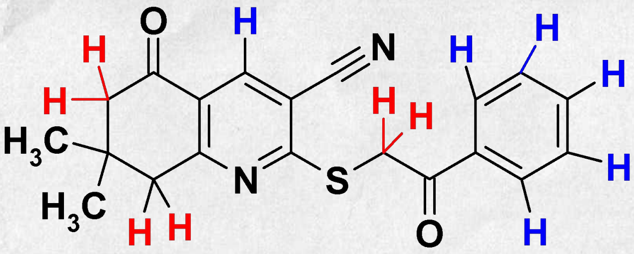
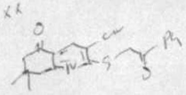
Кубанский государственный университет

Радиоспектроскопические методы исследования 3



244xx



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244XX (108)
EXP1 PULSE SEQUENCE: S2PUL
DATE 01-01-97
SOLVENT DMCO
FILE H9

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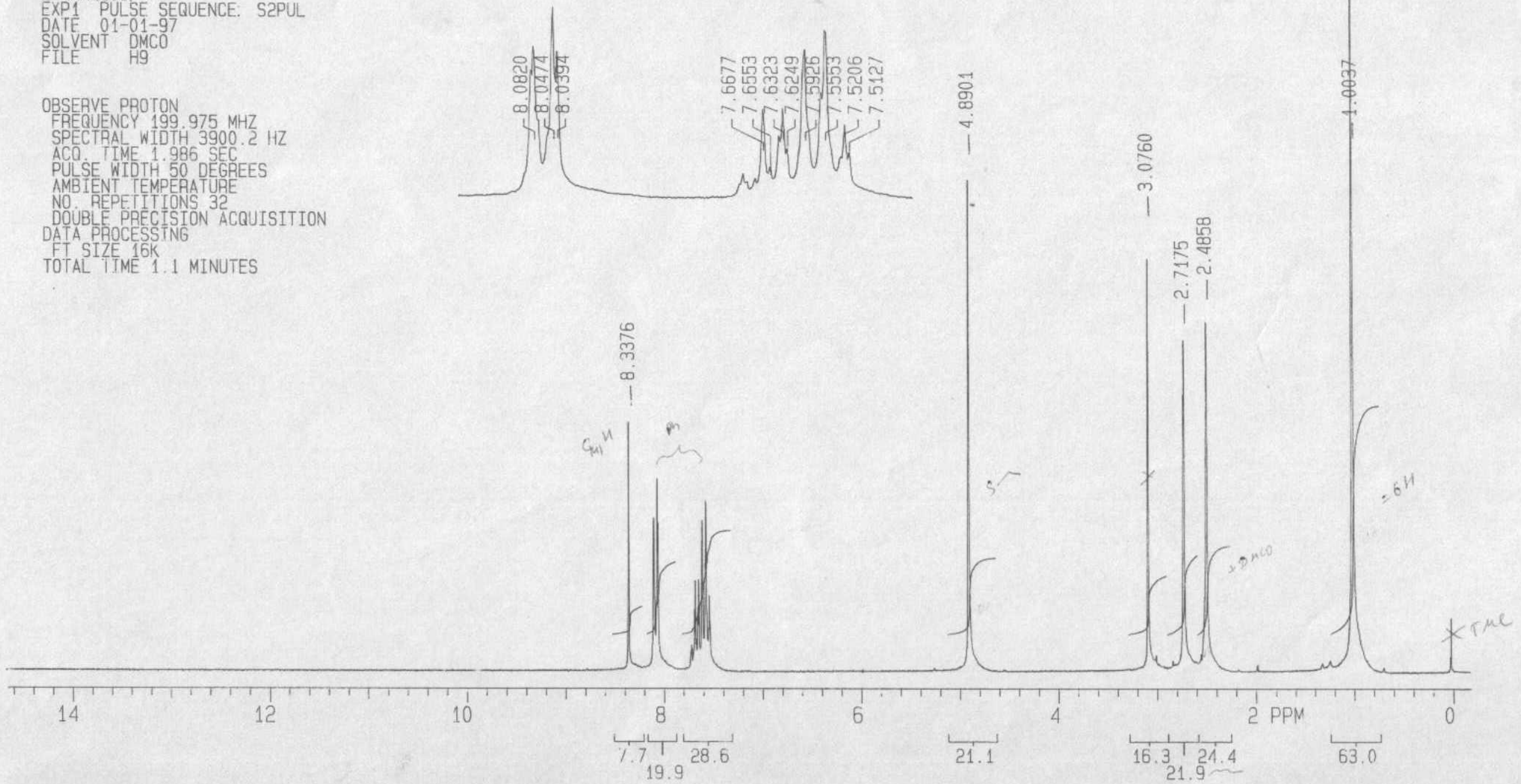
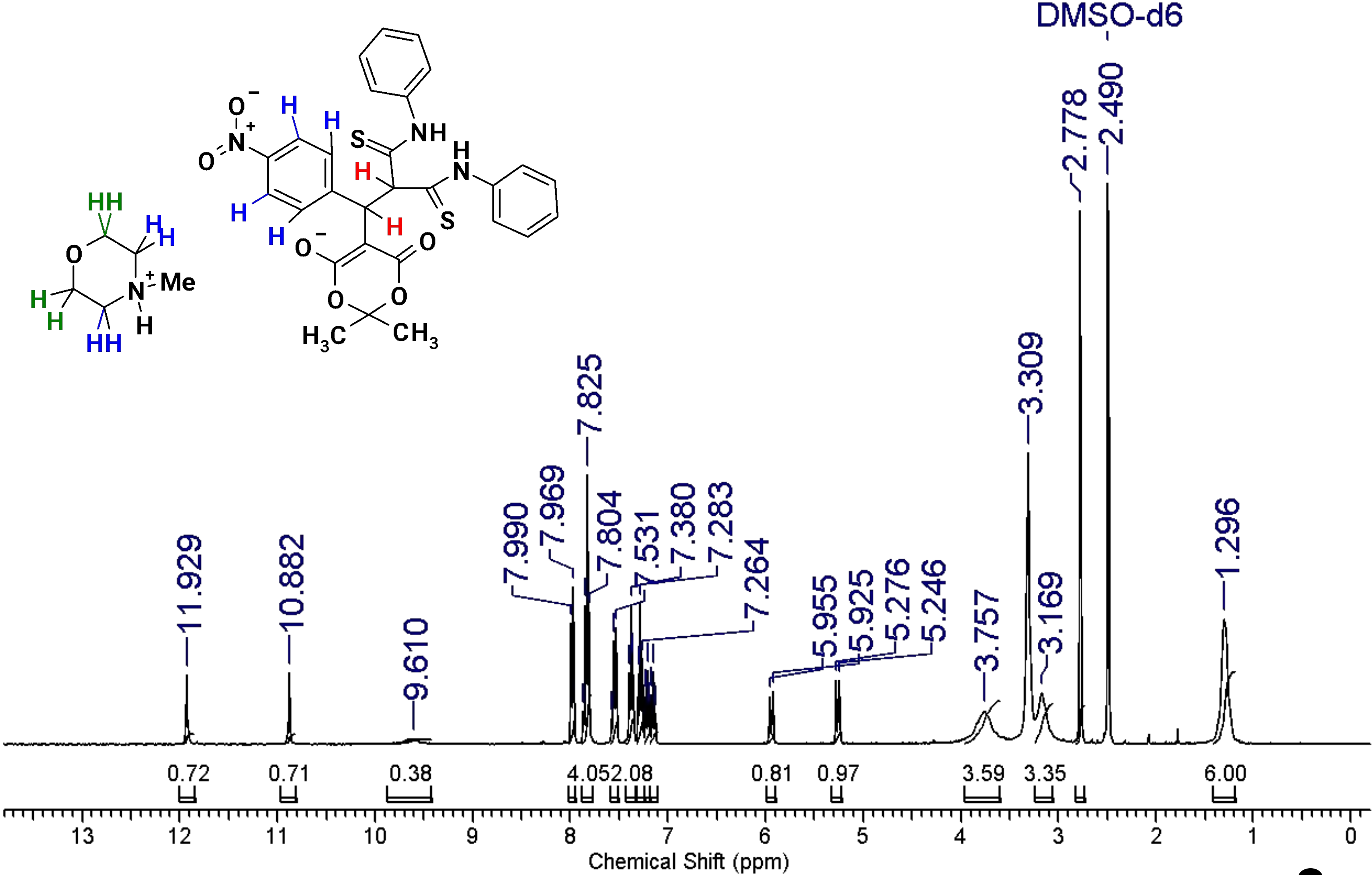
SPECTRAL WIDTH 3900.2 HZ
ACQ. TIME 1.986 SEC
PULSE WIDTH 50 DEGREES
AMBIENT TEMPERATURE
NO. REPETITIONS 32
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
FT SIZE 16K
TOTAL TIME 1.1 MINUTES

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9.610
7.990
7.969
7.825
7.804
7.531
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7.264
5.955
5.925
5.276
5.246
3.757
3.309
3.169
2.778
2.490
1.296
0.72
0.71
0.38
4.05
2.08
0.81
0.97
3.59
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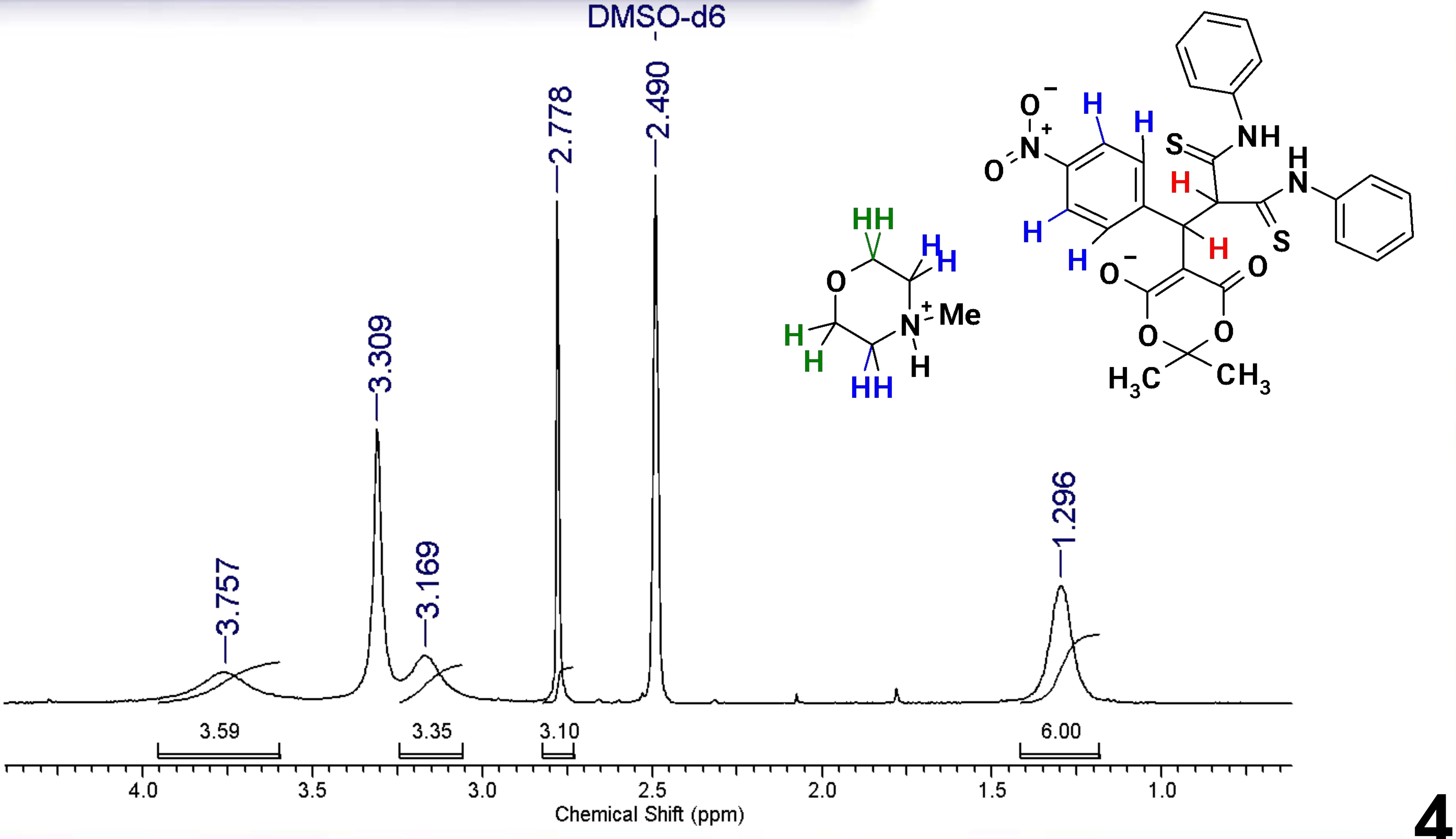
Chemical Shift (ppm)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3.309
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3.5
3.0
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2.0
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Me
H
HH
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NH
S
H
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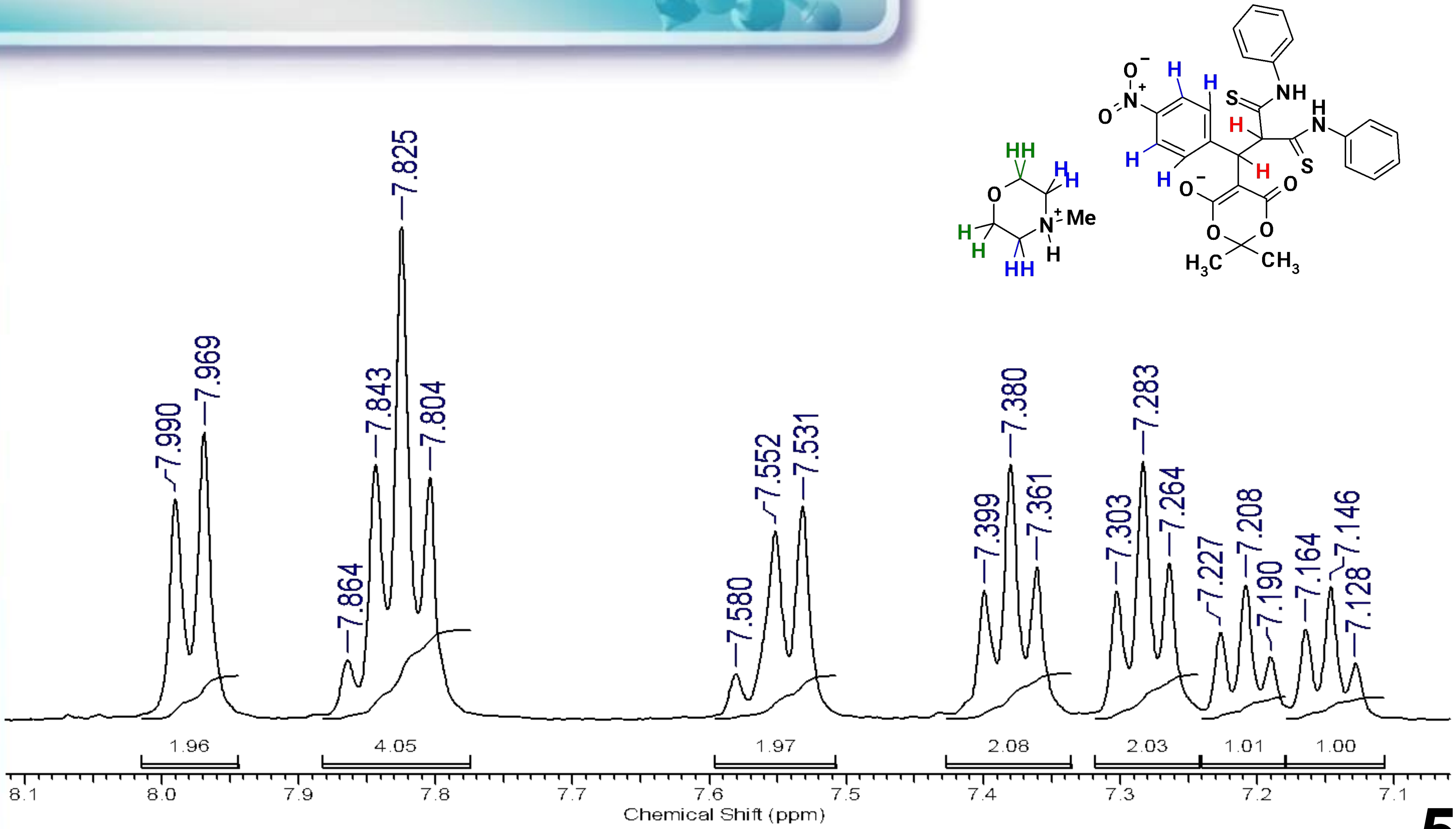
H₃C
CH₃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HH
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N
H
H
H
H
O
−
O
S
O
O
H₃C
CH₃
7.990
7.969
7.864
7.843
7.825
7.804
7.580
7.552
7.531
7.399
7.380
7.361
7.303
7.283
7.264
7.227
7.208
7.190
7.164
7.146
7.128
1.96
4.05
1.97
2.08
2.03
1.01
1.00
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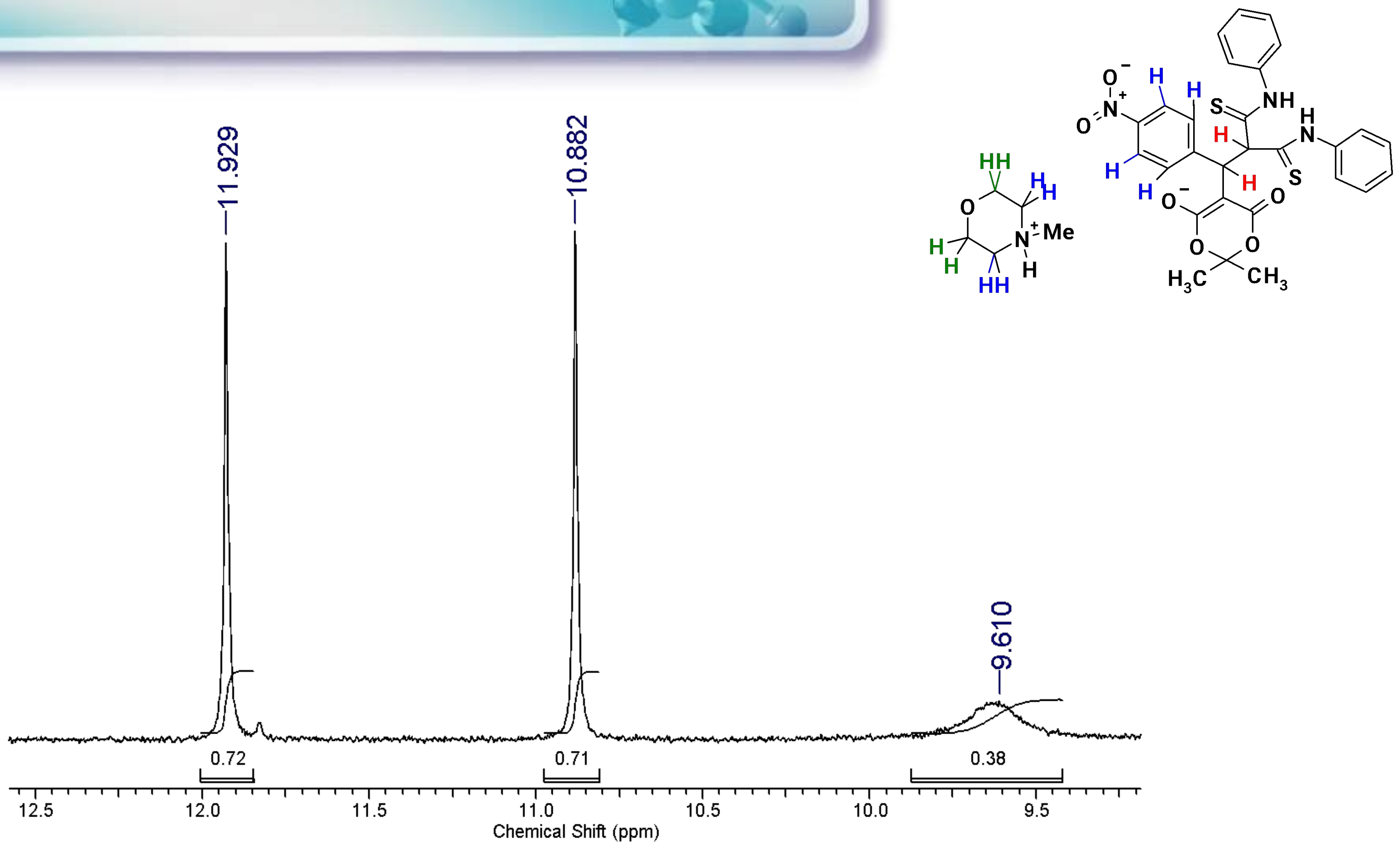
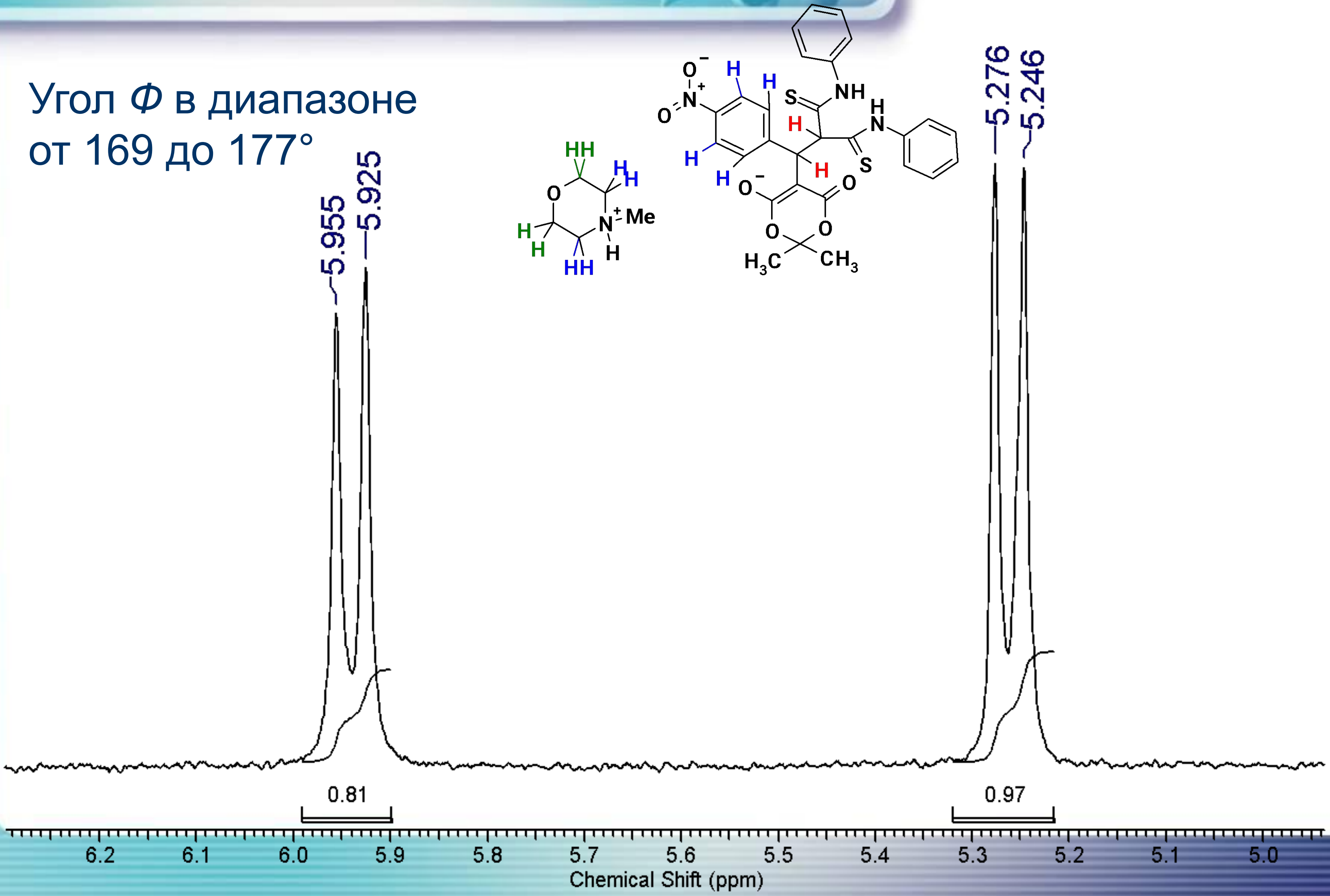
7.2
7.1
Chemical Shift (ppm)

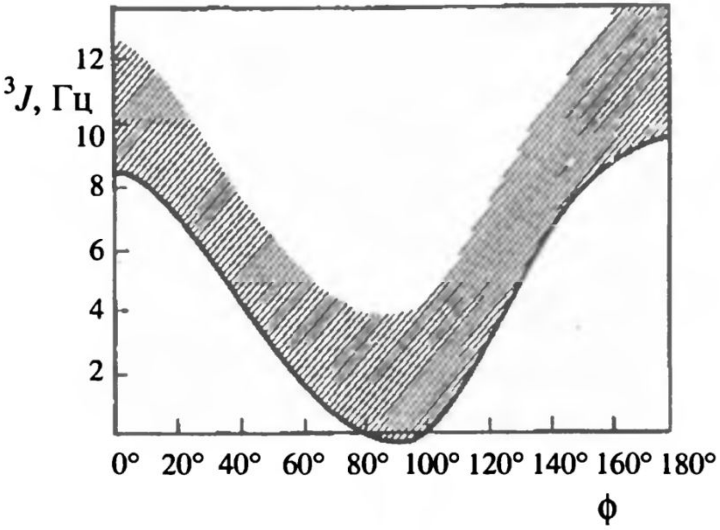

11.929
10.882
9.610
0.72
0.71
0.38
12.5
12.0
11.5
11.0
10.5
10.0
9.5
Chemical Shift (ppm)
HH
H
H
O
N
+
Me
H
H
H
HH
O
–
N
+
O
H
H
S
NH
H
N
H
H
H
H
S
O
–
O
O
O
H$_3$C
CH$_3$

Угол *Φ* в диапазоне от 169 до 177°

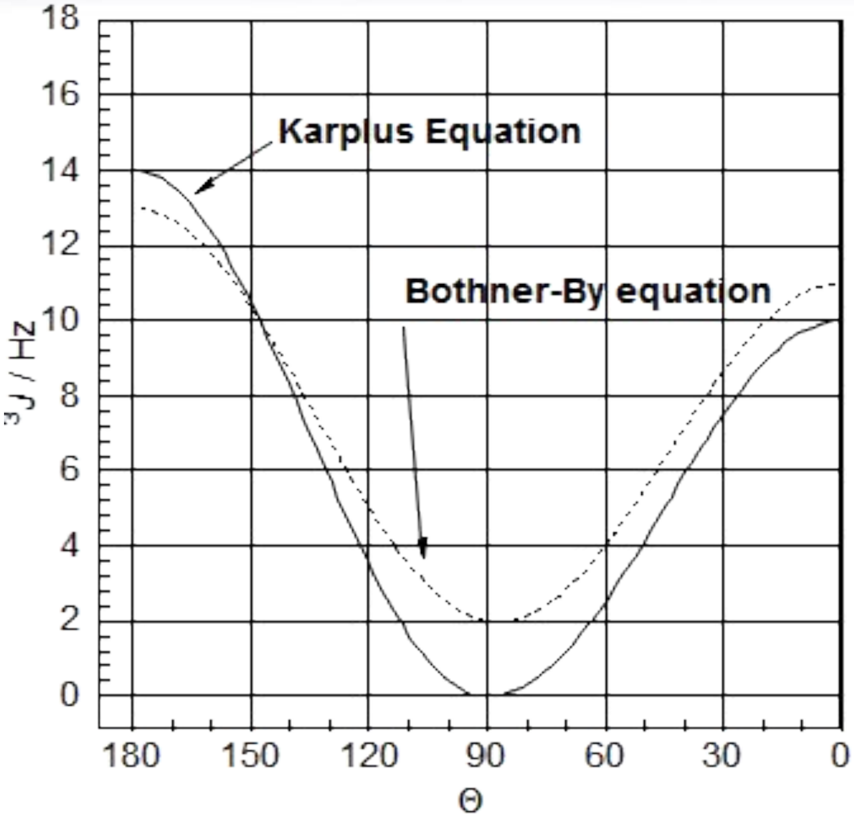


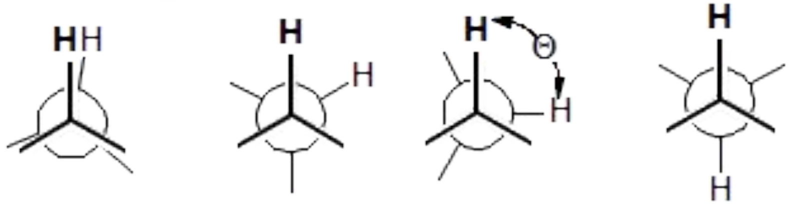
Уравнение Карплуса-Конроя

$$^3J = A + B\cos\varphi + C\cos2\varphi.$$



Кривая КК чественно хорошо согласуются с расчетами, проведенными для фрагмента H—C—C—H. Однако эксперимент показывает, что значения ^{3}Jнн для *ф* = 0 и 180° в общем на 2-4 Гц больше, чем рассчитанные. Поэтому для уравнения были предложены эмпирические постоянные **A = 7, B = - 1 и *C* = 5**. *Кривая Карплуса — Конроя* объясняет ряд важных закономерностей. Например, в олефиновых системах спин-спиновое взаимодействие между граис-протонами всегда больше, чем между цис-протонами. Поэтому легко различать *цис-* и транс-изомеры. Для 1,2-дизамещенных этанов справедливо соответствующее соотношение Jгош < *Jтранс.*





Θ = 0° ^3J = 7-11 Hz

Θ = 60° ^3J = 2-5 Hz

Θ = 90° ^3J = 0-2 Hz

Θ = 180° ^3J = 8-15 Hz

Karplus Equation

$^3J_{HH} = J_o \cdot \cos^2\Theta - K$

J_o = 14 (90-180°), J_o = 10 (0-90°), K = 0

Bothner-By equation

$^3J_{HH} = 7 - \cos\Theta + 5\cdot\cos 2\Theta$

The **Karplus** Equation for ${}^3J_{HH}$ (H-Csp^3-sp^{3}C-H) is:

$^3J = 7.8 - 1.0 \cos(phi) + 5.6 \cos(2*phi)$

This basic form of the Karplus equation does not correct for the electronegativity of the substituents.The **Altona** equations for vicinal ${}^3J_{HH}$ (H-Csp^3-sp^{3}C-H) are:

$^3J = p1 \cos^2(f) + p2 \cos(f) + p3 + S\, l_i\, (p4 + p5 \cos^2(e_i\, f + p6\, |l_i|))$

where the sum is over the four substituents. The order of substitution around each carbon makes a difference. The direction coefficient, e_i, is +1 for S_1 and S_3 and -1 for S_2 and S_4. The electronegativity of the substituents includes the "beta effect" and is given by:

$l_i = (C_a - C_H) + p7\, S\, (C_b - C_H)$

where C_a is the Huggin's electronegativity of the directly attached a atom, C_H is the electronegativity of hydrogen, and the sum is over the b atoms that are attached to the a atom. The substituent electronegativity for each attached group is listed under the substituent name. The coefficients have also been modified to use empirical chemical group substituent constants.

The **Diez, Altona, Donders** equation is:

$^3J = c00 + c01\ S\ l_i + c10\ \cos(f) + (c20 + c21\ S\ l_i)\ \cos(2f) + (s211\ S\ e_i\ l^2_i)\ \sin(2f)$

The coefficients for the Diez, Altona, Donders equations with chemical groups are:

c00 = 7.82 , c01 =-0.79 , c10 = -0.78 , c20 = 6.54 , c21 = -0.64 , s211 = 0.70

Please see: L. A. Donders, F. A. A. M. de Leeuw, C. Altona, "Relationship Between Proton-Proton NMR Coupling Constants and Substituent Electronegativities IV. An Extended Karplus Equation Accounting for Interactions Between Substituents and its Application to Coupling Constant Data Calculated by the Extended Huckel Method," *Magn. Reson. Chem.*, **1989**, *27*, 556-563.

The ^3J vinyl and ^4J allylic coupling constants are based on the modified Karplus Equation by **Garbisch:**

Please see: E. W. Garbisch, Jr., "Conformations. VI. Vinyl-Allylic Proton Spin Couplings," *J. Amer. Chem. Soc*, **1964**, *86*, 5561-5564.

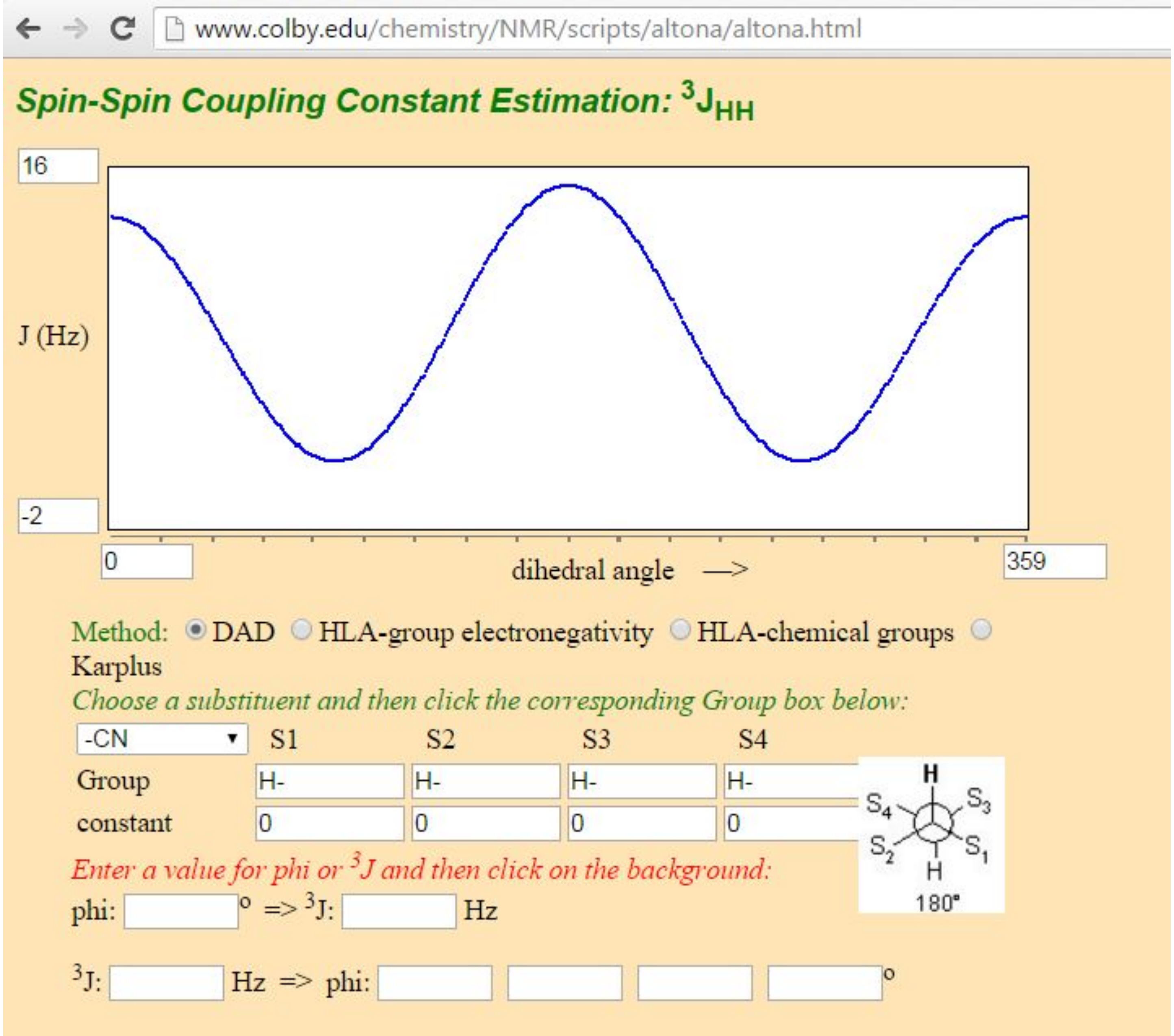
$^3J = 6.6 \cos^2(\mathrm{phi}) + 2.6 \sin^2(\mathrm{phi})$ $(0^\circ <= \mathrm{phi} <= 90^\circ)$

$^3J = 11.6 \cos^2(\mathrm{phi}) + 2.6 \sin^2(\mathrm{phi})$ $(90^\circ <= \mathrm{phi} <= 180^\circ)$

$^4J = 1.3 \cos^2(\mathrm{phi}) - 2.6 \sin^2(\mathrm{phi})$ $(0^\circ <= \mathrm{phi} <= 90^\circ)$

$^4J = - 2.6 \sin^2(\mathrm{phi})$ $(90^\circ <= \mathrm{phi} <= 180^\circ)$

http://www.colby.edu/chemistry/NMR/scripts/altona/altona.html



Spin-Spin Coupling Constant Estimation: $^3J_{HH}$

Method: ● DAD ○ HLA-group electronegativity ○ HLA-chemical groups ○ Karplus

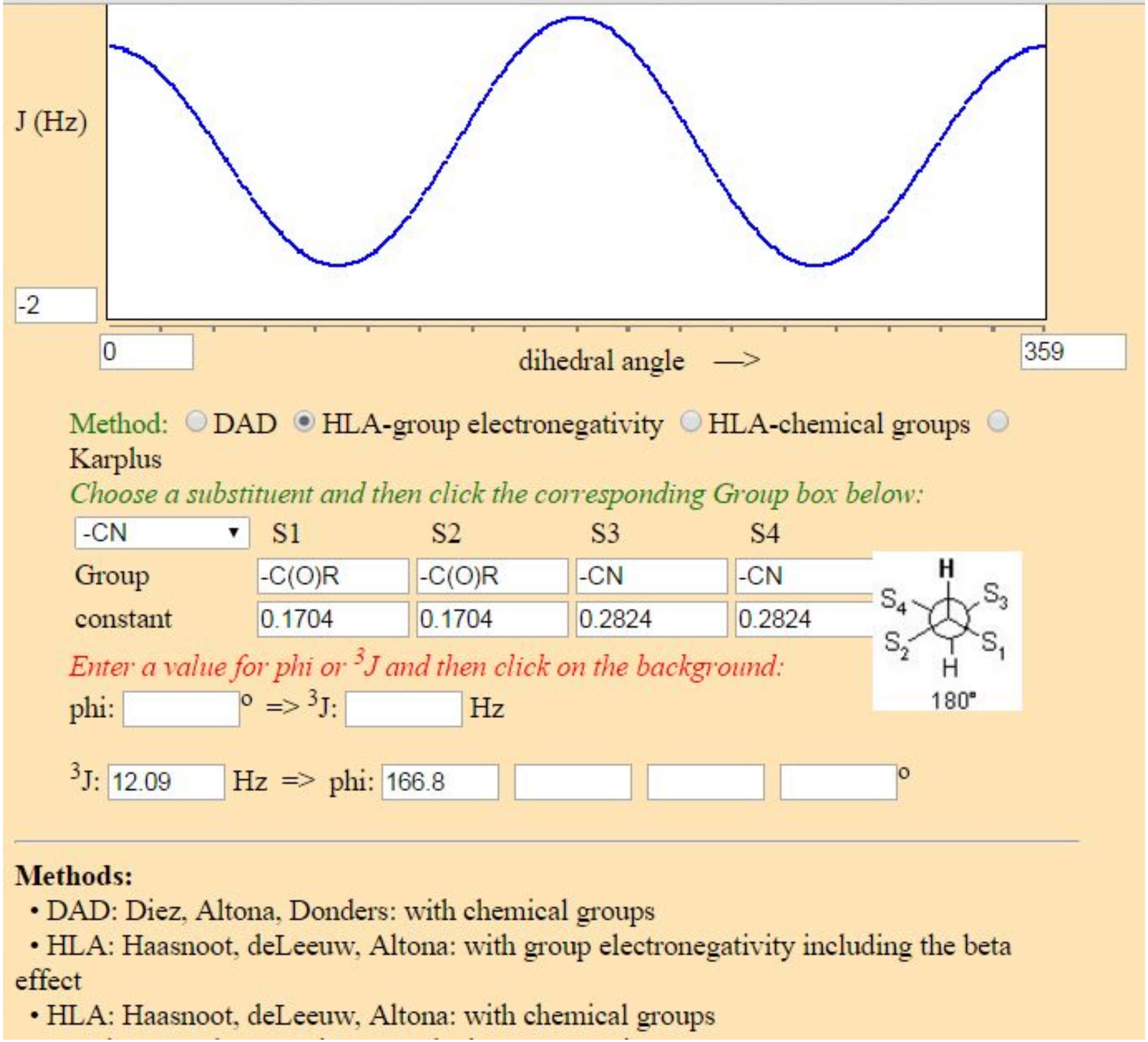
Choose a substituent and then click the corresponding Group box below:

-CN ▾	S1	S2	S3	S4
Group	H-	H-	H-	H-
constant	0	0	0	0

Enter a value for phi or ^3J and then click on the background:

phi: ° => ^3J: Hz

^3J: Hz => phi: °



Method: ○ DAD ● HLA-group electronegativity ○ HLA-chemical groups ○ Karplus

Choose a substituent and then click the corresponding Group box below:

-CN ▾	S1	S2	S3	S4
Group	-C(O)R	-C(O)R	-CN	-CN
constant	0.1704	0.1704	0.2824	0.2824

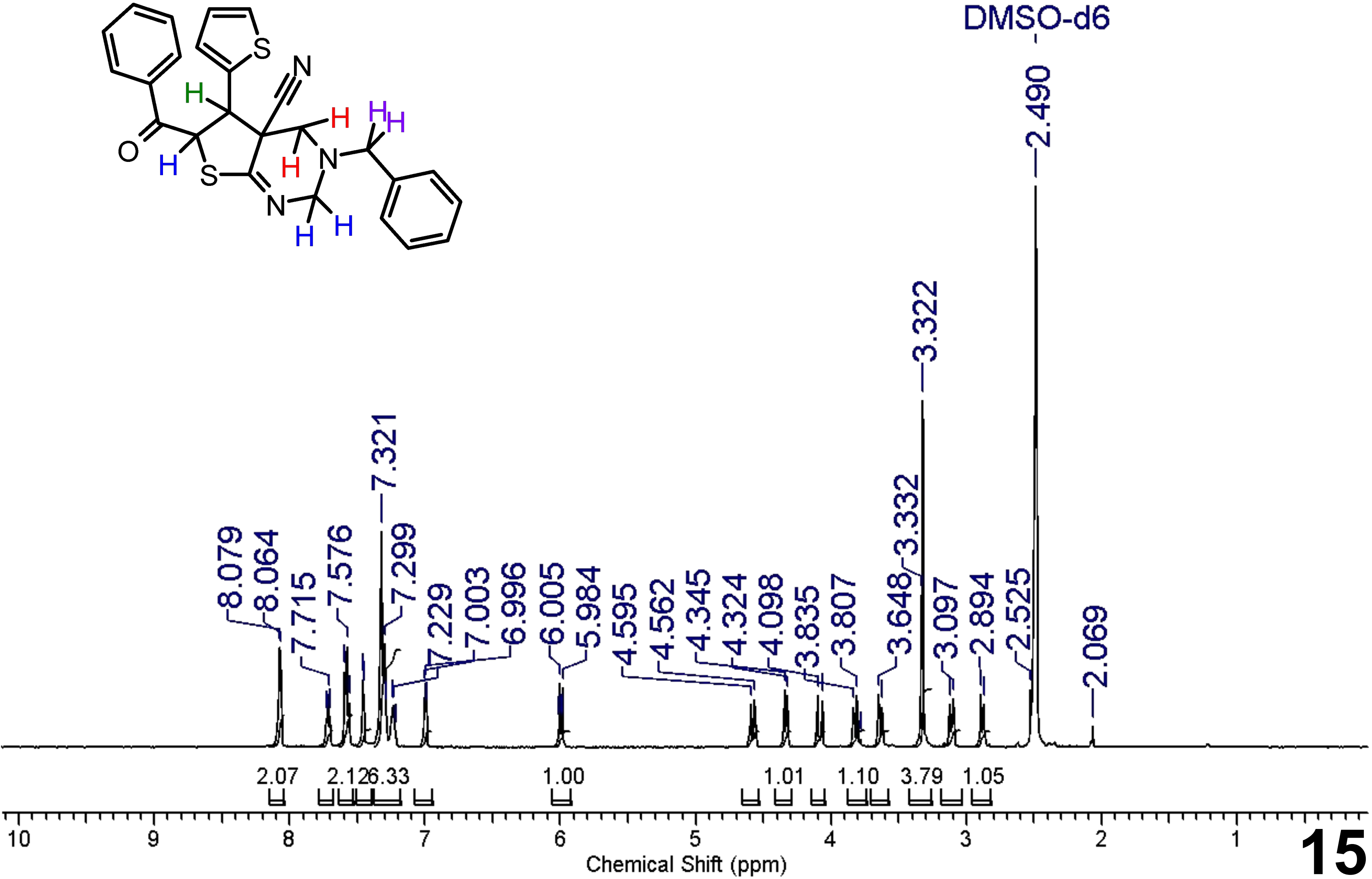
Enter a value for phi or ^3J and then click on the background:

phi: ° => ^3J: Hz

^3J: 12.09 Hz => phi: 166.8 °

Methods:

- DAD: Diez, Altona, Donders: with chemical groups
- HLA: Haasnoot, deLeeuw, Altona: with group electronegativity including the beta effect
- HLA: Haasnoot, deLeeuw, Altona: with chemical groups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7.003
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6.005
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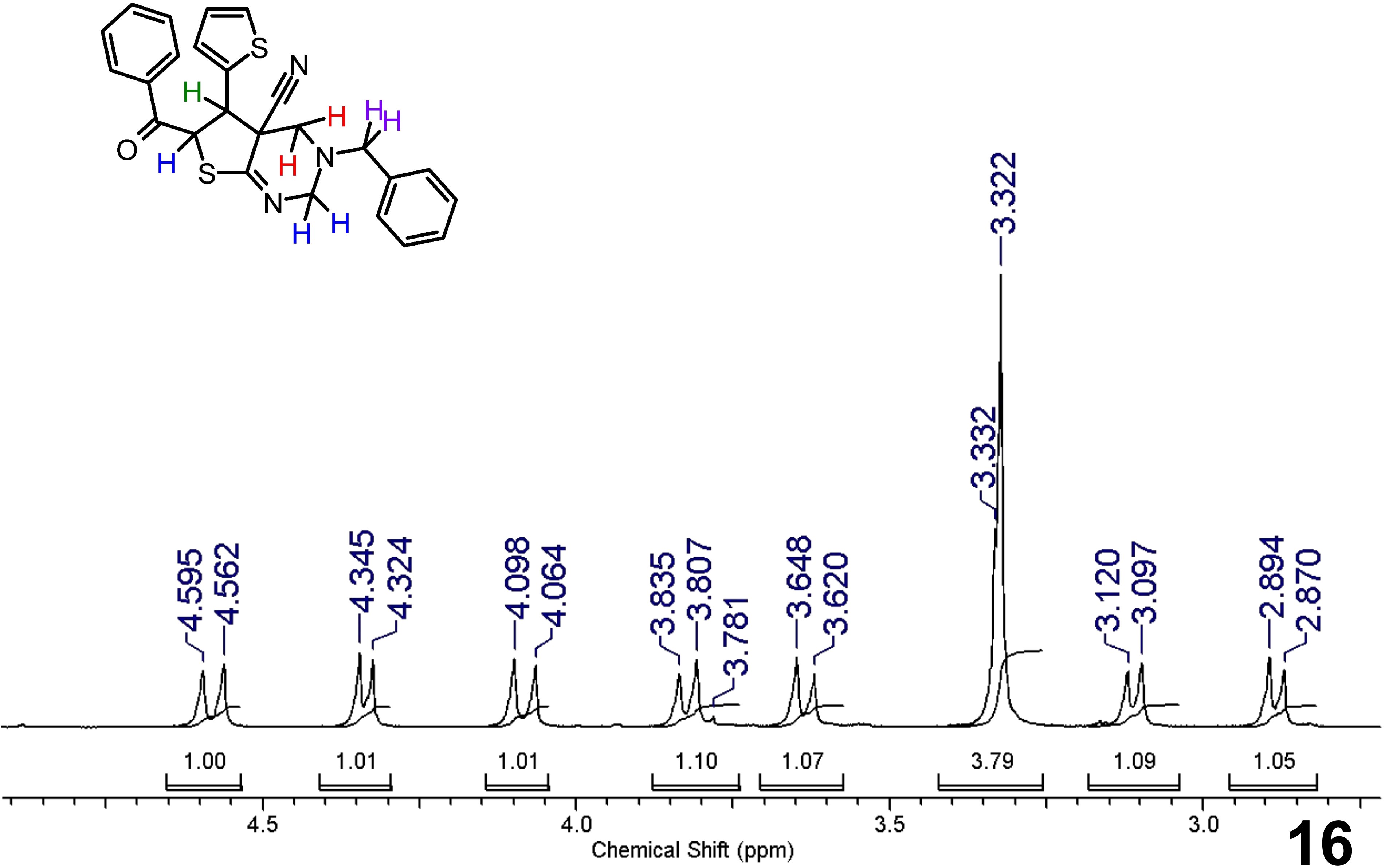
4.595
4.562
4.345
4.324
4.098
3.835
3.807
3.648
3.332
3.322
3.097
2.894
2.525
2.490
2.069
2.07
2.12
6.33
1.00
1.01
1.10
3.79
1.05
10
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)
O
S
S
N
N
N
H
H
H
H
H
H
H
H



O
S
S
N
N
N
H
H
H
H
H
H
H
H
4.595
4.562
4.345
4.324
4.098
4.064
3.835
3.807
3.781
3.648
3.620
3.332
3.322
3.120
3.097
2.894
2.870
1.00
1.01
1.01
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1.07
3.79
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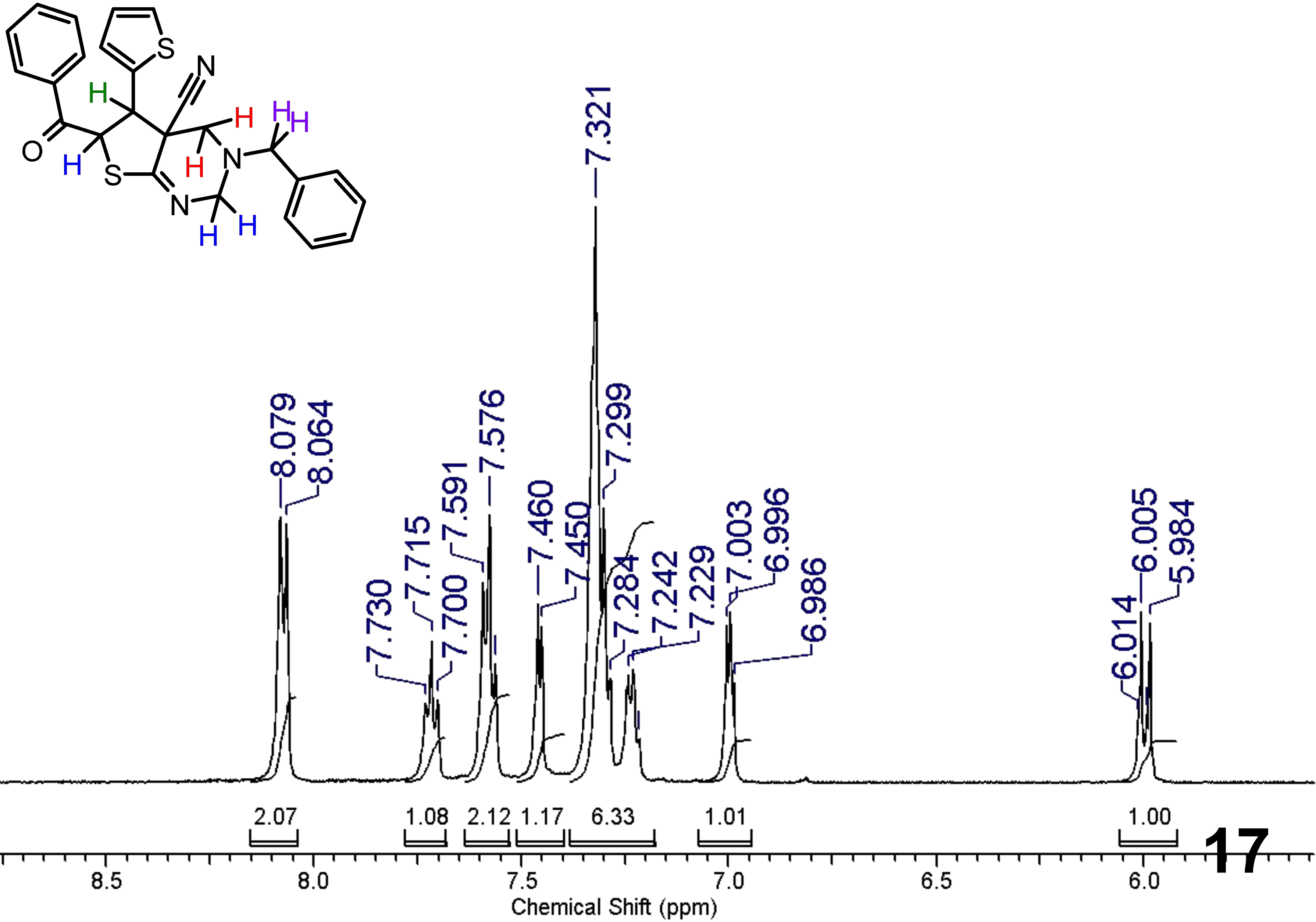
4.5
4.0
3.5
3.0
Chemical Shift (ppm)



O
S
N
H
8.079
8.064
7.730
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7.700
7.591
7.576
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7.299
7.284
7.242
7.229
7.003
6.996
6.986
6.014
6.005
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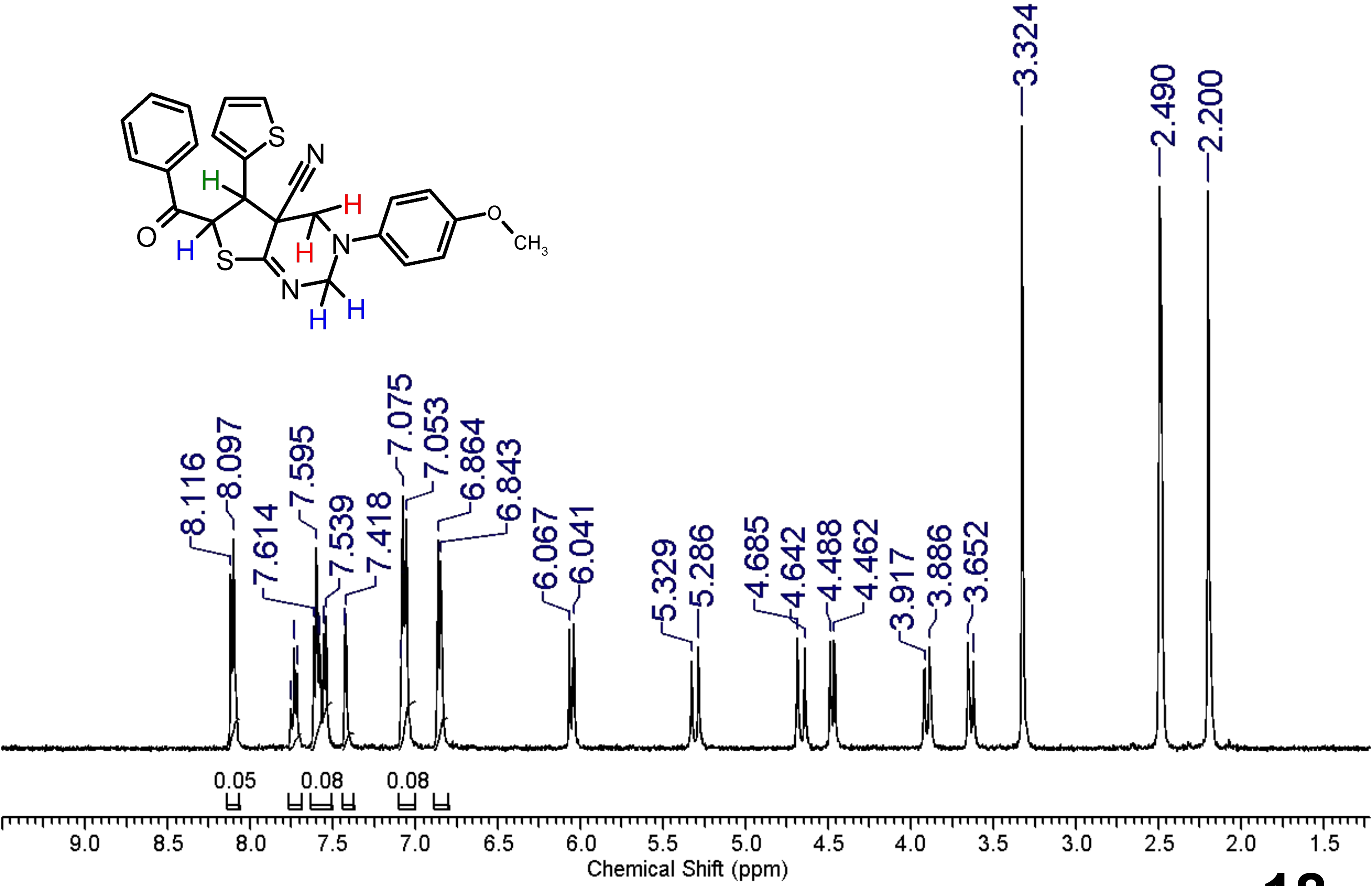
Chemical Shift (ppm)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H
H
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H
H
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7.418
7.075
7.053
6.864
6.843
6.067
6.041
5.329
5.286
4.685
4.642
4.488
4.462
3.917
3.886
3.652
3.324
2.490
2.200
0.05
0.08
0.08
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7.0
6.5
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3.5
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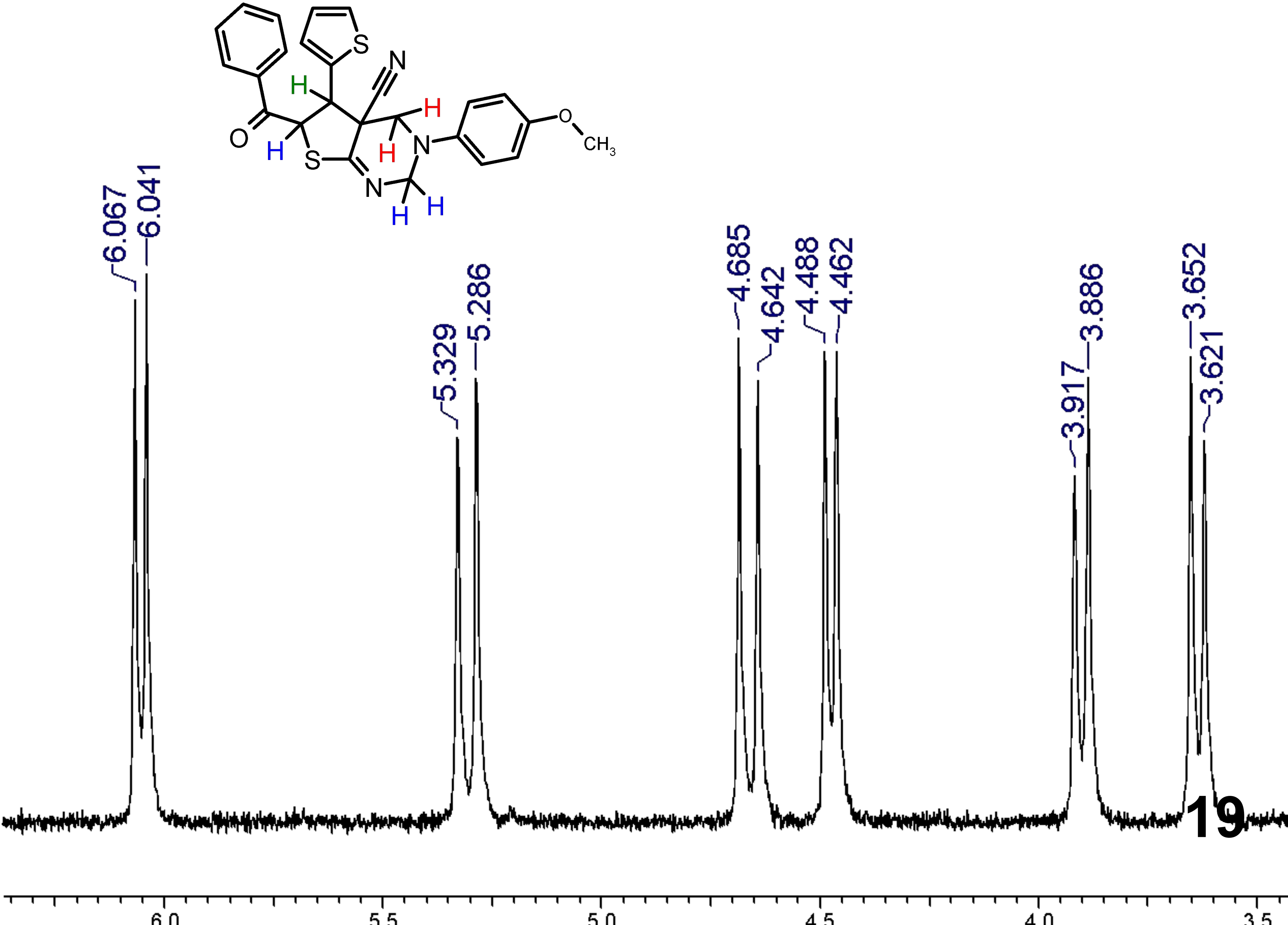
2.5
2.0
1.5
Chemical Shift (ppm)

18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4.488
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H
H
H
H
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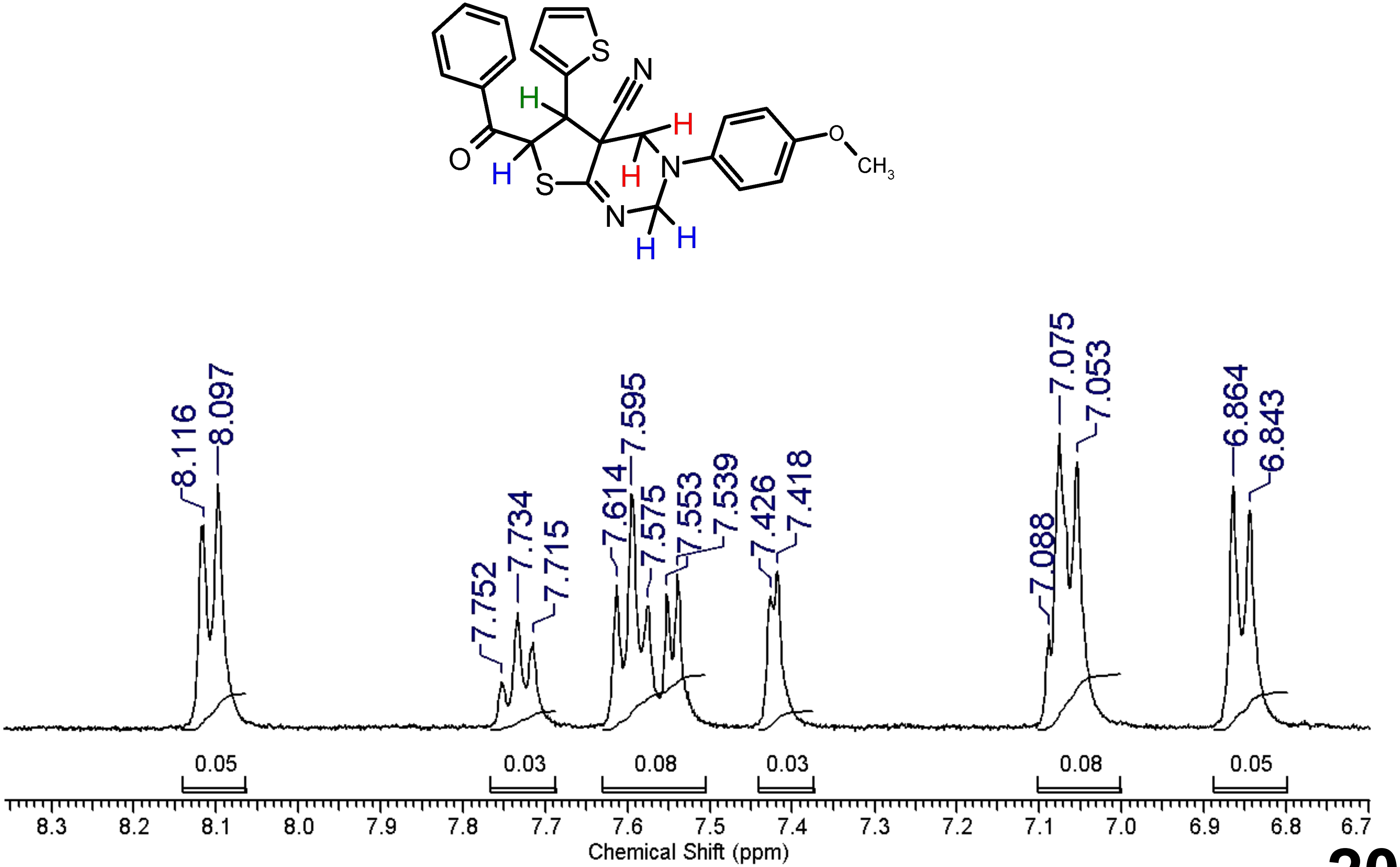
3.5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8.3
8.2
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8.0
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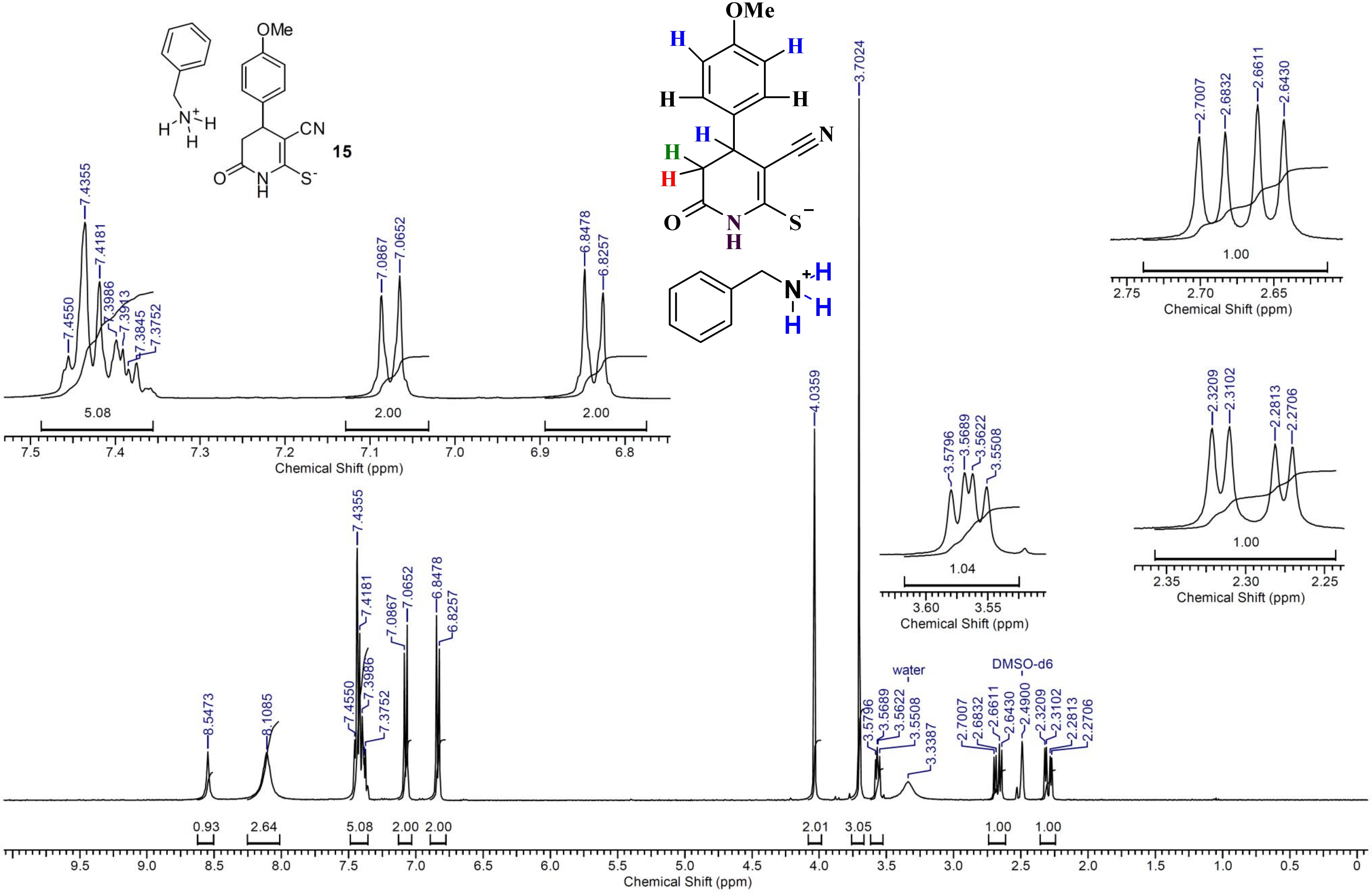
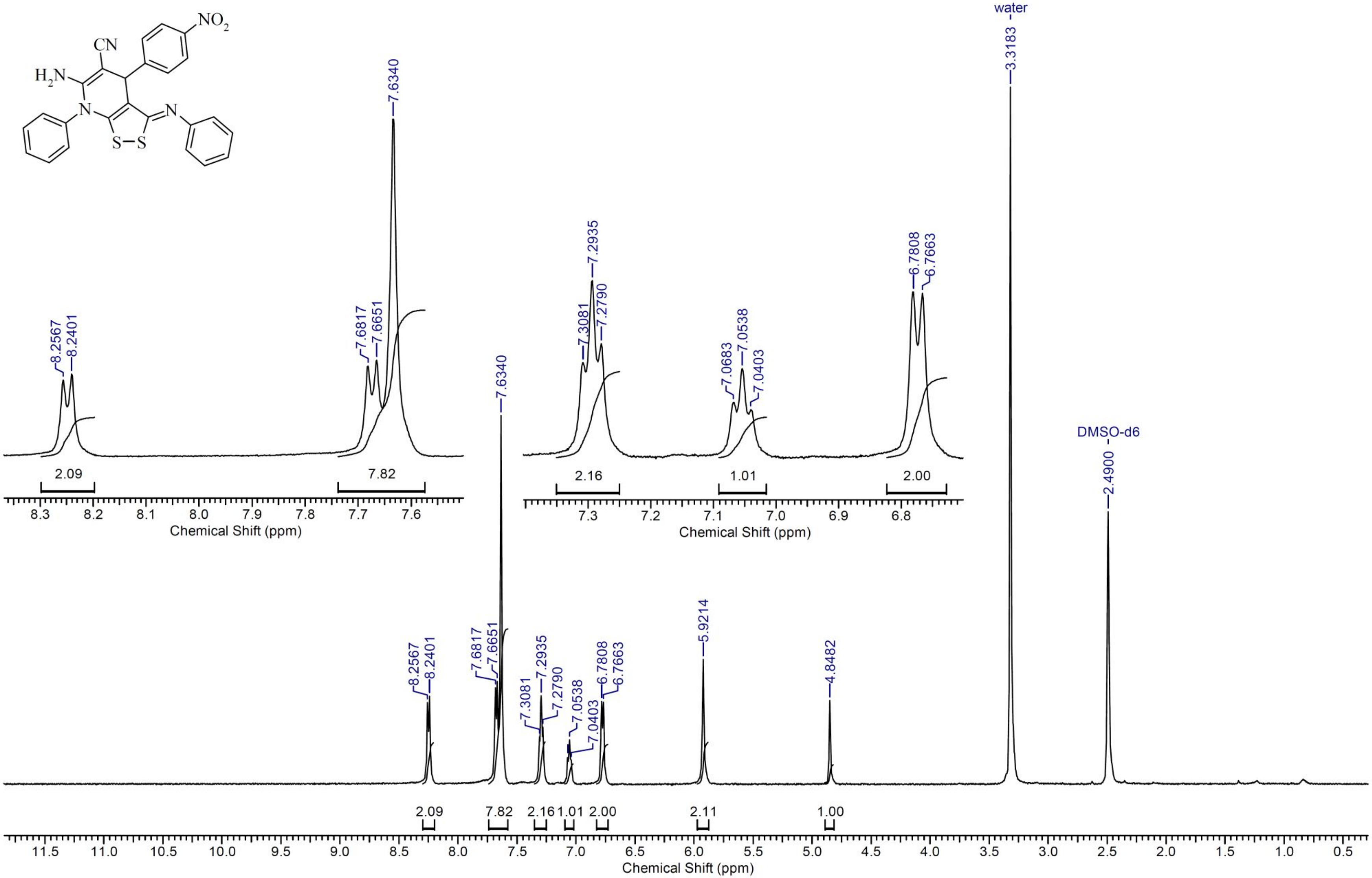
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
Chemical Shift (ppm)

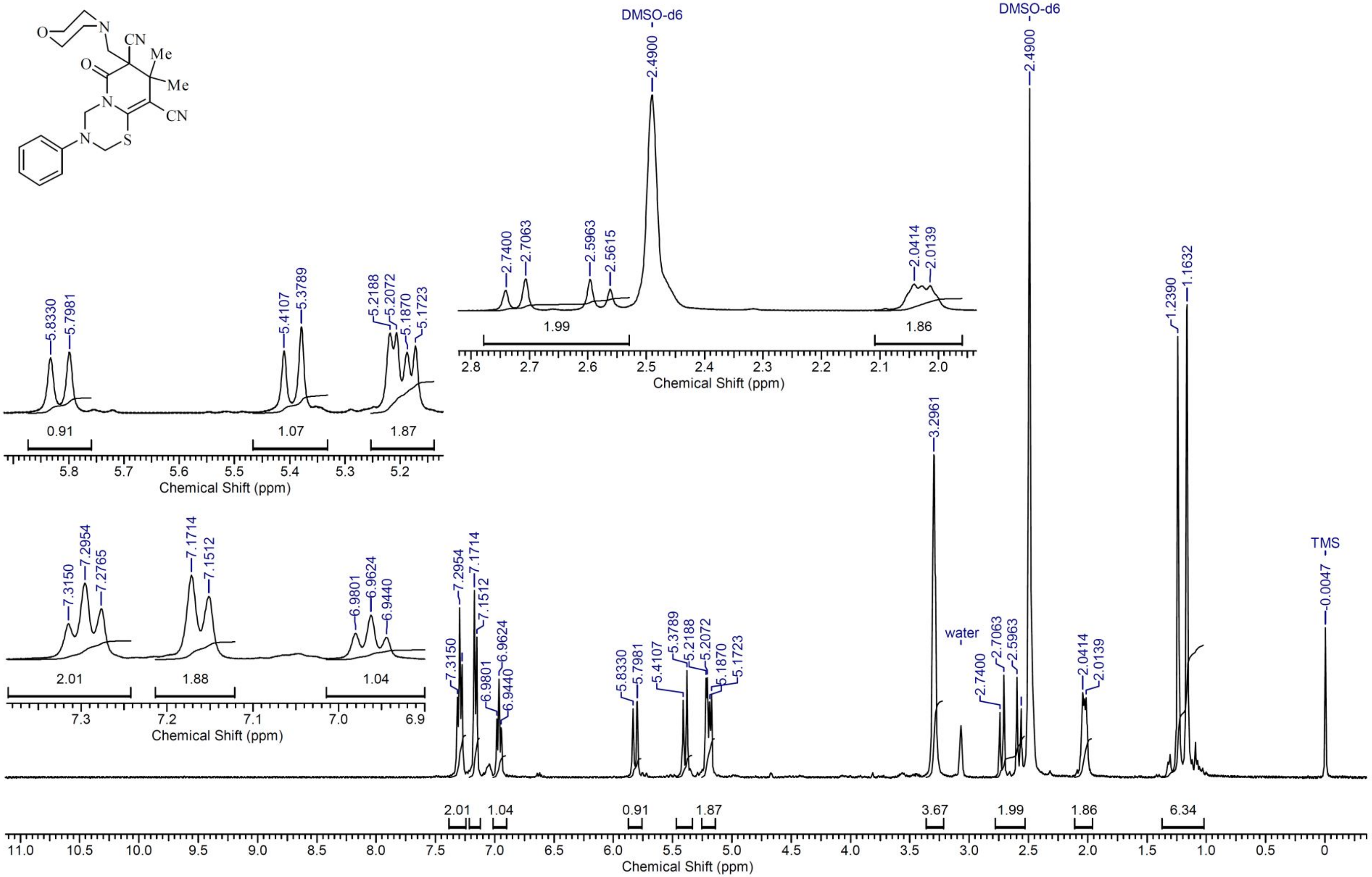
^{1}H NMR spectrum (400 MHz) of benzylammonium 3-cyano-4-(4-methoxyphenyl)-6-oxo-1,4,5,6-tetrahydropyridine-2-thiolate (**15**)



^{1}H NMR spectrum (500 MHz, DMSO-d_6) of 6-amino-4-(4-nitrophenyl)-7-phenyl-3-(phenylimino)-4,7-dihydro-3*H*-[1,2]dithiolo[b]pyridine-5-carbonitrile **4b**



^{1}H NMR spectrum (400 MHz, CCl_4–DMSO-*d*$_6$) of 8,8-dimethyl-7-(morpholin-4-ylmethyl)-6-oxo-3-phenyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrido[2,1-*b*][1,3,5]thiadiazin-7,9-dicarbonitrile (**5a**)



Thanks for your patience and attention

☺