Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Divergent Reactivity of α-Oximino Carbenoids: Facile Access to 2-Isoxazolines and 1-Azirines

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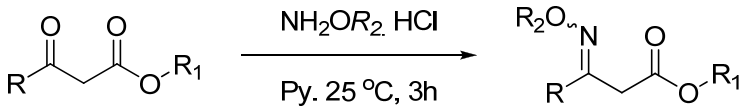
General methods: All reactions were carried out in flame or oven dried glasswares under nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 – 400 mesh) or aluminium oxide. Chromatograms 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 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.

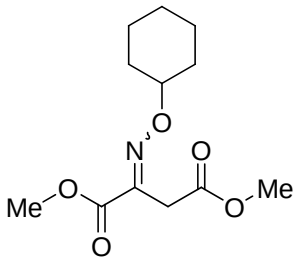
Materials: All solvents were distilled under nitrogen from the following drying agents immediately before use: acetonitrile and dichloroethane were distilled from P_2O_5. Anhydrous pyridine and DBU were purchased from commercial suppliers and used without further purification.

General procedure for β-oximino esters:



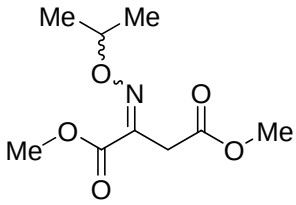
To a solution of β-ketoester (1.0 eq.) in pyridine at room temperature was added alkoxyamine hydrochloride (1.1 eq.) in one portion and the reaction mixture was stirred at RT for 3 h. Upon completion of the reaction as indicated by TLC, it was extracted with ethyl acetate, washed with water, brine and dried over anhydrous Na_2SO_4. The crude material was purified by column chromatography using hexane:ethyl acetate (19:1).

Dimethyl 2-(cyclohexyloxyimino)succinate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = <5:>95). Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39-4.32 (m, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.64 (s, 2H), 1.94-1.91 (m, 2H), 1.72-1.68 (m, 2H), 1.57-1.46 (m, 3H), 1.40-1.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 163.7, 144.7, 83.3, 52.9, 52.1, 31.4, 31.2, 25.4, 23.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{20}NO_5$: 258.1341. Found: 258.1347.

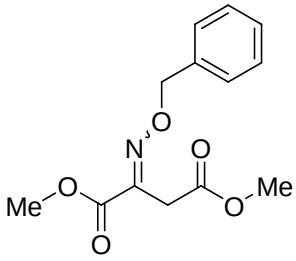
Dimethyl 2-(isopropoxyimino)succinate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = <5:>95). Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ

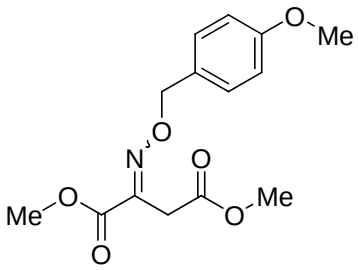
4.63-4.57 (m, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.62 (s, 2H), 1.29 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 163.7, 144.6, 76.7, 52.9, 52.1, 31.1, 21.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{16}NO_5$: 218.1028. Found: 218.1031.

Dimethyl 2-(benzyloxyimino)succinate:



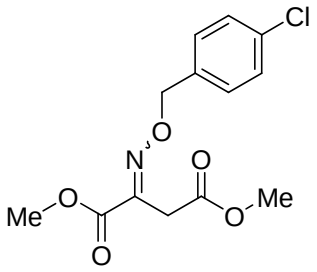
The title compound was prepared according to the general procedure. The product was obtained as pale yellow oil (*cis:trans* = <5:>95). Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H), 5.33 (s, 2H), 3.88 (s, 3H), 3.66 (s, 2H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 163.4, 145.7, 136.1, 128.5, 128.4, 128.2, 76.7, 53.0, 52.2, 31.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{12}N_5O$: 266.1042. Found: 266.1030.

Dimethyl 2-(4-methoxybenzyloxyimino)succinate:



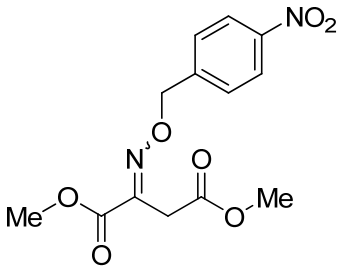
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = <5:>95). Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.25 (s, 2H), 3.88 (s, 3H), 3.81 (s, 3H), 3.63 (s, 2H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 163.4, 159.8, 145.4, 130.1, 128.1, 113.9, 76.7, 55.2, 53.0, 52.2, 31.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}NO_6$: 296.1134. Found: 296.1146.

Dimethyl 2-(4-chlorobenzyloxyimino)succinate:



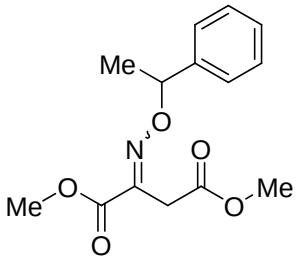
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = <5:>95). Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 5.29 (s, 2H), 3.88 (s, 3H), 3.66 (s, 2H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 163.2, 145.9, 134.6, 134.2, 129.5, 128.7, 76.7, 53.0, 52.2, 31.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{15}NO_5Cl$: 300.0639. Found: 300.0636.

Dimethyl 2-(4-nitrobenzyloxyimino)succinate:



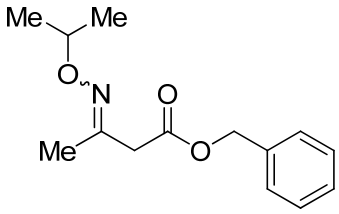
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = <5:>95). Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 5.43 (s, 2H), 3.88 (s, 3H), 3.71 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 163.0, 147.8, 146.6, 143.7, 128.2, 123.8, 76.4, 53.1, 52.4, 31.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{15}N_2O_7$: 311.0879. Found: 311.0879.

Dimethyl 2-(1-phenylethoxyimino)succinate:



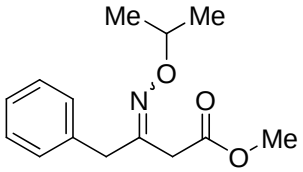
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = <5:>95). Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 5.49 (q, J = 6.4 Hz, 1H), 3.85 (s, 3H), 3.68 (s, 2H), 3.66 (s, 3H), 1.60 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 163.5, 145.3, 141.5, 128.4, 127.9, 126.1, 83.7, 52.9, 52.2, 31.4, 21.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}NO_5$: 280.1185. Found: 280.1189.

Benzyl 3-(isopropoxyimino)butanoate:



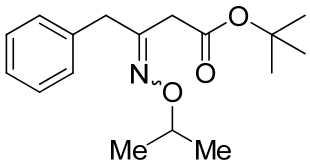
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 43:57). Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 5H), 5.15 & 5.14 (s, 2H), 4.33-4.25 (m, 1H), 3.36 & 3.26 (s, 2H), 1.96 & 1.90 (s, 3H), 1.22 & 1.16 (d, J = 6.4 Hz; d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 168.9, 150.2, 149.2, 135.7, 135.6, 128.5, 128.5, 128.3, 128.2, 128.1, 75.1, 75.0, 66.7, 66.5, 41.5, 35.5, 21.6, 21.6, 20.7, 14.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{20}NO_3$: 250.1443. Found: 250.1447.

Methyl 3-(isopropoxyimino)-4-phenylbutanoate:



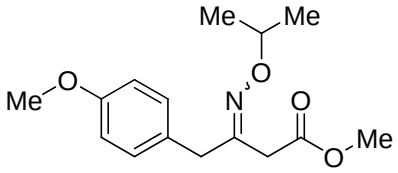
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 28 : 72). Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-1.18 (m, 5H), 4.41-4.35 (m, 1H), 3.80 & 3.62 (s, 2H), 3.62 & 3.61 (s, 3H), 3.17 & 3.12 (s, 2H), 1.27 & 1.23 (d, J = 6.0 Hz; d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.4, 151.8, 151.5, 136.2, 129.2, 129.1, 128.5, 128.5, 126.8, 126.5, 75.4, 75.2, 51.9, 51.8, 40.8, 38.8, 34.0, 33.2, 21.6, 21.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{20}NO_3$: 250.1443. Found: 250.1442.

***tert*-Butyl 3-(isopropoxyimino)-4-phenylbutanoate:**



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 25 : 75). Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.18 (m, 5H), 4.41-4.37 (m, 1H), 3.79 & 3.60 (s, 2H), 3.09 & 3.02 (s, 2H), 1.41 & 1.40 (s, 9H), 1.27 & 1.24 (d, J = 6.4 Hz; d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.1, 152.5, 152.1, 136.5, 136.5, 129.3, 129.3, 128.6, 128.5, 126.8, 126.5, 81.2, 80.9, 75.3, 75.2, 41.0, 40.2, 34.8, 34.1, 28.2, 28.0, 27.9, 21.7, 21.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{26}NO_3$: 292.1913. Found: 292.1917.

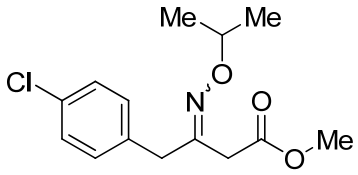
Methyl 3-(isopropoxyimino)-4-(4-methoxyphenyl)butanoate:



The title compound was prepared according to the general procedure. The product was obtained as pale yellow oil (*cis:trans* = 31:69). Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.09 (m, 2H), 6.85-6.81 (m, 2H), 4.42-4.34 (m, 1H), 3.79 (s, 3H), 3.73 & 3.55 (s, 2H), 3.63 & 3.62 (s, 3H), 3.15 & 3.11 (s, 2H), 1.27-1.23 (d, J = 6.0 Hz; d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.5, 158.5, 158.3, 152.4, 151.9, 130.3, 130.2, 128.2,

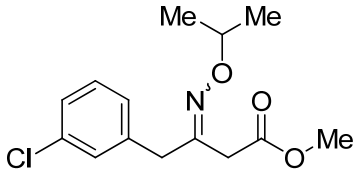
128.2, 114.0, 113.9, 75.4, 75.2, 55.2, 52.0, 51.8, 40.0, 38.8, 33.2, 21.7, 21.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{22}NO_4$: 280.1549. Found: 280.1543.

Methyl 4-(4-chlorophenyl)-3-(isopropoxyimino)butanoate:



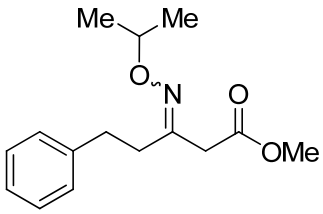
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 27:73). Yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.17-7.11 (m, 2H), 4.41-4.33 (m, 1H), 3.76 & 3.58 (s, 2H), 3.63 & 3.62 (s, 3H), 3.16 & 3.12 (s, 2H), 1.26 & 1.23 (d, J = 6.0 Hz; d, J = 6.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 169.3, 162.3, 151.3, 151.0, 134.8, 132.8, 130.6, 130.5, 128.7, 128.6, 75.6, 75.4, 52.0, 51.9, 40.2, 38.9, 33.5, 33.2, 21.7, 21.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{19}NO_3Cl$: 284.1053. Found: 284.1058.

Methyl 4-(3-chlorophenyl)-3-(isopropoxyimino)butanoate:



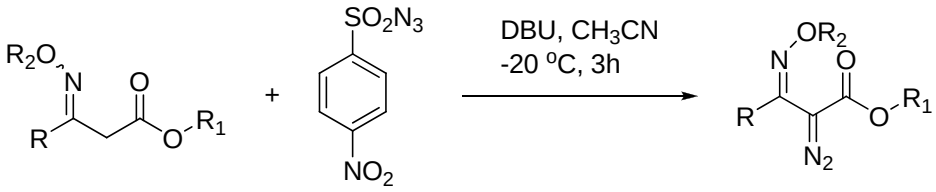
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 27:73). Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.20 (m, 3H), 7.12-7.07 (m, 1H), 4.43-4.35 (m, 1H), 3.77 & 3.60 (s, 2H), 3.64 & 3.63 (s, 3H), 3.17 & 3.13 (s, 2H), 1.27 & 1.23 (d, J = 6.4 Hz; d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.3, 151.0, 150.7, 138.4, 138.3, 134.4, 134.3, 129.8, 129.7, 129.4, 129.3, 127.4, 127.1, 126.8, 75.6, 75.5, 52.0, 51.9, 40.5, 38.9, 33.8, 33.3, 21.7, 21.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{19}NO_3Cl$: 284.1053. Found: 284.1048.

Methyl 3-(isopropoxyimino)-5-phenylpentanoate:



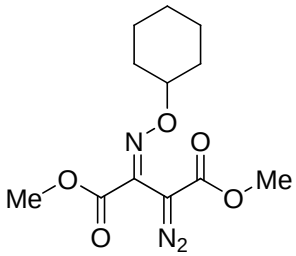
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 40:60). Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.21-7.18 (m, 3H), 4.35-4.28 (m, 1H), 3.68 & 3.67 (s, 3H), 3.27 & 3.11 (s, 2H), 2.89-2.80 (m, 2H), 2.69-2.56 (m, 2H), 1.23 & 1.18 (d, J = 6.0 Hz, d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.7, 153.2, 151.7, 141.2, 141.2, 128.5, 128.4, 128.3, 126.1, 75.2, 75.2, 52.1, 51.9, 40.1, 36.7, 34.6, 32.4, 31.5, 30.5, 21.7, 21.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{22}NO_3$: 264.1600. Found: 264.1598.

General procedure for α-diazo oxime ethers (1a-n):



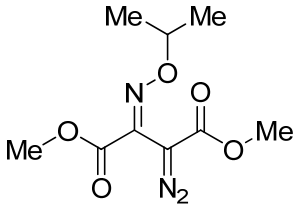
To a solution of β-oximino ester (1.0 eq.) and 4-nitrobenzenesulfonyl azide (1.1 eq.) in CH_3CN at -20 °C was added DBU (1.1 eq.) dropwise. The resulting orange color solution was stirred for 2h at -20 °C and slowly brought to RT. Upon completion of the reaction as indicated by TLC, the solvent was removed under reduced pressure and the crude material was purified by column chromatography using hexane:ethyl acetate (19:1).

(*E*)-dimethyl 2-(cyclohexyloxyimino)-3-diazosuccinate (1a):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32-4.26 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.95-1.91 (m, 2H), 1.72-1.67 (m, 2H), 1.54-1.46 (m, 3H), 1.41-1.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 162.2, 137.0, 83.6, 53.2, 52.5, 31.2, 25.3, 23.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{18}N_3O_5$: 284.1246. Found: 284.1243.

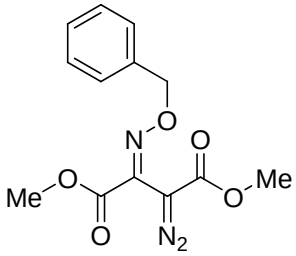
(*E*)-dimethyl 2-diazo-3-(isopropoxyimino)succinate (1b):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56-4.50 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.29 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 162.3,

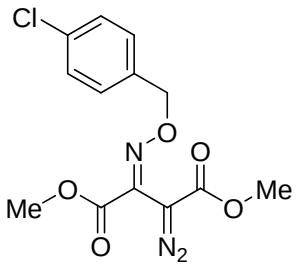
137.1, 78.8, 53.3, 52.6, 21.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{14}N_3O_5$: 244.0933. Found: 244.0931.

(*E*)- dimethyl 2-(benzyloxyimino)-3-diazosuccinate (1c):



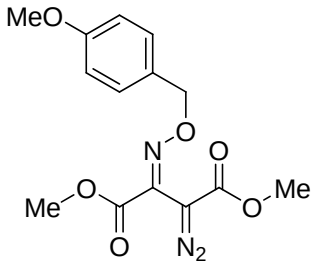
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 91-93 °C. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 5H), 5.26 (s, 2H), 3.88 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.0, 138.3, 135.7, 128.6, 128.6, 128.4, 76.7, 53.4, 52.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{14}N_3O_5$: 292.0933. Found: 292.0926.

(*E*)- dimethyl 2-(4-chlorobenzyloxyimino)-3-diazosuccinate (1d):



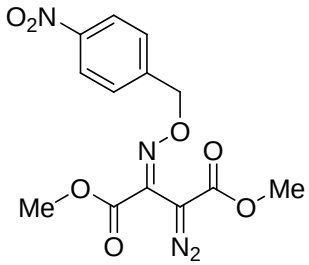
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 5.21 (s, 2H), 3.88 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 161.8, 138.6, 134.5, 134.2, 129.8, 128.8, 76.7, 53.4, 52.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}ClN_3O_5$: 326.0544. Found: 326.0542.

(*E*)- dimethyl 2-diazo-3-(4-methoxybenzyloxyimino)succinate (1e):



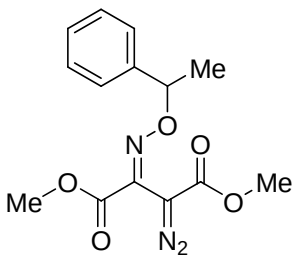
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 85-87 °C. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.19 (s, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.0, 159.9, 138.0, 130.2, 127.8, 113.9, 78.1, 55.3, 53.3, 52.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}N_3O_6$: 322.1039. Found: 322.1035.

(*E*)- dimethyl 2-diazo-3-(4-nitrobenzyloxyimino)succinate (1f):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 5.35 (s, 2H), 3.88 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 161.6, 148.0, 143.1, 139.4, 128.6, 123.9, 76.6, 53.5, 52.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}N_4O_7$: 337.0784. Found: 337.0775.

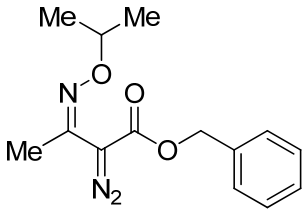
(*E*)-dimethyl 2-diazo-3-(1-phenylethoxyimino)succinate (1g):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 5.40

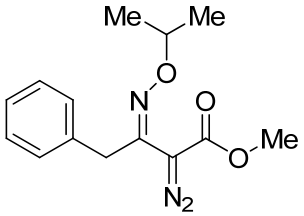
(q, J = 6.8 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 1.61 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 162.0, 141.1, 137.7, 128.5, 128.1, 126.2, 84.1, 53.3, 52.5, 21.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}N_3O_5$: 306.1090. Found: 306.1093.

(*Z*)- benzyl 2-diazo-3-(isopropoxyimino)butanoate (1h):



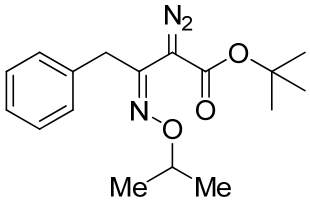
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 5H), 5.22 (s, 2H), 4.31-4-24 (m, 1H), 2.16 (s, 3H), 1.21 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 140.2, 135.6, 128.6, 128.4, 128.1, 75.9, 66.6, 21.4, 19.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}N_3O_3$: 276.1348. Found: 276.1351.

(*Z*)- methyl 2-diazo-3-(isopropoxyimino)-4-phenylbutanoate (1i):



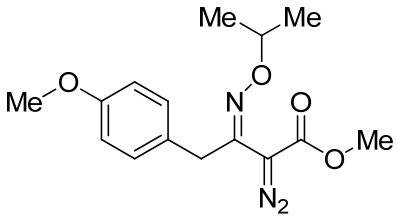
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (m, 5H), 4.42-4.35 (m, 1H), 3.93 (s, 2H), 3.73 (s, 3H), 1.27 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 142.8, 137.7, 128.8, 128.4, 126.6, 76.2, 51.9, 37.7, 21.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}N_3O_3$: 276.1348. Found: 276.1349.

(*Z*)-*tert*-butyl 2-diazo-3-(isopropoxyimino)-4-phenylbutanoate (1j):



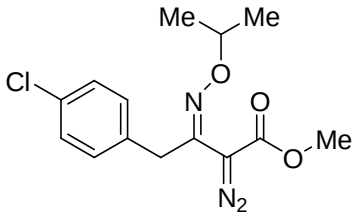
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 4.42-4.39 (m, 1H), 3.94 (s, 2H), 1.47 (s, 9H), 1.29 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.7, 137.8, 128.9, 128.3, 126.5, 82.1, 76.1, 37.6, 28.2, 21.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{24}N_3O_3$: 318.1818. Found: 318.1812.

(*Z*)- methyl 2-diazo-3-(isopropoxyimino)-4-(4-methoxyphenyl)butanoate (1k):



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 7.16 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 4.41-4.35 (m, 1H), 3.86 (s, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 1.26 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 158.4, 143.2, 129.8, 129.6, 113,8, 76.1, 55.2, 51.9, 36.8, 21.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{20}N_3O_4$: 306.1454. Found: 306.1458.

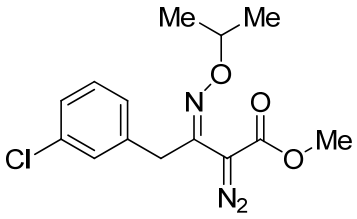
(Z)-methyl 4-(4-chlorophenyl)-2-diazo-3-(isopropoxyimino)butanoate (1l):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.4 Hz, 2H),

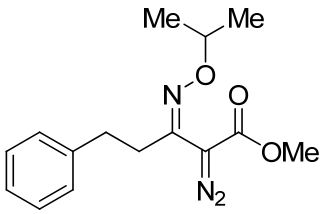
7.18 (d, J = 8.4 Hz, 2H), 4.41-4.33 (m, 1H), 3.89 (s, 2H), 3.72 (s, 3H), 1.26 (d, J = 6.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 162.3, 142.4, 136.2, 132.4, 130.2, 128.5, 76.3, 52.0, 37.1, 21.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{17}ClN_3O_3$: 310.0958. Found: 310.0953.

(Z)-methyl 4-(3-chlorophenyl)-2-diazo-3-(isopropoxyimino)butanoate (1m):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.13 (m, 4H), 4.41-4.35 (m, 1H), 3.90 (s, 2H), 3.74 (s, 3H), 1.26 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 142.1, 139.8, 134.2, 129.6, 129.0, 127.1, 126.9, 76.4, 52.0, 37.4, 21.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{17}ClN_3O_3$: 310.0958. Found: 310.0957.

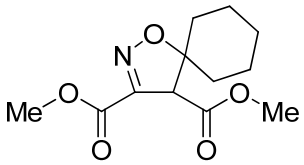
(*Z*)-methyl 2-diazo-3-(isopropoxyimino)-5-phenylpentanoate (1n):



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 7.23-7.15 (m, 5H), 4.31-4.25 (m, 1H), 3.79 (s, 3H), 2.92-2.81 (m, 4H), 1.18 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 143.0, 141.1, 128.6, 128.4, 126.0, 76.1, 52.1, 34.2, 34.0, 21.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{20}N_3O_3$: 290.1505. Found: 290.1504.

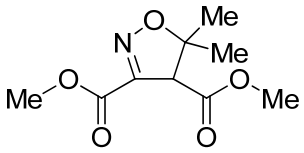
General procedure for 2-isoxazoles and 1-azirines: To a stirred suspension of $Rh_2(Piv)_4$ (2 mol%) in dichloroethane was added a solution of α-diazo oximine ethers in dichloroethane under nitrogen, and the reaction mixture was stirred under reflux (for 2-isoxazoles) or at RT (for 1-azirines) until 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 (silica gel, toluene: ethyl acetate = 50:1) to give desired products.

Dimethyl 1-oxa-2-azaspiro[4.5]dec-2-ene-3,4-dicarboxylate (2a):



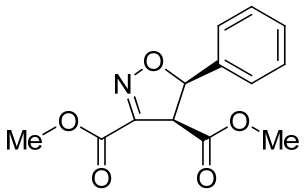
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 96-98 °C. Yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 4H), 3.75 (s, 3H), 1.92-1.83 (m, 2H), 1.77-1.67 (m, 2H), 1.64-1.57 (m, 5H), 1.38-1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 160.9, 149.3, 92.5, 60.3, 52.8, 52.6, 37.4, 31.4, 24.5, 22.3, 22.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{18}NO_5$: 256.1185. Found: 256.1185.

Dimethyl 5, 5-dimethyl-4,5-dihydroisoxazole-3,4-dicarboxylate (2b):



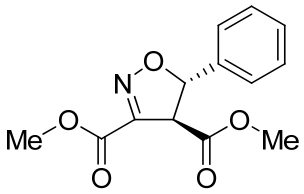
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 46%; ^{1}H NMR (400 MHz, $CDCl_3$) 3.96 (s, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 1.53 (s, 3H), 1.43 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 160.9, 149.2, 91.0, 60.6, 53.0, 52.8, 28.7, 22.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{14}NO_5$: 216.0872. Found: 216.0878.

***cis*-Dimethyl 5-phenyl-4,5-dihydroisoxazole-3,4-dicarboxylate (2c):**



The product was obtained as white solid. mp: 83-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 5H), 6.02 (d, J = 12.4 Hz, 1H), 4.60 (d, J = 12.4 Hz, 1H), 3.92 (s, 3H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 160.3, 149.5, 134.0, 129.1, 128.4, 126.7, 87.6, 57.3, 53.0, 52.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{14}NO_5$: 264.0872. Found: 264.0859.

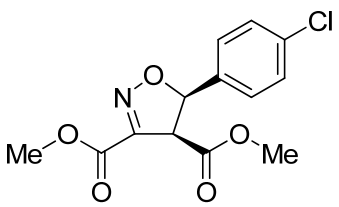
***trans*-Dimethyl 5-phenyl-4,5-dihydroisoxazole-3,4-dicarboxylate (2c'):**



The product was obtained as white solid. mp: 79-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 5H), 5.93 (d, J = 8.0 Hz, 1H), 4.33 (d, J = 7.6 Hz, 1H), 3.91 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 160.2, 148.7, 137.8, 129.2, 129.1, 125.5, 89.0, 59.7, 53.3, 53.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{14}NO_5$: 264.0872. Found: 264.0859.

The title compounds (**2c** and **2c'**) were prepared according to the general procedure. Yield: 65%;

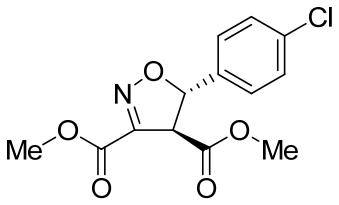
***cis*-Dimethyl 5-(4-chlorophenyl)-4,5-dihydroisoxazole-3,4-dicarboxylate (2d):**



The product was obtained as white solid. mp: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 5.99 (d, J = 12.4 Hz, 1H), 4.60 (d, J = 12.4

Hz, 1H), 3.92 (s, 3H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 160.1, 149.6, 135.1, 132.6. 128.7, 128.1, 86.8, 57.3, 53.1, 52.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}ClNO_5$: 298.0482. Found: 298.0483.

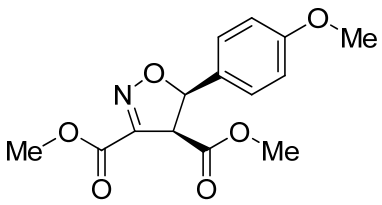
***trans*-Dimethyl 5-(4-chlorophenyl)-4,5-dihydroisoxazole-3,4-dicarboxylate (2d'):**



The product was obtained as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 5.90 (d, J = 8.0 Hz, 1H), 4.28 (d, J = 8.0 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 160.1, 148.7, 136.3, 135.2, 129.3, 126.9, 88.1, 59.8, 53.4, 53.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}ClNO_5$: 298.0482. Found: 298.0483.

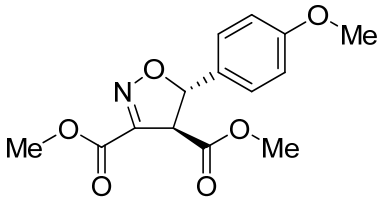
The title compounds (**2d** and **2d'**) were prepared according to the general procedure. Yield 63%;

***cis*-Dimethyl 5-(4-methoxyphenyl)-4,5-dihydroisoxazole-3,4-dicarboxylate (2e):**



The product was obtained as white solid. mp: 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.98 (d, J = 12.4 Hz, 1H) 4.55 (d, J = 12.0 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 160.4, 160.2, 149.6, 128.2, 125.9, 113.8, 87.6, 57.1, 55.3, 53.0, 52.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{15}NO_6$: Calcd for $C_{14}H_{16}NO_6$: 294.0978. Found: 294.0978.

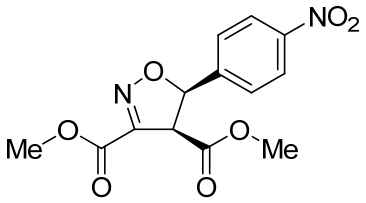
***trans*-Dimethyl 5-(4-methoxyphenyl)-4,5-dihydroisoxazole-3,4-dicarboxylate (2e'):**



The product was obtained as white solid. mp: 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 9.2 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.86 (d, J = 8.4 Hz, 1H), 4.32 (d, J = 8.4 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 160.3, 160.3, 148.7, 129.6, 127.2, 114.5, 89.2, 59.5, 55.4, 53.2, 53.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}NO_6$: 294.0978. Found: 294.0978.

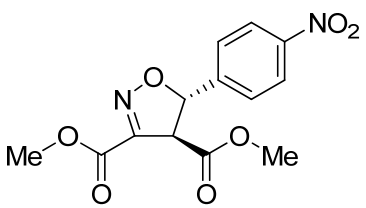
The title compounds (**2e** and **2e'**) were prepared according to the general procedure. Yield 50%;

***cis*-Dimethyl 5-(4-nitrophenyl)-4,5-dihydroisoxazole-3,4-dicarboxylate (2f):**



The product was obtained as white solid. mp: 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 6.11 (d, J = 12.4 Hz, 1H), 4.71 (d, J = 12.4 Hz, 1H), 3.93 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 159.9, 149.6, 148.3, 141.2, 127.7, 123.6, 86.0, 57.5, 53.3, 52.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}N_2O_7$: 309.0723. Found: 309.0731.

***trans*-Dimethyl 5-(4-nitrophenyl)-4,5-dihydroisoxazole-3,4-dicarboxylate (2f'):**

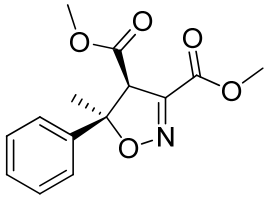


The product was obtained as white solid. mp: 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 6.04 (d, J =7.2 Hz, 1H), 4.30 (d, J = 7.2

Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 159.8, 148.7, 148.3, 144.8, 126.3, 124.4, 87.1, 59.9, 53.6, 53.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}N_2O_7$: 309.0723. Found: 309.0731.

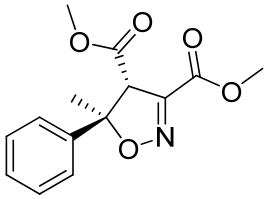
The title compounds (**2f** and **2f'**) were prepared according to the general procedure. Yield 73%;

***cis*-Dimethyl 5-methyl-5-phenyl-4,5-dihydroisoxazole-3,4-dicarboxylate (2g):**



The product was obtained as white solid. mp: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 4.22 (s, 1H), 3.90 (s, 3H), 3.17 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 160.5, 148.9, 138.4, 128.3, 128.2, 125.6, 94.3, 63.2, 53.0, 52.2, 28.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}NO_5$: 278.1028. Found: 278.1026.

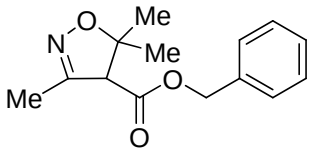
***trans*-Dimethyl 5-methyl-5-phenyl-4,5-dihydroisoxazole-3,4-dicarboxylate (2g'):**



The product was obtained as white solid. mp: 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.41-7.37 (m, 2H), 7.33-7.30 (m, 1H), 4.39 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 160.4, 149.3, 144.3, 128.8, 128.1, 124.0, 93.6, 62.3, 52.9, 52.9, 24.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}NO_5$: 278.1028. Found: 278.1026.

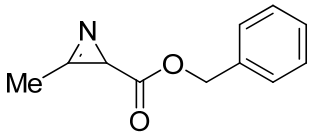
The title compounds (**2g** and **2g'**) were prepared according to the general procedure. Yield 50%;

Benzyl 3, 5, 5-trimethyl-4, 5-dihydroisoxazole-4-carboxylate (2h):



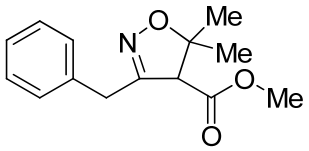
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 20%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.33 (m, 5H), 5.22 (d, J = 12.4 Hz, 1H), 5.14 (d, J = 12.4 Hz, 1H), 3.66 (s, 1H), 2.01 (s, 3H), 1.47 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (10MHz, $CDCl_3$) δ 167.9, 153.1, 135.0, 128.7, 128.6, 86.3, 67.3, 64.7, 28.3, 22.5, 13.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}NO_3$: 248.1287. Found: 248.1292.

Benzyl 3-methyl-2H-azirine-2-carboxylate (3h):



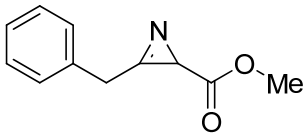
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 5H), 5.19 (d, J = 12.4 Hz, 1H), 5.14 (d, J = 12.4 Hz, 1H), 2.52 (s, 3H), 2.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 159.0, 135.5, 128.6, 128.3, 128.2, 66.8, 28.8, 12.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{12}NO_2$: 190.0868. Found: 190.0872.

Methyl 3-benzyl-5, 5-dimethyl-4, 5-dihydroisoxazole-4-carboxylate (2i):



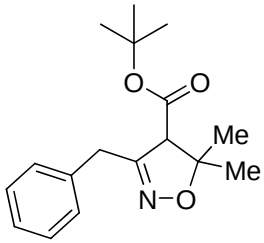
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 16%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.27-7.24 (m, 1H), 7.21-7.19 (m, 2H), 3.92 (d, J = 14.8 Hz, 1H), 3.67 (s, 3H), 3.60 (d, J = 15.2 Hz, 1H), 3.42 (s, 1H), 1.38 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 155.9, 135.4, 129.0, 128.9, 127.2, 86.5, 62.4, 52.2, 33.9, 28.1, 22.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}NO_3$: 248.1287. Found: 248.1288.

Methyl 3-benzyl-2H-azirine-2-carboxylate (3i):



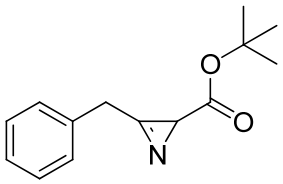
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 4.22 (d, J = 17.6 Hz, 1H), 4.14 (d, J = 17.6 Hz, 1H), 3.68 (s, 3H), 2.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 161.4, 131.5, 129.0, 129.0, 127.8, 52.2, 33.1, 29.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{12}NO_2$: 190.0868. Found: 190.0870.

***tert*-Butyl 3-benzyl-5,5-dimethyl-4,5-dihydroisoxazole-4-carboxylate (2j):**



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 16%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 3H), 7.21-7.19 (m, 2H), 3.94 (d, J = 15.2 Hz, 1H), 3.60 (d, J = 15.2 Hz, 1H), 3.31 (s, 1H), 1.46 (s, 9H), 1.38 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 156.5, 135.6, 129.0, 128.9, 127.1, 86.3, 82.4, 63.1, 33.8, 28.1, 27.9, 22.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{24}NO_3$: 290.1756. Found: 290.1757.

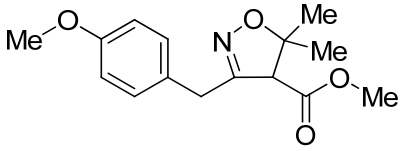
***tert*-Butyl 3-benzyl-2H-azirine-2-carboxylate (3j):**



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 4.15

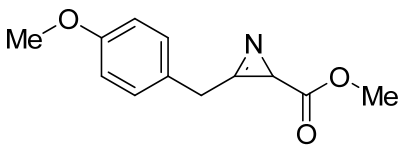
(s, 2H), 2.42 (s, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 161.8, 131.9, 129.1, 129.0, 127.7, 81.5, 33.2, 30.2, 28.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}NO_2$: 232.1338. Found: 232.1342.

Methyl 3-(4-methoxybenzyl)-5,5-dimethyl-4,5-dihydroisoxazole-4-carboxylate (2k):



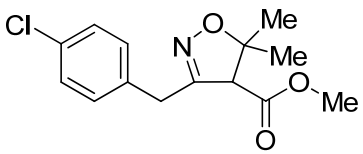
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 23%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 3.86 (d, J = 14.8 Hz, 1H), 3.79 (s, 3H), 3.68 (s, 3H), 3.54 (d, J = 15.2 Hz, 1H), 3.43 (s, 1H), 1.38 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 158.7, 156.3, 130.0, 127.2, 114.2, 86.4, 62.3, 55.2, 52.3, 32.9, 28.1, 22.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{20}NO_4$: 278.1392. Found: 278.1390.

Methyl 3-(4-methoxybenzyl)-2H-azirine-2-carboxylate (3k):



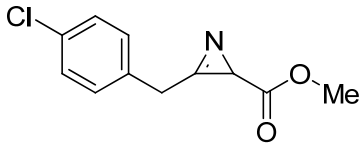
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.15 (d, J = 17.2 Hz, 1H), 4.07 (d, J = 17.2 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 2.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 161.5, 159.1, 130.1, 123.3, 114.4, 55.3, 52.1, 32.2, 29.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}NO_3$: 220.0974. Found: 220.0978.

Methyl 3-(4-chlorobenzyl)-5,5-dimethyl-4,5-dihydroisoxazole-4-carboxylate (2l):



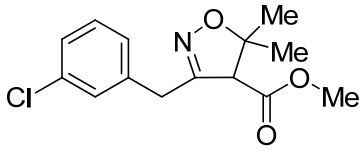
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 40-41 °C. Yield 20%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.88 (d, J = 14.8 Hz, 1H), 3.69 (s, 3H), 3.59 (d, J = 15.2 Hz, 1H), 3.43 (s, 1H), 1.40 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 155.4, 133.8, 133.1, 130.3, 129.0, 86.7, 62.3, 52.3, 33.2, 28.1, 22.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{17}ClNO_3$: 282.0897. Found: 282.0899.

Methyl 3-(4-chlorobenzyl)-2H-azirine-2-carboxylate (3l):



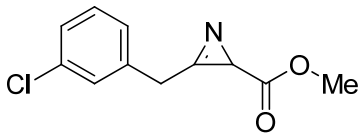
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 7.2 Hz, 2H), 4.18 (d, J = 17.6 Hz, 1H), 4.12 (d, J = 17.6 Hz, 1H), 3.70 (s, 3H), 2.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 161.2, 133.9, 130.4, 130.0, 129.2, 52.2, 32.5, 29.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{11}ClNO_2$: 224.0478. Found: 224.0479.

Methyl 3-(3-chlorobenzyl)-5,5-dimethyl-4,5-dihydroisoxazole-4-carboxylate (2m):



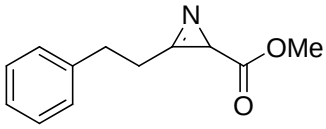
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 21%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 3H), 7.10-7.08 (m, 1H), 3.88 (d, J = 15.2 Hz, 1H), 3.69 (s, 3H), 3.59 (d, J = 15.2 Hz, 1H), 3.45 (s, 1H), 1.41 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 155.2, 137.3, 134.7, 130.1, 129.1, 127.5, 127.1, 86.8, 62.3, 52.3, 33.5, 28.1, 22.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{17}ClNO_3$: 282.0897. Found: 282.0898.

Methyl 3-(3-chlorobenzyl)-2H-azirine-2-carboxylate (3m):



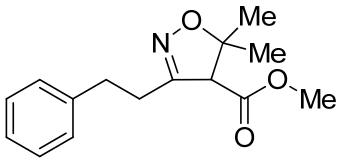
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.30 (m, 3H), 7.22-7.20 (m, 1H), 4.19 (d, J = 17.2 Hz, 1H), 4.12 (d, J = 18.0 Hz, 1H), 3.70 (s, 3H), 2.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 161.1, 134.8, 133.5, 130.2, 129.2, 128.1, 127.2, 52.3, 32.7, 29.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{11}ClNO_2$: 224.0478. Found: 224.0476.

Methyl 3-phenethyl-2H-azirine-2-carboxylate (3n):



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 7.34-7.22 (m, 5H), 3.70 (s, 3H), 3.17-3.07 (m, 4H), 2.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 161.8, 139.2, 128.7, 128.3, 126.8, 52.2, 30.3, 29.0, 28.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}NO_2$: 204.1025. Found: 204.1021.

Methyl 5,5-dimethyl-3-phenethyl-4,5-dihydroisoxazole-4-carboxylate

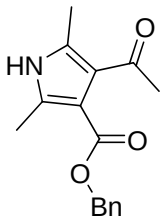


The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 23%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.22-7.20 (m, 3H), 3.72 (s, 3H), 3.55 (s, 1H), 2.95-2.88 (m, 2H), 2.86-2.80 (m, 1H), 2.62-2.55 (m, 1H), 1.40 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 156.1,

140.5, 128.5, 128.3, 126.3, 86.1, 63.8, 52.3, 32.3, 29.2, 28.2, 22.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{20}NO_3$: 262.1443. Found: 262.1448.

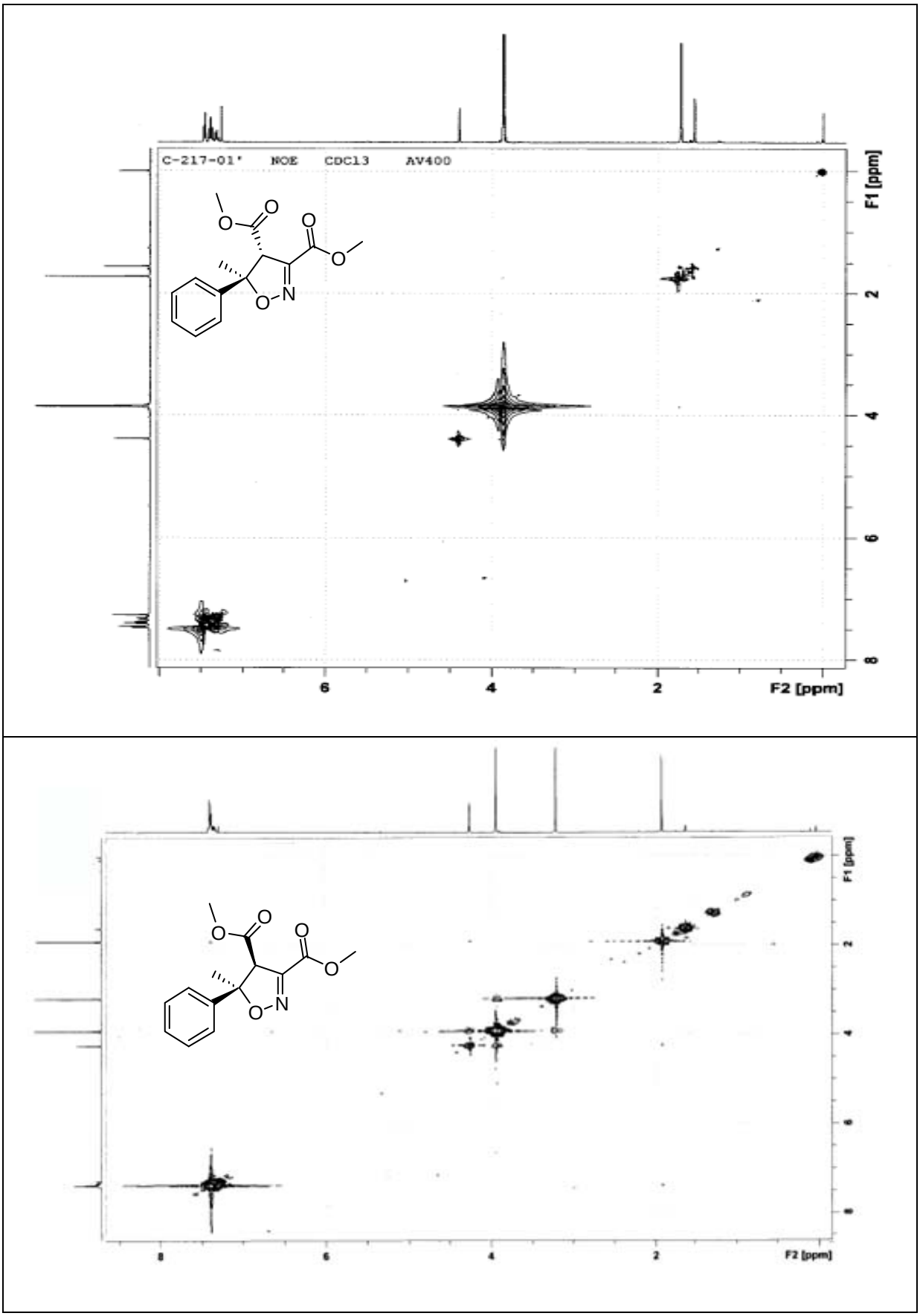
General procedure for pyrroles: To a mixture of $Rh_2(Piv)_4$ (2 mol%) and $Cu(acac)_2$ (0.6 equiv) was added a solution of α-diazo β-oximino esters (1.0 equiv) in dichloroethane. The reaction mixture was stirred at RT for 2 h, and was gradually warmed to 50 °C until the azirine intermediate was fully consumed. The solvent was evaporated under reduced pressure to give crude compound which was purified by column chromatography using hexane: ethylacetate (50:2) to give pyrroles.

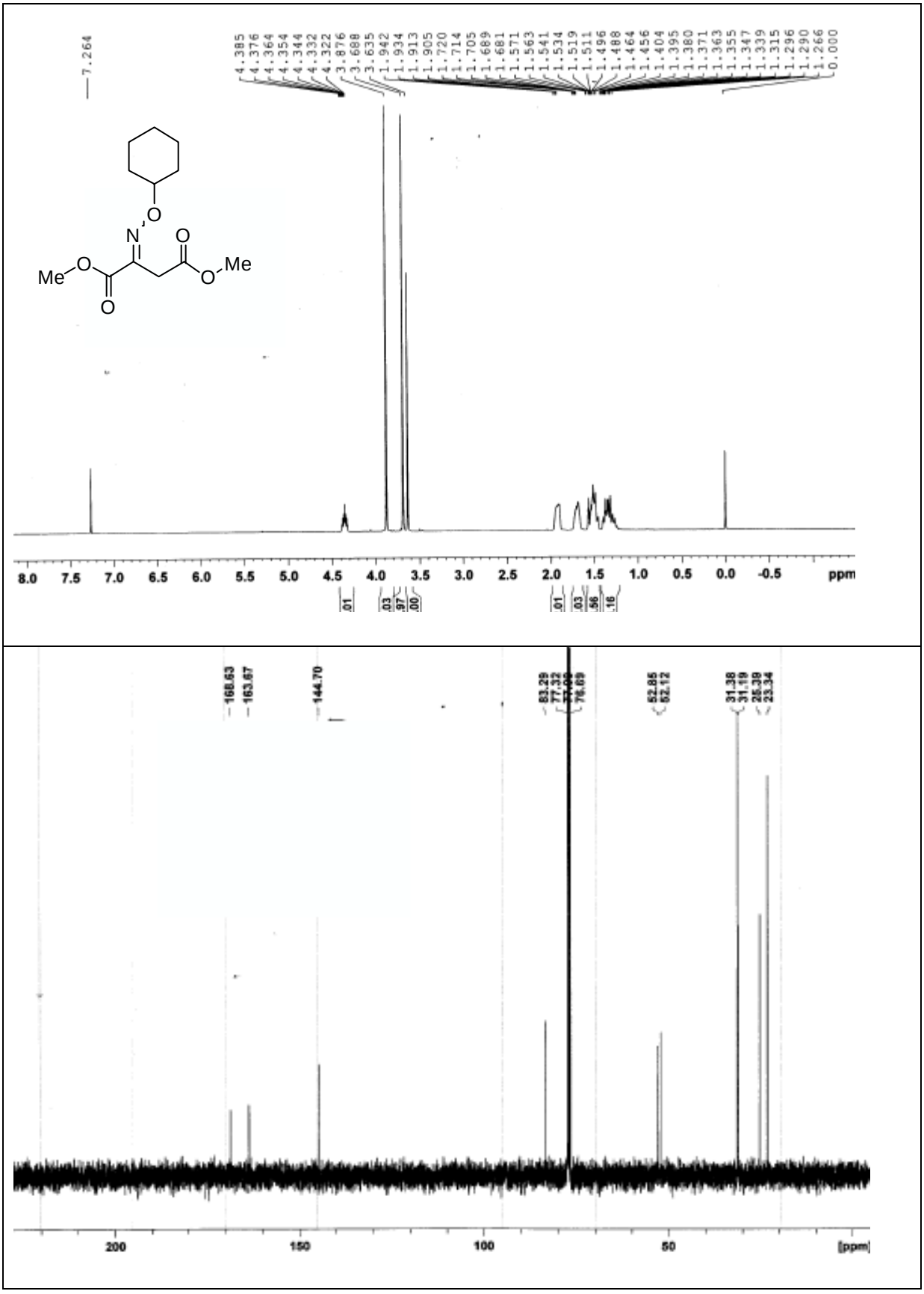
Benzyl 4-acetyl-2,5-dimethyl-1H-pyrrole-3-carboxylate (4):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, br, 1H), 7.43-7.33 (m, 5H), 5.32 (s, 2H), 2.61 (s, 3H), 2.50 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 161.2, 138.4, 136.0, 130.0, 128.7, 128.4, 128.3, 123.7, 117.6, 66.1, 31.3, 15.2, 12.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{18}NO_3$: 272.1287. Found: 272.1288.

NOESY spectra of **2g** and **2g'**

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4.376
4.364
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4.332
4.322
3.876
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3.635
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1.913
1.905
1.720
1.714
1.705
1.689
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1.563
1.541
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1.456
1.404
1.395
1.380
1.371
1.363
1.355
1.347
1.339
1.315
1.296
1.290
1.266
0.000
Me
O
N
O
O
Me
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 -0.5 ppm
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.03
.97
.00
.01
.03
.56
.16
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163.67
144.70
83.29
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77.00
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31.19
25.39
23.34
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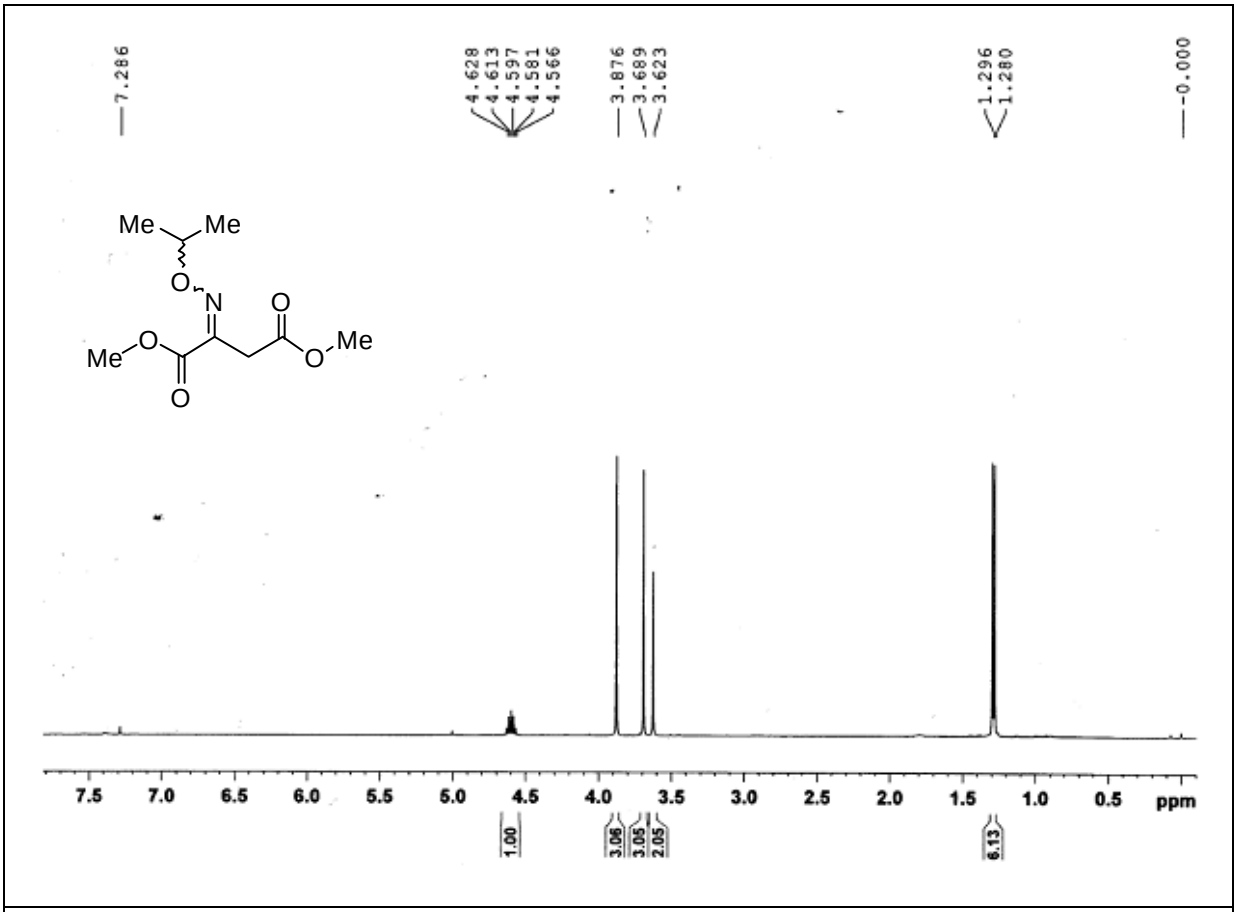
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4.597
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4.566
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0.000
Me
Me
O
N
O
Me
O
O
Me
O
7.5
7.0
6.5
6.0
5.5
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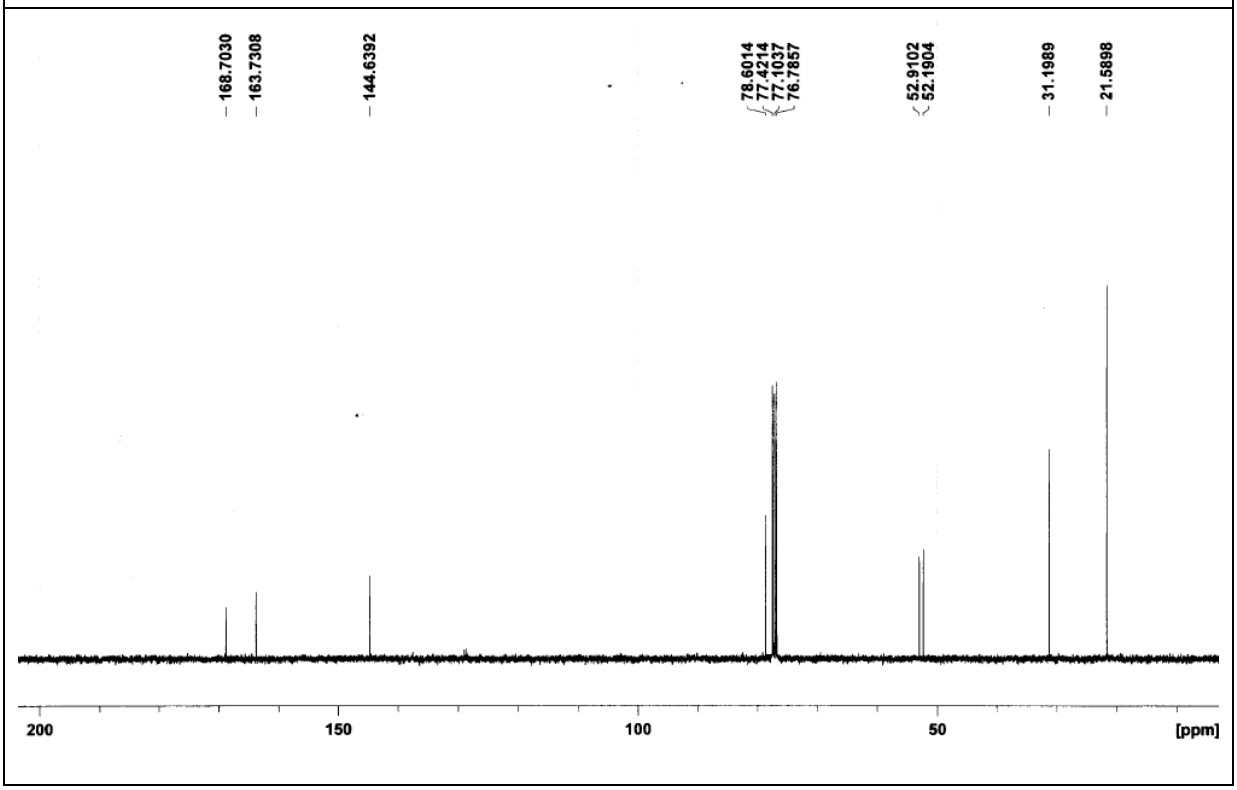
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
3.06
3.05
2.05
6.13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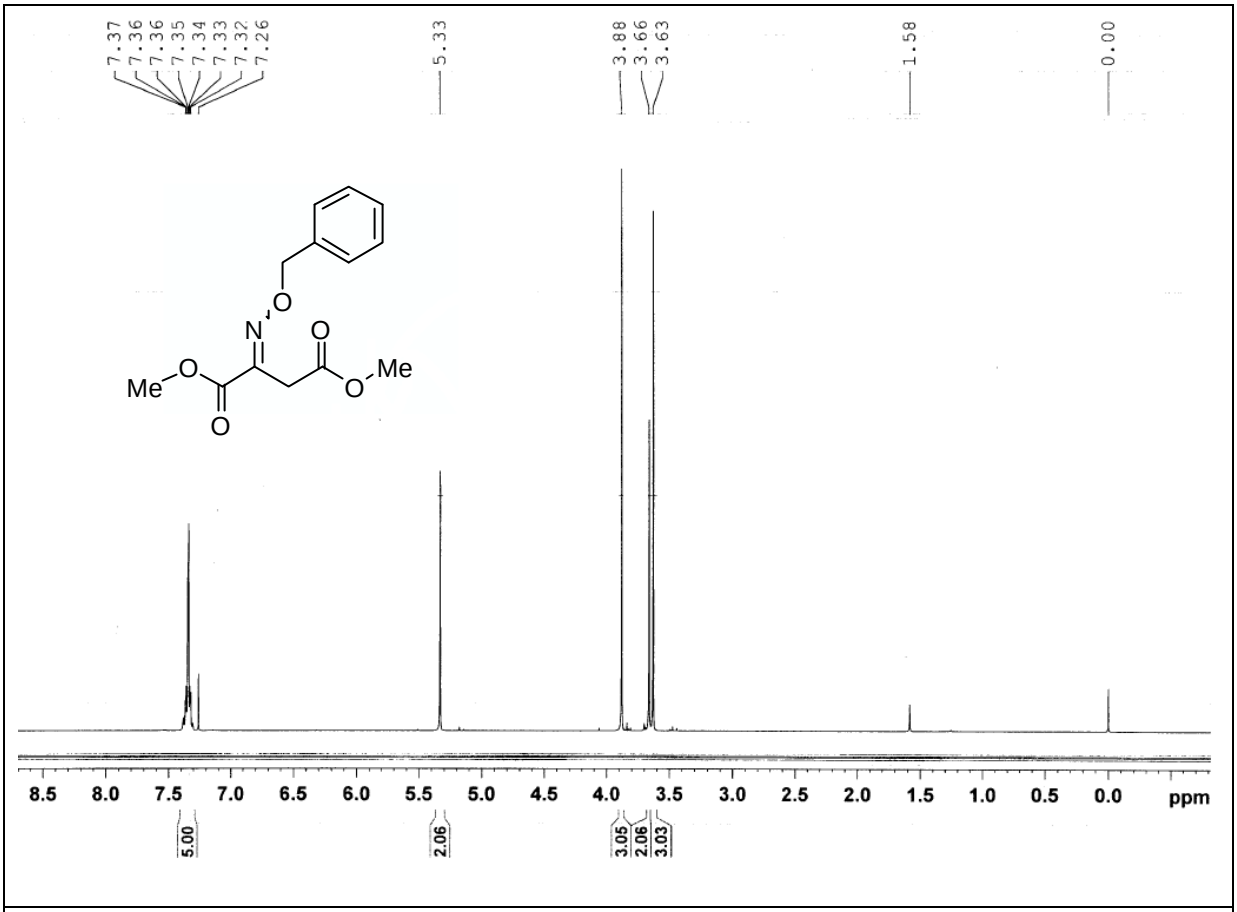
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7.36
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7.33
7.32
7.26
5.33
3.88
3.66
3.63
1.58
0.00
Me
O
N
O
O
Me
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
1.0
0.5
0.0
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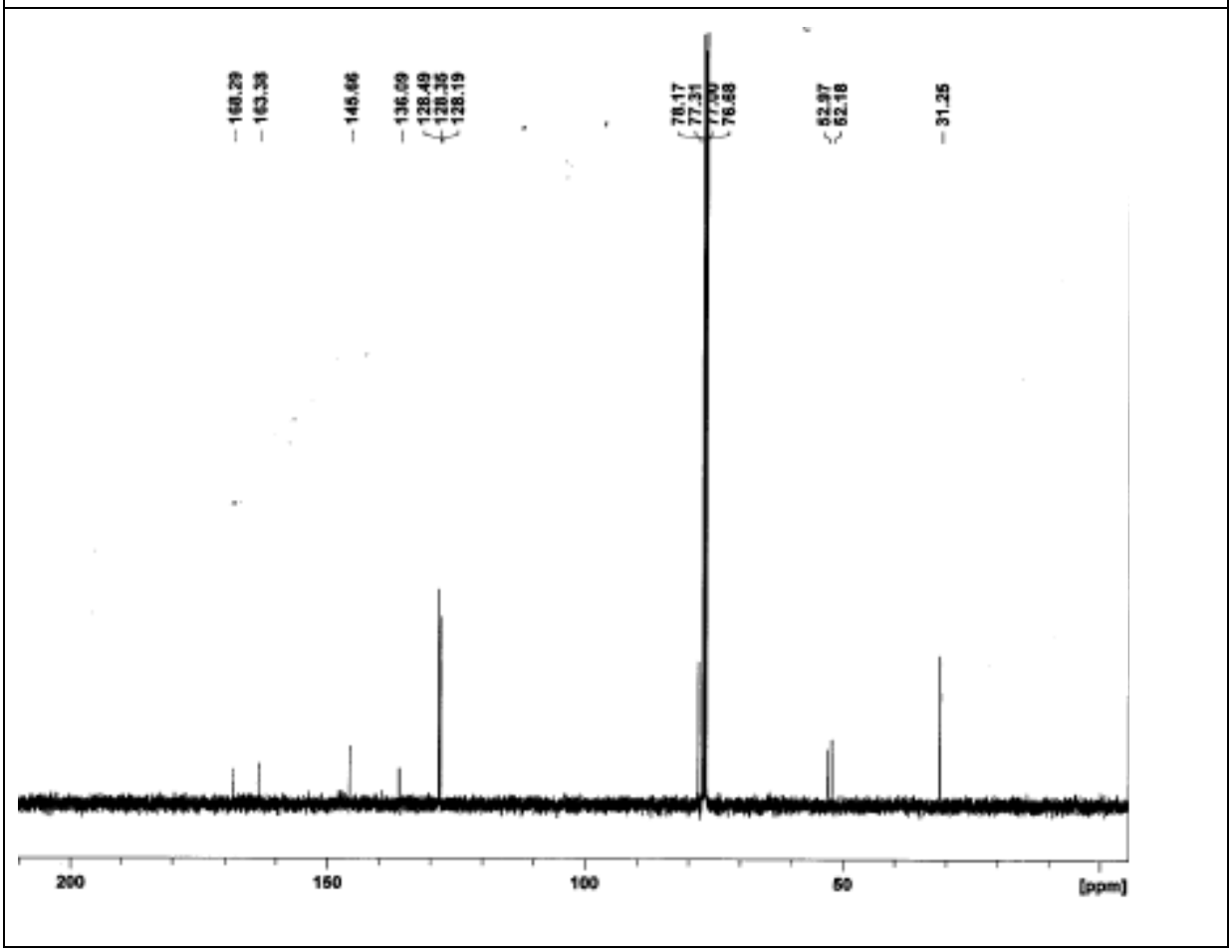
3.05
2.06
3.03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100
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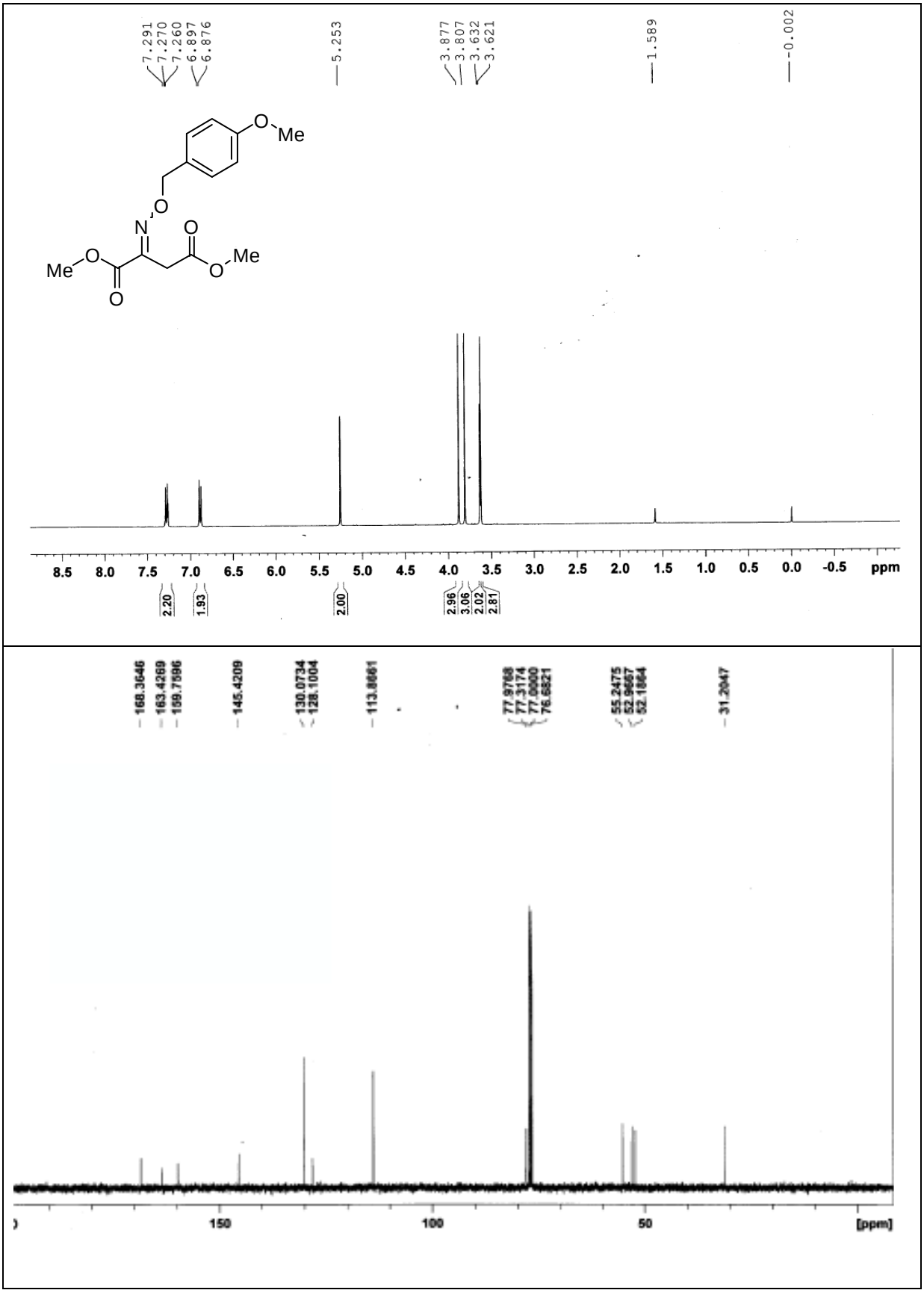
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3.807
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3.621
1.589
0.002
O
Me
O
N
O
Me
O
O
Me
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.20
1.93
2.00
2.96
3.06
2.02
2.81
168.3646
163.4269
159.7596
145.4209
130.0734
128.1004
113.8661
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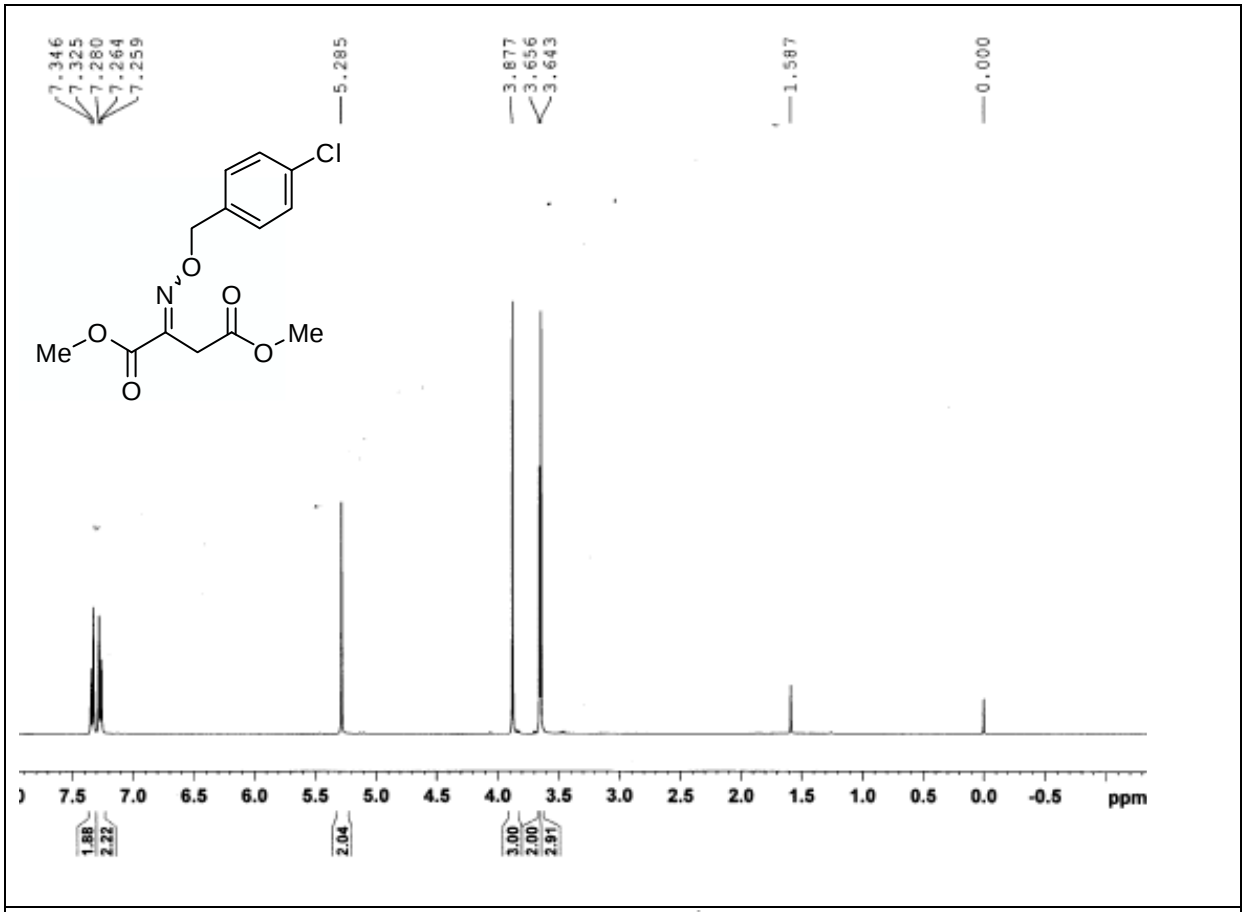
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0.000
Cl
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O
O
Me
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Me
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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0.0
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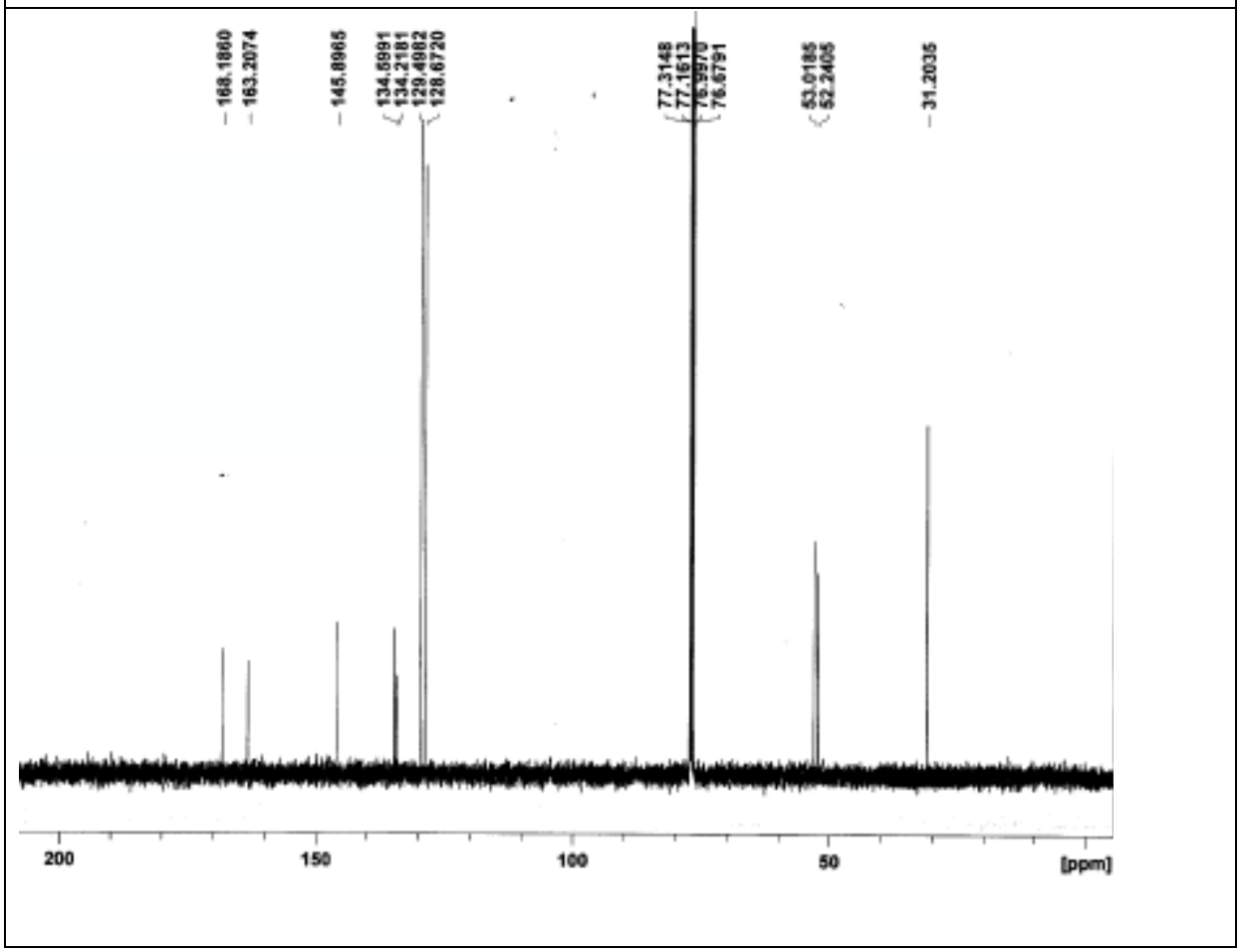
2.00
2.91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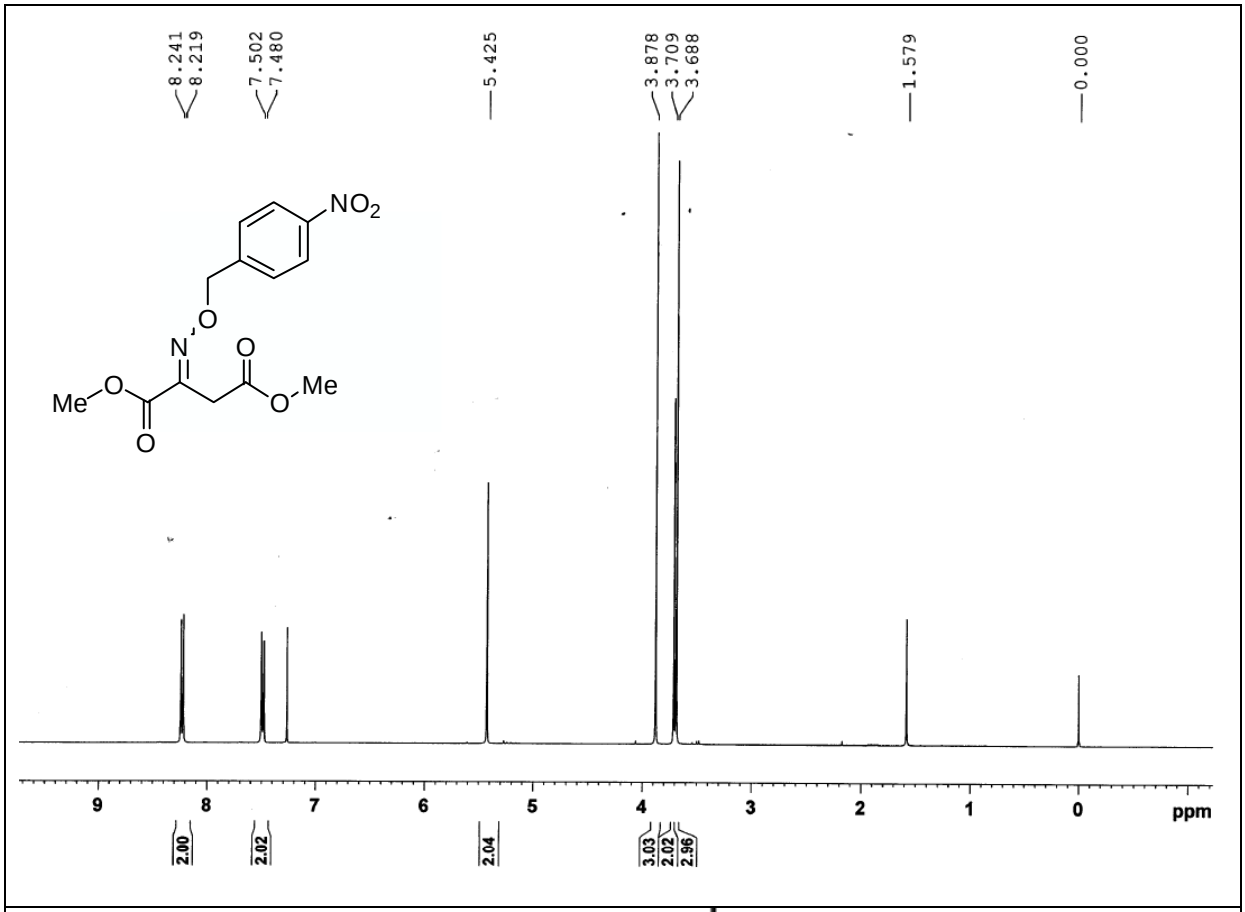
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3.688
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0.000
NO2
O
N
O
Me
O
O
O
Me
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8
7
6
5
4
3
2
1
0
ppm
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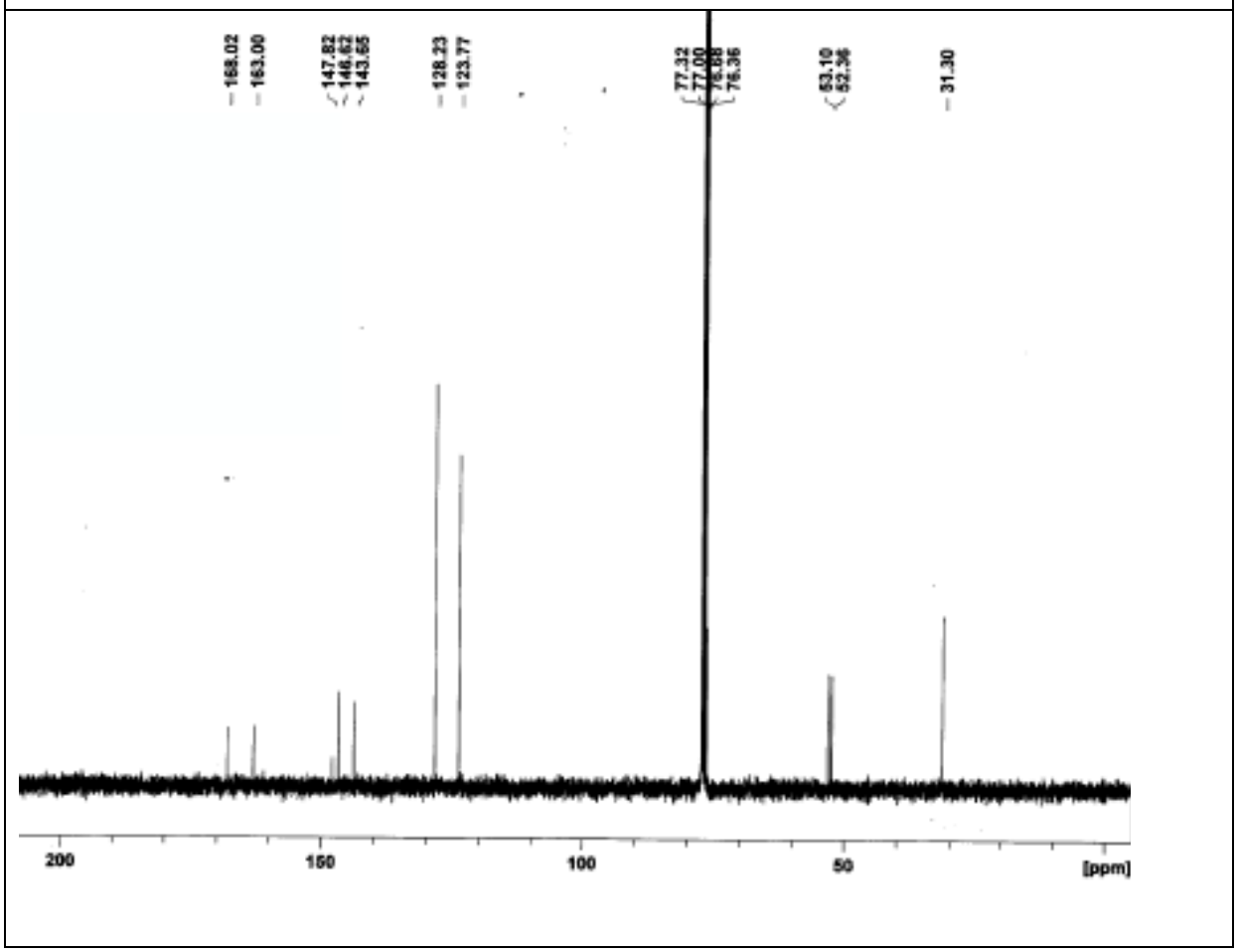
2.02
2.04
3.03
2.02
2.96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77.32
77.00
76.36
53.10
52.36
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100
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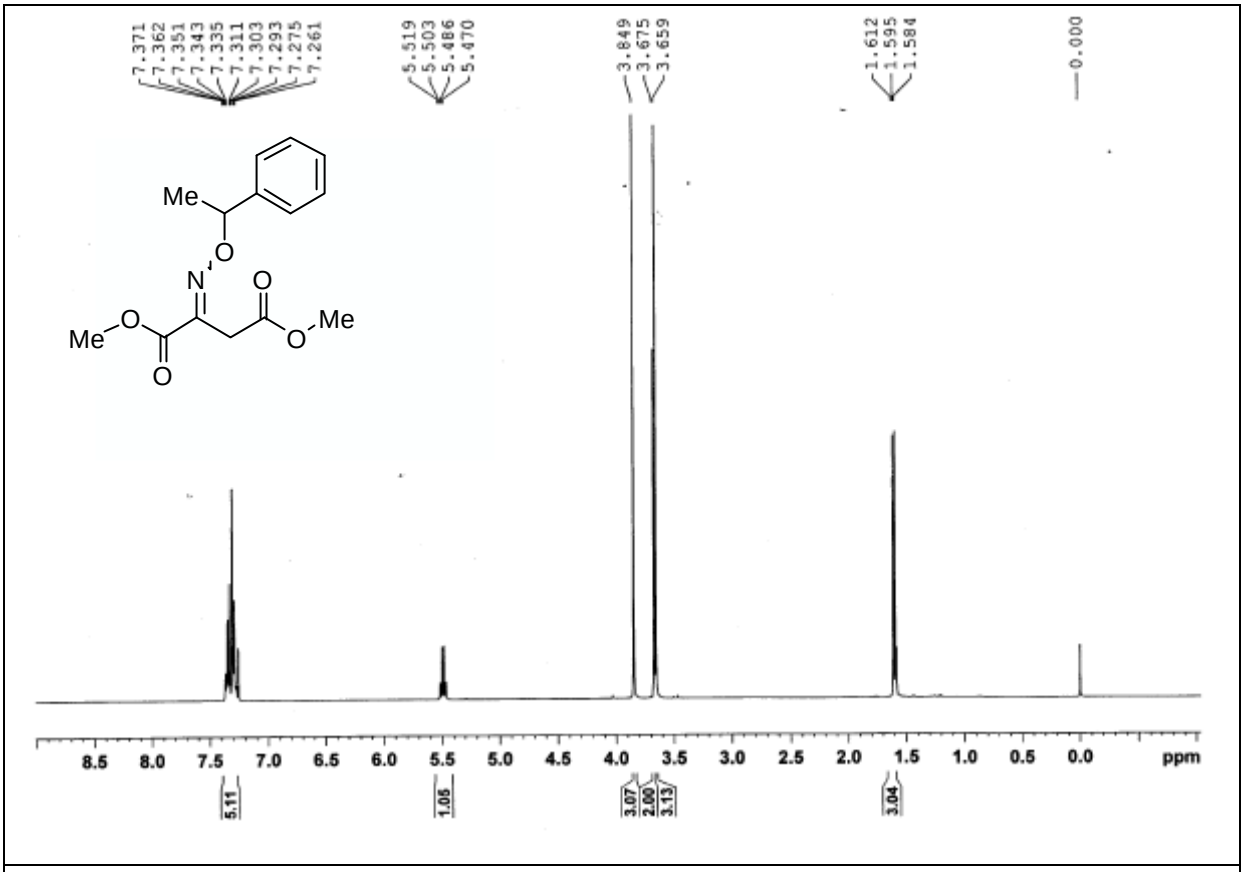
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7.343
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7.311
7.303
7.293
7.275
7.261
5.519
5.503
5.486
5.470
3.849
3.675
3.659
1.612
1.595
1.584
0.000
Me
O
N
O
Me
O
O
Me
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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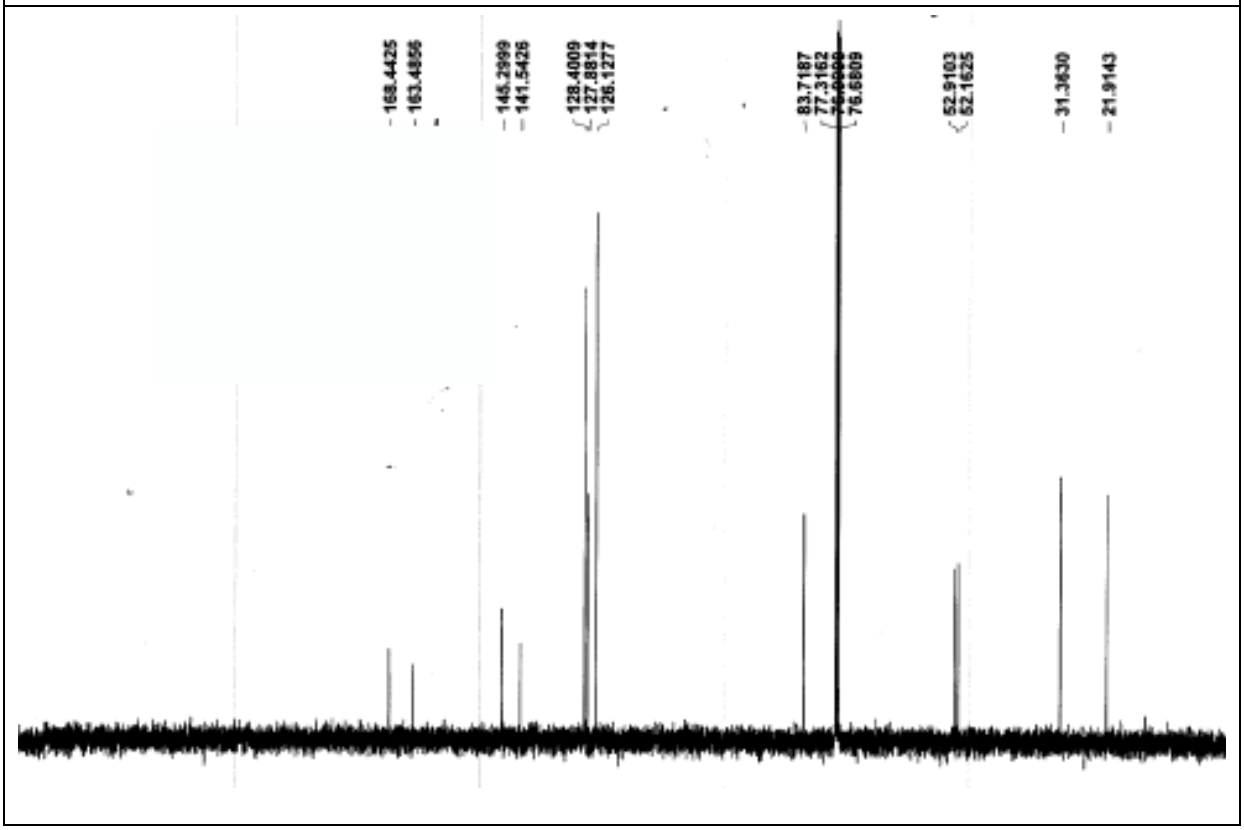
1.05
3.07
2.00
3.13
3.04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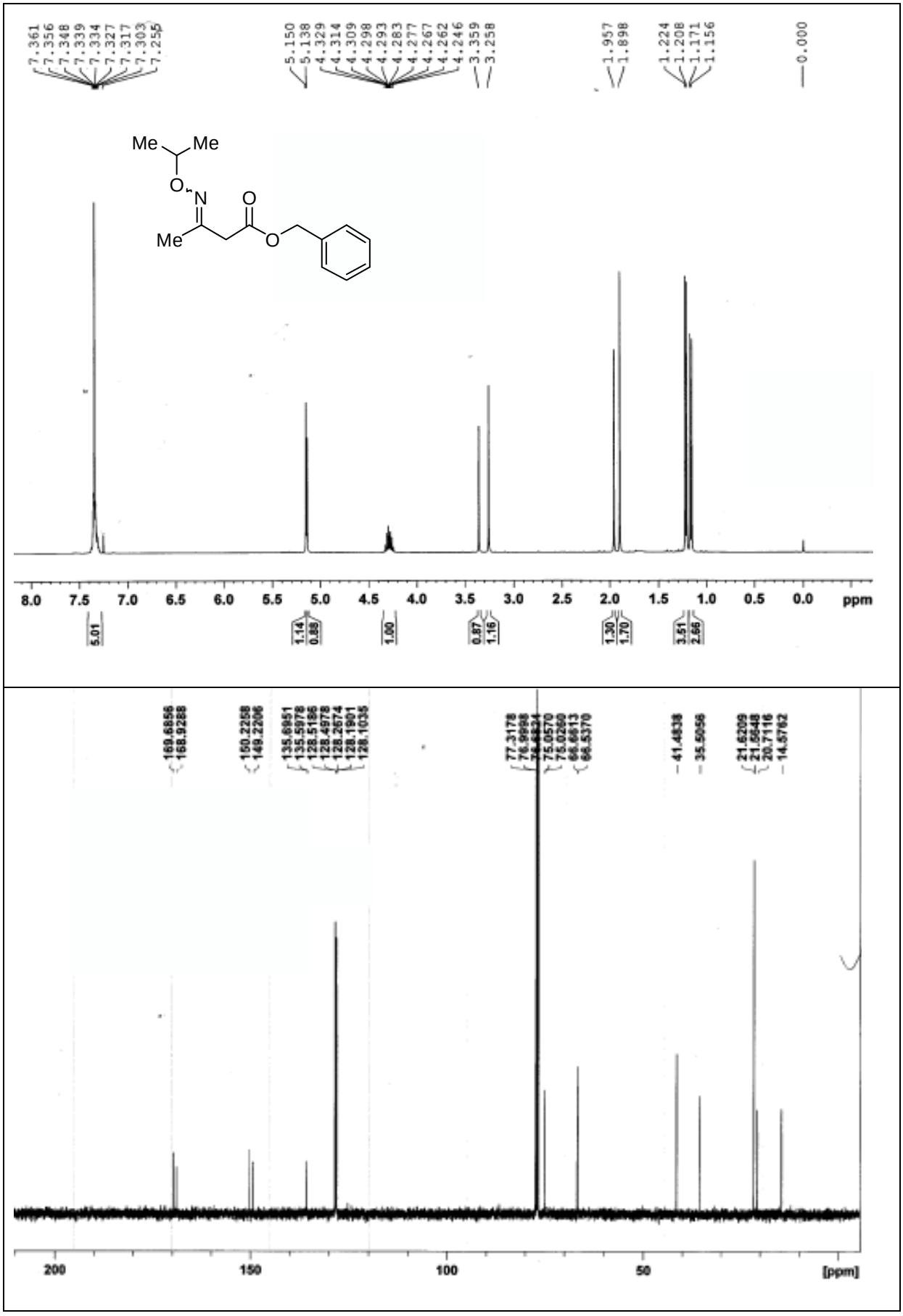
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7.303
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5.138
4.329
4.314
4.309
4.298
4.293
4.283
4.277
4.267
4.262
4.246
3.359
3.258
1.957
1.898
1.224
1.208
1.171
1.156
0.000
Me
Me
O
N
O
Me
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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1.00
0.87
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1.30
1.70
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2.66
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135.6951
135.5978
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128.4978
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128.1901
128.1035
77.3178
76.9998
75.0570
75.0260
66.6613
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100
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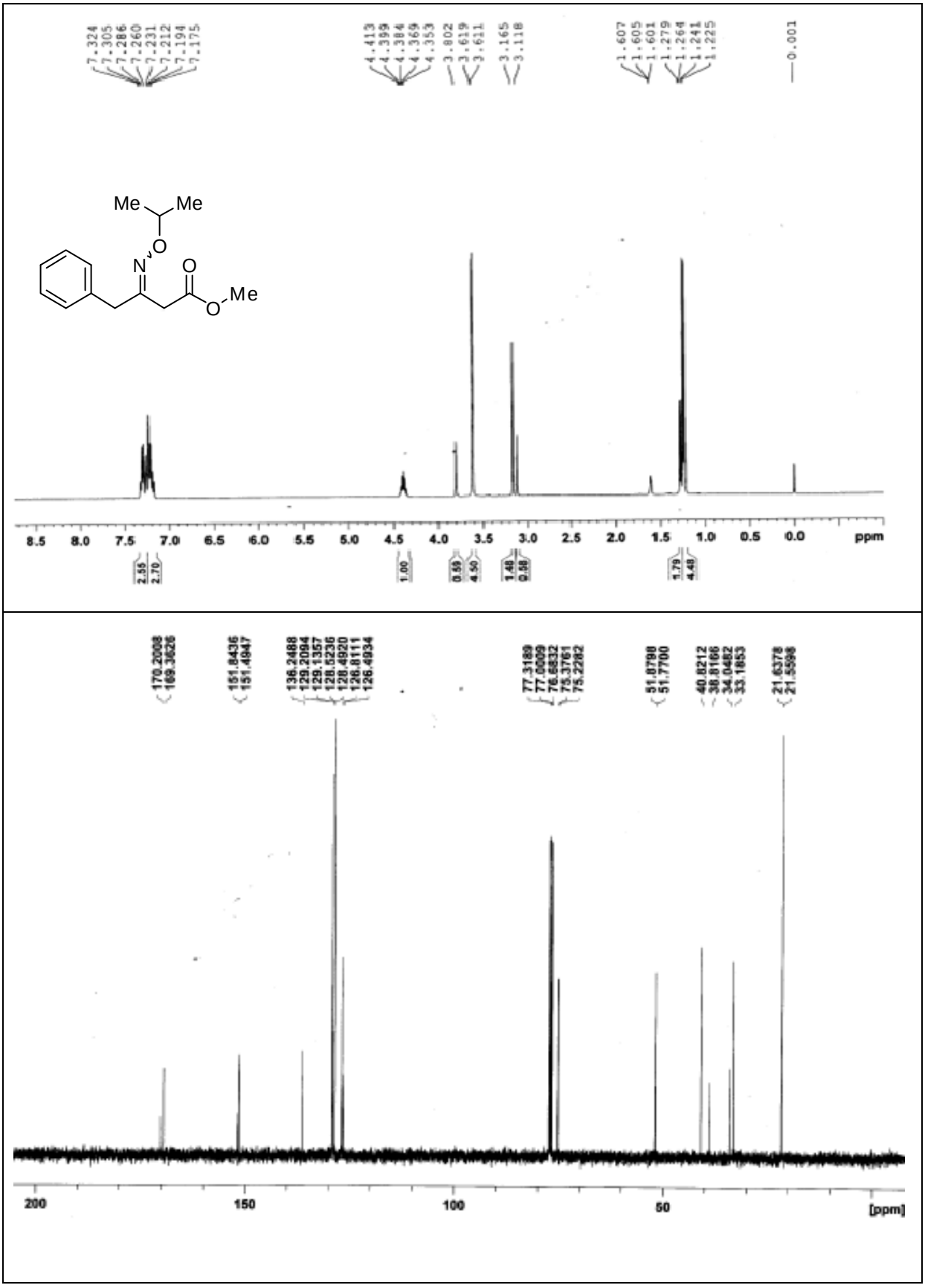
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7.175
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4.399
4.384
4.369
4.353
3.802
3.619
3.611
3.165
3.118
1.607
1.605
1.601
1.279
1.264
1.241
1.225
0.001
Me
Me
O
N
O
O
Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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1.48
0.58
1.79
4.48
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129.2094
129.1357
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128.4920
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126.4934
77.3189
77.0009
76.6832
75.3761
75.2282
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100
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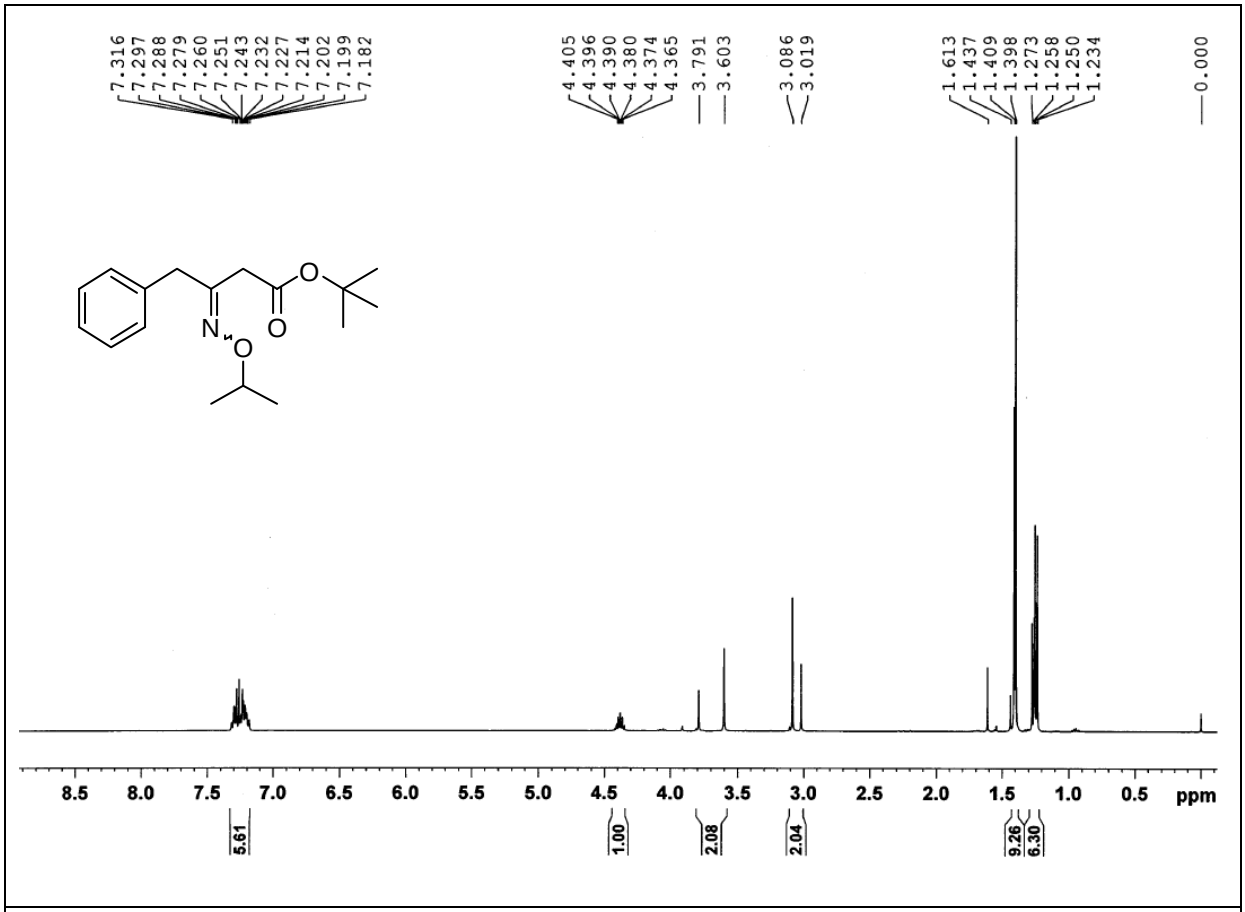
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7.243
7.232
7.227
7.214
7.202
7.199
7.182
4.405
4.396
4.390
4.380
4.374
4.365
3.791
3.603
3.086
3.019
1.613
1.437
1.409
1.398
1.273
1.258
1.250
1.234
0.000
O
O
N
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
1.0
0.5
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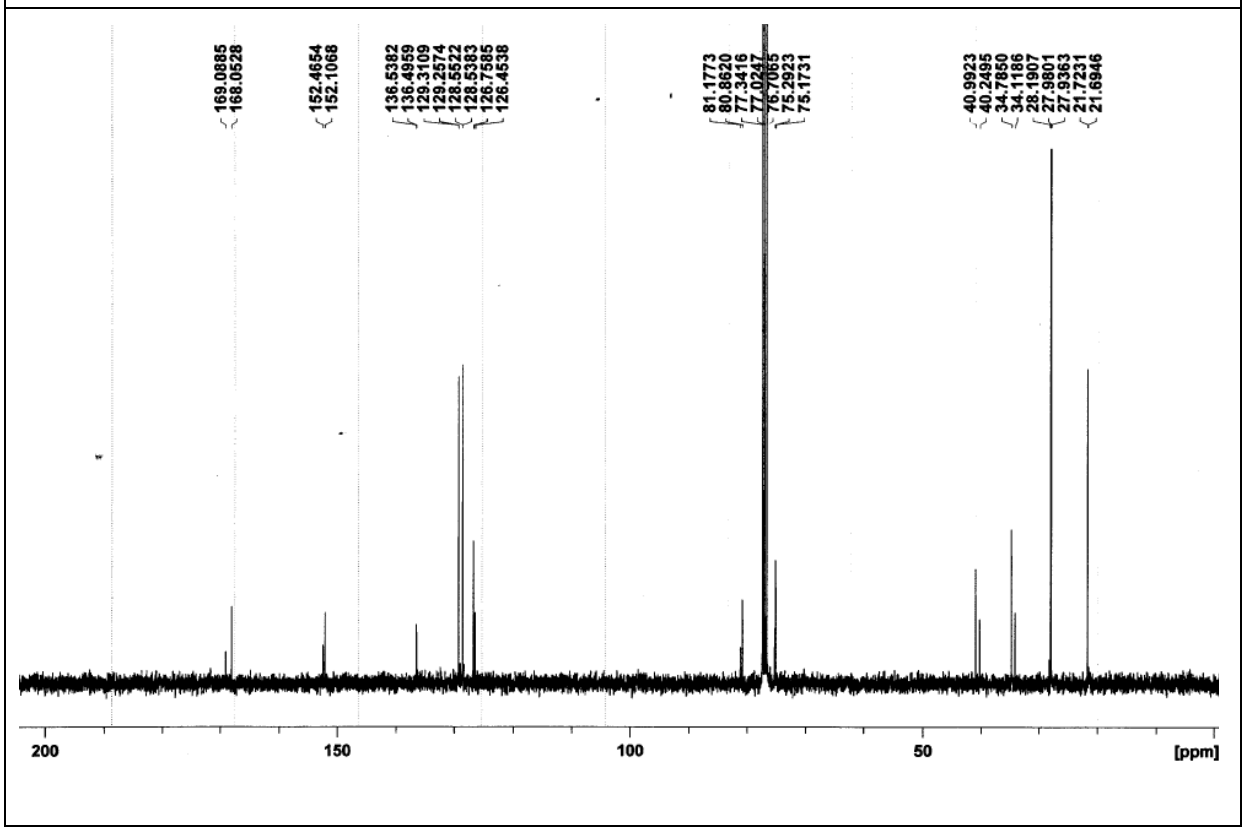
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128.5522
128.5383
126.7585
126.4538
81.1773
80.8620
77.3416
77.0247
76.7065
75.2923
75.1731
40.9923
40.2495
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28.1907
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100
50
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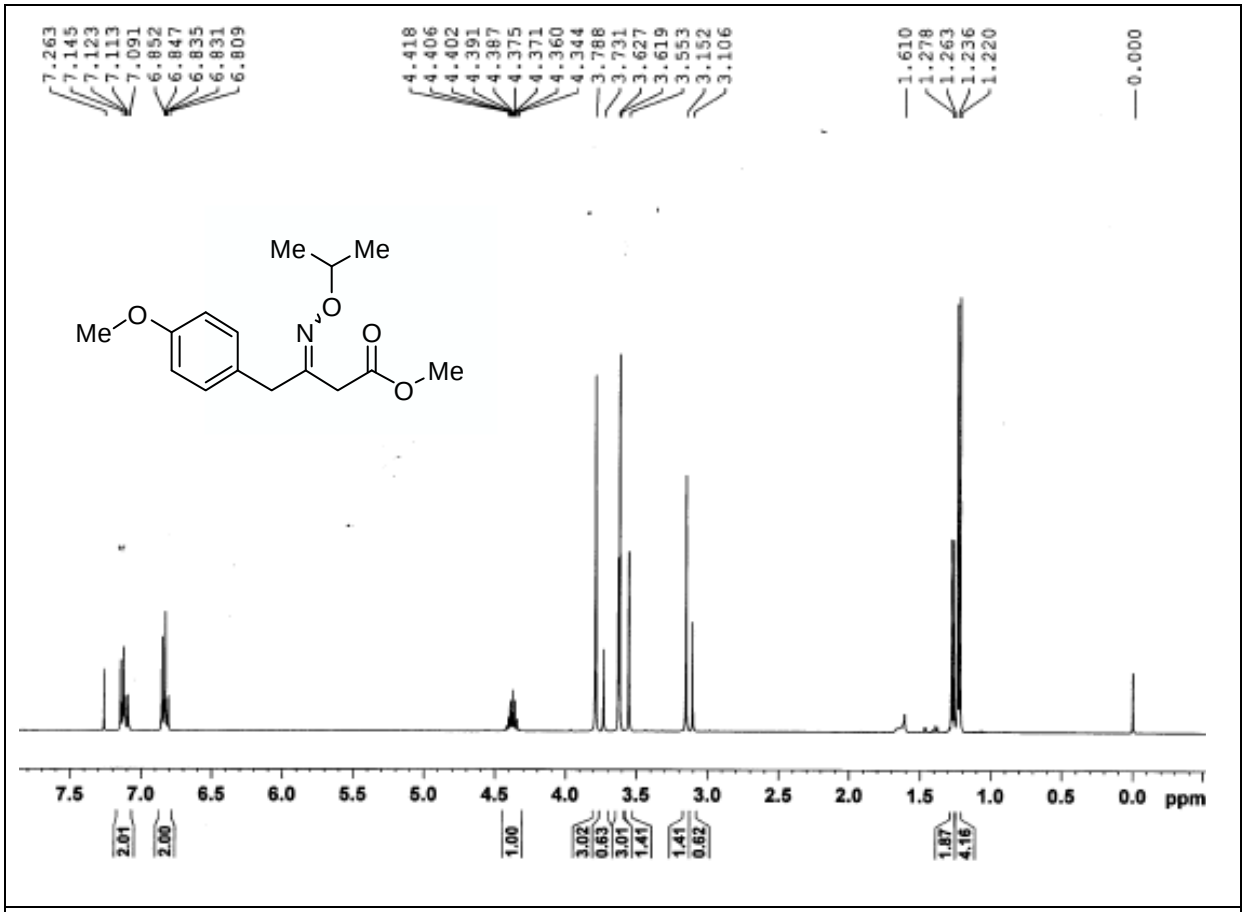
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6.809
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4.406
4.402
4.391
4.387
4.375
4.371
4.360
4.344
3.788
3.731
3.627
3.619
3.553
3.152
3.106
1.610
1.278
1.263
1.236
1.220
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Me
O
Me
O
N
O
O
Me
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
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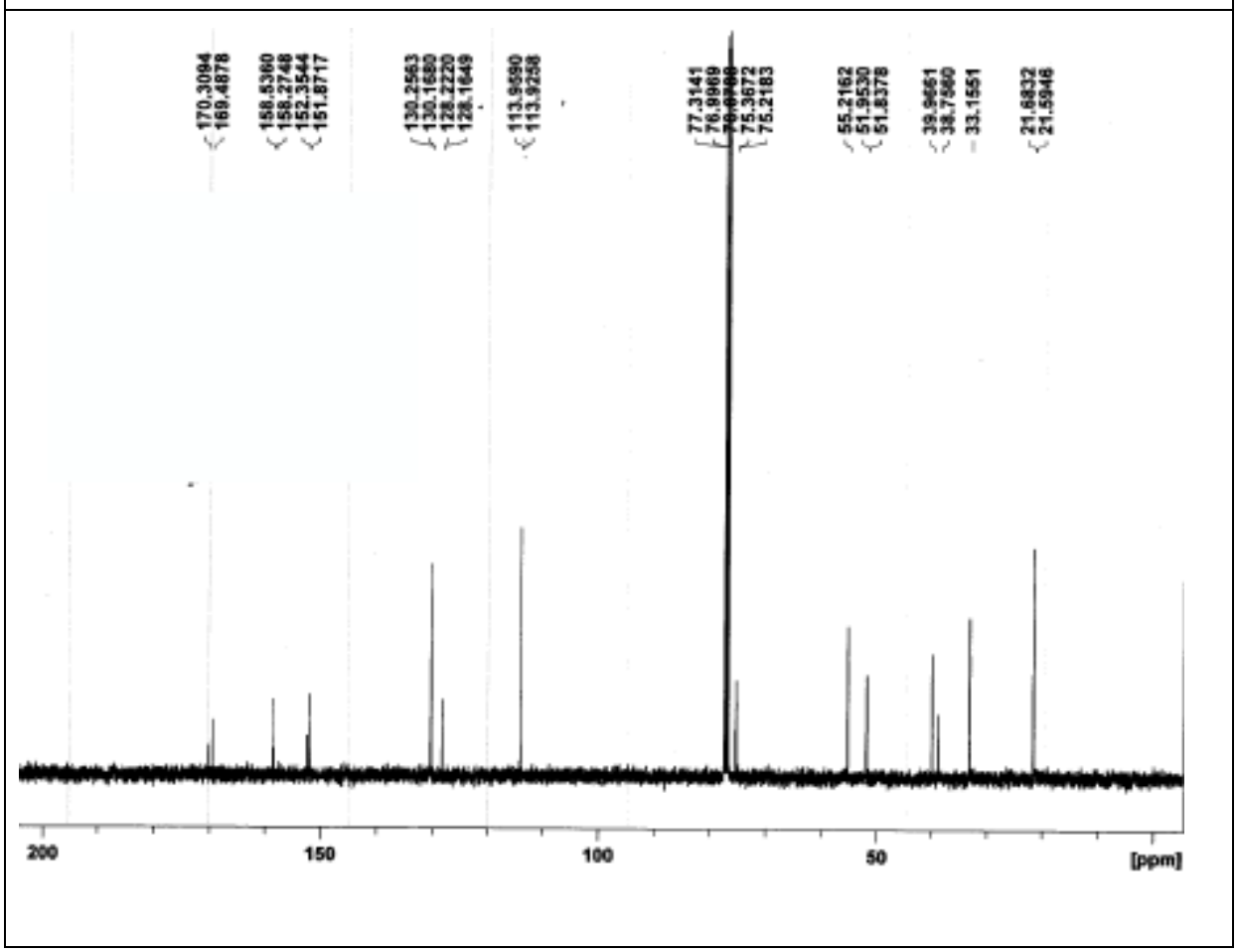
4.16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113.9258
77.3141
76.9969
75.3672
75.2183
55.2162
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39.9661
38.7980
33.1551
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21.5946
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100
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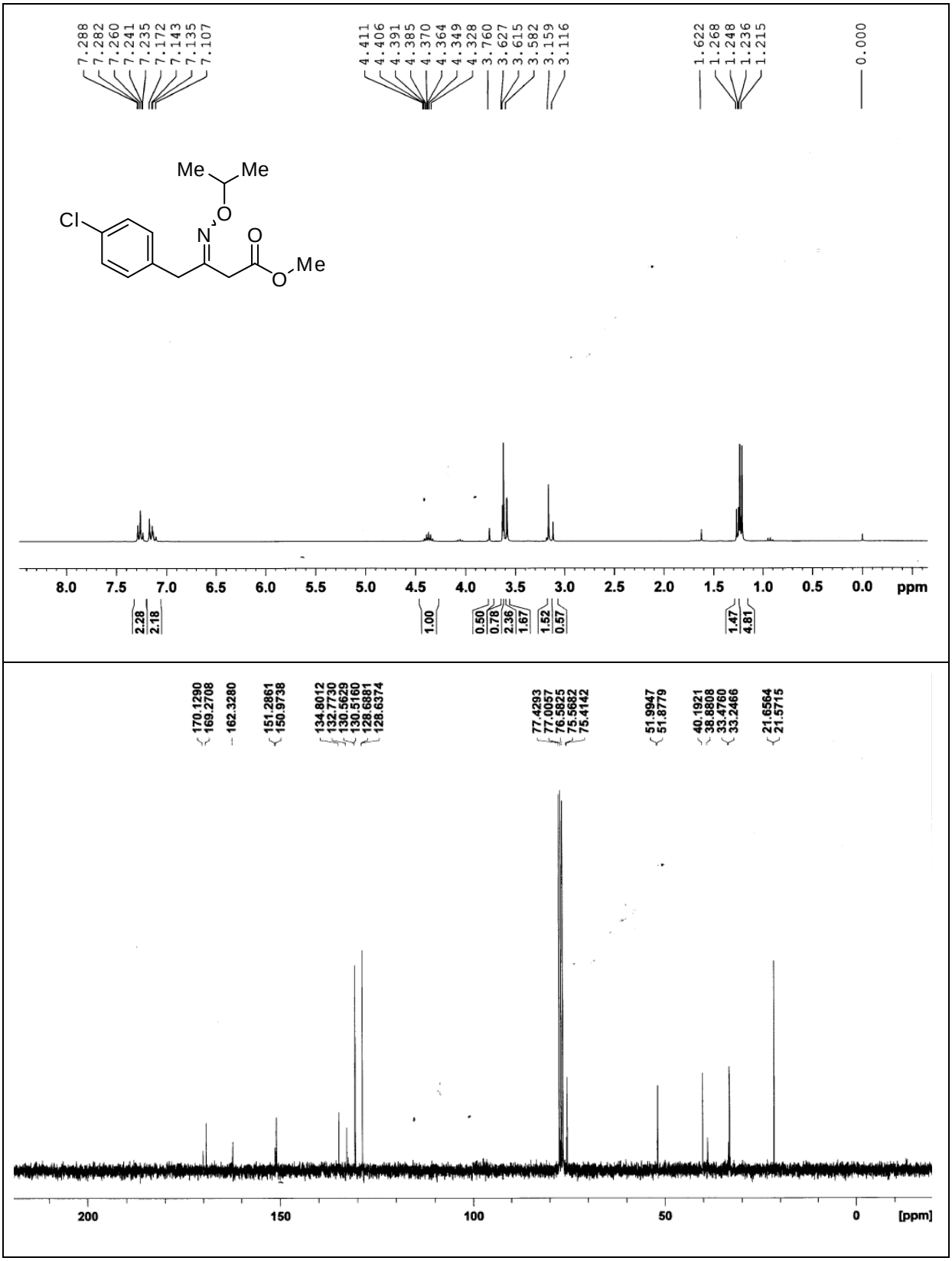
[ppm]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4.406
4.391
4.385
4.370
4.364
4.349
4.328
3.760
3.627
3.615
3.582
3.159
3.116
1.622
1.268
1.248
1.236
1.215
0.000
Me
Me
O
Cl
N
O
O
Me
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
0.5
0.0
ppm
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1.67
1.52
0.57
1.47
4.81
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162.3280
151.2861
150.9738
134.8012
132.7730
130.5629
130.5160
128.6881
128.6374
77.4293
77.0057
76.5825
75.5682
75.4142
51.9947
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38.8808
33.4760
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21.6564
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100
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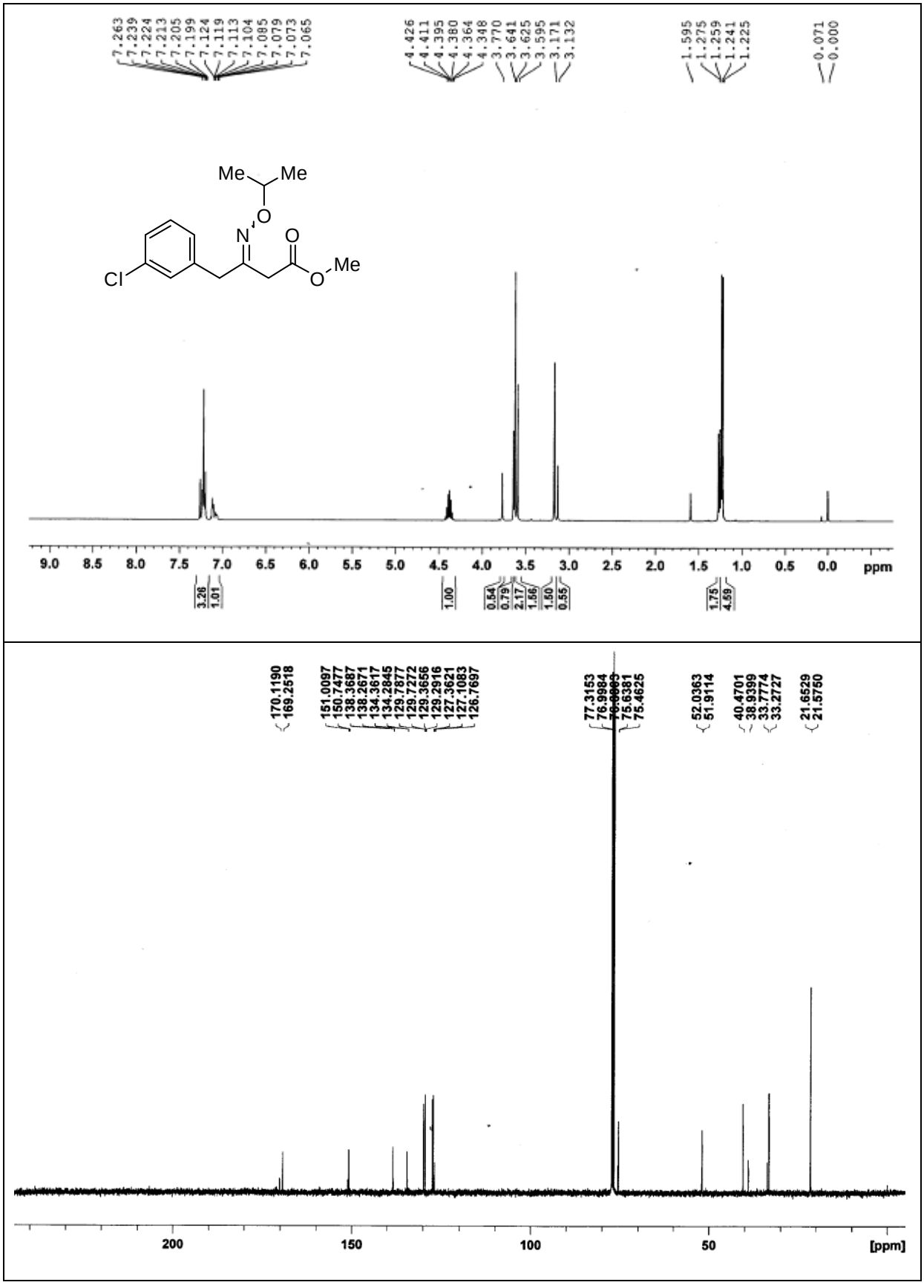
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7.119
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7.104
7.085
7.079
7.073
7.065
4.426
4.411
4.395
4.380
4.364
4.348
3.770
3.641
3.625
3.595
3.171
3.132
1.595
1.275
1.259
1.241
1.225
0.071
0.000
Me
Me
O
N
O
Cl
O
Me
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7.0
6.5
6.0
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5.0
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4.0
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2.0
1.5
1.0
0.5
0.0
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127.3621
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126.7697
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76.9984
76.6803
75.6381
75.4625
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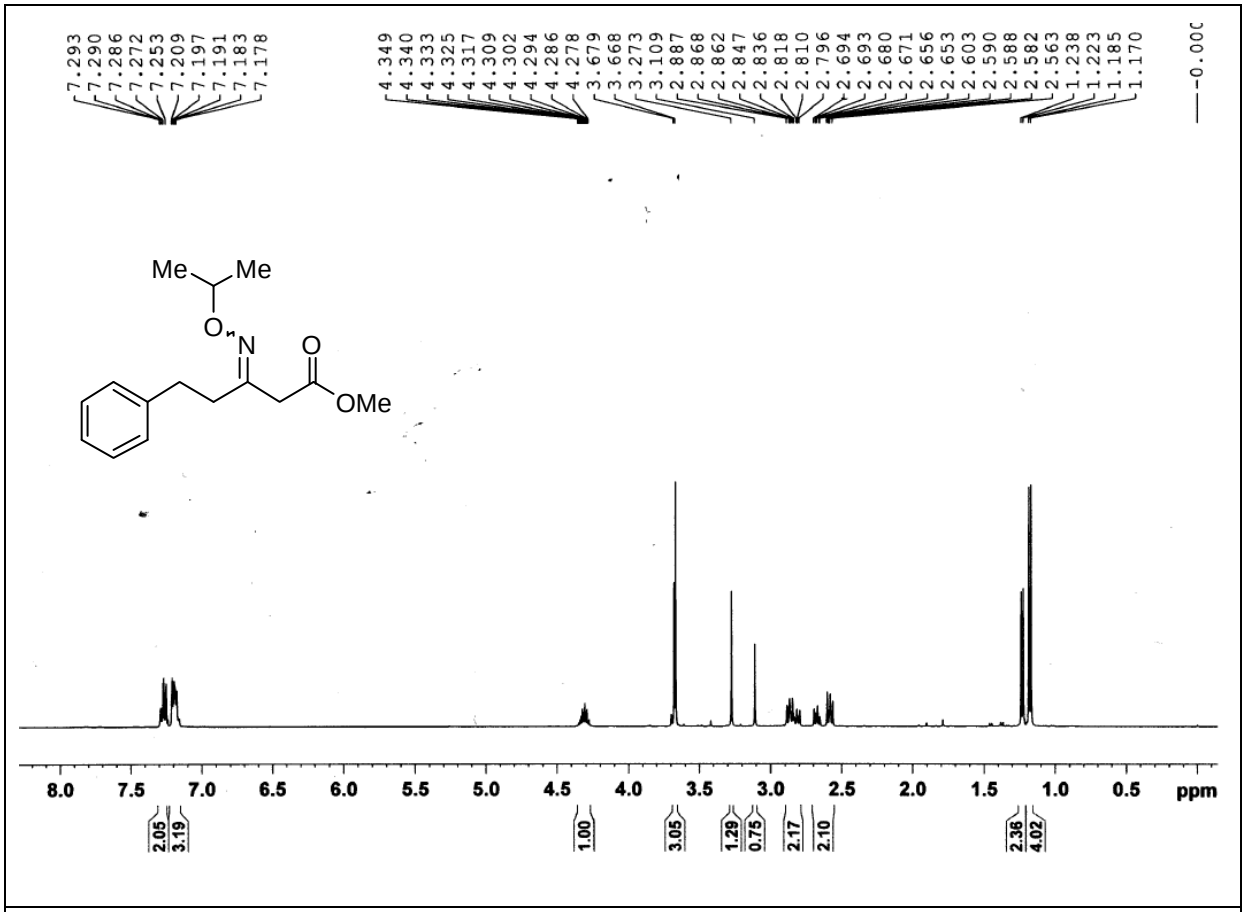
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4.325
4.317
4.309
4.302
4.294
4.286
4.278
3.679
3.668
3.273
3.109
2.887
2.868
2.862
2.847
2.836
2.818
2.810
2.796
2.694
2.693
2.680
2.671
2.656
2.653
2.603
2.590
2.588
2.582
2.563
1.238
1.223
1.185
1.170
Me
Me
O
N
O
OMe
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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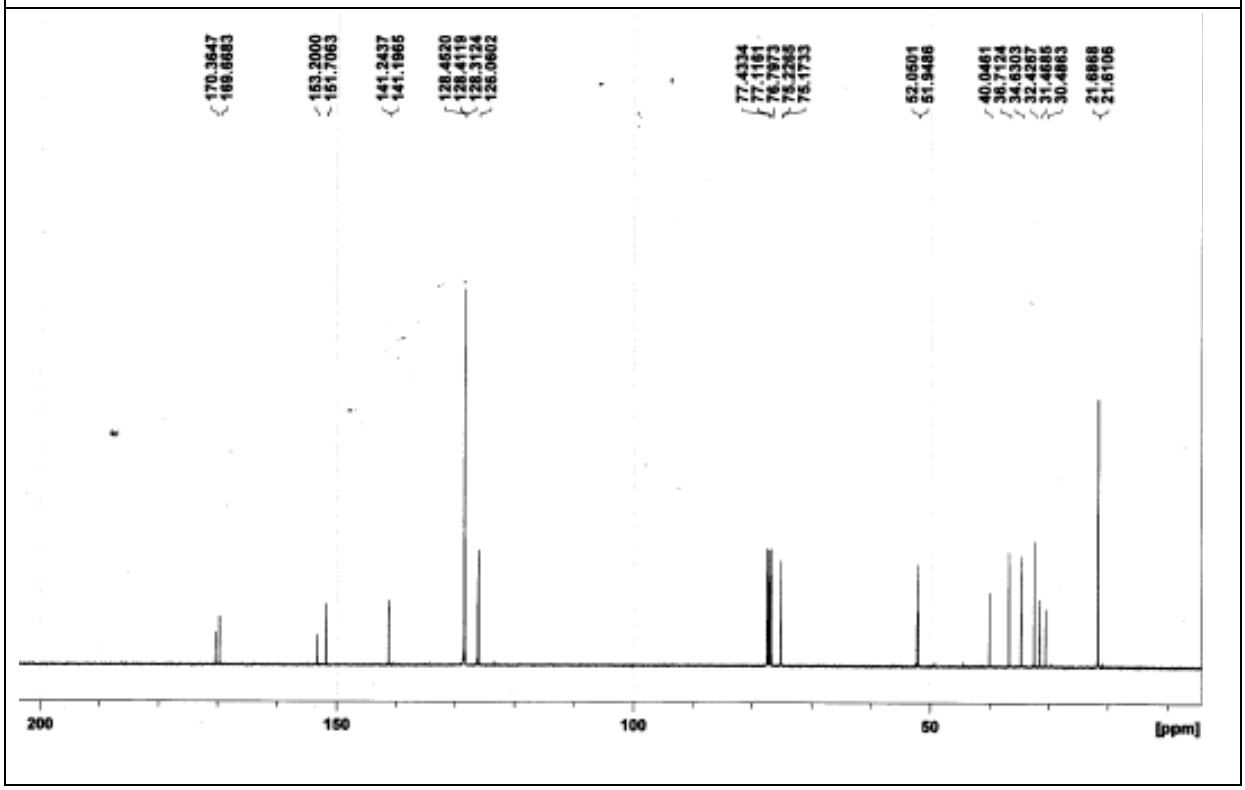
4.02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128.4520
128.4119
128.3124
126.0602
77.4334
77.1161
76.7973
75.2265
75.1733
52.0501
51.9486
40.0481
36.7124
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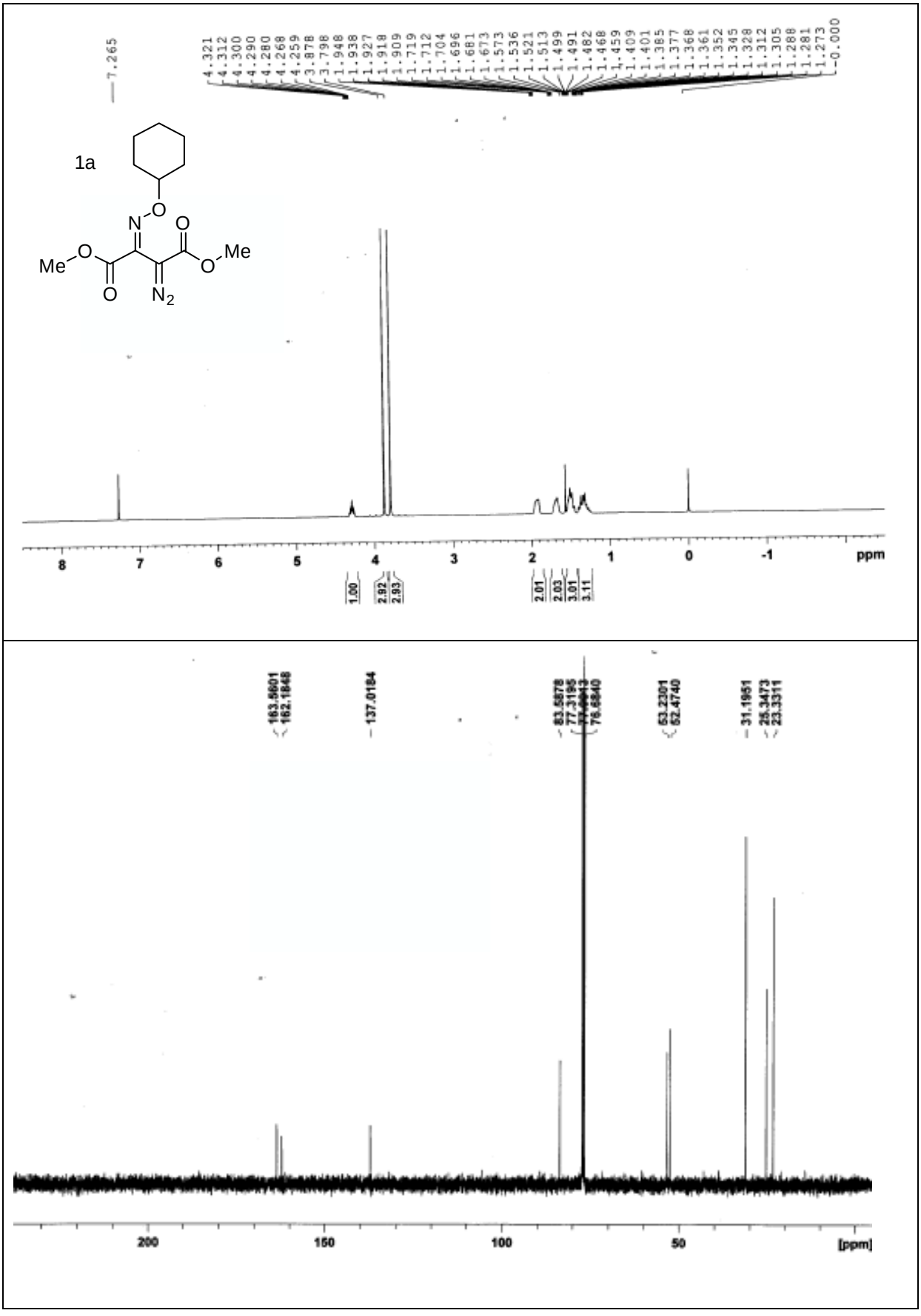
32.4267
31.4685
30.4863
21.6868
21.6106
200
150
100
50
[ppm]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O
O
Me
O
O
N2
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4.300
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4.268
4.259
3.878
3.798
1.948
1.938
1.927
1.918
1.909
1.719
1.712
1.704
1.696
1.681
1.673
1.573
1.536
1.521
1.513
1.499
1.491
1.482
1.468
1.459
1.409
1.401
1.385
1.377
1.368
1.361
1.352
1.345
1.328
1.312
1.305
1.288
1.281
1.273
0.000
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
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2.93
2.01
2.03
3.01
3.11
163.5601
162.1848
137.0184
83.5878
77.3195
76.6840
63.2301
62.4740
31.1951
25.3473
23.3311
200
150
100
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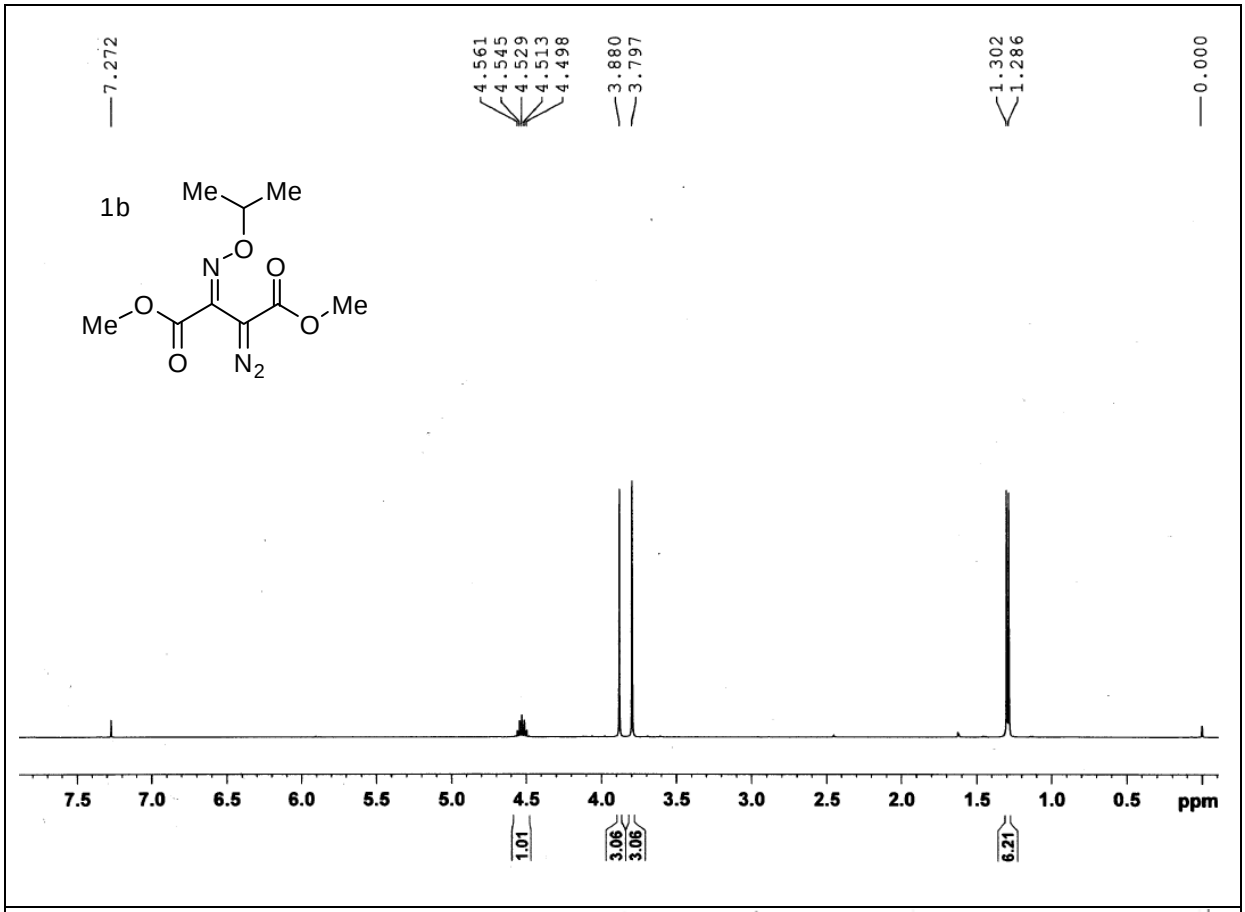
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3.797
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1.286
0.000
1b
Me
Me
O
N
O
Me
O
O
Me
O
O
N2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
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1.0
0.5
ppm
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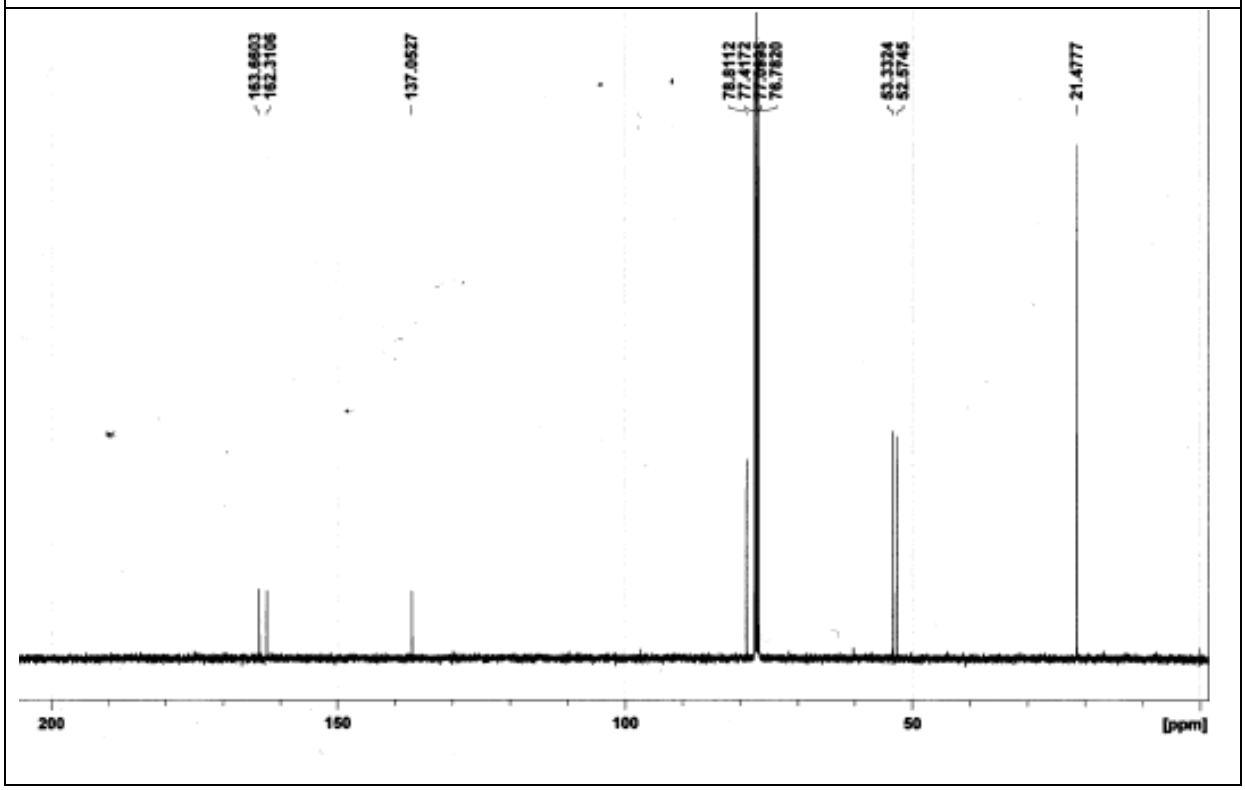
3.06
3.06
6.21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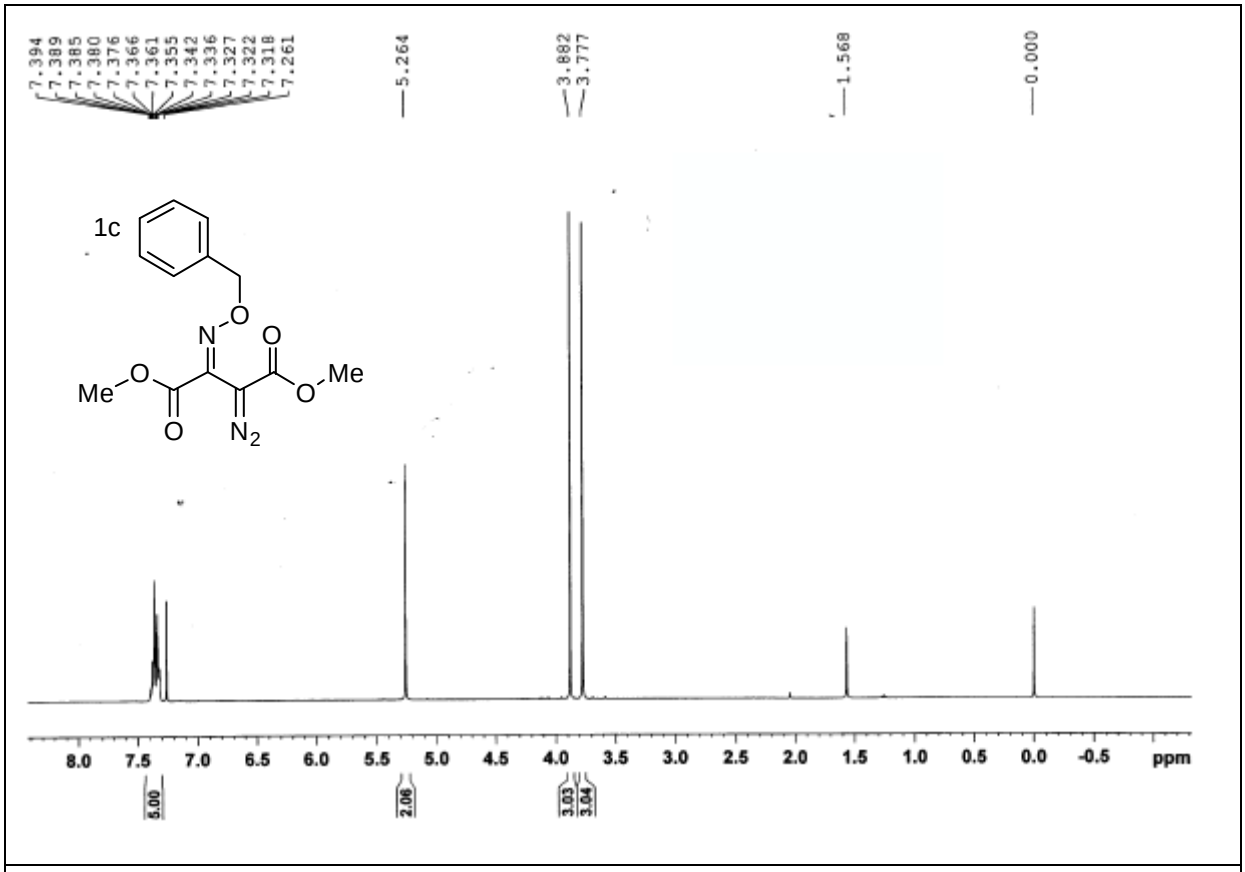
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7.355
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7.327
7.322
7.318
7.261
5.264
3.882
3.777
1.568
0.000
1c
Me
O
N
O
O
Me
O
N2
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
1.0
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ppm
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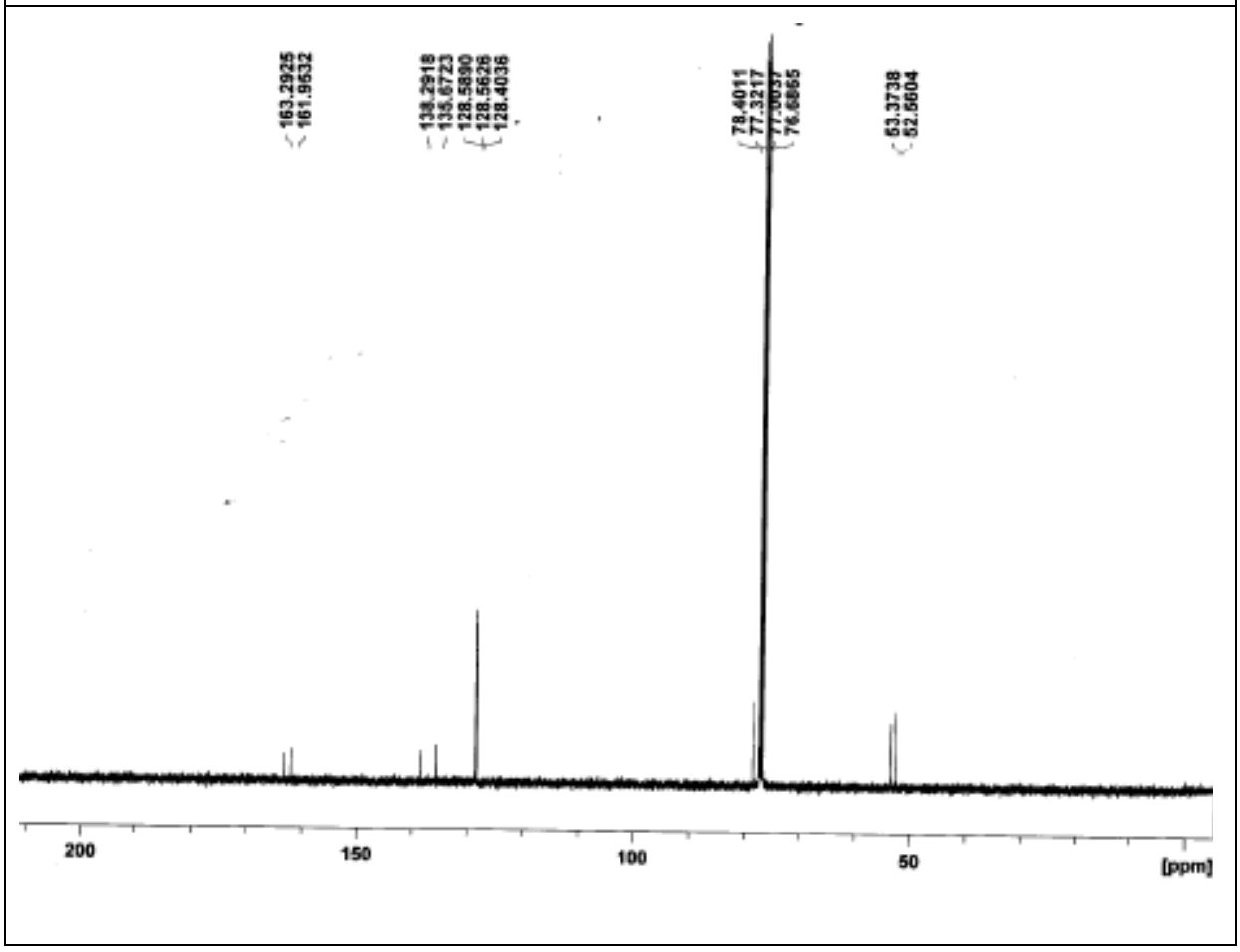
2.06
3.03
3.04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52.6604
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100
50
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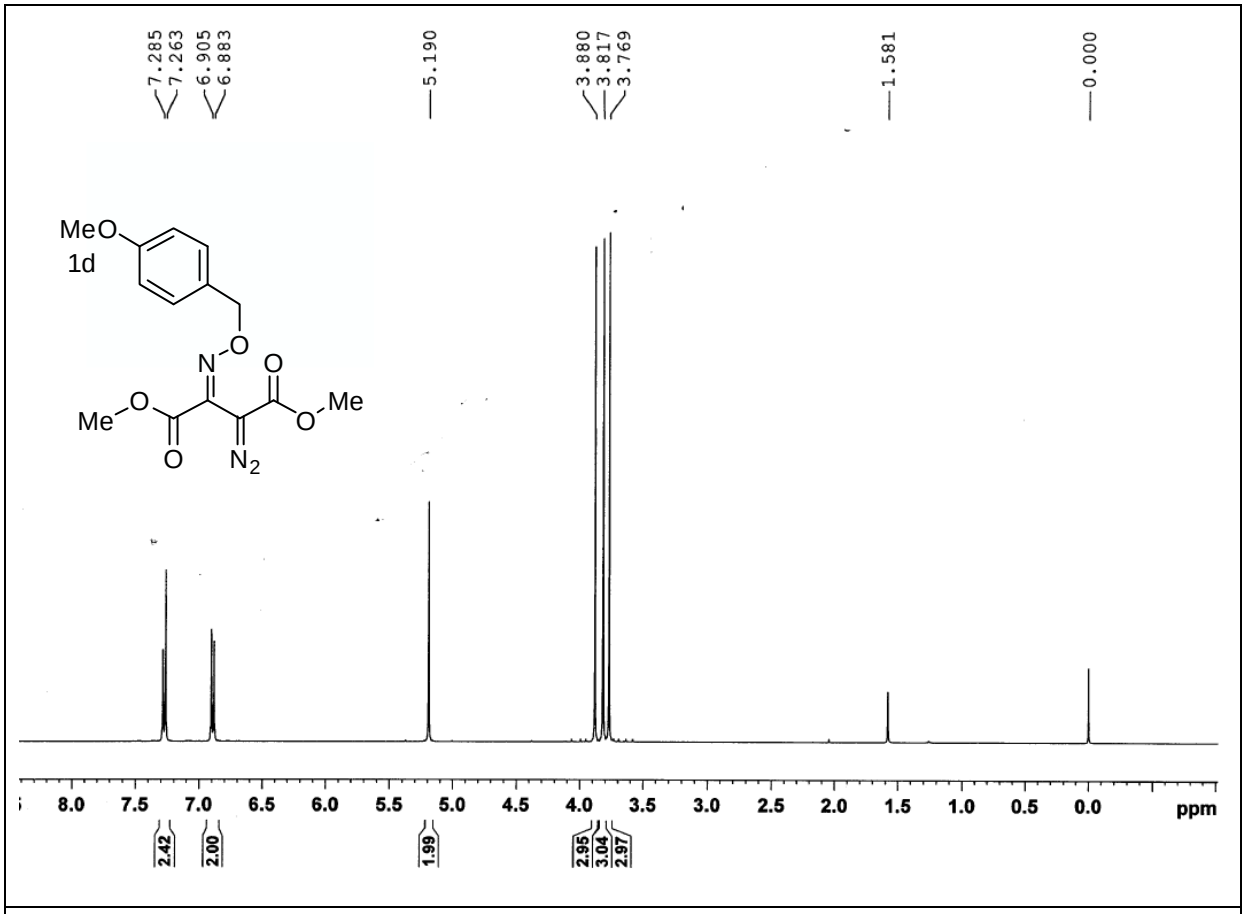
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3.817
3.769
1.581
0.000
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1d
N
O
O
Me
O
O
Me
O
N2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
0.5
0.0
ppm
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2.00
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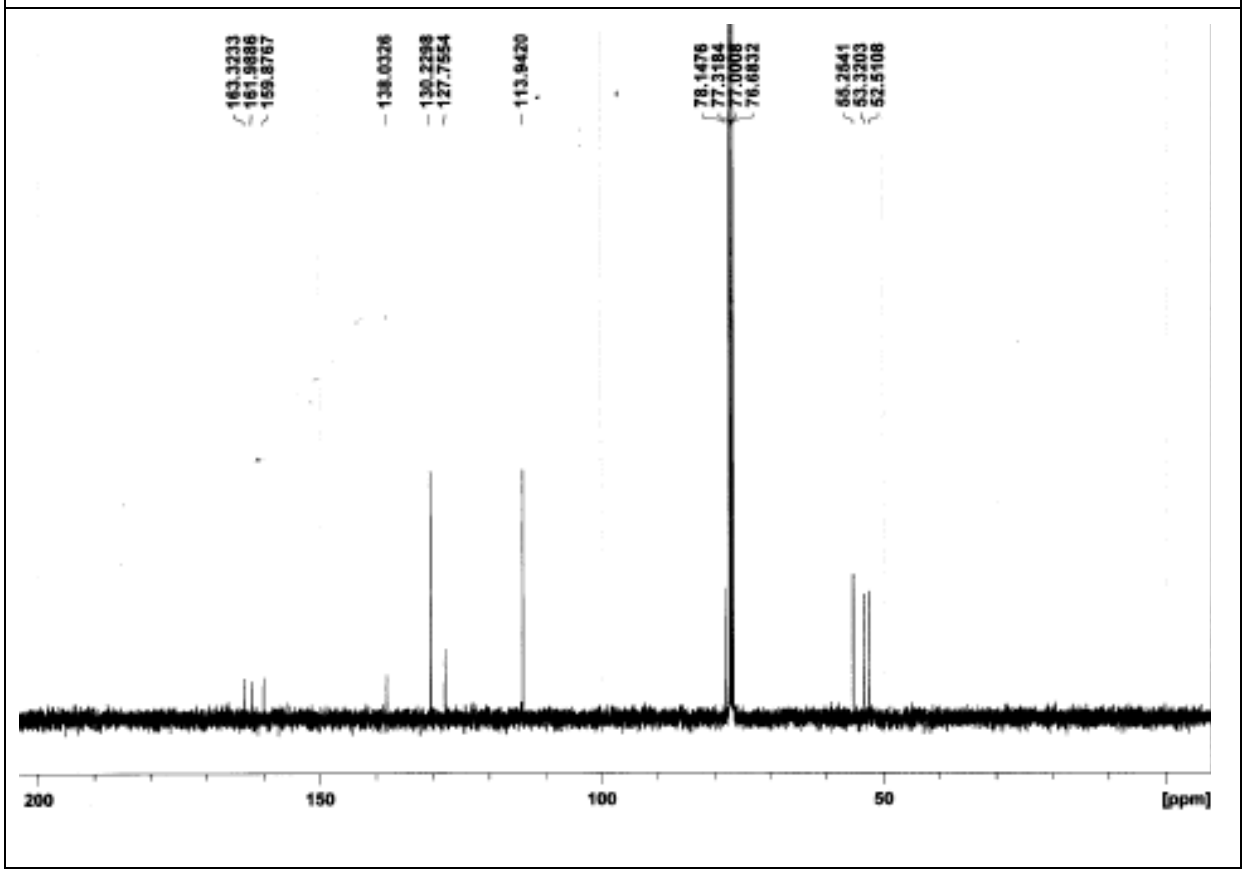
2.97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52.5108
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100
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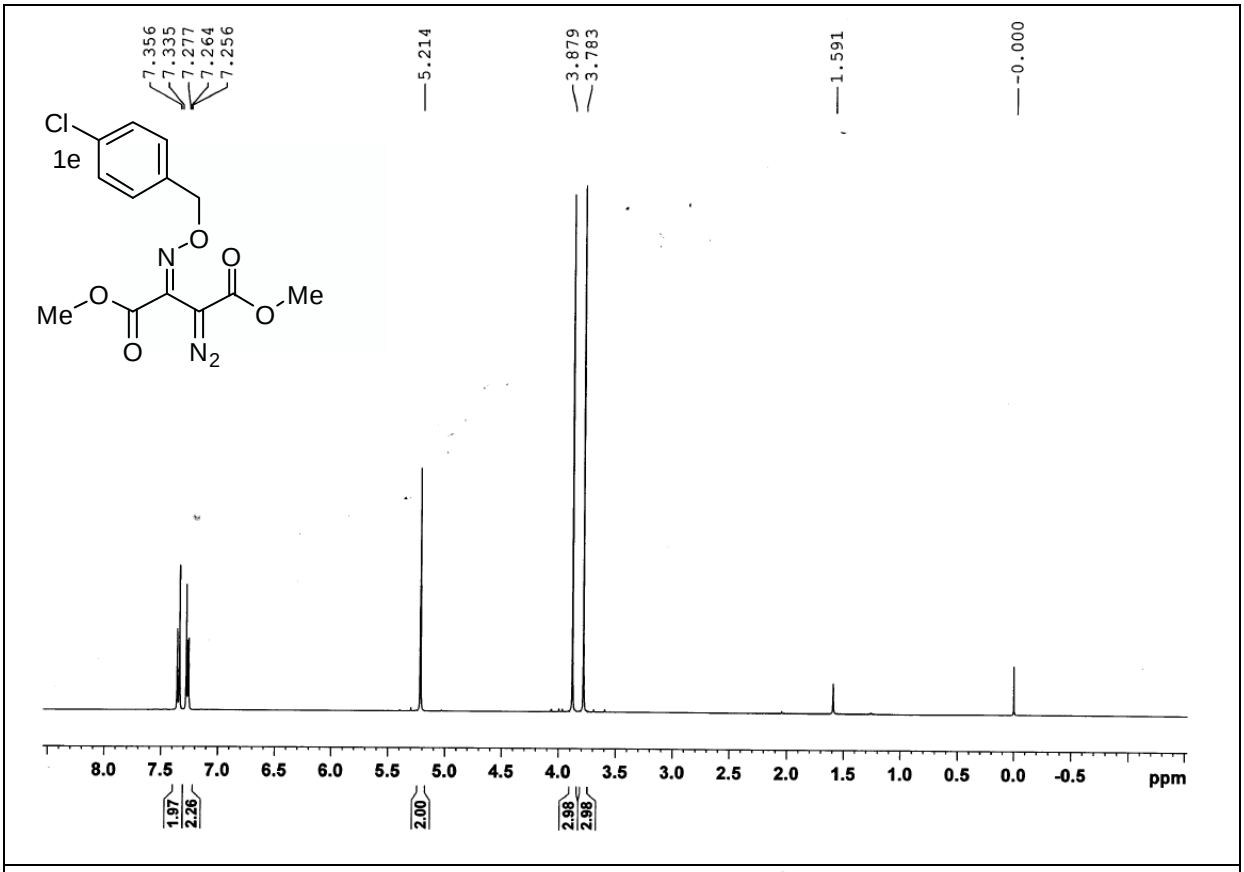
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7.335
7.277
7.264
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5.214
3.879
3.783
1.591
0.000
Cl
1e
N
O
O
Me
O
O
Me
O
N2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
0.5
0.0
-0.5
ppm
1.97
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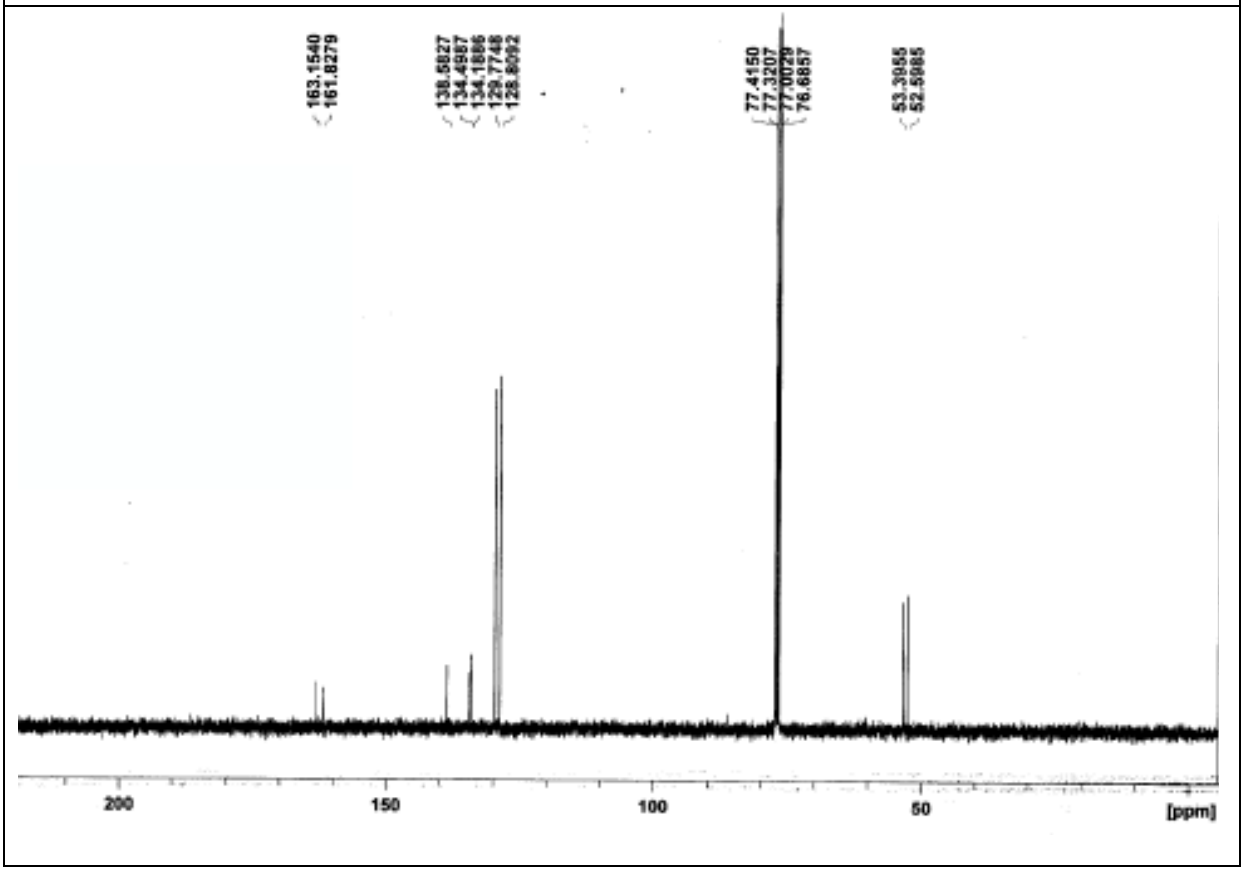
2.98
2.98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134.1886
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77.3207
77.0029
76.6857
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52.5985
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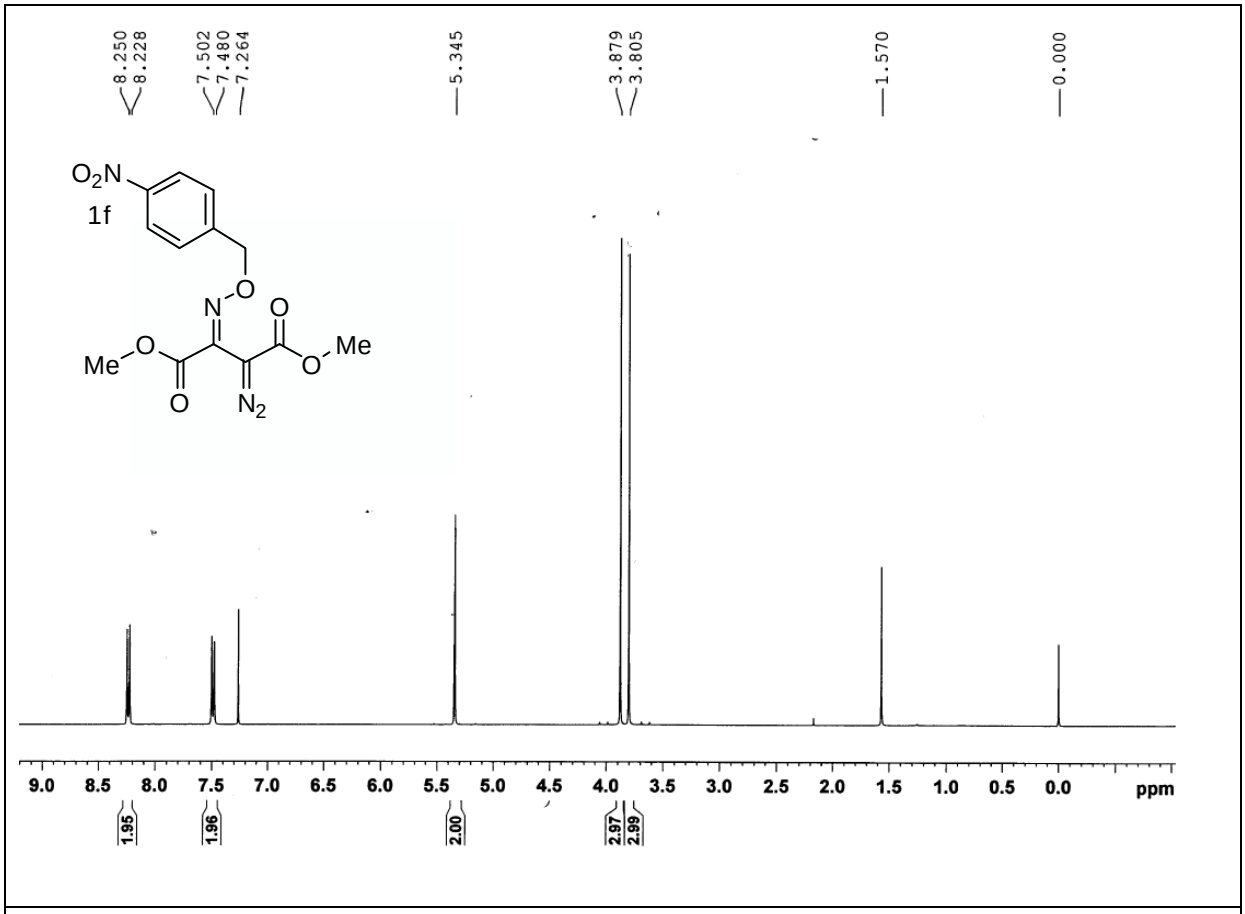
150
100
50
[ppm]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8.228
7.502
7.480
7.264
5.345
3.879
3.805
1.570
0.000
O2N
1f
N
O
O
Me
O
O
O
Me
O
N2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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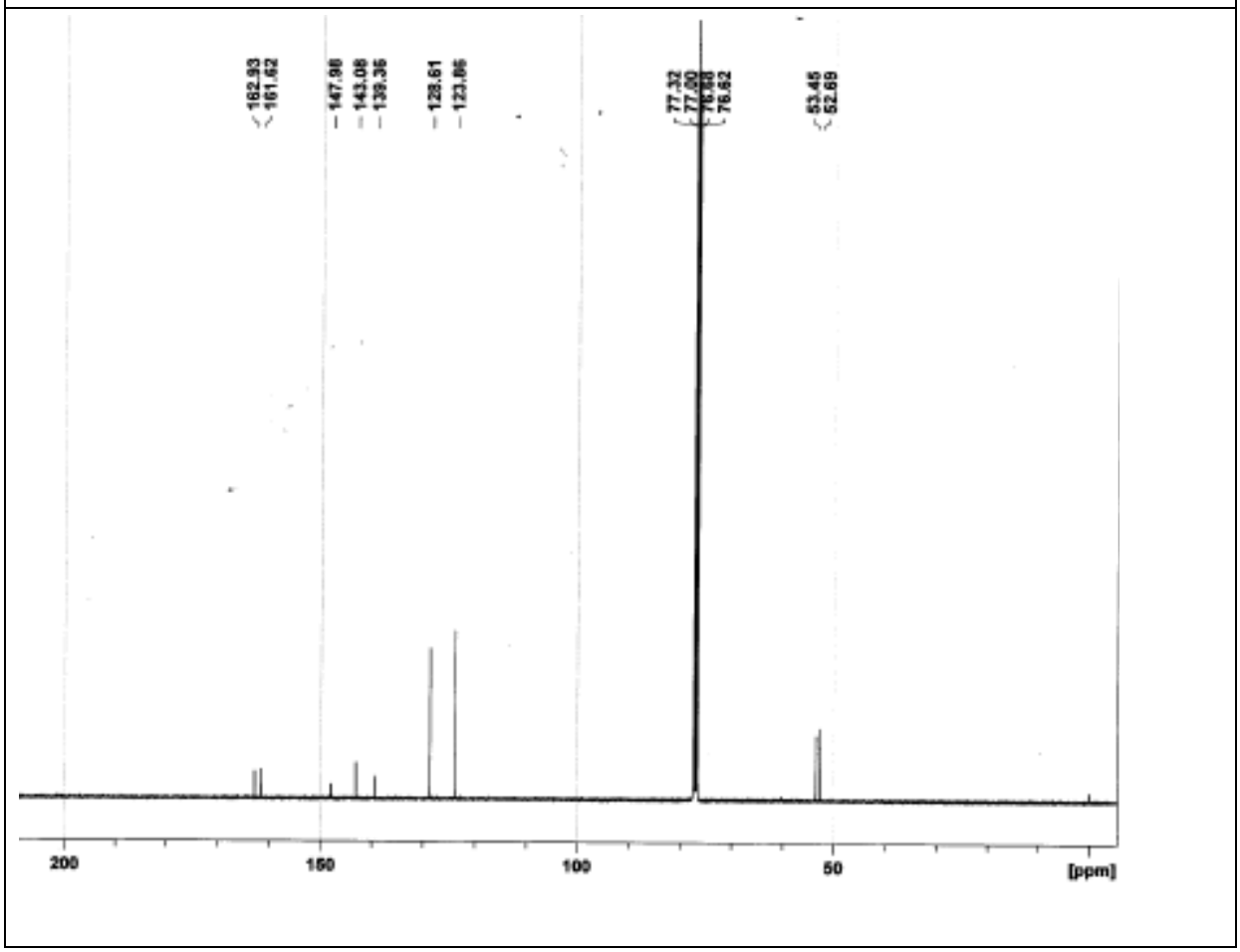
2.0
1.5
1.0
0.5
0.0
ppm
1.95
1.96
2.00
2.97
2.99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161.62
147.98
143.08
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128.61
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77.32
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76.62
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200
150
100
50
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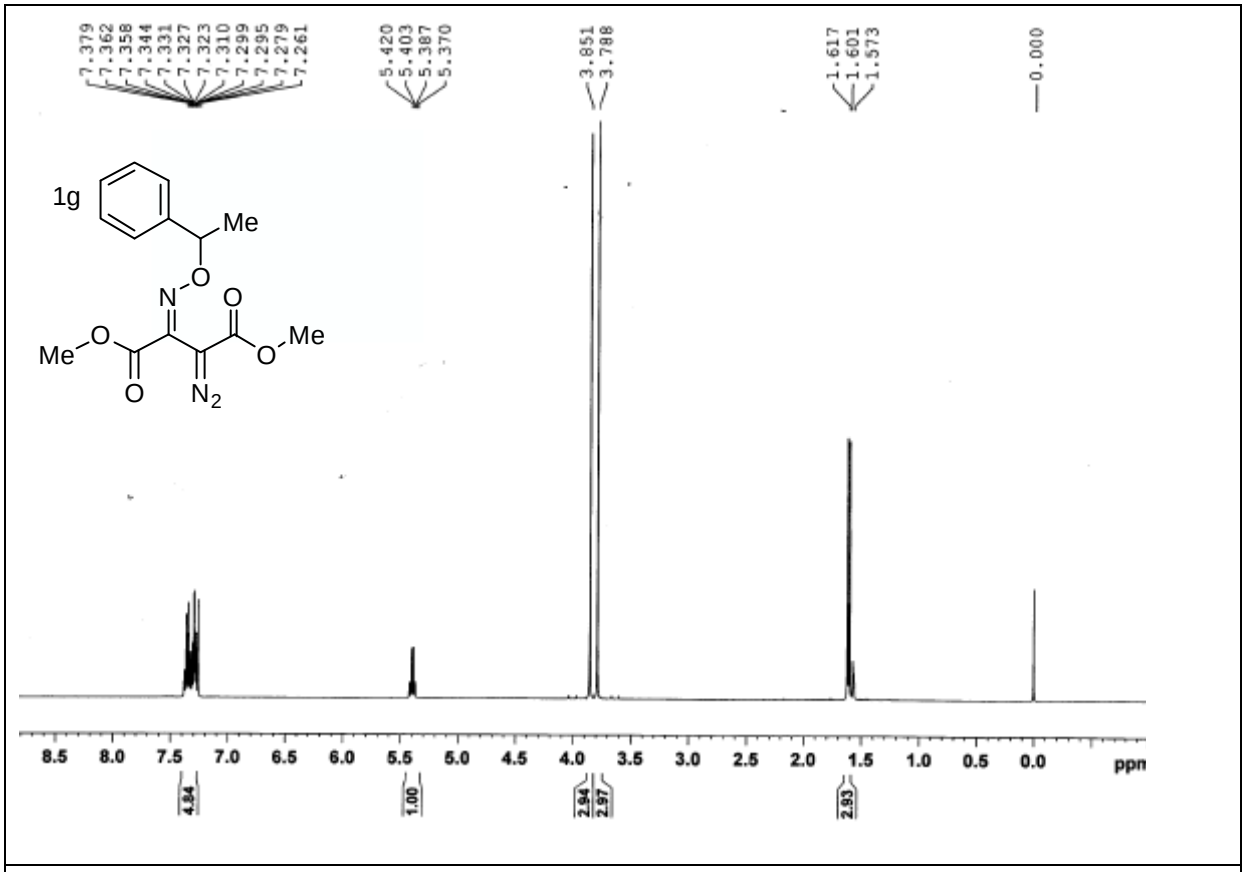
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7.358
7.344
7.331
7.327
7.323
7.310
7.299
7.295
7.279
7.261
5.420
5.403
5.387
5.370
3.851
3.788
1.617
1.601
1.573
0.000
1g
Me
O
N
O
Me
O
O
Me
O
N2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
1.0
0.5
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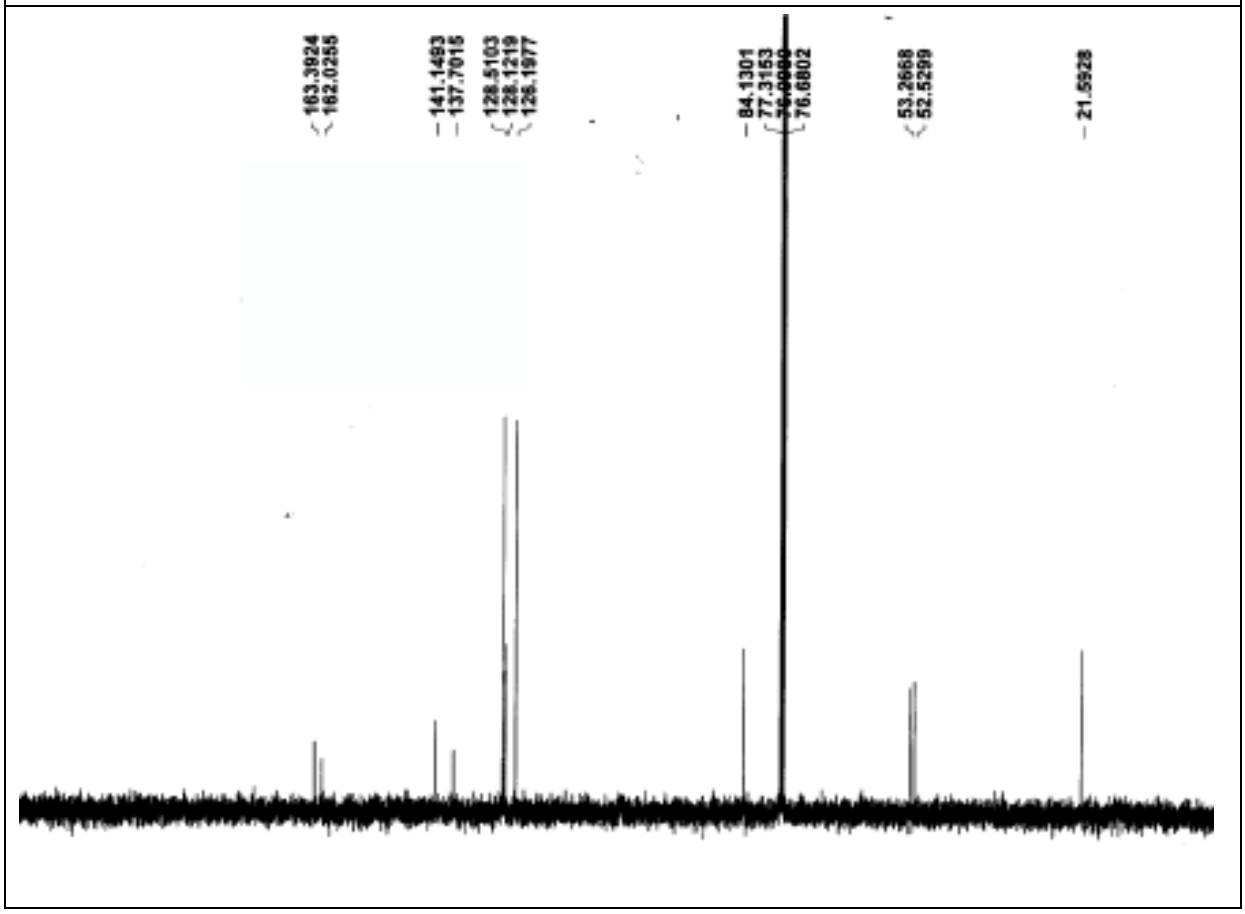
2.97
2.93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128.1219
126.1977
84.1301
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76.6802
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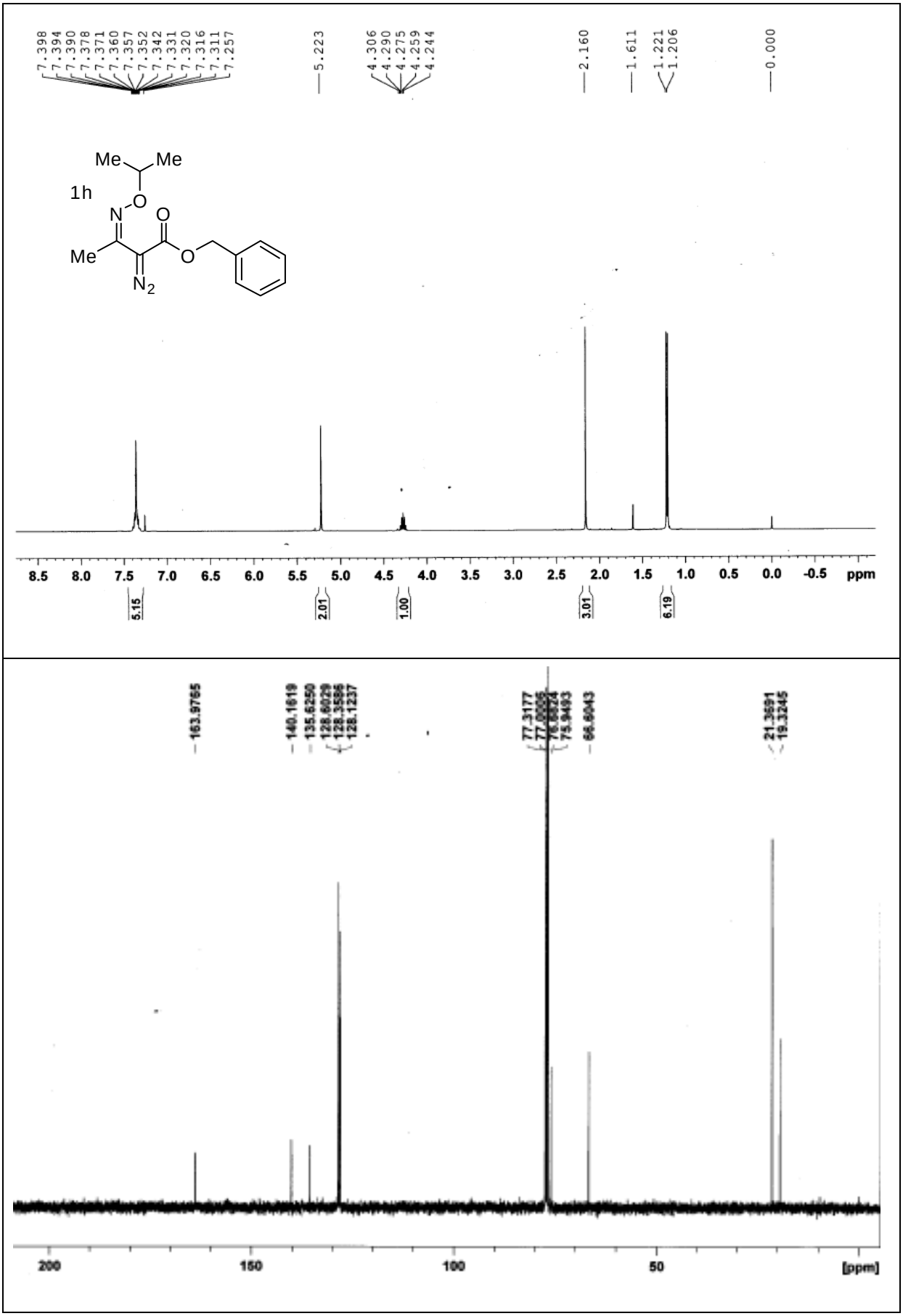
52.5299
21.5928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7.352
7.342
7.331
7.320
7.316
7.311
7.257
5.223
4.306
4.290
4.275
4.259
4.244
2.160
1.611
1.221
1.206
0.000
Me
Me
1h
N
O
O
Me
O
N2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
5.15
2.01
1.00
3.01
6.19
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135.6250
128.6029
128.3586
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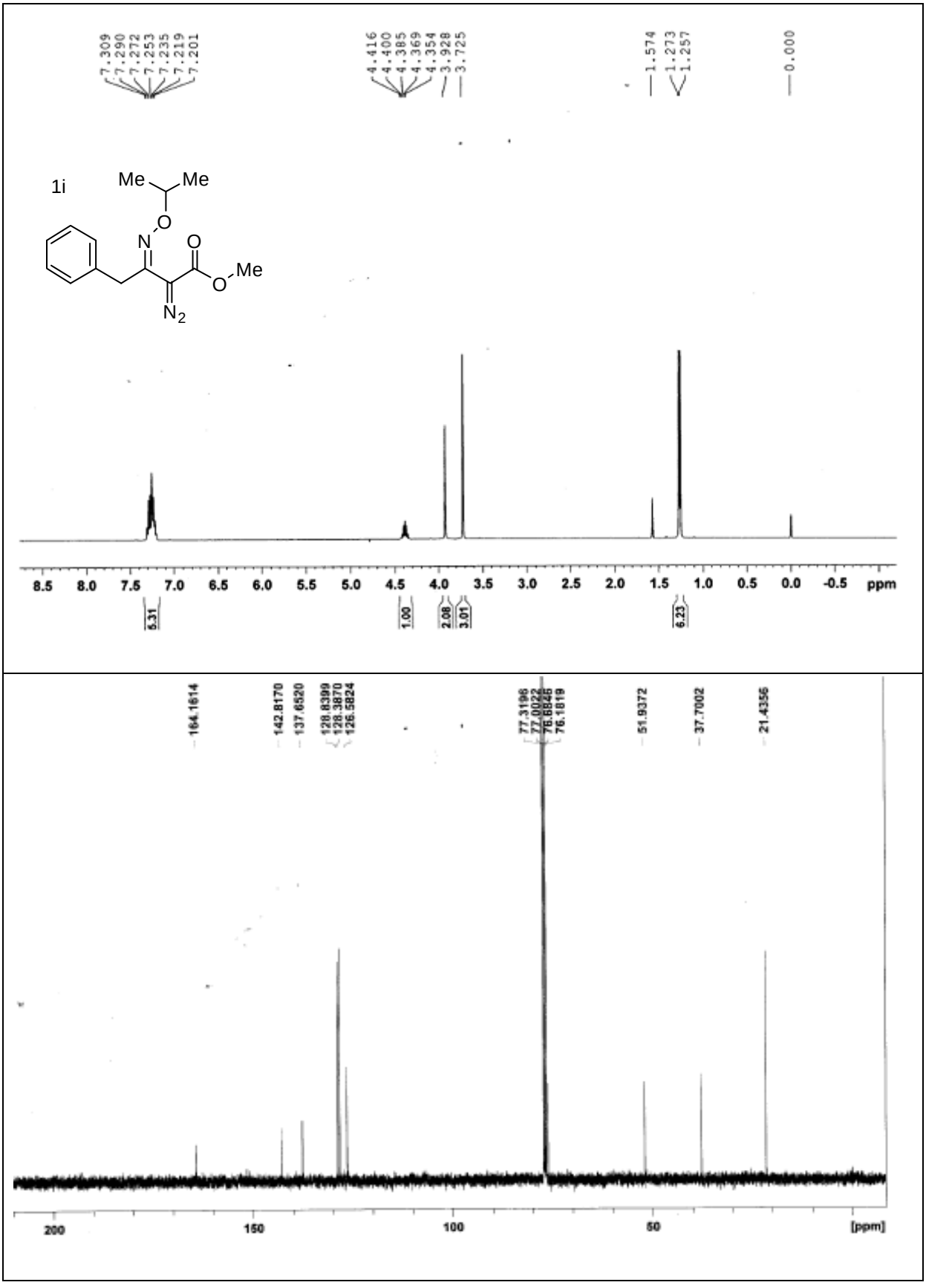
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7.219
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4.369
4.354
3.928
3.725
1.574
1.273
1.257
0.000
1i
Me
Me
O
N
O
O
Me
N2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
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1.00
2.08
3.01
6.23
164.1614
142.8170
137.6520
128.8399
128.3870
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100
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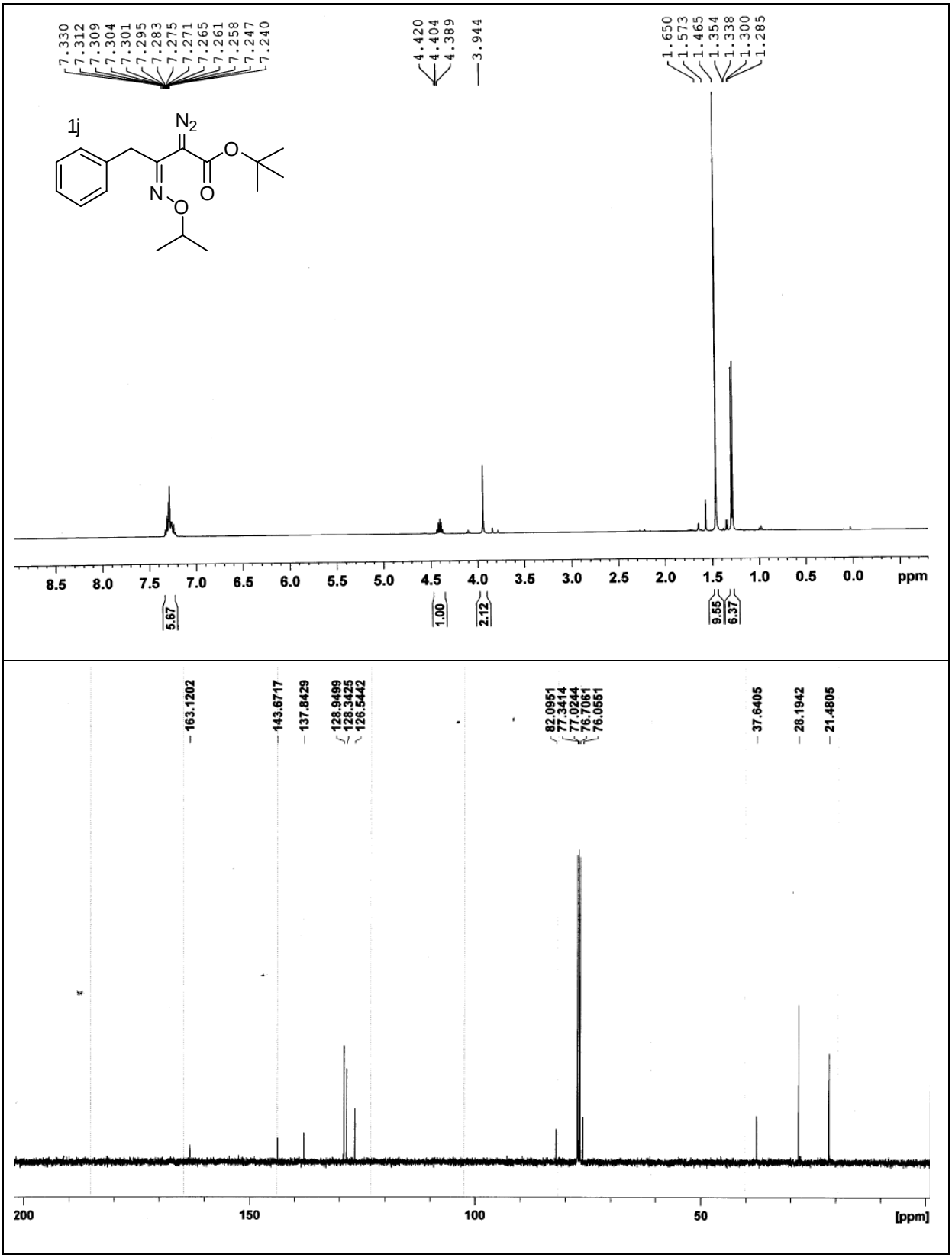
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7.283
7.275
7.271
7.265
7.261
7.258
7.247
7.240
4.420
4.404
4.389
3.944
1.650
1.573
1.465
1.354
1.338
1.300
1.285
1j
N2
O
O
N
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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6.37
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137.8429
128.9499
128.3425
126.5442
82.0951
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100
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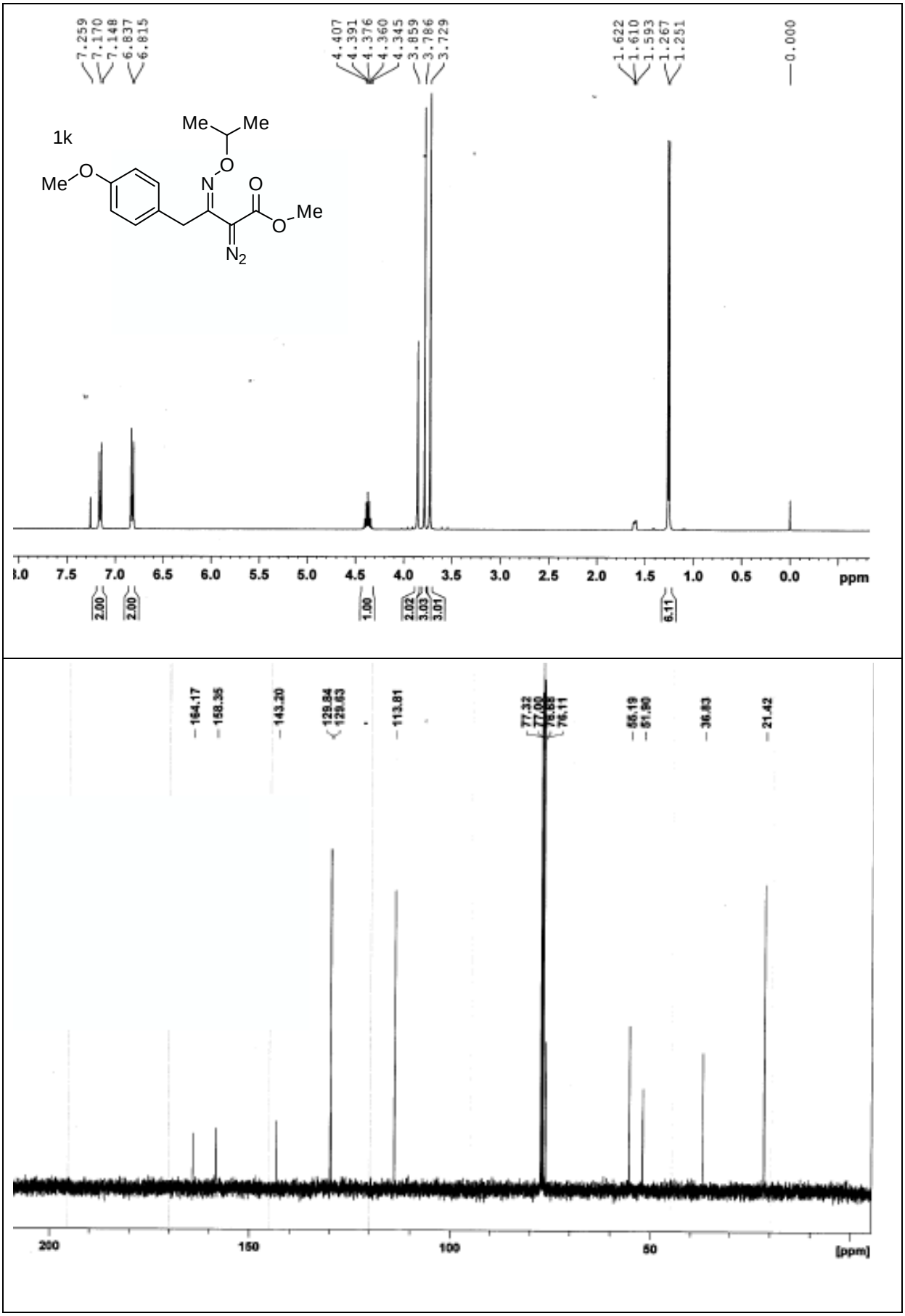
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4.376
4.360
4.345
3.859
3.786
3.729
1.622
1.610
1.593
1.267
1.251
0.000
1k
Me
Me
O
Me
O
N
O
O
Me
N2
ppm
2.00
2.00
1.00
2.02
3.03
3.01
6.11
164.17
158.35
143.20
129.84
129.63
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76.11
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100
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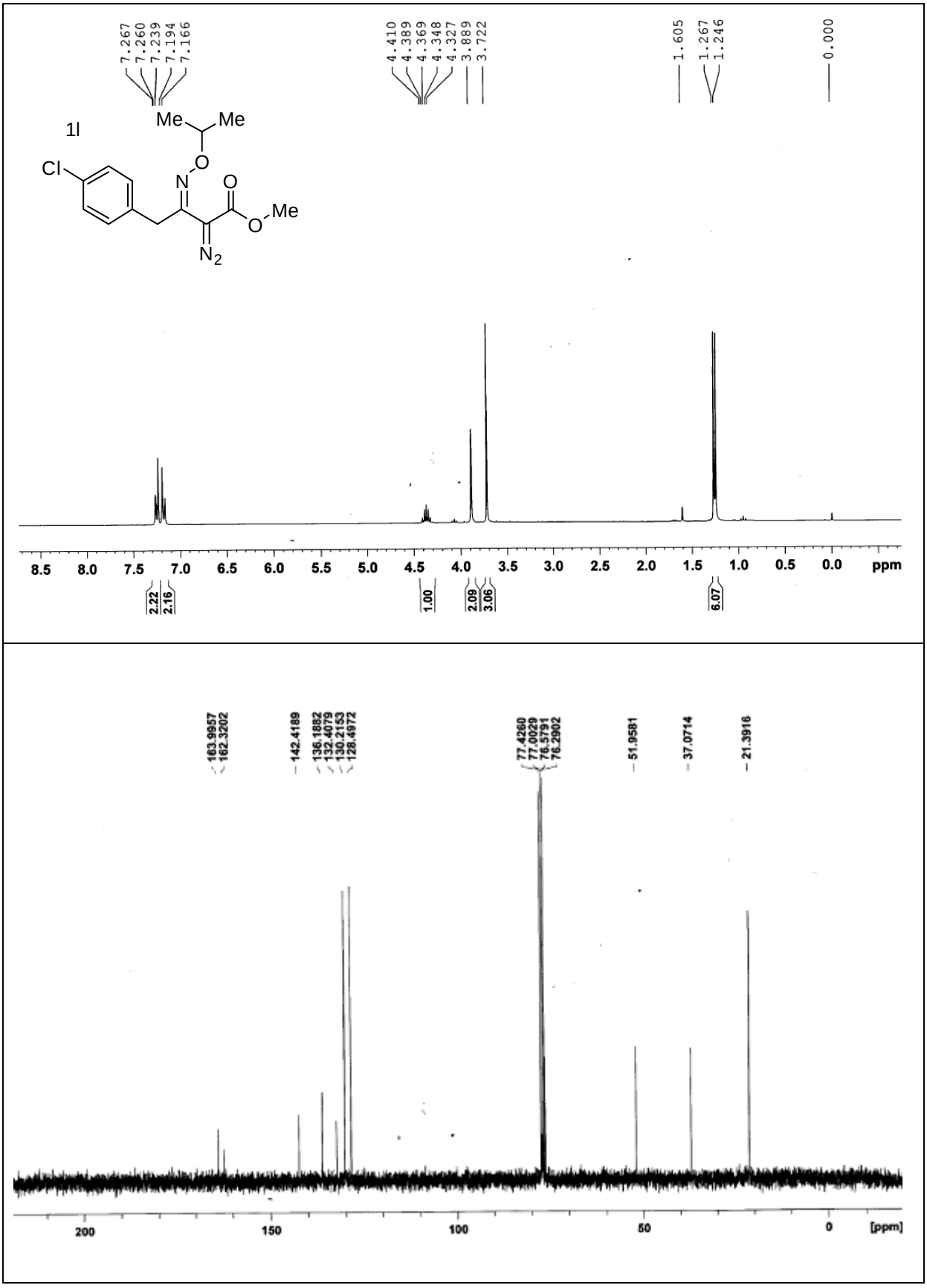
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4.327
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3.722
1.605
1.267
1.246
0.000
1l
Me
Me
O
Cl
N
O
O
Me
N2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.22
2.16
1.00
2.09
3.06
6.07
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162.3202
142.4189
136.1882
132.4079
130.2153
128.4972
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76.2902
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37.0714
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50
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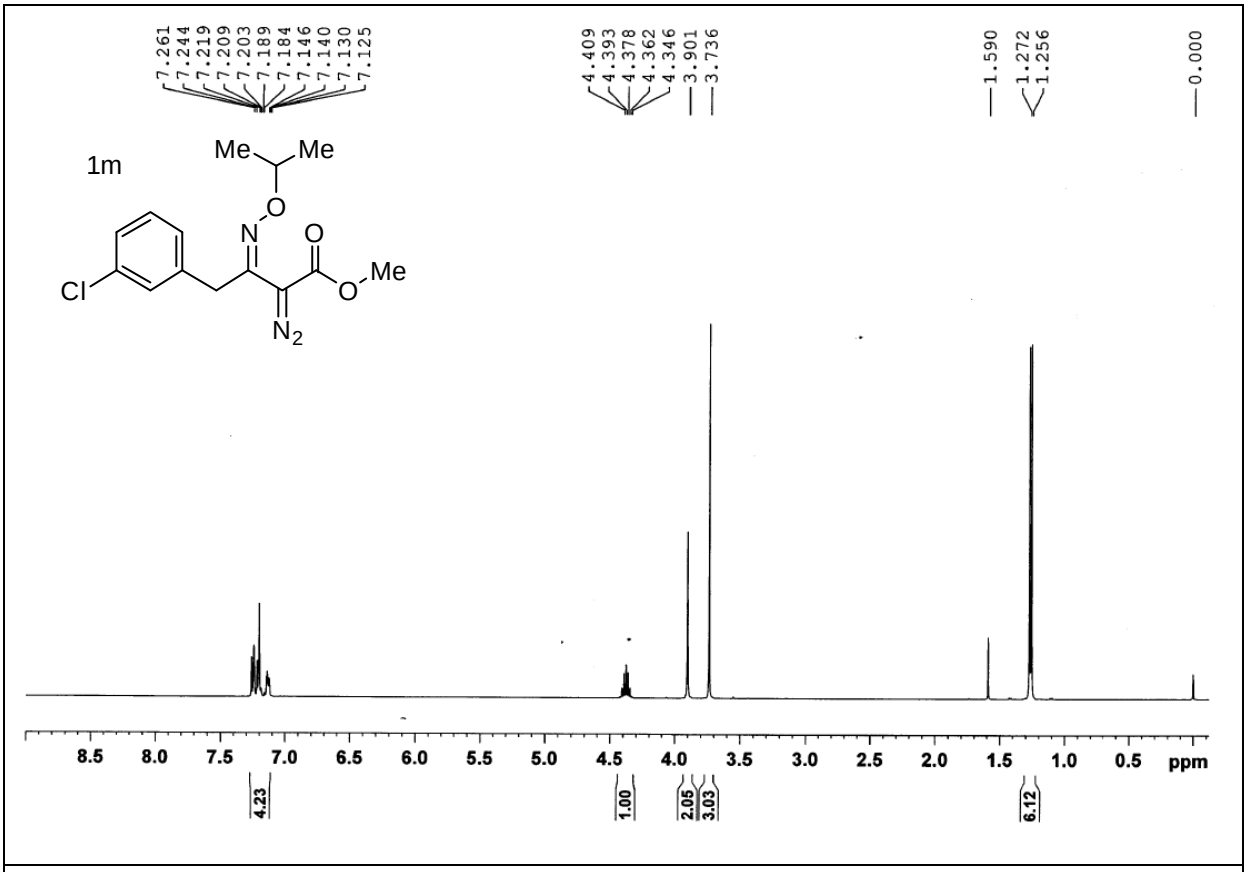
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7.184
7.146
7.140
7.130
7.125
4.409
4.393
4.378
4.362
4.346
3.901
3.736
1.590
1.272
1.256
0.000
1m
Me
Me
O
N
O
Cl
O
Me
N2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
1.5
1.0
0.5
ppm
4.23
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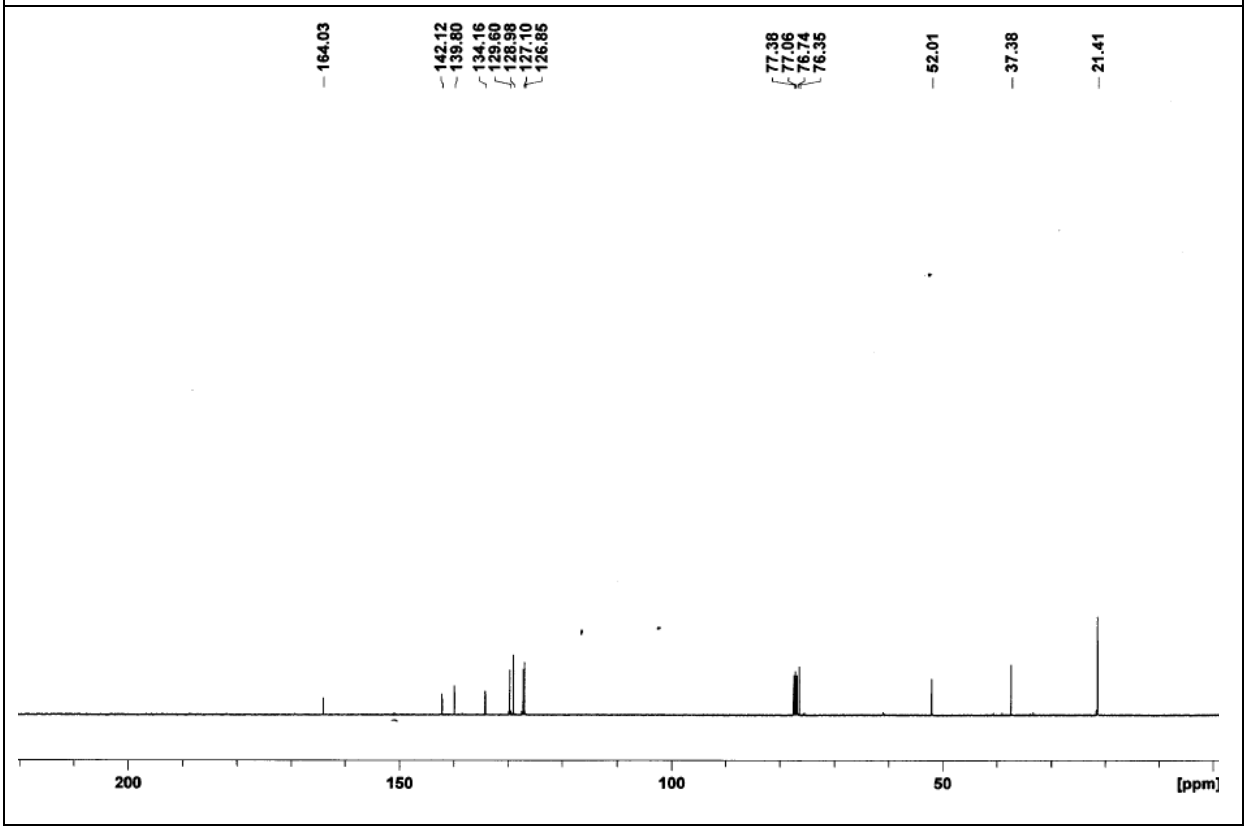
2.05
3.03
6.12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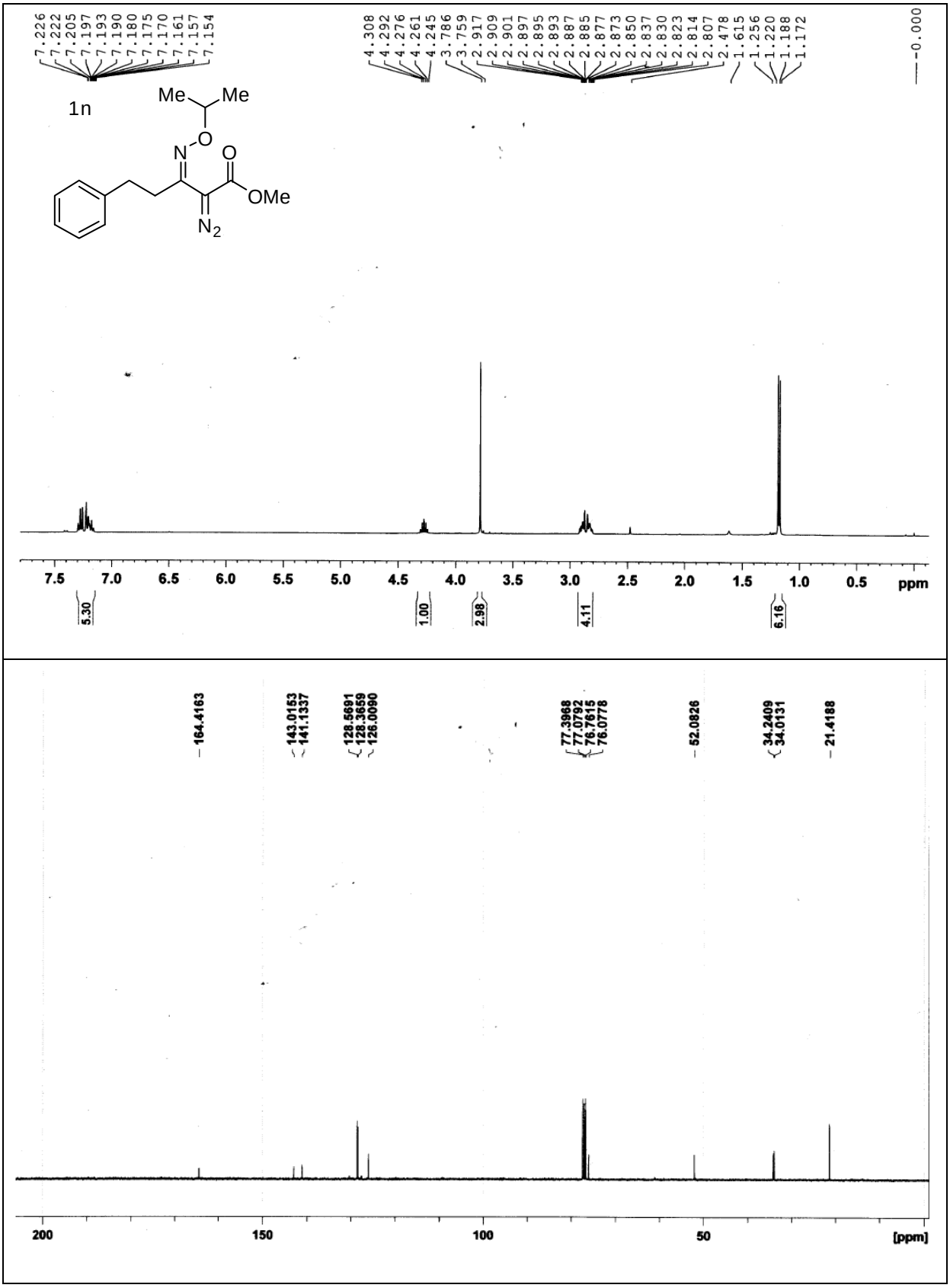
100
50
[ppm]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7.157
7.154
4.308
4.292
4.276
4.261
4.245
3.786
3.759
2.917
2.909
2.901
2.897
2.895
2.893
2.887
2.885
2.877
2.873
2.850
2.837
2.830
2.823
2.814
2.807
2.478
1.615
1.256
1.220
1.188
1.172
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1n
Me
Me
O
N
O
OMe
N2
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
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128.0090
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21.4188
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100
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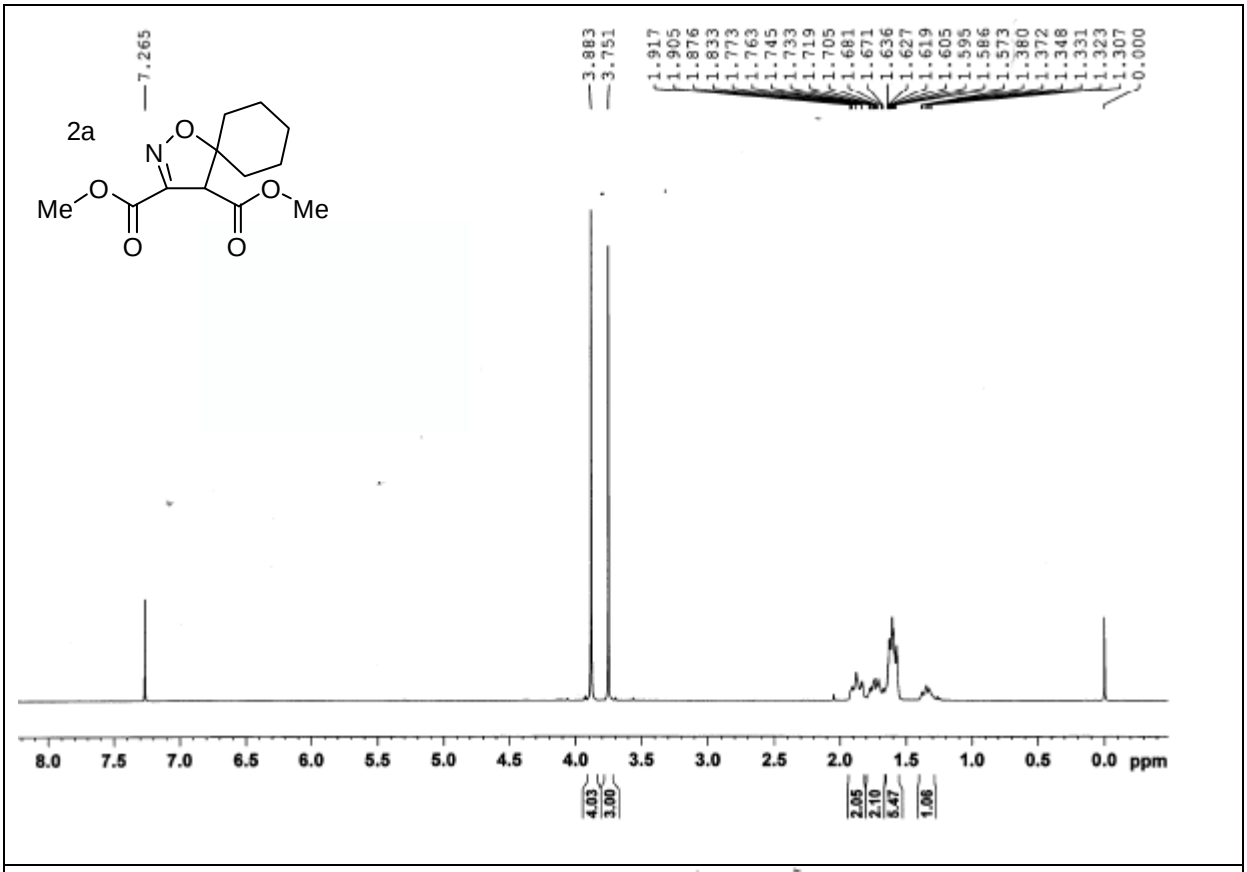
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O
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O
Me
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1.876
1.833
1.773
1.763
1.745
1.733
1.719
1.705
1.681
1.671
1.636
1.627
1.619
1.605
1.595
1.586
1.573
1.380
1.372
1.348
1.331
1.323
1.307
0.000
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.10
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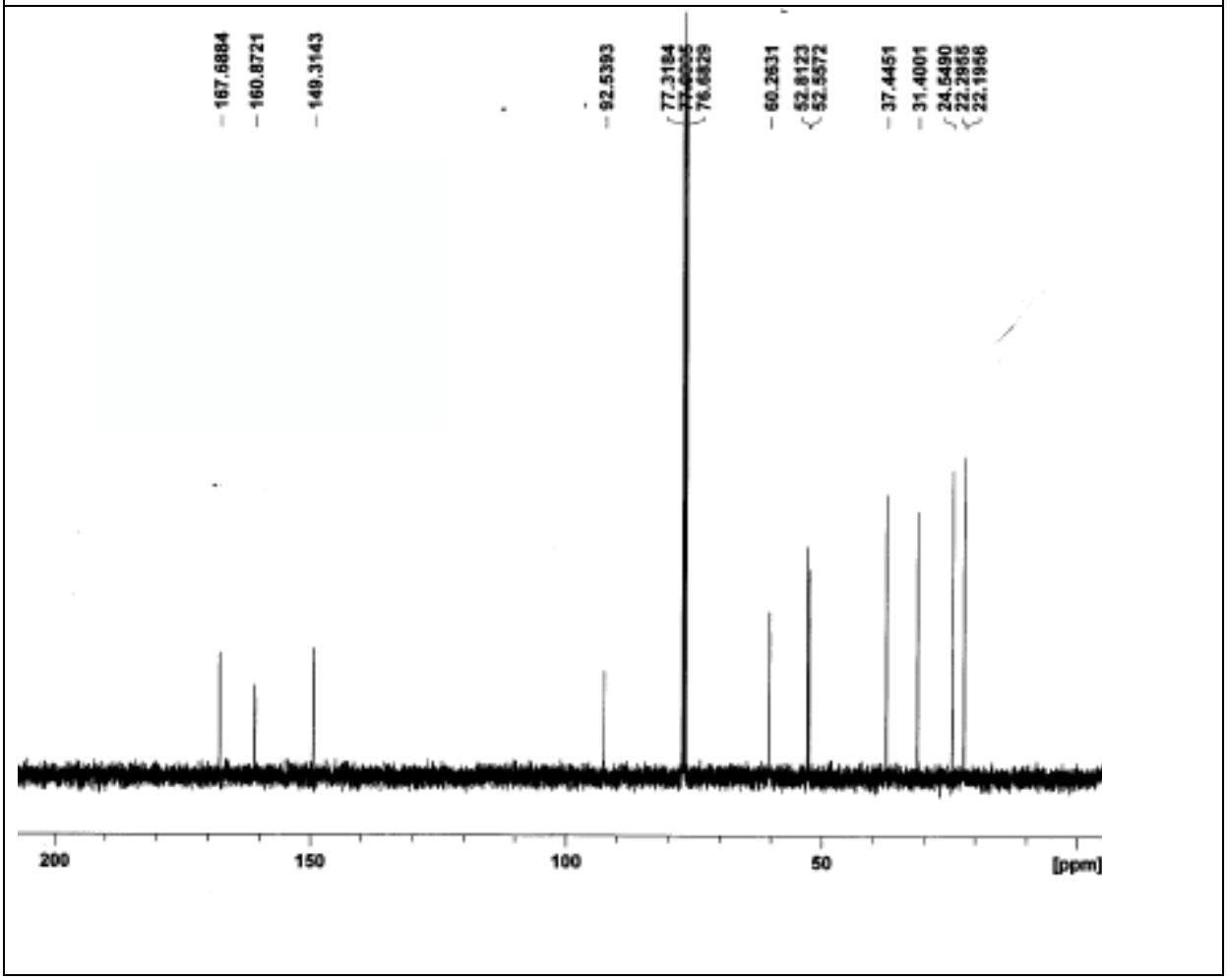
1.06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76.6829
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100
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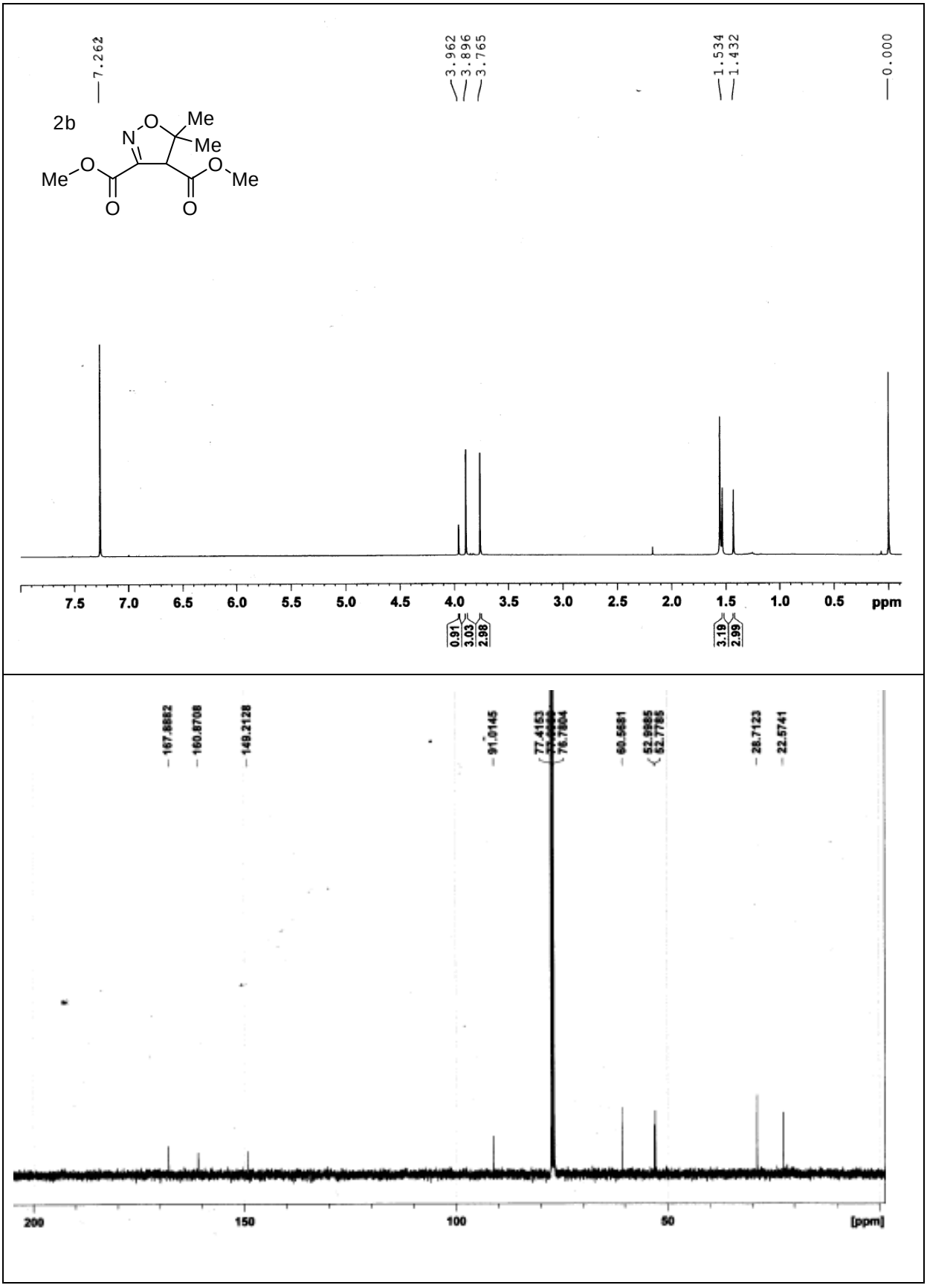
[ppm]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2b
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O
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O
Me
Me
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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3.19
2.99
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160.8708
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91.0145
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100
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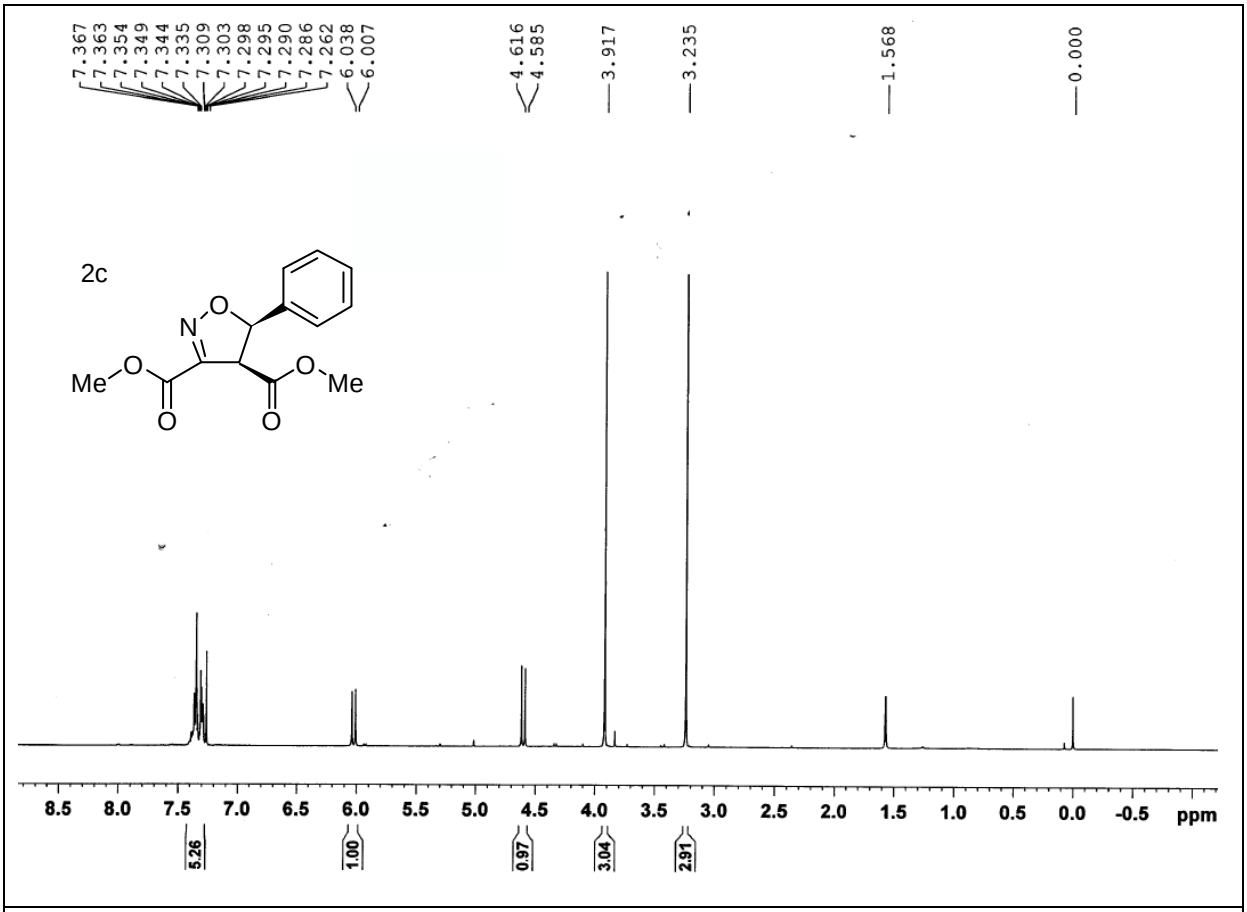
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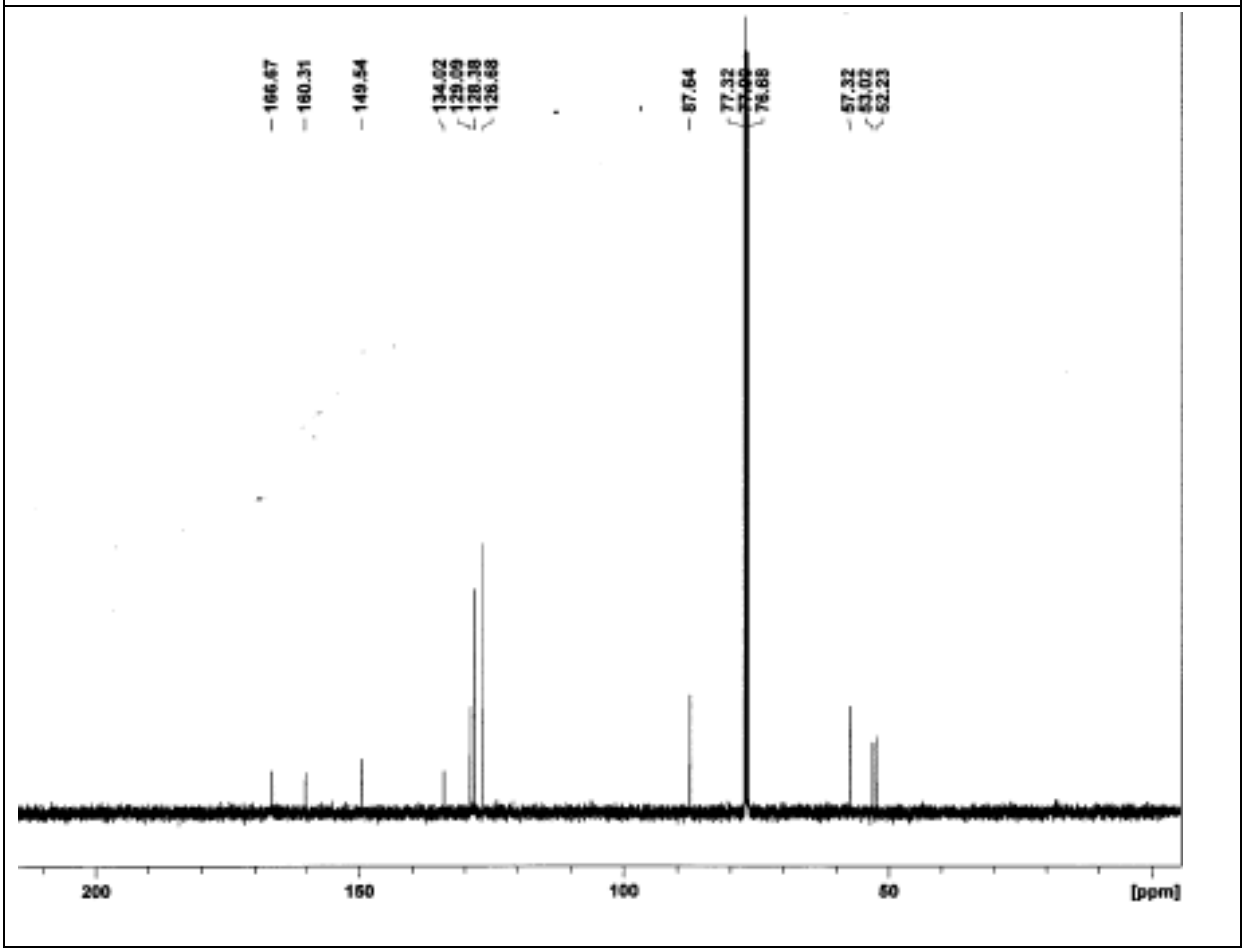
7.262
6.038
6.007
4.616
4.585
3.917
3.235
1.568
0.000
2c
N
O
Me
O
O
O
Me
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
5.26
1.00
0.97
3.04
2.91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160.31
149.54
134.02
129.09
128.38
126.88
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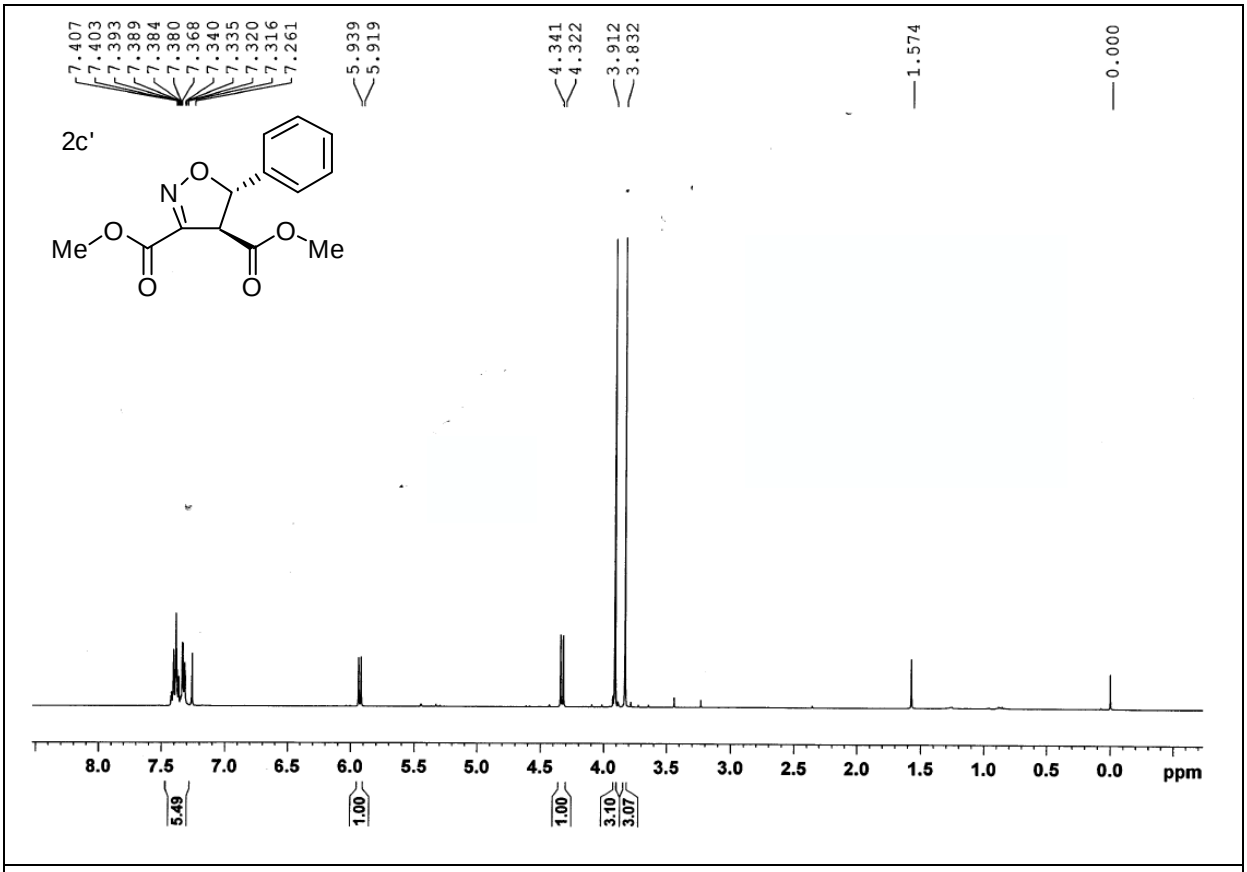
77.32
77.05
76.88
57.32
53.02
52.23
200
150
100
50
[ppm]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7.403
7.393
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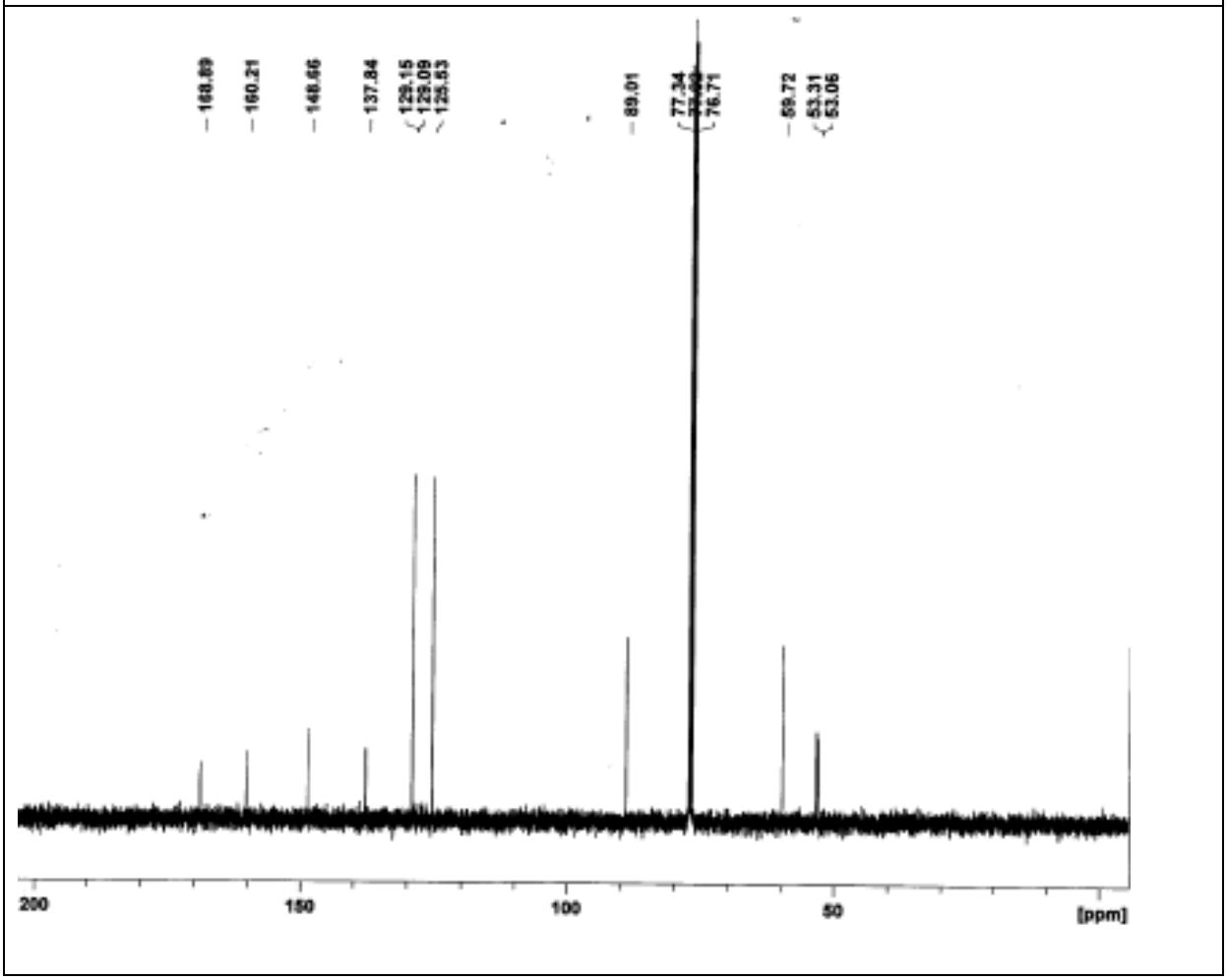
7.384
7.380
7.368
7.340
7.335
7.320
7.316
7.261
5.939
5.919
4.341
4.322
3.912
3.832
1.574
0.000
2c'
N
O
Me
O
O
Me
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.49
1.00
1.00
3.10
3.07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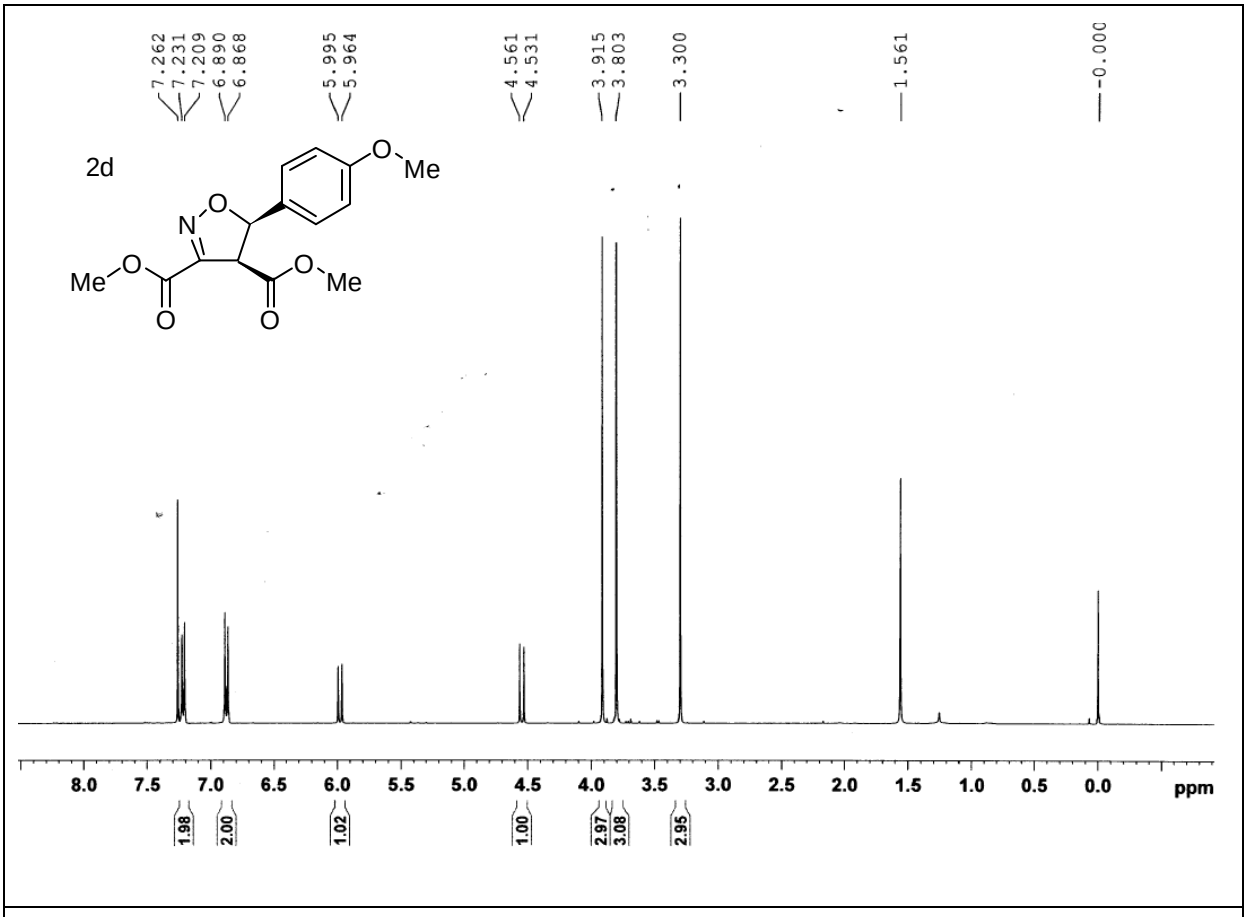
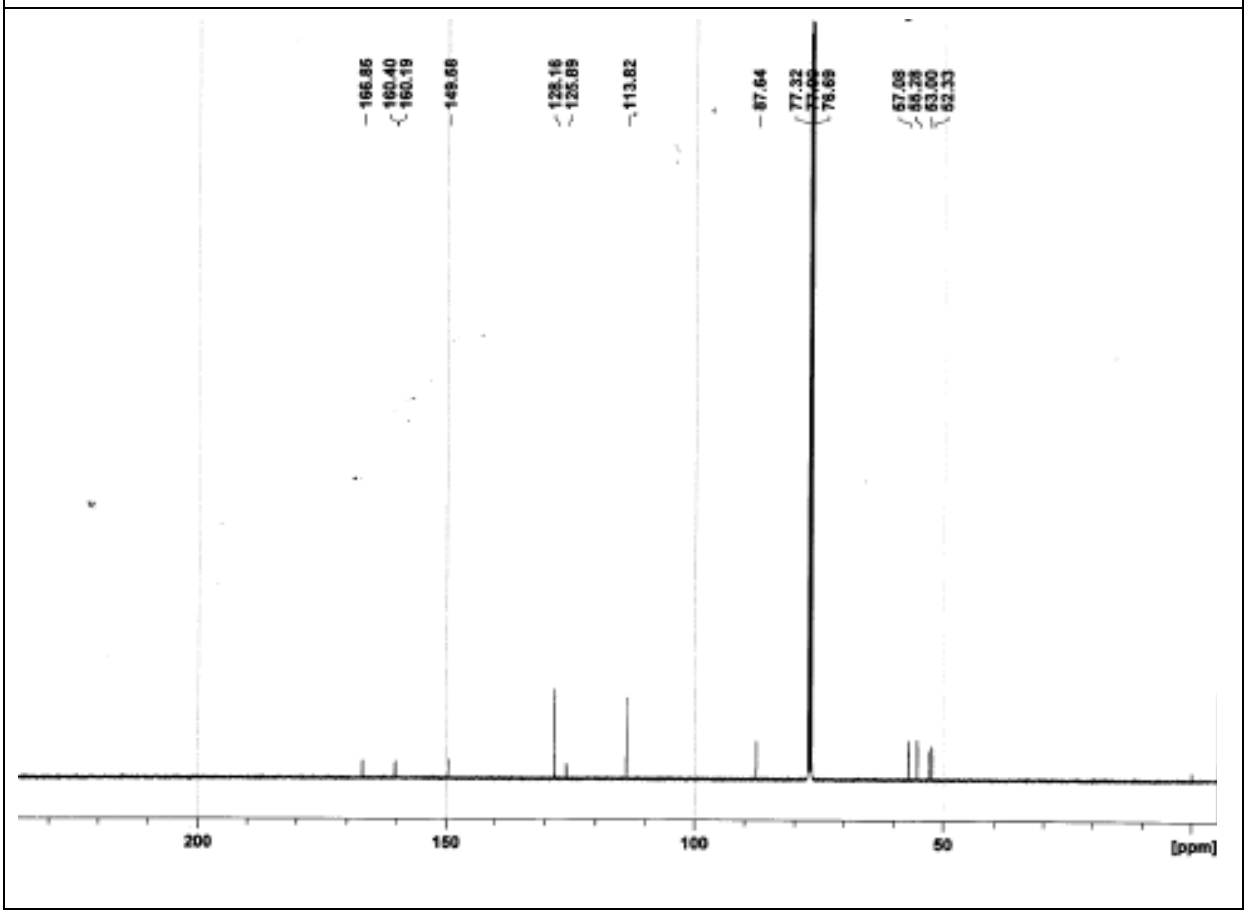
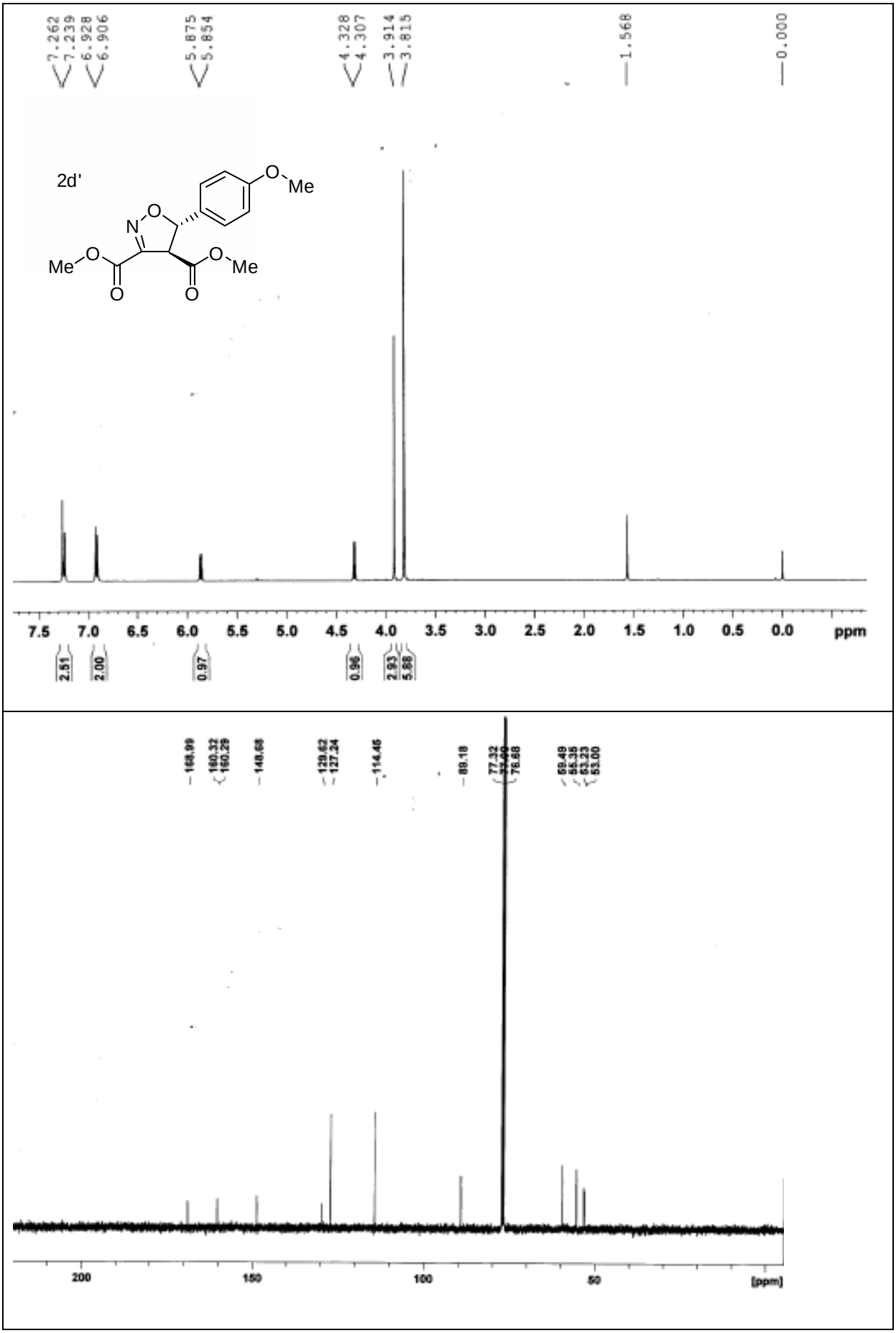
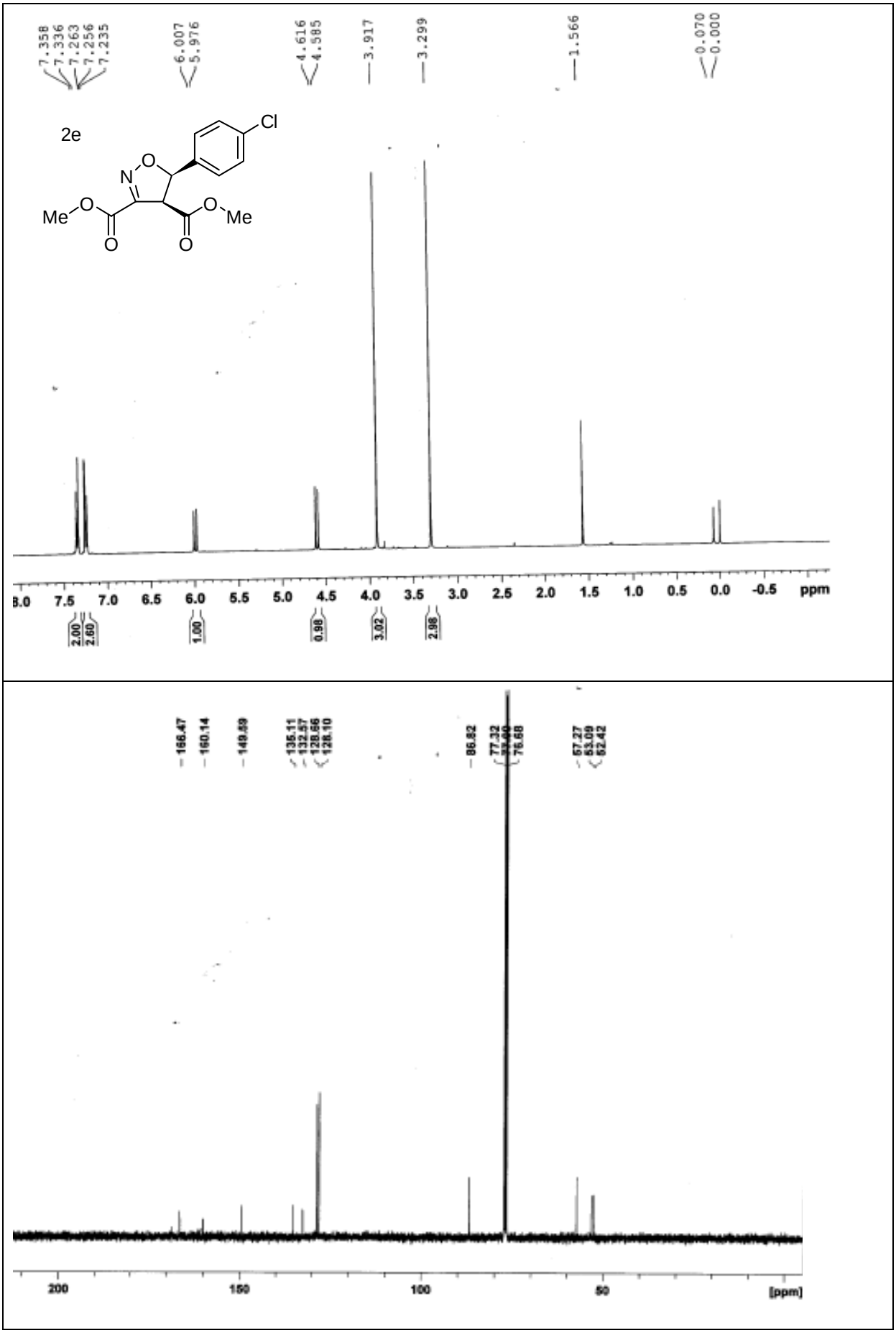
160.21
148.66
137.84
129.15
128.09
125.53
89.01
77.34
76.71
58.72
53.31
53.06
200
150
100
50
[ppm]


7.262
7.231
7.209
6.890
6.868
5.995
5.964
4.561
4.531
3.915
3.803
3.300
1.561
-0.000
2d
O
Me
N
O
Me
O
O
Me
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
1.98
2.00
1.02
1.00
2.97
3.08
2.95


166.85
160.40
160.19
149.68
128.16
125.89
113.82
87.64
77.32
78.69
57.08
55.28
53.00
52.33
200
150
100
50
[ppm]


7.262
7.239
6.928
6.906
5.875
5.854
4.328
4.307
3.914
3.815
1.568
0.000
2d'
O
Me
N
O
Me
O
O
Me
O
O
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
2.51
2.00
0.97
0.96
2.93
5.88
168.99
160.32
160.29
148.68
129.62
127.24
114.46
89.18
77.32
76.88
69.49
55.35
53.23
53.00
200
150
100
50
[ppm]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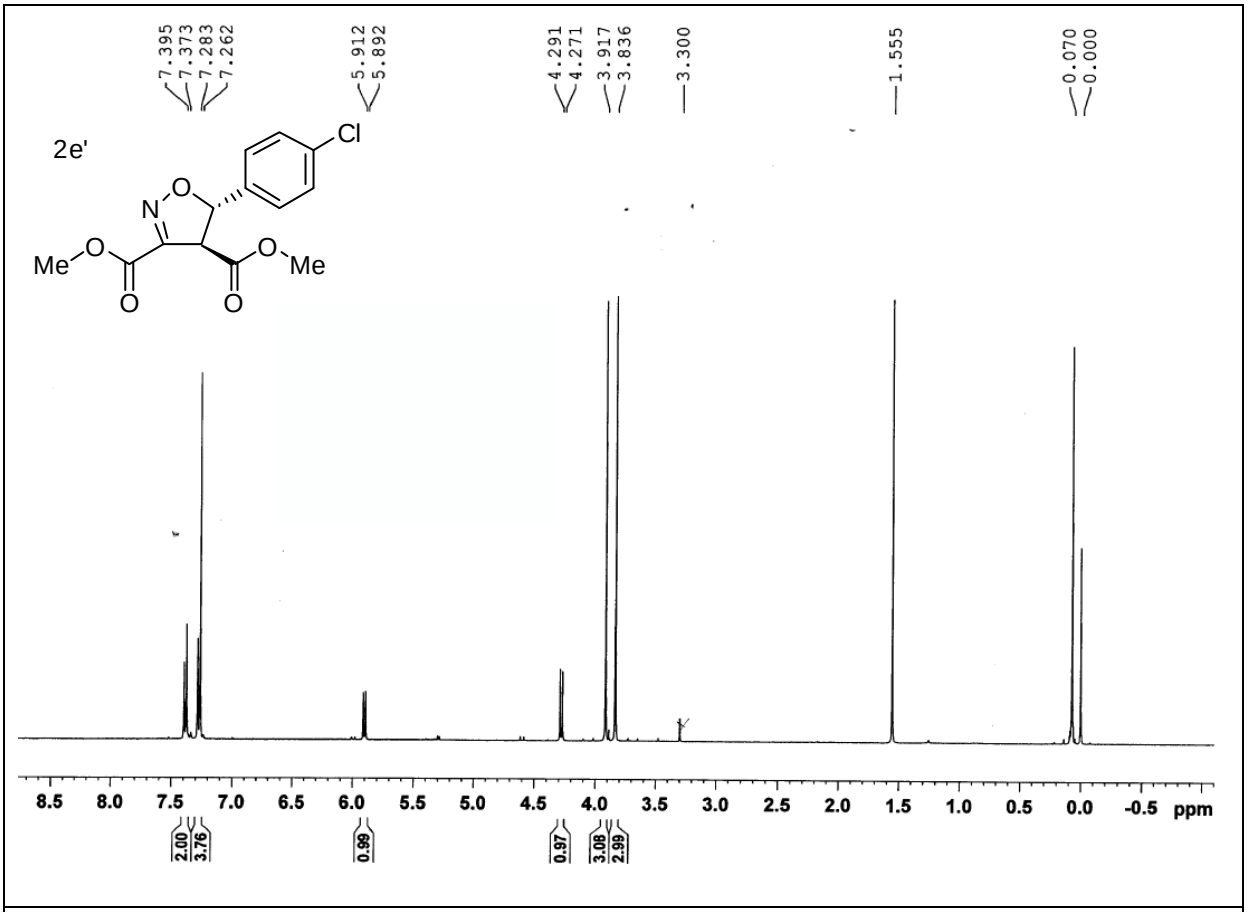
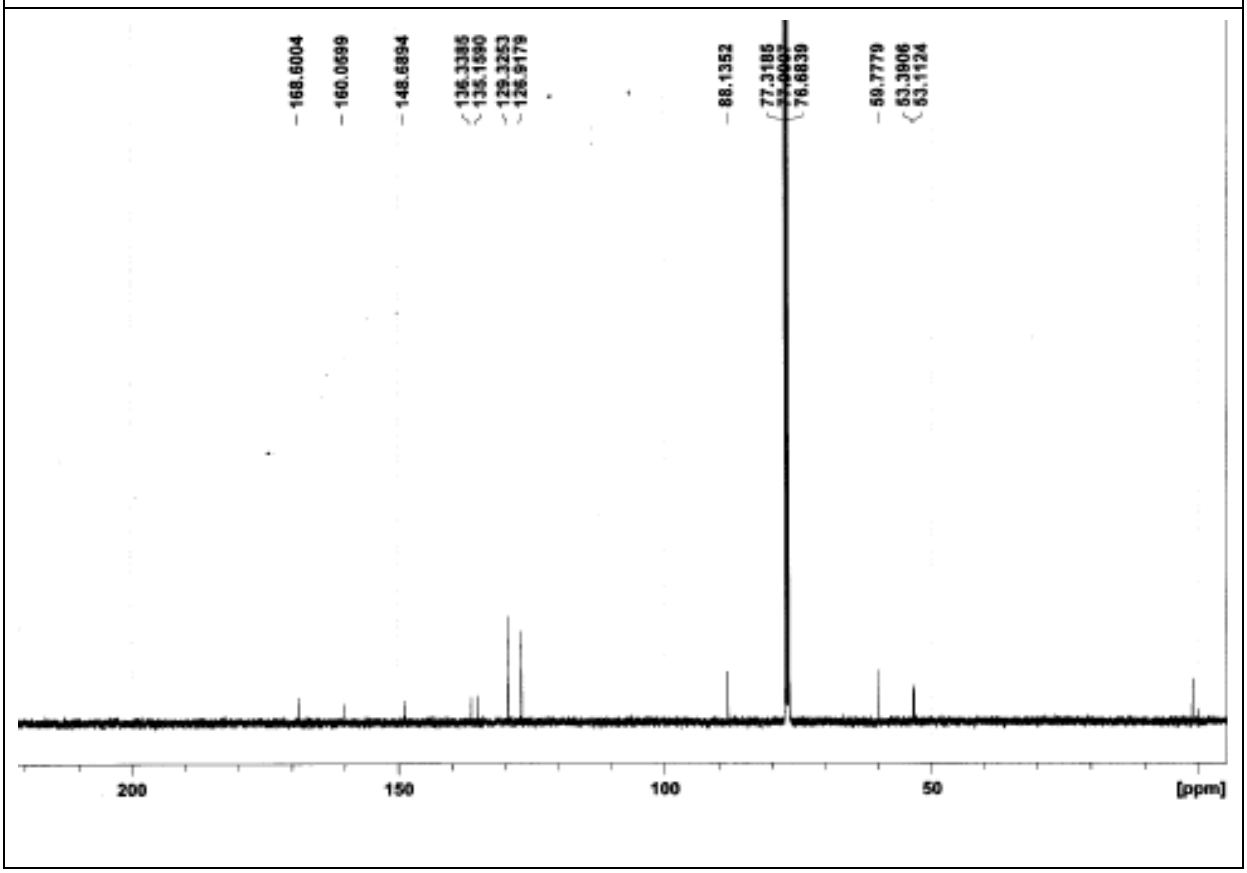
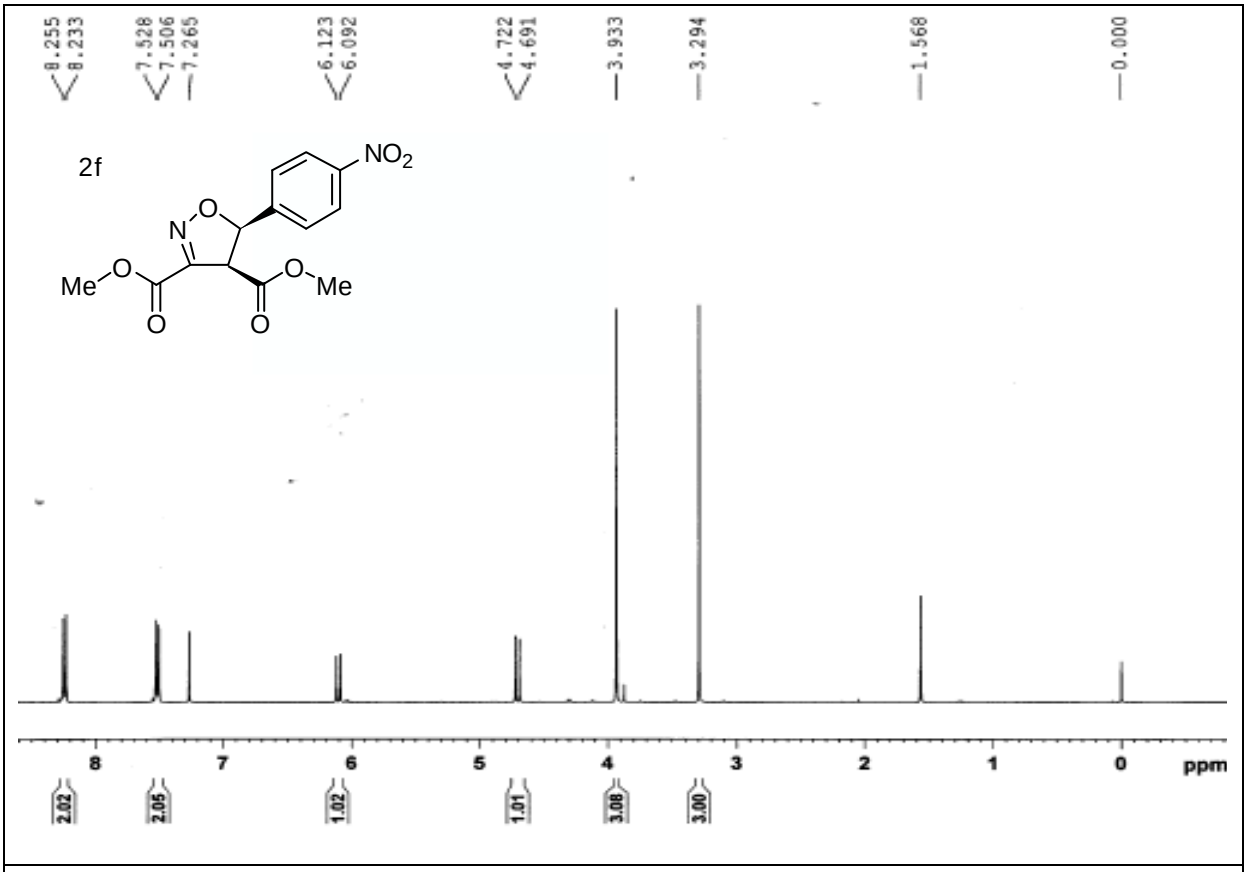
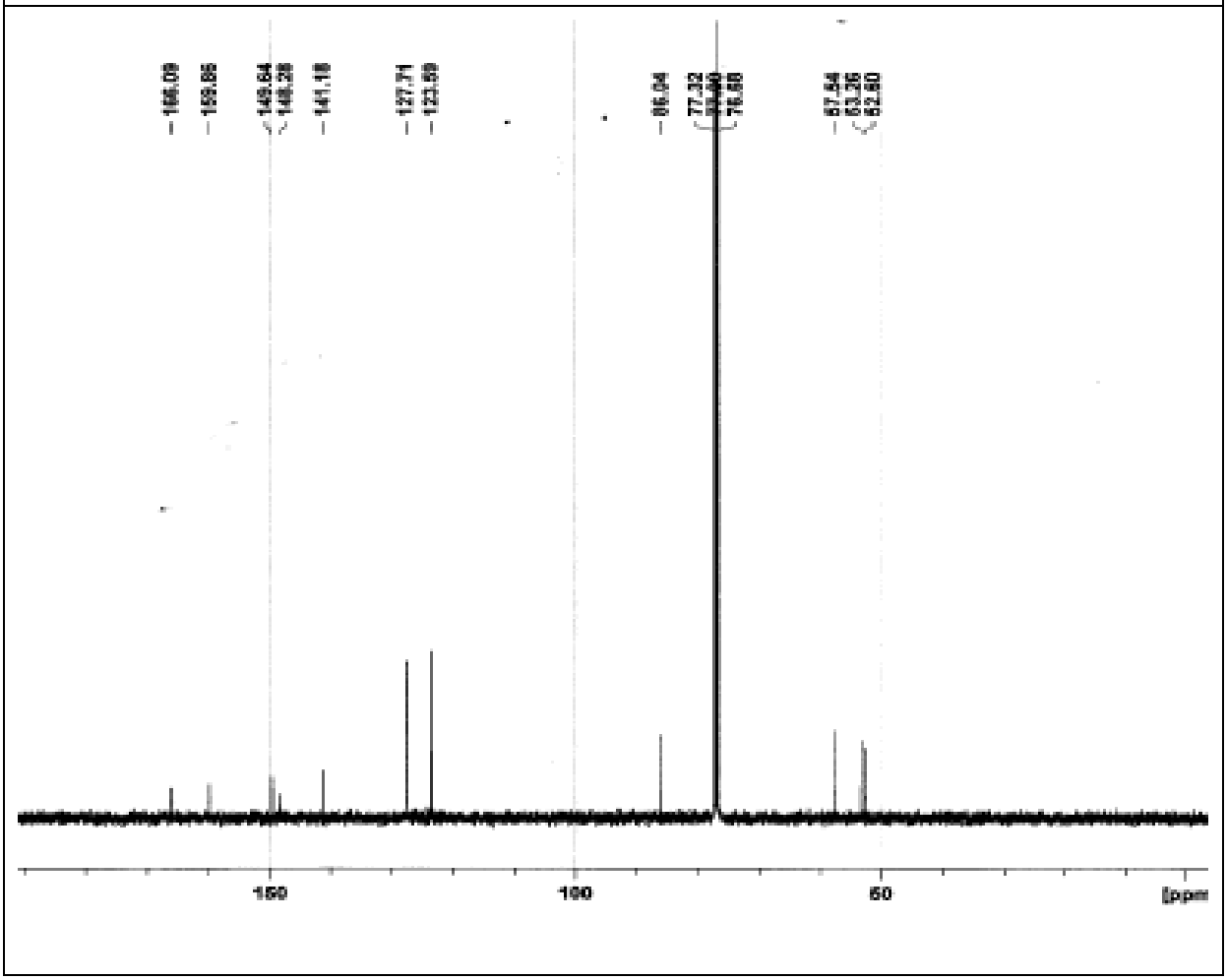
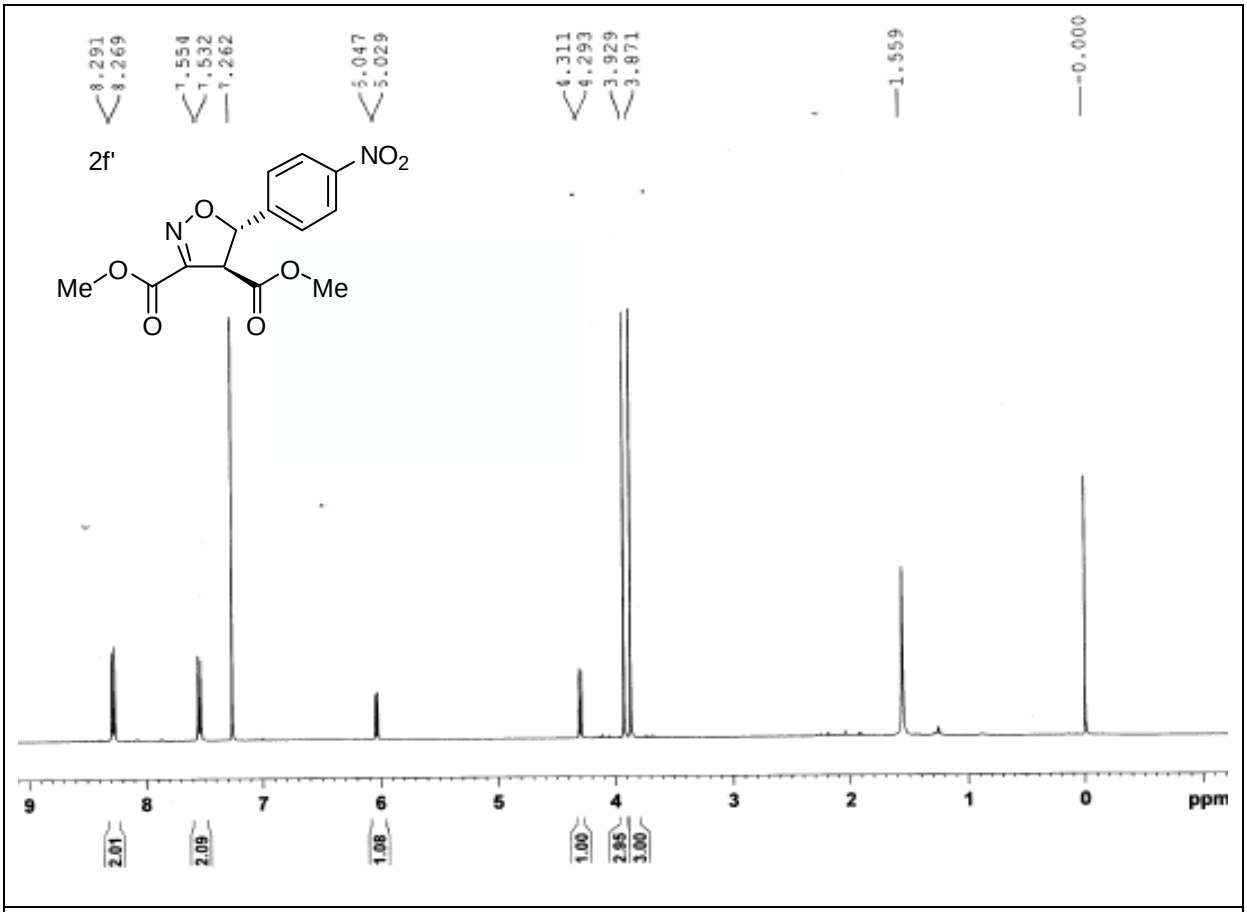
7.336
7.263
7.256
7.235
6.007
5.976
4.616
4.585
3.917
3.299
1.566
0.070
0.000
2e
Cl
N
O
Me
O
O
O
Me
O
ppm
2.00
2.60
1.00
0.98
3.02
2.98
166.47
160.14
149.59
135.11
132.57
128.66
128.10
86.82
77.32
76.68
67.27
53.09
52.42
200
150
100
50
[ppm]

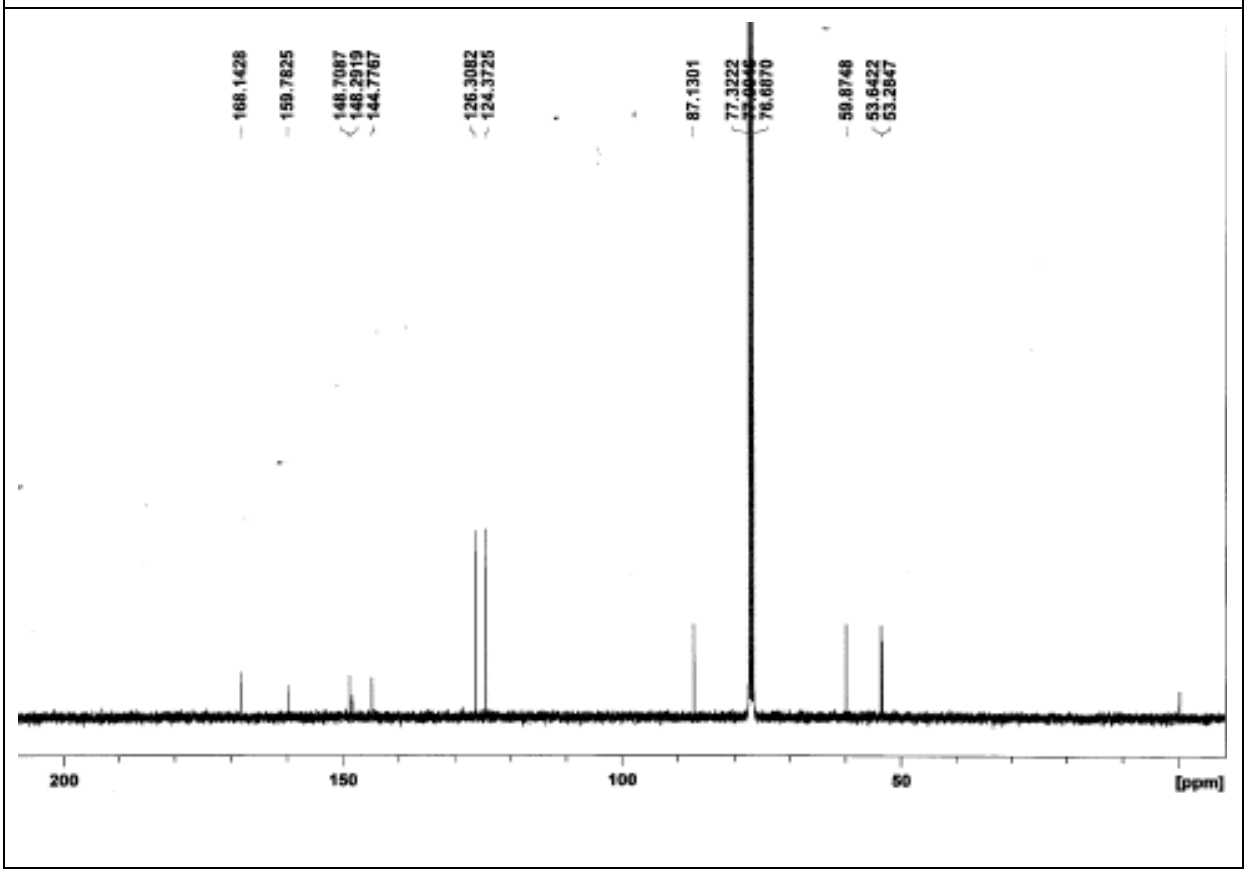

7.395
7.373
7.283
7.262
5.912
5.892
4.291
4.271
3.917
3.836
3.300
1.555
0.070
0.000
2e'
Cl
N
O
Me
O
O
O
Me
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.00
3.76
0.99
0.97
3.08
2.99

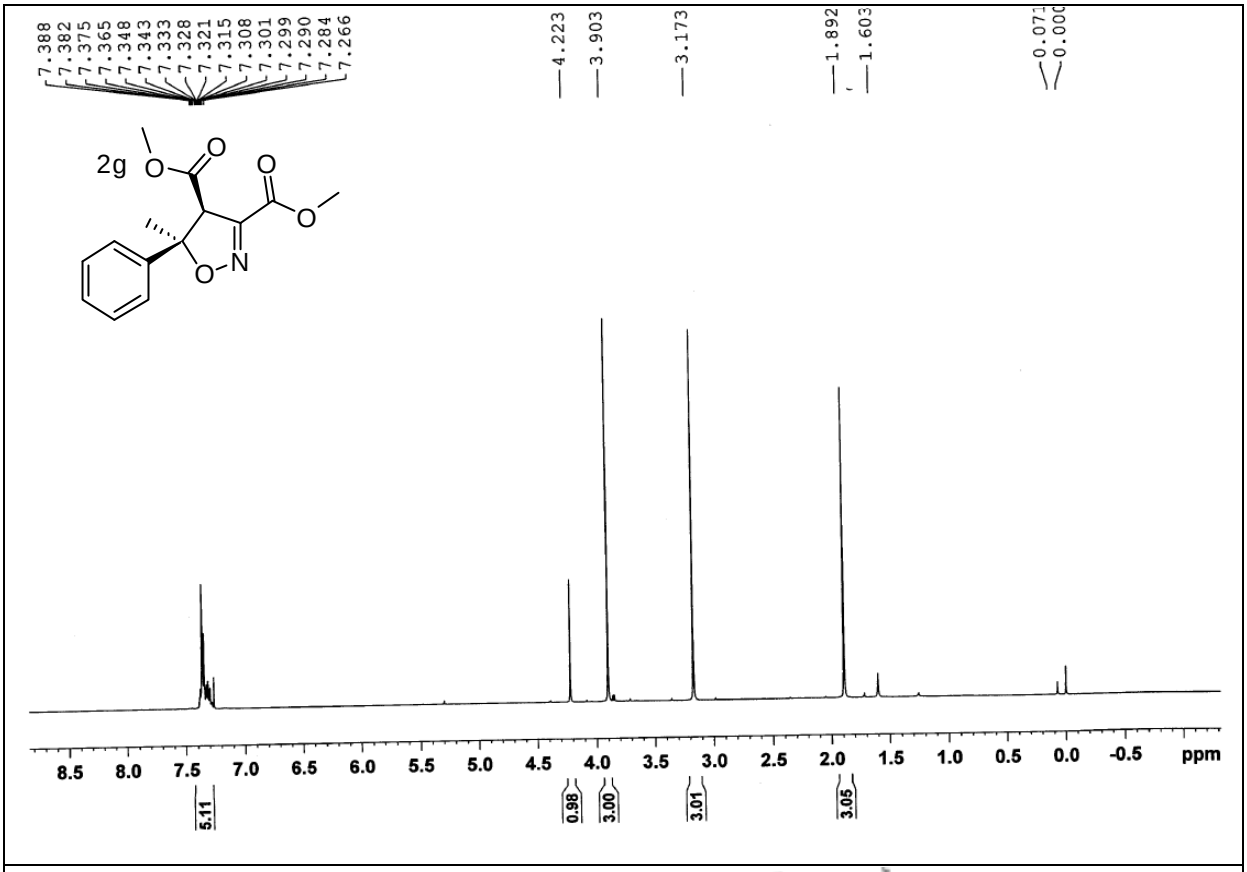

168.6004
160.0599
148.6894
136.3385
135.1590
129.3253
126.9179
88.1352
77.3185
76.6839
59.7779
53.3906
53.1124
200 150 100 50 [ppm]

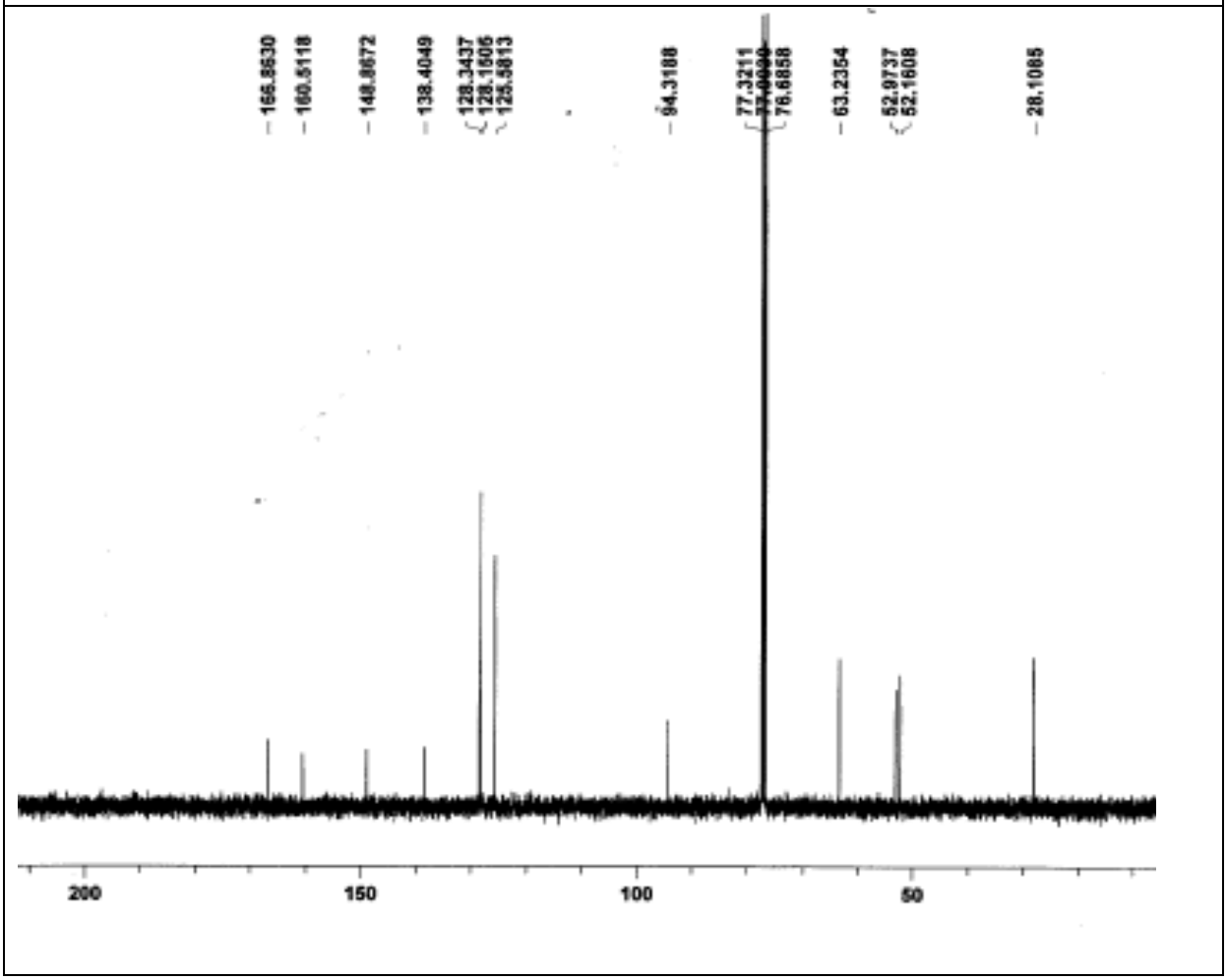

8.255
8.233
7.528
7.506
7.265
6.123
6.092
4.722
4.691
3.933
3.294
1.568
0.000
2f
NO2
N
O
Me
O
O
O
Me
8
7
6
5
4
3
2
1
0
ppm
2.02
2.05
1.02
1.01
3.08
3.00


166.09
159.85
149.84
148.28
141.18
127.71
123.59
86.04
77.32
76.88
67.64
63.26
62.80
150
100
50
ppm


8.291
8.269
7.554
7.532
7.262
5.047
5.029
4.311
4.293
3.929
3.871
1.559
0.000
2f'
NO2
N
O
Me
O
O
O
Me
ppm
2.01
2.09
1.08
1.00
2.95
3.00


168.1428
159.7825
148.7087
148.2919
144.7767
126.3082
124.3725
87.1301
77.3222
76.6870
59.8748
53.6422
53.2847
200
150
100
50
[ppm]


7.388
7.382
7.375
7.365
7.348
7.343
7.333
7.328
7.321
7.315
7.308
7.301
7.299
7.290
7.284
7.266
4.223
3.903
3.173
1.892
1.603
0.071
0.000
2g
O
O
O
O
N
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
-0.5
ppm
5.11
0.98
3.00
3.01
3.05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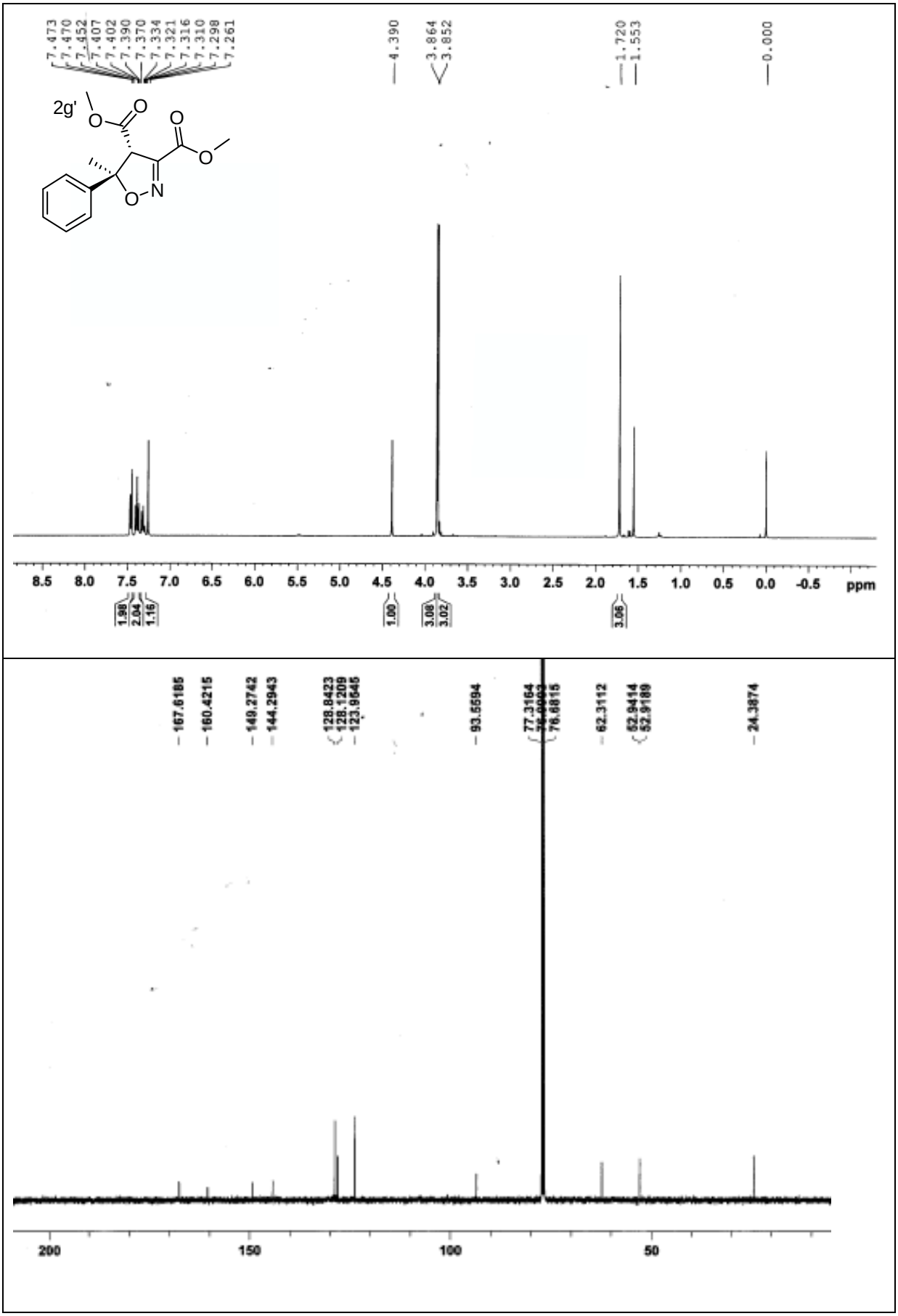
160.5118
148.8672
138.4049
128.3437
128.1506
125.5813
94.3188
77.3211
77.0000
76.6858
63.2354
52.9737
52.1608
28.1085
200
150
100
50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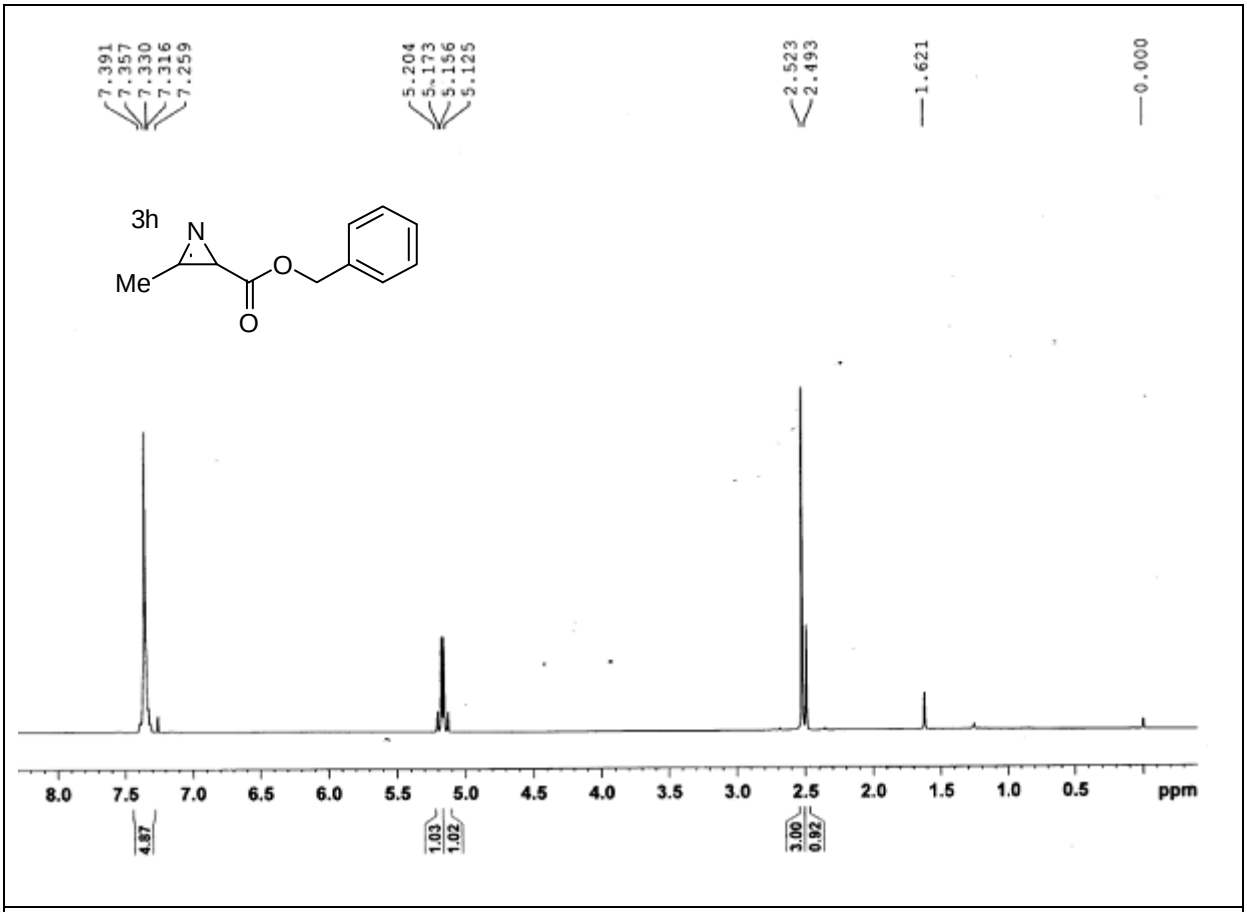
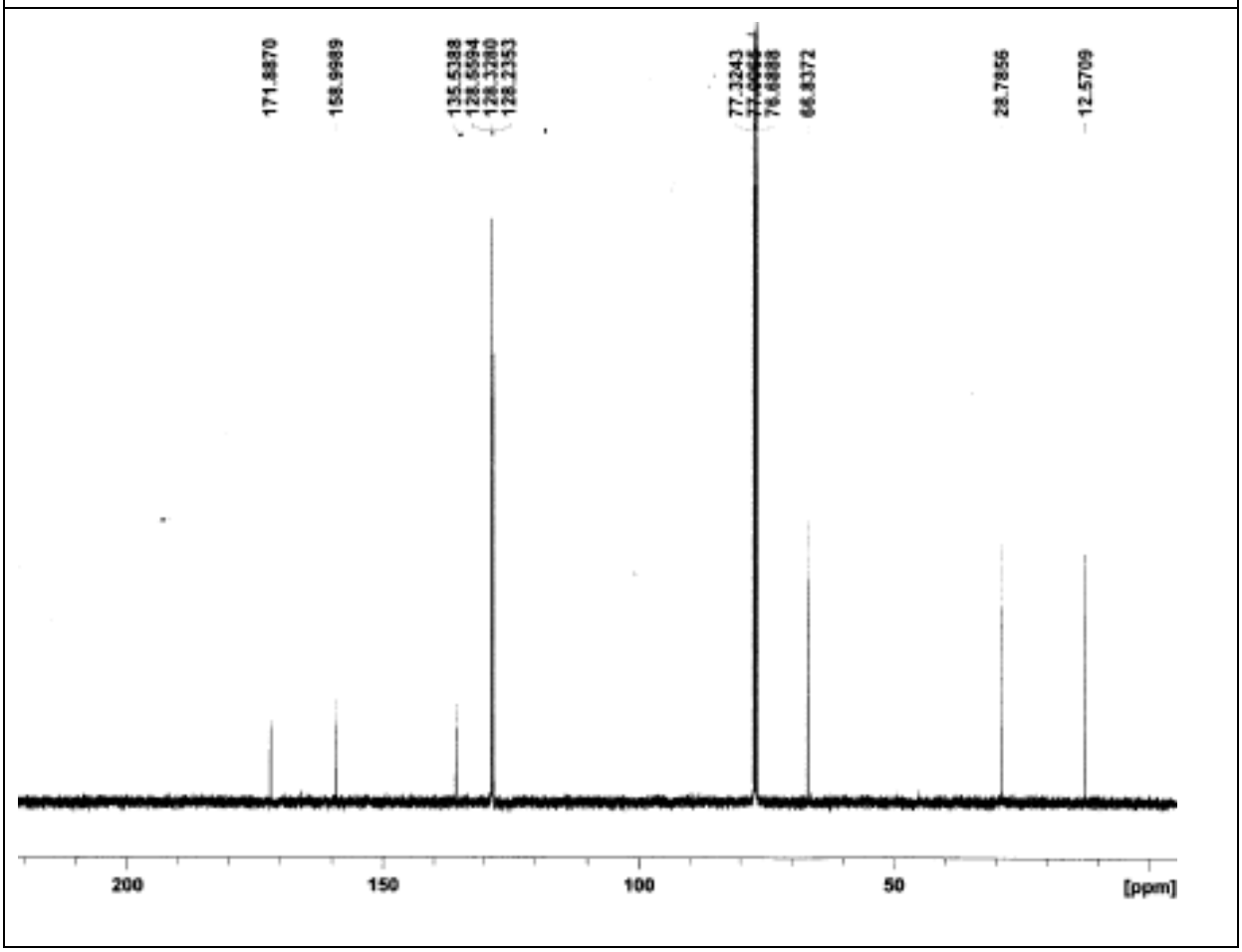
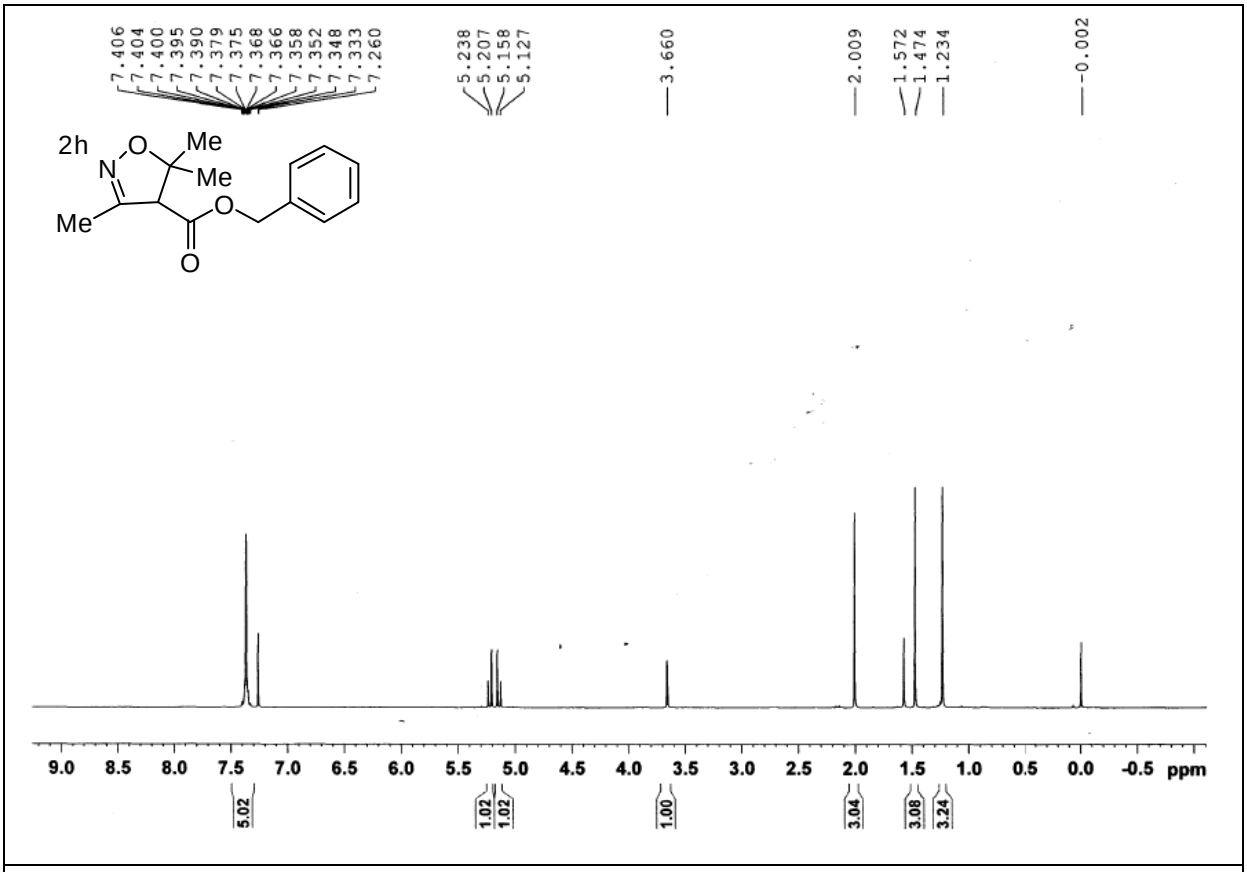
7.470
7.452
7.407
7.402
7.390
7.370
7.334
7.321
7.316
7.310
7.298
7.261
4.390
3.864
3.852
1.720
1.553
0.000
2g'
O
O
O
O
N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.98
2.04
1.16
1.00
3.08
3.02
3.06
167.6185
160.4215
149.2742
144.2943
128.8423
128.1209
123.9545
93.5594
77.3164
76.6815
62.3112
52.9414
52.9189
24.3874
200
150
100
50


7.391
7.357
7.330
7.316
7.259
5.204
5.173
5.156
5.125
2.523
2.493
1.621
0.000
3h
N
Me
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
4.87
1.03
1.02
3.00
0.92


171.8870
158.9989
135.5388
128.6594
128.3280
128.2353
77.2243
66.8372
28.7856
12.5709
200
150
100
50
[ppm]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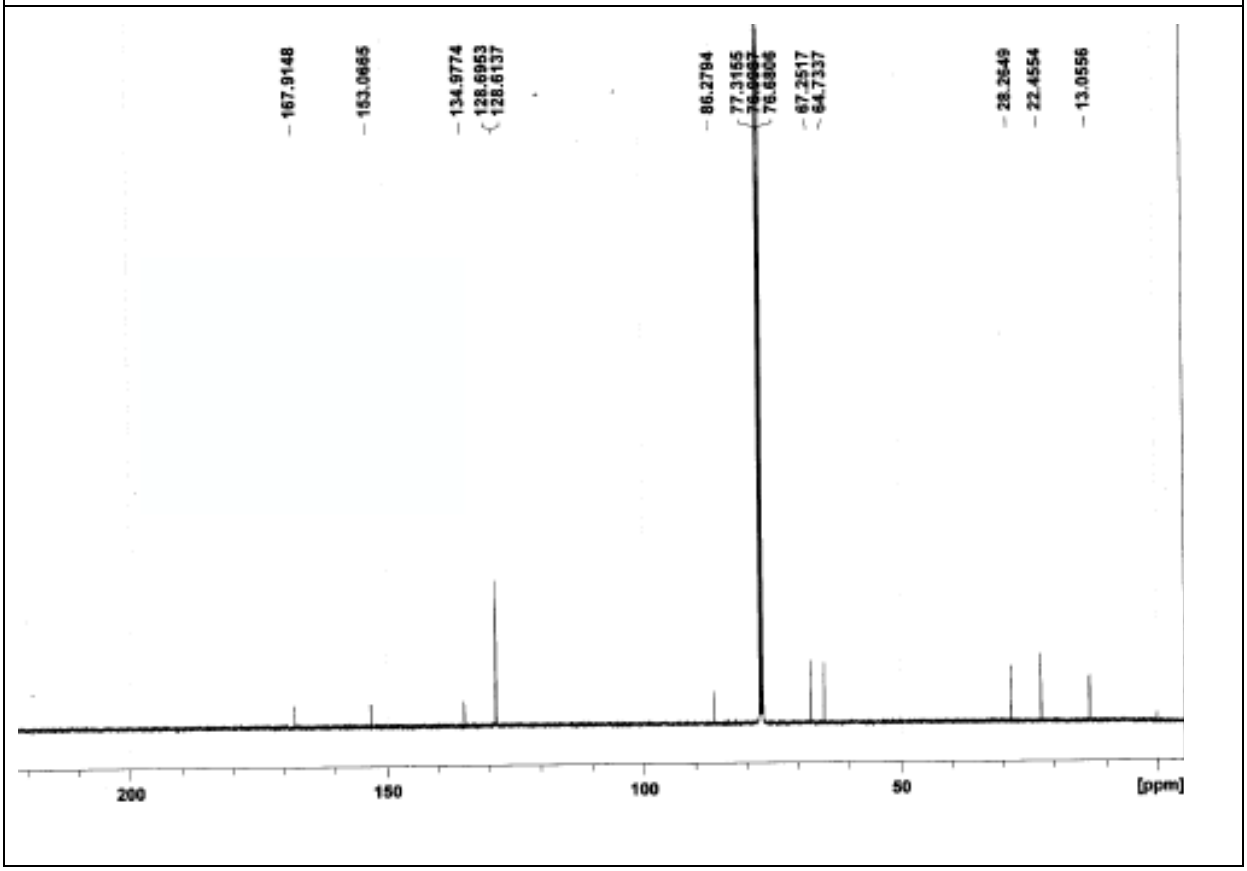
7.404
7.400
7.395
7.390
7.379
7.375
7.368
7.366
7.358
7.352
7.348
7.333
7.260
5.238
5.207
5.158
5.127
3.660
2.009
1.572
1.474
1.234
0.002
2h
O
N
Me
Me
Me
O
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
5.02
1.02
1.02
1.00
3.04
3.08
3.24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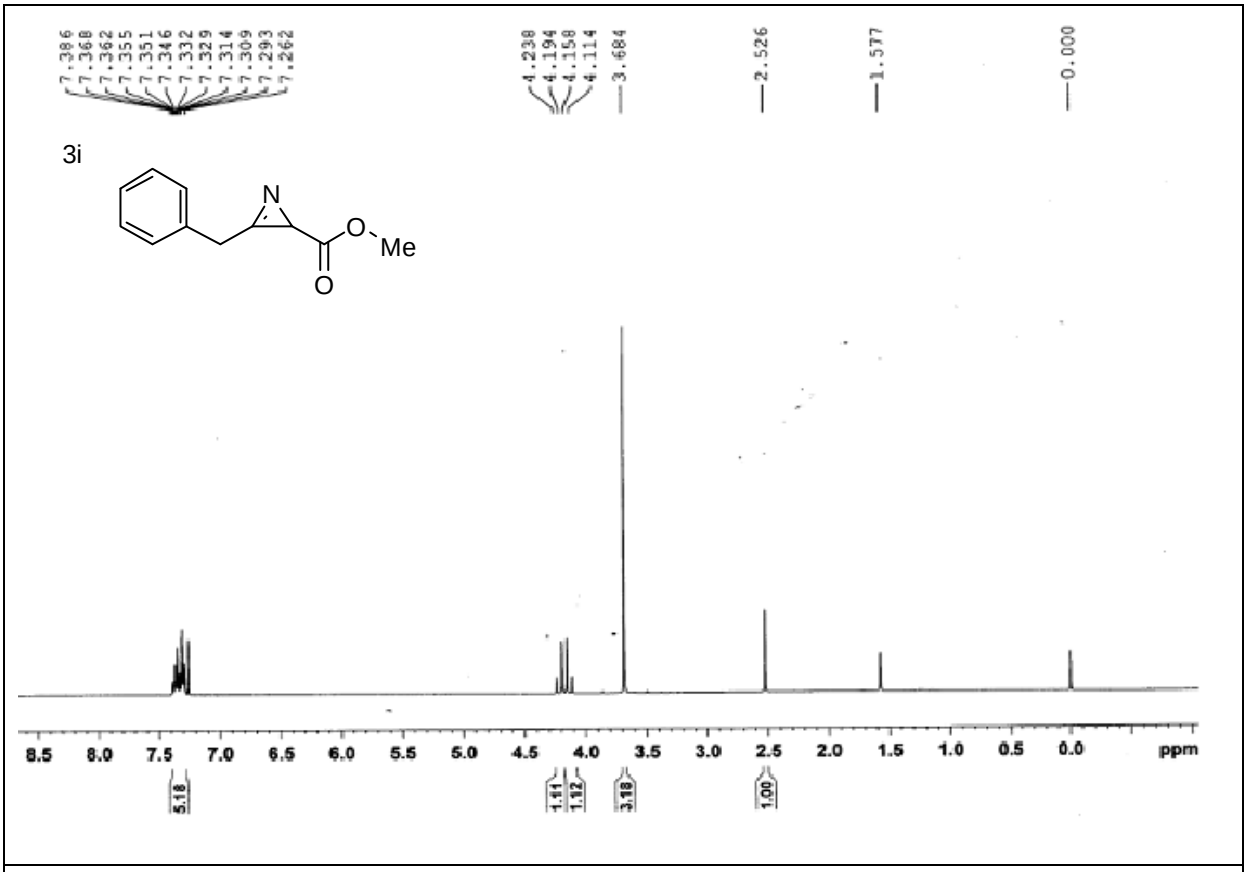
153.0665
134.9774
128.6953
128.6137
86.2794
77.3155
67.2517
64.7337
28.2649
22.4554
13.0556
200
150
100
50
[ppm]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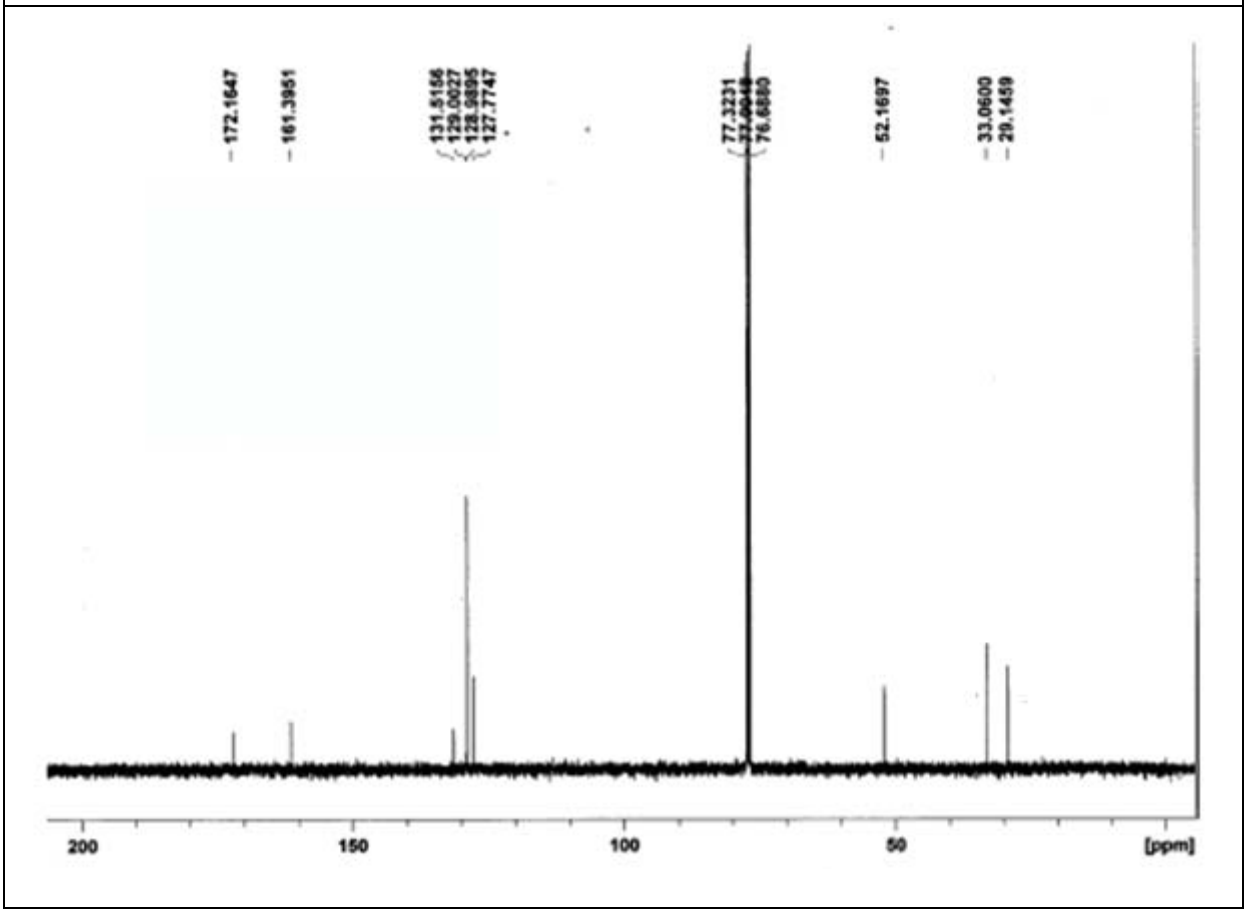
7.368
7.362
7.355
7.351
7.346
7.332
7.329
7.314
7.309
7.293
7.262
4.238
4.194
4.158
4.114
3.684
2.526
1.577
0.000
3i
N
O
Me
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.18
1.11
1.12
3.18
1.00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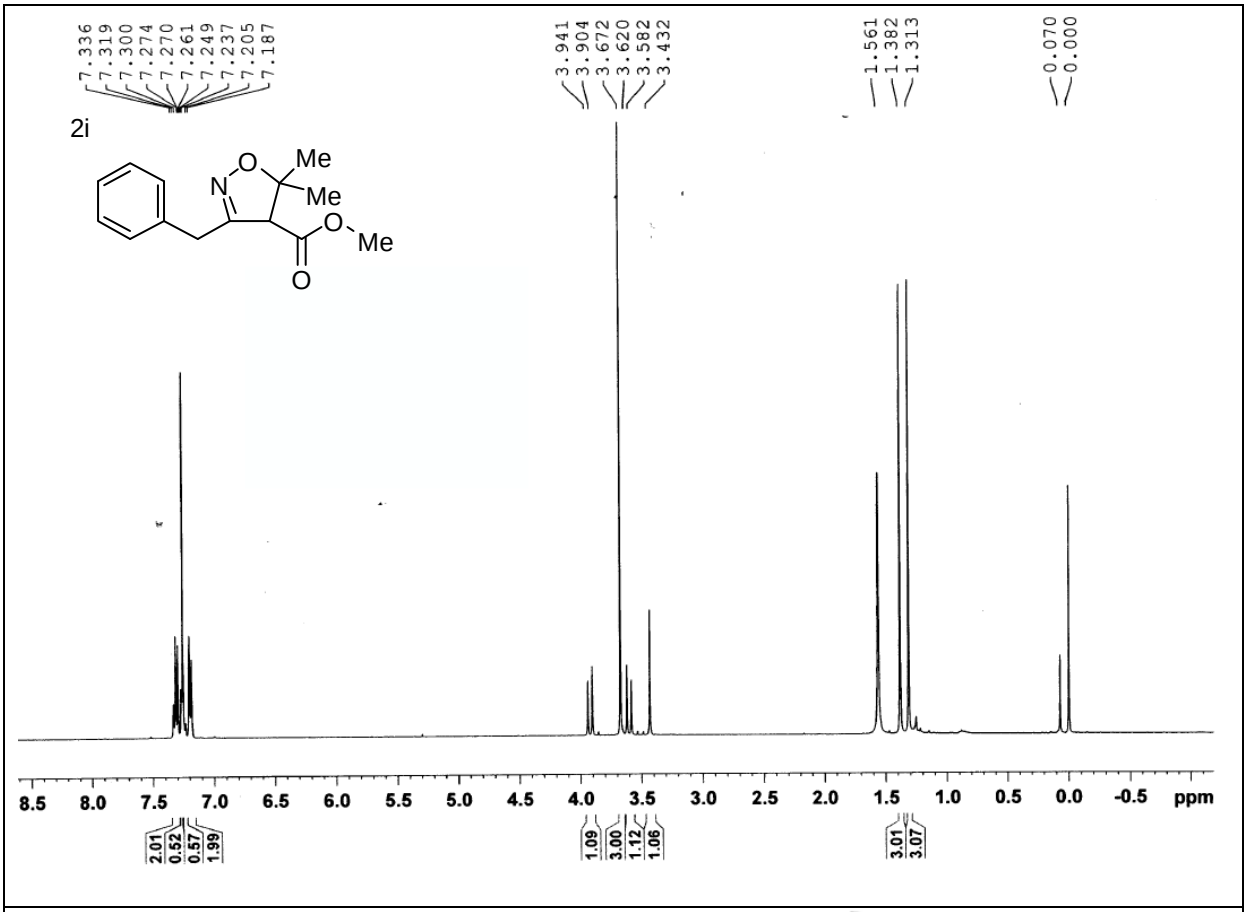
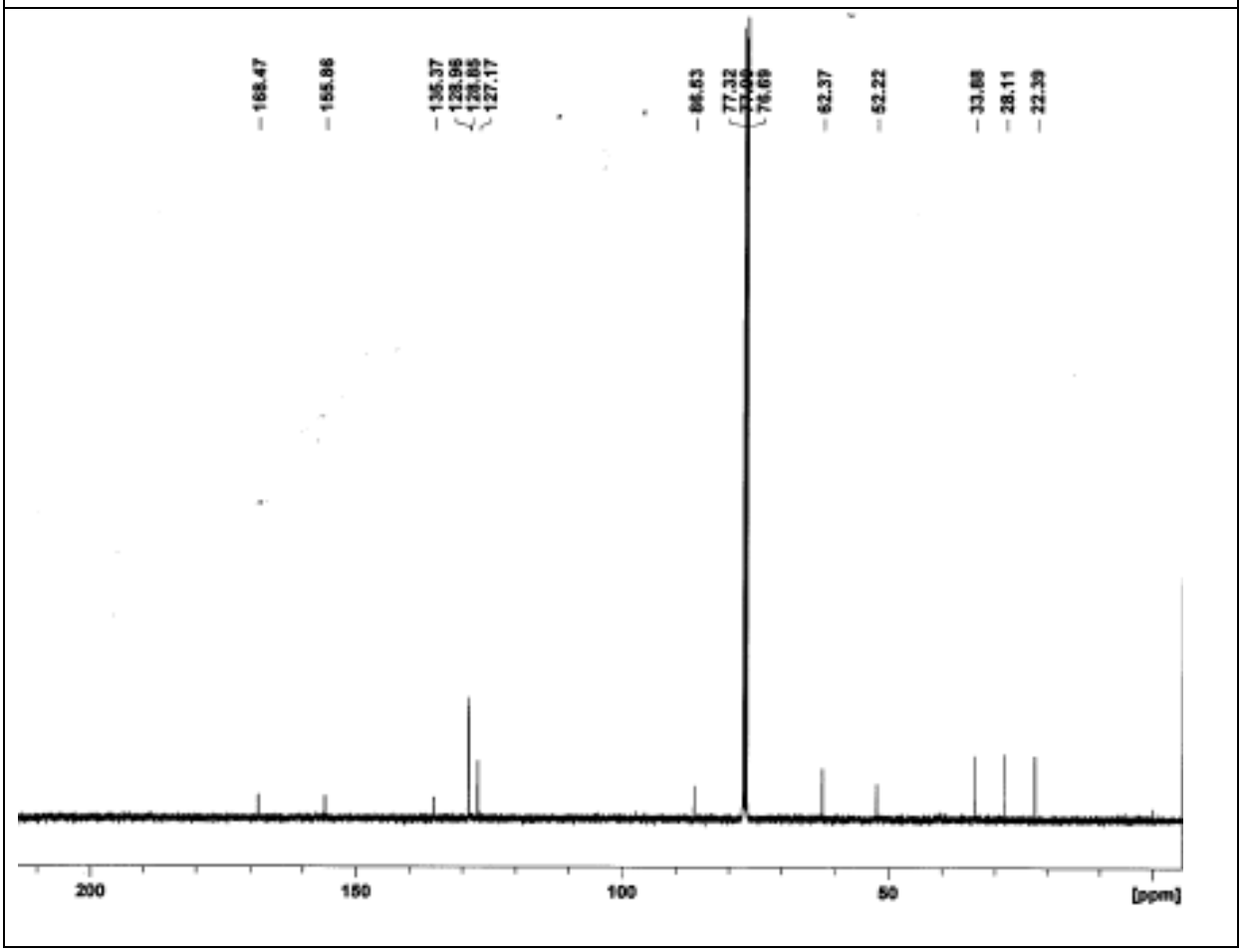
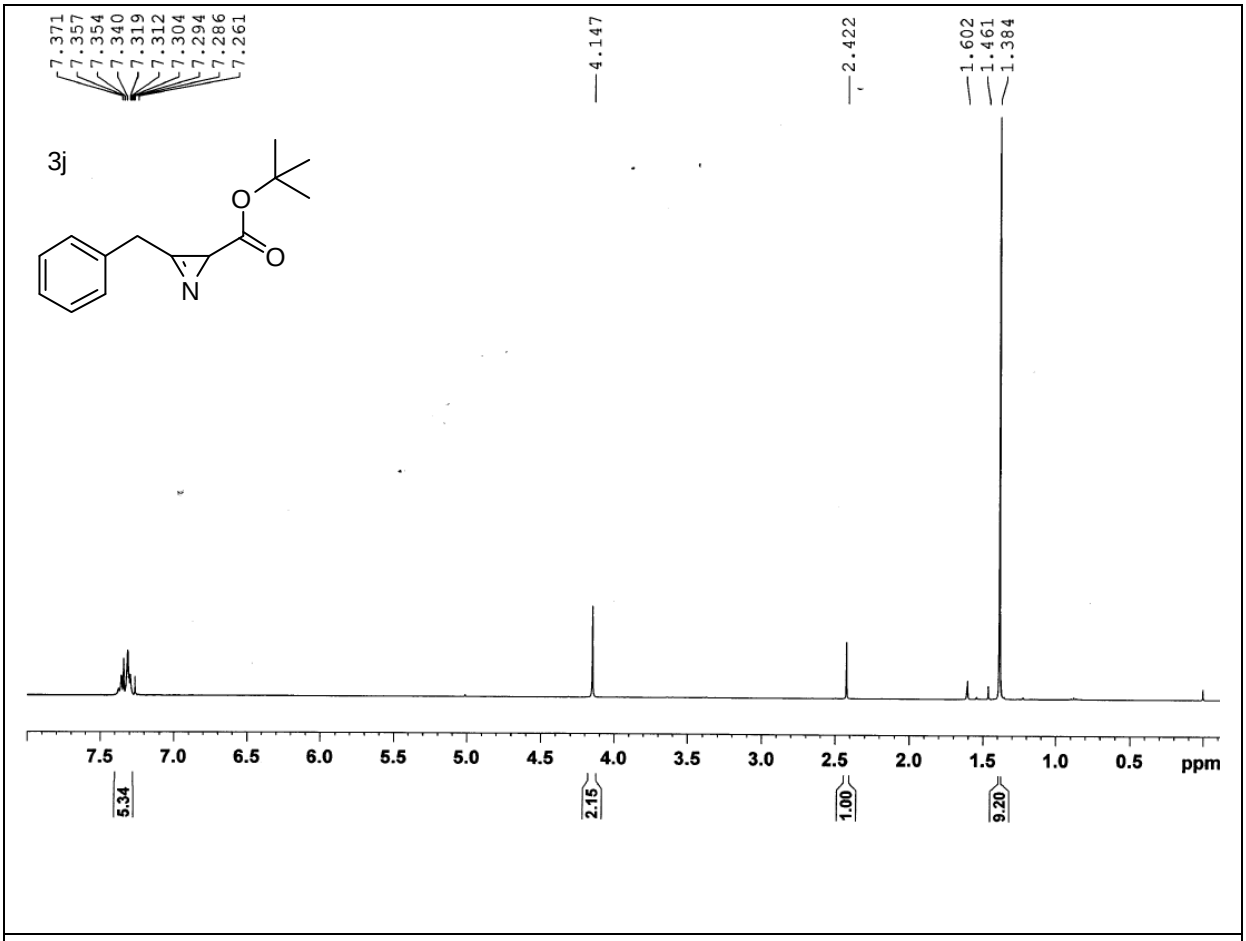
131.5156
129.0027
128.6895
127.7747
77.3231
76.6880
52.1697
33.0600
29.1459
200
150
100
50
[ppm]


7.336
7.319
7.300
7.274
7.270
7.261
7.249
7.237
7.205
7.187
3.941
3.904
3.672
3.620
3.582
3.432
1.561
1.382
1.313
0.070
0.000
2i
Me
Me
Me
O
N
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 0.0 -0.5 ppm
2.01
0.52
0.57
1.99
1.09
3.00
1.12
1.06
3.01
3.07


168.47
155.86
135.37
128.96
128.85
127.17
86.53
77.32
77.06
76.69
62.37
52.22
33.88
28.11
22.39
200 150 100 50 [ppm]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7.357
7.354
7.340
7.319
7.312
7.304
7.294
7.286
7.261
4.147
2.422
1.602
1.461
1.384
3j
O
O
N
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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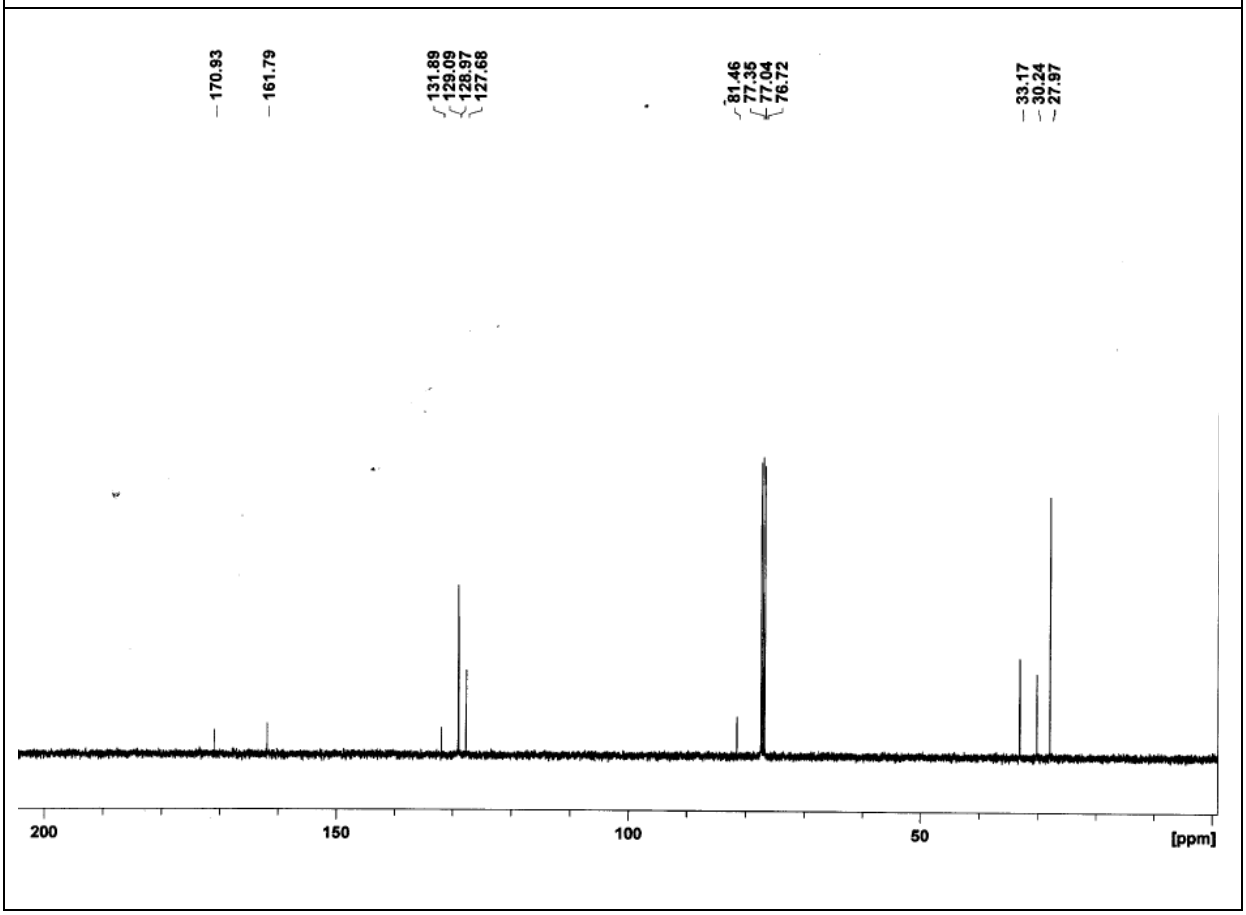
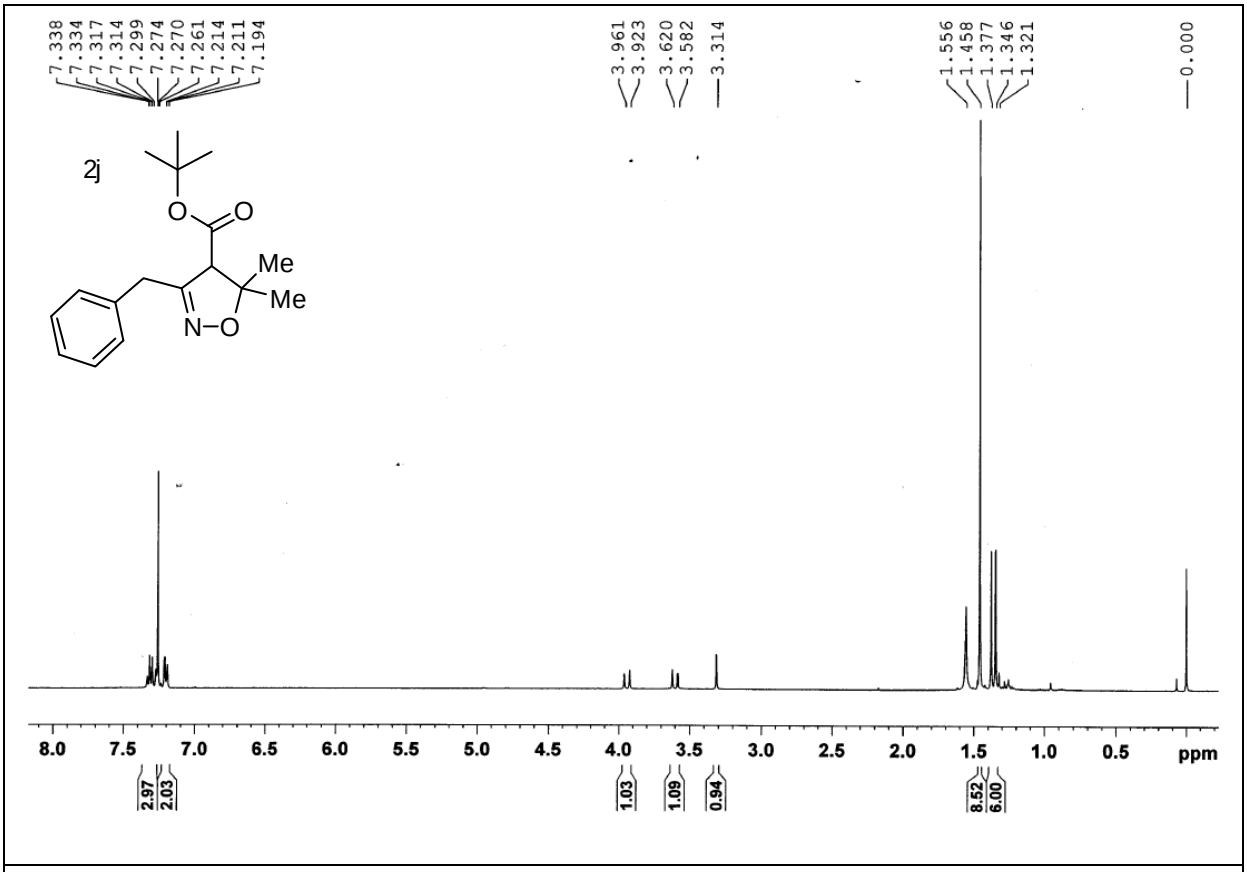
2.15
1.00
9.20


170.93
161.79
131.89
129.09
128.97
127.68
81.46
77.35
77.04
76.72
33.17
30.24
27.97
200
150
100
50
[ppm]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7.334
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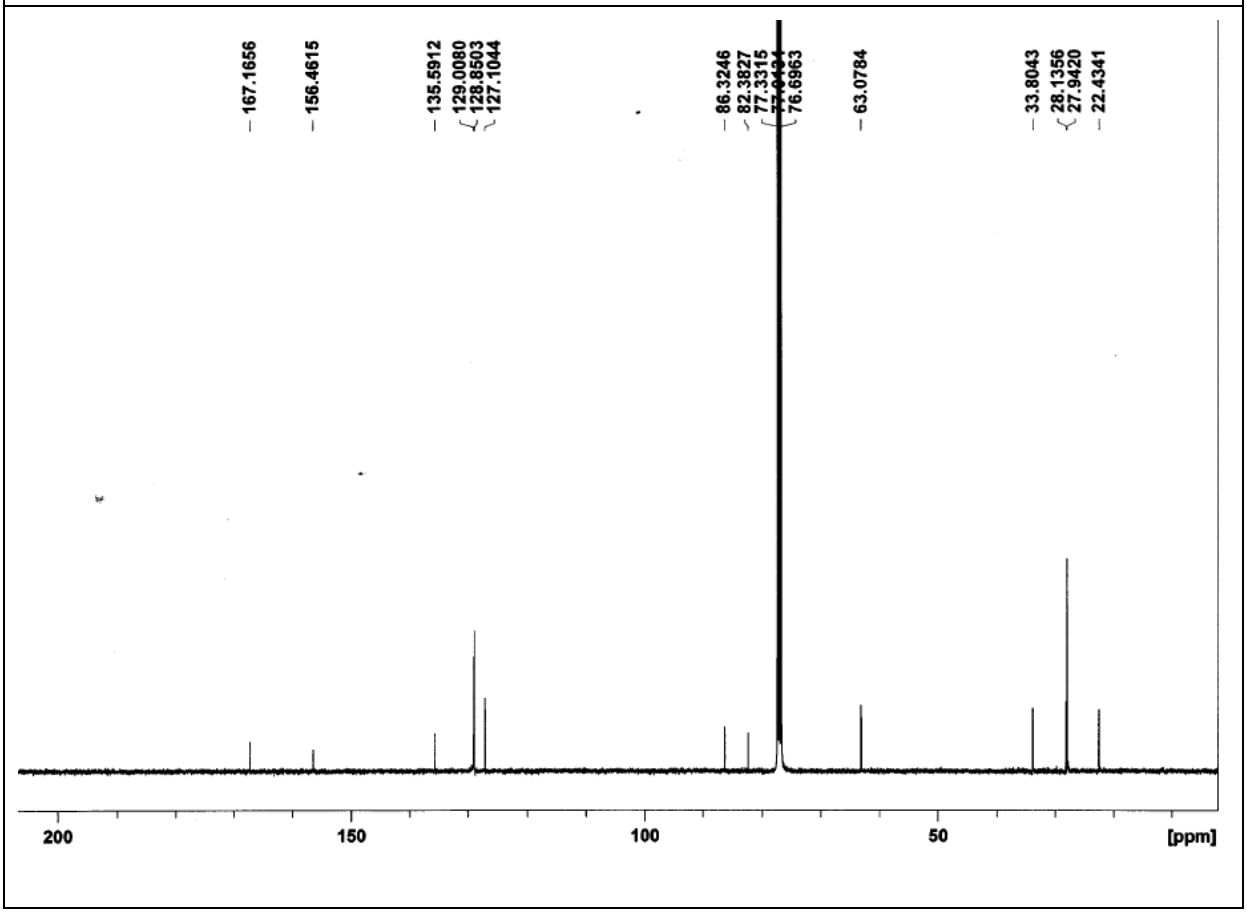
7.314
7.299
7.274
7.270
7.261
7.214
7.211
7.194
3.961
3.923
3.620
3.582
3.314
1.556
1.458
1.377
1.346
1.321
0.000
2j
O
O
Me
Me
N–O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.97
2.03
1.03
1.09
0.94
8.52
6.00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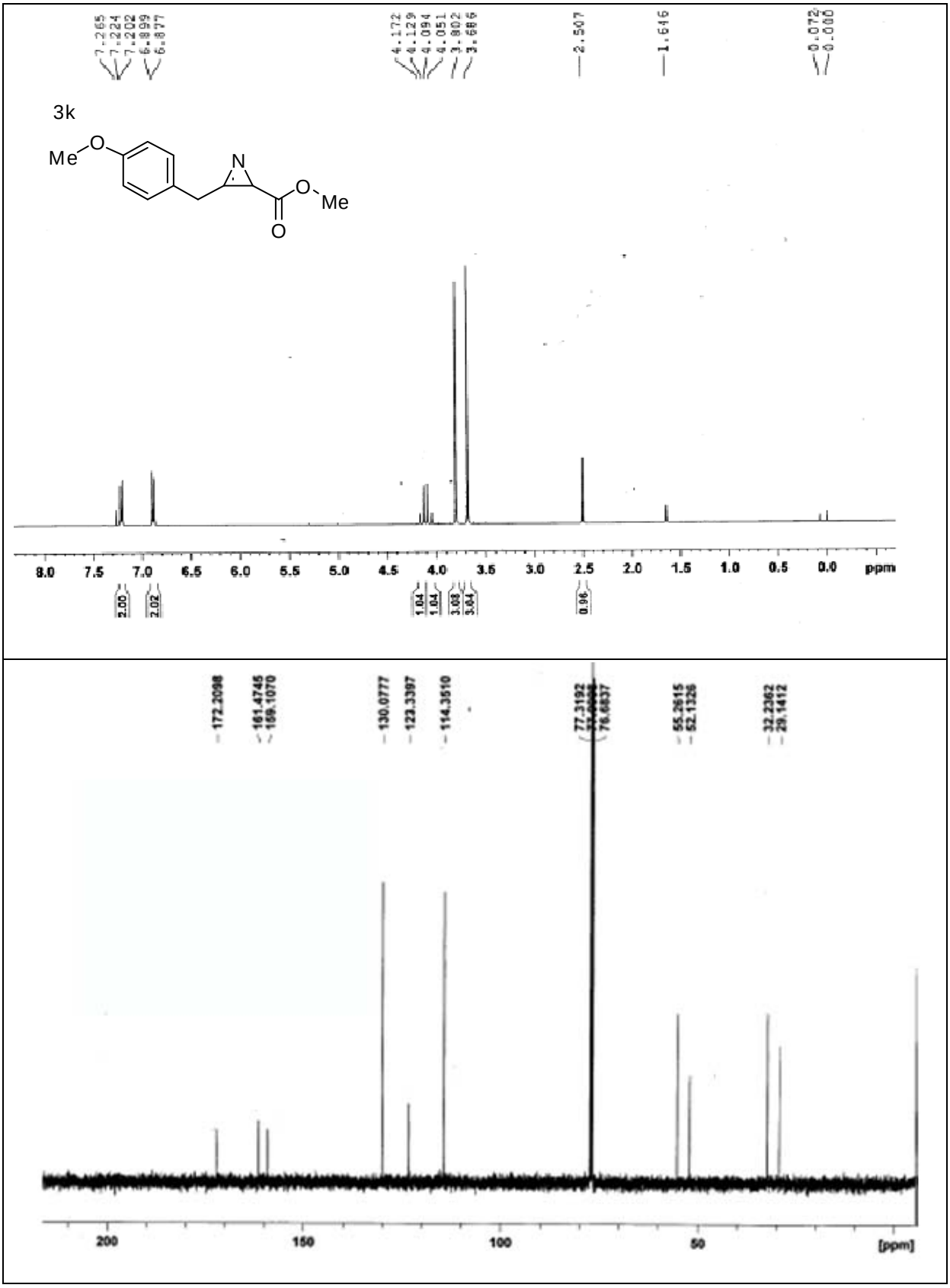
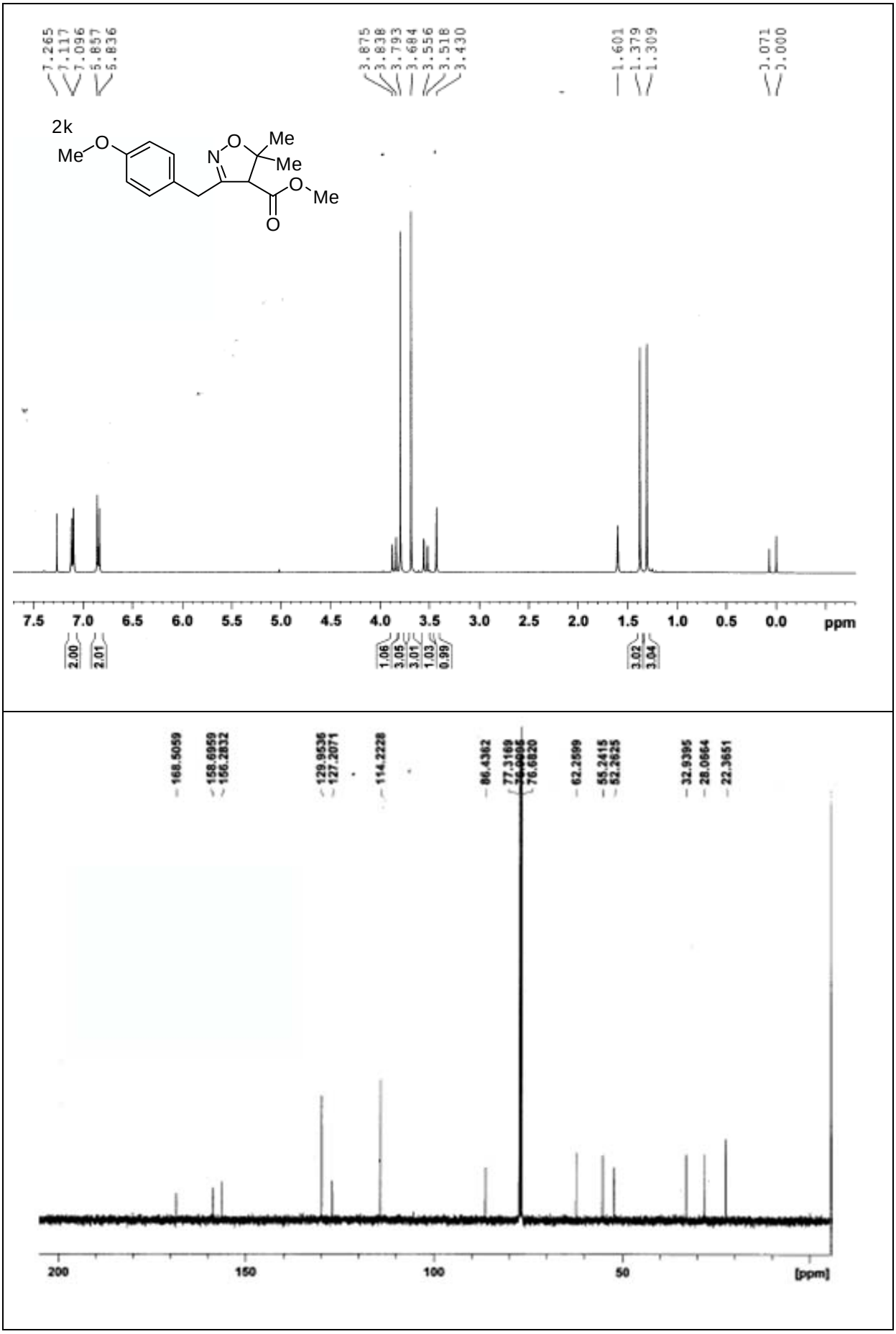
156.4615
135.5912
129.0080
128.8503
127.1044
86.3246
82.3827
77.3315
76.6963
63.0784
33.8043
28.1356
27.9420
22.4341
200
150
100
50
[ppm]


3k
Me
O
N
O
Me
O
7.265
7.224
7.202
6.899
6.877
4.172
4.129
4.094
4.051
3.902
3.686
2.507
1.616
0.072
0.000
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
2.00
2.02
1.04
1.04
3.08
3.04
0.96
172.2098
161.4745
159.1070
130.0777
123.3397
114.3510
77.3192
76.6837
55.2615
52.1328
32.2362
29.1412
200
150
100
50
[ppm]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7.117
7.096
5.857
5.836
3.875
3.838
3.793
3.684
3.556
3.518
3.430
1.601
1.379
1.309
3.071
3.000
2k
Me
O
N
O
Me
Me
O
Me
O
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
2.00
2.01
1.06
3.05
3.01
1.03
0.99
3.02
3.04
168.5059
158.6959
156.2832
129.9536
127.2071
114.2228
86.4362
77.3169
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55.2415
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32.9395
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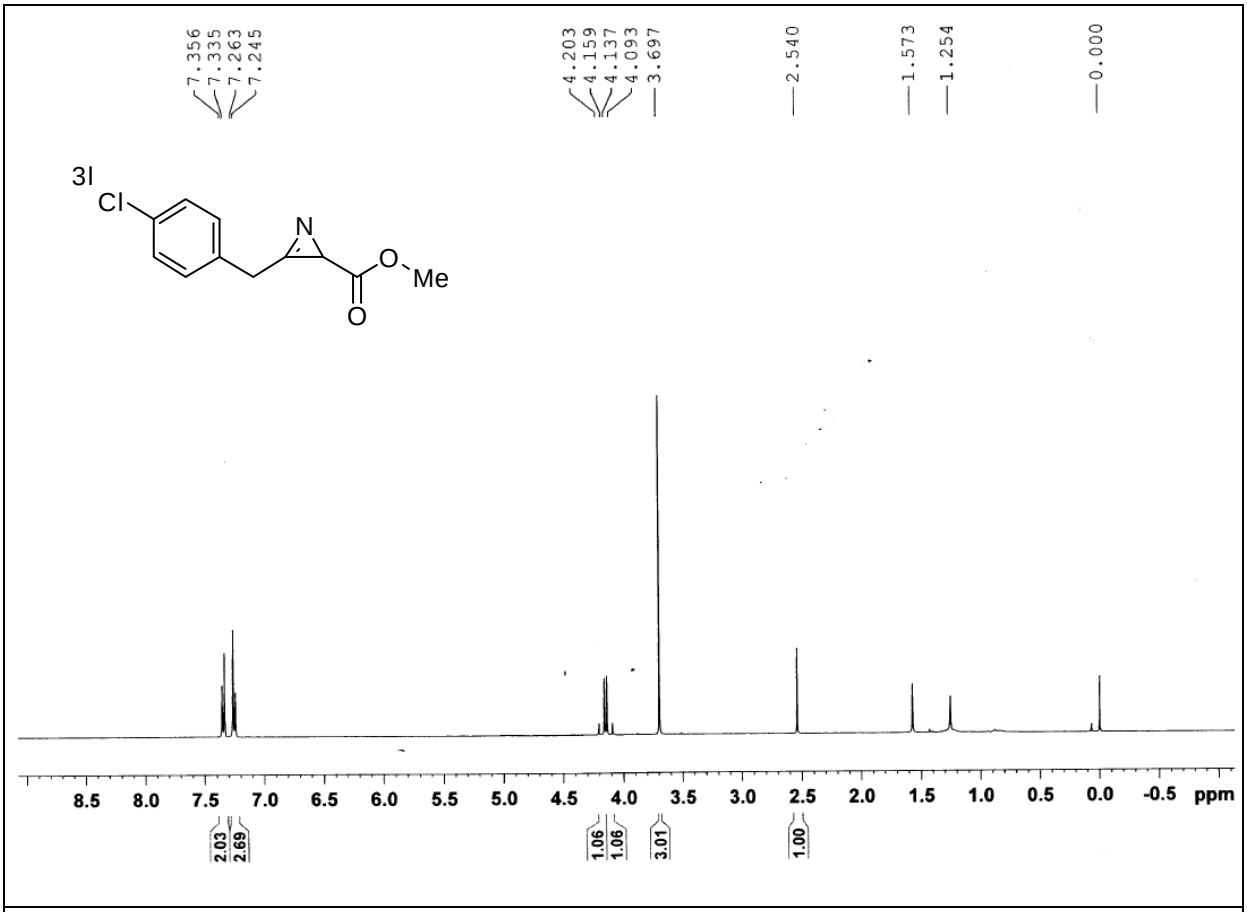
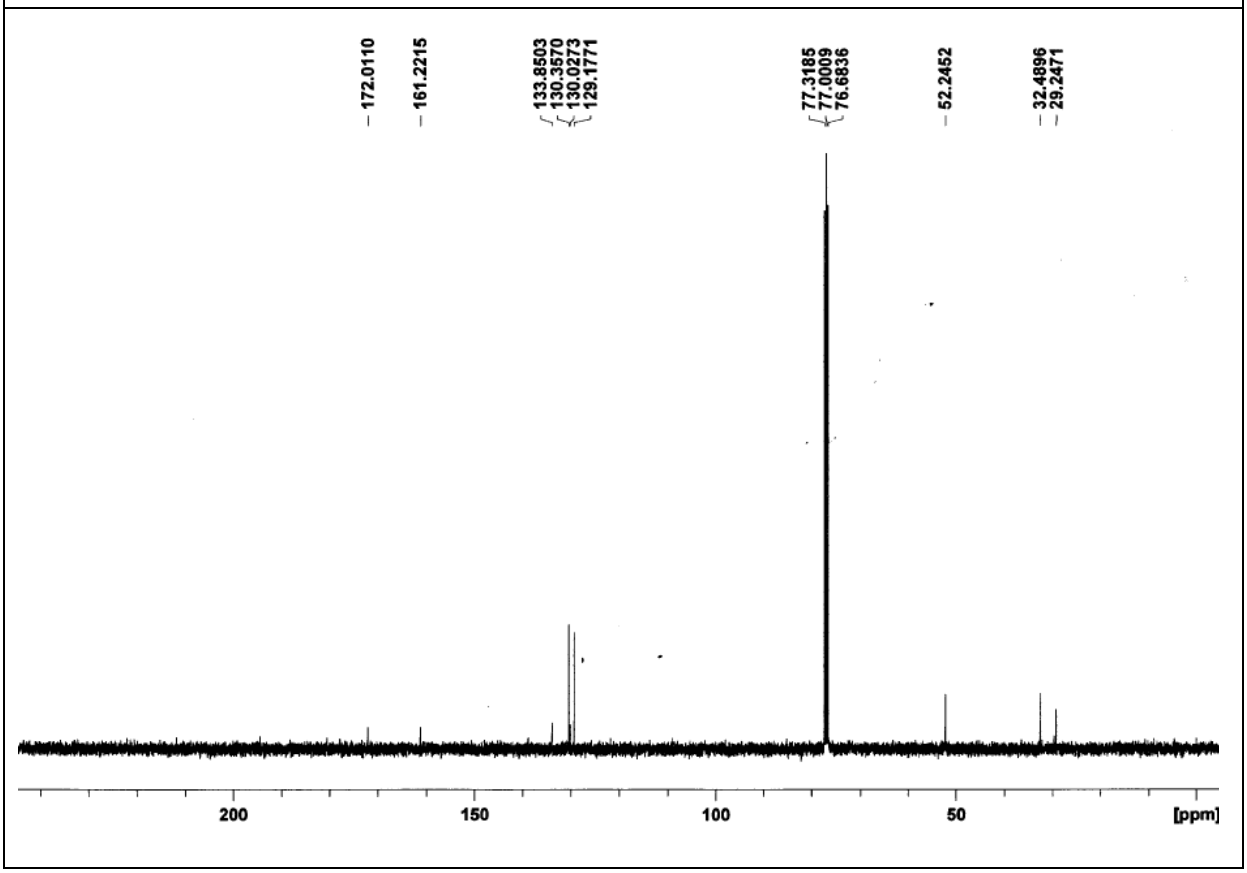
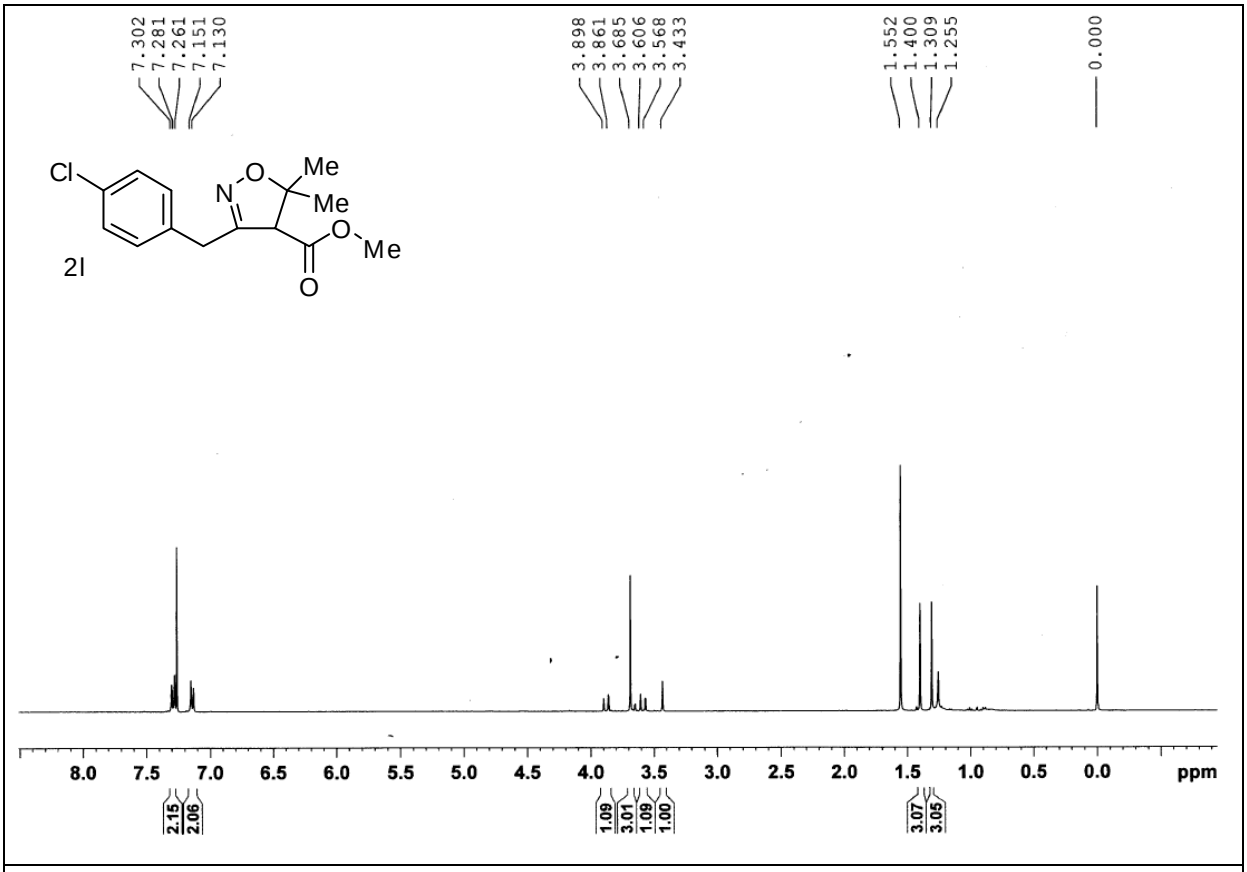
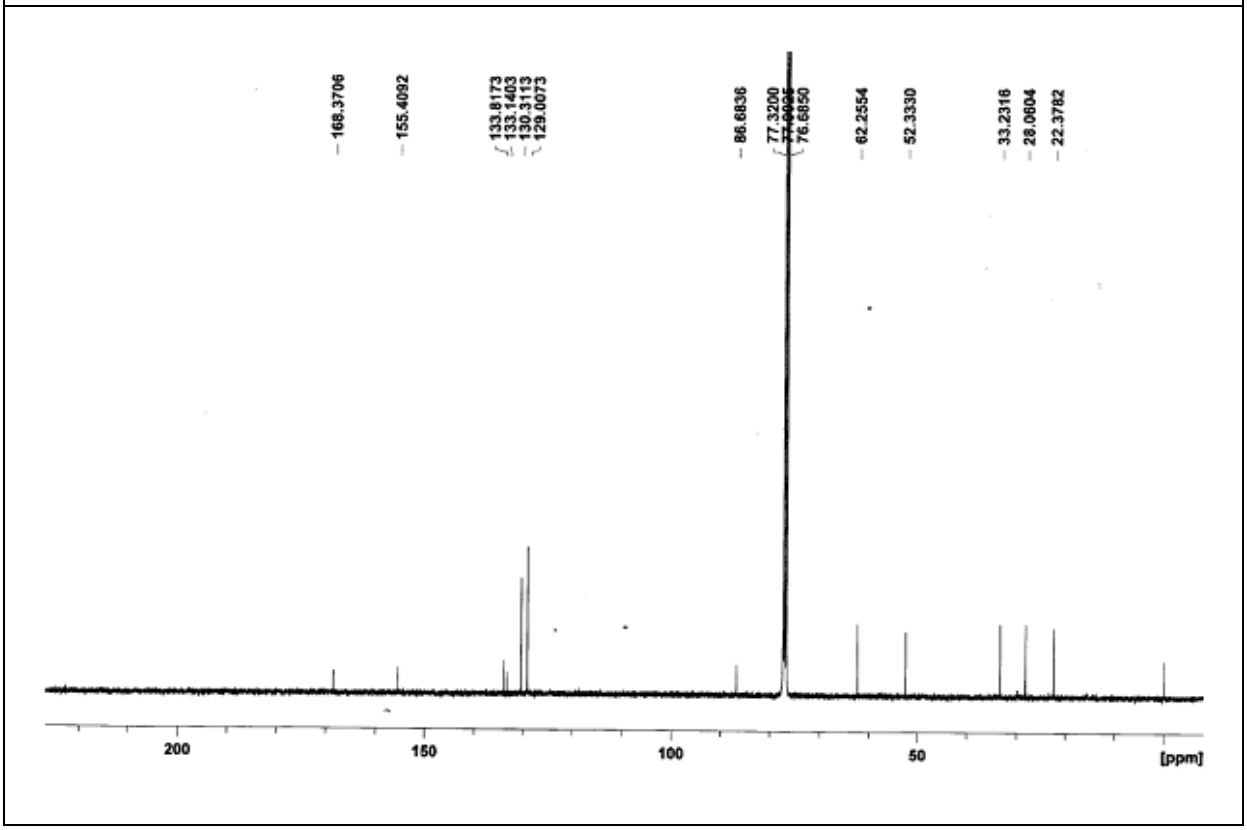
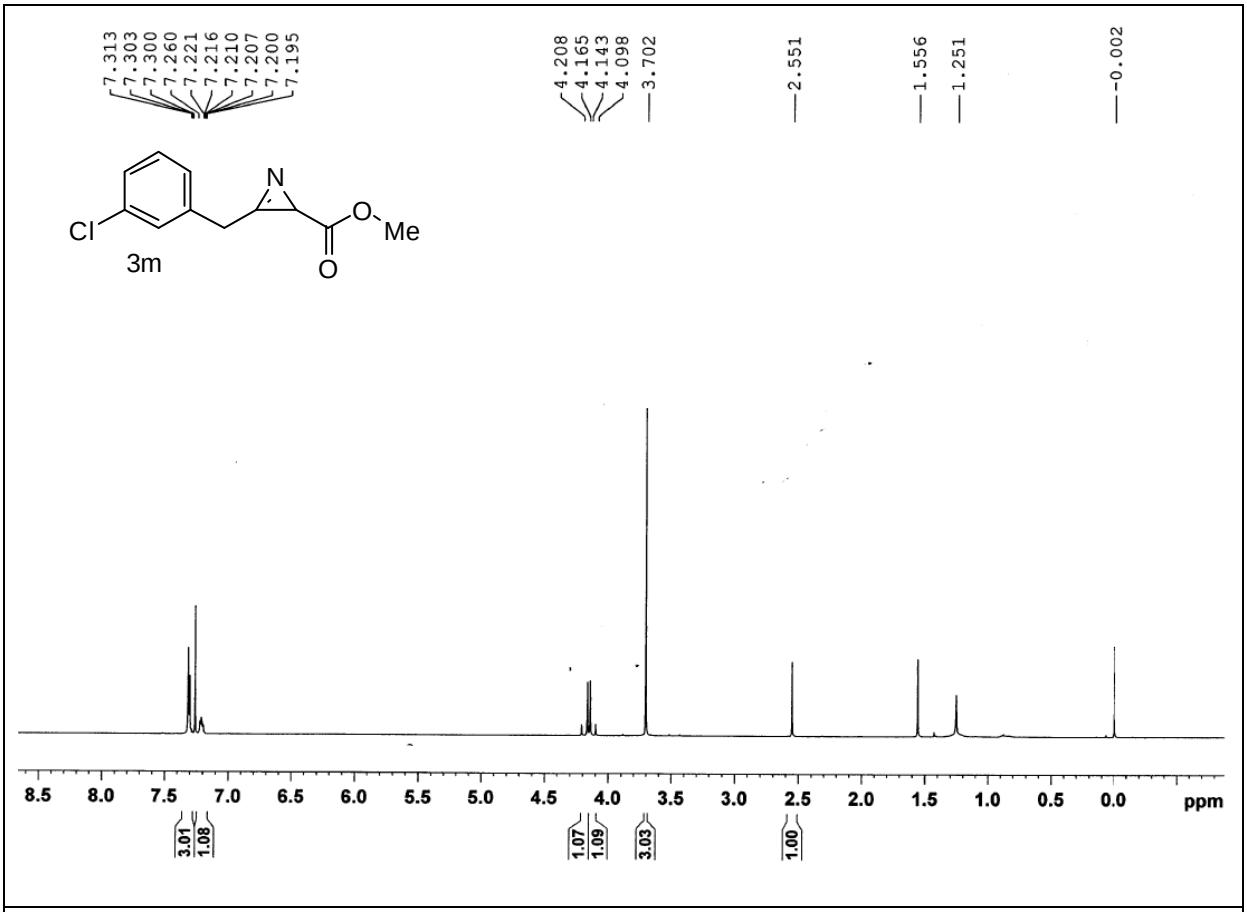
22.3651
200
150
100
50
[ppm]

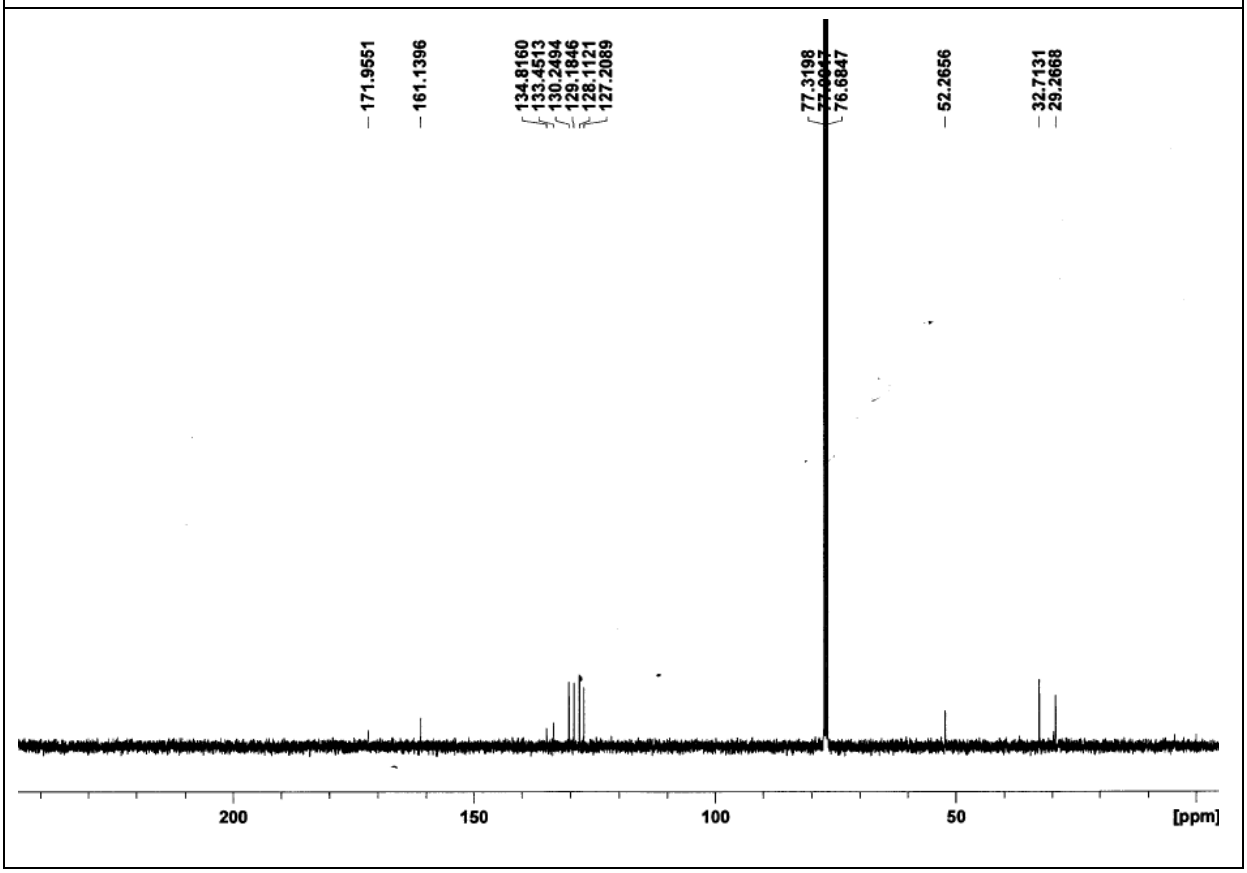

7.356
7.335
7.263
7.245
4.203
4.159
4.137
4.093
3.697
2.540
1.573
1.254
0.000
3l
Cl
N
O
Me
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.03
2.69
1.06
1.06
3.01
1.00

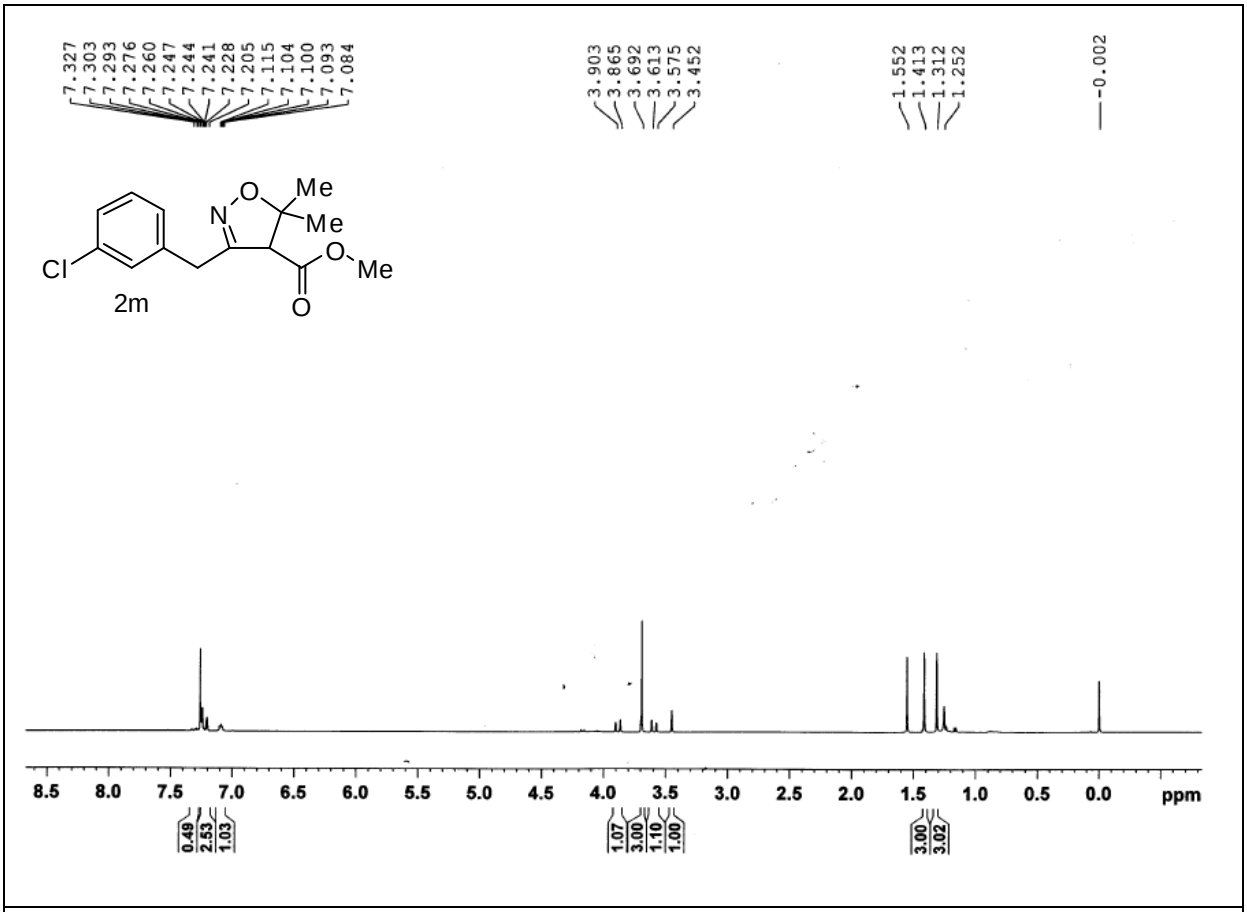

172.0110
161.2215
133.8503
130.3570
130.0273
129.1771
77.3185
77.0009
76.6836
52.2462
32.4896
29.2471
200 150 100 50 [ppm]


7.302
7.281
7.261
7.151
7.130
3.898
3.861
3.685
3.606
3.568
3.433
1.552
1.400
1.309
1.255
0.000
Cl
N
O
Me
Me
O
Me
O
2l
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
2.15
2.06
1.09
3.01
1.09
1.00
3.07
3.05


168.3706
155.4092
133.8173
133.1403
130.3113
129.0073
86.6836
77.3200
76.6850
82.2554
52.3330
33.2316
28.0604
22.3782
200
150
100
50
[ppm]


7.313
7.303
7.300
7.260
7.221
7.216
7.210
7.207
7.200
7.195
4.208
4.165
4.143
4.098
3.702
2.551
1.556
1.251
-0.002
Cl
N
O
Me
O
3m
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
3.01
1.08
1.07
1.09
3.03
1.00


171.9551
161.1396
134.8160
133.4513
130.2494
129.1846
128.1121
127.2089
77.3198
77.0847
76.6847
52.2656
32.7131
29.2668
200
150
100
50
[ppm]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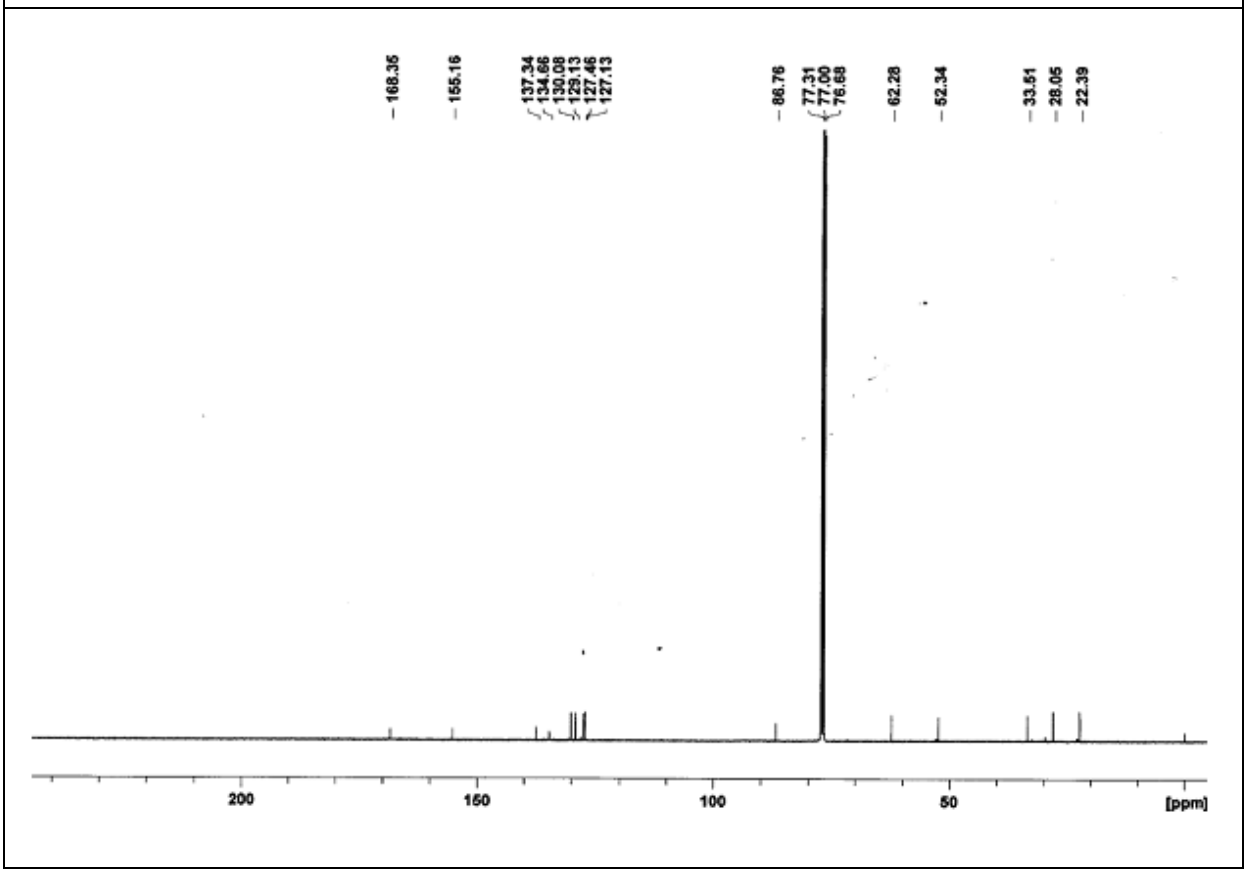
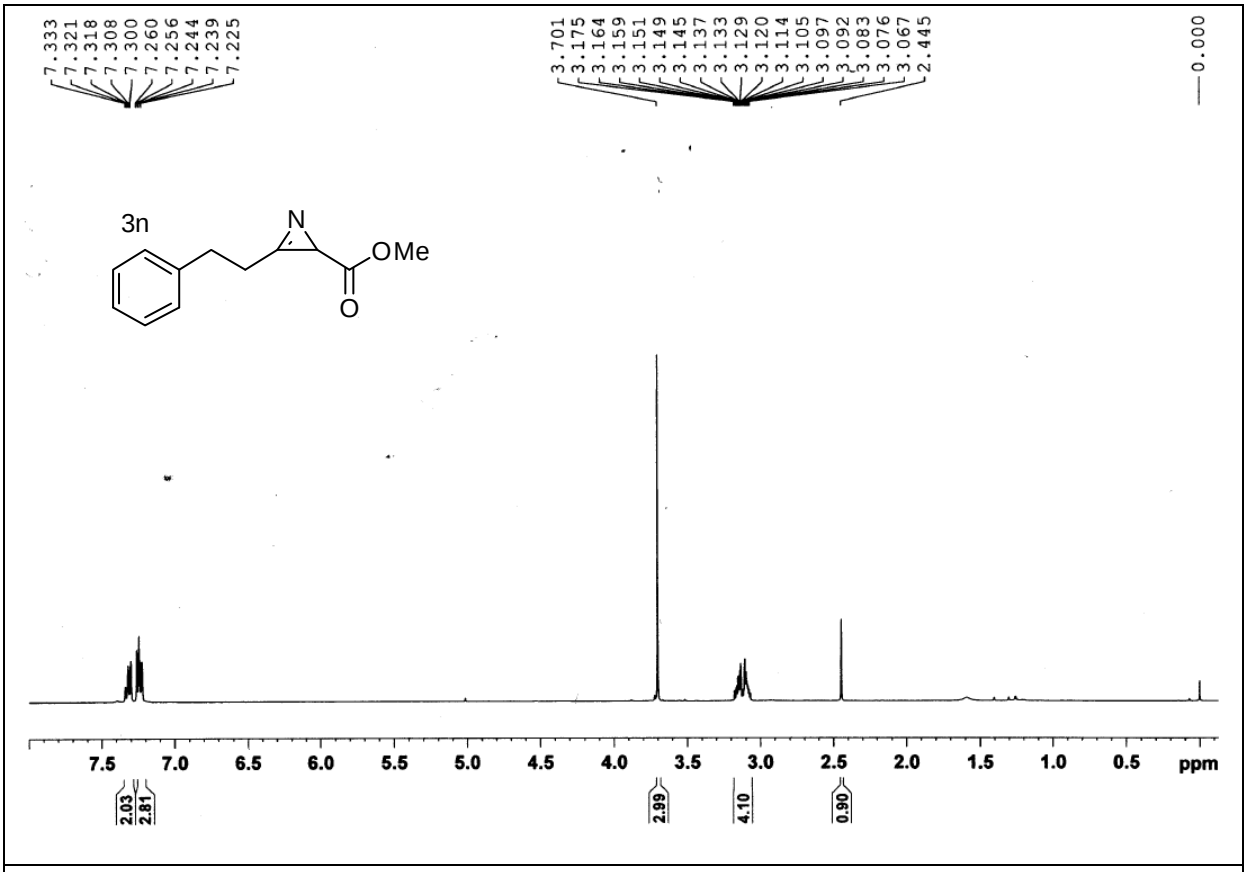
7.303
7.293
7.276
7.260
7.247
7.244
7.241
7.228
7.205
7.115
7.104
7.100
7.093
7.084
3.903
3.865
3.692
3.613
3.575
3.452
1.552
1.413
1.312
1.252
-0.002
Me
O
N
Me
O
Me
Cl
O
2m
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.49
2.53
1.03
1.07
3.00
1.10
1.00
3.00
3.02


168.35
155.16
137.34
134.66
130.08
129.13
127.46
127.13
86.76
77.31
77.00
76.68
62.28
52.34
33.51
28.05
22.39
200
150
100
50
[ppm]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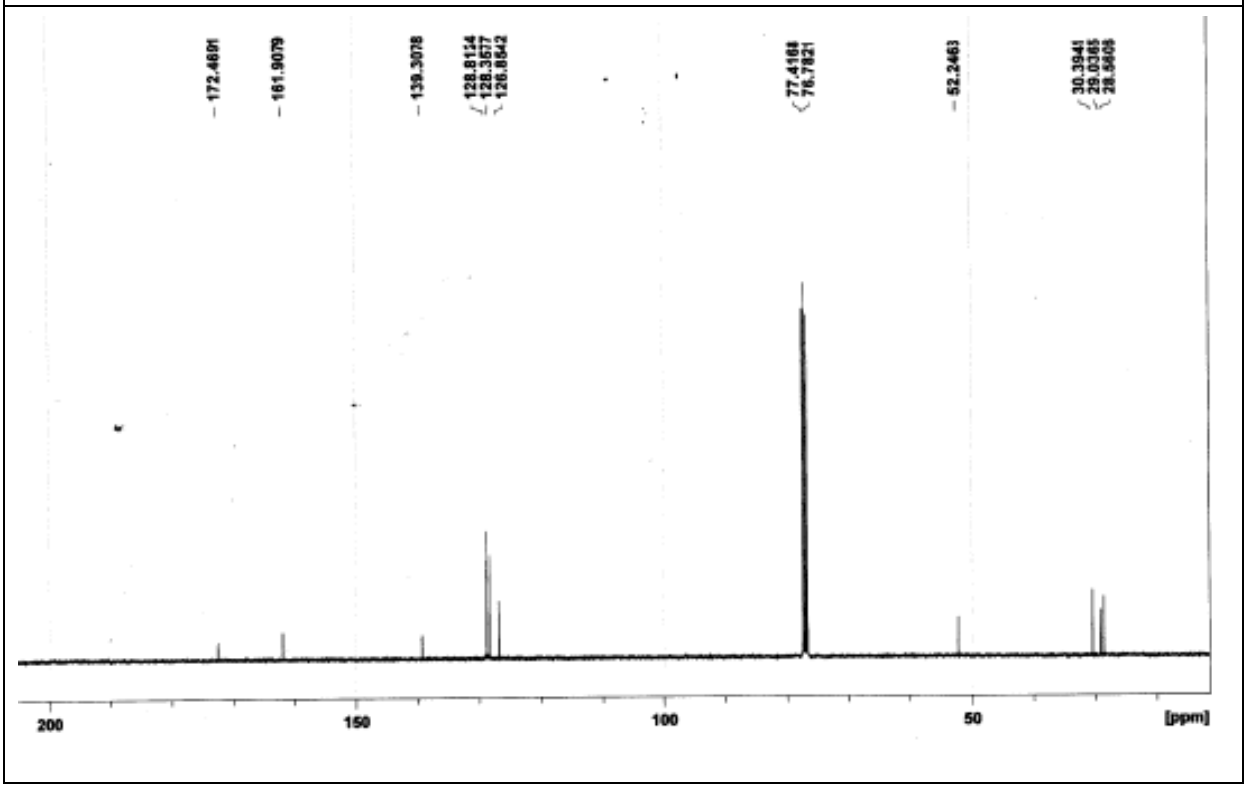
7.321
7.318
7.308
7.300
7.260
7.256
7.244
7.239
7.225
3.701
3.175
3.164
3.159
3.151
3.149
3.145
3.137
3.133
3.129
3.120
3.114
3.105
3.097
3.092
3.083
3.076
3.067
2.445
0.000
3n
N
OMe
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
2.81
2.99
4.10
0.90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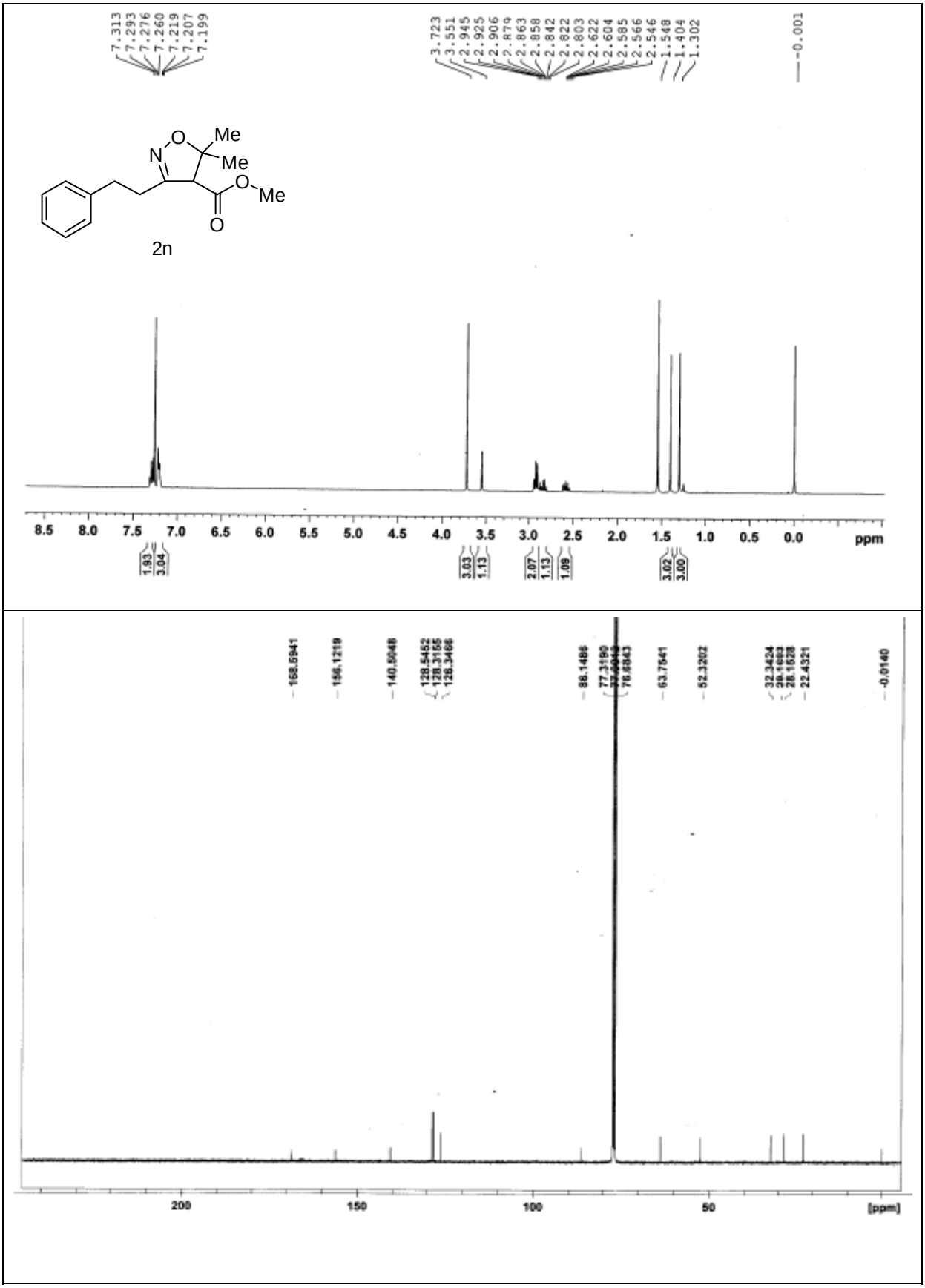
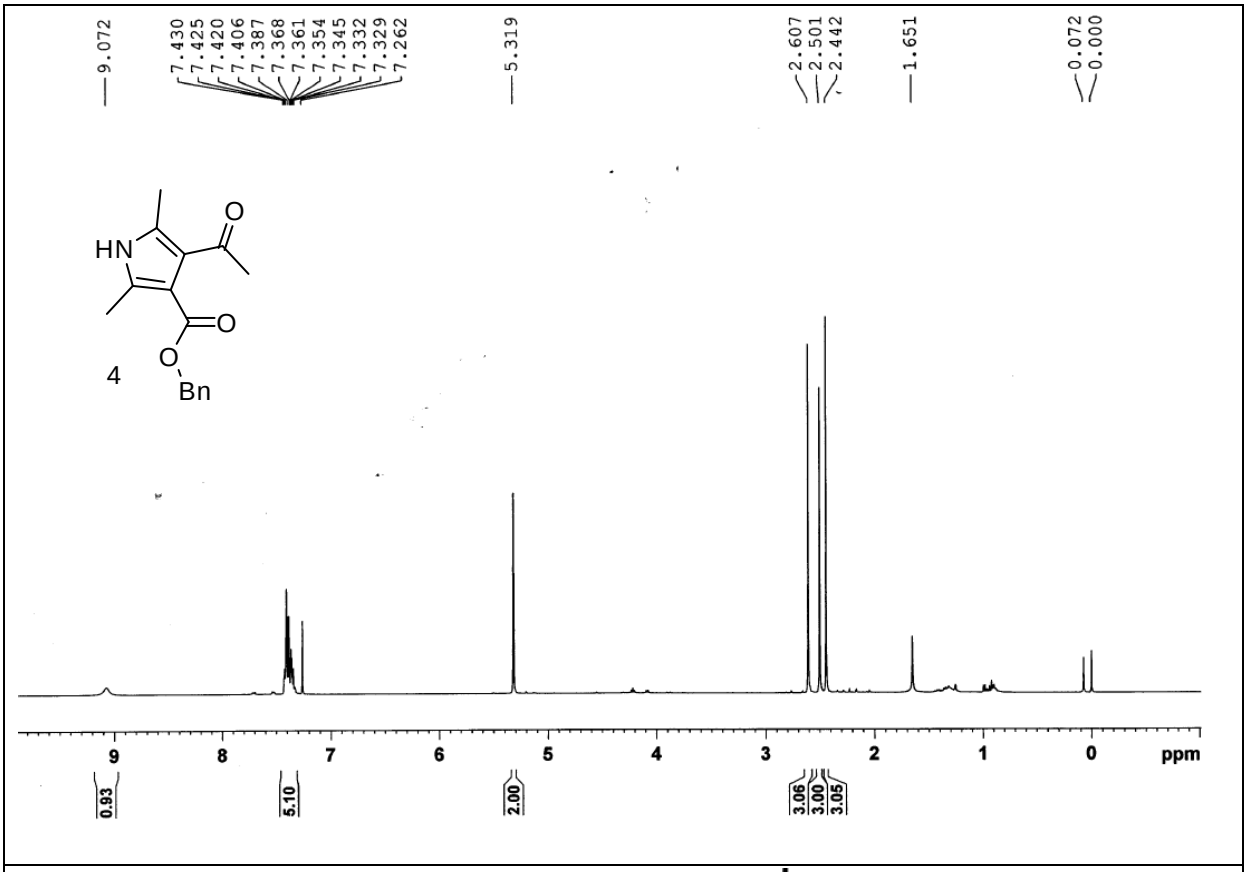
139.3078
128.8124
128.3677
126.8542
77.4168
76.7821
52.2463
30.3941
29.0385
28.5408
200
150
100
50
[ppm]


7.313
7.293
7.276
7.260
7.219
7.207
7.199
3.723
3.551
2.945
2.925
2.906
2.879
2.863
2.858
2.842
2.822
2.803
2.622
2.604
2.585
2.566
2.546
1.548
1.404
1.302
-0.001
Me
Me
O
N
O
Me
O
2n
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
1.93
3.04
3.03
1.13
2.07
1.13
1.09
3.02
3.00
168.5941
156.1219
140.6048
128.5452
128.3155
126.3466
86.1486
77.3190
76.6843
63.7641
52.3202
32.3424
28.1628
22.4321
-0.0140
200 150 100 50 [ppm]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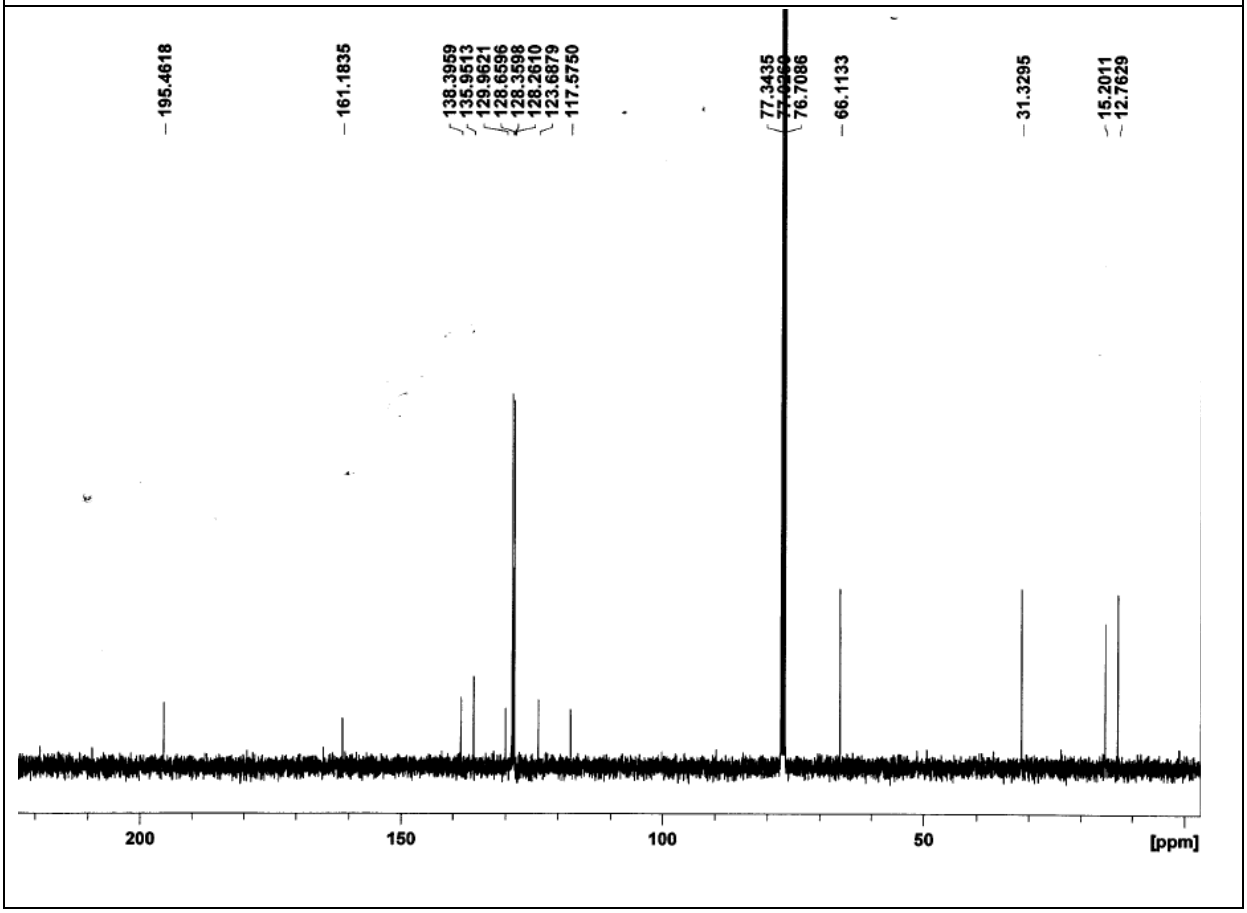
7.425
7.420
7.406
7.387
7.368
7.361
7.354
7.345
7.332
7.329
7.262
5.319
2.607
2.501
2.442
1.651
0.072
0.000
HN
O
O
O
4
Bn
9
8
7
6
5
4
3
2
1
0
ppm
0.93
5.10
2.00
3.06
3.00
3.05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135.9513
129.9621
128.6596
128.3598
128.2610
123.6879
117.5750
77.3435
76.7086
66.1133
31.3295
15.2011
12.7629
200
150
100
50
[ppm]