Base-Mediated Meerwein–Ponndorf–Verley Reduction of Aromatic and Heterocyclic Ketones

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Supporting Information – Table of Contents

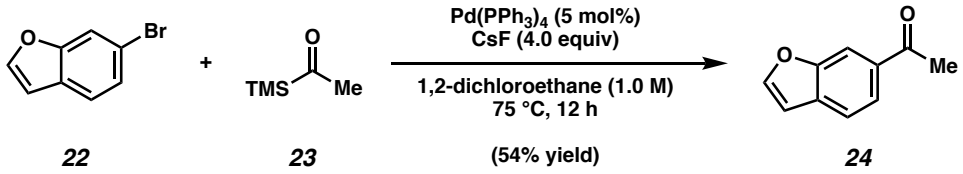
Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen or argon and commercially obtained reagents were used as received. Not-commercially available ketone substrates were synthesized following protocols specified in Section A in the Experimental Procedures. Alcohols **5** and (*R*)-**5** were synthesized following protocols specified in Section B and C in the Experimental Procedures, respectively. 1,2-Dicholoroethane, 1,4-dioxane, and isopropanol were obtained from Fischer Scientific and purified by distillation. 3-Pentanol (**3**) and 1-phenylethanol (**4**) were obtained from Sigma-Aldrich and purified by distillation. Prior to use, 1,4-dioxane, isopropanol, 3-pentanol (**3**) and 1-phenylethanol (**4**) were degassed by sparging with N_2 for 1 h. Ketone **1**[1] and **36**[2] were prepared according to literature procedures. **22**, **28**, **29**, **30**, **31**, and **34** were obtained from Sigma-Aldrich. **26**, **21**, **27**, **32**, **35**, and **37** was obtained from Combi-Blocks. Ketone **26** was obtained from Oxchem. Ketone **33** was obtained from Alfa Aesar. $Pd(PPh_3)_4$ (99%) was obtained from Strem Chemicals. Acetyltrimethylsilane (**23**) (97%) was obtained from Sigma-Aldrich. Cesium fluoride (99%+) was obtained from Strem Chemicals. Potassium phosphate (K_3PO_4) was obtained from Acros. Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm for analytical chromatography and 0.50 mm for preparative chromatography) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining techniques. Silicycle Siliaflash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Bruker spectrometers (at 300, 400, 500, and 600 MHz) and are reported relative to residual solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (at 75 and 125 MHz). IR spectra were recorded on a Perkin-Elmer UATR Two FT-IR spectrometer and are reported in terms of frequency absorption (cm^{-1}). DART-MS spectra were collected on a Thermo Exactive Plus MSD (Thermo Scientific) equipped with an ID-CUBE ion source and a Vapur Interface (IonSense Inc.). Both the source and MSD were controlled by Excalibur software v. 3.0. The analyte was spotted onto OpenSpot sampling cards (IonSense Inc.) using $CHCl_3$ or CH_2Cl_2 as the solvent. Ionization was accomplished using UHP He plasma with no additional ionization agents. The mass calibration was carried out using Pierce LTQ Velos ESI (+) and (–) Ion

calibration solutions (Thermo Fisher Scientific). Optical rotations were measured with a Rudolf Autopol III Automatic Polarimeter. Trace metal analysis was determined by inductively coupled plasma mass spectrometry on an Agilent 8800 Triple Quadrupole ICP-MS instrument. The level of all analytes of interest was determined in MS/MS mode, measured using He in the collision/reaction cell using an environmental calibration standard (elements not included in this standard: B, Ti, Rb, Ru, Rh, Pd, Ir, and Pt). The quantification was done using the ICP-MS MassHunter WorkStation v4.3, through the QuickScan acquisition. Nitric acid was obtained from Fisher Scientific (A467500). Determination of enantiopurity was carried out on a Mettler Toledo SFC (supercritical fluid chromatography) or Agilent HPLC (high performance liquid chromatography) using Daicel ChiralPak IC–3 and Daicel ChiralPak OD–H columns. Data for SFC and HPLC spectra are reported in enantiomeric excess (ee). For SFC and HPLC chromatograms see Section I of Experimental Procedures.

Experimental Procedures

A. Syntheses of Ketone Substrates

Representative Procedure for the Synthesis of Ketone Substrates (synthesis of ketone 24 is used as an example).

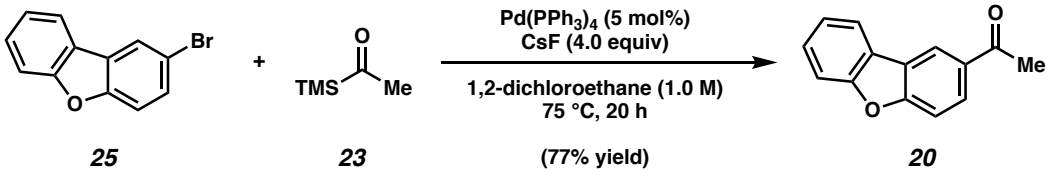


22 ***23*** ***24***

A flame-dried 1-dram vial was charged 6-bromobenzofuran (**22**) (130 mg, 0.660 mmol, 1.00 equiv) and a magnetic stir bar. In the glove box, CsF (401 mg, 2.64 mmol, 4.00 equiv) and $Pd(PPh_3)_4$ (38.1 mg, 0.0330 mmol, 0.0500 equiv) were added to the vial. The vessel was removed from the glove box and placed under an atmosphere of N_2 on the bench. Distilled 1,2-dichloroethane (0.700 mL, 1.00 M) and silane **23** (189 μL, 1.32 mmol, 2.0 equiv) were added and the vial was sealed with a Teflon-lined screw cap. The heterogeneous mixture was heated to 75 ºC for 12 h. After cooling to 23 ºC, the mixture was diluted with hexanes (0.5 mL), filtered over a plug of silica gel (1.00 cm OD x 5.00 cm, 10 mL EtOAc eluent), and the volatiles were removed under reduced pressure. The crude residue was purified by flash chromatography (19:1 Hexanes:EtOAc → 14:1 Hexanes:EtOAc) to yield ketone **24** (57.0 mg, 54% yield) as a yellow oil. Ketone **24**: R_f 0.42 (5:1 Hexanes:EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.89 (dd, J = 8.30, 1.38 Hz, 1H), 7.79 (d, J = 2.17 Hz, 1H), 7.66 (d, J = 8.30 Hz, 1H), 6.87–6.89 (m, 1H), 2.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8, 154.8, 148.4, 134.0, 132.0, 123.3, 121.2, 112.0, 107.0, 27.0; IR (film): 3118, 3003, 1673, 1425, 1271 cm^{-1}; HRMS-APCI (*m/z*) $[M+NH_4]^+$ calcd for $C_{10}H_{12}O_2N^+$, 178.08626; found 178.08536.

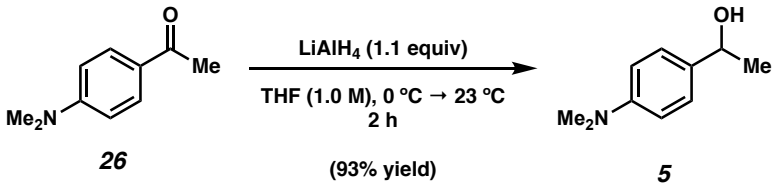
Note: Supporting information for the synthesis of ketone **36** has previously been reported.[2] The synthesis of the remaining substrate, **20**, is as follows:

Any modifications of the conditions shown in the representative procedure above are specified in the following scheme.



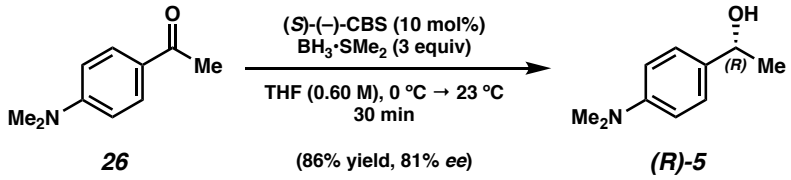
Ketone 20. Purification by flash chromatography (49:1 Hexanes:EtOAc) generated ketone **20** (263 mg, 77% yield) as a white solid. Ketone **20**: R_f 0.33 (9:1 Hexanes:EtOAc). Spectral data match those previously reported.[3]

B. Synthesis of Alcohol Reductant 5

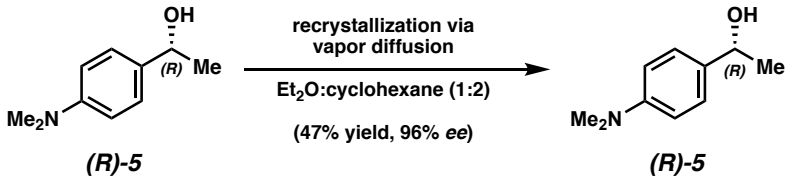


To a flame-dried flask equipped with a magnetic stir bar was added $LiAlH_4$ (2.56 g, 67.4 mmol, 1.10 equiv) in a glovebox. The flask was removed from the glovebox, THF (61.0 mL) was added, and the solution was cooled to 0 °C. To the solution was then added ketone **26** (2.00 g, 61.5 mmol each, 0.200 equiv) in 5 aliquots over 25 min. The reaction was then warmed to 23 °C. After stirring for 2 h, the reaction was cooled to 0 °C and quenched by the sequential addition of deionized water (5 mL), 10% aq. NaOH (7 ml), MeOH (20 mL), and deionized water (10 mL). The mixture was then warmed to 23 °C and stirred for 30 min. The mixture was then filtered over a pad of celite (100 mL EtOAc eluent). The resulting organic layer was dried over Na_2SO_4, filtered, and the volatiles were removed under reduced pressure. The crude residue was purified by flash chromatography (5:1 Hexanes:EtOAc → 3:1 Hexanes:EtOAc) to yield alcohol **5** (9.42 g, 93% yield) as a white solid. Alcohol **5**: R_f 0.33 (3:1 Hexanes:EtOAc). Spectral data match those previously reported.[4]

C. Synthesis of Enantioenriched Alcohol Reductant (*R*)-5



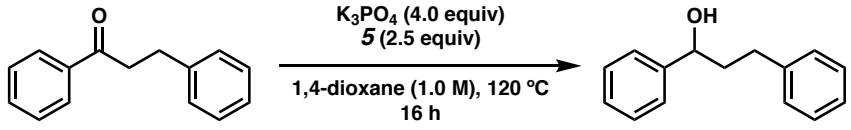
To a flame-dried flask equipped with a magnetic stir bar was added (*S*)-(–)-CBS catalyst (170 mg, 0.613 mmol, 0.100 equiv). The flask was removed from the glovebox and THF (6.13 mL) was added. Next, **26** (1.00 g, 6.13 mmol, 1.00 equiv) in a solution of THF (2.50 mL) was added to the reaction flask, which was then stirred to give a clear homogeneous solution and cooled to 0 °C. Subsequently, BH_3•SMe_2 (1.70 mL, 18.4 mmol, 3.00 equiv) was added (1 drop/2 sec) over 7.50 min. The reaction was stirred at 0 °C for 2 min, then warmed to 23 °C. After stirring for 30 min, the reaction was cooled to 0 °C and quenched by the dropwise addition of methanol (20 mL) and water (20 mL) and diluted with Et_2O (50 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with sat. aq. NH_4Cl (80 mL), sat. aq. $NaHCO_3$ (80 mL), and brine (80 mL). The organic layer was then dried over Na_2SO_4, filtered, and the volatiles were removed under reduced pressure. The crude residue was purified by flash chromatography (10:1 Hexanes:EtOAc → 3:1 Hexanes:EtOAc) to yield alcohol **(*R*)-5** (871 mg, 86% yield, 81% ee) as a white solid. Alcohol **(*R*)-5**: R_f 0.33 (3:1 Hexanes:EtOAc). The spectral data match those previously reported in the literature for ***rac*-5**.[4] The SFC data match those reported in the Experimental Procedures Section G.



A solution of **(*R*)-5** (25.0 mg, 0.151 mmol, 1.00 equiv) in Et_2O (1.00 mL) was filtered through a 0.45 μm Millipore Millex PTFE filter into a 1-dram vial. The vial was then placed within a 20 mL scintillation vial containing cyclohexane (2.00 mL). The scintillation vial was sealed and allowed to stand at 23 °C for 24 h, which led to the formation of white crystals. This vapor

diffusion crystallization process was repeated three times to lead to the recovery of alcohol **(*R*)-5** (11.8 mg, 47% yield, 96% ee) as a white crystalline solid. $[\alpha]_D^{23.1}$ = +51.6 (*c* = 1.00, $CHCl_3$). The spectral data match those previously reported in the literature for ***rac*-5**.[4] The major enantiomer product was assigned by comparison to published $[\alpha]_D$ values for **(*R*)-5**.[5]

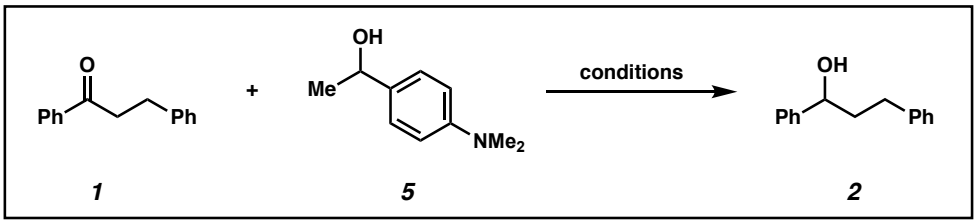
D. Survey of Reaction Conditions and Relevant Control Experiments



1 ***2***

Representative Procedure for Base-Mediated MPV Reduction from Table S1 (reduction of ketone 1 with alcohol 5 is used as an example). A 1-dram vial was charged with anhydrous powdered K_3PO_4 (85.0 mg, 0.400 mmol, 4.00 equiv) and a magnetic stir bar. The vial and its contents were flame-dried under reduced pressure, then allowed to cool under N_2. Ketone substrate **1** (21.0 mg, 0.100 mmol, 1.00 equiv) and alcohol reductant **5** (41.3 mg, 0.250 mmol, 2.50 equiv) were added. The vial was flushed with N_2, and then 1,4-dioxane (0.100 mL, 1.00 M) was added. Under a stream of N_2, the vial septum cap was quickly switched for a Teflon-lined screw cap, sealed, then further sealed with electrical tape. The reaction was stirred vigorously (800 rpm) at 120 °C for 16 h. After cooling to 23 °C, the mixture was diluted with hexanes (0.5 mL) and filtered over a plug of silica gel (1 cm OD x 5 cm, 10 mL EtOAc eluent). The volatiles were removed under reduced pressure and the yield of alcohol **2** was determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an external standard.

Any modifications of the conditions shown in the representative procedure above are specified below in Table S1.



Reaction Conditions	*Experimental Results*[a] *1*	*2*
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), dioxane (1.0 M), 120 °C, 16 h**	**0%**	**99%**
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), dioxane (1.0 M), 80 °C, 16 h**	**0%**	**99%**
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), dioxane (1.0 M), 120 °C, 3 h**	**<5%**	**98%**
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), 2-Me THF (1.0 M), 80 °C, 16 h**	**0%**	**99%**
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), *t*-amyl alcohol (1.0 M), 80 °C, 16 h**	**<5%**	**98%**
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), *n*-heptane (1.0 M), 80 °C, 16 h**	**11%**	**89%**
Control Experiments:		
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), dioxane (1.0 M), 120 °C, 16 h** ***Ran in the dark***	**0%**	**99%**
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), H_2O (2.0 equiv), dioxane (1.0 M), 120 °C, 16 h**	**<5%**	**95%**
5 **(2.5 equiv), K_3PO_4 (4.0 equiv), dioxane (1.0 M), 120 °C, 16 h** ***Ran under an atmosphere of air***	**12%**	**88%**

[a] **Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an external standard.**

Table S1. Survey of Reaction Conditions and Relevant Control Experiments

E. Trace Metal Analysis

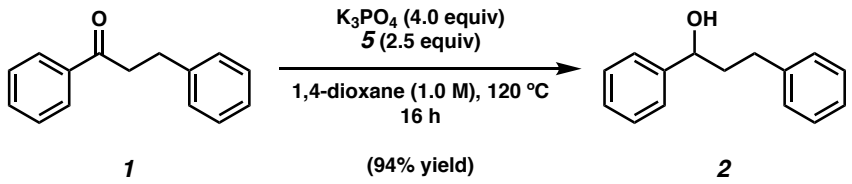
Representative Procedure for Trace Metal Analysis (preparation of K_3PO_4 is used as an example). A 15-mL conical tube was charged with K_3PO_4 (95.2 mg, 1.00 equiv) and the sample was diluted with milli-Q water (6.8 mL) to a final concentration of 1.4% (w/w). Subsequently, ICP-MS-grade 70% nitric acid (200 µl) was added to each sample (2% final nitric acid concentration).

Sample: K_3PO_4	
Metal	**Concentration (ppm) (average of two samples)**
Fe	0.00809
Al	0.000
Co	0.000
B	0.0240
Ti	0.0420
Mg	0.00189
Mn	7.84×10^{-5}
Sc	0.000
Rb	0.203
Ni	0.0303
Cu	0.000
Zn	0.000
Ru	9.46×10^{-6}
Rh	0.000
Pd	1.53×10^{-5}
Ag	0.000
Ir	1.17×10^{-6}
Pt	0.000

Sample: 1,4-dioxane	
Metal	**Concentration (ppm) (average of two samples)**
Fe	0.00369
Al	0.00384
Co	0.000130
B	0.00570
Ti	0.00250
Mg	0.01780
Mn	0.000151
Sc	0.00190
Rb	3.41×10^{-5}
Ni	0.354
Cu	0.000
Zn	0.000
Ru	0.000
Rh	0.000
Pd	1.06×10^{-5}
Ag	2.85×10^{-5}
Ir	0.000
Pt	0.000

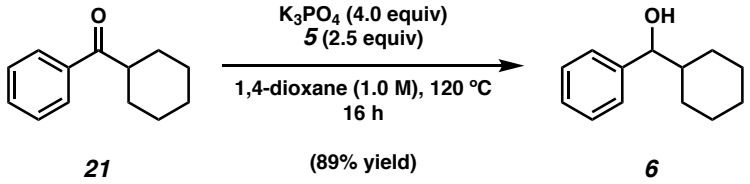
Sample: Alcohol Reductant 5	
Metal	**Concentration (ppm) (average of two samples)**
Fe	0.00352
Al	0.00121
Co	3.20×10^{-5}
B	0.0211
Ti	0.000642
Mg	0.0125
Mn	1.81×10^{-5}
Sc	0.000962
Rb	5.15×10^{-6}
Ni	0.113
Cu	0.000
Zn	0.000
Ru	0.000
Rh	9.31×10^{-7}
Pd	3.00×10^{-6}
Ag	7.91×10^{-6}
Ir	0.000
Pt	1.76×10^{-6}

F. Scope of Methodology

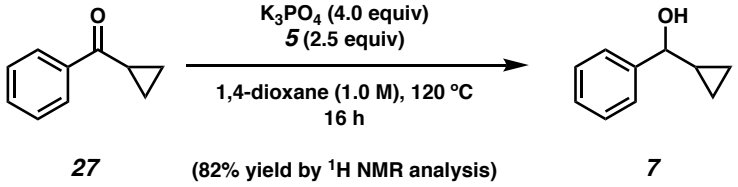


Representative Procedure for Base-Mediated MPV Reduction from Figure 2 (reduction of ketone 1 with alcohol 5 is used as an example). Alcohol 2. A 1-dram vial was charged with anhydrous powdered K_3PO_4 (85.0 mg, 0.400 mmol, 4.00 equiv) and a magnetic stir bar. The vial and its contents were flame-dried under reduced pressure, then allowed to cool under N_2. Ketone substrate **1** (21.0 mg, 0.100 mmol, 1.00 equiv) and alcohol reductant **5** (41.3 mg, 0.250 mmol, 2.50 equiv) were added. The vial was purged with N_2, and then 1,4-dioxane (0.100 mL, 1.00 M) was added. Under a stream of N_2, the vial septum cap was quickly switched for a Teflon-lined screw cap, sealed, then further sealed with electrical tape. The reaction was stirred vigorously (800 rpm) at 120 °C for 16 h. After cooling to 23 °C, the reaction was quenched by the addition of sat. aq. NH_4Cl (1.00 mL) and diluted with EtOAc (2.00 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 2.00 mL) and the combined organic layers were passed through a plug (1.00 cm OD) of silica gel (3.00 cm tall) and Na_2SO_4 (3.00 cm tall) using EtOAc (10.0 mL) as eluent. The volatiles were removed under reduced pressure. The crude residue was purified by flash chromatography (99:1 Hexanes:EtOAc → 19:1 Hexanes:EtOAc) to yield alcohol **2** (20 mg, 94% yield, average of two experiments) as a clear oil. Alcohol **2**: R_f 0.32 (5:1 Hexanes:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.33 (m, 4H), 7.32–7.26 (m, 3H), 7.23–7.16 (m, 3H), 4.78–4.61 (m, 1H), 2.85–2.61 (m, 2H), 2.23–1.97 (m, 2H), 1.87 (d, J = 3.5 Hz, 1H). Spectral data match those previously reported.[6]

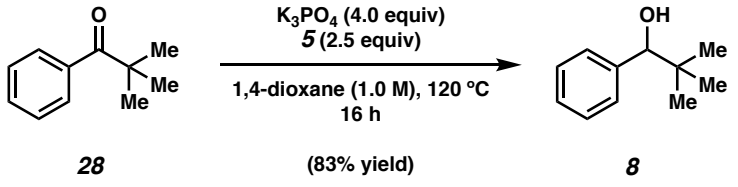
Any modifications of the conditions shown in the representative procedure above are specified in the following schemes, which depict all of the results shown in Figures 2 and 3.



Alcohol 6. Purification by flash chromatography (99:1 Hexanes:EtOAc → 19:1 Hexanes:EtOAc) generated alcohol **6** (17 mg, 89% yield, average of two experiments) as a crystalline white solid. Alcohol **6**: R_f 0.39 (5:1 Hexanes:EtOAc).). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.25 (m, 5H), 4.37 (dd, J = 7.2 Hz, 3.3 Hz, 1H), 2.03–1.92 (m, 1H), 1.84–1.72 (m, 2H), 1.71–1.57 (m, 3H), 1.41–1.33 (m, 1H), 1.29–1.00 (m, 4H), 0.99–0.87 (m, 1H). Spectral data match those previously reported.[7]

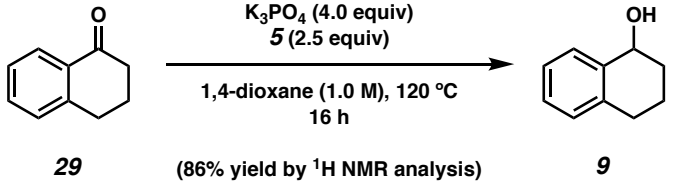


Alcohol 7. ^{1}H NMR analysis of the crude reaction mixture indicated an 82% yield of alcohol **7** relative to hexamethylbenzene external standard (average of two experiments). Purification by preparative thin-layer chromatography (3:1 Hexanes:EtOAc) provided an analytical sample of alcohol **7** as a clear oil. Alcohol **7**: R_f 0.30 (5:1 Hexanes:EtOAc).). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.40 (m, 2H), 7.39–7.33 (m, 2H), 7.32–7.27 (m, 1H), 4.02 (dd, J = 8.3, 3.0, 1H), 1.90 (d, J = 3.0, 1H), 1.28–1.18 (m, 1H), 0.69–0.61 (m, 1H), 0.60–0.52 (m, 1H), 0.52–0.44 (m, 1H), 0.42–0.34 (m, 1H). Spectral data match those previously reported.[8]

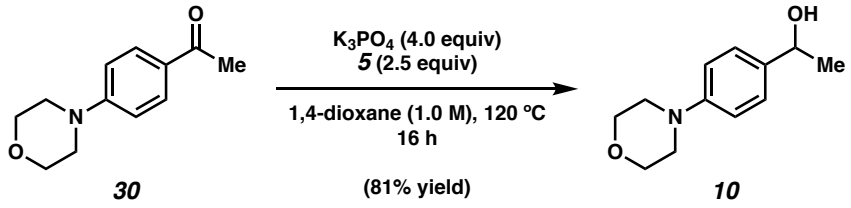


Alcohol 8. Purification by flash chromatography (24:1 Hexanes:EtOAc) generated alcohol **8** (14 mg, 83% yield, average of two experiments) as a white crystalline solid. Alcohol **8**: R_f 0.52 (5:1

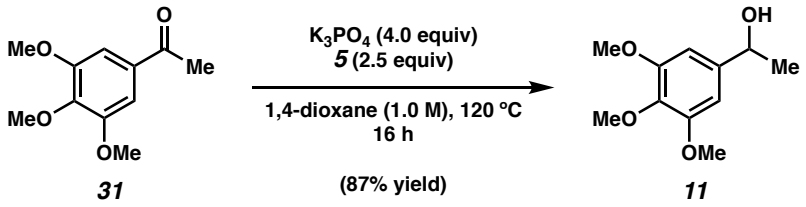
Hexanes:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.30 (m, 4H), 7.29–7.26 (m, 1H), 4.40 (d, J = 2.8, 1H), 1.84 (d, J = 2.8, 1H), 0.93 (s, 9H). Spectral data match those previously reported.[9]



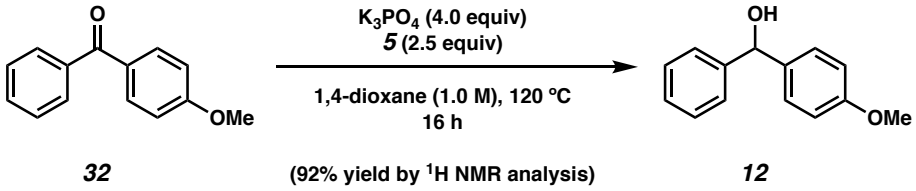
Alcohol 9. ^{1}H NMR analysis of the crude reaction mixture indicated an 86% yield of alcohol **9** relative to hexamethylbenzene external standard (average of two experiments). Purification by preparative thin-layer chromatography (9:1 PhH:Acetone) provided an analytical sample of alcohol **9** as a clear oil. Alcohol **9**: R_f 0.50 (9:1 PhH:Acetone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.39 (m, 1H), 7.24–7.17 (m, 2H), 7.14–7.05 (m, 1H), 4.84–4.71 (m, 1H), 2.88–2.78 (m, 1H), 2.87–2.67 (m, 1H), 2.05–1.95 (m, 2H), 1.95–1.87 (m, 1H), 1.85–1.73 (m, 1H), 1.71–1.60 (m, 1H). Spectral data match those previously reported.[10]



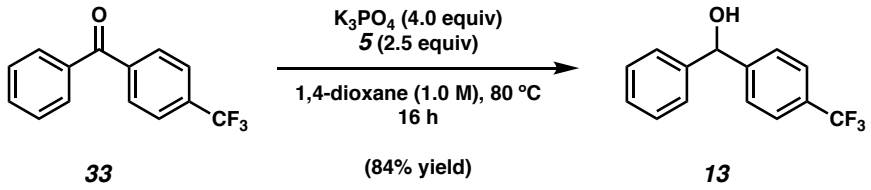
Alcohol 10. Purification by flash chromatography (2:2:1 CH_2Cl_2:Et_2O:Hexanes) generated alcohol **10** (17 mg, 81% yield, average of two experiments) as a pale yellow solid. Alcohol **10**: R_f 0.24 (1:1:1 CH_2Cl_2:Et_2O:Hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.28 (m, 2H), 6.93–6.87 (m, 2H), 4.85 (dq, J = 6.4, 3.5, 1H), 3.90–3.83 (m, 4H), 3.19–3.12 (m, 4H), 1.67 (d, J = 3.5, 1H), 1.48 (d, J = 6.4, 3H). Spectral data match those previously reported.[11]



Alcohol 11. Purification by flash chromatography (9:1 Hexanes:EtOAc → 2:1 Hexanes:EtOAc) generated alcohol **11** (18 mg, 87% yield, average of two experiments) as a clear oil. Alcohol **11**: R_f 0.33 (1:1 Hexanes:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60 (s, 2H), 4.89–4.77 (m, 1H), 3.86 (s, 6H), 3.83 (s, 3H), 1.99–1.80 (m, 1H), 1.48 (d, J = 6.4, 3H). Spectral data match those previously reported.[11]

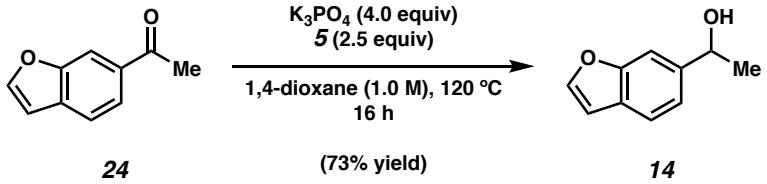


Alcohol 12. ^{1}H NMR analysis of the crude reaction mixture indicated a 92% yield of alcohol **12** relative to hexamethylbenzene external standard (average of two experiments). Purification by preparative thin-layer chromatography (3:3:2 CH_2Cl_2:Et_2O:Hexanes) provided an analytical sample of alcohol **12** as a pale yellow solid. Alcohol **12**: R_f 0.70 (1:1:1 CH_2Cl_2:Et_2O:Hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.31 (m, 4H), 7.31–7.23 (m, 3H), 6.93–6.81 (m, 2H), 5.82 (d, J = 3.0, 1H), 3.79 (s, 3H), 2.15 (d, J = 3.4, 1H). Spectral data match those previously reported.[7]

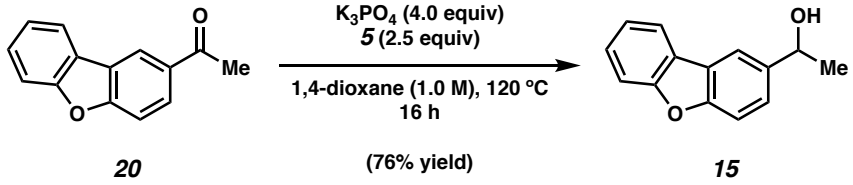


Alcohol 13. Purification by flash chromatography (9:1 Hexanes:Et_2O → 3:1 Hexanes:Et_2O) generated alcohol **13** (21 mg, 84% yield, average of two experiments) as a clear oil. Alcohol **13**: R_f 0.30 (5:1 Hexanes:Et_2O). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.3, 2H), 7.51 (d, J =

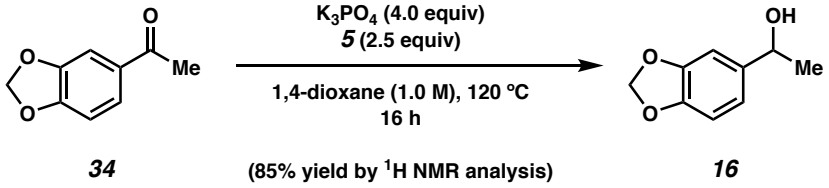
8.3, 2H), 7.42–7.34 (m, 4H), 7.34–7.28 (m, 1H), 5.88 (s, 1H), 2.46–2.32 (m, 1H). Spectral data match those previously reported.[7]



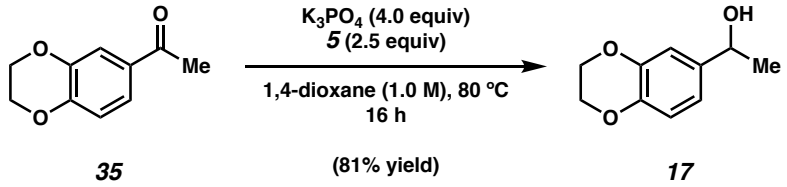
Alcohol 14. Purification by flash chromatography (90:9:1 → 15:9:1 Hexanes:PhH:Acetone) generated alcohol **14** (12 mg, 73% yield, average of two experiments) as a yellow oil. Alcohol **14**: R_f 0.39 (9:1 PhH:Acetone); ^{1}H NMR (500 MHz, C_6D_6): δ 7.50–7.46 (m, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.12 (ddd, J = 8.1, 1.4, 0.5 Hz, 1H), 6.35 (dd, J = 2.2, 1.1 Hz, 1H), 4.59 (q, J = 6.5 Hz, 1H), 1.29 (d, J = 6.5 Hz, 3H), 1.14, (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.3, 145.4, 142.8, 126.9, 121.2, 120.6, 108.4, 106.5, 70.7, 25.6; IR (film): 3350, 2972, 2926, 1430, 1265 cm^{-1}; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_{10}H_{11}O_2^+$, 163.0754; found 163.0746.



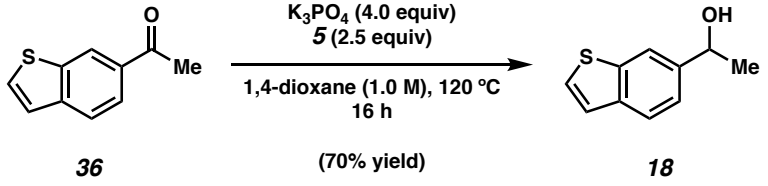
Alcohol 15. Purification by flash chromatography (90:9:1 → 25:9:1 Hexanes:PhH:Acetone) generated alcohol **15** (16 mg, 76% yield, average of two experiments) as a yellow solid. Alcohol **15**: R_f 0.35 (9:1 PhH:Acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.91 (m, 2H), 7.60–7.51 (m, 2H), 7.50–7.43 (m, 2H), 7.35 (td, J = 7.5, 1.0, 1H), 5.09 (dq, J = 6.4, 3.3, 1H), 1.90 (d, J = 3.3, 1H), 1.60 (d, J = 6.4, 3H). Spectral data match those previously reported.[12]



Alcohol 16. ^{1}H NMR analysis of the crude reaction mixture indicated an 85% yield of alcohol **16** relative to hexamethylbenzene external standard. Purification by preparative thin-layer chromatography (13:1:1 PhH:Et_2O:CH_3CN) provided an analytical sample of alcohol **16** as a yellow oil. Alcohol **16**: R_f 0.30 (13:1:1 PhH:Et_2O:CH_3CN); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.90 (s, 1H), 6.82 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 2H), 4.86–4.79 (m, 1H), 1.70 (d, *J* = 3.4 Hz, 1H), 1.46 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.9, 147.0, 140.1, 118.8, 108.2, 106.2, 101.1, 70.4, 25.3; IR (film): 3361, 2972, 2890, 1487, 1240 cm^{-1}; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_9H_{11}O_3^+$, 167.0703; found 167.0699.

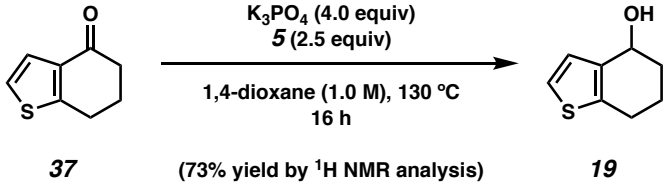


Alcohol 17. Purification by flash chromatography (98:1:1 → 28:1:1 PhH:Et_2O:CH_3CN) generated alcohol **17** (15 mg, 81% yield, average of two experiments) as a yellow oil. Alcohol **17**: R_f 0.32 (13:1:1 PhH:Et_2O:CH_3CN). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.92–6.88 (m, 1H), 6.86–6.81 (m, 2H), 4.80 (dq, *J* = 6.4, 3.6, 1H), 4.25 (s, 4H), 1.69 (d, *J* = 3.6, 1H), 1.46 (d, *J* = 6.4, 3H). Spectral data match those previously reported.[13]



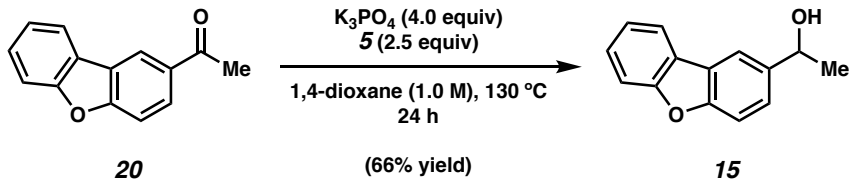
Alcohol 18. Purification by flash chromatography (90:9:1 → 40:9:1 Hexanes:PhH:Acetone) generated alcohol **8** (12 mg, 70% yield, average of two experiments) as a yellow oil. Alcohol **18**: R_f 0.38 (9:1 PhH:Acetone); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.80 (d, *J* = 8.2 Hz,

1H), 7.43 (d, J = 5.5 Hz, 1H), 7.38 (dd, J = 8.3, 1.3 Hz, 1H), 7.32 (d, J = 5.5 Hz, 1H), 5.10–5.0 (m, 1H), 1.85 (d, J = 3.4 Hz, 1H), 1.56 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.3, 140.1, 139.2, 126.6, 123.8, 123.7, 122.3, 119.2, 70.7, 25.5; IR (film): 3351, 2971, 1398, 1197, 1074 cm^{-1}; HRMS-APCI (*m/z*) $[M]^+$ calcd for $C_{10}H_{10}OS^+$, 178.0447; found 178.0437.



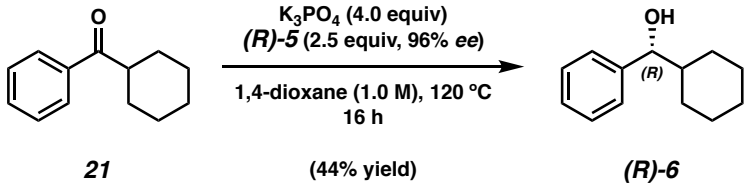
Alcohol 19. ^{1}H NMR analysis of the crude reaction mixture indicated a 73% yield of alcohol **19** relative to hexamethylbenzene external standard. Purification by preparative thin-layer chromatography (1:1:1 Hexanes:Et_2O:CH_2Cl_2) provided an analytical sample of alcohol **19** as a white crystalline solid. Alcohol **19**: R_f 0.48 (1:1:1 Hexanes:Et_2O:CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (dt, J = 5.2, 0.7 Hz, 1H), 7.03 (d, J = 5.2 Hz, 1H), 4.82–4.75 (m, 1H), 2.89–2.79 (m, 1H), 2.77–2.67 (m, 1H), 2.06–1.94 (m, 2H), 1.93–1.79 (m, 2H), 1.64 (d, J = 7.0 Hz 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0, 138.1, 126.7, 122.9, 65.6, 32.5, 25.2, 20.1; IR (film): 3235, 2936, 2921, 1431, 982 cm^{-1}; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_8H_{11}OS^+$, 155.0525; found 155.0521.

G. Gram-Scale Base-Mediated MPV Reduction



Alcohol 15. An 8-dram vial was charged with anhydrous powdered K_3PO_4 (4.04 g, 19.0 mmol, 4.00 equiv) and a magnetic stir bar. The vial and its contents were flame-dried under reduced pressure, then allowed to cool under N_2. Ketone substrate **20** (1.00 g, 4.76 mmol, 1.00 equiv) and alcohol reductant **5** (1.96 g, 11.9 mmol, 2.50 equiv) were then added. The vial was flushed with N_2 and subsequently 1,4-dioxane (4.76 mL, 1.00 M) was added. Under a stream of N_2, the vial septum cap was quickly switched for a Teflon-lined screw cap, sealed, then further sealed with electrical tape. The reaction was then stirred vigorously (800 rpm) at 130 °C for 24 h. After cooling to 23 °C, the reaction was quenched by the addition of sat. aq. NH_4Cl (8.00 mL) and diluted with EtOAc (6.00 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 6.00 mL) and the combined organic layers were passed through a plug (1.00 cm OD) of silica gel (3.00 cm tall) and Na_2SO_4 (3.00 cm tall) using EtOAc (10.0 mL) as eluent. The volatiles were removed under reduced pressure. The crude residue was purified by flash chromatography (60:9:1 Hexanes:PhH:Acetone → 5:9:1 Hexanes:PhH:Acetone) to yield alcohol **15** (664 mg, 66% yield) as a yellow solid. Alcohol **15**: R_f 0.32 (5:1 Hexanes:EtOAc). Spectral data match those previously reported.[12]

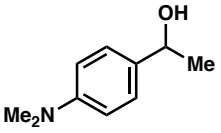
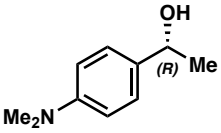
H. Stereospecific Base-Mediated MPV Reduction

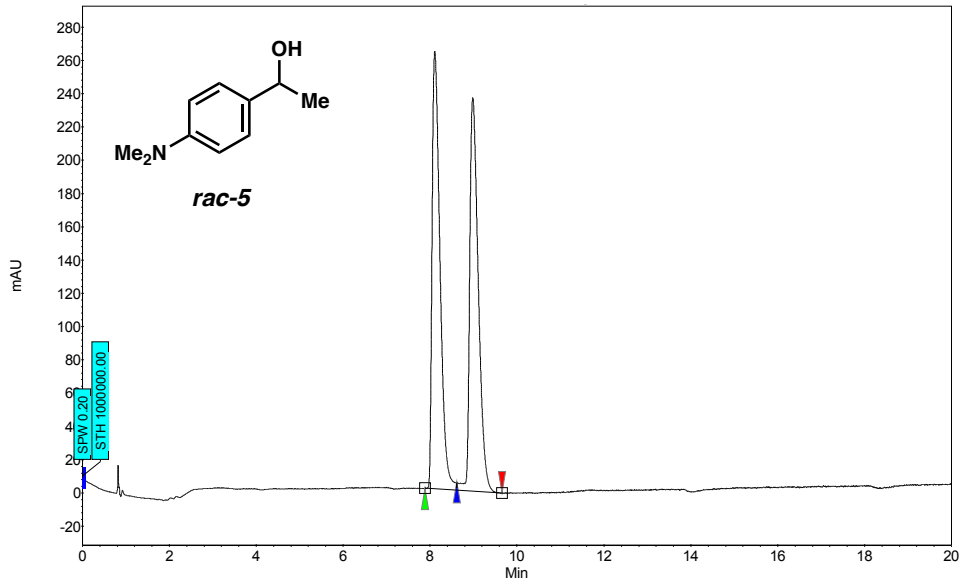


Alcohol (*R*)-6. A 1-dram vial was charged with anhydrous powdered K_3PO_4 (85.0 mg, 0.400 mmol, 4.00 equiv) and a magnetic stir bar. The vial and its contents were flame-dried under reduced pressure, then allowed to cool under N_2. Ketone substrate **21** (18.8 mg, 0.100 mmol, 1.00 equiv) and alcohol reductant **(*R*)-5** (41.3 mg, 0.250 mmol, 2.50 equiv) were added. The vial was purged with N_2 and subsequently, 1,4-dioxane (0.100 mL, 1.00 M) was added. Under a stream of N_2, the vial septum cap was quickly switched for a Teflon-lined screw cap, sealed, then further sealed with electrical tape. The reaction was stirred vigorously (800 rpm) at 120 °C for 16 h. After cooling to 23 °C, the reaction was quenched by the addition of sat. aq. NH_4Cl (1.00 mL) and diluted with EtOAc (2.00 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 2.00 mL) and the combined organic layers were passed through a plug (1.00 cm OD) of silica gel (3.00 cm tall) and Na_2SO_4 (3.00 cm tall) using EtOAc (10.0 mL) as eluent. The volatiles were removed under reduced pressure. The crude residue was purified by flash chromatography (99:1 Hexanes:EtOAc → 19:1 Hexanes:EtOAc) to yield alcohol **(*R*)-6** (8.4 mg, 44% yield, 48% ee) as a white crystalline solid. Alcohol **(*R*)-6**: R_f 0.39 (5:1 Hexanes:EtOAc). $[\alpha]_D^{21.1}$ = +20.8 (c = 0.50, $CHCl_3$). The spectral data match those previously reported in the literature for ***rac*-6**.[7] The major enantiomer product was assigned by comparison to published $[\alpha]_D$ values for **(*R*)-6**.[14]

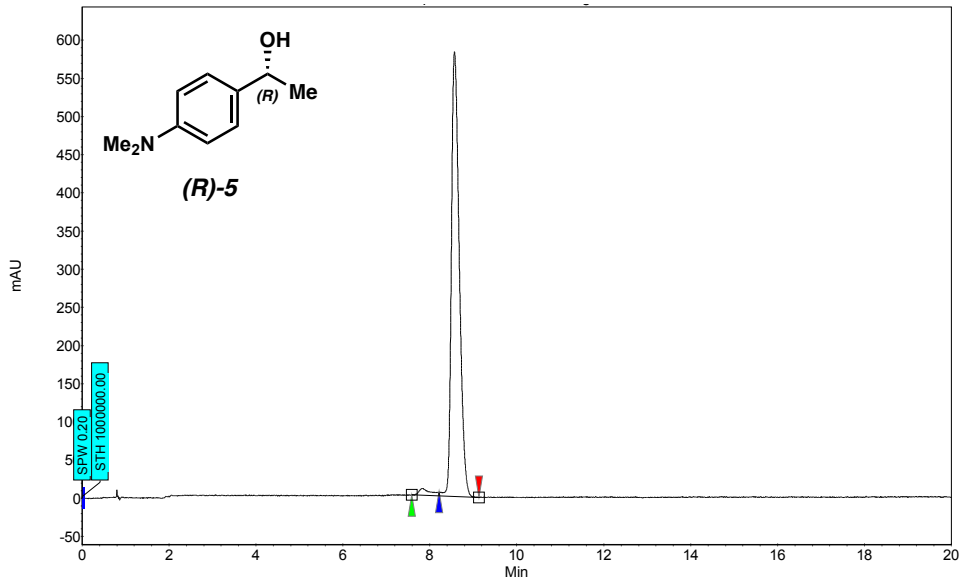
G. Verification of Enantiopurity

Chiral SFC & HPLC Assays

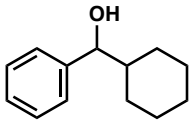
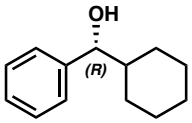
Compound	SFC Method Column/Temp. Abs. Wavelength	Solvent	Method Flow Rate	Retention Times (min)	Enantiomeric Ratio (er)
 ***rac-5***	Daicel ChiralPak IC-3/35 °C λ_{abs} = 210 nm	5% isopropanol in CO_2	3.5 mL/min	7.88/8.61	50:50
 ***(R)-5***	Daicel ChiralPak IC-3/35 °C λ_{abs} = 210 nm	5% isopropanol in CO_2	3.5 mL/min	7.58/8.22	98:2

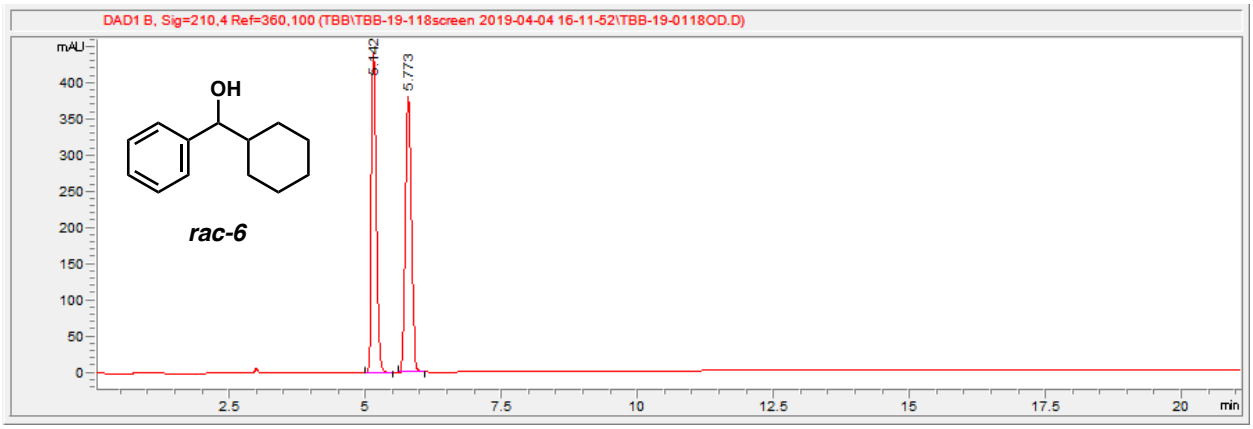


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.88	8.11	8.61	0.00	50.43	263.1	55.4	50.434
2	UNKNOWN	8.61	8.99	9.66	0.00	49.57	236.6	54.5	49.566
Total						100.00	499.7	109.9	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.58	7.82	8.22	0.00	2.18	8.7	2.7	2.176
2	UNKNOWN	8.22	8.57	9.13	0.00	97.82	582.5	122.1	97.824
Total						100.00	591.1	124.8	100.000

Compound	HPLC Method Column/Temp. Abs. Wavelength	Solvent	Method Flow Rate	Retention Times (min)	Enantiomeric Ratio (er)
 ***rac-6***	Daicel ChiralPak OD-H/23 °C λ_{abs} = 210 nm	10% isopropanol in Hexanes	1 mL/min	5.14/5.77	50:50
 ***(R)-6***	Daicel ChiralPak OD-H/23 °C λ_{abs} = 210 nm	10% isopropanol in Hexanes	1 mL/min	5.16/5.70	74:26



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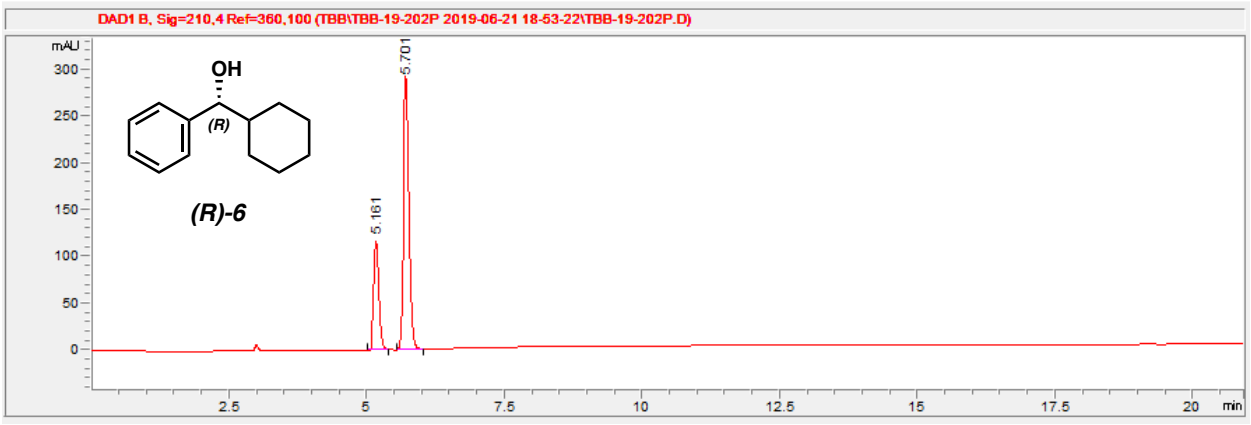

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2	5.701	2094.1	291.8	0.1107	74.081	0.837

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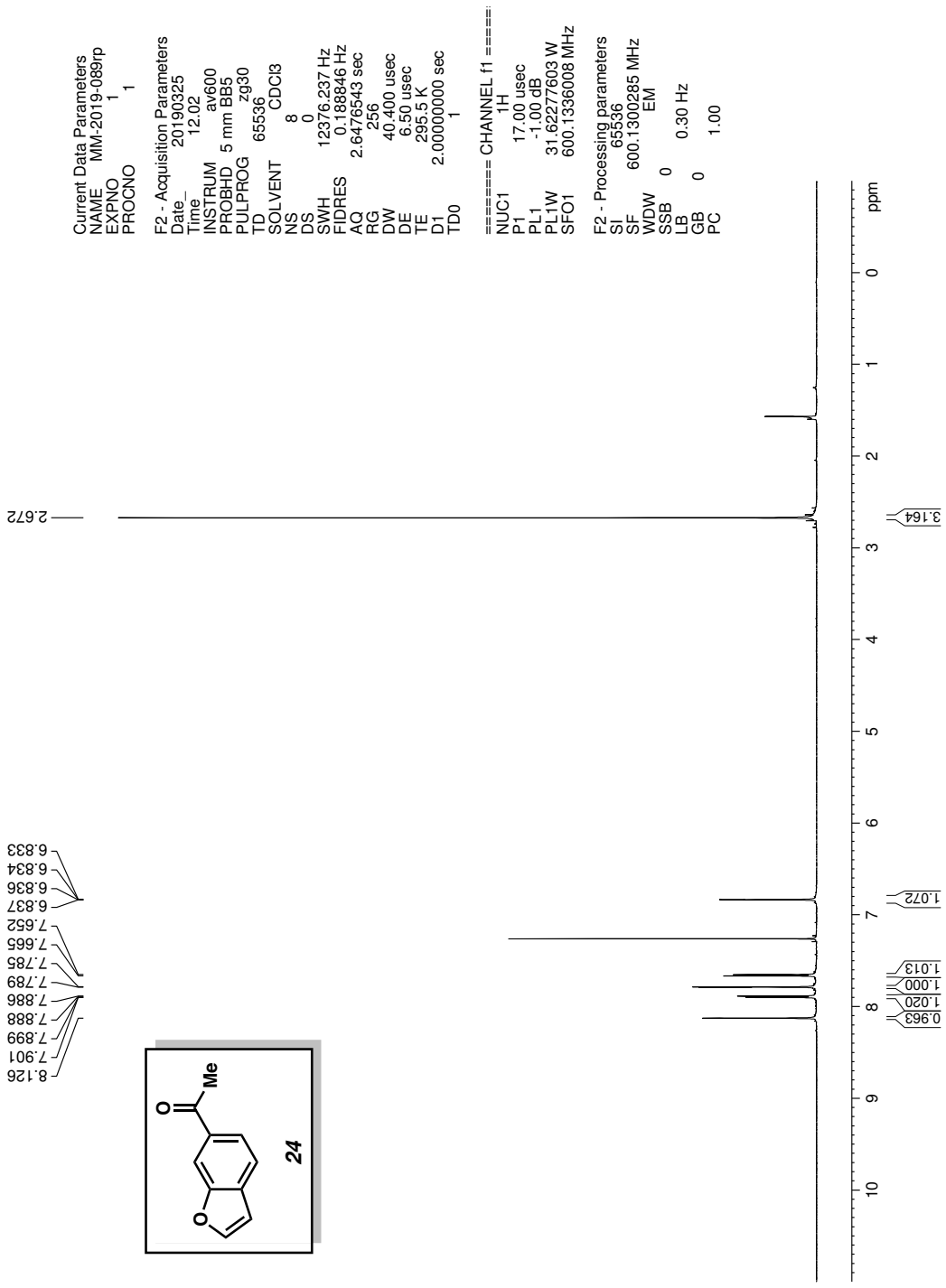
^{1}H NMR Spectra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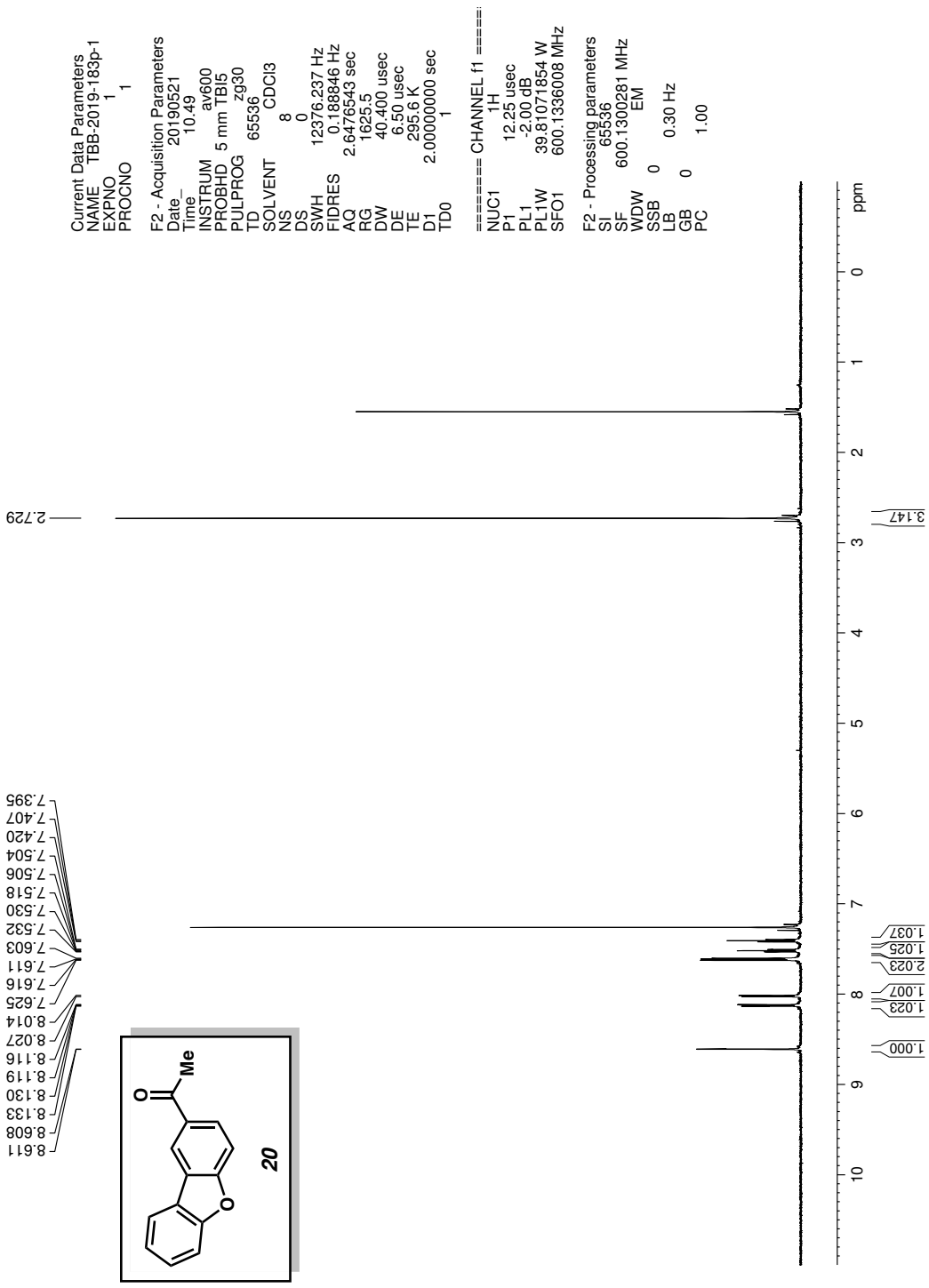
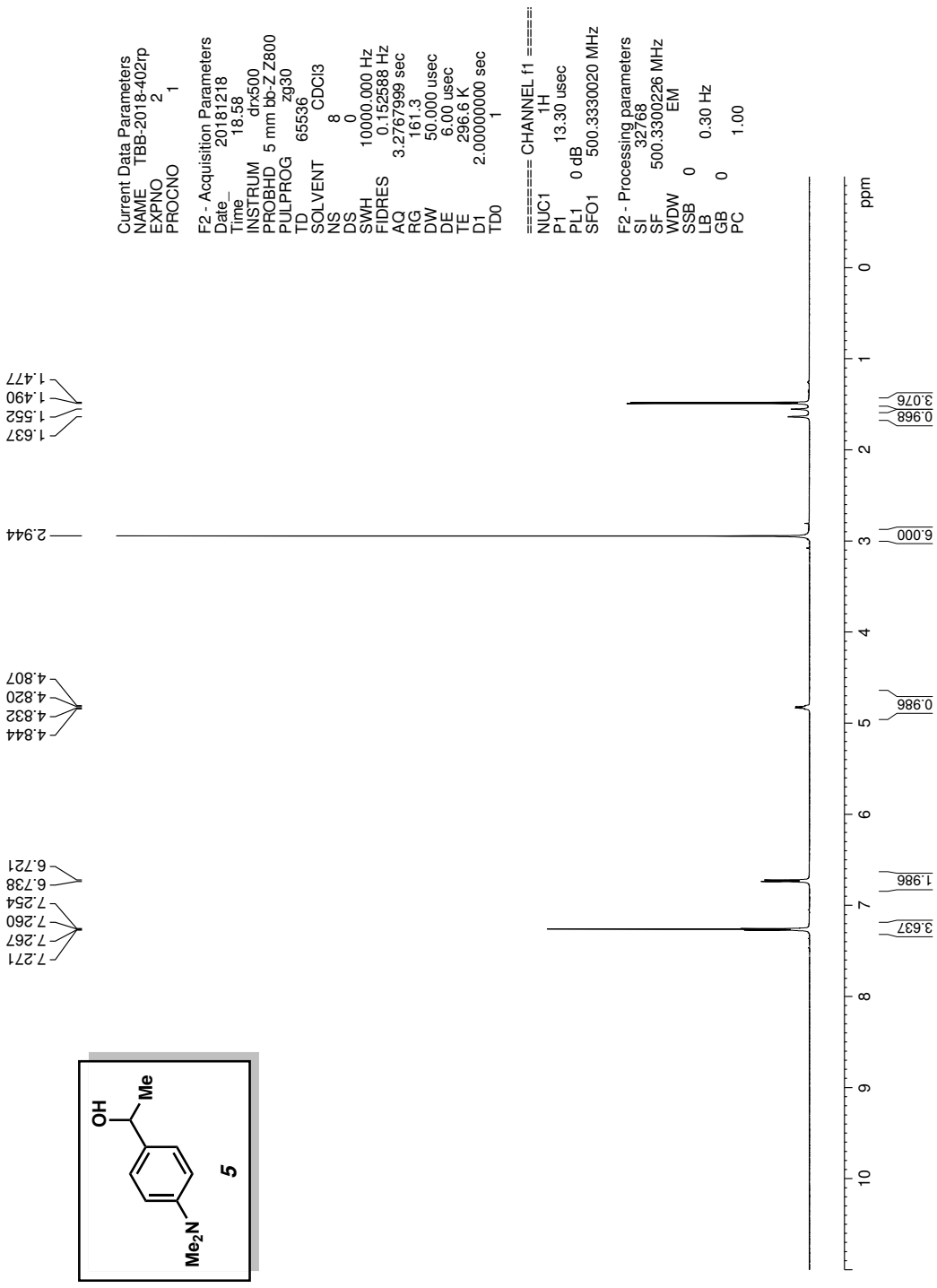
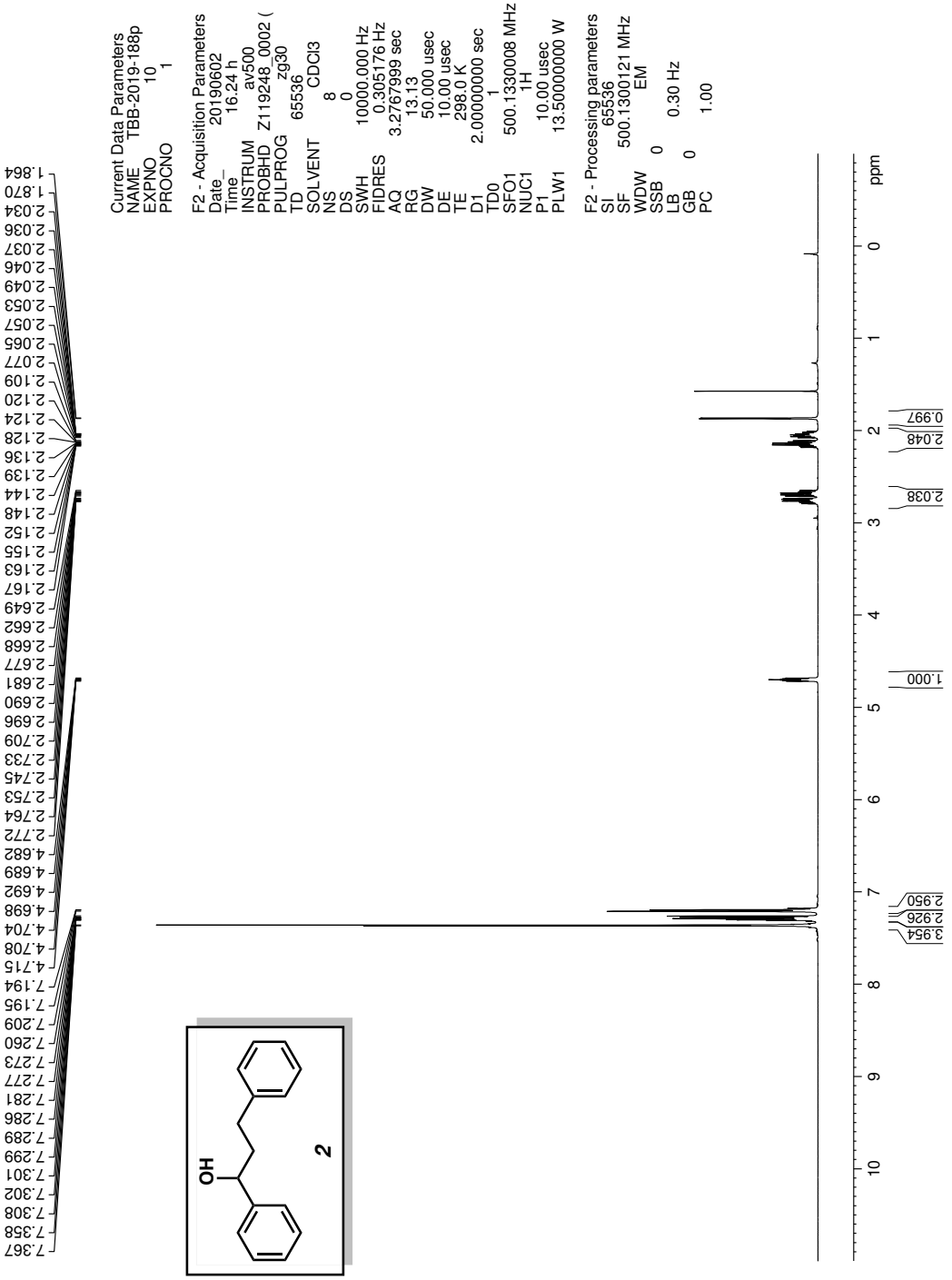
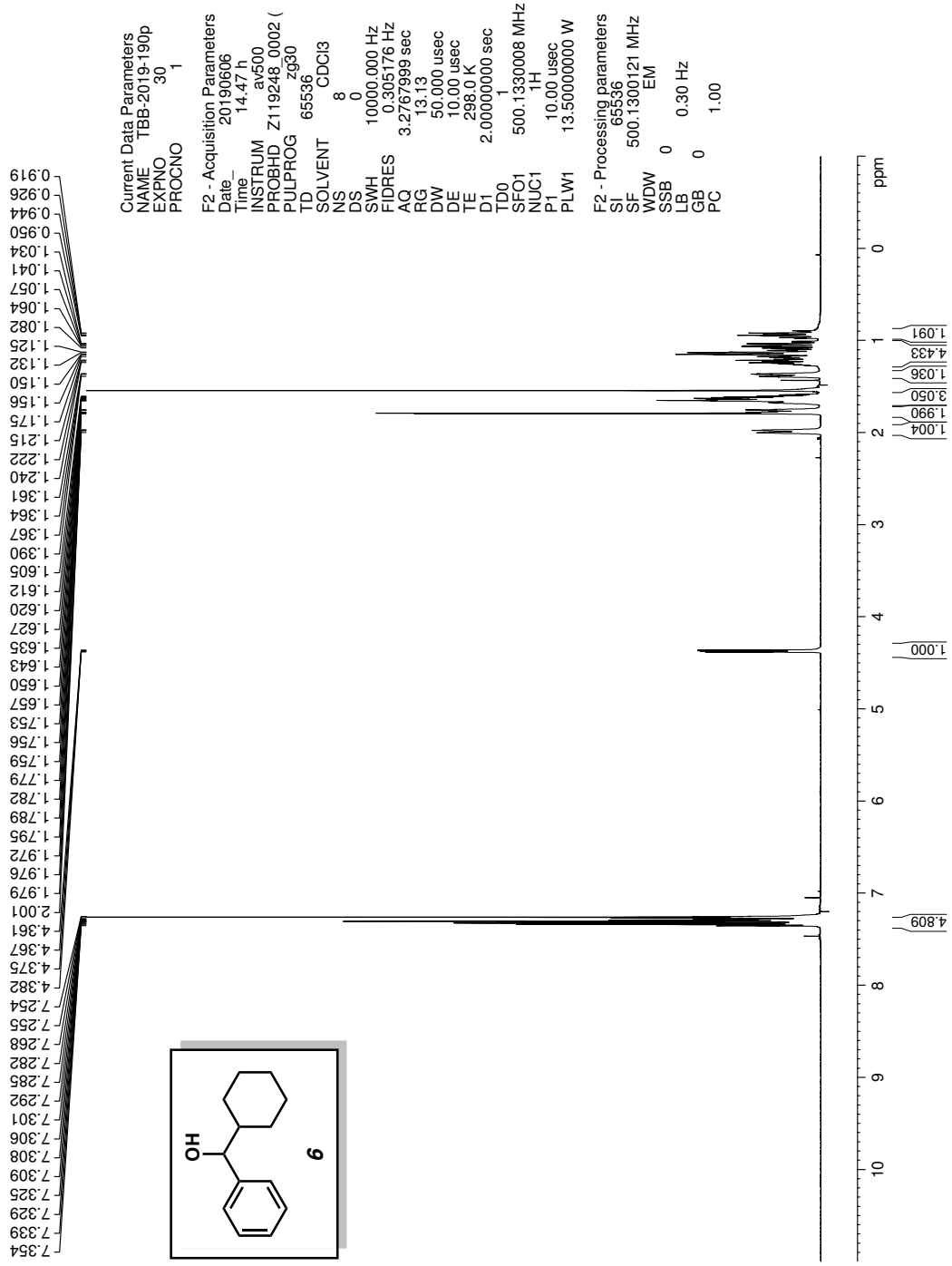
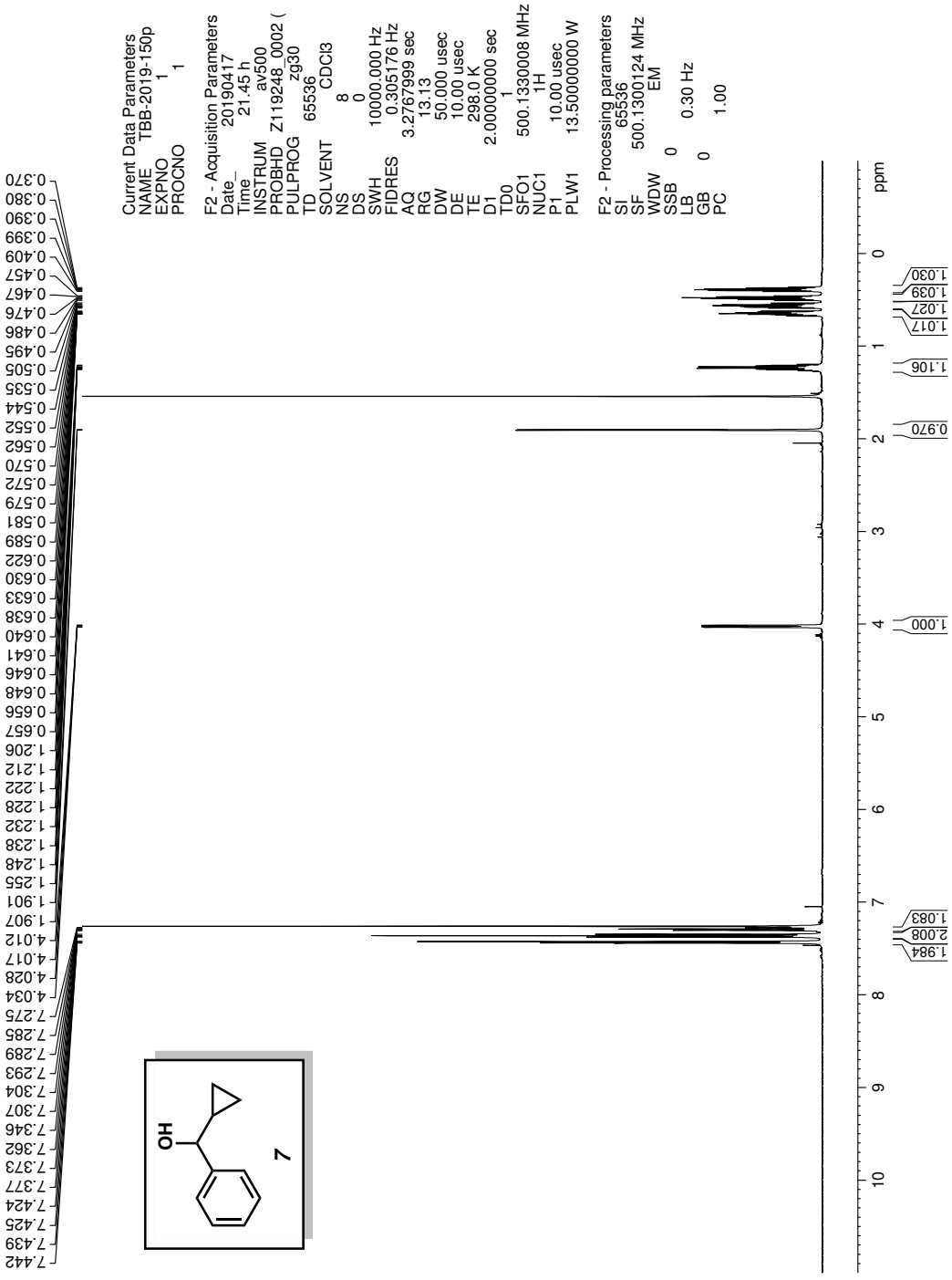
SI 65536
SF 600.1300285 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.672
6.833
6.834
6.836
6.837
7.652
7.665
7.785
7.789
7.886
7.888
7.899
7.901
8.126
3.164
1.072
1.013
1.000
1.020
0.963
Me
O
O
24
ppm

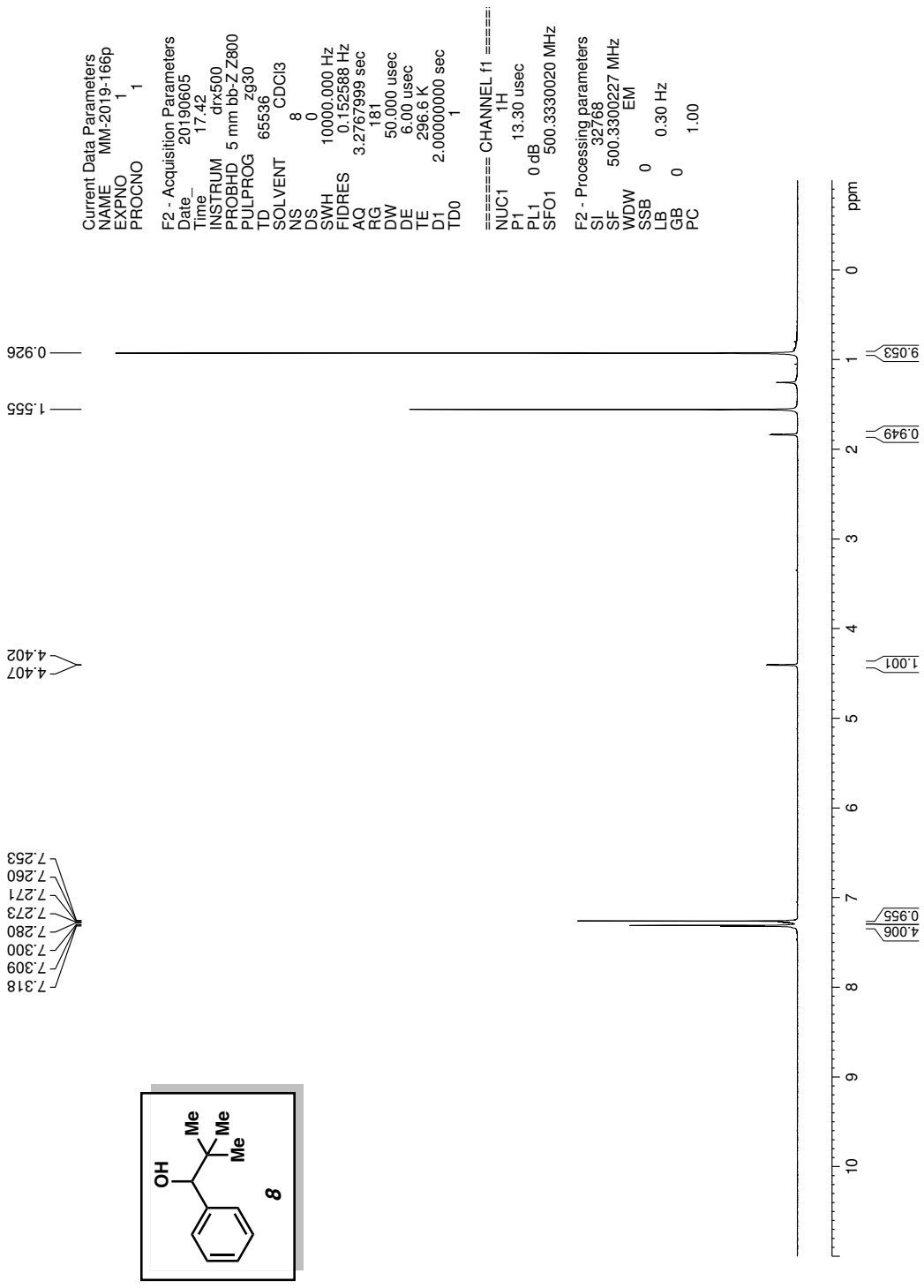

Current Data Parameters
NAME TBB-2019-183p-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190521
Time 10.49
INSTRUM av600
PROBHD 5 mm TBI5
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.64776543 sec
RG 1625.5
DW 40.400 usec
DE 6.50 usec
TE 295.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.25 usec
PL1 -2.00 dB
PL1W 39.81071854 W
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300281 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.729
8.611
8.608
8.133
8.130
8.119
8.116
8.027
8.014
7.625
7.616
7.611
7.603
7.532
7.530
7.518
7.506
7.504
7.420
7.407
7.395
Me
O
O
20
3.147
1.037
1.025
2.023
1.007
1.023
1.000
ppm

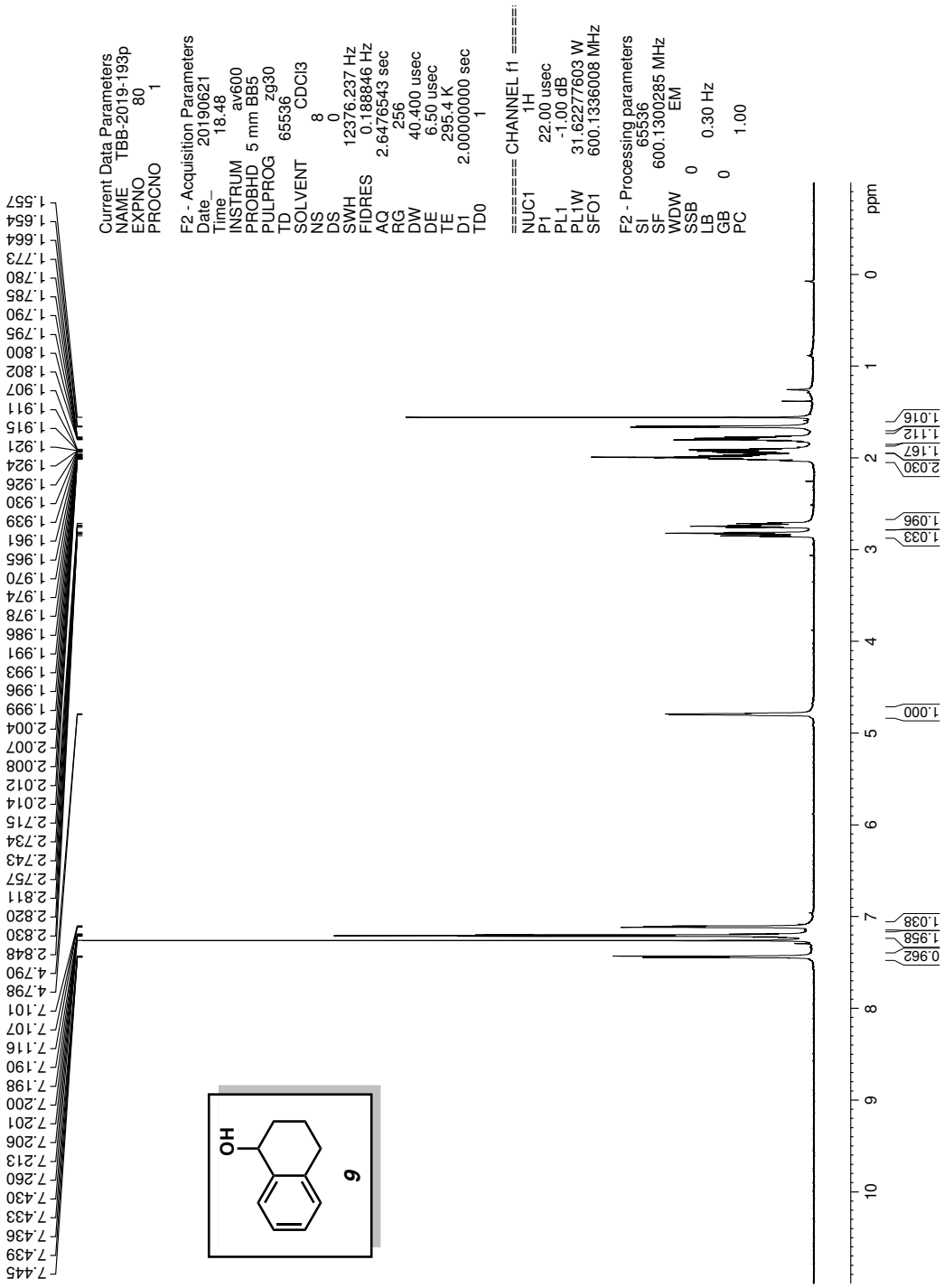

Current Data Parameters
NAME TBB-2018-402rp
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181218
Time_ 18.58
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 161.3
DW 50.000 usec
DE 6.00 usec
TE 296.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 0 dB
SFO1 500.3330020 MHz
F2 - Processing parameters
SI 32768
SF 500.3300226 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.271
7.267
7.260
7.254
6.738
6.721
4.844
4.832
4.820
4.807
2.944
1.637
1.552
1.490
1.477
3.637
1.986
0.986
6.000
0.968
3.076
ppm
OH
Me
Me2N
5

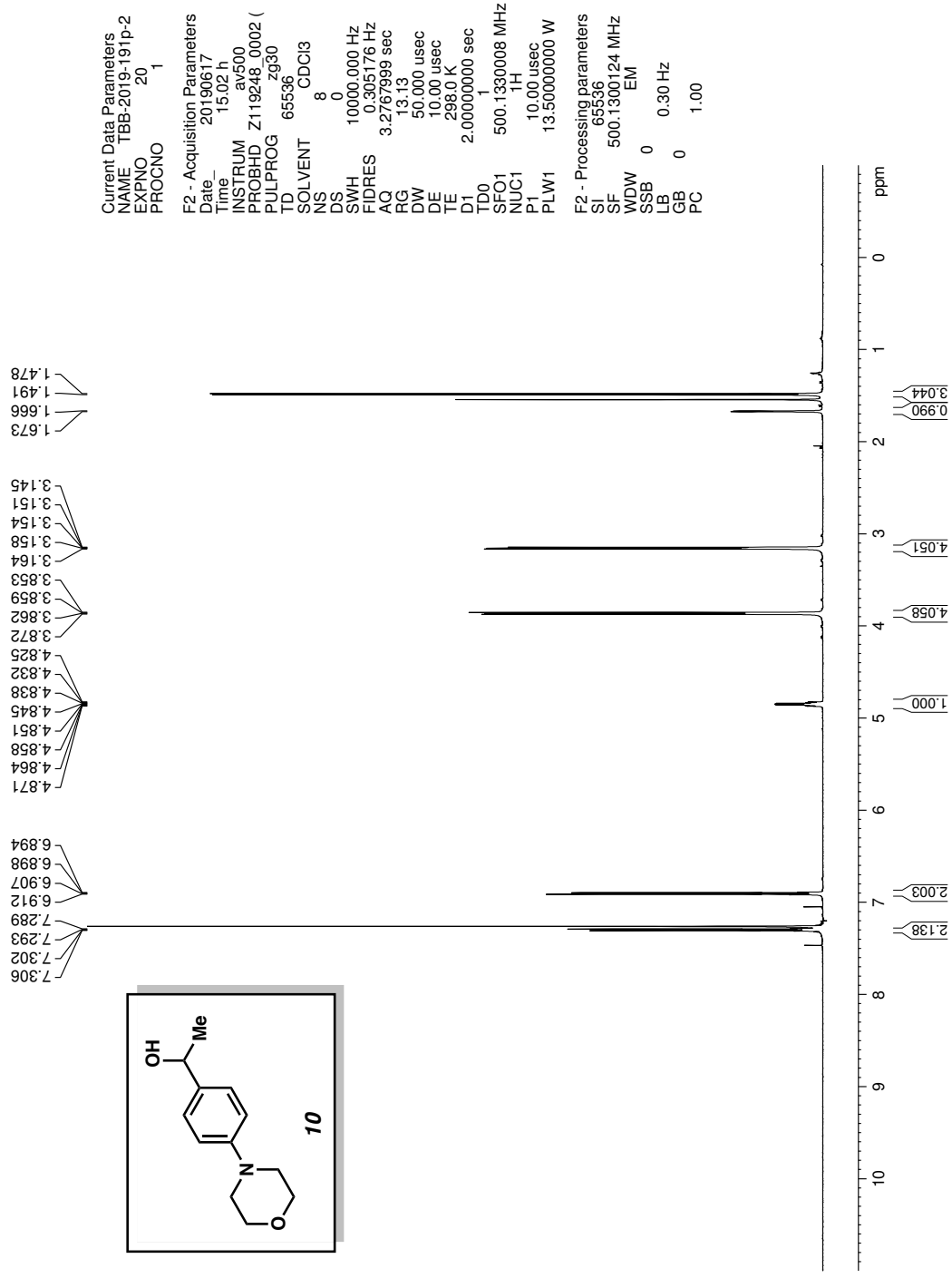

Current Data Parameters
NAME TBB-2019-188p
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190602
Time 16.24 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 13.13
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
2
ppm
1.000
2.048
2.038
0.997
3.954
2.926
2.950

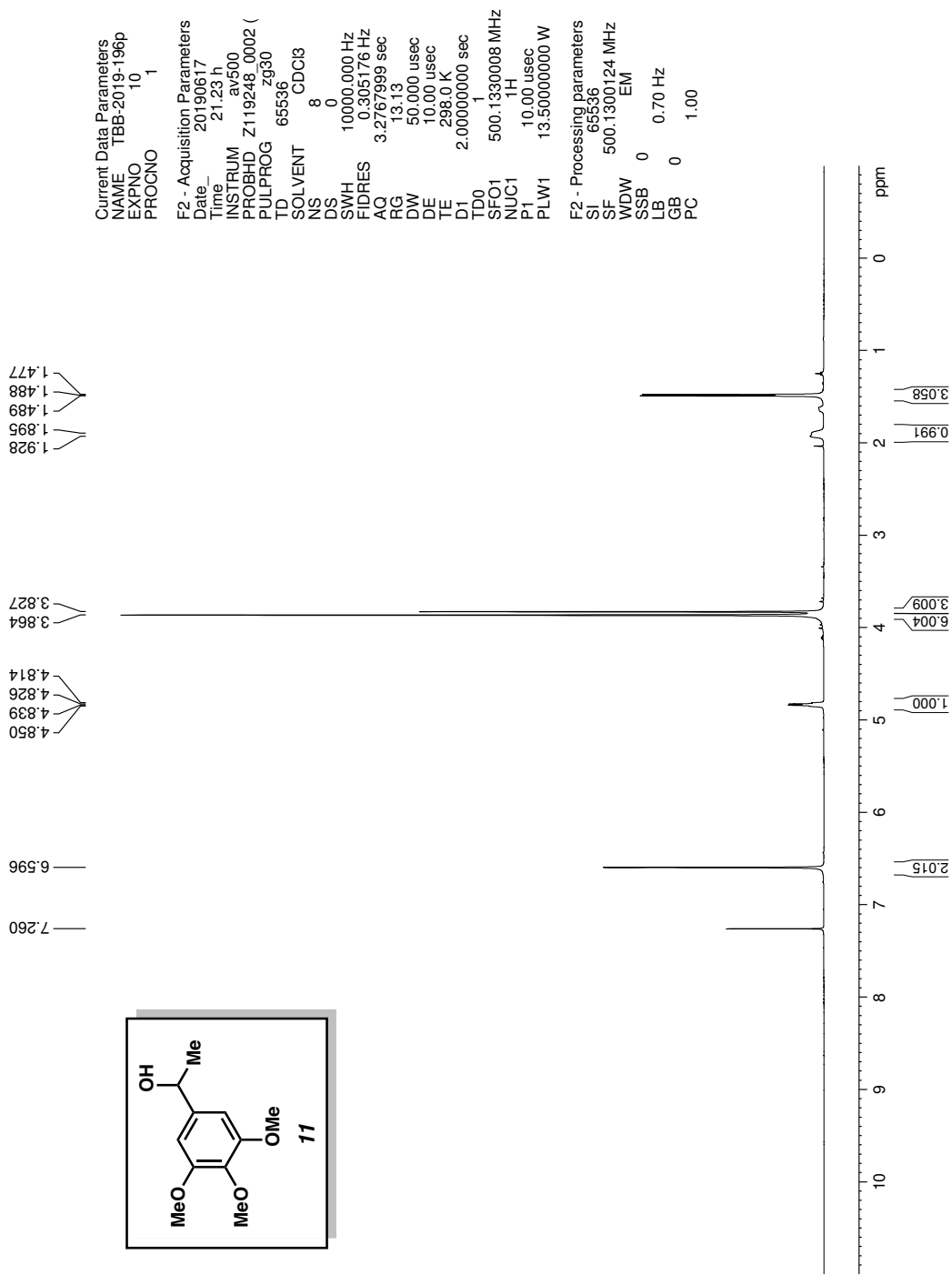

Current Data Parameters
NAME TBB-2019-190p
EXPNO 30
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190606
Time 14.47 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 13.13
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
6
ppm
1.091
4.433
1.036
3.050
1.990
1.004
1.000
4.809

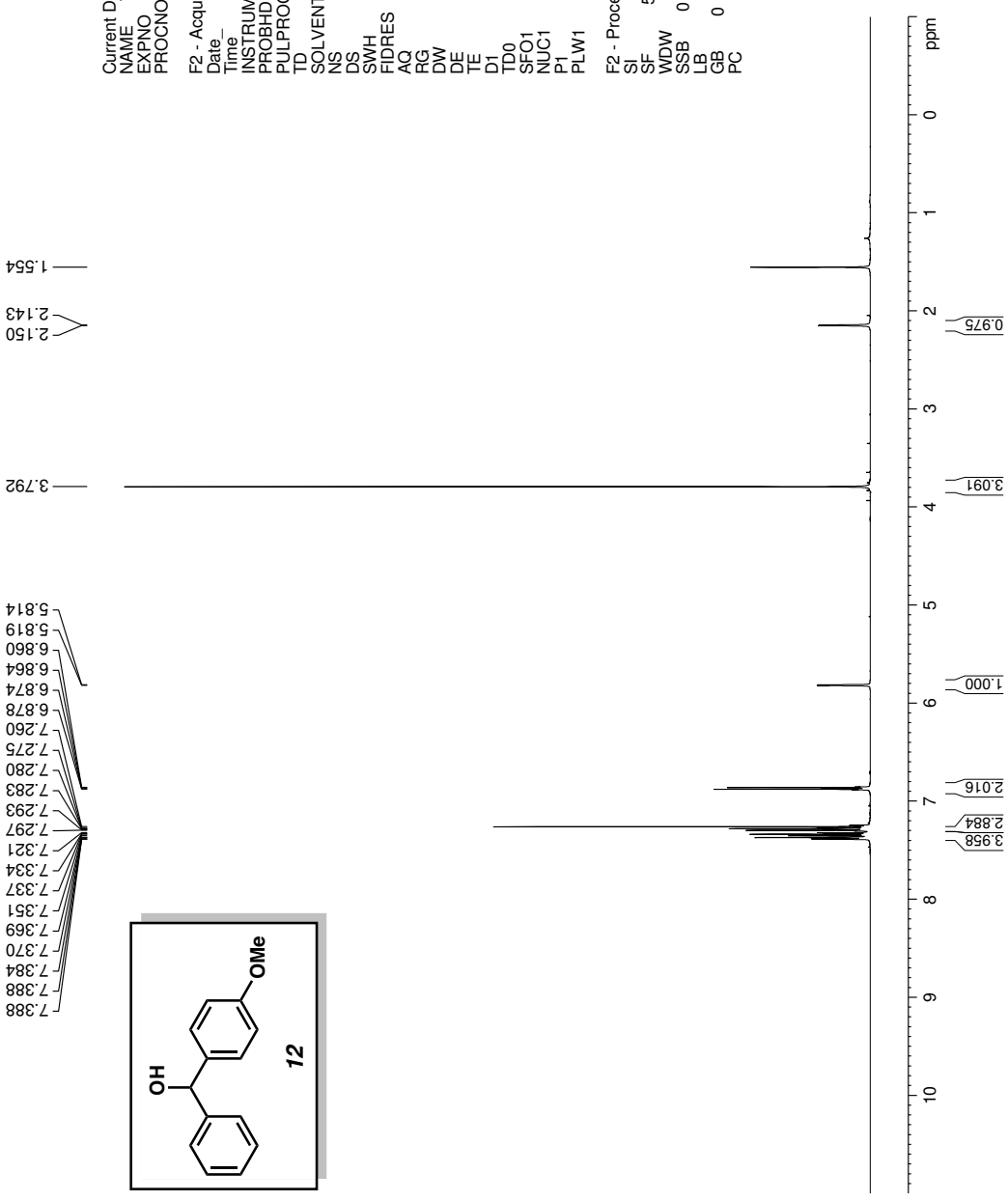

Current Data Parameters
NAME TBB-2019-150p
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190417
Time 21.45 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 13.13
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
7
ppm
1.030
1.039
1.027
1.017
1.106
0.970
1.000
1.083
2.008
1.984

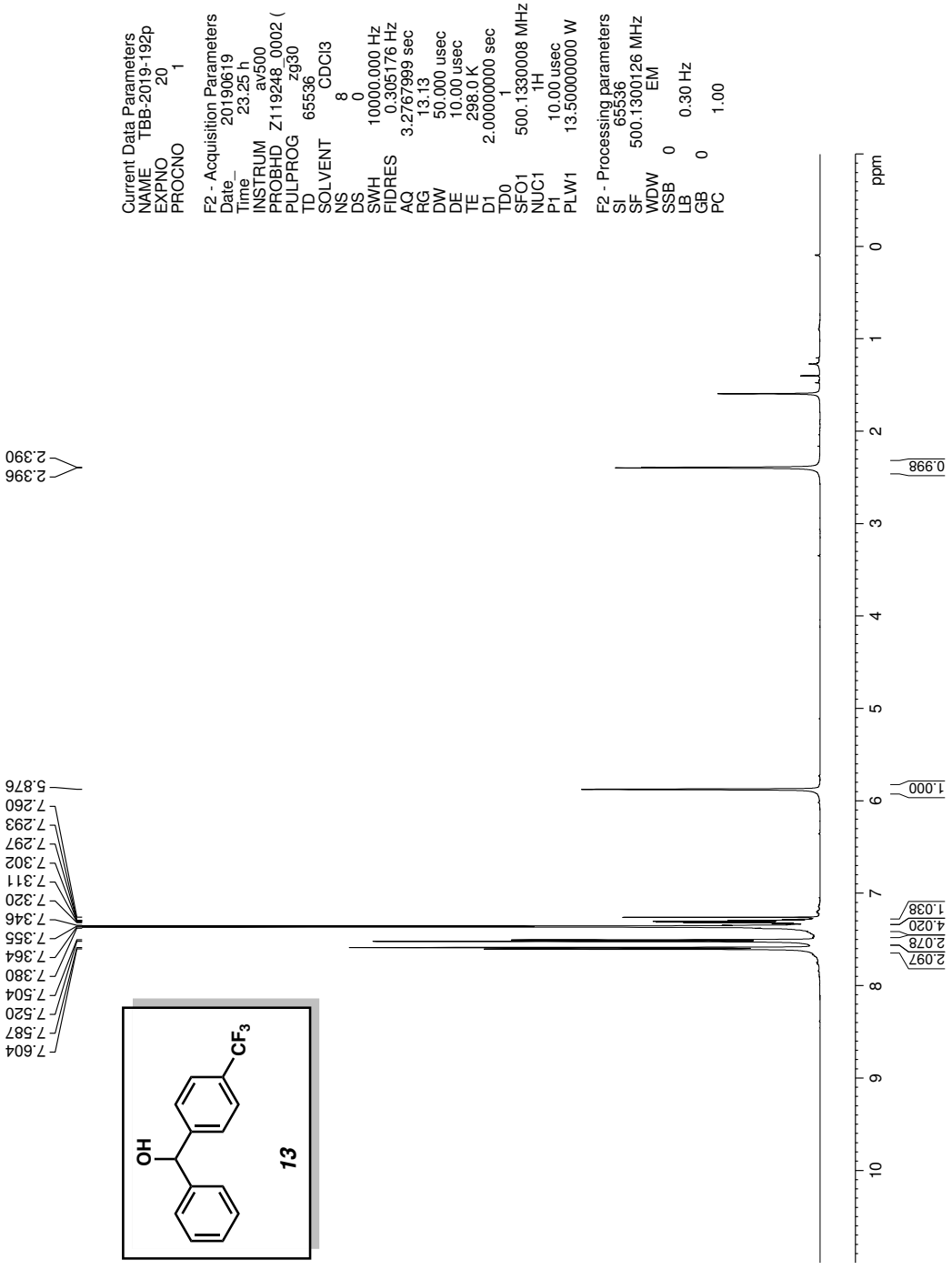

Current Data Parameters
NAME MM-2019-166p
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190605
Time_ 17.42
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 181
DW 50.000 usec
DE 6.00 usec
TE 296.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 0 dB
SFO1 500.3330020 MHz
F2 - Processing parameters
SI 32768
SF 500.3300227 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.926
1.555
4.402
4.407
7.253
7.260
7.271
7.273
7.280
7.300
7.309
7.318
9.053
0.949
1.001
0.955
4.006
ppm
OH
Me
Me
Me
8

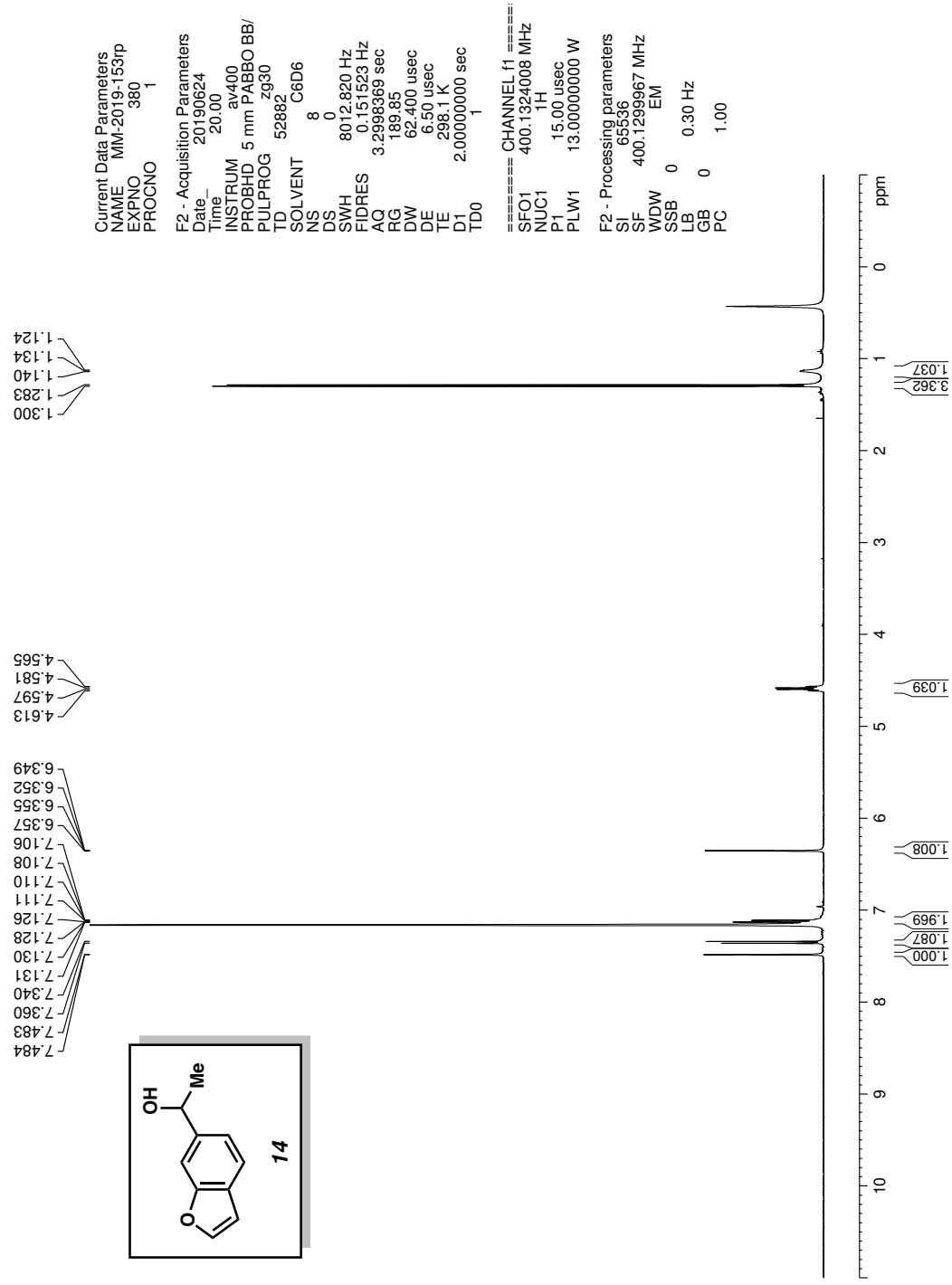

Current Data Parameters
NAME TBB-2019-193p
EXPNO 80 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190621
Time_ 18.48
INSTRUM av600
PROBHD 5 mm BB5
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 256
DW 40.400 usec
DE 6.50 usec
TE 295.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 22.00 usec
PL1 -1.00 dB
PL1W 31.62277603 W
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300285 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
9
ppm
0.962
1.958
1.038
1.000
1.033
1.096
2.030
1.167
1.112
1.016

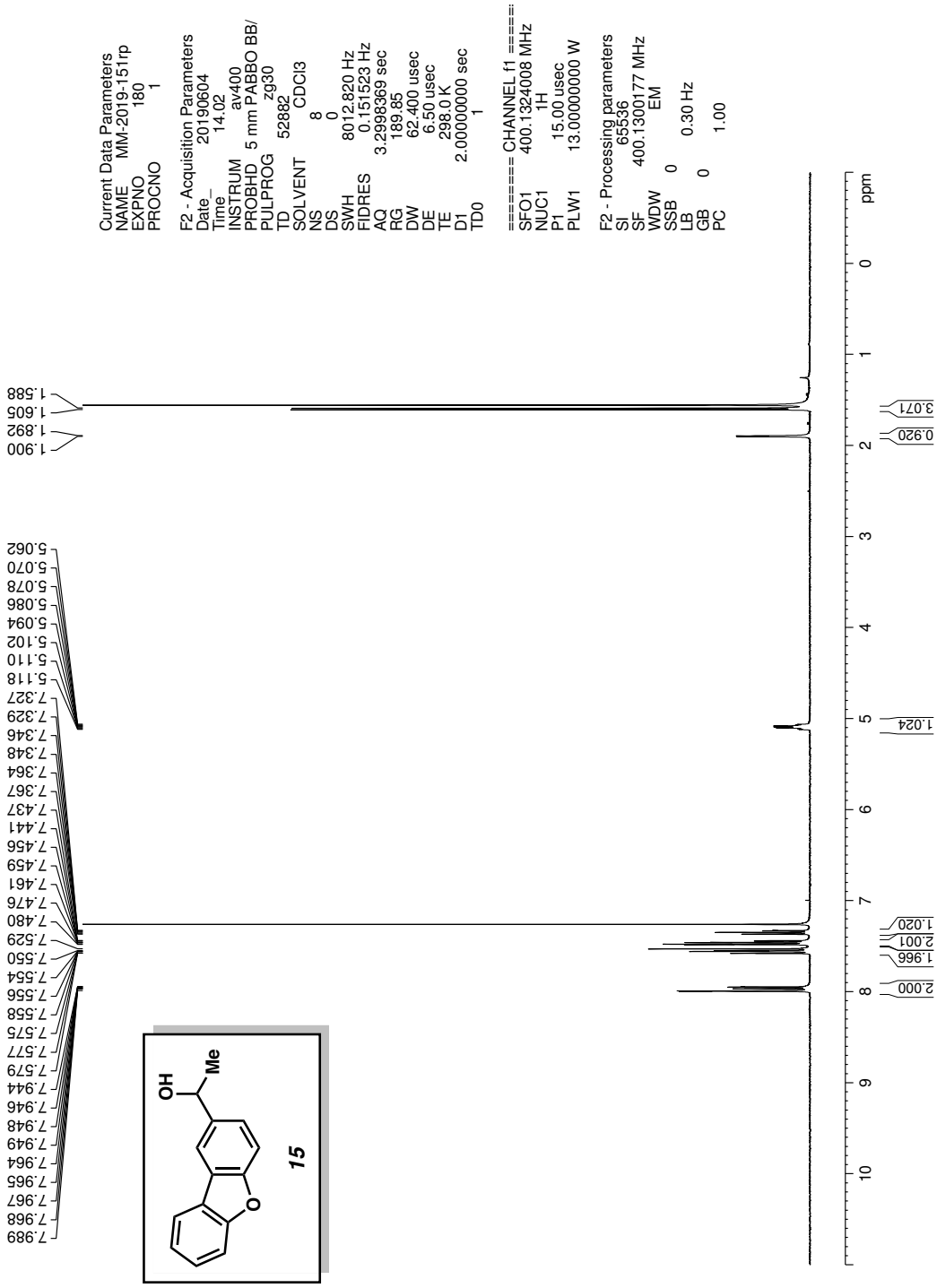

Current Data Parameters
NAME TBB-2019-191p-2
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190617
Time 15.02 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 13.13
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.306
7.302
7.293
7.289
6.912
6.907
6.898
6.894
4.871
4.864
4.858
4.851
4.845
4.838
4.832
4.825
3.872
3.862
3.859
3.853
3.164
3.158
3.154
3.151
3.145
1.673
1.666
1.491
1.478
2.138
2.003
1.000
4.058
4.051
0.990
3.044
OH
Me
N
O
10
ppm

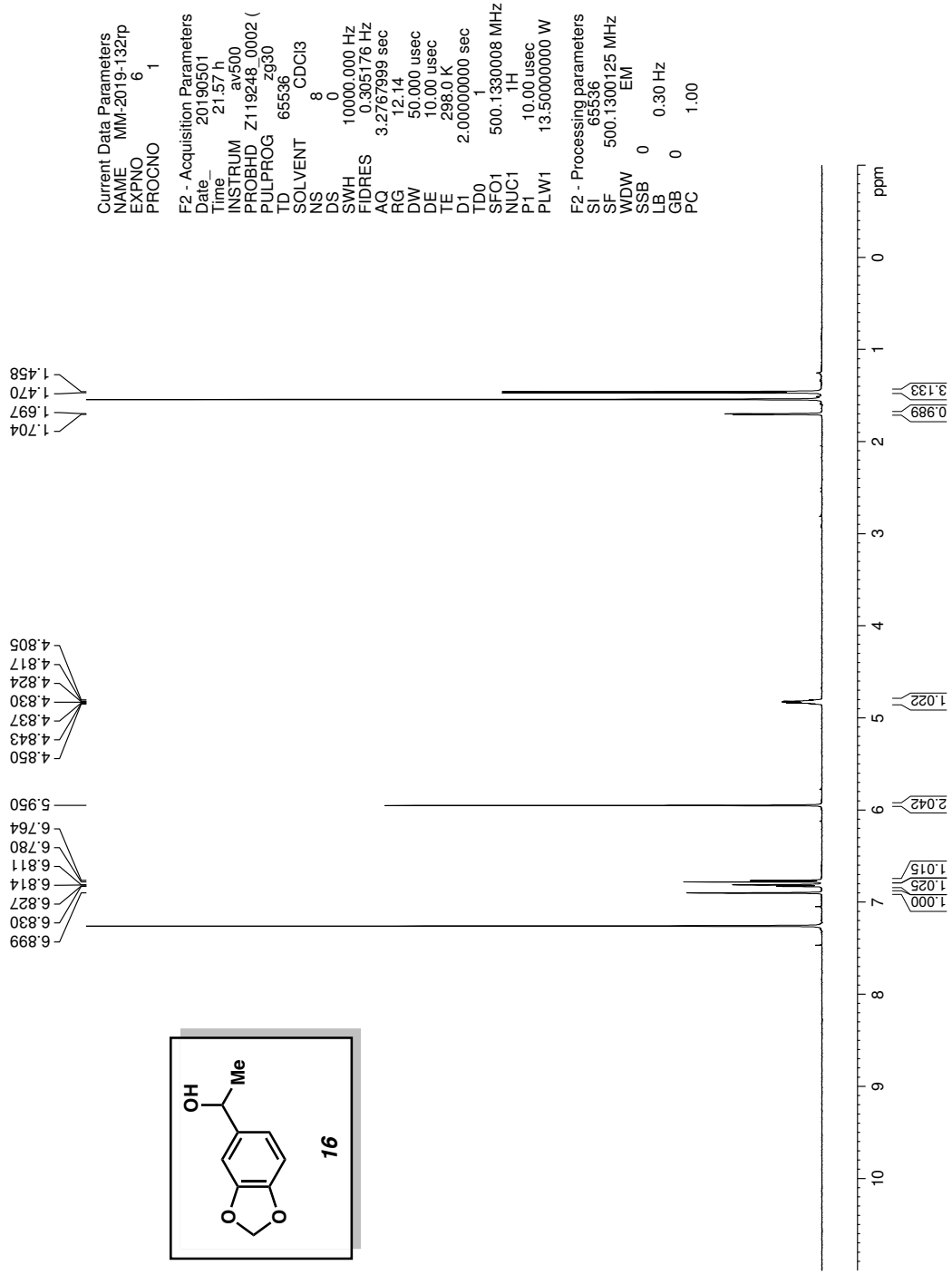

Current Data Parameters
NAME TBB-2019-196p
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190617
Time 21.23 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 13.13
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300124 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
1.477
1.488
1.489
1.895
1.928
3.827
3.864
4.814
4.826
4.839
4.850
6.596
7.260
3.058
0.991
3.009
6.004
1.000
2.015
ppm
OH
Me
OMe
MeO
MeO
11

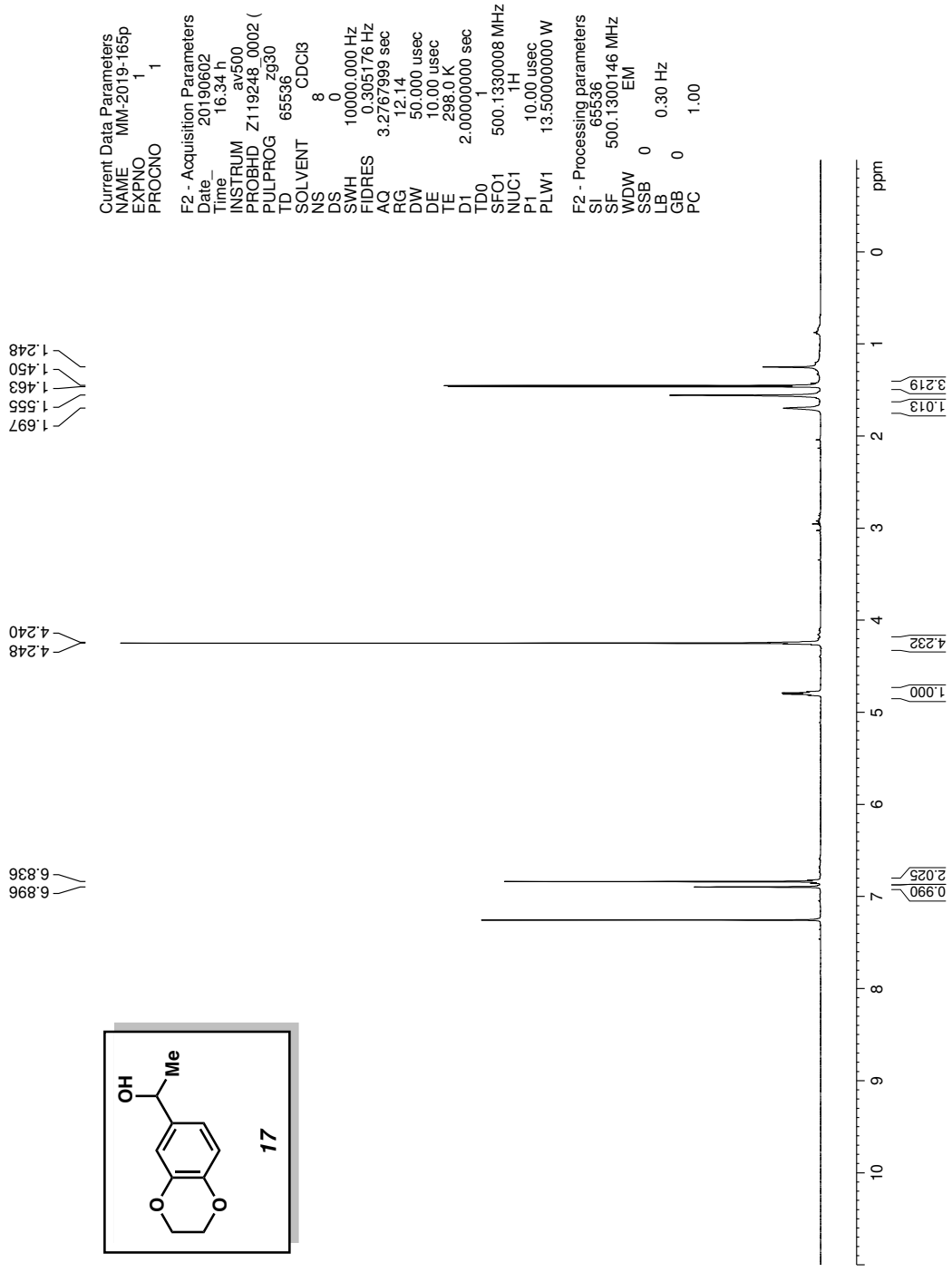

Current Data Parameters
NAME TBB-2019-198p-2
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190619
Time 20.39 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 13.13
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.554
2.143
2.150
3.792
5.814
5.819
6.860
6.864
6.874
6.878
7.260
7.275
7.280
7.283
7.293
7.297
7.321
7.334
7.337
7.351
7.369
7.370
7.384
7.388
7.388
0.975
3.091
1.000
2.016
2.884
3.958
ppm
OH
OMe
12

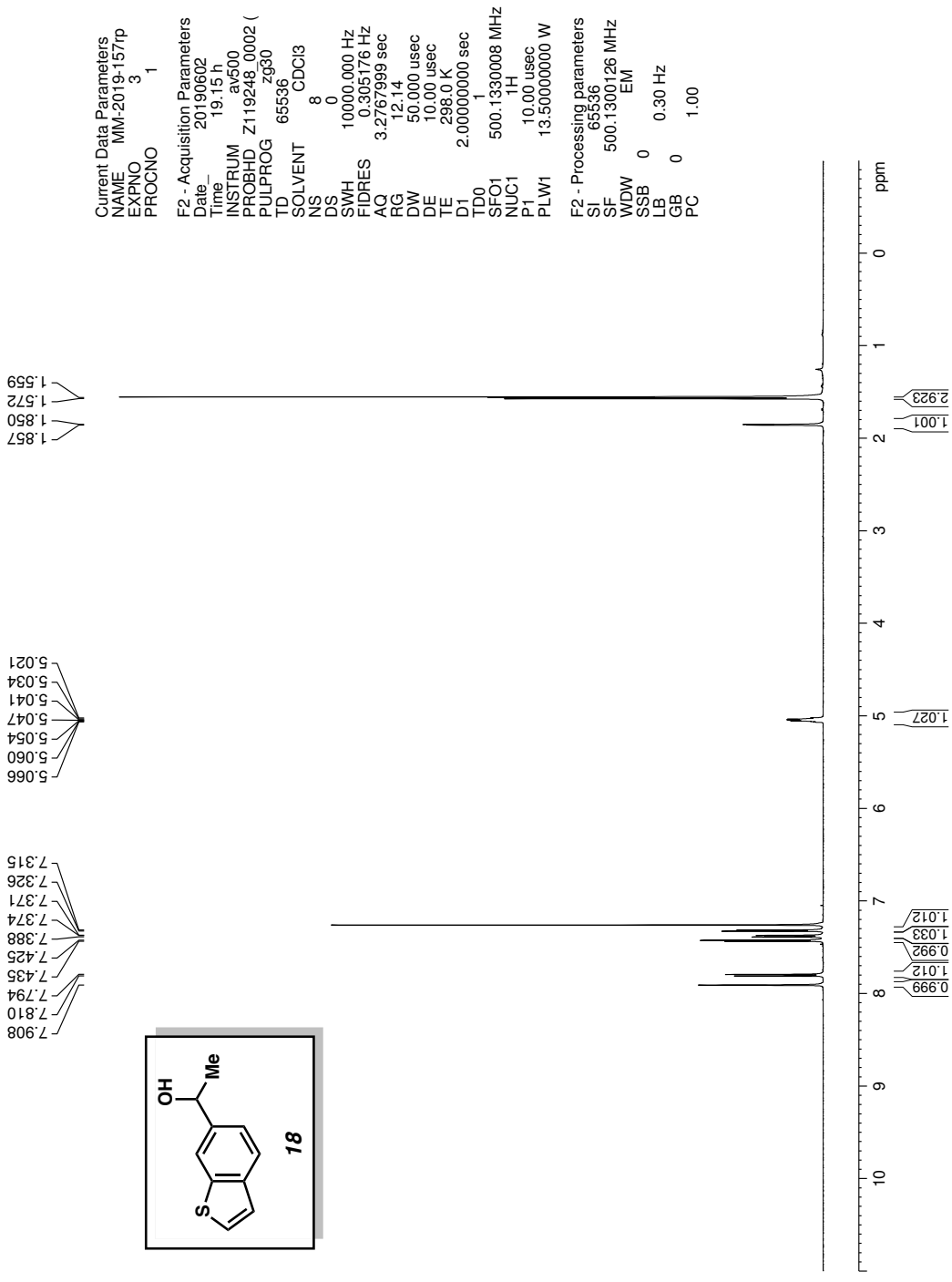

Current Data Parameters
NAME TBB-2019-192p
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190619
Time_ 23.25 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 13.13
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.396
2.390
5.876
7.604
7.587
7.520
7.504
7.380
7.364
7.355
7.346
7.320
7.311
7.302
7.297
7.293
7.260
0.998
1.000
1.038
4.020
2.078
2.097
ppm
OH
CF3
13

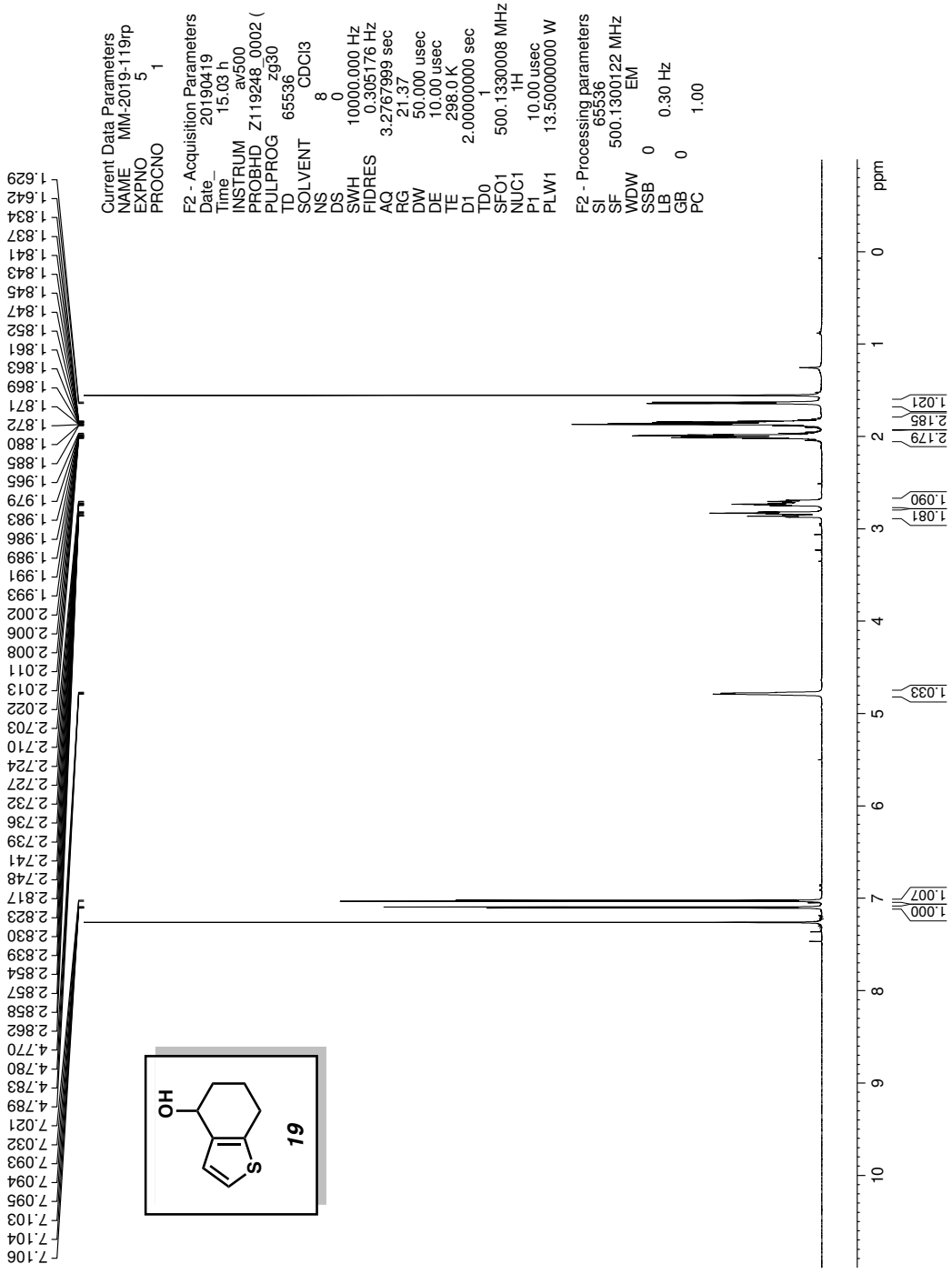

Current Data Parameters
NAME MM-2019-153rp
EXPNO 380
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190624
Time 20.00
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT C6D6
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1299967 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.124
1.134
1.140
1.283
1.300
4.565
4.581
4.597
4.613
6.349
6.352
6.355
6.357
7.106
7.108
7.110
7.111
7.126
7.128
7.130
7.131
7.340
7.360
7.483
7.484
OH
Me
O
14
3.362
1.037
1.039
1.008
1.969
1.087
1.000
ppm


Current Data Parameters
NAME MM-2019-151rp
EXPNO 180
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190604
Time 14.02
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ======
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1300177 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.900
1.892
1.605
1.588
5.062
5.070
5.078
5.086
5.094
5.102
5.110
5.118
7.327
7.329
7.346
7.348
7.364
7.367
7.437
7.441
7.456
7.459
7.461
7.476
7.480
7.529
7.550
7.554
7.556
7.558
7.575
7.577
7.579
7.944
7.946
7.948
7.949
7.964
7.965
7.967
7.968
7.989
OH
Me
O
15
3.071
0.920
1.024
1.020
2.001
1.966
2.000
ppm

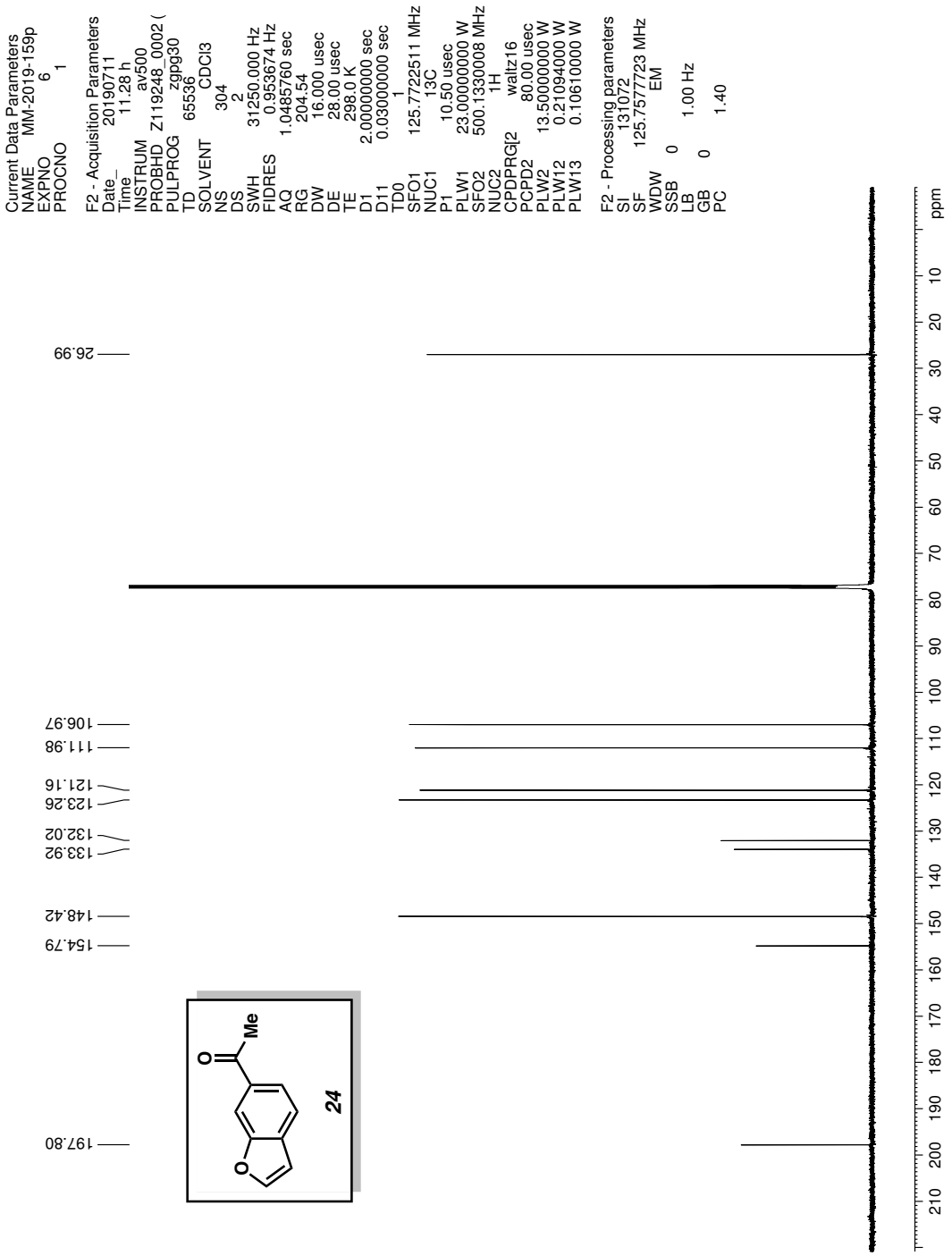

Current Data Parameters
NAME MM-2019-132rp
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190501
Time_ 21.57 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
6.899
6.830
6.827
6.814
6.811
6.780
6.764
5.950
4.850
4.843
4.837
4.830
4.824
4.817
4.805
1.704
1.697
1.470
1.458
1.000
1.025
1.015
2.042
1.022
0.989
3.133
OH
Me
O
O
16
ppm

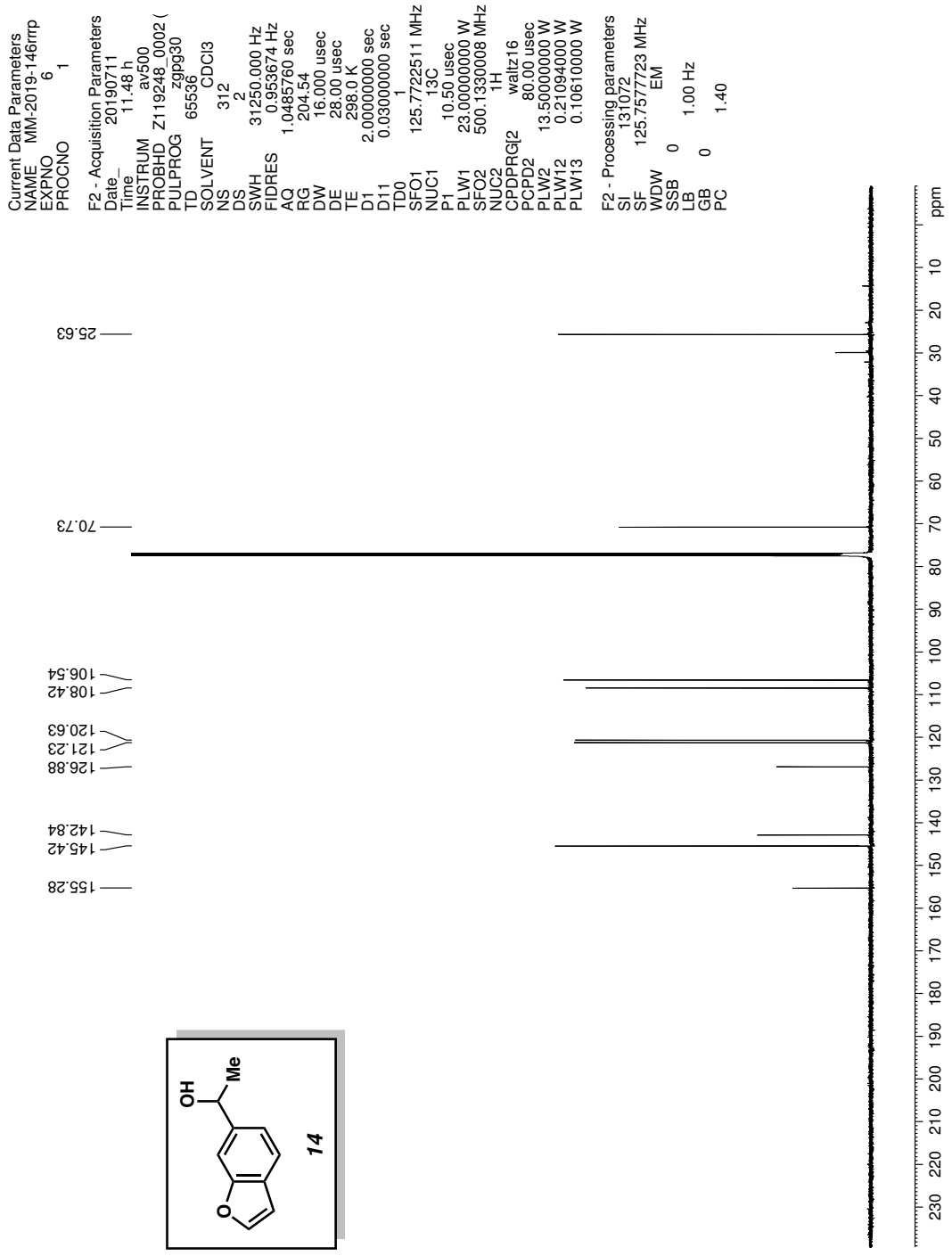

Current Data Parameters
NAME MM-2019-165p
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190602
Time 16.34 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.697
1.555
1.463
1.450
1.248
4.248
4.240
6.896
6.836
3.219
1.013
4.232
1.000
2.025
0.990
ppm
OH
Me
O
O
17

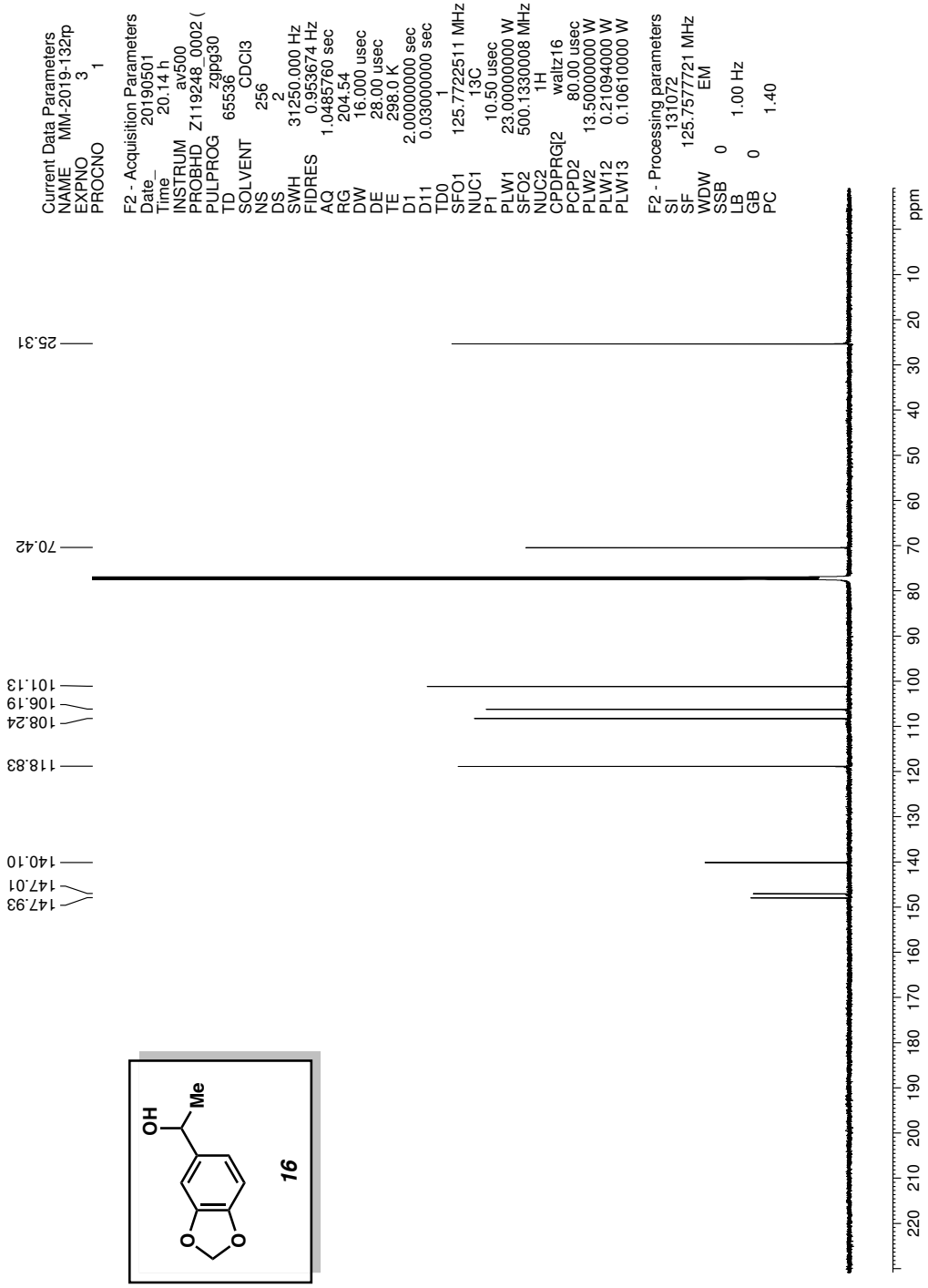

Current Data Parameters
NAME MM-2019-157rp
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190602
Time 19.15 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.857
1.850
1.572
1.559
5.066
5.060
5.054
5.047
5.041
5.034
5.021
7.908
7.810
7.794
7.435
7.425
7.388
7.374
7.371
7.326
7.315
OH
Me
S
18
2.923
1.001
1.027
0.999
1.012
0.992
1.033
1.012
ppm

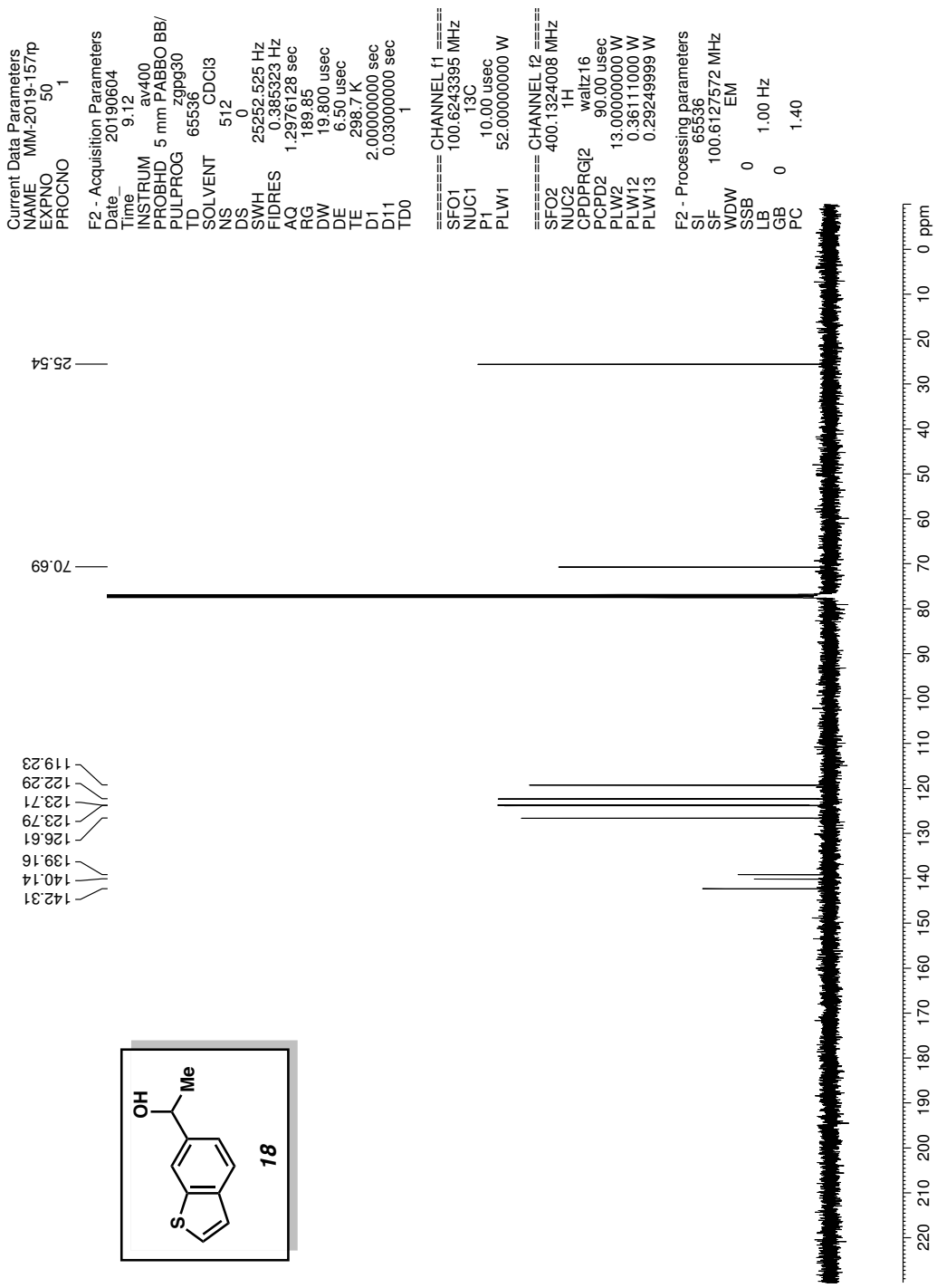

Current Data Parameters
NAME MM-2019-119rp
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190419
Time 15.03 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 21.37
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
S
19
ppm
1.000
1.007
1.033
1.081
1.090
2.179
2.185
1.021

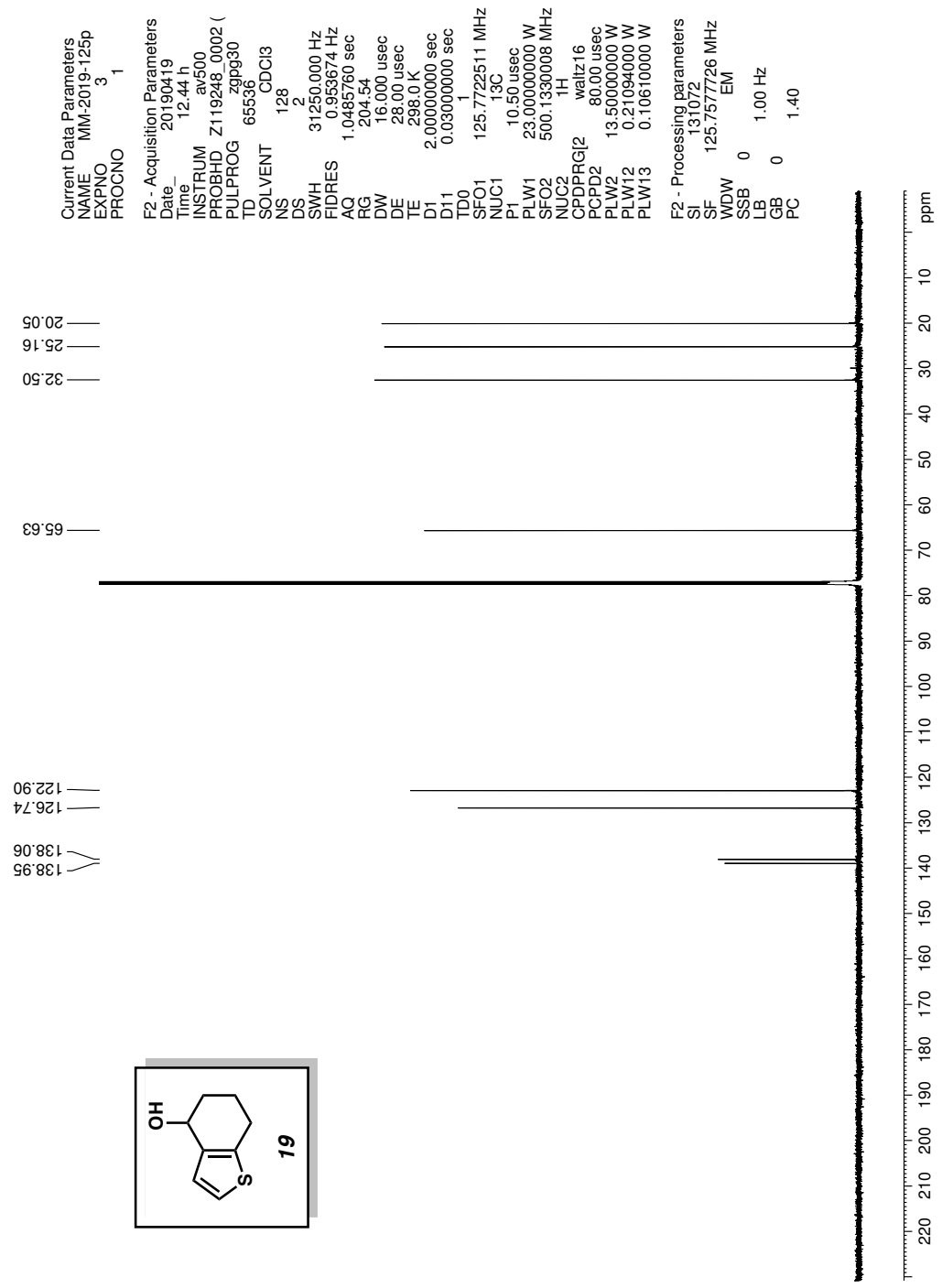
^{13}C NMR Spectra


Current Data Parameters
NAME MM-2019-159p
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190711
Time 11.28 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 304
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577723 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
26.99
106.97
111.98
121.16
123.26
132.02
133.92
148.42
154.79
197.80
O
Me
O
24
ppm


Current Data Parameters
NAME MM-2019-146rrp
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190711
Time 11.48 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 312
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577723 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
25.63
70.73
106.54
108.42
120.63
121.23
126.88
142.84
145.42
155.28
ppm
OH
Me
O
14


Current Data Parameters
NAME MM-2019-132rp
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190501
Time 20.14 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577721 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
25.31
70.42
101.13
106.19
108.24
118.83
140.10
147.01
147.93
OH
Me
16
ppm


Current Data Parameters
NAME MM-2019-157rp
EXPNO 50
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190604
Time 9.12
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 189.85
DW 19.800 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 =====
SFO1 100.6243395 MHz
NUC1 13C
P1 10.00 usec
PLW1 52.00000000 W
======== CHANNEL f2 =====
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W
PLW13 0.29249999 W
F2 - Processing parameters
SI 65536
SF 100.6127572 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
25.54
70.69
119.23
122.29
123.71
123.79
126.61
139.16
140.14
142.31
OH
Me
S
18
0 ppm


Current Data Parameters
NAME MM-2019-125p
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190419
Time 12.44 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577726 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
20.05
25.16
32.50
65.63
122.90
126.74
138.06
138.95
OH
S
19
ppm