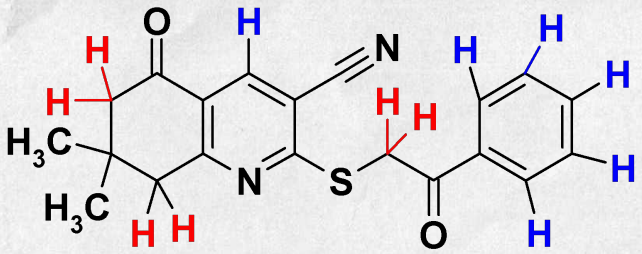
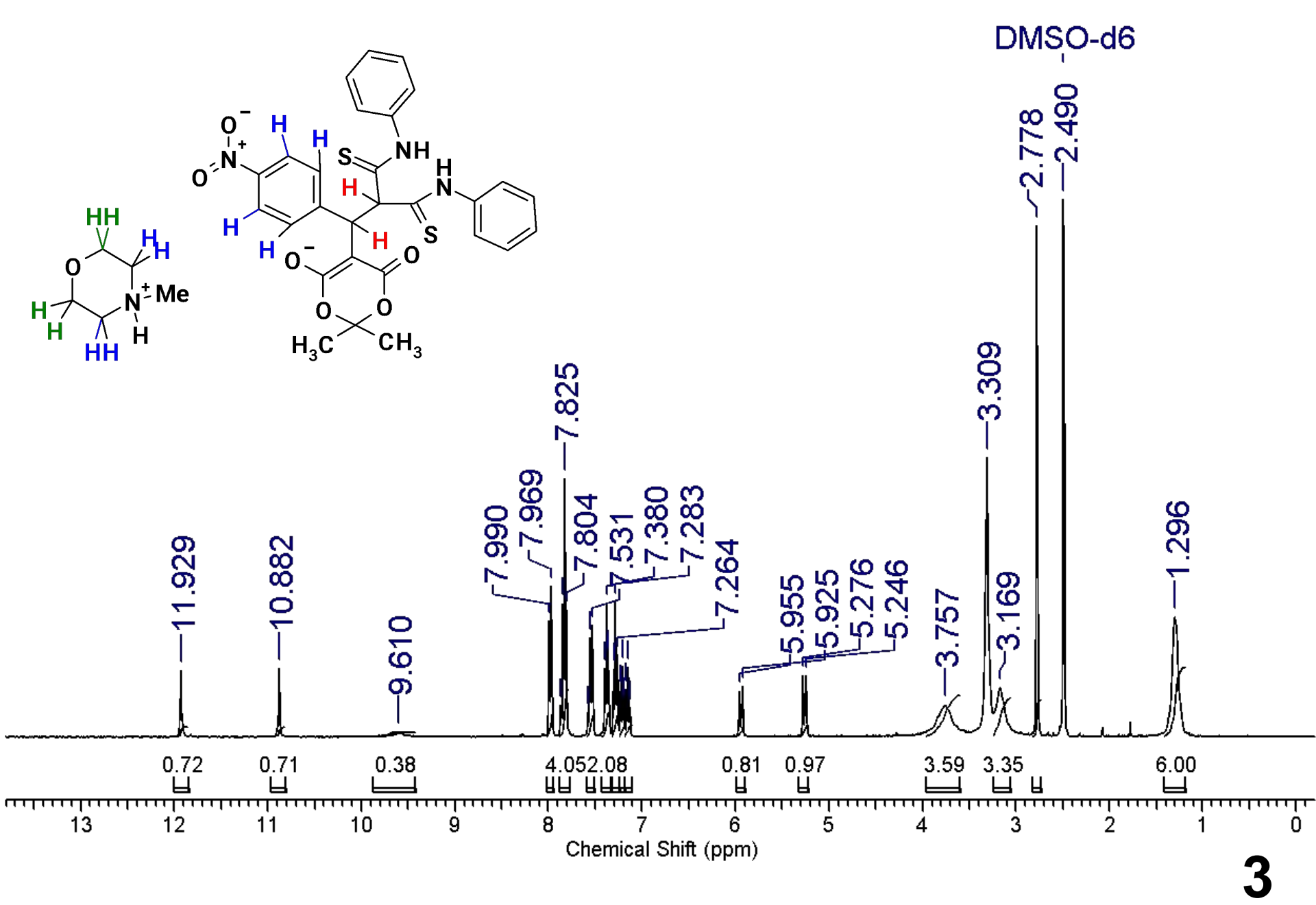
Радиоспектроскопические методы исследования 3

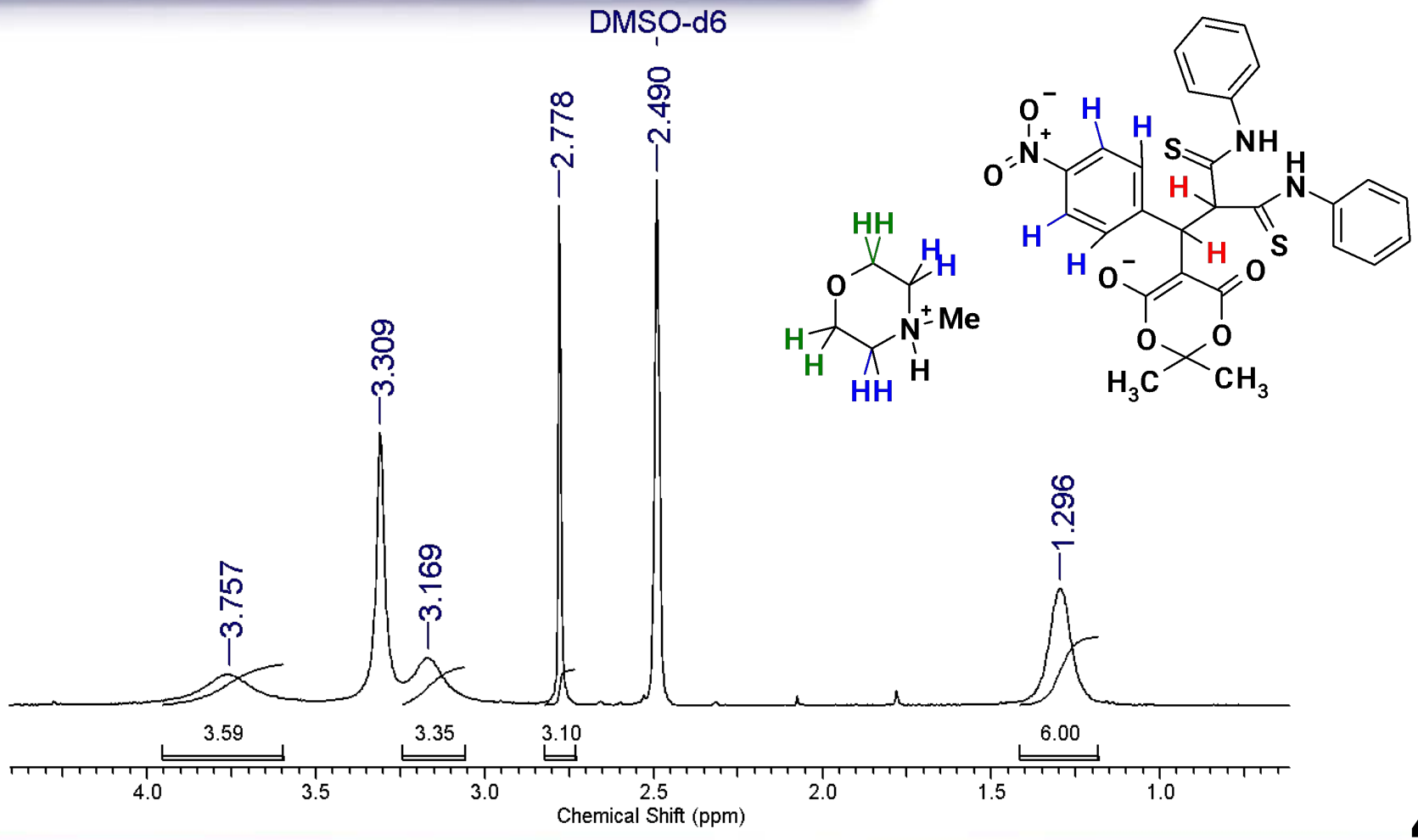


244XX (108)
EXP1 PULSE SEQUENCE: S2PUL
DATE 01-01-97
SOLVENT DMCO
FILE H9

OBSERVE PROTON
FREQUENCY 199.975 MHZ
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


DMSO-d6
11.929
10.882
9.610
7.990
7.969
7.825
7.804
7.531
7.380
7.283
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
3.35
6.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

3


DMSO-d6
2.778
2.490
3.309
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3.169
1.296
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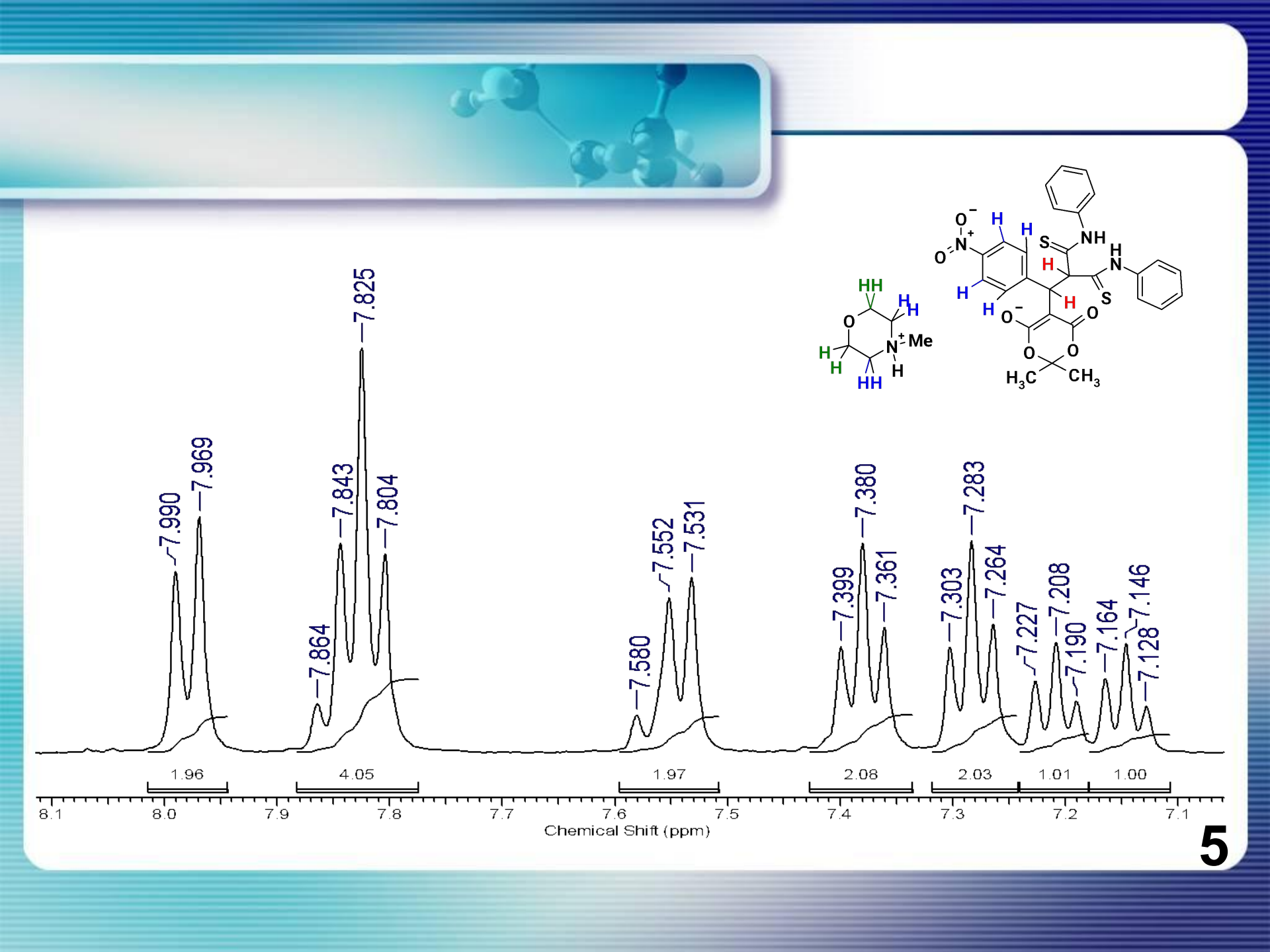
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


7.990
7.969
7.864
7.843
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7.804
7.580
7.552
7.531
7.399
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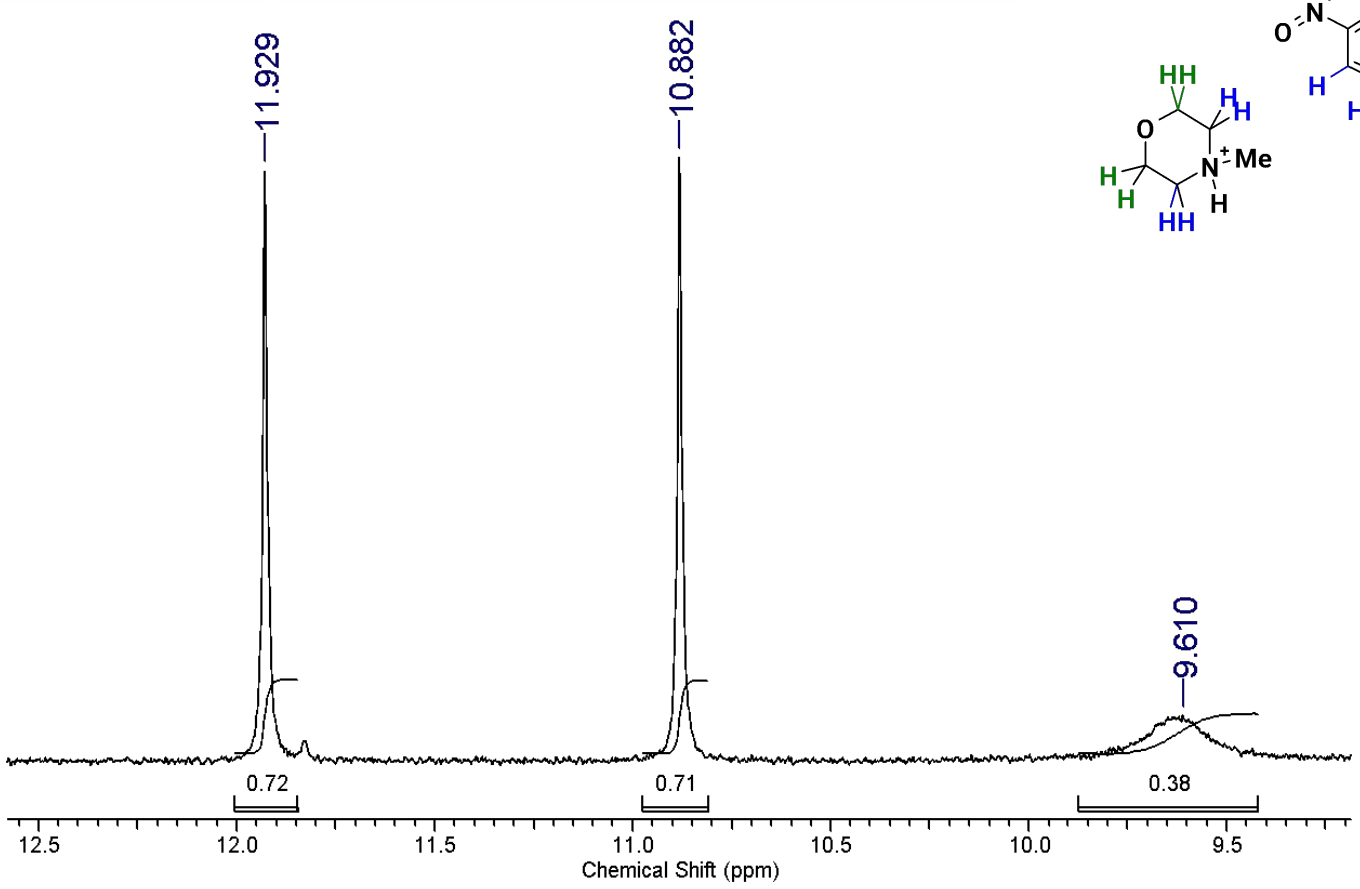
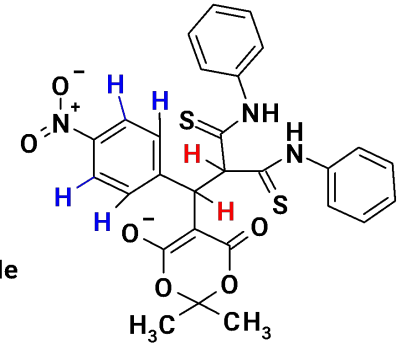
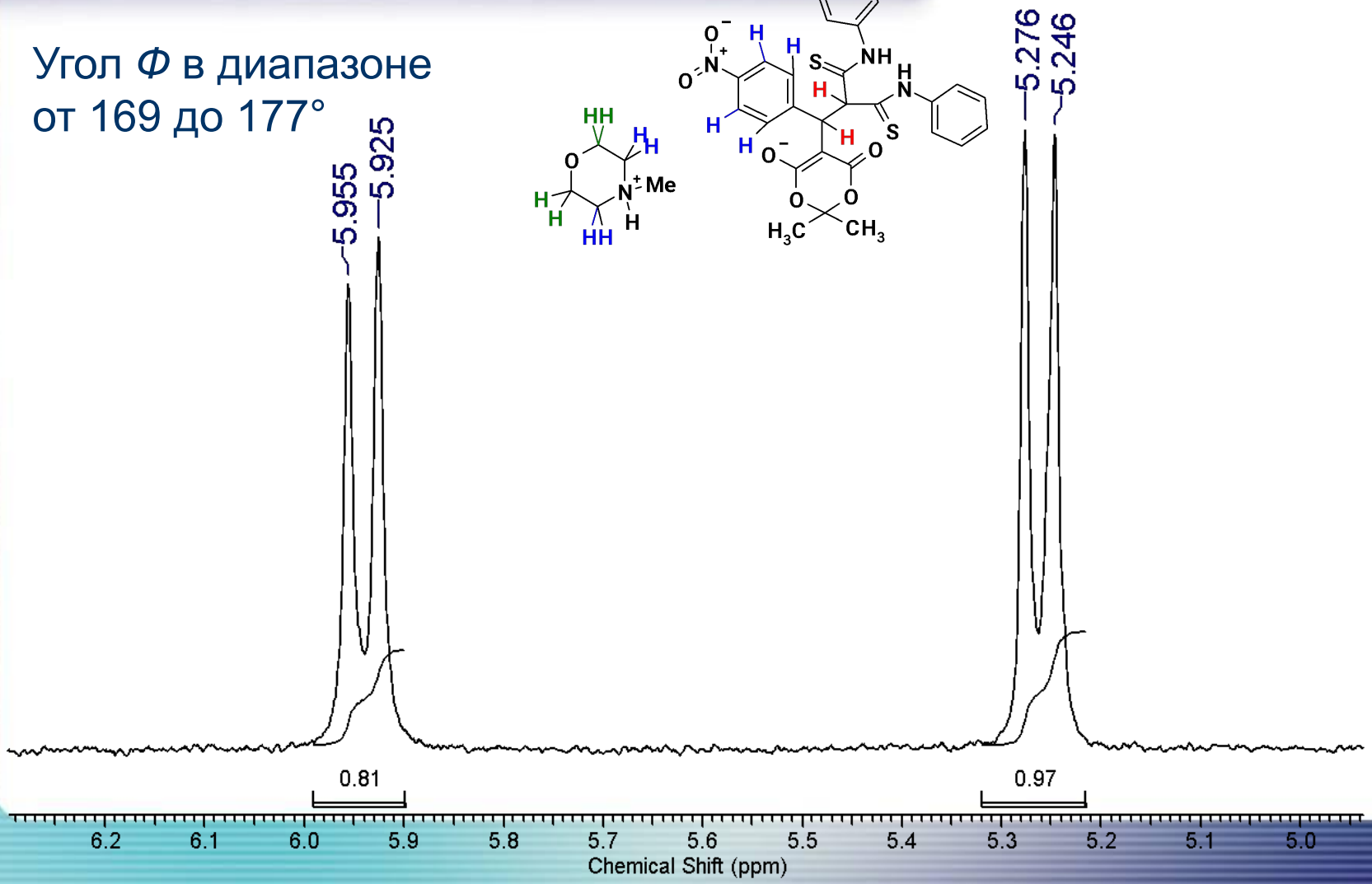
7.303
7.283
7.264
7.227
7.208
7.190
7.164
7.146
7.128
1.96
4.05
1.97
2.08
2.03
1.01
1.00
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)


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

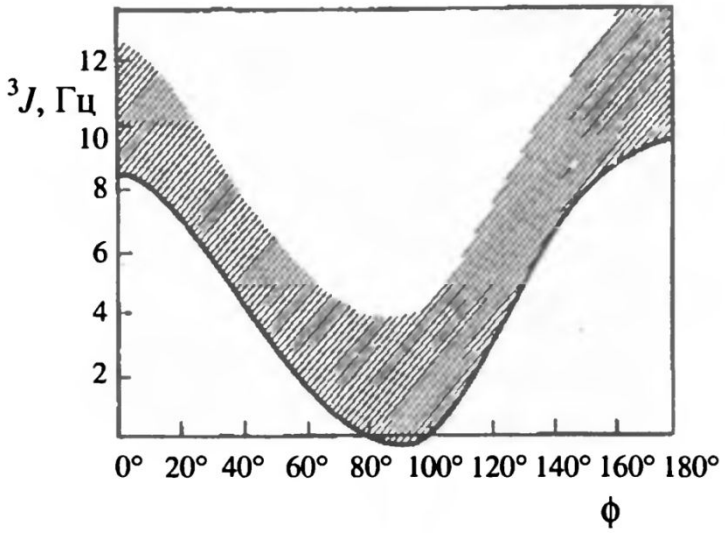

O
N
O
H
H
S
NH
H
N
H
H
H
S
H
O
O
O
O
H3C
CH3

Угол *Ф* в диапазоне
от 169 до 177°

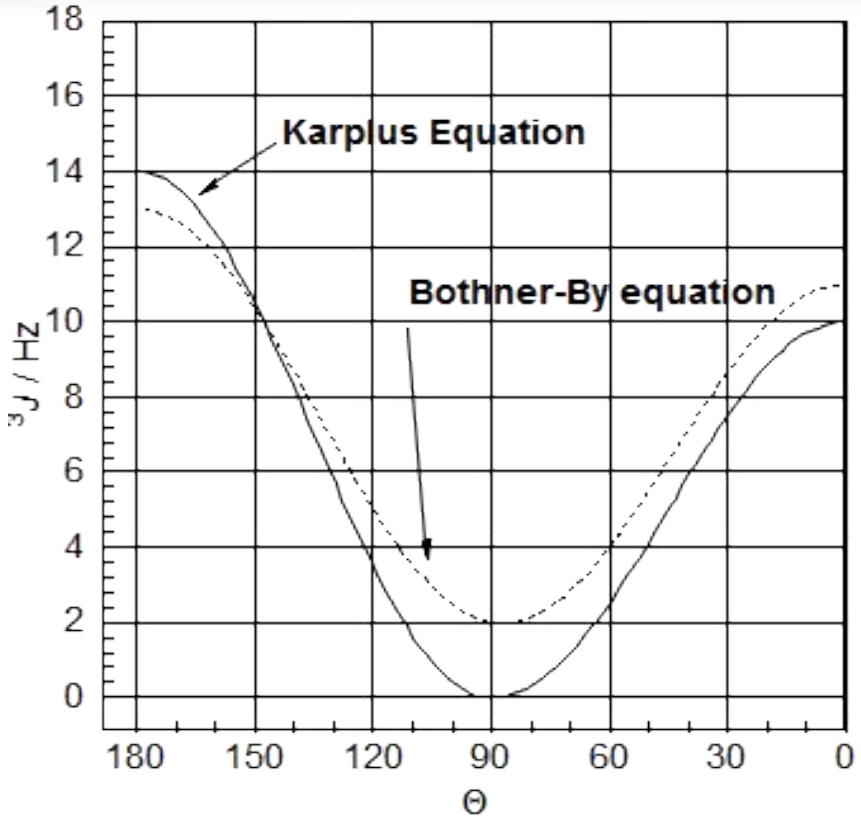


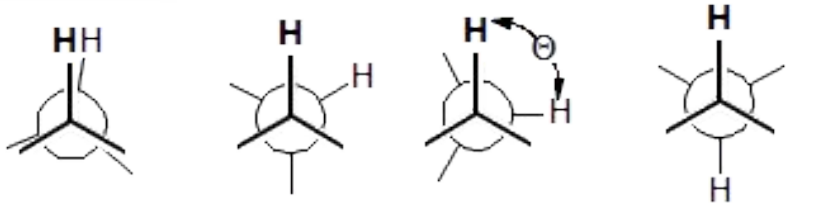
Уравнение Карплуса-Конроя

$$^3J = A + B\cos\varphi + C\cos 2\varphi.$$



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:

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

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 ^{3}J vinyl and ^{4}J 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.

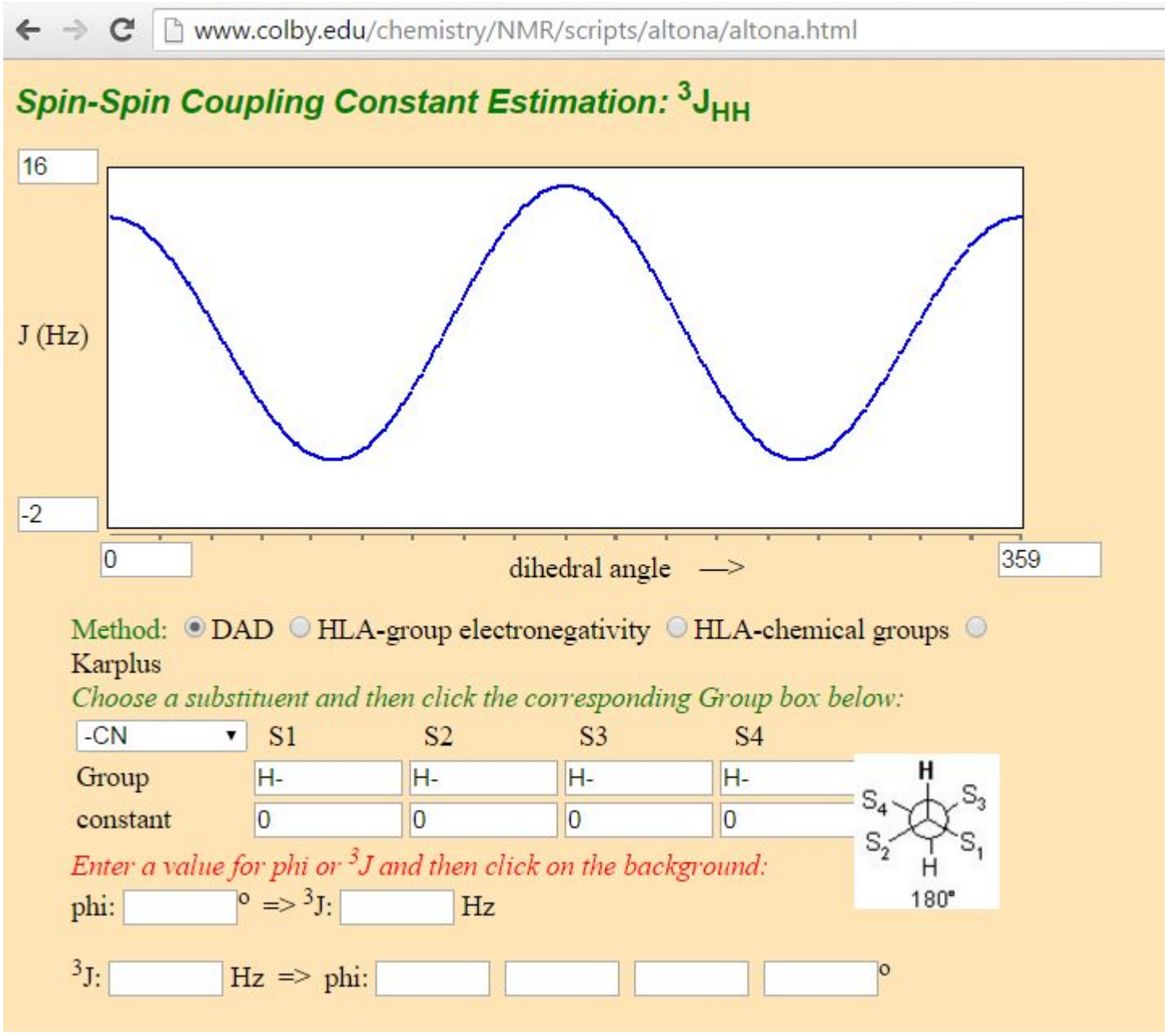
$^{3}J = 6.6 \cos^{2}(\text{phi}) + 2.6 \sin^{2}(\text{phi})$ $(0^{o} <= \text{phi} <= 90^{o})$

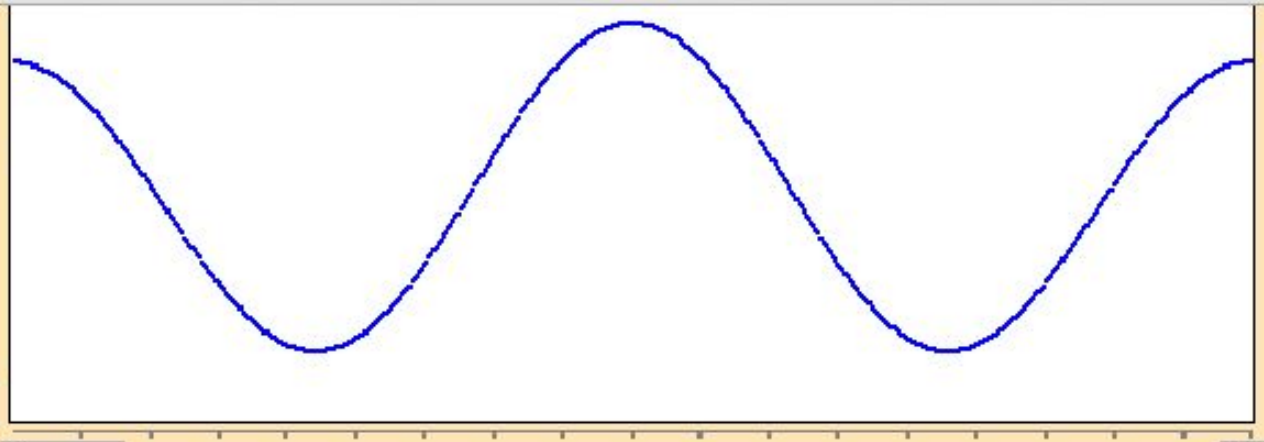
$^{3}J = 11.6 \cos^{2}(\text{phi}) + 2.6 \sin^{2}(\text{phi})$ $(90^{o} <= \text{phi} <= 180^{o})$

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

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

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

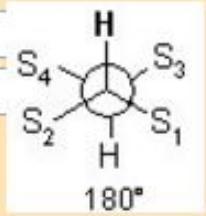




Method: DAD HLA-group electronegativity HLA-chemical groups Karplus

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:

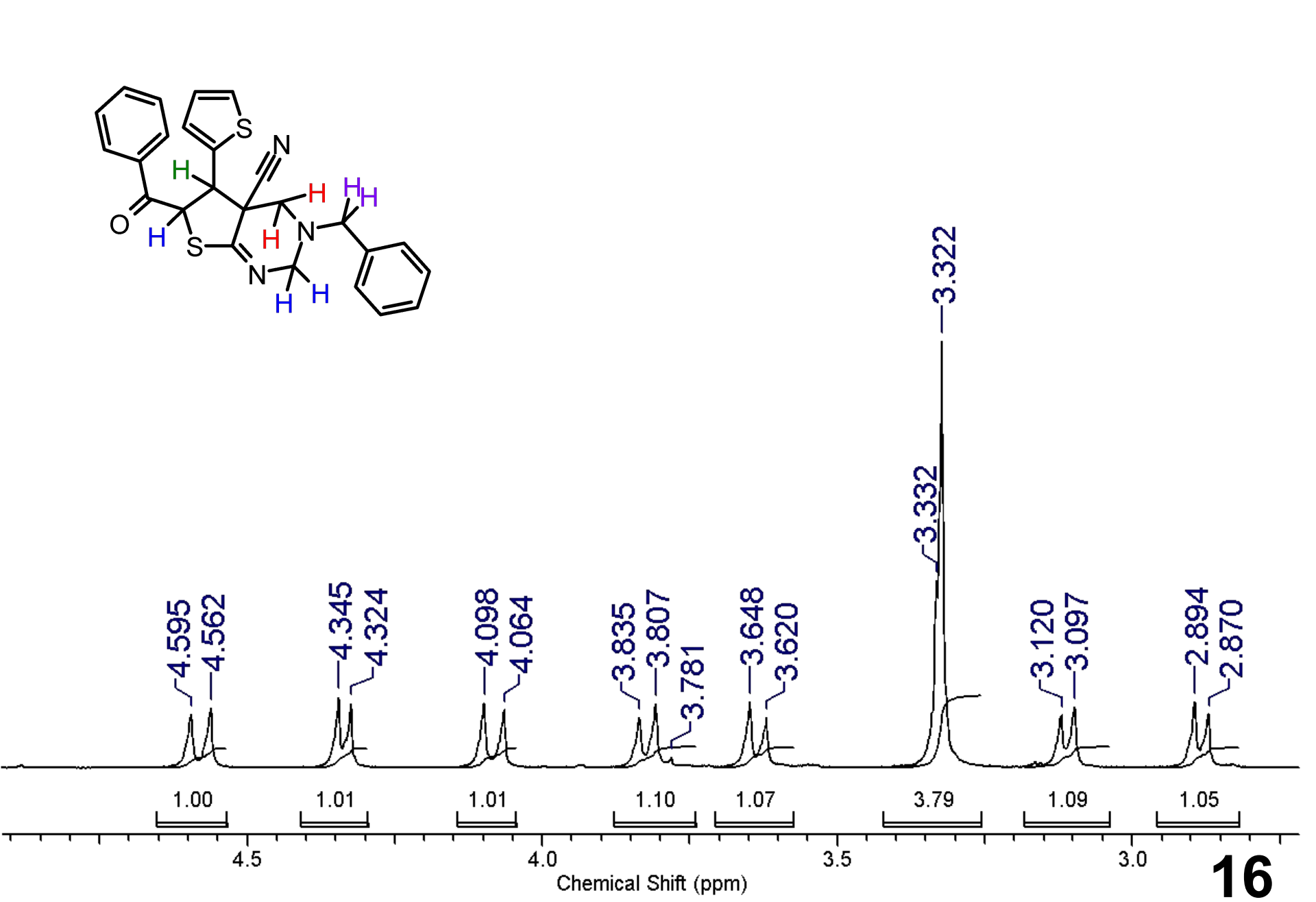
phi: ° => ^3J: Hz

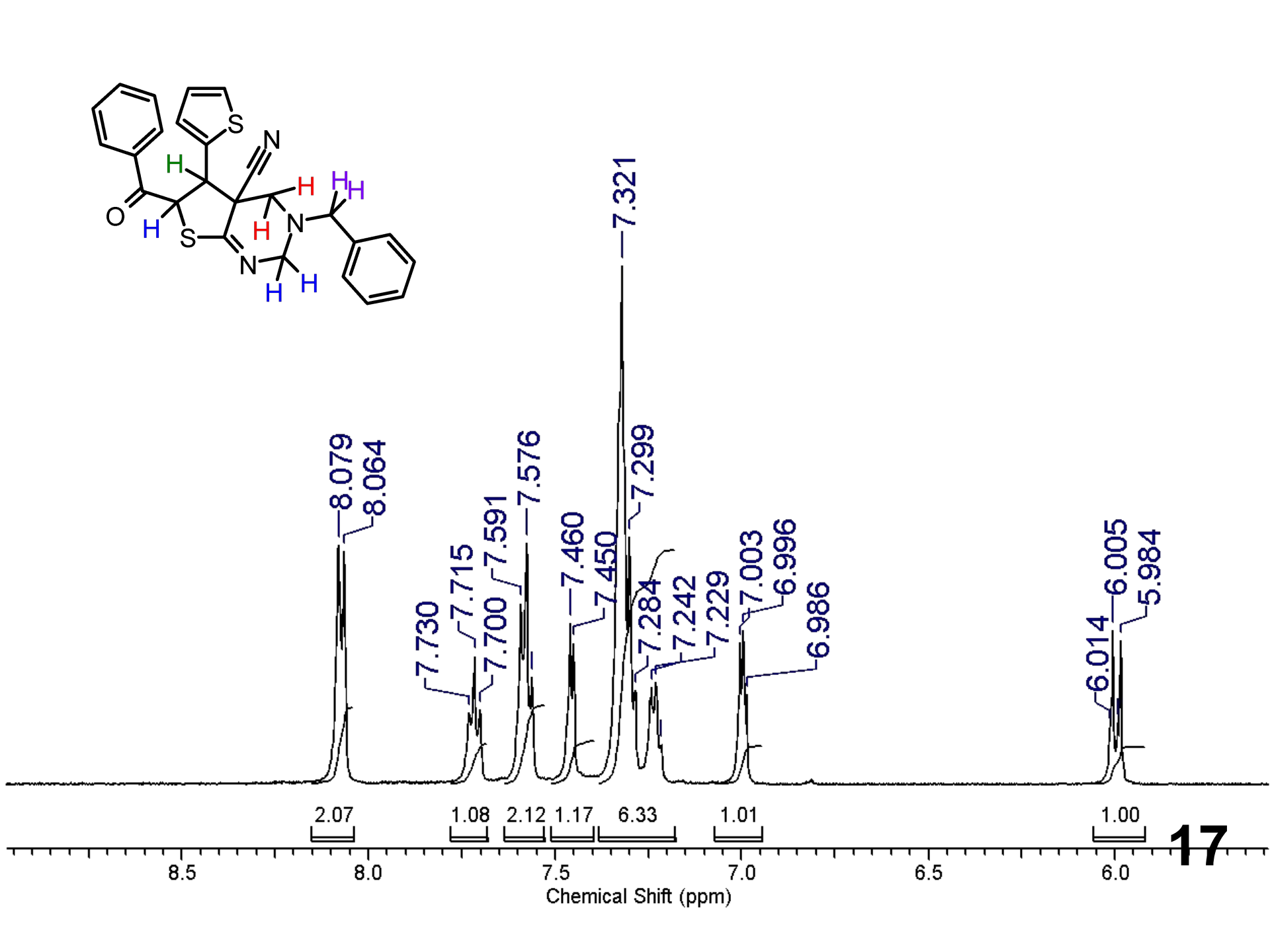
^3J: 12.09 Hz => phi: 166.8 °

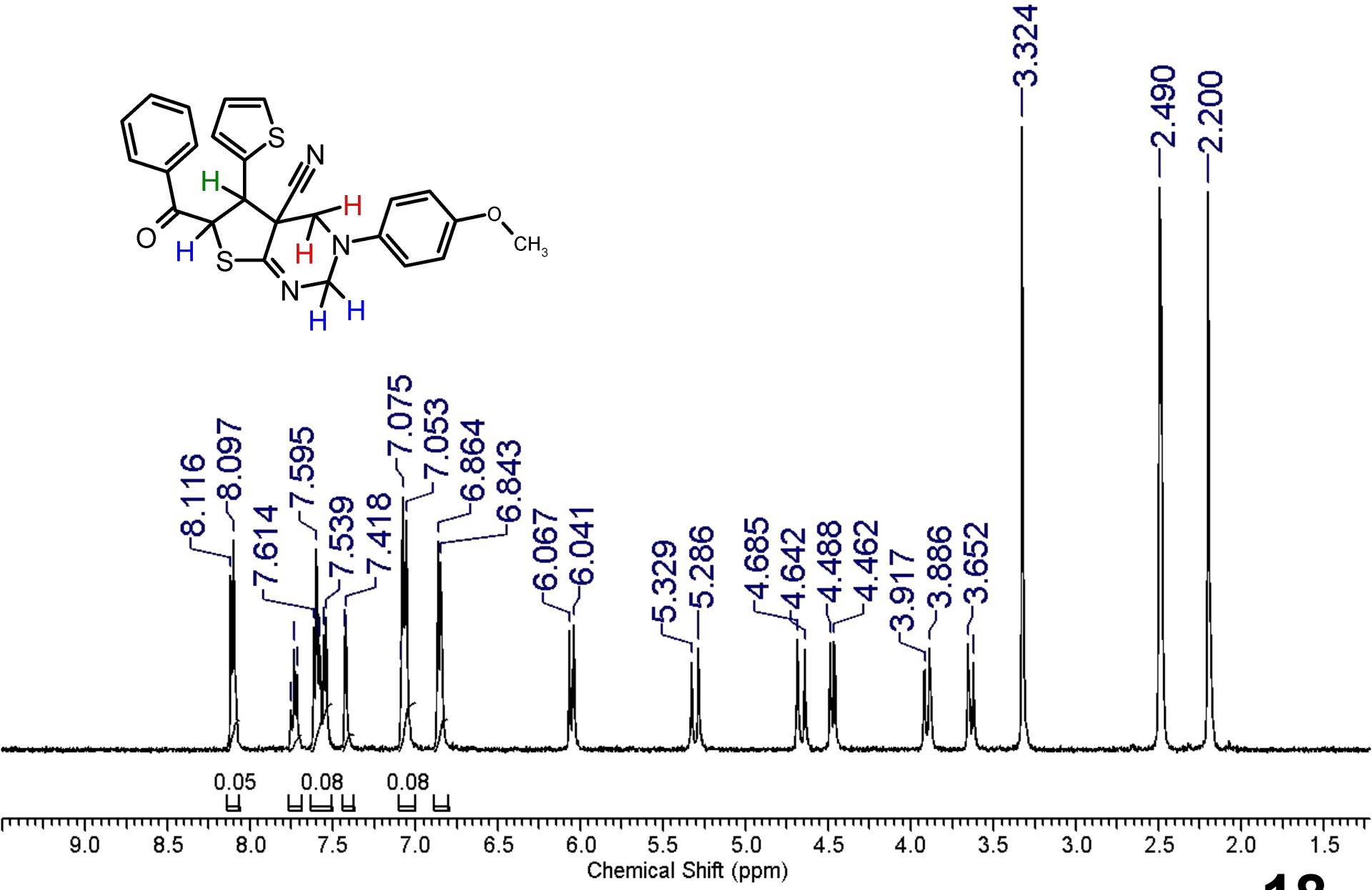
Methods:

- 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

DMSO-d6
8.079
8.064
7.715
7.576
7.321
7.299
7.229
7.003
6.996
6.005
5.984
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)


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
1.10
1.07
3.79
1.09
1.05
4.5
4.0
3.5
3.0
Chemical Shift (ppm)


8.079
8.064
7.730
7.715
7.700
7.591
7.576
7.460
7.450
7.321
7.299
7.284
7.242
7.229
7.003
6.996
6.986
6.014
6.005
5.984
2.07
1.08
2.12
1.17
6.33
1.01
1.00
8.5
8.0
7.5
7.0
6.5
6.0
Chemical Shift (ppm)
17


8.116
8.097
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6.067
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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
9.0
8.5
8.0
7.5
7.0
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4.0
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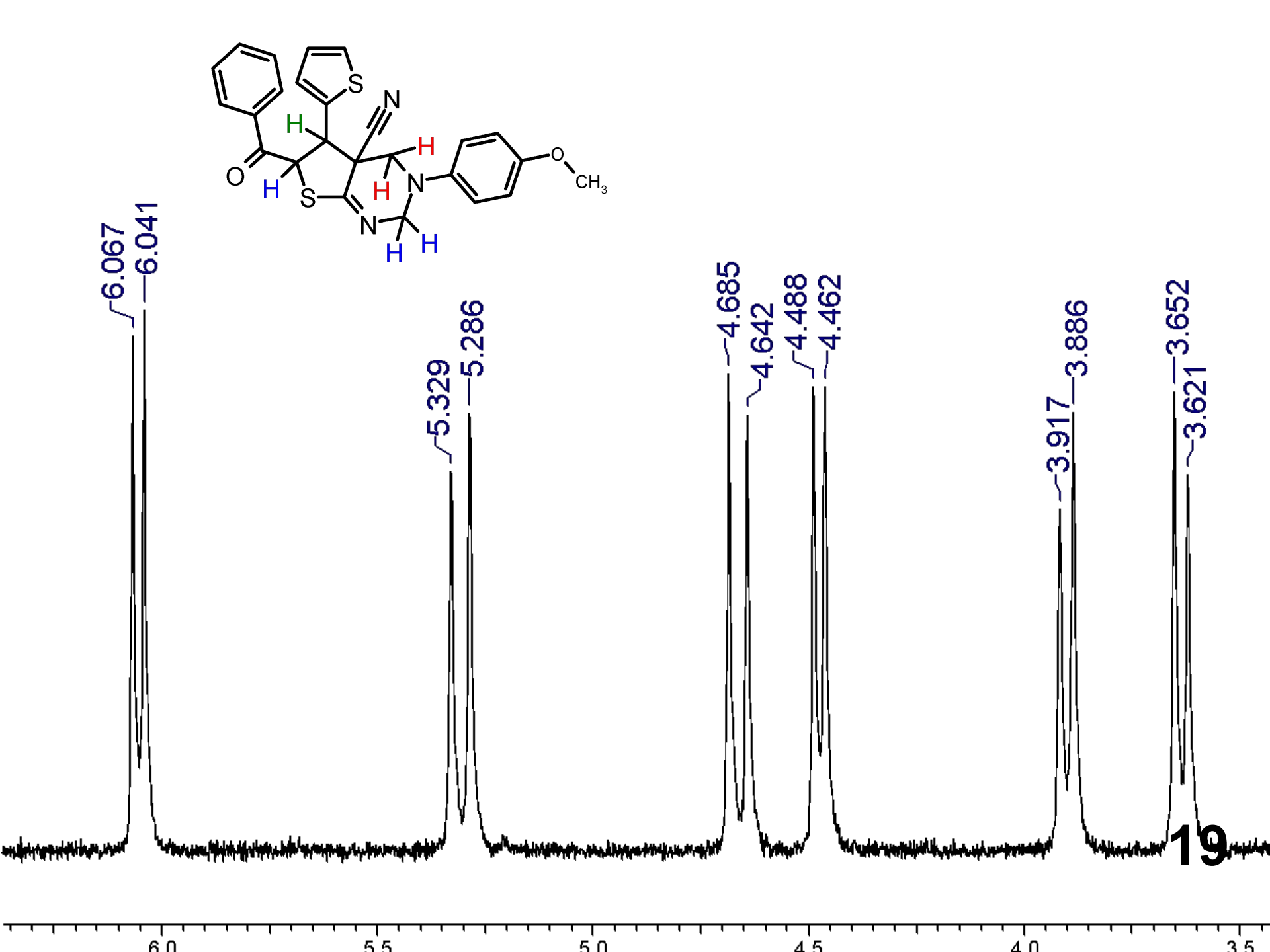
1.5
Chemical Shift (ppm)


6.067
6.041
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5.286
4.685
4.642
4.488
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19
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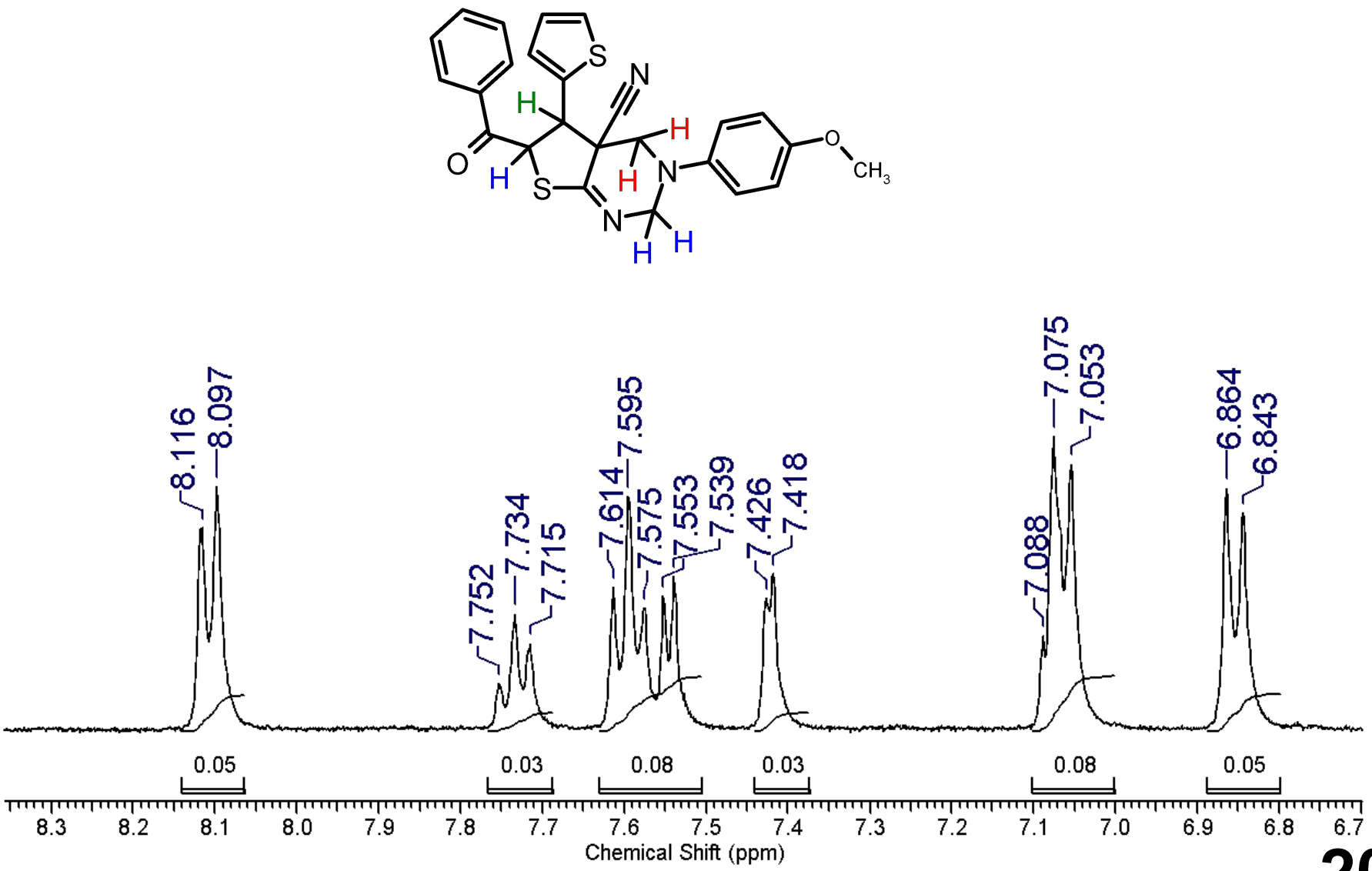
5.5
5.0
4.5
4.0
3.5


8.116
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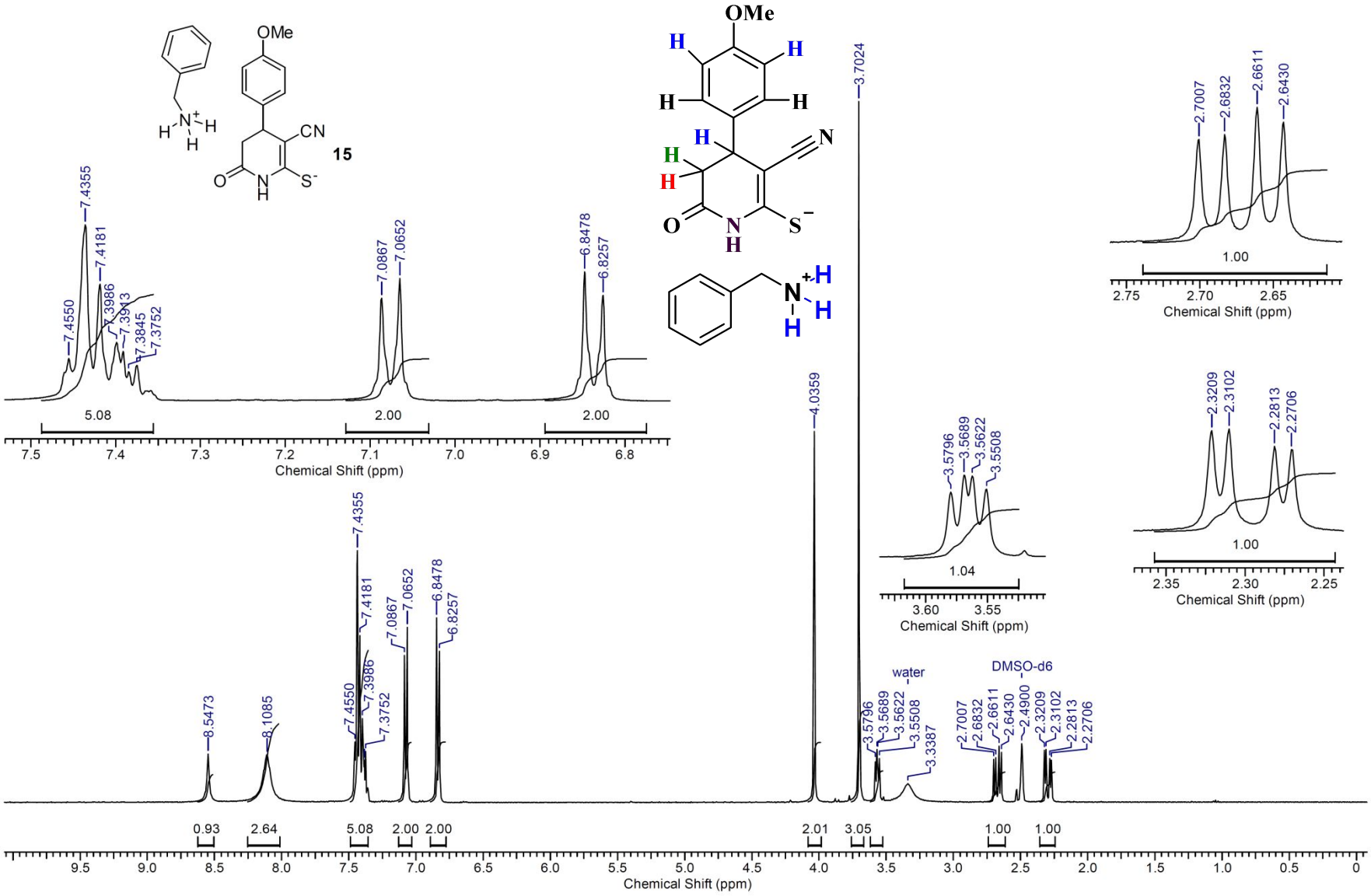
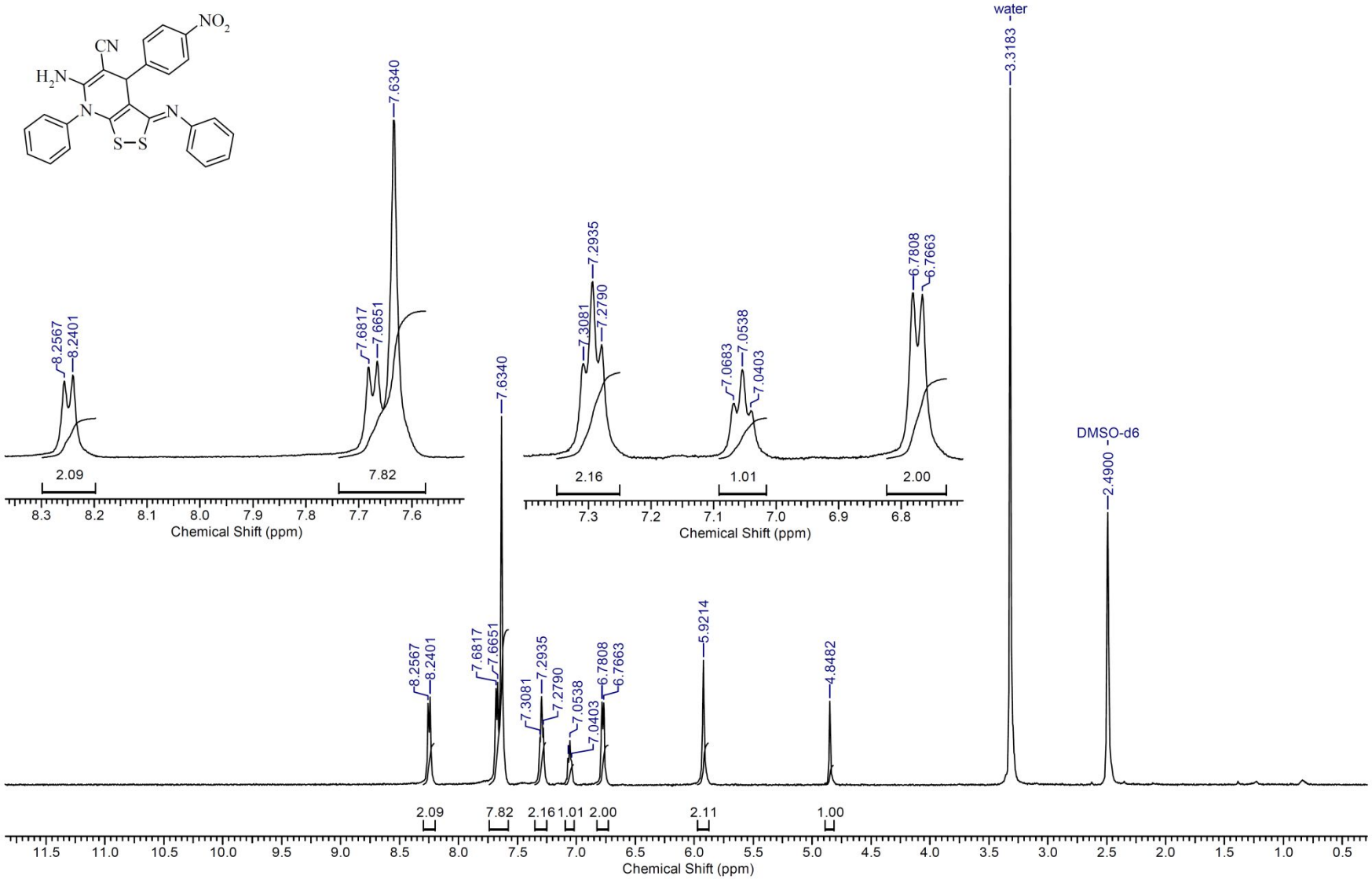
7.088
7.075
7.053
6.864
6.843
0.05
0.03
0.08
0.03
0.08
0.05
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
Chemical Shift (ppm)

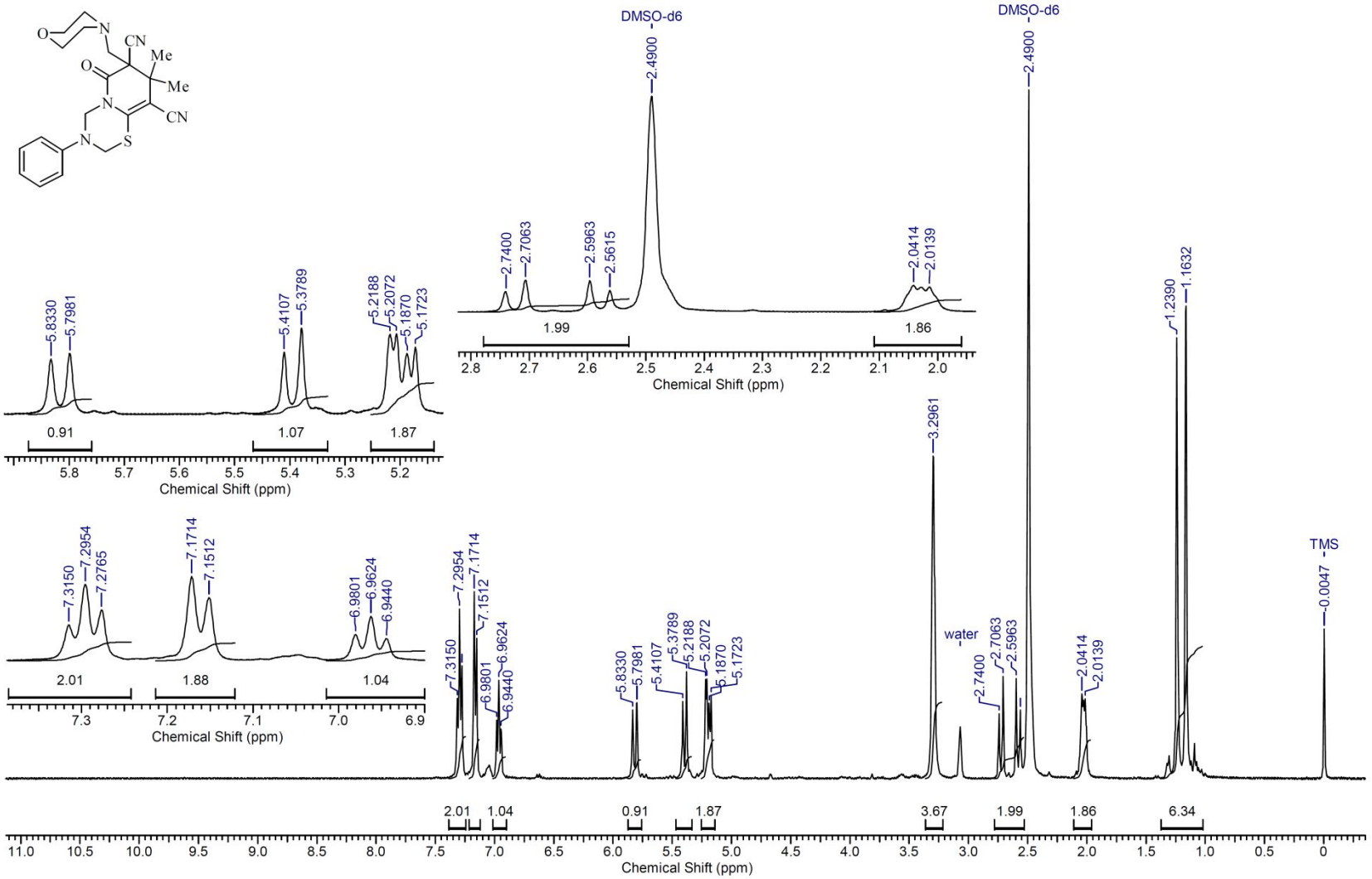
^{1}H NMR spectrum (400 MHz) of benzylammonium 3-cyano-4-(4-methoxyphenyl)-6-oxo-1,4,5,6-tetrahydropyridine-2-thiolate (**15**)



^{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
☺