Bis-Triazologlycolipid mimetics - Low molecular weight organogelator

Arasappan Hemamalini[a], Thangamuthu Mohan Das[a,b]*

[a]*Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai – 600 025, INDIA.*
[b]*Department of Chemistry, School of Basic and Applied Sciences, Central University of Tamil Nadu, Thiruvarur -610 004; Ph. No. +919489054264; Fax 04366 – 225312; E-mail: tmohandas@cutn.ac.in*

New J. Chem.
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

General procedure for *bis*-propargylated derivatives and its corresponding NMR data are provided in ESI.

^{1}H NMR, ^{13}C NMR, DEPT-135, 2D NMR and Mass spectrum are available in the ESI

Figure 6: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 3.

Figure 7: ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 3.

Figure 8: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 5a.

Figure 9: ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 5a.

Figure 10: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 7a.

Figure 11: ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 7a.

Figure 12: DEPT-135 spectrum (75 MHz, $CDCl_3$) of compound, 7a.

Figure 13: ^{1}H-^{13}C correlation spectrum (300 MHz, $CDCl_3$) of compound, 7a.

Figure 14: Mass spectrum of compound, 7a.

Figure 15: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 4.

Figure 16: ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 4.

Figure 17: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 6b.

Figure 18: ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 6b.

Figure 19: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 8b.

Figure 20: ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 8b.

Figure 21: DEPT-135 spectrum (75 MHz, $CDCl_3$) of compound, 8b.

Figure 22 Mass spectrum of compound, 8b.

Figure 23 ^{1}H NMR expansion spectrum (300 MHz, $CDCl_3$) of compound, 5a.

Figure 24 ^{1}H NMR expansion spectrum (300 MHz, $CDCl_3$) of compound, 6b.

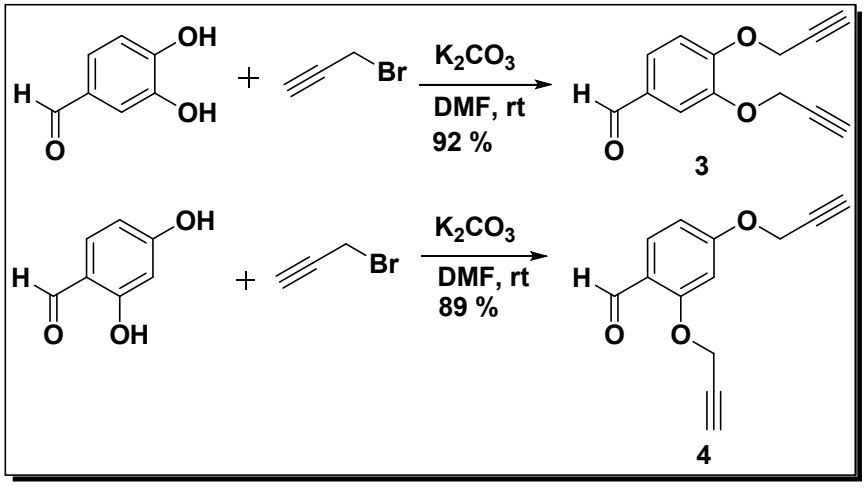
Figure 25 ^{1}H NMR expansion spectrum (300 MHz, $CDCl_3$) of compound, 7a.

Figure 26 ^{1}H NMR expansion spectrum (300 MHz, $CDCl_3$) of compound, 8b.

Table: 1 Optimisation of solvents

Entry No	Solvent	Yield (%)
1	Tertiary butanol	-
2	Acetonitrile	-
3	Tetrahydrofuran	89

While assigning the spectral data, several abbreviations were used and these include 'Ar' for aromatic, 'Sac' for saccharide 'Alk' for alkene and "trz" for triazole respectively.



Synthesis of *bis*-propargylated aldehydes (**3**) and (**4**).

1. General procedure for the synthesis of *bis* alkylated aldehyde, 3 & 4:

To a solution of dihydroxy benzaldehyde, (1 mmol) in dry DMF (15 ml) were added potassium carbonate (5 equiv.) and after stirring the solution for 5minutes vigorously, propargyl bromide (2.2 equiv.) was added and the reaction mixture kept for stirring for 24 hrs. After careful work up, the product was further purified by column chromatography.

Spectroscopic data for compounds **3** and **4** are as follows.

1.1 Physicochemical and spectrochemical data of 3,4-bis(prop-2-ynyloxy)benzaldehyde (3):

Colourless crystal, Yield: 89 % (0.19 g), mp 96-98 ºC, ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1H, -CHO), 7.51-7.45 (m, 2H, Ar-H), 7.11 (d, J = 8.1 Hz, 1H, Ar-H), 4.79 (d, J = 2.4 Hz, 2H, -CH_2), 4.76 (d, J = 2.4 Hz, 2H, -CH_2), 2.50 (m, 2H, -C≡H), ^{13}C NMR (75 MHz, $CDCl_3$) : δ 190.7, 152.7, 147.8, 130.8, 126.7, 113.2, 112.6, 77,7, 77.5, 76.7, 76.5, 56.8, 56.7. Elemental Analysis: C, 72.89; H, 4.71, Found: C, 72.82; H, 4.69.

1.2 Physicochemical and spectrochemical data of 2,4-bis(prop-2-ynyloxy)benzaldehyde (4):

Colourless crystal, Yield: 77 % (0.72 g), mp 104-106 ºC, ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.32 (s, 1H, -CHO), 7.85 (d, J = 9 Hz, 1H, Ar-H), 6.70 (s, 1H, Ar-H), 6.67 (d, J = 1.8 Hz, 1H, Ar-H), 4.81 (d, J = 2.4 Hz, 2H, -CH_2), 4.77 (d, J = 2.4 Hz, 2H, -CH_2), 2.60 (s, 2H, -C≡H), ^{13}C NMR (75 MHz, $CDCl_3$): δ:188.1, 163.6, 161.4, 130.6, 120.1, 107.5, 100.4, 77.5, 77.0, 76.7, 76.5, 56.5, 56.1, Elemental Analysis: C, 72.89; H, 4.71, Found: C, 72.85 ; H, 4.67.

2. General procedure for the synthesis of *α*, *β*-unsaturated *β*-C-glycosidic ketones, 5a, 5b, 6a, 6b:

To a solution of *β-C*-glycosidic ketone, **1**, **2** (1 mmol) in dry DCM (5 ml) were added pyrrolidine (30% mol) and *bis*-propargylated-benzaldehyde **3**, **4** (1.2 mmol). After stirring at room temperature for given period of time, the reaction mixture was evaporated under reduced pressure and extracted by EtOAc-water. The ethylacetate layer was dried over anhyd. Na_2SO_4 and concentrated to dryness. The product was

further purified by column chromatography.

Spectroscopic data for compounds **5a**, **5b**, **6a** and **6b** are as follows.

2.1 Physicochemical and spectral data for (E)-1-(4,6-*O*-butylidene-*β*-D-glucopyranosyl)-4-(3,4-bis prop-1'-oxo-2'-yne phenyl)-but-3-ene-2-one (5a)

White solid, Yield: 91 % (0.43 g), mp 156-158 ºC, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, J = 15.9 Hz, 1H, Alk-H), 7.28 (s, 1H, Ar-H), 7.22 (d, J = 8.4 Hz, 1H, Ar-H), 7.08 (d, J = 8.1 Hz, 1H, Ar-H), 6.68 (d, J = 16.2 Hz, 1H, Alk-H), 4.82 (s, 4H, -CH_2), 4.55 (t, J = 5Hz, 1H, Sac-H), 4.15 (dd, J = 3.9 Hz, J = 9.6 Hz, 1H, Sac-H),3.98-3.92 (m, 1H, Sac-H), 3.74 (t, J = 8.7 Hz, 1H, Sac-H), 3.47-3.35 (m, 3H, Sac-H), 3.26 (t, J = 9.0 Hz,1H, Sac-H), 3.17-3.11 (m, 2H, Sac-H, -CH_2), 2.97 (dd, J = 6.9 Hz, J = 16.1 Hz, -CH_2), 1.66-1.62 (m, 2H, -CH_2), 1.44 (q, J = 7.5 Hz, 2H, -CH_2), 0.94 (t, J = 7.2 Hz, 3H, Sac-H), ^{13}C NMR (75 MHz, $CDCl_3$) : δ:198.0, 149.9, 147.6, 143.5, 128.3, 125.1, 123.8, 114.2, 113.9, 102.5, 80.5,78.0, 77.9, 76.4, 76.4, 76.2, 75.4, 74.5, 70.6, 68.3, 57.0, 56.7, 43.4, 36.2, 30.9, 17.5, 13.9, Elemental Analysis: C, 66.37; H, 6.43, Found: C, 66.35; H, 6.41.

2.2 Physicochemical and spectral data for (E)-1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-4-(3,4-bis prop-1'-oxo-2'-yne phenyl)-but-3-ene-2-one (5b)

Syrupy liquid, Yield: 89 % (0.52 g), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, J = 16.2 Hz, 1H, Alk-H), 7.28 (m, 2H, Ar-H), 7.27 (d, J = 8.4 Hz, Ar-H), 7.07 (d, J = 8.4 Hz, 1H, Ar-H), 6.63 (d, J = 16.2 Hz, 1H, Alk-H), 5.24 (t, J = 9.3 Hz, 1H, Sac-H), 5.08 (t, J = 9.8 Hz, 1H, Sac-H), 4.99 (t, J = 9.6 Hz, 1H, Sac-H), 4.81 (d, J = 2.4 Hz, 4H, -CH_2), 4.26 (dd, J = 4.8 Hz, J = 12.6 Hz, 1H, Sac-H), 4.15-4.12 (m, 1H, Sac-H), 4.03 (dd, J = 2.1 Hz, J = 12.3 Hz, 1H, Sac-H), 3.74-3.70 (m, 1H, Sac-H), 3.02 (dd, J = 8.4 Hz, J = 16.2 Hz, 1H, -CH_2), 2.67 (dd, J = 3.2 Hz, J = 16.2 Hz, 1H, -CH_2), 2.58-2.55 (m, 2H, -C≡C), 2.02 (t, J = 2.9 Hz, 12H, -$OCOCH_3$), ^{13}C NMR (75 MHz, $CDCl_3$) : δ 196.0, 170.6,170.2, 170.0, 169.6,

149.9, 147.6,143.4, 128.2, 125.0, 123.8, 114.2, 113.7, 78.0, 77.9, 76.6, 76.4, 75.7, 74.2, 71.7, 68.5, 62.1, 56.9, 56.7, 42.5,29.7, 20.7 (2C), 20.6, Elemental Analysis: C, 61.64; H, 5.52, Found: C, 61.60; H, 5.49; N, 32.81.

2.3 Physicochemical and spectral data for (E)-1-(4,6-*O*-butylidene-*β*-D-glucopyranosyl)-4-(2,4-bis prop-1'-oxo-2'-yne phenyl)-but-3-ene-2-one (6a)

Syrupy liquid, Yield: 79 % (0.89 g), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, J = 16.2 Hz, 1H, Alk-H), 7.52 (d, J = 8.7 Hz, 1H, Ar-H), 6.77 (s, 1H, Ar-H), 6.72-6.62 (m, 2H, Ar-H, Alk-H), 4.77 (d, J = 2.4 Hz, 2H, -CH_2), 4.74 (d, J = 2.4 Hz, 2H, -CH_2), 4.53 (t, J = 5.1 Hz, 1H, Ace-H), 4.16-4.11 (m, 2H, Sac-H), 3.96-3.89 (m, 1H, Sac-H), 3.73 (t, J = 8.7 Hz, 1H, Sac-H), 3.43 (t, J = 8.9 Hz, 2H, Sac-H), 3.25 (t, J = 9.0 Hz, 1H, Sac-H), 3.11 (dd, J = 4.3 Hz, J = 16.2 Hz, 1H, -CH_2), 2.99 (dd, J = 6.9 Hz, J = 16.1 Hz, 1H, -CH_2), 2.57 (t, 2.1 Hz, 2H, -C≡CH), 1.65-1.60 (m, 2H, -CH_2), 1.42 (q, J = 7.8 Hz, 2H, -CH_2), 0.92 (t, J = 7.4 Hz, 3H, -CH_3), ^{13}C NMR (75 MHz, $CDCl_3$) : δ 198.6, 160.7, 157.8, 138.7, 130.0, 125.3, 117.7, 107.4, 102.5, 100.8, 80.4, 77.9, 75.4, 74.8, 70.6, 68.4, 56.3, 56.0, 43.3, 36.2, 17.5, 13.9, Elemental Analysis: C, 66.37; H, 6.43, Found: C, 66.33; H, 6.38.

2.4 Physicochemical and spectral data for (E)-1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-4-(2,4-bis prop-1'-oxo-2'-yne phenyl)-but-3-ene-2-one (6b)

Syrupy liquid, Yield: 79 % (0.89 g), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, J = 16.2 Hz, 1H, Alk-H), 7.52 (d, J = 8.7 Hz, 1H, Ar-H), 6.75-6.63 (m, 3H, Alk-H, Ar-H), 5.23 (t, J = 9.3 Hz, 1H, Sac-H), 5.08 (t, J = 9.8 Hz, 1H, Sac-H), 4.99 (t, J = 9.8 Hz, 1H, Sac-H), 4.79 (s, 2H, -CH_2), 4.74 (s, 2H, -CH_2), 4.27 (dd, J = 4.8 Hz, J = 12.3 Hz, 1H, Sac-H), 4.16-4.00 (m, 4H, Sac-H), 3.72 (dd, J = 3H, J = 9.8 Hz, 1H, Sac-H), 3.02 (dd, J = 8.4 Hz, J = 16.2 Hz, 1H, Sac-H), 2.67 (dd, J = 3 Hz, J = 16.2 Hz, 1H, Sac-H), 2.59 (d, J = 2.1 Hz,

2H, -C≡H), 2.05-2.01 (m, 12H, -$COCH_3$), ^{13}C NMR (75 MHz, $CDCl_3$) : δ 196.5, 170.7, 170.3, 170.0, 169.6, 160.7, 157.8, 138.5, 130.1, 125.2, 117.6, 107.4, 100.8, 77.9, 77.8, 76.5, 76.2, 75.7, 74.3 (2C), 71.8, 68.6, 62.1, 60.4, 56.3, 56.0, 42.3, 30.9, 21.0, 20.7 (2C), 20.6 (2C), 14.2, Elemental Analysis: C, 61.64; H, 5.52, Found: C, 61.61 ; H, 5.47.

Synthesis of Gels:

The gelation ablity of the bis-triazologlycolipids was determined by the "inversion tube method." All the synthesized triazologlycolipids was tested for gelation by the method where 1 mg of the compound was dissolved in 1 mL of the solvent in a close capped vial to result in 1% CGC. The mixture was heated till all the solid gets dissolved and the vial was cooled to 25 °C and left for 12h at this temperature and then turned upside down. When the gelator formed is immobilized at this stage, it is said to be a Gel and it is denoted by "G". Some of them forms partial gel is denoted as "PG". Some of them which are insoluble is represented as "I" and those which got precipitated is denoted as "P".

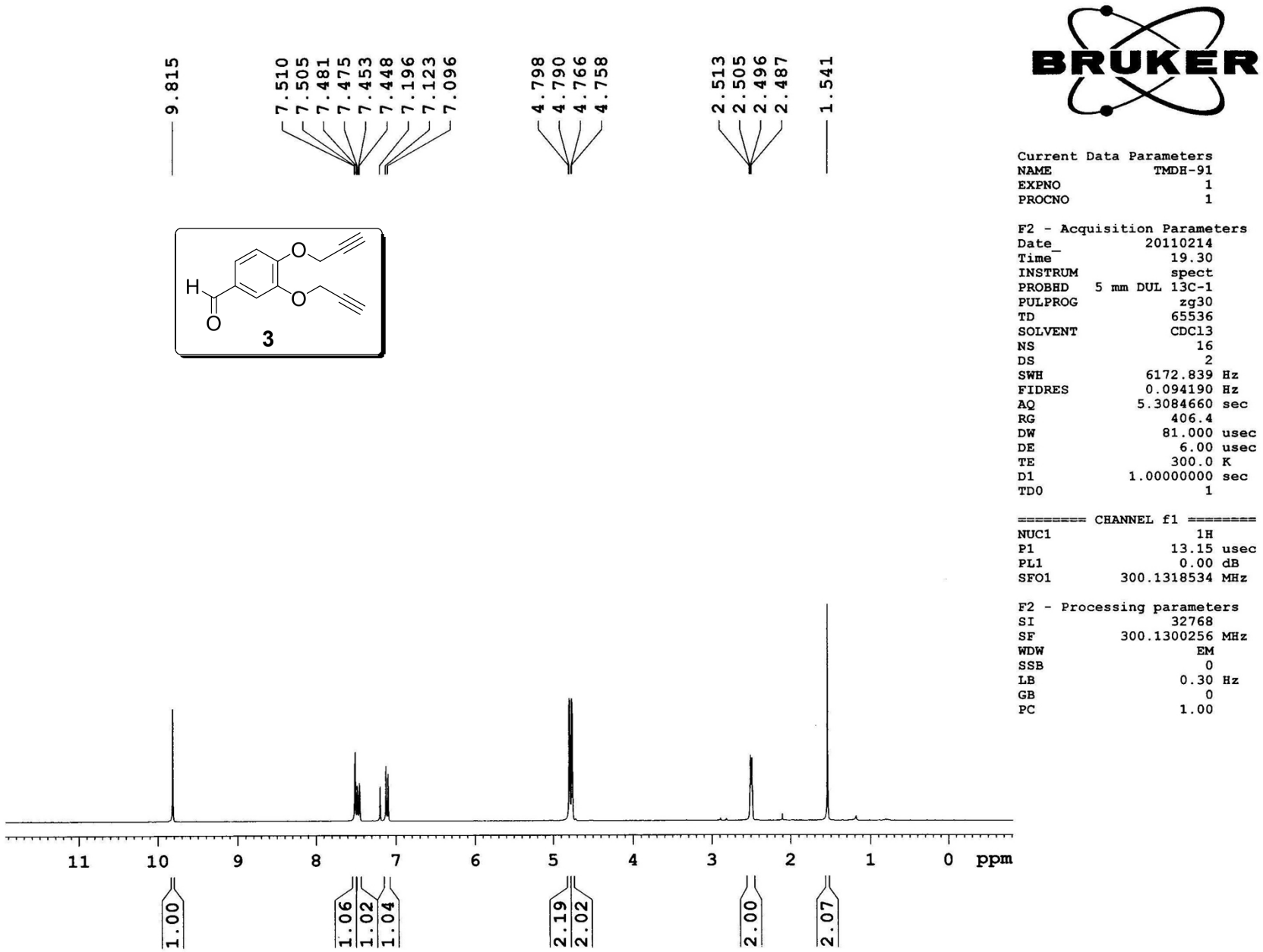
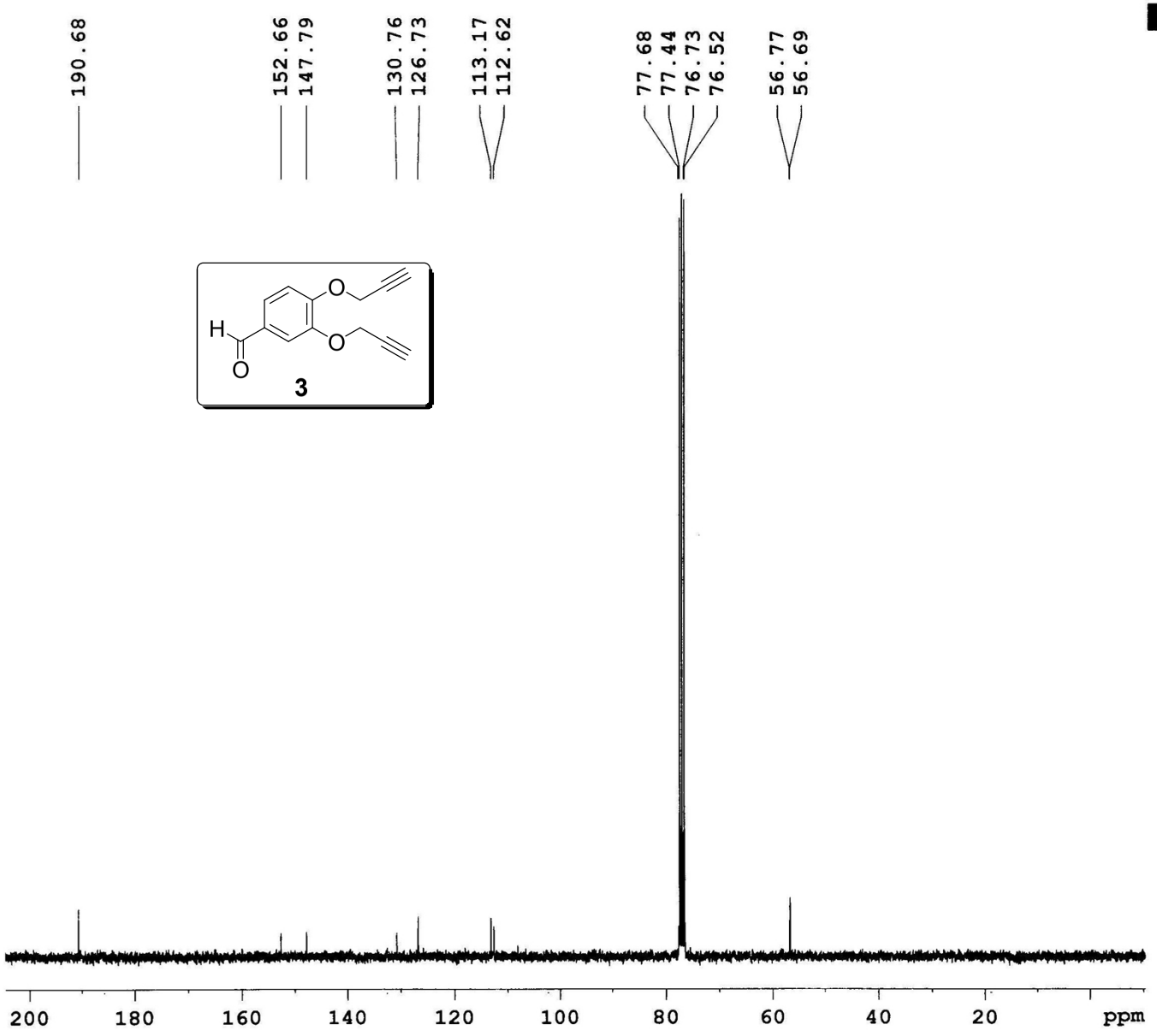


Figure 6 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 3.




```
Current Data Parameters
NAME                  TMDH-91
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20110214
Time                  19.44
INSTRUM               spect
PROBHD    5 mm DUL 13C-1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     433
DS                       4
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                     362
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                    7.40 usec
PL1                  -2.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.68 dB
PL13                 16.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                     32768
SF              75.4677490 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40
```

Figure 7 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 3.

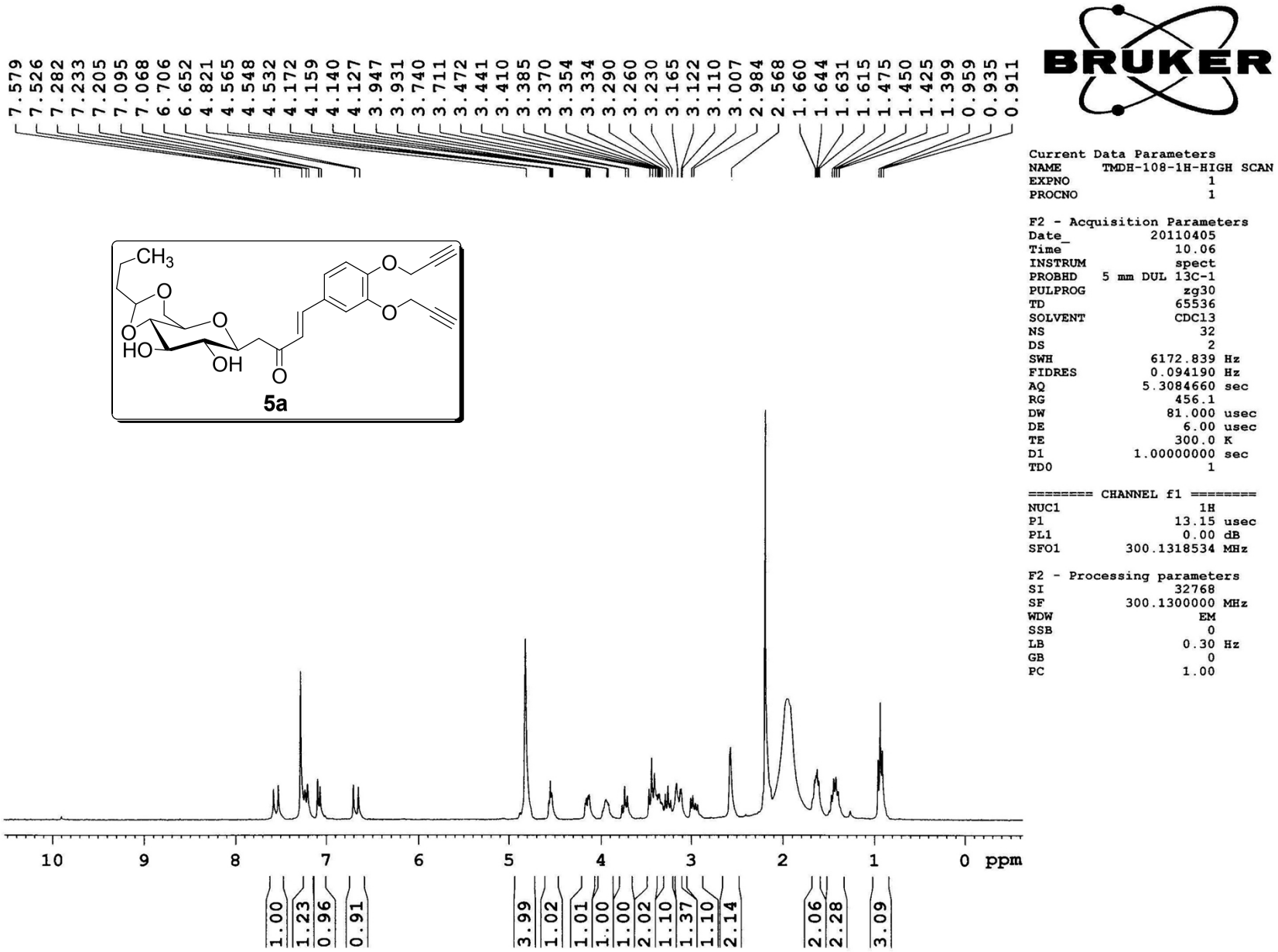
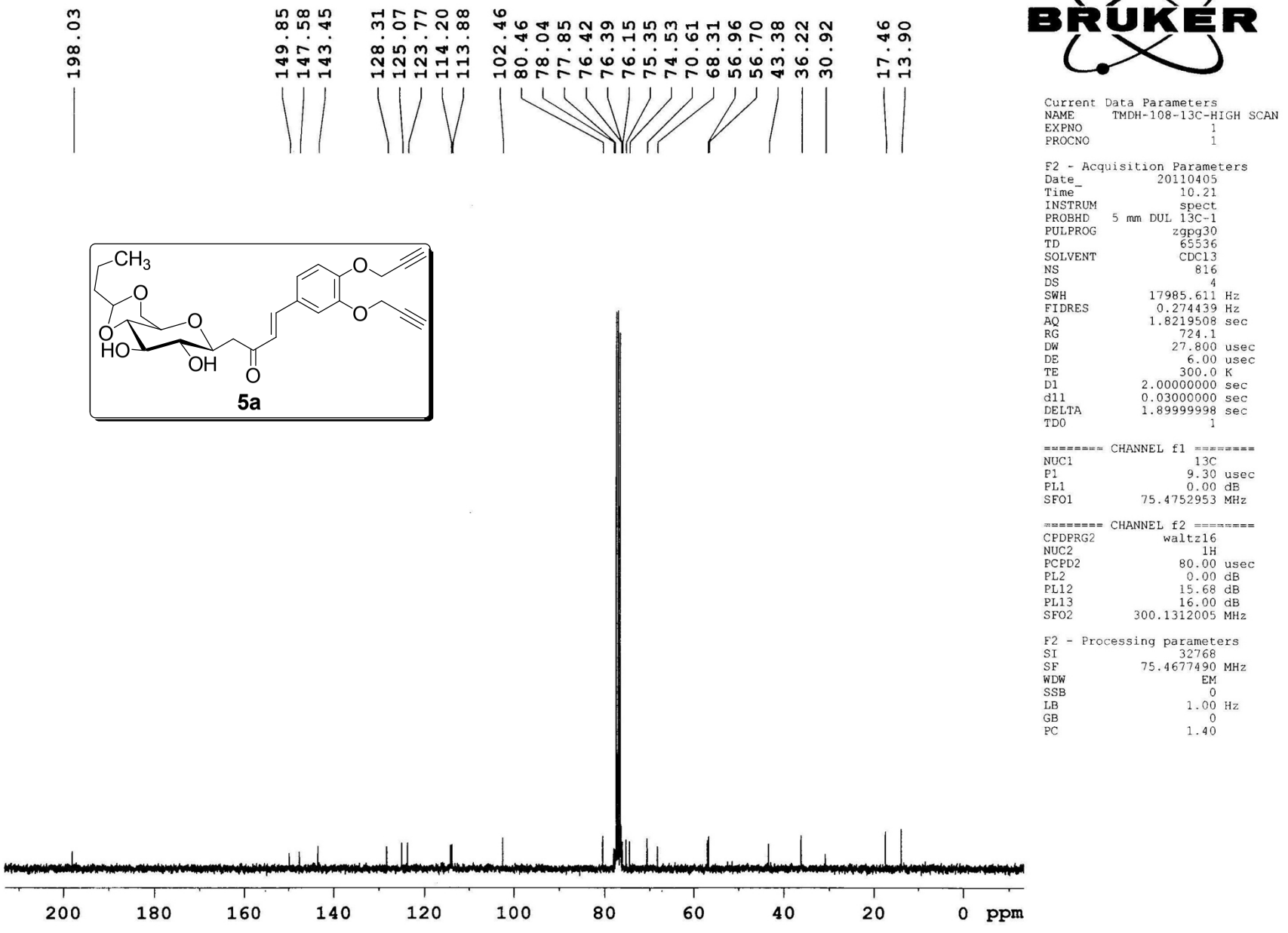


Figure 8 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 5a.



BRUKER

```
Current Data Parameters
NAME      TMDH-108-13C-HIGH SCAN
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110405
Time                10.21
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   816
DS                     4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                 724.1
DW                27.800 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.30 usec
PL1                 0.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.68 dB
PL13               16.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure 9 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 5a.

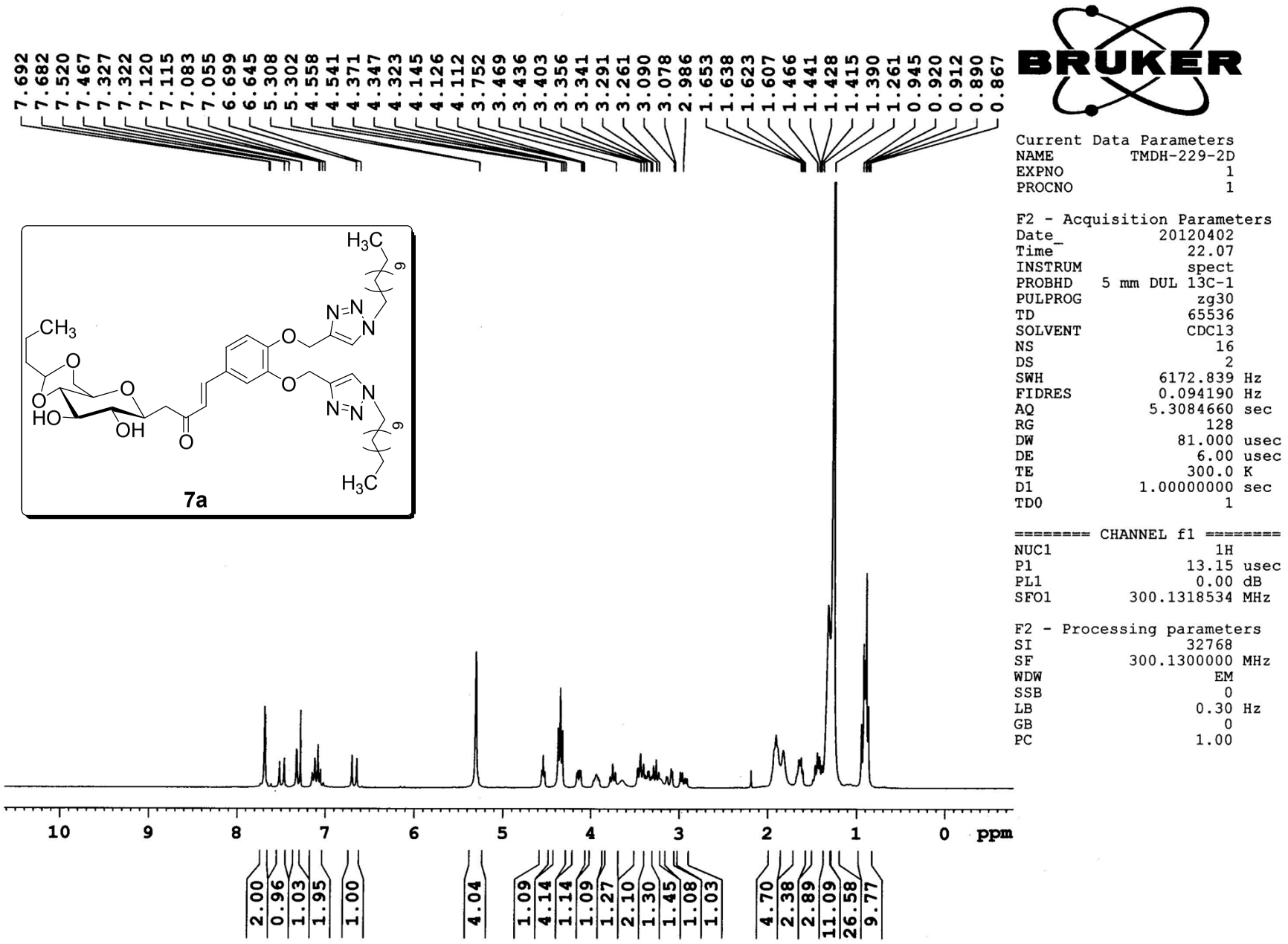


Figure 10 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 7a.

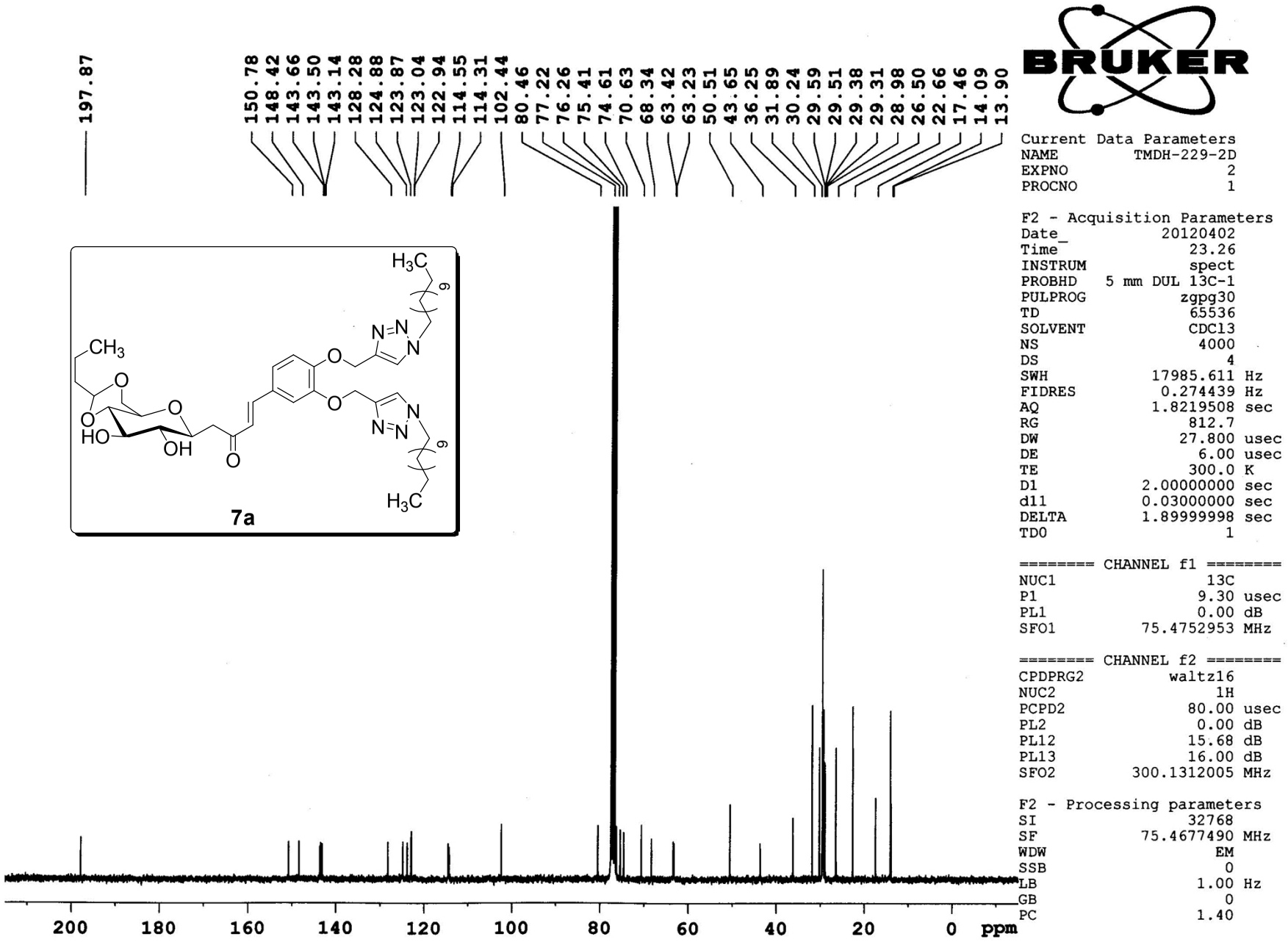


Figure 11 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 7a.

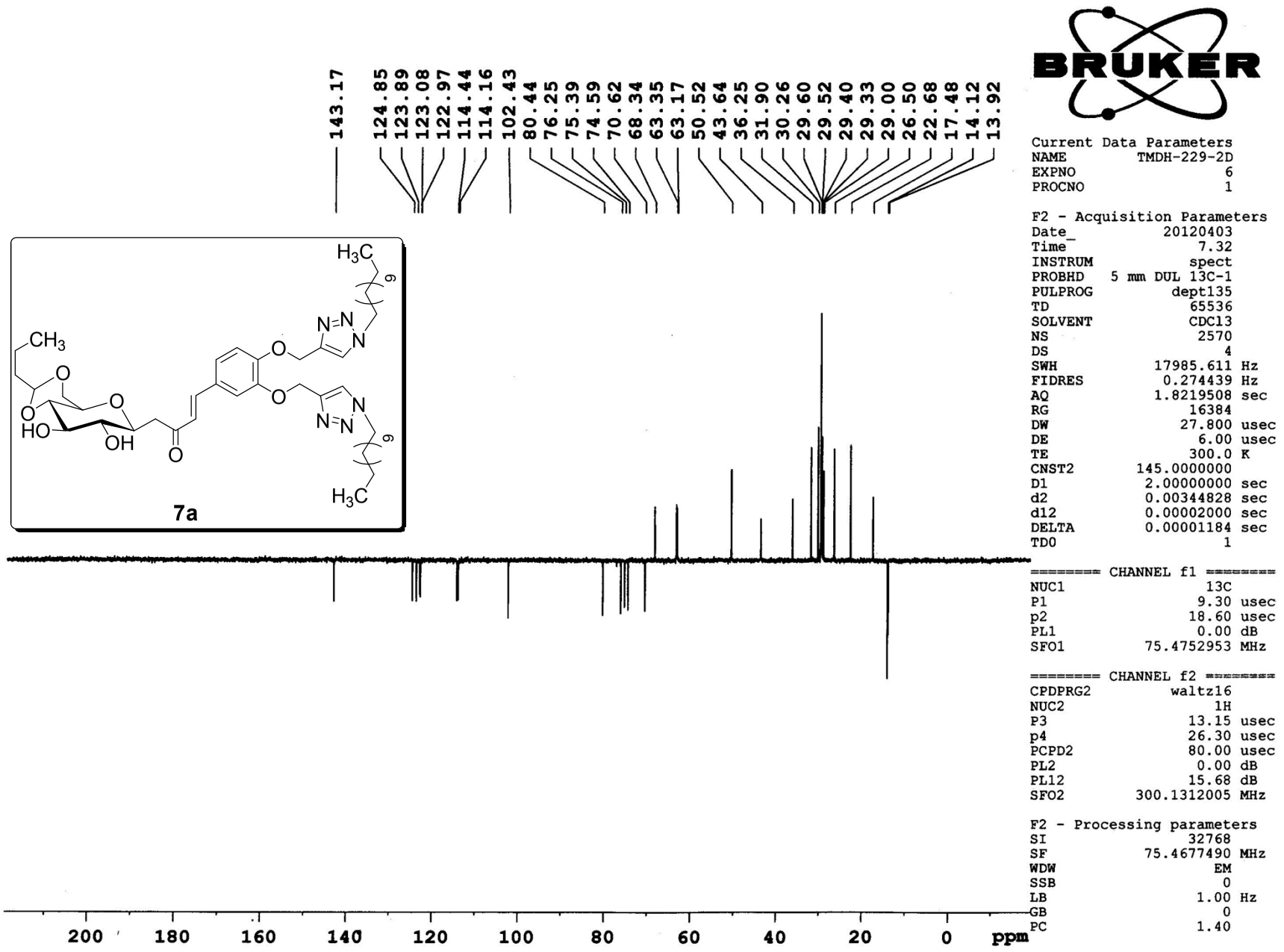


Figure 12 DEPT-135 spectrum (75 MHz, $CDCl_3$) of compound, 7a.

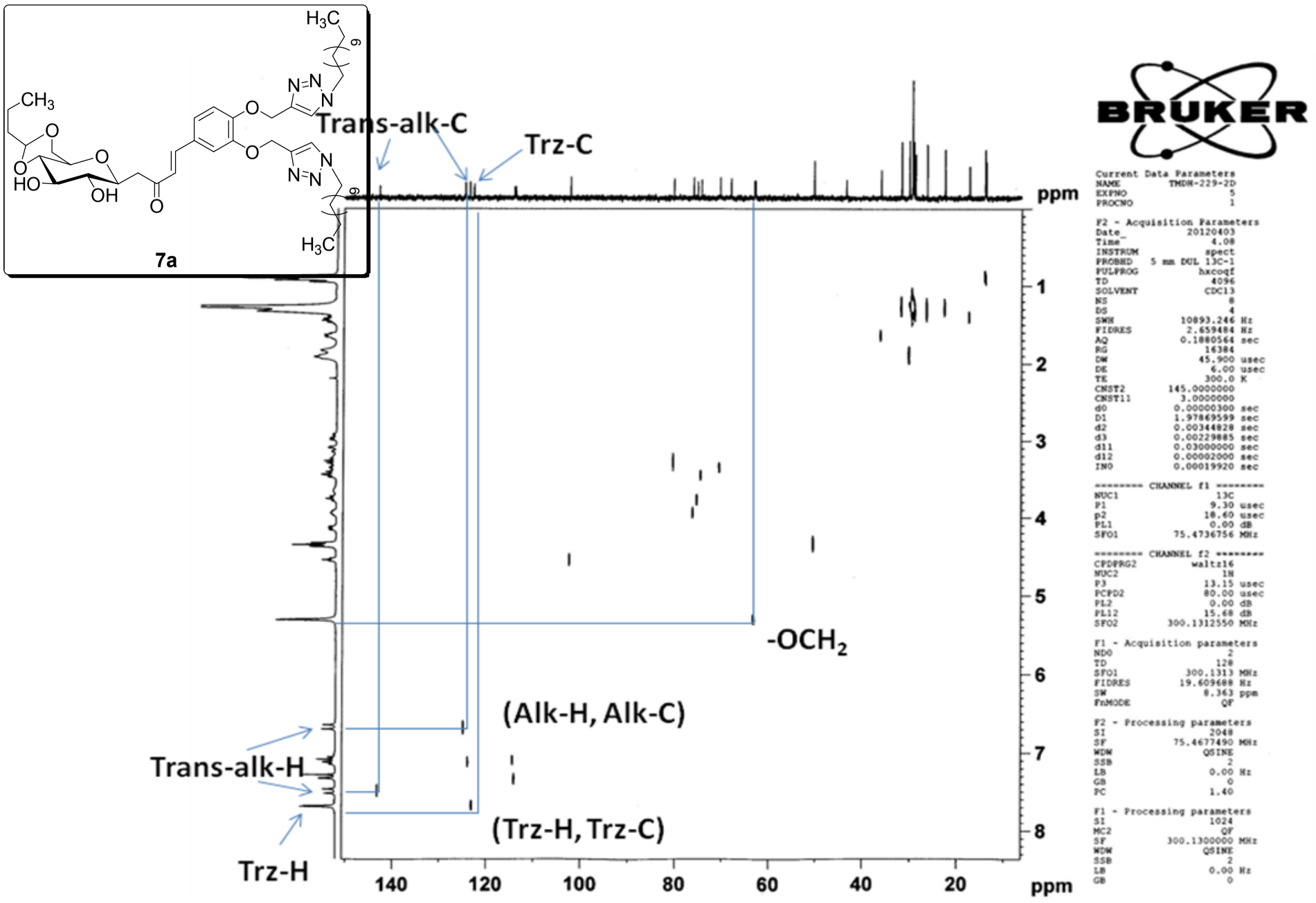


Figure 13 ^{1}H-^{13}C correlation spectrum (300 MHz, 75 MHz, $CDCl_3$) of compound, 7a.

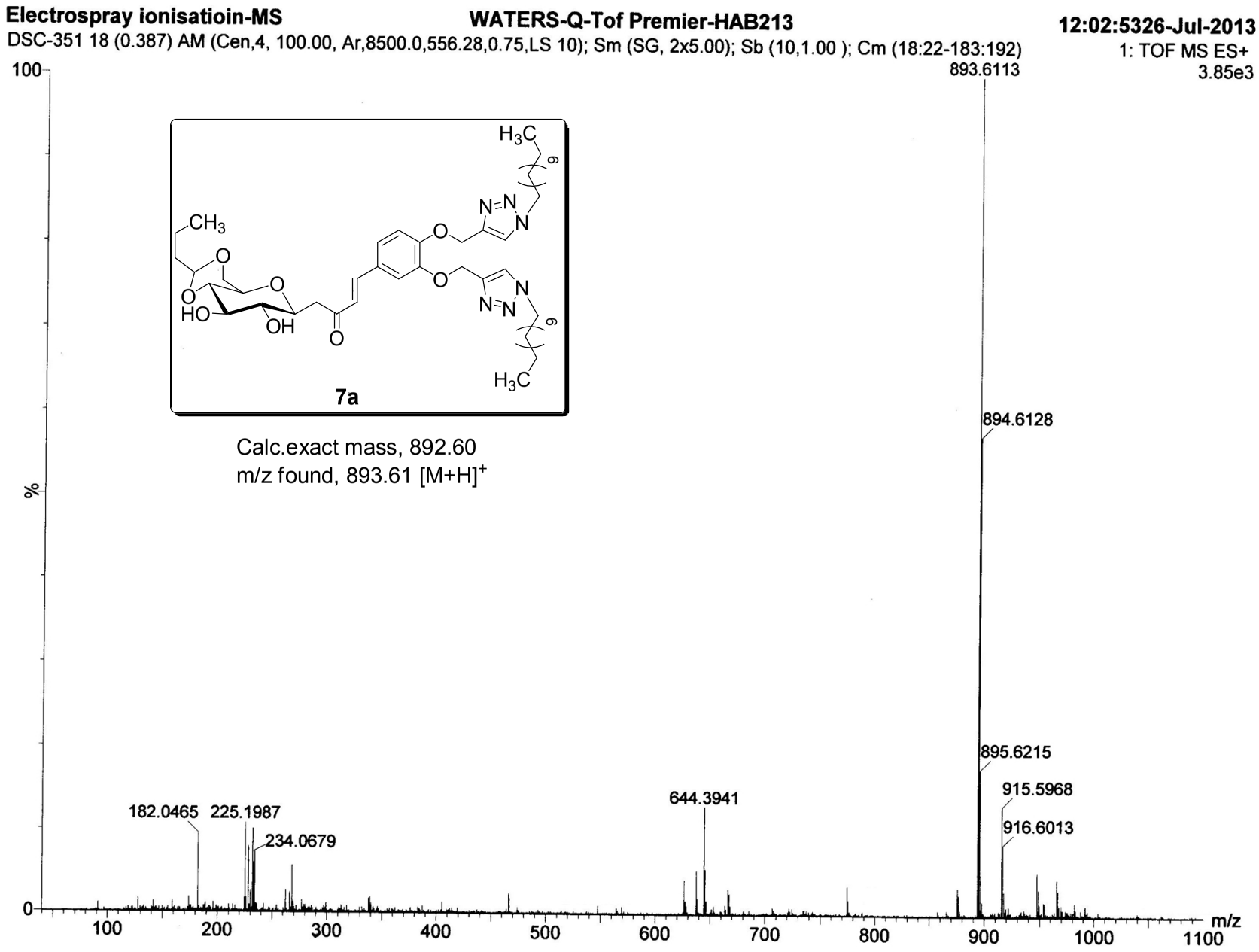


Figure 14 Mass spectrum of compound, 7a.

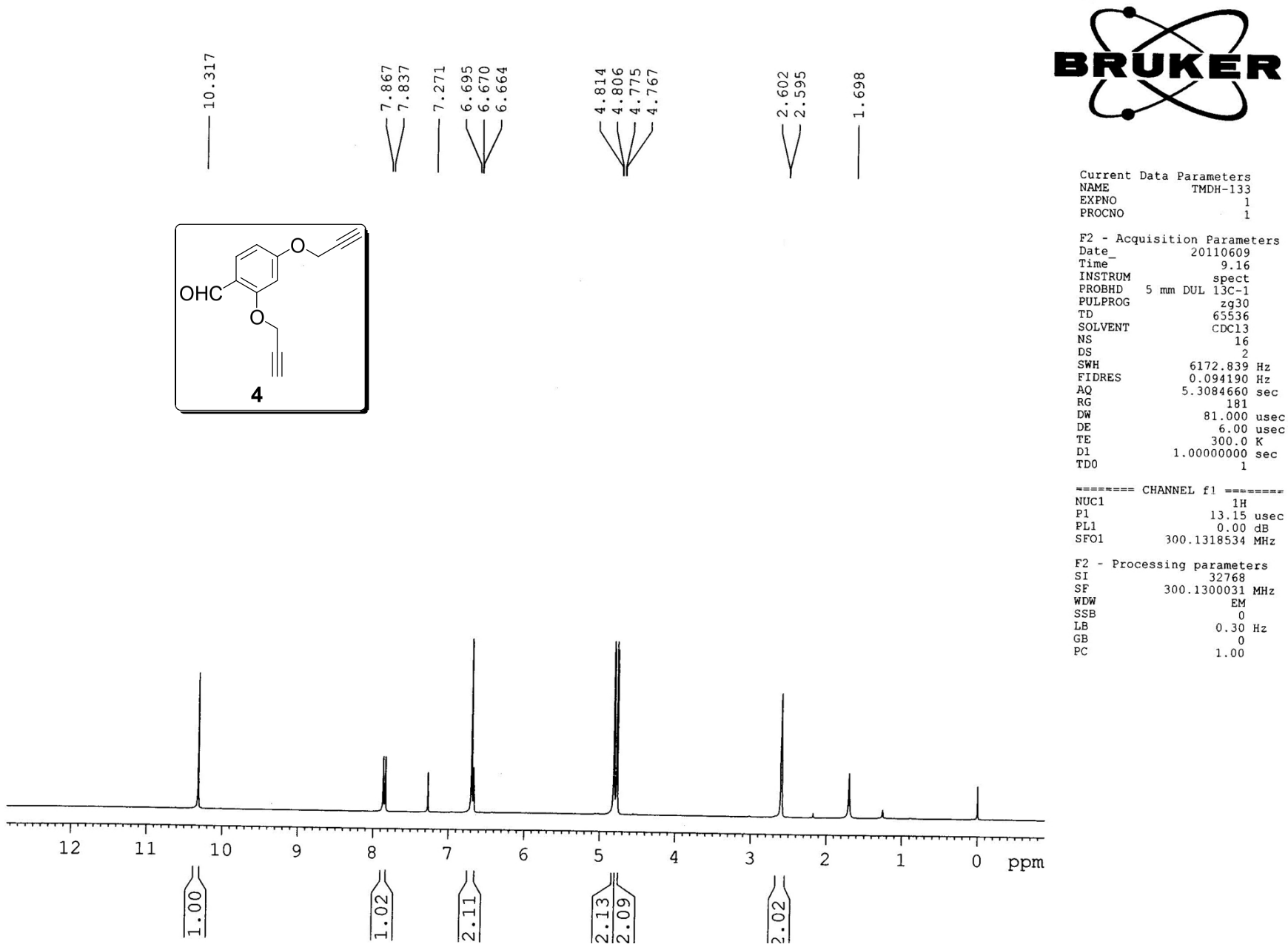
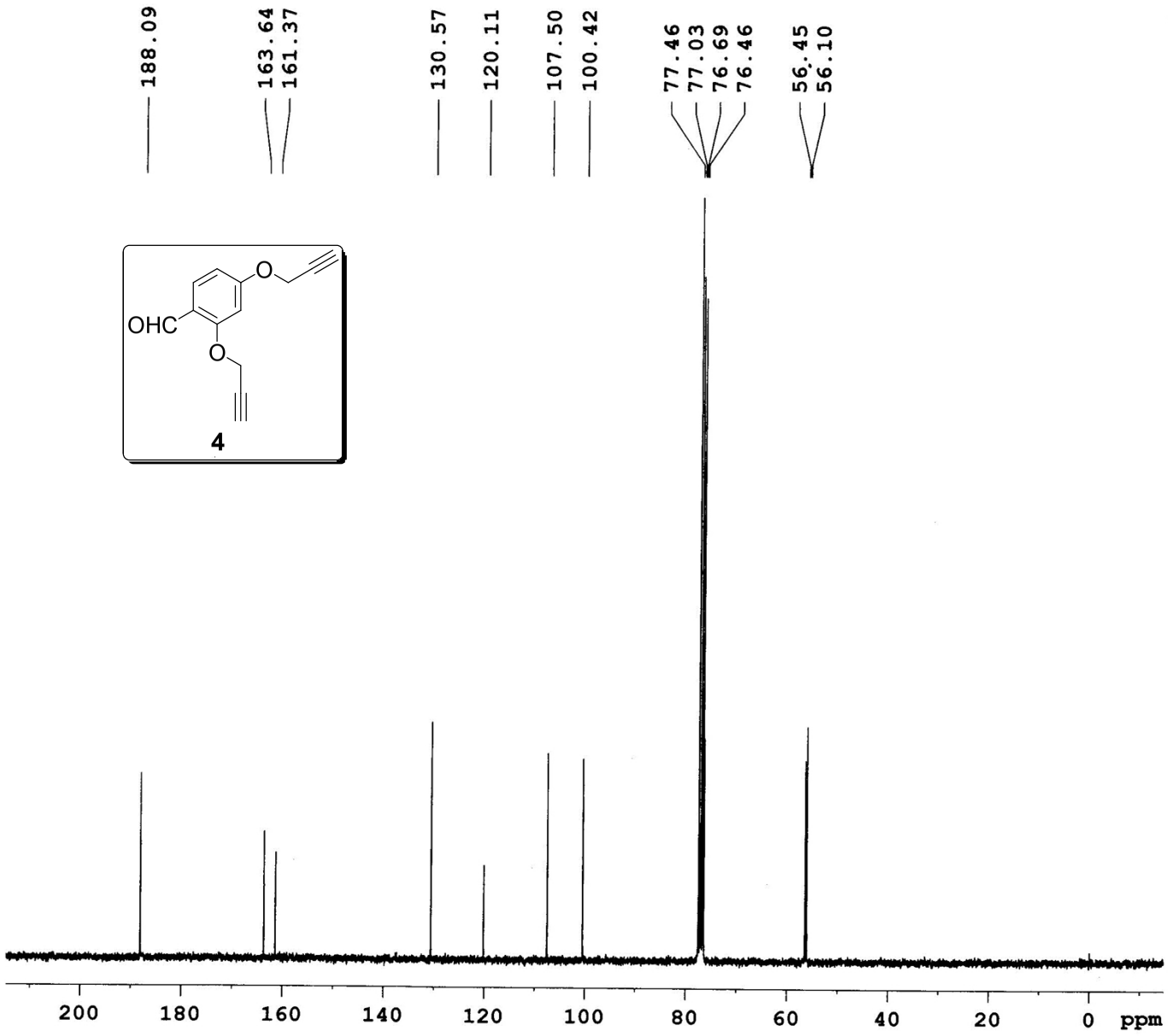


Figure 15 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 4.



BRUKER

```
Current Data Parameters
NAME                  TMDH-133
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20110609
Time                      9.24
INSTRUM                  spect
PROBHD     5 mm DUL 13C-1
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         810
DS                           4
SWH                17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                         512
DW                    27.800 usec
DE                     6.00 usec
TE                     300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.30 usec
PL1                      0.00 dB
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    15.68 dB
PL13                    16.00 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF                75.4677490 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                       1.40
```

Figure 16 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 4.

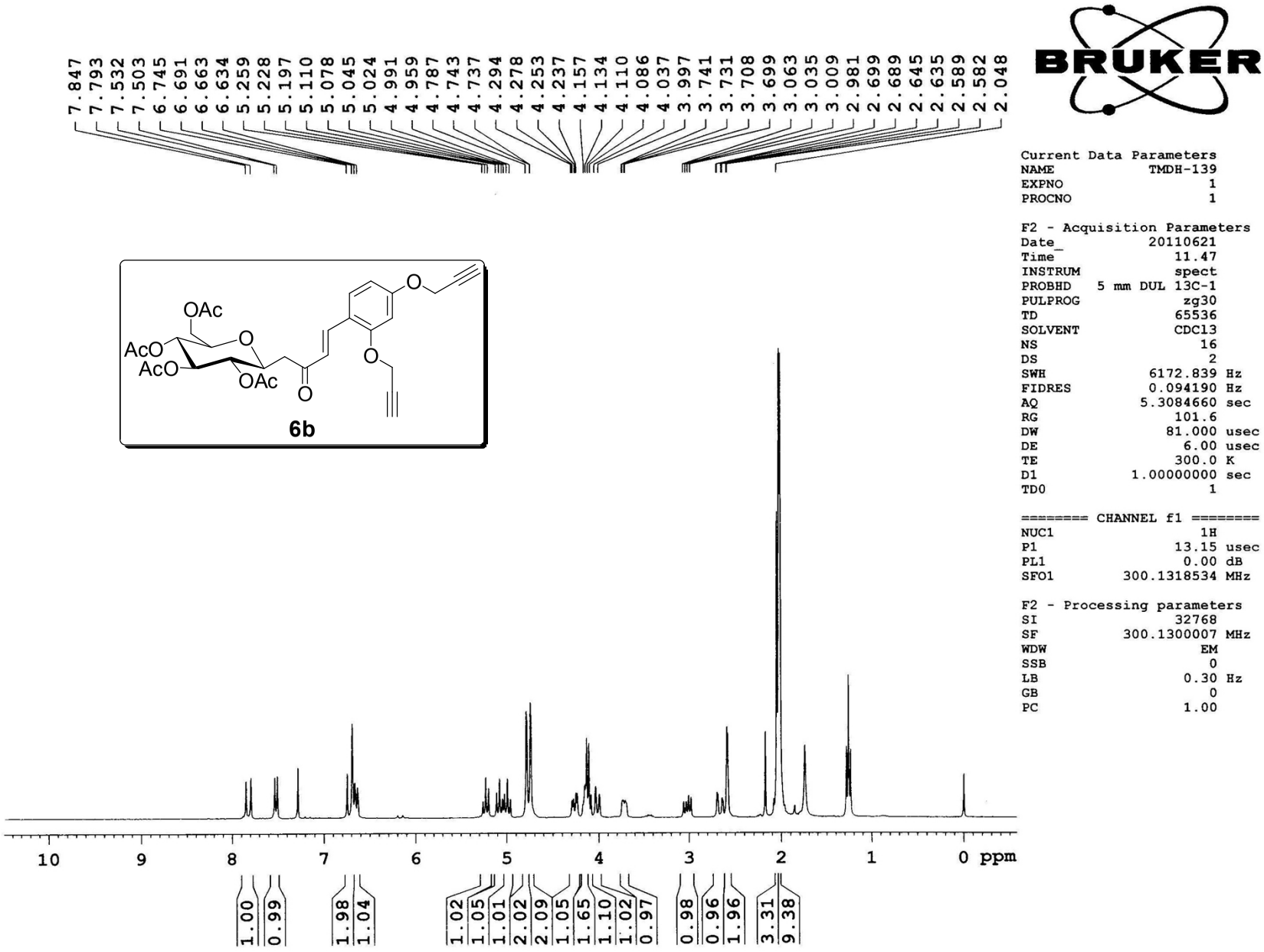
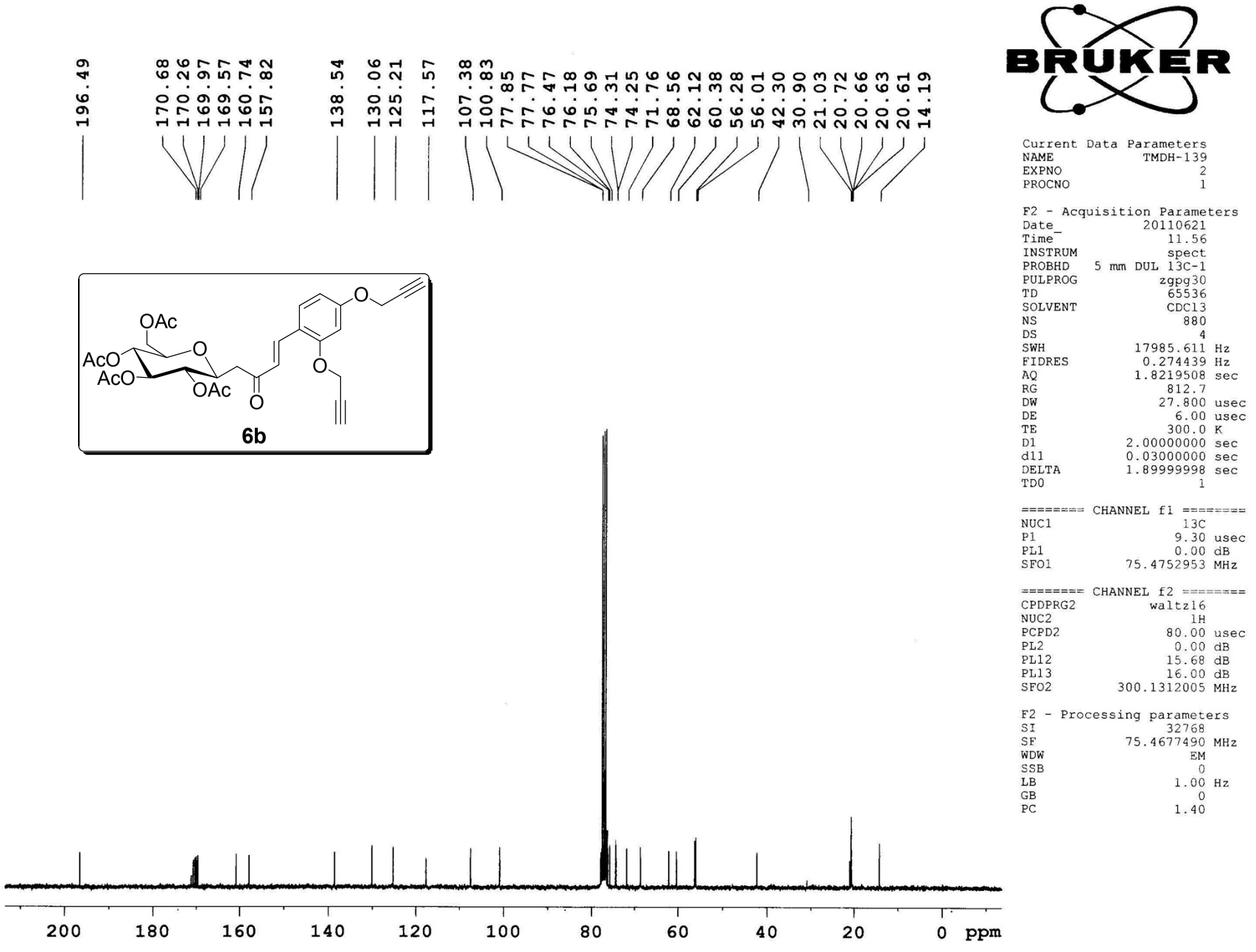


Figure 17 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 6b.



BRUKER

Current Data Parameters
NAME TMDH-139
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110621
Time 11.56
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 880
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 812.7
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.68 dB
PL13 16.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure 18 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 6b.

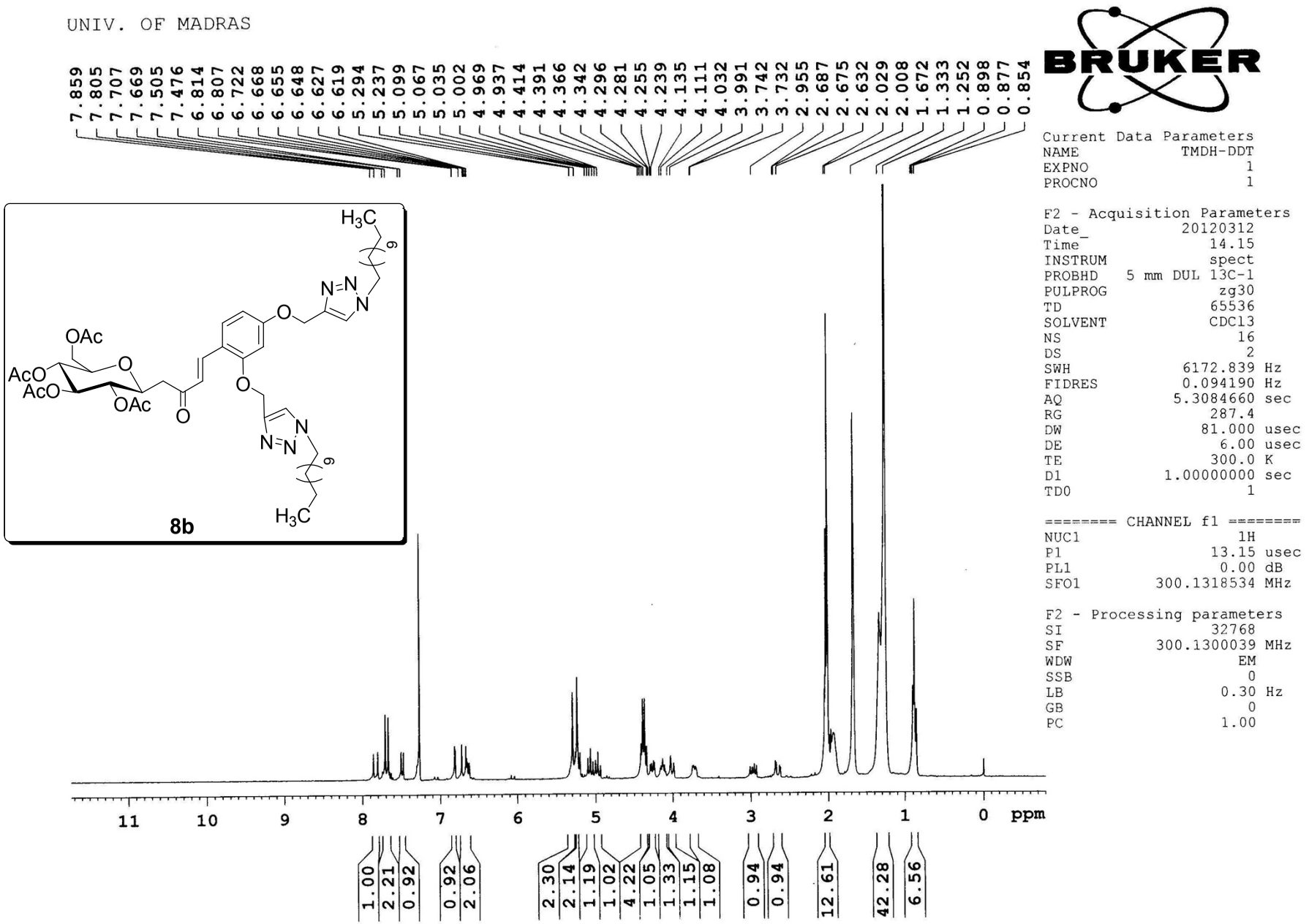


Figure 19 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound, 8b.

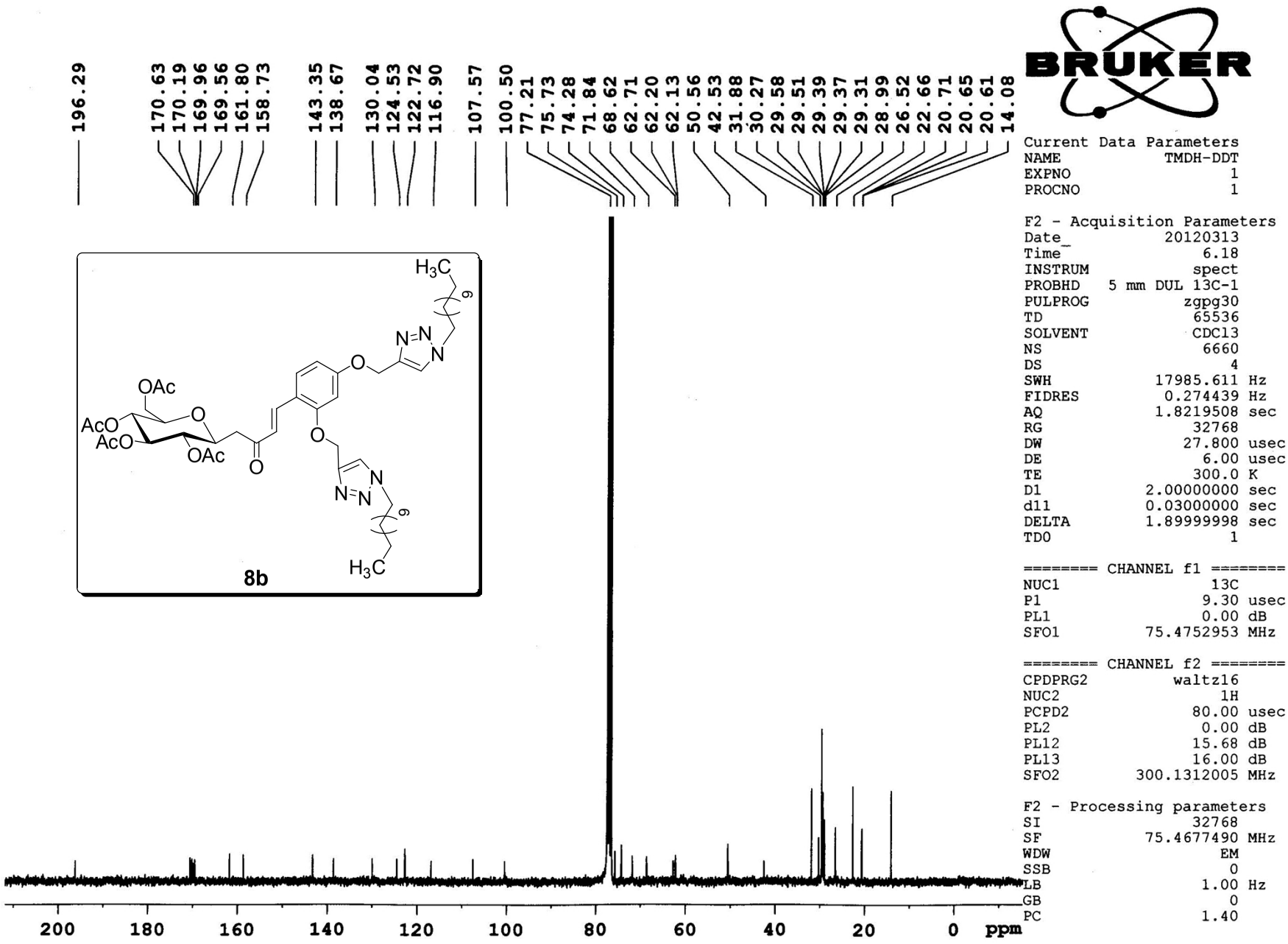


Figure 20 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound, 8b.

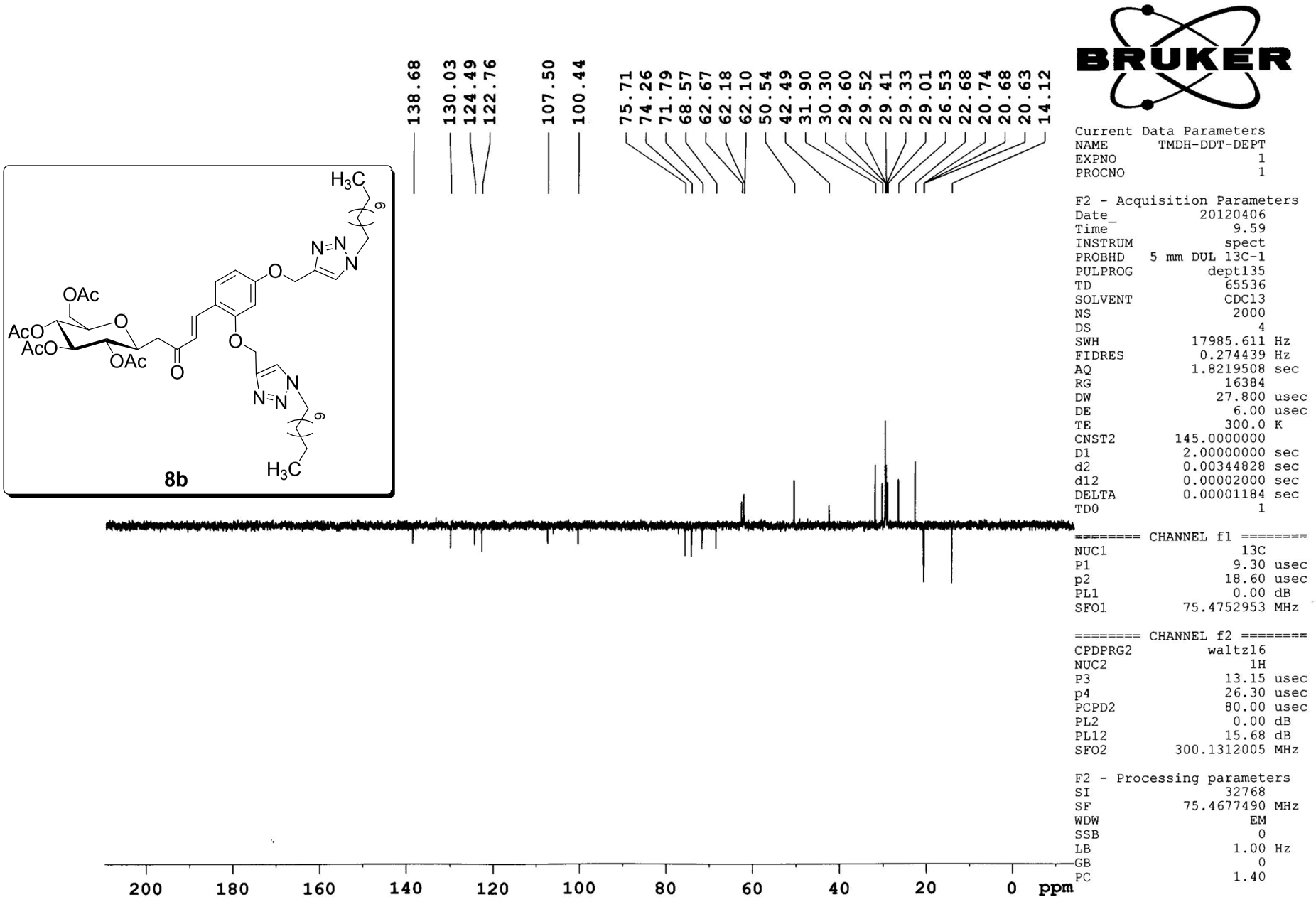


Figure 21 DEPT-135 spectrum (75 MHz, $CDCl_3$) of compound, 8b.

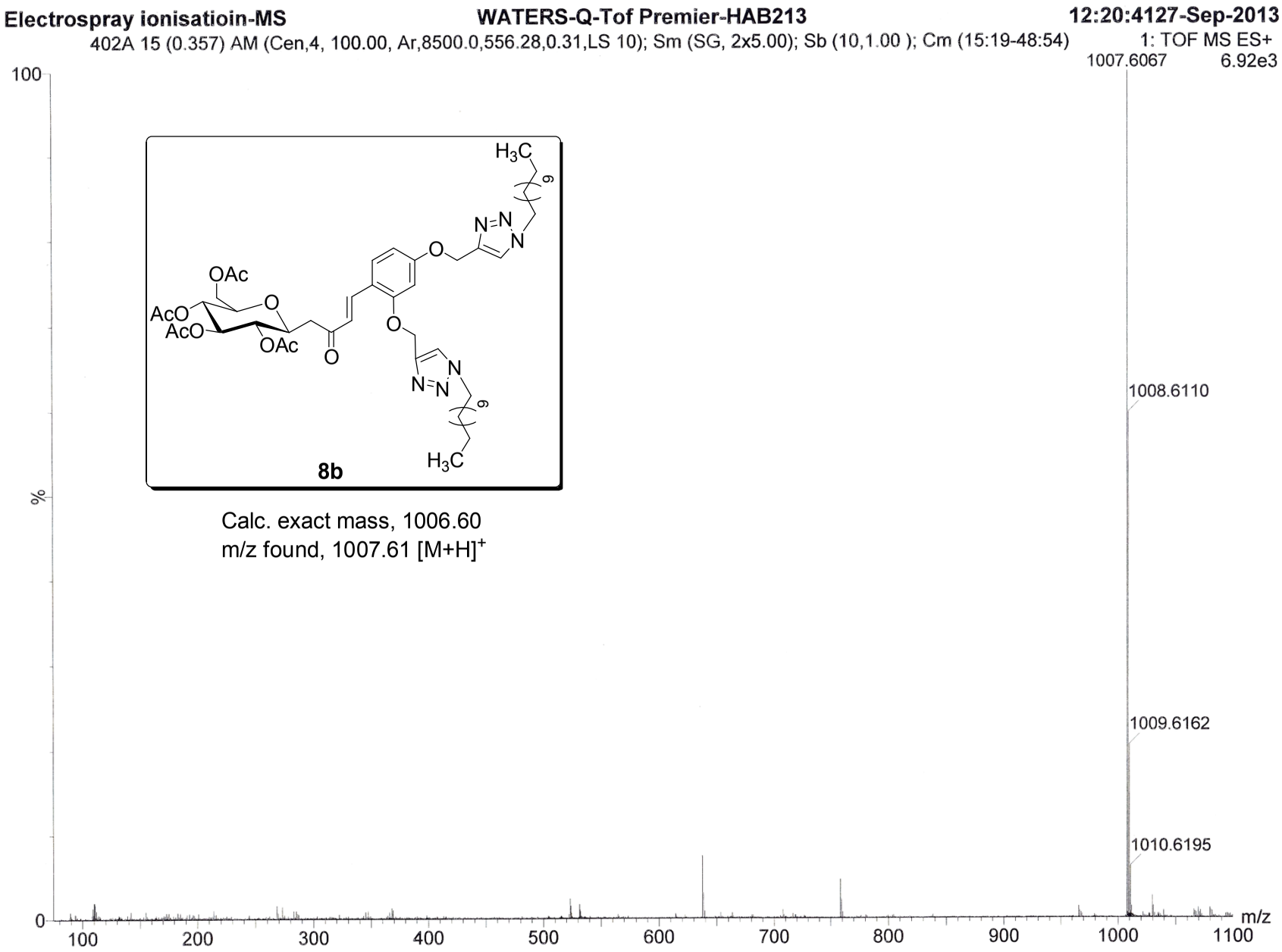


Figure 22 Mass spectrum of compound, 8b.

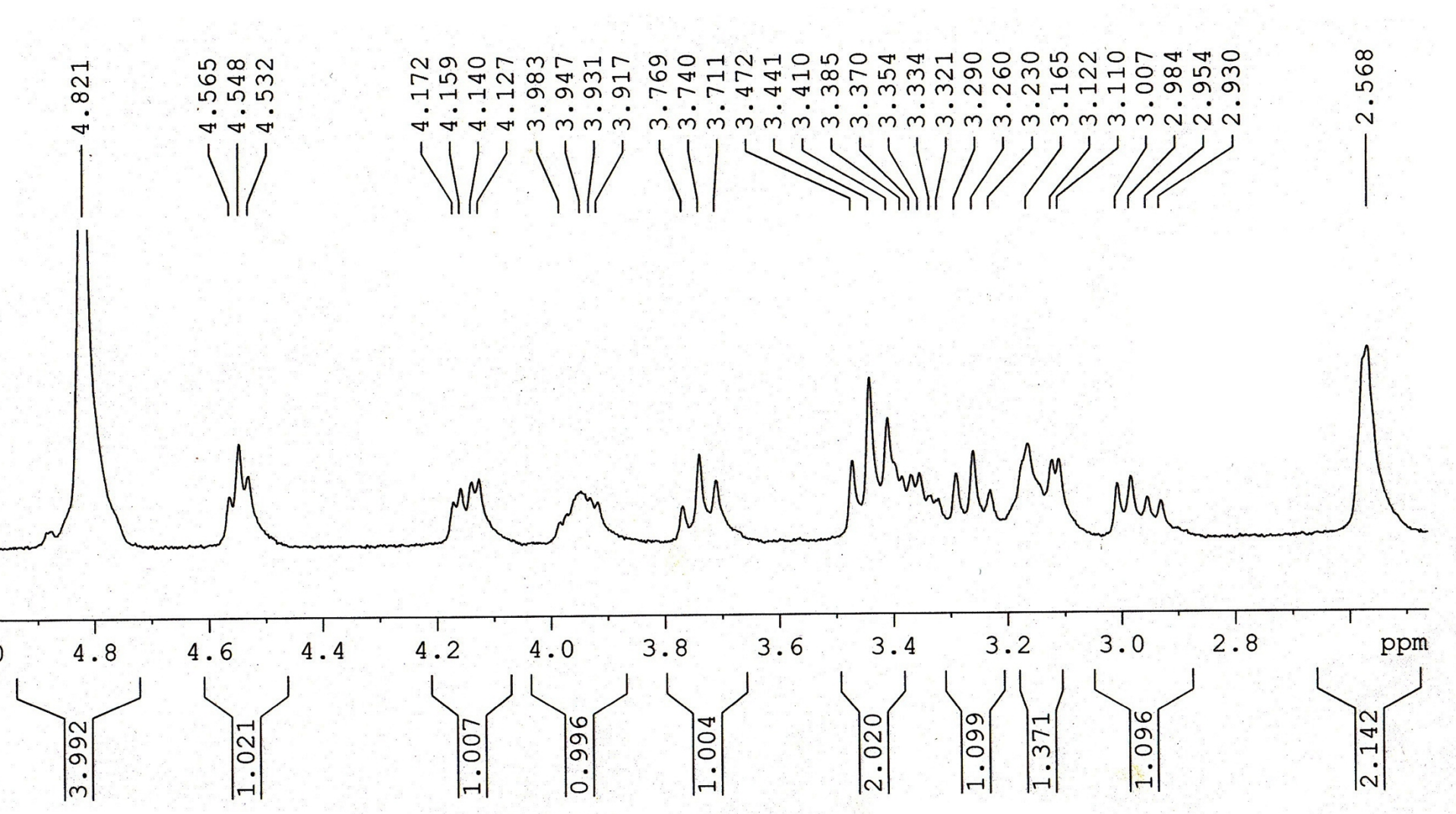


Figure 23 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) expansion of compound, 5a.

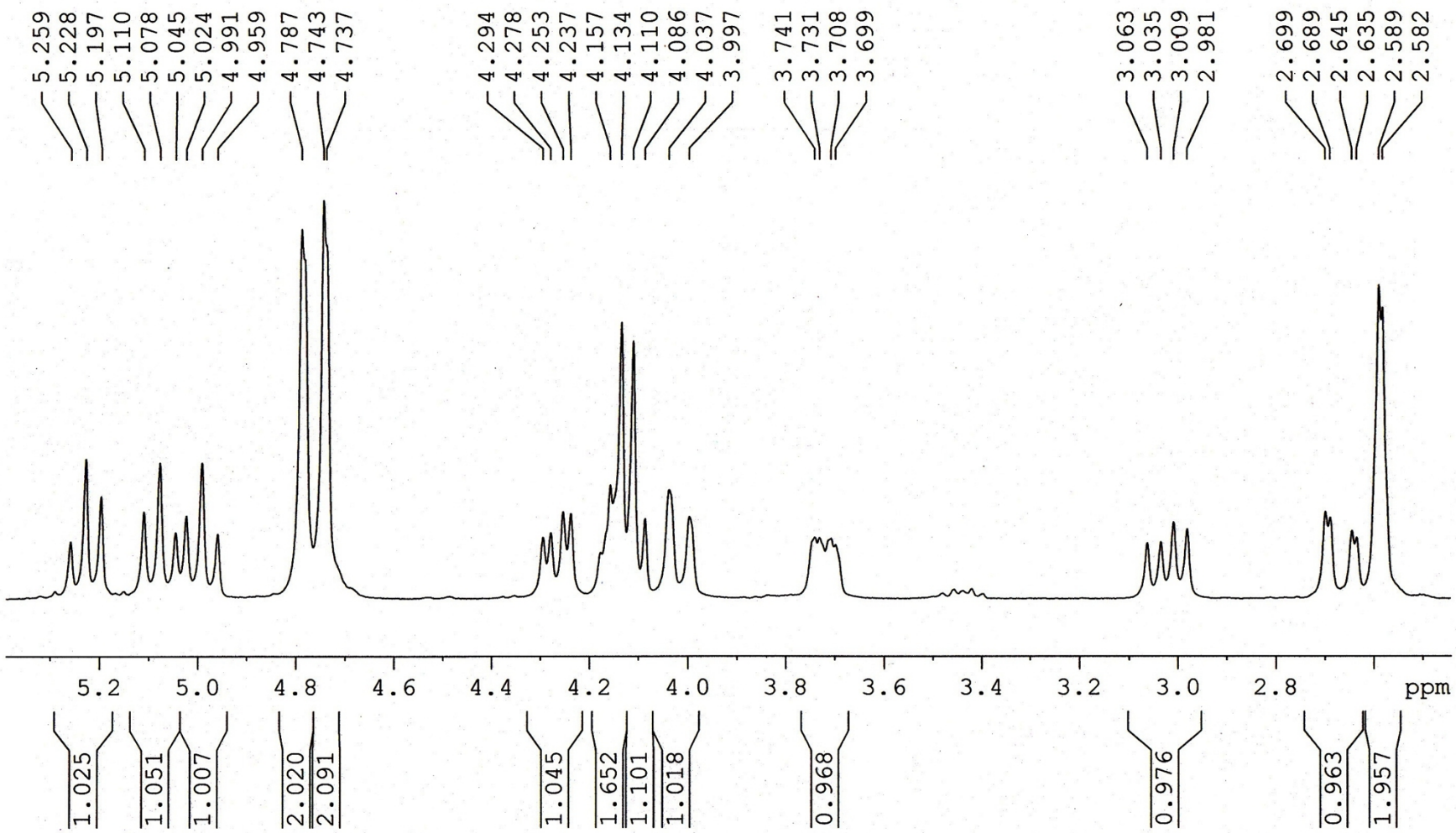


Figure 24 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) expansion of compound, 6b.

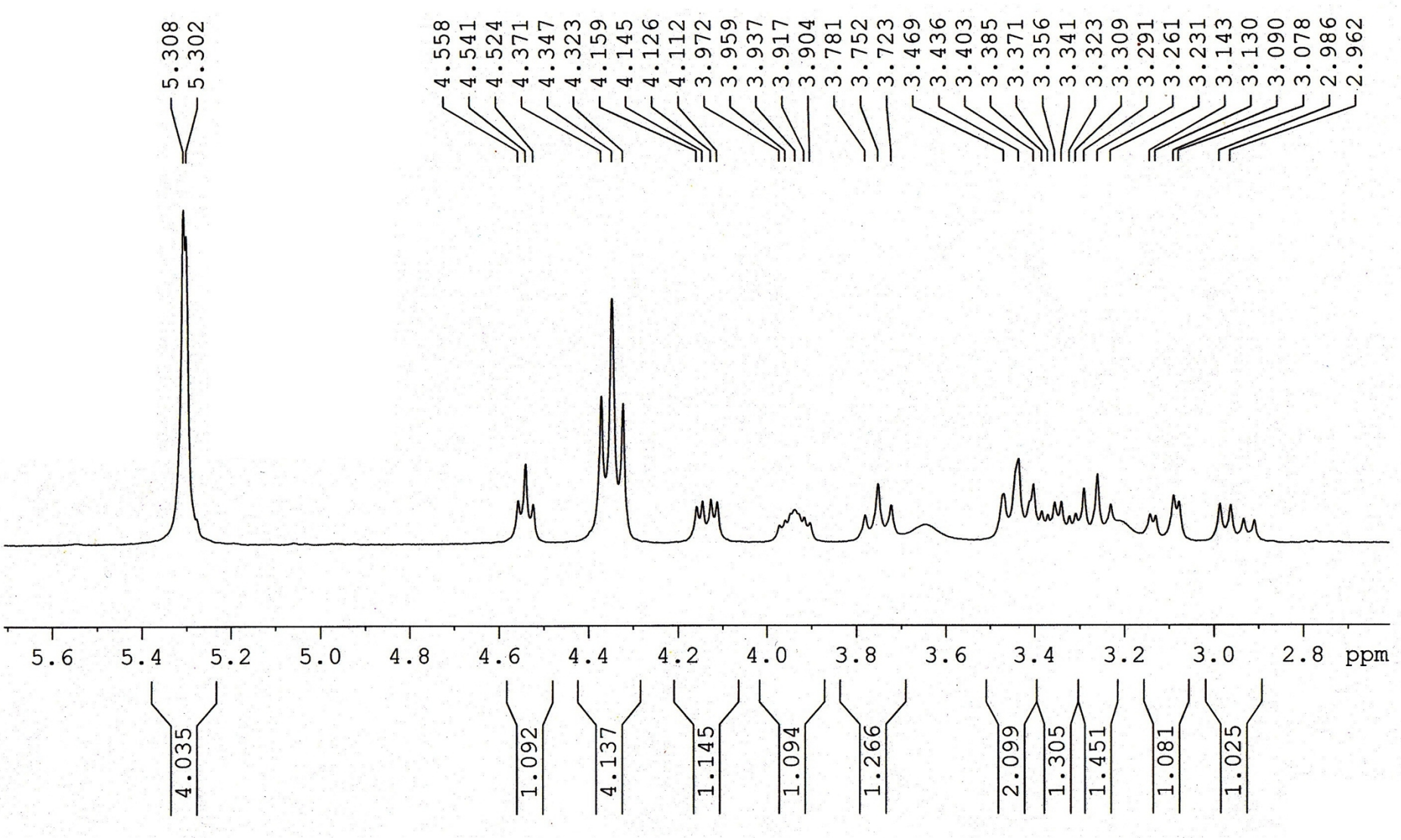


Figure 25 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) expansion of compound, 6b.

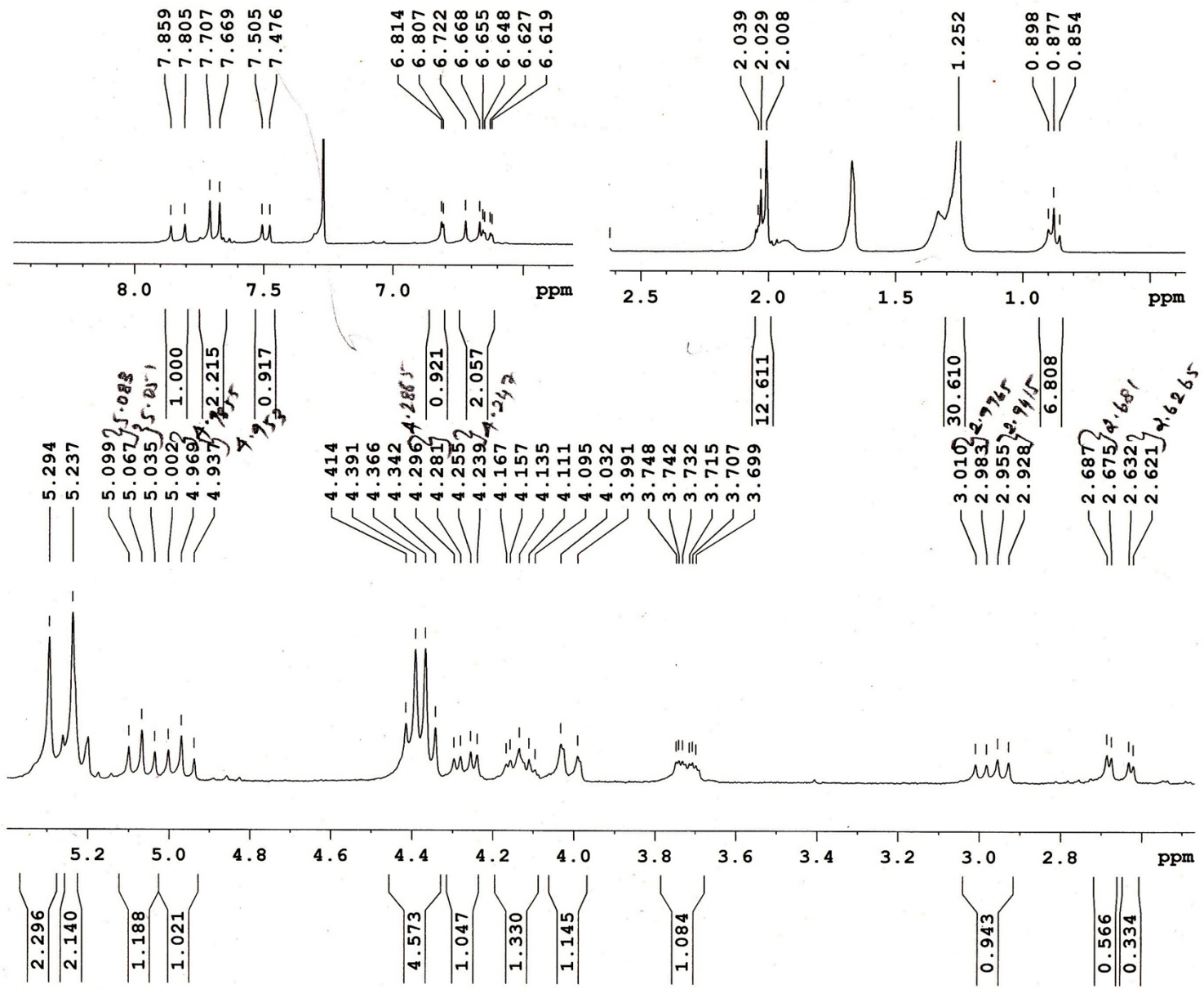


Figure 26 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) expansion of compound, 8b.