A New Concise Strategy for Synthesis of Dibenzo[*b*,*f*]thiepins and Related Fused Symmetrical Thiepin Derivatives

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SUPPORTING INFORMATION

General information. All reactions were performed under nitrogen atmosphere unless otherwise stated. NMR spectra were recorded at 300.1 MHz for ^{1}H and 75.5 MHz for ^{13}C, respectively, using the residual solvent signal as reference. The IR spectra were acquired using a FT-IR instrument. Melting points were determined on a capillary melting point apparatus. Bis(phenylsulfonyl) sulfide was prepared following a literature procedure.[8] All other reagents and solvents were commercially available and used as received, except THF, which was distilled from sodium and benzophenone. Column chromatography was performed on silica gel (40–63 μm).

Bis(aryl) sulfide 7. To a solution of the acetal **5** (2.0 g, 6.9 mmol) in THF (40 mL) was added *n*-BuLi (2.5 M in hexanes, 3.4 mL, 8.5 mmol) dropwise at −78 °C. The resulting mixture was stirred at −78 °C for 30 min followed by addition of a solution of $(PhSO_2)_2S$ (1.10 g, 3.5 mmol) in THF (30 mL) during 15 min. The reaction mixture was allowed to warm to room temperature over 16 h. Workup as above, followed by column chromatography [*n*-heptane/EtOAc (1:2)] afforded the sulfide **7** (0.90 g, 58%) as a white solid; mp 133–136.5 °C; IR (neat) 2886, 1594, 1506, 1458, 1444, 1383, 1265, 1253, 1204, 1165, 1082, 1041, 1027, 989, 978, 951, 867, 854, 835, 756 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.07 (s, 2H), 6.79 (s, 2H), 6.11 (s, 2H), 4.13–3.93 (m, 8H), 3.76 (s, 6H), 3.61 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 149.5 (s), 148.5 (s), 130.8 (s), 125.6 (s), 115.6 (d), 109.8 (d), 100.5 (d), 64.9 (t), 55.6 (q), 55.6 (q); Anal. Calcd for $C_{22}H_{26}O_8S$: C, 58.65; H, 5.82. Found: C, 58.26; H, 5.73.

Dialdehyde 9. A solution of aq. $HClO_4$ (70%, 0.09 mL) in H_2O (3.0 mL) was added to a solution of compound **7** (0.30 g, 0.67 mmol) in acetone (10 mL) at room temperature. The resulting mixture was stirred at room temperature for 1 h. Workup as above, followed by trituration with Et_2O provided the dialdehyde **9** (230 mg, 95%) as a white solid; mp 202–204 °C; IR (neat) 2860, 1665, 1585, 1497, 1380, 1260, 1214, 1149, 1038, 868, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.36 (s, 2H), 7.46 (s, 2H), 6.67 (s, 2H), 3.96 (s, 6H), 3.77 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 190.0 (d), 154.5 (s), 149.3 (s), 133.0 (s), 129.0 (s), 114.7 (d), 111.9 (d), 56.5 (q), 56.5 (q); *m/z* (ESI+) 363 $[M + H]^+$. Anal. Calcd for $C_{18}H_{18}O_6S$: C, 59.66; H, 5.01. Found: C, 59.82; H, 5.14.

2,3,7,8-Tetramethoxydibenzo[*b,f*]thiepin (10). The procedure above was used, employing the dialdehyde **9** (181 mg, 0.50 mmol) as the substrate. Purification of the crude product by column chromatography [*n*-heptane/EtOAc (1:2)] yielded the thiepin **10** (132 mg, 80%) as an off-white solid; mp 197–199 °C; IR (neat) 2921, 1590, 1500, 1465, 1453, 1440, 1431, 1348, 1237, 1197, 1176, 1163, 1150, 1046, 1029, 961, 856, 800, 768 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.98 (s, 2H), 6.93 (s, 2H), 6.73 (s, 2H), 3.89 (s, 6H), 3.85 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 150.1 (s),

149.2 (s), 133.4 (s), 132.6 (d), 125.8 (s), 115.2 (d), 111.8 (d), 56.2 (q), 56.2 (q). HRMS (FAB+) *m/z* 330.0925 [M^+], $C_{18}H_{18}O_4S$ requires 330.0926.

Diacetal 13. To a solution of anhydrous diisopropylamine (0.52 mL, 3.7 mmol) in THF (10 mL) was added *t*-BuLi (1.7 M in pentane, 2.2 mL, 3.7 mmol) at −78 °C. After stirring at −78 °C for 30 min a solution of the acetal **12**[16] (1.0 g, 3.0 mmol) in THF (7 mL) was added during 15 min. After stirring for 40 min at −78 °C, $(SO_2Ph)_2S$ (0.50 g, 1.59 mmol) in THF (5 mL) was added during 10 min at −78 °C, and the reaction mixture was thereafter allowed to warm to room temperature over 16 h. A solution of sat. NH_4Cl (20 mL) was added, and the resulting mixture was extracted with Et_2O (2 × 30 mL). The combined organic phases were washed with water (2 × 30 mL), brine (30 mL) and dried over Na_2SO_4. Evaporation of the solvents in vacuo and trituration of the residue with MeOH gave compound **13** (810 mg, 78%) as an off white solid; mp 203–206.5 °C; IR (neat) 1448, 1439, 1369, 1220, 1188, 1136, 1086, 1064, 975, 956, 750, 727 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.09 (d, J = 8.5 Hz, 2H), 7.92–7.90 (m, 4H), 7.71–7.55 (m, 8H), 7.44–7.39 (m, 2H), 7.29–7.23 (m, 2H), 3.95–3.93 (m, 4H), 3.65–3.60 (m, 4H); ^{13}C NMR (DMSO-d_6) δ 137.0 (s), 137.0 (s), 134.8 (d), 129.7 (d), 129.4 (s), 127.0 (s), 126.7 (d), 126.1 (d), 125.1 (s), 123.8 (d), 121.4 (d), 114.4 (d), 97.9 (d), 64.7 (t). Anal. Calcd for $C_{34}H_{28}N_2O_8S_3$: C, 59.29; H, 4.10; N, 4.07. Found: C, 59.11; H, 4.15; N, 4.02.

Dialdehyde 14. A similar procedure as described for compound **8** was used, starting with the diacetal **13** (0.50 g, 0.73 mmol) in 1,4-dioxane (7 mL), and aq. $HClO_4$ (70%, 0.12 mL) in H_2O (2 mL). The reaction mixture was stirred at room temperature for 8 h. Workup as for **8**, and subsequent recrystallization from CH_3CN gave the dialdehyde **14** (430 mg, 98%) as an off white solid; mp 211–213 °C; IR (neat) 1665, 1449, 1432, 1386, 1378, 1193, 1159, 1140, 1086, 972, 847, 754, 748, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.77 (s, 2H), 8.24–8.19 (m, 4H), 7.91–7.88 (m, 4H), 7.58–7.53 (m, 1H), 7.49–7.35 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 185.9 (d), 138.8 (s), 137.8 (s), 137.6 (s), 135.0 (d), 129.7 (d), 127.5 (d), 127.2 (d), 126.3 (s), 126.0 (d), 124.2 (s), 122.5 (d), 114.8 (d). HRMS (FAB+) *m/z* 601.0570 [M + H]$^+$, $C_{30}H_{20}N_2O_6S_3$ + H requires 601.0562.

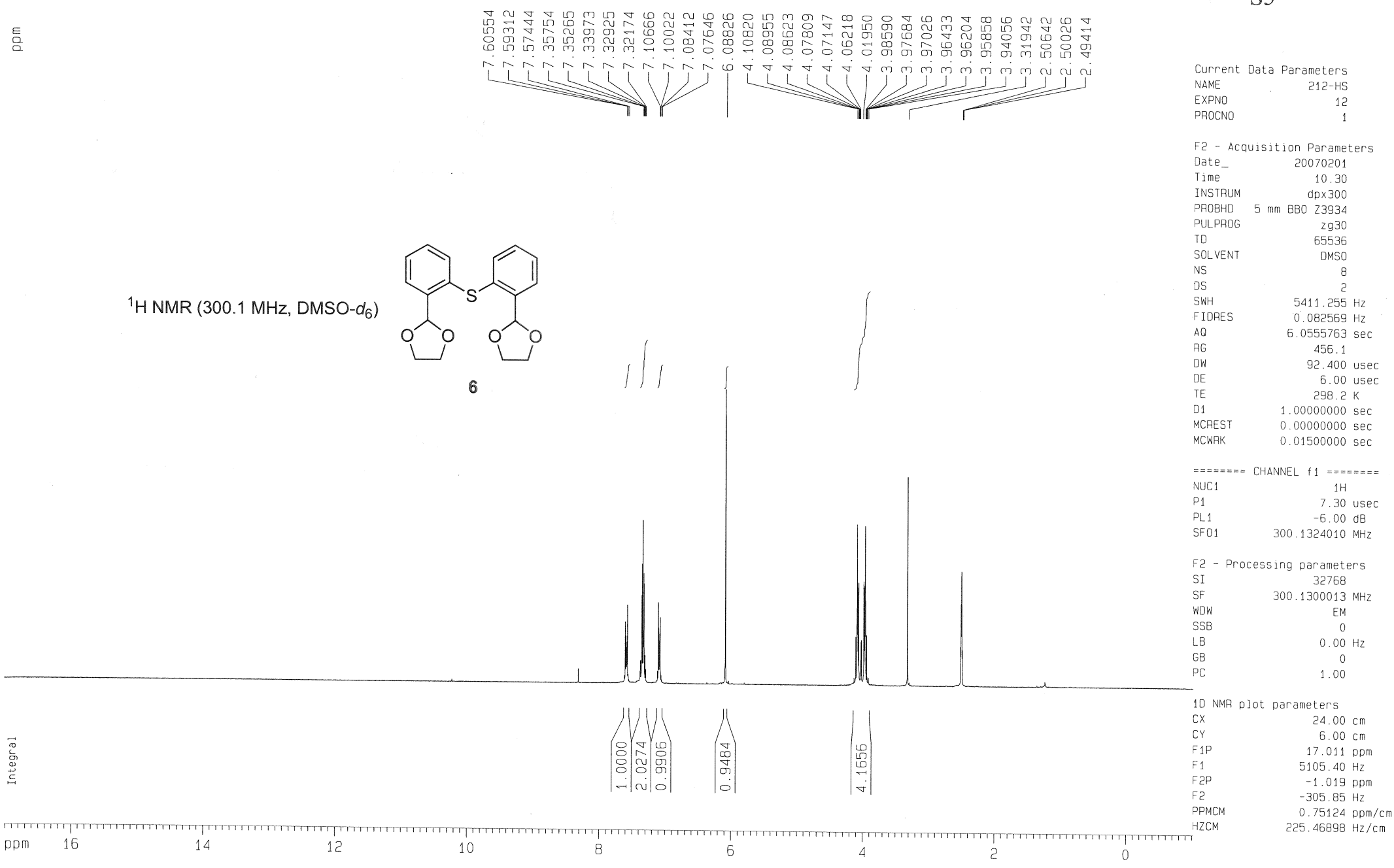
2,12-Di(phenylsulfonyl)thiepino[2,3-*b*:7,6-*b*′]bisindole (11). The same procedure as described for compound **1** was employed, starting with **14** (200 mg, 0.33 mmol) dissolved in THF (90 mL), $TiCl_4$ (1.9 mL, 17.4 mmol), Zn (2.3 g, 35 mmol), pyridine (0.4 mL) and THF (80 mL). The crude product was subjected to column chromatography [*n*-hexane/EtOAc (4:1)] to give the fused thiepin **11** (150 mg, 79%) as yellowish crystalline solid; mp: 230–232 °C; IR (neat) 1443, 1383, 1361, 1186, 1168, 1150, 1129, 1103, 1082, 959, 790, 767, 752, 740, 721 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.11–8.04 (m, 6H), 7.72–7.67 (m, 2H), 7.61–7.55 (m, 6H),

7.45–7.40 (m, 2H), 7.33–7.27 (m, 4H); ^{13}C NMR (DMSO-d_6) δ 137.2 (s), 136.5 (s), 135.0 (d), 129.8 (d), 127.9 (s), 127.5 (s), 126.9 (d), 126.5 (d), 124.6 (d), 124.2 (d), 121.5 (s), 119.3 (d), 115.2 (d). Anal. Calcd for $C_{30}H_{20}N_2O_4S_3$: C, 63.36; H, 3.54; N, 4.93. Found: C, 63.22; H, 3.55; N, 4.86.

Diacetal 16. The synthesis of **16** was performed according to the procedure described above for compound **6** starting with the acetal **15**[17a] (1.14 g, 4.0 mmol), *n*-BuLi (2.5 M in hexanes, 1.9 mL, 4.8 mmol) using THF (20 mL) as the solvent, followed by addition of $(PhSO_2)_2S$ (630 mg, 2.0 mmol) dissolved in THF (15 mL). The crude product was subjected to gradient column chromatography [*n*-hexane/EtOAc (4:1 → 2:1)] to give **16** (652 mg, 74%) as a white solid; mp 184–185 °C; IR (neat) 2886, 1362, 1197, 1078, 1057, 1018, 992, 949, 935, 793, 756, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.80–7.75 (m, 4H), 7.34–7.23 (m, 4H), 6.58 (s, 2H), 4.21–4.06 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 143.7 (s), 140.1 (s), 138.5 (s), 125.6 (d), 125.0 (d), 123.3 (s), 123.2 (d), 122.9 (d), 99.3 (d), 65.8 (t). Anal. Calcd for $C_{22}H_{18}O_4S_3$: C, 59.70; H, 4.10. Found: C, 59.84; H, 4.12.

Dialdehyde 17. A procedure similar to that described for compound **8** was used, starting with the diacetal **16** (443 mg, 1.0 mmol) in acetone (40 mL) and aq. $HClO_4$ (70%, 0.3 mL) in H_2O (3 mL). The mixture was stirred for 24 h at room temperature. After workup as for **8**, the crude product was triturated with Et_2O to give the dialdehyde **17** (335 mg, 94%) as a yellow solid; mp 223–225 °C; IR (neat) 1656, 1589, 1478, 1425, 1296, 1248, 1194, 1160, 940, 755, 726, 713 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.58 (s, 2H), 7.91–7.88 (m, 2H), 7.83–7.80 (m, 2H), 7.54–7.49 (m, 2H), 7.39–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 183.8 (d), 142.6 (s), 141.5 (s), 139.4 (s), 133.7 (s), 129.2 (d), 126.3 (d), 124.5 (d), 124.0 (d). Anal. Calcd for $C_{18}H_{10}O_2S_3$: C, 60.99; H, 2.84. Found: C, 61.18; H, 2.73.

Thiepino[3,2-*b*:6,7-*b*′]bis[1]benzothiophene (18). This compound was prepared according to the procedure for described for **1** with the same amounts of reagents and solvents employing **17** (179 mg, 0.5 mmol) as the starting material. Purification of the crude product by column chromatography (*n*-heptane) gave compound **18** (138 mg, 86%) as a yellow crystalline solid; mp 213–215.5 °C; IR (neat) 1431, 1317, 1252, 1220, 1098, 1018, 950, 922, 856, 836, 760, 751, 743, 723 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 8.14 (ddd, J = 8.1, 1.3, 0.7 Hz, 2H), 7.92 (ddd, J = 7.9, 1.3, 0.7 Hz, 2H), 7.52 (ddd, J = 8.1, 7.9, 1.3 Hz, 2H), 7.44 (ddd, J = 7.9, 7.9, 1.3 Hz, 2H), 7.28 (s, 2H); ^{13}C NMR (acetone-d_6) δ 142.8 (s), 142.1 (s), 139.5 (s), 128.5 (d), 126.7 (d), 126.2 (d), 123.7 (d), 123.4 (s), 123.2 (d). Anal. Calcd for $C_{18}H_{10}S_3$: C, 67.04; H, 3.13; S, 29.83. Found: C, 66.97; H, 3.02; S, 29.87.



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PROCNO	1

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SOLVENT	DMSO
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RG	456.1
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TE	298.2 K
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MCWRK	0.01500000 sec

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PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

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SF	300.1300013 MHz
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SSB	0
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GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
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F2P	-1.019 ppm
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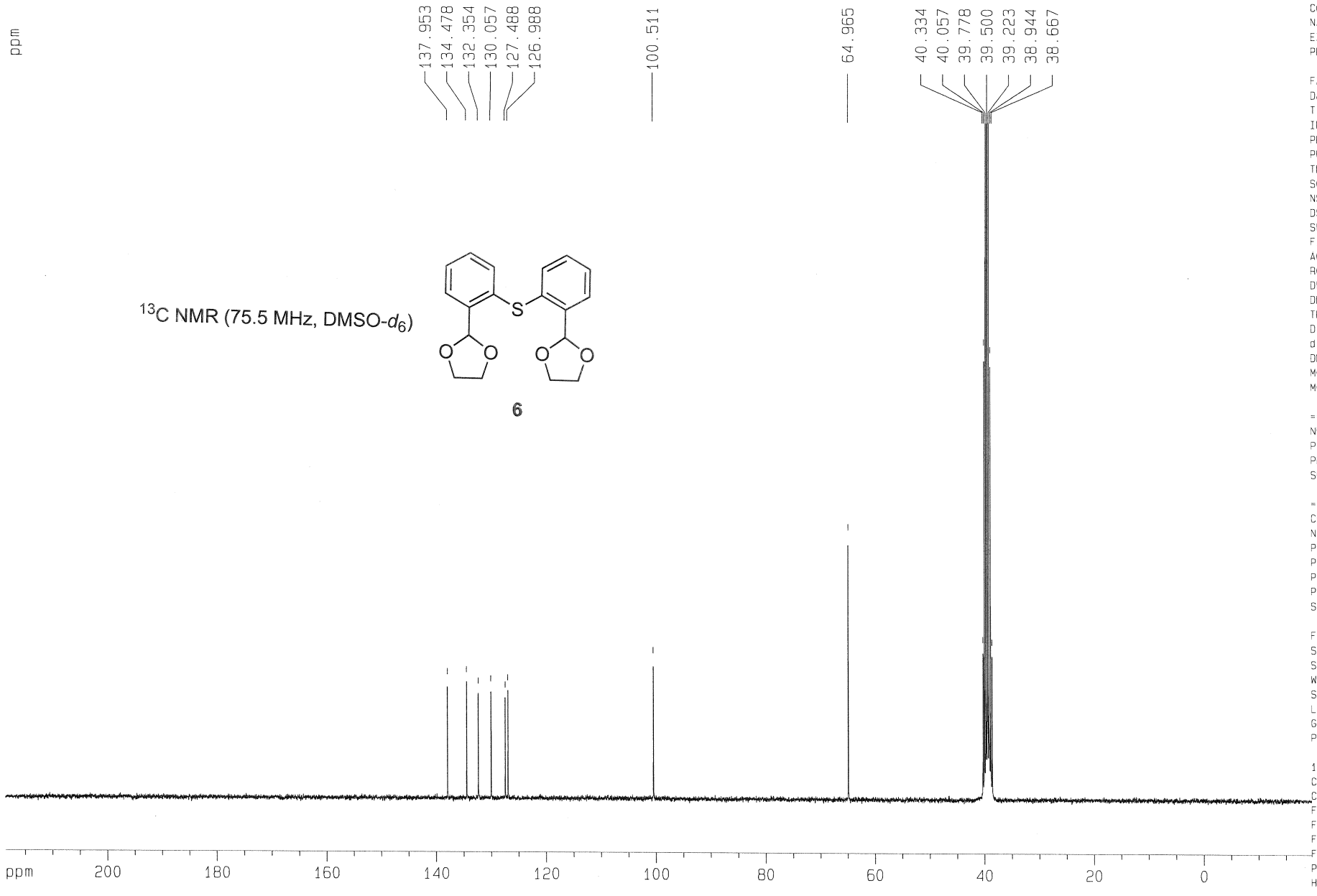

^{13}C NMR (75.5 MHz, DMSO-d_6)

6

Current Data Parameters
NAME 212-HS (kol)
EXPNO 12
PROCNO 1

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Time 10.41
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PULPROG zgpg30
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SOLVENT DMSO
NS 3072
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
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RG 5160.6
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TE 298.2 K
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MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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P1 7.00 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
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NUC2 1H
PCPD2 90.00 usec
PL2 -6.00 dB
PL12 15.82 dB
PL13 120.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
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SF 75.4677872 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
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CY 19.00 cm
F1P 218.649 ppm
F1 16500.93 Hz
F2P -19.673 ppm
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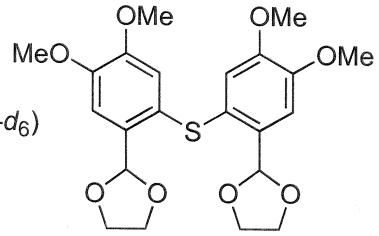
^{1}H NMR (300.1 MHz, DMSO-d_6)



7

Current Data Parameters
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EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
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PULPROG zg30
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SOLVENT DMSO
NS 16
DS 2
SWH 5411.255 Hz
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AQ 6.0555763 sec
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DE 6.00 usec
TE 293.2 K
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MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
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F2 - Processing parameters
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WDW EM
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LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
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CY 8.00 cm
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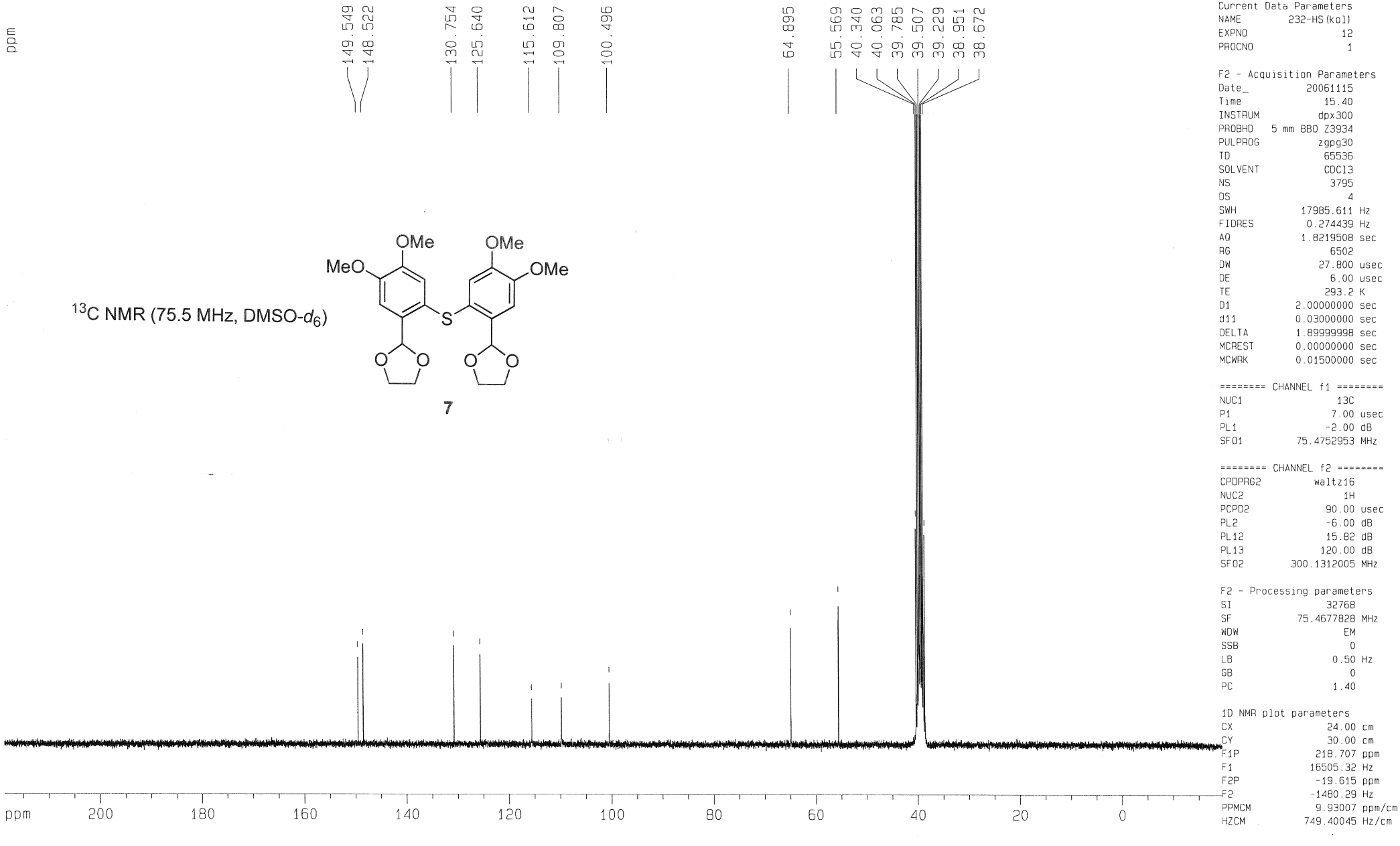
HZCM 225.46898 Hz/cm



^{13}C NMR (75.5 MHz, DMSO-d_6)

7

Current Data Parameters
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EXPNO 12
PROCNO 1

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SOLVENT CDCl3
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FIDRES 0.274439 Hz
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RG 6502
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DE 6.00 usec
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MCWRK 0.01500000 sec

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P1 7.00 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
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PCPD2 90.00 usec
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PL12 15.82 dB
PL13 120.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
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WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.40

1D NMR plot parameters
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CY 30.00 cm
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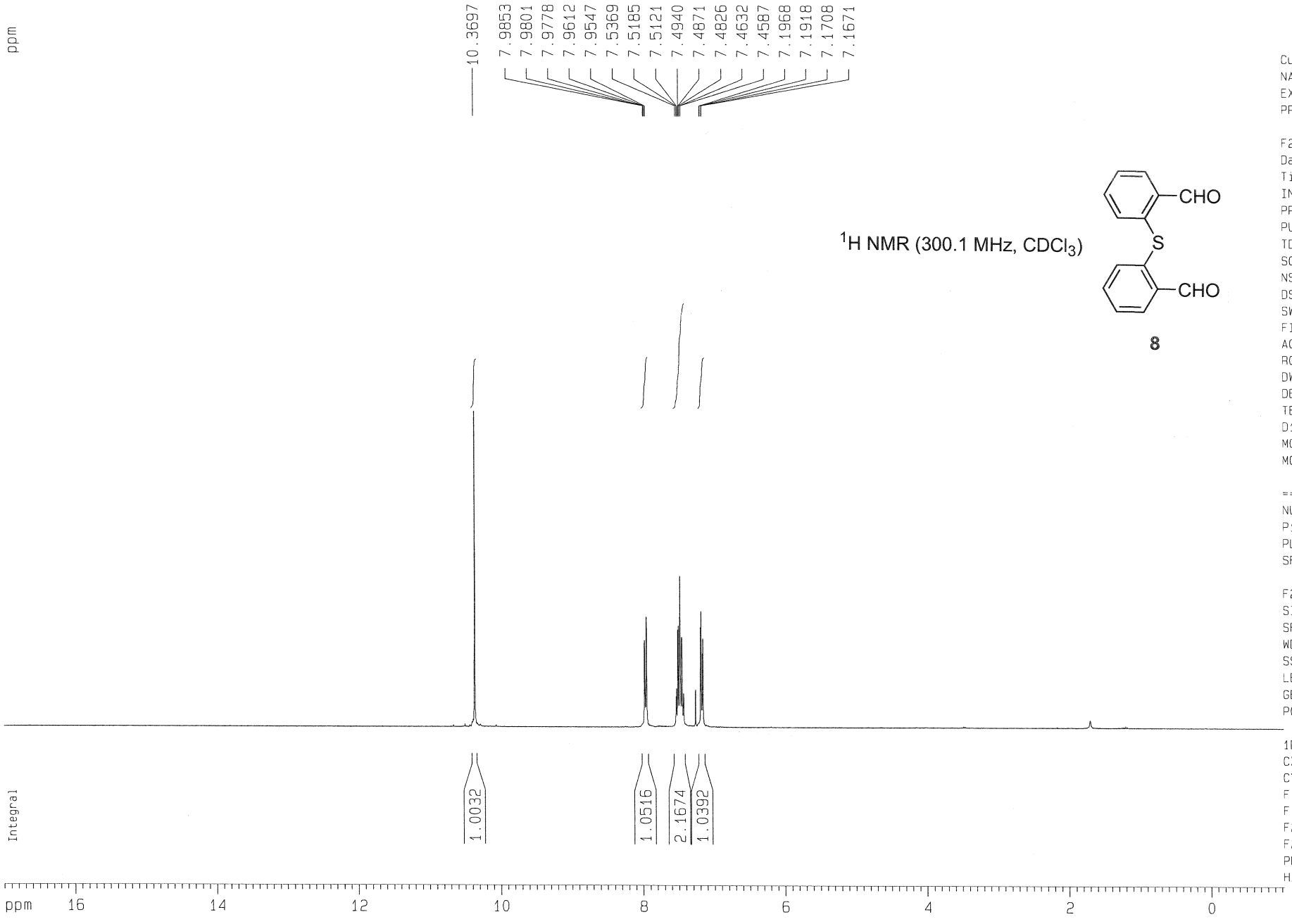

^{1}H NMR (300.1 MHz, $CDCl_3$)

8

Current Data Parameters

NAME	218-HS
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	5411.255 Hz
FIDRES	0.082569 Hz
AQ	6.0555763 sec
RG	406.4
DW	92.400 usec
DE	6.00 usec
TE	298.2 K
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MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

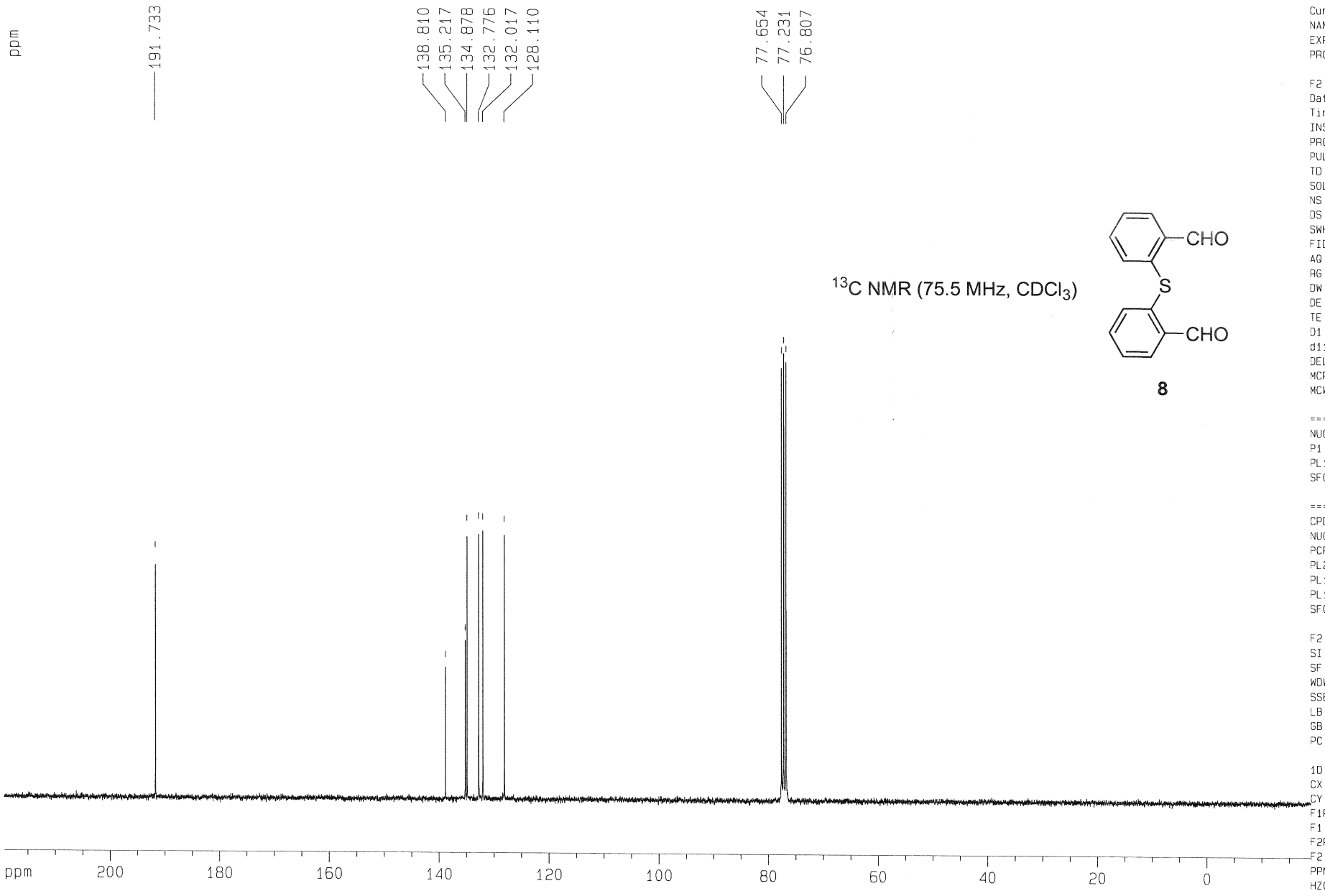
NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300033 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	6.00 cm
F1P	17.004 ppm
F1	5103.41 Hz
F2P	-1.026 ppm
F2	-307.85 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



^{13}C NMR (75.5 MHz, $CDCl_3$)

8

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Current Data Parameters
NAME          218-HS(kol)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20070301
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PULPROG          zgpg30
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SOLVENT            DMSO
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DS                    4
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AQ            1.8219508 sec
RG               5792.6
DW               27.800 usec
DE                6.00 usec
TE                298.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
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PL1              -2.00 dB
SF01        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2              -6.00 dB
PL12             15.82 dB
PL13            120.00 dB
SF02       300.1312005 MHz

F2 - Processing parameters
SI                32768
SF          75.4677347 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40

1D NMR plot parameters
CX               24.00 cm
CY                5.00 cm
F1P             219.344 ppm
F1            16553.43 Hz
F2P             -18.977 ppm
F2            -1432.18 Hz
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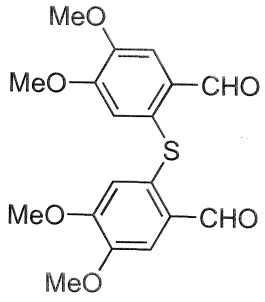
^{1}H NMR (300.1 MHz, $CDCl_3$)



9

Current Data Parameters

NAME	236-HS
EXPNO	9
PROCNO	1

F2 - Acquisition Parameters

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PULPROG	zg30
TD	65536
SOLVENT	CDCl3
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DS	2
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FIDRES	0.082569 Hz
AQ	6.0555763 sec
RG	512
DW	92.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300033 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	8.00 cm
F1P	17.004 ppm
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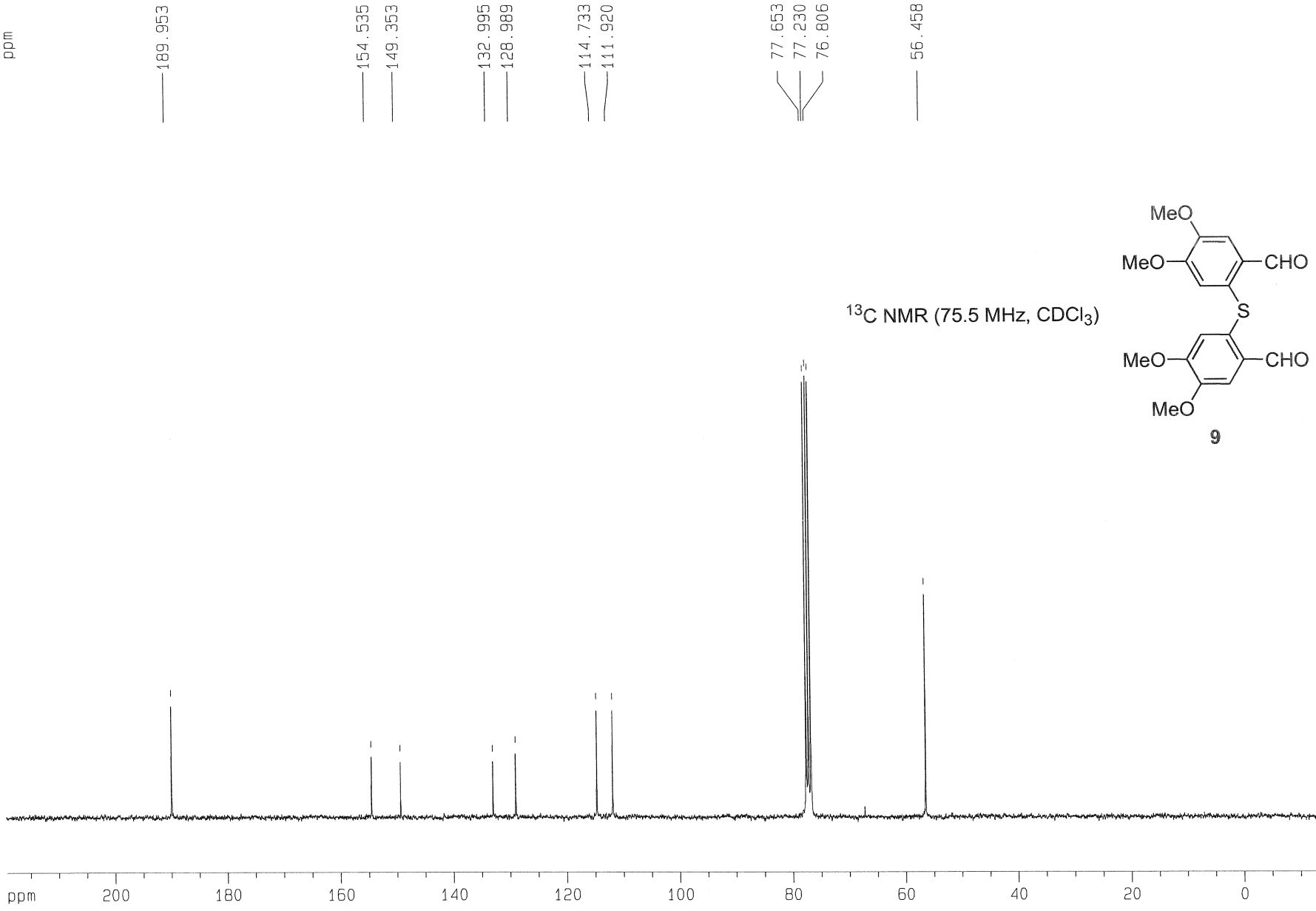
F2P	-1.026 ppm
F2	-307.85 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



^{13}C NMR (75.5 MHz, $CDCl_3$)

9

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Current Data Parameters
NAME          236-HS (kol)
EXPNO                    9
PROCNO                   1

F2 - Acquisition Parameters
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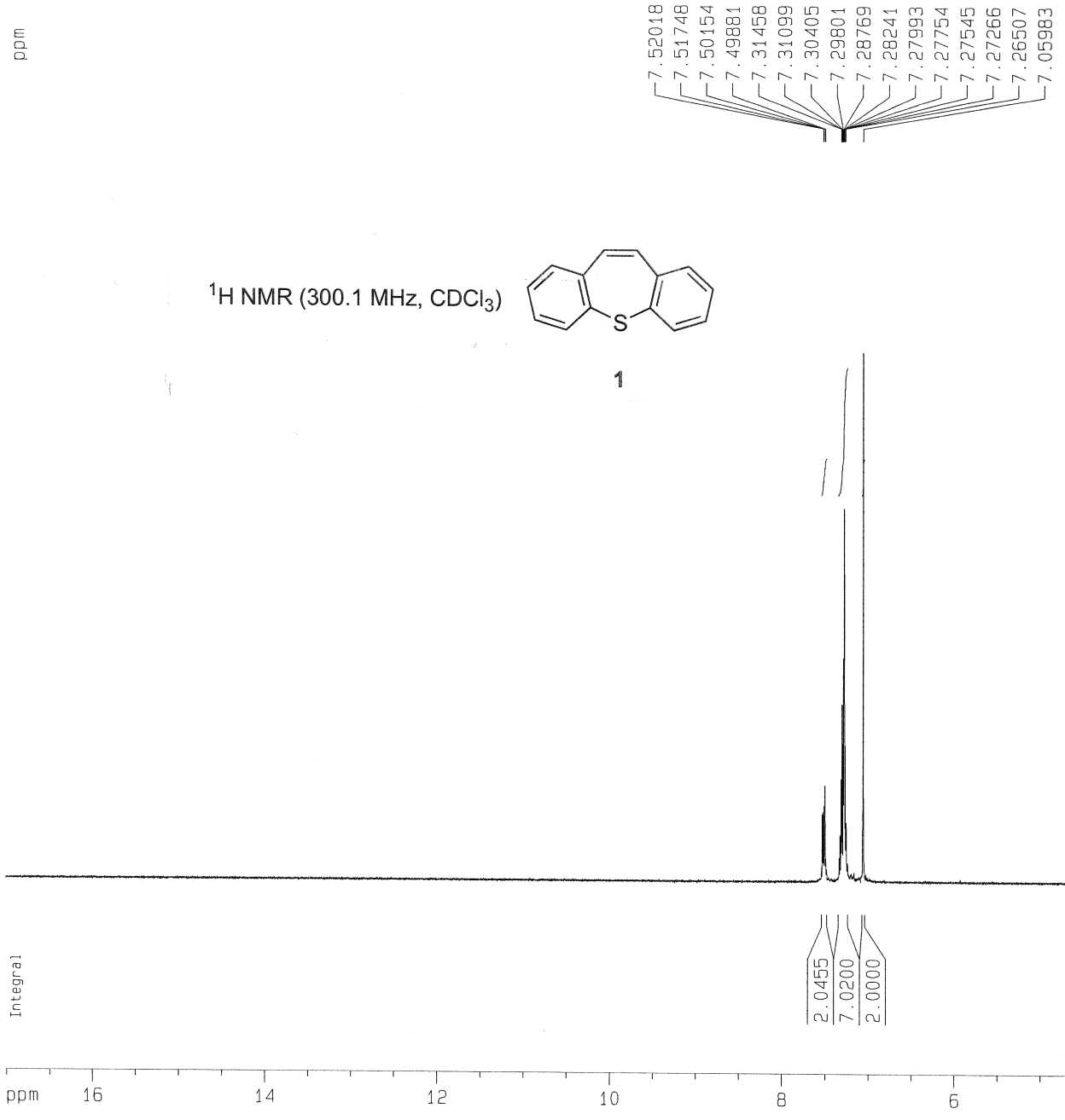
PULPROG          zgpg30
TD               65536
SOLVENT          CDCl3
NS                1427
DS                   4
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG               5792.6
DW              27.800 usec
DE               6.00 usec
TE              298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1              7.00 usec
PL1             -3.00 dB
SFO1        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2          80.00 usec
PL2             -6.00 dB
PL12            16.50 dB
PL13            16.00 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                32768
SF          75.4677336 MHz
WDW                EM
SSB                 0
LB              3.00 Hz
GB                  0
PC               1.40

1D NMR plot parameters
CX              24.00 cm
CY               4.00 cm
F1P            219.359 ppm
F1           16554.54 Hz
F2P           -18.963 ppm
F2           -1431.08 Hz
PPMCM          9.93008 ppm/cm
HZCM         749.40045 Hz/cm
```



^{1}H NMR (300.1 MHz, $CDCl_3$)

1

Current Data Parameters

NAME	225-HS(1)
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070227
Time	17.25
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	5411.255 Hz
FIDRES	0.082569 Hz
AQ	6.0555763 sec
RG	812.7
DW	92.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

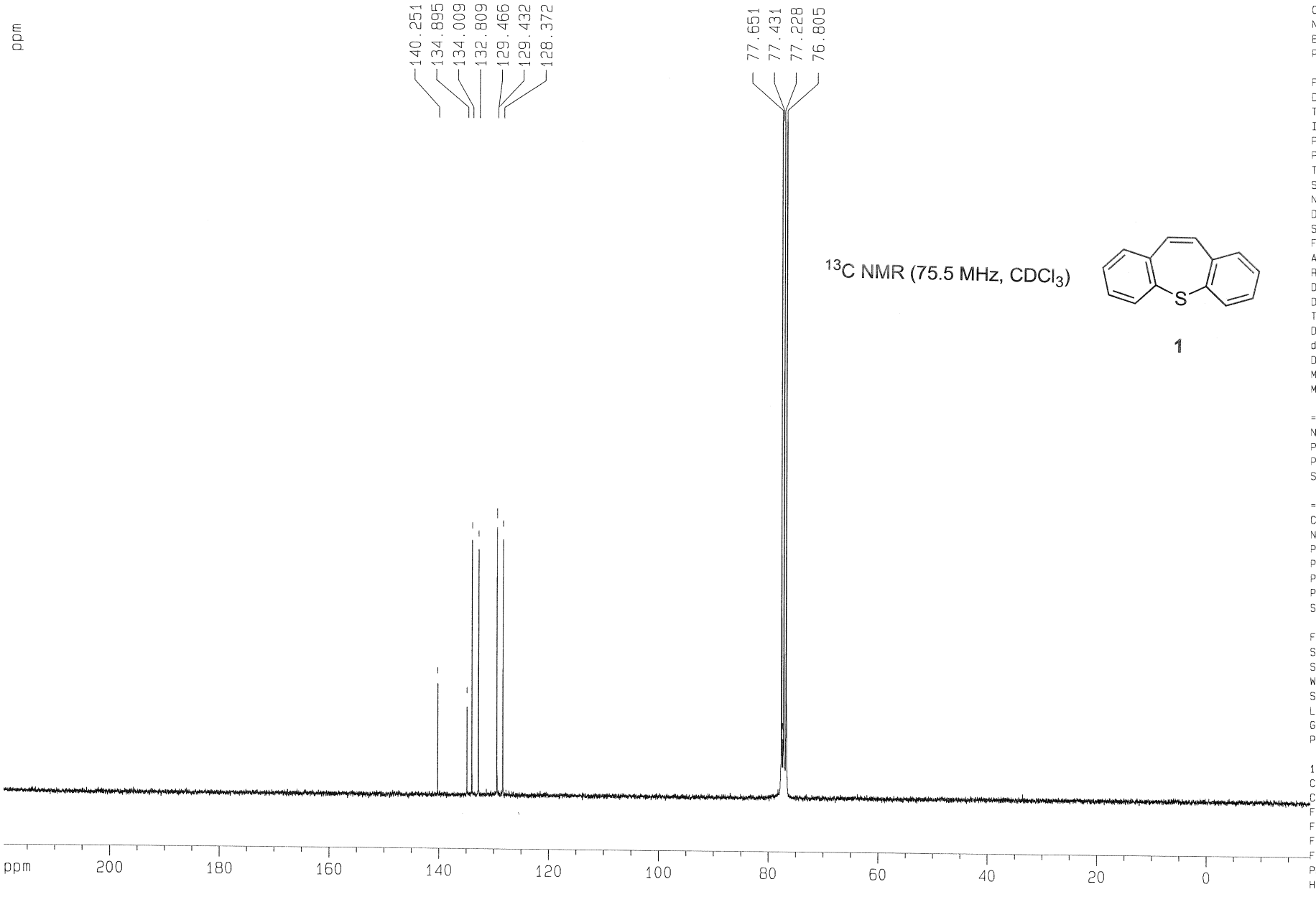
NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300011 MHz
WDW	EM
SSB	0
LB	-0.05 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	1.50 cm
F1P	17.011 ppm
F1	5105.52 Hz
F2P	-1.019 ppm
F2	-305.73 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



^{13}C NMR (75.5 MHz, $CDCl_3$)

1

```
Current Data Parameters
NAME          225-HS(kol)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070227
Time                17.28
INSTRUM             dpx300
PROBHD   5 mm BBO Z3934
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                  12288
DS                      4
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                 6502
DW               27.800 usec
DE                6.00 usec
TE                298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

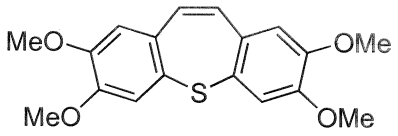
======== CHANNEL f1 ========
NUC1                  13C
P1                 7.00 usec
PL1               -2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             90.00 usec
PL2               -6.00 dB
PL12              15.82 dB
PL13             120.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677330 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40

1D NMR plot parameters
CX                24.00 cm
CY                 5.00 cm
F1P             219.366 ppm
F1             16555.09 Hz
F2P             -18.955 ppm
F2             -1430.53 Hz
PPMCM           9.93008 ppm/cm
HZCM          749.40051 Hz/cm
```

^{1}H NMR (300.1 MHz, $CDCl_3$)



10

Current Data Parameters

NAME	241-HS (2)
EXPNO	9
PROCNO	1

F2 - Acquisition Parameters

Date_	20061212
Time	9.45
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	5411.255 Hz
FIDRES	0.082569 Hz
AQ	6.0555763 sec
RG	256
DW	92.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

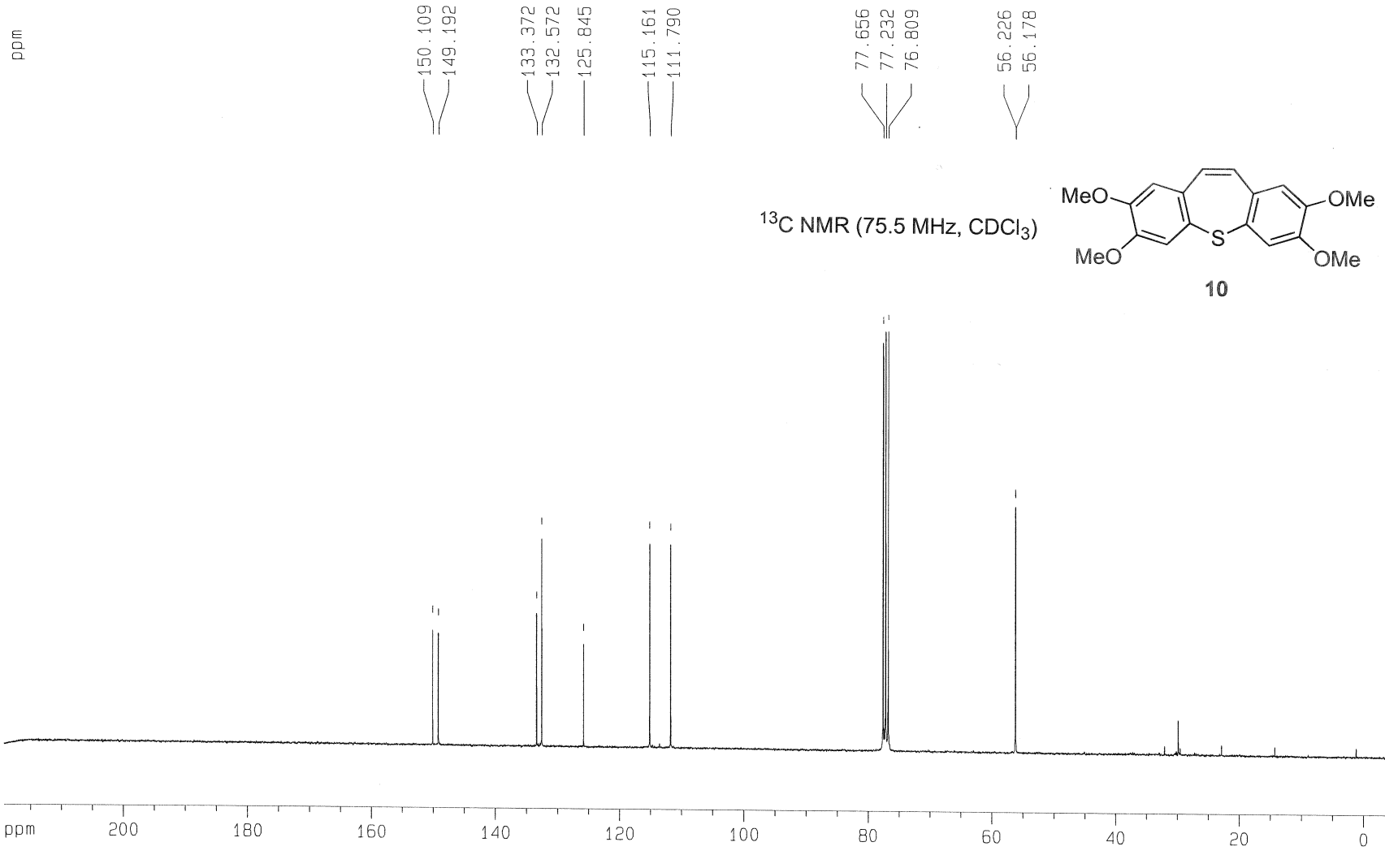
NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300031 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	5.00 cm
F1P	17.005 ppm
F1	5103.57 Hz
F2P	-1.025 ppm
F2	-307.68 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



^{13}C NMR (75.5 MHz, $CDCl_3$)

10

```
Current Data Parameters
NAME          241-HS (kol)
EXPNO                    9
PROCNO                   1

F2 - Acquisition Parameters
Date_             20061212
Time                 16.41
INSTRUM              dpx300
PROBHD    5 mm BBO Z3934
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     8192
DS                        4
SWH              17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                   5160.6
DW                27.800 usec
DE                 6.00 usec
TE                 298.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

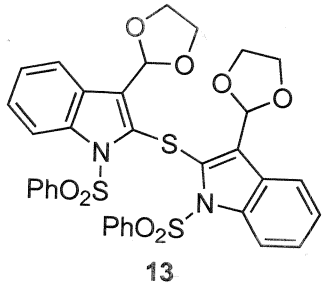
======== CHANNEL f1 ========
NUC1                   13C
P1                 7.00 usec
PL1                -3.00 dB
SF01          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2             80.00 usec
PL2                -6.00 dB
PL12               16.50 dB
PL13               16.00 dB
SF02         300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF           75.4677347 MHz
WDW                      EM
SSB                       0
LB                 1.00 Hz
GB                        0
PC                 1.40

1D NMR plot parameters
CX                24.00 cm
CY                 4.00 cm
F1P             219.344 ppm
F1              16553.43 Hz
F2P             -18.977 ppm
F2              -1432.18 Hz
PPMCM            9.93008 ppm/cm
HZCM           749.40045 Hz/cm
```

^{1}H NMR (300.1 MHz, DMSO-d_6)



13

Current Data Parameters

NAME	188-HS(1)
EXPNO	12
PROCNO	1

F2 - Acquisition Parameters

Date_	20070201
Time	10.21
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	8
DS	2
SWH	5411.255 Hz
FIDRES	0.082569 Hz
AQ	6.0555763 sec
RG	456.1
DW	92.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

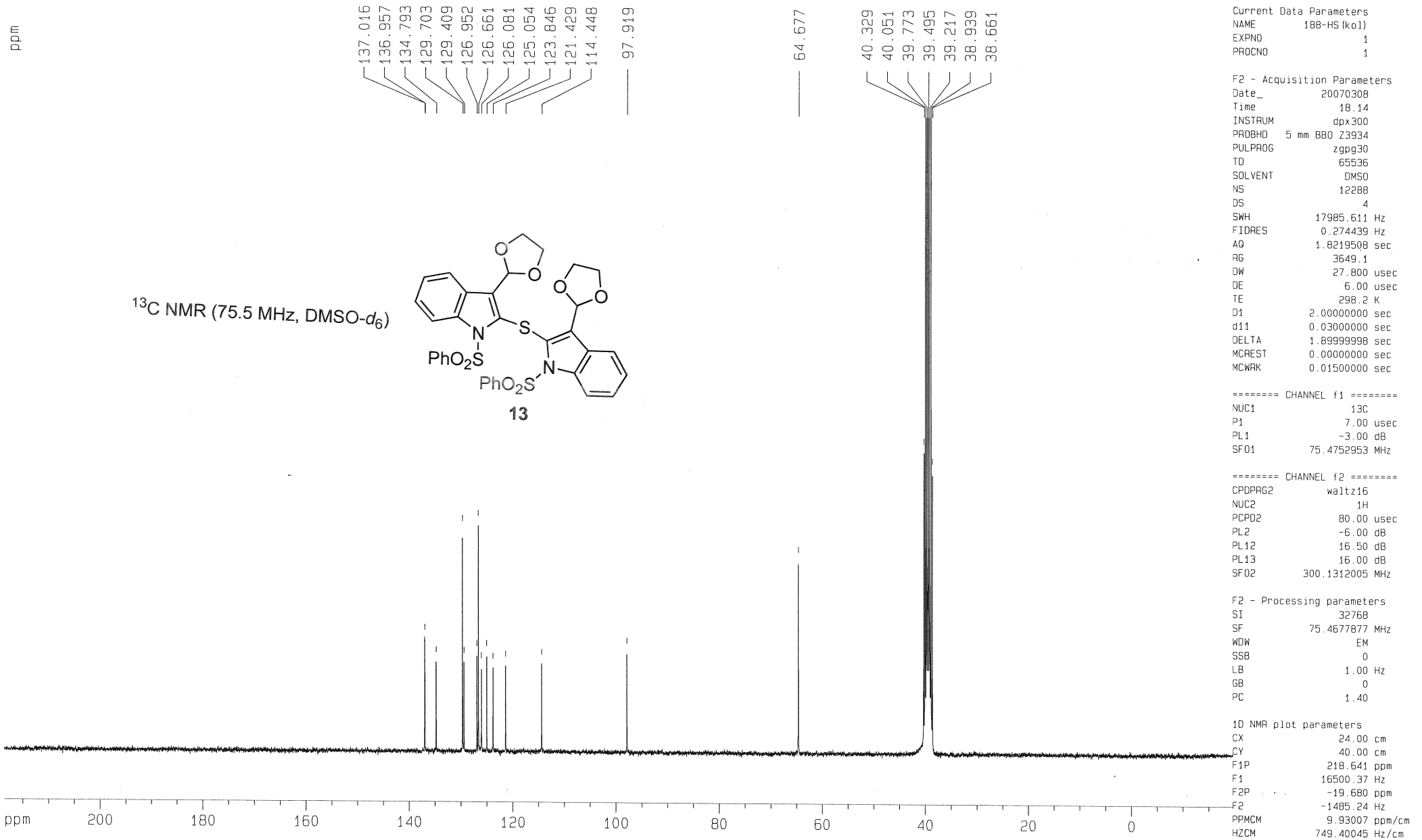
NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300013 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	8.00 cm
F1P	17.011 ppm
F1	5105.40 Hz
F2P	-1.019 ppm
F2	-305.85 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



^{13}C NMR (75.5 MHz, DMSO-d_6)

13

Current Data Parameters
NAME 188-HS(kol)
EXPNO 1
PROCNO 1

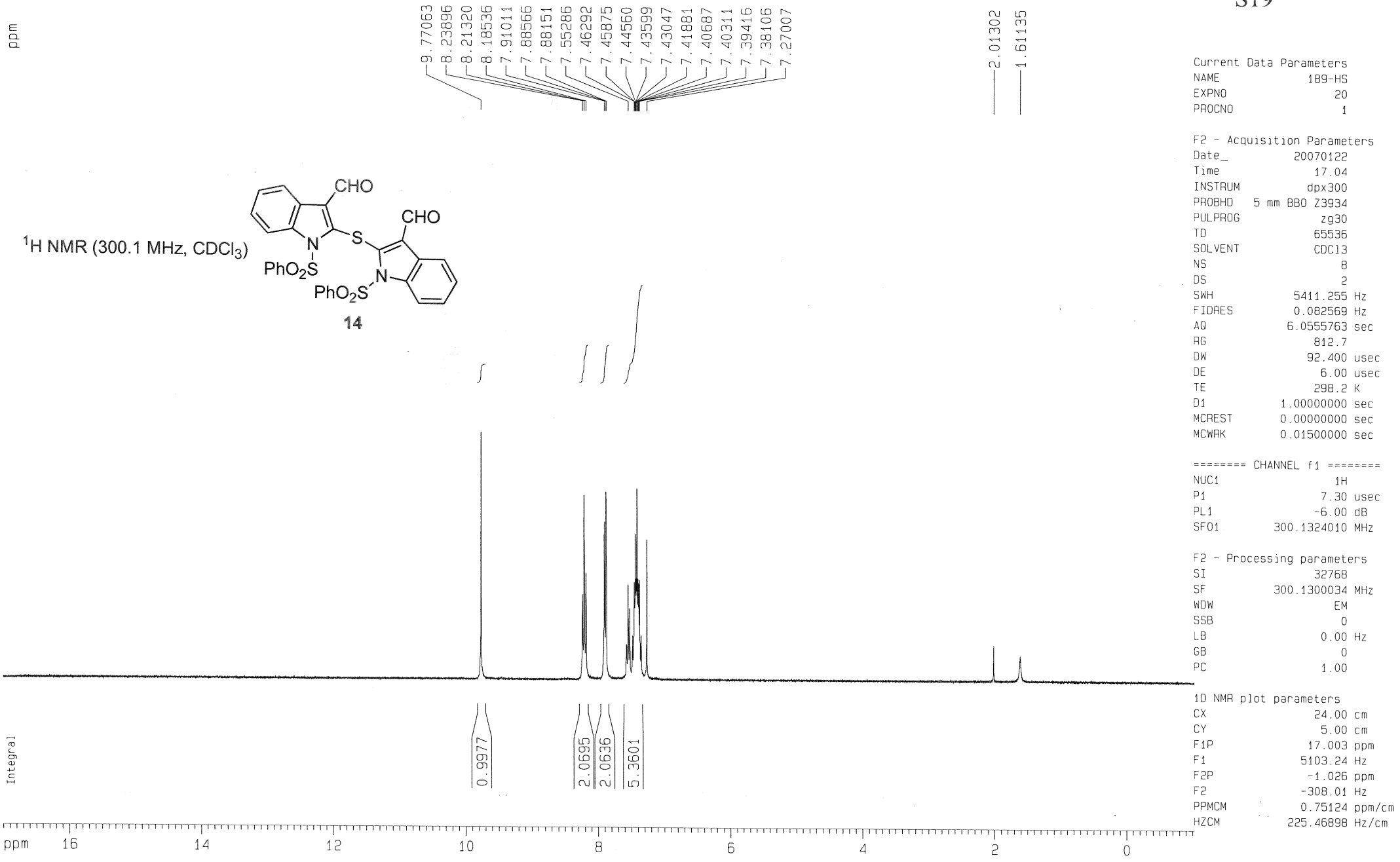
F2 - Acquisition Parameters
Date_ 20070308
Time 18.14
INSTRUM dpx300
PROBHD 5 mm BBO Z3934
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 12288
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 3649.1
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 16.50 dB
PL13 16.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677877 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 24.00 cm
CY 40.00 cm
F1P 218.641 ppm
F1 16500.37 Hz
F2P -19.680 ppm
F2 -1485.24 Hz
PPMCM 9.93007 ppm/cm
HZCM 749.40045 Hz/cm



Current Data Parameters

NAME	189-HS
EXPNO	20
PROCNO	1

F2 - Acquisition Parameters

Date_	20070122
Time	17.04
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	5411.255 Hz
FIDRES	0.082569 Hz
AQ	6.0555763 sec
RG	812.7
DW	92.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

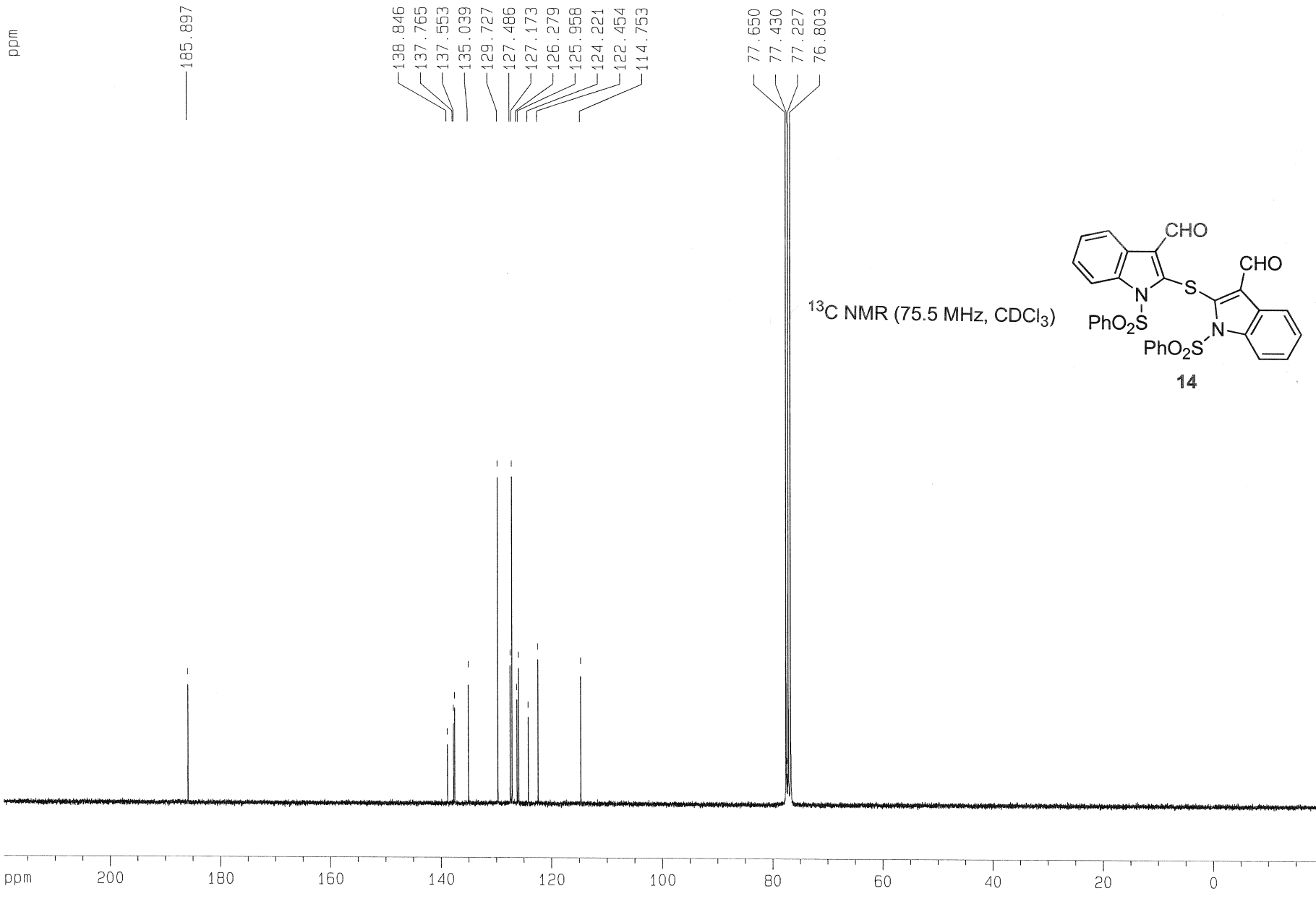
NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300034 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	5.00 cm
F1P	17.003 ppm
F1	5103.24 Hz
F2P	-1.026 ppm
F2	-308.01 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



^{13}C NMR (75.5 MHz, $CDCl_3$)

14

rent Data Parameters

NAME	189-HS(kol)
EXPNO	20
PROCNO	1

F2 - Acquisition Parameters

Date_	20070122
Time	17.24
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	12288
DS	4
SWH	17985.611 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	4096
DW	27.800 usec
DE	6.00 usec
TE	298.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	13C
P1	7.00 usec
PL1	-3.00 dB
SF01	75.4752953 MHz

======== CHANNEL f2 ========

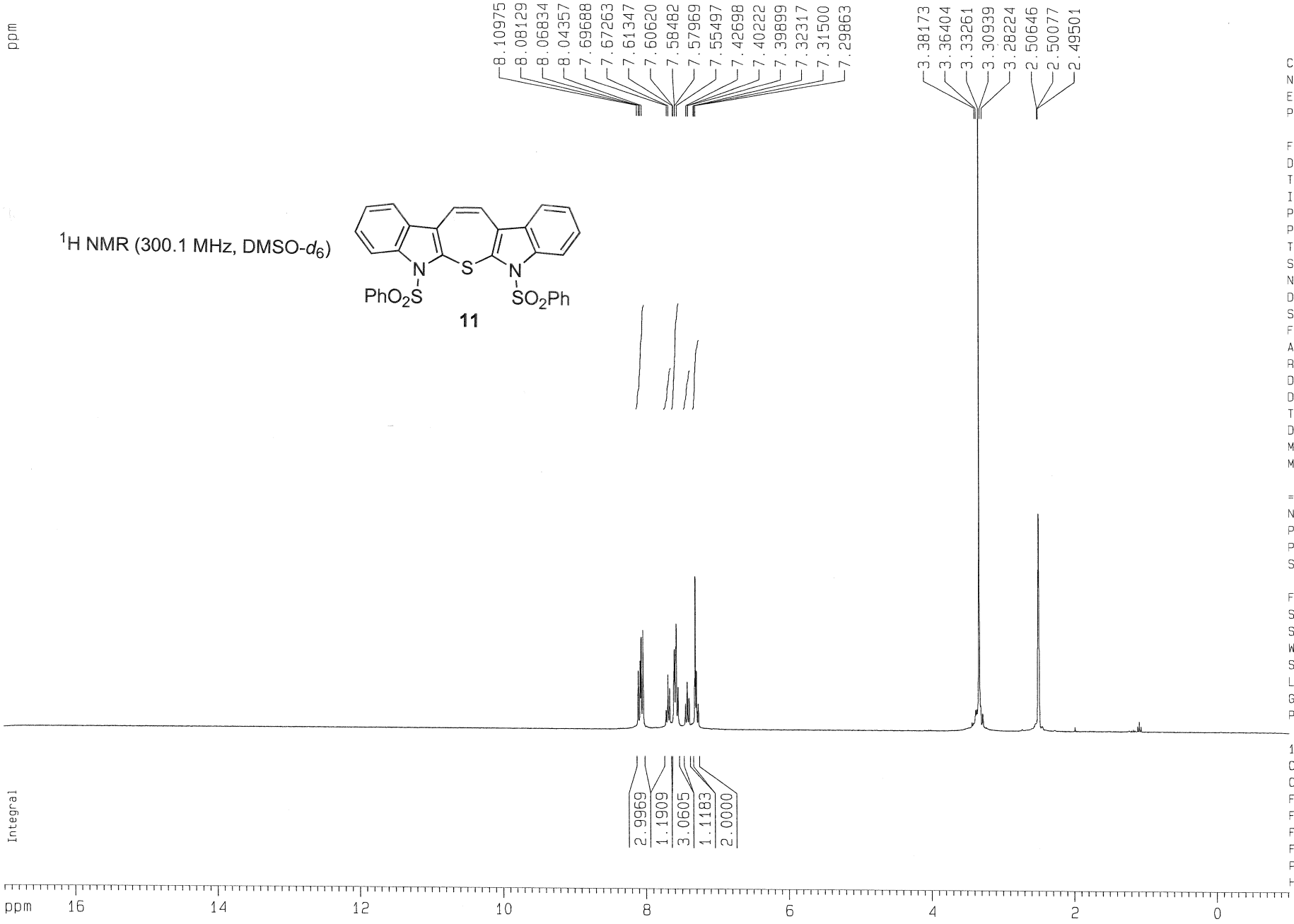
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-6.00 dB
PL12	16.50 dB
PL13	16.00 dB
SF02	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	75.4677330 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	24.00 cm
CY	6.00 cm
F1P	219.366 ppm
F1	16555.09 Hz
F2P	-18.955 ppm
F2	-1430.53 Hz
PPMCM	9.93008 ppm/cm
HZCM	749.40051 Hz/cm



^{1}H NMR (300.1 MHz, DMSO-d_6)

11

Current Data Parameters

NAME	tj_205_HS
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070705
Time	17.22
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	8
DS	2
SWH	5411.255 Hz
FIDRES	0.082569 Hz
AQ	6.0555763 sec
RG	574.7
DW	92.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

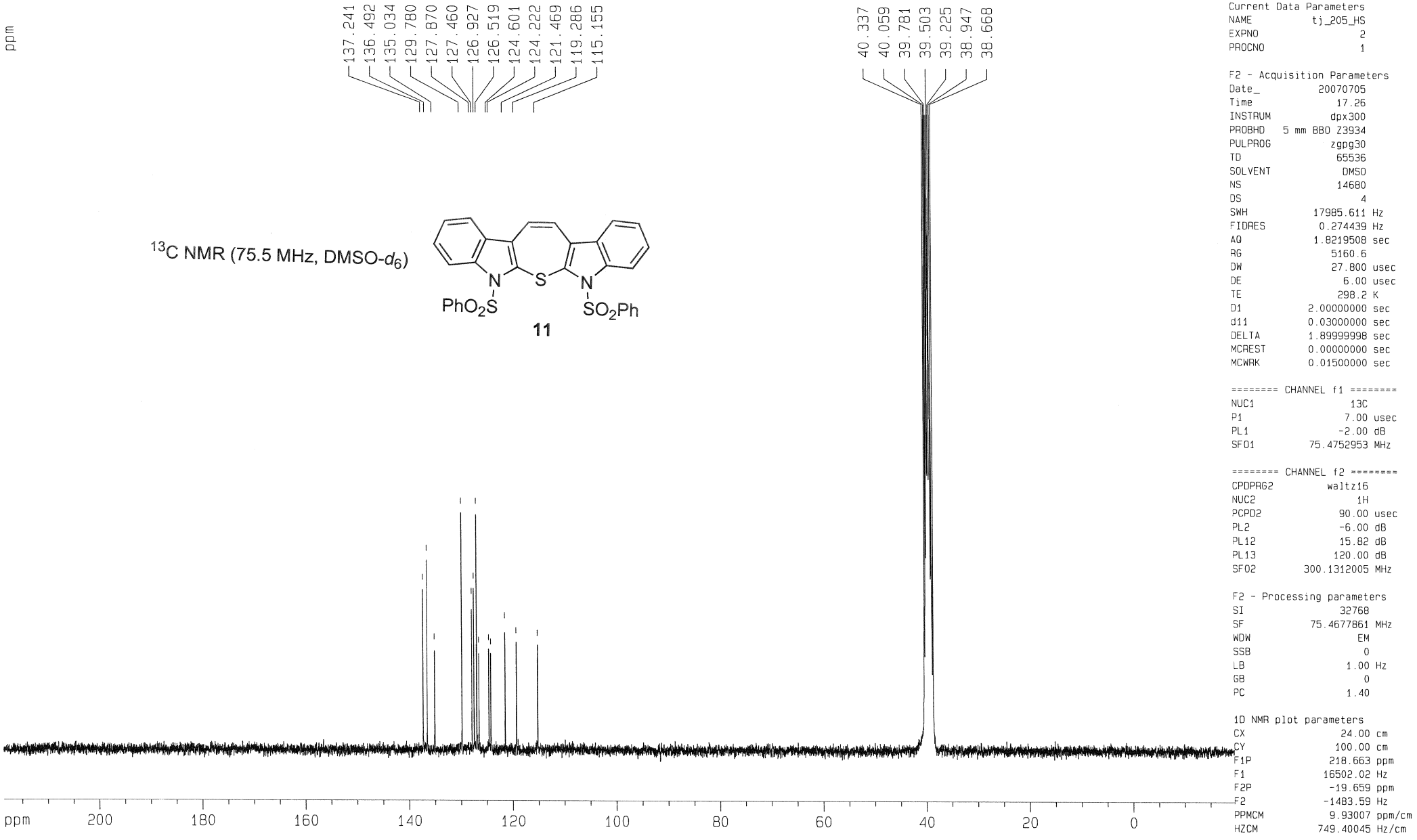
NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300013 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	25.00 cm
F1P	17.011 ppm
F1	5105.40 Hz
F2P	-1.019 ppm
F2	-305.85 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



Current Data Parameters

NAME	tj_205_HS
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20070705
Time	17.26
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	14680
DS	4
SWH	17985.611 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	5160.6
DW	27.800 usec
DE	6.00 usec
TE	298.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	13C
P1	7.00 usec
PL1	-2.00 dB
SFO1	75.4752953 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-6.00 dB
PL12	15.82 dB
PL13	120.00 dB
SFO2	300.1312005 MHz

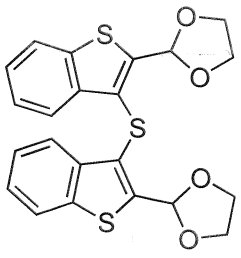
F2 - Processing parameters

SI	32768
SF	75.4677861 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	24.00 cm
CY	100.00 cm
F1P	218.663 ppm
F1	16502.02 Hz
F2P	-19.659 ppm
F2	-1483.59 Hz
PPMCM	9.93007 ppm/cm
HZCM	749.40045 Hz/cm

^{1}H NMR (300.1 MHz, $CDCl_3$)



16

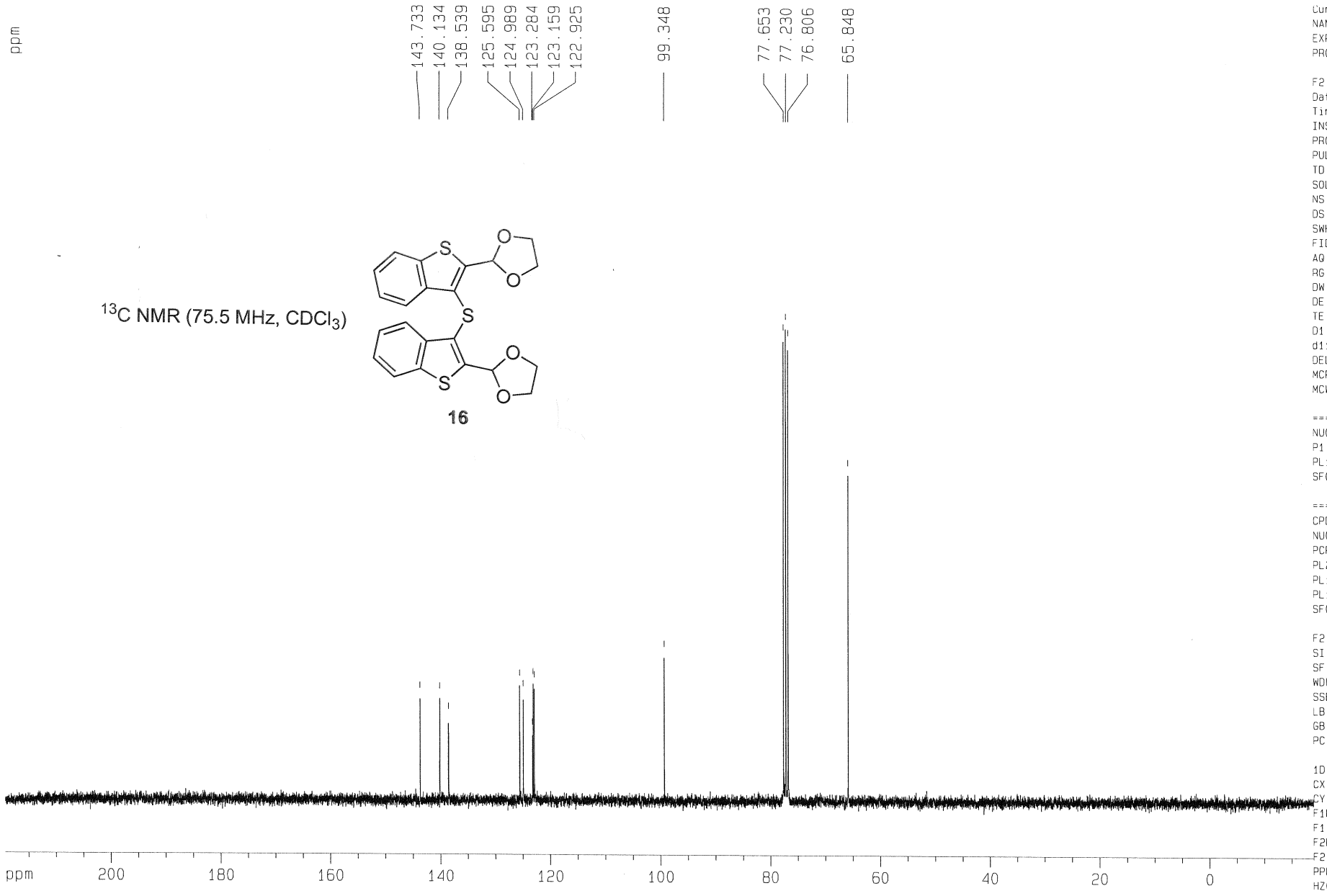
Current Data Parameters
NAME 242-HS(3)
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061207
Time 12.00
INSTRUM dpx300
PROBHD 5 mm BBO Z3934
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 5411.255 Hz
FIDRES 0.082569 Hz
AQ 6.0555763 sec
RG 256
DW 92.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.30 usec
PL1 -6.00 dB
SFO1 300.1324010 MHz

F2 - Processing parameters
SI 32768
SF 300.1300033 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 24.00 cm
CY 4.00 cm
F1P 17.004 ppm
F1 5103.41 Hz
F2P -1.026 ppm
F2 -307.85 Hz
PPMCM 0.75124 ppm/cm
HZCM 225.46898 Hz/cm



Current Data Parameters
NAME 242-HS(kol)
EXPNO 20
PROCNO 1

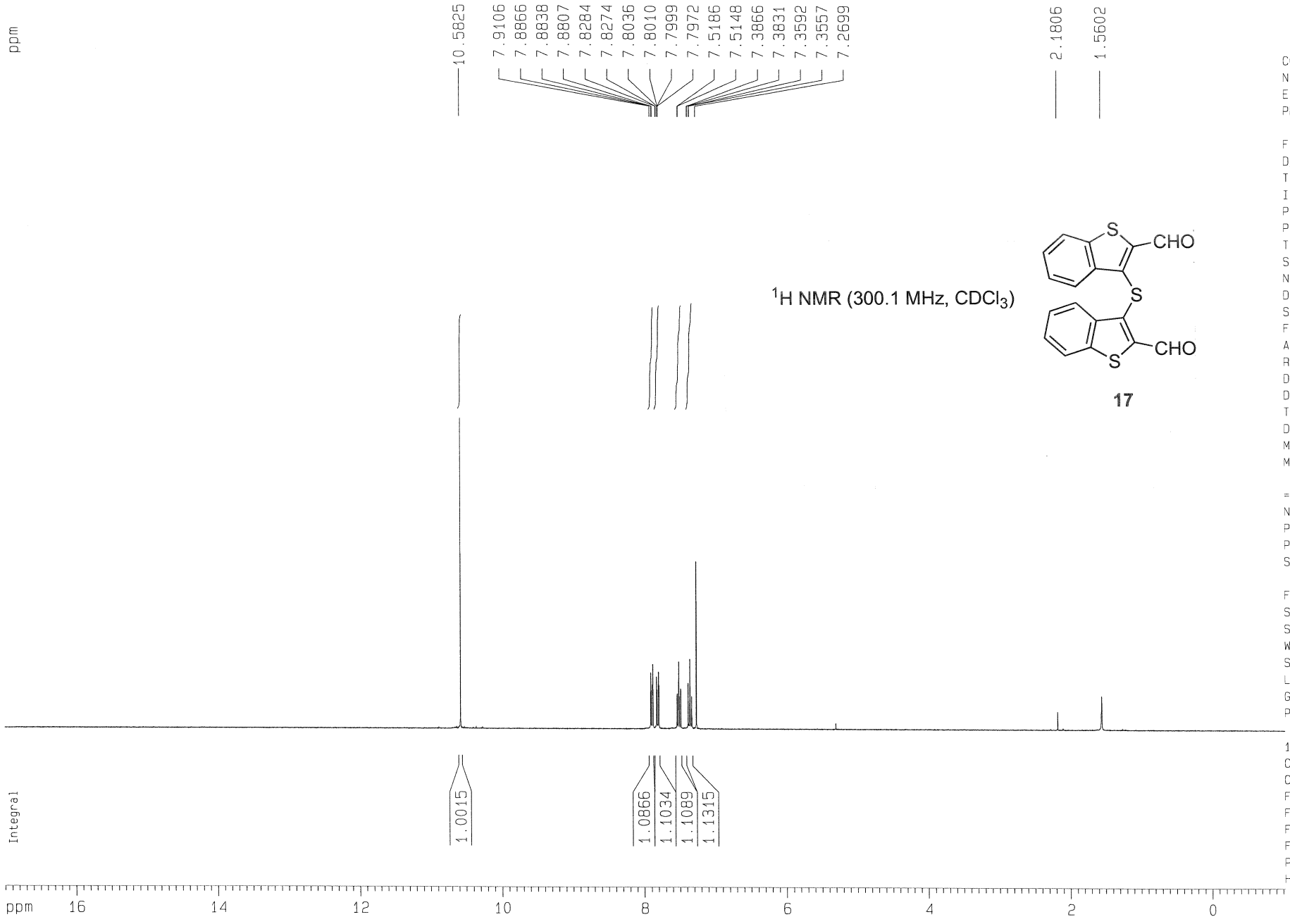
F2 - Acquisition Parameters
Date_ 20070125
Time 11.00
INSTRUM dpx300
PROBHD 5 mm BBO Z3934
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 301
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4597.6
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -6.00 dB
PL12 15.82 dB
PL13 120.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677347 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 24.00 cm
CY 6.00 cm
F1P 219.344 ppm
F1 16553.43 Hz
F2P -18.977 ppm
F2 -1432.18 Hz
PPMCM 9.93008 ppm/cm
HZCM 749.40051 Hz/cm



^{1}H NMR (300.1 MHz, $CDCl_3$)

17

Current Data Parameters

NAME	245-HS(1)
EXPNO	12
PROCNO	1

F2 - Acquisition Parameters

Date_	20061221
Time	16.29
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	5411.255 Hz
FIDRES	0.082569 Hz
AQ	6.0555763 sec
RG	1290.2
DW	92.400 usec
DE	6.00 usec
TE	299.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

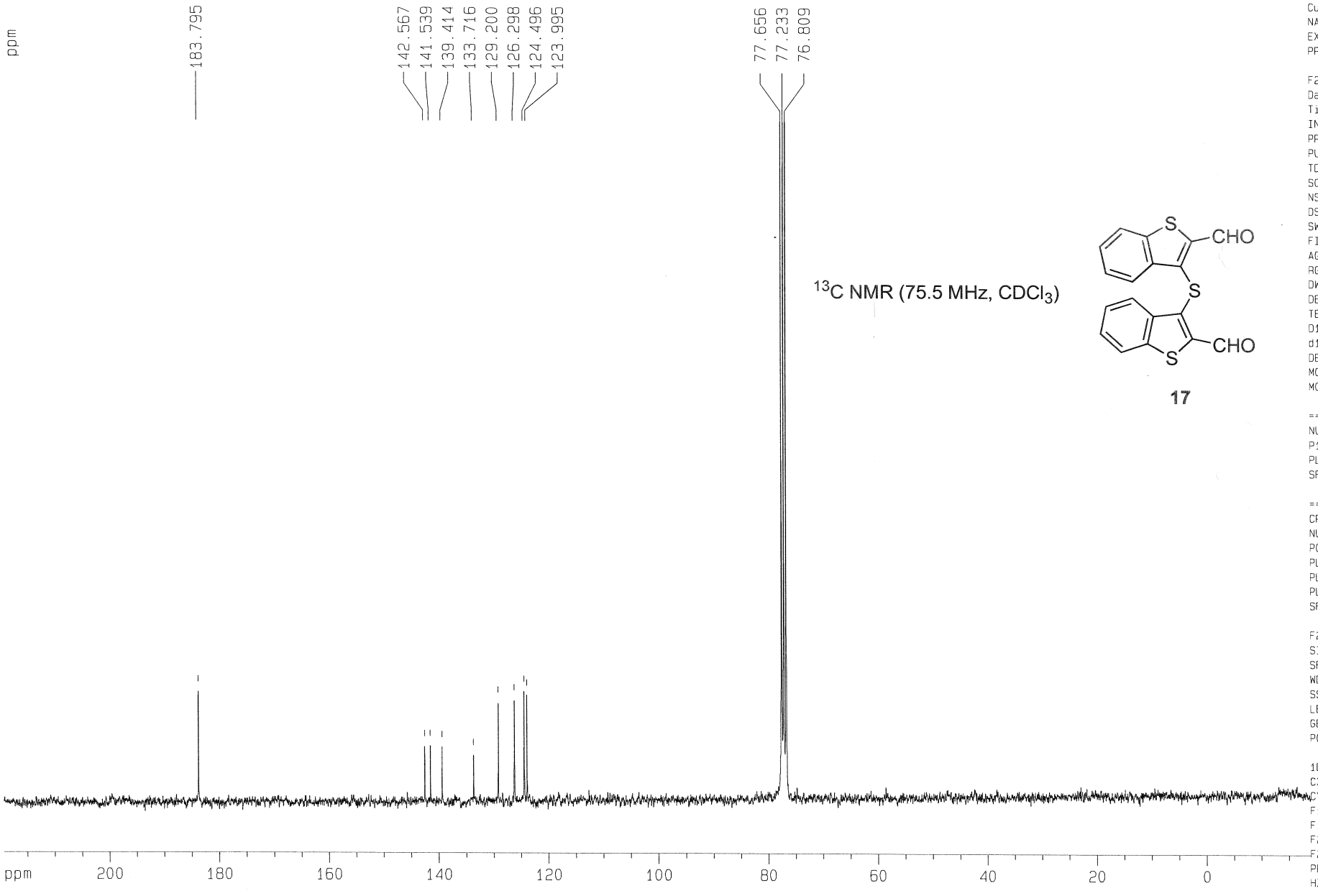
NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300033 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	6.00 cm
F1P	17.004 ppm
F1	5103.41 Hz
F2P	-1.026 ppm
F2	-307.85 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



^{13}C NMR (75.5 MHz, $CDCl_3$)

17

```
Current Data Parameters
NAME          245-HS (kol)
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_              20070124
Time                  10.03
INSTRUM             dpx300
PROBHD    5 mm BBO Z3934
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1237
DS                       4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                4597.6
DW                27.800 usec
DE                 6.00 usec
TE                298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 7.00 usec
PL1                -2.00 dB
SF01         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             90.00 usec
PL2                -6.00 dB
PL12               15.82 dB
PL13              120.00 dB
SF02        300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF          75.4677330 MHz
WDW                     EM
SSB                      0
LB                  3.50 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                 24.00 cm
CY                  2.00 cm
F1P              219.366 ppm
F1             16555.09 Hz
F2P              -18.955 ppm
F2             -1430.53 Hz
PPMCM             9.93008 ppm/cm
HZCM            749.40051 Hz/cm
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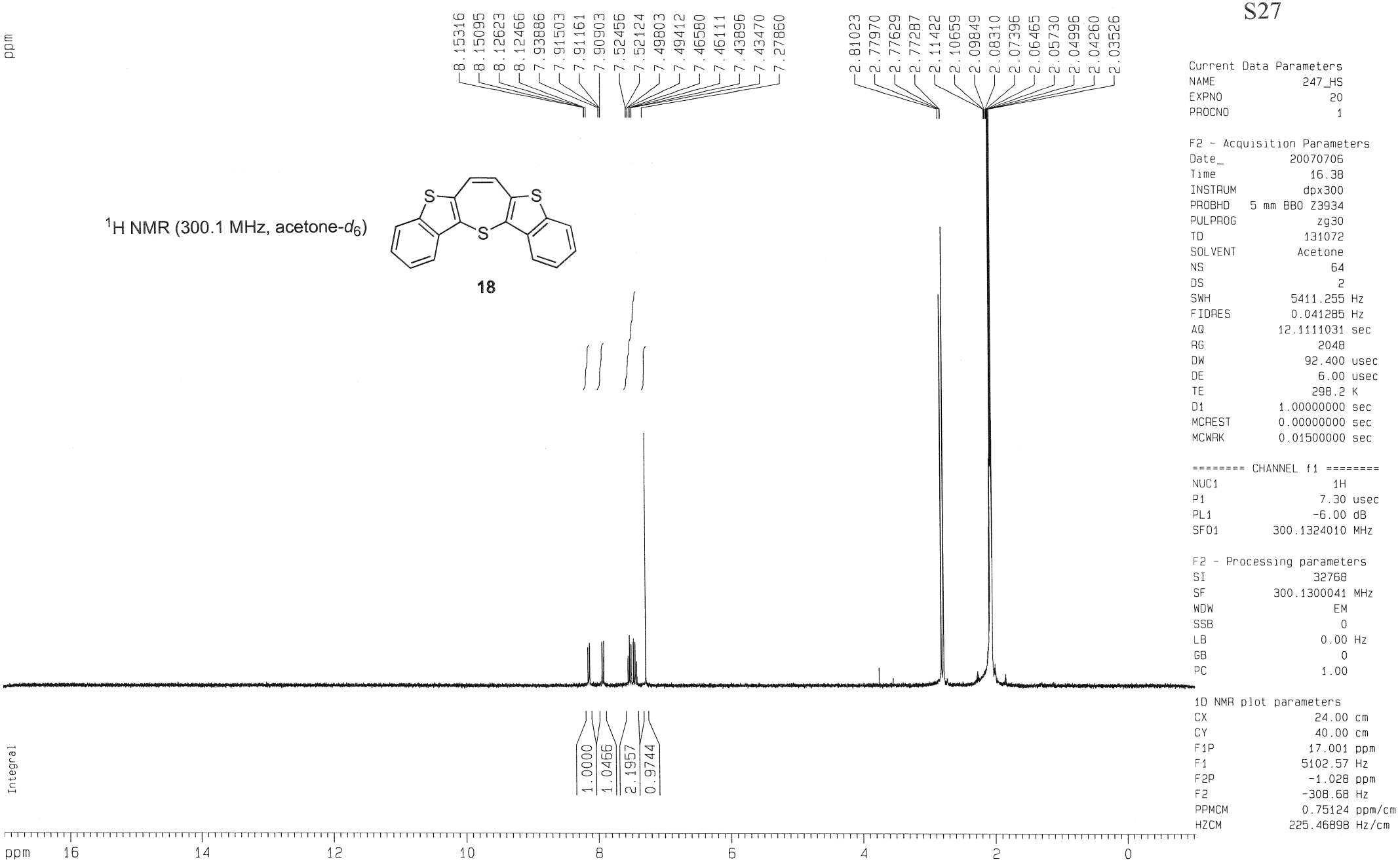


^{1}H NMR (300.1 MHz, acetone-d_6)

18

Current Data Parameters

NAME	247_HS
EXPNO	20
PROCNO	1

F2 - Acquisition Parameters

Date_	20070706
Time	16.38
INSTRUM	dpx300
PROBHD	5 mm BBO Z3934
PULPROG	zg30
TD	131072
SOLVENT	Acetone
NS	64
DS	2
SWH	5411.255 Hz
FIDRES	0.041285 Hz
AQ	12.1111031 sec
RG	2048
DW	92.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

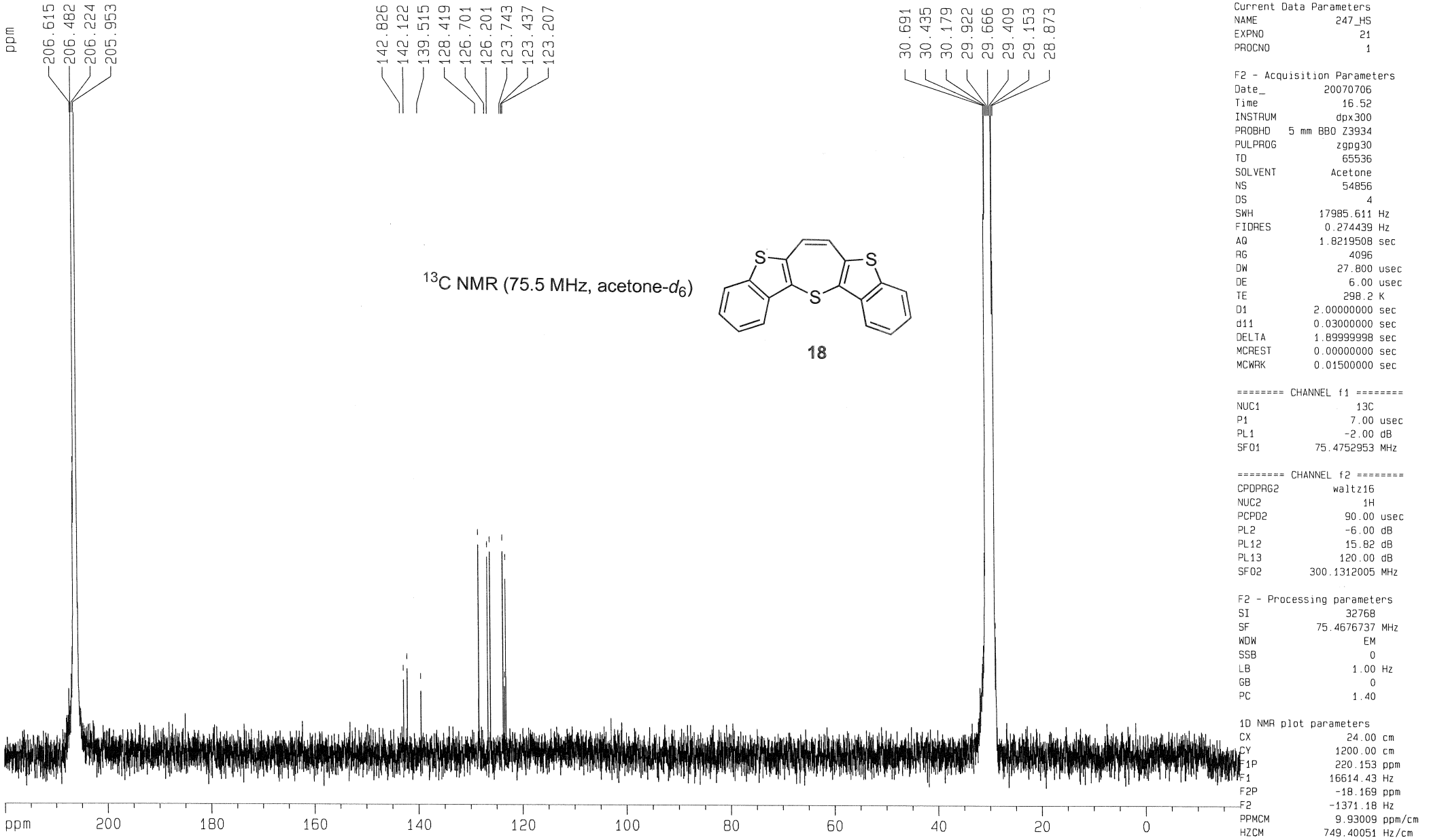
NUC1	1H
P1	7.30 usec
PL1	-6.00 dB
SFO1	300.1324010 MHz

F2 - Processing parameters

SI	32768
SF	300.1300041 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	24.00 cm
CY	40.00 cm
F1P	17.001 ppm
F1	5102.57 Hz
F2P	-1.028 ppm
F2	-308.68 Hz
PPMCM	0.75124 ppm/cm
HZCM	225.46898 Hz/cm



^{13}C NMR (75.5 MHz, acetone-d_6)

18

Current Data Parameters
NAME 247_HS
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070706
Time 16.52
INSTRUM dpx300
PROBHD 5 mm BBO Z3934
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 54856
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4096
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 -2.00 dB
SF01 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -6.00 dB
PL12 15.82 dB
PL13 120.00 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4676737 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 24.00 cm
CY 1200.00 cm
F1P 220.153 ppm
F1 16614.43 Hz
F2P -18.169 ppm
F2 -1371.18 Hz
PPMCM 9.93009 ppm/cm
HZCM 749.40051 Hz/cm