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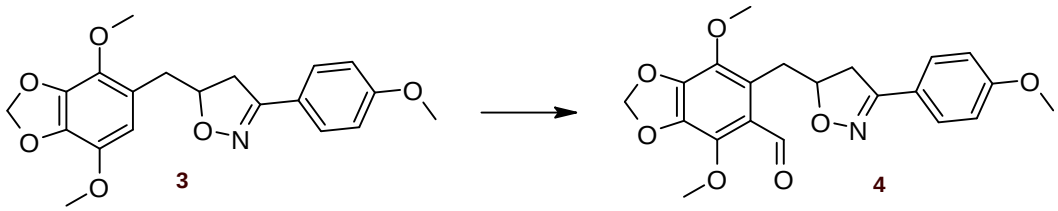
Baeyer–Villiger rearrangement of polyalkoxybenzaldehydes with benzene ring opening

Dmitry V. Tsyganov, Aida I. Samigullina and Victor V. Semenov

Table of content:

Chemistry. Materials and methods. Melting points were measured using a Boetius melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 instrument [working frequencies of 500.13 MHz (^{1}H) and of 125.76 MHz (^{13}C), respectively]. Chemical shift values were reported in parts per million (ppm) and referenced to the appropriate NMR solvent peaks. Spin–spin coupling constants (*J*) were reported in Hertz (Hz). NMR spectra were prepared using original software designed at N. D. Zelinsky Institute of Organic Chemistry RAS (Moscow, Russian Federation). Low resolution mass spectra (*m*/*z*) were recorded on a Finnigan MAT/INCOS 50 mass spectrometer at 70 eV using direct probe injection. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). Elemental analysis was performed on the automated Perkin-Elmer 2400 CHN microanalyzer. Thin layer chromatography (TLC) analysis was performed using Merck 60 F_{254} plates. Flash chromatography was accomplished using Silica (Acros, 0.035– 0.070 mm, 60 Å). Solvents and reagents were purified by standard procedures.

Synthesis *of 6-[(3-(4-methoxyphenyl)-4,5-dihydro-1,2-oxazol-5-yl)methyl]-2H-4,7-dimethoxy-1,3-benzodioxole-5-carbaldehyde* **(4)**

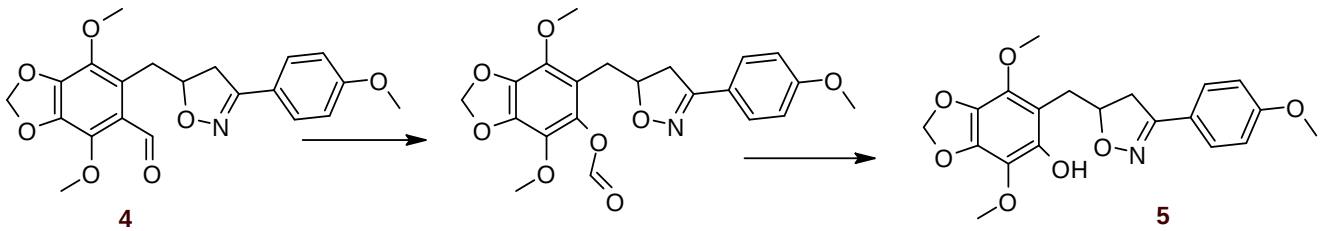


1. Preparation of the formylation mixture: Ethyl formate as a single portion (11.0 g, 148 mmol) was added to a suspension of PCl_5 (26.7 g, 128 mmol) in dry CH_2Cl_2 (40 mL) and refluxed for 4 h ($CaCl_2$ tube). A solution of dichloromethyl ethyl ether (128 mmol) was obtained.

2. A solution of *6-[(3-(4-methoxyphenyl)-4,5-dihydro-1,2-oxazol-5-yl)methyl]-2H-4,7-dimethoxy-1,3-benzodioxole* **3** [S1] (3.71 g, 10.0 mmol) and dichloromethyl ethyl ether (1.50 g, 13.0 mmol) and dry CH_2Cl_2 (20 mL) was added dropwise to a solution of $SnCl_4$ (9.1 g, 35 mmol) in dry CH_2Cl_2 (20 mL) with stirring at room temp. The reaction mixture was kept for 5 h at 20 °C and poured into water (100 mL). The organic layer was separated, washed with water (3 × 50 mL), and dried over $MgSO_4$. After removal of the solvent, product **4** was recrystallized from EtOH. White powder; 3.25 g (81 %); mp 119-121 °C (EtOH);

^{1}H NMR (DMSO-d_6) δ: 3.07 (dd, 1H, $ArCH_2$, J = 7.0, J = 10.0), 3.17 (dd, 1H, $ArCH_2$, J = 7.0, J = 10.0), 3.17 (dd, 1H,(H4), J = 7.0, J = 13.0) 3.33 (dd, 1H,(H4), J = 10.0, J = 16.0) 3.80 (s, 3H, OMe), 3.84 (s, 3H, OMe), 3.89 (s, 3H, OMe), 4.73 (m, 1H, H(5)), 6.20 (s, 2H, OCH_2O), 7.01 (d, 2H, Ar, J = 9.0), 7.60 (d, 2H, Ar, J = 9.0), 10.25 (s, 1H, CHO). EIMS m/z: 399 ($[M]^+$, 100%), 223 (44), 209(43), 176(52), 121(46), 92(31), 77(51), 64(23), 52(18). Calc for $C_{21}H_{21}NO_7$ C, 63.15; H, 5.30; N, 3.51 Found C63.21; H, 5.39; N, 3.57.

4,7-Dimethoxy-6-[(3-(4-methoxyphenyl)-4,5-dihydro-1,2-oxazol-5-yl)methyl]-2H-1,3-benzodioxol-5-ol **(5)**



1. To a suspension of aldehyde **4** (3.0 g, 7.51 mmol) and SeO_2 (25 mg, 0.23 mmol) in *tert*-butanol (30 ml), H_2O_2 (35%, 1.3 ml, 15.03 mmol) was added dropwise at 50 °C, stirred at 55-60 °C for 3 hours and left overnight. The resulting orange solution with an oily precipitate was treated at 20 °C with a solution of Na_2SO_3 (1.0 g) in water (10 ml), *tert*-butanol was evaporated, the residue was extracted with ethyl acetate (2x10 ml), washed with water (2x10 ml), dried and evaporated. Formic acid ester of the phenol (2.7 g, 83%) was obtained as an orange oil, which was used further without purification.

2. To a solution of the above ester in MeOH (20 ml), triethylamine (0.76 g, 7.51 mmol) was added dropwise, this was stirred at 20 °C for 1 h, and evaporated. A solution of HCl (10 M, 2 ml) in water (5 ml) and CH_2Cl_2 (30 ml) were added to the resulting residue, this was stirred for 1 h, and the aqueous layer was separated. The organic layer was washed with water (3×10 ml), dried and evaporated. The product was isolated using column chromatography (EtOAc/petroleum ether, 1:1, R_f =0.5) to yield 2.20 g (76%) of phenol **5** (purity 95%, white crystals, mp 82-84 °C (EtOAc/petroleum ether, 1:1).

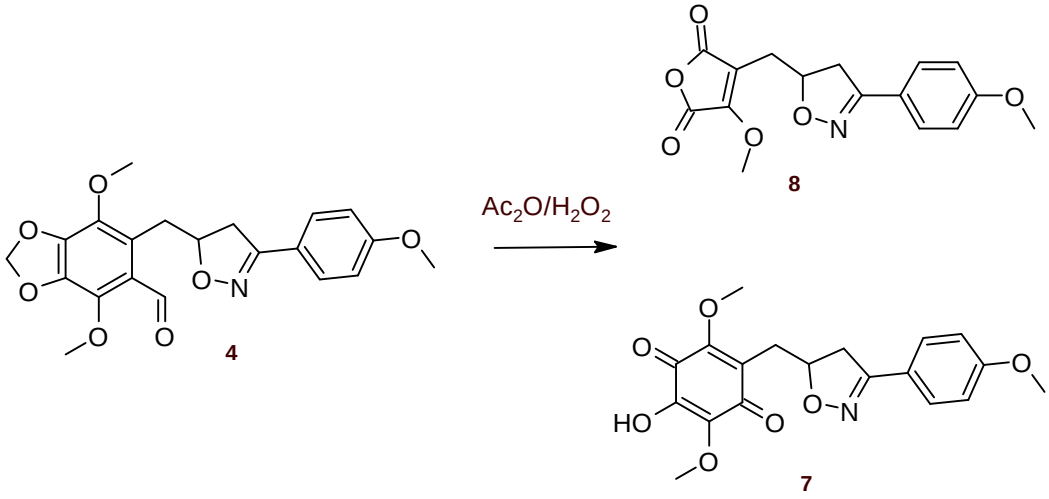
^{1}H NMR ($CDCl_3$) δ: 2.94 (dd, 1H, $ArCH_2$, *J* = 8.0, *J* = 13.0), 3.05 (dd, 1H, $ArCH_2$, *J* = 8.0, *J* = 13.0), 3.17 (m, 2H, (H4), 3.81 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.98 (s, 3H, OMe), 4.96 (m, 1H, H(5)), 5.75 (s, 1H, OH) 5.87 (s, 2H, OCH_2O), 6.89 (d, 2H, Ar, *J* = 11.0), 7.59 (d, 2H, Ar, *J* = 11.0)

^{13}C NMR ($CDCl_3$) δ: 160.93, 156.60, 141.54, 137.15, 136.79, 131.28, 128.27 (2C), 127.12, 122.64, 114.05 (2C), 107.86, 101.11, 80.60, 60.37, 59.97, 55.37, 39.41, 28.92.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$; calcd. $C_{20}H_{21}NO_7$+ H 387.1318; found 387.1329.

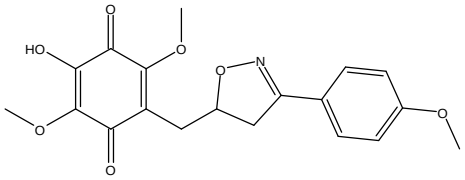
Calc for $C_{20}H_{21}NO_7$ C, 62.01; H, 5.46; N, 3.62. Found C62.12; H, 5.51; N, 3.59.

Baeyer–Villiger oxidative rearrangement of carbaldehyde **4**



To Ac_2O (25 ml) and H_2SO_4 (2 drops) with stirring and cooling, H_2O_2 (35%, 9 ml) was added dropwise at a temperature <45-55 °C, this was stirred for 30 min, and isoxazolinaldehyde **4** (5.0 g) was added in portions at a temperature <35 °C (cooling), and stirred for 6 h. Acetic anhydride was evaporated on a rotary evaporator, the products were isolated by column chromatography (EtOAc/petroleum ether = 1:1): 1st fraction was maleic anhydride derivative **8** (1 g, 25%), and 2nd fraction was quinone **7** (1.2 g, 26%).

2-Hydroxy-3,6-dimethoxy-5-[(3-(4-methoxyphenyl)-4,5-dihydro-1,2-oxazol-5-yl)methyl]cyclohexa-2,5-diene-1,4-dione **(7)**



Yield**,** 1.2 g (26%), orange crystals**,** mp 152-154 °C decomp. (MeOH), R_f = 0.3, EtOAc/petroleum ether = 1:1

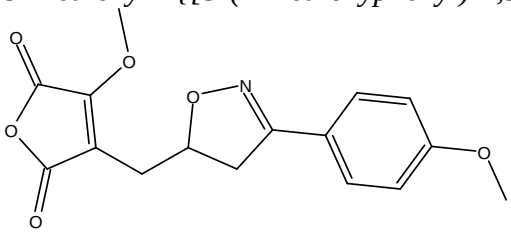
^{1}H NMR (DMSO-d_6) δ: 2.59 (dd, 1H, $ArCH_2$, *J* = 6.0, *J* = 10.0), 2.72 (dd, 1H, ArCH2, *J* = 7.0, *J* = 12.0), 3.06 (dd, 1H,(H4), *J* = 10.0, *J* = 17.0) 3.41 (dd, 1H,(H4), *J* = 10.0, *J* = 17.0) 3.79 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.92 (s, 3H, OMe), 4.74 (m, 1H, H(5)), 6.20 (s, 2H, OCH2O), 7.00 (d, 2H, Ar, *J* = 9.0), 7.59 (d, 2H, Ar, *J* = 9.0), 10.45 (br.s, 1H, OH).

^{13}C NMR (DMSO-d_6) δ: 183.47, 180.20, 160.66, 156.17, 154.42, 143.55, 138.00, 128.16 (2C), 124.29, 121.88, 114.27 (2C), 78.79, 61.04, 60.07, 55.32, 28.51.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$; calcd. $C_{19}H_{19}NO_7$+ H 373.3567; found 373.3578.

Calc for $C_{19}H_{19}NO_7$ C, 61.12; H, 5.13; N, 3.75. Found C, 61.24; H, 5.17; N, 3.85

3-Methoxy-4-{[3-(4-methoxyphenyl)-4,5-dihydro-1,2-oxazol-5-yl]methyl}furan-2,5-dione (**8**)



Yield 1.0 g (25%), white crystals, mp 143-144 °C (EtOAc/petroleum ether = 1:1), R_f = 0.6, EtOAc/petroleum ether = 1:1).

^{1}H NMR (DMSO-d_6) δ: 2.67 (dd, 1H, $ArCH_2$, *J* = 5.0, *J* = 8.0), 2.84 (dd, 1H, ArCH2, *J* = 8.0, *J* = 15.0), 3.16 (dd, 1H,(H4), *J* = 7.0, *J* = 17.0) 3.51 (dd, 1H,(H4), *J* = 10.0, *J* = 17.0) 3.80 (s, 3H, OMe), 4.21 (s, 3H, OMe), 4.85 (m, 1H, H(5)), 6.20 (s, 2H, OCH2O), 7.00 (d, 2H, Ar, *J* = 9.0), 7.59 (d, 2H, Ar, *J* = 9.0), 10.45 (br.s, 1H, OH). ^{13}C NMR (DMSO-*d*6) δ: 165.66, 160.78, 156.63, 155.36, 128.27 (2C), 121.66, 114.29 (2C), 111.15, 78.06, 60.13, 55.34, 27.67.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$; calcd. for $C_{15}H_{16}NO_6$ + H 318.0962; found 318.0972.

Calc for $C_{16}H_{15}NO_6$ C, 60.57; H, 4.77; N, 4.41. Found C, 60.72; H, 4.86; N, 4.53.

Single crystal X-ray diffraction data

X-ray diffraction data for compounds **7** and **8** were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[S2] The structure was solved by direct methods using SHELXT[S3] and refined on *F*[S3] using SHELXL-2018[S4] in the OLEX2 program.[S5] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. The locations of hydrogen atoms H17 and H17A of compound **7** were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters. All other hydrogen atoms for both compounds were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite[S6] was used for molecular graphics.

Data of compound **7** are refined as an inversion twin. The phenyl substituent C^{14}–C^{19} in the crystal of compound **7** is disordered over two positions with the contribution of main component of 0.568.

Table S1. Crystal data and structure refinement for compounds **7** and **8**.

Compound	**7**	**8**
Empirical formula	$C_{19}H_{19}NO_7$	$C_{16}H_{15}NO_6$
Formula weight	373.35	317.29
Temperature, K	100(1)	100(1)
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
Unit cell dimensions: a, b, c, Å α, β, γ, °	4.79523(7) 8.20587(11) 43.0852(6) 90 90 90	8.29006(9) 14.54498(18) 11.91274(13) 90 94.3701(10) 90
Volume, $Å^3$	1695.36(4)	1432.25(3)
Z, Z′	4, 1	8, 1
ρ_{calc}, g/cm^3	1.463	1.471
μ, mm^{-1}	0.949	0.962
F(000)	784	664
Crystal size, mm^3	0.05 x 0.06 x 0.11	0.04 x 0.05 x 0.33
θ, deg	4.104≤θ≤79.542	4.807≤ θ ≤79.552
Reflections collected	13607	16647
Independent reflections	3493	3102

	[R(int) = 0.0350]	[R(int) = 0.0311]
Reflections with $I > 2\sigma(I)$	3277	2886
Parameters / restraints	261 / 0	210 / 0
Goodness-of-fit on F^2	1.075	1.046
R_1 / wR_2 [$I>2\sigma(I)$]	0.0435 / 0.1137	0.0345 / 0.0920
R_1 / wR_2 (all reflections)	0.0463 / 0.1155	0.0364 / 0.0935
ρ_{max}/ρ_{min} ($e\text{Å}^{-3}$)	0.206 / -0.210	0.269 / -0.250
Extinction coefficient	0.0017(5)	-
CCDC number	2291864	2291865

Molecular and crystal structures of compounds 7 and 8

The compounds **7** and **8** forms orthorhombic and monoclinic crystals (Sp. groups $P2_12_12_1$ and $P2_1/n$, respectively) with by the one molecule in the independent part of the unit cell without inclusion of the solvent molecules (Figures S1,S2). Five-membered 1,2-oxazole cycle has different conformation in the crystals of two compounds. So, in the molecule 8 the cycle is more planar, while for molecule **7** the conformation of the cycle – envelope, characteristic of five-membered rings: four atoms are in the plane, and one atom deviates from this plane. The values of torsion angle C(3)-O(2)-N(1)-C(5) are -17.7(3)° and -3.69(11)° for molecules **7** and **8**, respectively. The selected bond lengths, valence and torsion angles are given in Tables S2 and S3. The methoxy group O(12)–C(12) for both molecules is in the plane of the phenyl ring. Other methoxy groups are deviated from the planes of the aromatic cycles. Thus, in the case of groups O(19)-C(21) (**7**) and O(15)-C(19) (**8**) deviations can be caused due to intramolecular interactions of C-H…O type. The main supramolecular structure in the crystal **7** is centrosymmetric dimer formed due to hydrogen bond O–H ···O type (Figure S3). Parameters of the hydrogen bonding are given in the Table S4.

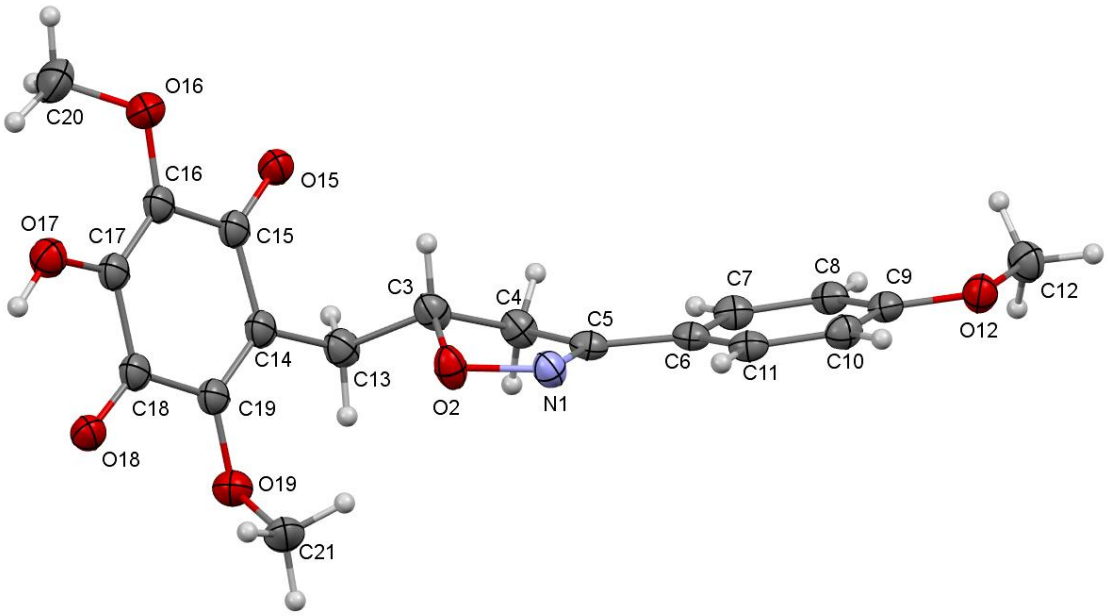


Figure S1. The structure of **7** with numeration of the non-hydrogen atoms. Anisotropic displacement parameters are drawn at 50% probability level.

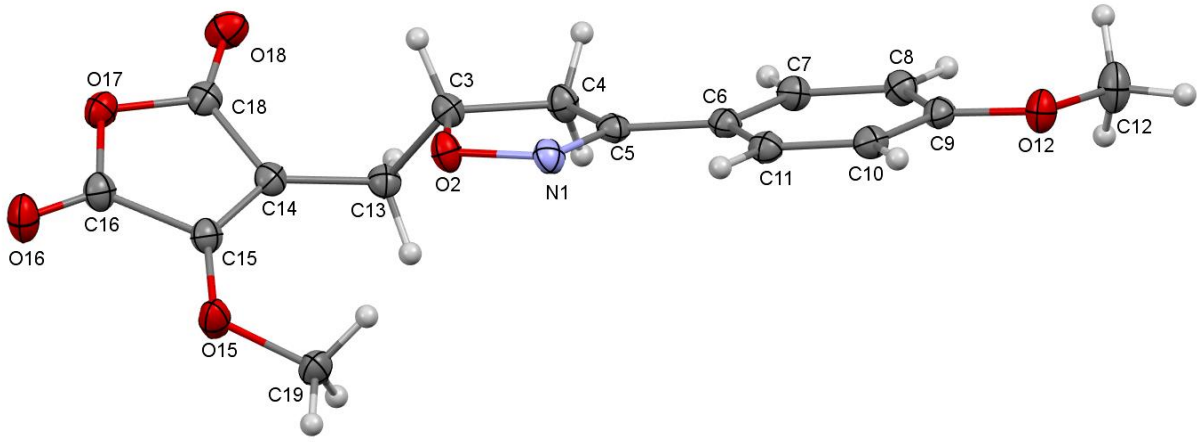


Figure S2. The structure of **8** with numeration of the non-hydrogen atoms. Anisotropic displacement parameters are drawn at 50% probability level.

Table S2. Selected bond length (Å) and angle (°) in the crystals for compounds **7** and **8**.

compound **7**		compound **8**	
Bond (Å)			
Bond	Bond length, Å	Bond	Bond length, Å
O(2)-N(1)	1.422(3)	O(2)-N(1)	1.4169(11)
O(2)-C(3)	1.459(3)	O(2)-C(3)	1.4639(12)
N(1)-C(5)	1.286(3)	N(1)-C(5)	1.2858(14)
C(3)-C(4)	1.512(4)	C(3)-C(4)	1.5275(14)
C(4)-C(5)	1.503(4)	C(4)-C(5)	1.5005(14)
C(5)-C(6)	1.467(3)	C(5)-C(6)	1.4678(14)
C(3)-C(13)	1.524(12)	C(3)-C(13)	1.5268(14)
C(13)-C(14)	1.509(11)	C(13)-C(14)	1.5020(14)
O(12)-C(9)	1.360(3)	O(12)-C(9)	1.3620(12)
O(12)-C(12)	1.427(3)	O(12)-C(12)	1.4255(14)

O(15)-C(15)	1.222(8)	O(15)-C(15)	1.3233(13)
O(16)-C(16)	1.355(7)	O(15)-C(19)	1.4508(13)
O(16)-C(20)	1.343(10)	O(18)-C(18)	1.1934(14)
O(18)-C(18)	1.217(8)	O(16)-C(16)	1.1914(14)
O(19)-C(19)	1.352(3)	O(17)-C(16)	1.3765(13)
O(19)-C(21)	1.454(4)	O(17)-C(18)	1.4094(13)
Angle (°)			
Angle	Angle value, °	Angle	Angle value, °
N(1)-O(2)-C(3)	106.39(17)	N(1)-O(2)-C(3)	109.44(7)
C(5)-N(1)-O(2)	108.8(2)	C(5)-N(1)-O(2)	109.53(8)
O(2)-C(3)-C(4)	103.1(2)	O(2)-C(3)-C(4)	104.93(8)
C(3)-C(4)-C(5)	98.9(2)	C(3)-C(4)-C(5)	101.29(8)
O(2)-C(3)-C(13)	107.6(9)	O(2)-C(3)-C(13)	108.91(8)
N(1)-C(5)-C(6)	121.0(2)	N(1)-C(5)-C(6)	121.15(9)
C(9)-O(12)-C(12)	117.9(2)	C(9)-O(12)-C(12)	117.04(9)
C(3)-C(13)-C(14)	109.4(10)	C(3)-C(13)-C(14)	112.72(8)
C(16)-O(16)-C(20)	115.8(8)	C(16)-O(17)-C(18)	106.88(8)
C(19)-O(19)-C(21)	113.7(2)	C(15)-O(15)-C(19)	117.98(8)

Table S3. Selected torsion angle (°) in the crystals for compounds **7** and **8**.

Torsion angle (°)			
Angle	Angle value, °	Angle	Angle value, °
O(2)-N(1)-C(5)-C(4)	-2.8(3)	O(2)-N(1)-C(5)-C(4)	-2.20(12)
C(3)-O(2)-N(1)-C(5)	-17.7(3)	C(3)-O(2)-N(1)-C(5)	-3.69(11)
N(1)-O(2)-C(3)-C(13)	150.8(6)	N(1)-O(2)-C(3)-C(13)	130.78(8)
O(2)-C(3)-C(13)-C(14)	64.9(16)	O(2)-C(3)-C(13)-C(14)	67.34(11)
C(4)-C(5)-C(6)-C(7)	-2.0(4)	C(7)-C(6)-C(5)-C(4)	0.01(15)
C(3)-C(13)-C(14)-C(15)	69.0(18)	C(3)-C(13)-C(14)-C(18)	86.22(11)
C(12)-O(12)-C(9)-C(8)	4.2(4)	C(12)-O(12)-C(9)-C(8)	-3.54(15)
C(21)-O(19)-C(19)-C(14)	107.0(7)	C(19)-O(15)-C(15)-C(14)	-0.24(19)
C(20)-O(16)-C(16)-C(17)	-50.6(10)		

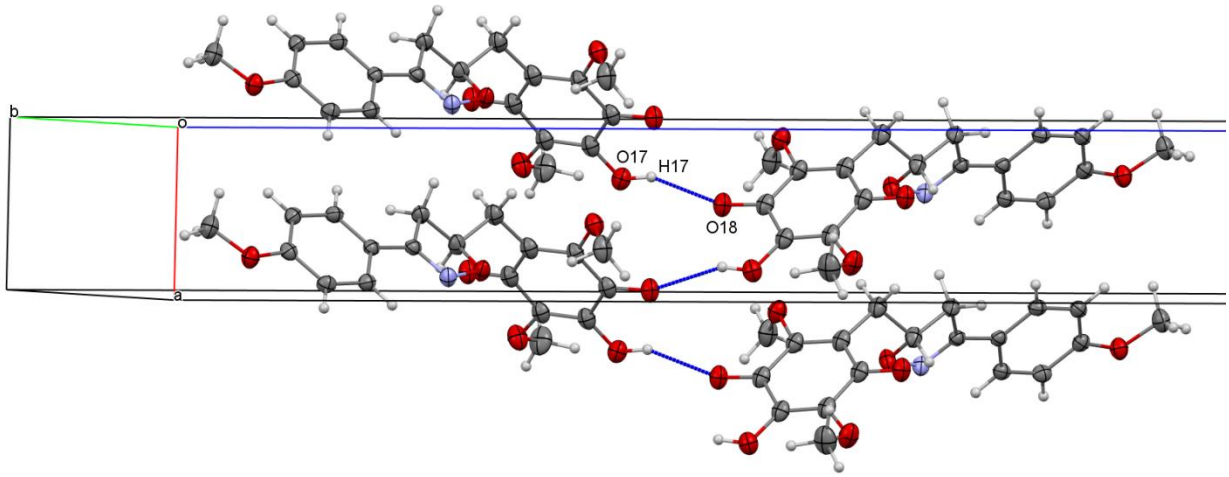


Figure S3. The main motif –a spiral chain – due to O–H···O hydrogen bond. Hydrogen bonds are shown by blue dashed lines.

Table S4. Parameters of hydrogen bonds for **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(17)-H(17)...O(18)#1	0.87(3)	2.21(5)	3.032(11)	158(11)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+3/2,-z+1

References

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S3. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3.

S4. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3.

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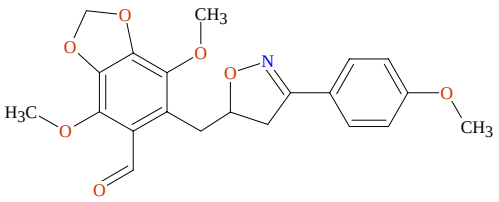
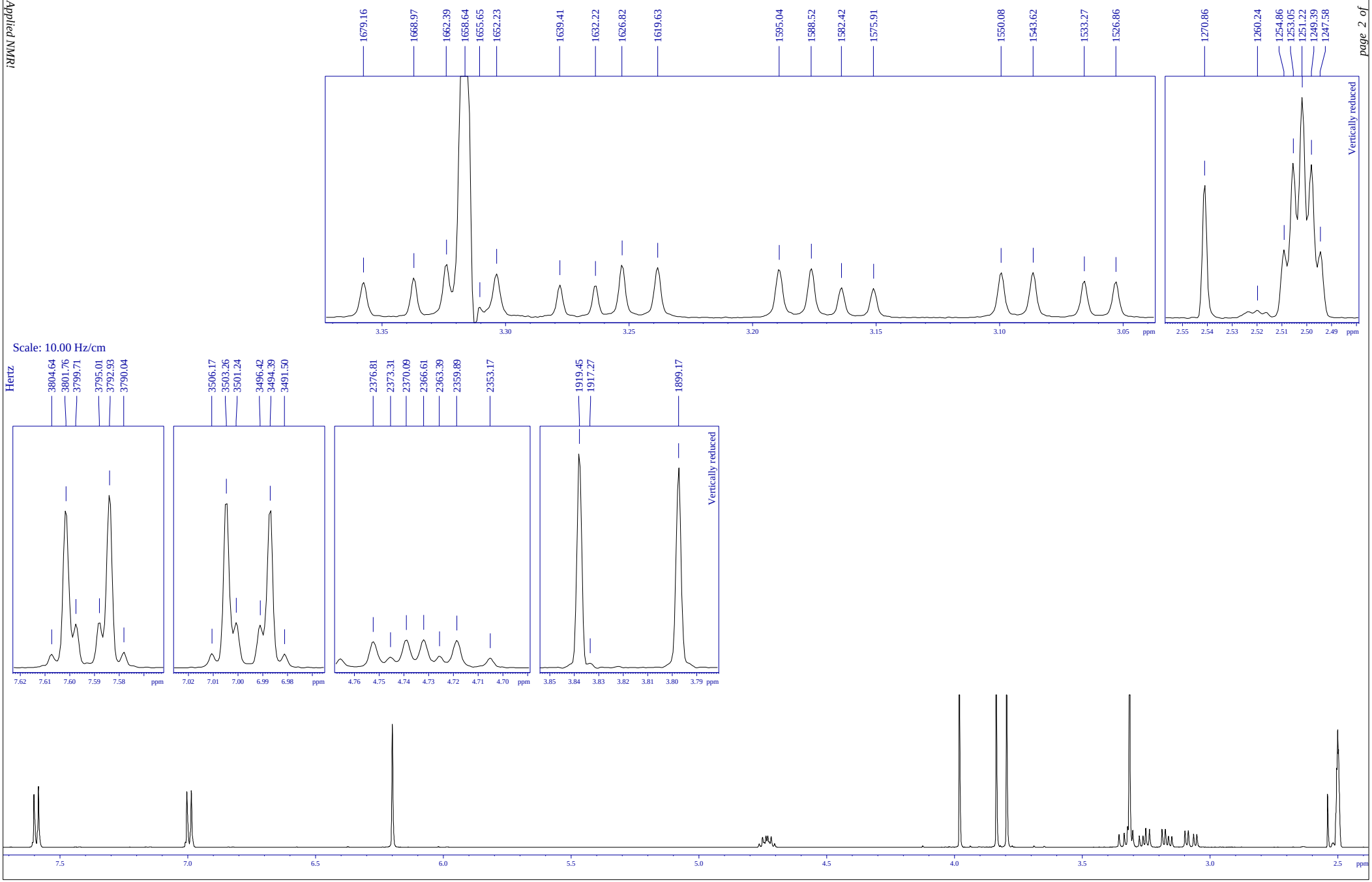
The Best Applied NMR!

4 (NMR/17217961)



Found protons = 19 impurity* < 0.1 %

4 (NMR/17217961)



4 (NMR/17217961)

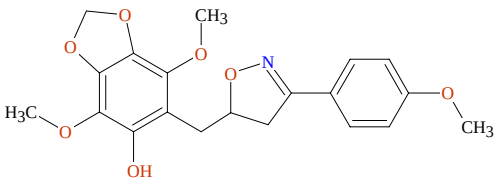
Peaks List

#	Address [points]	Frequency [Hz]	[ppm]	Intensity [cm]
1	12665.6	5130.737	10.2588	6.22
2	17010.9	3804.645	7.6073	0.29
3	17020.4	3801.759	7.6015	3.41
4	17027.1	3799.714	7.5975	0.93
5	17042.5	3795.008	7.5880	0.97
6	17049.3	3792.935	7.5839	3.71
7	17058.8	3790.037	7.5781	0.33
8	17989.0	3506.170	7.0105	0.30
9	17998.5	3503.261	7.0047	3.59
10	18005.2	3501.237	7.0007	0.96
11	18020.9	3496.423	6.9910	0.90
12	18027.6	3494.393	6.9870	3.43
13	18037.0	3491.503	6.9812	0.29
14	19316.0	3101.212	6.2008	7.67
15	21689.7	2376.808	4.7524	0.55
16	21701.1	2373.309	4.7454	0.23
17	21711.7	2370.094	4.7390	0.60
18	21723.1	2366.614	4.7320	0.60
19	21733.7	2363.390	4.7256	0.25
20	21745.1	2359.889	4.7186	0.58
21	21767.1	2353.167	4.7051	0.21
22	22952.2	1991.516	3.9820	18.31
23	23188.3	1919.452	3.8379	17.05
24	23195.5	1917.266	3.8335	0.38
25	23254.8	1899.172	3.7974	15.65
26	23975.7	1679.164	3.3575	0.76
27	24009.1	1668.971	3.3371	0.85
28	24030.7	1662.389	3.3239	1.14
29	24043.0	1658.640	3.3164	16.12
30	24052.8	1655.649	3.3104	0.23
31	24064.0	1652.228	3.3036	0.94
32	24106.0	1639.407	3.2780	0.70
33	24129.5	1632.220	3.2636	0.70
34	24147.2	1626.820	3.2528	1.12
35	24170.8	1619.630	3.2384	1.07
36	24251.4	1595.035	3.1892	1.04
37	24272.7	1588.520	3.1762	1.05
38	24292.7	1582.421	3.1640	0.64
39	24314.1	1575.906	3.1510	0.62
40	24398.7	1550.081	3.0994	0.97
41	24419.9	1543.622	3.0864	0.96
42	24453.8	1533.270	3.0657	0.78
43	24474.8	1526.863	3.0529	0.77
44	25313.7	1270.861	2.5411	3.95
45	25348.4	1260.244	2.5198	0.22
46	25366.1	1254.861	2.5091	1.97
47	25372.0	1253.045	2.5054	4.48
48	25378.0	1251.220	2.5018	6.39
49	25384.0	1249.395	2.4981	4.44
50	25389.9	1247.578	2.4945	1.93
51	29478.0	0.002	0.0000	4.28

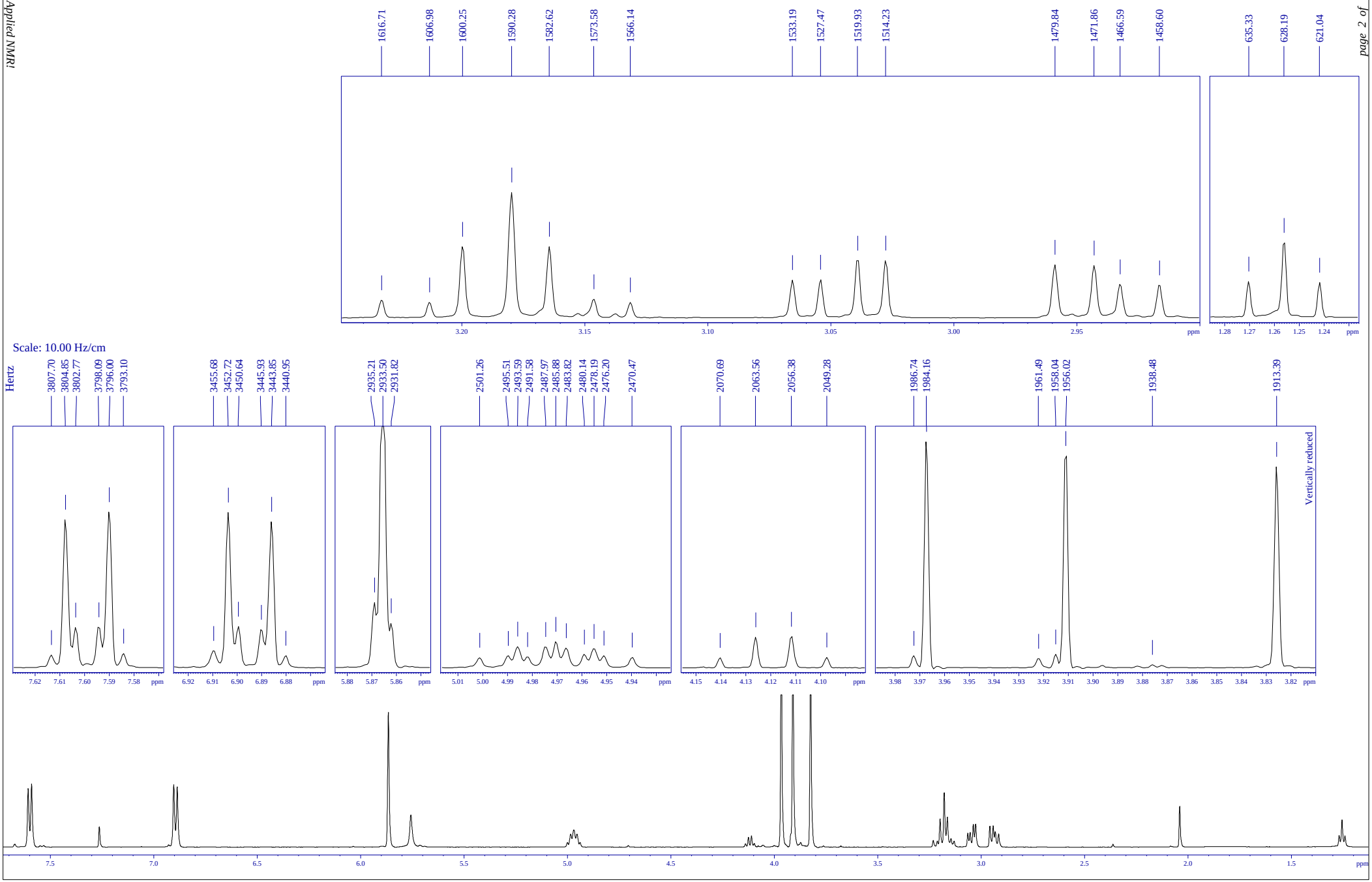
The Best Applied NMR!

5 (NMR/29340046)

Found protons = 24 impurity* < 0.1 %



5 (NMR/29340046)



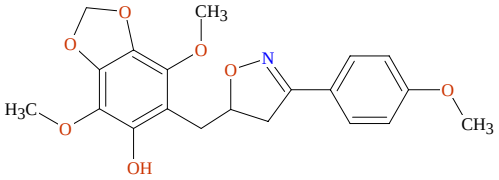
5 (NMR/29340046)

Peaks List

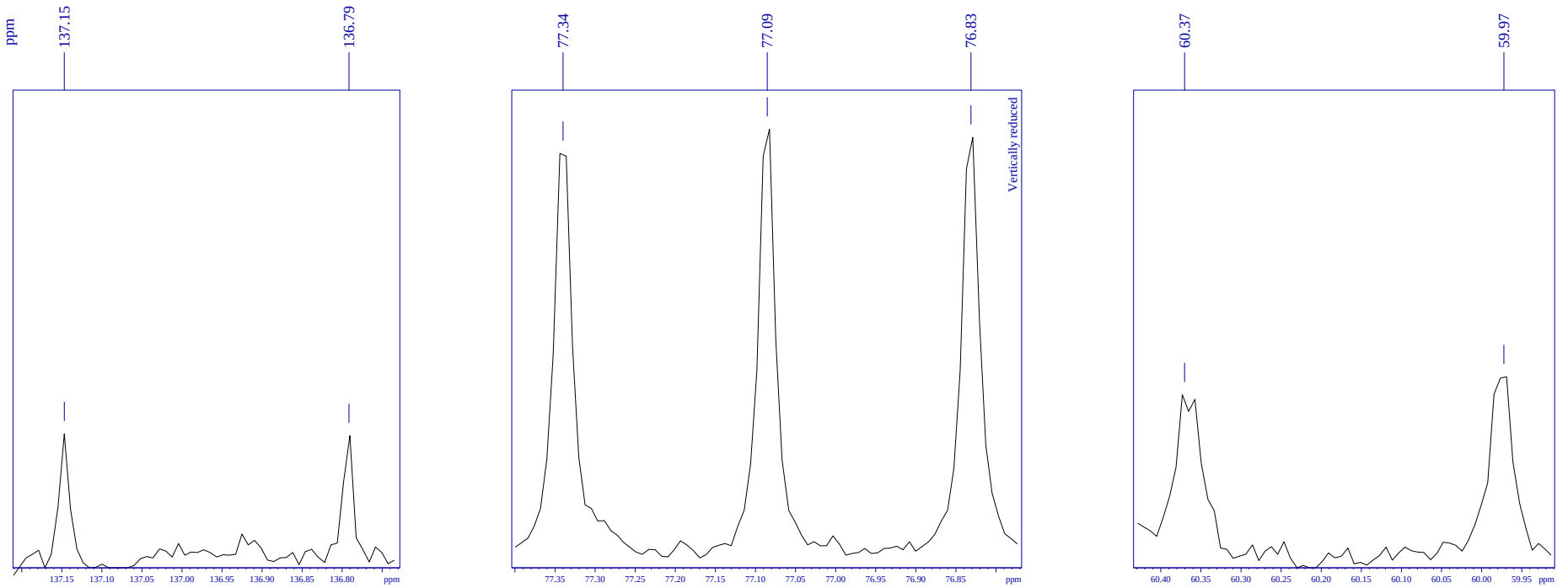
#	Address [points]	Frequency [Hz]	[ppm]	Intensity [cm]
1	17004.9	3807.705	7.6134	0.26
2	17014.3	3804.851	7.6077	3.03
3	17021.1	3802.770	7.6036	0.82
4	17036.4	3798.085	7.5942	0.85
5	17043.3	3795.996	7.5900	3.19
6	17052.8	3793.102	7.5842	0.29
7	17579.2	3632.454	7.2630	1.49
8	18158.4	3455.681	6.9096	0.35
9	18168.1	3452.718	6.9036	3.15
10	18175.0	3450.638	6.8995	0.83
11	18190.4	3445.927	6.8901	0.79
12	18197.2	3443.854	6.8859	2.97
13	18206.7	3440.947	6.8801	0.25
14	19863.9	2935.210	5.8689	1.32
15	19869.5	2933.497	5.8655	6.37
16	19875.0	2931.821	5.8621	0.90
17	20047.5	2879.184	5.7569	0.77
18	21285.9	2501.264	5.0012	0.21
19	21304.7	2495.509	4.9897	0.24
20	21311.0	2493.585	4.9859	0.43
21	21317.6	2491.582	4.9819	0.22
22	21329.4	2487.969	4.9746	0.43
23	21336.3	2485.881	4.9705	0.53
24	21343.0	2483.820	4.9663	0.40
25	21355.1	2480.143	4.9590	0.27
26	21361.5	2478.189	4.9551	0.39
27	21368.0	2476.198	4.9511	0.25
28	21386.8	2470.469	4.9397	0.21
29	22696.8	2070.689	4.1403	0.20
30	22720.1	2063.558	4.1260	0.62
31	22743.7	2056.380	4.1117	0.64
32	22766.9	2049.277	4.0975	0.21
33	22971.9	1986.736	3.9724	0.84
34	22980.3	1984.163	3.9673	16.00
35	23054.6	1961.495	3.9220	0.65
36	23065.9	1958.035	3.9151	0.94
37	23072.5	1956.015	3.9110	15.39
38	23130.0	1938.479	3.8760	0.21
39	23212.2	1913.388	3.8258	14.06
40	24184.4	1616.707	3.2326	0.37
41	24216.3	1606.980	3.2131	0.32
42	24238.3	1600.253	3.1997	1.46
43	24271.0	1590.280	3.1797	2.53
44	24296.1	1582.615	3.1644	1.44
45	24325.7	1573.584	3.1463	0.38
46	24350.1	1566.144	3.1315	0.32
47	24458.1	1533.189	3.0656	0.77
48	24476.8	1527.475	3.0542	0.78
49	24501.5	1519.929	3.0391	1.21
50	24520.2	1514.234	3.0277	1.16
51	24632.9	1479.837	2.9589	1.08
52	24659.0	1471.863	2.9430	1.06
53	24676.3	1466.587	2.9324	0.69
54	24702.5	1458.599	2.9164	0.68
55	26137.1	1020.782	2.0410	2.82
56	27400.1	635.332	1.2703	0.74
57	27423.6	628.190	1.2561	1.58
58	27447.0	621.040	1.2418	0.71
59	29482.0	0.002	0.0000	6.84

5 (NMR/29340046)

160.93 156.60 141.54 137.15 136.79 131.28 128.27 127.12 122.64 114.05 107.86 101.11 80.60 77.34 77.09 76.83 60.37 59.97 55.37 39.41 28.92



5 (NMR/29340046)



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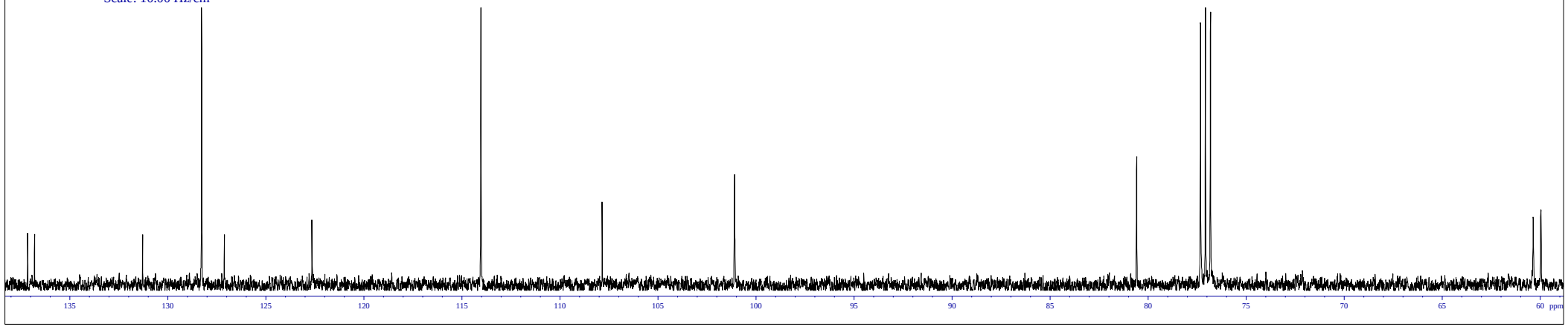


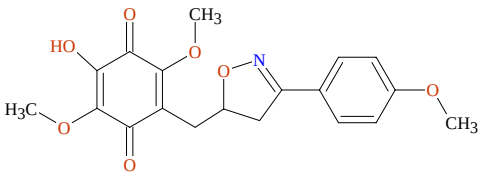
5 (NMR/29340046)

Peaks List

#	Address [points]	Frequency [Hz]	[ppm]	Intensity [cm]
1	9973.5	20237.705	160.9261	2.41
2	10519.0	19693.695	156.6002	2.92
3	12418.1	17799.730	141.5398	2.96
4	12972.0	17247.297	137.1469	1.95
5	13016.8	17202.598	136.7915	1.96
6	13711.9	16509.369	131.2791	1.92
7	14091.2	16131.146	128.2715	13.40
8	14237.0	15985.737	127.1153	1.91
9	14800.7	15423.559	122.6450	2.59
10	15885.0	14342.183	114.0461	14.00
11	16665.0	13564.201	107.8597	3.14
12	17516.7	12714.853	101.1059	4.32
13	20102.7	10135.766	80.5975	4.92
14	20513.5	9726.113	77.3400	10.50
15	20545.6	9694.073	77.0853	10.93
16	20577.6	9662.127	76.8312	10.63
17	22653.3	7592.051	60.3704	2.63
18	22703.5	7541.983	59.9723	3.00
19	23284.5	6962.580	55.3650	3.85
20	25295.8	4956.646	39.4142	6.71
21	26619.7	3636.300	28.9151	6.47

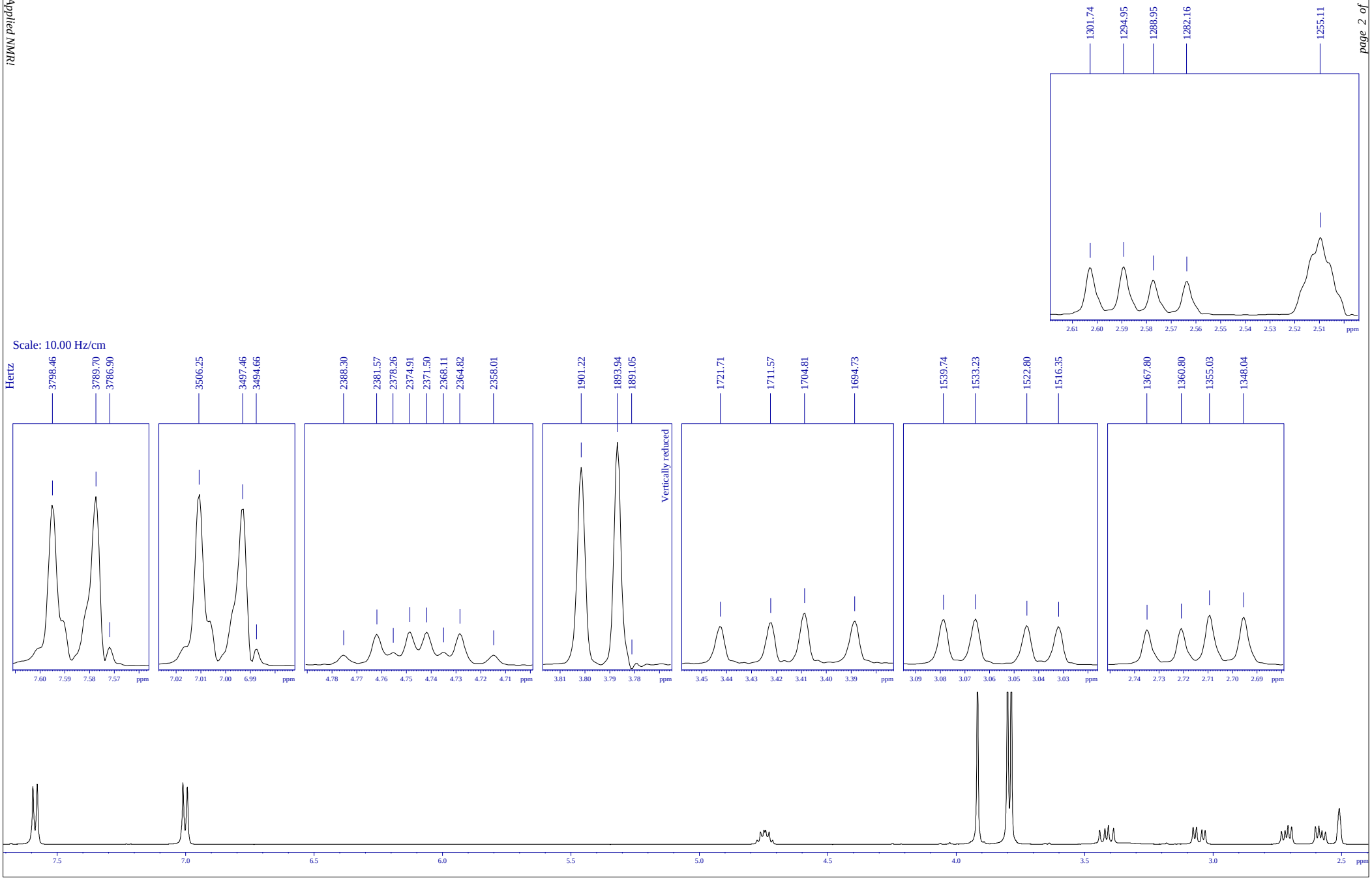
7 (NMR/29330183)

Found protons = 15 impurity* < 0.1 %



The Best Applied NMR!

7 (NMR/29330183)



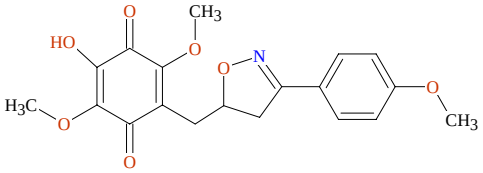
7 (NMR/29330183)

Peaks List

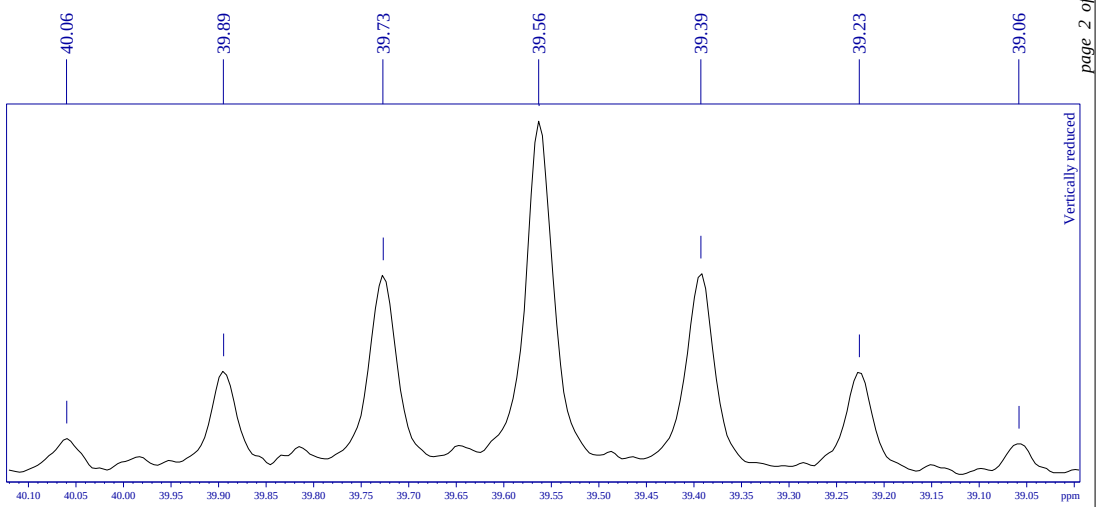
#	Address [points]	Frequency [Hz]	[ppm]	Intensity [cm]
1	12343.8	5233.213	10.4637	0.29
2	17045.2	3798.463	7.5950	3.35
3	17073.9	3789.702	7.5774	3.53
4	17083.1	3786.900	7.5718	0.38
5	18002.7	3506.249	7.0107	3.59
6	18031.5	3497.458	6.9931	3.32
7	18040.7	3494.658	6.9875	0.34
8	21666.0	2388.296	4.7753	0.21
9	21688.1	2381.572	4.7619	0.65
10	21698.9	2378.260	4.7553	0.26
11	21709.9	2374.908	4.7486	0.70
12	21721.1	2371.502	4.7418	0.69
13	21732.2	2368.110	4.7350	0.27
14	21743.0	2364.821	4.7284	0.66
15	21765.3	2358.008	4.7148	0.21
16	23070.3	1959.754	3.9185	15.05
17	23262.1	1901.221	3.8015	14.20
18	23285.9	1893.940	3.7869	16.00
19	23295.4	1891.050	3.7811	−0.27
20	23850.3	1721.709	3.4425	0.81
21	23883.5	1711.571	3.4223	0.90
22	23905.7	1704.813	3.4087	1.10
23	23938.7	1694.727	3.3886	0.93
24	24446.6	1539.743	3.0787	0.96
25	24467.9	1533.234	3.0657	0.96
26	24502.1	1522.795	3.0448	0.83
27	24523.2	1516.351	3.0319	0.81
28	25010.0	1367.796	2.7349	0.74
29	25032.9	1360.801	2.7209	0.77
30	25051.8	1355.030	2.7094	1.05
31	25074.7	1348.041	2.6954	1.01
32	25226.5	1301.736	2.6028	1.01
33	25248.7	1294.946	2.5892	1.02
34	25268.4	1288.951	2.5772	0.74
35	25290.6	1282.160	2.5637	0.72
36	25379.2	1255.113	2.5096	1.63
37	29492.0	0.000	0.0000	3.28

7 (NMR/29330183)

183.47 180.20 160.66 156.17 154.42 143.55 138.00 128.16 124.92 121.88 114.27 78.79 61.04 60.07 55.32 40.06 39.89 39.73 39.56 39.39 39.23 39.06 28.51



7 (NMR/29330183)



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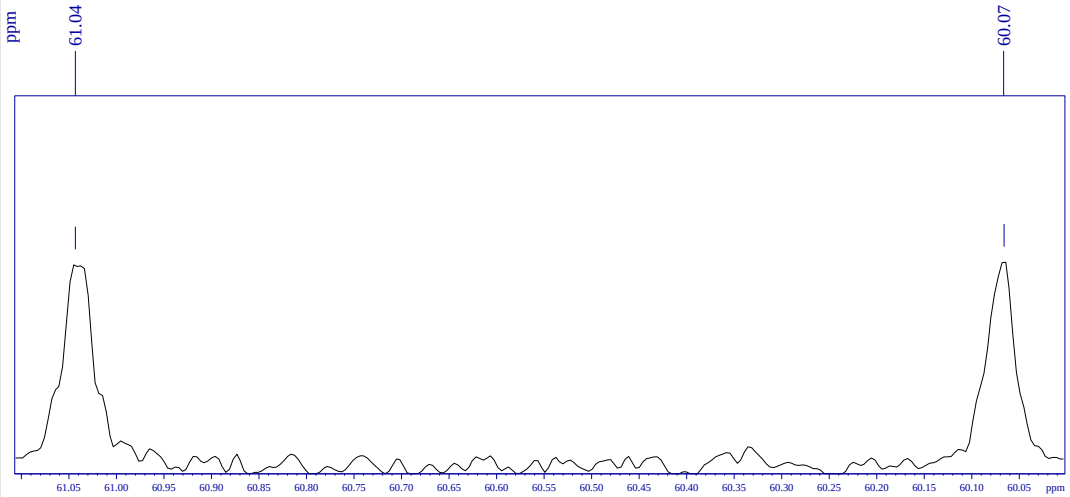
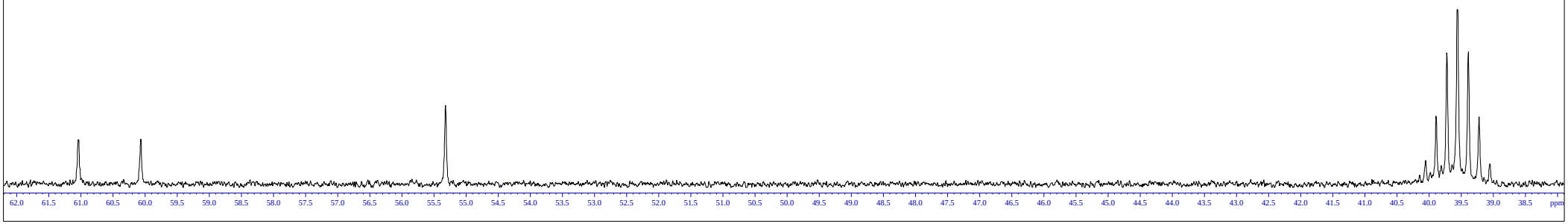




7 (NMR/29330183)

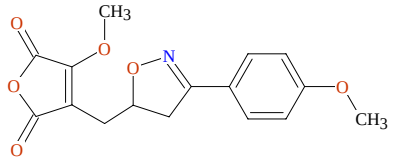
Peaks List

#	Address [points]	Frequency [Hz]	[ppm]	Intensity [cm]
1	12203.3	23072.287	183.4660	2.68
2	13059.4	22661.469	180.1992	2.75
3	18179.3	20204.762	160.6640	3.40
4	19356.5	19639.916	156.1725	3.49
5	19816.2	19419.301	154.4182	2.84
6	22665.6	18052.074	143.5463	3.01
7	24119.5	17354.426	137.9987	2.08
8	26699.0	16116.692	128.1566	12.04
9	27548.0	15709.304	124.9171	3.37
10	28343.1	15327.783	121.8833	3.34
11	30339.0	14370.121	114.2682	12.50
12	39636.9	9908.613	78.7912	5.07
13	44288.4	7676.667	61.0432	2.69
14	44544.5	7553.775	60.0660	2.74
15	45788.3	6956.959	55.3203	4.74
16	49787.9	5037.821	40.0597	1.42
17	49831.1	5017.070	39.8947	4.09
18	49875.1	4995.963	39.7268	7.89
19	49918.1	4975.343	39.5629	14.00
20	49962.7	4953.940	39.3927	7.99
21	50006.4	4932.977	39.2260	4.07
22	50050.4	4911.860	39.0581	1.22
23	52814.9	3585.355	28.5100	5.02

The Best Applied NMR!

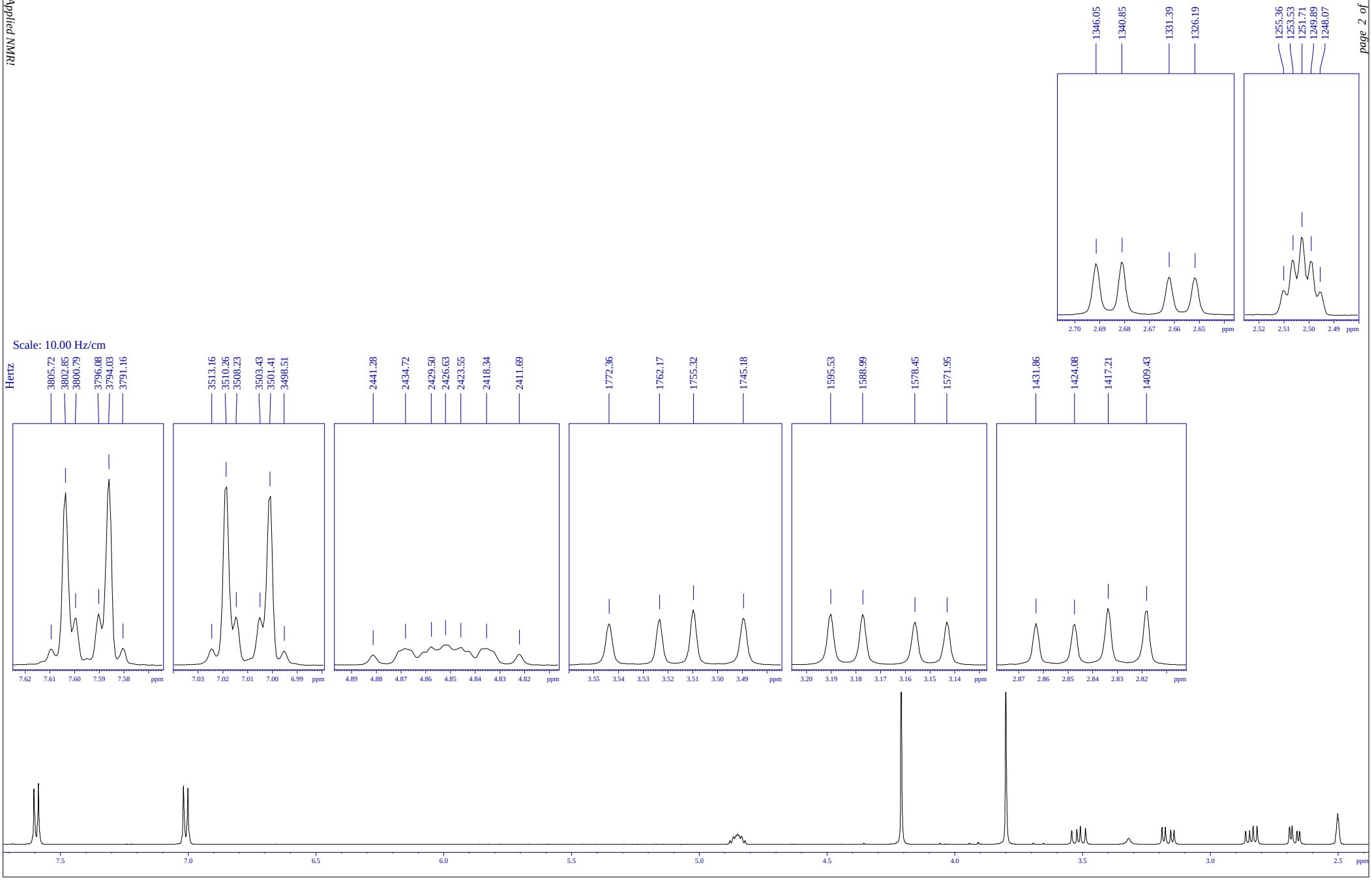
8 (NMR/29330182)

Found protons = 15 impurity* = 0.2 %



The Best Applied NMR!

8 (NMR/29330182)

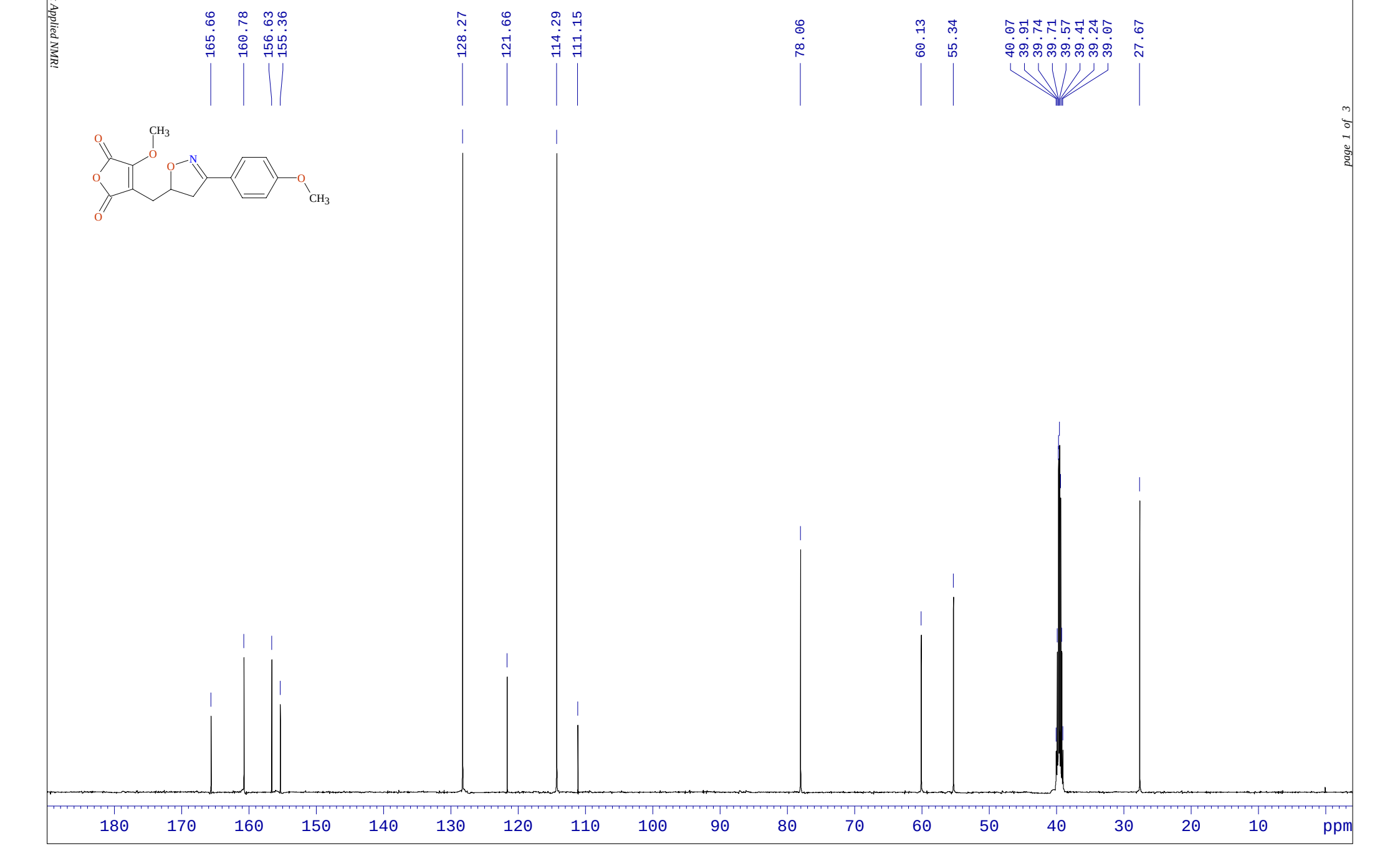


8 (NMR/29330182)

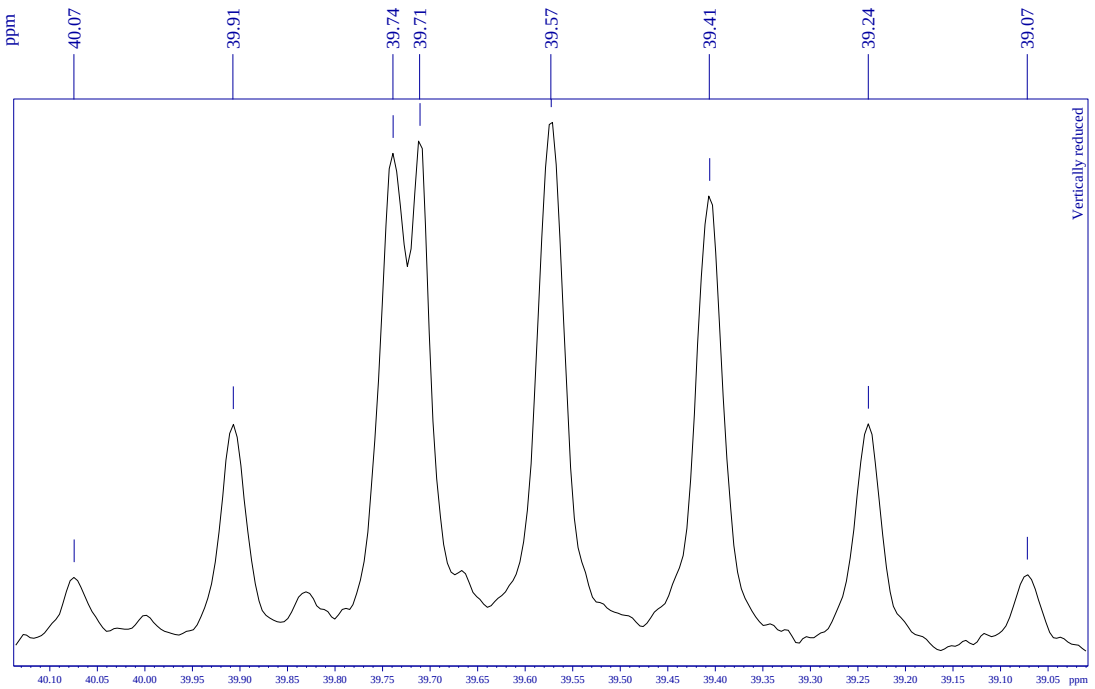
Peaks List

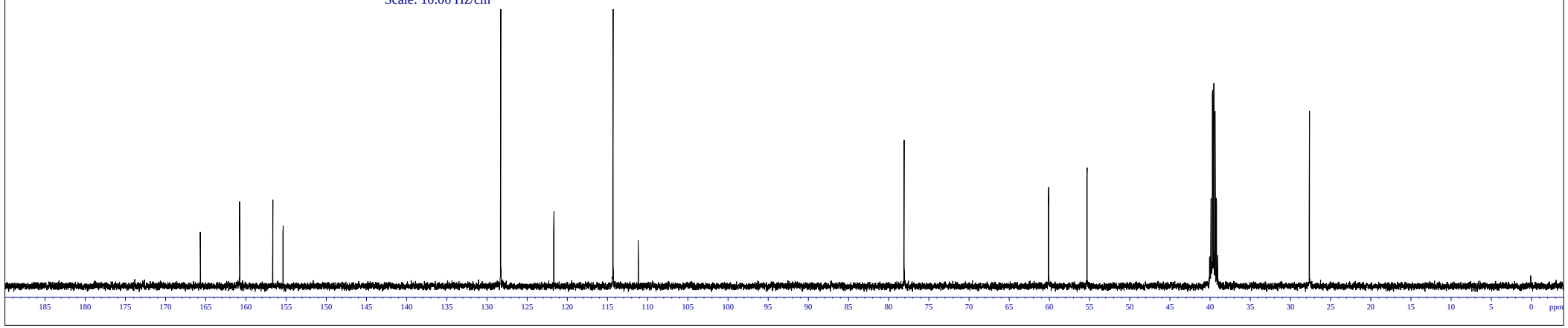
#	Address [points]	Frequency [Hz]	[ppm]	Intensity [cm]
1	17010.4	3805.717	7.6095	0.33
2	17019.8	3802.846	7.6037	3.55
3	17026.6	3800.790	7.5996	0.99
4	17042.0	3796.077	7.5902	1.05
5	17048.7	3794.025	7.5861	3.86
6	17058.1	3791.165	7.5804	0.35
7	17969.1	3513.161	7.0245	0.34
8	17978.6	3510.264	7.0187	3.75
9	17985.2	3508.231	7.0146	0.99
10	18001.0	3503.425	7.0050	0.98
11	18007.6	3501.411	7.0010	3.55
12	18017.1	3498.513	6.9952	0.30
13	21481.4	2441.277	4.8813	0.21
14	21502.9	2434.723	4.8682	0.34
15	21520.0	2429.498	4.8577	0.38
16	21529.4	2426.634	4.8520	0.41
17	21539.5	2423.548	4.8458	0.36
18	21556.6	2418.336	4.8354	0.35
19	21578.4	2411.693	4.8221	0.22
20	22579.7	2106.100	4.2111	16.00
21	23250.8	1901.319	3.8016	15.96
22	23673.3	1772.363	3.5438	0.86
23	23706.7	1762.174	3.5234	0.95
24	23729.2	1755.319	3.5097	1.14
25	23762.4	1745.181	3.4895	0.98
26	24037.8	1661.121	3.3214	0.26
27	24252.8	1595.529	3.1902	1.05
28	24274.2	1588.992	3.1772	1.05
29	24308.7	1578.450	3.1561	0.89
30	24330.1	1571.946	3.1431	0.88
31	24789.1	1431.859	2.8630	0.86
32	24814.6	1424.075	2.8474	0.86
33	24837.1	1417.211	2.8337	1.16
34	24862.6	1409.431	2.8181	1.14
35	25070.3	1346.045	2.6914	1.07
36	25087.3	1340.848	2.6810	1.10
37	25118.3	1331.390	2.6621	0.79
38	25135.4	1326.187	2.6517	0.78
39	25367.5	1255.356	2.5101	0.52
40	25373.4	1253.534	2.5064	1.16
41	25379.4	1251.710	2.5028	1.64
42	25385.4	1249.887	2.4991	1.13
43	25391.3	1248.067	2.4955	0.49
44	29481.0	0.001	0.0000	3.24

8 (NMR/29330182)



8 (NMR/29330182)





8 (NMR/29330182)

Peaks List

#	Address [points]	Frequency [Hz]	[ppm]	Intensity [cm]
1	16868.9	20833.521	165.6638	2.02
2	18149.4	20219.100	160.7780	3.24
3	19237.0	19697.262	156.6285	3.21
4	19568.8	19538.020	155.3622	2.27
5	26670.2	16130.533	128.2666	13.84
6	28401.4	15299.830	121.6610	2.85
7	30333.4	14372.805	114.2895	14.00
8	31155.4	13978.342	111.1528	1.72
9	39829.3	9816.301	78.0572	5.48
10	44527.9	7561.761	60.1295	3.69
11	45782.4	6959.818	55.3430	4.44
12	49784.0	5039.675	40.0744	1.10
13	49827.9	5018.617	39.9070	3.28
14	49872.0	4997.478	39.7389	7.13
15	49879.4	4993.925	39.7106	7.36
16	49915.5	4976.567	39.5726	7.63
17	49959.3	4955.595	39.4059	6.53
18	50003.0	4934.609	39.2390	3.28
19	50046.8	4913.591	39.0718	1.14
20	53035.9	3479.287	27.6666	6.52