Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of 2-Aminofurans and 2-Unsubstituted Furans *via* Carbenoid-mediated [3+2] Cycloaddition

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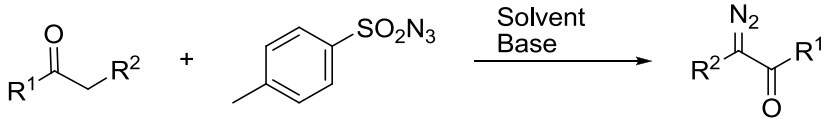
Table of Contents

General methods: All reactions were carried out in flame or oven dried glasswares under nitrogen atmosphere with freshly distilled dry 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 RT on 300 M Hz Bruker ACF 300, 400 M Hz Bruker DPX 400, 500 M Hz Bruker AMX 500, and 400 M Hz *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.

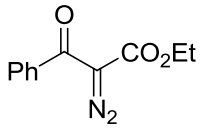
General procedure for the α-diazo compounds (1a - 1r):



Method A: To a solution of β-ketoester or ketone (1.0 eq.) and 4-methylbenzenesulfonyl azide (1.2 eq.) in CH_3CN at 0 °C was added DBU (1.2 eq.) dropwise under nitrogen. The resulting solution was stirred at 0 °C for 3 h and slowly brought to RT. Upon completion as indicated by thin layer chromatography (TLC), the reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The reaction mixture was concentrated under reduced pressure, and the crude material was purified by column chromatography (hexane/ethyl acetate = 9:1).

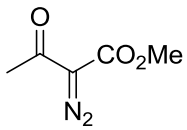
Method B: To a solution of β-diketone (1.0 eq.) and 4-methylbenzenesulfonyl azide (1.2 eq.) in ethanol at RT was added triethylamine (1.2 eq.) dropwise under nitrogen. The reaction mixture was stirred for 3 h at RT. Upon completion as indicated by thin layer chromatography (TLC), the reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The reaction mixture was concentrated under reduced pressure, and the crude material was purified by column chromatography (hexane/ethyl acetate = 9:1).

Ethyl 2-diazo-3-oxo-3-phenylpropanoate (1a):



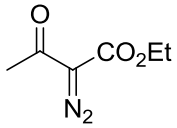
The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 - 7.61 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.53 - 7.41 (m, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 161.0, 137.1, 132.3, 128.3, 127.9, 61.6, 14.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{11}N_2O_3$: 219.0770. Found: 219.0765.

Methyl 2-diazo-3-oxobutanoate (1b):



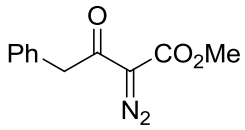
The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield: 82%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.0, 161.8, 52.1, 28.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_5H_7N_2O_3$: 143.0457. Found: 143.0462.

Ethyl 2-diazo-3-oxobutanoate (1b'):



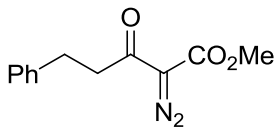
The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.28 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.2, 161.4, 61.4, 28.2, 14.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_6H_9N_2O_3$: 157.0613. Found: 157.0609

Methyl 2-diazo-3-oxo-4-phenylbutanoate (1c):



The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.25 (m, 5H), 4.19 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 161.6, 134.0, 129.7, 128.5, 127.1, 52.3, 45.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{11}N_2O_3$: 219.0770. Found: 219.0765.

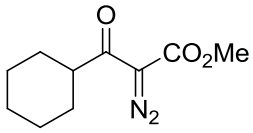
Methyl 2-diazo-3-oxo-5-phenylpentanoate (1d):



The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.20 (m, 5H), 3.85 (s, 3H), 3.21 (t, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 161.7,

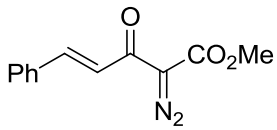
140.8, 128.5, 128.5, 126.1, 52.2, 41.8, 30.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}N_2O_3$: 233.0926. Found: 233.0931.

Methyl 3-cyclohexyl-2-diazo-3-oxopropanoate (1e):



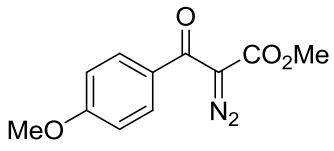
The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 3.35 - 3.28 (m, 1H), 1.81 - 1.67 (m, 5H), 1.47 - 1.19 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 161.7, 52.1, 46.8, 28.7, 25.8, 25.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{15}N_2O_3$: 211.1083. Found: 211.1090.

(E)-methyl 2-diazo-3-oxo-5-phenylpent-4-enoate (1f):



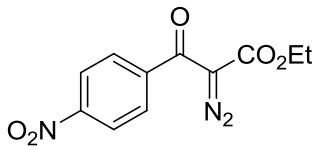
The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 20.8 Hz, 1H), 7.77 (d, *J* = 21.2 Hz, 1H), 7.64 - 7.61 (m, 2H), 7.40 - 7.38 (m, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 161.9, 143.0, 134.6, 130.6, 128.9, 128.7, 121.7, 52.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{11}N_2O_3$: 231.0770. Found: 231.0767

Methyl 2-diazo-3-(4-methoxyphenyl)-3-oxopropanoate (1g):



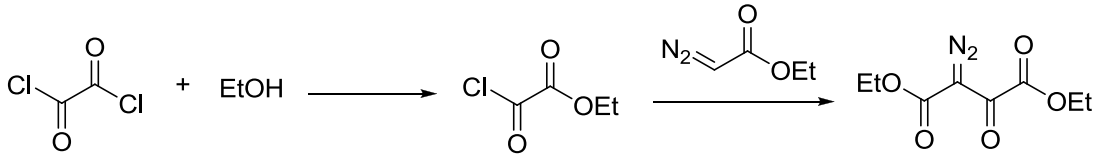
The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 12.0 Hz, 2H), 6.92 (d, *J* = 11.6 Hz, 2H), 3.86 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 163.2, 161.8, 131.0, 129.3, 113.2, 55.4, 52.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{11}N_2O_4$: 235.0719. Found: 235.0716.

Ethyl 2-diazo-3-(4-nitrophenyl)-3-oxopropanoate (1h):



The title compound was prepared according to Method A. The product was obtained as red oil. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.30 - 8.26 (m, 2H), 7.77 - 7.74 (m, 2H), 4.25 (q, *J* = 6.8 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 185.6, 160.3, 149.6, 142.5, 129.3, 123.1, 62.0, 14.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{10}N_3O_5$: 264.0620. Found: 264.0622.

Diethyl 2-diazo-3-oxosuccinate (1i):



The title compound was prepared according to the following procedure.

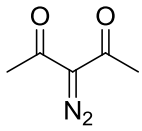
Ethyl 2-chloro-2-oxoacetate: To oxalyl chloride (20 mmol, 1.72 mL) at 0 ℃ was added ethanol (10 mmol, 0.58 mL) dropwise with a syringe pump over 1 h. Upon completion of addition, the mixture was allowed to warm to RT over 2 h. The crude material was distilled under vacuum to give the desired product (1.02g, 75%);

Diethyl 2-diazo-3-oxosuccinate: To ethyl 2-chloro-2-oxoacetate (0.5 mmol, 55 μL) in 5 mL THF at 0 ℃ was added a solution of EDA (1.5 mmol, 158 μL) in 3 mL THF, and the mixture was stirred for another 3 h at 0 °C. Upon completion as indicated by thin layer chromatography (TLC), the reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The reaction mixture was concentrated under reduced

pressure, and the crude material was purified by column chromatography (hexane/ethyl acetate = 9:1).

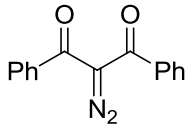
The product was obtained as yellow oil. Yield 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.35 (m, 4H), 1.35 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 159.9, 62.8, 62.3, 14.2, 13.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_8H_{11}N_2O_5$: 215.0668. Found: 215.0665.

3-Diazopentane-2,4-dione (1j):



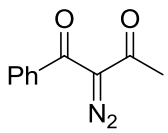
The title compound was prepared according to Method B. The product was obtained as yellow oil. Yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 28.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_5H_7N_2O_2$: 127.0512. Found: 127.0508.

2-Diazo-1,3-diphenylpropane-1,3-dione (1k):



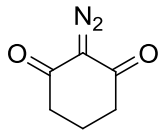
The title compound was prepared according to Method B. The product was obtained as yellow solid. mp: 105 - 107 °C. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.58 (m, 4H), 7.47 - 7.44 (m, 2H), 7.36 - 7.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.5, 137.0, 132.6, 128.4, 128.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{11}N_2O_2$: 251.0821. Found: 251.0812.

2-Diazo-1-phenylbutane-1,3-dione (1l):



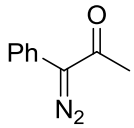
The title compound was prepared according to Method B. The product was obtained as white solid. mp: 55 - 56 °C. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 - 7.63 (m, 2H), 7.59 - 7.50 (m, 1H), 7.48 - 7.47 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 185.1, 137.3, 132.7, 128.9, 127.4, 29.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_9N_2O_2$: 189.0664. Found: 189.0660.

2-Diazocyclohexane-1,3-dione (1m):



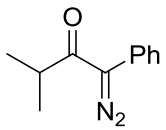
The title compound was prepared according to Method B. The product was obtained as yellow solid. mp: 46 - 48 °C. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (t, J = 6.4 Hz, 4H), 2.09 - 2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 36.8, 18.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_6H_7N_2O_2$: 139.0508. Found: 139.0509.

1-Diazo-1-phenylpropan-2-one (1n):



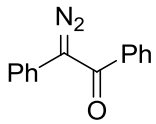
The title compound was prepared according to Method A. The product was obtained as orange solid. mp: 57 - 58 °C. Yield 74%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 - 7.43 (m, 2H), 7.41 - 7.38 (m, 2H), 7.26 - 7.25 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5, 129.0, 126.9, 125.8, 125.5, 26.9; HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_9H_8N_2ONa$: 183.0534. Found: 183.0528.

2-Diazo-3-methyl-1-phenylbutan-1-one (1o):



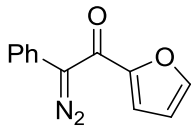
The title compound was prepared according to Method A. The product was obtained as red oil. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.52 (m, 2H), 7.43 - 7.39 (m, 2H), 7.27 - 7.24 (m, 1H), 3.02 - 2.95 (m, 1H), 1.20 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 130.3, 129.0, 126.9, 126.0, 36.5, 18.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}N_2O$: 189.1028. Found: 189.1023.

2-Diazo-1,2-diphenylethanone (1p):



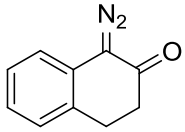
The title compound was prepared according to Method A. The product was obtained as red solid. mp: 78 - 79 °C. Yield 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 - 7.60 (m, 2H), 7.52 - 7.43 (m, 3H), 7.42 - 7.38 (m, 4H), 7.28 - 7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 138.0, 131.7, 129.1, 128.5, 127.8, 127.0, 126.1, 126.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{11}N_2O$: 223.0871. Found: 223.0878.

2-Diazo-1-(furan-2-yl)-2-phenylethanone (1q):



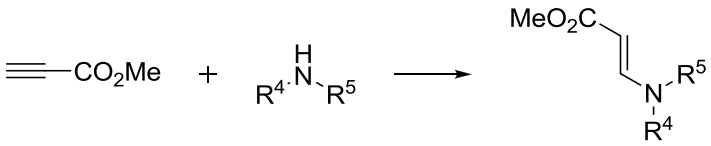
The title compound was prepared according to Method A. The product was obtained as yellow solid. mp: 109 - 110 °C. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.60 (m, 2H), 7.58 (d, J = 0.8 Hz, 1H), 7.52 - 7.52 (m, 2H), 7.46 - 7.42 (m, 1H), 6.49 (d, J = 1.6 Hz, 1H), 6.41 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 152.4, 144.4, 129.0, 127.2, 126.2, 125.9, 116.7, 112.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_9N_2O_2$: 213.0664. Found: 213.0665.

1-Diazo-3,4-dihydronaphthalen-2(1H)-one (1r):



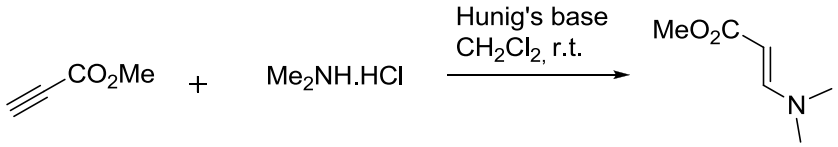
The title compound was prepared according to Method A. The product was obtained as red oil. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.28 (m, 1H), 7.23 - 7.21 (m, 1H), 7.12 - 7.08 (m, 1H), 6.98 - 6.96 (m, 1H), 3.02 (t, J = 6.8 Hz, 2H), 2.68 - 2.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 131.3, 128.4, 127.5, 125.4, 124.5, 120.4, 36.9, 27.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_9N_2O$: 173.0715. Found: 173.0713.

General procedure for the synthesis of 3-aminoalkenoate (2b - d):



To a solution of methyl propiolate (5.0 mmol, 1.0 eq.) in THF (25 mL) was added amine (6.0 mmol, 1.2 eq.) at RT, and the reaction mixture was stirred overnight. Solvent was removed under reduced pressure, and crude compound was purified by column chromatography (hexane/ethyl acetate = 3:2).

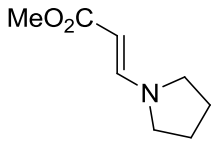
Methyl (E)-3-(dimethylamino) prop-2-enoate (2a):



To a solution of methyl propiolate (5.0 mmol, 1.0 eq.) in CH_2Cl_2 (50 mL) at RT was added dimethyl ammonium chloride (7.5 mmol, 1.5 eq.) and Hunig's base (7.5 mmol, 1.5 eq.) successively. Upon completion as indicated by TLC, the reaction was quenched with water, extracted with CH_2Cl_2, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure, and the crude material was purified by column chromatography (hexane/ethyl acetate = 3:2).

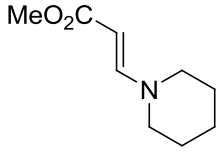
The product was obtained as yellow solid. mp: 50 - 51 °C. Yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 12.9 Hz, 1H), 4.52 (d, J = 12.9 Hz, 1H), 3.66 (s, 3H), 2.88 (s, br, 6H).

Methyl (E)-3-pyrrolidin-1-ylprop-2-enoate (2b):



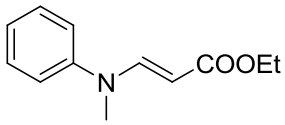
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 72 - 73 °C. Yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 12.8 Hz, 1H), 4.47 (d, *J* = 12.8 Hz, 1H), 3.65 (s, 3H), 3.23 - 3.18 (m, 4H), 1.92 (s, 4H).

(E)-methyl 3-(piperidin-1-yl)acrylate (2c):



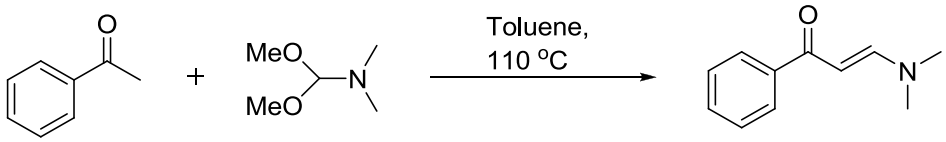
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 40 - 41 °C. Yield 92%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 12.9 Hz, 1H), 4.61 (d, *J* = 13.2 Hz, 1H), 3.64 (s, 3H), 3.17 (m, 4H), 1.59 (m, 6H).

(E)-Ethyl 3-(methyl(phenyl)amino)acrylate (2d):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 86%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 13.2 Hz, 1H), 7.37 - 7.33 (m, 2H), 7.14 - 7.10 (m, 3H), 4.94 (d, *J* = 13.2 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.24 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

(E)-3-(dimethylamino)-1-phenylprop-2-en-1-one (2e):



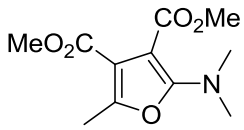
To a stirred solution of acetophenone (5.0 mmol, 1.0 eq.) in toluene (5.0 mL) was added 1,1-dimethoxy-N,N-dimethylmethanamine (7.0 mmol, 1.4 eq.), and the mixture was stirred at 110 °C. Upon completion as indicated by TLC, the reaction was quenched with water,

extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure, and the crude material was purified by column chromatography (hexane/ethyl acetate = 1:1). The product was obtained as yellow solid (500 mg). mp: 90 - 91 °C. Yield 57 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.38 (m, 2H), 7.80 (d, *J* = 12.4 Hz, 1H), 7.45 - 7.39 (m, 3H), 5.71 (d, *J* = 12.4 Hz, 1H), 3.14 (s, 3H), 2.93 (s, 3H).

General procedure for aminofurans (3aa - 3la, 3bb - 3be):

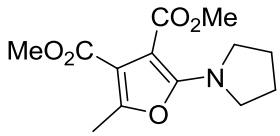
$Cu(hfacac)_2 \cdot H_2O$ (0.012 mmol, 6 mol %) was dried under vacuum at RT until it turned gray white. To a stirred solution of enamine (0.20 mmol, 1.0 eq.) in dichloroethane (1.0 mL) at RT was added a solution of diazo compound (0.24 mmol, 1.2 eq.) in dichloroethane (1.0 mL) dropwise over 10 min. The reaction mixture was stirred under N_2 at 60 ^oC until the diazo compound was fully consumed (4 h). The reaction mixture was stirred for another 12 h with exposure to air through a needle until the intermediate was completely consumed as indicated by TLC. The reaction mixture was concentrated under reduced pressure, and the crude material was purified by column chromatography using hexane/ethyl acetate (9:1) to yield 2-aminofuran.

Dimethyl 2-(dimethylamino)-5-methyl-furan-3,4-dicarboxylate (3ba):



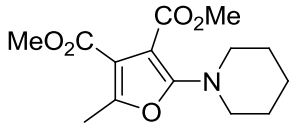
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 74%; ^1H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.71 (s, 3H), 2.99 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 164.1, 159.8, 146.6, 114.5, 90.7, 51.7, 51.3, 40.7, 12.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{16}NO_5$: 242.1028. Found: 242.1033.

Dimethyl 2-methyl-5-pyrrolidin-1-yl-furan-3,4-dicarboxylate (3bb):



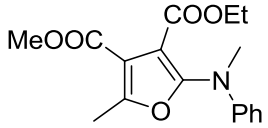
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 54%; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.73 (s, 3H), 3.53 - 3.50 (m, 4H), 2.30 (s, 3H), 1.94 - 1.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.2, 157.7, 145.7, 114.6, 87.5, 51.7, 51.1, 49.4, 25.5, 12.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{18}NO_5$: 268.1185. Found: 268.1184.

Dimethyl 2-methyl-5-(piperidin-1-yl)furan-3,4-dicarboxylate (3bc):



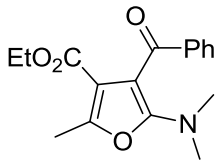
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.75 (s, 3H), 3.38 - 3.35 (m, 4H), 2.33 (s, 3H), 1.67 - 1.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.9, 159.9, 147.2, 114.3, 92.6, 51.7, 51.4, 50.1, 25.6, 24.1, 12.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{20}NO_5$: 282.1341. Found: 282.1344.

3-Ethyl 4-methyl 5-methyl-2-(methyl(phenyl)amino)furan-3,4-dicarboxylate (3bd):



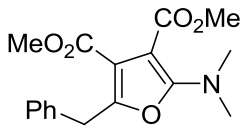
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.21 (m, 2H), 6.91 - 6.88 (m, 1H), 6.80 - 6.77 (m, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 3.33 (s, 3H), 2.46 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 162.4, 153.8, 152.9, 146.5, 129.0, 120.5, 115.4, 113.6, 107.1, 60.7, 51.7, 39.0, 14.0, 13.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{20}NO_5$: 318.1341. Found: 318.1338.

Ethyl 4-benzoyl-5-(dimethylamino)-2-methylfuran-3-carboxylate (3b'e):



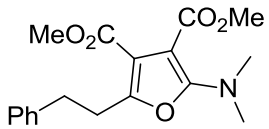
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 - 7.80 (m, 2H), 7.49 - 7.41 (m, 1H), 7.39 - 7.37 (m, 2H), 3.71 (q, *J* = 7.2 Hz, 2H), 2.91 (s, 3H), 2.45 (s, 3H), 0.78 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 163.9, 157.9, 148.5, 140.7, 131.9, 128.8, 128.2, 115.2, 97.9, 60.1, 40.3, 13.4, 12.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{20}NO_4$: 302.1392. Found: 302.1396.

Dimethyl 2-benzyl-5-(dimethylamino)furan-3,4-dicarboxylate (3ca):



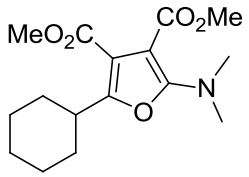
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.22 (m, 5H), 4.01 (s, 2H), 3.83 (s, 3H), 3.74 (s, 3H), 2.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.1, 160.1, 147.4, 137.2, 128.6, 128.5, 126.6, 115.3, 90.2, 51.9, 51.4, 40.5, 32.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{20}NO_5$: 318.1341. Found: 318.1345.

Dimethyl 2-(dimethylamino)-5-phenethylfuran-3,4-dicarboxylate (3da):



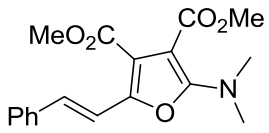
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.25 (m, 2H), 7.21 - 7.15 (m, 3H), 3.77 (s, 3H), 3.74 (s, 3H), 3.02 - 2.99 (m, 2H), 2.98 (s, 6H), 2.92 - 2.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.1, 159.8, 149.1, 140.7, 128.4, 128.4, 126.1, 114.8, 90.5, 51.7, 51.3, 40.6, 34.4, 28.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{22}NO_5$: 332.1498. Found: 332.1493.

Dimethyl 2-cyclohexyl-5-(dimethylamino)furan-3,4-dicarboxylate (3ea):



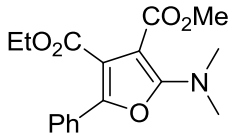
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.72 (s, 3H), 3.02 (s, 6H), 2.90 - 2.82 (m, 1H), 1.82 - 1.64 (m, 5H), 1.52 - 1.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.1, 159.6, 153.0, 112.8, 90.3, 51.8, 51.3, 40.6, 36.3, 31.0, 26.1, 25.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{24}NO_5$: 310.1654. Found: 310.1657.

(E)-Dimethyl 2-(dimethylamino)-5-styrylfuran-3,4-dicarboxylate (3fa):



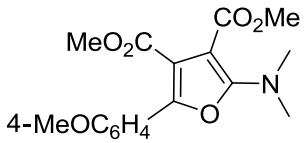
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 - 7.23 (m, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 6.94 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 3.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 164.1, 159.5, 145.1, 136.7, 128.7, 128.4, 127.9, 126.6, 116.5, 114.1, 91.3, 52.0, 51.5, 40.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{20}NO_5$: 330.1341. Found: 330.1343.

4-Ethyl 3-methyl 2-(dimethylamino)-5-phenylfuran-3,4-dicarboxylate (3aa):



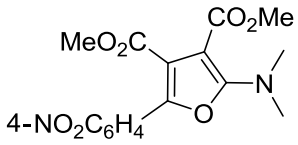
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 8.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 3H), 3.17 (s, 6H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 163.1, 160.8, 140.9, 129.2, 128.6, 127.8, 124.9, 116.0, 91.8, 61.6, 51.2, 40.7, 14.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{20}NO_5$: 318.1341. Found: 318.1342.

Dimethyl 2-(dimethylamino)-5-(4-methoxyphenyl)furan-3,4-dicarboxylate (3ga):



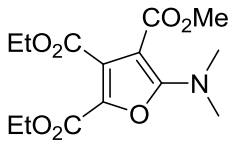
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 - 7.50 (m, 2H), 6.91 - 6.89 (m, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 3.75 (s, 3H), 3.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.2, 160.5, 159.4, 141.9, 126.8, 121.9, 114.1, 114.0, 91.7, 55.3, 52.4, 51.3, 40.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{20}NO_6$: 334.1291. Found: 334.1291.

4-Ethyl 3-methyl 2-(dimethylamino)-5-(4-nitrophenyl)furan-3,4-dicarboxylate (3ha):



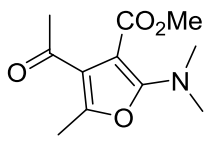
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 - 8.19 (m, 2H), 7.66 - 7.64 (m, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 3.22 (s, 6H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 162.6, 161.1, 146.1, 137.8, 134.9, 124.3, 124.2, 120.5, 92.4, 62.1, 51.4, 40.6, 14.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{19}N_2O_7$: 363.1192. Found: 363.1189.

2,3-Diethyl 4-methyl 5-(dimethylamino)furan-2,3,4-tricarboxylate (3ia):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 (q, *J* = 9.6 Hz, 2H), 4.28 (q, *J* = 9.2 Hz, 2H), 3.73 (s, 3H), 3.20 (s, 6H), 1.39 (t, *J* = 9.2 Hz, 3H), 1.31 (t, *J* = 9.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 162.1, 161.8, 157.5, 129.9, 129.5, 91.5, 61.8, 60.9, 51.4, 40.5, 14.2, 14.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{20}NO_7$: 314.1240. Found: 314.1239.

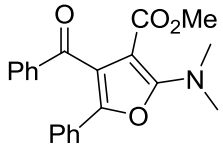
Methyl 4-acetyl-2-(dimethylamino)-5-methylfuran-3-carboxylate (3ja):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 3.08 (s, 6H), 2.36 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 163.6, 161.4, 144.0,

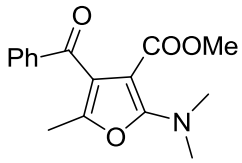
124.2, 89.7, 50.9, 41.1, 30.8, 12.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{16}NO_4$: 226.1079. Found: 226.1076.

Methyl 4-benzoyl-2-(dimethylamino)-5-phenylfuran-3-carboxylate (3ka):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.93 (m, 2H), 7.55 - 7.51 (m, 1H), 7.45 - 7.41 (m, 4H), 7.26 - 7.23 (m, 2H), 7.19 - 7.17 (m, 1H), 3.32 (s, 3H), 3.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 163.0, 160.9, 140.2, 137.8, 133.2, 129.2, 129.0, 128.6, 127.4, 124.5, 121.7, 93.0, 50.5, 40.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{20}NO_4$: 350.1392. Found: 350.1401.

3-Ethyl 4-methyl 5-methyl-2-(methyl(phenyl)amino)furan-3,4-dicarboxylate (3la):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.85 - 7.83 (m, 2H), 7.53 - 7.49 (m, 1H), 7.44 - 7.40 (m, 2H), 3.19 (s, 3H), 3.13 (s, 6H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 163.3, 160.7, 143.6, 138.9, 132.5, 128.7, 128.3, 121.7, 91.1, 50.3, 40.7, 12.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{18}NO_4$: 288.1236. Found: 288.1235.

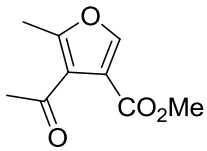
General procedures for 2-unsubstituted furans:

Cu (hfacac)$_2$·H$_2$O (0.012 mmol, 6 mol %) was dried under vacuum at RT until it turned gray white. To a solution of enamine (0.20 mmol, 1.0 eq.) in dichloroethane (1.0 mL) at RT was added a solution of diazo compound (0.24 mmol, 1.2 eq.) in dichloroethane (1.0 mL) dropwise over 10 min.

Method A: The reaction mixture was stirred at RT for 4 h under N_2 (**4re** for overnight) until the diazo compound was fully consumed. The reaction mixture was concentrated under reduced pressure, and the crude material was purified by column chromatography using hexane/ethyl acetate (19:1) to give 2-unsubstituted furan.

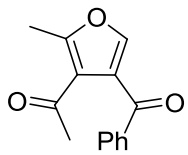
Method B: The reaction mixture was heated at 60 ^{o}C under N_2 until the diazo compound is fully consumed. Solvent was removed under reduced pressure, and the crude mixture was dissolved in THF (2.5 mL). The solution was treated with *p*-Toluenesulfonic acid (0.40 mmol, 2.0 eq.) and heated at 60 $^{\circ}$C under N_2 overnight. The reaction mixture was concentrated under reduced pressure, and the crude material was purified by column chromatography using hexane/ethyl acetate (19:1) to give 2-unsubstitued furan.

Methyl 4-acetyl-5-methyl-furan-3-carboxylate (4ja):



The title compound was prepared according to Method B. The product was obtained as colorless oil. Yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 3.84 (s, 3H), 2.53 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 163.0, 158.1, 146.4, 121.6, 117.8, 51.9, 31.2, 13.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{11}O_4$: 183.0657. Found: 183.0661.

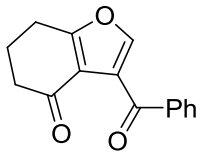
1-(4-Benzoyl-2-methylfuran-3-yl)ethanone (4je):



The title compound was prepared according to Method B. The product was obtained as colorless oil. Yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 - 7.90 (m, 2H), 7.64 - 7.60 (m,

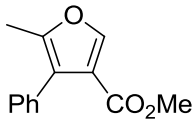
1H), 7.52 (s, 1H), 7.50 - 7.44 (m, 2H), 2.55 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 189.5, 158.8, 145.3, 138.2, 133.3, 129.4, 128.7, 125.9, 122.3, 30.7, 13.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}O_3$: 217.0865. Found: 217.0860.

3-Benzoyl-6,7-dihydrobenzofuran-4(5H)-one (4me):



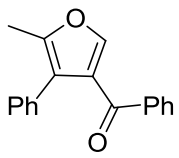
The title compound was obtained without acid treatment at 80 ^{o}C. The product was obtained as yellow oil. Yield 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 - 7.88 (m, 2H), 7.66 (s, 1H), 7.60 - 7.58 (m, 1H), 7.49 - 7.45 (m, 2H), 2.98 (t, *J* = 6.4 Hz, 2H), 2.57 - 2.54 (m, 2H), 2.25 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 189.0, 167.9, 145.3, 137.8, 133.3, 129.6, 128.4, 123.8, 120.0, 38.2, 23.5, 22.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{13}O_3$: 241.0865. Found: 241.0862.

Methyl 5-methyl-4-phenylfuran-3-carboxylate (4na):



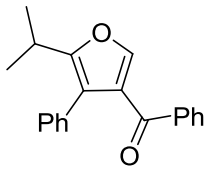
The title compound was prepared according to Method A. The product was obtained as colorless oil. Yield 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.41 - 7.37 (m, 2H), 7.35 - 7.30 (s, 3H), 3.72 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 150.8, 146.7, 131.9, 130.0, 127.8, 127.2, 120.9, 118.4, 51.2, 12.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}O_3$: 217.0865. Found: 217.0860.

(5-Methyl-4-phenylfuran-3-yl)(phenyl)methanone (4ne):



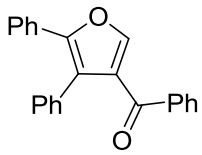
The title compound was prepared according to Method A. The product was obtained as colorless oil. Yield 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 - 7.82 (m, 2H), 7.72 (s, 1H), 7.52 - 7.51 (m, 1H), 7.42 - 7.39 (m, 2H), 7.35 - 7.32 (m, 2H), 7.28 - 7.26 (m, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 150.8, 146.9, 138.8, 132.5, 132.1, 129.6, 129.4, 128.3, 128.1, 127.0, 125.9, 121.5, 12.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{15}O_2$: 263.1072. Found: 263.1076.

(5-Isopropyl-4-phenylfuran-3-yl)(phenyl)methanone (4oe):



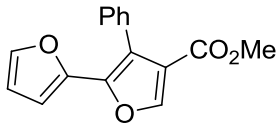
The title compound was prepared according to Method A. The product was obtained as colorless oil. Yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 - 7.82 (m, 2H), 7.73 (s, 1H), 7.54 - 7.50 (m, 1H), 7.42 - 7.38 (m, 2H), 7.35 - 7.32 (m, 2H), 7.31 - 7.24 (m, 3H), 3.13 - 3.06 (m, 1H), 1.28 (d, *J* =6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 158.9, 147.0, 138.9, 132.5, 132.2, 129.8, 129.3, 128.3, 128.1, 127.0, 125.8, 119.7, 26.0, 21.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{19}O_2$: 291.1385. Found: 291.1391.

(4, 5-Diphenylfuran-3-yl)(phenyl)methanone (4pe):



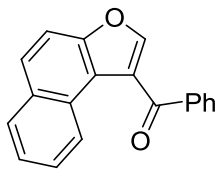
The title compound was prepared according to Method A. The product was obtained as colorless oil. Yield 59%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.85 - 7.84 (m, 2H), 7.53 - 7.25 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 150.8, 147.1, 138.7, 132.7, 132.3, 130.1, 130.0, 129.4, 128.5, 128.4, 128.4, 128.1, 127.6, 127.5, 126.2, 122.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{23}H_{17}O_2$: 325.1229. Found: 325.1225.

Methyl 3-phenyl-2,2'-bifuran-4-carboxylate (4qa):



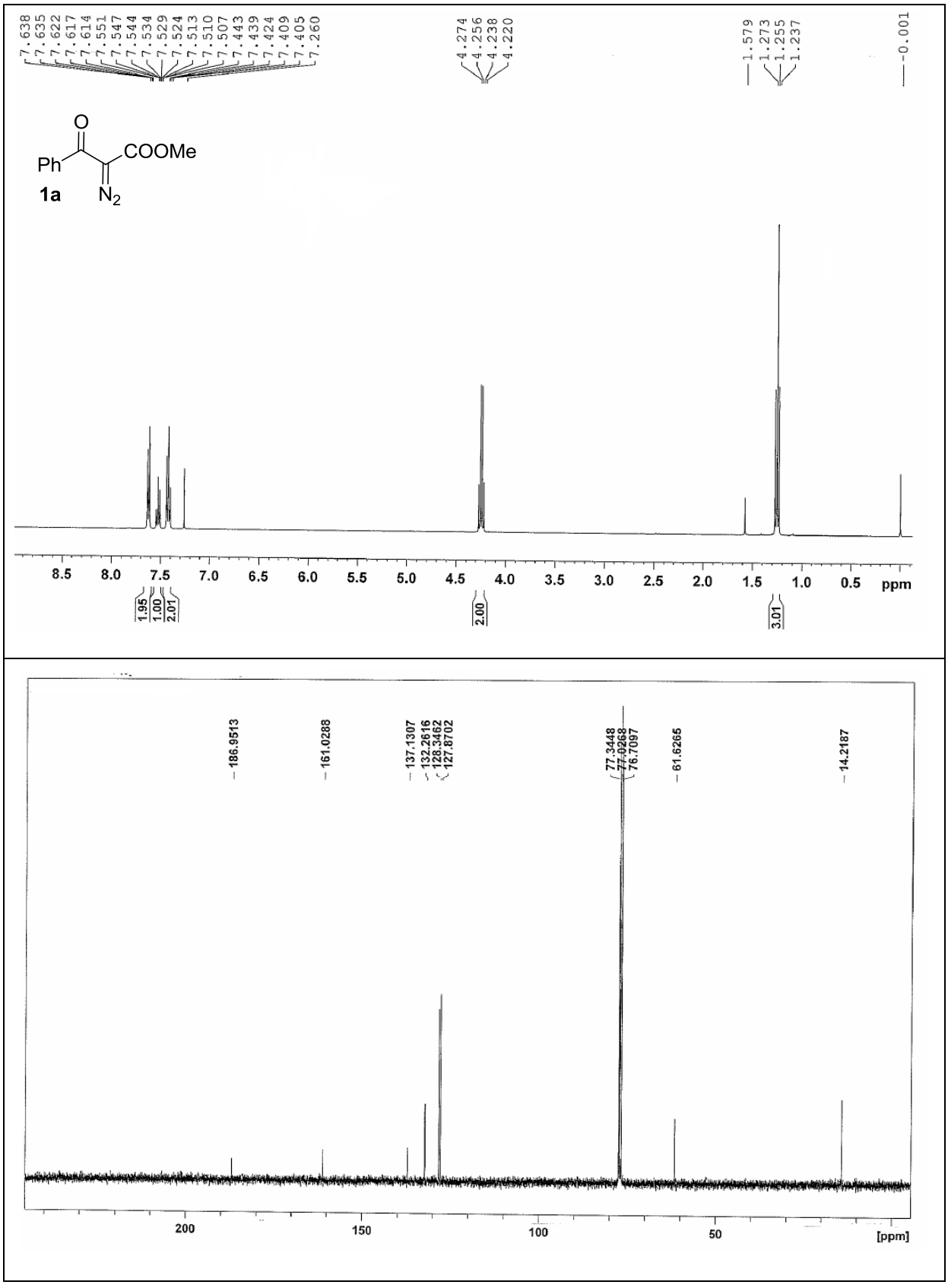
The title compound was prepared according to Method A. The product was obtained as colorless oil. Yield 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.42 - 7.37 (m, 5H), 7.36 - 7.36 (m, 1H), 6.33 (dd, J_1 = 3.2 Hz, J_2 = 1.6 Hz, 1H), 6.20 (dd, J_1 = 3.6 Hz, J_2 = 1.6 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 147.3, 144.8, 143.9, 142.4, 131.0, 130.2, 128.0, 127.9, 121.1, 119.9, 111.2, 107.8, 51.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{13}O_4$: 269.0814. Found: 269.0813.

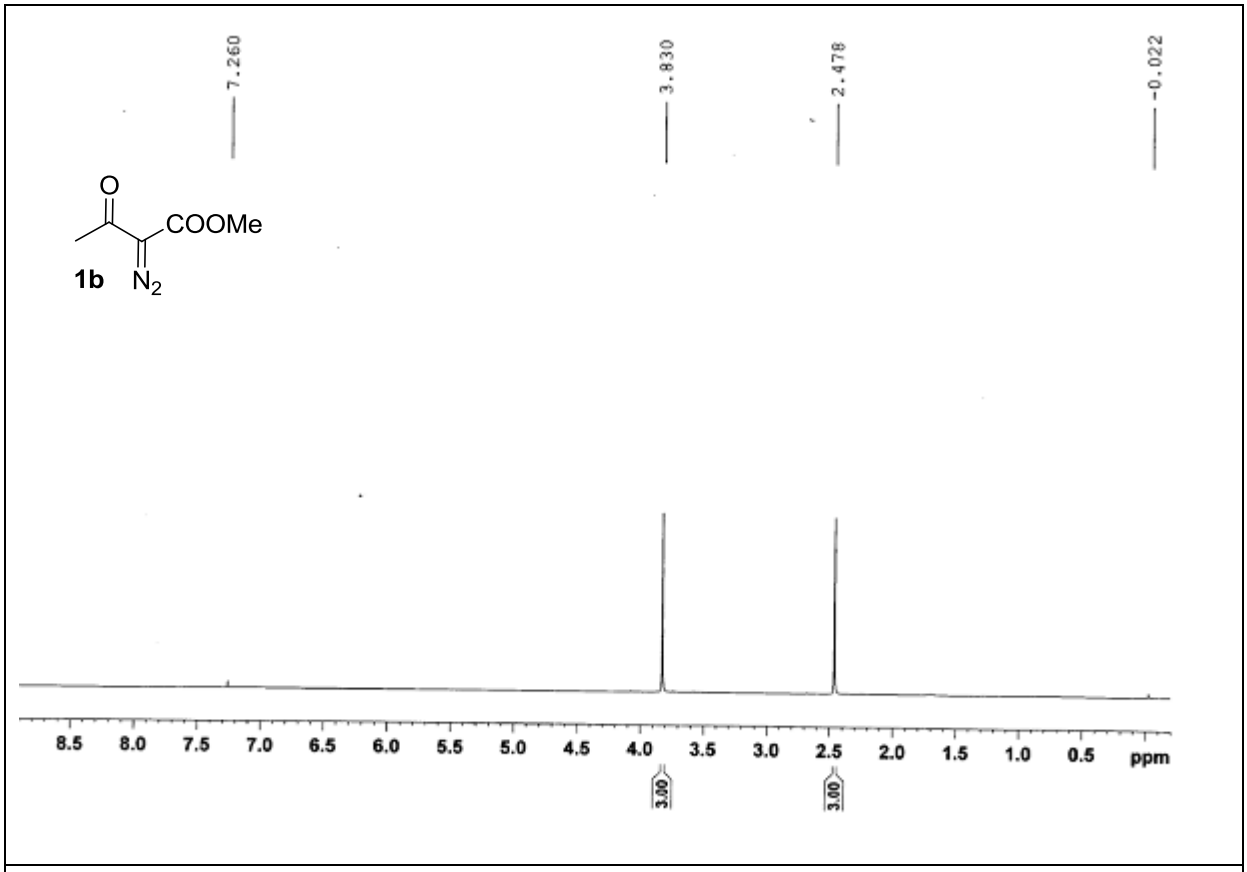
Naphtho[2,1-b]furan-1-yl(phenyl)methanone (4re):

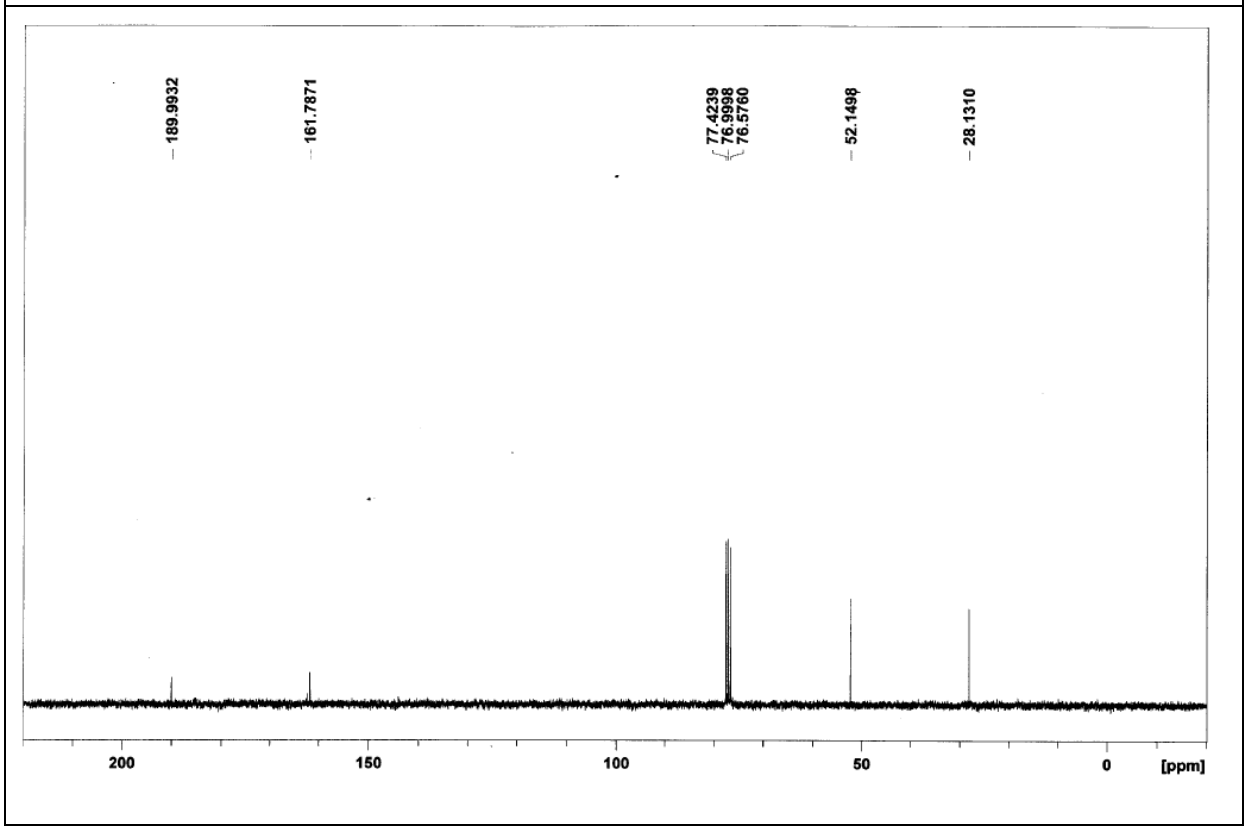


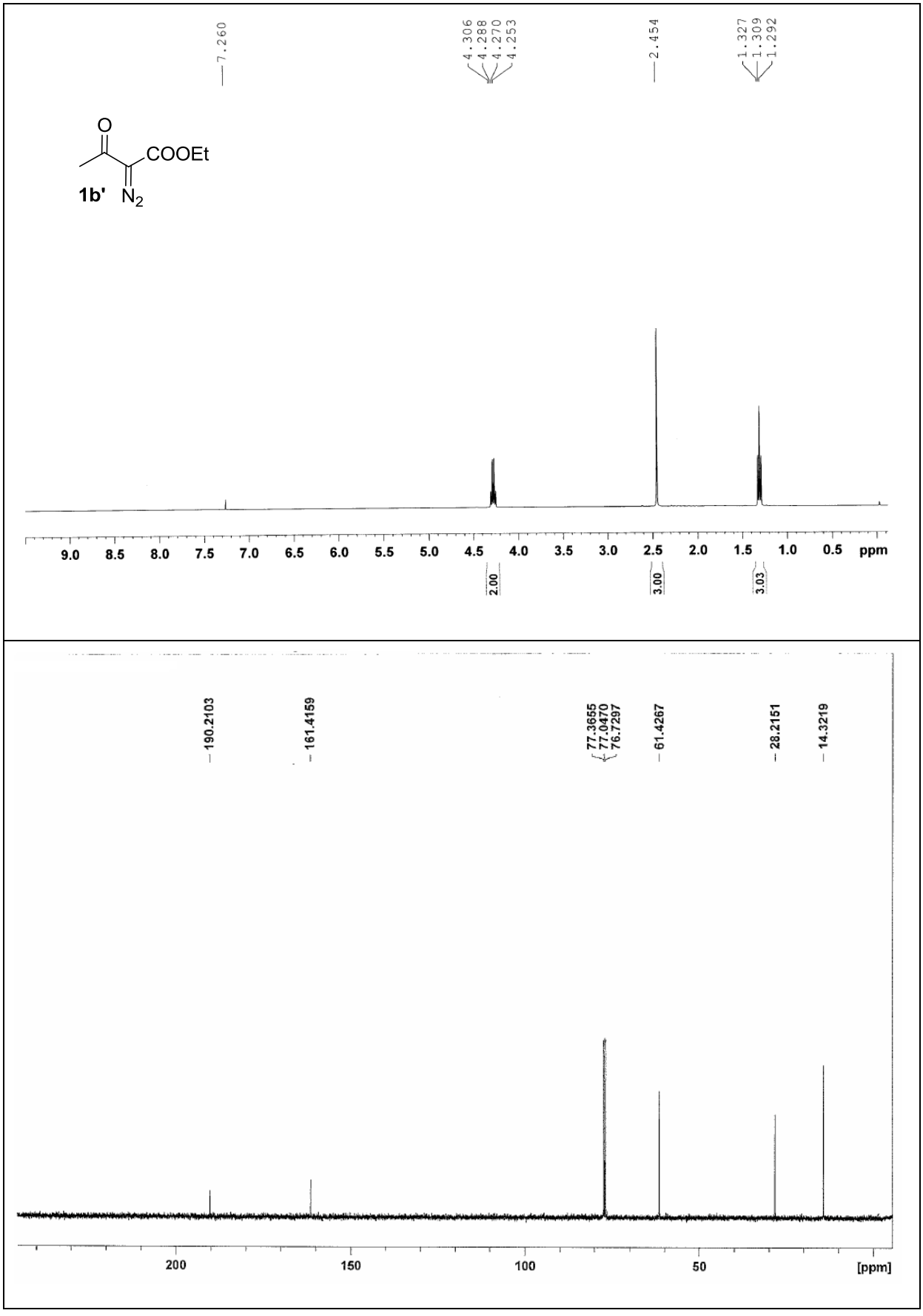
The title compound was prepared according to Method A. The product was obtained as yellow oil. Yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 - 8.88 (m, 1H), 8.04 - 7.95 (m, 4H), 7.88 - 7.86 (m, 1H), 7.72 - 7.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 154.0, 151.4, 139.3, 133.0, 131.3, 129.8, 128.7, 128.6, 128.1, 127.9, 126.8, 126.2, 125.3, 123.9, 119.9, 112.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{13}O_2$: 173.0916. Found: 273.0915.

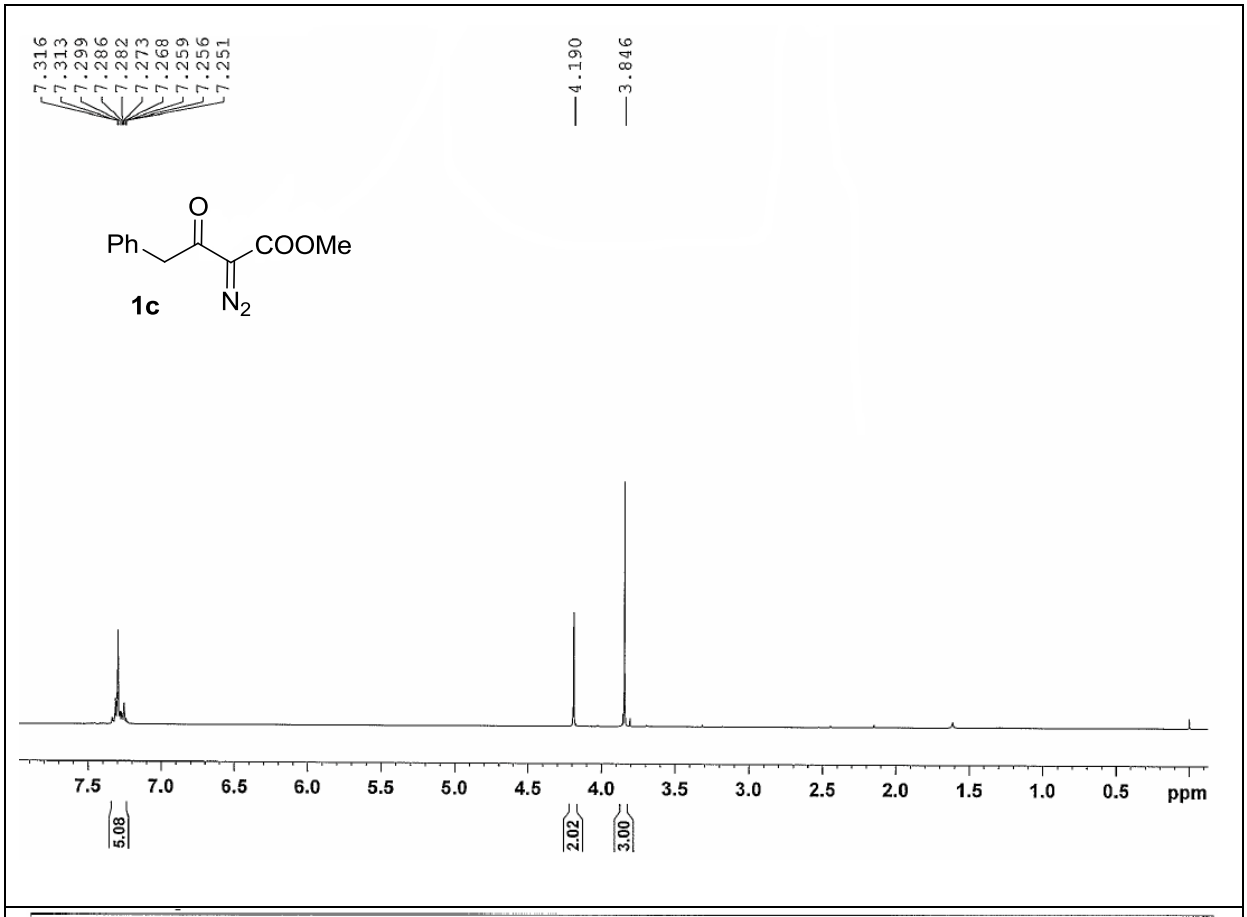
^{1}H and ^{13}C NMR spectra of α-diazo compounds

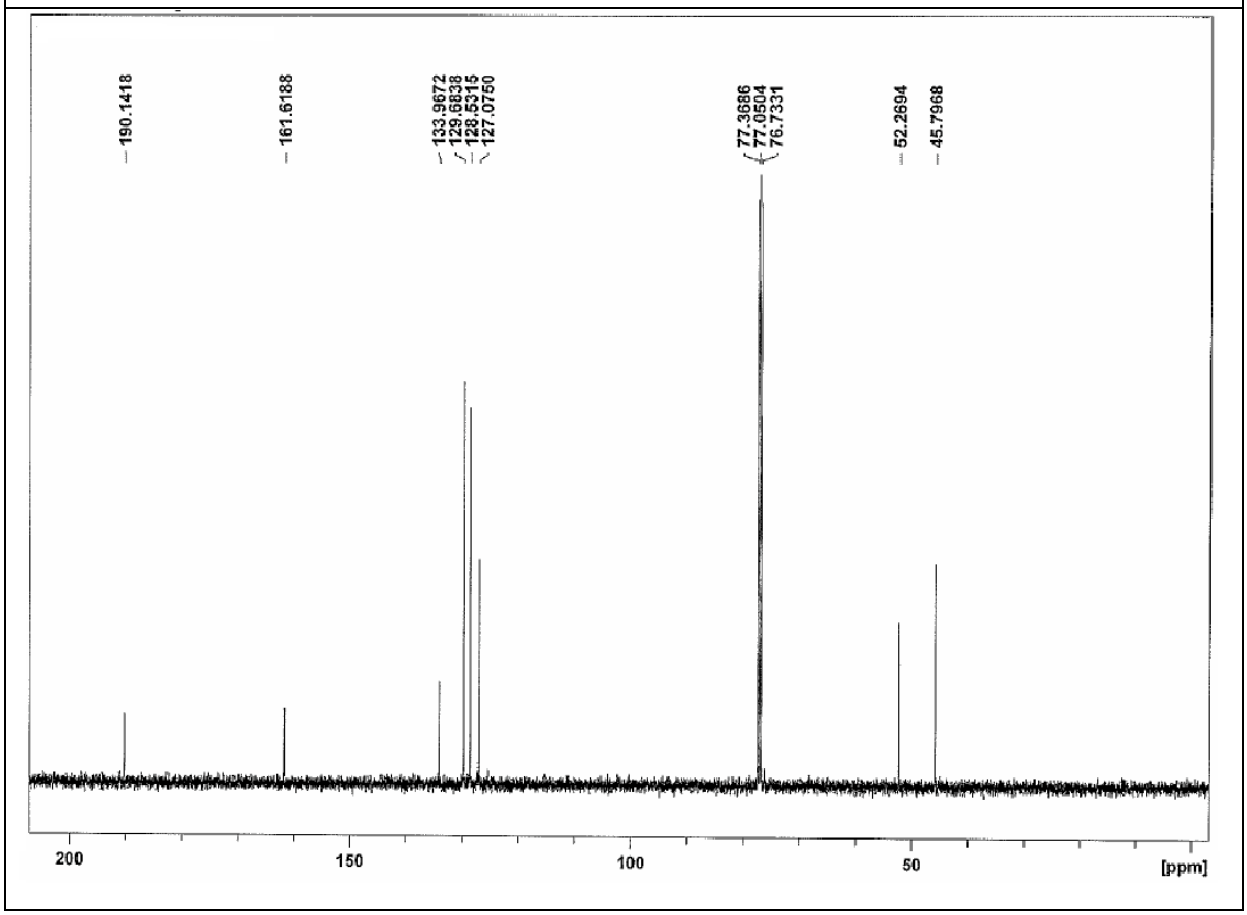


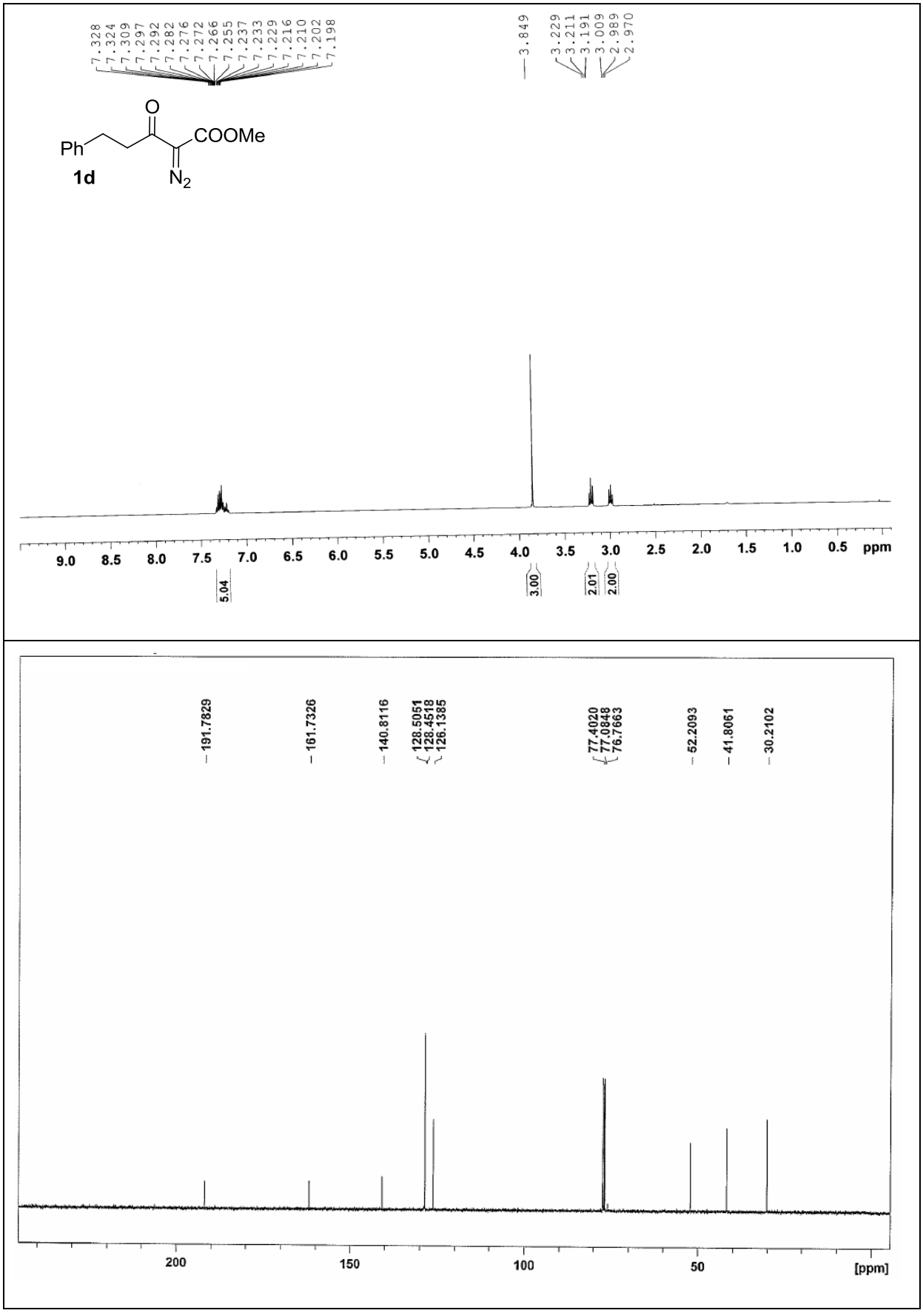

7.260
3.830
2.478
-0.022
O
COOMe
1b
N_2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.00
3.00


189.9932
161.7871
77.4239
76.9998
76.5760
52.1498
28.1310
200 150 100 50 0 [ppm]





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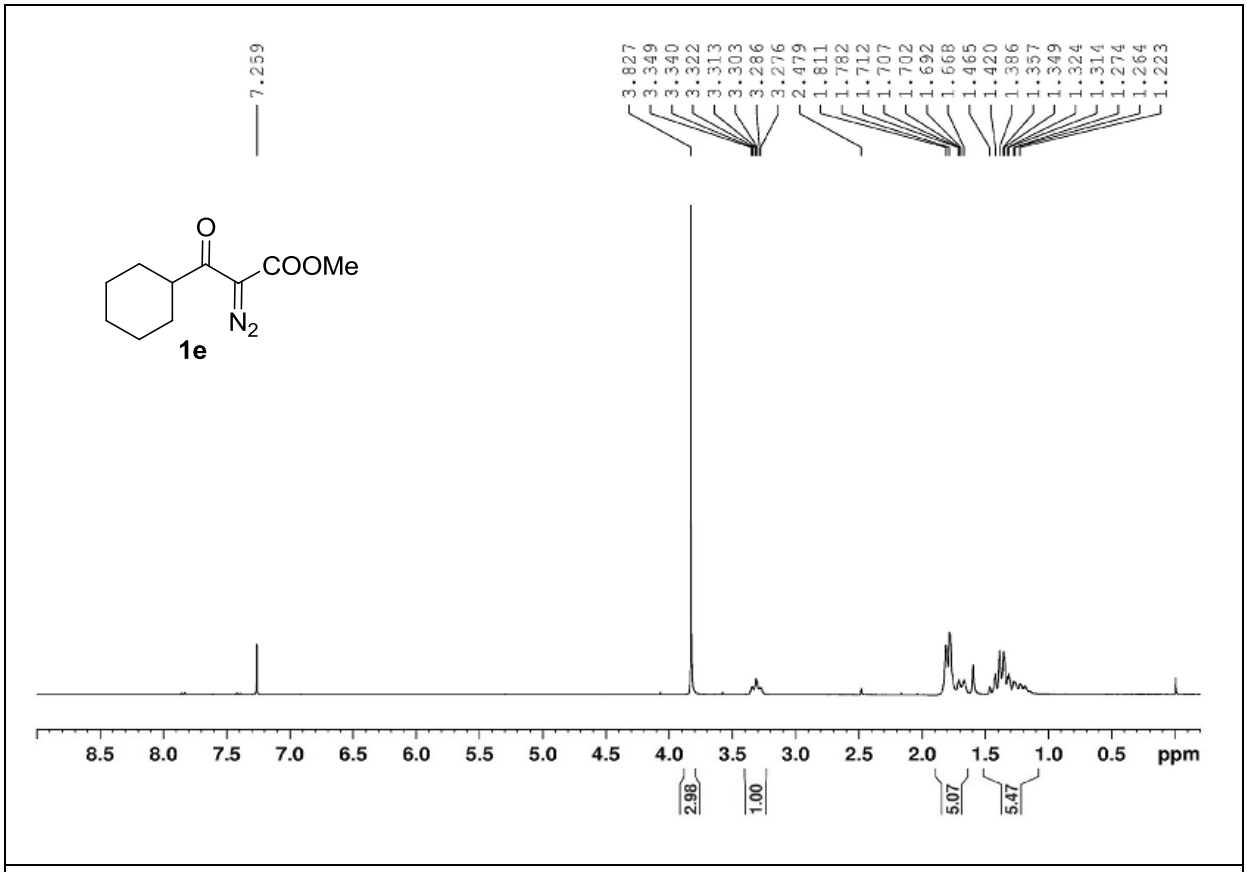
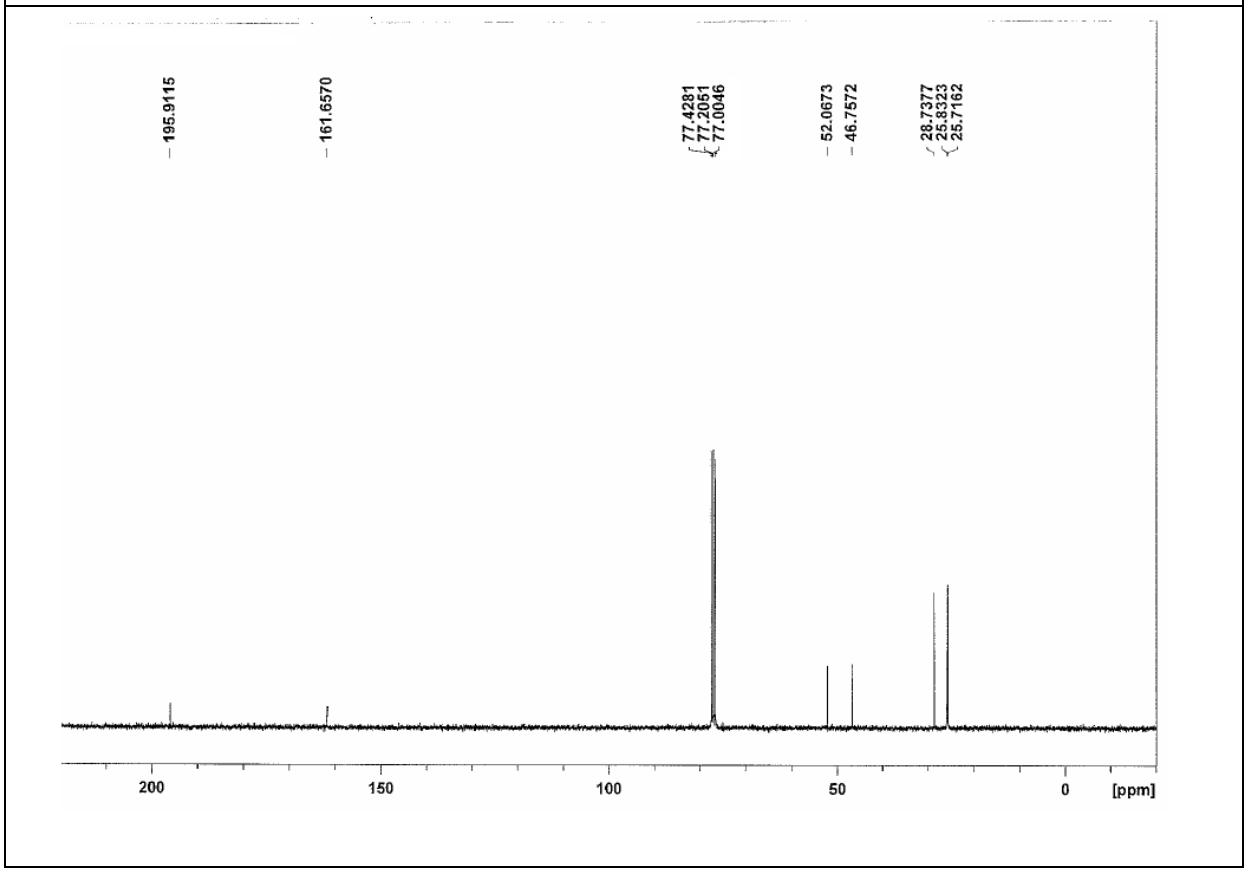
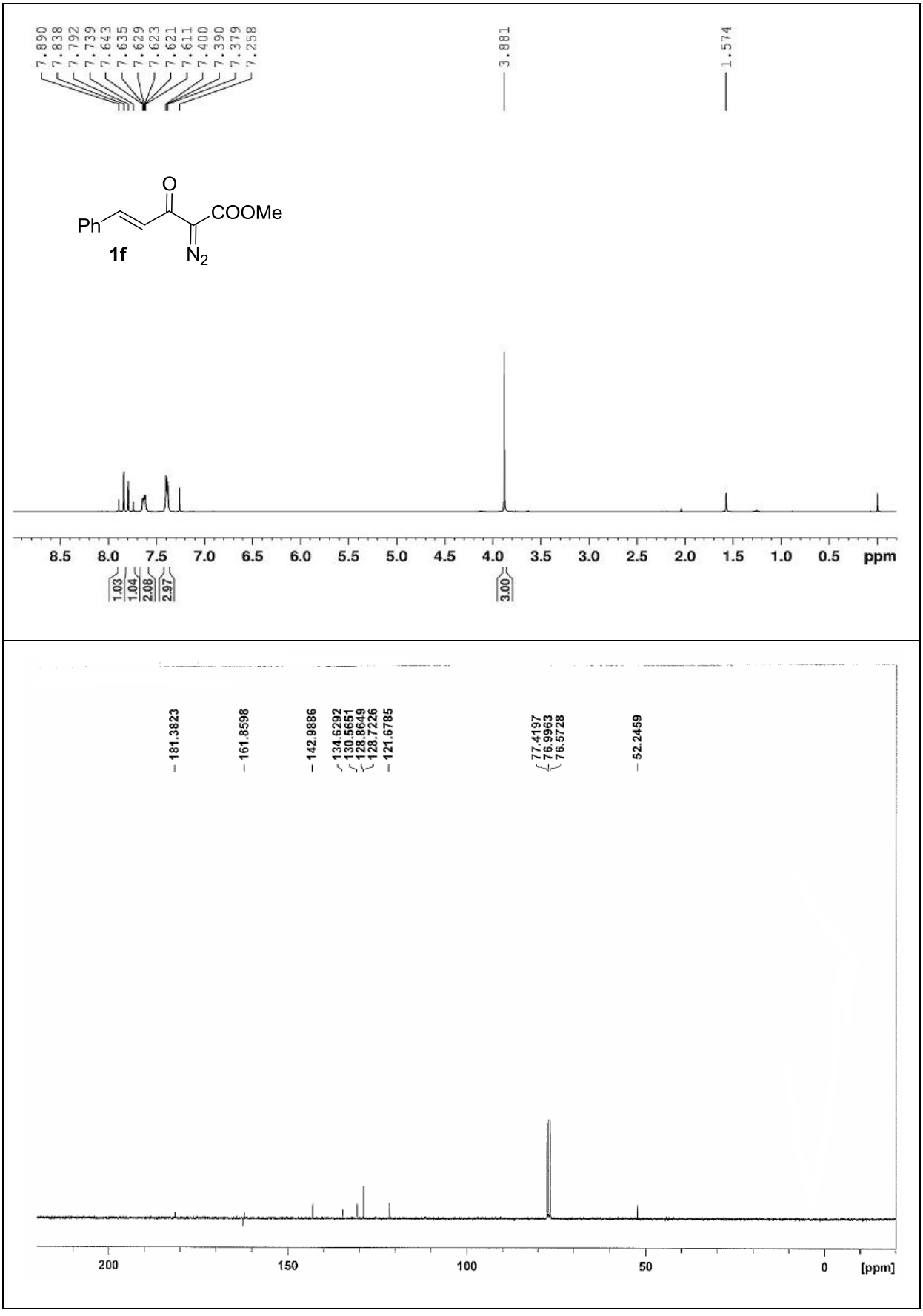
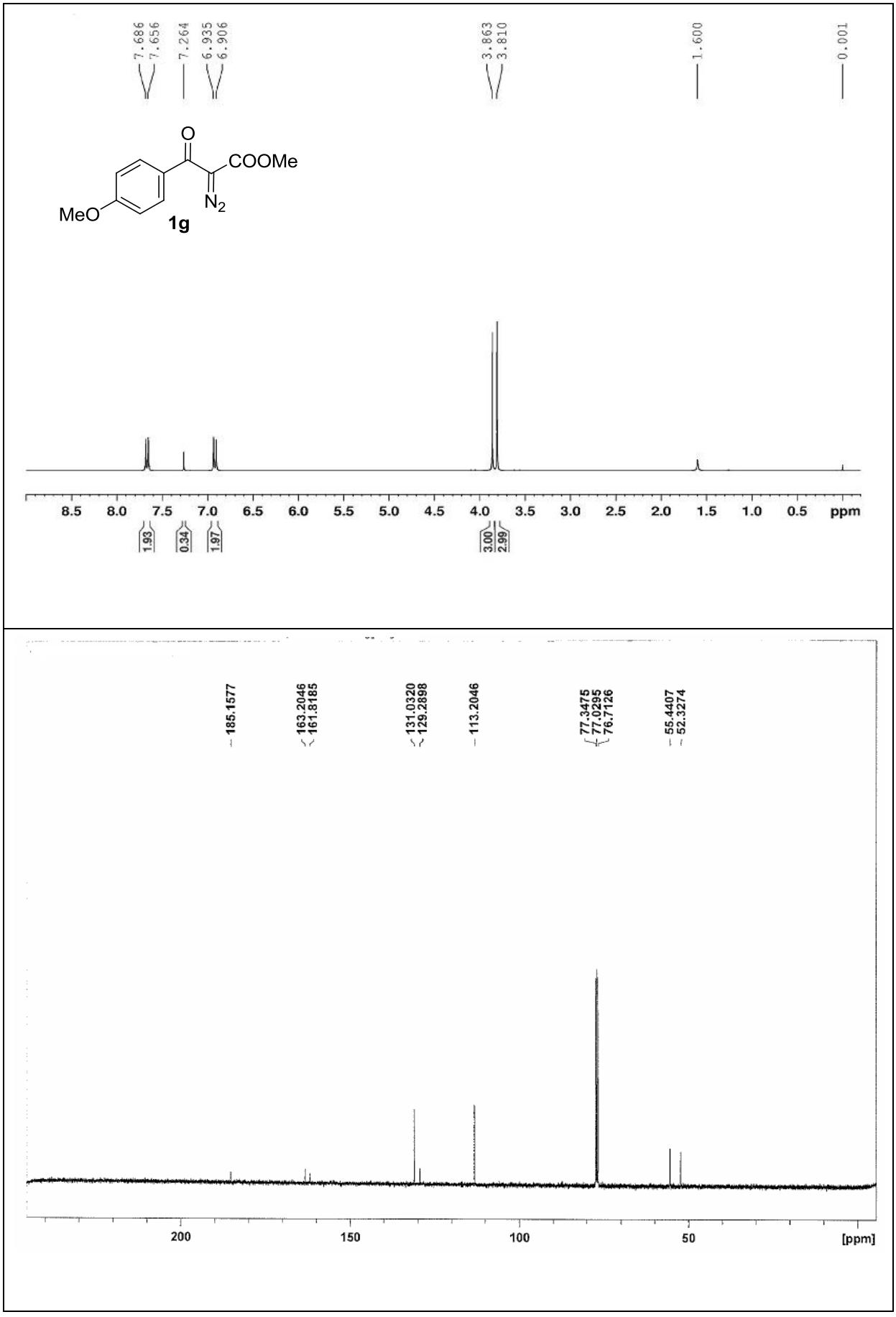
7.324
7.309
7.297
7.292
7.282
7.276
7.272
7.266
7.255
7.237
7.233
7.229
7.216
7.210
7.202
7.198
3.849
3.229
3.211
3.191
3.009
2.989
2.970
O
COOMe
Ph
1d
N2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.04
3.00
2.01
2.00
191.7829
161.7326
140.8116
128.5051
128.4518
126.1385
77.4020
77.0848
76.7663
52.2093
41.8061
30.2102
200 150 100 50 [ppm]


7.259
3.827
3.349
3.340
3.322
3.313
3.303
3.286
3.276
2.479
1.811
1.782
1.712
1.707
1.702
1.692
1.668
1.465
1.420
1.386
1.357
1.349
1.324
1.314
1.274
1.264
1.223
O
COOMe
N2
1e
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
2.98
1.00
5.07
5.47


195.9115
161.6570
77.4281
77.2061
77.0046
52.0673
46.7572
28.7377
25.8323
25.7162
200 150 100 50 0 [ppm]


7.890
7.838
7.792
7.739
7.643
7.635
7.629
7.623
7.621
7.611
7.400
7.390
7.379
7.258
3.881
1.574
O
Ph
COOMe
1f
N2
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
1.03
1.04
2.08
2.97
3.00
181.3823
161.8598
142.9886
134.6292
130.5651
128.8649
128.7226
121.6785
77.4197
76.9963
76.5728
52.2459
200
150
100
50
0
[ppm]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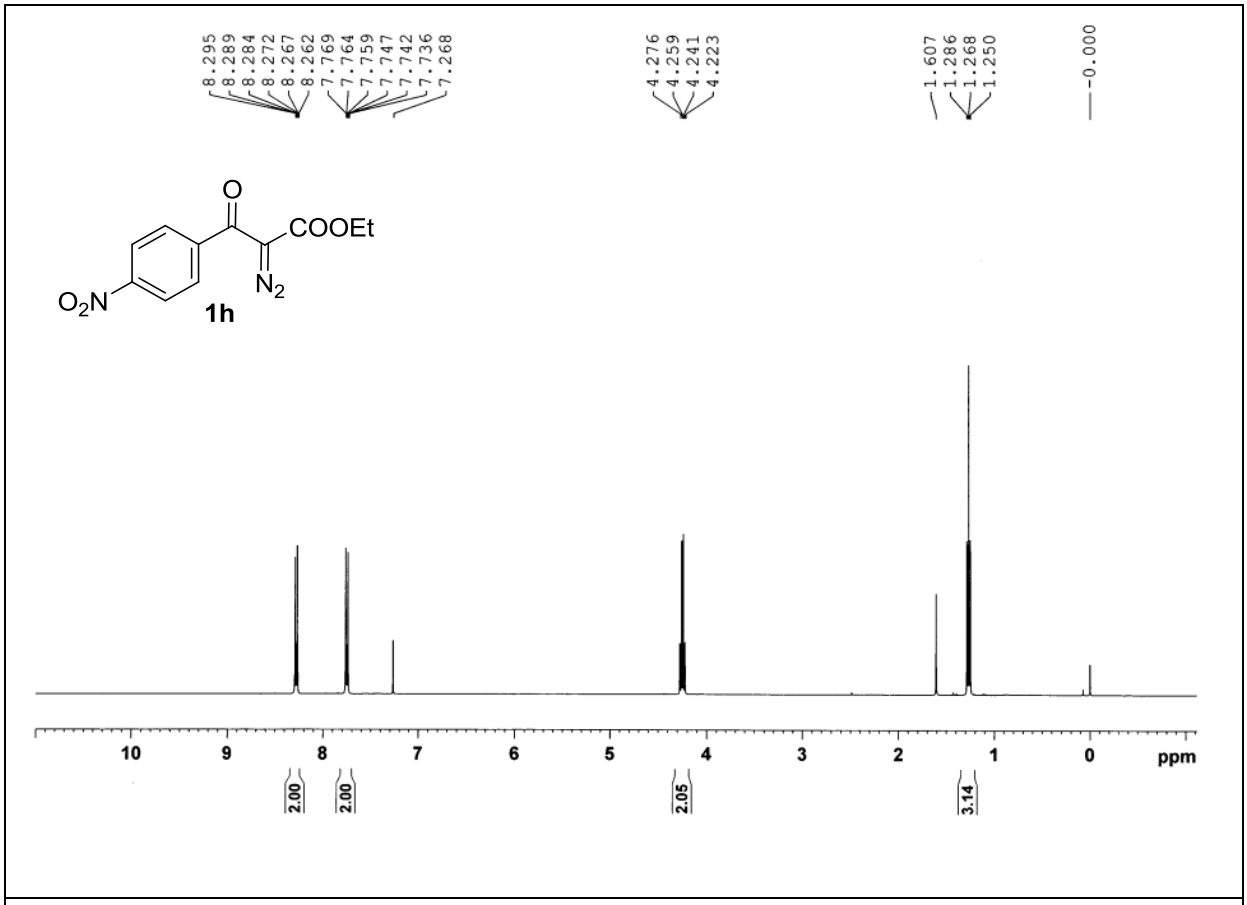
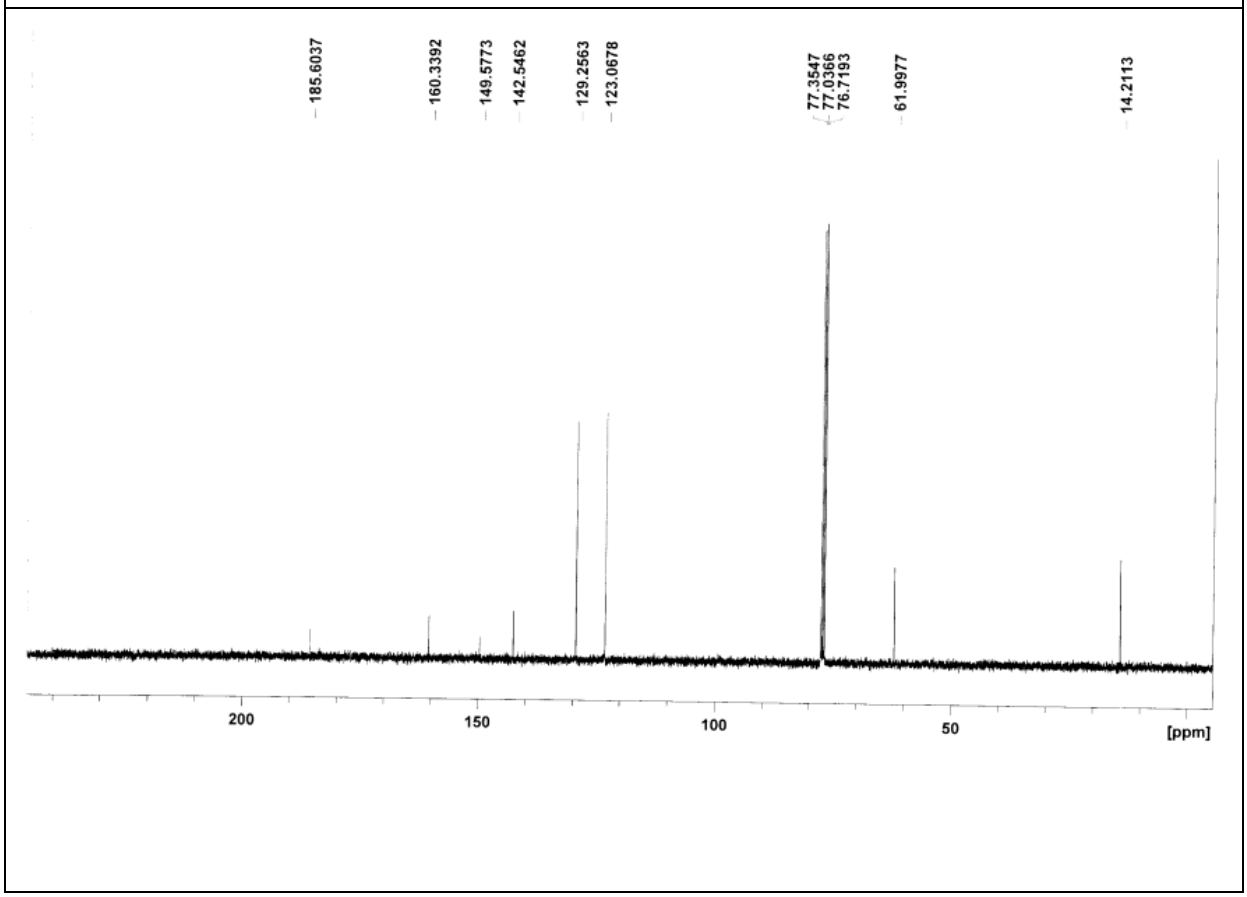
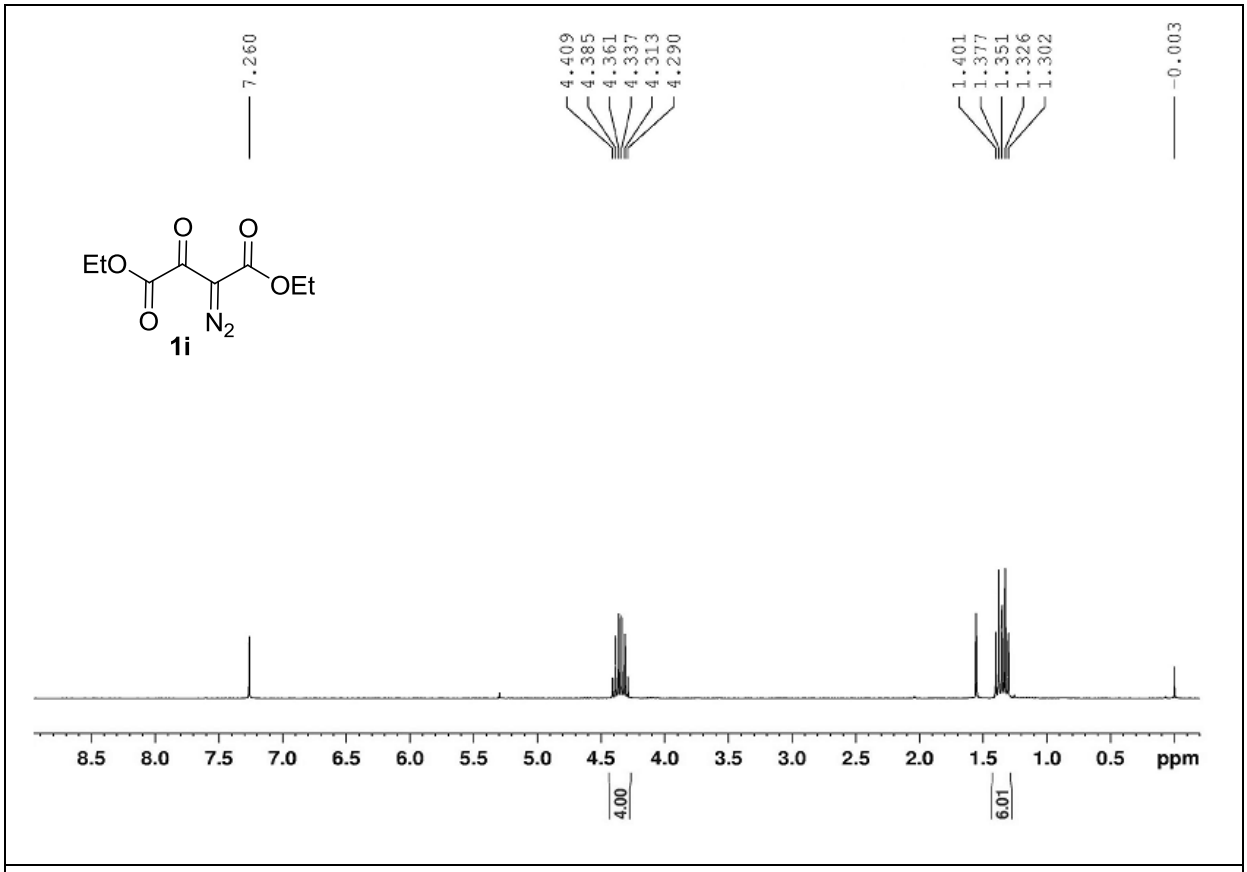
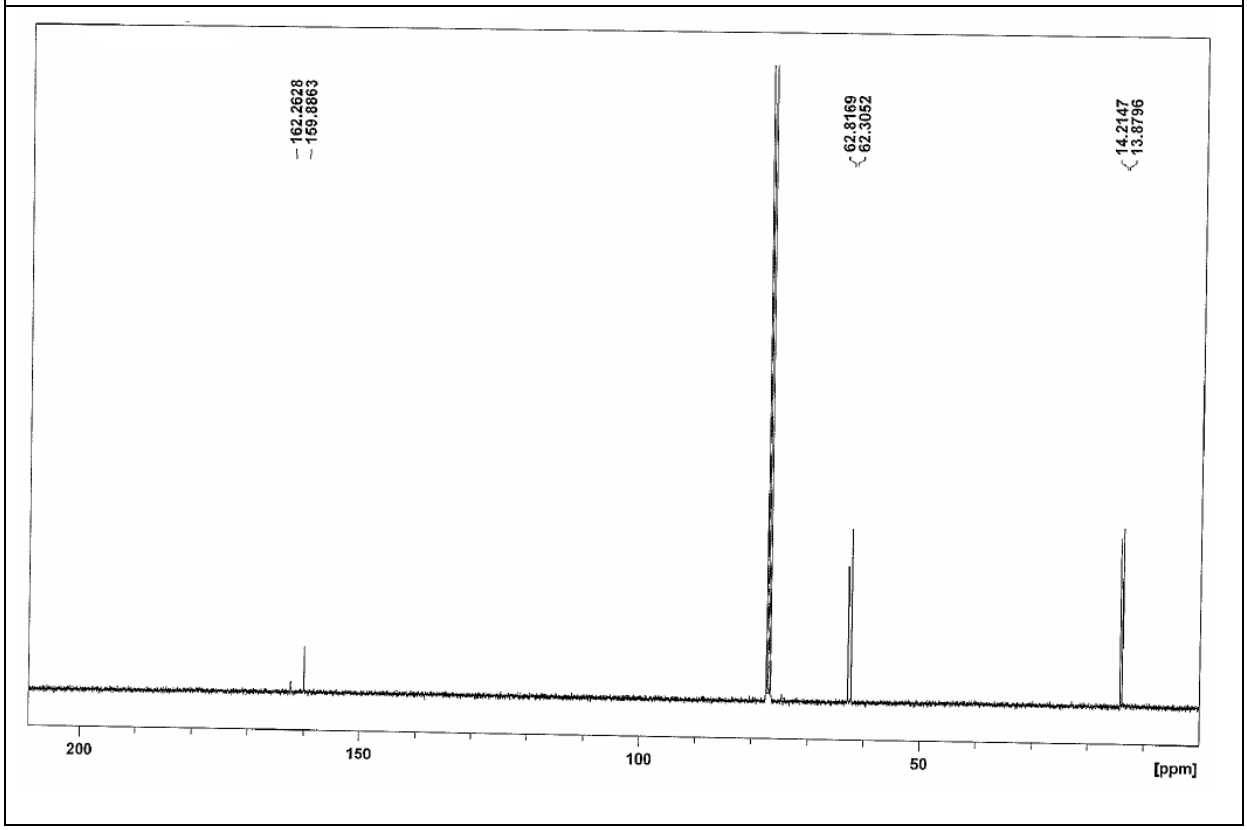
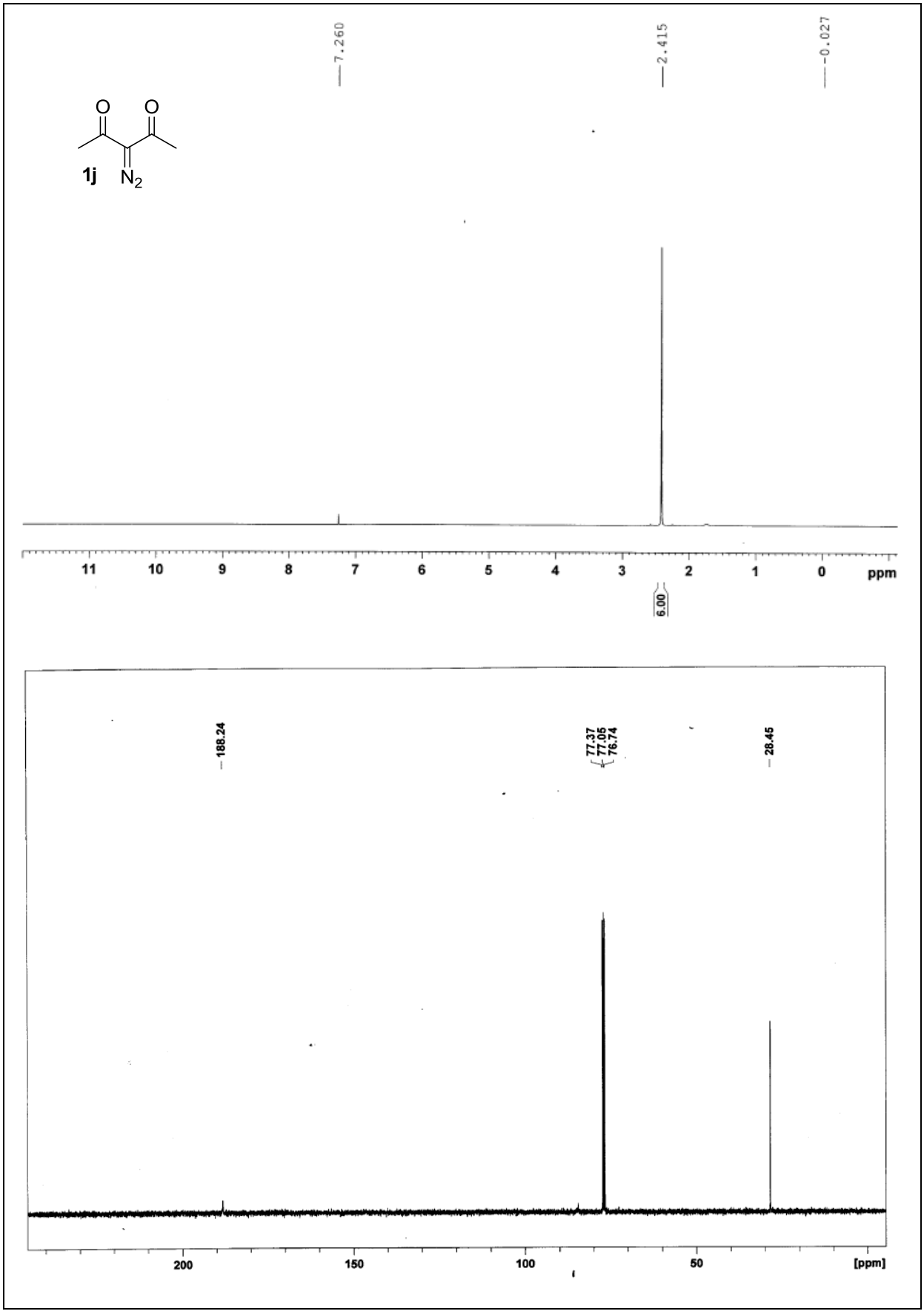
7.656
7.264
6.935
6.906
3.863
3.810
1.600
0.001
O
COOMe
N2
MeO
1g
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.93
0.34
1.97
3.00
2.99
185.1577
163.2046
161.8185
131.0320
129.2898
113.2046
77.3475
77.0295
76.7126
55.4407
52.3274
200
150
100
50
[ppm]

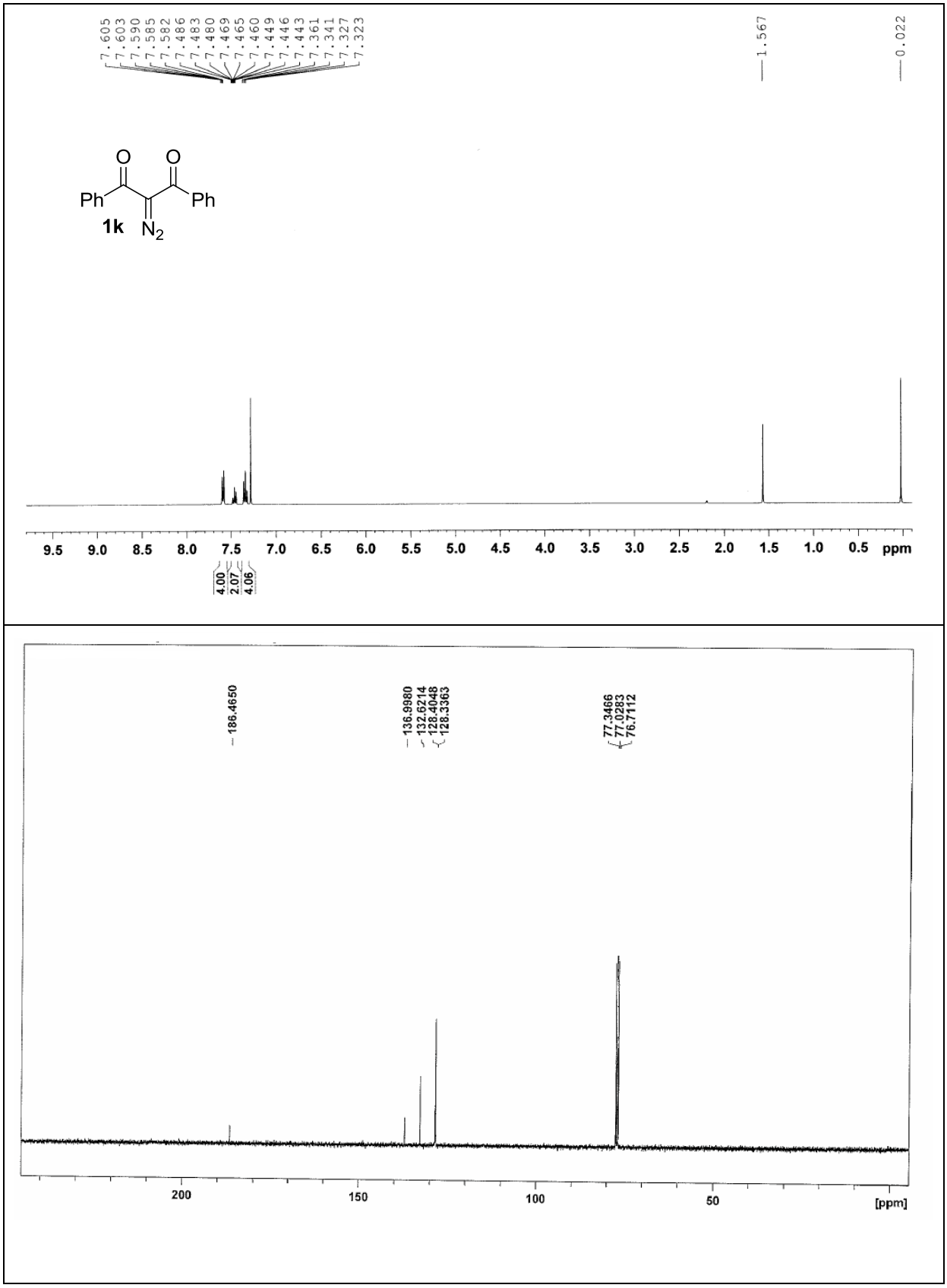

8.295
8.289
8.284
8.272
8.267
8.262
7.769
7.764
7.759
7.747
7.742
7.736
7.268
4.276
4.259
4.241
4.223
1.607
1.286
1.268
1.250
0.000
O
COOEt
N2
O2N
1h
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
2.05
3.14

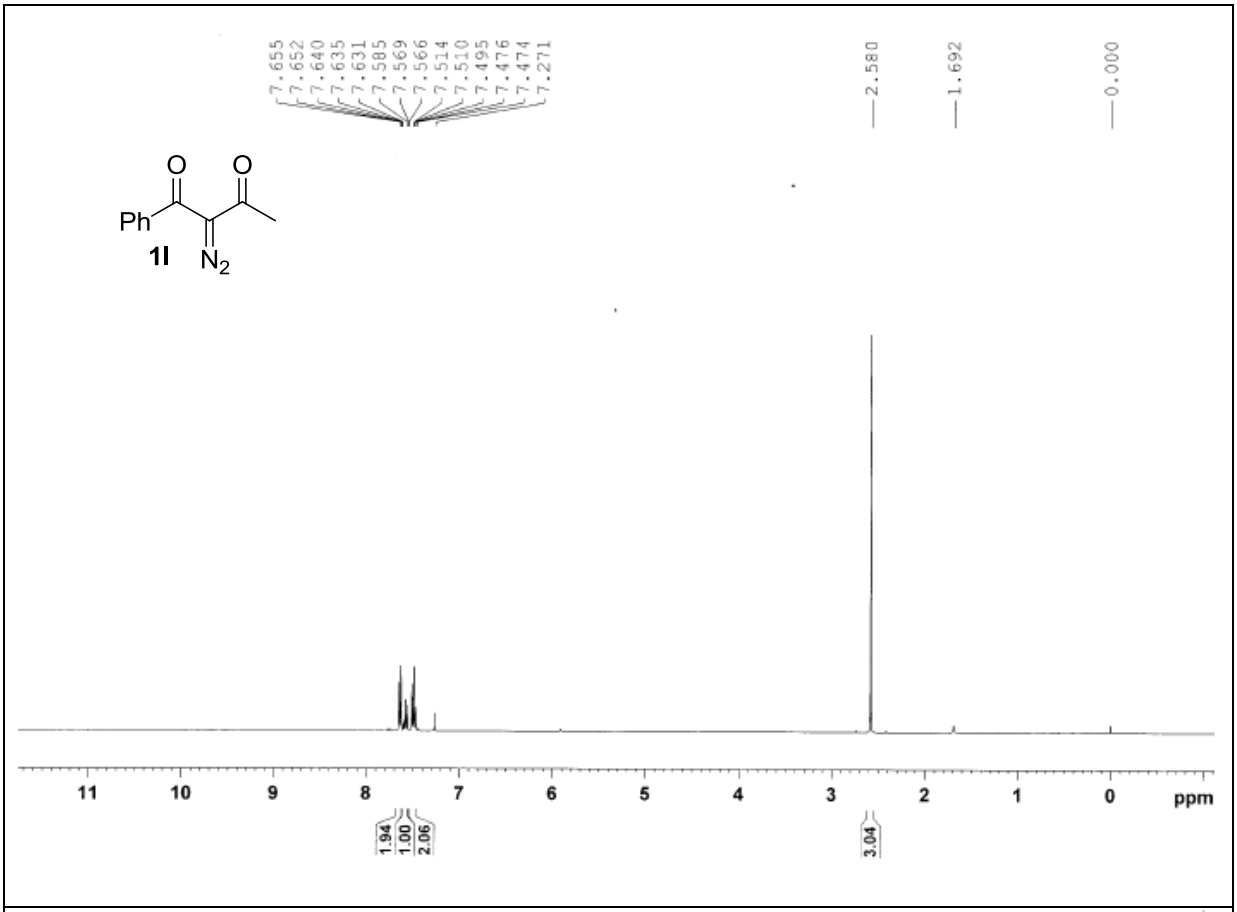

185.6037
160.3392
149.5773
142.5462
129.2563
123.0678
77.3547
77.0366
76.7193
61.9977
14.2113
200
150
100
50
[ppm]

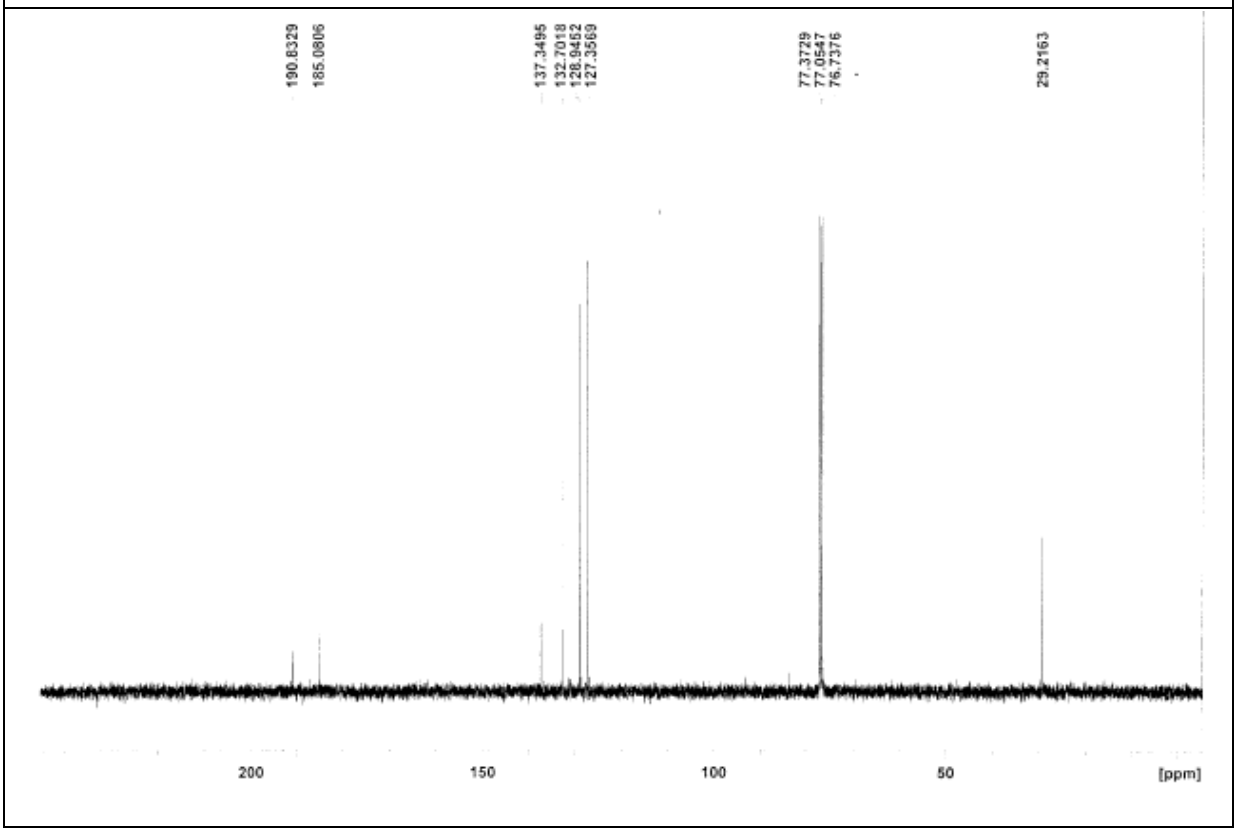

7.260
4.409
4.385
4.361
4.337
4.313
4.290
1.401
1.377
1.351
1.326
1.302
-0.003
EtO
O
O
OEt
O
N2
1i
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
6.01

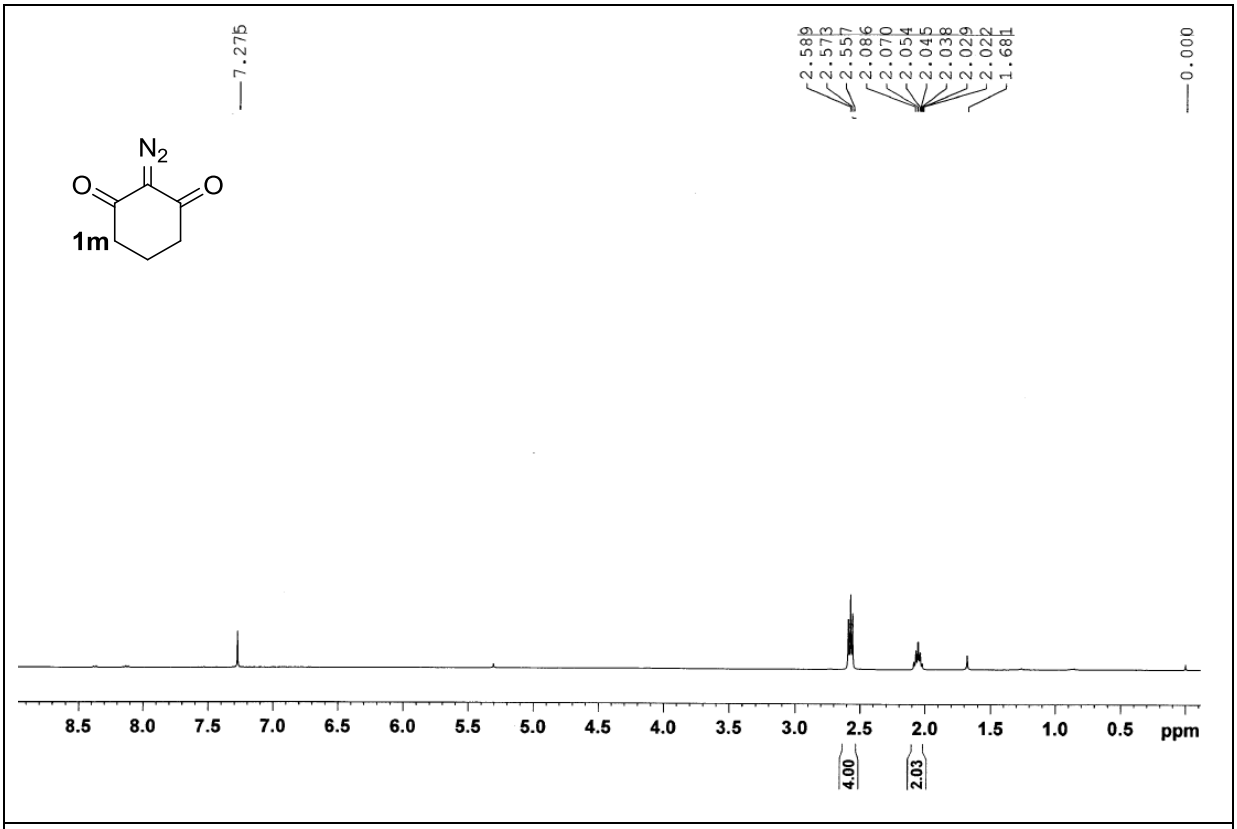

162.2628
159.8863
62.8169
62.3052
14.2147
13.8796
200
150
100
50
[ppm]






7.655
7.652
7.640
7.635
7.631
7.585
7.569
7.566
7.514
7.510
7.495
7.476
7.474
7.271
2.580
1.692
0.000
O
O
Ph
1l
N2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
1.00
2.06
3.04


190.8329
185.0806
137.3495
132.7018
128.9452
127.3569
77.3729
77.0547
76.7376
29.2163
200
150
100
50
[ppm]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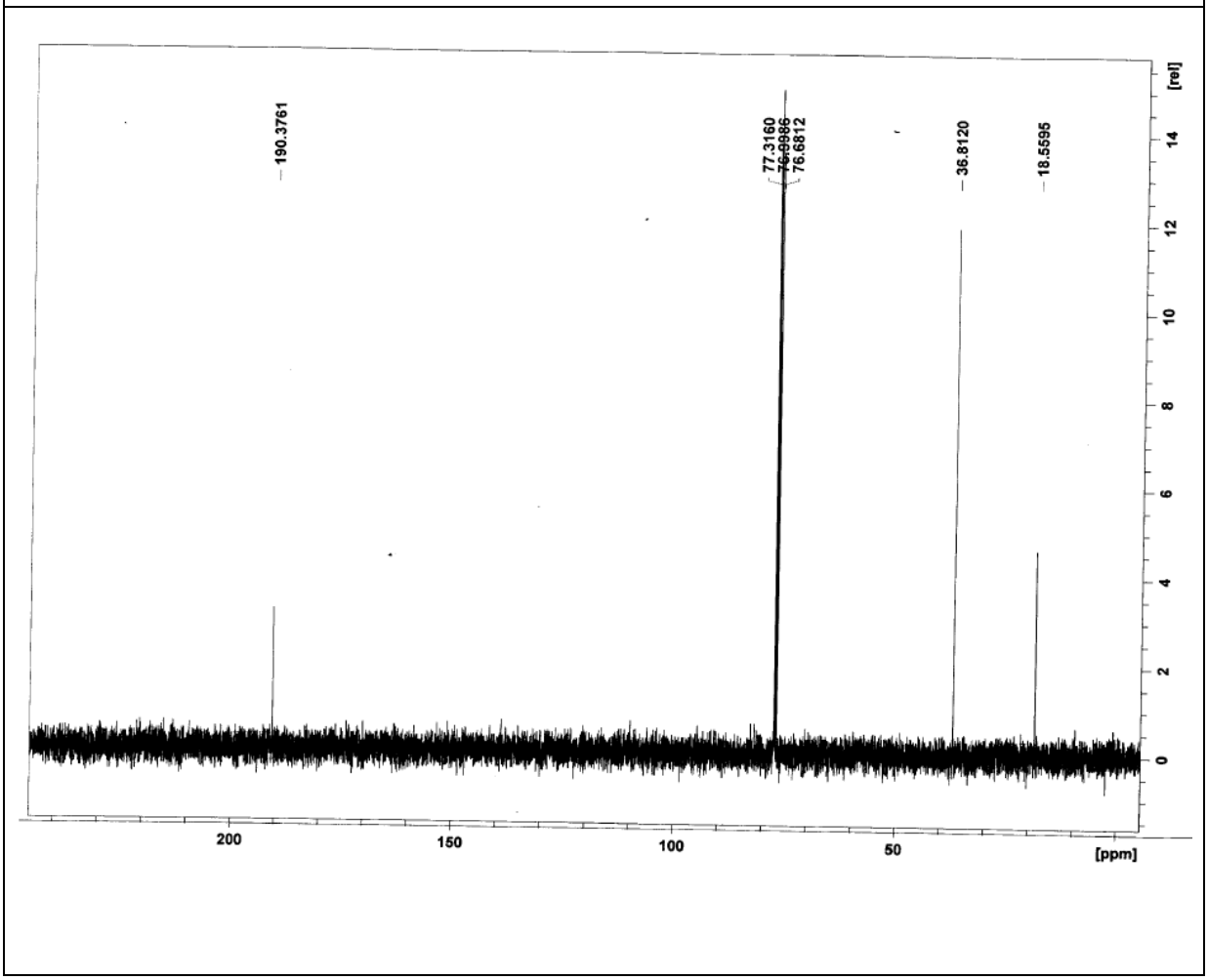
2.573
2.557
2.086
2.070
2.054
2.045
2.038
2.029
2.022
1.681
0.000
N2
O
O
1m
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
2.03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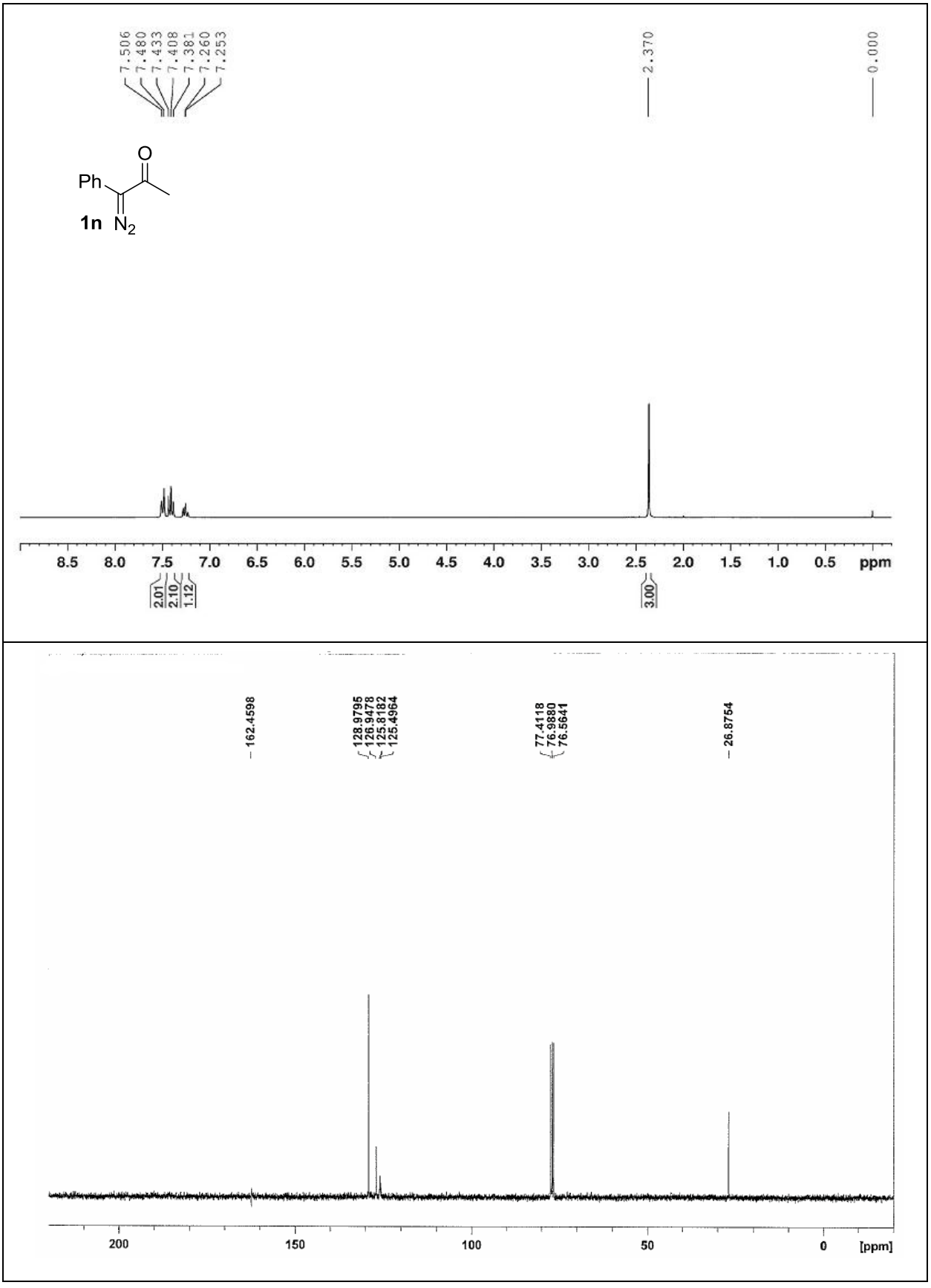
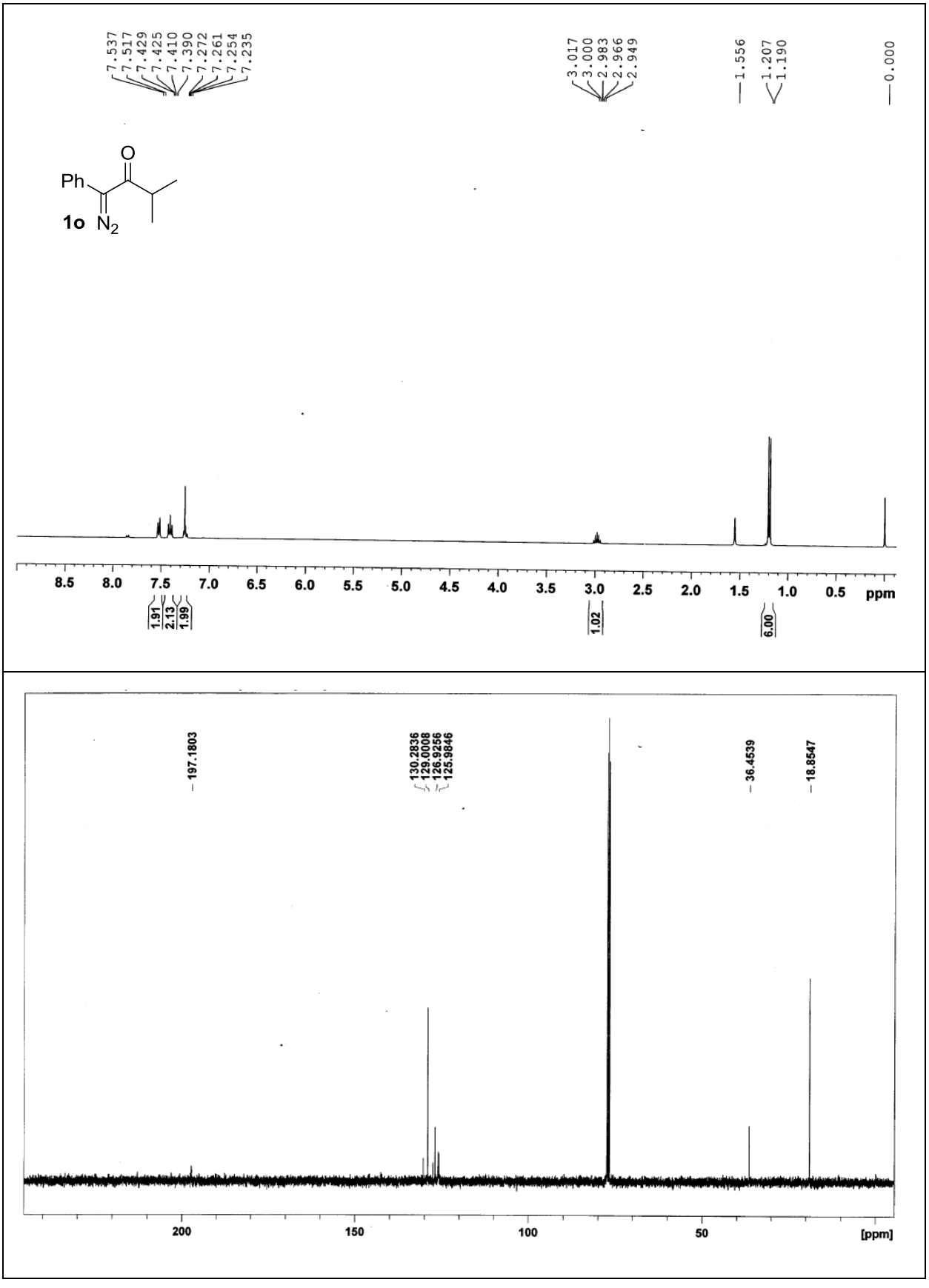
77.3160
76.9986
76.6812
36.8120
18.5595
[rel]
14
12
10
8
6
4
2
0
200
150
100
50
[ppm]

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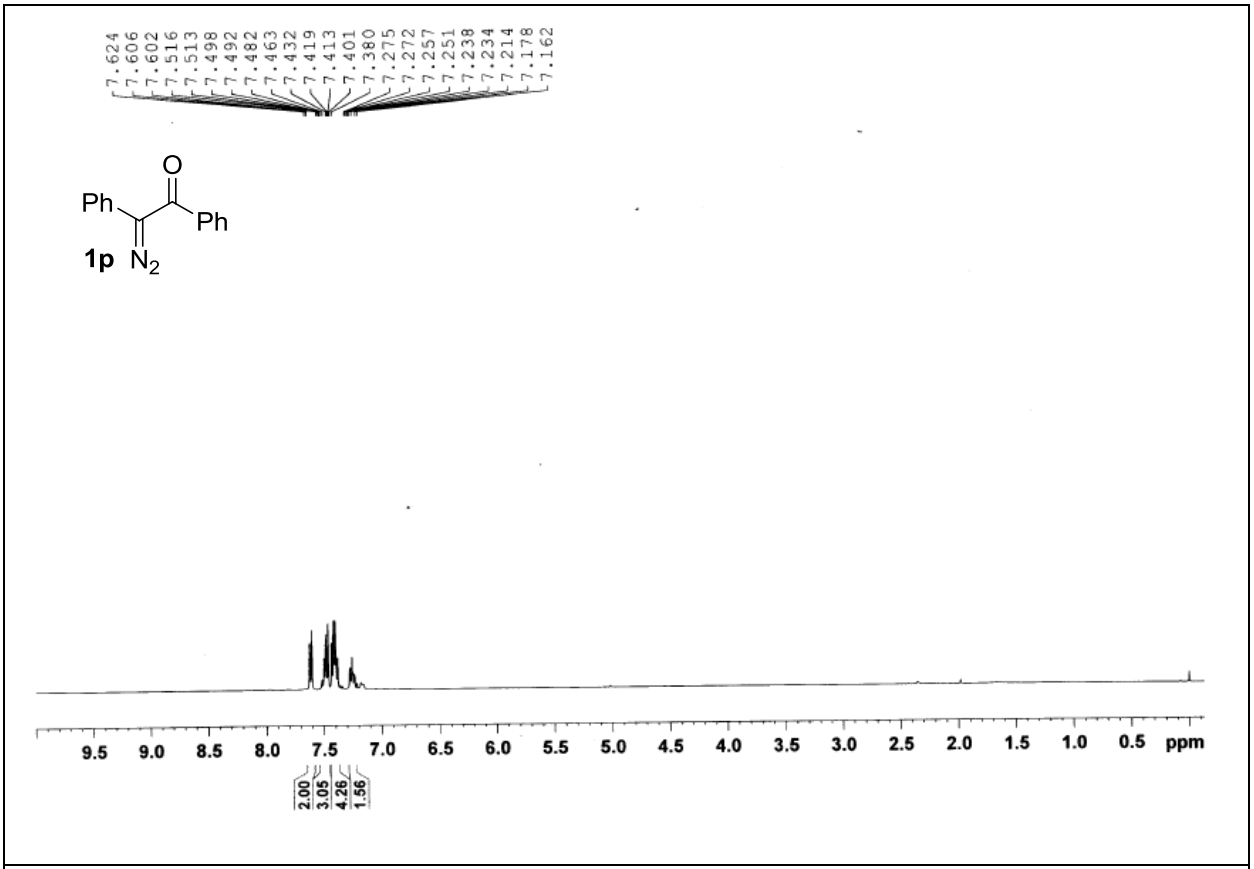
7.517
7.429
7.425
7.410
7.390
7.272
7.261
7.254
7.235
3.017
3.000
2.983
2.966
2.949
1.556
1.207
1.190
0.000
O
Ph
1o N2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.91
2.13
1.99
1.02
6.00
197.1803
130.2836
129.0008
126.9256
125.9846
36.4539
18.8547
200 150 100 50 [ppm]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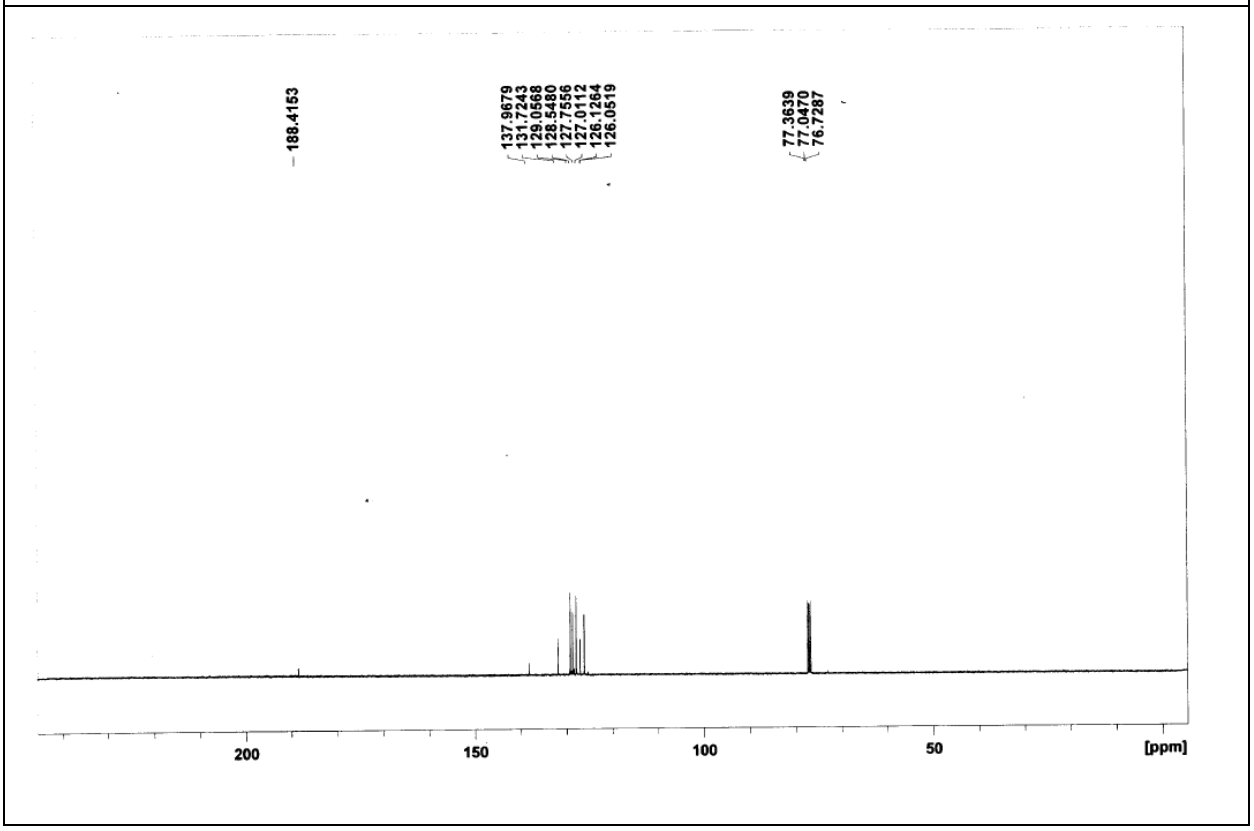
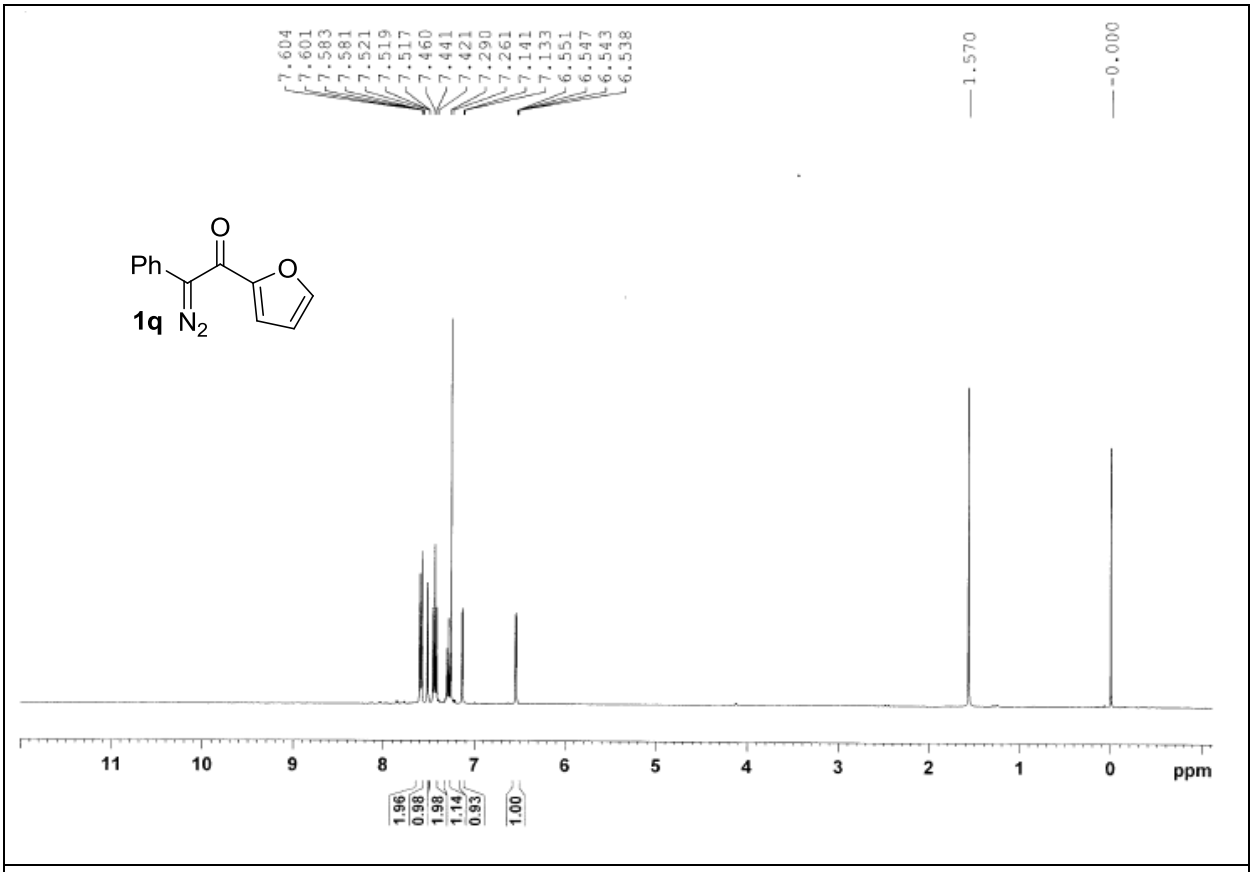
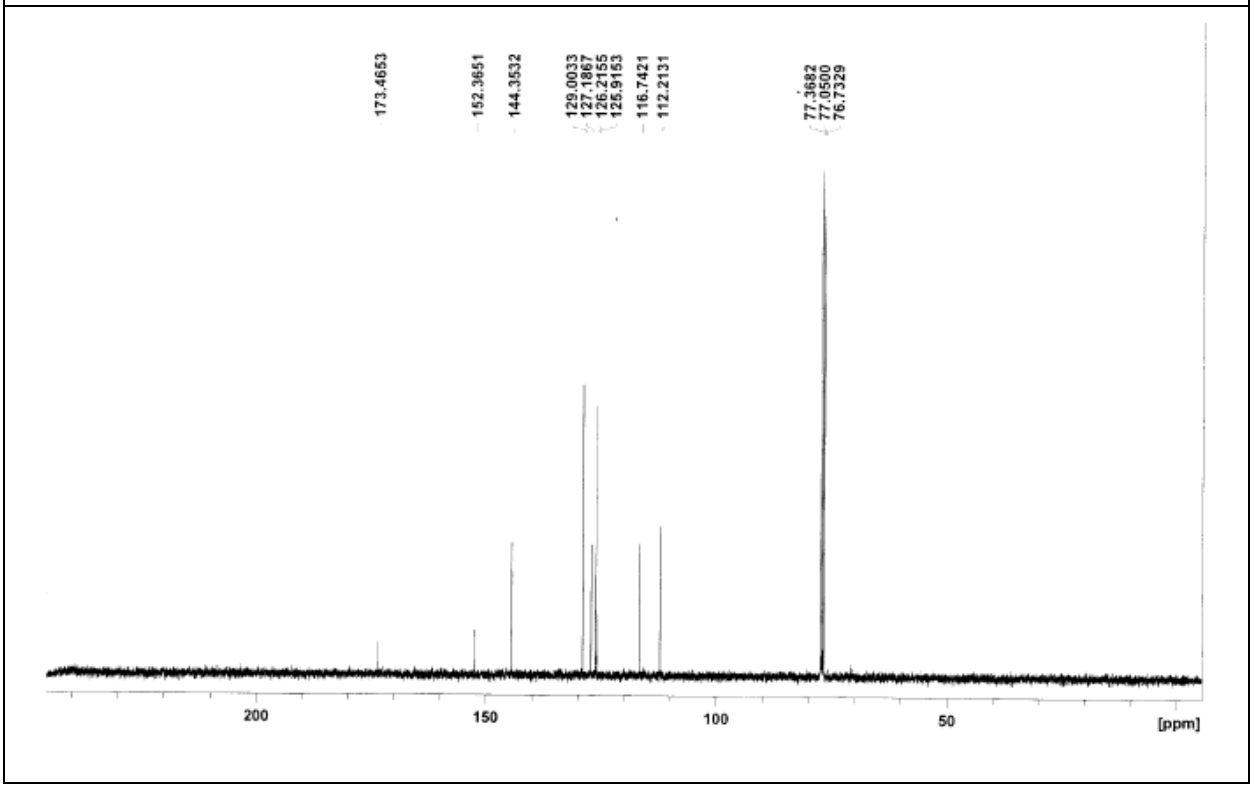
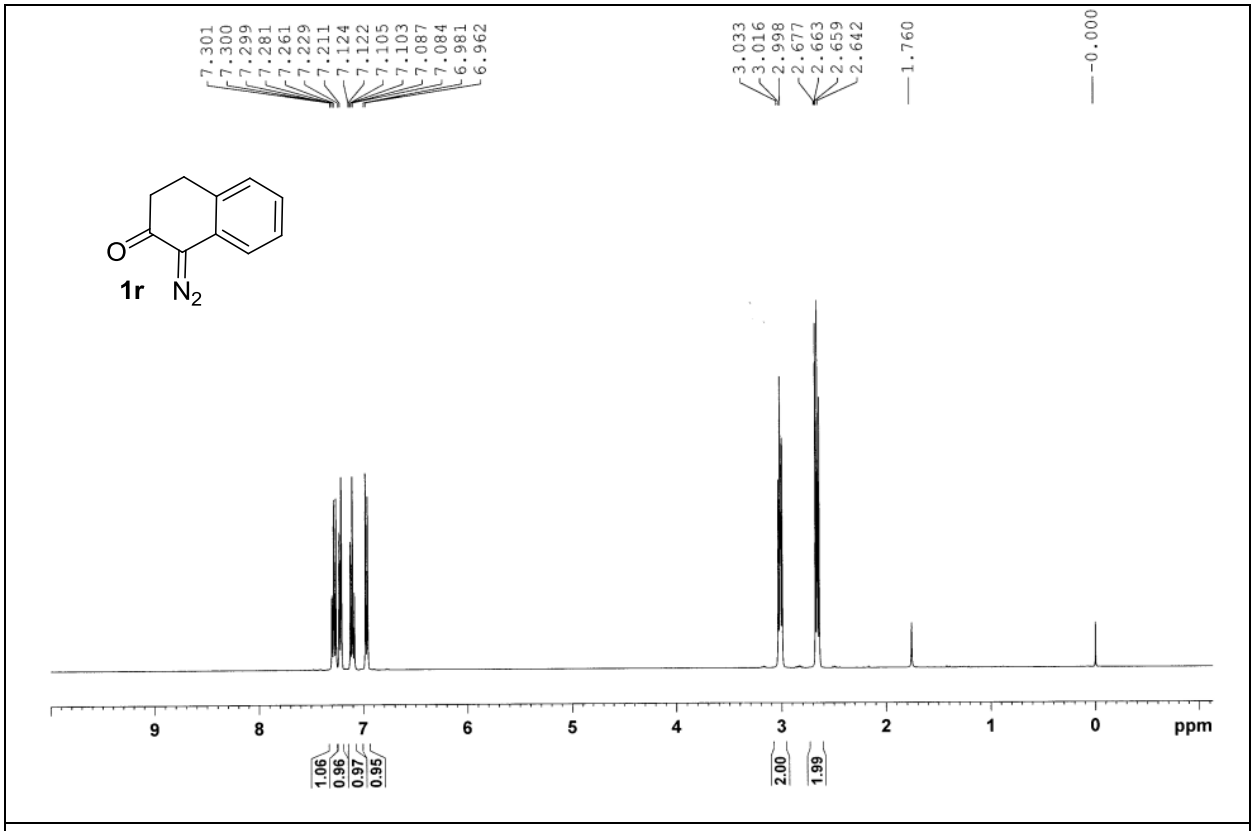
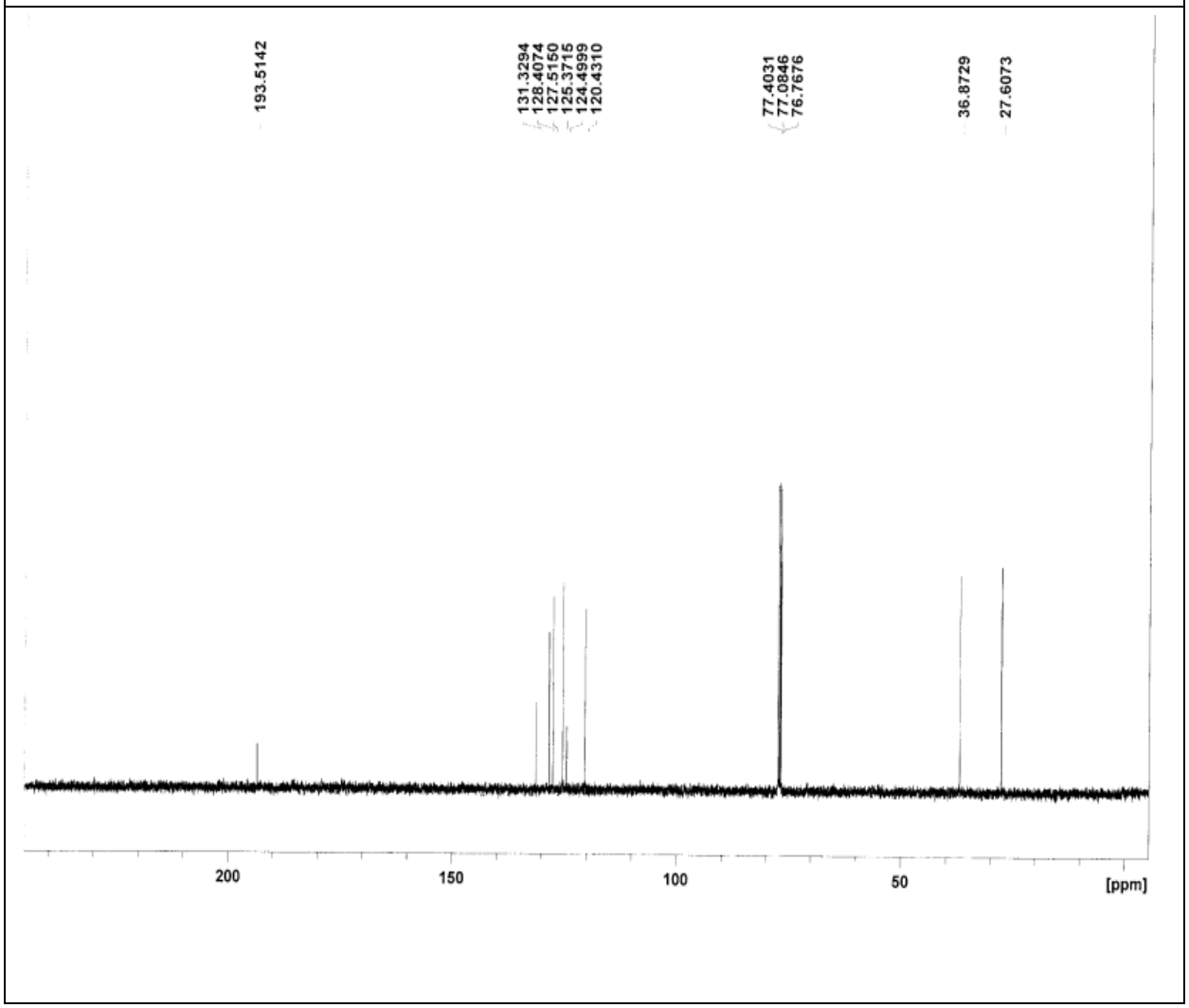
7.606
7.602
7.516
7.513
7.498
7.492
7.482
7.463
7.432
7.419
7.413
7.401
7.380
7.275
7.272
7.257
7.251
7.238
7.234
7.214
7.178
7.162
O
Ph
Ph
1p
N2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
3.05
4.26
1.56


188.4153
137.9679
131.7243
129.0568
128.5480
127.7556
127.0112
126.1264
126.0519
77.3639
77.0470
76.7287
200
150
100
50
[ppm]

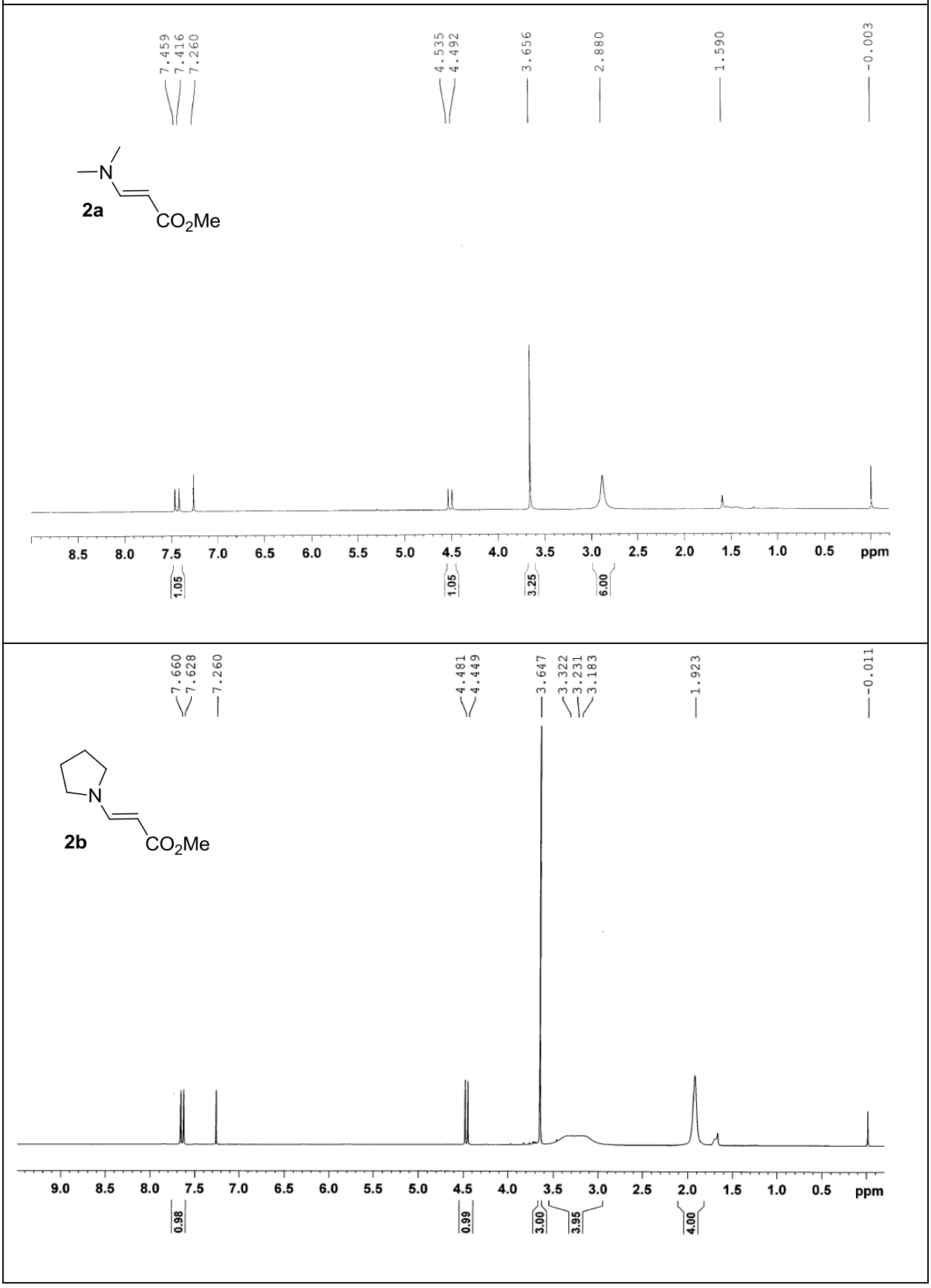

7.604
7.601
7.583
7.581
7.521
7.519
7.517
7.460
7.441
7.421
7.290
7.261
7.141
7.133
6.551
6.547
6.543
6.538
1.570
0.000
Ph
O
O
1q
N2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
0.98
1.98
1.14
0.93
1.00

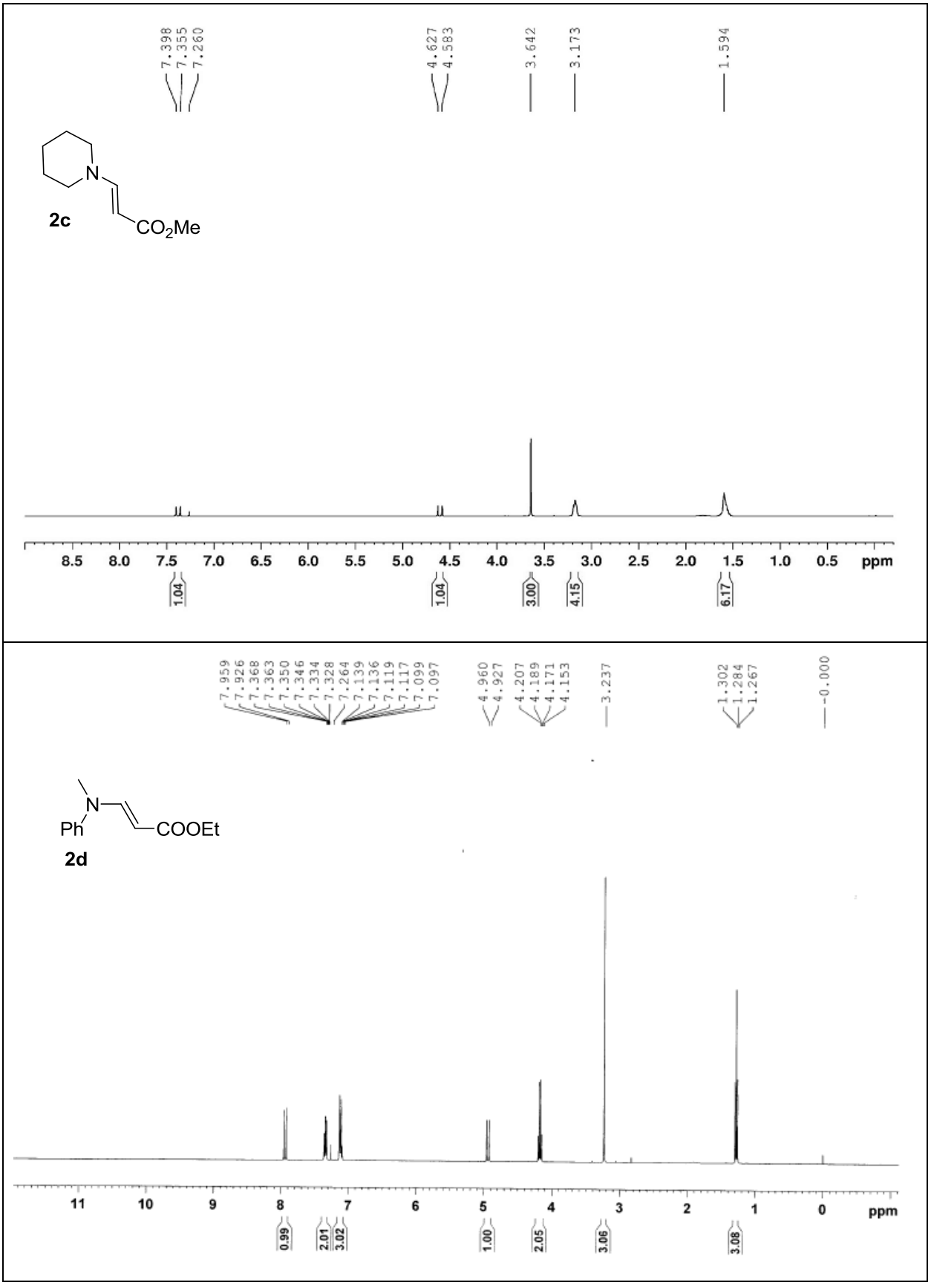

173.4653
152.3651
144.3532
129.0033
127.1867
126.2155
125.9153
116.7421
112.2131
77.3682
77.0500
76.7329
200
150
100
50
[ppm]

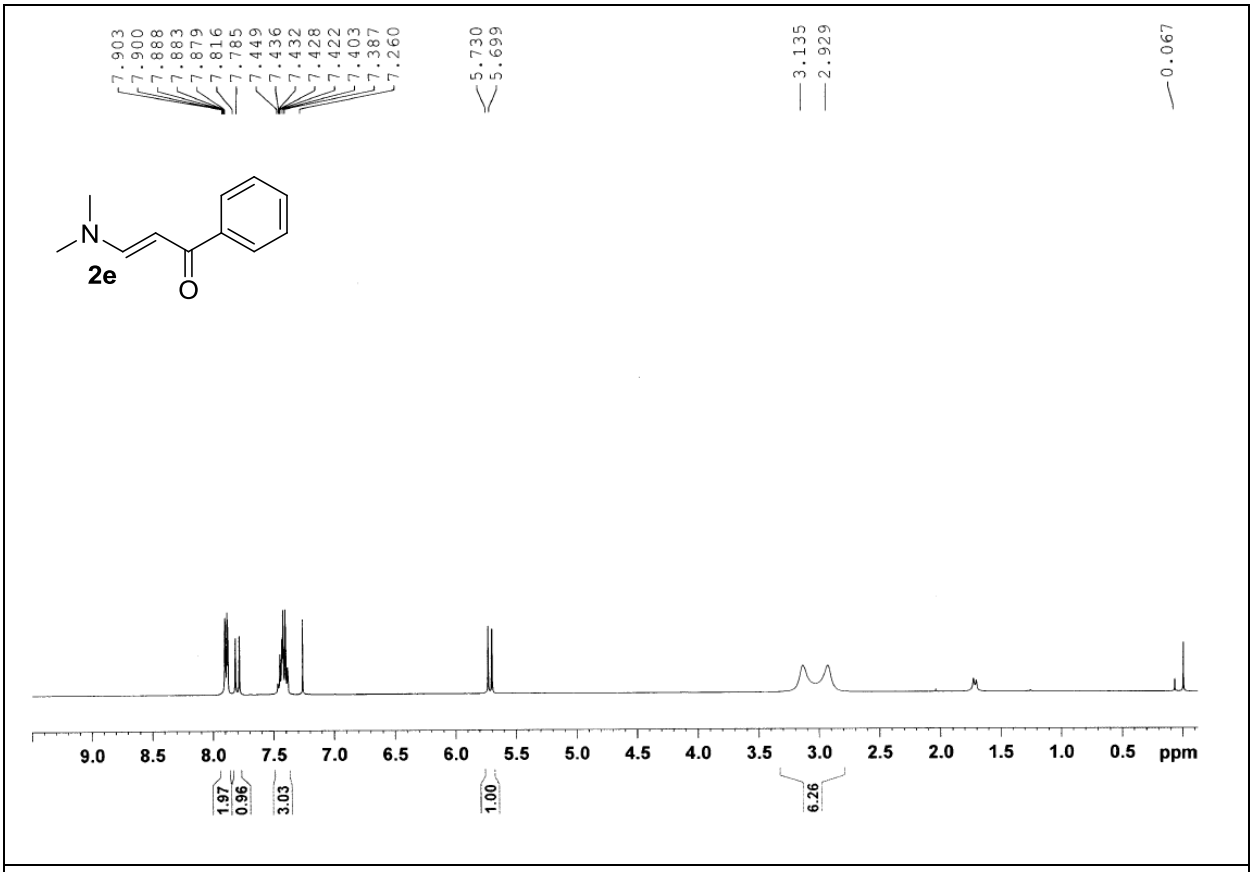

7.301
7.300
7.299
7.281
7.261
7.229
7.211
7.124
7.122
7.105
7.103
7.087
7.084
6.981
6.962
3.033
3.016
2.998
2.677
2.663
2.659
2.642
1.760
0.000
O
1r
N2
9
8
7
6
5
4
3
2
1
0
ppm
1.06
0.96
0.97
0.95
2.00
1.99


193.5142
131.3294
128.4074
127.5150
125.3715
124.4999
120.4310
77.4031
77.0846
76.7676
36.8729
27.6073
200
150
100
50
[ppm]

^{1}H spectra of enamines



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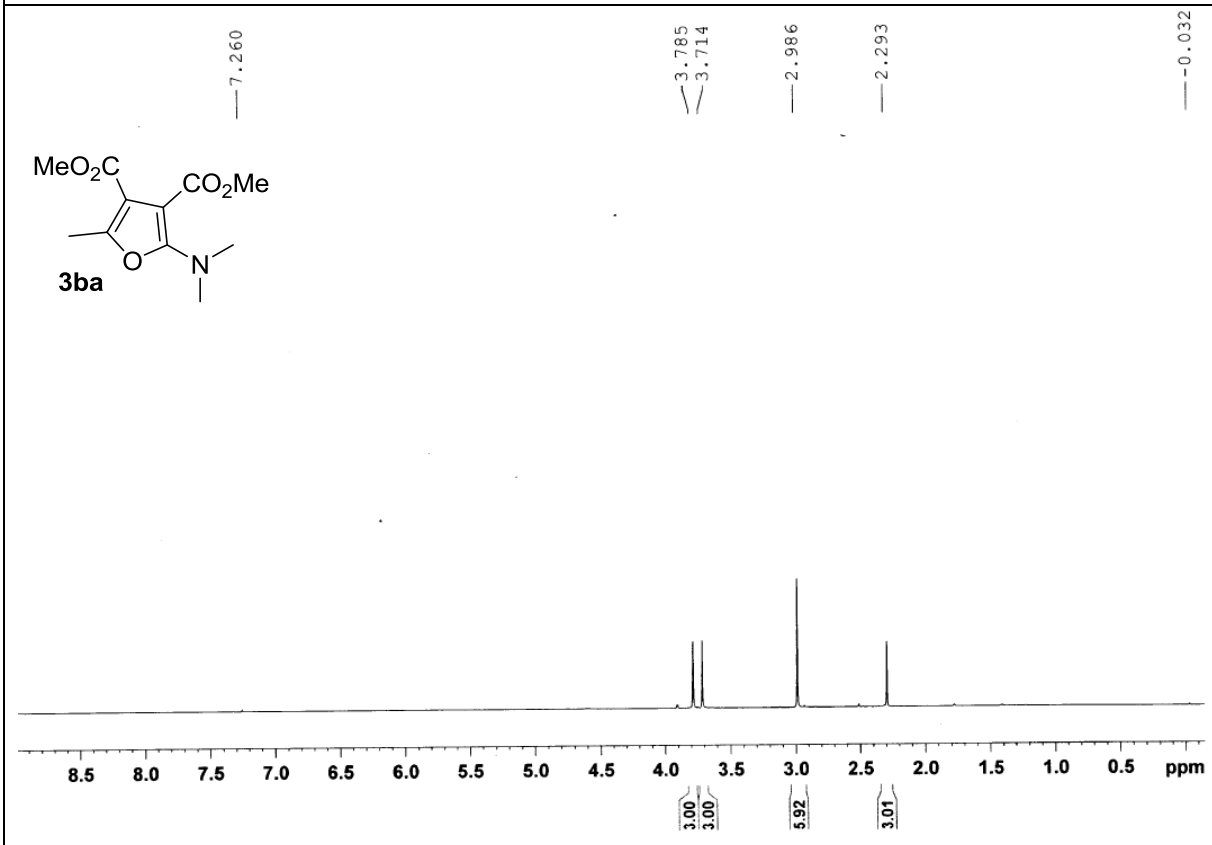
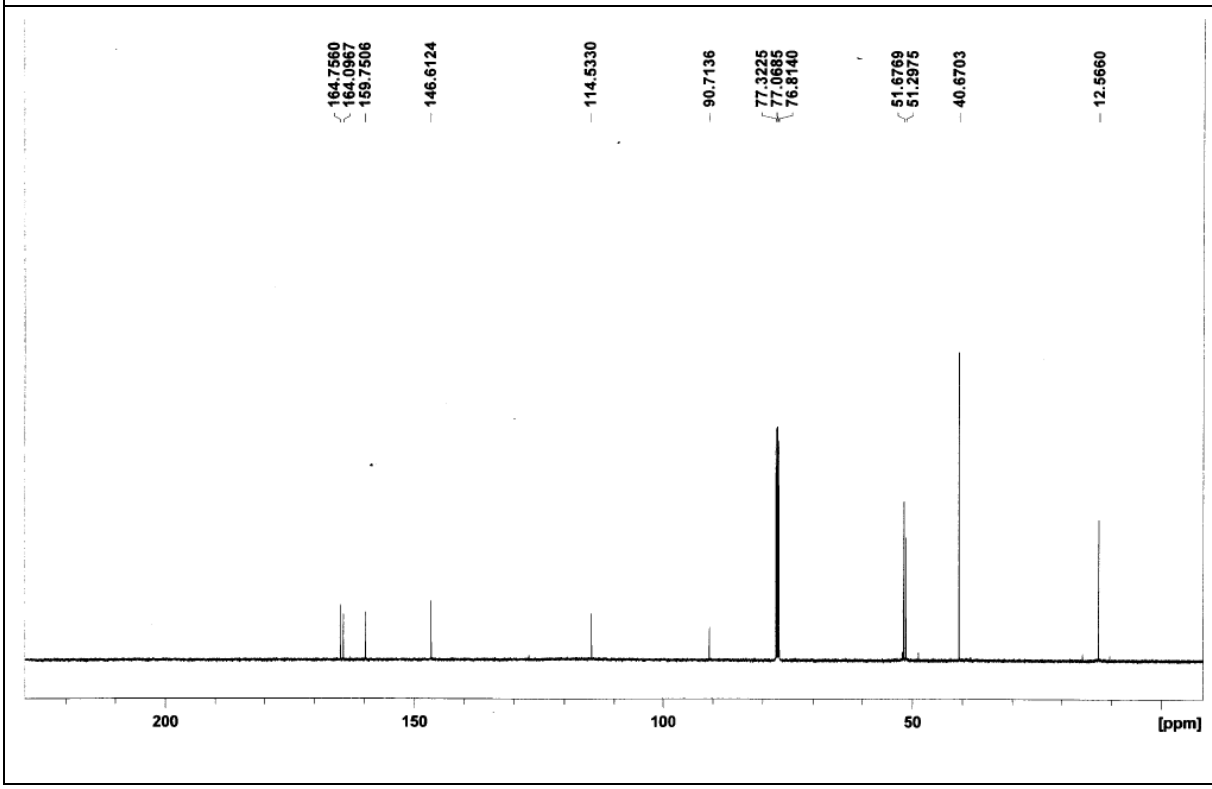
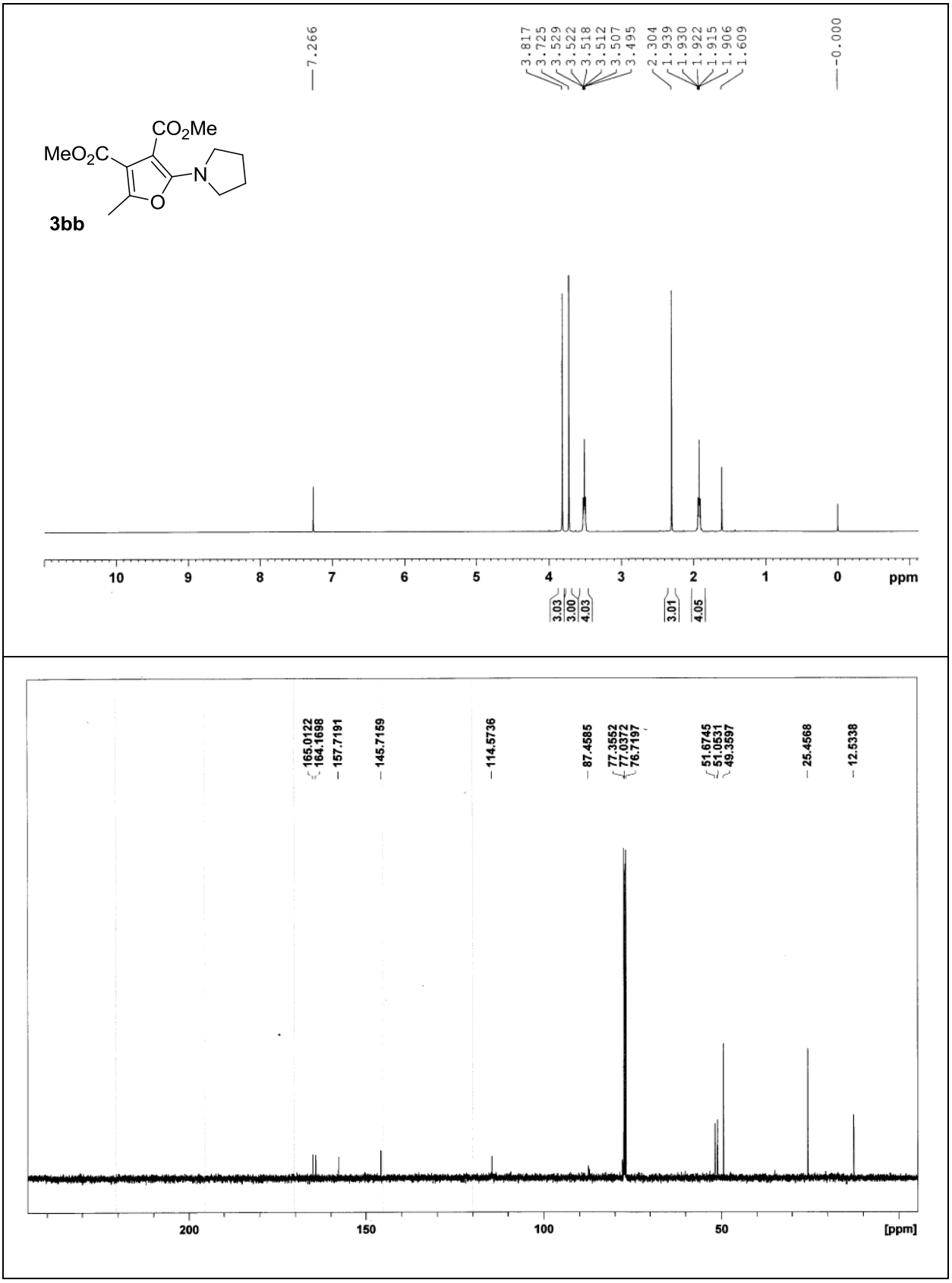
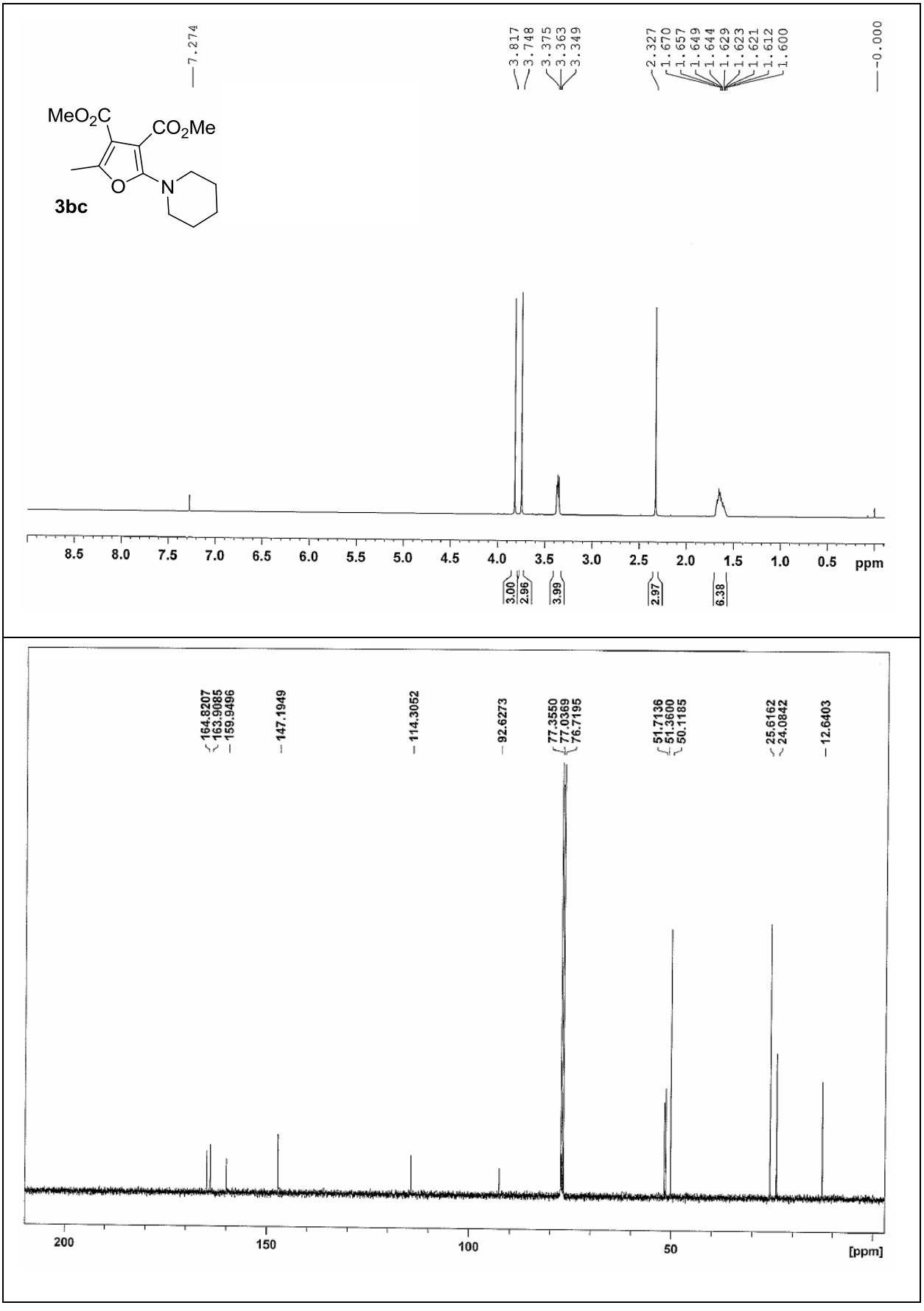
7.900
7.888
7.883
7.879
7.816
7.785
7.449
7.436
7.432
7.428
7.422
7.403
7.387
7.260
5.730
5.699
3.135
2.929
0.067
N
2e
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.97
0.96
3.03
1.00
6.26

^{1}H and ^{13}C NMR spectra of 2-aminofurans





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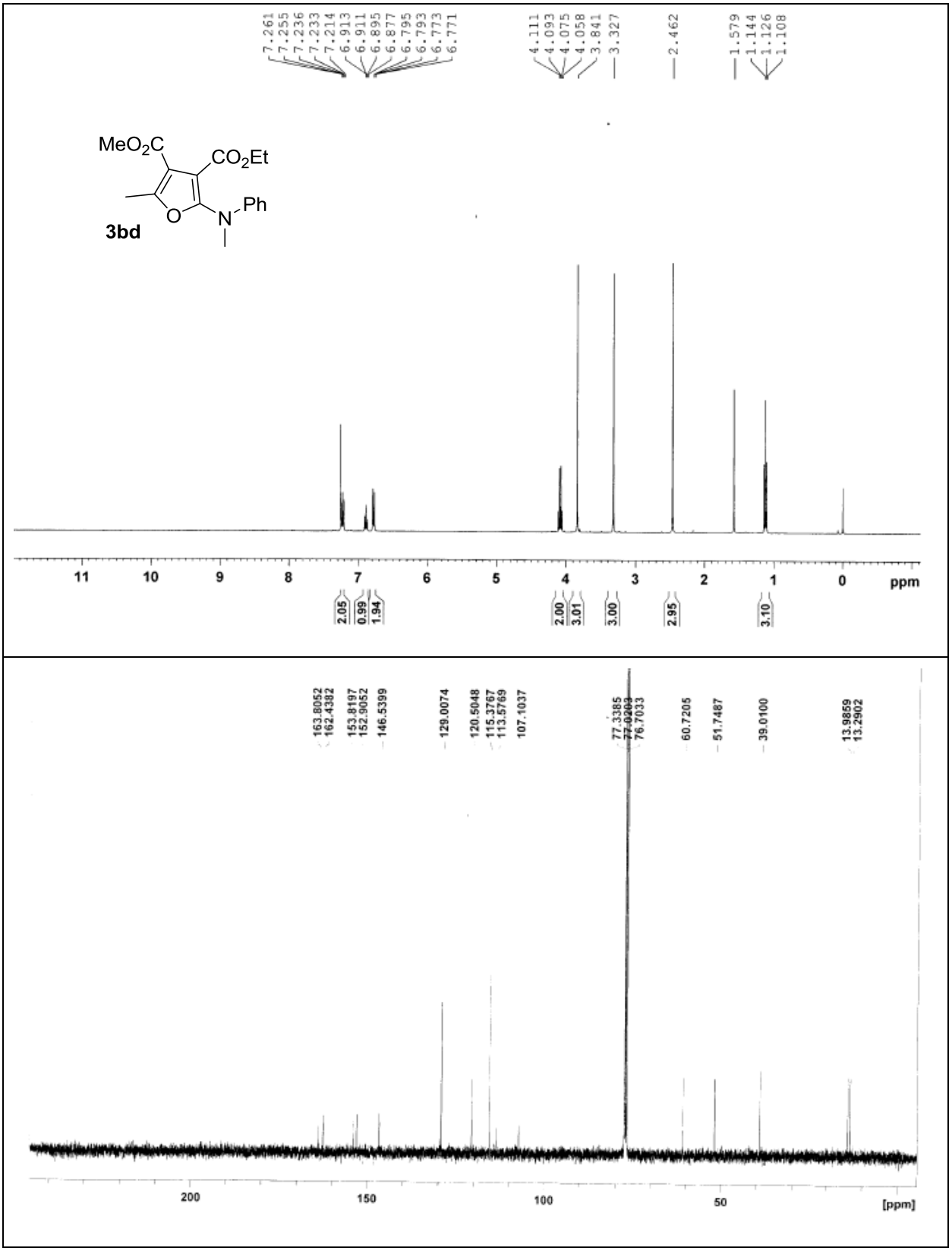
3.817
3.748
3.375
3.363
3.349
2.327
1.670
1.657
1.649
1.644
1.629
1.623
1.621
1.612
1.600
0.000
MeO2C
CO2Me
O
N
3bc
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.00
2.96
3.99
2.97
6.38
164.8207
163.9085
159.9496
147.1949
114.3052
92.6273
77.3550
77.0369
76.7195
51.7136
51.3600
50.1185
25.6162
24.0842
12.6403
200
150
100
50
[ppm]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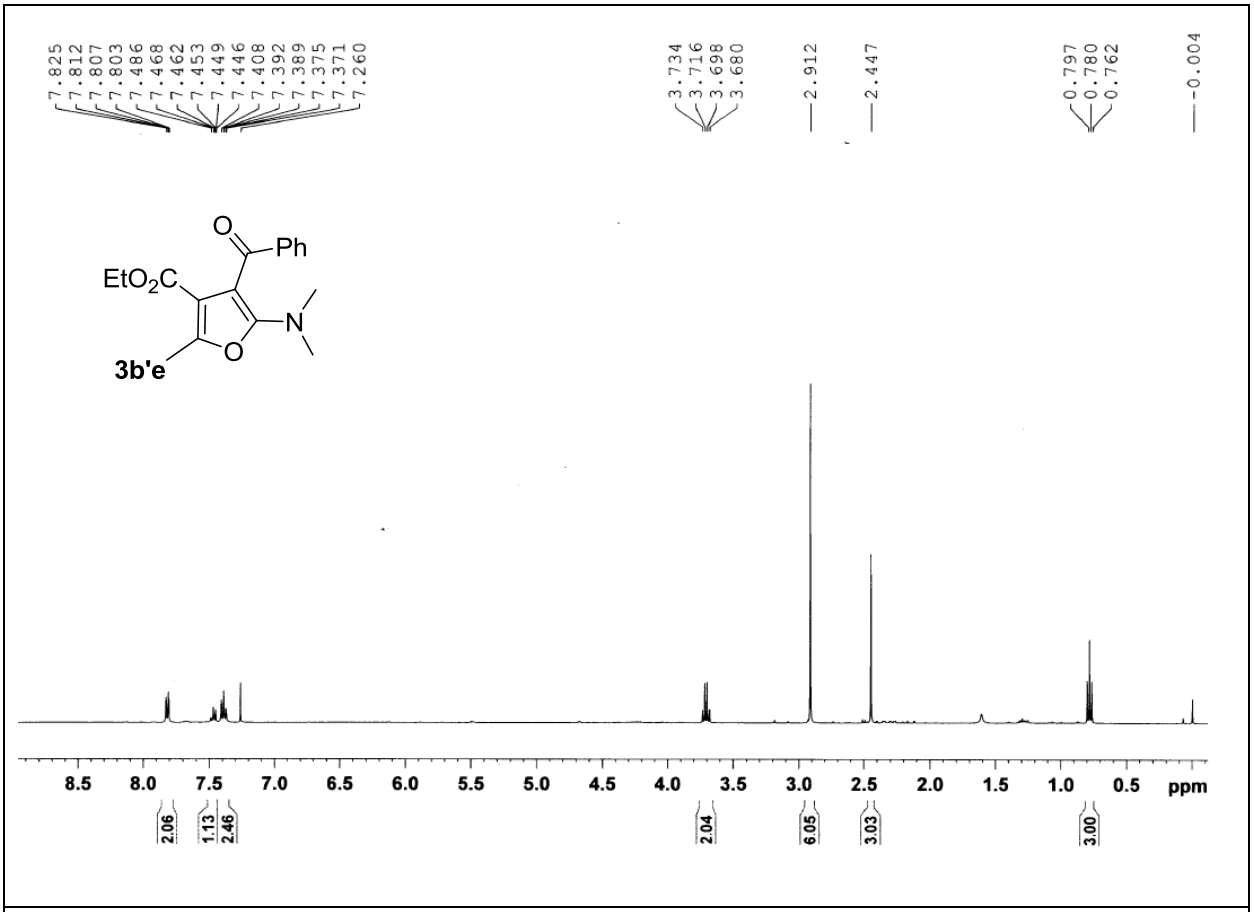
7.255
7.236
7.233
7.214
6.913
6.911
6.895
6.877
6.795
6.793
6.773
6.771
4.111
4.093
4.075
4.058
3.841
3.327
2.462
1.579
1.144
1.126
1.108
MeO2C
CO2Et
O
N
Ph
3bd
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
0.99
1.94
2.00
3.01
3.00
2.95
3.10
163.8052
162.4382
153.8197
152.9052
146.5399
129.0074
120.5048
115.3767
113.5769
107.1037
77.3385
77.0269
76.7033
60.7205
51.7487
39.0100
13.9859
13.2902
200
150
100
50
[ppm]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7.807
7.803
7.486
7.468
7.462
7.453
7.449
7.446
7.408
7.392
7.389
7.375
7.371
7.260
3.734
3.716
3.698
3.680
2.912
2.447
0.797
0.780
0.762
-0.004
O
Ph
EtO2C
N
O
3b'e
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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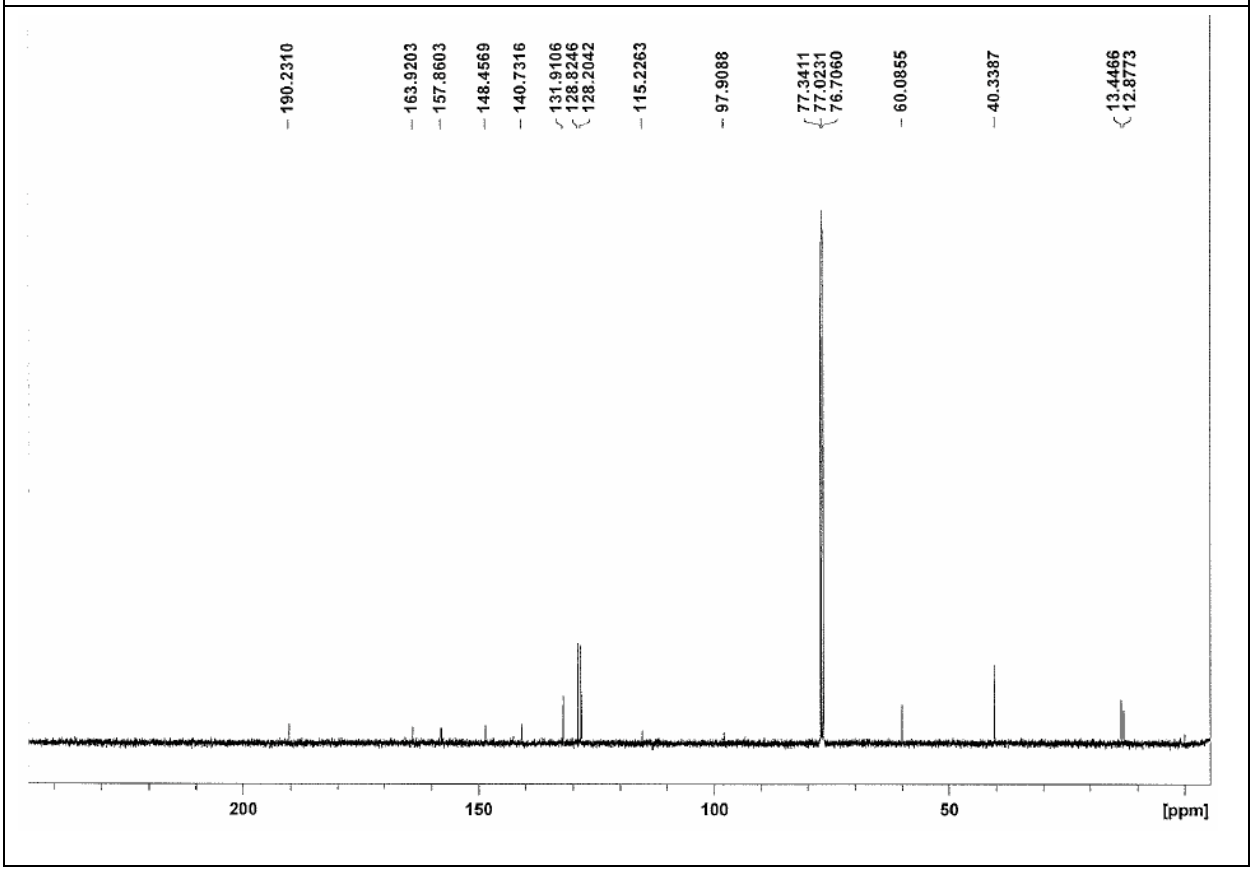
1.13
2.46
2.04
6.05
3.03
3.00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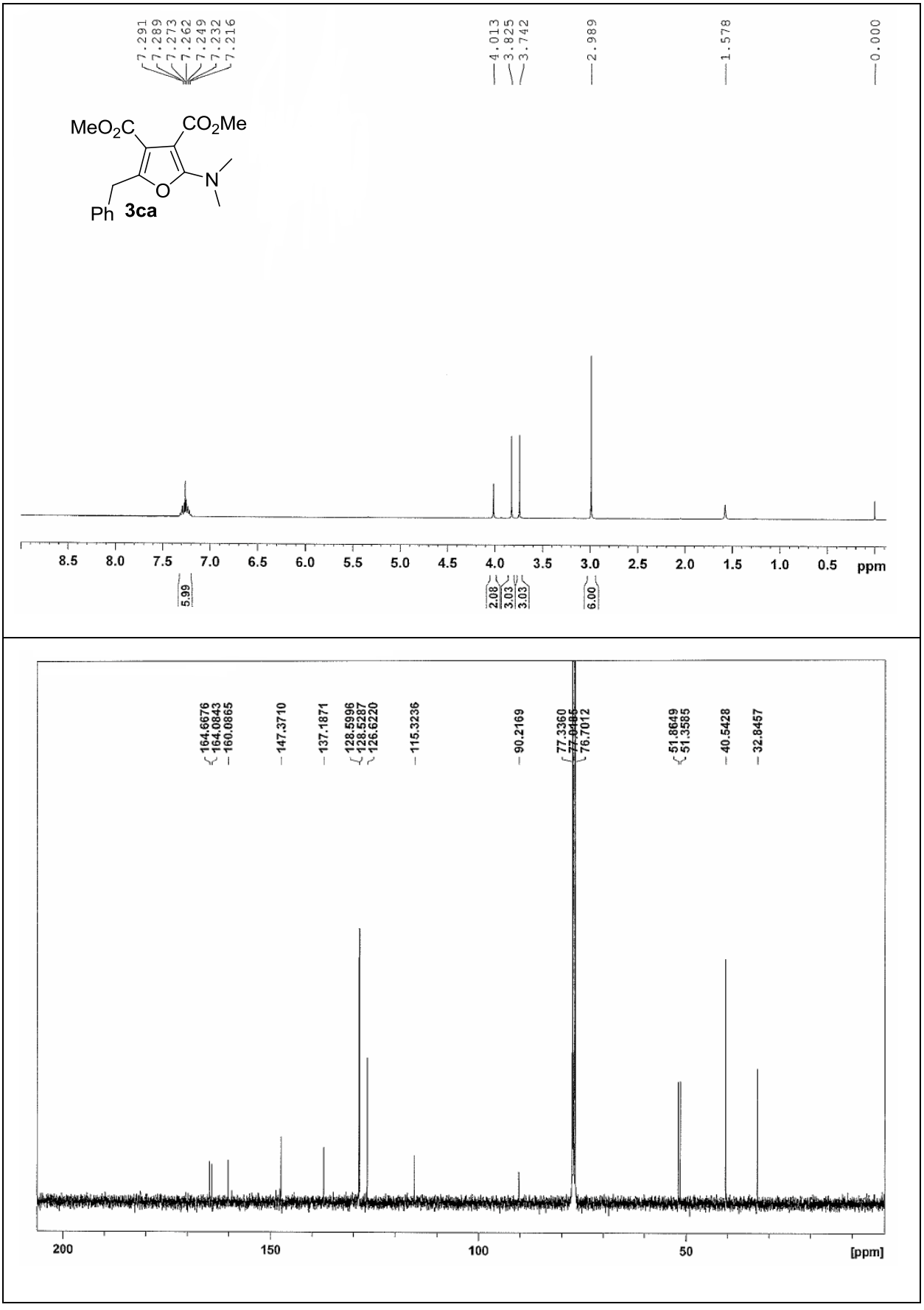
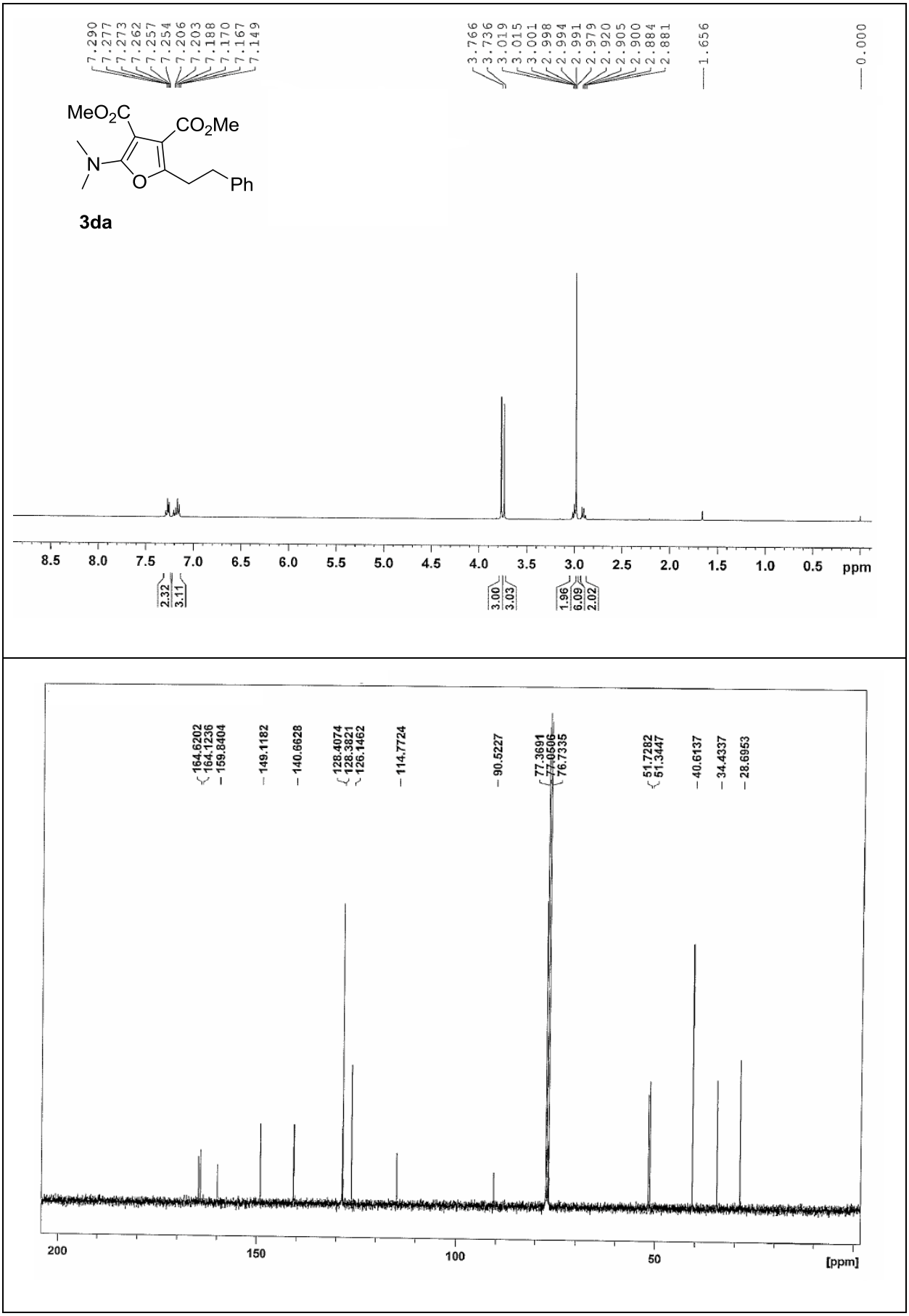
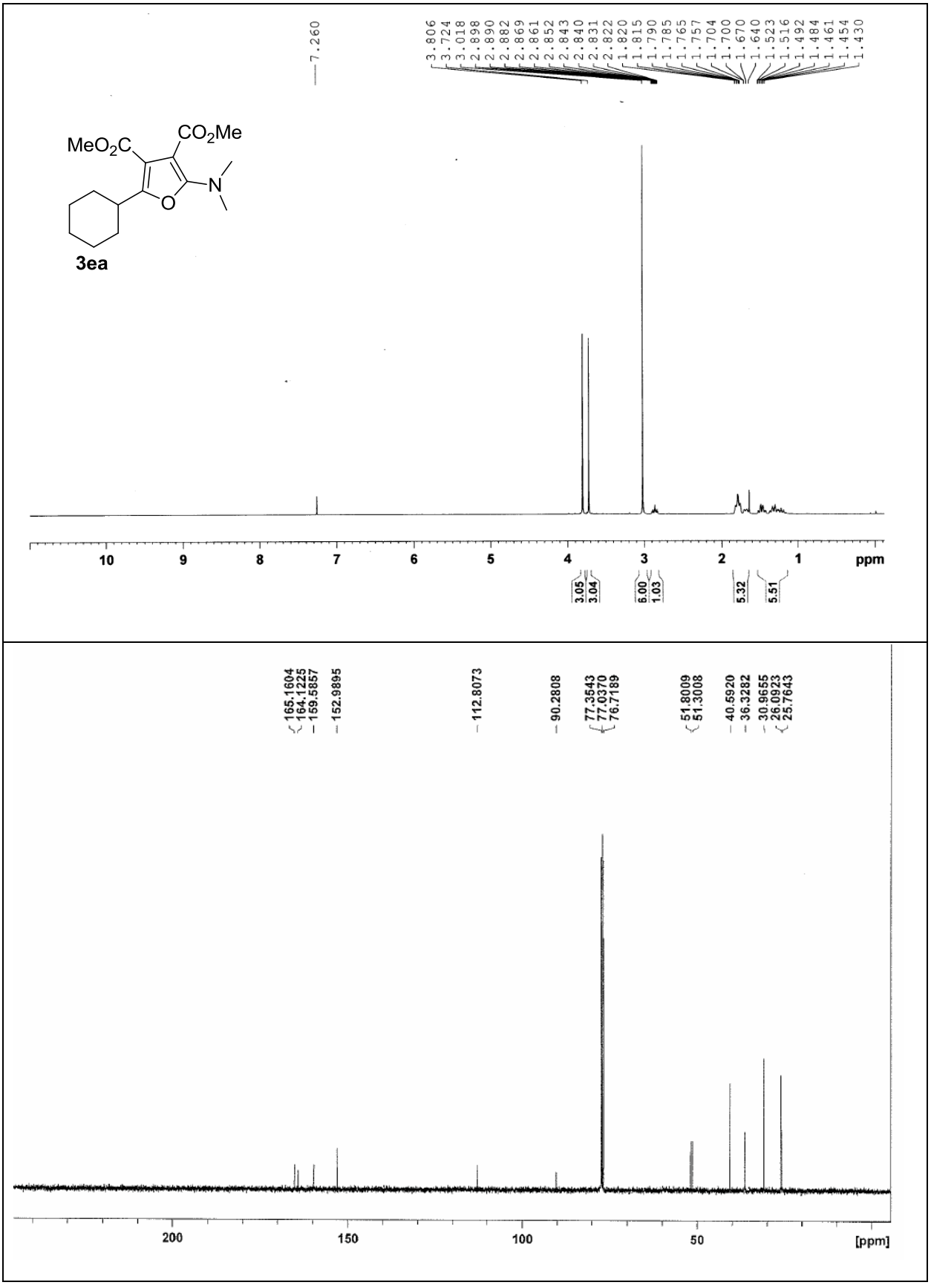
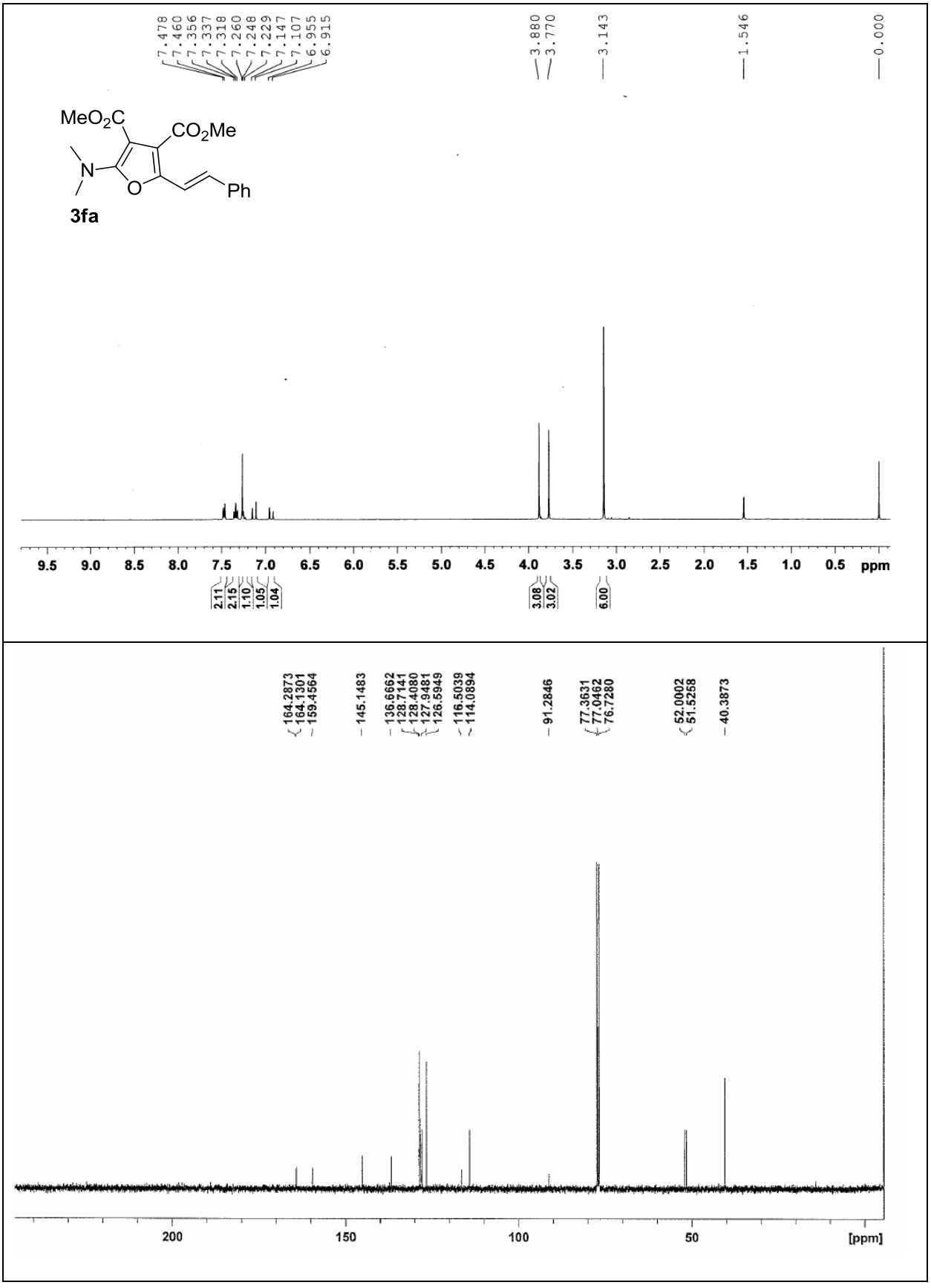
157.8603
148.4569
140.7316
131.9106
128.8246
128.2042
115.2263
97.9088
77.3411
77.0231
76.7060
60.0855
40.3387
13.4466
12.8773
200
150
100
50
[ppm]




7.290
7.277
7.273
7.262
7.257
7.254
7.206
7.203
7.188
7.170
7.167
7.149
3.766
3.736
3.019
3.015
3.001
2.998
2.994
2.991
2.979
2.920
2.905
2.900
2.884
2.881
1.656
0.000
MeO2C
CO2Me
N
O
Ph
3da
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
2.32
3.11
3.00
3.03
1.96
6.09
2.02
164.6202
164.1236
159.8404
149.1182
140.6628
128.4074
128.3821
126.1462
114.7724
90.5227
77.3691
77.0506
76.7335
51.7282
51.3447
40.6137
34.4337
28.6953
200
150
100
50
[ppm]

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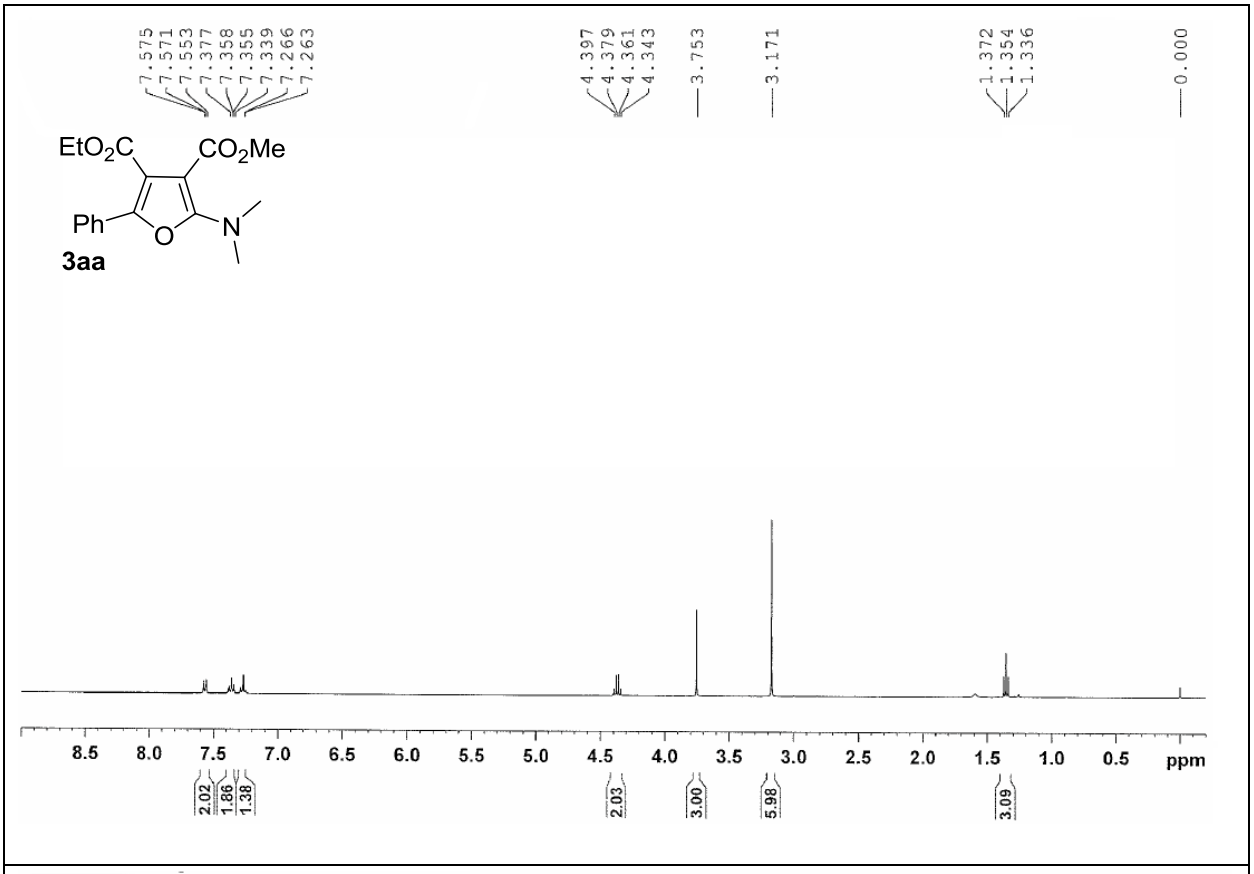
7.337
7.318
7.260
7.248
7.229
7.147
7.107
6.955
6.915
3.880
3.770
3.143
1.546
0.000
MeO2C
CO2Me
N
O
Ph
3fa
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.11
2.15
1.10
1.05
1.04
3.08
3.02
6.00
164.2873
164.1301
159.4564
145.1483
136.6662
128.7141
128.4080
127.9481
126.5949
116.5039
114.0894
91.2846
77.3631
77.0462
76.7280
52.0002
51.5258
40.3873
200 150 100 50 [ppm]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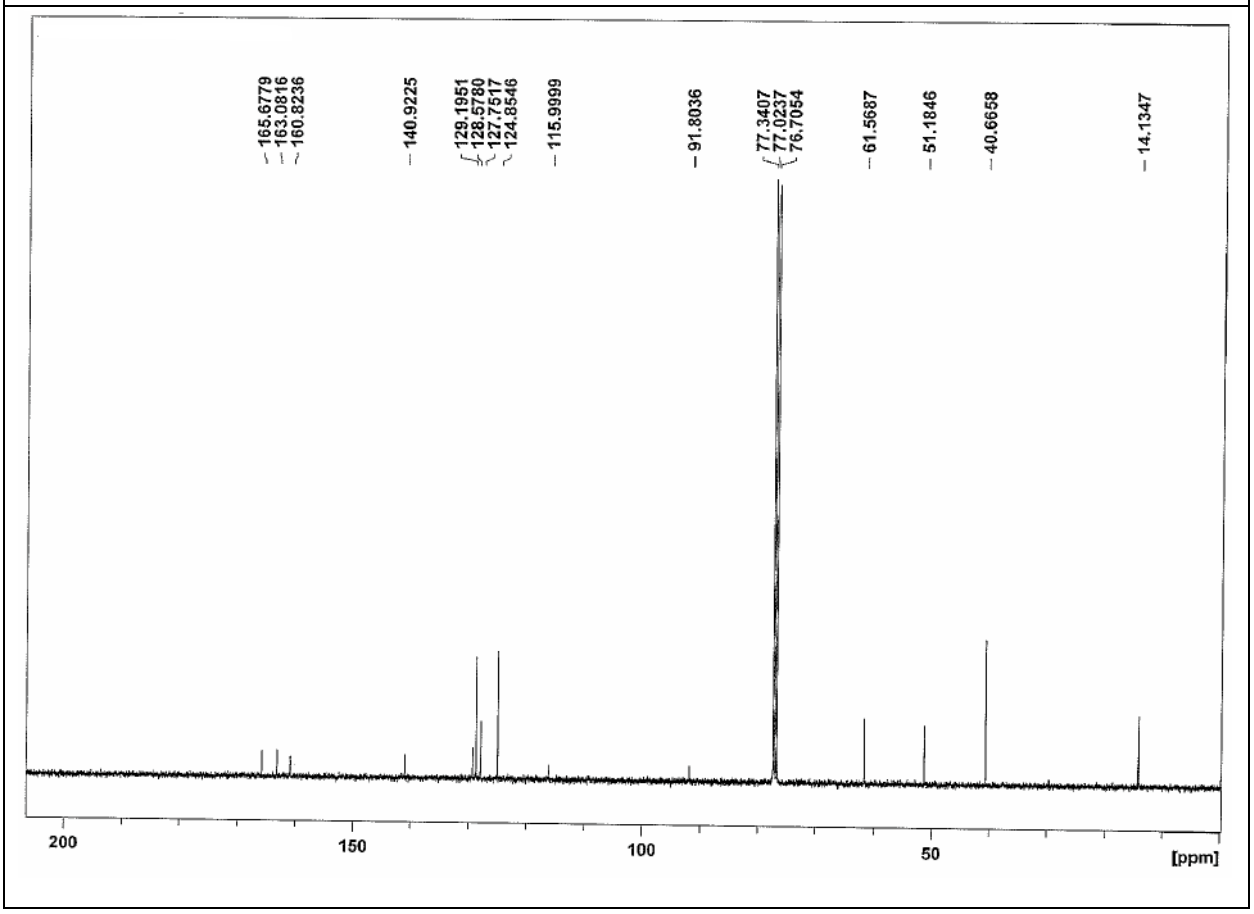
7.553
7.377
7.358
7.355
7.339
7.266
7.263
4.397
4.379
4.361
4.343
3.753
3.171
1.372
1.354
1.336
0.000
EtO2C
CO2Me
Ph
O
N
3aa
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
1.86
1.38
2.03
3.00
5.98
3.09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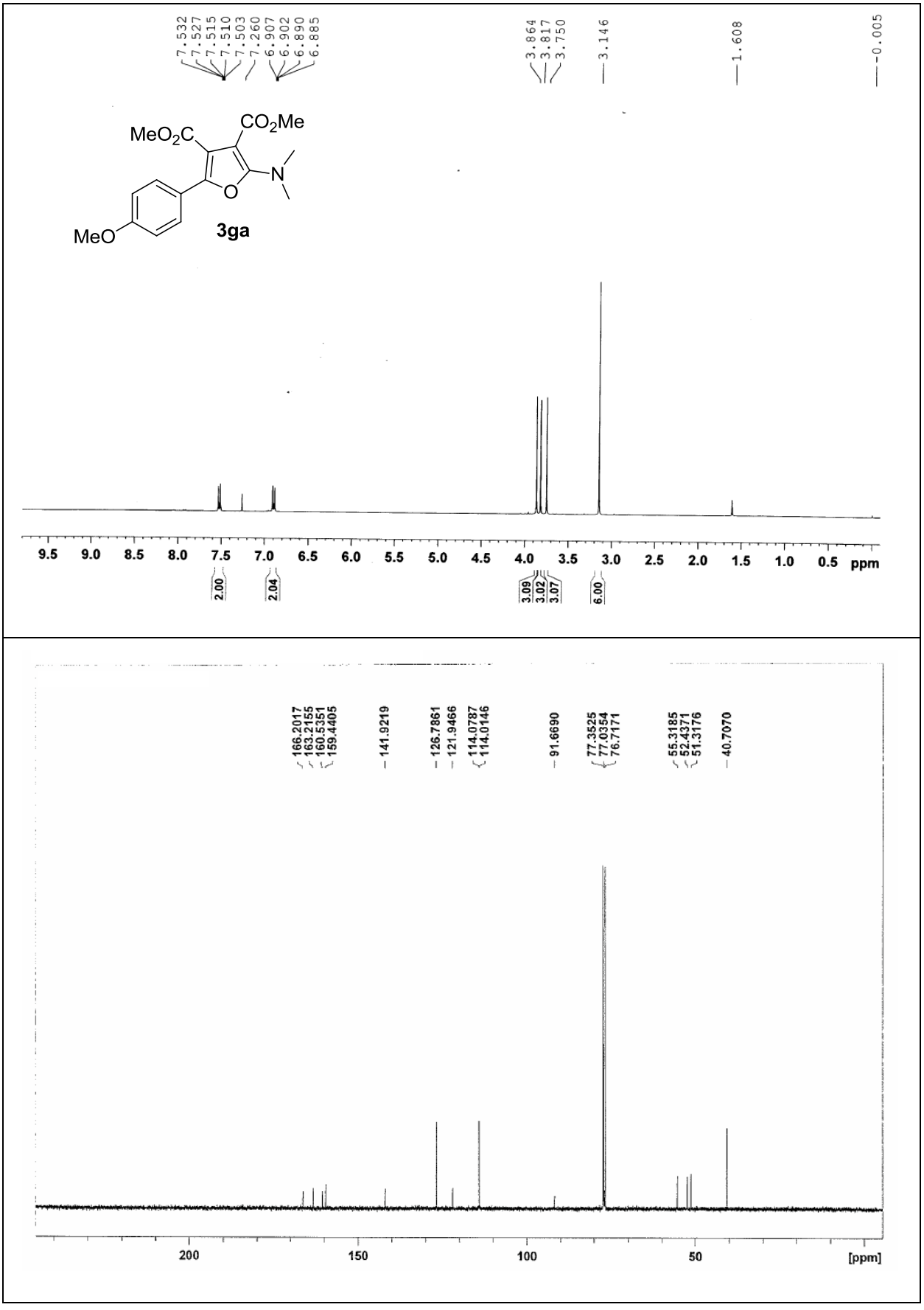
160.8236
140.9225
129.1951
128.5780
127.7517
124.8546
115.9999
91.8036
77.3407
77.0237
76.7054
61.5687
51.1846
40.6658
14.1347
200
150
100
50
[ppm]


7.532
7.527
7.515
7.510
7.503
7.260
6.907
6.902
6.890
6.885
3.864
3.817
3.750
3.146
1.608
-0.005
MeO2C
CO2Me
N
O
MeO
3ga
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
2.00
2.04
3.09
3.02
3.07
6.00
166.2017
163.2155
160.5351
159.4405
141.9219
126.7861
121.9466
114.0787
114.0146
91.6690
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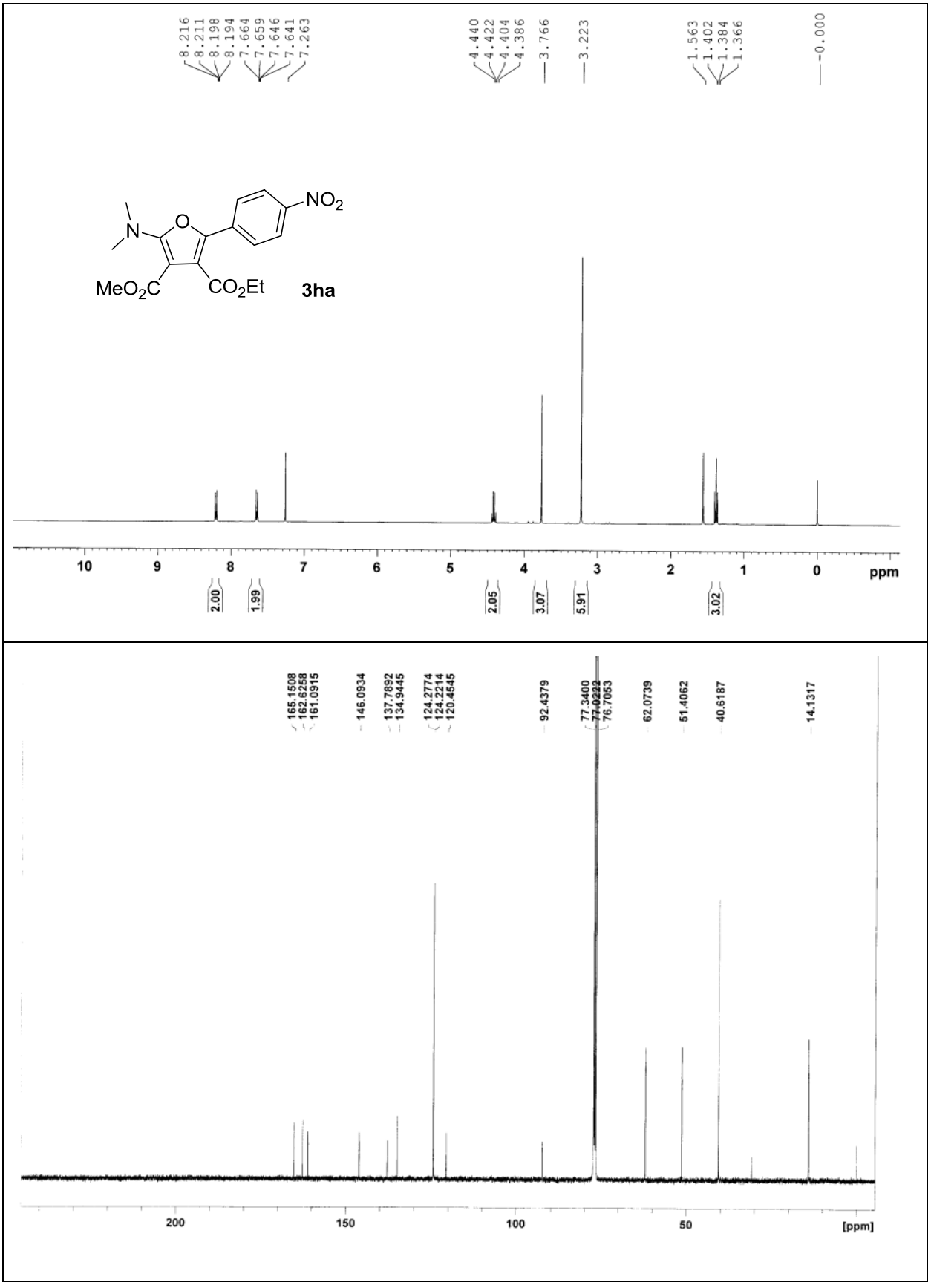
77.0354
76.7171
55.3185
52.4371
51.3176
40.7070
200
150
100
50
[ppm]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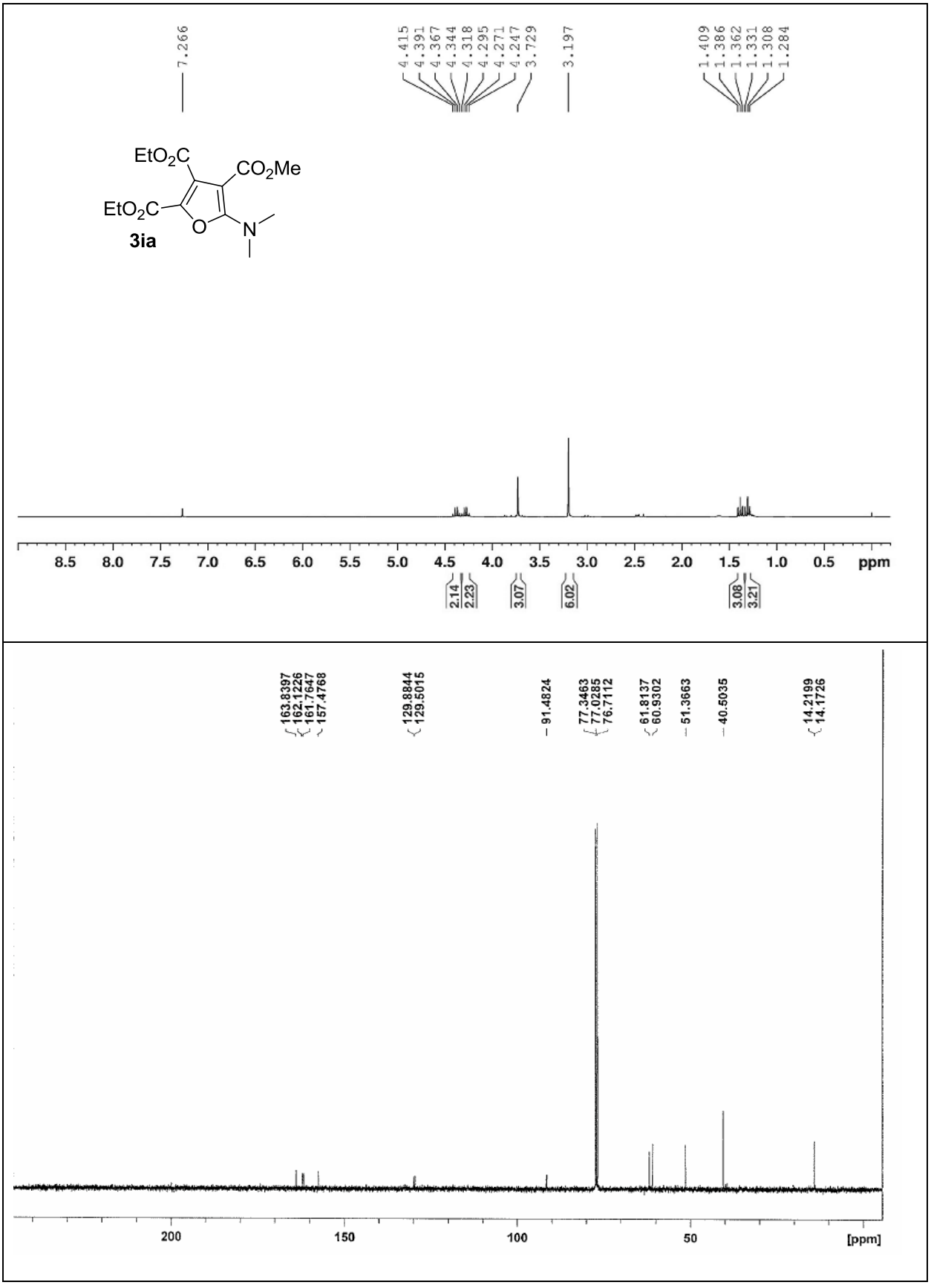
8.211
8.198
8.194
7.664
7.659
7.646
7.641
7.263
4.440
4.422
4.404
4.386
3.766
3.223
1.563
1.402
1.384
1.366
0.000
NO2
N
O
MeO2C
CO2Et
3ha
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.99
2.05
3.07
5.91
3.02
165.1508
162.6268
161.0915
146.0934
137.7892
134.9445
124.2774
124.2214
120.4545
92.4379
77.3400
77.0233
76.7053
62.0739
51.4062
40.6187
14.1317
200
150
100
50
[ppm]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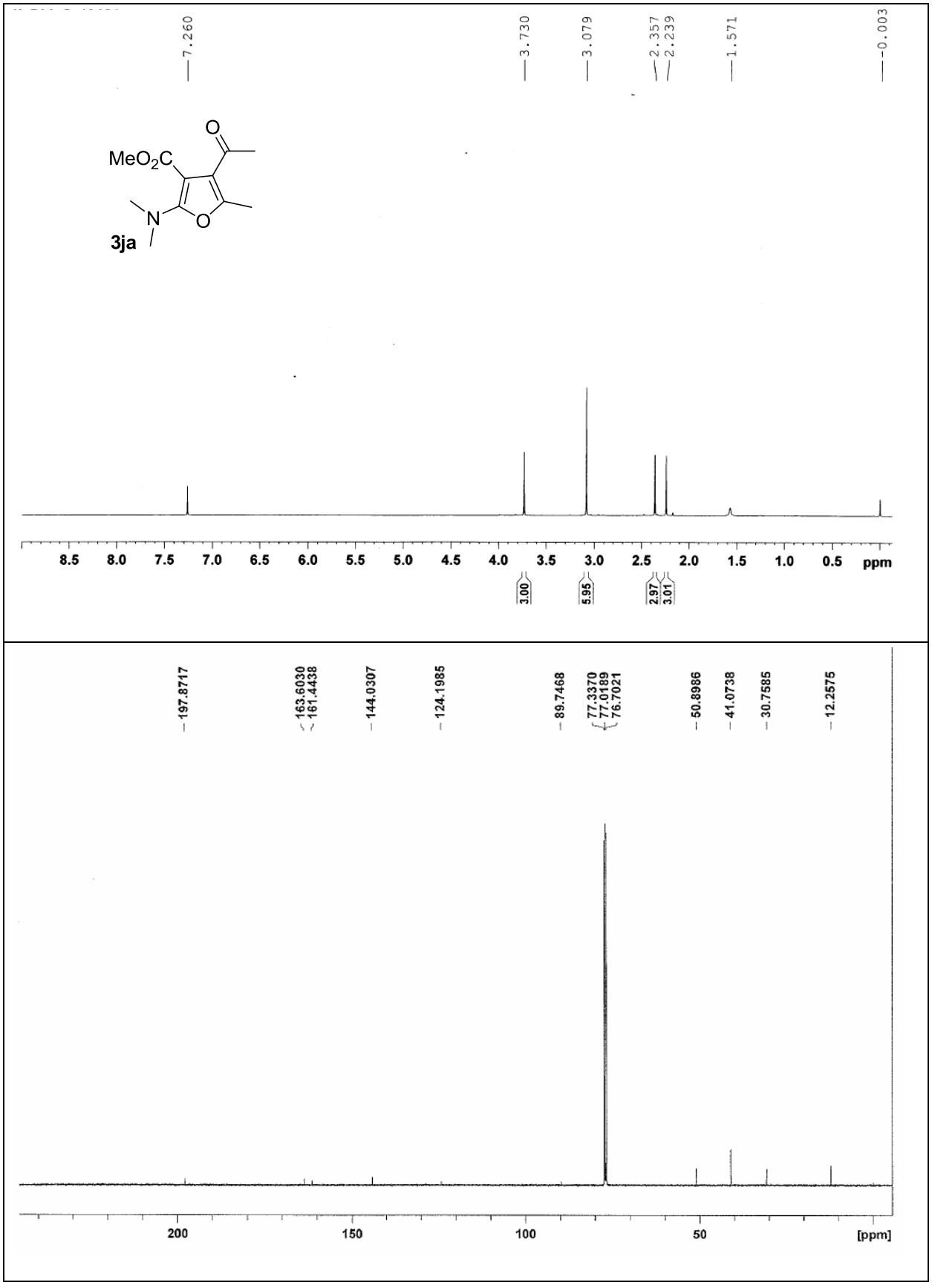
4.391
4.367
4.344
4.318
4.295
4.271
4.247
3.729
3.197
1.409
1.386
1.362
1.331
1.308
1.284
EtO2C
CO2Me
EtO2C
O
N
3ia
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.14
2.23
3.07
6.02
3.08
3.21
163.8397
162.1226
161.7647
157.4768
129.8844
129.5015
91.4824
77.3463
77.0285
76.7112
61.8137
60.9302
51.3663
40.5035
14.2199
14.1726
200
150
100
50
[ppm]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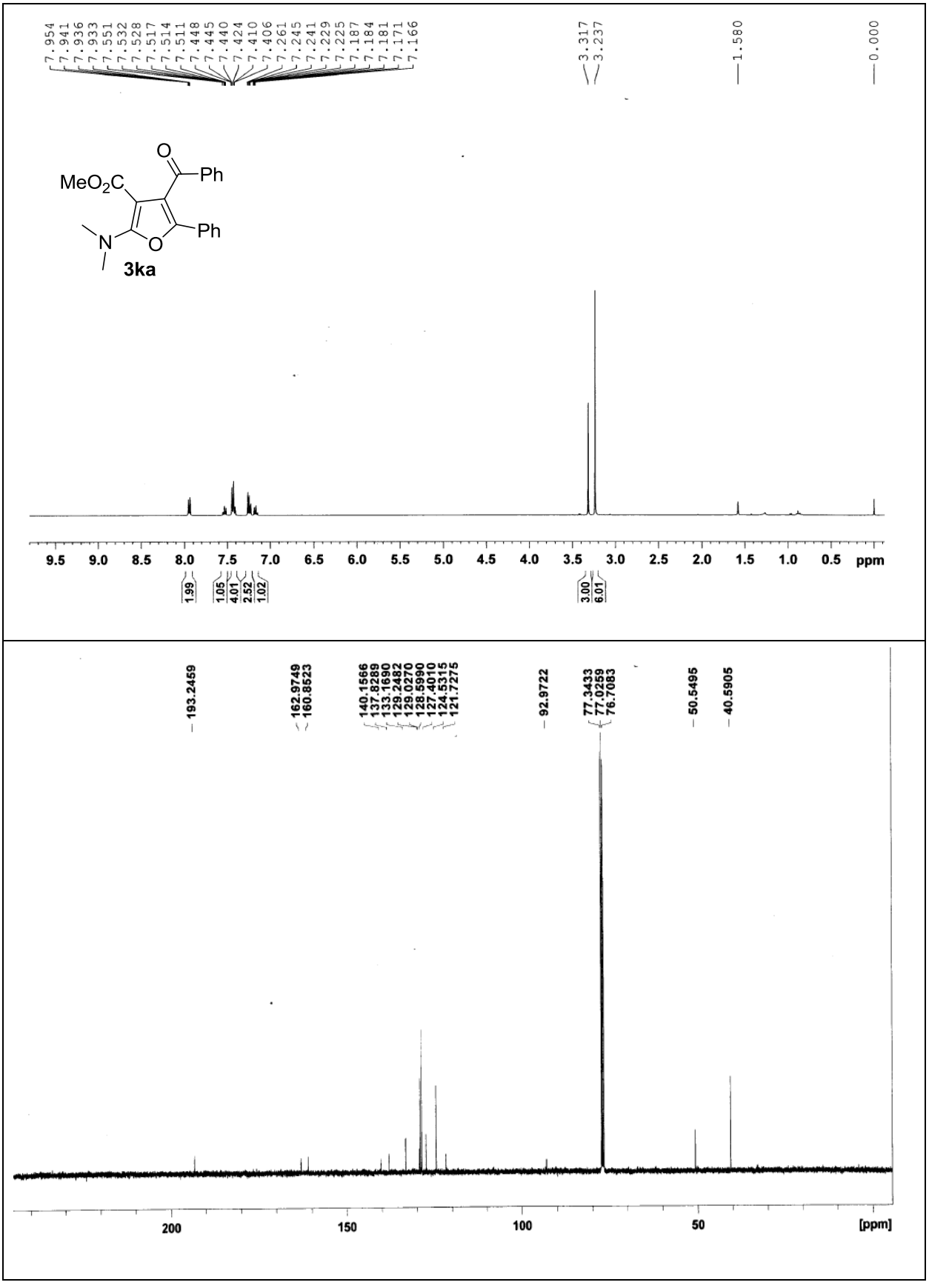
3.730
3.079
2.357
2.239
1.571
0.003
MeO2C
O
N
O
3ja
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.00
5.95
2.97
3.01
197.8717
163.6030
161.4438
144.0307
124.1985
89.7468
77.3370
77.0189
76.7021
50.8986
41.0738
30.7585
12.2575
200 150 100 50 [ppm]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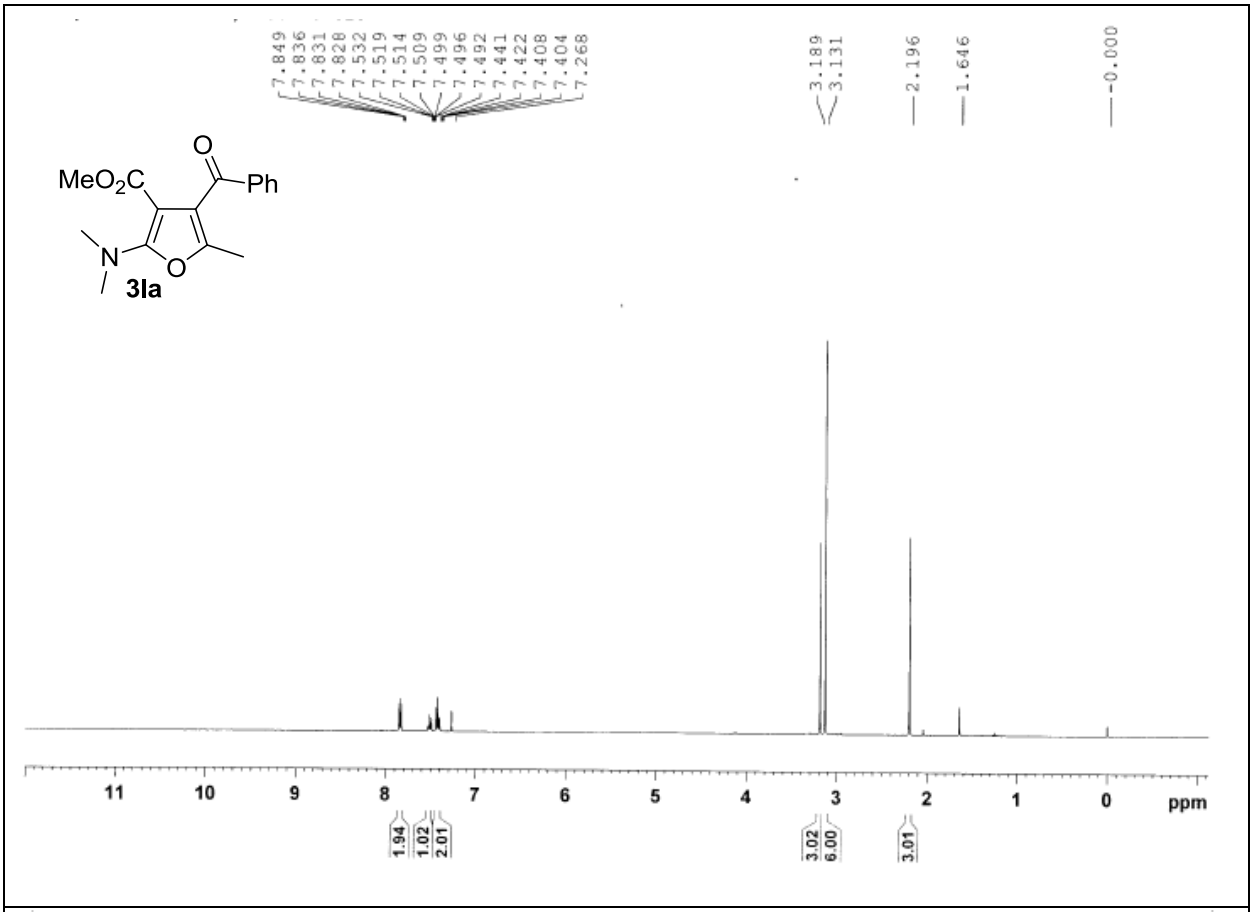
7.941
7.936
7.933
7.551
7.532
7.528
7.517
7.514
7.511
7.448
7.445
7.440
7.424
7.410
7.406
7.261
7.245
7.241
7.229
7.225
7.187
7.184
7.181
7.171
7.166
3.317
3.237
1.580
0.000
MeO2C
O
Ph
Ph
N
O
3ka
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.99
1.05
4.01
2.52
1.02
3.00
6.01
193.2459
162.9749
160.8523
140.1566
137.8289
133.1690
129.2482
129.0270
128.5990
127.4010
124.5315
121.7275
92.9722
77.3433
77.0259
76.7083
50.5495
40.5905
200
150
100
50
[ppm]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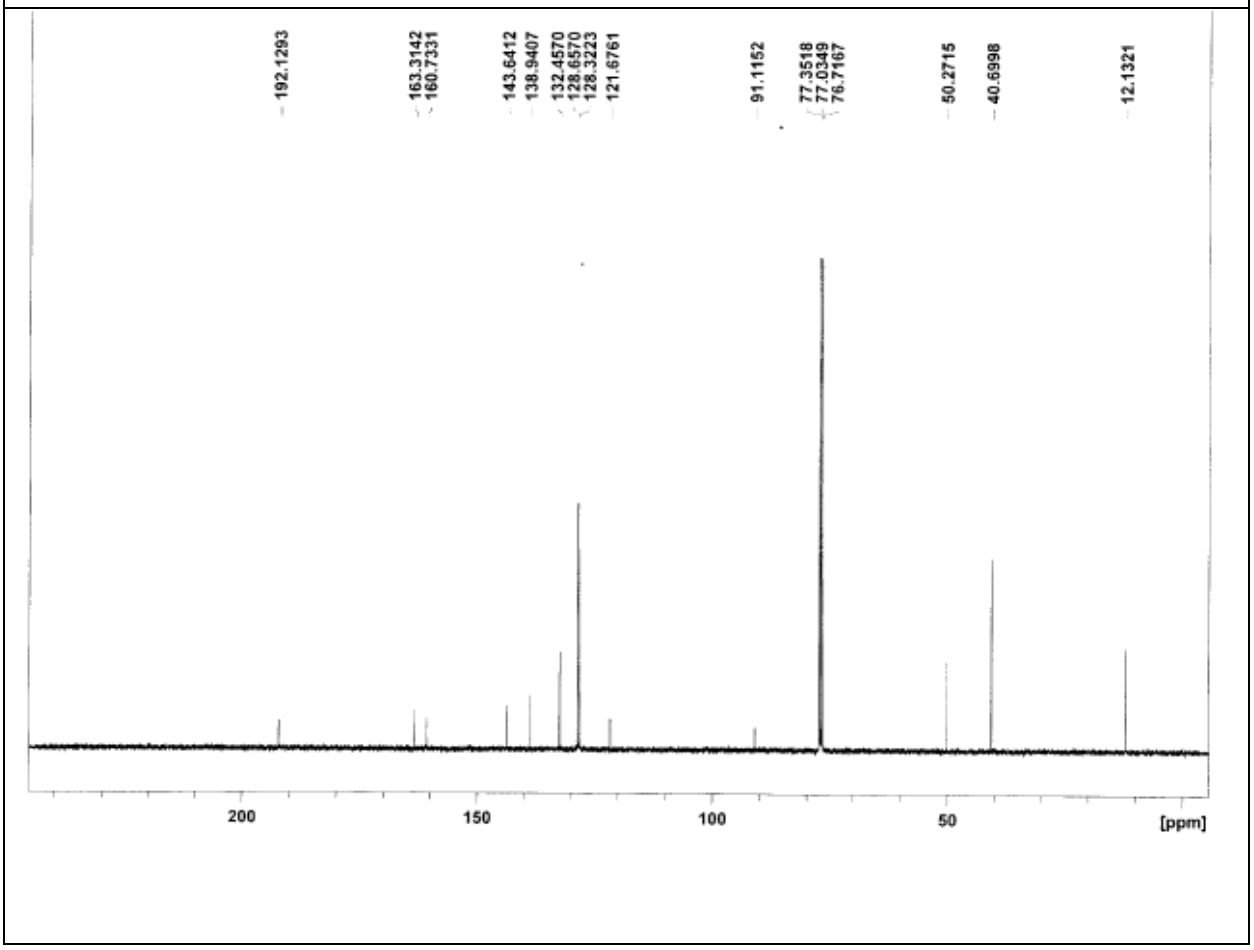
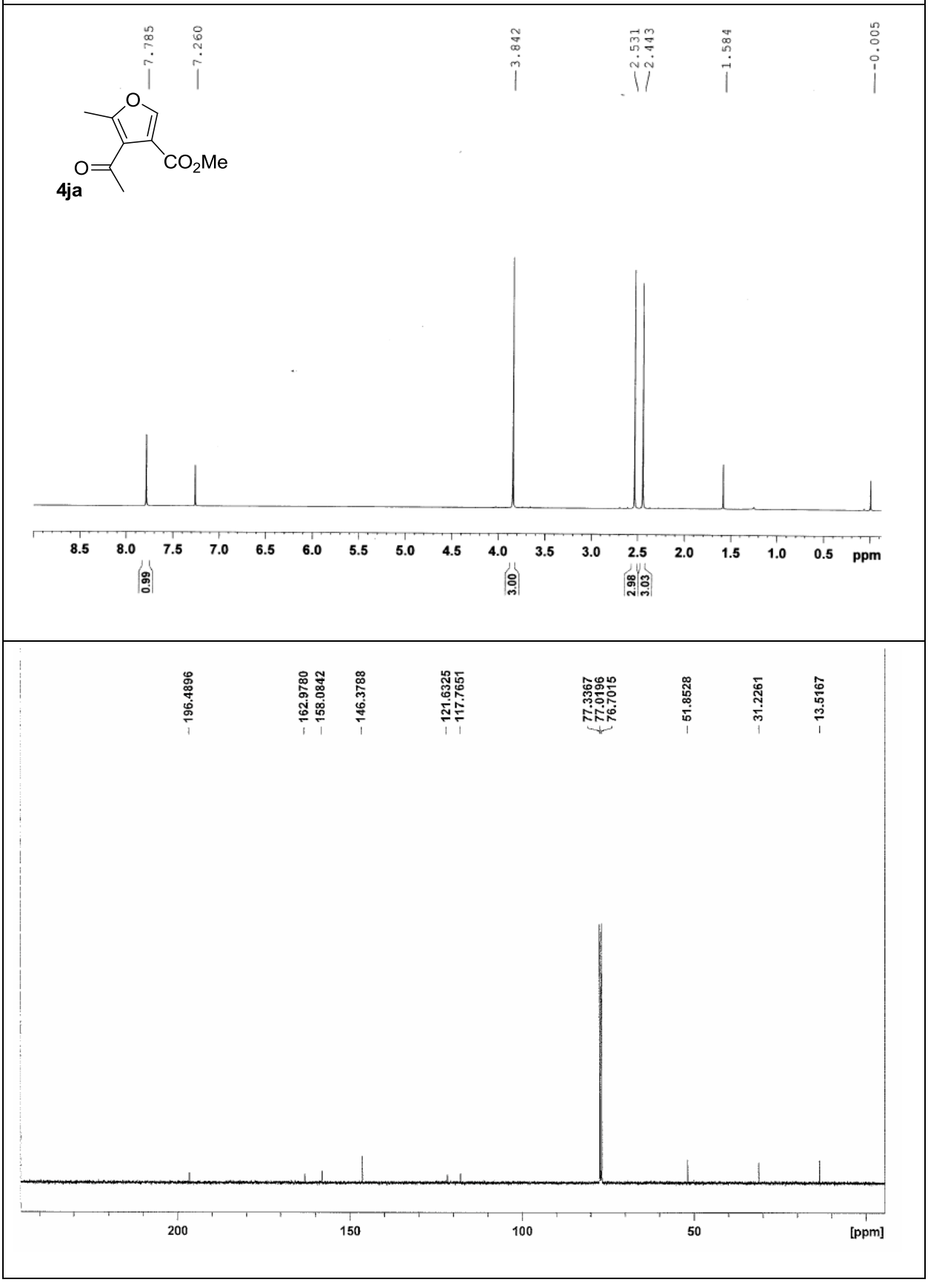
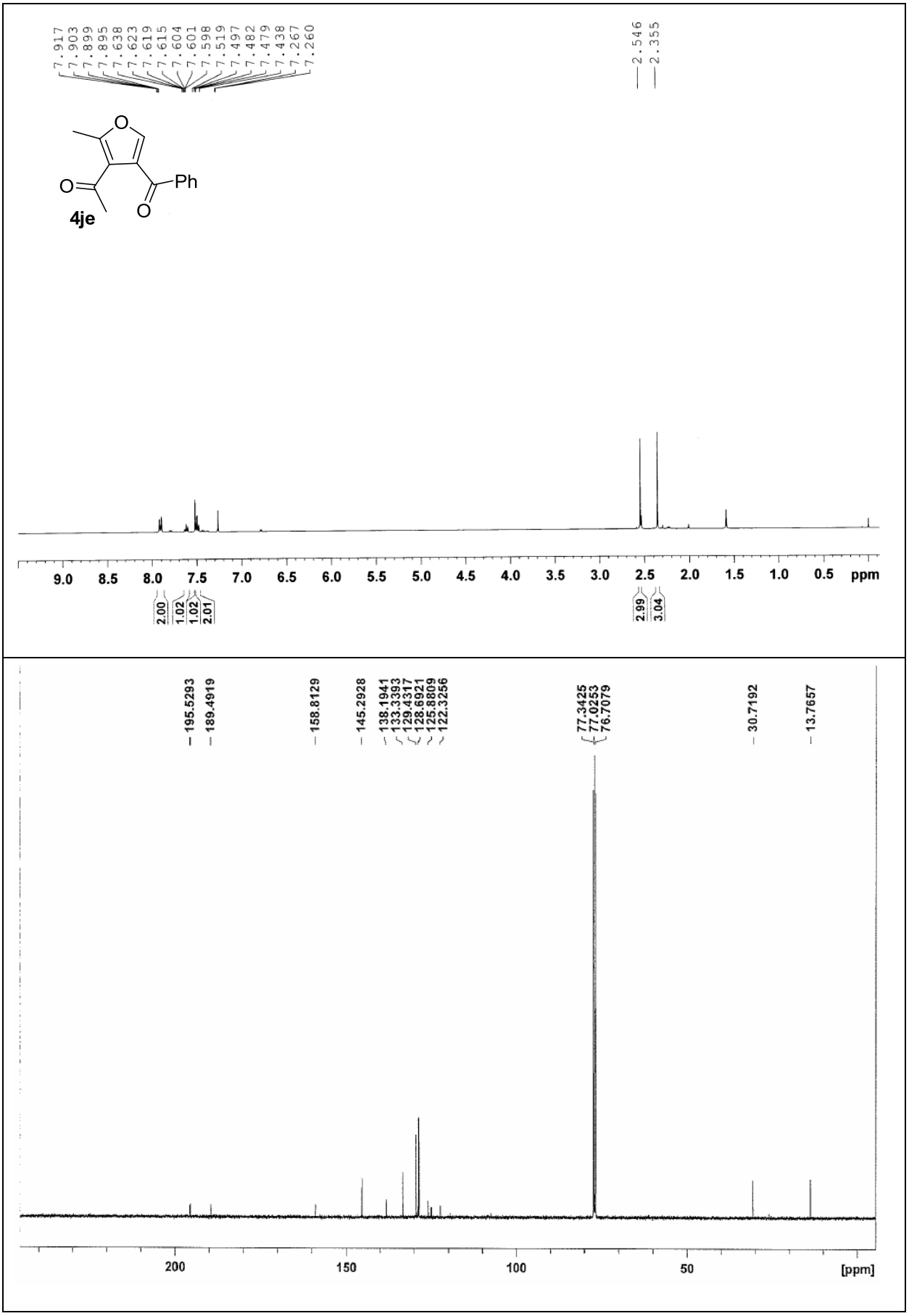
7.836
7.831
7.828
7.532
7.519
7.514
7.509
7.499
7.496
7.492
7.441
7.422
7.408
7.404
7.268
3.189
3.131
2.196
1.646
0.000
MeO2C
O
Ph
N
O
3la
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
1.02
2.01
3.02
6.00
3.01


192.1293
163.3142
160.7331
143.6412
138.9407
132.4570
128.6570
128.3223
121.6761
91.1152
77.3518
77.0349
76.7167
50.2715
40.6998
12.1321
200
150
100
50
[ppm]

^{1}H and ^{13}C NMR spectra of 2-unsubstituted furans

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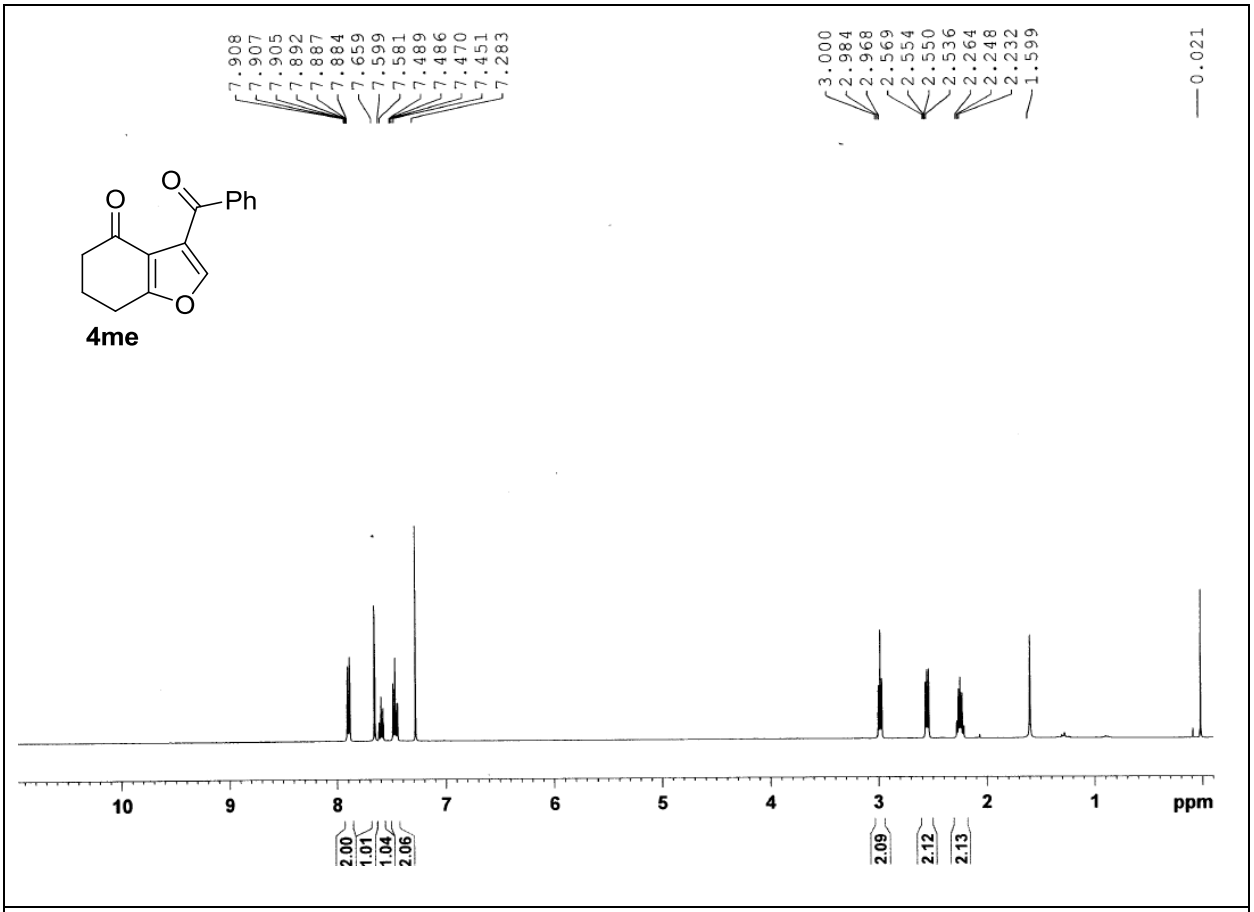
7.903
7.899
7.895
7.638
7.623
7.619
7.615
7.604
7.601
7.598
7.519
7.497
7.482
7.479
7.438
7.267
7.260
2.546
2.355
O
O
Ph
O
4je
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.02
1.02
2.01
2.99
3.04
195.5293
189.4919
158.8129
145.2928
138.1941
133.3393
129.4317
128.6921
125.8809
122.3256
77.3425
77.0253
76.7079
30.7192
13.7657
200
150
100
50
[ppm]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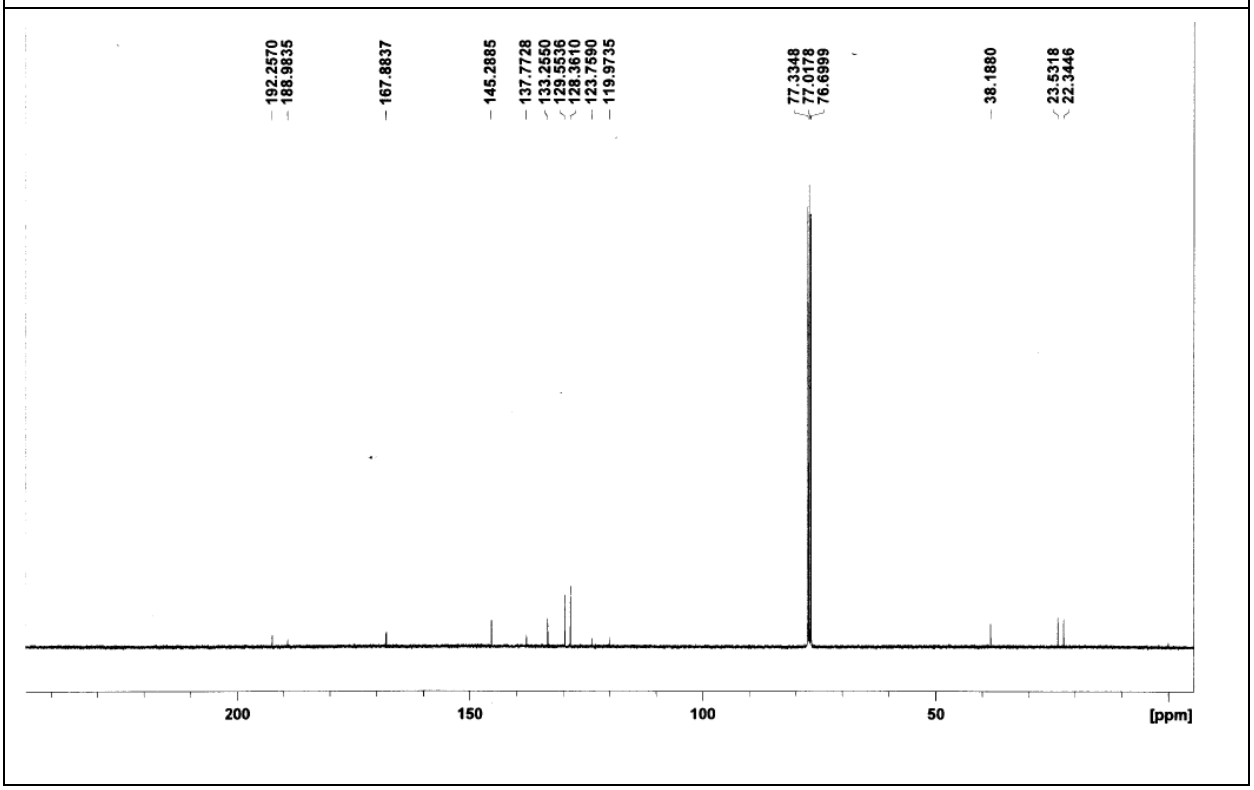
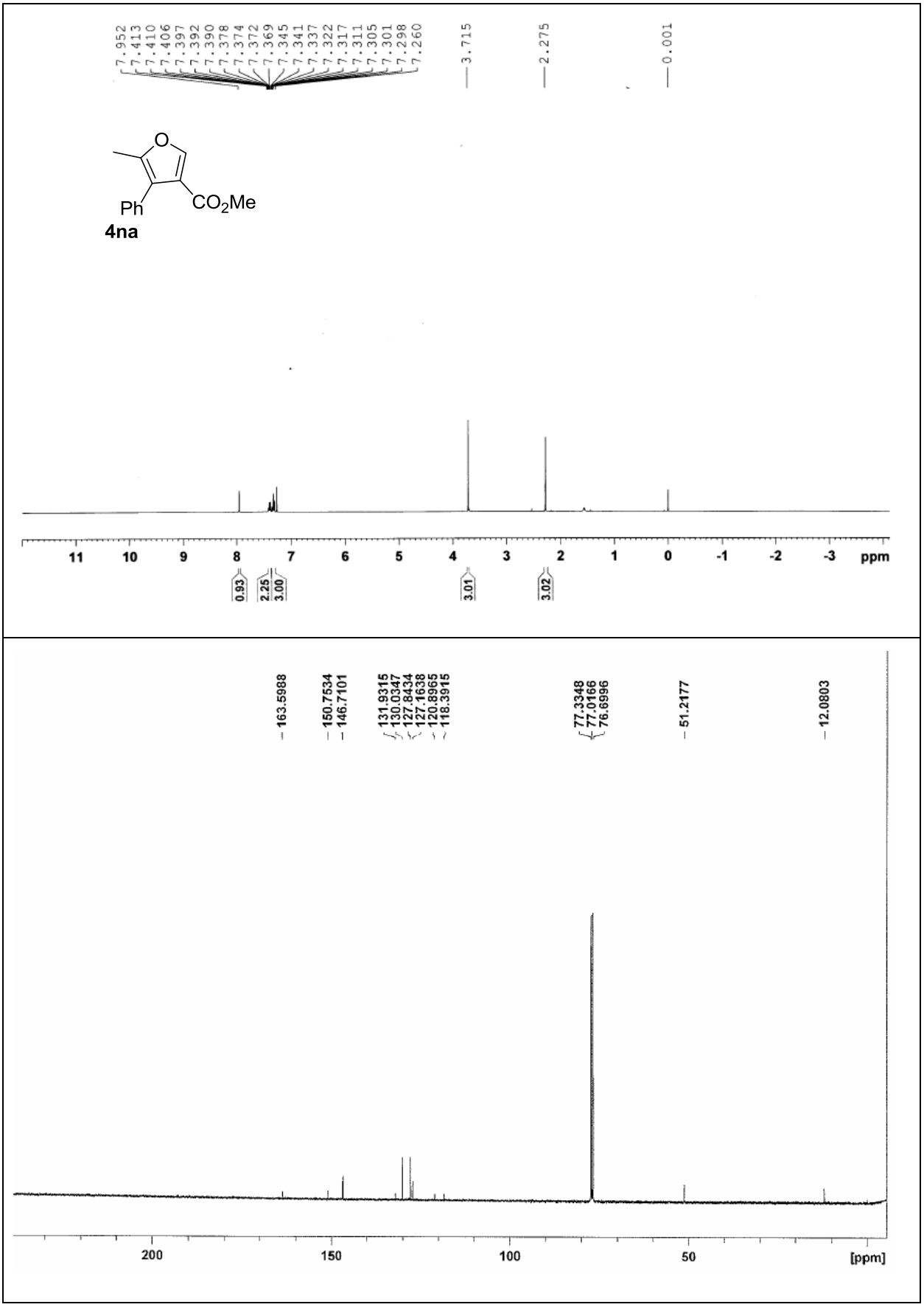
7.907
7.905
7.892
7.887
7.884
7.659
7.599
7.581
7.489
7.486
7.470
7.451
7.283
3.000
2.984
2.968
2.569
2.554
2.550
2.536
2.264
2.248
2.232
1.599
0.021
O
O
Ph
O
4me
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.01
1.04
2.06
2.09
2.12
2.13


192.2570
188.9835
167.8837
145.2885
137.7728
133.2550
129.5536
128.3610
123.7590
119.9735
77.3348
77.0178
76.6999
38.1880
23.5318
22.3446
200
150
100
50
[ppm]


7.952
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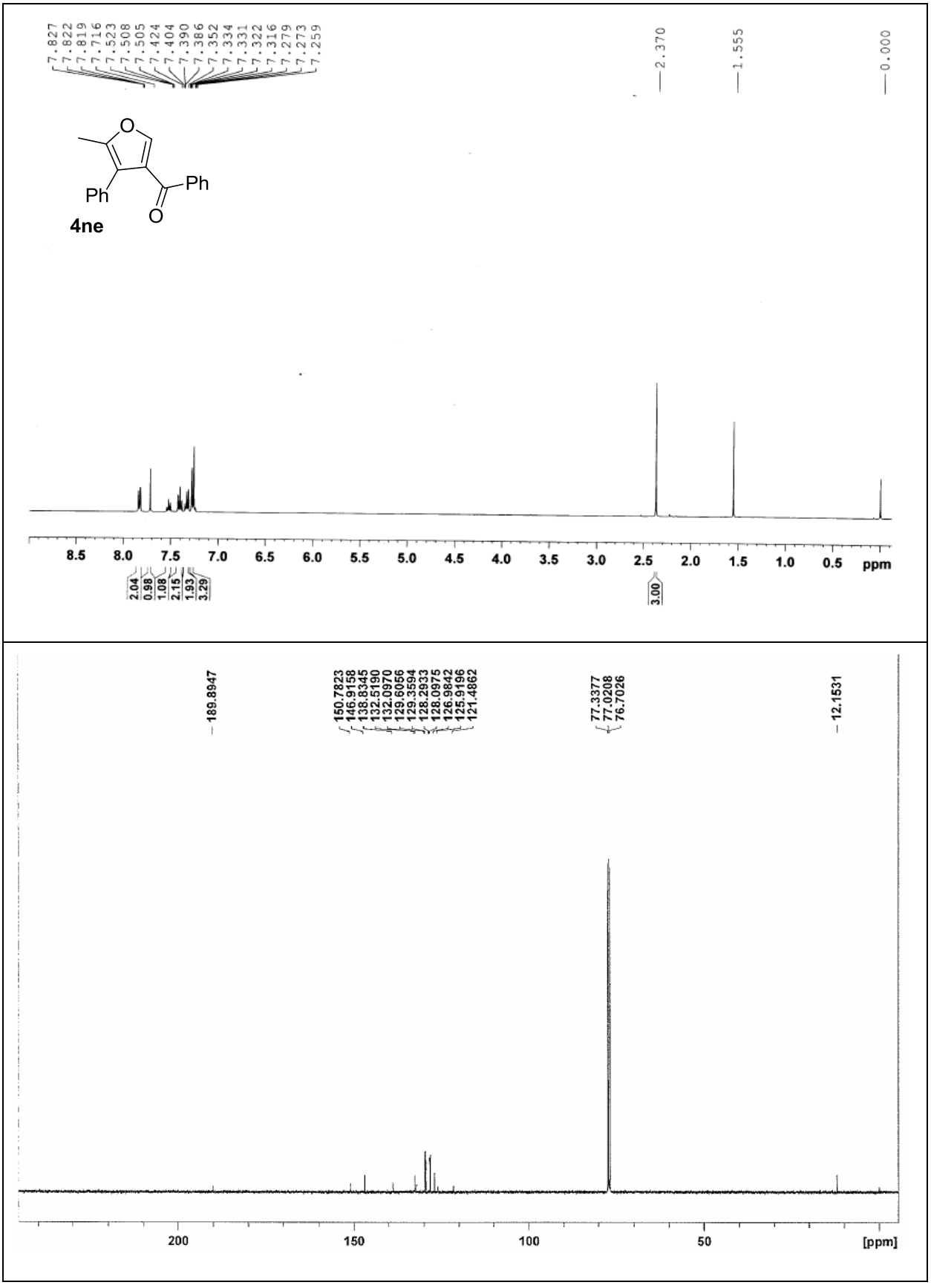
7.410
7.406
7.397
7.392
7.390
7.378
7.374
7.372
7.369
7.345
7.341
7.337
7.322
7.317
7.311
7.305
7.301
7.298
7.260
3.715
2.275
0.001
O
Ph
CO2Me
4na
11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
0.93
2.25
3.00
3.01
3.02
163.5988
150.7534
146.7101
131.9315
130.0347
127.8434
127.1638
120.8965
118.3915
77.3348
77.0166
76.6996
51.2177
12.0803
200 150 100 50 [ppm]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7.819
7.716
7.523
7.508
7.505
7.424
7.404
7.390
7.386
7.352
7.334
7.331
7.322
7.316
7.279
7.273
7.259
2.370
1.555
0.000
O
Ph
Ph
O
4ne
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
2.04
0.98
1.08
2.15
1.93
3.29
3.00
189.8947
150.7823
146.9158
138.8345
132.5190
132.0970
129.6056
129.3594
128.2933
128.0975
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121.4862
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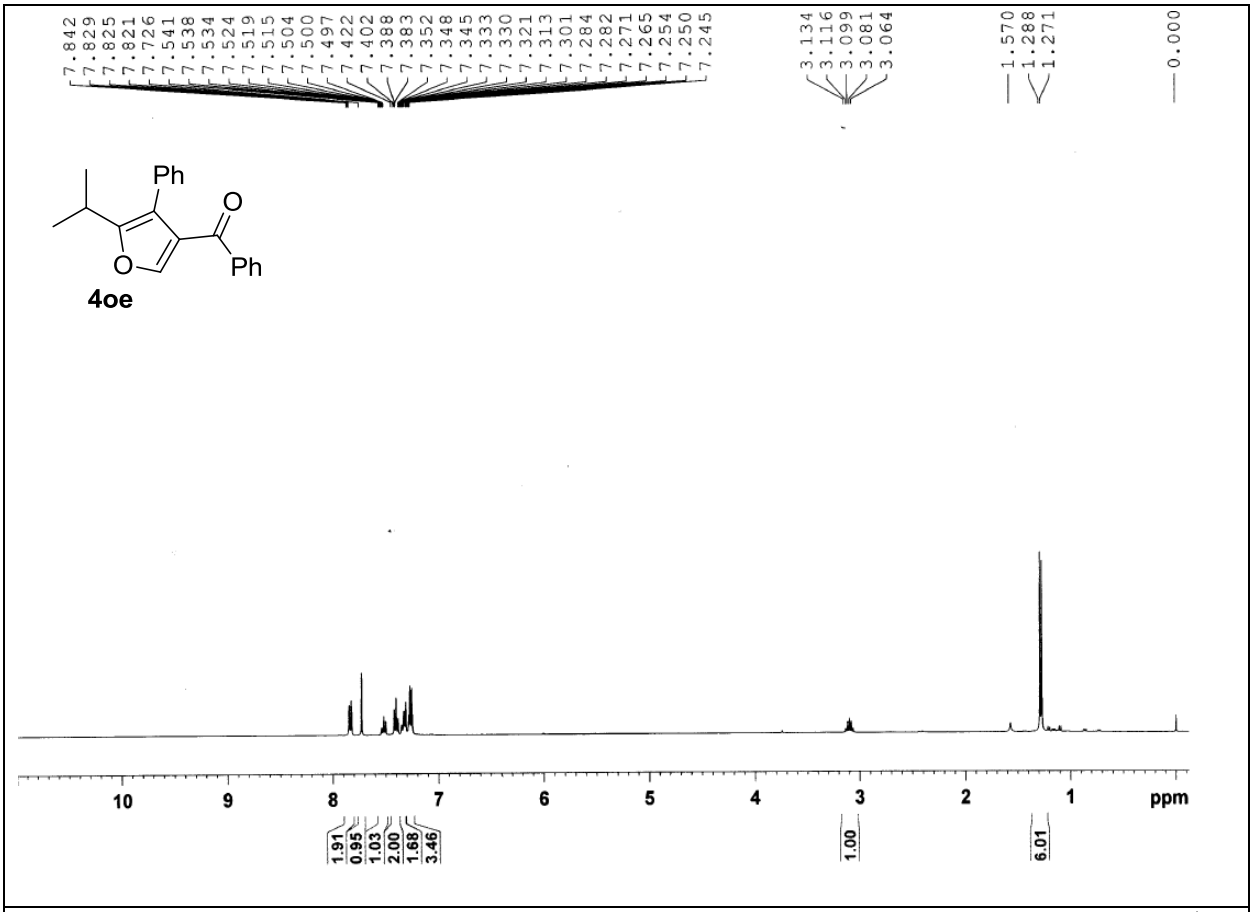
77.0208
76.7026
12.1531
200
150
100
50
[ppm]


7.842
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7.825
7.821
7.726
7.541
7.538
7.534
7.524
7.519
7.515
7.504
7.500
7.497
7.422
7.402
7.388
7.383
7.352
7.348
7.345
7.333
7.330
7.321
7.313
7.301
7.284
7.282
7.271
7.265
7.254
7.250
7.245
3.134
3.116
3.099
3.081
3.064
1.570
1.288
1.271
0.000
Ph
O
O
Ph
4oe
10
9
8
7
6
5
4
3
2
1
ppm
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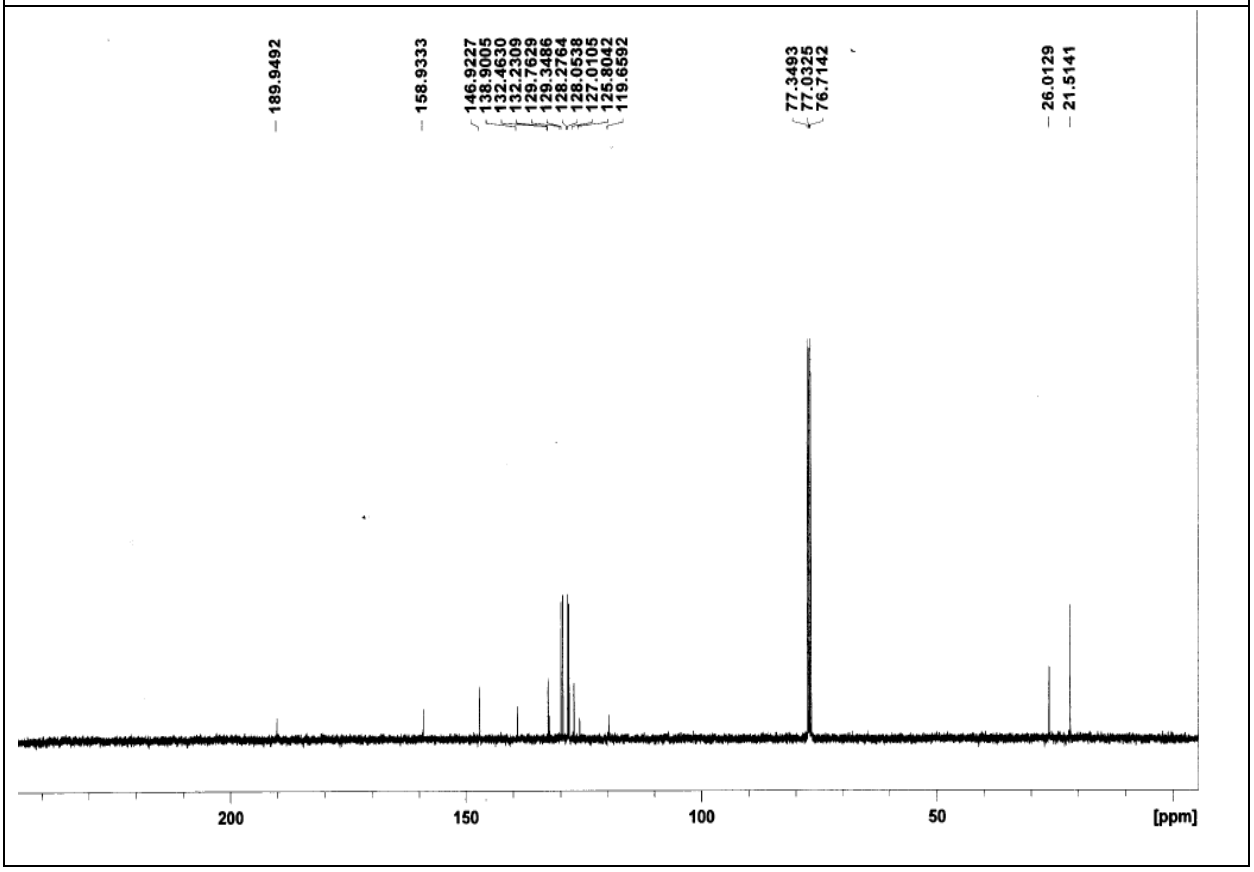
0.95
1.03
2.00
1.68
3.46
1.00
6.01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146.9227
138.9005
132.4630
132.2309
129.7629
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128.2764
128.0538
127.0105
125.8042
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77.3493
77.0325
76.7142
26.0129
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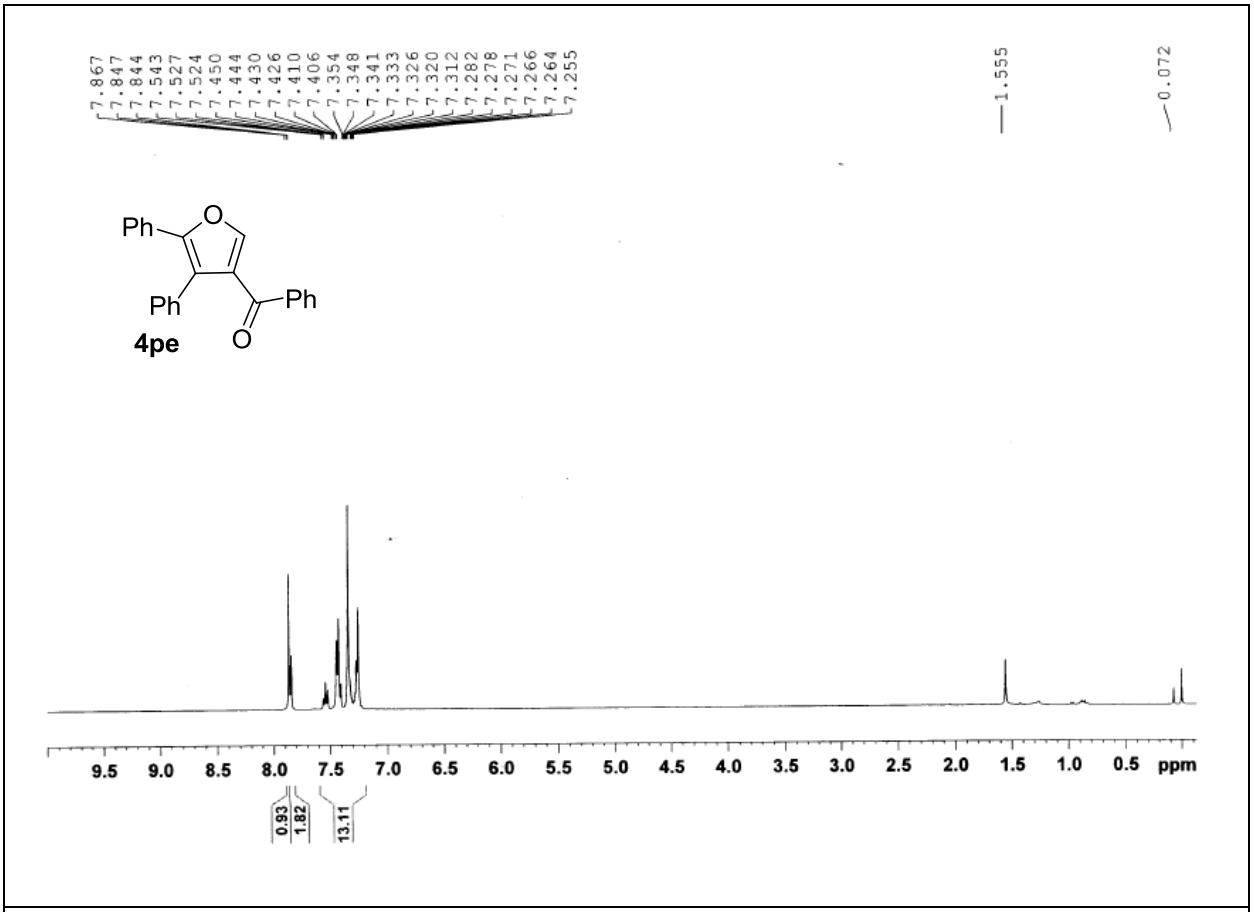
200
150
100
50
[ppm]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7.524
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7.444
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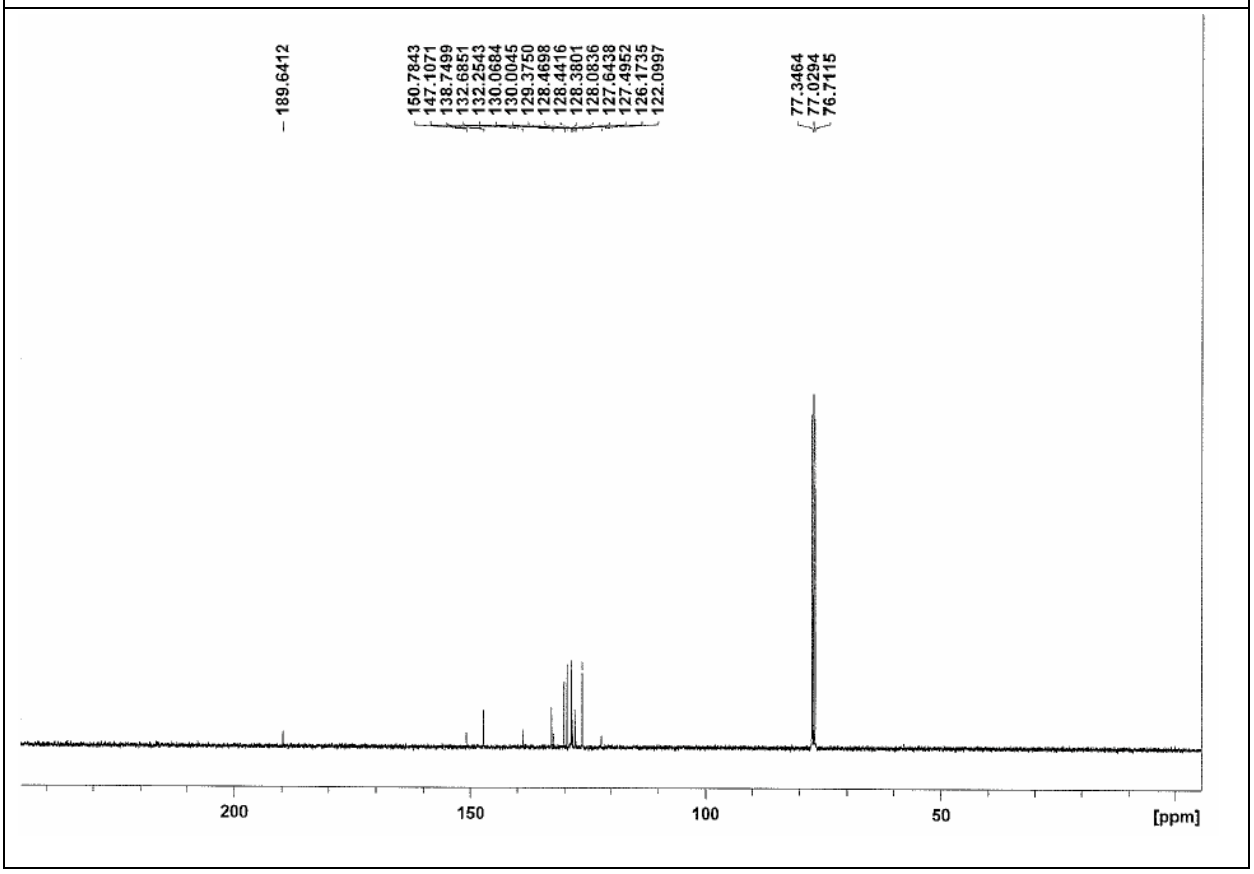
7.426
7.410
7.406
7.354
7.348
7.341
7.333
7.326
7.320
7.312
7.282
7.278
7.271
7.266
7.264
7.255
1.555
0.072
Ph
O
Ph
Ph
Ph
O
4pe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.93
1.82
13.11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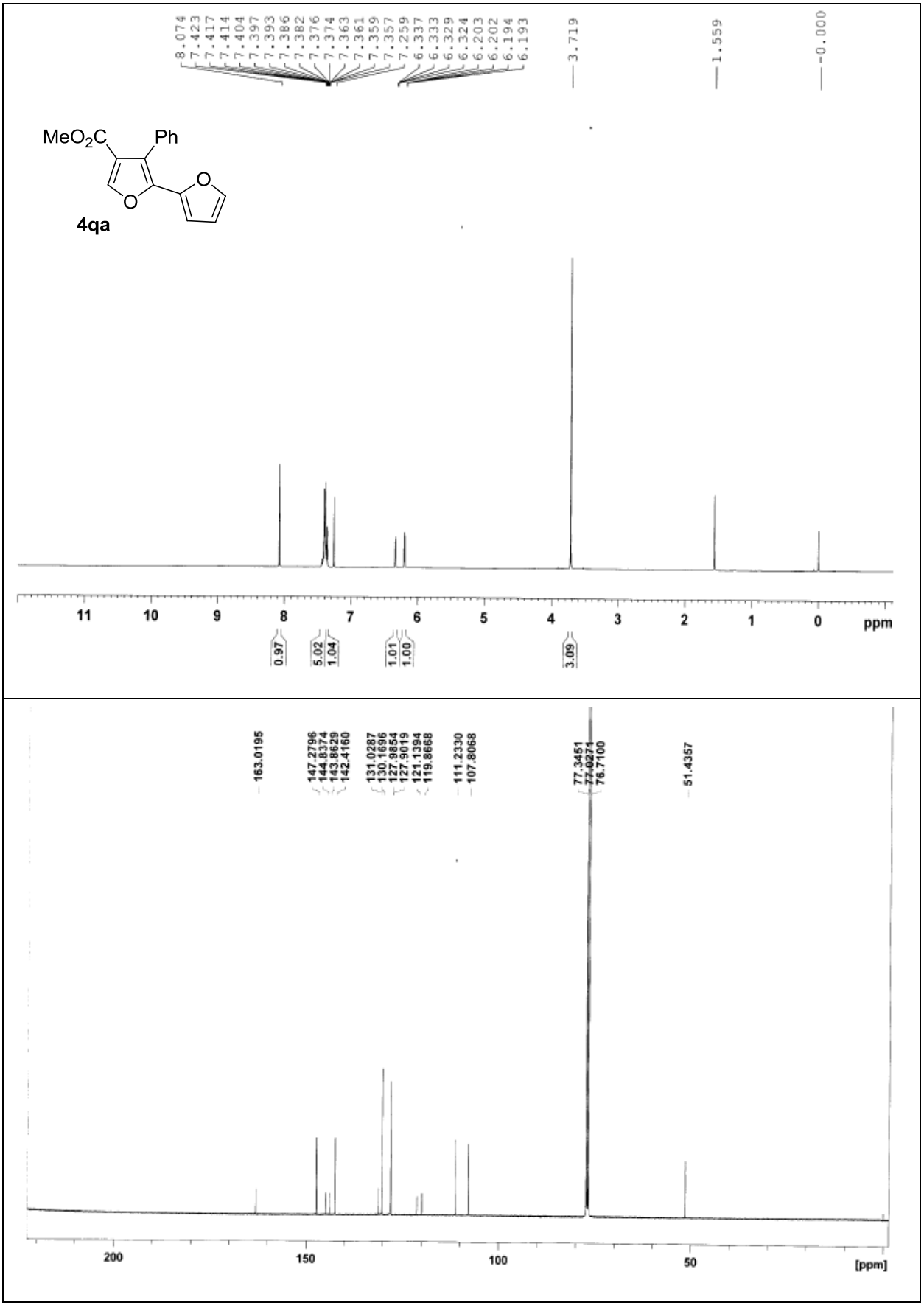
132.2543
130.0684
130.0045
129.3750
128.4698
128.4416
128.3801
128.0836
127.6438
127.4952
126.1735
122.0997
77.3464
77.0294
76.7115
200
150
100
50
[ppm]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7.414
7.404
7.397
7.393
7.386
7.382
7.376
7.374
7.363
7.361
7.359
7.357
7.259
6.337
6.333
6.329
6.324
6.203
6.202
6.194
6.193
3.719
1.559
0.000
MeO2C
Ph
O
O
4qa
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
5.02
1.04
1.01
1.00
3.09
163.0195
147.2796
144.8374
143.8629
142.4160
131.0287
130.1696
127.9854
127.9019
121.1394
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107.8068
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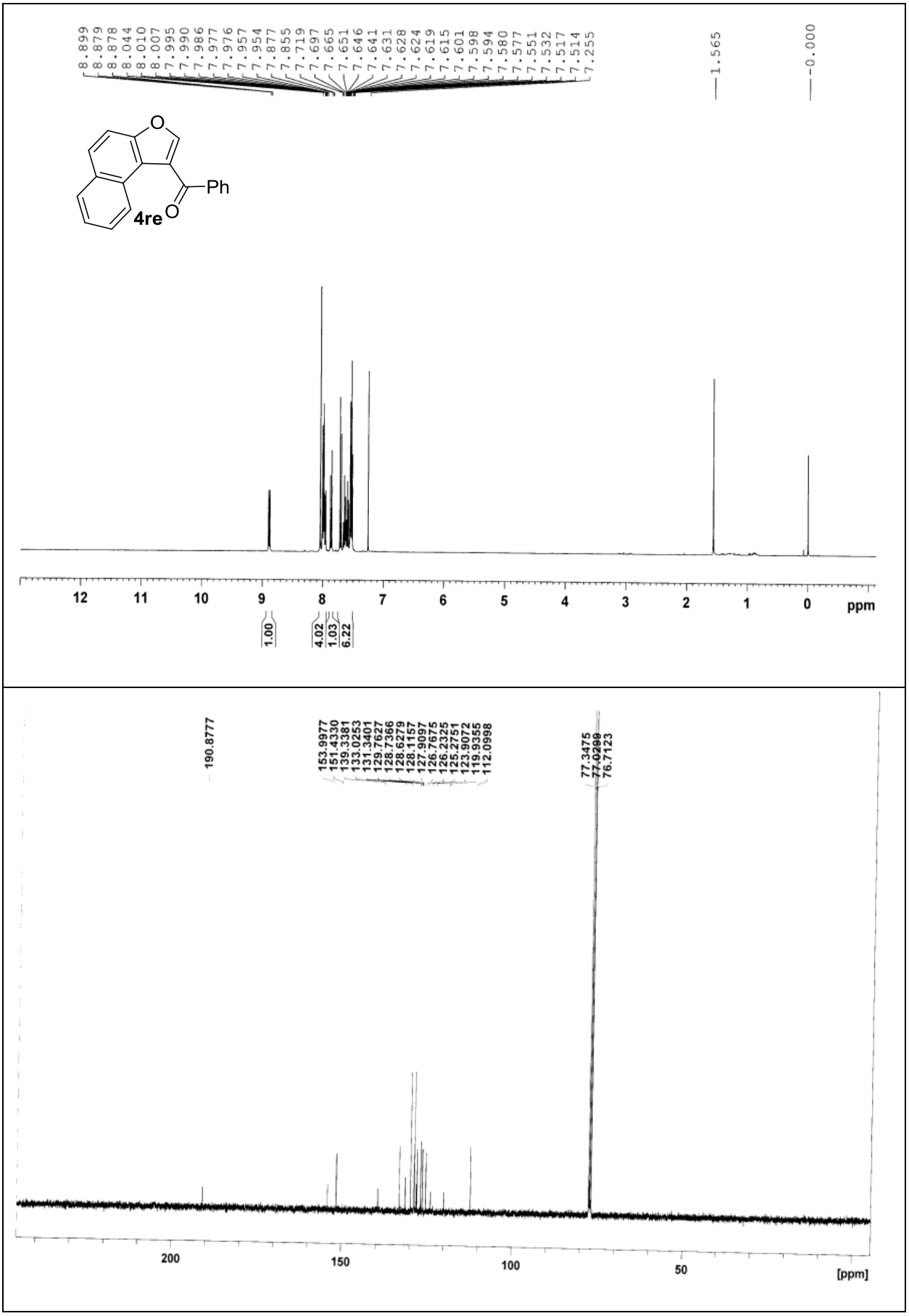
200
150
100
50
[ppm]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7.977
7.976
7.957
7.954
7.877
7.855
7.719
7.697
7.665
7.651
7.646
7.641
7.631
7.628
7.624
7.619
7.615
7.601
7.598
7.594
7.580
7.577
7.551
7.532
7.517
7.514
7.255
1.565
0.000
O
Ph
O
4re
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.02
1.03
6.22
190.8777
153.9977
151.4330
139.3381
133.0253
131.3401
129.7627
128.7366
128.6279
128.1157
127.9097
126.7675
126.2325
125.2751
123.9072
119.9355
112.0998
77.3475
77.0299
76.7123
200
150
100
50
[ppm]