Total Synthesis of Russuphelol: A Case of Mistaken Chirality

M. Quamar Salih and Christopher M. Beaudry*

Department of Chemistry, Oregon State University, Corvallis, OR 97331

christopher.beaudry@oregonstate.edu

Supporting Information

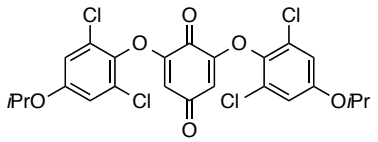
Table of Contents

1. General Experimental Details 2
2. Experimental Procedures 3 - 8
3. Comparison of NMR Data 9
4. ^{1}H and ^{13}C Spectral Data 10 - 31
5. UV/Vis and physical properties of Russuphelol 32
6. Low Temperature NMR Data 33 - 35

Experimental Section

All reactions were carried out under an inert Ar atmosphere in oven-dried glassware. Flash column chromatography (FCC) was carried out with SiliaFlash P60, 60 Å silica gel. Reactions and column chromatography were monitored with EMD silica gel 60 F254 plates and visualized with vanillin stains. Dichloromethane (DCM) and acetonitrile (MeCN) were dried by passage through activated alumina columns. Dioxane was dried with CaH and distilled onto 3 Å molecular sieves. All other reagents and solvents were used without further purification from commercial sources.

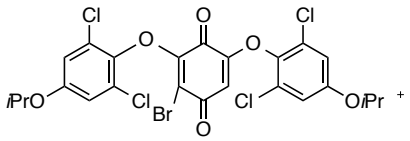
Instrumentation: FT-IR spectra were obtained on NaCl plates with a PerkinElmer Spectrum Vision spectrometer. Proton and carbon NMR spectra (^{1}H NMR and ^{13}C NMR) were recorded in deuterated chloroform ($CDCl_3$) unless otherwise noted on a Bruker 700 MHz Avance III Spectrometer with carbon-optimized cryoprobe and Bruker 400 MHz DPX-400 spectrometer and calibrated to residual solvent peaks (7.29 in ^{1}H and 77.0 ppm ^{13}C). Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, br = broad, m = multiplet. Melting points were determined with a Cole–Parmer instrument and are uncorrected.



7

2,6-Bis(2,6-dichloro-4-isopropoxyphenoxy)cyclohexa-2,5-diene-1,4-dione (7). To a solution of phenol **6** (663 mg, 3.00 mmol) in DMF (12 mL, 0.25 M) was added NaH (132 mg, 3.30 mmol, 60% in mineral oil). The mixture was stirred for 15 min after which dichloroquinone **5** (292 mg, 1.65 mmol) was slowly added. The reaction mixture was stirred for 16 h upon which time TLC indicated consumption of all quinone starting material. The reaction mixture was carefully quenched with 2M HCl solution (2 mL). The mixture was diluted with H_2O and extracted with DCM (30 mL x 3). The organic layers were combined, washed with H_2O, saturated NaCl solution, dried over $MgSO_4$, and concentrated. Purification by FCC (10:1 Hexanes:EtOAc) yielded **7** (644 mg, 1.19 mmol, 72%) as a yellow solid.

Data for **7**: R_f 0.15 (8:1 Hexanes: EtOAc); mp = 183-184 °C; IR (thin film) 3091, 2980, 1701, 1647, 1602; ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.95 (s, 4 H), 5.59 (s, 2 H), 4.53 (sept, *J* = 6.1 Hz, 2 H), 1.38 (d, *J* = 6.1 Hz, 12 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 186.1, 174.2, 156.4, 154.8, 138.0, 128.6, 116.4, 110.7, 71.4, 21.8; HRMS (ESI) calcd for $C_{24}H_{21}O_6Cl$ [M+H]: 545.0100, found 545.0092.

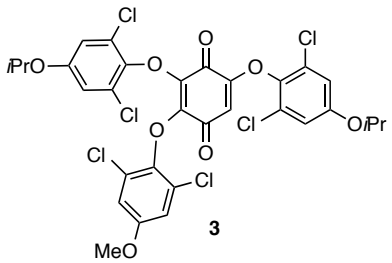


4

2-Bromo-3,5-bis(2,6-dichloro-4-isopropoxyphenoxy)cyclohexa-2,5-diene-1,4-dione (4). To a solution of quinone **7** (335 mg, 0.618 mmol) in (1:1) HOAc/DCM (6.18 mL, 0.10 M) was added $PyrHBr_3$ (198 mg, 0.618 mmol). The reaction mixture was stirred for 1 h upon which time TLC indicated consumption of all quinone starting material. The reaction mixture was quenched with 2M HCl solution (10 mL). The mixture was diluted with H_2O and extracted with DCM (20 mL x 4). The organic layers were combined, washed with 2M HCl solution (2 x 10 mL), H_2O, saturated NaCl solution, dried over $MgSO_4$, and concentrated to yield **4** (378 mg, 0.605 mmol, 98%) as a red solid.

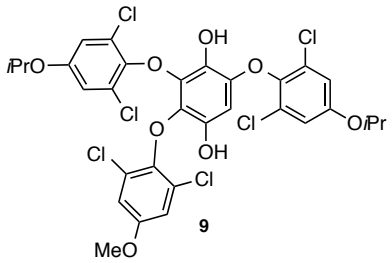
Data for **4**: R_f 0.45 (6:1 Hexanes: EtOAc); mp = 123-134.5 °C; IR (thin film) 3008, 2978, 1691, 1656, 1639, 1596; ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.93 (s, 2 H), 6.90 (s, 2 H), 5.80 (s, 1 H), 4.50 (m, 2 H), 1.38 (d, *J* = 6.1 Hz, 6 H), 1.37 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 179.1, 172.1, 156.5, 155.0, 154.3,

152.8, 141.8, 137.8, 128.4, 126.9, 118.4, 116.4, 116.2, 109.9, 71.5, 71.3, 21.9, 21.8; HRMS (ESI) calcd for $C_{24}H_{20}O_6Cl_4Br$ [M+H]: 622.9197, found 622.9210



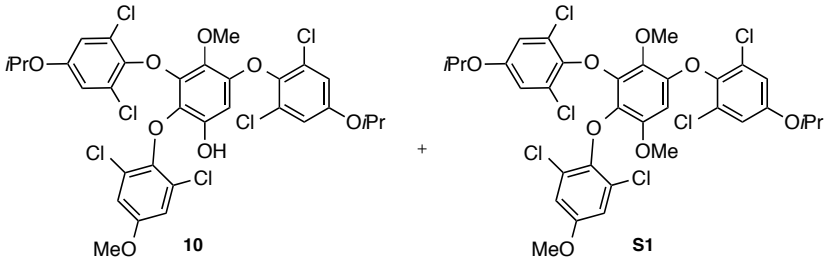
3,5-Bis(2,6-dichloro-4-isopropoxyphenoxy)-2-(2,6-dichloro-4-methoxyphenoxy)cyclohexa-2,5-diene-1,4-dione (3). To a solution of phenol **8** (21 mg, 0.11 mmol) in DMF (2 mL, 0.05 M) was added Cs_2CO_3 (36 mg, 0.11 mmol). The mixture was stirred for 15 min after which bromoquinone **4** (63 mg, 0.10 mmol) was added. The reaction mixture was stirred for 14 h (in the dark) upon which time TLC indicated consumption of all quinone starting material. The reaction mixture was quenched with 2M HCl solution (10 mL). The mixture was diluted with H_2O and extracted with DCM (25 mL x 3). The organic layers were combined, washed with H_2O, saturated NaCl solution, dried over $MgSO_4$, and concentrated. Purification by FCC (10:1 to 7:1 Hexanes:EtOAc) yielded **3** (49 mg, 0.066 mmol, 66.6%) as a red wax. This material was dissolved in $CHCl_3$ (1 ml) and crystalized by vapor diffusion (pentane / $CHCl_3$) solution to obtain a single crystal suitable for diffraction.

Data for **3**: R_f 0.33 (7:1 Hexanes: EtOAc); mp = 128-130 ^oC; IR (thin film) 3007, 2978, 1737, 1685, 1661, 1607; ^1H NMR (700 MHz, $CDCl_3$) δ 6.92 (s, 2 H), 6.805 (s, 2 H), 6.803 (s, 2 H), 5.45 (s, 1 H), 4.51 (sept, *J* = 6.0 Hz, 1 H), 4.45 (sept, *J* = 6.0 Hz, 1 H), 3.77 (s, 3 H), 1.37 (d, *J* = 6.0 Hz, 6 H), 1.32 (d, *J* = 6.0 Hz, 6 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 180.4, 174.8, 156.4, 156.1, 154.6, 154.3, 142.4, 141.9, 139.8, 139.1, 138.0, 128.5, 126.88, 126.85, 116.4, 116.2, 114.2, 107.8, 71.4, 71.3, 55.9, 21.83, 21.79; HRMS (ESI) calcd for $C_{31}H_{25}O_8Cl_6$ [M+H]: 734.9681, found 734.9688.



3,5-Bis(2,6-dichloro-4-isopropoxyphenoxy)-2-(2,6-dichloro-4-methoxyphenoxy)benzene-1,4-diol (9). To a solution of quinone **3** (61 mg, 0.083 mmol) in THF (0.8 mL, 0.1 M) was added saturated $Na_2S_2O_4$ solution drop wise (0.08 mL). The mixture changes color from orange to clear in 15 min. Upon which time TLC indicated consumption of all quinone starting material. The reaction mixture was quenched with 2M HCl solution (1 mL). The mixture was diluted with H_2O and extracted with DCM (10 mL x 3). The organic layers were combined, dried over $MgSO_4$, and concentrated to yield **9** (61 mg, 0.083 mmol, 99%) as a white solid.

Data for **9**: R_f 0.30 (7:1 Hexanes: EtOAc); mp = 163-165 ^oC; IR (thin film) 3128 (br), 2976, 1684, 1660, 1605; ^1H NMR (700 MHz, $CDCl_3$) δ 6.91 (s, 2 H), 6.83 (s, 2 H), 6.76 (s, 2 H), 6.01 (s, 1 H), 5.46 (br s, 1 H), 4.96 (br s, 1 H), 4.51 (sept, *J* = 6.2 Hz, 1 H), 4.44 (sept, *J* = 6.2 Hz, 1 H), 3.77 (s, 3 H), 1.38 (d, *J* = 6.0 Hz, 6 H), 1.33 (d, *J* = 6.2 Hz, 6 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.8, 155.5, 153.7, 143.6, 142.6, 141.2, 140.7, 140.6, 135.7, 130.7, 130.1, 129.8, 128.3, 127.0, 116.4, 115.8, 114.5, 96.0, 71.3, 71.0, 56.0, 21.95, 21.86; HRMS (ESI) calcd for $C_{31}H_{27}O_8Cl_6$ [M+H]: 736.9837, found 736.9872.

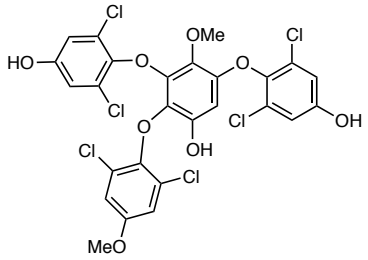


3,5-Bis(2,6-dichloro-4-isopropoxyphenoxy)-2-(2,6-dichloro-4-methoxyphenoxy)-4-methoxyphenol (10). To a solution of hydroquinone **9** (42 mg, 0.057 mmol) in (3:1) DCM/MeOH (0.57 mL, 0.01 M) was added $TMSCHN_2$ (57 μL, 0.114 mmol, 2M solution in hexane). The reaction mixture was stirred at rt for 2 h upon which time TLC indicated four spots. The reaction mixture was quenched with saturated $Na_2S_2O_4$ solution (1 mL). The mixture was diluted with H_2O and extracted with DCM (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. Purification by FCC (10:1

Hexanes: EtOAc) yielded dimethyl **S1** (1 mg, 0.0013 mmol, 3%), monomethyl **10** (13mg, 0.0173 mmol, 31%) and recovered hydroquinone **9** (23mg, 0.0312 mmol, 55%)

Data for **10**: R_f 0.30 (10:1 Hexanes: EtOAc); IR (thin film) 3087, 2976, 1684, 1660, 1605; ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.93 (s, 2 H), 6.83 (s, 2 H), 6.78 (s, 2 H), 5.87 (s, 1 H), 5.71 (br s, 1 H), 4.51 (sept, *J* = 6.1 Hz, 1 H), 4.43 (sept, *J* = 6.0 Hz, 1 H), 3.77 (s, 3 H), 3.53 (s, 3 H), 1.38 (d, *J* = 6.2 Hz, 6 H), 1.33 (d, *J* = 6.2 Hz, 6 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.8, 155.3, 153.6, 147.3, 143.9, 143.6, 142.8, 141.1, 139.9, 132.3, 129.9, 129.8, 129.4, 128.4, 126.6, 116.6, 116.5, 116.4, 116.2, 116.0, 114.4, 95.1, 71.3, 71.2, 71.1, 61.5, 56.0, 21.91, 21.88, 21.84, 21.76; HRMS (ESI) calcd for $C_{32}H_{29}O_8$ Cl_6 [M+H]: 750.9994, found 751.0024

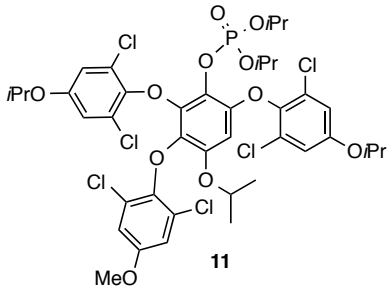
Data for **S1**: R_f 0.33 (10:1 Hexanes: EtOAc); IR (thin film) 2976, 1597, 1562, 1498; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 2 H), 6.81 (s, 2 H), 6.79 (s, 2 H), 5.78 (s, 1 H), 4.52 (sept, *J* = 6.1 Hz, 1 H), 4.44 (sept, *J* = 6.1 Hz, 1 H), 3.76 (s, 3 H), 3.68 (s, 3 H), 3.56 (s, 3 H), 1.38 (d, *J* = 6.0 Hz, 6 H), 1.33 (d, *J* = 6.0 Hz, 6 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.2, 154.9, 153.6, 146.9, 146.4, 144.3, 143.6, 142.0, 140.2, 133.6, 132.2, 129.9, 127.4, 127.0, 116.6, 116.5, 116.2, 114.3, 114.2, 93.7, 71.3, 71.2, 61.5, 57.0, 55.9, 21.9, 21.8; HRMS (ESI) calcd for $C_{33}H_{31}O_8Cl_6$ [M+H]: 765.0150, found 765.0114.



Russuphelol (1). To a solution of **10** (12 mg, 0.016 mmol) in DCM (0. 16 mL, 0.1 M) was added BCl_3 (0.1 ml, 0.10 mmol, 1 M in DCM solution). The reaction mixture was stirred for 4 h at rt upon which time TLC indicated consumption of all starting material. The reaction mixture was slowly quenched with MeOH (2 mL), stirred for 30 min and concentrated. Purification by FCC (2:1 to 1:1 Hexanes: EtOAc) yielded russuphelol (**1**) (6.9 mg, 0.0103 mmol, 64 %) as a white solid, which matched reported data (See table below). This material was dissolved in (1:1) $CHCl_3$/MeOH and crystalized by vapor diffusion (pentane / MeOH,$CHCl_3$) to obtain a single crystal suitable for diffraction.s

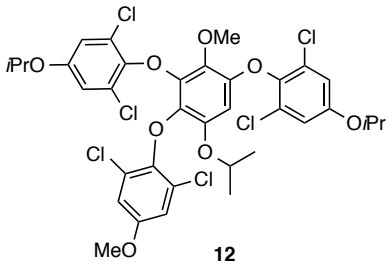
Data for **1**: R_f 0.1 (2:1 Hexanes: EtOAc); mp = 210 ^{o}C; IR (thin film) 3365 (br), 2925, 2853, 1604, 1469, 1435, 1212; ^{1}H NMR (700 MHz, *d*-MeOD) δ 6.80 (s, 2 H), 6.76 (s, 2 H), 6.61 (s, 2 H), 5.50 (s, 1 H), 3.64 (s,

3 H), 3.40 (s, 3 H); ^{13}C NMR (176 MHz, *d*-MeOD) δ 157.8, 157.70, 155.8, 149.0, 146.9, 146.4, 144.4, 143.9, 141.0, 133.8, 132.4, 131.6, 129.8, 128.7, 117.9, 117.2, 116.2, 97.4, 62.6, 57.3; HRMS (ESI) calcd for $C_{26}H_{17}O_8Cl_6$ [M+H]: 666.9055, found 666.9065



2,6-Bis(2,6-dichloro-4-isopropoxyphenoxy)-3-(2,6-dichloro-4-methoxyphenoxy)-4-isopropoxyphenyl diisopropyl phosphate (11). To a solution of quinone **3** (55 mg, 0.075 mmol) in benzene (0.75 mL, 0.1 M) was added triisopropylphosphite (47 mg, 0.225 mmol). The mixture was stirred vigorously for 48 h after which time TLC indicated consumption of all quinone starting material. The reaction mixture was directly loaded on to a column and purified (4:1 Hexanes:EtOAc) to yield **11** (44 mg, 0.0466 mmol , 62%) as an yellow oil.

Data for **11**: R_f 0.15 (8:1 Hexanes: EtOAc); IR (thin film) 2977, 2932, 1595, 1459; ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.92 (s, 2 H), 6.79 (s, 2 H), 6.71 (s, 2 H), 5.00 (m, 2 H), 4.51 (sept, *J* = 6.0 Hz, 1 H), 4.42 (sept, *J* = 6.0 Hz, 1 H), 3.99 (sept, *J* = 6.2 Hz, 1 H), 1.37 (m, 12 H), 1.32 (d, *J* = 6.1 Hz, 6 H), 1.29 (d, *J* = 6.1 Hz, 6 H), 0.80 (d, *J* = 5.8 Hz, 6 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.3, 155.1, 154.7, 153.6, 144.6, 144.0, 143.9, 143.7, 141.31, 141.29, 140.6, 133.3, 130.0, 127.6, 126.6, 116.6, 116.4, 113.9, 96.2, 73.3 (d, *j* = 7.1 Hz), 71.25, 71.24, 70.6, 55.9, 23.8 (d, *j* = 2.1 Hz), 21.9, 21.8, 20.9; HRMS (ESI) calcd for $C_{40}H_{46}O_{11}PCl_6$ [M+H]: 943.0863, found 943.0909.



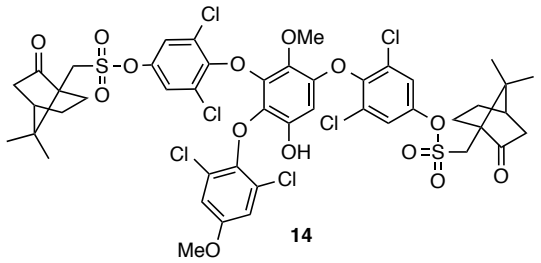
2,2'-((4-(2,6-dichloro-4-methoxyphenoxy)-5-isopropoxy-2-methoxy-1,3-phenylene)bis(oxy))bis(1,3-dichloro-5-isopropoxybenzene) (12). (i) To a solution of **11** (38 mg, 0.040 mmol) in isopropanol (0.4 mL, 0.1 M) was added KOH (22 mg, 0.40 mmol). The reaction mixture was stirred vigorously for 16 h upon which time TLC indicated consumption of all starting material. The reaction mixture was quenched with 2M HCl solution (2 mL). The mixture was diluted with H_2O and extracted with DCM (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The crude material was carried over to the next reaction.

(ii) To a solution of crude phenol (~0.040 mmol) in acetone (0.4 mL, 0.1 M) were added K_2CO_3 (22 mg, 0.16 mmol) and MeI (23 mg, 0.16 mmol). The reaction mixture was stirred for 18 h upon which time TLC indicated consumption of all starting material. The reaction mixture was quenched with 2M HCl solution (0.5 mL). The mixture was diluted with H_2O and extracted with DCM (10 mL x 3). The organic layers were combined, dried over $MgSO_4$, and concentrated. Purification by FCC (10:1 Hexanes: EtOAc) yielded triisopropyl russuphelol **12** (22 mg, 0.0277 mmol, 70%) as a clear oil.

Data for **12**: R_f 0.50 (6:1 Hexanes: EtOAc); IR (thin film) 2977, 2931, 1597, 1563, 1494, 1464; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2 H), 6.84 (s, 2 H), 6.78 (s, 2 H), 5.72 (s, 1 H), 4.52 (sept, *J* = 6.1 Hz, 1 H), 4.46 (sept, *J* = 6.1 Hz, 1 H), 4.10 (sept, *J* = 6.1 Hz, 1 H), 3.764 (s, 3 H), 3.761 (s, 3 H), 1.37 (d, *J* = 6.0 Hz, 6 H), 1.33 (d, *J* = 5.9 Hz, 6 H), 0.94 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.1, 154.9, 153.6, 146.1, 144.5, 144.1, 143.8, 142.4, 140.2, 133.8, 133.4, 129.9, 127.4, 127.3, 116.5, 116.4, 114.1, 96.1, 71.3, 71.2, 70.8, 61.5, 55.9, 21.9 (2C), 21.2; HRMS (ESI) calcd for $C_{35}H_{34}O_8Cl_6$ [M+H]: 793.0385, found 793.0379.

Russuphelol (1). To a solution of **12**(20 mg, 0.025 mmol) in DCM (0.25 mL, 0.1 M) was added BCl_3 (0.25 mL, 0.25 mmol, 1M solution in DCM). The reaction mixture was stirred for 2 h upon which time TLC indicated consumption of all starting material. The reaction mixture was quenched with MeOH (0.25 mL), stirred for 15 min and concentrated. Purification by FCC (2:1 to 1:1 Hexanes:EtOAc) yielded **1** (11.6

mg, 0.0173 mmol, 69%) as a white solid, with spectroscopic data identical the material synthesized previously.



3,5-dichloro-4-(3-(2,6-dichloro-4-(((((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl)sulfonyl)oxy)phenoxy)-6-(2,6-dichloro-4-methoxyphenoxy)-5-hydroxy-2-methoxyphenoxy)phenyl (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (14). To a solution of russuphelol (**1**) (3.0 mg, 4.48 μmol) in DCM (0.1 mL, 0.045 M) was added DMAP (1.3 mg, 10.6 μmol) and (1*S*, 4*R*)- camphorsulfuryl chloride (1.7mg, 9.8 μmol). The mixture was stirred for 1 h after which time TLC indicated new spot. The reaction mixture was directly loaded on to a column and purified (3:1 to 2:1 Hexanes:EtOAc) to yield **14** (3.8 mg, 3.46 μmol , 77%) as a clear wax.

Data for **14**: R_f 0.35 (2:1 Hexanes: EtOAc); IR (thin film) 3392 (br), 2921, 2851, 1747, 1573, 1450; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.45 (s, 2 H), 7.27 (s, 2 H), 6.84 (s, 2 H), 5.89 (m, 1 H), 5.79 (bs, 1 H), 3.89 (d, *J* = 15.0 Hz, 1 H), 3.85 (d, *J* = 15.1 Hz, 1 H), 3.79 (s, 3 H), 3.53 (s, 3 H), 3.28 (d, *J* = 15.1 Hz, 1 H), 3.24 (d, *J* = 15.1 Hz, 1 H), 2.54 (m, 2 H), 2.47 (m, 2 H), 2.20 (m, 2 H), 2.14 (m, 2 H), 2.04 (m, 2 H), 1.80 (m, 2 H), 1.53 (m, 2 H), 1.20 (s, 3 H), 1.18 (s, 3 H), 0.97 (s, 3 H), 0.95 (s, 3 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 213.91, 213.89, 156.0, 148.13, 146.3, 145.8, 145.4, 144.1, 143.5, 143.3, 140.6, 132.2, 130.5, 129.8, 128.3, 126.9, 123.4, 122.70, 114.5, 95.8, 61.6, 58.2, 58.1, 56.0, 48.4, 48.22, 48.18, 48.13, 42.84, 42.81, 42.49, 42.48, 29.7, 26.9, 25.2, 25.1, 19.9, 19.8, 14.24, 14.19; HRMS (ESI) calcd for $C_{46}H_{45}O_{14}S_2Cl_6$ [M+H]: 1095.0382, found 1095.0388.

Comparison of NMR data for russuphelol (**1**)

Solvent peak for *d*-MeOD was calibrated to 3.21 ppm in ^{1}H and 49.8 ppm in ^{13}C spectrum.

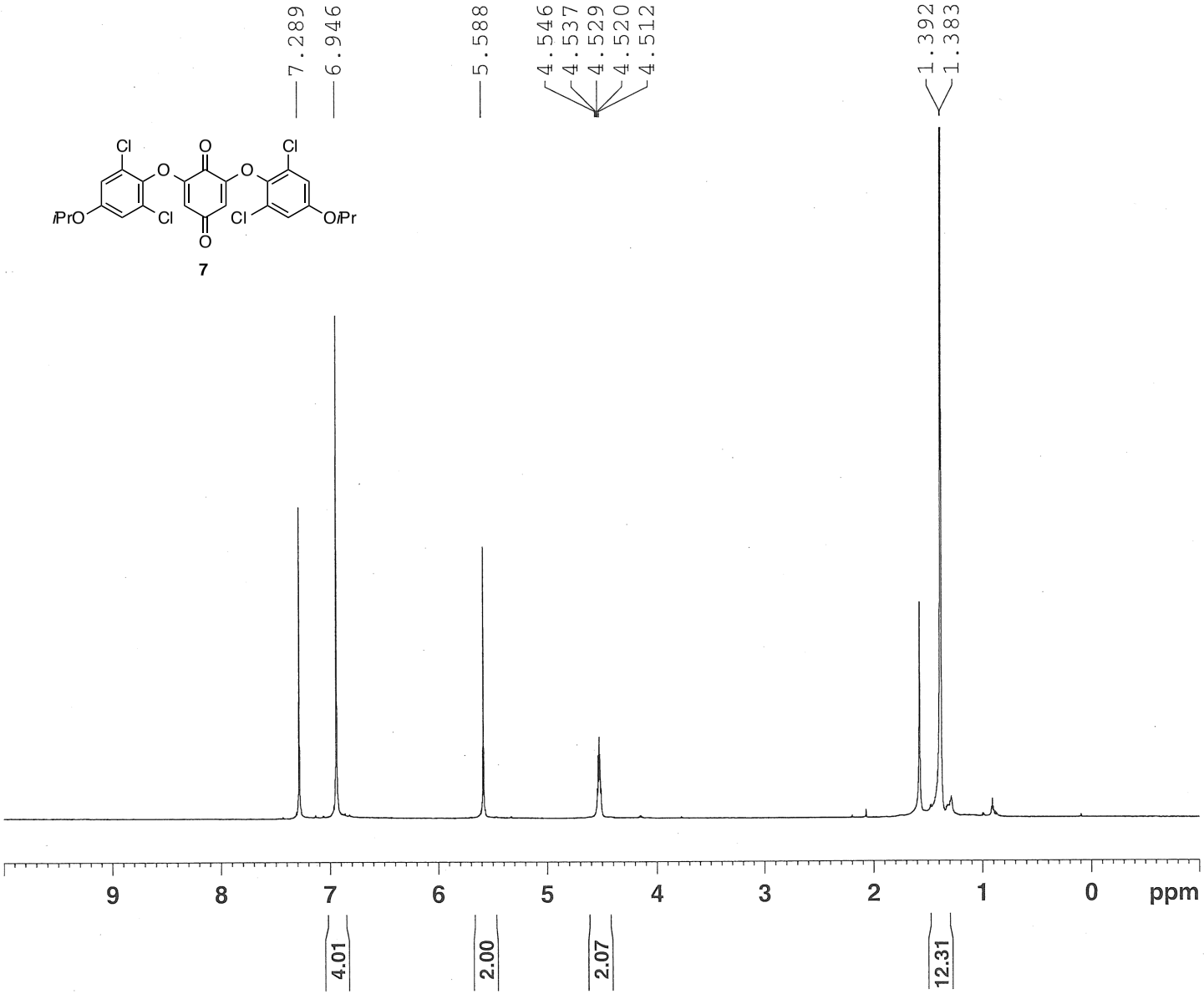
^{1}H NMR data of isolated and synthetic russuphelol in *d*-MeOD

Isolation	Synthetic	Δ
6.80	6.80	0.00
6.75	6.76	0.01
6.62	6.61	-0.01
5.57	5.55	-0.02
3.63	3.64	0.01
3.40	3.40	0.00

^{13}C data for isolated and synthetic russuphelol in *d*-MeOD

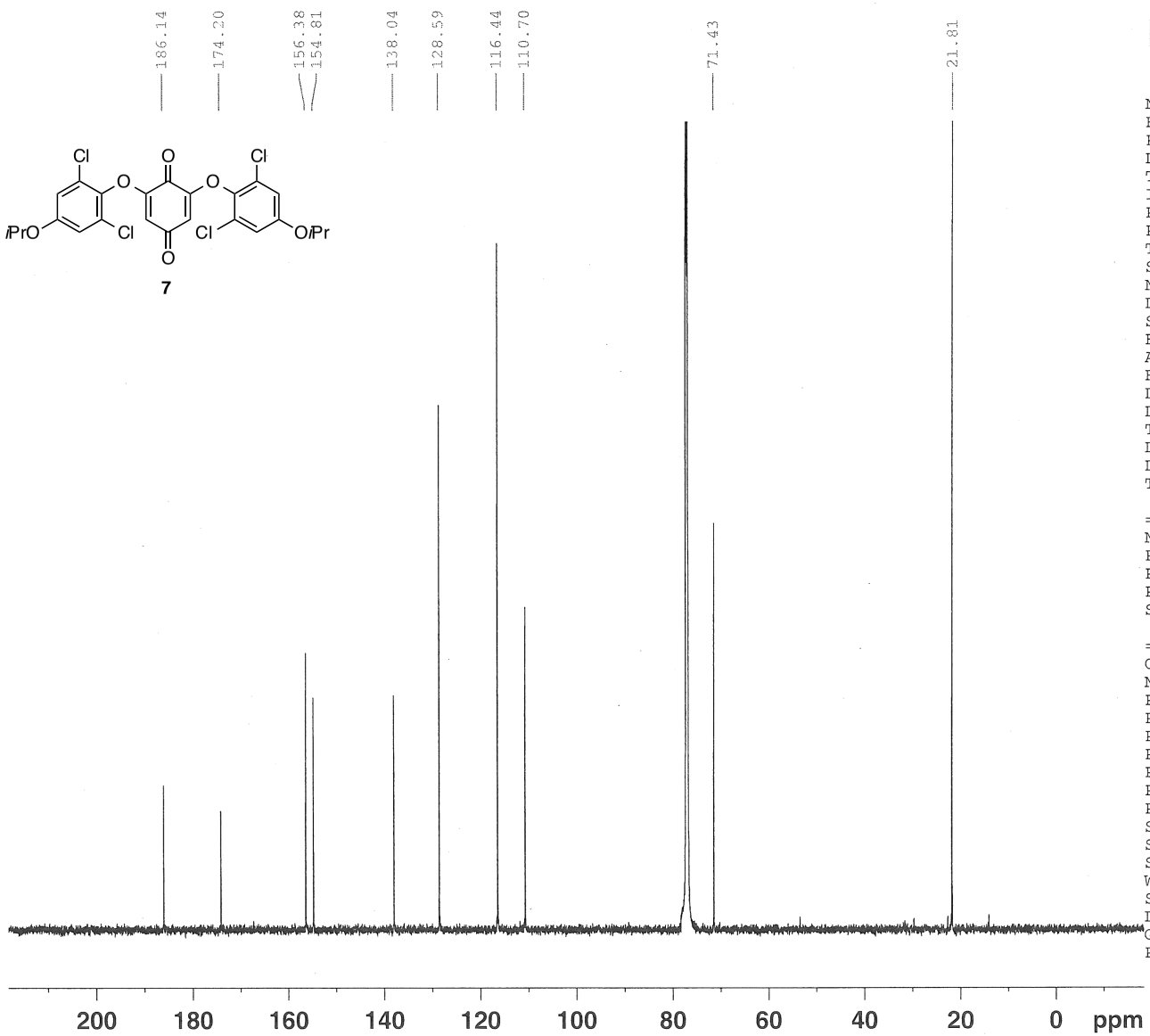
Isolation	Synthetic	Δ
157.6	157.8	0.2
157.6	157.7	0.1
155.7	155.8	0.1
148.9	149.0	0.1
146.8	146.9	0.1
146.3	146.4	0.1
144.4	144.4	0.0
143.9	143.9	0.0
141.0	141.0	0.0
133.8	133.8	0.0
132.4	132.4	0.0
131.6	131.6	0.0
129.7	129.8	0.1
128.6	128.7	0.1
117.9	117.9	0.0
117.2	117.2	0.0
116.2	116.2	0.0
97.3	97.4	0.1
62.6	62.6	0.0
57.3	57.3	0.0

4170-2




```
NAME              4170-2
EXPNO                  1
PROCNO                 1
Date_           20131030
Time               17.36
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             zg30
TD                 95236
SOLVENT            CDCl3
NS                     4
DS                     0
SWH            11904.762 H
FIDRES          0.125003 H
AQ             3.9999621 s
RG                  22.6
DW                42.000 u
DE                  6.50 u
TE                 298.2 K
D1            2.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                  9.40 u
PL1                -3.20 d
PL1W         33.59817505 W
SFO1         700.1516910 M
SI                131072
SF           700.1471400 M
WDW                   EM
SSB                    0
LB                  0.30 H
GB                     0
PC                  1.00
```

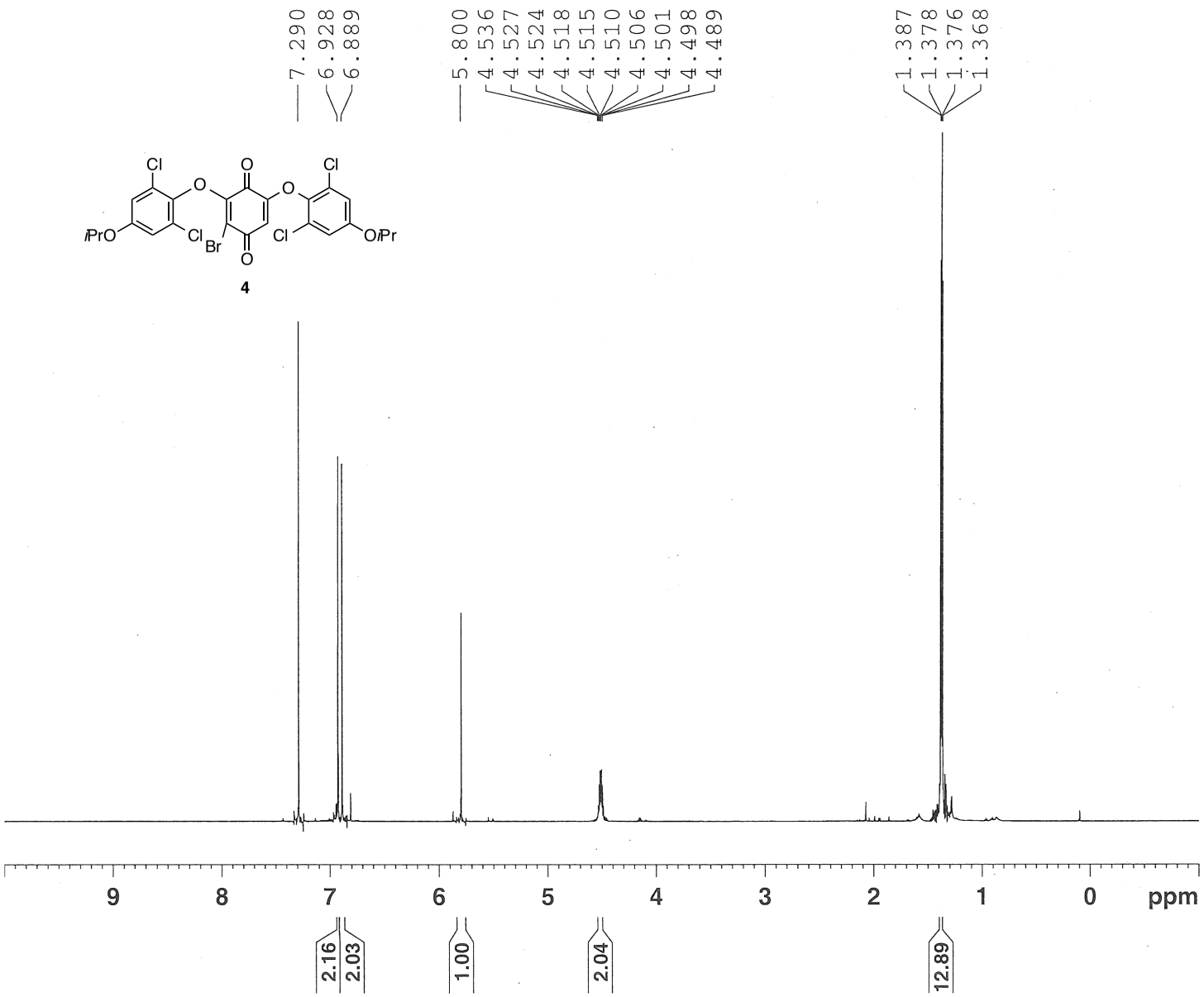
4206-2



BRUKER

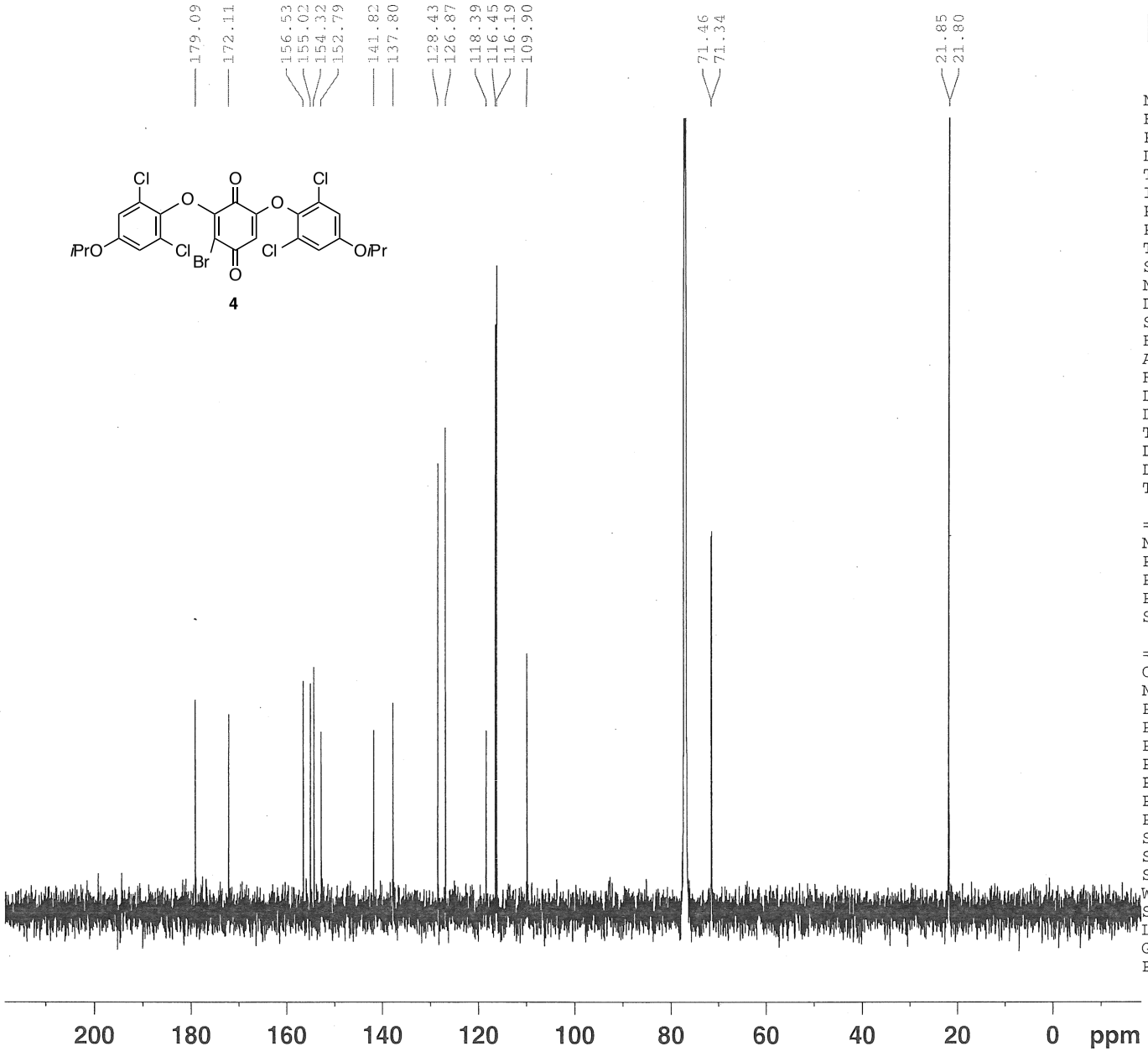
NAME	4206-2
EXPNO	2
PROCNO	1
Date_	20131224
Time	18.14
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	1
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0697436 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

4197-x



NAME	4197-x
EXPNO	1
PROCNO	1
Date_	20131126
Time	12.04
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	8
DS	0
SWH	11904.762 H
FIDRES	0.125003 H
AQ	3.9999621 s
RG	40.3
DW	42.000 u
DE	6.50 u
TE	298.1 K
D1	2.00000000 s
TD0	1
======== CHANNEL f1 =====	
NUC1	1H
P1	9.40 u
PL1	-3.20 d
PL1W	33.59817505 W
SFO1	700.1516910 M
SI	131072
SF	700.1471400 M
WDW	EM
SSB	0
LB	0.30 H
GB	0
PC	1.00

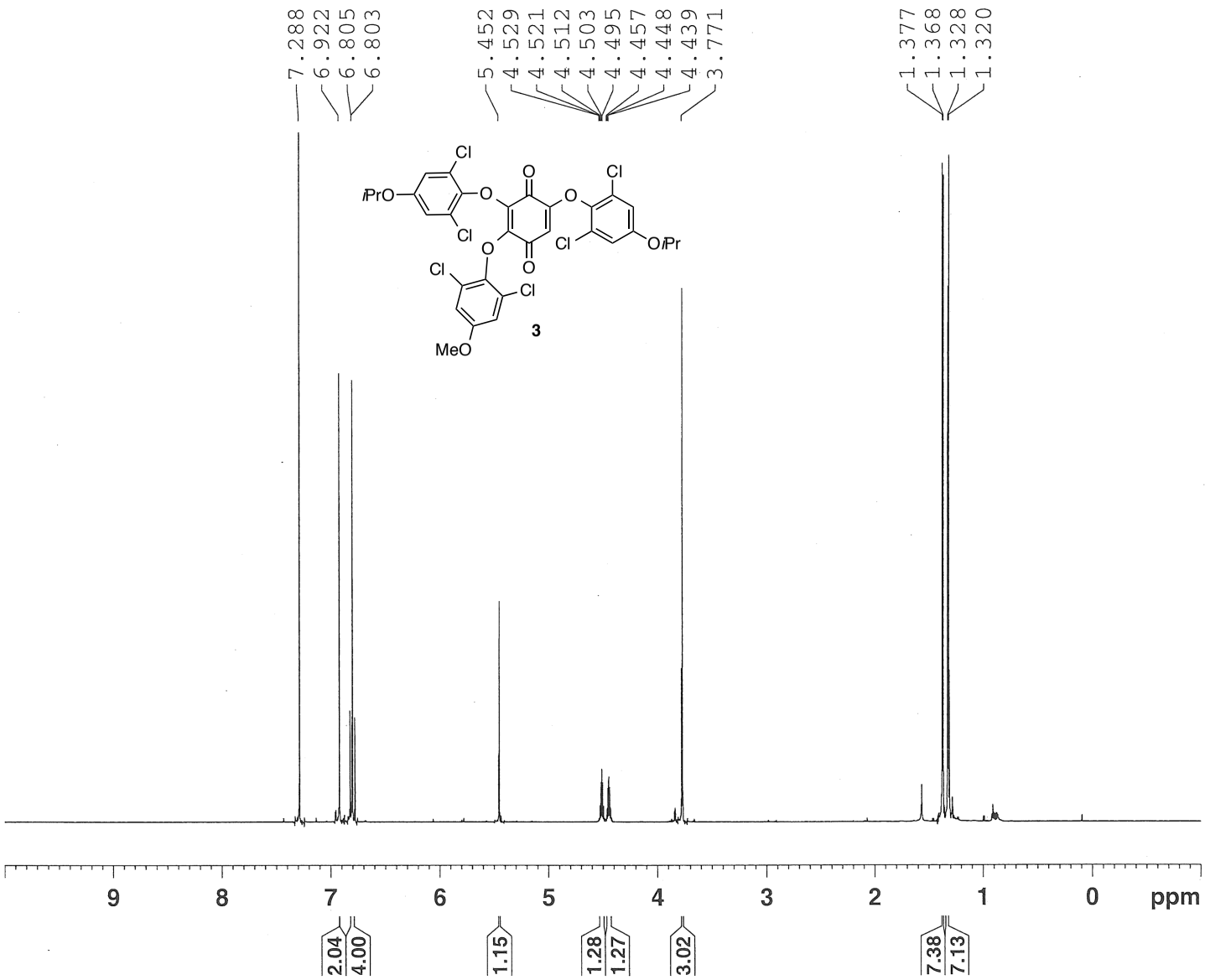
4197-x



BRUKER

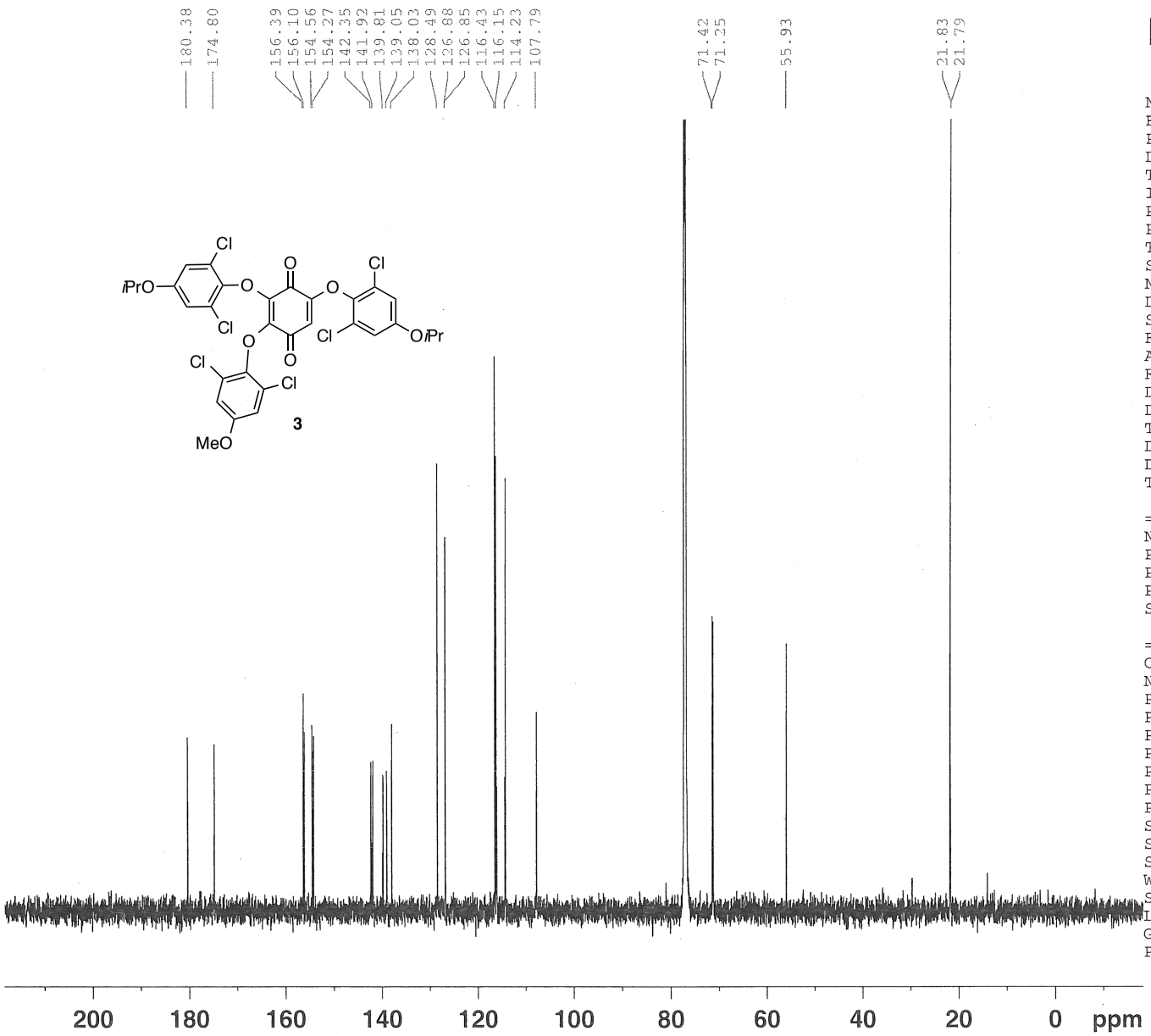
NAME	4197-x
EXPNO	2
PROCNO	1
Date_	20131126
Time	12.06
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	64
DS	1
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0697436 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

4190-3



NAME	4190-3
EXPNO	1
PROCNO	1
Date_	20131122
Time	12.04
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	8
DS	0
SWH	11904.762 H
FIDRES	0.125003 H
AQ	3.9999621 s
RG	22.6
DW	42.000 u
DE	6.50 u
TE	298.2 K
D1	2.00000000 s
TD0	1
======== CHANNEL f1 =====	
NUC1	1H
P1	9.40 u
PL1	-3.20 d
PL1W	33.59817505 W
SFO1	700.1516910 M
SI	131072
SF	700.1471400 M
WDW	EM
SSB	0
LB	0.30 H
GB	0
PC	1.00

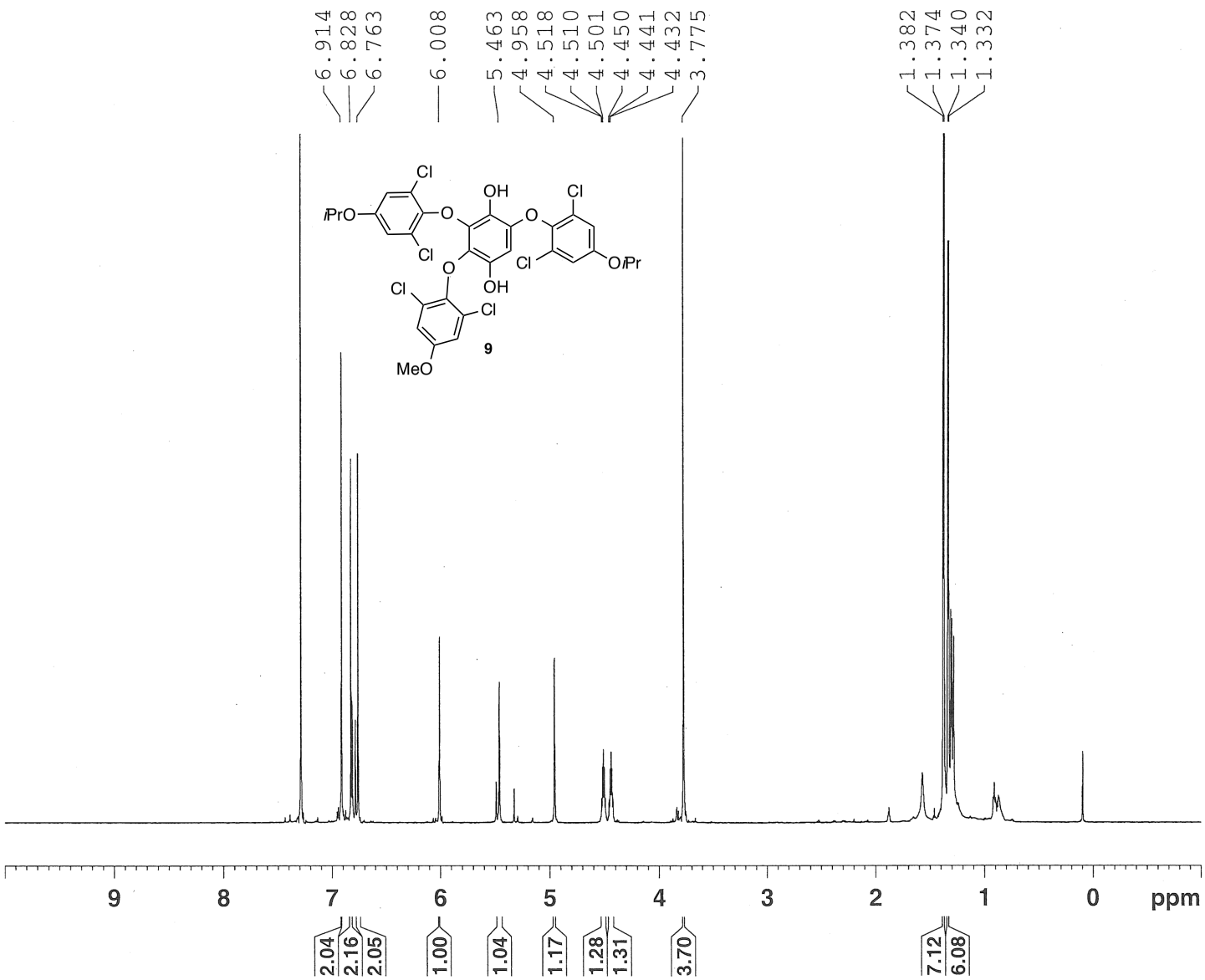
4190-3



BRUKER

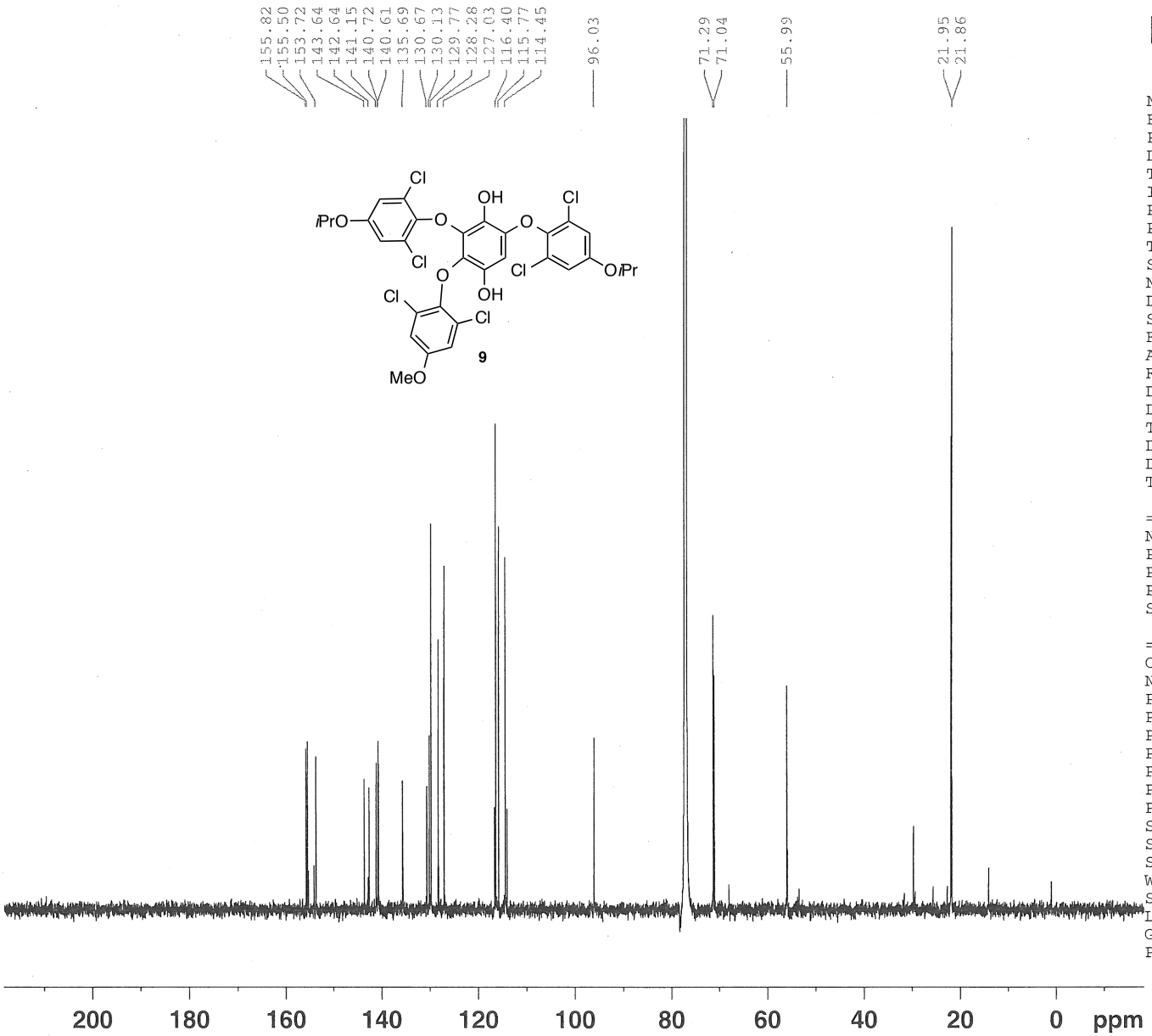
NAME	4190-3	
EXPNO	2	
PROCNO	1	
Date_	20131122	
Time	12.10	
INSTRUM	spect	
PROBHD	5 mm CPDCH 13C	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	201	
DS	1	
SWH	41666.668	Hz
FIDRES	0.635783	Hz
AQ	0.7864820	sec
RG	203	
DW	12.000	usec
DE	16.50	usec
TE	298.2	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.00	usec
PL1	4.50	dB
PL1W	38.14553833	W
SFO1	176.0697436	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	65.00	usec
PL2	-3.20	dB
PL12	13.60	dB
PL13	120.00	dB
PL2W	33.59817505	W
PL12W	0.70196527	W
PL13W	0.00000000	W
SFO2	700.1499406	MHz
SI	32768	
SF	176.0521380	MHz
WDW	EM	
SSB	0	
LB	3.00	Hz
GB	0	
PC	1.40	

4204-x




```
NAME              42004-x
EXPNO                   1
PROCNO                  1
Date_            20131206
Time                10.10
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG              zg30
TD                  95236
SOLVENT             CDCl3
NS                      8
DS                      1
SWH            11904.762 H
FIDRES          0.125003 H
AQ             3.9999621 s
RG                   20.2
DW                 42.000 u
DE                   6.50 u
TE                  298.4 K
D1            2.00000000 s
TD0                     1

======== CHANNEL f1 =====
NUC1                   1H
P1                   9.40 u
PL1                 -3.20 d
PL1W         33.59817505 W
SFO1         700.1516910 M
SI                131072
SF           700.1471400 M
WDW                    EM
SSB                     0
LB                   0.30 H
GB                      0
PC                   1.00
```

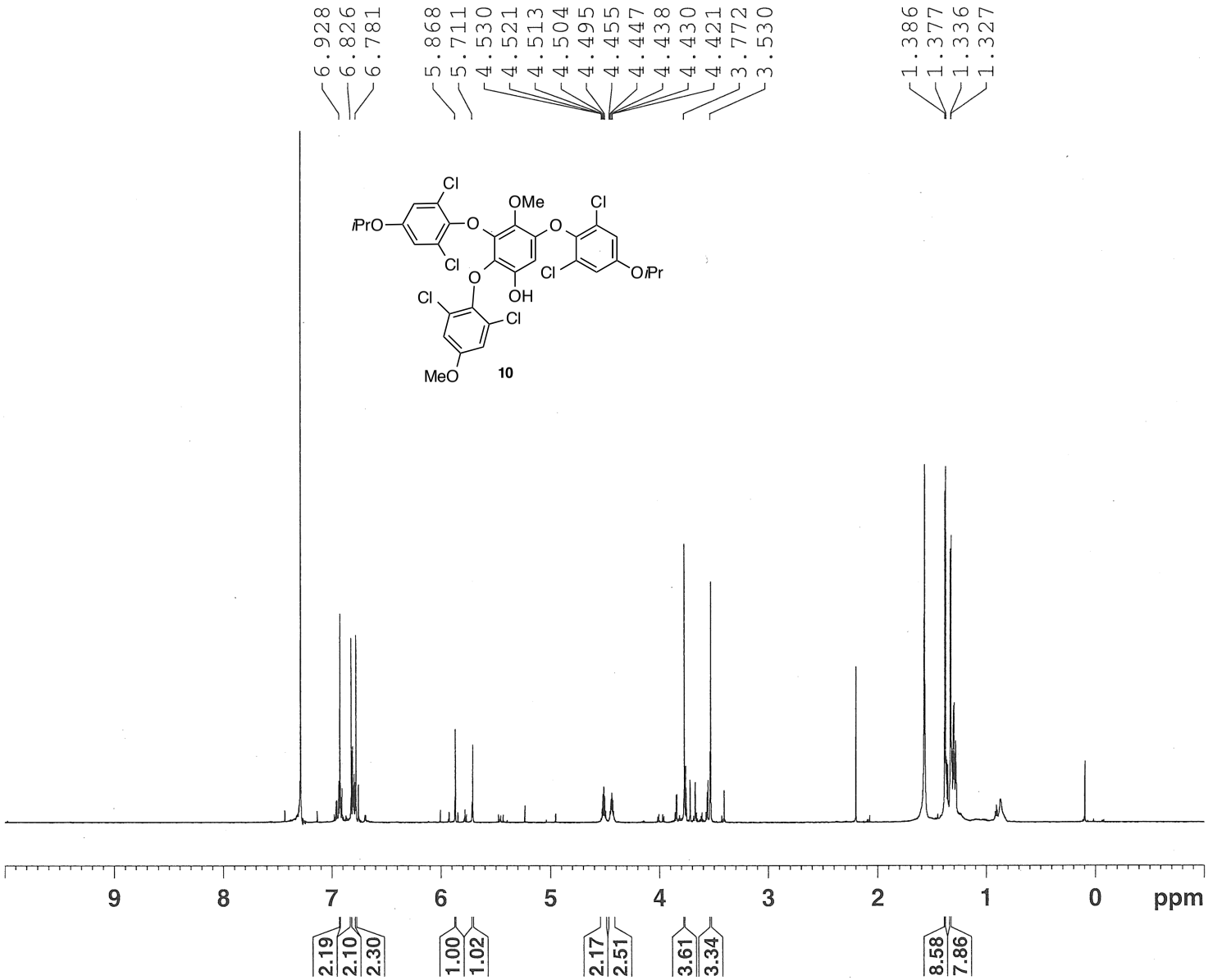
4204-x



BRUKER

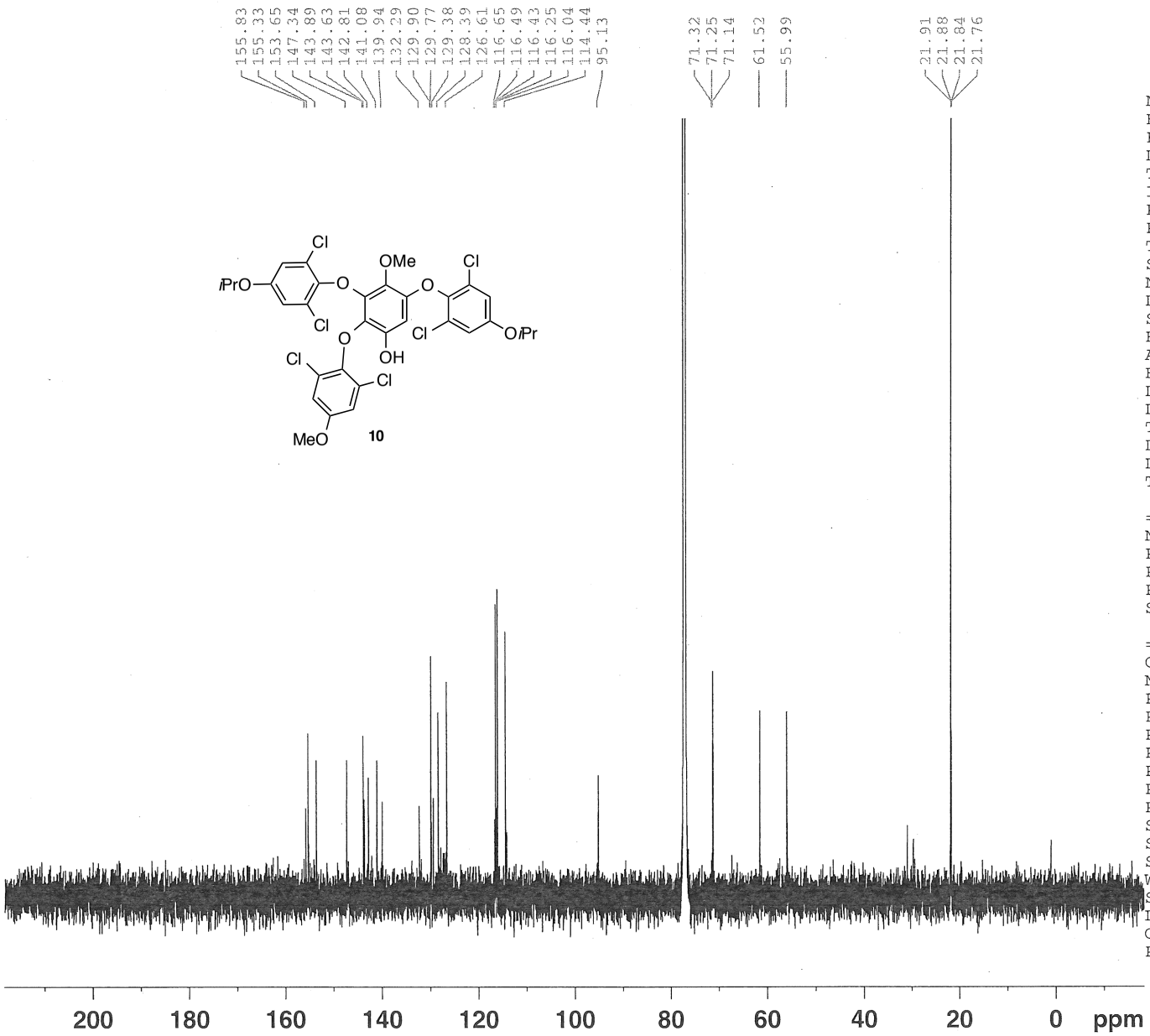
NAME	42004-x
EXPNO	2
PROCNO	1
Date_	20131206
Time	10.13
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	753
DS	1
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0697436 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

4231-2



NAME	4231-2
EXPNO	1
PROCNO	1
Date_	20140124
Time	18.34
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	8
DS	0
SWH	11904.762 H
FIDRES	0.125003 H
AQ	3.9999621 s
RG	40.3
DW	42.000 u
DE	6.50 u
TE	298.1 K
D1	2.00000000 s
TD0	1
======== CHANNEL f1 =====	
NUC1	1H
P1	9.40 u
PL1	-3.20 d
PL1W	33.59817505 W
SFO1	700.1516910 M
SI	131072
SF	700.1471400 M
WDW	EM
SSB	0
LB	0.30 H
GB	0
PC	1.00

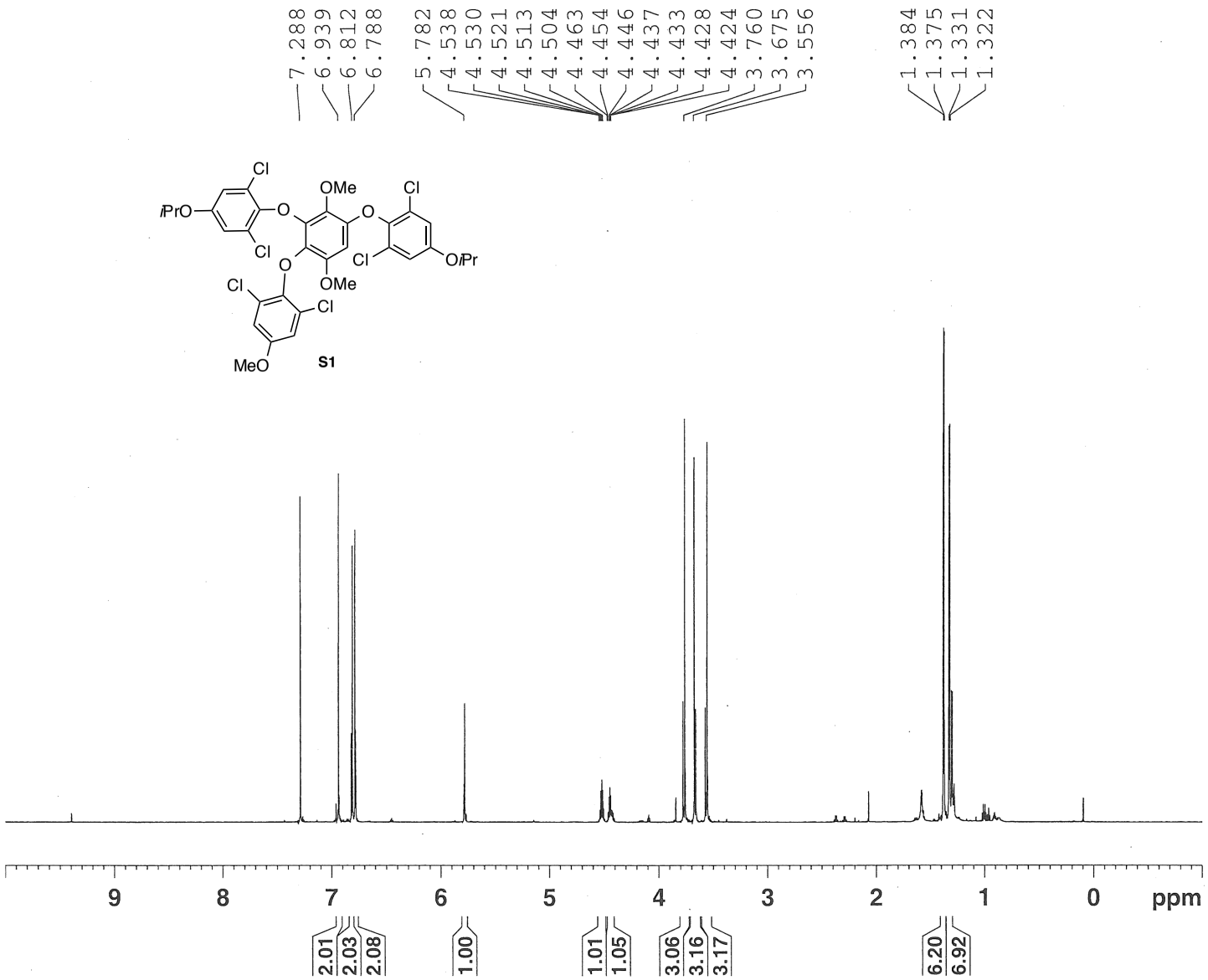
4231-2



10

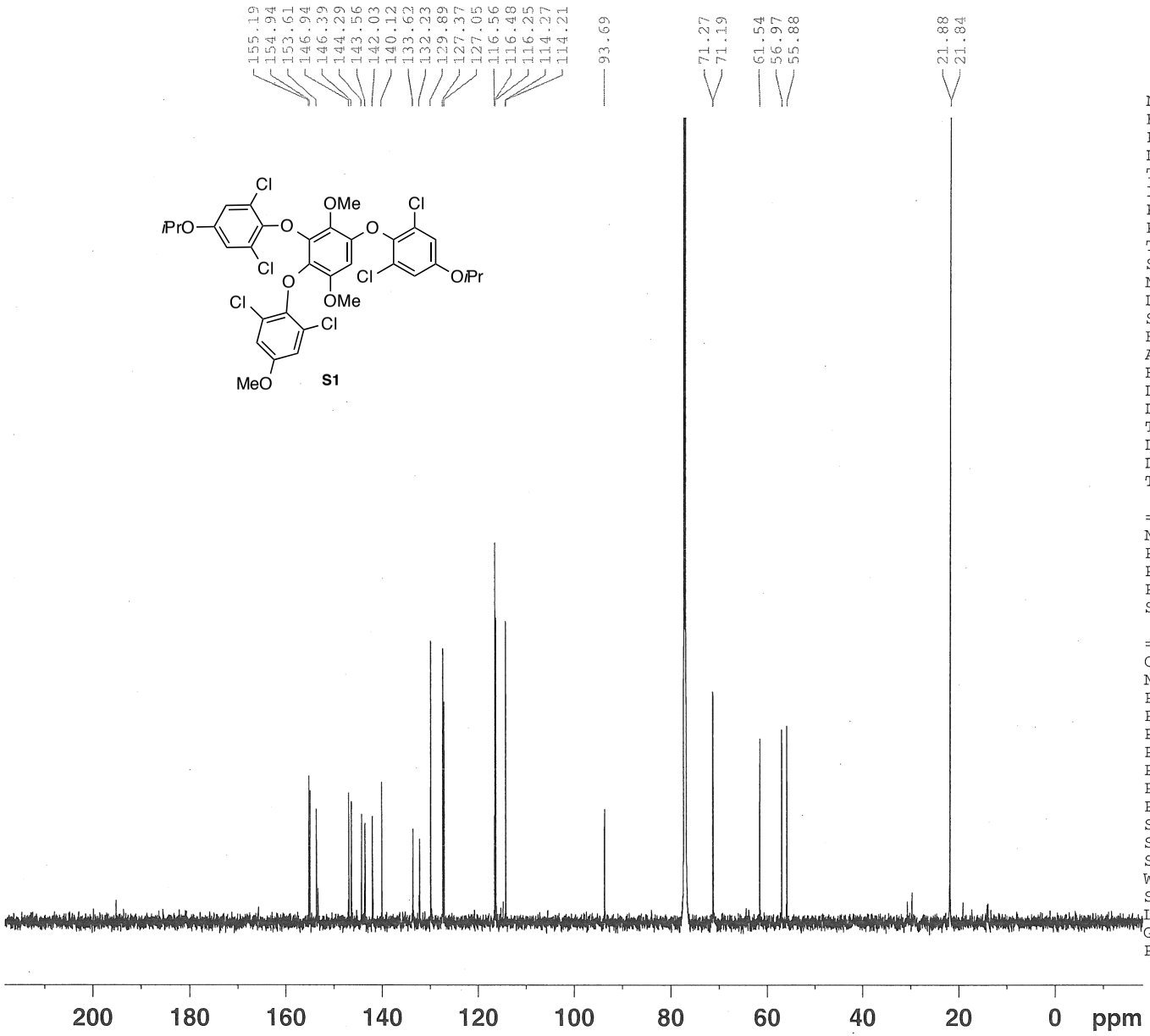
NAME	4231-2
EXPNO	2
PROCNO	1
Date_	20140124
Time	18.37
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1068
DS	1
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0697436 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

4235-1



NAME	4235-1
EXPNO	1
PROCNO	1
Date_	20140128
Time	12.36
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	8
DS	0
SWH	11904.762 H
FIDRES	0.125003 H
AQ	3.9999621 s
RG	22.6
DW	42.000 u
DE	6.50 u
TE	298.4 K
D1	2.00000000 s
TD0	1
======== CHANNEL f1 =====	
NUC1	1H
P1	9.40 u
PL1	-3.20 d
PL1W	33.59817505 W
SFO1	700.1516910 M
SI	131072
SF	700.1471400 M
WDW	EM
SSB	0
LB	0.30 H
GB	0
PC	1.00

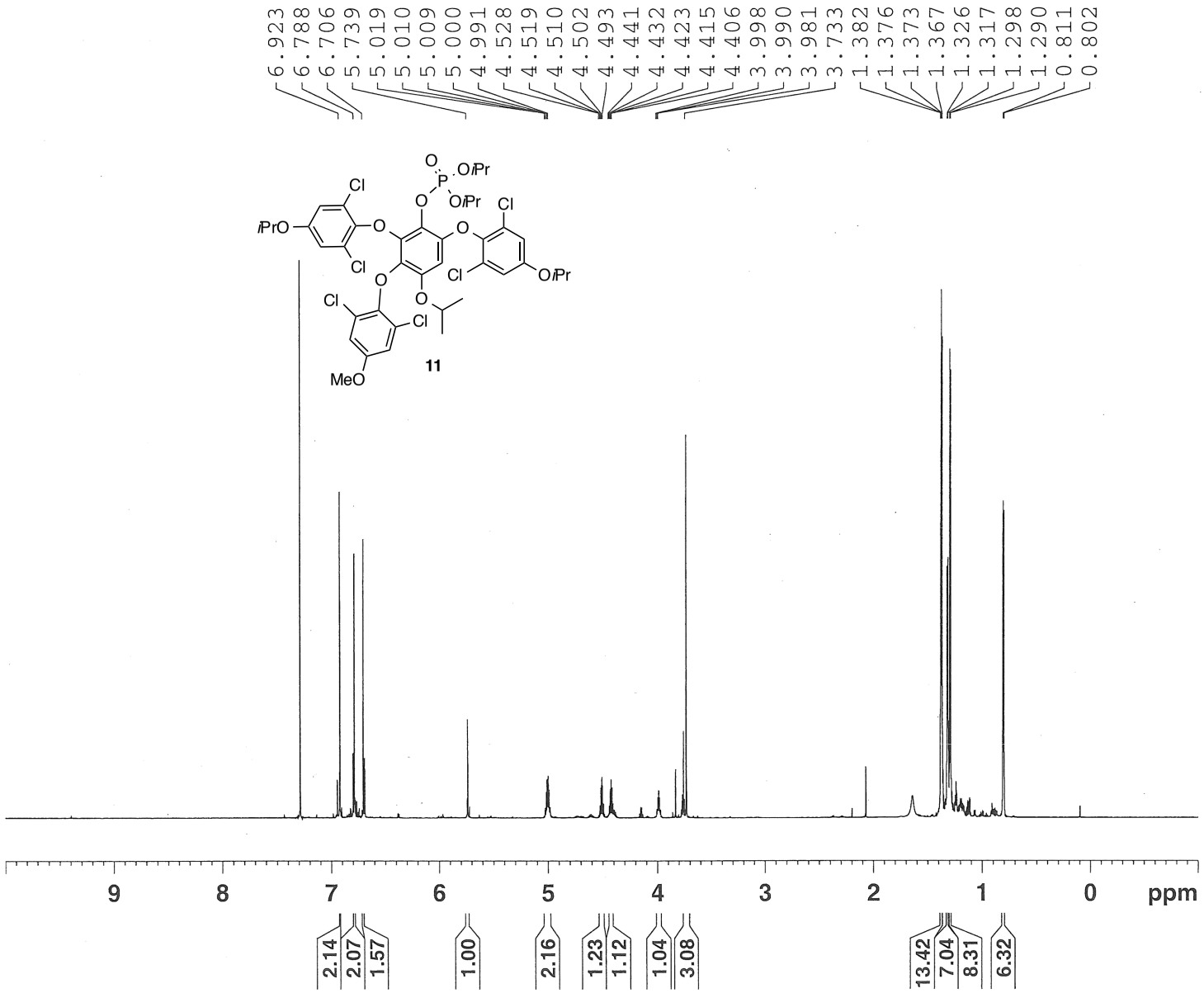
4235-1



BRUKER

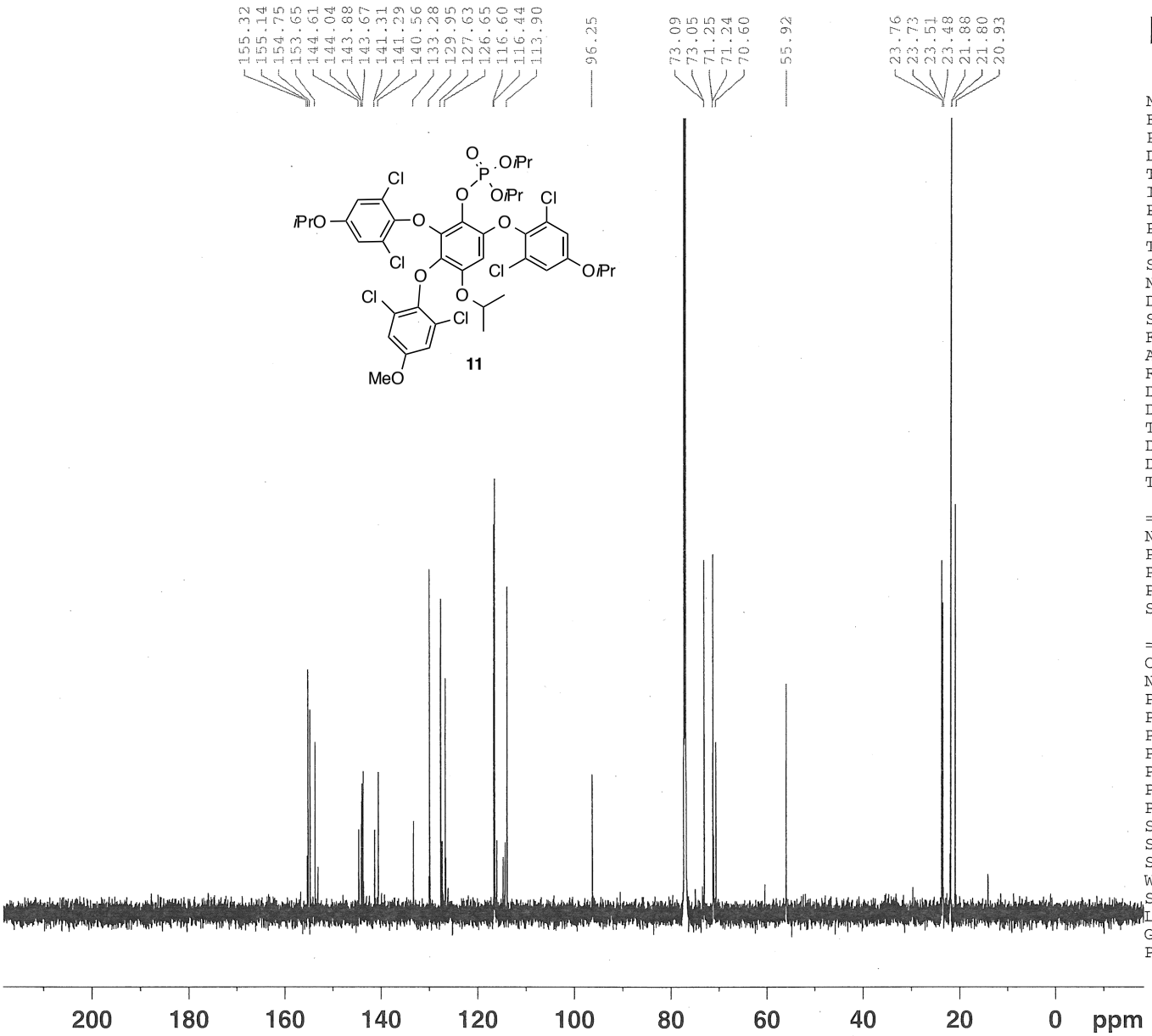
NAME	4235-1	
EXPNO	2	
PROCNO	1	
Date_	20140128	
Time	12.43	
INSTRUM	spect	
PROBHD	5 mm CPDCH 13C	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	142	
DS	4	
SWH	41666.668	Hz
FIDRES	0.635783	Hz
AQ	0.7864820	sec
RG	203	
DW	12.000	usec
DE	16.50	usec
TE	298.3	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.00	usec
PL1	4.50	dB
PL1W	38.14553833	W
SFO1	176.0697436	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	65.00	usec
PL2	-3.20	dB
PL12	13.60	dB
PL13	120.00	dB
PL2W	33.59817505	W
PL12W	0.70196527	W
PL13W	0.00000000	W
SFO2	700.1499406	MHz
SI	32768	
SF	176.0521380	MHz
WDW	EM	
SSB	0	
LB	3.00	Hz
GB	0	
PC	1.40	

4237-2



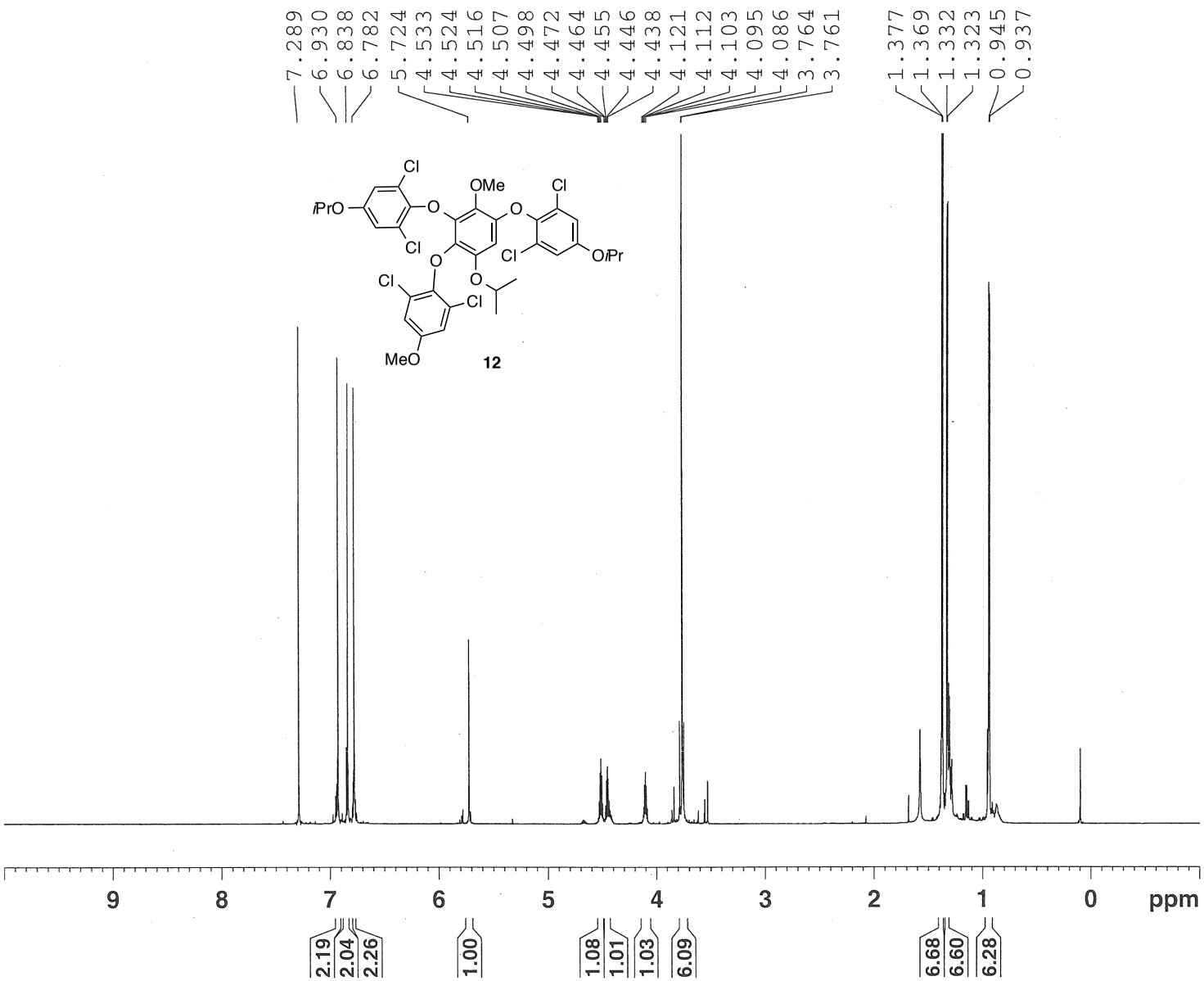

```
NAME              4237-2
EXPNO                  1
PROCNO                 1
Date_           20140203
Time               19.28
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             zg30
TD                 95236
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           11904.762 H
FIDRES         0.125003 H
AQ           3.9999621 s
RG                  40.3
DW                42.000 u
DE                  6.50 u
TE                 298.1 K
D1           2.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                  9.40 u
PL1                -3.20 d
PL1W        33.59817505 W
SFO1        700.1516910 M
SI               131072
SF          700.1471400 M
WDW                   EM
SSB                    0
LB                  0.30 H
GB                     0
PC                  1.00
```

4237-2



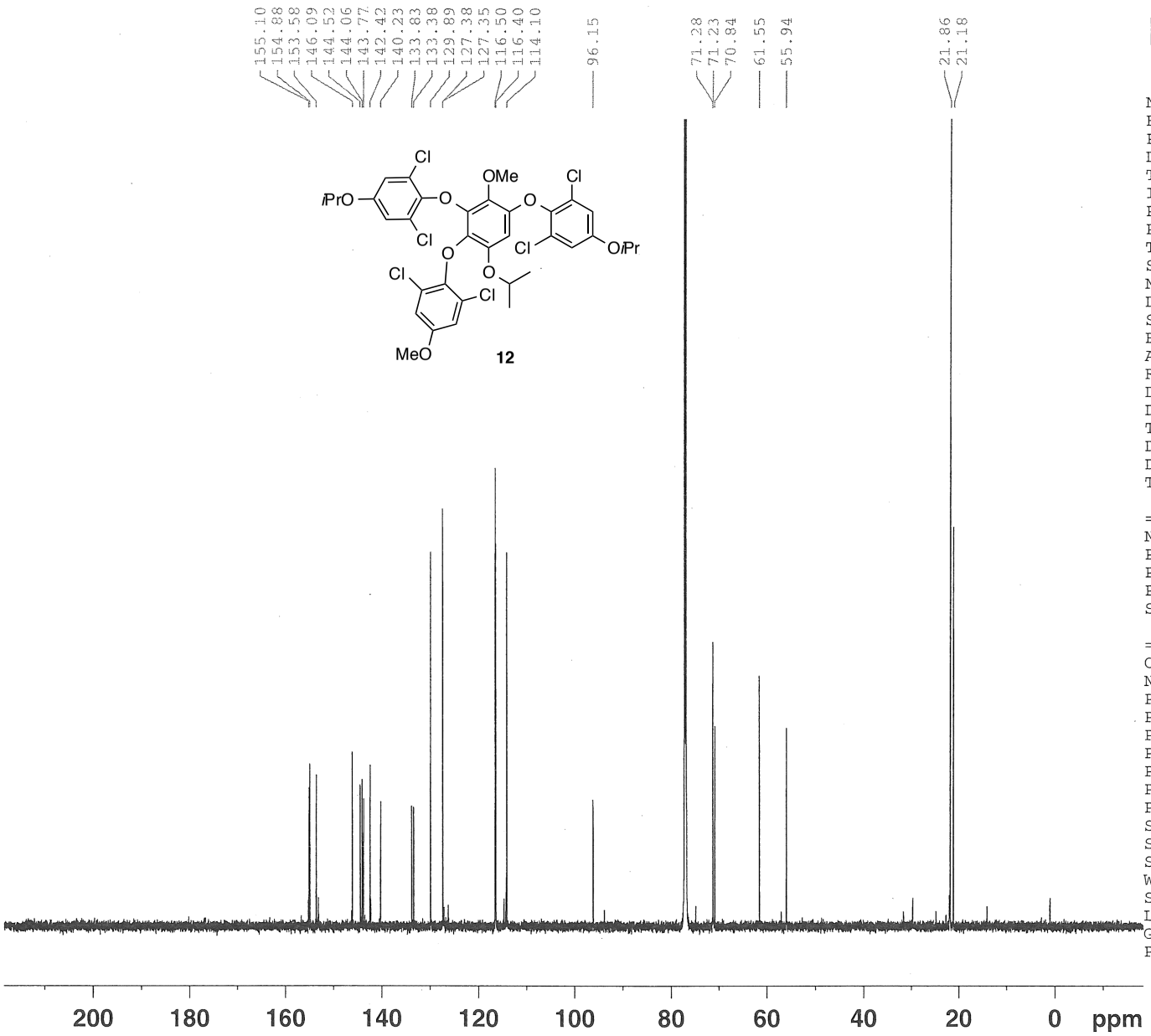
NAME	4237-2
EXPNO	2
PROCNO	1
Date_	20140203
Time	19.32
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	216
DS	1
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0697436 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

4247-1




```
NAME                4247-1
EXPNO                    1
PROCNO                   1
Date_             20140228
Time                 14.47
INSTRUM              spect
PROBHD    5 mm CPDCH 13C
PULPROG               zg30
TD                   95236
SOLVENT              CDCl3
NS                       8
DS                       0
SWH             11904.762 H
FIDRES           0.125003 H
AQ              3.9999621 s
RG                    20.2
DW                  42.000 u
DE                    6.50 u
TE                   298.1 K
D1             2.00000000 s
TD0                      1

======== CHANNEL f1 =====
NUC1                    1H
P1                    9.40 u
PL1                  -3.20 d
PL1W          33.59817505 W
SFO1          700.1516910 M
SI                 131072
SF            700.1471400 M
WDW                    EM
SSB                     0
LB                   0.30 H
GB                      0
PC                   1.00
```

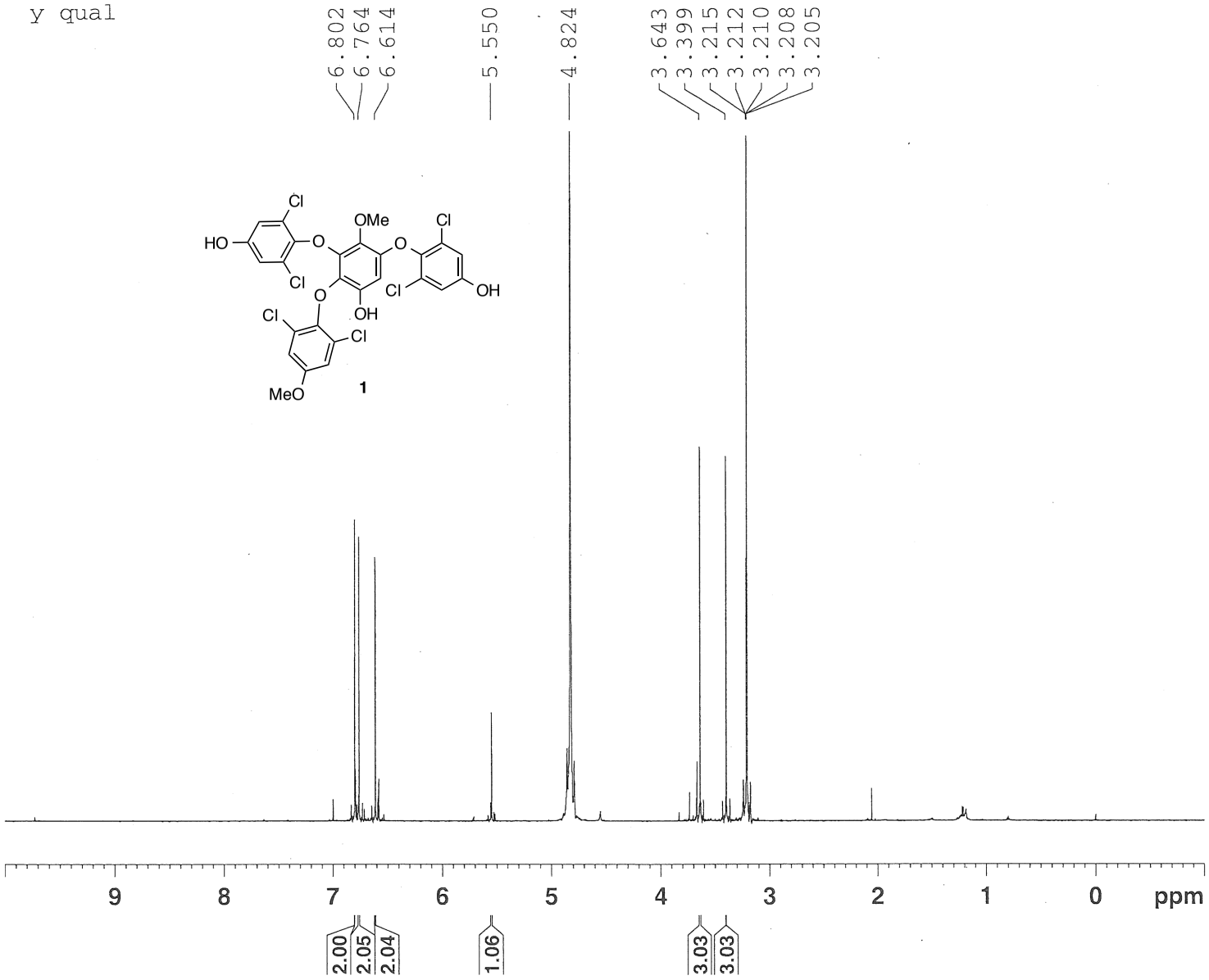
4247-1



BRUKER

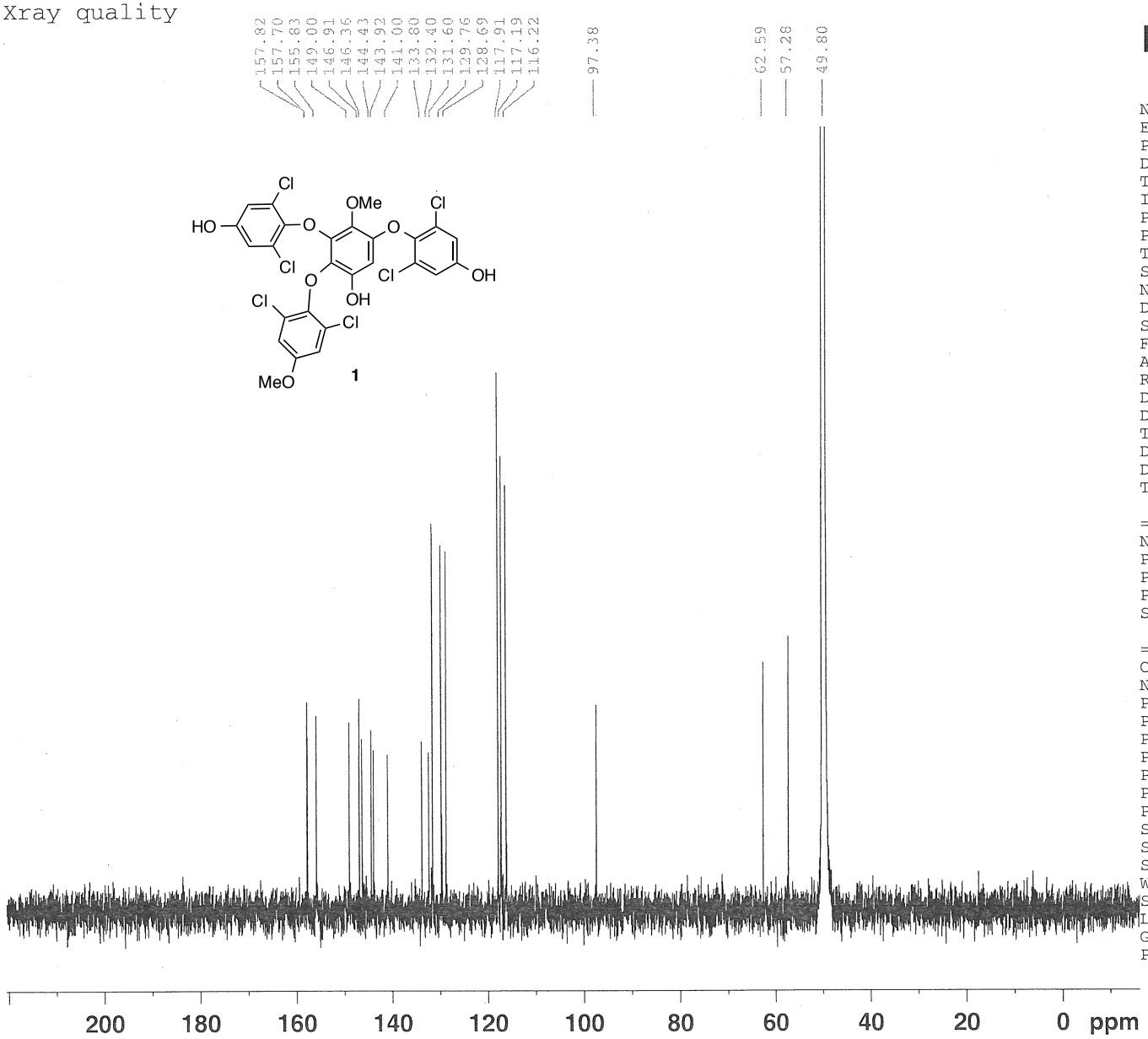
NAME	4247-1
EXPNO	2
PROCNO	1
Date_	20140228
Time	14.49
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0697436 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

ssuphel
y qual




```
NAME              Russ-1
EXPNO                  1
PROCNO                 1
Date_           20140605
Time               11.59
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             zg30
TD                 95236
SOLVENT             MeOD
NS                     8
DS                     0
SWH            11904.762 H
FIDRES          0.125003 H
AQ             3.9999621 s
RG                  25.4
DW                42.000 u
DE                 6.50 u
TE                298.2 K
D1           2.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                  9.40 u
PL1                -3.20 d
PL1W        33.59817505 W
SFO1        700.1516910 M
SI               131072
SF          700.1472269 M
WDW                  EM
SSB                   0
LB                 0.30 H
GB                    0
PC                 1.00
```

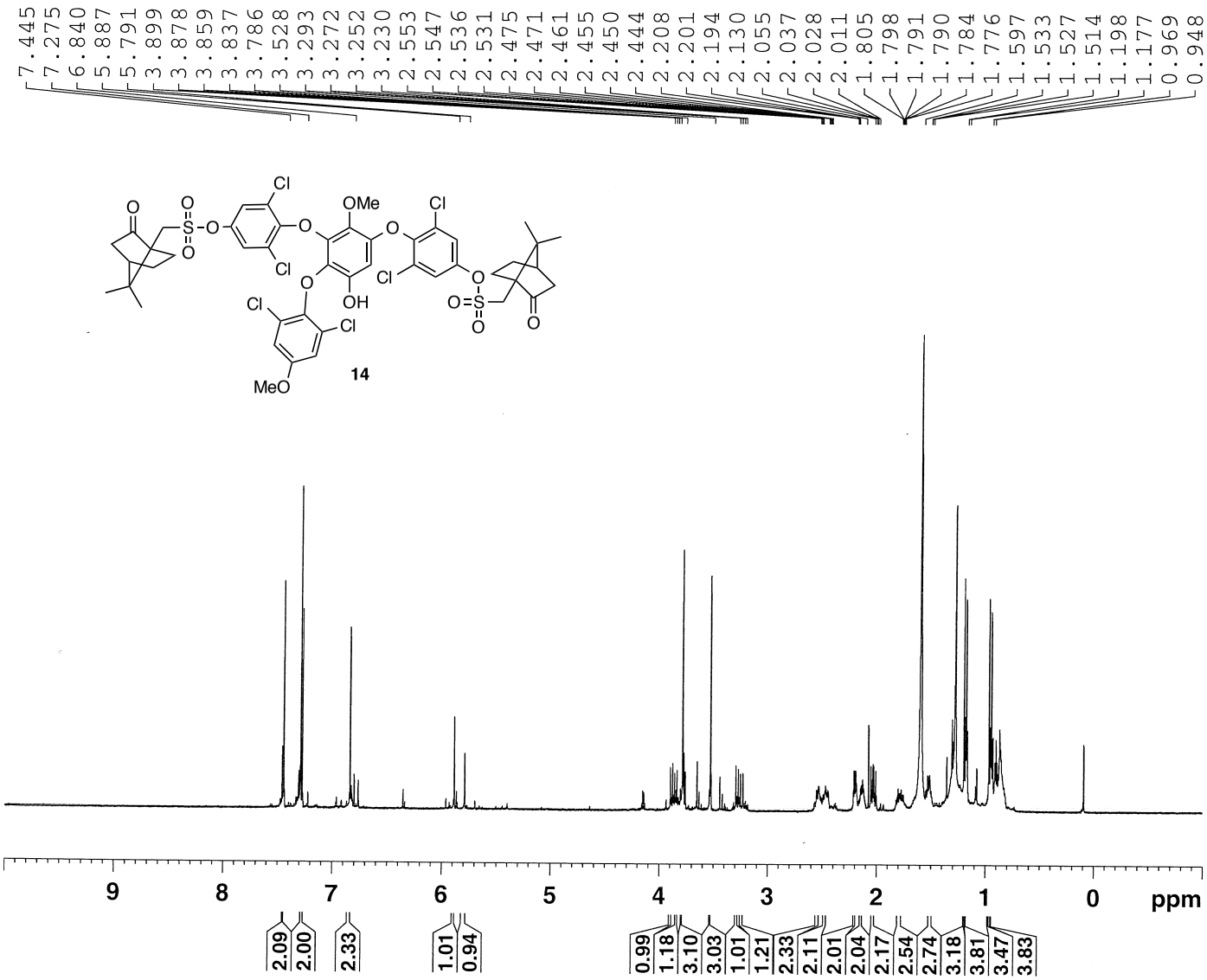
Russuphelol
Xray quality



BRUKER

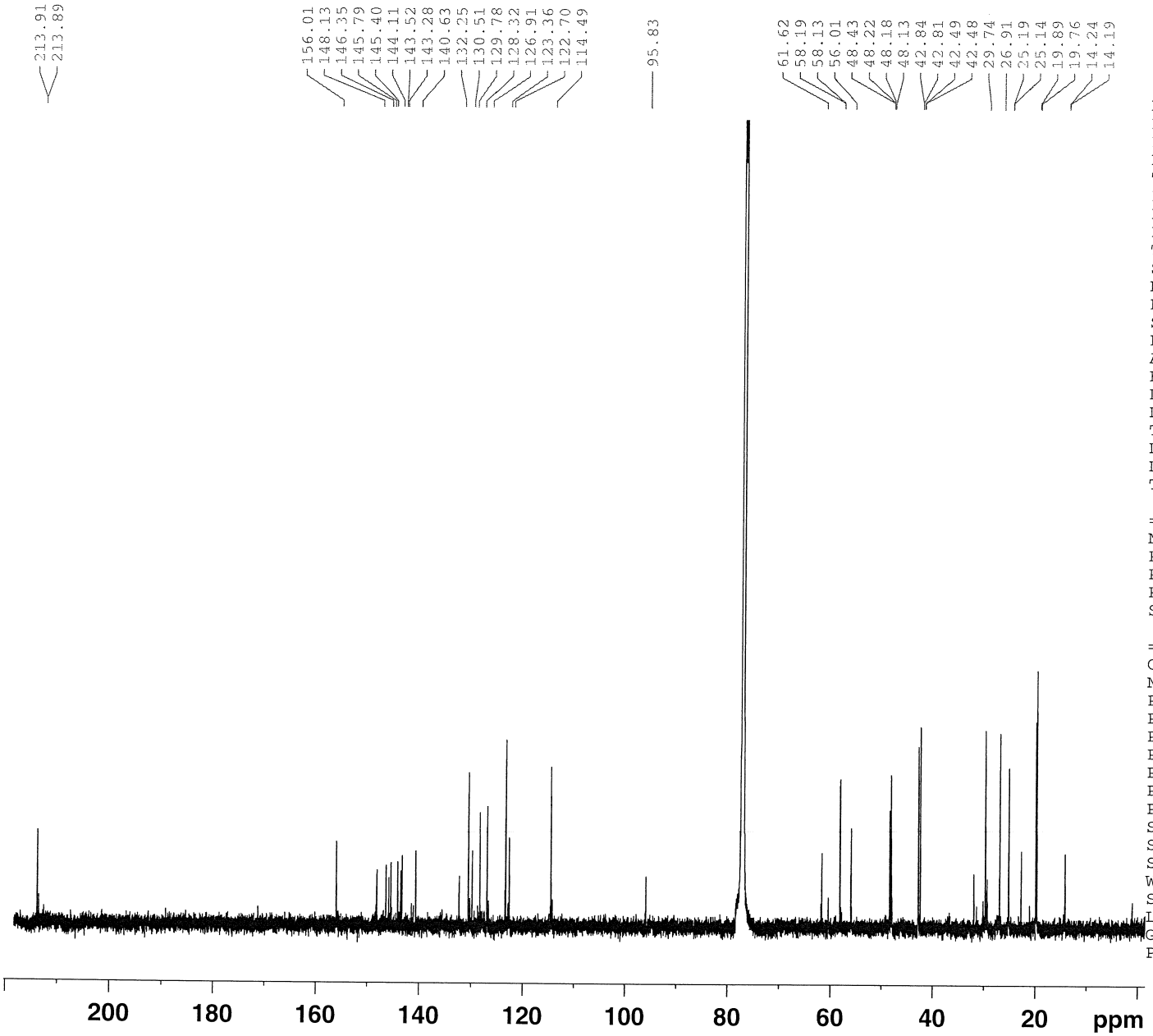
NAME	Russ-1
EXPNO	2
PROCNO	1
Date_	20140605
Time	11.14
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	MeOD
NS	911
DS	1
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0697436 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0517514 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

4284-1



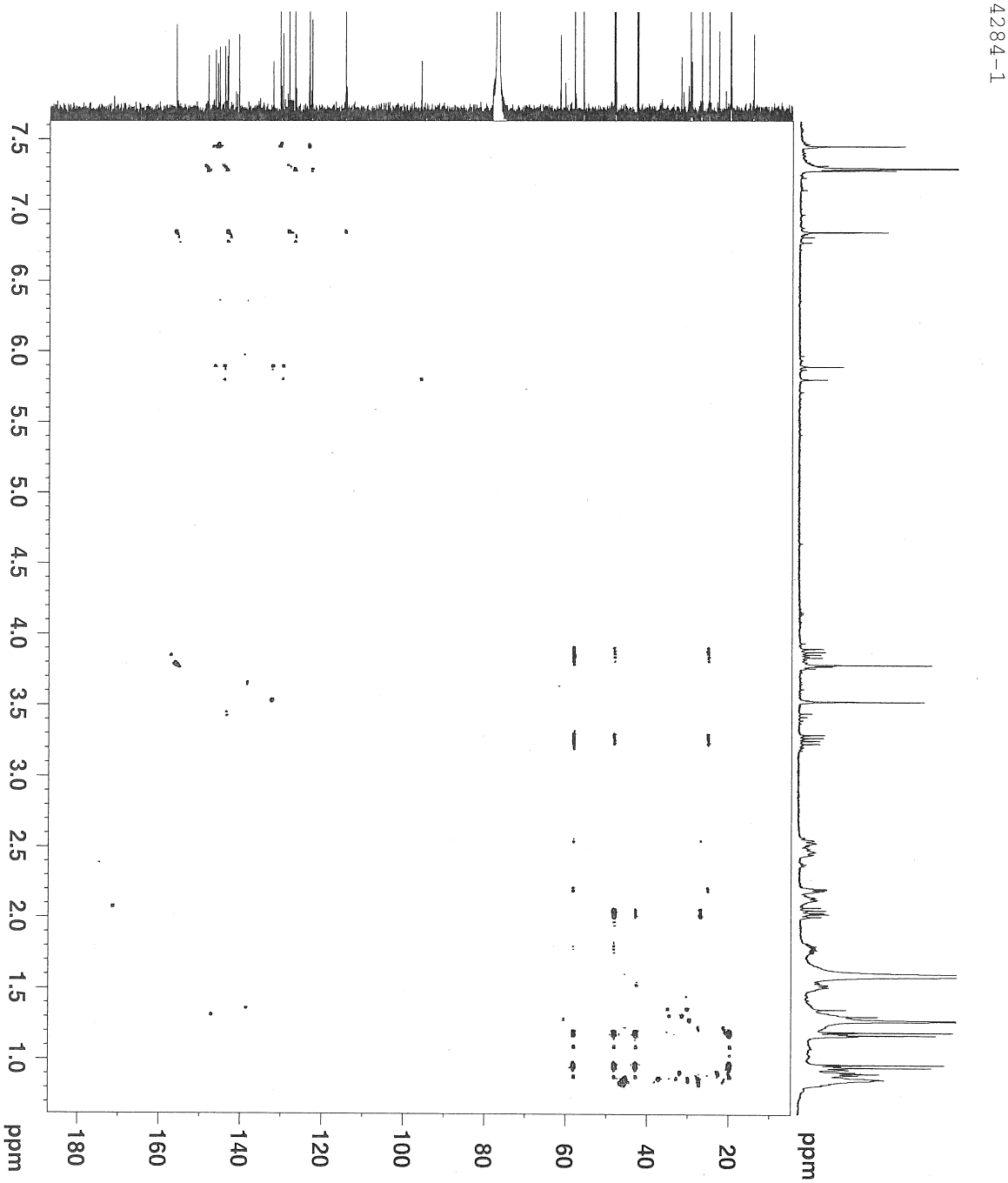
NAME	4284-1
EXPNO	5
PROCNO	1
Date_	20140531
Time	21.05
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	8
DS	0
SWH	11904.762 H
FIDRES	0.125003 H
AQ	3.9999621 s
RG	16
DW	42.000 u
DE	6.50 u
TE	298.3 K
D1	2.00000000 s
TD0	1
======== CHANNEL f1 =====	
NUC1	1H
P1	9.40 u
PL1	-3.20 d
PL1W	33.59817505 W
SFO1	700.1516910 M
SI	131072
SF	700.1471400 M
WDW	EM
SSB	0
LB	0.30 H
GB	0
PC	1.00

4284-1



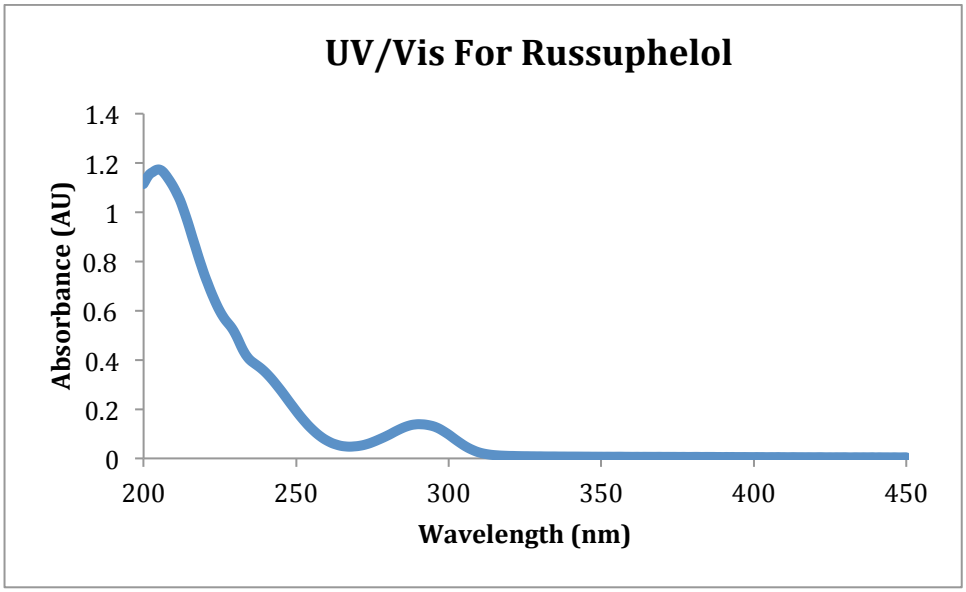
NAME	4284-1
EXPNO	6
PROCNO	1
Date_	20140531
Time	21.11
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	5000
DS	1
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0697436 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

HMBC for **14**




```
NAME                    4284-1
EXPNO                        8
PROCNO                       1
Date_                 20140601
Time                      1.47
INSTRUM                   spect
PROBHD   5 mm CPDCH 13C
PULPROG              hmbcetgp13nd
TD                        0x59
SOLVENT                   CDCl3
NS                            8
DS                            1
SWH                   7002.801 Hz
FIDRES                1.709668 Hz
AQ                    0.2925044 sec
RG                         2032
DW                       71.400 usec
DE                        6.50 usec
TE                     298.0000 K
CNST6                145.0000000
CNST7                160.0000000
CNST13                 8.0000000
CNST30                 0.59811154
D0                     0.00000300 sec
D1                     1.50000000 sec
D6                     0.06250000 sec
D16                    0.00020000 sec
IN0                    0.00001280 sec

========== CHANNEL f1 ==========
NUC1                         1H
P1                         9.40 usec
P2                        18.80 usec
PL1                       -3.20 dB
PLIW                  33.59817505 W
SFO1                700.1506407 MHz

========== CHANNEL f2 ==========
NUC2                         13C
P3                         9.00 usec
P24                     2000.00 usec
PL2                        4.50 dB
PL2W                  38.14553833 W
SFO2                176.0697152 MHz
SF7                        12.32 dB
SPNAM7          Crp80comp.4
SPOAL7                      0.500
SPOFFS7                     0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1                   SINE.100
GPNAM3                   SINE.100
GPNAM4                   SINE.100
GPNAM5                   SINE.100
GPNAM6                   SINE.100
GP21                     80.000 %
GP22                     14.00 %
GP23                     -4.00 %
GP25                     -2.00 %
GP26                   1000.00 usec
P16                          512
NDO                            2
TD                           512
SFO1                 176.0697 MHz
FIDRES               76.375435 Hz
SW                   222.095 ppm
FnMODE               Echo-Antiecho
SP                        -1.00
WDW                    QSINE 2
SSB                            0
LB                      0.00 Hz
GB                             0
PC                          1.00
SI                          1024
MC2                 echo-antiecho
SF                   176.0521380 MHz
WDW                    QSIND 2
SSB                            0
LB                      0.00 Hz
GB                             0
```

Russuphelol UV/Vis Data

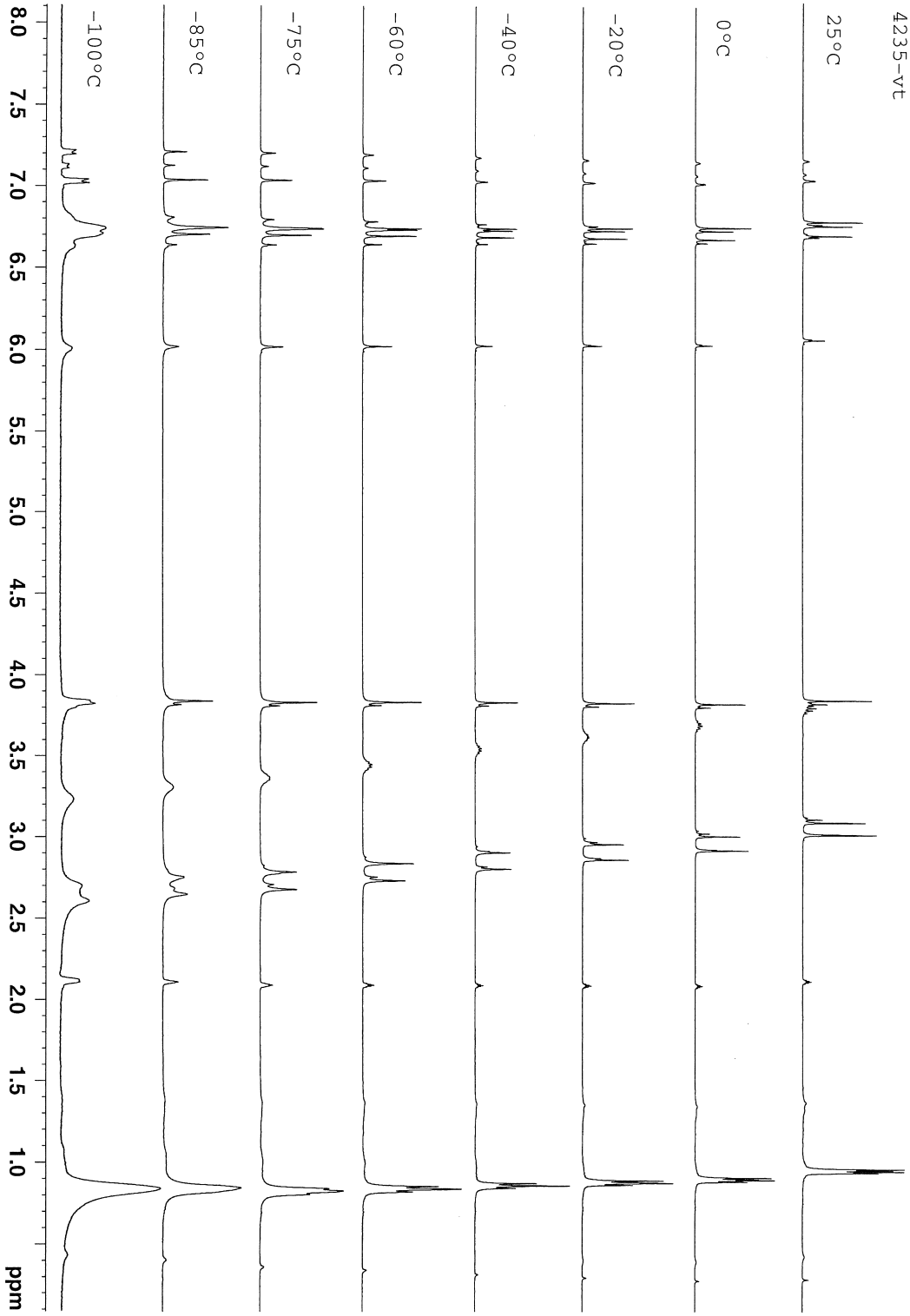


λmax = 286 nm

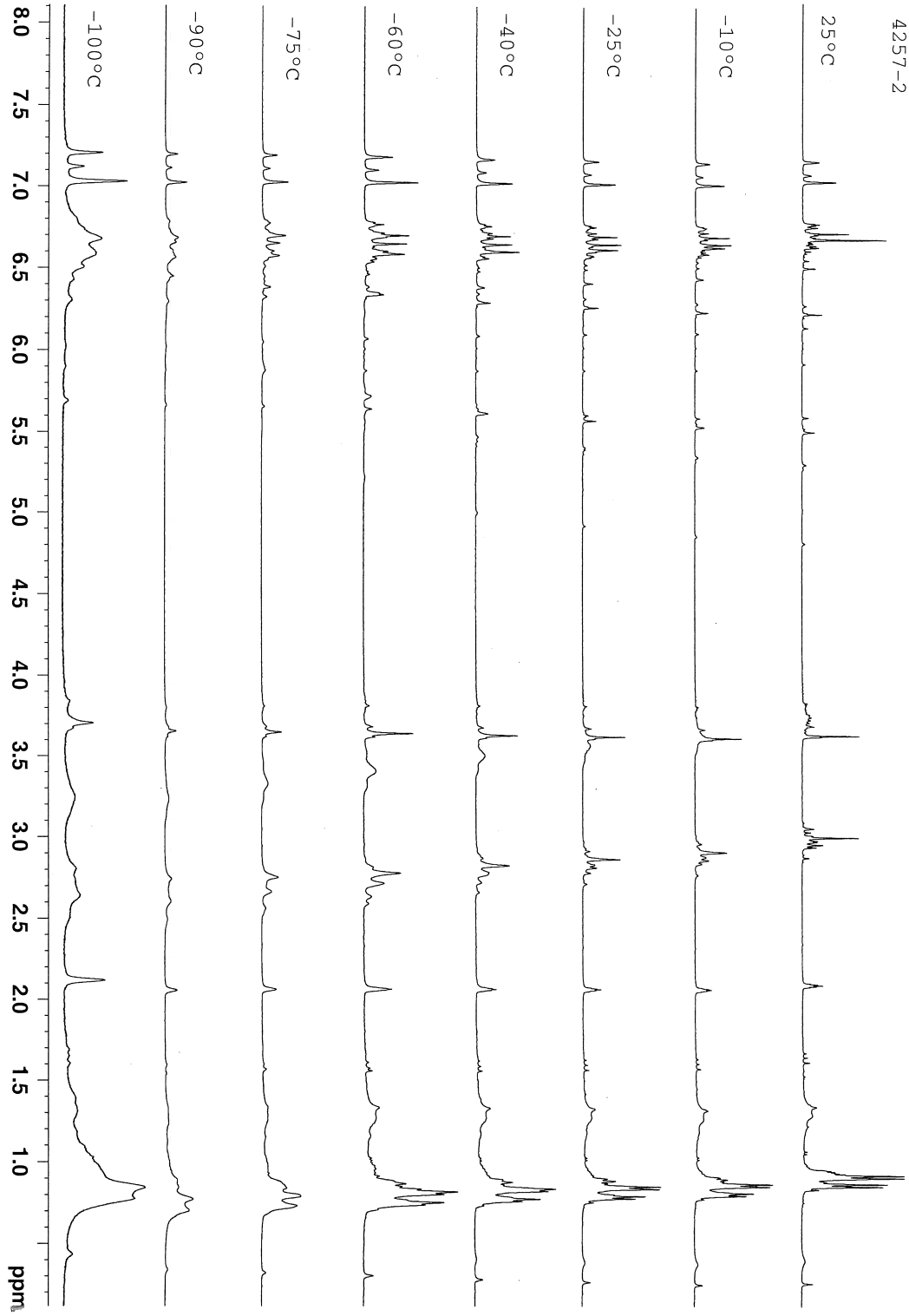
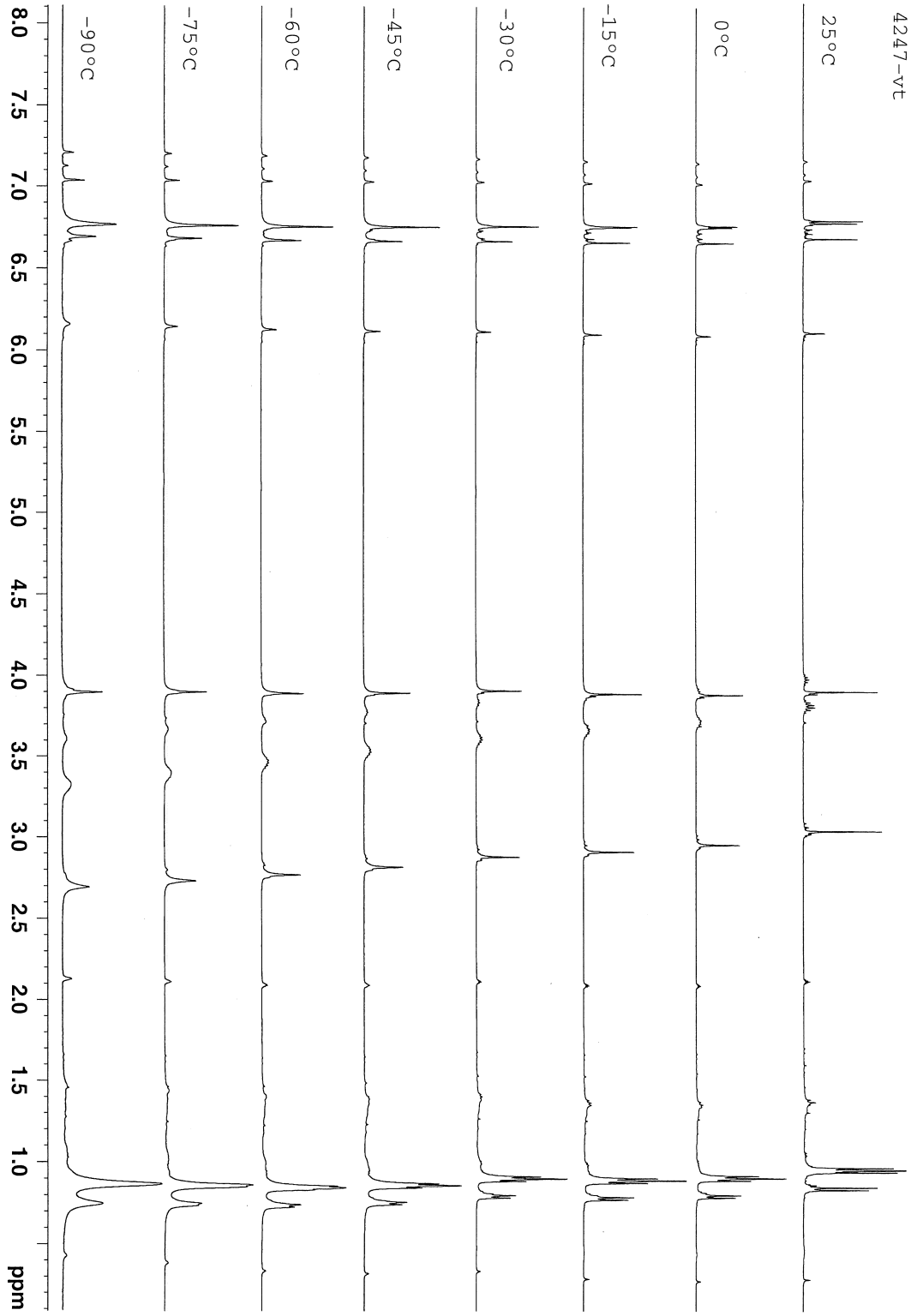
	Isolated	Synthetic
Color	brown	white
Appearance	powder	crystals
Melting point (°C)	233-235	210
λmax	280	286

Low Temperature NMR Data

VTNMR for **S1** in *d*-Toluene



VTNMR for **10** in *d*-Toluene



VTNMR for **12** in *d*-Toluene