Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPLEMENTARY INFORMATION FOR

Nickel nanoparticles assisted regioselective synthesis of pyrazoloquinolinone and triazoloquinazolinone derivatives

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Experimental

All the chemicals involved in the synthesis were purchased from Alfa Aesar, Sigma Aldrich, Merck and were used without further purification. Purity of the products were confirmed by infrared (IR), ^{1}H-NMR, ^{13}C-NMR and mass spectra besides X-ray diffraction (XRD) and melting point data. Melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded in KBr pellets on a Perkin Elmer Spectrum 400 FTIR instrument, and the frequencies are expressed in cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker Avance II-400 spectrometer in DMSO-d_6 (Chemical shifts in δ with TMS as internal standard). Mass spectral data were obtained with a JEOL D-300 (ESI) mass spectrometer. Single crystal XRD data was obtained with Xcalibur-Eos-Gemini instrument and powder XRD analysis was done with X'Pert Pro instrument. The EDAX and SEM imaging were carried out by scanning electron microscope of make JSM-6360 (JEOL) and the TEM imaging was done using transmission electron microscope of make JEM-2100, 200 kV(JEOL)**.** All reactions were monitored by thin layer chromatography (TLC) using precoated aluminum sheets (silica gel 60 F 254 0.2-mm thickness) and developed in an iodine chamber.

X-ray crystallography

The single crystal X-ray diffraction (XRD) data were collected at 293 K with Mo Ka radiation (l ¼ 0.71073 °A) using Agilent Xcalibur (Eos, Gemini) diffractometer equipped with a graphite monochromator. The software used for data collection CrysAlis PRO (Agilent, 2011), data reduction CrysAlis PRO and cell refinement CrysAlis PRO. The structure were solved by direct methods and refined by Olex2.refine.

General procedure for preparation of 5a-h, 6a-j

In a 50 ml round bottom flask, 3-Amino-1*H*-1,2,4-triazole/3-Amino-5-methyl-1*H*-pyrazole (1 mmol), aldehyde (1 mmol) and dimedone (1 mmol), nickel nanoparticle (10 mol %) were refluxed in acetonitrile (10 ml) for 10 minutes. On cooling, solid crystals separated out. The nickel nanoparticles were retrieved magnetically and the reaction mixture was filtered. The residue was dried and analyzed.

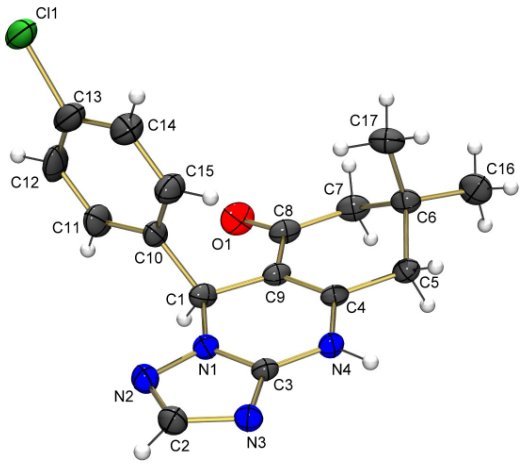


Table S.I.1. X-ray crystallography data for compound **5c**. (CCDC 1024257)

Empirical formula	$C_{17}H_{17}Cl\ N_4O$
Formula weight	328.80
Crystal system	Triclinic
Space group	P-1
a(Å)	6.0023(11)
b(Å)	12.317(2)
c(Å)	12.460(2)
α(°)	67.981(17)
β(°)	77.245(15)
γ(°)	80.977(15)
Volume (Å)	830.1(3)
ρ (calculated) (g cm^{-3})	1.3154
T(K)	291.9(9)
Absorption coefficient (mm^{-1})	0.240
Total reflection collected	6065
Independent reflection	3734
Refine parameter	209
θ range (°)	6.78 to 57.48
Final R Indexes [1>=2σ(I)]	R1 = 0.0535
Final R indexes [all data]	R1 = 0.0850
Goodness-of-fit on F^2	1.036

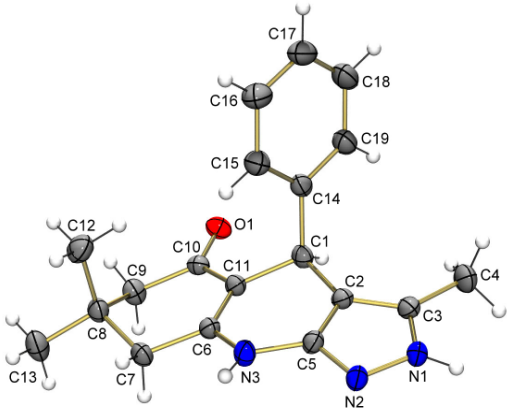
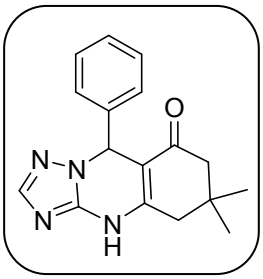


Table S.I.2. X-ray crystallography data for compound **6a**. (CCDC 1024256)

Empirical formula	$C_{19}H_{21}N_3O$
Formula weight	307.39
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	10.1735(11)
b(Å)	14.3043(10)
c(Å)	11.2897(9)
α(°)	90.00
β(°)	96.376(8)
γ(°)	90.00
Volume (Å)	1632.8(3)
ρ (calculated) (g cm^{-3})	1.2545
T(K)	292.34(10)
Absorption coefficient (mm^{-1})	0.079
Total reflection collected	7067
Independent reflection	3707
Refine parameter	211
θ range (°)	6.38 to 57.38
Final R Indexes [1>=2σ(I)]	R1 = 0.0588
Final R indexes [all data]	R1 = 0.1646
Goodness-of-fit on F^2	0.988

ANALYTICAL DATA

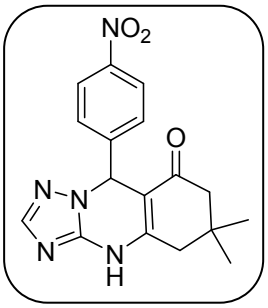
6,6-dimethyl-9-phenyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (5a):



Light yellow crystal, Yield: 90 %, Melting point: 249-251^{O}C .

IR (KBr): 3445, 2962, 1650, 1594, 1374, 1252, 721 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.14 (s, 1H), 7.68 (s, 1H), 7.17-7.29 (m, 5H), 6.19 (s, 1H), 2.52-2.59 (m, 2H), 2.19 (d, *J* = 16Hz, 1H), 2.05 (d, *J* =16Hz, 1H), 1.03 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 26.77, 28.45, 32.16, 49.74, 57.89, 105.55, 126.92, 127.69, 128.23, 141.55, 146.82, 150.24, 150.39, 192.96. ESI- MS: *m/z* 295 $[M+H]^{+}$.

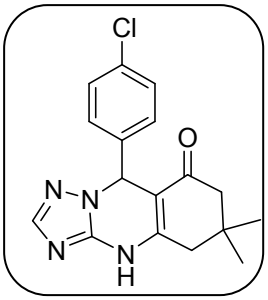
6,6-dimethyl-9-(4-nitrophenyl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (5b):



Pale yellow crystal, Yield: 93%, Melting point: 301-302^{O}C.

IR (KBr): 3412, 3090, 2964, 1646, 1579, 1351, 1253, 729 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.31 (s, 1H), 8.14 (d, *J* = 8Hz, 2H), 7.73 (s, 1H), 7.47 (d, *J* = 8Hz, 2H), 6.36 (s, 1H), 2.56 (d, *J* = 16Hz, 1H), 2.49 (d, *J* = 16Hz, 1H), 2.19 (d, *J* = 16Hz, 1H), 2.05(d, *J* = 16Hz, 1H), 1.03 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 26.92, 28.26, 32.21, 49.63, 57.49, 104.72, 123.55, 128.46, 146.81, 146.89, 148.38, 150.40, 150.97, 193.01. ESI-MS: *m/z* 340 $[M+H]^{+}$.

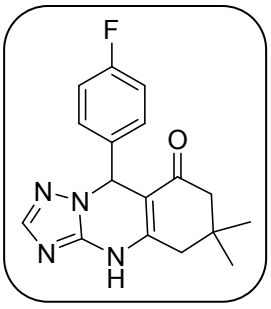
9-(4-chlorophenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (5c):



Pale yellow crystal, Yield: 92%, Melting point: 297-298^{O}C.

IR (KBr): 3436, 3094, 2961, 1649, 1578, 1367, 1254, 760 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 10.95 (s, 1H), 7.45 (s, 1H), 7.09 (d, *J* = 8Hz, 2H), 6.95 (d, *J* = 8Hz, 2H), 5.97 (s, 1H), 2.25-2.34 (m, 2H), 1.95 (d, *J* = 16Hz, 1H), 1.81 (d, *J* = 16Hz, 1H), 0.79 (s, 3H), 0.71 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 26.87, 28.36, 32.17, 49.71, 57.34, 105.16, 128.25, 128.86, 132.26, 140.49, 146.76, 150.17, 150.55, 192.98. ESI-MS: *m/z* 329 $[M+H]^{+}$.

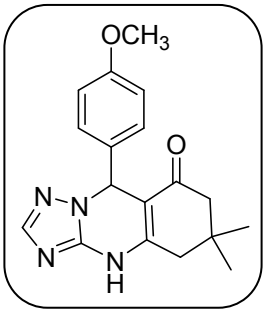
9-(4-fluorophenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (5d):



Colourless crystal, Yield: 90%, Melting point: 303-305^{O}C.

IR (KBr): 3450, 3091, 2963, 1649, 1581, 1365, 1255, 762 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.16 (s, 1H), 7.69 (s, 1H), 7.22-7.23 (m, 2H), 7.08-7.10 (m, 2H), 6.22 (s, 1H), 2.53-2.58 (m, 2H), 2.19 (d, *J* = 16Hz, 1H), 2.06 (d, *J* = 16Hz, 1H), 1.03 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 27.36, 28.87, 32.66, 50.23, 57.73, 105.86, 115.39, 129.50, 138.34, 147.24, 150.59, 160.74, 163.16, 193.45. ESI-MS: *m/z* 313 $[M+H]^{+}$.

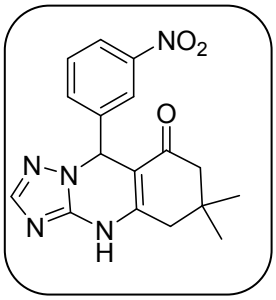
9-(4-methoxyphenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (5e):



Colourless crystal, Yield: 88% , Melting point: 230-232^{O}C.

IR (KBr): 3436, 2961, 1649, 1580, 1367, 1246, 745 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 10.87 (s,1H), 7.45 (s, 1H), 6.87 (d, *J* = 8Hz, 2H), 6.60 (d, *J* = 8Hz, 2H), 5.93 (s, 1H), 3.47 (s, 3H), 2.28-2.37 (m, 2H), 1.98 (d, *J* = 16Hz, 1H), 1.83 (d, *J* = 16Hz, 1H), 0.82 (s, 3H), 0.75 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 26.79, 28.49, 32.15, 49.78, 54.99, 57.30, 105.71, 113.54, 128.09, 133.82, 146.72, 150.14, 158.66, 192.94. ESI-MS: *m/z* 325 $[M+H]^{+}$.

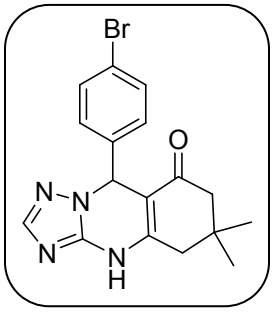
6,6-dimethyl-9-(3-nitrophenyl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (5f):



Pale yellow solid, Yield: 85%, Melting point: 290-292^{O}C.

IR (KBr): 3436, 3082, 2960, 1645, 1580, 1367, 1256, 732 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.09 (s,1H), 7.84- 7.90 (m, 2H), 7.52 (s, 1H), 7.37-7.44 (m, 2H), 6.20 (s, 1H), 2.28-2.40 (m, 2H), 1.99 (d, *J* = 16Hz, 1H), 1.86 (d, *J* = 16Hz, 1H), 0.829 (s, 3H), 0.756 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 26.85, 28.31, 32.23, 49.65, 57.39, 104.59, 121.66, 122.81, 130.04, 133.71, 143.45, 146.77, 147.58, 150.42, 151.13, 193.09. ESI-MS: *m/z* 340 $[M+H]^{+}$.

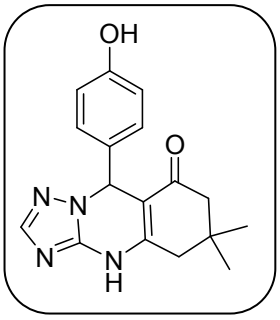
9-(4-bromophenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (5g):



Yellow crystal, Yield: 91%, Melting point: 282-285^{O}C.

IR (KBr): 3436, 3090, 2965, 1650, 1584, 1367, 1255, 759 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.19 (s, 1H), 7.70 (s, 1H), 7.47 (d, *J* = 8Hz, 2H), 7.13 (d, *J* = 8Hz, 2H), 6.19 (s, 1H), 2.54-2.58 (m, 2H), 2.19 (d, *J* = 16Hz, 1H), 2.05 (d, *J* = 16Hz, 1H), 1.03 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 26.87, 28.36, 32.18, 49.71, 57.43, 105.12, 120.85, 129.22, 131.18, 140.91, 146.75, 150.18, 150.56, 192.99. ESI-MS: *m/z* 373 $[M]^{+}$, 375 $[M+2]^{+}$.

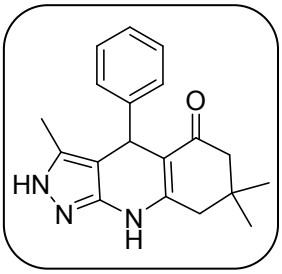
9-(4-hydroxyphenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (5h):



Pale yellow solid, Yield: 89%, Melting point: 303-304^{O}C.

IR (KBr): 3348, 3096, 2932, 1631, 1587, 1370, 1269, 731 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.04 (s, 1H), 9.39 (s, 1H), 7.65 (s, 1H), 6.96 (d, *J* = 8Hz, 2H), 6.62 (d, *J* = 8Hz, 2H), 6.08 (s, 1H), 2.57-2.68 (m, 2H), 2.18 (d, *J* = 16Hz, 1H), 2.05 (d, *J* = 16Hz, 1H), 1.03 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 26.79, 28.51, 32.14, 49.80, 52.99, 57.33, 105.86, 114.84, 132.21, 128.07, 146.69, 149.83, 150.03, 156.87, 192.94. ESI-MS: *m/z* 311$[M+H]^{+}$.

3,7,7-trimethyl-4-phenyl-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6a):

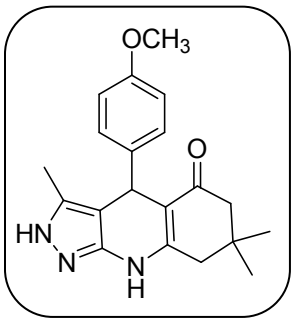


Colourless crystal, Yield: 96%, Melting point: 230-232^{O}C.

IR (KBr): 3237, 3065, 2963, 1590, 1548, 1253, 760 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.48 (s,1H), 9.44 (s, 1H), 6.79-6.92 (m, 5H), 4.68 (s, 1H), 2.19 (d, *J* = 16Hz, 1H), 2.13 (d, *J* = 16Hz, 1H), 1.85 (d, *J* = 16Hz, 1H), 1.68 (d, *J* = 16Hz, 1H), 1.65 (s, 3H), 0.76 (s, 3H), 0.69 (s,

3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.35, 26.82, 28.83, 31.87, 35.08, 40.96, 50.39, 103.91, 106.94, 125.11, 127.67, 134.79, 146.23, 148.39, 152.78, 192.78. ESI-MS: *m/z* 308 $[M+H]^+$.

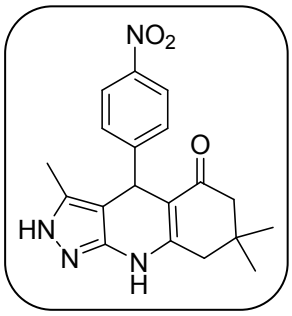
4-(4-methoxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6b):



Pale Yellowish solid, Yield: 95%, Melting point: 295-297^{O}C.

IR (KBr): 3240, 3065, 2963, 1590, 1548, 1253, 760 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.71 (s,1H), 9.65 (s, 1H), 6.99 (d, *J* = 8Hz, 2H), 6.71 (d, *J* = 8Hz, 2H), 4.86 (s, 1H), 2.41 (d, *J* = 16Hz, 1H), 2.34 (d, *J* = 16Hz, 1H), 2.07 (d, *J* = 16Hz, 1H), 1.89 (d, *J* = 16Hz, 1H), 1.88 (s, 3H), 0.98 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.33, 26.82, 28.85, 31.85, 34.09, 40.95, 50.43, 54.79, 104.15, 107.23, 112.99, 128.01, 134.7, 140.72, 146.26, 152.44, 156.79, 192.79. ESI-MS: *m/z* 338 $[M+H]^+$.

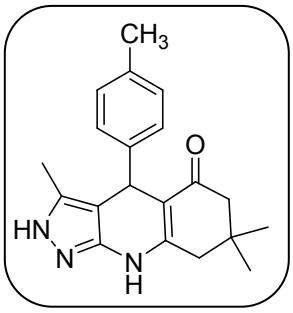
3,7,7-trimethyl-4-(4-nitrophenyl)-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-b]quinolin-5(4*H*)-one (6c):



Yellow crystal, Yield: 98%, Melting point: 300-302^{O}C.

IR (KBr): 3262, 3068, 2952, 1593, 1547, 1255, 740 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.61 (s,1H), 9.63 (s, 1H), 7.82 (d, *J* = 8Hz, 2H), 7.14 (d, *J* = 8Hz, 2H), 4.84 (s, 1H), 2.18-2.21 (m, 2H), 1.86 (d, *J* = 16Hz, 1H), 1.68 (d, *J* = 16Hz, 1H), 1.62 (s, 3H), 0.75 (s, 3H), 0.68 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.28, 26.89, 28.86, 31.90, 35.46, 40.92, 50.22, 102.51, 105.89, 123.19, 128.38, 135.39, 145.19, 146.05, 153.34, 155.89, 192.81. ESI-MS: *m/z* 353 $[M+H]^+$.

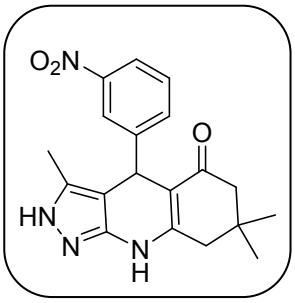
3,7,7-trimethyl-4-(*p*-tolyl)-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6d):



Pale yellowish crystal, Yield: 94%, Melting point: 310-312^{O}C.

IR (KBr): 3234, 3070, 2961, 1590, 1547, 1254, 777 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.45 (s,1H), 9.39 (s, 1H), 6.69-6.75 (m, 4H), 4.62 (s, 1H), 3.09 (s, 3H), 2.17 (d, *J* = 16Hz, 1H), 2.09 (d, *J* = 16Hz, 1H), 1.83 (d, *J* = 16Hz, 1H), 1.69 (d, *J* = 16Hz, 1H), 1.63 (s, 3H), 0.74 (s, 3H), 0.67 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.34, 20.49, 26.79, 28.88, 31.85, 34.59, 40.95, 50.41, 104.03, 107.09, 127.02, 128.23, 133.87, 134.71, 145.49, 146.24, 152.58, 192.75. ESI-MS: *m/z* 322 $[M+H]^+$.

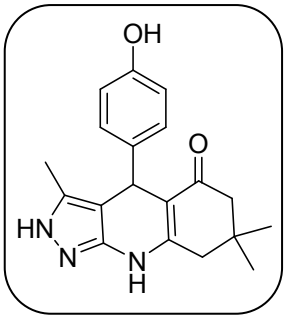
3,7,7-trimethyl-4-(3-nitrophenyl)-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6e):



Yellow crystal, Yield: 93%, Melting point: 298-300^{O}C.

IR (KBr): 3210, 3065, 2958, 1588, 1547, 1257, 729 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.87 (s,1H), 9.89 (s, 1H), 7.92 (d, *J* = 8Hz, 2H), 7.60 (s, 1H), 7.47 (d, *J* = 8Hz, 2H), 5.11 (s, 1H), 2.39-2.47 (m, 2H), 2.10 (d, *J* = 16Hz, 1H), 1.92 (d, *J* = 16Hz, 1H), 1.88 (s, 3H), 0.99 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.32, 26.66, 28.76, 31.93, 35.93, 40.89, 50.19, 102.72, 106.06, 120.40, 121.49, 129.25, 134.08, 135.39, 146.08, 147.46, 150.50, 153.37, 192.89. ESI-MS: *m/z* 353 $[M+H]^+$.

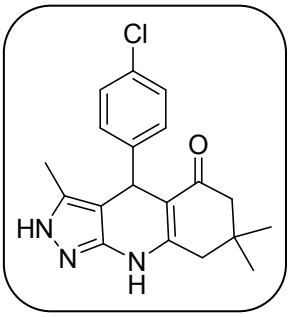
4-(4-hydroxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6f):



Light pinkish solid, Yield: 95%, Melting point: 272-275^{O}C.

IR (KBr): 3256, 3067, 2961, 1588, 1546, 1253, 759 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.49 (s,1H), 9.41 (s, 1H), 8.80 (s, 1H), 6.69 (d, *J* = 8Hz, 2H), 6.34 (d, *J* = 8Hz, 2H), 4.63 (s, 1H), 2.22 (d, *J* = 16.8Hz, 1H), 2.15 (d, *J* = 16.8Hz, 1H), 1.89 (d, *J* = 16Hz, 1H), 1.76 (d, *J* = 16Hz, 1H), 1.70 (s, 3H), 0.80 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.35, 26.81, 28.86, 31.84, 33.99, 40.97, 50.47, 104.39, 107.39, 114.37, 127.92, 134.61, 139.09, 146.28, 152.37, 154.73, 192.81. ESI-MS: *m/z* 324 [M+H]$^{+}$.

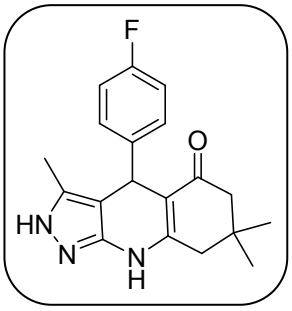
4-(4-chlorophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6g):



Colourless crystal, Yield: 97%, Melting point: 305-307^{O}C.

IR (KBr): 3257, 3070, 2962, 1590, 1547, 1254, 785 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.79 (s,1H), 9.76 (s, 1H), 7.21 (d, *J* = 8Hz, 2H), 7.11 (d, *J* = 8Hz, 2H), 4.92 (s, 1H), 2.43 (d, *J* = 16.8Hz, 1H), 2.35 (d, *J* = 16.8Hz, 1H), 2.08 (d, *J* = 16Hz, 1H), 1.91 (d, *J* = 16Hz, 1H), 1.87 (s, 3H), 0.98 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.30, 26.64, 28.75, 31.87, 34.61, 40.92, 50.33, 103.35, 106.57, 127.62, 128.99, 129.55, 134.99, 146.16, 147.31, 152.88, 192.81. ESI-MS: *m/z* 342 [M+H]$^{+}$.

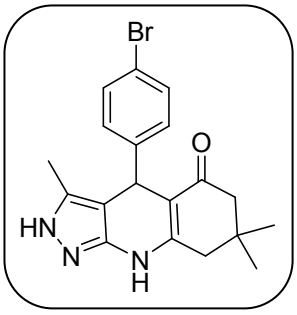
4-(4-fluorophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6h):



Colourless crystal, Yield: 96%, Melting point: 338-340^{O}C.

IR (KBr): 3243, 3068, 2959, 1587, 1546, 1253, 791cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.77 (s,1H), 9.73 (s, 1H), 6.98-7.12 (m, 4H), 4.93 (s, 1H), 2.42 (d, *J* = 16Hz, 1H), 2.35 (d, *J* = 8Hz, 1H), 2.08 (d, *J* = 16Hz, 1H), 1.91 (d, *J* = 8Hz, 1H), 1.87 (s, 3H), 0.98 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.29, 26.83, 28.75, 31.87, 34.35, 40.93, 50.35, 103.68, 106.85, 114.36, 128.79, 134.89, 144.57, 146.19, 152.74, 161.20, 192.83. ESI-MS: *m/z* 326 [M+H]$^{+}$.

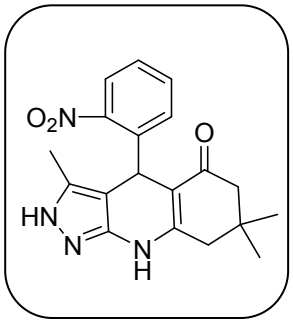
4-(4-bromophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6i):



Colourless crystal, Yield: 96%, Melting point: 315-317 ^{O}C.

IR (KBr): 3237, 3070, 2959, 1589, 1547, 1253, 784 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.74 (s,1H), 9.71 (s, 1H), 7.30 (d, *J* = 8Hz, 2H), 7.02 (d, *J* = 8Hz, 2H), 4.86 (s, 1H), 2.38 (d, *J* = 17.2Hz, 1H), 2.31 (d, *J* = 17.2Hz, 1H), 2.04 (d, *J* = 16Hz, 1H), 1.87 (d, *J* = 16Hz, 1H), 1.83 (s, 3H), 0.94 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.33, 26.84, 28.75, 31.88, 34.69, 40.91, 50.31, 103.27, 106.52, 118.04, 129.43, 130.54, 135.08, 146.07, 147.72, 152.92, 192.83. ESI-MS: *m/z* 386 [M]$^{+}$, 389 [M+2]$^{+}$.

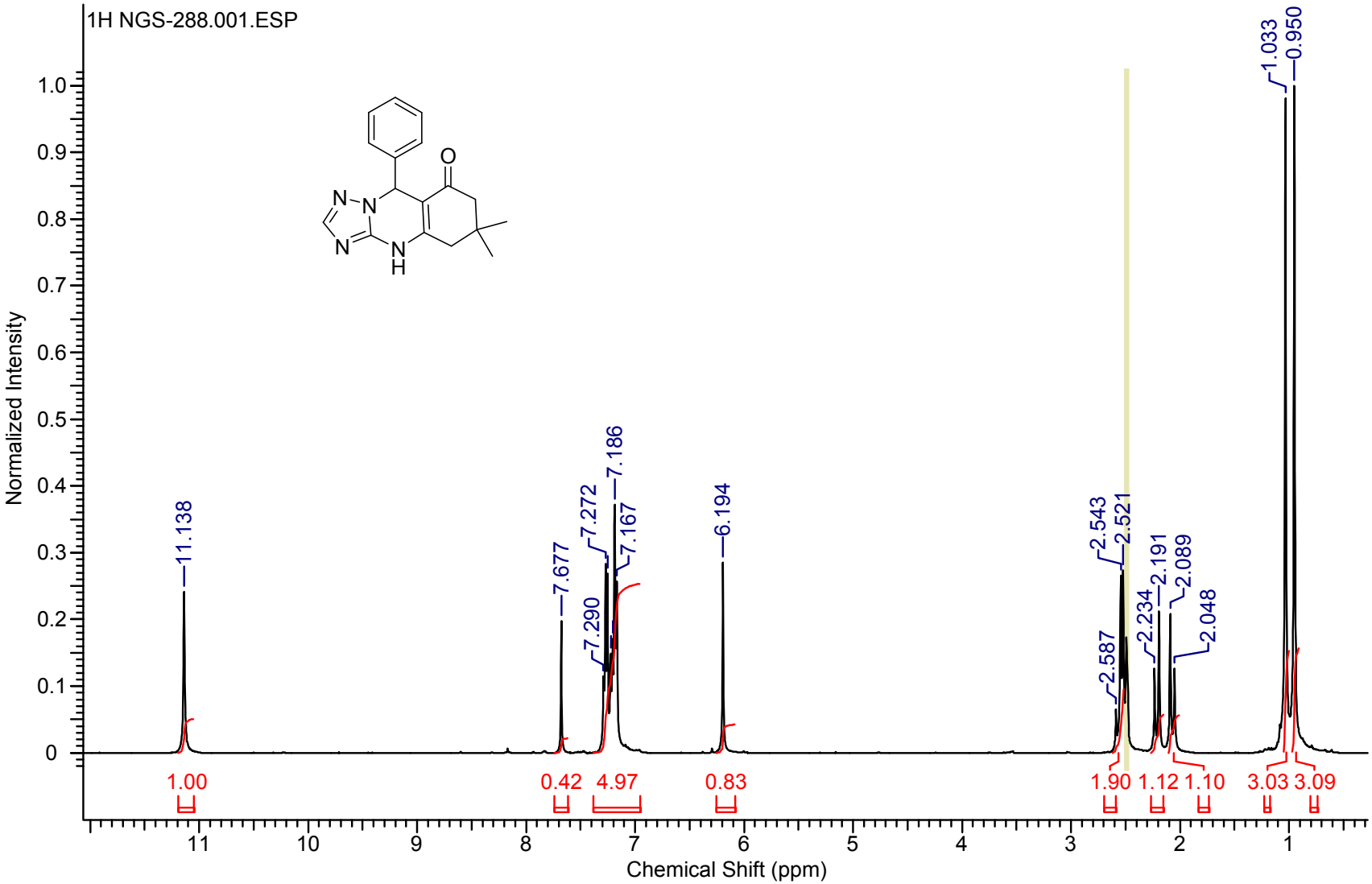
3,7,7-trimethyl-4-(2-nitrophenyl)-6,7,8,9-tetrahydro-2*H*-pyrazolo[3,4-*b*]quinolin-5(4*H*)-one (6j):



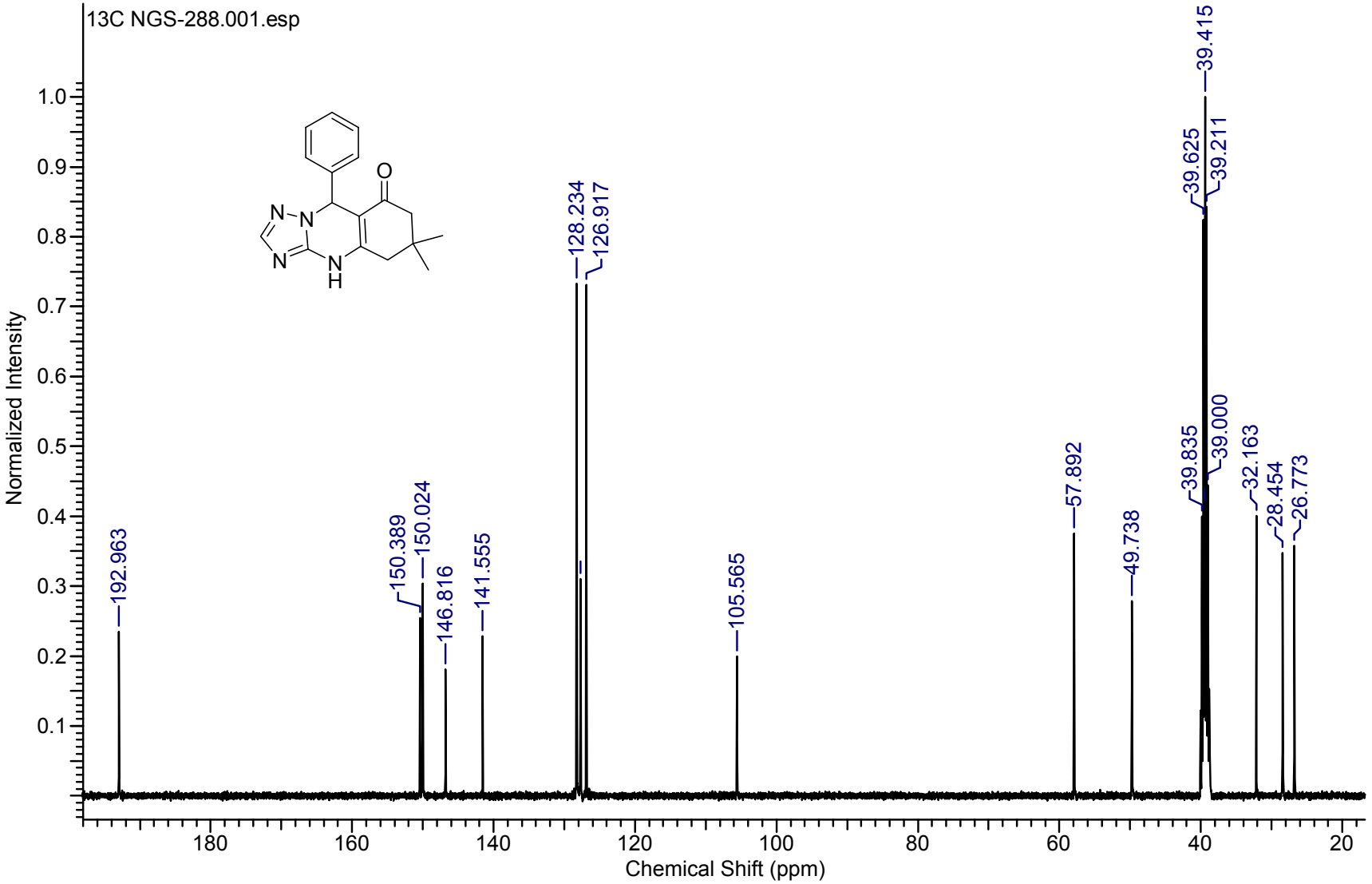
Yellow solid, Yield: 91%, Melting point: 262-265 ^{O}C.

IR (KBr): 3263, 3061, 2958, 1590, 1549, 1258, 734 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 11.93 (s,1H), 9.89 (s, 1H), 7.67 (d, *J* = 8Hz, 1H), 7.46 (t, *J* = 8Hz, 1H), 7.23 (t, *J* = 8Hz, 1H), 7.09 (d, *J* = 8Hz, 1H), 5.54 (s, 1H), 2.41 (d, *J* = 16Hz, 1H), 2.29 (d, *J* = 16Hz, 1H), 2.01 (d, *J* = 16Hz, 1H), 1.93 (s, 3H), 1.79 (d, *J* = 16Hz, 1H), 0.95 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 9.37, 26.52, 28.67, 29.66, 31.94, 40.69, 49.81, 102.23, 107.04, 122.55, 126.21, 131.04, 132.59, 136.33, 140.70, 142.29, 148.21, 152.59, 192.78. ESI-MS: *m/z* 353[M+H]$^{+}$.

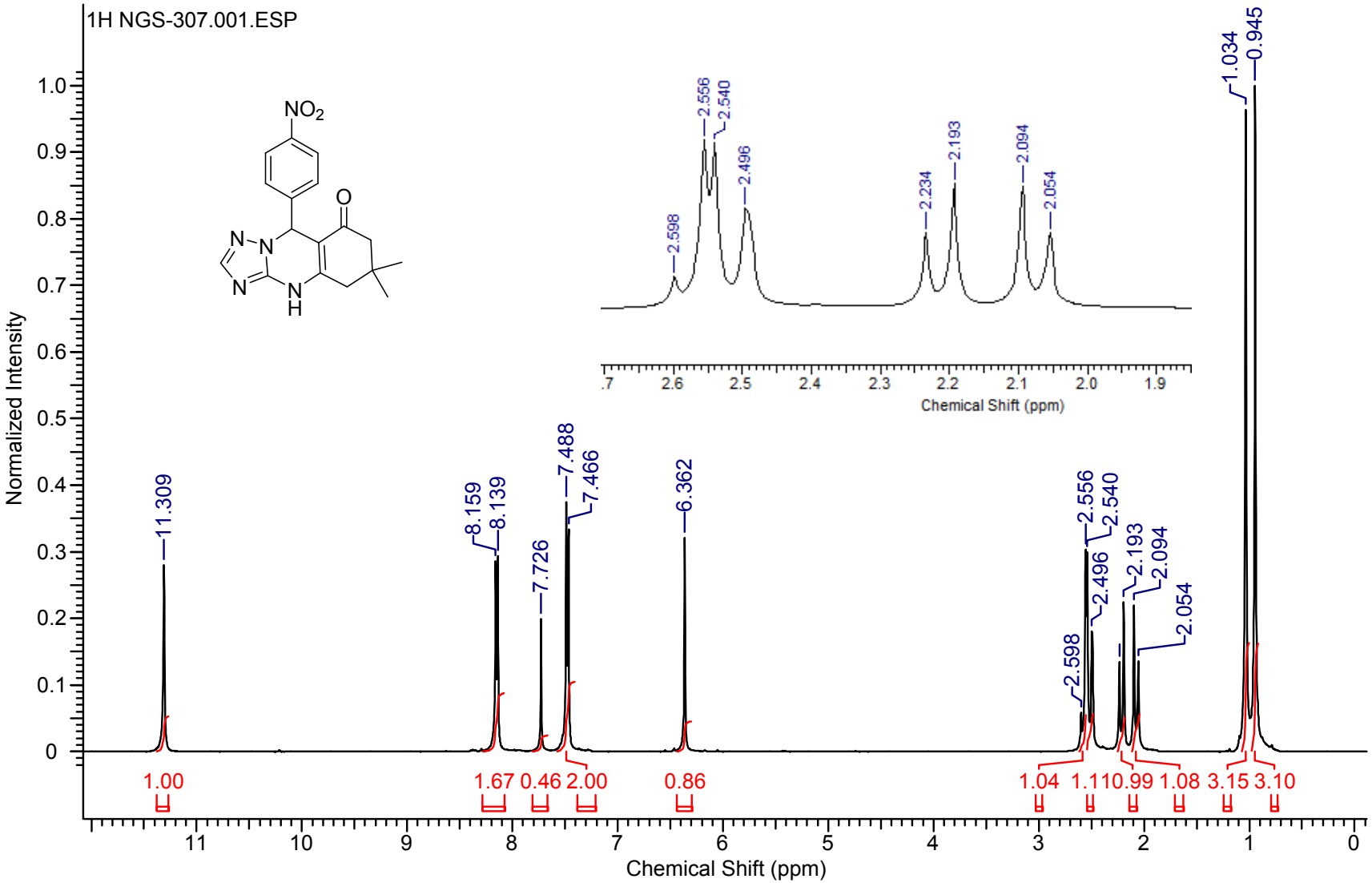
5a


1H NGS-288.001.ESP
Normalized Intensity
Chemical Shift (ppm)
11.138
7.677
7.290
7.272
7.186
7.167
6.194
2.587
2.543
2.521
2.234
2.191
2.089
2.048
1.033
0.950
1.00
0.42
4.97
0.83
1.90
1.12
1.10
3.03
3.09

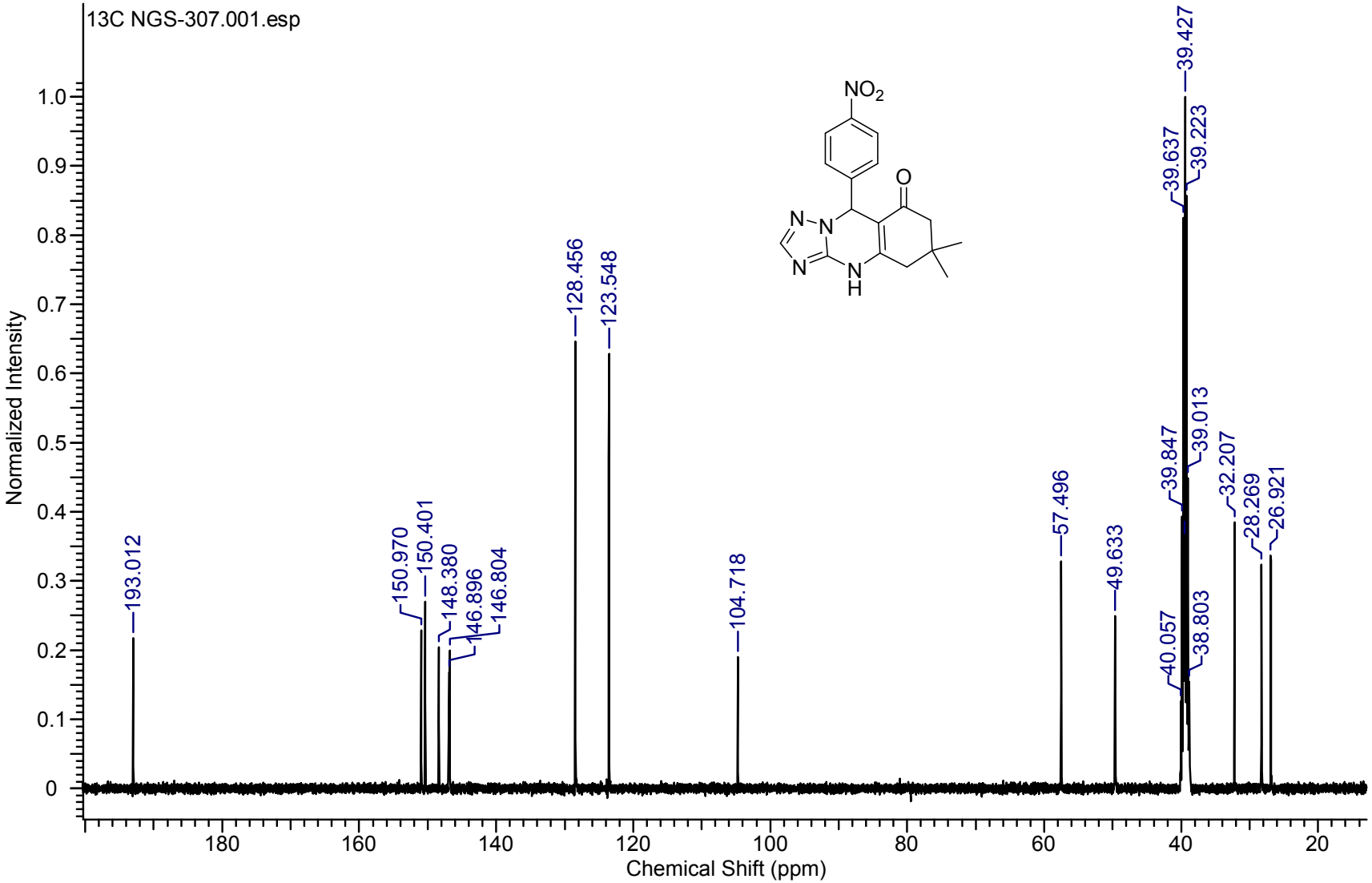
5a


13C NGS-288.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.963
150.389
150.024
146.816
141.555
128.234
126.917
105.565
57.892
49.738
39.835
39.625
39.415
39.211
39.000
32.163
28.454
26.773

5b


1H NGS-307.001.ESP
NO2
O
N
N
N
H
Normalized Intensity
Chemical Shift (ppm)
11.309
8.159
8.139
7.726
7.488
7.466
6.362
2.598
2.556
2.540
2.496
2.234
2.193
2.094
2.054
1.034
0.945
1.00
1.67
0.46
2.00
0.86
1.04
1.11
0.99
1.08
3.15
3.10

5b


13C NGS-307.001.esp
Normalized Intensity
Chemical Shift (ppm)
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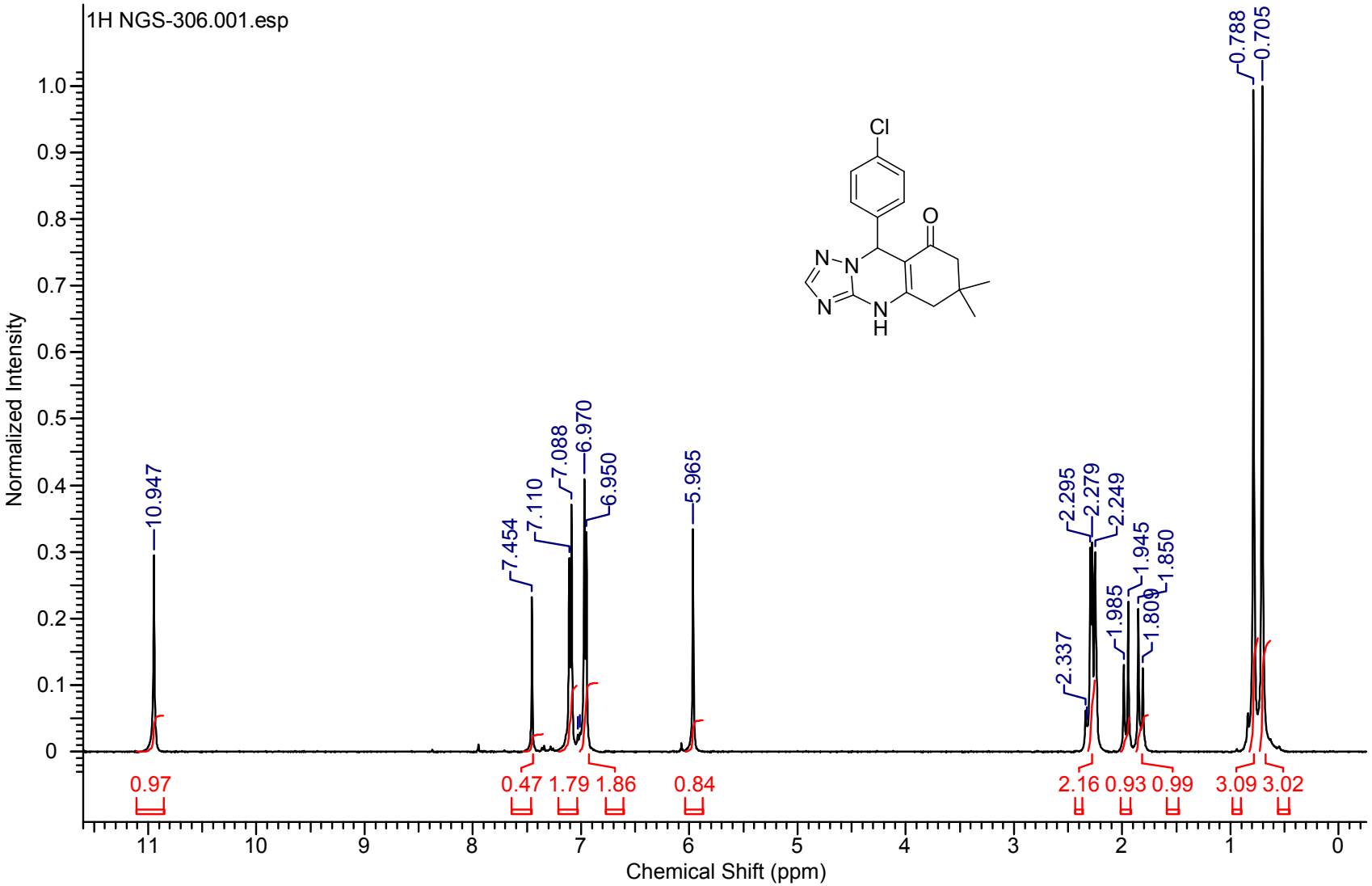
150.401
148.380
146.896
146.804
128.456
123.548
104.718
57.496
49.633
40.057
39.847
39.637
39.427
39.223
39.013
38.803
32.207
28.269
26.921
NO2
O
N
N
N
H

5c


1H NGS-306.001.esp
Normalized Intensity
Chemical Shift (ppm)
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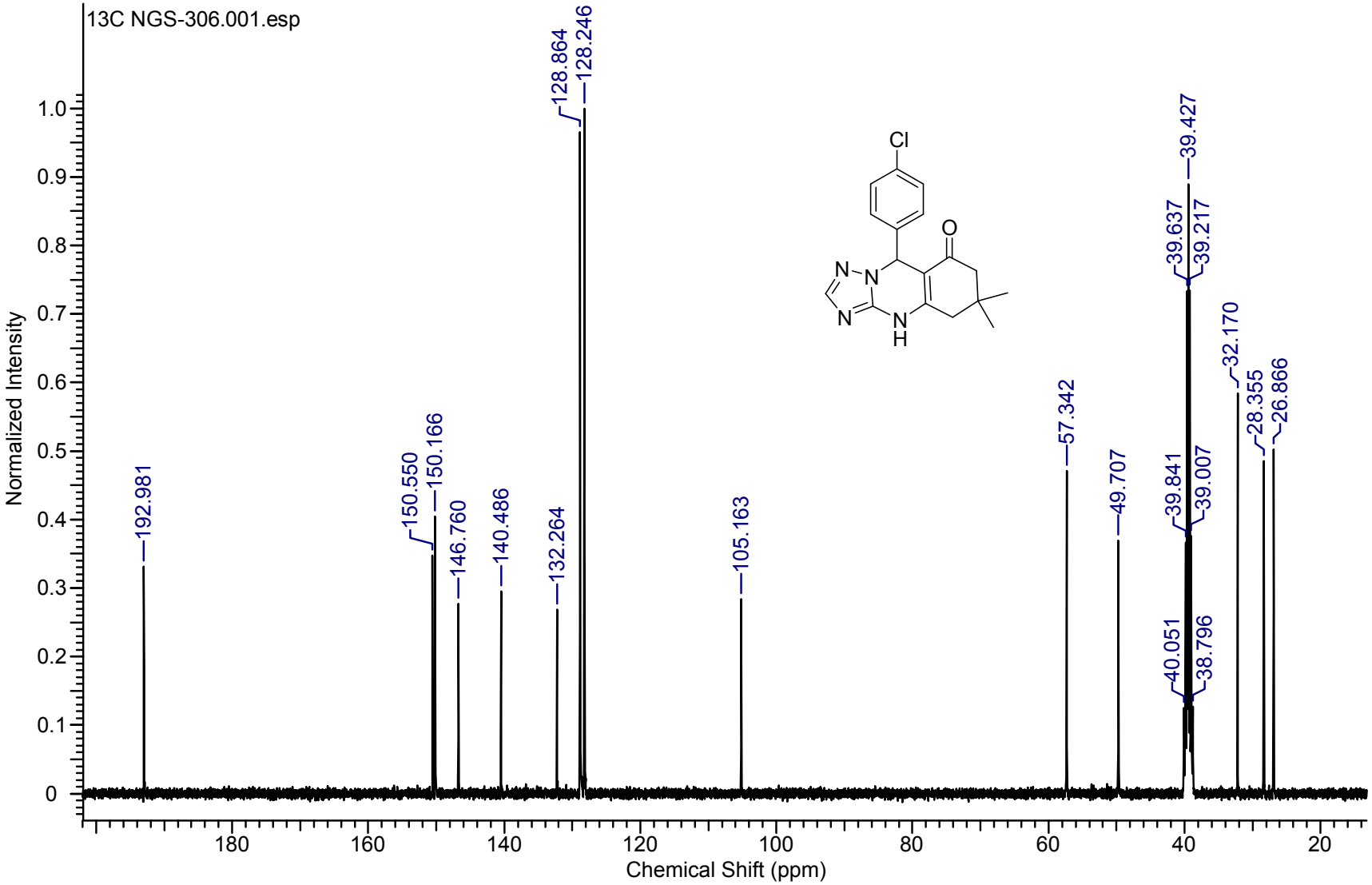
7.110
7.088
6.970
6.950
5.965
2.337
2.295
2.279
2.249
1.985
1.945
1.850
1.809
0.788
0.705
0.97
0.47
1.79
1.86
0.84
2.16
0.93
0.99
3.09
3.02
Cl
O
N
N
N
N
H

5c


13C NGS-306.001.esp
Normalized Intensity
Chemical Shift (ppm)
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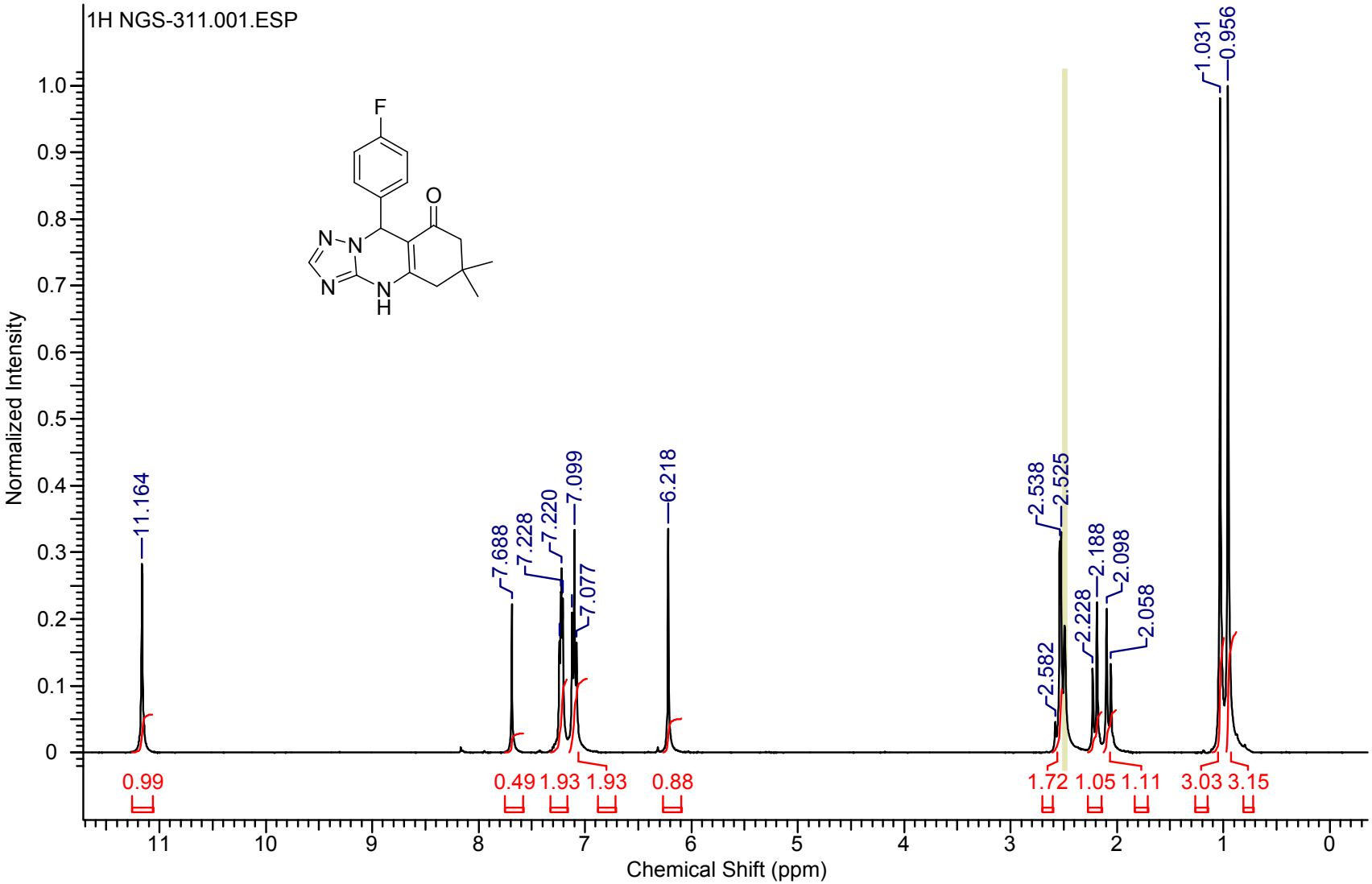
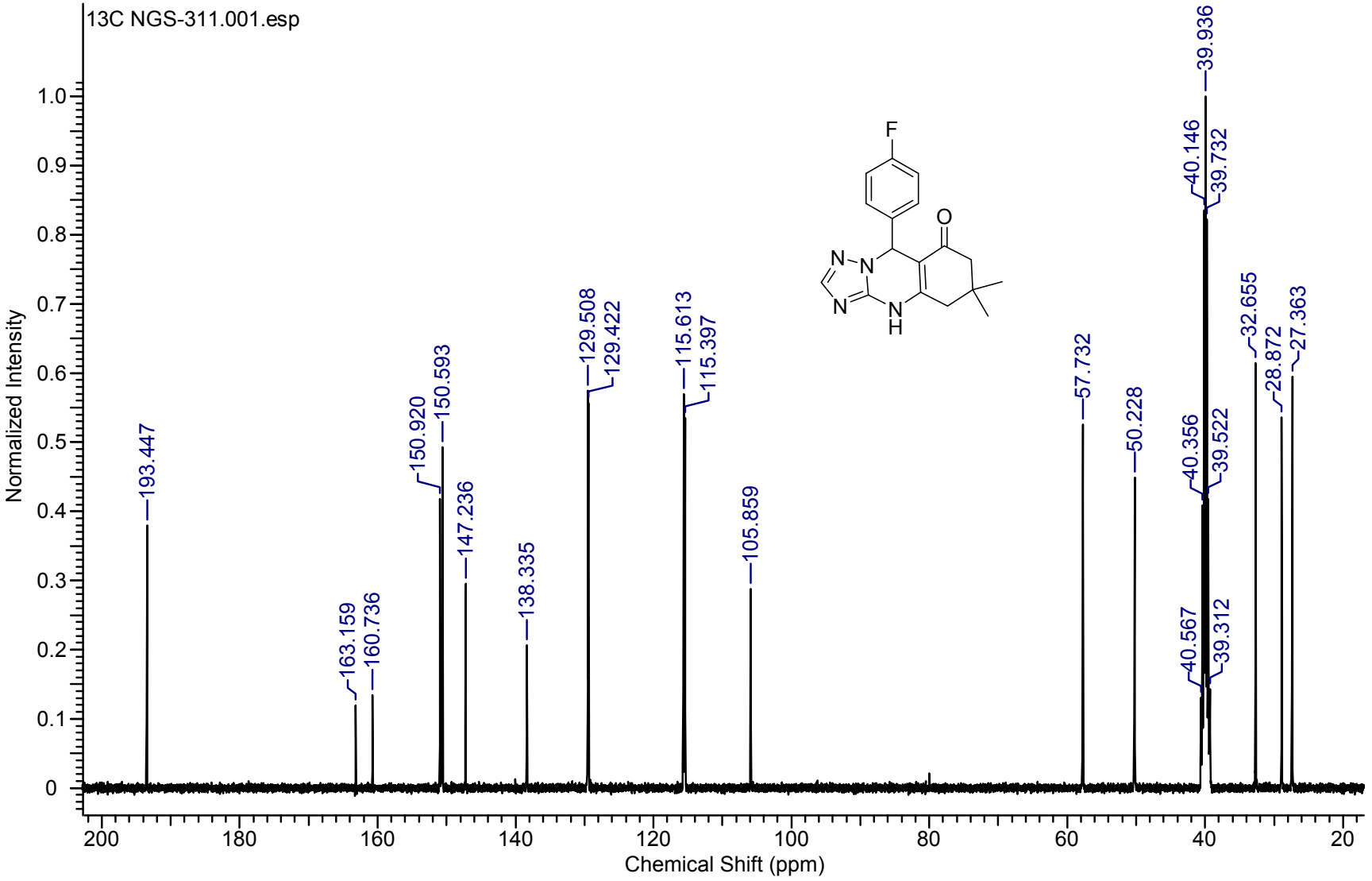
150.166
146.760
140.486
132.264
128.864
128.246
105.163
57.342
49.707
40.051
39.841
39.637
39.427
39.217
39.007
38.796
32.170
28.355
26.866
Cl
O
N
N
N
H

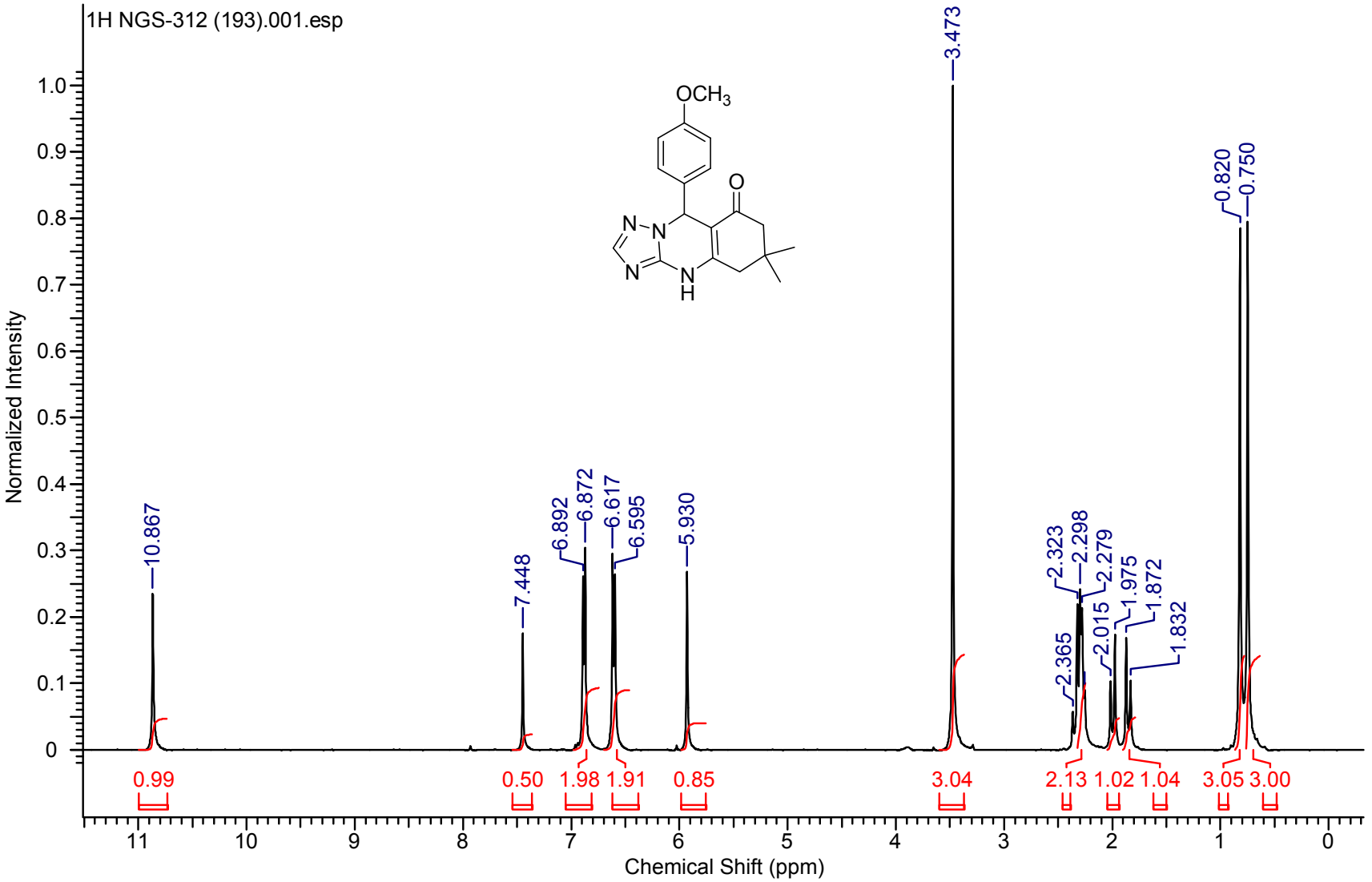
5d


1H NGS-311.001.ESP
F
O
N
N
N
N
H
Normalized Intensity
Chemical Shift (ppm)
11.164
7.688
7.228
7.220
7.099
7.077
6.218
2.538
2.525
2.582
2.228
2.188
2.098
2.058
1.031
0.956
0.99
0.49
1.93
1.93
0.88
1.72
1.05
1.11
3.03
3.15

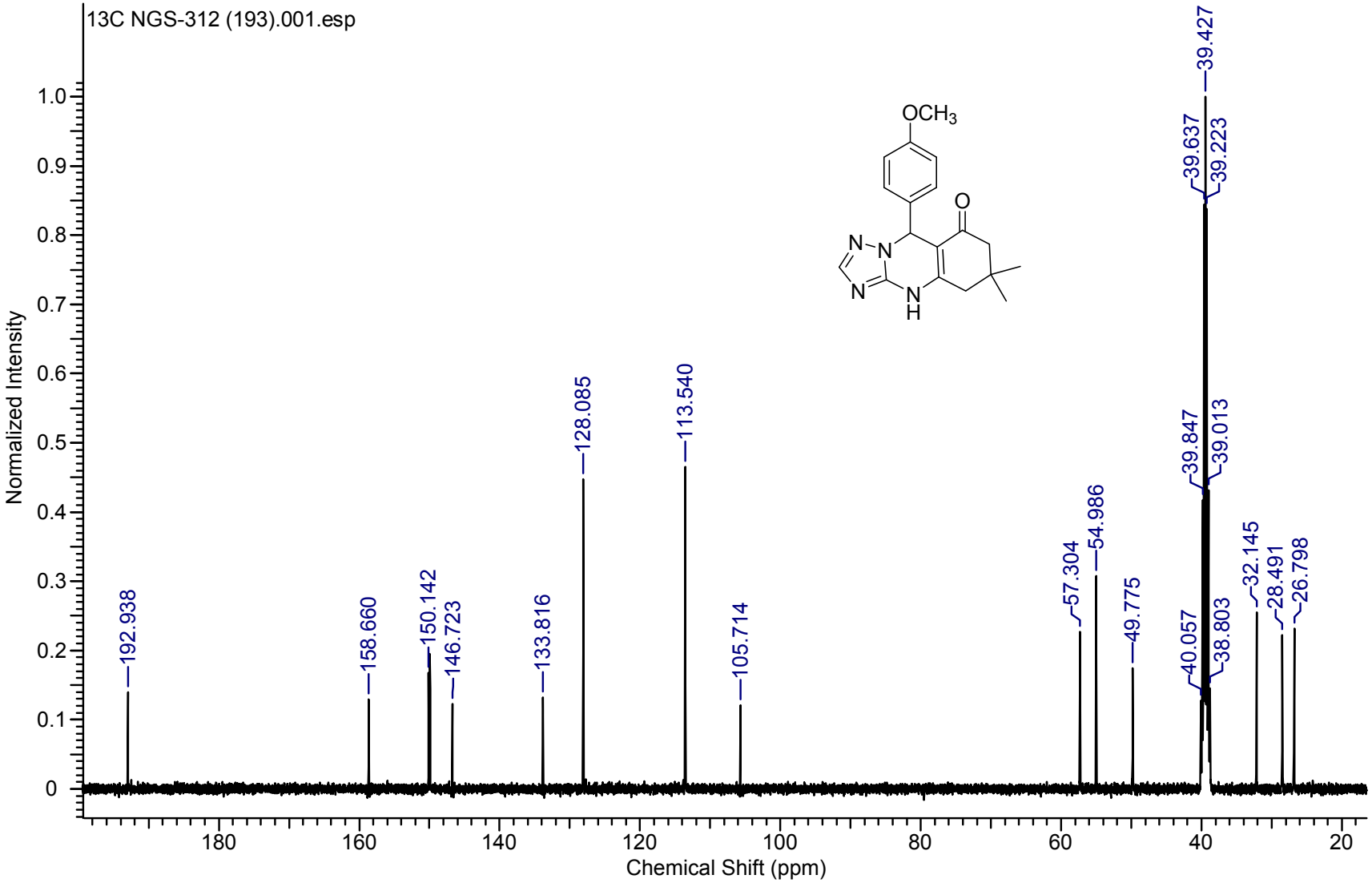
5d


13C NGS-311.001.esp
Normalized Intensity
Chemical Shift (ppm)
193.447
163.159
160.736
150.920
150.593
147.236
138.335
129.508
129.422
115.613
115.397
105.859
57.732
50.228
40.567
40.356
40.146
39.936
39.732
39.522
39.312
32.655
28.872
27.363
F
O
N
N
N
N
H

5e


1H NGS-312 (193).001.esp
OCH3
O
N
N
N
N
H
Normalized Intensity
Chemical Shift (ppm)
10.867
7.448
6.892
6.872
6.617
6.595
5.930
3.473
2.323
2.298
2.279
2.365
2.015
1.975
1.872
1.832
0.820
0.750
0.99
0.50
1.98
1.91
0.85
3.04
2.13
1.02
1.04
3.05
3.00

5e


13C NGS-312 (193).001.esp
Normalized Intensity
Chemical Shift (ppm)
192.938
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150.142
146.723
133.816
128.085
113.540
105.714
57.304
54.986
49.775
40.057
39.847
39.637
39.427
39.223
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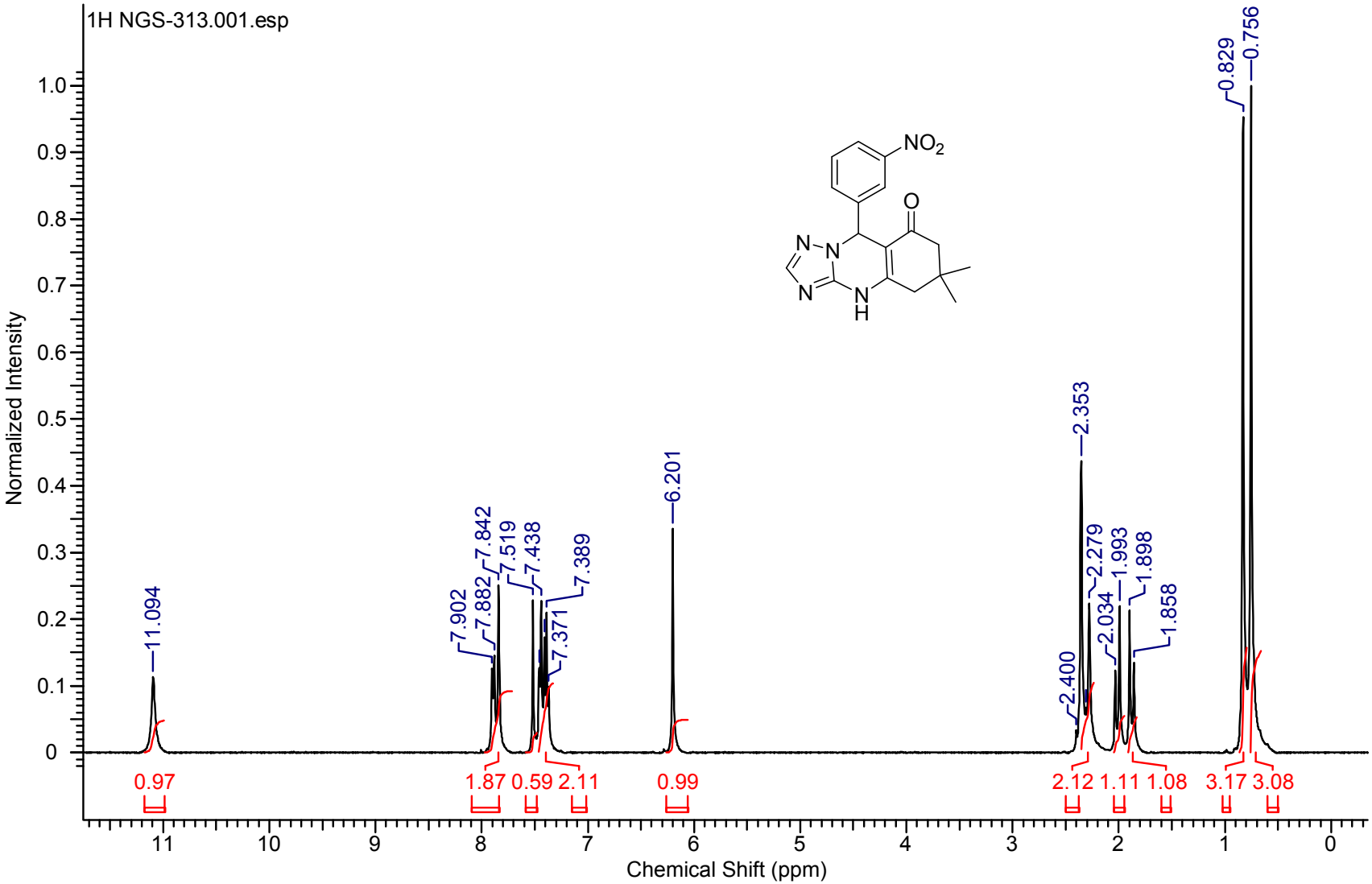
38.803
32.145
28.491
26.798
OCH3
O
N
N
N
N
H

5f


1H NGS-313.001.esp
Normalized Intensity
Chemical Shift (ppm)
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7.882
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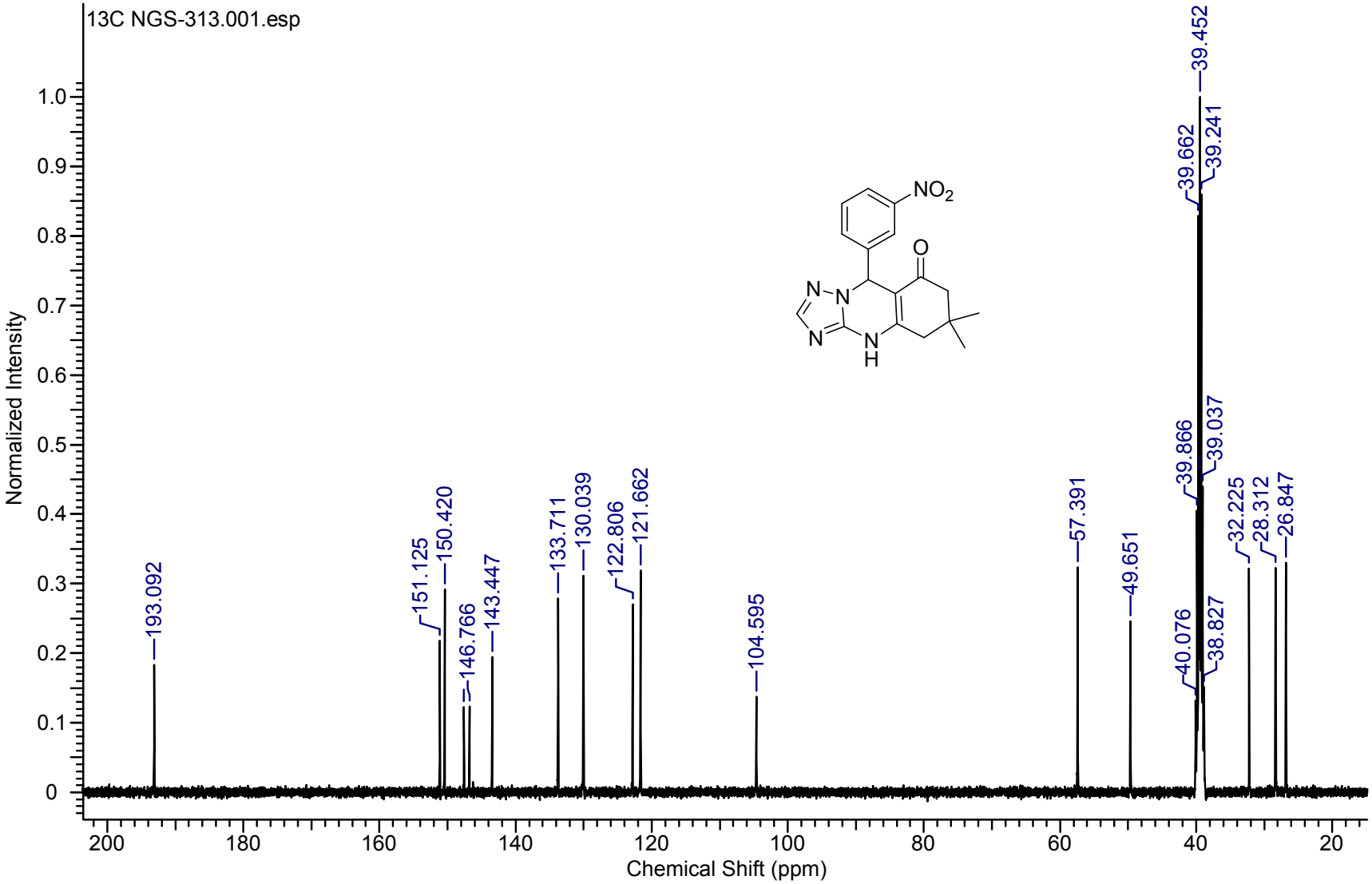
7.519
7.438
7.389
7.371
6.201
2.400
2.353
2.279
2.034
1.993
1.898
1.858
0.829
0.756
0.97
1.87
0.59
2.11
0.99
2.12
1.11
1.08
3.17
3.08
NO2
O
N
N
N
H

5f


13C NGS-313.001.esp
Normalized Intensity
Chemical Shift (ppm)
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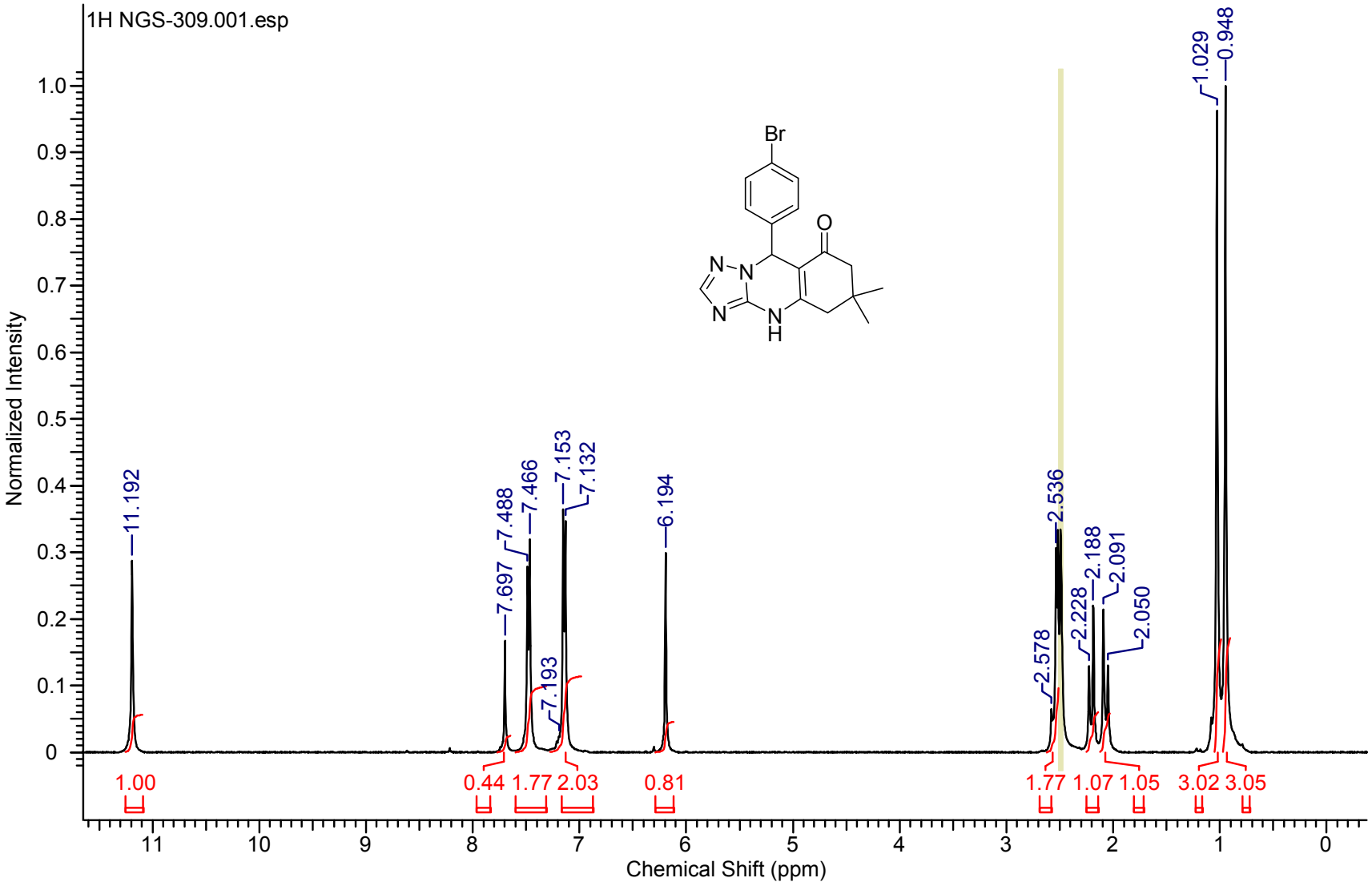
150.420
146.766
143.447
133.711
130.039
122.806
121.662
104.595
57.391
49.651
40.076
39.866
39.662
39.452
39.241
39.037
38.827
32.225
28.312
26.847
NO2
O
N
N
N
N
H

5g


1H NGS-309.001.esp
Normalized Intensity
Chemical Shift (ppm)
Br
O
N
N
N
N
H
11.192
7.697
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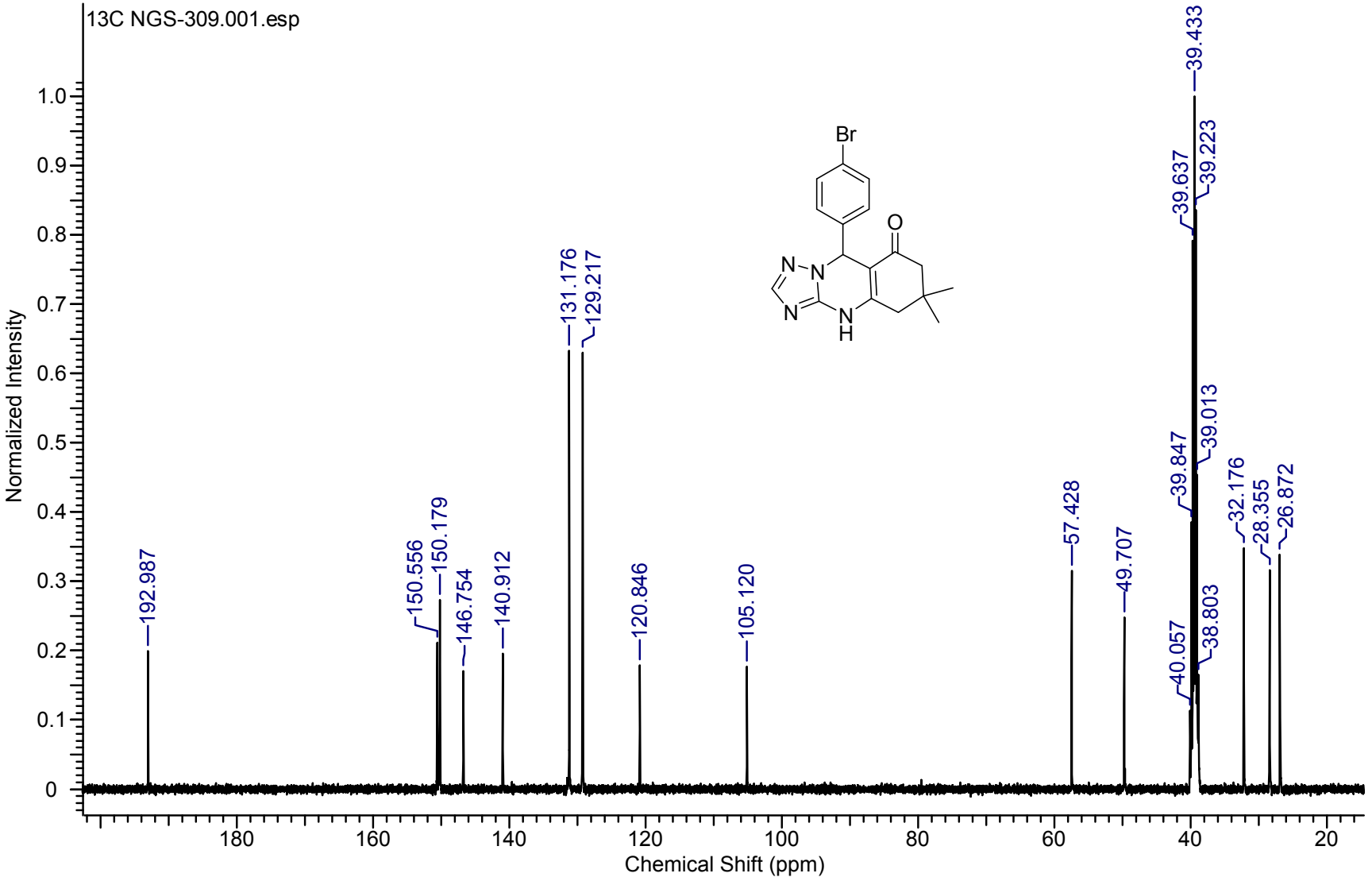
7.466
7.193
7.153
7.132
6.194
2.578
2.536
2.228
2.188
2.091
2.050
1.029
0.948
1.00
0.44
1.77
2.03
0.81
1.77
1.07
1.05
3.02
3.05

5g


13C NGS-309.001.esp
Normalized Intensity
Chemical Shift (ppm)
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140.912
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120.846
105.120
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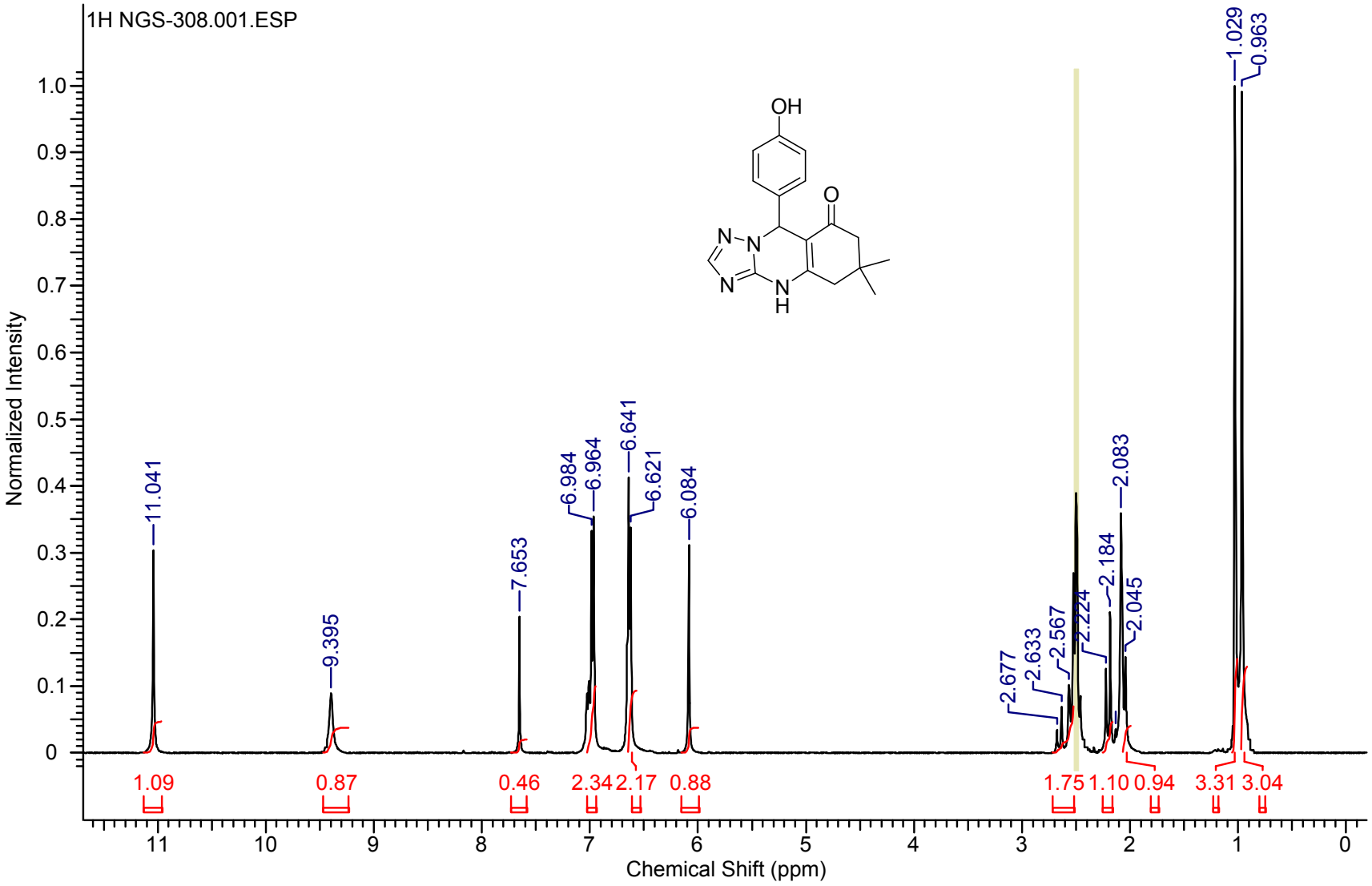
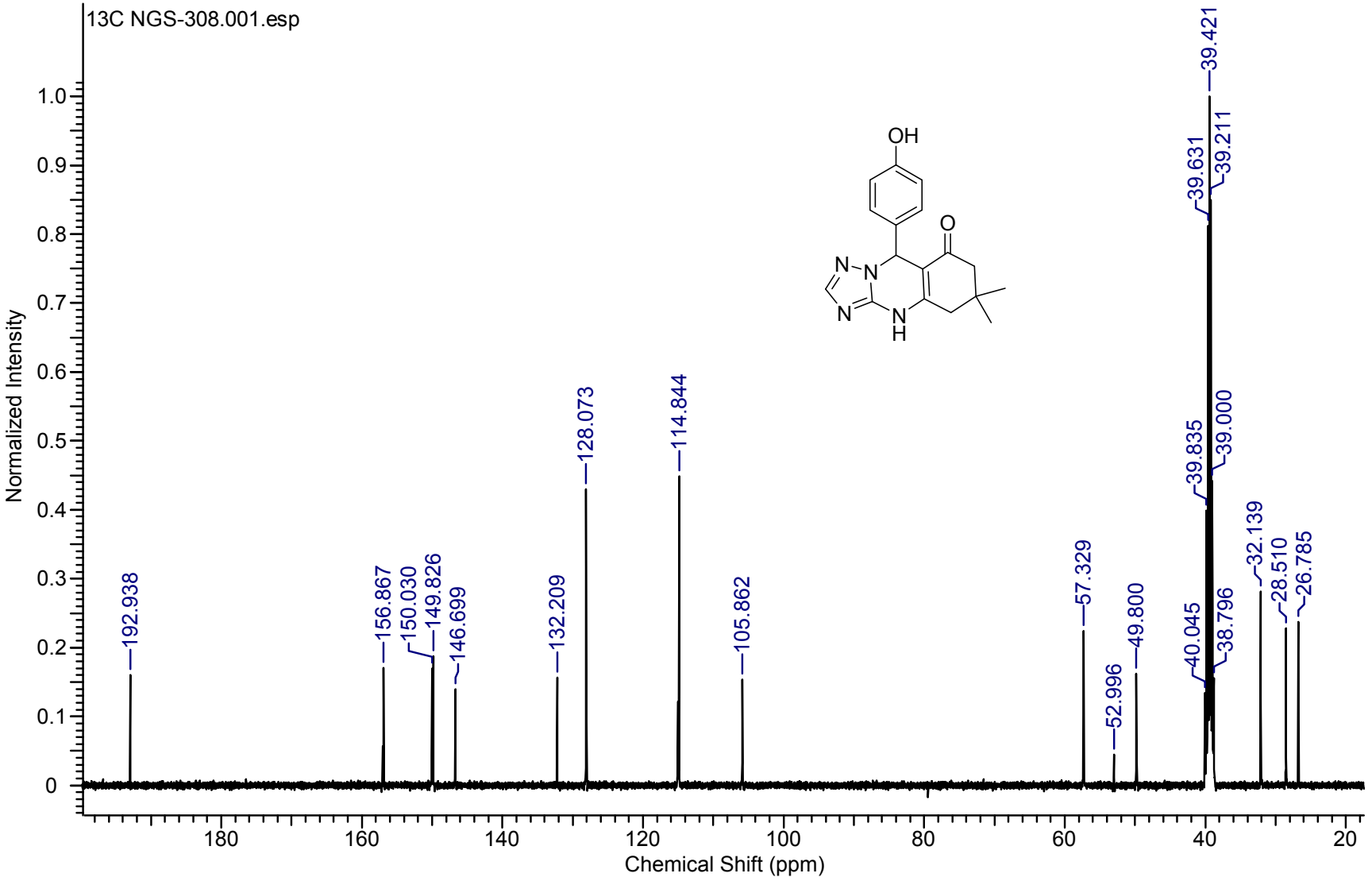
49.707
40.057
39.847
39.637
39.433
39.223
39.013
38.803
32.176
28.355
26.872
Br
O
N
N
N
N
H

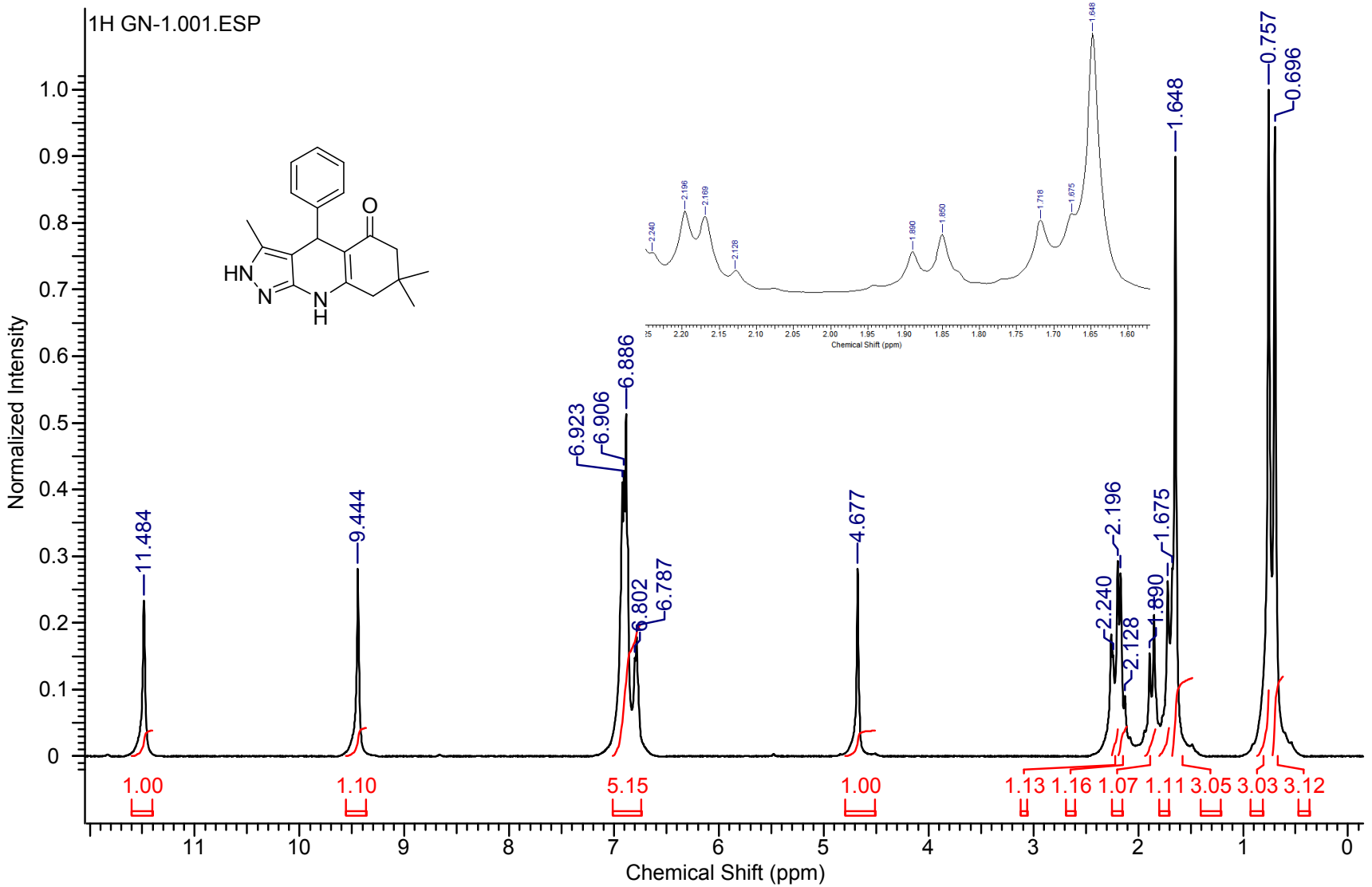
5h


1H NGS-308.001.ESP
Normalized Intensity
Chemical Shift (ppm)
11.041
9.395
7.653
6.984
6.964
6.641
6.621
6.084
2.677
2.633
2.567
2.224
2.184
2.083
2.045
1.029
0.963
1.09
0.87
0.46
2.34
2.17
0.88
1.75
1.10
0.94
3.31
3.04
OH
O
N
N
N
N
H

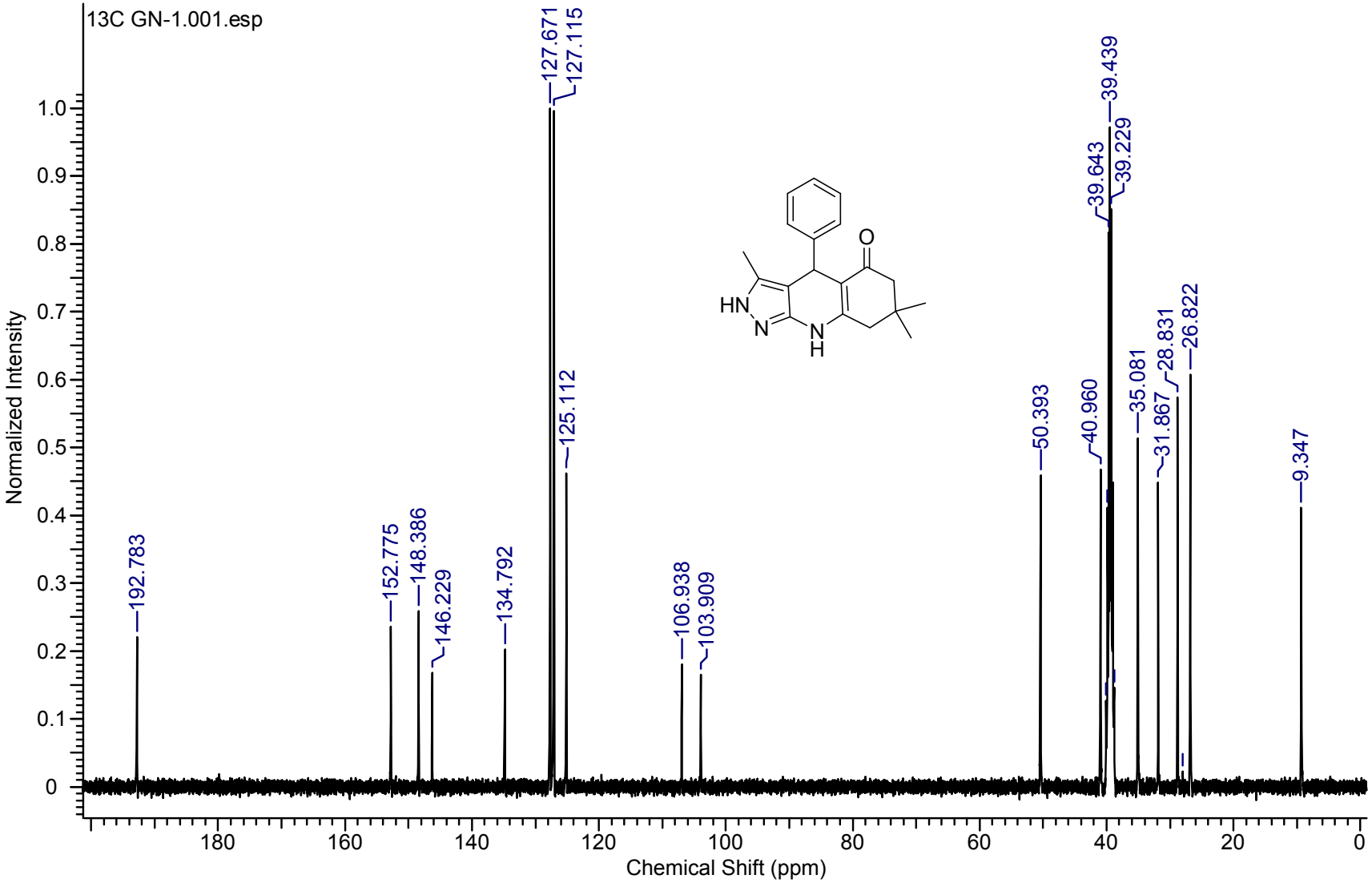
5h


13C NGS-308.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.938
156.867
150.030
149.826
146.699
132.209
128.073
114.844
105.862
57.329
52.996
49.800
40.045
39.835
39.631
39.421
39.211
39.000
38.796
32.139
28.510
26.785
OH
O
N
N
N
N
H

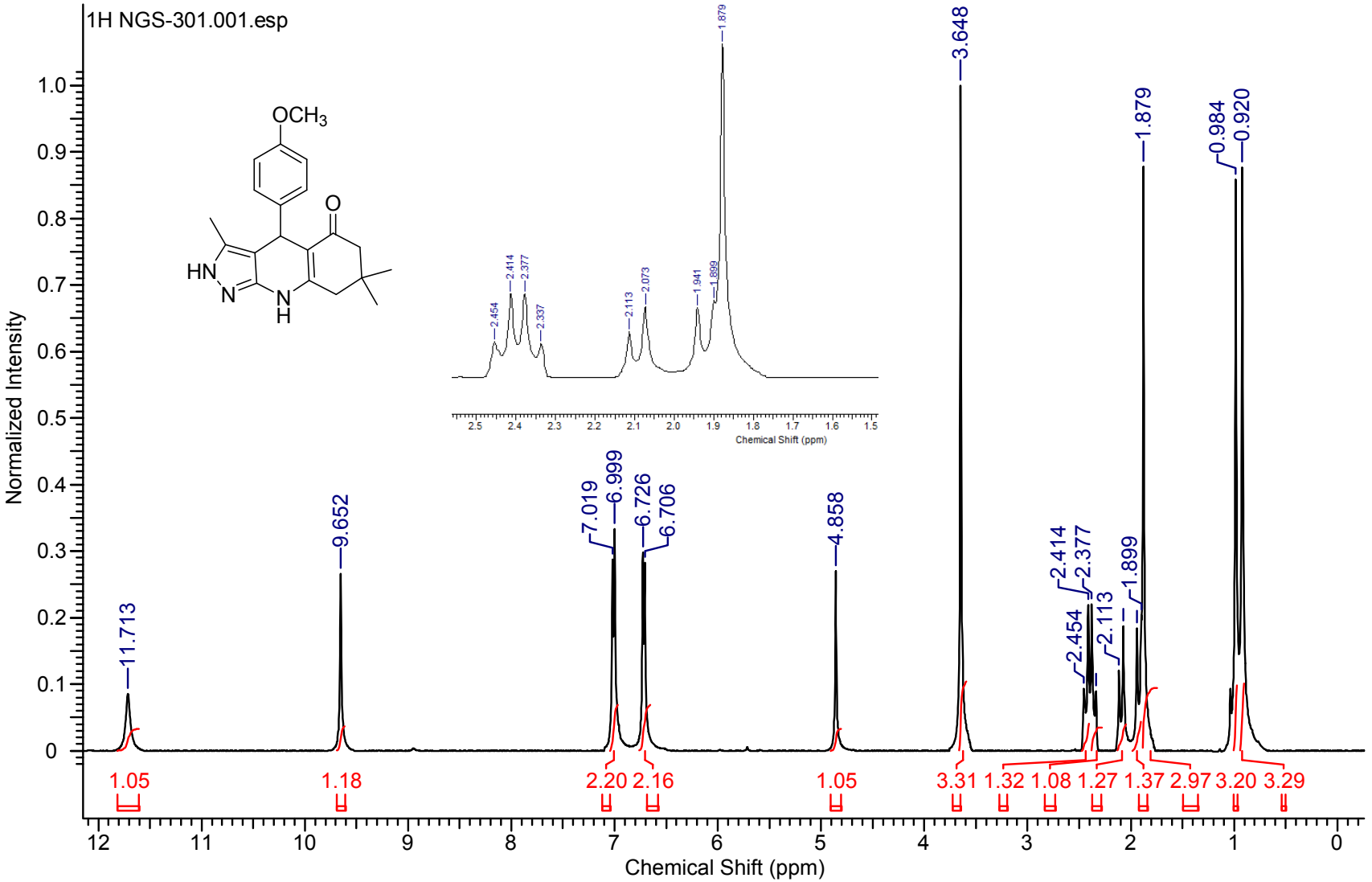
6a


1H GN-1.001.ESP
Normalized Intensity
Chemical Shift (ppm)
11.484
9.444
6.923
6.906
6.886
6.802
6.787
4.677
2.240
2.196
2.169
2.128
1.890
1.850
1.718
1.675
1.648
0.757
0.696
1.00
1.10
5.15
1.00
1.13
1.16
1.07
1.11
3.05
3.03
3.12
HN
N
N
H
O

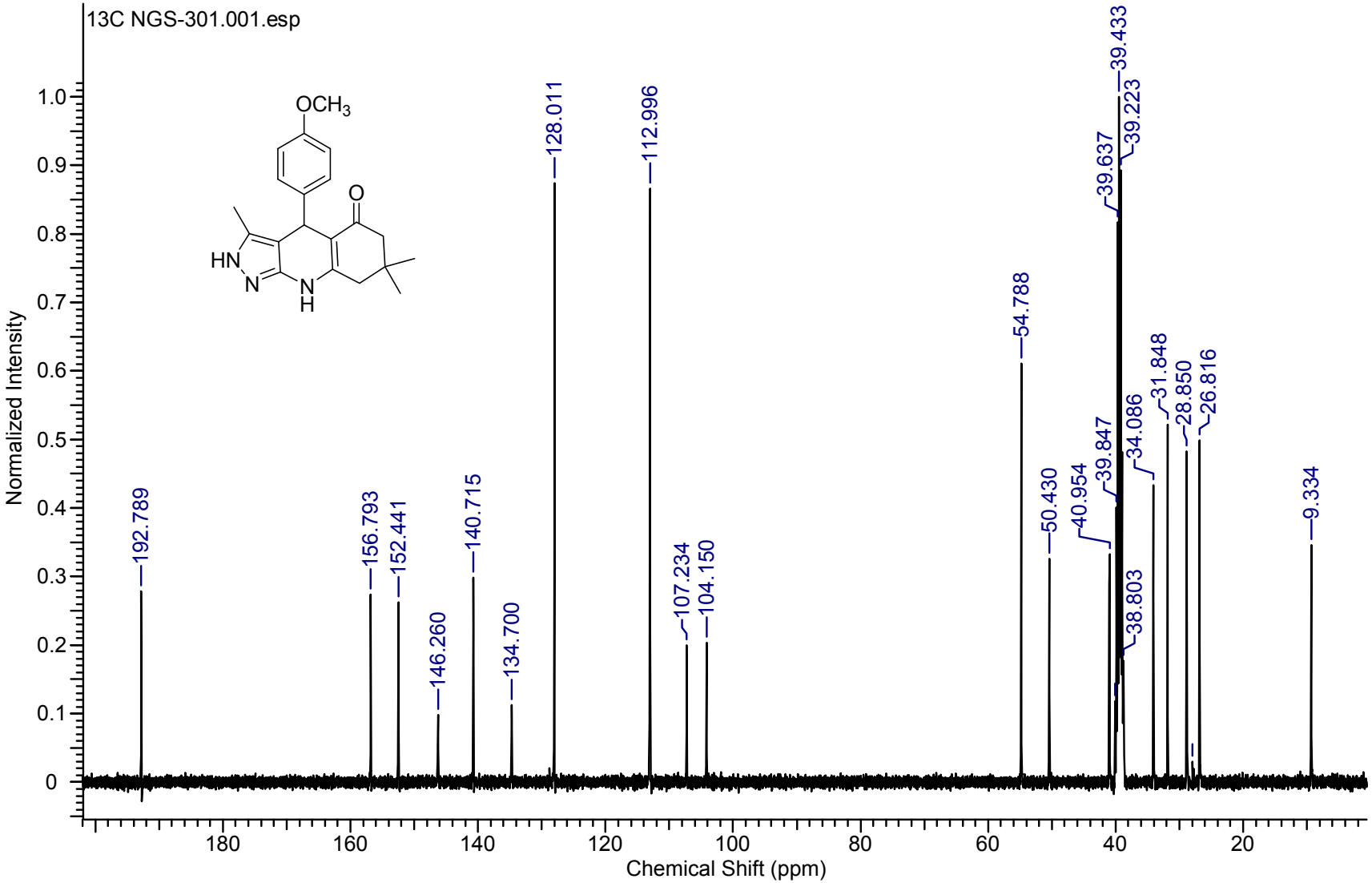
6a


13C GN-1.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.783
152.775
148.386
146.229
134.792
127.671
127.115
125.112
106.938
103.909
50.393
40.960
39.643
39.439
39.229
35.081
31.867
28.831
26.822
9.347
HN
N
N
H
O

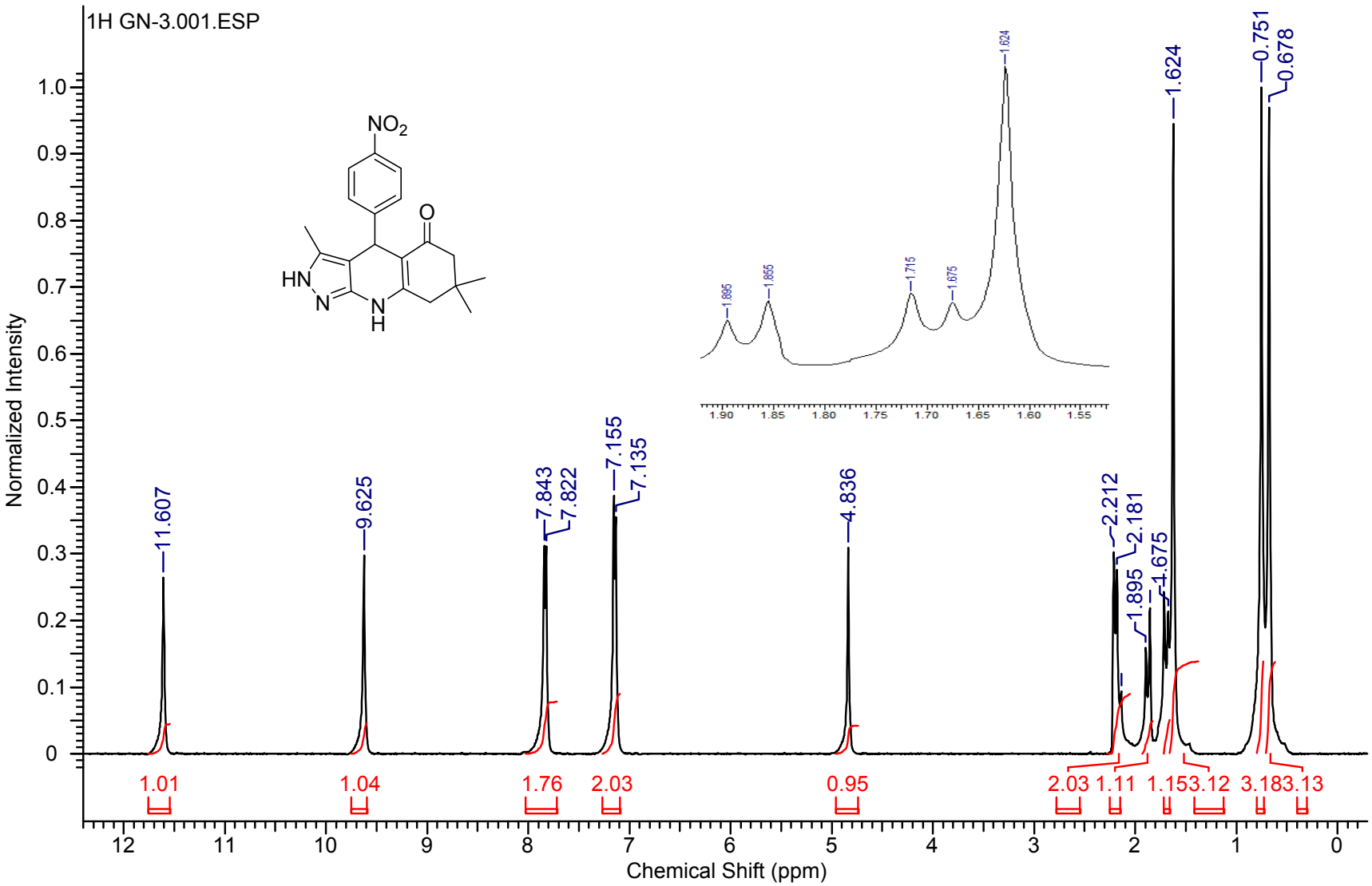
6b


1H NGS-301.001.esp
OCH3
O
HN
N
N
H
Normalized Intensity
Chemical Shift (ppm)
11.713
9.652
7.019
6.999
6.726
6.706
4.858
3.648
2.414
2.377
2.454
2.113
1.899
1.879
0.984
0.920
1.05
1.18
2.20
2.16
1.05
3.31
1.32
1.08
1.27
1.37
2.97
3.20
3.29

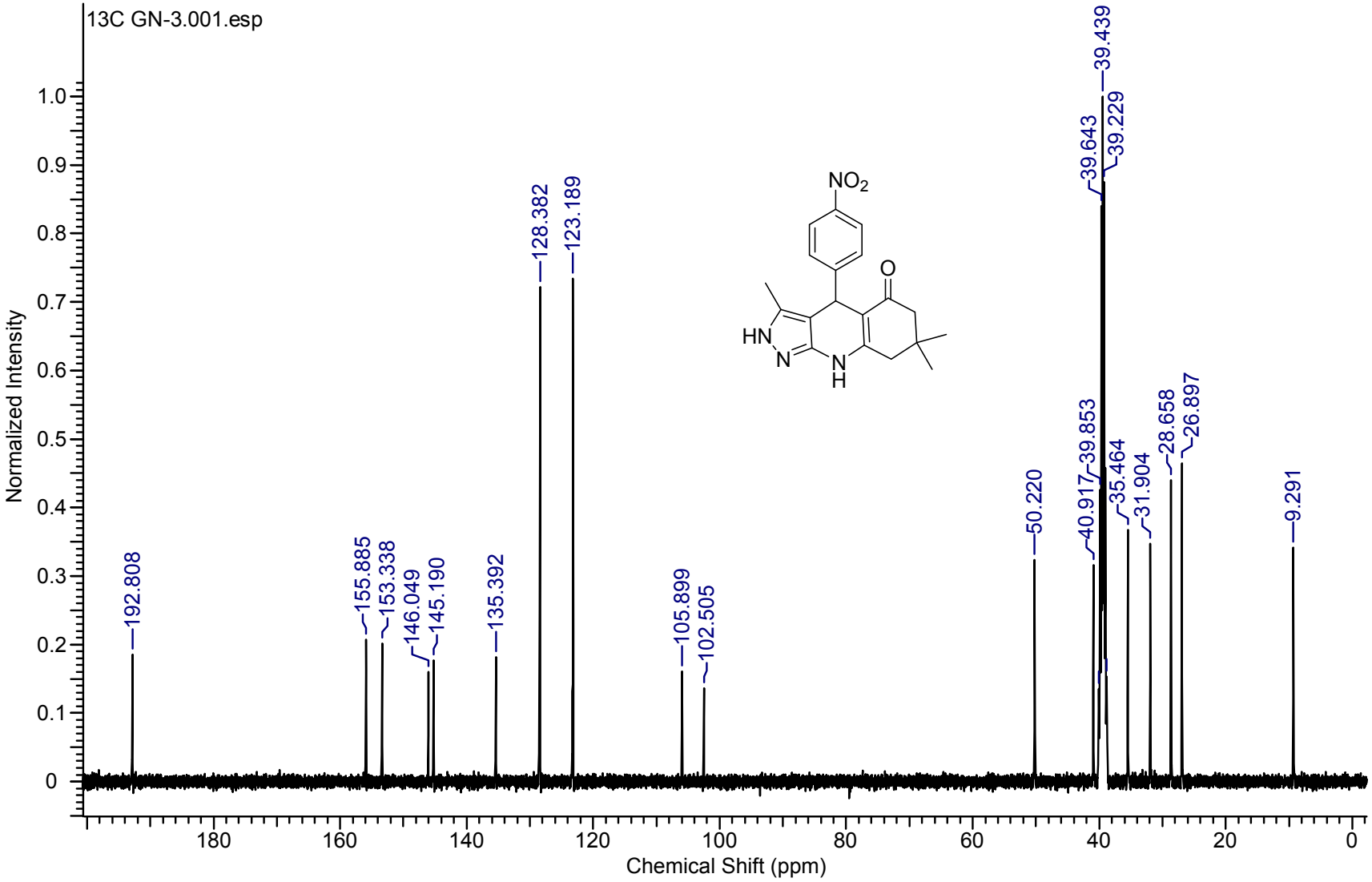
6b


13C NGS-301.001.esp
OCH3
O
HN
N
N
H
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
192.789
156.793
152.441
146.260
140.715
134.700
128.011
112.996
107.234
104.150
54.788
50.430
40.954
39.847
39.637
39.433
39.223
38.803
34.086
31.848
28.850
26.816
9.334
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

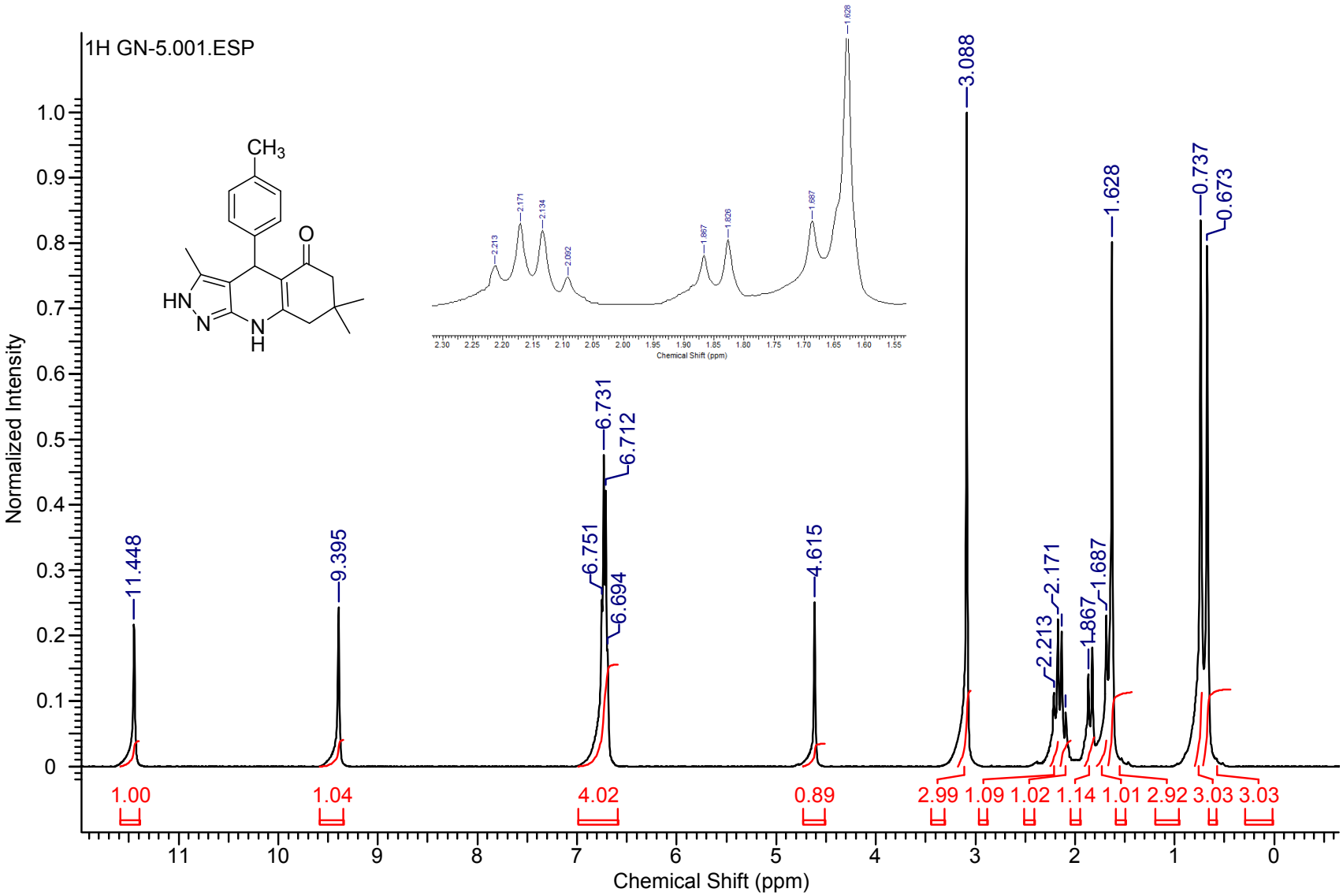
6c


1H GN-3.001.ESP
NO2
O
HN
N
N
H
Normalized Intensity
Chemical Shift (ppm)
11.607
9.625
7.843
7.822
7.155
7.135
4.836
2.212
2.181
1.895
1.675
1.624
0.751
0.678
1.01
1.04
1.76
2.03
0.95
2.03
1.11
1.15
3.12
3.18
3.13

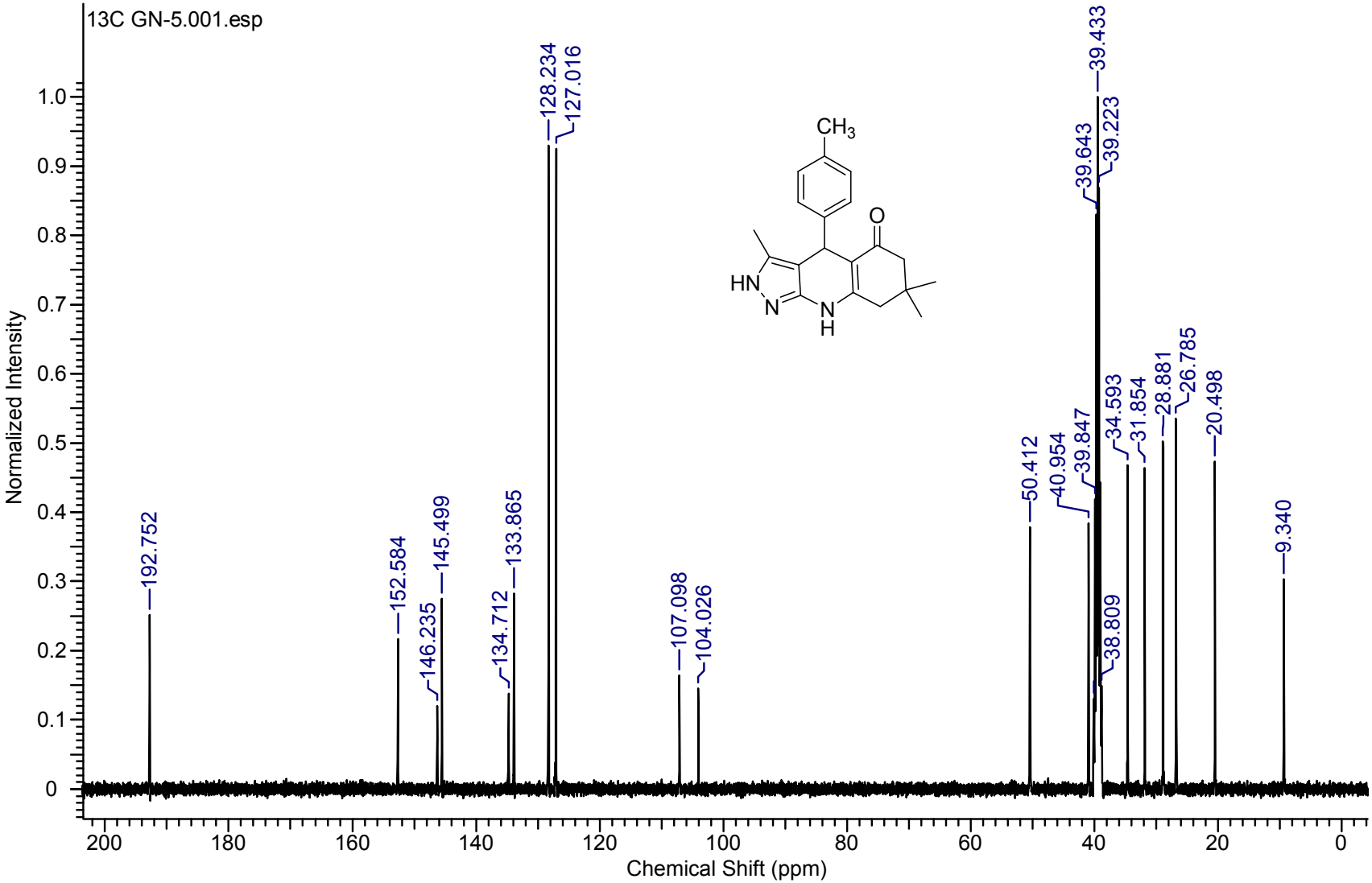
6c


13C GN-3.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.808
155.885
153.338
146.049
145.190
135.392
128.382
123.189
105.899
102.505
50.220
40.917
39.853
39.643
39.439
39.229
35.464
31.904
28.658
26.897
9.291
NO2
O
HN
N
N
H

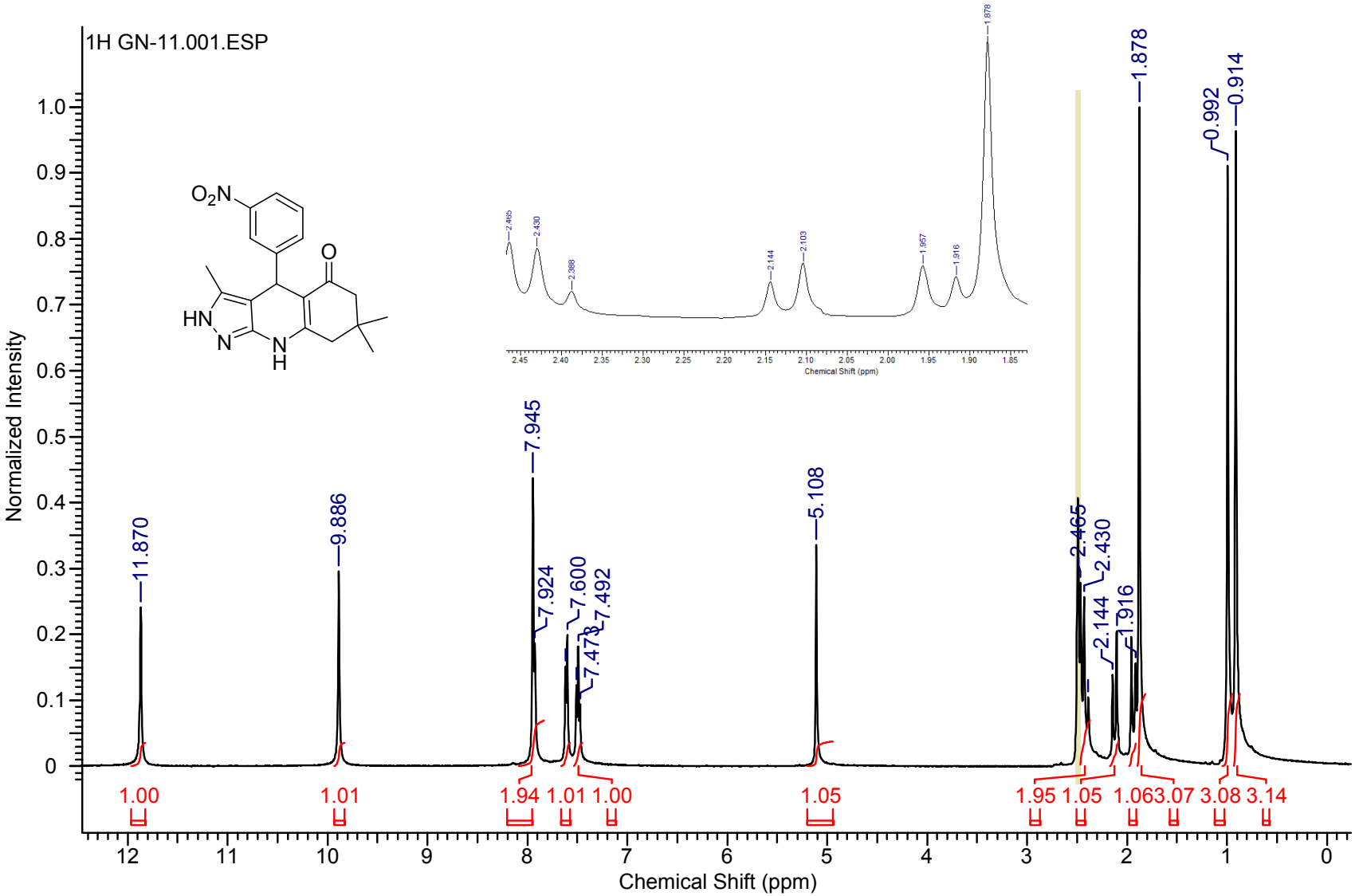
6d


1H GN-5.001.ESP
Normalized Intensity
Chemical Shift (ppm)
11.448
9.395
6.751
6.731
6.712
6.694
4.615
3.088
2.213
2.171
1.867
1.687
1.628
0.737
0.673
1.00
1.04
4.02
0.89
2.99
1.09
1.02
1.14
1.01
2.92
3.03
3.03

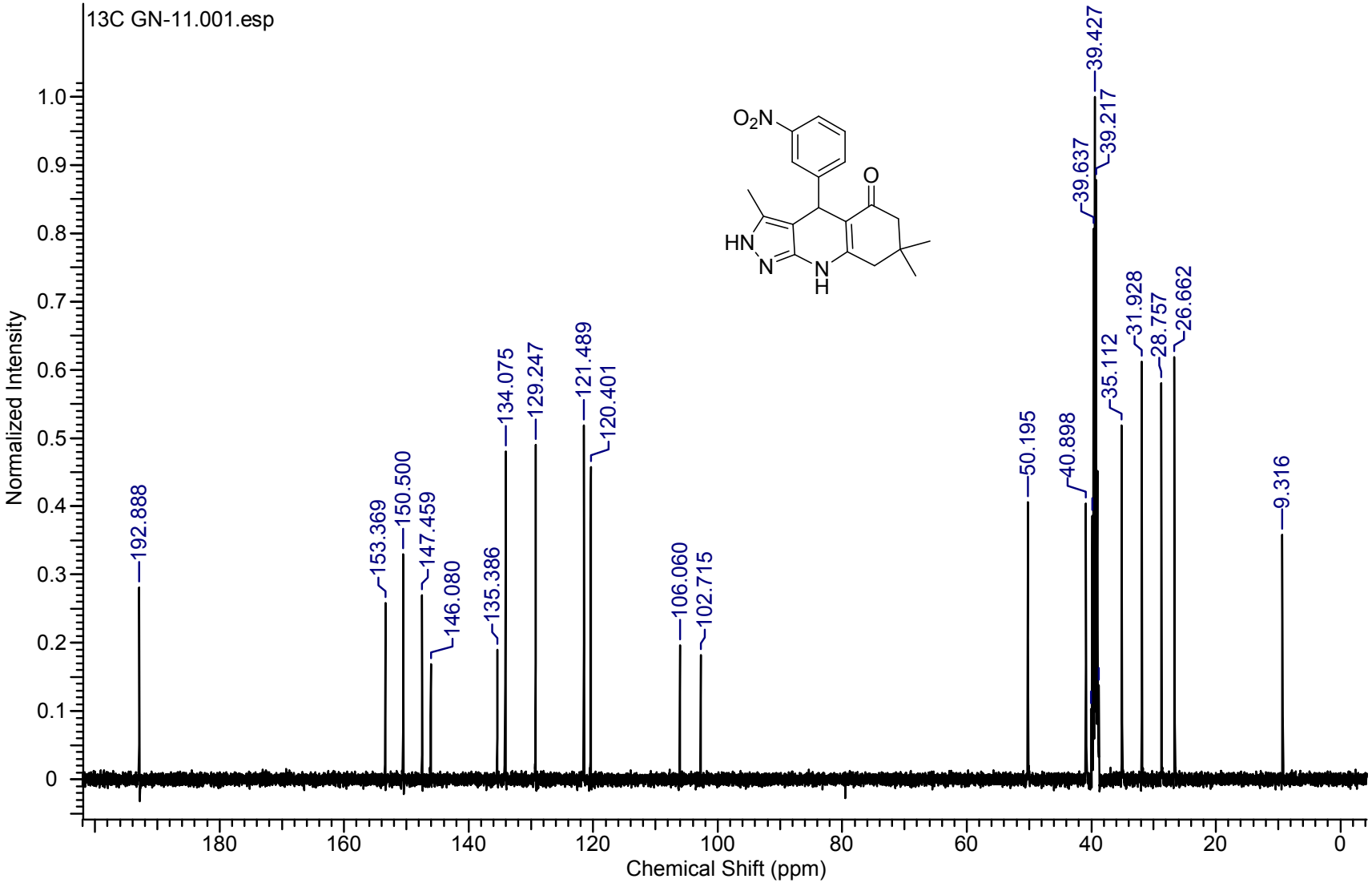
6d


13C GN-5.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.752
152.584
146.235
145.499
134.712
133.865
128.234
127.016
107.098
104.026
50.412
40.954
39.847
39.643
39.433
39.223
38.809
34.593
31.854
28.881
26.785
20.498
9.340
CH3
O
HN
N
N
H

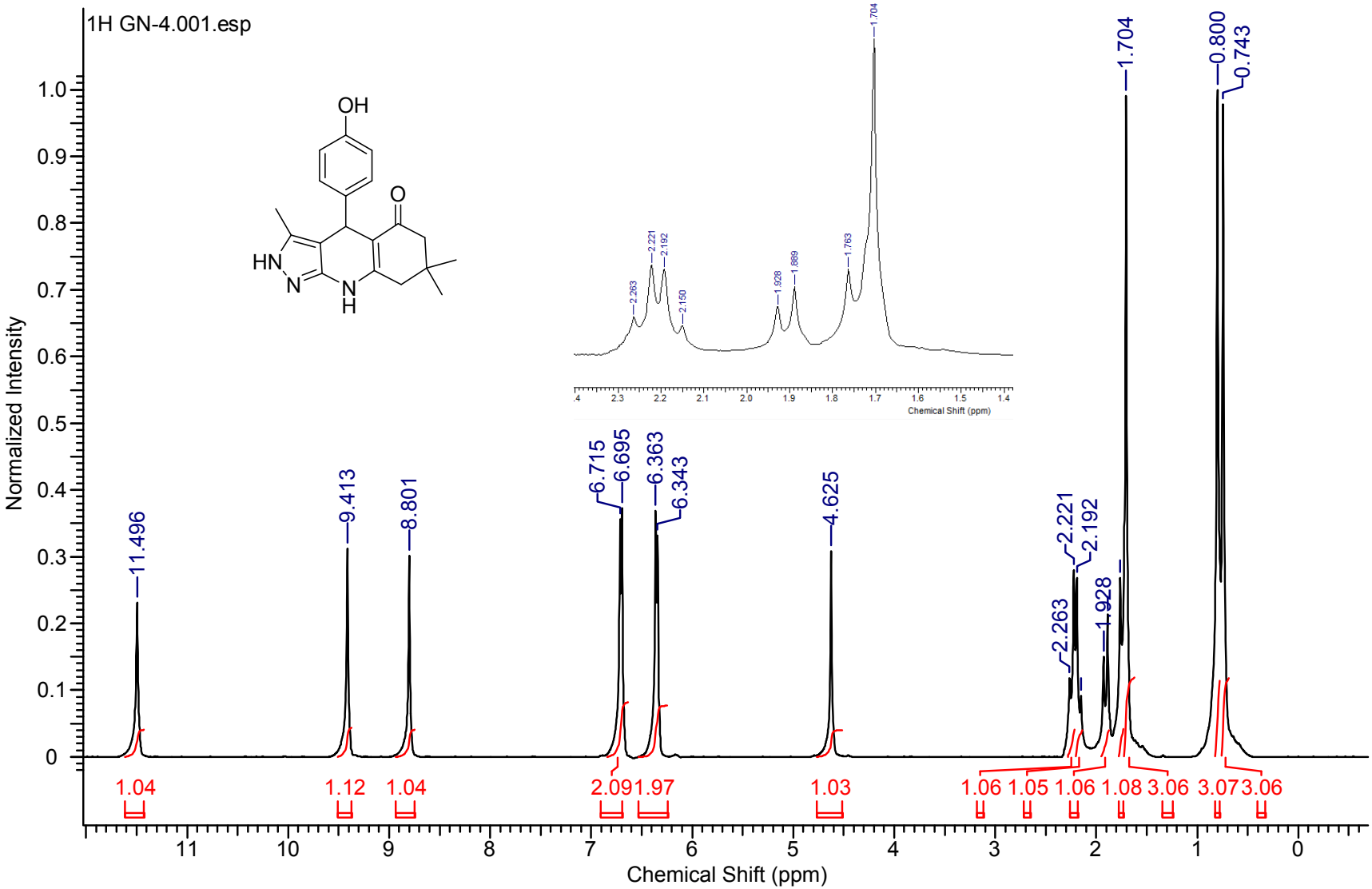
6e


1H GN-11.001.ESP
Normalized Intensity
Chemical Shift (ppm)
11.870
9.886
7.945
7.924
7.600
7.492
7.473
5.108
2.465
2.430
2.144
1.916
1.878
0.992
0.914
1.00
1.01
1.94
1.01
1.00
1.05
1.95
1.05
1.06
3.07
3.08
3.14
O2N
HN
N
N
H
O

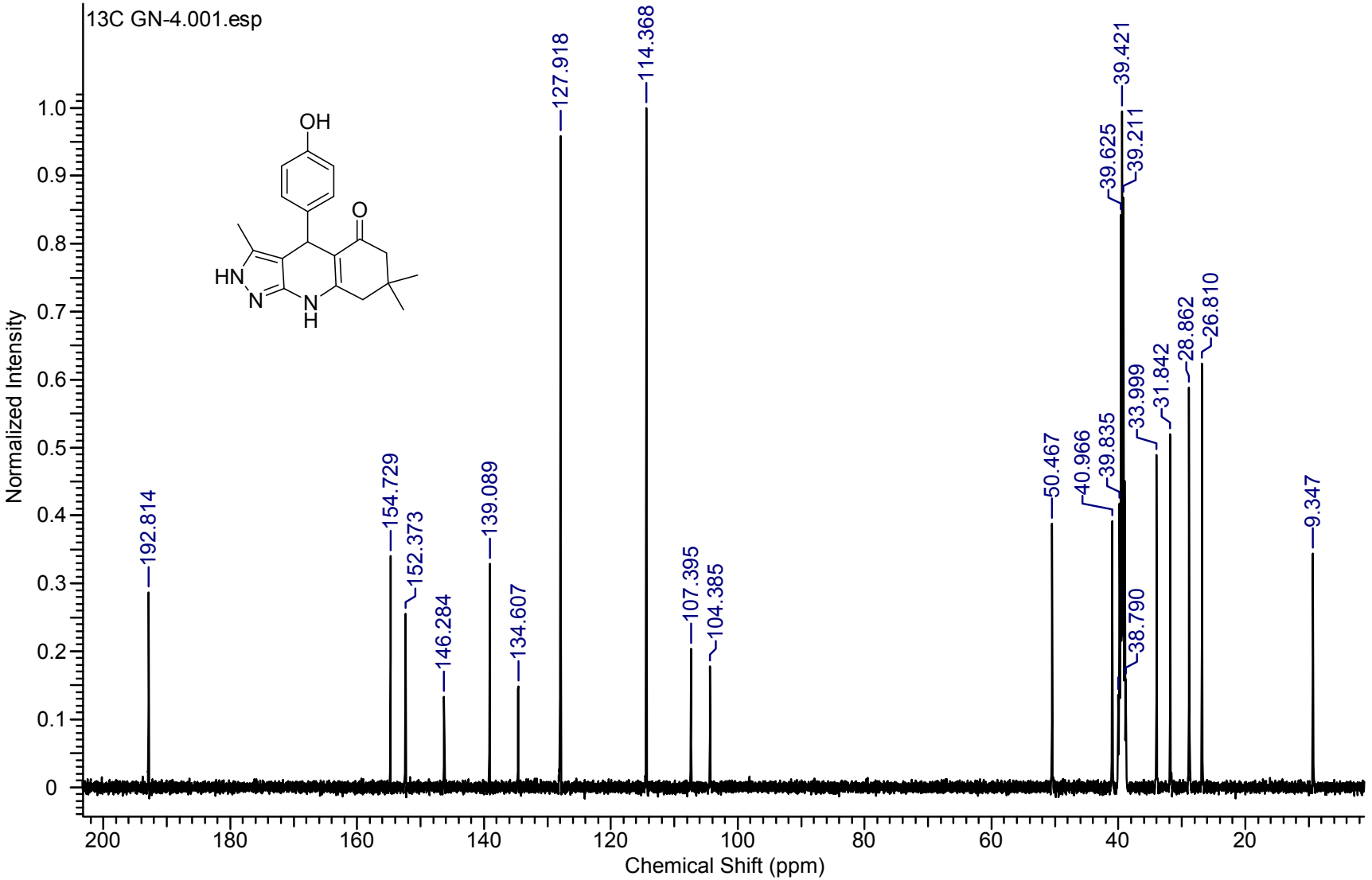
6e


13C GN-11.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.888
153.369
150.500
147.459
146.080
135.386
134.075
129.247
121.489
120.401
106.060
102.715
50.195
40.898
39.637
39.427
39.217
35.112
31.928
28.757
26.662
9.316
O2N
O
HN
N
N
H

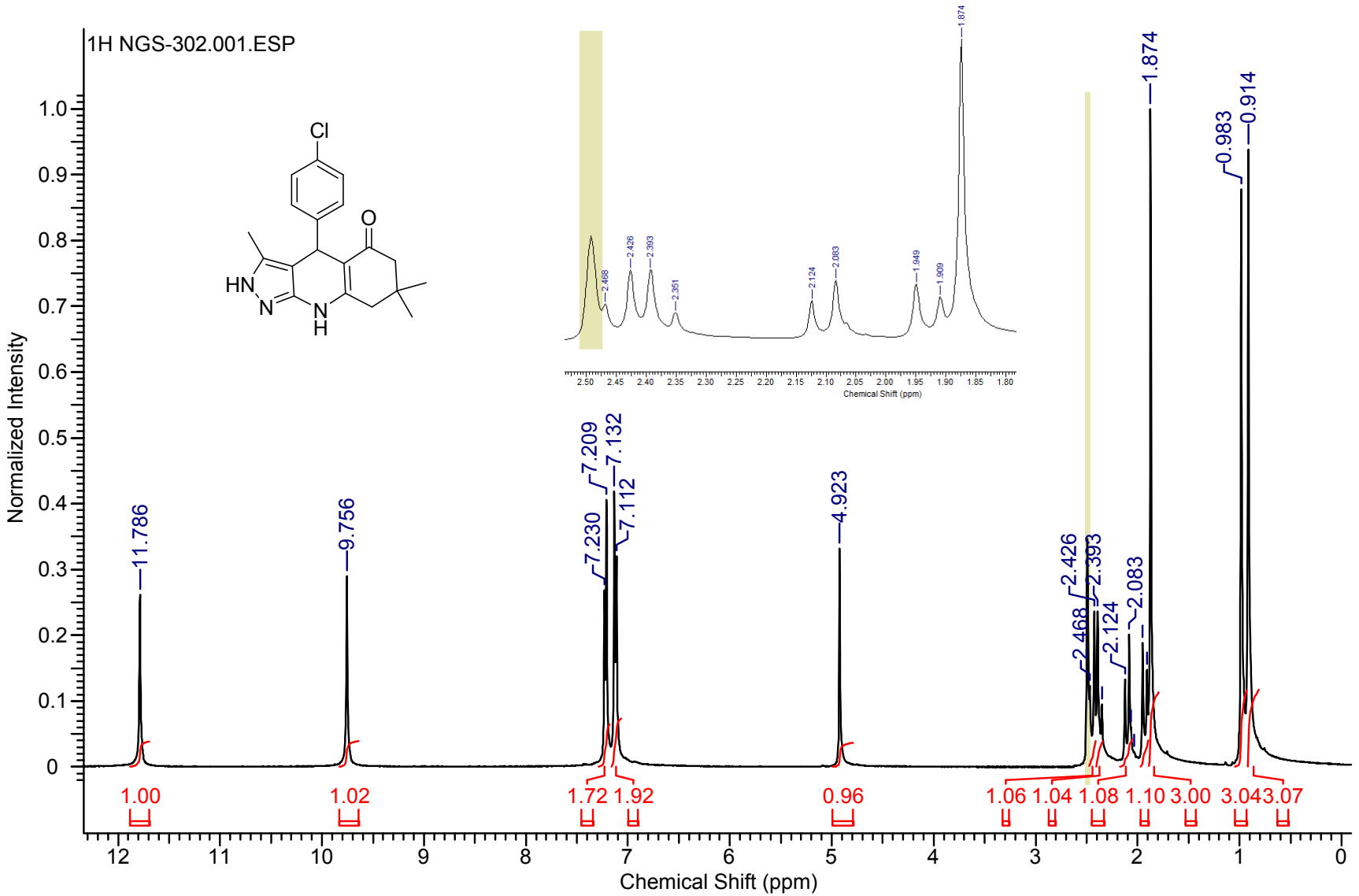
6f


1H GN-4.001.esp
OH
O
HN
N
N
H
Normalized Intensity
Chemical Shift (ppm)
11.496
9.413
8.801
6.715
6.695
6.363
6.343
4.625
2.263
2.221
2.192
1.928
1.704
0.800
0.743
1.04
1.12
1.04
2.09
1.97
1.03
1.06
1.05
1.06
1.08
3.06
3.07
3.06

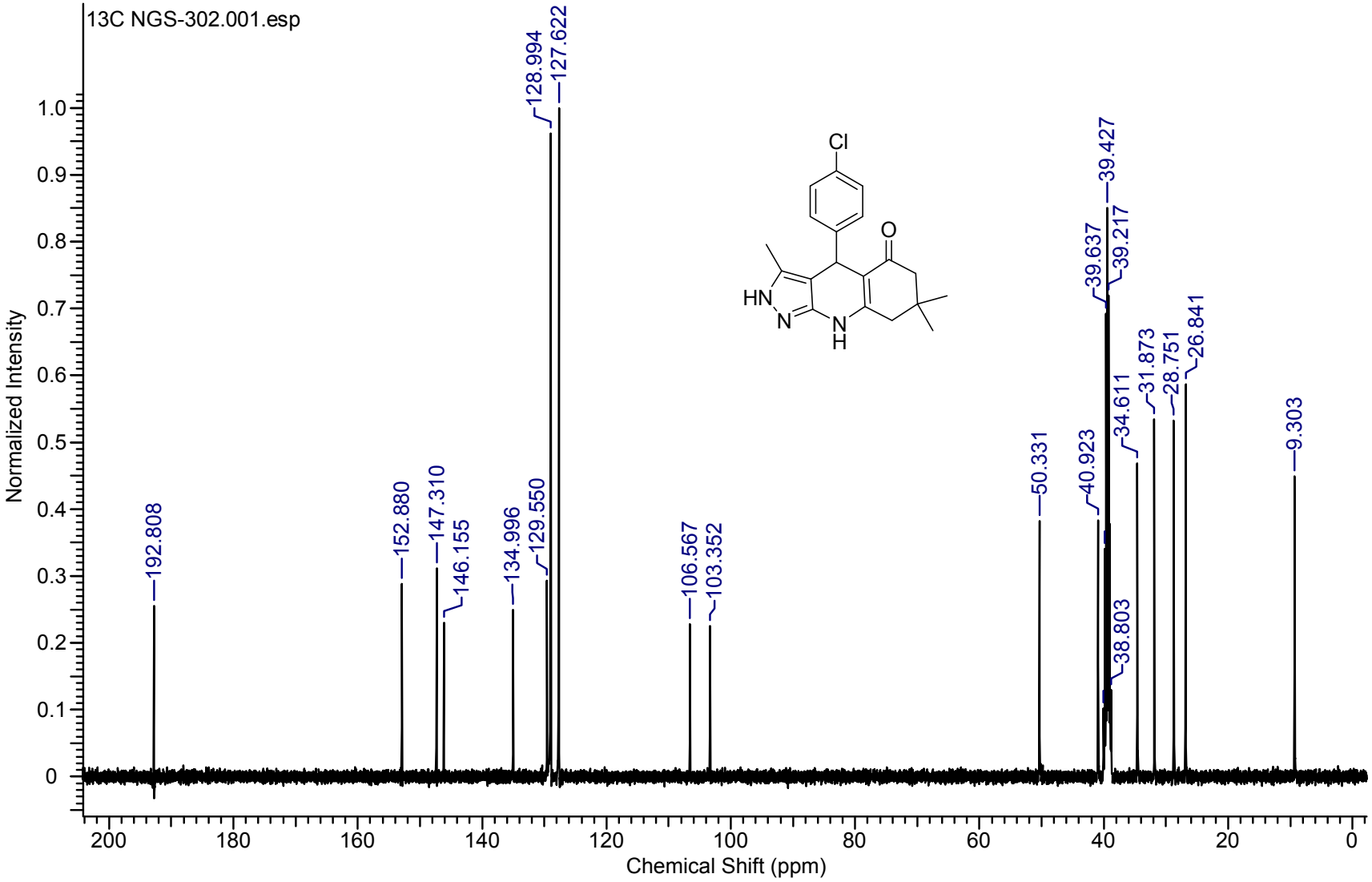
6f


13C GN-4.001.esp
OH
O
HN
N
N
H
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
192.814
154.729
152.373
146.284
139.089
134.607
127.918
114.368
107.395
104.385
50.467
40.966
39.835
39.625
39.421
39.211
38.790
33.999
31.842
28.862
26.810
9.347
200
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

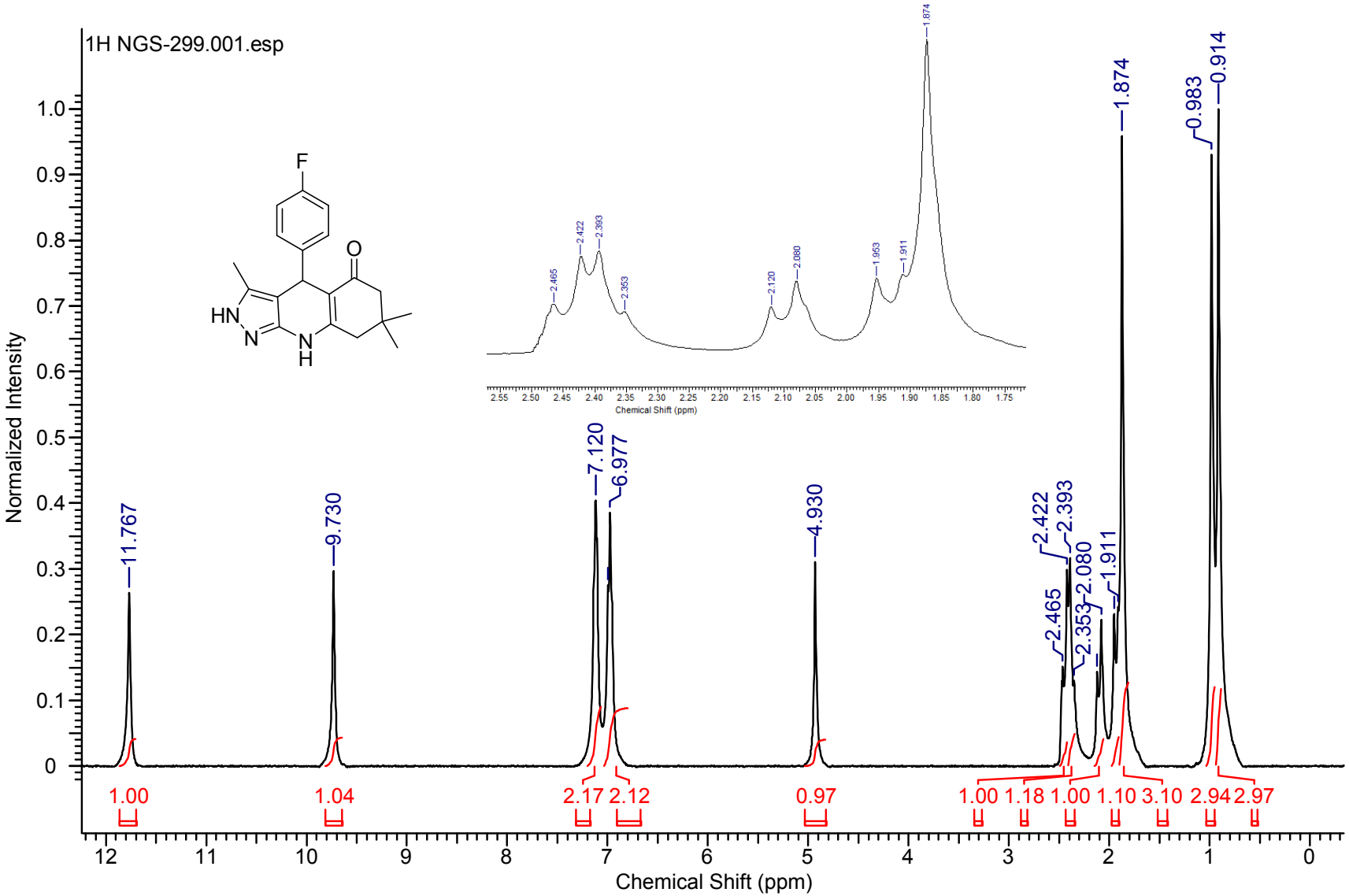
6g


1H NGS-302.001.ESP
Cl
O
HN
N
N
H
Normalized Intensity
Chemical Shift (ppm)
11.786
9.756
7.209
7.132
7.230
7.112
4.923
2.426
2.393
2.468
2.124
2.083
1.874
0.983
0.914
1.00
1.02
1.72
1.92
0.96
1.06
1.04
1.08
1.10
3.00
3.04
3.07

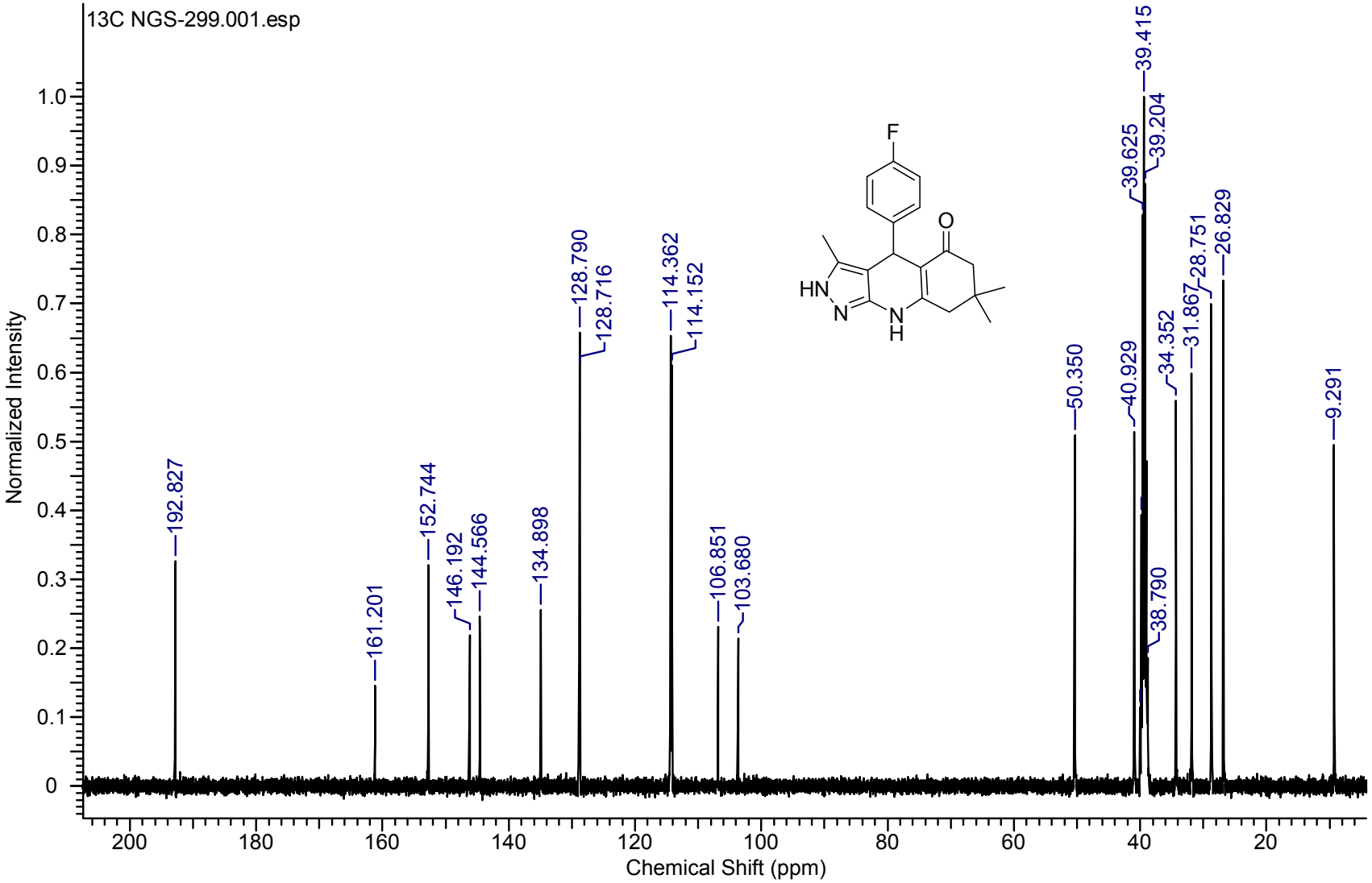
6g


13C NGS-302.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.808
152.880
147.310
146.155
134.996
129.550
128.994
127.622
106.567
103.352
50.331
40.923
39.637
39.427
39.217
38.803
34.611
31.873
28.751
26.841
9.303
Cl
O
HN
N
N
H

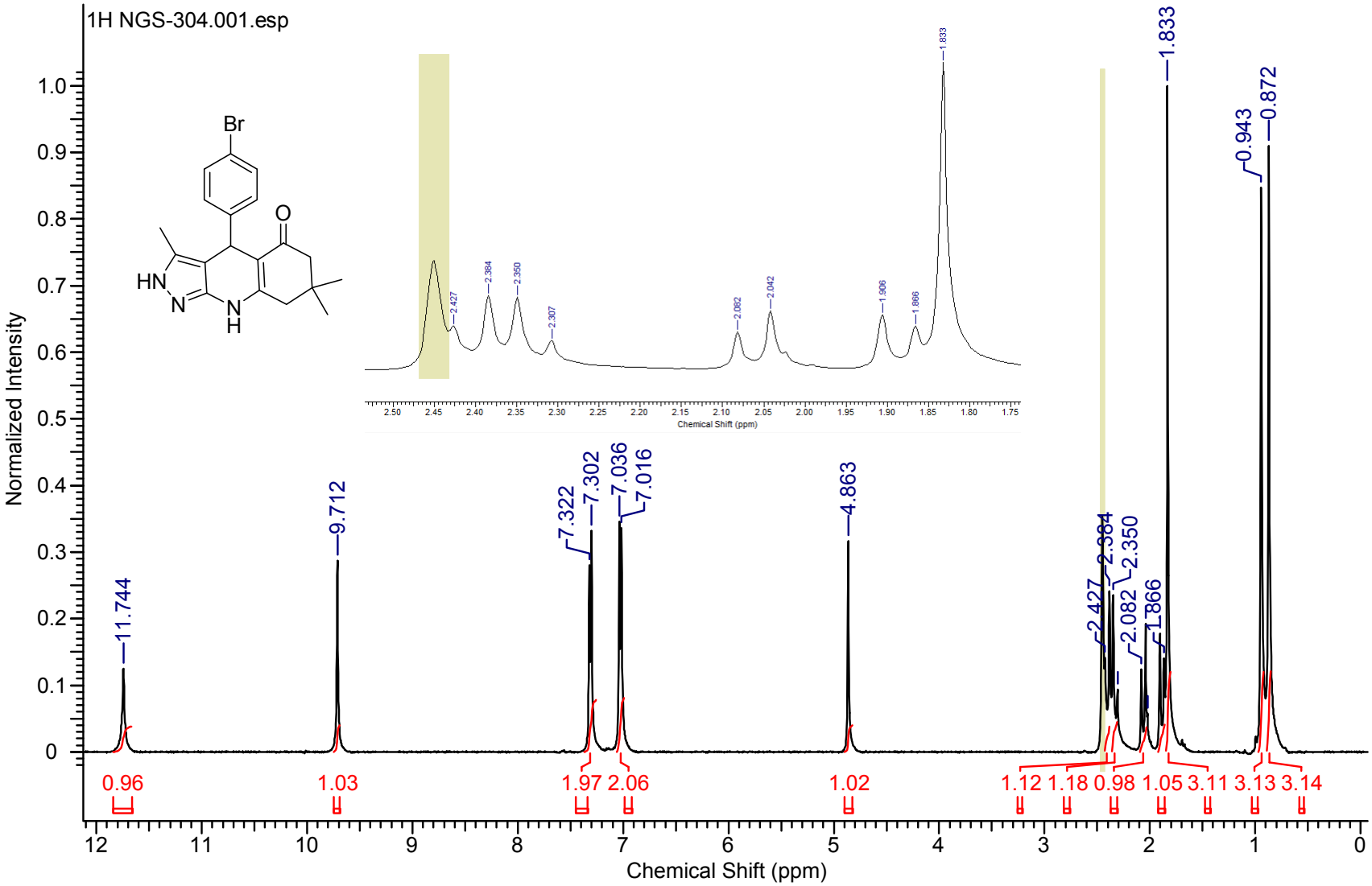
6h


1H NGS-299.001.esp
Normalized Intensity
Chemical Shift (ppm)
11.767
9.730
7.120
6.977
4.930
2.422
2.393
2.465
2.353
2.080
1.911
1.874
0.983
0.914
1.00
1.04
2.17
2.12
0.97
1.00
1.18
1.00
1.10
3.10
2.94
2.97
F
O
HN
N
N
H

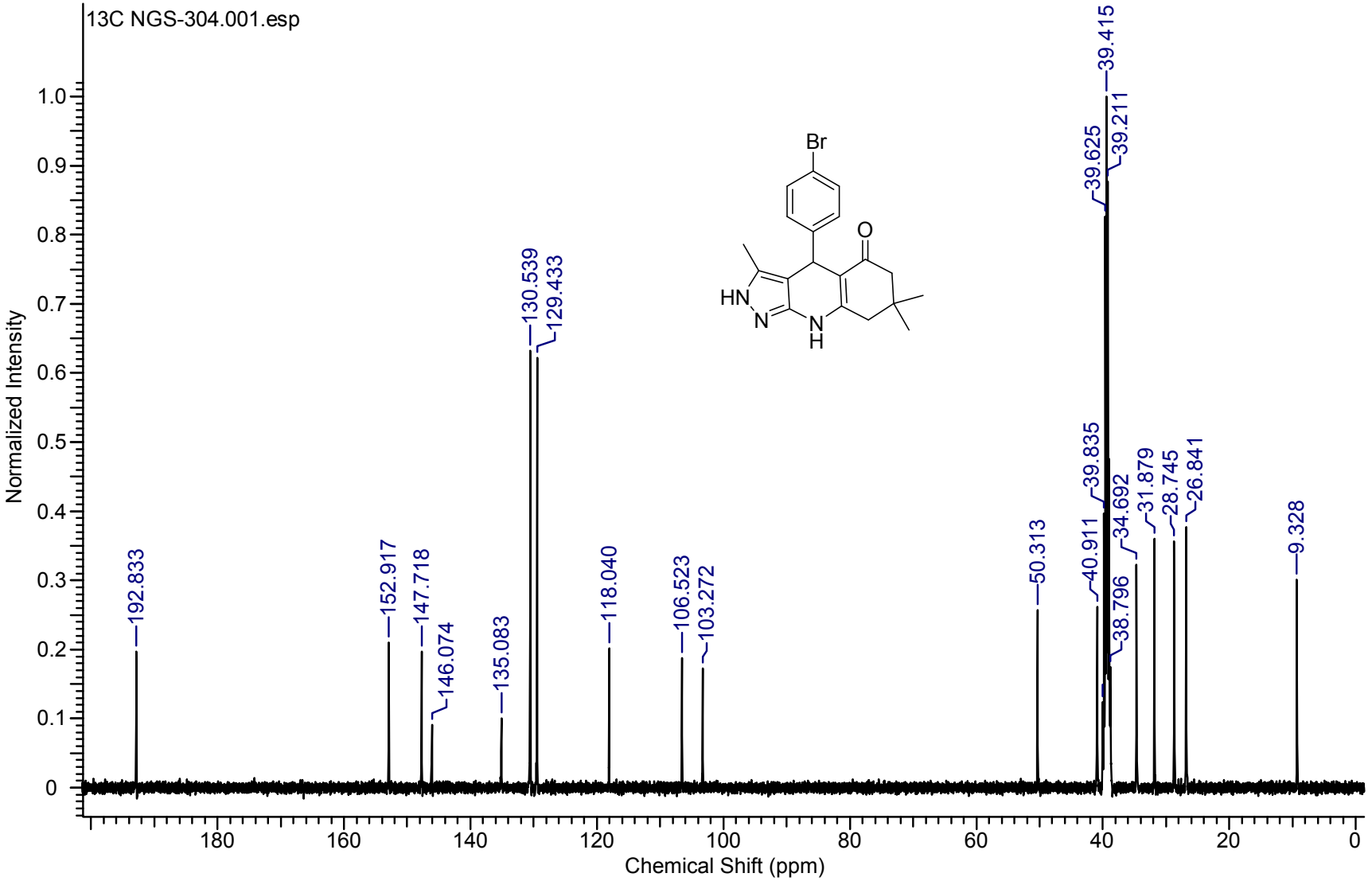
6h


13C NGS-299.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.827
161.201
152.744
146.192
144.566
134.898
128.790
128.716
114.362
114.152
106.851
103.680
50.350
40.929
39.625
39.415
39.204
38.790
34.352
31.867
28.751
26.829
9.291
F
O
HN
N
N
H

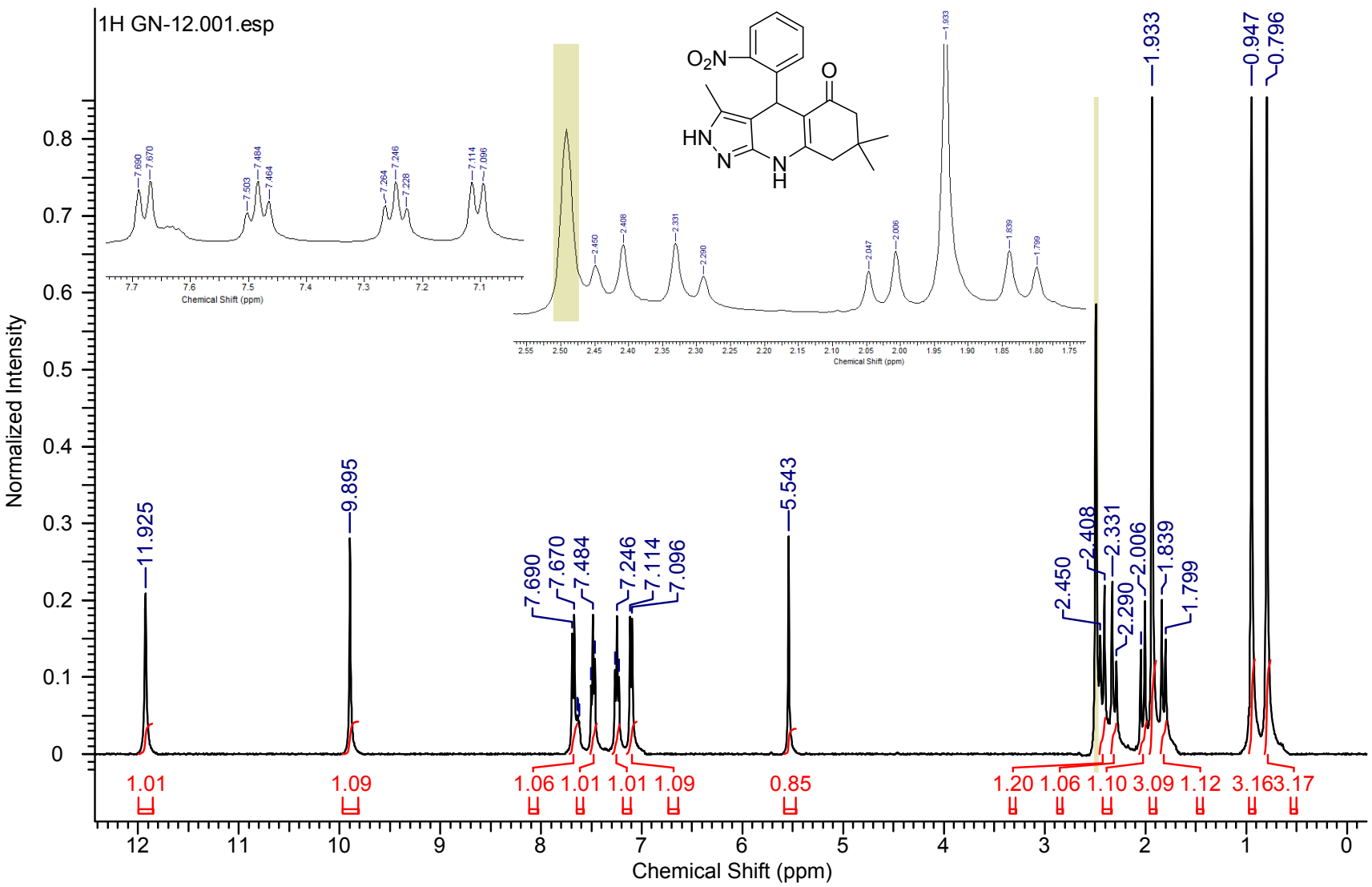
6i


1H NGS-304.001.esp
Br
O
HN
N
N
H
Normalized Intensity
Chemical Shift (ppm)
11.744
9.712
7.322
7.302
7.036
7.016
4.863
2.427
2.384
2.350
2.082
1.866
1.833
0.943
0.872
0.96
1.03
1.97
2.06
1.02
1.12
1.18
0.98
1.05
3.11
3.13
3.14

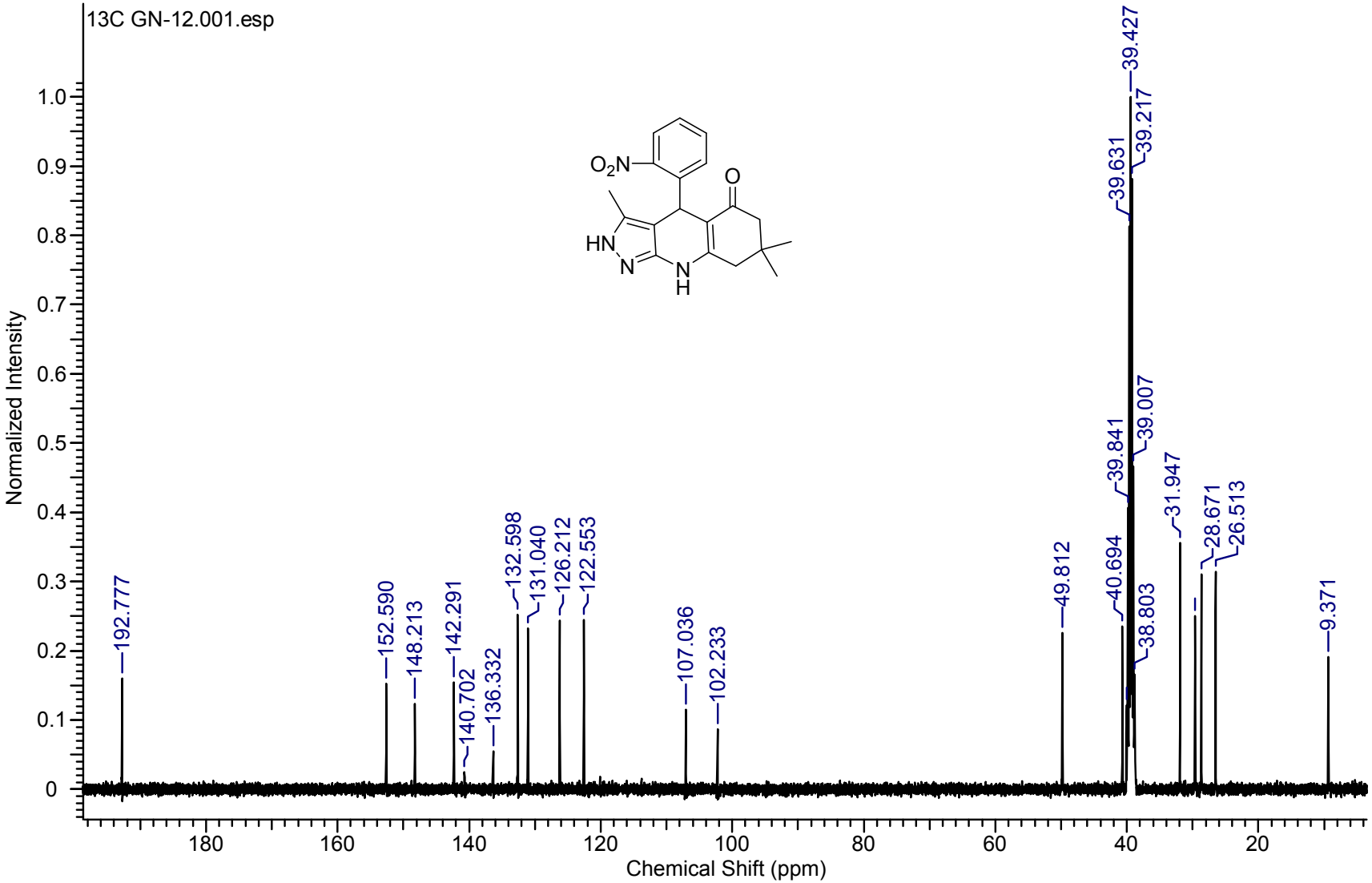
6i


13C NGS-304.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.833
152.917
147.718
146.074
135.083
130.539
129.433
118.040
106.523
103.272
50.313
40.911
39.835
39.625
39.415
39.211
38.796
34.692
31.879
28.745
26.841
9.328
Br
O
HN
N
N
H

6j


1H GN-12.001.esp
Normalized Intensity
Chemical Shift (ppm)
11.925
9.895
7.690
7.670
7.484
7.246
7.114
7.096
5.543
2.450
2.408
2.331
2.290
2.006
1.839
1.799
1.933
0.947
0.796
1.01
1.09
1.06 1.01 1.01 1.09
0.85
1.20 1.06 1.10 3.09 1.12 3.16 3.17
O2N
HN
N
N
H
O

6j


13C GN-12.001.esp
Normalized Intensity
Chemical Shift (ppm)
192.777
152.590
148.213
142.291
140.702
136.332
132.598
131.040
126.212
122.553
107.036
102.233
49.812
40.694
39.841
39.631
39.427
39.217
39.007
38.803
31.947
28.671
26.513
9.371
O2N
HN
N
N
H
O