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Arylhydrazones of α-keto esters *via* methanolysis of dichlorodiazabutadienes: synthesis and structural study

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General remarks.

Unless stated otherwise, all the reagents used in this study were obtained from the commercial sources (Aldrich, TCI-Europe, Strem, ABCR). NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300 MHz); chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 53.84 ppm; residual $CHDCl_2$ in CD_2Cl_2: δ_H = 5.32 ppm); ^{1}H and ^{13}C assignments were established using NOESY, HSQC and HMBC experiments; numbering schemes as shown in the Inserts. IR: Perkin-Elmer Spectrum One spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNS/O analyzer. Mass-spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source; MeOH, CH_2Cl_2 or MeOH/CH_2Cl_2 mixture was used as a solvent. Thermogravimetric analysis (TGA) and differential thermal analysis were determined using a Netzsch TG 209F1 Libra apparatus. Solvents were purified by distillation over the indicated drying agents and were transferred under Ar: Et_2O (Mg/anthracene), CH_2Cl_2 (CaH_2), hexane (Na/K). Flash chromatography: Merck Geduran® Si 60 (40–63 μm).

Computational details. The full geometry optimization of model structure *Z*-**2a** based on the appropriate experimental X-ray geometry as a starting point have been carried out with the help of the ORCA 4.2.1 program package [S1]. The ground multiplicity state of the model system is the singlet, and spin-restricted approximation (closed electron shell) was applied. Symmetry operations were not applied during the geometry optimization procedure for greater freedom of variation of geometric parameters. The convergence tolerances for the geometry optimization procedure were: energy change = 5.0×10^{-6} Eh, maximal gradient = 3.0×10^{-4} Eh/Bohr, RMS gradient = 1.0×10^{-4} Eh/Bohr, maximal displacement = 4.0×10^{-3} Bohr, and RMS displacement = 2.0×10^{-3} Bohr. The Hessian matrix was calculated for the optimized model structure in order to prove the location of correct minimum on the potential energy surface (no imaginary frequencies were found). The topological analysis of the electron density distribution with the help of the QTAIM method was performed by using the Multiwfn program (version 3.7) [S2]. The VMD program [S3] was used for visualization of non-

covalent interactions in 3D using NCI analysis technique [S4]. The Cartesian atomic coordinates for the optimized equilibrium geometry of model structure *Z*-**2a** are presented in Table S1.

Table S1 Cartesian atomic coordinates for the optimized equilibrium geometry of model structure *Z*-**2a**.

Atom	X	Y	Z
O	0.93986932165597	6.96842333281888	3.46385764581195
O	-0.04405449792026	5.86499587836067	1.76346404512756
N	2.90124038951362	4.90258832680511	3.55678875486536
N	3.16039561850036	5.90623443758132	4.35313682923079
H	2.50268592704668	6.68634933208871	4.37700854357925
C	0.89139239403085	5.98555749269295	2.72542752145458
C	1.84851009325873	4.87388034759281	2.77395717651270
C	1.73428595799713	3.68114296652033	1.91242783533310
C	0.51938369264650	3.02527040396100	1.70177155553538
H	-0.38383481891696	3.40925181674003	2.15258953576907
C	0.46095673865783	1.87501641144420	0.93170153384497
H	-0.48850302890721	1.37544396634116	0.78874720737366
C	1.61131389400180	1.35691251845994	0.35336281033673
H	1.56221914340088	0.45966134765691	-0.24957803781194
C	2.82480841001276	1.99999044926331	0.55513475169419
H	3.72792866530302	1.60918335062508	0.10461887919442
C	2.88533526910474	3.14813836389543	1.32660629331760
H	3.83042353159157	3.64879196414262	1.48328072261562
C	-0.98247564728087	6.94782662709259	1.67246967183781
H	-1.64974131201590	6.68385266339956	0.85971302039977
H	-0.47191047140548	7.88315479018722	1.45631487185997
H	-1.53783477129704	7.05465810550828	2.60151699111878
C	4.27479694753005	5.90156700671666	5.18824490226186
C	5.13512318537018	4.80677481473232	5.27070532261023
H	4.93248371561462	3.93250046588239	4.67124918264152
C	6.22352156594060	4.86033513062950	6.12330641053942
H	6.88424823750148	4.00614533604461	6.18869787519237
C	6.47026648025631	5.98795595173798	6.89755103479671
H	7.32430323770774	6.01933178620331	7.55975496843902
C	5.60950614061449	7.07398676841261	6.81167385880958
H	5.78888577253961	7.95894332513017	7.40767356168015
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H	3.85130897278695	7.88808743147866	5.89370258143479

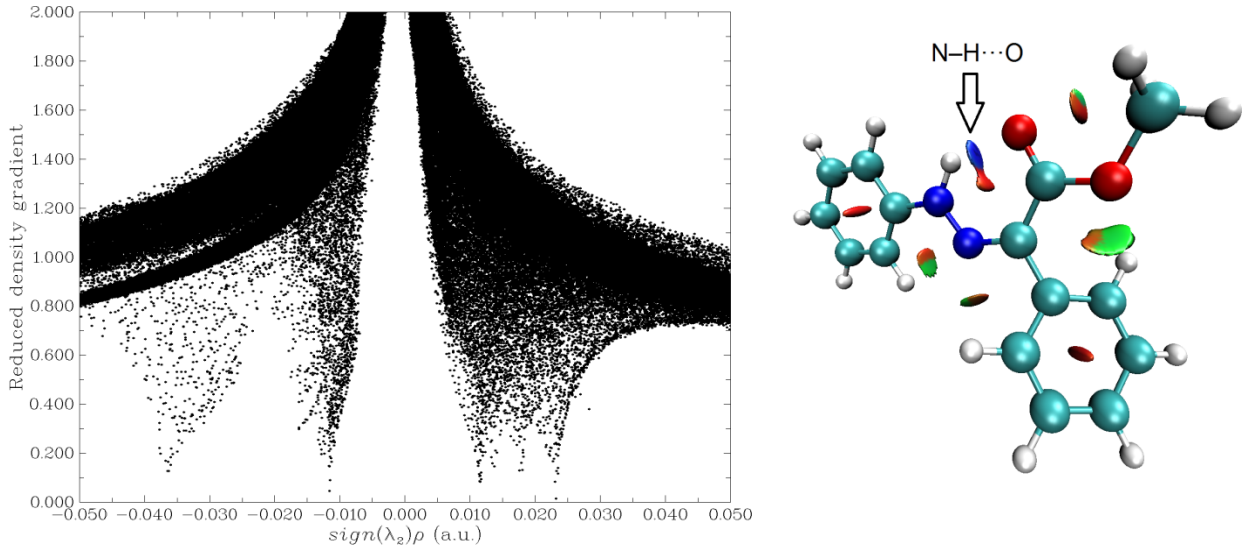
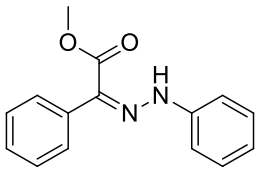


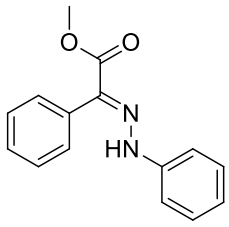
Figure S1 NCI plot for the optimized equilibrium model structure *Z*-**2a** and visualization of intramolecular hydrogen bonding N–H···O in 3D using NCI analysis technique.

Synthetic part.

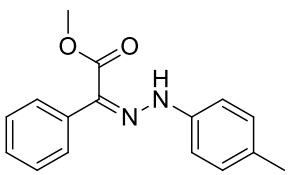
The corresponding dichlorodiazabutadiene (10 mg) was dissolved in aqueous MeOH (30 ml) and stirred for 2 hours. The reaction mixture was evaporated to dryness and purified by column chromatography on silica gel using a mixture of hexane and dichloromethane.



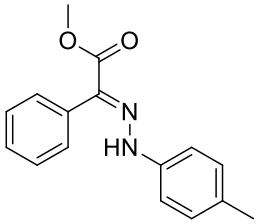
Methyl (*Z*)-2-phenyl-2-(2-phenylhydrazono)acetate *Z*-**2a**, yellow solid (30%), mp 125 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.47 (s, 1H, NH), 7.71 (s, 2H, arom), 7.48–7.30 (m, 7H, arom), 7.06 (t, J = 6.7 Hz, 1H, arom), 3.91 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 138.5, 131.8, 124.8, 124.1, 123.9, 123.3, 123.0, 118.0, 109.7, 47.2.



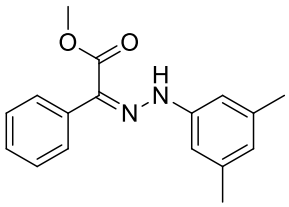
Methyl (*E*)-2-phenyl-2-(2-phenylhydrazono)acetate *E*-**2a**, yellow solid (35%), mp 95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H, NH), 7.64–7.45 (m, 3H, arom), 7.42–7.18 (m, 4H, arom), 7.16 (d, J = 8.6 Hz, 2H, arom),7.05–6.93 (m, 1H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 142.5, 134.1, 129.7, 129.7, 129.5, 129.3, 129.0, 122.3, 114.1, 52.4.



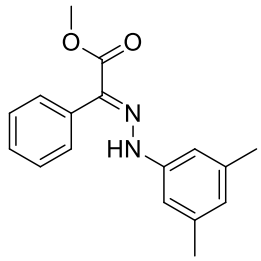
Methyl (*Z*)-2-phenyl-2-(2-(p-tolyl)hydrazono)acetate *Z*-**2b**, yellow solid (41%), mp 112 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 1H, NH), 7.55 (dt, J = 10.6, 5.7 Hz, 3H, arom), 7.36 (d, J = 6.7 Hz, 2H, arom), 7.08 (q, J = 8.5 Hz, 4H, arom), 3.88 (s, 3H, CH_3), 2.31 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 135.6, 128.8, 127.2, 125.2, 125.2, 125.0, 124.9, 124.5, 109.4, 47.7, 16.1.



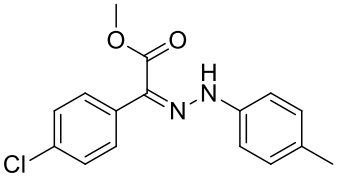
Methyl (*E*)-2-phenyl-2-(2-(*p*-tolyl)hydrazono)acetate *E*-**2b**, yellow solid (33%), mp 104 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.45 (s, 1H, NH), 7.72–7.62 (m, 2H, arom), 7.48–7.25 (m, 3H, arom), 7.31–7.11 (m, 4H, arom), 3.90 (d, J = 1.0 Hz, 3H, CH_3), 2.35 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 136.2, 127.5, 125.3, 124.0, 123.3, 122.9, 109.6, 47.1, 16.2.



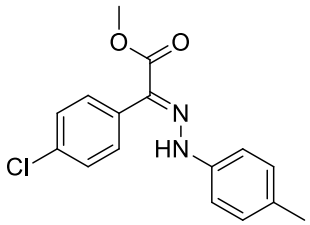
Methyl (*Z*)-2-(2-(3,5-dimethylphenyl)hydrazono)-2-phenylacetate *Z*-**2c**, yellow solid (35%), mp 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.48 (s, 1H), 7.74 (d, J = 7.9 Hz, 2H), 7.46 (dt, J = 12.3, 7.0 Hz, 3H), 7.01 (s, 2H), 6.75 (s, 1H), 3.93 (s, 3H), 2.40 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 138.5, 134.5, 132.0, 124.2, 123.3, 123.0, 122.7, 120.0, 107.6, 47.1, 16.9.



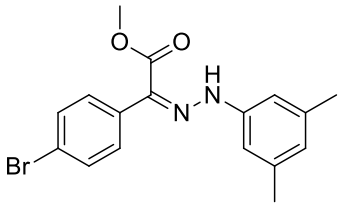
Methyl (*E*)-2-(2-(3,5-dimethylphenyl)hydrazono)-2-phenylacetate *E*-**2c**, yellow solid (45%), mp 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.54 (dt, J = 12.6, 6.9 Hz, 4H), 7.35 (d, J = 7.8 Hz, 2H), 6.78 (s, 2H), 6.64 (s, 1H), 3.89 (s, 3H), 2.29 (s, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 157.7, 137.8, 134.5, 129.1, 126.7, 125.2, 125.0, 124.9, 124.4, 119.6, 107.3, 47.8, 16.7.



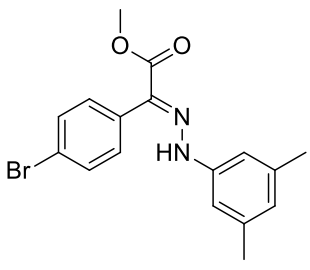
Methyl (*Z*)-2-(4-chlorophenyl)-2-(2-(p-tolyl)hydrazono)acetate *Z*-**2d**, yellow solid (32%), mp 101 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.50 (s, 1H, NH), 7.62 (d, J = 8.5 Hz, 2H, arom), 7.39 (s, 2H,arom), 7.24 – 7.13 (m, 4H, arom), 3.90 (s, 3H, OCH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.4, 163.9, 140.6, 135.04, 133.3, 132.4, 129.8, 128.0, 125.6, 114.3, 51.7, 20.8.



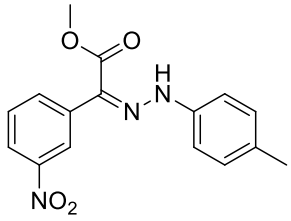
Methyl (*E*)-2-(4-chlorophenyl)-2-(2-(p-tolyl)hydrazono)acetate *E*-**2d**, yellow solid (39%), mp 86 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H,NH), 7.57 (dd, J = 18.3, 8.5 Hz, 2H, arom), 7.33 (dd, J = 15.6, 8.5 Hz, 2H, arom), 7.22–7.04 (m, 4H, arom), 3.88 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 135.7, 132.4, 132.1, 130.6, 129.8, 128.1, 128.0, 114.3, 114.1, 52.4, 20.7.



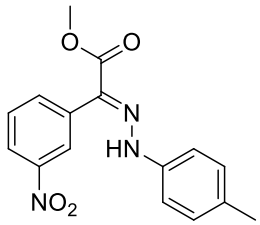
Methyl (*Z*)-2-(4-bromophenyl)-2-(2-(3,5-dimethylphenyl)hydrazono)acetate *Z*-**2e**, yellow solid (37%), mp 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.44 (s, 1H, NH), 7.54 (s, 4H, arom), 6.93 (s, 2H, arom), 6.71 (s, 1H, arom), 3.89 (s, 3H, OCH_3), 2.34 (s, 6H, CH_3,). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 142.8, 139.2, 135.4, 131.0, 130.2, 126.0, 124.8, 121.6, 112.2, 51.8, 21.4.



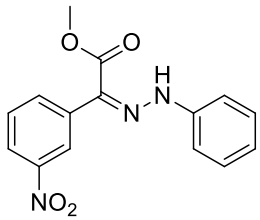
Methyl (*E*)-2-(4-bromophenyl)-2-(2-(3,5-dimethylphenyl)hydrazono)acetate *E*-**2e**. yellow solid (43%), mp 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H, NH), 7.70 (d, J = 8.3 Hz, 2H,arom), 7.23 (d, J = 8.3 Hz, 2H,arom), 6.80 (s, 2H,arom), 6.66 (s, 1H,arom), 3.89 (s, 3H, OCH_3), 2.30 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 139.2, 132.8, 132.3, 130.8, 130.2, 128.6, 124.5, 124.0, 111.9, 52.4, 21.3.



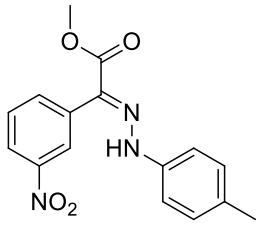
Methyl (*Z*)-2-(3-nitrophenyl)-2-(2-(p-tolyl)hydrazono)acetate *Z*-**2f**, yellow solid (32%), mp 102 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.64 (s, 1H, NH), 8.56 (s, 1H, arom), 8.17 (d, J = 8.0 Hz, 1H, arom), 8.02 (d, J = 7.5 Hz, 1H, arom), 7.54 (t, J = 8.0 Hz, 1H, arom), 7.20 (q, J = 8.5 Hz, 4H, arom), 3.93 (s, 3H, OCH_3), 2.35 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 156.2, 148.0, 138.2, 136.3, 134.1, 128.6, 123.6, 123.2, 121.7, 115.8, 114.8, 55.6, 51.9.



Methyl (*E*)-2-(3-nitrophenyl)-2-(2-(p-tolyl)hydrazono)acetate *E*-**2f**, yellow solid (35%), mp 80 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, J = 8.0 Hz, 1H, NH), 8.25 (s, 1H, arom), 8.03 (s, 1H, arom), 7.73 (dd, J = 14.5, 7.2 Hz, 2H, arom), 7.10 (q, J = 8.4 Hz, 4H, arom), 3.89 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 143.3, 139.7, 135.5, 132.6, 131.6, 130.6, 129.9, 124.4, 114.6, 114.3, 100.7, 52.5, 20.7.



Methyl (*Z*)-2-(3-nitrophenyl)-2-(2-phenylhydrazono)acetate *Z*-**2g**, yellow solid (37%), mp 131 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.63 (s, 1H, NH), 8.56 (s, 1H, arom), 8.17 (d, J = 8.1 Hz, 1H, arom), 8.02 (d, J = 7.8 Hz, 1H, arom), 7.54 (t, J = 8.0 Hz, 1H, arom), 7.39–7.31 (m, 4H, arom), 7.08 (t, J = 7.0 Hz, 1H, arom), 3.94 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 162.3, 148.0, 142.5, 138.0, 134.2, 129.5, 128.7, 124.9, 123.4, 122.0, 114.6, 52.0.



Methyl (*E*)-2-(3-nitrophenyl)-2-(2-phenylhydrazono)acetate *E*-**2g**, yellow solid (43%), mp 159 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, J = 7.1 Hz, 1H, arom), 8.25 (s, 1H, NH), 8.08 (s, 1H, arom), 7.75 (dt, J = 13.8, 7.1 Hz, 2H, arom), 7.32 (t, J = 7.3 Hz, 2H, arom), 7.18 (d, J = 8.0 Hz, 2H, arom), 7.04 (t, J = 7.2 Hz, 1H, arom), 3.90 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 142.0, 135.4, 131.5, 130.6, 129.4, 124.6, 124.5, 123.1, 114.4, 107.0, 95.4, 52.6.

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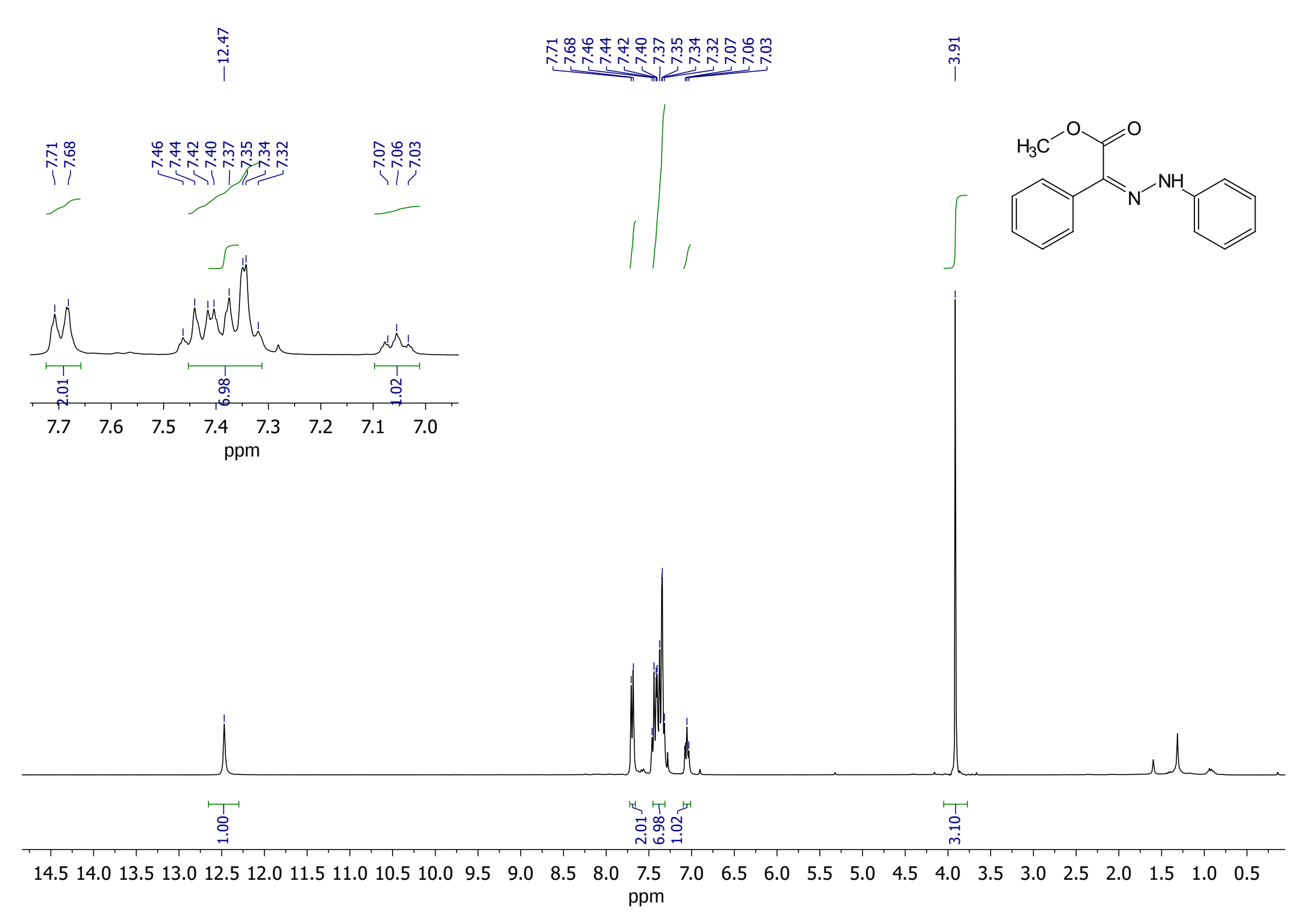
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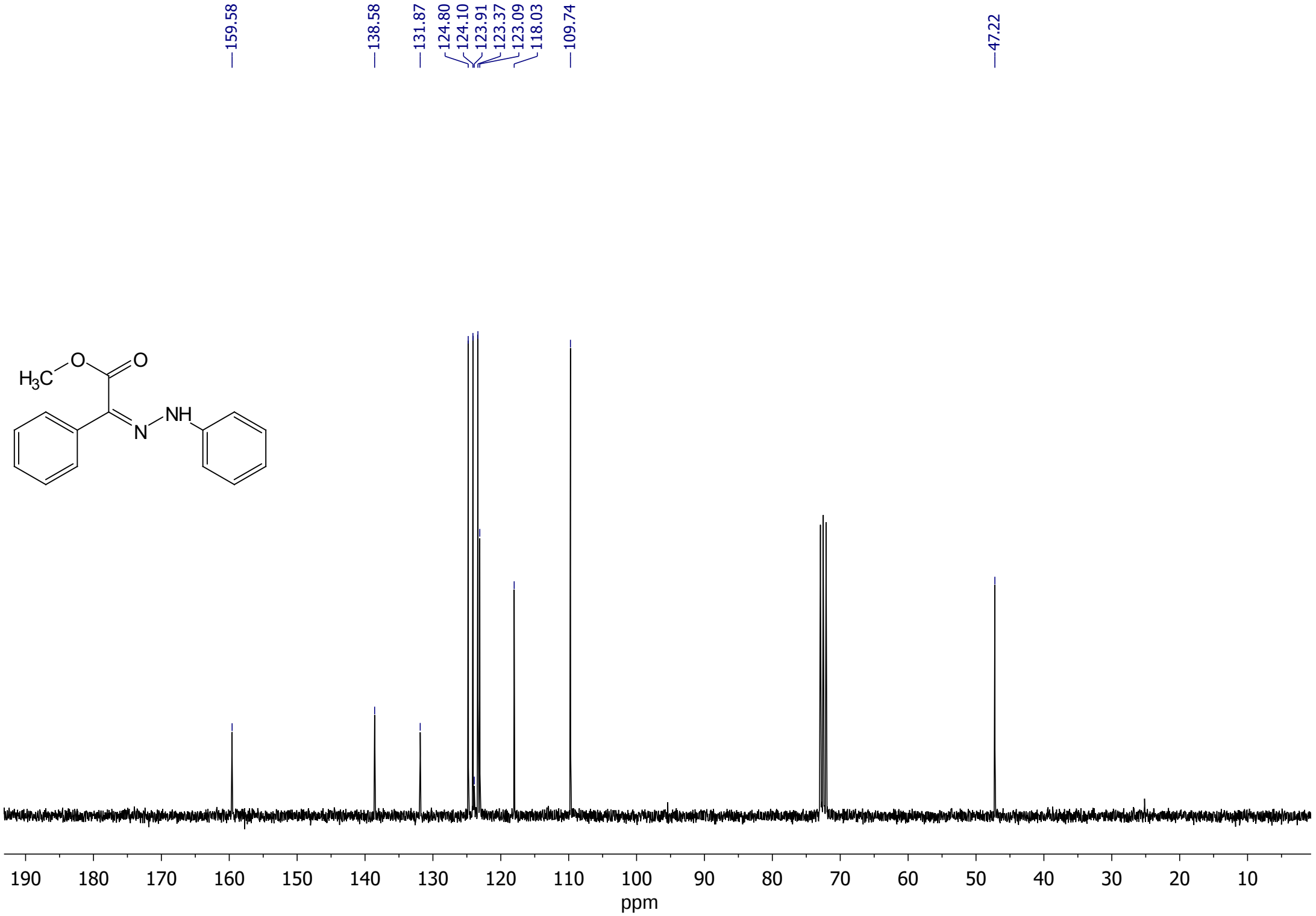
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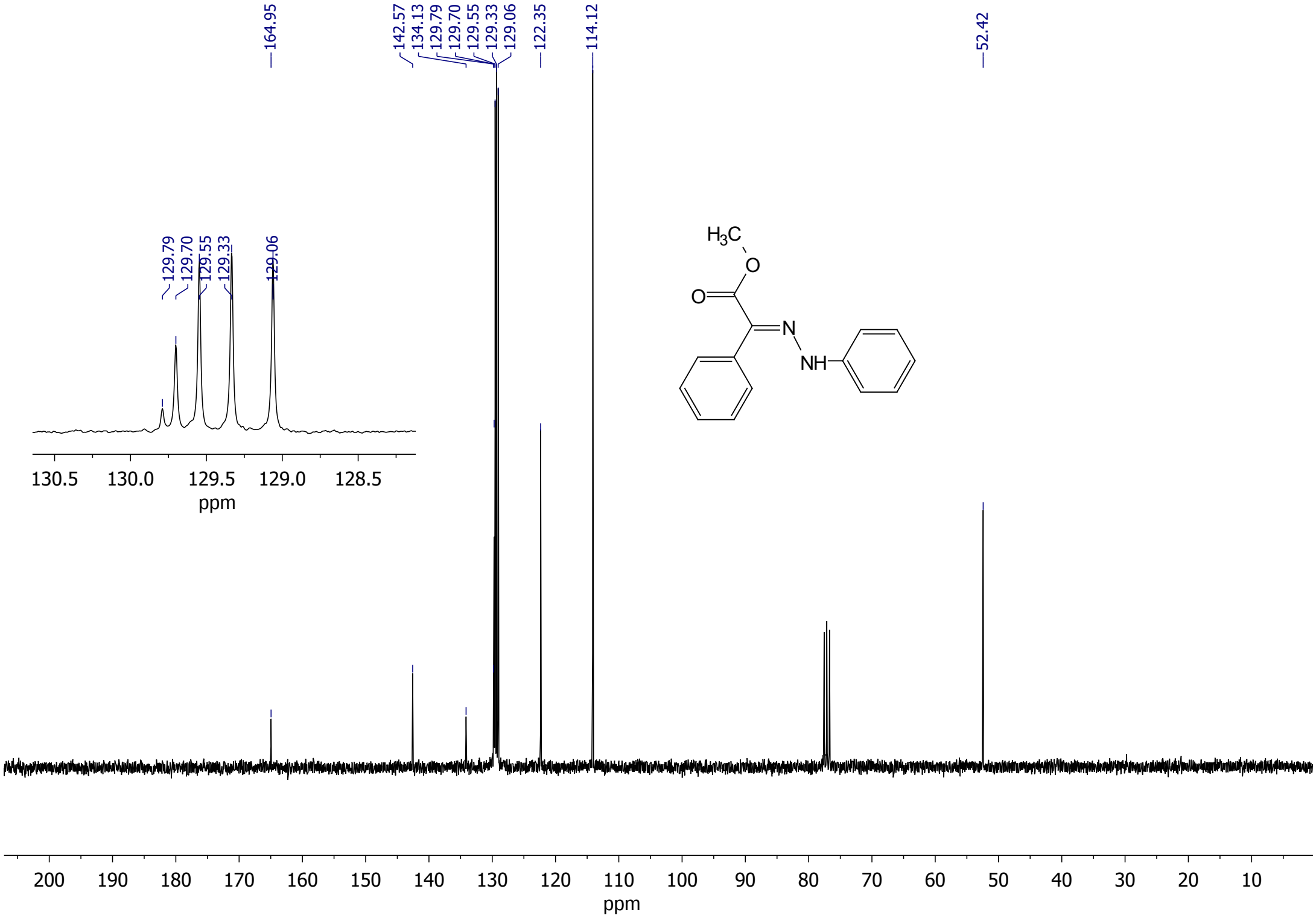
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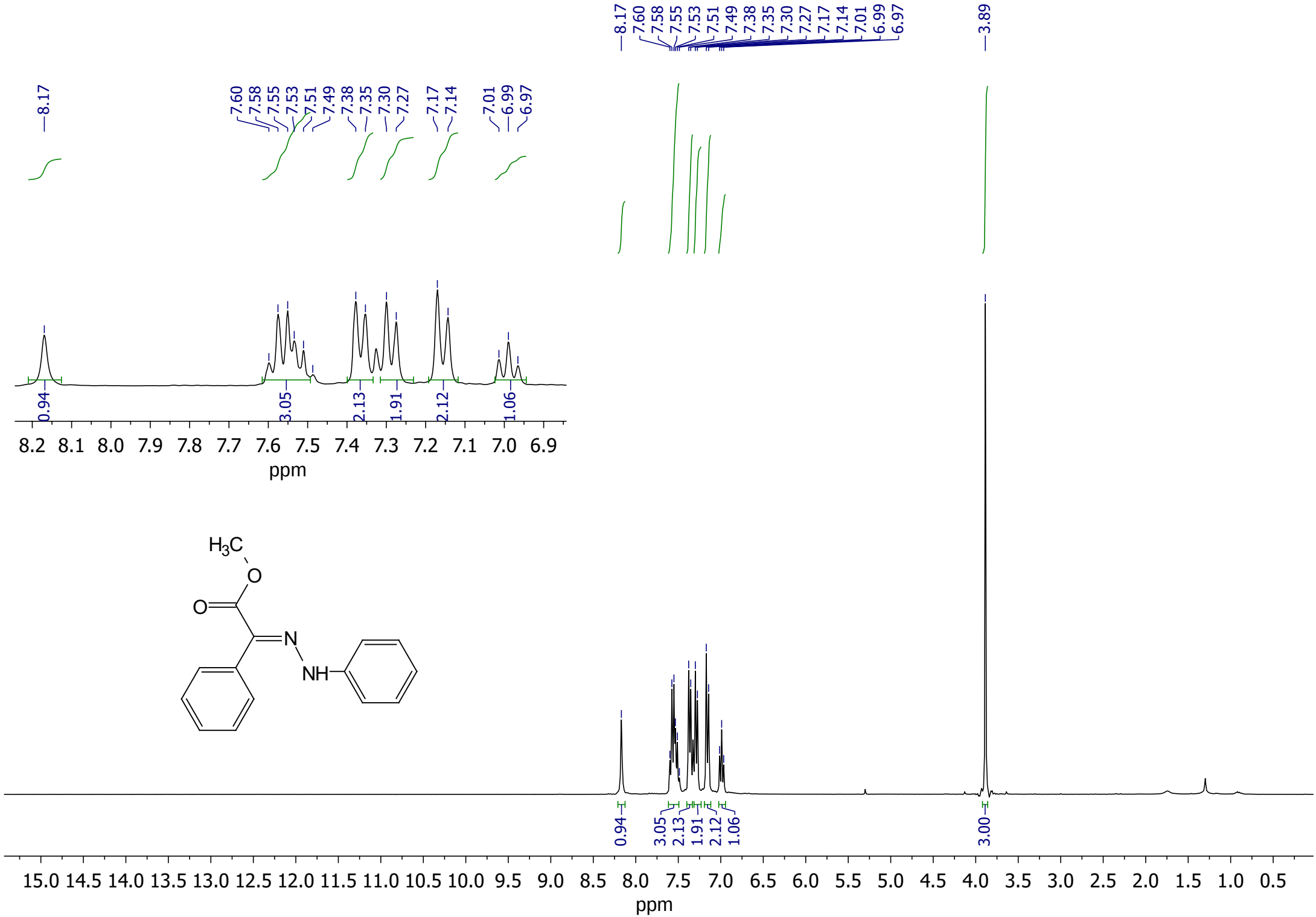
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7.27
7.17
7.14
7.01
6.99
6.97
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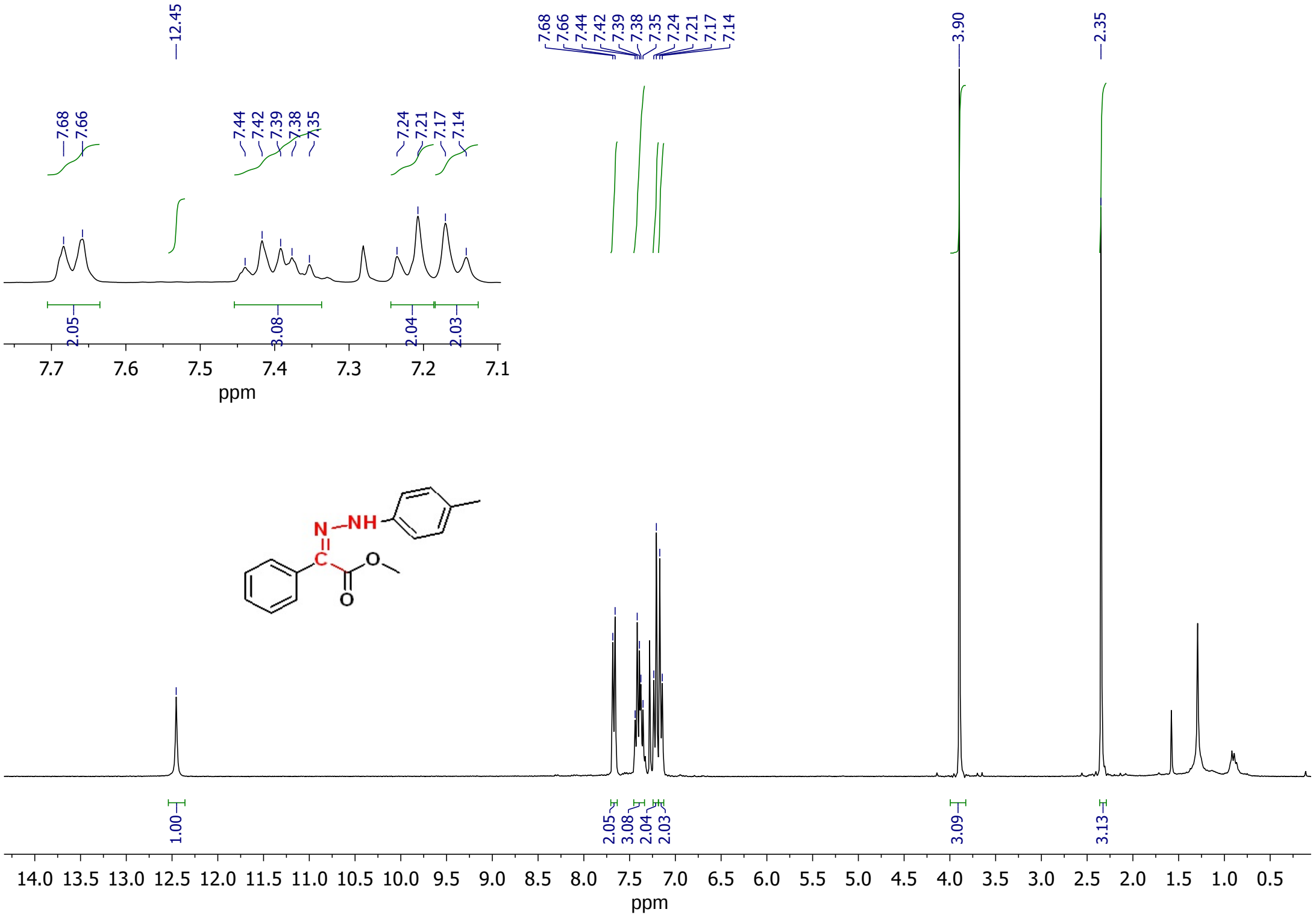
2.13
1.91
2.12
1.06
3.00
ppm
H3C
O
O
N
NH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7.35
7.24
7.21
7.17
7.14
3.90
2.35
2.05
3.08
2.04
2.03
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm
N
NH
C
O
O
1.00
2.05
3.08
2.04
2.03
3.09
3.13
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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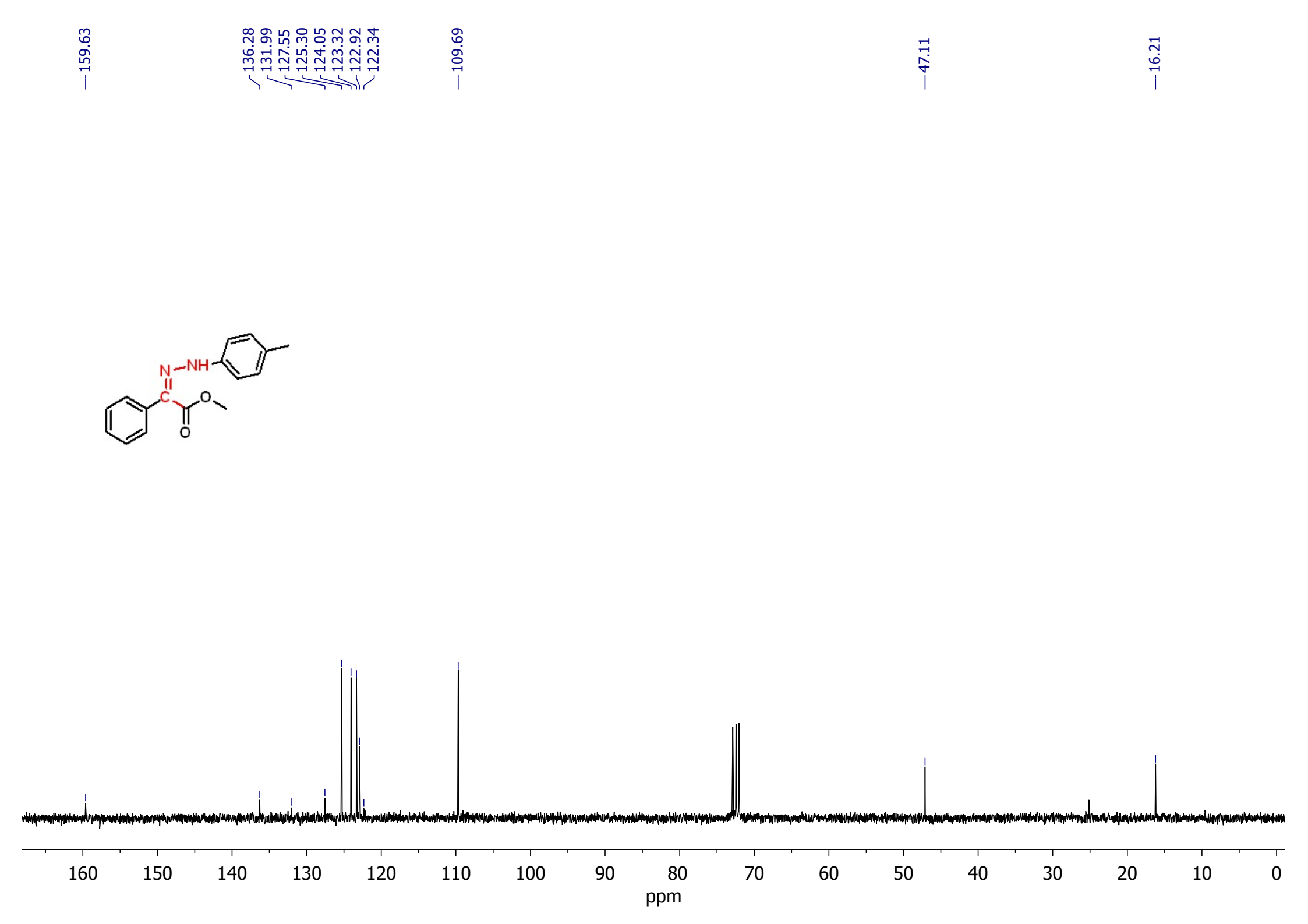
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136.28
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125.30
124.05
123.32
122.92
122.34
109.69
47.11
16.21
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NH
C
O
O
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140
130
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100
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60
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20
10
0
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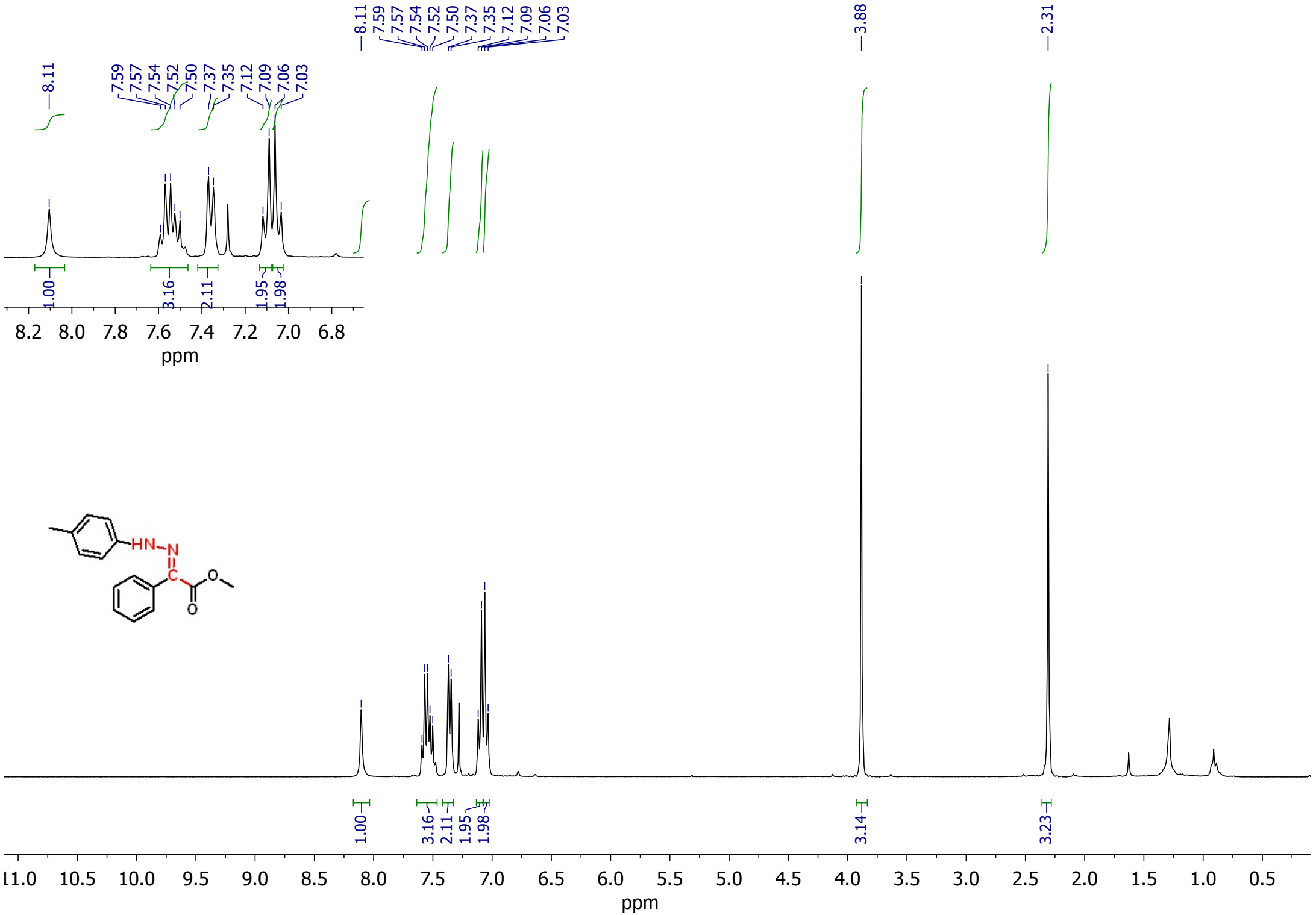
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7.37
7.35
7.12
7.09
7.06
7.03
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1.98
3.14
3.23
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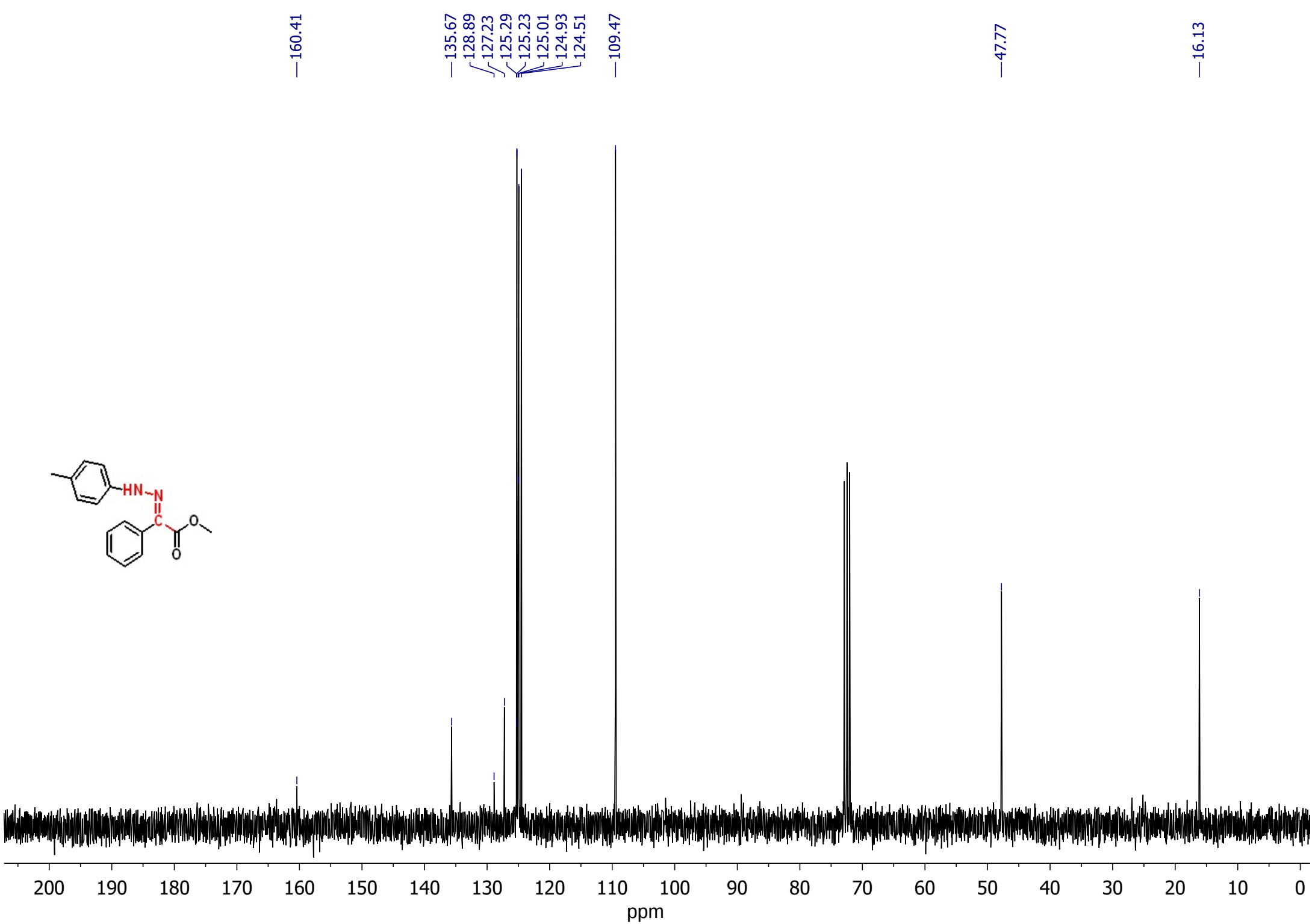
C
O
O
ppm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124.93
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N
C
O
O
200
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140
130
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60
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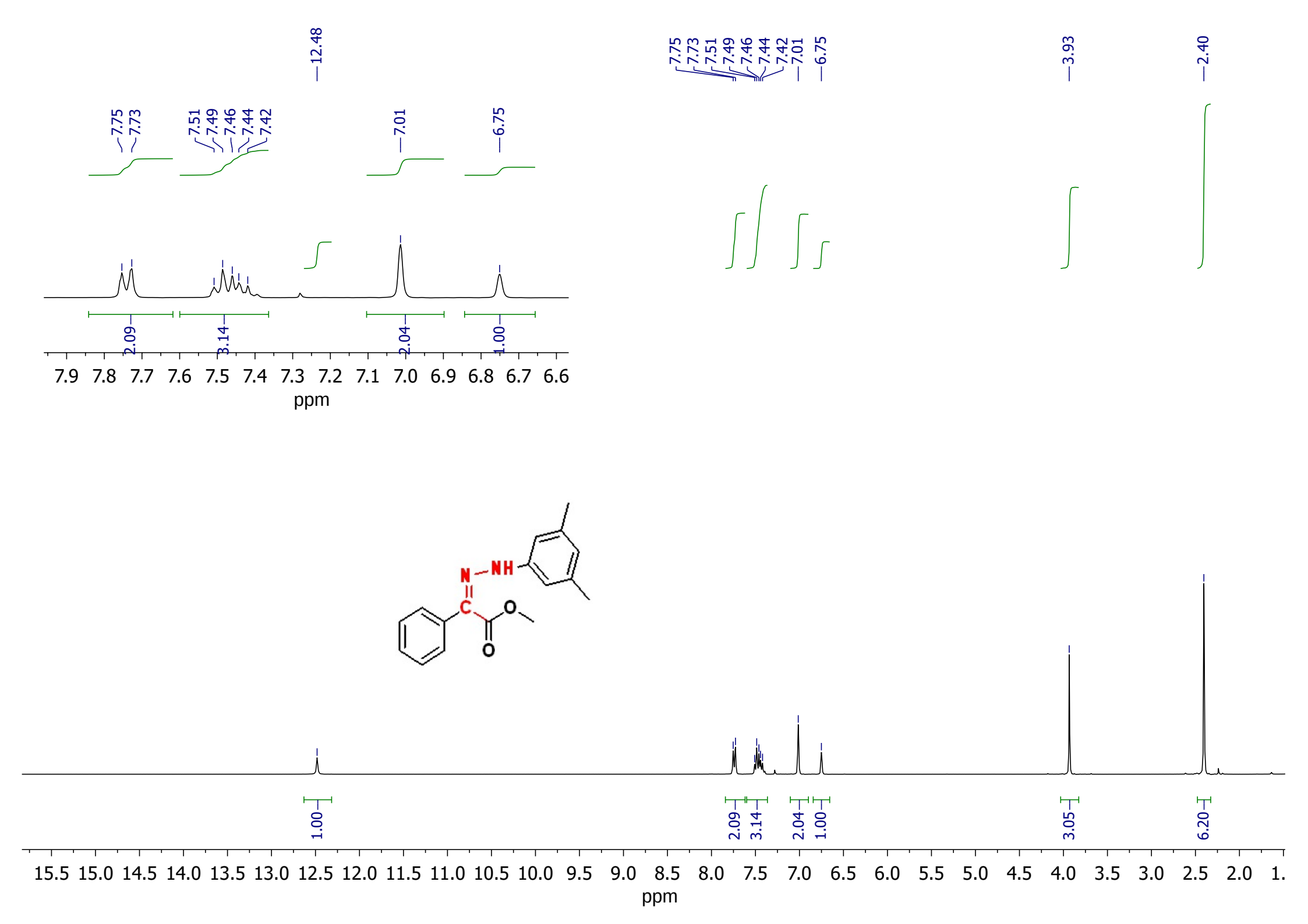
20
10
0
ppm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7.42
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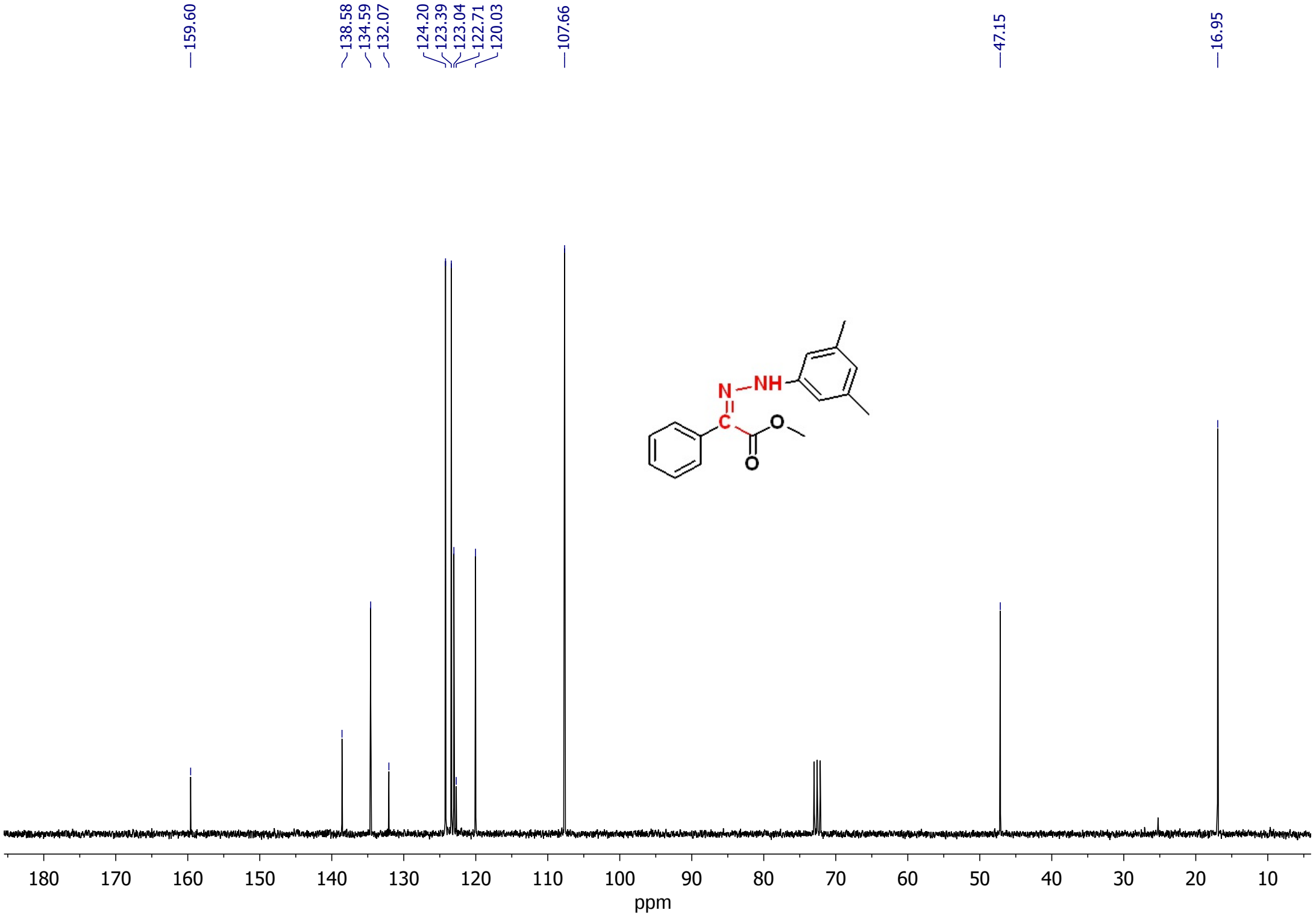
6.75
3.93
2.40
2.09
3.14
2.04
1.00
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
ppm
N
NH
C
O
O
1.00
2.09
3.14
2.04
1.00
3.05
6.20
15.5 15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.
ppm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138.58
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107.66
47.15
16.95
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NH
C
O
O
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150
140
130
120
110
100
90
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70
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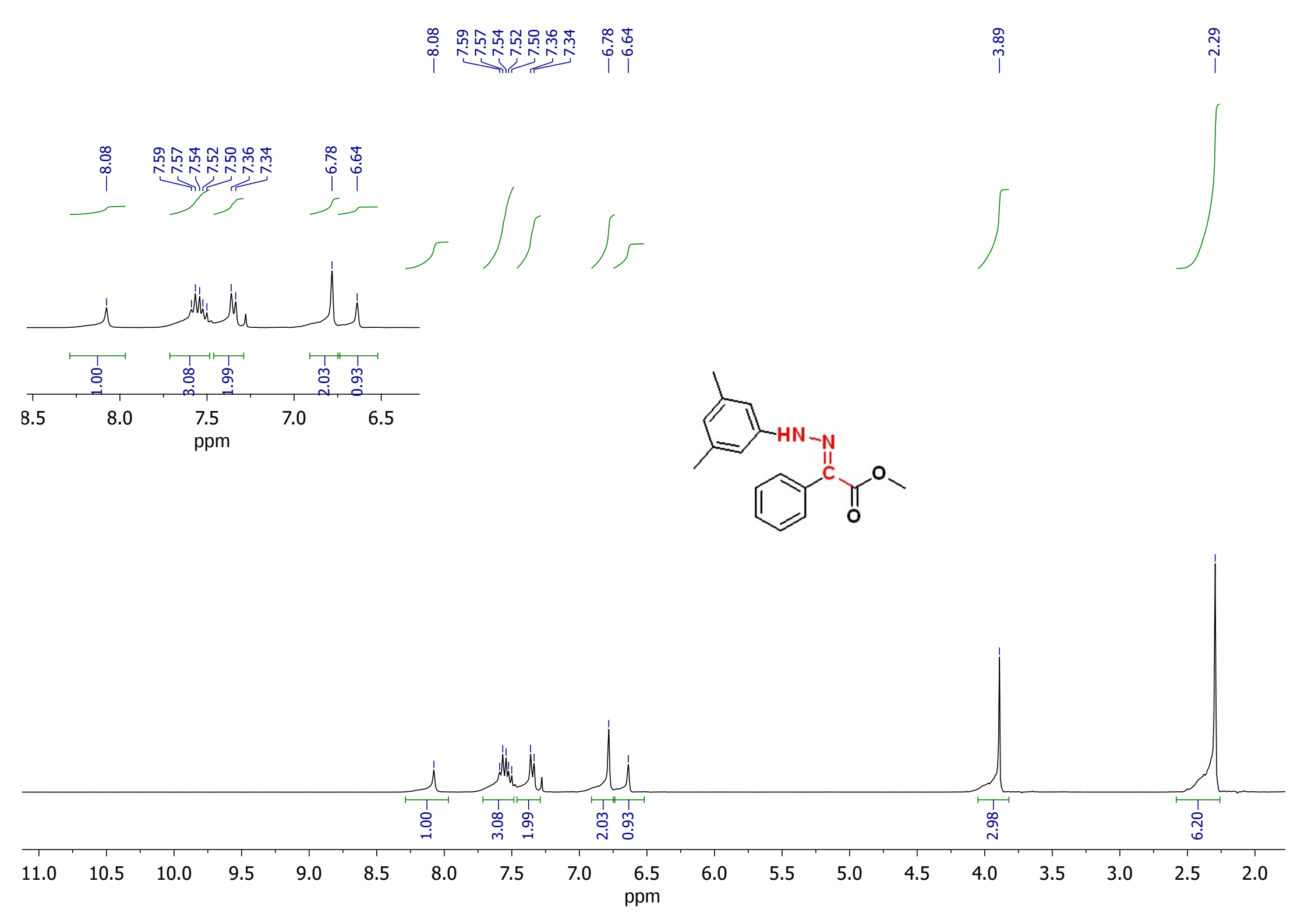
40
30
20
10
ppm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7.36
7.34
6.78
6.64
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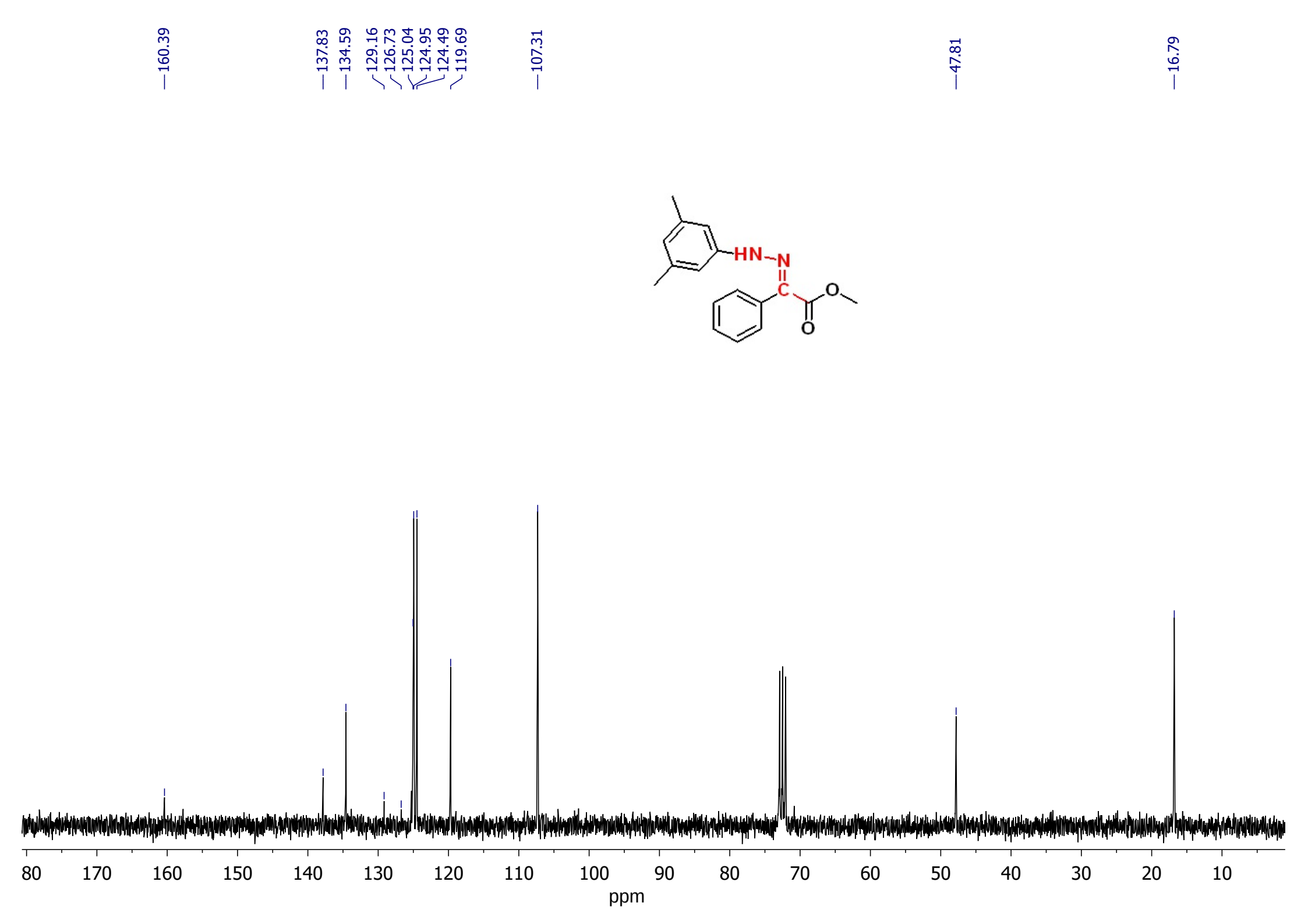
3.08
1.99
2.03
0.93
2.98
6.20
HN
N
C
O
O
ppm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137.83
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126.73
125.04
124.95
124.49
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107.31
47.81
16.79
HN
N
C
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O
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160
150
140
130
120
110
100
90
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70
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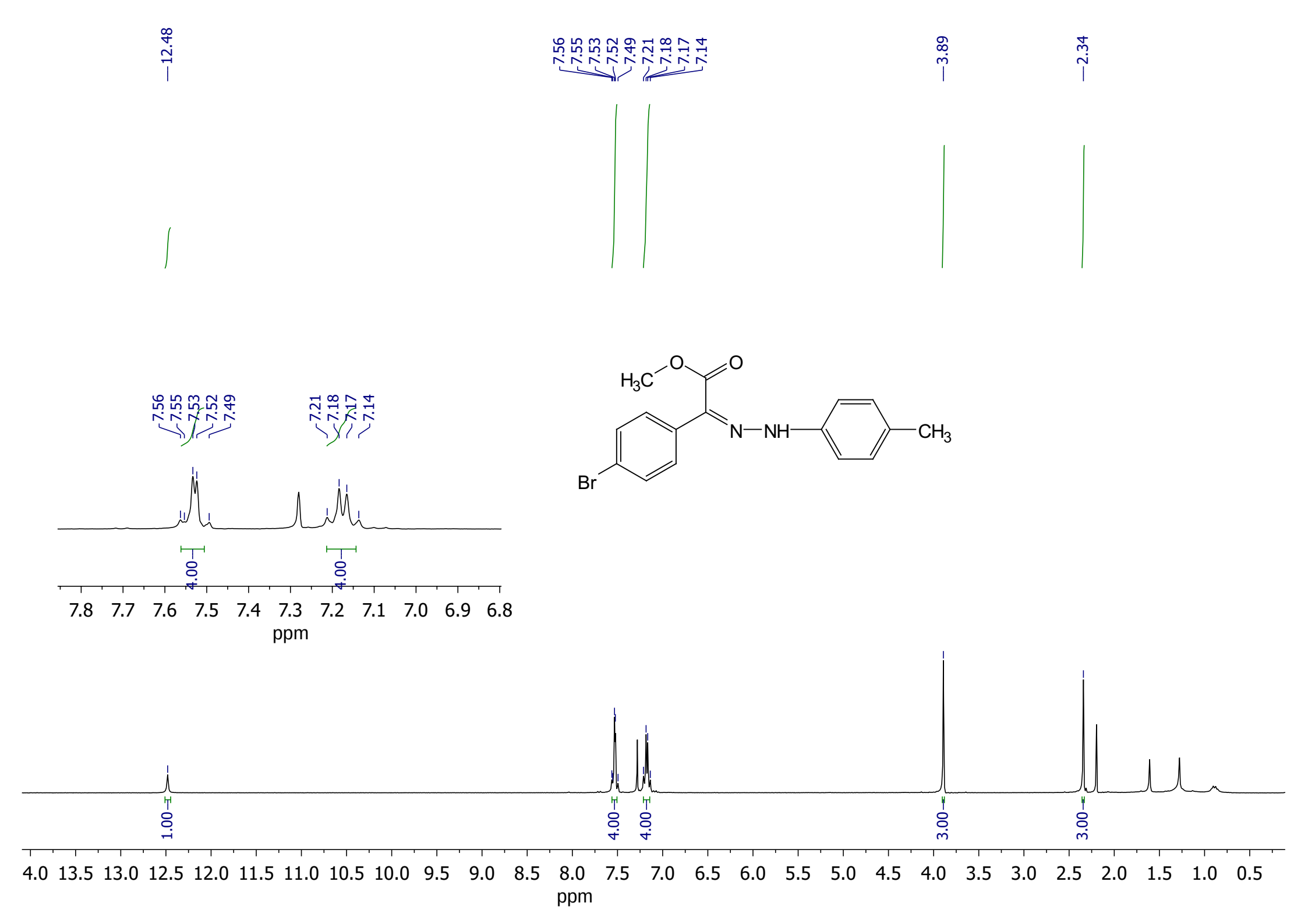
30
20
10
ppm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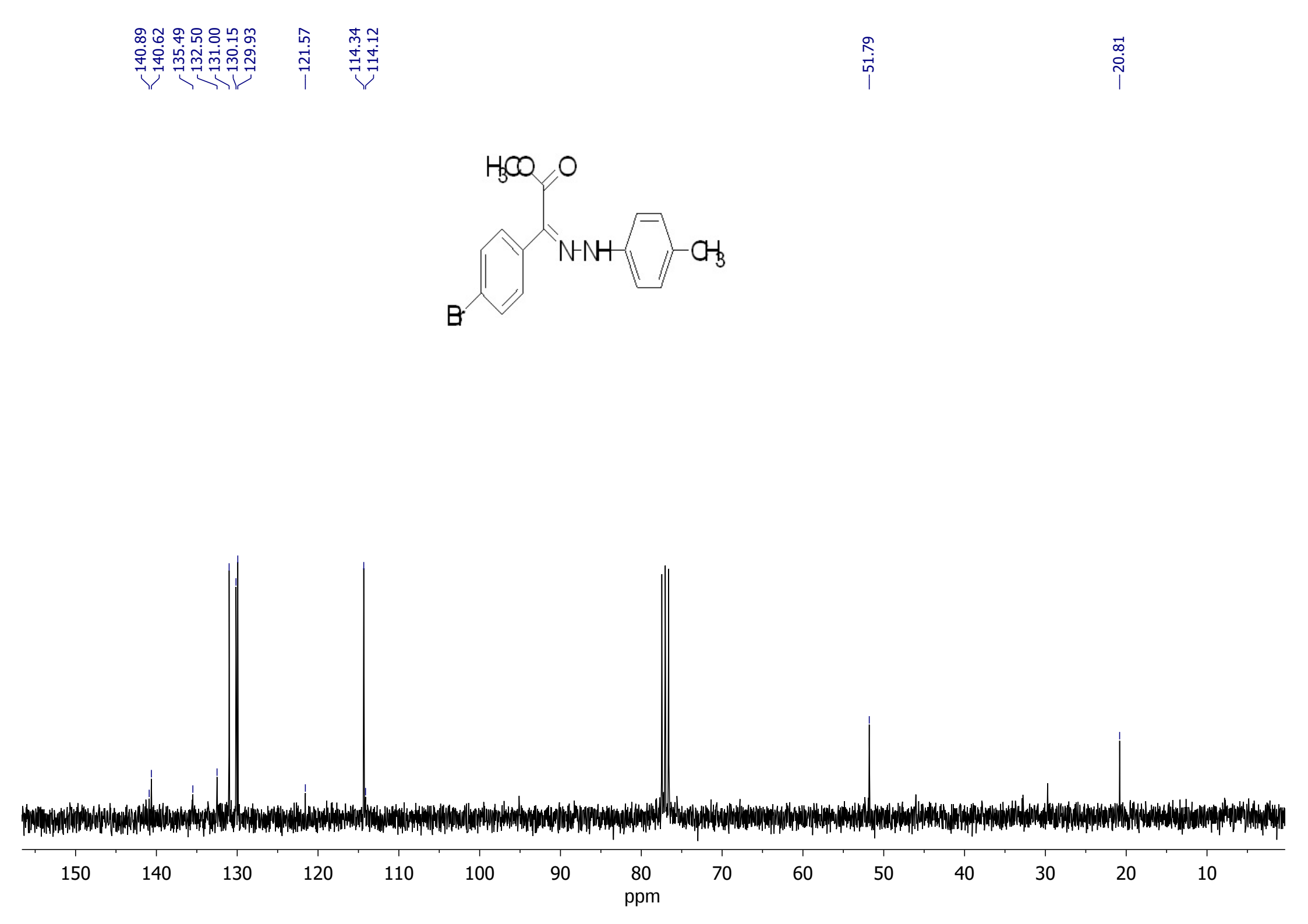
7.56
7.55
7.53
7.52
7.49
7.21
7.18
7.17
7.14
3.89
2.34
O
O
H3C
N
NH
CH3
Br
4.00
4.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
ppm
1.00
4.00
4.00
3.00
3.00
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm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140.62
135.49
132.50
131.00
130.15
129.93
121.57
114.34
114.12
51.79
20.81
150
140
130
120
110
100
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80
70
60
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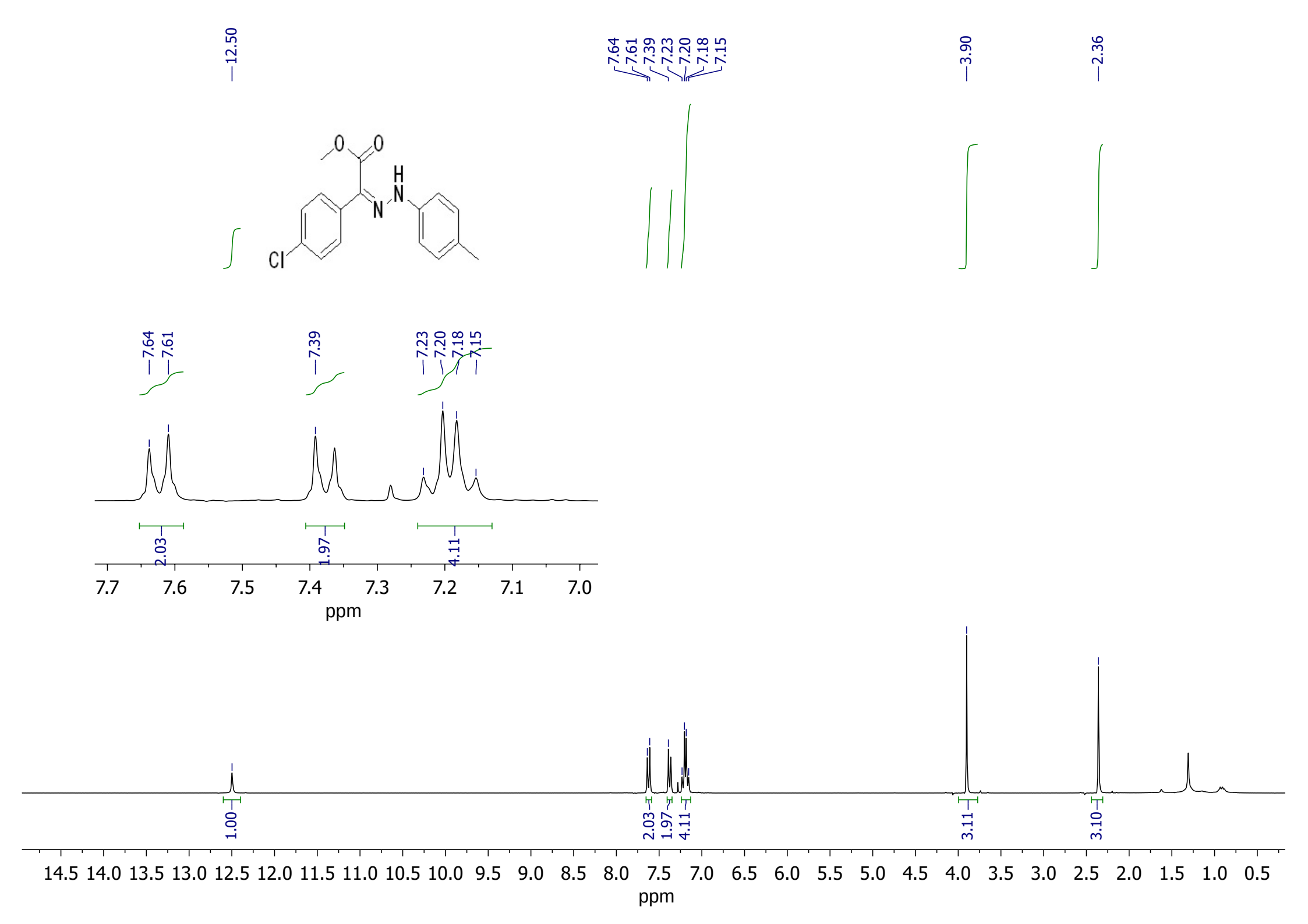
40
30
20
10
ppm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7.64
7.61
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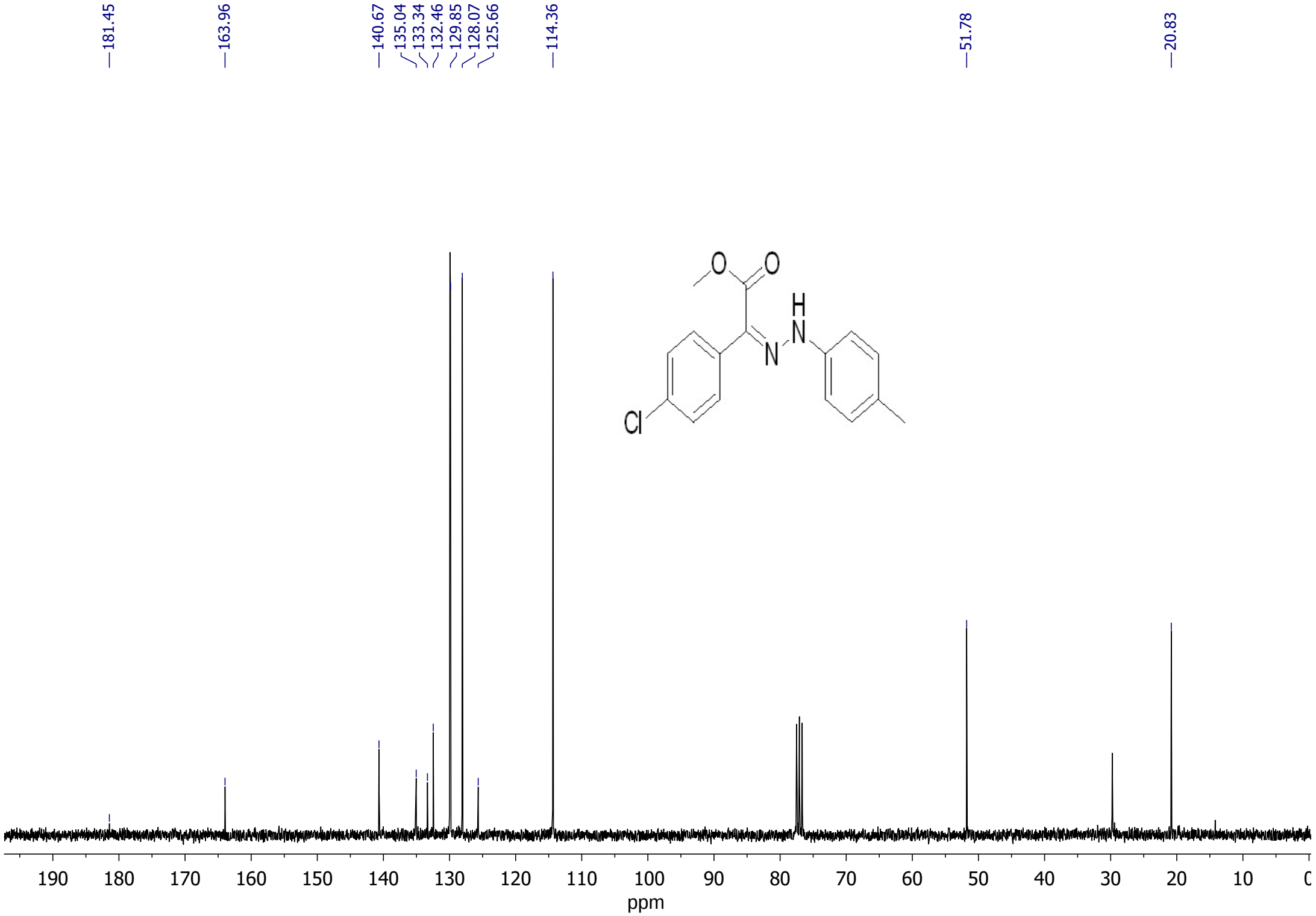
7.20
7.18
7.15
3.90
2.36
O
O
H
N
N
Cl
2.03
1.97
4.11
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm
1.00
2.03
1.97
4.11
3.11
3.10
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm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129.85
128.07
125.66
114.36
51.78
20.83
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O
H
N
N
Cl
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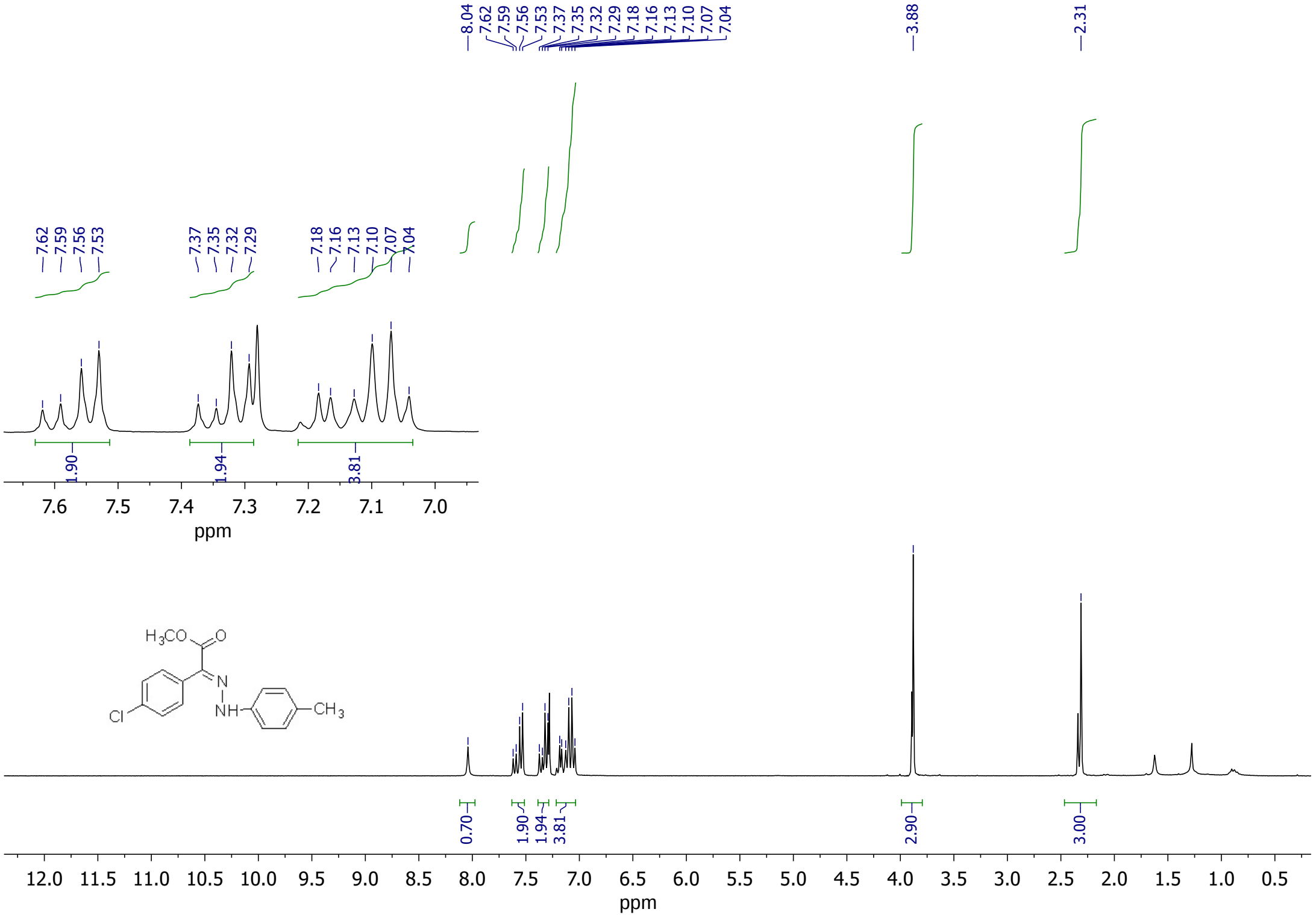
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.62
7.59
7.56
7.53
7.37
7.35
7.32
7.29
7.18
7.16
7.13
7.10
7.07
7.04
3.88
2.31
1.90
1.94
3.81
ppm
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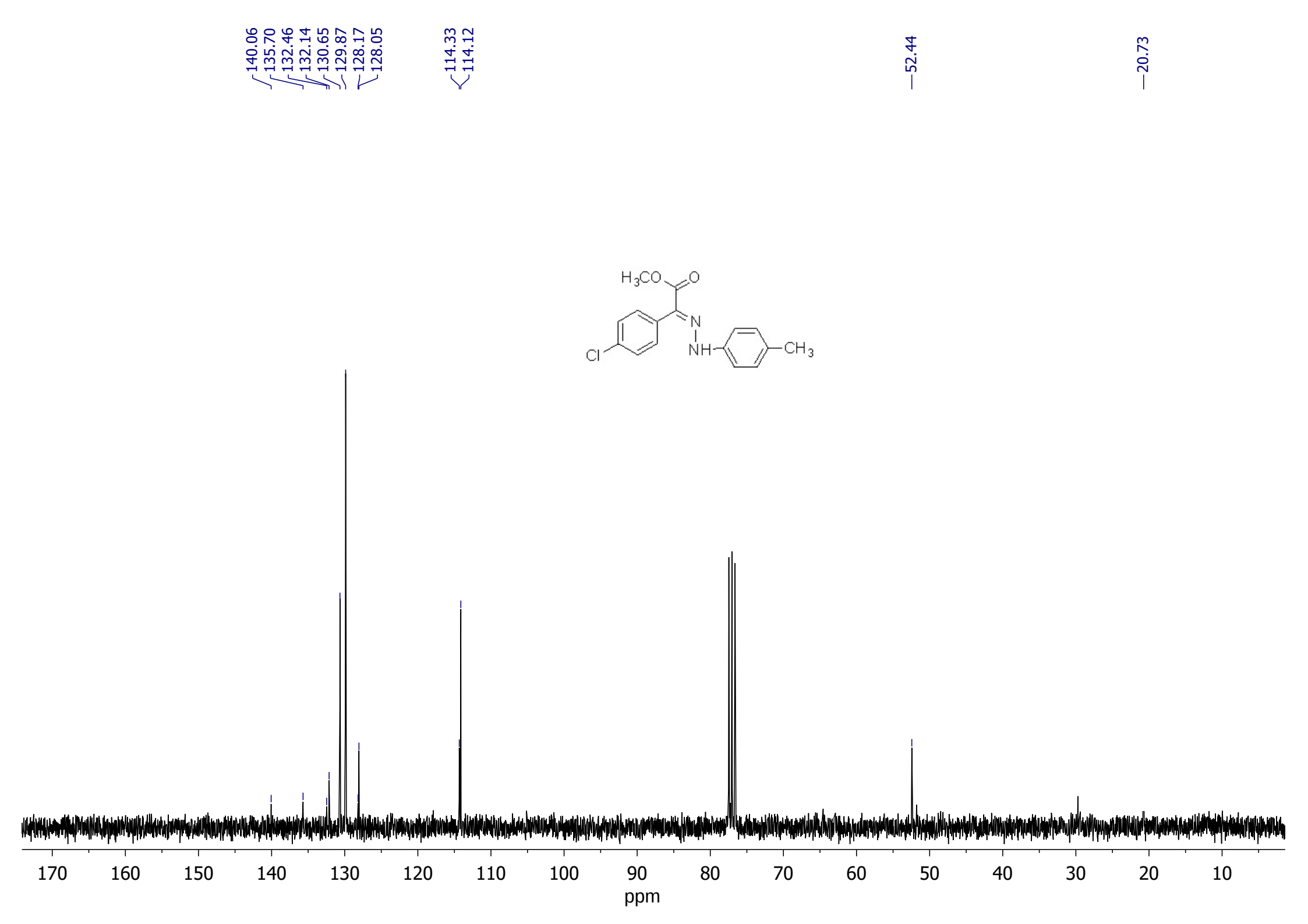
O
N
NH
CH3
Cl
0.70
1.90
1.94
3.81
2.90
3.00
ppm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132.46
132.14
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129.87
128.17
128.05
114.33
114.12
52.44
20.73
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O
N
NH
CH3
Cl
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160
150
140
130
120
110
100
90
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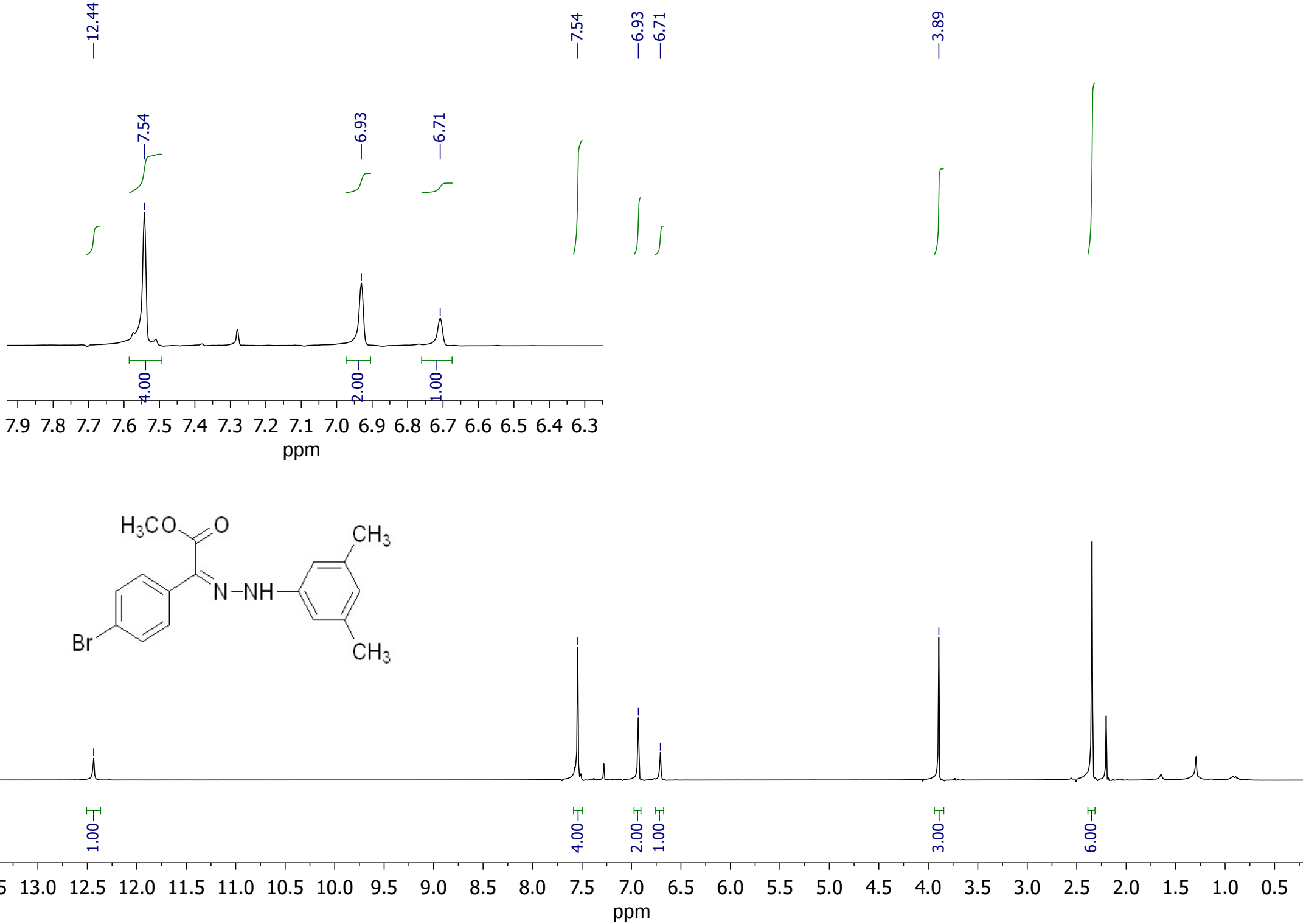
70
60
50
40
30
20
10
ppm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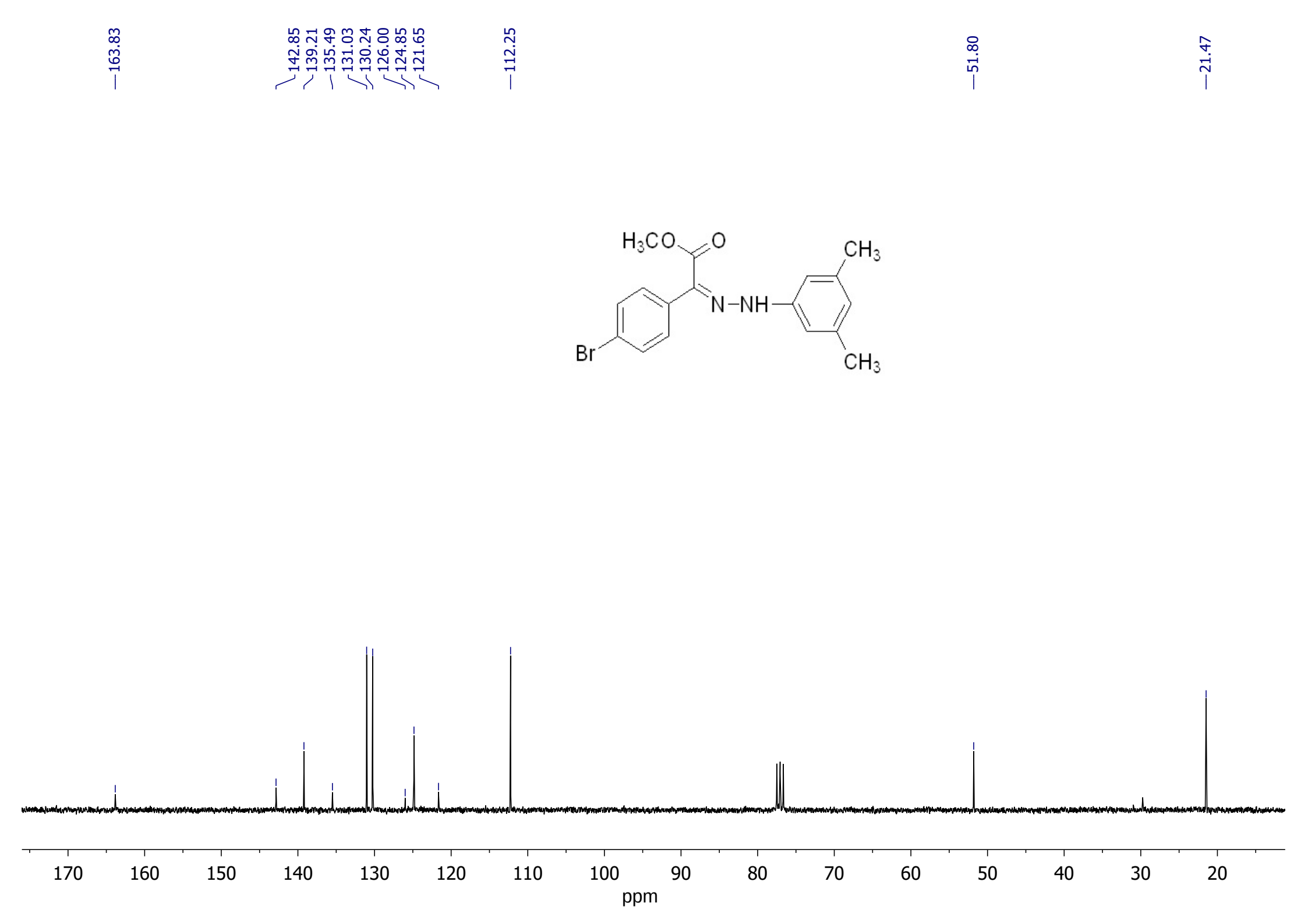
2.00
1.00
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
ppm
H3CO
O
CH3
N–NH
Br
CH3
1.00
4.00
2.00
1.00
3.00
6.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm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142.85
139.21
135.49
131.03
130.24
126.00
124.85
121.65
112.25
51.80
21.47
H3CO
O
N–NH
CH3
CH3
Br
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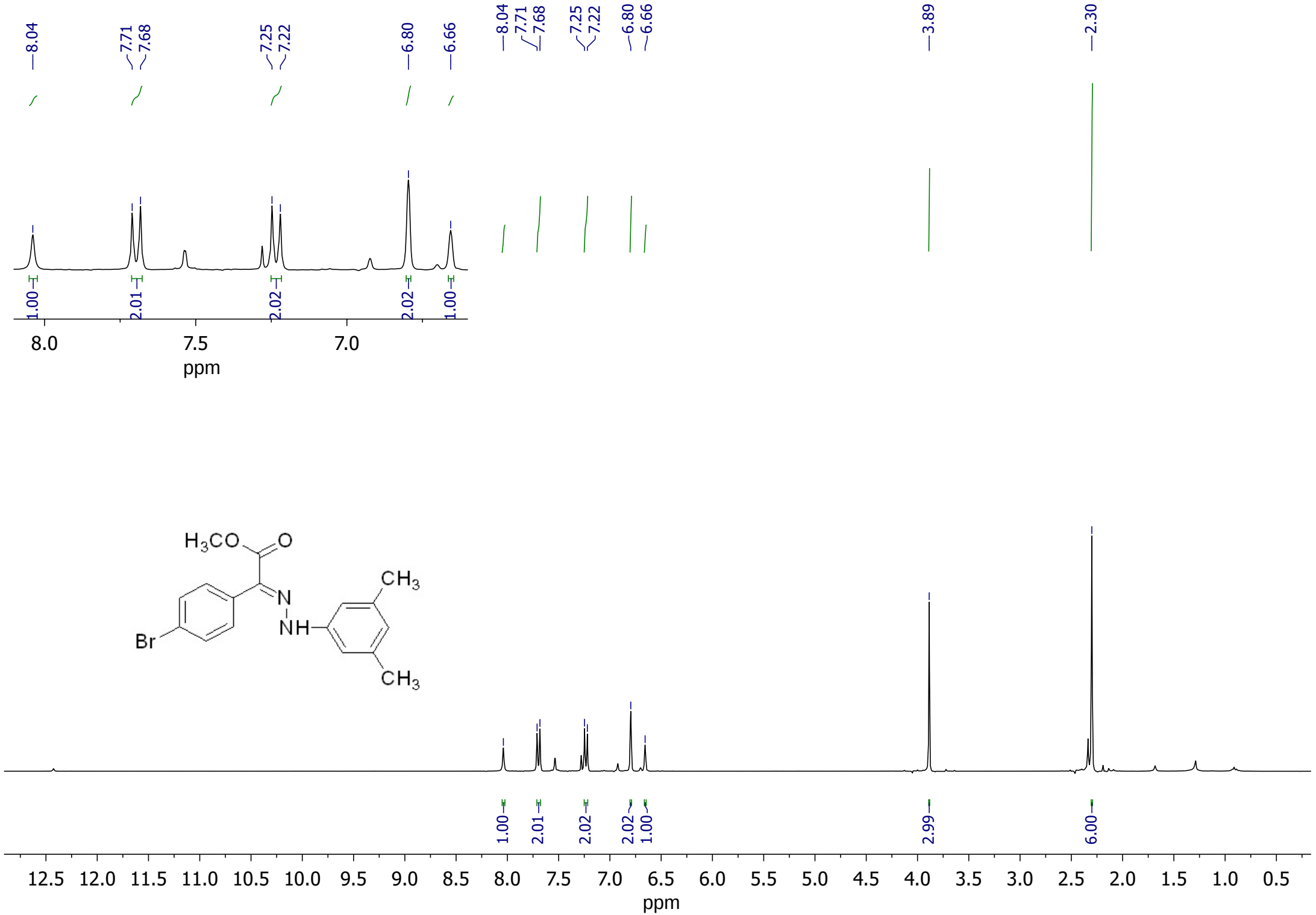
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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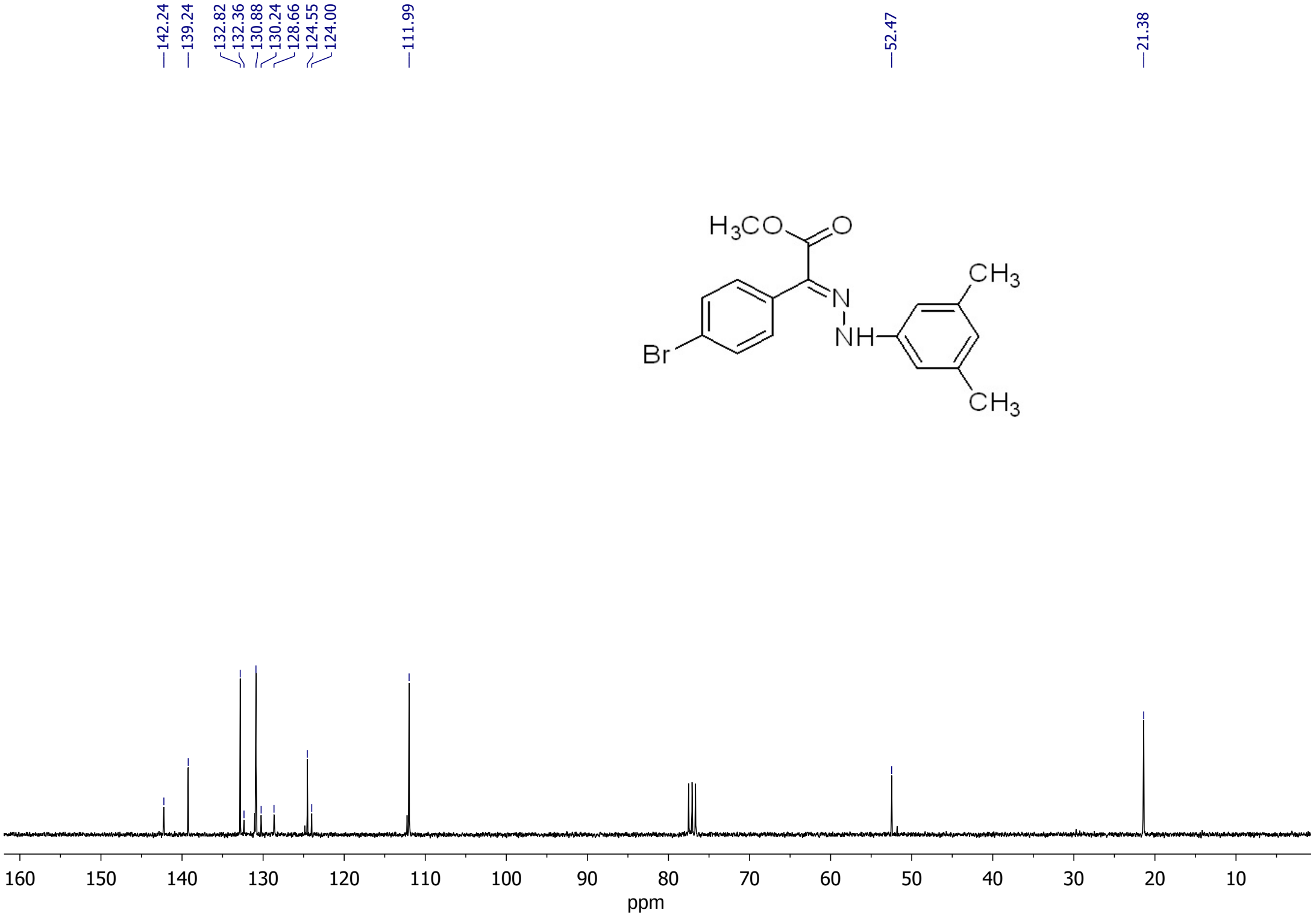
1.00
2.01
2.02
2.02
1.00
2.99
6.00
H3CO
O
N
NH
Br
CH3
CH3
8.0
7.5
7.0
ppm
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm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130.24
128.66
124.55
124.00
111.99
52.47
21.38
H3CO
O
N
NH
Br
CH3
CH3
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150
140
130
120
110
100
90
80
70
60
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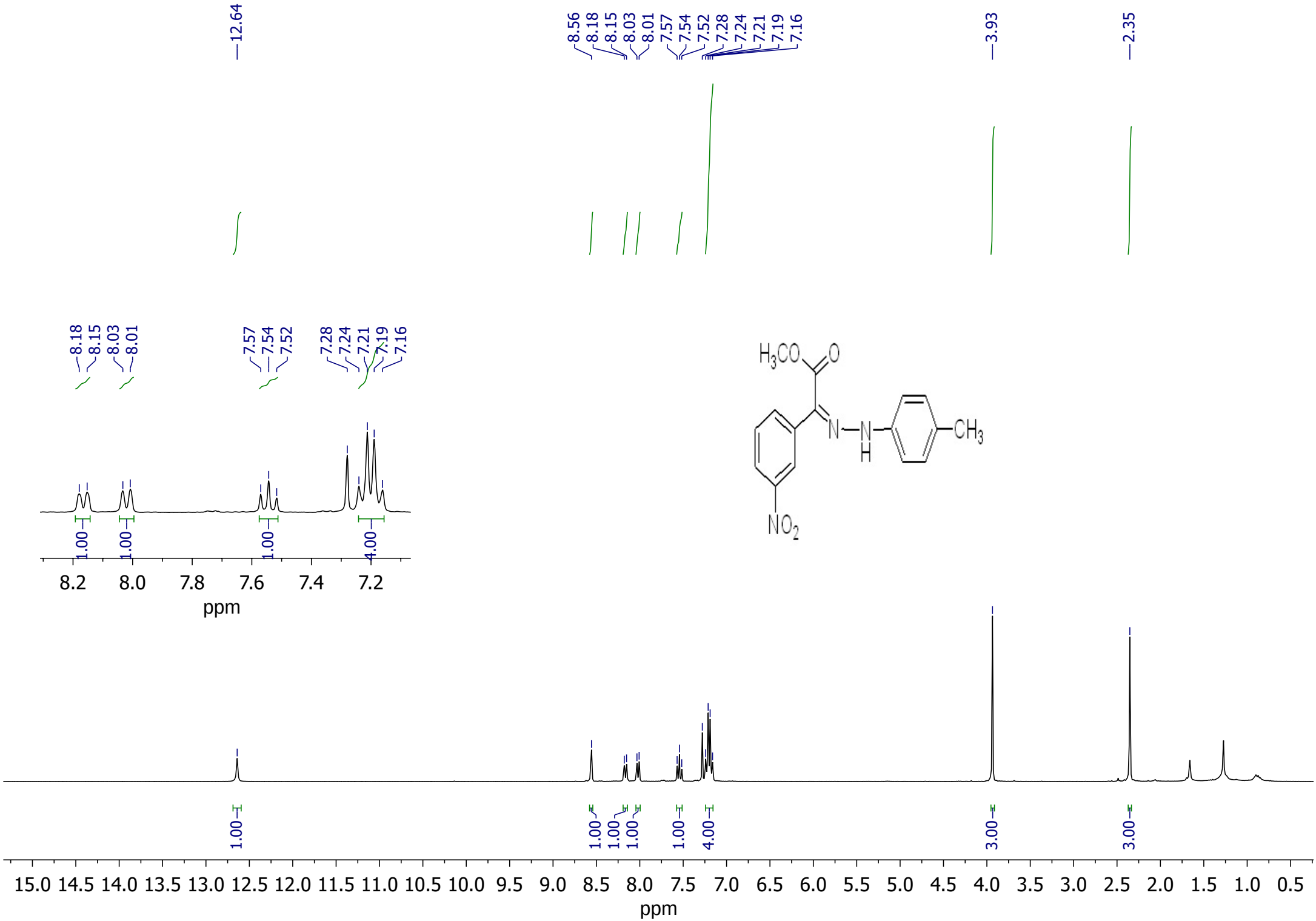
30
20
10
ppm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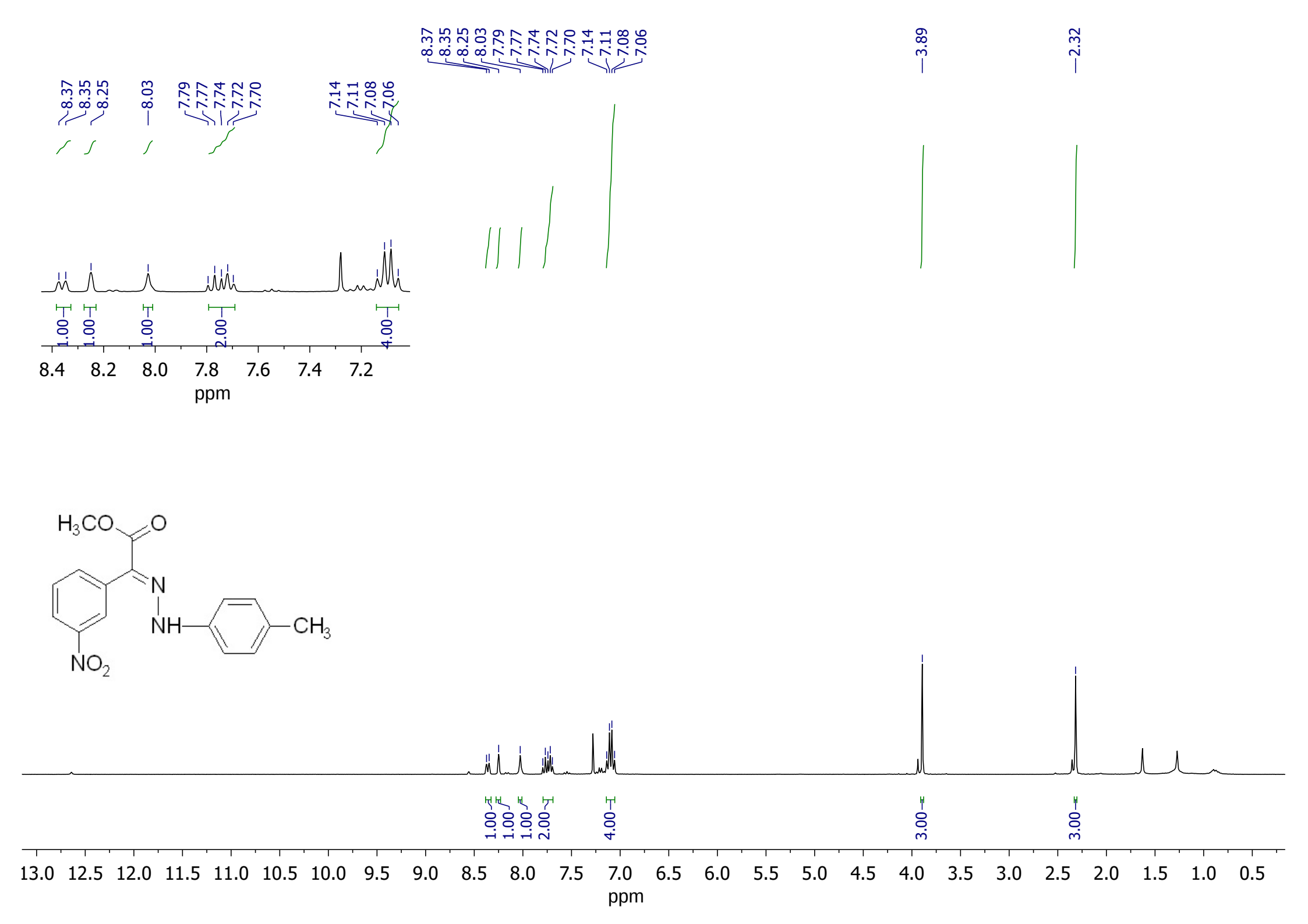
7.54
7.52
7.28
7.24
7.21
7.19
7.16
3.93
2.35
1.00
1.00
1.00
1.00
4.00
3.00
3.00
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
8.18
8.15
8.03
8.01
7.57
7.54
7.52
7.28
7.24
7.21
7.19
7.16
1.00
1.00
1.00
4.00
8.2 8.0 7.8 7.6 7.4 7.2
ppm
H3CO
O
N
N
H
CH3
NO2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7.74
7.72
7.70
7.14
7.11
7.08
7.06
3.89
2.32
1.00
1.00
1.00
2.00
4.00
3.00
3.00
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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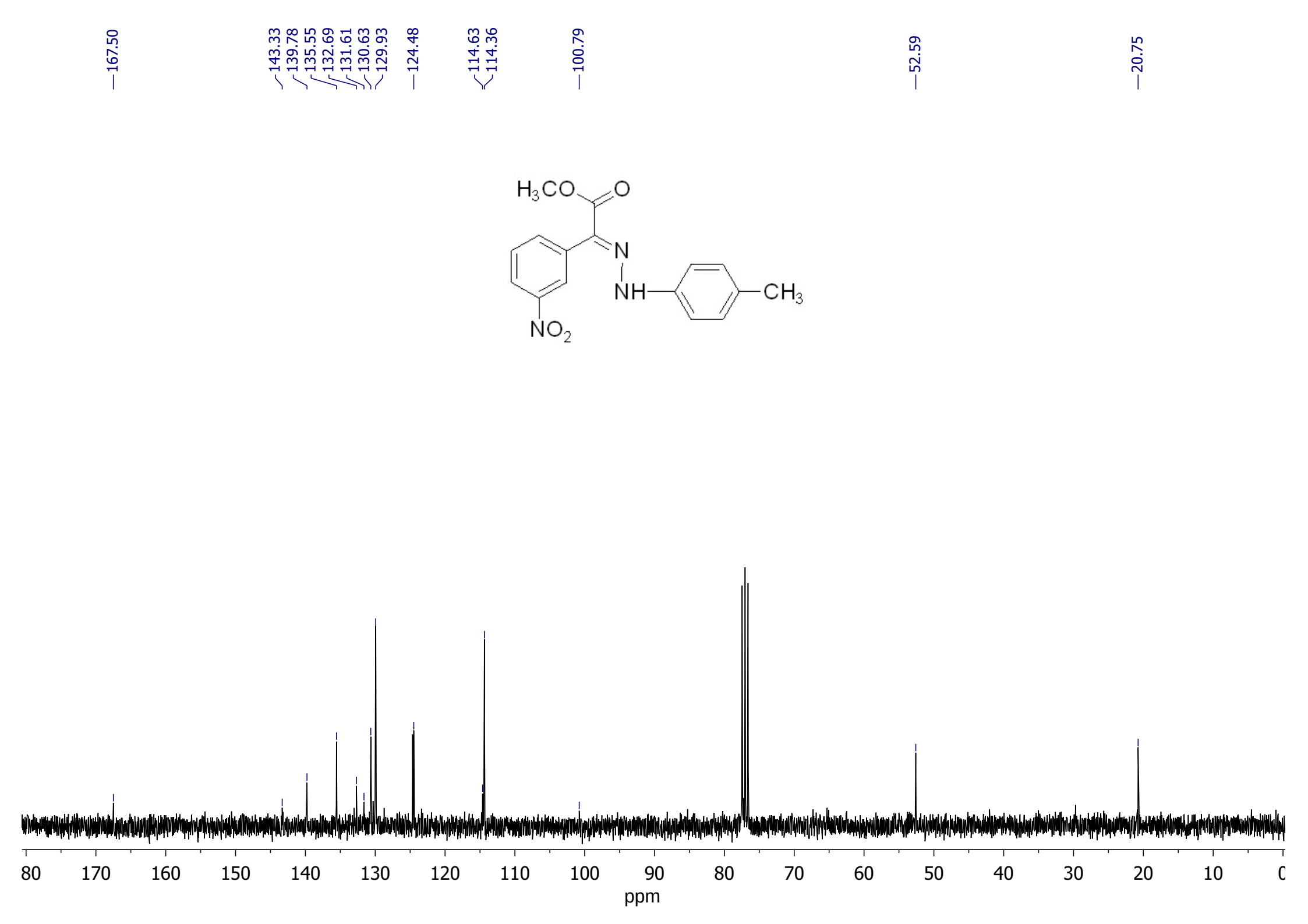
2.0
1.5
1.0
0.5
ppm
H3CO
O
N
NH
CH3
NO2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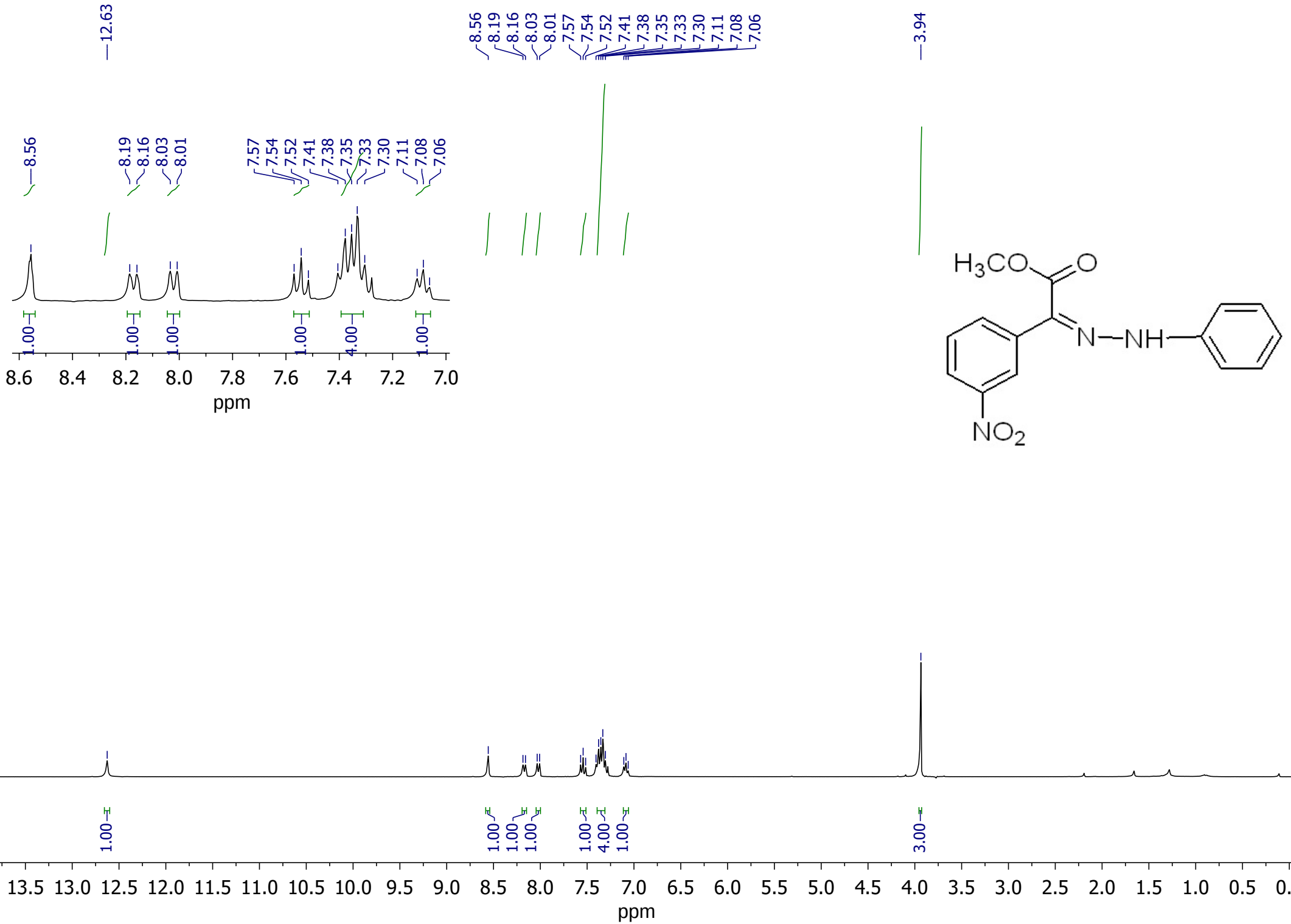
129.93
124.48
114.63
114.36
100.79
52.59
20.75
H3CO
O
N
NH
CH3
NO2
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.56
8.19
8.16
8.03
8.01
7.57
7.54
7.52
7.41
7.38
7.35
7.33
7.30
7.11
7.08
7.06
3.94
1.00
1.00
1.00
1.00
4.00
1.00
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
H3CO
O
N
NH
NO2
1.00
1.00
1.00
1.00
4.00
1.00
3.00
4.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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4.0
3.5
3.0
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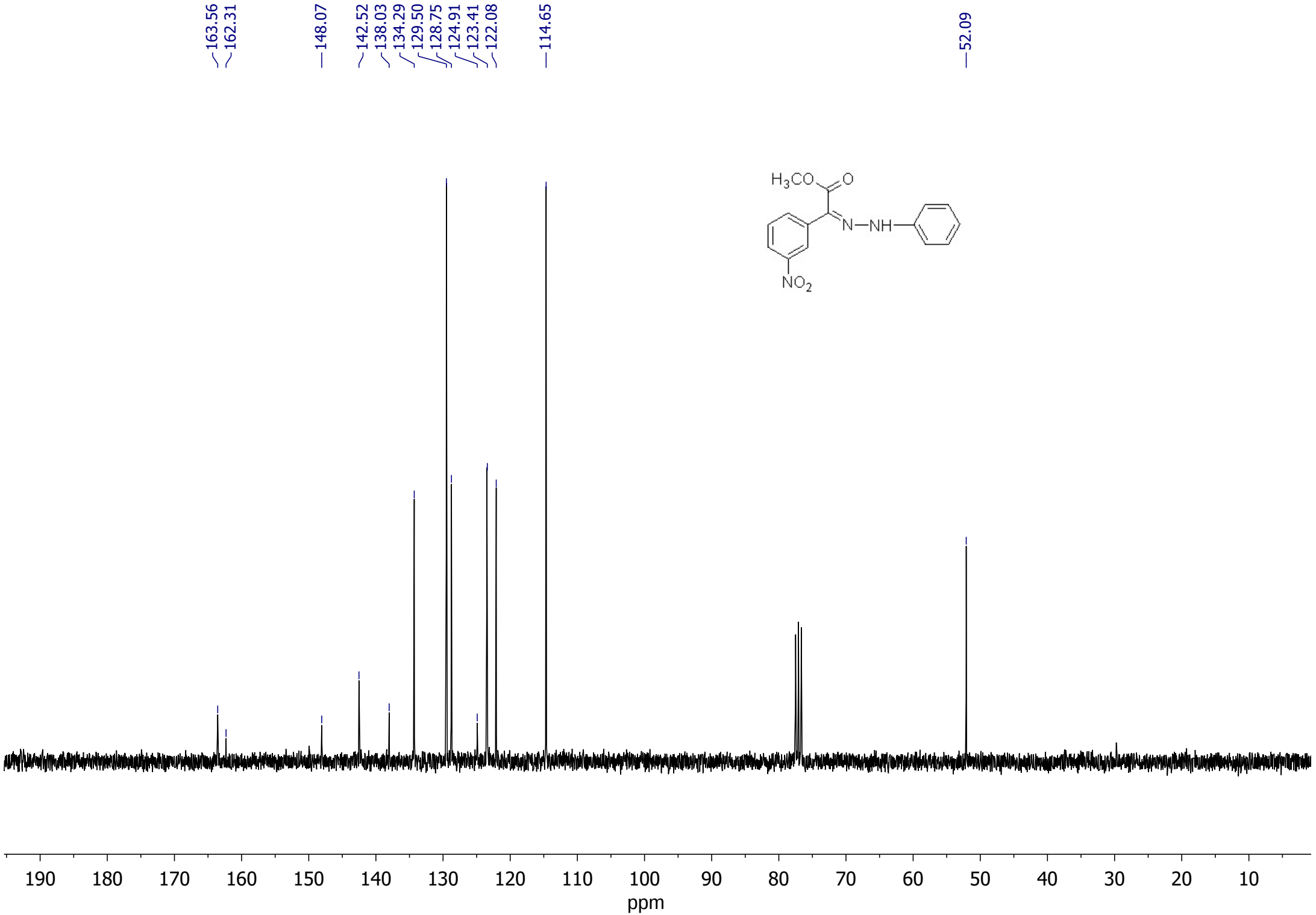
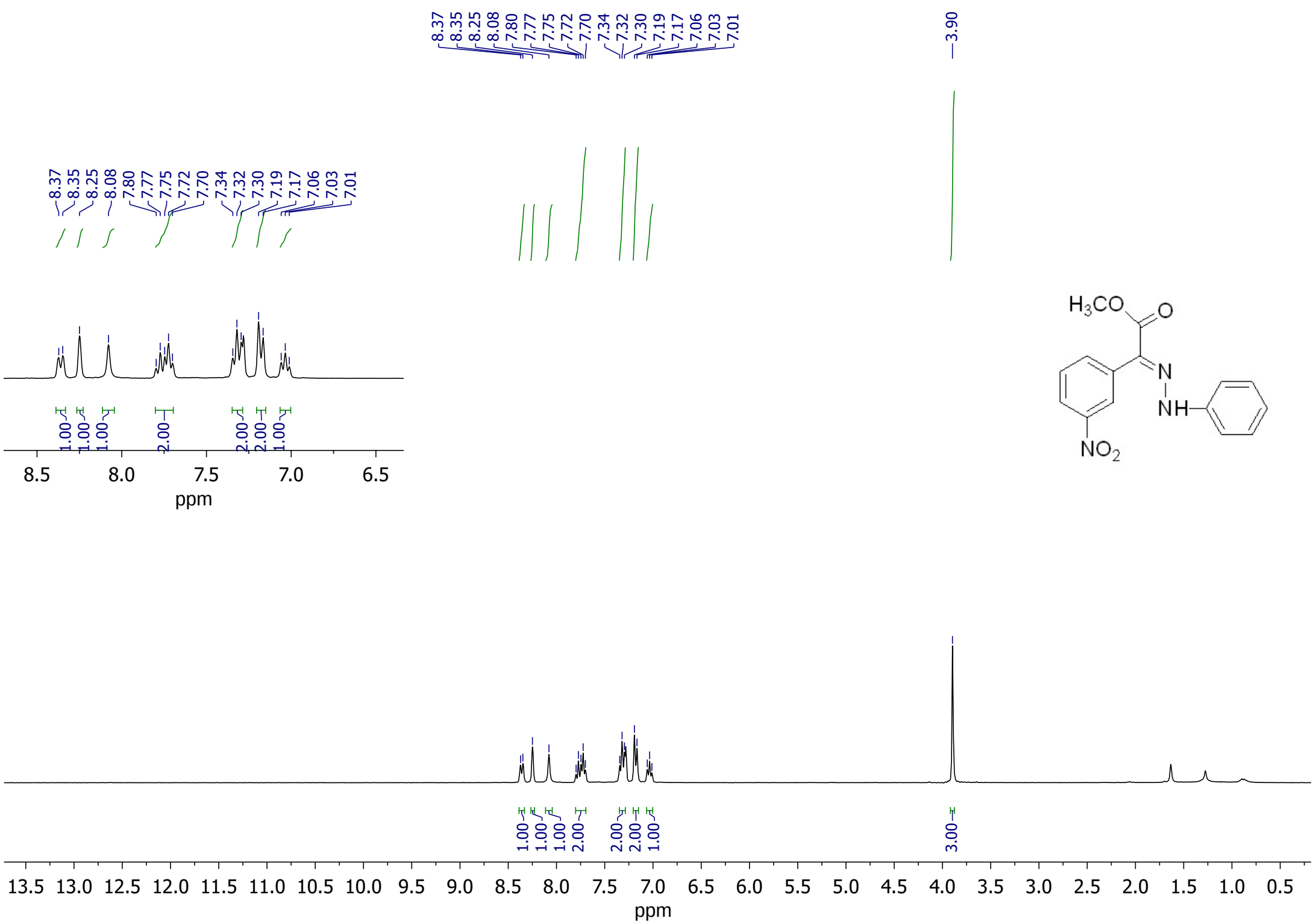
2.0
1.5
1.0
0.5
0.0
ppm


163.56
162.31
148.07
142.52
138.03
134.29
129.50
128.75
124.91
123.41
122.08
114.65
52.09
H3CO
O
N—NH
NO2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.77
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7.72
7.70
7.34
7.32
7.30
7.19
7.17
7.06
7.03
7.01
3.90
1.00
1.00
1.00
2.00
2.00
2.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
ppm
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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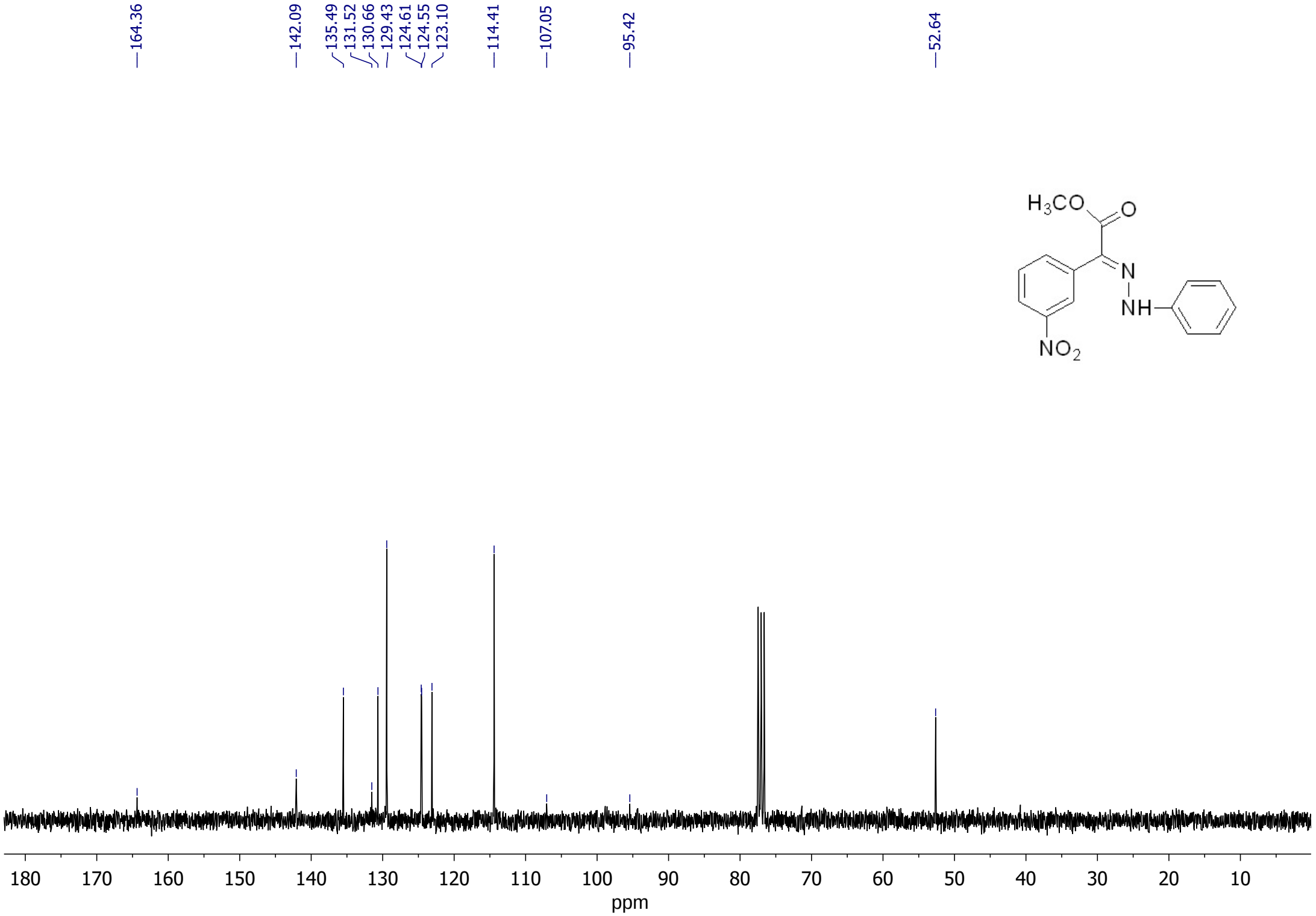
2.5
2.0
1.5
1.0
0.5
ppm
H3CO
O
N
NH
NO2


164.36
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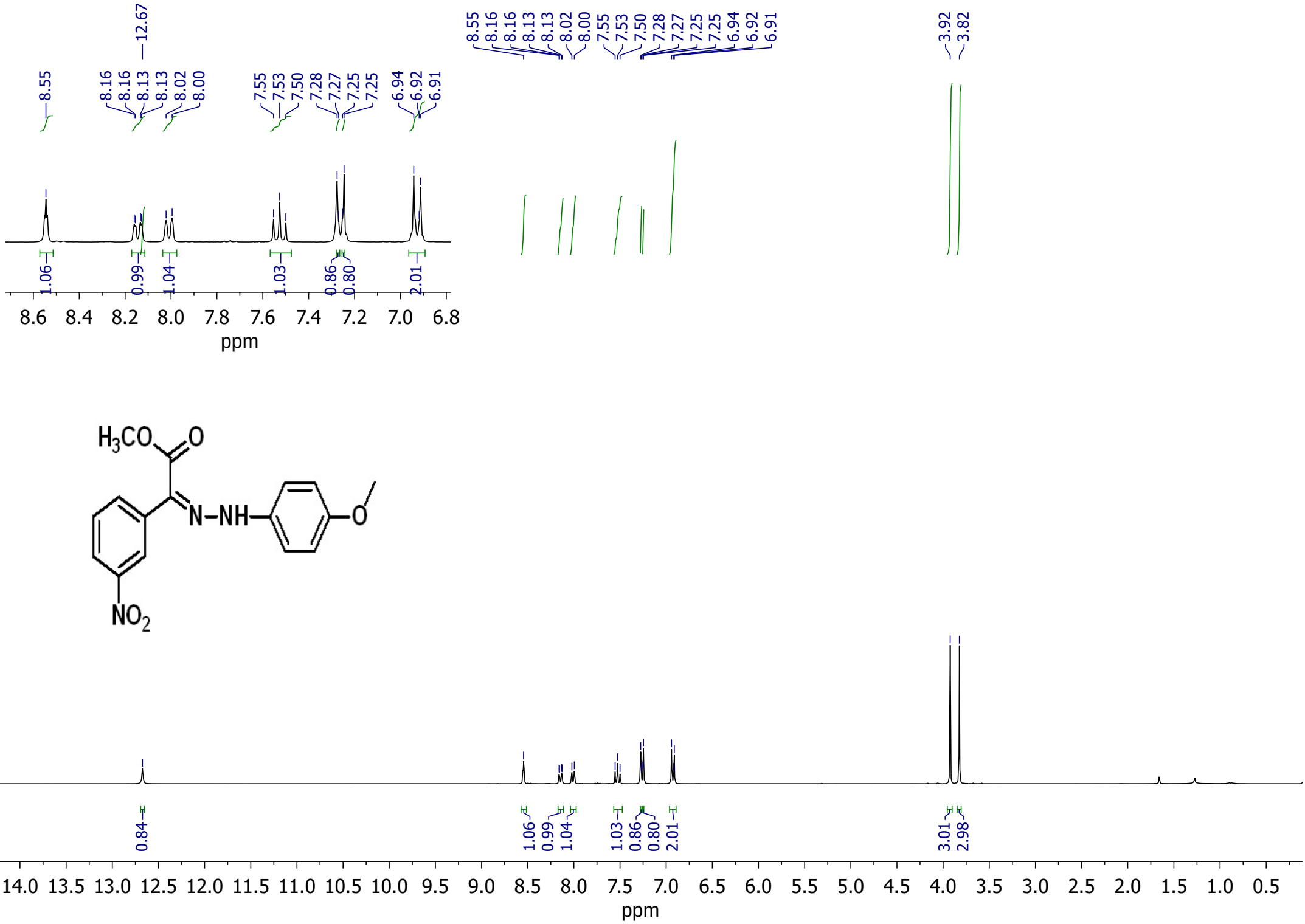
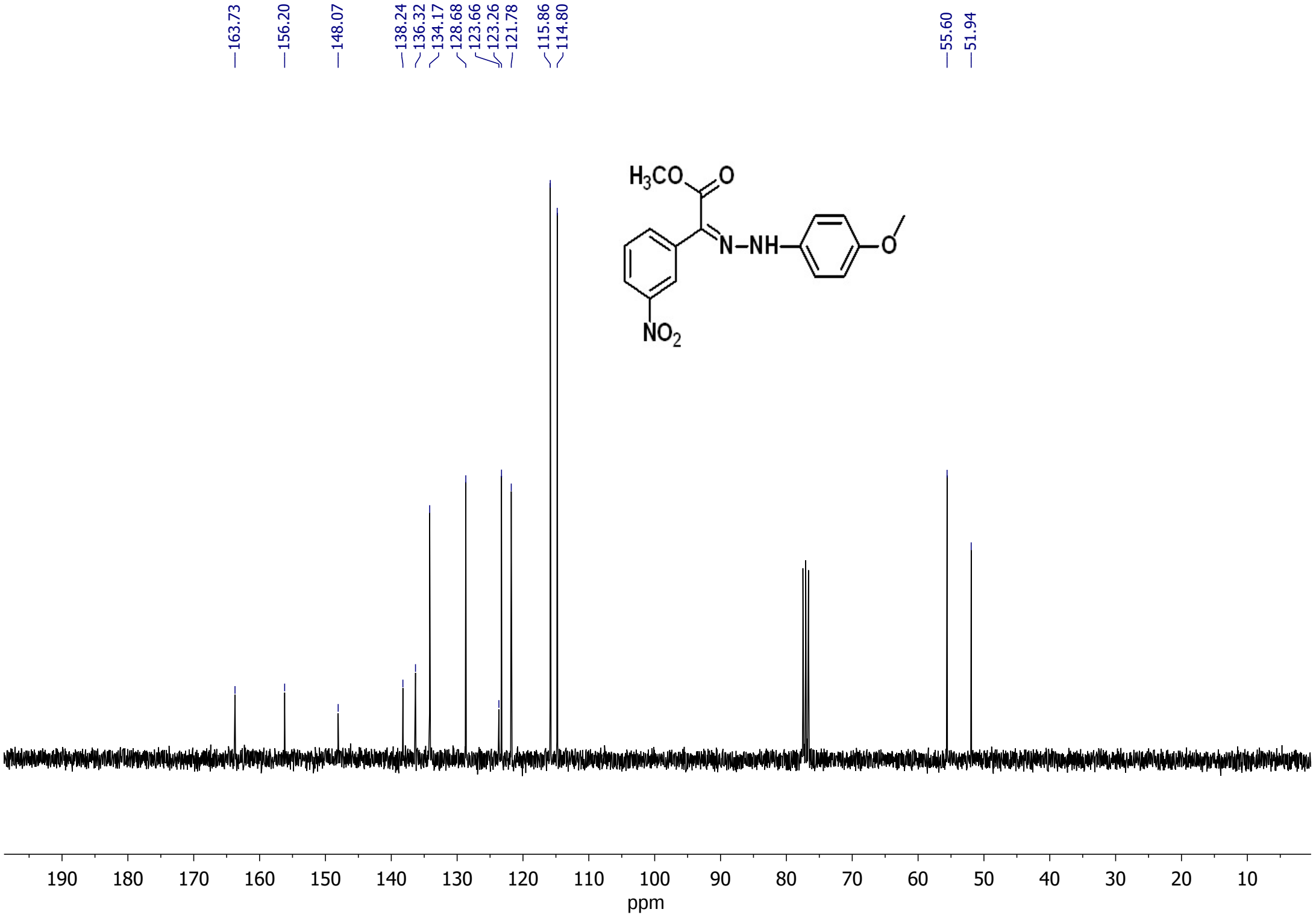
131.52
130.66
129.43
124.61
124.55
123.10
114.41
107.05
95.42
52.64
H3CO
O
N
NH
NO2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


12.67
8.55
8.16
8.16
8.13
8.13
8.02
8.00
7.55
7.53
7.50
7.28
7.27
7.25
7.25
6.94
6.92
6.91
3.92
3.82
1.06
0.99
1.04
1.03
0.86
0.80
2.01
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
ppm
H3CO
O
N–NH
O
NO2
0.84
1.06
0.99
1.04
1.03
0.86
0.80
2.01
3.01
2.98
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


163.73
156.20
148.07
138.24
136.32
134.17
128.68
123.66
123.26
121.78
115.86
114.80
55.60
51.94
H3CO
O
N–NH
O
NO2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm