SUPPLEMENTARY INFORMATION FOR

Synthetic, mechanistic and kinetic studies on the organo-nano catalyzed synthesis of oxygen and nitrogen containing Spiro compounds under ultrasonic condition

Nongthombam Geetmani Singh,[a] Makroni Lily,[b] Soungaijam Premila Devi,[b] Noimur Rahman,[a] Aziz Ahmed,[c] Asit Kumar Chandra,[b] and Rishanlang Nongkhlaw[a]*

[a]*Organic synthesis Lab, Centre for Advanced Studies in Chemistry, North Eastern Hill University, Shillong, Meghalaya-793022, India*
[b]*Computational Lab, Centre for Advanced Studies in Chemistry, North Eastern Hill University, Shillong-793022, India.*

[c]*Indian Institute of Technology, Patna 800013, India*

∗ E-mail: rlnongkhlaw@nehu.ac.in; Tel.: +91-364-2722628; fax: +91-364-2550076;

Table of content **Page No.**

Experimental

All the chemicals involved in the synthesis were purchased from Alfa Aesar, Sigma Aldrich & Merck and were used without further purification. The purity of the products were confirmed by infrared (FT-IR), ^{1}H-NMR, ^{13}C-NMR and mass spectra besides X-ray diffraction (XRD) data. FT-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 a Bruker Avance II-400 spectrometer in DMSO-d6 (chemical shifts in δ with TMS as internal standard). Mass spectral data were obtained with a Waters ZQ-4000 mass spectrometer. Elemental analyses were carried out on a Heraeus CHN-O-Rapid analyzer. Single crystal XRD data were obtained with an Xcalibur-Eos-Gemini instrument and powder XRD analysis was conducted with a Rigaku TT RAX 3XRD instrument. VSM analysis was carried out in Lakeshore, model: 7410 series instrument. All reactions were monitored by thin layer chromatography (TLC) using pre-coated aluminum sheets (silica gel 60 F 254 0.2 mm thickness) and developed in an iodine chamber. The TEM images were captured using a transmission electron microscope of JEM-2100 make, 200 kV (JEOL). SEM and EDS imaging were carried out with scanning electron microscope of JSM-6360 (JEOL) make.

X-ray crystallography (Single crystal XRD)

The single crystal X-ray diffraction (XRD) data were collected at 291/294 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.

Preparation of Fe_2O_3 Nanoparticle: A weakly acidified aqueous solution of Fe^{2+}/Fe^{3+} (1:2) was reduced using 1.5M NaOH under vigorous stirring condition for 1-2 hours. A black precipitate was obtained which was recovered with an external magnet and washed repeatedly till the pH became neutral. The synthesised Fe_3O_4 nanoparticles were further oxidised to ɣ-Fe_2O_3 through calcination.

Encapsulation of Fe_2O_3 Nanoparticle with silica: A suspension of Fe_2O_3 nanoparticles (1g) in methanol was ultrasonicated for 10 minutes at 50^{o}C. 5ml of tetraethylorthosilicate

(TEOS) was transfused into the solution and further ultrasonicated for 2 hours. On completion, the nanoparticles were recovered by an external magnet and washed with methanol followed by diethyl ether.

Functionalization of vitamin B_1 on Fe_2O_3@SiO_2 Nanoparticle: An aqueous solution of Fe_2O_3@SiO_2 (1g) in methanol was ultrasonicated for 30 minutes in the presence of triethylamine (1.5ml). Subsequently, thiamine hydrochloride (0.6g) was added to the solution and further ultrasonicated for 3 hours at 50°C. On completion, the nanoparticles were filtered, washed with water followed by diethyl ether. The nanoparticles were then subjected to acidification by HCl, in order to convert the alkaline Fe_2O_3@SiO_2@thiamine moiety to Fe_2O_3@SiO_2@thiamine hydrochloride.

General procedure for preparation of 4a-e, 5a–e, 6a-e, 7a-e, 8a-e, 9a-b, 10a-b, 11a-b, 12a-c, 13a-b

In a 50 ml round bottom flask, isatin (1mmol), malononitrile / 3-amino-5-methyl-1H-pyrazole (1 mmol), 1,3-diketone (1 mmol), Fe_2O_3@SiO_2@vitB_1-Np (2 mol%), Millipore water (10 ml) were ultrasonicated for 10-20 minutes (depending on the derivative). On completion (monitored by TLC) the solution was diluted and the nanocatalysts were recovered using a magnet. Finally, the mixture was filtered and washed several times with water then, eventually recrystallized from ethanol.

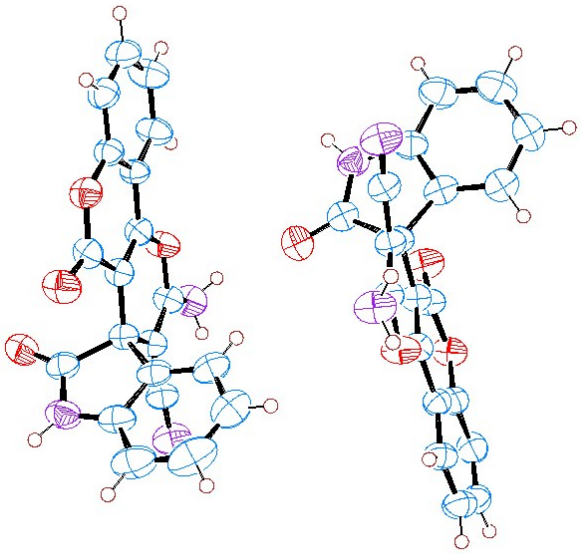


Table S.I.1. X-ray crystallography data for compound **5a** (CCDC 1443510).

Empirical formula	$2(C_{20}H_{11}N_3O_4)$
Formula weight	714.66
Crystal system	Triclinic
Space group	P-1
a(Å)	10.3603(15)
b(Å)	13.054(2)
c(Å)	14.655(3)
α(°)	75.239(15)
β(°)	84.652(14)
γ(°)	69.915(14)
Volume (Å)	1799.9(6)
ρ (calculated) (g cm^{-3})	1.3185
T(K)	291.6(2)
Absorption coefficient (mm^{-1})	0.095
Total reflection collected	12261
Independent reflection	8117
Refine parameter	488
θ range (°)	6.64 to 58.12°
Final R Indexes [1>=2σ(I)]	R_1 = 0.0942, wR_2 = 0.2287
Final R indexes [all data]	R_1 = 0.1796, wR_2 = 0.2954
Goodness-of-fit on F^2	0.995

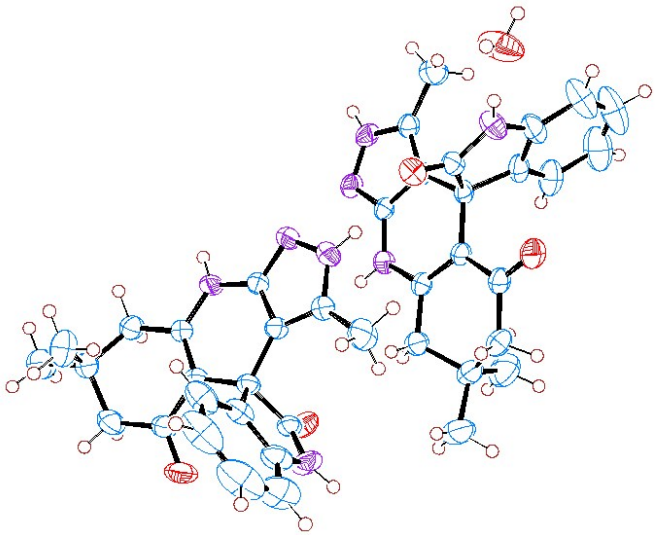
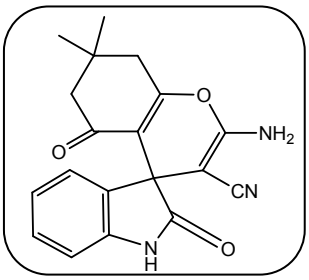


Table S.I.2. X-ray crystallography data for compound **9a** (CCDC 1443423).

Empirical formula	$2(C_{20}H_{20}N_4O_2)+H_2O$
Formula weight	714.83
Crystal system	Orthorhombic
Space group	Pbcn
a(Å)	15.4558(7)
b(Å)	18.7716(10)
c(Å)	26.3270(12)
α(°)	90
β(°)	90
γ(°)	90
Volume (Å)	167638.3(6)
ρ (calculated) (g cm^{-3})	1.2431
T(K)	294.3(5)
Absorption coefficient (mm^{-1})	0.084
Total reflection collected	36255
Independent reflection	7807
Refine parameter	489
θ range (°)	6.12 to 52.74°
Final R Indexes [1>=2σ(I)]	R1 = 0.0561, wR_2 = 0.1147
Final R indexes [all data]	R1 = 0.0955, wR_2 = 0.1366
Goodness-of-fit on F^2	1.039

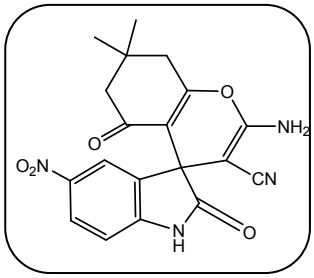
ANALYTICAL DATA

2-amino-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (4a):



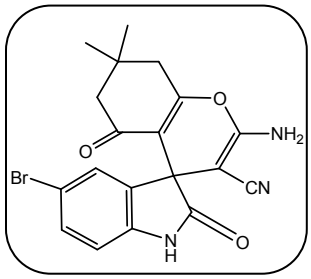
IR (KBr): 3377, 3315, 3148, 2959, 2193, 1722, 1682, 1656, 1472, 1349, 1223, 1055 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.33 (s, 1H), 7.17 (s, 2H), 7.06 (t, 1H, *J* = 7.2 Hz), 6.89 (d, 1H, *J*=7.2 Hz), 6.81 (t, 1H, *J* = 7.2 Hz), 6.70 (d, 1H, *J* = 8.4 Hz), 2.42 (m, 2H), 2.09 (d, 1H, *J* = 16 Hz), 2.01(d, 1H, *J* = 16 Hz), 0.95 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 194.8, 177.9, 164.1, 158.7, 142.0, 134.3, 129.1, 128.1, 123.0, 117.3, 110.7, 109.1, 57.4, 49.9, 46.7, 31.9, 27.5, 26.9. ESI-MS: *m/z* 336 $[M+1]^+$. Anal. Calcd. for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53%; Found: C, 67.91; H, 5.05; N, 12.65%.

2-amino-7,7-dimethyl-5'-nitro-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (4b):



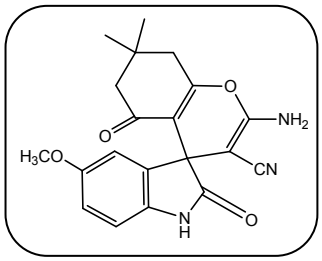
IR (KBr): 3393, 3264, 2964, 2190, 1742, 1681, 1650, 1481, 1338, 1228, 1061 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.19 (s, 1H), 8.14 (d, 1H, *J* = 8.8Hz), 7.96 (s, 1H), 7.46 (s, 1H), 7.01 (d, 1H, *J* = 8.8 Hz), 2.53- 2.68 (m, 2H), 2.19 (d, 1H, *J* = 16 Hz), 2.12 (d, 1H, *J* = 16Hz), 1.01 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 195.3, 178.5, 165.1, 159.0, 148.6, 142.3, 135.3, 125.7, 118.8, 117.0, 109.7, 109.3, 55.7, 49.7, 46.9, 32.0, 27.6, 26.9. ESI-MS: *m/z* 381 $[M+1]^+$.

2-amino-5'-bromo-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (4c):



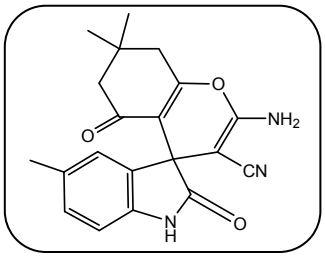
IR (KBr): 3367, 3292, 3161, 2958, 2872, 2194, 1727, 1681, 1655, 1475, 1350, 1223, 1057 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.31 (s, 1H), 7.06-7.09 (m, 3H), 6.98 (d, 1H, *J* = 12Hz), 6.50 (d, 1H, *J* = 8.4Hz), 2.25-2.37 (m, 2H), 1.86-1-94 (m, 2H), 0.76 (s, 6H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 195.0, 177.6, 164.5, 158.8, 141.4, 136.7, 130.8, 125.9, 117.1, 113.2, 111.1, 110.1, 56.6, 49.8, 46.9, 31.9, 27.4, 27.1. ESI-MS: *m/z* 413 $[M^+]$, 415$[M+2]^+$.

2-amino-5'-methoxy-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (4d):



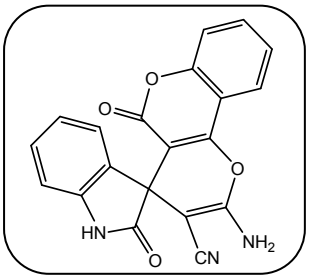
IR (KBr): 3380, 3296 3091, 2963, 2870, 1676, 1481, 1345, 1241, 1066 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 9.99 (s, 1H), 7.00 (s, 2H), 6.45 (t, 2H, *J* = 8.4Hz), 6.36 (s, 1H), 3.41 (s, 3H), 2.26-2.31 (m, 2H), 1.92 (d, 1H, *J* = 16Hz), 1.86 (d, 1H, *J* = 16Hz), 0.78 (s, 3H), 0.76 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 195.3, 178.3, 164.5, 159.1, 155.4, 136.1, 135.8, 117.8, 112.9, 111.1, 110.5, 109.9, 57.9, 55.7, 50.4, 47.7, 32.3, 28.0, 27.5. ESI-MS: *m/z* 366 $[M+1]^+$.

2-amino-5',7,7-trimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (4e):



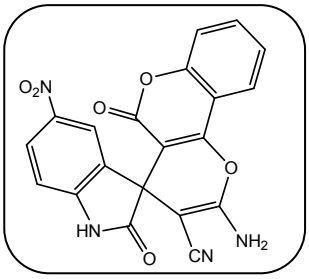
IR (KBr): 3366, 3312, 2958, 2193, 1718, 1680, 1658, 1492, 1349, 1225, 1056 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.29 (s,1H), 7.21 (s, 2H), 6.93 (d, 1H, *J* = 7.2Hz), 6.77 (s, 1H), 6.67 (d, 1H, *J* = 7.2 Hz), 2.51-2.54 (m, 2H), 2.13-2.19 (m, 5H), 1.02 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 194.8, 177.9, 164.0, 158.6, 139.5, 134.4, 130.4, 128.3, 123.5, 117.3, 110.7, 108.9, 57.6, 49.9, 46.7, 31.9, 27.4, 27.1, 20.6. ESI-MS: *m/z* 350 $[M+1]^+$.

2'-amino-2,5'-dioxo-5'*H*-spiro[indoline-3,4'-pyrano[3,2-*c*]chromene]-3'-carbonitrile (5a):



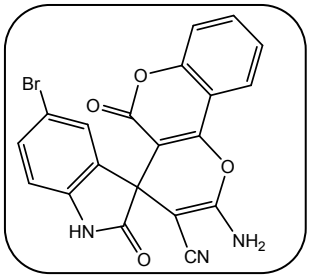
IR (KBr): 3436, 3295, 2206, 1711, 1675, 1642, 1471, 1361, 1217, 1082 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.62 (s, 1H), 7.86 (d, 1H, *J* = 8.4Hz), 7.69 (t, 1H, *J* = 7.2Hz), 7.61 (s, 2H), 7.48 (d, 1H, *J* = 7.2Hz), 7.43 (t, 1H, *J* = 8.4Hz) 7.12-7.14 (m, 2H), 6.85 (t, 1H, *J* = 7.2Hz), 6.77 (d, 1H, *J* = 7.2Hz). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.1, 158.4, 158.2, 155.0, 152.0, 142.1, 133.6, 133.0, 128.8, 124.9, 124.0, 122.6, 122.0, 116.9, 116.6, 112.4, 109.4, 101.3, 56.9, 48.5. ESI-MS: *m/z* 358 $[M+1]^+$. Anal. Calcd. for $C_{20}H_{11}N_3O_4$: C, 67.23; H, 3.10; N, 11.76%; Found: C, 67.30; H, 3.06; N, 11.80%.

2'-amino-5-nitro-2,5'-dioxo-5'*H*-spiro[indoline-3,4'-pyrano[3,2-*c*]chromene]-3'-carbonitrile (5b):



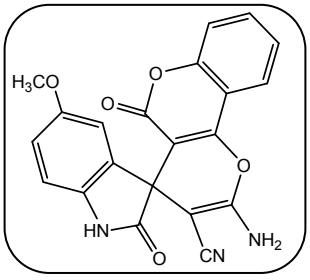
IR (KBr): 3376, 3313, 3214, 2203, 1743, 1674, 1625, 1478, 1365, 1216, 1071 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.38 (s, 1H), 8.30 (s, 1H), 8.16 (d, 1H, *J* = 7.6Hz), 7.91 (d, 1H, *J* = 8.8Hz), 7.80 (s, 2H), 7.73 (t, 1H, *J* = 7.2Hz), 7.51 (t, 1H, *J* = 8.4Hz), 7.45 (d, 1H, *J* = 8.4Hz), 7.04 (d, 1H, *J* = 8.4Hz). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.8, 158.7, 158.6, 155.7, 152.0, 148.5, 142.7, 133.9, 133.7, 126.2, 125.0, 122.7, 120.5, 116.7, 116.6, 112.6, 109.6, 100.1, 55.5, 47.7. ESI-MS: *m/z* 403 $[M+1]^+$.

2'-amino-5-bromo-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c]chromene]-3'-carbonitrile (5c):



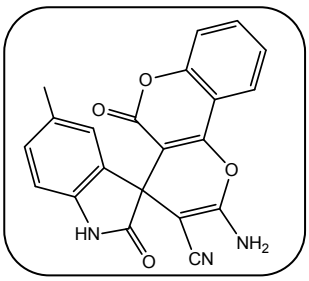
IR (KBr): 3330, 3247, 2202, 1739, 1672, 1472, 1360, 1220, 1087 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.82 (s, 1H), 7.93 (d, 1H, *J* = 8.4Hz), 7.75-7.79 (m, 3H), 7.68 (s, 1H), 7.49-7.57 (m, 2H), 7.39 (d, 1H, *J* = 7.2Hz), 6.82 (d, 1H, *J* = 7.6Hz). ^{13}C NMR (DMSO-D6, 100 MHz): δ 176.8, 158.5, 158.4, 155.3, 152.0, 141.4, 135.3, 133.6, 131.6, 127.2, 124.9, 122.6, 116.9, 116.6, 113.7, 112.5, 111.3, 100.6, 56.2, 47.7. ESI-MS: *m/z* 434$[M^+]$ and 436 $[M+2]^+$.

2'-amino-5-methoxy-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c]chromene]-3'-carbonitrile (5d)



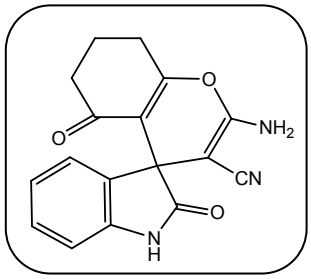
IR (KBr): 3350, 3288, 3172, 2958, 2835, 2204, 1702, 1679, 1492, 1362, 1205, 1084 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.50 (s, 1H), 7.93 (d, 1H, *J* = 7.2Hz), 7.76 (t, 1H, *J* = 7.2Hz), 7.67 (s, 2H), 7.54 (t, 1H, *J* = 7.2Hz), 7.49 (d, 1H, *J* = 8.8Hz), 6.92 (s, 1H), 6.74-6.79 (m, 2H), 3.65 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.0, 158.3, 158.2, 155.2, 155.0, 152.0, 135.3, 134.2, 133.5, 124.9, 122.6, 117.0, 116.6, 113.7, 112.5, 110.8, 109.8, 101.3, 57.0, 55.3, 48.0. ESI-MS: *m/z* 388 $[M+1]^+$.

2'-amino-5-methyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c]chromene]-3'-carbonitrile (5e)



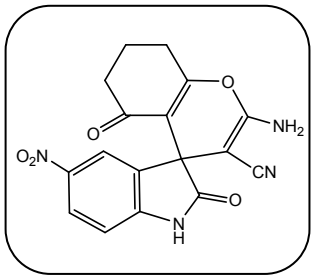
IR (KBr): 3329, 3246, 2206, 1738, 1671, 1492, 1359, 1223, 1081 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.57 (s, 1H), 7.94 (d, 1H, *J* = 8.4Hz), 7.76 (t, 1H, *J* = 7.2Hz), 7.65 (s, 2H), 7.54 (t, 1H, *J* = 7.2Hz), 7.49 (d, 1H, *J* = 8.8Hz), 6.99-7.03 (m, 2H), 6.73 (d, 1H, *J* = 8.4Hz), 2.19 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.0, 158.3, 158.2, 154.9, 151.9, 139.6, 133.6, 133.1 130.9, 129.1, 124.9, 124.6, 122.6, 117.0, 116.6, 112.4, 109.2, 101.4, 57.1, 47.5, 20.5. ESI-MS: *m/z* 372 $[M+1]^+$.

2-amino-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (6a):



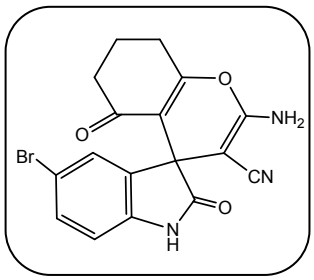
IR (KBr): 3370, 3301, 3131, 2959, 2191, 1707, 1682, 1466, 1353, 1210, 1077 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.33 (s, 1H), 7.15 (s, 2H), 6.69-7.05 (m, 4H), 1.83-2.42 (m, 6H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 194.9, 178.0, 165.9, 158.5, 141.9, 134.4, 128.0, 123.1, 121.5, 117.3, 111.8, 109.0, 57.4, 46.8, 36.3, 26.6, 19.7. ESI-MS: *m/z* 307 $[M^+]$.

2-amino-5'-nitro-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (6b):



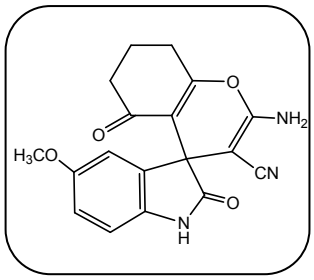
IR (KBr): 3459, 3363, 3182, 2945, 2196, 1744, 1683, 1482, 1337, 1202, 1073 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.01 (s, 1H), 7.96 (d, 1H, *J* = 8.4Hz), 7.85 (s, 1H), 7.28 (s, 2H), 6.83 (d, 1H, *J* = 8.4Hz), 2.48-2.51 (m, 2H), 2.05-2.06 (m, 2H), 1.73-1.79 (m, 2H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 195.4, 178.6, 167.1, 158.8, 148.5, 142.3, 135.4, 125.7, 119.1, 117.0, 110.7, 109.2, 55.8, 46.9, 36.0, 26.7, 19.5. ESI-MS: *m/z* 353 $[M+1]^+$. Anal. Calcd. for $C_{17}H_{12}N_4O_5$: C, 57.96; H, 3.43; N, 15.90%; Found: C, 58.07; H, 3.50; N, 15.79%.

2-amino-5'-bromo-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (6c):



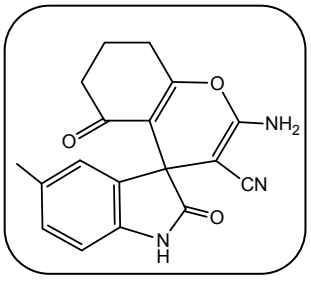
IR (KBr): 3386, 3286, 3047, 2973, 2896, 2188, 1710, 1660, 1475, 1327, 1221, 1079 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.77 (s, 1H), 6.93-7.51 (m, 5H), 2.15-2.82 (m, 6H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 195.1, 177.7, 163.4, 158.6, 141.2, 135.4, 130.8, 126.0, 123.8, 121.5, 117.1, 107.5, 58.4, 47.0, 36.2, 26.6, 19.6. ESI-MS: *m/z* 485$[M^+]$ and 487 $[M+2]^+$.

2-amino-5'-methoxy-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (6d)



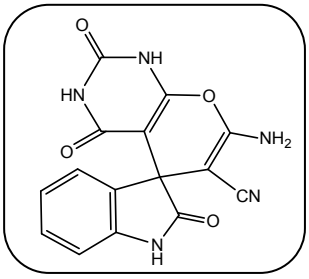
IR (KBr): 3370, 3288, 3172, 2946, 2832, 2189, 1702, 1661, 1492, 1328, 1221, 1079 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.21 (s, 1H), 7.21 (s, 2H), 6.63-6.71 (m, 3H), 3.66 (s, 3H), 2.62-2.65 (m, 2H), 2.20-2.24 (m, 2H), 1.90-1.93 (m, 2H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 194.9, 177.9, 165.9, 158.8, 154.8, 135.8, 135.2, 117.3, 112.4, 111.7, 110.2, 109.3, 57.5, 55.2, 47.2, 36.3, 26.7, 19.7. ESI-MS: *m/z* 338 $[M+H]^+$.

2-amino-5'-methyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (6e):



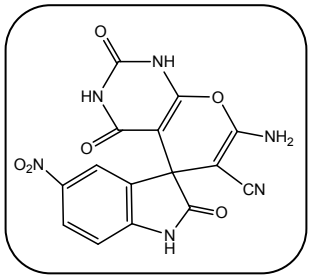
IR (KBr): 3361, 3144, 2950, 2875, 2195, 1710, 1660, 1491, 1351, 1213, 1075 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.29 (s, 1H), 7.21 (s, 2H), 6.92 (d, 1H, *J* = 7.2Hz), 6.81 (s, 1H), 6.65 (d, 1H, *J* = 8.8Hz), 2.28-2.66 (m, 2H), 2.19-2.27 (m, 5H), 1.89-1.93 (m, 2H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 194.9, 178.0, 165.9, 158.5, 139.4, 134.4, 130.3, 128.3, 123.7, 117.3, 111.8, 108.8, 57.6, 46.8, 36.3, 26.6, 20.6, 19.7. ESI-MS: *m/z* 322 $[M+1]^+$.

7'-amino-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (7a):



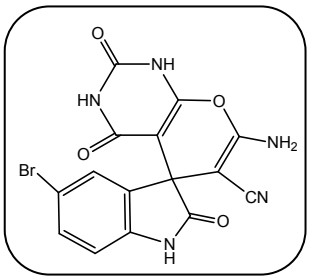
IR (KBr): 3404, 3334, 3236, 3063, 2872, 2200, 1725, 1671, 1472, 1329, 1216, 1111 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 12.23 (s, 1H), 11.06 (s, 1H), 10.41 (s, 1H), 7.30 (s, 2H), 7.04-7.09 (m, 2H), 6.82 (t, 1H, *J* = 7.2Hz), 6.69 (d, 1H, *J* = 7.2Hz). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.5, 161.3, 158.1, 153.2, 149.1, 142.0, 133.4, 128.3, 123.7, 121.7, 116.8, 109.2, 86.7, 57.7, 46.5. ESI-MS: *m/z* 324 $[M+1]^+$. Anal. Calcd. for $C_{15}H_9N_5O_4$: C, 55.73; H, 2.81; N, 21.66%; Found: C, 55.86; H, 2.77; N, 21.79%.

7'-amino-5-nitro-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (7b):



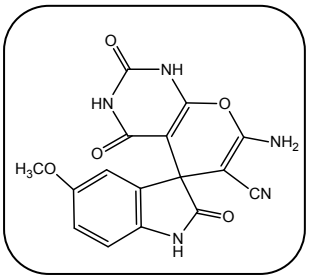
IR (KBr): 3443, 3296, 2824, 2200, 1749, 1668, 1477, 1345, 1231, 1061 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 12.38 (s, 1H), 11.22 (s, 1H), 11.18 (s, 1H), 8.24 (s, 1H), 8.15 (d, 1H, *J* = 7.6Hz), 7.56 (s, 2H), 7.01 (d, 1H, *J* = 8.8Hz). ^{13}C NMR (DMSO-D6, 100 MHz): δ 178.3, 161.6, 158.6, 153.8, 149.2, 148.5, 142.5, 134.5, 125.8, 119.9, 116.7, 109.3, 85.7, 56.1, 46.7. ESI-MS: *m/z* 369 $[M+1]^+$.

7'-amino-5-bromo-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (7c):



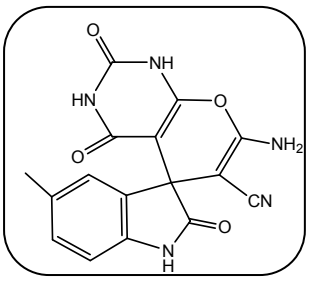
IR (KBr): 3431, 3294, 2823, 2196, 1720, 1694, 1475, 1337, 1220, 1085 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 12.53 (s, 1H), 11.37 (s, 1H), 10.83 (s, 1H), 7.56-7.66 (m, 4H), 6.96 (s, 1H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.2, 161.4, 158.3, 153.5, 149.1, 141.3, 138.8, 135.8, 131.0, 126.7, 116.7, 113.4, 86.1, 56.9, 46.8. ESI-MS: *m/z* 400 $[M]^+$, 402 $[M+2]^+$.

7'-amino-5-methoxy-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (7d):



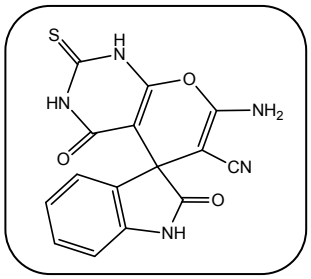
IR (KBr): 3406, 3298, 3099, 3924, 2836, 2199, 1729, 1692, 1473, 1327, 1204, 1025 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 12.28 (s, 1H), 11.11 (s, 1H), 10.29 (s, 1H), 7.35 (s, 2H), 6.82 (s, 1H), 6.67-6.73 (m, 2H), 3.66 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.5, 161.3, 158.1, 155.0, 153.2, 149.2, 135.3, 134.7, 116.9, 113.0, 110.5, 109.5, 86.7, 57.8, 55.3, 47.0. ESI-MS: *m/z* 354$[M+1]^+$.

7'-amino-5-methyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (7e):



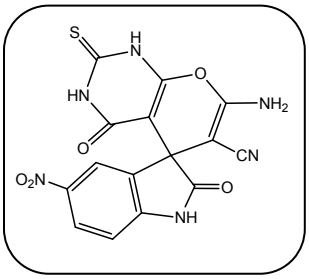
IR (KBr): 3335, 3257, 2923, 2828, 2209, 1730, 1650, 1491, 1345, 1224, 1114 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 12.06 (s, 1H), 10.88 (s, 1H), 10.14 (s, 1H), 7.41 (s, 2H), 7.13 (d, 1H, *J* = 8.8Hz), 6.70 (s, 1H), 6.59 (d, 1H, *J* = 8.8Hz), 1.96 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.5, 163.7, 161.3, 158.1, 150.4, 138.4, 133.5, 131.8, 130.5, 128.6, 116.9, 111.3, 86.8, 57.8, 46.5, 20.4. ESI-MS: *m/z* 338$[M+1]^+$.

7'-amino-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (8a)



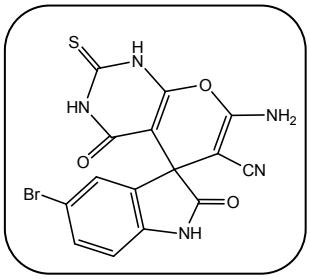
IR (KBr): 3428, 3316, 3206, 2923, 2848, 2202, 1692, 1572, 1470, 1344, 1218, 1056 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 13.81 (s, 1H), 12.44 (s, 1H), 10.47 (s, 1H), 7.36 (s, 2H), 7.07-7.12 (m, 2H), 6.83 (s, 1H), 6.71 (d, 1H, *J* = 7.2Hz). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.1, 173.8, 159.0, 158.0, 152.7, 142.0, 132.9, 128.5, 123.9, 121.8, 116.7, 109.2, 91.5, 57.4, 46.5. ESI-MS: *m/z* 340 $[M+1]^+$. Anal. Calcd. for $C_{15}H_9N_5O_3S$: C, 53.09; H, 2.67; N, 20.64%; Found: C, 52.86; H, 2.71; N, 20.79%.

7'-amino-5-nitro-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (8b):



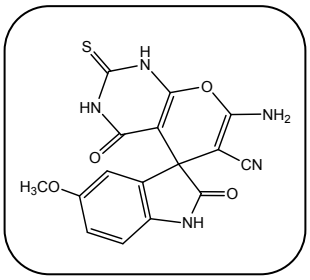
IR (KBr): 3368, 3284, 3099, 2922, 2862, 2198, 1718, 1685, 1579, 1484, 1342, 1230, 1107 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 12.54 (s, 1H), 11.27 (s, 1H), 8.33 (s, 1H), 8.17 (d, 1H, *J* = 8.4Hz), 7.59 (s, 2H), 7.01 (d, 1H, *J* = 8.8Hz). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.9, 174.0, 159.3, 158.4, 153.3, 148.6, 142.6, 133.9, 126.0, 120.3, 116.5, 109.4, 90.5, 55.9, 46.7. ESI-MS: *m/z* 385 $[M+1]^+$.

7'-amino-5-bromo-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (8c):



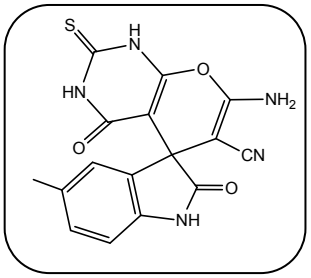
IR (KBr): 3418, 3349, 3304, 2939, 2859, 2199, 1703, 1670, 1579, 1473, 1341, 1218, 1055 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 12.52 (s, 1H), 10.67 (s, 1H), 7.17-7.49 (m, 4H), 6.75 (d, 1H, *J* = 7.2Hz). ^{13}C NMR (DMSO-D6, 100 MHz): δ 176.9, 173.9, 159.2, 158.1, 152.9, 141.4, 135.3, 131.2, 127.0, 116.6, 113.6, 111.1, 90.9, 56.7, 48.5. ESI-MS: *m/z* 416 $[M]^+$ and 418 $[M+2]^+$.

7'-amino-5-methoxy-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (8d):



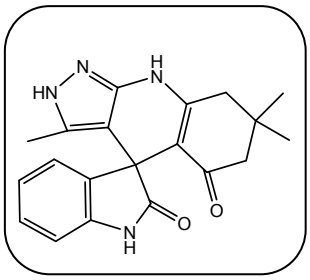
IR (KBr): 3354, 3242, 2952, 2849, 2203, 1703, 1681, 1582, 1492, 1341, 1210, 1049 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 12.28 (s, 1H), 10.14 (s, 1H), 7.19 (s, 2H), 6.68 (s, 1H), 6.46-6.53 (m, 2H), 3.45 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.0, 173.8, 159.0, 157.9, 155.1, 152.7, 135.3, 116.8, 113.3, 110.7, 109.5, 91.5, 57.5, 55.3, 47.0. ESI-MS: *m/z* 370 $[M+1]^+$.

7'-amino-5-methyl-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (8e):



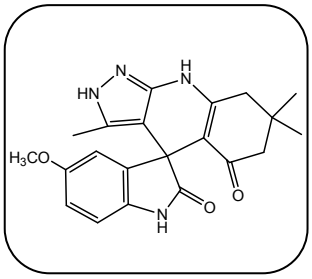
IR (KBr): 3405, 3258, 2922, 2862, 2197, 1716, 1658, 1589, 1486, 1348, 1221, 1112 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 12.48 (s, 1H), 11.11 (s, 1H), 10.44 (s, 1H), 7.62 (s, 2H), 7.00 (s, 1H), 6.82 (d, 1H, *J* = 7.6Hz), 2.26 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.1, 173.9, 163.7, 159.0, 158.0, 138.5, 133.0, 131.8, 130.6, 128.7, 116.8, 108.9, 91.5, 57.5, 46.6, 20.4. ESI-MS: *m/z* 354 $[M+1]^+$.

3',7',7'-trimethyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(2'*H*)-dione (9a):



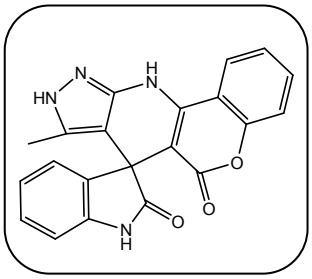
IR (KBr): 3329, 3118, 2960, 2898, 1723, 1647, 1473, 1348, 1229, 1085 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.67 (s, 1H), 9.96 (s, 1H), 9.76 (s, 1H), 6.79 (t, 1H, *J* = 7.2Hz), 6.46-6.81 (m, 3H), 2.15-2.27 (m, 2H), 1.79 (d, 1H, *J* = 16Hz), 1.68 (d, 1H, *J* = 16Hz), 1.31 (s, 3H), 0.76 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 192.0, 179.6, 154.1, 145.9, 141.5, 137.5, 134.3, 126.7, 122.5, 121.2, 108.3, 105.1, 101.3, 50.3, 48.1, 41.2, 32.0, 28.2, 26.9, 8.6. ESI-MS: *m/z* 349 $[M+1]^+$. Anal. Calcd. for $C_{20}H_{20}N_4O_2$: C, 68.95; H, 5.79; N, 16.08%; Found: C, 69.10; H, 5.81; N, 15.99%.

5-methoxy-3',7',7'-trimethyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(2'*H*)-dione (9b):



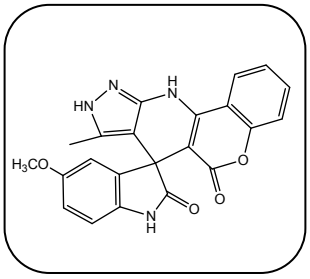
IR (KBr): 3366, 3306, 3073, 2958, 2922, 1701, 1686, 1491, 1337, 1262, 1032 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.92 (s, 1H), 10.04 (s, 1H), 9.99 (s, 1H), 6.60-6.67 (m, 2H), 6.29 (s, 1H), 3.57 (s, 3H), 2.39-2.47 (m, 2H), 2.04 (d, 1H, *J* = 16.8Hz), 1.93 (d, 1H, *J* = 15.6Hz), 1.58 (s, 3H), 1.01 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 192.0, 179.5, 154.6, 154.1, 145.9, 138.8, 135.0, 134.4, 110.9, 109.6, 108.5, 105.0, 101.3, 55.0, 50.3, 48.6, 41.2, 32.0, 28.2, 26.6, 8.6. ESI-MS: *m/z* 379 $[M+1]^+$.

8-methyl-6*H*-spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3'-indoline]-2',6(9*H*,11*H*)-dione (10a):



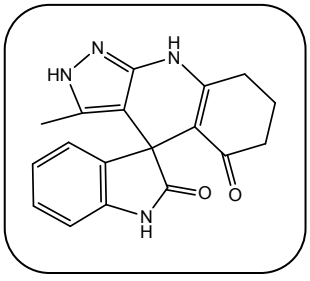
IR (KBr): 3340, 3232, 3047, 1707, 1644, 1485, 1344, 1229, 1085 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.97 (s, 1H), 10.63 (s, 1H), 10.37 (s, 1H), 7.91 (d, 1H, *J* = 7.6Hz), 7.43-7.47 (m, 1H), 7.25 (d, 1H, *J* = 7.6Hz), 7.17 (t, 1H, *J* = 7.2Hz), 6.79-6.89 (m, 4H), 1.31 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.9, 167.1, 159.9, 154.4, 148.7, 143.2, 136.0, 134.0, 131.4, 129.3, 128.6, 123.2, 122.0, 121.3, 119.1, 117.4, 109.4, 103.2, 100.4, 47.2, 8.6. ESI-MS: *m/z* 371 $[M+1]^+$. Anal. Calcd. for $C_{21}H_{14}N_4O_3$: C, 68.10; H, 3.81; N, 15.13%; Found: C, 67.96; H, 3.85; N, 15.20%.

5'-methoxy-8-methyl-6*H*-spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3'-indoline]-2',6(9*H*,11*H*)-dione (10b):



IR (KBr): 3392, 3225, 3047, 2982, 2844, 1719, 1632, 1492, 1346, 1202, 1084 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.97 (s, 1H), 10.62 (s, 1H), 10.18 (s, 1H), 7.91 (d, 1H, *J* = 8.8Hz), 7.46 (t, 1H, *J* = 8.4Hz), 6.97 (s, 1Hz), 6.87-6.91 (m, 2H), 6.72-6.77 (m, 2H), 3.58 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 177.8, 167.0, 159.9, 155.0, 154.5, 148.6, 136.4, 136.0, 134.1, 131.5, 130.6, 122.0, 119.1, 117.4, 112.9, 112.3, 110.4, 109.7, 100.5, 55.1, 47.7, 8.6. ESI-MS: *m/z* 401 $[M+1]^+$.

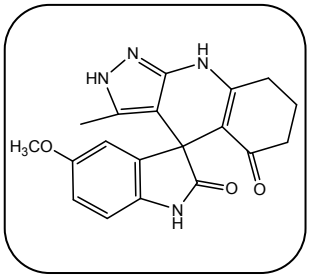
3'-methyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(2'*H*)-dione (11a):



IR (KBr): 3245, 3073, 2954, 1703, 1619, 1470, 1339, 1221, 1078 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.89 (s, 1H), 10.20 (s, 1H), 10.01 (s, 1H), 7.04 (t, 1H, *J* = 7.2Hz), 6.72-6.79 (m, 3H), 2.58-2.63 (m, 2H), 2.08-2.13 (m, 2H), 1.83-1.86 (m, 2H), 1.54 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 192.4, 179.7, 156.0, 145.7, 141.5, 137.5, 134.3, 126.7, 122.6, 121.1, 108.2,

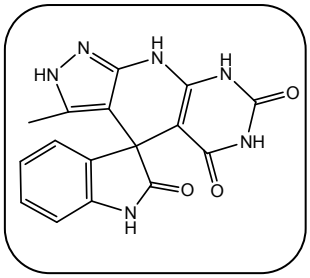
106.4, 101.3, 59.0, 48.2, 36.8, 27.9, 21.1, 8.6. ESI-MS: *m/z* 321 $[M+1]^+$. Anal. Calcd. for $C_{18}H_{16}N_4O_2$: C, 67.49; H, 5.03; N, 17.49%; Found: C, 67.51; H, 5.08; N, 17.60%.

5-methoxy-3'-methyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(2'*H*)-dione (11b):



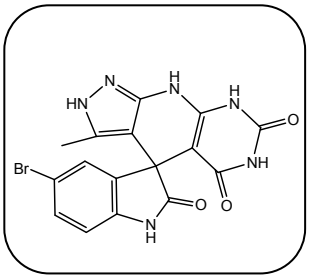
IR (KBr): 3425, 3354, 3205, 3081, 2961, 1731, 1686, 1489, 1216, 1076 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 10.89 (s, 1H), 10.17 (s, 1H), 7.49 (s, 1H), 6.82 (s, 1H), 6.72 (d, 1H, *J* = 8.4Hz), 3.71 (s, 3H), 2.55-.2.75 (m, 2H), 2.08-2.15 (m, 2H), 1.92-1.98 (m, 2H), 1.51 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 204.8, 177.9, 155.5, 154.8, 144.0, 141.4, 134.5, 133.4, 132.0, 114.0, 111.4, 110.1, 97.5, 58.9, 58.2, 55.4, 33.6, 20.9, 12.9. ESI-MS: *m/z* 351 $[M+1]^+$.

3'-methyl-8',9'-dihydrospiro[indoline-3,4'-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyrimidine]-2,5',7'(2'*H*,6'*H*)-trione (12a):



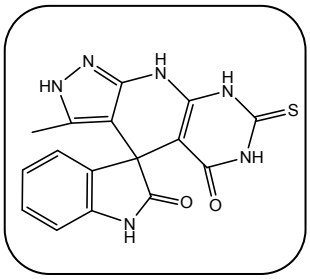
IR (KBr): 3359, 3065, 2926, 2869, 1716, 1640, 1469, 1332, 1217, 1041 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 11.78 (s, 1H), 10.29 (s, 1H), 10.14 (s, 1H), 9.92 (s, 1H), 8.89 (s, 1H), 6.84-6.88 (m, 1H), 6.54-6.59 (m, 3H), 1.31 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 178.9, 162.0, 149.8, 147.5, 145.1, 141.6, 136.2, 134.6, 127.2, 123.1, 121.5, 108.6, 99.9, 84.9, 47.2, 8.5. ESI-MS: *m/z* 337 $[M+1]^+$. Anal. Calcd. for $C_{16}H_{12}N_6O_3$: C, 57.14; H, 3.60; N, 24.99%; Found: C, 57.22; H, 3.58; N, 25.03%.

5-bromo-3'-methyl-8',9'-dihydrospiro[indoline-3,4'-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyrimidine]-2,5',7'(2'H,6'H)-trione (12c):



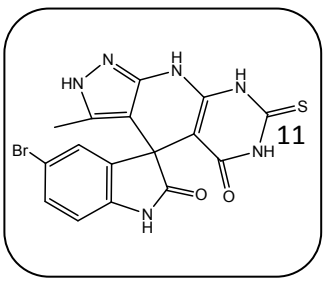
IR (KBr): 3246, 3012, 2857, 1728, 1634, 1469, 1327, 1213, 1094 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 12.09 (s, 1H), 10.58 (s, 1H), 10.53 (s, 1H), 10.17 (s, 1H), 9.16 (s, 1H), 7.28 (d, 1H, *J* = 7.2Hz), 6.99 (s, 1H), 6.76 (d, 1H, *J* = 7.6Hz), 1.58 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 178.6, 162.6, 149.7, 147.7, 145.0, 141.0, 138.6, 134.6, 130.0, 125.9, 113.2, 110.6, 99.2, 84.3, 47.4, 8.6. ESI-MS: *m/z* 414 $[M]^+$ and 416 $[M+2]^+$.

3'-methyl-7'-thioxo-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyrimidine]-2,5'(2'H)-dione (13a):



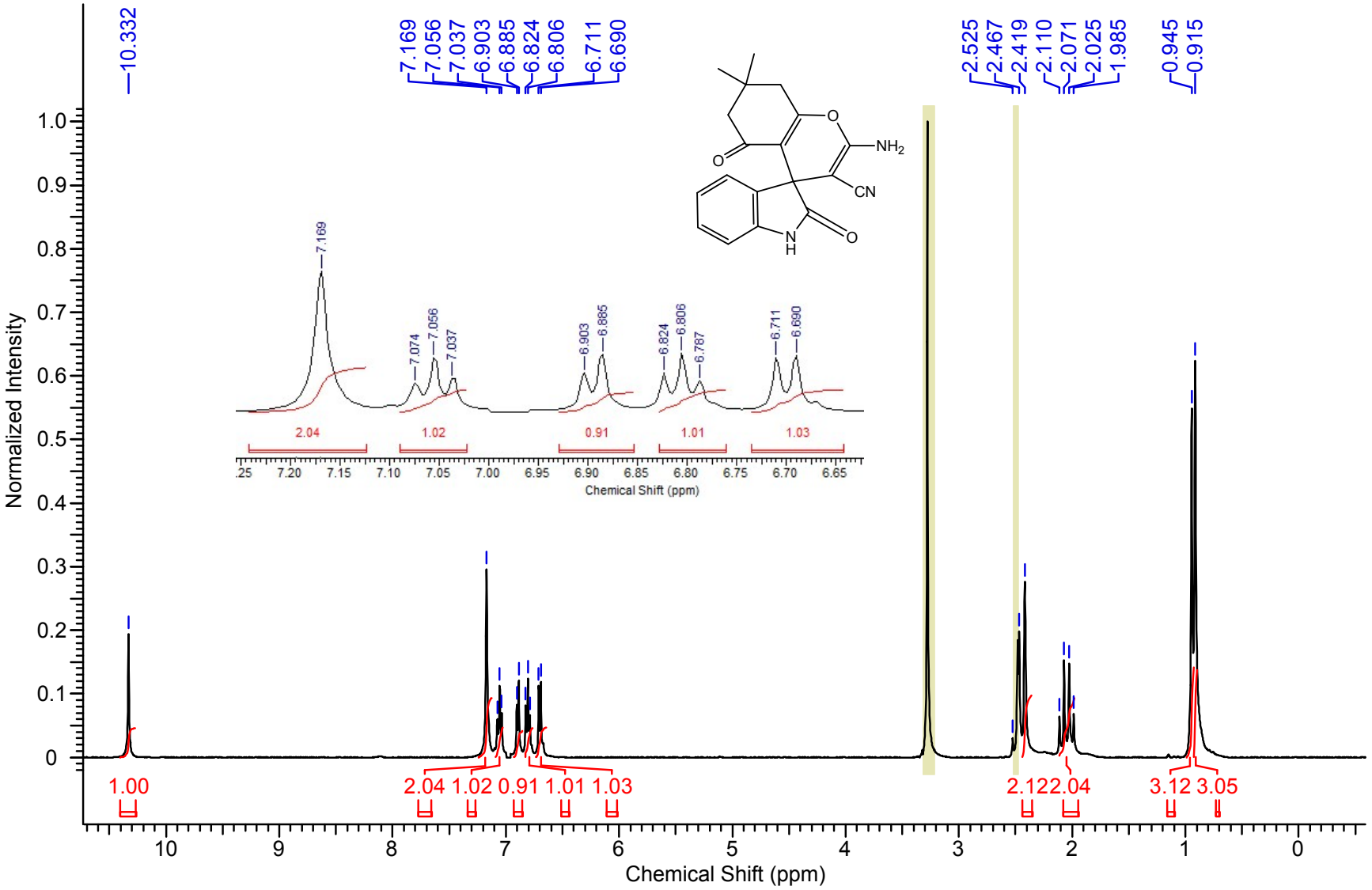
IR (KBr): 3344, 3221, 2945, 2879, 1688, 1567, 1471, 1340, 1217, 1095 cm^{-1}. ^1H NMR (DMSO-D6, 400 MHz): δ 12.09 (s, 1H), 12.00 (s, 1H), 11.67 (s, 1H), 10.42 (s, 1H), 8.91 (s, 1H), 7.11 (t, 1H, *J* = 7.2Hz), 6.79-6.88 (m, 3H), 1.54 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 178.4, 173.4, 159.3, 146.9, 144.3, 141.6, 135.6, 134.8, 127.5, 123.2, 121.6, 108.7, 99.5, 89.2, 47.2, 8.5. ESI-MS: *m/z* 353 $[M+1]^+$. Anal. Calcd. for $C_{16}H_{12}N_6O_2S$: C, 54.54; H, 3.43; N, 23.85%; Found: C, 54.45; H, 3.44; N, 23.93%.

5-bromo-3'-methyl-7'-thioxo-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyrimidine]-2,5'(2'H)-dione (13b):

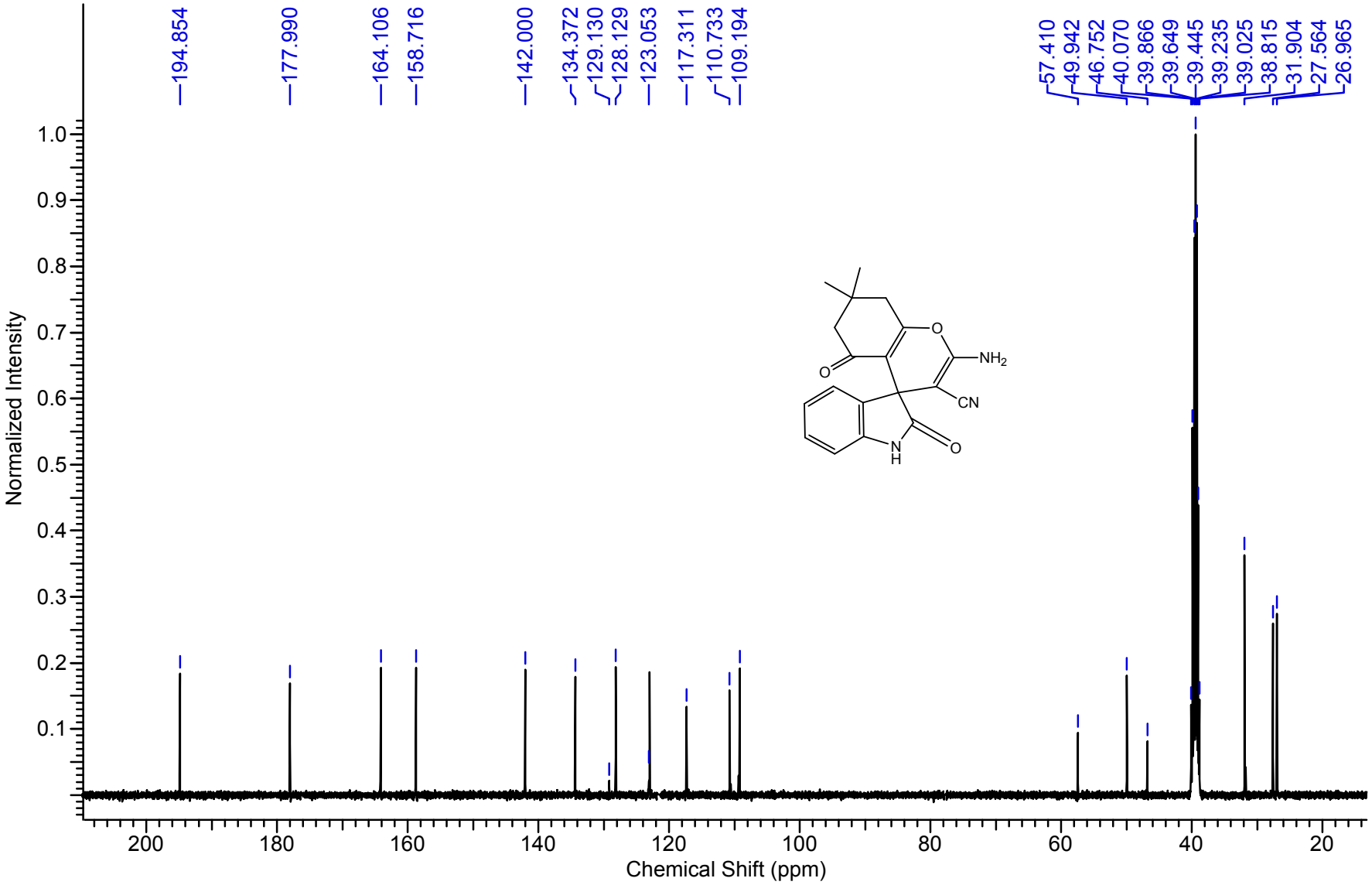


IR (KBr): 3405, 3216, 2926, 1708, 1603, 1473, 1236, 1169, 1082 cm^{-1}. ^{1}H NMR (DMSO-D6, 400 MHz): δ 12.07 (s, 1H), 10.59 (s, 1H), 10.49 (s, 1H), 10.23 (s, 1H), 8.95 (s, 1H), 7.08 (s, 1H), 6.77 (d, 1H, *J* = 8.8Hz), 6.71 (d, 1H, *J* = 7.2Hz), 1.58 (s, 3H). ^{13}C NMR (DMSO-D6, 100 MHz): δ 178.0, 173.5, 159.4, 147.1, 144.3, 140.9, 137.9, 134.9, 130.3, 127.8, 126.1, 110.7, 98.9, 88.6, 46.8, 8.6. ESI-MS: *m/z* 429 $[M]^+$ and 431 $[M+2]^+$.

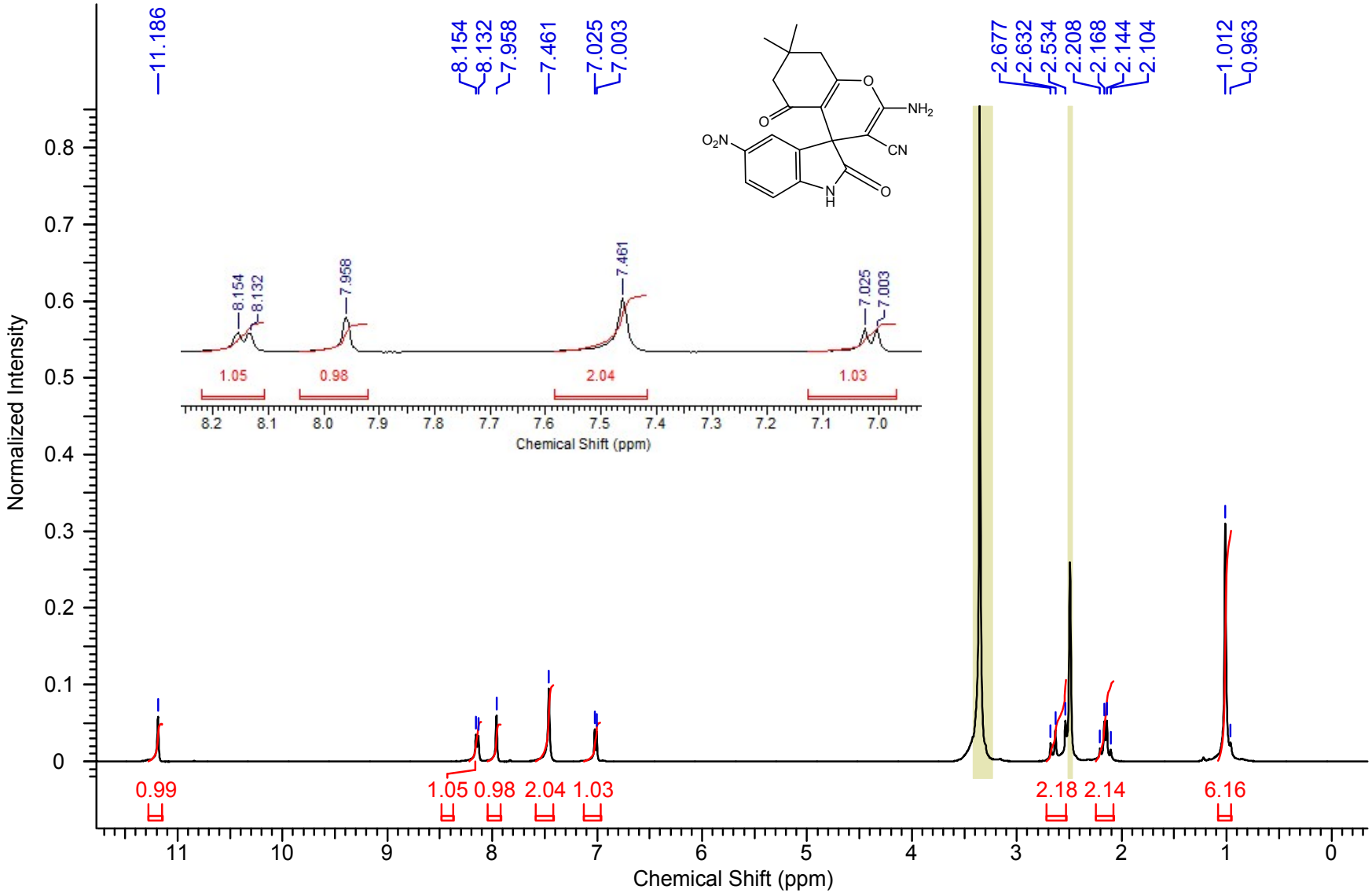
^{1}H-NMR of P-1(**4a**)



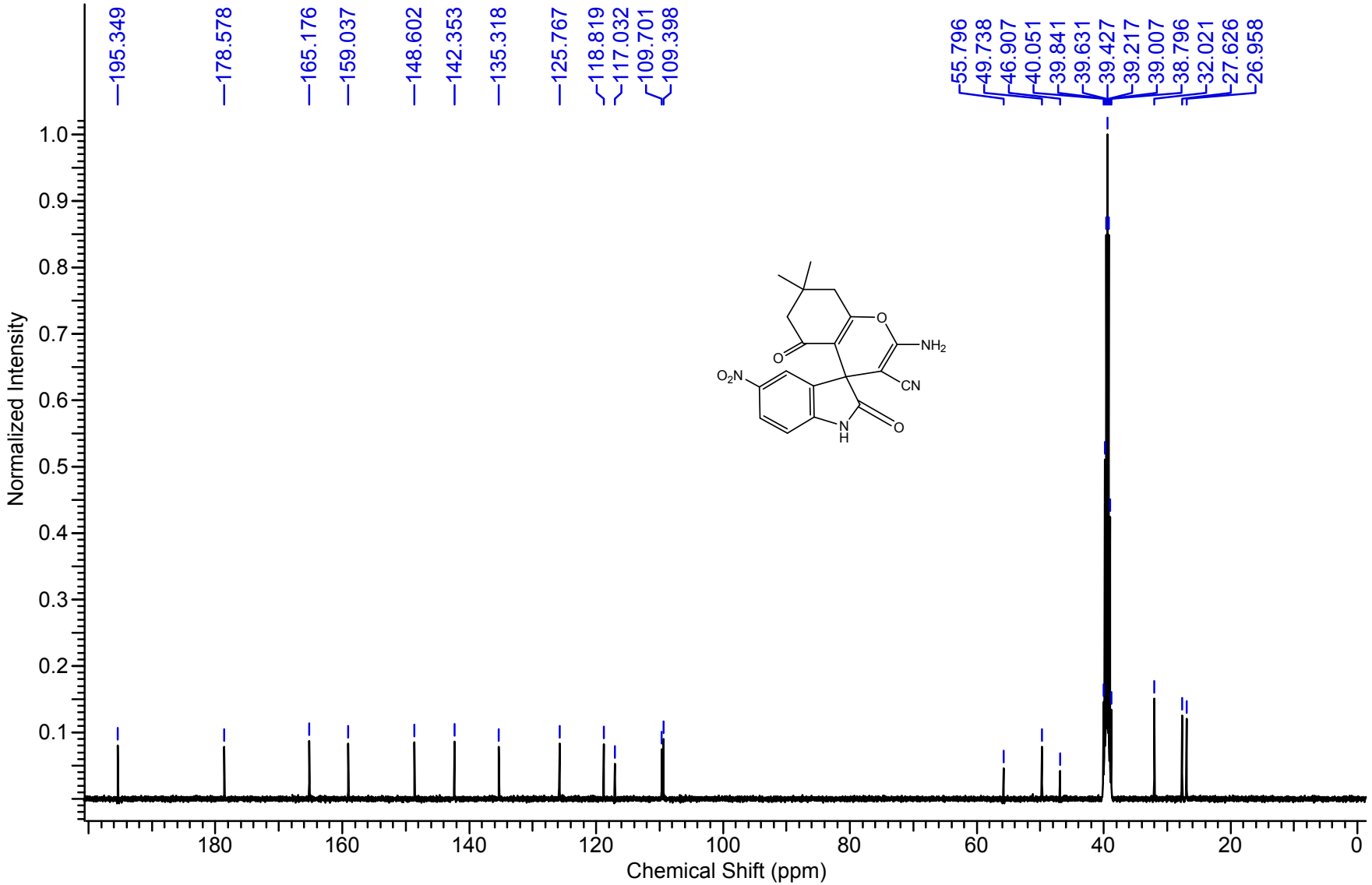
^{13}C-NMR of P-1(**4a**)



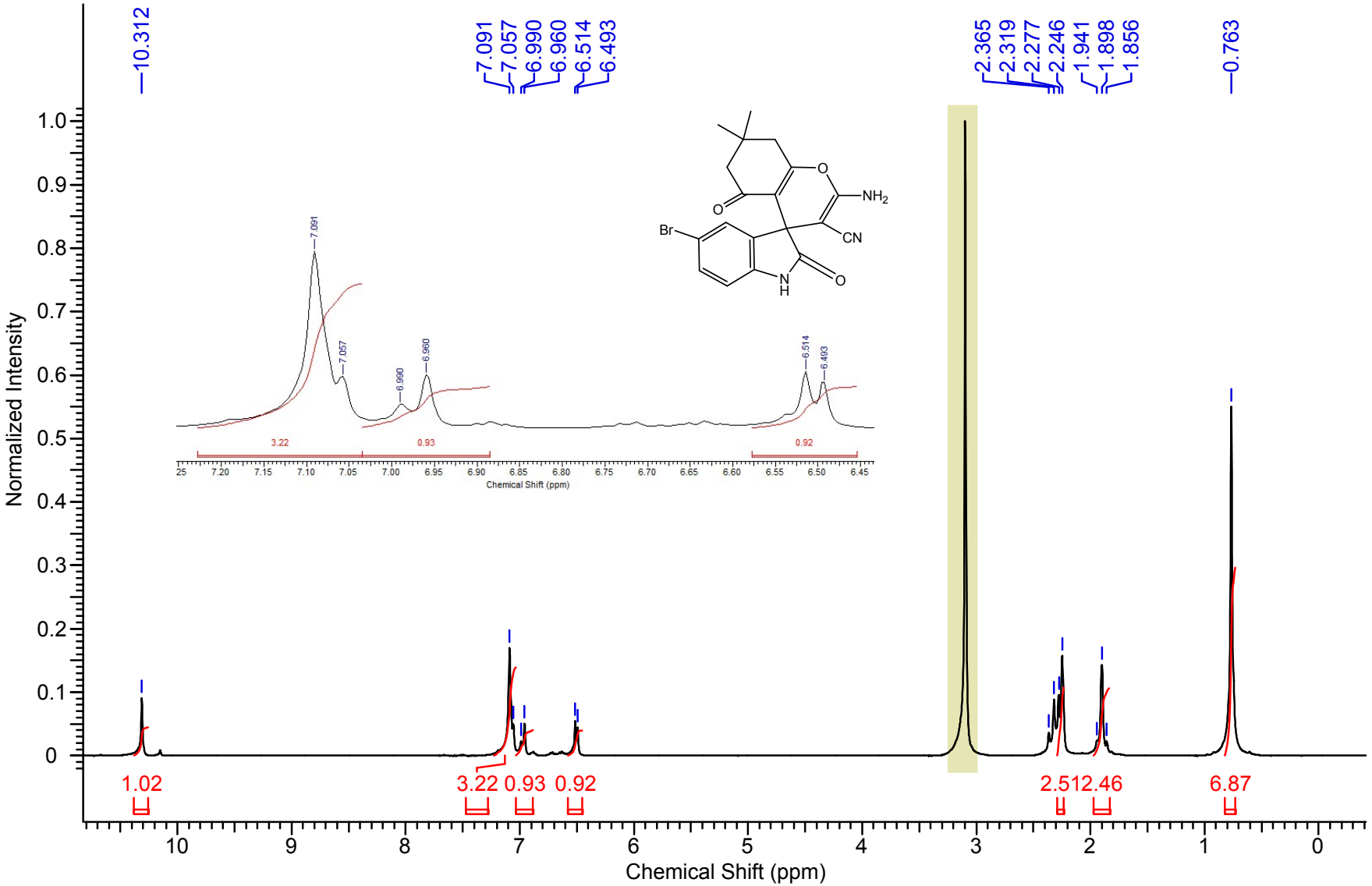
^{1}H-NMR of P-17(**4b**)



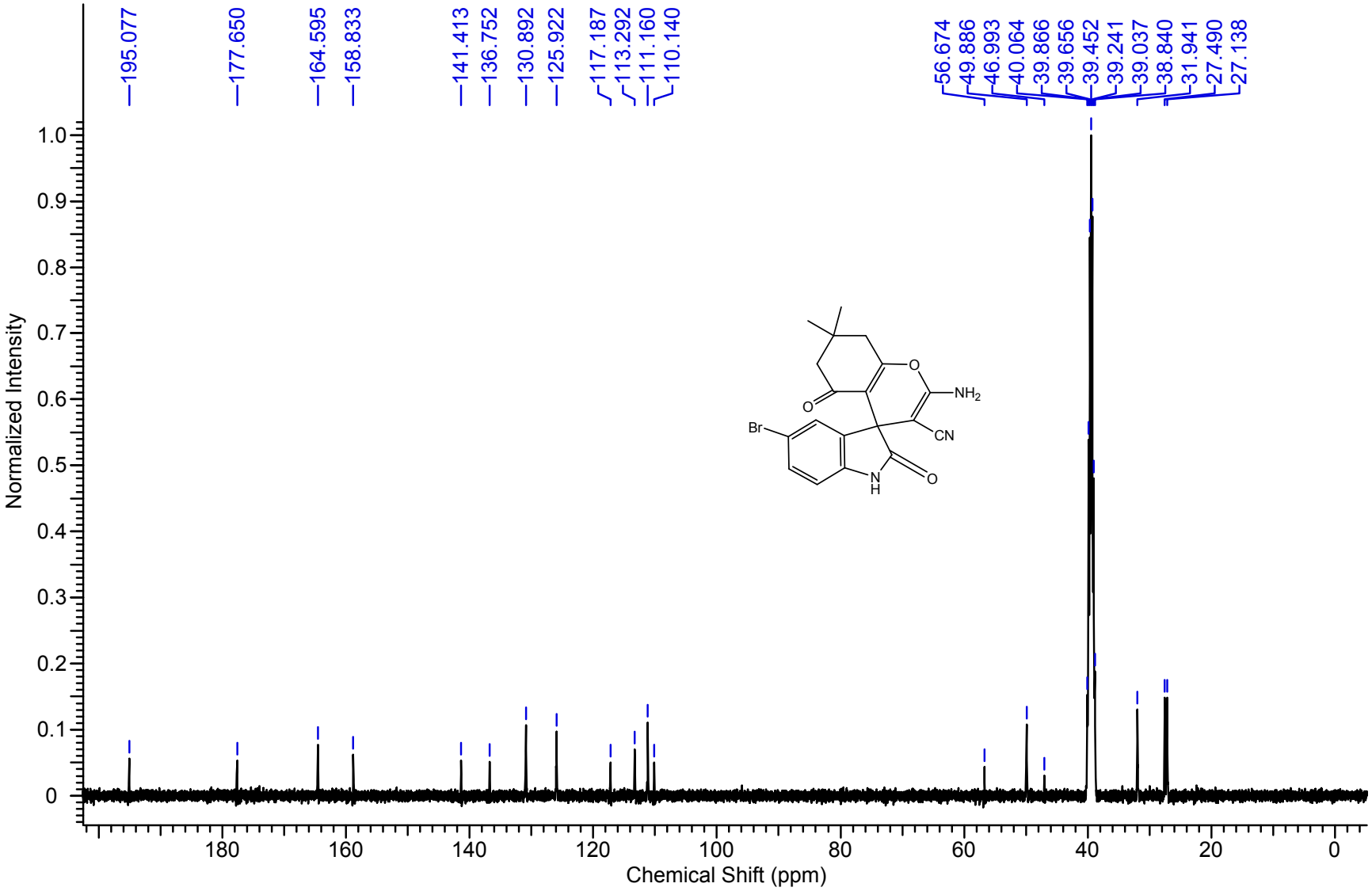
^{13}C-NMR of P-17(**4b**)



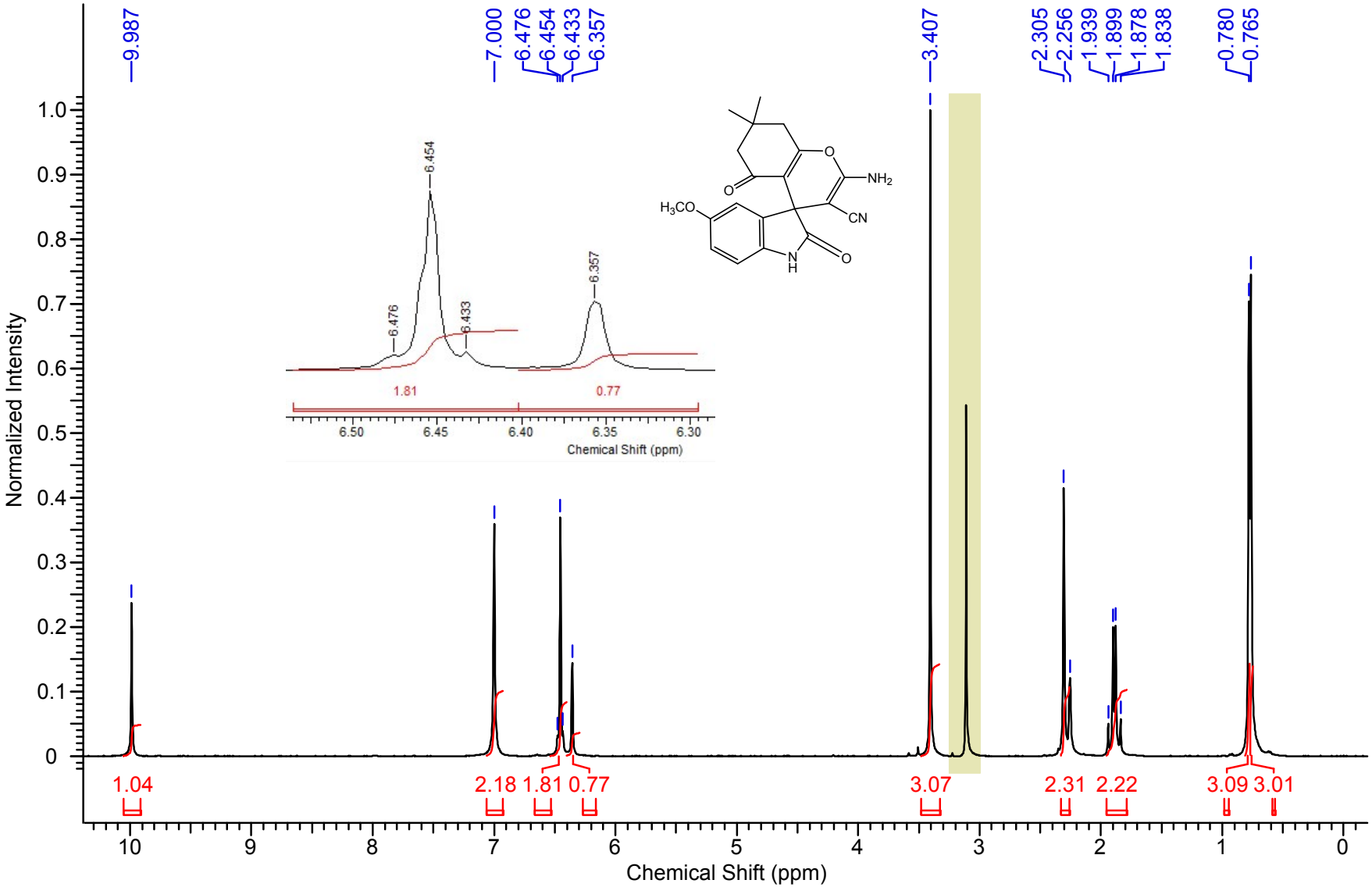
^{1}H-NMR of P-369(**4c**)



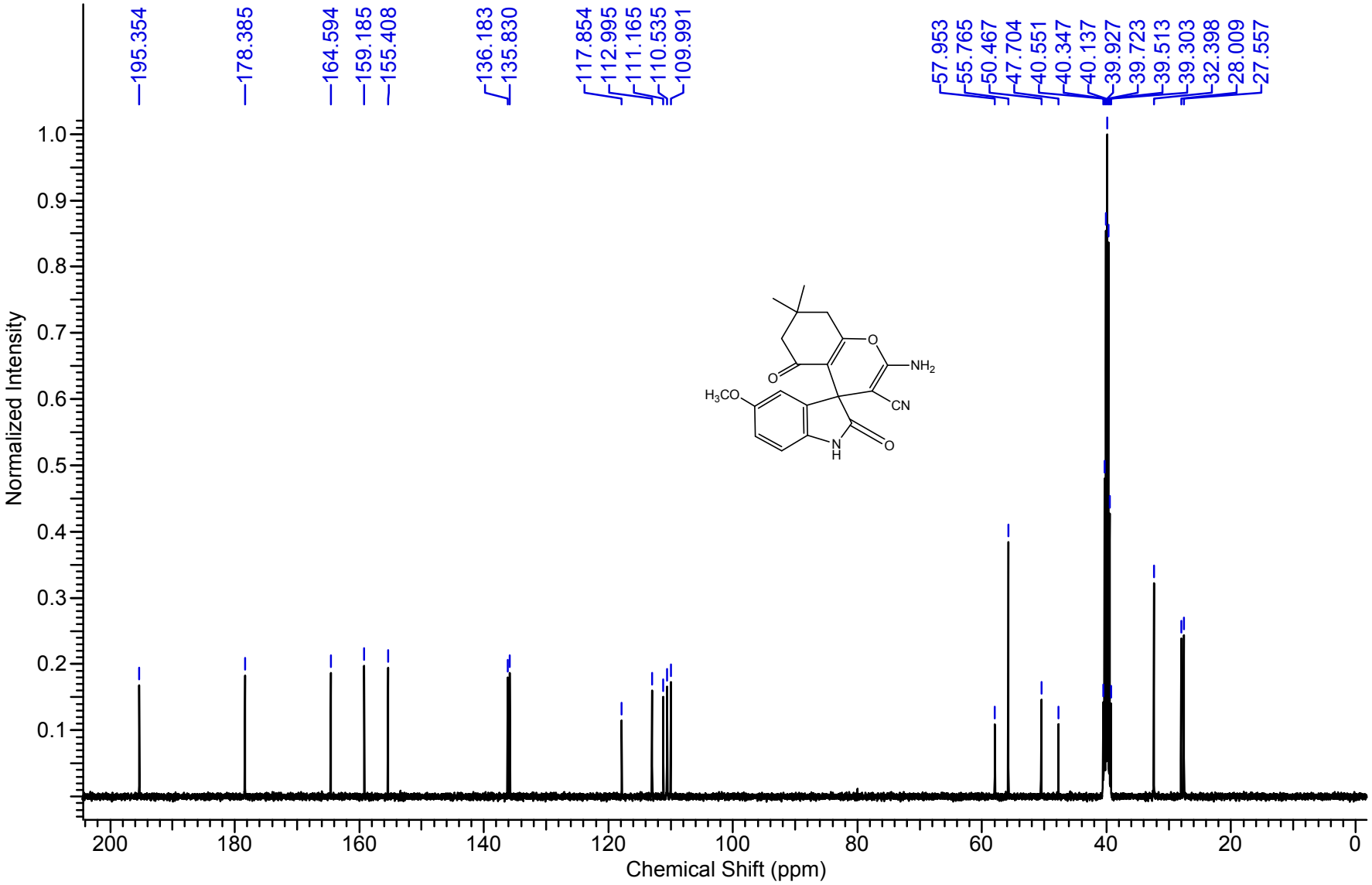
^{13}C-NMR of P-369(**4c**)



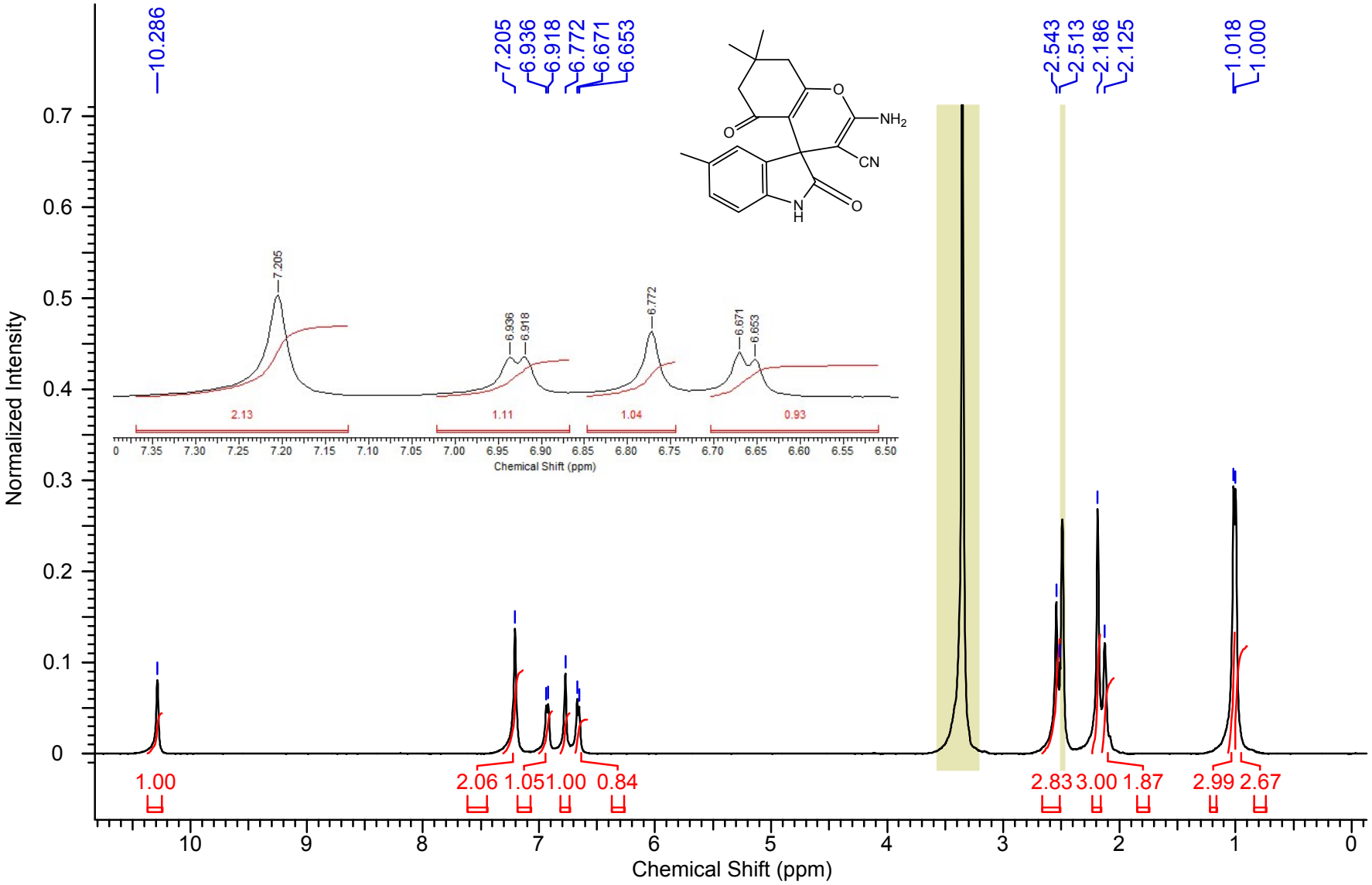
^{1}H-NMR of P-384(**4d**)



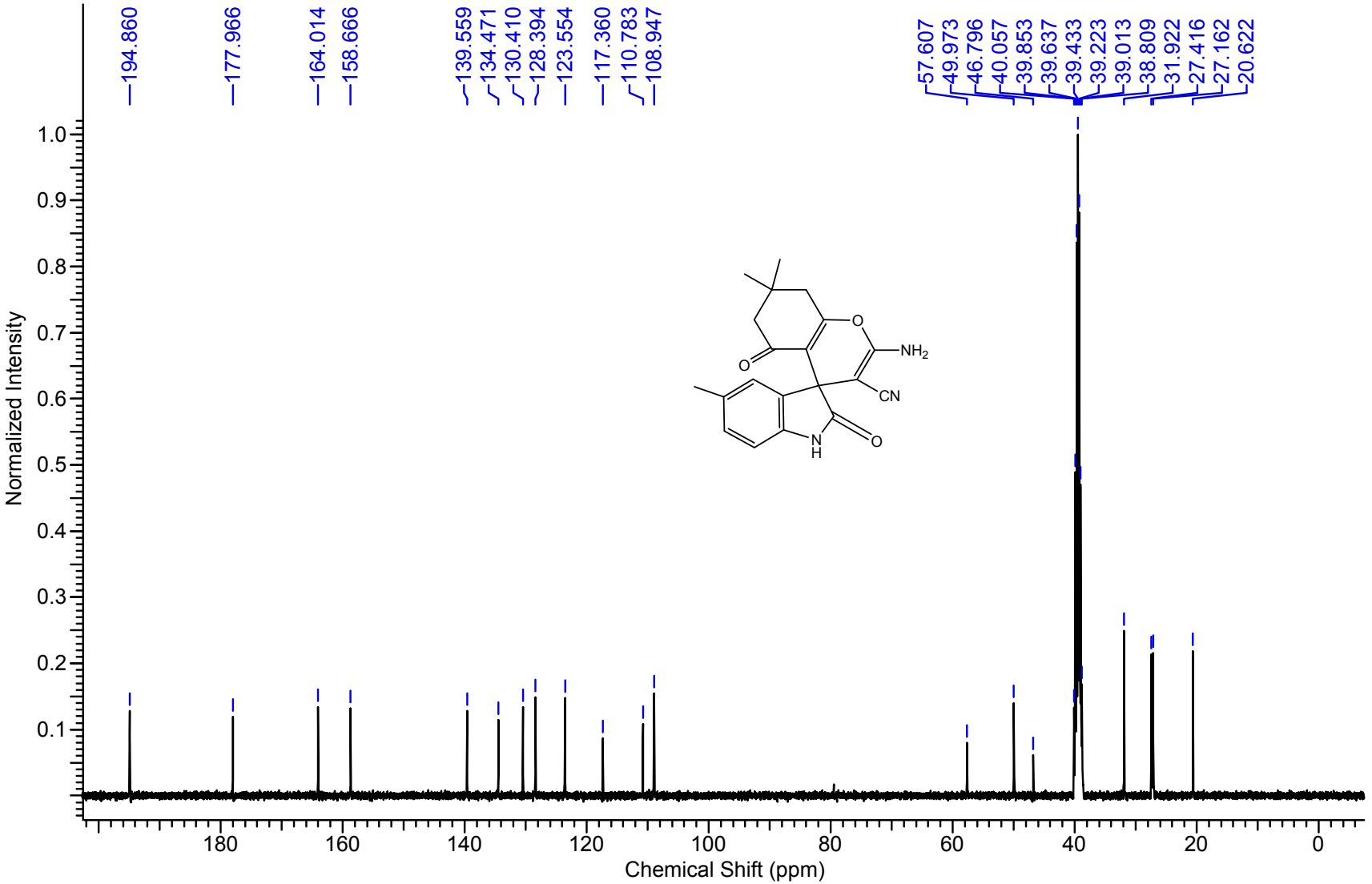
^{13}C-NMR of P-384(**4d**)



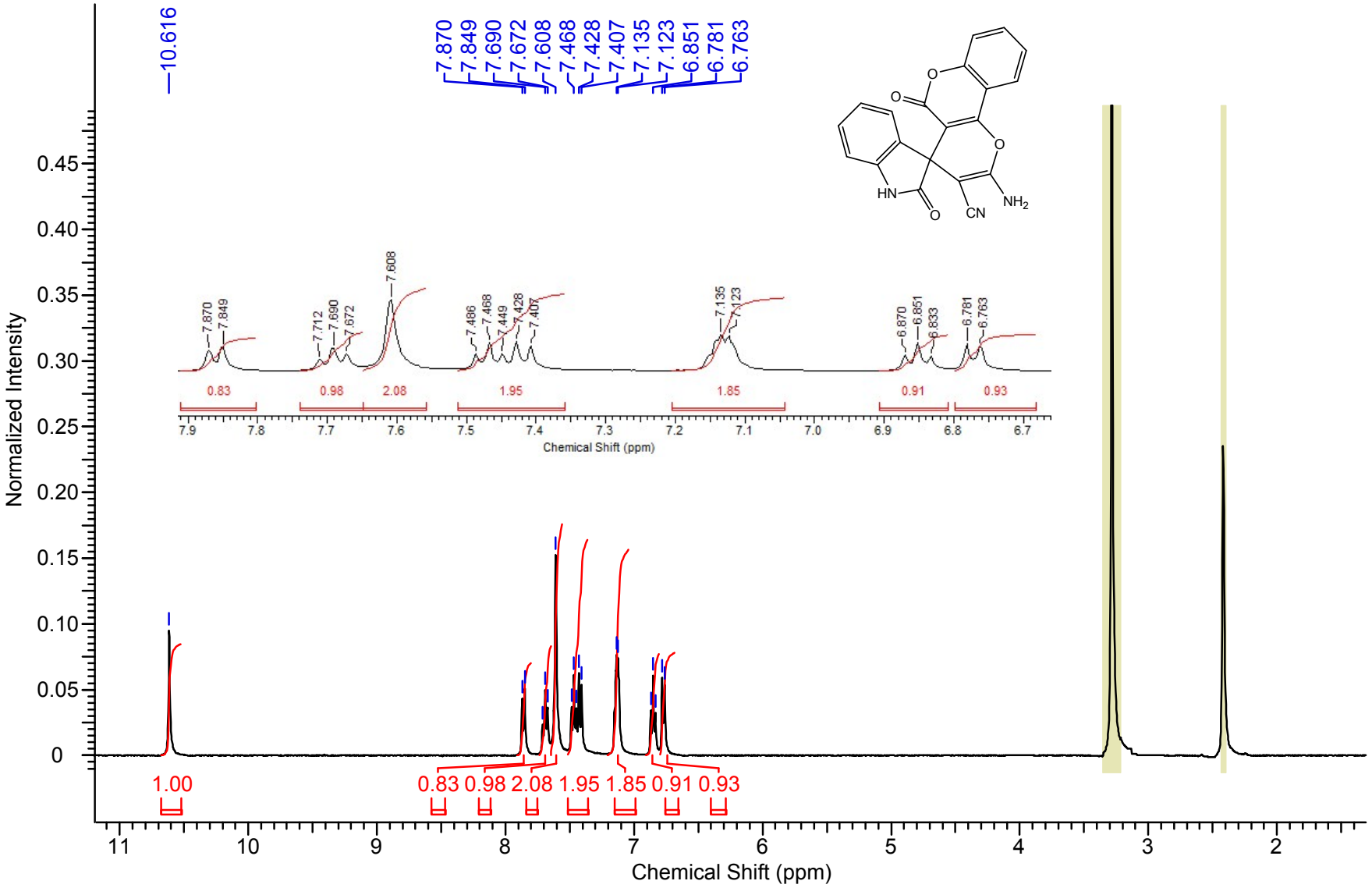
^{1}H-NMR of P-14(**4e**)



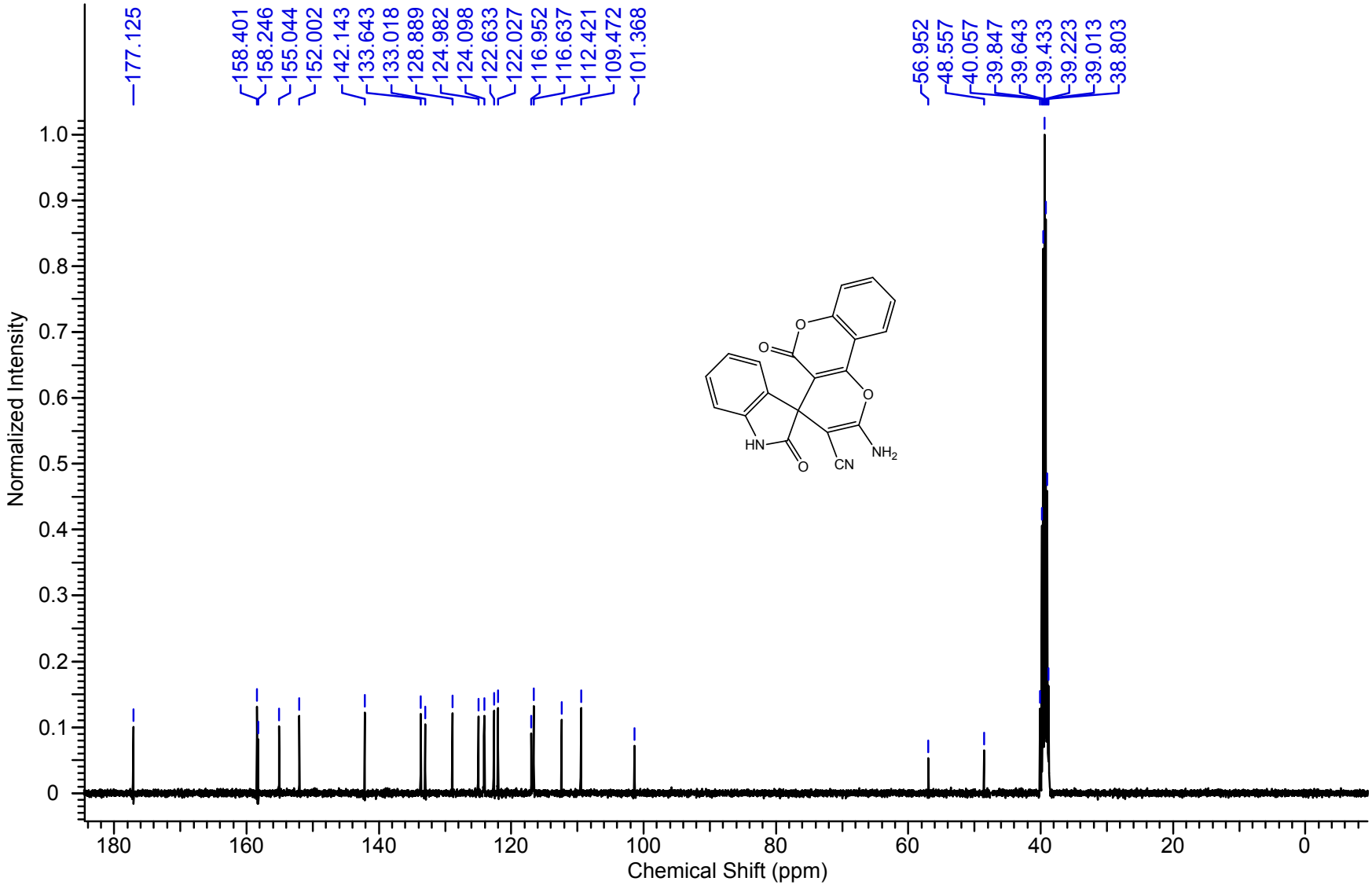
^{13}C-NMR of P-14(**4e**)



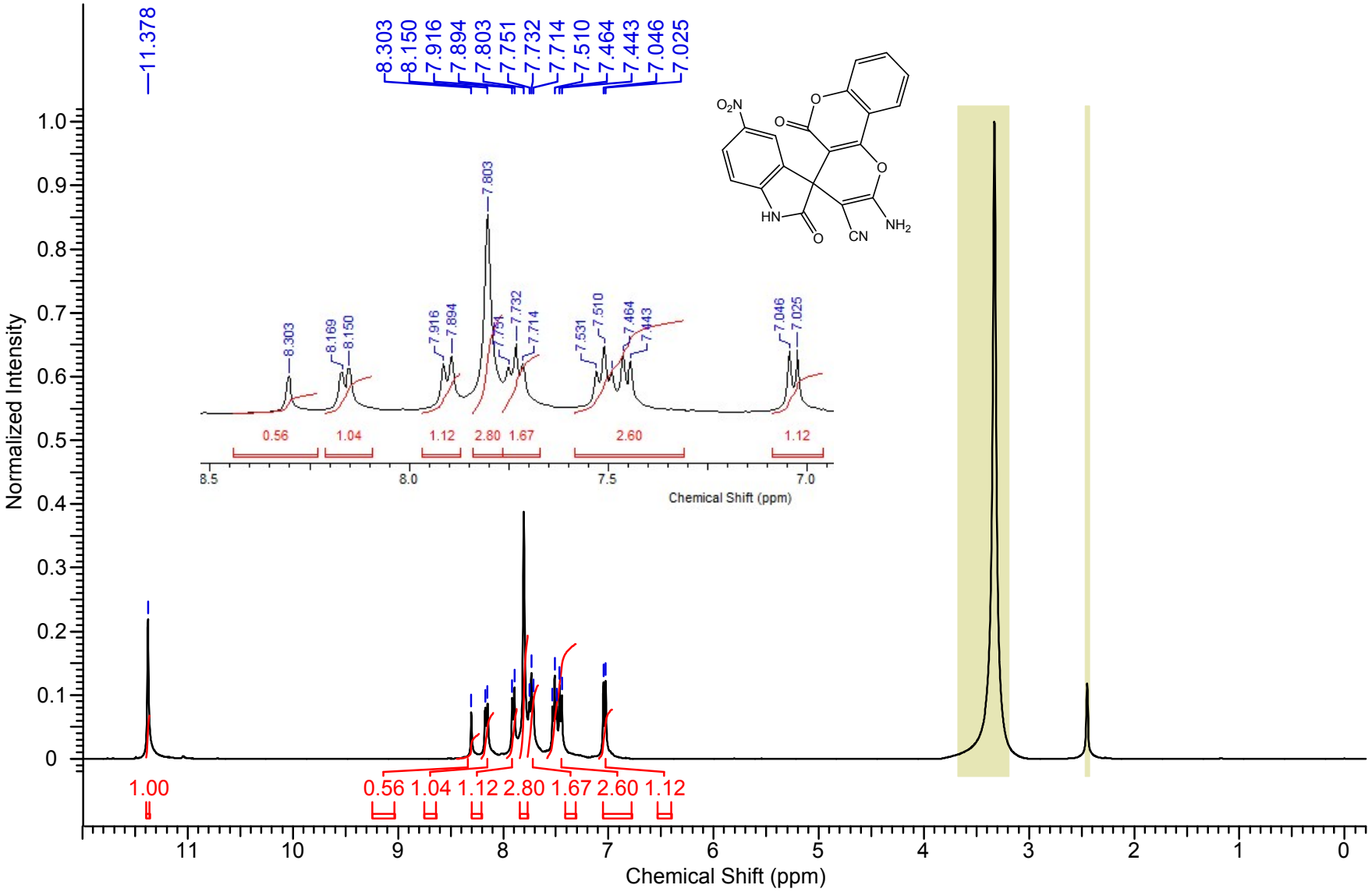
^{1}H-NMR of P-3(**5a**)



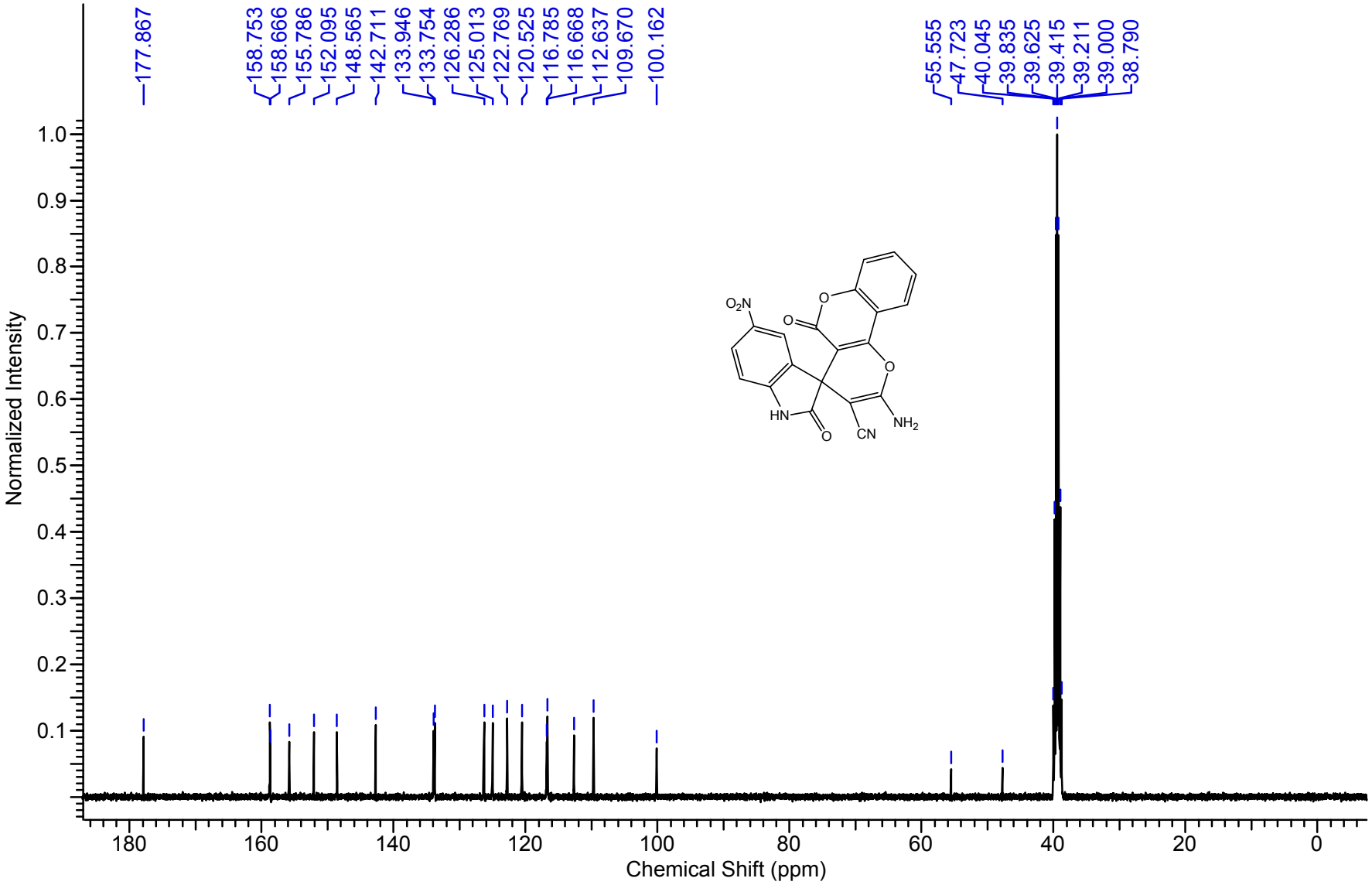
^{13}C-NMR of P-3(**5a**)



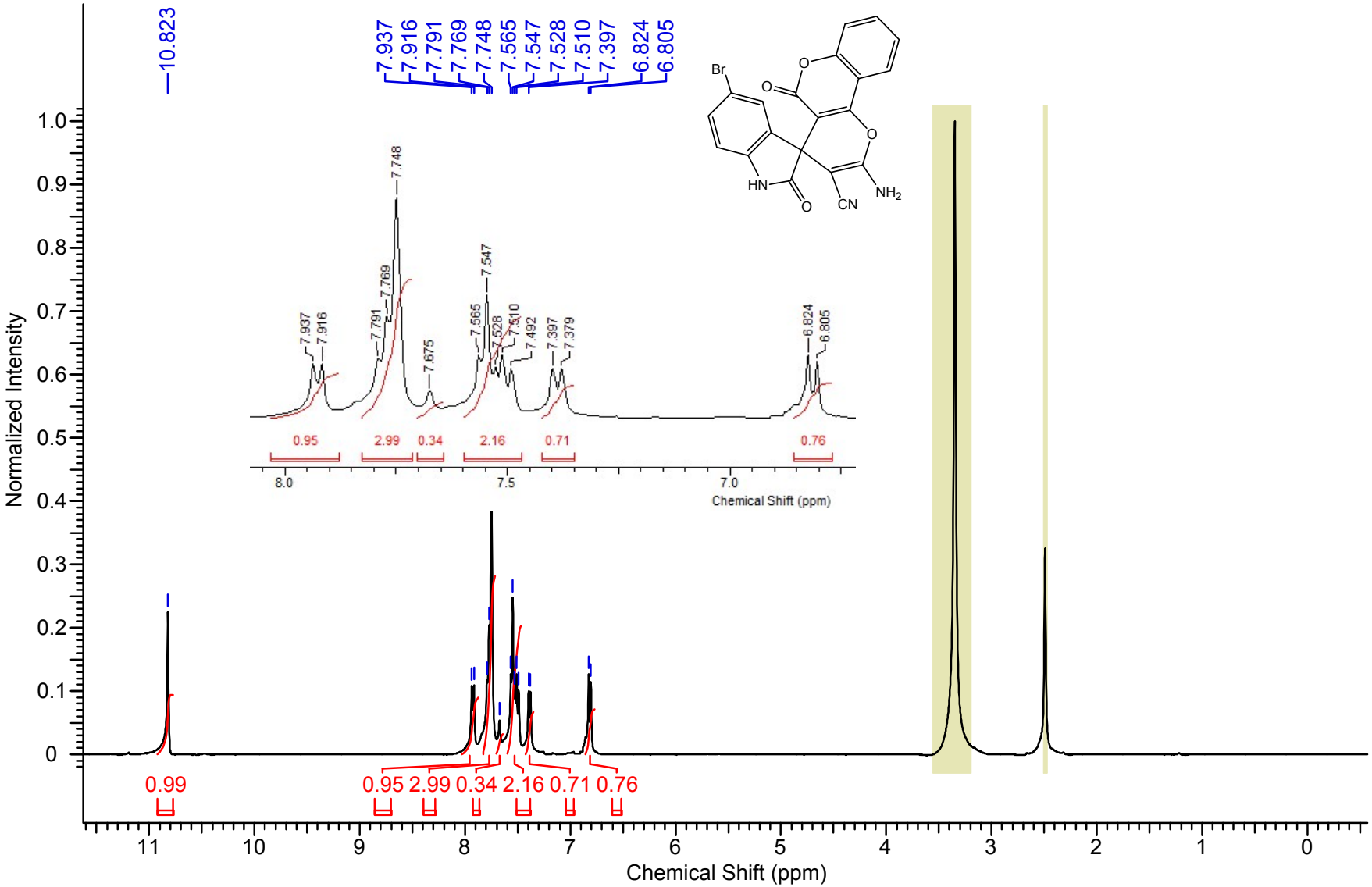
^{1}H-NMR of P-18(**5b**)



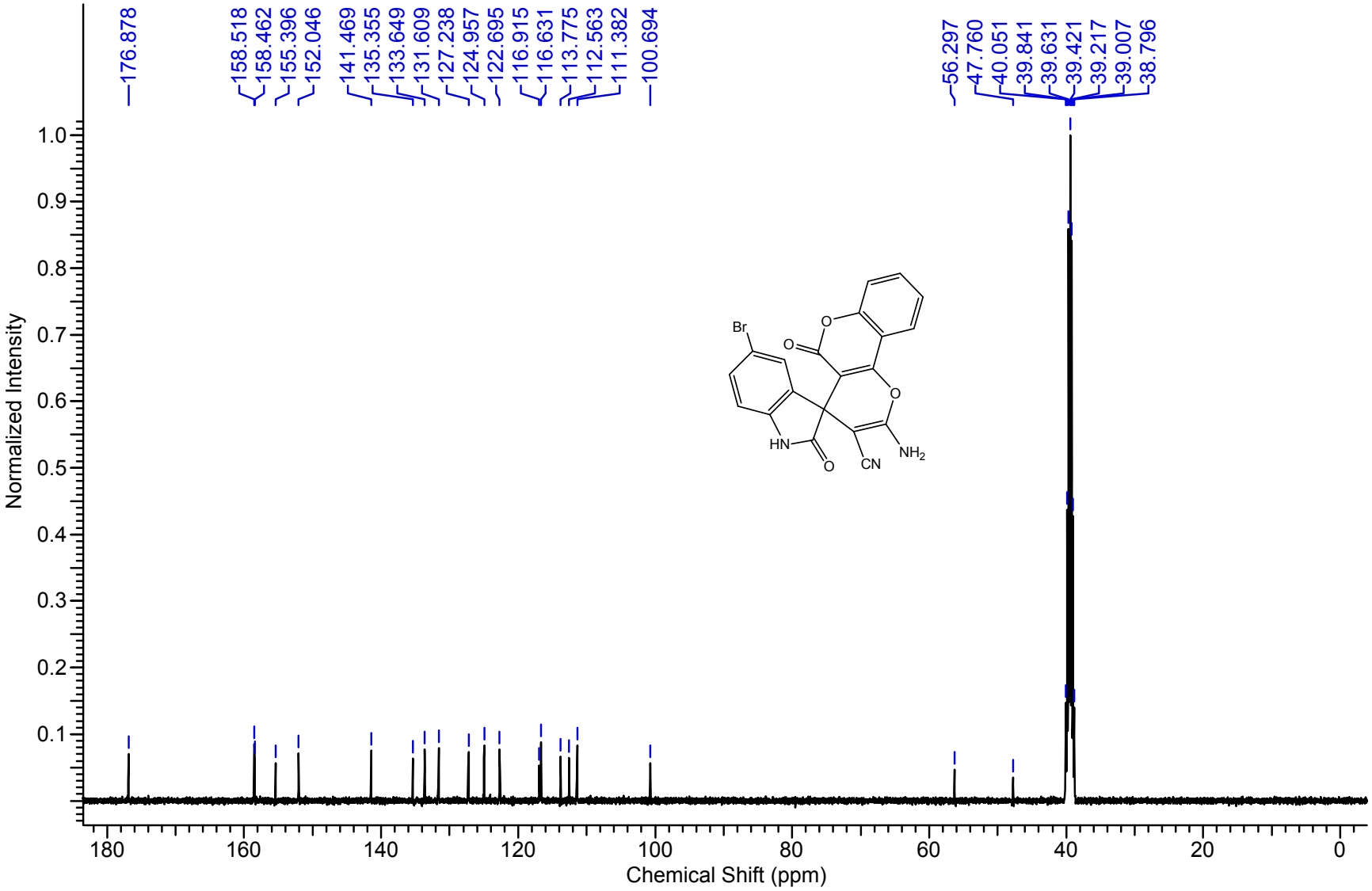
^{13}C-NMR of P-18(**5b**)



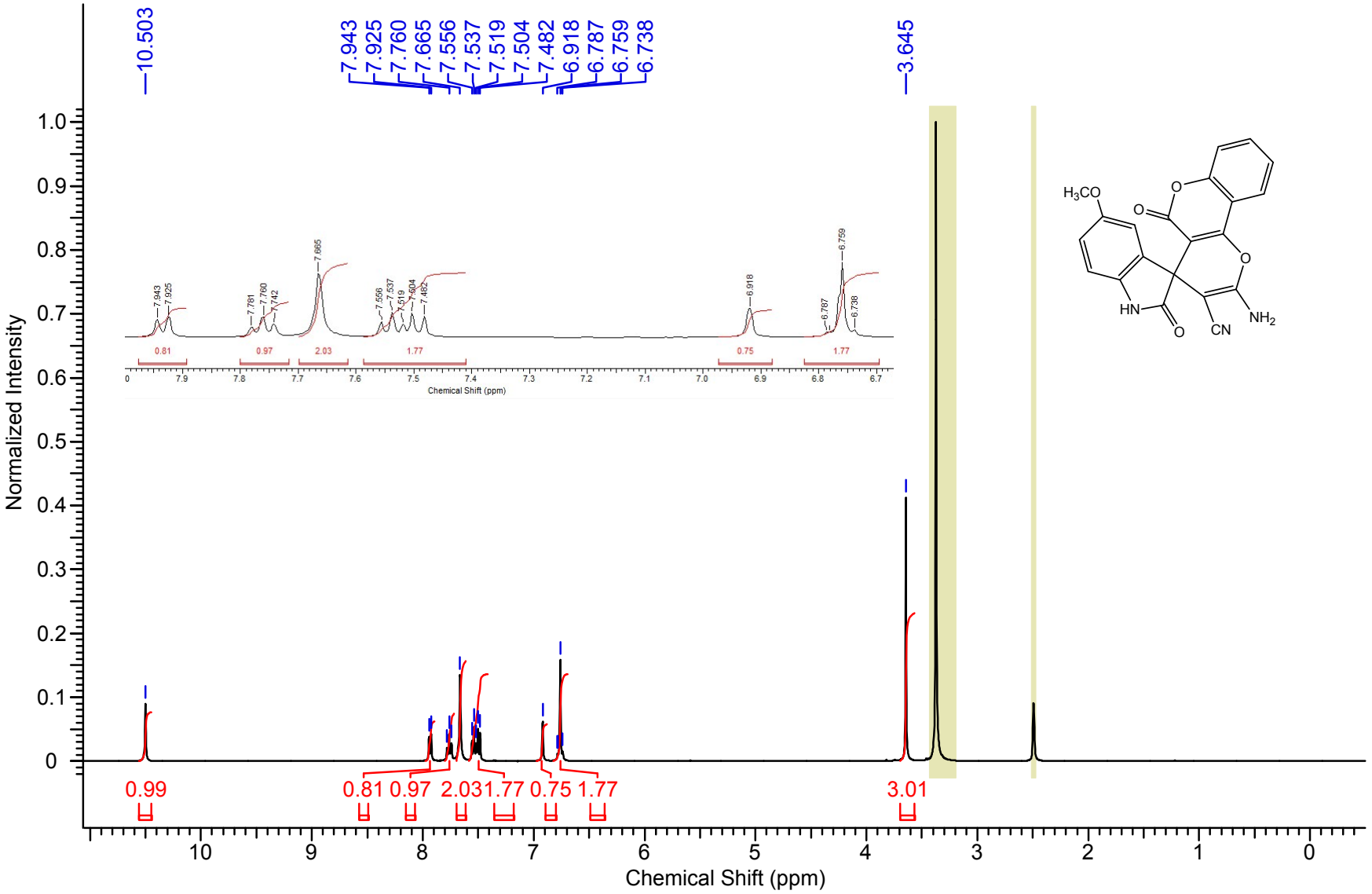
^{1}H-NMR of P-370(**5c**)



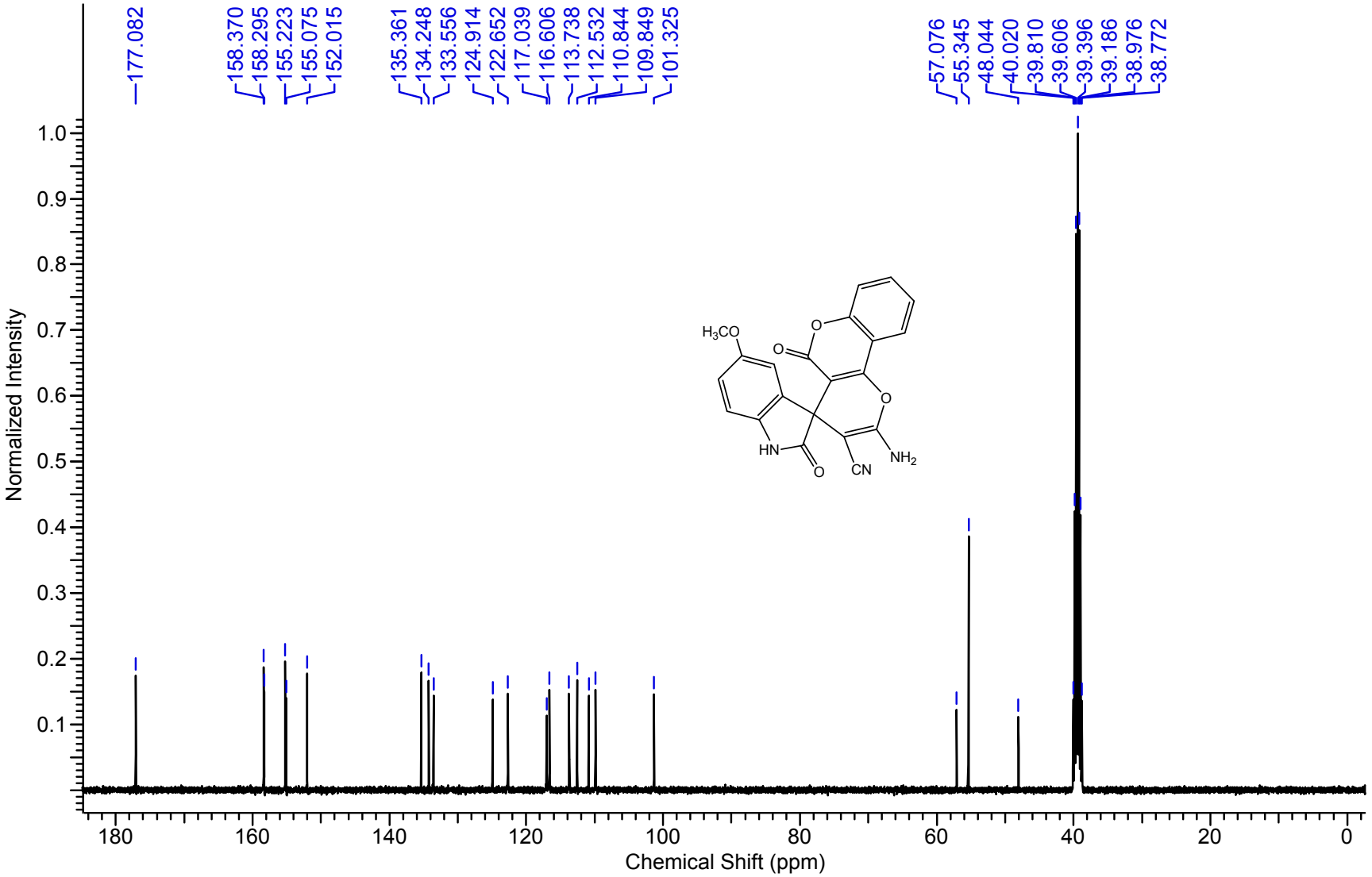
^{13}C-NMR of P-370(**5c**)



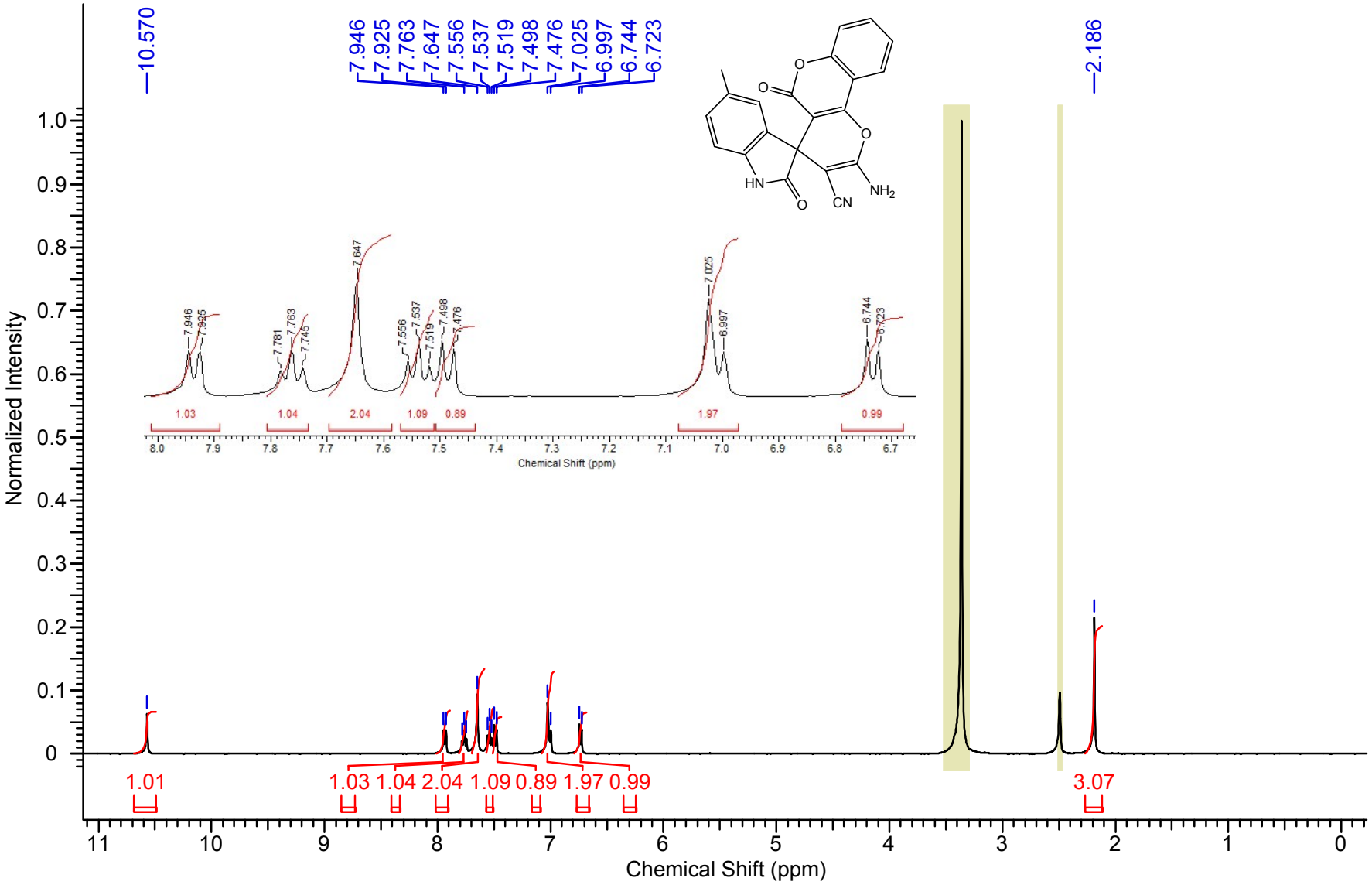
^{1}H-NMR of P-385(**5d**)



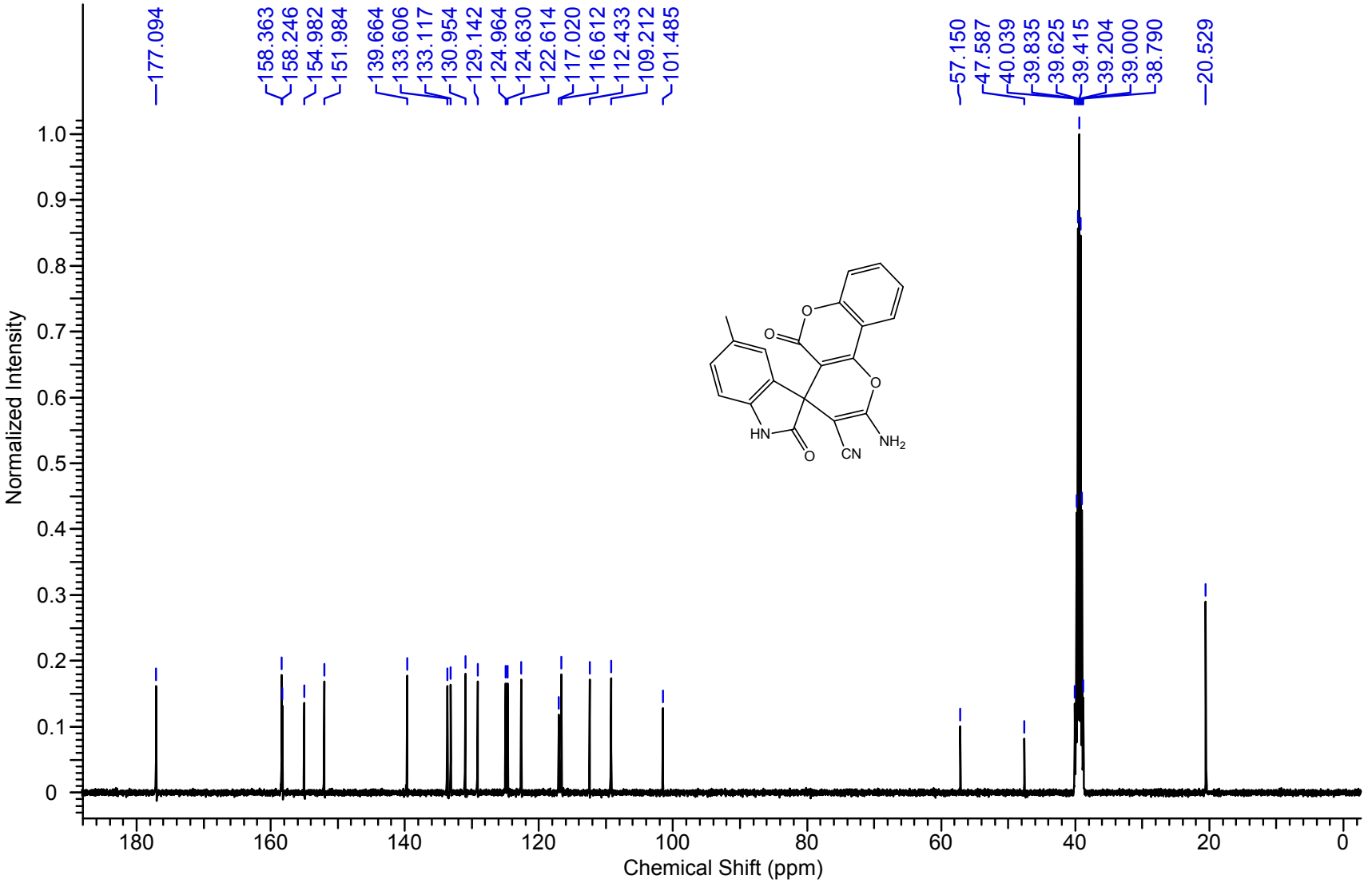
^{13}C-NMR of P-385(**5d**)



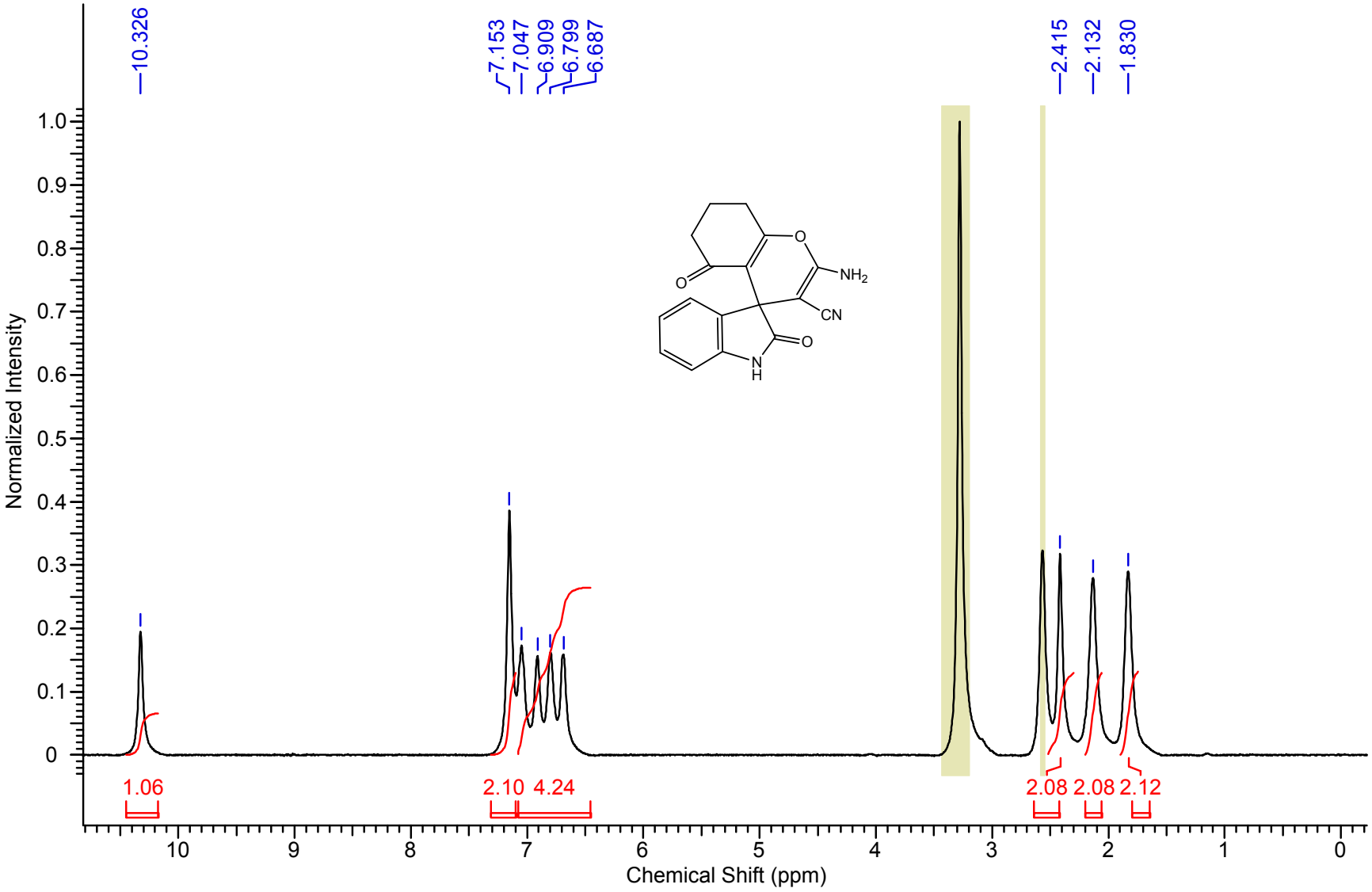
^{1}H-NMR of P-15(**5e**)



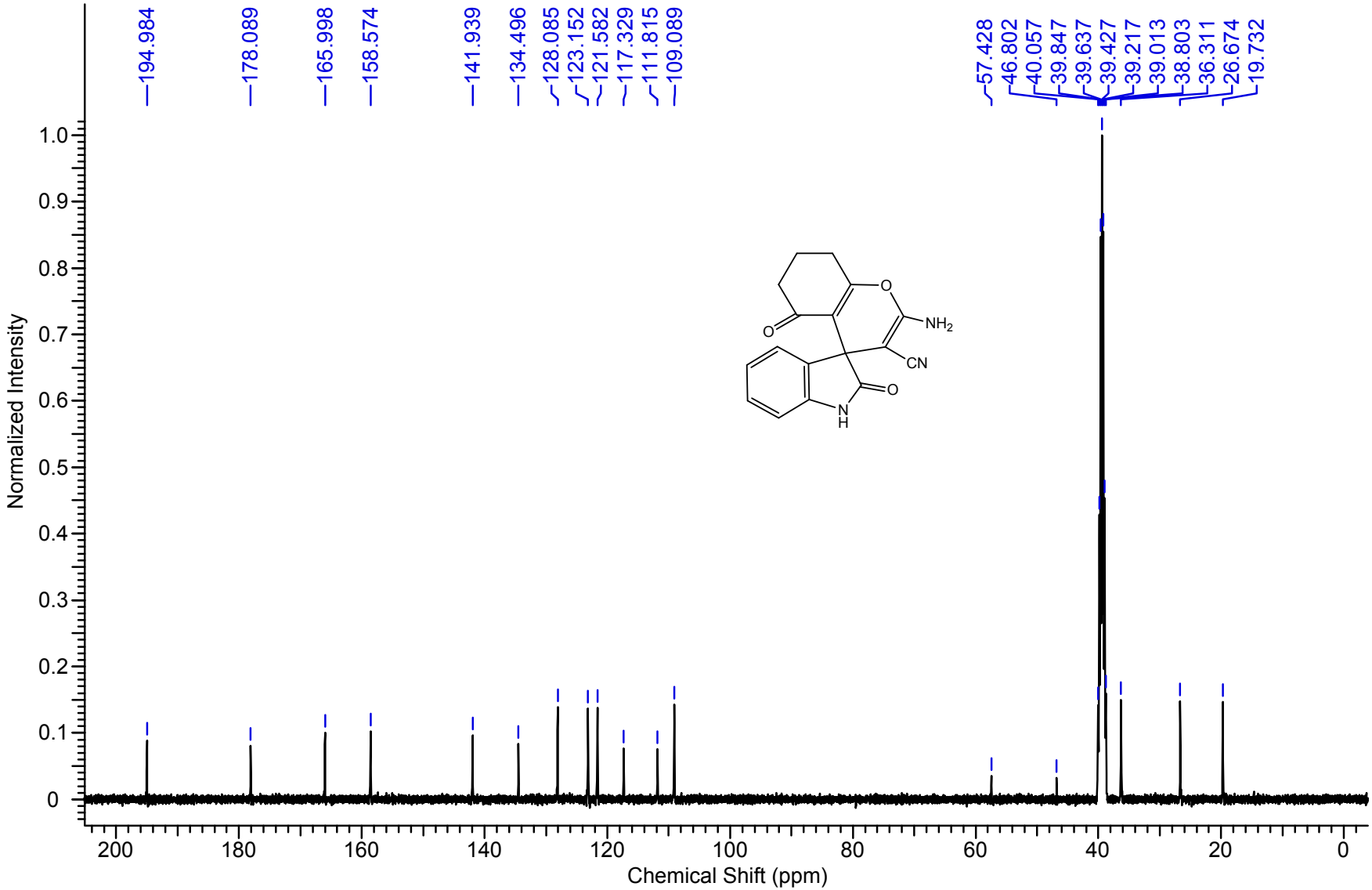
^{13}C-NMR of P-15(**5e**)



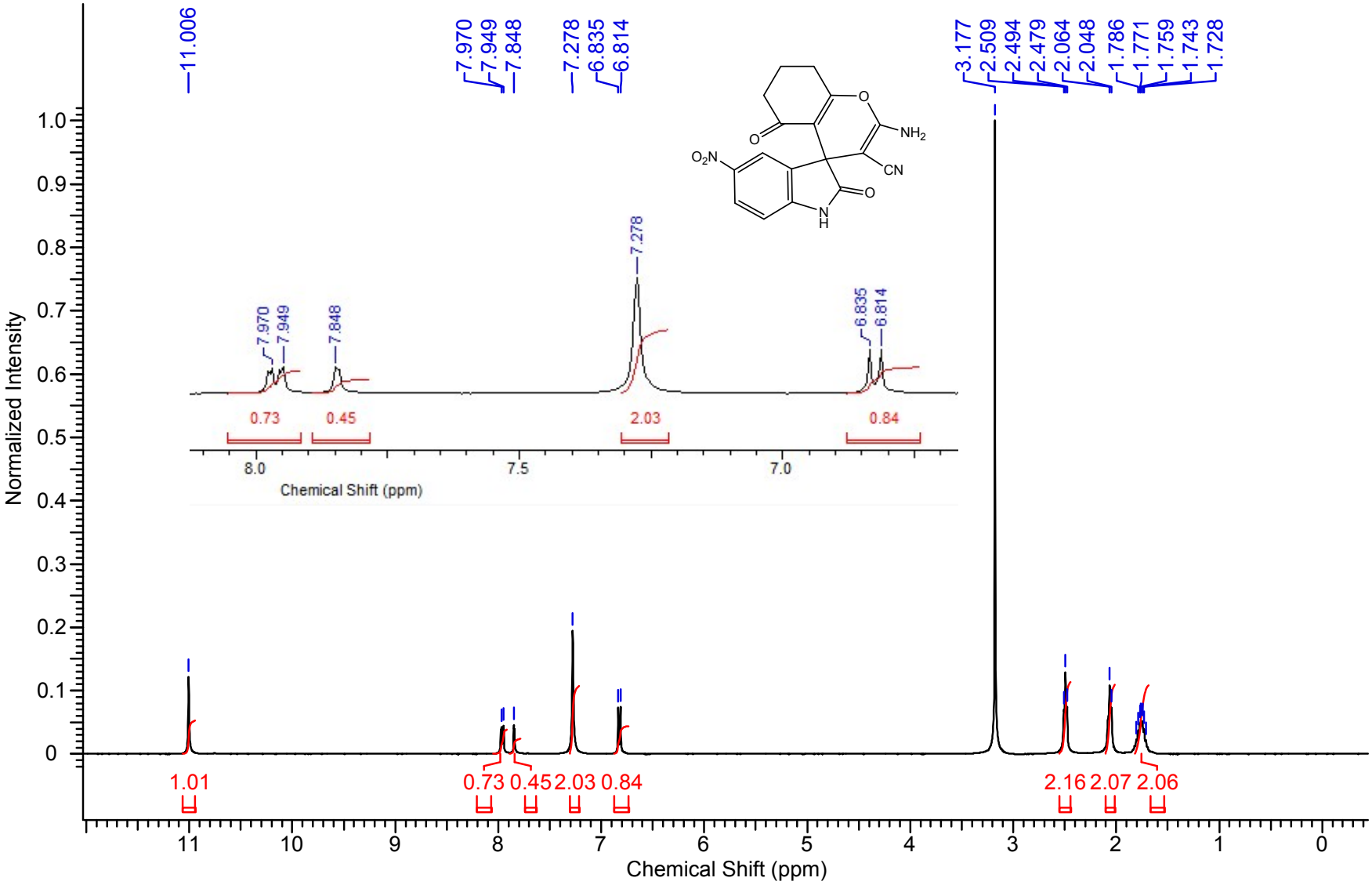
^{1}H-NMR of P-10(**6a**)



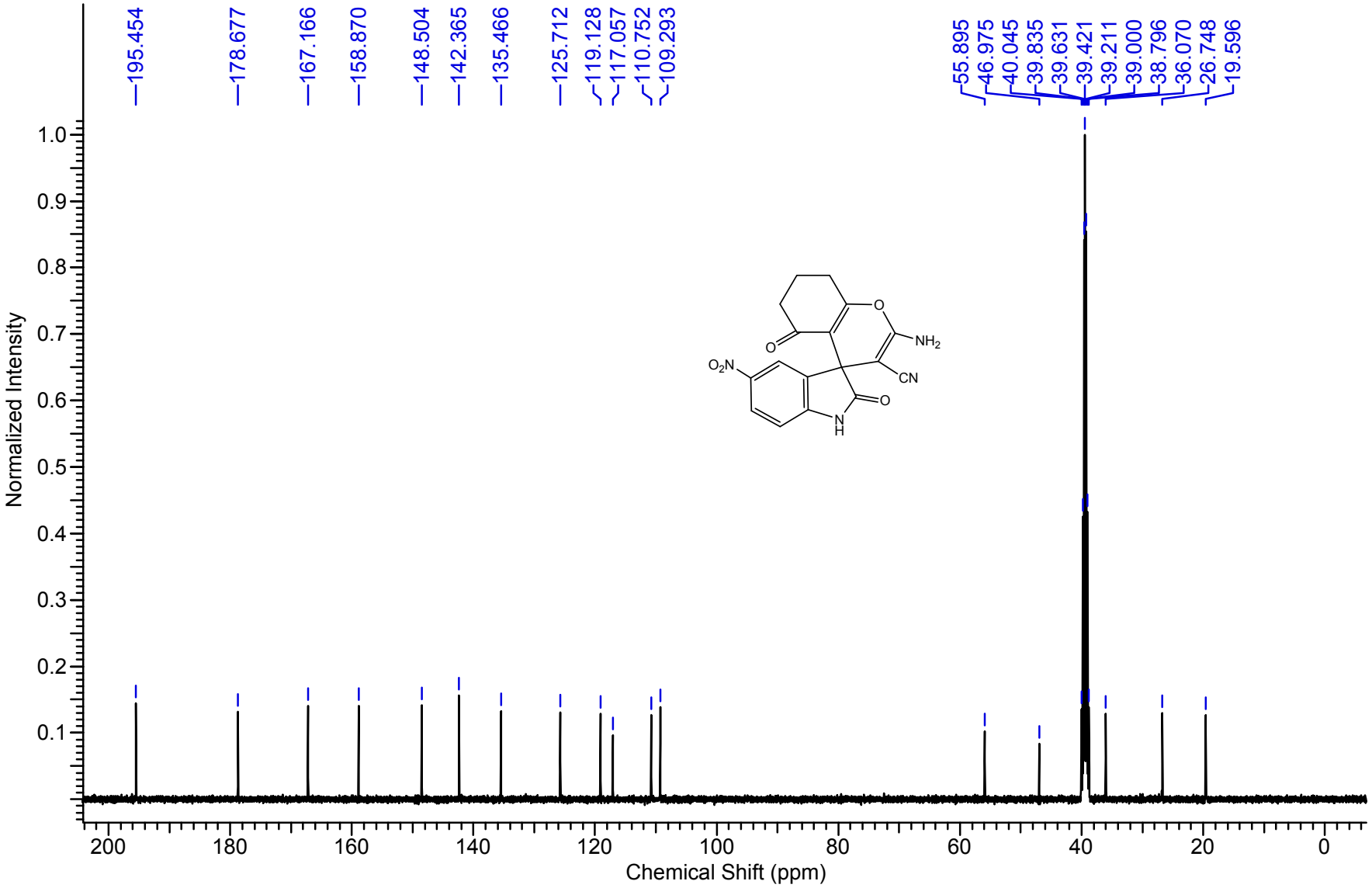
^{13}C-NMR of P-10(**6a**)



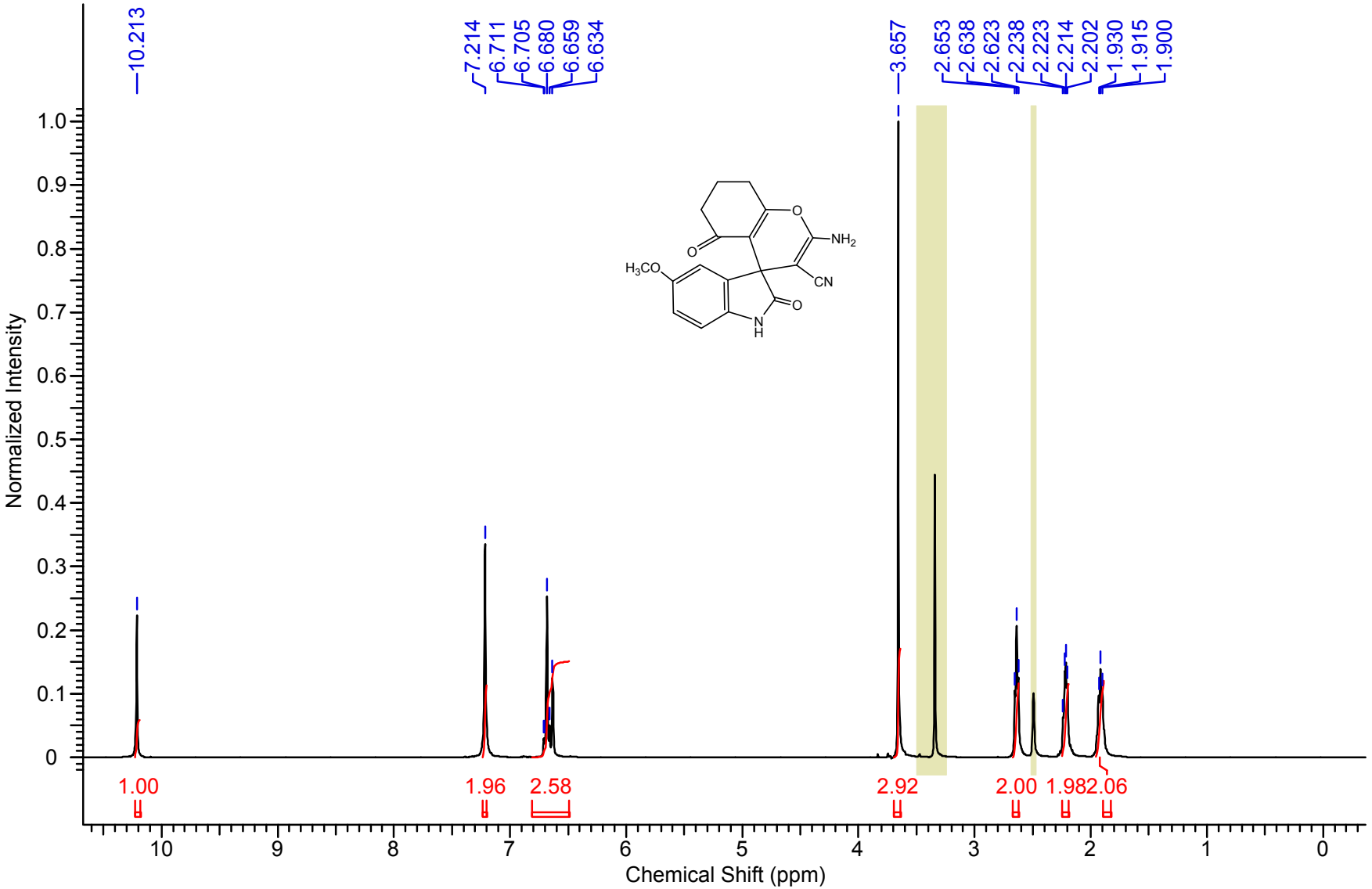
^{1}H-NMR of P-378(**6b**)



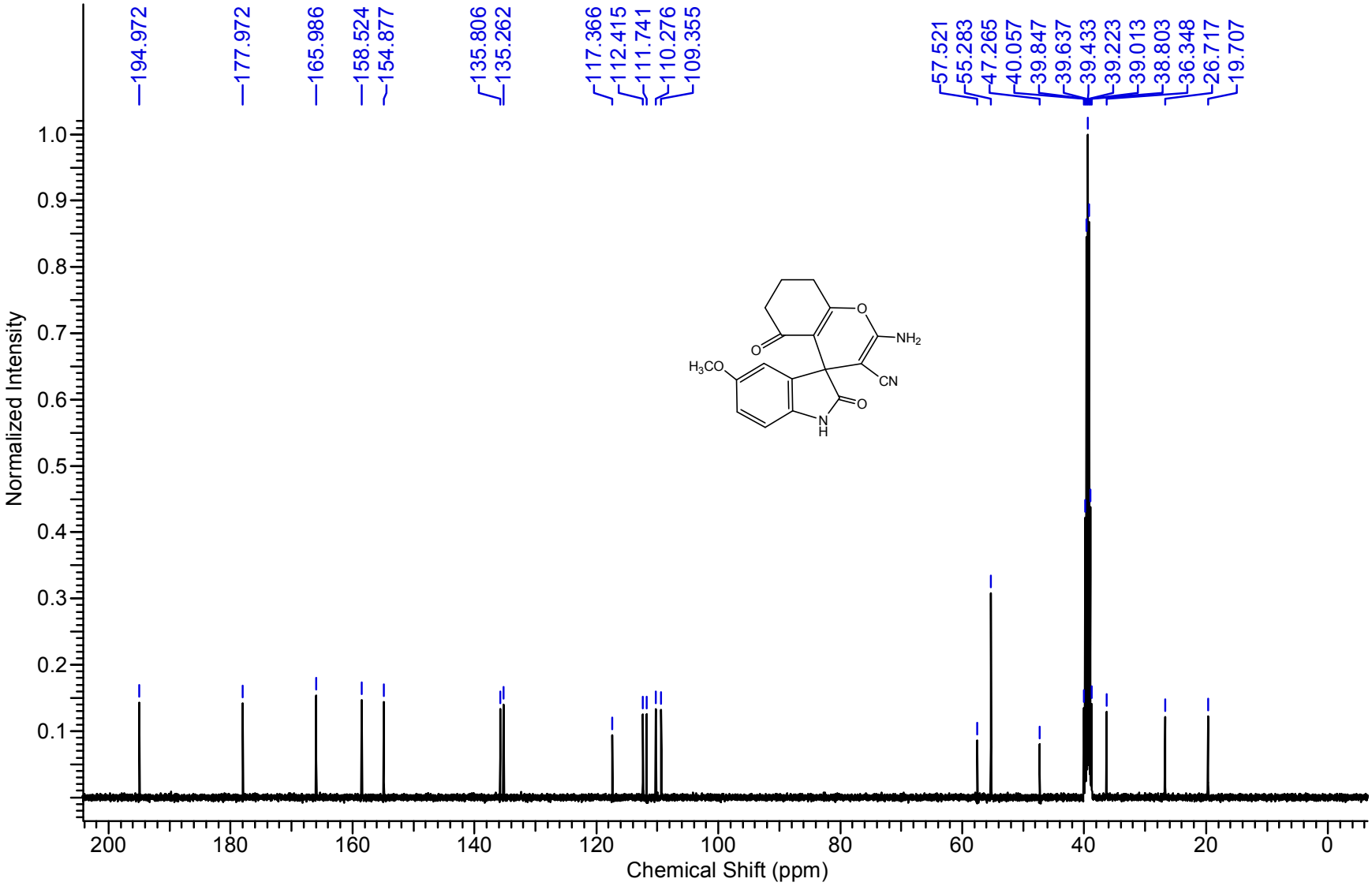
^{13}C-NMR of P-378(**6b**)



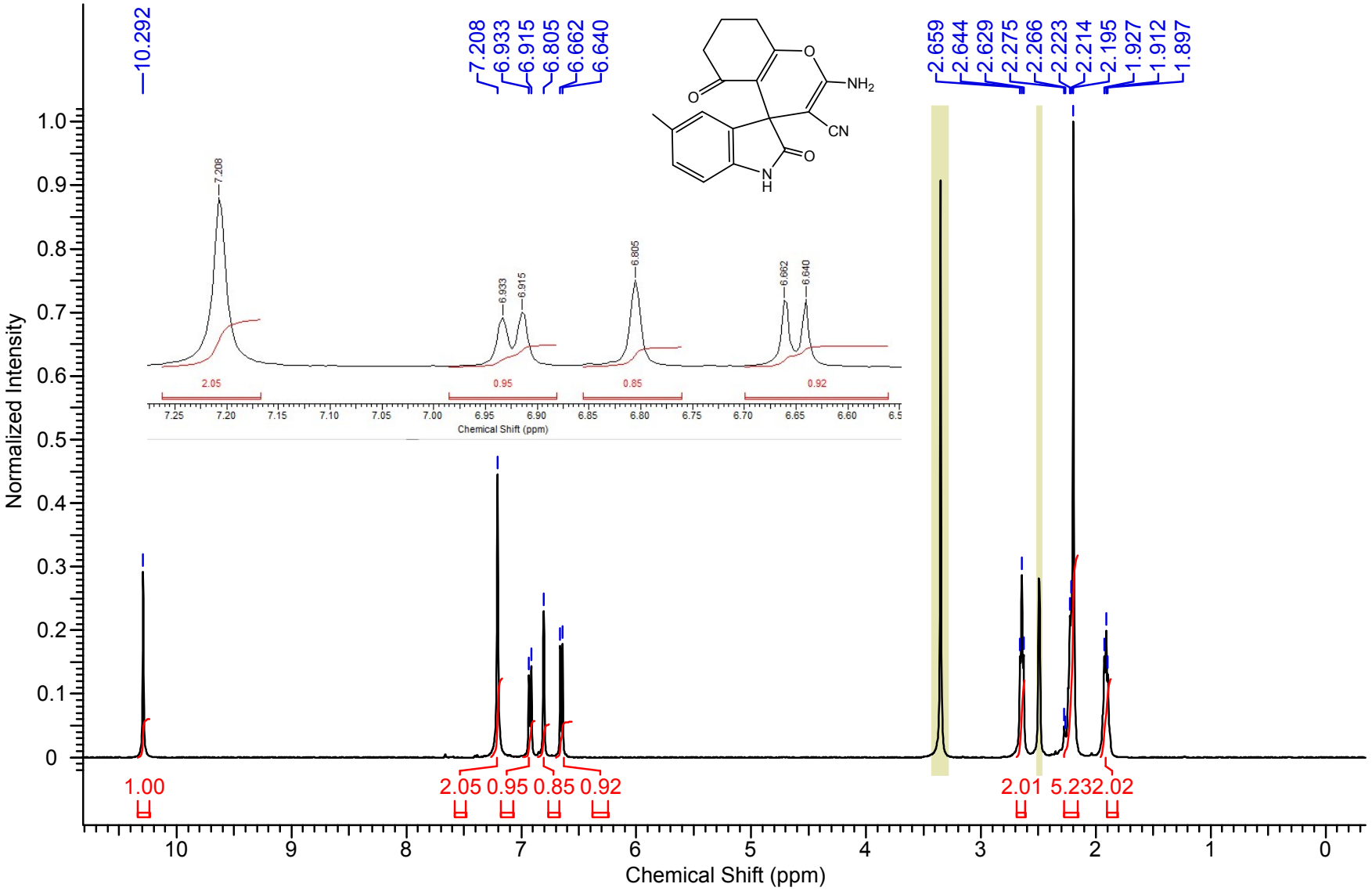
^{1}H-NMR of P-387(**6d**)



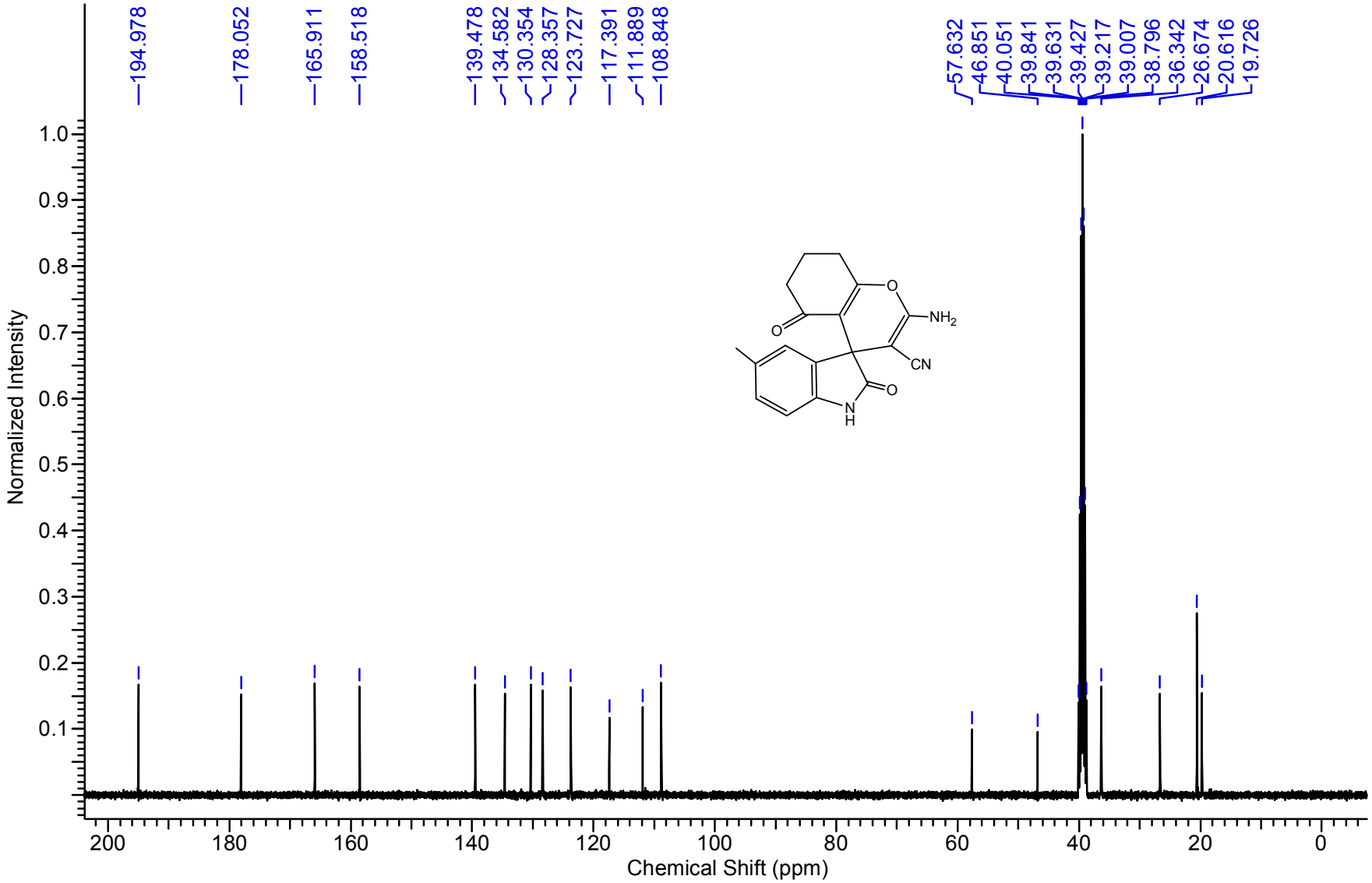
^{13}C-NMR of P-387(**6d**)



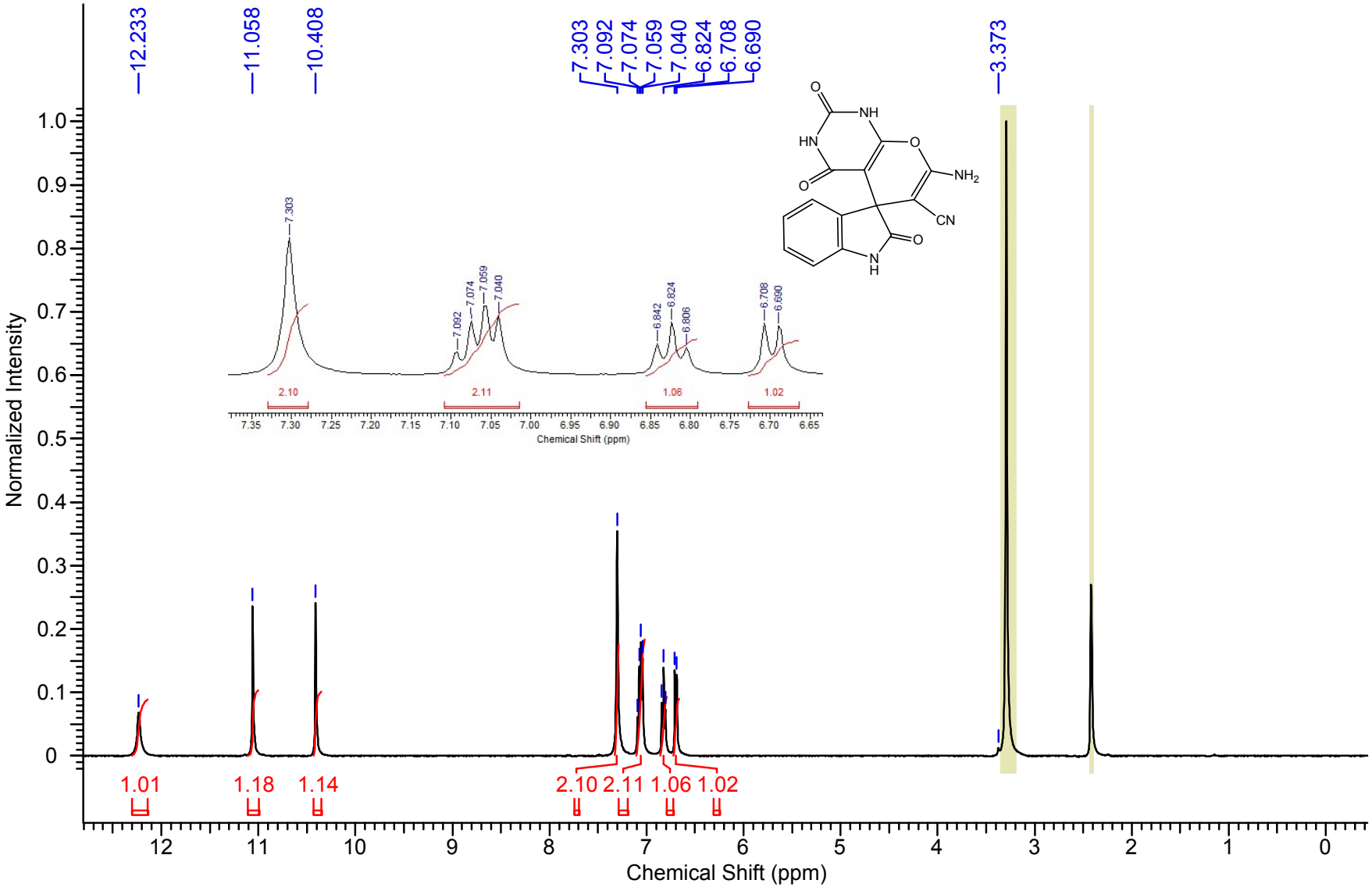
^{1}H-NMR of P-381(**6e**)



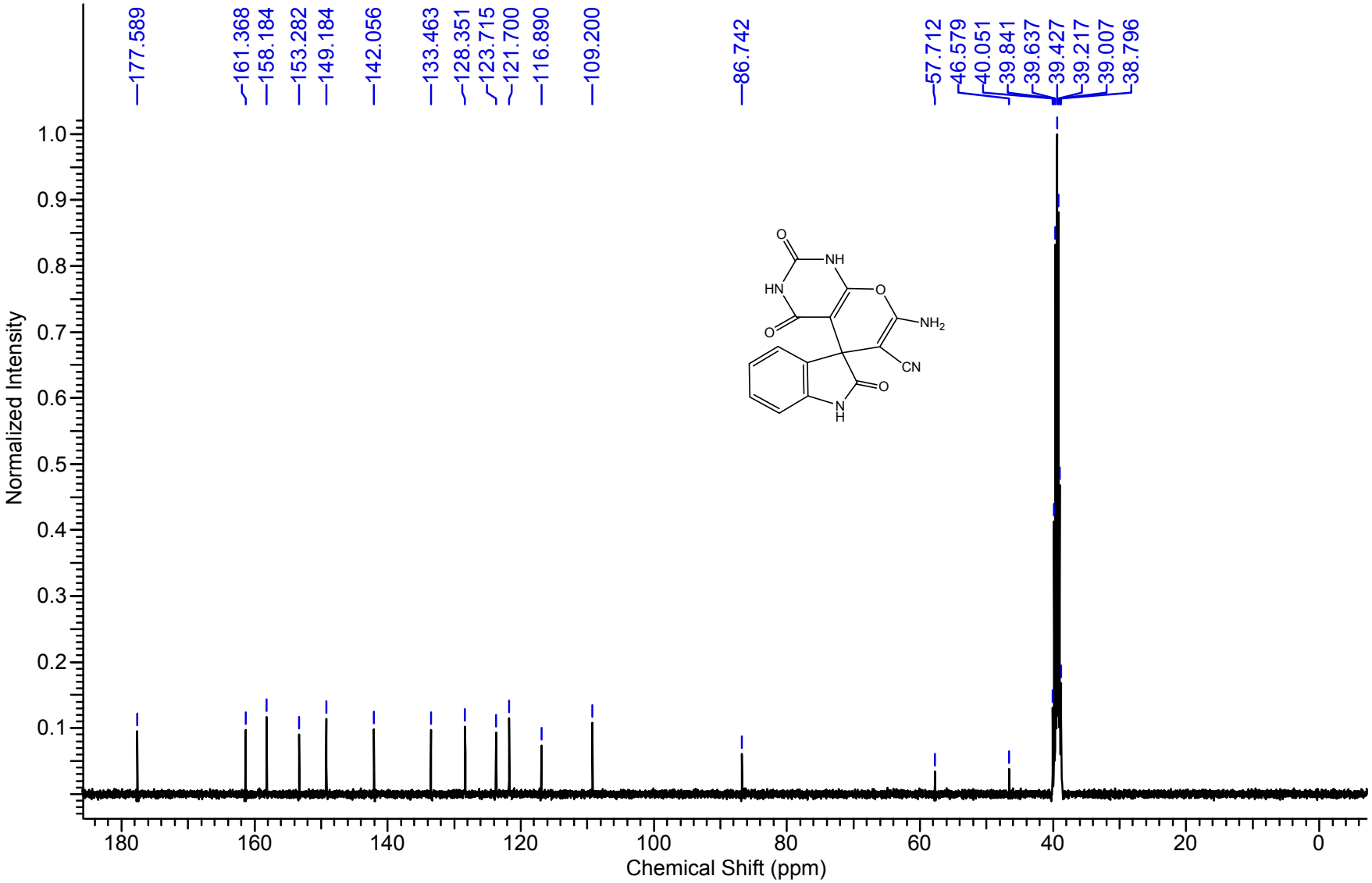
^{13}C-NMR of P-381(**6e**)



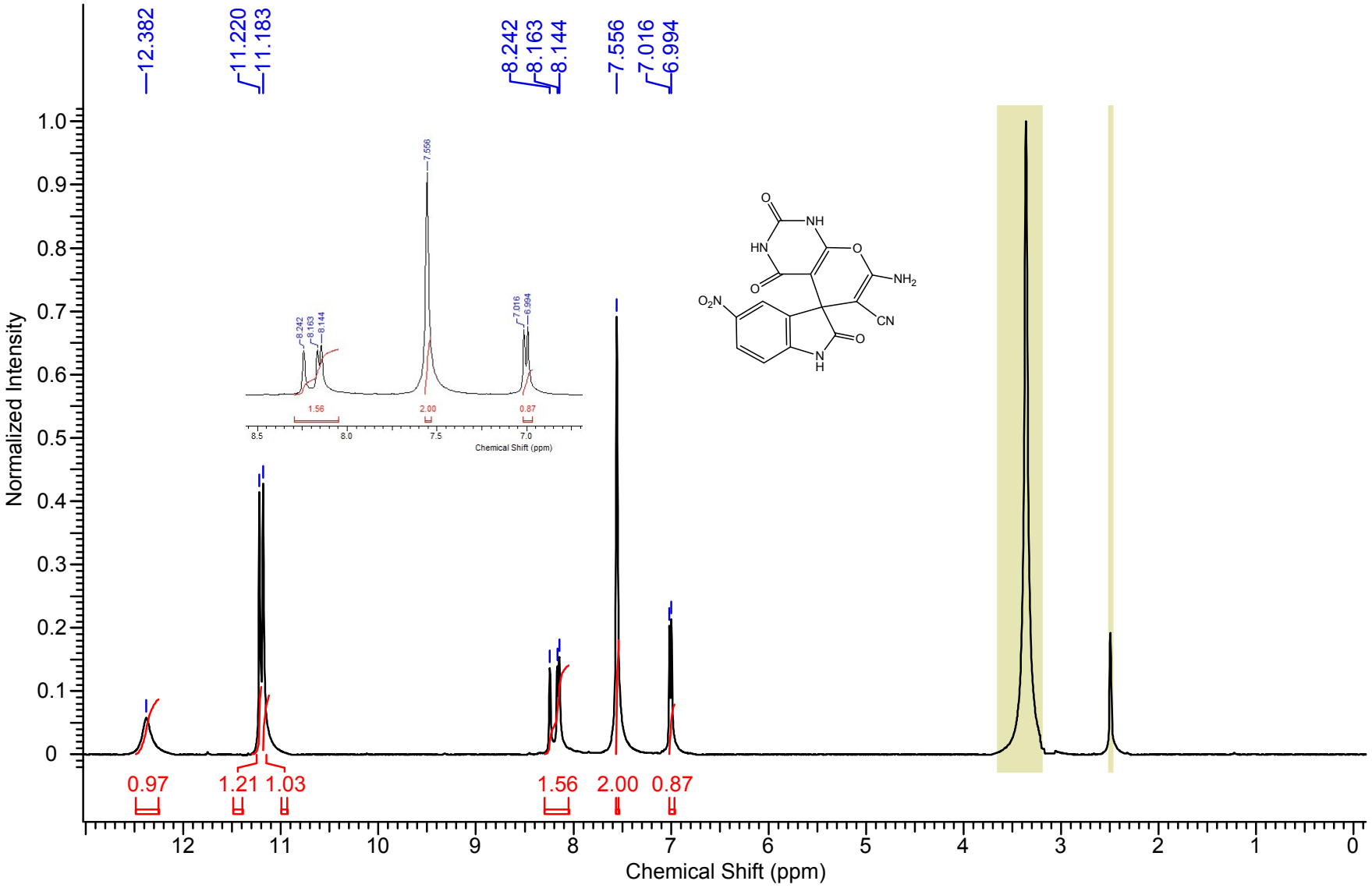
^{1}H-NMR of P-2(**7a**)



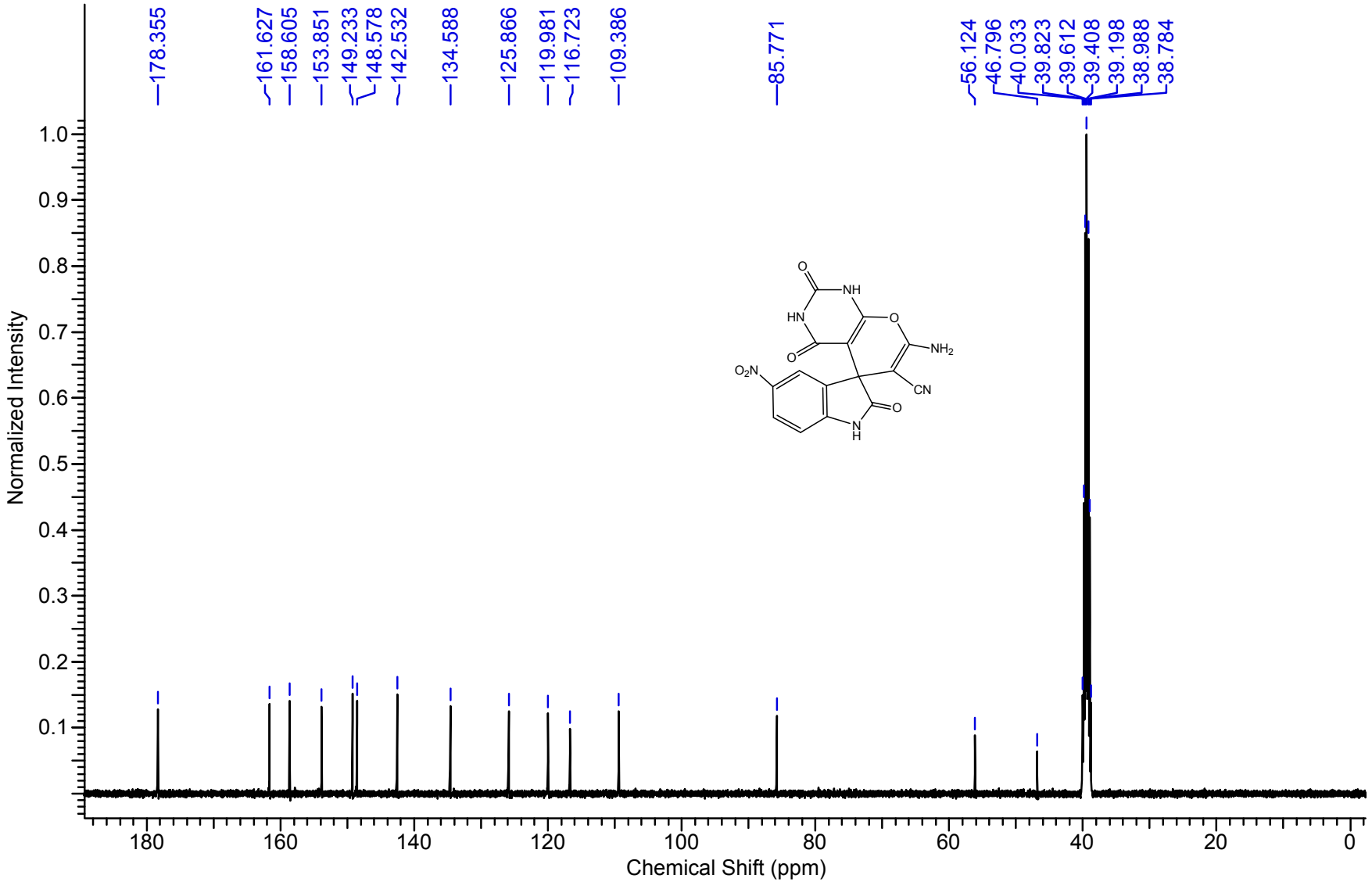
^{13}C-NMR of P-2(**7a**)



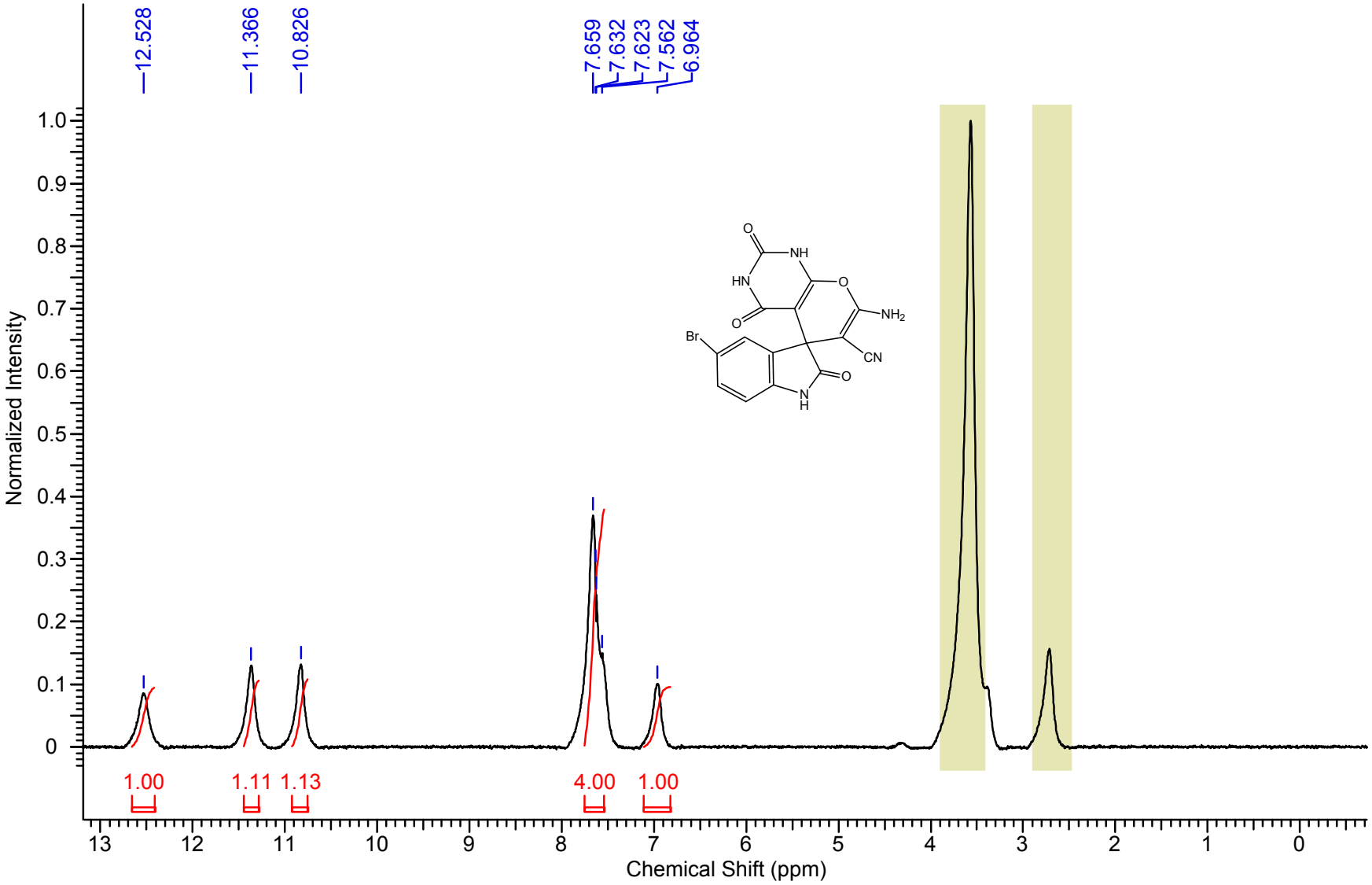
^{1}H-NMR of P-19(**7b**)



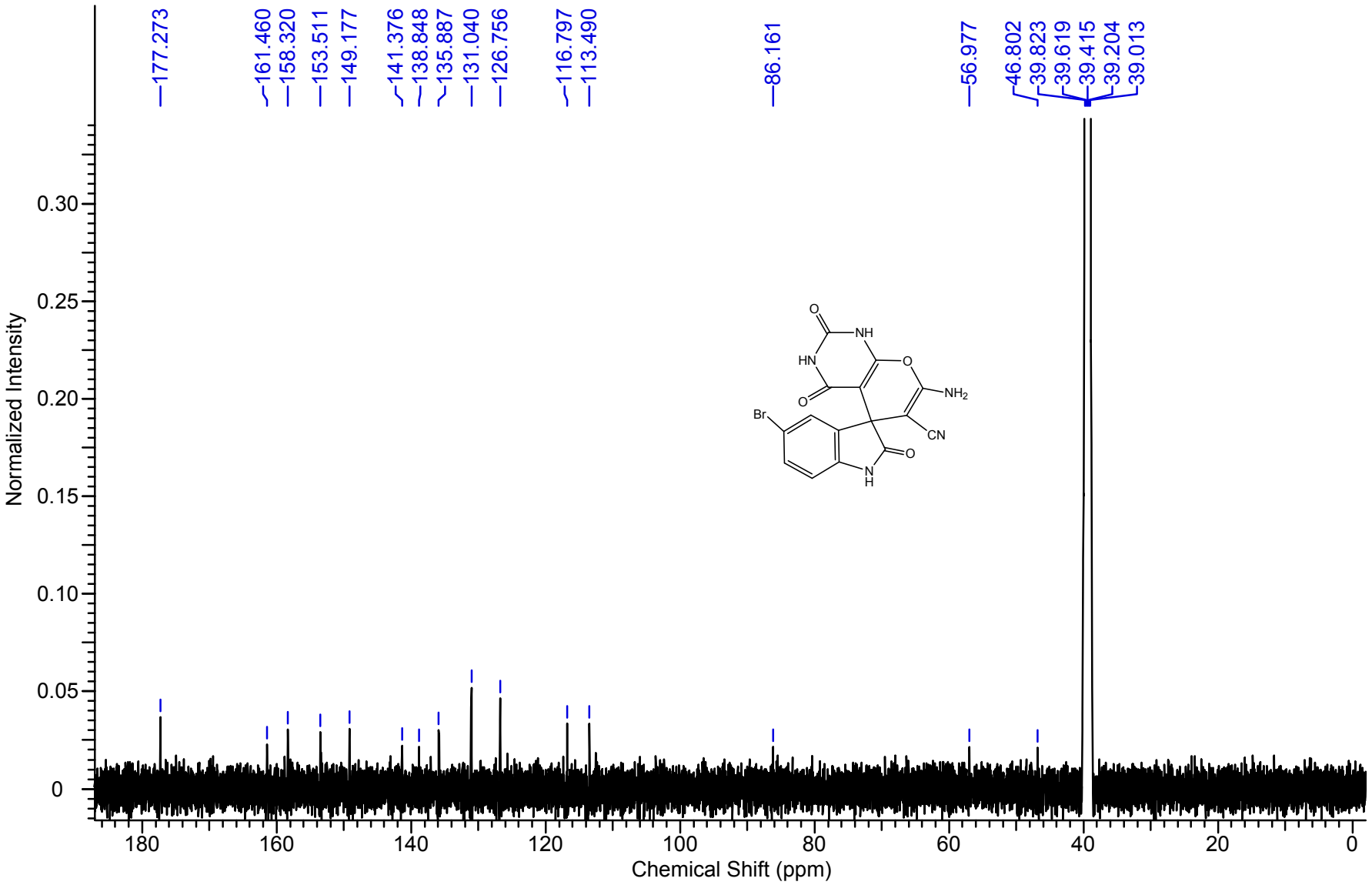
^{13}C-NMR of P-19(**7b**)



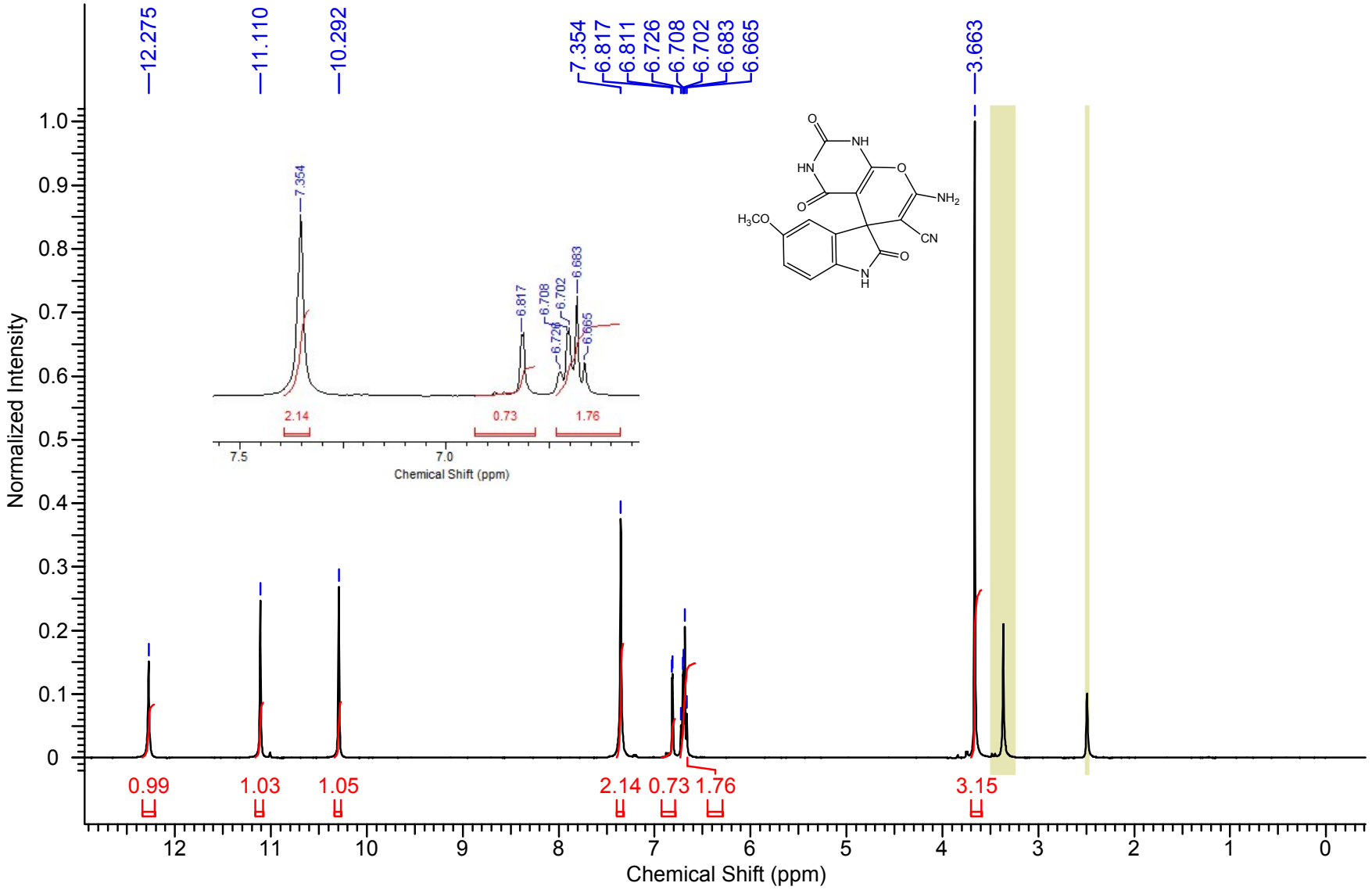
^{1}H-NMR of P-372(**7c**)



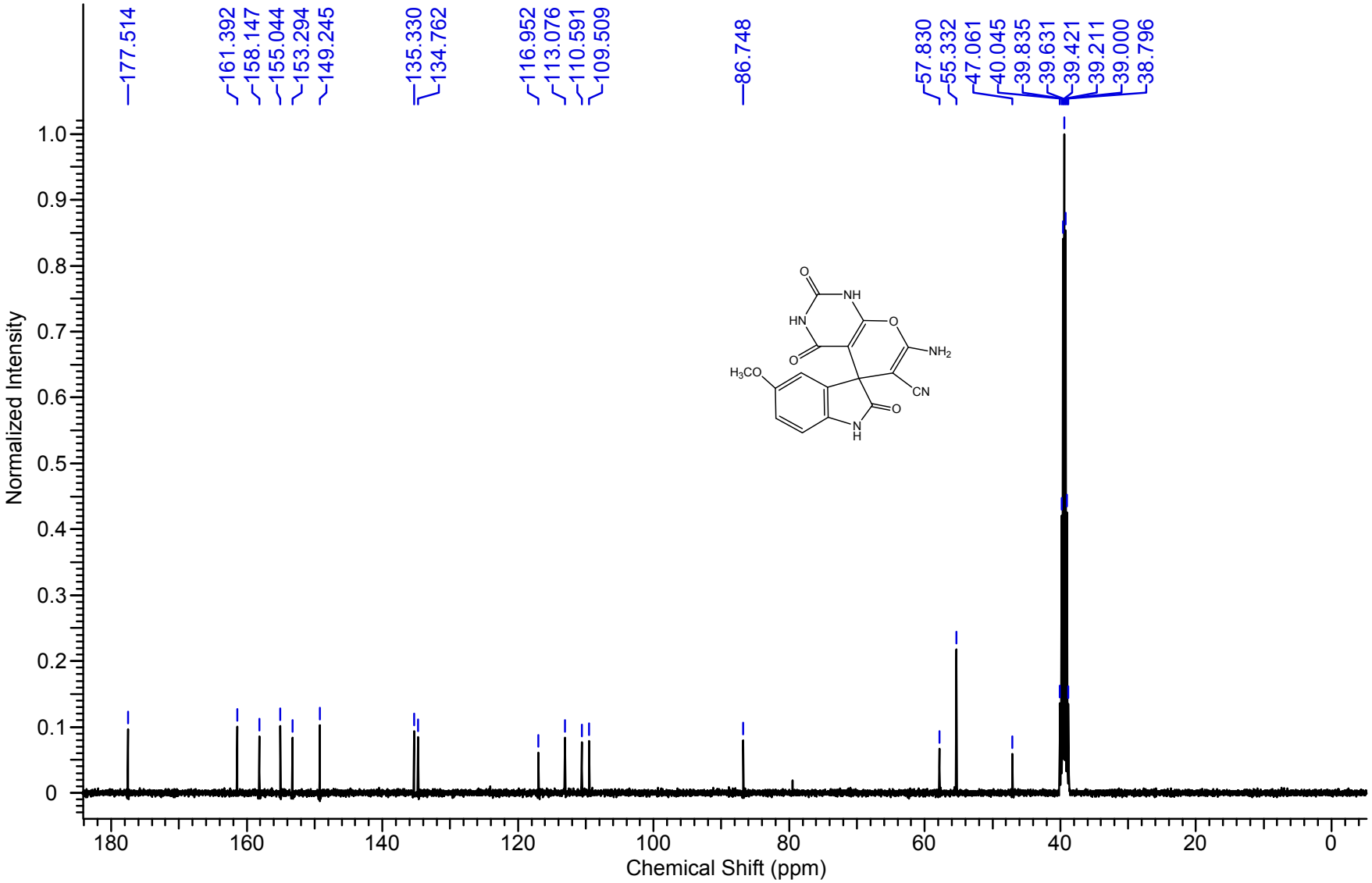
^{13}C-NMR of P-372(**7c**)



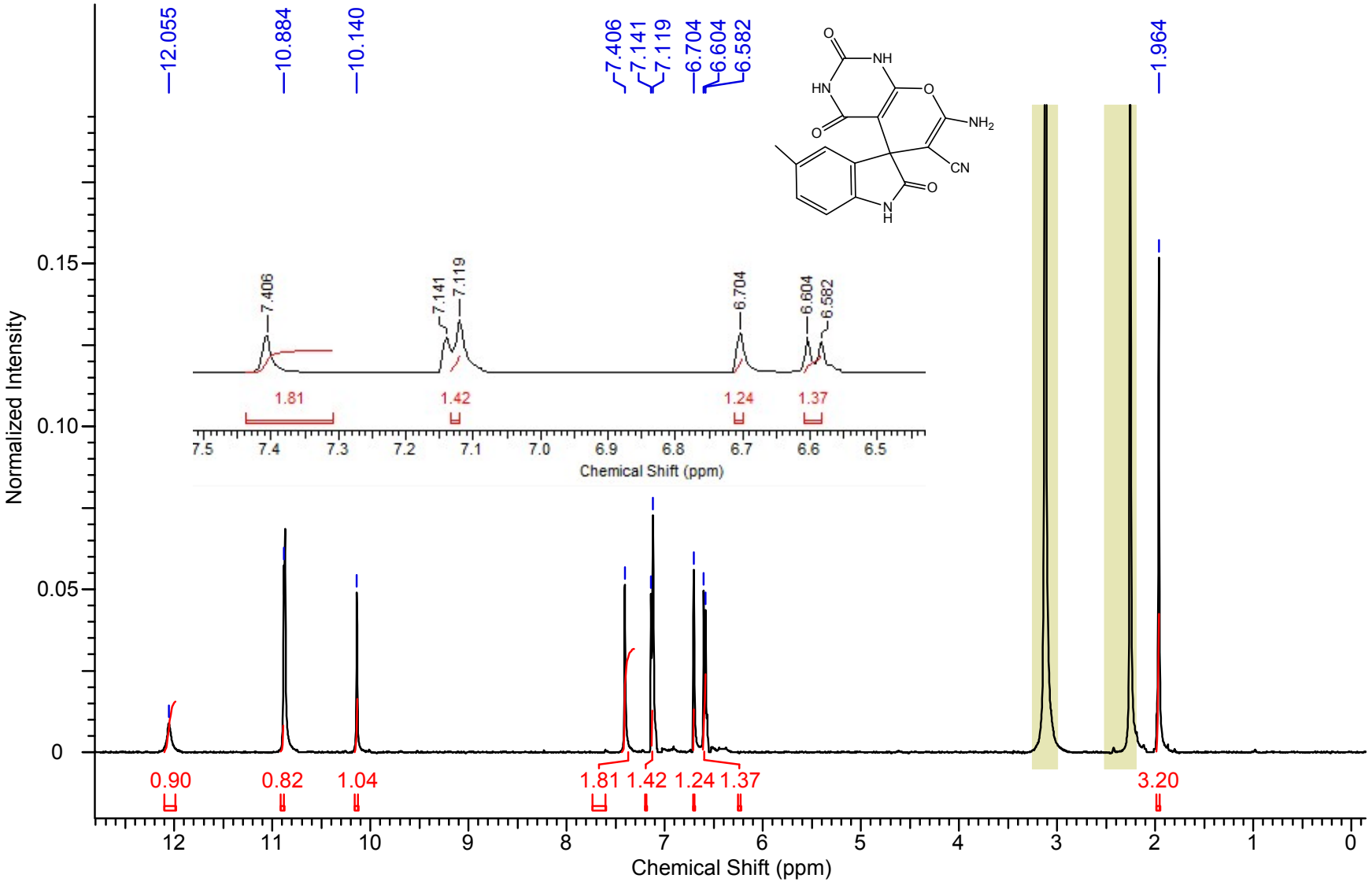
^{1}H-NMR of P-386(**7d**)



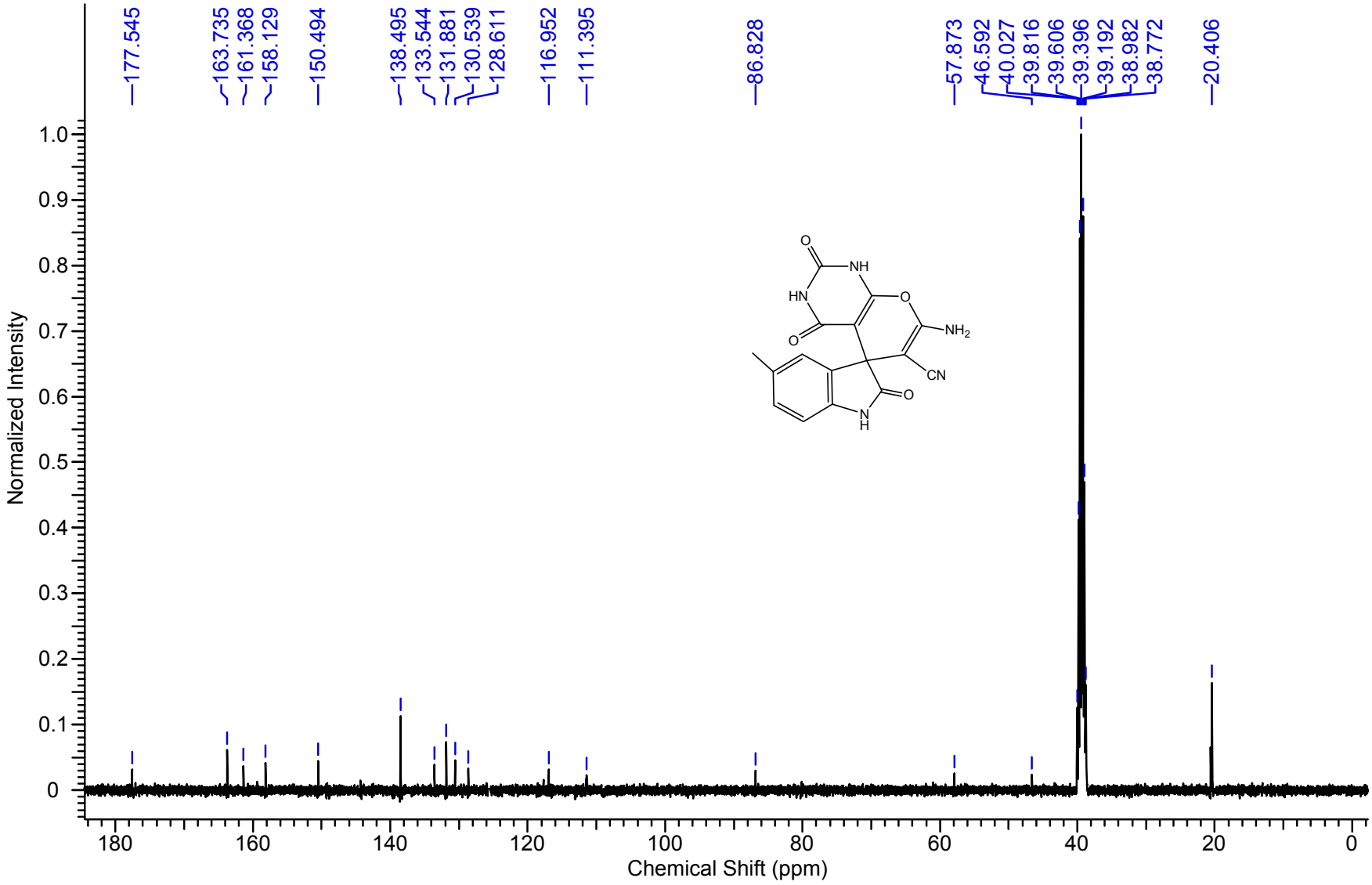
^{13}C-NMR of P-386(**7d**)



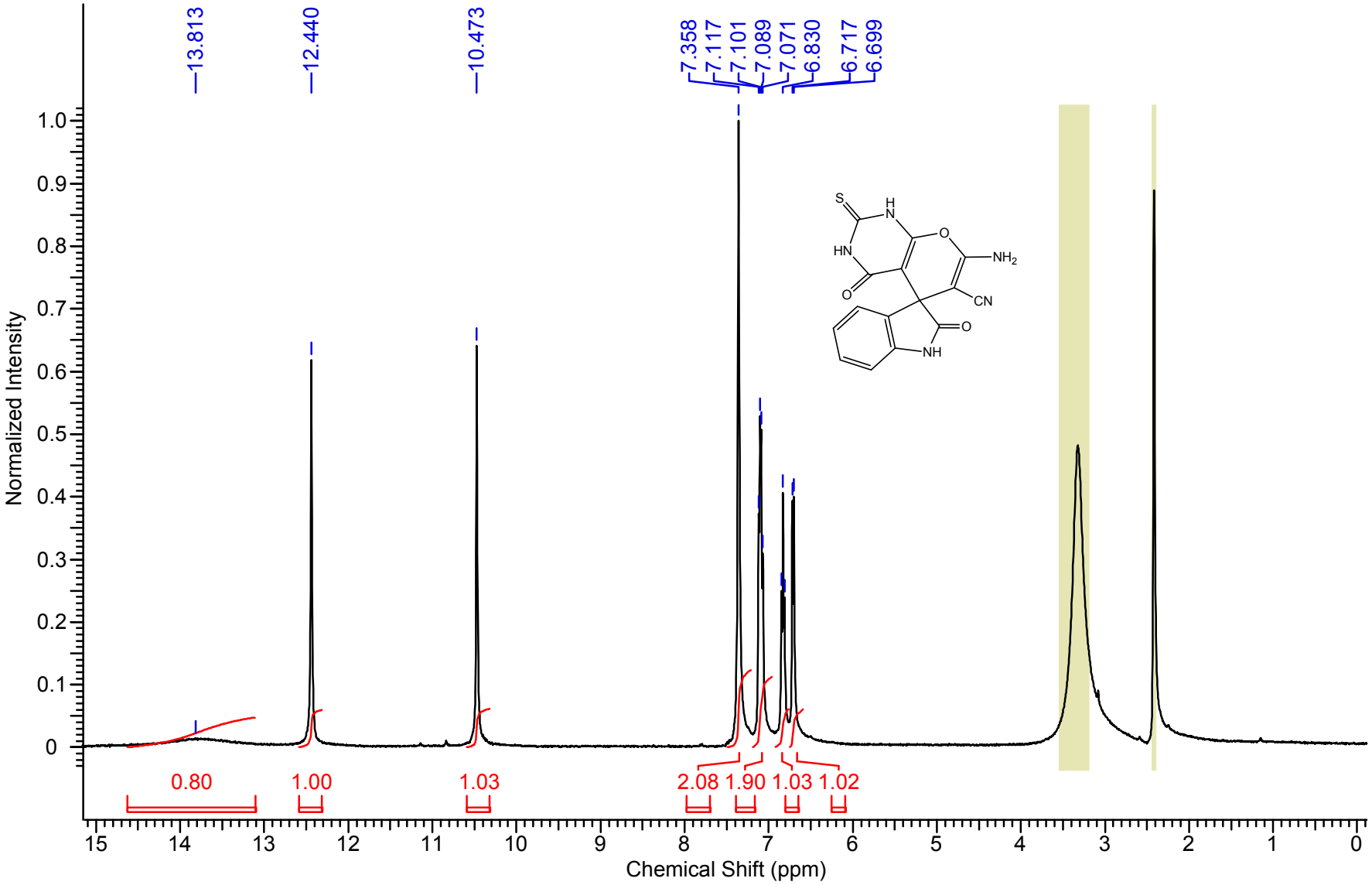
^{1}H-NMR of P-382(**7e**)



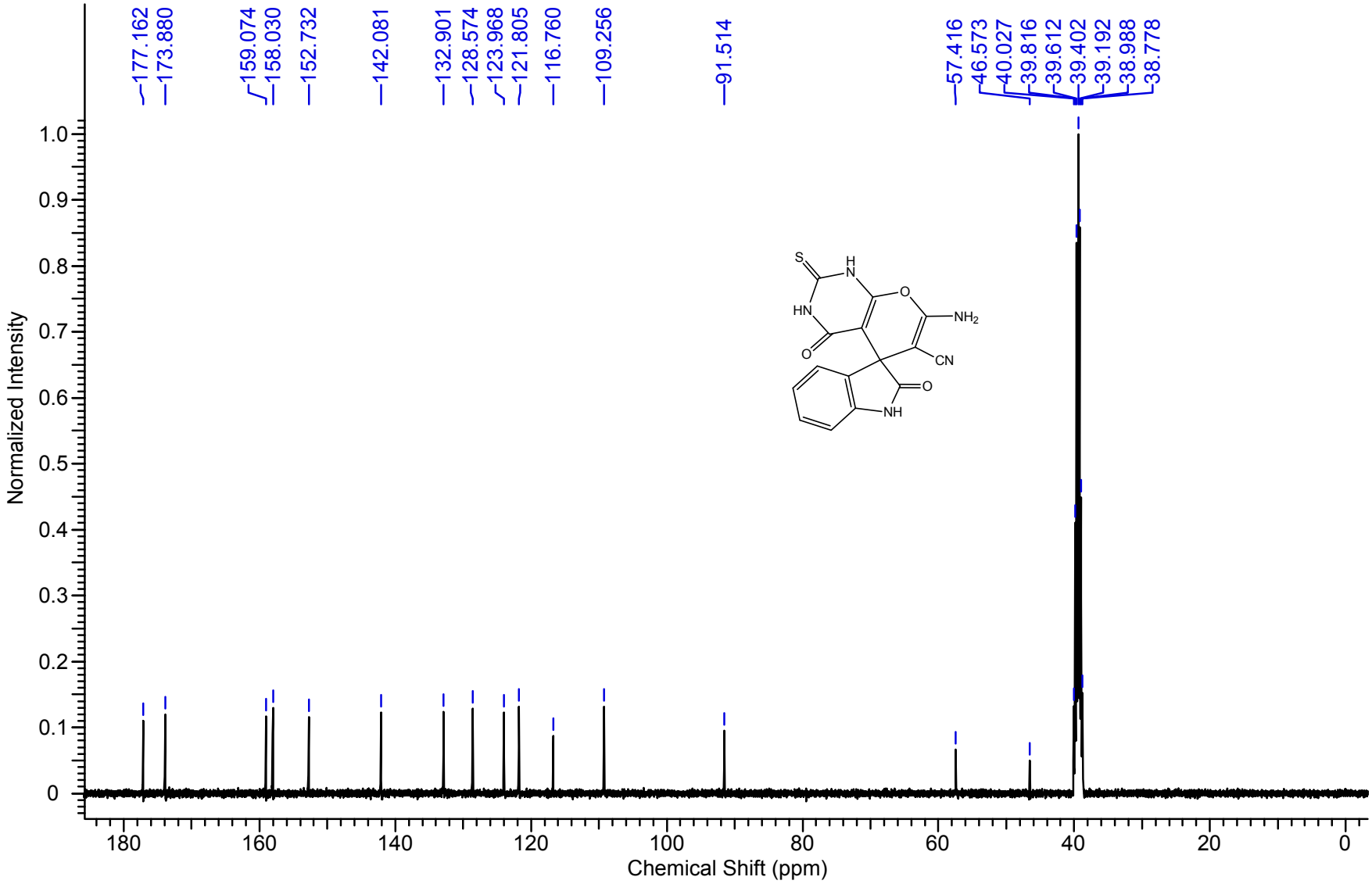
^{13}C-NMR of P-382(**7e**)



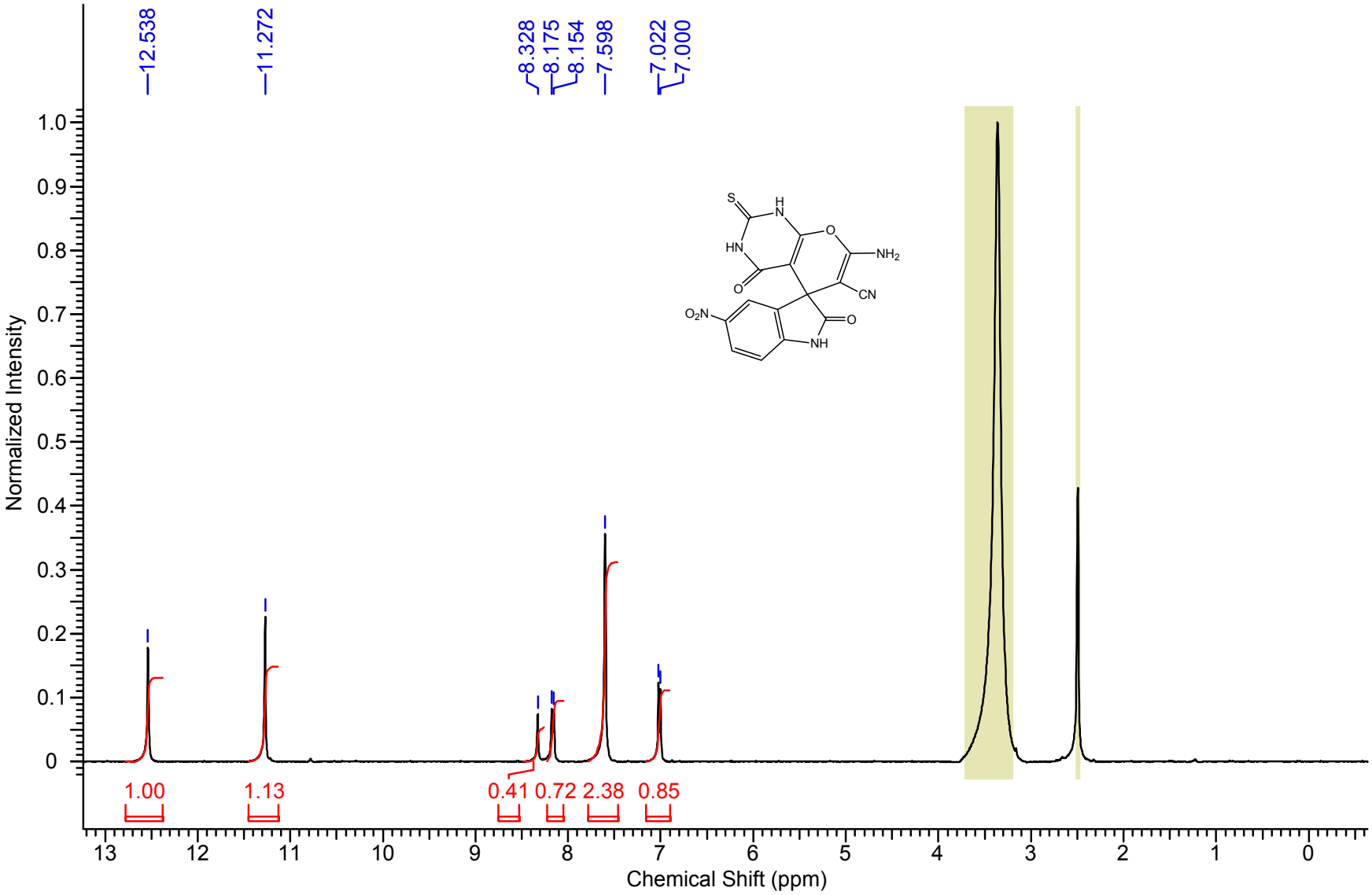
^{1}H-NMR of P-12(**8a**)



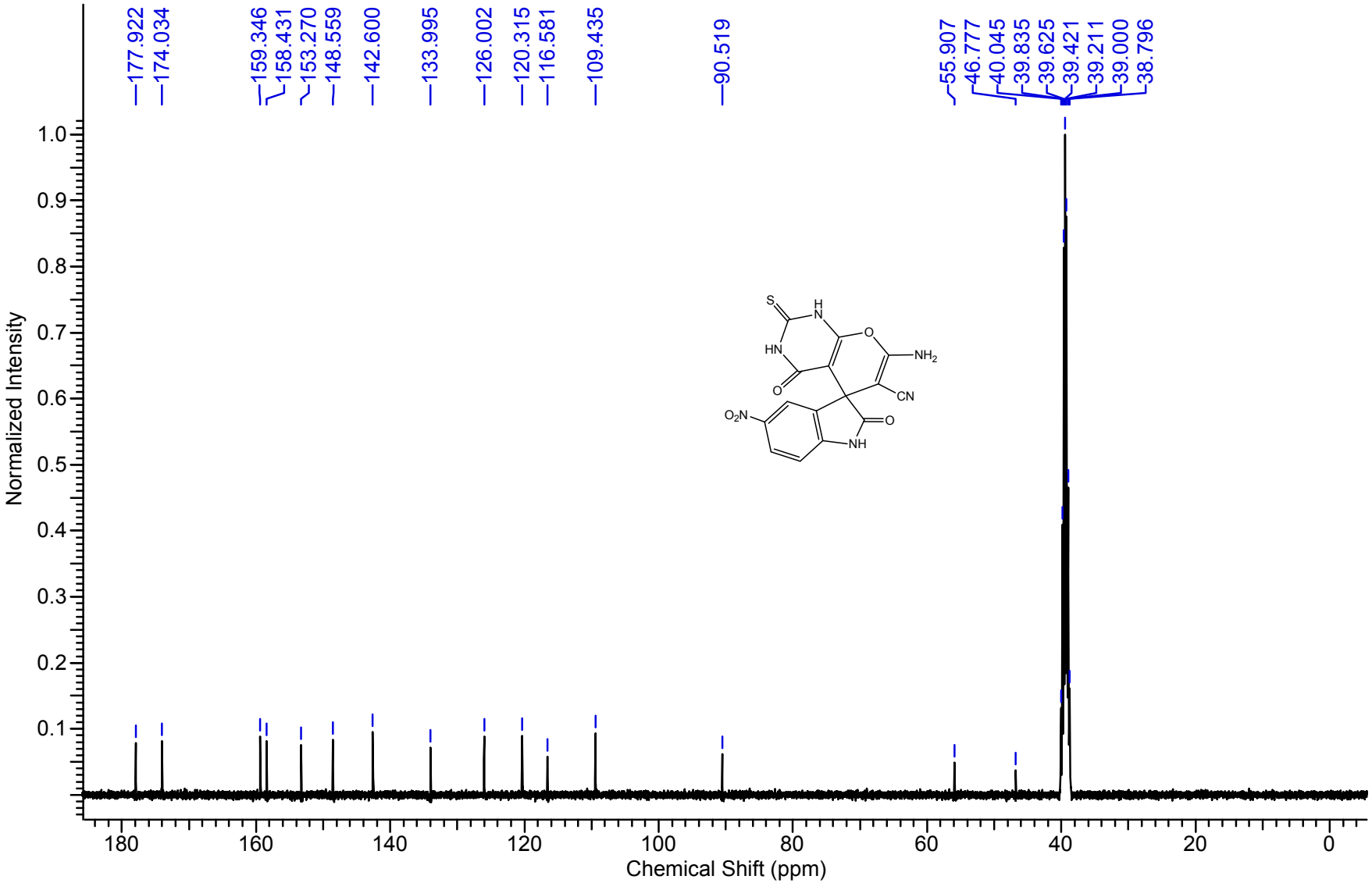
^{13}C-NMR of P-12(**8a**)



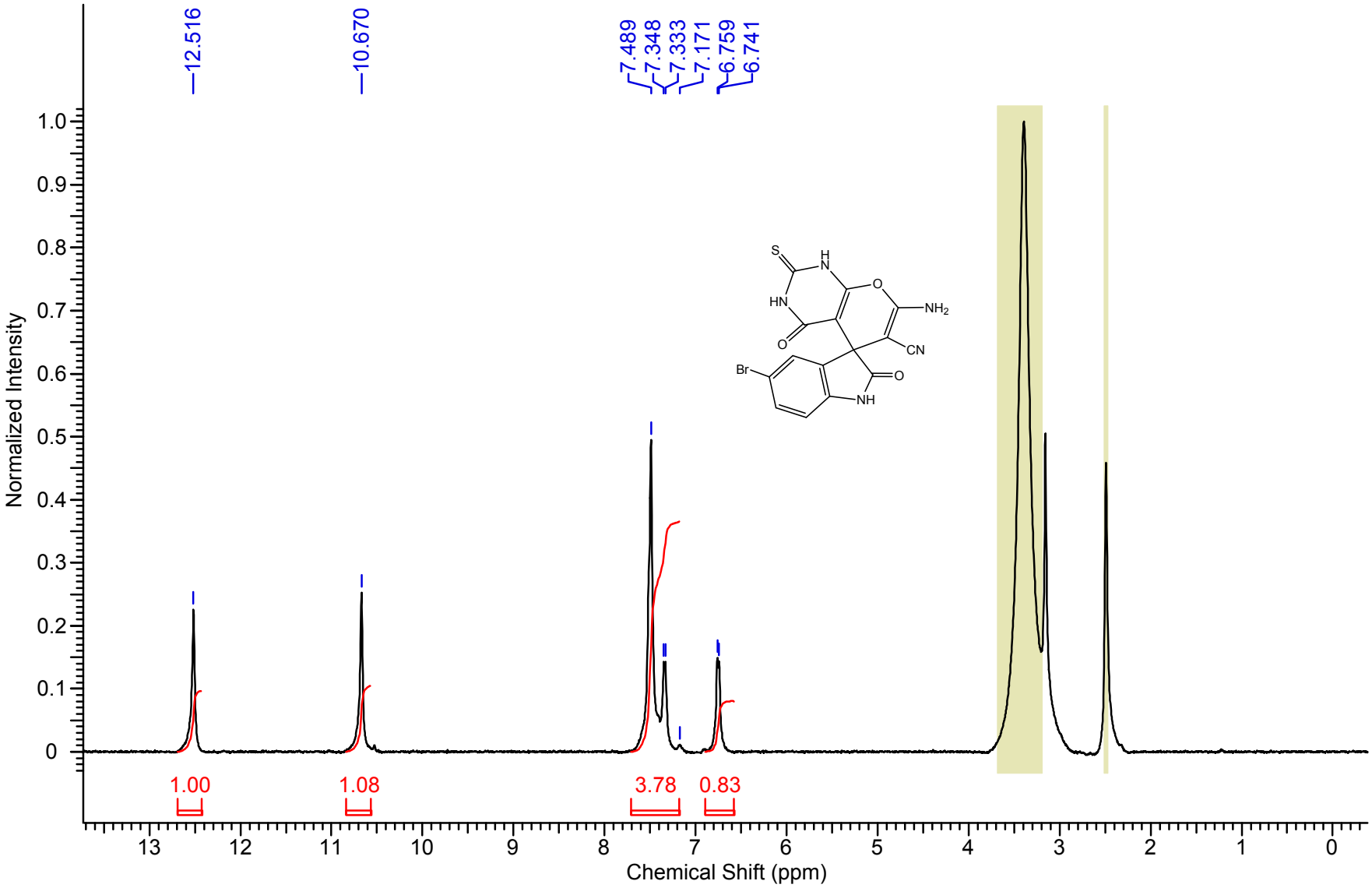
^{1}H-NMR of P-377(**8b**)



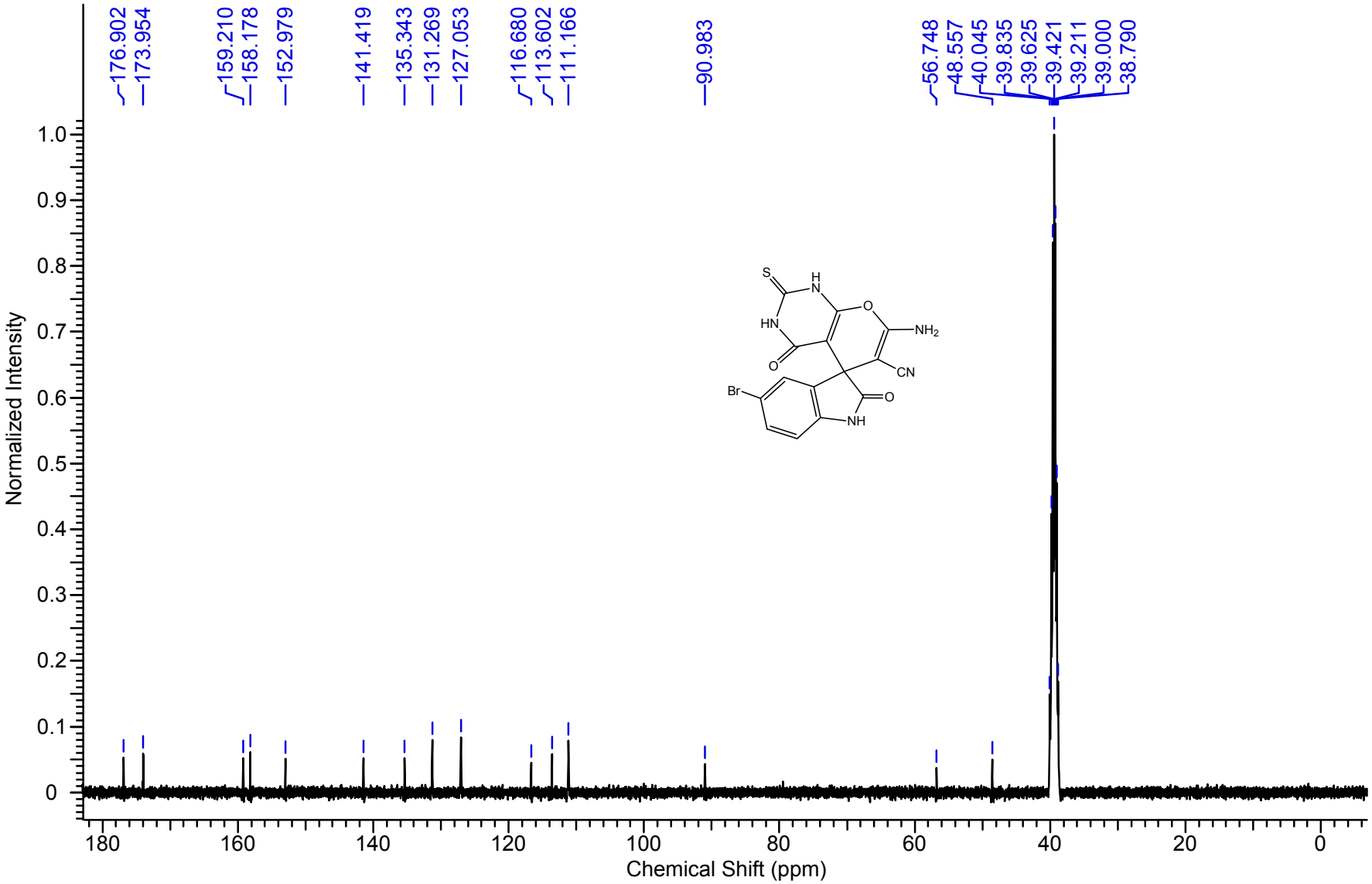
^{13}C-NMR of P-377(**8b**)



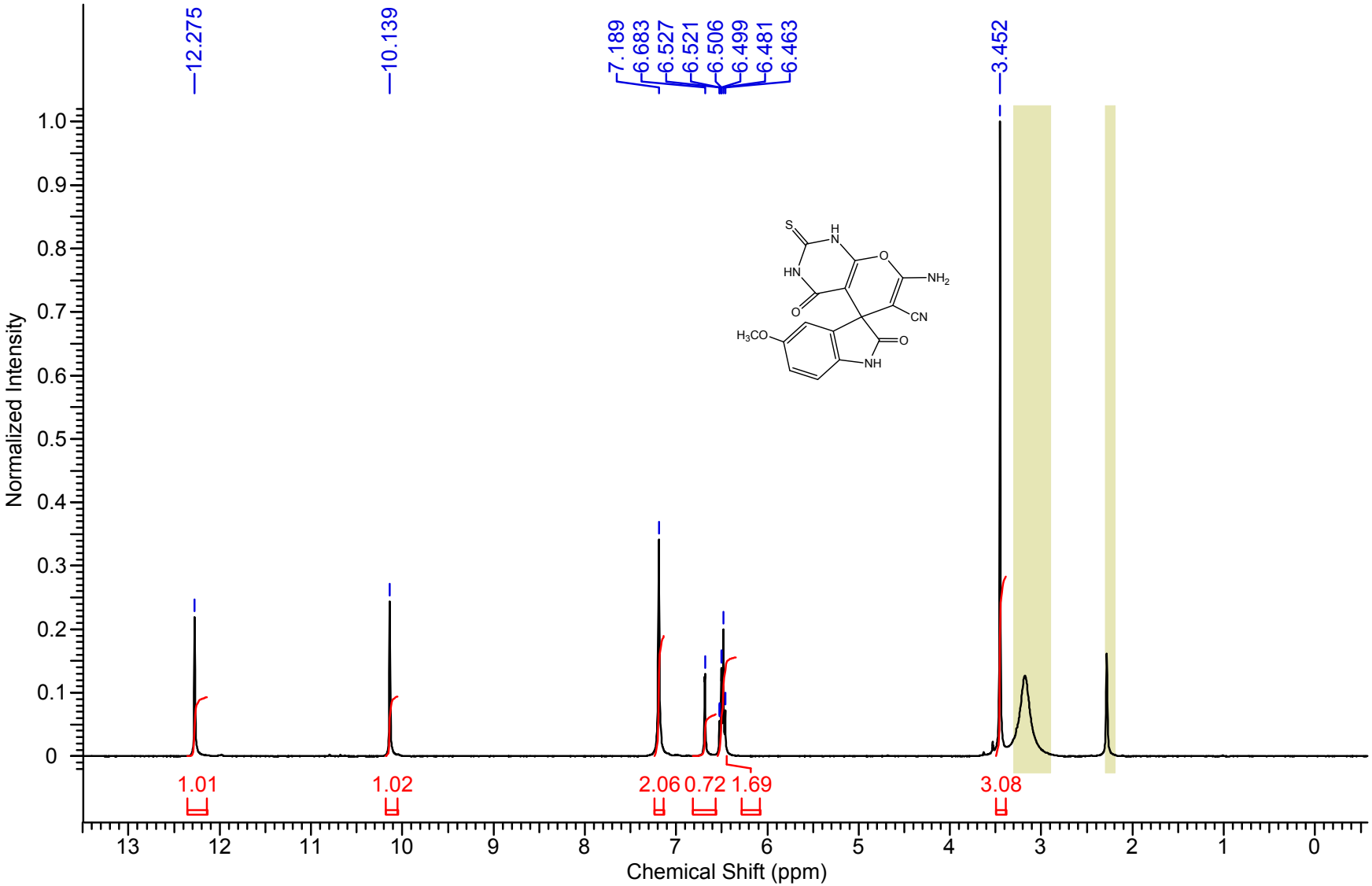
^{1}H-NMR of P-375(**8c**)



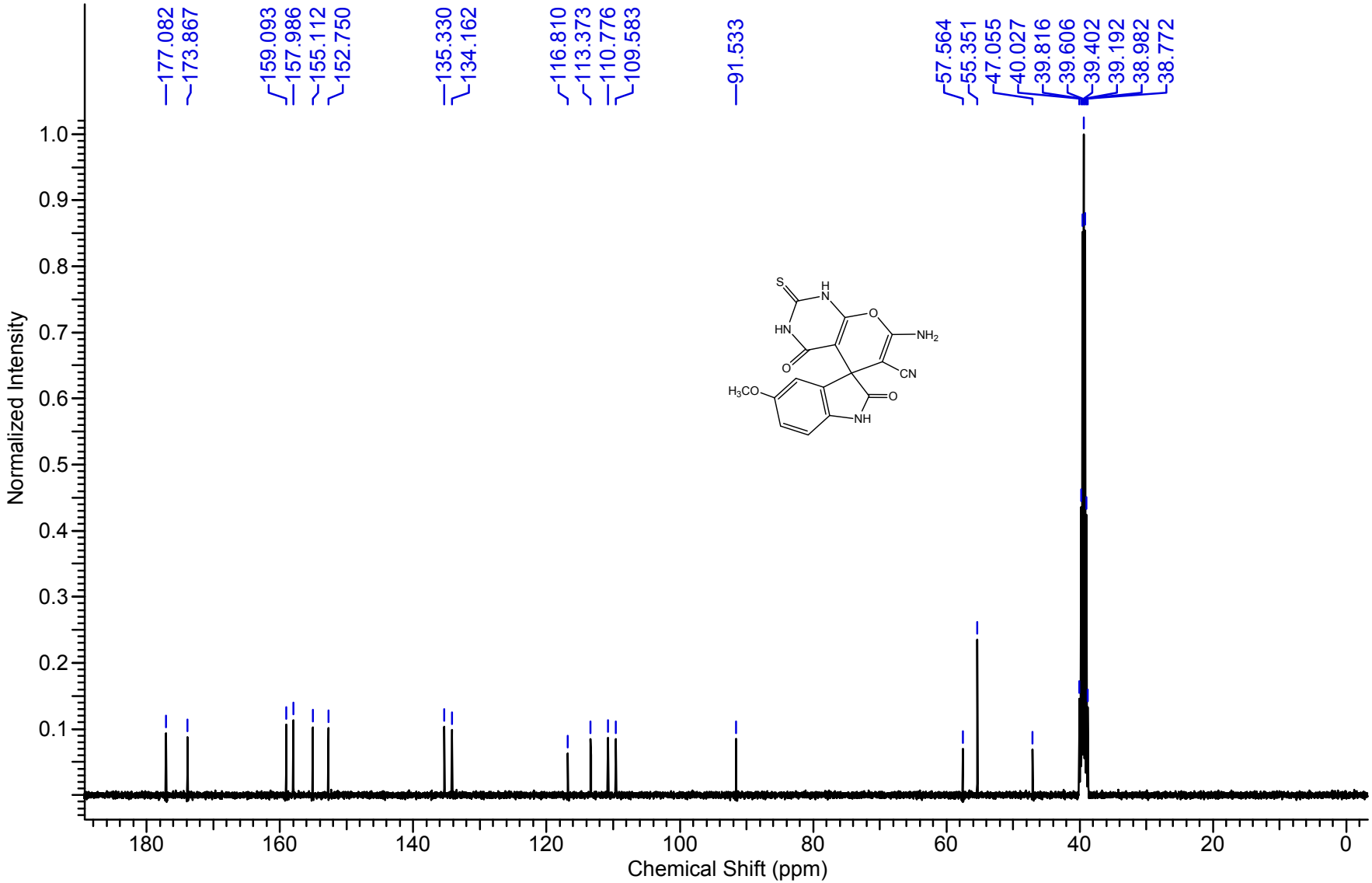
^{13}C-NMR of P-375(**8c**)



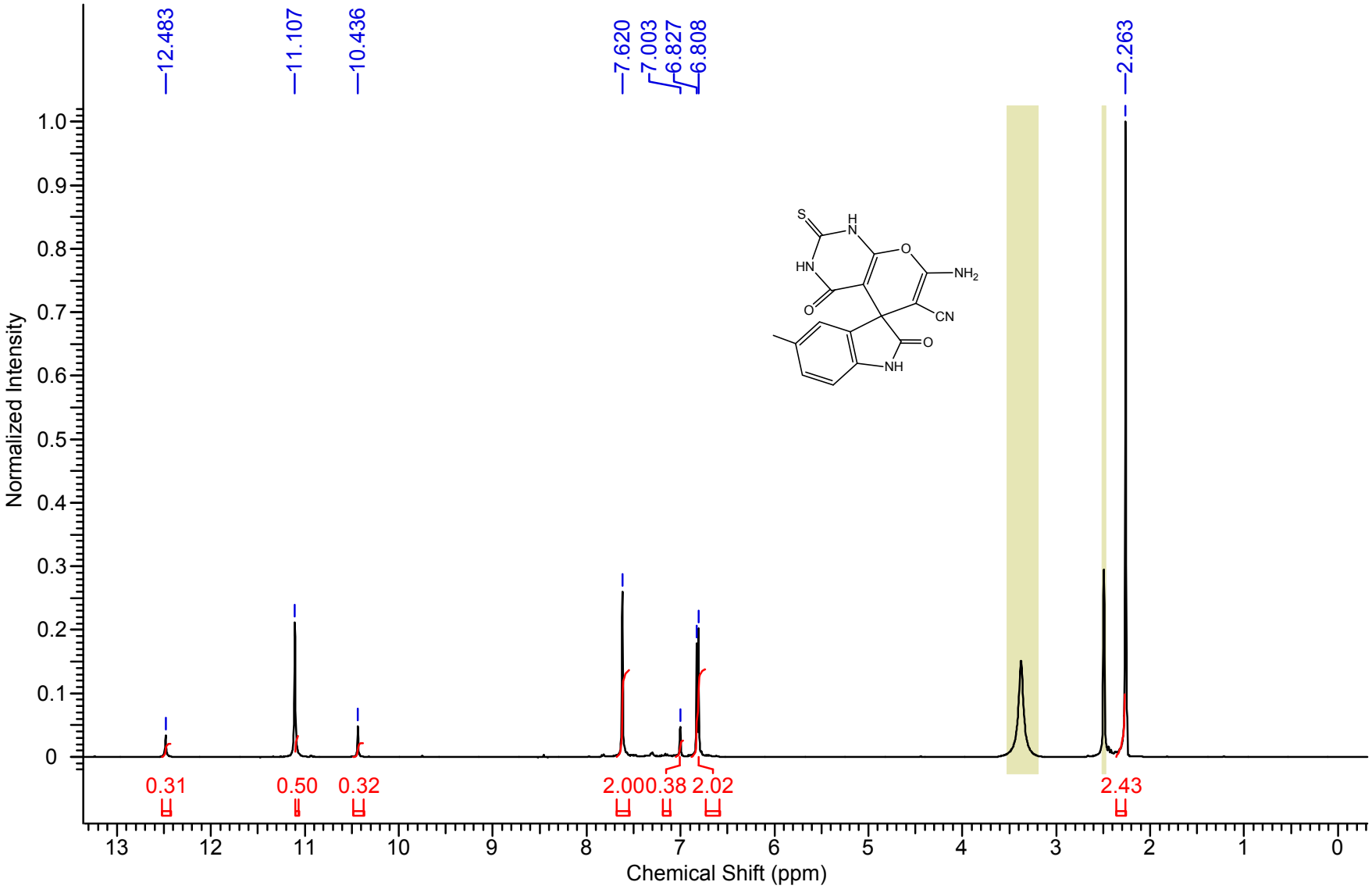
^{1}H-NMR of NGS-388(**8d**)



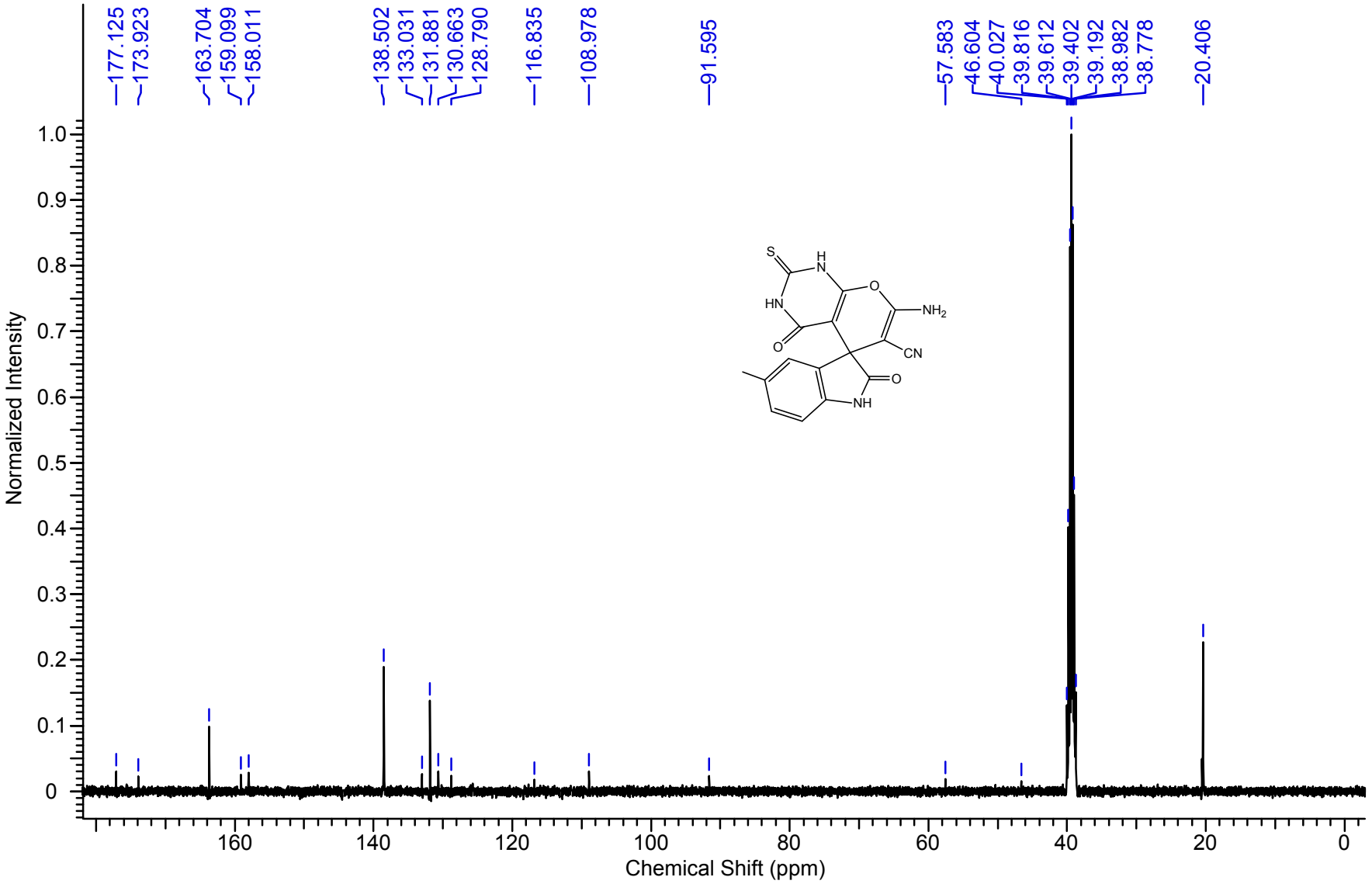
^{13}C-NMR of NGS-388(**8d**)



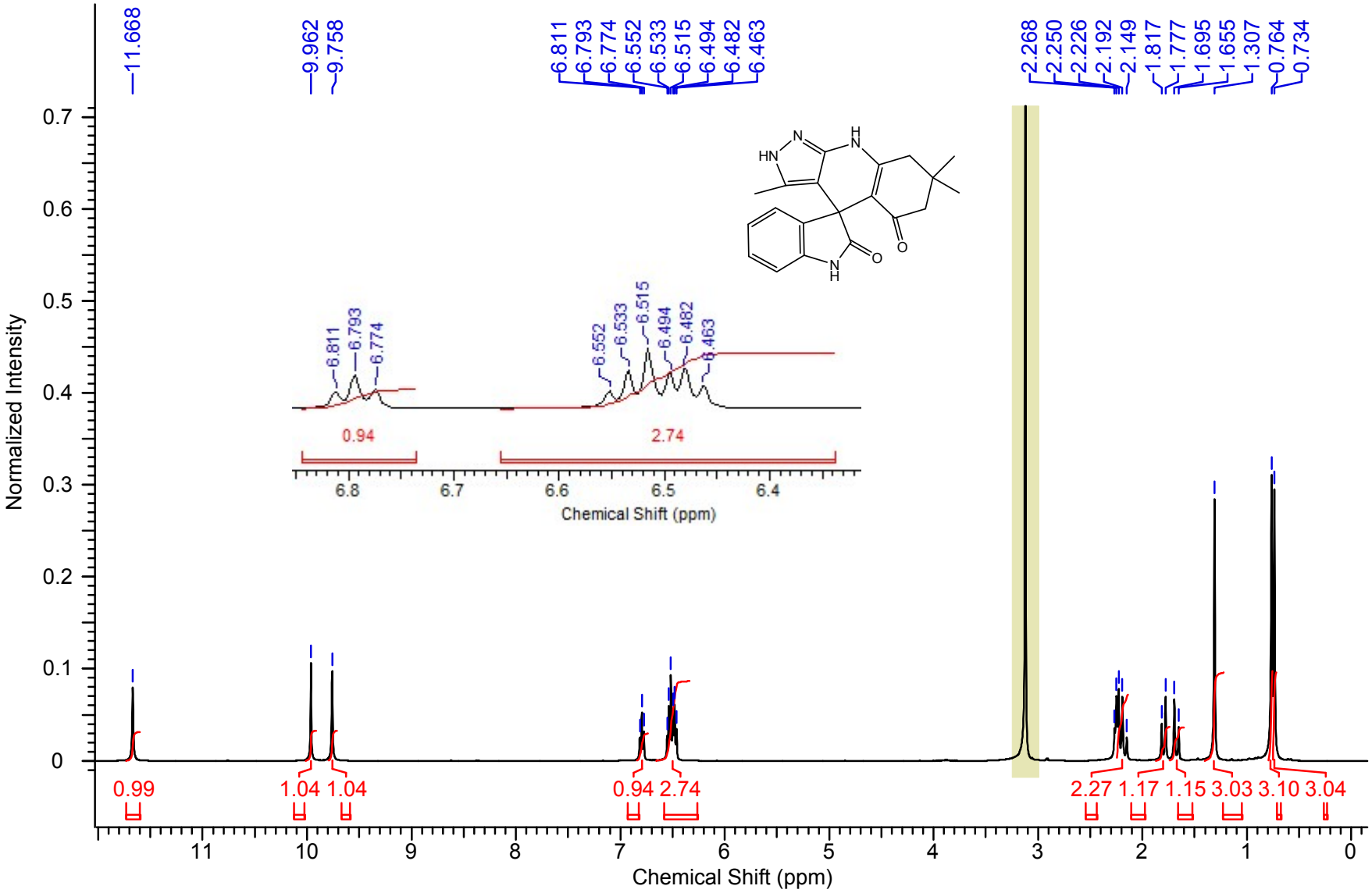
^{1}H-NMR of P-383(**8e**)



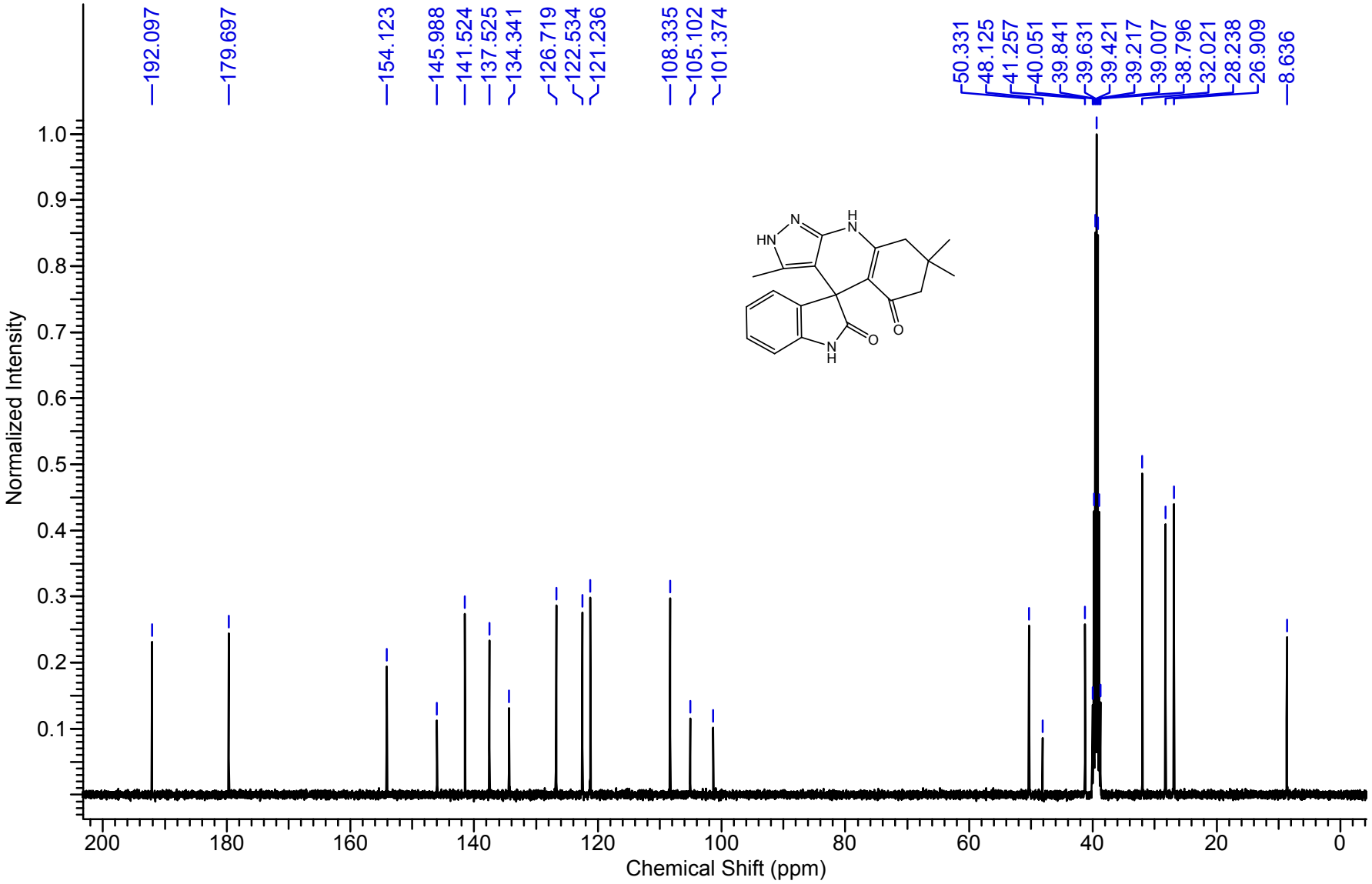
^{13}C-NMR of P-383(**8e**)



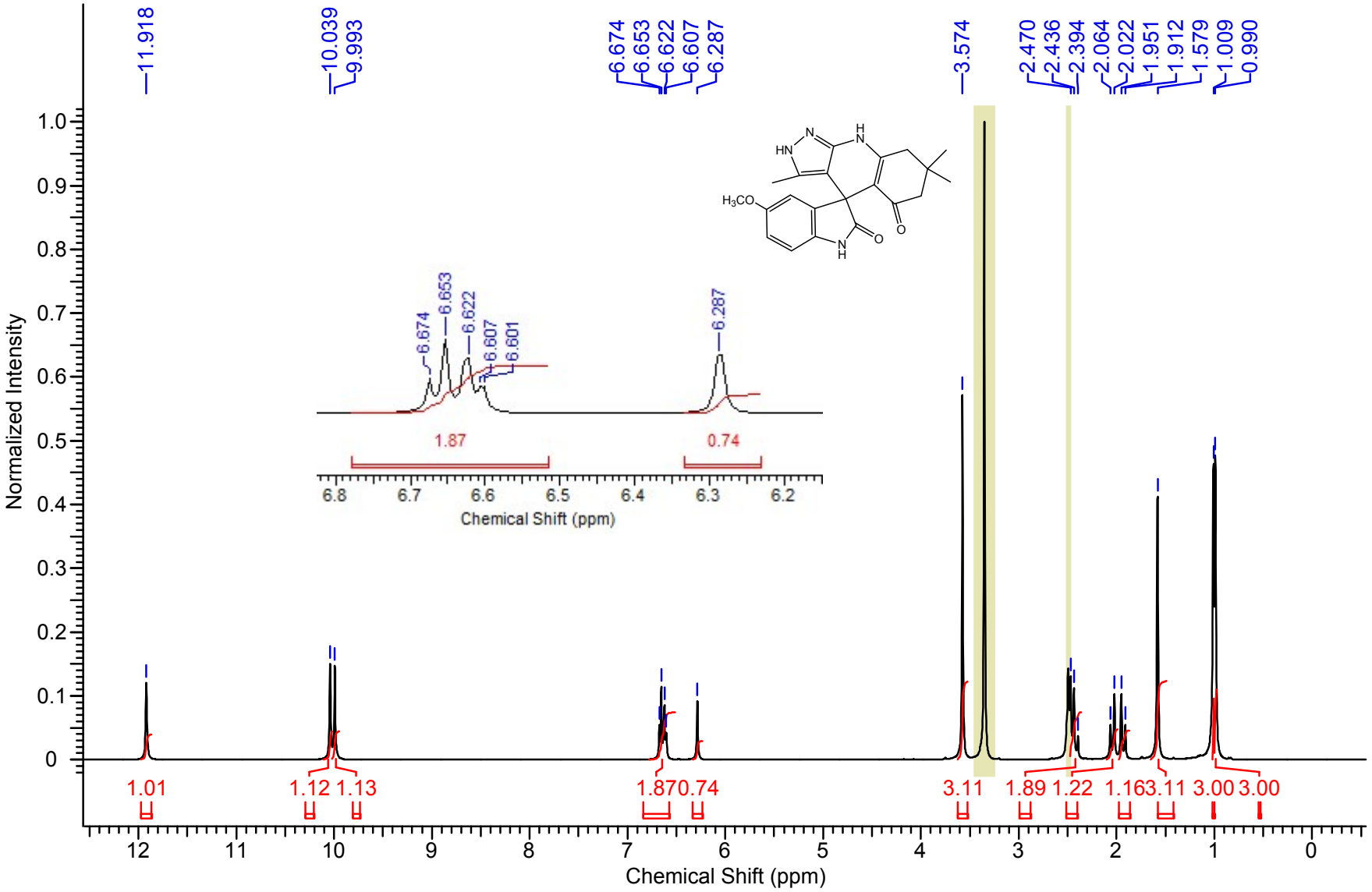
^{1}H-NMR of NGS-400(**9a**)



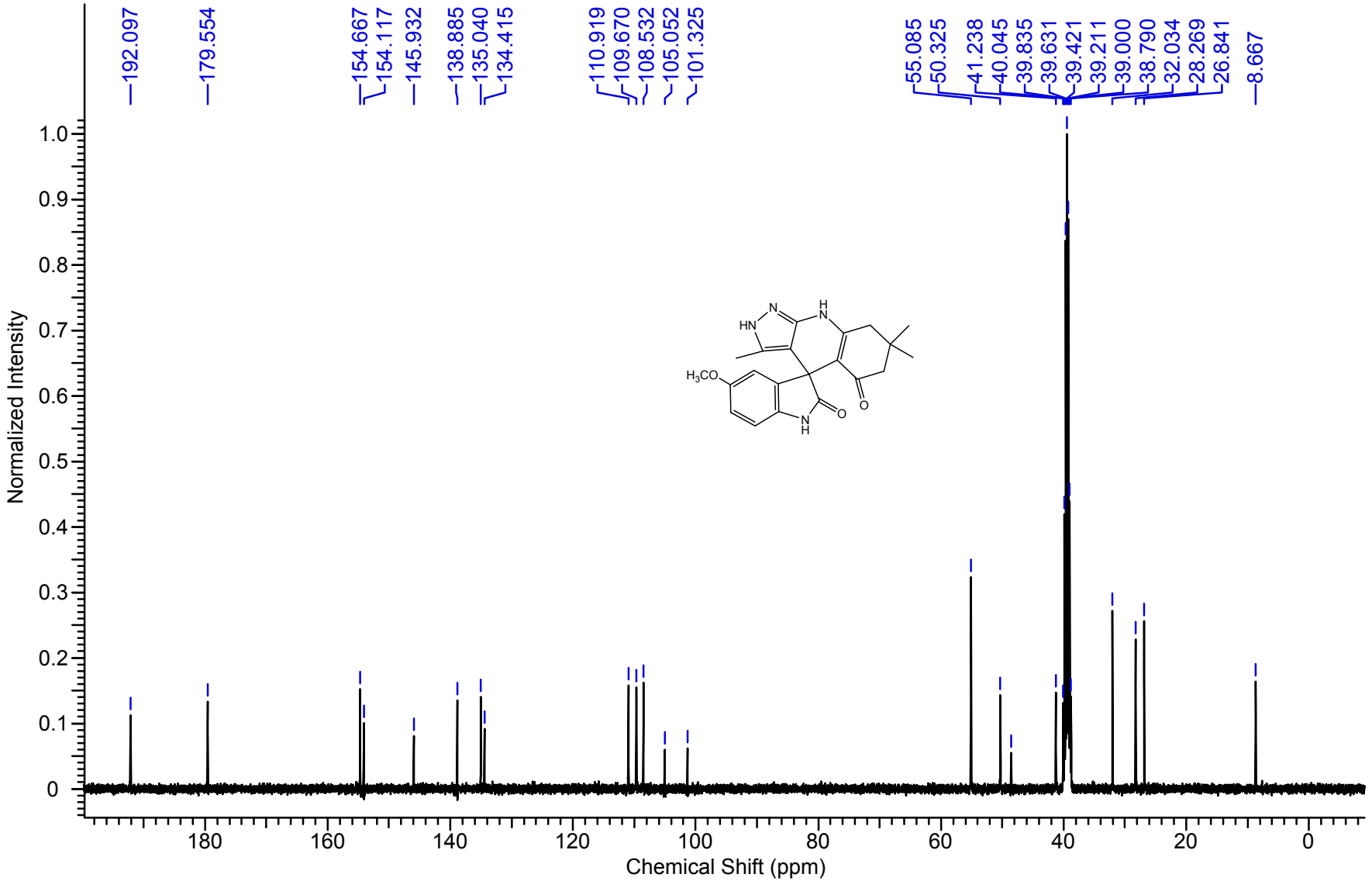
^{13}C-NMR of NGS-400(**9a**)



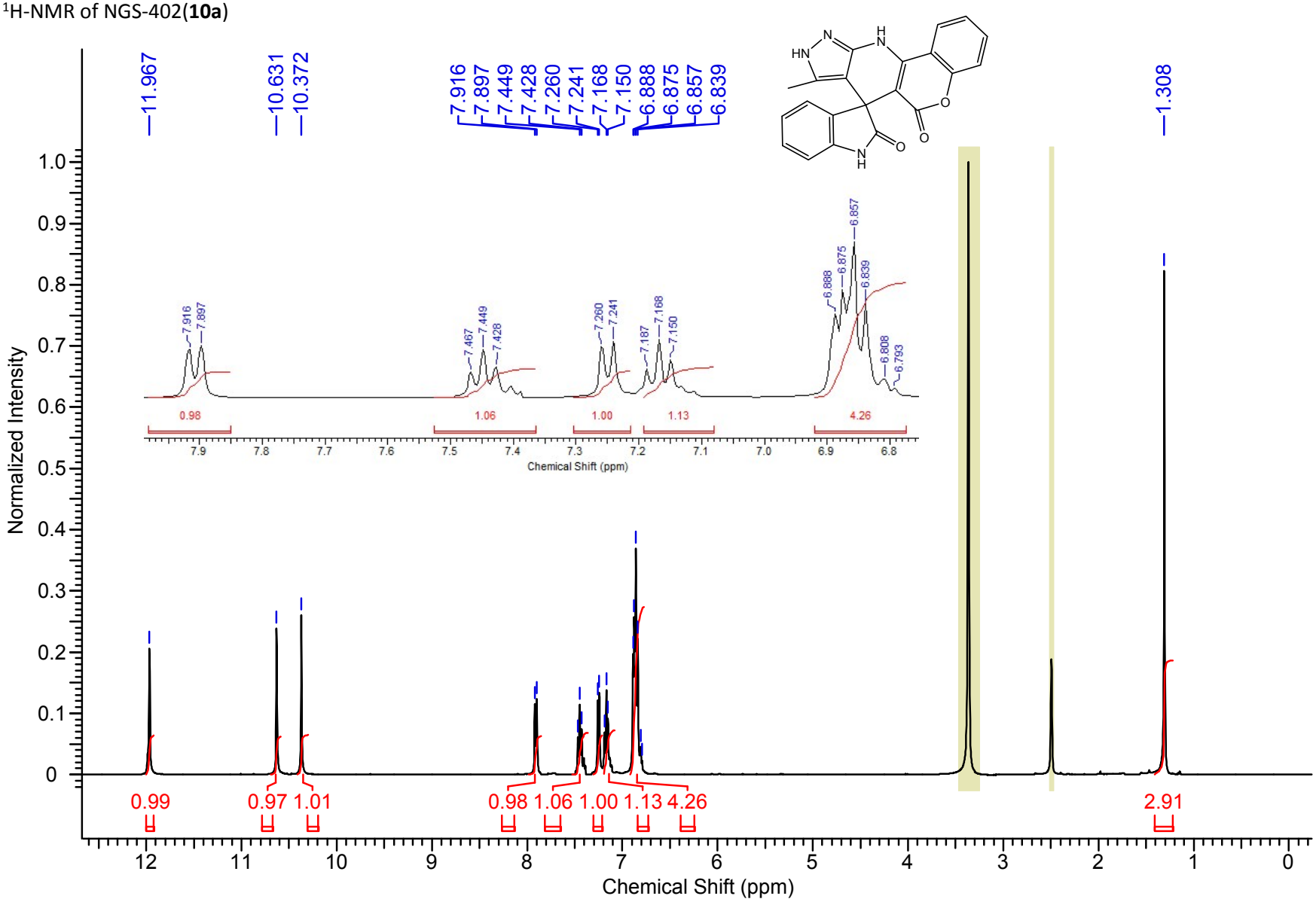
^{1}H-NMR of NGS-413(**9b**)



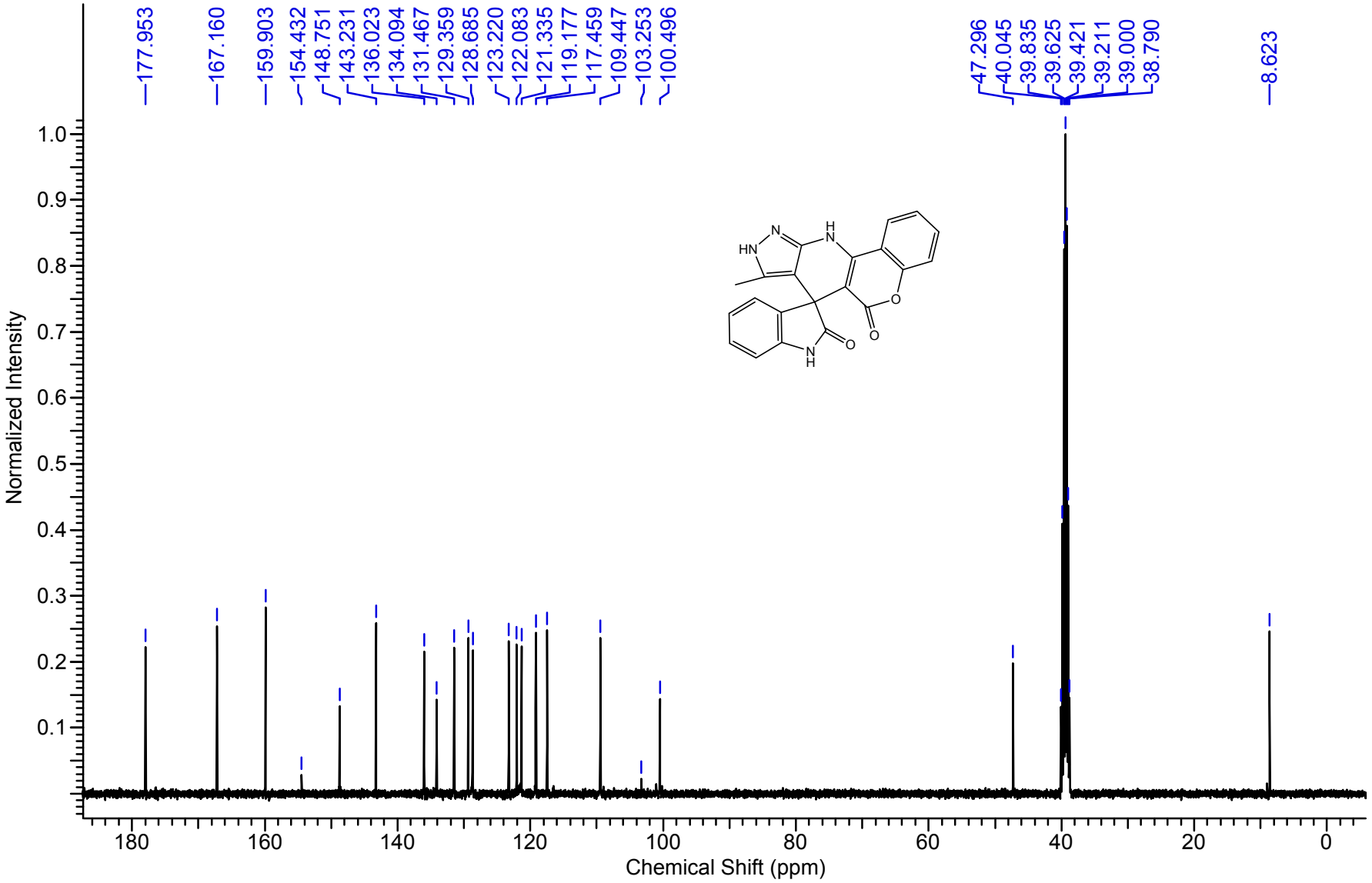
^{13}C-NMR of NGS-413(**9b**)



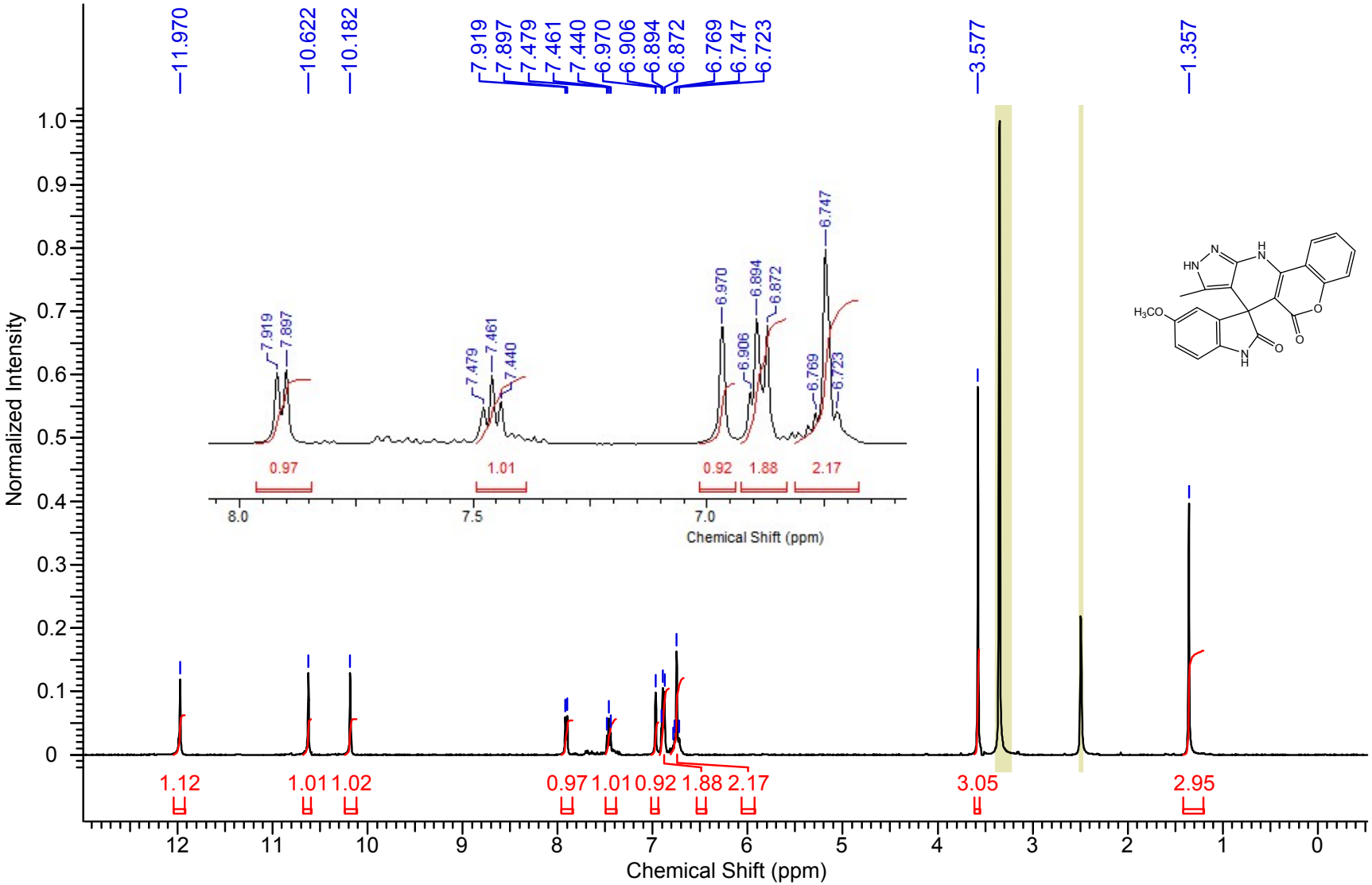
^{1}H-NMR of NGS-402(**10a**)



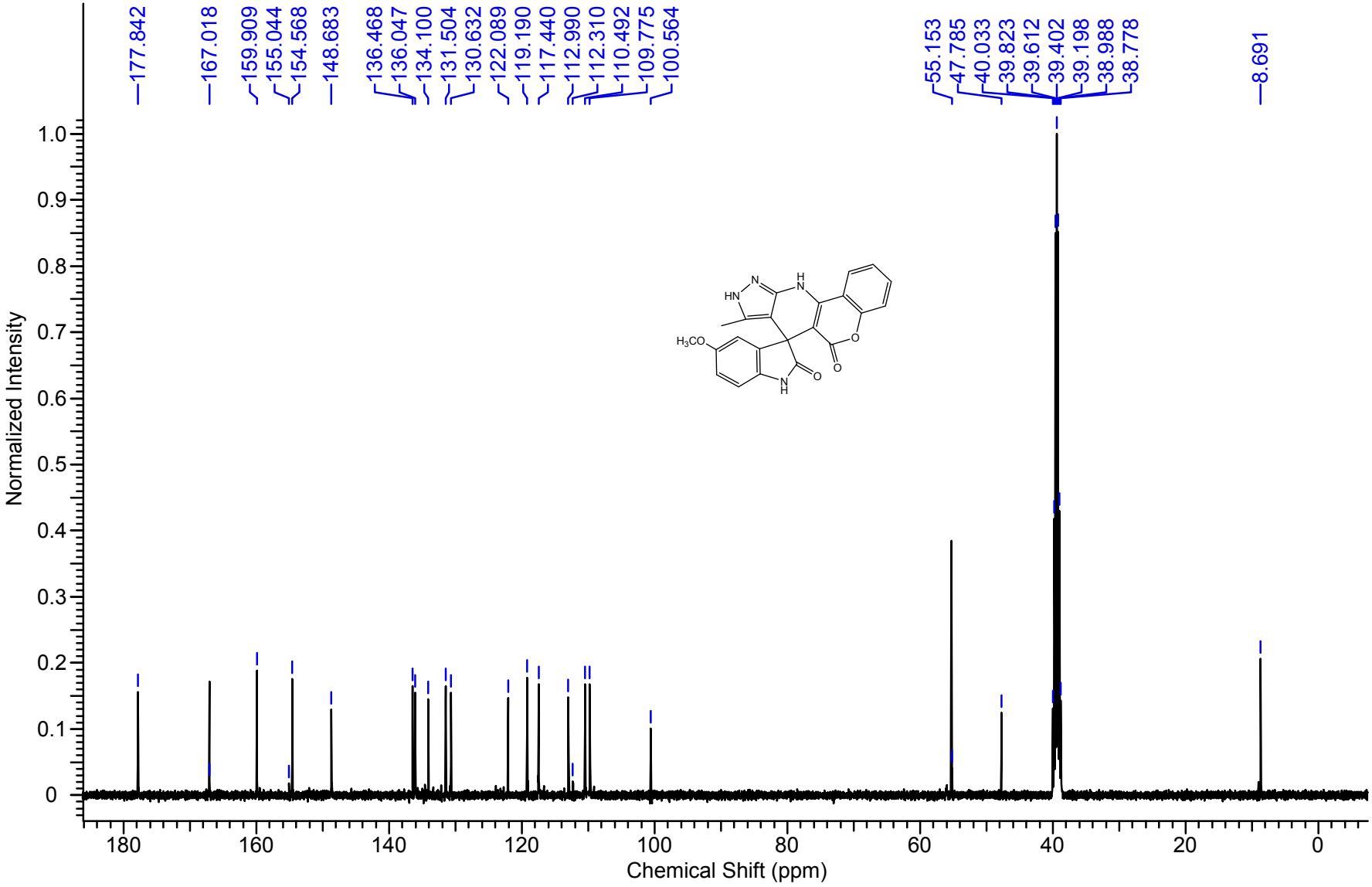
^{13}C-NMR of NGS-402(**10a**)



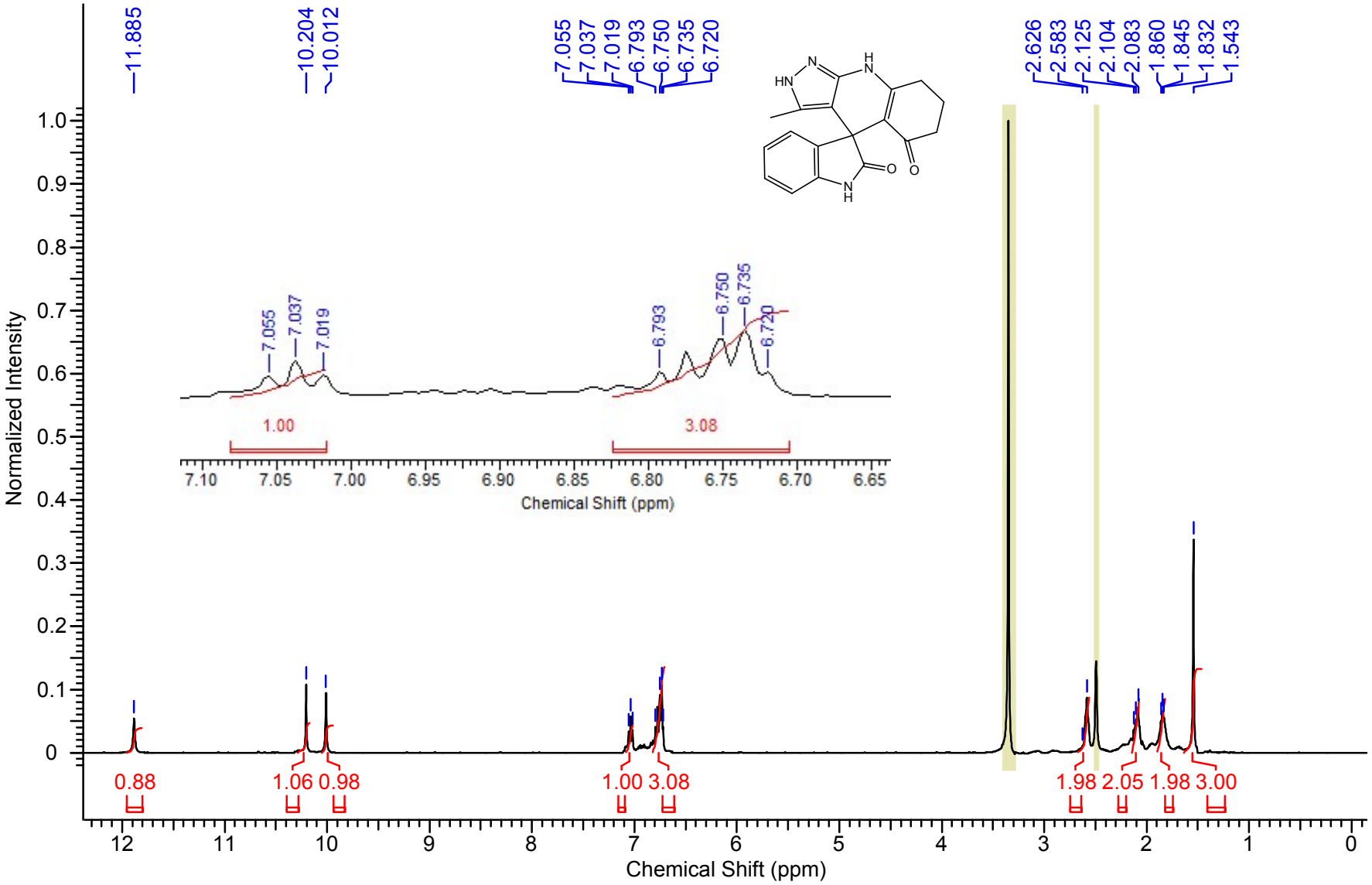
^{1}H-NMR of NGS-414(**10b**)



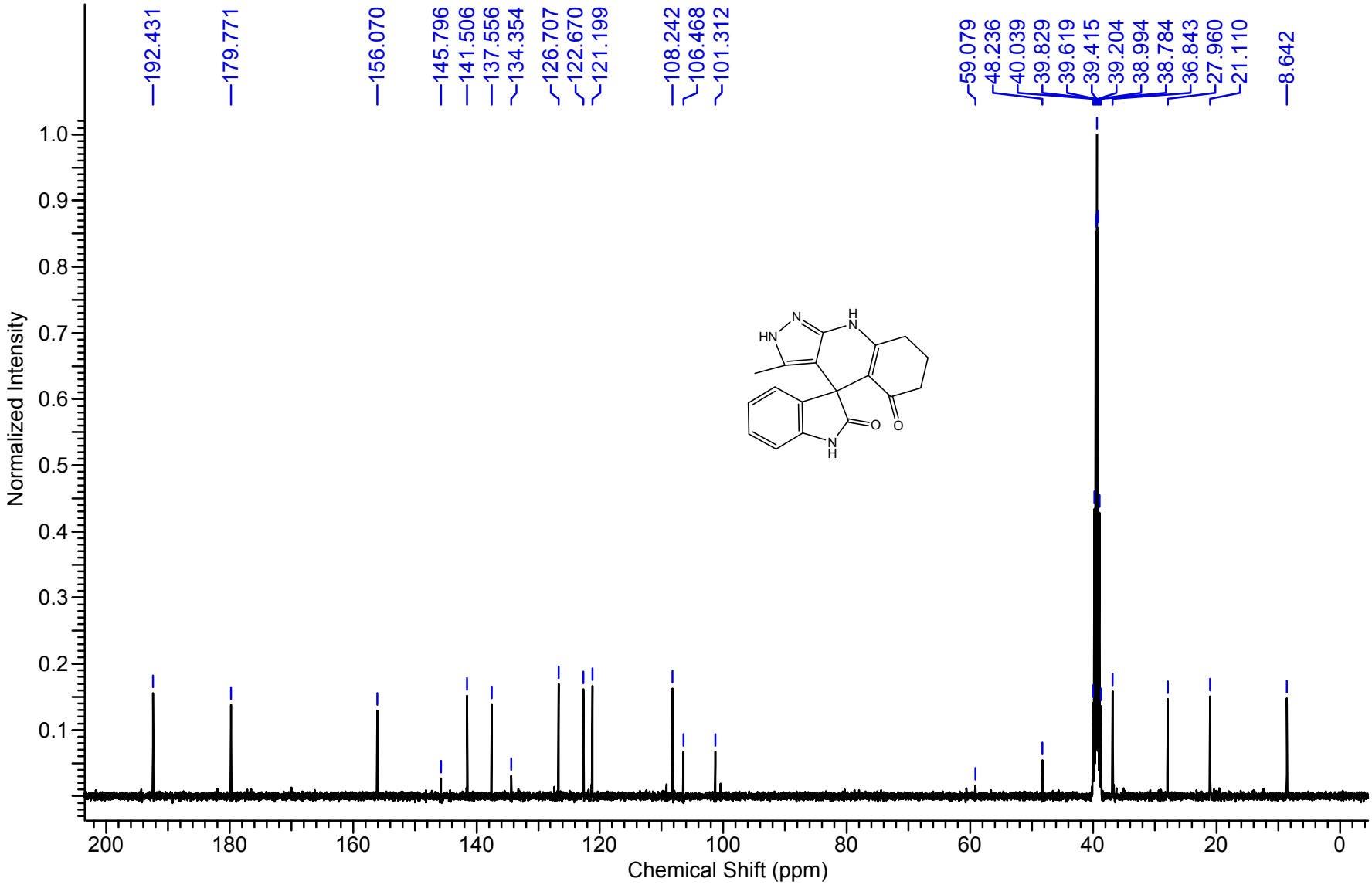
^{13}C-NMR of NGS-414(**10b**)


177.842
167.018
159.909
155.044
154.568
148.683
136.468
136.047
134.100
131.504
130.632
122.089
119.190
117.440
112.990
112.310
110.492
109.775
100.564
55.153
47.785
40.033
39.823
39.612
39.402
39.198
38.988
38.778
8.691
Normalized Intensity
Chemical Shift (ppm)
HN
N
H
N
H3CO
O
O
O
N
H

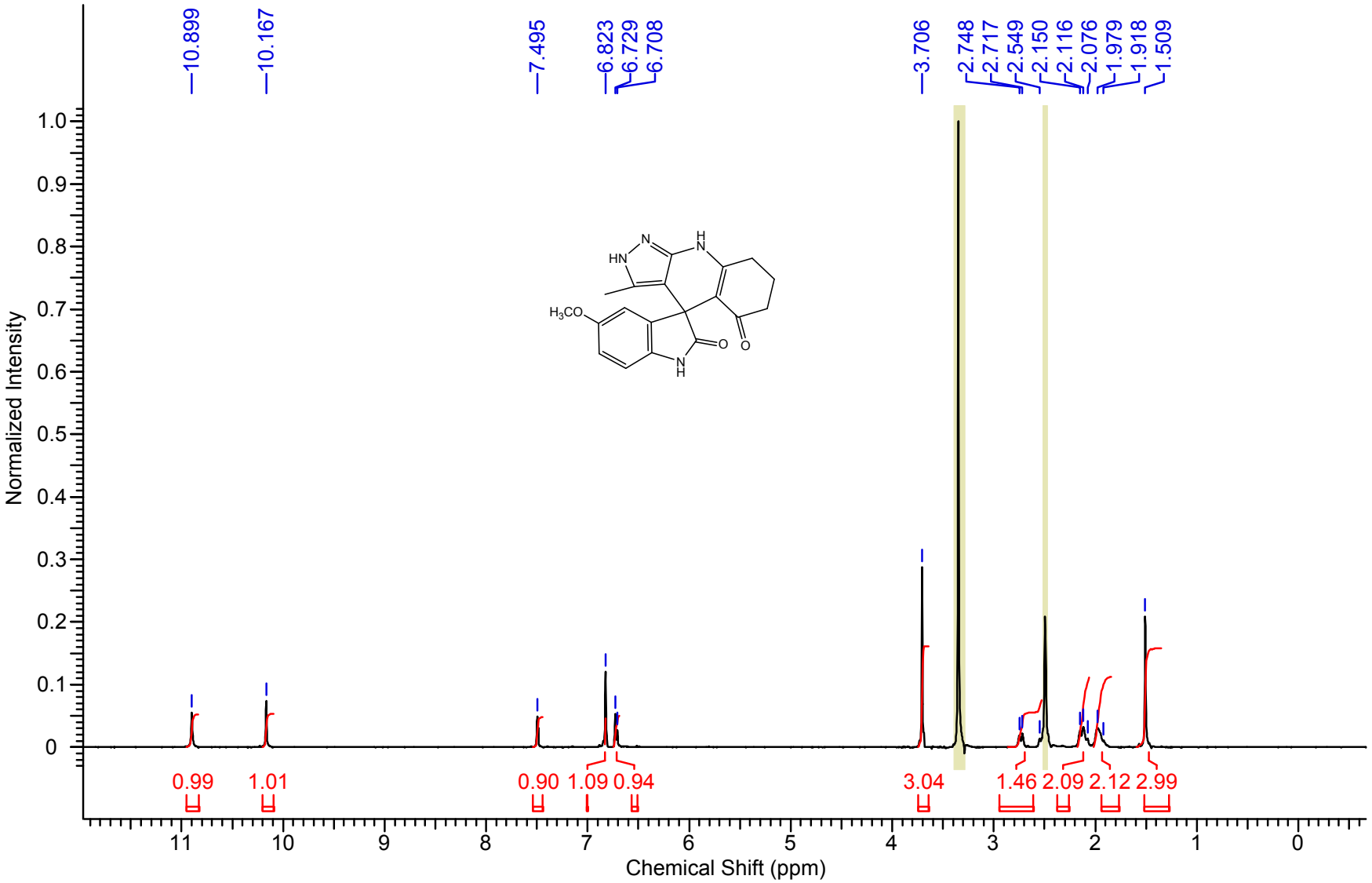
^{1}H-NMR of NGS-406(**11a**)



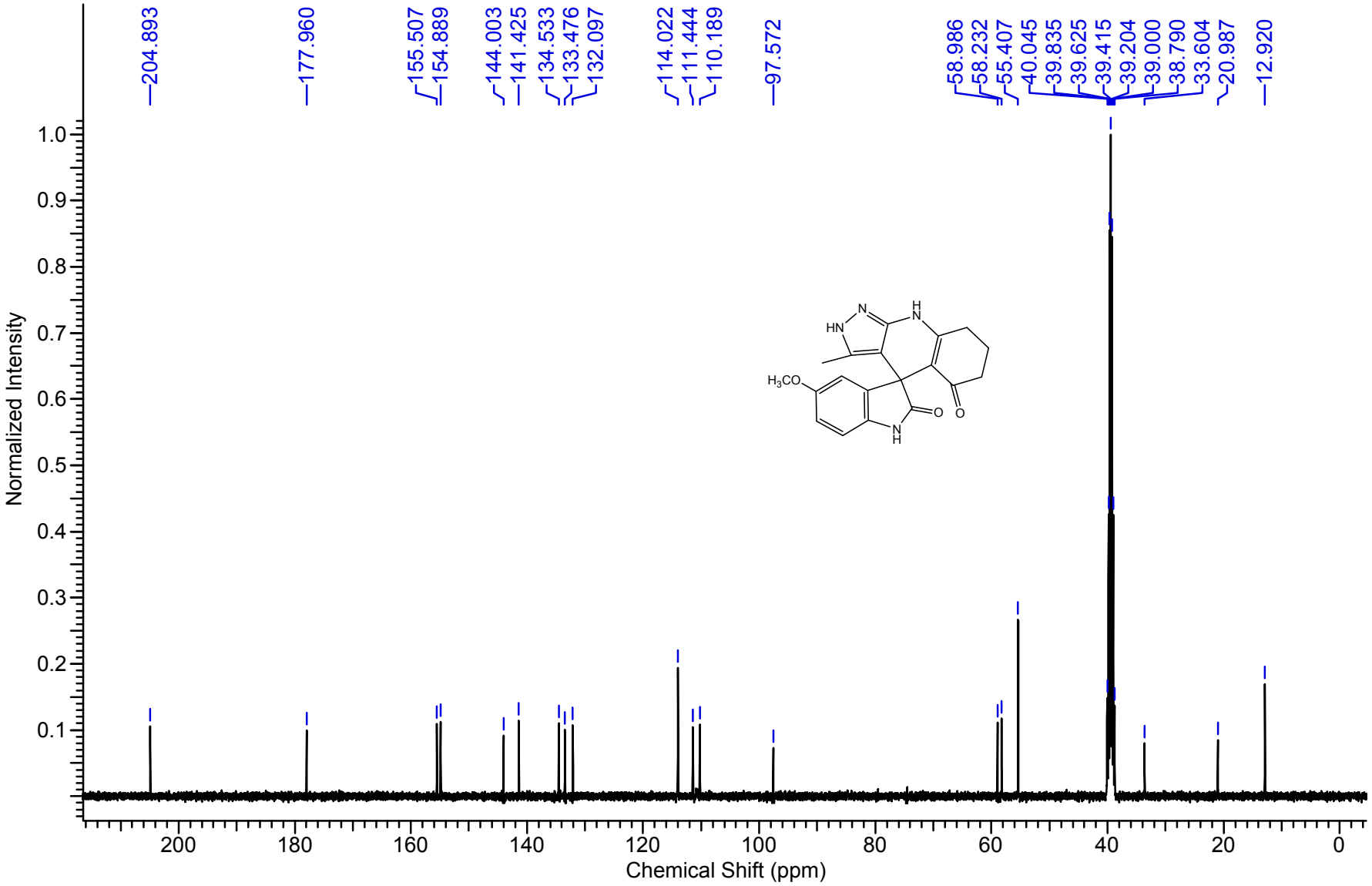
^{13}C-NMR of NGS-406(**11a**)



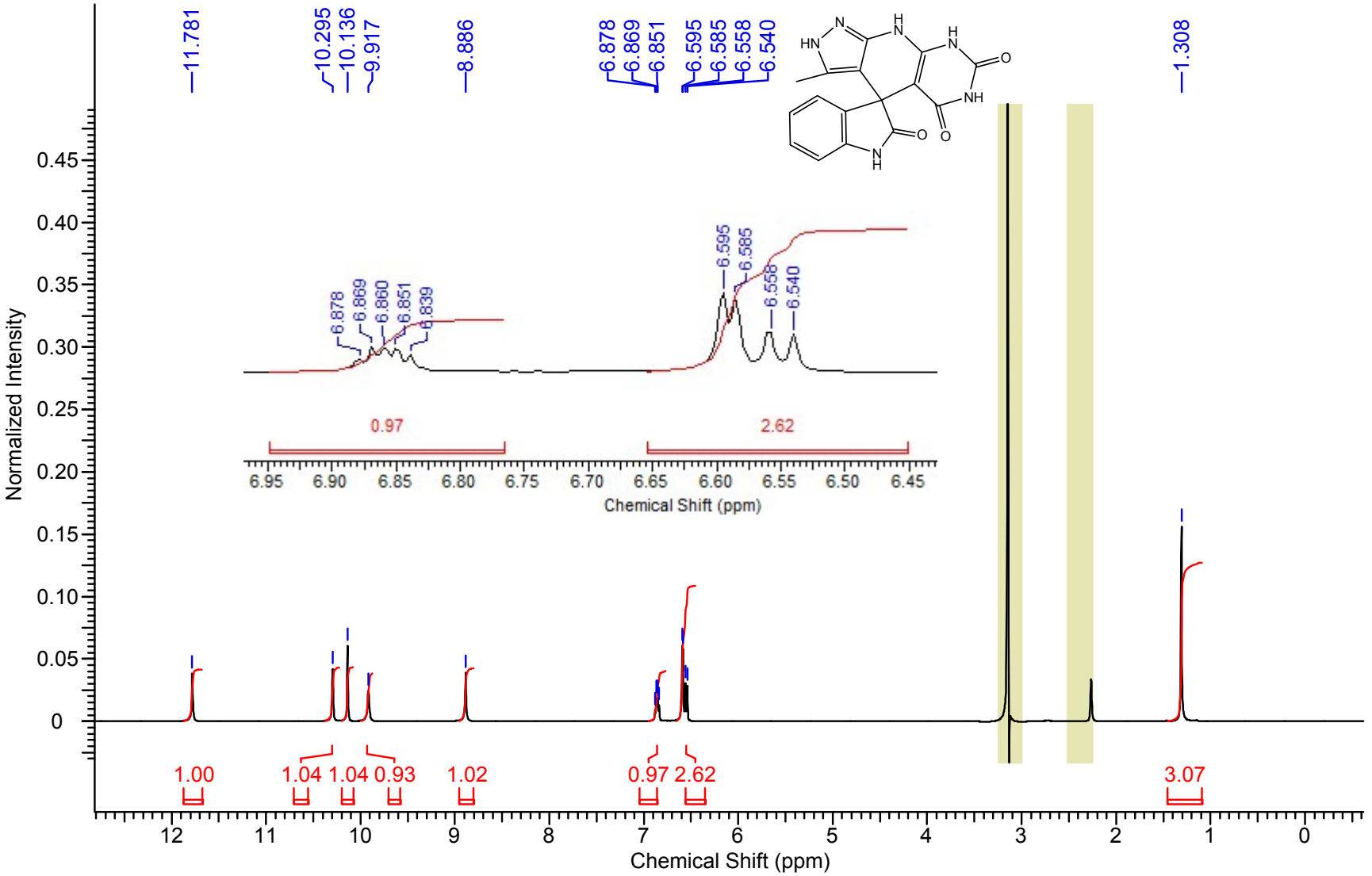
^{1}H-NMR of NGS-415(**11b**)



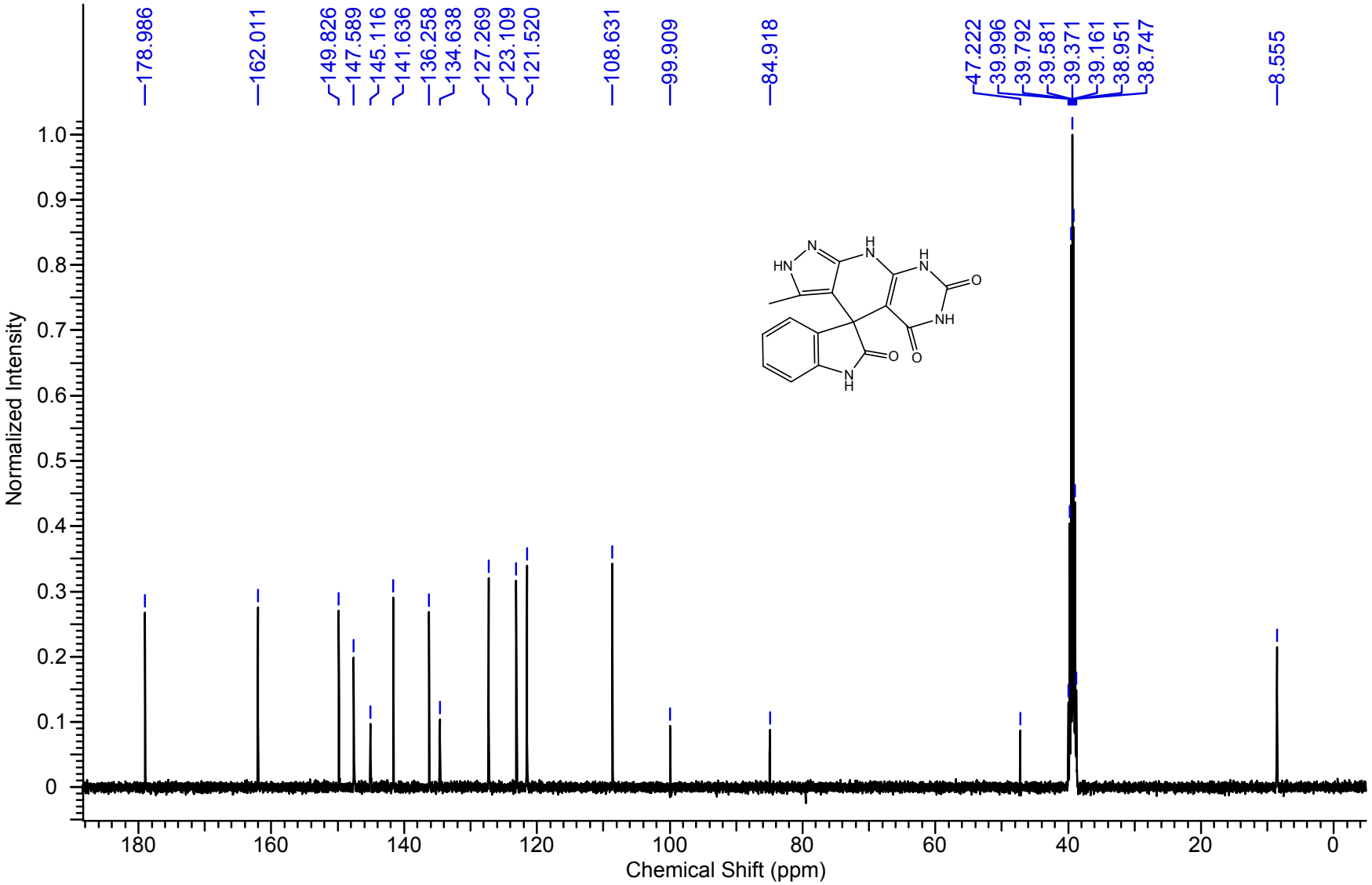
^{13}C-NMR of NGS-415(**11b**)



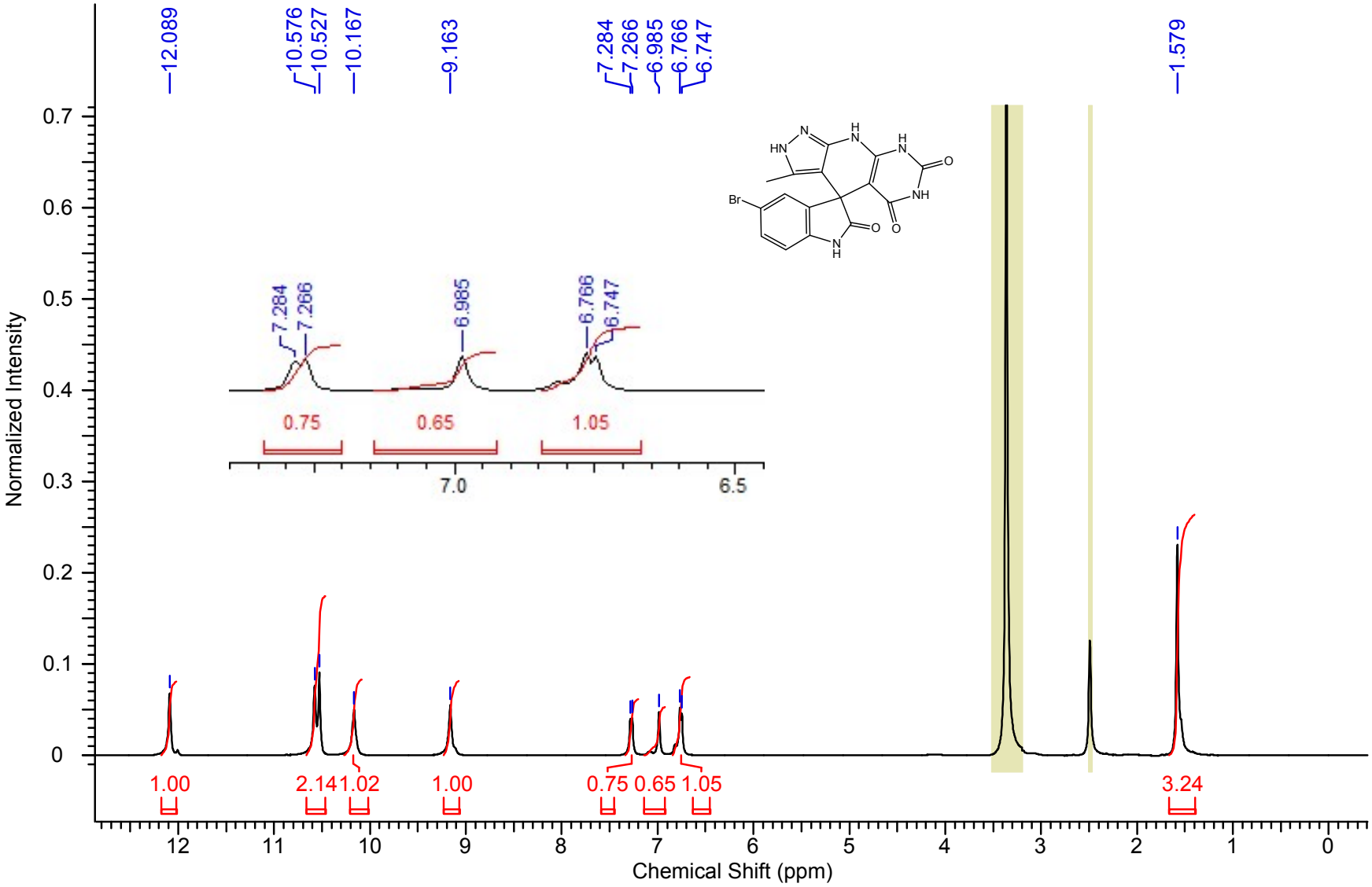
^{1}H-NMR of NGS-404(**12a**)



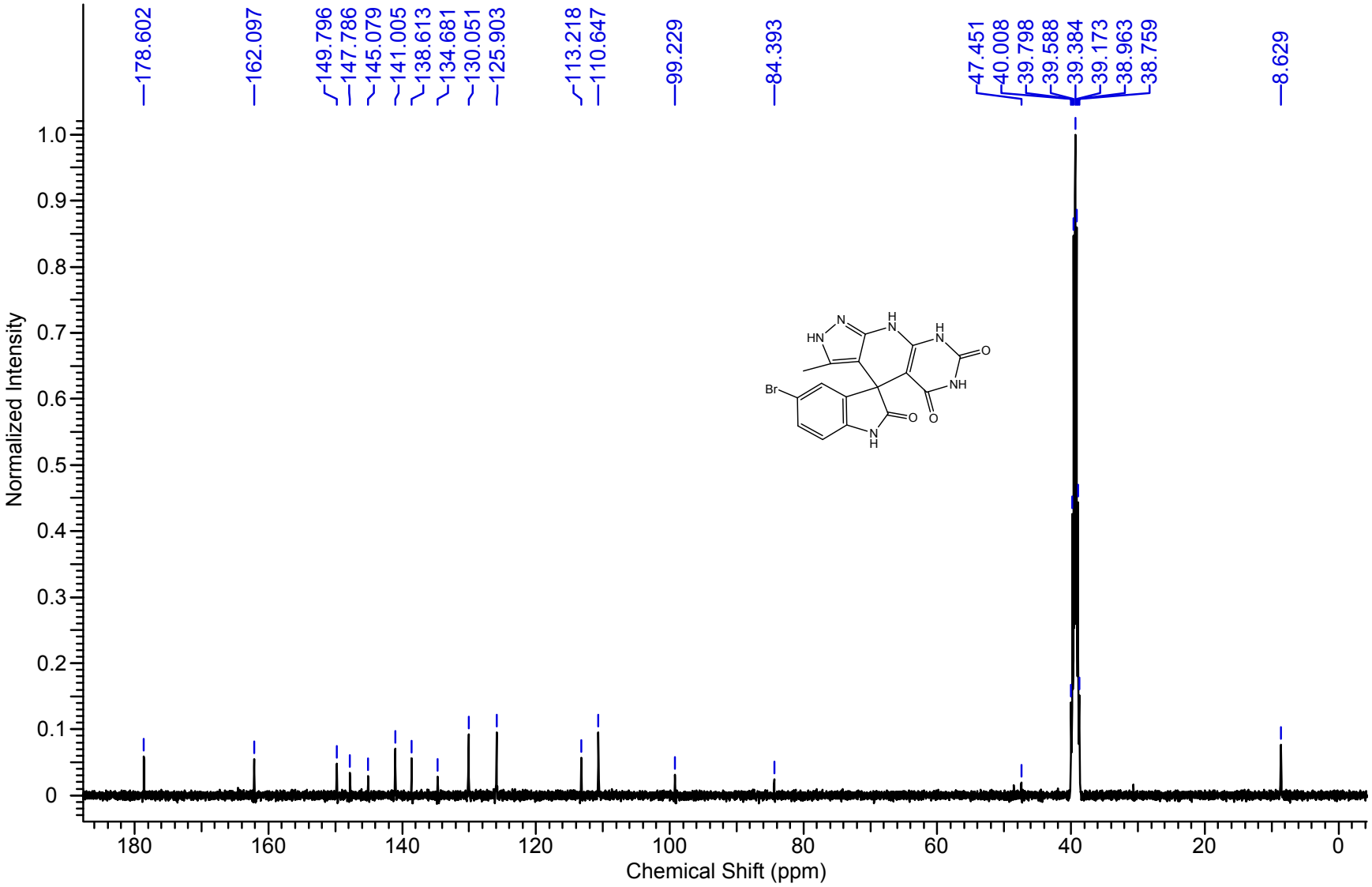
^{13}C-NMR of NGS-404(**12a**)



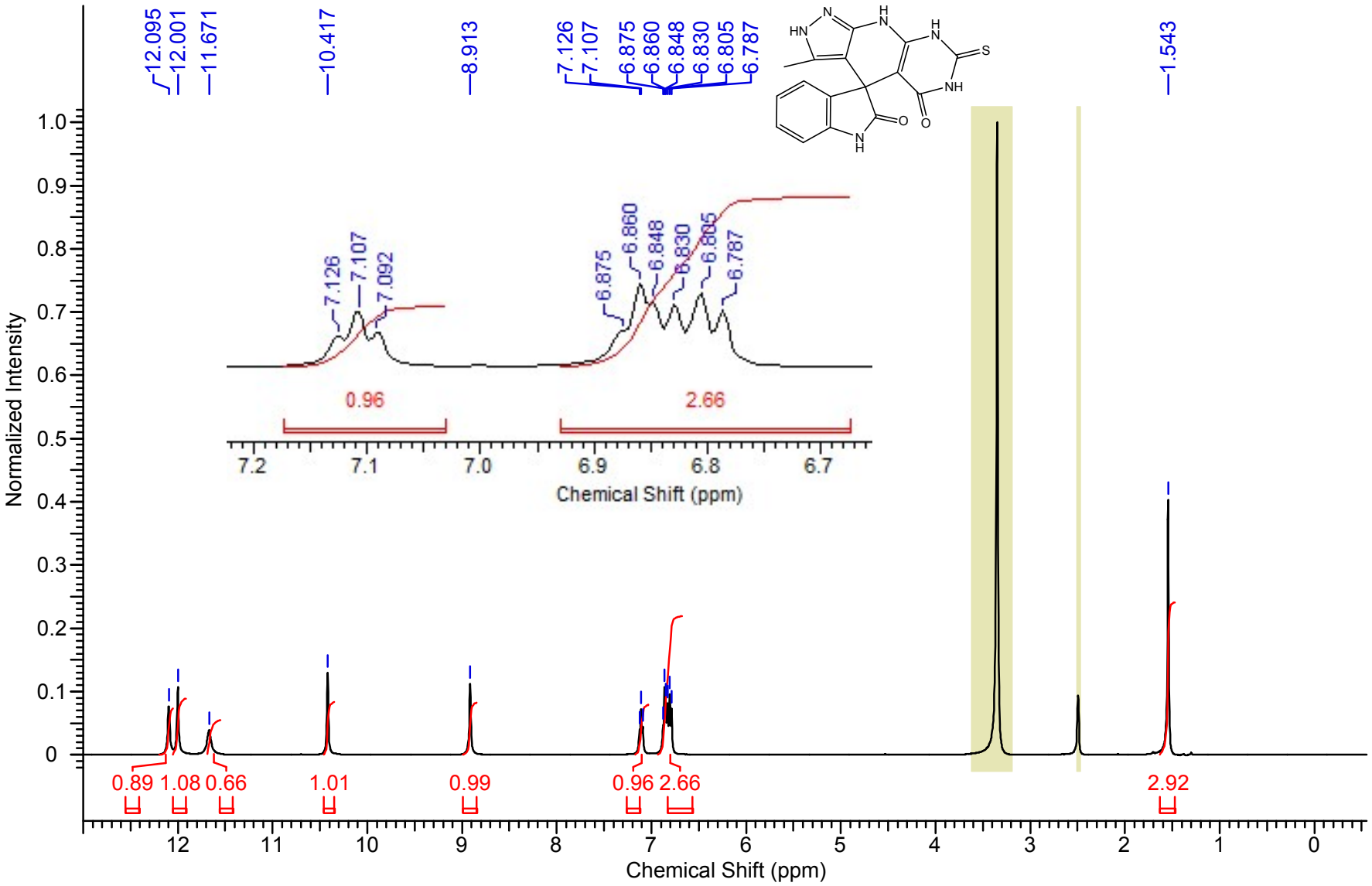
^{1}H-NMR of NGS-411(**12c**)



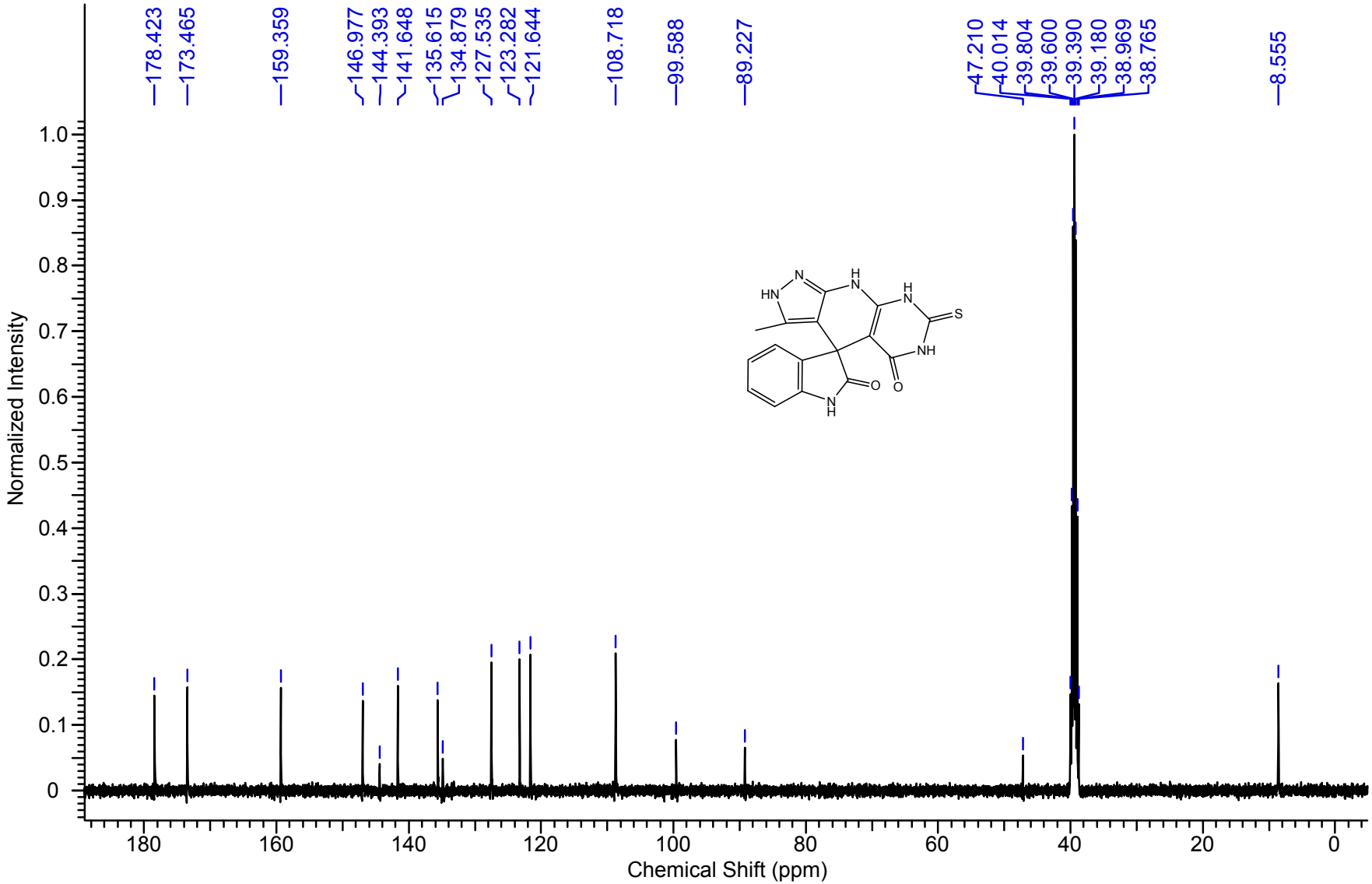
^{13}C-NMR of NGS-411 (**12c**)



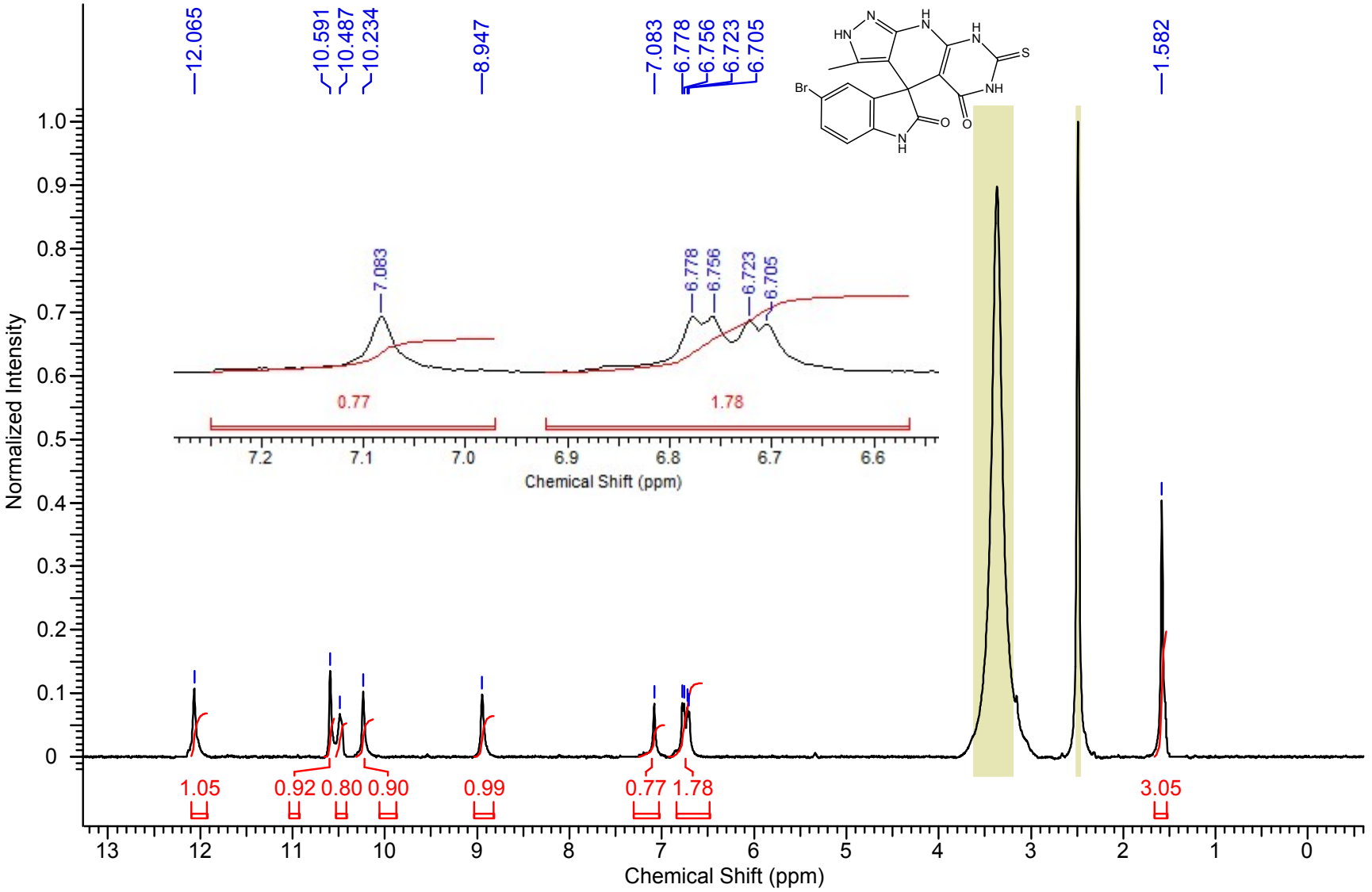
^{1}H-NMR of NGS-405b (**13a**)



^{13}C-NMR of NGS-405b (**13a**)



[1]H-NMR of NGS-412(**13b**)



^{13}C-NMR of NGS-412 (**13b**)