

Supporting Information

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

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Contents:

Table S1. NMR data of isolated halocyanine A (1) and synthetic halocyanine A HCl salt (1).	S2
¹ H and ¹³ C NMR Spectra.....	S3–S44

Table S1. NMR data of isolated halocyamine A (1) and synthetic halocyamine A HCl salt (1) in DMSO-*d*₆.

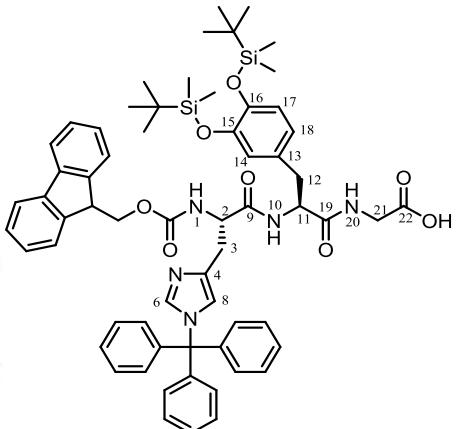
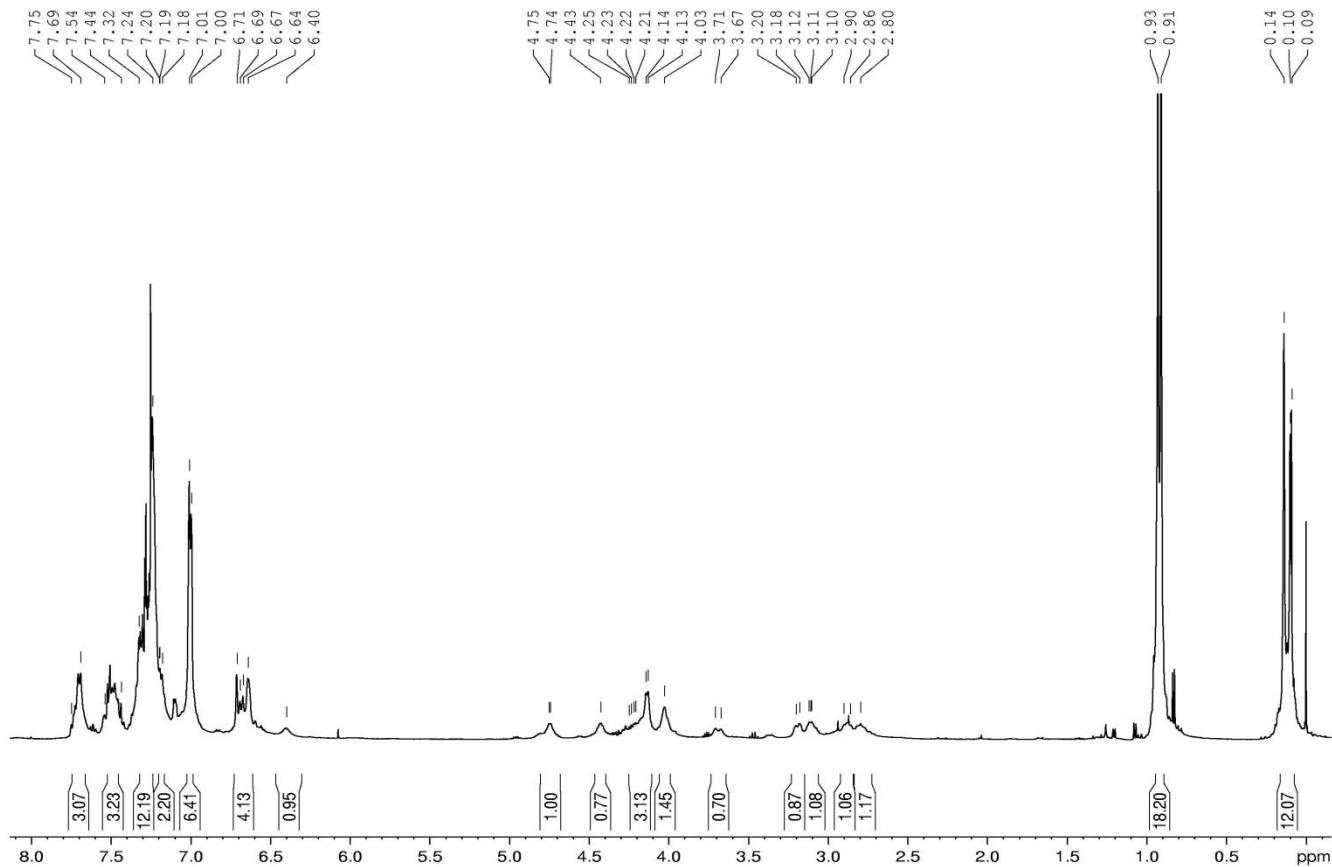
Atom No.	¹ H [δ, mult., J (Hz)]		¹³ C (δ)	
	Isolated (1) ¹	Synthetic (1)	Isolated (1) ¹	Synthetic (1)
1	Not observed	Not observed (8.37 [3H, br s]) [*]	-	-
2	3.84 (1H, t, 5.0)	3.61 (1H, br s)	53.10	53.8
3	3.03 (1H, dd, 15.5, 5.0), 2.93 (1H, dd, 15.5, 7.5)	2.91–2.89 (1H, m), 2.73 (1H, dd, 14.3, 7.5)	29.62	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.

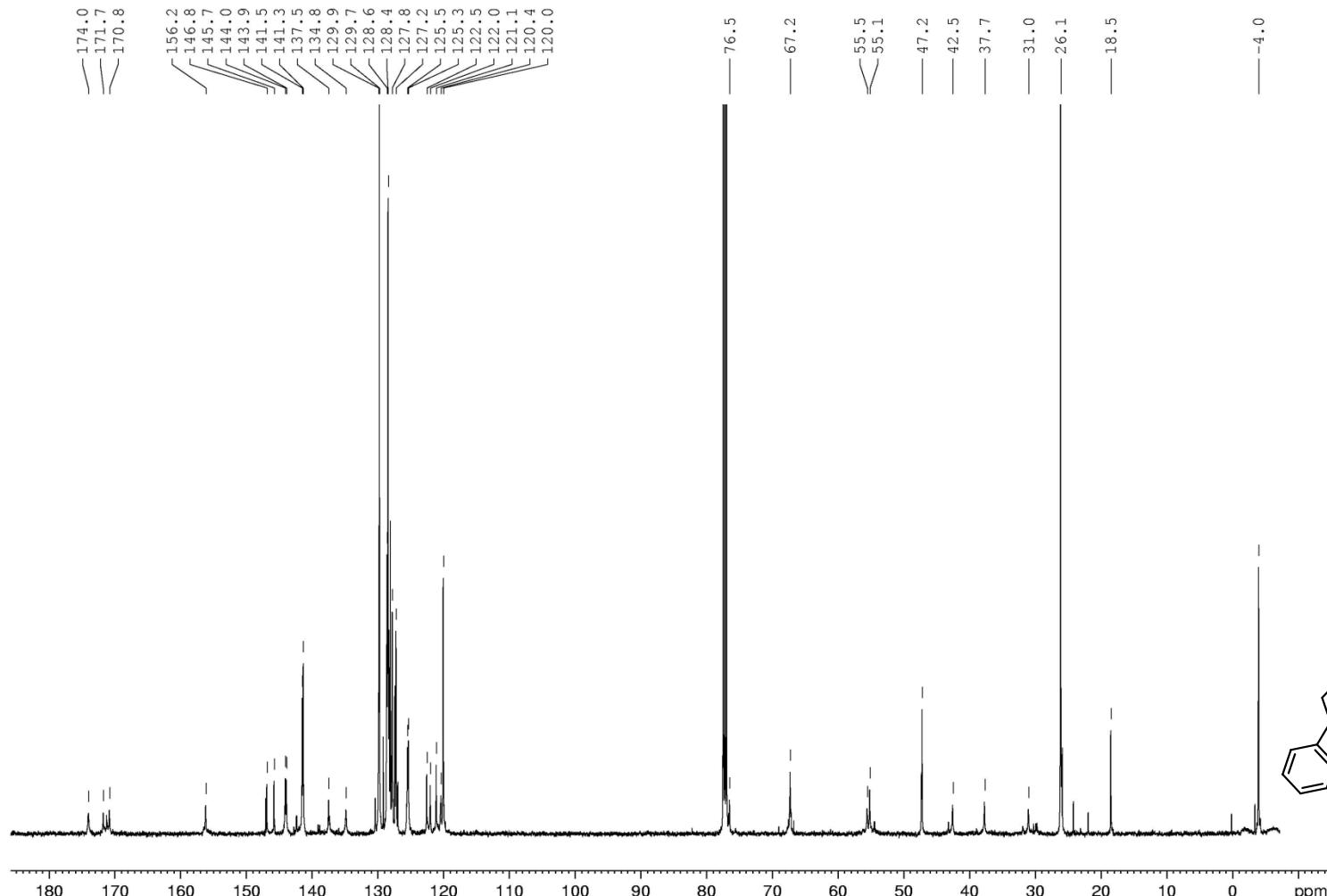
[#]3.00 ppm, dd, *J* = 14.0 and 5.6 Hz, in CH₃OD

Reference

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



¹H NMR (CDCl₃, 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**).

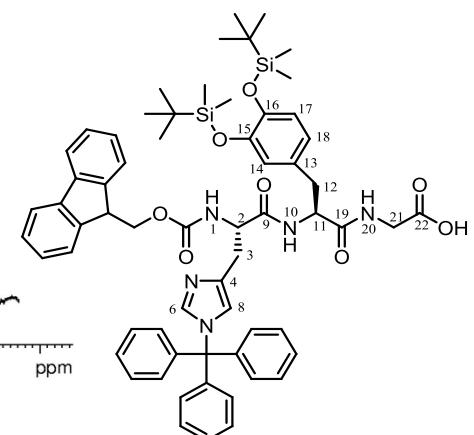
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PROCNO 1

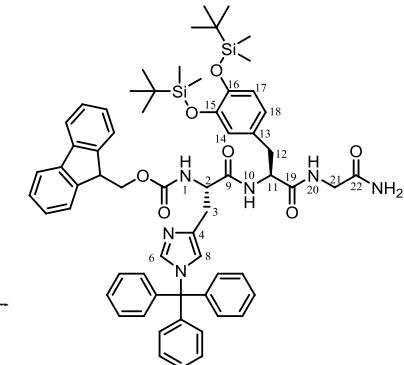
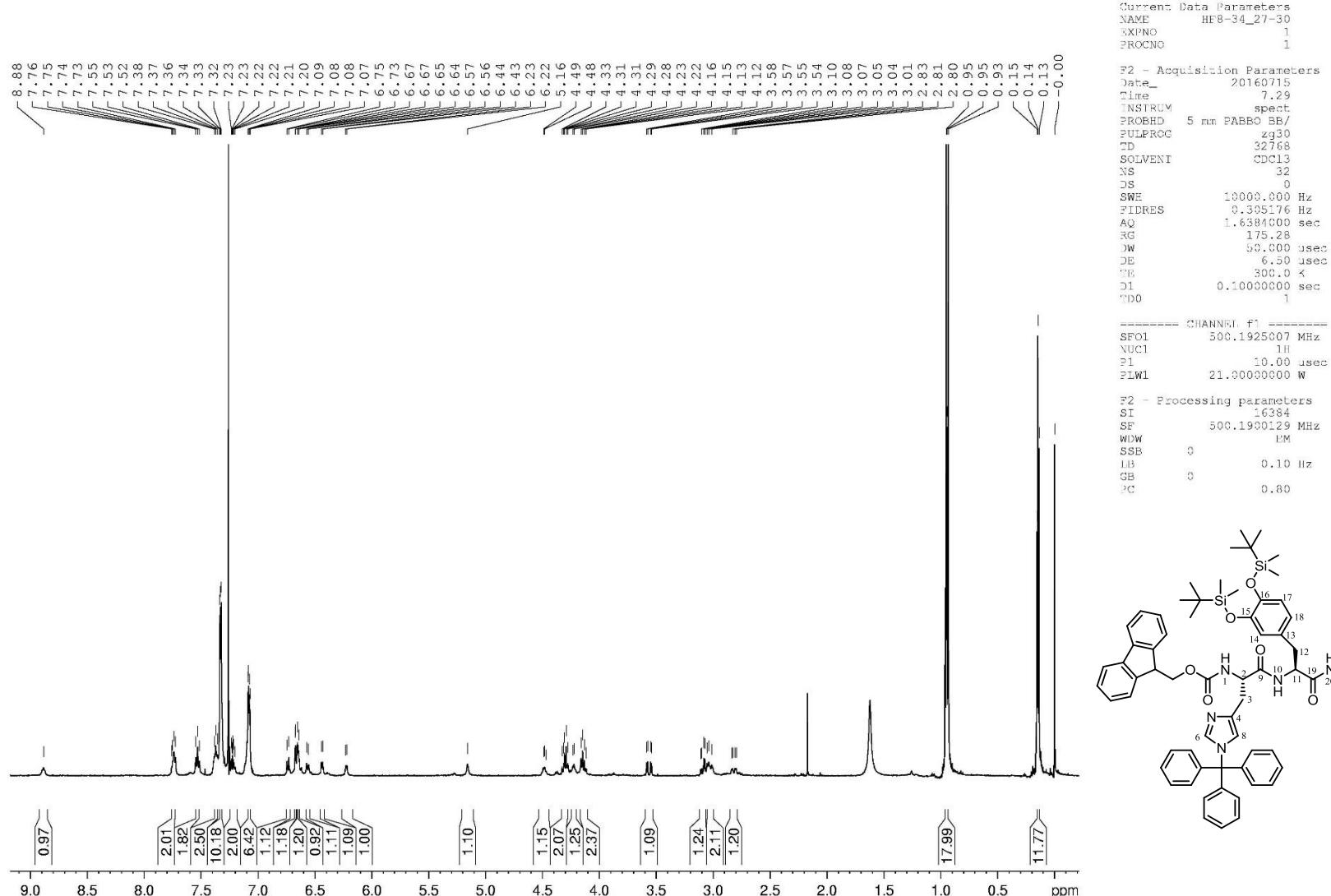
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PULPROG zgpg
TD 65536
SOLVENT CDCl₃
NS 8000
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 749.15
DW 16.800 usec
DE 6.50 usec
TE 300.0 K
D1 0.63058811 sec
D11 0.03000000 sec
TD0 1

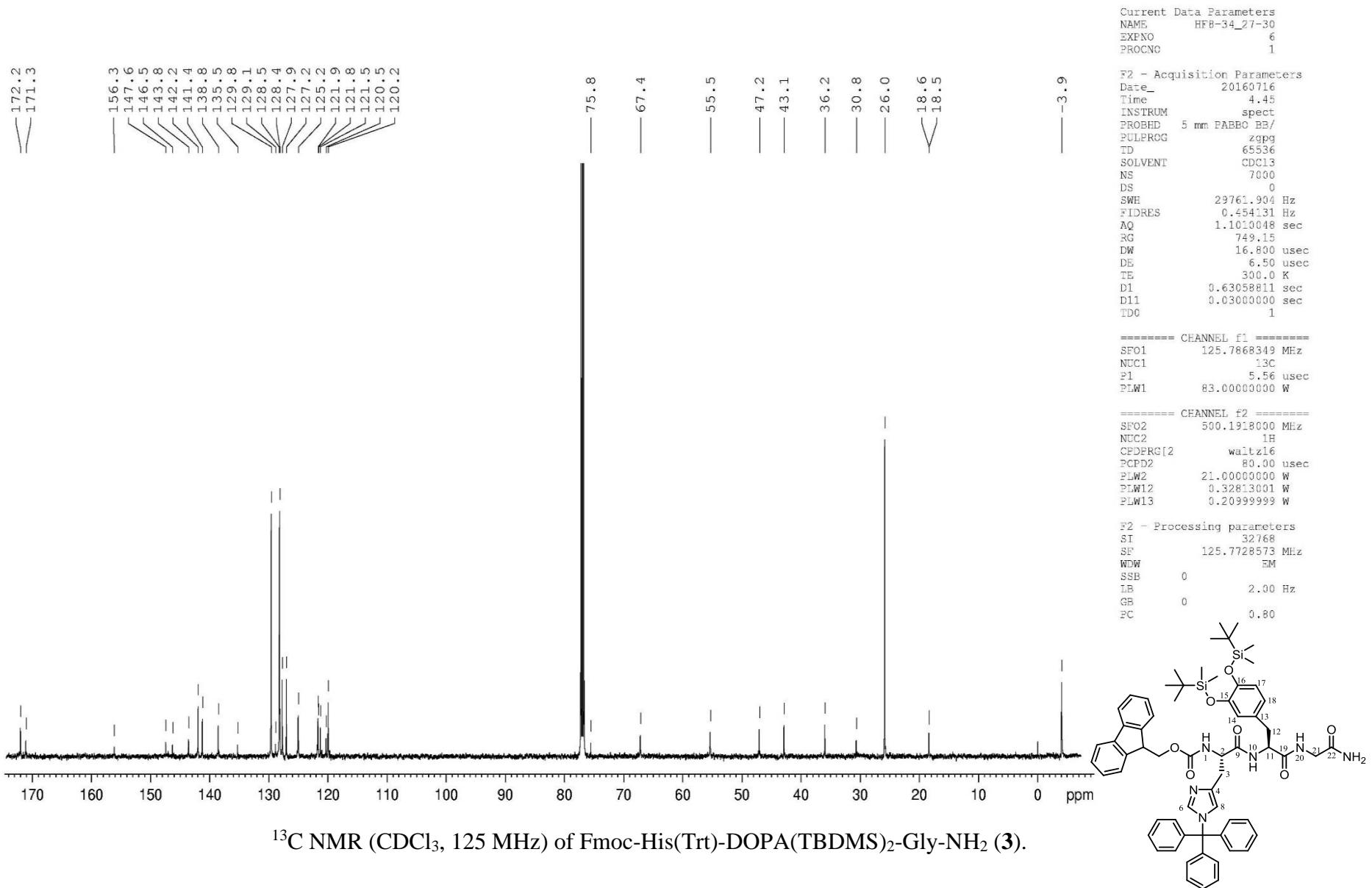
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NUC1 ¹³C
P1 5.56 usec
PLW1 83.00000000 W

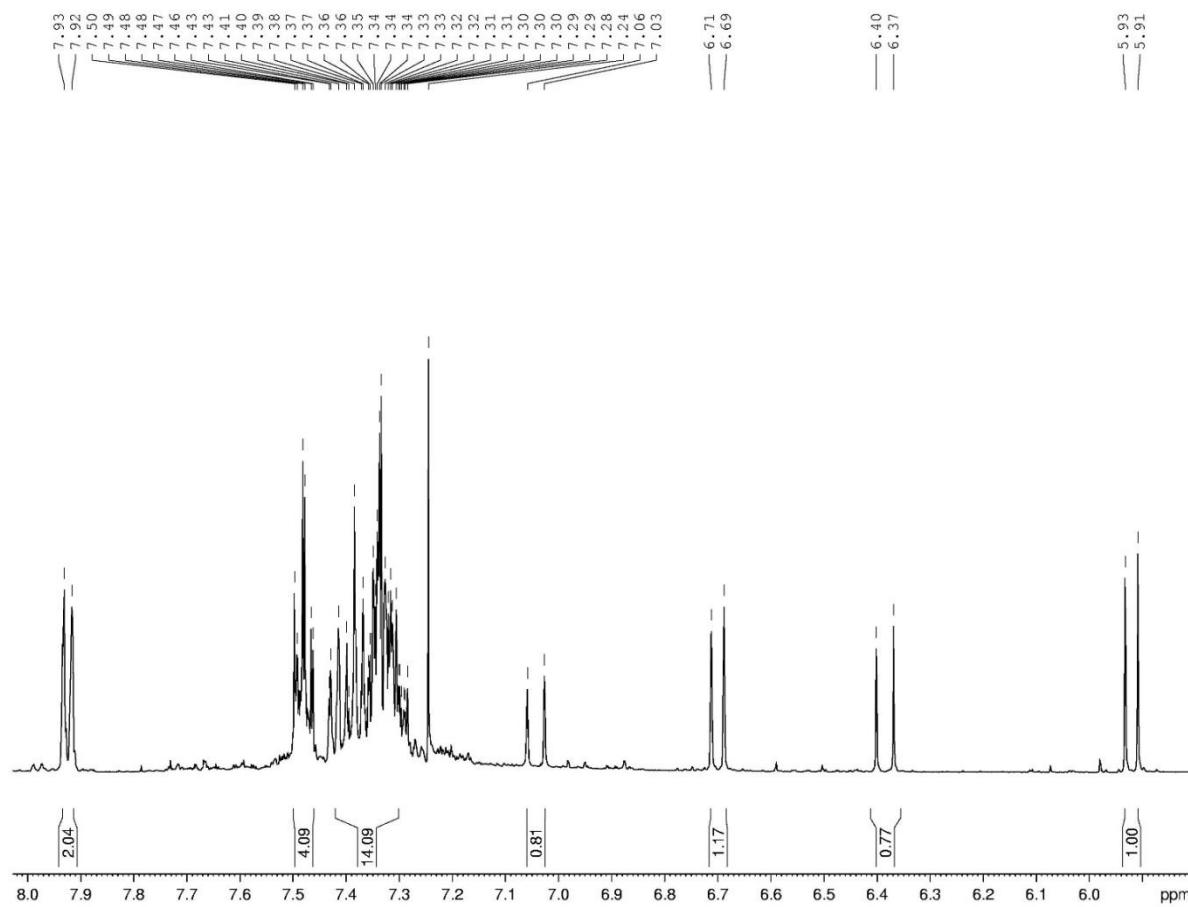
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SFO2 500.1918000 MHz
NUC2 ¹H
CPDPFG[2] waltz16
PCPD2 80.00 usec
PLW2 21.00000000 W
PLW12 0.32813001 W
PLW13 0.20999999 W

F2 - Processing parameters
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SF 125.7728610 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.80







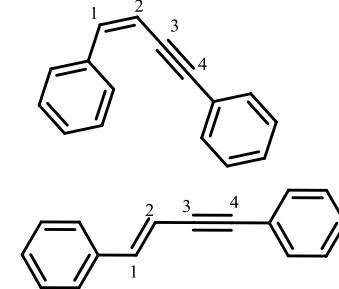


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 EXPNO 1
 PROCNO 1

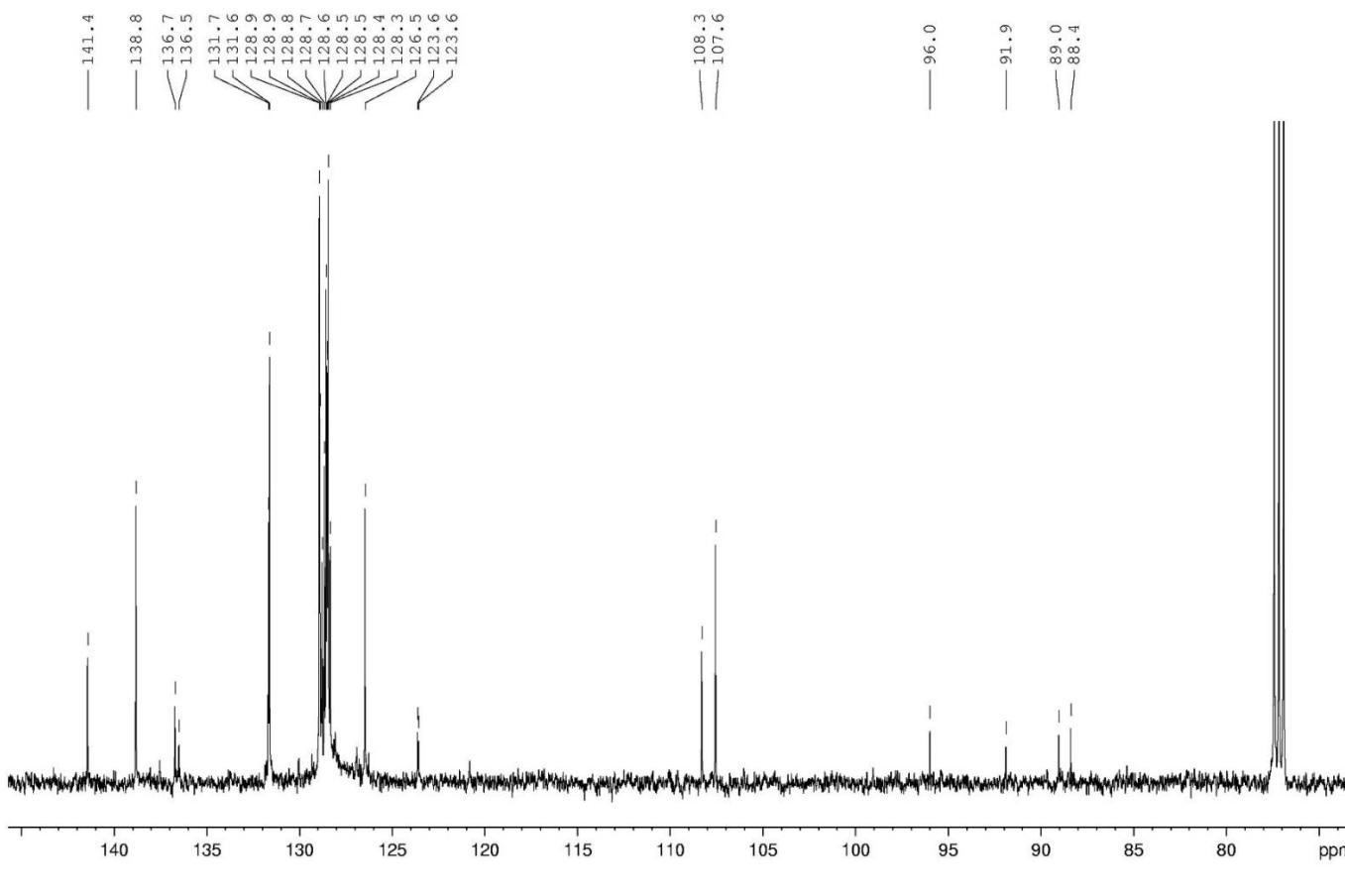
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 TD 32768
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 NS 16
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 SWE 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 1.6384000 sec
 RG 122.68
 DW 50.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 0.1000000 sec
 T0 1

===== CHANNEL f1 =====
 SP01 500.1325007 MHz
 NUC1 1H
 PI 10.00 usec
 PLW1 21.0000000 W

F2 - Processing parameters
 SI 16384
 SF 500.1300202 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 0.80



¹H NMR (CDCl₃, 500 MHz) of a mixture of (Z)-but-1-en-3-yne-1,4-diylbenzene (**5**) and (E)-but-1-en-3-yne-1,4-diylbenzene (**6**).



¹³C 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**).

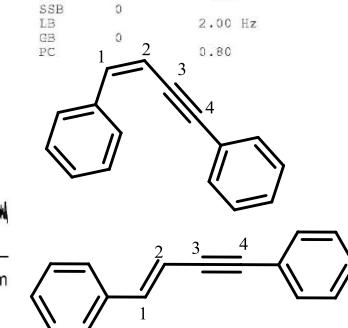
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EXPNO: 3
PROCNO: 1

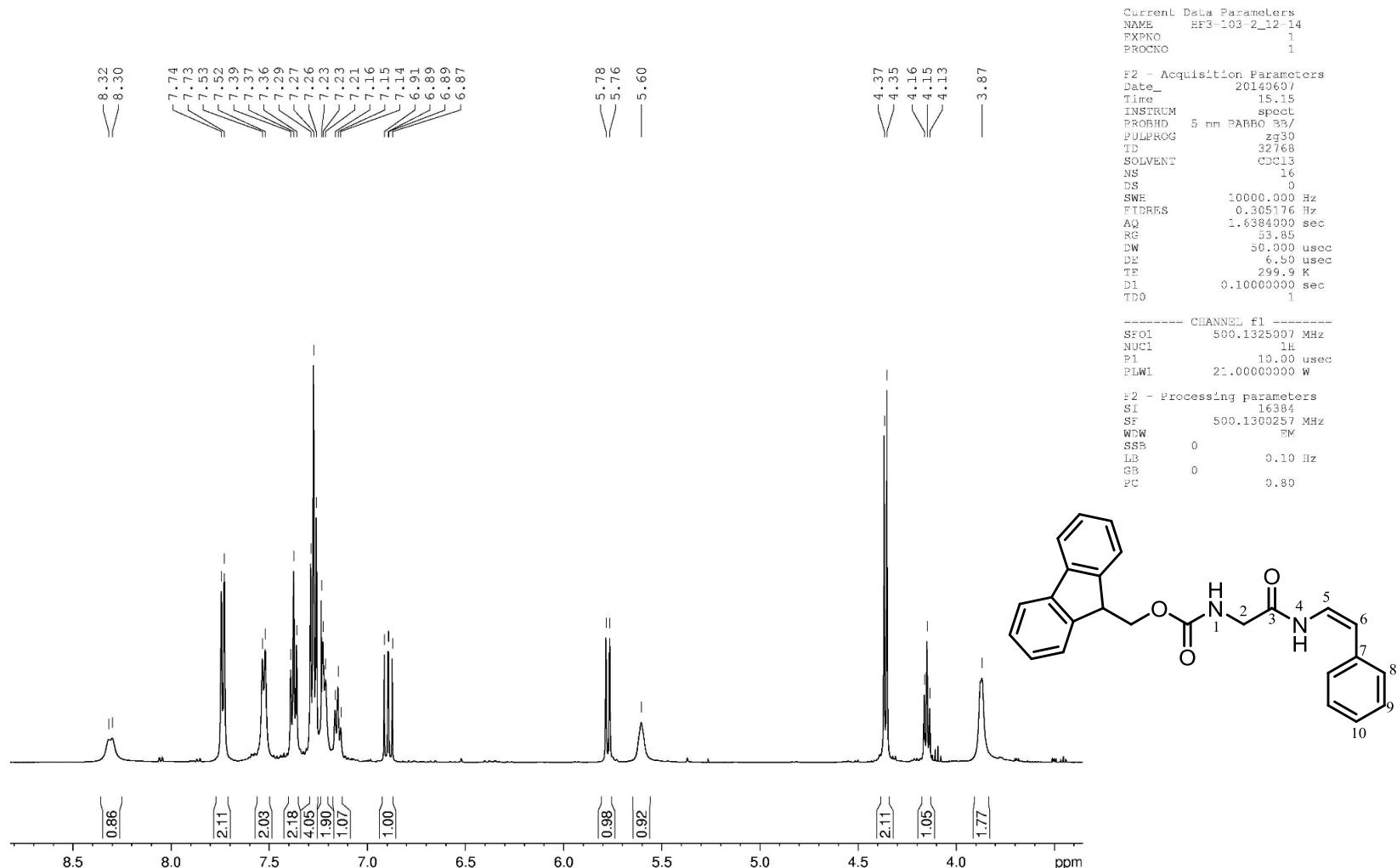
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PULPROG: zgpg3
TD: 65536
SOLVENT: CDCl₃
NS: 300
DS: 0
SWH: 29761.904 Hz
FIDRES: 0.454131 Hz
AQ: 1.1010048 sec
RG: 749.15
DW: 16.800 usec
DE: 6.50 usec
TE: 300.0 K
D1: 0.63058811 sec
D11: 0.03000000 sec
TD0: 1

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NUC1: ¹³C
PL: 5.56 usec
P1W1: 63.0000000 W

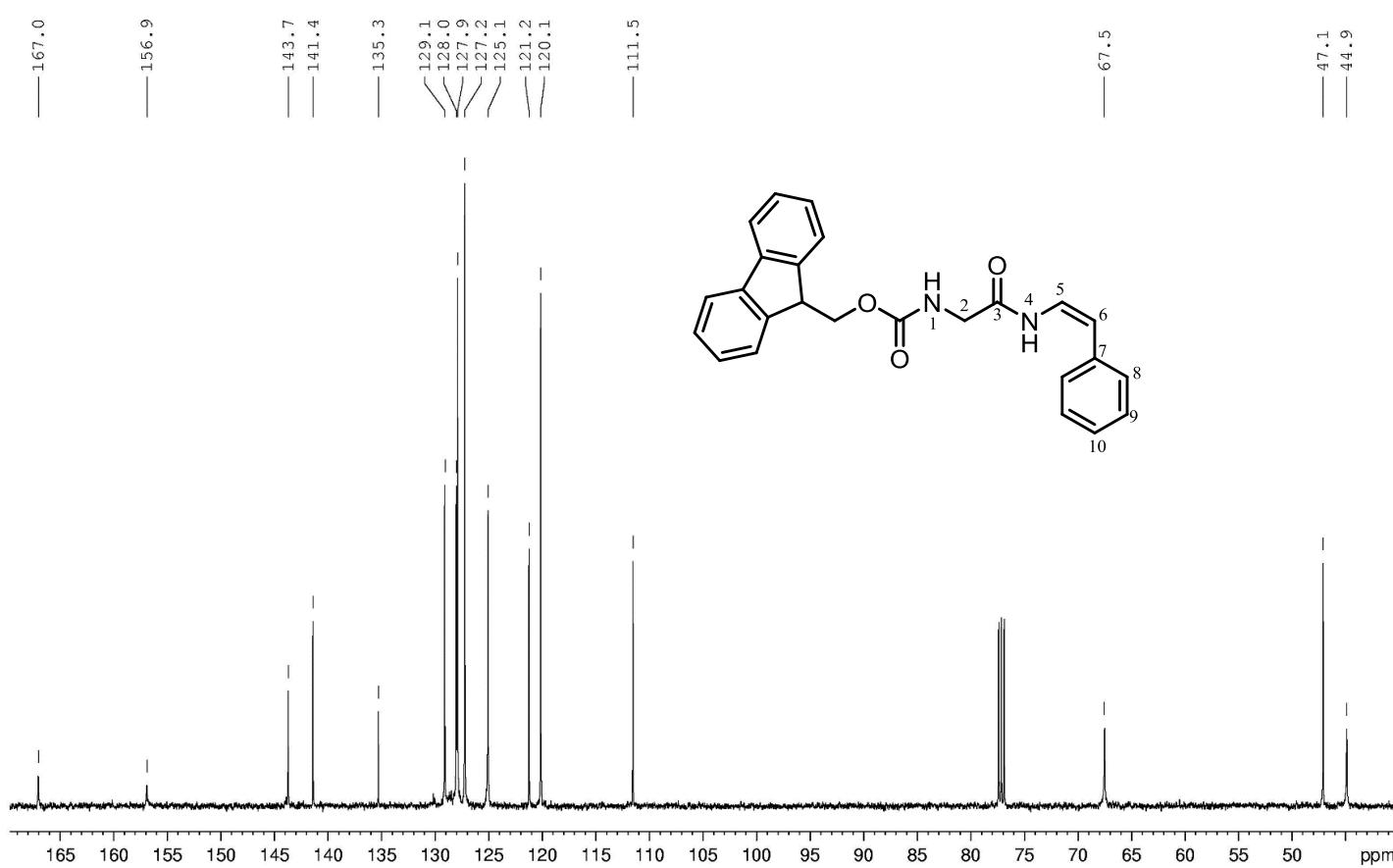
----- CHANNEL f2 -----
SFO2: 500.1318000 MHz
NUC2: ¹H
CPDPG[2]: waltz16
PCPDG2: 80.00 usec
P1W2: 21.0000000 W
P1W12: 0.32813001 W
P1W13: 0.20999999 W

F2 - Processing parameters
SI: 32768
SF: 125.7577723 MHz
WDW: EM
SSB: 0
LB: 2.00 Hz
GB: 0.80
PC:





¹H NMR (CDCl₃, 500 MHz) of (Z)-(9H-fluoren-9-yl)methyl (2-oxo-2-(styrylamino)ethyl)carbamate (**10**).

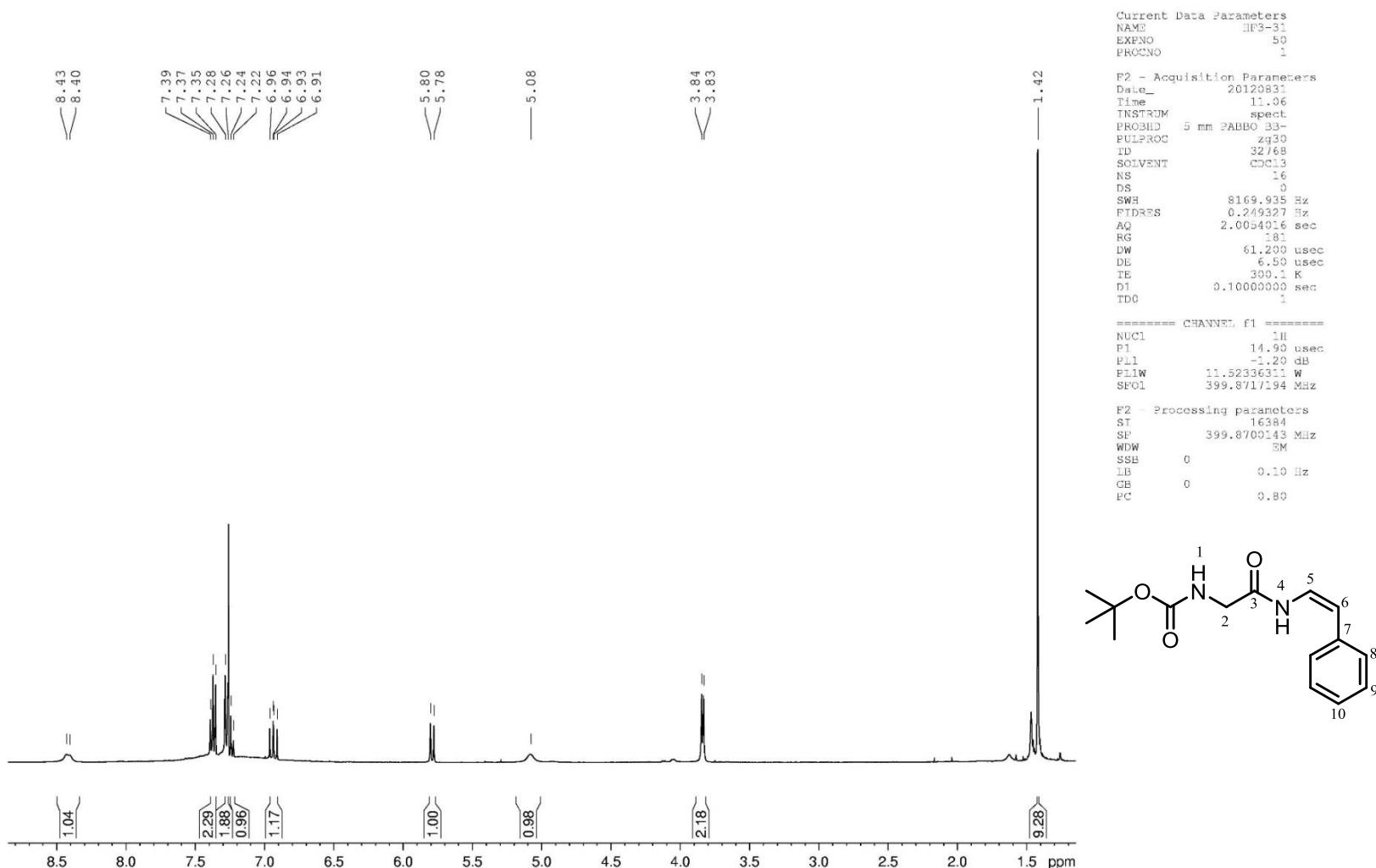


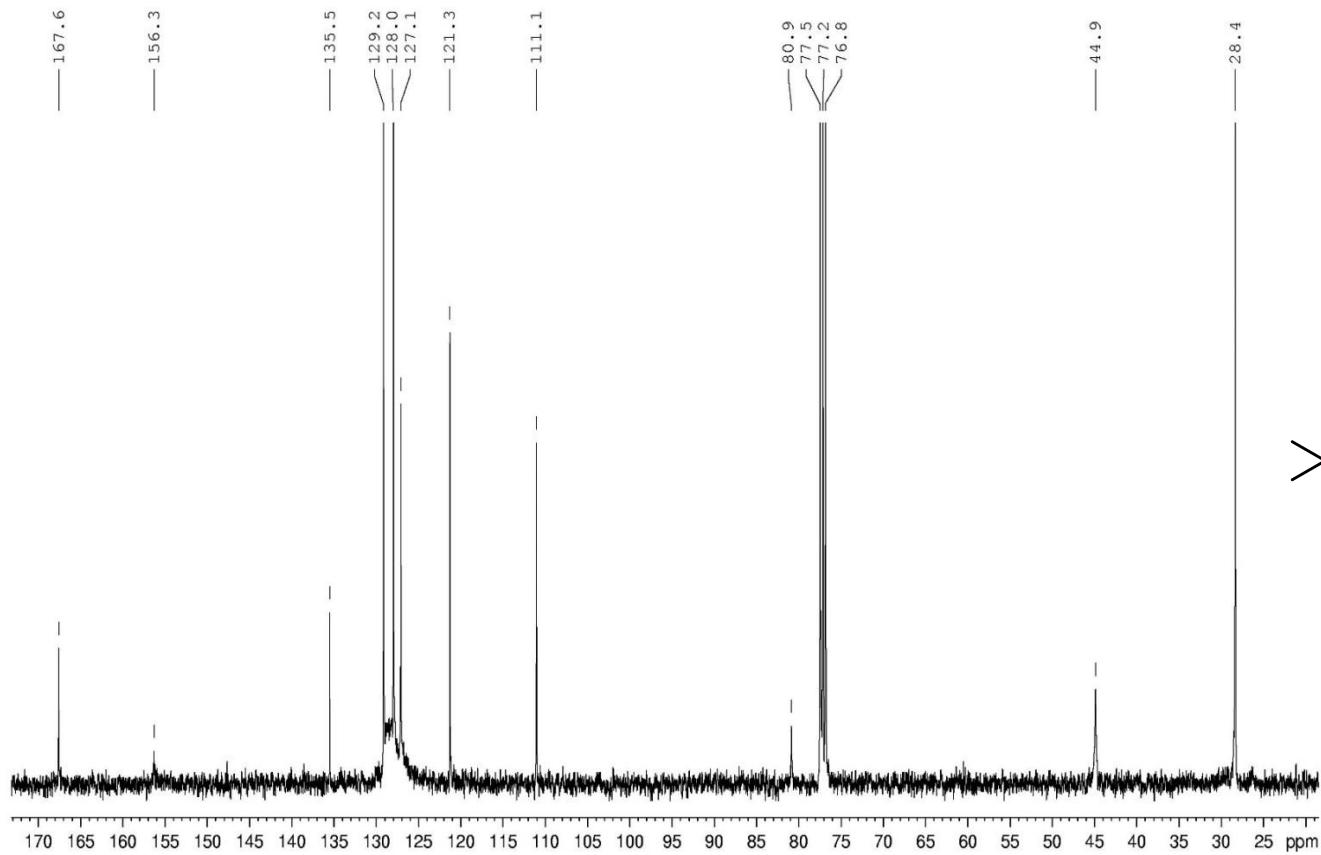
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PRCNO 1
F2 - Acquisition Parameters
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PULPROG zgpg
TD 65536
SOLVENT CDCl₃
NS 200
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 769.15
DW 16.800 usec
DE 6.50 usec
TE 300.1 K
D1 0.63058811 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SF01 125.7717479 MHz
NUC1 13C
P1 5.56 usec
PLW1 83.00000000 W

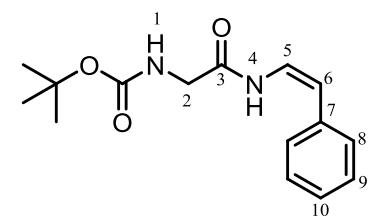
===== CHANNEL f2 =====
SF02 500.1318000 MHz
NUC2 1H
CPDPFG[2] waltz16
PCPD2 80.00 usec
PLW2 21.00000000 W
PLW12 0.32813C01 W
PLW13 0.20999999 W

F2 - Processing parameters
SI 32768
SF 125.7577810 MHz
WM EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.80

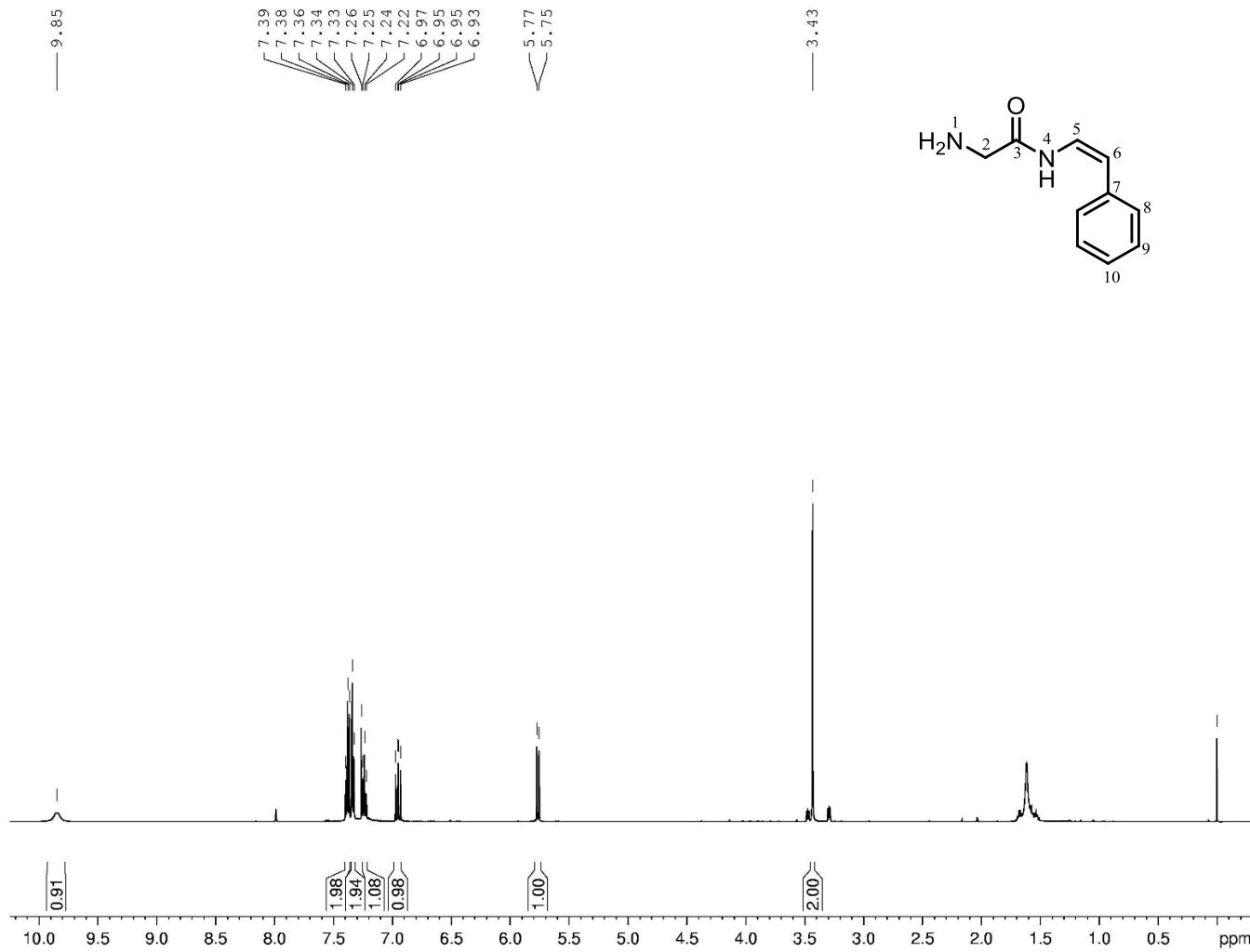




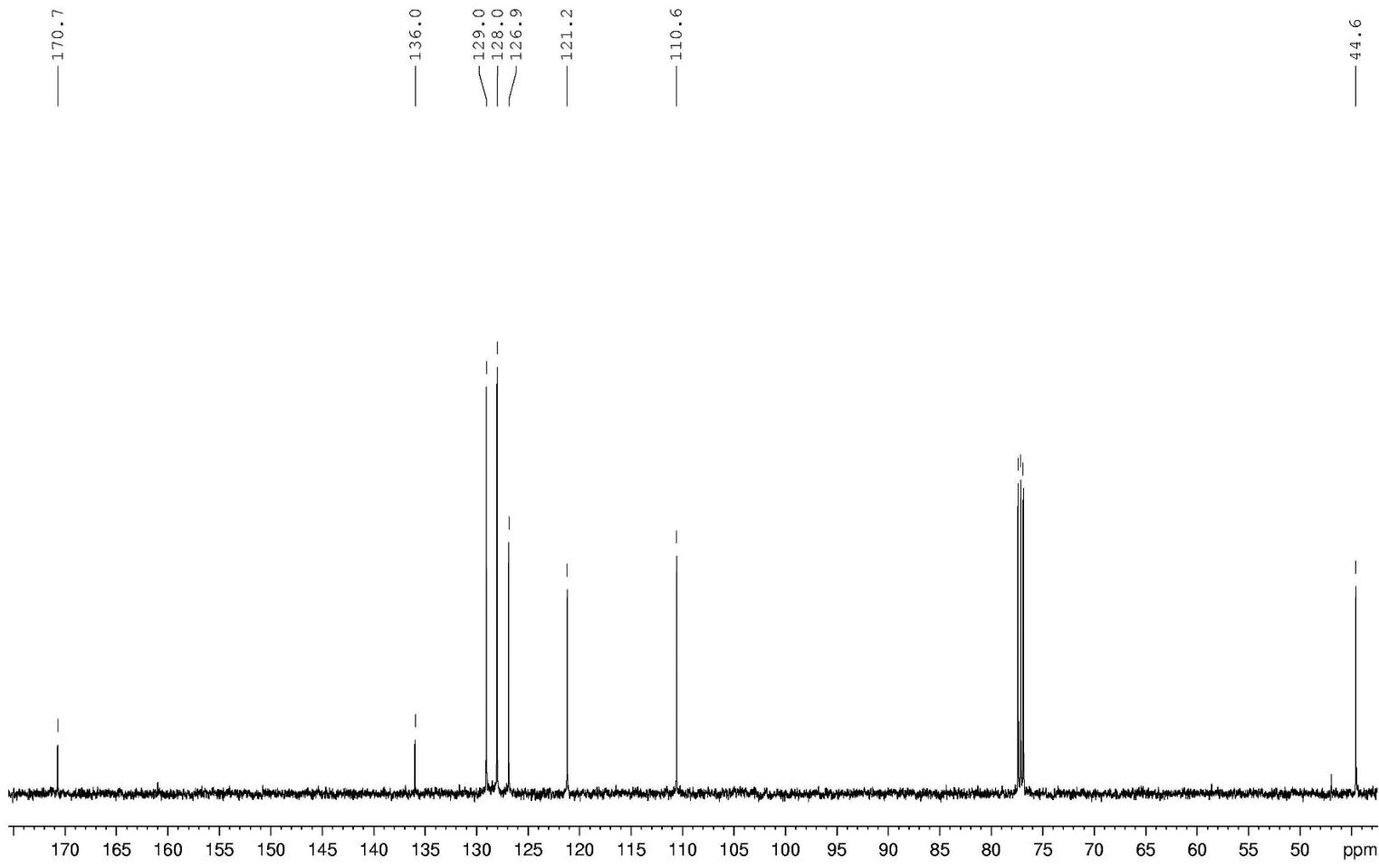
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 PROCNO 1
 F2 - Processing parameters
 SI 32768
 SF 100.6127571 MHz
 WDW FID
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 0.80



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



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



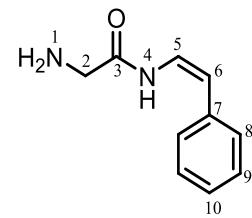
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EXPNO 2
PROCNO 1

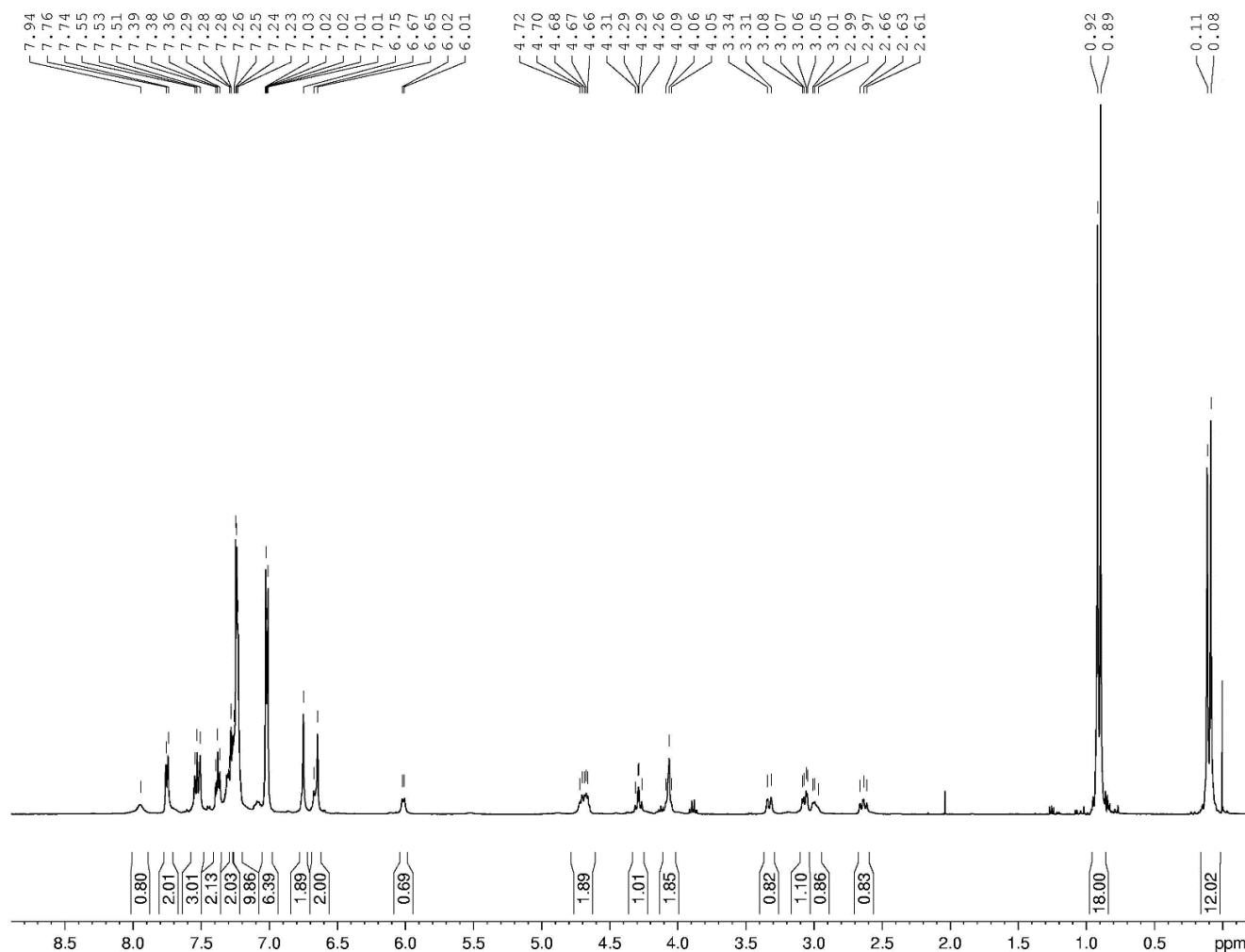
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PULPROG zgpg
TD 65536
SOLVENT CDCl₃
NS 131
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 749.15
DW 16.800 usec
DE 6.50 usec
TE 300.0 K
D1 0.63058811 sec
D11 0.0300000 sec
TDO 1

===== CHANNEL f1 =====
SFO1 125.7717479 MHz
NUC1 ¹³C
P1 5.56 usec
PLW1 83.0000000 W

===== CHANNEL f2 =====
SFO2 500.1318000 MHz
NUC2 ¹H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 21.0000000 W
PLW12 0.32813001 W
PLW13 0.20999999 W

F2 - Processing parameters
SI 32768
SF 125.7577751 MHz
WDW EM
SSB 0 2.00 Hz
LB 0
GB C
PC 0.80





Current Data Parameters
NAME HF7-139
EXPNO 2
PROCNO 1

```

F2 - Acquisition Parameters
Date_      20160417
Time_      20.13
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PULPROG_ zg30
TD_        32768
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NS_        16
DS_        0
SWH_       10000.000 Hz
FIDRES_   0.30576 Hz
AQ_        1.6384000 sec
RG_        27.23
DW_        50.000 usec
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TE_        300.0 K
DI_        0.1000000 sec
TDC_       1

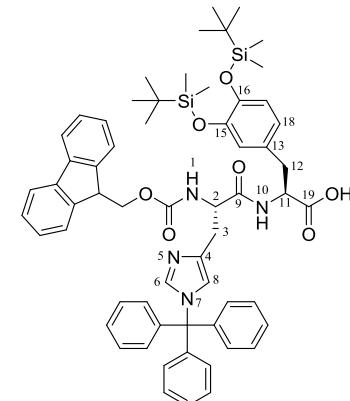
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NUC1          1H  
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PLW1      21.0000000 W
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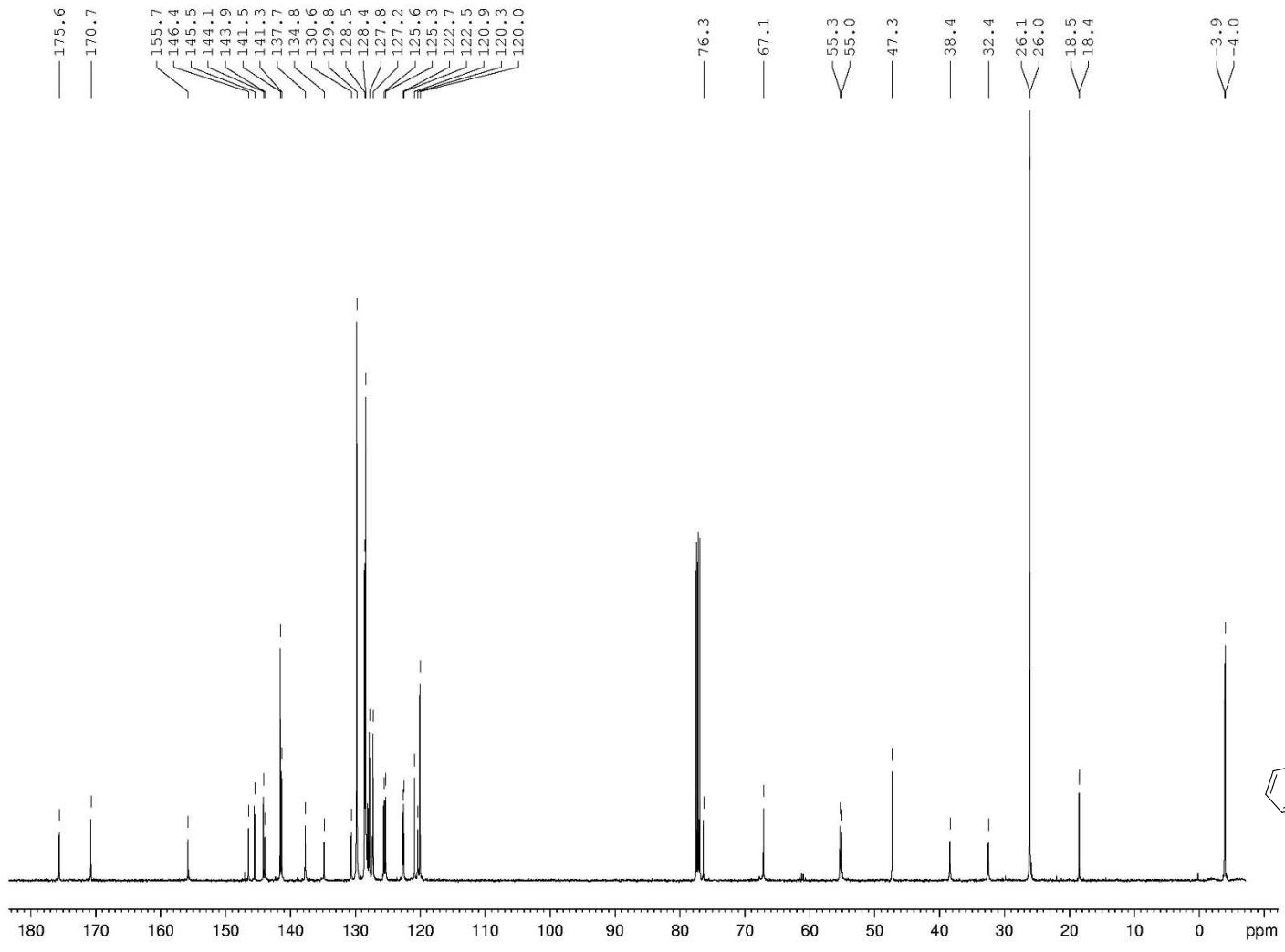
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F2 - Processing parameters
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WDW          EM
SSB          0
LB          0.10 Hz
SB          0
PC          0.80

```



¹H NMR (CDCl₃, 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).

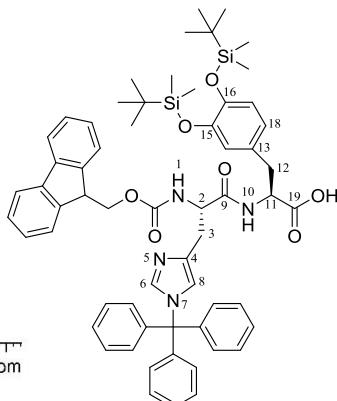
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EXPNO 6
PROCNO 1

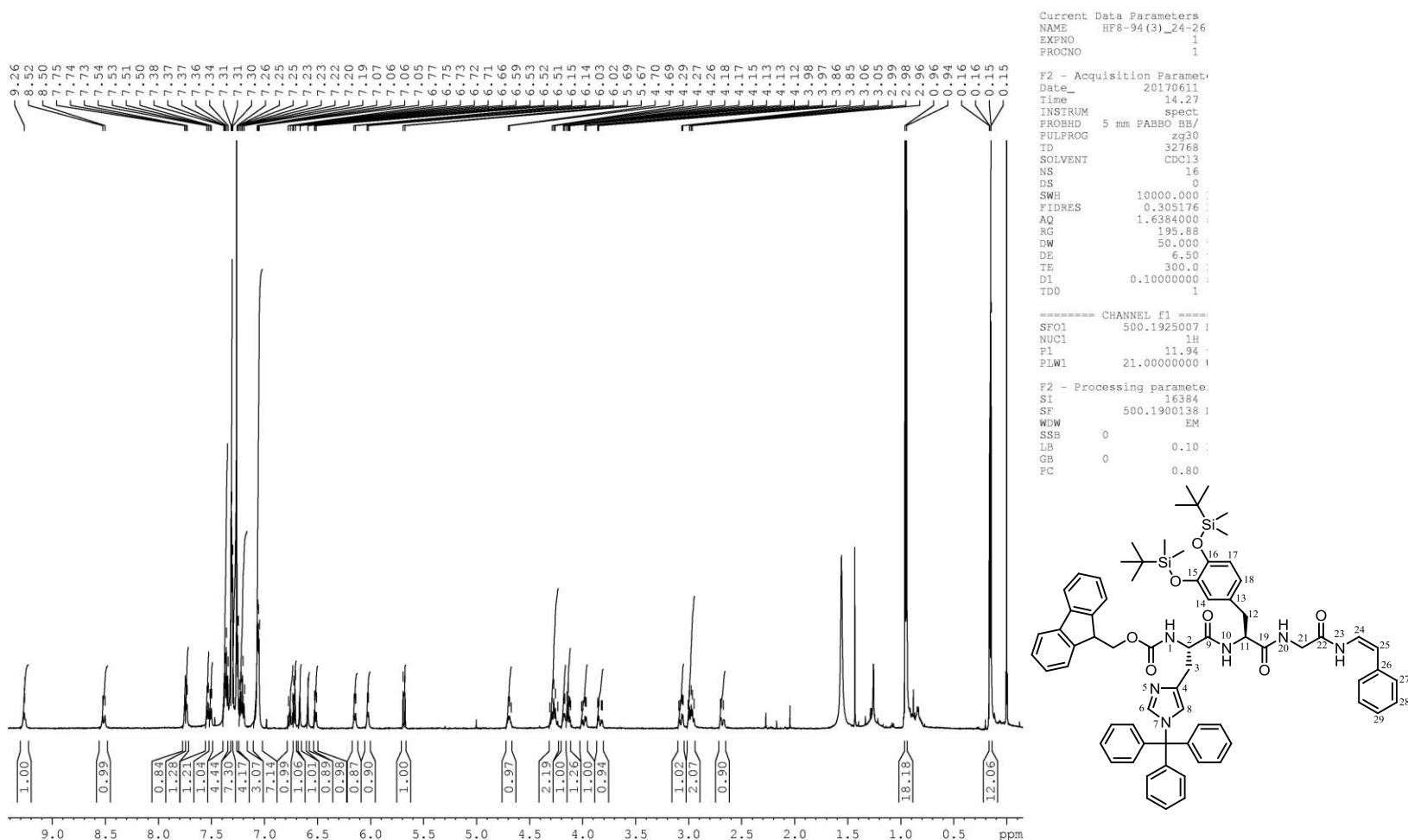
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TD 65536
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NS 4000
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 743.15
DW 16.800 usec
DE 6.50 usec
TE 300.0 K
D1 0.63058811 sec
D11 0.03000000 sec
TD0 1

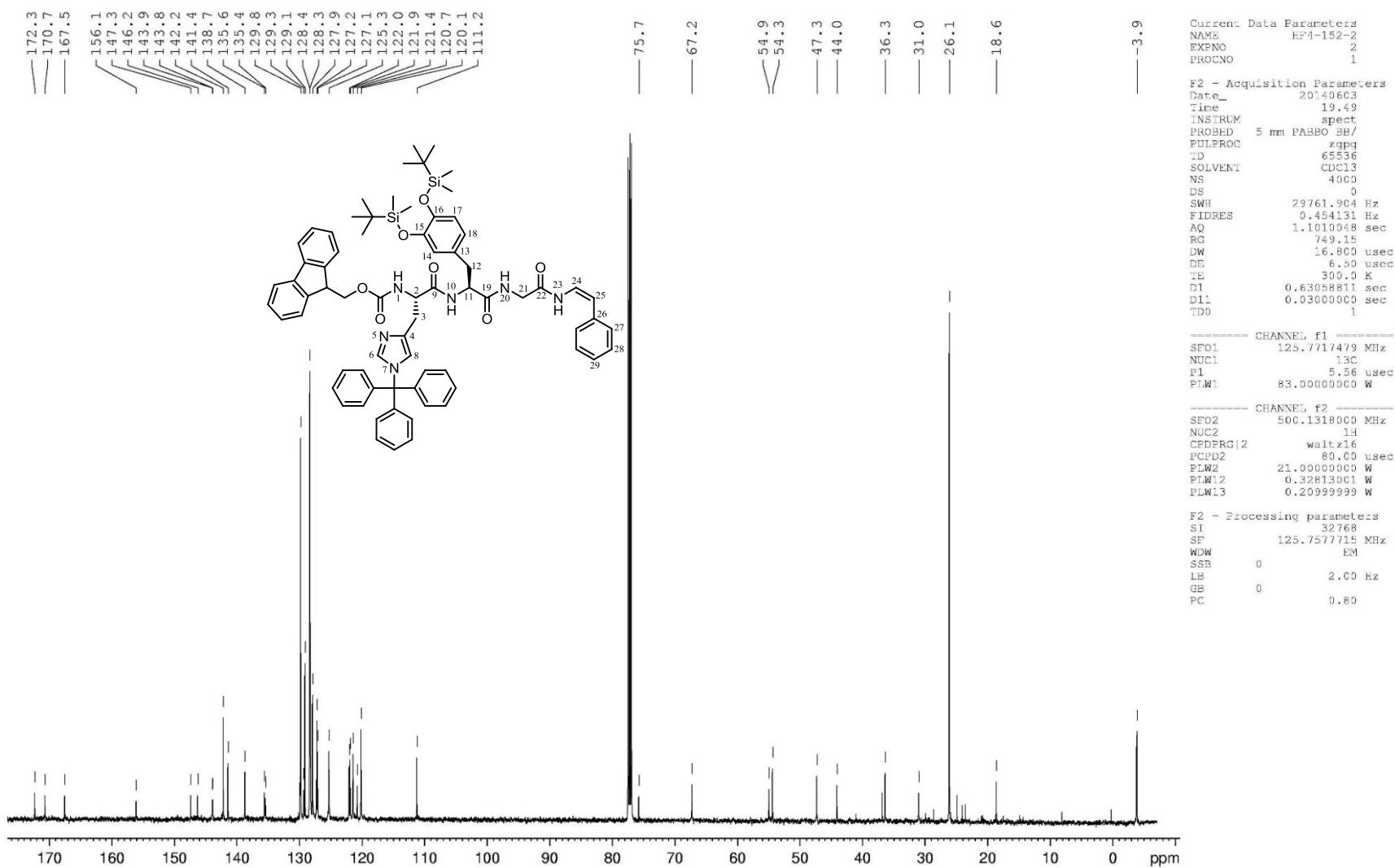
===== CHANNEL f1 =====
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NUC1 13C
P1 5.56 usec
PLW1 83.00000003 W

===== CHANNEL f2 =====
SFO2 500.1918000 MHz
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PLW13 0.20999999 W

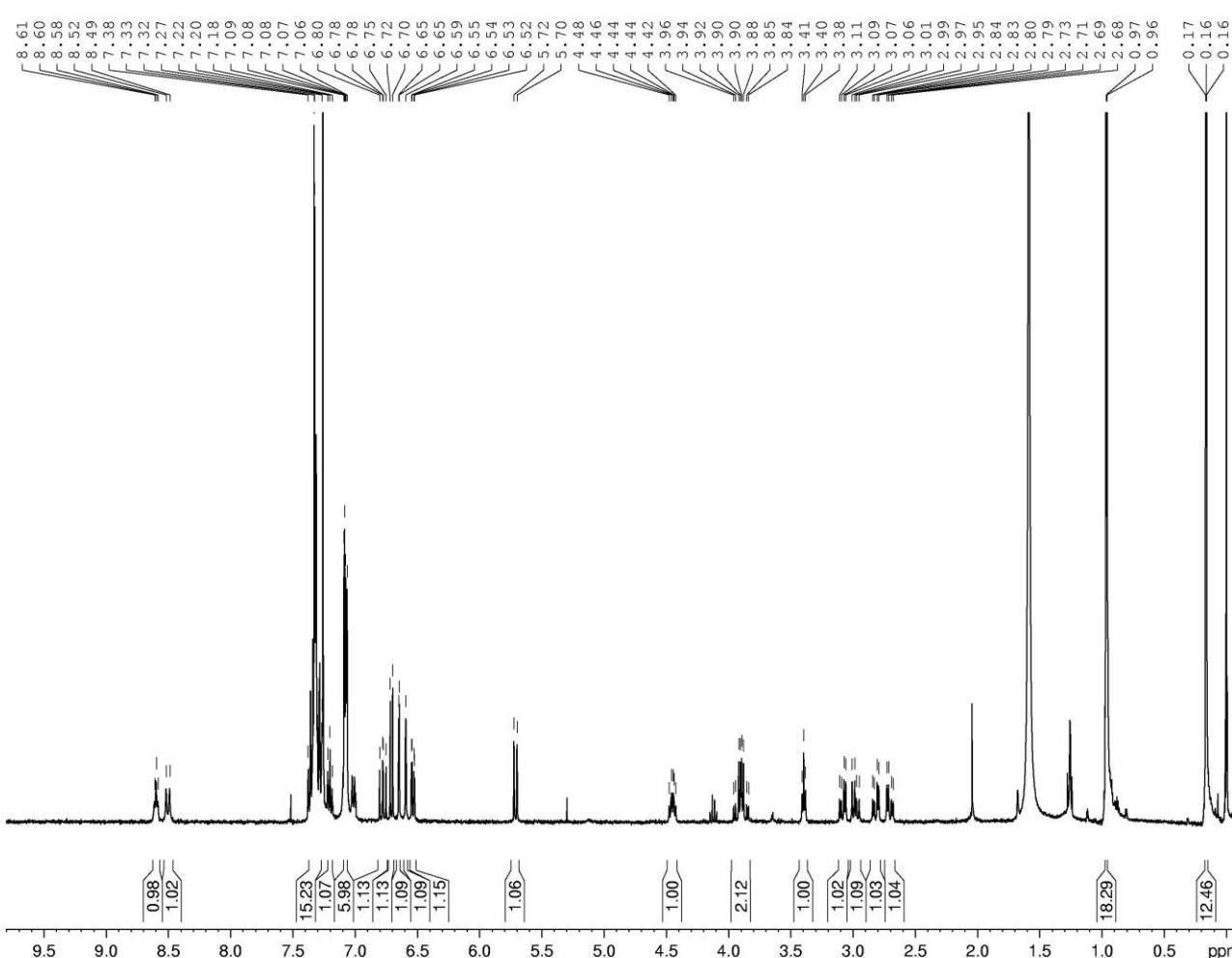
F2 - Processing parameters
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SF 125.1728631 MHz
WDW LM
SSB C
LB 2.00 Hz
GB C
PC 0.80







^{13}C NMR (CDCl₃, 125 MHz) of (9H-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**).



Current Data Parameters
NAME HF8-96(2)
EXPNO 1
PROCNO 1

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F2 - Acquisition Parameters
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PULPROG  zg30
TD        32768
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NS         64
DS          0
SWH       8012.820 Hz
FIDRES   0.244532 Hz
AQ        2.0447233 sec
RG        512
DW        62.400 used
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TE        300.0 K
D1        0.1000000 sec
TDO      1

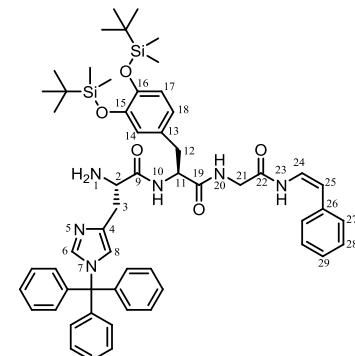
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PLLW          40.00000000 W
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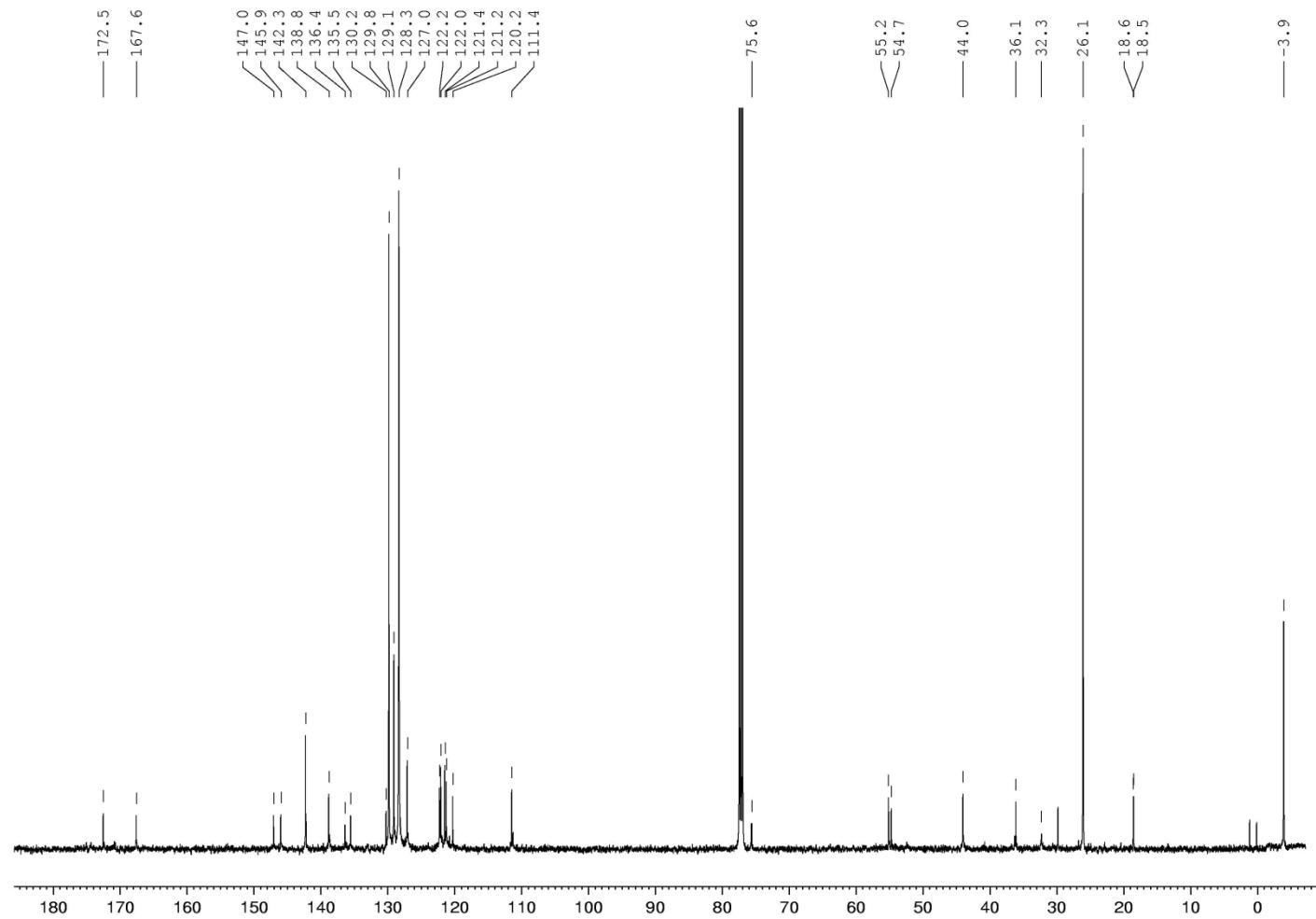
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F2 - Processing parameters
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SF        400.1300095 MHz
WDW          EM
SSB          0
LB          0.10 Hz
GB          0
PC          0.80

```



¹H NMR (CDCl₃, 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-1H-imidazol-4-yl)propanamide (**14**).



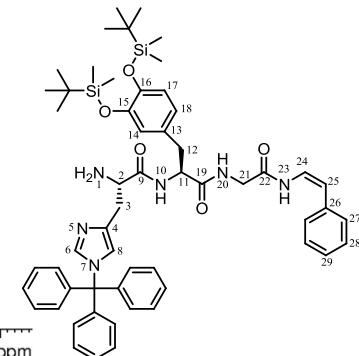
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EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
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Time 18.17
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PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 6000
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

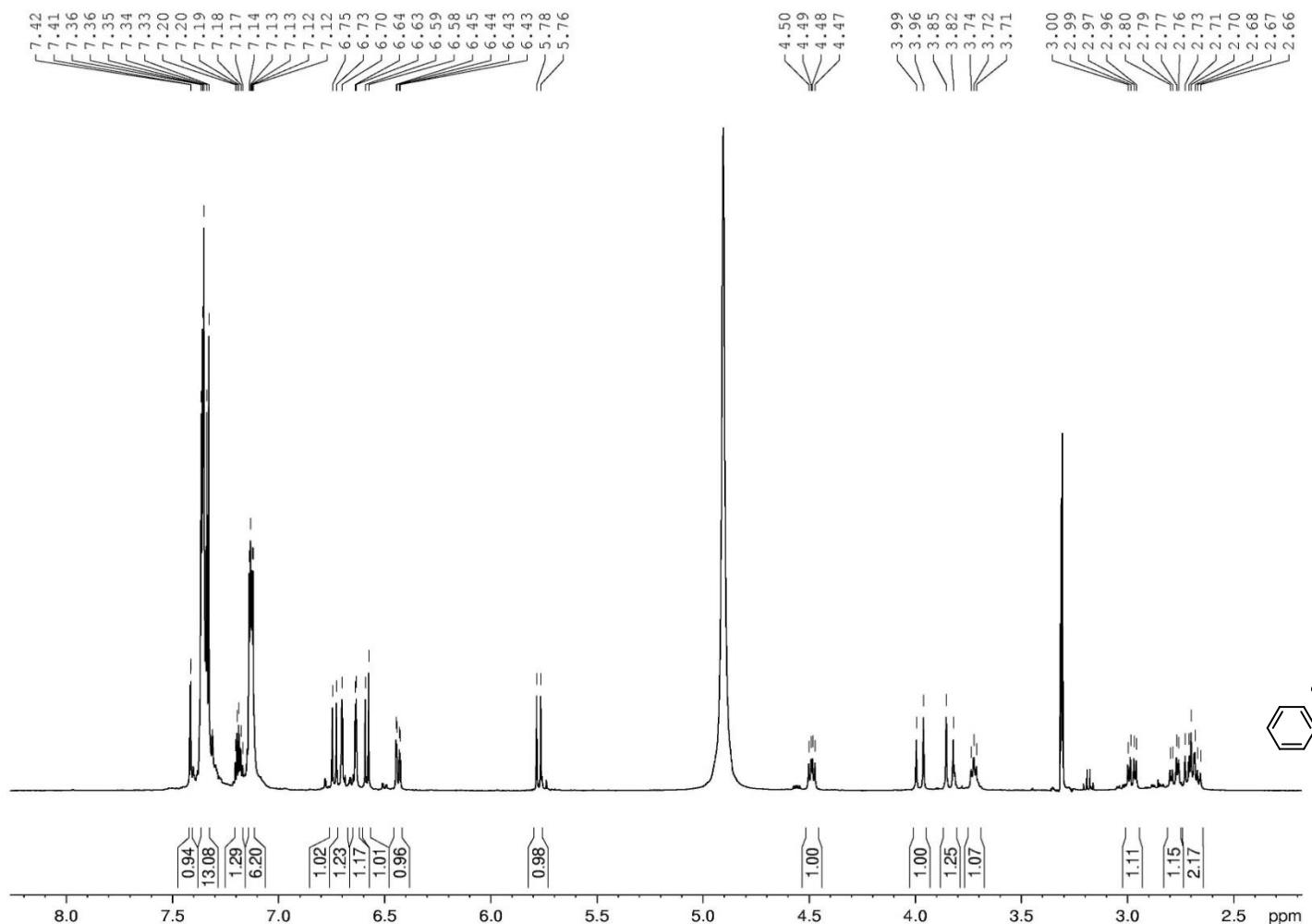
===== CHANNEL f1 =====
SFO1 125.7717479 MHz
NUC1 13C
P1 5.56 usec
PLW1 83.0000000 W

===== CHANNEL f2 =====
SFO2 500.1318000 MHz
NUC2 1H
CPDPFG[2] waltz16
PCPD2 80.00 usec
PLW2 21.0000000 W
PLW12 0.32813001 W
PLW13 0.20399999 W

F2 - Processing parameters
SI 32768
SF 125.7577720 MHz
WDW EM
SSB 0 2.00 Hz
LB 0
GB 0 0.80
PC



^{13}C NMR (CDCl_3 , 125 MHz) of (S)-2-amino-N-((S)-3-(3,4-bis((tert-butylidimethylsilyl)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**).

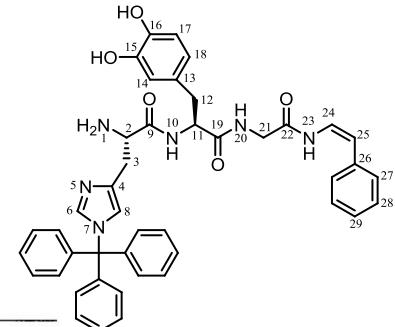


Current Data Parameters
 NAME HF8-11_6-8
 EXPO 1
 PROCNO 1

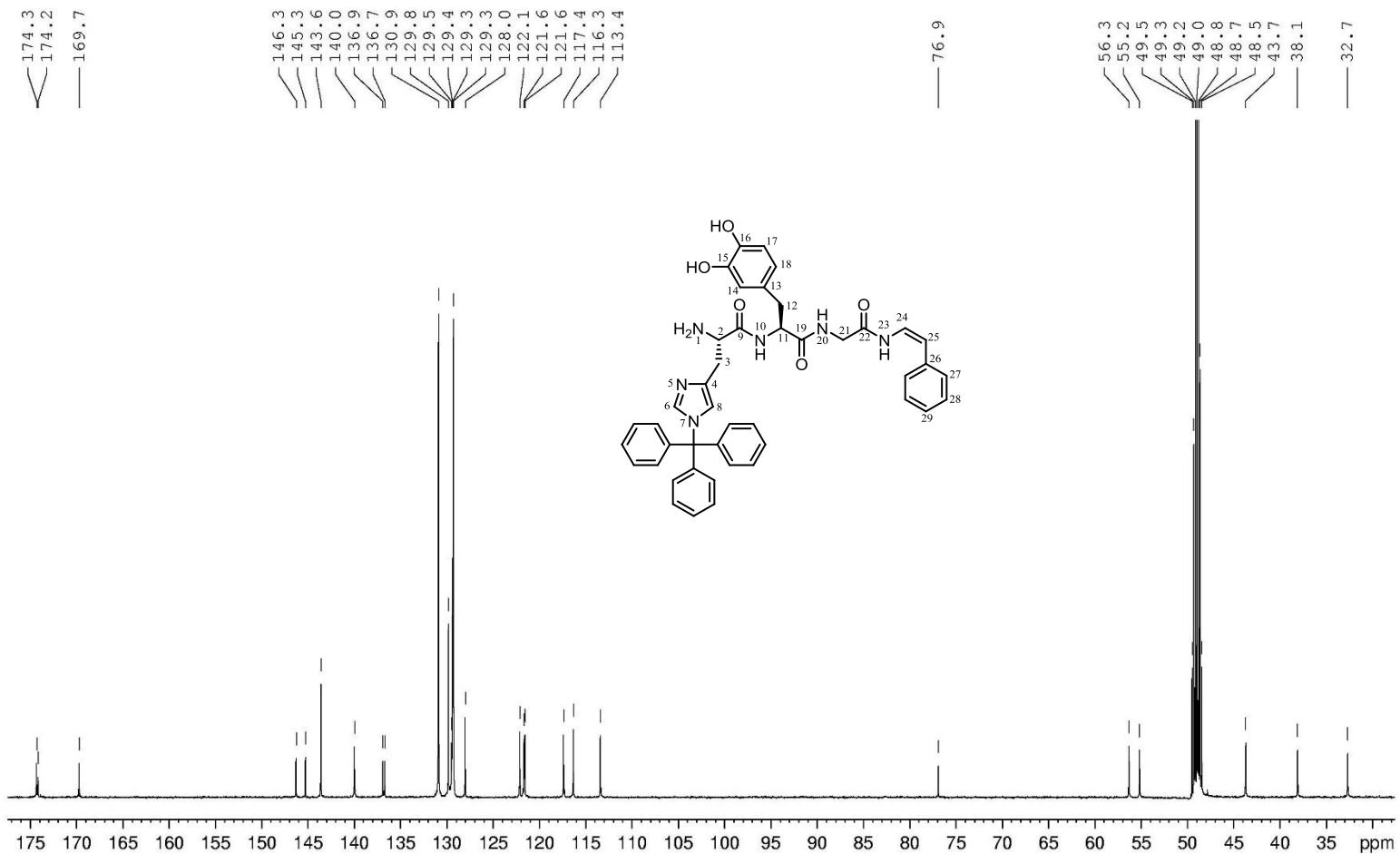
F2 - Acquisition Parameters
 Date 20160617
 Time 18.24
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 32768
 SG1VENT MeOD
 NS 16
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 1.6384000 sec
 RG 88.42
 DW 50.000 usec
 DE 6.50 usec
 TE 295.1 K
 D1 0.1000000 sec
 TDO 1

===== CHANNEL f1 =====
 SF01 500.1925007 MHz
 NUC1 1H
 P1 10.00 usec
 PLW1 21.0000000 W

F2 - Processing parameters
 SI 16384
 SF 500.1900098 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 0.80



¹H NMR (CD₃OD, 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**).



^{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**).

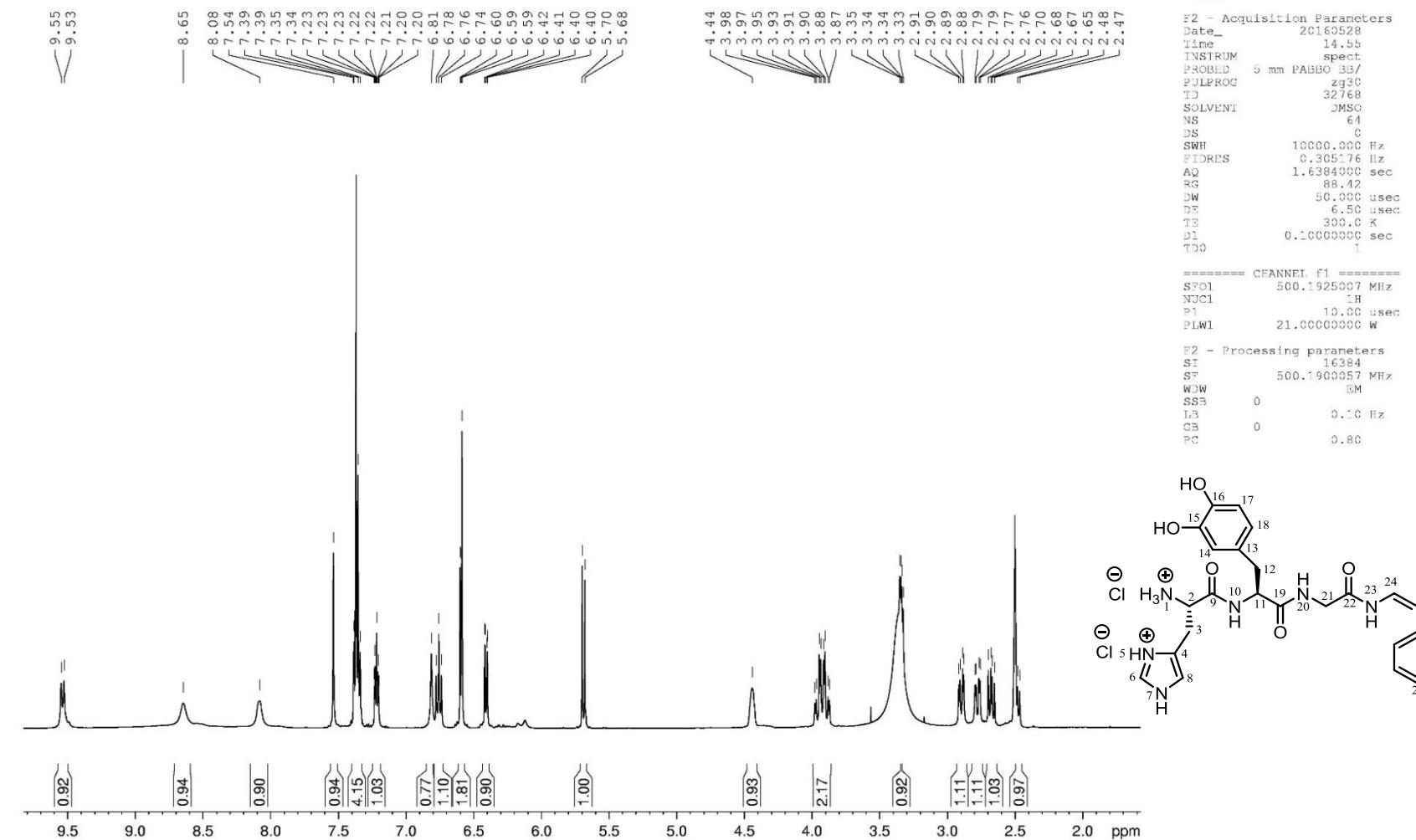
Current Data Parameters
NAME HF8-11_6-8
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160618
Time 5.48
INSTRUM spect
PROBHD 5 mm PAR30 BB/
PULPROG zgppg
TD 65536
SOLVENT MeOD
NS 7000
DS 0
SWH 29761.901 Hz
FIDRES 0.154131 Hz
AQ 1.1010048 sec
RG 749.15
DW 16.800 usec
DE 6.50 usec
TE 295.7 K
D1 0.63058811 sec
D11 0.03000000 sec
TD0 1

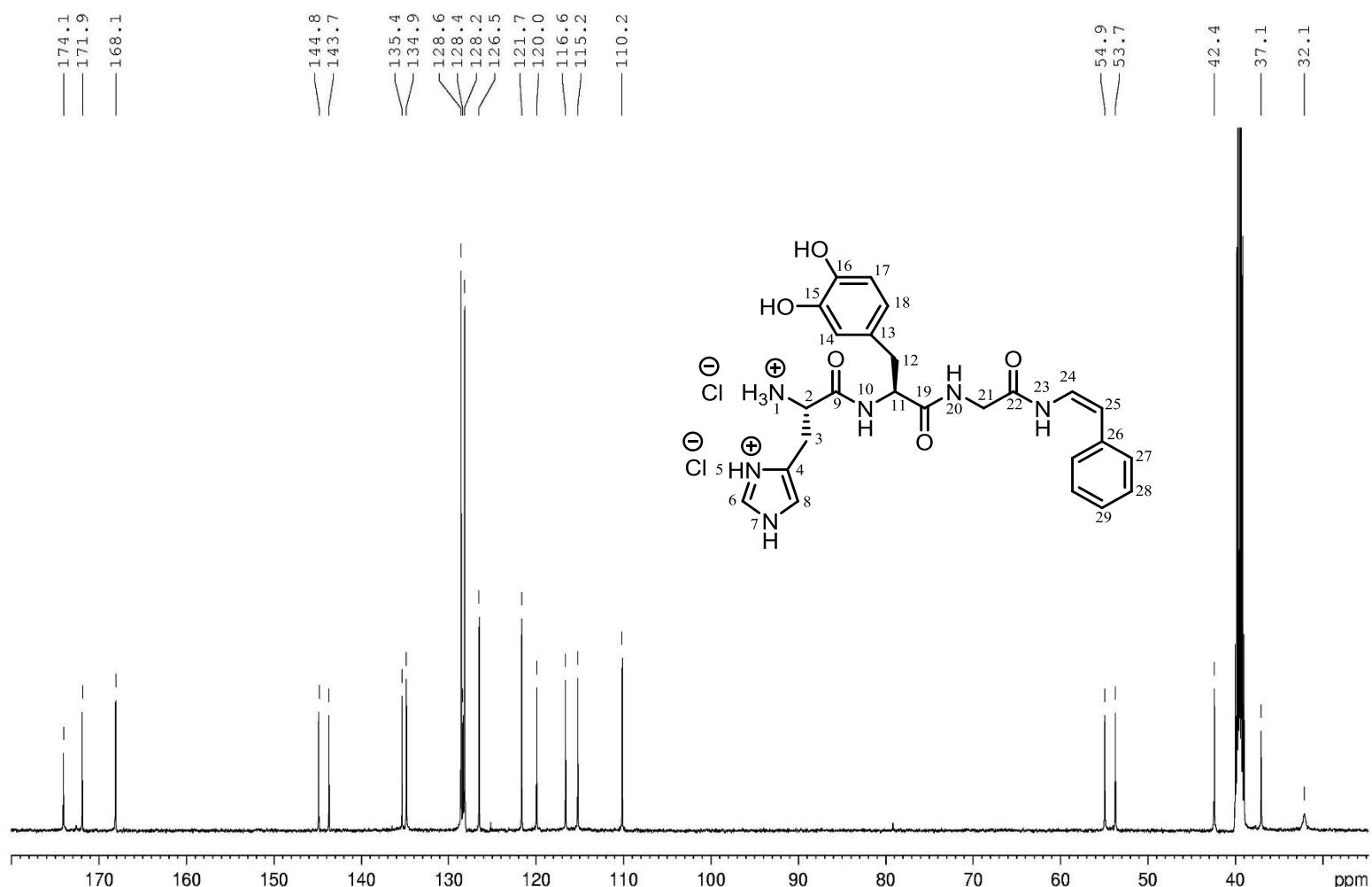
===== CHANNEL f1 ======
SFO1 125.7868349 MHz
NUC1 ^{13}C
P1 5.36 usec
PLW1 83.0000000 W

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

F2 - Processing parameters
SI 32768
SF 125.7727020 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
FC 0.80



¹H 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**).



^{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**).

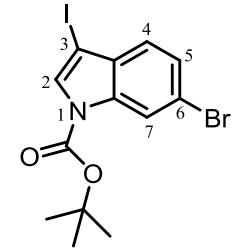
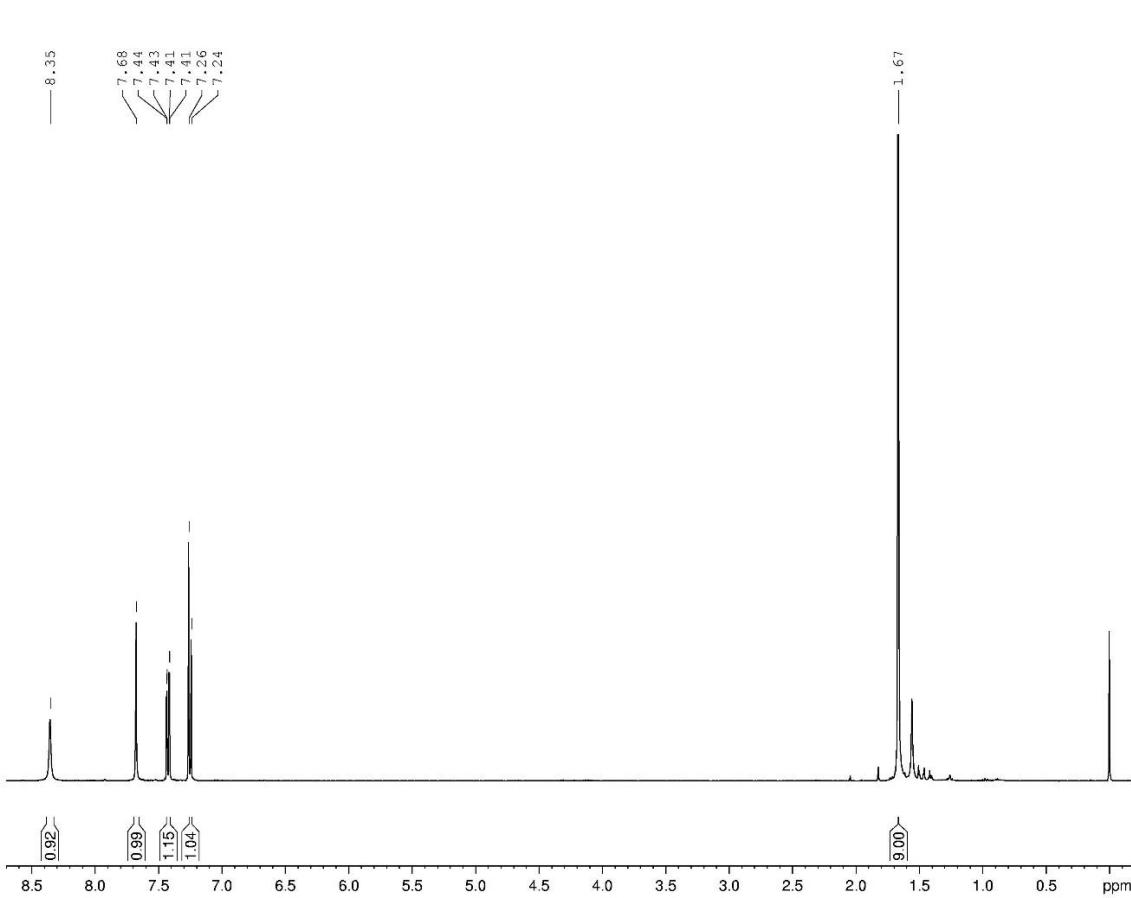
Current Data Parameters
NAME HF7-184
EXPNO 5
PROCNO 1

P2 - Acquisition Parameters
Date_ 20160529
Time 9.23
INSTRUM spect
PROBHD 5 mm PABBO BR/
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

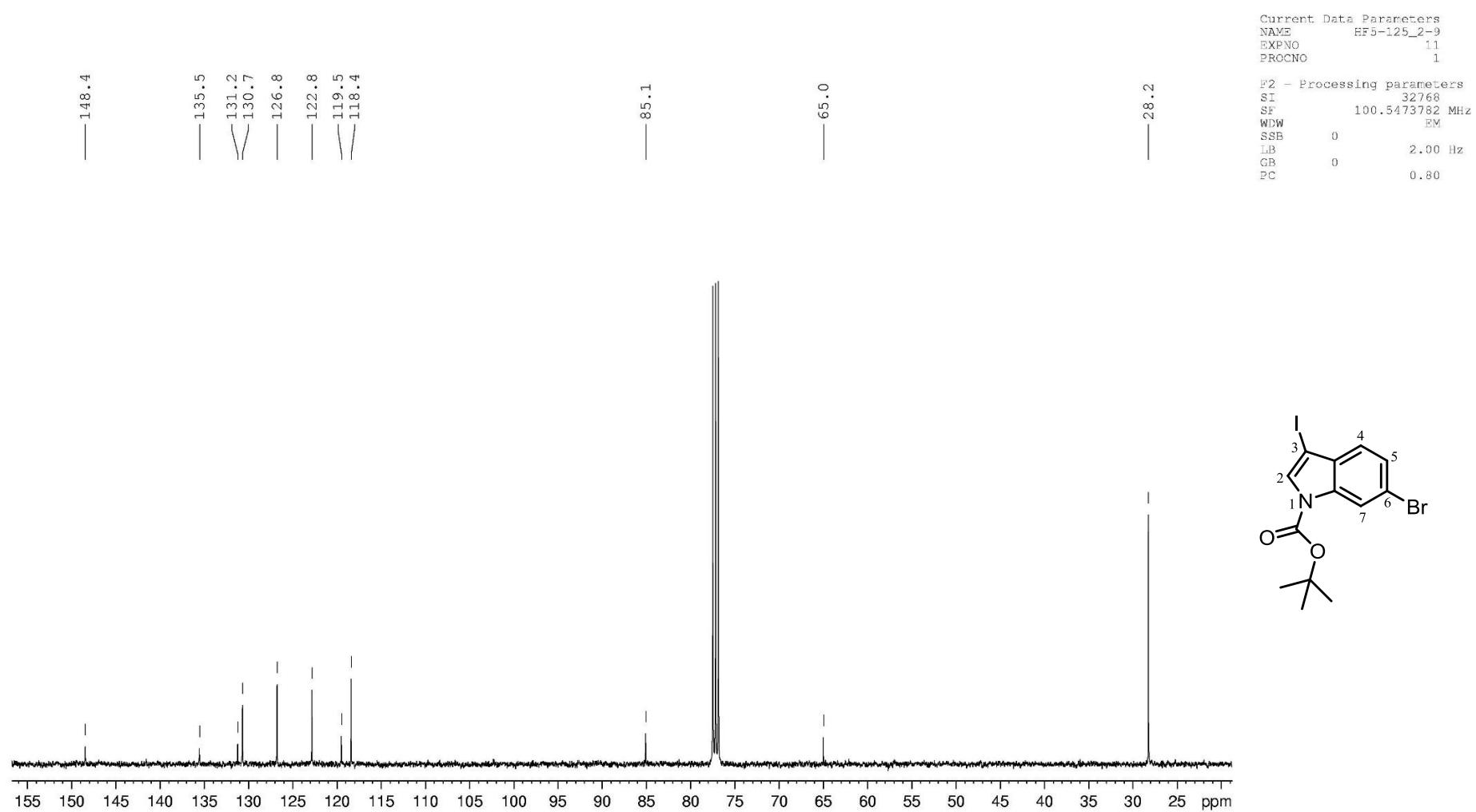
===== CHANNEL f1 =====
SFO1 125.7868349 MHz
NUC1 13C
F1 5.56 usec
PLW1 83.00000000 W

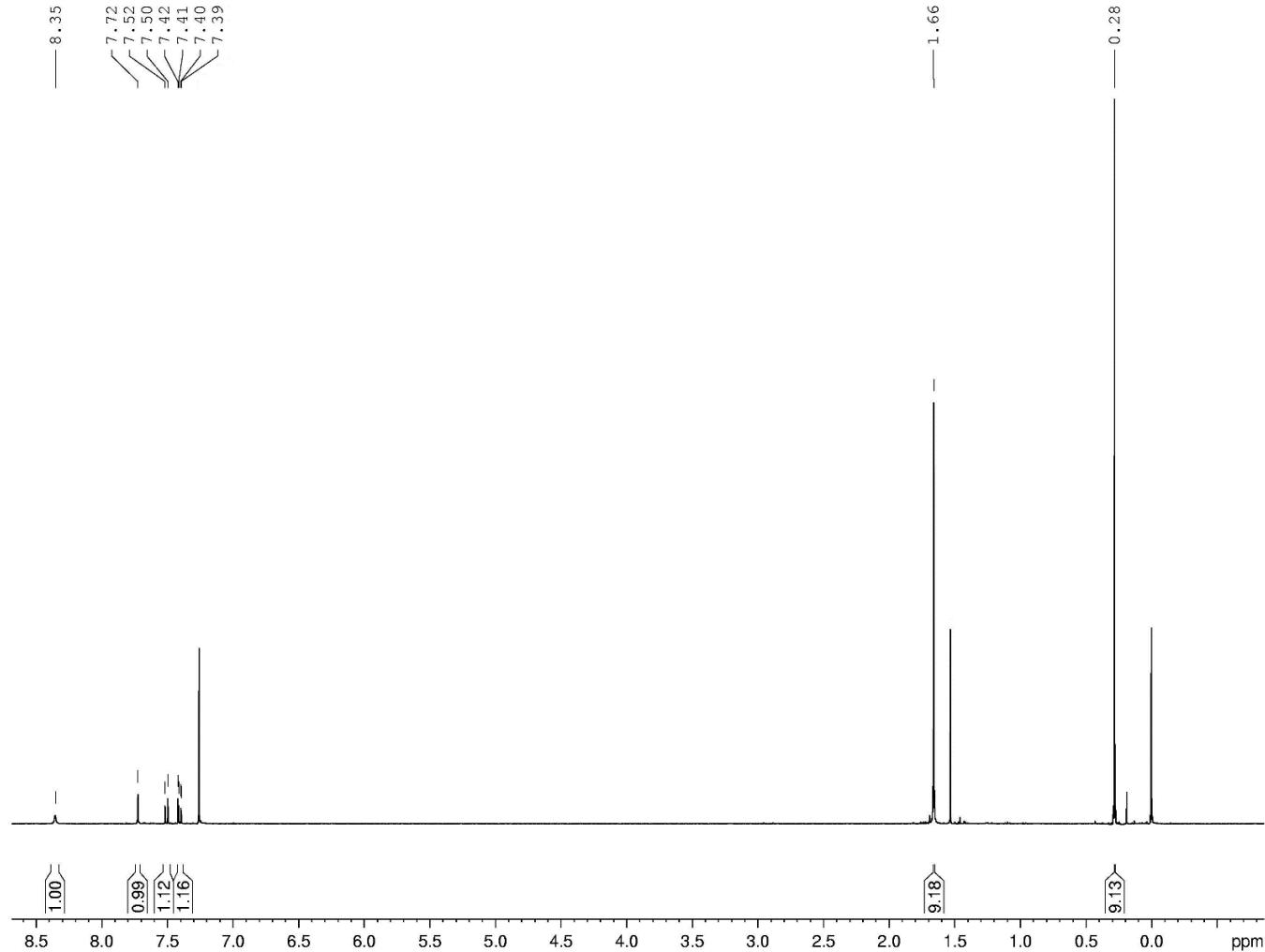
===== CHANNEL f2 =====
SFO2 500.1918000 MHz
NUC2 1H
CPDPFG[2] waltz16
PCPD2 80.00 usec
PLW2 21.00000000 W
PLW12 0.32813001 W
PLW13 0.20999999 W

P2 - Processing parameters
SI 32768
SF 125.7729343 MHz
WDW FID
SSB 0
LB 2.00 Hz
GB 0
FC 0.80



¹H NMR (CDCl₃, 400 MHz) of *tert*-Butyl-6-bromo-3-iodo-1*H*-indole-1-carboxylate (**19**).



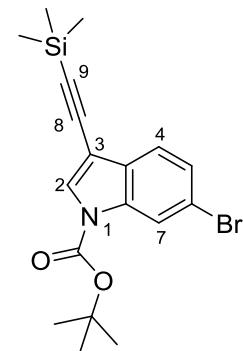


Current Data Parameters
NAME EF7-25
EXPNO 1
PROCNO 1

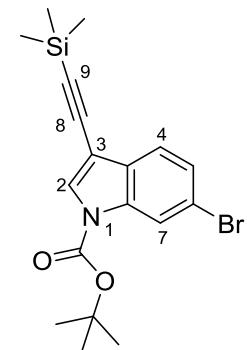
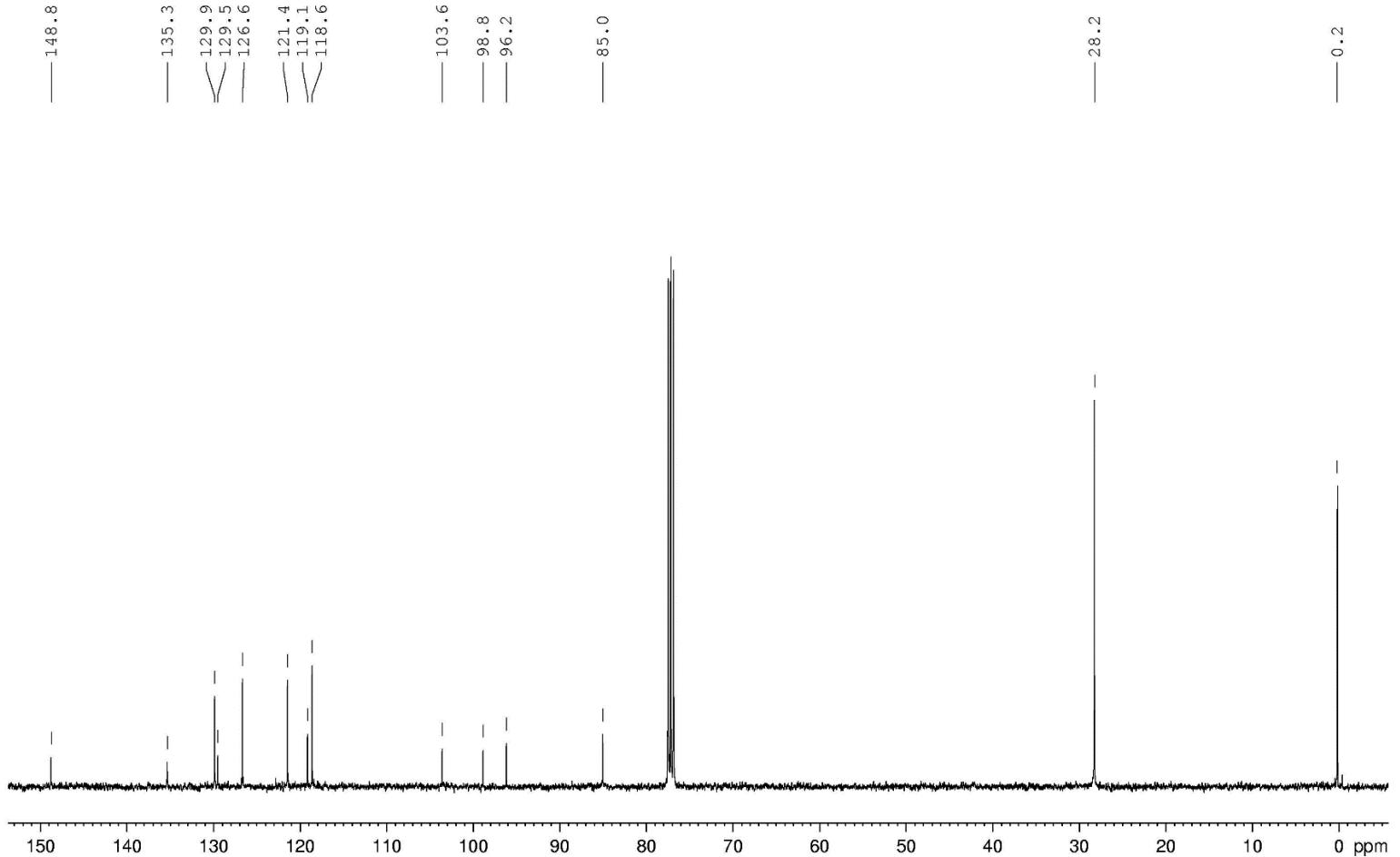
F2 - Acquisition Parameters
Date 20151122
Time 10.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 6
DS 0
SW1 8012.820 Hz
ETDRES 0.244532 Hz
AQ 2.0447233 sec
RG 456
DW 62.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.1000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 1H
P1 7.32 usec
PL1 -6.00 dB
P1W 40.0000000 W
SF01 400.1320007 MHz

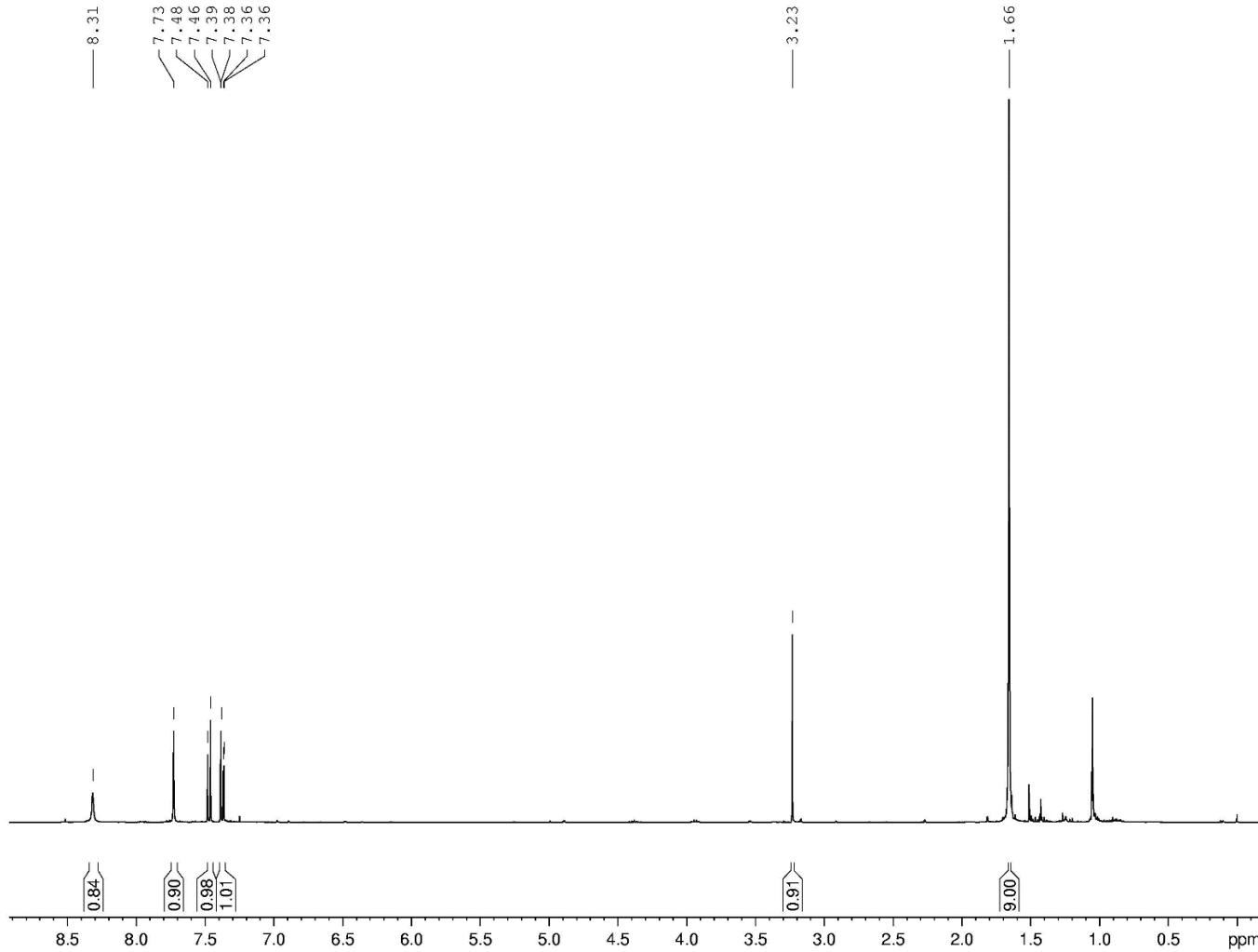
F2 - Processing parameters
SI 16384
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0 0.10 Hz
GB 0
PC 0.80



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



¹³C NMR (CDCl₃, 100 MHz) of *tert*-butyl 6-bromo-3-((trimethylsilyl)ethynyl)-1*H*-indole-1-carboxylate (**20**).

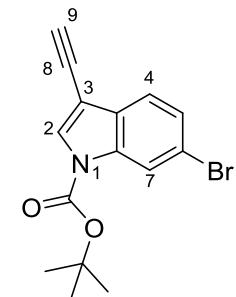


Current Data Parameters
 NAMR HF4-77
 EXPNO 10
 PROCNO 1

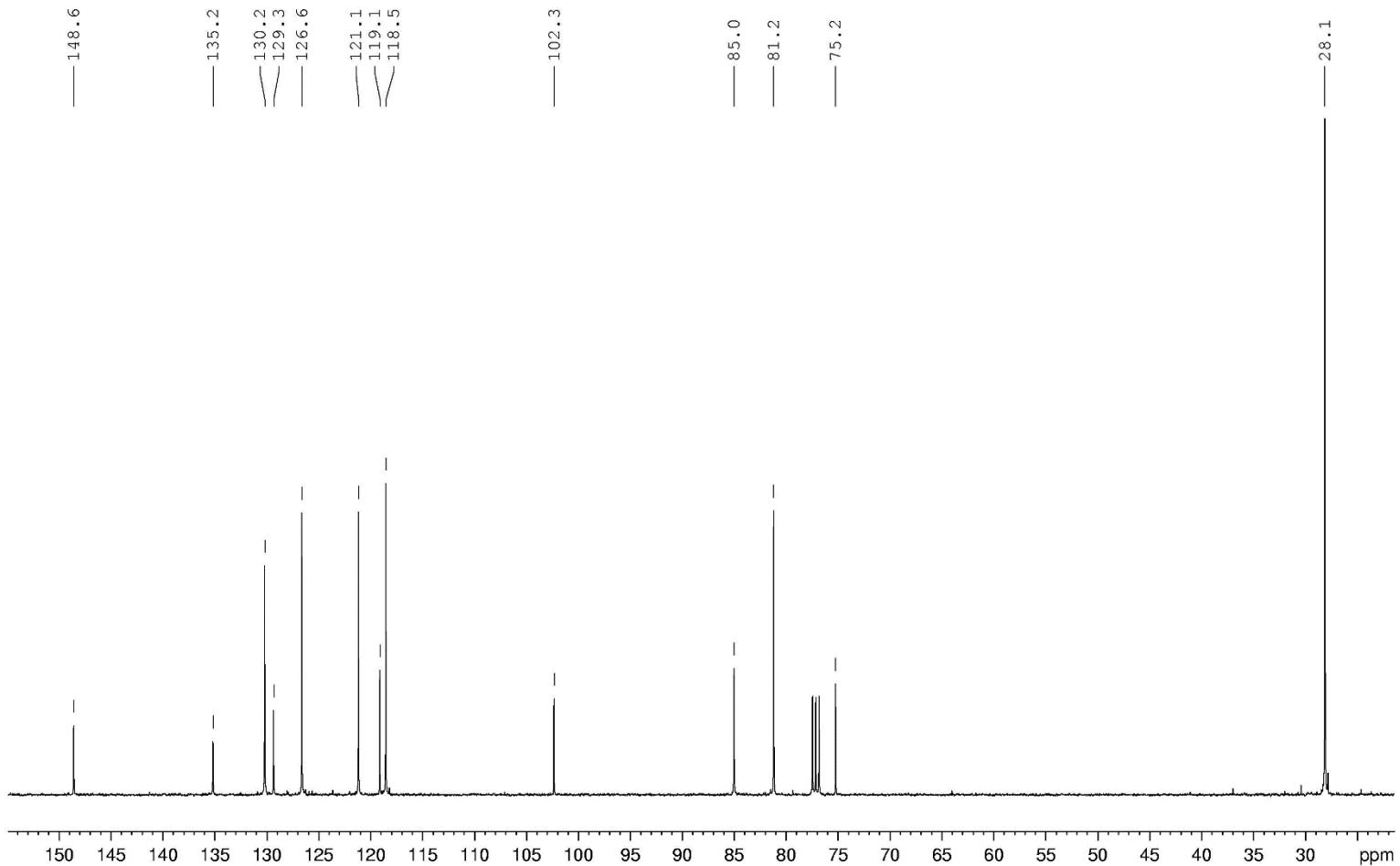
P2 - Acquisition Parameters
 Date_ 20140109
 Time 14.27
 INSTRUM spect
 PROBHD 5 mm PABBO BB
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 8169.935 Hz
 FIDRES 0.249327 Hz
 AQ 2.0054016 sec
 RG 36
 DW 61.200 usec
 DE 6.50 usec
 TE 300.0 K
 D1 0.1000000 sec
 TDO 1

----- CHANNEL f1 -----
 NUC1 1E
 PL 14.90 usec
 PLL -1.70 dB
 PELW 12.92942619 Hz
 SFOL 399.8717194 MHz

P2 - Processing parameters
 SI 16384
 SF 399.8700187 MHz
 WDW PM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 0.80

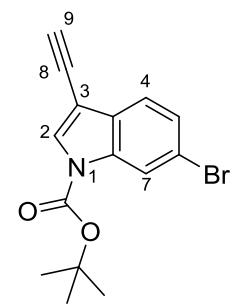


¹H NMR (CDCl₃, 400 MHz) of *tert*-butyl 6-bromo-3-ethynyl-1*H*-indole-1-carboxylate (**17**).

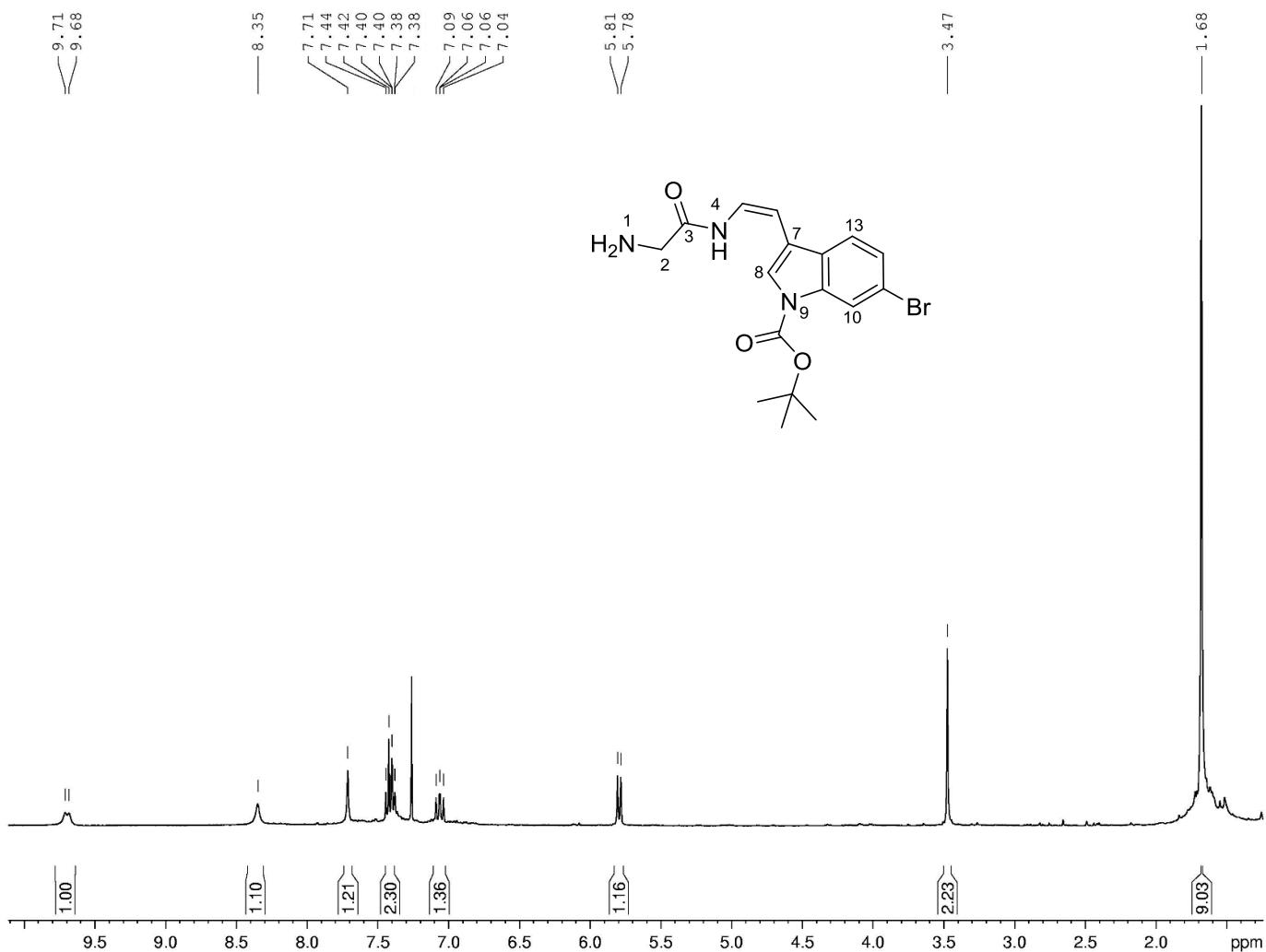


Current Data Parameters
NAME HF4-77
EXPNO 12
PRCNO 1

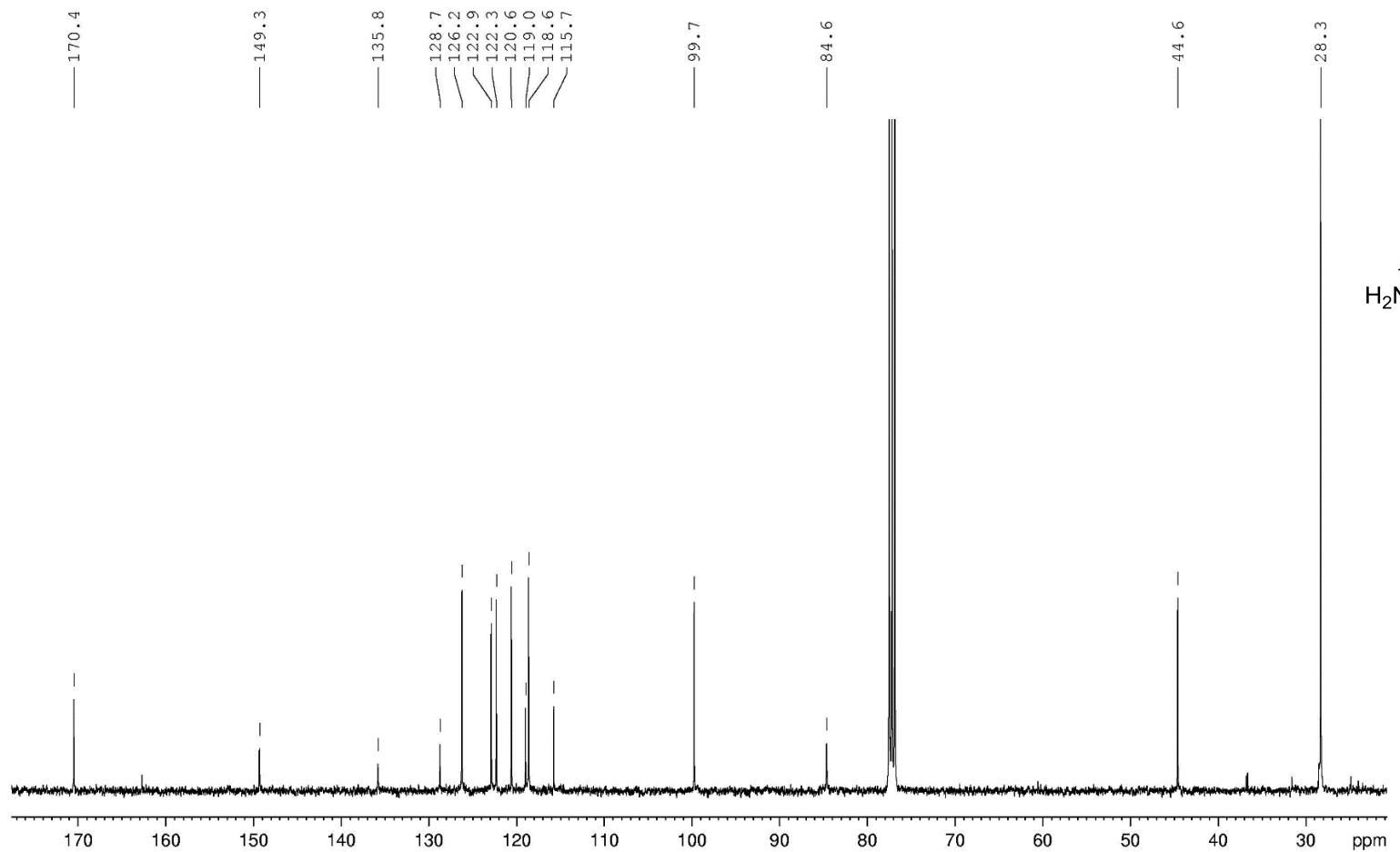
F2 - Processing parameters
SI 32768
SF 100.5473870 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.80



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

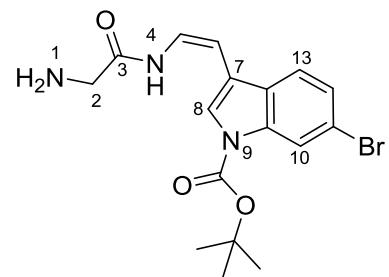


^1H NMR (CDCl_3 , 400 MHz) of *tert*-butyl (Z)-3-(2-(2-aminoacetamido)vinyl)-6-bromo-1*H*-indole-1-carboxylate (**21**).

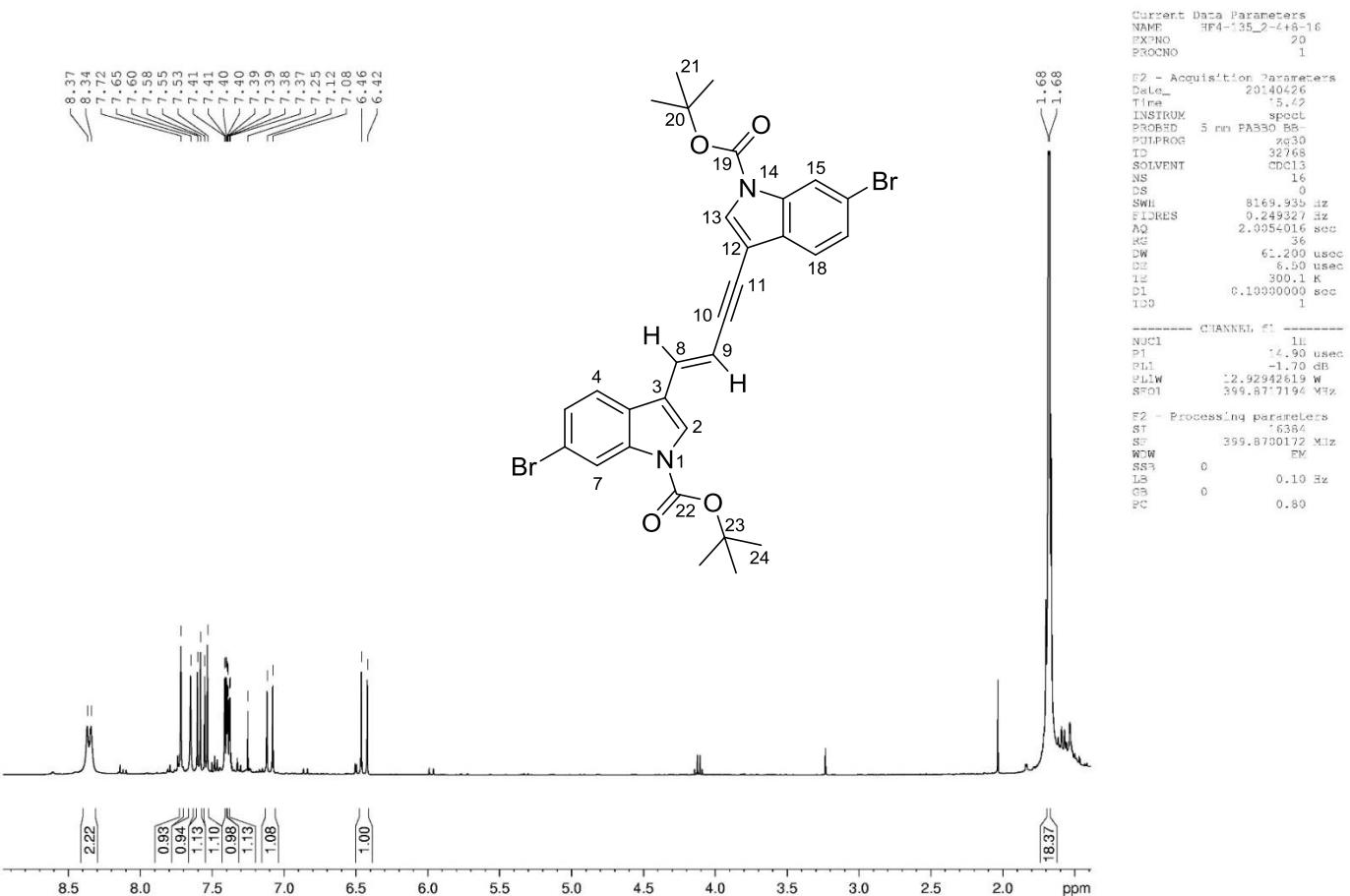


Current Data Parameters
NAME HF4-144_33-44
EXPNO 10
PROCNO 1

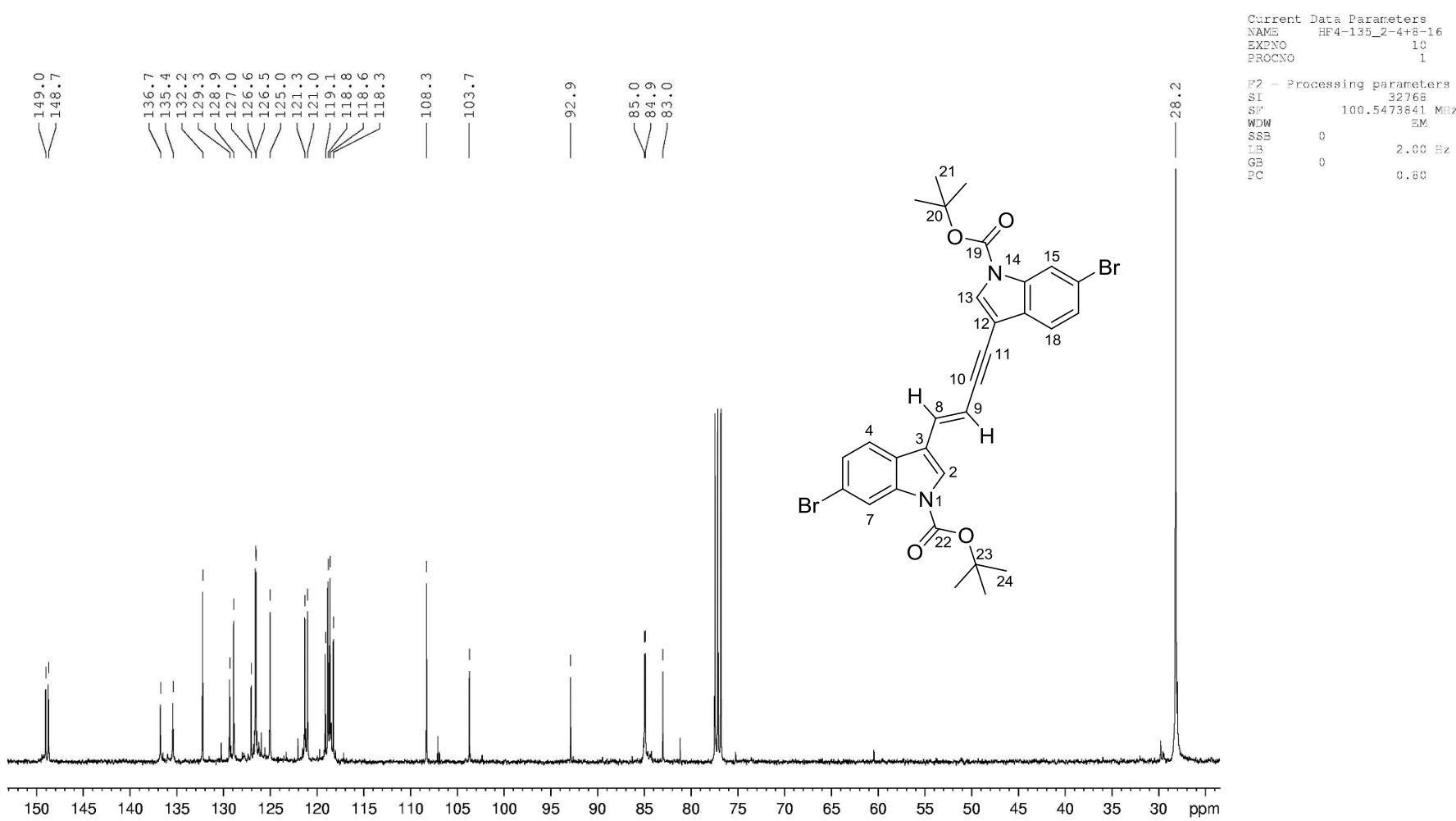
F2 - Processing parameters
SI 32768
SF 100.5473797 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.80



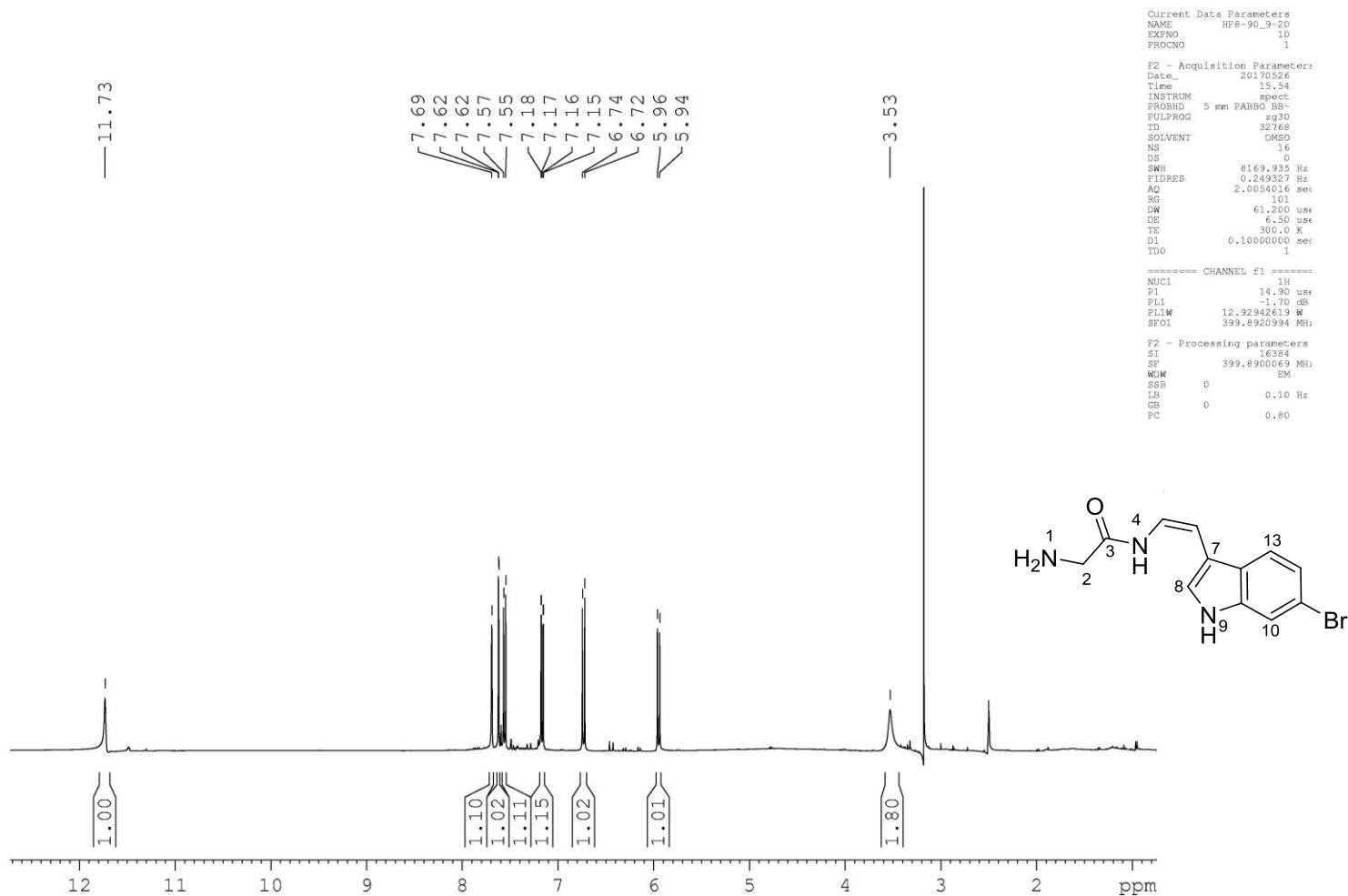
^{13}C NMR (CDCl_3 , 100 MHz) of *tert*-butyl (Z)-3-(2-(2-aminoacetamido)vinyl)-6-bromo-1*H*-indole-1-carboxylate (**21**).



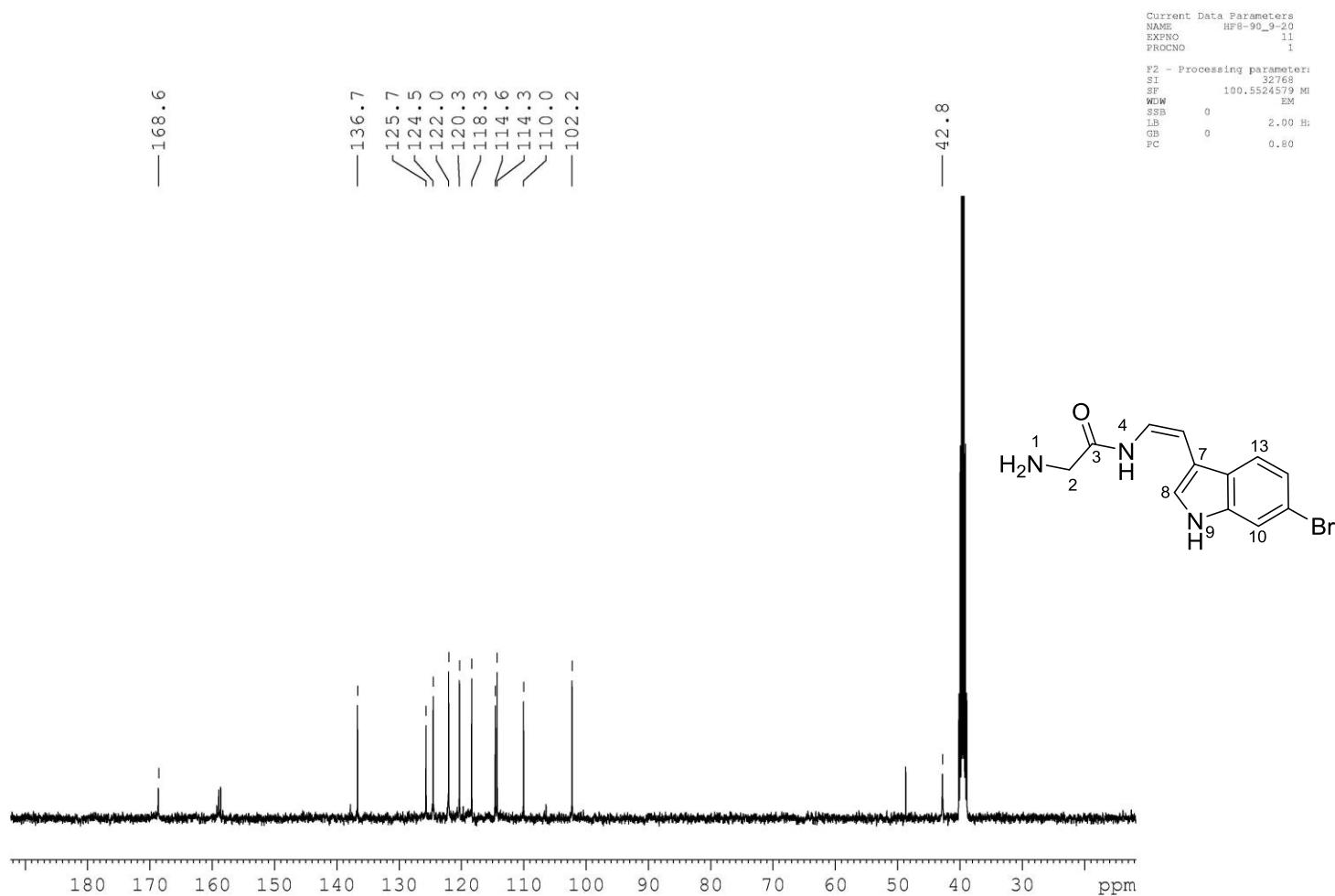
¹H NMR (CDCl₃, 400 MHz) of (*E*)-di-*tert*-butyl 3,3'-(but-1-en-3-yn-1,4-diyl)bis(6-bromo-1*H*-indole-1-carboxylate) (**22**).



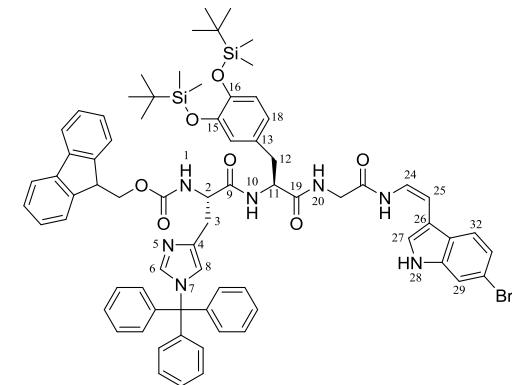
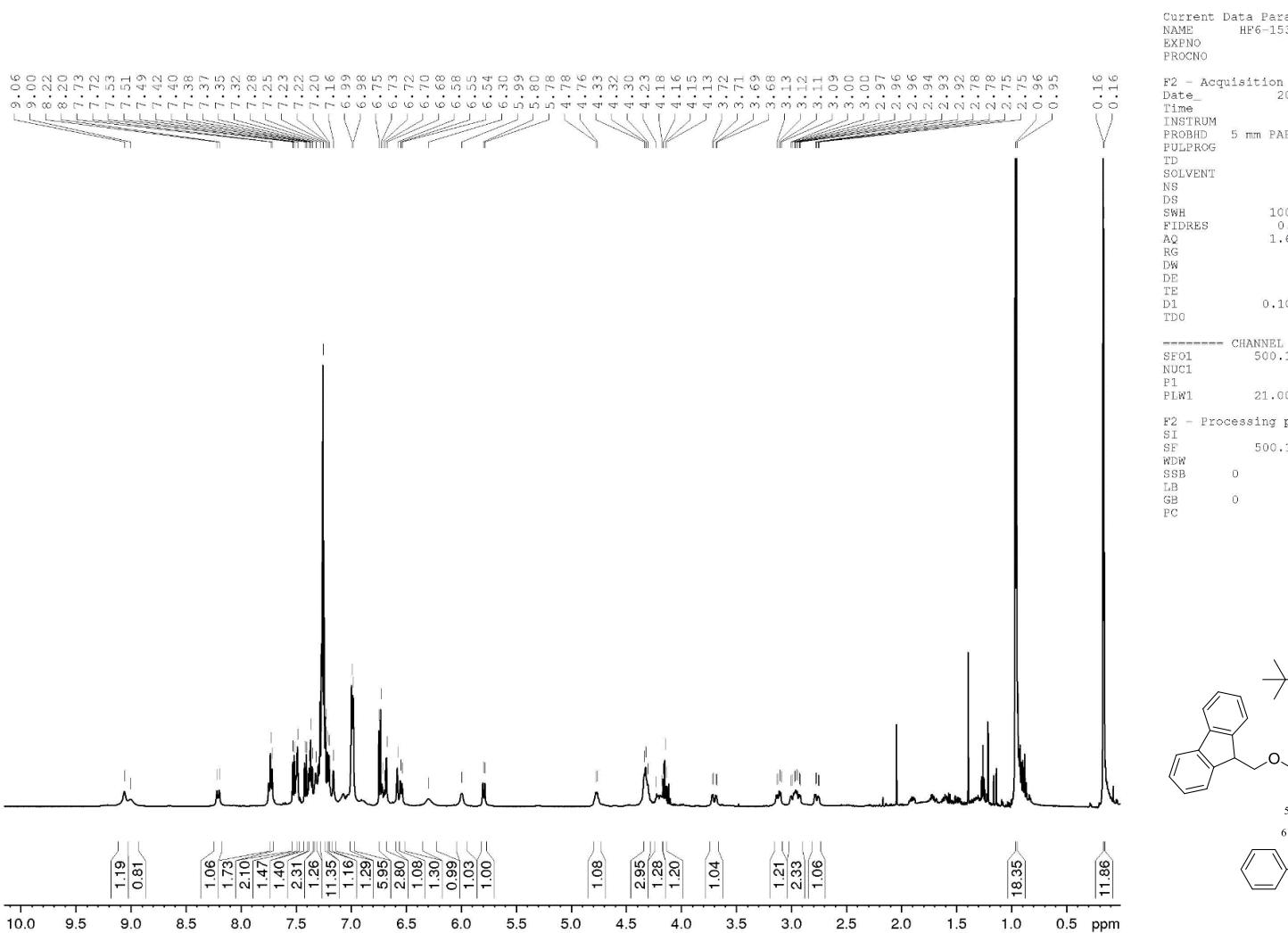
^{13}C NMR (CDCl_3 , 100 MHz) of (*E*)-di-*tert*-butyl 3,3'-(but-1-en-3-yn-1,4-diyl)bis(6-bromo-1*H*-indole-1-carboxylate) (**22**).



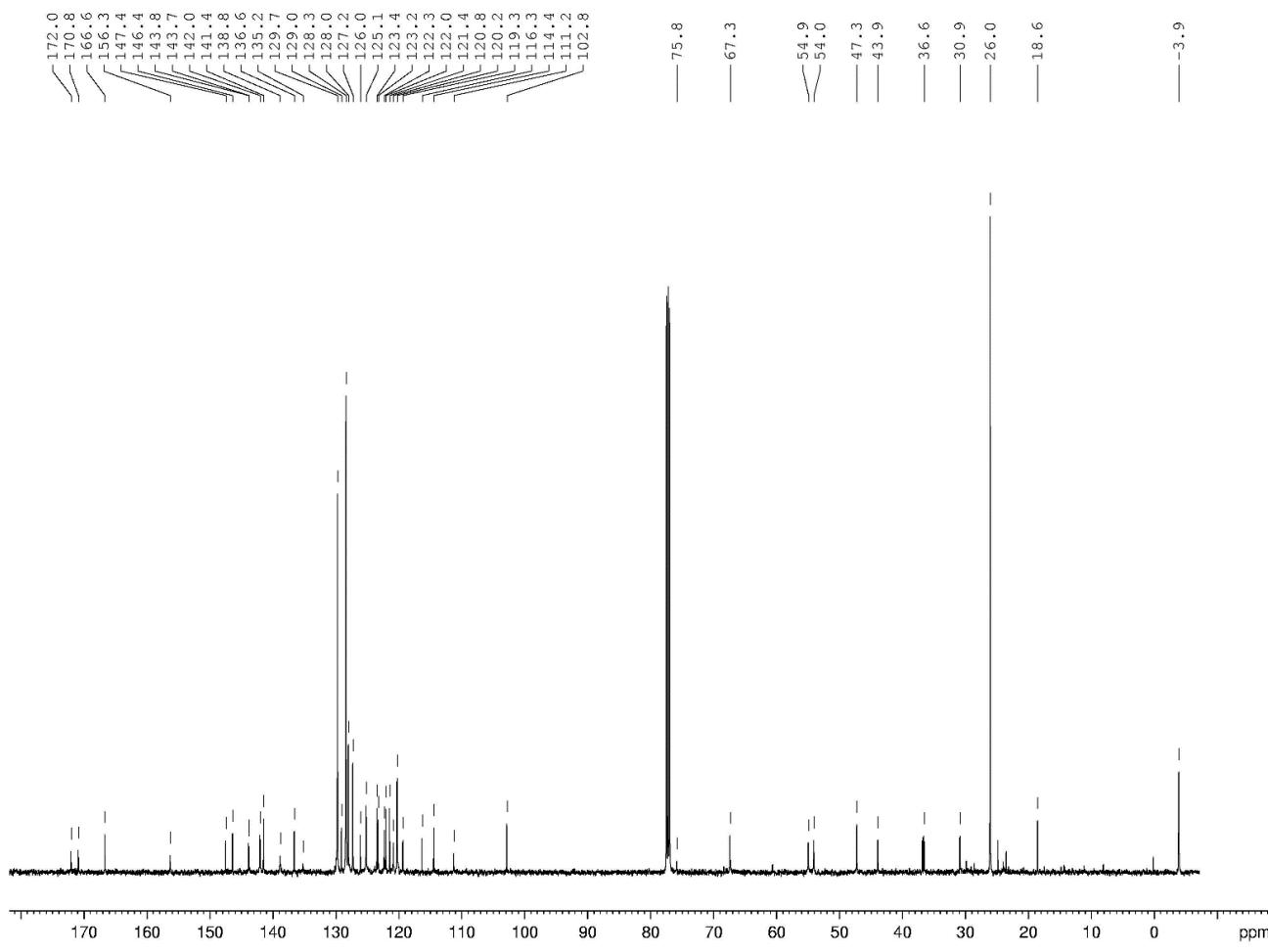
¹H NMR (DMSO-*d*₆, 400 MHz) of (*Z*)-2-amino-*N*-(2-(6-bromo-1*H*-indol-3-yl)vinyl)acetamide (**16**).



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



¹H NMR (CDCl₃, 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 (9H-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**).

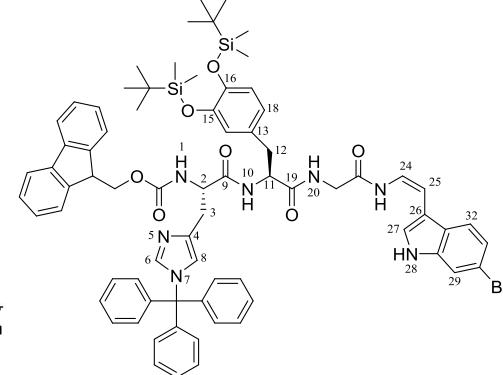
Current Data Parameters
NAME HF6_153_35_40
EXPNO 2
PROCNO 1

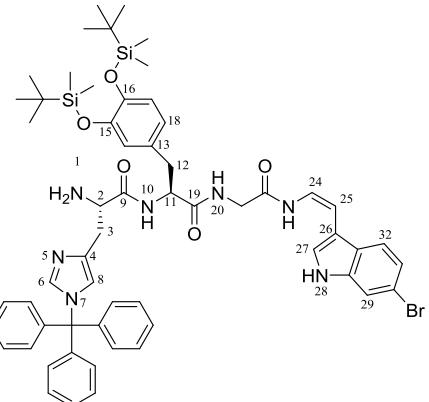
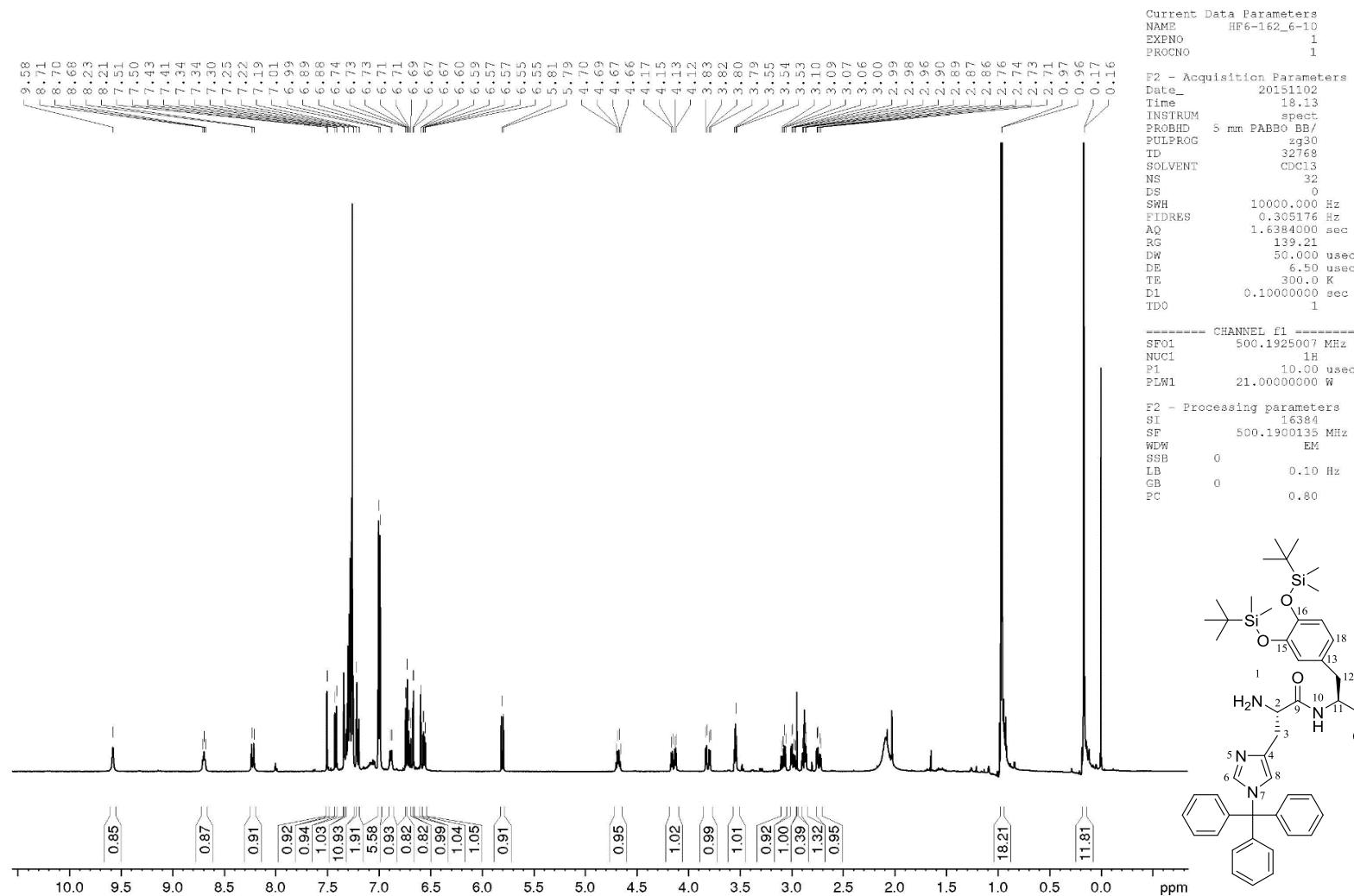
F2 - Acquisition Parameters
Date_ 2015.03.1
Time 14.54
INSTRUM spect
PROBHD 5 mm TBI PRO BB/
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 2
DS 0
SWH 29761.334 Hz
FIDRES 0.454233 Hz
AQ 1.1010078 sec
RG 749.15
DW 16.800 used
DE 6.50 used
TE 300.0 K
D1 0.63058811 sec
D11 0.03000000 sec
TD0 1

----- CHANNEL f1 -----
SFO1 125.7868349 MHz
NUC1 ¹³C
PL 5.56 usec
FLW1 83.0000000 W

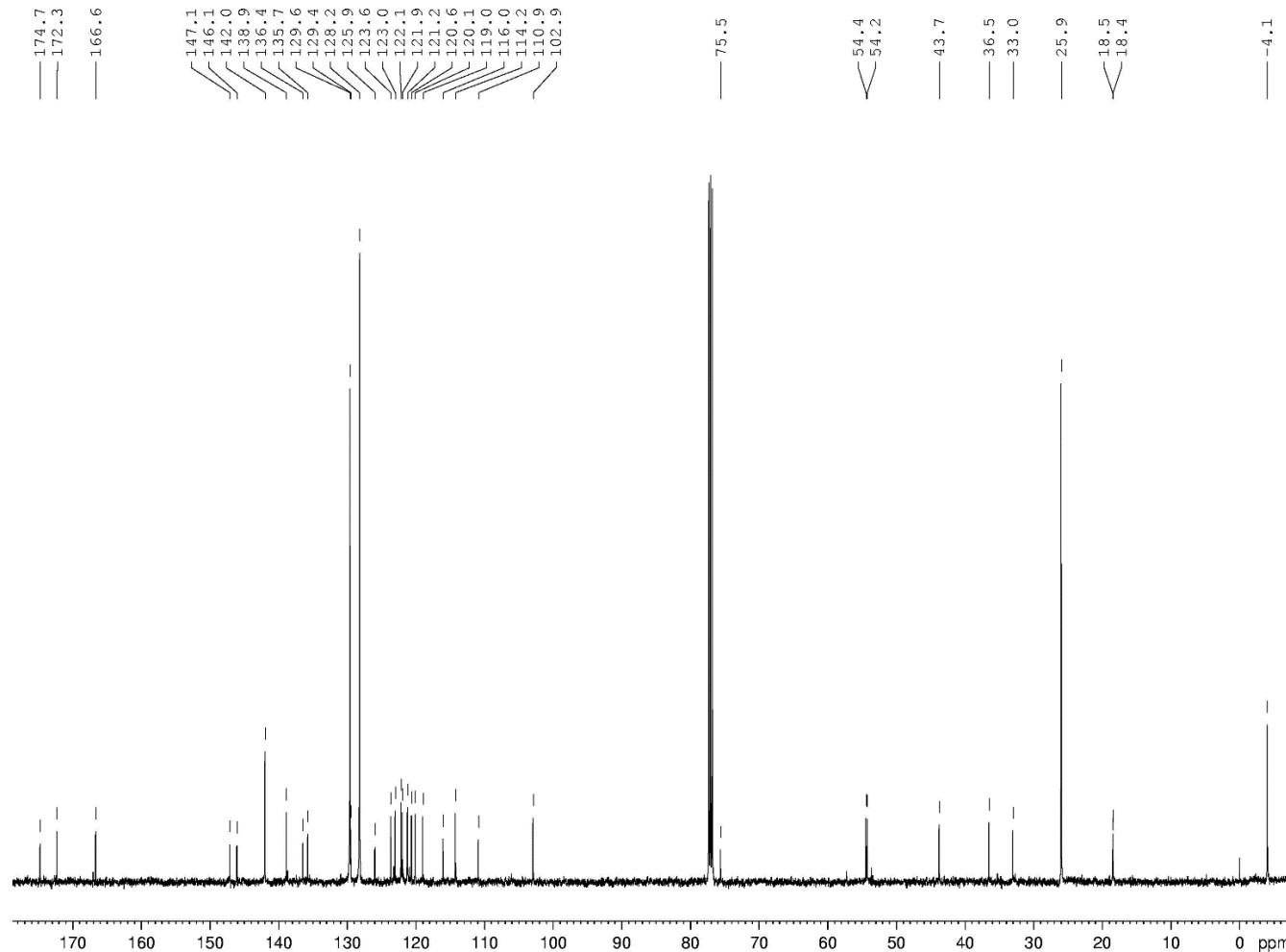
----- CHANNEL f2 -----
SFO2 500.1318000 MHz
NUC2 ¹H
CPDPRG[2] waltz16
CPDW2 80.00 usec
FLW2 21.0000000 W
FLW2 0.32813031 W
FLW3 0.20593999 W

F2 - Processing parameters
ST 35768
SF 125.7720592 MHz
WDW 0 EM
SSB 0 2.00 Hz
LB 0 0.80
GSI 0
PC



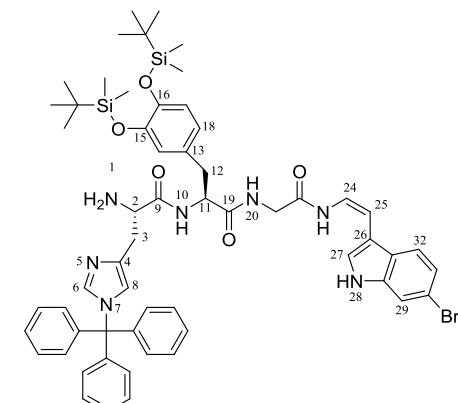


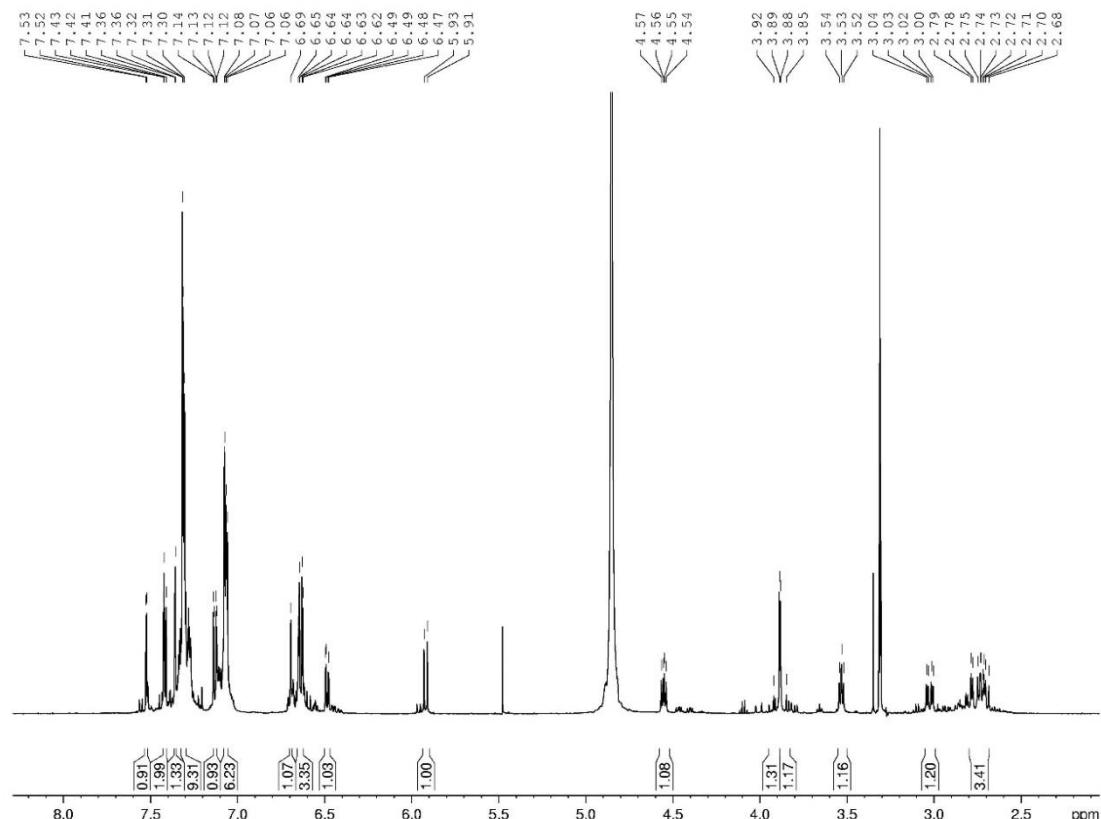
¹H NMR (CDCl₃, 500 MHz) of (S)-2-amino-N-((S)-3-(3,4-bis((tert-butyldimethylsilyl)oxy)phenyl)-1-((2-(((Z)-2-(6-bromo-1H-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-1-oxopropan-2-yl)-3-(1-trityl-1H-imidazol-4-yl)propanamide (**24**).



^{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**).

Current Data Parameters
 NAME EF6-162-6-10
 EXPNO 5
 PROCN0
 F2 - Acquisition Parameters
 Date 20151103
 Time 6.08
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg
 ID 65536
 SOLVENT CDCl3
 NS 225
 DS 0
 SWH 29761.904 Hz
 EDRES 0.654135 sec
 AQ 1.101004 sec
 RG 749.15
 DW 16.800 used
 DE 6.50 used
 TF 300.0 K
 TP 0.6305881 sec
 D1 0.0300000 sec
 TDO
 CHANNEL f1
 SF01 125.7868343 MHz
 NUC1 13C
 PI 5.56 usec
 PW1 83.0000000 W
 CHANNEL f2
 SF02 300.1918000 MHz
 NUC2 1H
 CPDRG12 waltz16
 TCDP2 80.00 usec
 TM2 21.10000000 W
 TM12 0.32E30C W
 TM13 0.20999999 W
 F2 - Processing parameters
 ST 32768
 SF 125.7728755 MHz
 WDD 0
 SSB 0
 LB 2.00 Hz
 GB 0
 ZC 0.80





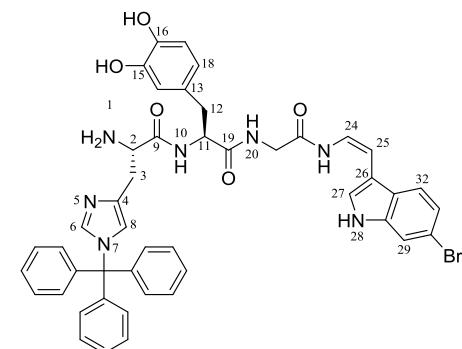
¹H NMR (CD₃OD, 500 MHz) of (*S*)-2-amino-N-((*S*)-1-((2-((*Z*)-2-(6-bromo-1*H*-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-3-(3,4-dihydroxyphenyl)-1-oxopropan-2-yl)-3-(1-trityl-1*H*-imidazol-4-yl)propanamide (**25**).

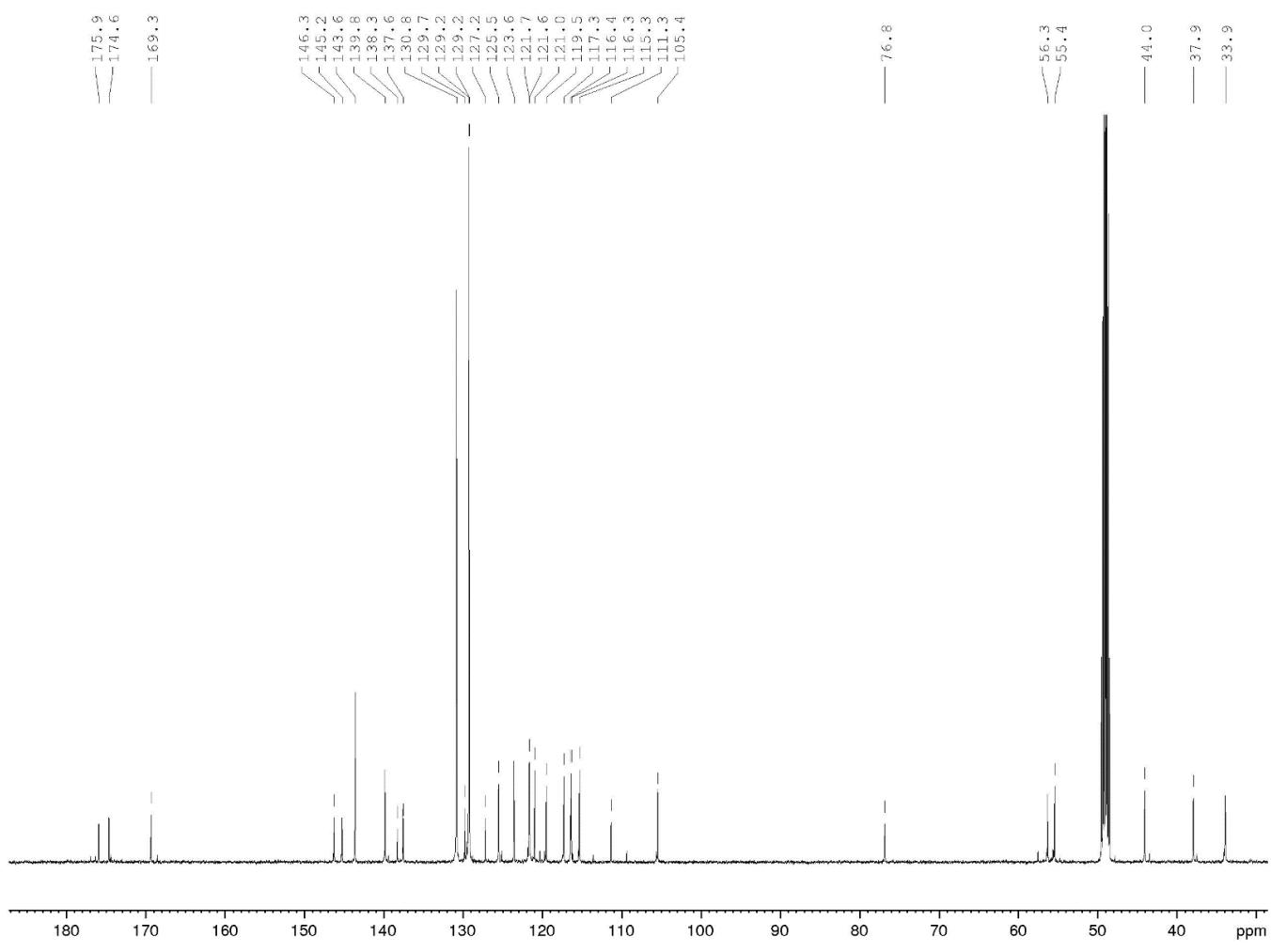
Current Data Parameters
NAME: HE7-103 (2)
EXNO: 4
PROCNO: 1

P2 - Acquisition Parameters
Date: 20160225
Time: 8:34
INSTRUM: spect
PROBOD: 5 mm PABBO BB/
SHPPROC: zg30
TD: 32768
SOLVENT: MeOH
NS: 16
DS: 0
SW1: 10000.000 Hz
P1: 0.300178 Hz
AQ: 1.6536400 sec
RG: 96.27
DW: 50.000 usec
DE: 6.50 usec
TE: 300.0 K
D1: 0.1000000 sec
TDO: 1

CHANNEL 1
SIQ1: 500.1925007 MHz
NUC1: 1H
P1: 10.00 usec
PWL: 21.00000000 W

P2 - Processing parameters
SI: 16384
ST: 500.1903101 MHz
WDW: EM
SSB: 0
LB: 0.10 Hz
ETR: 0
PC: 0.80



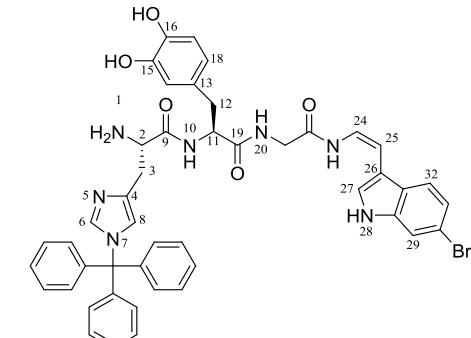


Current Data Parameters
NAME HF7-103(2)
EXPNO 8
PROCNO 1
P2 - Acquisition Parameters
Date 20160226
Time 5.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg
TD 65536
SOLVENT MeD
NS 7682
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 749.15
DW 16.800 usec
DE 6.50 usec
TB 300.0 K
D1 0.63058811 sec
D11 0.03000000 sec
TD0 8

===== CHANNEL f1 =====
SF01 125.7868349 MHz
NUC1 13C
P1 5.56 usec
PLW1 83.00000000 W

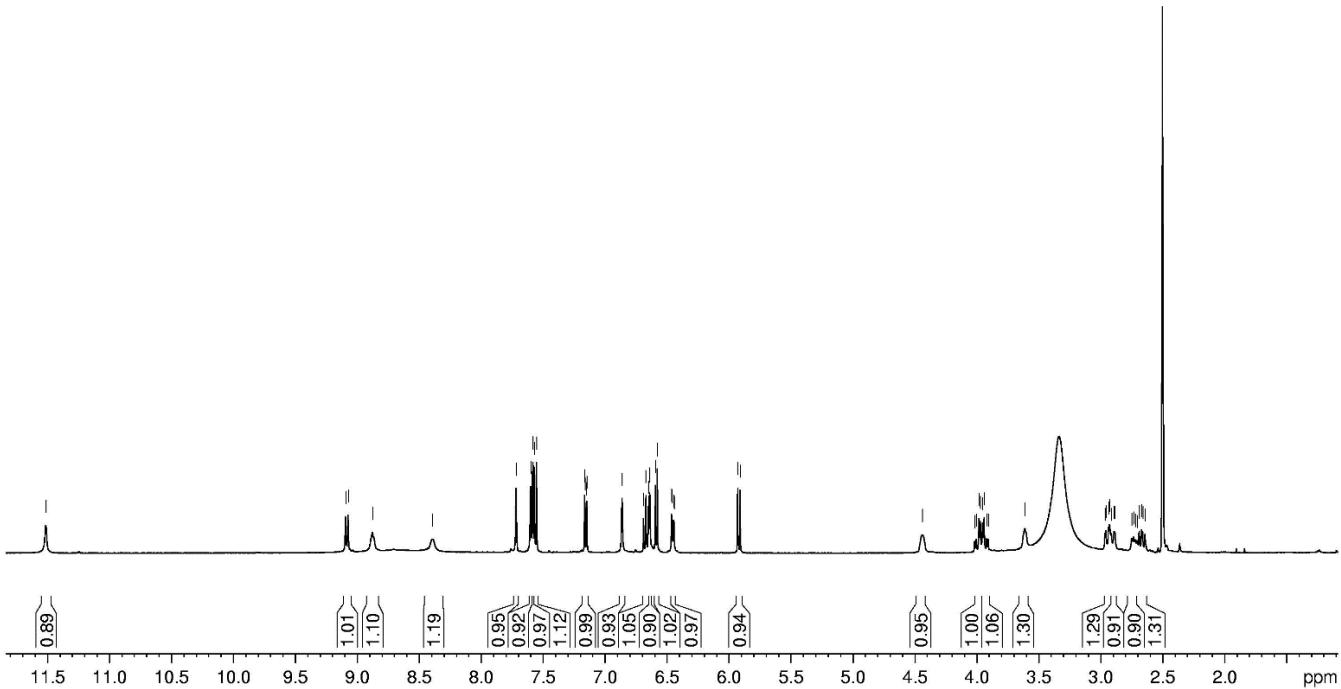
===== CHANNEL f2 =====
SF02 500.1918000 MHz
NUC2 1H
CPDPFG[2] waltz16
PCPD2 80.00 usec
PLW2 21.0000000 W
PLW12 0.32813001 W
PLW13 0.20999999 W

F2 - Processing parameters
SI 32768
SF 125.7727016 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.80



¹³C NMR (CD₃OD, 125 MHz) of (S)-2-amino-N-((S)-1-((2-((Z)-2-(6-bromo-1H-indol-3-yl)vinyl)amino)-2-oxoethyl)amino)-3-(3,4-dihydroxyphenyl)-1-oxopropan-2-yl)-3-(1-trityl-1H-imidazol-4-yl)propanamide (**25**).

11.51



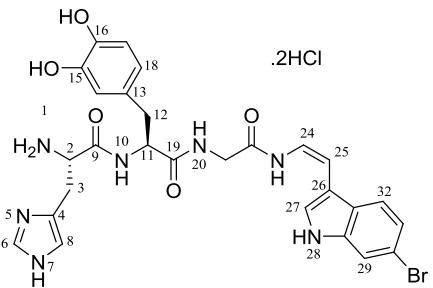
¹H NMR (DMSO-*d*₆, 500 MHz) of halocyamine A dihydrochloride salt (**1**).

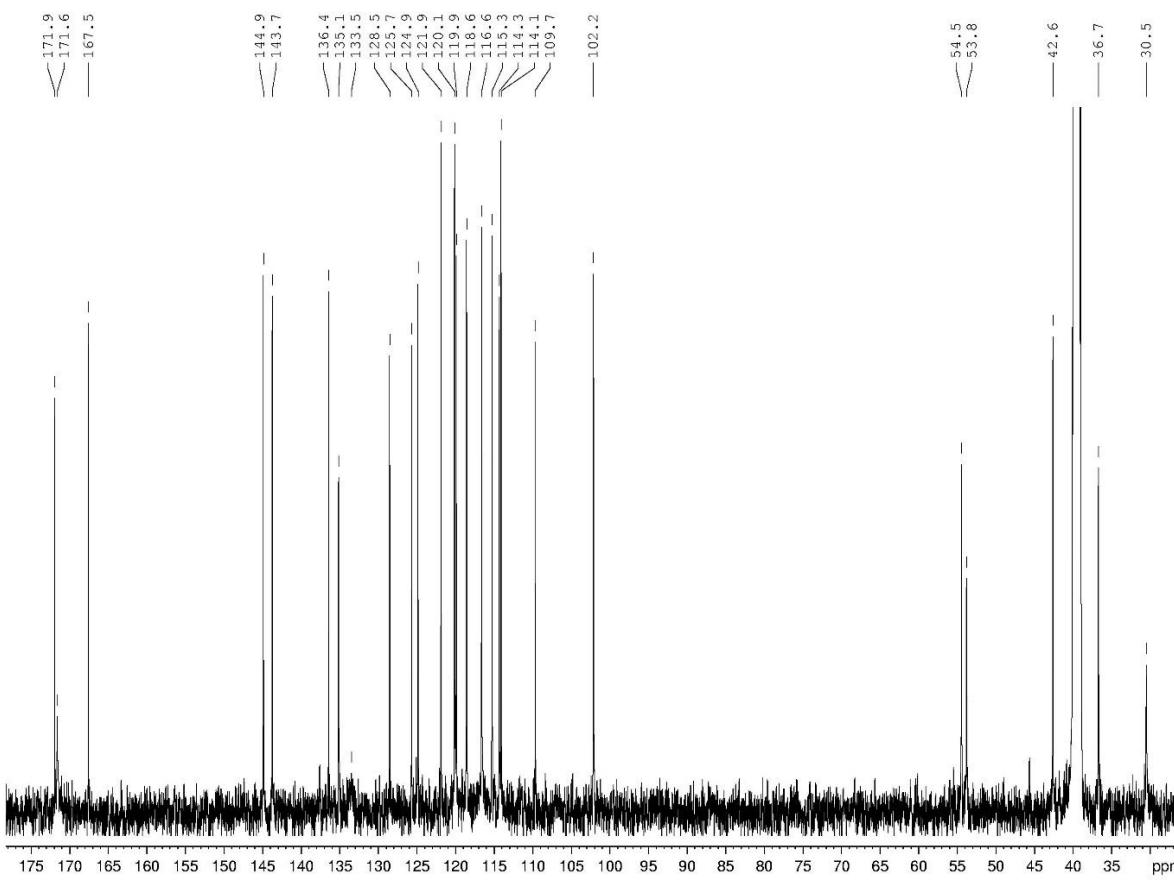
Current Data Parameters
NAME HF8-28(2)_1C-43
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160702
Time 11.07
INSTRUM spect
PROBHD 5 mm PABBC 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
DI 0.1000000 sec
TDC 1

----- CHANNEL f1 -----
SP01 500.1925007 MHz
NUC1 1H
PI 10.00 usec
PLW1 21.0000000 W

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





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

Current Data Parameters
NAMT 1HFB 28(2)=0.43
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160703
Time_ 6.75
INSTRUM spect
PROBHD 5 mm DABRD BB/
PULPROG zgpg
TD 65536
SOLVENT DMSO
NS 1000
DS 1
SWH 29761.901 Hz
ETDRS 0.15/13.3 Hz
AQ 1.10100E-8 sec
RG 749.15
DW 16.800 usec
DE 6.50 usec
TE 300.0 °K
C1 0.63058811 sec
C1 0.03000000 sec
TD0 8

----- CHANNEL F1 -----
SFO1 25.78663E9 MHz
NUC1 ^{13}C
PC 5.56 usec
P1W1 63.00000000 W

----- CHANNEL F2 -----
SFO2 500.1918000 MHz
NUC2 ^1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW1 21.00000000 W
PLW2 5.32813001 W
PLW3 0.20993999 W

F2 - Processing parameters
SC 32768
SF 125.7729351 MHz
WDW EM
SSB 0
LB 2.00 Hz
GZ 0
PC 0.80

