

Ozonolysis in solvent/water mixtures: direct conversion of alkenes to aldehydes and ketones

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Sample preparative application (w/purification through distillation)				SI-3
Compound	Role	SI included	CAS	
3(8-acetoxyoctyl)-1,2,4-trioxolane (ozonide)	Product (unknown)	Experimental na procedures		SI-3
“ “	“ “	^1H , ^{13}C		SI-4,5
9-acetoxynonanal (1)	Product (known)	^{13}C	29541-97-7	SI-6
hexanal, 6-benzoyloxy-4-methyl (2)	Product (known)	^{13}C	172608-79-6	SI-7
Benzophenone (3)	Product (known)	^{13}C	119-64-9	SI-8
5-acetyl-2-methyl cyclohexanone (4)	Product (known)	^1H , ^{13}C	56893-77-7	SI-9,10
4-acetoxy benzaldehyde (5)	Product (known)	^{13}C	878-00-2	SI-11
4-nitrobenzaldehyde (6)	Product (known)	^{13}C	555-16-8	SI-12

(To print chemical spectra with embedded structures, print as “Document and Markups”.)

General Experimental Conditions: All reagents and solvents were used as supplied commercially, except CH₂Cl₂, which was distilled from CaH₂. ¹H/¹³C NMR spectra were recorded on 300/75 or 400/100 MHz spectrometers. Progress of reactions involving peroxides were monitored by TLC, using a *N,N'*-dimethylphenylenediamine indicator;¹ hydroperoxides and H₂O₂ yield a reddish-pink spot immediately while ozonides provide a pink or green-red color after standing or mild heating. Aqueous washes were monitored for the presence of H₂O₂ with peroxide test strips. Ozonolysis was conducted with a 5g/hr ozonizer using dried (Drierite) O₂ as the input gas.

Sample medium-scale application (purification through distillation)

5-Acetyl-2-methyl-cyclohexanone (4):² Into a 0 °C solution of dihydrocarvone (4.940 g, 32.4 mmol) and water (10.0 mL, 555 mmol) in 213 mL acetone in a round-bottom flask was added Sudan red (trace) until a faint pink-red color could be observed. A stream of O₃/O₂ (approximately 2% O₃, effective delivery of approximately 0.5 mmol/min) was introduced below the surface of the solution via a pipette. After the color of the indicator had been discharged, the ozonizer was set to 0 V, and the solution was purged with O₂ (2 min). The solution was diluted with 100 mL of H₂O and the mixture extracted with 130 mL CH₂Cl₂. The separated aqueous layer was back extracted with 30 mL CH₂Cl₂ and the combined organic layers were washed with 30 mL H₂O. No residual H₂O₂ could be detected in the organic layer (peroxide test strips), which was dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by bulb-to-

¹ Smith, L. L. Hill, F. L. *J. Chromatogr.*, **1972**, 66, 101.

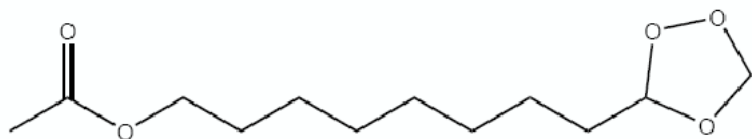
² Schreiber, S. L.; Liew, W. F. *Tetrahedron Letters*, **1984**, 24, 2363-6 (reported without experimental characterization).

bulb distillation (155 °C, 13 mm) to afford 5-acetyl-2-methyl-cyclohexanone (3.933g, 78%) as a yellow oil: R_f = 0.23 (40% Et₂O/Hex); ¹H NMR (300 MHz, CDCl₃): δ 2.78 (m, 1H), 2.43 (d, J = 9, 2H), 2.34 (apparent sextet, J = 6.3, 1H), 2.15 (s, 3H), 2.2-2.05 (2H), 1.68 (apparent qd/ddd, J = 13.3, 3.4, 1H), 1.39 (apparent qd/ddd, J = 13.1, 3.4, 1H), 0.98 (d, J = 9.5, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 211.5, 208.3, 52.0, 44.5, 42.7, 34.5, 28.3, 27.8, 14.3. HRMS calcd. for C₉H₁₅O₂ (M⁺); 155.1072; found, 155.1066.

3-(8-Acetoxyoctyl)-1,2,4-trioxolane (ozonide of 9-decenyl acetate, new compound):

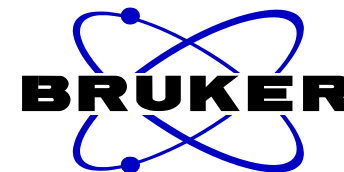
Into a -78 °C solution of 9-decenyl acetate (0.528 g, 2.6 mmol) in 20 mL CH₂Cl₂ in a flame dried round bottom flask was added a stream of O₃/O₂ (approximately 2% O₃, effective delivery of approximately 0.5 mmol/min). After the solution assumed the blue tint of free ozone, the ozonizer voltage was turned to zero and the solution was purged with O₂ for two minutes. The residue obtained upon concentration *in vacuo* (caution!) was purified by flash chromatography on SiO₂ with 10% EtOAc/hexanes to afford 3-(8-acetoxyoctyl)-1,2,4-trioxolane (416.6 mg, 63%) as a colorless oil: R_f = 0.4 (10% EA/hex); ¹H NMR (400 MHz, CDCl₃): δ 5.04 (s, 1H), 4.98 (t, J = 5.0, 1H), 4.87 (s, 1H), 3.91 (t, J = 6.7, 2H), 1.88 (s, 3H), 1.57 (m, 2H), 1.49 (m, 2H), 1.31-1.19 (10H). ¹³C NMR (100 MHz, CDCl₃): δ 170.6, 103.5, 93.8, 64.2, 31.4, 30.9, 29.1, 28.9, 28.4, 25.7, 23.6, 20.6. HRMS calcd. for C₁₂H₂₃O₅ (M⁺); 247.1546; found, 247.1545.

1D Proton NMR



8-acetoxyoctyl-1,2,4-trioxolane

5.043
4.989
4.977
4.965
4.880
3.924
3.908
3.891
1.894
1.604
1.588
1.575
1.566
1.554
1.499
1.483
1.466
1.305
1.295
1.286
1.192

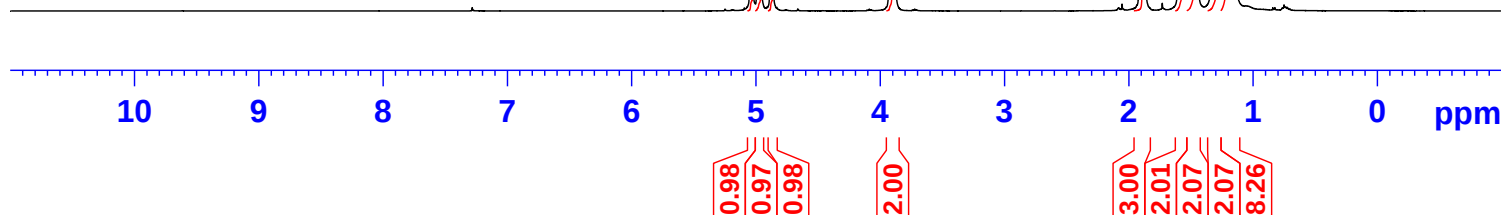


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PROCNO 1

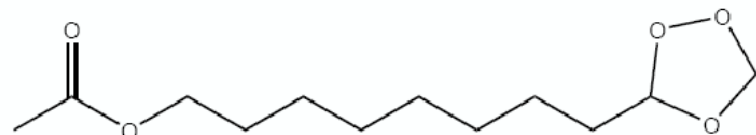
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13C NMR



8-acetoxyoctyl-1,2,4-trioxolane

170.69

103.50

93.77

77.54

77.22

76.90

64.24

31.42

30.94

29.11

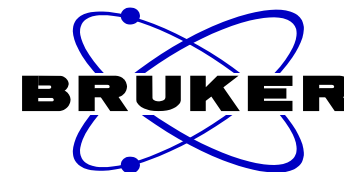
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28.43

25.70

23.62

20.64



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PROCNO 1

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FIDRES 0.673677 Hz
AQ 0.7422452 sec
RG 4597.6
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TD0 1

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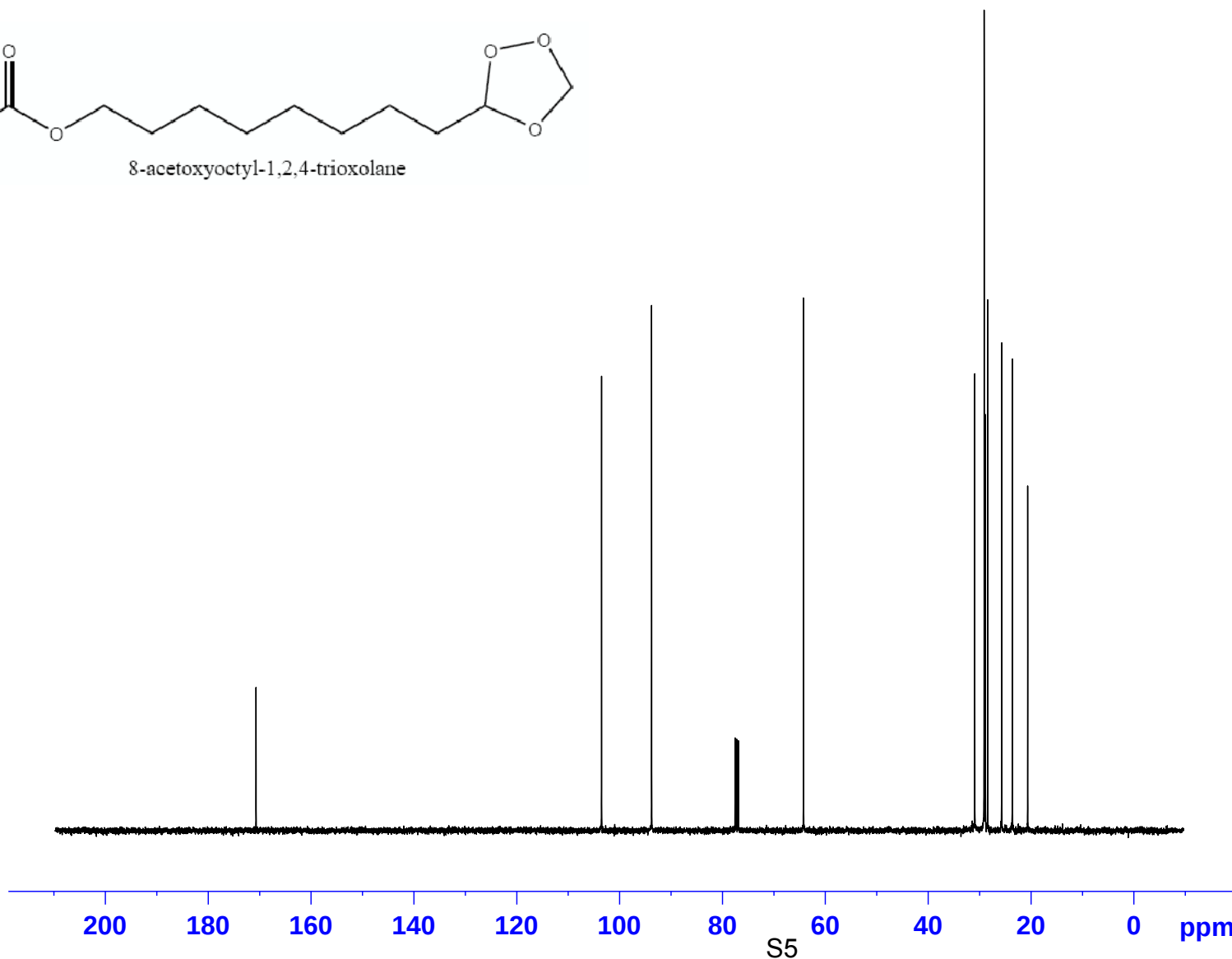
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PL12 12.90 dB
PL13 13.82 dB
SF02 400.1316005 MHz

F2 - Processing parameters

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13C

202.76

171.15

77.51

77.09

76.66

64.48

43.81

29.17

28.99

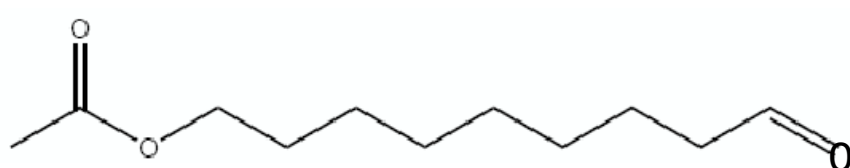
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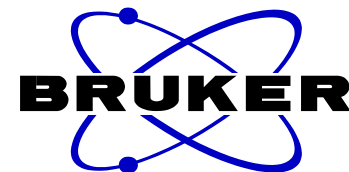
25.78

21.95

20.95



1



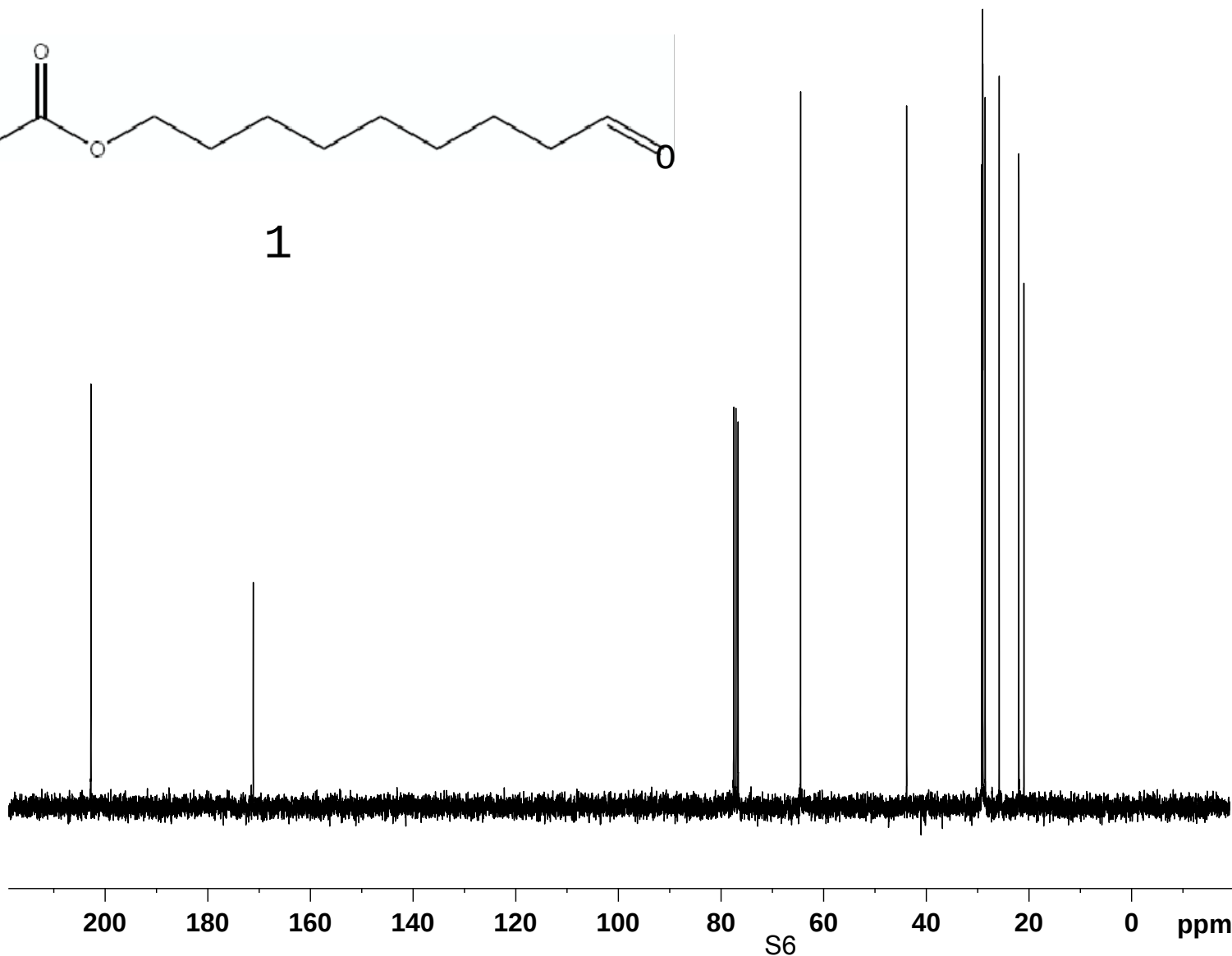
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SOLVENT CDC13
NS 62
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FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 8192
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DE 6.00 usec
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d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

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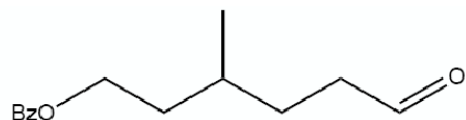
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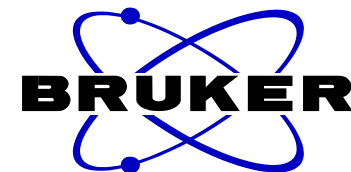
S6

ppm

1D Proton NMR



2



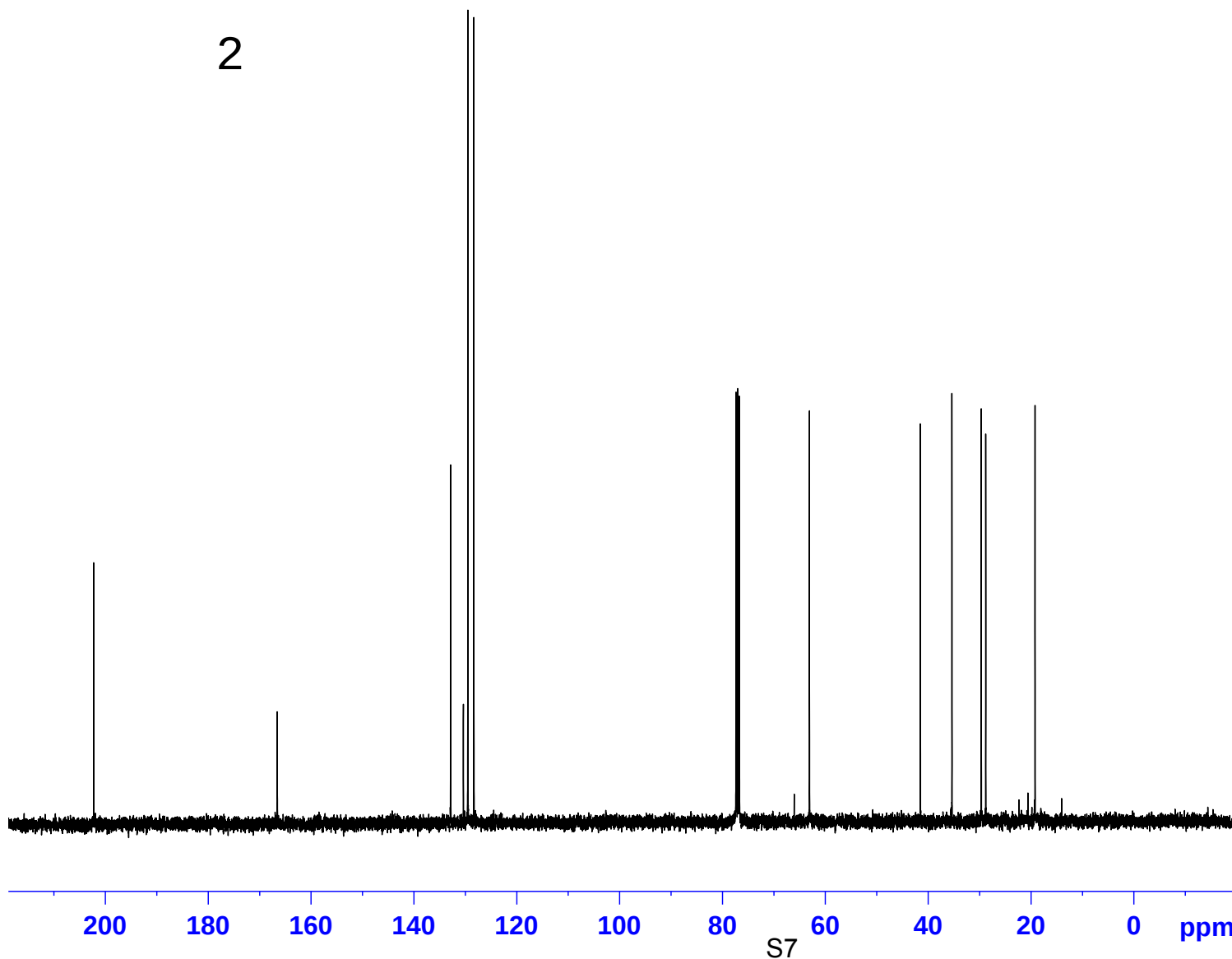
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TD 32768
SOLVENT CDCl3
NS 322
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FIDRES 0.731836 Hz
AQ 0.6832628 sec
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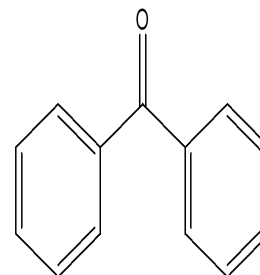
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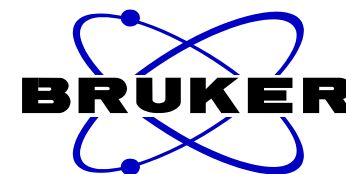
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PC 1.40



13C



3



Current Data Parameters

NAME ces-iii-87-F1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070918
Time 22.18
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PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 42
DS 4
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 32768
DW 27.800 usec
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TE 300.0 K
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d11 0.03000000 sec
DELTA 1.89999998 sec
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===== CHANNEL f1 =====

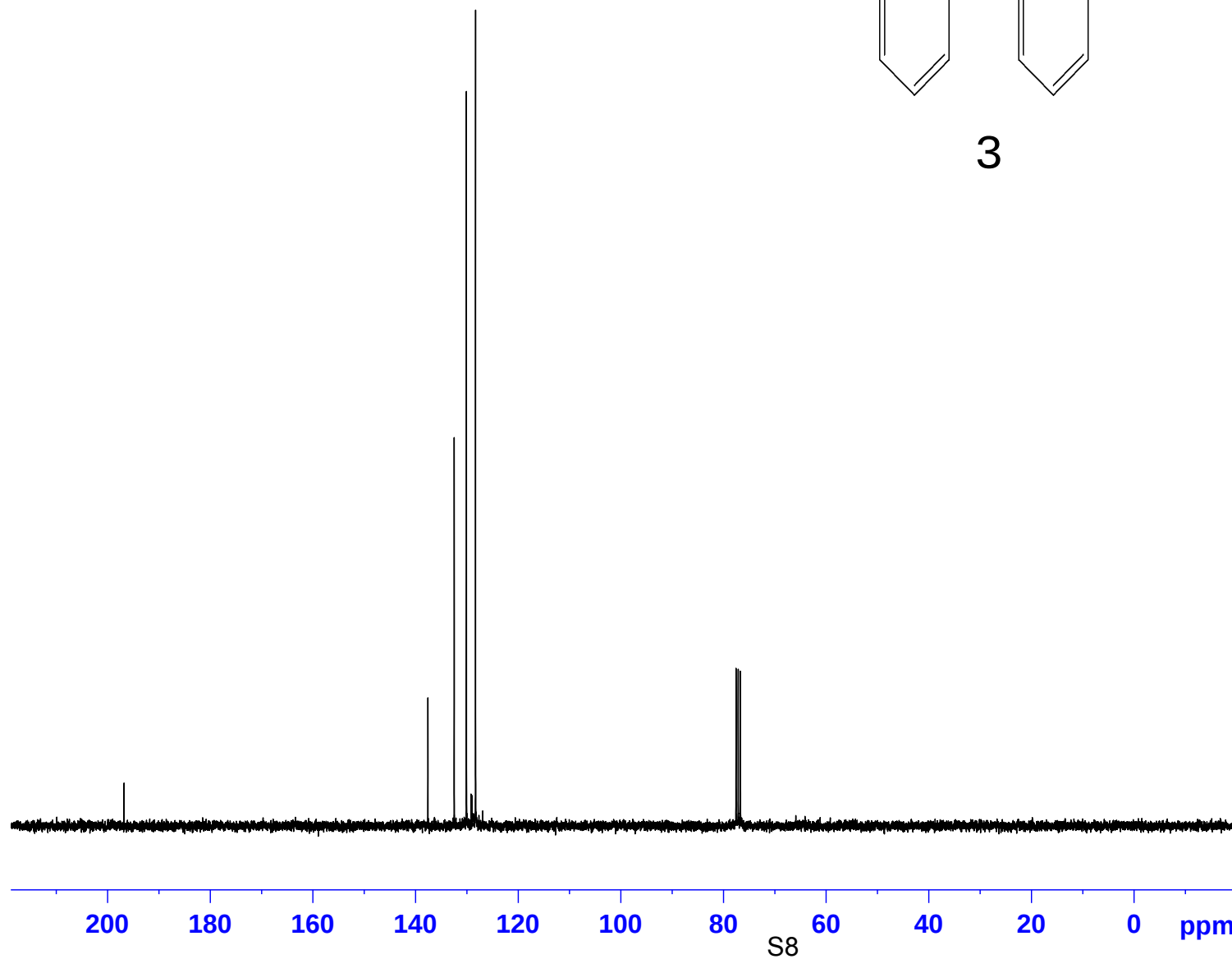
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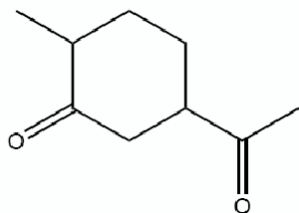
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PL13 21.16 dB
PL2 0.00 dB
SF02 300.1312005 MHz

F2 - Processing parameters

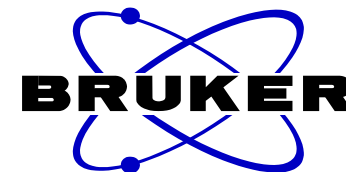
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1D Proton



4

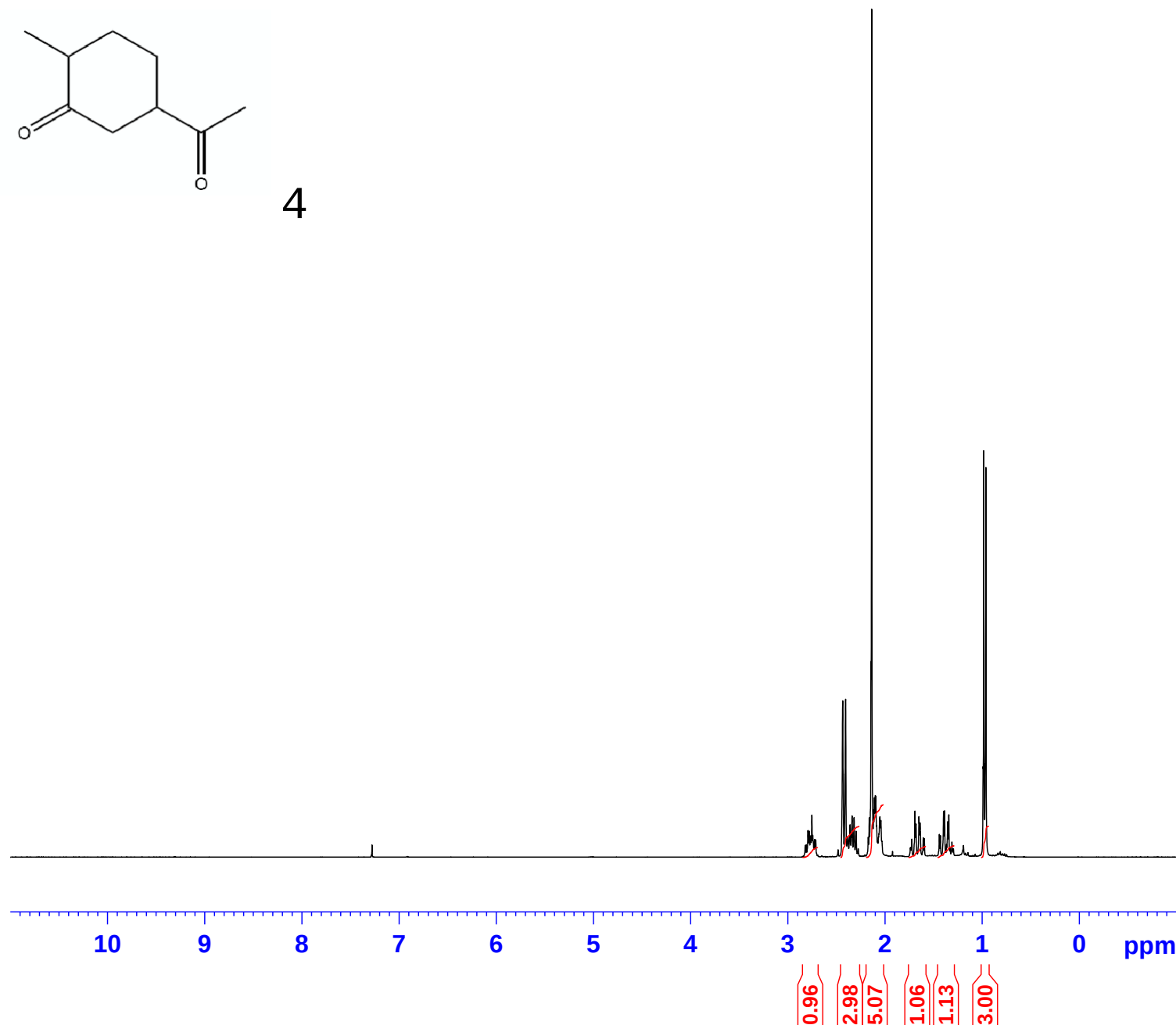


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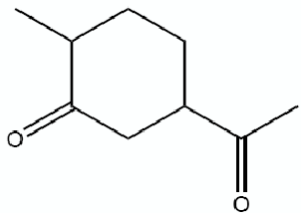
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FIDRES 0.188380 Hz
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RG 90.5
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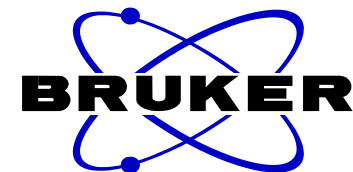
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13C



4



Current Data Parameters

NAME ces-iii-86-F2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

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SOLVENT CDCl3
NS 13
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FIDRES 0.548877 Hz
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RG 32768
DW 27.800 usec
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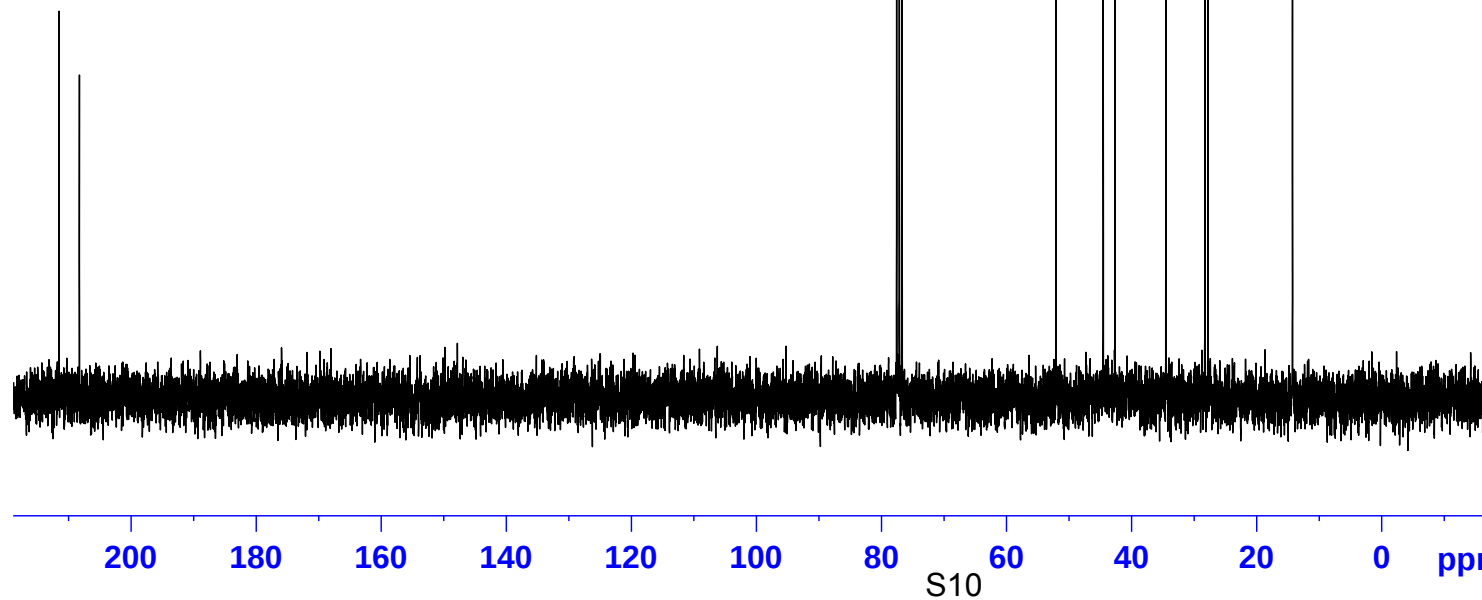
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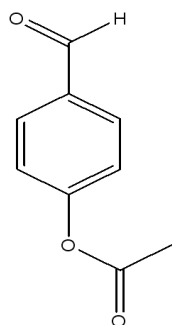
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S10

13C



5



Current Data Parameters

NAME ces-iii-96
EXPNO 2
PROCNO 1

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TD 32768
SOLVENT CDCl3
NS 74
DS 4
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 32768
DW 27.800 usec
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DELTA 1.89999998 sec
TD0 1

===== CHANNEL f1 =====

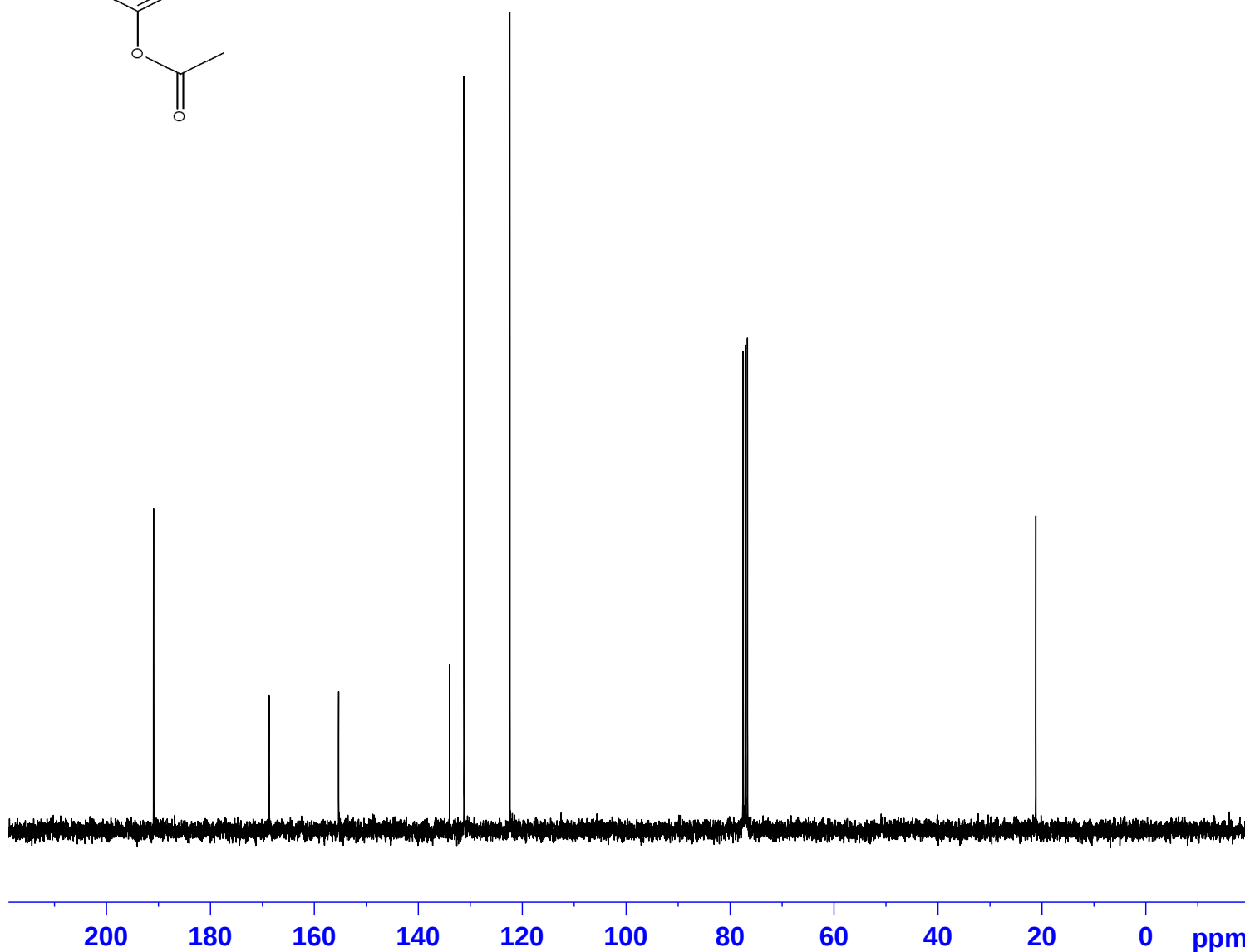
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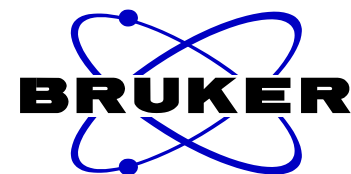
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F2 - Processing parameters

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S11



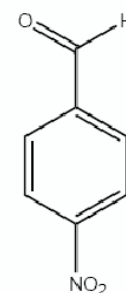
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FIDRES 0.731836 Hz
AQ 0.6832628 sec
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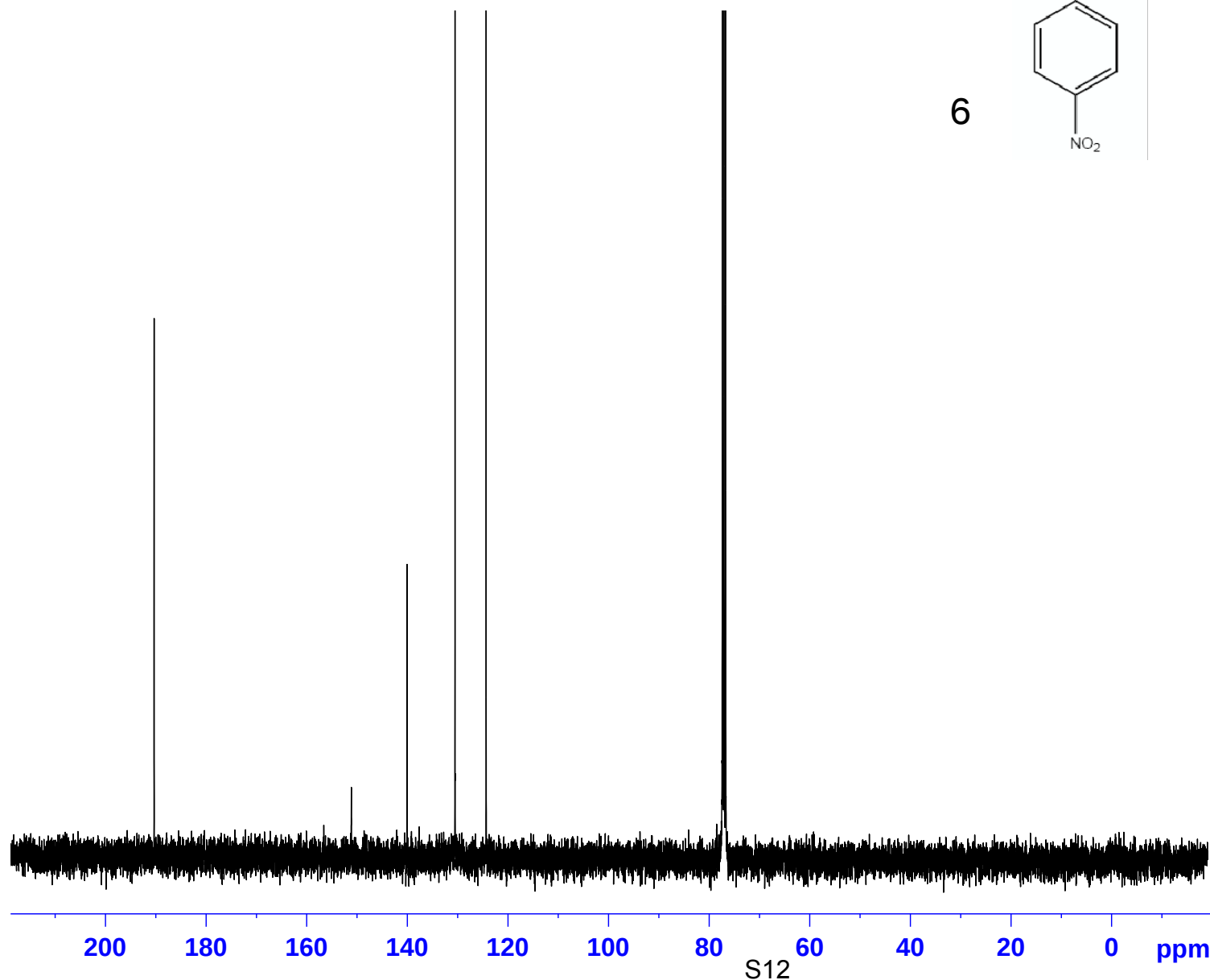
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PCPD2 70.00 usec
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PL13 13.82 dB
PL2 -4.00 dB
SF02 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



6



S12