Supporting Information

Synthesis and Biological Evaluation of the Ascidian Blood-Pigment Halocyamine A

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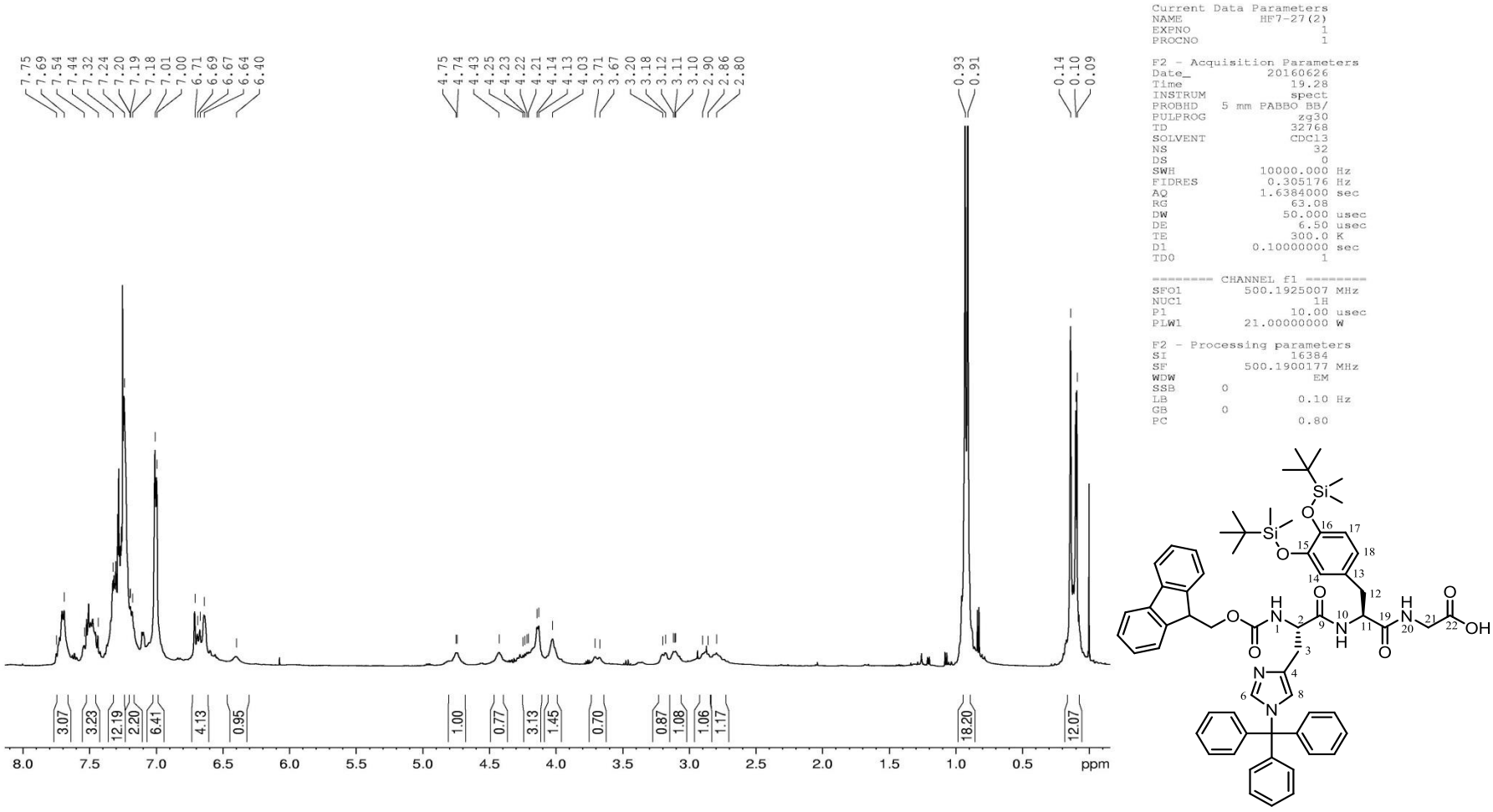
Table S1. NMR data of isolated halocyamine A (1) and synthetic halocyamine A HCl salt (1) in DMSO-d_6.

Atom No.	^{1}H [δ, mult., *J* (Hz)]		^{13}C (δ)	
	Isolated (1)[1]	**Synthetic (1)**	**Isolated (1)[1]**	**Synthetic (1)**
1	Not observed	Not observed (8.37 [3H, br s])*	-	-
2	3.84 (1H, t, 5.0)	3.61 (1H, br s)	53.10	53.8
3	3.03 (1H, dd, 15.5, 5.0), 2.93 (1H, dd, 15.5, 7.5)	2.91–2.89 (1H, m), 2.73 (1H, dd, 14.3, 7.5)	29.62	30.5
4	-	-	132.88	133.4
5	-	-	-	-
6	7.65 (1H, s)	7.60 (1H, s)	135.13	135.1
7	Not observed	Not observed	-	-
8	6.90 (1H, s)	6.86 (1H, s)	116.37	Not observed (118.2)*
9	-	-	170.27	171.6
10	8.84 (1H, br d, 6.8)	8.40 (1H, br s)	-	-
11	4.43 (1H, m)	4.44 (1H, br s)	54.94	54.5
12	2.98#, 2.65 (1H, dd, 14.0, 10.5),	2.95 (1H, dd, 14.0, 4.1), 2.66 (1H, dd, 14.0, 9.6)	36.46	36.7
13	-	-	128.42	128.5
14	6.81 (1H, d, 1.8)	6.64 (1H, d, 1.5)	116.76	116.6
15	-	-	145.03	144.9
16	-	-	143.72	143.7
17	6.59 (1H, d, 8.0)	6.59 (1H, d, 8.0)	115.24	115.3
18	6.47 (1H, dd, 8.0, 1.8)	6.45 (1H, dd, 8.0, 1.5)	119.47	119.9
19	-	-	171.96	171.9
20	9.16 (1H, br t, 6.5)	8.88 (1H, br s)	-	-
21	3.97 (2H, d, 5.5)	3.99 (1H, dd, 16.6, 5.8), 3.93 (1H, dd, 16.6, 5.8)	42.72	42.6
22	-	-	167.39	167.5
23	9.04 (1H, d, 10.5)	9.08 (1H, d, 10.0)	-	-
24	6.69 (1H, t, 9.5)	6.67 (1H, dd, 10.0, 9.7)	118.39	118.6
25	5.92 (1H, d, 9.5)	5.92 (1H, d, 9.7)	102.10	102.2
26	-	-	109.59	109.7
27	7.73 (1H, s)	7.72 (1H, s)	124.72	124.9
28	11.85 (1H, s)	11.51 (1H, br s)	-	-
28a	-	-	136.43	136.4
29	7.61 (1H, d, 2.0)	7.58 (1H, d, 1.6)	114.12	114.1
30	-	-	114.24	114.3
31	7.15 (1H, dd, 8.5, 2.0)	7.16 (1H, dd, 8.3, 1.6)	121.73	121.9
32	7.55 (1H, d, 8.5)	7.56 (1H, d, 8.3)	119.90	120.1
32a	-	-	125.59	125.7

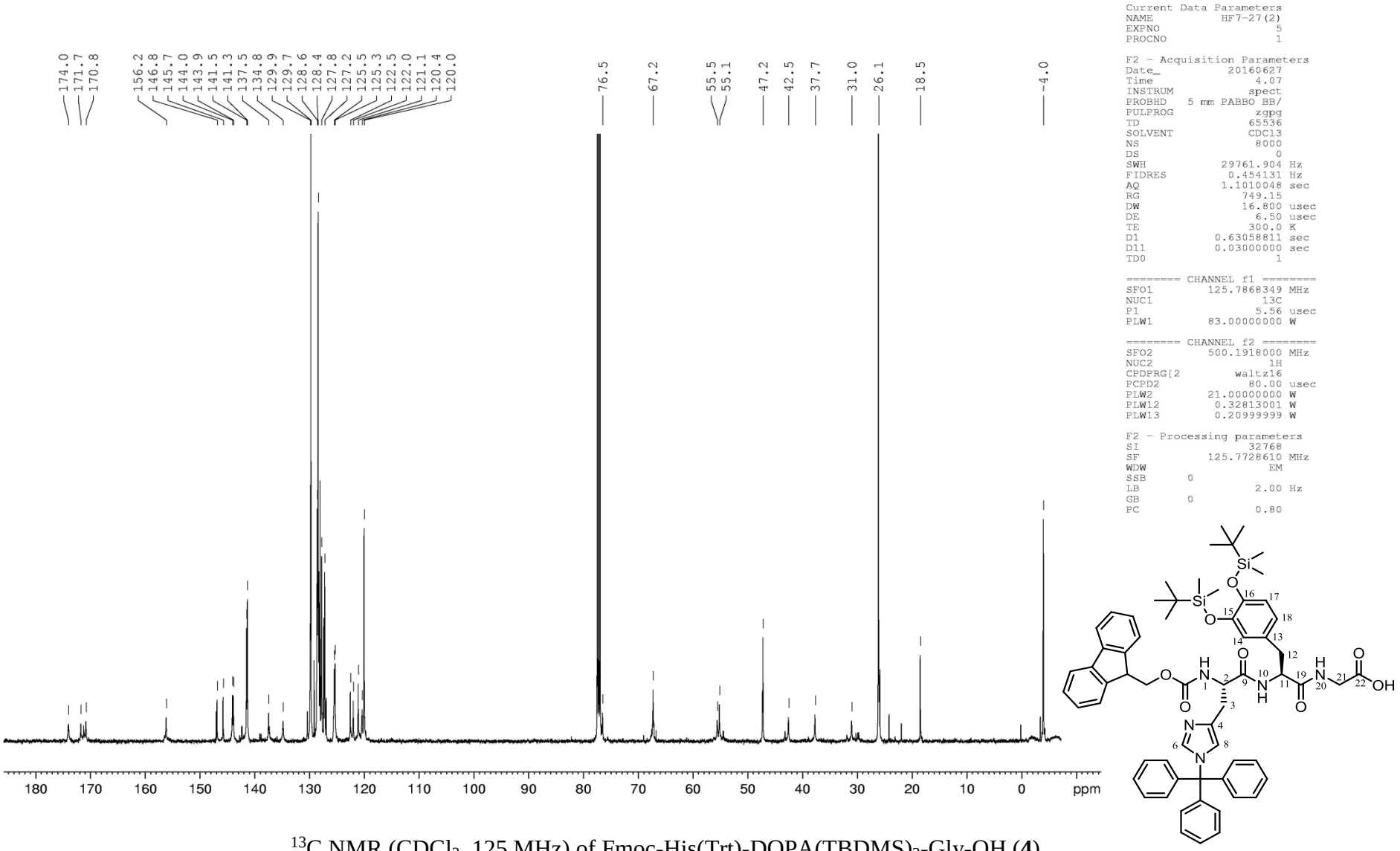
*signals observed for synthetic halocyamine A TFA salt in DMSO-d_6.
#3.00 ppm, dd, *J* = 14.0 and 5.6 Hz, in CH_3OD

Reference

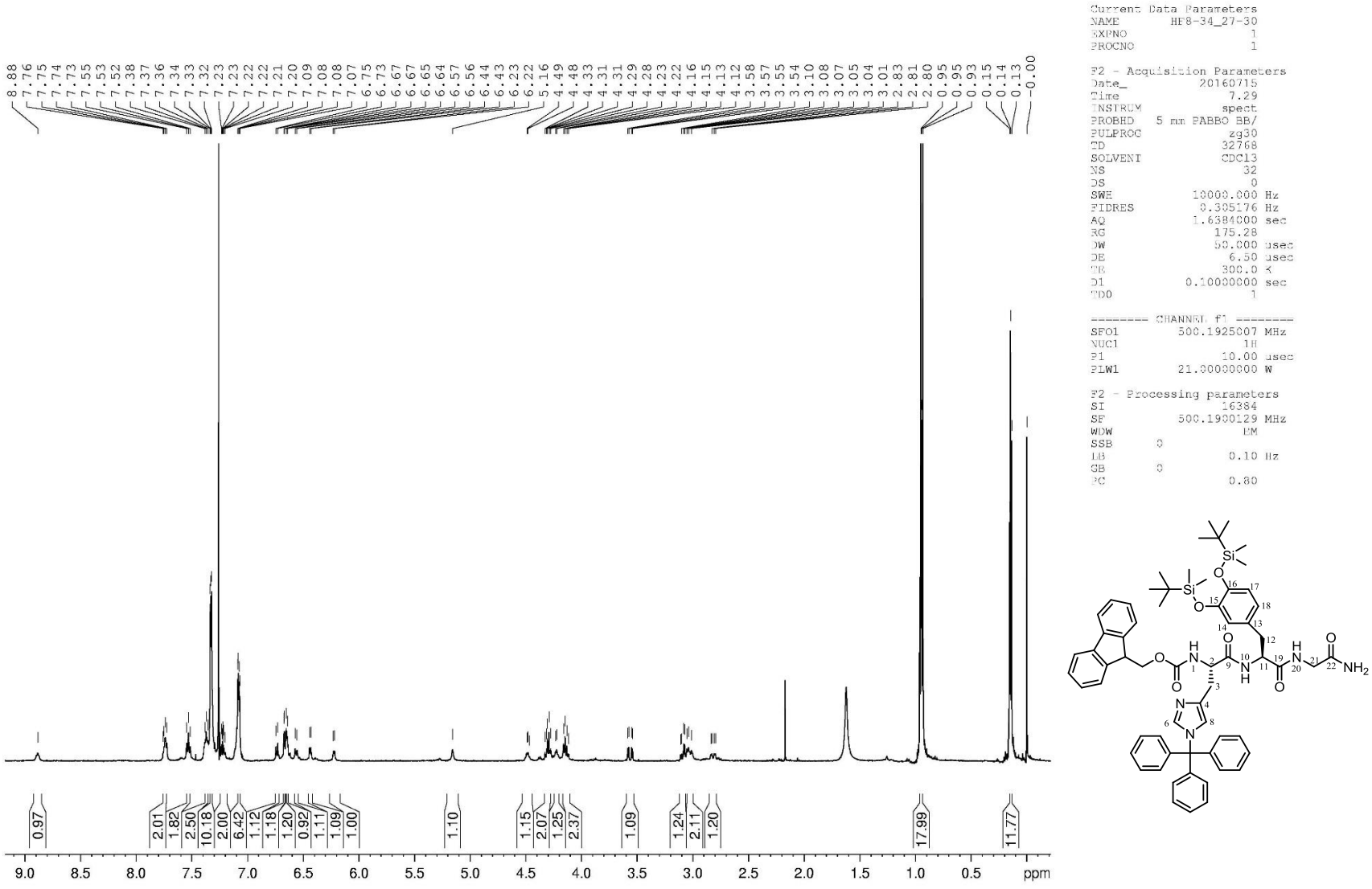
(1) K. Azumi, H. Yokosawa, S. Ishii, *Biochemistry* 1990, ***29***, 159–165.



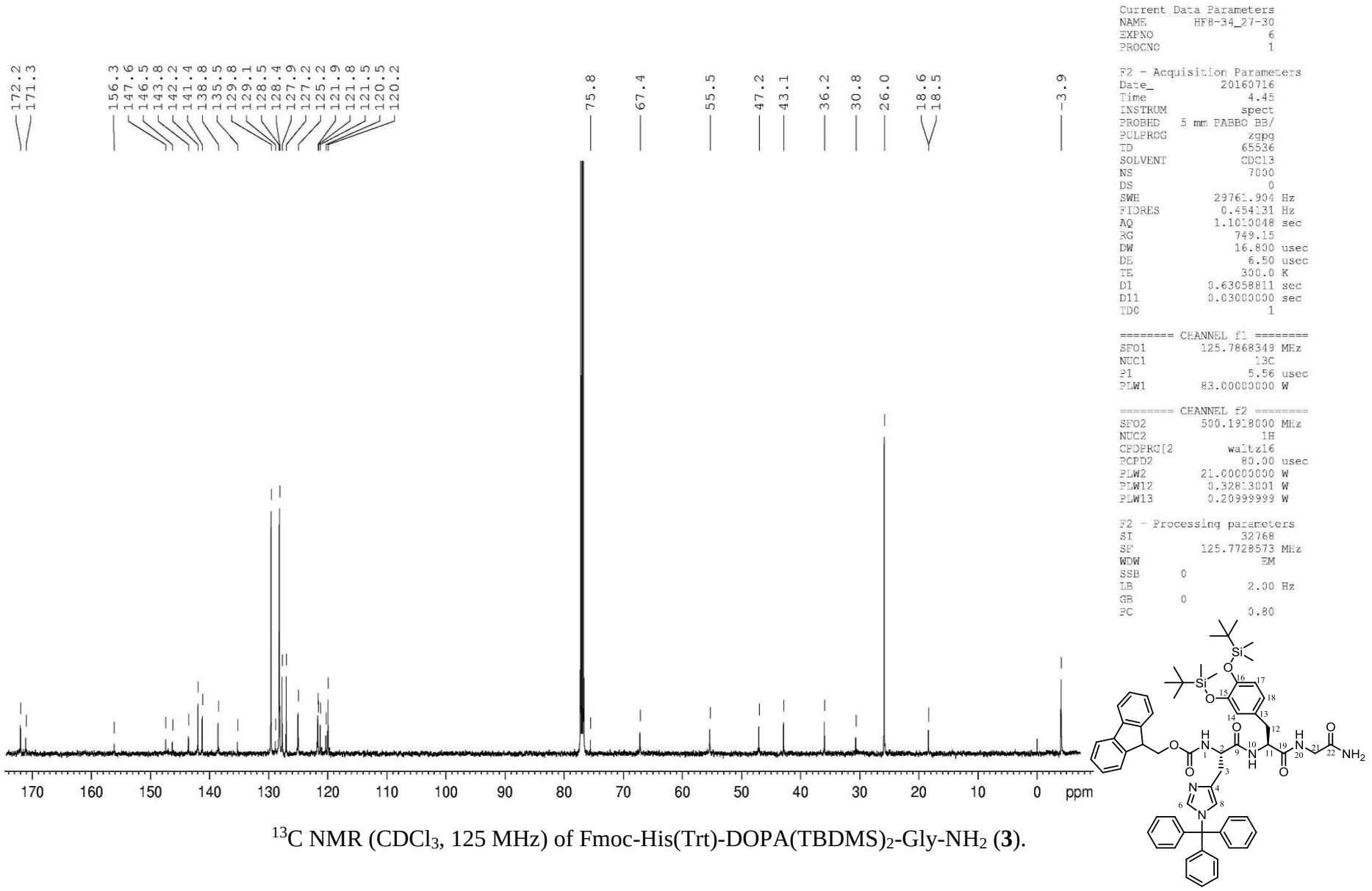
^{1}H NMR ($CDCl_3$, 500 MHz) of Fmoc-His(Trt)-DOPA(TBDMS)$_2$-Gly-OH (**4**).



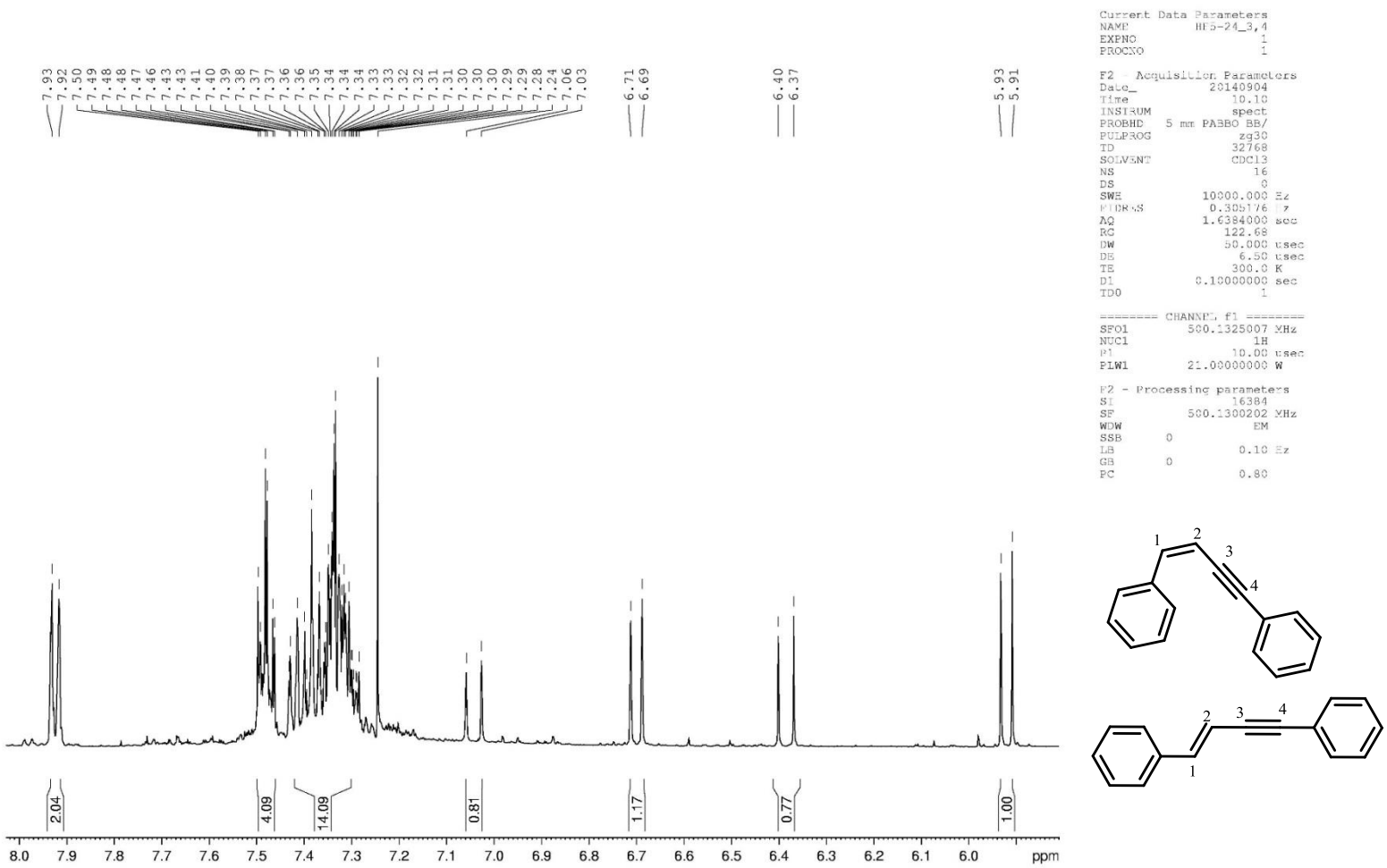
^{13}C NMR ($CDCl_3$, 125 MHz) of Fmoc-His(Trt)-DOPA(TBDMS)$_2$-Gly-OH (**4**).



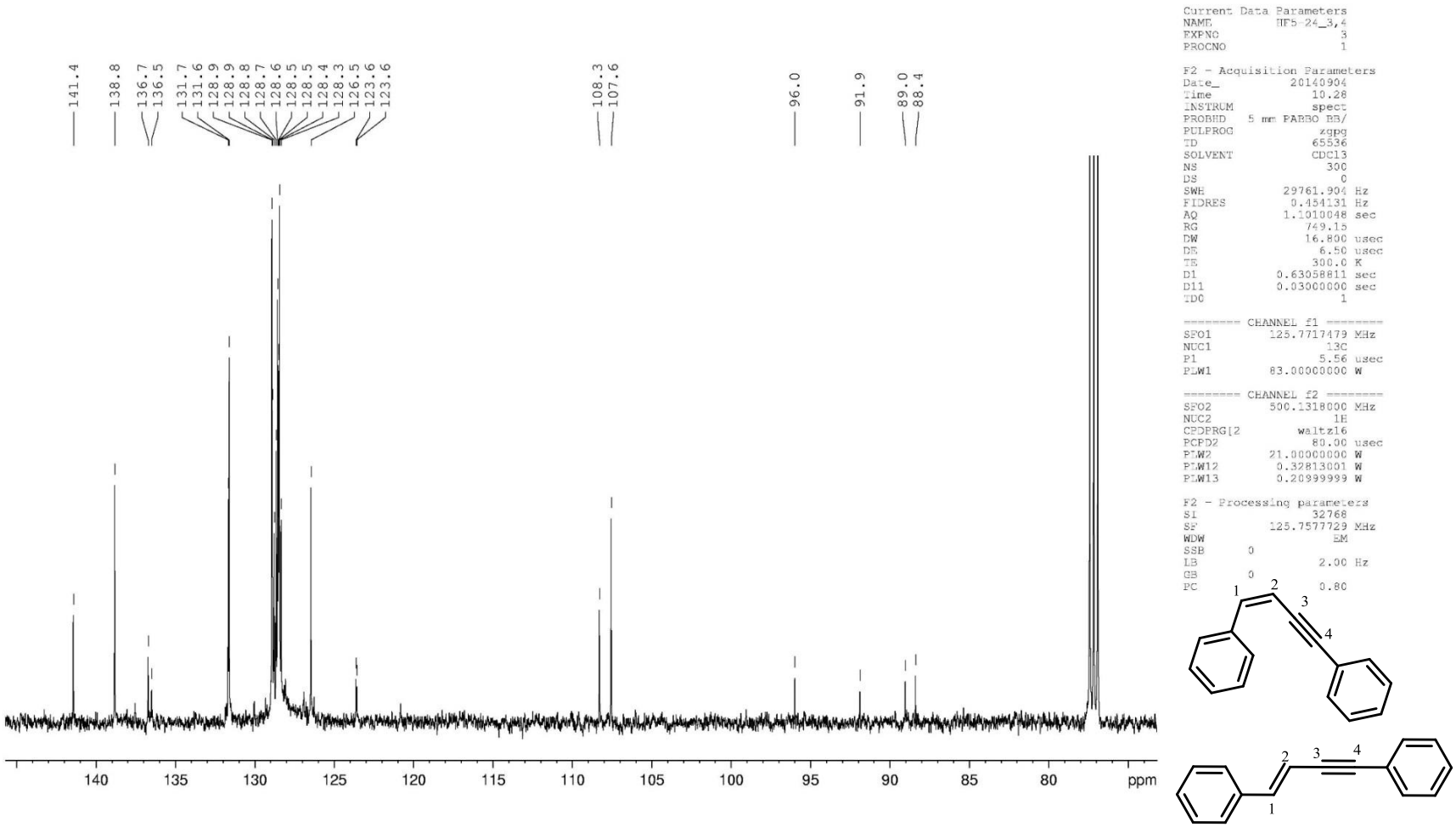
^{1}H NMR ($CDCl_3$, 500 MHz) of Fmoc-His(Trt)-DOPA(TBDMS)$_2$-Gly-NH_2 (**3**).



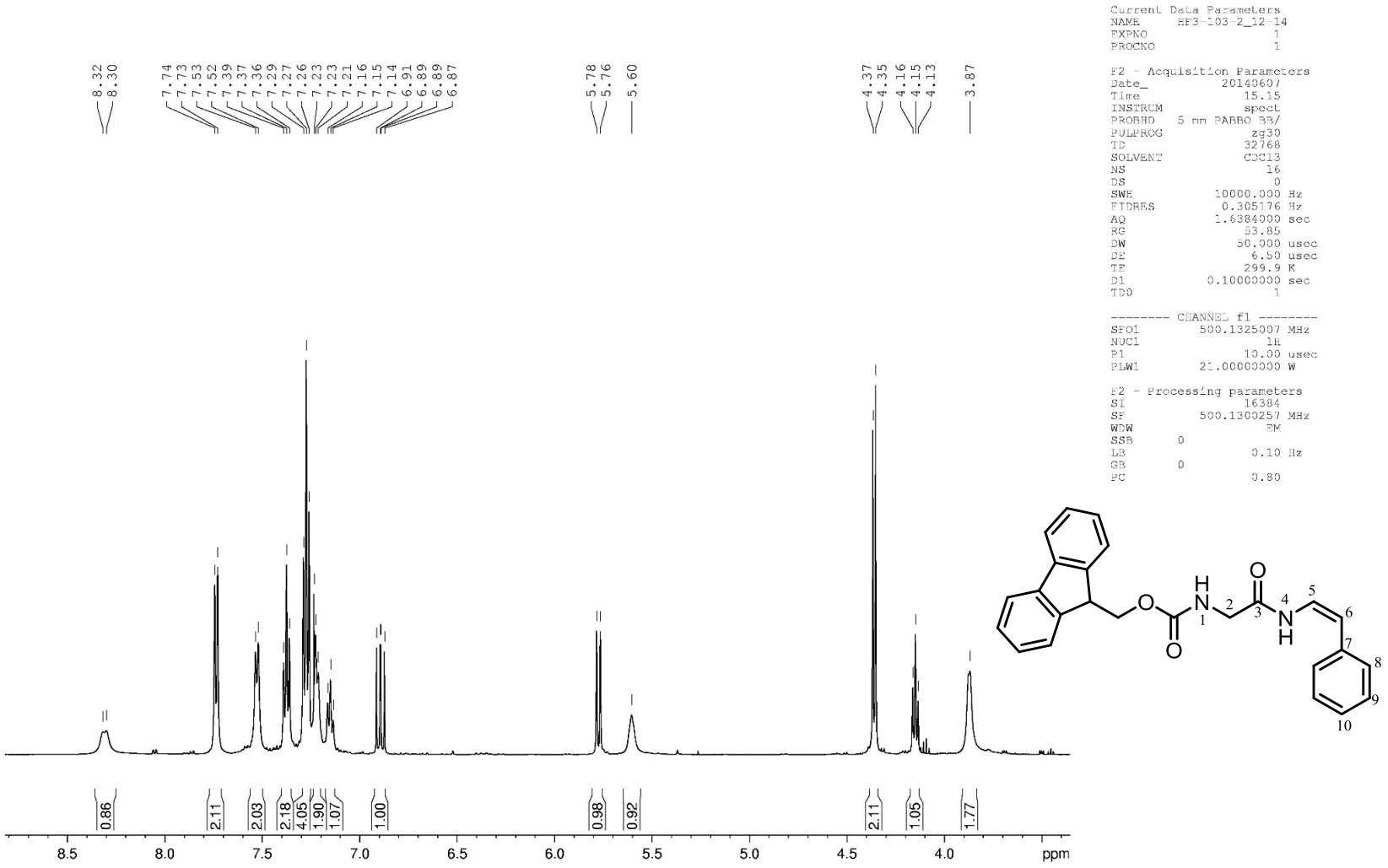
^{13}C NMR ($CDCl_3$, 125 MHz) of Fmoc-His(Trt)-DOPA(TBDMS)$_2$-Gly-NH_2 (**3**).



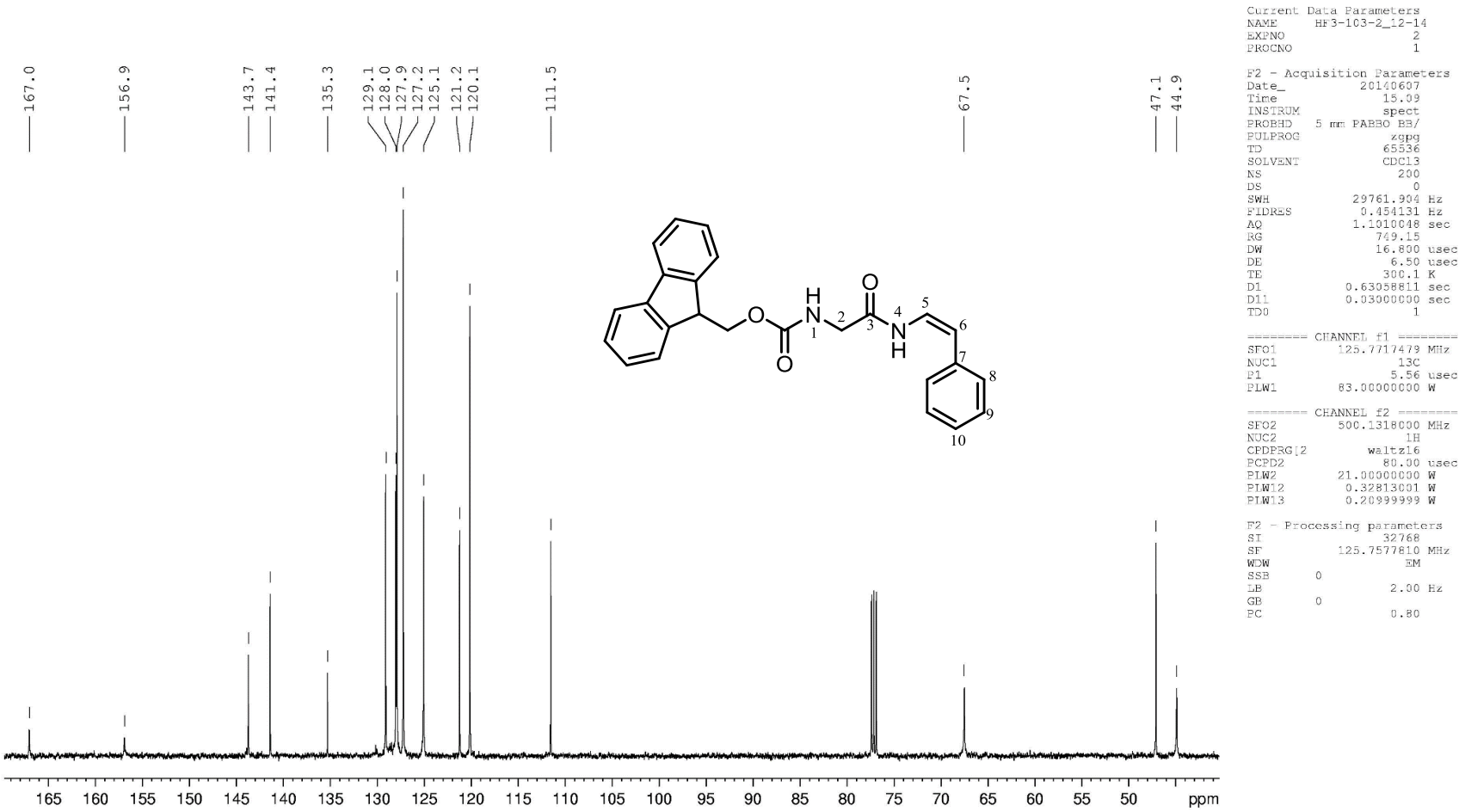
^{1}H NMR ($CDCl_3$, 500 MHz) of a mixture of (*Z*)-but-1-en-3-yne-1,4-diyldibenzene (**5**) and (*E*)-but-1-en-3-yne-1,4-diyldibeneze (**6**).



^{13}C NMR ($CDCl_3$, 125 MHz) of a mixture of (*Z*)-but-1-en-3-yne-1,4-diyldibenzene (**5**) and (*E*)-but-1-en-3-yne-1,4-diyldibeneze (**6**).



^{1}H NMR ($CDCl_3$, 500 MHz) of (*Z*)-(9*H*-fluoren-9-yl)methyl (2-oxo-2-(styrylamino)ethyl)carbamate (**10**).

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TD0                   1

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P1                   5.56 usec
PLW1         83.00000000 W

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PLW12         0.32813001 W
PLW13         0.20999999 W

F2 - Processing parameters
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GB        0
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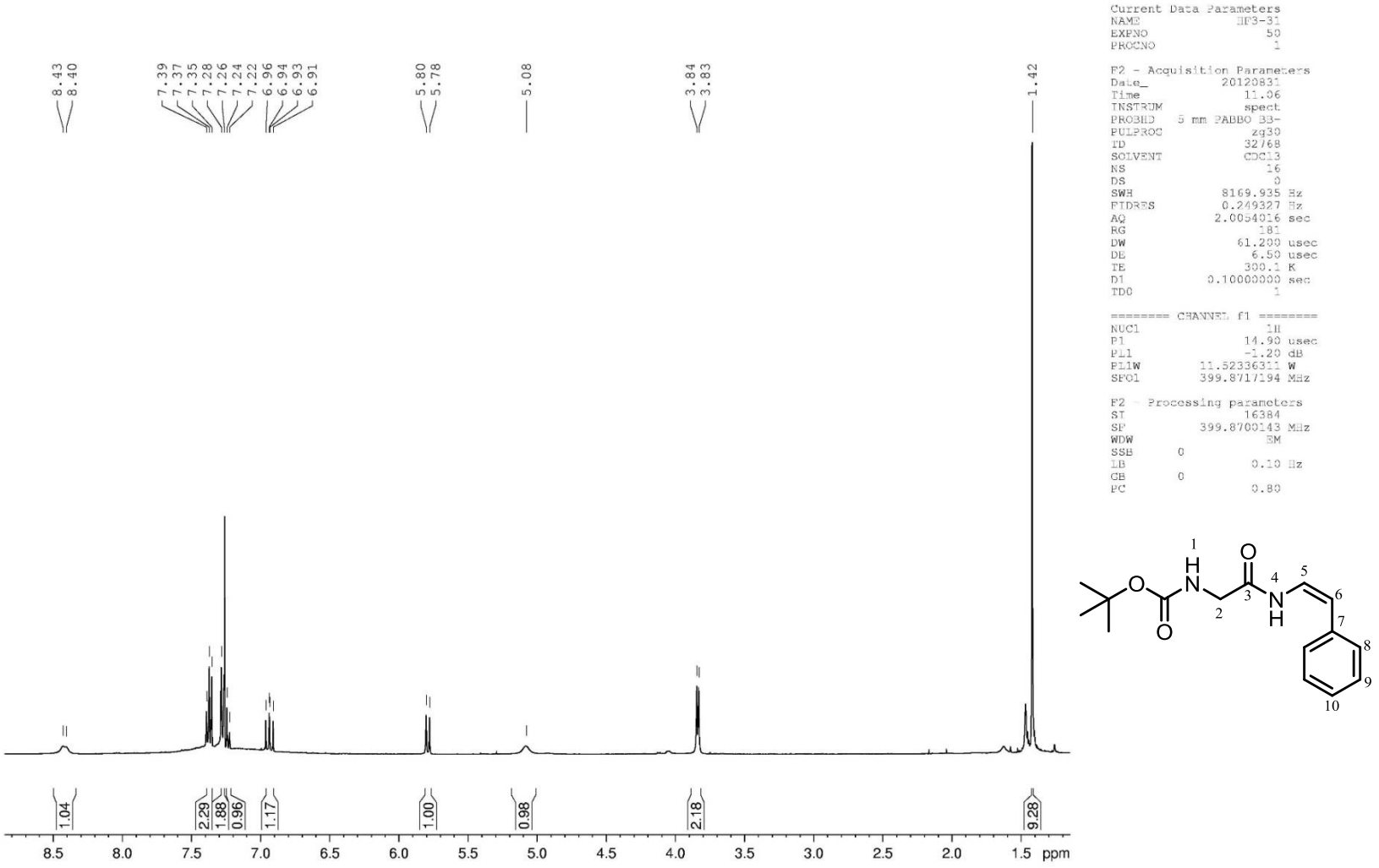
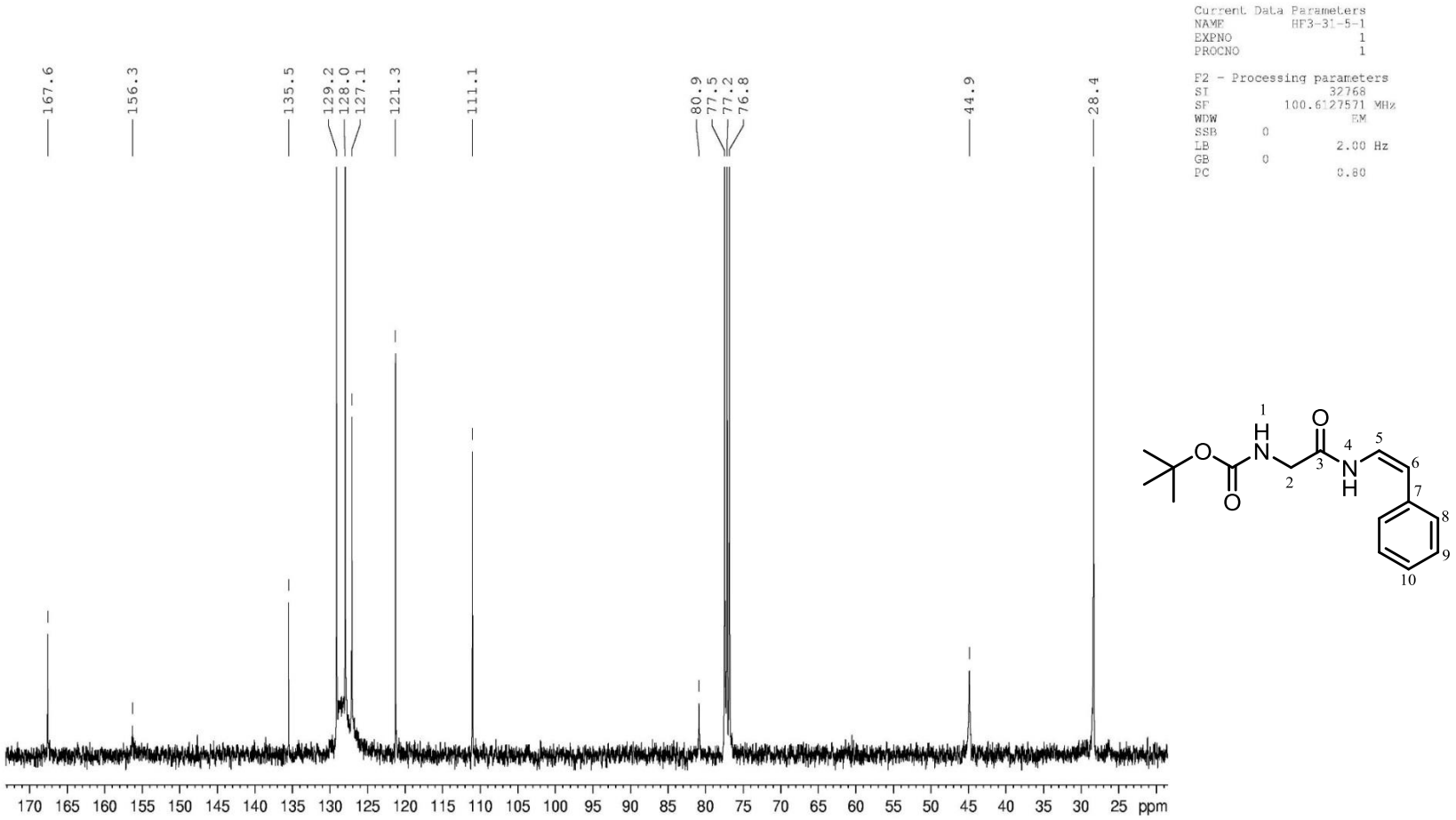
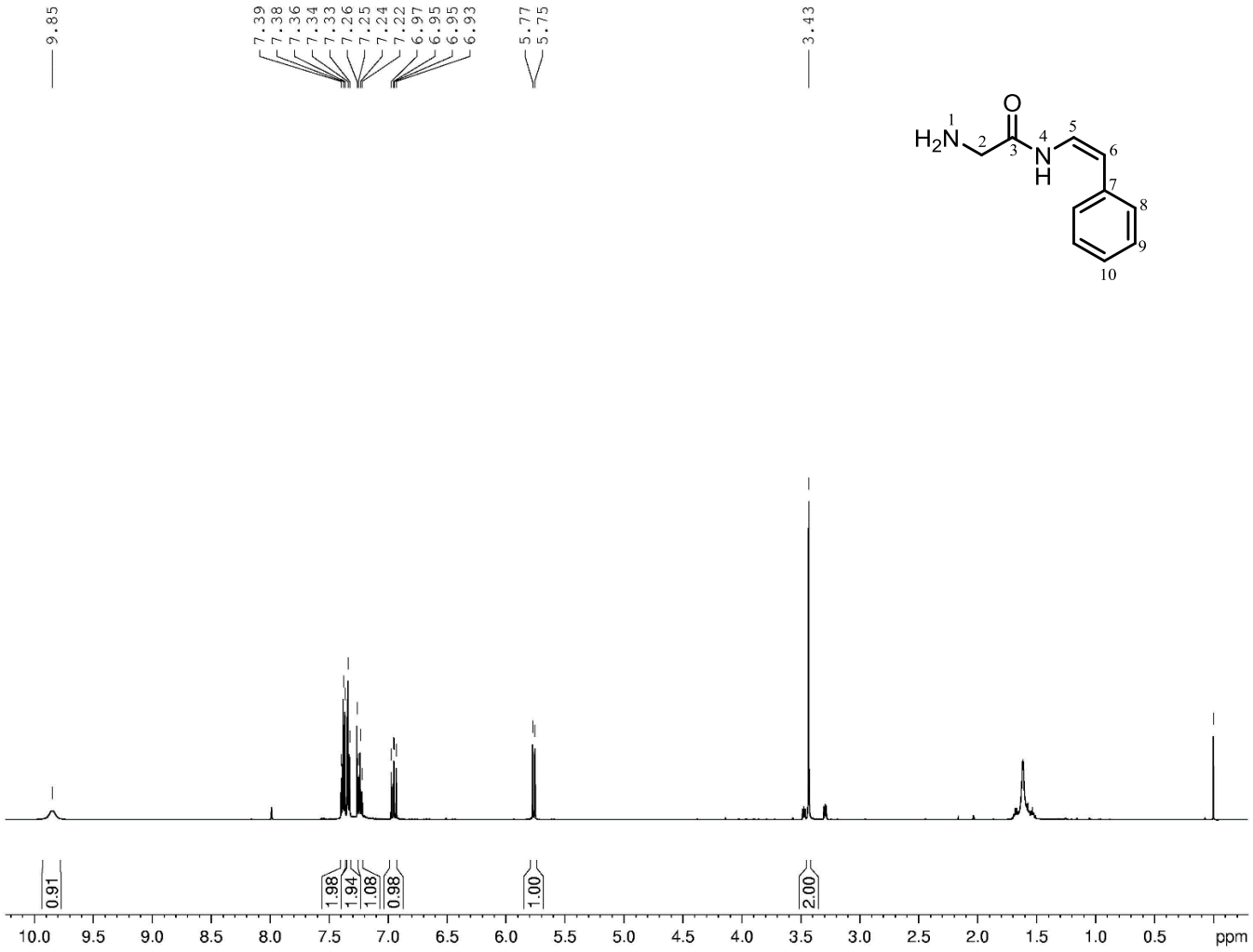
^{13}C NMR ($CDCl_3$, 125 MHz) of (*Z*)-(9*H*-fluoren-9-yl)methyl (2-oxo-2-(styrylamino)ethyl)carbamate (**10**).



^{1}H NMR ($CDCl_3$, 400 MHz) of *tert*-butyl (*Z*)-(2-oxo-2-(styrylamino)ethyl)carbamate (**12**).



^{13}C NMR ($CDCl_3$, 100 MHz) of *tert*-butyl (*Z*)-(2-oxo-2-(styrylamino)ethyl)carbamate (**12**).

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PC                 0.80
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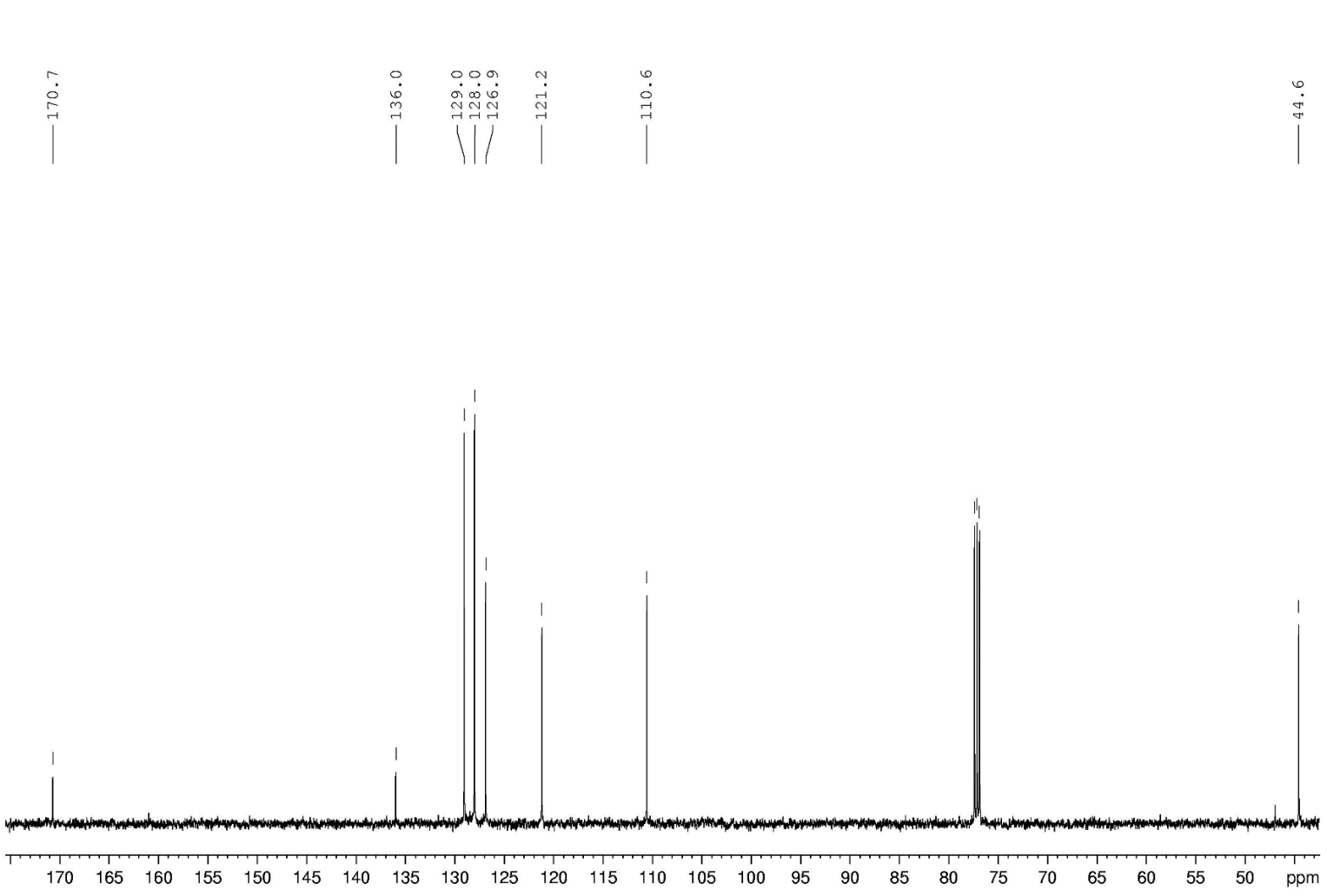
^{1}H NMR ($CDCl_3$, 500 MHz) of (*Z*)-2-amino-*N*-styrylacetamide (**8**).

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FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               749.15
DW               16.800 usec
DE                6.50 usec
TE               300.0 K
D1            0.63058811 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         125.7717479 MHz
NUC1                  13C
P1                   5.56 usec
PLW1         83.00000000 W

======== CHANNEL f2 ========
SFO2         500.1318000 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         21.00000000 W
PLW12         0.32813001 W
PLW13         0.20999999 W

F2 - Processing parameters
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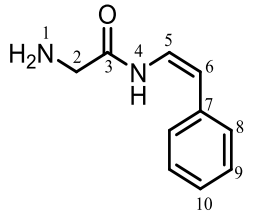
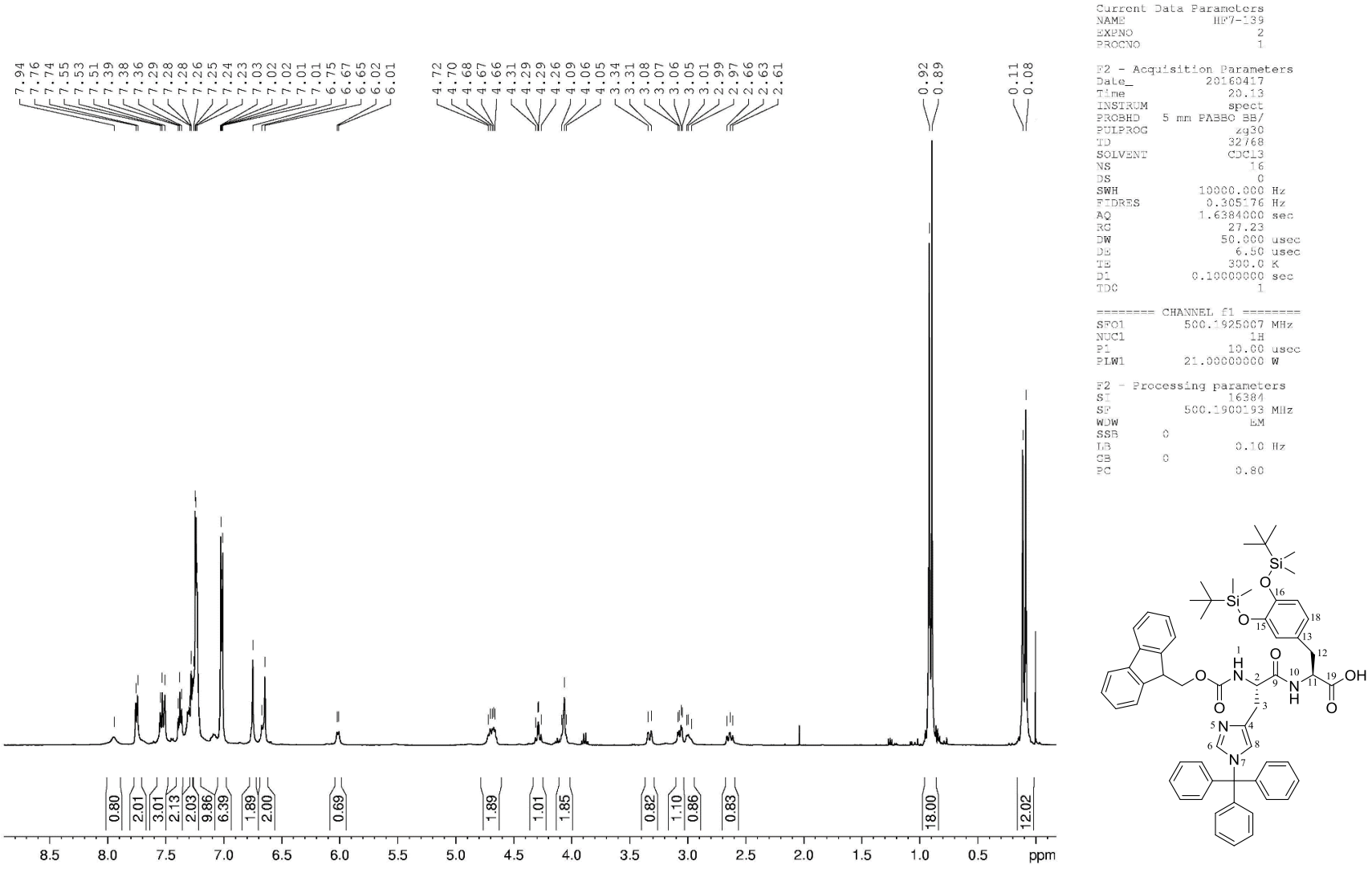


^{13}C NMR ($CDCl_3$, 125 MHz) of (*Z*)-2-amino-*N*-styrylacetamide (**8**).

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DE                    6.50 usec
TE                   300.0 K
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TD0                       1

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P1                     10.00 usec
PLW1           21.00000000 W

F2 - Processing parameters
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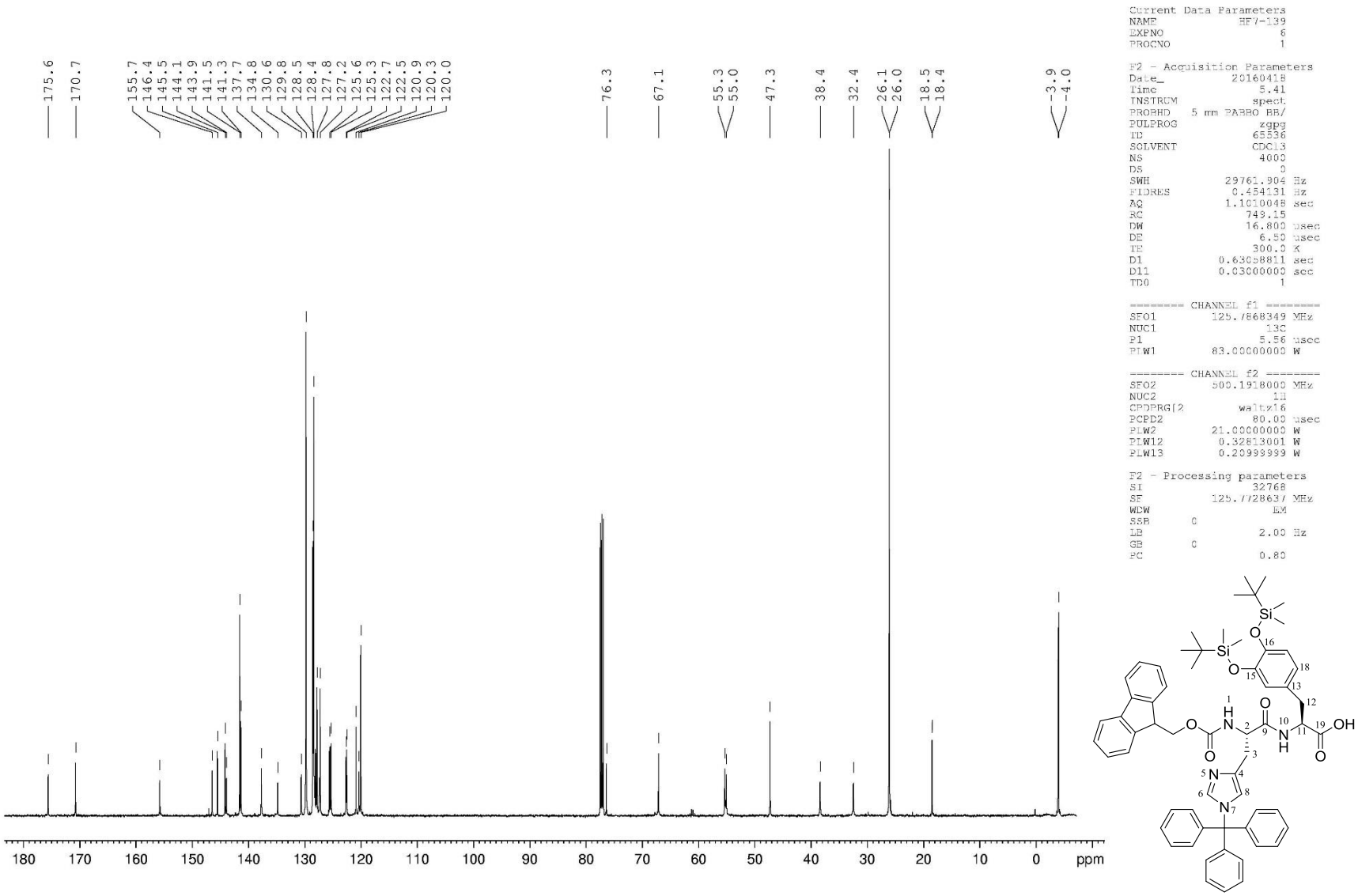
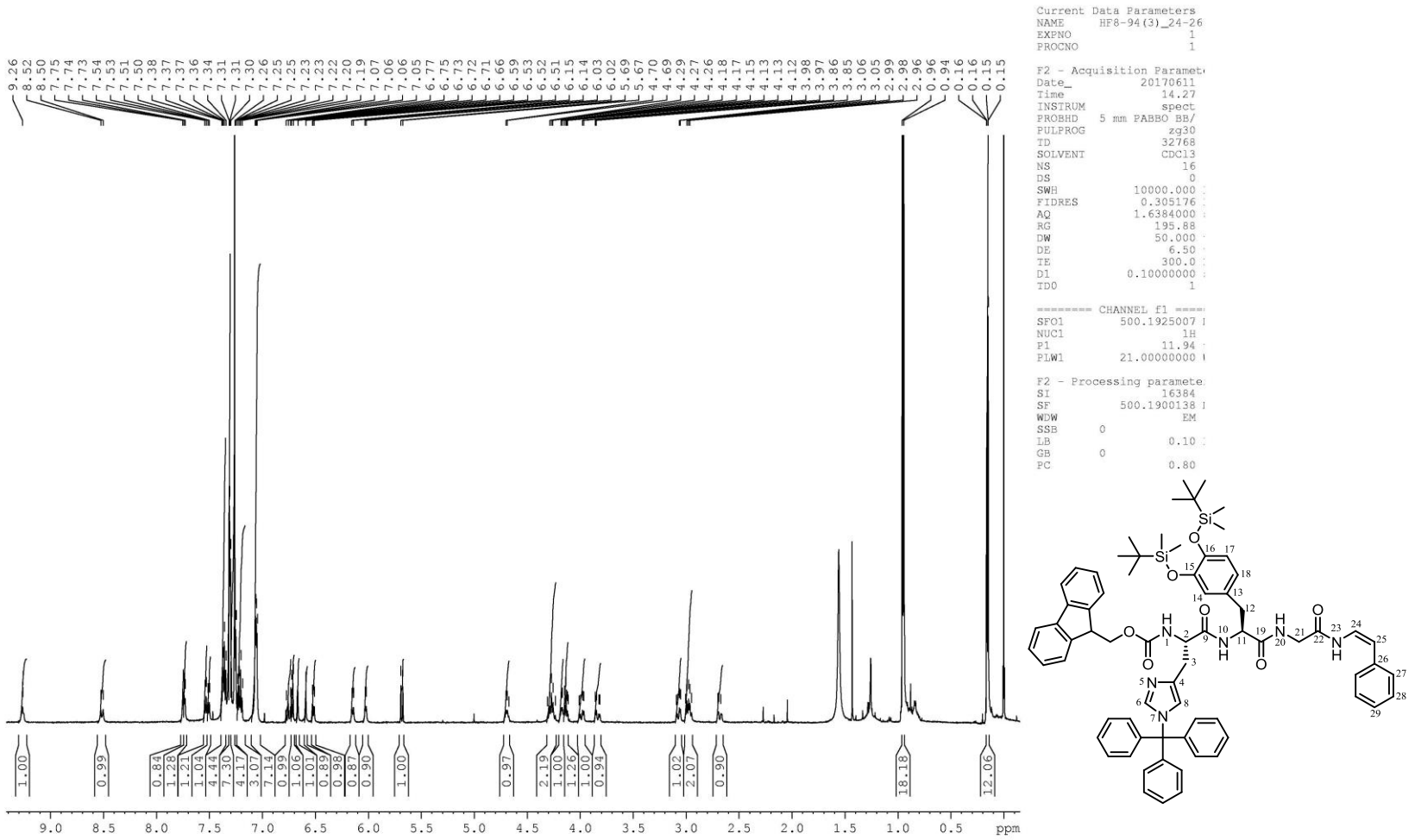
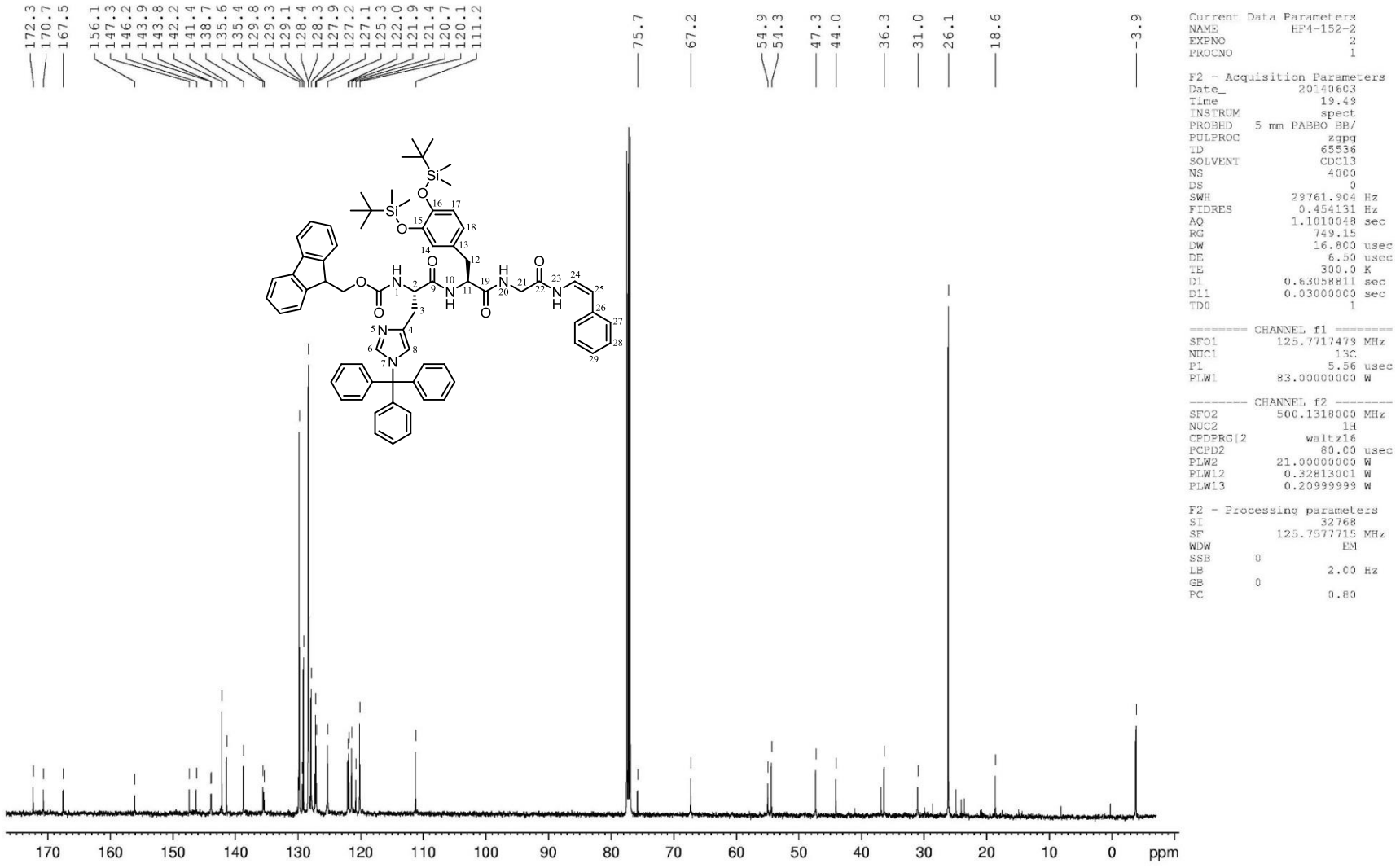
^{1}H NMR ($CDCl_3$, 500 MHz) of Fmoc-His(Trt)-DOPA(TBDMS)$_2$-OH (**7**).



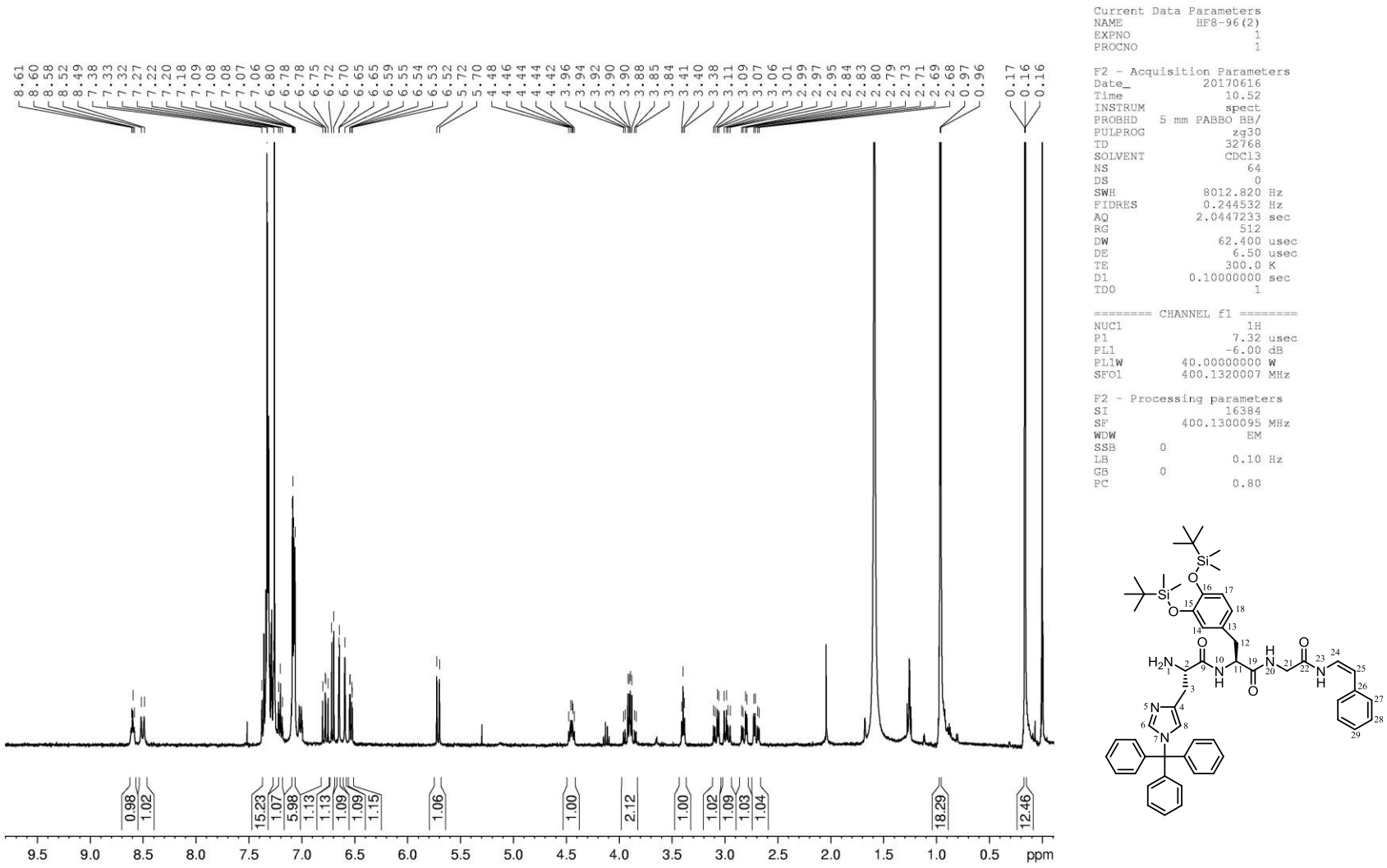
^{13}C NMR ($CDCl_3$, 125 MHz) of Fmoc-His(Trt)-DOPA(TBDMS)$_2$-OH (**7**).



^{1}H NMR ($CDCl_3$, 500 MHz) of (9*H*-fluoren-9-yl)methyl ((*S*)-1-(((*S*)-3-(3,4-bis((*tert*-butyldimethylsilyl)oxy)phenyl)-1-oxo-1-((2-oxo-2-(((*Z*)-styryl)amino)ethyl)amino)propan-2-yl)amino)-1-oxo-3-(1-trityl-1*H*-imidazol-4-yl)propan-2-yl)carbamate (**13**).



^{13}C NMR ($CDCl_3$, 125 MHz) of (9*H*-fluoren-9-yl)methyl ((*S*)-1-(((*S*)-3-(3,4-bis((*tert*-butyldimethylsilyl)oxy)phenyl)-1-oxo-1-((2-oxo-2-(((*Z*)-styryl)amino)ethyl)amino)propan-2-yl)amino)-1-oxo-3-(1-trityl-1*H*-imidazol-4-yl)propan-2-yl)carbamate (**13**).

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F2 - Processing parameters
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WDW                         EM
SSB          0
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GB           0
PC                        0.80
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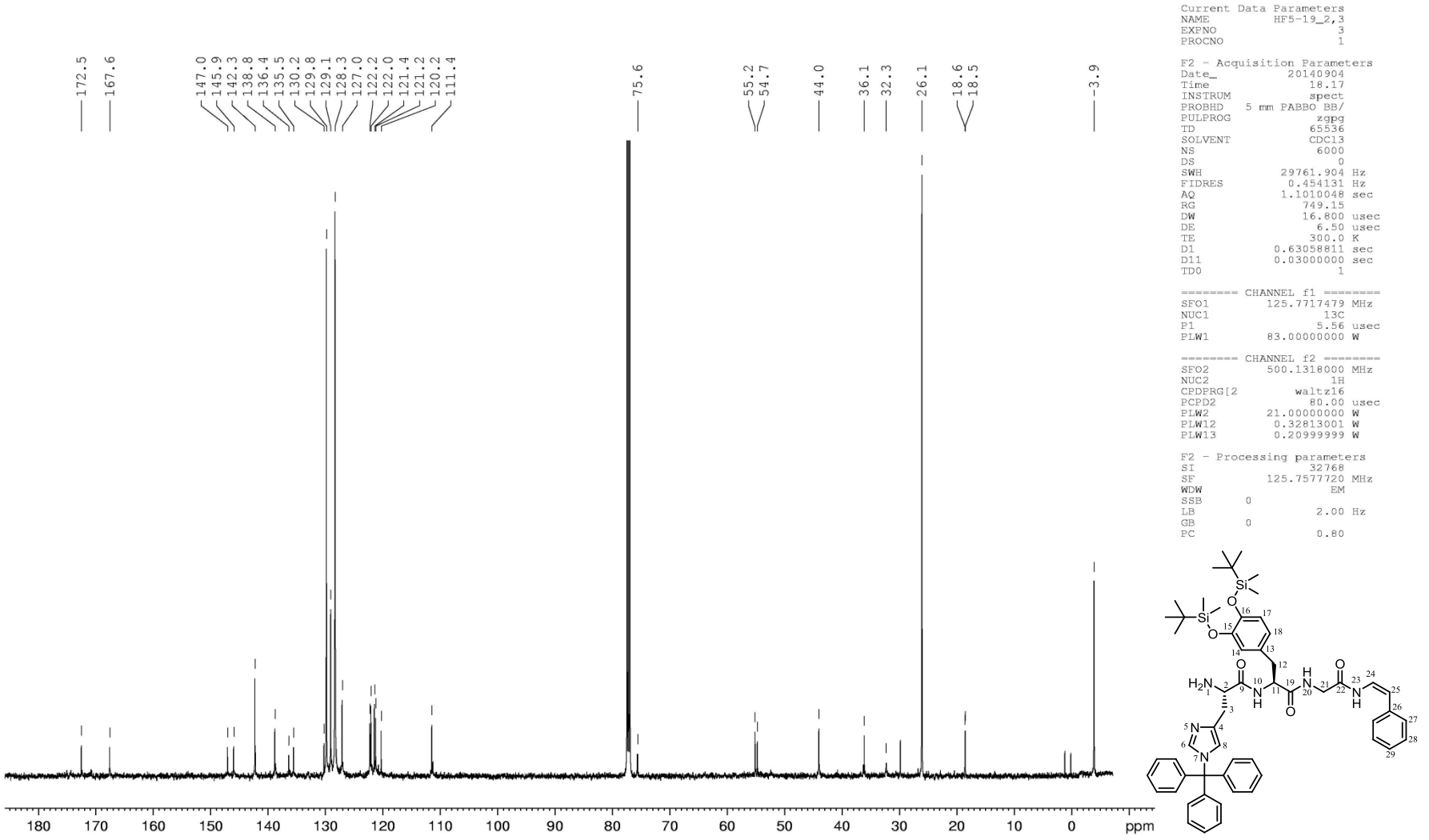
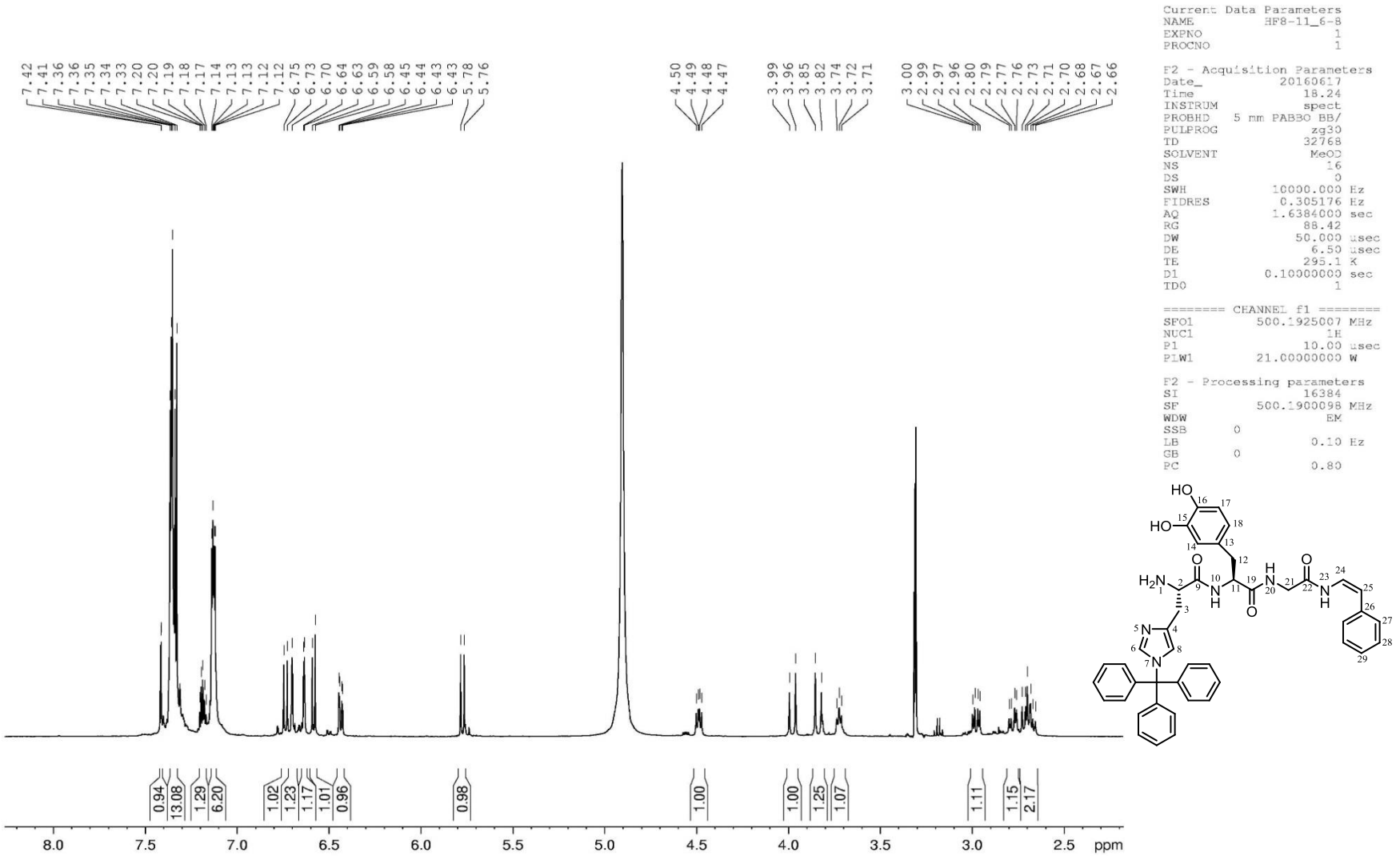
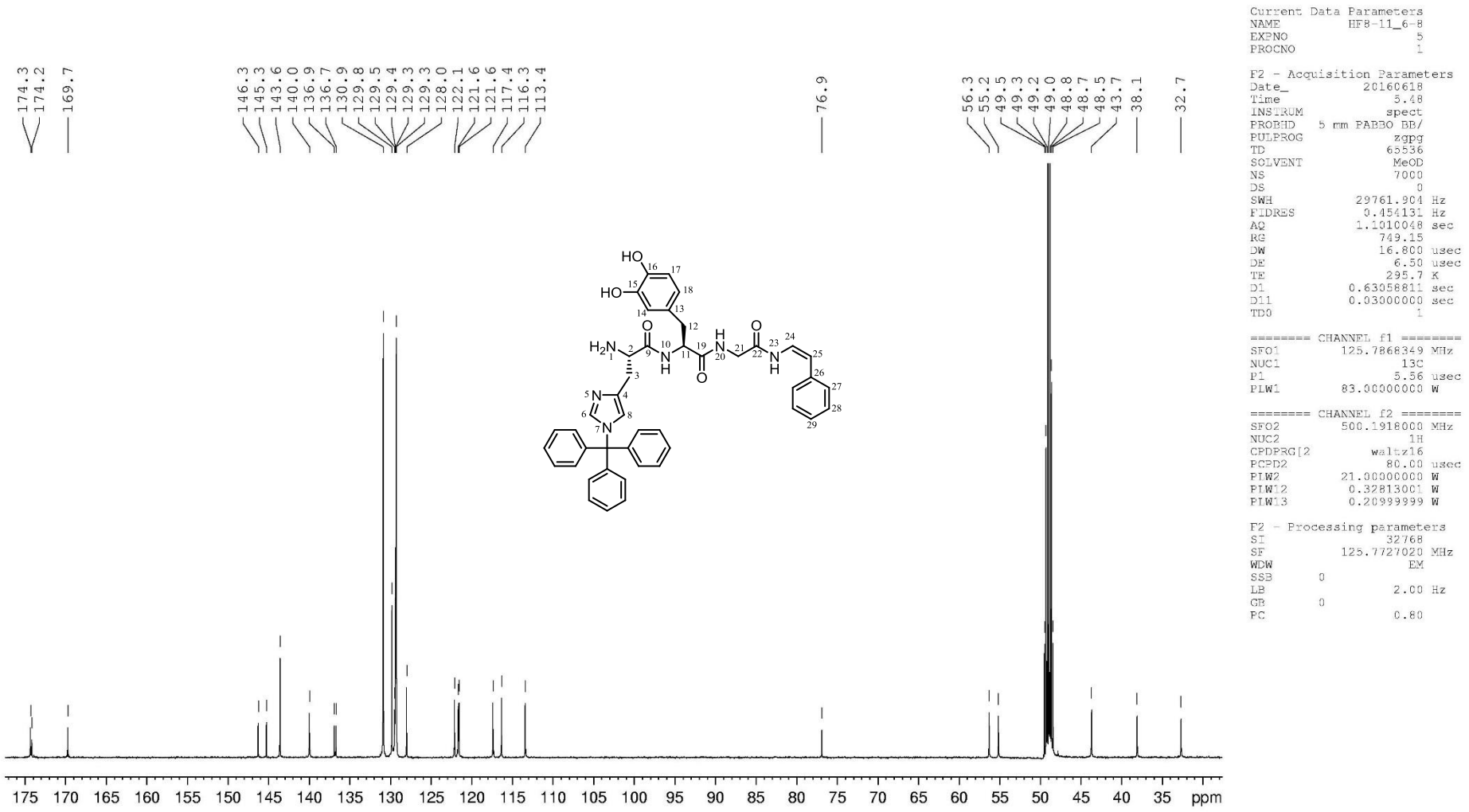
^{1}H NMR ($CDCl_3$, 400 MHz) of (*S*)-2-amino-*N*-((*S*)-3-(3,4-bis((*tert*-butyldimethylsilyl)oxy)phenyl)-1-oxo-1-((2-oxo-2-(((*Z*)-styryl)amino)ethyl)amino)propan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**14**).



^{13}C NMR ($CDCl_3$, 125 MHz) of (*S*)-2-amino-*N*-((*S*)-3-(3,4-bis((*tert*-butyldimethylsilyl)oxy)phenyl)-1-oxo-1-((2-oxo-2-(((*Z*)-styryl)amino)ethyl)amino)propan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**14**).



^{1}H NMR (CD_3OD, 500 MHz) of (*S*)-2-amino-*N*-((*S*)-3-(3,4-dihydroxyphenyl)-1-oxo-1-((2-oxo-2-(((*Z*)-styryl)amino)ethyl)amino)propan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**15**).

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TE               295.7 K
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D11           0.03000000 sec
TD0                    1

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NUC1                 13C
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PLW12         0.32813001 W
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F2 - Processing parameters
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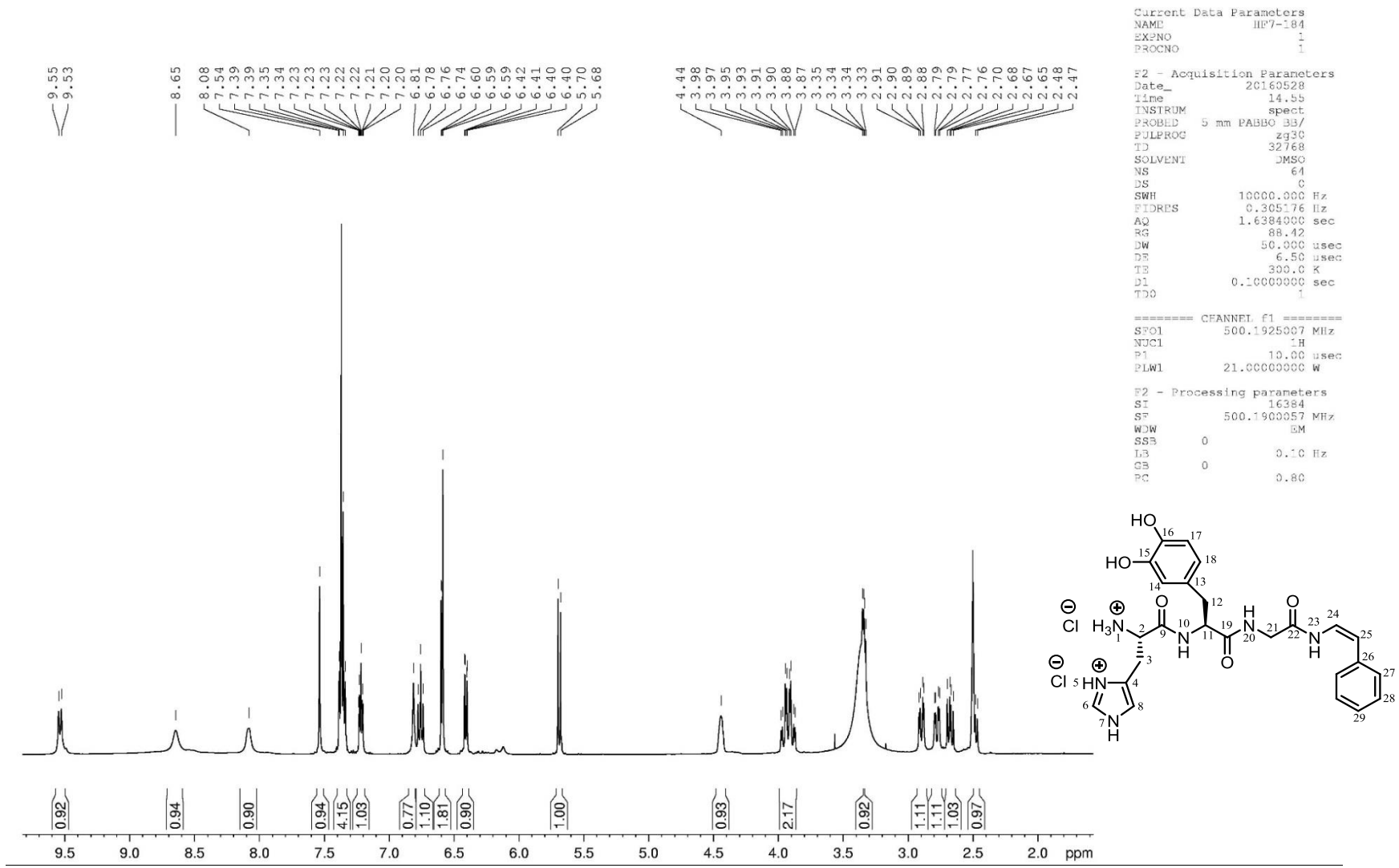
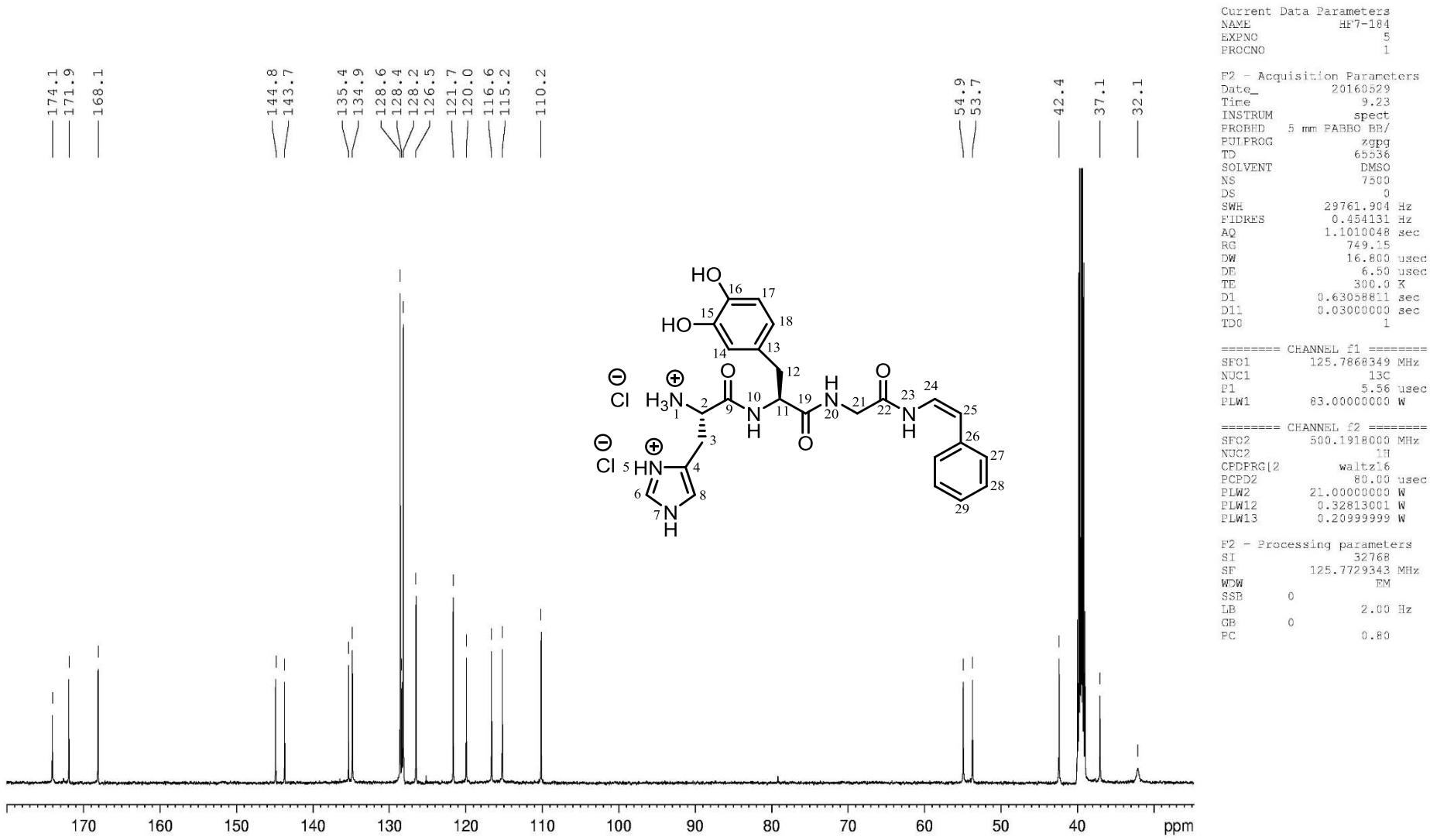
SF           125.7727020 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                0.80
```

^{13}C NMR (CD_3OD, 125 MHz) of (*S*)-2-amino-*N*-((*S*)-3-(3,4-dihydroxyphenyl)-1-oxo-1-((2-oxo-2-(((*Z*)-styryl)amino)ethyl)amino)propan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**15**).



^{1}H NMR (DMSO-d_6, 500 MHz) of 4-((*S*)-2-ammonio-3-(((*S*)-3-(3,4-dihydroxyphenyl)-1-oxo-1-((2-oxo-2-(((*Z*)-styryl)amino)ethyl)amino)propan-2-yl)amino)-3-oxopropyl)-1*H*-imidazol-3-ium chloride (**2**).

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Current Data Parameters
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PROCNO                      1

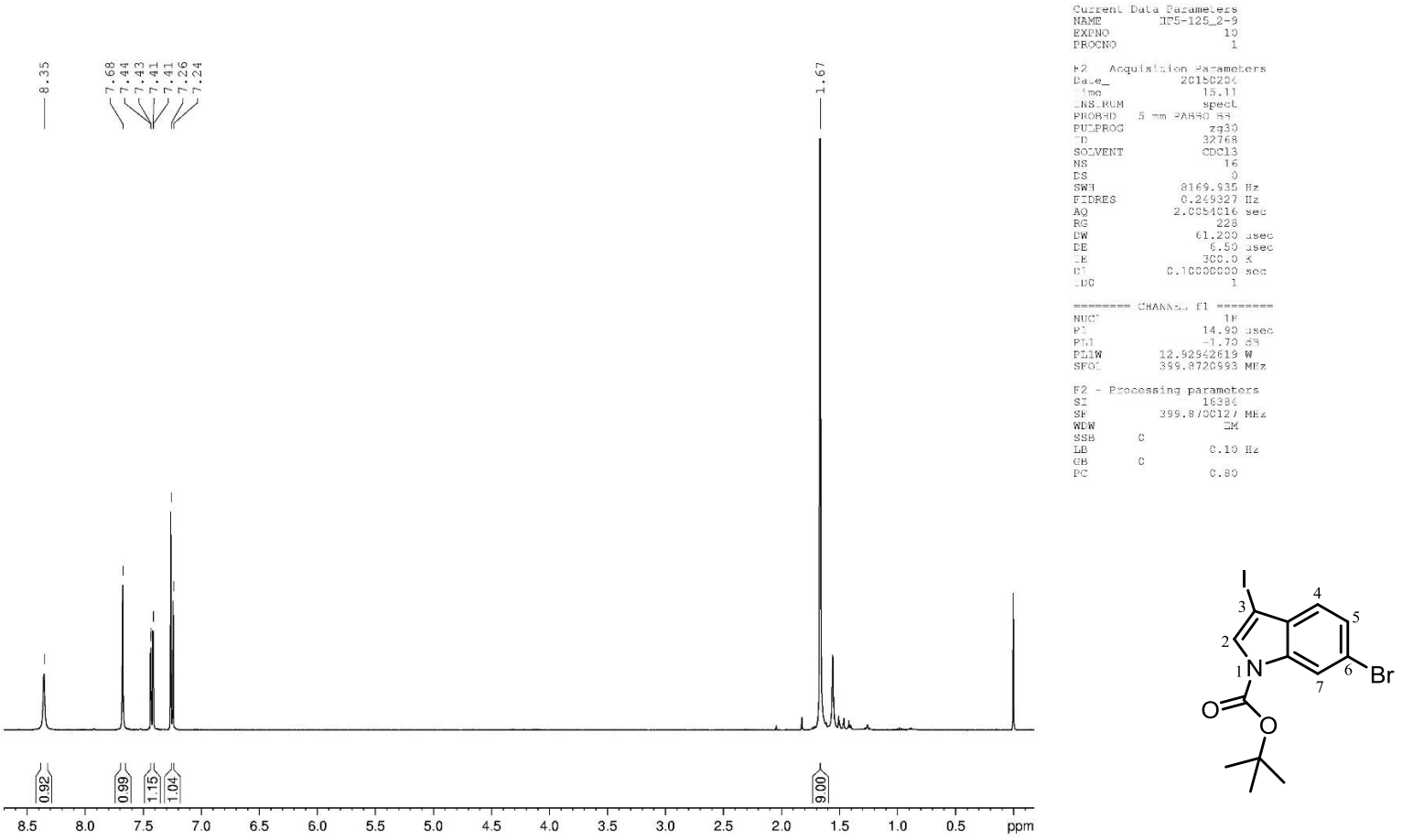
F2 - Acquisition Parameters
Date_               20160529
Time                    9.23
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg
TD                     65536
SOLVENT                DMSO
NS                      7500
DS                         0
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010048 sec
RG                    749.15
DW                    16.800 usec
DE                     6.50 usec
TE                    300.0 K
D1                 0.63058811 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              125.7868349 MHz
NUC1                      13C
P1                       5.56 usec
PLW1              83.00000000 W

======== CHANNEL f2 ========
SFO2              500.1918000 MHz
NUC2                      1H
CPDPRG[2               waltz16
PCPD2                   80.00 usec
PLW2              21.00000000 W
PLW12              0.32813001 W
PLW13              0.20999999 W

F2 - Processing parameters
SI                        32768
SF                125.7729343 MHz
WDW                          EM
SSB           0
LB                        2.00 Hz
GB            0
PC                        0.80
```

^{13}C NMR (DMSO-d_6, 125 MHz) of 4-((*S*)-2-ammonio-3-(((*S*)-3-(3,4-dihydroxyphenyl)-1-oxo-1-((2-oxo-2-(((*Z*)-styryl)amino)ethyl)amino)propan-2-yl)amino)-3-oxopropyl)-1*H*-imidazol-3-ium chloride (**2**).



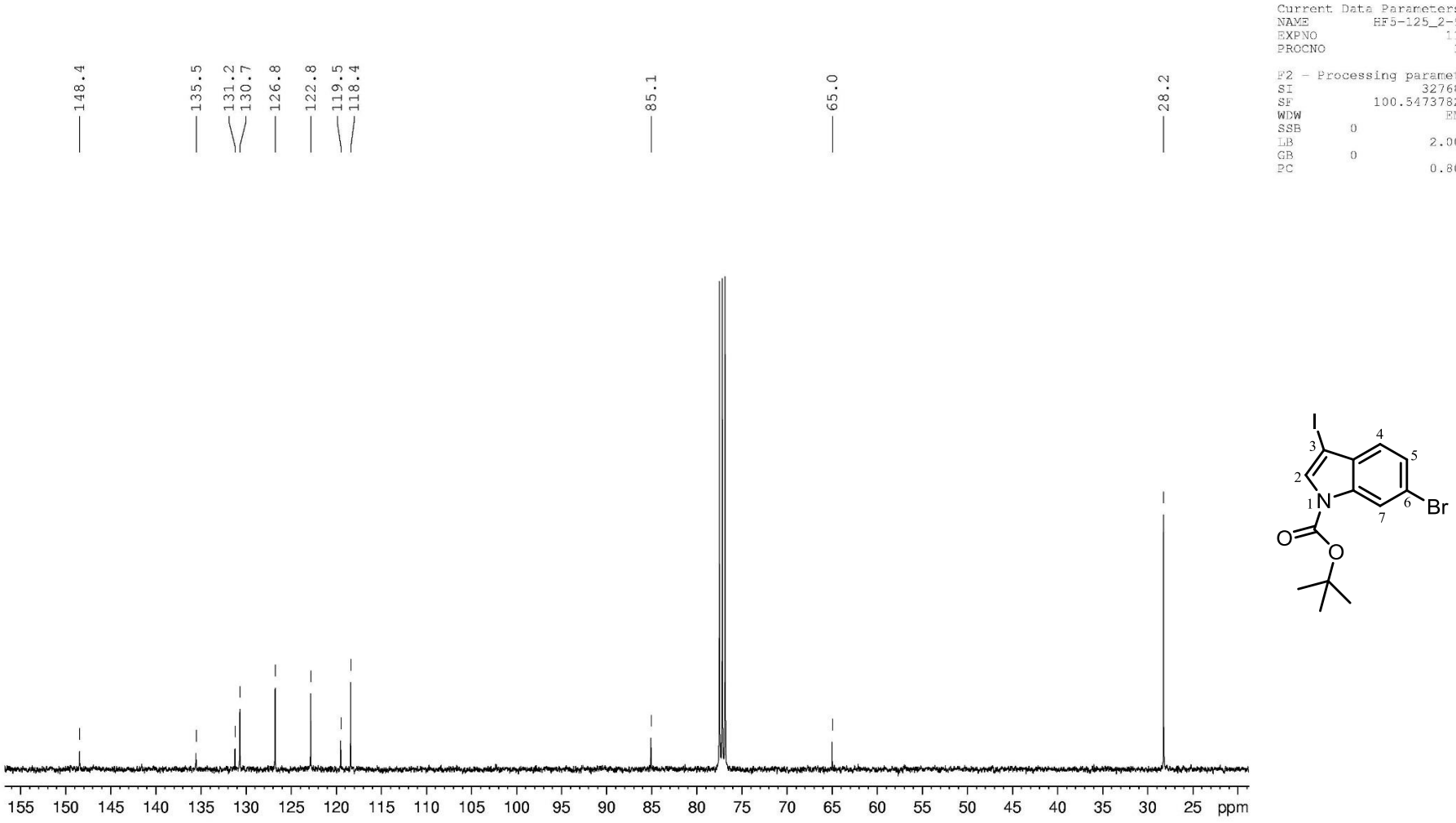

```
Current Data Parameters
NAME          HF5-125_2-9
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_          20150204
Time              15.11
INSTRUM           spect
PROBHD   5 mm PABBO BB
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   0
SWH           8169.935 Hz
FIDRES        0.249327 Hz
AQ            2.0054016 sec
RG                228
DW               61.200 usec
DE                6.50 usec
TE                300.0 K
D1           0.10000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1                14.90 usec
PL1               -1.70 dB
PL1W        12.92962619 W
SFO1        399.8720993 MHz

F2 - Processing parameters
SI                16384
SF          399.8700127 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                0.80
```


^{1}H NMR ($CDCl_3$, 400 MHz) of *tert*-Butyl-6-bromo-3-iodo-1*H*-indole-1-carboxylate (**19**).

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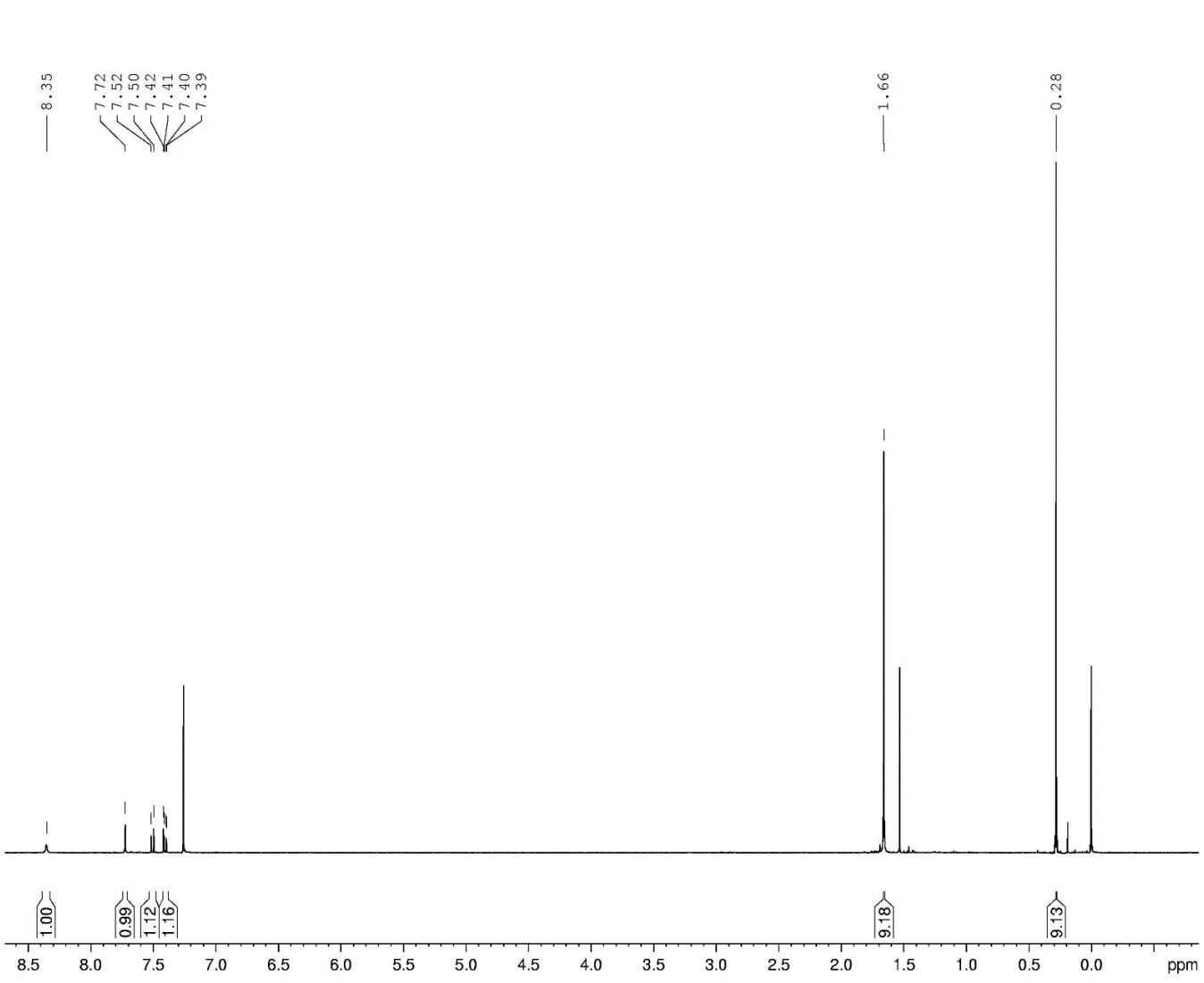
Current Data Parameters
NAME          HF5-125_2-9
EXPNO                  11
PROCNO                  1

F2 - Processing parameters
SI                   32768
SF           100.5473782 MHz
WDW                     EM
SSB       0
LB                  2.00 Hz
GB        0
PC                  0.80
```


^{1}H NMR ($CDCl_3$, 400 MHz) of *tert*-Butyl-6-bromo-3-iodo-1*H*-indole-1-carboxylate (**19**)

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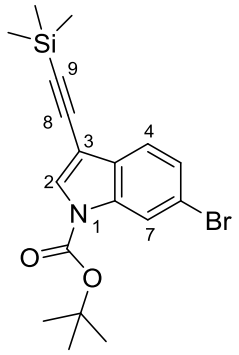
Current Data Parameters
NAME                  EF7-25
EXPNO                      1
PROCNO                     1

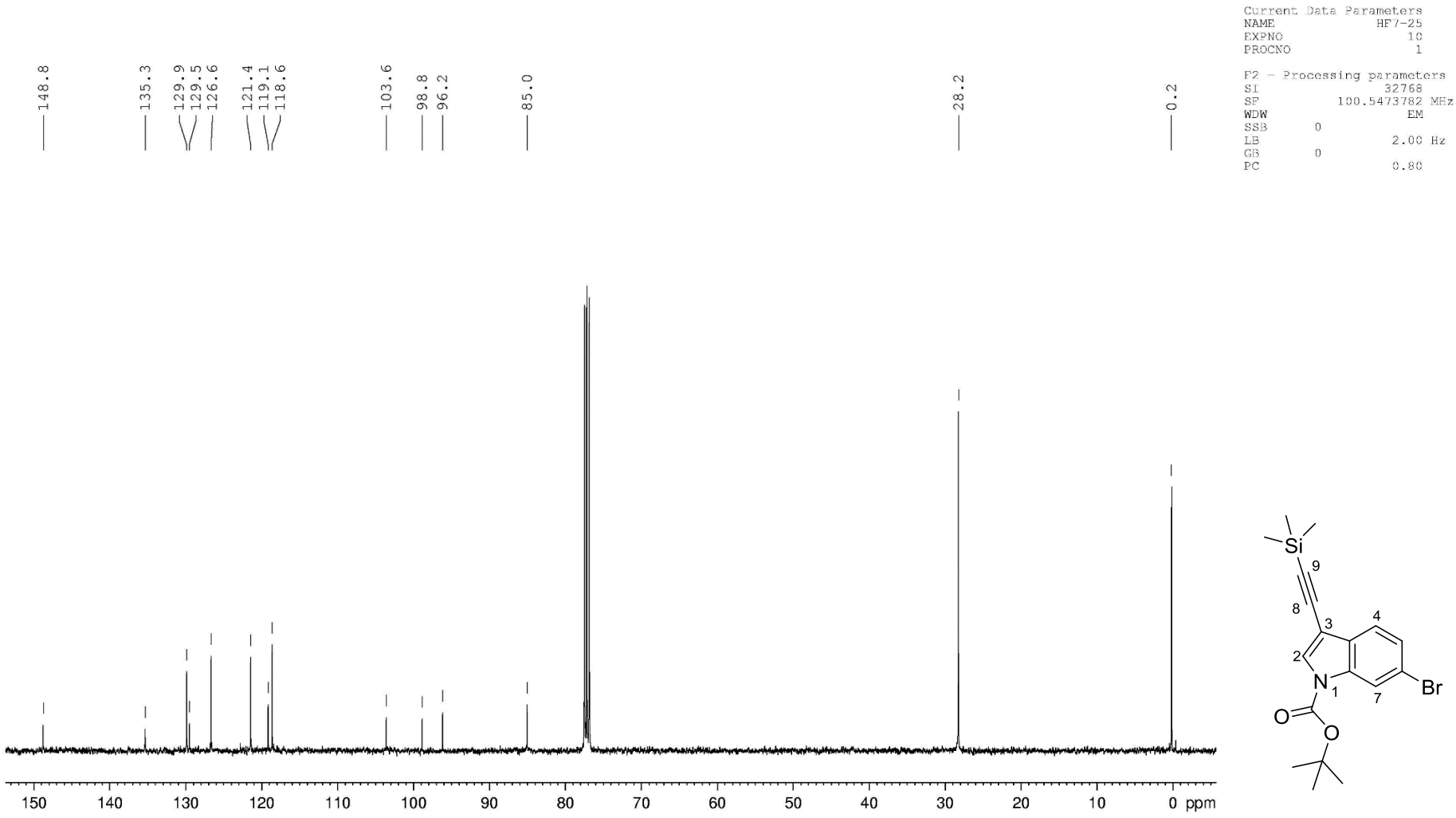
F2 - Acquisition Parameters
Date_              20151122
Time                   10.46
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 2.0447233 sec
RG                       456
DW                    62.400 usec
DE                     6.50 usec
TE                    300.0 K
D1              0.10000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     7.32 usec
PL1                   -6.00 dB
PL1W          40.00000000 W
SFO1          400.1320007 MHz

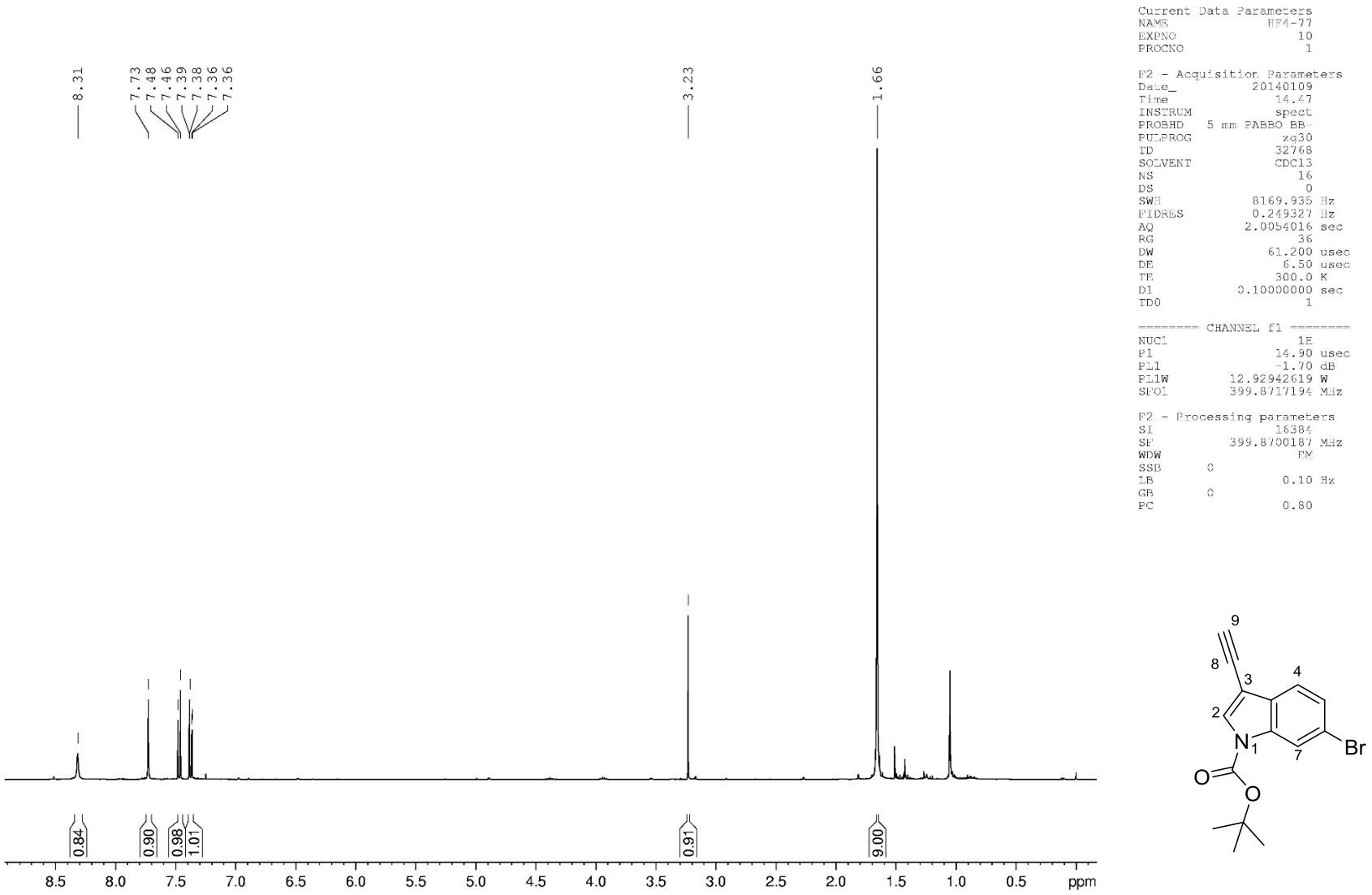
F2 - Processing parameters
SI                    16384
SF            400.1300094 MHz
WDW                      EM
SSB       0
LB                     0.10 Hz
GB        0
PC                     0.80
```



^{1}H NMR ($CDCl_3$, 400 MHz) of *tert*-butyl 6-bromo-3-((trimethylsilyl)ethynyl)-1*H*-indole-1-carboxylate (**20**).



^{13}C NMR ($CDCl_3$, 100 MHz) of *tert*-butyl 6-bromo-3-((trimethylsilyl)ethynyl)-1*H*-indole-1-carboxylate (**20**).



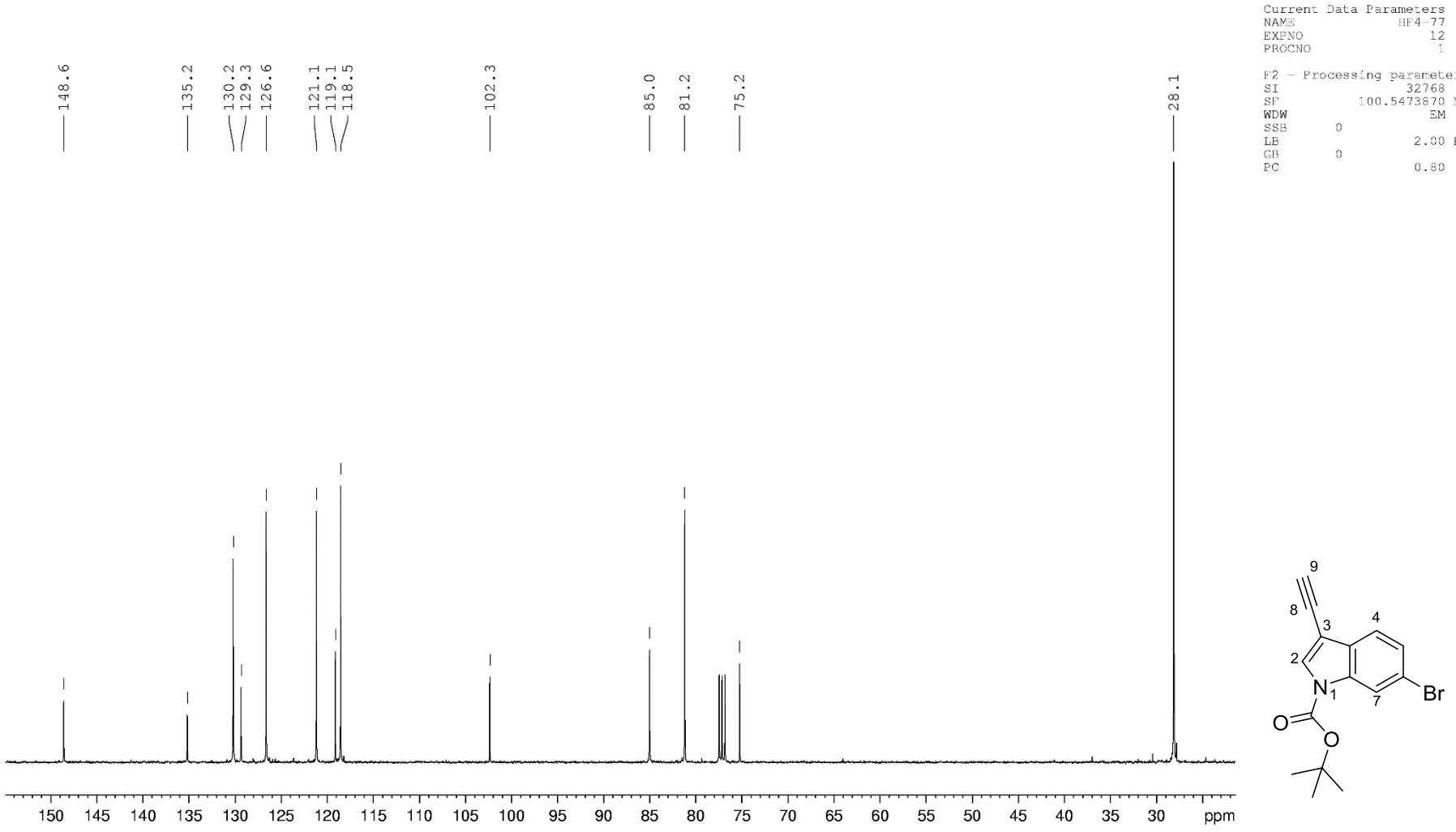

```
Current Data Parameters
NAME                  HF4-77
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140109
Time                  14.47
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8169.935 Hz
FIDRES            0.249327 Hz
AQ                2.0054016 sec
RG                       36
DW                  61.200 usec
DE                   6.50 usec
TE                  300.0 K
D1             0.10000000 sec
TD0                       1

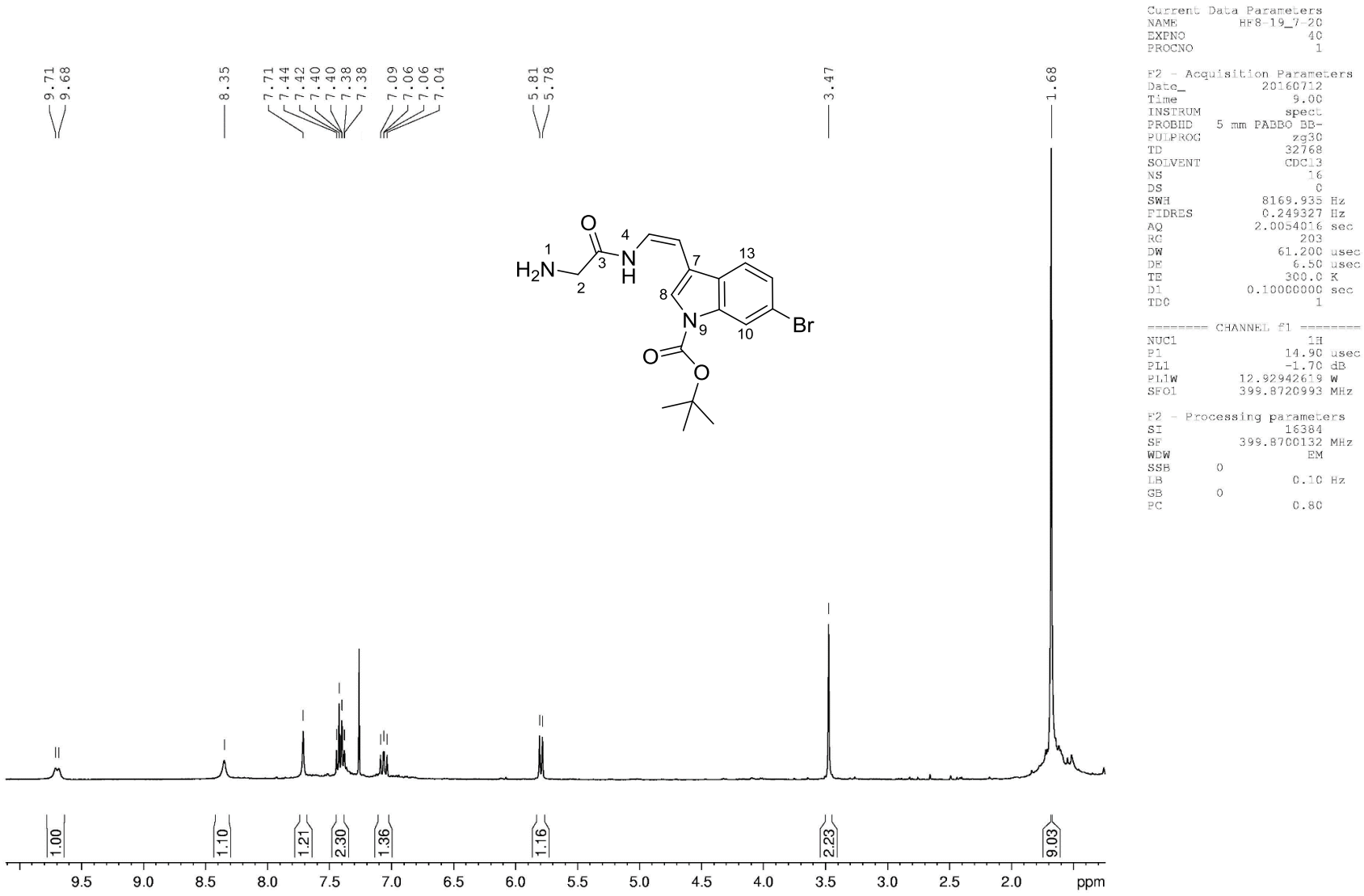
-------- CHANNEL f1 --------
NUC1                     1H
P1                   14.90 usec
PL1                  -1.70 dB
PL1W          12.92942619 W
SFO1          399.8717194 MHz

F2 - Processing parameters
SI                    16384
SF            399.8700187 MHz
WDW                      EM
SSB          0
LB                    0.10 Hz
GB           0
PC                    0.80
```


^{1}H NMR ($CDCl_3$, 400 MHz) of *tert*-butyl 6-bromo-3-ethynyl-1*H*-indole-1-carboxylate (**17**).



^{13}C NMR ($CDCl_3$, 100 MHz) of *tert*-butyl 6-bromo-3-ethynyl-1*H*-indole-1-carboxylate (**17**).

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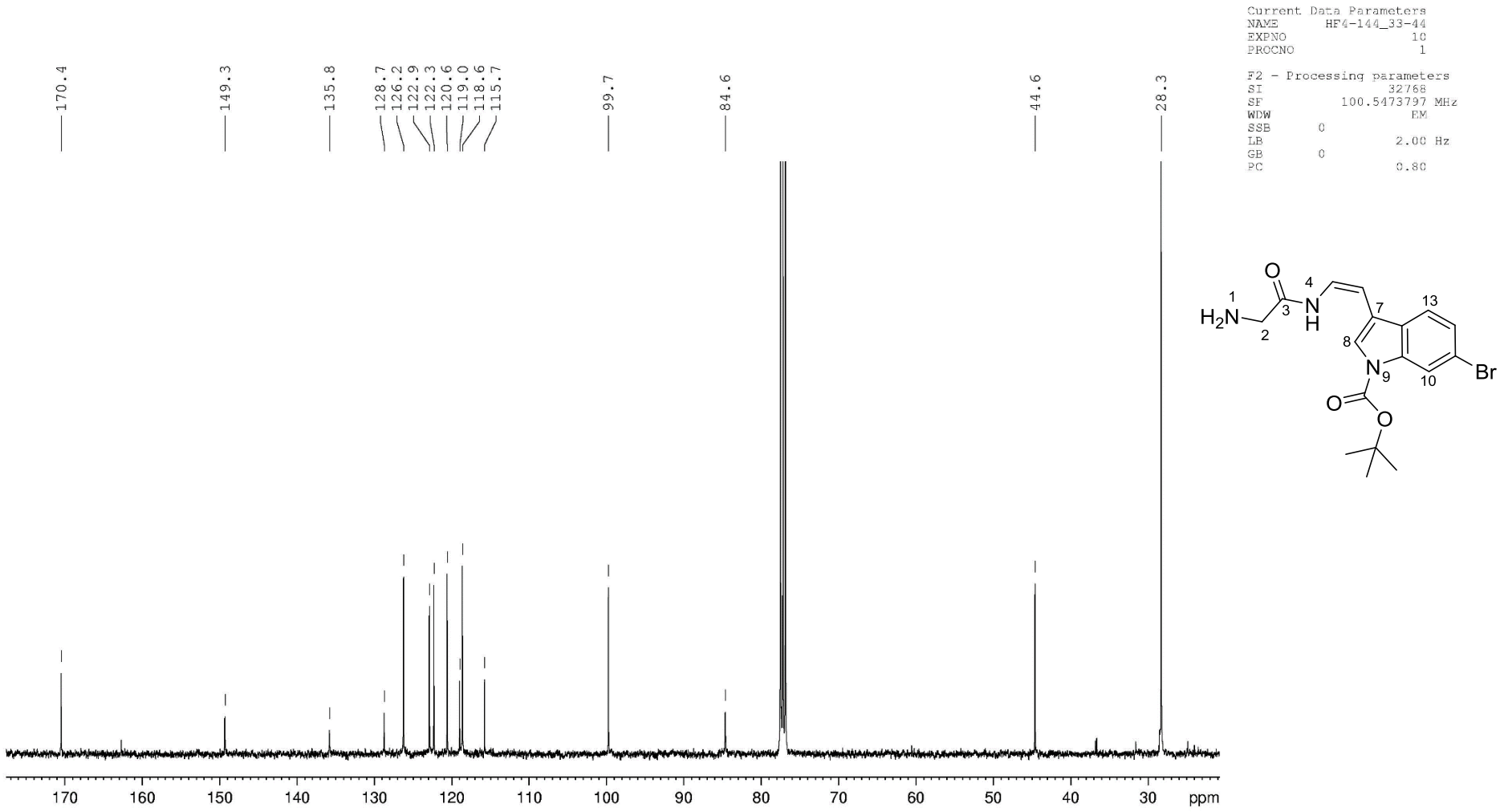
Current Data Parameters
NAME          HF8-19_7-20
EXPNO                  40
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160712
Time                9.00
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8169.935 Hz
FIDRES          0.249327 Hz
AQ              2.0054016 sec
RG                   203
DW                61.200 usec
DE                 6.50 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

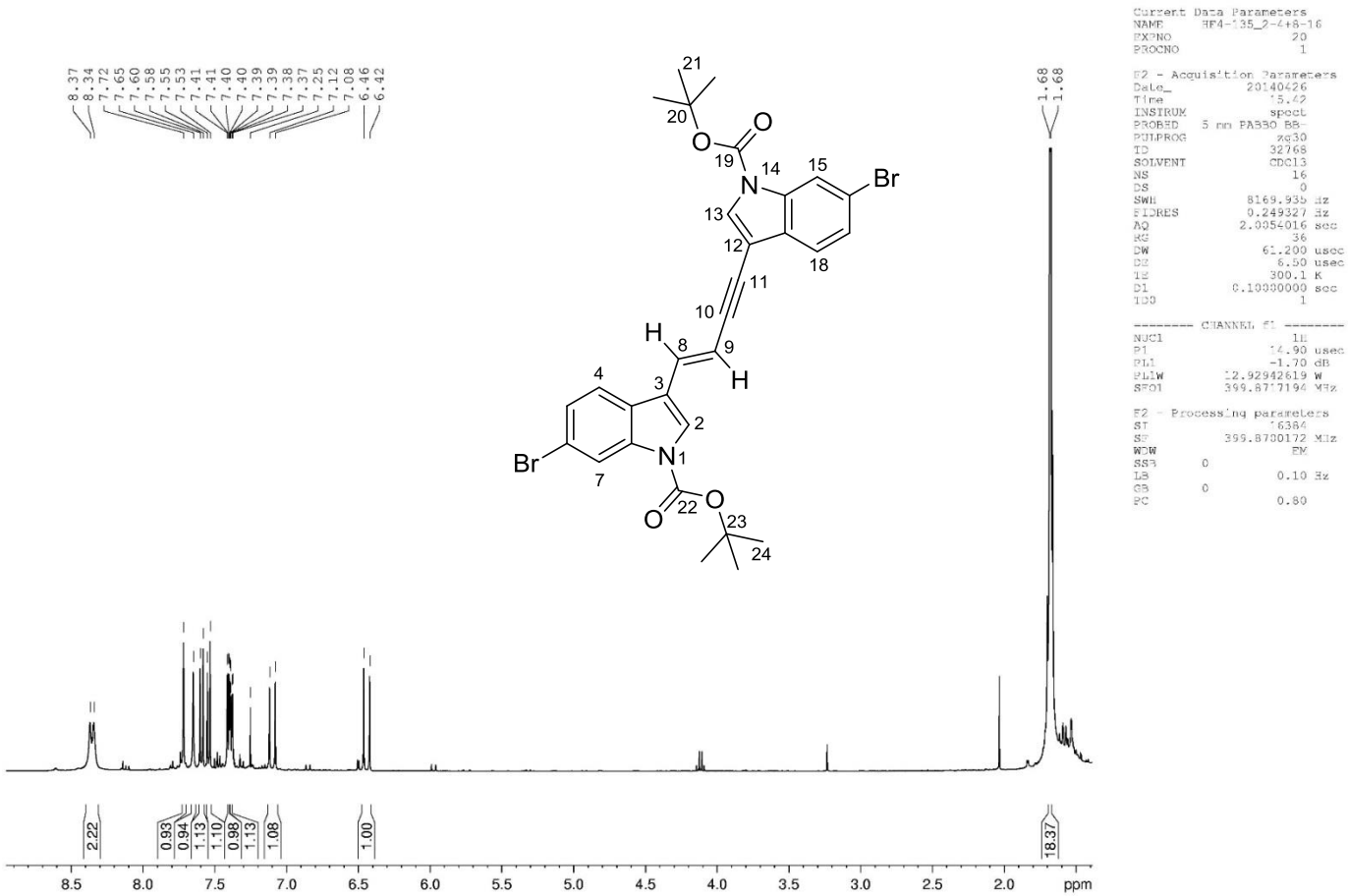
======== CHANNEL f1 ========
NUC1                  1H
P1                 14.90 usec
PL1                -1.70 dB
PL1W         12.92942619 W
SFO1         399.8720993 MHz

F2 - Processing parameters
SI                 16384
SF          399.8700132 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 0.80
```

^{1}H NMR ($CDCl_3$, 400 MHz) of *tert*-butyl (Z)-3-(2-(2-aminoacetamido)vinyl)-6-bromo-1*H*-indole-1-carboxylate (**21**).



^{13}C NMR ($CDCl_3$, 100 MHz) of *tert*-butyl (Z)-3-(2-(2-aminoacetamido)vinyl)-6-bromo-1*H*-indole-1-carboxylate (**21**).

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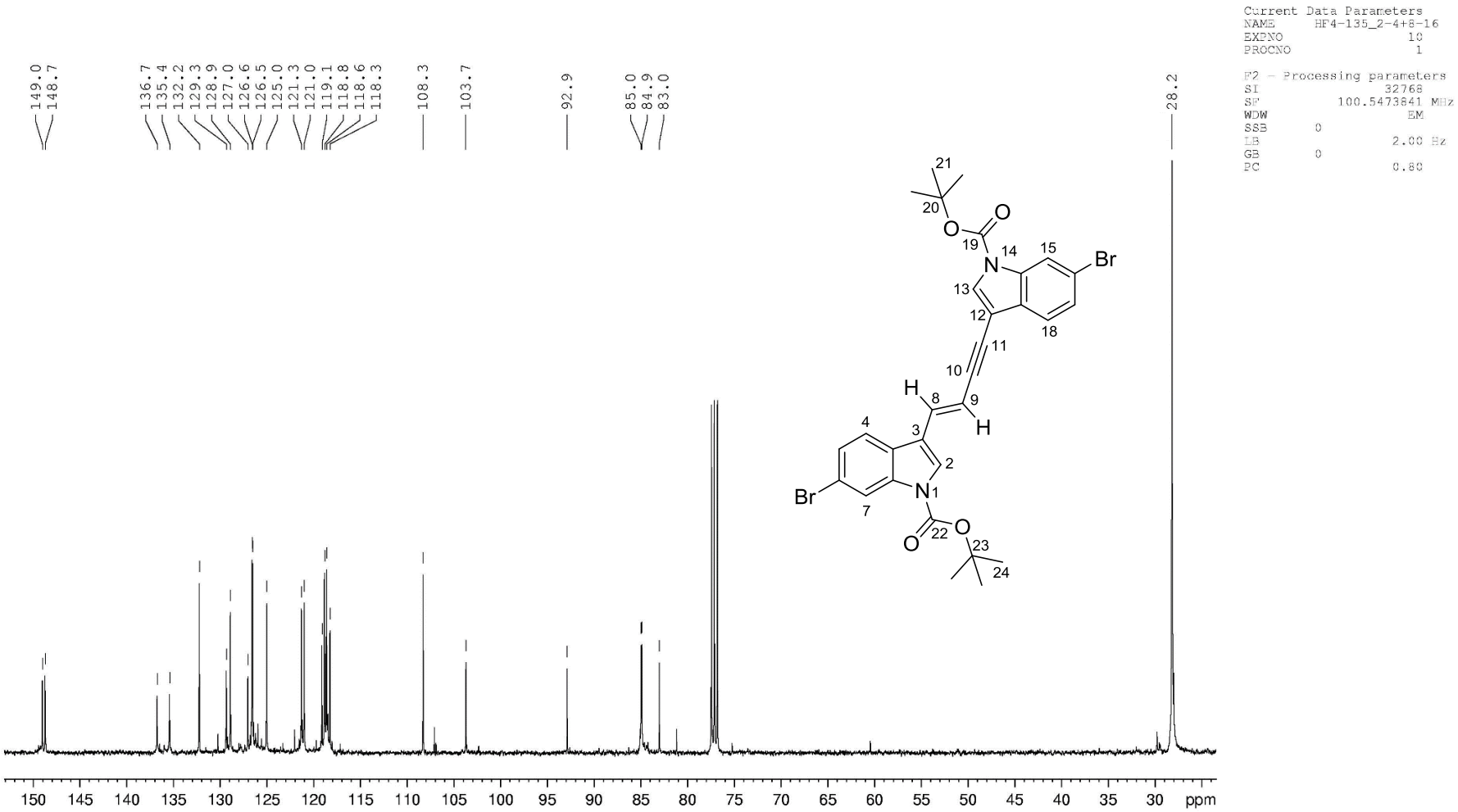
Current Data Parameters
NAME      HF4-135_2-448-16
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140426
Time                  15.42
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH               8169.935 Hz
FIDRES            0.249327 Hz
AQ                2.0054016 sec
RG                       36
DW                  61.200 usec
DE                   6.50 usec
TE                  300.1 K
D1                0.10000000 sec
TD0                      1

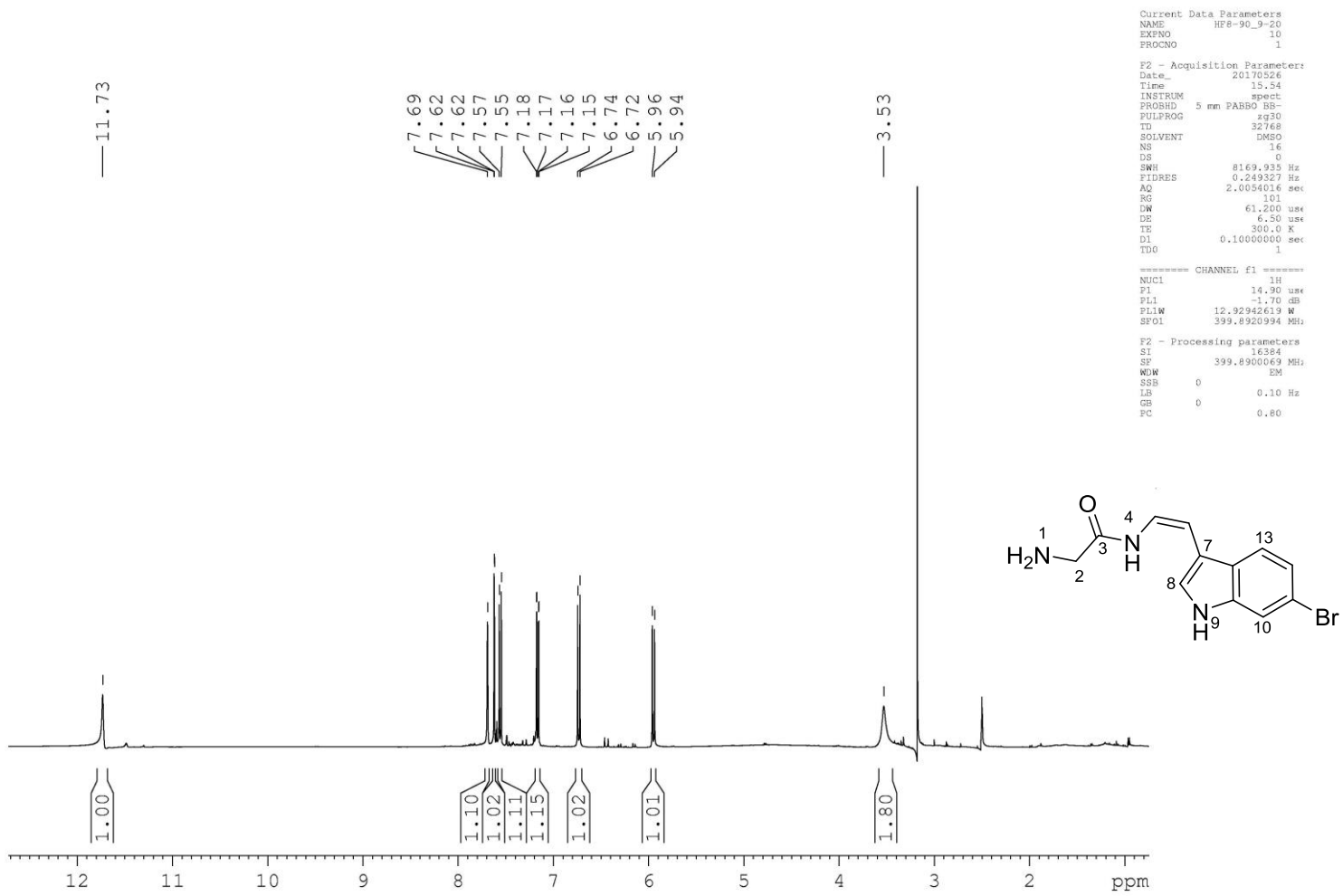
======== CHANNEL f1 ========
NUC1                     1H
P1                    14.90 usec
PL1                   -1.70 dB
PL1W            12.92942619 W
SFO1            399.8777194 MHz

F2 - Processing parameters
SI                    16384
SF              399.8700172 MHz
WDW                      EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    0.80
```

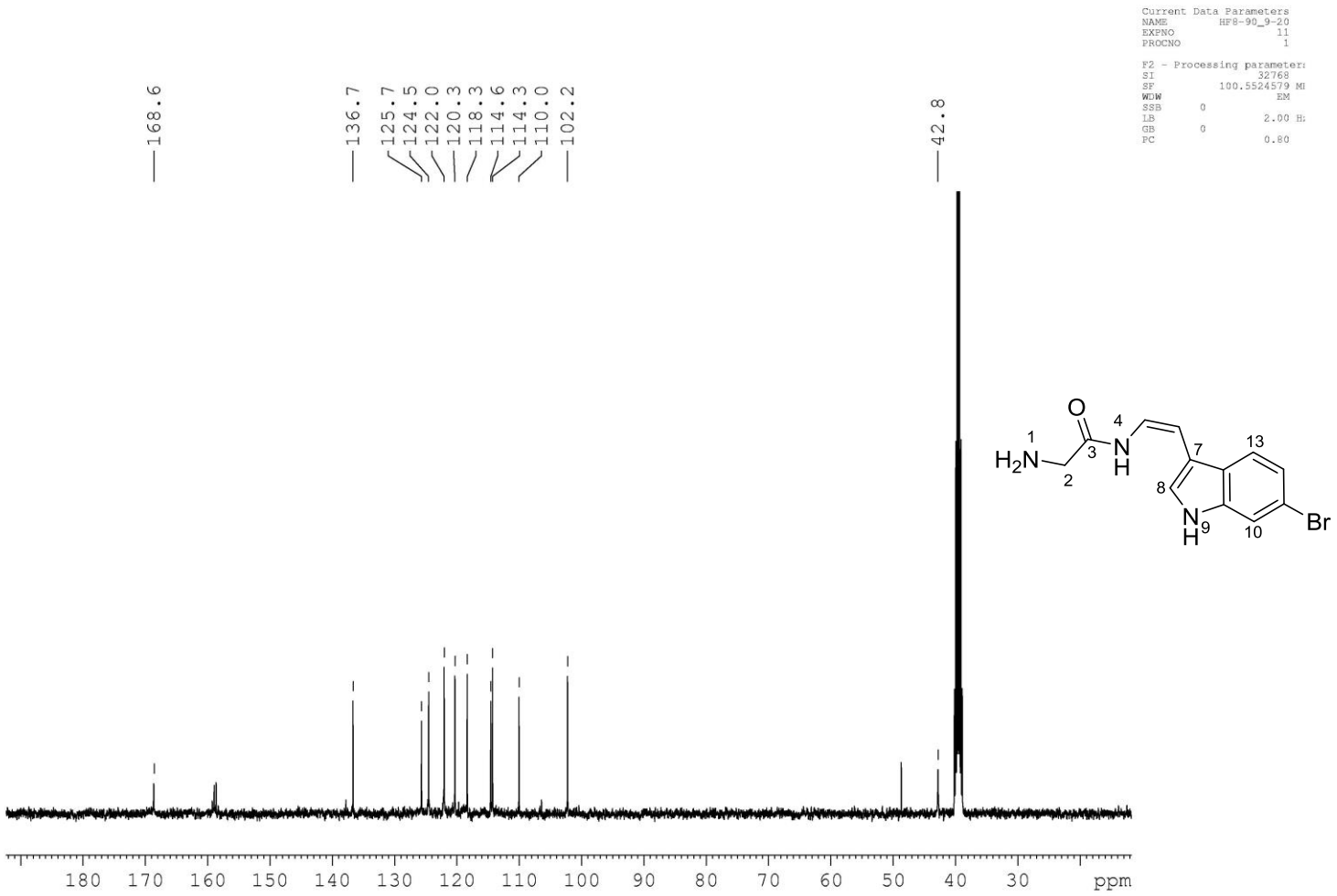
^{1}H NMR ($CDCl_3$, 400 MHz) of (*E*)-di-*tert*-butyl 3,3'-(but-1-en-3-yne-1,4-diyl)bis(6-bromo-1*H*-indole-1-carboxylate) (**22**).



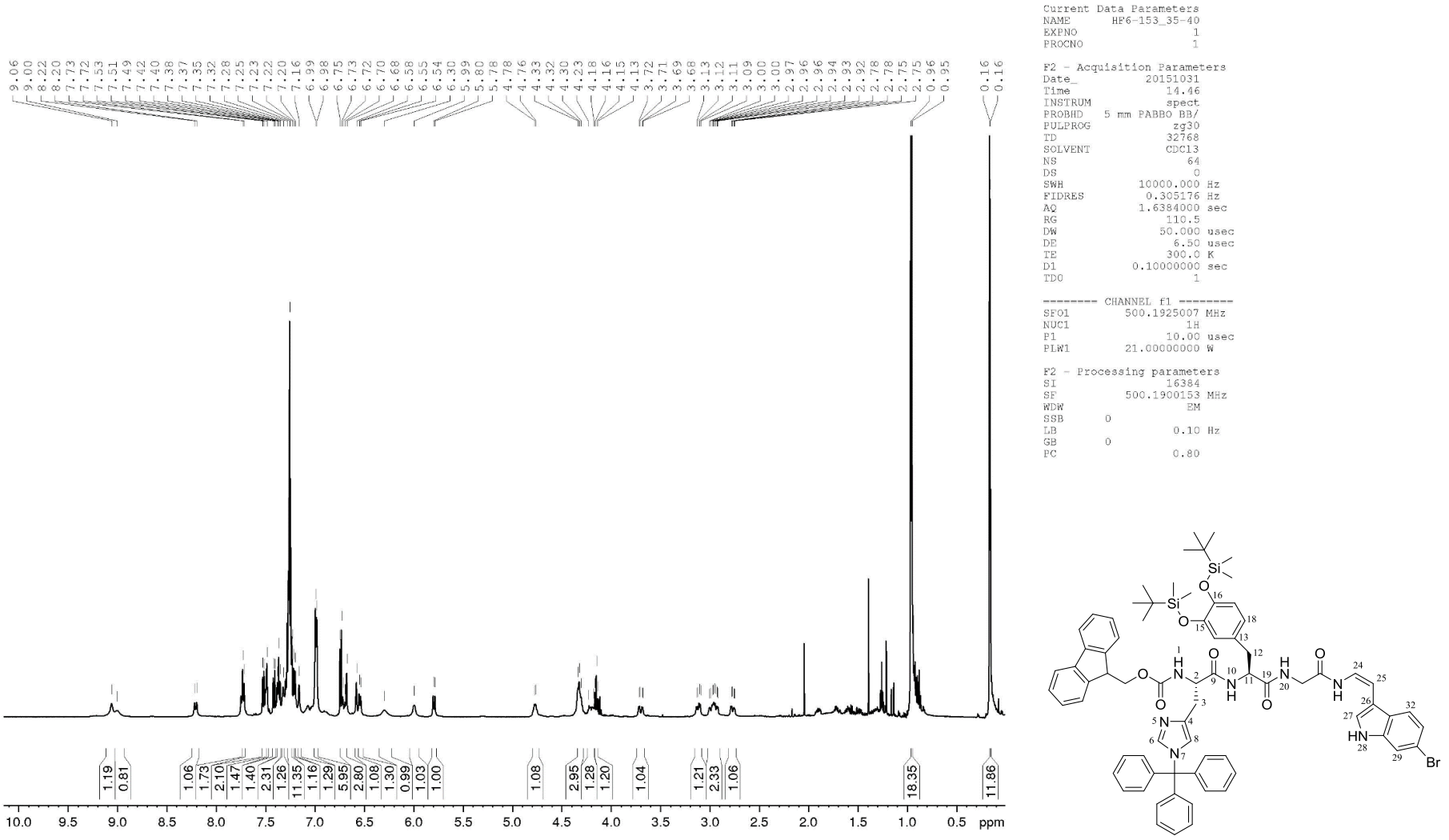
^{13}C NMR ($CDCl_3$, 100 MHz) of (*E*)-di-*tert*-butyl 3,3'-(but-1-en-3-yne-1,4-diyl)bis(6-bromo-1*H*-indole-1-carboxylate) (**22**).



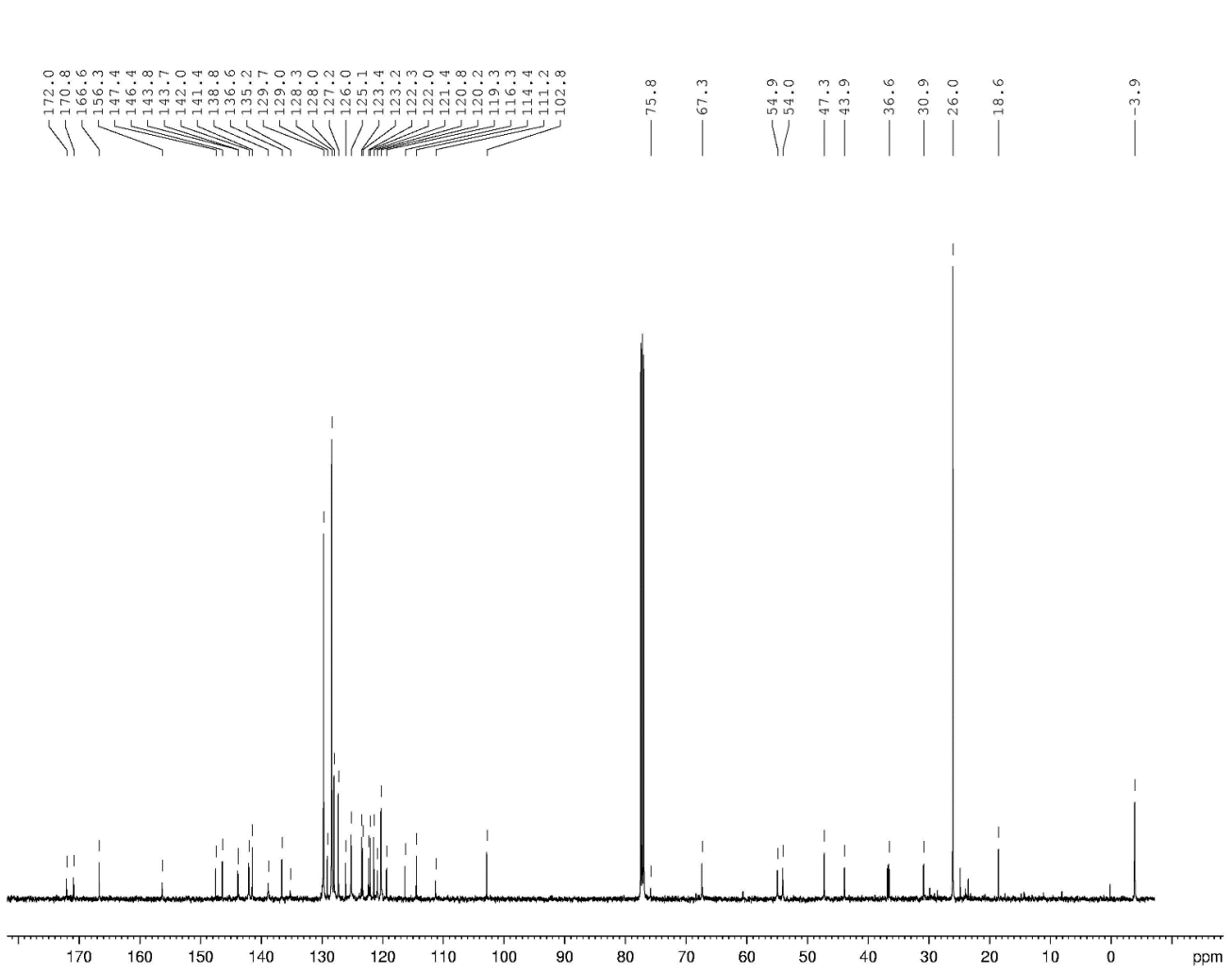
^{1}H NMR (DMSO-d_6, 400 MHz) of (*Z*)-2-amino-*N*-(2-(6-bromo-1*H*-indol-3-yl)vinyl)acetamide (**16**).

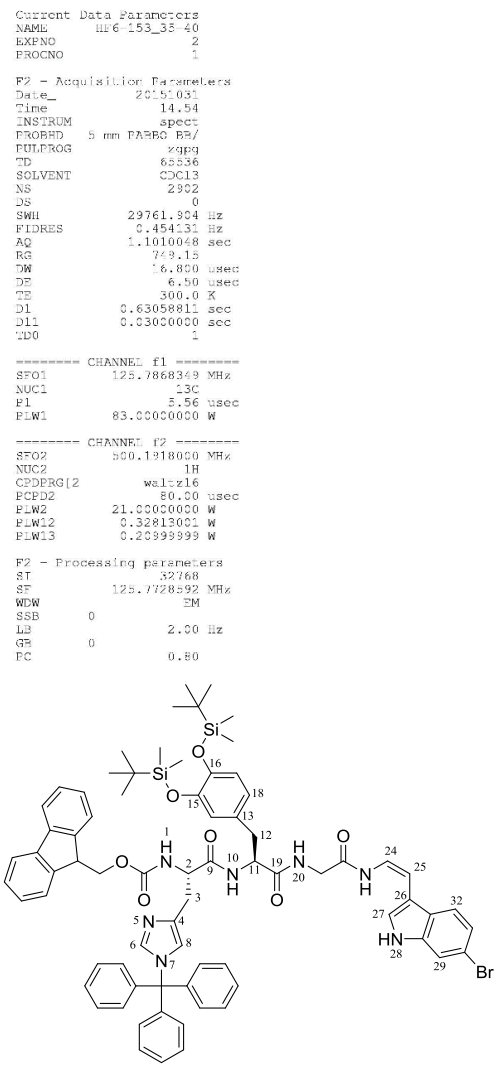


^{13}C NMR (DMSO-d_6, 100 MHz) of (*Z*)-2-amino-*N*-(2-(6-bromo-1*H*-indol-3-yl)vinyl)acetamide (**16**).

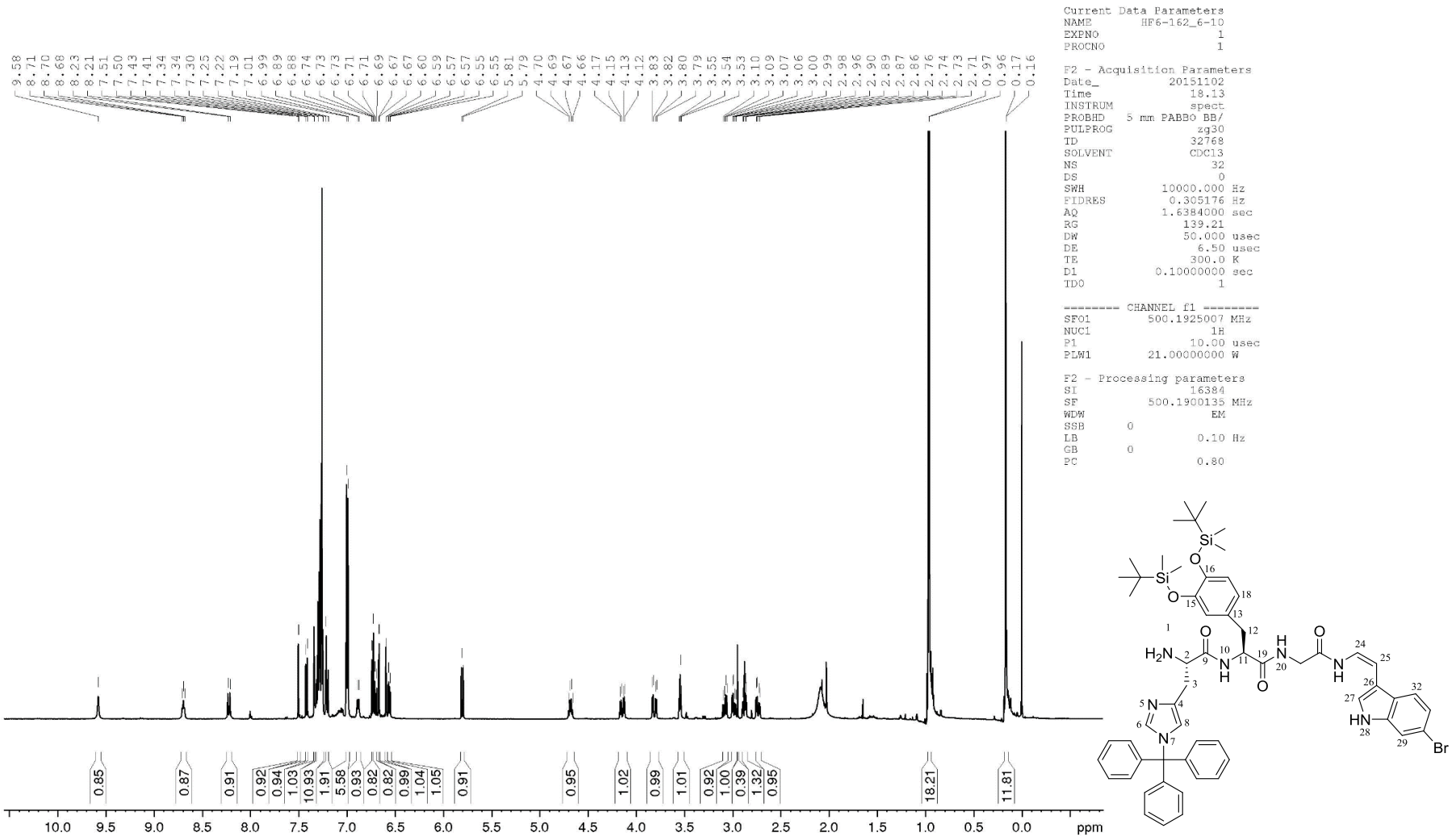


^{1}H NMR ($CDCl_3$, 500 MHz) of (9*H*-fluoren-9-yl)methyl ((*S*)-1-(((*S*)-3-(3,4-bis((*tert*-butyldimethylsilyl)oxy)phenyl)-1-((2-(((*Z*)-2-(6-bromo-1*H*-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-1-oxopropan-2-yl)amino)-1-oxo-3-(1-trityl-1*H*-imidazol-4-yl)propan-2-yl)carbamate (**23**).

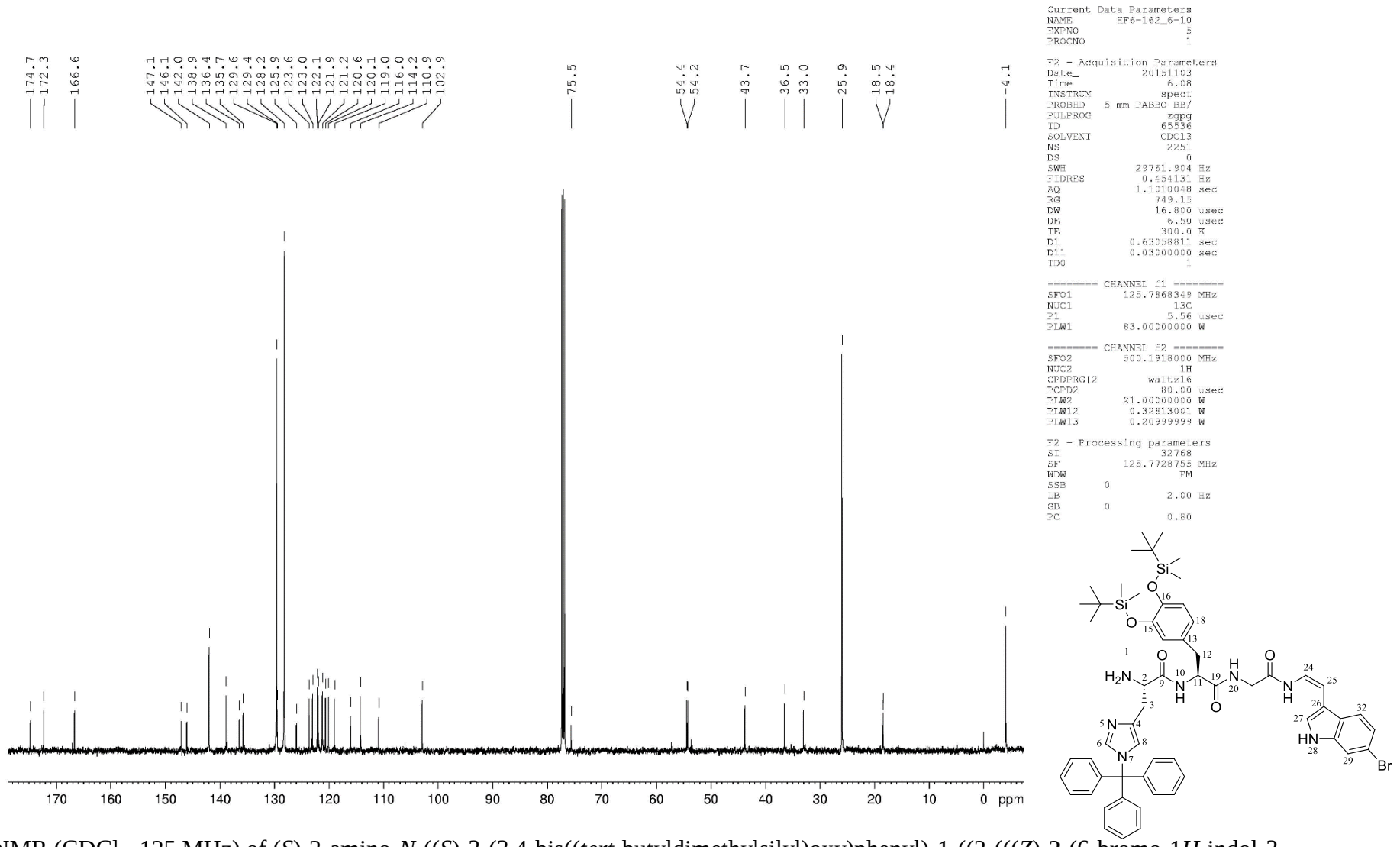




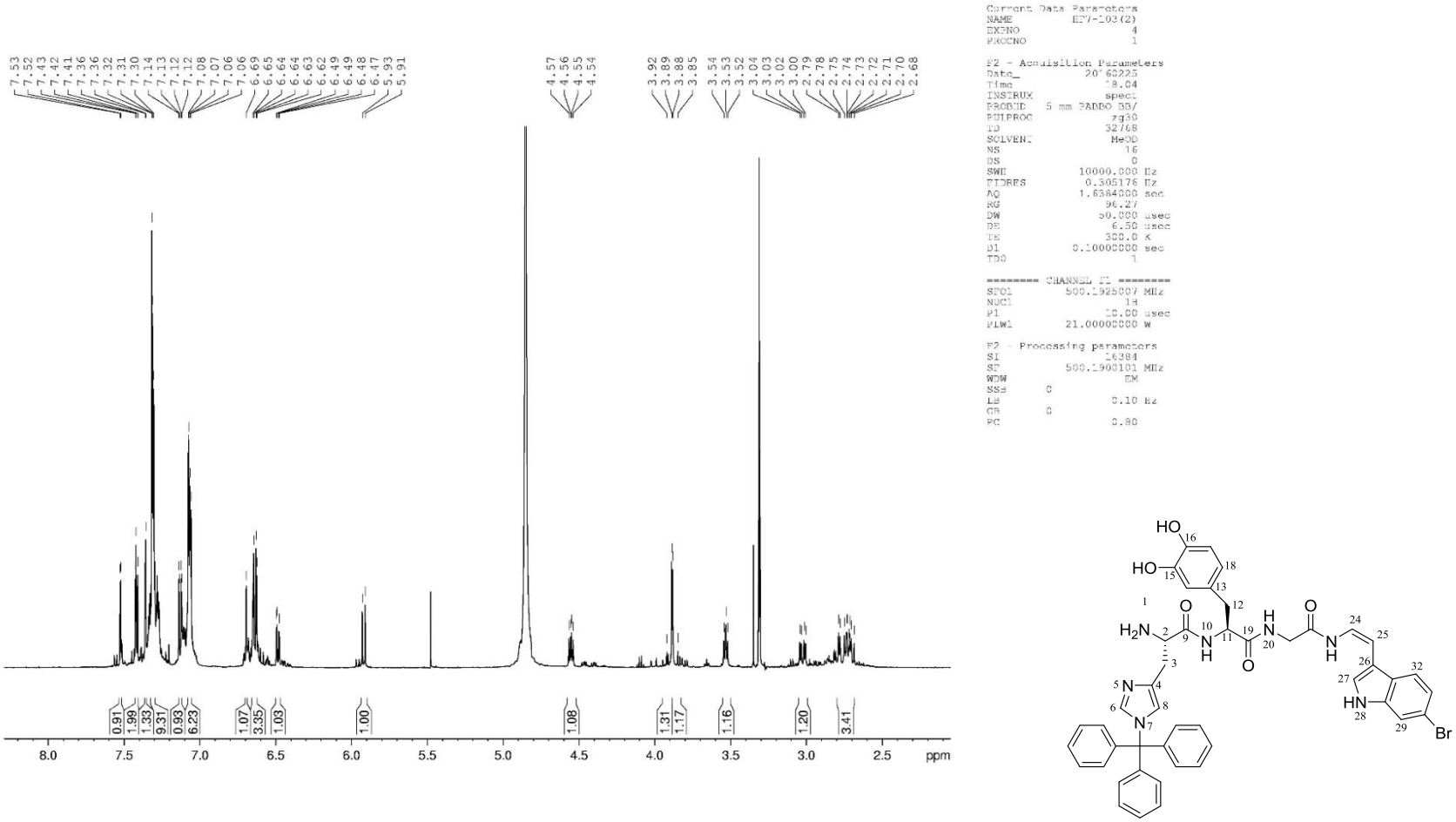
^{13}C NMR ($CDCl_3$, 125 MHz) of (9*H*-fluoren-9-yl)methyl ((*S*)-1-(((*S*)-3-(3,4-bis((*tert*-butyldimethylsilyl)oxy)phenyl)-1-((2-(((*Z*)-2-(6-bromo-1*H*-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-1-oxopropan-2-yl)amino)-1-oxo-3-(1-trityl-1*H*-imidazol-4-yl)propan-2-yl)carbamate (**23**).



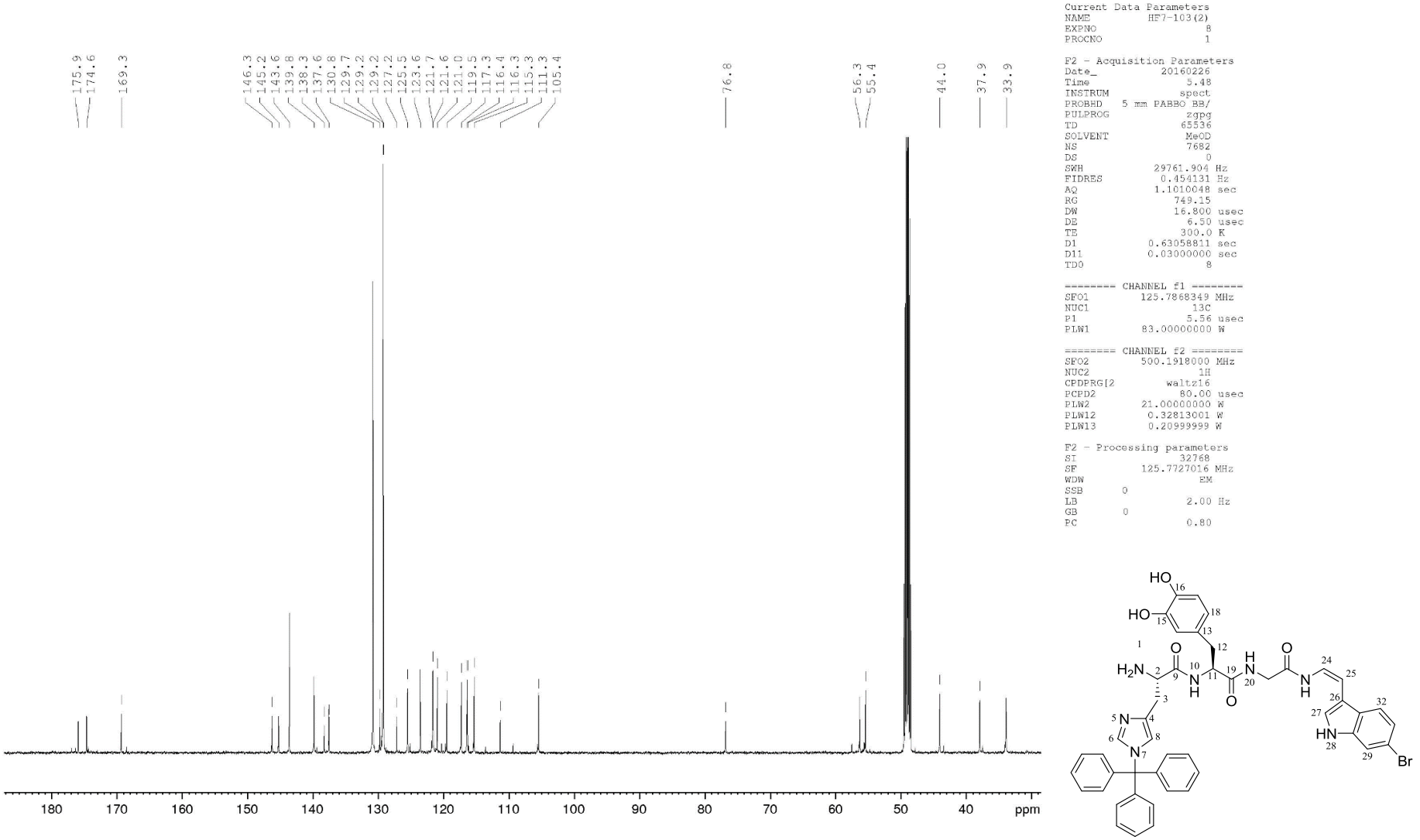
^{1}H NMR ($CDCl_3$, 500 MHz) of (*S*)-2-amino-*N*-((*S*)-3-(3,4-bis((*tert*-butyldimethylsilyl)oxy)phenyl)-1-((2-(((*Z*)-2-(6-bromo-1*H*-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-1-oxopropan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**24**).



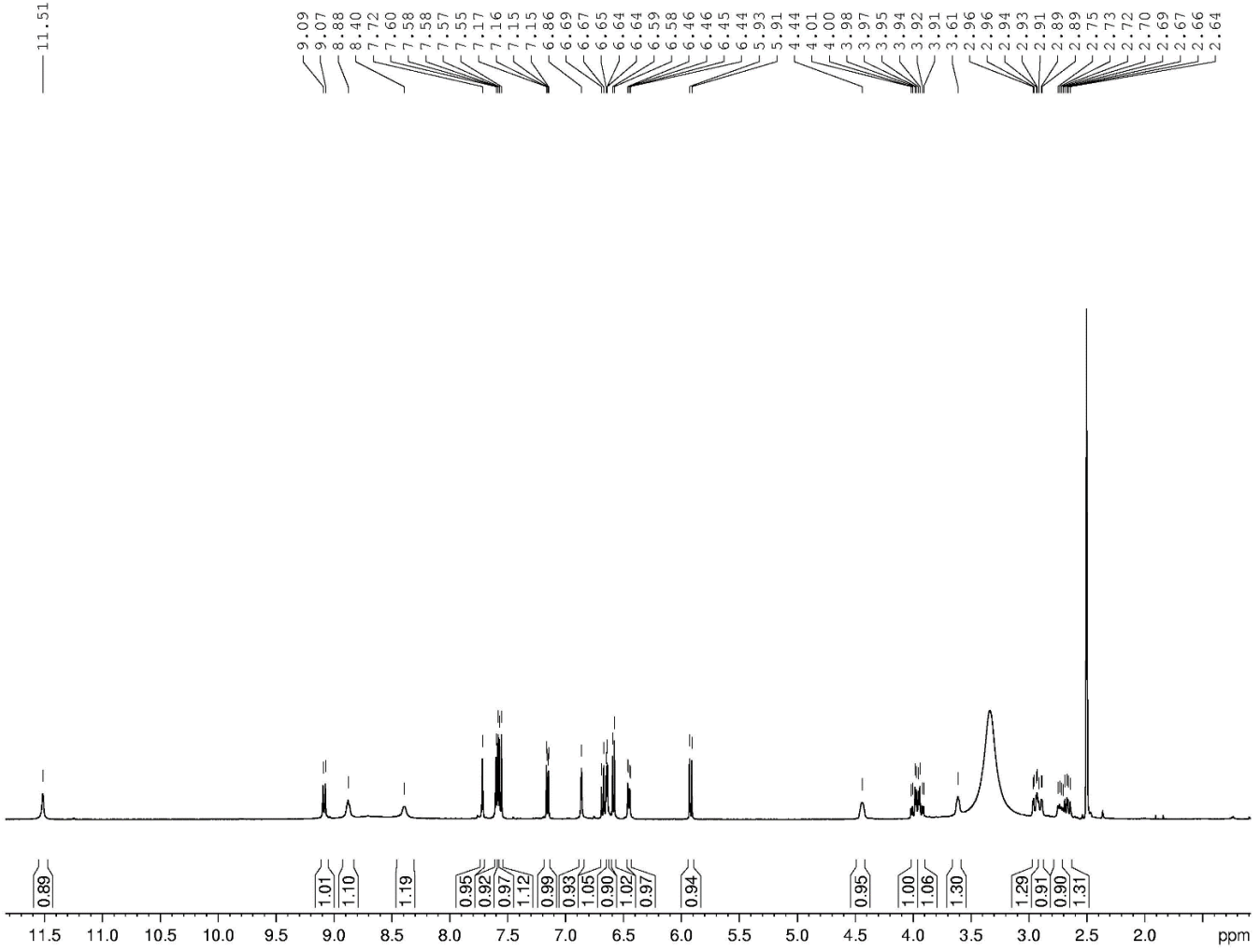
^{13}C NMR ($CDCl_3$, 125 MHz) of (*S*)-2-amino-*N*-((*S*)-3-(3,4-bis((*tert*-butyldimethylsilyl)oxy)phenyl)-1-((2-(((*Z*)-2-(6-bromo-1*H*-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-1-oxopropan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**24**).



^{1}H NMR (CD_3OD, 500 MHz) of (*S*)-2-amino-*N*-((*S*)-1-((2-(((*Z*)-2-(6-bromo-1*H*-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-3-(3,4-dihydroxyphenyl)-1-oxopropan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**25**).



^{13}C NMR (CD_3OD, 125 MHz) of (*S*)-2-amino-*N*-((*S*)-1-((2-(((*Z*)-2-(6-bromo-1*H*-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-3-(3,4-dihydroxyphenyl)-1-oxopropan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**25**).

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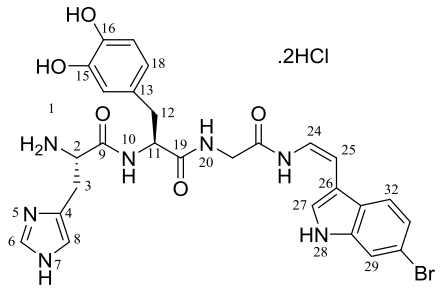
Current Data Parameters
NAME      HF8-28(2)_40-43
EXPNO                   1
PROCNO                  1

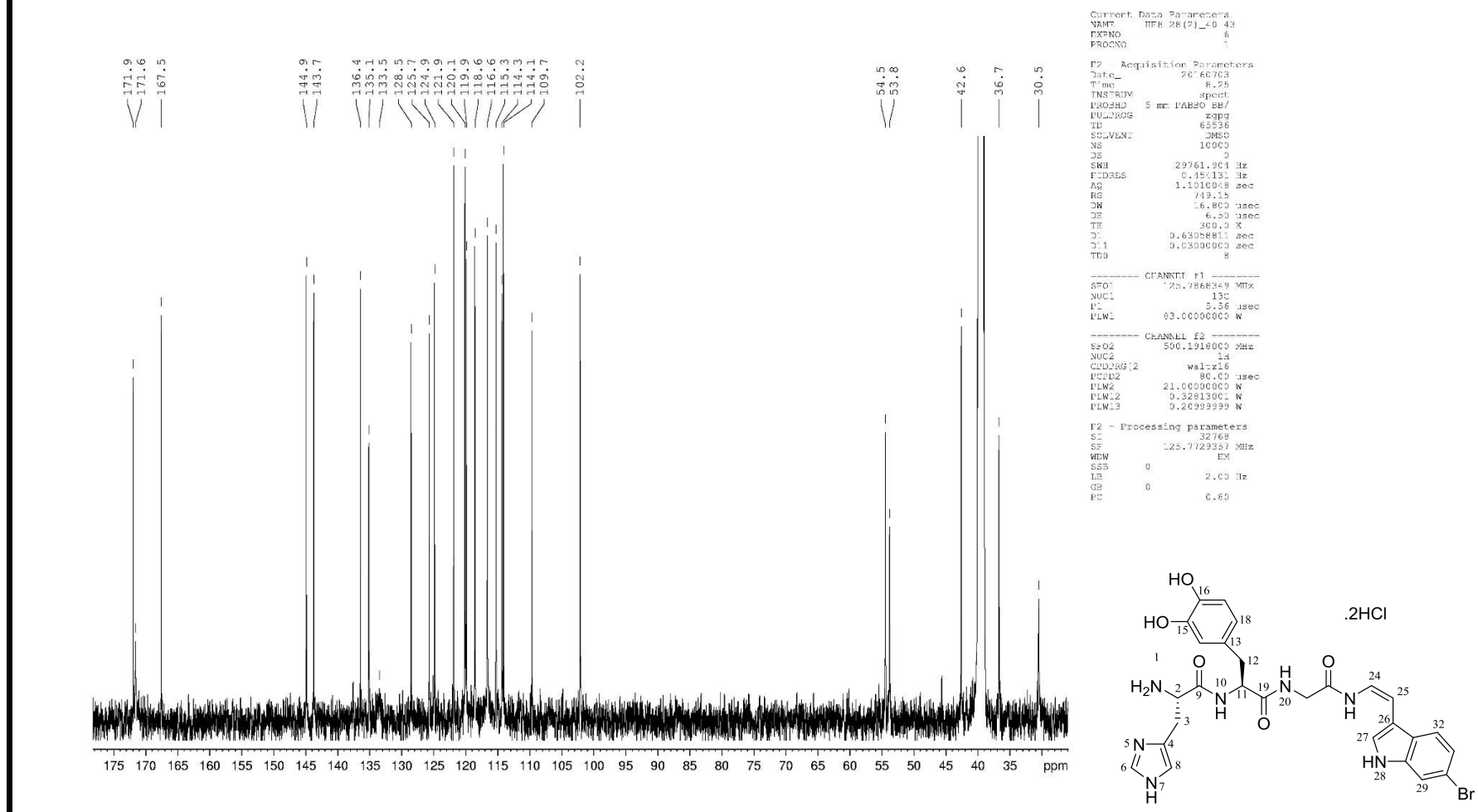
F2 - Acquisition Parameters
Date_           20160702
Time              11.07
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT             DMSO
NS                    32
DS                     0
SWH           10000.000 Hz
FIDRES        0.305176 Hz
AQ            1.6384000 sec
RG               175.28
DW              50.000 usec
DE               6.50 usec
TE              300.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1925007 MHz
NUC1                   1H
P1                  10.00 usec
PLW1        21.00000000 W

F2 - Processing parameters
SI                 16384
SF           500.1900057 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 0.80
```



^{1}H NMR (DMSO-d_6, 500 MHz) of halocyamine A dihydrochloride salt (**1**).



^{13}C NMR (DMSO-d_6, 125 MHz) of halocyamine A dihydrochloride salt (**1**).