Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A Short and Efficient Total Synthesis of the Bromotyrosine-derived Alkaloid Psammaplysene A

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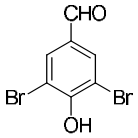
Contents

General information

Anhydrous benzene and PhMe were freshly distilled from sodium benzophenone ketyl under N_2. Anhydrous DCM, MeCN, and Et_3N were freshly distilled over CaH_2. Silica gel plates pre-coated on glass were used for thin layer chromatography (TLC) using UV light, iodine vapor, or 7% ethanolic phosphomolybdic acid and heating as the visualizing methods. Silica gel was used for flash column chromatography. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials. Reagents were obtained commercially and used as received.
^{1}H and ^{13}C NMR spectra were recorded in the indicated solvent at room temperature (400, 500, or 600 MHz for ^{1}H and 100, 125, or 150 MHz for ^{13}C, respectively). Spectral splitting patterns are designated as follows: s, singlet; br, broad; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were taken on an FT-IR spectrophotometer. High-resolution mass spectra (HRMS) were measured by the ESI or EI method.

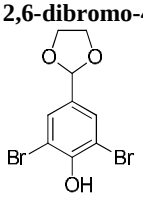
Experimental Details:

3,5-dibromo-4-hydroxybenzaldehyde (7)[1]



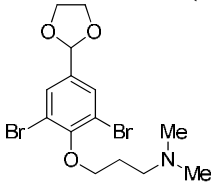
A solution of Br_2 (5.04 g, 1.61 mL, 31.5 mmol) in AcOH (16 mL) was added slowly to a mixture of 4-hydroxybenzaldehyde **5** (1.83 g, 15 mmol), sodium acetate (3.8 g, 46.5 mmol) and AcOH (36 mL) at room temperature over 20 min. After addition, the reaction was kept stirring for 1h at room temperature. The resulting mixture was then poured into 200 mL of water, and a solid precipitated. After filtration, the solid was washed with H_2O and dried in vacuum to afford compound **7** as a pale solid (3.94 g, 94%).
R_f = 0.48 (100% EtOAc); IR (KBr): 3199 (br), 2858, 1672, 1579, 1482, 1415, 1230, 1199, 1149 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.00 (s, 2H), 6.42 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 154.4, 133.6 (×2), 131.3, 110.7 (×2) ; HRMS (EI+): calcd for $C_7H_4Br_2O_2$: 277.8579, found: 277.8578.

2,6-dibromo-4-(1,3-dioxolan-2-yl)phenol



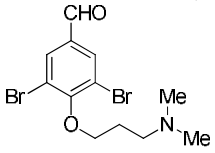
A solution of 3,5-dibromo-4-hydroxybenzaldehyde **7** (2.8 g, 10 mmol), ethylene glycol (840 μL, 15 mmol), and camphorsulfonic acid (70 mg, 0.3 mmol) in 50 mL benzene was refluxed for 2 h, while any water produced was collected in a Dean-Stark trap. Once the reaction was complete, the solution was cooled and then quenched with saturated aquenous Na_2CO_3 (50 mL). The separated benzene layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford glycol acetal, which was directly used for the next step without purification. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.56 (s, 2H), 6.03 (brs, 1H), 5.70 (s, 1H), 4.11- 4.08 (m, 2H), 4.03–3.99 (m, 2H).

3-[2,6-dibromo-4-(1,3-dioxolan-2-yl)phenoxy]-*N*,*N*-dimethylpropylamine (8)



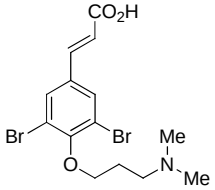
A mixture of glycol acetal, *N*,*N*-dimethyl-3-chloropropylamine (1.36 mL, 12 mmol), Cs_2CO_3 (8.14 g, 25mmol, 2.5 equiv), NaI (374 mg, 2.5mmol, 0.25 equiv), and CH_3CN (50 mL) was stirred at 80 °C for 12h. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, DCM/CH_3OH, 10:1) to afford the product **8** (3.31 g, 81% from **7**) as a colorless oil.
R_f = 0.71 (20% MeOH in DCM); IR (film): 2951, 2884, 1550, 1455, 1360, 1259, 1096, 1038, 988 cm^{-1}; ^1H NMR (500 MHz,$CDCl_3$) δ 7.61 (s, 2H), 5.72 (s, 1H), 4.11–4.00 (m, 6H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.35 (s, 6H), 2.13–2.07 (m, 2H);^{13}C NMR (150 MHz, $CDCl_3$) δ 153.86, 136.76, 130.97 (×2), 118.40 (×2), 101.87, 71.82 , 65.49 (×2), 56.42 , 45.32 (×2), 28.03; HRMS (EI+): calcd for $C_{14}H_{19}Br_2NO_3$: 406.9732, found: 406.9731.

3,5-dibromo-4-[3-(dimethylamino)propoxy]benzaldehyde (9)



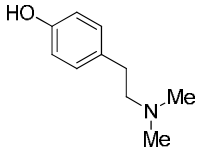
To a solution of **8** (819 mg, 2 mmol) in CH_3OH (20 ml) was added 3M HCl (20 mL), and the reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was then adjusted to pH 7 with saturated aqueous $NaHCO_3$. The reaction mixture was extracted with DCM (3 × 50 mL) and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, DCM/CH_3OH, 6:1) to afford the product **9** (708 mg, 97%) as a colorless solid.
MP.: 166–167 °C; R_f = 0.63 (20% MeOH in DCM); IR (KBr): 2952, 2680, 1688, 1547, 1469, 1366, 1257, 1185 cm^{-1}; ^1H NMR (500 MHz,$CDCl_3$) δ 9.86 (s, 1H), 8.03 (s, 2H), 4.19 (t, *J* = 5.5 Hz, 2H), 3.40 (t, *J* = 8.0 Hz, 2H), 2.87 (s, 6H), 2.54–2.48 (m, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 188.37, 157.22, 134.63, 134.03 (×2), 119.31 (×2), 70.21 , 55.78 , 43.33 (×2), 25.51; HRMS (EI+): calcd for $C_{12}H_{15}Br_2NO_2$: 362.9470, found: 362.9468.

(*E*)-3-[3,5-dibromo-4-(3-(dimethylamino)propoxy)phenyl]acrylic acid (3)[2]



A round-bottom flask with a reflux condenser was charged with benzaldehyde **9** (158 mg, 0.43 mmol), piperidine (8μL, 0.08 mmol) and toluene (1.5 mL). Then malonic acid (47 mg, 0.45 mmol) and triethylamine (78μL, 0.6 mmol) were added, and the reaction mixture was stirred at reflux. Two additional portion of malonic acid (47mg, 0.45 mmol) was added to the reaction mixture after stirring of 1 h and 3 h, respectively. After refluxing for 5 h, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, DCM/CH_3OH, 2:1) to provide the acid **3** (140 mg, 80%) as a white solid.
MP.: 198–199 °C; R_f = 0.35 (20% MeOH in DCM); IR (KBr): 3448 (br), 2951, 1636, 1559, 1456, 1410, 1260 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.80 (s, 2H), 7.38 (d, *J* = 16.2 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 4.16 (t, *J* = 5.4 Hz, 2H), 3.51 (t, *J* = 7.8 Hz, 2H), 2.96 (s, 6H), 2.34–2.30 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 173.22, 154.12, 138.72 , 136.20, 132.81 (×2), 126.92, 119.39 (×2), 71.28, 56.62, 43.54 (×2), 26.46.

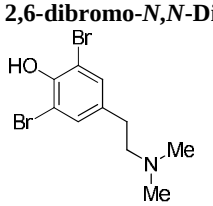
***N*,*N*-Dimethyltyramine (10)**



To a solution of tyramine hydrochloride **6** (1.736 g, 10 mmol) and $NaHCO_3$ (1.68 g, 20 mmol) in MeOH (50 mL)

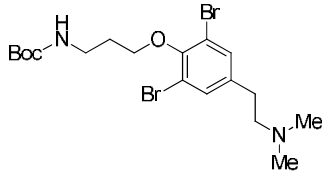
were added 37% aqueous formalin (3.0 mL, 40 mmol) and 10% Pd/C (1.15 g), and the mixture was stirred at room temperature for 5 h under hydrogen. The reaction mixture was filtered off through a plug of Celite with washing by MeOH and the combined filtrate was concentrated to provide *N*,*N*-dimethyltyramine **10** (1.62 g, 98%) as colorless crystals. The residue was used in the next reaction without further purification.
R_f = 0.3 (20% MeOH in DCM); IR (KBr): 2933, 2795, 1611, 1514, 1468, 1388, 1256, 1170, 866 cm^{-1}; ^1H NMR (400 MHz,$CDCl_3$) δ 9.24 (brs, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 8.4, 3.2 Hz, 2H), 2.76- 2.71 (m, 2H), 2.63- 2.59 (m, 2H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.44, 130.12, 129.53 (×2), 115.76 (×2), 61.44, 44.83(×2), 32.52; HRMS (EI+): calcd for $C_{10}H_{15}NO$: 165.1154, found: 165.1150.

2,6-dibromo-*N*,*N*-Dimethyltyramine (11)[3]



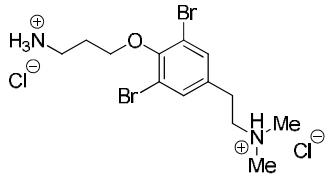
A solution of KBr (3.9 g) and Br_2 (790 μL) in water (13 mL) was added dropwise to a solution of **10** (1.16 g, 7 mmol) in a mixed solvent of methanol/water 1:1 (7 mL). After stirring for 0.5 h at room temperature, the reaction was quenched by adding saturated aqueous Na_2SO_3 (5 mL) and adjusted to pH 7 with saturated aqueous $NaHCO_3$. The solid precipitated was filtered off, washed with water and dried under reduced pressure. The residue was purified by column chromatography (SiO_2, DCM/CH_3OH, 7:1) to afford **11** (1.83 g, 81%) as a colorless solid.
MP.: 206- 208 °C; R_f = 0.5 (20% MeOH in DCM); IR (KBr): 3378 (br), 2957, 2689, 1476, 1312, 1151 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) δ 10.3 (brs, 1H) 7.49 (s, 2H), 3.24- 3.20 (m, 2H), 2.95- 2.91 (m, 2H), 2.74 (s, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 151.69, 133.75(×2), 131.27, 112.52 (×2), 59.47, 43.63 (×2), 30.12;

***N*-Boc-2,6-dibromo-*N*,*N*-Dimethyltyramine (12)[2]**



A mixture of **11** (1.0 g, 3.1 mmol), Boc-protected 3-bromo-propylamine (959 mg, 4.03 mmol), Cs_2CO_3 (2.52 g, 7.75mmol, 2.5 equiv), NaI (116 mg, 0.775mmol, 0.25 equiv), and CH_3CN (20 mL) was stirred in a sealed tube at 80 °C for 12h. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, DCM/CH_3OH, 10:1) to afford the product **12** (1.38 g, 93%) as a colorless solid.
MP.: 41–43 °C; R_f = 0.65 (20% MeOH in DCM); IR (KBr): 2974, 1708, 1458, 1253, 1173 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.45 (s, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 6.6 Hz, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 6H), 2.02–1.98 (m, 2H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, CD_3OD) δ 158.47, 152.79, 140.27, 134.09 (×2), 119.02 (×2), 79.94, 72.12, 61.52, 45.22 (×2), 38.64, 33.02, 31.28, 28.80 (×3).

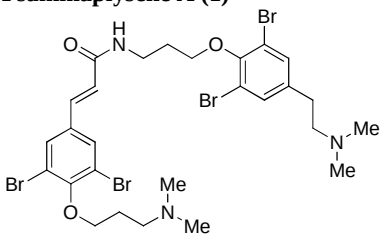
3-[2,6-Dibromo-4-(2-dimethylamino-ethyl)-phenoxy]-propylamine dihydrochloride (4)[2]



To a solution of **12** (167 mg, 0.348 mmol) in CH_3OH (10 ml) was added 3M HCl (3.5 mL), and the reaction mixture was stirred at the same temperature for 2 h. The solvent was removed under reduced pressure and the obtained solid **4** was showed by NMR as pure compound (155 mg, 98%) without purification.
MP.: 266–268 °C; R_f = 0.25 (33% MeOH in DCM); IR (KBr): 3422 (br), 2958, 1458, 1255, 1059 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.63 (s, 2H), 4.12 (t, *J* = 6.0 Hz, 2H), 3.38–3.35 (m, 2H), 3.31–3.28 (m, 2H), 3.06–3.03 (m,

2H), 2.93 (s, 6H), 2.24–2.20 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 152.43, 139.66, 134.26 (×2), 118.96 (×2), 71.58, 60.71, 44.70 (×2), 38.86, 32.18, 29.17.

Psammaplysene A (1)[2]



To a mixture of acid **3** (101 mg, 0.25 mmol) and amine **4** (108 mg, 0.24 mmol) in DCM was added TEA (100 μL, 0.74 mmol), DMAP (15 mg, 0.123 mmol), DIC (62 mg, 0.49 mmol), and the reaction mixture was stirred at room temperature for 10 h. The reaction mixture was extracted with DCM (3 × 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, DCM/CH_3OH, 3:1) to afford **1** (157 mg, 85%) as a white solid.

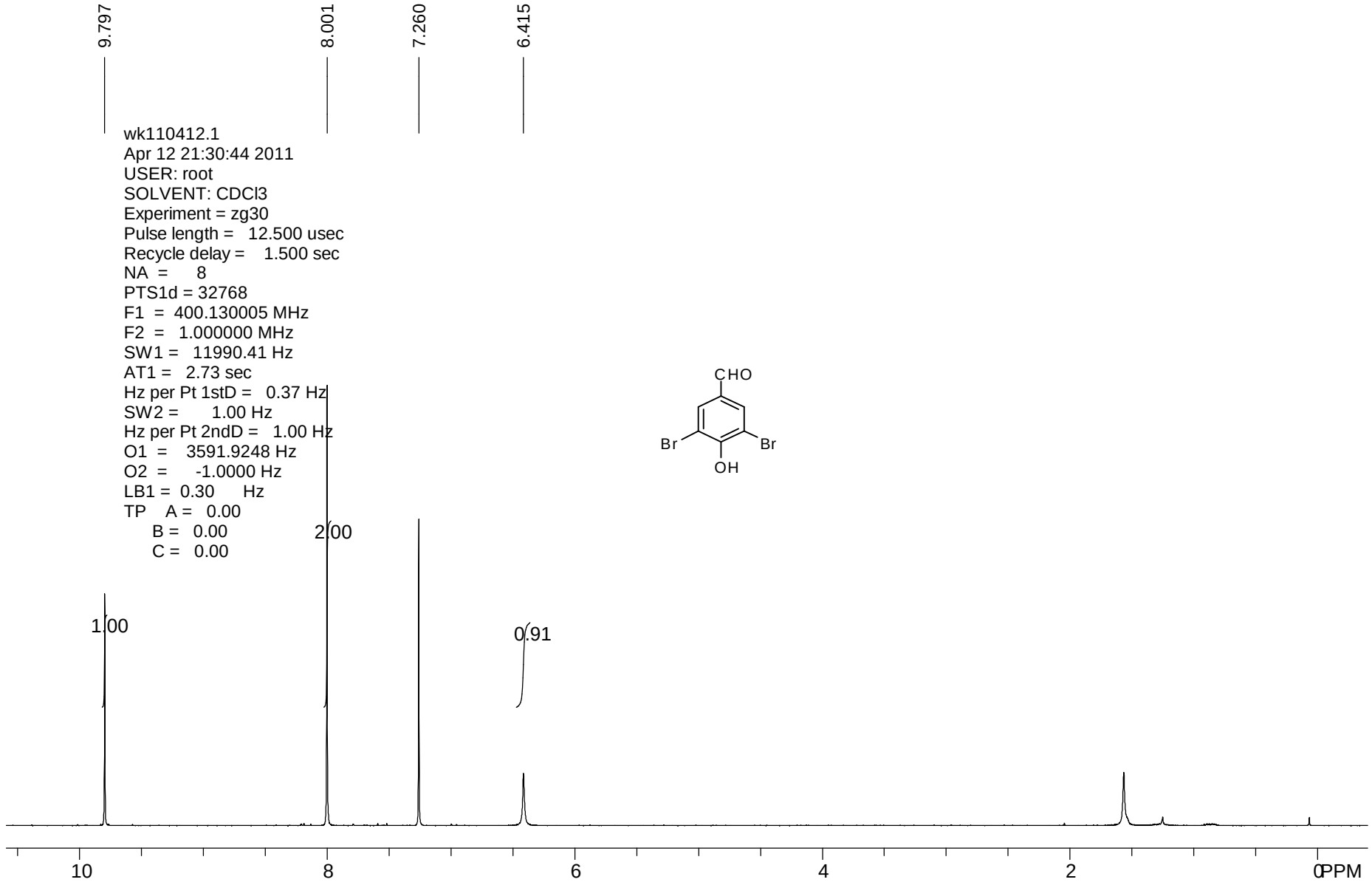
MP.: 115–116 °C; R_f=0.4 (20% MeOH in DCM); IR (KBr): 3285 (br), 2945, 2766, 1659, 1624, 1542, 1457, 1261, 1039, 974 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 7.76 (s, 2H), 7.44 (s, 2H), 7.37 (d, J = 15.6 Hz, 1H), 6.58 (d, J = 15.6 Hz, 1H), 4.06–4.03 (two overlapping triplets appearing as a multiplet, J = 6.4 Hz for both, 4H), 3.59 (t, J = 7.2 Hz, 2H), 2.74–2.65 (m, 4H), 2.55–2.51 (m, 2H), 2.32 (s, 6H), 2.29 (s, 6H), 2.16–2.02 (m, 4H); ^{13}C NMR (100 MHz, CD_3OD) δ 167.79, 155.18, 152.68, 140.42, 138.06 , 135.33, 134.08 (×2), 133.00 (×2), 124.01, 119.67 (×2), 119.00 (×2), 72.85, 72.07, 61.59, 57.39, 45.38 (×2), 45.29 (×2), 38.07, 33.14, 30.87, 28.86.

References

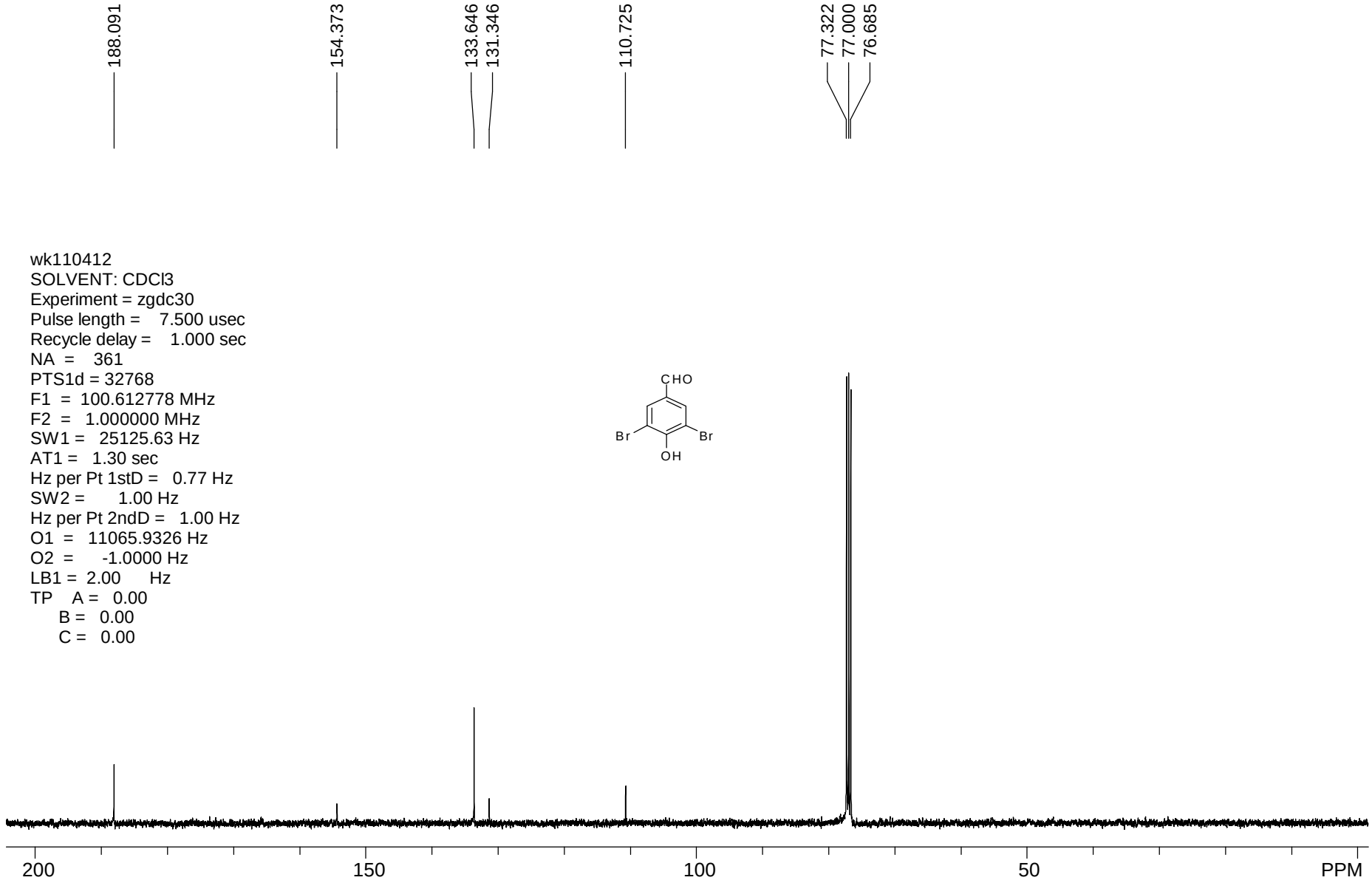
1. L. He, L. Zhang, X. Liu, X. Li, M. Zheng, H. Li, K. Yu, K. Chen, X. Shen, H. Jiang and H. Liu, *J. Med. Chem.*, **2009**, 52, 2465–2481.
2. S. N. Georgiades and J. Clardy, *Org. Lett.*, **2005**, 7, 4091–4094.
3. H. Kigoshi, K. Kanematsu, K. Yokota and D. Uemura, *Tetrahedron*, **2000**, 56, 9063–9070.

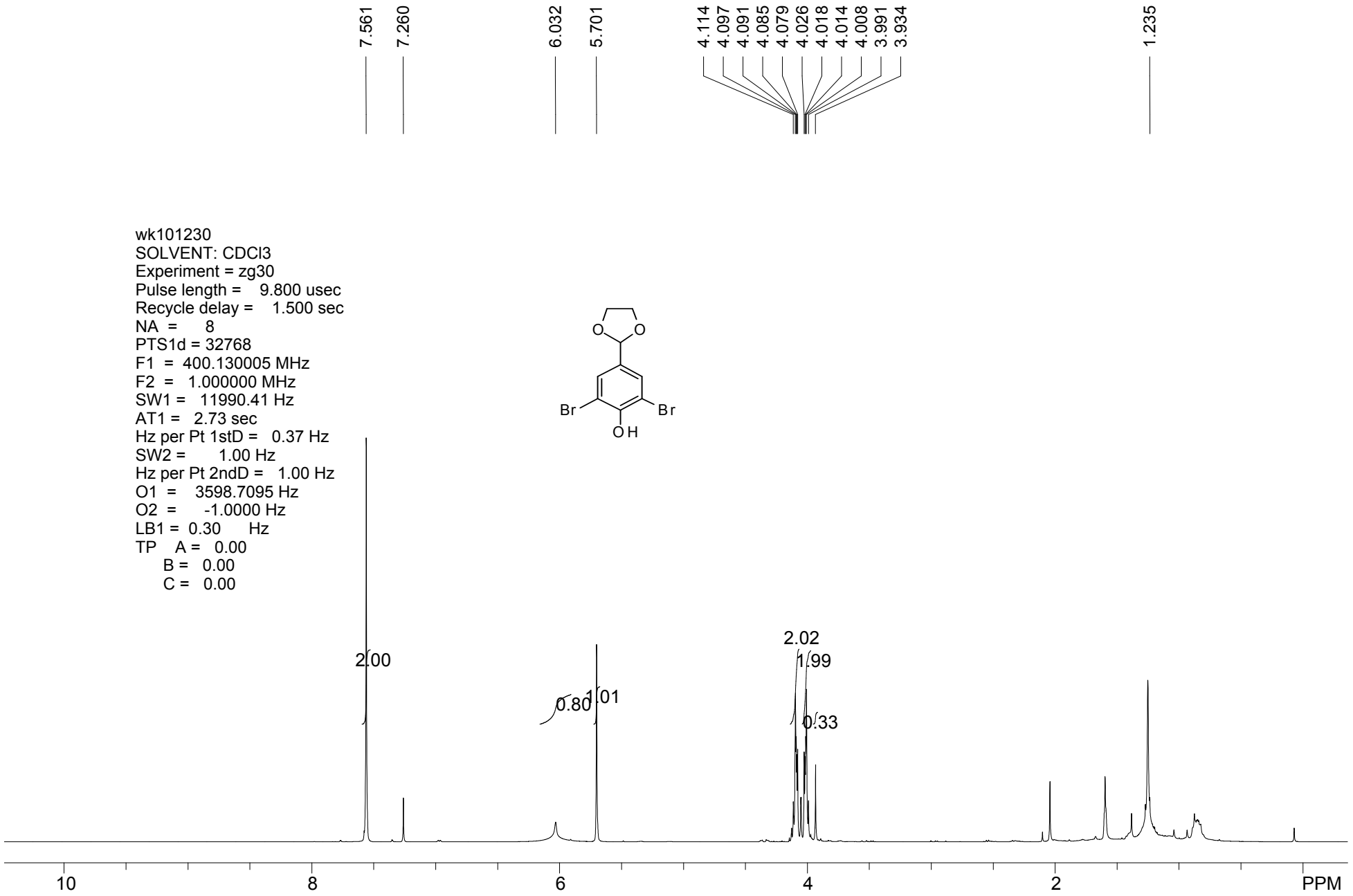
Copies of ^{1}H NMR and ^{13}C NMR Spectra of Compounds

3,5-dibromo-4-hydroxybenzaldehyde (7)



3,5-dibromo-4-hydroxybenzaldehyde (7)

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XJJ170711

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3-[2,6-dibromo-4-(1,3-dioxolan-2-yl)phenoxy]-N,N-dimethylpropylamine (8)

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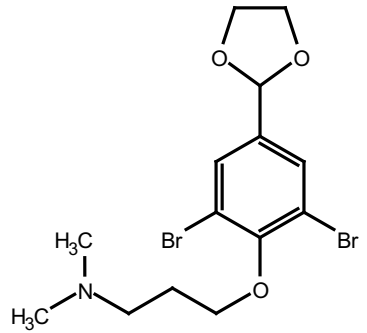

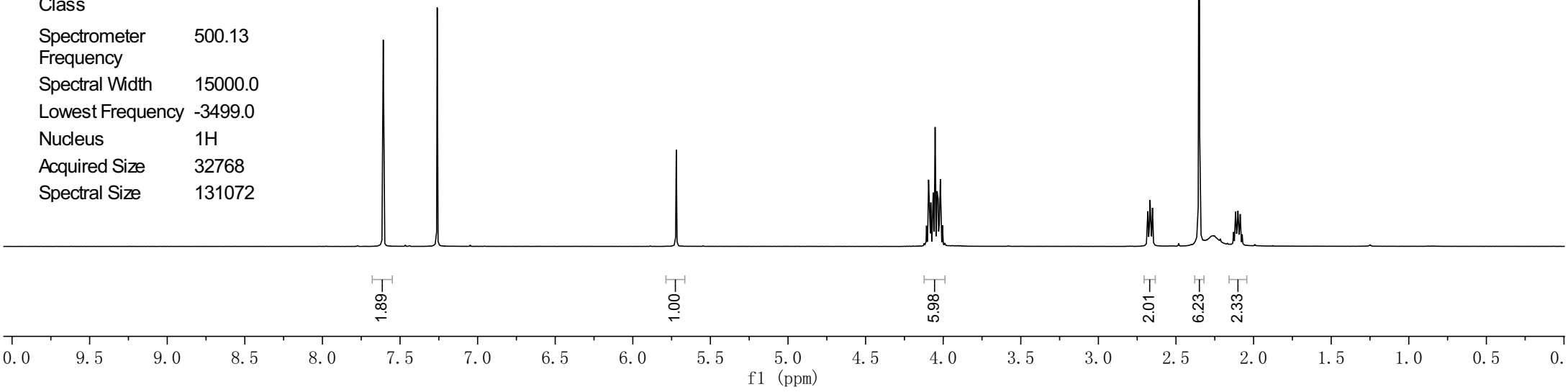

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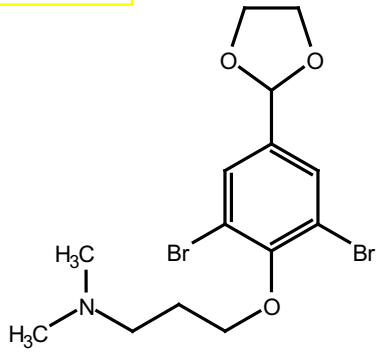
3-[2,6-dibromo-4-(1,3-dioxolan-2-yl)phenoxy]-N,N-dimethylpropylamine (8)



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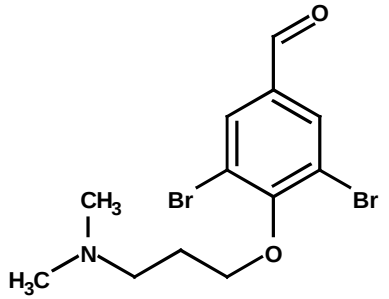
3,5-dibromo-4-[3-(dimethylamino)propoxy]benzaldehyde (9)



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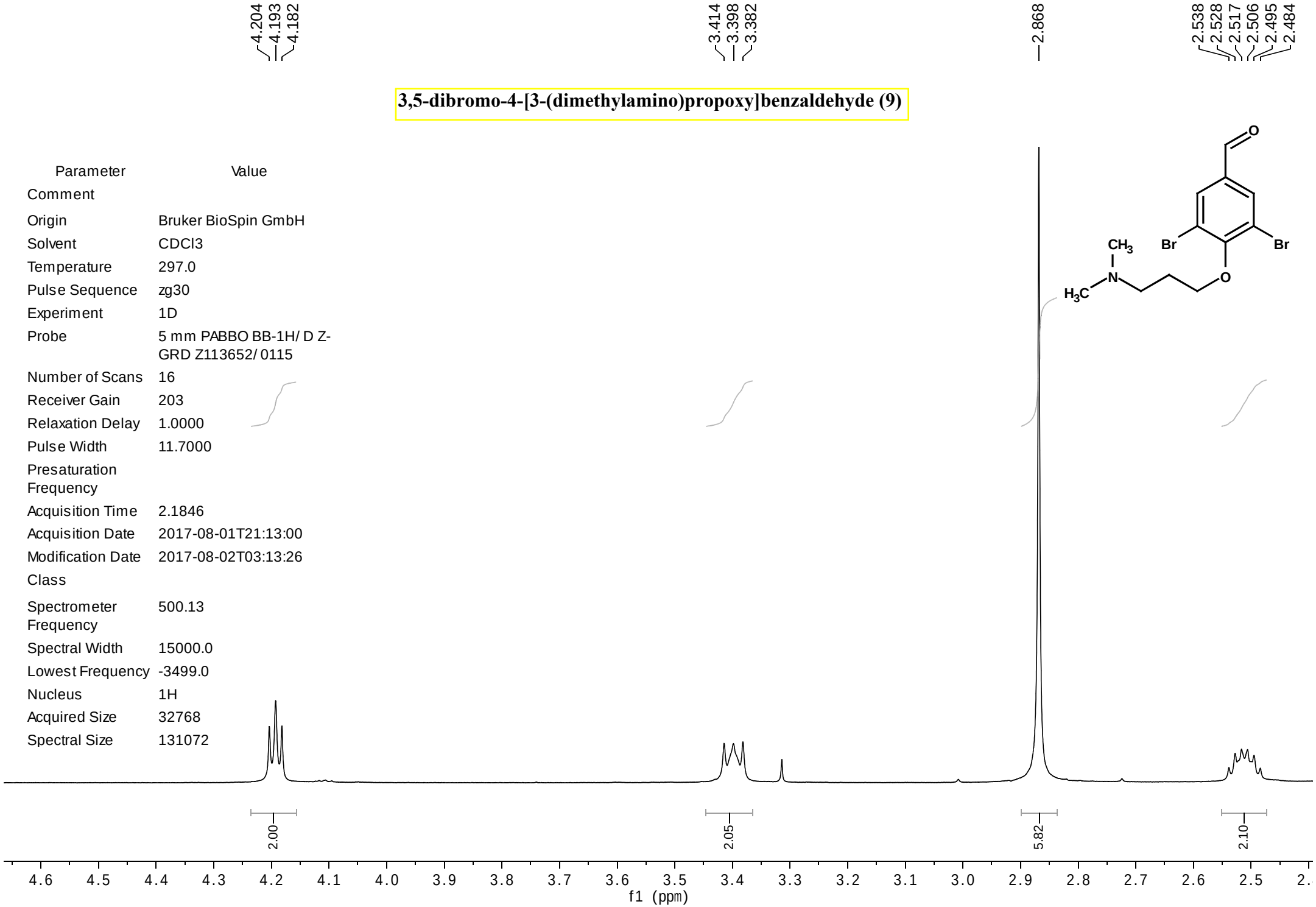
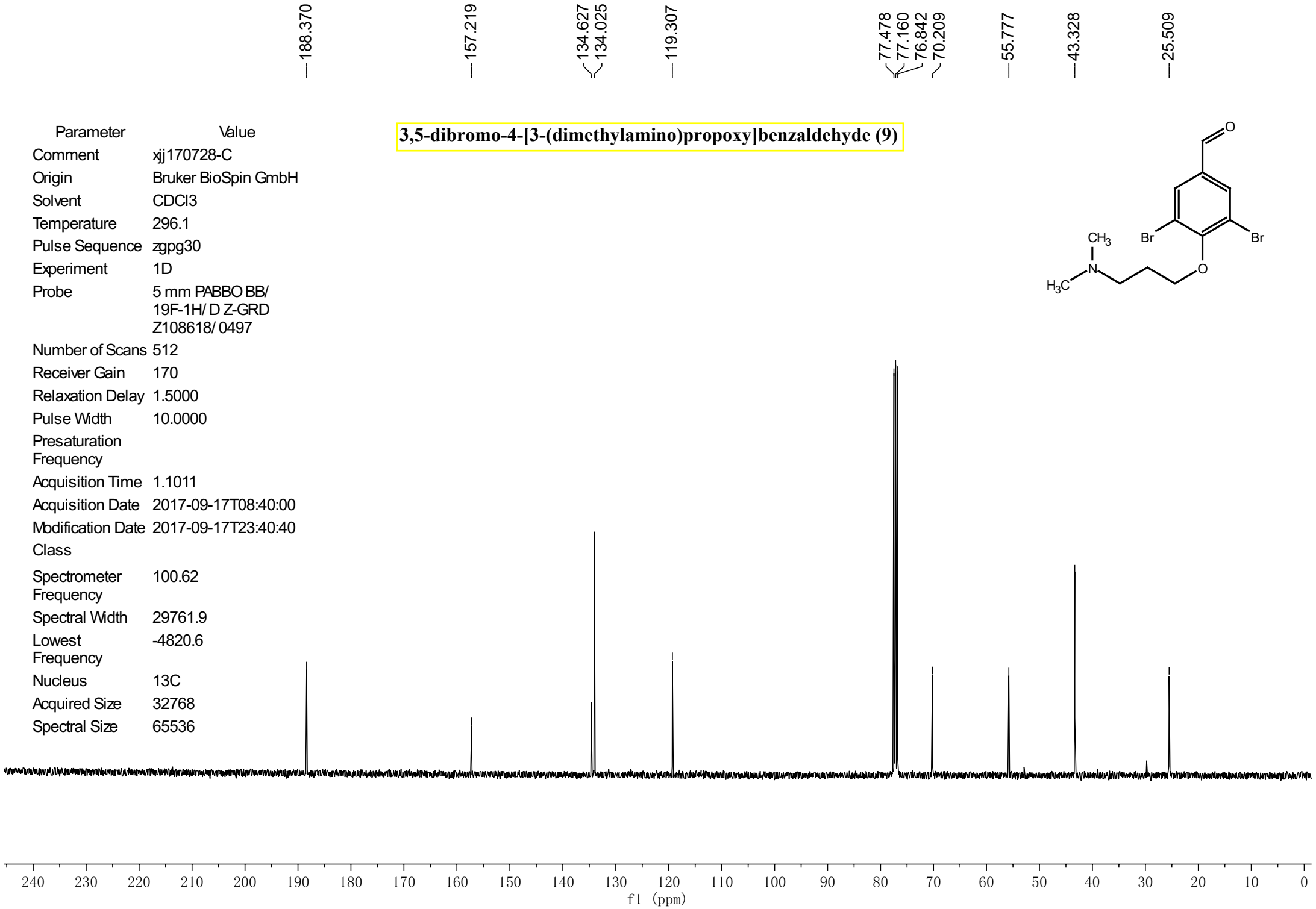
Lowest Frequency	-3499.0
Nucleus	1H
Acquired Size	32768
Spectral Size	131072


4.204
4.193
4.182
3.414
3.398
3.382
2.868
2.538
2.528
2.517
2.506
2.495
2.484
3,5-dibromo-4-[3-(dimethylamino)propoxy]benzaldehyde (9)
Parameter Value
Comment
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.0
Pulse Sequence zg30
Experiment 1D
Probe 5 mm PABBO BB-1H/ D Z-GRD Z113652/ 0115
Number of Scans 16
Receiver Gain 203
Relaxation Delay 1.0000
Pulse Width 11.7000
Presaturation Frequency
Acquisition Time 2.1846
Acquisition Date 2017-08-01T21:13:00
Modification Date 2017-08-02T03:13:26
Class
Spectrometer Frequency 500.13
Spectral Width 15000.0
Lowest Frequency -3499.0
Nucleus 1H
Acquired Size 32768
Spectral Size 131072
O
CH3
Br
Br
N
O
H3C
2.00
2.05
5.82
2.10
4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.
f1 (ppm)

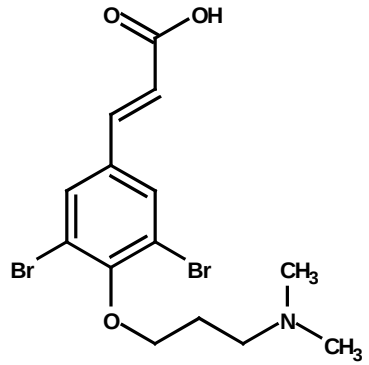

188.370
157.219
134.627
134.025
119.307
77.478
77.160
76.842
70.209
55.777
43.328
25.509
Parameter Value
Comment xjj170728-C
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 296.1
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0497
Number of Scans 512
Receiver Gain 170
Relaxation Delay 1.5000
Pulse Width 10.0000
Presaturation Frequency
Acquisition Time 1.1011
Acquisition Date 2017-09-17T08:40:00
Modification Date 2017-09-17T23:40:40
Class
Spectrometer Frequency 100.62
Spectral Width 29761.9
Lowest Frequency -4820.6
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
3,5-dibromo-4-[3-(dimethylamino)propoxy]benzaldehyde (9)
O
CH3
Br
Br
N
O
H3C
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

XJJ170717-1

7.800 | 7.389 | 7.362 | 6.484 | 6.458 | 4.836 | 4.166 | 4.157 | 4.148 | 3.520 | 3.507 | 3.494 | 3.312 | 3.310 | 3.307 | 2.962 | 2.344 | 2.335 | 2.325 | 2.318 | 2.308 | 2.299

(E)-3-[3,5-dibromo-4-(3-(dimethylamino)propoxy)phenyl]acrylic acid (3)

Parameter	Value
Comment	Zhejiang University Agilent 600 DD2 Onenmr Sample: XJJ170717-1 in Methanol
Origin	Varian
Solvent	cd3od
Temperature	27.0
Pulse Sequence	s2pul
Experiment	1D
Probe	onenmr
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7039
Acquisition Date	2017-07-21T17:15:58
Modification Date	2017-07-21T17:16:20
Spectrometer Frequency	599.77
Spectral Width	9615.4
Lowest Frequency	-1209.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536



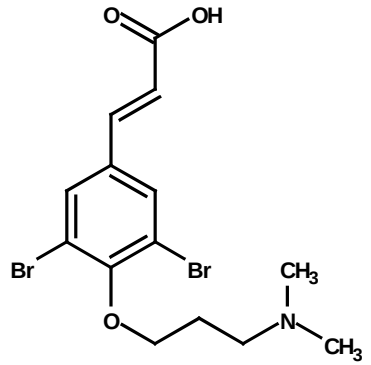
1.76 | 0.99 | 0.98 | 2.00 | 2.15 | 5.83 | 2.11

f1 (ppm)

4.166 4.157 4.148 3.520 3.507 3.494 3.312 3.310 3.307 2.962 2.344 2.335 2.325 2.318 2.308 2.299

(E)-3-[3,5-dibromo-4-(3-(dimethylamino)propoxy)phenyl]acrylic acid (3)

Parameter	Value
Comment	Zhejiang University Agilent 600 DD2 Onenmr Sample: XJJ170717-1 in Methanol
Origin	Varian
Solvent	cd3od
Temperature	27.0
Pulse Sequence	s2pul
Experiment	1D
Probe	onenmr
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7039
Acquisition Date	2017-07-21T17:15:58
Modification Date	2017-07-21T17:16:20
Spectrometer Frequency	599.77
Spectral Width	9615.4
Lowest Frequency	-1209.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

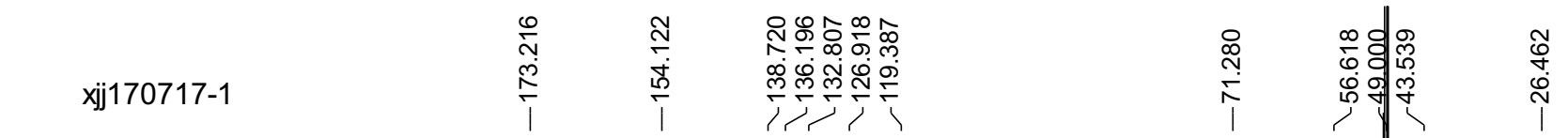


2.00 2.15 5.83 2.11

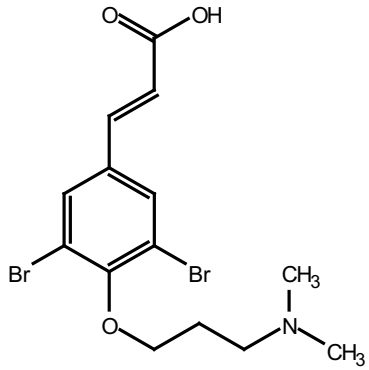
4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3

f1 (ppm)

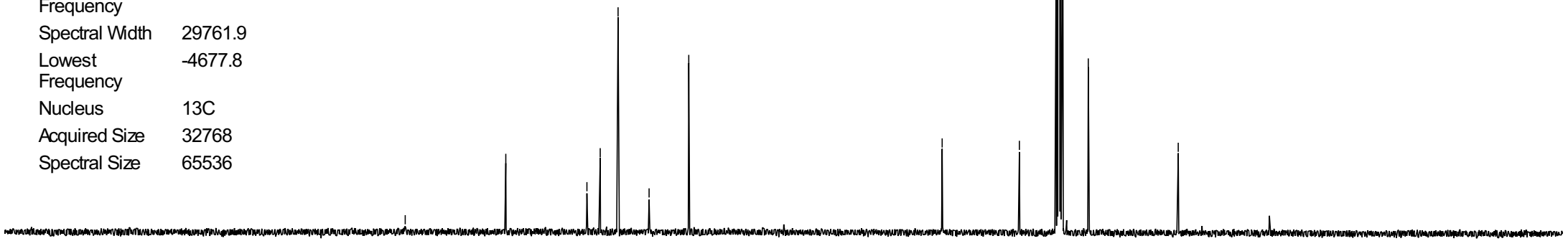
xjj170717-1

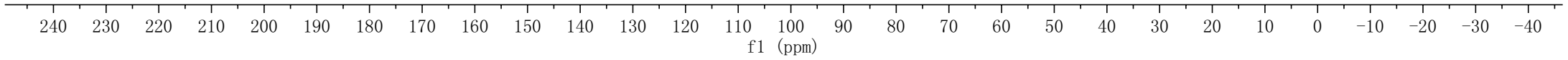


(E)-3-[3,5-dibromo-4-(3-(dimethylamino)propoxy)phenyl]acrylic acid (3)

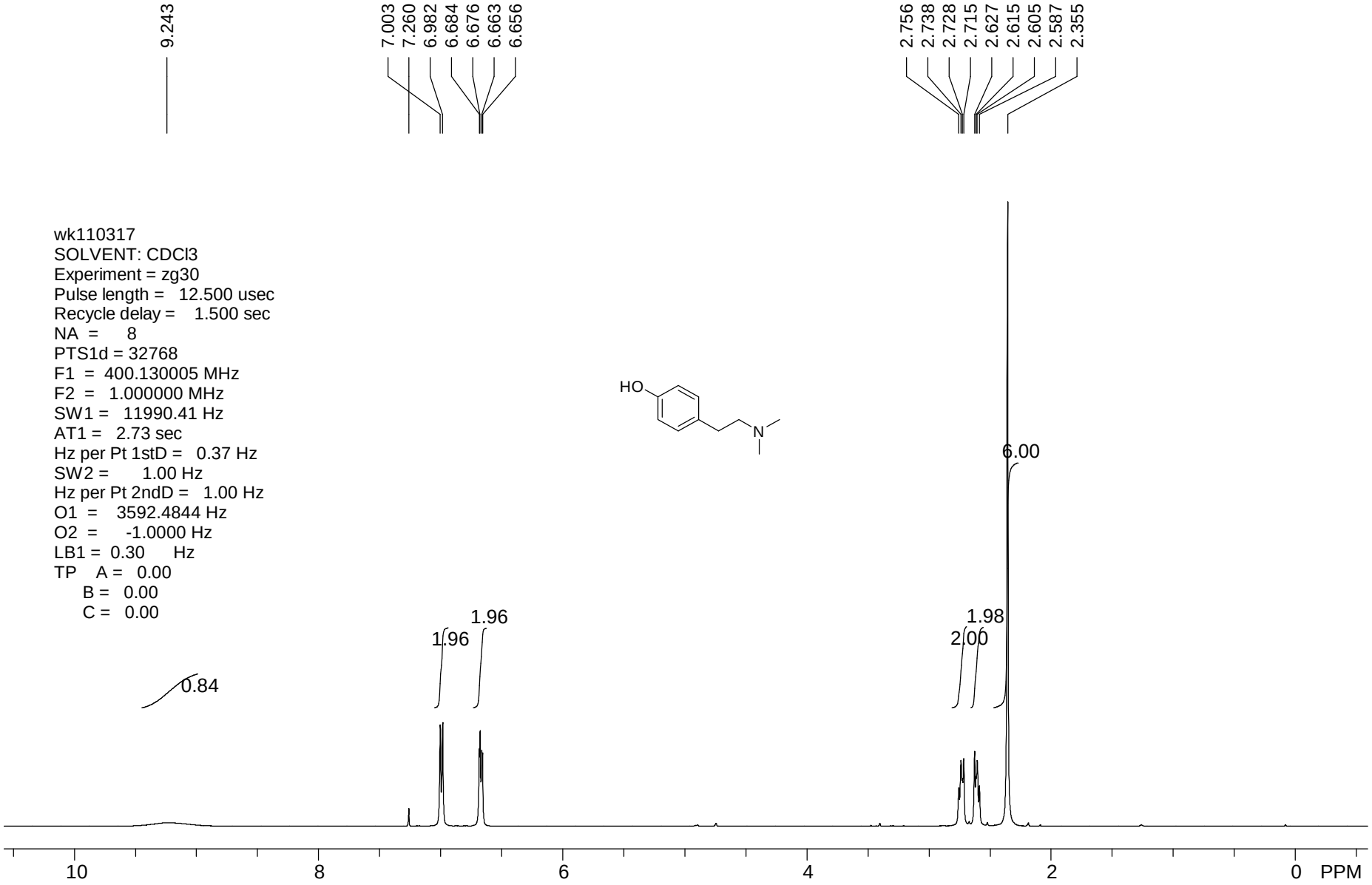


Parameter	Value
Comment	xjj170717-1c
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	293.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0497
Number of Scans	512
Receiver Gain	193
Relaxation Delay	1.5000
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	1.1011
Acquisition Date	2017-09-17T11:06:00
Modification Date	2017-09-18T02:06:06
Class	
Spectrometer Frequency	100.62
Spectral Width	29761.9
Lowest Frequency	-4677.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

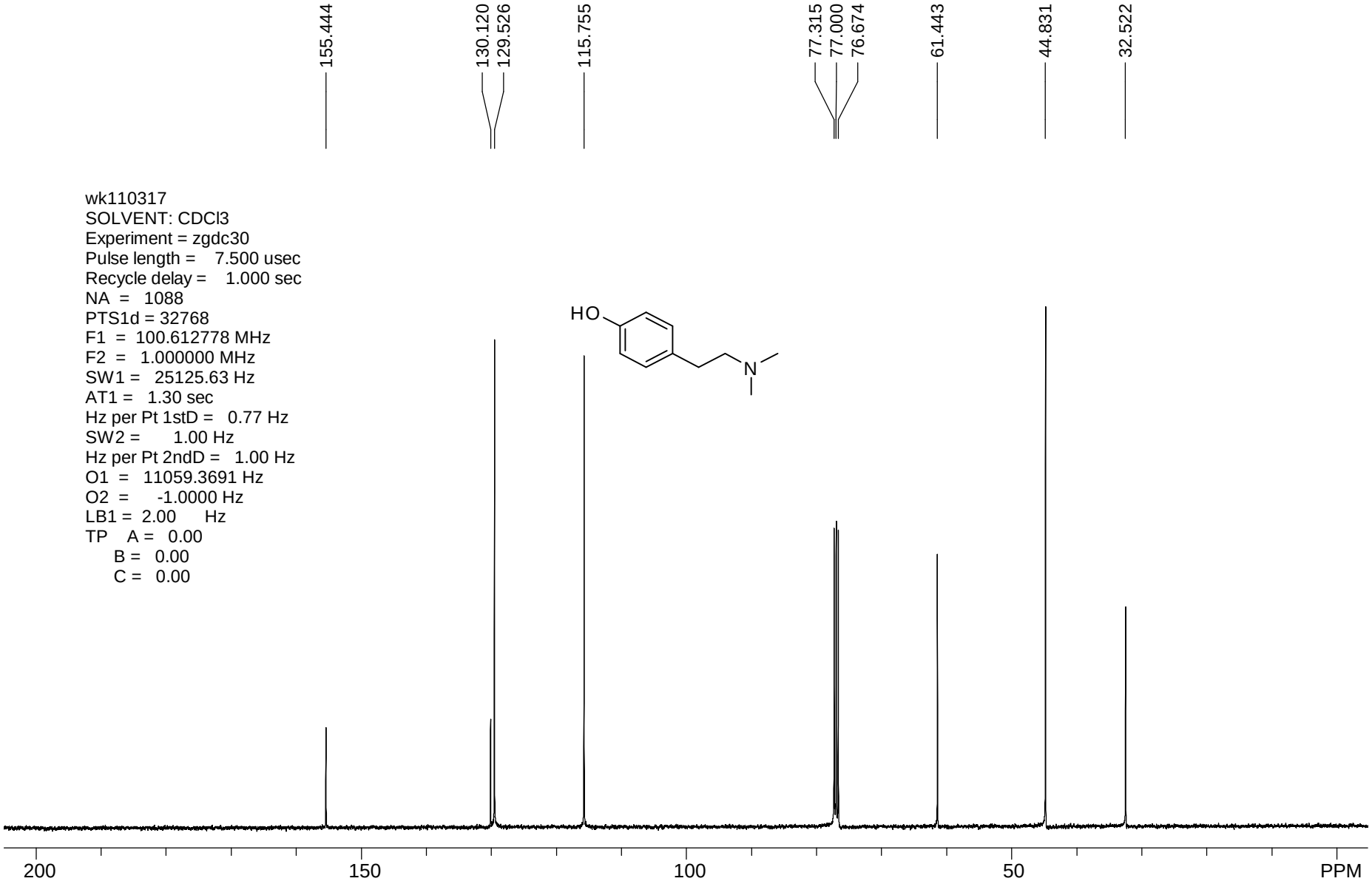




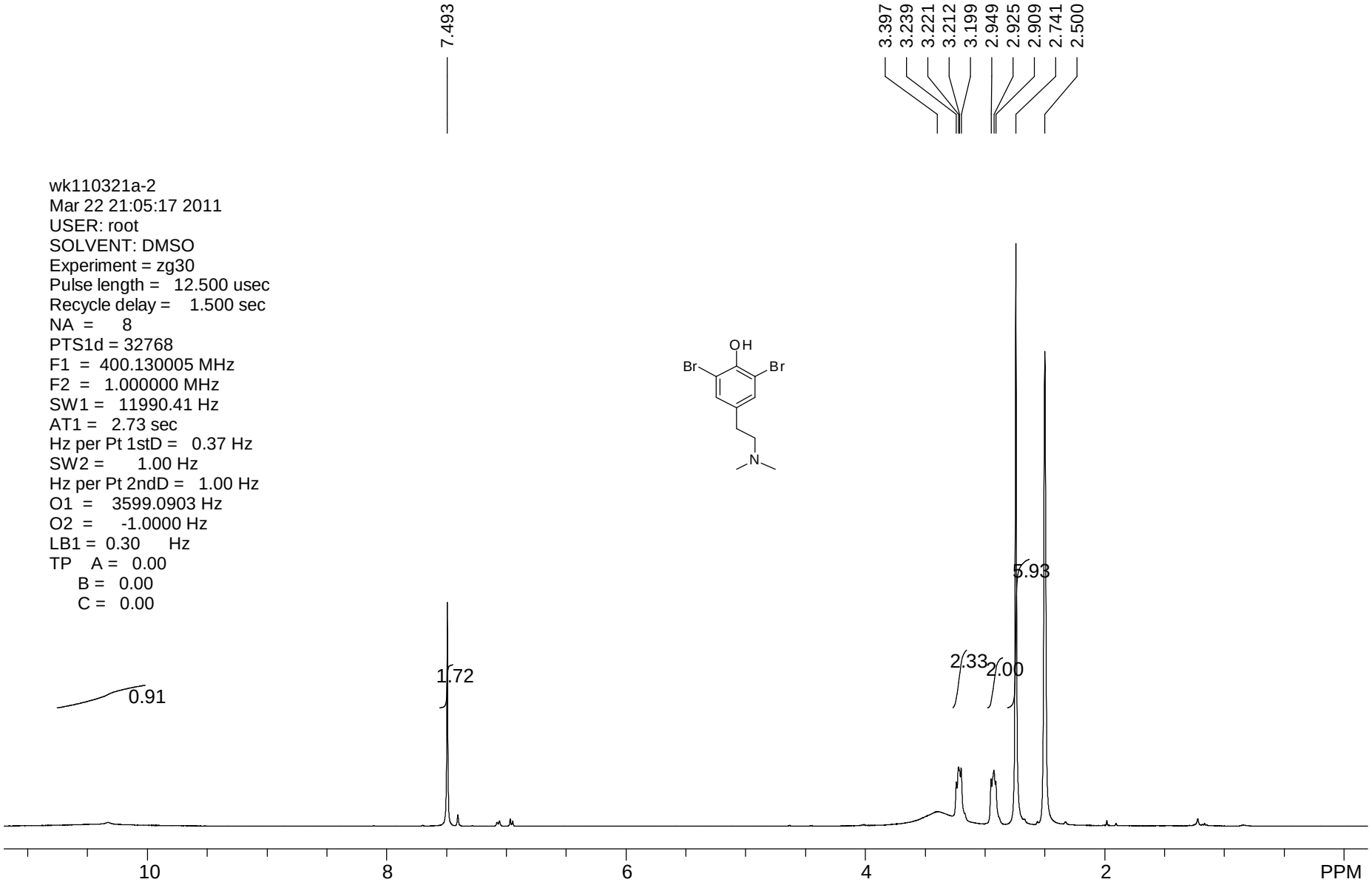
_N,N_-Dimethyltyramine (10)



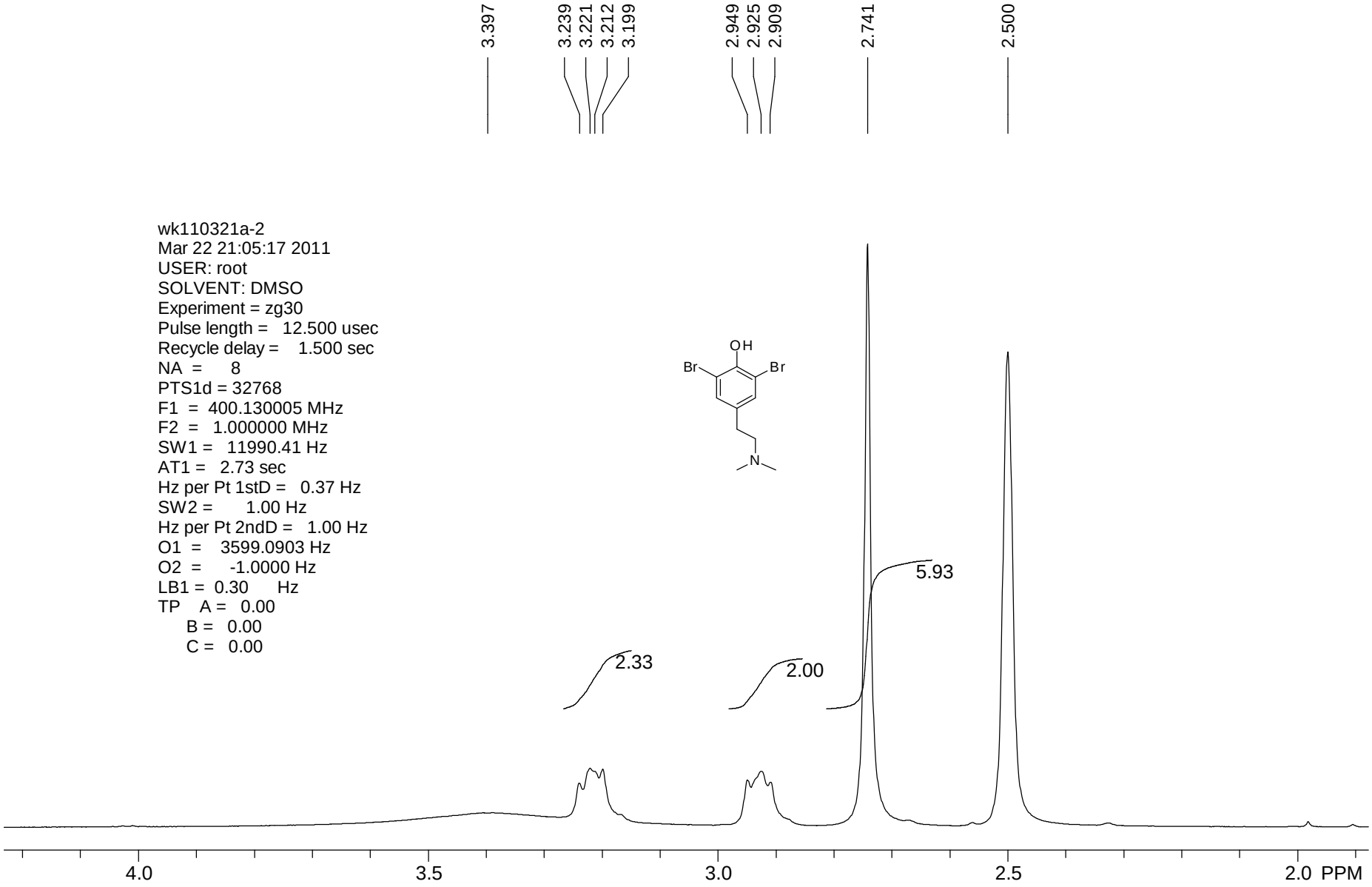
_N,N_-Dimethyltyramine (10)



2,6-dibromo-*N,N*-Dimethyltyramine (11)



2,6-dibromo-*N*,*N*-Dimethyltyramine (11)

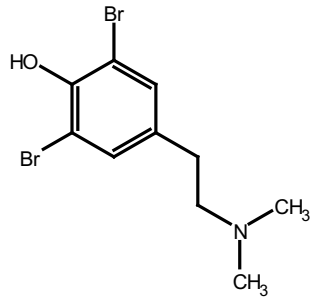


XJJ170721

151.691
133.753
131.272
112.520
59.471
49.213
49.000
48.787
43.630
30.122

Parameter	Value
Comment	xjj170721-C
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0497
Number of Scans	512
Receiver Gain	193
Relaxation Delay	1.5000
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	1.1011
Acquisition Date	2017-09-17T09:34:00
Modification Date	2017-09-18T00:34:42
Class	
Spectrometer Frequency	100.62
Spectral Width	29761.9
Lowest Frequency	-4677.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

2,6-dibromo-*N*,*N*-Dimethyltyramine (11)



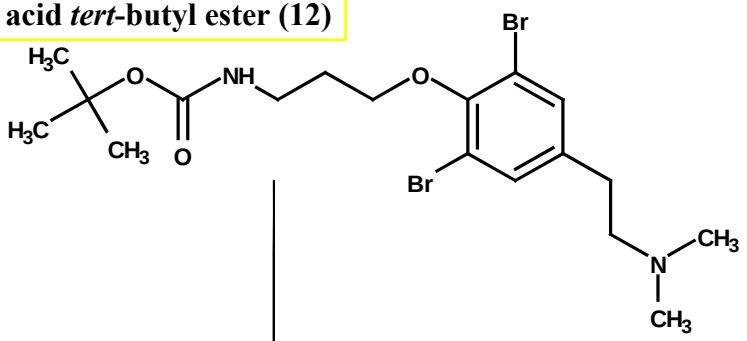
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

XJJ170407

7.451 4.825 4.015 4.005 3.994 3.324 3.313 3.302 3.300 3.297 2.748 2.736 2.722 2.583 2.569 2.557 2.311 2.010 1.999 1.988 1.430

{3-[2,6-Dibromo-4-(2-dimethylamino-ethyl)phenoxy]propyl}carbamic acid *tert*-butyl ester (12)

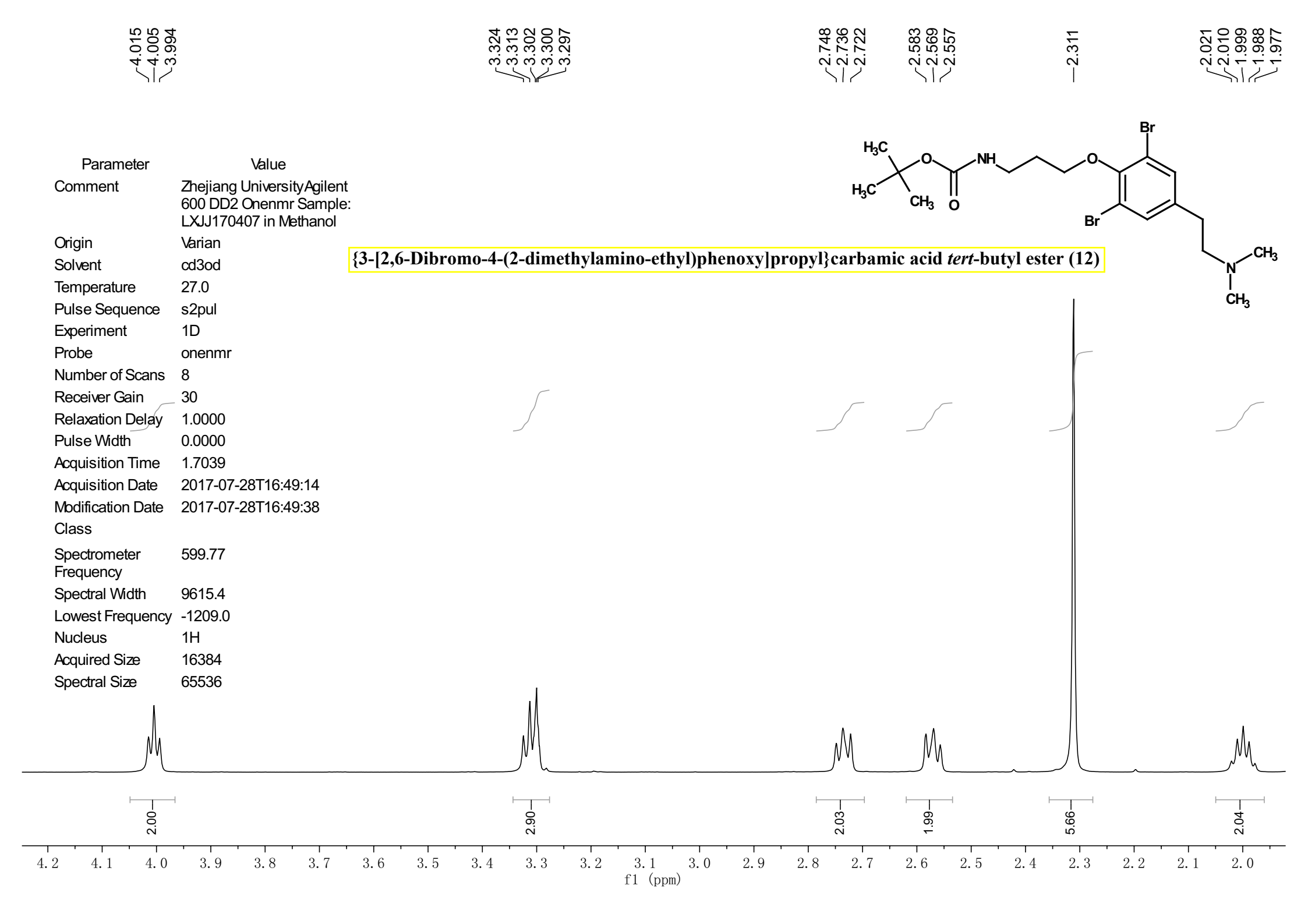


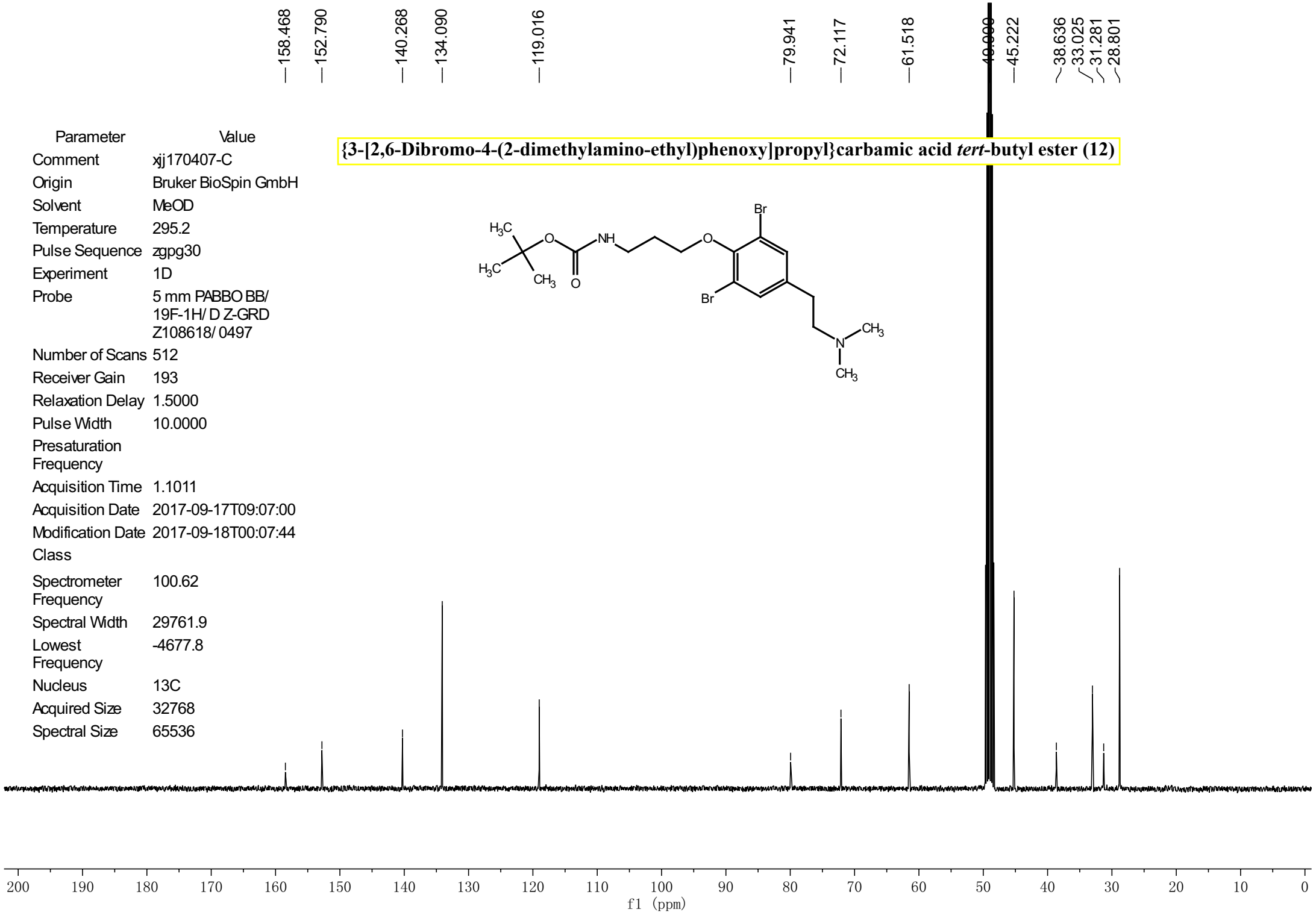
Parameter	Value
Comment	Zhejiang University Agilent 600 DD2 Onenmr Sample: LXJJ170407 in Methanol
Origin	Varian
Solvent	cd3od
Temperature	27.0
Pulse Sequence	s2pul
Experiment	1D
Probe	onenmr
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7039
Acquisition Date	2017-07-28T16:49:14
Modification Date	2017-07-28T16:49:38
Class	
Spectrometer Frequency	599.77
Spectral Width	9615.4
Lowest Frequency	-1209.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

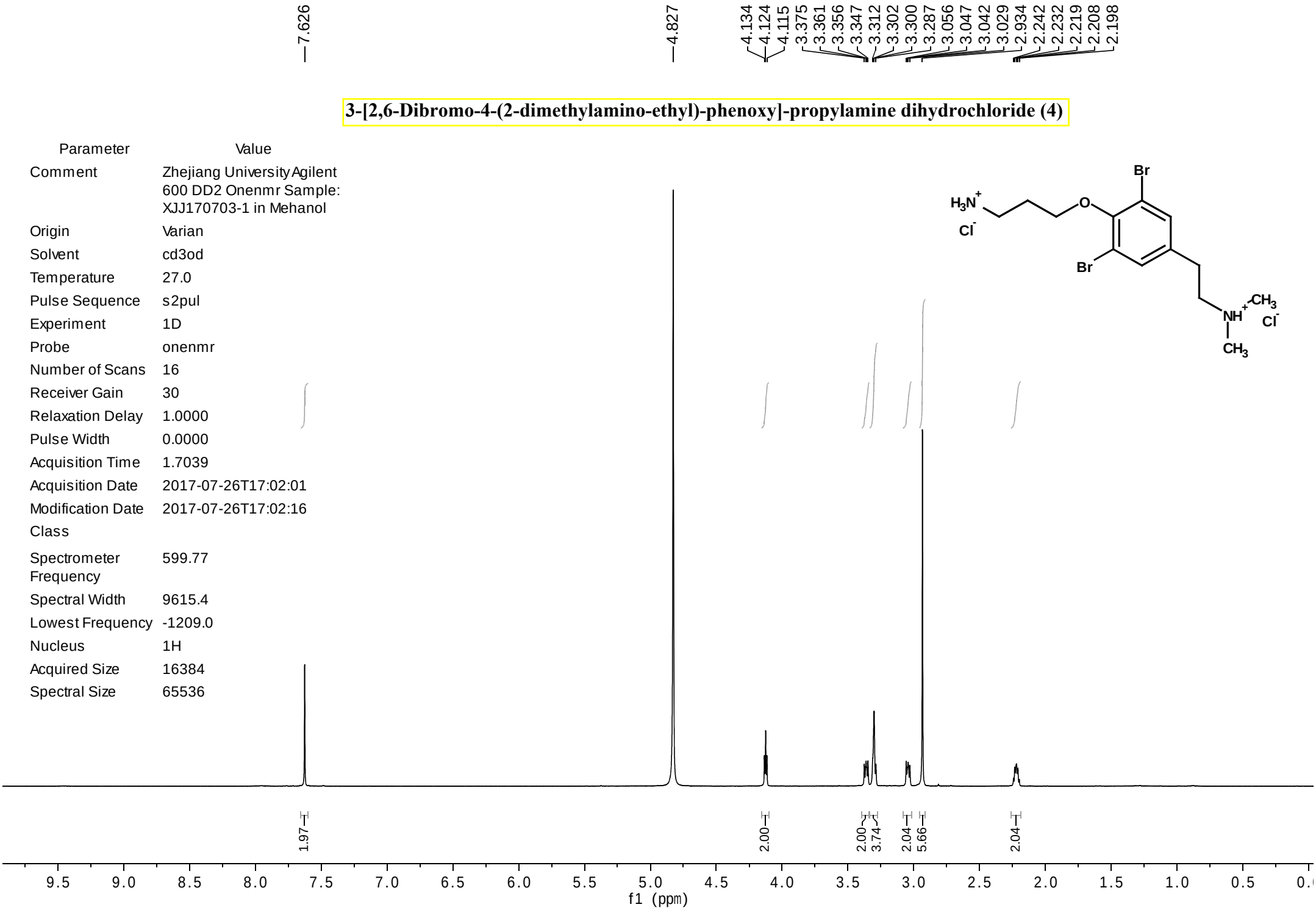
1.80 2.00 2.90 2.03 1.99 5.66 2.04 8.71

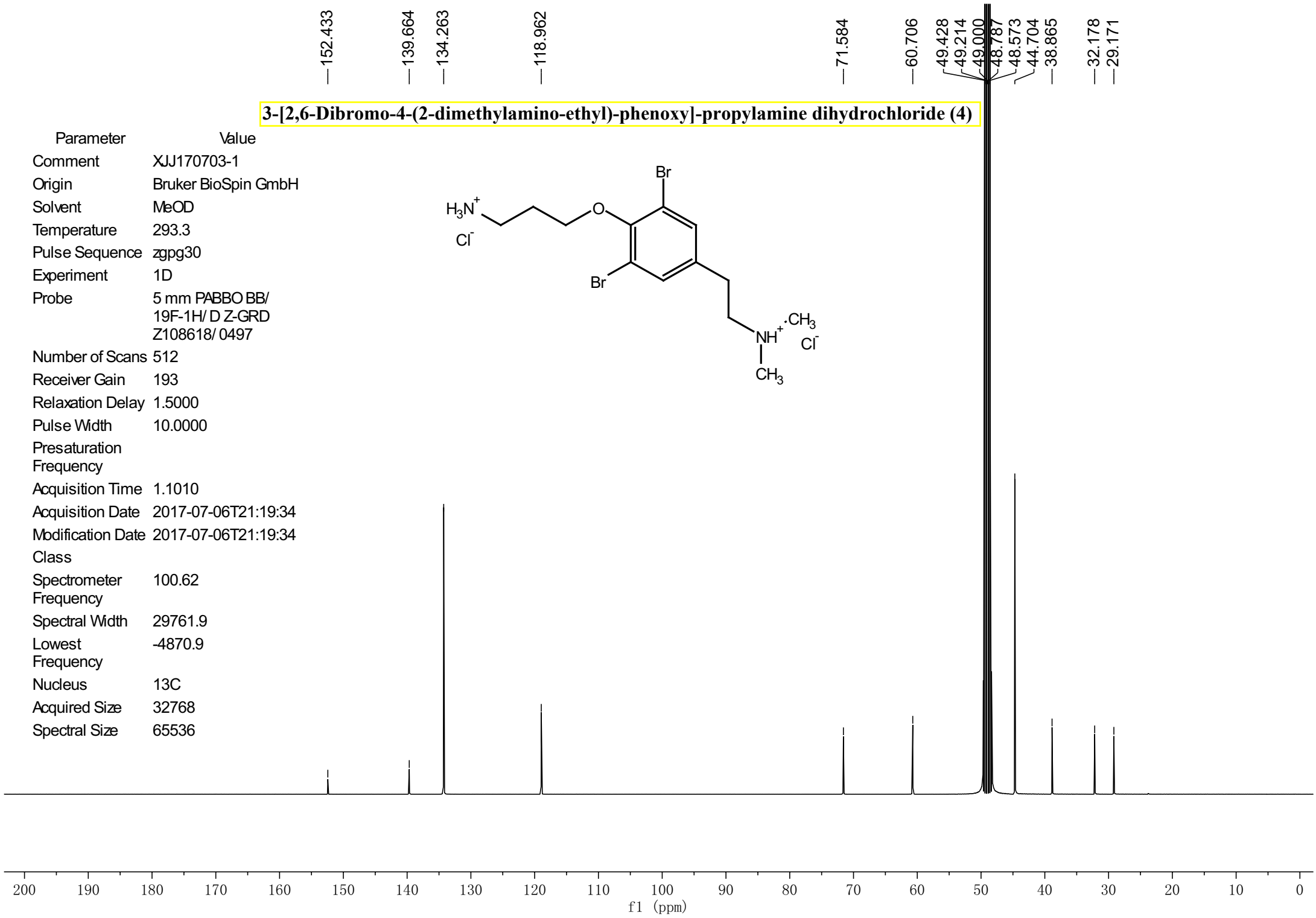
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

f1 (ppm)

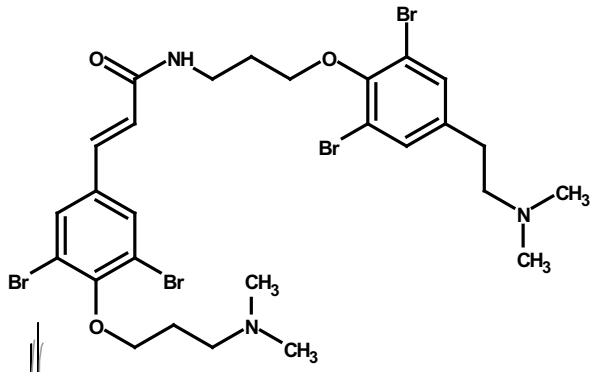

4.015
4.005
3.994
3.324
3.313
3.302
3.300
3.297
2.748
2.736
2.722
2.583
2.569
2.557
2.311
2.021
2.010
1.999
1.988
1.977
Parameter Value
Comment Zhejiang UniversityAgilent 600 DD2 Onenmr Sample: LXJJ170407 in Methanol
Origin Varian
Solvent cd3od
Temperature 27.0
Pulse Sequence s2pul
Experiment 1D
Probe onenmr
Number of Scans 8
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.7039
Acquisition Date 2017-07-28T16:49:14
Modification Date 2017-07-28T16:49:38
Class
Spectrometer Frequency 599.77
Spectral Width 9615.4
Lowest Frequency -1209.0
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
{3-[2,6-Dibromo-4-(2-dimethylamino-ethyl)phenoxy]propyl}carbamic acid tert-butyl ester (12)
H3C
O
NH
O
Br
Br
CH3
CH3
N
CH3
H3C
CH3
O
2.00
2.90
2.03
1.99
5.66
2.04
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
f1 (ppm)


158.468
152.790
140.268
134.090
119.016
79.941
72.117
61.518
40.000
45.222
38.636
33.025
31.281
28.801
{3-[2,6-Dibromo-4-(2-dimethylamino-ethyl)phenoxy]propyl}carbamic acid tert-butyl ester (12)
Parameter Value
Comment xjj170407-C
Origin Bruker BioSpin GmbH
Solvent MeOD
Temperature 295.2
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0497
Number of Scans 512
Receiver Gain 193
Relaxation Delay 1.5000
Pulse Width 10.0000
Presaturation Frequency
Acquisition Time 1.1011
Acquisition Date 2017-09-17T09:07:00
Modification Date 2017-09-18T00:07:44
Class
Spectrometer Frequency 100.62
Spectral Width 29761.9
Lowest Frequency -4677.8
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

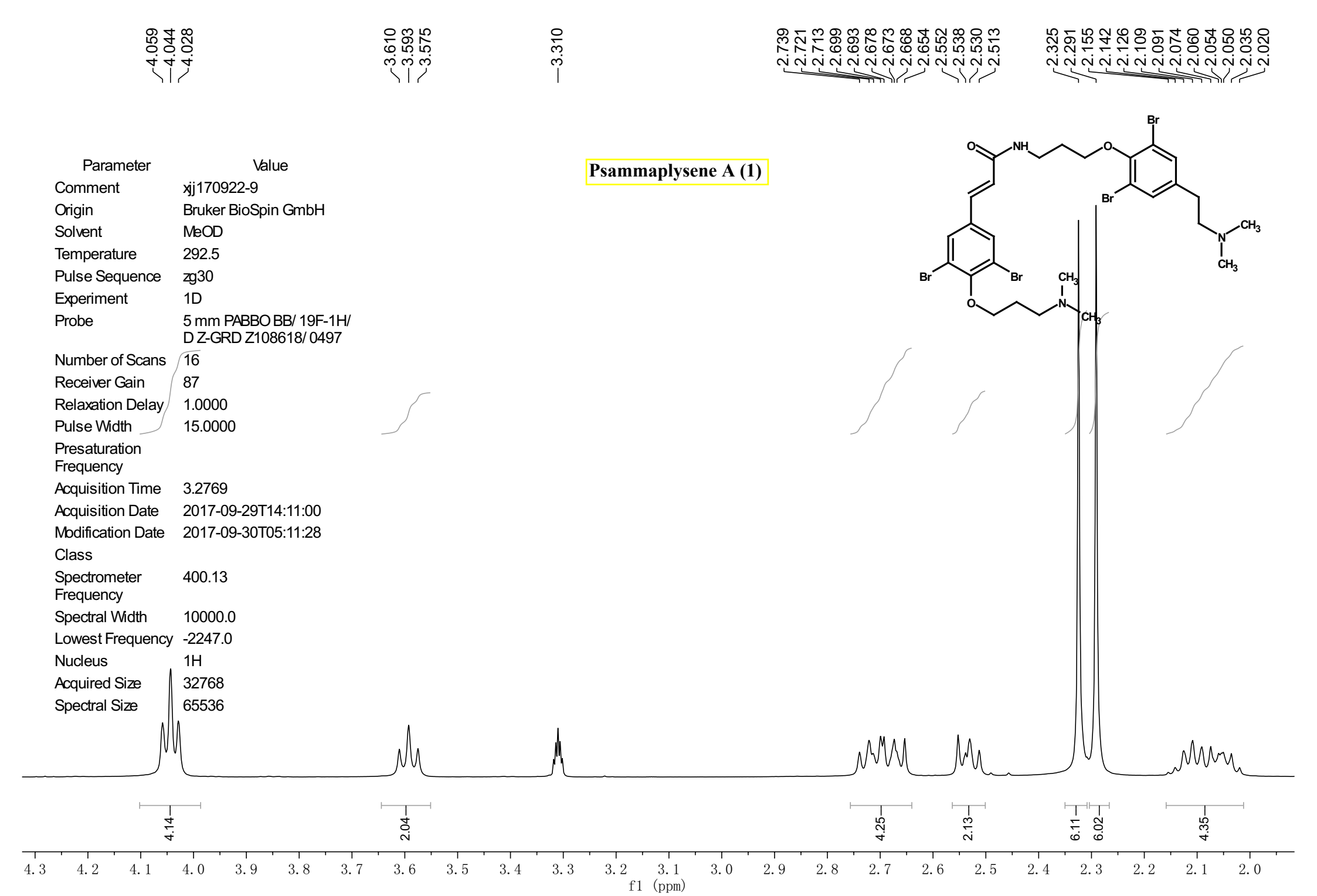

7.626
4.827
4.134
4.124
4.115
3.375
3.361
3.356
3.347
3.312
3.302
3.300
3.287
3.056
3.047
3.042
3.029
2.934
2.242
2.232
2.219
2.208
2.198
3-[2,6-Dibromo-4-(2-dimethylamino-ethyl)-phenoxy]-propylamine dihydrochloride (4)
Parameter Value
Comment Zhejiang University Agilent 600 DD2 Onenmr Sample: XJJ170703-1 in Mehanol
Origin Varian
Solvent cd3od
Temperature 27.0
Pulse Sequence s2pul
Experiment 1D
Probe onenmr
Number of Scans 16
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.7039
Acquisition Date 2017-07-26T17:02:01
Modification Date 2017-07-26T17:02:16
Class
Spectrometer Frequency 599.77
Spectral Width 9615.4
Lowest Frequency -1209.0
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
Br
H3N+
Cl-
O
Br
NH+
CH3
Cl-
CH3
1.97
2.00
2.00
3.74
2.04
5.66
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

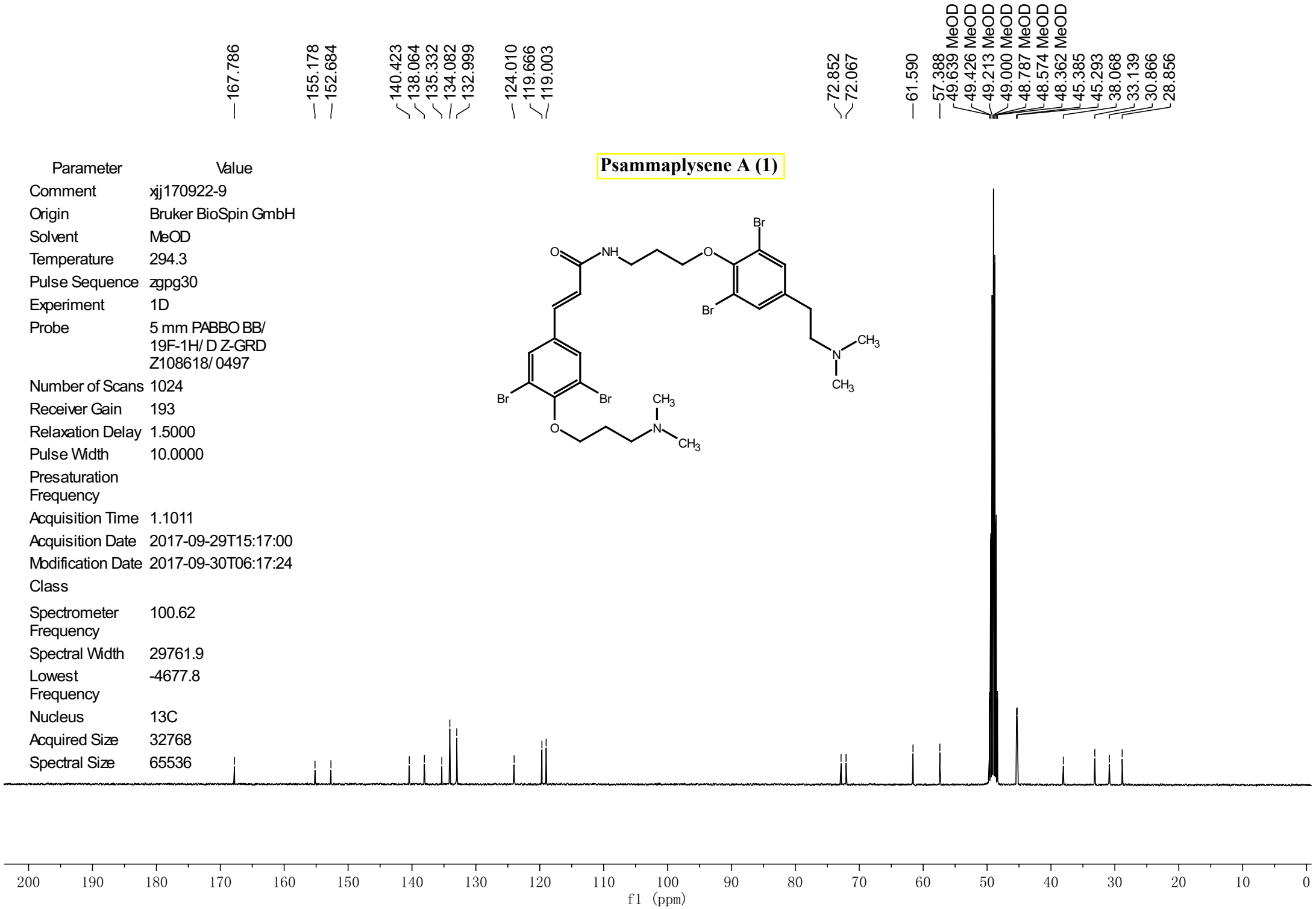

152.433
139.664
134.263
118.962
71.584
60.706
49.428
49.214
49.000
48.787
48.573
44.704
38.865
32.178
29.171
3-[2,6-Dibromo-4-(2-dimethylamino-ethyl)-phenoxy]-propylamine dihydrochloride (4)
Parameter Value
Comment XJJ170703-1
Origin Bruker BioSpin GmbH
Solvent MeOD
Temperature 293.3
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0497
Number of Scans 512
Receiver Gain 193
Relaxation Delay 1.5000
Pulse Width 10.0000
Presaturation Frequency
Acquisition Time 1.1010
Acquisition Date 2017-07-06T21:19:34
Modification Date 2017-07-06T21:19:34
Class
Spectrometer Frequency 100.62
Spectral Width 29761.9
Lowest Frequency -4870.9
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
Br
H3N+
Cl-
O
Br
NH+
CH3
Cl-
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Psammaplysene A (1)



Parameter	Value
Comment	xjj170922-9
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	292.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0497
Number of Scans	16
Receiver Gain	87
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	3.2769
Acquisition Date	2017-09-29T14:11:00
Modification Date	2017-09-30T05:11:28
Class	
Spectrometer Frequency	400.13
Spectral Width	10000.0
Lowest Frequency	-2247.0
Nucleus	1H
Acquired Size	32768
Spectral Size	65536


4.059
4.044
4.028
3.610
3.593
3.575
3.310
2.739
2.721
2.713
2.699
2.693
2.678
2.673
2.668
2.654
2.552
2.538
2.530
2.513
2.325
2.291
2.155
2.142
2.126
2.109
2.091
2.074
2.060
2.054
2.050
2.035
2.020
Parameter Value
Comment xjj170922-9
Origin Bruker BioSpin GmbH
Solvent MeOD
Temperature 292.5
Pulse Sequence zg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0497
Number of Scans 16
Receiver Gain 87
Relaxation Delay 1.0000
Pulse Width 15.0000
Presaturation Frequency
Acquisition Time 3.2769
Acquisition Date 2017-09-29T14:11:00
Modification Date 2017-09-30T05:11:28
Class
Spectrometer Frequency 400.13
Spectral Width 10000.0
Lowest Frequency -2247.0
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Psammaplysene A (1)
Br
O
NH
O
Br
Br
N
CH3
CH3
Br
Br
CH3
O
N
CH3
4.14
2.04
4.25
2.13
6.11
6.02
4.35
4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
f1 (ppm)


167.786
155.178
152.684
140.423
138.064
135.332
134.082
132.999
124.010
119.666
119.003
72.852
72.067
61.590
57.388
49.639 MeOD
49.426 MeOD
49.213 MeOD
49.000 MeOD
48.787 MeOD
48.574 MeOD
48.362 MeOD
45.385
45.293
38.068
33.139
30.866
28.856
Psammaplysene A (1)
Parameter Value
Comment xjj170922-9
Origin Bruker BioSpin GmbH
Solvent MeOD
Temperature 294.3
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0497
Number of Scans 1024
Receiver Gain 193
Relaxation Delay 1.5000
Pulse Width 10.0000
Presaturation Frequency
Acquisition Time 1.1011
Acquisition Date 2017-09-29T15:17:00
Modification Date 2017-09-30T06:17:24
Class
Spectrometer Frequency 100.62
Spectral Width 29761.9
Lowest Frequency -4677.8
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
Br
O
NH
O
Br
CH3
N
CH3
Br
Br
CH3
O
N
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)