

Supporting Information

Synthesis of Diarylsulfones with Simple Arenes and $K_2S_2O_8$ through Double C-S Bond Formation

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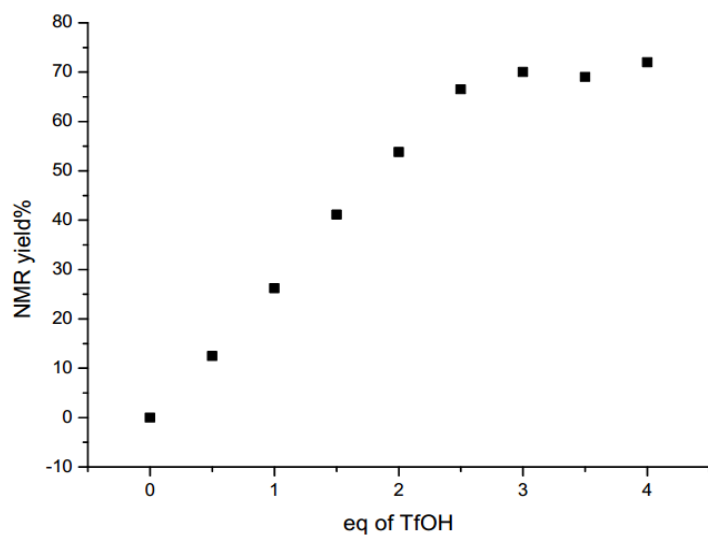
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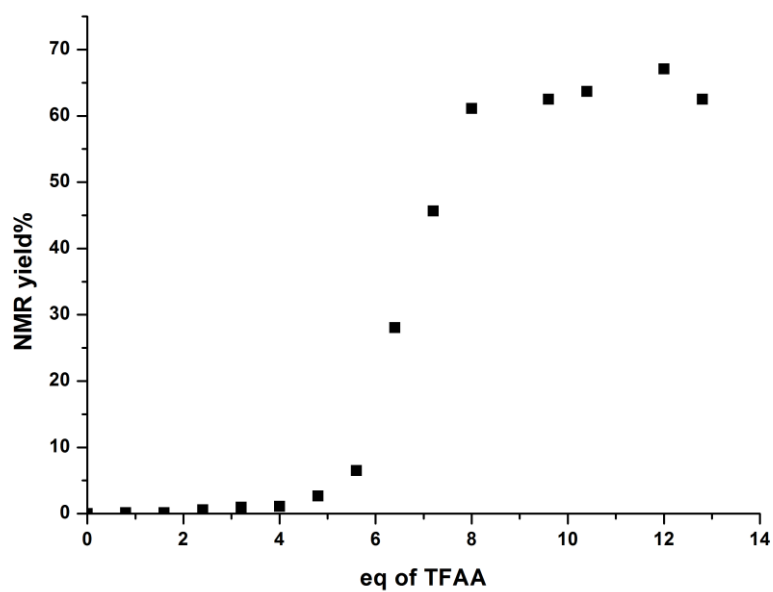
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<chem>c1ccccc1</chem> $\xrightarrow[80^\circ\text{C}, 9\text{h}]{\text{K}_2\text{S}_2\text{O}_8\ 1.0\text{eq}, \text{TFAA}\ 11\text{eq}, \text{TfOH}\ x\text{eq}, \text{DCE}\ 0.3\text{ml}}$ <chem>O=S(=O)(c1ccccc1)c2ccccc2</chem> 5.0eq									
eq of TfOH	0	0.5	1	1.5	2	2.5	3	3.5	4
NMR yield%	0	12.5	26.2	41.1	53.8	66.5	70	69	72



<chem>c1ccccc1</chem> $\xrightarrow[80^\circ\text{C}, 6\text{h}]{\text{K}_2\text{S}_2\text{O}_8\ 1.0\text{eq}, \text{TfOH}\ 4.0\text{eq}, \text{TFAA}\ x\text{eq}, \text{DCE}\ 0.3\text{ml}}$ <chem>O=S(=O)(c1ccccc1)c2ccccc2</chem> 5.0eq							
eq of TFAA	0	0.8	1.6	2.4	3.2	4	4.8
NMR yield%	0	0.16	0.14	0.57	0.97	1.1	2.67
eq of TFAA	5.6	6.4	7.2	8	9.6	10.4	12
NMR yield%	6.5	28.04	45.64	61.1	62.5	63.7	67.1

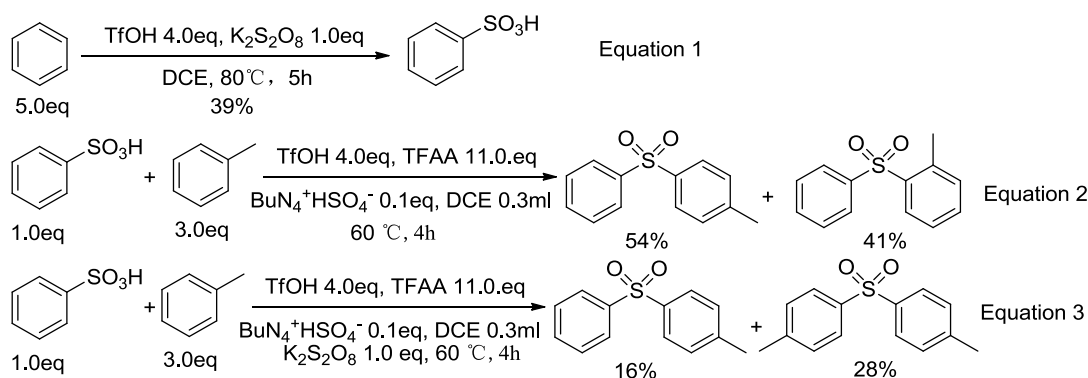


General procedure:

For symmetric diarylsulfones: $K_2S_2O_8$ (0.2 mmol, 54 mg), tetrabutylammonium hydrogen sulfate (0.1eq, 6.8mg), DCE 0.3 ml, arene(5.0eq) and TFAA (11eq, 0.3 ml) were added into a 10 ml sealed tube followed by adding TfOH (4.0 eq, 71 ul). The mixture was stirred at R.T or higher temperature for about 6 h. Then extract with dichloromethane (DCM) and wash it by water. The organic phase was purified by flash column chromatography to give the desired product.

For unsymmetric diarylsulfones: $K_2S_2O_8$ (0.2 mmol, 54 mg), tetrabutylammonium hydrogen sulfate (0.1eq, 6.8mg), DCE 0.3 ml, one of arenes (2.0 eq) and TfOH (4.0 eq, 71 ul) were added into a 10 ml sealed tube. After stirring at proper temperature for about 4 h, the other arene (3.0 eq) and TFAA (11eq, 0.3 ml) were added. The reaction was continued for another 4 h. Then extract with DCM and wash it by water. The organic phase was purified by flash column chromatography to give the desired product.

Mechanism study:



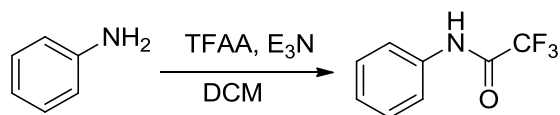
Equation 1: $K_2S_2O_8$ (0.2 mmol, 54 mg), DCE 0.3 ml, benzene (5 eq, 90 ul) and TfOH (5.0 eq, 90ul) were added into a 10 ml sealed tube. After stirring at 80 °C for 5 h, the mixture was transferred into a 50ml round-bottom flask to remove the solvent. Add CH_3COOK (0.2mmol) into the residual as an internal standard and dissolve with D_2O . The yield is 39% by NMR.

Equation 2: Benzenesulfonic acid (0.2mmol, 32mg), tetrabutylammonium hydrogen sulfate (0.1eq, 6.8mg), DCE 0.3 ml, toluene (3 eq, 48 ul), TfOH (4.0 eq, 72ul) and TFAA (11.0eq, 0.3ml) were added into a 10 ml sealed tube. After stirring at 60 °C for 4 h, the mixture was extracted with DCM and washed with water. After removing the solvent, add 4-nitrobenzaldehyde (0.1mmol) into the residual as an internal standard and dissolve with $CDCl_3$. The yield of **24** and its region isomer were 54% and is 41% respectively by NMR.

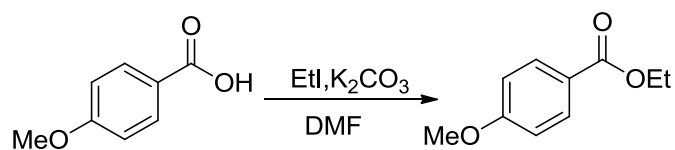
Equation 3: Benzenesulfonic acid (0.2mmol, 32mg), $K_2S_2O_8$ (1.0eq, 54 mg), tetrabutylammonium hydrogen sulfate (0.1eq, 6.8mg), DCE 0.3 ml, toluene (3 eq, 48 ul), TfOH (4.0 eq, 72ul) and TFAA (11.0eq, 0.3ml) were added into a 10 ml sealed tube. After stirring at 60 °C for 4 h, the mixture was extracted with DCM and washed with water. After removing the solvent, add 4-nitrobenzaldehyde (0.1mmol) into the residual as an internal standard and dissolve with $CDCl_3$. The yield calculated based on benzenesulfonic acid of **24** and **3** were 16% and 28% respectively by NMR.

All commercial materials (Alfa Aesar, Aladdin, J&K Chemical LTD.) were used without further purification. All solvents were analytical grade. The potassium persulfate were ground to powder. The melting points were measured on WRS-1B from Shanghai INESA Physico Optical Instrument Co., Ltd. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE^{III} 400 MHz spectrometer in CDCl_3 or d_6 -DMSO using TMS or solvent peak as a standard. All ^{13}C NMR spectra were recorded with complete proton decoupling. Low-resolution mass spectral analyses were performed with an Waters AQUITY UPLCTM/MS. Most reactions were carried out in sealed tube with Teflon cap or round-bottom flask. Analytical TLC was performed on Yantai Chemical Industry Research Institute silica gel 60 F254 plates and flash column chromatography was performed on Qingdao Haiyang Chemical Co. Ltd silica gel 60 (200-300mesh). The rotavapor was BUCHI's Rotavapor R-3.

Some substrates were prepared from simple arenes with simple reactions:



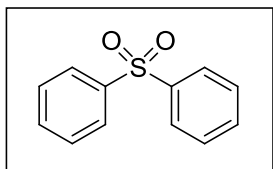
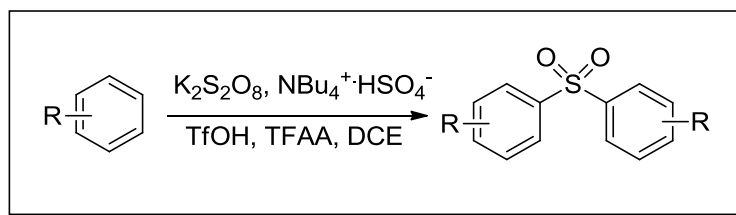
To a 100 ml round-bottom flask, was added aniline(20mmol,1.8ml), triethylamine(1.0eq, 2.8ml) and DCM 40 ml. TFAA (1.0eq, 2.8ml) was added dropwise to the mixture over 30min at ice bath. Then warm to room temperature and stir for about 4 hours. The mixture was washed by water and purified by column chromatography (Hexane : EtOAc = 5: 1 to 1:1) to get the desired product 3.6g (I.Y=95 %). It matched with the reported spectrum⁸.



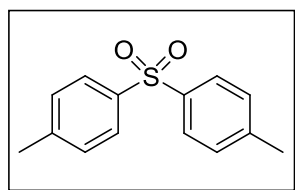
To a 100 ml round-bottom flask, was added 4-methoxybenzoic acid (10 mmol, 1.52 g), K_2CO_3 (1.0 eq, 1.4 g), iodoethane (1.5 eq, 1.7 ml) and DMF 20 ml. The mixture was stirred at 50 °C overnight. Then extracted with DCM, washed by water and purified by column chromatography (Hexane : EtOAc = 10:1) to get the desired product 1.6g (I.Y=90 %). It matched with the reported spectrum⁹.



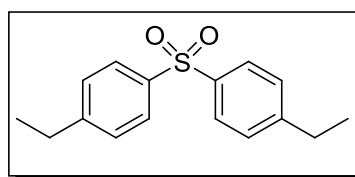
To a 50 ml round-bottom flask, was added 1-methyl-1H-pyrrole (20mmol, 1.8ml), TFAA (1.0eq, 2.8ml) and DCM 20 ml. TfOH (1.0eq, 1.8ml) was added dropwise to the mixture over 30min at ice bath. Then warm to room temperature and stir for about 6 hours. The mixture was washed by water and purified by column chromatography (Hexane : EtOAc = 15:1) to get the desired product 2g (I.Y=65%). It matched with the reported spectrum¹⁰.



Sulfonyldibenzene(2): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3 ml), benzene (1.0 mmol, 90 μl), TFAA (2.2 mmol, 306 μl) and TfOH (0.8 mmol, 71 μl) was added, the reaction was carried out at 80 $^\circ\text{C}$ for 6 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 15 : 1) to get 71mg product, which is a kind of white solid giving 81% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.94 (d, $J = 7.72$ Hz, 4H), 7.54 – 7.46 (m, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 141.59, 133.24, 129.31, 127.63; LRMS (ESI) calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 219.04, found 218.97. m.p. 124.0-124.2 $^\circ\text{C}$.

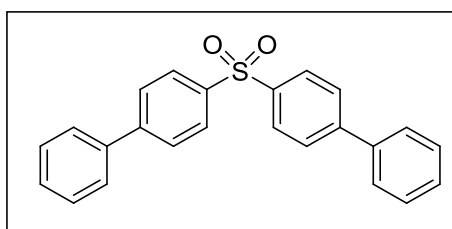
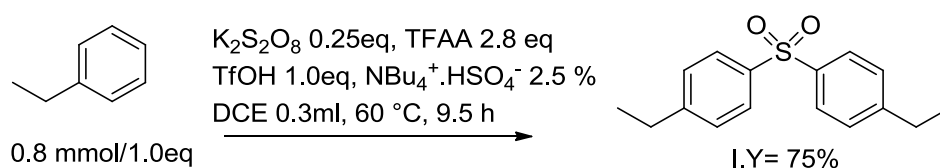


4,4'-sulfonylbis(methylbenzene)(3): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), toluene (1.0 mmol, 100 μl), TFAA (2.2 mmol, 300 μl) and TfOH (0.8 mmol, 71 μl) was added, the reaction was carried out at 60 $^\circ\text{C}$ for 7 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 69 mg 4,4'-sulfonylbis(methylbenzene) which is a kind of white solid with 71% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.80 (d, $J = 7.96$ Hz, 4H), 7.25 (d, $J = 7.72$ Hz, 4H), 2.35(s, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 143.92, 139.03, 129.83, 127.48, 21.48. LRMS (ESI) calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 247.07, found 247.18. m.p.150.8-153.7 $^\circ\text{C}$.

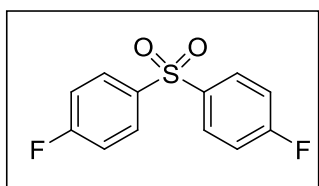


4,4'-sulfonylbis(ethylbenzene)(4): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), ethylbenzene (1.0 mmol, 123ul), TFAA (2.2 mmol, 300 ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 60 °C for 6 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 103 mg 4,4'-sulfonylbis(ethylbenzene) which is a kind of white solid with 87% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.84 (d, J = 8.12 Hz, 4H), 7.30 (d, J = 8.08 Hz, 4H), 2.67(q, J = 7.52 Hz, 4H), 1.22(t, J = 7.60 Hz, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 150.14, 139.33, 128.82, 127.80, 28.93, 15.19. LRMS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 275.10, found 275.20. m.p.90.4-90.6 °C.

If the condition was instead as follow, the isolated yield is 75%.

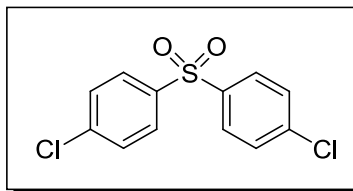


4,4'-sulfonyldibiphenyl(5): $\text{K}_2\text{S}_2\text{O}_8$ (0.3 mmol, 82 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.03 mmol, 10 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), biphenyl (1.5 mmol, 232mg), TFAA (2.7 mmol, 250 ul) and TfOH (1.3 mmol, 117 ul) was added, the reaction was carried out at 80 °C for 7 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 4 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 4 : 1) to get 222 mg 4,4'-sulfonyldibiphenyl which is a kind of white solid with 98% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 8.03 (d, J = 8.28 Hz, 4H), 7.71 (d, J = 8.24 Hz, 4H), 7.56 (d, J = 7.12 Hz, 4H), 7.47 – 7.40 (m, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 138.67, 136.02, 134.49, 134.11, 132.54, 129.88, 20.09, 19.54; LRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 371.10, found 371.19. m.p.211.2-214.5 °C.

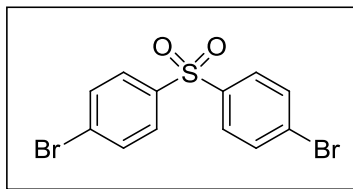


4,4'-sulfonylbis(fluorobenzene)(6): $\text{K}_2\text{S}_2\text{O}_8$ (0.3 mmol, 82 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.03 mmol, 10 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), fluorobenzene(500ul), Tf_2O (400 ul) and TfOH (0.6 mmol, 52 ul) was added, the

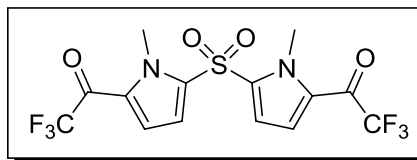
reaction was carried out at 80 °C for 11 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na₂SO₄, which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 137 mg 4,4'-sulfonylbis(fluorobenzene) which is a kind of white solid with 90% yield. ¹H-NMR (400 MHz, CDCl₃) δ (ppm) 7.97 (dd, *J* = 8.80 Hz, *J* = 5.08 Hz, 4H), 7.19 (t, *J* = 8.48 Hz, 4H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 164.47 (d, *J* = 254.51 Hz), 137.59 (d, *J* = 3.13 Hz), 130.44 (d, *J* = 9.54 Hz), 116.70 (d, *J* = 22.59 Hz) The spectrum data is in accordance with literature reported^[3]. m.p.93.0-96.9 °C.



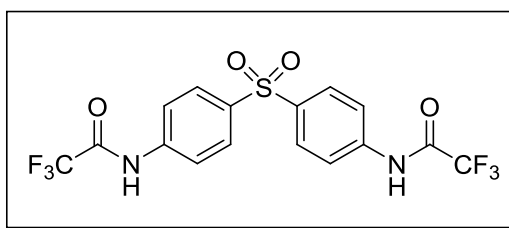
4,4'-sulfonylbis(chlorobenzene)(7): K₂S₂O₈ (0.2 mmol, 54 mg) and NBu₄⁺.HSO₄⁻ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), chlorobenzene(1.0 mmol, 100ul), TFAA (2.2 mmol, 300 ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 85 °C for 6 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na₂SO₄, which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 92 mg 4,4'-sulfonylbis(chlorobenzene) which is a kind of white solid with 73% yield. ¹H-NMR (400 MHz, CDCl₃) δ (ppm) 7.77 (d, *J* = 8.40 Hz, 4H), 7.37 (d, *J* = 8.40 Hz, 4H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 140.19, 139.77, 129.78, 129.16; The spectrum data is in accordance with literature reported^[1]. m.p.138.8-142.1 °C.



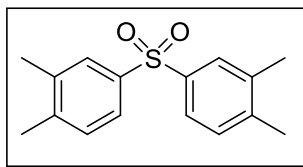
4,4'-sulfonylbis(bromobenzene)(8): K₂S₂O₈ (5 mmol, 1.35 g) and NBu₄⁺.HSO₄⁻ (0.3 mmol, 85 mg) was added into a 100ml sealed tube charged with a magnetic bar, following that, bromobenzene(30 mmol, 3.2 ml), TFAA (40 mmol, 5.6 ml) and TfOH (25 mmol, 2.2 ml) was added, the reaction was carried out at 85 °C for 8h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na₂SO₄, which was removed under reduced pressure. The residual was decolorization by activated carbon in acetone after column chromatography (Hexane : EtOAc = 10 : 1) to get 3.8 g 4,4'-sulfonylbis(bromobenzene) which is a kind of white solid with 98% yield. ¹H-NMR (400 MHz, CDCl₃) δ (ppm) 7.77 (d, *J* = 8.64 Hz, 4H), 7.64 (d, *J* = 8.56 Hz, 4H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 140.33, 132.88, 129.29, 128.93; The spectrum data is in accordance with literature reported^[2]. m.p.155.7-158.1 °C.



1,1'-(5,5'-sulfonylbis(1-methyl-1H-pyrrole-5,2-diyl))bis(2,2,2-trifluoroethanone)(9): $\text{K}_2\text{S}_2\text{O}_8$ (0.24 mmol, 65 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.024 mmol, 8.2 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 2,2,2-trifluoro-1-(1-methyl-1H-pyrrol-2-yl)ethanone (1.2 mmol, 220mg), TFAA (2.64 mmol, 367 ul) and TfOH (0.96 mmol, 85 ul) was added, the reaction was carried out at 60 °C for 5 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 5 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 5 : 1) to get 123 mg 1,1'-(5,5'-sulfonylbis(1-methyl-1H-pyrrole-5,2-diyl)) bis(2,2,2-trifluoroethanone) which is a kind of white solid with 61% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.56(s, 2H), 7.449(s, 2H), 4.00(s, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 171.33(q, J = 36.62 Hz), 134.44, 127.43, 125.69, 121.57(q, J = 4.09 Hz), 116.39(q, J = 288.44 Hz), 38.93. LRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{F}_6\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 417.03, found 417.03. m.p.193.7-195.4 °C.

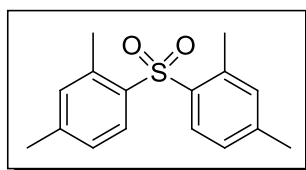


N,N'-(4,4'-sulfonylbis(4,1-phenylene))bis(2,2,2-trifluoroacetamide)(10): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 2,2,2-trifluoro-N-phenylacetamide (1.0 mmol, 190mg), TFAA (2.2 mmol, 300 ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 80 °C for 6 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 5 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 5 : 1) to get 109 mg N,N'-(4,4'-sulfonyl bis(4,1-phenylene))bis(2,2,2-trifluoroacetamide) which is a kind of white solid with 62% yield. $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ (ppm) 11.65(s, 2H), 8.00 (d, J = 8.68 Hz, 4H), 7.91 (d, J = 8.64 Hz, 4H); $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ (ppm) 154.90(q, J = 35.84 Hz), 141.00, 137.39, 128.65, 121.42, 115.50(q, J = 284.66 Hz). LRMS (ESI) calcd for $\text{C}_{16}\text{H}_9\text{F}_6\text{O}_4\text{S}$ $[\text{M}-\text{H}]^-$: 439.03, found 439.21. m.p.133.4-135.0 °C.



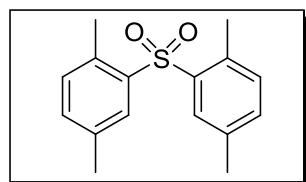
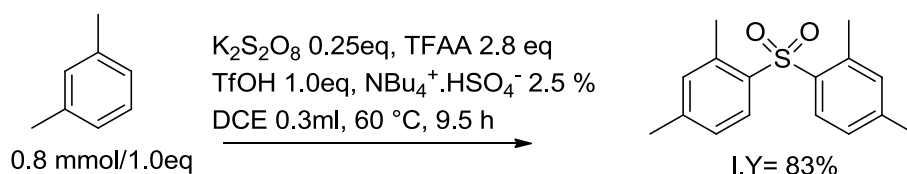
4,4'-sulfonylbis(1,2-dimethylbenzene)(11): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$

(0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), *o*-xylene (1.0 mmol, 121 μ l), TFAA (2.2 mmol, 300 μ l) and TfOH (0.8 mmol, 71 μ l) was added, the reaction was carried out at 50 $^{\circ}$ C for 7 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 4 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 4 : 1) to get 96 mg 4,4'-sulfonylbis(1,2-dimethylbenzene) which is a kind of white solid with 88% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.66 (m, 4H), 7.21 (d, J = 7.80 Hz, 2H), 2.25 (m, 12H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 142.60, 139.27, 137.98, 130.33, 128.22, 125.04, 19.91, 19.81; LRMS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 275.10, found 275.10. m.p.153.62-155.6 $^{\circ}$ C.



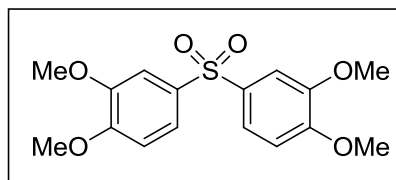
4,4'-sulfonylbis(1,3-dimethylbenzene)(12): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), *m*-xylene (1.0 mmol, 121 μ l), TFAA (2.2 mmol, 300 μ l) and TfOH (0.8 mmol, 71 μ l) was added, the reaction was carried out at 40 $^{\circ}$ C for 15 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 4 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 4 : 1) to get 101 mg 4,4'-sulfonylbis(1,3-dimethylbenzene) which is a kind of white solid with 92% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 8.05 (d, J = 8.12 Hz, 2H), 7.15 (d, J = 7.92 Hz, 2H), 7.00 (s, 2H), 2.33 (s, 6H), 2.28 (s, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 144.02, 137.38, 136.12, 133.19, 129.71, 126.54, 21.19, 19.79; LRMS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 275.10, found 275.10. m.p.115.6-119.3 $^{\circ}$ C.

If the condition was instead as follow, the isolated yield is 83%.

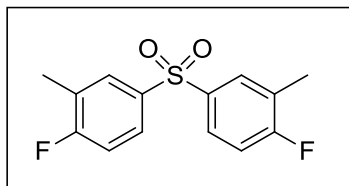


2,2'-sulfonylbis(1,4-dimethylbenzene)(13): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), *p*-xylene (1.0 mmol, 121 μ l), TFAA (2.2 mmol, 300 μ l) and TfOH (0.8 mmol, 71 μ l) was added, the reaction was carried out at 50 $^{\circ}$ C for 7 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 4 : 1 as the eluent), the reaction was quenched by

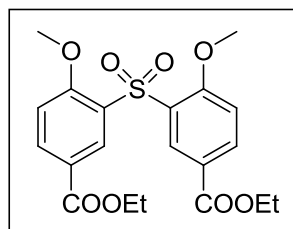
brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 4 : 1) to get 88 mg 2,2'-sulfonylbis(1,4-dimethylbenzene) which is a kind of white solid with 88% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 8.00 (s, 2H), 7.26 (d, J = 7.56 Hz, 2H), 7.08 (d, J = 7.68 Hz, 2H), 2.39 (s, 6H), 2.67 (s, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 138.67, 136.02, 134.49, 134.11, 132.54, 129.88, 20.09, 19.54; LRMS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 275.10, found 275.14. m.p.143.1-143.4 $^\circ\text{C}$.



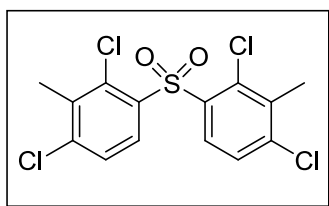
4,4'-sulfonylbis(1,2-dimethoxybenzene)(14): $\text{K}_2\text{S}_2\text{O}_8$ (0.3 mmol, 82 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.03 mmol, 10 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 1,2-dimethoxybenzene (1.8 mmol, 230 μl), TFAA (1.8 mmol, 250 μl) and TfOH (0.6 mmol, 52 μl) was added, the reaction was carried out at room temperature for 7 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 1 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 2 : 1) to get 190 mg 4,4'-sulfonylbis(1,2-dimethoxybenzene) which is a kind of white solid with 95% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.50 (d, J = 8.48 Hz, 2H), 7.34 (s, 2H), 6.88 (d, J = 8.48 Hz, 2H), 3.87 (s, 12H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 152.84, 149.25, 133.85, 121.49, 110.85, 109.68, 56.29, 56.21; LRMS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_6\text{S}$ $[\text{M}+\text{H}]^+$: 339.08.10, found 339.10. m.p.156.1-157.7 $^\circ\text{C}$.



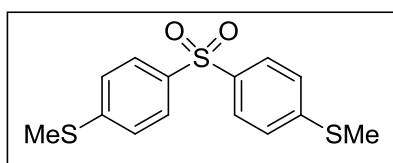
3,3'-sulfonylbis(1-fluoro-2-methylbenzene)(15): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 1-fluoro-2-methylbenzene (1.0 mmol, 110 μl), TFAA (2.2 mmol, 300 μl) and TfOH (0.8 mmol, 71 μl) was added, the reaction was carried out at 85 $^\circ\text{C}$ for 6 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 93 mg 3,3'-sulfonylbis(1-fluoro-2-methylbenzene) which is a kind of white solid with 83% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.81 – 7.77 (m, 4H), 7.11 (t, J = 8.80 Hz, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 164.03 (d, J = 252.74 Hz), 137.26 (d, J = 3.47 Hz), 131.21 (d, J = 6.71 Hz), 127.63 (d, J = 9.57 Hz), 126.83 (d, J = 18.55 Hz), 116.14 (d, J = 23.65 Hz), 14.55 (d, J = 3.36 Hz). m.p.100.9-103.2 $^\circ\text{C}$.



diethyl 3,3'-sulfonylbis(4-methoxybenzoate)(16): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), TFAA(300ul) and TfOH (1.0 mmol, 90 ul) was added, the reaction was carried out at 80 °C for 4h. After adding ethyl 4-methoxybenzoate (1.0mmol, 163ul), the reaction was running for another 5h. The reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 1 : 1) to get 123 mg diethyl 3,3'-sulfonylbis(4-methoxybenzoate) which is a kind of white solid with 78% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 8.81 (d, J = 2.04 Hz, 2H), 8.22(dd, J = 8.68Hz, J = 2.04 Hz, 2H), 6.91(d, J = 8.72 Hz, 2H), 4.38(q, J = 7.12 Hz, 1H), 3.71(s, 2H), 1.39(t, J = 7.12 Hz 3H),; ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 165.24, 160.39, 136.83, 133.02, 128.75, 122.92, 111.96, 61.35, 56.42, 14.47. LRMS (ESI) calcd for $C_{20}H_{23}O_8S$ $[M+H]^+$: 423.10, found 423.44. m.p.182.6-184.2 °C.

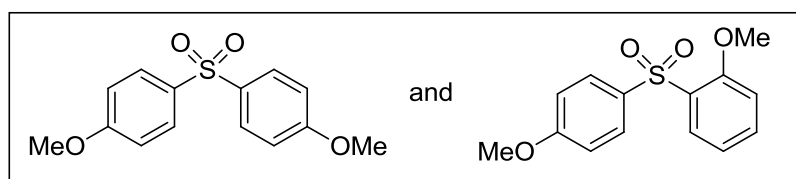


4,4'-sulfonylbis(1,3-dichloro-2-methylbenzene)(17): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 1,3-dichloro-2-methylbenzene (1.0 mmol, 128ul), TFAA (2.2 mmol, 300 ul) and TfOH (1.0 mmol, 89 ul) was added, the reaction was carried out at 90 °C for 7 h. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 92 mg 4,4'-sulfonylbis(1,3-dichloro-2- methylbenzene) which is a kind of white solid with 81% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (d, J = 8.46 Hz, 2H), 7.54 (d, J = 8.64 Hz, 4H), 2.45 (s, 6H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 141.46, 137.30, 136.63, 133.35, 130.77, 127.70, 17.77. m.p.165.2-167.6 °C.

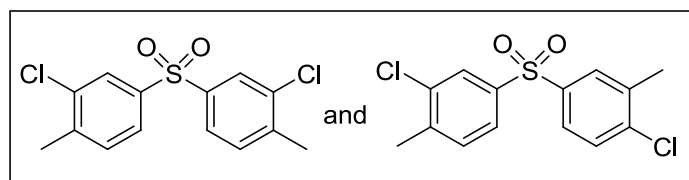


(sulfonylbis(4,1-phenylene))bis(methylsulfane)(18): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar,

following that, DCE (0.3ml), TFAA (2.2 mmol, 300 ul) and TfOH (0.8 mmol, 71 ul) was added, the mixture was stirred at 80 °C for 1 h. Add methyl(phenyl)sulfane (1.4 mmol, 165ul), stir for another 5 h at 50°C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 5 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na₂SO₄, which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 8 : 1) to get 97 mg (sulfonylbis(4,1-phenylene))bis(methylsulfane) which is a kind of white solid with 81% yield. ¹H-NMR (400 MHz, CDCl₃) δ (ppm) 7.78 (d, *J* = 8.12 Hz, 4H), 7.26 (d, *J* = 8.08 Hz, 4H), 2.47(s, 6H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 146.98, 137.96, 128.22, 125.98, 15.22. LRMS (ESI) calcd for C₁₄H₁₄O₂S₃ [M+H]⁺: 311.12, found 311.21. m.p.121.0-123.8 °C.

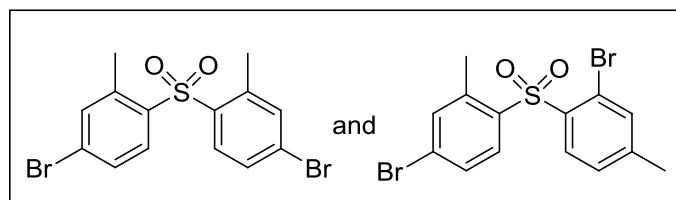


4,4'-sulfonylbis(methoxybenzene)(19a) and 1-methoxy-2-((4-methoxyphenyl)sulfonyl)benzene(19b): K₂S₂O₈ (0.3 mmol, 82 mg) and NBu₄⁺.HSO₄⁻ (0.03 mmol, 10 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, anisole (400 ul), TFAA (200 ul) and TfOH (0.6 mmol, 52 ul) was added, the reaction was carried out at 50 °C for 9 h. After observing obvious product spots on the TLC (Hexane : EtOAc = 4 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na₂SO₄, which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 4 : 1) to get 89 mg 4,4'-sulfonylbis(methoxybenzene) which is a kind of white solid with 53% yield and 47 mg 1-methoxy-2-((4-methoxyphenyl)sulfonyl)benzene which is also a kind of white solid with 28% yield at the same time. For 4, 4'-sulfonylbis(methoxybenzene) : ¹H-NMR (400 MHz, CDCl₃) δ (ppm) 7.82 (d, *J* = 8.96 Hz, 4H), 6.92 (d, *J* = 8.92 Hz, 4H), 3.80 (s, 6H) ; ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 163.14, 133.95, 129.31, 114.48, 55.67; LRMS (ESI) calcd for C₁₄H₁₅O₄S [M+H]⁺: 279.06, found 279.06. m.p.121.4-124.9 °C. For 1-methoxy-2-((4-methoxyphenyl)sulfonyl)benzene : ¹H-NMR (400 MHz, CDCl₃) δ (ppm) 8.12 (dd, *J* = 1.68 Hz, *J* = 7.88 Hz, 1H), 7.90 (d, *J* = 9.88 Hz, 2H), 7.50 (m, 1H), 7.07 (m, 1H), 7.50 (d, *J* = 9.84 Hz, 2H), 6.91(m, 1H) ; ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 163.29, 156.99, 135.30, 133.13, 130.77, 129.70, 129.66, 120.54, 113.77, 112.51, 55.97, 55.69; LRMS (ESI) calcd for C₁₄H₁₅O₄S [M+H]⁺: 279.06, found 279.06. m.p.122-124.3 °C.

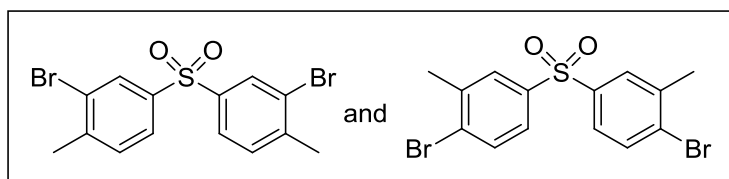


4,4'-sulfonylbis(2-chloro-1-methylbenzene)(20a) and 2-chloro-4-(4-chloro-3-methylphenylsulfonyl)-1-methylbenzene(20b): K₂S₂O₈ (0.2 mmol, 54 mg) and NBu₄⁺.HSO₄⁻ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 1-chloro-2-methylbenzene (1.0 mmol, 117 ul), TFAA (300 ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 70 °C for 6 h. After observing

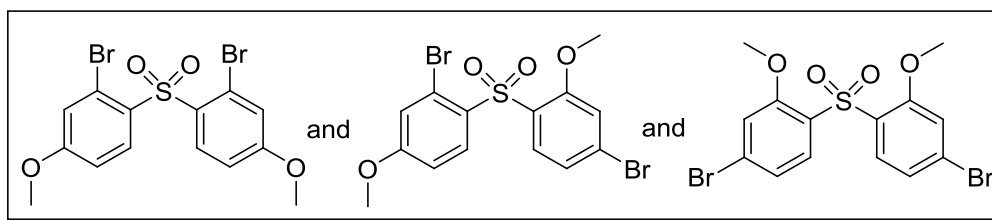
obvious product spots on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 59 mg 4,4'-sulfonylbis(2-chloro-1-methylbenzene) which is a kind of white solid with 47% yield and 40 mg 2-chloro-4-(4-chloro-3-methyl phenylsulfonyl)-1-methylbenzene which is also a kind of white solid with 32% yield at the same time. For 4,4'-sulfonylbis (2-chloro-1-methylbenzene) : $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.78 (s, 2H), 7.67 (dd, $J = 8.32$ Hz, $J = 1.60$ Hz, 2H), 7.45 (d, $J = 8.32$ Hz, 2H), 2.41 (s, 6H) ; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 140.30, 139.81, 138.04, 130.21, 129.88, 126.44, 20.32. m.p.110.9-113.3 $^\circ\text{C}$. For 2-chloro-4-(4-chloro-3-methylphenyl sulfonyl)-1-methyl benzene : $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.88 (s, 2H) , 7.78(s, 2H), 7.70(m, 4H), 7.46 (d, $J = 8.36$ Hz, 2H), 7.36 (d, $J = 8.00$ Hz, 2H), 2.42(s, 3H), 2.41(s, 3H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 142.55, 140.51, 140.39, 139.74, 138.09, 135.66, 131.91, 130.25, 129.94, 128.26, 126.50, 125.84, 20.47, 20.35. m.p.105.7-107.3 $^\circ\text{C}$.



4,4'-sulfonylbis(1-bromo-3-methylbenzene)(21a) and 2-bromo-1-(4-bromo-2-methyl phenylsulfonyl)-4-methylbenzene(21b): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 1-bromo-3-methylbenzene (121 μl), TFAA (300 μl) and TfOH (0.8 mmol, 71 μl) was added, the reaction was carried out at 80 $^\circ\text{C}$ for 6 h. After observing obvious product spots on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 99 mg 4,4'-sulfonylbis(1-bromo-3-methylbenzene) which is a kind of white solid with 55% yield and 66 mg 2-bromo-1-(4-bromo-2-methyl phenylsulfonyl)-4-methylbenzene which is also a kind of white solid with 38% yield at the same time. For 4,4'-sulfonylbis (1-bromo-3-methylbenzene)) : $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 8.01 (d, $J = 8.44$ Hz, 2H), 7.53 (d, $J = 8.48$ Hz, 2H), 7.39 (s, 2H), 2.29 (s, 6H) ; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 139.79, 137.66, 135.59, 131.40, 129.54, 128.70, 19.95. m.p.126.9-127.5 $^\circ\text{C}$; For 2-bromo-1-(4-bromo-2-methyl phenylsulfonyl)-4-methyl benzene : $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 8.25 (d, $J = 8.12$ Hz, 1H), 8.15 (d, $J = 8.48$ Hz, 1H), 7.53 (d, $J = 8.44$ Hz, 1H), 7.47 (s, 1H), 7.38 (s, 1H), 7.34 (d, $J = 8.12$ Hz, 1H), 2.40(s, 3H), 2.28(s, 3H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 146.36, 139.65, 137.16, 136.72, 136.17, 135.20, 133.20, 131.99, 129.27, 128.64, 128.47, 120.87, 21.26, 20.00. m.p.101.1-101.8 $^\circ\text{C}$.

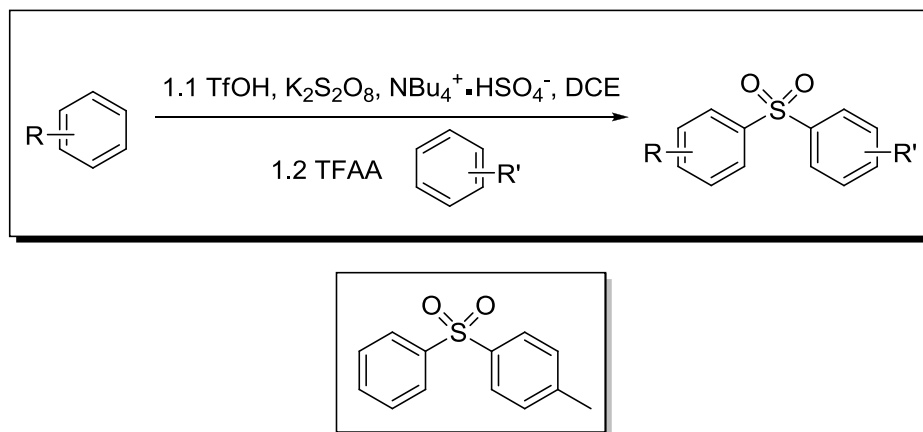


4,4'-sulfonylbis(2-bromo-1-methylbenzene)(22a) and 4,4'-sulfonylbis(1-bromo-2-methylbenzene)(22b): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 1-bromo-2-methylbenzene (121 ul), TFAA (300 ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 70 °C for 6 h. After observing obvious product spots on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 92 mg 4,4'-sulfonylbis(2-bromo-1-methylbenzene) which is a kind of white solid with 57% yield and 56 mg 4,4'-sulfonylbis(1-bromo-2-methylbenzene) which is also a kind of white solid with 35% yield at the same time. For 4,4'-sulfonylbis(2-bromo-1-methylbenzene) : 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 (d, J = 1.08 Hz, 2H), 7.65 (d, J = 8.48 Hz, 2H), 7.59 (dd, J = 8.46 Hz, J = 1.58 Hz, 2H), 2.43 (s, 6H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 140.46, 139.96, 133.57, 131.20, 129.50, 126.41, 29.80. m.p.1112-113.2 °C; For 2-bromo-1-(4-bromo-2-methyl phenylsulfonyl)-4-methylbenzene : 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07 (s, 2H), 7.75 (d, J = 8.00 Hz, 2H), 7.36 (d, J = 7.96 Hz, 2H), 2.44(s, 6H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 144.33, 140.30, 131.55, 131.33, 126.41, 125.61, 23.21. m.p.104.5-105.0 °C.

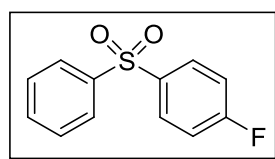


4,4'-sulfonylbis(3-bromo-1-methoxybenzene)(23a), 2-bromo-1-(4-bromo-2-methoxy phenylsulfonyl)-4-methoxybenzene(23b) and 4,4'-sulfonylbis(1-bromo-3-methoxy benzene)(23c): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 1-bromo- 3-methoxybenzene (1.0 mmol, 126 ul), TFAA (300 ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at r.t. for 6 h. After observing obvious product spots on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 70 mg 4,4'-sulfonylbis(3-bromo-1-methoxybenzene) which is a kind of white solid with 40% yield, 53 mg 2-bromo-1-(4-bromo-2-methoxyphenyl sulfonyl)-4-methoxybenzene which is a kind of white solid with 30% yield and 28mg 4,4'-sulfonylbis(1-bromo-3-methoxy which is also a kind of white solid with 16% yield at the same time. For 4,4'- sulfonylbis(3-bromo-1-methoxybenzene) : 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 8.41 (d, J = 8.92 Hz, 2H), 7.12(d, J = 2.04 Hz, 2H), 6.99 (dd, J = 8.96 Hz, J = 2.04 Hz, 2H), 3.85 (s, 6H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 163.74, 135.40, 130.93, 121.95, 120.57, 112.59, 56.08; LRMS (ESI) calcd for $C_{14}H_{13}Br_2N_2O_4S$ $[M+H]^+$: 434.88, found 435.03. m.p.123.5-126.1 °C. For 2-bromo-1-(4-bromo-2-methoxyphenyl sulfonyl)-4-methoxy benzene : 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22 (d, J = 8.92 Hz, 1H), 8.02(d, J = 8.44 Hz, 1H), 7.20(d, J = 9.88 Hz, 1H), 7.03 (d, J = 2.24 Hz, 1H), 6.96 (s, 1H), 6.91(dd, J = 8.92 Hz, J = 2.24 Hz, 1H), 3.79(s, 3H), 3.60(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 163.57, 157.25, 134.42, 133.10,

131.81, 129.92, 127.17, 123.66, 121.89, 120.25, 116.02, 112.74, 56.41, 56.06. LRMS (ESI) calcd for $C_{14}H_{13}Br_2N_2O_4S$ $[M+H]^+$: 434.88, found 435.03. m.p.144.2-145.4 °C. For 4,4'-sulfonylbis (1-bromo-3-methoxy) : 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, J = 8.40 Hz, 2H), 7.67 (d, J = 7.60 Hz, 2H), 6.96 (s, 2H), 3.62 (s, 6H) ; ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 157.51, 132.44, 129.66, 127.97, 123.57, 115.98, 56.47. LRMS (ESI) calcd for $C_{14}H_{13}Br_2N_2O_4S$ $[M+H]^+$: 434.88, found 435.03. m.p.202.6-205.7 °C.



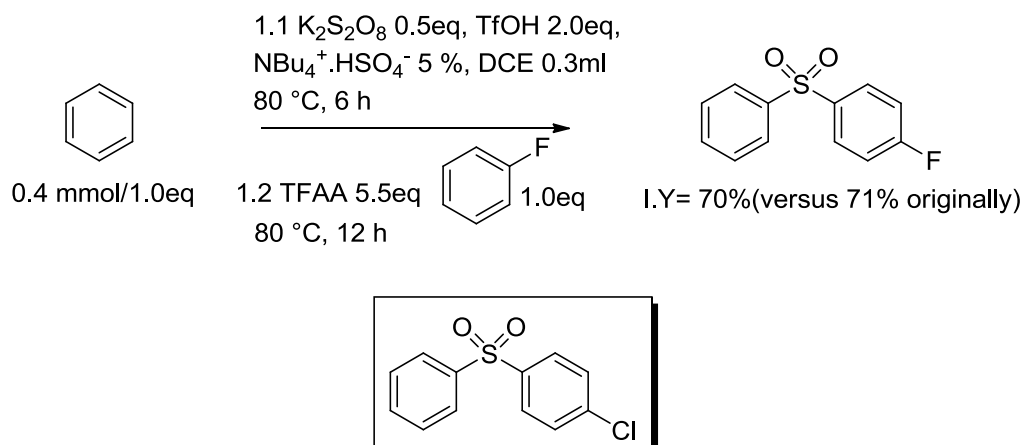
1-methyl-4-(phenylsulfonyl)benzene(24): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), toluene (0.4 mmol, 36ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 50 °C for 5h. Then TFAA(300ul) and benzene (0.6 mmol, 64ul) were added, stirring for another 5h at 40°C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 52 mg 1-methyl-4-(phenylsulfonyl)benzene which is a kind of white solid with 56% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, J = 7.72Hz, 2H), 7.36(d, J = 7.60Hz, 2H), 7.50(m, 3H), 7.28(d, J = 7.76 Hz, 2H), 2.37(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 144.23, 142.03,138.69, 133.06, 129.97, 129.33, 127.67, 127.57, 21.58. LRMS (ESI) calcd for $C_{13}H_{13}O_2S$ $[M+H]^+$: 233.06, found 233.24. m.p.104.4-108.7 °C.



1-fluoro-4-(phenylsulfonyl)benzene(25): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), benzene (0.4 mmol, 36ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 80 °C for 5h. Then TFAA(300ul) and fluorobenzene (0.6 mmol, 64ul) were added, stirring for another 5h at 80°C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 67 mg 1-fluoro-4-(phenylsulfonyl)benzene which is a kind of white solid

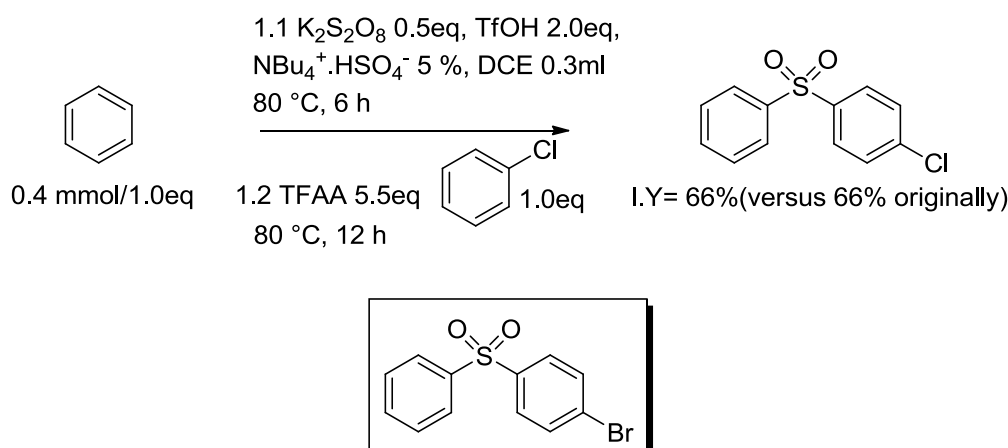
with 71% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.94 – 7.92 (m, 4H), 7.36(t, $J = 7.36\text{Hz}$, 1H), 7.51(t, $J = 7.20\text{ Hz}$, 2H), 7.17(t, $J = 8.24\text{ Hz}$, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 165.56(d, $J_{\text{C-F}} = 254.36\text{ Hz}$), 141.59, 137.85(d, $J_{\text{C-F}} = 3.07\text{ Hz}$), 133.44, 130.58(d, $J_{\text{C-F}} = 9.51\text{ Hz}$), 129.49, 127.68, 116.71(d, $J_{\text{C-F}} = 22.56\text{ Hz}$). The spectrum data is in accordance with literature reported^[6]. m.p.112.1-112.4 °C.

If the condition was instead as follow, the isolated yield is 70%.

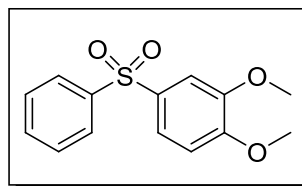
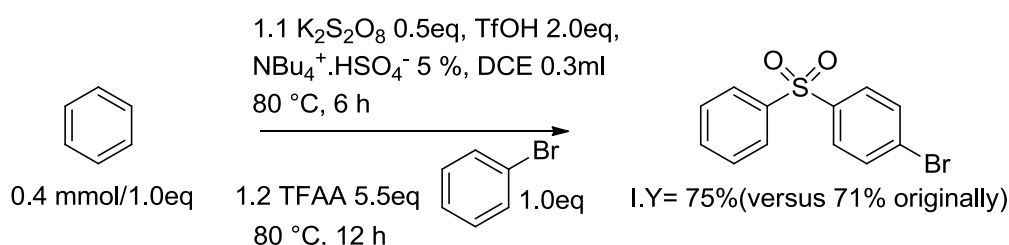


1-chloro-4-(phenylsulfonyl)benzene(26): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), benzene (0.4 mmol, 36ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 80 °C for 6h. Then TFAA(300ul) and chlorobenzene (0.6 mmol, 62ul) were added, stirring for another 10h at 80°C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 55 mg 1-chloro-4-(phenylsulfonyl)benzene which is a kind of white solid with 60% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.92 (d, $J = 8.00\text{ Hz}$, 2H), 7.87(d, $J = 8.24\text{Hz}$, 2H), 7.57(t, $J = 7.24\text{ Hz}$, 1H), 7.52 – 7.45(m, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 141.31, 140.26, 139.98, 133.54, 129.71, 129.52, 129.22, 127.54. The spectrum data is in accordance with literature reported^[4]. m.p.155.1-158.0 °C.

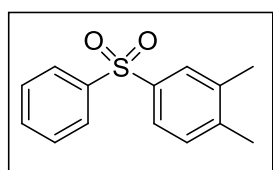
If the condition was instead as follow, the isolated yield is 66%.



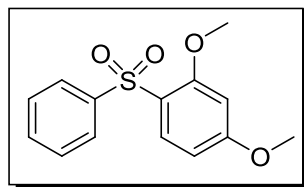
1-bromo-4-(phenylsulfonyl)benzene(27): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), benzene (0.4 mmol, 36ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 80 °C for 6h. Then TFAA(300ul) and bromobenzene (0.6 mmol, 63ul) were added ,stirring for another 10h at 80°C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 84 mg 1-bromo-4-(phenylsulfonyl)benzene which is a kind of white solid with 71% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, J = 7.76 Hz, 2H), 7.89(d, J = 7.52Hz, 2H), 7.62 (d, J = 6.76 Hz, 2H), 7.56(t, J = 6.48 Hz, 1H), 7.53(d, J = 6.80 Hz, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 141.24, 140.79, 133.58, 132.71, 129.54, 129.30, 128.55, 127.75. The spectrum data is in accordance with literature reported^[5]. m.p.108.0-1110.1 °C. If the condition was instead as follow, the isolated yield is 75%.



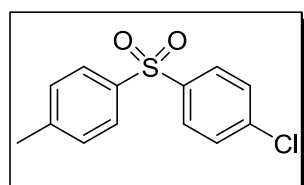
1,2-dimethoxy-4-(phenylsulfonyl)benzene(28): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), benzene (0.4 mmol, 36ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 80 °C overnight. Then TFAA(300ul) and 1,2-dimethoxybenzene (0.6 mmol, 76ul) were added ,stirring for another 5h at room temperature. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 70 mg 1,2-dimethoxy-4-(phenylsulfonyl)benzene which is a kind of white solid with 63% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, J = 7.44 Hz, 2H), 7.56 – 7.45 (m, 4H), 7.37(s, 1H), 6.91(d, J = 8.48 Hz, 1H), 3.89(s, 6H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 153.16, 149.38, 142.37, 133.19, 132.97, 129.30, 127.34, 122.02, 110.98, 110.04, 56.35, 56.29. LRMS (ESI) calcd for $C_{14}H_{15}O_4S$ $[M+H]^+$: 279.06, found 278.96. m.p.114.8-115.7 °C.



1,2-dimethyl-4-(phenylsulfonyl)benzene(29): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), benzene (0.6 mmol, 54ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 85 °C for 6h. Then TFAA(300ul) and 1,2-dimethylbenzene (0.4 mmol, 49ul) were added ,stirring for another 3h at 40°C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 75 mg 1,2-dimethyl-4-(phenylsulfonyl)benzene which is a kind of white solid with 76% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, J = 7.00 Hz, 2H), 7.69 – 7.66 (m, 2H), 7.53 – 7.51 (m, 3H), 7.24(d, J = 7.44 Hz, 2H), 2.28(s, 6H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 143.01, 142.16, 138.77, 138.18, 133.01, 130.48, 129.27, 128.48, 127.52, 125.31, 20.03, 19.90. LRMS (ESI) calcd for $C_{14}H_{15}O_2S$ $[M+H]^+$: 247.07, found 247.01. m.p.107.8-111.2 °C.

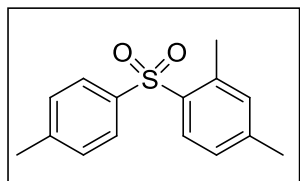


2,4-dimethoxy-1-(phenylsulfonyl)benzene(30): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), benzene (0.4 mmol, 36ul) and TfOH (0.8 mmol, 71 ul) was added, the reaction was carried out at 80 °C overnight. Then TFAA(300ul) and 1,3-dimethoxybenzene (0.6 mmol, 76ul) were added ,stirring for another 5h at room temperature. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 59 mg 2,4-dimethoxy-1-(phenylsulfonyl)benzene which is a kind of white solid with 53% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (d, J = 8.80 Hz, 1H), 7.92 (d, J = 7.92 Hz, 2H), 7.52(t, J = 7.40 Hz, 1H), 7.45(t, J = 7.12 Hz, 2H), 6.57(d, J = 7.92 Hz, 2H), 6.37(s, 1H), 3.82(s, 3H), 3.71(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 165.75, 158.75, 142.22, 132.71, 131.81, 128.54, 128.16, 121.43, 104.77, 99.55, 55.94, 55.84. LRMS (ESI) calcd for $C_{14}H_{15}O_4S$ $[M+H]^+$: 279.06, found 278.96. m.p.118.3-118.9 °C.

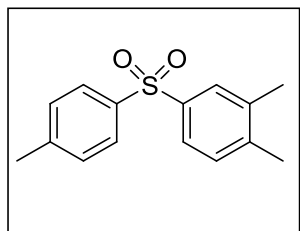


1-chloro-4-tosylbenzene(31): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), toluene (0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 50 °C for 4h. Then TFAA(300ul) and chlorobenzene (0.6 mmol, 62ul) were added ,stirring for another 3h at 70°C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1

as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 71 mg 1-chloro-4-tosylbenzene which is a kind of white solid with 66% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.85 (d, J = 8.32 Hz, 2H), 7.80 (d, J = 8.00 Hz, 2H), 7.44 (d, J = 8.32 Hz, 2H), 7.29(d, J = 8.00 Hz, 2H), 2.39(s, 3H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 144.60, 140.66, 139.72, 138.34, 130.13, 129.62, 129.06, 127.79. The spectrum data is in accordance with literature reported^[4]. m.p.119.1-120.0 °C.

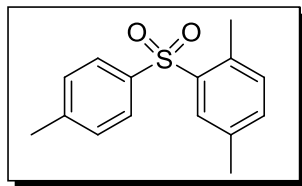


2,4-dimethyl-1-tosylbenzene(32): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), toluene (0.4 mmol, 43ul) and TfOH (1.1 mmol, 100 ul) was added, the reaction was carried out at 50 °C for 6h. Then TFAA(300ul) and 1,3-dimethylbenzene (0.6 mmol, 62ul) were added ,stirring overnight at room temperature.. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 80 mg 2,4-dimethyl-1-tosylbenzene which is a kind of white solid with 77% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 8.07 (d, J = 8.08 Hz, 1H), 7.43 (d, J = 8.16 Hz, 2H), 7.26 (d, J = 7.96 Hz, 2H), 7.16(d, J = 8.04 Hz, 1H), 7.02(s, 1H), 2.40(s, 3H), 2.38(s, 3H), 2.34(s,3H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 144.32, 143.79, 138.76, 137.73, 136.34, 133.40, 129.64, 129.51, 127.63, 127.08, 21.58, 21.35, 20.13. LRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 261.09, found 261.17. m.p.46.1-48.2 °C.

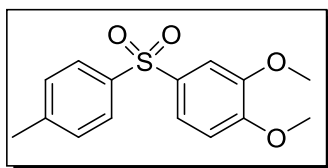


1,2-dimethyl-4-tosylbenzene(33): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), toluene (0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 60 °C for 4h. Then TFAA(300ul) and 1,2-dimethylbenzene (0.6 mmol, 64ul) were added ,stirring for another 4h at room temperature.. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 84 mg 1,2-dimethyl-4-tosylbenzene which is a kind of white solid with 81% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.80 (d, J = 8.16 Hz, 2H), 7.67 (s, 1H), 7.65 (d, J = 8.04 Hz, 1H), 7.27(d, J = 8.00 Hz, 2H), 7.23(d, J = 7.84 Hz, 1H), 2.38(s, 3H),

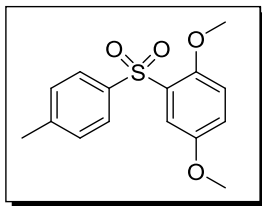
2.27(s,6H); ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm) 143.92, 142.76, 139.32, 139.26, 138.11, 130.44, 129.92, 128.39, 127.63, 125.19, 21.63, 20.02, 19.91. LRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 261.09, found 261.17. m.p.121.2-123.0 $^{\circ}\text{C}$ ^[20].



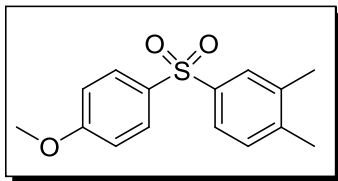
1,4-dimethyl-2-tosylbenzene(34): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), toluene (0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 60 $^{\circ}\text{C}$ for 4h. Then TFAA(300ul) and 1,4-dimethylbenzene (0.6 mmol, 74ul) were added ,stirring overnight at room temperature.. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 61 mg 1,4-dimethyl-2-tosylbenzene which is a kind of white solid with 58% yield. ^1H -NMR (400 MHz, CDCl_3) δ (ppm) 8.02 (s, 1H), 7.73 (d, J = 8.12 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.08(d, J = 7.68 Hz, 1H), 2.40(s, 3H), 2.37(s, 6H); ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm) 143.89, 138.80, 138.57, 136.42, 134.72, 134.23, 132.63, 129.66, 129.61, 127.69, 21.59, 20.93, 19.73. LRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 261.09, found 261.17. m.p.104.0-105.7 $^{\circ}\text{C}$.



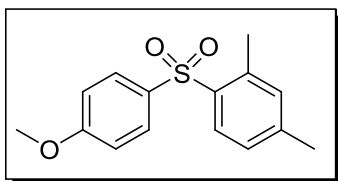
1,2-dimethoxy-4-tosylbenzene(35): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), toluene(0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 60 $^{\circ}\text{C}$ for 4h. Then TFAA(300ul) and 1,2-dimethoxybenzene (0.6 mmol, 76ul) were added ,stirring for another 4h at room temperature. After observing an obvious product spot on the TLC (Hexane : EtOAc = 5 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 77 mg 1,2-dimethoxy-4-tosylbenzene which is a kind of white solid with 66% yield. ^1H -NMR (400 MHz, CDCl_3) δ (ppm) 7.81 (d, J = 7.80 Hz, 2H), 7.55 (d, J = 8.24 Hz, 1H), 7.38(s, 1H), 7.28(d, J = 7.68 Hz, 2H), 6.92(d, J = 7.68 Hz, 1H), 3.90(s, 6H), 2.38(s, 3H); ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm) 152.97, 149.30, 143.86, 139.39, 133.58, 129.90, 127.36, 121.76, 110.92, 109.88, 56.29, 56.24, 21.56. LRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 293.08, found 293.16. m.p.127.2-130.6 $^{\circ}\text{C}$.



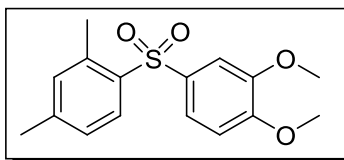
1,4-dimethoxy-2-tosylbenzene(36): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), toluene(0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 60 °C for 4h. Then TFAA(300ul) and 1,4-dimethoxybenzene (0.6 mmol, 83mg) were added ,stirring for another 4h at room temperature. After observing an obvious product spot on the TLC (Hexane : EtOAc = 5 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 76 mg 1,4-dimethoxy-2-tosylbenzene which is a kind of white solid with 65% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, J = 8.16 Hz, 2H), 7.67 (d, J = 3.04 Hz, 1H), 7.27(s, 1H), 7.28(d, J = 8.08 Hz, 2H), 7.05(dd, J = 9.00 Hz, J = 3.08 Hz, 1H), 6.83(d, J = 9.00 Hz, 1H), 3.83(s, 3H), 3.70(s, 3H), 2.40(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 153.26, 151.17, 143.86, 138.47, 129.87, 129.13, 128.41, 121.39, 114.35, 113.83, 56.52, 56.07, 21.56. LRMS (ESI) calcd for $C_{15}H_{17}O_4S$ $[M+H]^+$: 293.08, found 293.16. m.p.84.3-86.1 °C.



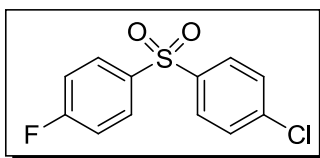
4-(4-methoxyphenylsulfonyl)-1,2-dimethylbenzene(37): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), anisole(0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at room temperature for 4h. Then TFAA(300ul) and *o*-xylene (0.6 mmol, 73ul) were added ,stirring overnight at room temperature. After observing an obvious product spot on the TLC (Hexane : EtOAc = 5 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 59 mg 4-(4-methoxyphenylsulfonyl)-1,2-dimethylbenzene which is a kind of white solid with 54% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (d, J = 8.44 Hz, 2H), 7.66 (s, 1H), 7.63(d, J = 8.16 Hz, 1H), 7.21(d, J = 7.88 Hz, 1H), 6.94(d, J = 8.44 Hz, 2H), 3.82(s, 3H), 2.28(s, 6H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 163.28, 142.58, 139.66, 138.09, 133.84, 130.43, 129.78, 128.22, 125.01, 114.53, 55.72, 20.01, 19.92. LRMS (ESI) calcd for $C_{15}H_{17}O_3S$ $[M+H]^+$: 277.08, found 277,22. m.p.75-76 °C.



1-(4-methoxyphenylsulfonyl)-2,4-dimethylbenzene(38): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), anisole(0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at room temperature for 4h. Then TFAA(300ul) and *o*-xylene (0.6 mmol, 73ul) were added ,stirring overnight at room temperature. After observing an obvious product spot on the TLC (Hexane : EtOAc = 5 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 60 mg 1-(4-methoxyphenylsulfonyl)-2,4-dimethylbenzene which is a kind of white solid with 55% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (d, J = 8.04 Hz, 1H), 7.77 (d, J = 8.72 Hz, 2H), 7.15(d, J = 8.00 Hz, 1H), 7.01(s, 1H), 6.93(d, J = 8.72 Hz, 1H), 3.82(s, 3H), 2.40(s, 3H), 2.33(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 163.16, 144.18, 137.60, 133.42, 133.25, 129.85, 129.37, 127.08, 114.27, 55.71, 21.36, 21.14. LRMS (ESI) calcd for $C_{15}H_{17}O_3S$ $[M+H]^+$: 277.08, found 277,15. m.p.124.7-125.8 $^{\circ}C$.

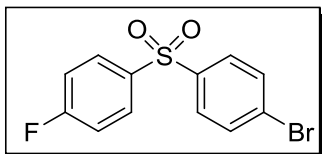


1-(3,4-dimethoxyphenylsulfonyl)-2,4-dimethylbenzene(39): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), *m*-xylene(0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at room temperature for 4h. Then TFAA(300ul) and 1,2-dimethoxybenzene (0.6 mmol, 73ul) were added ,stirring overnight at room temperature. After observing an obvious product spot on the TLC(Hexane : EtOAc = 5 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 86 mg 1-(3,4-dimethoxyphenyl sulfonyl)-2,4-dimethylbenzene which is a kind of white solid with 71% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J = 8.08 Hz, 1H), 7.44 (d, J = 8.36 Hz, 1H), 7.30(s, 1H), 7.15(d, J = 8.04 Hz, 1H), 7.02(s, 1H), 6.89(d, J = 8.48 Hz, 1H), 3.89(s, 3H), 3.87(s, 3H), 2.42(s, 3H), 2.34(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 152.85, 149.11, 144.21, 137.65, 136.65, 133.47, 133.31, 129.35, 127.10, 121.84, 110.65, 110.10, 56.30, 56.27, 21.37, 20.19. LRMS (ESI) calcd for $C_{16}H_{19}O_4S$ $[M+H]^+$: 307.09, found 307.19. m.p.118.5-120.7 $^{\circ}C$.

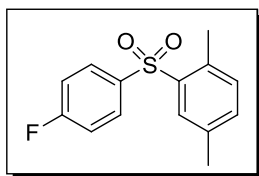


1-chloro-4-(4-fluorophenylsulfonyl)benzene(40): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), fluorobenzene (0.4 mmol, 38ul) and TfOH (1.0 mmol, 88 ul) was added, the reaction was carried out at 80 $^{\circ}C$ for 4h. Then TFAA(300ul) and fluorobenzene (0.6 mmol, 64ul) were added, stirring overnight at 60 $^{\circ}C$. After observing an obvious product spot on

the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 72 mg 1-chloro-4-(4-fluorophenylsulfonyl)benzene which is a kind of white solid with 66% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.94 (dd, $J = 7.84\text{Hz}$, $J = 5.28\text{Hz}$ 2H), 7.85(d, $J = 8.16\text{Hz}$, 2H), 7.29(d, $J = 8.24\text{ Hz}$, 1H), 7.18(t, $J = 8.48\text{ Hz}$, 2H), 7.13(d, $J = 8.28\text{ Hz}$, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 165.66(d, $J_{\text{C-F}} = 255.12\text{ Hz}$), 140.14, 140.10, 137.38(d, $J_{\text{C-F}} = 3.14\text{ Hz}$), 130.60(d, $J_{\text{C-F}} = 9.50\text{ Hz}$), 129.81, 129.14, 116.86(d, $J_{\text{C-F}} = 23.46\text{ Hz}$). m.p.110.2-111.0 $^\circ\text{C}$.

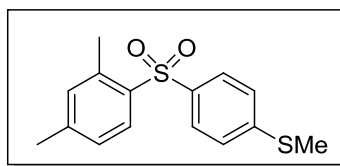


1-bromo-4-(4-fluorophenylsulfonyl)benzene(41): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), bromobenzene (0.4 mmol, 43ul) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 80 $^\circ\text{C}$ for 5h. Then TFAA(300ul) and fluorobenzene (0.6 mmol, 64ul) were added, stirring for another 3h at 80 $^\circ\text{C}$. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 107 mg 1-bromo-4-(4-fluorophenylsulfonyl)benzene which is a kind of white solid with 86% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.94 (dd, $J = 7.60\text{ Hz}$, $J = 5.32\text{Hz}$, 2H), 7.85(d, $J = 7.96\text{Hz}$, 2H), 7.63(d, $J = 8.00\text{ Hz}$, 1H), 7.18(t, $J = 8.20\text{ Hz}$, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) 165.69(d, $J_{\text{C-F}} = 255.12\text{ Hz}$), 140.65, 137.35(d, $J_{\text{C-F}} = 3.12\text{ Hz}$), 132.82, 130.62(d, $J_{\text{C-F}} = 9.58\text{ Hz}$), 129.22, 128.73, 116.89(d, $J_{\text{C-F}} = 23.36\text{ Hz}$). m.p.101.5-102.2 $^\circ\text{C}$.

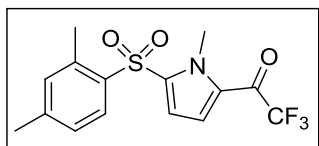


2-(4-fluorophenylsulfonyl)-1,4-dimethylbenzene(42): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), p-xylene (0.4 mmol, 50ul) and TfOH (1.0 mmol, 89 ul) was added, the reaction was carried out at 40 $^\circ\text{C}$ for 5h. Then TFAA(300ul) and fluorobenzene (0.6 mmol, 57ul) were added, stirring for another 5h at 80 $^\circ\text{C}$. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 64 mg 2-(4-fluorophenylsulfonyl)-1,4-dimethylbenzene which is a kind of white solid with 60% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) 8.02 (s, 1H), 7.88(dd, $J = 8.36\text{Hz}$, $J = 5.16\text{Hz}$ 2H), 7.29(d, $J = 7.52\text{ Hz}$, 1H), 7.17(t, $J = 8.48\text{ Hz}$, 2H), 7.13(d, $J = 7.76\text{ Hz}$,

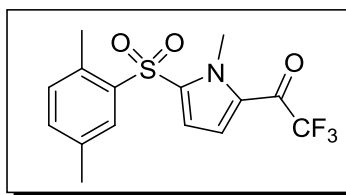
1H), 2.41(s, 3H), 2.38(s, 3H); ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm) 165.32(d, $J_{\text{C-F}} = 253.12$ Hz), 138.35, 137.62(d, $J_{\text{C-F}} = 3.09$ Hz), 136.70, 134.77, 134.60, 132.81, 130.49(d, $J_{\text{C-F}} = 9.43$ Hz), 129.75, 116.38(d, $J_{\text{C-F}} = 22.24$ Hz), 20.98, 19.79. m.p. 109.7-111.3 $^{\circ}\text{C}$.



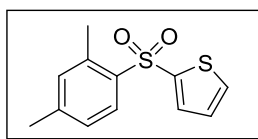
4-((2,4-dimethylphenyl)sulfonyl)phenyl(methyl)sulfane(43): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), *m*-xylene (0.4 mmol, 52ul), TfOH (1.0 mmol, 90 ul) and TFAA(300ul) were added, the reaction was carried out at 50 $^{\circ}\text{C}$ for 1h. Then methyl(phenyl)sulfane (0.8 mmol, 94ul) were added, stirring 6 h at room temperature. After observing an obvious product spot on the TLC (Hexane : EtOAc = 8 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 10 : 1) to get 80 mg 4-((2,4-dimethylphenyl)sulfonyl)phenyl(methyl)sulfane which is a kind of white solid with 53% yield. ^1H -NMR (400 MHz, CDCl_3) δ (ppm) 8.06 (d, $J = 8.08$ Hz, 1H), 7.72 (d, $J = 8.40$ Hz, 2H), 7.25(d, $J = 8.36$ Hz, 2H), 7.01(s, 1H), 7.17(d, $J = 8.00$ Hz, 1H), 7.02(s, 1H), 2.47(s, 3H), 2.40 (s, 3H), 2.34(s, 3H); ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm) 146.17, 144.40, 137.63, 137.21, 136.16, 133.41, 129.43, 127.88, 127.11, 125.20, 20.13, 14.73. LRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 293.06, found 293.32. m.p. 93.1-95.2 $^{\circ}\text{C}$.



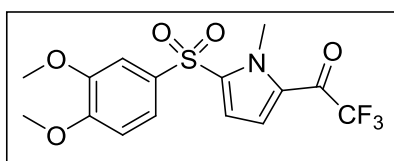
1-(5-(2,4-dimethylphenylsulfonyl)-1-methyl-1H-pyrrol-2-yl)-2,2,2-trifluoroethanone(44): $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 54 mg) and $\text{NBu}_4^+.\text{HSO}_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 2,2,2-trifluoro-1-(1-methyl-1H-pyrrol-2-yl)ethanone (0.6 mmol, 107mg) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 50 $^{\circ}\text{C}$ overnight. Then TFAA(300ul) and *m*-xylene (0.4 mmol, 51ul) were added, stirring for another 3h at 40 $^{\circ}\text{C}$. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 89 mg 1-(5-(2,4-dimethylphenylsulfonyl)-1-methyl-1H-pyrrol-2-yl)-2,2,2-trifluoroethanone which is a kind of white solid with 65% yield. ^1H -NMR (400 MHz, CDCl_3) δ (ppm) 7.98 (dd, $J = 8.08$ Hz, $J = 1.04$ Hz, 1H), 7.51(s, 1H), 7.41(s, 1H), 7.15(d, $J = 1.04$ Hz, 1H), 7.06(s, 1H), 3.97(s, 1H), 2.52(s, 3H), 2.35(s, 3H); ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm) 171.17(q, $J = 36.62$ Hz), 144.67, 137.42, 136.82, 134.86, 133.55, 129.00, 127.39, 126.84, 125.21, 122.15(q, $J = 3.81$ Hz), 116.37(q, $J = 288.56$ Hz), 38.83, 21.37, 20.19. LRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 346.06, found 345.98. m.p. 118.7-120.7 $^{\circ}\text{C}$.



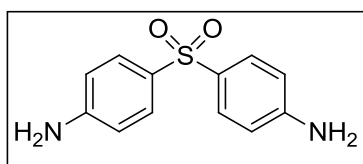
1-(5-(2,5-dimethylphenylsulfonyl)-1-methyl-1H-pyrrol-2-yl)-2,2,2-trifluoroethanone(45): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 2,2,2-trifluoro-1-(1-methyl-1H-pyrrol-2-yl)ethanone (0.6 mmol, 107mg) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 50 °C overnight. Then TFAA(300ul) and *p*-xylene (0.4 mmol, 51ul) were added, stirring for another 3h at 40 °C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 88 mg 1-(5-(2,5-dimethylphenylsulfonyl)-1-methyl-1H-pyrrol-2-yl)-2,2,2-trifluoroethanone which is a kind of white solid with 64% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (s, 1H), 7.44(s, 1H), 7.37(s, 1H), 7.20(d, J = 7.72 H, 1H), 7.06(d, J = 7.72 H, 1H), 3.91(s, 1H), 2.44(s, 3H), 2.31(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 171.20(q, J = 36.36 Hz), 139.29, 136.81, 134.89, 134.45, 132.78, 129.10, 126.67, 125.24, 122.20(q, J = 3.88 Hz), 116.35(q, J = 293.26 Hz), 38.82, 20.92, 19.79. LRMS (ESI) calcd for $C_{15}H_{15}F_3NO_3S$ $[M+H]^+$: 346.06, found 345.98. m.p.117.6-118.3 °C.



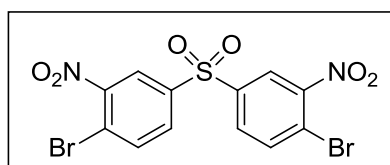
2-(2,4-dimethylphenylsulfonyl)thiophene(46): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+.HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), *m*-xylene (0.4 mmol, 46ul) and TfOH (0.4 mmol, 36 ul) was added, the reaction was carried out at 50 °C for 5h. Then TFAA(300ul) and thiophene (1.6 mmol, 128ul) were added, stirring for another 5h at room temperature. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent) , the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 47 mg 2-(2,4-dimethylphenylsulfonyl)thiophene which is a kind of white solid with 47% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, J = 8.12 Hz, 1H), 7.65(d, J = 3.64Hz, 1H), 7.61(d, J = 4.92 Hz, 1H), 7.16(d, J = 4.92 Hz, 1H), 7.06 (m, 2H), 2.55(s, 3H), 2.36(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 144.68, 143.61, 137.98, 136.96, 133.55, 133.24, 133.09, 129.33, 127.46, 127.38. LRMS (ESI) calcd for $C_{12}H_{13}O_2S_2$ $[M+H]^+$: 253.03, found 252.98. m.p.116.1-116.7 °C.



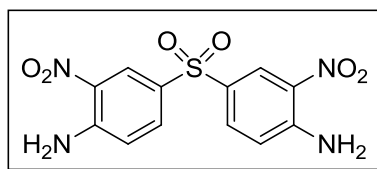
1-(5-(3,4-dimethoxyphenylsulfonyl)-1-methyl-1H-pyrrol-2-yl)-2,2,2-trifluoroethanone(47): $K_2S_2O_8$ (0.2 mmol, 54 mg) and $NBu_4^+ \cdot HSO_4^-$ (0.02 mmol, 6.8 mg) was added into a 10ml sealed tube charged with a magnetic bar, following that, DCE (0.3ml), 2,2,2-trifluoro-1-(1-methyl-1H-pyrrol-2-yl)ethanone (0.6 mmol, 107mg) and TfOH (1.6 mmol, 138 ul) was added, the reaction was carried out at 50 °C for 5h. Then TFAA(300ul) and 1,2-dimethoxybenzene (0.4 mmol, 51ul) were added, stirring for another 5h at 40 °C. After observing an obvious product spot on the TLC (Hexane : EtOAc = 10 : 1 as the eluent), the reaction was quenched by brine solution, extract three times with DCM. Collect the organic phase to dry over anhydrous Na_2SO_4 , which was removed under reduced pressure. The residual was purified by column chromatography (Hexane : EtOAc = 20 : 1) to get 80 mg 1-(5-(3,4-dimethoxyphenylsulfonyl)-1-methyl-1H-pyrrol-2-yl)-2,2,2-trifluoroethanone which is a kind of white solid with 53% yield. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 (d, J = 6.84 Hz, 1H), 7.52(s, 1H), 7.45(s, 1H), 7.39(s, 1H), 6.95 (d, J = 8.52 Hz, 1H), 3.99(s, 3H), 3.93(s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ (ppm) 177.02(q, J = 36.98 Hz), 153.32, 149.49, 134.38, 133.81, 127.59, 125.52, 121.78(q, J = 4.12 Hz), 121.42, 116.41(q, J = 288.56 Hz), 111.05, 109.54, 56.41, 56.35, 38.82. LRMS (ESI) calcd for $C_{15}H_{15}F_3NO_5S$ $[M+H]^+$: 378.05, found 377.96. m.p.119.1-123.6 °C.



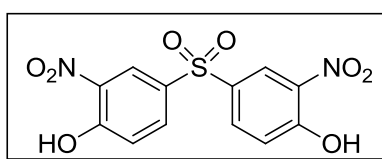
Dapsone: 4, 4'-sulfonylbis(bromobenzene) (6mmol, 2.3g) was added into a 50ml sealed tube followed by Cu_2O (0.1eq, 86mg), NH_3 (25% in H_2O , 13ml) and DMSO 20 ml. The mixture was heated at 90 °C for 20 h followed by extracting with EtOAc and washing with water. The organic phase was purified by column chromatography (from Hexane: EtOAc = 5: 1 to Hexane: EtOAc = 1 : 1) to get 1.5g Dapsone as white solid, the isolated yield is 98%. 1H -NMR (400 MHz, d_6 -acetone) δ (ppm) 7.56 (d, J = 8.48 H, 4H), 6.70 (d, J = 8.52 H, 4H), 5.43(s, 4H); ^{13}C -NMR (100 MHz, d_6 -acetone) δ (ppm) 152.44, 130.17, 128.85, 113.23. LRMS (ESI) calcd for $C_{12}H_{13}N_2O_2S$ $[M+H]^+$: 248.16, found 249.21. m.p.173.5-175.0 °C.



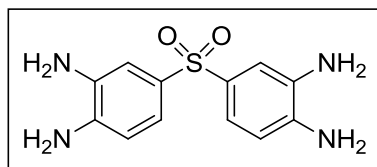
4,4'-sulfonylbis(1-bromo-2-nitrobenzene)(48): Add 4,4'-sulfonylbis(bromobenzene) (9mmol, 3.4g) into a 100ml round-bottom flask charged with a magnetic bar. After adding 40ml conc. H_2SO_4 and heating to 80 °C, KNO_3 (27mmol, 3.7g) was added in several portions. After 3h, the mixture was poured into ice water, collect the appearing solid and dry under reduced pressure to give 4.3g 4,4'-sulfonylbis(1-bromo-2-nitrobenzene) with 91% isolated yield. 1H -NMR (400 MHz, d_6 -DMSO) δ (ppm) 8.69 (s, 2H), 8.21(s, 4H); ^{13}C -NMR (100 MHz, d_6 -DMSO) δ (ppm) 150.09, 139.98, 136.74, 132.28, 125.03, 120.46. m.p.237.9-241.7 °C.



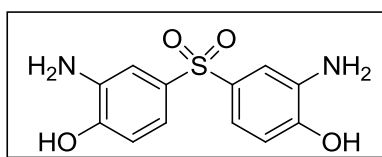
4,4'-sulfonylbis(2-nitroaniline)(49): Add 4,4'-sulfonylbis(1-bromo-2-nitrobenzene) (3mmol, 1.4g) into a 50ml round-bottom flask charged with a magnetic bar. After adding $\text{NH}_3\cdot\text{H}_2\text{O}$ (25%, 1.5ml) and DMSO 6ml, the mixture was stirred at 50°C for 3h. Add water and collect the appearing solid via filtration with suction giving 4,4'-sulfonylbis(2-nitroaniline) with quantitative yield. $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ (ppm) 8.45 (d, $J = 1.92$ Hz, 2H), 8.08(s, 4H), 7.78(dd, $J = 9.04$ Hz, $J = 2.08$ Hz, 2H), 7.11(d, $J = 9.04$ Hz, 2H); $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ (ppm) 148.68, 132.60, 129.17, 126.69, 126.32, 120.76. m.306.2-308.3 °C



4,4'-sulfonylbis(2-nitrophenol)(50): Add 4,4'-sulfonylbis(1-bromo-2-nitrobenzene) (4mmol, 1.9g) into a 50ml round-bottom flask charged with a magnetic bar. After adding NaOH 1.3g, DMSO 10ml and H_2O 2.4ml, the mixture was stirred at 50°C for 2h. Add dilute HCl solution and collect the appearing solid via filtration with suction giving 4,4'-sulfonylbis(2-nitrophenol) with quantitative yield. $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ (ppm) 8.42 (d, $J = 2.16$ Hz, 2H), 8.04(dd, $J = 8.84$ Hz, $J = 2.16$ Hz, 2H), 7.26(d, $J = 8.84$ Hz, 2H); $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ (ppm) 156.13, 137.21, 133.24, 130.55, 125.61, 120.46. m.234.9-235.8 °C.



4,4'-sulfonylbis(benzene-1,2-diamine)(51): Add 4,4'-sulfonylbis(2-nitroaniline) (4mmol, 1.25g), Pd/C(10%wt, 67mg), EtOH 15ml and $\text{NH}_2\text{-NH}_2\cdot\text{H}_2\text{O}$ (20.0eq, 4ml) into a 50ml round-bottom flask charged with a magnetic bar under protection with Argon. After 24h under 60°C, the solvent was removed under reduced pressure to get the reddish-brown sticky product with 96% isolated yield. $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ (ppm) 6.90 (d, $J = 1.96$ Hz, 2H), 6.85(dd, $J = 8.12$ Hz, $J = 1.96$ Hz, 2H), 6.52(d, $J = 8.16$ Hz, 4H), 5.26(s, 4H), 4.85(s, 2H; $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ (ppm)139.45, 134.45, 129.80, 117.00, 112.51, 111.82. LRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{N}_4\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 279.08, found 279.28.



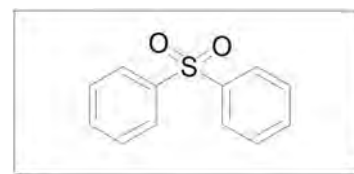
4,4'-sulfonylbis(2-aminophenol)(52): Add 4,4'-sulfonylbis(2-nitrophenol) (3mmol, 1.1g), Pd/C(10%wt, 50mg), EtOH 4ml, 1,4-dioxane 6ml and $\text{NH}_2\text{-NH}_2\cdot\text{H}_2\text{O}$ (20.0eq, 3ml) into a 50ml

round-bottom flask charged with a magnetic bar under protection with Argon. After 24h under 95°C, the solvent was removed under reduced pressure to get the reddish-brown sticky product with 94% isolated yield. ¹H-NMR (400 MHz, *d*₆-DMSO) δ (ppm) 6.93 (d, *J* = 2.28 Hz, 2H), 8.86(dd, *J* = 8.20 Hz, *J* = 2.24 Hz, 2H), 6.64(d, *J* = 8.20 Hz, 2H); ¹³C-NMR (100 MHz, *d*₆-DMSO) δ (ppm) 151.33, 137.89, 130.63, 116.48, 113.58, 111.05. LRMS (ESI) calcd for C₁₂H₁₃N₂O₄S [M-H]⁻: 279.05, found 279.18

References

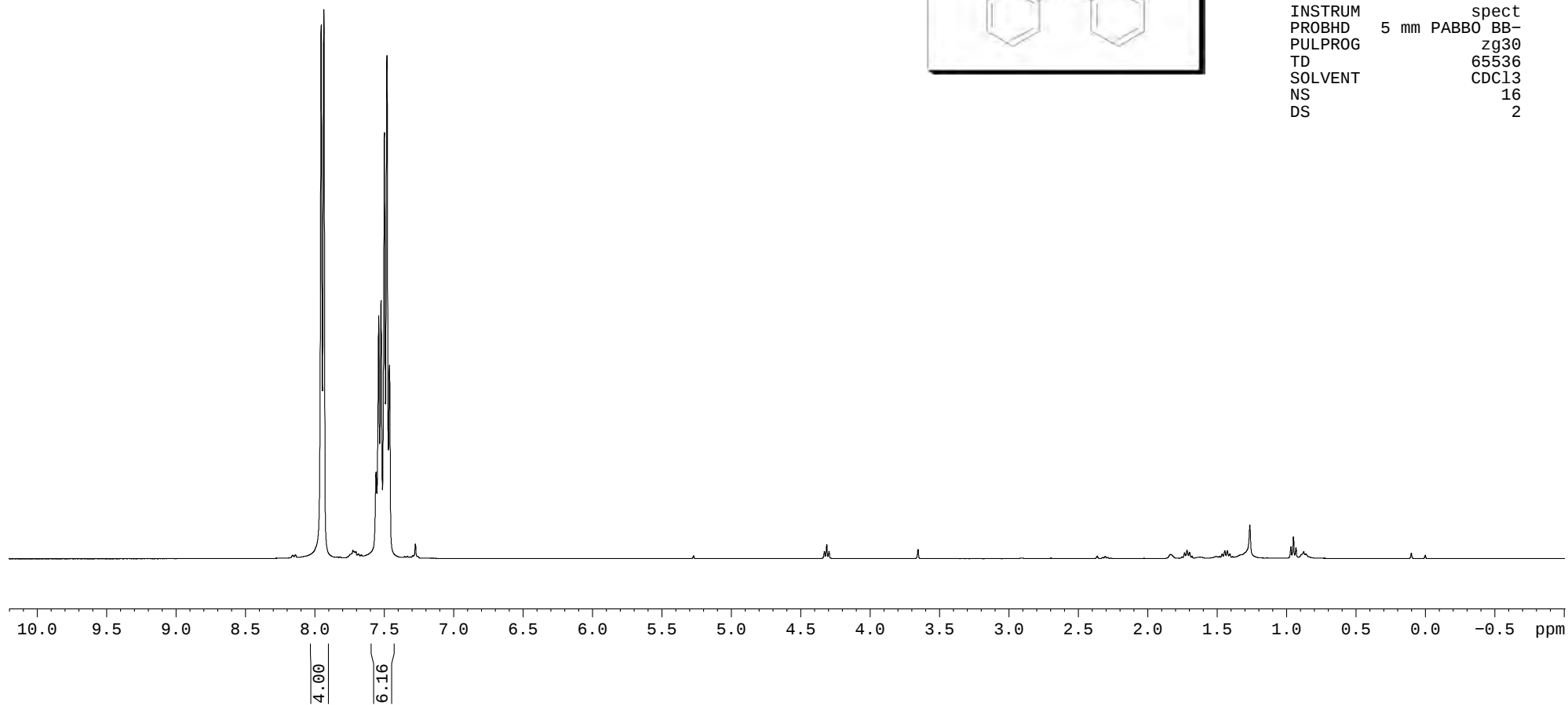
- [1] JOC, 2007, 72, 5847-5850.
- [2] Chemistry of Materials 2013, V25(13), P2630-2637
- [3] Journal of Polymer Science, Part A: Polymer Chemistry 2005, V43(14), P2964-2976
- [4] IJC-B Vol.44B(10) [October 2005], 2183-2185
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- [7] Gesellschaft 1907, V40, P641-48.
- [8] Huchel, Uschi; Journal of Carbohydrate Chemistry 2010, V29(2).
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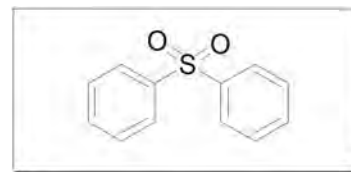
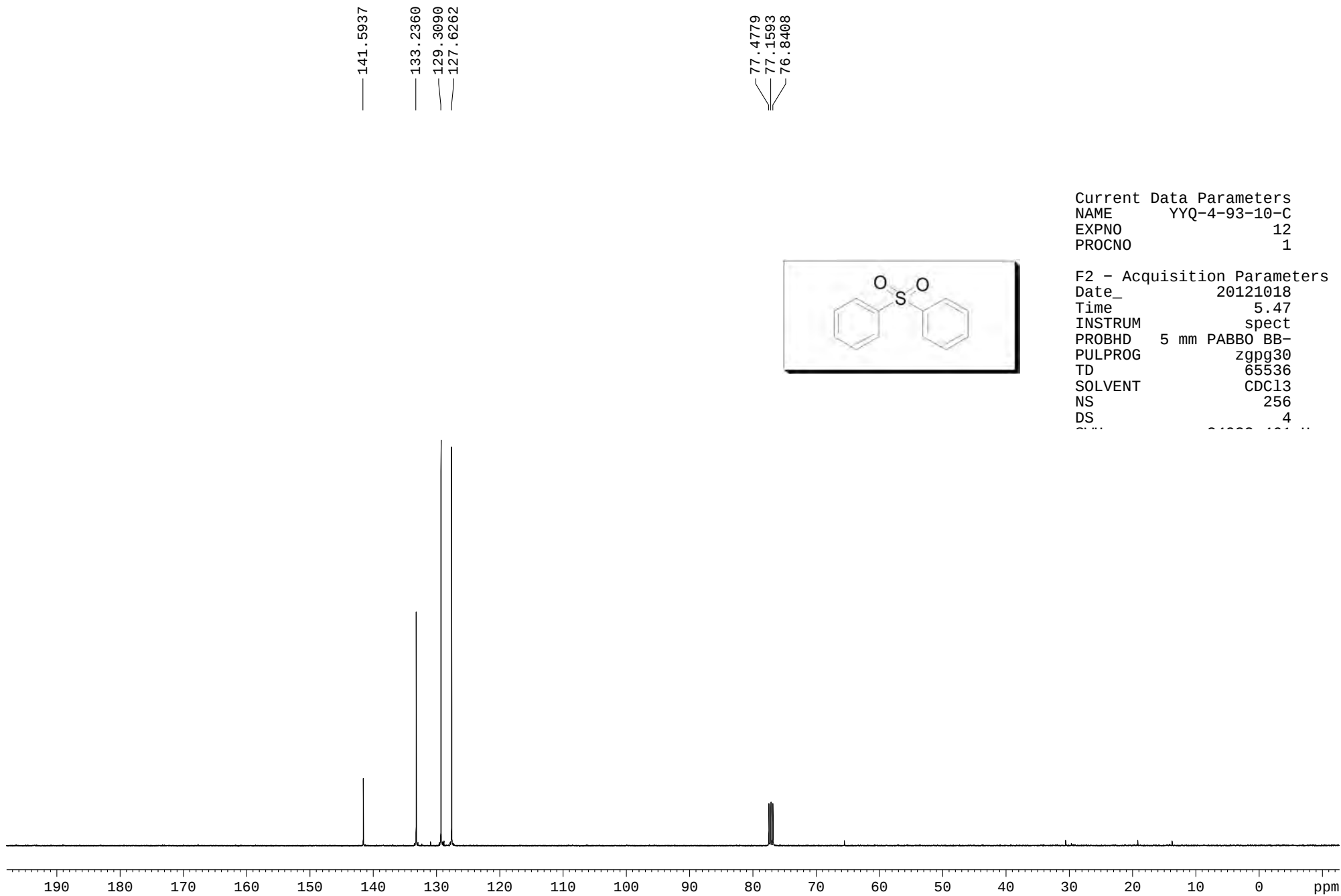
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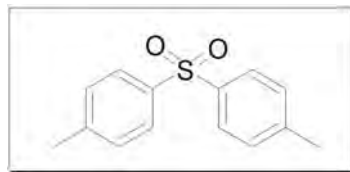
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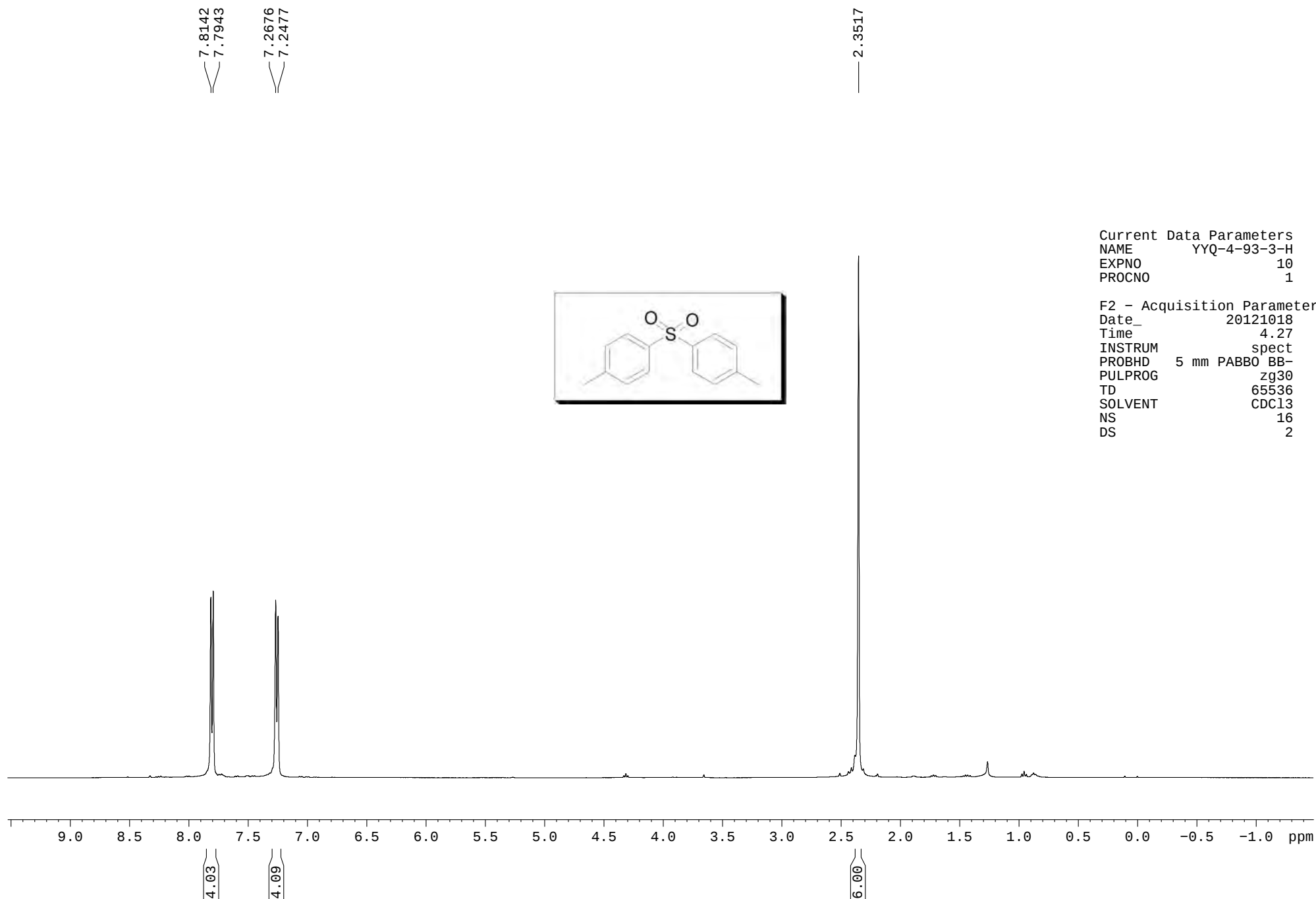
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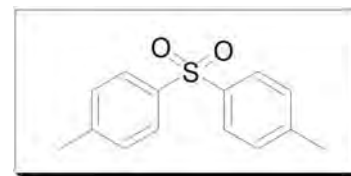
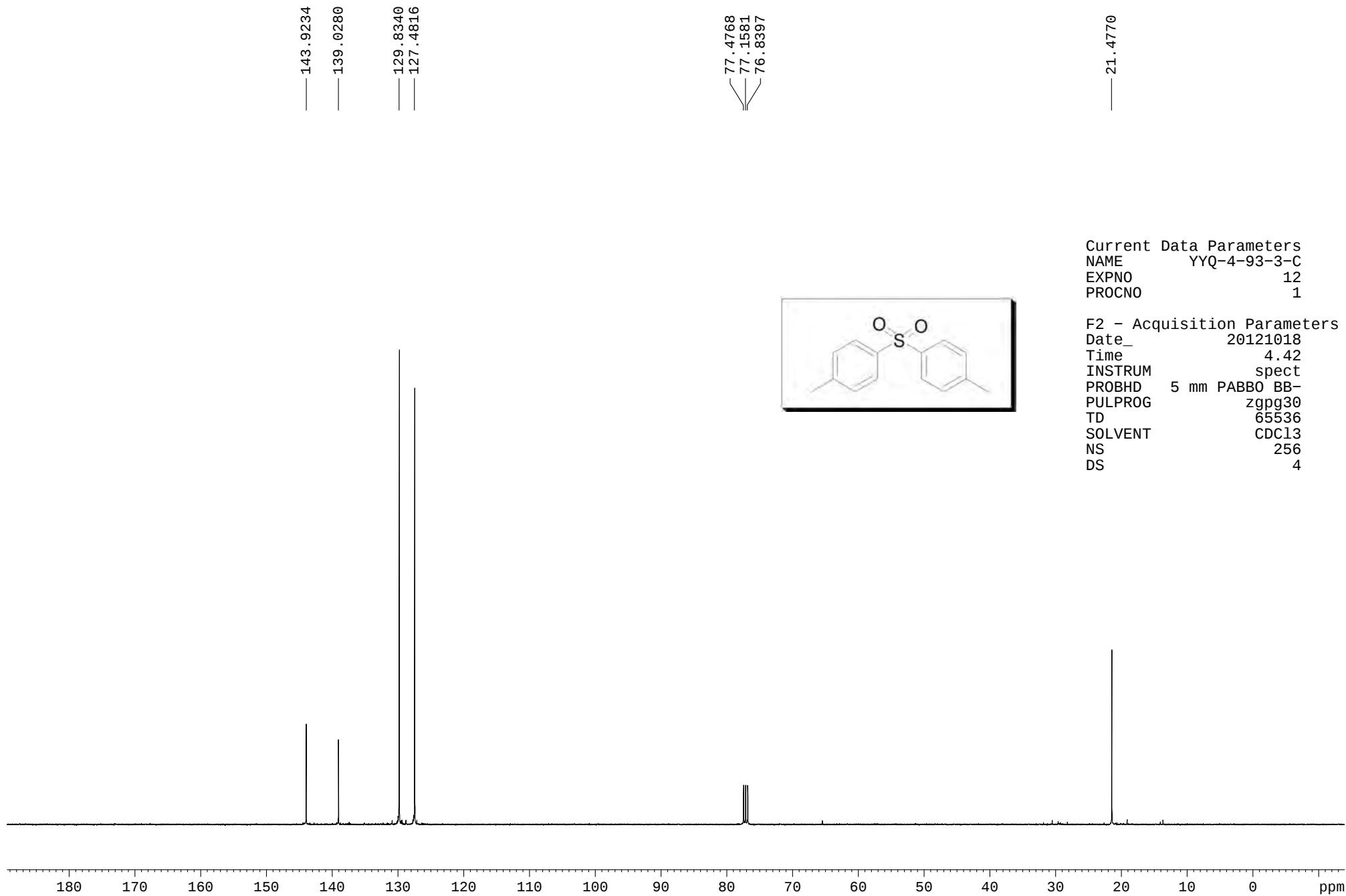
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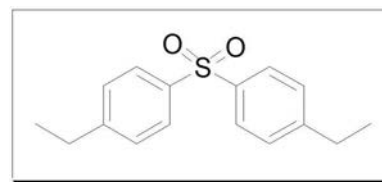
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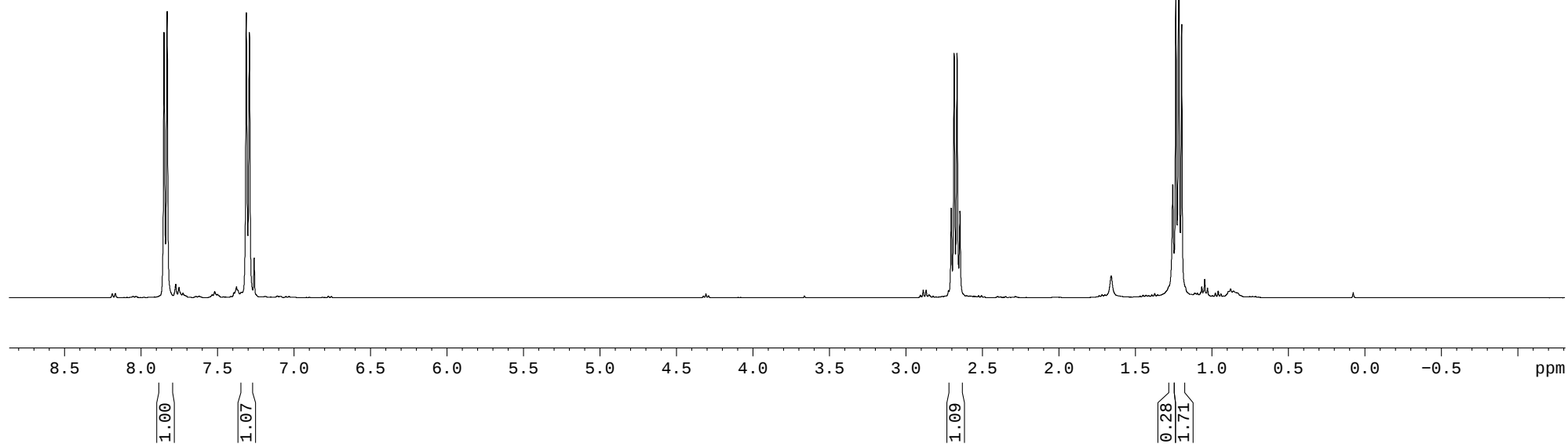
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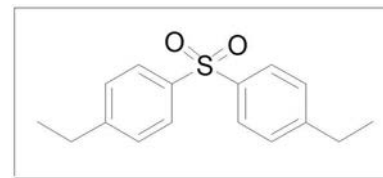
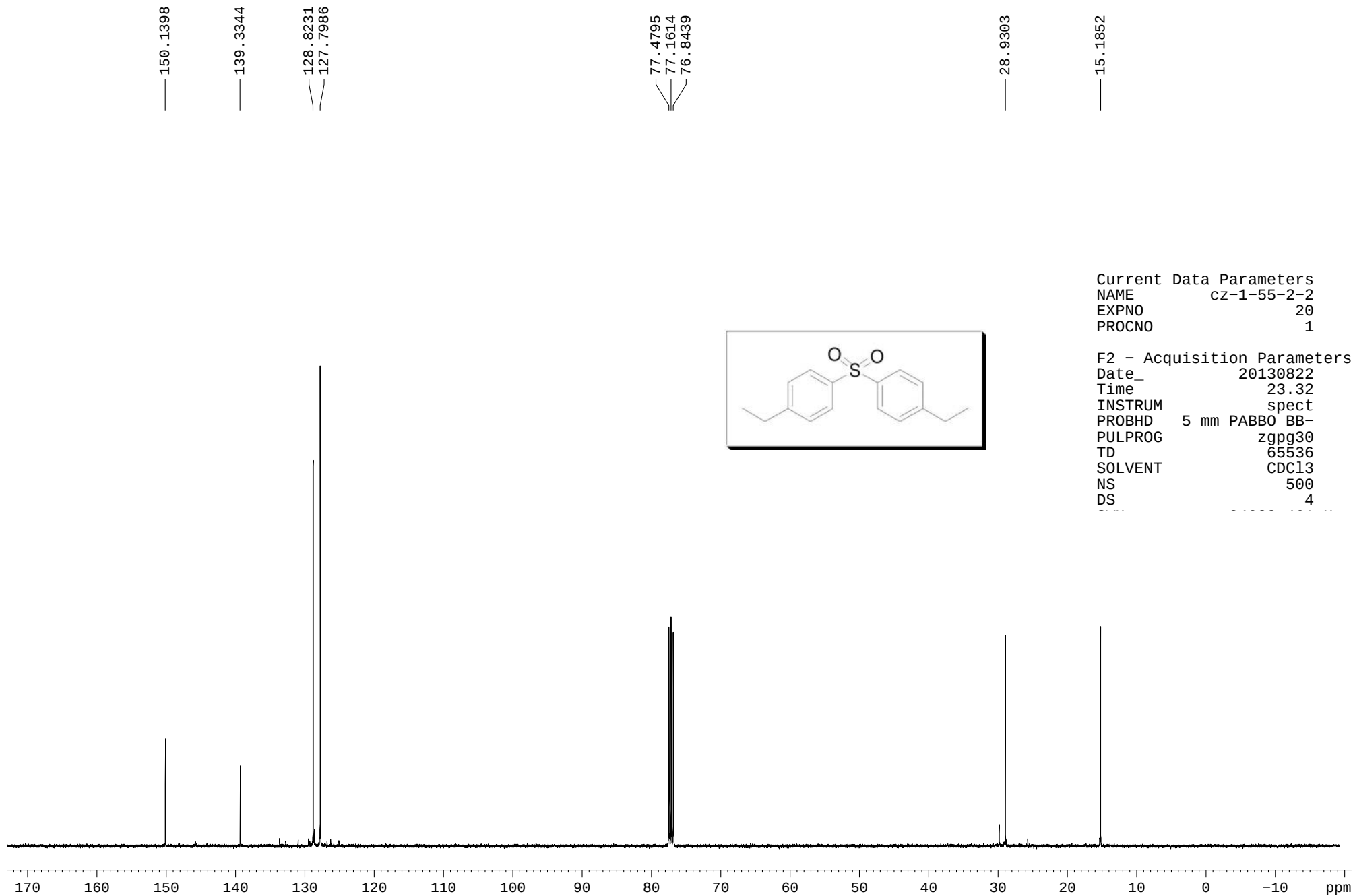
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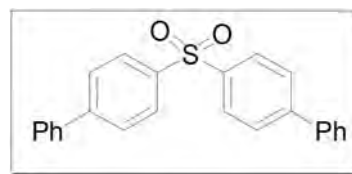
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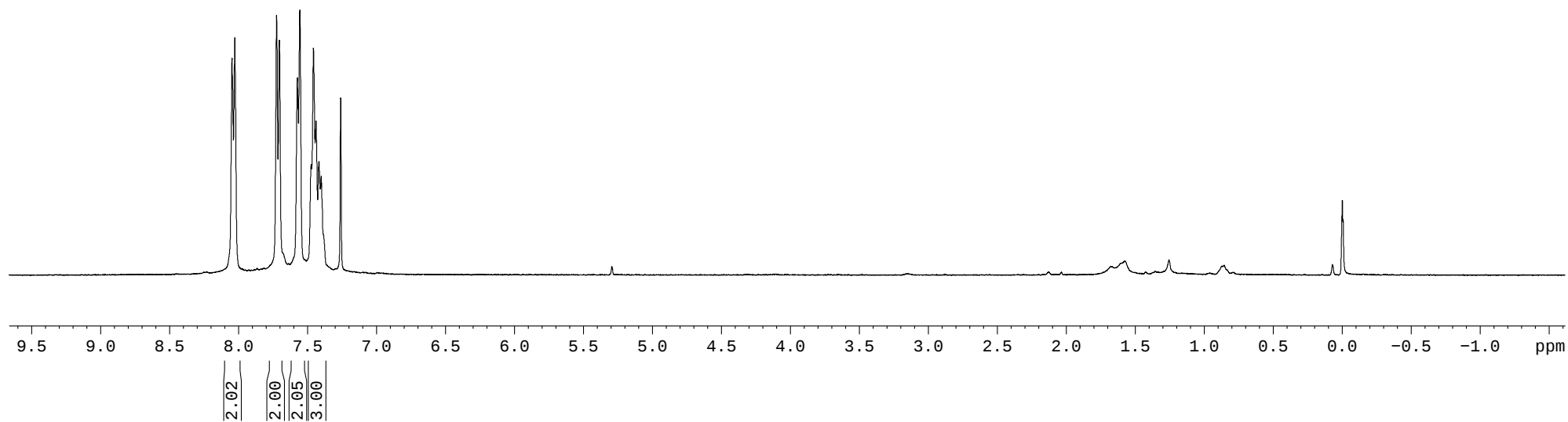
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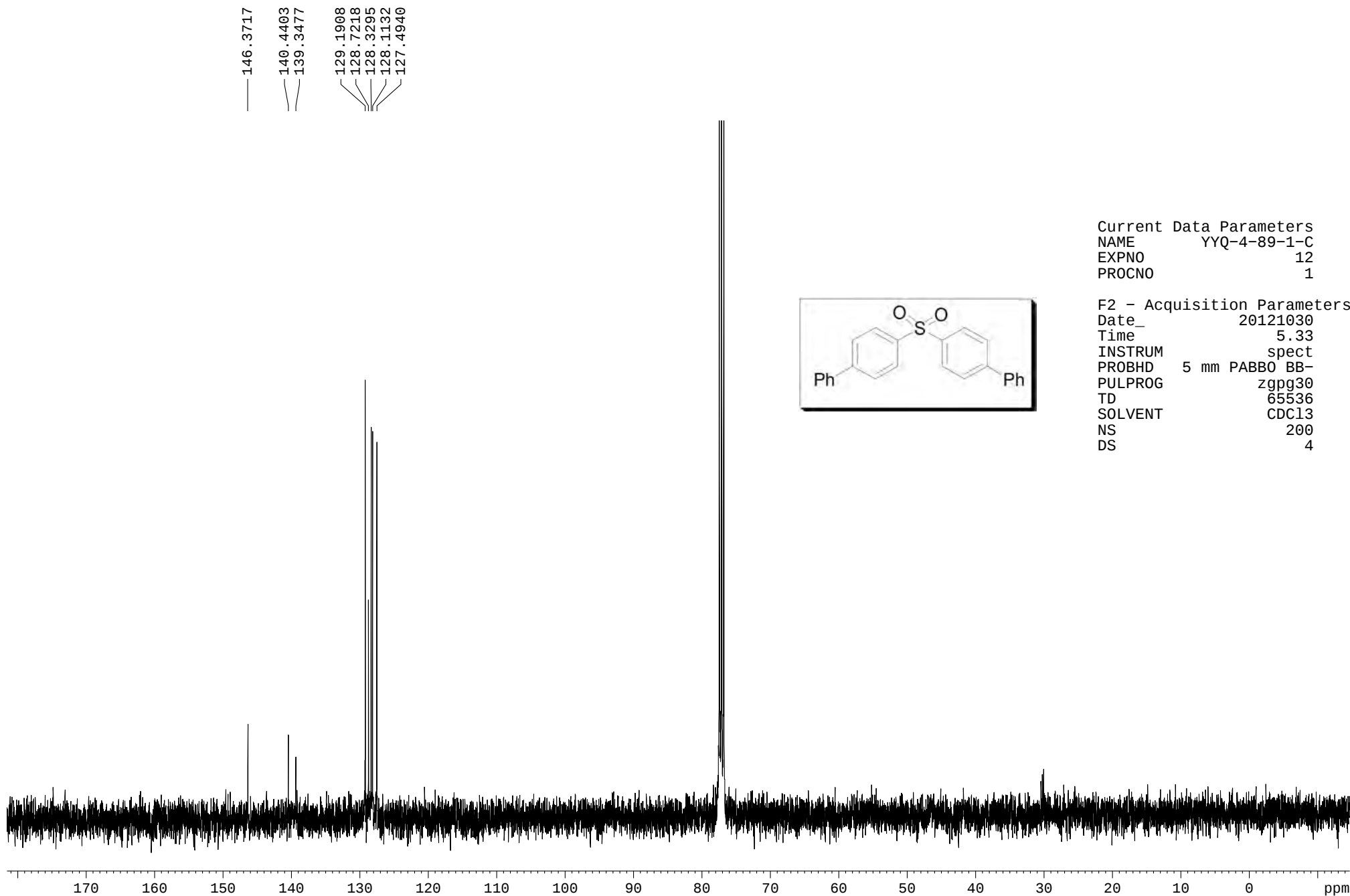
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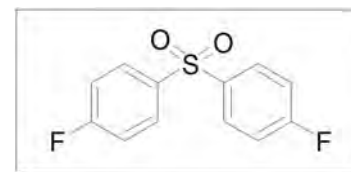
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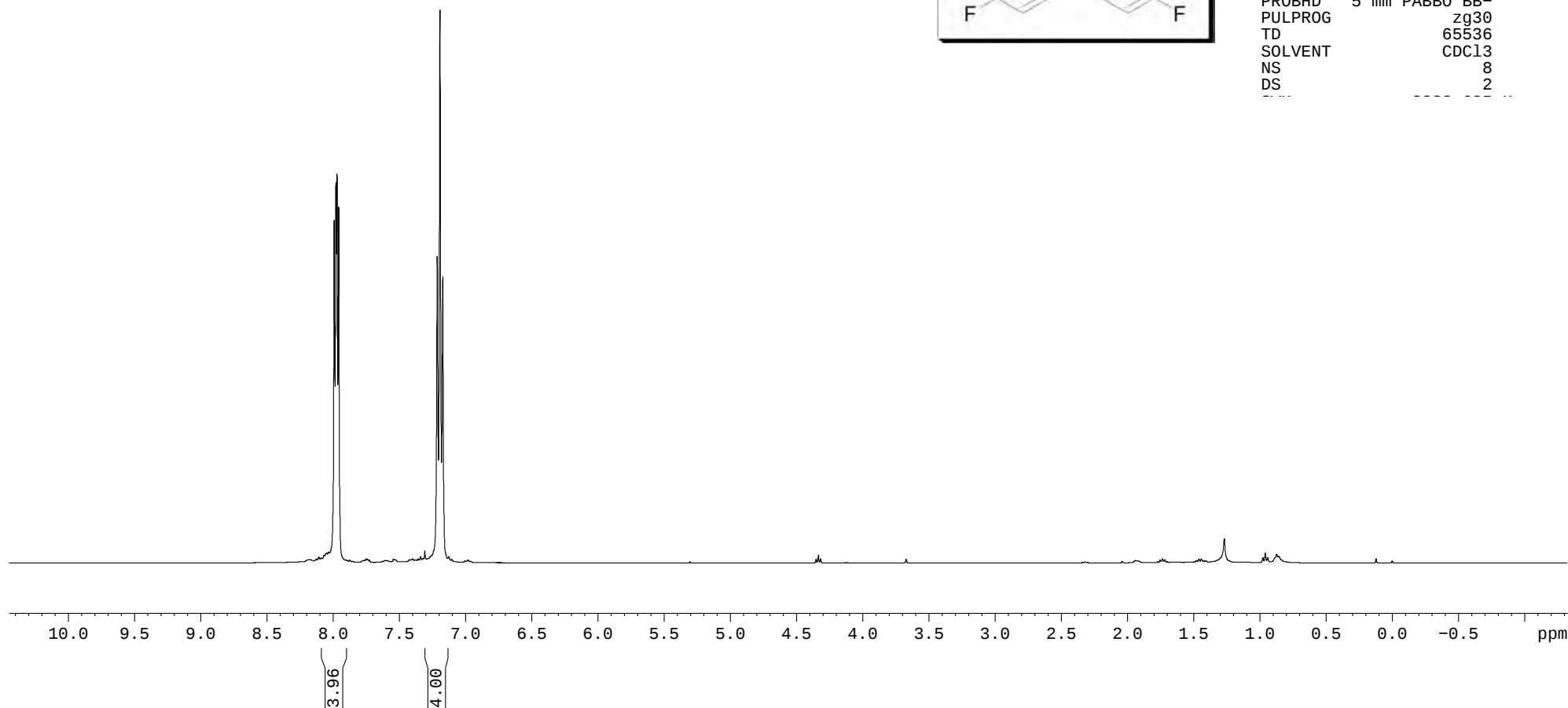
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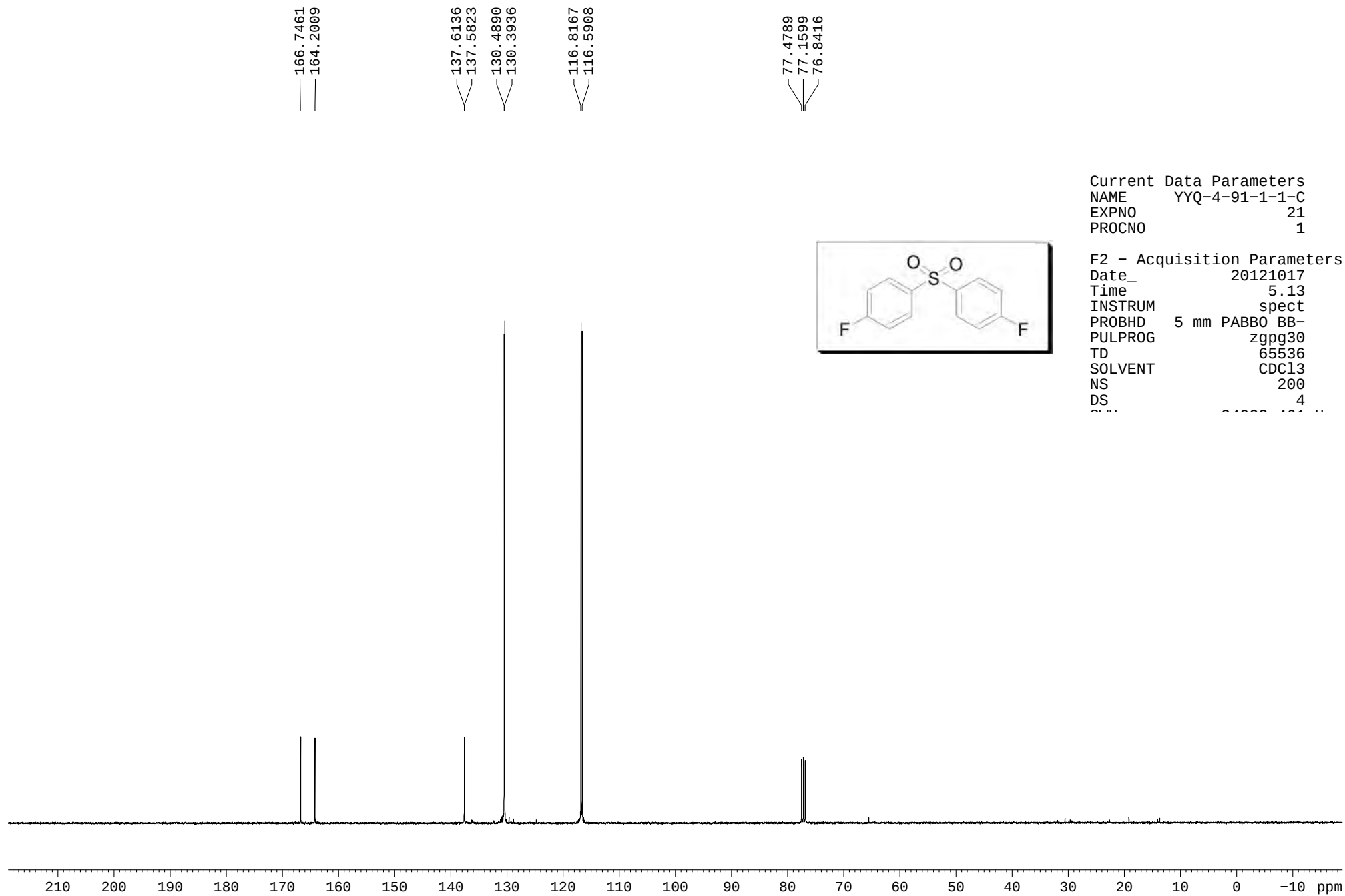
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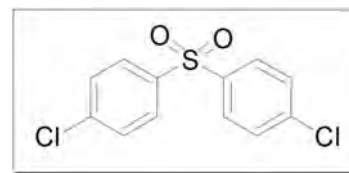




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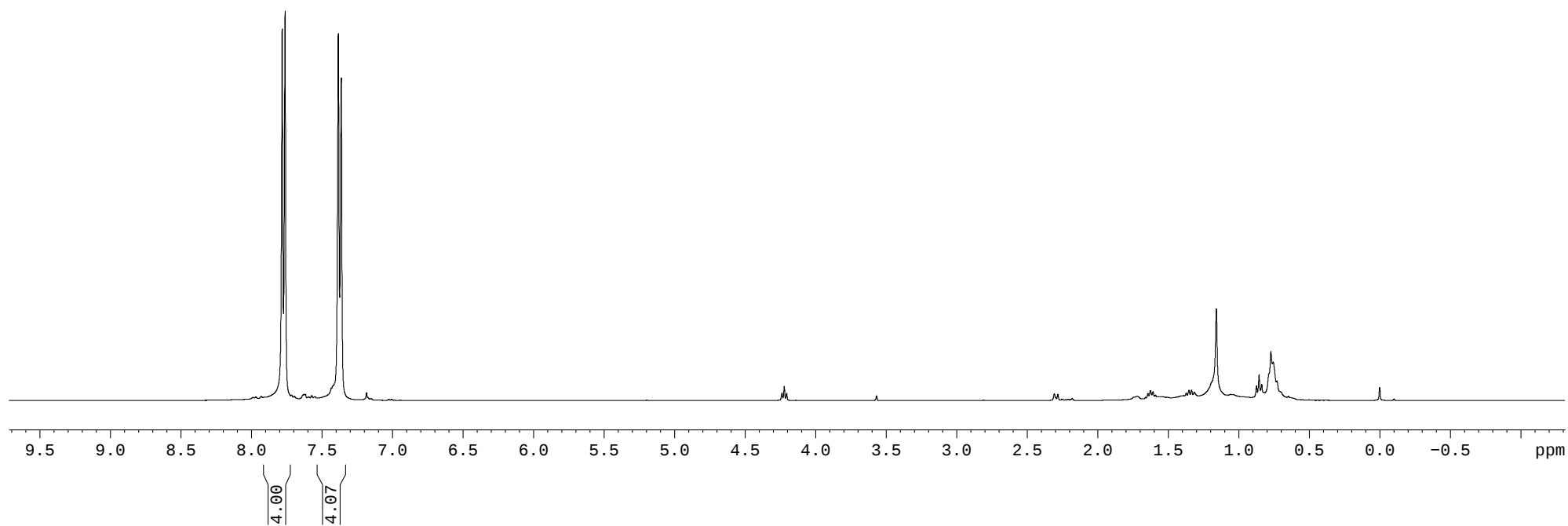
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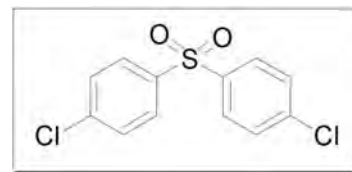
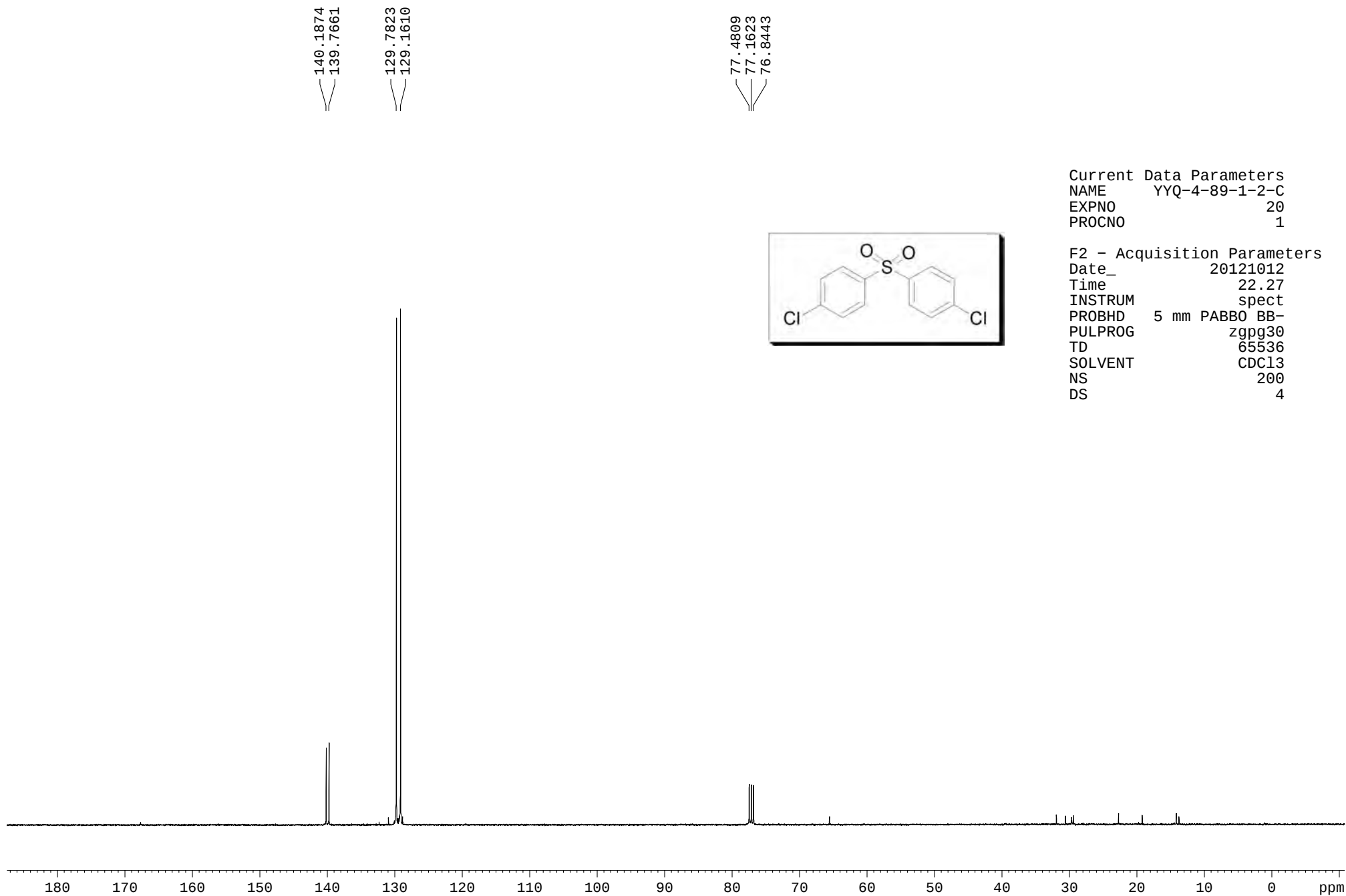
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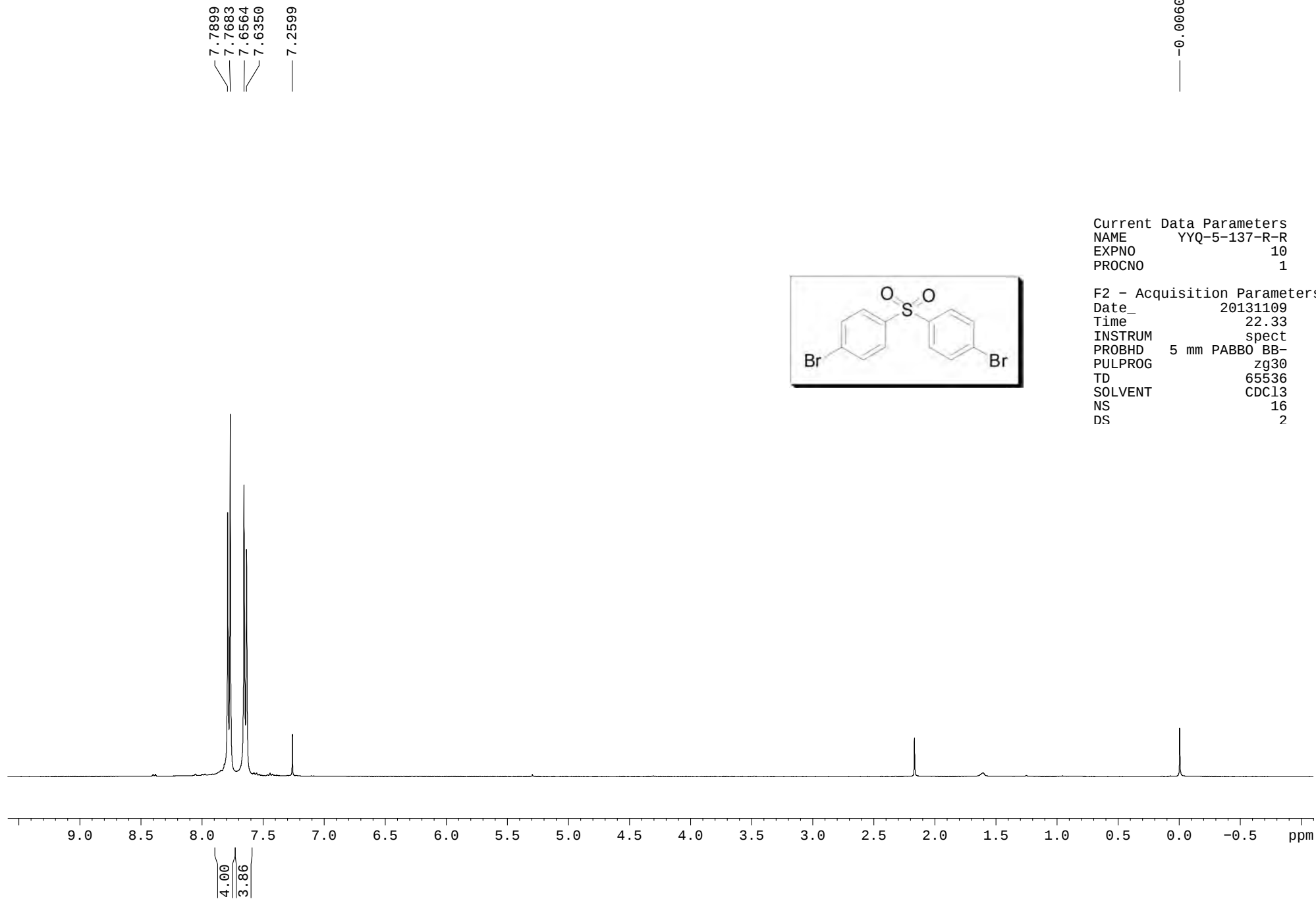


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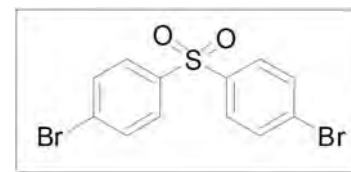
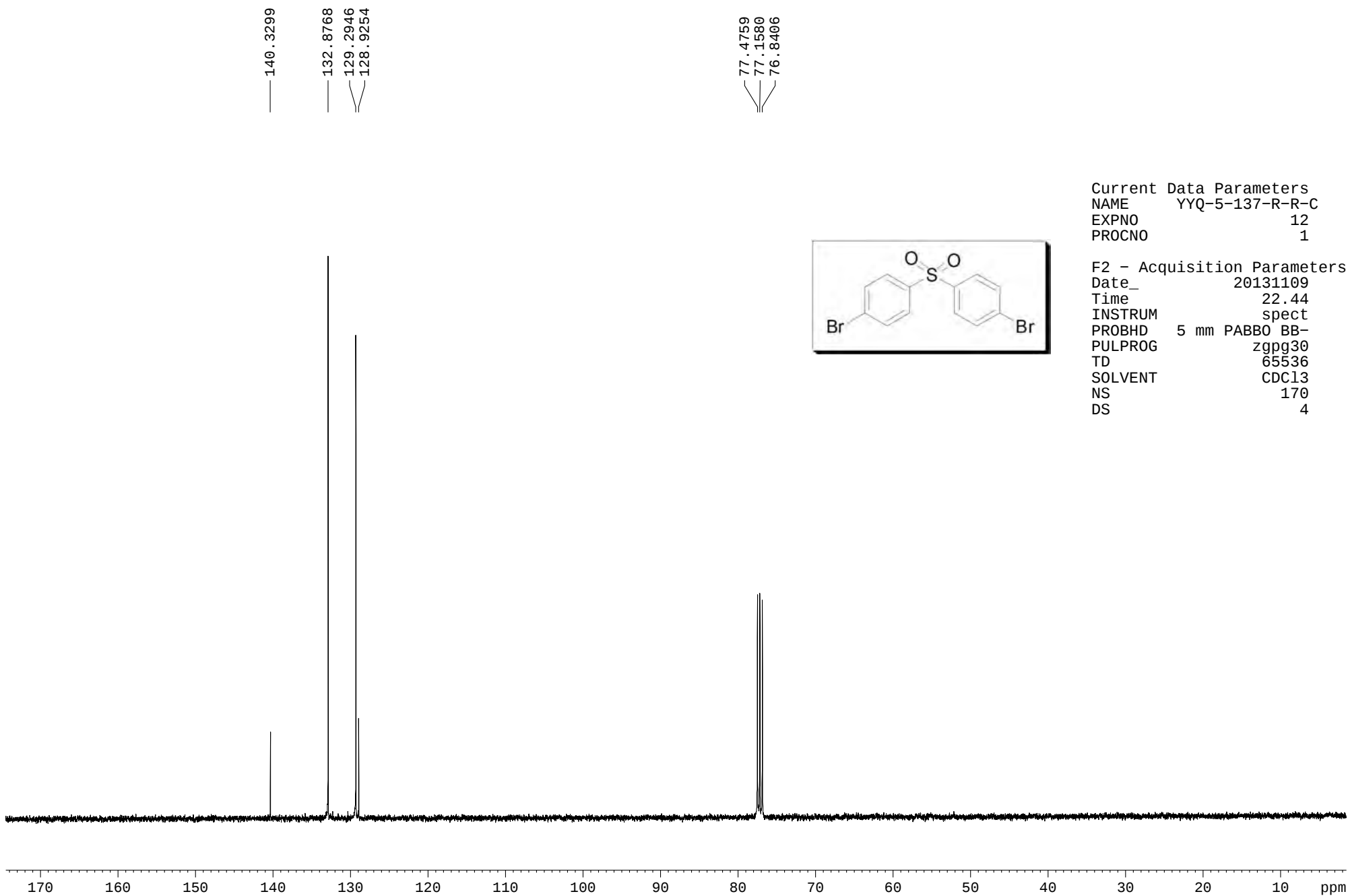
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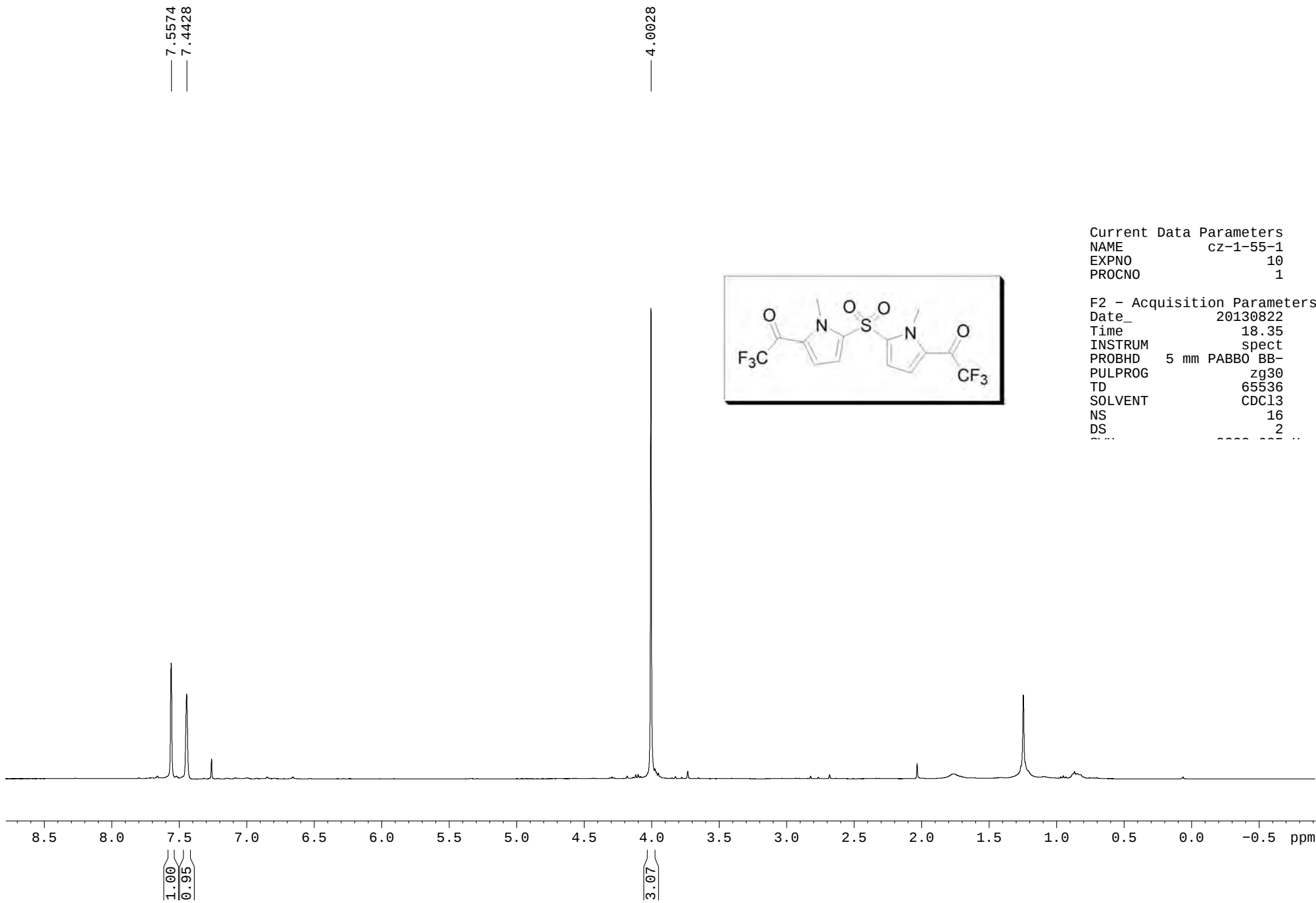
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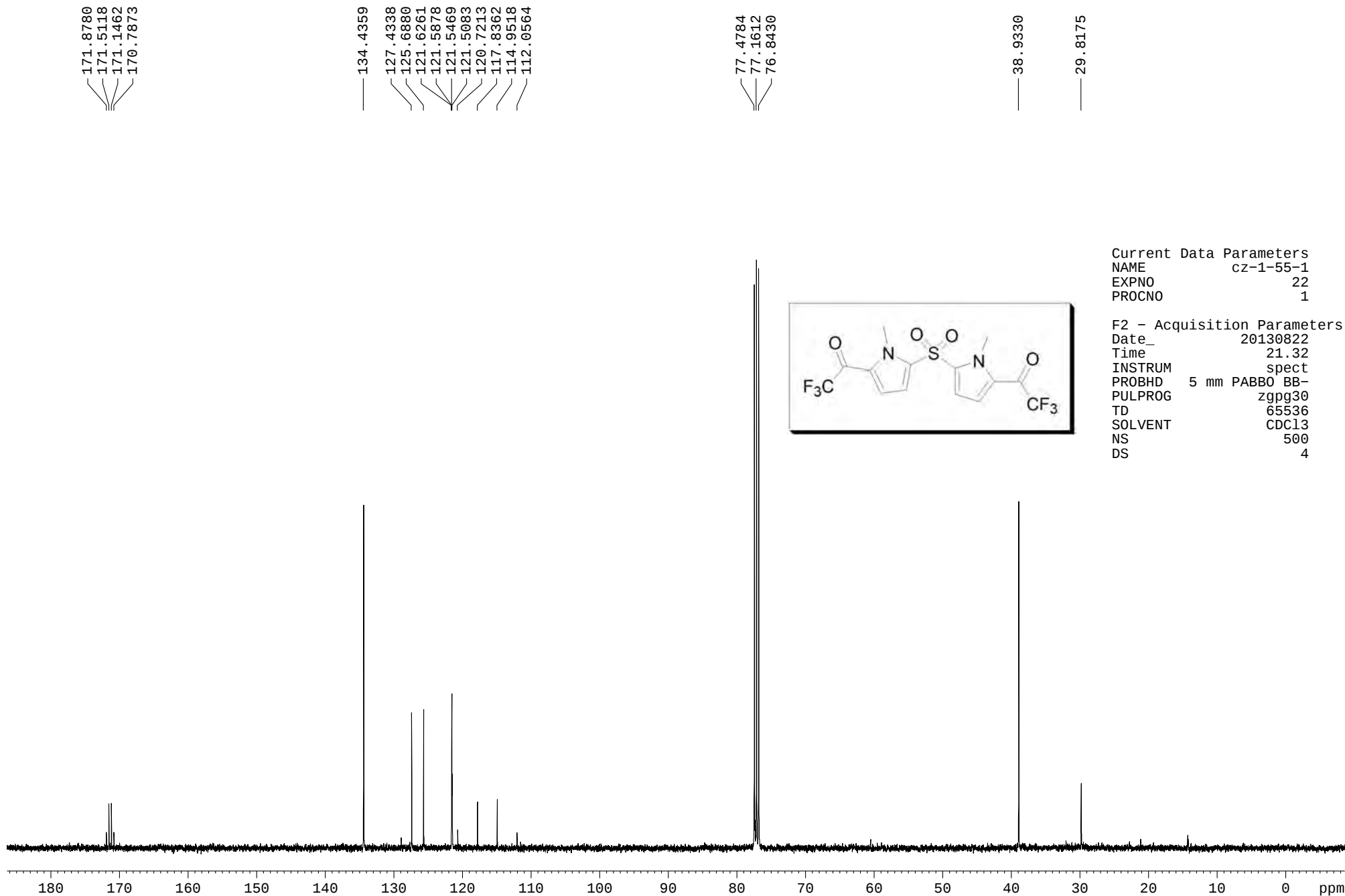
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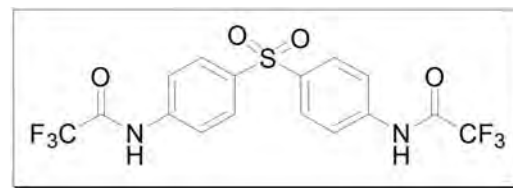
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EXPNO 10
PROCNO 1

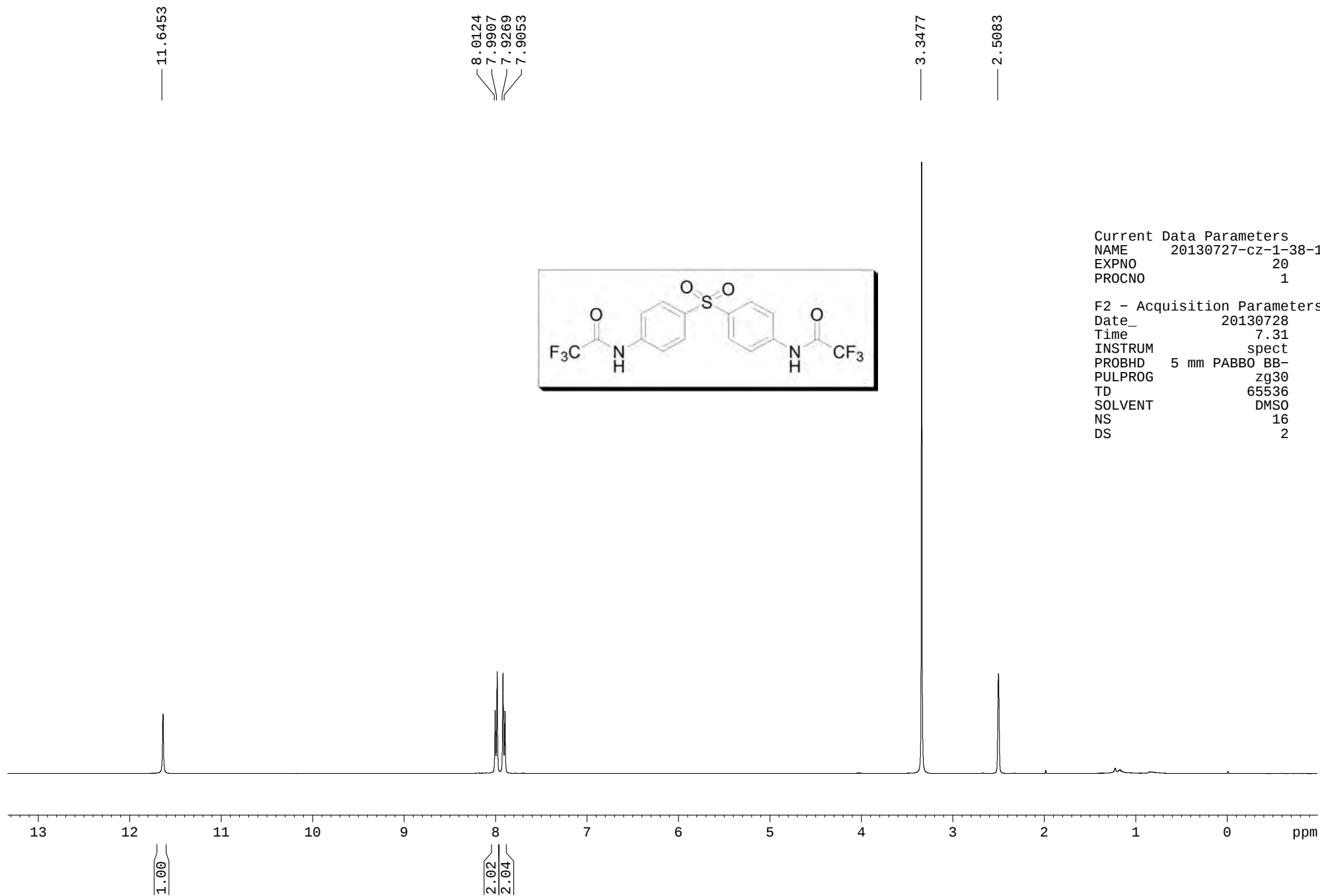
F2 - Acquisition Parameters
Date_ 20130822
Time 18.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2

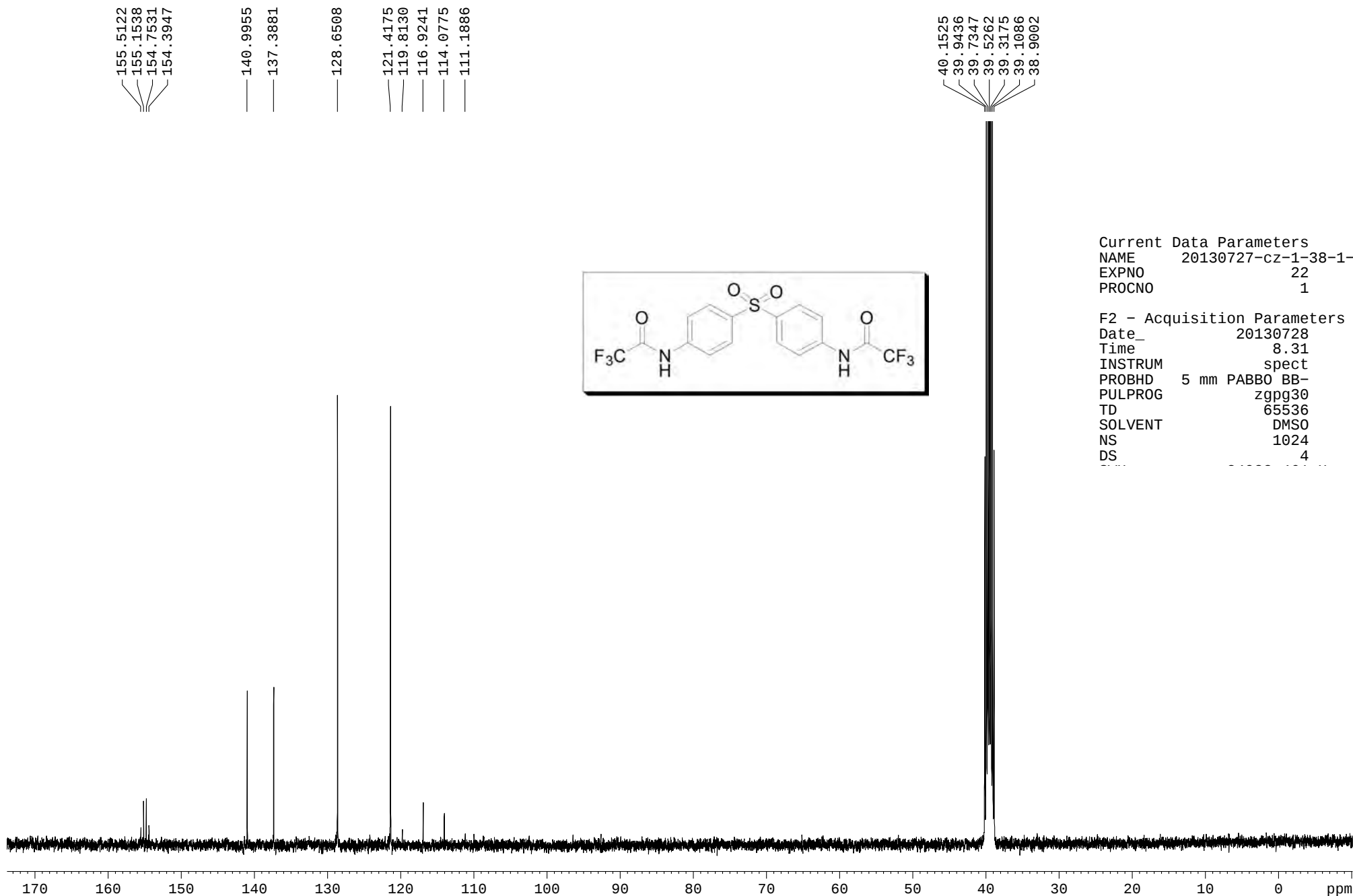
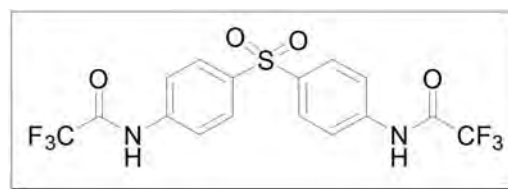




Current Data Parameters
 NAME 20130727-cz-1-38-1
 EXPNO 20
 PROCNO 1

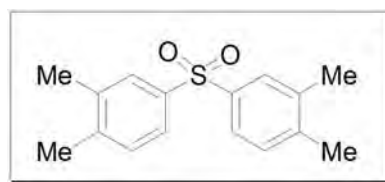
F2 - Acquisition Parameters
 Date_ 20130728
 Time 7.31
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 16
 DS 2





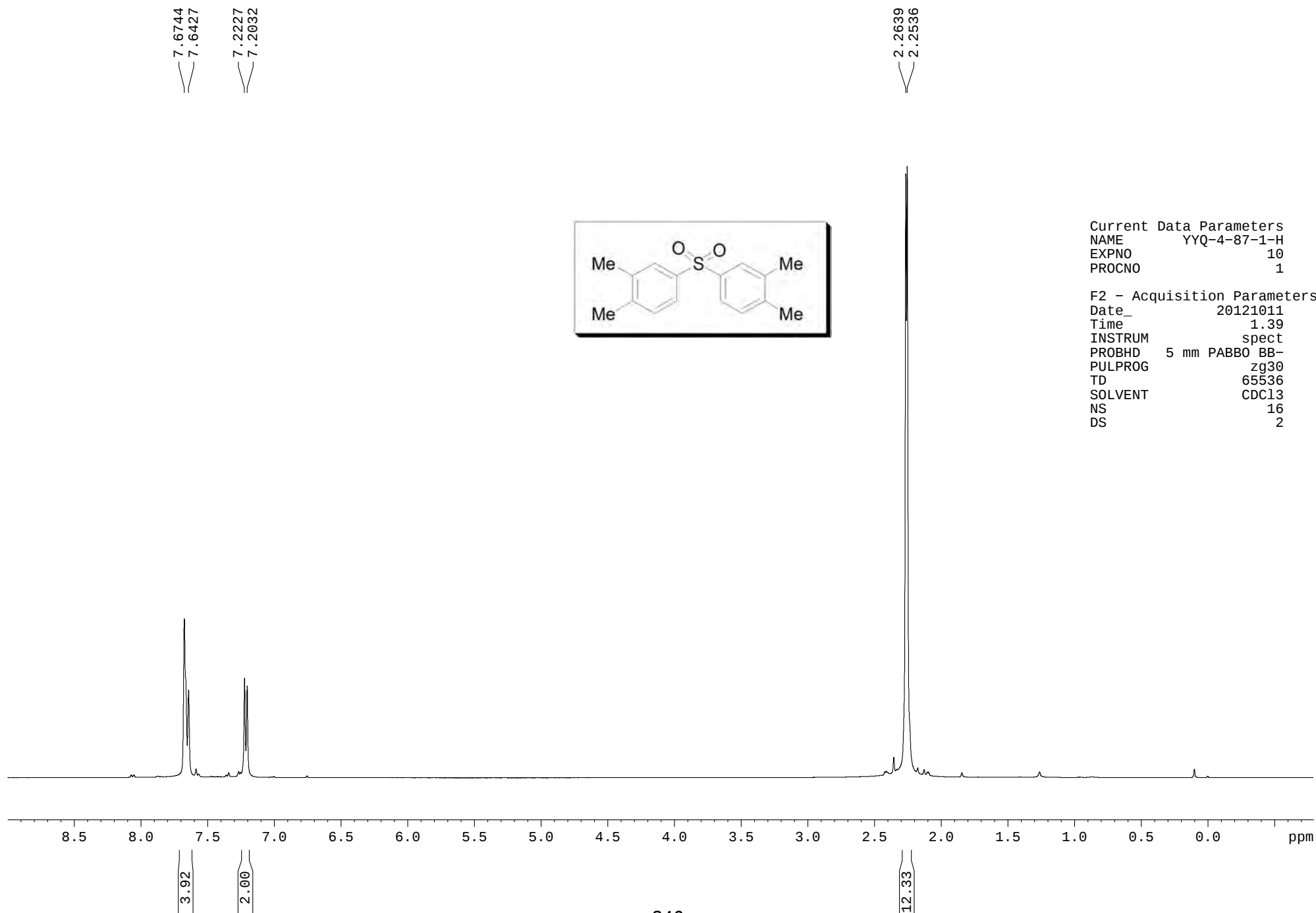
Current Data Parameters
 NAME 20130727-cz-1-38-1-c
 EXPNO 22
 PROCNO 1

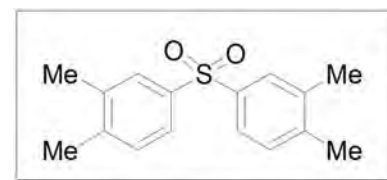
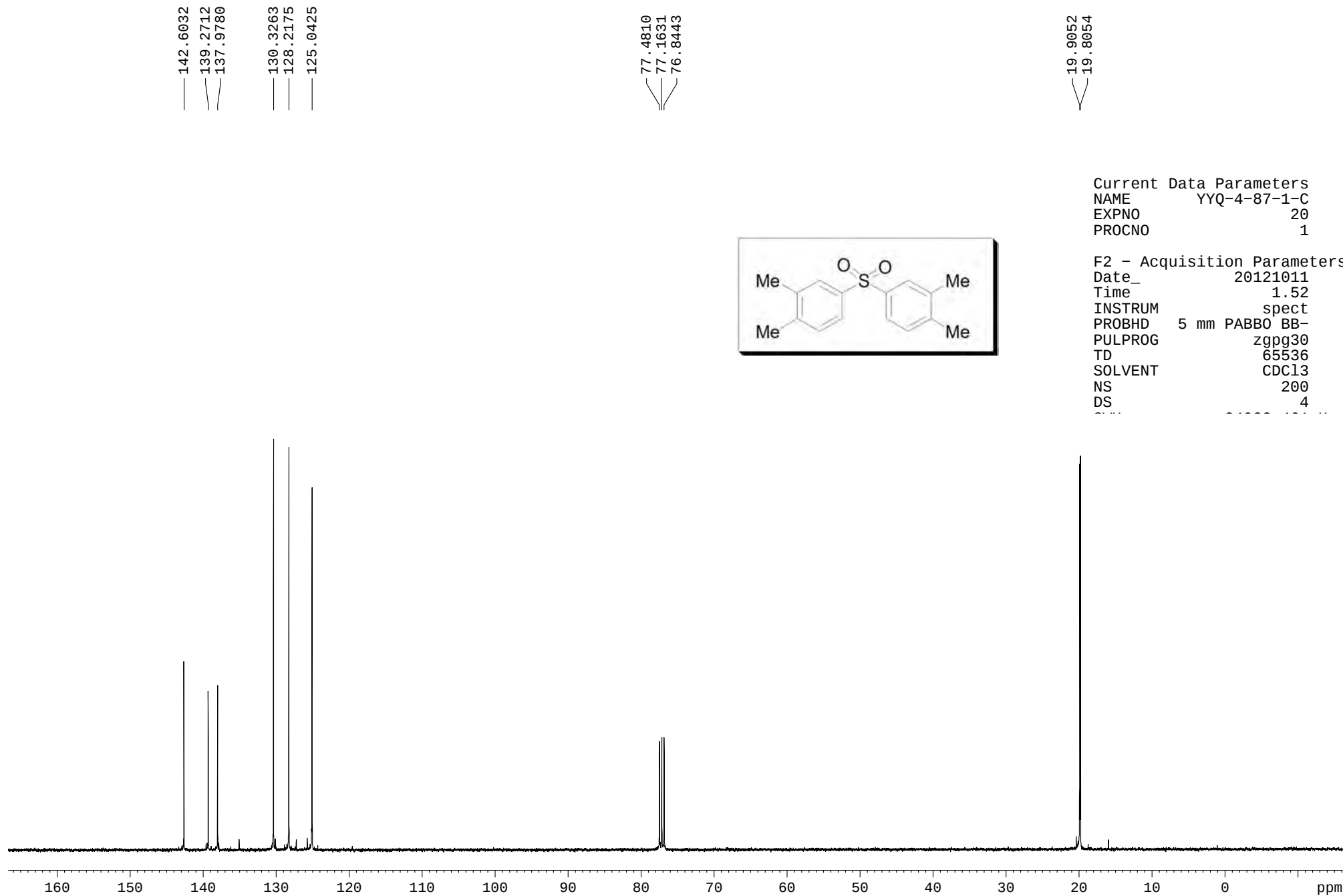
F2 - Acquisition Parameters
 Date_ 20130728
 Time 8.31
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 1024
 DS 4



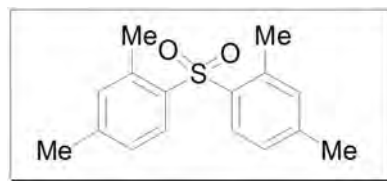
Current Data Parameters
 NAME YYQ-4-87-1-H
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20121011
 Time 1.39
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2



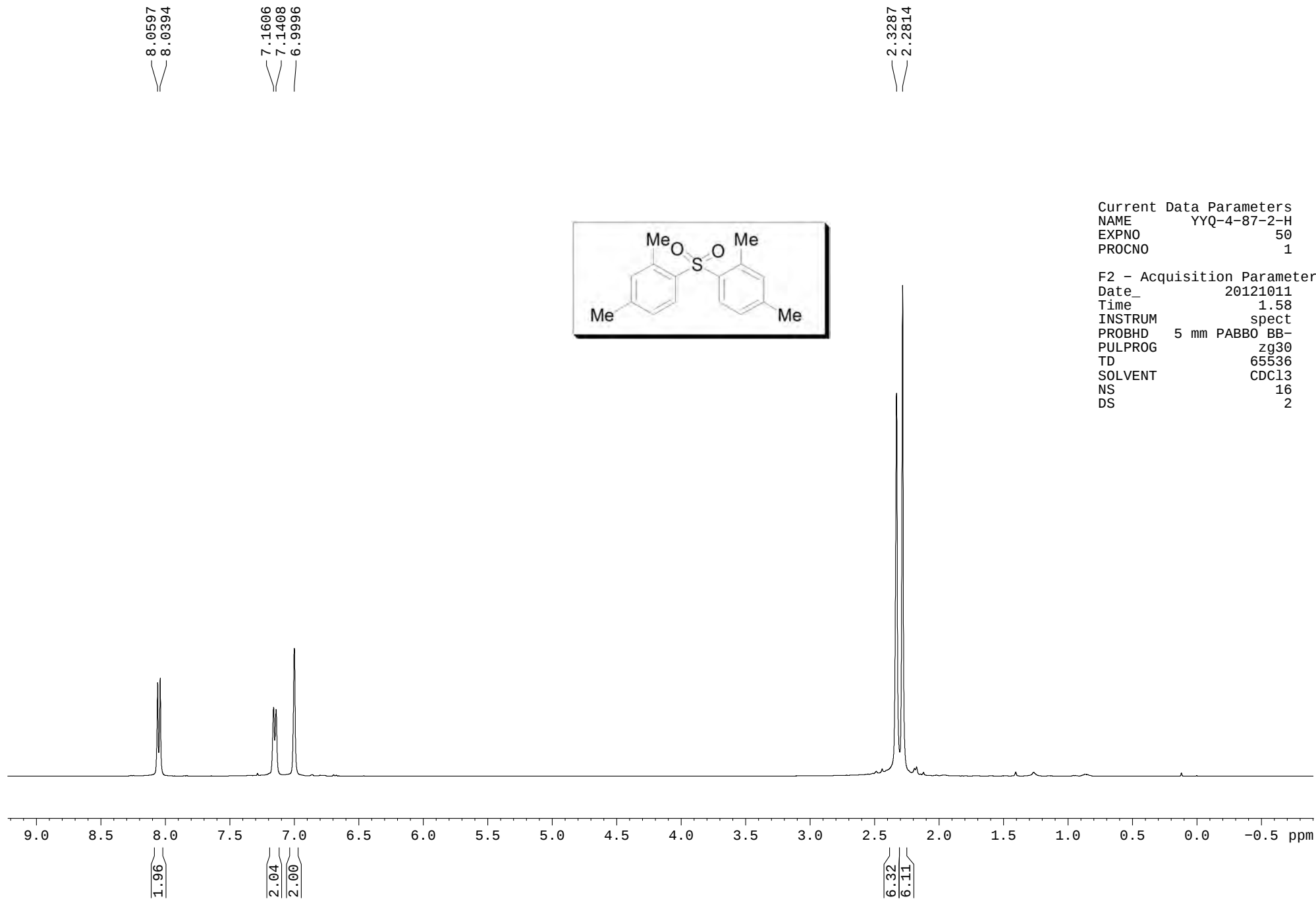


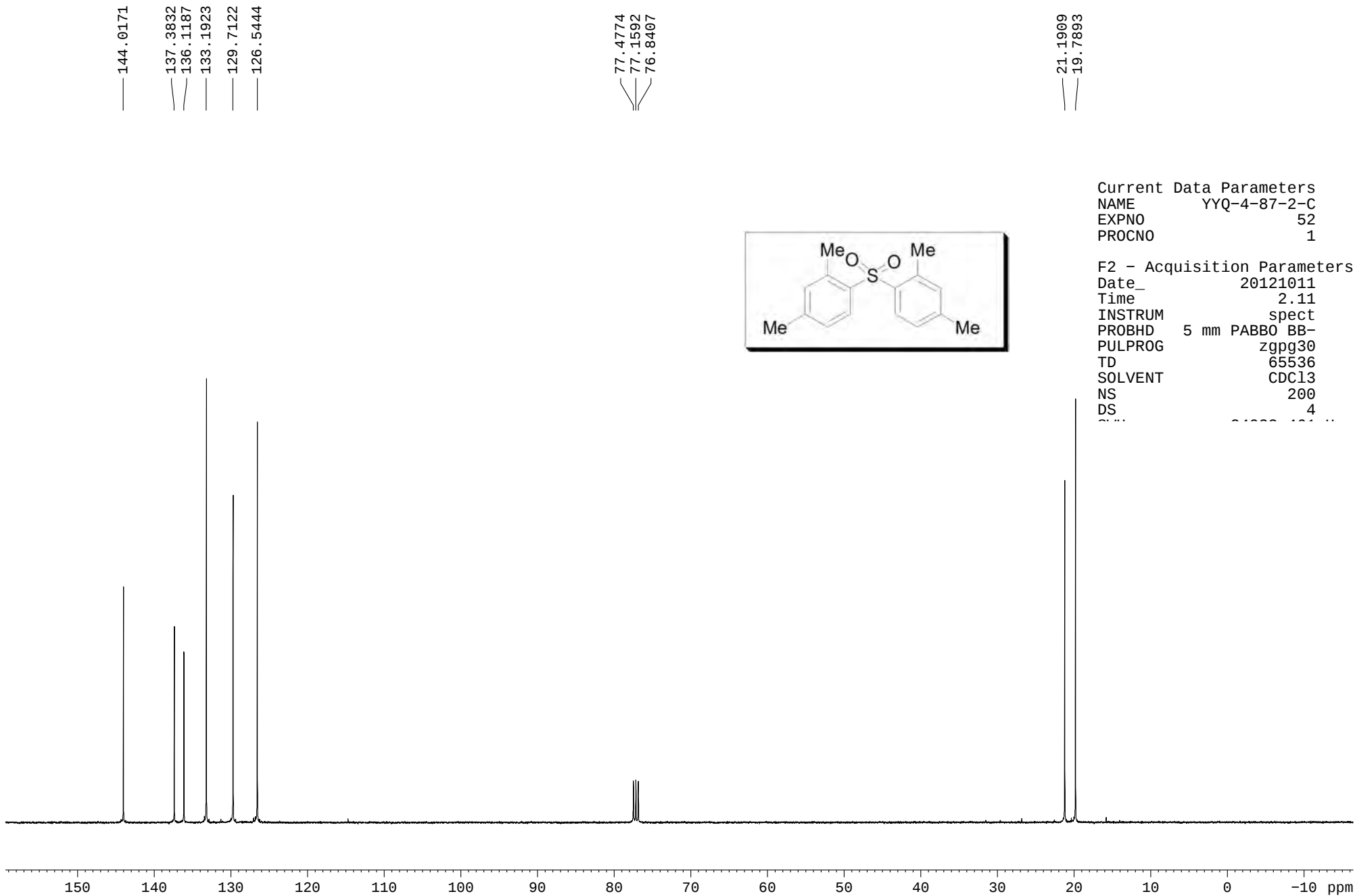
Current Data Parameters
 NAME YYQ-4-87-1-C
 EXPNO 20
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20121011
 Time 1.52
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 200
 DS 4



Current Data Parameters
NAME YYQ-4-87-2-H
EXPNO 50
PROCNO 1

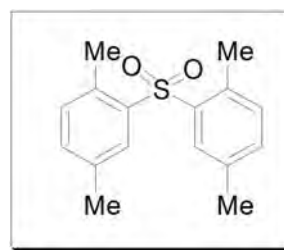
F2 - Acquisition Parameters
Date_ 20121011
Time 1.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2





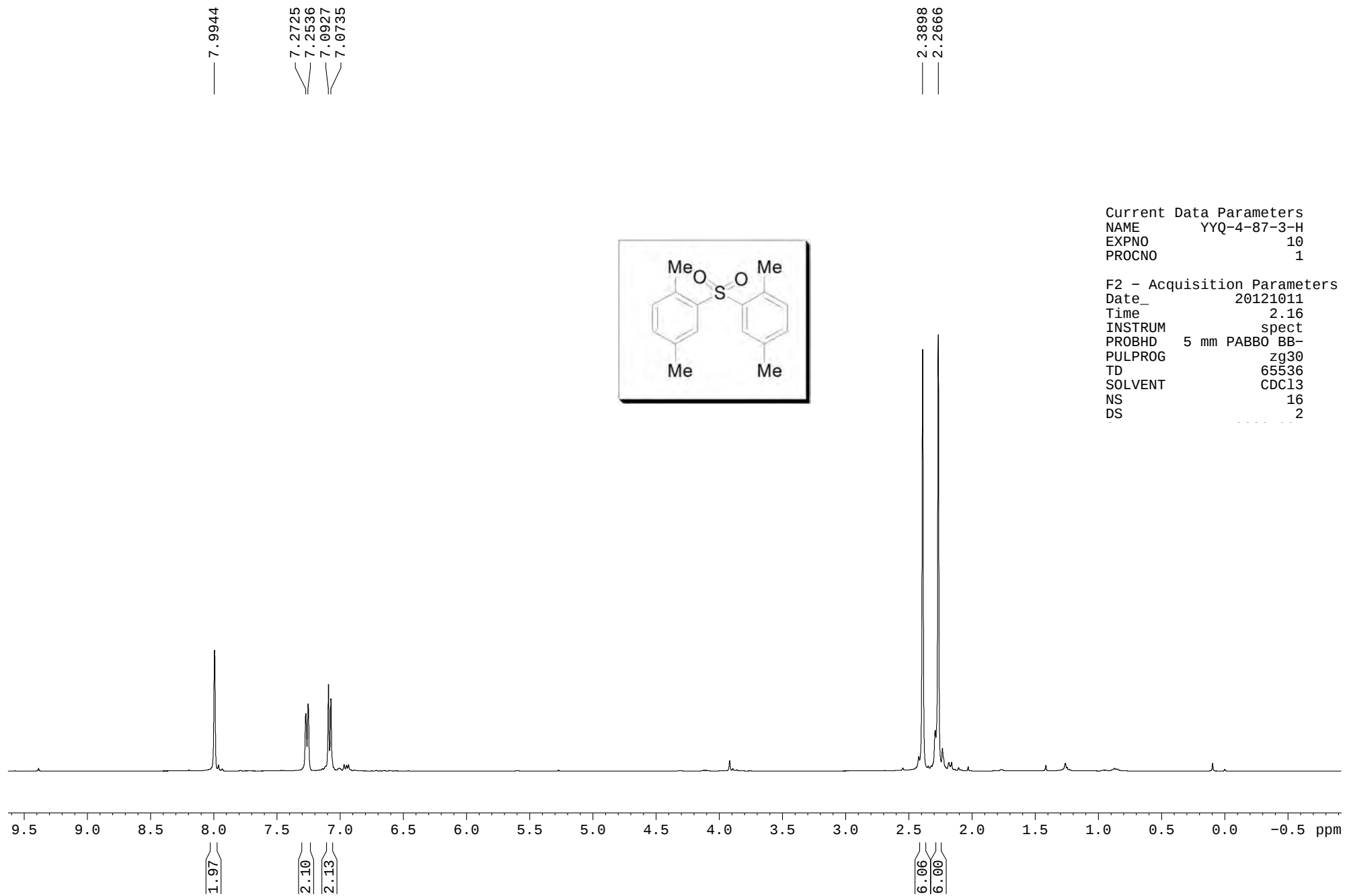
Current Data Parameters
NAME YYQ-4-87-2-C
EXPNO 52
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121011
Time 2.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4



Current Data Parameters
 NAME YYQ-4-87-3-H
 EXPNO 10
 PROCNO 1

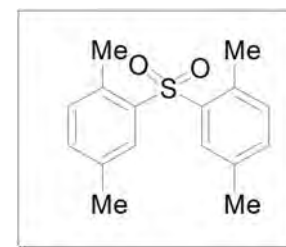
F2 - Acquisition Parameters
 Date_ 20121011
 Time 2.16
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2



138.6686
136.0236
134.4894
134.1134
132.5425
129.8827

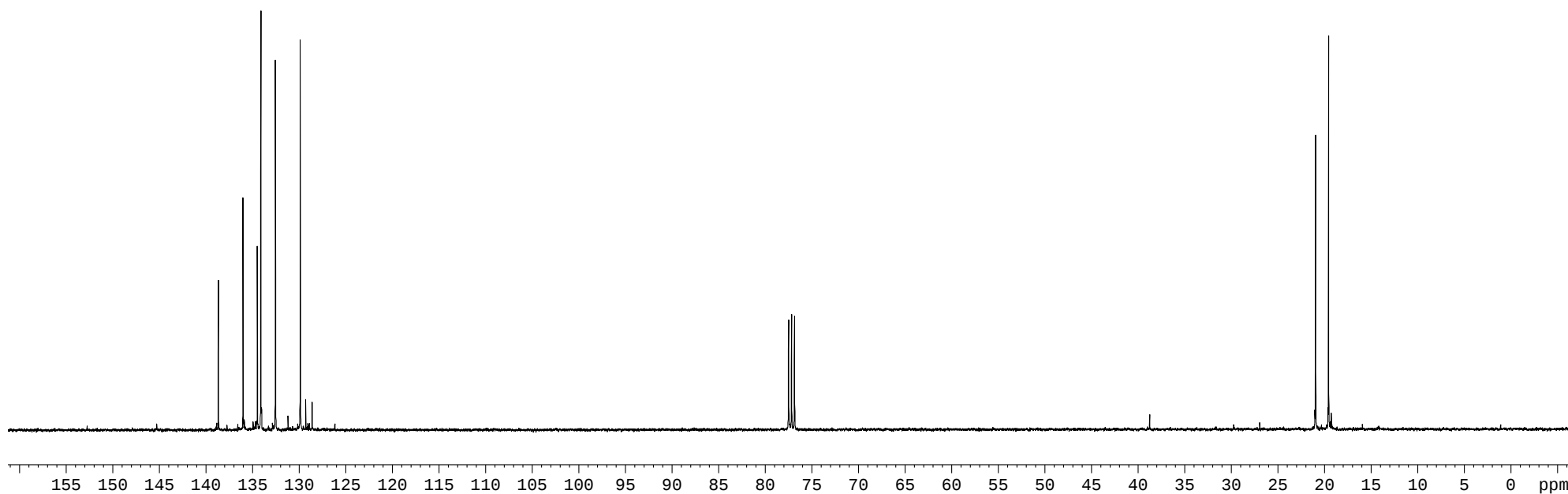
77.4848
77.1665
76.8479

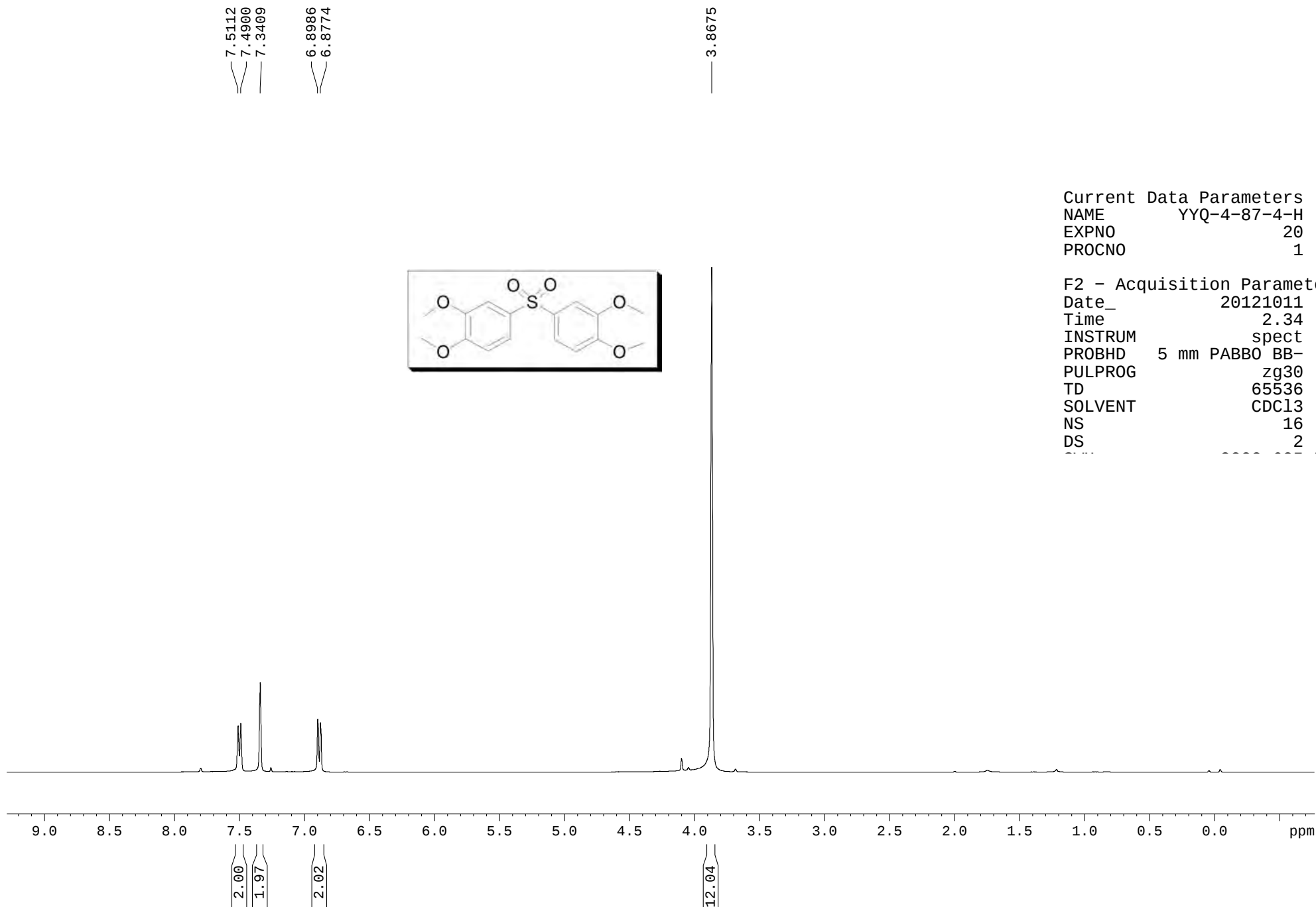
20.9340
19.5434



Current Data Parameters
NAME YYQ-4-87-3-C
EXPNO 12
PROCNO 1

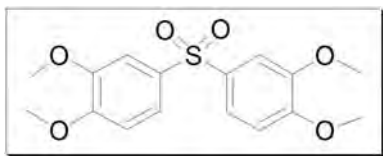
F2 - Acquisition Parameters
Date_ 20121011
Time 2.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4





Current Data Parameters
NAME YYQ-4-87-4-H
EXPNO 20
PROCNO 1

F2 - Acquisition Parameter
Date_ 20121011
Time 2.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



152.84
149.25

133.85

121.49

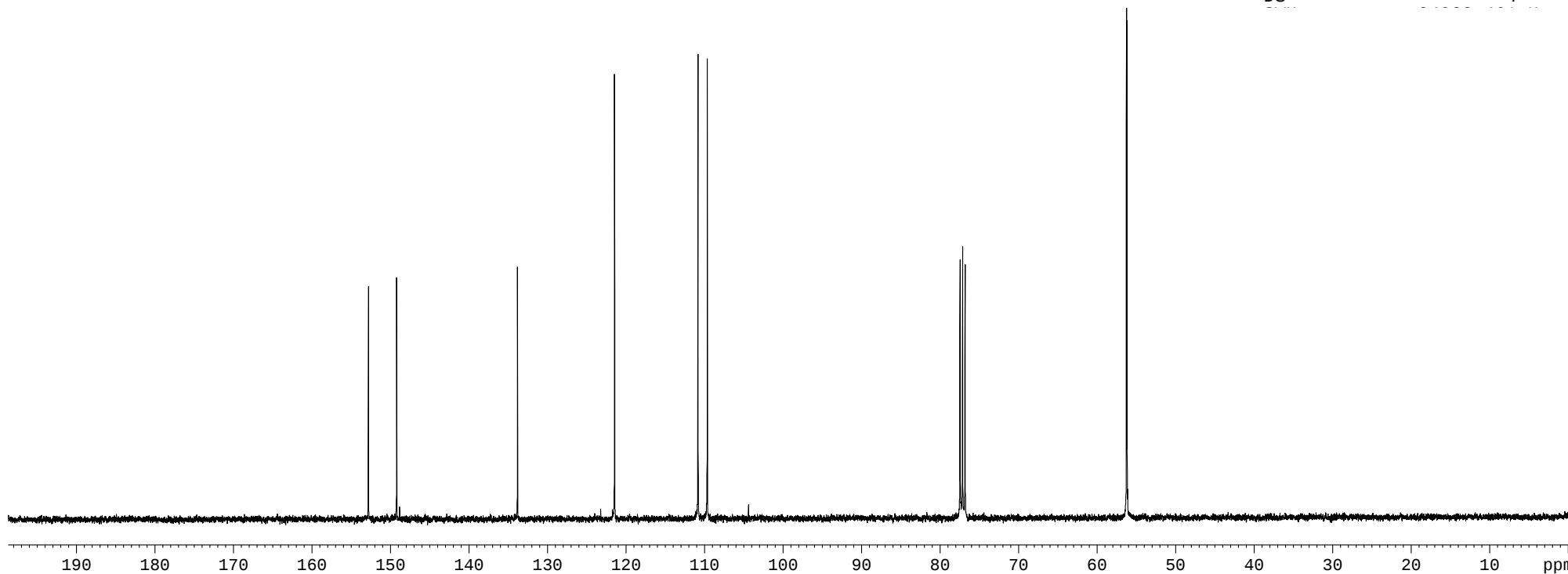
110.85
109.68

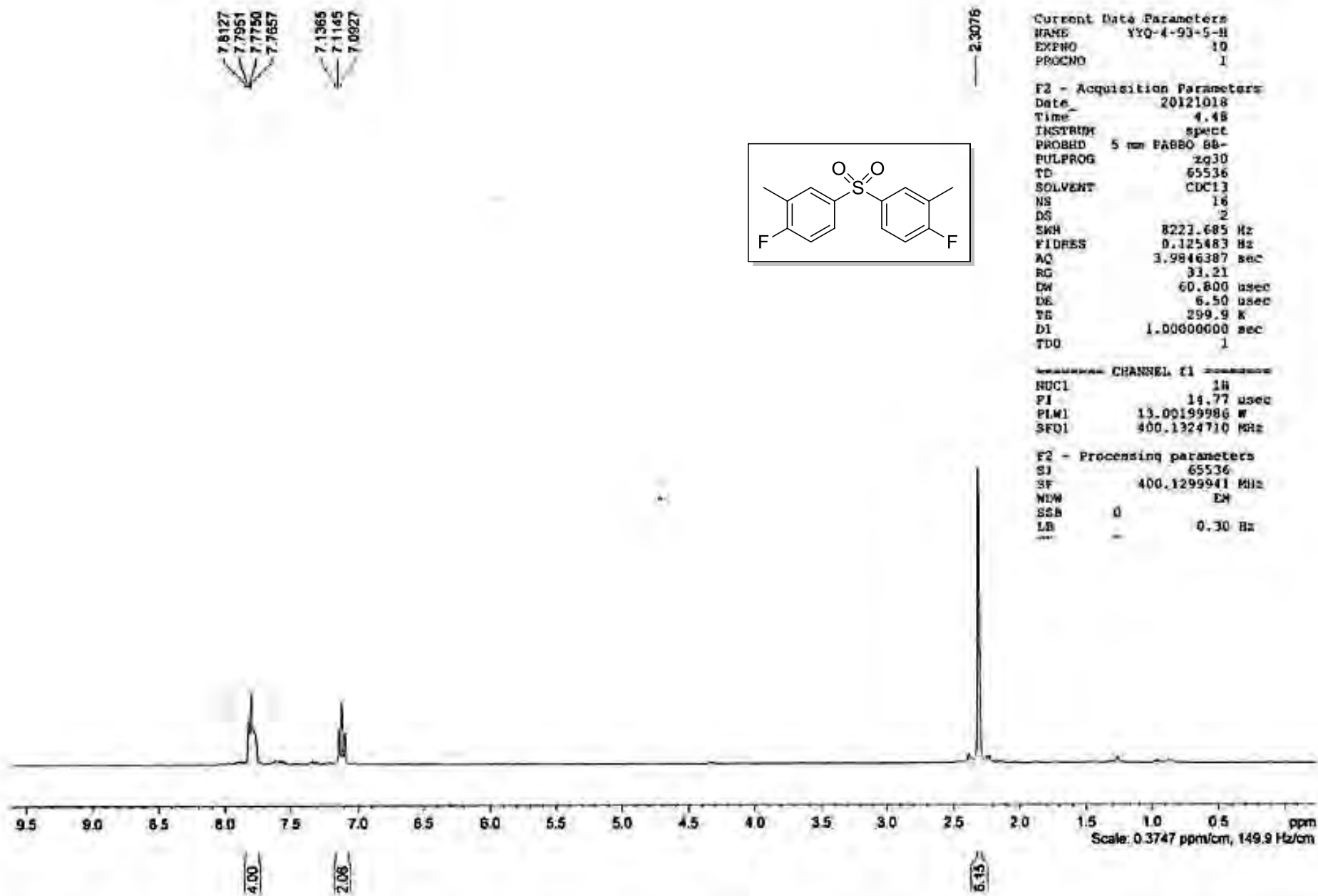
77.48
77.16
76.84

56.29
56.21

Current Data Parameters
NAME YYQ-4-87-4-C
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121011
Time 2.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 200
DS 4



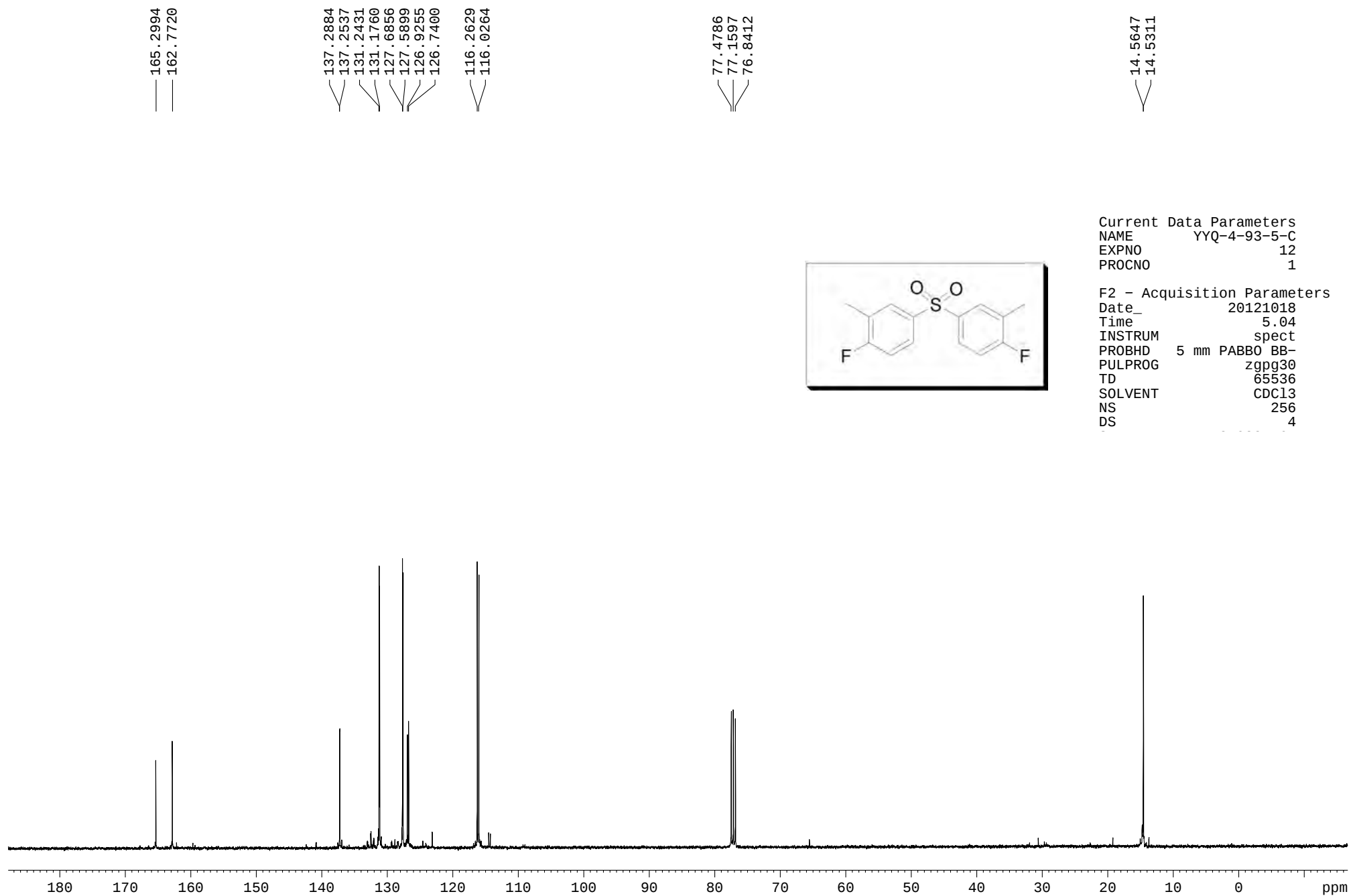


Current Data Parameters
 NAME YIQ-4-93-5-H
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date 20121018
 Time 4.48
 INSTRUM spect
 PROBHD 5 mm FASBO 88-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8221.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 31.21
 CW 60.800 usec
 DE 6.50 usec
 TE 299.9 K
 DI 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.77 usec
 PLW1 13.00199986 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1299941 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz



165.2994
162.7720

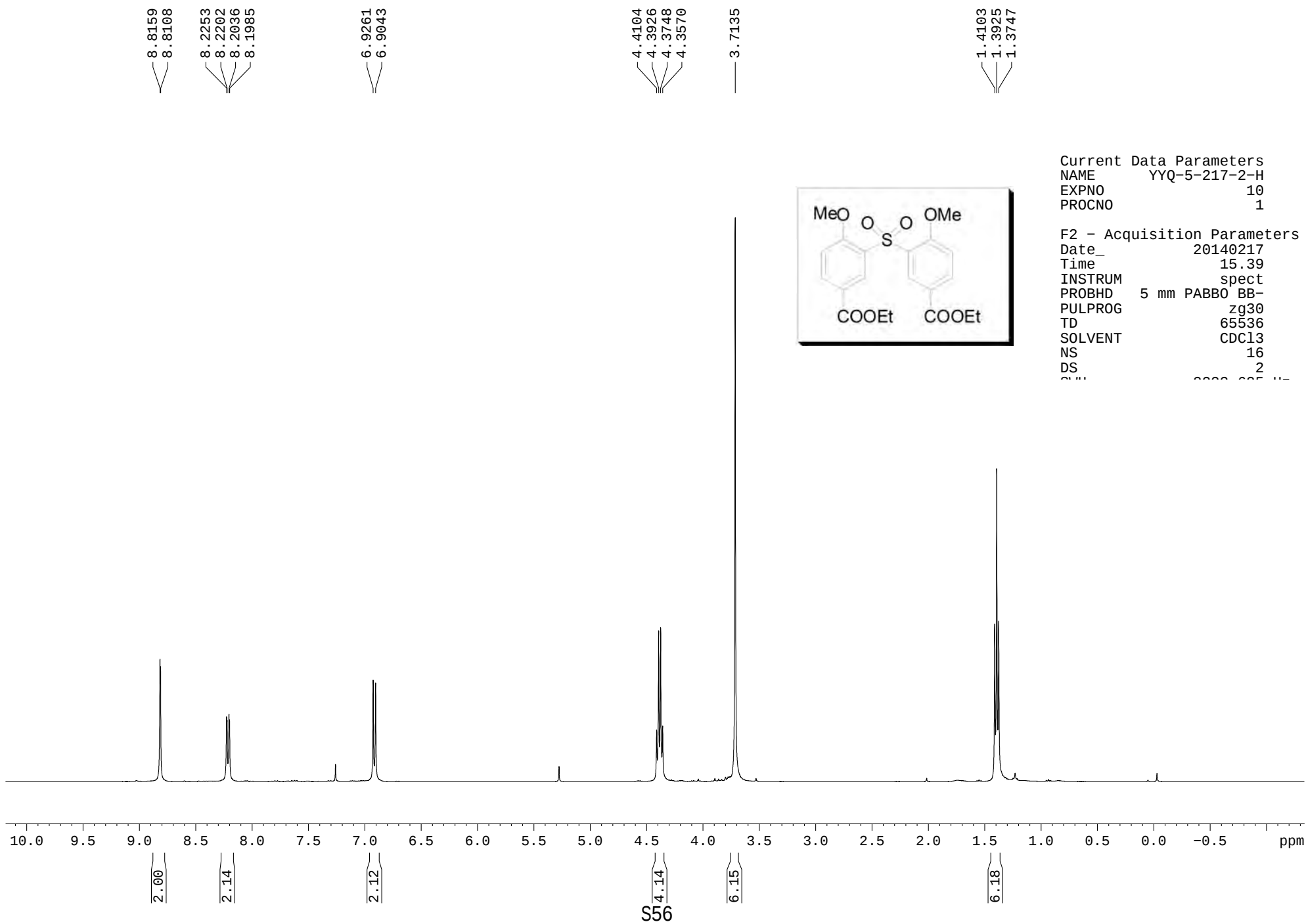
137.2884
137.2537
131.2431
131.1760
127.6856
127.5899
126.9255
126.7400
116.2629
116.0264

77.4786
77.1597
76.8412

14.5647
14.5311

Current Data Parameters
NAME YYQ-4-93-5-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121018
Time 5.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4



— 165.24
— 160.39

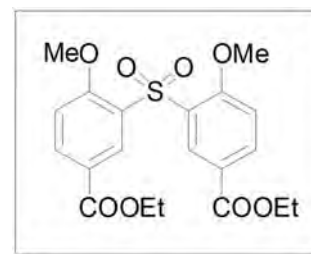
— 136.83
— 133.02
— 128.75
— 122.92

— 111.96

77.48
77.16
76.84

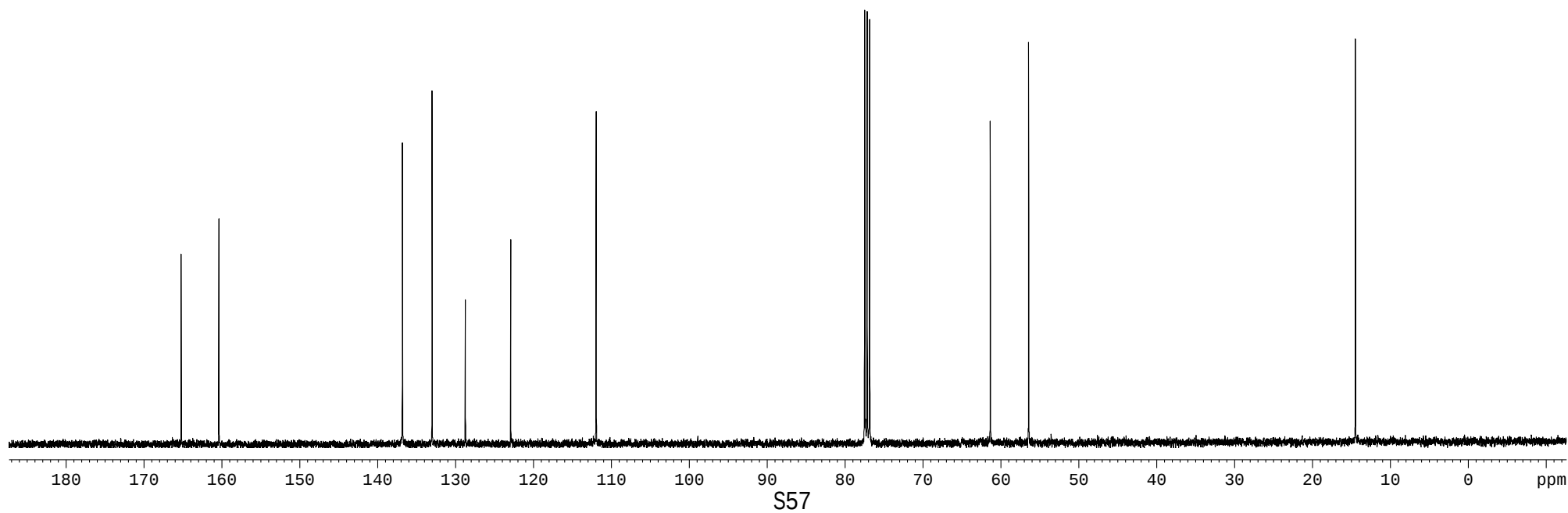
— 61.35
— 56.42

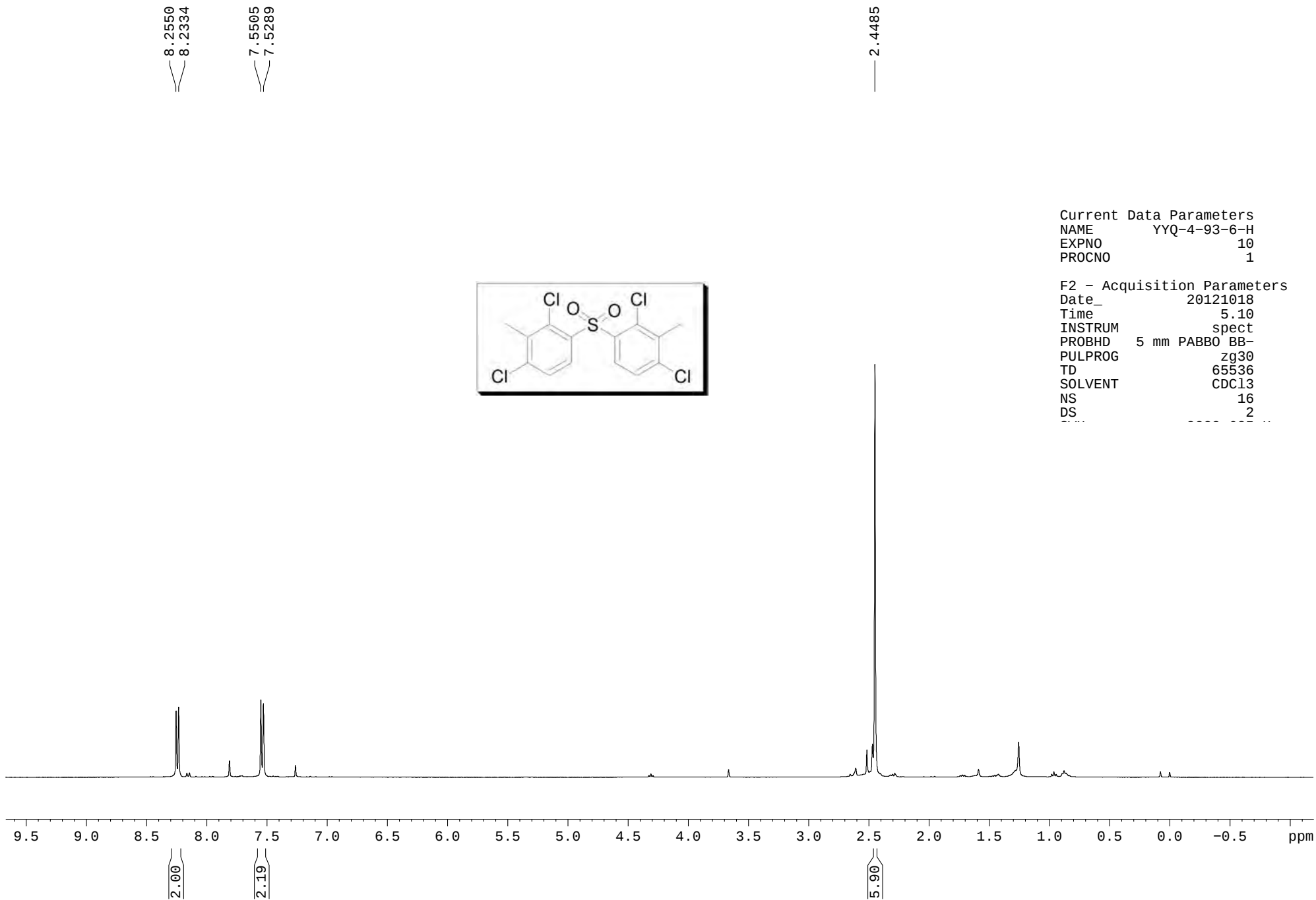
— 14.47



Current Data Parameters
NAME YYQ-5-217-1-2-C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140217
Time 16.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4
~... ..

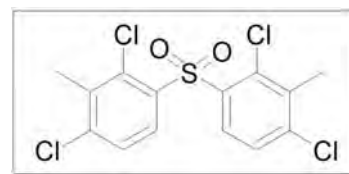




— 141.4603
— 137.2960
— 136.6291
— 133.3474
— 130.7668
— 127.7006

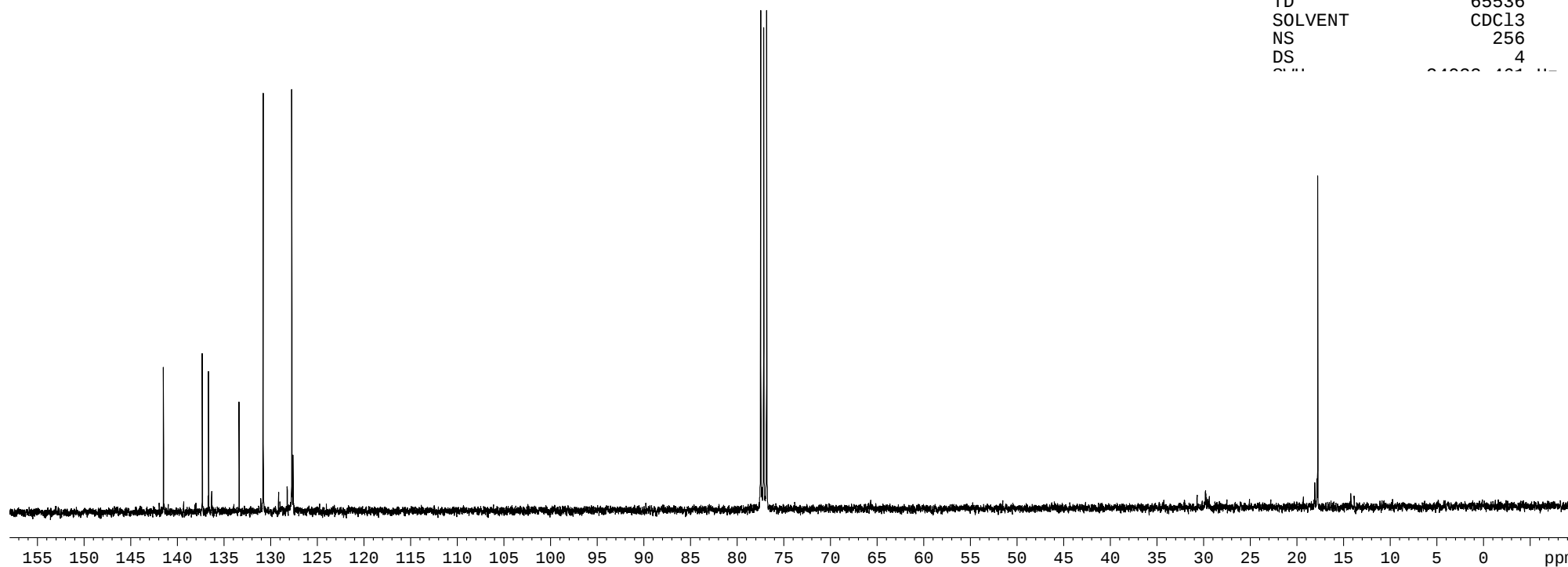
77.4766
77.1590
76.8415

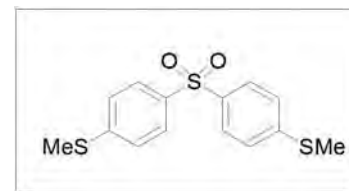
— 17.7655



Current Data Parameters
NAME YYQ-4-93-6-C
EXPNO 12
PROCNO 1

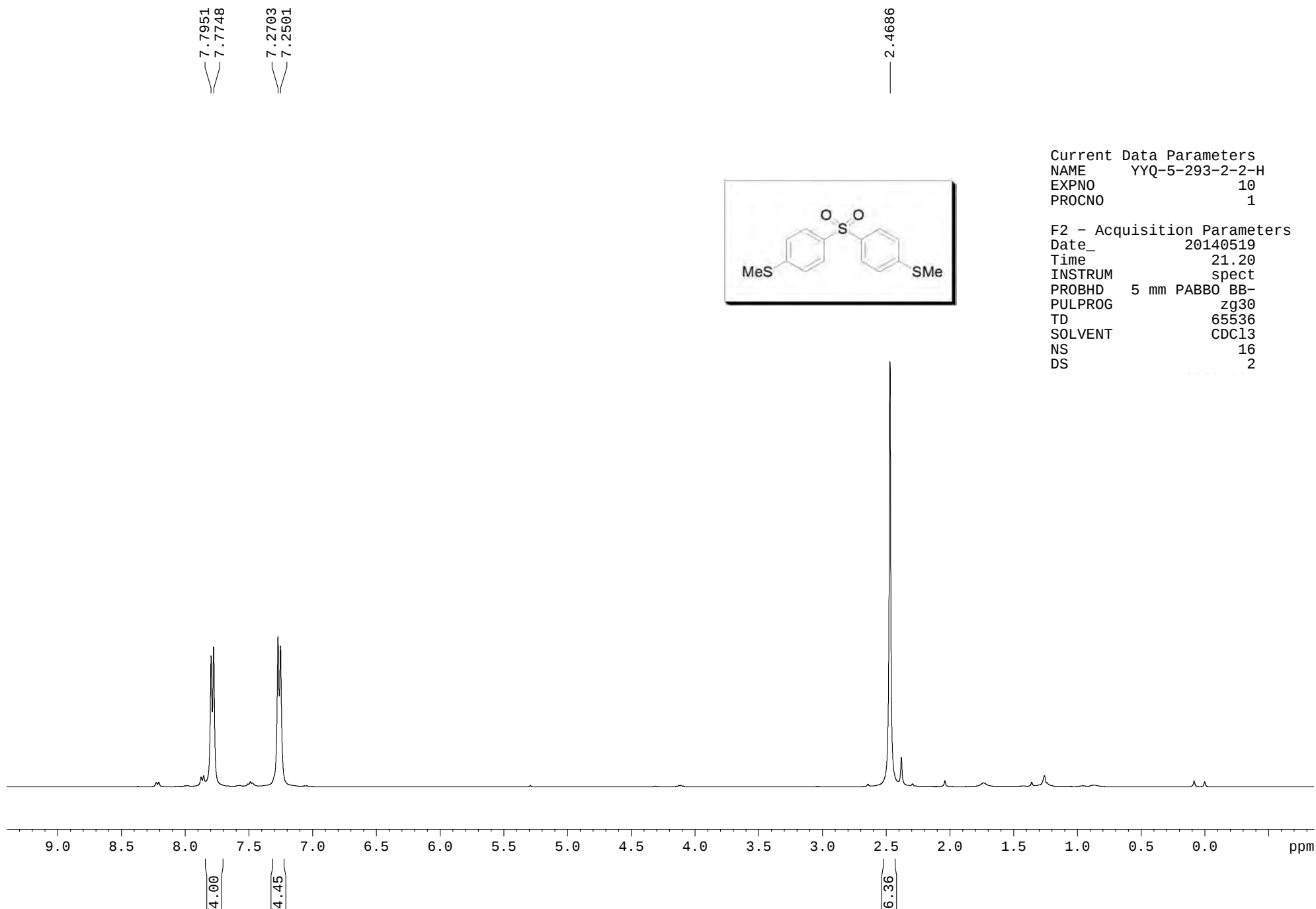
F2 - Acquisition Parameters
Date_ 20121018
Time 5.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
AQ 0.10000000

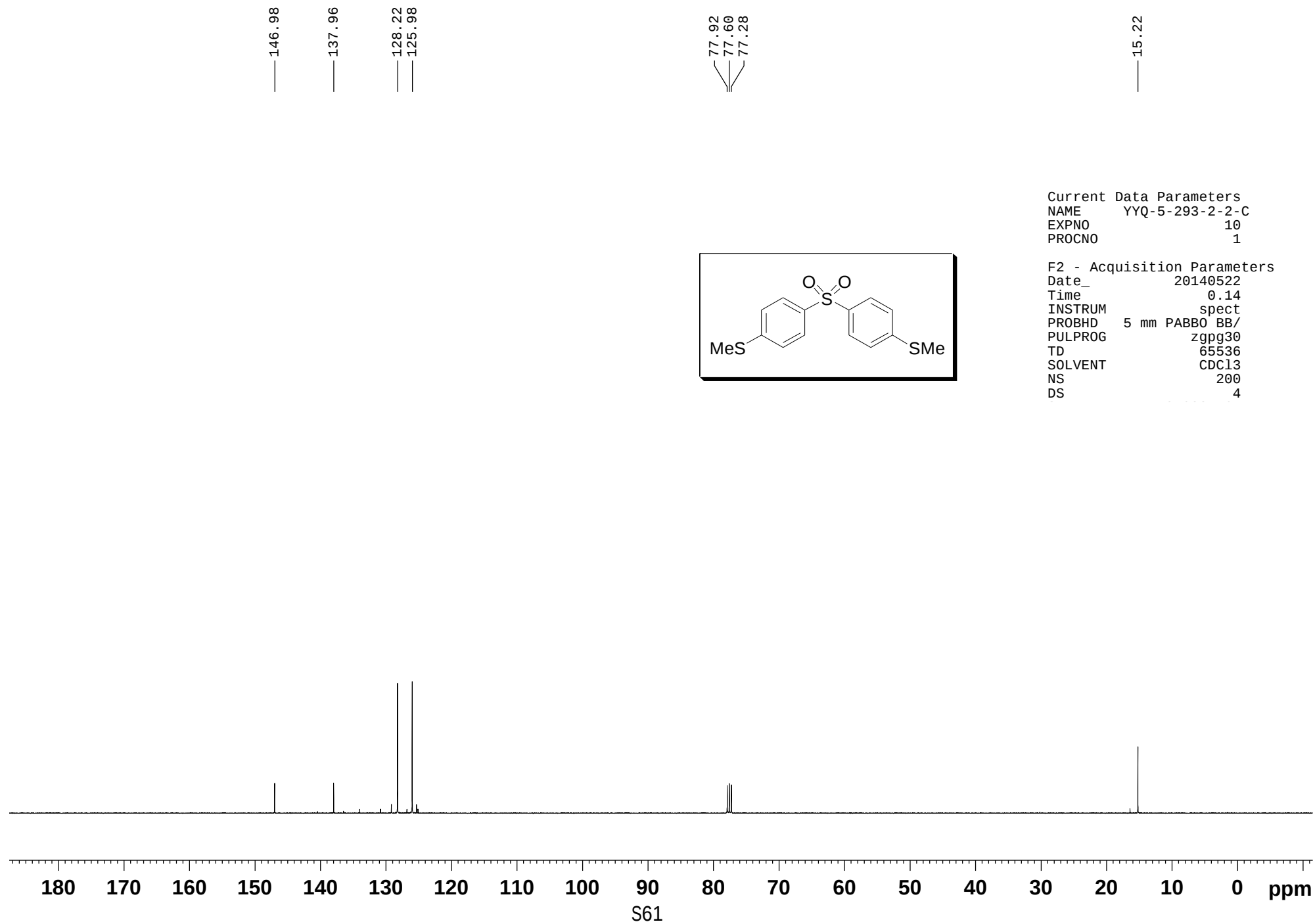


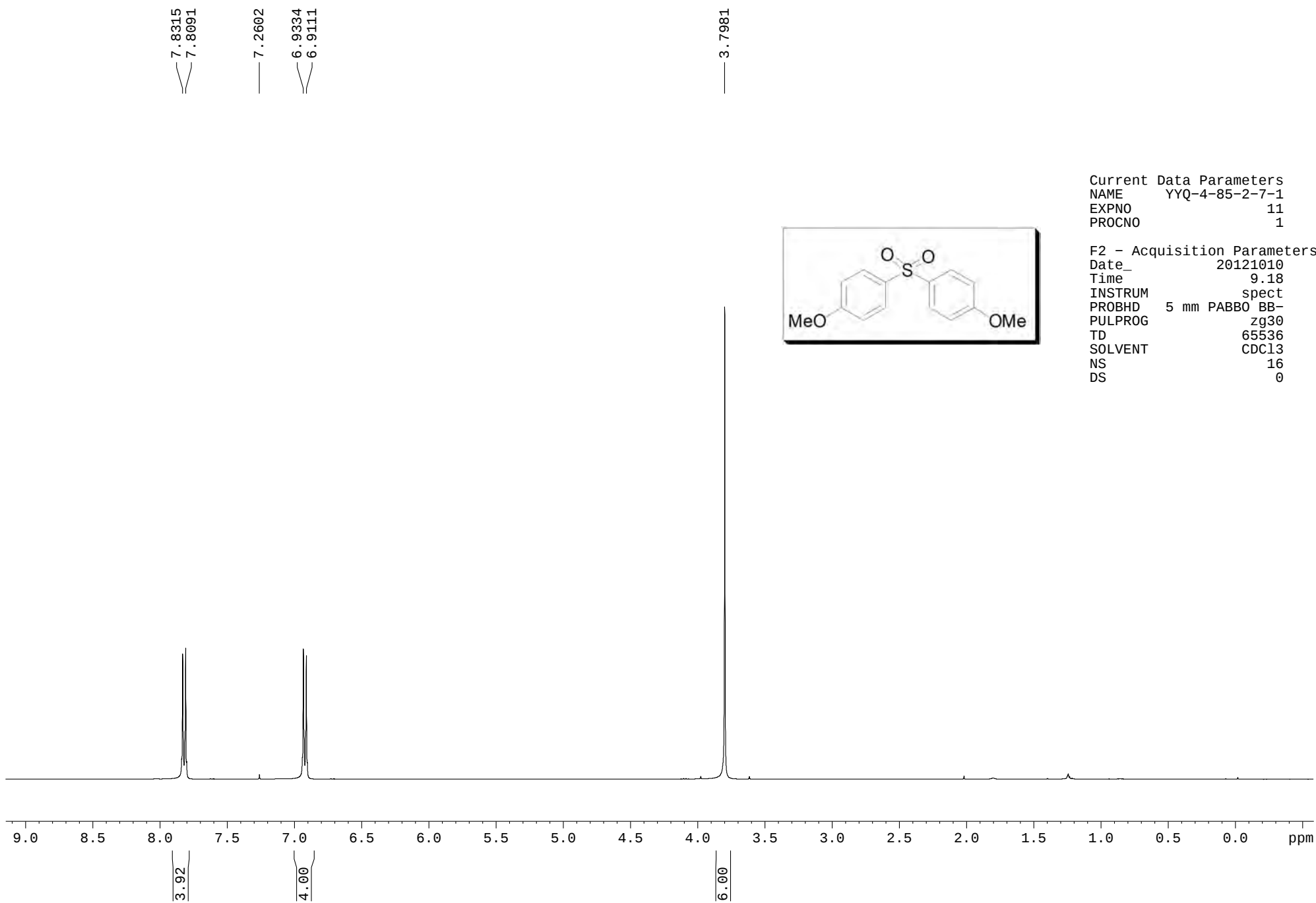


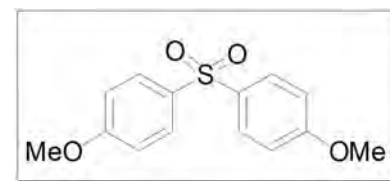
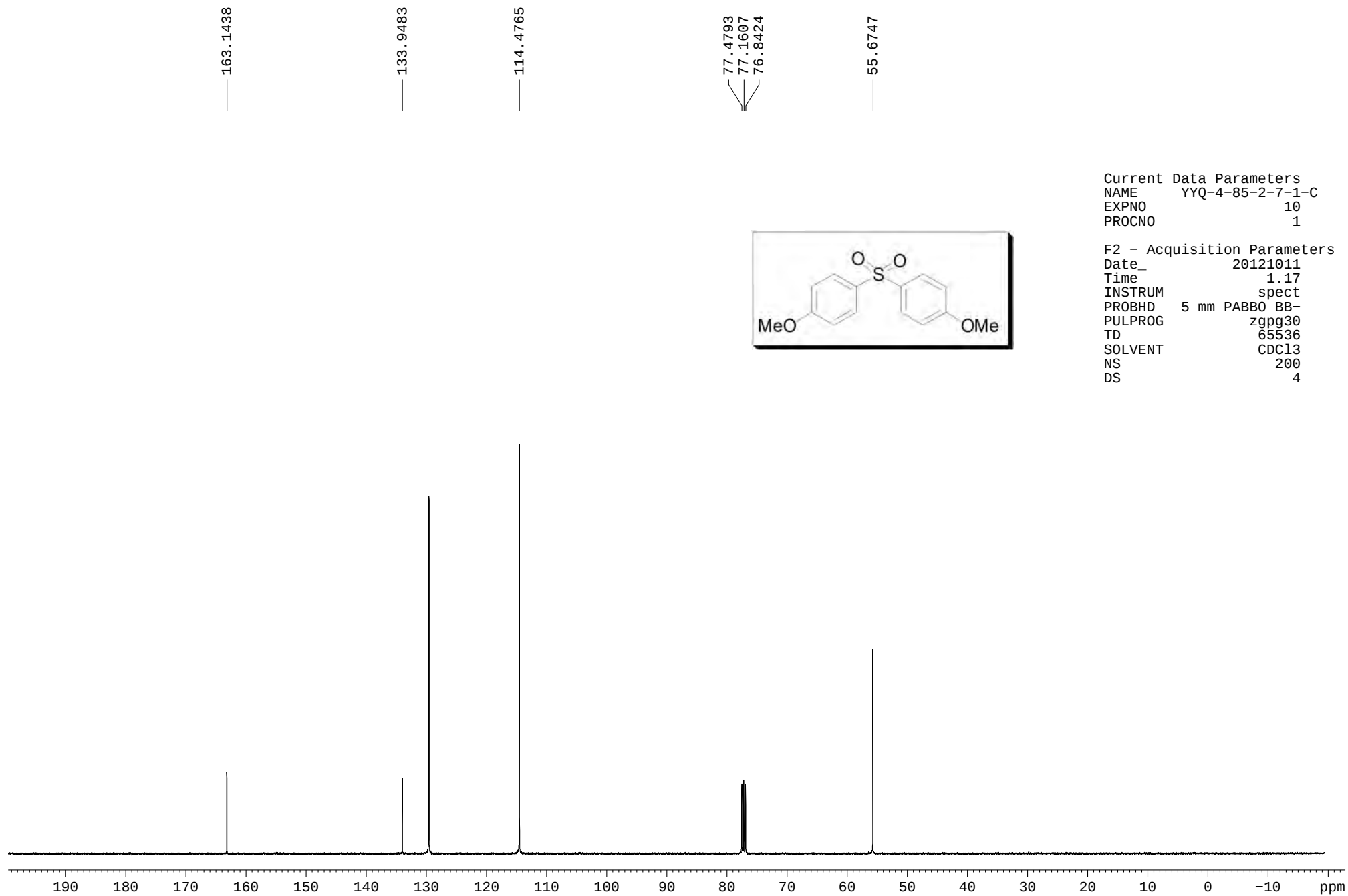
Current Data Parameters
 NAME YYQ-5-293-2-2-H
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140519
 Time 21.20
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2



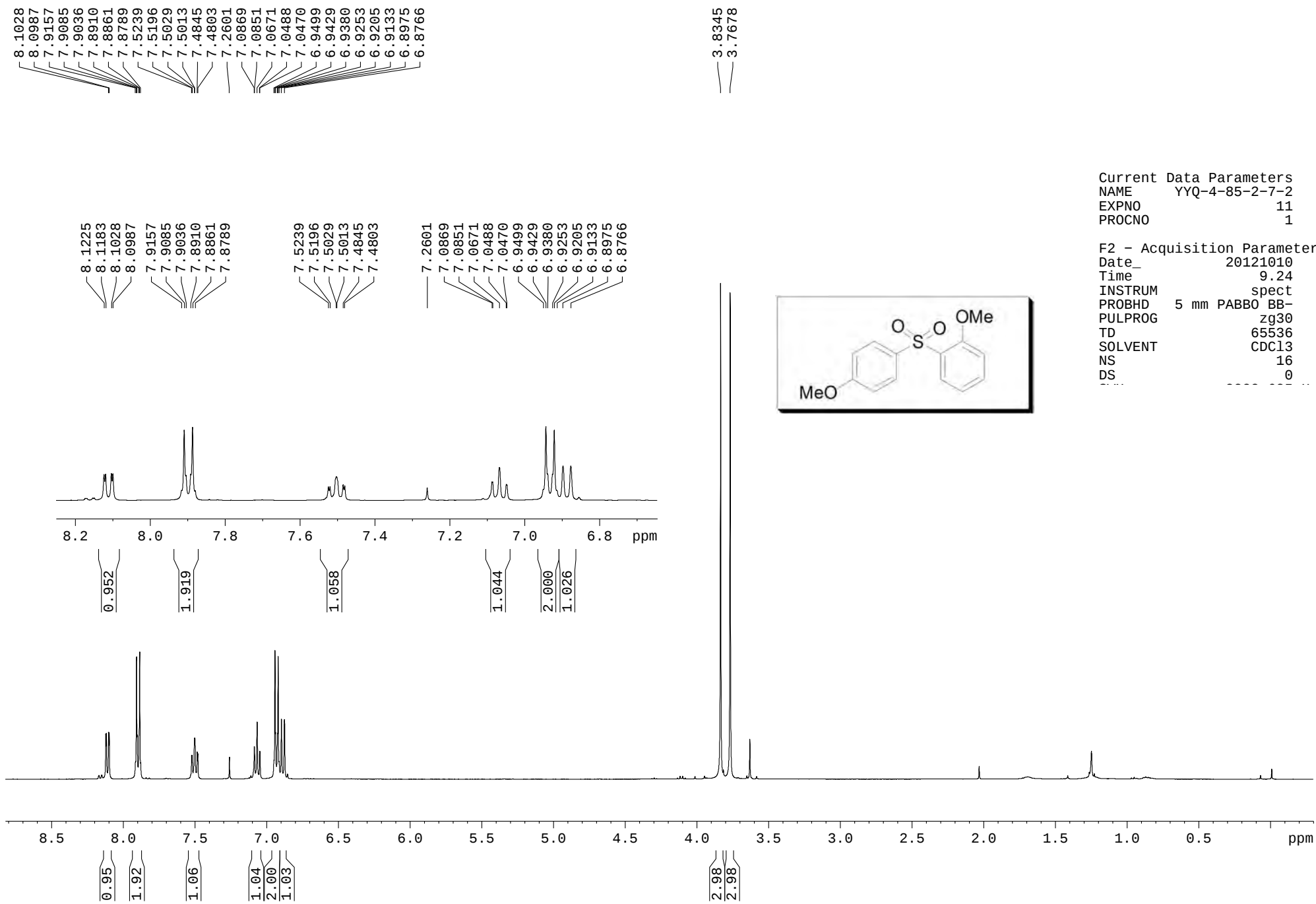






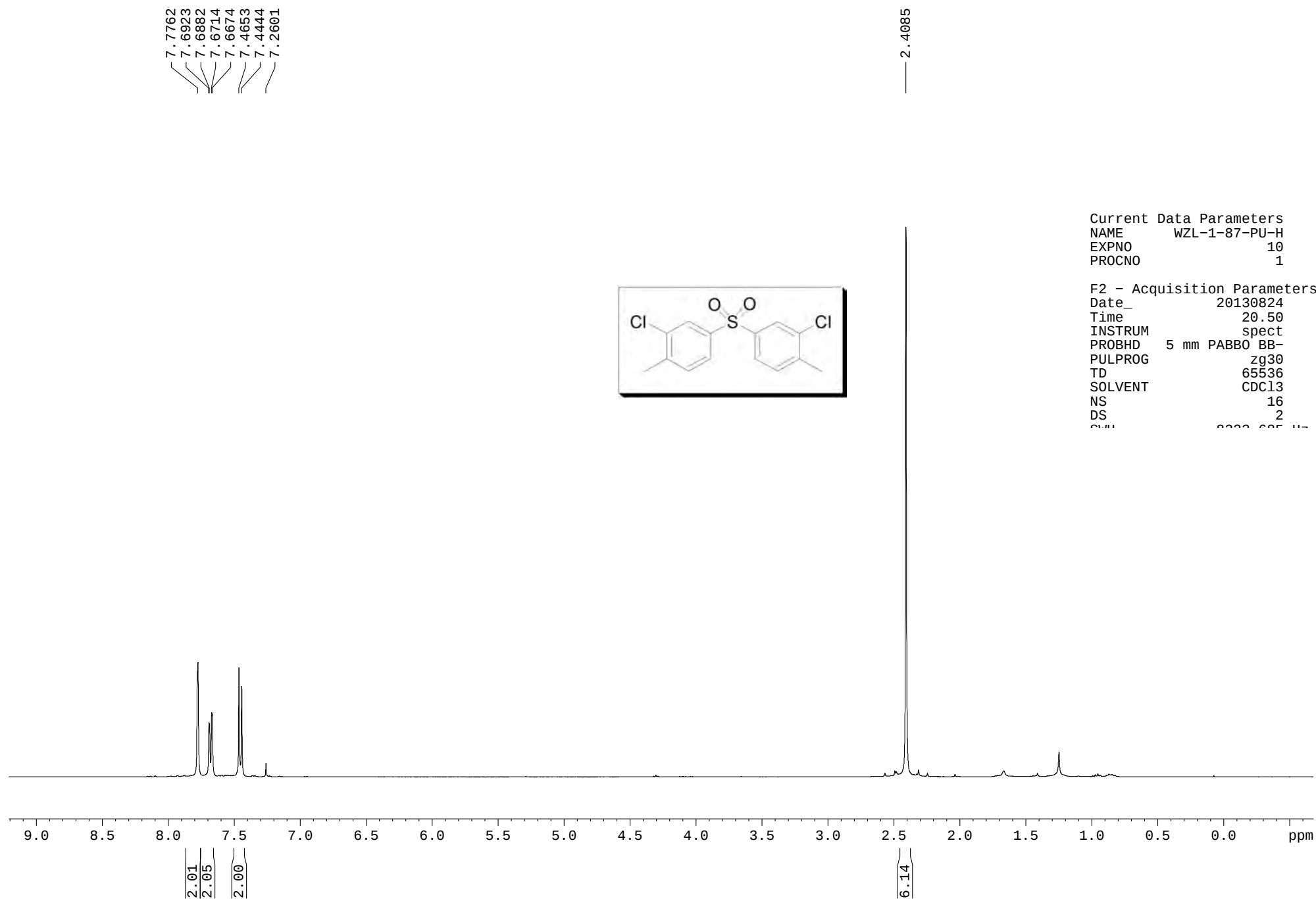
Current Data Parameters
NAME YYQ-4-85-2-7-1-C
EXPNO 10
PROCNO 1

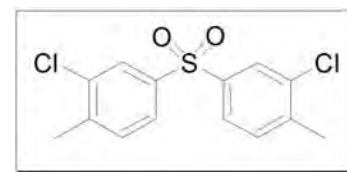
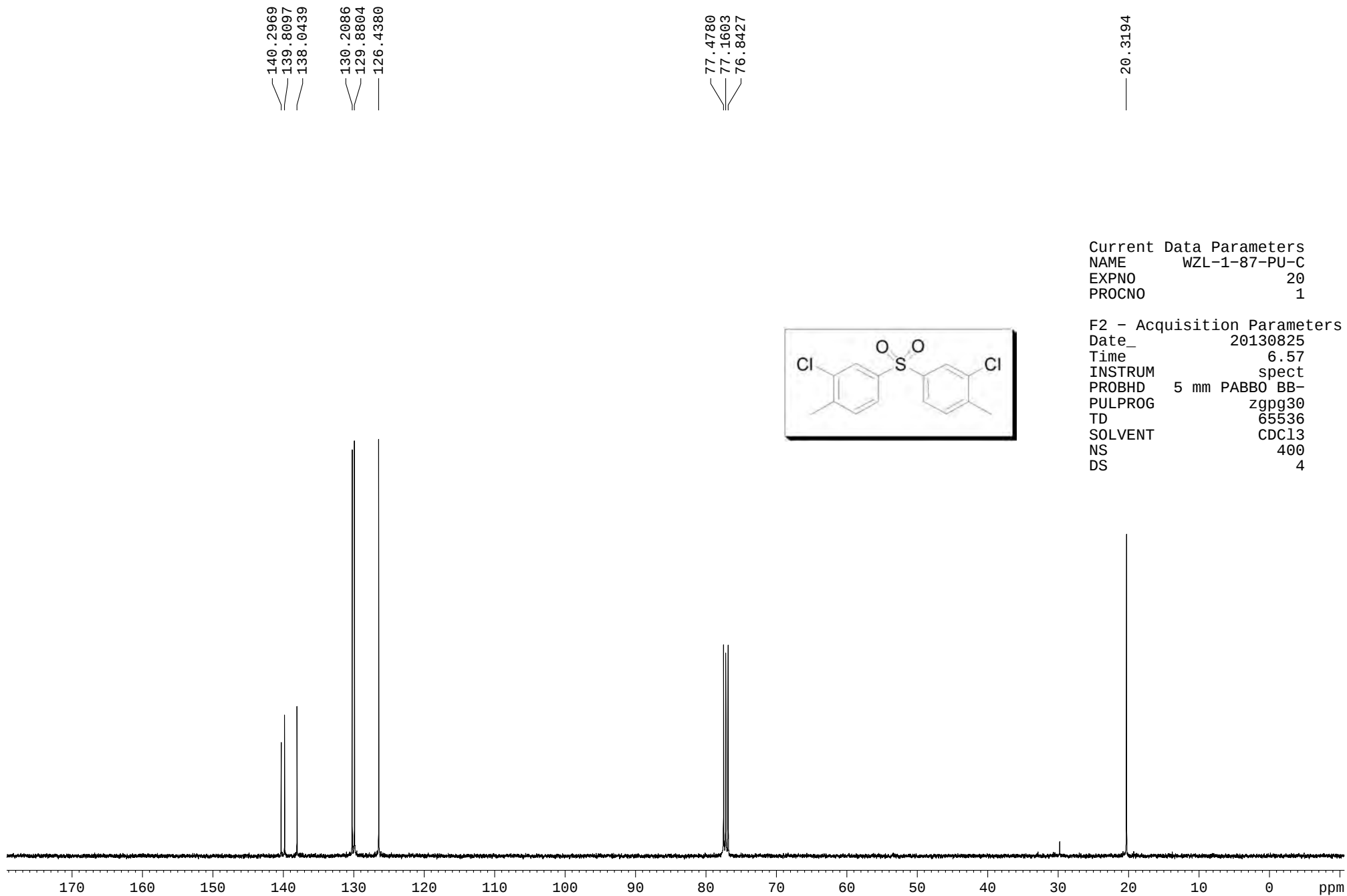
F2 - Acquisition Parameters
Date_ 20121011
Time 1.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4



Current Data Parameters
NAME YYQ-4-85-2-7-2
EXPNO 11
PROCNO 1

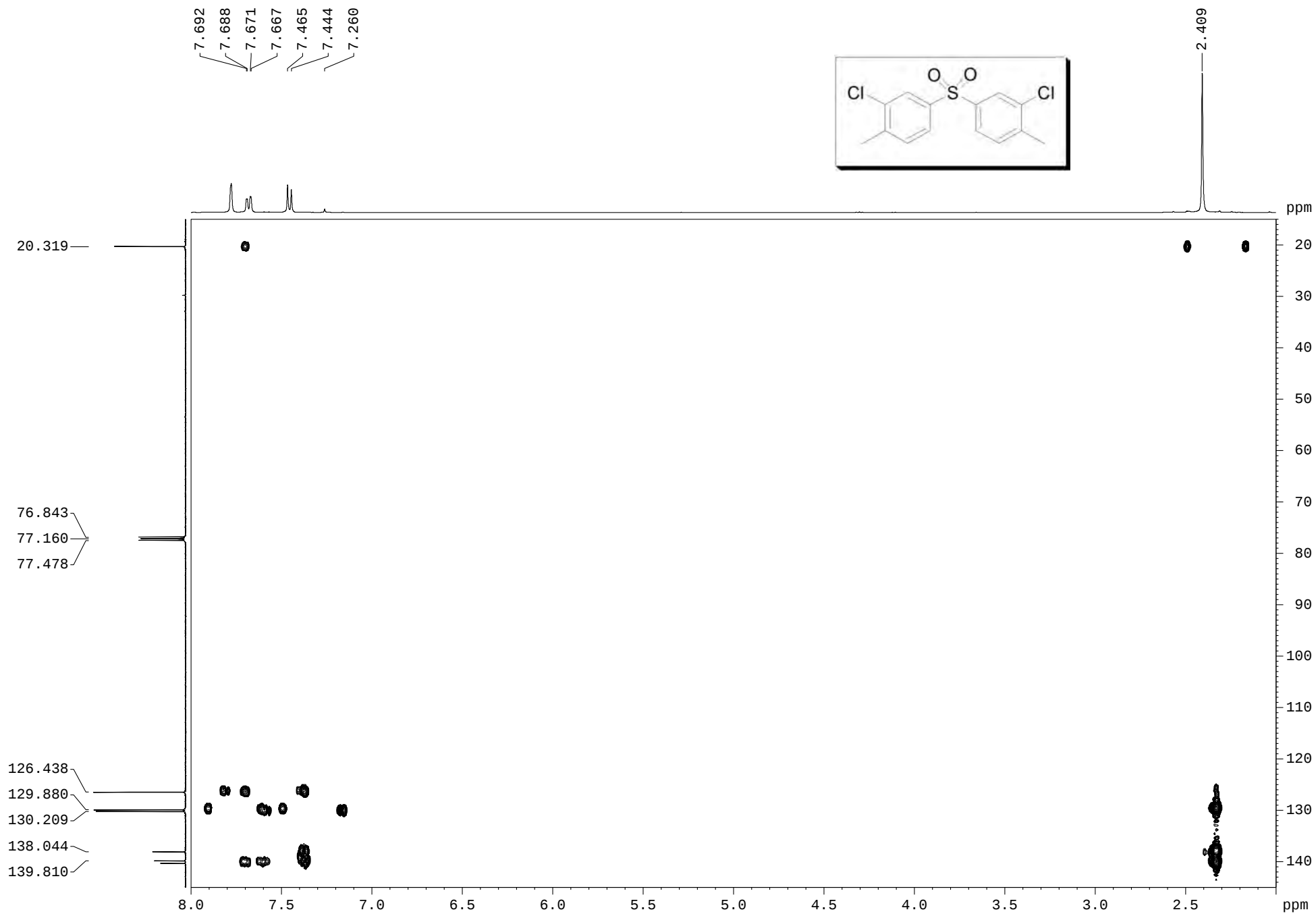
F2 - Acquisition Parameters
Date_ 20121010
Time 9.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 0





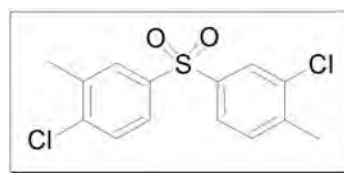
Current Data Parameters
NAME WZL-1-87-PU-C
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130825
Time 6.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4



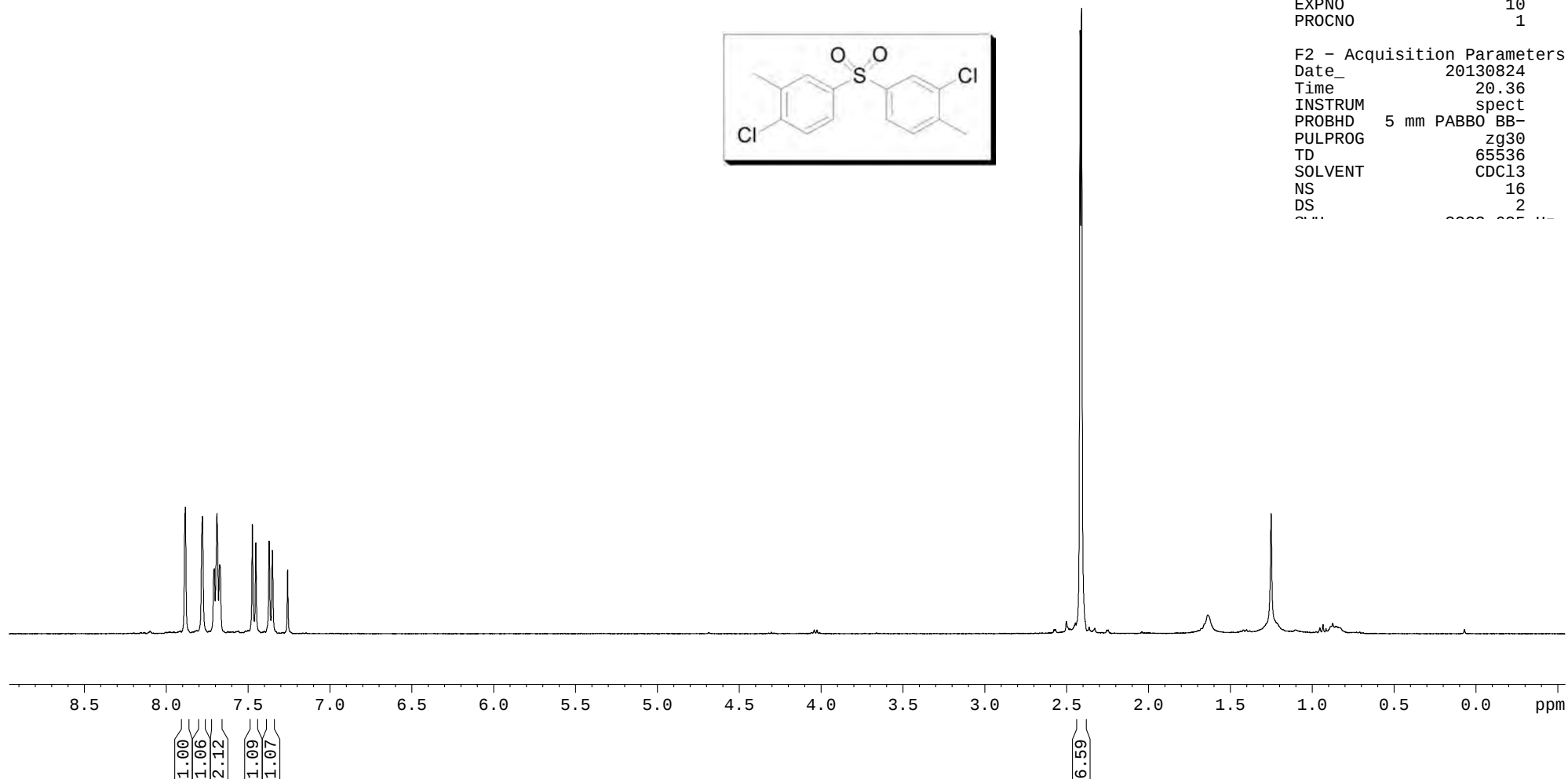
7.8829
7.7783
7.7062
7.6900
7.6738
7.4735
7.4526
7.3709
7.3509

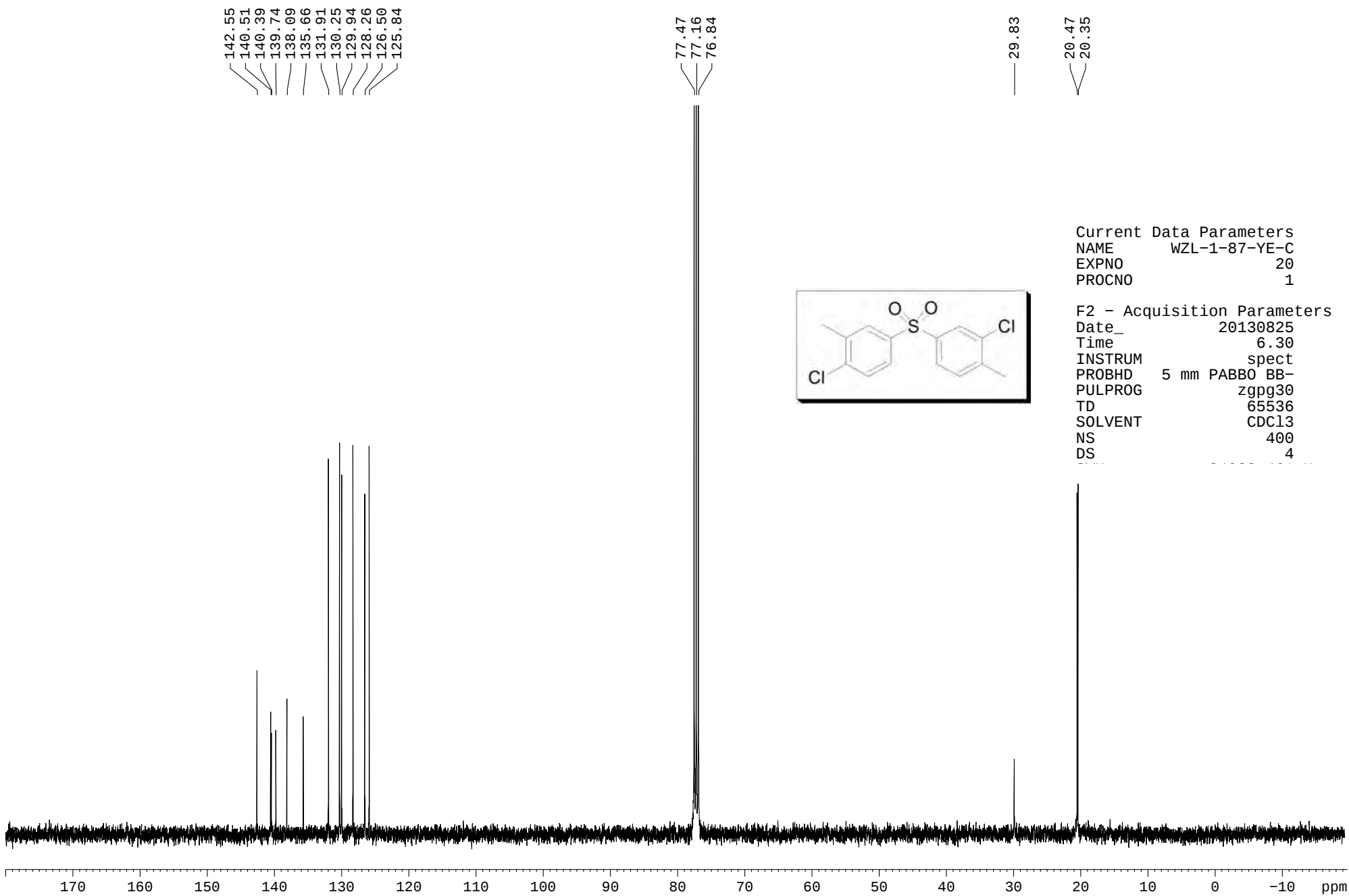
2.4163
2.4079



Current Data Parameters
NAME WZL-1-87-YE-H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130824
Time 20.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
AQ 0.000 0.000 0.000





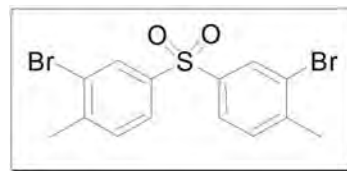
Current Data Parameters
NAME WZL-1-87-YE-C
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130825
Time 6.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4

7.7622
7.7595
7.6657
7.6448
7.5936
7.5895
7.2595

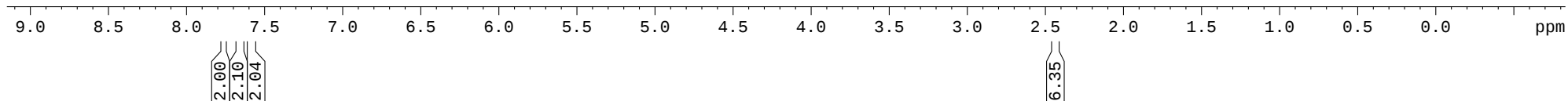
2.4339

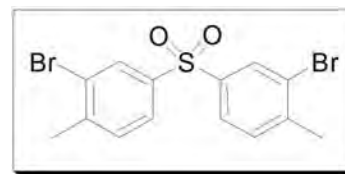
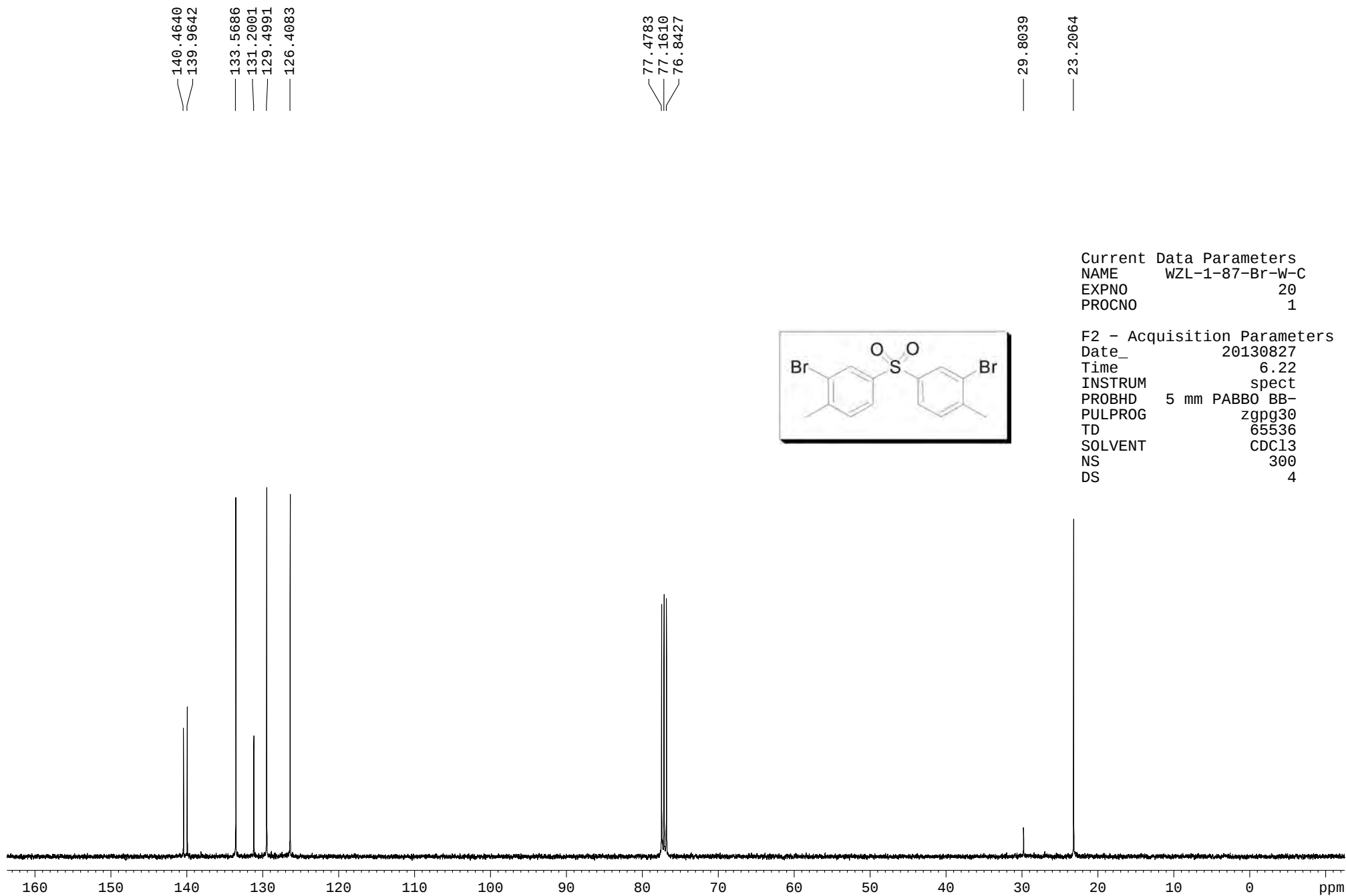
1.2484



Current Data Parameters
NAME WZL-1-87-Br-W-H
EXPNO 10
PROCNO 1

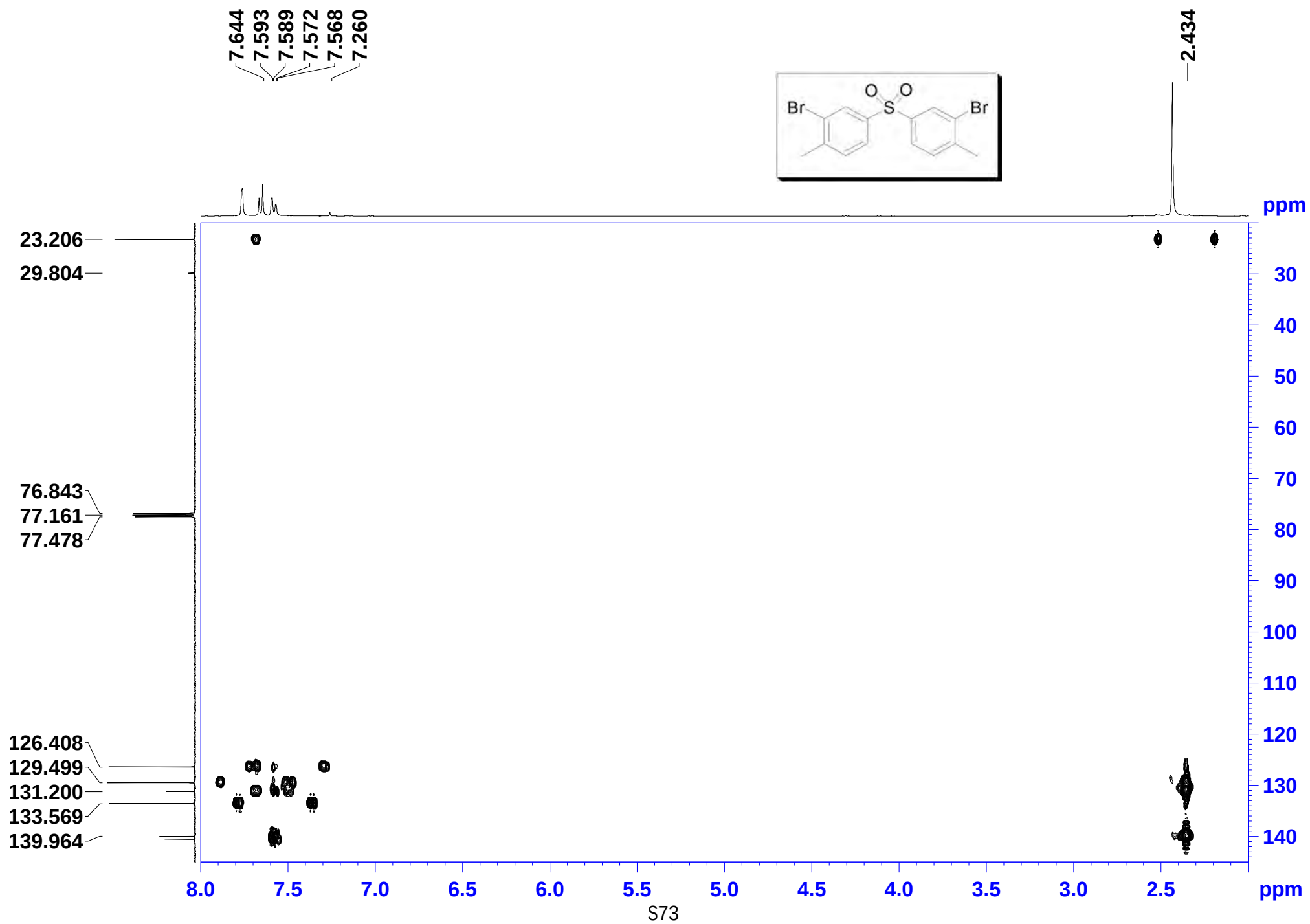
F2 - Acquisition Parameters
Date_ 20130826
Time 12.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2

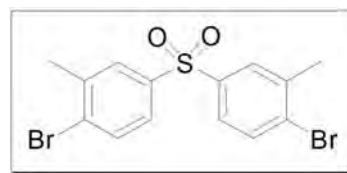




Current Data Parameters
NAME WZL-1-87-Br-W-C
EXPNO 20
PROCNO 1

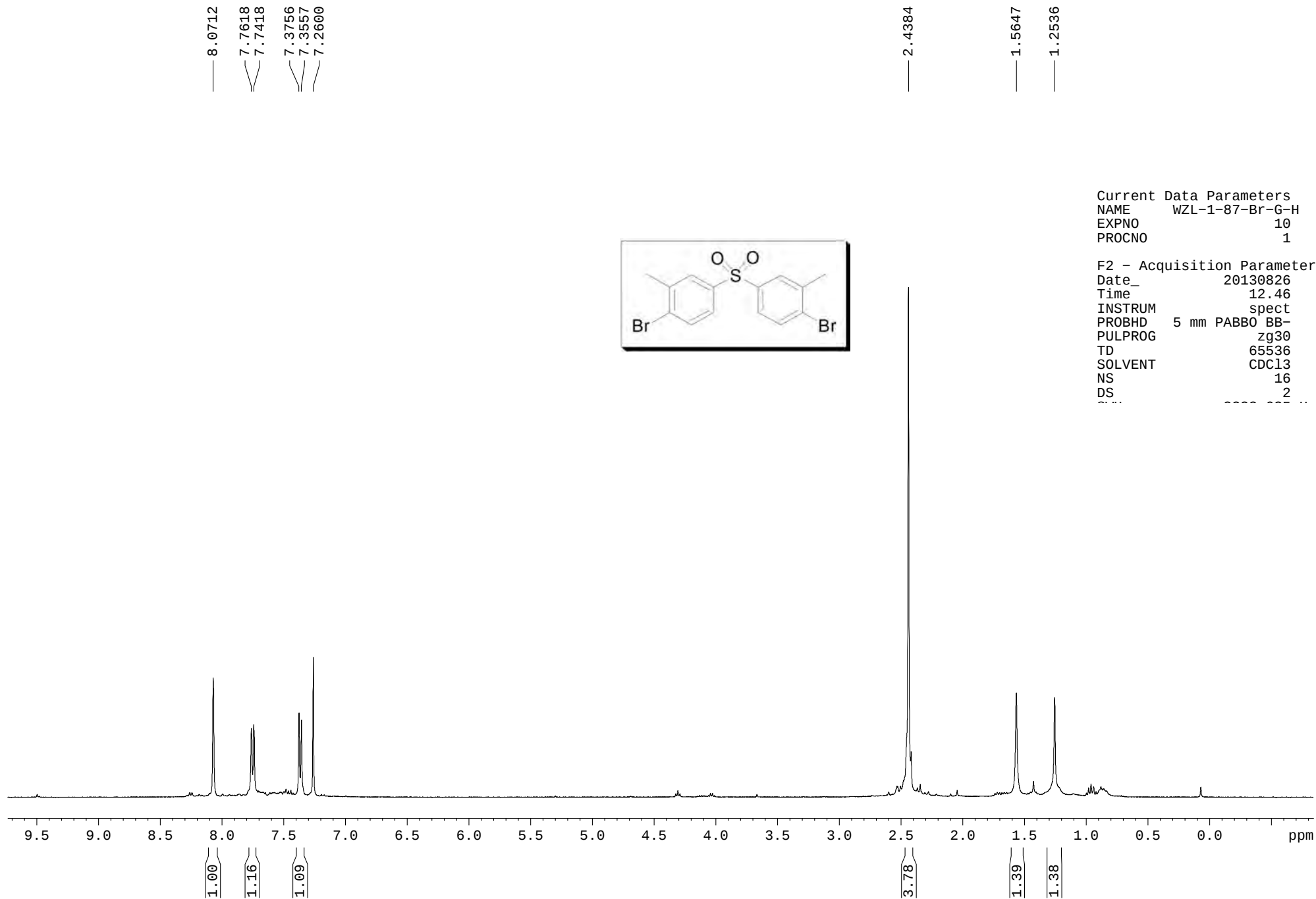
F2 - Acquisition Parameters
Date_ 20130827
Time 6.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 4

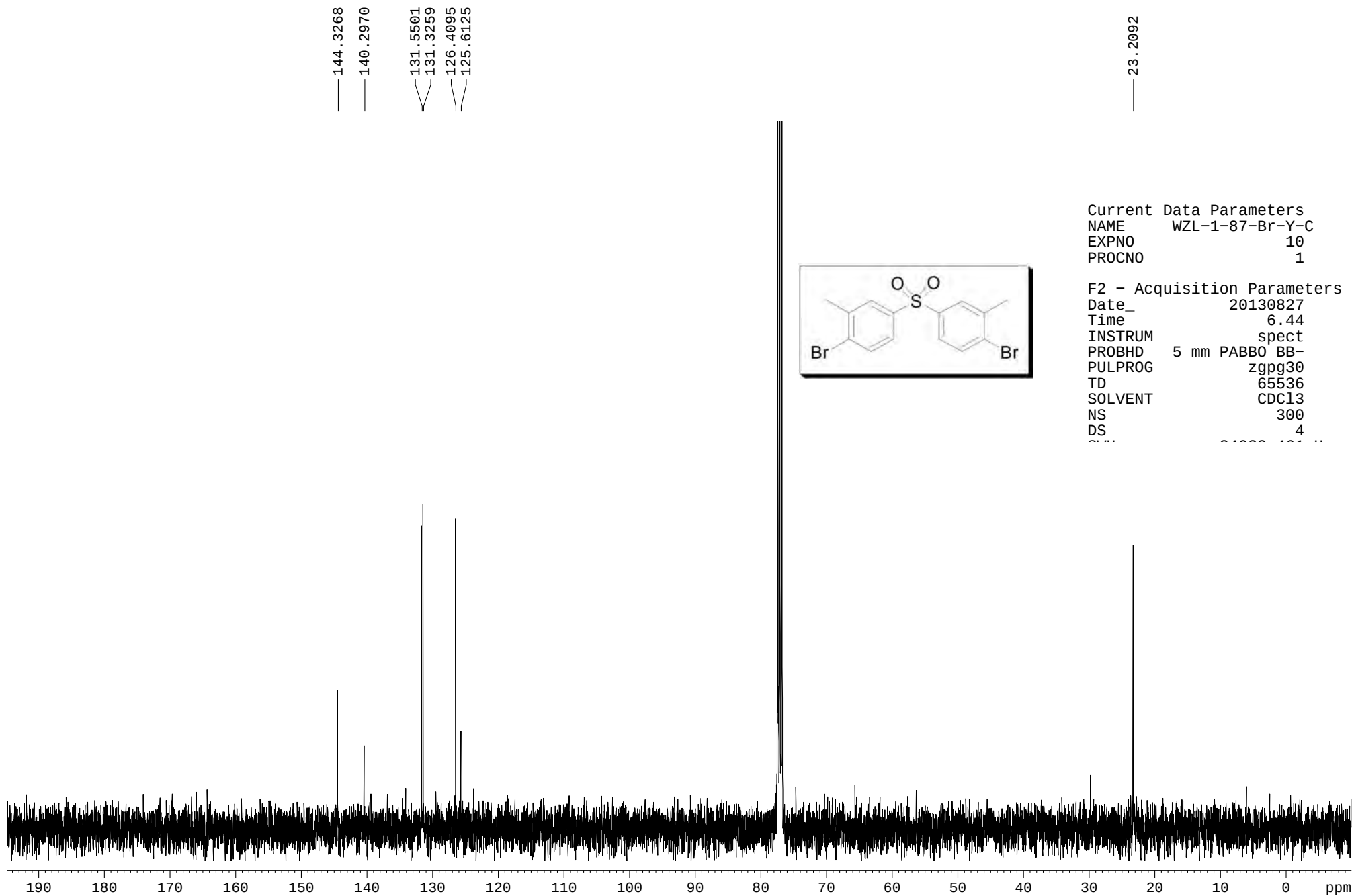




Current Data Parameters
NAME WZL-1-87-Br-G-H
EXPNO 10
PROCNO 1

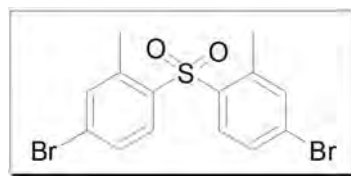
F2 - Acquisition Parameters
Date_ 20130826
Time 12.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2





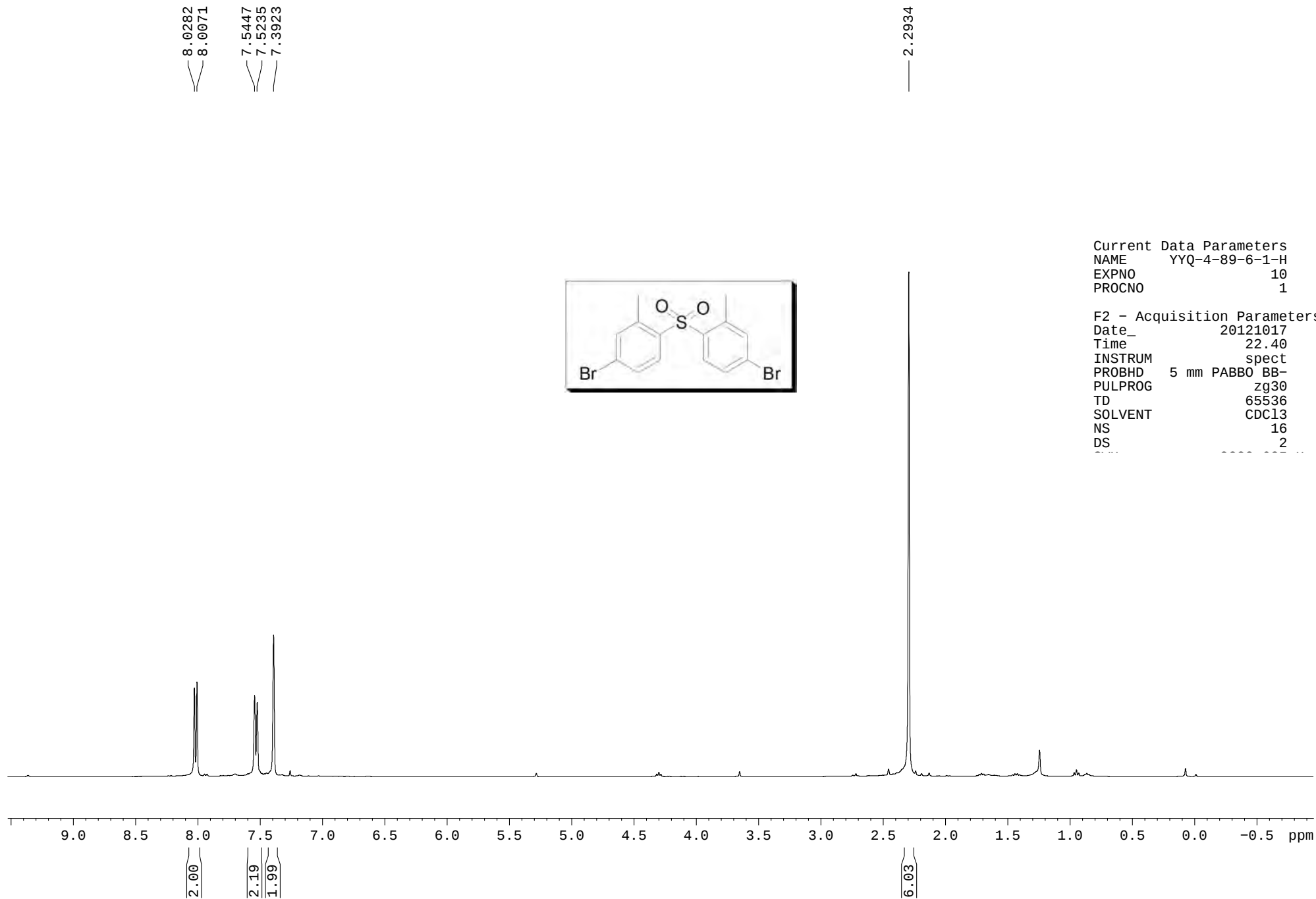
Current Data Parameters
NAME WZL-1-87-Br-Y-C
EXPNO 10
PROCNO 1

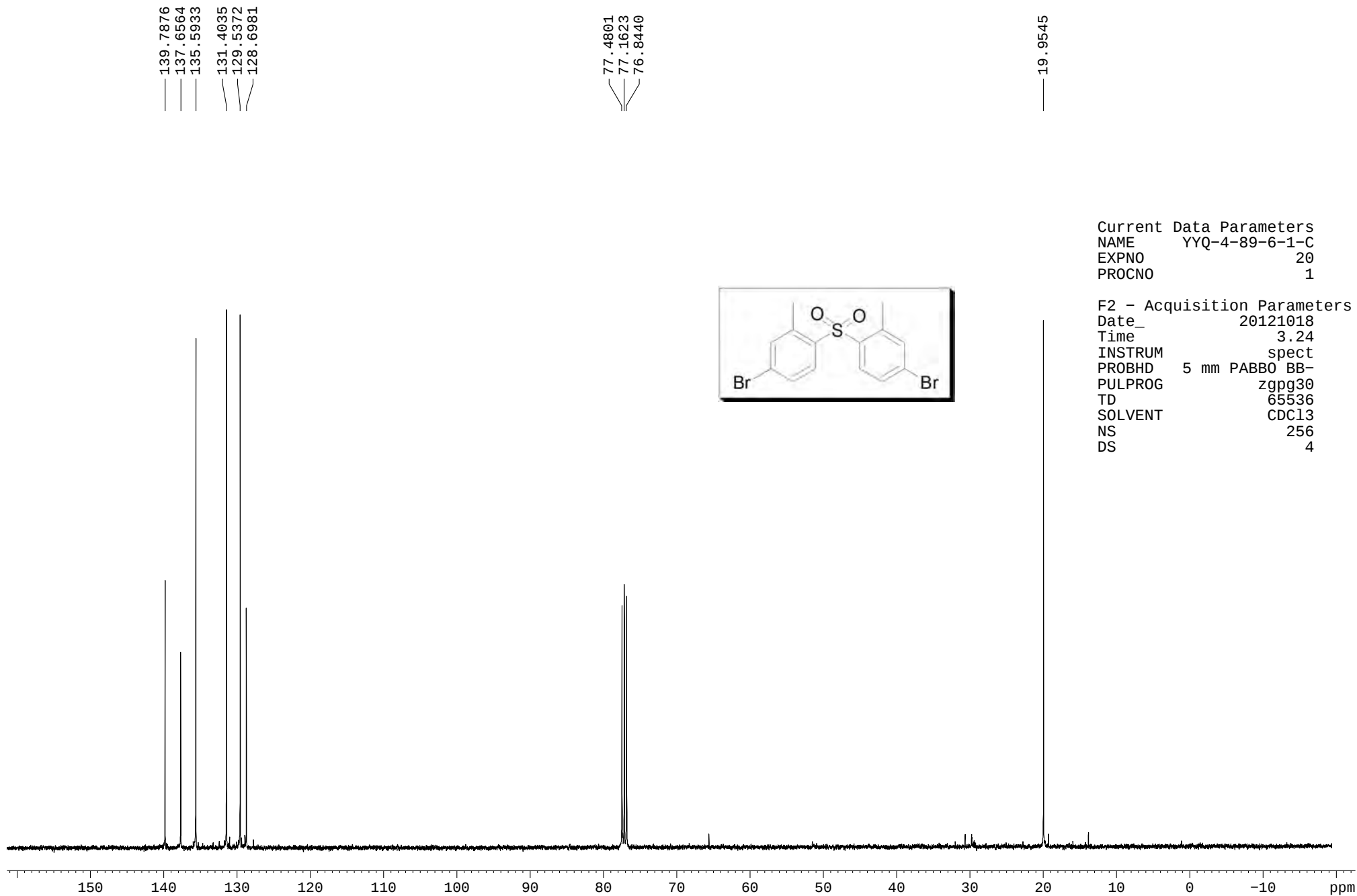
F2 - Acquisition Parameters
Date_ 20130827
Time 6.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 4



Current Data Parameters
 NAME YYQ-4-89-6-1-H
 EXPNO 10
 PROCNO 1

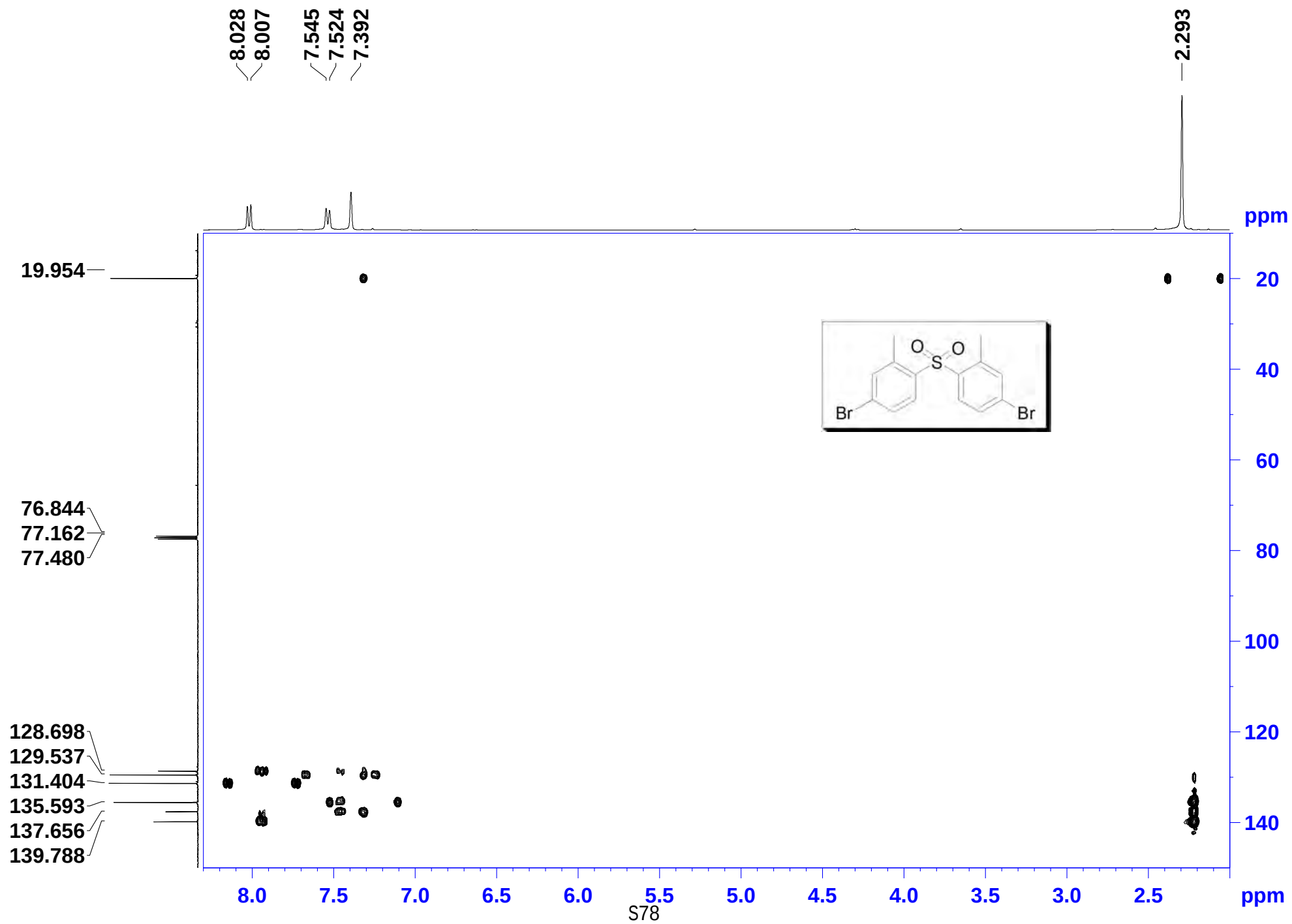
F2 - Acquisition Parameters
 Date_ 20121017
 Time 22.40
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2





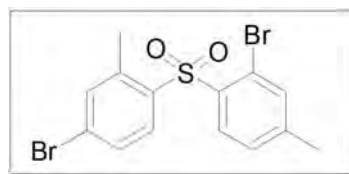
Current Data Parameters
NAME YYQ-4-89-6-1-C
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121018
Time 3.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4



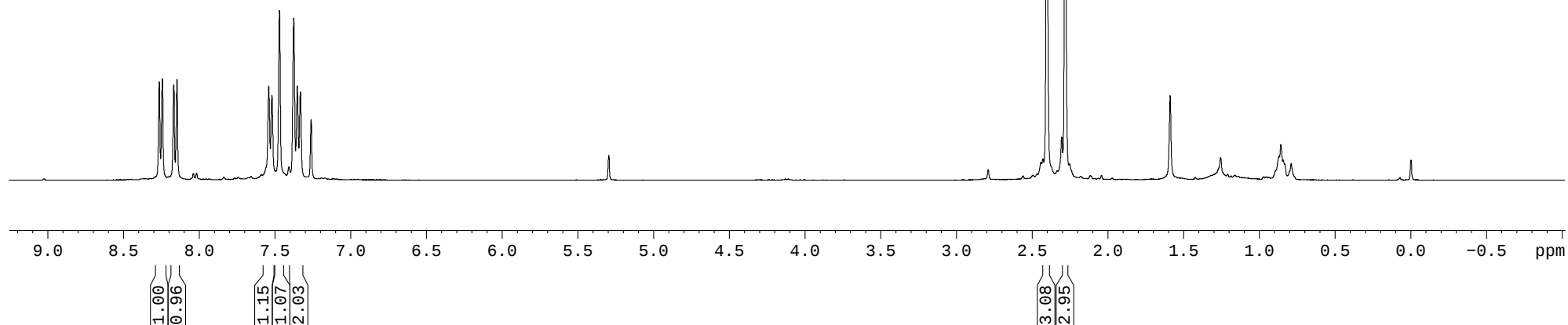
8.2634
8.2431
8.1676
8.1464
7.5410
7.5199
7.4701
7.3762
7.3521
7.3318
7.2603

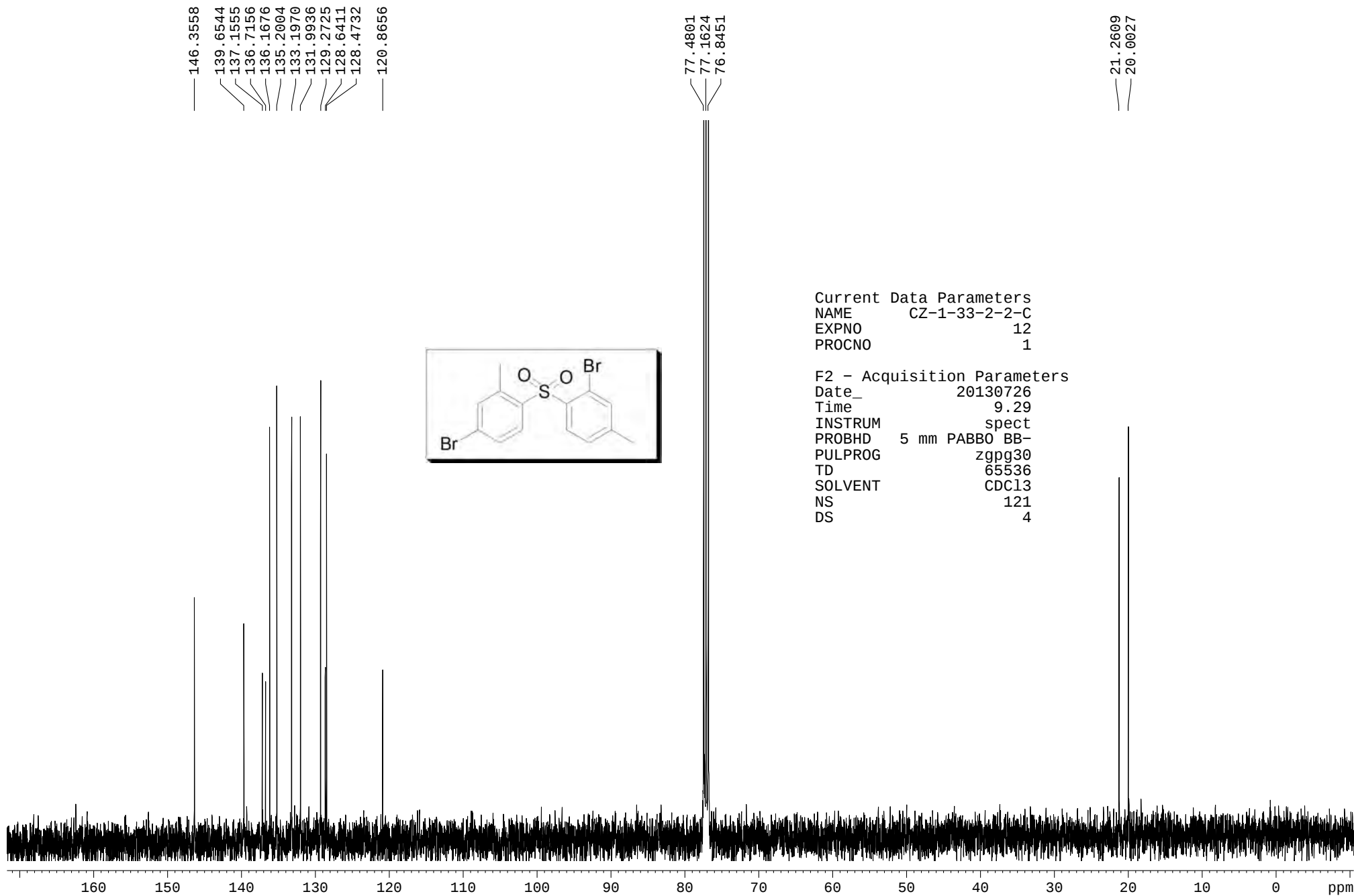
2.4010
2.2798



Current Data Parameters
NAME CZ-1-33-2-2
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130726
Time 9.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



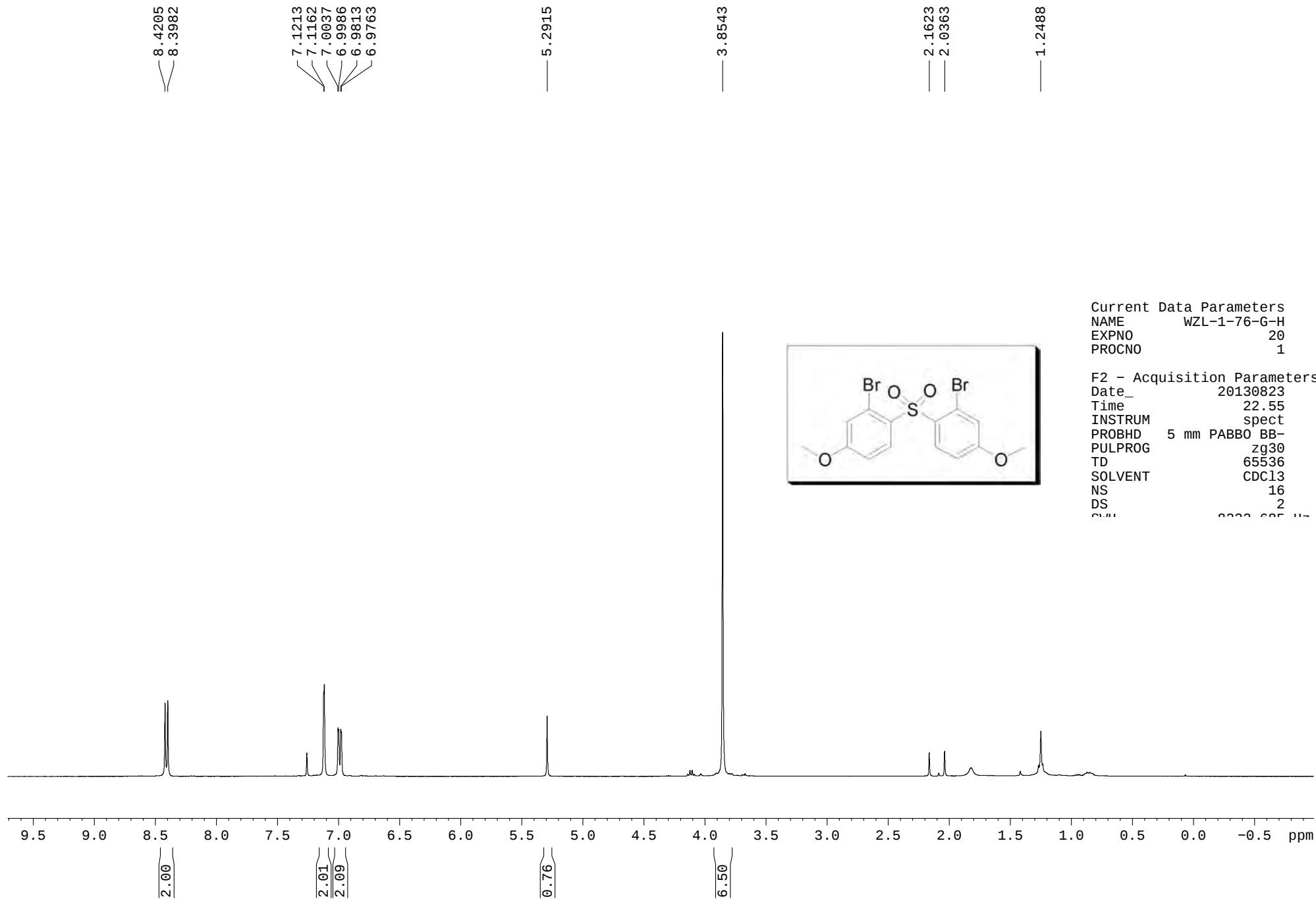


Current Data Parameters

NAME CZ-1-33-2-2-C
EXPNO 12
PROCNO 1

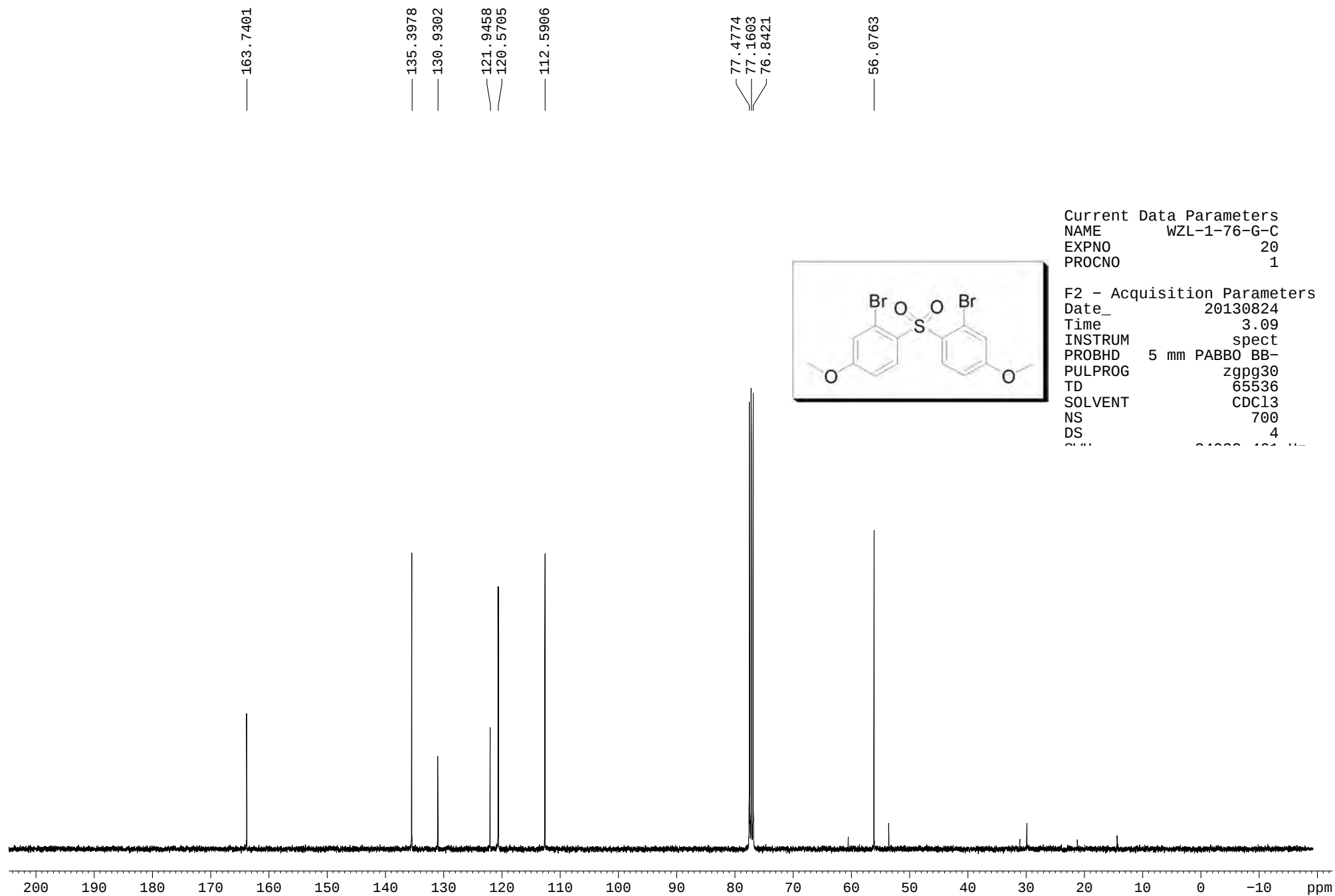
F2 - Acquisition Parameters

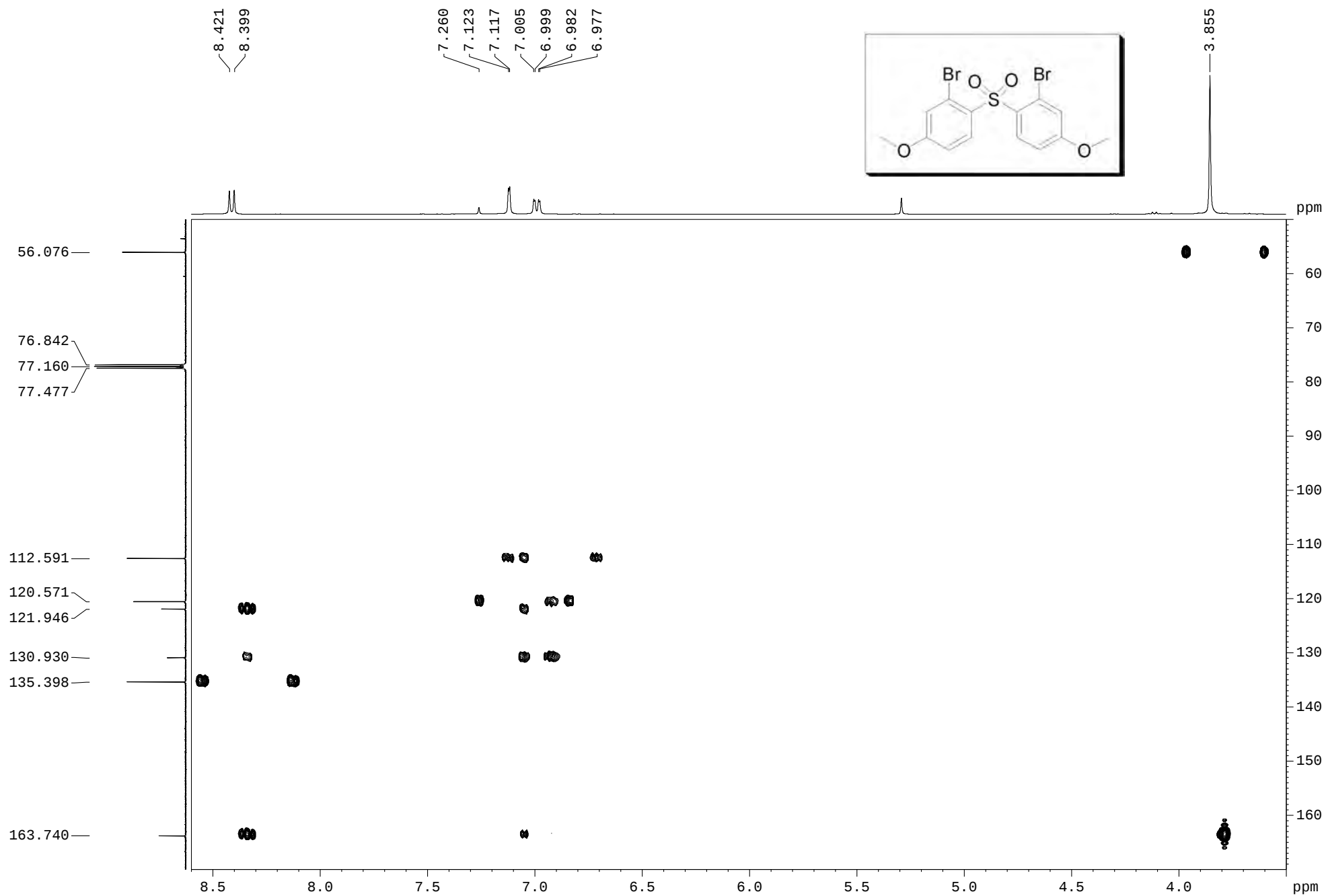
Date_ 20130726
Time 9.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 121
DS 4

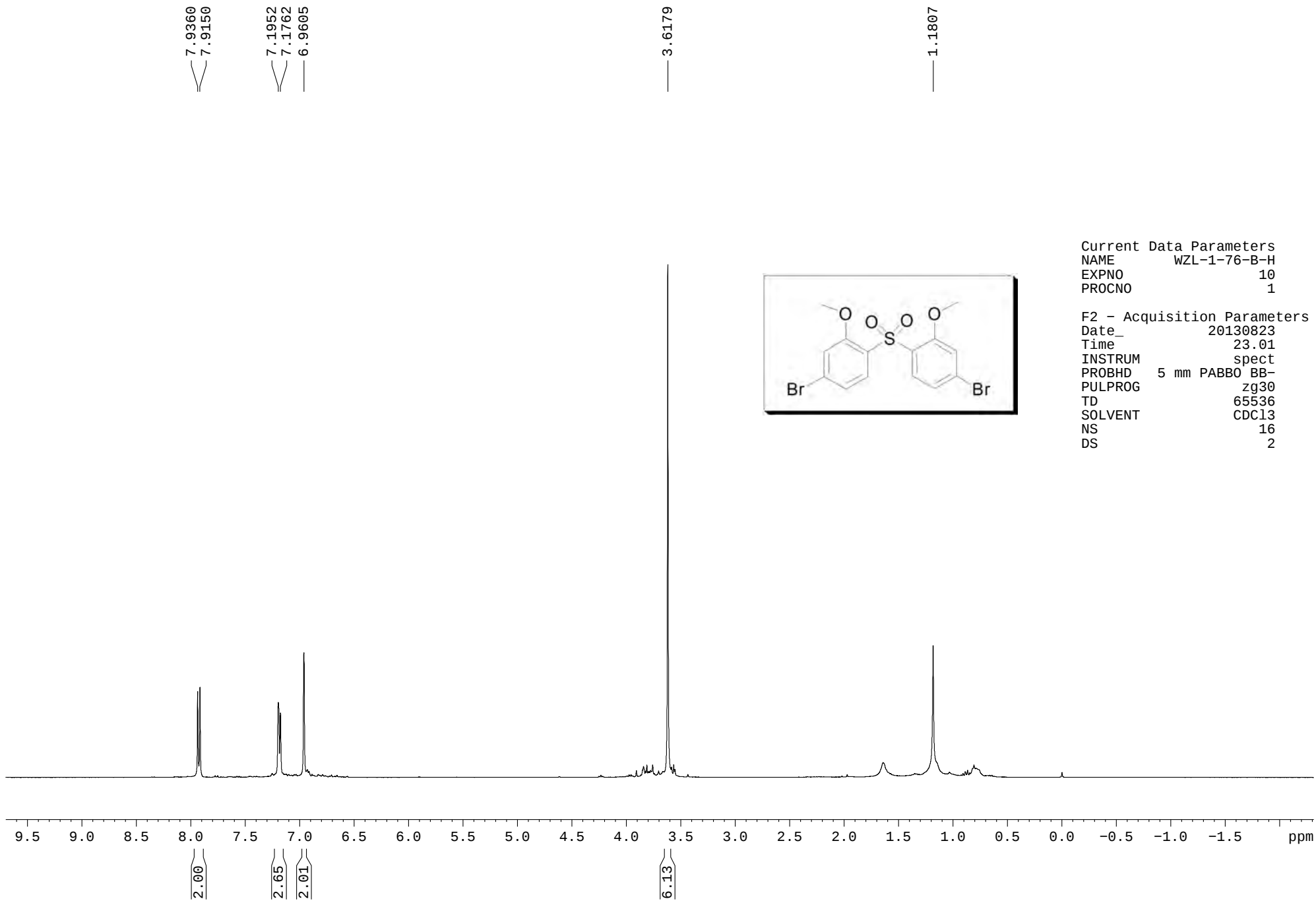


Current Data Parameters
NAME WZL-1-76-G-H
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130823
Time 22.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SFO 300.135 MHz

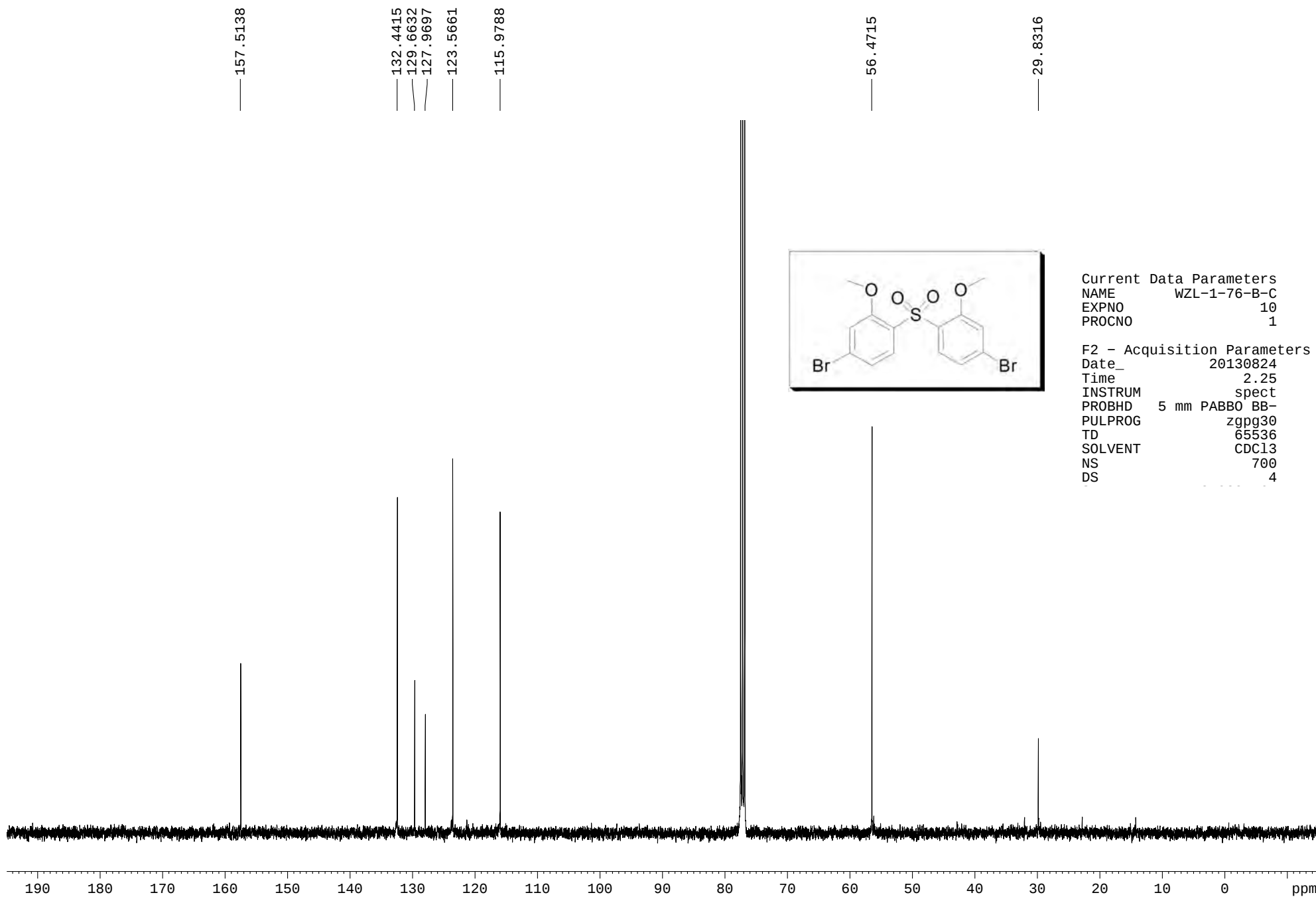


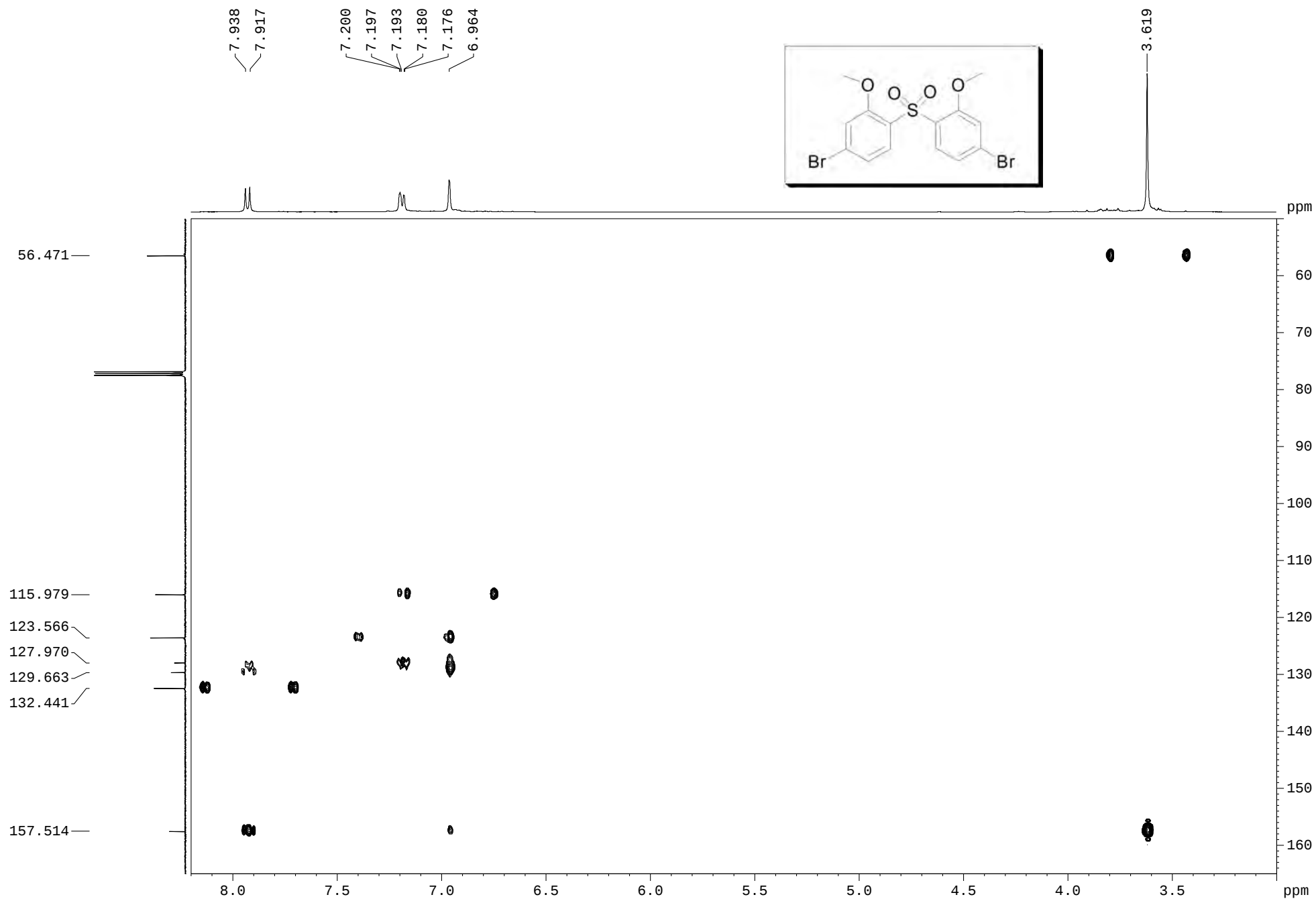
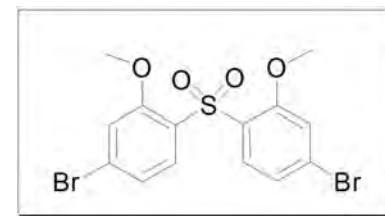


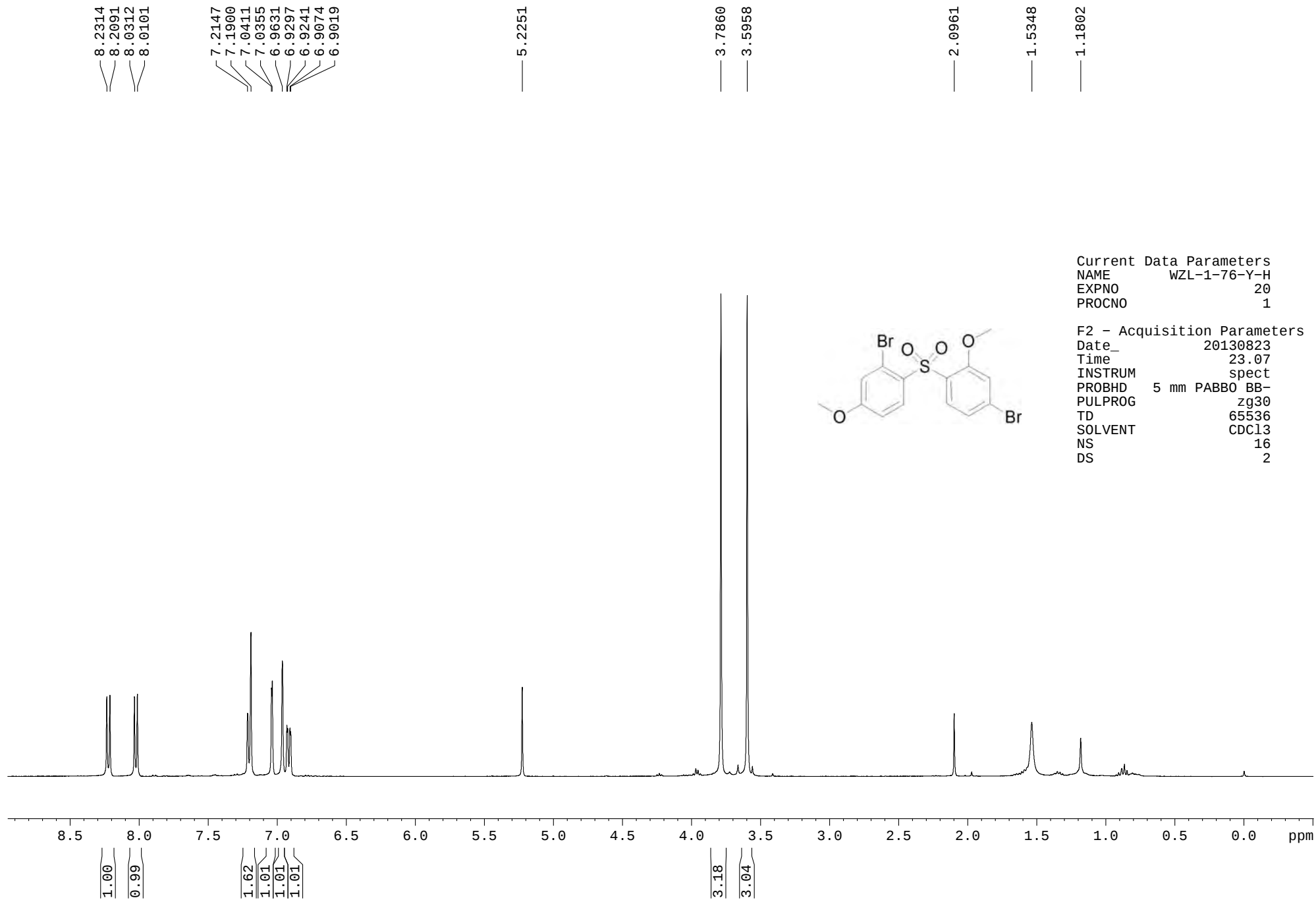


Current Data Parameters
NAME WZL-1-76-B-H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130823
Time 23.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2

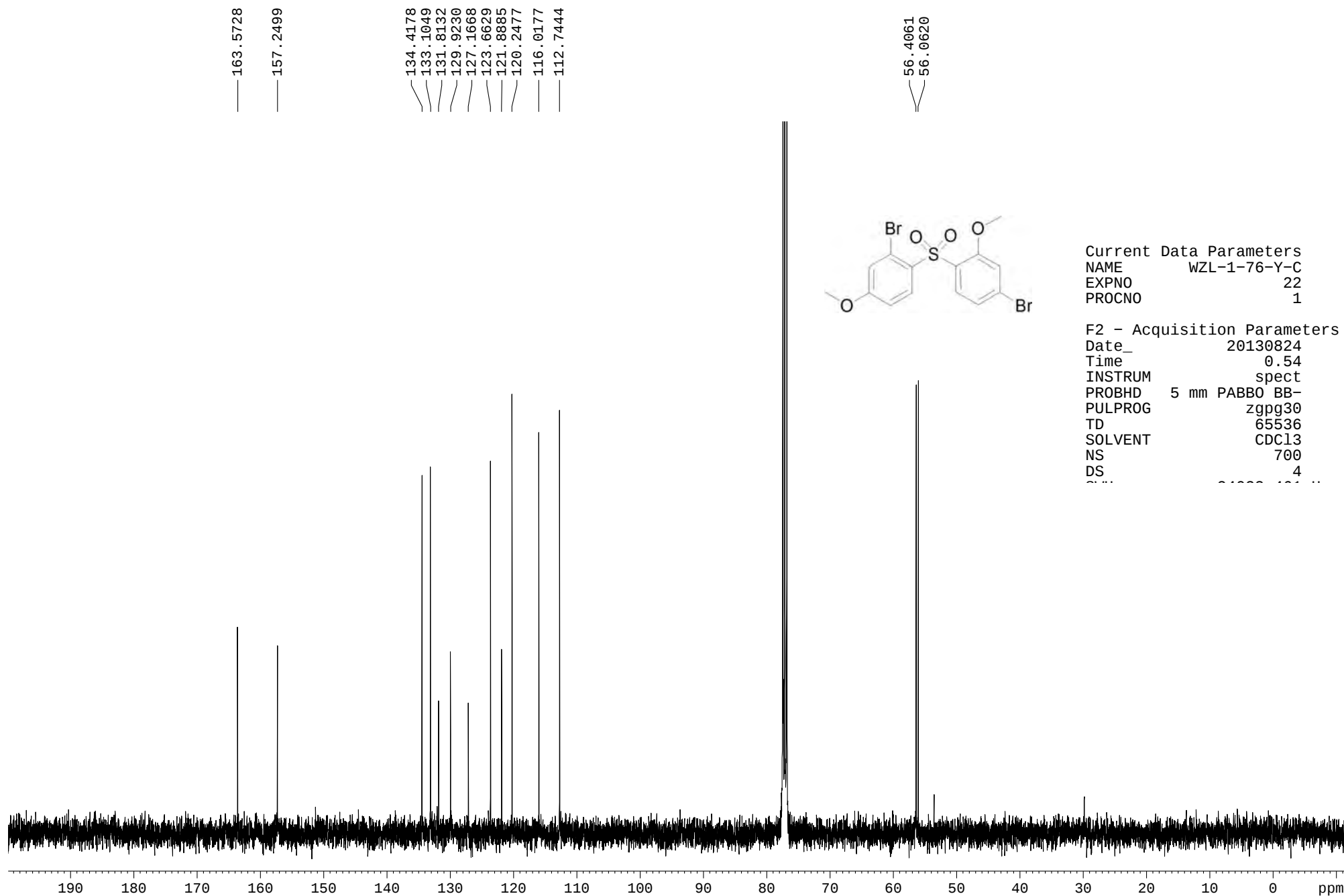






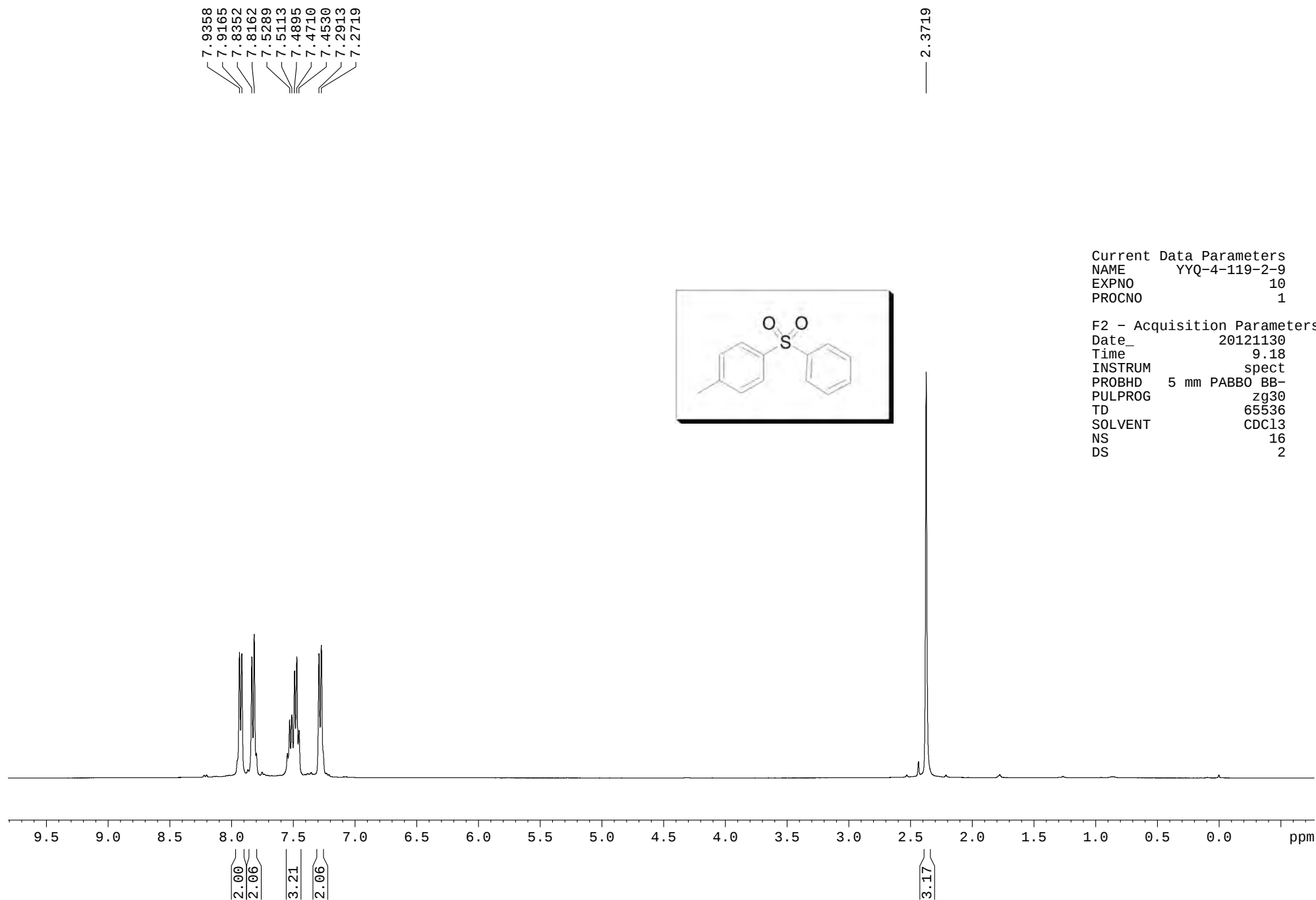
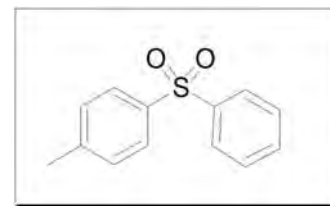
Current Data Parameters
NAME WZL-1-76-Y-H
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130823
Time 23.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



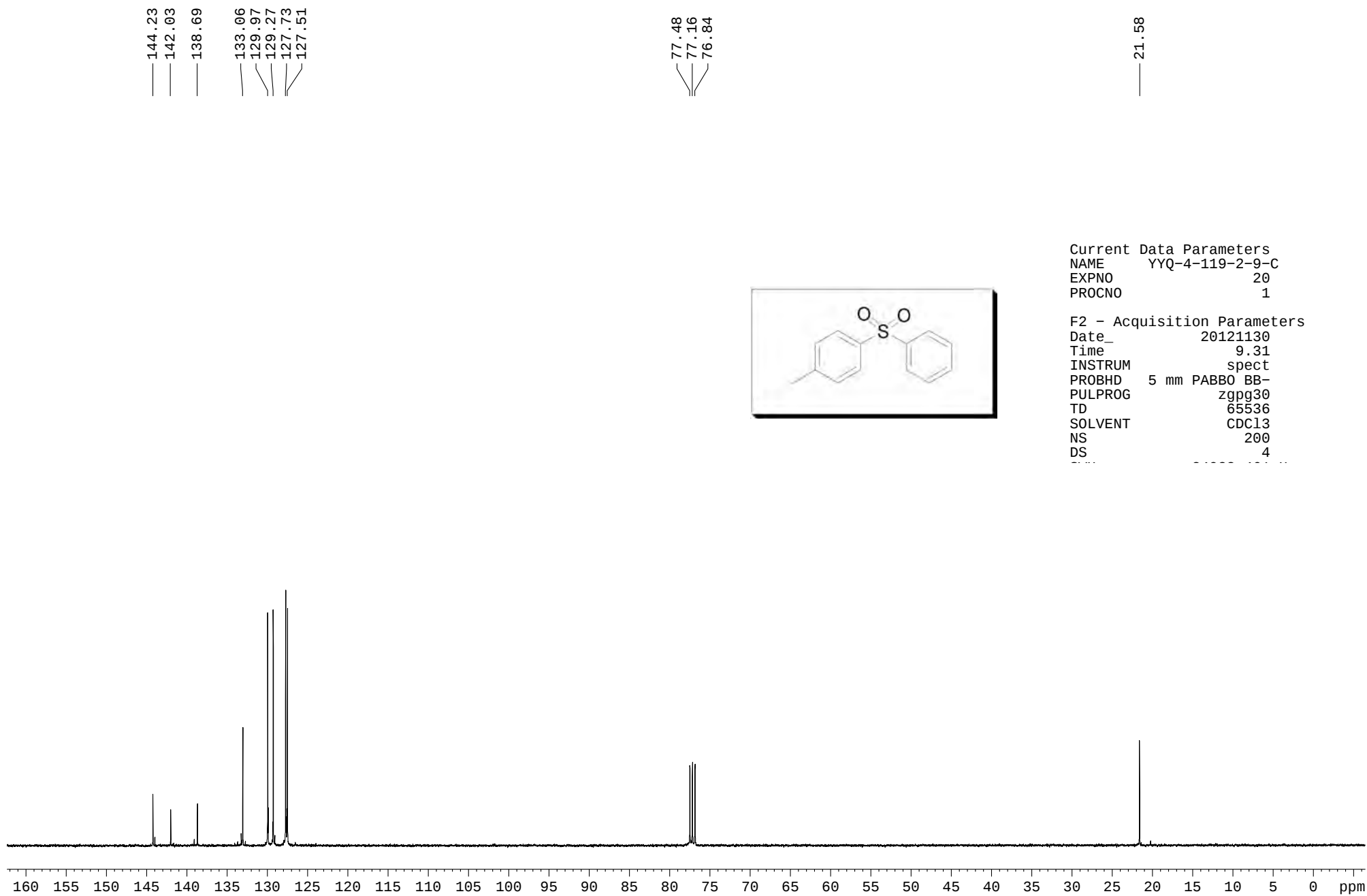
Current Data Parameters
NAME WZL-1-76-Y-C
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130824
Time 0.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 700
DS 4



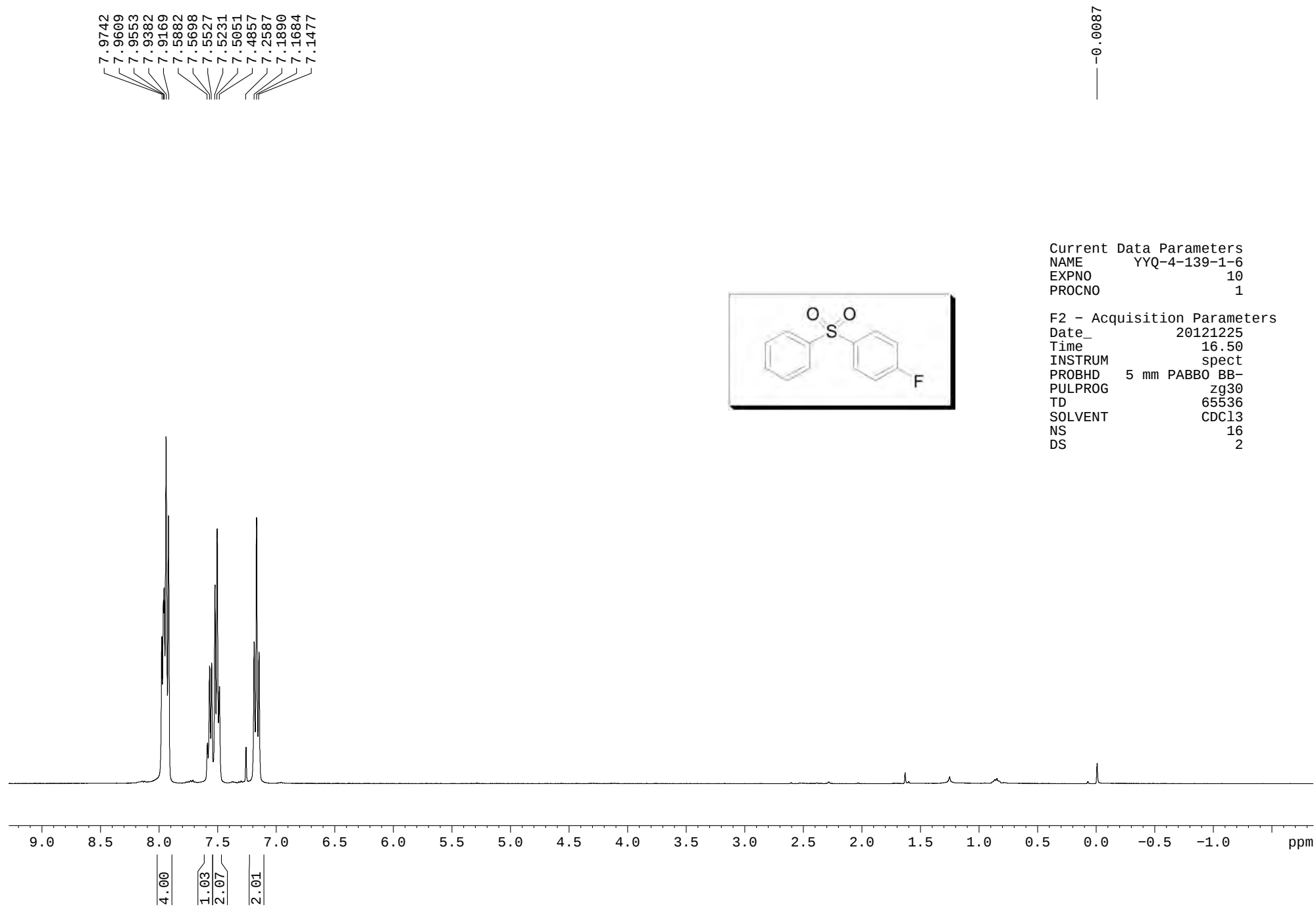
Current Data Parameters
NAME YYQ-4-119-2-9
EXPNO 10
PROCNO 1

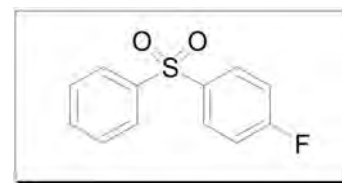
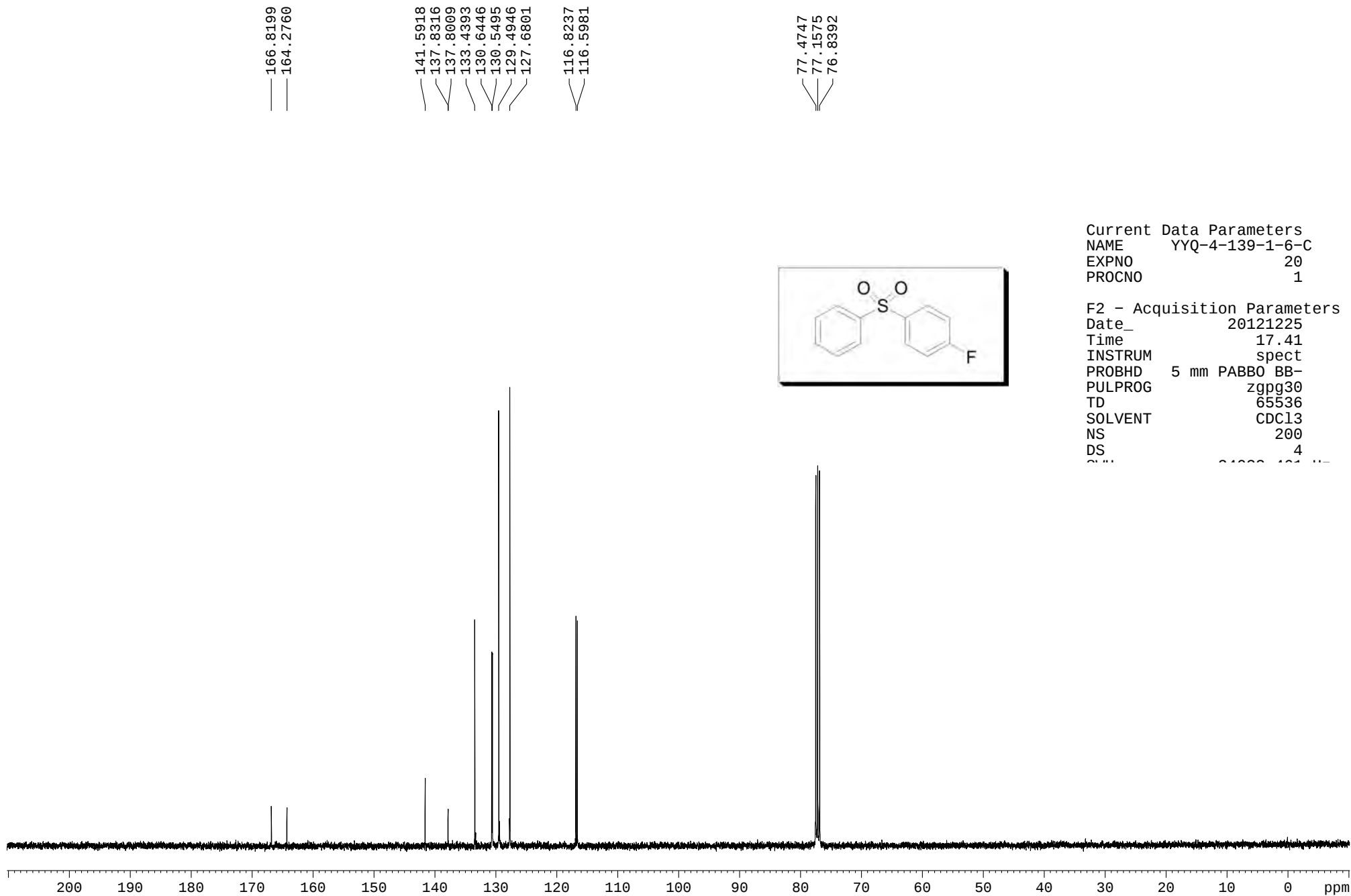
F2 - Acquisition Parameters
Date_ 20121130
Time 9.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



Current Data Parameters
NAME YYQ-4-119-2-9-C
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121130
Time 9.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4

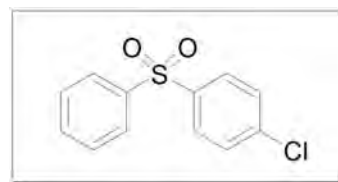




Current Data Parameters
NAME YYQ-4-139-1-6-C
EXPNO 20
PROCNO 1

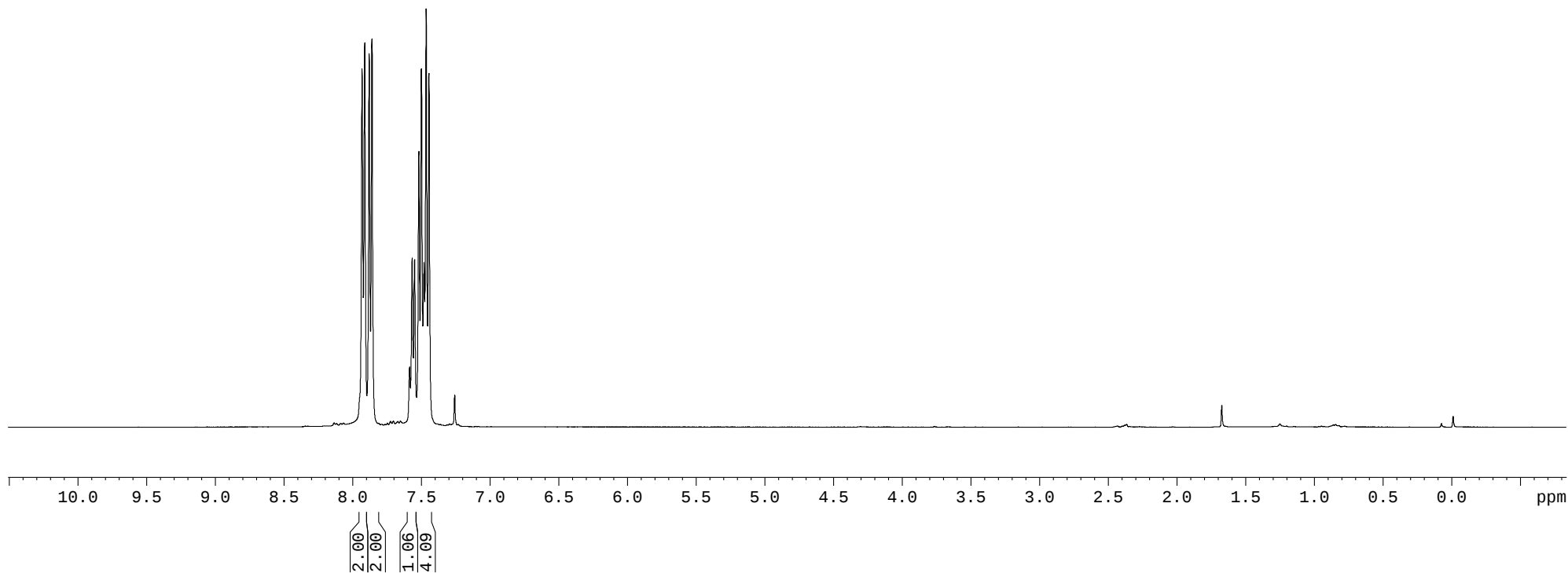
F2 - Acquisition Parameters
Date_ 20121225
Time 17.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4
SFO 300.136 MHz

7.9335
7.9135
7.8808
7.8602
7.5862
7.5681
7.5519
7.5497
7.5195
7.5016
7.4814
7.4658
7.4453
7.2580



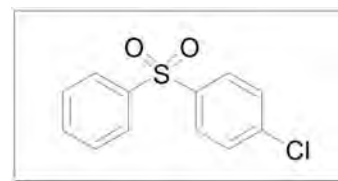
Current Data Parameters
NAME YYQ-4-123-1-9
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121206
Time 12.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



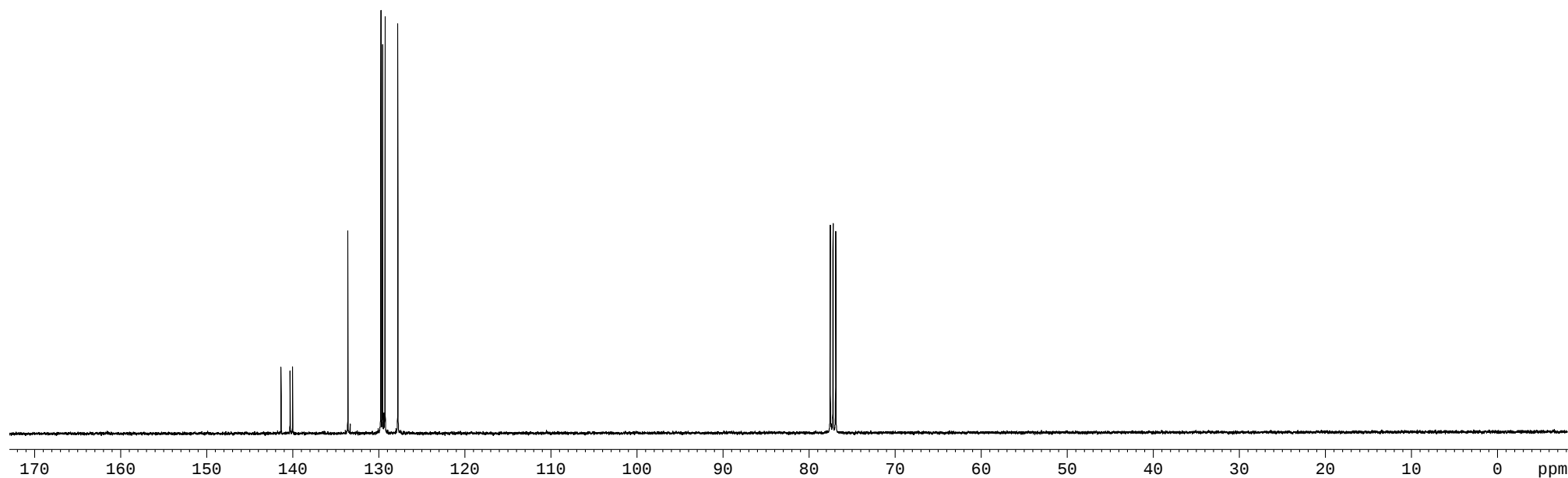
141.3113
140.2631
139.9756
133.5449
129.7107
129.5151
129.2224
127.7351

77.4821
77.1637
76.8462

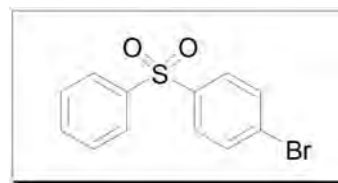


Current Data Parameters
NAME YYQ-4-123-1-9-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121206
Time 12.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4

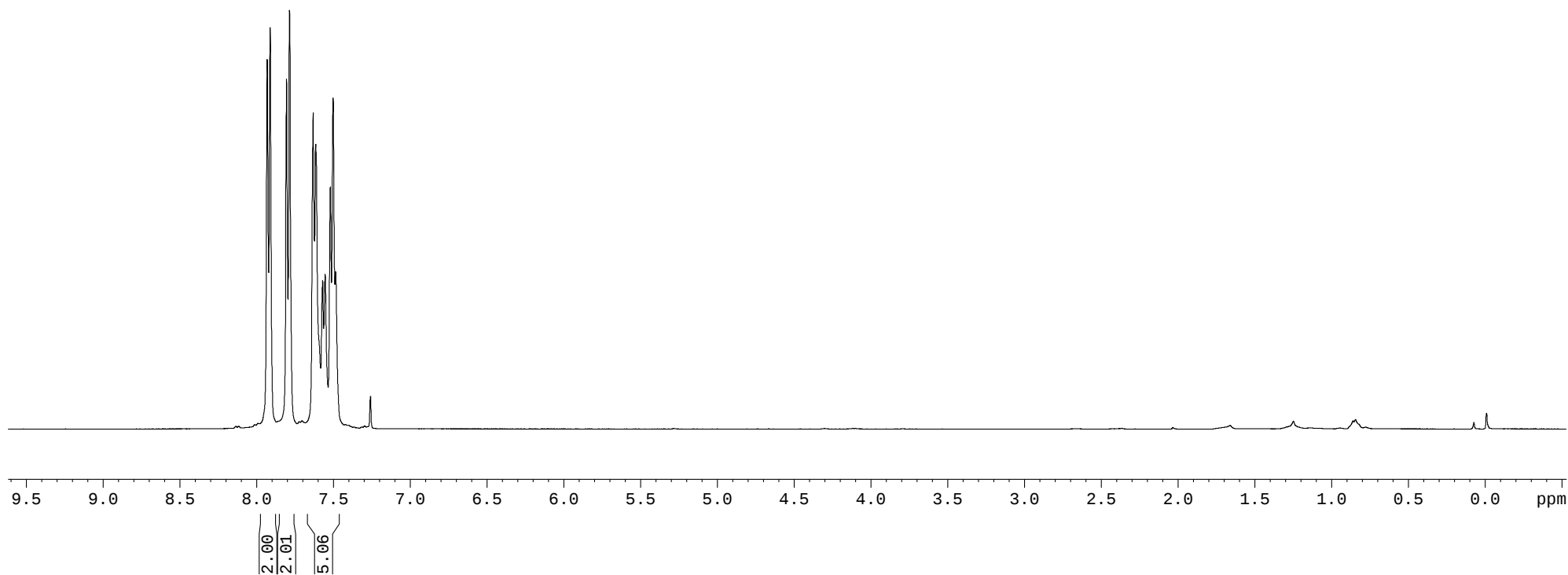


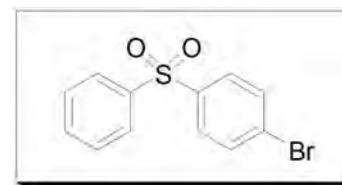
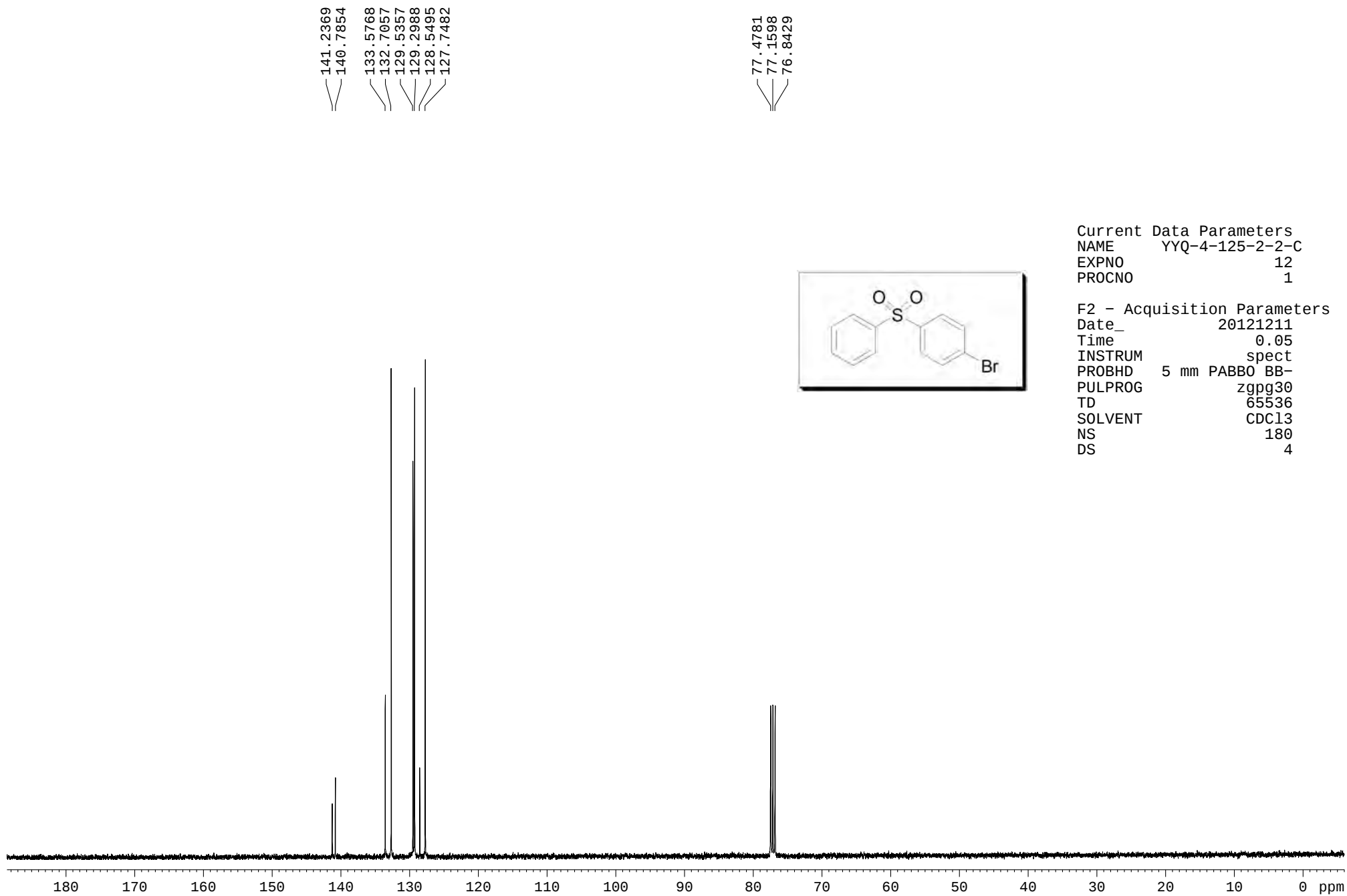
7.9324
7.9130
7.8061
7.7873
7.6327
7.6158
7.5714
7.5552
7.5213
7.5035
7.4865
7.2592



Current Data Parameters
NAME YYQ-4-125-2-2-H
EXPNO 10
PROCNO 1

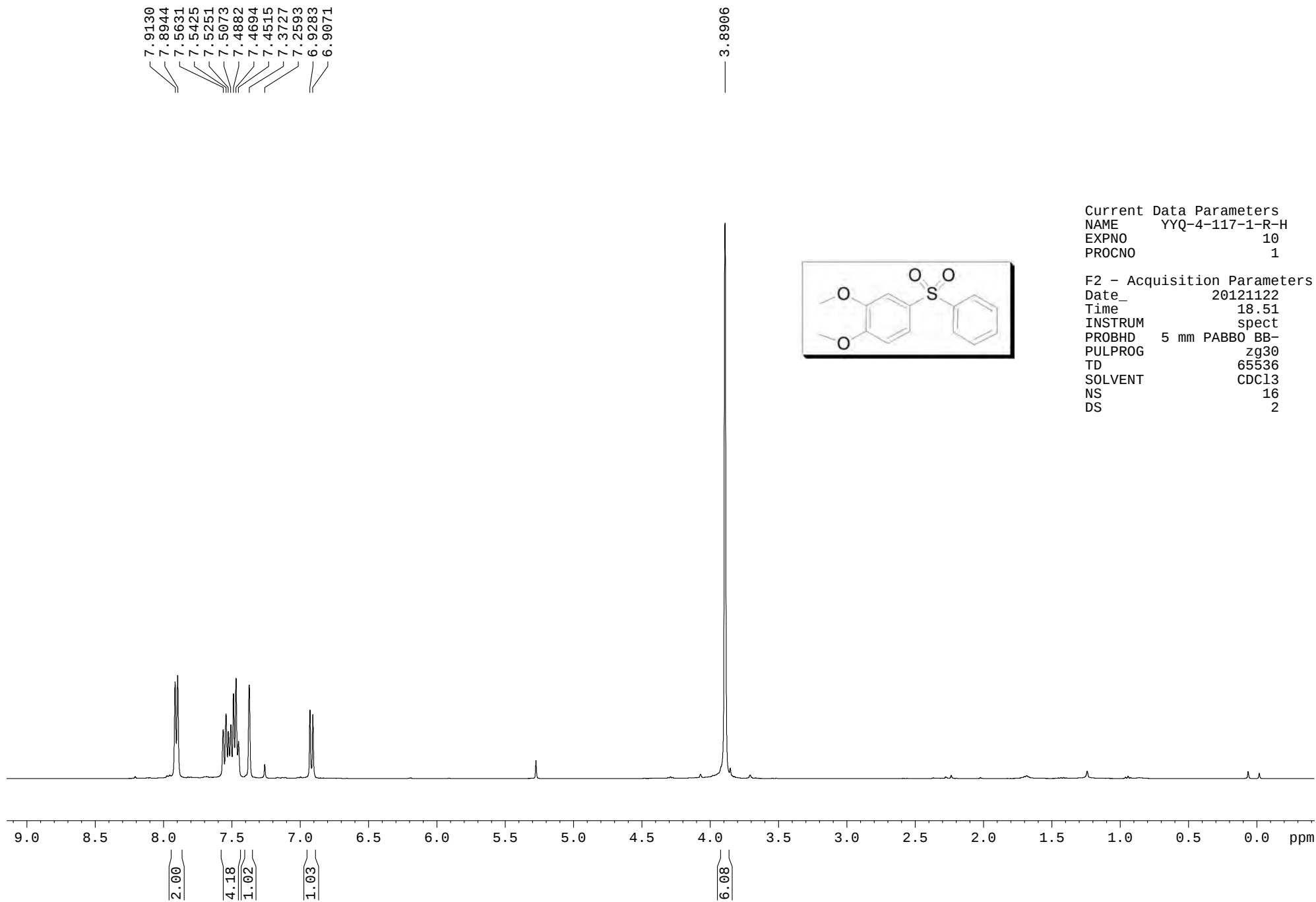
F2 - Acquisition Parameters
Date_ 20121210
Time 23.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
AQ 0.000 0.000 0.000





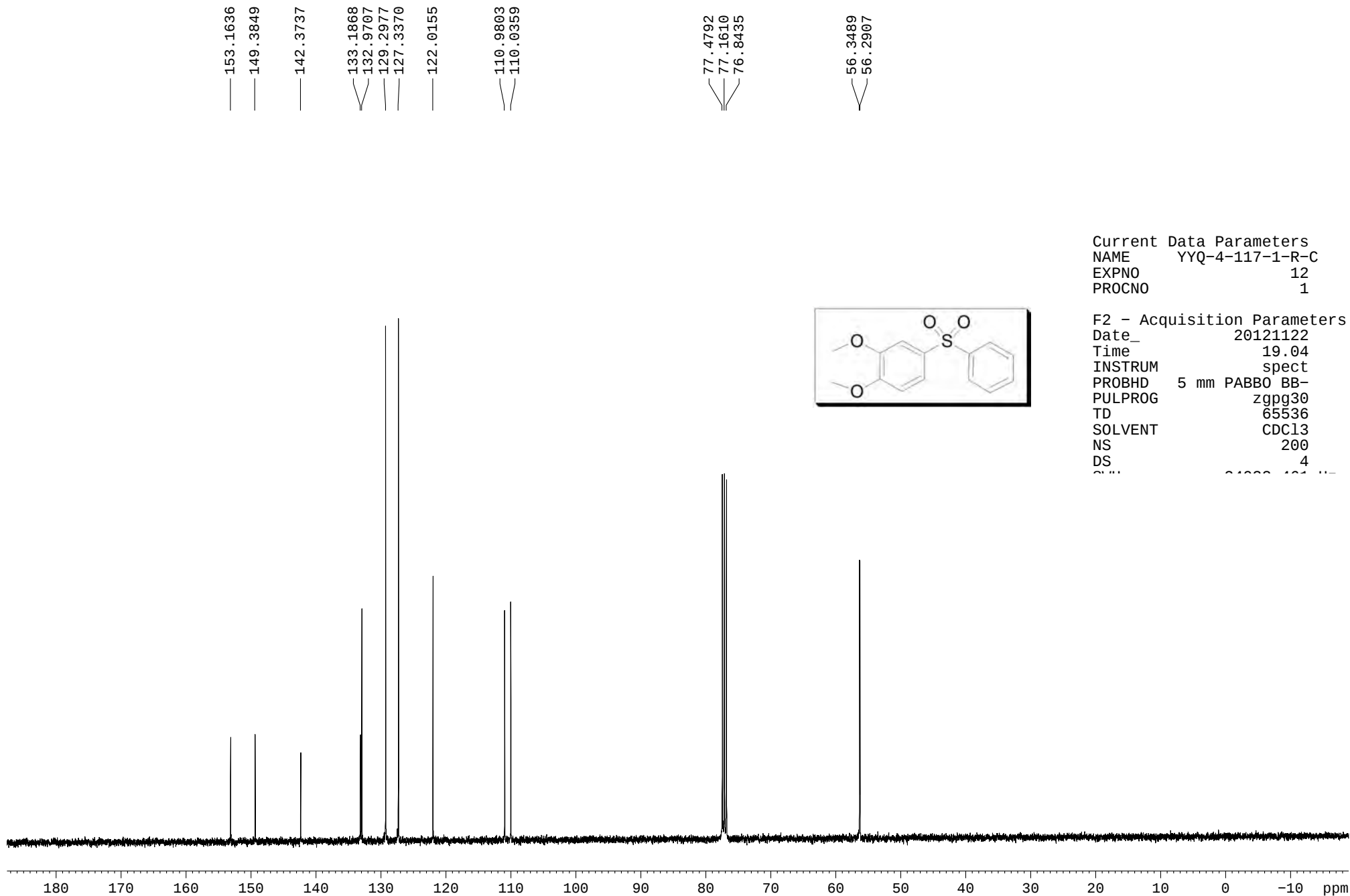
Current Data Parameters
NAME YYQ-4-125-2-2-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121211
Time 0.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 180
DS 4



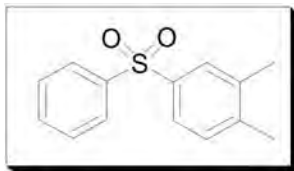
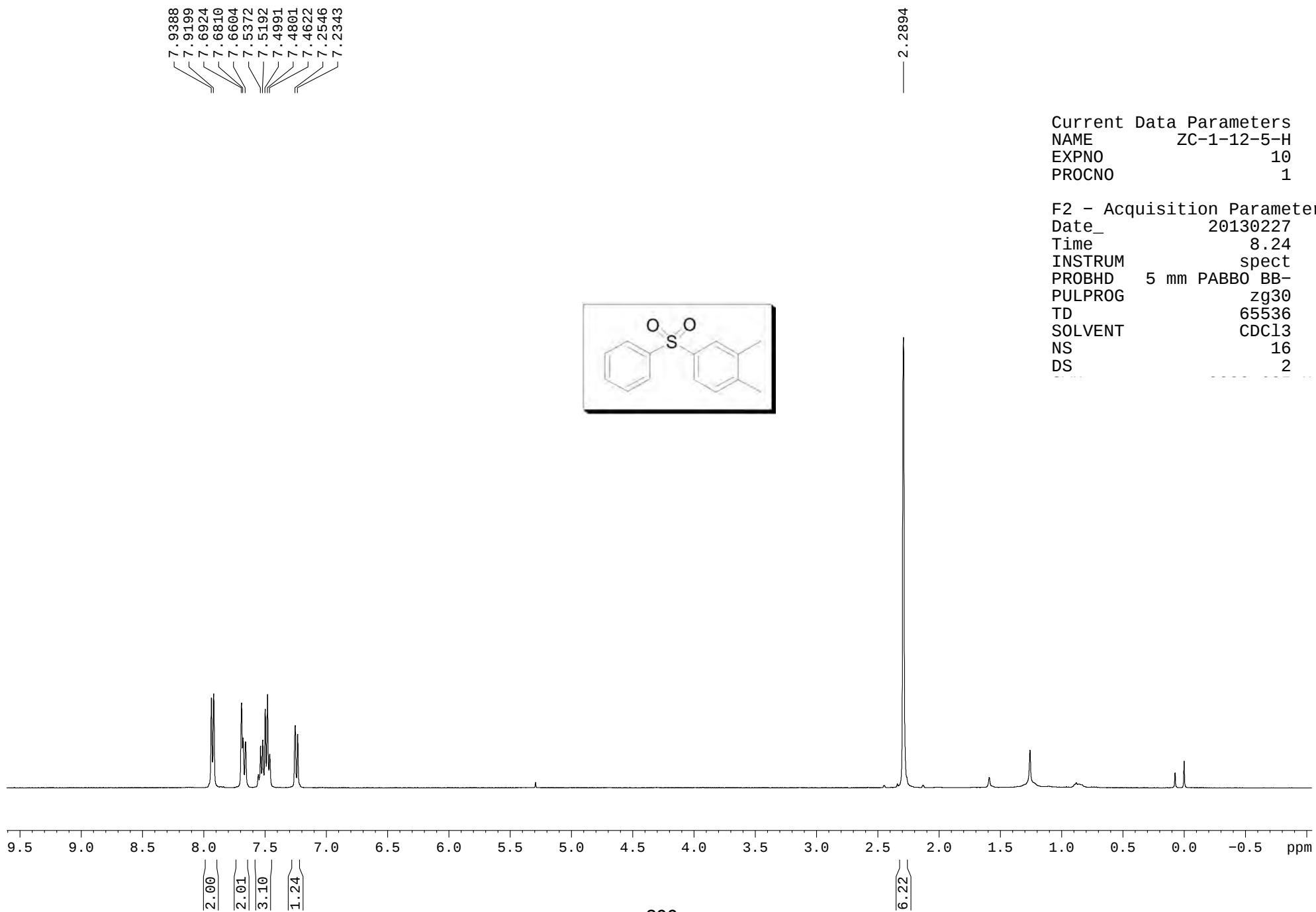
Current Data Parameters
NAME YYQ-4-117-1-R-H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121122
Time 18.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



Current Data Parameters
NAME YYQ-4-117-1-R-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121122
Time 19.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4
SFO 300.136 MHz



Current Data Parameters
NAME ZC-1-12-5-H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameter
Date_ 20130227
Time 8.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2

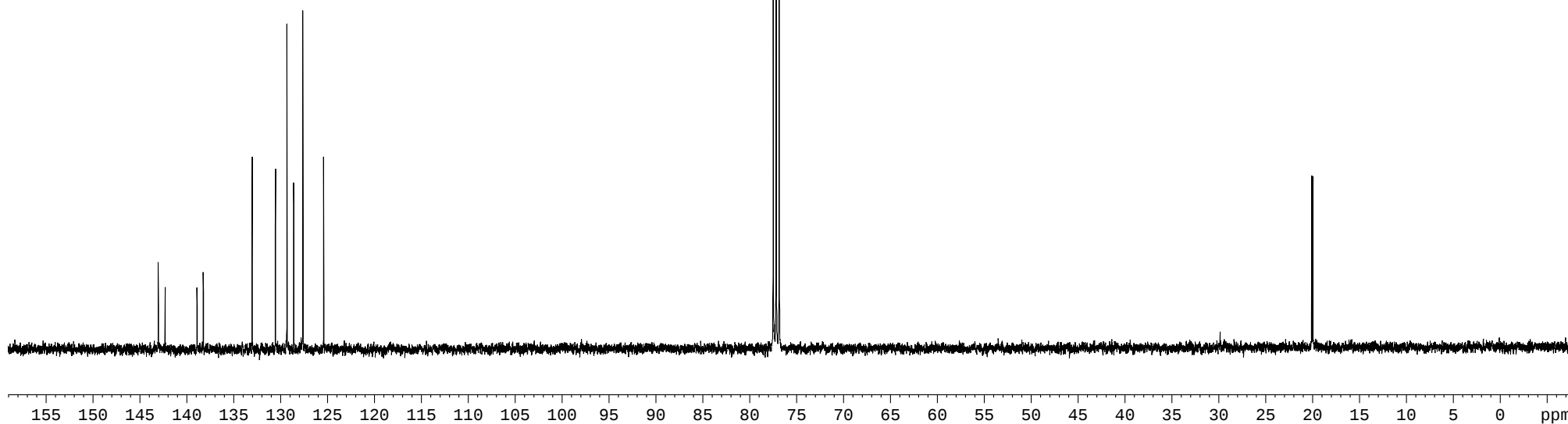
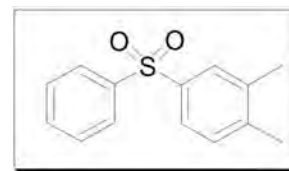
143.0230
142.2943
138.8951
138.2240
133.0263
130.5344
129.3111
128.5840
127.6115
125.3997

77.4807
77.1626
76.8455

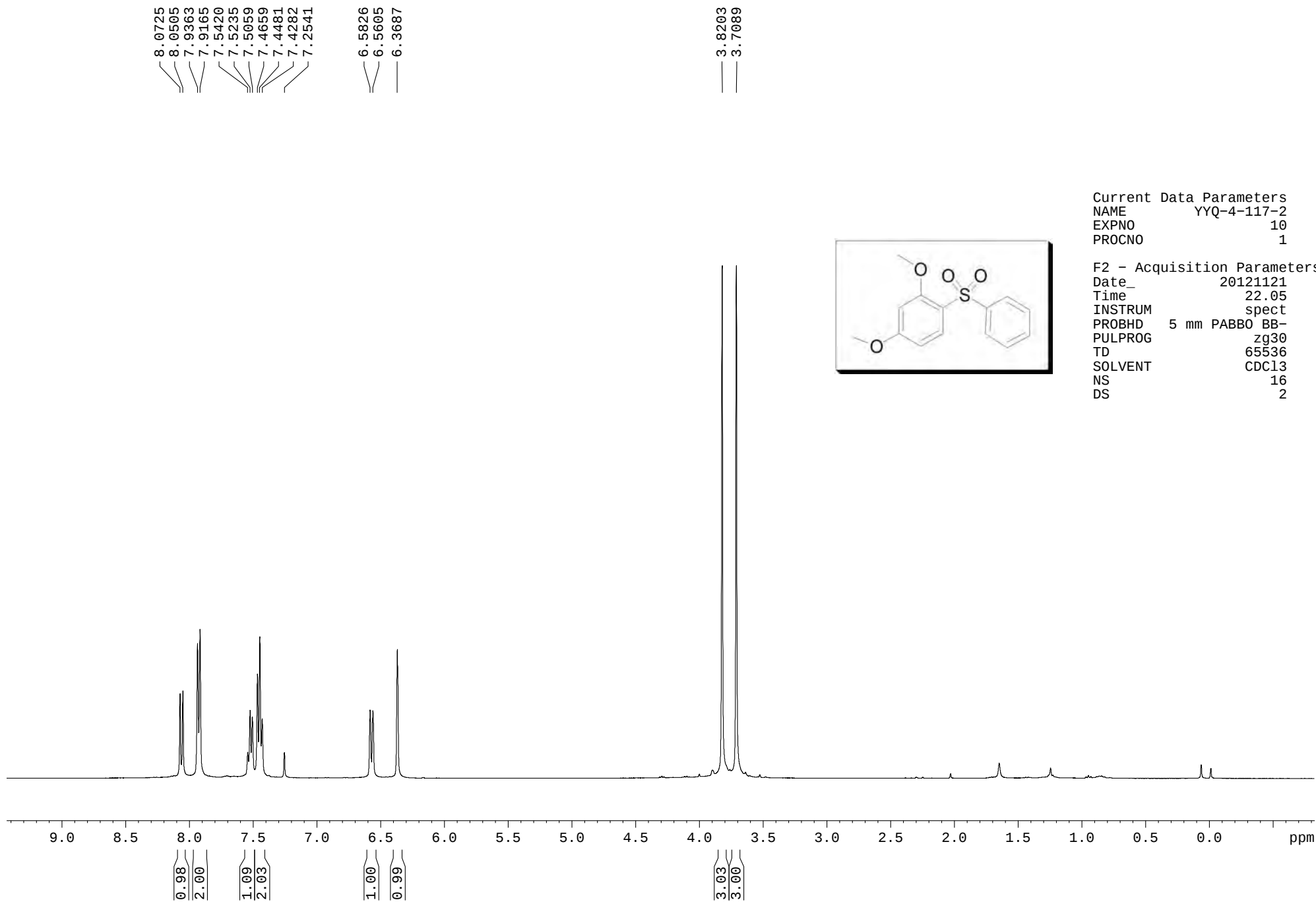
20.0764
19.9476

Current Data Parameters
NAME ZC-4-12-5-C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130227
Time 19.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4
SFO 400.141 MHz



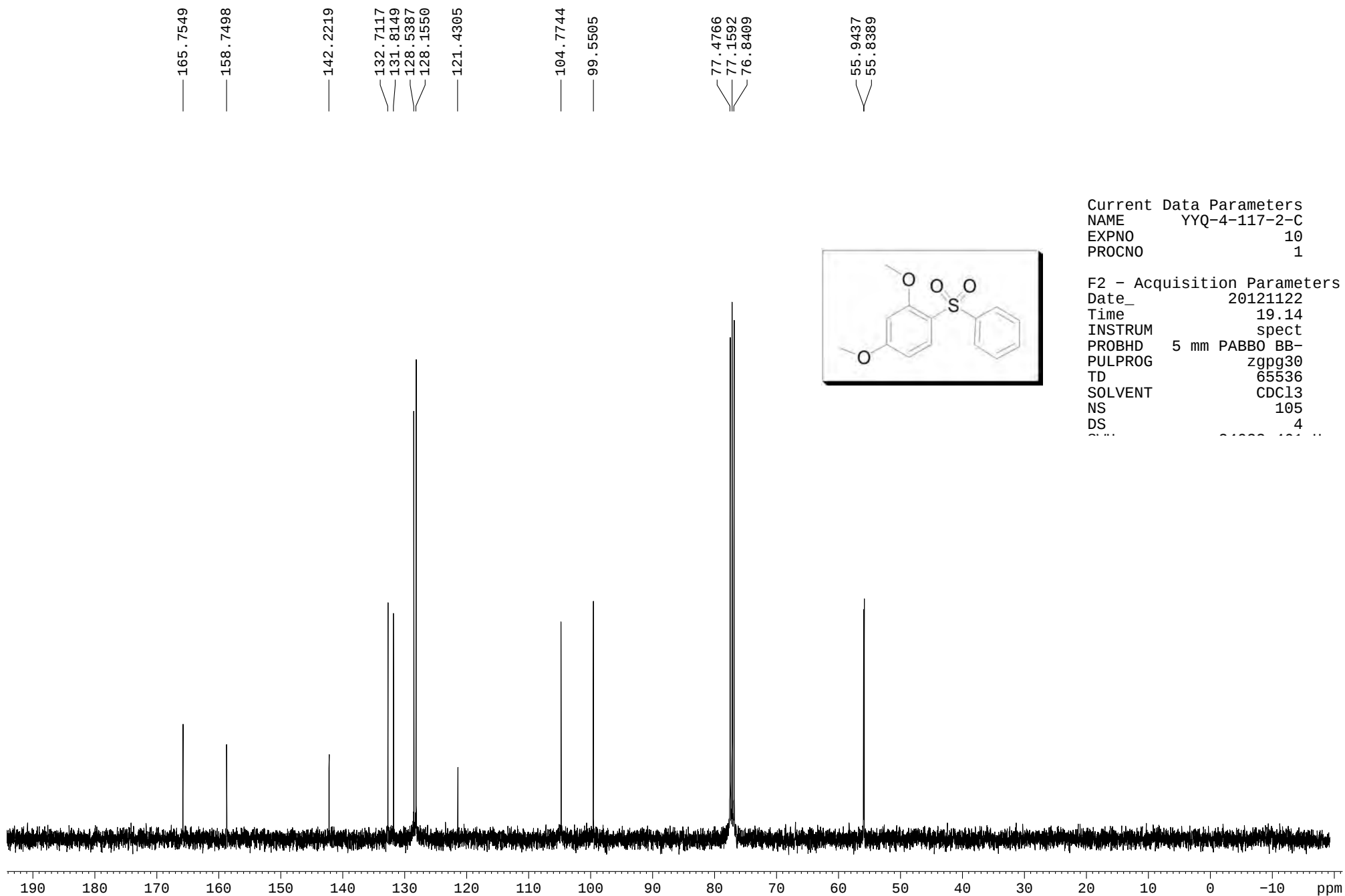
S100



Current Data Parameters
NAME YYQ-4-117-2
EXPNO 10
PROCNO 1

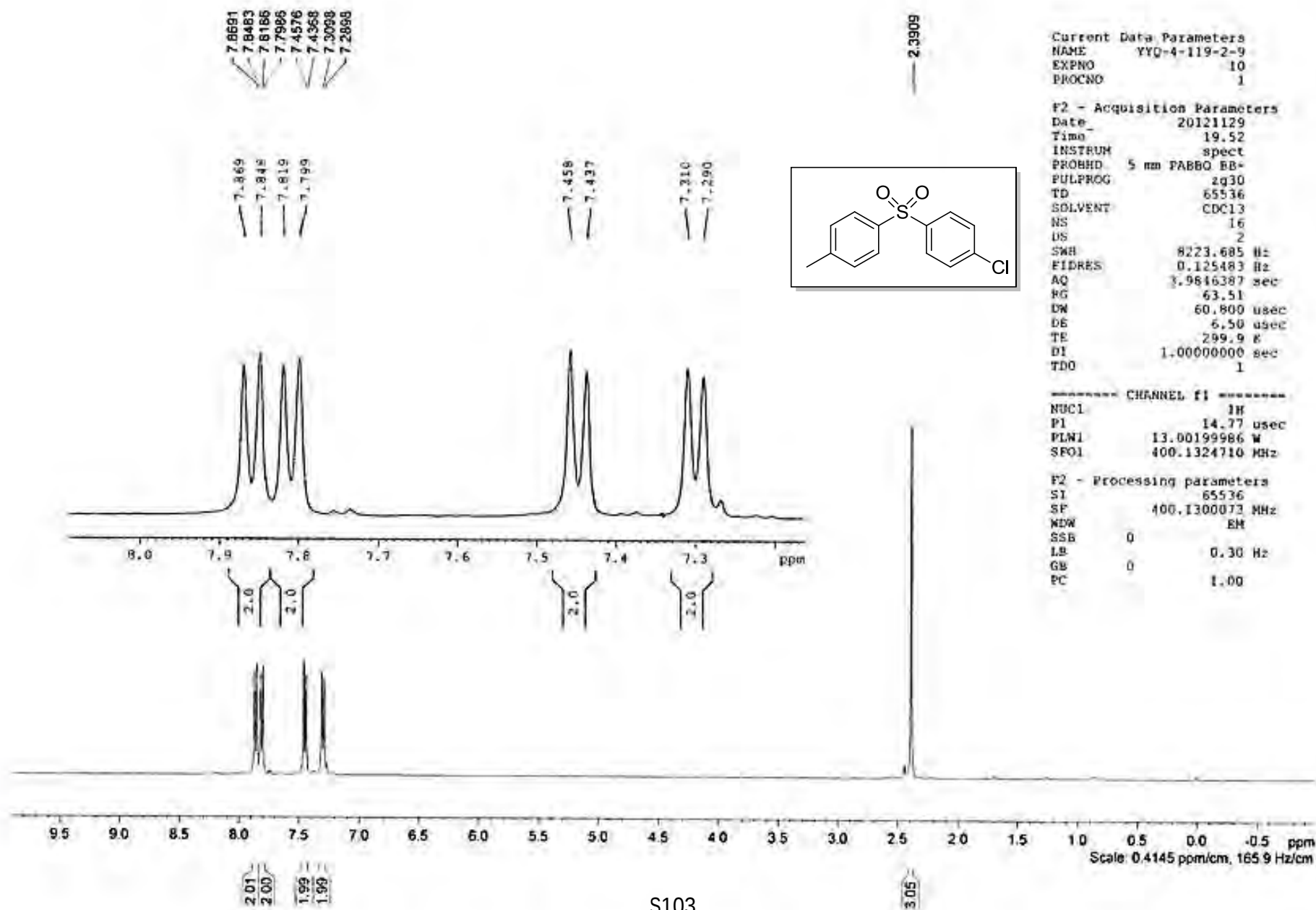
F2 - Acquisition Parameters
Date_ 20121121
Time 22.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2

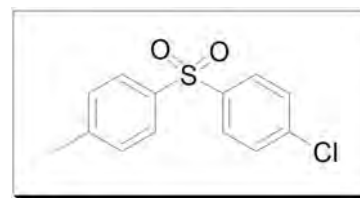
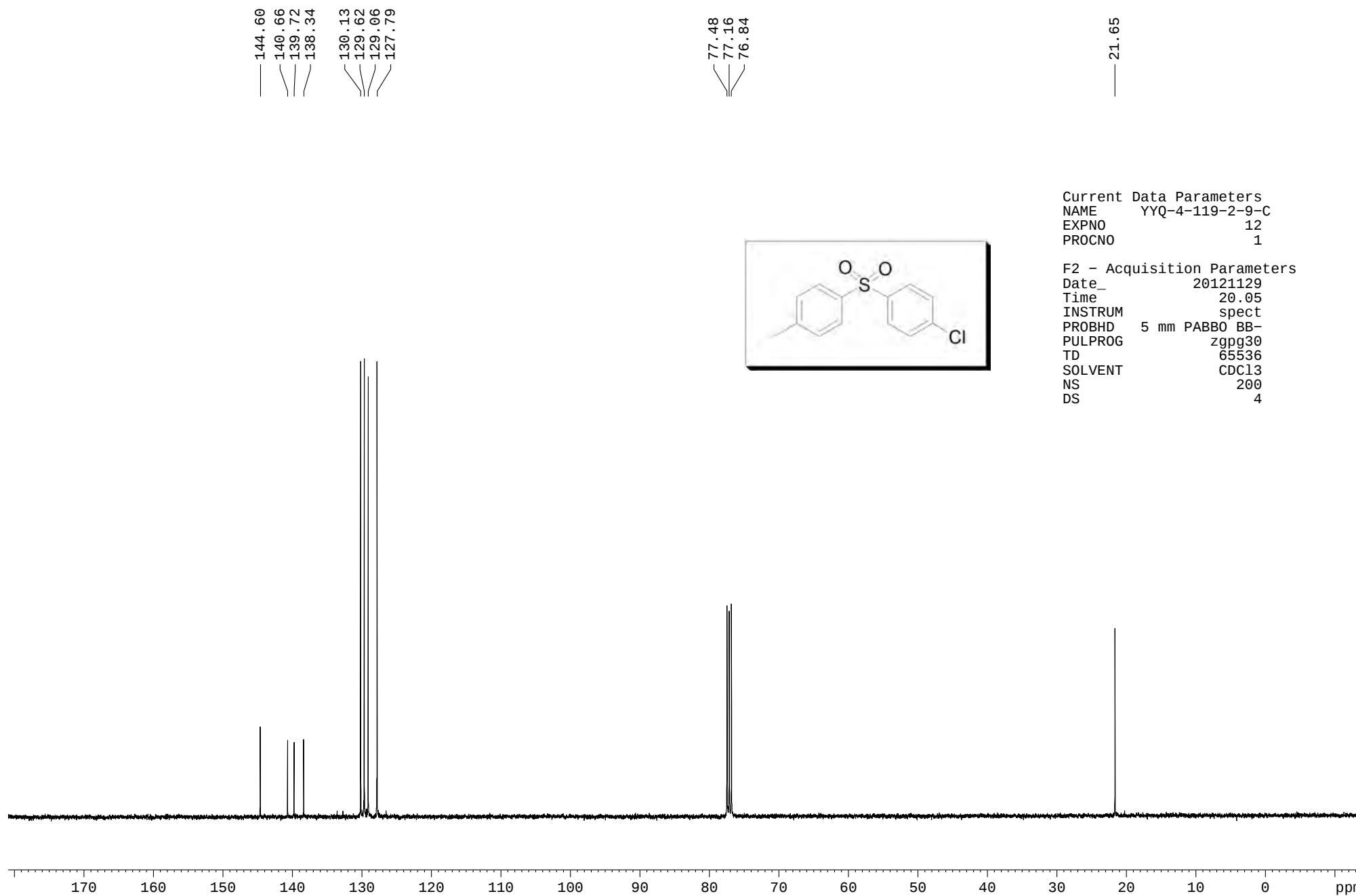
S101



Current Data Parameters
NAME YYQ-4-117-2-C
EXPNO 10
PROCNO 1

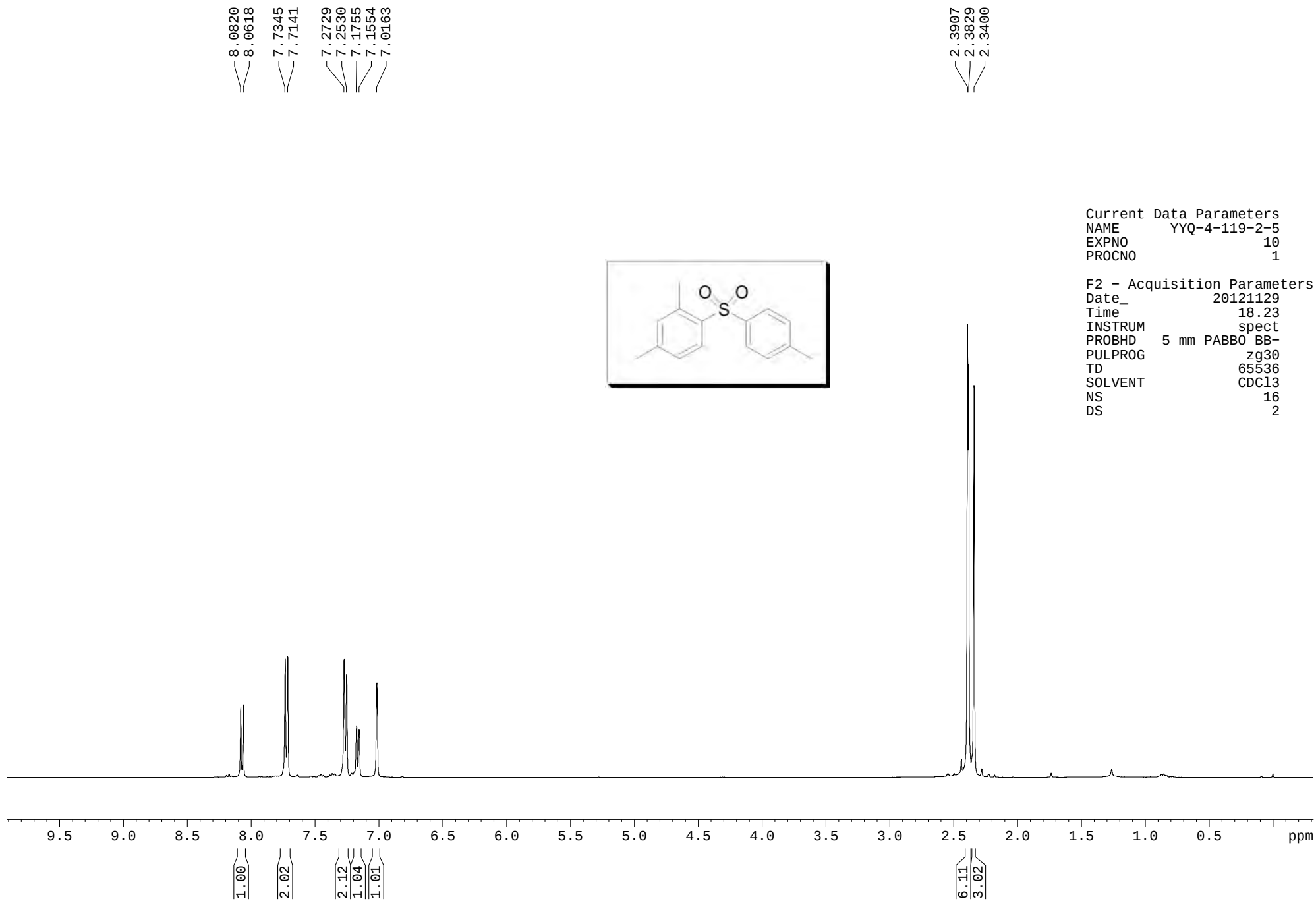
F2 - Acquisition Parameters
Date_ 20121122
Time 19.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 105
DS 4
SWH 10000.000 MHz





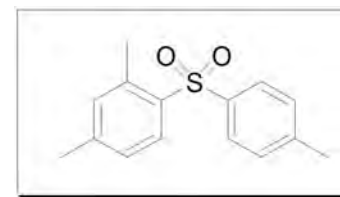
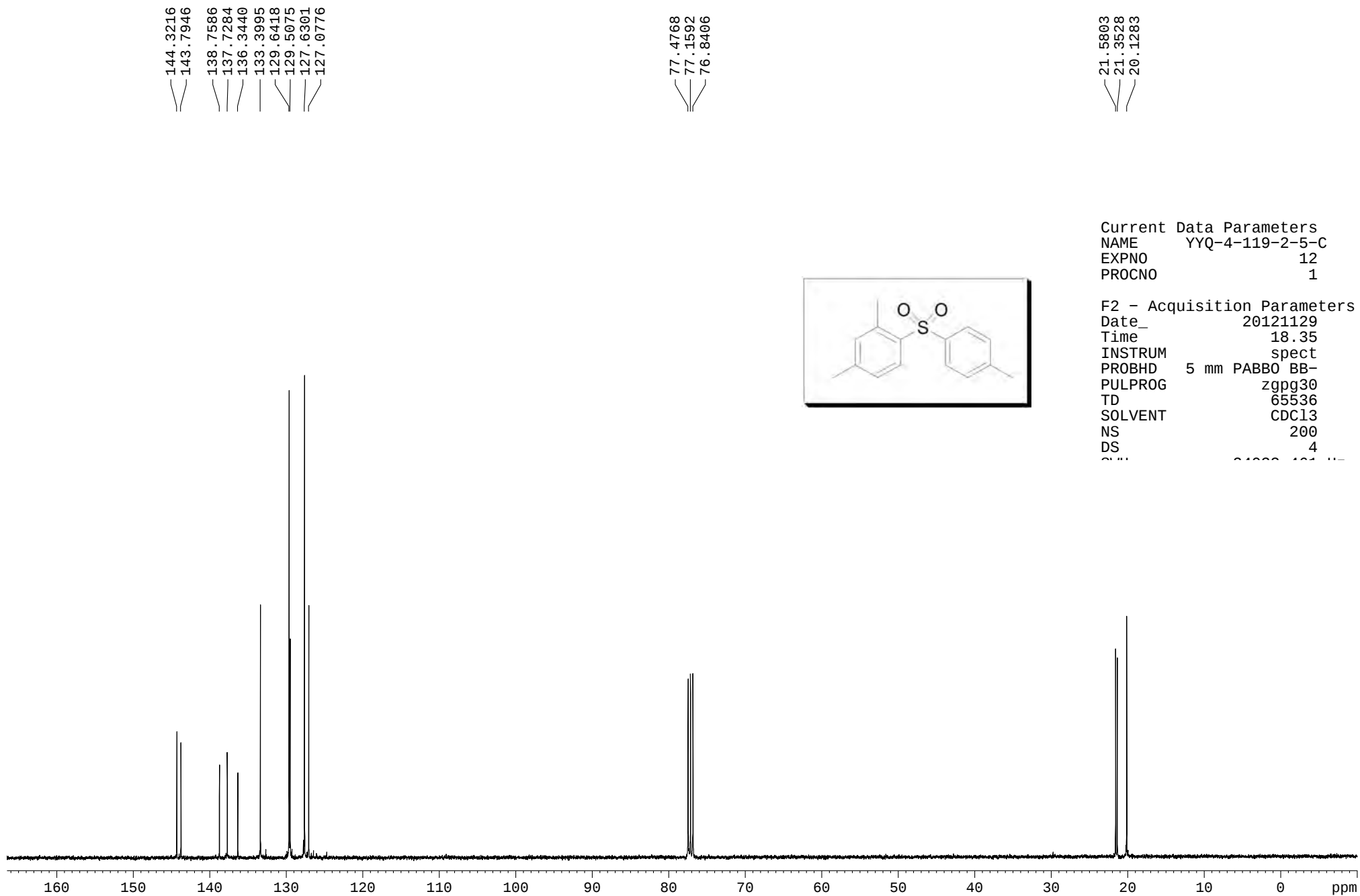
Current Data Parameters
NAME YYQ-4-119-2-9-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121129
Time 20.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4



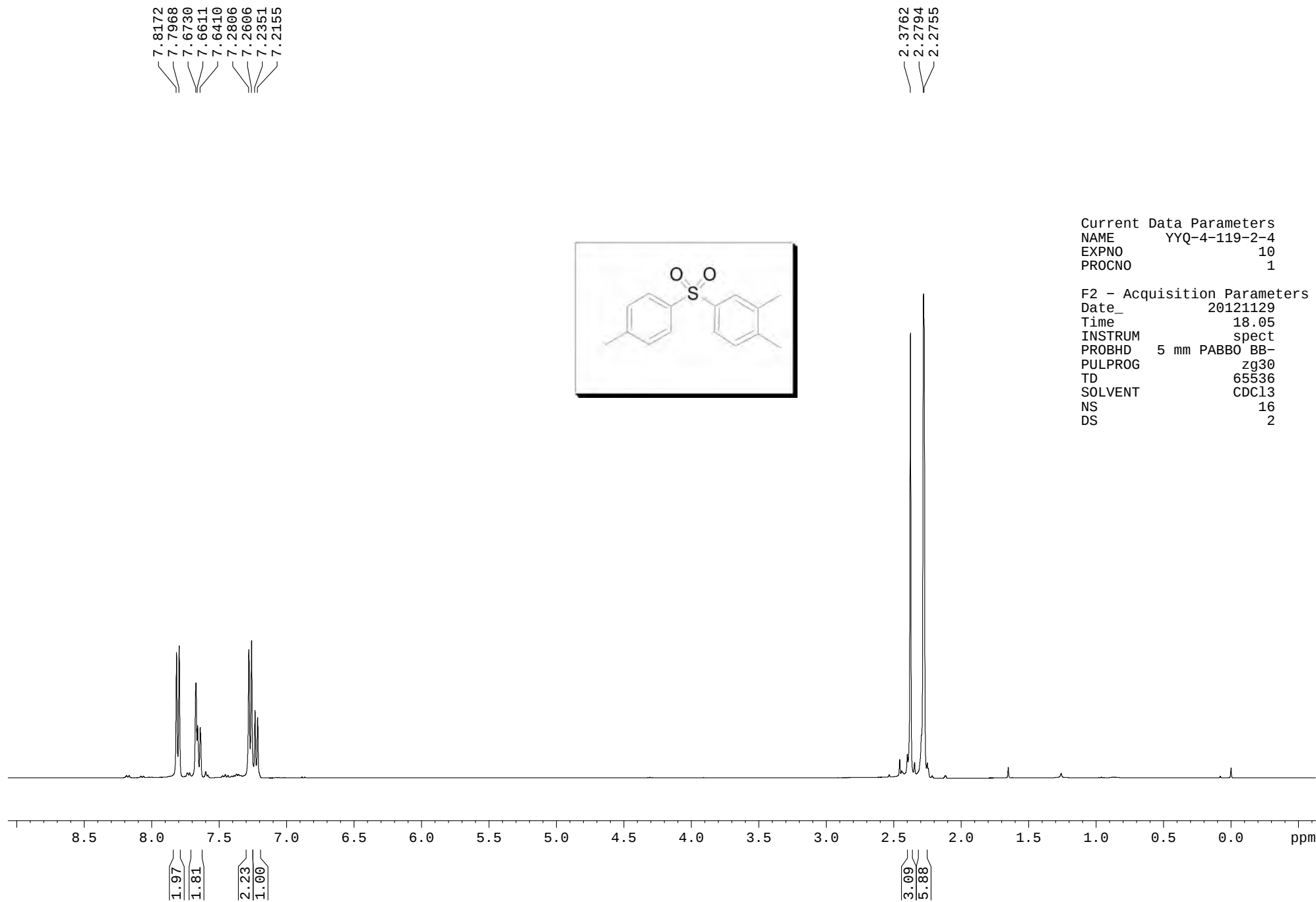
Current Data Parameters
NAME YYQ-4-119-2-5
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121129
Time 18.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



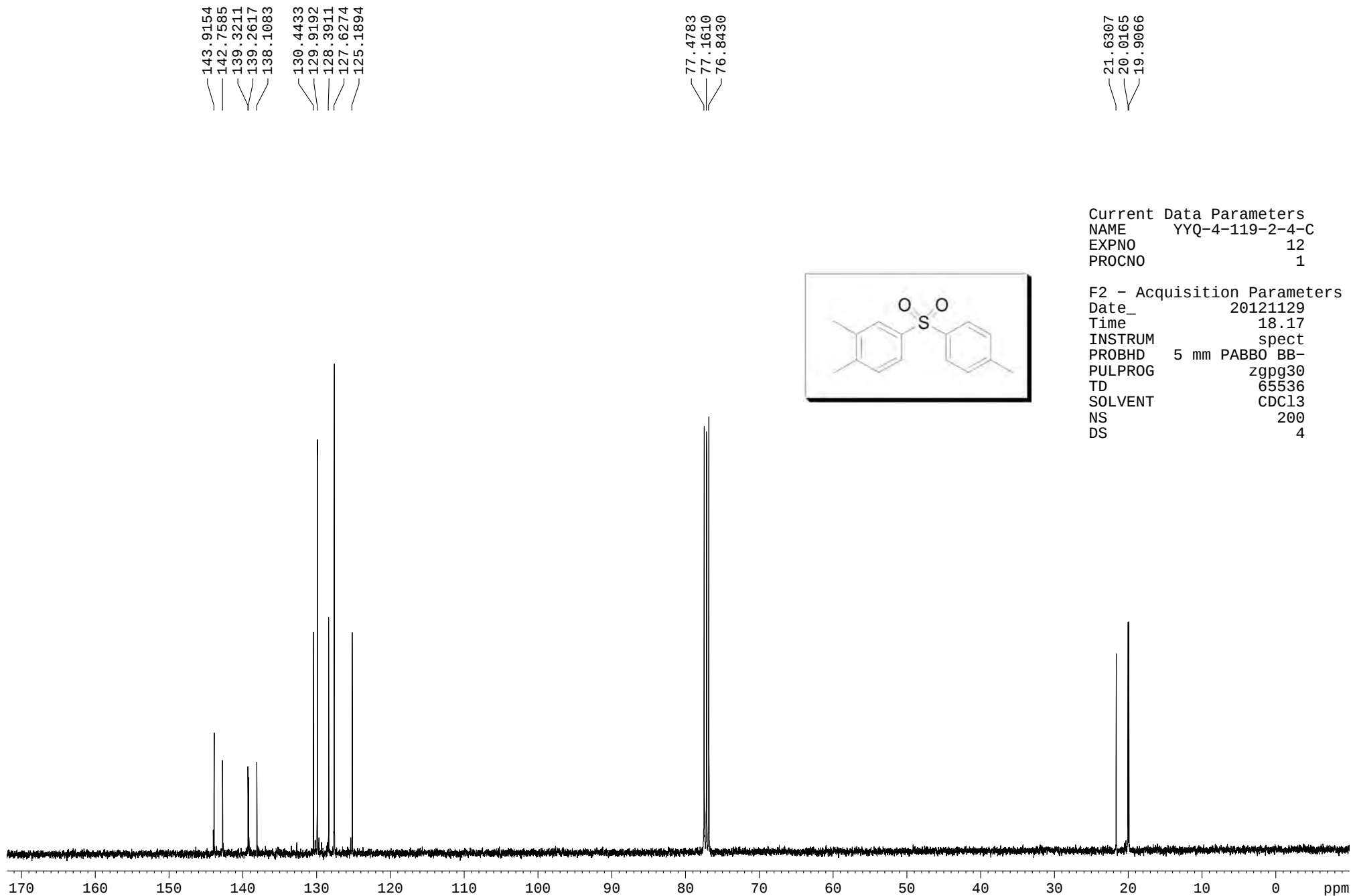
Current Data Parameters
NAME YYQ-4-119-2-5-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121129
Time 18.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4
AQ 0.16000000



Current Data Parameters
NAME YYQ-4-119-2-4
EXPNO 10
PROCNO 1

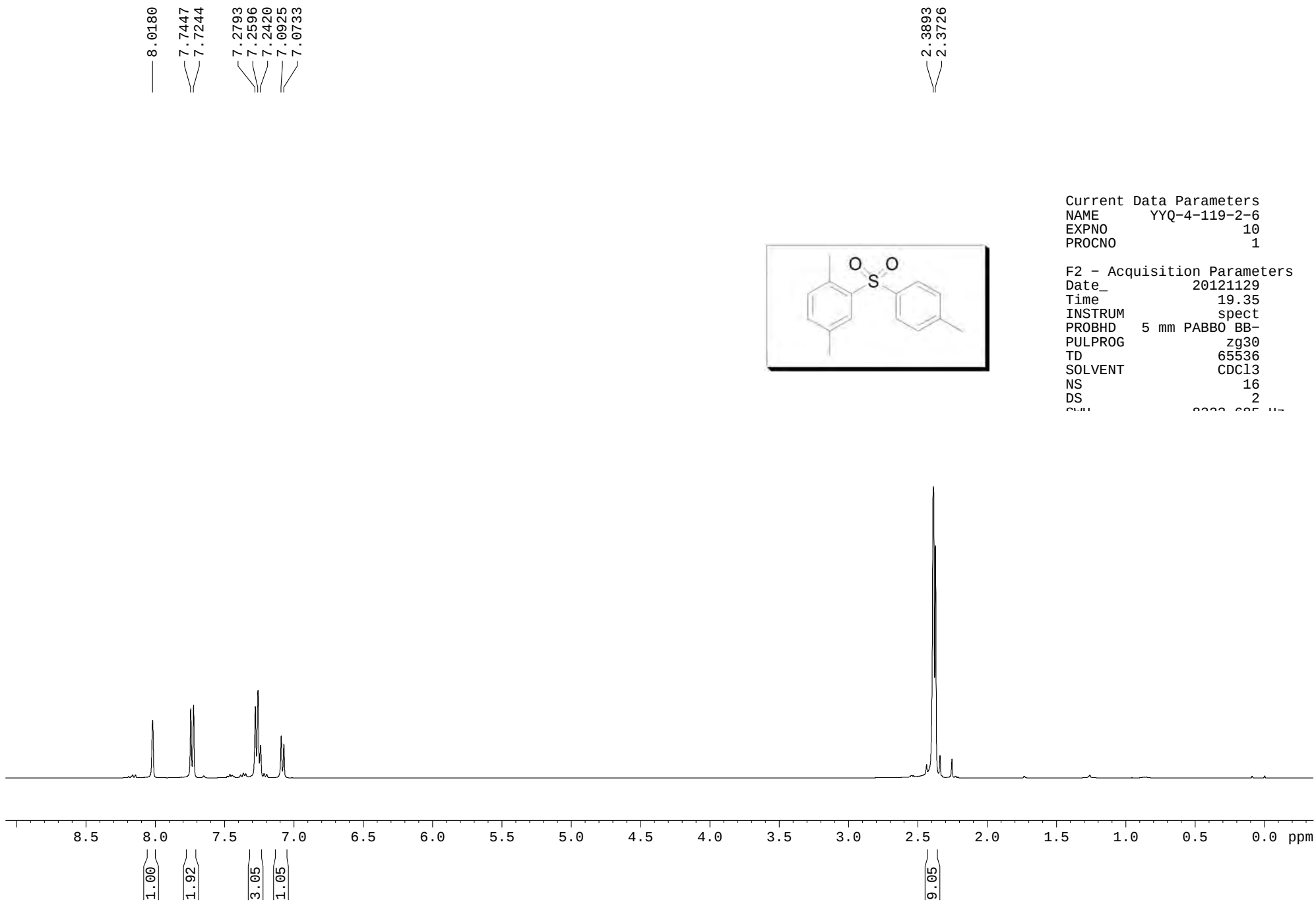
F2 - Acquisition Parameters
Date_ 20121129
Time 18.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2

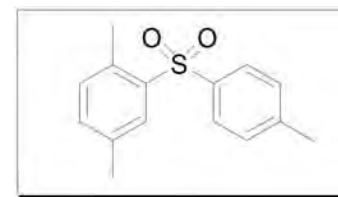
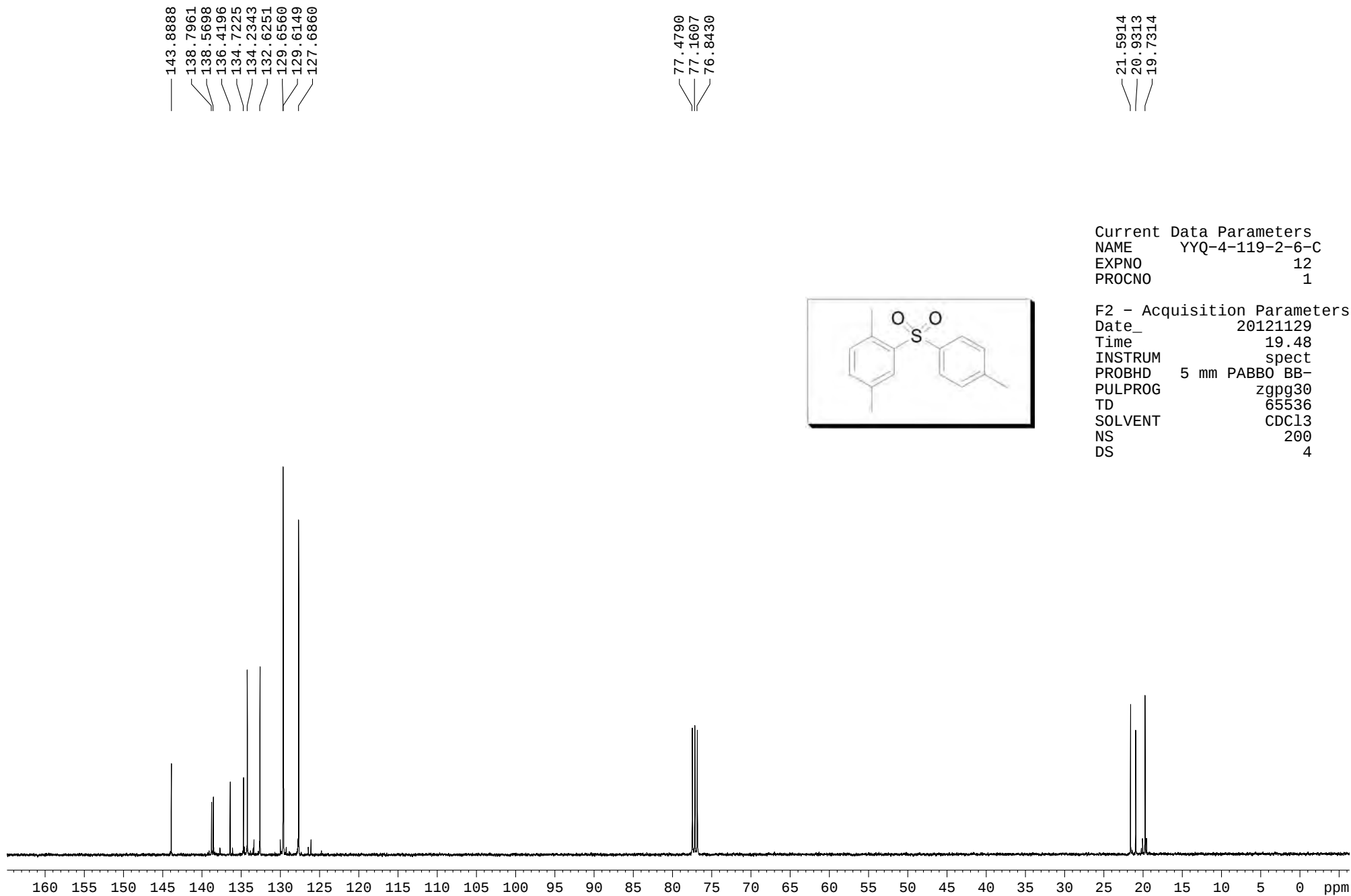


Current Data Parameters
NAME YYQ-4-119-2-4-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121129
Time 18.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4

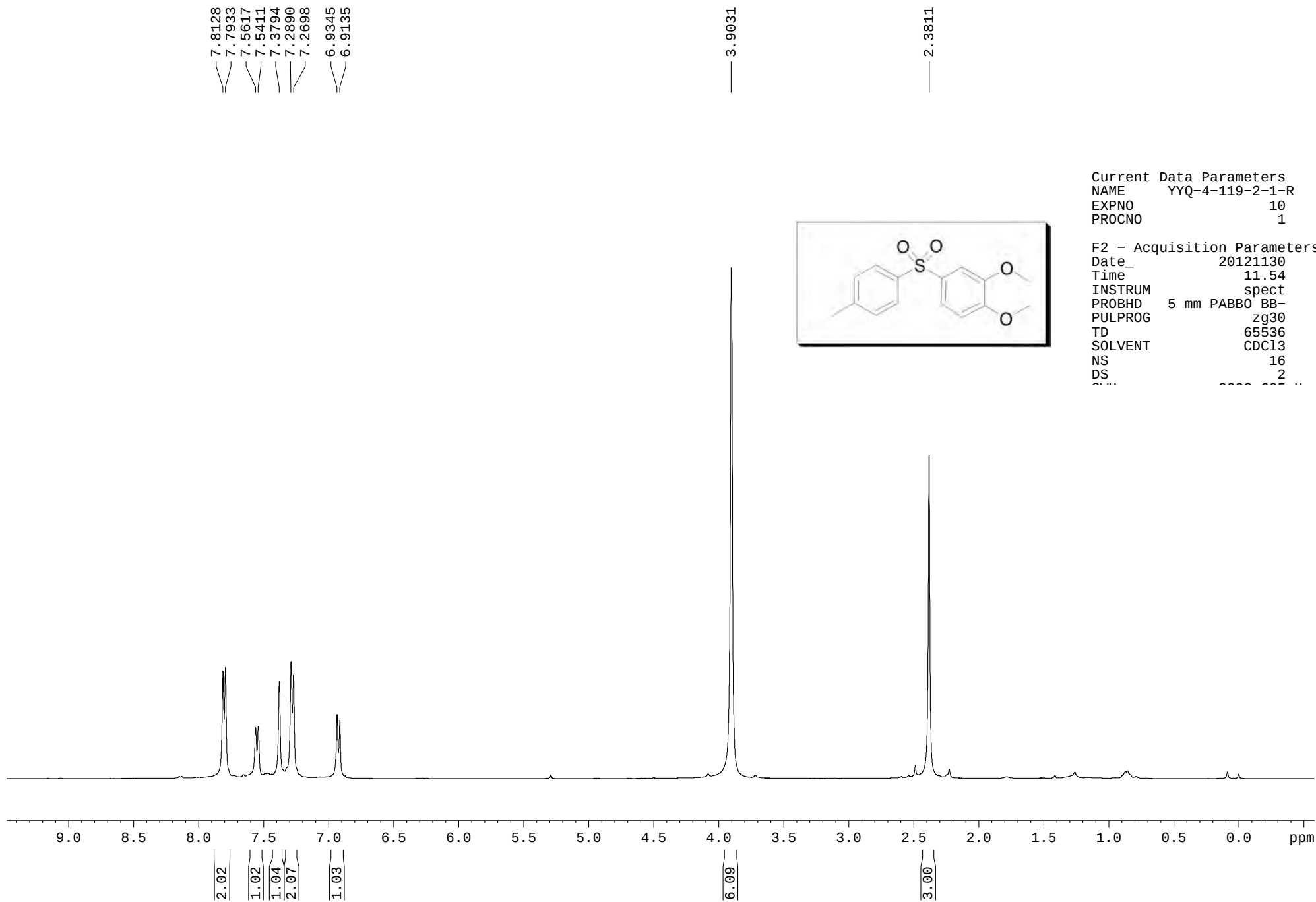
S108



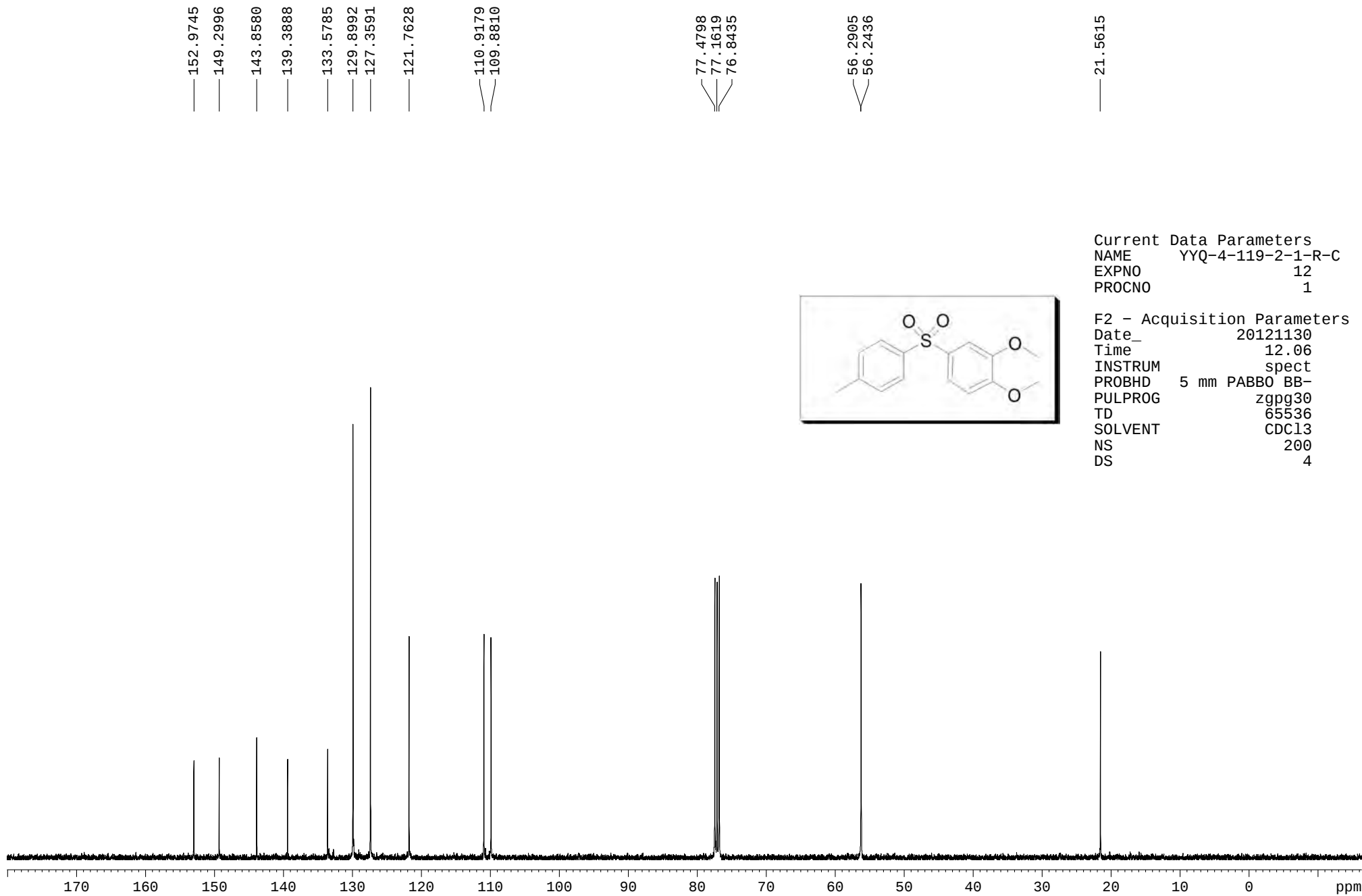


Current Data Parameters
NAME YYQ-4-119-2-6-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121129
Time 19.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4

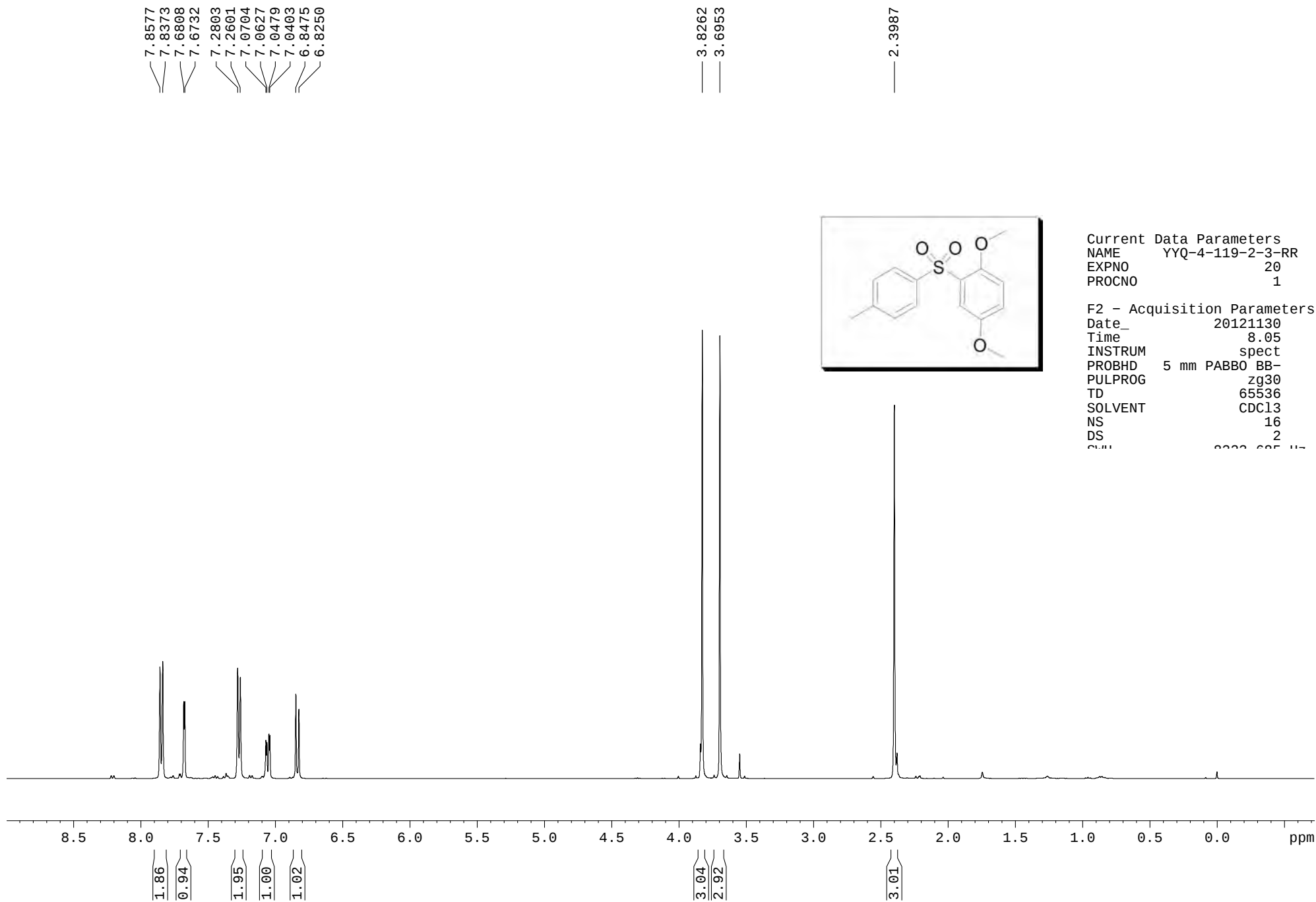


S111



Current Data Parameters
NAME YYQ-4-119-2-1-R-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121130
Time 12.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4



S113

—153.2607
—151.1680

—143.8609

—138.4735

—129.8652
—129.1298
—128.4083

—121.3935

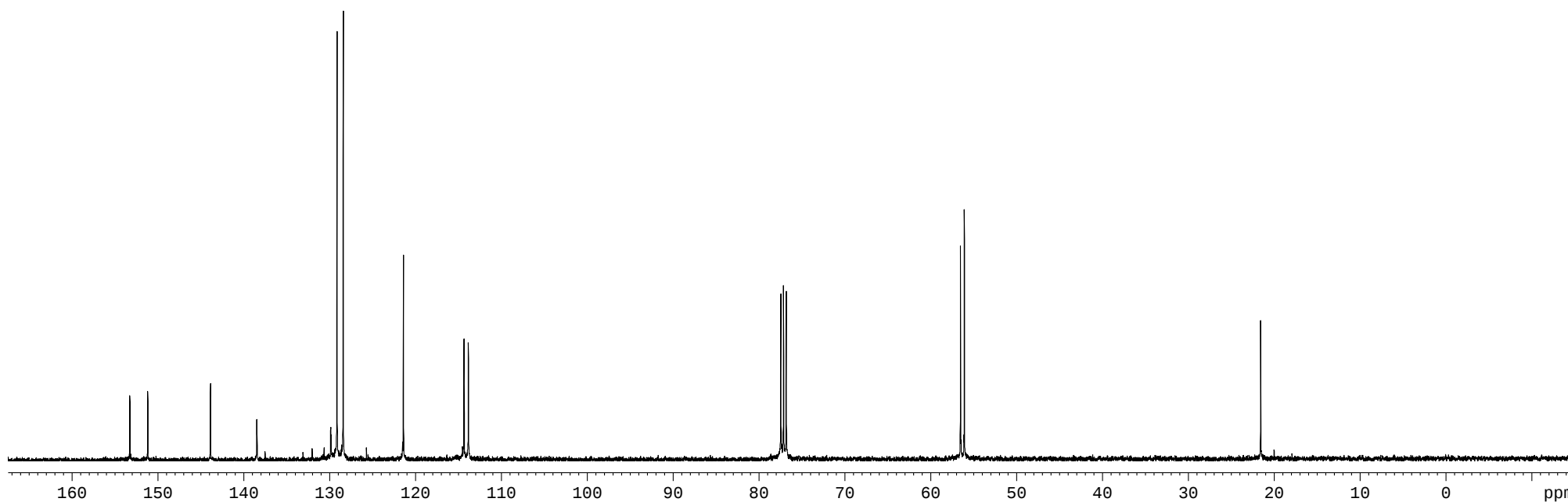
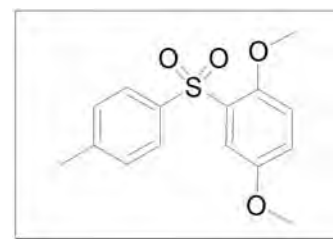
—114.3465
—113.8336

—56.5242
—56.0692

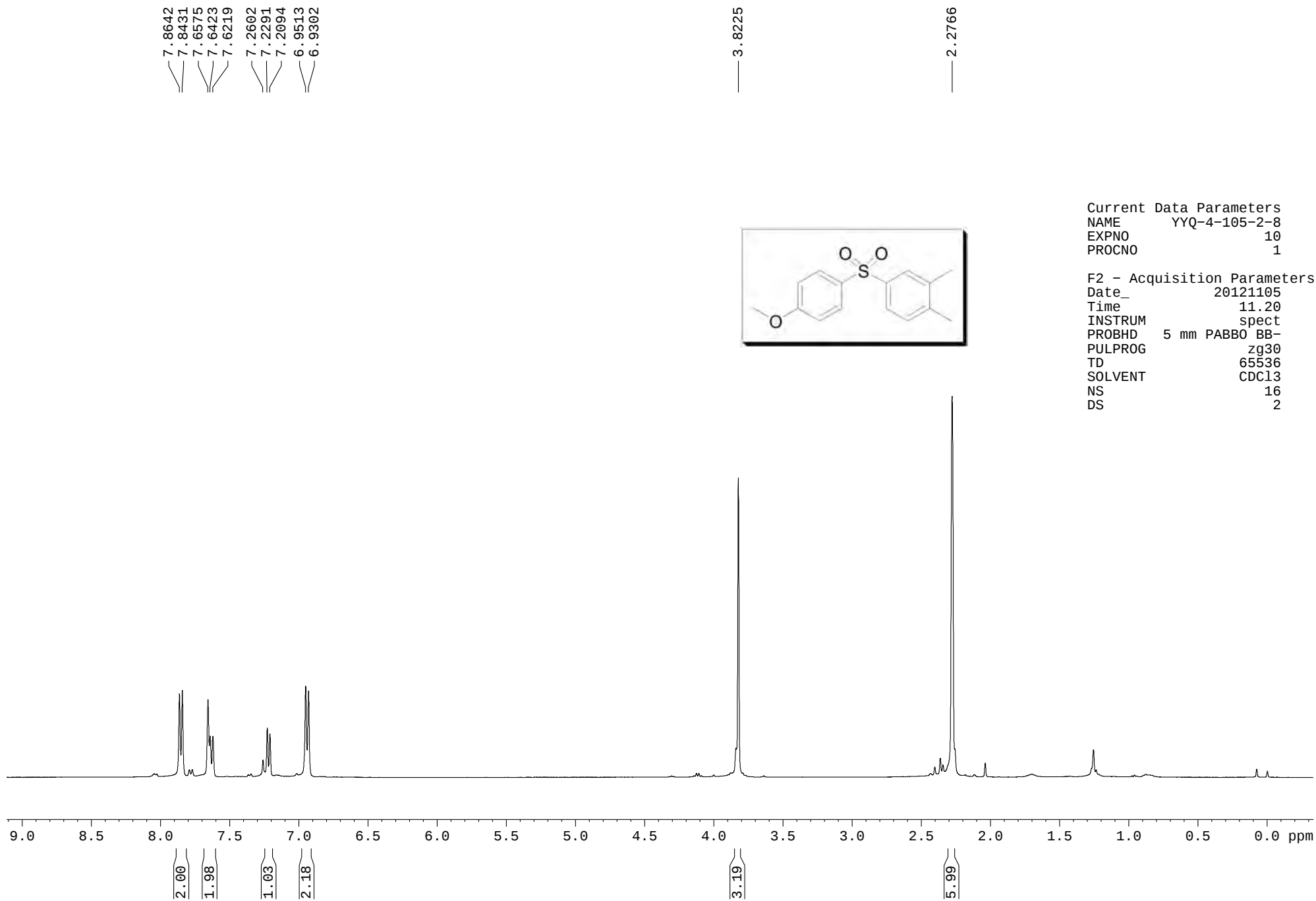
—21.5641

Current Data Parameters
NAME YYQ-4-119-2-2-2-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121129
Time 12.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4
SWH 34300 Hz

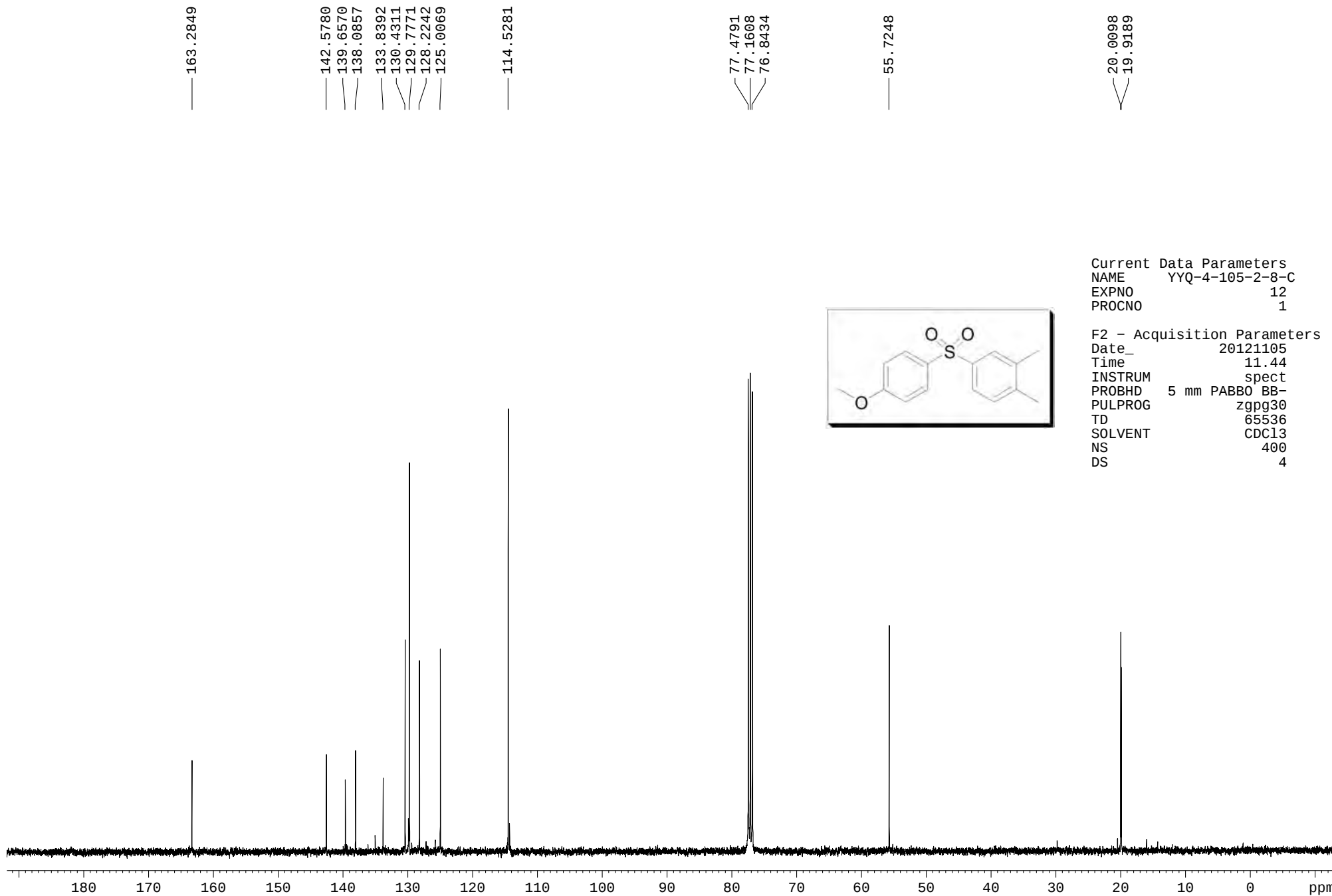


S114



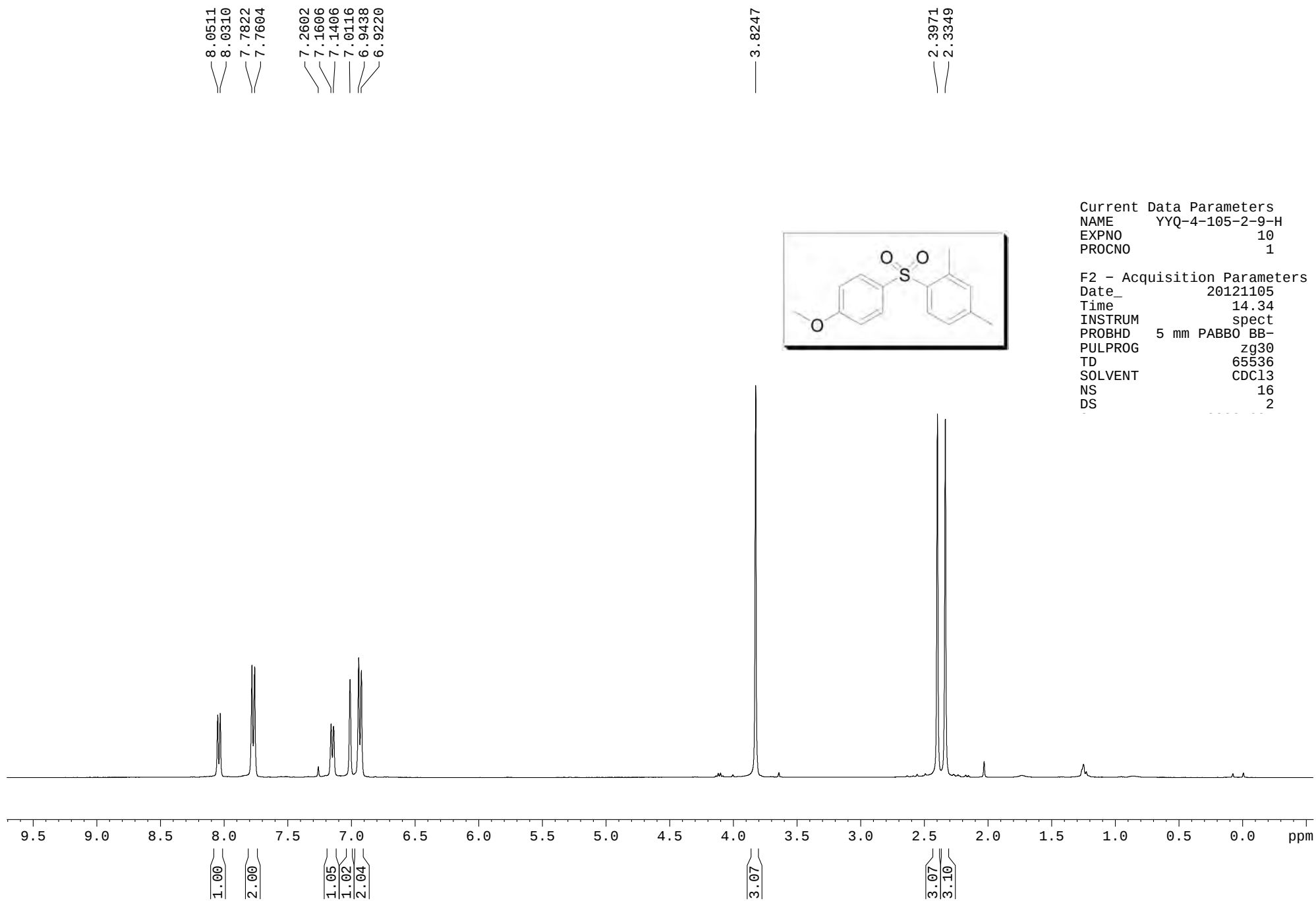
Current Data Parameters
NAME YYQ-4-105-2-8
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121105
Time 11.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



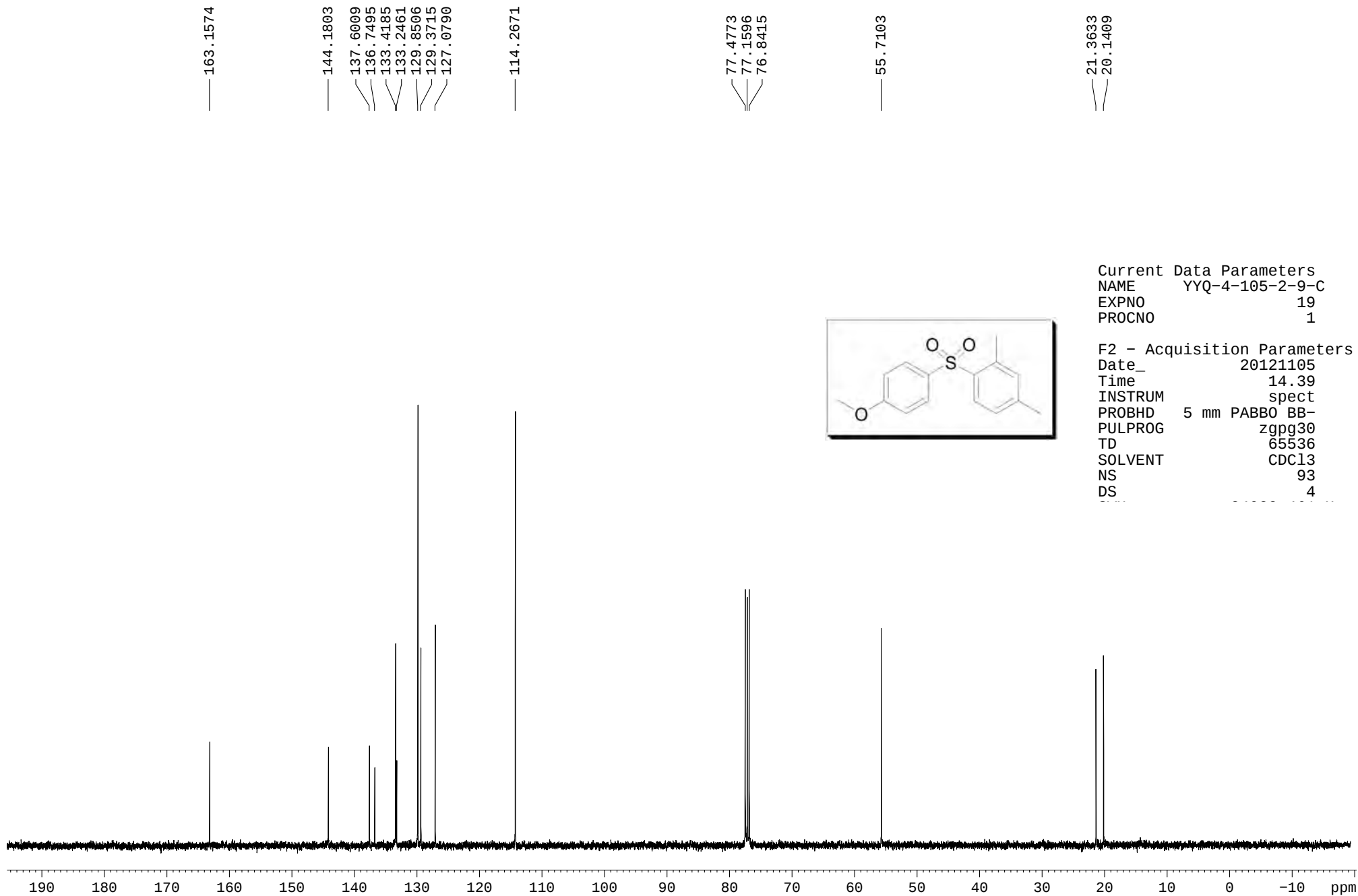
Current Data Parameters
NAME YYQ-4-105-2-8-C
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121105
Time 11.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4



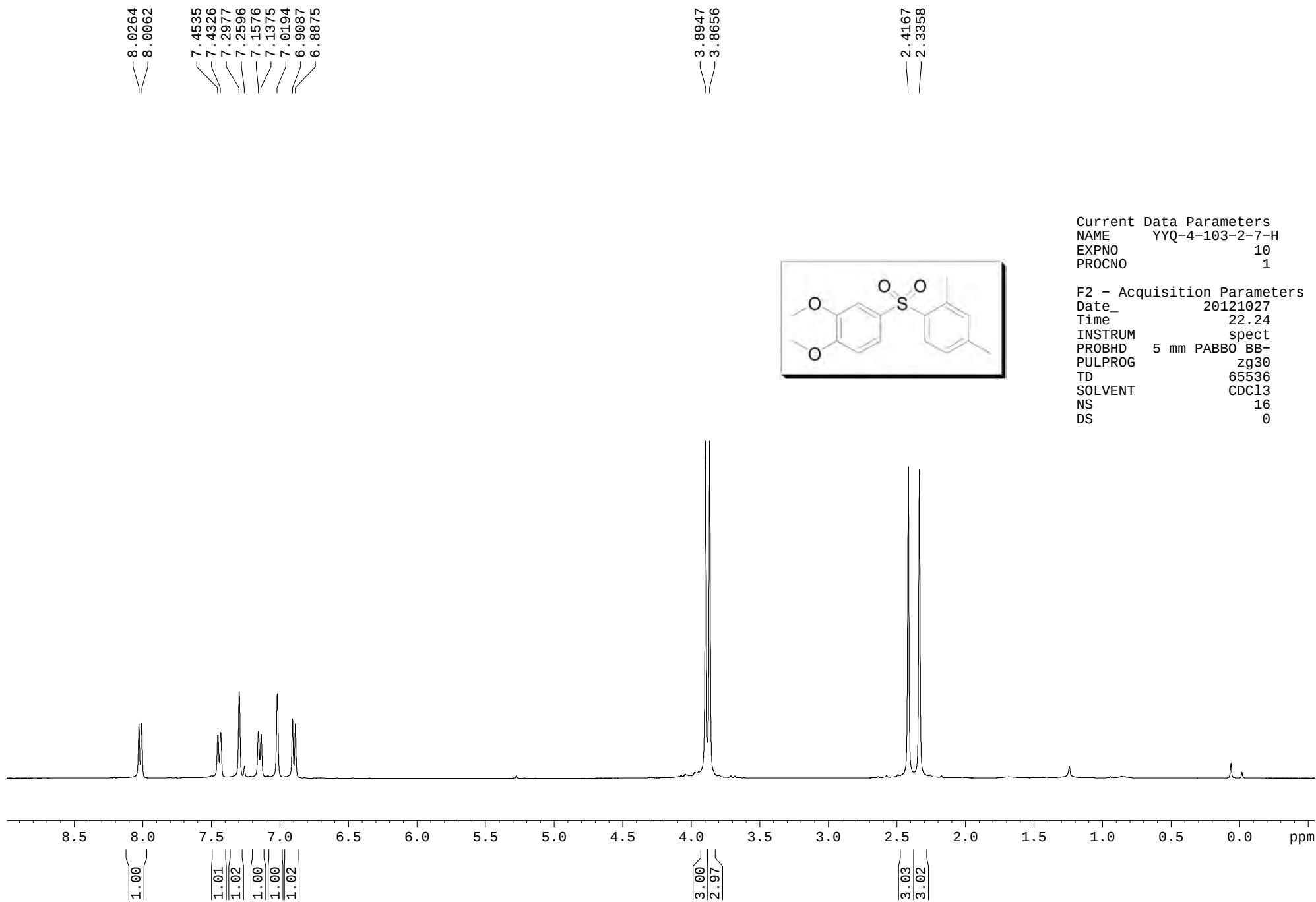
Current Data Parameters
NAME YYQ-4-105-2-9-H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121105
Time 14.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



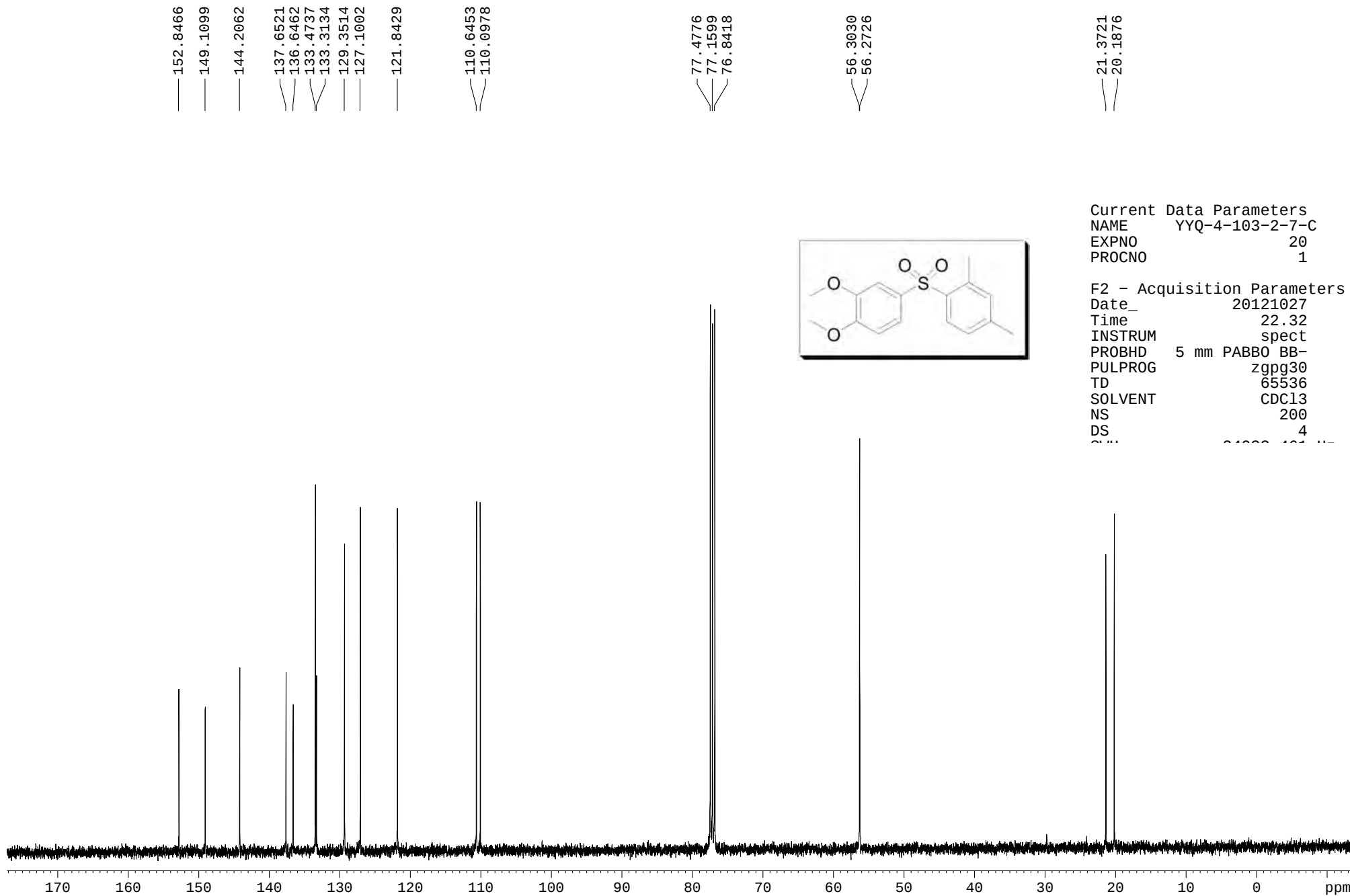
Current Data Parameters
NAME YYQ-4-105-2-9-C
EXPNO 19
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121105
Time 14.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 93
DS 4



Current Data Parameters
NAME YYQ-4-103-2-7-H
EXPNO 10
PROCNO 1

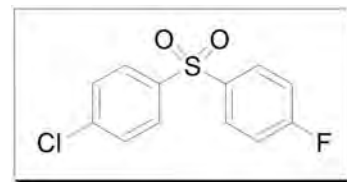
F2 - Acquisition Parameters
Date_ 20121027
Time 22.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0



Current Data Parameters
 NAME YYQ-4-103-2-7-C
 EXPNO 20
 PROCNO 1

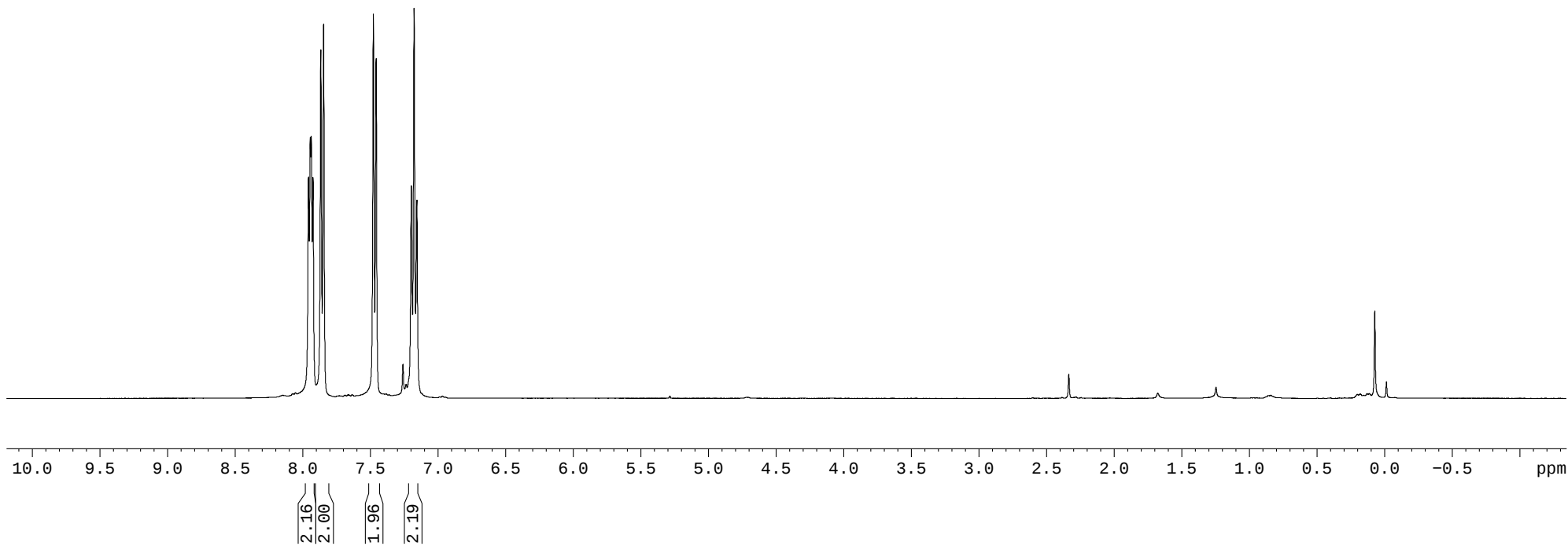
F2 - Acquisition Parameters
 Date_ 20121027
 Time 22.32
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 200
 DS 4

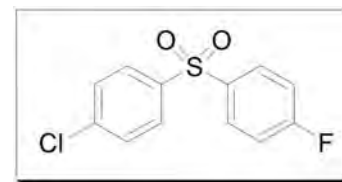
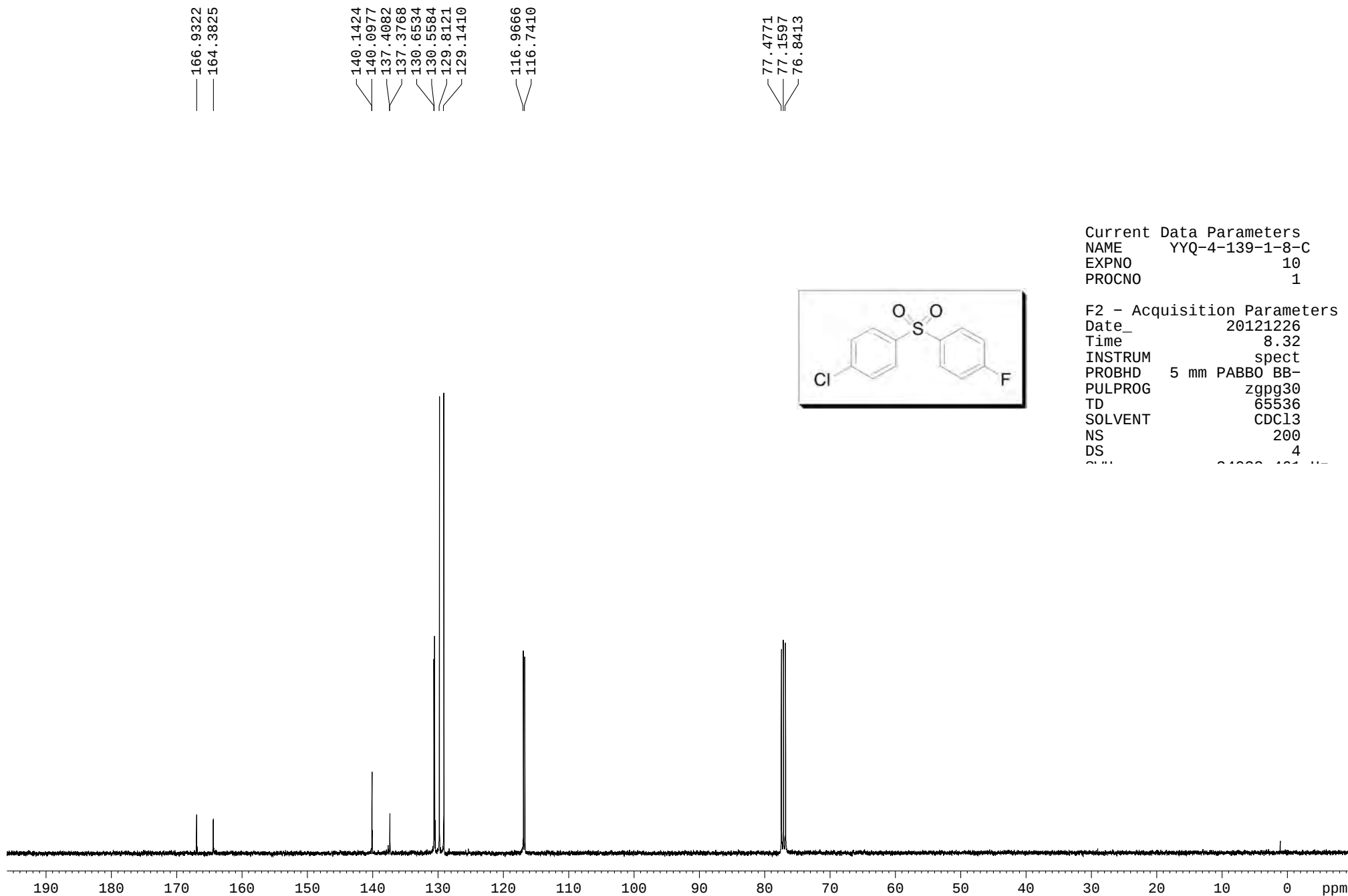
7.9583
7.9451
7.9387
7.9256
7.8674
7.8470
7.4789
7.4583
7.1983
7.1776
7.1568



Current Data Parameters
NAME YYQ-4-139-1-8
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121225
Time 22.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2

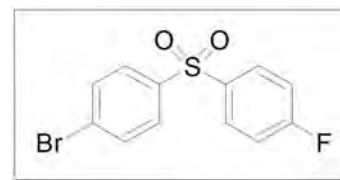




Current Data Parameters
 NAME YYQ-4-139-1-8-C
 EXPNO 10
 PROCNO 1

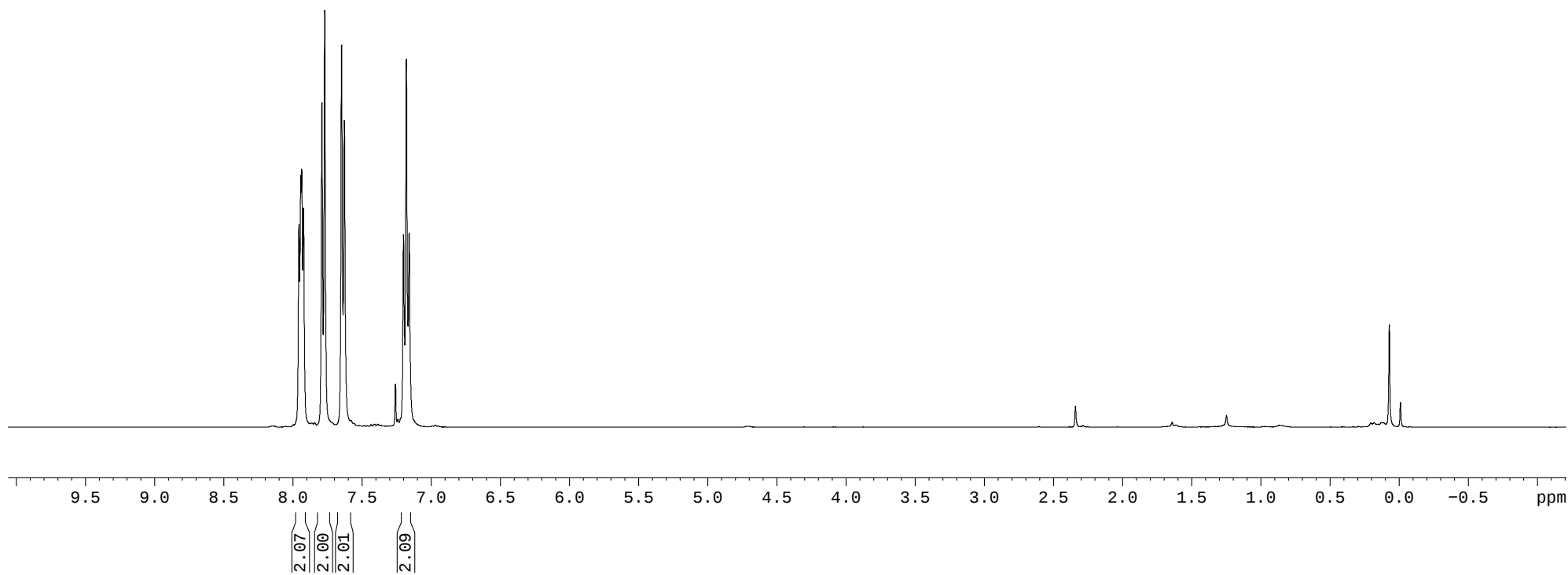
F2 - Acquisition Parameters
 Date_ 20121226
 Time 8.32
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 200
 DS 4
 ...

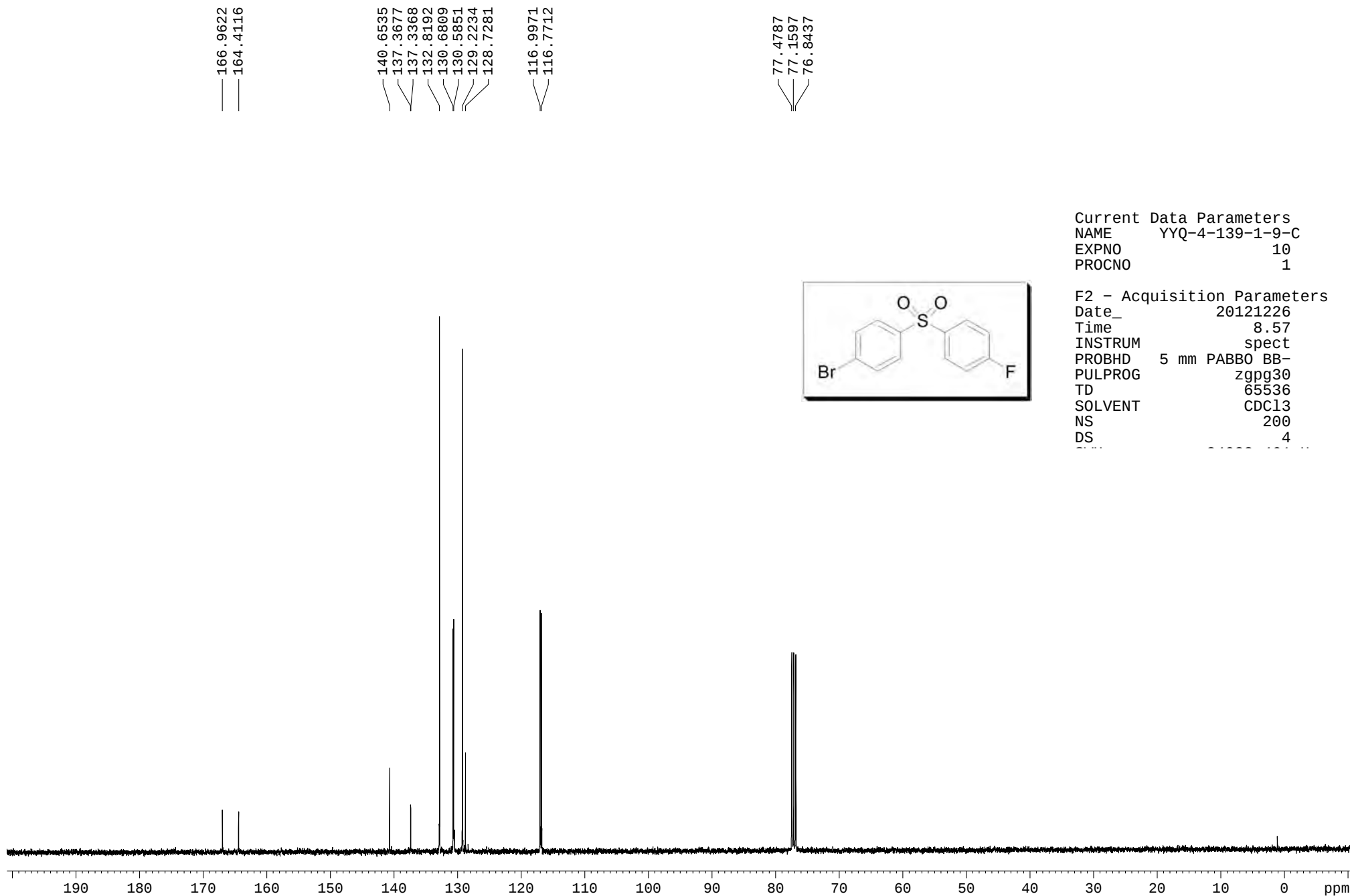
7.9567
7.9434
7.9377
7.9245
7.7908
7.7709
7.6484
7.6289
7.2596
7.2008
7.1803
7.1600



Current Data Parameters
NAME YYQ-4-139-1-9
EXPNO 10
PROCNO 1

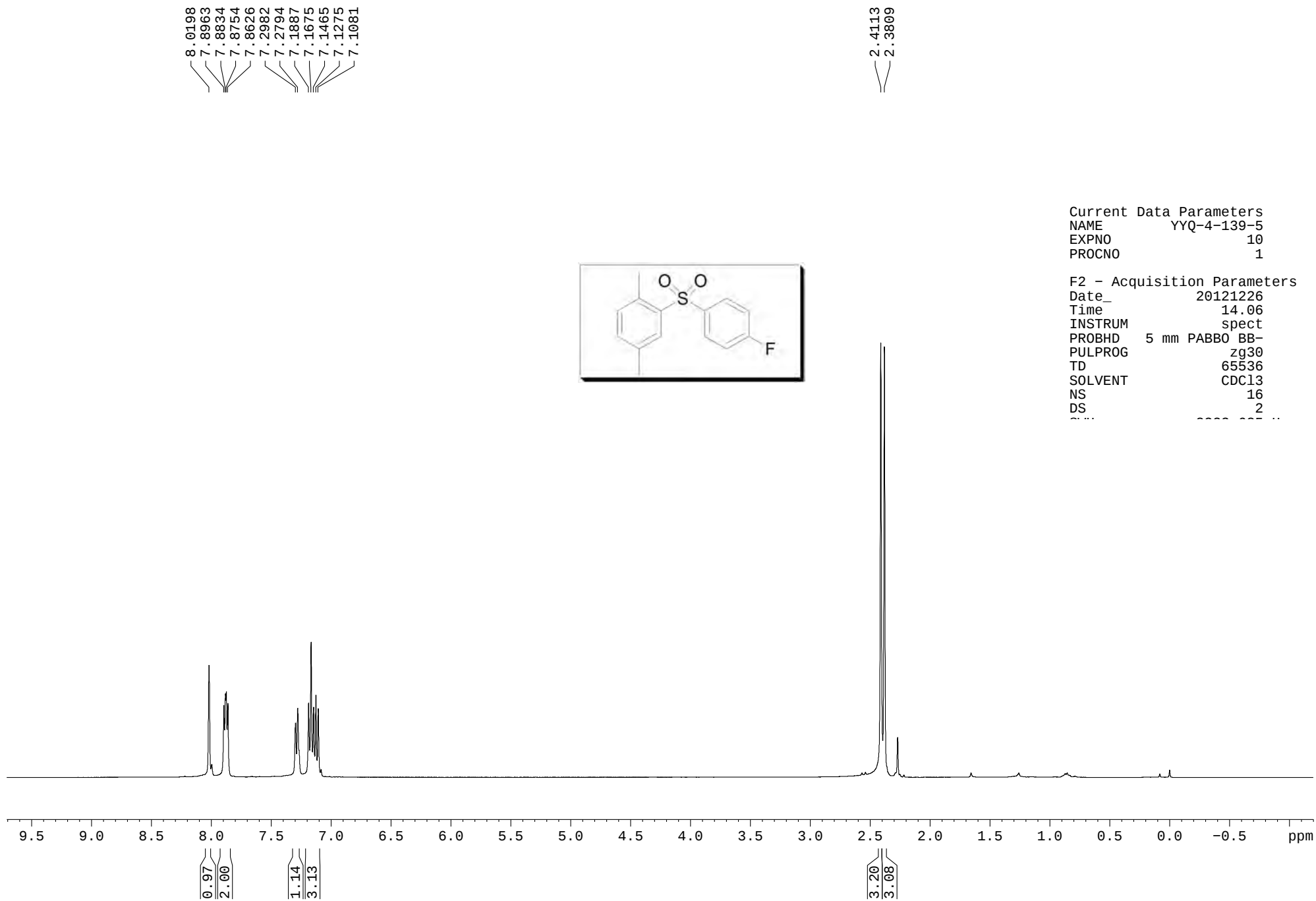
F2 - Acquisition Parameters
Date_ 20121225
Time 22.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 2000.000 MHz





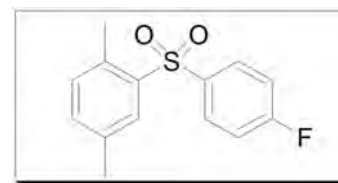
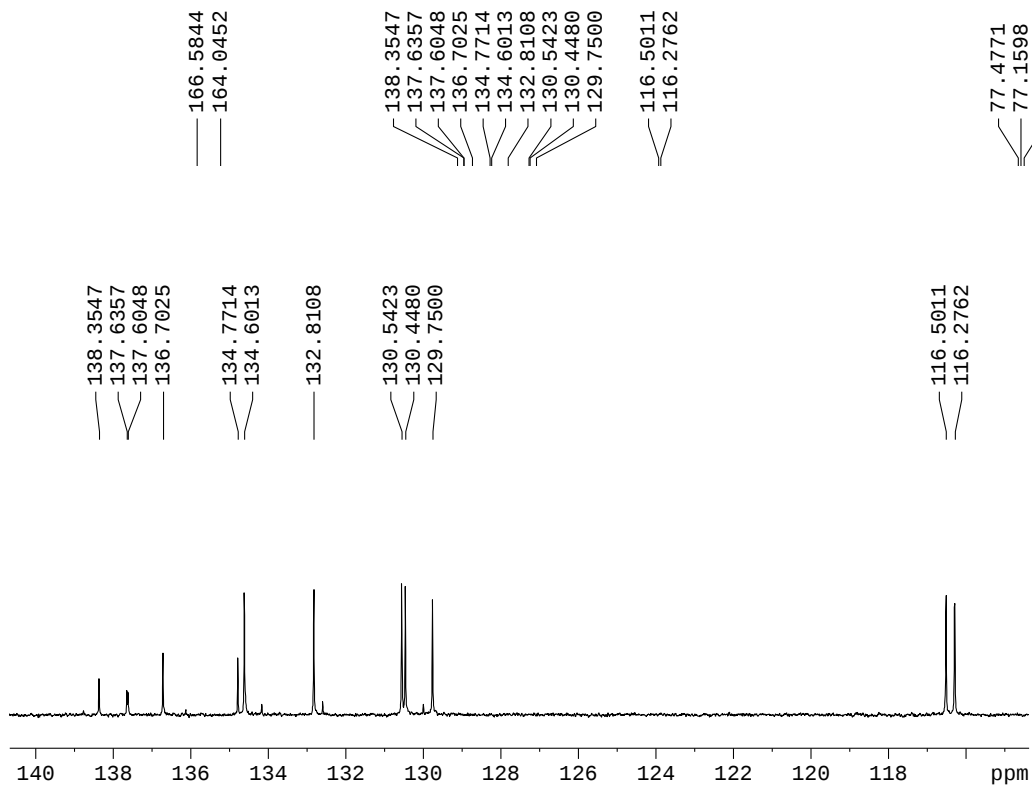
Current Data Parameters
NAME YYQ-4-139-1-9-C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121226
Time 8.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 200
DS 4



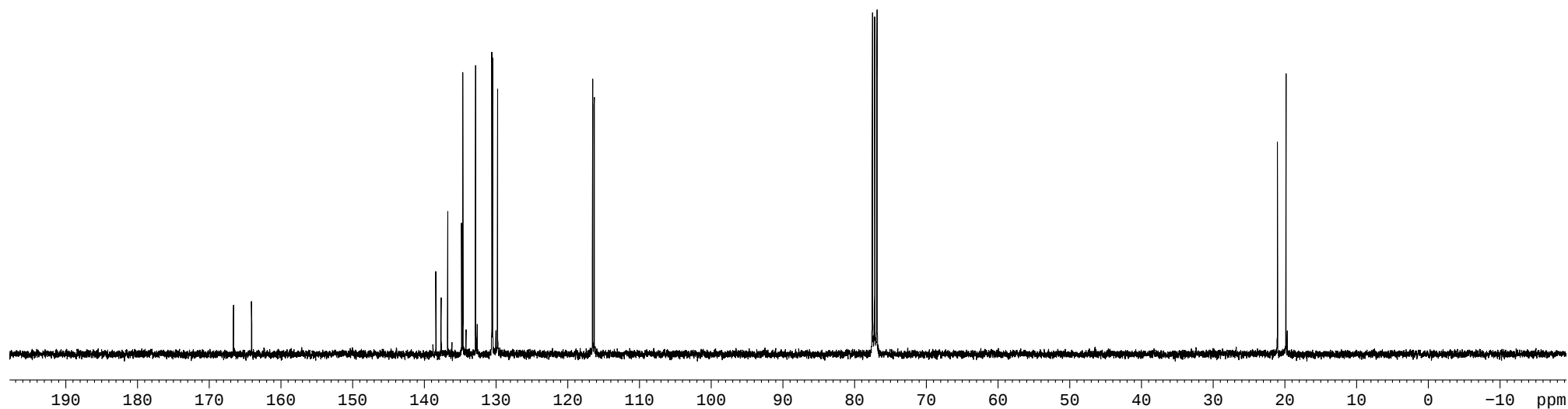
Current Data Parameters
NAME YYQ-4-139-5
EXPNO 10
PROCNO 1

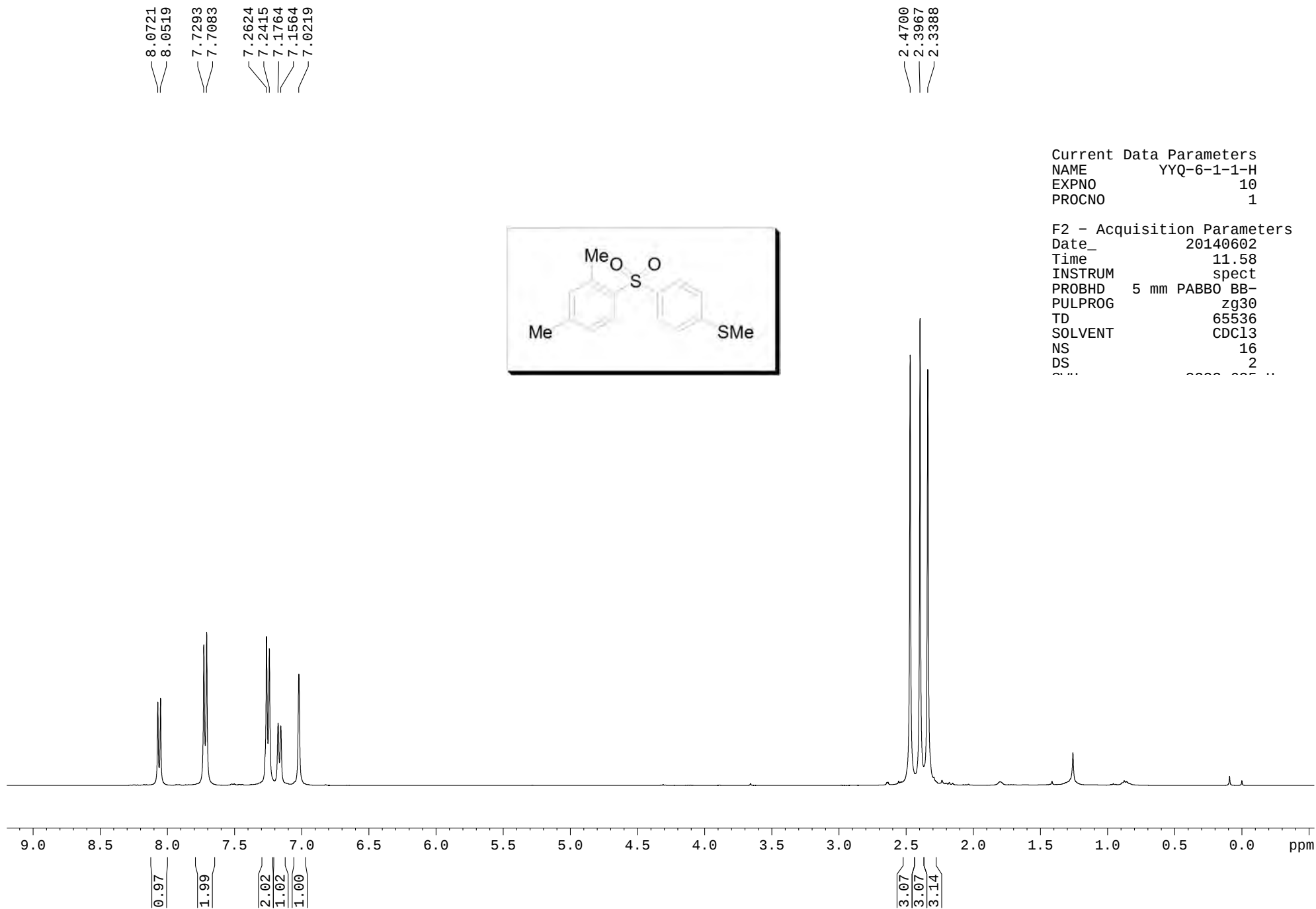
F2 - Acquisition Parameters
Date_ 20121226
Time 14.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2

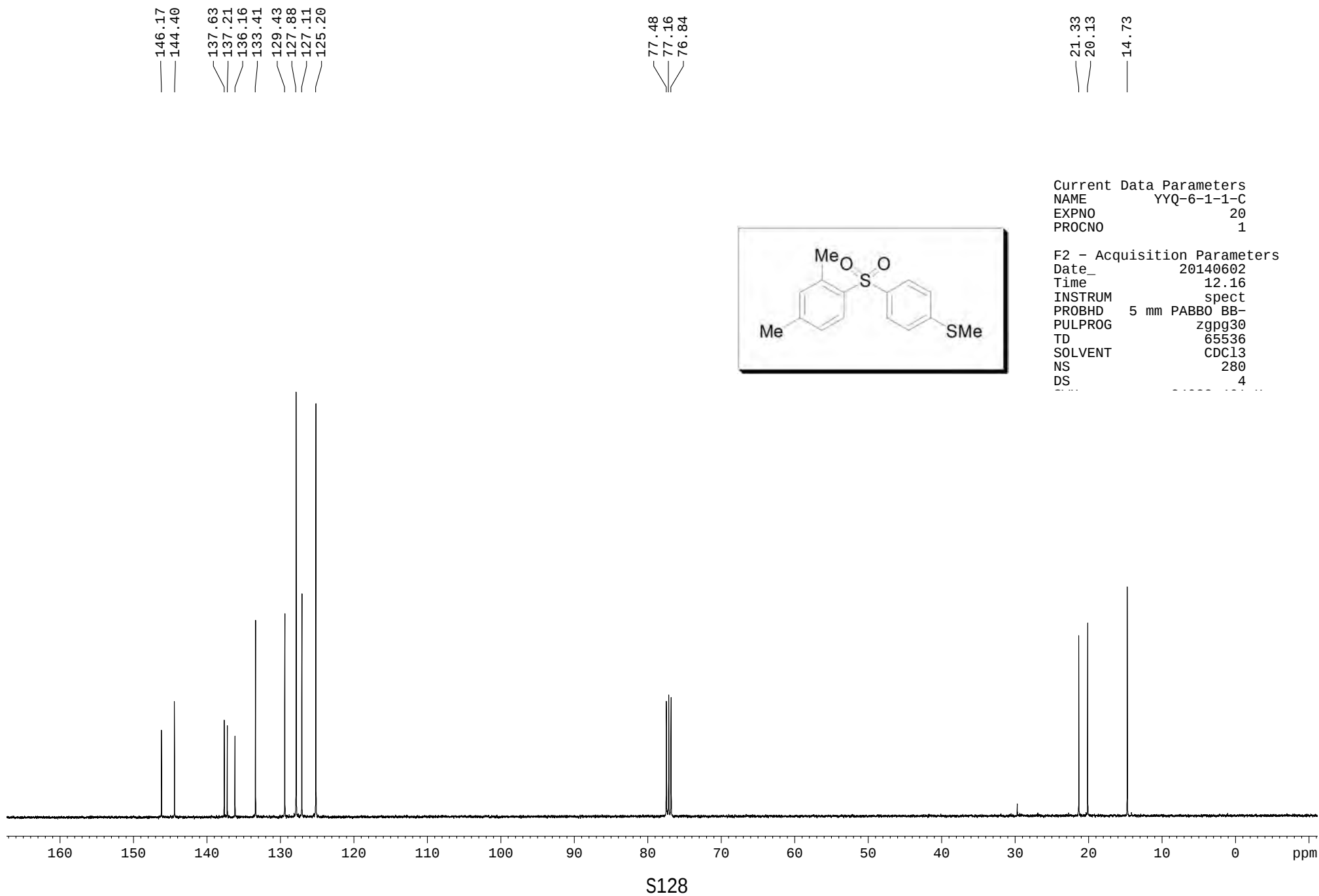


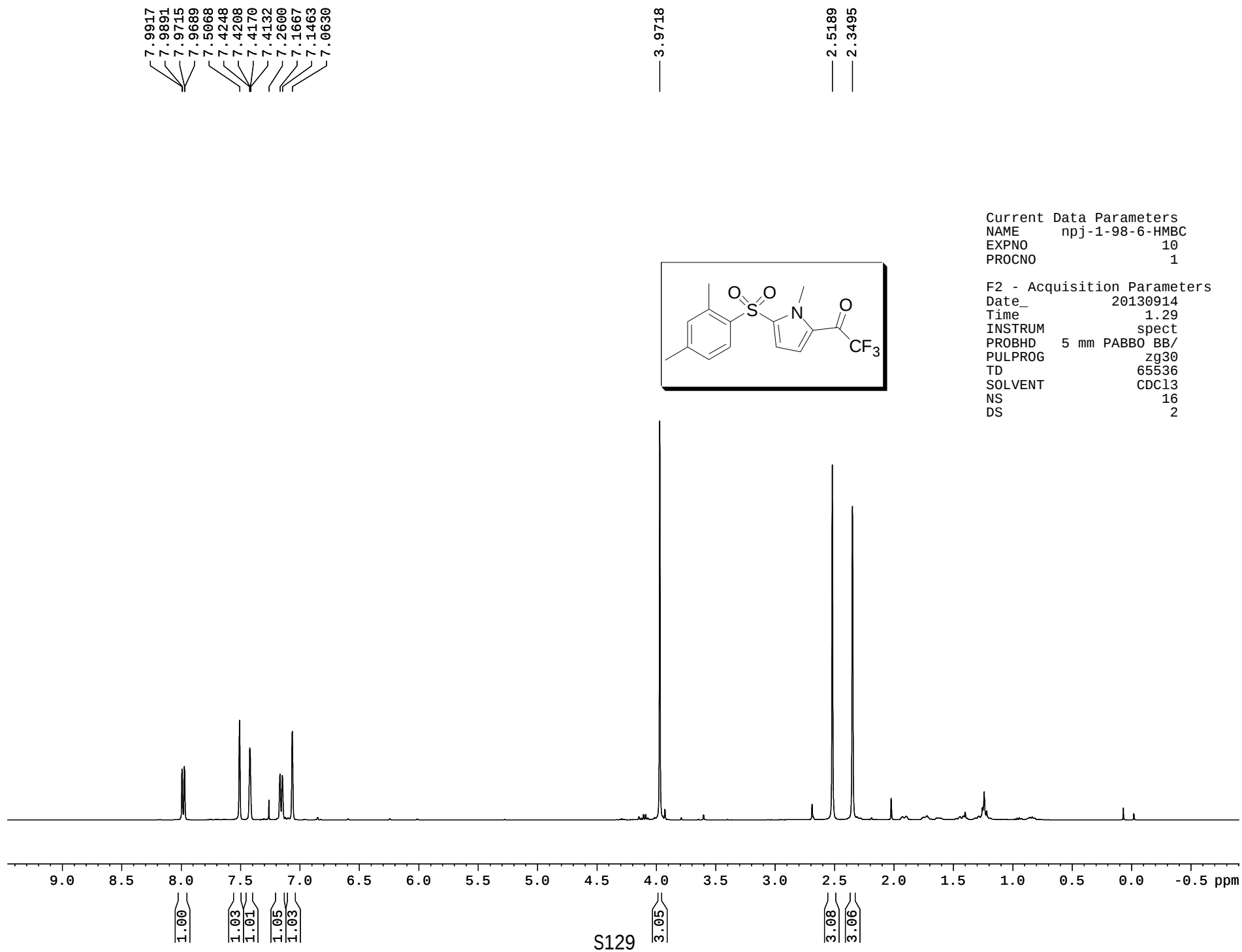
Current Data Parameters
NAME YYQ-4-139-5-C
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121226
Time 14.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 180
DS 4



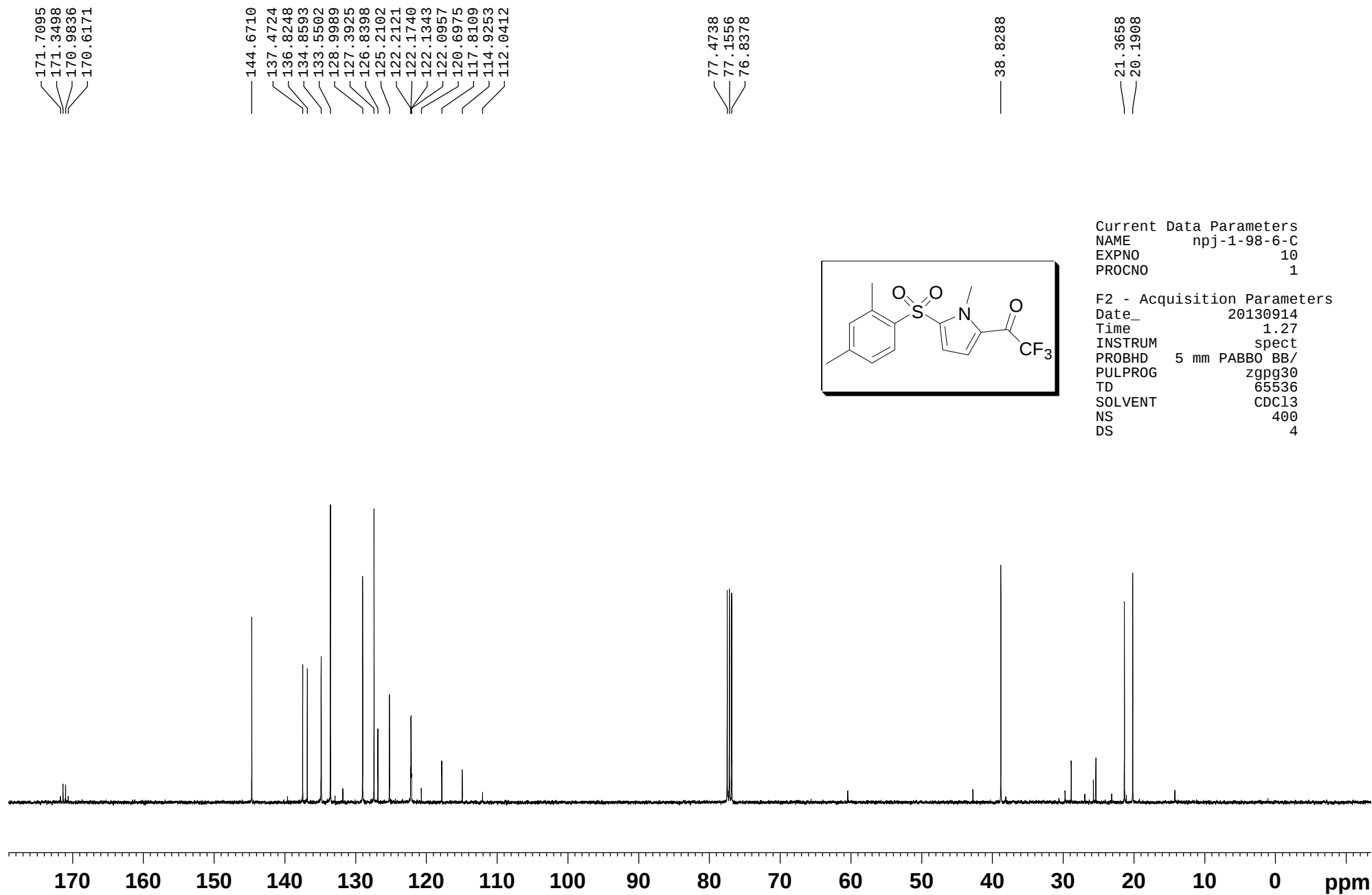






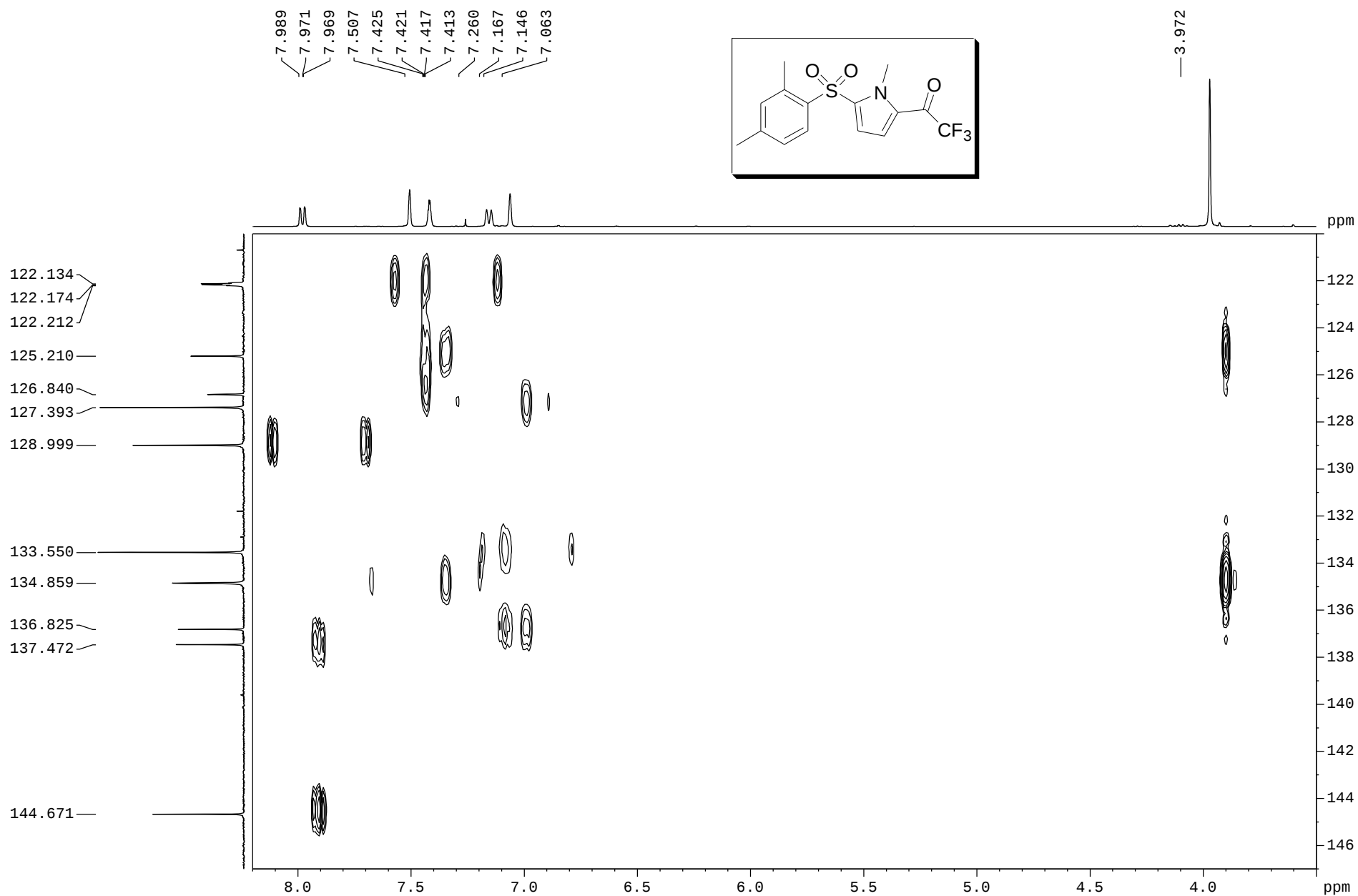
Current Data Parameters
NAME npj-1-98-6-HMBC
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130914
Time 1.29
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2



Current Data Parameters
NAME npj-1-98-6-C
EXPNO 10
PROCNO 1

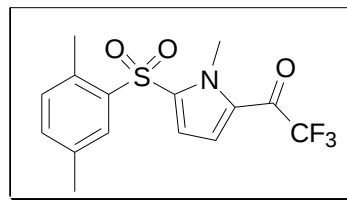
F2 - Acquisition Parameters
Date_ 20130914
Time 1.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4



7.9439
7.5421
7.4539
7.3026
7.2815
7.1609
7.1416

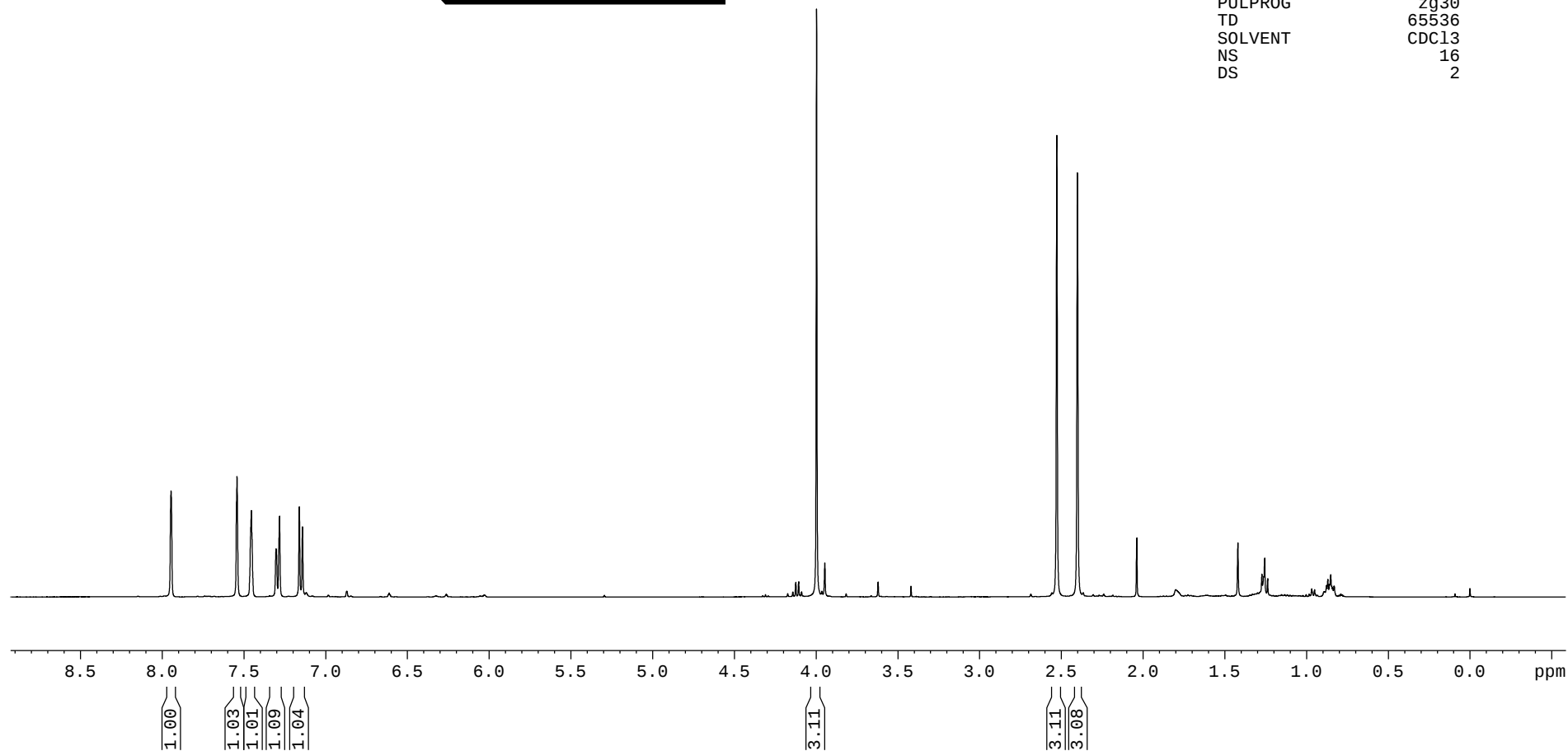
3.9969

2.5273
2.4009



Current Data Parameters
NAME npj-1-98-1-HMBC
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130914
Time 0.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2



S132

171.74
171.38
171.02
170.67

139.29
136.81
134.89
134.45
132.78
129.10
126.67
125.24
122.27
122.23
122.19
122.15
120.69
117.82
114.89
112.02

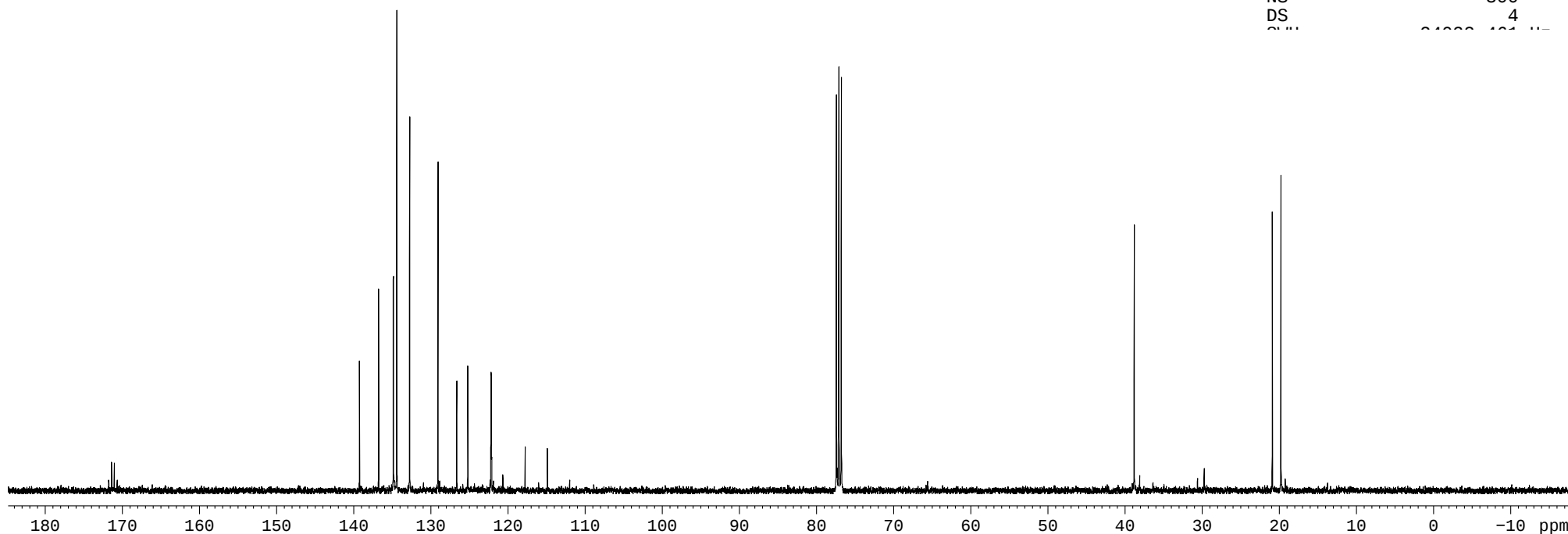
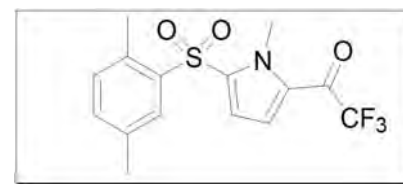
77.44
77.12
76.80

38.82

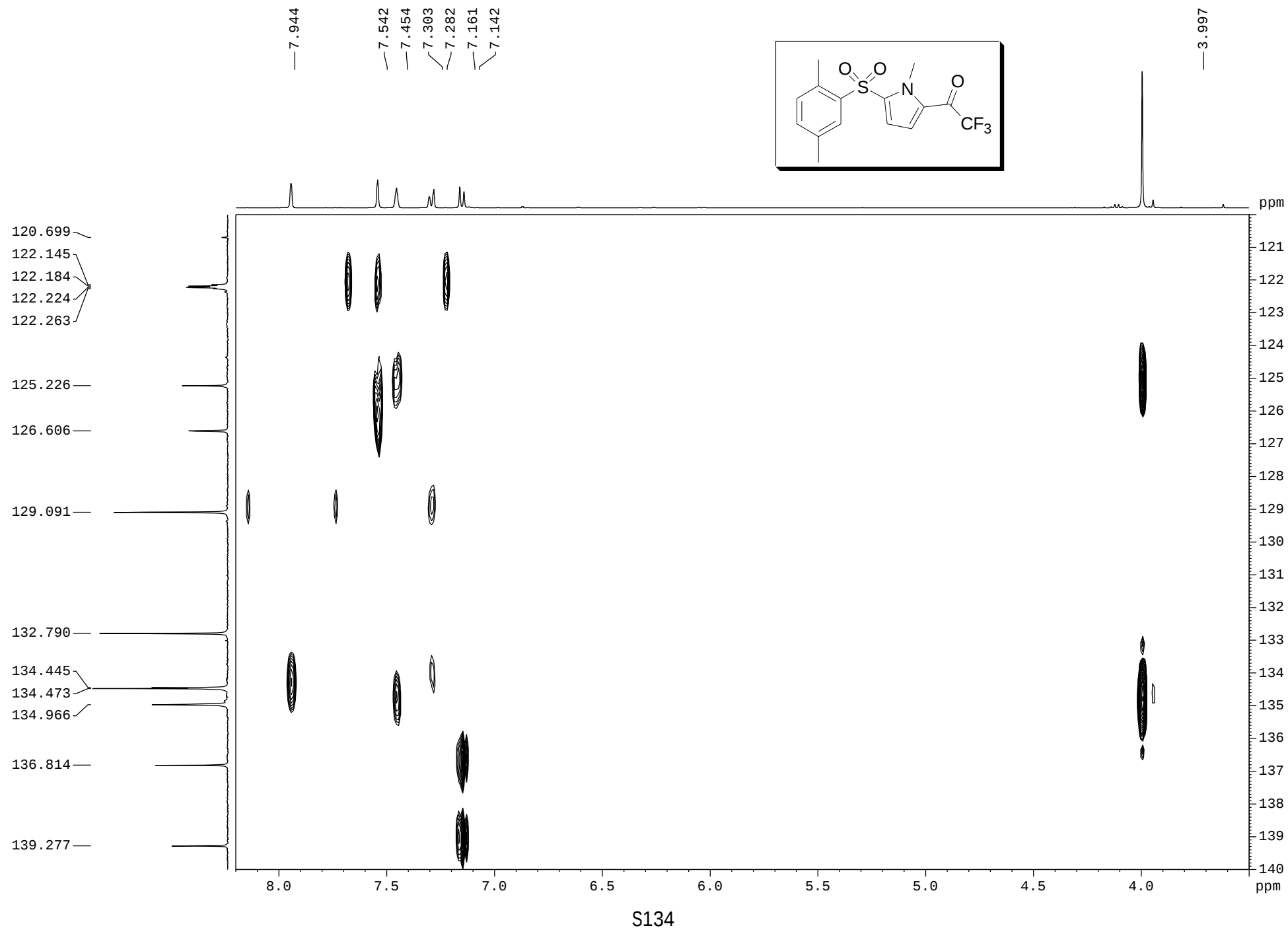
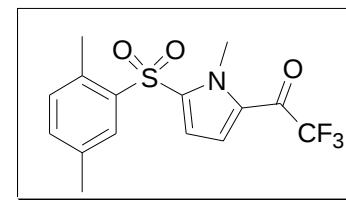
20.92
19.79

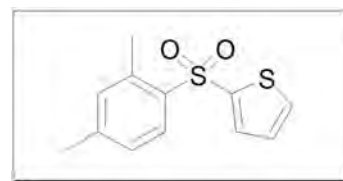
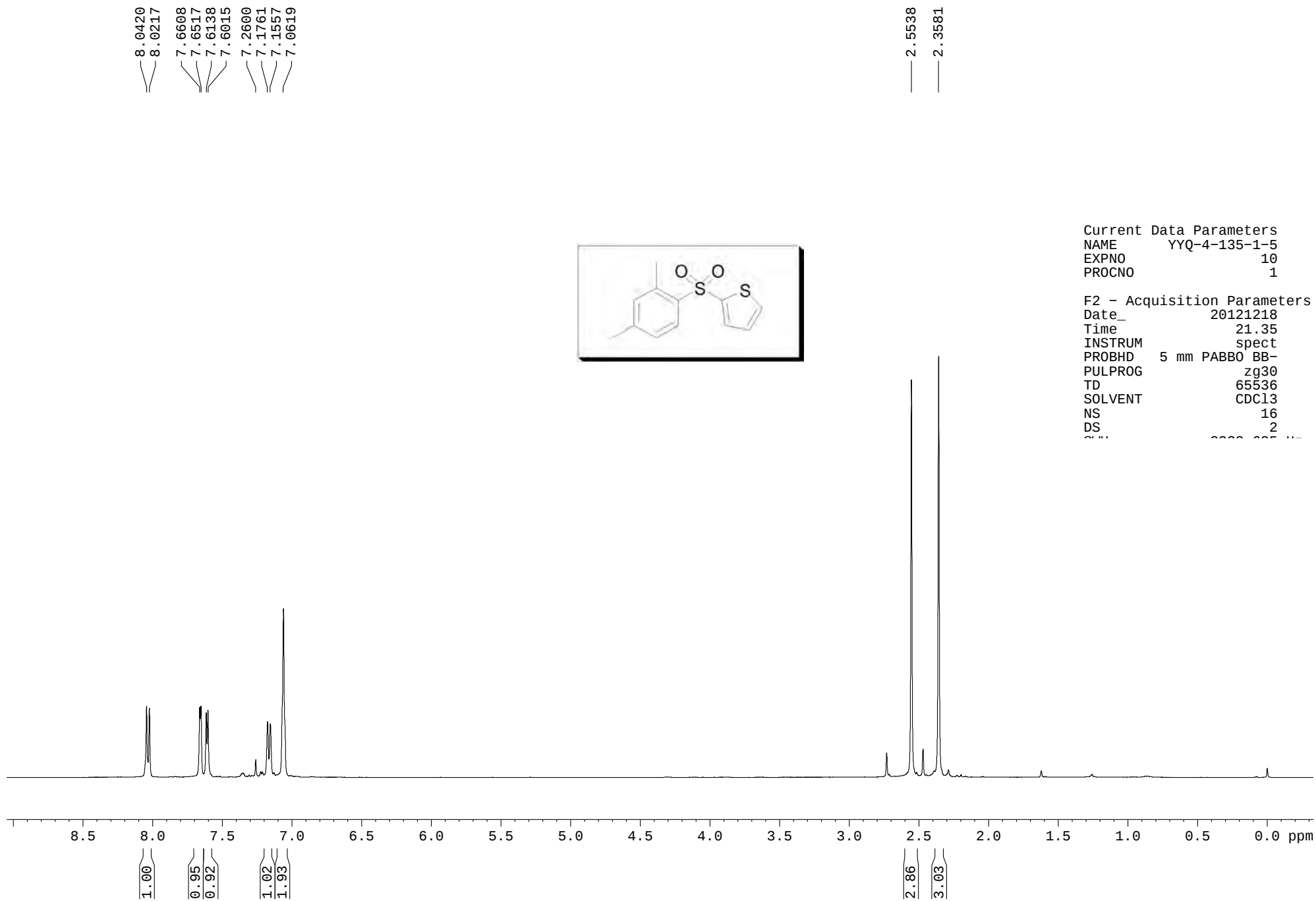
Current Data Parameters
NAME cz-1-50-2-2
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130821
Time 21.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 4



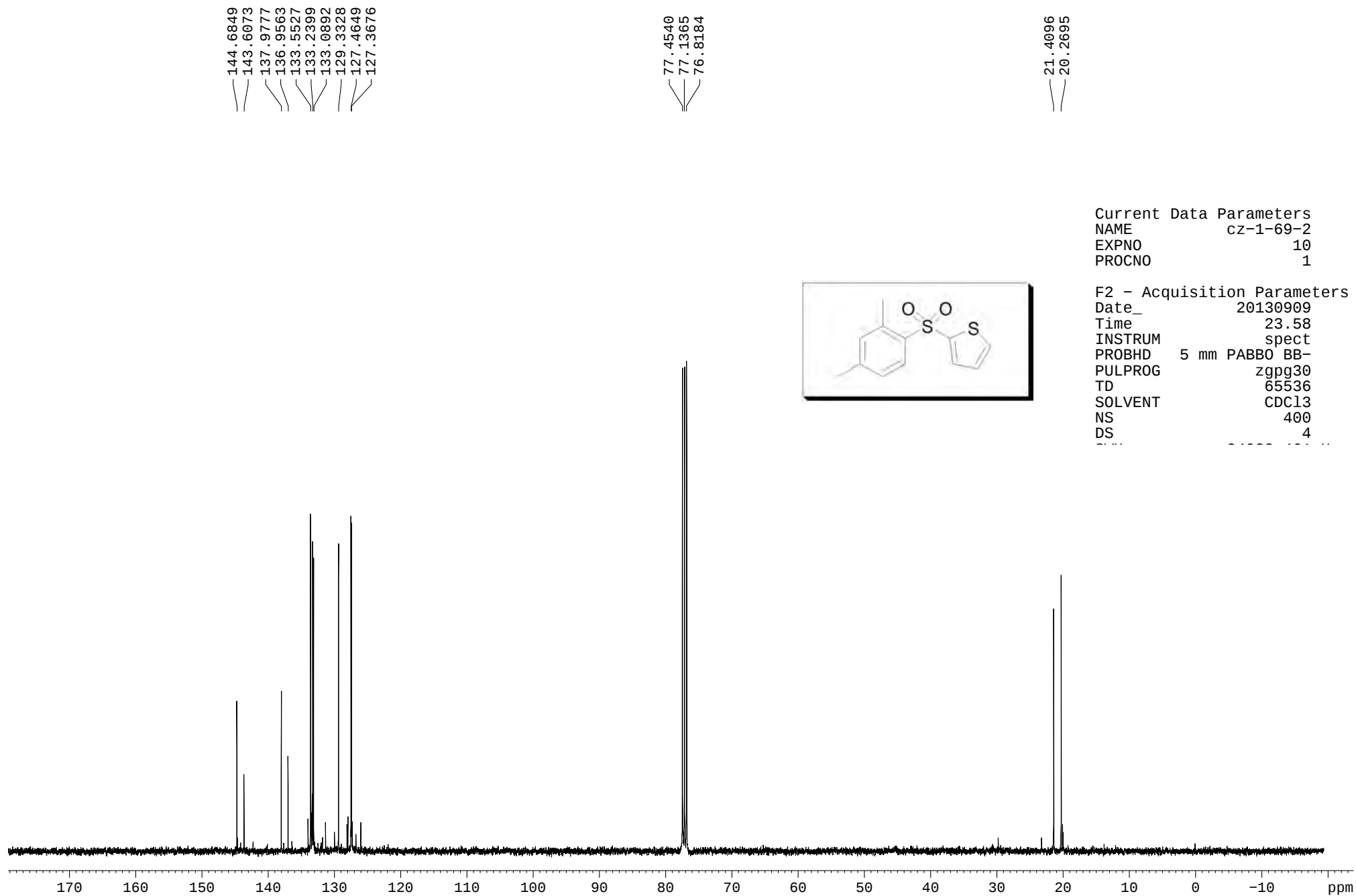
S133





Current Data Parameters
NAME YYQ-4-135-1-5
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121218
Time 21.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
AQ 0.02000000



144.6849
143.6073
137.9777
136.9563
133.5527
133.2399
133.0892
129.3328
127.4649
127.3676

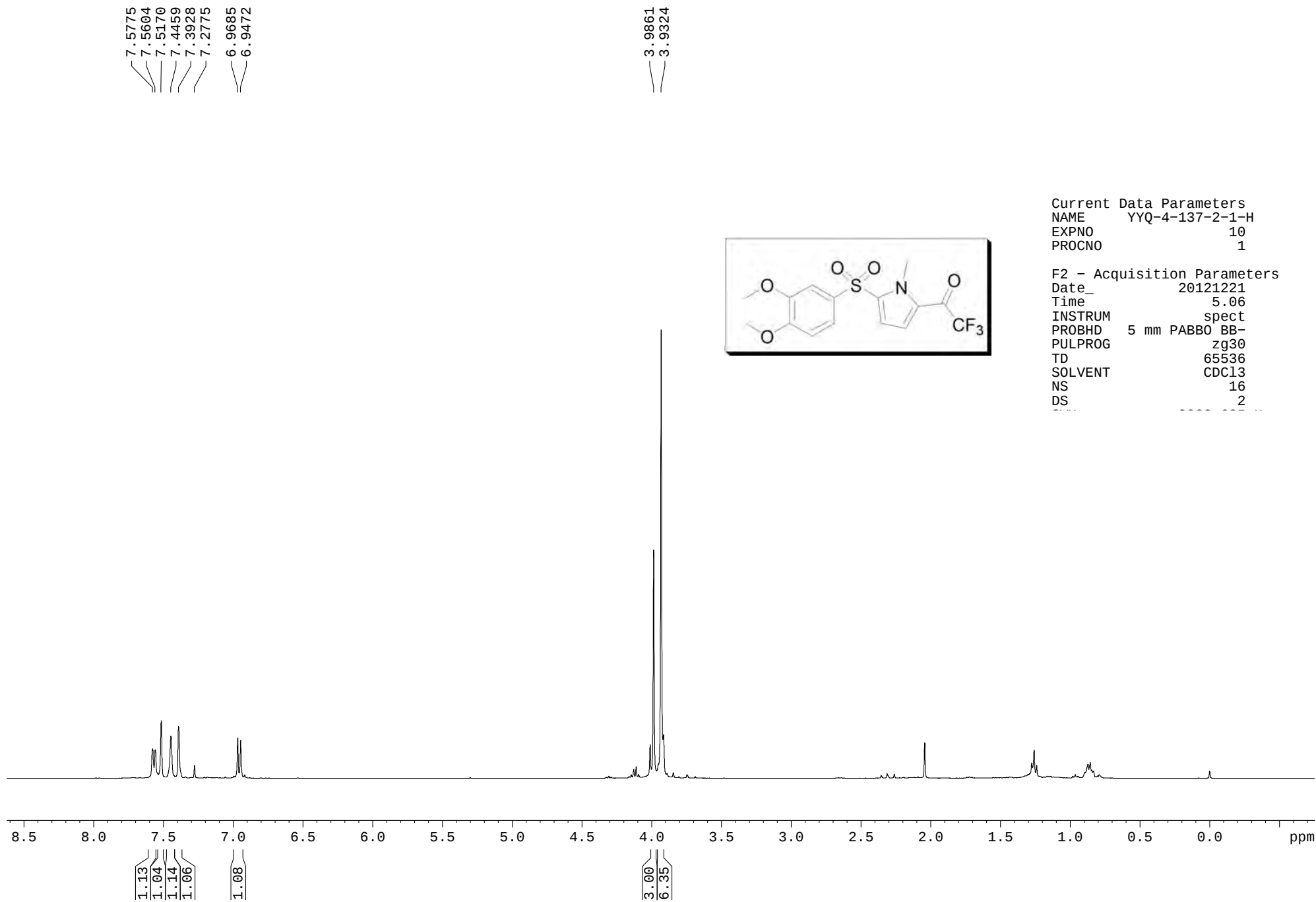
77.4540
77.1365
76.8184

21.4096
20.2695

Current Data Parameters
NAME cz-1-69-2
EXPNO 10
PROCNO 1

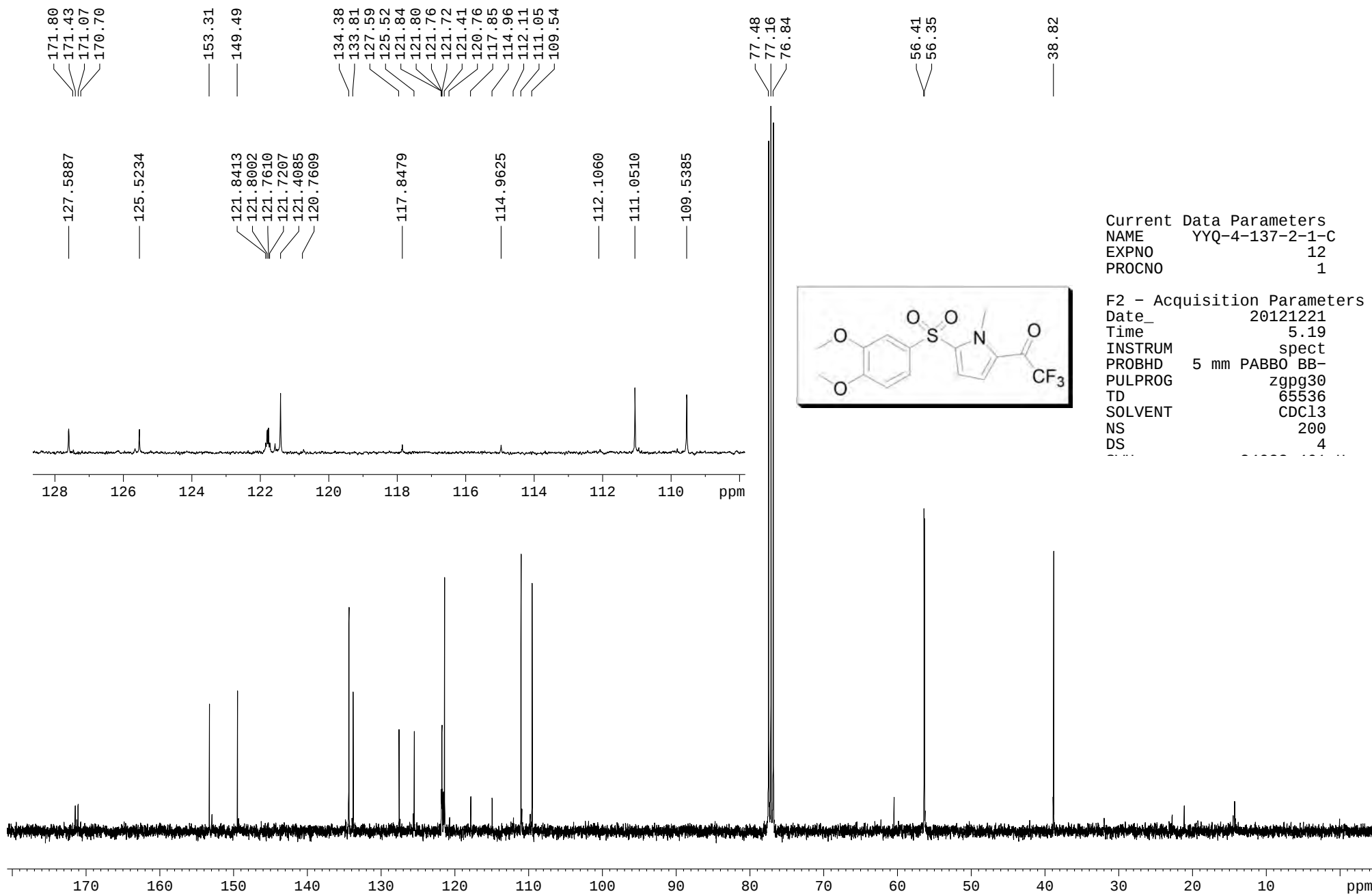
F2 - Acquisition Parameters
Date_ 20130909
Time 23.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4

S136



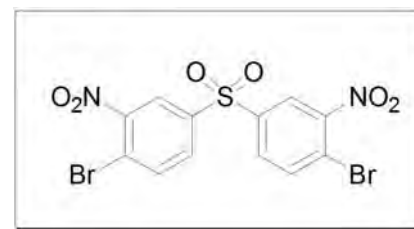
Current Data Parameters
 NAME YYQ-4-137-2-1-H
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20121221
 Time 5.06
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2



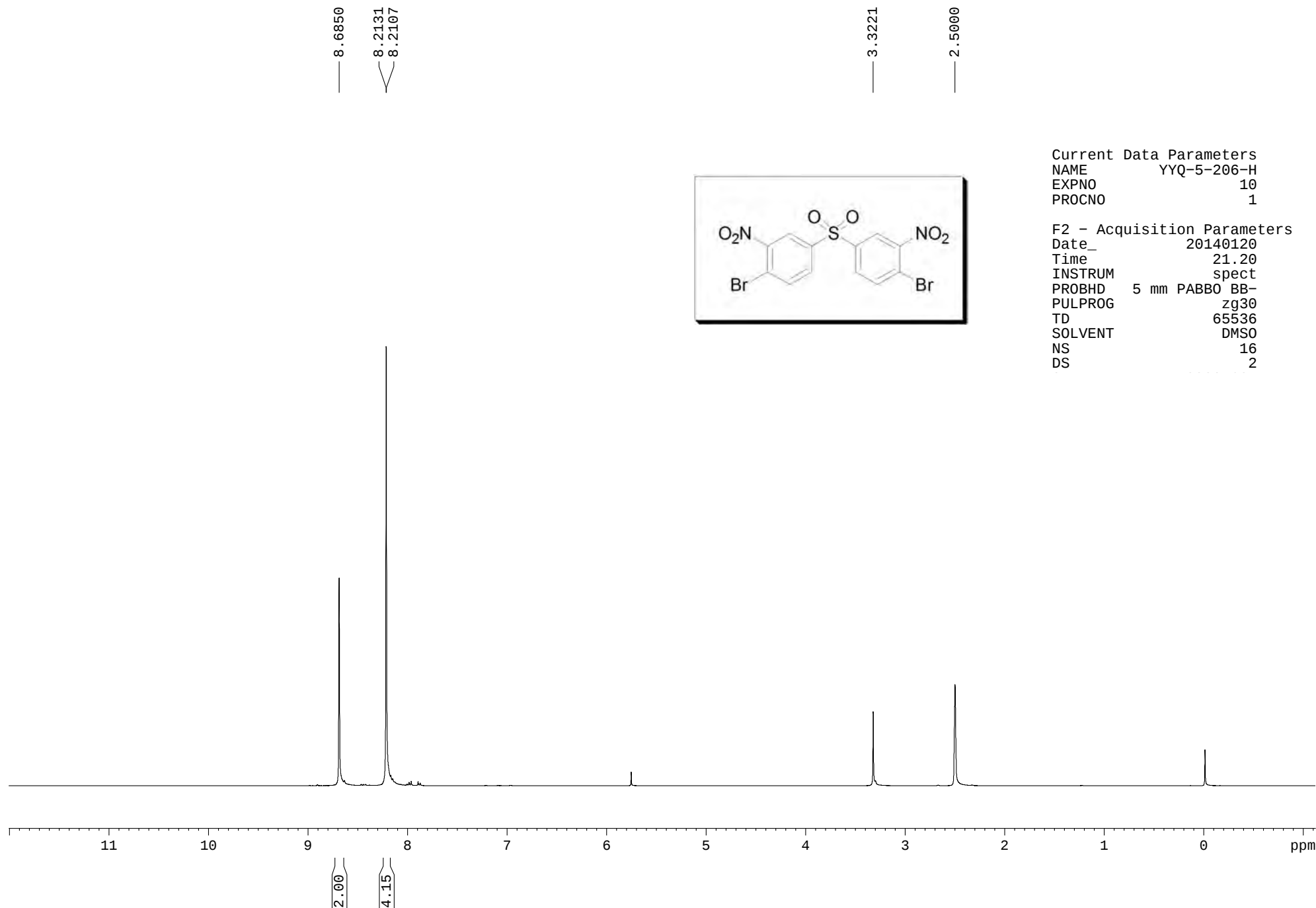
Current Data Parameters
NAME YYQ-4-137-2-1-C
EXPNO 12
PROCNO 1

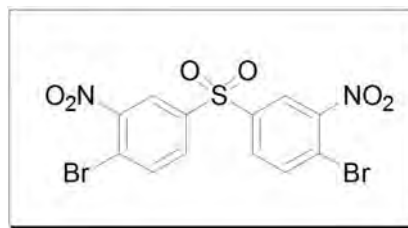
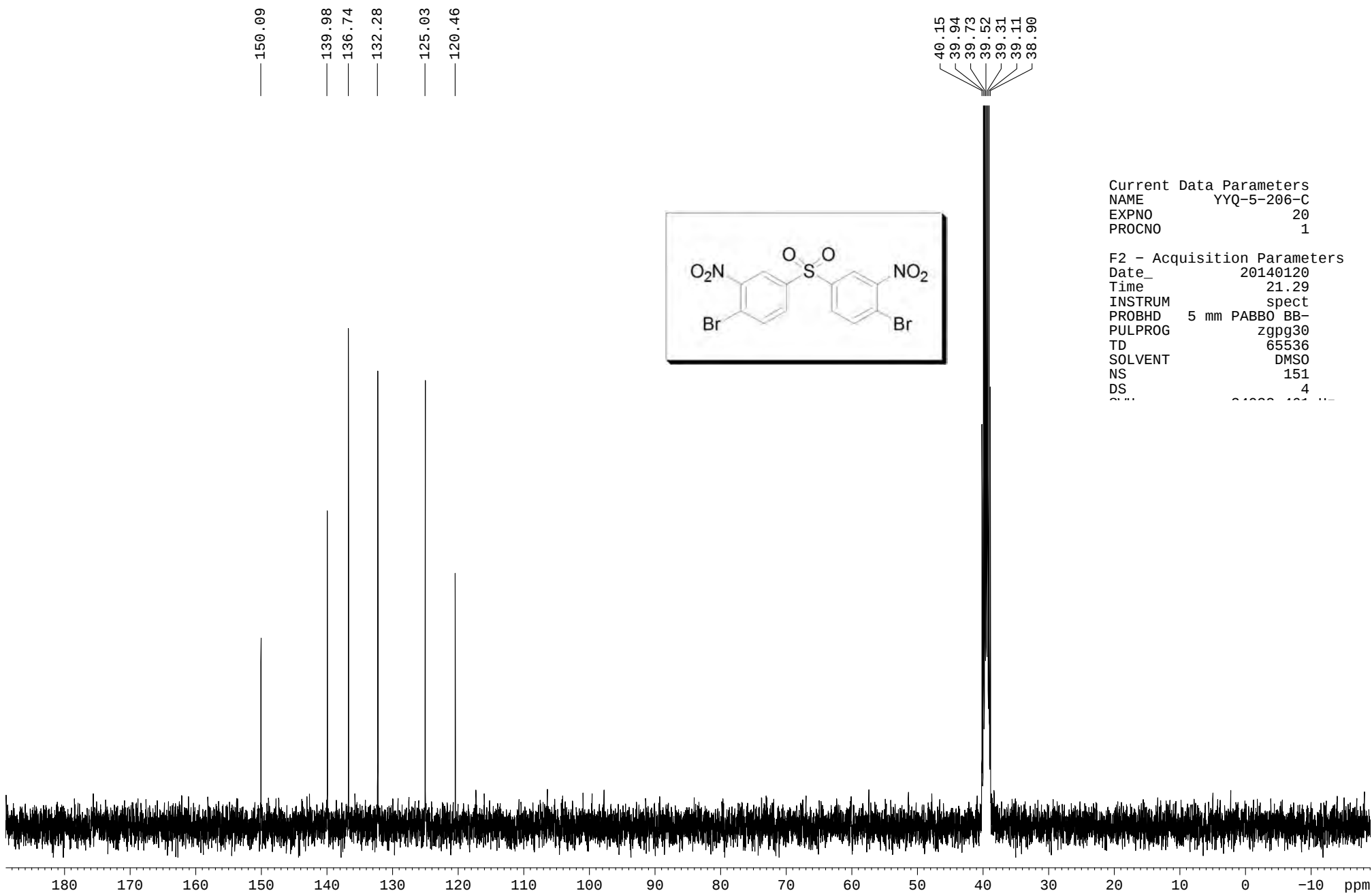
F2 - Acquisition Parameters
Date_ 20121221
Time 5.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4



Current Data Parameters
NAME YYQ-5-206-H
EXPNO 10
PROCNO 1

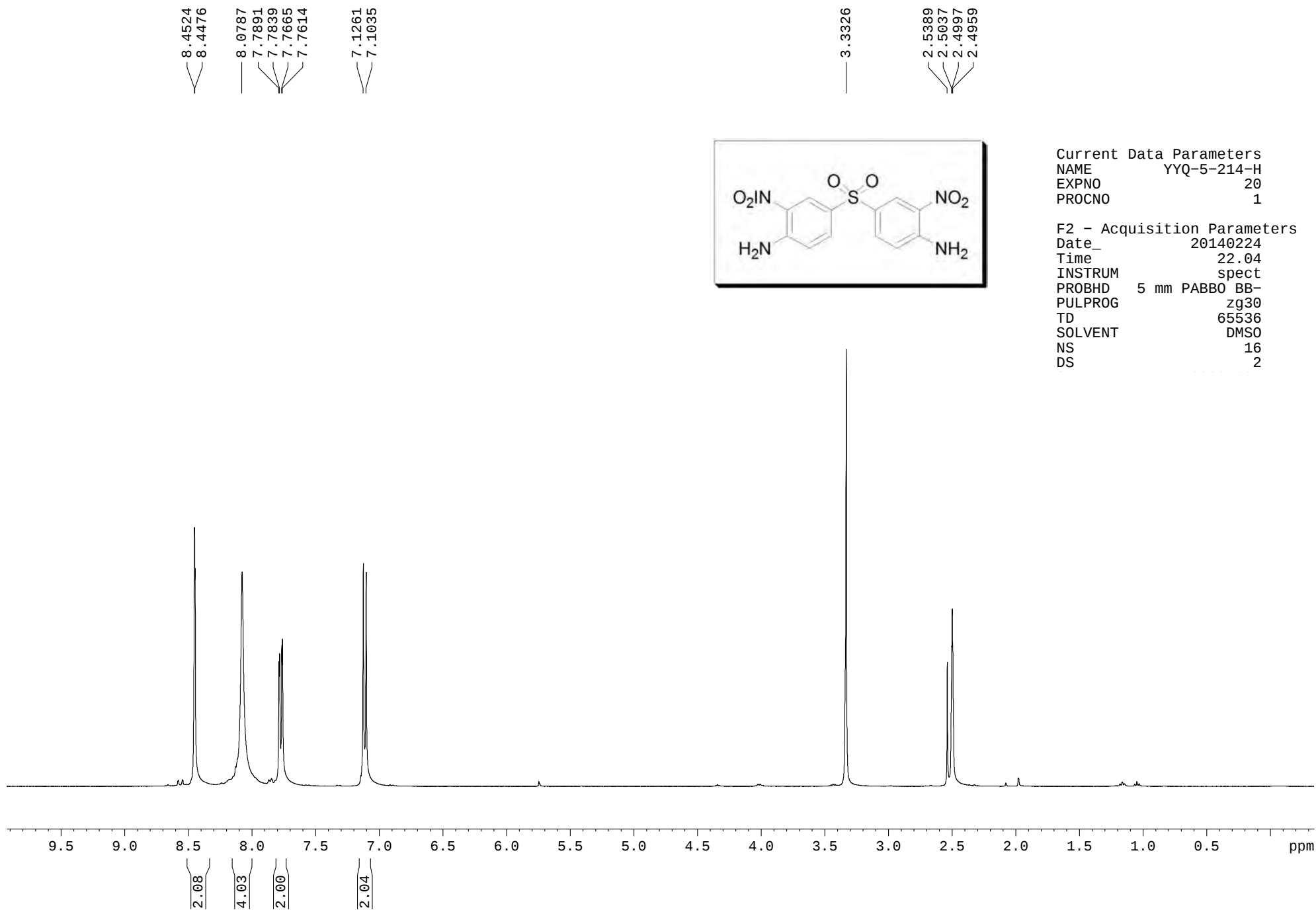
F2 - Acquisition Parameters
Date_ 20140120
Time 21.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2

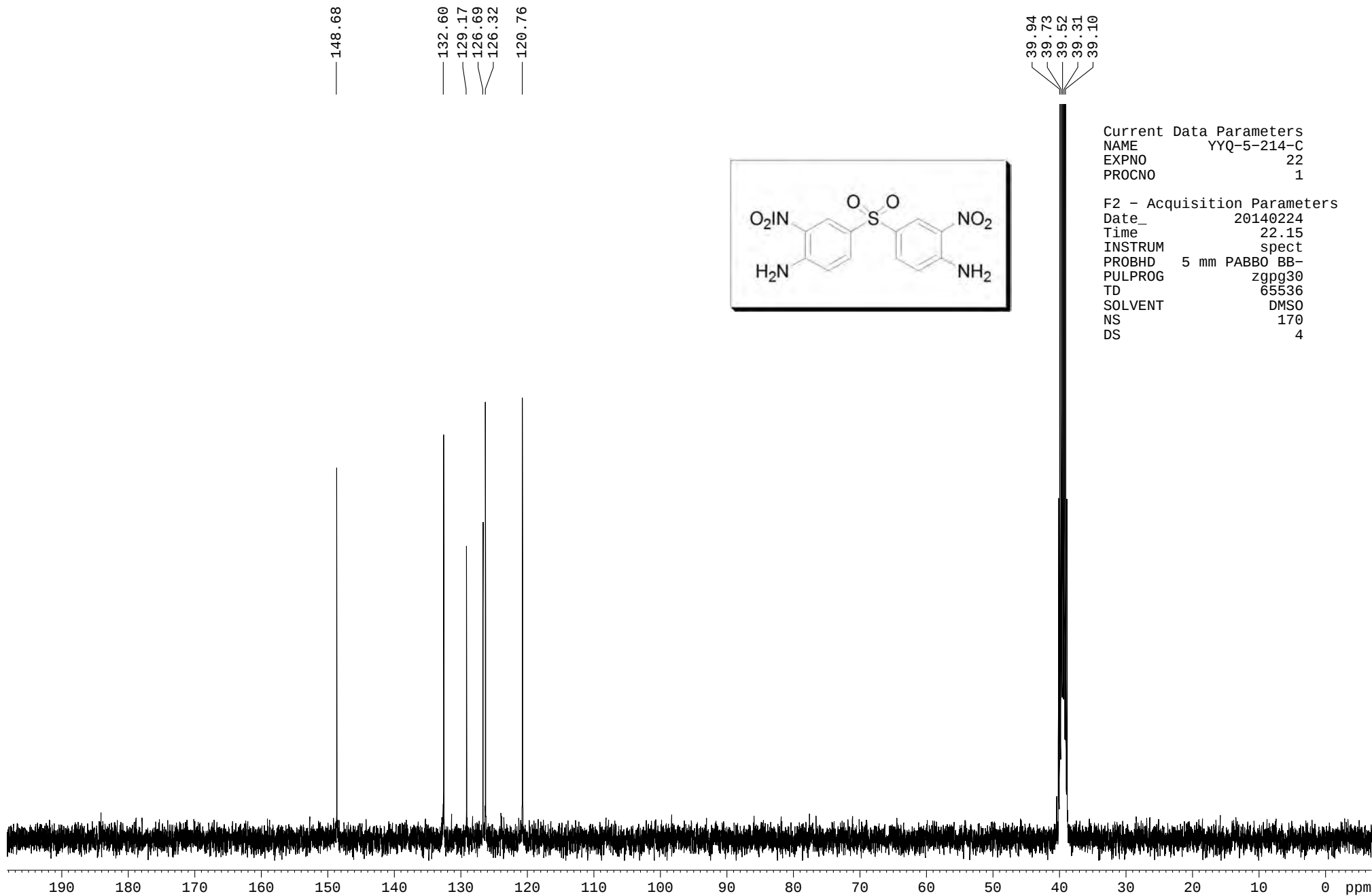




Current Data Parameters
NAME YYQ-5-206-C
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140120
Time 21.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 151
DS 4
AQ 0.13000000

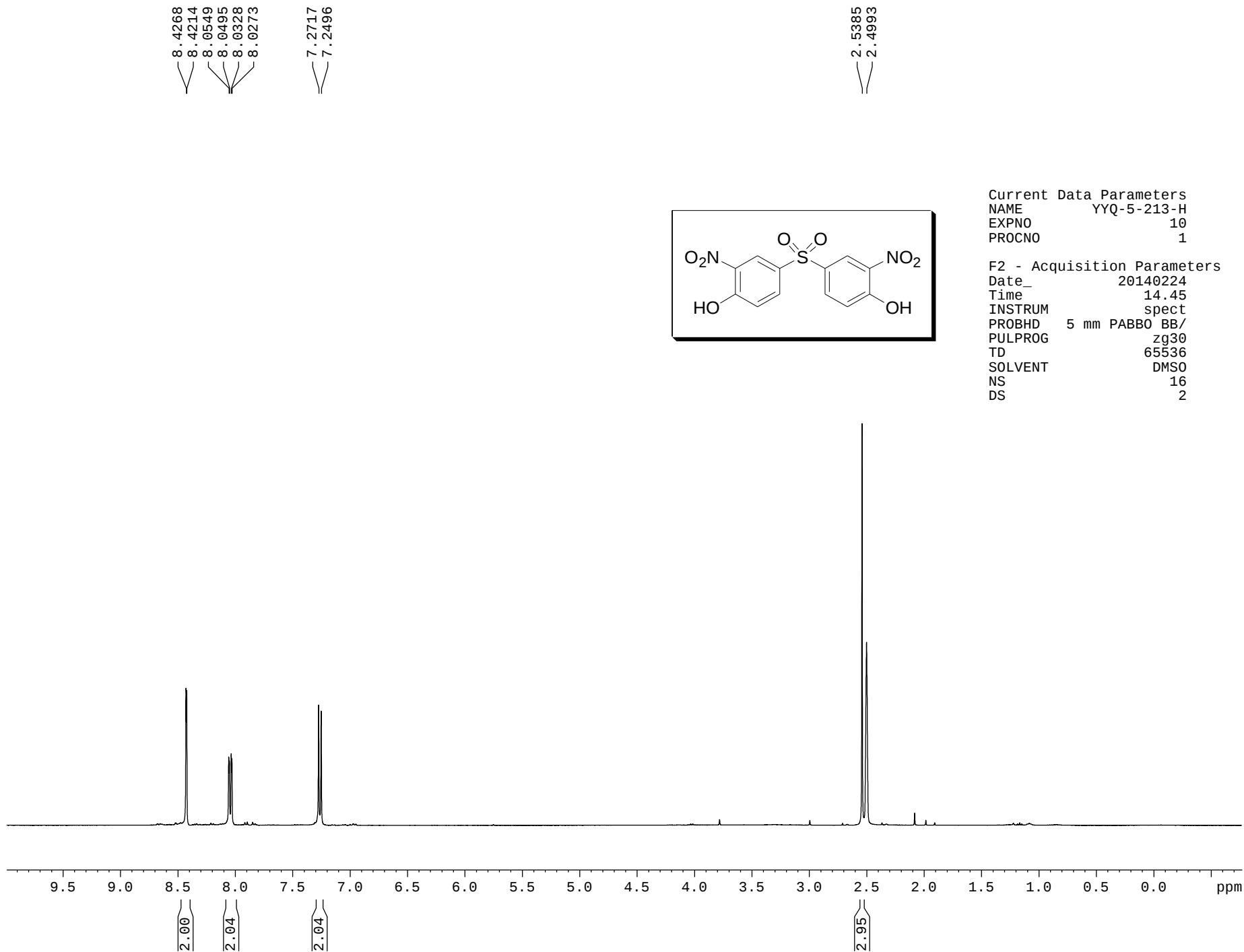


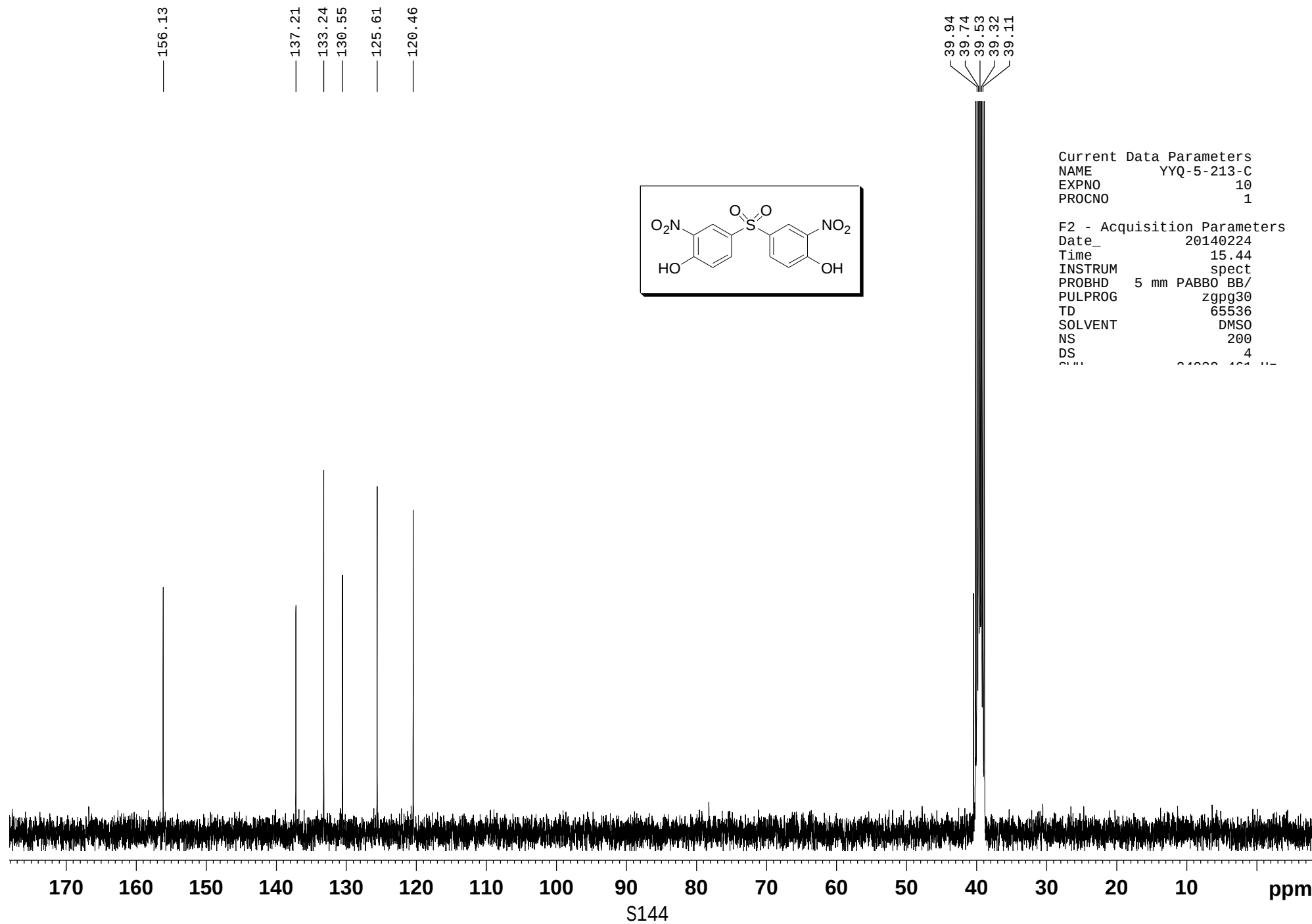


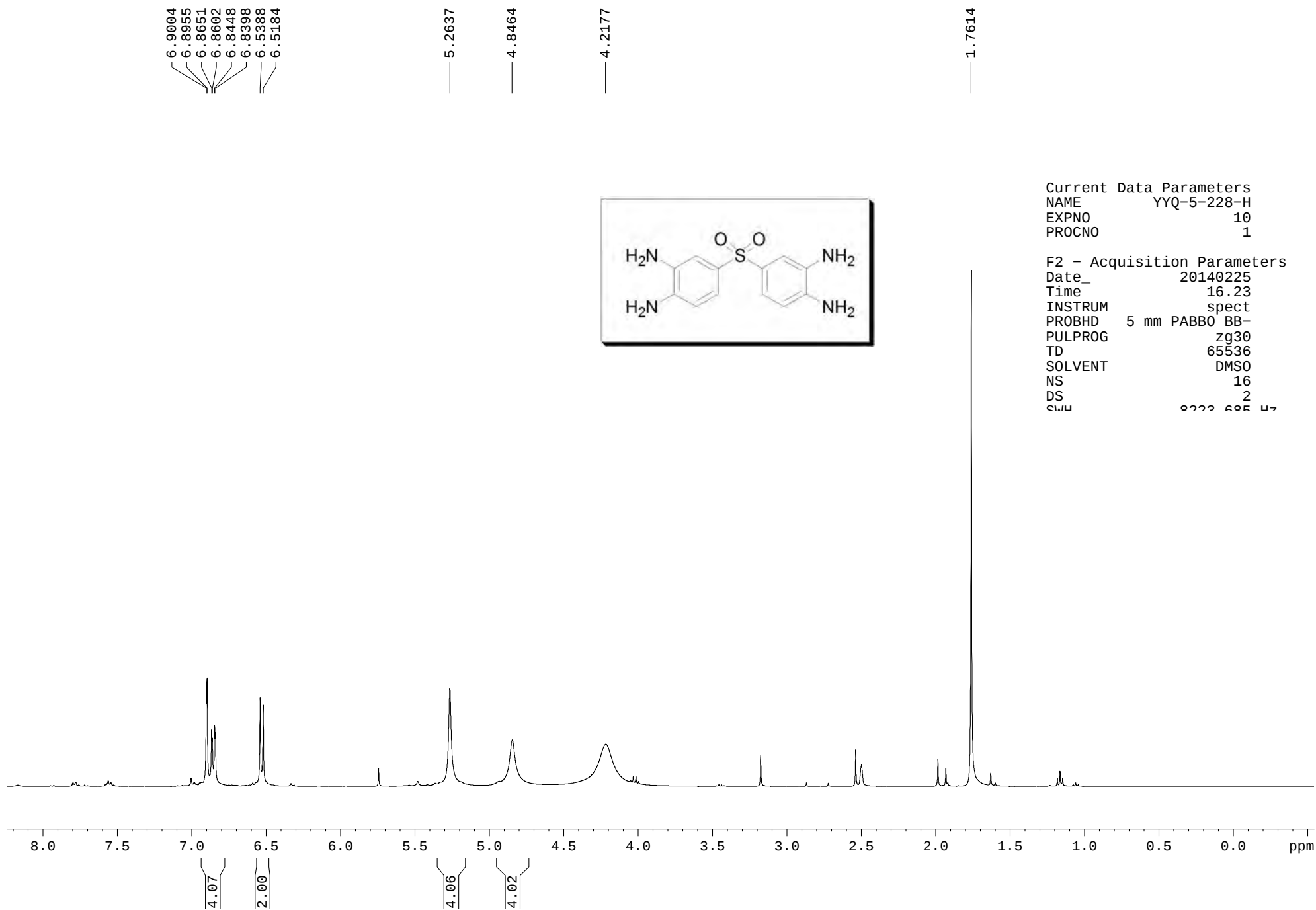
Current Data Parameters
NAME YYQ-5-214-C
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140224
Time 22.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 170
DS 4

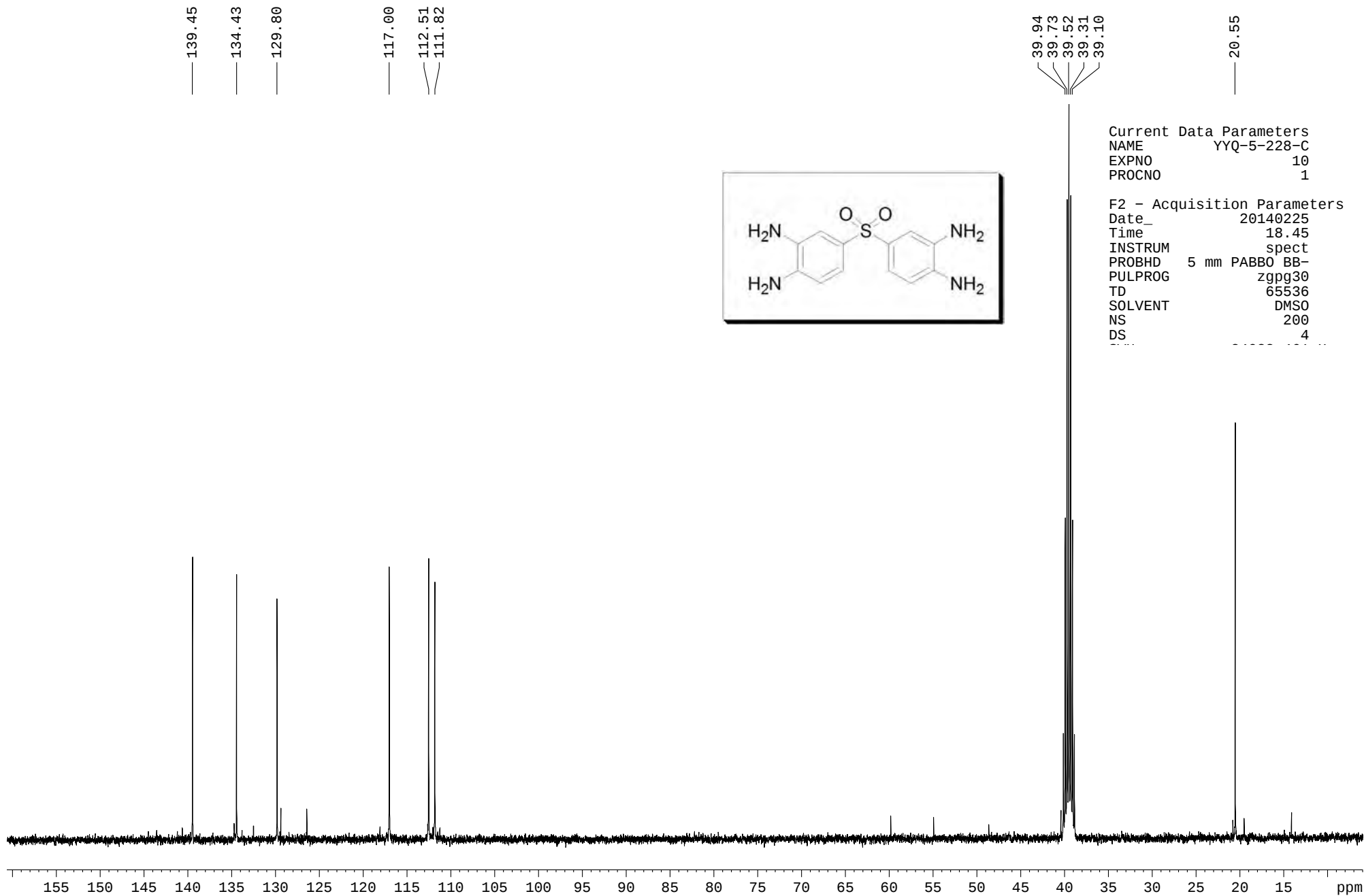
S142





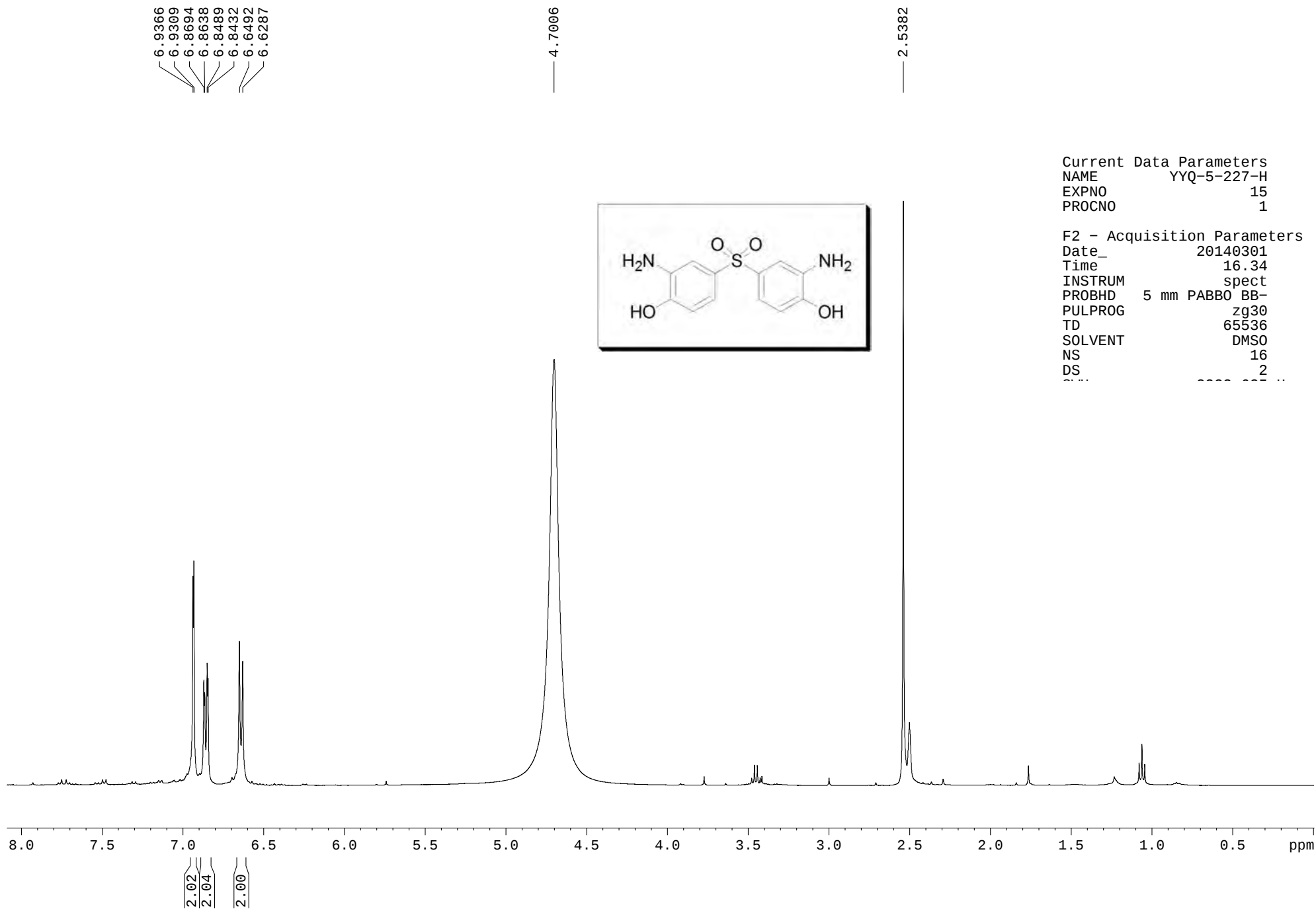


S145



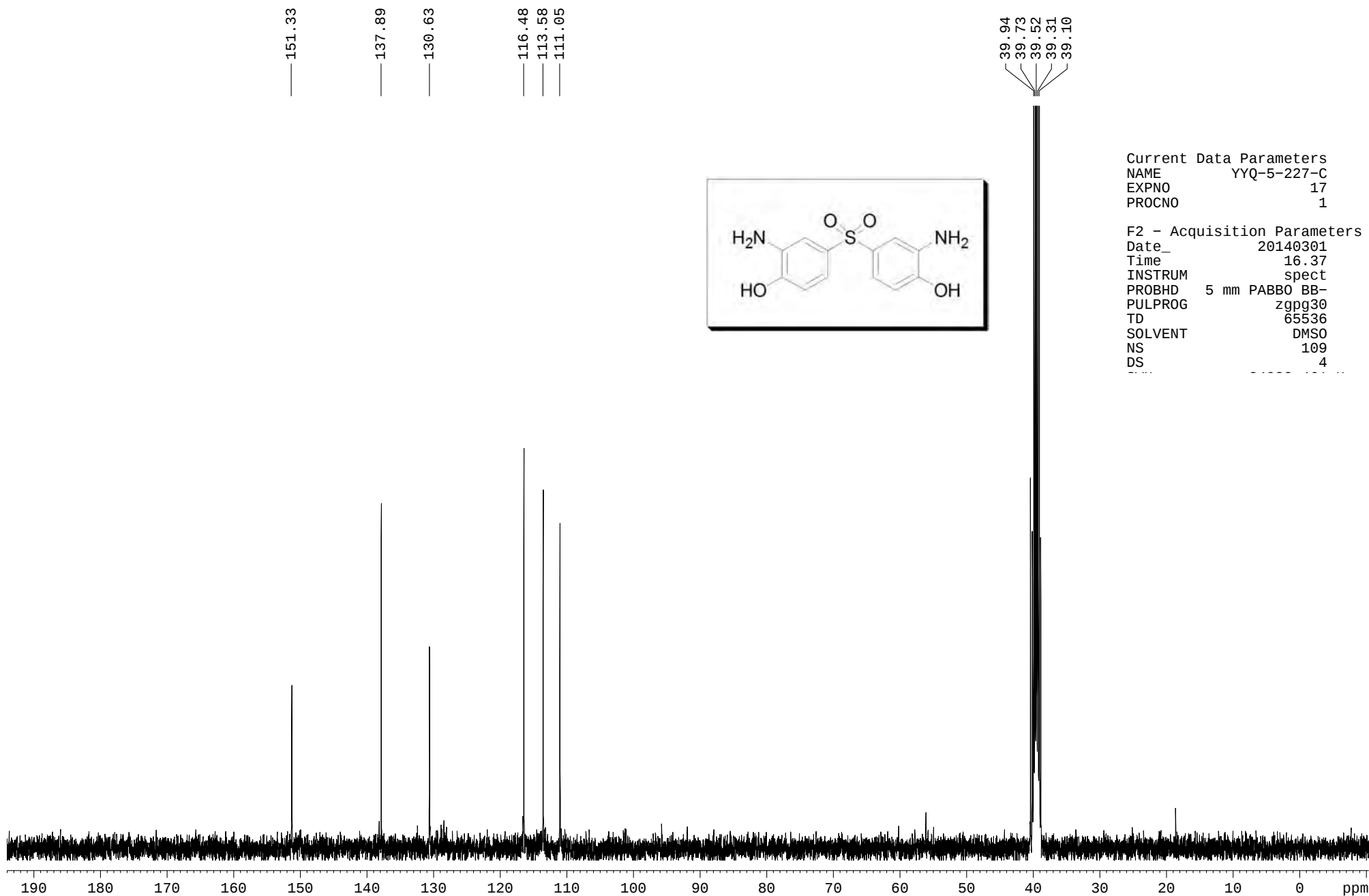
Current Data Parameters
NAME YYQ-5-228-C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140225
Time 18.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 200
DS 4



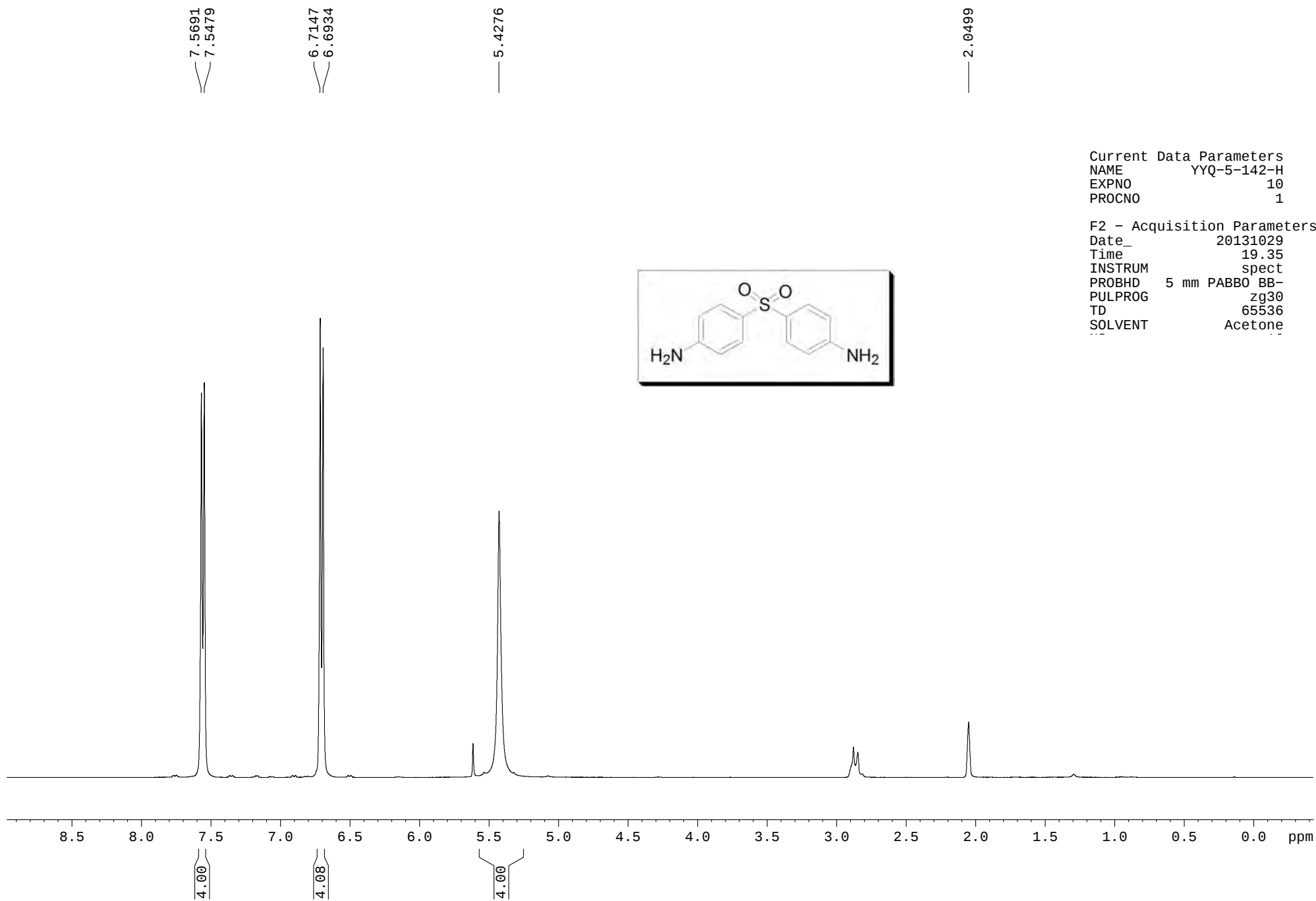
Current Data Parameters
NAME YYQ-5-227-H
EXPNO 15
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140301
Time 16.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2



Current Data Parameters
NAME YYQ-5-227-C
EXPNO 17
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140301
Time 16.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 109
DS 4



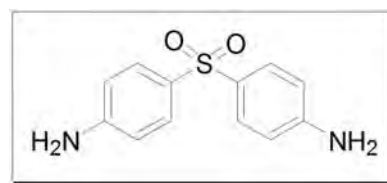
205.3696
205.2819

152.4408

130.1720
128.8543

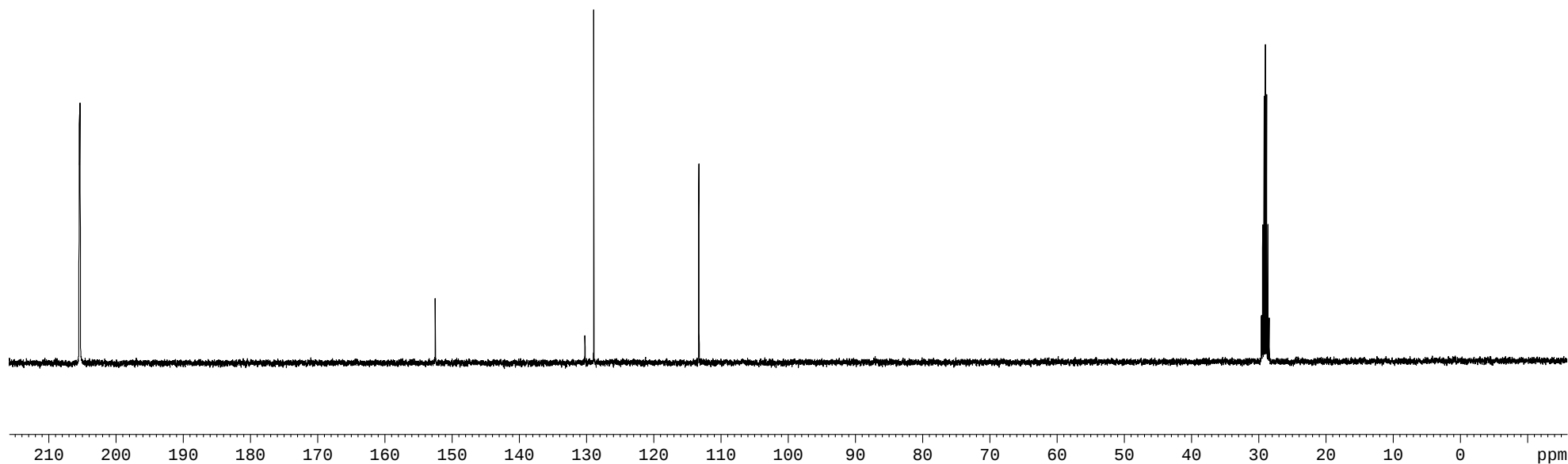
113.2341

29.5099
29.3317
29.1390
29.1247
28.9470
28.7551
28.5619
28.3693



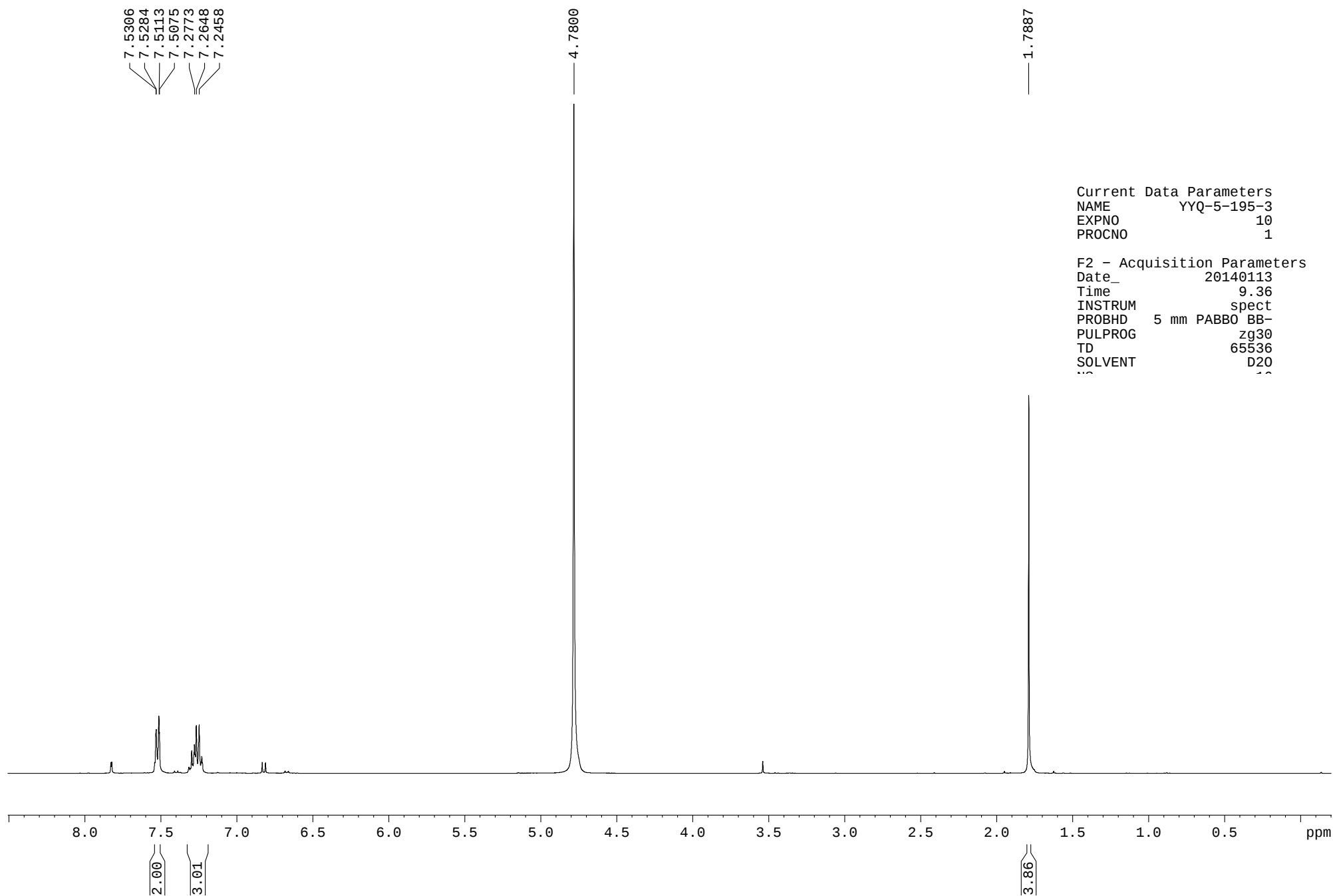
Current Data Parameters
NAME YYQ-5-142-C
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131029
Time 19.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 89
DS 4



S150

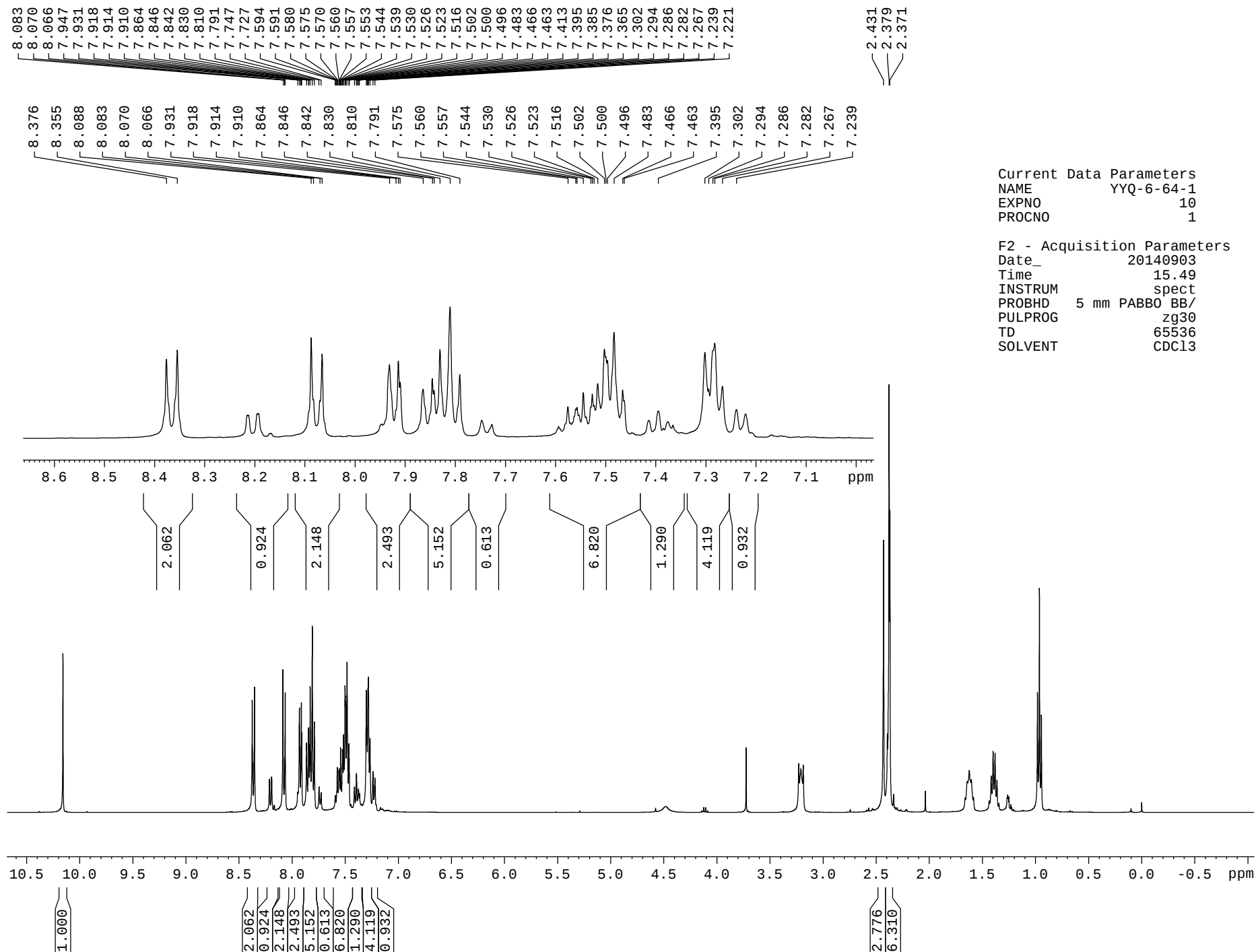
Mechanism study: Equation 1



Current Data Parameters
NAME YYQ-5-195-3
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140113
Time 9.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT D2O

Mechanism study: Equation 2



Mechanism study: Equation 3

