Supporting Information

for

Unconventional Site-Selectivity in Palladium-Catalyzed Cross-Couplings of Dichloroheteroarenes under Ligand-Controlled and Ligand-Free Systems

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I. Experimental Details

A. General Materials and Methods

NMR spectra were recorded at 298 K on a Bruker DRX 500 MHz (500.233 MHz for ^{1}H, 125.795 MHz for ^{13}C, 470.639 MHz for ^{19}F), a Bruker Avance III 600 MHz (600.130 MHz for ^{1}H or 150.903 MHz for ^{13}C) spectrometer, or a Bruker Ascend 400 MHz (400.130 MHz for ^{1}H NMR, 100.613 for ^{13}C). ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference [^{1}H NMR: $CHCl_3$ (7.26 ppm), C_6D_5H (7.16 ppm), DMSO-d_5 (2.50 ppm); ^{13}C NMR: $CDCl_3$ (77.16 ppm), ^{13}C NMR: C_6D_6 (128.06 ppm), DMSO-d_6 (39.52 ppm)]. Multiplicities are reported as follows: singlet (s), broad singlet (br s) doublet (d), doublet of doublets (dd), doublet of doublets of doublets (ddd), triplet (t), quartet (q), and multiplet (m). GC data were collected using a Shimadzu GC-2010 Plus with a flame ionization detector equipped with a SH-Rxi-5ms capillary column (15 m x 0.25 mm ID x 0.25 μm df). GCMS data were collected with a Shimadzu GC-2030 paired with a Shimadzu GCMS-QP2020 NX and equipped with a SH-Rxi-5ms capillary column (30 m x 0.25 mm ID x 0.25 μm df). LC-MS analyses were performed on either an Agilent 6538 Q-TOF MS or a Bruker micro-TOF MS, both coupled to an Agilent 1290 Infinity UHPLC system. A 50 mm long Eclipse Plus C18 column (Agilent Technologies, Santa Barbara, CA; i.d. 2.1 mm, 1.8 μm particle size) was used for separation. A 6-minute gradient was used at a flow rate of 0.6 mL/min: 0-1 min 95% buffer A (100% H2O with 0.1% formic acid), followed by a gradient from 1-4 minutes of 5-95% buffer B (100% acetonitrile with 0.1% formic acid), 1 minute 95% buffer B, and returning to 95% buffer A for 1 minute. The mass spectrometers were operated in positive-ion mode with electrospray ionization. All reactions that require heating were conducted in aluminum single-size vial reaction blocks (Chemglass) fitted to an IKA stirring hot plate equipped with a temperature probe.

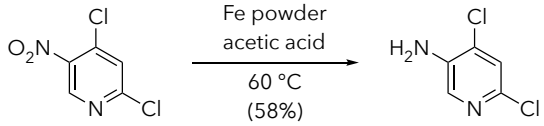
Unless otherwise noted below, all commercially-obtained chemicals were used as received. PEPPSI-SIPr and PEPPSI-IPr were obtained from Sigma Aldrich. (η^3-1-^{t}Bu-indenyl)$_2$(μ-Cl)$_2$Pd$_2$, (η^3-1-^{t}Bu-indenyl)Pd(IPr)(Cl), and (η^3-1-^{t}Bu-indenyl)Pd(IPent)(Cl) were obtained from Umicore. Other (η^3-1-^{t}Bu-indenyl)Pd(NHC)(Cl) precatalysts were prepared from the corresponding *N*-heterocyclic carbene ligands IMes, SIMes, SIMix, or SIPr (each obtained from Strem Chemicals or Sigma Aldrich) according to a literature procedure.[1] Unless otherwise noted, dichloroheteroarenes and arylboronic acid starting materials were obtained from Oakwood Chemical. 4,5-Dichloro-3(2H)-pyridazinone (**S45**)[2] and 3,4,5-trichloropyridazine (**S46**)[3] were prepared according to literature procedures. Potassium fluoride, 1,4-dioxane, benzyl bromide, iodine, potassium *tert*-butoxide, tetrabutylammonium hexafluorophosphate, and palladium (II) chloride were obtained from Acros Organics. Potassium carbonate, methylmagnesium bromide, triphenylphosphine, tri-*tert*-butylphosphine, 4-vinylphenylboronic acid, 2,4-dichloro-3-cyanopyridine, and 2,4-dichloro-5-methylpyridine were obtained from Alfa Aesar. 2,4-dichloro-5-nitropyridine and 3,3'-bromomethyloxetane were obtained from Combi-Blocks. 2,4-Dichloro-1,8-naphthyridine and 3-amino-2,4-dichloropyridine were obtained from Millipore Sigma. 3-Amino-2,4-dichloropyridine was obtained from Synthonix. Sodium carbonate, THF, toluene, and methanol were obtained from Fisher Scientific. Magnesium turnings, *tert*-butyl bromide, cyclopentyl bromide, benzothiophene (thianaphthene), 2-bromo-5-methylpyridine, lithium chloride, tetrabutylammonium bromide and chloride, tris(dibenzylideneacetone)dipalladium(0), diphenylphosphinoferrocene, tri-*o*-tolylphosphine, and tricyclohexylphosphine were obtained from Oakwood

chemical. Diisobutylaluminum hydride (DIBAL), magnesium bromide diethyl etherate, propylene carbonate, potassium bromide, and *n*-butyllithium were obtained from Sigma-Aldrich. Palladium (II) acetate, trimethyl phosphine, Q-Phos, and CataCXium A were obtained from Strem Chemical. 2,4-Dichloroquinoline, zinc dichloride, and $Pd(PPh_3)_4$ were obtained from TCI Chemicals. Benzene was obtained from Beantown Chemical. For the purposes of Kumada or Negishi cross-couplings or for preparation of Grignard reagents, THF was purified on a JC Meyer solvent dispensing system and stored under N_2 prior to use. For the purpose of Suzuki-Miyaura cross-couplings, THF was used as received from Fisher Scientific. For the purpose of Suzuki-Miyaura cross-couplings under ligand-free reaction conditions, DMF was purified on a JC Meyer solvent dispensing system and stored under N_2 prior to use. 1,4-Dioxane required for Pd/dppf-mediated Suzuki-Miyaura cross-couplings was used as received from Acros Organics but kept under N_2 prior to and during use. Grignard reagents were titrated according to a literature procedure.[4]

Deuterated solvents ($CDCl_3$, C_6D_6, DMSO-d_6) were obtained from Cambridge Isotopes and stored over molecular sieves. Manual flash column chromatography was performed on SiliCycle silica gel 60 (40-63 μm particle size) and thin layer chromatography was performed on SiliCycle TLC plates pre-coated with extra hard silica gel 60 F_{254}. Automated flash column chromatography was performed with a Biotage Selekt equipped with Biotage Sfär silica flash cartridges (20 μm particle size; 50 Å pore width) for normal phase separations, or Silica C18 cartridges (30 μm particle size; 100 Å pore width) for reversed phase separations.

B. Synthesis and Characterization of Reagents

1. Chlorinated Heteroarenes

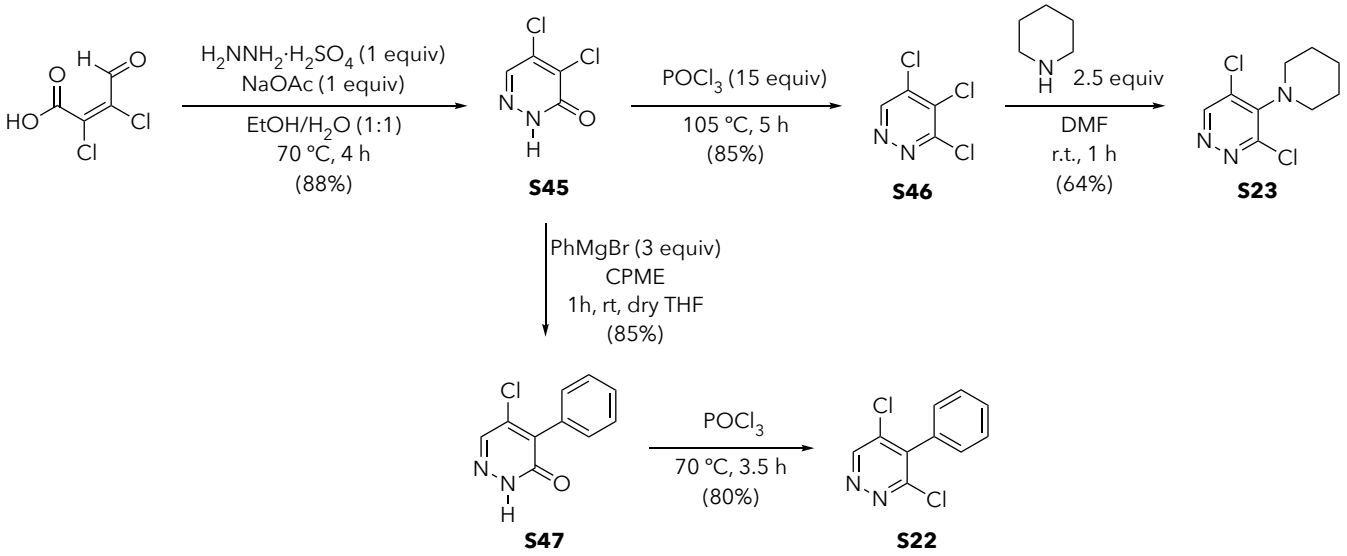


S16

3-Amino-4,6-dichloropyridine **(S16)**: Glacial acetic acid (14.2 mL) was heated to 60 °C in a round-bottom flask equipped with a Vigreux reflux condenser and stir bar. Iron powder (4.175 g, 74.8 mmol, 3.5 equiv) and 2,4-dichloro-5-nitropyridine (4.122 g, 21.36 mmol, 1.0 equiv) were added to the flask consecutively while stirring. The mixture was allowed to stir at 60 °C for 2.5 h. Partway through the reaction time, the mixture thickened such that stirring was encumbered, so an additional 8 mL glacial acetic acid was added to the flask. The resulting suspension was vacuum-filtered through celite and the filter cake was washed thoroughly with ethyl acetate. Solvent was removed from the filtrate under reduced pressure, and the resulting solids were taken up in ethyl acetate. The organic solution was washed with saturated aqueous sodium bicarbonate, deionized water (3x), and brine. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting white solid was dried under vacuum overnight, affording **S16** as a very pale pink solid (2.030 g, 58% yield). ^{1}H NMR

(500 MHz, $CDCl_3$, δ): 7.88 (s, 1H), 7.21 (s, 1H), 4.16 (br s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 139.7, 139.3, 136.2, 129.7, 123.9

Scheme S1. Dichloropyridazines Synthetic Map



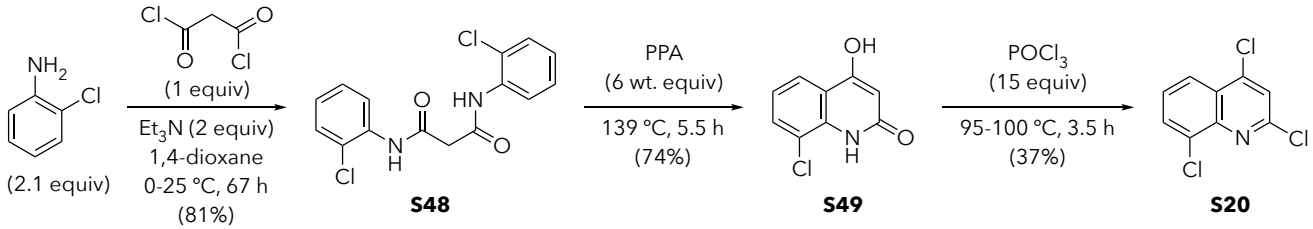
5-Chloro-4-phenyl-3(2H)-pyridazinone (**S47**): Compound **S47** was prepared according to a procedure adapted from the literature.[5] 4,5-Dichloro-3(2H)-pyridazinone (**S45**)[2] (1.2 g, 7.27 mmol, 1.0 equiv) was added to an oven-dried 50 mL Schlenk flask equipped with a stir bar. The flask was fitted with a rubber septum, the septum was secured with copper wire, and the flask was evacuated and backfilled with N_2 (3x). Dry THF (12 mL) was transferred into the flask by cannula. The flask was cooled in an ice bath, and a solution of phenylmagnesium bromide (1.6 *M* in CPME, 13.6 mL, 21.82 mmol, 3.0 equiv) was added dropwise over 10 min by cannula. The flask was removed from the ice bath and the reaction was stirred at room temperature for 1 h. The flask was returned to the ice bath, opened to air, and quenched by the slow addition of aqueous NH_4Cl (12 mL; 100 g/L). The resulting mixture was partitioned between deionized water and ethyl acetate. The aqueous layer was extracted with ethyl acetate (2x). The combined organic fractions were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting solids were triturated in hexanes, filtered, and dried under vacuum to afford **S47** as a white solid (1.277 g, 85% yield). ^1H NMR (500 MHz, DMSO-d_6, δ): 13.40 (br s, 1H), 8.03 (s, 1H), 7.47-7.40 (multiple overlapping signals, 5H). Spectral data are consistent with the literature report.[5]

3,5-Dichloro-4-phenylpyridazine (**S22**): Phosphorous(V) oxychloride (3.4 mL) and **S47** (1.266 g, 6.127 mmol, 1.0 equiv) were combined in an oven-dried round-bottom flask equipped with a stir bar. The flask was then fitted with a Vigreux reflux condenser and sealed with a rubber septum fastened with copper wire. An outgassing line, which was assembled with PVC tubing, a needle adapter, and a needle, was routed from the condenser through a mineral oil bubbler, which was in turn routed through an aqueous KOH trap. An in-gas needle was introduced to the condenser, and the system was purged with N_2. The in-gas line was closed off such that hydrogen chloride evolution could be monitored visually. The reaction mixture was heated to 70 °C and stirred for 3.5 h. Stirring was

continued while the reaction cooled to ambient temperature. The reaction was quenched by slow, dropwise addition of aqueous NaOH (5 mol % in water) while stirring until bubbling ceased. The mixture was diluted with water and filtered affording a brown solid. The wet solid was taken up in benzene, and then concentrated under reduced pressure; this process was repeated once. The resulting solids were dried under vacuum overnight to afford **S22** as a brown solid (1.109 g, 80% yield). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 9.54 (s, 1H), 7.58-7.51 (multiple overlapping signals, 3H), 7.46-7.43 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, δ): 155.6, 151.6, 138.8, 137.9, 131.7, 129.7, 128.71, 128.68. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{10}H_6Cl_2N_2$ 223.9908; Found 223.9896.

3,5-Dichloro-4-(1-piperidinyl)-pyridazine (**S23**): 3,4,5-Trichloropyridazine (**S46**)[3] (550.3 mg, 3.0 mmol, 1.0 equiv) was combined with DMF (9.38 mL) and a stir bar in a 5-dram vial. The vial was fitted with a septum and placed under an atmosphere of N_2 gas. Piperidine (744 μL, 7.5 mmol, 2.5 equiv) was added dropwise through the septum via a 100 μL syringe to the stirring solution, resulting in rapid evolution of HCl gas and increased turbidity. The reaction was stirred at ambient temperature for 1 h. DMF was removed under vacuum, and the residue was purified by flash column chromatography on silica gel in 10% acetone in hexanes (R_f = 0.22). The combined fractions were dried under vacuum to afford **S23** as a white solid with minor brown discoloration (445 mg, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.68 (s, 1H), 3.36-3.34 (m, 4H), 1.77-1.64 (multiple overlapping signals, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 155.5, 148.0, 143.1, 123.9, 50.6, 25.6, 23.7. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_9H_{11}Cl_2N_3$ 231.0330; Found 231.0326.

Scheme S2. Synthesis of 2,4,8-Trichloroquinoline (**S20**)

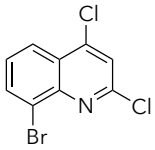


***N*^{1},*N*^{3}-Bis(2-chlorophenyl)-propanediamide** (**S48**): Compound **S48** was prepared according to a modified literature procedure.[6] Malonyl dichloride was purified by simple vacuum distillation prior to use; triethylamine was distilled from calcium hydride, sparged with N_2, and stored over 4 Å molecular sieves prior to use. 2-Chloroaniline (2.679 g, 21 mmol, 2.1 equiv) was weighed into a 100-mL round bottom flask, followed by dry 1,4-dioxane (24 mL) and a stir bar. The flask was fitted with a rubber septum and the septum was secured with copper wire. An ingas needle and smaller diameter outgassing needle were introduced through the septum, and the contents of the flask were sparged with N_2 for 15 min. Dry triethylamine (2 equiv, 20 mmol, 2.8 mL) was added through the septum via 1-mL syringe, and the sealed flask was cooled in an ice bath. Under N_2, a solution of malonyl dichloride (973 μL, 10 mmol, 1 equiv) in dry 1,4-dioxane (28.5 mL) was added dropwise to the cooled stirring solution through the septum via a 10-mL syringe over 20 min. The solution became bright yellow and evolution of HCl gas was observed. The

flask was removed from the ice bath and stirred at ambient temperature for 67 h. The flask was opened to air and the bright yellow mixture was poured into a 500-mL beaker. While stirring, aqueous HCl (2 *M*, 36 mL) was added slowly to the mixture. The mixture was stirred for an additional 30 min, resulting in precipitation of yellow solids. The solids were collected by vacuum filtration, washed with water, and dried under vacuum, affording **S48** as a yellow powder (2.6132 g, 81% yield). A minor dioxane impurity (3 mol%, 0.8% by mass) was detected by ^{1}H-NMR analysis. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 10.04 (s, 2H), 7.90 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.51 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.43 (ddd, *J* = 8.7, 8.0, 1.3, 2H) 7.19 (ddd, *J* = 8.7, 8.0, 1.3, 2H), 3.75 (s, 2H). Spectral data are consistent with the literature.[6]

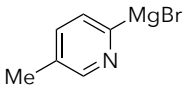
8-Chloro-4-hydroxy-2(1H)-quinolinone (**S49**): *N*^{1}, *N*^{3}-Bis(2-chlorophenyl)-propanediamide (**S48**) (1.661 g, 5.14 mmol, 1.0 equiv) and polyphosphoric acid (9.965 g, 6.0 wt. equiv) were measured into a round-bottom flask equipped with stir bar. The flask was fitted with a water-cooled coil-type jacketed condenser fitted with a rubber septum secured by copper wire. The system was placed under an atmosphere of N_2 gas, and the mixture was heated to 139 °C for 5.5 h. The system was allowed to cool to handling temperature and the mixture was poured into ice water, inducing precipitation and hardening of the tar-like mixture. The transfer was completed with alternating washes of ethyl acetate and water. The resulting slurry was stirred overnight to break up the tar, resulting in a suspension of precipitated fine solids. The suspension was decanted from residual tar and the precipitate was collected by filtration, washed with water, and dried under vacuum to afford **S49** as a pale brown powder (737 mg, 74% yield). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 11.61 (br s, 1H), 10.37 (br s, 1H), 7.78 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 5.81 (s, 1H). Spectral data are consistent with the literature.[7]

2,4,8-Trichloroquinoline (**S20**): 8-Chloro-4-hydroxy-2(1H)-quinolinone (**S49**) (737.4 mg, 3.77 mmol, 1.0 equiv) and phosphorous(V) oxychloride ($POCl_3$) (5.3 mL, 56.6 mmol, 15.0 equiv) were combined in a round-bottom flask equipped with a stir bar. The flask was fitted with a water-cooled coil-type jacketed condenser fitted with a rubber septum secured by copper wire. The system was placed under an atmosphere of N_2 and heated at 95-100°C for 3.5 h. Evolving hydrogen chloride gas was routed through a mineral oil bubbler and then through an aqueous KOH trap using PVC tubing. Excess $POCl_3$ was removed by short-path vacuum distillation. Residual $POCl_3$ was quenched by dropwise addition of aqueous NaOH (5 mol %) then diluted with deionized water, inducing precipitation. The dark brown precipitate was filtered, washed with water, triturated in hexanes by sonication, and vacuum filtered through celite. The filtrate was concentrated under reduced pressure, but excessive residual water was observed by ^{1}H NMR. The solids were redissolved in chloroform, and the solution was washed with brine (2x), passed through a plug of magnesium sulfate, and concentrated under reduced pressure. The resulting solids were dried under vacuum overnight to afford **S20** as a pale yellow solid (324 mg, 37% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.13 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.3 Hz, 1H). 7.58 (s, 1H), 7.57 (dd, *J* = 8.5, 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 151.0, 144.9, 144.8, 133.4, 131.8, 127.8, 126.7, 123.4, 123.2. HRMS (TOF MS ESI+) m/z: [M]+ Calcd for $C_9H_4Cl_3N$ 230.9409; Found 230.9471.

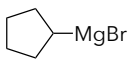


8-Bromo-2,4-dichloroquionoline (**28**): Compound **28** was prepared according to a modified literature procedure.[8] 2-Bromoaniline (230 μL, 1 mmol, 1.0 equiv), malonic acid (208 mg, 2 mmol, 2 equiv) and phosphorous(V) oxychloride ($POCl_3$) (2.0 mL) were combined in a 10 mL oven-dried Schlenk flask equipped with a stir bar. The flask was fitted with a water-cooled coil-type jacketed condenser equipped with a rubber septum secured by copper wire. The system was placed under an atmosphere of N_2 and heated at 100 °C for 6 h. Evolving hydrogen chloride gas was routed through a mineral oil bubbler and then through an aqueous KOH trap using PVC tubing. The reaction mixture was allowed to cool to room temperature and was subsequently poured onto crushed ice with stirring. The resulting mixture was extracted with excess dichloromethane and washed with sat. $NaHCO_3$ (aq) until the aqueous layer was slightly basic (pH 8). The layers were separated, and the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (R_f = 0.58 in 98:2 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.18 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.12 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.58 (s, 1H), 7.50 (dd, *J* = 8.4, 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ δ): 150.9, 145.5, 144.7, 135.3, 128.1, 126.5, 124.13, 124.05, 123.0. HRMS (ESI$^+$) m/z: [M]+: Calcd for $C_9H_4Cl_2BrN$ 274.8904; Found 274.8904.

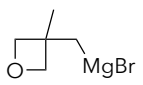
2. Grignard Reagents



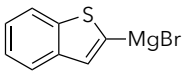
5-Methyl-2-pyridylmagnesium bromide (**S50**): Compound **S50** was prepared according to a modified literature procedure.[9] To an oven-dried 25 mL Schlenk flask equipped with a stir bar, under N_2, was added freshly crushed magnesium turnings (80.2 mg, 3.3 mmol, 1.1 equiv), dry degassed THF (6.0 mL), dry lithium chloride (127.2 mg, 3 mmol, 1.0 equiv), and diisobutylaluminum hydride (30 μL of a 1.0 *M* solution in THF, 0.03 mmol, 0.01 equiv). The reaction mixture was stirred for 5 min, followed by the dropwise addition of a solution of 2-bromo-5-methylpyridine (516.1 mg, 3.0 mmol, 1.0 equiv) in dry degassed THF (3.0 mL). The reaction was stirred at 23 °C for 1 h, resulting in a dark red solution that was used without further purification.



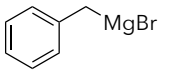
Cyclopentylmagnesium bromide (**S51**): To an oven-dried 25 mL Schlenk flask equipped with a stir bar, under N_2, was added freshly crushed magnesium turnings (53.5 mg, 2.2 mmol, 1.1 equiv) and dry degassed THF (6.7 mL). Cyclopentyl bromide (475 μL, 4 mmol, 1.0 equiv) was then added dropwise to the reaction mixture. The reaction mixture was heated to reflux for 3 h, resulting in a light brown solution that was used without further purification.



3,3'-Methyloxetanylmagnesium bromide (**S52**): To an oven-dried 25 mL Schlenk flask equipped with a stir bar, under N_2, was added freshly crushed magnesium turnings (106.9 mg, 4.4 mmol, 1.1 equiv), dry degassed THF (6.0 mL), and diisobutylaluminum hydride (40 μL of a 1.0 *M* solution in THF, 0.04 mmol, 0.01 equiv). The reaction mixture was stirred for 5 min, followed by the dropwise addition of a solution of 3-bromomethyl-3-methyloxetane (462 μL, 4.0 mmol, 1.0 equiv) in dry degassed THF (7 mL). The reaction mixture was heated to reflux for 2.5 h resulting in a colorless solution containing a white precipitate. This mixture was used without further purification.



2-Benzothiophenylmagnesium bromide (**S53**): Compound **S53** was prepared according to a modified literature procedure.[7] To an oven-dried 25 mL Schlenk flask ("Flask A") equipped with a stir bar, under N_2, was added benzothiophene (1.073 g, 8 mmol, 1 equiv) and dry degassed THF (13 mL). The resulting solution was cooled to -84 °C. *n*-BuLi (3.2 mL of a 2.5 *M* solution in hexanes, 8 mmol, 1.0 equiv) was added dropwise, and the mixture was stirred for 2 h while warming to 0 °C. In a separate 50 mL Schlenk flask ("Flask B") equipped with a stir bar, under nitrogen, was added magnesium bromide ethyl etherate (2.066 g, 3.0 mmol, 1.0 equiv) and dry degassed THF (14 mL). The cold contents of Flask A were added to the slurry in Flask B. The reaction mixture was stirred at 23 °C until all solids were dissolved, resulting in a rusty colored solution that was used without further purification.



Benzylmagnesium bromide (**S54**): To an oven-dried 25 mL Schlenk flask equipped with a stir bar, under N_2, was added freshly crushed magnesium turnings (106.9 mg, 4.4 mmol, 1.1 equiv), dry degassed THF (6.0 mL), and diisobutylaluminum hydride (40 µL of 1.0 *M* solution in THF, 0.04 mmol, 0.01 equiv). The resulting mixture was stirred for 5 min, followed by the dropwise addition of benzyl bromide (475µL, 4 mmol, 1.0 equiv) in dry degassed THF (7 mL). The reaction mixture was heated to reflux for 3 h, resulting in a clear solution containing a small quantity of white crystals. This mixture was used without further purification.

C. Suzuki Cross-Couplings with Pd/IPr

1. General Procedures

GC-Scale Reactions. The specified solids required in the Suzuki-Miyaura reactions were added to a 1-dram reaction vial in order of increasing mass: palladium catalyst (palladium source and free ligand) or precatalyst, the specified dihalopyridine substrate if solid (0.08 mmol, 1 equiv), arylboronic acid (0.08 mmol, 1.0 equiv), potassium carbonate or cesium carbonate, and then a stir bar. Liquid reagents were pre-measured by syringe and added in quick succession: benzene, THF, or 1,4-dioxane (0.32 mL, 0.25 *M*) via 1-mL syringe, followed by N_2-sparged deionized water via 50-µL syringe. Note: dihalopyridine substrates were added last if liquid, via microliter syringe. A septum cap equipped with an N_2-ingas and outgassing needle was fastened to the 1-dram reaction vial and the headspace was sparged for 30-45 seconds. With continuous sparging, the vial was unscrewed from the septum cap and lowered while the cap was replaced with a PTFE-lined cap. The reaction was stirred vigorously at the specified temperature for the specified duration.

Scaled-Up Reactions for Product Isolation. Precatalyst (η^3-1-^{t}Bu-indenyl)Pd(IPr)Cl (8.4 mg, 0.012 mmol, 3.0 mol%) was weighed into a 1-dram vial followed by solid substrate, if applicable (2,4-dichloropyridine, quinoline, or 3,5-dichloropyridazine, 0.4 mmol, 1 equiv), arylboronic acid (0.4 mmol, 1.0 equiv), potassium carbonate, and a stir bar. Liquid reagents were pre-measured by syringe and added in quick succession: benzene or THF (1.6 mL, 0.25 *M*) via a 1-mL syringe followed by N_2-sparged deionized water via a 100-µL or 250-µL syringe. In cases where the substrate was a liquid, the substrate was added last via microliter syringe (0.4 mmol, 1 equiv). A septum cap equipped with an N_2-ingas and outgassing needle was fastened to the 1-dram reaction vial and the mixture was

sparged for 30-45 seconds. With continuous sparging, the vial was unscrewed from the septum cap and lowered while the cap was replaced with a PTFE-lined cap. The reaction was stirred vigorously at the specified temperature for the specified duration. The cap was removed, the reaction mixture was diluted in ethyl acetate then filtered through a plug of celite. The reaction outcome was assessed by GC and TLC (isomeric ratios were determined by GC). The mixture was purified by flash column chromatography or crystallization under the specified conditions, and the product was dried under vacuum.

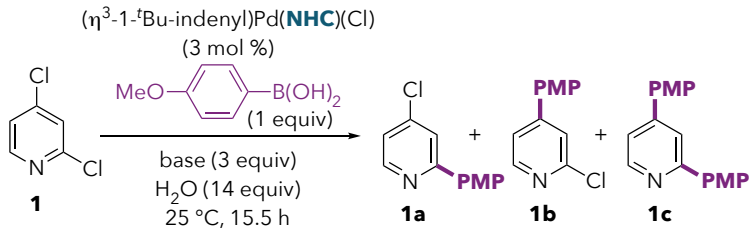
Conditions A: potassium carbonate (221.1 mg, 1.6 mmol, 4.0 equiv), deionized water (250 µL, 13.8 mmol, 34.6 equiv), THF, 60 °C.

Conditions B: potassium carbonate (165.8 mg, 1.2 mmol, 3.0 equiv), deionized water (100 µL, 5.53 mmol, 13.8 equiv), THF, 25 °C.

Conditions C: potassium carbonate (165.8 mg, 1.2 mmol, 3.0 equiv), deionized water (100 µL, 5.53 mmol, 13.8 equiv), benzene, 25 °C.

2. Optimization (Table 1)

Table S1. Optimization of the C4-Selective Suzuki-Miyaura Coupling with Pd/IPr[a]



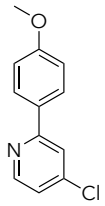
entry	trial	NHC	base	solvent	additive (equiv)	**1a** (%)	**1b** (%)	**1c** (%)	**1a** : **1b**
1	1	SIPr	KF	THF	--	4	35	4	1 : 8.8
2	2	SIPr	KF	THF	--	5	44	5	1 : 8.8
3	Average	SIPr	KF	THF	--	5	39	5	1 : 7.8
4	1	SIPr	K_2CO_3	THF	--	7.4	67.7	9.1	1 : 9.1
5	2	SIPr	K_2CO_3	THF	--	6.2	63.0	10.3	1 : 10.1
6	Average	SIPr	K_2CO_3	THF	--	6.8	65.4	9.7	1 : 9.6
7	1	IPr	K_2CO_3	THF	--	6	69	8	1 : 11.5
8	2	IPr	K_2CO_3	THF	--	7	68	7	1 : 9.7
9	Average	IPr	K_2CO_3	THF	--	7	69	8	1 : 9.9
10	1	IPr	K_2CO_3	C_6H_6	--	8	69	6.0	1 : 8.6
11	2	IPr	K_2CO_3	C_6H_6	--	8	70	6.4	1 : 8.8
12	Average	IPr	K_2CO_3	C_6H_6	--	8	70	6.2	1 : 8.8
13	1	IPr	K_2CO_3	$PhCH_3$	--	8	75	4	1 : 9.4
14	2	IPr	K_2CO_3	$PhCH_3$	--	8	72	4	1 : 9.0
15	Average	IPr	K_2CO_3	$PhCH_3$	--	8	74	4	1 : 9.2
16	1	IPr	K_2CO_3	DMF	--	8	46	17	1 : 5.8
17	2	IPr	K_2CO_3	DMF	--	8	48	14	1 : 5.9
18	Average	IPr	K_2CO_3	DMF	--	8	47	15	1 : 5.9
19	1	IPr	K_2CO_3	PC[b]	--	9	43	16	1 : 4.8
20	2	IPr	K_2CO_3	PC[b]	--	9	46	18	1 : 5.1
21	Average	IPr	K_2CO_3	PC[b]	--	9	45	17	1 : 5.0
22[c]	1	--	K_2CO_3	C_6H_6	--	2	<1	n.d.	--
23[c]	2	--	K_2CO_3	C_6H_6	--	1	<1	n.d.	--

24[c]	Average	--	K_2CO_3	C_6H_6	--	2	<1	n.d.	--
25[d]	1	--	K_2CO_3	THF	--	2	1	n.d.	--
26[d]	2	--	K_2CO_3	THF	--	1	<1	n.d.	--
27[d]	Average	--	K_2CO_3	THF	--	1	<1	n.d.	--
28	1	SIPr	K_2CO_3	C_6H_6	--	9	61	8	1 : 6.8
29	2	SIPr	K_2CO_3	C_6H_6	--	9	66	7	1 : 7.3
30	Average	SIPr	K_2CO_3	C_6H_6	--	9	64	8	1 : 7.1
31	1	SIMes	K_2CO_3	C_6H_6	--	21	30	3	1 : 1.4
32	2	SIMes	K_2CO_3	C_6H_6	--	27	39	3	1 : 1.4
33	Average	SIMes	K_2CO_3	C_6H_6	--	24	35	3	1 : 1.5
34	1	IMes	K_2CO_3	C_6H_6	--	21	35	3	1 : 1.6
35	2	IMes	K_2CO_3	C_6H_6	--	24	44	3	1 : 1.7
36	Average	IMes	K_2CO_3	C_6H_6	--	23	40	3	1 : 1.7
37	1	SIMix	K_2CO_3	C_6H_6	--	8	36	2	1 : 4.5
38	2	SIMix	K_2CO_3	C_6H_6	--	8	31	2	1 : 3.9
39	Average	SIMix	K_2CO_3	C_6H_6	--	8	34	2	1 : 4.3
40	1	IPent	K_2CO_3	C_6H_6	--	1	31	21	1 : 31
41	2	IPent	K_2CO_3	C_6H_6	--	1	37	24	1 : 37
42	Average	IPent	K_2CO_3	C_6H_6	--	1	34	23	1 : 34
43	1	IPr	K_2CO_3	THF	NBu_4Br (1)	<1	3	n.d.	--
44	2	IPr	K_2CO_3	THF	NBu_4Br (1)	1	4	n.d.	--
45	Average	IPr	K_2CO_3	THF	NBu_4Br (1)	<1	3	n.d.	--
46	1	IPr	K_2CO_3	THF	NBu_4Br (3)	<1	2	n.d.	--
47	2	IPr	K_2CO_3	THF	NBu_4Br (3)	<1	2	n.d.	--
48	Average	IPr	K_2CO_3	THF	NBu_4Br (3)	<1	2	n.d.	--
49	1	IPr	K_2CO_3	THF	NBu_4Cl (3)	<1	1	n.d.	--
50	2	IPr	K_2CO_3	THF	NBu_4Cl (3)	<1	<1	n.d.	--
51	Average	IPr	K_2CO_3	THF	NBu_4Cl (3)	<1	1	n.d.	--
52	1	IPr	K_2CO_3	THF	NBu_4OH (3)[e]	1	4	n.d.	--
53	2	IPr	K_2CO_3	THF	NBu_4OH (3)[e]	1	4	n.d.	--
54	Average	IPr	K_2CO_3	THF	NBu_4OH (3)[e]	1	4	n.d.	--
55	1	IPr	K_2CO_3	dioxane	--	6.7	77.1	7.6	1 : 12
56[f]	1	IPr	K_2CO_3	dioxane	--	2.8	43.0	25.4	1 : 15
57	1	IPr	K_2CO_3	toluene	--	8.8	78.2	4.8	1 : 9
58[f]	1	IPr	K_2CO_3	toluene	--	8.5	44.6	15.4	1 : 5

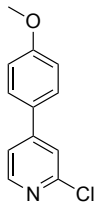
[a]Reactions were conducted according to the General Procedure for GC-scale reactions. GC yields calibrated against undecane as an internal standard. Calculated yield values were rounded to the nearest integer. Entries reported as <1 indicate a calibrated GC yield less than 0.5%; nd = not detected. [b]PC = propylene carbonate. [c]No NHC ligand; Pd source was $(\eta^3\text{-}1\text{-}^t\text{Bu-indenyl})_2(\mu\text{-Cl})_2Pd_2$ (1.5 mol %). [d]No NHC ligand; Pd source was $PdCl_2$ (3 mol %). [e]NBu_4OH was added as a solution in water (156 μL of a 40% aqueous solution, 3 equiv) added; no additional water added to the reaction. [f]Reaction was conducted at 100 °C.

Discussion: Unlike our optimized ligand-free conditions (*vide infra*), the addition of tetraalkylammonium salts to the Pd/IPr catalytic conditions inhibits cross-coupling (Table S1, entries 43-54). The use of high temperatures in the Pd/IPr conditions does not lead to significant improvements in C4-selectivity (compare entry 55 to 56, and entry 57 to 58), indicating that the high-temperatures used in ligand-free conditions are not solely responsible for the greatly enhanced selectivity under 'Jeffery' conditions.

3. Isolation and Characterization of Products (Table 1 and Scheme 2)

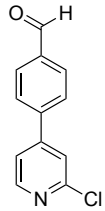


4-Chloro-2-(4-methoxyphenyl)pyridine (1a). Compound **1a** was prepared according to a modified literature procedure[10]. $Pd(OAc)_2$ (33.7 mg, 0.15 mmol, 5 mol %), 1,1'-bis(diphenylphosphino)ferrocene (109.8 mg, 0.15 mmol, 5 mol %), Cs_2CO_3 (2.44 g, 7.5 mmol 2.5 equiv) and *p*-methoxyphenylboronic acid (455.8 mg, 3 mmol, 1 equiv) were added to an oven-dried 5-dram vial in a N_2-filled glovebox. The vial was sealed with a septum and removed from the glovebox, and 2,4-dichloropyridine (**1,** 322 µL, 3 mmol, 1 equiv), deionized water (378 µL, 21 mmol, 7 equiv), and 1,4-dioxane (12 mL) were added through the septum. The reaction was allowed to stir at 70 °C for 19 h. Purification via flash column chromatography (R_f = 0.50 in 20% ethyl acetate in hexanes) yielded **1a** as an off-white solid (504 mg, 76% yield). Spectral data are consistent with the literature.[11]



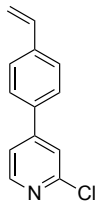
2-Chloro-4-(4-methoxyphenyl)pyridine (1b). Compound **1b** was prepared according to the general procedure using Conditions B and 2,4-dichloropyridine (43.2 µL, 0.4 mmol, 1.0 equiv) with stirring for 16.5 h. Three separate reactions were perfomed using *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv), *p*-methoxyphenylboronic acid pinacol ester (93.6 mg, 0.4 mmol, 1.0 equiv), or *p*-methoxyphenylboronic acid neopentyl glycol ester (88.0 mg, 0.4 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel (R_f = 0.29 in 10% acetone in hexanes) provided **1b** and other isolated side products as white solids with varying degrees of brown discoloration. *p*-Methoxyphenylboronic acid method: (63.3 mg, 72% yield); *p*-methoxyphenylboronic acid pinacol ester method: (61.5 mg, 70% yield; diarylated side product **1c**: 15.2 mg, 13% yield); *p*-methoxyphenylboronic acid neopentyl glycol ester method: (55.4 mg, 63% yield; diarylated side product **1c**: 10.5 mg, 9% yield). **1b**: (600 MHz, $CDCl_3$, δ): 8.36 (d, *J* = 5.2 Hz, 1H), 7.6-7.5 (m, 2H), 7.48 (d, *J* = 1.1 Hz, 1H), 7.37 (dd, *J* = 1.6, 5.3 Hz, 1H), 7.01-6.98 (m, 2H), 3.85 (s, 3H). Spectral data are consistent with the literature.[12] 2,4-bis(4-methoxyphenyl)pyridine (**1c**): (600 MHz, $CDCl_3$, δ): 8.65 (d, *J* = 5.2 Hz, 1H), 8.00 (m, 2H), 7.83 (s, 1H), 7.65 (m, 2H), 7.35 (dd, *J* = 5.2, 1.4 Hz, 1H), 7.04-7.01 (multiple peaks, 4H), 3.88 (coincidentally overlapping singlets, 6H). Spectral data are consistent with the literature.[13]

Larger-Scale Preparation of 1b: Compound **1b** was prepared according to the general procedure using Conditions B with 2,4-dichloropyridine (216 µL, 2.0 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (303.9 mg, 2.0 mmol, 1.0 equiv) with stirring for 27 h. Purification by flash column chromatography on silica gel (R_f = 0.29 in 10% acetone in hexanes) provided **1b** as a white solid with slight yellow discoloration (265.8 mg, 61% yield). Spectral data are consistent with the literature.[12]

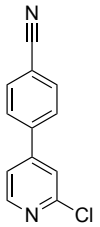


4-(2-Chloro-4-pyridinyl)benzaldehyde (4b). Compound4**3b** was prepared according to the general procedure using Conditions B, 2,4-dichloropyridine (43.2 µL, 0.4 mmol, 1.0 equiv) and *p*-formylphenylboronic acid (60.0 mg, 0.4 mmol, 1.0 equiv) with stirring for 16 h. Purification by flash column chromatography on silica (R_f = 0.22 in 10% acetone in hexanes) provided **4b** as a white solid (38.8 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 10.08 (s, 1H), 8.48 (d, *J* = 5.2 Hz, 1H), 8.01-7.99 (m, 2H), 7.78-7.76 (m, 2H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.46 (dd, *J* = 5.2, 1.5 Hz, 1H). Spectral data are consistent with

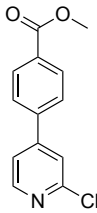
the literature.[14] The C2-mononarylated isomer **S4a** was isolated as a minor product in low purity (7.5 mg, <9% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 10.9 (s, 1H), 8.64 (d, *J* = 5.3 Hz, 1H), 8.17-8.15 (m, 2H), 8.01-7.99 (m, 2H), 7.18 (d, *J* = 1.8 Hz, 1H), 7.32 (dd, *J* = 1.8, 5.3 Hz, 1H). The minor product of diarylation **4c** was also isolated (8.3 mg, 7% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 10.12 (s, 1H), 10.11 (s, 1H), 8.84 (d, *J* = 5.0 Hz, 1H), 8.26-8.24 (m, 2H), 8.05-8.02 (multiple peaks, 5H), 7.88-7.86 (m, 2H), 7.55 (dd, *J* = 1.6, 5.0 Hz, 1H).



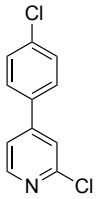
2-Chloro-4-(4-vinylphenyl)pyridine (5b). Compound **5b** was prepared according to the general procedure using Conditions B, 2,4-dichloropyridine (43.2 µL, 0.4 mmol, 1.0 equiv) and *p*-vinylphenylboronic acid (60.0 mg, 0.4 mmol, 1.0 equiv) with stirring for 16.5 h. Purification by flash column chromatography on silica (R_f = 0.21 in 2.5% acetone in hexanes) provided **5b** as an off-white solid (55.7 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.39 (d, *J* = 5.2 Hz, 1H), 7.56-7.55 (m, 2H), 7.51-7.49 (multiple overlapping signals, 3H), 7.39 (d, *J* = 5.2 Hz, 1H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.83 (d, *J* = 17.6 Hz, 1H), 5.34 (d, *J* = 10.9 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 152.3, 151.0, 150.1, 139.1, 135.9 (two signals are coincidentally overlapping), 127.2, 127.1, 121.7, 120.2, 115.5. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{13}H_{10}ClN$ 215.0502; Found 215.04922.



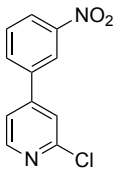
4-(2-Chloro-4-pyridinyl)benzonitrile (6b). Compound **6b** was prepared according to the general procedure using Conditions B, 2,4-dichloropyridine (43.2 µL, 0.4 mmol, 1.0 equiv) and *p*-cyanophenylboronic acid (58.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 16.5 h. Purification by flash column chromatography on silica (R_f = 0.19 in 10% acetone in hexanes) provided **6b** as a white crystalline solid (60.3 mg, 70% yield); ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.47 (d, *J* = 5.2 Hz, 1H), 7.78-7.77 (m, 2H), 7.71-7.70 (m, 2H), 7.52 (d, *J* = 1.1 Hz, 1H), 7.42 (dd, *J* = 5.2, 1.1 Hz, 1H). The spectral data are consistent with the literature.[15] The C2-mononarylated isomer **S6a** was isolated as a minor product in low purity (7.8 mg, <9% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.63 (d, *J* = 5.2 Hz, 1H), 8.11-8.10 (m, 2H), 7.78-7.77 (multiple overlapping signals, 3H), 7.33 (dd, *J* = 5.2, 1.8 Hz, 1H). The minor product of diarylation **S6c** was also isolated (14.3 mg, 13% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.84 (d, *J* = 5.0 Hz, 1H), 8.19-8.18 (m, 2H), 7.94 (s, 1H), 7.83-7.79 (multiple overlapping signals, 6H), 7.52 (dd, *J* = 5.0, 1.3 Hz, 1H).



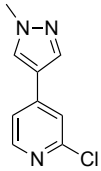
4-(2-Chloro-4-pyridinyl)benzoic acid methyl ester (7b). Compound **7b** was prepared according to the general procedure using Conditions B, 2,4-dichloropyridine (43.2 µL, 0.4 mmol, 1.0 equiv) and *p*-(methoxycarbonyl)phenylboronic acid (72.0 mg, 0.4 mmol, 1.0 equiv) with stirring for 16 h. Purification by flash column chromatography on silica (R_f = 0.24 in 5% acetone in hexanes) provided **7b** as a white microcrystalline solid (59.8 mg, 60% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.43 (d, *J* = 4.9 Hz, 1H), 8.13-8.12 (m, 2H), 7.65-7.64 (m, 2H), 7.53 (s, 1H), 7.42 (d, *J* = 4.9 Hz, 1H), 3.93 (s, 3H). Spectral data are consistent with the literature.[15]



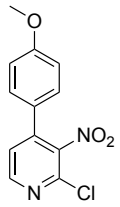
2-Chloro-4-(4-chlorophenyl)pyridine (8b). Compound **8b** was prepared according to the general procedure using Conditions B, 2,4-dichloropyridine (43.2 μL, 0.4 mmol, 1.0 equiv) and *p*-chlorophenylboronic acid (62.5 mg, 0.4 mmol, 1.0 equiv) with stirring for 16 h. Purification by flash column chromatography on silica (R_f = 0.25 in 5% THF in hexanes) resulted in partial separation of **8b** from the C2-monoarylated isomer. Coeluted fractions were purified by evaporative crystallization from acetone and water, providing **8b** as an off-white solid (59 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.43 (d, *J* = 5.2 Hz, 1H), 7.55-7.52 (m, 2H), 7.50 (d, *J*= 1.6 Hz, 1H), 7.47-7.45 (m, 2H), 7.38 (dd, *J* = 5.2, 1.6 Hz, 1H). Spectral data are consistent with the literature.[15]



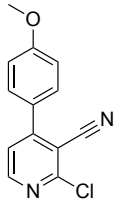
2-Chloro-4-(3-nitrophenyl)pyridine (9b). Compound **9b** was prepared according to the general procedure (except on the 1.0 mmol scale) using Conditions B, 2,4-dichloropyridine (108.0 μL, 1.0 mmol, 1.0 equiv) and *m*-nitrophenylboronic acid (166.9 mg, 1.0 mmol, 1.0 equiv) with stirring for 16 h. Purification by flash column chromatography on silica (R_f = 0.24 in 10% acetone in hexanes) provided **9b** as a white crystalline solid (156.7 mg, 67% yield); mp 159-161 °C [uncorrected, measured against benzoic acid (113-117 °C)]. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.52 (dd, *J* = 5.2, 0.5 Hz, 1H), 8.48 (dd, *J* = 1.8, 1.8 Hz, 1H), 8.33 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H), 7.95 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H), 7.71 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.60 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.48 (dd, *J* = 5.2, 1.8 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 152.9, 150.7, 149.1, 149.0, 138.8, 133.0, 130.6, 124.4, 122.3, 122.2, 120.5. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{11}H_7ClN_2O_2$ 234.0196; Found 234.0193.



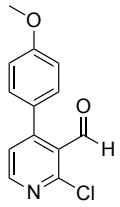
2-Chloro-4-(1-methyl-1H-pyrazol-4-yl)pyridine (10b). Compound **10b** was prepared according to the general procedure using Conditions B, with the modification that the reaction was heated to 75 °C, and with 2,4-dichloropyridine (43.2 μL, 0.4 mmol, 1.0 equiv) and (1-methyl-1*H*-pyrazol-4-yl)boronic acid (75.5 mg, 0.6 mmol, 1.5 equiv) with stirring for 35 h. Products were purified via flash column chromatography using a step gradient: 0.75% methanol in CH_2Cl_2 until elution of the C2-monoarylated product **S10a**, 3% methanol in CH_2Cl_2 until elution of **10b**, 5% methanol in CH_2Cl_2 until elution of the diarylated product **S10c** (R_f values in 0.75% methanol/CH_2Cl_2: C2-monoarylated isomer **S10a** = 0.17, C4-monoarylated isomer **10b** = 0.31, diarylated product **S10c** = 0.09). Product **10b** was isolated as an off-white solid (52 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.27 (d, *J* = 5.3 Hz, 1H), 7.80 (s, 1H), 7.72 (s, 1H), 7.34 (d, *J* = 1.3 Hz, 1H), 7.22 (dd, *J* = 5.3, 1.3 Hz, 1H), 3.94 (s, 3H). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.43 (s, 1H), 8.30 (dd, *J* = 5.3, 0.6 Hz, 1H), 8.12 (d, *J* = 0.6 Hz, 1H), 7.71 (dd, *J* = 1.5, 0.6 Hz, 1H), 7.57 (dd, *J* = 5.3, 1.5 Hz, 1H), 3.88 (s, 3H). Spectral data are consistent with the literature.[16] The C2-mononarylated isomer (**S10a**) was isolated as a minor product in low purity (10 mg, <13% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.42 (d, *J* = 5.4 Hz, 1H), 7.93 (s, 1H), 7.92 (s, 1H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.10 (dd, *J* = 5.4, 1.9 Hz, 1H), 3.95 (s, 3H). The minor product of diarylation (**S10c**) was also isolated (9 mg, 9% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.48 (dd, *J* = 5.2, 0.7 Hz, 1H), 7.97 (s, 1H), 7.95 (s, 1H), 7.87 (d, *J* = 0.7 Hz, 1H), 7.76 (s, 1H), 7.50 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.15 (dd, *J* = 5.2, 1.7 Hz, 1H), 3.97 (s, 3H), 3.96 (s, 3H).



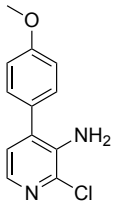
2-Chloro-4-(4-methoxyphenyl)-3-nitropyridine (11b). Compound **11b** was prepared according to the general procedure using Conditions A, 2,4-dichloro-3-nitro-pyridine (77.2 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 9 h. Purification by flash column chromatography on silica gel in 10-15% acetone/hexanes (R_f = 0.25 in 10% acetone in hexanes) provided **11b** as a colorless crystalline solid (70.3 mg, 66% yield), with evidence of yellow impurity (1H NMR shows there is a 6% impurity comprising C2-monoarylated isomer **S11a**); mp 110-113 °C [uncorrected, measured against benzoic acid (110-113 °C)]. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.49 (d, J = 5.1 Hz, 1H), 7.36-7.33 (multiple peaks, 3H), 6.99-6.97 (m, 2H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 161.5, 150.0, 145.1 (this small quaternary peak was selected from among impurity peaks based on comparison with an ACD labs simulated spectrum), 144.3, 142.3, 129.2, 125.0, 124.3, 115.0, 55.5. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{12}H_9ClN_2O_3$ 264.0302; Found 264.0298.



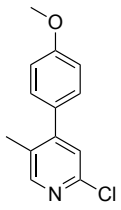
2-Chloro-4-(4-methoxyphenyl)-3-pyridinecarbonitrile (12b). Compound **12b** was prepared according to the general procedure using Conditions A, 2,4-dichloro-3-cyano-pyridine (69.2 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 12 h. Purification by flash column chromatography on silica gel (R_f = 0.21 in 10% acetone in hexanes) provided **12b** as a colorless crystalline solid (66.4 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.52 (d, J = 5.3 Hz, 1H), 7.60-7.57 (m, 2H), 7.36 (d, J = 5.3 Hz, 1H), 7.07-7.04 (m, 2H), 3.88 (s, 3H). Spectral data are consistent with the literature.[17] The minor product of diarylation (**S12c**) was also isolated (4.4 mg, 3% yield; R_f = 0.10 in 10% acetone in hexanes). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.77 (d, J = 5.1 Hz, 1H), 7.91-7.90 (m, 2H), 7.62-7.58 (m, 2H), 7.31 (d, J = 5.1 Hz, 1H), 7.07-7.04 (multiple peaks, 4H), 3.89 (coincidentally overlapping singlets, 6H).



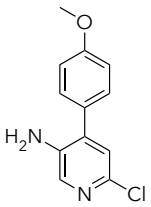
2-Chloro-4-(4-methoxyphenyl)-3-pyridinecarboxaldehyde (13b). Compound **13b** was prepared according to the general procedure using Conditions C, 2,4-dichloro-3-pyridinecarboxaldehyde (70.4 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 12 h. Purification by flash column chromatography on silica gel (R_f = 0.21 in 10% acetone in hexanes) provided **13b** as a yellow solid (51.4 mg, 52% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 10.14 (s, 1H), 8.49 (d, J = 5.1 Hz, 1H), 7.31 (d, J = 5.1 Hz, 1H), 7.29-7.26 (m, 2H), 7.02-7.00 (m, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 190.3, 161.0, 154.4, 151.5, 151.1, 130.8, 128.1, 127.6, 124.8, 114.5, 55.5. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{13}H_{10}ClNO_2$ 247.0400; Found 247.0385. The C2-mononarylated isomer **S13a** was isolated as a minor product in low purity (9.9 mg, <10% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.97 (s, 1H), 8.65 (d, J = 5.3 Hz, 1H), 7.51-7.49 (m, 2H), 7.38 (d, J = 5.3 Hz, 1H), 7.03-7.02 (m, 2H), 3.88 (s, 3H).



2-Chloro-4-(4-methoxyphenyl)-3-pyridinamine (14b). Compound **14b** was prepared according to the general procedure using Conditions C, 3-amino-2,4-dichloro-pyridine (65.2 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 18.5 h. Purification by flash column chromatography on silica gel (R_f = 0.42 in 25% ethyl acetate in hexanes) provided **14b** as a white crystalline solid (56.7 mg, 60% yield); mp 113-116 °C [uncorrected, measured against benzoic acid (111-113 °C)]. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.79 (d, *J* = 4.8 Hz, 1H), 7.38-7.35 (m, 2H), 7.01-6.98 (m, 2H), 6.95 (d, *J* = 4.8 Hz, 1H), 4.19 (br s, 2H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 159.9, 138.1, 137.6, 137.3, 135.2, 129.6, 128.7, 124.2, 114.7, 55.5. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{12}H_{11}ClN_2O$ 234.0560; Found 234.0557. The C2-monoarylated isomer **S14a** was isolated as a minor product (12.2 mg, 13% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.98 (d, *J* = 5.2 Hz, 1H), 7.62-7.59 (m, 2H), 7.15 (d, *J* = 5.2 Hz, 1H), 7.02-7.00 (m, 2H), 4.23 (br s, 2H), 3.86 (s, 3H). The minor product of diarylation **S14c** was also isolated (16.7 mg, 14% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.13 (d, *J* = 4.9 Hz, 1H), 7.68-7.66 (m, 2H), 7.46-7.44 (m, 2H), 7.03-7.00 (multiple peaks, 4H), 6.98 (d, *J* = 4.9 Hz, 1H), 3.90 (br s, 2H), 3.864 (s, 3H), 3.859 (s, 3H).

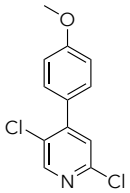


2-Chloro-4-(4-methoxyphenyl)-5-methylpyridine (15b). Compound **15b** was prepared according to the general procedure using Conditions B, 2,4-dichloro-5-methylpyridine (64.8 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 18.5 h. Purification by flash column chromatography on silica gel (R_f = in 5% acetone in hexanes) resulted in partial purification of the C4-monoarylated isomer. One fraction containing coeluted monoarylated isomers and diarylated product was purified further by preparatory TLC in the same eluent. Product **15b** was extracted from the silica gel with acetone and combined with remaining **15b** fractions obtained from flash column chromatography, providing an off-white solid (49.9 mg, 53% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.24 (s, 1H), 7.26-7.24 (m, 2H), 7.19 (s, 1H), 7.00-6.98 (m, 2H), 3.86 (s, 3H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 159.9, 152.1, 150.9, 149.2, 130.3, 129.91, 129.87, 124.2, 114.2, 55.5, 17.0. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{13}H_{12}ClNO$ 233.0607; Found 233.0603. The minor product of diarylation **S15c** was also isolated (21.8 mg, 18% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.52 (s, 1H), 7.96-7.94 (m, 2H), 7.52 (s, 1H), 7.33-7.31 (m, 2H), 7.01-7.98 (multiple peaks, 4H), 3.87 (s, 3H), 3.86 (s, 3H), 2.30 (s, 3H).

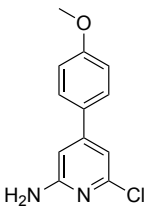


6-Chloro-4-(4-methoxyphenyl)-3-pyridinamine (16b). Compound **16b** was prepared according to the general procedure using Conditions C, 5-amino-2,4-dichloropyridine (78.2 mg, 0.48 mmol, 1.2 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 21 h. Purification was performed by reversed phase flash column chromatography with a 12 g C18 silica column, using an initial automated program comprising of a flow rate of 36 mL/min of water:acetonitrile (98:2 to 6:94) over 30 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 50-53% MeCN in water. After the elution, the initial program was resumed. The C4 monoarylated product **16b** coeluted with the C2 monoarylated isomer **S16a** at 52-53% MeCN. Fractions containing **16b** were partitioned between dichloromethane and saturated brine. The organic layers were combined and dried over magnesium sulfate and solvent was removed under reduced pressure affording a mixture of the product

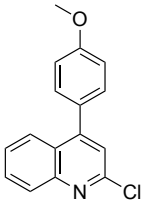
isomers. Further purification attempts were unsuccessful, and the final product **16b** was obtained as a rust colored solid in 94% purity (74.4 mg, 74% yield based on 94% purity). ^{1}H NMR (400 MHz, C_6D_6, δ): 7.55 (s, 1H), 6.55-7.00 (m, 2H), 6.90 (s, 1H), 6.66-6.71 (m, 2H), 3.28 (s, 3H), 2.88 (br s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, δ): 160.6, 141.5, 139.9, 137.5, 136.9, 130.1, 124.6, 125.3, 115.1, 55.2. HRMS (ESI$^+$) m/z: [M]+: Calcd for $C_{12}H_{11}ClN_2O$ 234.0560; Found 234.0562.



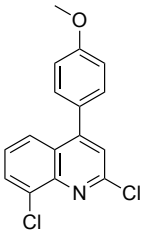
2,5-Dichloro-4-(4-methoxyphenyl)pyridine (17b). Compound **17b** was prepared according to the general procedure using Conditions C, 2,4,5-trichloropyridine (73.0 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 21 h. Purification was performed by reversed phase flash column chromatography with a 12 g C18 silica column, using an initial automated program comprising a flow rate of 30 mL/min of water:methanol (98:2 to 0:100) over 40 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 65-60% MeOH in water. After the elution, the initial program was resumed. The C4 monoarylated product eluted at 67% MeOH. Fractions containing product **17b** were partitioned between ethyl acetate and saturated brine. The organic layers were combined and dried over magnesium sulfate and solvent was removed under reduced pressure affording an off-white solid (44.0 mg, 43% yield). ^{1}H NMR (500 MHz, C_6D_6, δ): 8.16 (s, 1H), 6.94-7.02 (m, 2H), 6.87 (s, 1H), 6.66-6.71 (m, 2H), 3.26 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, δ): 160.5, 149.9, 149.51, 149.46, 130.2, 128.9, 128.0, 125.3, 113.8, 54.5 ppm. HRMS (ESI$^+$) m/z: [M]+: Calcd for $C_{12}H_9Cl_2NO$ 253.0061; Found 253.0073.



6-Chloro-4-(4-methoxyphenyl)-2-pyridinamine (18b). Compound **18b** was prepared according to the general procedure using Conditions C, 2-amino-4,6-dichloro-pyridine (65.2 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 25.5 h. Purification by flash column chromatography on silica gel (R_f = 0.22 in 25% ethyl acetate in hexanes) provided **18b** as a colorless crystalline solid with minor brown discoloration (45.1 mg, 48% yield); mp 167-172 °C [uncorrected, measured against benzoic acid (115-118 °C)]. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.51-7.49 (m, 2H), 6.96 (m, 2H), 6.86 (d, J = 1.3 Hz, 1H), 6.53 (d, J = 1.3 Hz, 1H), 4.61 (br s, 2H), 3.85 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 160.8, 158.8, 152.6, 150.2, 130.0, 128.2, 114.6, 111.5, 103.8, 55.5. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{12}H_{11}ClN_2O$ 234.0560; Found 234.0551. The C2-monoarylated isomer **S18a** was isolated as a minor product (R_f = 0.30 in 25% ethyl acetate in hexanes; 12.6 mg, 13% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.88-7.86 (m, 2H), 7.03 (d, J = 1.5 Hz, 1H), 6.97-6.95 (m, 2H), 6.40 (d, J = 1.5 Hz, 1H), 4.57 (br s, 2H), 3.85 (s, 3H). The column eluent was modified to 5% methanol in CH_2Cl_2 to elute the diarylated product **S18c**, isolated in low purity (R_f = 0.02 in 25% ethyl acetate in hexanes; 19.7 mg, <16% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.94-7.91 (m, 2H), 7.60-7.57 (m, 2H), 7.22 (d, J = 1.3 Hz, 1H), 7.00-6.96 (multiple peaks, 4H), 6.58 (d, J = 1.3 Hz, 1H), 4.62 (br s, 2H), 3.859 (s, 3H), 3.856 (s, 3H).

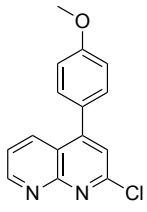


2-Chloro-4-(4-methoxyphenyl)quinoline (19b). Compound **19b** was prepared according to the general procedure using Conditions B on a 3.0 mmol scale using 2,4-dichloroquinoline (**19**, 594.2 mg, 3.0 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (455.9 mg, 3.0 mmol, 1.0 equiv) with stirring for 19 h. The product mixture was diluted in ethyl acetate, filtered through celite, and solvent was removed under reduced pressure (as described in the general procedure) Purification method 1: The concentrated residue was dissolved in excess acetone in a conical flask, then water was added until the solution appeared to become saturated. Slow evaporation of the acetone/water solution from the flask induced crystallization. Yellow-tinted crystals were collected from three crops, separated from solvent, and dried in air to provide product **19b** (454 mg, 56% yield). Purification method 2: The concentrated residue was purified on a Biotage Selekt automated column using 100 grams of high-capacity silica (*see General Materials and Methods*), a linear gradient of 2-20% acetone in hexanes over 12 column volumes, at a flow rate of 120 mL/min (R_f = 0.60 in 10% acetone in hexanes. GC analysis indicated coelution of the C2- and C4-monoarylated isomers (**S19a** and **19b**); however, large colorless crystals of **19b** formed selectively within the fractions, and were collected in two separate crops and dried under air to provide product **19b** (403.2 mg, 50% yield); mp 152-154 °C [uncorrected, measured against benzoic acid (113-117 °C)]. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.08 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.73 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.0, 1.2 1H), 7.46-7.43 (m, 2H), 7.32 (s, 1H), 7.08-7.05 (m, 2H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 160.4, 151.5, 150.5, 148.6, 130.9, 130.5, 129.15, 129.12, 126.9, 126.1, 125.9, 122.1, 114.3, 55.6. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{16}H_{12}ClNO$ 269.0607; Found 269.0606.

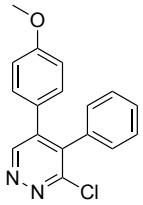


2,8-Dichloro-4-(4-methoxyphenyl)quinoline (20b). Compound **20b** was prepared according to the general procedure using Conditions C, 2,4,8-trichloroquinoline (102.3 mg, 0.44 mmol, 1.1 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 15.5 h. The product was purified by reversed phase flash column chromatography with a 12 g C18 silica column, using an initial automated program utilizing a flow rate of 13 mL/min of water:acetonitrile (98:2 to 5:95) over 30 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 61-70% MeCN in water. After the elution, the initial program was resumed. The C4 monoarylated product **20b** eluted cleanly at 65-67% MeCN, but the C2-monoarylated isomer **S20a** and the 2,4-diarylated product **S20c** subsequently coeluted with each other. Fractions containing **20b** were partitioned between ethyl acetate and saturated brine. The organic layers were combined and dried over magnesium sulfate, concentrated, and dried furnishing **20b** as a white solid (65.9 mg, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.86 (dd, *J* = 1.8, 1.4 Hz, 1H), 7.84 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.43-7.40 (multiple peaks, 3H), 7.38 (s, 1H), 7.08-7.05 (m, 2H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 160.6, 152.1, 151.5, 145.0, 133.1, 130.9, 130.6, 128.9, 127.5, 126.7, 125.3, 123.2, 114.4, 55.6. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{16}H_{11}Cl_2NO$ 303.0218; Found 303.0217. The minor products **S20a** and **S20c** were further purified by (normal-phase) flash column chromatography in 5-20% acetone in hexanes. The C2-monoarylated isomer **S20a** was isolated as a minor product in low purity (4.0 mg, <3% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.24-8.22 (m, 2H), 8.13 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.01 (s, 1H), 7.87 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.48 (dd, *J* = 8.4, 7.5 Hz, 1H), 7.07-7.04 (m, 2H), 3.90 (s, 3H). The minor product of 2,4-diarylation **S20c** was also isolated in low purity (7.3 mg, <5% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ):

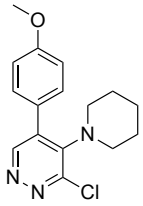
8.30-8.27 (m, 2H), 7.83-7.81 (multiple peaks, 3H), 7.49-7.46 (m, 2H), 7.33 (dd, *J* = 8.4, 7.5 Hz, 1H), 7.09-7.07 (m, 2H), 7.07-7.04 (m, 2H), 3.92 (s, 3H), 3.89 (s, 3H).



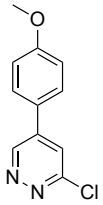
2-Chloro-4-(4-methoxyphenyl)-1,8-naphthyridine (21b). Compound **21b** was prepared according to the general procedure using Conditions B, with the modification that catalyst **3f** (9.8 mg, 0.012 mmol, 3.0 mol%) was used instead of **3b**, 2,4-dichloro-1,8-naphthyridine (79.6 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 12 h. Purification by flash column chromatography on silica gel (R_f = 0.22 in 20% pyridine in hexanes) provided **21b** as a white solid (72.1 mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.04 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.28 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.38-7.37 (multiple peaks, 3H), 7.05-7.03 (m, 2H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 160.7, 156.1, 154.0, 153.7, 152.3, 135.6, 130.8, 127.8, 123.0, 122.2, 120.6, 114.5, 55.5. HRMS (TOF MS ESI+) m/z: [M]+ Calcd for $C_{15}H_{11}ClN_2O$ 270.0560; Found 270.0567.



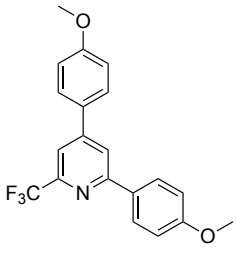
3-Chloro-5-(4-methoxyphenyl)-4-phenylpyridazine (22b). Compound **22b** was prepared according to the general procedure using Conditions A, 3,5-dichloro-4-phenylpyridazine (**S22**, 135.0 mg, 0.6 mmol, 1.5 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 22 h. Product **22b** was purified on an automated column using 10 grams of high-capacity silica, a linear gradient of 5-40% acetone in hexanes over 11 column volumes (R_f = 0.36 in 20% acetone in hexanes). Product **22b** was isolated as a white solid (81.5 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.12 (s, 1H), 7.34-7.33 (m, 3H), 7.15-7.14 (m, 2H), 7.03-7.01 (m, 2H), 6.77-6.75 (m, 2H), 3.74 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 160.3, 157.0, 151.6, 140.5, 137.7, 133.4, 130.9, 129.7, 128.9, 128.6, 126.0, 114.3, 55.3. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{17}H_{13}ClN_2O$ 296.0716; Found 296.0706. The minor product of diarylation **S22c** was also isolated in low purity (10.1 mg, <7% yield, R_f = 0.15 in 20% acetone in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.15 (s, 1H), 7.28-7.26 (m, 2H), 7.21-7.17 (m, 3H), 7.03-7.01 (m, 2H), 6.93-6.91 (m, 2H), 6.79-6.75 (multiple peaks, 4H), 3.782 (s, 3H), 3.778 (s, 3H).



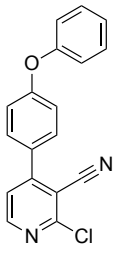
3-Chloro-5-(4-methoxyphenyl)-4-(1-piperidinyl)pyridazine (23b). Compound **23b** was prepared according to the general procedure using Conditions A, modified to heat at 66 °C instead of 60 °C, with 3,5-dichloro-4-(1-piperidinyl)-pyridazine (**S23**, 92.8 mg, 0.4 mmol, 1.0 equiv), and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 8 days (however, yields were comparable when the reaction was run for only 3 days). Product **23b** was purified on an automated column using 10 grams of high-capacity silica, a linear gradient of 5-40% acetone in hexanes over 11 column volumes (although **23b** eluted after 13 column volumes) at a flow rate of 40 mL/min (R_f = 0.21 in 20% acetone in hexanes), providing **23b** as a red-brown solid (38.7 mg, 32% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.74 (s, 1H), 7.28-7.26 (m, 2H), 7.00-6.98 (m, 2H), 3.85 (s, 3H), 2.99-2.97 (m, 4H), 1.51-1.47 (m, 2H), 1.43-1.39 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 159.8, 156.5, 149.3, 143.0, 130.7, 126.4, 126.3, 114.4, 55.4, 50.2, 25.5, 23.8. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{16}H_{18}ClN_3O$ 303.1138; Found 303.1129.



3-Chloro-5-(4-methoxyphenyl)pyridazine (24b). Prior to the reaction, 3,5-dichloropyridazine (purchased as a reddish brown solid) was purified by trituration in pentanes and filtration through a sintered funnel; the filtrate was concentrated and dried furnishing 3,5-dichloropyridazine starting material as a white solid (70% recovery). Compound **24b** was prepared according to the general procedure using Conditions A, purified 3,5-dichloropyridazine (59.6 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 6 h. Purification by flash column chromatography on silica gel (R_f = 0.22 in 15% acetone in hexanes) provided **24b** as a white crystalline solid with minor red-brown discoloration (68.8 mg, 78% yield); mp 94–97 °C [uncorrected, measured against benzoic acid (113-117 °C)]. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.24 (d, J = 1.5 Hz, 1H), 7.55-7.54 (multiple peaks, 3H), 6.97 (d, J =7.4 Hz, 2H), 3.80 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, δ): 161.9, 157.2, 148.5, 140.7, 128.6, 125.0, 123.6, 115.2, 55.5. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{11}H_9ClN_2O$ 220.0403; Found 220.0403.



2,4-Bis-(4-methoxyphenyl)-6-(trifluoromethyl)pyridine (S25c). Compound **S34c** was prepared according to the general procedure using Conditions B, 2,4-dichloro-6-(trifluoromethyl)pyridine (86.4 mg, 0.4 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (60.8 mg, 0.4 mmol, 1.0 equiv) with stirring for 12 h. Purification by flash column chromatography on silica (R_f = 0.34 in 7% acetone in hexanes) provided **S25c** as a white crystalline solid (61.8 mg, 43% yield); mp 95-98 °C [uncorrected, measured against benzoic acid (109-111 °C)]. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.09-8.06 (m, 2H), 7.96 (d, J = 1.3 Hz, 1H), 7.70 (d, J = 1.3 Hz, 1H), 7.67-7.64 (m, 2H), 7.06-7.00 (multiple peaks, 4H), 3.88 (s, 3H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 161.2, 161.1, 158.1, 150.4, 148.7 (q, J_{CF} = 33.9 Hz), 130.8, 129.9, 128.7, 128.5, 122.0 (q, J_{CF} = 274.5 Hz), 119.4, 115.5 (q, J_{CF} = 2.7 Hz), 114.8, 114.3, 55.54, 55.49. ^{19}F NMR (471 MHz, $CDCl_3$, δ): -68.0.

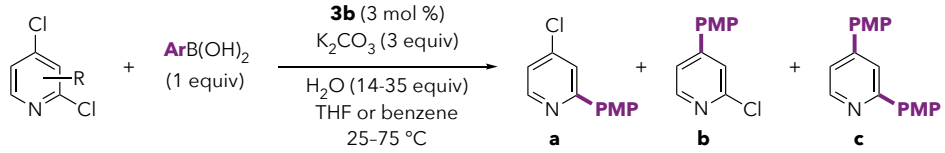


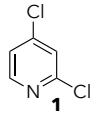
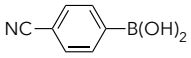
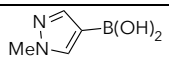
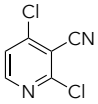
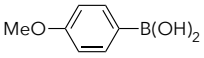
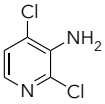
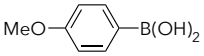
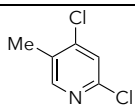
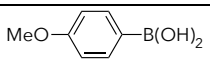
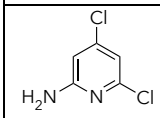
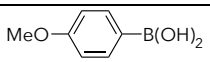
2-Chloro-4-(4-phenoxyphenyl)-3-pyridinecarbonitrile (39b). Compound **39b** was prepared according to the general procedure using Conditions A on a 1.0 mmol scale, 2,4-dichloro-3-cyanopyridine (173.0 mg, 1.0 mmol, 1.0 equiv) and *p*-phenoxyphenylboronic acid (214.0 mg, 1.0 mmol, 1.0 equiv) with stirring for 19 h. Purification by flash column chromatography on silica gel (R_f = 0.26 in 10% acetone in hexanes) provided **39b** as a white solid (188 mg, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.52 (d, J = 5.2 Hz, 1H), 8.59-8.56 (m, 2H), 7.41-7.37 (multiple peaks, 3H), 7.20-7.17 (m, 1H), 7.12-7.08 (multiple peaks, 4H). Spectral data are consistent with the literature.[17]

4. Discussion About Mass Balance

The moderate isolated yields in Scheme 2 (ligand-controlled conditions) are generally due to a combination of factors: (1) unreacted starting material, (2) formation of diarylated product, and (3) material loss during purification of the target product by column chromatography due to partial coelution of regioisomers.

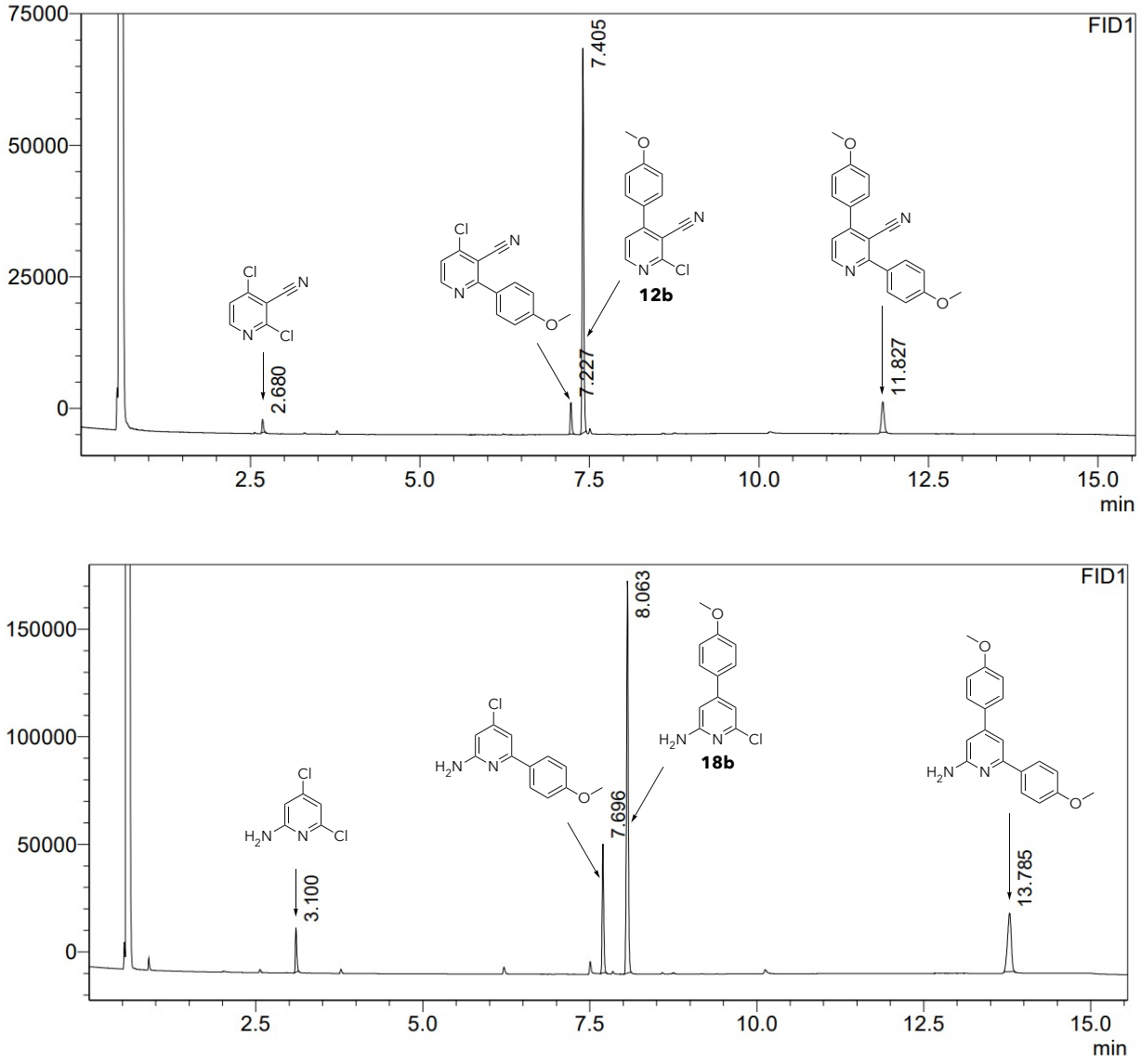
In several examples above, we report isolated yields of the minor regioisomer as well as the diarylated regioisomer. These isolated yields are summarized below. In some cases, the mass balances are above 90%. In cases with lower mass balance, there was significant material loss during isolation of products.



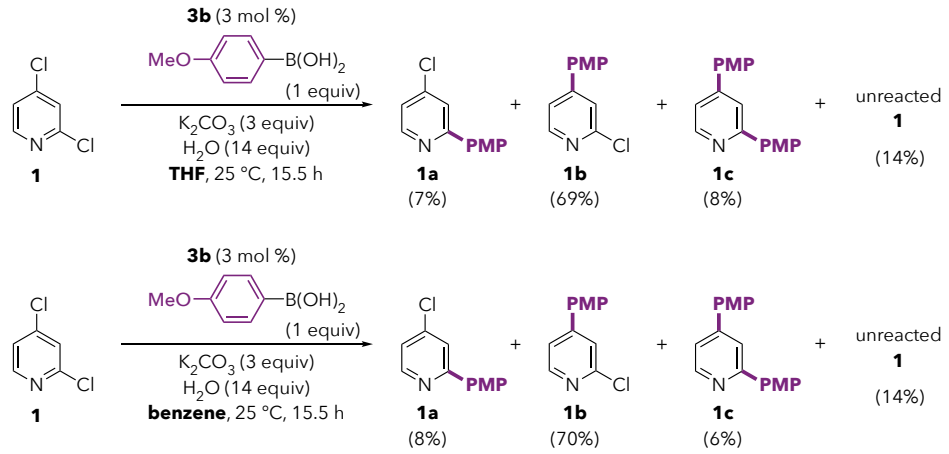
Substrate	$ArB(OH)_2$	estimated unreacted substrate based on crude GC (uncalibrated, %)[a]	**a** (%)	**b** (%)	**c** (%)	Sum of substrate + **a** + **b** + **c** (%)
 **1**		6	9	71 (**6b**)	13	99
1		2	13	67 (**10b**)	9	91
		2	6[b]	68 (**12b**)	3	79
		6	13	60 (**14b**)	14	93
		11	2[b]	53 (**15b**)	18	84
		4	13	48 (**18b**)	16	81

[a]Yield calculated by extrapolation from the isolated yield of the C4 product (**b**) and the ratio of C4 product to remaining starting material signals by GC analysis of the crude reaction mixture. [b]Yield calculated by extrapolation from the isolated yield of the C4 product (**b**) and the ratio of C4:C2 product signals by GC analysis of the crude reaction mixture.

The GC chromatograms below illustrate the crude reaction mixtures prior to purification for two of the reactions from the table above with lower mass balance (reactions to form **12b** and **18b**). There are no significant unidentified peaks.



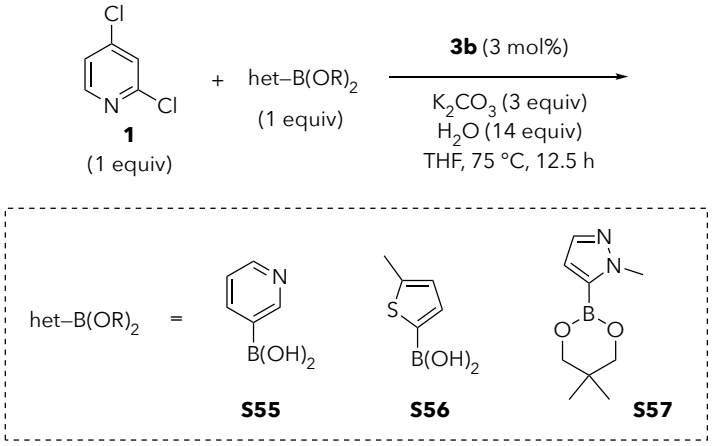
In the optimization table (Table 1), a standard was added to the reactions and calibrated GC yields were obtained. We generally see good mass balance accounted for by major and minor regioisomers, unreacted starting material, and diarylation products. Examples are illustrated below, corresponding to entries 3 and 5 of Table 1:

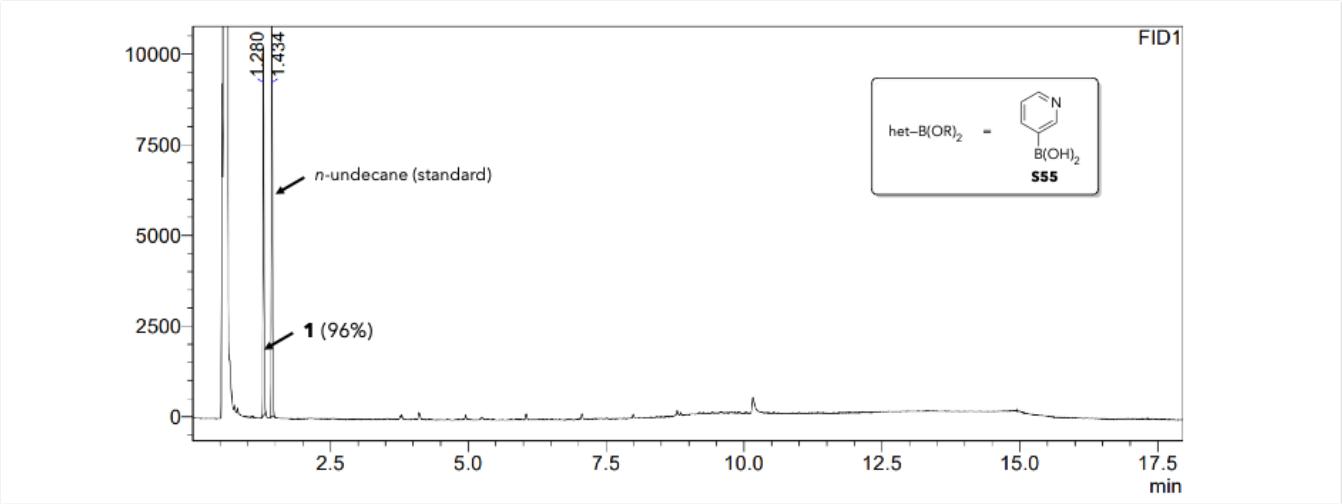


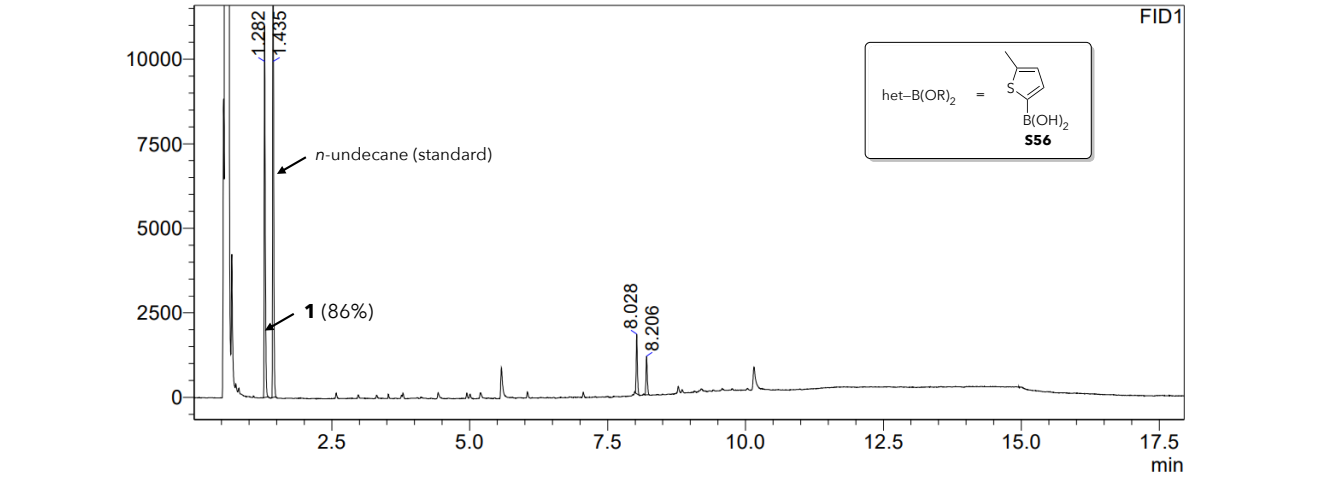
5. Scope Limitations of the Suzuki Coupling

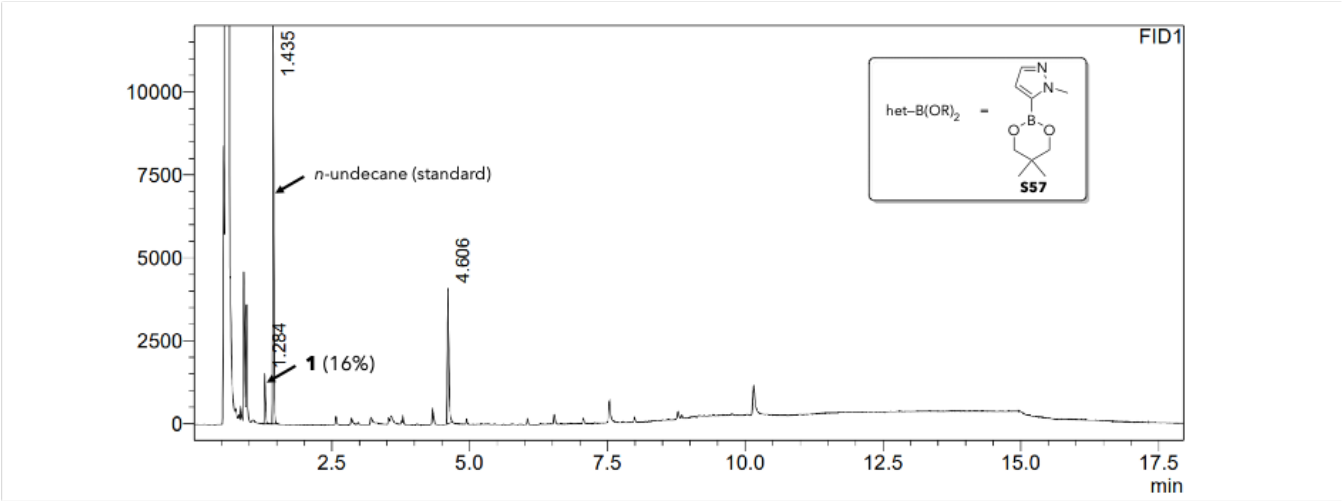
Boron Nucleophile Limitations. Heteroaryl boronic acids and esters **S55**-**S57** were ineffective in the Suzuki cross-coupling with **1** under the optimized conditions using catalyst **3b** (General Procedure for GC-Scale Reactions) at room temperature or even at a higher temperature (75 °C, below). For **S55** and **S56**, most of the starting material **1** remained after the reaction time. For **S57**, most of the starting material was consumed, but only small amounts of products were detected by GC. The GC chromatograms of these crude reactions are depicted below.

Scheme S3. Boron Nucleophile Limitations









Substrate Limitations: Overview. Some substrates did not provide the desired cross-coupling selectivity. These substrates are categorized below as 2,4-dihalopyridines that lead to overarylation (**25** and **26**), brominated 2,4-

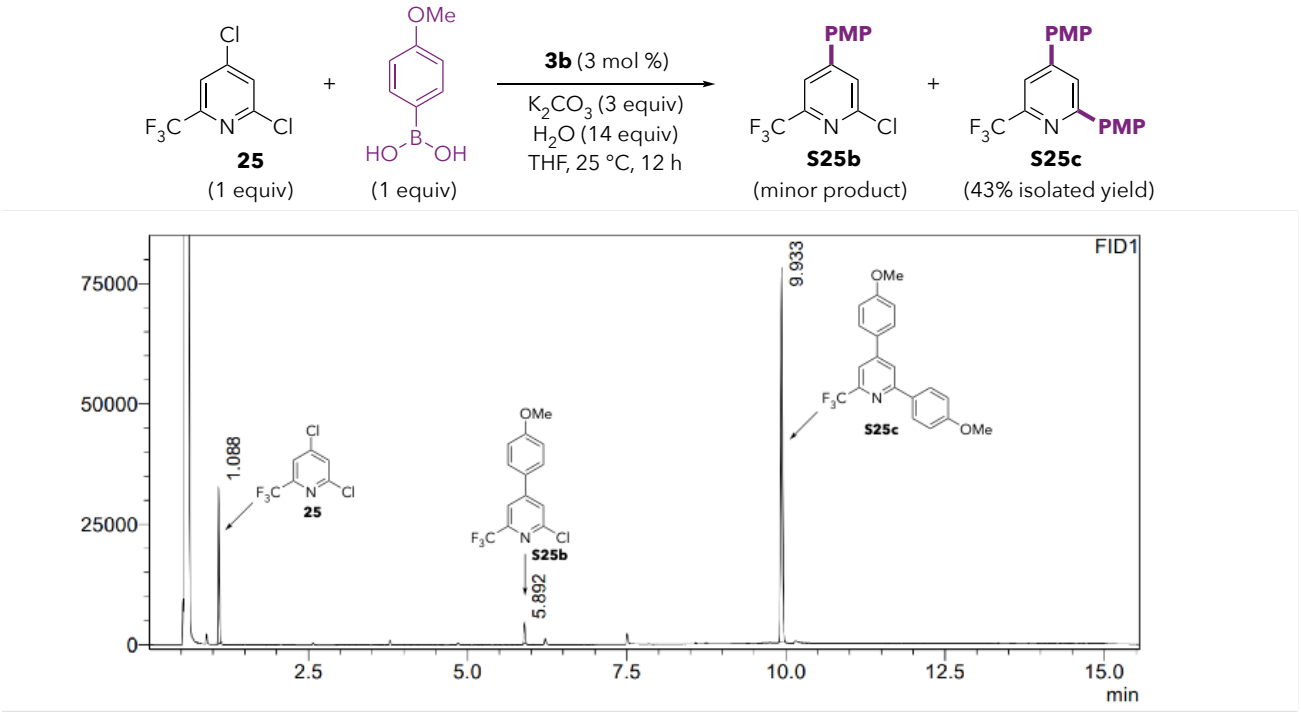
dichloropyridine or quinolines that react at bromide instead of chloride (**27** and **28**), and 2,5-dichloropyridine and pyrimidine (**29** and **30**), substrates for which the Pd/IPr catalytic system provides conventional selectivity next to nitrogen. The reactions below were conducted according to the General Procedure for GC-Scale Reactions.

Substrates Resulting in Overarylation. Reactions of both substrates **25** and **26** afford diarylated product **S25c** and **1c** as the major products by crude GC analysis.

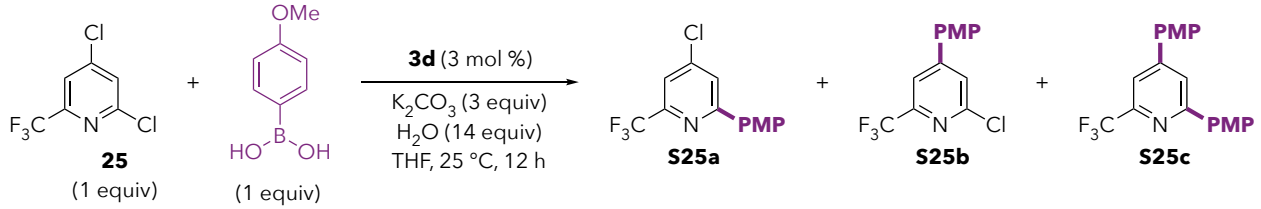
For the reaction of **25** with catalyst **3b**, a small amount of C4-monarylated product **S25b** is detected by crude GC, but the major product is **S25c** from diarylation (Scheme S4). Product **S25c** was isolated and characterized (*vide supra*). The monoarylated product was not isolated, but its identity was tentatively assigned on the basis of its mass (by GCMS analysis) and inference based on the usual selectivity exhibited by **3b** (Pd/IPr, which favors reaction at C4 with other 2,4-dichloropyridines) and **3d** (Pd/IMes, which gives nearly a 1:1 mixture of C2- and C4-arylated products with other 2,4-dichloropyridines). When **3d** (Pd/IMes) is used as the catalyst for the Suzuki coupling of **25**, much less diarylation is observed, and two monoarylated products are formed in a 1.5:1 ratio (assigned as **S25b** and **S25a**, Scheme S5). Notably, only one of these two monoarylated products is observed in the reaction using catalyst **3b**, and based on the usual selectivity with **3b** we infer that this product is **S25b**.

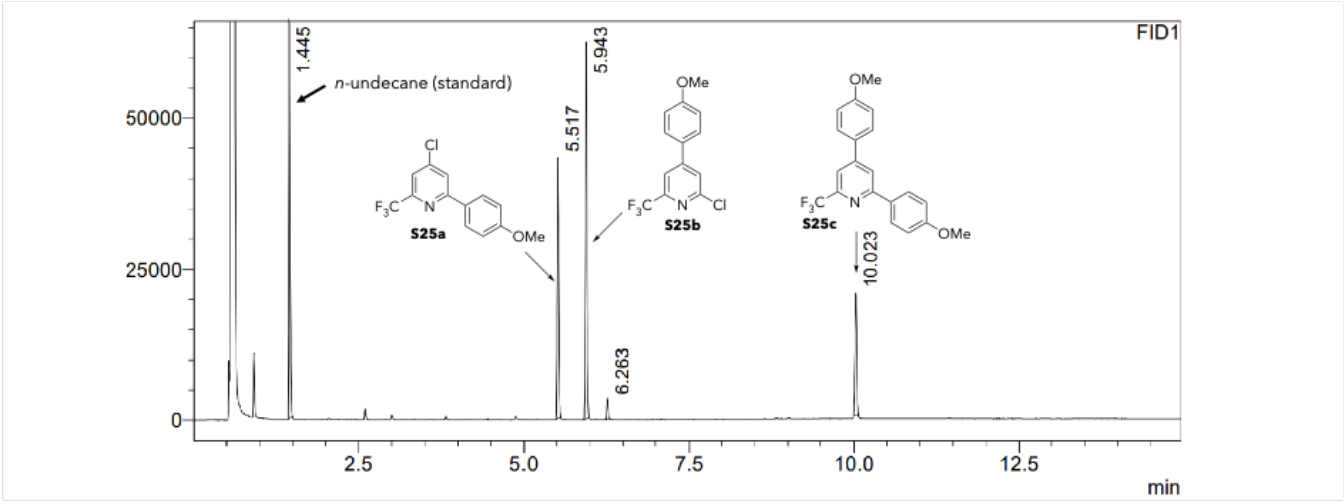
Dibromo substrate **26** undergoes extensive diarylation using catalyst **3b** (Scheme S6). Product **1c** has been isolated and characterized (*vide supra*), and the identities of the minor monoarylated products **S26a** and **S26b** are supported by GCMS analysis. The regiochemistry of **S26a** and **S26b** was inferred based on the usual selectivity exhibited by **3b** (Pd/IPr, which favors reaction at C4 with 2,4-dichloropyridines) and subsequently confirmed using C4-selective cross-coupling conditions recently reported by Fairlamb[18] (*vide infra*).

Scheme S4. Suzuki reaction of **25** using Pd/IPr catalyst **3b**.

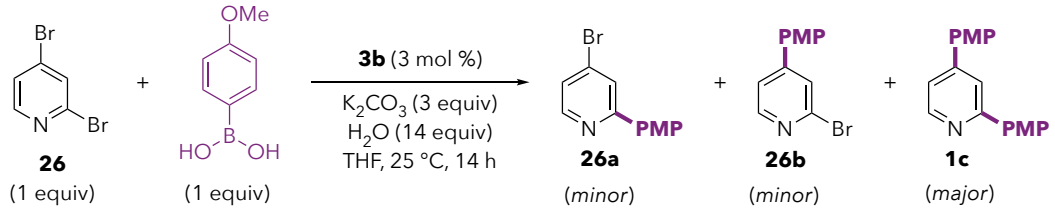


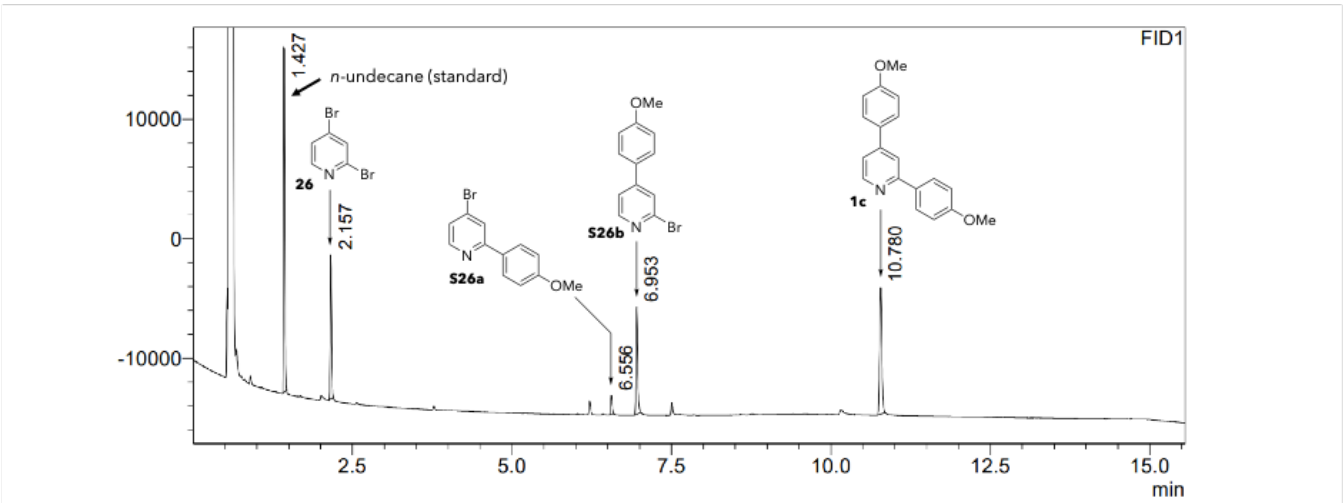
Scheme S5. Suzuki reaction of **25** using Pd/SIMes catalyst **3d**.





Scheme S6. Suzuki reaction of **26** using Pd/IPr catalyst **3b**.

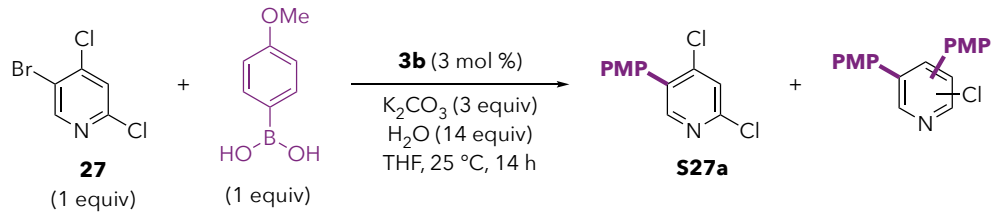


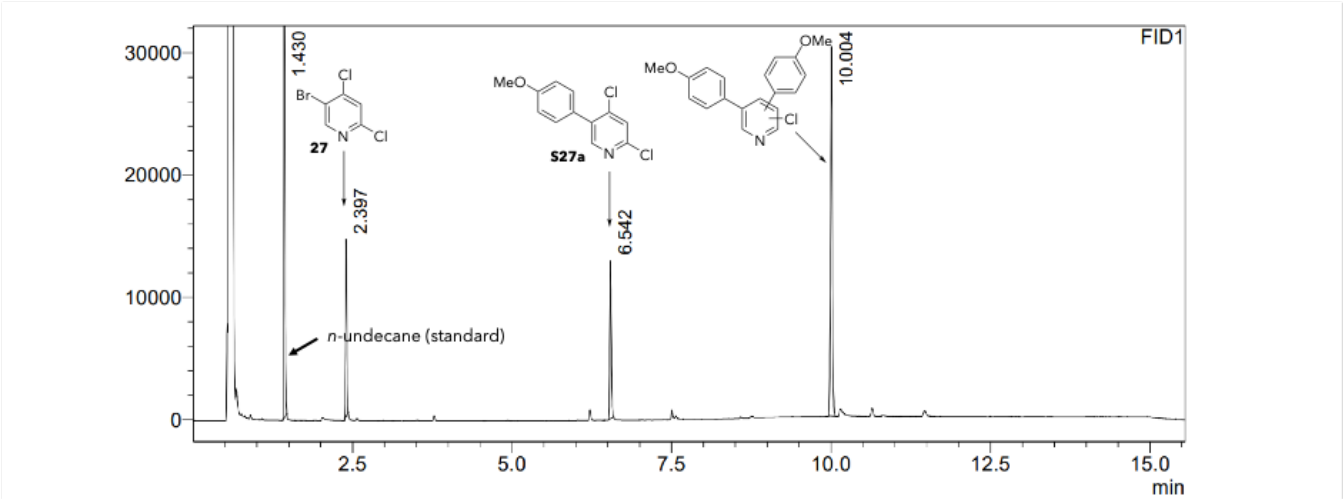


Substrates Resulting in Reaction at Bromide. Substrates **27** and **28** undergo extensive reaction at bromide under the optimized conditions, providing a mixture of dichloro-monoarylated products **S27a** and **S28a** and

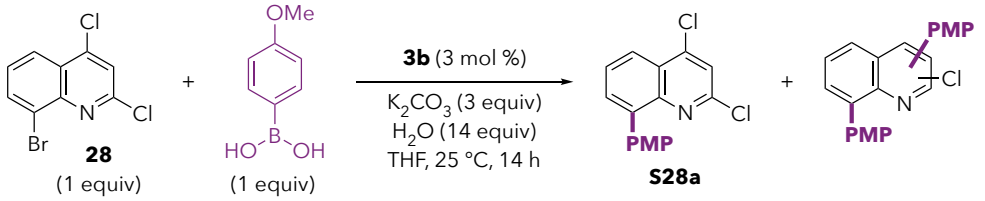
diarylated products resulting from reaction at bromide and one of the chlorides (Schemes S7-S8). Product identities were assigned based on GCMS analysis.

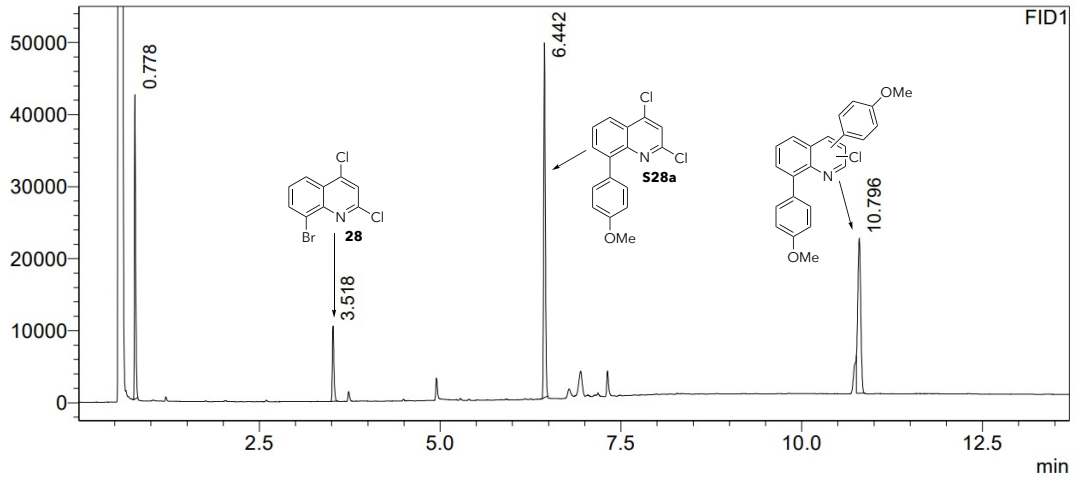
Scheme S7. Suzuki reaction of **27** using Pd/IPr catalyst **3b**.





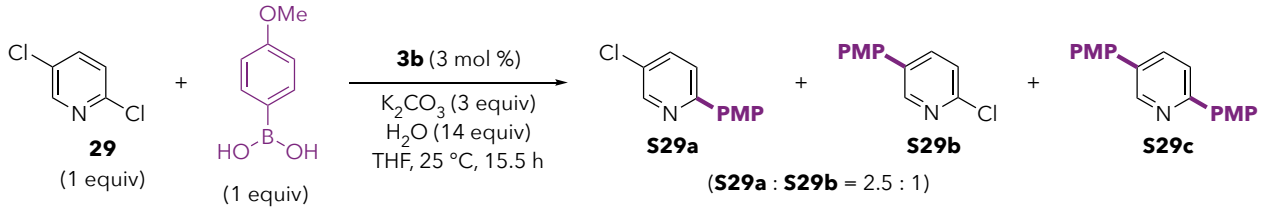
Scheme S8. Suzuki reaction of **28** using Pd/IPr catalyst **3b**.

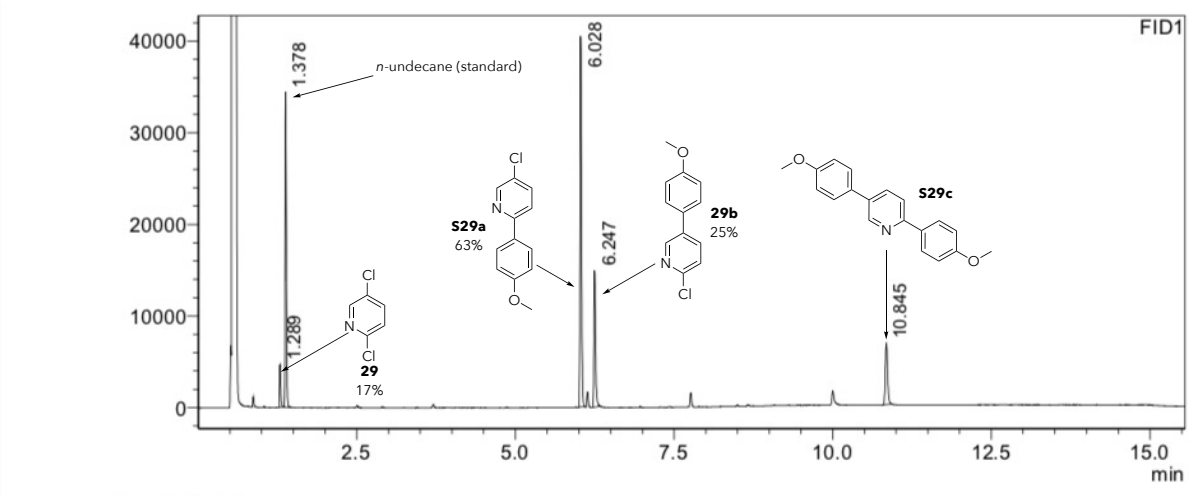




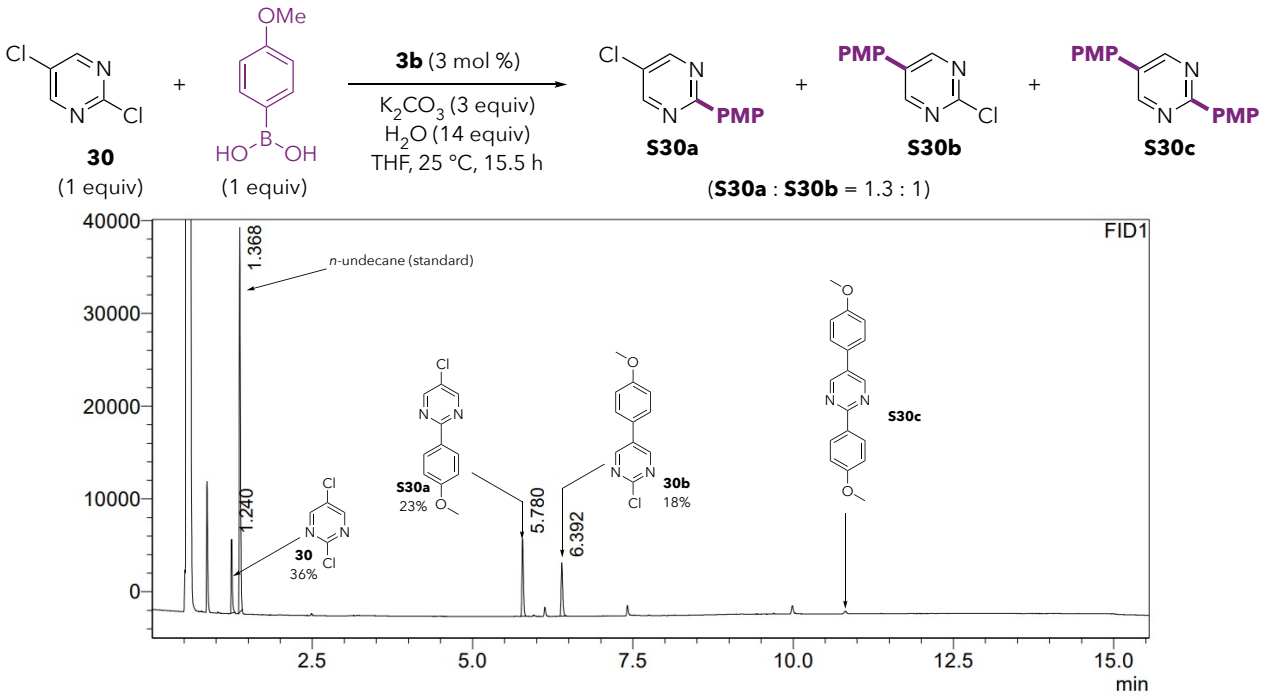
Substrates Resulting in Cross-Coupling at the Conventional Site Next to Nitrogen. 2,5-Dichloropyridine (**29**) and 2,5-dichloropyrimidine (**30**) favor reaction at C2 under the optimized system according to crude GC and GCMS analysis (ratio of **S29b** to **S29a** = 1 : 2.5, **S30b** to **S30a** = 1 : 1.3 based on the ratio of signal integrations by GC, Schemes S9-S10). As such, the use of catalyst **3b** does not enable unconventional selectivity with this substrate. The identities of the monoarylated products were assigned by a combination of GCMS analysis and comparison to the results obtained with a $Pd(OAc)_2$/dppf catalytic system, a system that normally favors conventional C2-selectivity in the reaction of other dichlorinated pyridines.[10] The identity of the diarylated products **S29c** and **S30c** were assigned based on their masses obtained by GCMS analysis.

Scheme S9. Suzuki reaction of **29** using Pd/IPr catalyst **3b**.





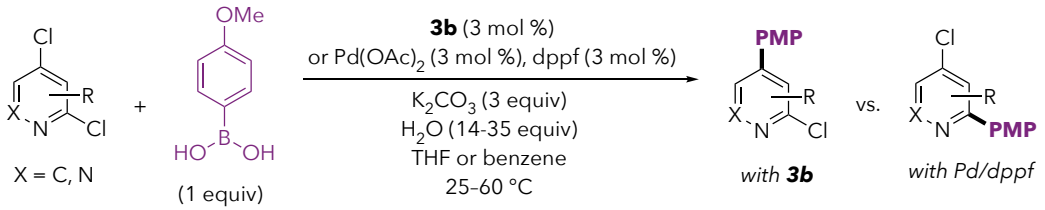
Scheme S10. Suzuki reaction of **30** using Pd/IPr catalyst **3b**.



6. Comparison of Results with IPr (C4-Selective) vs. dppf (C2-Selective)

C4-selectivity remains ligand-controlled for the substrates depicted in Scheme 2, as evidenced by the observation of different major products when using catalyst **3b** (ligand = IPr) versus using $Pd(OAc)_2$/dppf (Table S2).

Table S2. Retention time (RT) of major products by GC-FID for reactions catalyzed by **3b** or by $Pd(OAc)_2$/dppf.



entry	substrate	**3b** (min)	Pd/dppf (min)
1	**S11**	7.11	7.21
2	**S13**	7.21	7.16
3	**S14**	7.25	7.02
4	**S15**	6.52	6.68
5	**S16**	7.81	7.88
6	**S18**	8.03	7.69
7	**S21**	7.10	7.20
8	**S22**	6.79	6.48
9	**S23**	7.62	7.98
10	**S24**	7.22	6.62

D. Kumada Cross Couplings with Pd/IPr

1. General Procedures

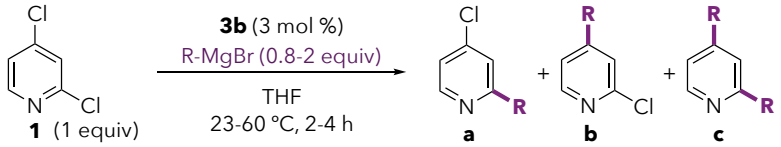
GC-Scale Reactions. The precatalyst **3b** (1.7 mg, 0.0024 mmol, 3.0 mol%) was added to an oven-dried 1-dram vial equipped with a stir bar. The vial was transferred to a N_2 atmosphere glovebox, and the Grignard reagent (0.77-2 equiv) was added as a solution in THF followed by 2,4-dichloropyridine (0.08 mmol, 1 equiv). The vial was sealed with a PTFE-lined cap and removed from the glovebox. The reaction was stirred for 2-4 hours at 23-60 °C. The reaction mixture was opened to air and quenched with EtOAc (~3.2 mL), and the internal standard undecane was added (7.5 µL, 0.036 mmol). The vial was shaken to mix the contents, and the mixture was filtered through celite prior to analysis by GC and GCMS.

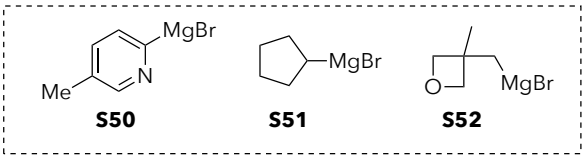
Scaled-Up Reactions for Product Isolation. The precatalyst **3b** (8.4 mg, 0.012 mmol, 3.0 mol%) was added to an oven-dried 1- or 5-dram vial equipped with a stir bar. The vial was transferred to a N_2 atmosphere glovebox, and the Grignard reagent (0.77-2 equiv) as a solution in THF was added followed by the addition of 2,4-dichloropyridine (1 equiv). The vial was sealed with a PTFE-lined cap and removed from the glovebox. The reaction was stirred for 2-5 hours at 23 °C, then the vial was opened to air. The reaction mixture was diluted with EtOAc and washed with sat. aqueous NH_4Cl (3 x 10 mL), sat. aqueous $NaHCO_3$ (3 x 10 mL), and brine (2 x 10 mL) in a separatory funnel. The organic layer was extracted with additional EtOAc (3 x 10 mL) and the combined organic layers were dried over anhydrous $MgSO_4$. The crude reaction mixture was analyzed by GC, concentrated under vacuum, and purified by normal or reversed phase flash column chromatography.

2. Optimization

Kumada reactions were performed according to the general procedure for GC-scale reactions.

Table S3. Optimization of Kumada Cross-Couplings



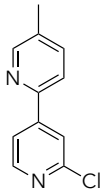


entry	T (°C)	time (h)	R-MgBr (equiv)	**a** : **b** [a]	**1** (%)[b]
1	23	2	**S50** (1)	<1 : 100	16
2[c]	23	2	**S50** (1)	--[d]	100
3[e]	23	2	**S50** (1)	--[d]	72
4	23	3	**S51** (1)	1 : 8	5
5	23	3	**S51** (0.8)	1 : 7	13
6[c]	23	3	**S51** (1)	--[d]	56
7	23	3	**S52** (1)	<1 : 39	30
8	23	3	**S52** (2)	<1 : 60	7
9[c]	23	3	**S52** (1)	--[d]	98
10[f]	60	4	**S52** (1)	--[d]	64

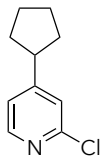
[a] Ratios based on the ratio of signals for **a** and **b** in the GC chromatogram. [b]GC yield of recovered starting material calibrated against undecane. In entry 3, the starting material was 2-bromo-4-chloropyridine instead of **1**. [c]No catalyst (metal free control). [d]"--" means no cross-coupled products **a** or **b** were observed. [e]2-Bromo-4-chloropyridine was used instead of **1** in combination with $Pd(OAc)_2$ (5 mol %) and dppf (5 mol %) as the catalytic system instead of **3b**. [f]$Pd(OAc)_2$ (5 mol %) and dppf (5 mol %) was used as the catalytic system instead of **3b**.

Discussion: Catalyst-free controls using reagents **S50**–**S52** (Table S3, entries 2, 6, 9) show no formation of products **a** or **b**, indicating that there is no background S_NAr reactivity. Entries 1, 5, and 8 represent the optimized conditions that were used for scale-up reactions. Interestingly, products **a** and **c** were not observed in the cross couplings with **S50** and **S52**. The use of 2-bromo-4-chloropyridine as the substrate for reaction with **S50** (entry 3), a substrate that should be strongly biased toward reaction at C2, also did not lead to any detectable cross-coupled products. Reaction of the pyridyl Grignard **S50** at C2 would lead to a 2,2'-bipyridine derivative which can chelate to Pd or Mg, providing a compound that is insoluble or not volatile and therefore invisible by GC-FID. Similarly in the case of Grignard **S52**, product **a** is not obtained even when using $Pd(OAc)_2$/dppf (entry 10), although considerably more starting material was consumed. It is possible that the C2-functionalized product **a** resulting from reaction of Grignard **S52** is prone to decomposition.

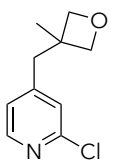
3. Isolation and Characterization of Kumada Products from Scheme 3



2-Chloro-5'-methyl-4,2'-bipyridine (31b). Product **31b** was prepared according to the general procedure using **3b** (8.4 mg, 0.012 mmol, 3 mol %), 5-methyl-2-pyridylmagnesium bromide (**S50**, 1.6 mL of a 0.25 *M* solution in THF, 0.40 mmol, 1.00 equiv), and **1** (43.2 μL, 0.40 mmol, 1.00 equiv). The reaction was stirred at 23 °C for 2 h. The crude GC chromatogram indicated the presence of unreacted **1**. Purification was performed by flash column chromatography (R_f= 0.46 in 90:10 Hex:EtOAc) yielded a white solid (49.7 mg, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.58-8.61 (m, 1H), 8.49 (d, *J* = 5.2 Hz, 1H), 7.96-7.99 (m, 1H), 7.82 (dd, J= 5.2, 1.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.9 Hz, 1H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 152.7, 151.0, 150.8, 149.7, 137.8, 134.6, 121.7, 120.7, 119.8. HRMS (ESI$^+$) m/z: [M]+: Calcd for $C_{11}H_9ClN_2$ 204.0454; Found 204.0455. The C2 monoarylated isomer **S31a** has been reported in previous literature, and the signals for product **31b** are not consistent with those reported for **S31a**.[19]



2-Chloro-4-cyclopentylpyridine (32b). Product **32b** was prepared according to the general procedure using **3b** (8.4 mg, 0.012 mmol, 3 mol %), cyclopentylmagnesium bromide (**S51**, 1.34 mL of a 0.299 ± 0.004 *M* solution in THF, 0.40 mmol, 0.77 equiv), and **1** (56.2 μL, 0.52 mmol, 1.00 equiv). The reaction was stirred at 23 °C for 4 h. The crude GC chromatogram indicated the presence of unreacted **1**. Purification was performed by reversed phase flash column chromatography with a 12 g C18 silica column, using an initial automated program comprising a flow rate of 30 mL/min of water:acetonitrile (98:2 to 0:100) over 31 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 58-69% MeCN in water over 11 column volumes. After the elution, the initial program was resumed. The C4 monoarylated product **32b** eluted at 61-64% MeCN. Fractions containing **32b** were partitioned between dichloromethane and saturated brine. The organic layers were combined and dried over magnesium sulfate and solvent was removed under reduced pressure affording **32b** as a light brown oil (50.8 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.24 (d, *J* = 5.2 Hz, 1 H), 7.17 (s, 1H), 7.06 (d, *J* = 5.2 Hz, 1H), 2.92-3.01 (m, 1H), 2.02-2.12 (m, 2H), 1.75-1.85 (m, 2H), 1.65-1.75 (m, 2H), 1.51-1.61 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 159.3, 151.7. 149.5, 123.1, 121.6, 45.1, 34.0, 25.6. HRMS (ESI$^+$) m/z: [M]+: Calcd for $C_{10}H_{12}ClN$ 181.0658; Found 181.0666.

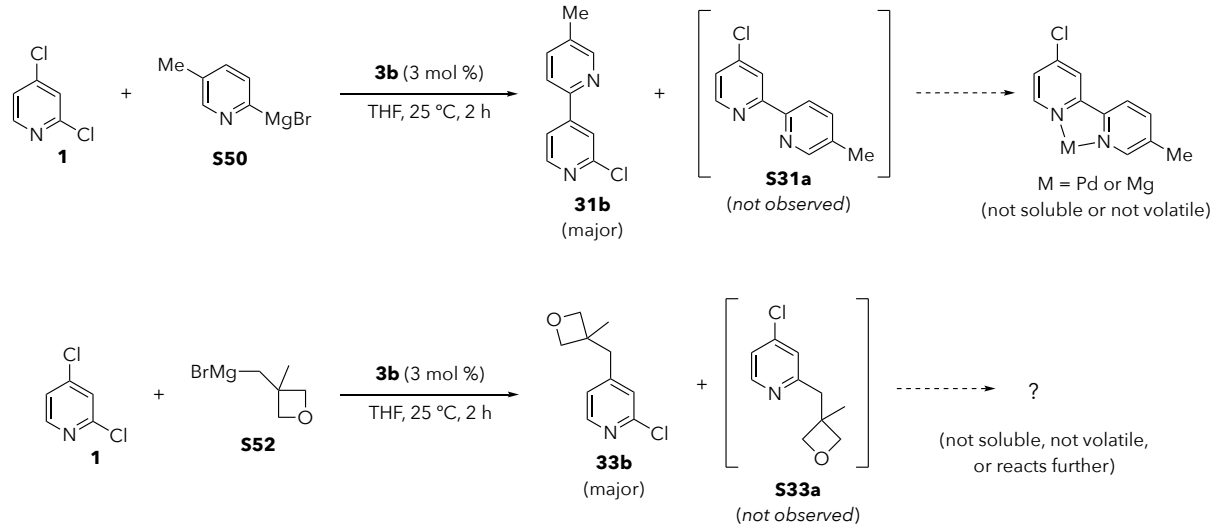


2-Chloro-4-(3,3'-methyloxetanyl)pyridine (33b). Product **33b** was prepared according to the general procedure using **3b** (8.4 mg, 0.012 mmol, 3 mol %), 3,3'-methyloxetanylmagnesium bromide (**S52**, 5.71 mL of a 0.14 *M* solution in THF, 0.80 mmol, 2.0 equiv), and **1** (43.2 μL, 0.40 mmol, 1.00 equiv). The reaction was stirred at 23 °C for 3 h. Purification was performed by reversed phase flash column chromatography with a 12 g C18 silica column, using an initial automated program comprising a flow rate of 25 mL/min of water:acetonitrile (98:2 to 8:92) over 21 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 46-49% MeCN in water. After the elution, the initial program was resumed. The C4 monoarylated product **33b** coeluted with an aliphatic impurity at 49% MeCN. Fractions containing **33b** were partitioned between ethyl acetate and saturated brine. The organic layers were combined and dried over magnesium sulfate and solvent was removed under reduced pressure. The aliphatic impurity was removed *in vacuo* yielding an off white colored solid (46.5 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.30 (d,

J = 5.0 Hz, 1H), 7.11 (s, 1H), 6.99 (d, J = 5.0 Hz), 4.59 (d, J = 5.8 Hz, 2H), 4.37 (d, J = 5.8 Hz, 2H), 2.96 (s, 2H), 1.28 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 151.8, 150.5, 149.6, 125.0, 123.4, 82.7, 82.1, 43.9, 39.7, 23.3 ppm. HRMS (ESI^+) m/z: [M]+: Calcd for $C_{10}H_{12}ClNO$ 197.0607; Found 197.0599.

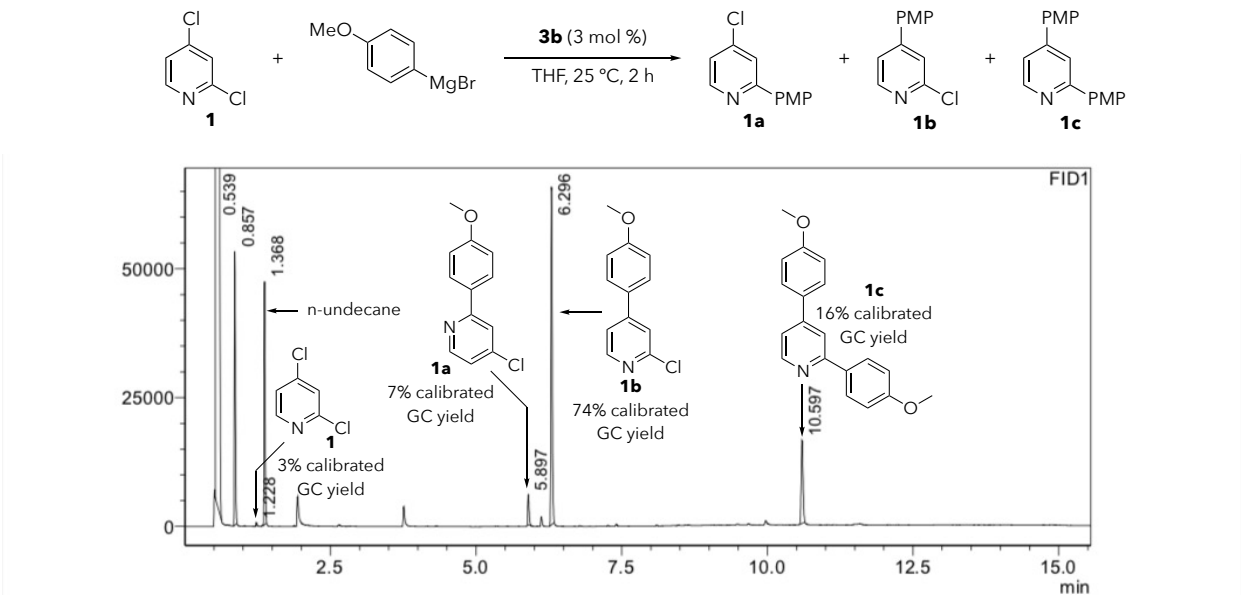
4. Discussion about Decomposition of Putative Products S31a and S33a

Although typical C4:C2 selectivity for Pd/IPr-catalyzed Suzuki, Kumada, and Negishi couplings of **1** is about 10:1 (range 7:1 to 13:1 for the reactions reported in the manuscript), the reactions of **1** with a pyridyl or a methyloxetanyl Grignard reagent (**S50** and **S52**) lead to the C4-functionalized products **31b** and **33b** as the only products observed. We hypothesize that this apparently high selectivity is misleading, and the selectivity in these reactions is likely similar to the other Pd/IPr-catalyzed reactions in the manuscript. It is likely that some amount of C2-functionalized products (**S31a** and **S33a**) *are* formed, but these products undergo further reaction in a way that makes them undetected by crude GC-FID, GC-MS, or NMR due to poor volatility or solubility. The hypothesized decompositions are represented below:

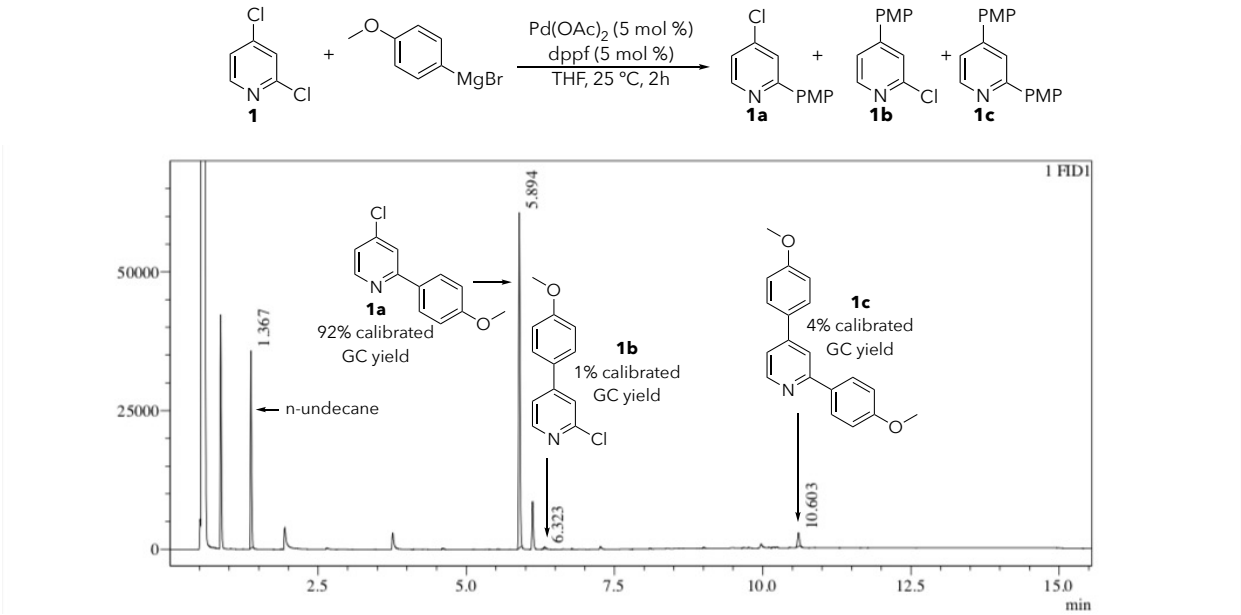


Evidence to support the hypothesis that **S31a** and **S33a** (but not other C2-functionalized products) undergo decomposition includes the following:

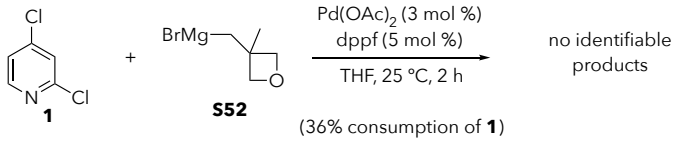
(1) With the exception of the reactions with **S50** and **S52**, good mass balance in seen in the other Kumada couplings, as well as in the Suzuki and Negishi couplings (see Sections I.C.4 and I.G.6). As an example, the following reaction was performed, affording known products that have all been previously isolated and calibrated against an internal standard for GC-FID analysis. As illustrated, there is no evidence for decomposition of the C2-functionalized product **1a**. The C4:C2 product ratio is 11:1, which is comparable to other cross-couplings performed with substrate **1** using Pd/IPr. The mass balance in the crude GC chromatogram adds up to 100% (estimated error is ±3%), indicating that all material is accounted for.

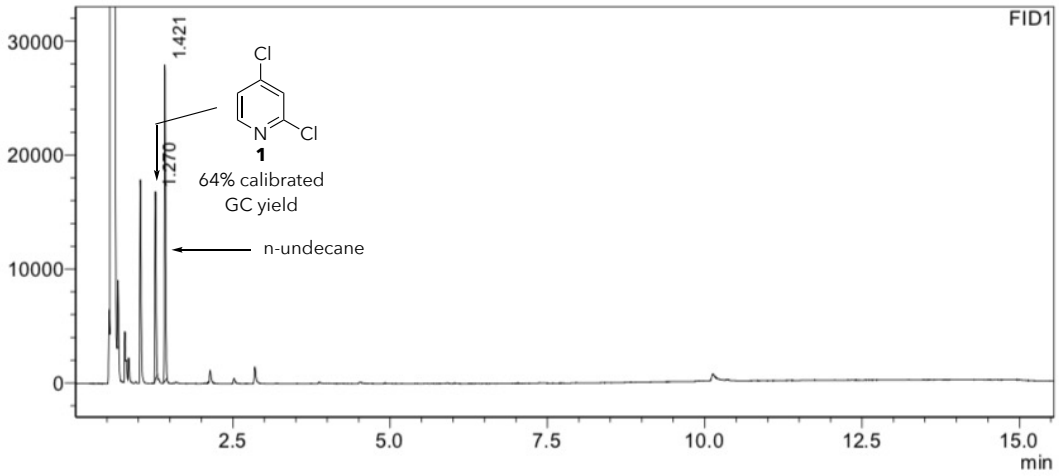


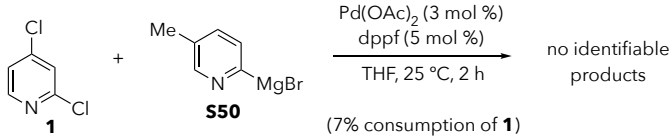
(2) Efforts to bias the reaction of **1** to favor formation of the C2-functionalized products **S31a** and **S33a**, using the ligand dppf, have been largely unsuccessful. The ligand dppf normally promotes highly-selective and efficient C2-functionalization,[10] as illustrated in the Kumada coupling below:

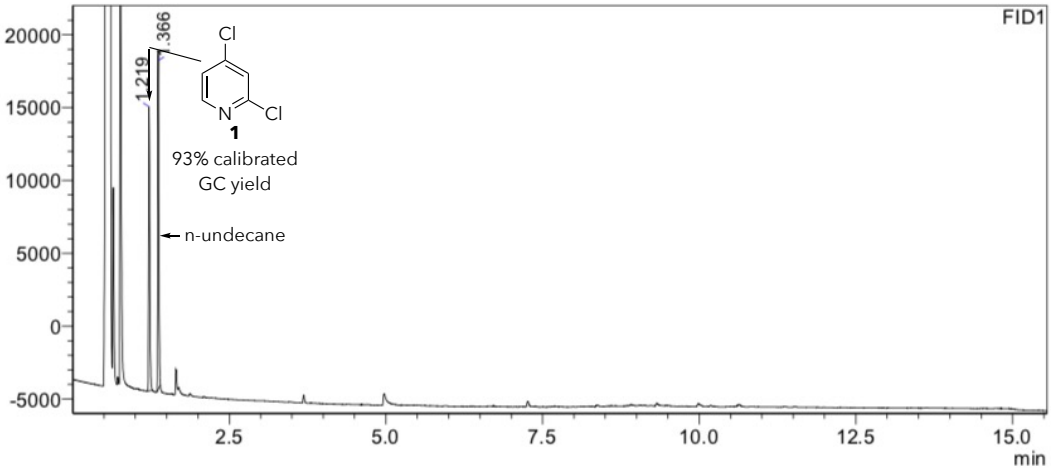


However, when this catalytic system is applied to the Kumada coupling of **1** with **S50** and **S52**, no cross-coupled products are observed despite partial consumption of **1**:

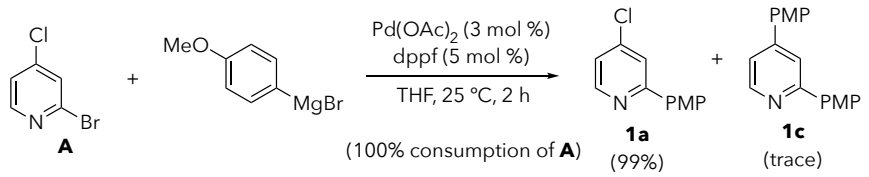


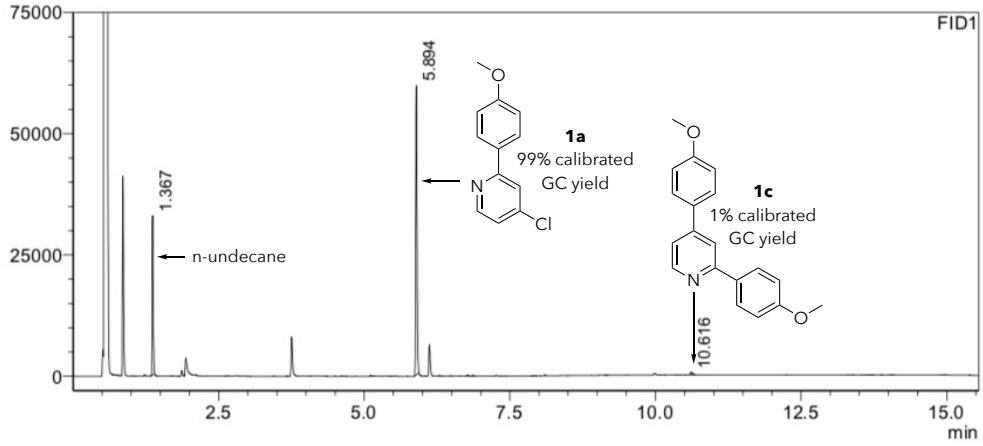




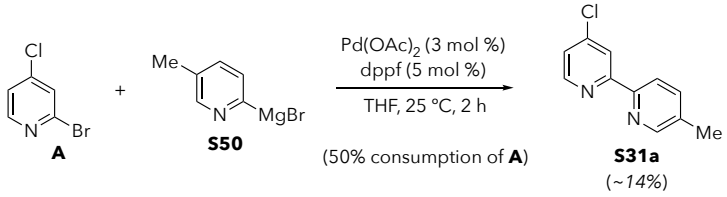


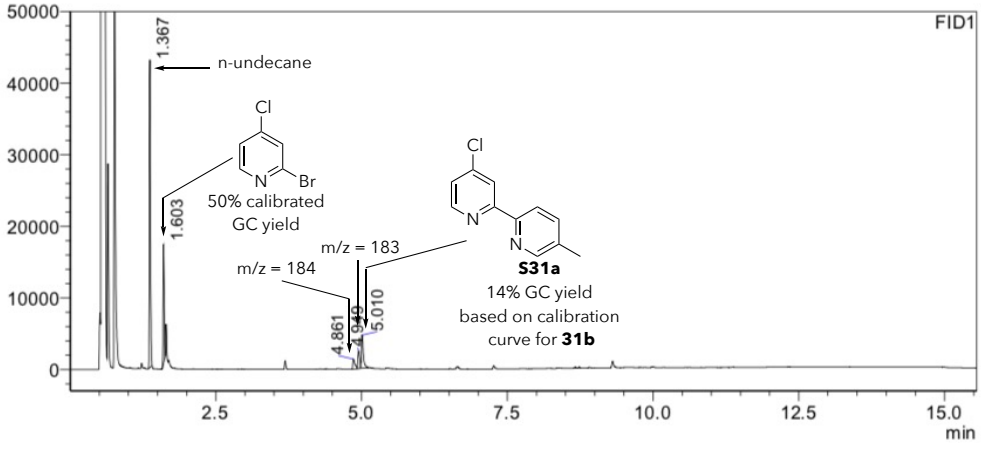
(3) The use of the Pd/dppf catalytic system for the cross-coupling of 2-bromo-4-chloropyridine would be expected to lead to improved cross-coupling at C2, because this substrate has enhanced reactivity at C2 due to the 2-Br substituent. Indeed, excellent mass balance is observed in the reaction between 2-bromo-4-chloropyridine and a simple aryl Grignard reagent:

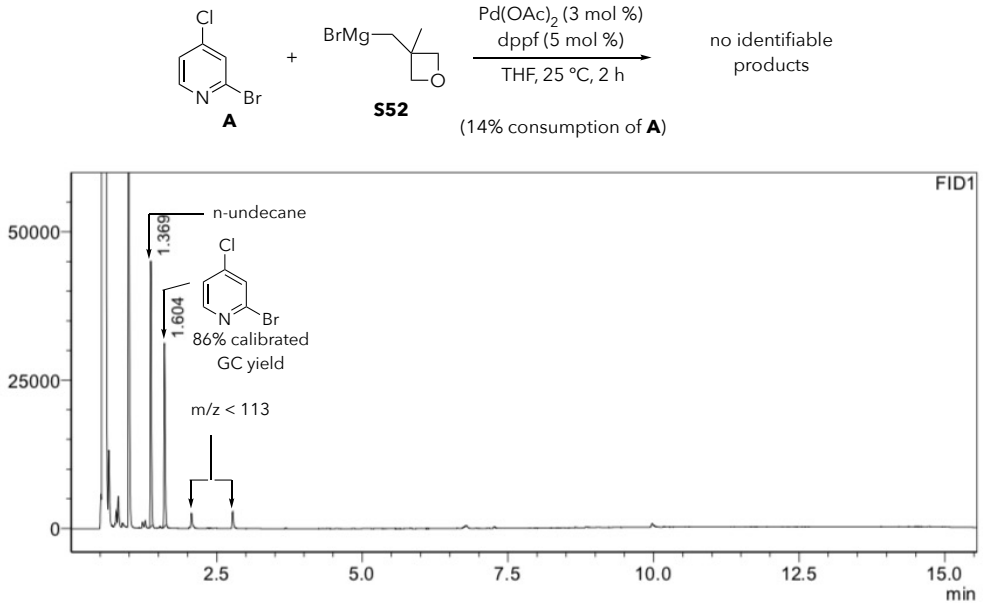




However, the use of this system for the reactions with Grignard reagents **S50** and **S52** leads to none or only a small amount of detectable C2-functionalized products, despite partial consumption of the starting material. These results are consistent with conversion of the C2-functionalized products into materials that are not identified by crude GC-FID, GC-MS, or NMR due to poor solubility or volatility. We are continuing to explore the nature of these decomposition pathways in our lab.







E. Negishi Cross-Couplings with Pd/IPr

1. General Procedures

GC-Scale Reactions. In a glovebox, Grignard reagent (0.77-1 equiv as a solution in THF) and a solution of $ZnCl_2$ in THF (1 *M*, equimolar with the Grignard reagent) were combined in an oven-dried 1-dram vial ("vial A") equipped with a stir bar and stirred for at least 0.5 hours at ambient temperature. Outside of the glovebox, the precatalyst **3b** (1.7 mg, 0.0024 mmol, 3.0 mol %) was added to a separate oven-dried 1-dram vial equipped with a stir bar ("vial B"), and this vial was transferred into the glovebox. The contents of vial A, comprising the organozinc reagent (0.77-1 equiv), and 2,4-dichloropyridine (0.08 mmol, 1 equiv) were added to vial B. Vial B was sealed with a PTFE-lined cap and removed from the glovebox. Reactions were stirred for 0.75-4 hours at 23-60 °C. The reaction mixture was opened to air, diluted with ethyl acetate (~3 mL), and the internal standard undecane was added (7.5 µL, 0.036 mmol). The vial was shaken to mix the contents, and the mixture was filtered through celite prior to analysis by GC and GCMS.

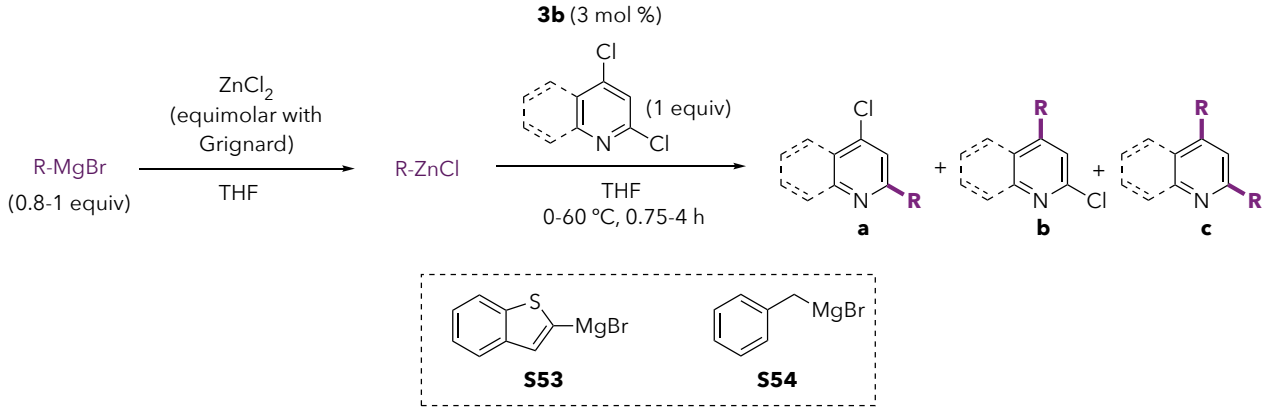
Scaled-Up Reactions for Product Isolation. In a glovebox, Grignard reagent (0.77-1 equiv as a solution in THF) and a solution of $ZnCl_2$ in THF (1 *M*, equimolar with the Grignard reagent). were combined in an oven-dried 1- or 5-dram vial ("vial A") equipped with a stirbar. The mixture was stirred for 0.5 hours at ambient temperature. Outside of the glovebox, the precatalyst **3b** (8.4 mg, 0.012 mmol, 3.0 mol %) was added to a separate oven-dried 1- or 5-dram vial equipped with a stir bar ("vial B"), and this vial was transferred into the glovebox. The contents of vial A, comprising the organozinc reagent (0.77-1 equiv), and 2,4-dichloropyridine (0.08 mmol, 1 equiv) were added to vial B. Vial B was sealed with a PTFE-lined cap and removed from the glovebox. Reactions were stirred for 0.75-4 hours at 60 °C unless otherwise indicated. The reaction mixture was opened to air, diluted with ethyl acetate (~3 mL), and washed with sat. NH_4Cl (3 x 10 mL), sat. $NaHCO_3$ (3 x 10 mL), and brine (2 x 10 mL) in a separatory

funnel. The organic layer was extracted with additional ethyl acetate (3 x 10 mL) and the combined organic layers were dried over anhydrous $MgSO_4$. The crude product was analyzed by GC and purified by normal or reversed phase column chromatography.

2. Optimization

Negishi reactions were performed according to the general procedure for GC-scale reactions. Yield of remaining starting material (**1**) is calibrated against the undecane internal standard. Ratio of products **a** and **b** are assuming equal response factor between the isomers.

Table S4. Optimization of Negishi Cross Couplings.

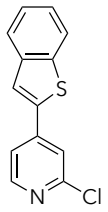


entry	T (°C)	time (h)	R-MgBr (equiv)	**a** : **b** [a]	**1** (%)[b]
1	60	0.75	**S59** (1)	1 : 68	2
2	60	0.75	**S59** (0.8)	1 : 7.7	33
3[c]	60	0.75	**S59** (1)	--[d]	98
4	60	3	**S60** (1)	<1 : 99	0
5	23	3	**S60** (1)	1 : 45	8
6	0	3	**S60** (1)	1 : 9	21
7[c]	60	3	**S60** (1)	--[d]	96
8	60	2	MeMgBr (1)	<1 : 99	51
9[e]	60	4	MeMgBr (1)	1 : 16	0
10[e]	60	4	MeMgBr (0.8)	1 : 4	0

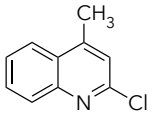
[a] Ratios based on the ratio of signals for **a** and **b** in the GC chromatograph. [b]All reactions were performed with 2,4-dichloropyridine (**1**) unless otherwise indicated. GC yield of recovered starting material calibrated against undecane. [c]No catalyst (metal free control). [d]"--" means no cross-coupled products **a** or **b** were detected. [e]2,4-Dichloroquinoline (**19**) was used instead of **1**.

Discussion: Catalyst-free controls (Table S4, entries 3 and 7) show no reaction, indicating that there is no background S_NAr reactivity. Entries 2, 6, and 10 represent optimized conditions that were used for scale-up reactions. Although the results of entry 1 appear promising only low yields of product B could be isolated.

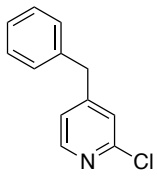
3. Isolation and Characterization of Negishi Products from Scheme 3



4-Benzothiophen-2-yl-2-chloropyridine (34b). Product **34b** was prepared according to the general procedure using **3b** (8.4 mg, 0.012 mmol, 3 mol %), benzothiophenylzinc chloride (**S53**, 2.35 mL of a 0.170 ± 0.001 *M* solution in THF, 0.40 mmol, 0.80 equiv), and **1** (54.0 µL, 0.50 mmol, 1.00 equiv). The reaction was stirred at 60 °C for 0.75 h. Purification was performed by reversed phase flash column chromatography with a 12 g C18 silica column, using an initial automated program comprising a flow rate of 12 mL/min of water:acetonitrile (98:2 to 5:95) over 35 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 61-70% MeCN in water. After the elution, the initial program was resumed. The C4-monoarylated product **34b** coeluted with the diarylated product at 65-67% MeCN in water. Fractions containing **34b** were partitioned between ethyl acetate and saturated brine. The organic layers were combined and dried over magnesium sulfate and concentrated under reduced pressure. Compound **34b** was further purified by normal phase flash column chromatography (R_f= 0.36 in 80:20 Hex:EtOAc), affording **34b** as an off-white colored solid (68.9 mg, 70% yield). Spectral data are consistent with those previously reported.[20]



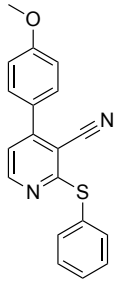
2-Chloro-4-methylquinoline (35b). Compound (**35b**) was prepared according to the general procedure using **3b** (8.4 mg, 0.012 mmol, 3 mol %), methylzinc chloride (1.00 mL of 0.67 ± 0.02 *M* solution in THF, 0.40 mmol, 0.77 equiv), and 2,4-dichloroquinoline (103.0 mg, 0.52 mmol, 1.00 equiv). The reaction was stirred at 60 °C for 4 h. Purification was performed by reversed phase flash column chromatography with a 12 g C18 silica column, using an initial automated program comprising a flow rate of 30 mL/min of water:acetonitrile (98:2 to 6:94) over 35 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 56% MeCN in water. After the elution, the initial program was resumed. The C4 monoarylated product eluted at 56% MeCN. Fractions containing **35b** were partitioned between dichloromethane and saturated brine. The organic layers were combined and dried over magnesium sulfate and solvent was removed under reduced pressure affording **35b** as a white solid (50.5 mg, 71% yield). Spectral data are consistent with those previously reported.[21]



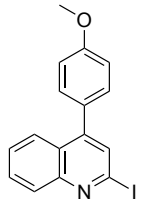
4-Benzyl-2-chloropyridine (36b). Compound (**36b**) was prepared according to the general procedure using **3b** (8.4 mg, 0.012 mmol, 3 mol %), benzylzinc chloride (**S54**, 4.82 mL of a 0.083 *M* solution in THF, 0.40 mmol, 1.00 equiv), and 2,4-dichloropyridine (43.2 µL, 0.40 mmol, 1.00 equiv). The reaction was stirred at 0 °C for 3 h. Purification was performed by reversed phase flash column chromatography with a 12 g C18 silica column, using an initial automated program comprising a flow rate of 35 mL/min of water:acetonitrile (98:2 to 5:95) over 35 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 70-73% MeCN in water. After the elution, the initial program was resumed. The C4 monoarylated product **36b** eluted at 72-73% MeCN. Fractions containing **36b** were partitioned between dichloromethane and saturated brine. The organic layers were combined and dried over magnesium sulfate and solvent was removed under reduced pressure affording **36b** as a light brown oil (52.3 mg, 64% yield). ^{1}H NMR (500 MHz, C_6D_6, δ): 7.95 (d, *J* = 5.0 Hz, 1H), 7.00-7.10 (multiple peaks, 3H), 6.75-6.80

(multiple peaks, 3H), 6.33 (dd, J = 5.0, 0.7 Hz, 1H), 3.27 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, δ): 153.4, 152.7, 150.2, 138.8, 129.5, 129.3, 127.3, 124.9, 123.2, 41.0 ppm. HRMS (ESI+) m/z: [M]+: Calcd for $C_{12}H_{11}ClN$ 203.0502; Found 203.0519.

F. Multistep Syntheses using C4-Selective Cross-Coupling with Pd/IPr (Scheme 4)

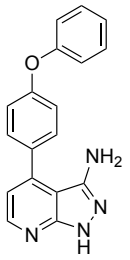


4-(4-Methoxyphenyl)-2-(phenylthio)-3-pyridinecarbonitrile (37). Thiophenol (40.8 µL, 0.4 mmol, 1.0 equiv) was added dropwise to a stirring solution of 2-chloro-4-(4-methoxyphenyl)-3-pyridinecarbonitrile (**12b**, 97.9 mg, 0.4 mmol, 1.0 equiv), triethylamine (111.5 µL, 0.8 mmol, 2.0 equiv), and DMF (0.4 mL) in a 1-dram reaction vial. The vial was sparged with N_2 gas using the technique described in the "general procedure" on S9, sealed with a PTFE-lined cap, and heated to 60 °C for 18.3 h. After cooling, a crystalline precipitate formed. The mixture was poured into a 125 mL Erlenmeyer flask and diluted with 30 mL of deionized water, inducing precipitation of the desired product and solubilizing byproducts. The precipitate was filtered and saved, and the liquid filtrate was extracted with ethyl acetate. The organic phase was concentrated, affording mixed white and orange solids. The solids were washed with diethyl ether over a fritted funnel until all orange discoloration had passed into the filtrate. The combined organic solids were dried under vacuum furnishing **37** as a colorless crystalline solid with slight yellow discoloration (92.2 mg, 72% yield); mp 156–158 °C [uncorrected, measured against benzoic acid (113-117 °C)]. ^1H NMR (500 MHz, C_6D_6, δ): 7.84 (d, J = 5.2 Hz, 1H), 7.59-7.57 (m, 2H), 7.24-7.22 (m, 2H), 7.12-7.04 (multiple peaks, 3H), 7.00-6.67 (m, 2H), 6.29 (d, J = 5.2 Hz, 1H), 3.23 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, δ): 164.9, 161.6, 153.4, 151.3, 136.4, 130.3, 129.5, 129.4, 129.3, 119.7, 115.8, 114.6, 105.5, 54.9 (two signals are coincidentally overlapping). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 164.5, 161.4, 153.7, 151.8, 135.6, 130.1, 129.6, 129.4, 128.8, 127.9, 120.0, 115.9, 114.6, 105.1, 55.6. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{19}H_{14}N_2OS$ 318.0827; Found 318.0812.



2-Iodo-4-(4-methoxyphenyl)-quinoline (38). Reaction conditions were adapted from a literature procedure describing the di-iodination of 2,4-dichloropyridine.[22] 2-Chloro-4-(4-methoxyphenyl)quinoline (**19b**, 107.9 mg, 0.4 mmol, 1.0 equiv), NaI (179.9 mg, 1.2 mmol, 3.0 equiv), and acetonitrile (0.45 mL) were combined in a 1-dram vial with stir bar. Acetyl chloride (2.1 equiv 0.84 mmol, 59.9 µL) was added dropwise to the stirring mixture. The vial was sparged with N_2 gas using the technique described under "general procedure" on S9 sealed with a PTFE cap, and heated to reflux for 67 h. TLC analysis indicated complete consumption of quinoline starting material **19b**. The product mixture was quenched by dropwise addition of deionized water (8.5 mL) while stirring. An aqueous solution of 10% K_2CO_3/5% $NaHSO_3$ was added to the mixture, and the mixturew was shaken and extracted with $CHCl_3$ (3x). The organic fractions were combined, dried over Mg_2SO_4, filtered, concentrated, and purified by column chromatography on silica (R_f = 0.46 in 10% ethyl acetate in hexanes) to separate product **38** from polar impurities detected by TLC. Product fractions were concentrated and dried affording **38** as a white crystalline solid (119 mg, 82% yield); mp 114-117 °C [uncorrected, measured against benzoic acid (112-114 °C)]. ^1H NMR (500 MHz, $CDCl_3$, δ): 8.06 (d, J = 8.4

Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.64 (s, 1H), 7.47 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.40-7.37 (m, 2H), 7.04-7.01 (m, 2H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 160.3, 149.97, 149.50, 131.6, 130.8, 130.1, 129.3, 128.6, 127.1, 126.3, 126.2, 119.2, 114.3, 55.5. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{16}H_{12}INO$ 360.9964; Found 360.9963.



4-(4-phenoxyphenyl)-1H-Pyrazolo[3,4-b]pyridin-3-amine (40).

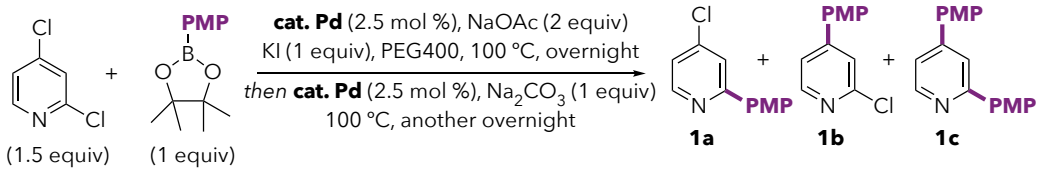
2-Chloro-4-(4-phenoxyphenyl)-3-pyridinecarbonitrile (**39b**, 122.7 mg, 0.4 mmol, 1.0 equiv), hydrazine-monohydrate (200.2 mg, 4.0 mmol, 10.0 equiv), and *i*PrOH (6.2 mL) were combined with a stir bar in a 25 mL round-bottom flask equipped with water-cooled jacketed condenser. The condenser was sealed with a rubber septum secured by copper wire, the system was sparged with N_2 gas, and the reaction was heated to 90 °C with stirring for 15 h under an atmosphere of N_2. The mixture was cooled, and trace impurities were detected by TLC. Solvent was removed under reduced pressure, and the solids were columned on silica (R_f = 0.27 in 4.5% methanol in CH_2Cl_2). All rinses and transfers were completed with $CHCl_3$. Solvent was removed under reduced pressure, furnishing a bright yellow solid. Drying under vacuum afforded **40** (119.3 mg, 99% yield). ^1H NMR (500 MHz, $CDCl_3$, δ): 10.82 (br s, 1H), 8.50 (d, *J* = 4.8 Hz, 1H), 7.58-7.55 (m, 2H), 7.42-7.39 (m, 2H), 7.20-7.17 (m, 1H), 7.16-7.14 (m, 2H), 7.12-7.10 (m, 2H), 6.95 (d, *J* = 4.8 Hz, 1H), 4.05 (br s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 158.8, 156.3, 153.5, 149.4, 147.5, 145.3, 131.7, 130.4, 130.1, 124.3, 119.8, 118.6, 115.8, 104.1.

G. *Ligand-Free Suzuki Cross-Couplings*

1. *Ligand-Free Control Reaction Based on Previously-Reported Conditions (Scheme 5b)*

Reactions were set up according to the literature procedure[15] (Table S5, entries 1-3) with the indicated modifications (entries 4-12).

Table S5. Analysis of the Role of Ligand in the Previously-Reported Conditions[15] for C4-Selective Suzuki Cross-Coupling[a]



entry	trial	Pd source	additional ligand (mol %)	**1a** (%)	**1b** (%)	**1c** (%)	**1a** : **1b**
1	1	PEPPSI-IPr	--	<1	80	2	<1 : 80
2	2	PEPPSI-IPr	--	<1	84	2	<1 : 84
3	Average	PEPPSI-IPr	--	<1	82	2	<1 : 82
4	1	**3b**	--	<1	69	1	<1 : 69
5	2	**3b**	--	<1	81	1	<1 : 81
6	Average	**3b**	--	<1	75	1	<1 : 75
7	1	$Pd(OAc)_2$	PPh_3 (5)	28	14	2	1.9 : 1
8	2	$Pd(OAc)_2$	PPh_3 (5)	32	18	2	1.8 : 1
9	Average	$Pd(OAc)_2$	PPh_3 (5)	30	16	2	1.9 : 1
10	1	$PdCl_2$	--	<1	54	1	<1 : 54
11	2	$PdCl_2$	--	<1	66	1	<1 : 66
12	Average	$PdCl_2$	--	<1	60	1	<1 : 60

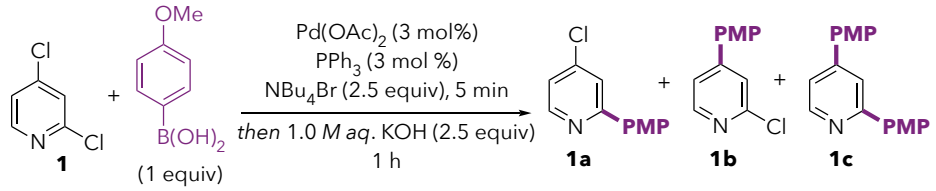
[a]GC yields calibrated against undecane as the internal standard.

Discussion: Selectivity under Yang's high-temperature conditions is significantly better than what is observed under the Pd/IPr-catalyzed room temperature conditions employed in our work. However, ligand-free control reactions using $PdCl_2$ (Table S5, entries 10-12) demonstrate that the same extremely high selectivity is observed in the absence of IPr. The selectivity under the conditions reported in reference 15 is therefore not ligand-controlled. When PPh_3 is used as a ligand in combination with $Pd(OAc)_2$ (entries 7-9, a catalytic system analogous to Fairlamb's work with dibromopyridine),[18] the reaction favors C2-arylated product **1a**, but with poor yield. In all other entries, extremely high selectivity for product **1b** is observed.

2. Coupling of 1 under Fairlamb's Recently Reported Pd/PPh3 Conditions

The Suzuki coupling in Table S6 was set up according to conditions reported by Fairlamb et al., who observed C4-selective cross-coupling of 2,4-dibromopyridine.[18] Reactions were conducted on a 0.16 mmol reaction scale.

Table S6. Reaction of **1** under Fairlamb's Conditions



entry	solvent	Temp. (°C)	**1a** (%)	**1b** (%)	**1c** (%)	**1a** : **1b**
1	THF	40	90.6	5.2	4.9	17 : 1
2	dioxane	110	85.4	0.6	12.8	142 : 1

Discussion: Intriguingly, although these conditions promote C4-selective Suzuki coupling of 2,4-di*bromo*pyridine, 2,4-di*chloro*pyridine undergoes preferential C2-coupling.

3. General Procedures for the Ligand-Free 'Jeffery' Conditions Reported Herein

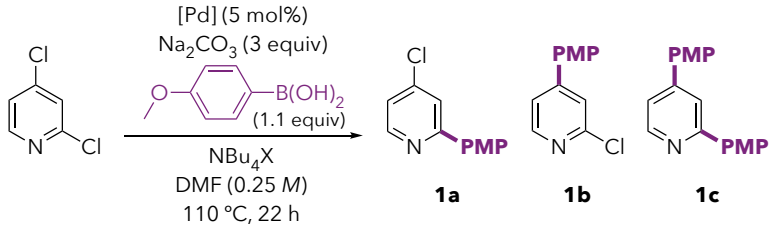
GC-Scale Reactions. Solids were added to a 1-dram reaction vial in order of increasing mass: palladium catalyst (typically 0.008 mmol, 5 mol %), *p*-methoxyphenylboronic acid (26.7 mg, 0.18 mmol, 1.1 equiv), sodium carbonate (50.9 mg, 0.48 mmol, 3.0 equiv), tetrabutylammonium salt (0-5 equiv), and a stir bar. Inside a nitrogen-atmosphere glovebox, liquid reagents were pre-measured by syringe and added in quick succession: DMF (0.64 mL) via 1-mL syringe, followed by 2,4-dichloropyridine (17.2 µL, 0.16 mmol, 1.0 equiv) via 25-µL syringe. The reaction vial was sealed under nitrogen with either a septum screwcap or a solid PTFE-lined screwcap. When indicated, N_2-sparged deionized water was added through the septum cap outside the glovebox via 25- or 50-µL syringe, and the puncture was sealed with electrical tape. The reaction was stirred vigorously at the indicated temperature for 22 h. The reaction vial was opened to air, diluted with ethyl acetate (~ 3 mL), and *n*-undecane (15 µL, 0.44 equiv) was added as an internal standard via 25-µL syringe. An aliquot was filtered through celite into a separate vial for GC analysis.

Scaled-Up Reactions for Product Isolation. $PdCl_2$ (4.4 mg, 0.025 mmol, 5.0 mol%) was weighed into a 1-dram vial followed by solid substrate if applicable (2,5-dichloropyridine, pyrimidine, or 2,4-dichloroquinoline, 0.5 mmol, 1 equiv), arylboronic acid (0.5 mmol, 1.1 equiv), sodium carbonate (159 mg, 1.5 mmol, 3.0 equiv), tetrabutylammonium bromide (806 mg, 2.5 mmol, 5.0 equiv) and a stir bar. DMF (2 mL) was added inside a nitrogen-atmosphere glovebox and sealed with either a septum screwcap or a solid PTFE-lined screwcap. Unless otherwise indicated, N_2-sparged deionized water (45 µL, 2.5 mmol, 5.0 equiv) was added through the septum cap outside the glovebox via 50-µL syringe (*note: conversion in 0.5 mmol scale reactions was more adversely affected by dry conditions compared to 0.16 mmol scale reactions*), followed by 2,4-dichloropyridine substrate (if liquid), and the puncture was sealed with electrical tape. The reaction was stirred vigorously at 110 °C for the indicated time. After cooling to ambient temperature, the cap was removed, the reaction mixture was diluted with ethyl acetate and,

in cases where calibrated GC yields are reported, *n*-undecane (46.9 μL, 0.44 equiv) was added as an internal standard via 50-μL syringe. The reaction mixture was then filtered through a plug of celite. The reaction outcome was assessed by GC and TLC (isomeric ratios were determined by GC). The mixture was purified by flash column chromatography and/or reversed phase chromatography as indicated, and the product was dried under vacuum.

4. Optimization of the Ligand-Free Conditions (Table 2)

Table S7. Optimization of Ligand-Free Suzuki Coupling

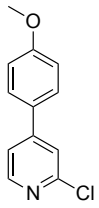


entry	trial	Pd source	NBu_4X (equiv)	**1a** (%)	**1b** (%)	**1c** (%)	**1a** : **1b**
1	1	$PdCl_2$	Br (3)	0.3	82	0.4	1 : >99
2	2	$PdCl_2$	Br (3)	0.6	80	0.4	1 : >99
3	Average	$PdCl_2$	Br (3)	0.5	81	0.4	1 : >99
4	1	$PdCl_2$	Br (5)	0.4	87	0.4	1 : >99
5	2	$PdCl_2$	Br (5)	0.5	80	0.4	1 : >99
6	Average	$PdCl_2$	Br (5)	0.5	84	0.4	1 : >99
7	1	$Pd(OAc)_2$	Br (3)	0.7	75	0.4	1 : >99
8	2	$Pd(OAc)_2$	Br (3)	0.6	71	0.3	1 : >99
9	Average	$Pd(OAc)_2$	Br (3)	0.7	73	0.4	1 : >99
10	1	Pd_2dba_3	Br (3)	0.4	61	0.2	1 : >99
11	2	Pd_2dba_3	Br (3)	0.5	52	0.2	1 : >99
12	Average	Pd_2dba_3	Br (3)	0.5	57	0.2	1 : >99
13	1	$PdCl_2$	Cl (3)	0.8	72	0.4	1 : 90
14	2	$PdCl_2$	Cl (3)	1.3	72	0.6	1 : 55
15	Average	$PdCl_2$	Cl (3)	1.1	72	0.5	1 : 65
16	1	$PdCl_2$	Br (1)	1.2	67	0.8	1 : 56
17	2	$PdCl_2$	Br (1)	1.2	71	0.6	1 : 59
18	Average	$PdCl_2$	Br (1)	1.2	69	0.7	1 : 58
19	1	$PdCl_2$	PF_6 (3)	2.6	44	2.4	1 : 17
20	2	$PdCl_2$	PF_6 (3)	3.4	52	3.8	1 : 15
21	Average	$PdCl_2$	PF_6 (3)	3.0	48	3.1	1 : 16
22[b]	1	$PdCl_2$	---	1.9	70	1.6	1 : 37
23[b]	2	$PdCl_2$	---	2.2	68	1.5	1 : 31
24[b]	Average	$PdCl_2$	---	2.1	69	1.6	1 : 33
25	1	$PdCl_2$	---	3.3	55	3.0	1 : 17
26	2	$PdCl_2$	---	3.7	58	3.2	1 : 16
27	Average	$PdCl_2$	---	3.5	56	3.1	1 : 16
28	1	$PdCl_2$	Br (1)	1.2	67	0.8	1 : 56
29	2	$PdCl_2$	Br (1)	1.2	71	0.6	1 : 59
30	Average	$PdCl_2$	Br (1)	1.2	69	0.7	1 : 58
31[c]	1	$PdCl_2$	Br (3)	1	80	0.6	1 : 80
32[c]	2	$PdCl_2$	Br (3)	0.8	78	0.5	1 : 98
33[c]	Average	$PdCl_2$	Br (3)	0.9	79	0.6	1 : 88
34[d]	1	$PdCl_2$	Br (3)	1.1	82	0.6	1 : 75
35[d]	2	$PdCl_2$	Br (3)	1.0	84	0.8	1 : 84
36[d]	Average	$PdCl_2$	Br (3)	1.1	83	0.7	1 : 75
37[e]	1	$PdCl_2$	Br (3)	0.8	40	0.5	1 : 50

38[e]	2	$PdCl_2$	Br (3)	0.8	49	0.4	1 : 61
39[e]	Average	$PdCl_2$	Br (3)	0.8	45	0.5	1 : 56
40[f]	1	$PdCl_2$	Br (3)	0.3	8	0.4	1 : 27
41[f]	2	$PdCl_2$	Br (3)	0.3	10	0.5	1 : 33
42[f]	Average	$PdCl_2$	Br (3)	0.3	9	0.5	1 : 29
43[c]	1	$PdCl_2$	Br (5)	0.8	85	0.4	1 : >99
44[c]	2	$PdCl_2$	Br (5)	0.7	84	0.6	1 : >99
45[c]	Average	$PdCl_2$	Br (5)	0.8	85	0.5	1 : >99

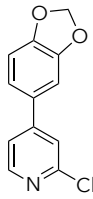
[a]Reactions were conducted according to the General Procedure on S37 for GC-scale reactions. GC yields calibrated against undecane as an internal standard. Calculated yield values were rounded to the nearest integer. [b]With KBr (3 equiv). [c]With H_2O (5 equiv). [d]With H_2O (10 equiv). [e]With 1 mol% $PdCl_2$. *f*Reaction run at 25 °C.

5. Isolation and Characterization of Cross-Coupled Products (Scheme 6)

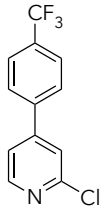


2-Chloro-4-(4-methoxyphenyl)pyridine (1b). Compound **1b** was prepared according to the general procedure under ligand-free conditions using 2,4-dichloropyridine (54 µL, 0.5 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (83.6 mg, 0.55 mmol, 1.1 equiv) with stirring for 30 h. Purification by flash column chromatography on silica gel in 6-20% ethyl acetate/hexanes (R_f = 0.42 in 15% ethyl acetate in hexanes) provided **1b** as a white solid (82.1 mg, 75% yield). Spectral data are consistent with previously reported data and literature.[12]

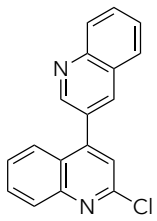
Larger-Scale Preparation of 1b: Compound **1b** was prepared according to the general procedure under ligand-free conditions using 2,4-dichloropyridine (270 µL, 2.5 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (417.9 mg, 2.75 mmol, 1.1 equiv) with stirring for 40 h. Purification by flash column chromatography on silica gel in 6-20% ethyl acetate/hexanes (R_f = 0.42 in 15% ethyl acetate in hexanes) provided **1b** as a white solid (347 mg, 63% yield). Spectral data are consistent with previously reported data and literature.[12]



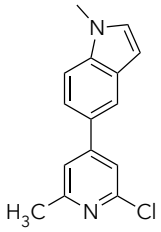
4-(1,3-benzodioxol-5-yl)-2-chloro-pyridine (41b). Compound **41b** was prepared according to the general procedure under ligand-free conditions using 2,4-dichloropyridine (54 µL, 0.5 mmol, 1.0 equiv) and 3,4-(methylenedioxy)benzeneboronic acid (91.3 mg, 0.55 mmol, 1.1 equiv) with stirring for 34 h. Purification by flash column chromatography on silica gel in 2-21% ethyl acetate/hexanes (R_f = 0.35 in 15% ethyl acetate in hexanes) provided **41b** as a white solid (75 mg, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.36 (d, *J* = 5.2 Hz, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.32 (dd, *J* = 5.2, 1.7 Hz, 1H), 7.11 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.06 (d, *J* = 1.7 Hz, 1 H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 152.3, 151.2, 150.1, 149.2, 148.7, 131.0, 121.7, 121.4, 120.2, 109.1, 107.3, 101.8. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{12}H_8ClNO_2$ 233.0244; Found 233.0245.



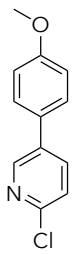
2-Chloro-4-[4-(trifluoromethyl)phenyl]-pyridine (42b). Compound **42b** was prepared according to the general procedure under ligand-free conditions using 2,4-dichloropyridine (54 μL, 0.5 mmol, 1.0 equiv) and *p*-(trifluoromethyl)phenylboronic acid (104.5 mg, 0.55 mmol, 1.1 equiv) with stirring for 23 h. Purification by flash column chromatography on silica gel using a linear gradient of 1-28% ethyl acetate/hexanes over 9 column volumes (R_f = 0.40 in 15% ethyl acetate in hexanes) provided **42b** as a white solid (79.1 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.46 (d, *J* = 5.2 Hz, 1H), 7.76 (d, *J* = 8.4, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 1.3 Hz, 1H), 7.43 (dd, *J* = 5.2, 1.3 Hz, 1H). Spectral data are consistent with literature.[23]



2-Chloro-4-(3-quinolinyl)-quinoline (43b). Compound **43b** was prepared according to the general procedure under ligand-free conditions using 2,4-dichloroquinoline (99 mg, 0.5 mmol, 1.0 equiv) and 3-quinolineboronic acid (95.1 mg, 0.55 mmol, 1.1 equiv) with stirring for 27.5 h. Purification by flash column chromatography on silica gel in 20% ethyl acetate/hexanes (R_f = 0.33 in 20% ethyl acetate in hexanes) provided **43b** as a tan solid (94.1 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.05 (d, *J* = 1.9 Hz, 1 H), 8.32 (d, *J* = 1.4 Hz, 1 H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H) 7.94 (d, *J* = 8.1 Hz, 1H), 7.83-7.87 (multiple peaks, 3H), 7.68 (dd, *J* = 15.2, 7.4 Hz, 1H), 7.56 (dd, *J* = 15.2, 7.4 Hz, 1H), 7.47 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 150.5, 150.4, 148.6, 148.22, 148.15, 136.7, 131.0, 130.8, 130.0, 129.7, 129.5, 128.3, 127.8, 127.7, 127.6, 125.7, 125.5, 122.9. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{18}H_{11}ClN_2$ 290.0611; Found 290.0615.



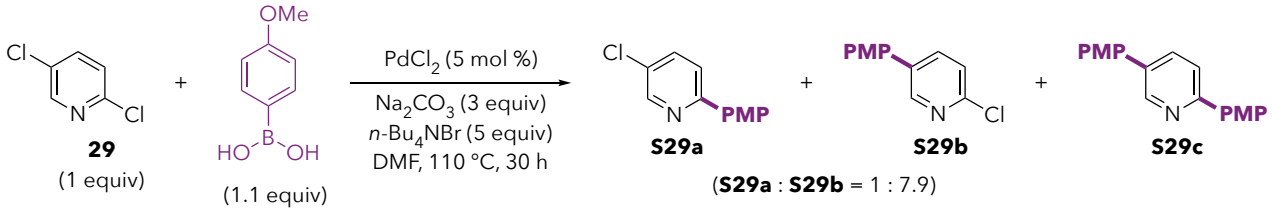
2-Chloro-6-methyl-4-(1-methyl-1H-indol-5-yl)-pyridine (44b). Compound **44b** was prepared according to the general procedure under ligand-free conditions using 2,4-dichloro-6-methylpyridine (81 mg, 0.5 mmol, 1.0 equiv) and 1-methyl-5-indolyl-boronic acid (96.2 mg, 0.55 mmol, 1.1 equiv) with stirring for 30 h. Purification by flash column chromatography on silica gel in 5-20% ethyl acetate/hexanes (R_f = 0.45 in 20% ethyl acetate in hexanes) provided **44b** as a white solid (62.2 mg, 49% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.88 (m, 1.6 Hz, 1H), 7.45 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.41 (d, *J* = 0.8 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 0.8 Hz, 1H), 7.11 (d, *J* = 3.1 Hz, 1H), 6.56 (dd, *J* = 3.1, 0.7 Hz, 1H), 3.81 (s, 3H), 2.58 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 159.3, 153.2, 151.1, 137.4, 130.3, 129.1, 128.4, 120.7, 120.1, 119.9, 119.0, 110.0, 101.9, 33.1, 24.4. HRMS (ESI Q-TOF) m/z: [M]+ Calcd for $C_{15}H_{13}ClN_2$ 256.0767; Found 256.0772.

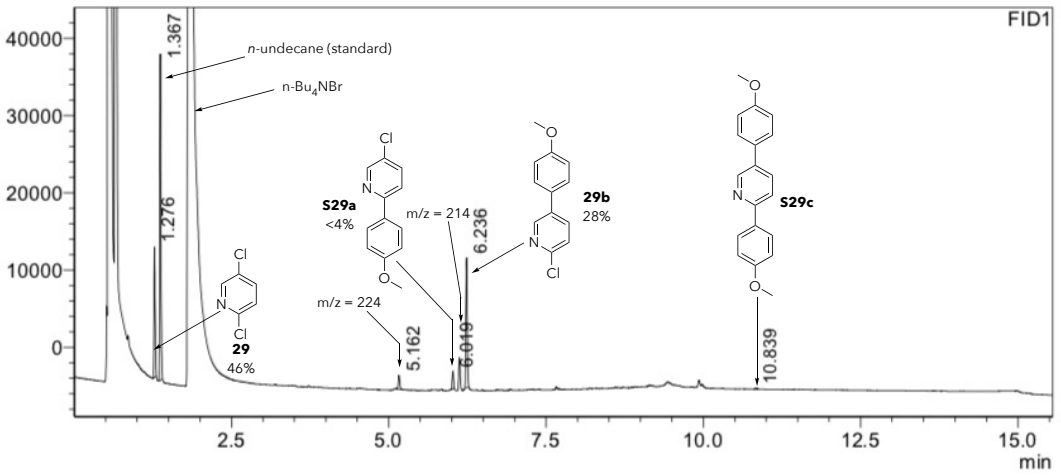


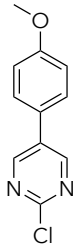
2-Chloro-5-(4-methoxyphenyl)-pyridine (29b). Compound **29b** was prepared according to the general procedure under ligand-free conditions, with the modification that no water was added. The reaction vial was charged with 2,5-dichloropyridine (74 mg, 0.5 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (83.6 mg, 0.55 mmol, 1.1 equiv) and stirred for 30 h. Purification by flash column chromatography on silica gel in 1-36% ethyl acetate/hexanes (R_f = 0.41 in 15% ethyl acetate in hexanes) resulted in coelution of **29b** and the diarylated product (the estimated crude yield of diarylated product is ~1% based on GC analysis). Further purification was performed using reversed phase flash column

chromatography with a 30 g C18 silica column, using an initial automated program comprising a flow rate of 35 mL/min of water:acetonitrile (98:2 to 1:99) over 20 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 98% MeCN in water. Fractions containing **29b** were partitioned between ethyl acetate and saturated brine. The organic layers were combined and dried over magnesium sulfate and dried *in vacuo* providing **29b** as a white solid (22.4 mg, 20% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.57 (dd, *J* = 2.6, 0.6 Hz, 1H), 7.79 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.46- 7.51 (m, 2H), 7.36 (dd, *J* = 8.3, 0.6 Hz, 1H), 6.98-7.03 (m, 2H), 3.86 (s, 3H). The product of C2-arylation was also isolated (4.5 mg, 4%). Spectral data for both monoarylated products are consistent with the literature.[11] Side products resulting from diarylation and homocoupling of **29** (m/z = 224) were each detected by GCMS (Scheme S11). These side products, as well as remaining starting material, appears to account for most of the remaining mass balance.

Scheme S11. Suzuki reaction of **29** under ligand-free conditions.



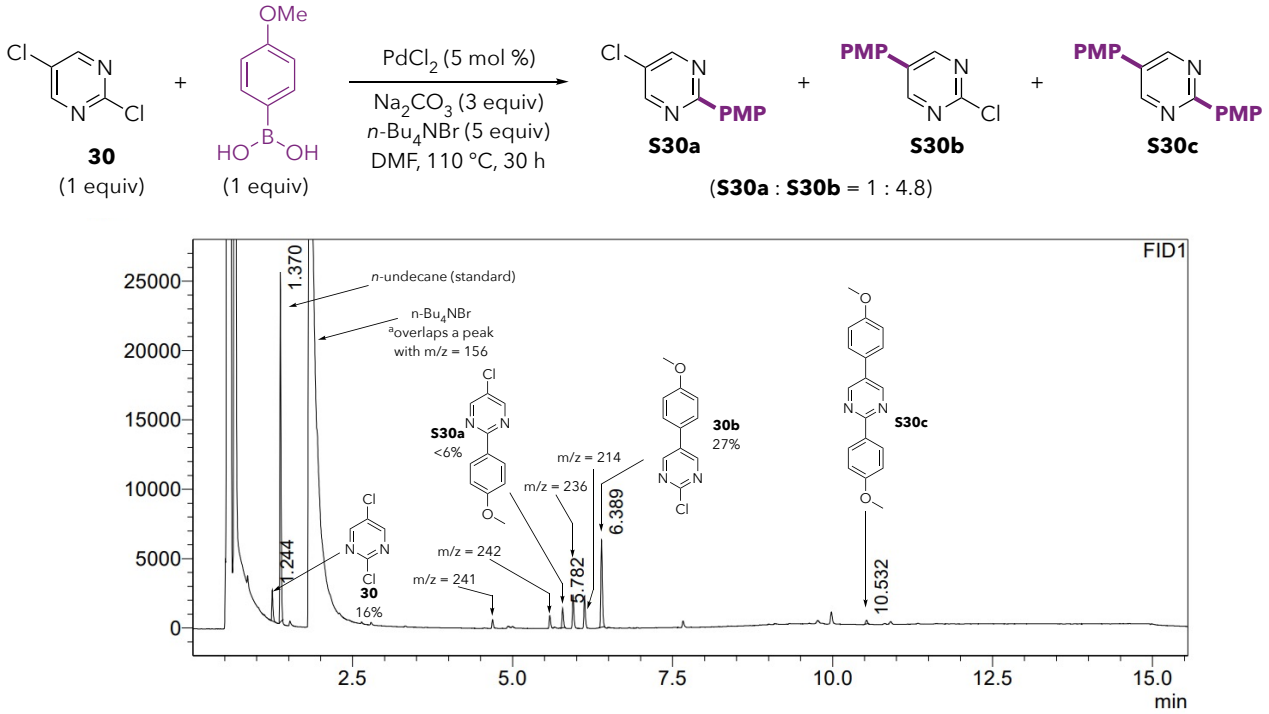




2-Chloro-5-(4-methoxyphenyl)-pyrimidine (30b). Compound **30b** was prepared according to the general procedure under ligand-free conditions with the modification that no water was added. The reaction vial was charged with 2,5-dichloropyrimidine (74.5 mg, 0.5 mmol, 1.0 equiv) and *p*-methoxyphenylboronic acid (83.6 mg, 0.55 mmol, 1.1 equiv) and stirred for 30 h. Purification by flash column chromatography on silica gel in 1-45% ethyl acetate/hexanes (R_f = 0.31 in 15% ethyl acetate in hexanes) resulted in coelution of the C5 isomer and a bipyrimidine side product. Fractions containing product **30b** were combined and solvent was removed under reduced pressure. Further purification was performed using reversed phase flash column chromatography with a 30 g C18 silica column, using an initial automated

program comprising a flow rate of 35 mL/min of water:acetonitrile (98:2 to 1:99) over 20 column volumes. When the product began eluting, the program was paused and reset to elute the analyte at 50-55% MeCN in water. Fractions containing **30b** were partitioned between ethyl acetate and saturated brine. The organic layers were combined and dried over magnesium sulfate and dried *in vacuo* providing **30b** as a white solid (18.5 mg, 17% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.78 (s, 2H), 7.46-7.53 (m, 2H), 7.00-7.08 (m, 2H), 3.87 (s, 3H). Spectral data are consistent with the literature.[24] The crude reaction mixture was analyzed by GCMS; in addition to remaining starting material, a small amount of C2-arylated product, and trace diarylated product, several small peaks corresponding to unidentified side products were observed (Scheme S12).

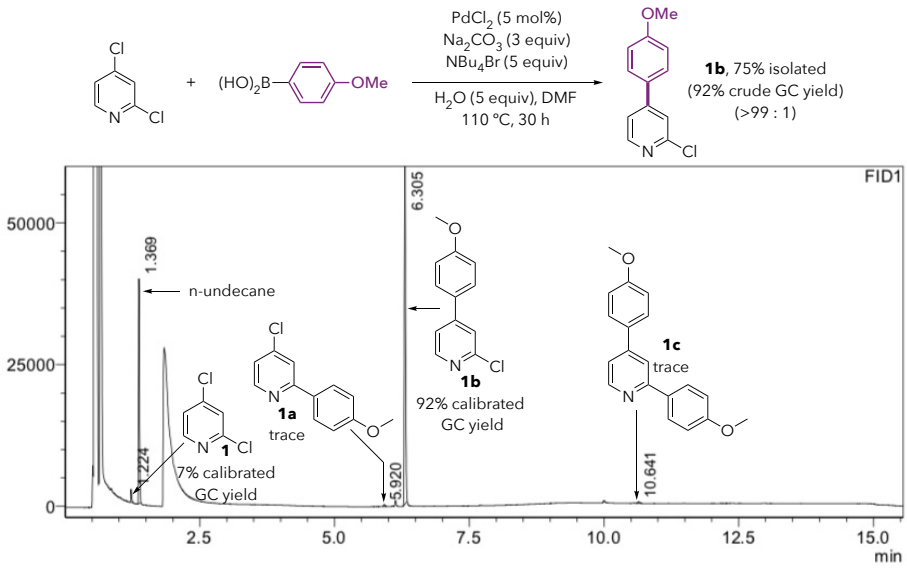
Scheme S12. Suzuki reaction of **30** under ligand-free conditions.

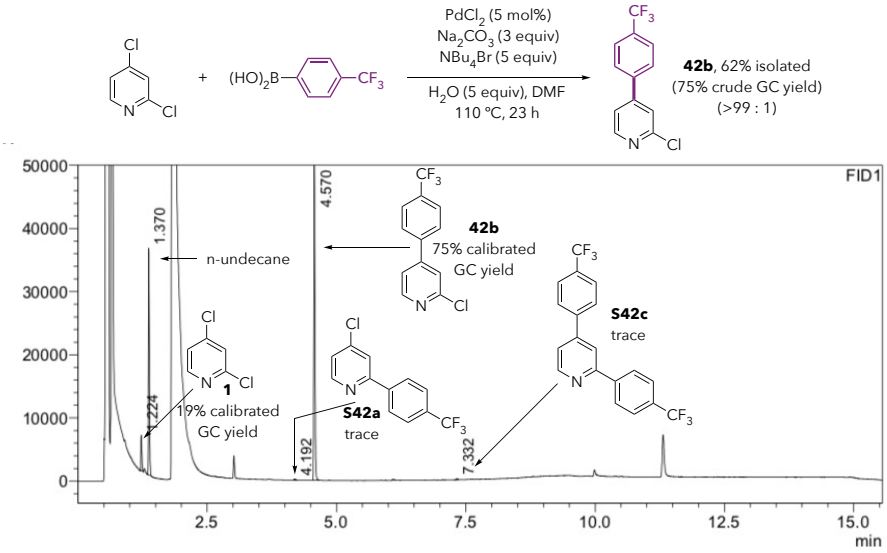


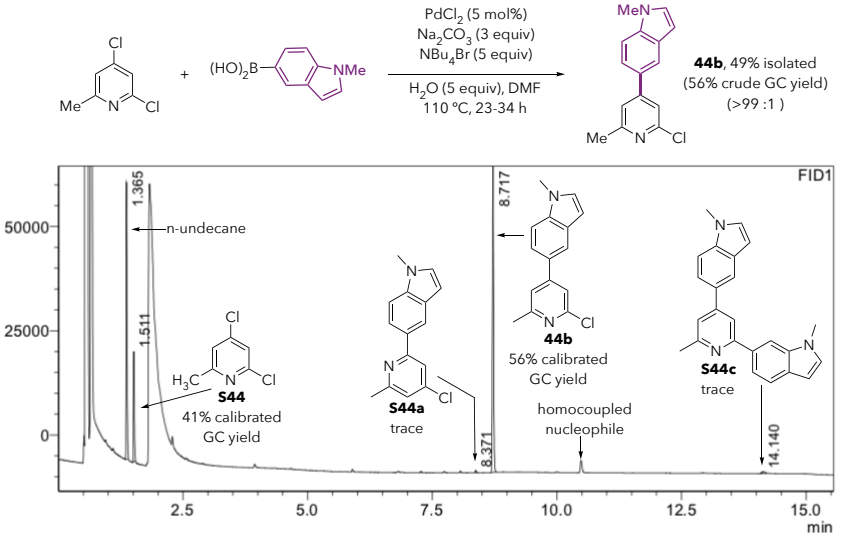
[a]A side product that overlaps with NBu_4Br was detected in a column fraction during purification and analyzed by GCMS providing a m/z = 157. This mass is consistent with a side product resulting from an S_NAr reaction between dimethylamine and 2,5-dichloropyrimidine. Dimethylamine is a common contaminant in DMF.

6. Discussion about Mass Balance

Lower yields under the ligand-free conditions are near-exclusively explained by unreacted starting material as well as some material loss during product isolation, as illustrated by the three GC chromatograms below that are representative of the reactions shown in Scheme 6 (product was not isolated from the trials shown below due to the addition of internal standard, undecane, after completion of the reaction). We tentatively hypothesize that the reactions stall due to aggregation of Pd nanoparticles into unreactive Pd black, leaving a significant portion of starting material unreacted.


PdCl2 (5 mol%)
Na2CO3 (3 equiv)
NBu4Br (5 equiv)
H2O (5 equiv), DMF
110 °C, 30 h
1b, 75% isolated
(92% crude GC yield)
(>99 : 1)
FID1
n-undecane
1.369
1.224
1
7% calibrated
GC yield
1a
trace
5.920
6.305
1b
92% calibrated
GC yield
1c
trace
10.641
min

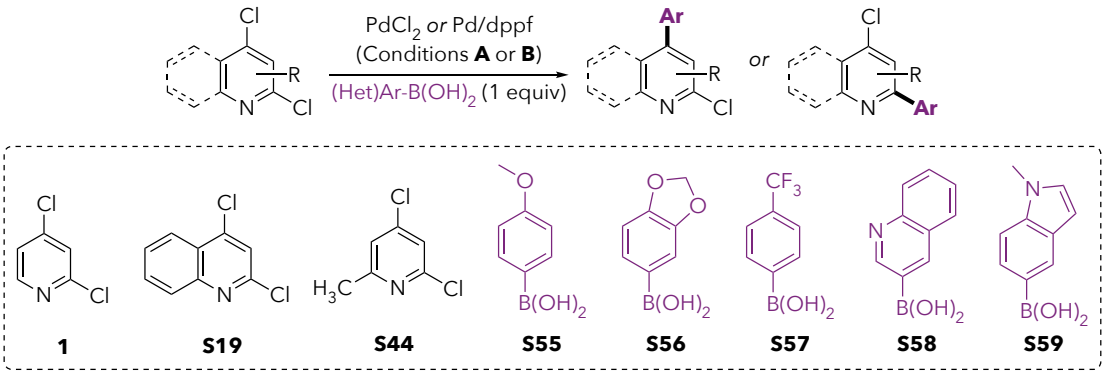

PdCl2 (5 mol%)
Na2CO3 (3 equiv)
NBu4Br (5 equiv)
H2O (5 equiv), DMF
110 °C, 23 h
42b, 62% isolated
(75% crude GC yield)
(>99 : 1)
FID1
n-undecane
1.370
1.224
1
19% calibrated
GC yield
4.192
S42a
trace
4.570
42b
75% calibrated
GC yield
7.332
S42c
trace
min


PdCl2 (5 mol%)
Na2CO3 (3 equiv)
NBu4Br (5 equiv)
H2O (5 equiv), DMF
110 °C, 23-34 h
44b, 49% isolated
(56% crude GC yield)
(>99 :1)
FID1
n-undecane
1.365
1.511
S44
41% calibrated
GC yield
S44a
trace
8.371
8.717
44b
56% calibrated
GC yield
homocoupled
nucleophile
S44c
trace
14.140
min

7. Comparison of Ligand-Free Results (C4-Selective) vs. C2-Selective Conditions

The ligand-free conditions described herein promote Suzuki-Miyaura cross-coupling of 2,4-dichloropyridines and quinoline with high C4-selectivity and promote C5-selective coupling of 2,5-dichloropyridine and pyrimidine. In contrast, Pd/dppf is a highly C2-selective catalyst for each of these substrates. Tables S8 and S9 demonstrate orthogonality between these two catalytic systems, based on the distinct GC retention times of the major products under each of these conditions.

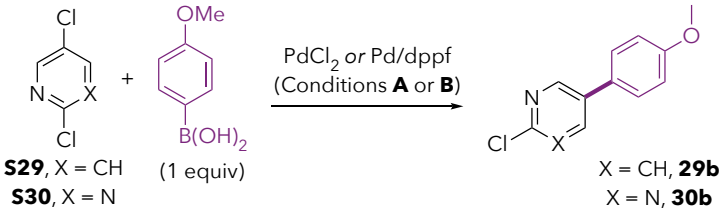
Table S8. Retention times (RT) of C4- and C2-arylated products by GC-FID for ligand-free reactions versus $Pd(OAc)_2$/dppf -catalyzed reactions.[a]



entry	substrate	nucleophile	RT with **A** (min)	RT with **B** (min)
1	**1**	**S55**	6.31	5.91
2	**1**	**S56**	6.84	6.46
3	**1**	**S57**	4.58	4.18
4	**S19**	**S58**	10.22	10.85
5	**S44**	**S59**	8.73	8.37

[a]Conditions A: $PdCl_2$ (5 mol%), Na_2CO_3 (3 equiv), $N(n\text{-}Bu)_4Br$ (5 equiv), H_2O (5 equiv), DMF (0.25 *M*), 110 °C, 22-34h. Conditions B: $Pd(OAc)_2$ /dppf (5 mol%), Cs_2CO_3 (2.5 equiv), H_2O (7 equiv), 1,4-dioxane (0.25 *M*), 60 °C, 12 h.

Table S9. Retention times (RT) of C5- and C2-arylated products by GC-FID for ligand-free reactions versus $Pd(OAc)_2$/dppf -catalyzed reactions[a]



entry	substrate	nucleophile	RT with **A** (min)	RT with **B** (min)
1	**S29**	**S55**	6.24	6.02
5	**S30**	**S55**	6.39	5.78

[a]Conditions A: $PdCl_2$ (5 mol%), Na_2CO_3 (3 equiv), $N(n\text{-}Bu)_4Br$ (5 equiv), H_2O (5 equiv), DMF (0.25 *M*), 110 °C, 22-34h. Conditions B: $Pd(OAc)_2$ /dppf (5 mol%), Cs_2CO_3 (2.5 equiv), H_2O (7 equiv), 1,4-dioxane (0.25 *M*), 60 °C, 12 h.

II. References

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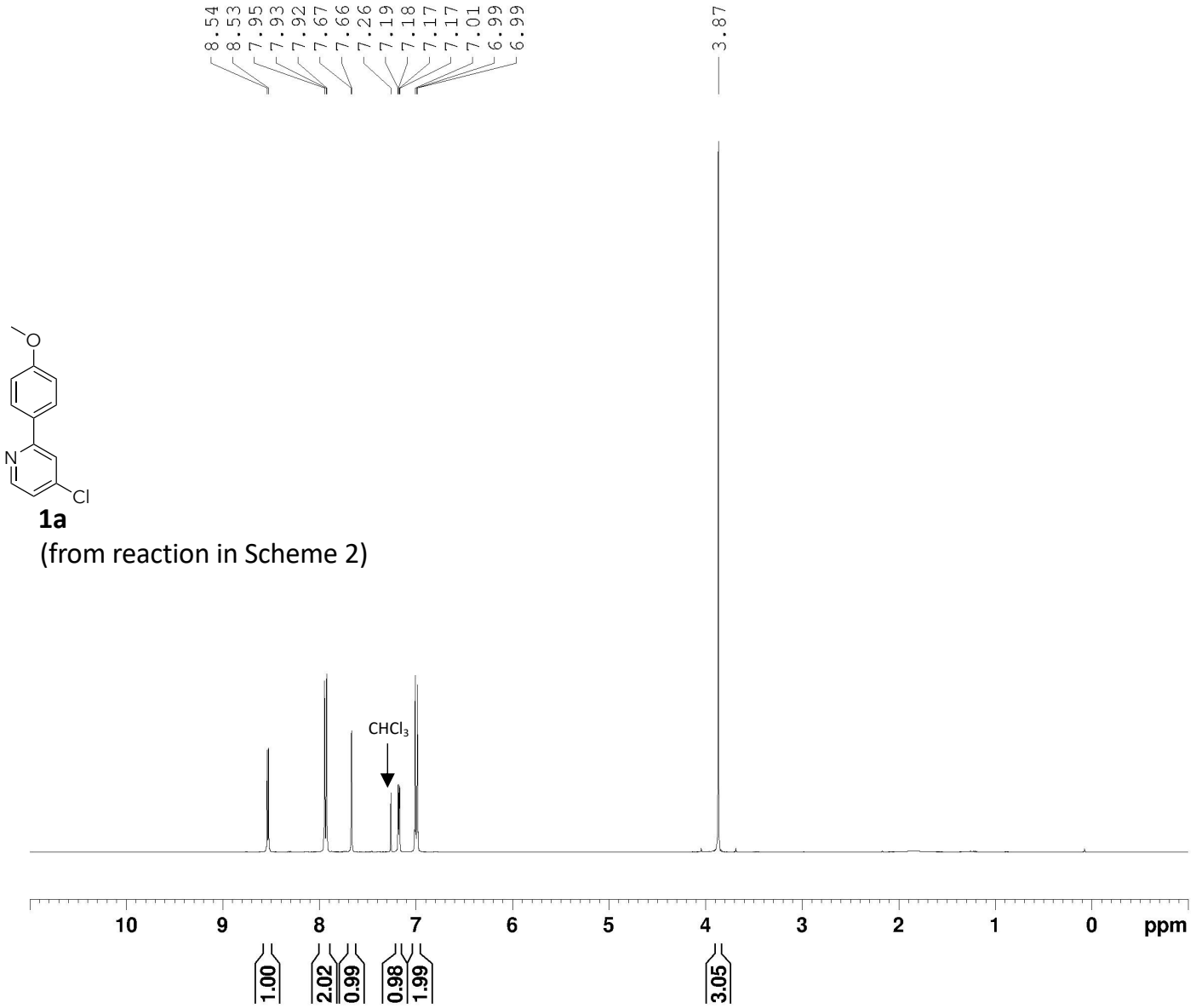
III. NMR Spectra



1a

(from reaction in Scheme 2)

```
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PROCNO                 1

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PROBHD    Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9976959 sec
RG                   101
DW                61.000 usec
DE                13.89 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1         24.03499985 W

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                  1.00
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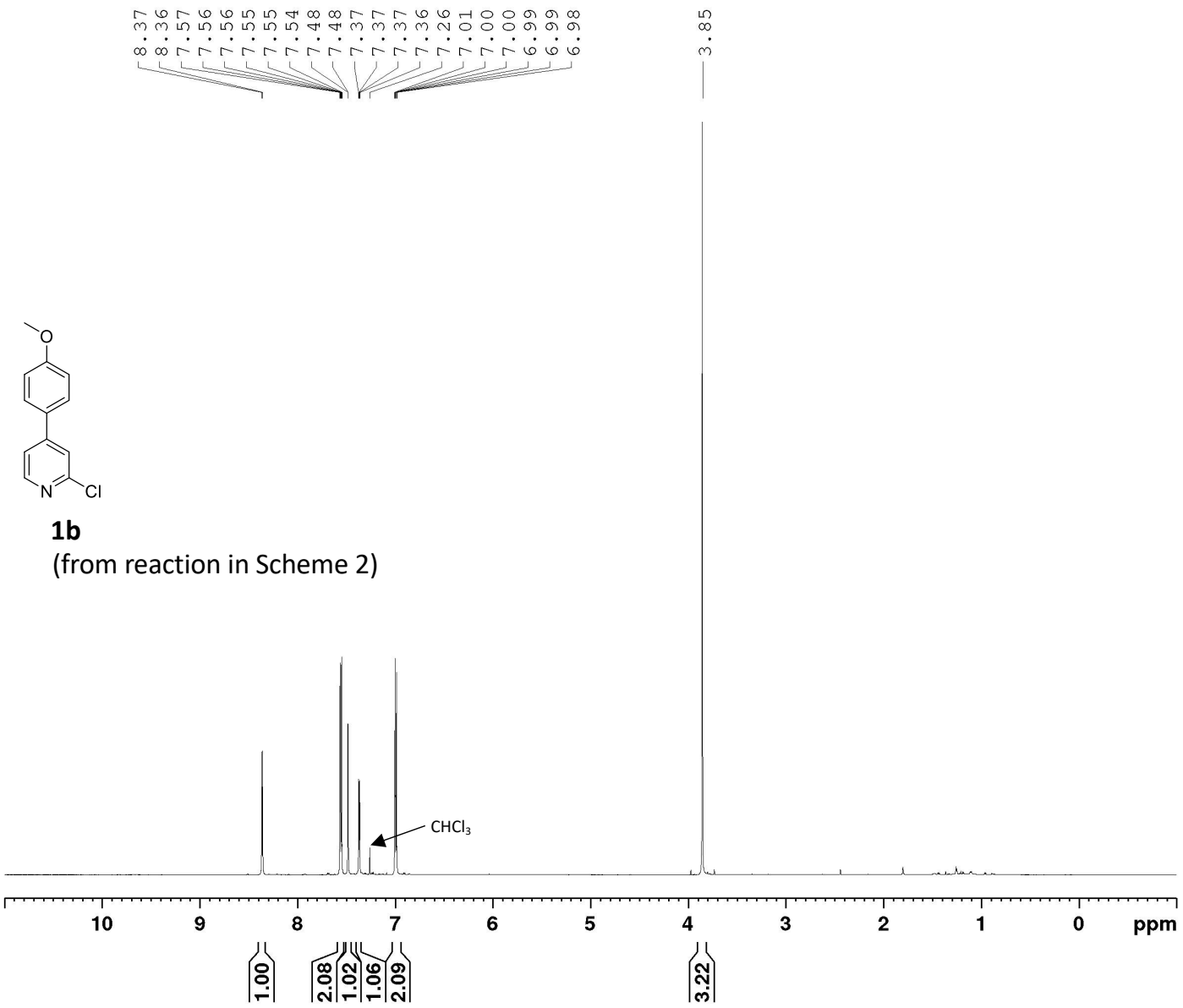
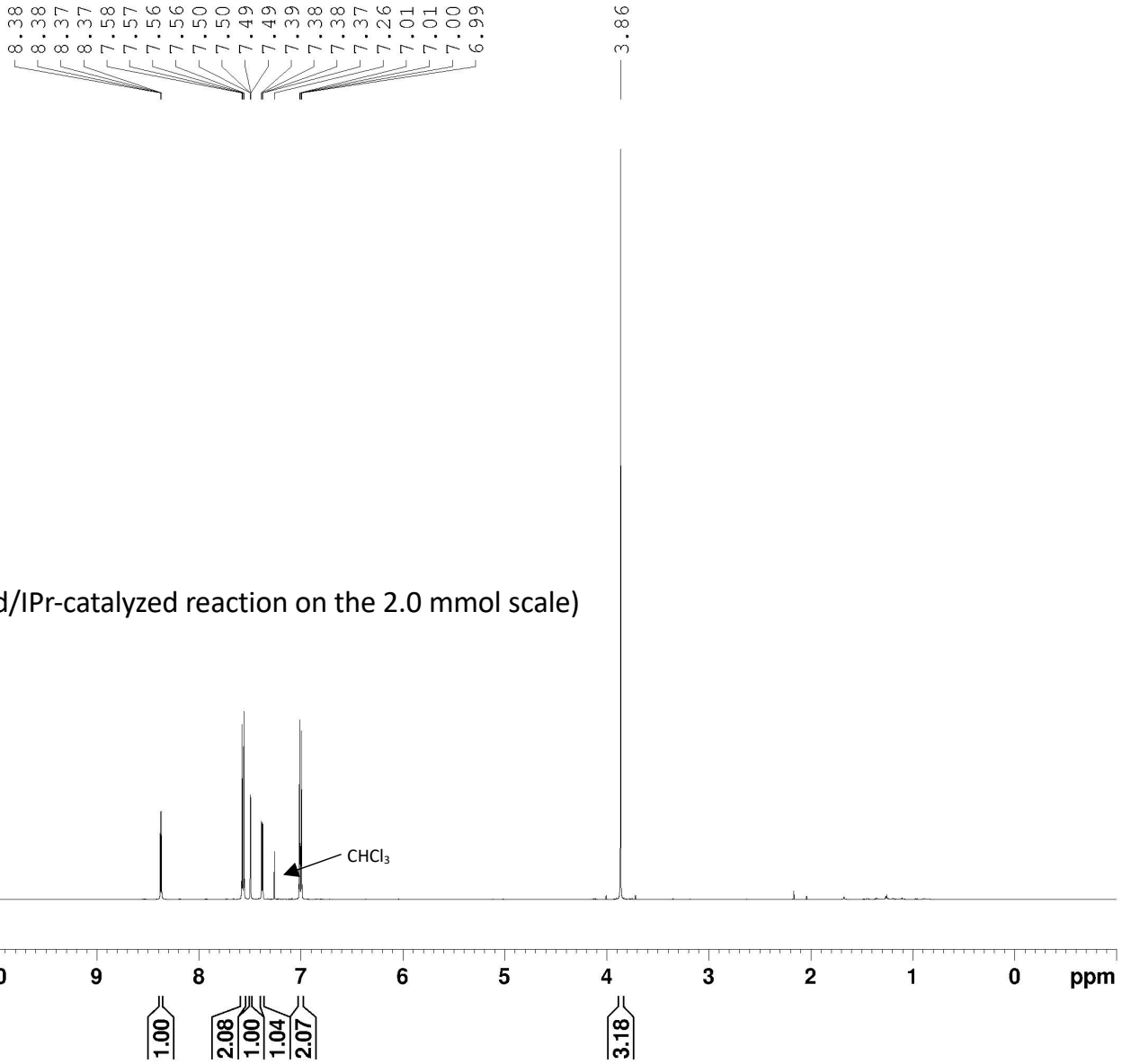


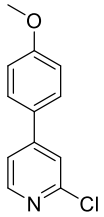
1b
(from reaction in Scheme 2)

```
Current Data Parameters
NAME      JPN-1-174-7_C4-mono
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_           20200610
Time                12.30 h
INSTRUM             spect
PROBHD    Z127277_0002 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH             12019.230 Hz
FIDRES           0.366798 Hz
AQ              2.7262976 sec
RG                   4.41
DW                 41.600 usec
DE                 10.00 usec
TE                 300.0 K
D1             1.00000000 sec
TD0                    1
SFO1          600.1337060 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1           5.59999990 W

F2 - Processing parameters
SI                  65536
SF            600.1300144 MHz
WDW                    EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```





1b

(from Pd/IPr-catalyzed reaction on the 2.0 mmol scale)

```
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EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220419
Time              17.32 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ            3.2767999 sec
RG                 86.13
DW                50.000 usec
DE                16.00 usec
TE                300.0 K
D1           2.00000000 sec
TD0                    1
SFO1        500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1        11.44699955 W

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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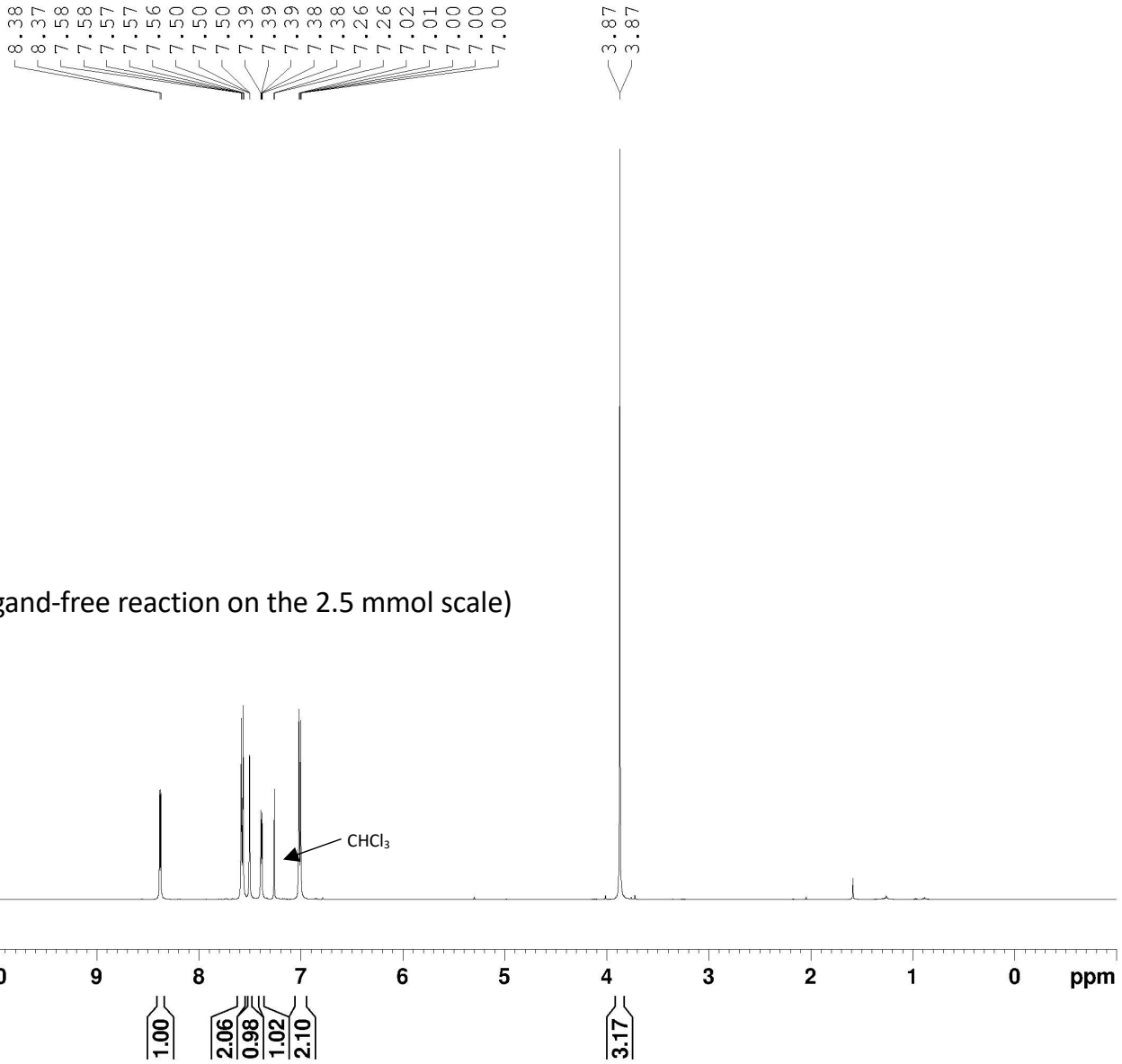

1b

(from ligand-free reaction on the 2.5 mmol scale)

```
Current Data Parameters
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EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220419
Time              17.42 h
INSTRUM            spect
PROBHD    Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ             3.2767999 sec
RG                151.18
DW                50.000 usec
DE                16.00 usec
TE                300.0 K
D1           2.00000000 sec
TD0                    1
SFO1        500.2330889 MHz
NUC1                1H
P0                 4.00 usec
P1                12.00 usec
PLW1        11.44699955 W

F2 - Processing parameters
SI                 65536
SF          500.2300117 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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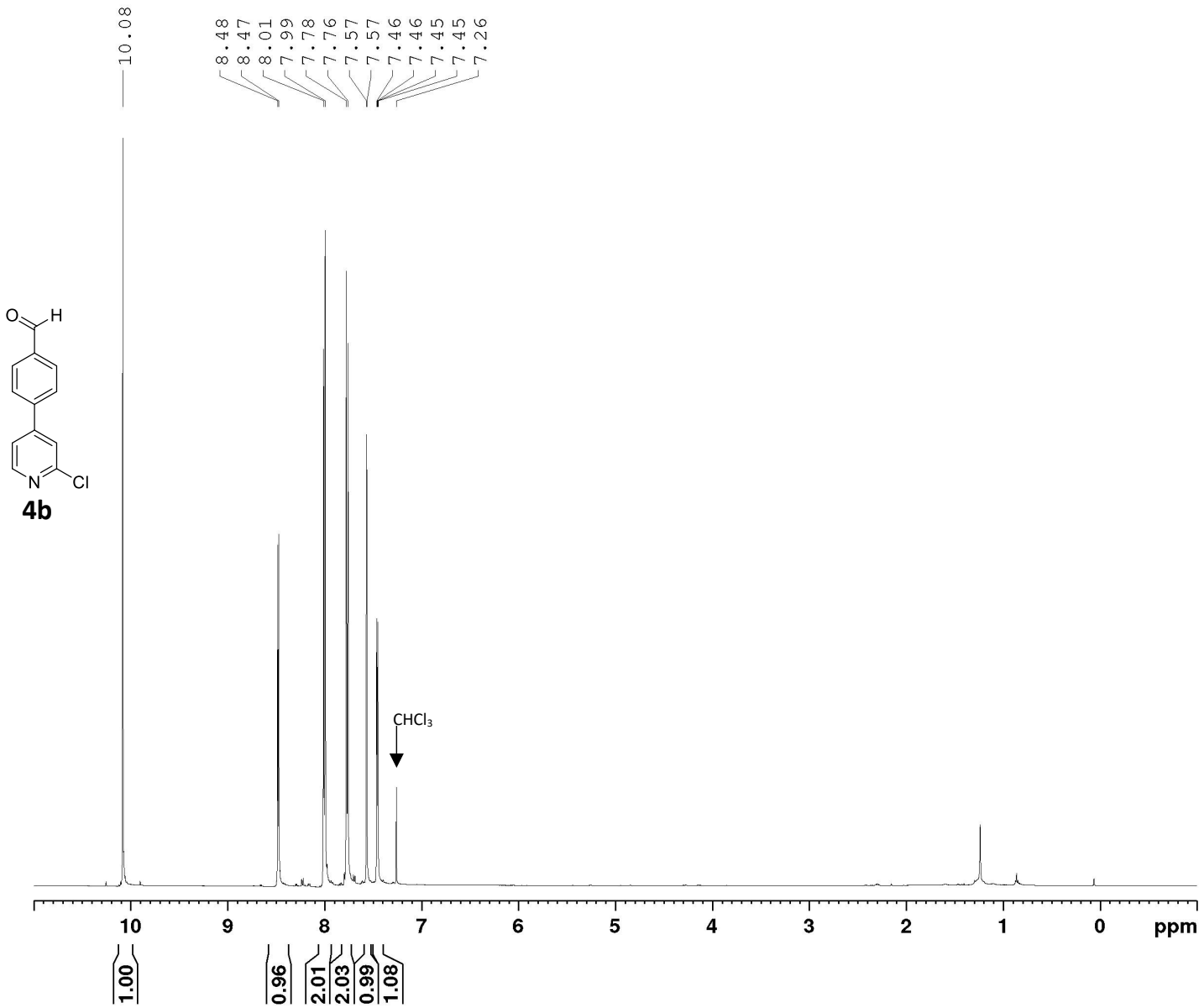


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EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211120
Time                5.51 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                 76.94
DW                50.000 usec
DE                16.00 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1          500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1          11.44699955 W

F2 - Processing parameters
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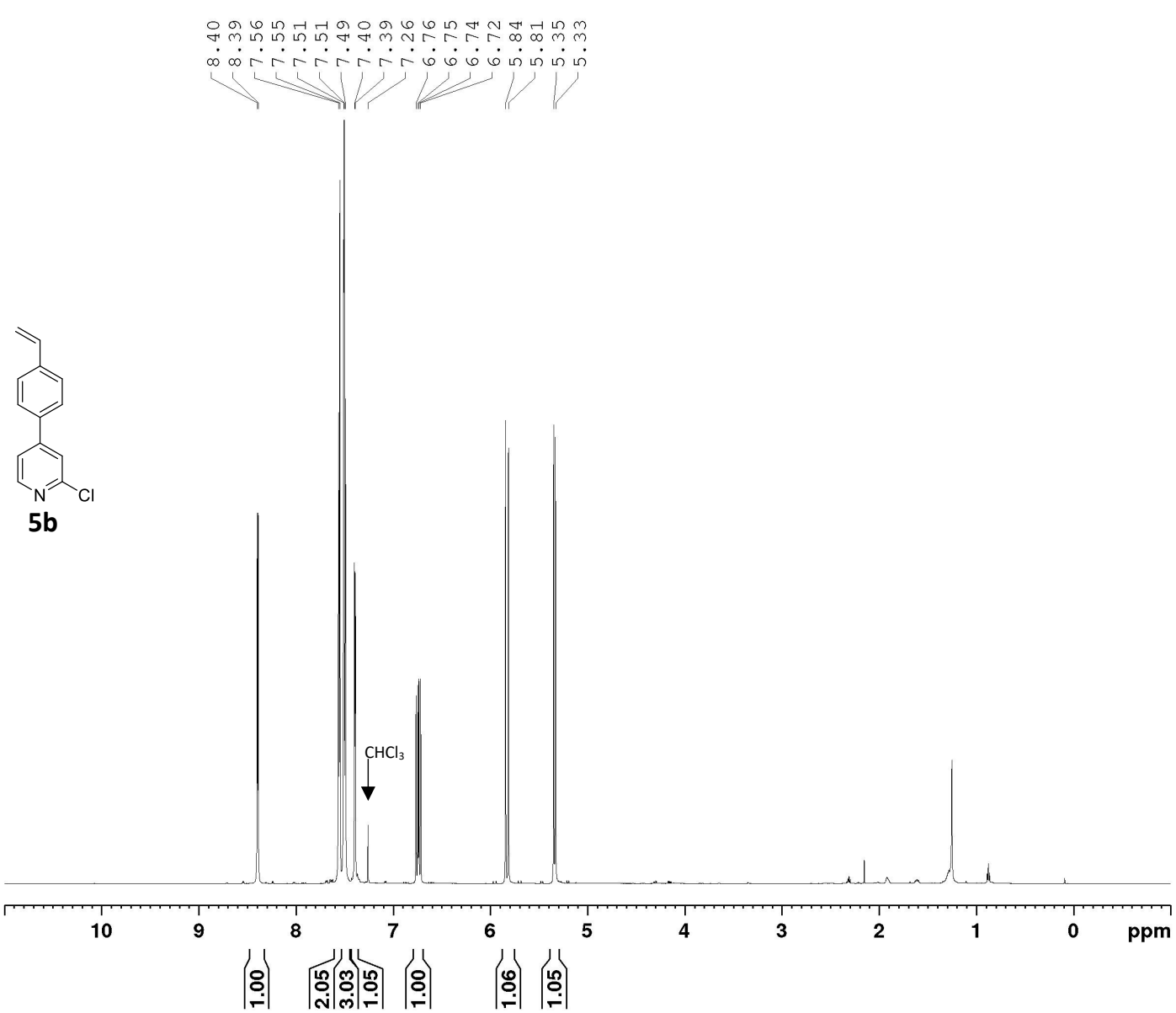
SF            500.2300120 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
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EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20200608
Time              16.21 h
INSTRUM             spect
PROBHD    Z127277_0002 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH           12019.230 Hz
FIDRES         0.366798 Hz
AQ             2.7262976 sec
RG                  4.41
DW                41.600 usec
DE                10.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                    1
SFO1         600.1337060 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1          5.59999990 W

F2 - Processing parameters
SI                  65536
SF           600.1300145 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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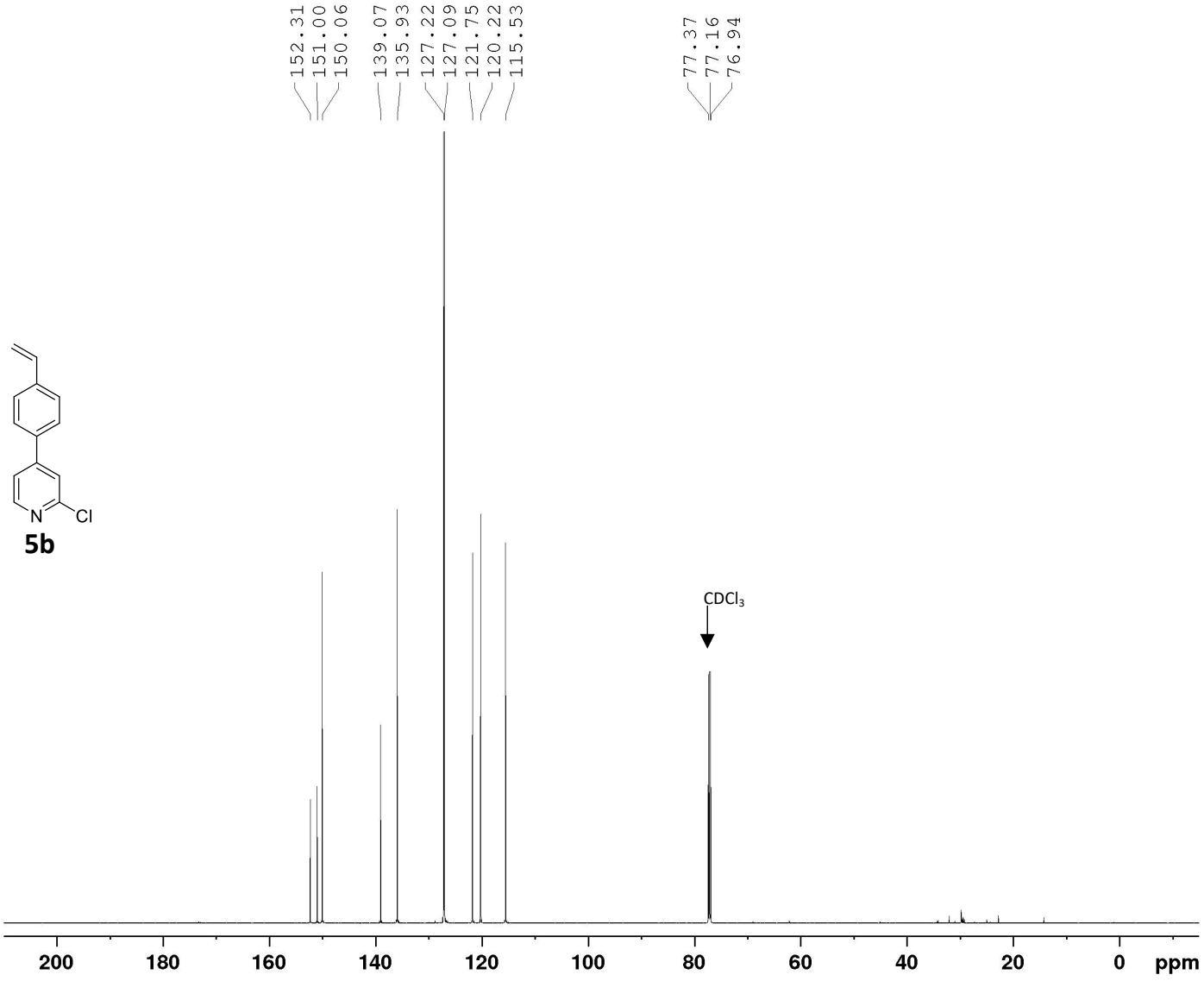


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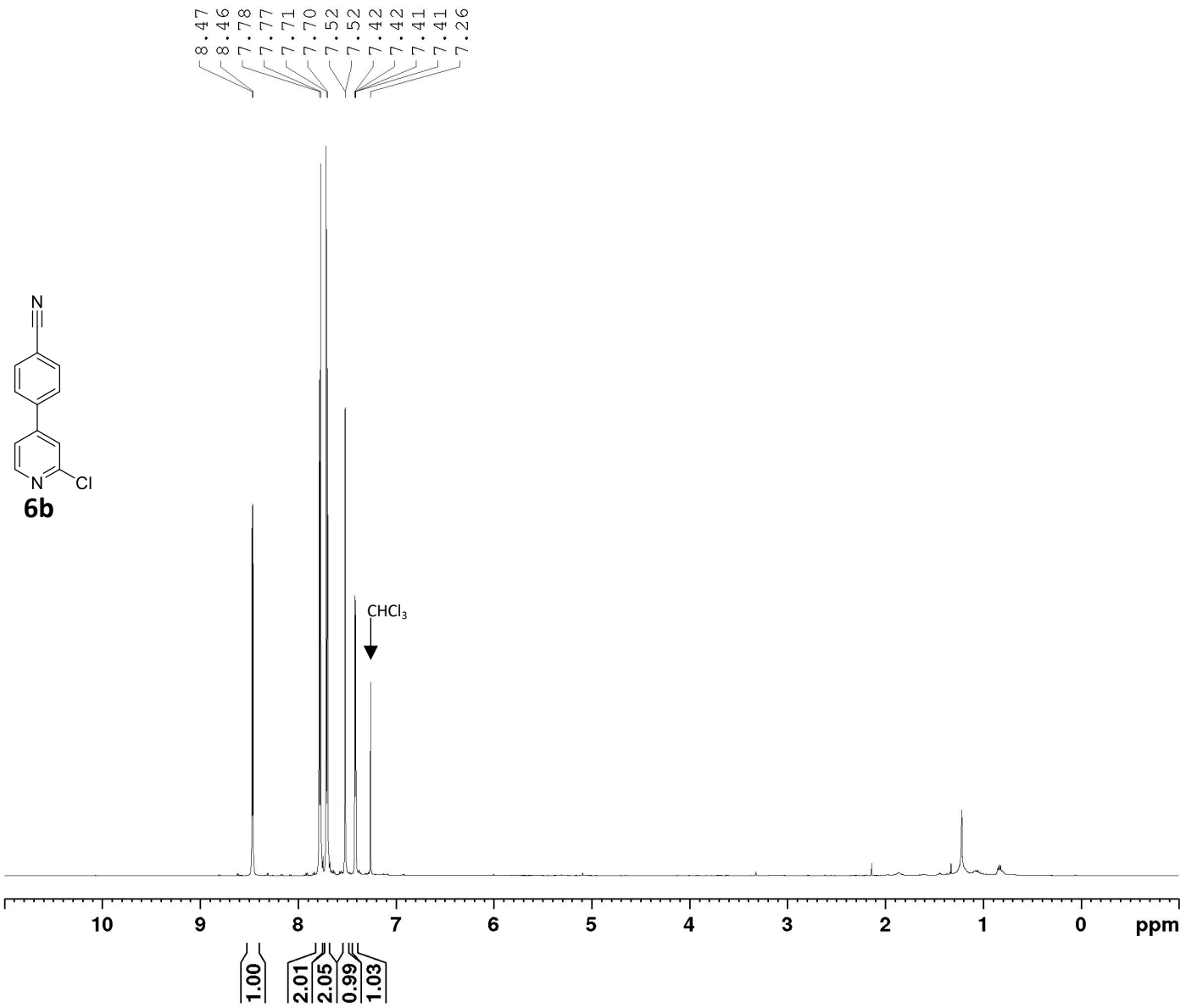
Current Data Parameters
NAME      JPN-1-171-3_C4-mono_dried
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20200608
Time              17.13 h
INSTRUM            spect
PROBHD   Z127277_0002 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.9087659 sec
RG                184.4
DW               13.867 usec
DE                18.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        150.9178981 MHz
NUC1                13C
P0                 4.00 usec
P1                12.00 usec
PLW1        91.00000000 W
SFO2        600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2         5.59999990 W
PLW12        0.07314300 W
PLW13        0.03679000 W

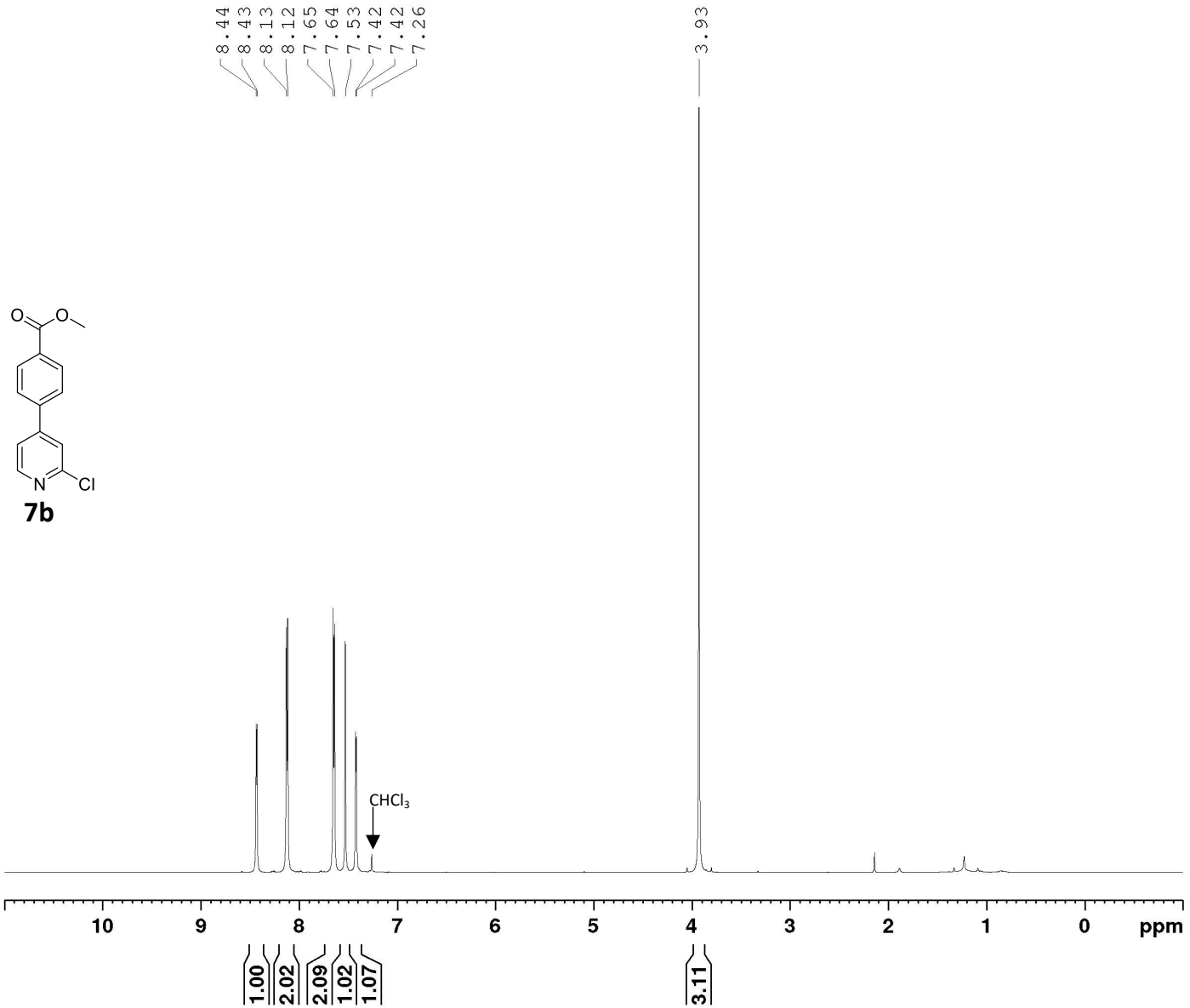
F2 - Processing parameters
SI                32768
SF          150.9028016 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```




```
Current Data Parameters
NAME      JPN-1-171-2_C4-mono_dried
EXPNO                22
PROCNO                1

F2 - Acquisition Parameters
Date_          20200608
Time              17.21 h
INSTRUM           spect
PROBHD   Z127277_0002 (
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  64
DS                   2
SWH          12019.230 Hz
FIDRES         0.366798 Hz
AQ             2.7262976 sec
RG                4.41
DW               41.600 usec
DE               10.00 usec
TE               300.0 K
D1            1.00000000 sec
TD0                  1
SFO1         600.1337060 MHz
NUC1                1H
P0                2.67 usec
P1                8.00 usec
PLW1          5.59999990 W

F2 - Processing parameters
SI               65536
SF           600.1300145 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

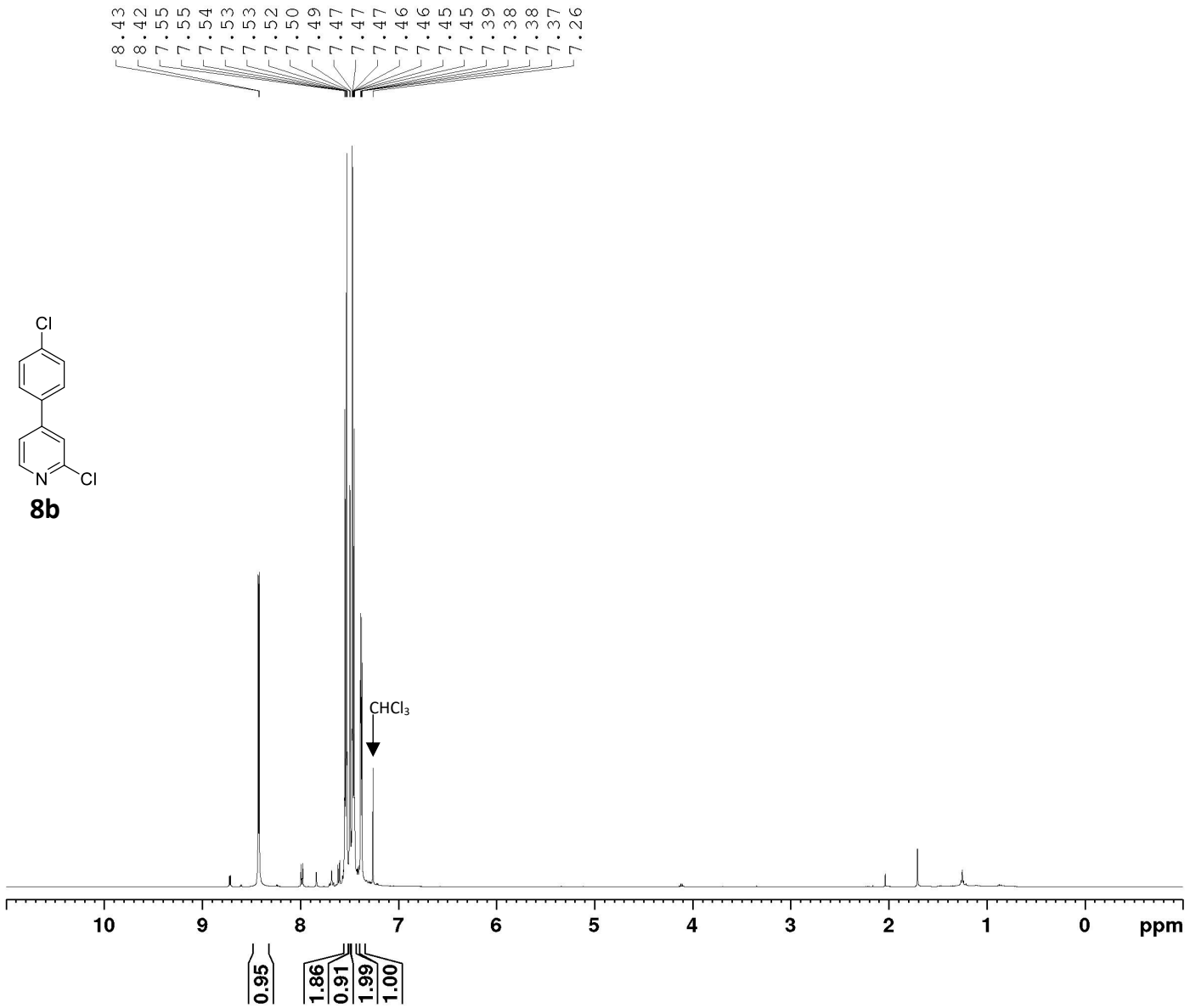


7b

```
Current Data Parameters
NAME      JPN-1-174-4_C4-mono
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20200610
Time                  12.06 h
INSTRUM               spect
PROBHD    Z127277_0002 (
PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        64
DS                         2
SWH               12019.230 Hz
FIDRES             0.366798 Hz
AQ                 2.7262976 sec
RG                      4.41
DW                    41.600 usec
DE                    10.00 usec
TE                    300.0 K
D1                1.00000000 sec
TD0                        1
SFO1            600.1337060 MHz
NUC1                      1H
P0                     2.67 usec
P1                     8.00 usec
PLW1             5.59999990 W

F2 - Processing parameters
SI                     65536
SF              600.1300144 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```

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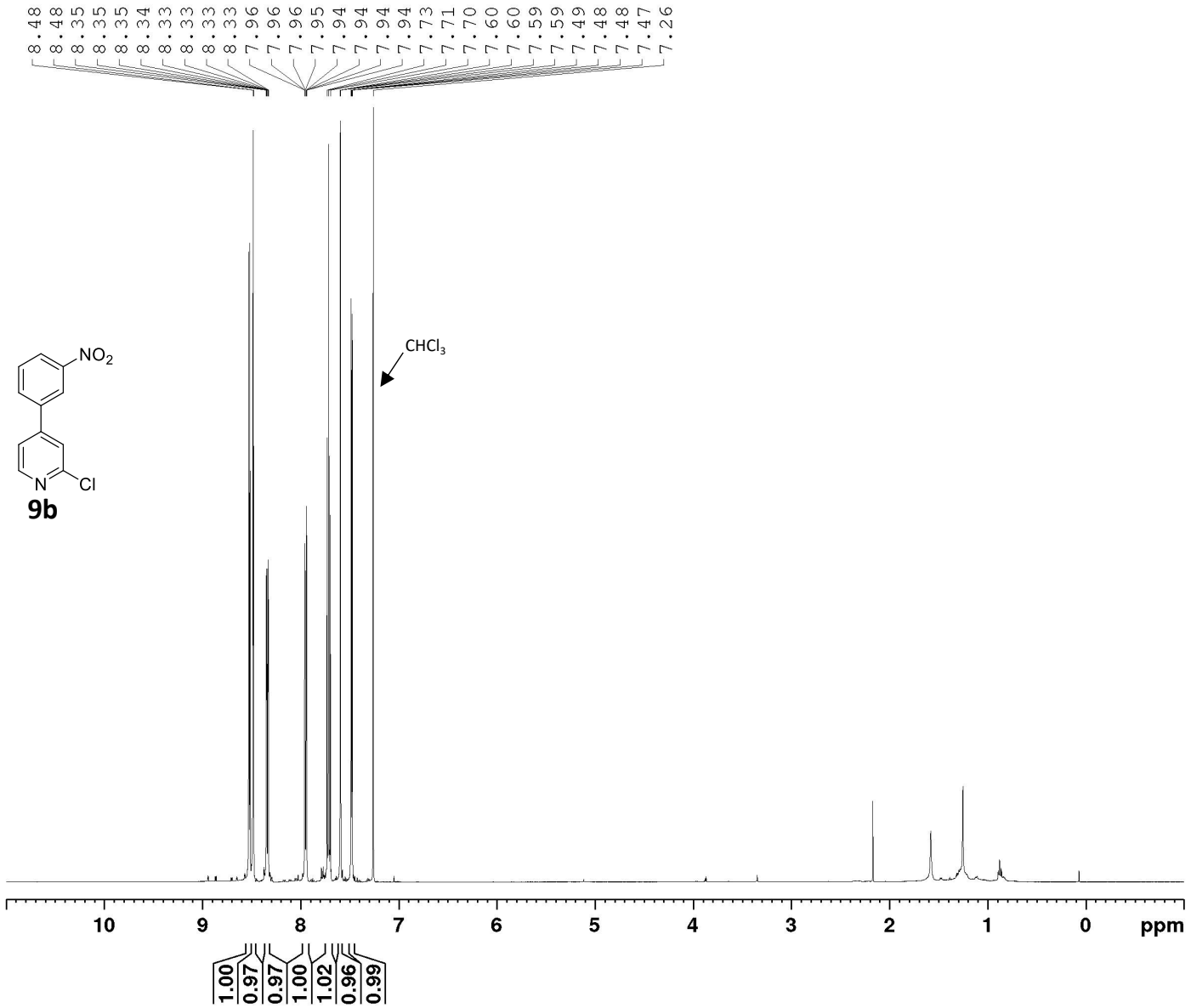
Current Data Parameters
NAME      JPN-1-174-3a_C4-mono
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_            20200811
Time                23.22 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH             10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                  86.13
DW                 50.000 usec
DE                 16.00 usec
TE                 300.0 K
D1              2.00000000 sec
TD0                     1
SFO1          500.2330889 MHz
NUC1                   1H
P0                  4.00 usec
P1                 12.00 usec
PLW1          11.44699955 W

F2 - Processing parameters
SI                  65536
SF            500.2300122 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```




```
Current Data Parameters
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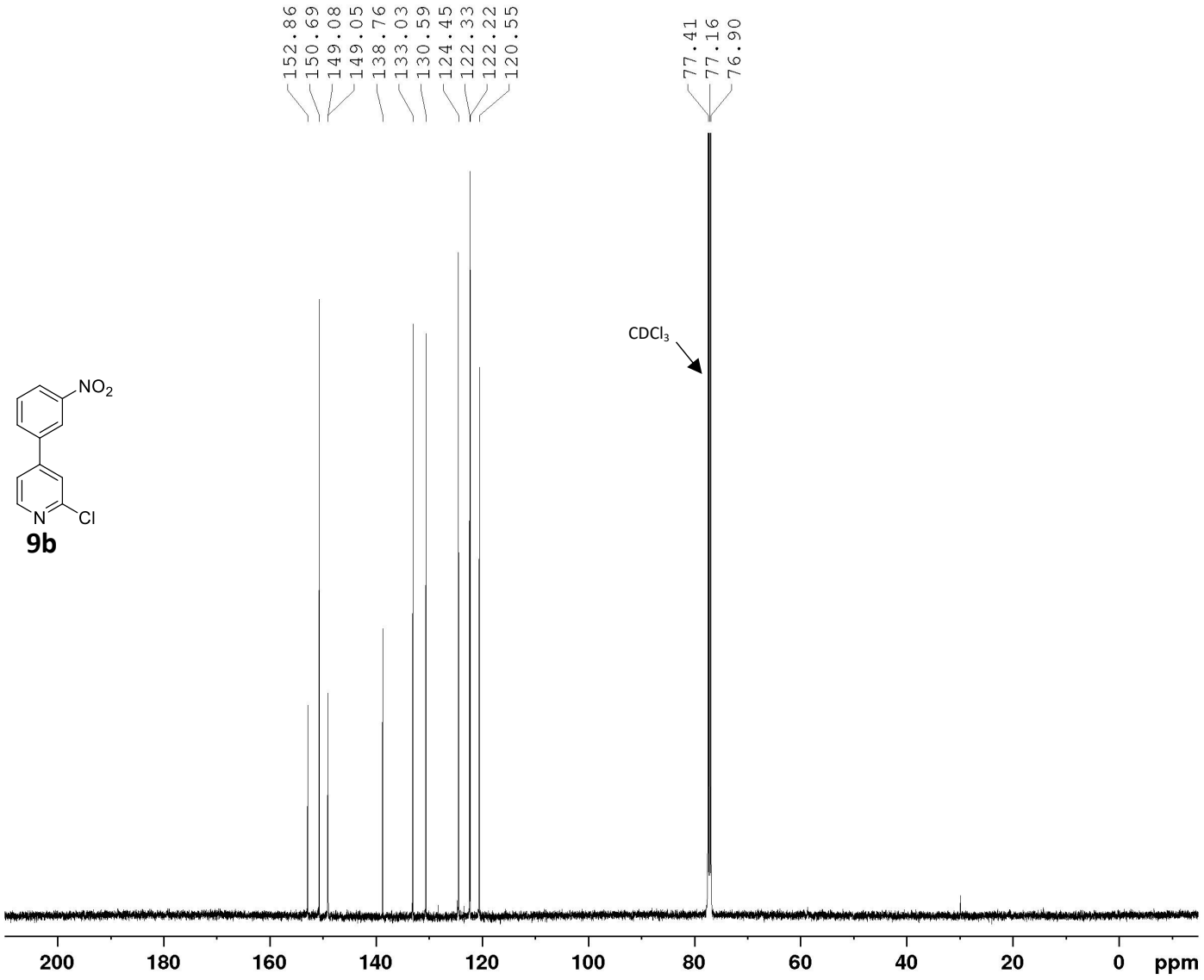
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211121
Time                1.47 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ             3.2767999 sec
RG                151.18
DW                50.000 usec
DE                16.00 usec
TE                298.0 K
D1            2.00000000 sec
TD0                    1
SFO1         500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1         11.44699955 W

F2 - Processing parameters
SI                 65536
SF           500.2300121 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

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Current Data Parameters
NAME         JPN-1-193-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211121
Time                2.43 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1         125.7955118 MHz
NUC1                 13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

F2 - Processing parameters
SI                32768
SF           125.7829172 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
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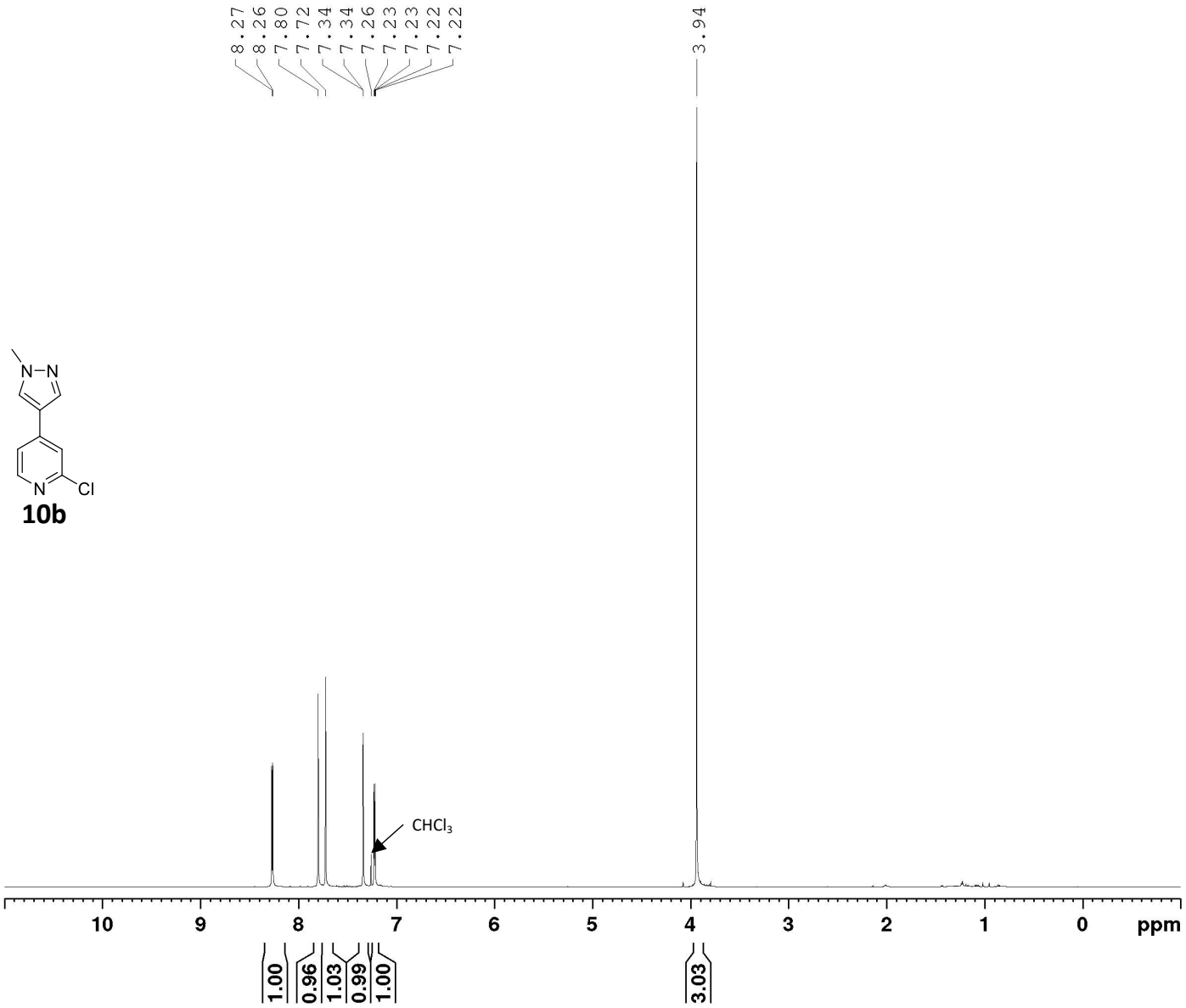
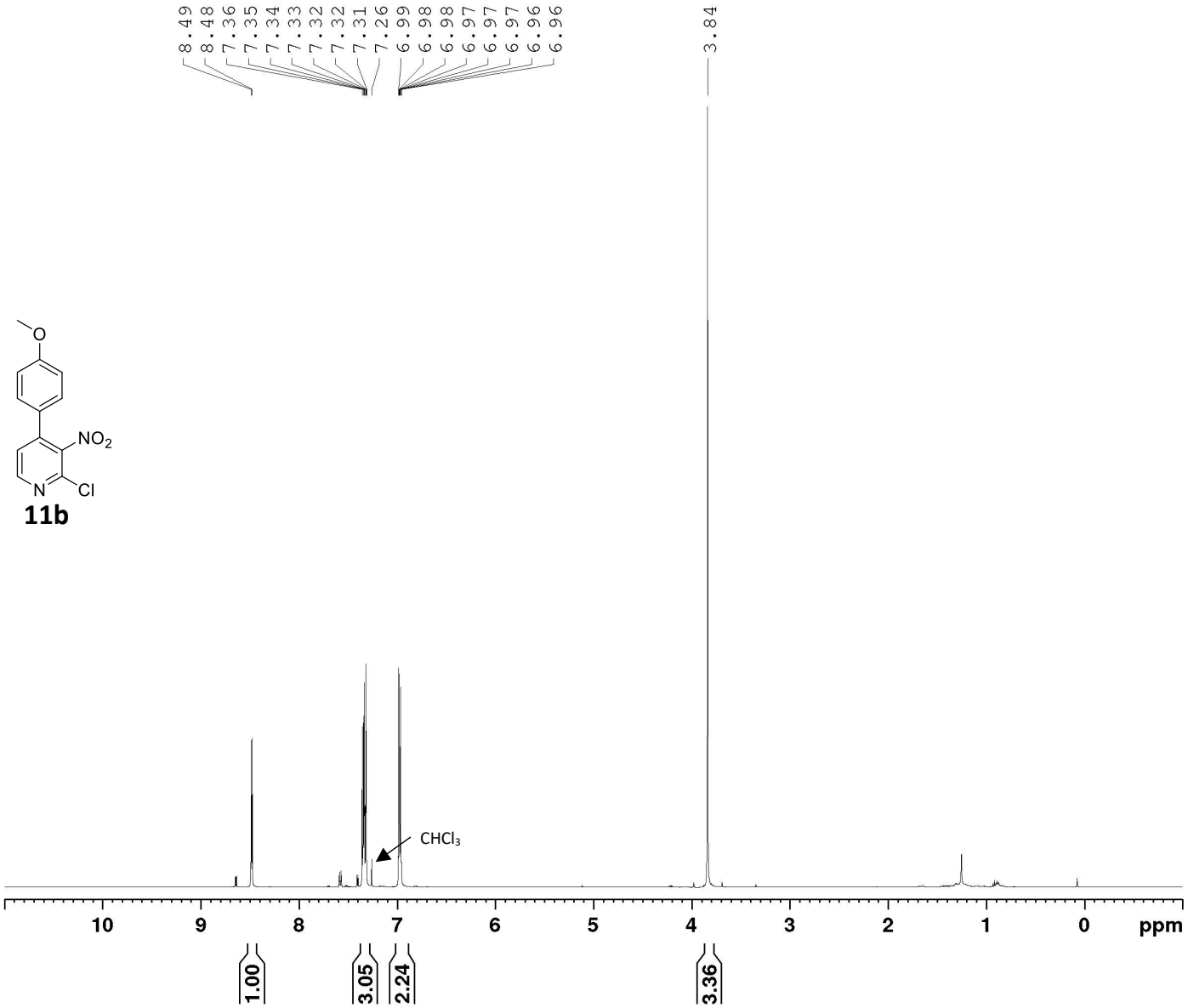


10b

```
Current Data Parameters
NAME      JPN-2-11a_C4-mono_MeOH_column_cc
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200829
Time              17.06 h
INSTRUM           spect
PROBHD   Z125869_0055 (
PULPROG           zg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ             3.2767999 sec
RG                37.93
DW               50.000 usec
DE               16.00 usec
TE               300.0 K
D1            2.00000000 sec
TD0                   1
SFO1         500.2330889 MHz
NUC1                 1H
P0                4.00 usec
P1               12.00 usec
PLW1         11.44699955 W

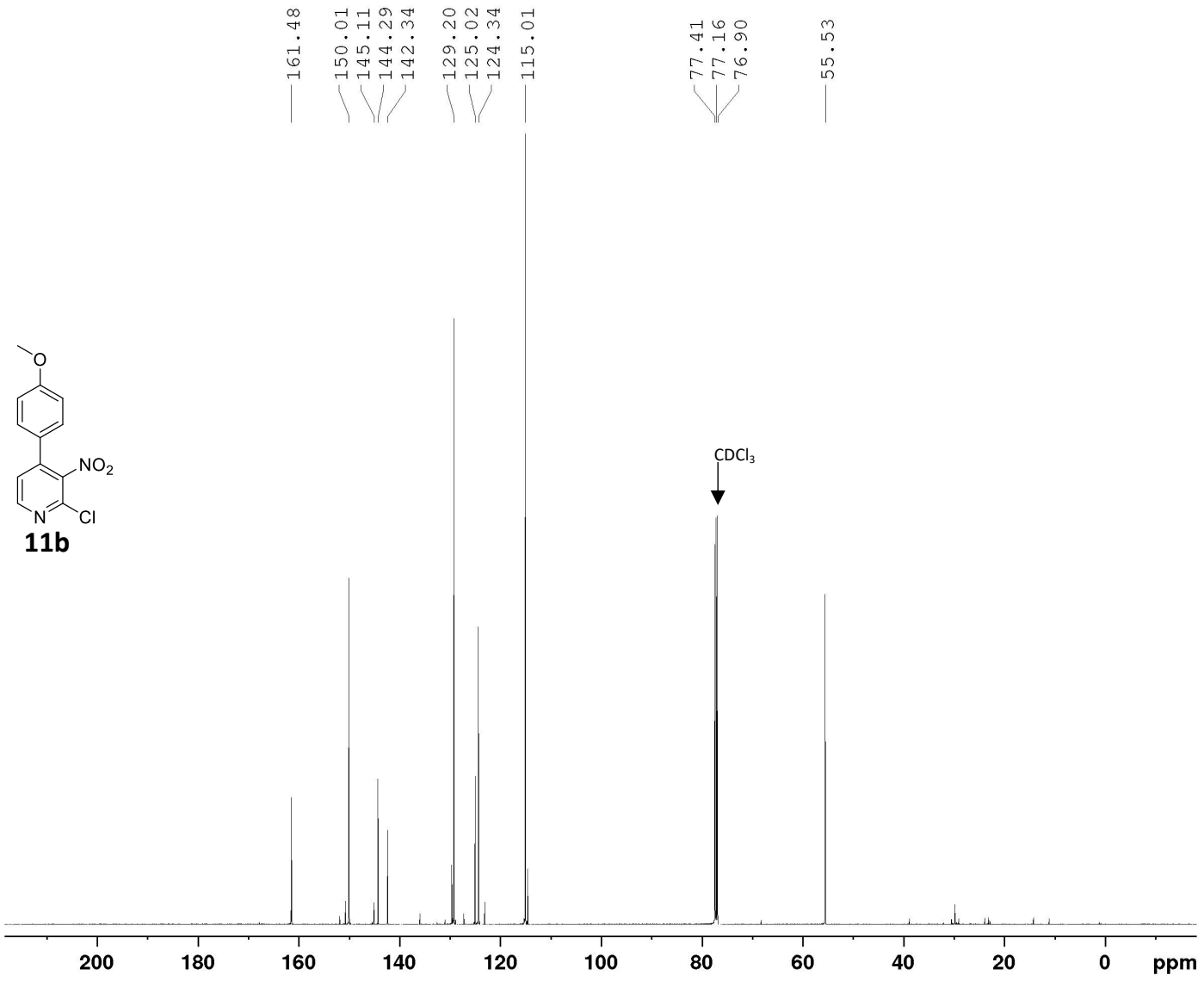
F2 - Processing parameters
SI                65536
SF           500.2300122 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```




```
Current Data Parameters
NAME         JPN-1-163-3
EXPNO                 16
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211119
Time                2.34 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10000.000 Hz
FIDRES            0.305176 Hz
AQ              3.2767999 sec
RG                 37.93
DW                50.000 usec
DE                16.00 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1          500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1          11.44699955 W

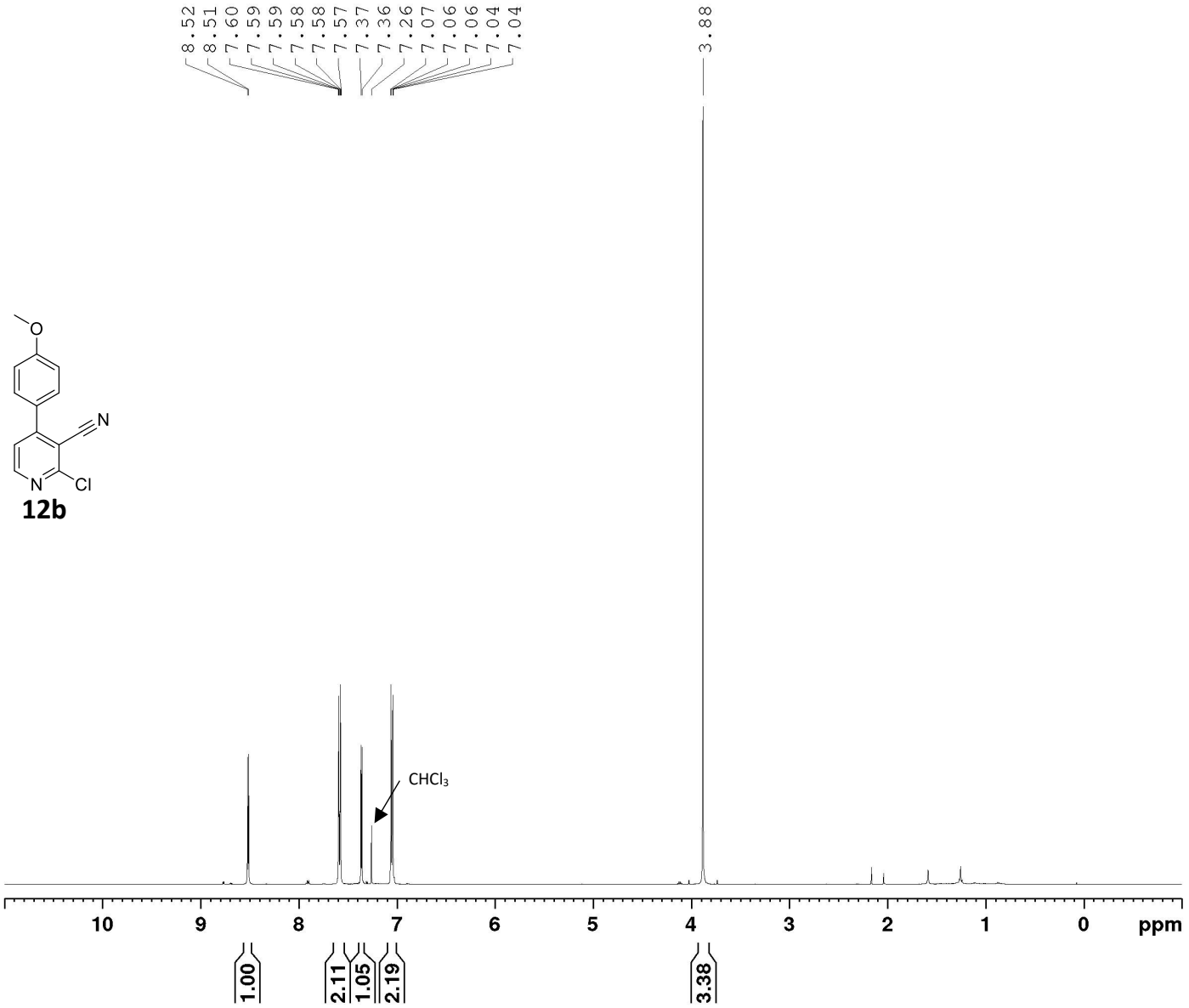
F2 - Processing parameters
SI                 65536
SF            500.2300119 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME         JPN-1-163-3
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211119
Time                3.30 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7955118 MHz
NUC1               13C
P0                 3.33 usec
P1                10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

F2 - Processing parameters
SI                32768
SF          125.7829219 MHz
WDW                EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

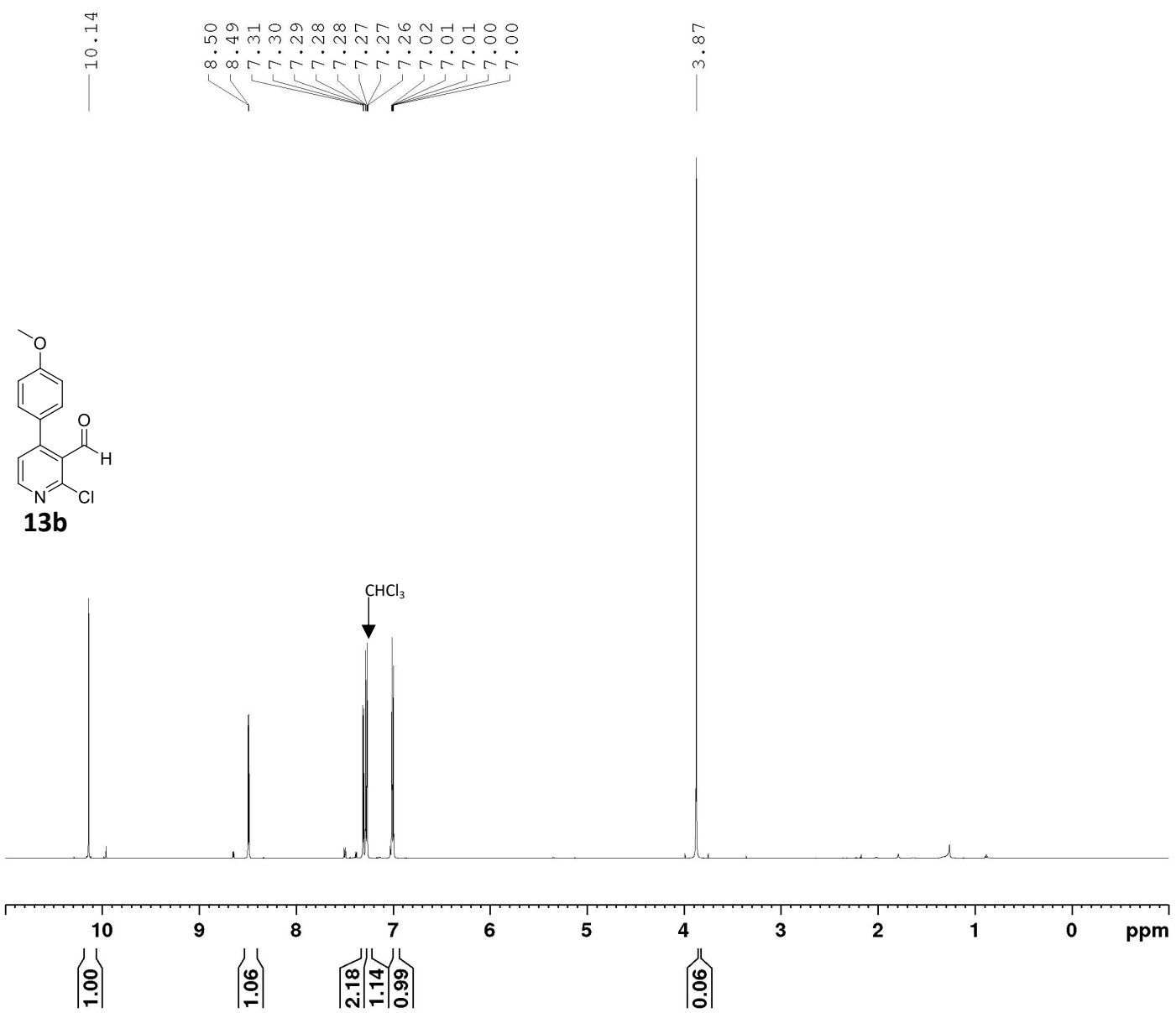


12b

```
Current Data Parameters
NAME      JPN-1-166-1_repeat_c4-mono
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200601
Time                9.25 h
INSTRUM            spect
PROBHD   Z119470_0370 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            10000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                137.36
DW                 50.000 usec
DE                  6.50 usec
TE                 300.0 K
D1             1.00000000 sec
TD0                    1
SFO1          500.2330889 MHz
NUC1                  1H
P0                  3.13 usec
P1                  9.38 usec
PLW1          20.00000000 W

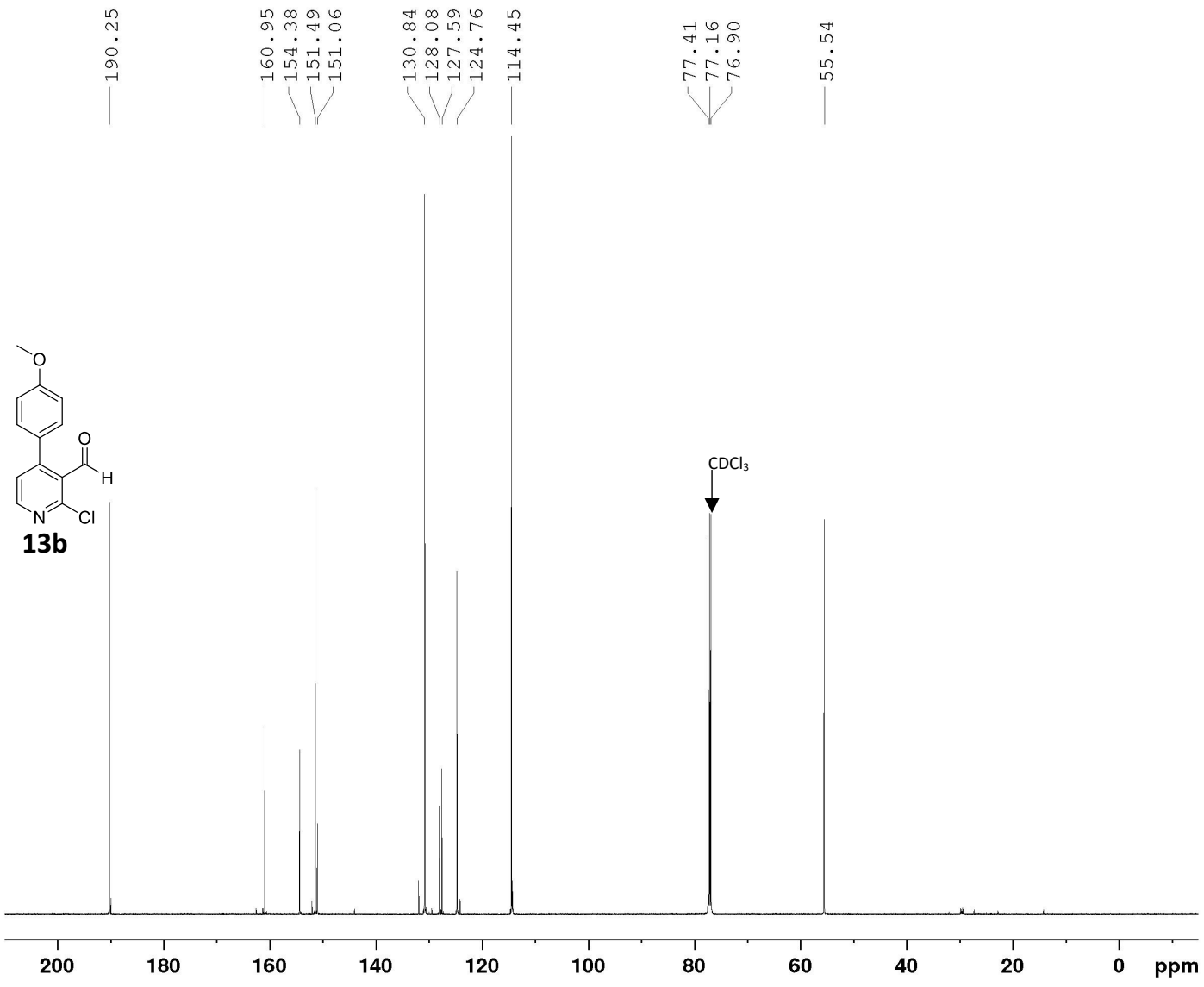
F2 - Processing parameters
SI                 32768
SF            500.2300128 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



Current Data Parameters
NAME JPN-1-167-1_C4-Mono
EXPNO 24
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200608
Time 20.22 h
INSTRUM spect
PROBHD Z127277_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 2.7262976 sec
RG 4.41
DW 41.600 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337060 MHz
NUC1 1H
P0 2.67 usec
P1 8.00 usec
PLW1 5.59999990 W

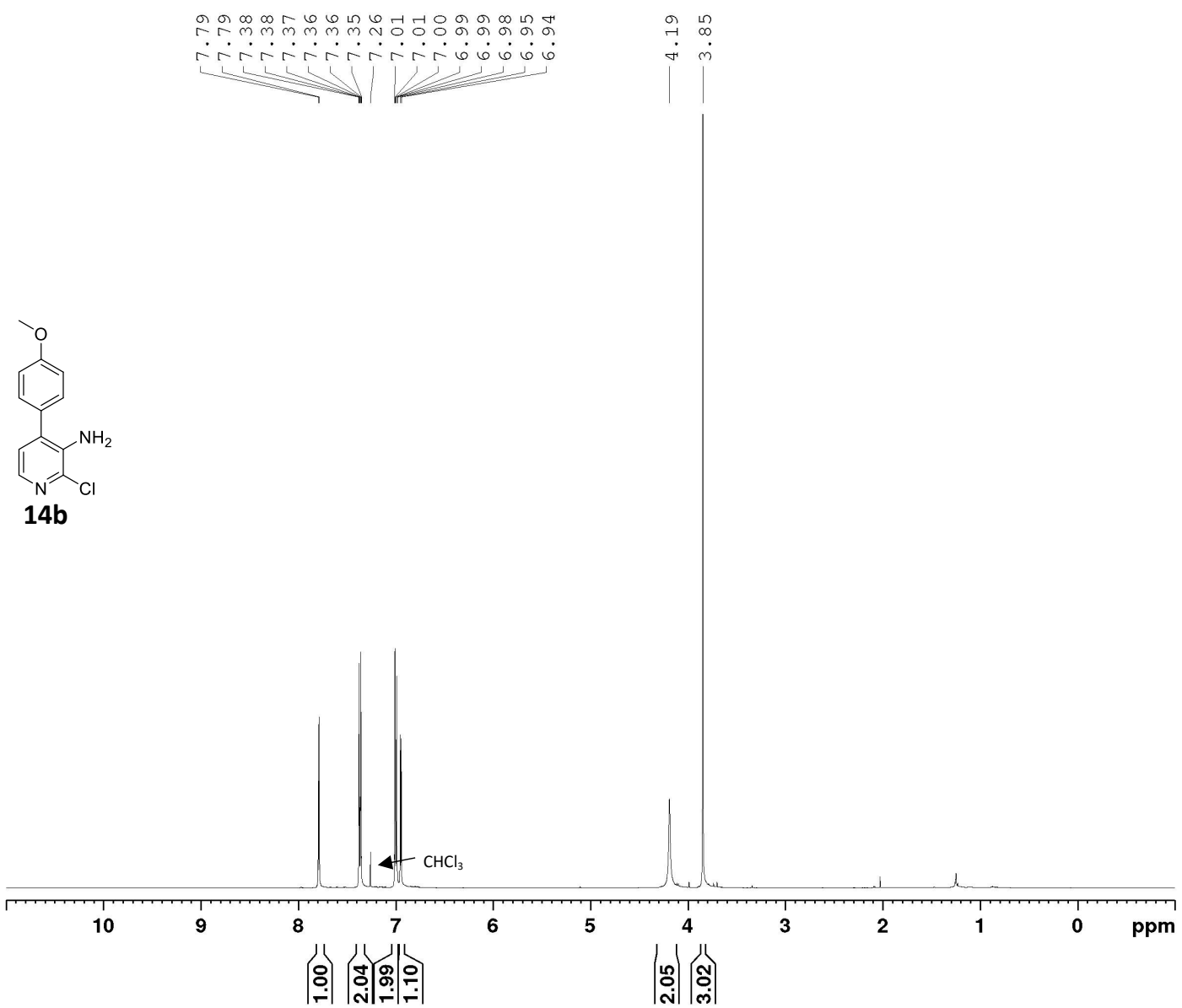
F2 - Processing parameters
SI 65536
SF 600.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00




```
Current Data Parameters
NAME      JPN-1-167-1_C4-Mono
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20200811
Time                  21.16 h
INSTRUM               spect
PROBHD    Z125869_0055 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               29761.904 Hz
FIDRES             0.908261 Hz
AQ                1.1010048 sec
RG                   190.44
DW                   16.800 usec
DE                   18.00 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1           125.7955118 MHz
NUC1                    13C
P0                    3.33 usec
P1                   10.00 usec
PLW1           56.90299988 W
SFO2           500.2320009 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           11.44699955 W
PLW12           0.25756001 W
PLW13           0.12955000 W

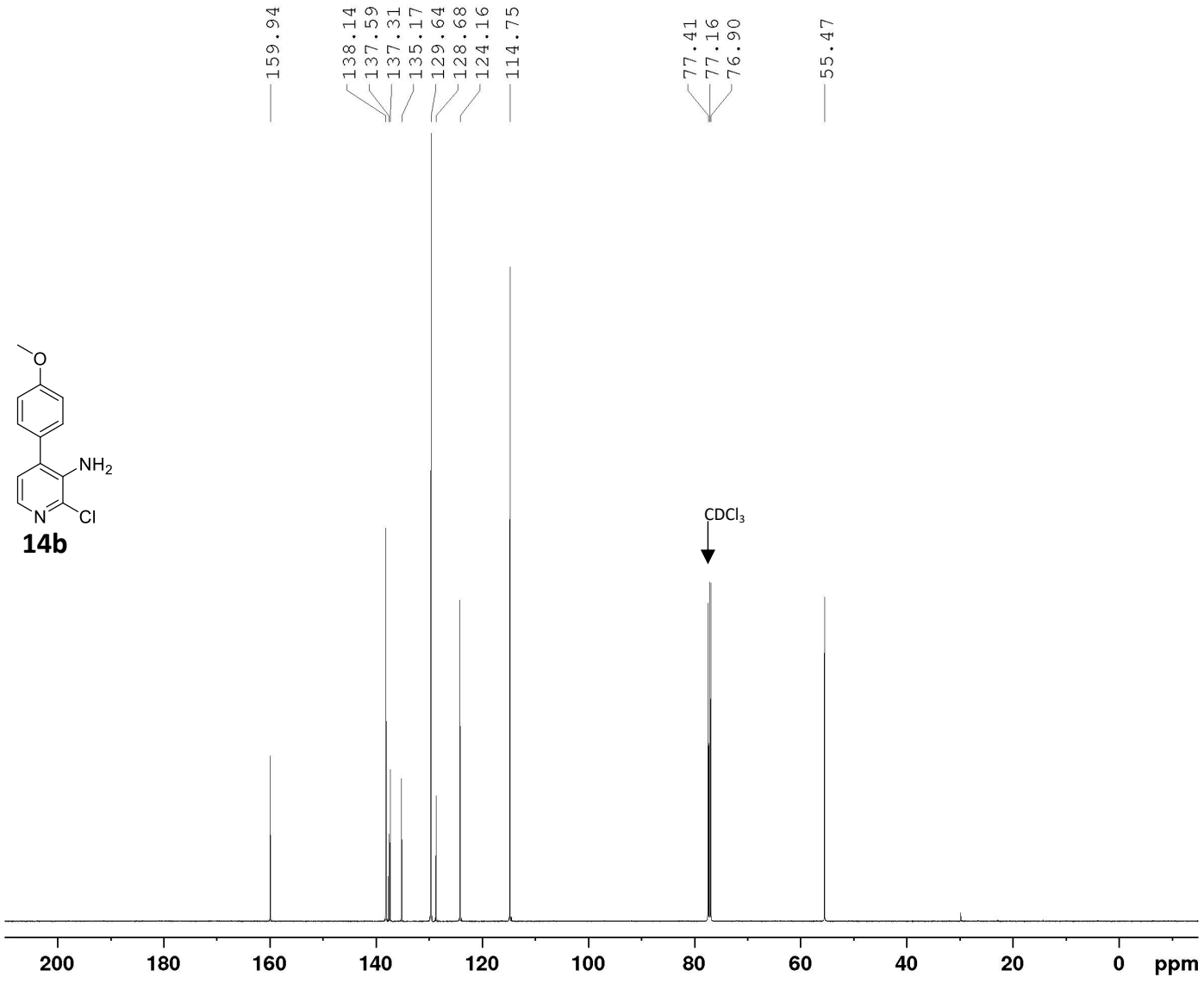
F2 - Processing parameters
SI                    32768
SF             125.7829218 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```




```
Current Data Parameters
NAME      JPN-2-17-1_C4-mono
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_            20200914
Time                10.52 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH             10000.000 Hz
FIDRES              0.305176 Hz
AQ                3.2767999 sec
RG                    30.54
DW                 50.000 usec
DE                 16.00 usec
TE                 300.0 K
D1              2.00000000 sec
TD0                     1
SFO1          500.2330889 MHz
NUC1                   1H
P0                 4.00 usec
P1                12.00 usec
PLW1          11.44699955 W

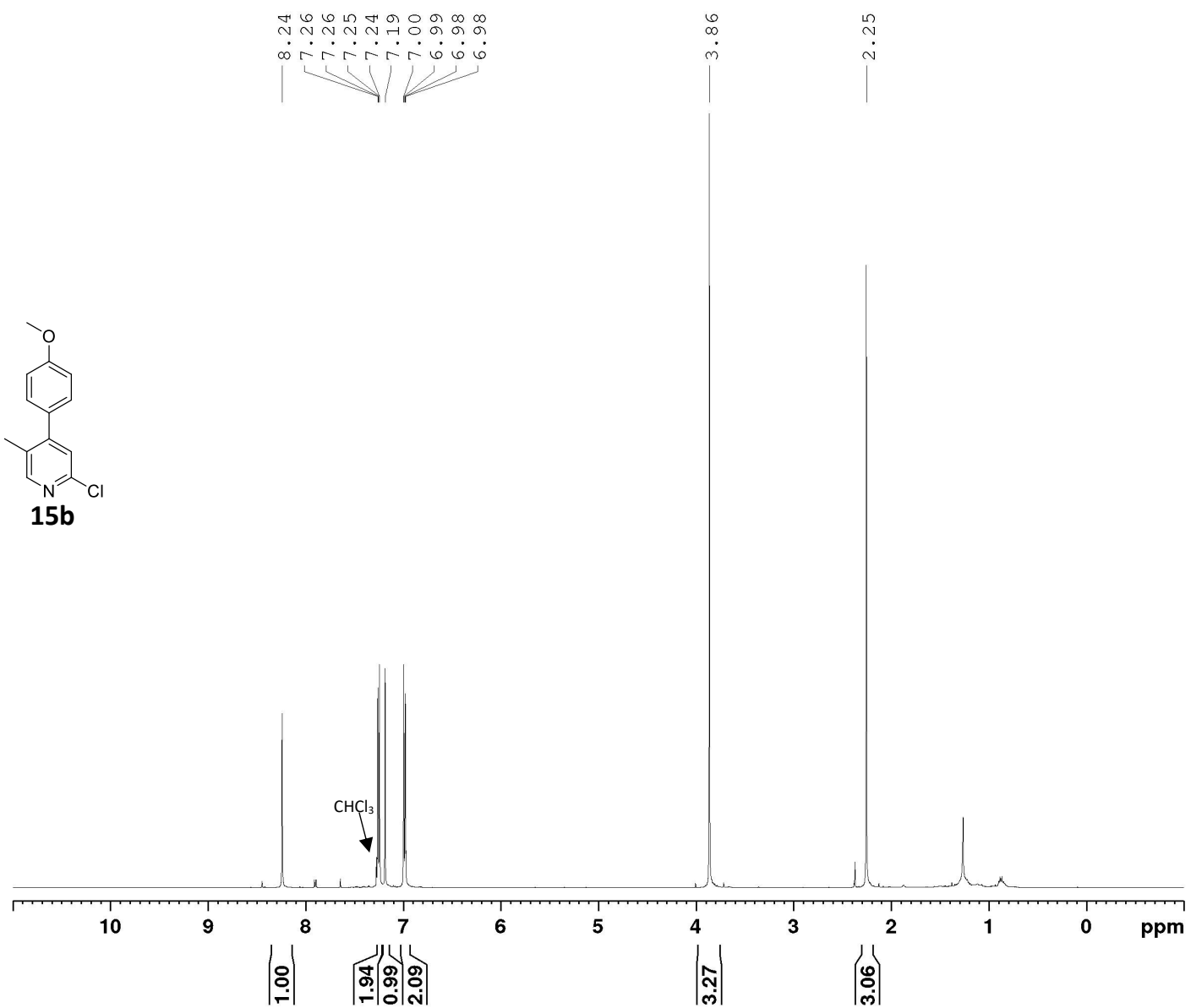
F2 - Processing parameters
SI                  65536
SF            500.2300120 MHz
WDW                    EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME          JPN-2-17-1
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211119
Time                9.19 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         125.7955118 MHz
NUC1                 13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

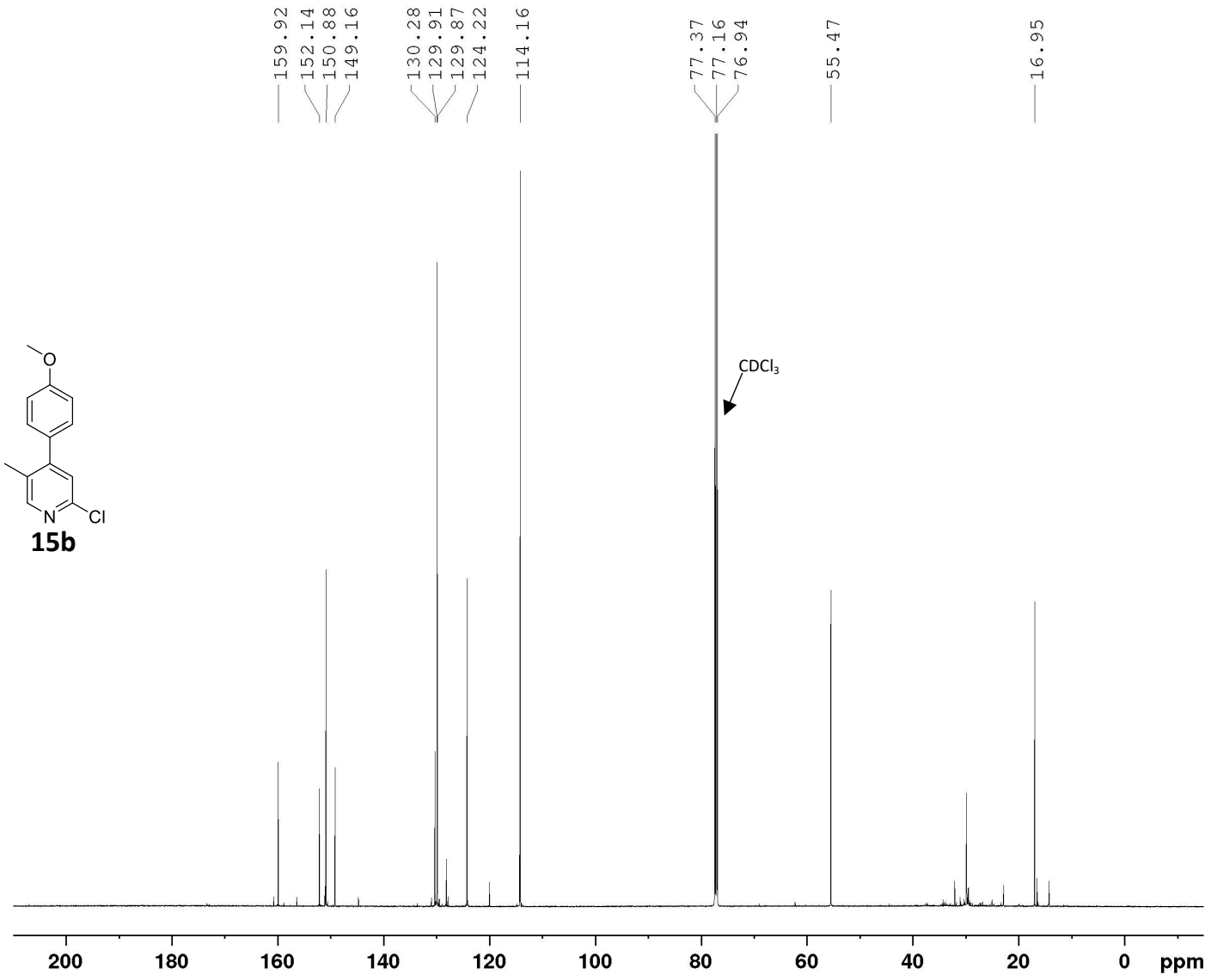
F2 - Processing parameters
SI                32768
SF           125.7829236 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```




```
Current Data Parameters
NAME      JPN-2-17-2_C4-mono
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_            20200914
Time                4.30 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                 25.21
DW                50.000 usec
DE                16.00 usec
TE                300.0 K
D1             2.00000000 sec
TD0                     1
SFO1          500.2330889 MHz
NUC1                   1H
P0                 4.00 usec
P1                12.00 usec
PLW1          11.44699955 W

F2 - Processing parameters
SI                  65536
SF            500.2300047 MHz
WDW                    EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

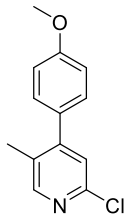



```
Current Data Parameters
NAME          JPN-2-17-2
EXPNO                 11
PROCNO                 1

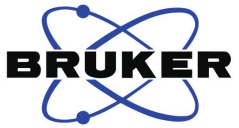
F2 - Acquisition Parameters
Date_           20200519
Time              16.32 h
INSTRUM             spect
PROBHD   Z127277_0002 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.9087659 sec
RG                184.4
DW               13.867 usec
DE                18.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        150.9178981 MHz
NUC1                13C
P0                 4.00 usec
P1                12.00 usec
PLW1        91.00000000 W
SFO2        600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2         5.59999990 W
PLW12        0.07314300 W
PLW13        0.03679000 W

F2 - Processing parameters
SI                32768
SF          150.9027914 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

HSQC



15b




```
Current Data Parameters
NAME        JPN-2-1-167-4
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20211103
Time                20.15 h
INSTRUM              spect
PROBHD    Z125869_0055 (
PULPROG          hsqcetgp
TD                   1024
SOLVENT              CDCl3
NS                      8
DS                     16
SWH              7002.801 Hz
FIDRES          13.677346 Hz
AQ               0.0731136 sec
RG                  190.44
DW                  71.400 usec
DE                  16.00 usec
TE                  298.0 K
CNST2          145.0000000
D0               0.00000300 sec
D1               1.50000000 sec
D4               0.00172414 sec
D11              0.03000000 sec
D16              0.00020000 sec
IN0              0.00001990 sec
TDav                    1
ZGOPTNS
SFO1           500.2330889 MHz
NUC1                   1H
P1                  12.00 usec
P2                  24.00 usec
PLW1           11.44699955 W
SFO2           125.7948829 MHz
NUC2                   13C
CPDPRG[2             garp
P3                  10.00 usec
P4                  20.00 usec
PCPD2               70.00 usec
PLW2           56.90299988 W
PLW12           1.16129994 W
GPNAM[1]       SMSQ10.100
GPZ1                80.00 %
GPNAM[2]       SMSQ10.100
GPZ2                20.10 %
P16               1000.00 usec

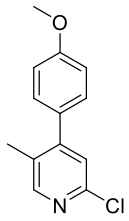
F1 - Acquisition parameters
TD                     256
SFO1            125.7949 MHz
FIDRES         196.293976 Hz
SW                199.735 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                    1024
SF             500.2300477 MHz
WDW                 QSINE
SSB                     2
LB                      0 Hz
GB                      0
PC                   1.40

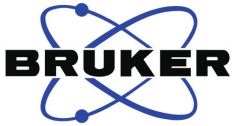
F1 - Processing parameters
SI                    1024
MC2         echo-antiecho
SF              125.7829335 MHz
WDW                 QSINE
SSB                     2
LB                      0 Hz
GB                      0
```

^{13}C at 130 ppm correlated to the *meta* C-H protons

HMBC



15b




```
Current Data Parameters
NAME       JPN-2-1-167-4
EXPNO                 11
PROCNO                 1

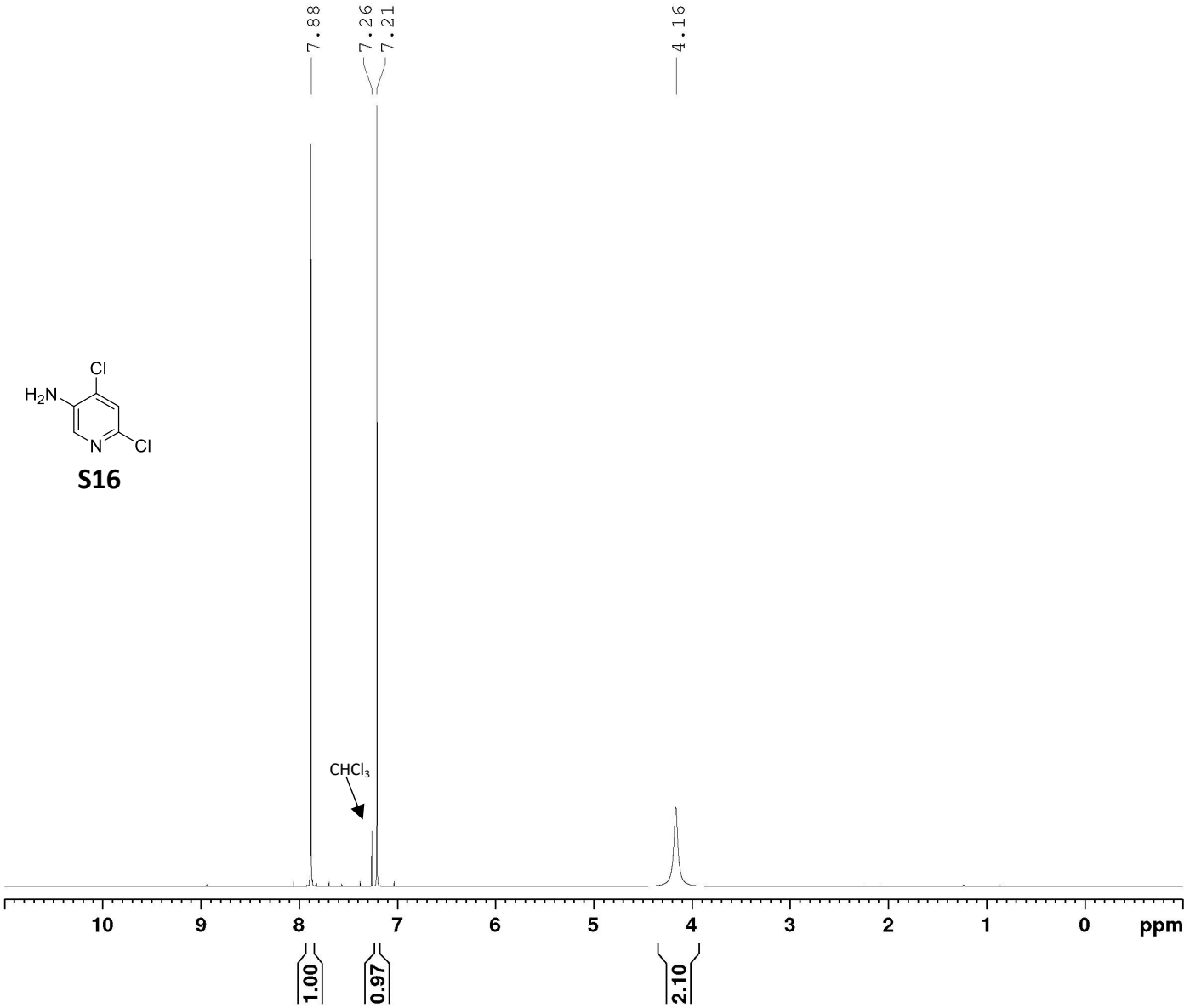
F2 - Acquisition Parameters
Date_           20211103
Time              19.20 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG     hmbcgplpndqf
TD                  4096
SOLVENT             CDCl3
NS                     4
DS                    16
SWH             4587.156 Hz
FIDRES          2.239822 Hz
AQ              0.4464640 sec
RG                190.44
DW                109.000 usec
DE                 16.00 usec
TE                298.0 K
CNST2         145.0000000
CNST13         10.0000000
D0             0.00000300 sec
D1             1.50000000 sec
D2             0.00344828 sec
D6             0.05000000 sec
D16            0.00020000 sec
IN0            0.00001810 sec
TDav                   1
SFO1          500.2323359 MHz
NUC1                  1H
P1                 12.00 usec
P2                 24.00 usec
PLW1          11.44699955 W
SFO2          125.7955118 MHz
NUC2                 13C
P3                 10.00 usec
PLW2          56.90299988 W
GPNAM[1]       SMSQ10.100
GPZ1               50.00 %
GPNAM[2]       SMSQ10.100
GPZ2               30.00 %
GPNAM[3]       SMSQ10.100
GPZ3               40.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1           125.7955 MHz
FIDRES        431.629822 Hz
SW               219.597 ppm
FnMODE                QF

F2 - Processing parameters
SI                   4096
SF            500.2300475 MHz
WDW                 QSINE
SSB                     0
LB                      0 Hz
GB                      0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2                    QF
SF            125.7829335 MHz
WDW                 QSINE
SSB                     0
LB                      0 Hz
GB                      0
```

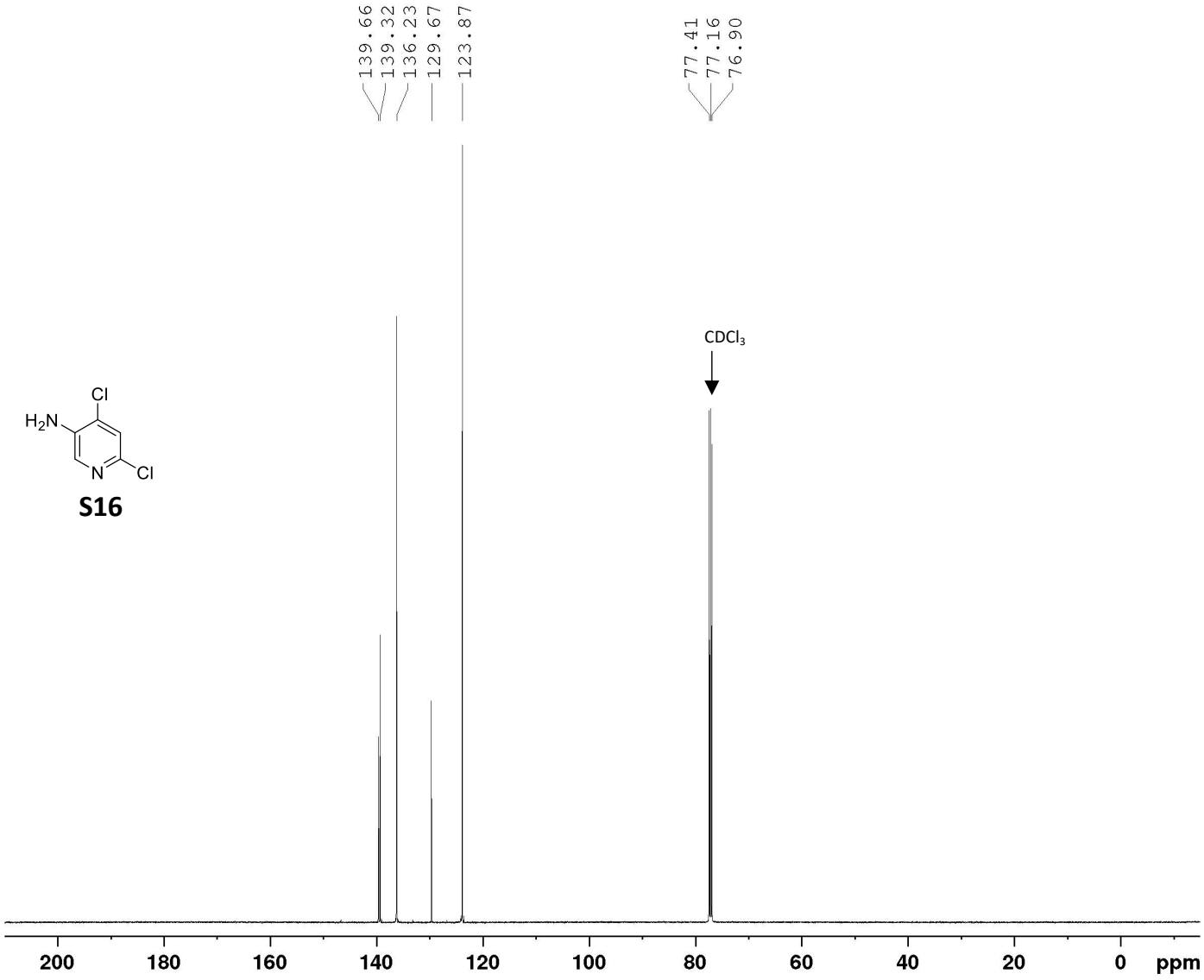
Meta C-H protons correlate to methyl on the C5 carbon




```
Current Data Parameters
NAME      JPN-2-54_(5-amino-2,4-DCP)
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211127
Time              18.56 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ             3.2767999 sec
RG                  47.3
DW                50.000 usec
DE                16.00 usec
TE                298.0 K
D1           2.00000000 sec
TD0                     1
SFO1         500.2330889 MHz
NUC1                   1H
P0                 4.00 usec
P1                12.00 usec
PLW1         11.44699955 W

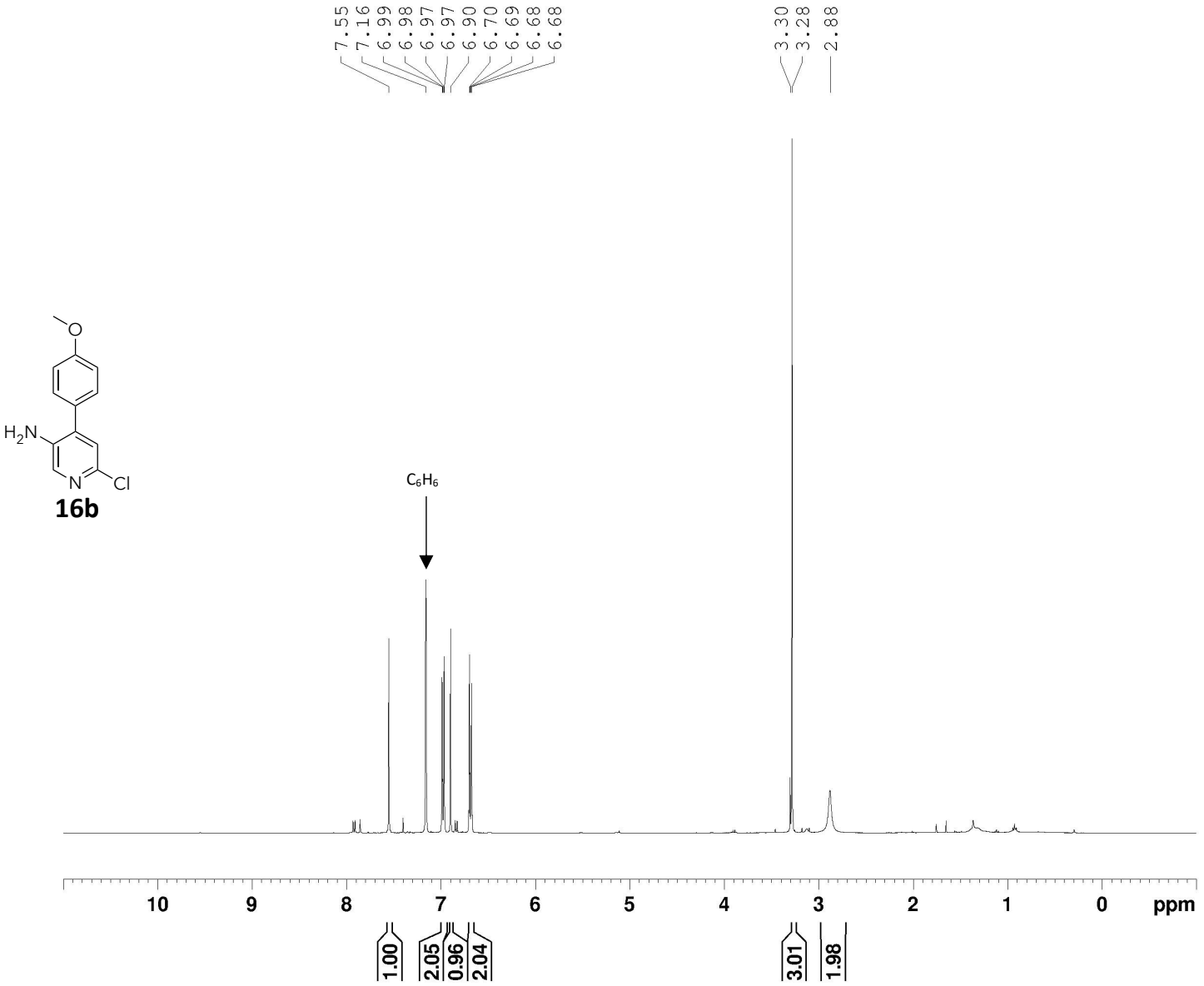
F2 - Processing parameters
SI                  65536
SF           500.2300120 MHz
WDW                    EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME      JPN-2-54_(5-amino-2,4-DCP)
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211127
Time              19.52 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.44
DW               16.800 usec
DE               18.00 usec
TE               298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7955118 MHz
NUC1                13C
P0                3.33 usec
P1               10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

F2 - Processing parameters
SI                32768
SF          125.7829244 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

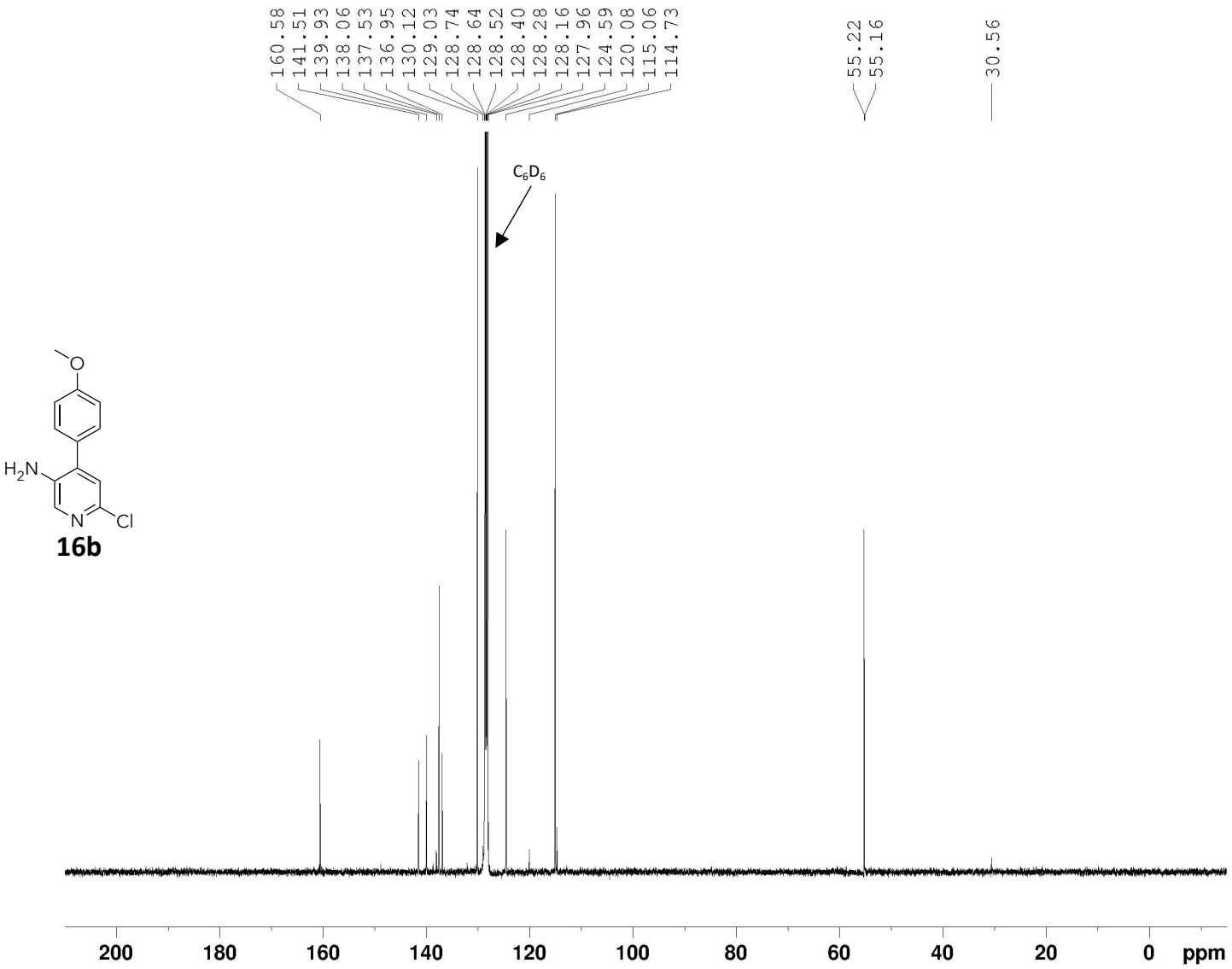


16b

Current Data Parameters
NAME NL-1-94-1Hx2
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210807
Time 12.32 h
INSTRUM Avance Neo
PROBHD Z152088_0031 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 16
DS 2
SWH 8196.722 Hz
FIDRES 0.250144 Hz
AQ 3.9976959 sec
RG 101
DW 61.000 usec
DE 13.89 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P0 2.67 usec
P1 8.00 usec
PLW1 24.03499985 W

F2 - Processing parameters
SI 65536
SF 400.1299967 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



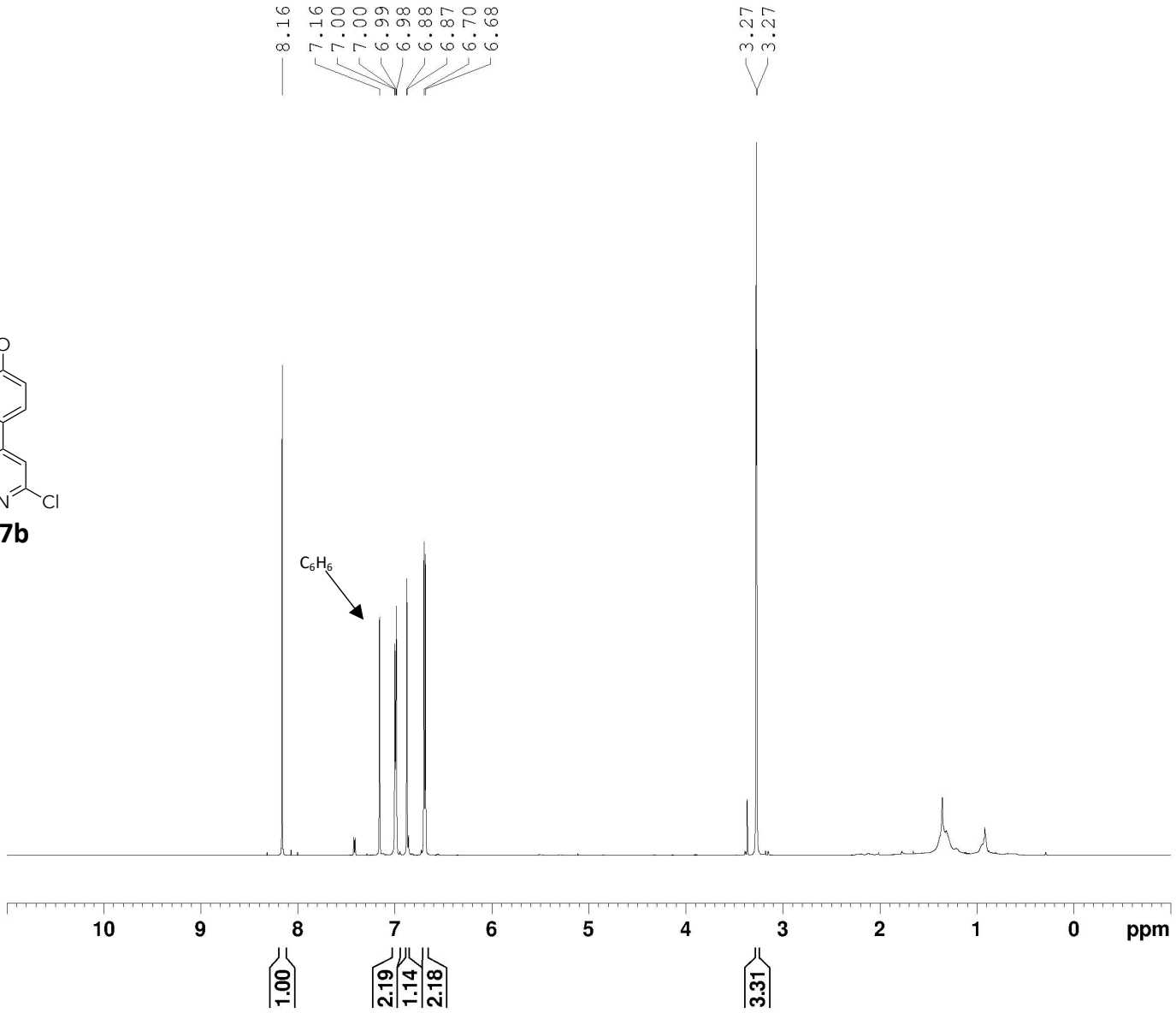
BRUKER

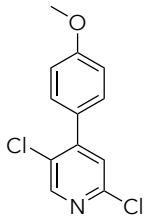
```
Current Data Parameters
NAME          NL-1-94-1Hx2
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_              20210807
Time                 19.40 h
INSTRUM         Avance Neo
PROBHD     Z152088_0031 (
PULPROG             zgpg30
TD                   65536
SOLVENT              C6D6
NS                   1024
DS                      4
SWH             23809.523 Hz
FIDRES           0.726609 Hz
AQ               1.3762560 sec
RG                   8.125
DW                  21.000 usec
DE                   6.50 usec
TE                  298.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                     1
SFO1           100.6228298 MHz
NUC1                  13C
P0                   2.67 usec
P1                   8.00 usec
PLW1           86.55400085 W
SFO2           400.1316005 MHz
NUC2                  1H
CPDPRG[2           waltz65
PCPD2                90.00 usec
PLW2           24.03499985 W
PLW12           0.18990999 W
PLW13           0.09552100 W

F2 - Processing parameters
SI                   32768
SF             100.6126977 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

proton 300k c6d6





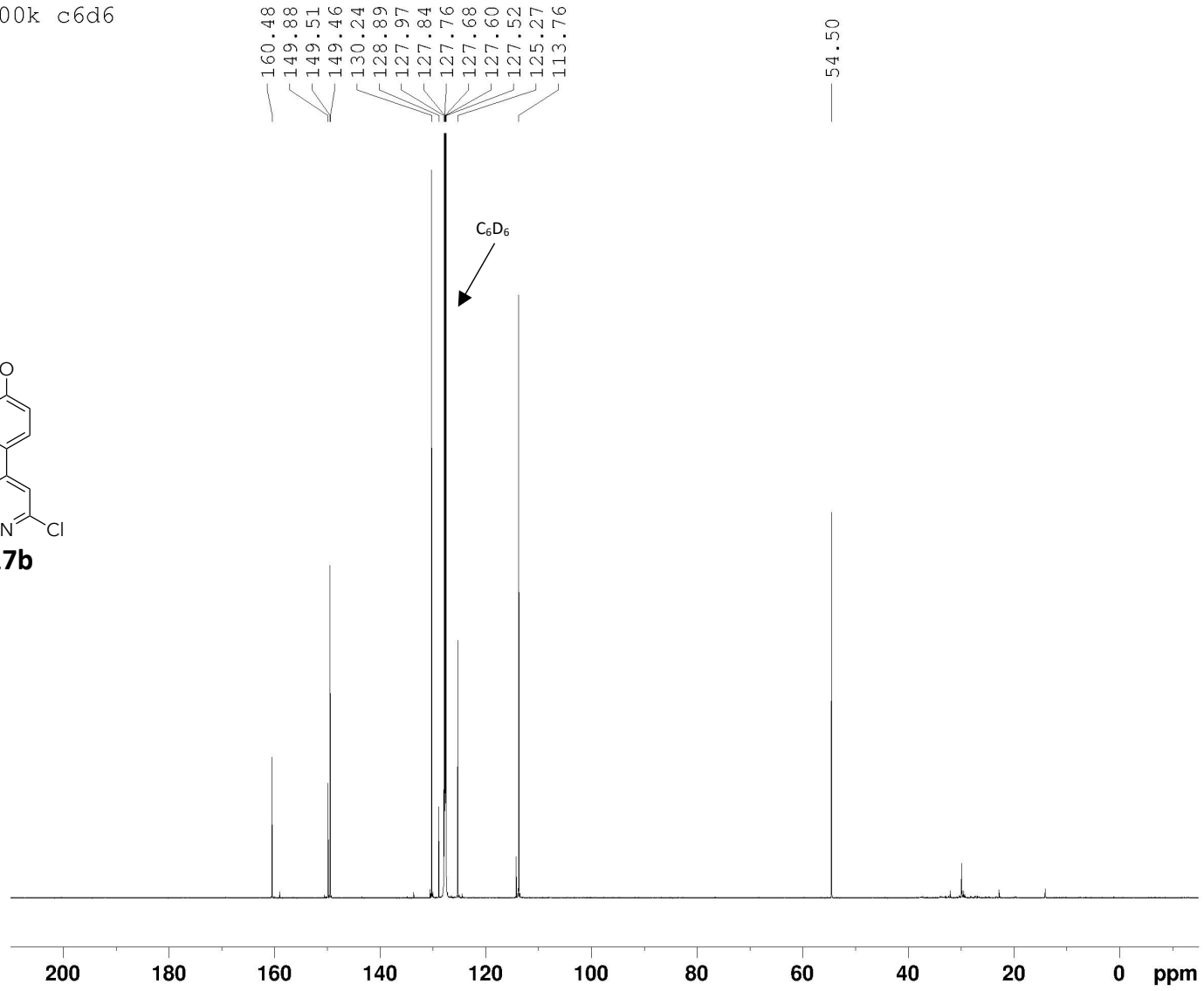
17b

Current Data Parameters
NAME NL-1-93-1n-inadequate-08-27-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210827
Time 12.31 h
INSTRUM spect
PROBHD Z127277_0002 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 2.7262976 sec
RG 6.41
DW 41.600 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337060 MHz
NUC1 1H
P0 2.67 usec
P1 8.00 usec
PLW1 5.59999990 W

F2 - Processing parameters
SI 65536
SF 600.1299970 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

300k c6d6

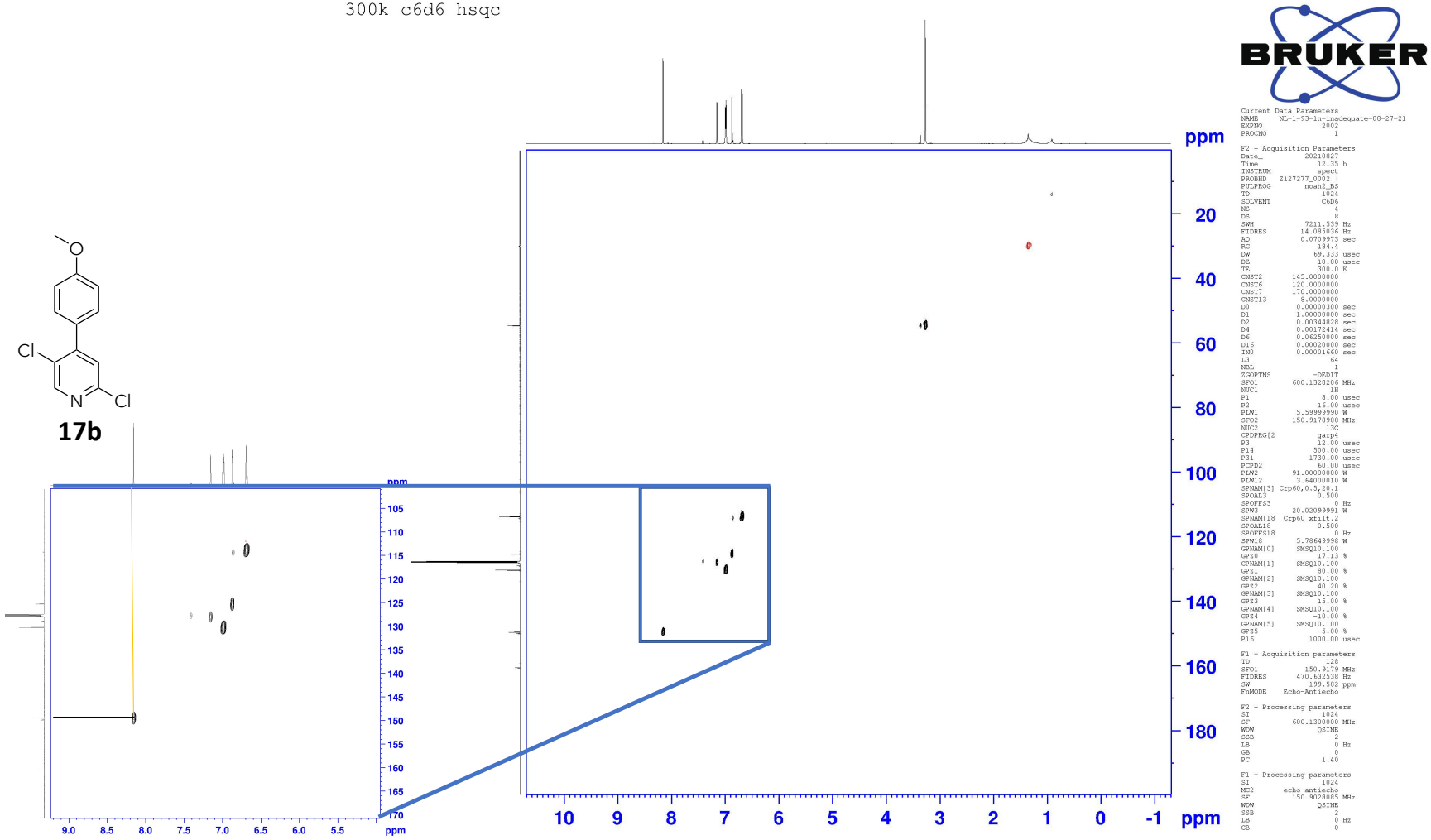


Current Data Parameters
NAME NL-1-93-1n-inadequate-08-27-2
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210830
Time 9.42 h
INSTRUM spect
PROBHD Z127277_0002 (
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 1024
DS 4
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.9087659 sec
RG 184.4
DW 13.867 usec
DE 18.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9178981 MHz
NUC1 13C
P0 4.00 usec
P1 12.00 usec
PLW1 91.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 5.59999990 W
PLW12 0.07314300 W
PLW13 0.03679000 W

F2 - Processing parameters
SI 32768
SF 150.9028090 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

300k c6d6 hsqc



BRUKER

```
Current Data Parameters
NAME      NL-1-93-1n-inadequate-08-27-21
EXPNO              2002
PROCNO                1

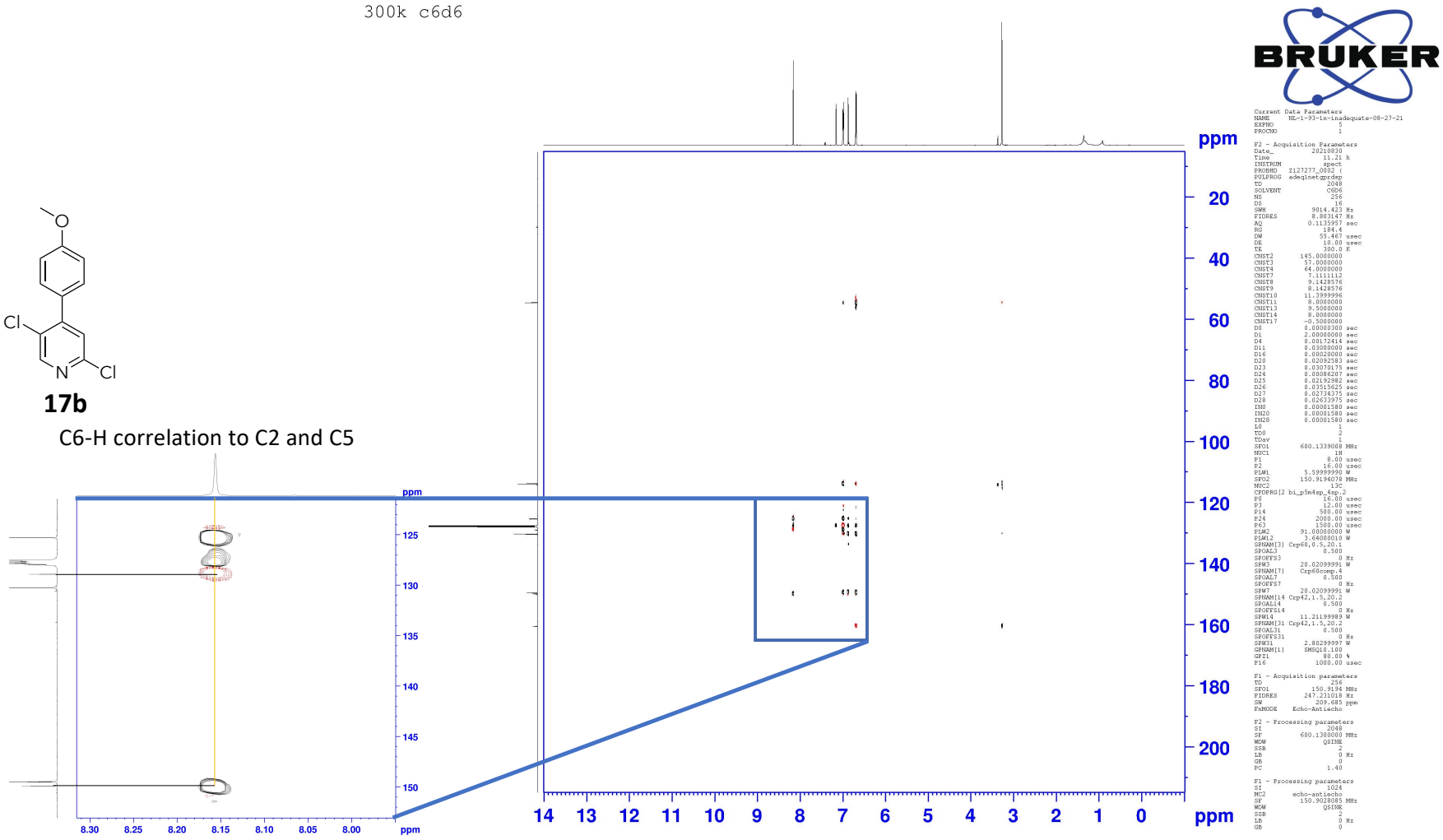
F2 - Acquisition Parameters
Date_          20210827
Time              12.35 h
INSTRUM             spect
PROBHD   2127277_0002 1
PULPROG         noah2_BS
TD                 1024
SOLVENT            C6D6
NS                    4
DS                    8
SWH            7211.539 Hz
FIDRES        14.085036 Hz
AQ             0.0709973 sec
RG                184.4
DW               69.333 usec
DE               10.00 usec
TE               300.0 K
CNST2         145.0000000
CNST6         120.0000000
CNST7         170.0000000
CNST13          8.0000000
D0             0.00000300 sec
D1             1.00000000 sec
D2             0.00344828 sec
D4             0.00172414 sec
D6             0.06250000 sec
D16            0.00020000 sec
IN0            0.00001660 sec
L3                   64
NBL                   1
ZGOPTNS             -DEDIT
SFO1          600.1328206 MHz
NUC1                  1H
P1                 8.00 usec
P2                16.00 usec
PLW1           5.59999990 W
SFO2          150.9178988 MHz
NUC2                 13C
CPDPRG[2            garp4
P3                12.00 usec
P14              500.00 usec
P31             1730.00 usec
PCPD2             60.00 usec
PLW2          91.00000000 W
PLW12          3.64000010 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3             0.500
SPOFFS3                0 Hz
SPW3          20.02099991 W
SPNAM[18  Crp60_xfilt_2
SPOAL18            0.500
SPOFFS18               0 Hz
SPW18          5.78649998 W
GPNAM[0]      SMSQ10.100
GPZ0              17.13 %
GPNAM[1]      SMSQ10.100
GPZ1              80.00 %
GPNAM[2]      SMSQ10.100
GPZ2              40.20 %
GPNAM[3]      SMSQ10.100
GPZ3              15.00 %
GPNAM[4]      SMSQ10.100
GPZ4             -10.00 %
GPNAM[5]      SMSQ10.100
GPZ5              -5.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  128
SFO1          150.9179 MHz
FIDRES        470.632538 Hz
SW            199.582 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                 1024
SF            600.1300000 MHz
WDW                QSINE
SSB                   2
LB                    0 Hz
GB                    0
PC                 1.40

F1 - Processing parameters
SI                 1024
MC2         echo-antiecho
SF            150.9028085 MHz
WDW                QSINE
SSB                   2
LB                    0 Hz
GB                    0
```

1,1 ADEQUATE



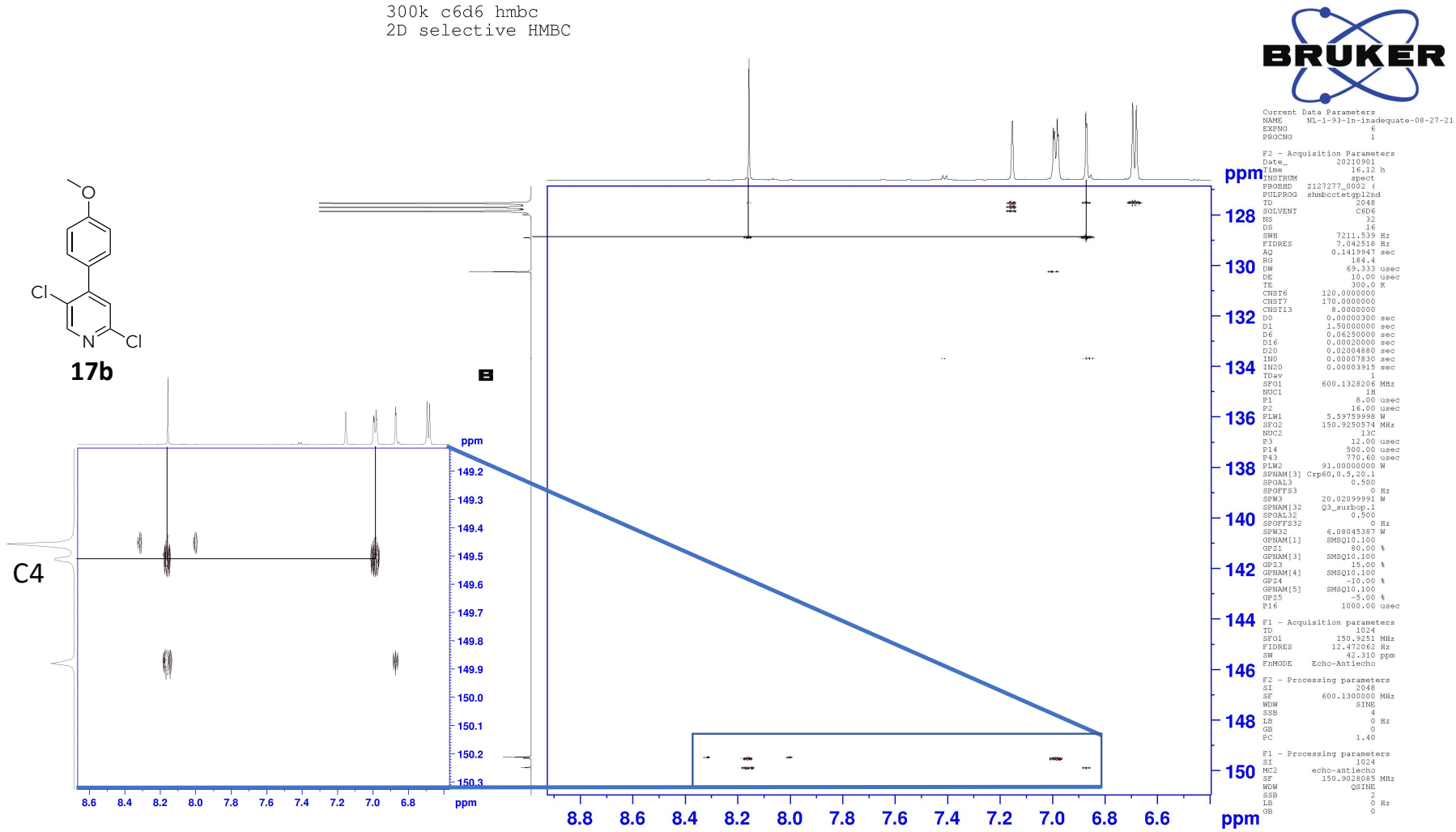
Current Data Parameters
NAME NL-1-93-1n-1nadequate-08-27-21
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210830
Time 11.21 h
INSTRUM spect
PROBHD Z127277_0002 (
PULPROG adeq1net.prdap
TD 2048
SOLVENT C6D6
NS 256
DS 16
SWH 9014.423 Hz
FIDRES 8.803147 Hz
AQ 0.1135957 sec
RG 184.4
DW 55.467 usec
DE 10.00 usec
TE 300.0 K
CNST2 145.0000000
CNST3 57.0000000
CNST4 64.0000000
CNST7 7.1111112
CNST8 9.1428576
CNST9 8.1428576
CNST10 11.3999996
CNST11 8.0000000
CNST13 9.5000000
CNST14 8.0000000
CNST17 -0.5000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00020000 sec
D20 0.02092583 sec
D23 0.03070175 sec
D24 0.00086207 sec
D25 0.02192982 sec
D26 0.03515625 sec
D27 0.02734375 sec
D28 0.02633975 sec
IN0 0.00001580 sec
IN20 0.00001580 sec
IN28 0.00001580 sec
L0 1
TD0 2
TDav 1
SFO1 600.1339008 MHz
NUC1 1H
P1 8.00 usec
P2 16.00 usec
PLW1 5.59999990 W
SFO2 150.9194078 MHz
NUC2 13C
CPDPRG[2 bi_p5m4sp_4sp.2
P0 16.00 usec
P3 12.00 usec
P14 500.00 usec
P24 2000.00 usec
P63 1500.00 usec
PLW2 91.00000000 W
PLW12 3.64000010 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3 0.500
SPOFFS3 0 Hz
SPW3 20.02099991 W
SPNAM[7] Crp60comp.4
SPOAL7 0.500
SPOFFS7 0 Hz
SPW7 20.02099991 W
SPNAM[14 Crp42,1.5,20.2
SPOAL14 0.500
SPOFFS14 0 Hz
SPW14 11.21199989 W
SPNAM[31 Crp42,1.5,20.2
SPOAL31 0.500
SPOFFS31 0 Hz
SPW31 2.80299997 W
GPNAM[1] SMSQ10.100
GPZ1 80.00 %
P16 1000.00 usec

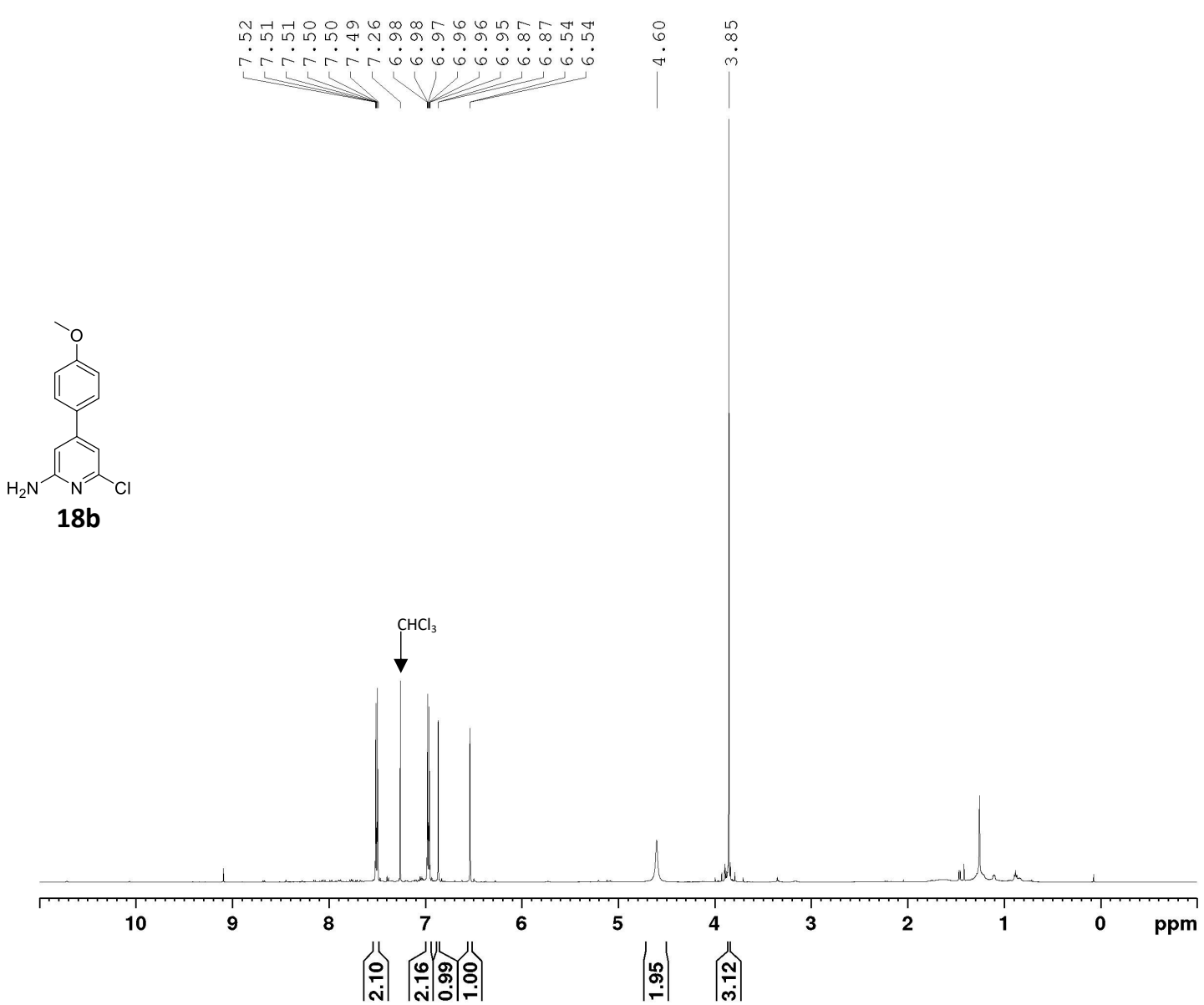
F1 - Acquisition parameters
TD 256
SFO1 150.9194 MHz
FIDRES 247.231018 Hz
SW 209.685 ppm
FnMODE Echo-Antiecho

F2 - Processing parameters
SI 2048
SF 600.1300000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 echo-antiecho
SF 150.9028085 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0



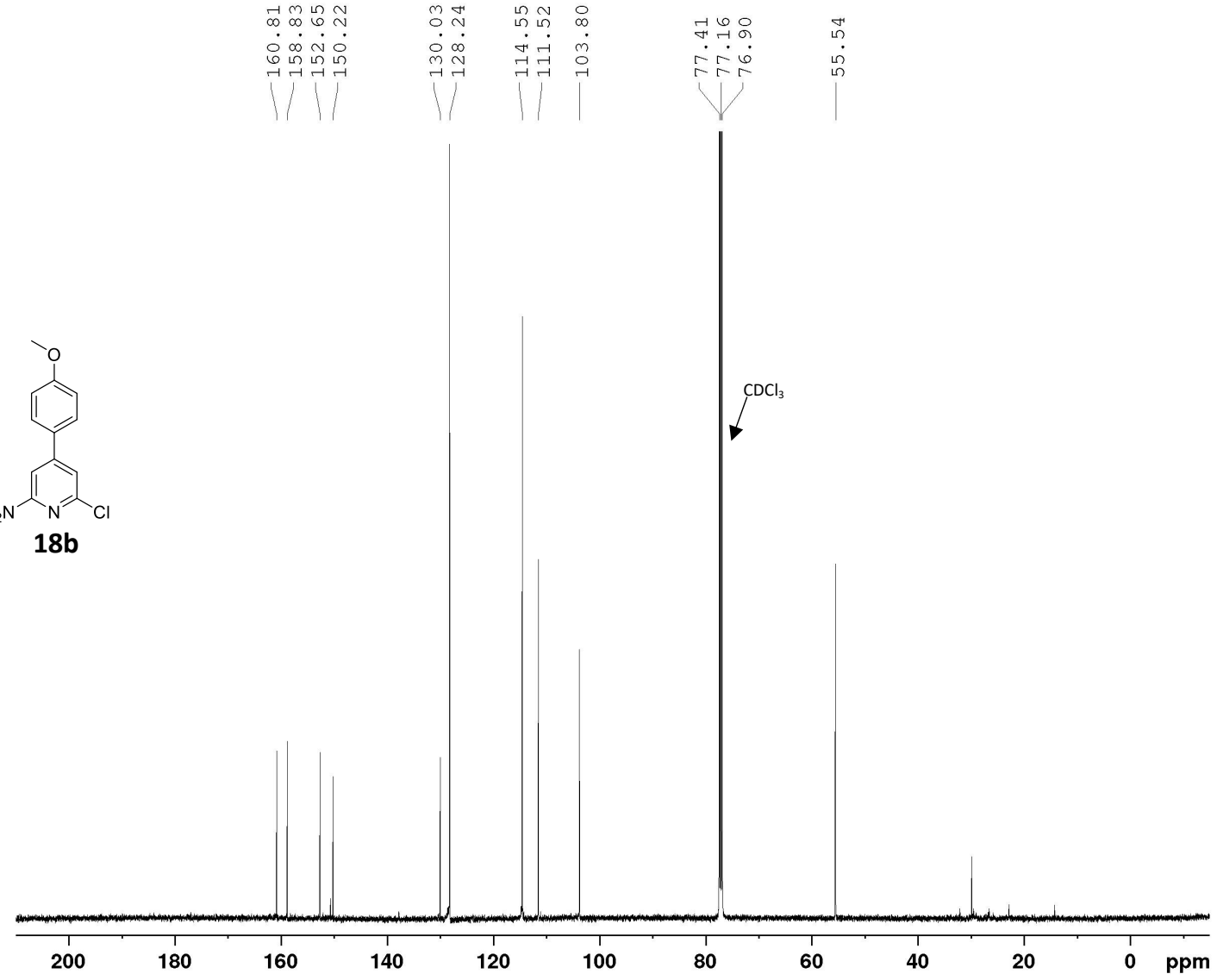
C4 reasoned by process of elimination, HMBC correlations, and chemical shift. Optimized 3-bond correlations. C(129ppm) weak correlation to C6-H, and a strong correlation to C3-H results in identification as C5. Absence of correlation from C(149.5) to C3-H and strong correlation to C6-H results in identification of C4.



Current Data Parameters
NAME JPN-2-16-2
EXPNO 16
PROCNO 1

F2 - Acquisition Parameters
Date_ 20211120
Time 1.49 h
INSTRUM spect
PROBHD Z125869_0055 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 151.18
DW 50.000 usec
DE 16.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.2330889 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 11.44699955 W

F2 - Processing parameters
SI 65536
SF 500.2300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

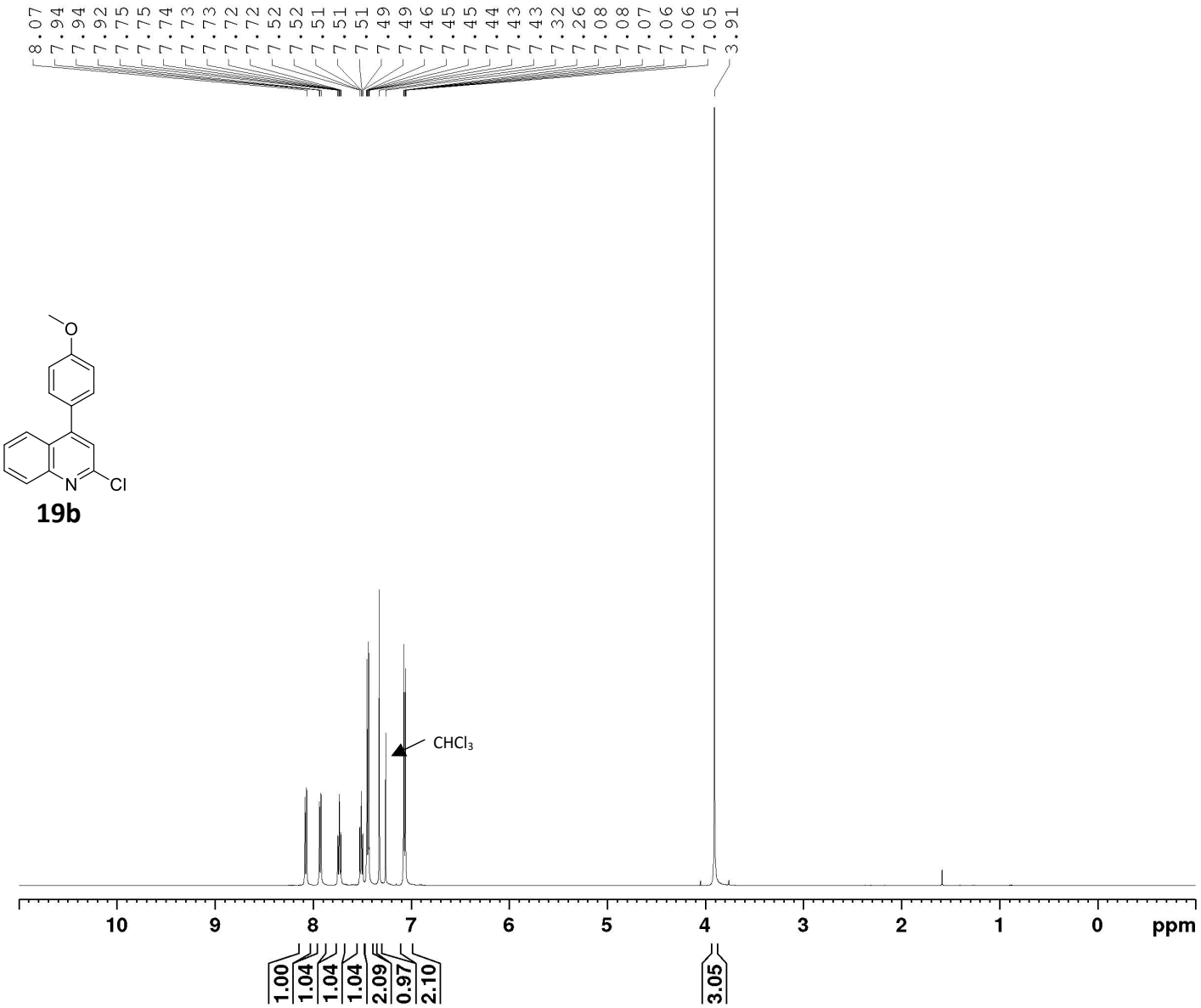


18b

```
Current Data Parameters
NAME          JPN-2-16-2
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211120
Time                2.45 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ              1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1         125.7955118 MHz
NUC1                 13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

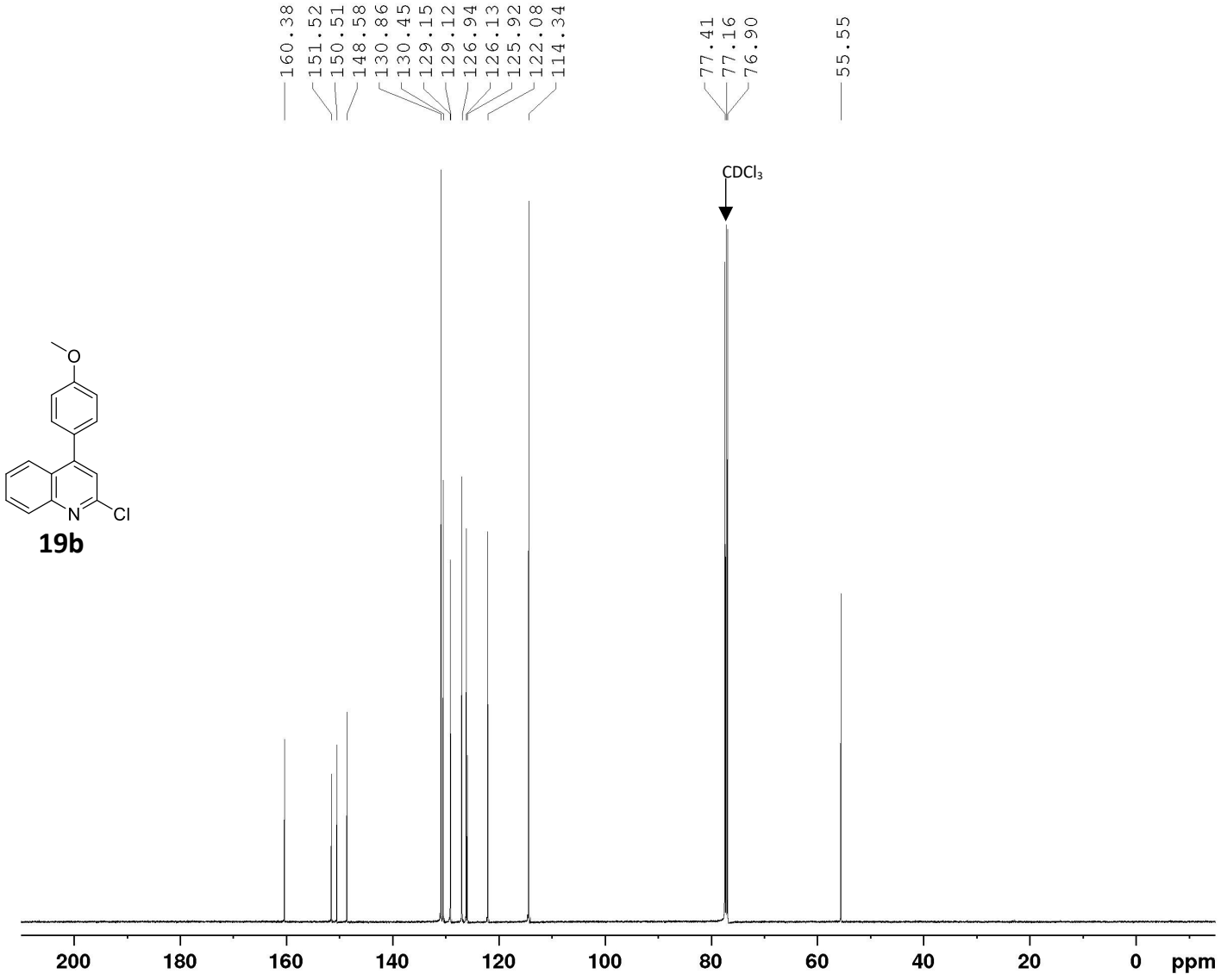
F2 - Processing parameters
SI                 32768
SF           125.7829170 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```




```
Current Data Parameters
NAME      JPN-2-8_repeat_C4-mono_crop
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201130
Time              17.10 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10000.000 Hz
FIDRES            0.305176 Hz
AQ                3.2767999 sec
RG                  122.05
DW                 50.000 usec
DE                 16.00 usec
TE                 300.0 K
D1             2.00000000 sec
TD0                    1
SFO1          500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                 12.00 usec
PLW1          11.44699955 W

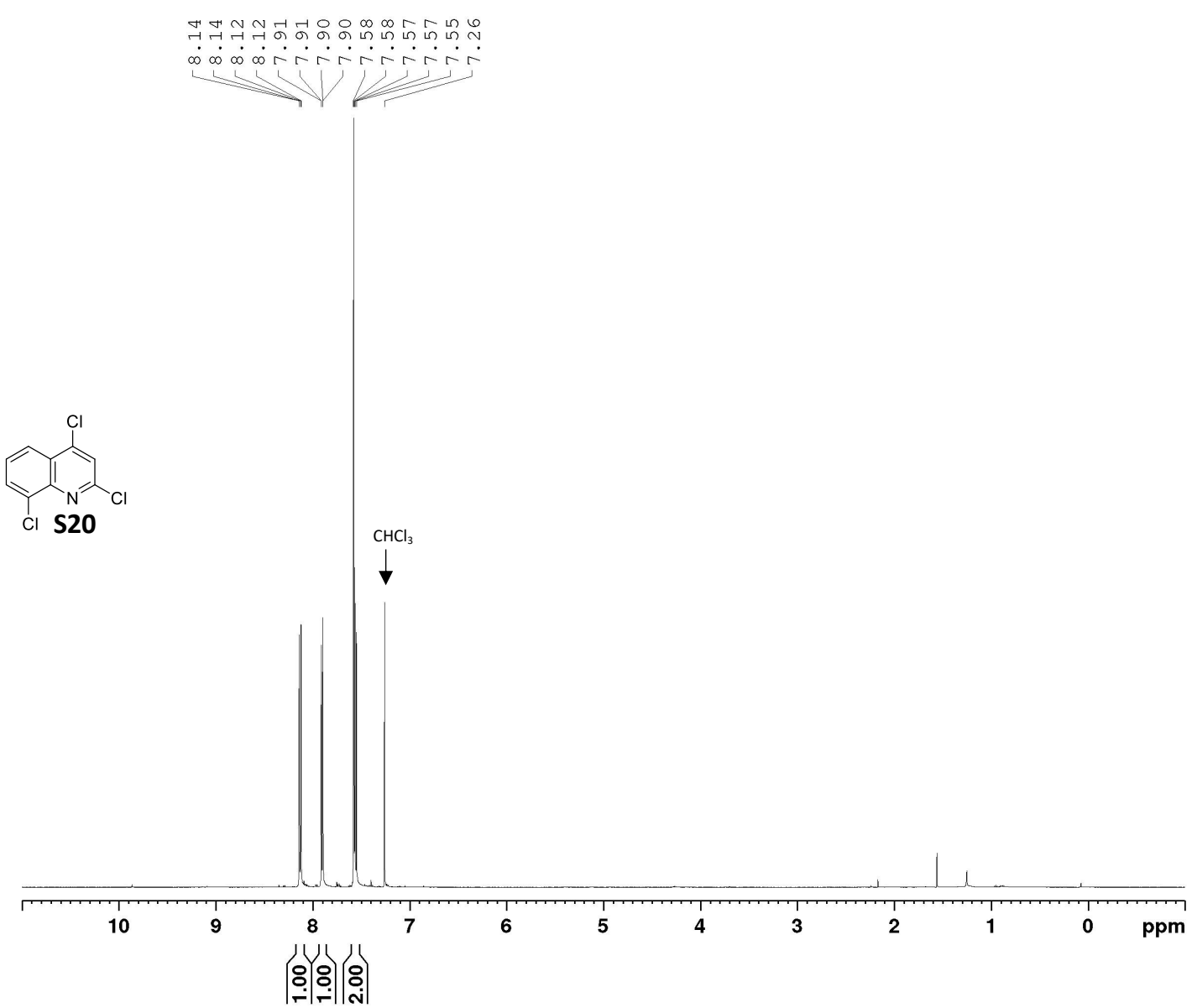
F2 - Processing parameters
SI                 65536
SF            500.2300120 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME      JPN-2-8_repeat
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211119
Time               6.24 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         125.7955118 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

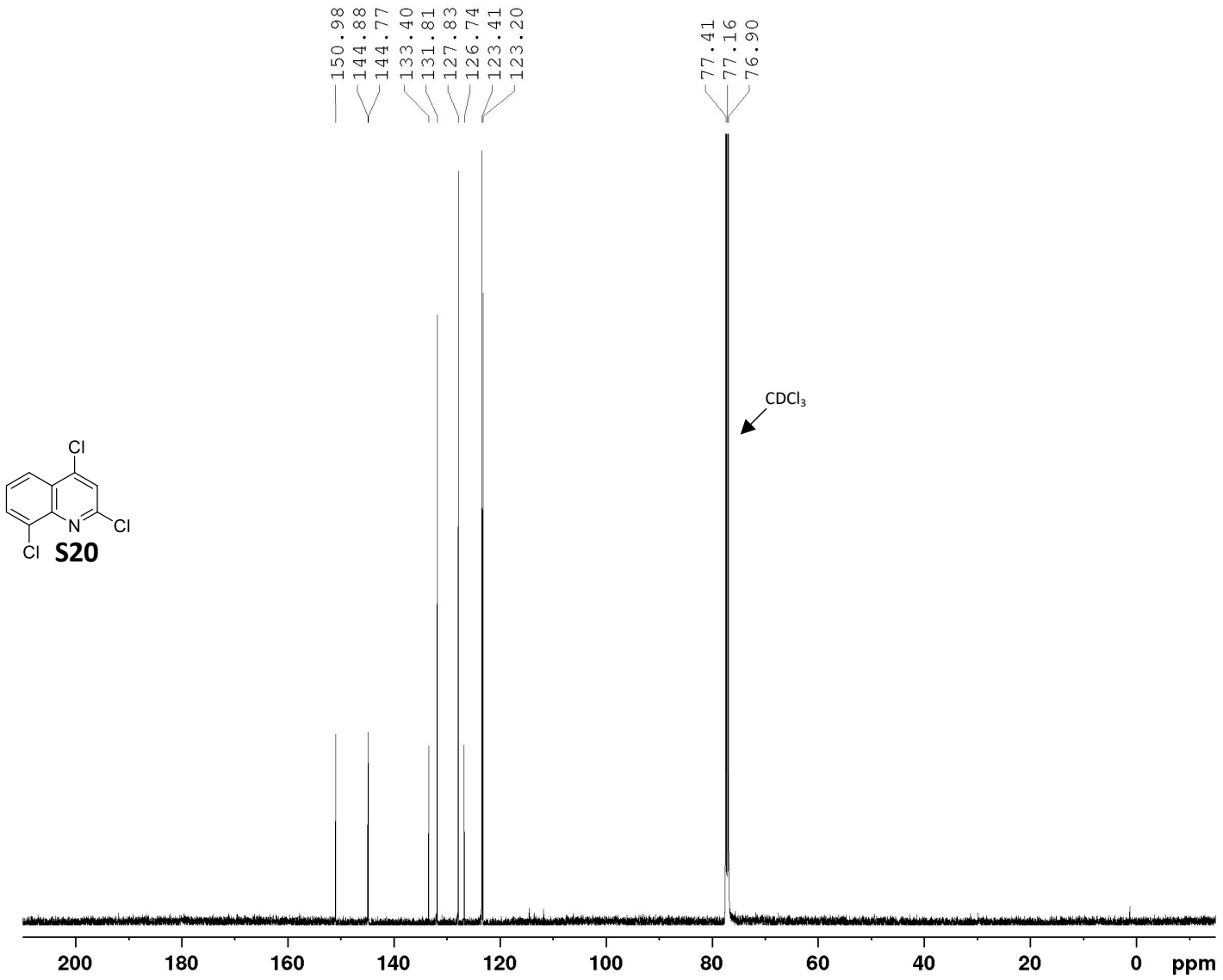
F2 - Processing parameters
SI                 32768
SF           125.7829201 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```




```
Current Data Parameters
NAME          JPN-2-42-3
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210209
Time               10.24 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                151.18
DW                 50.000 usec
DE                 16.00 usec
TE                 300.0 K
D1             2.00000000 sec
TD0                    1
SFO1         500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1         11.44699955 W

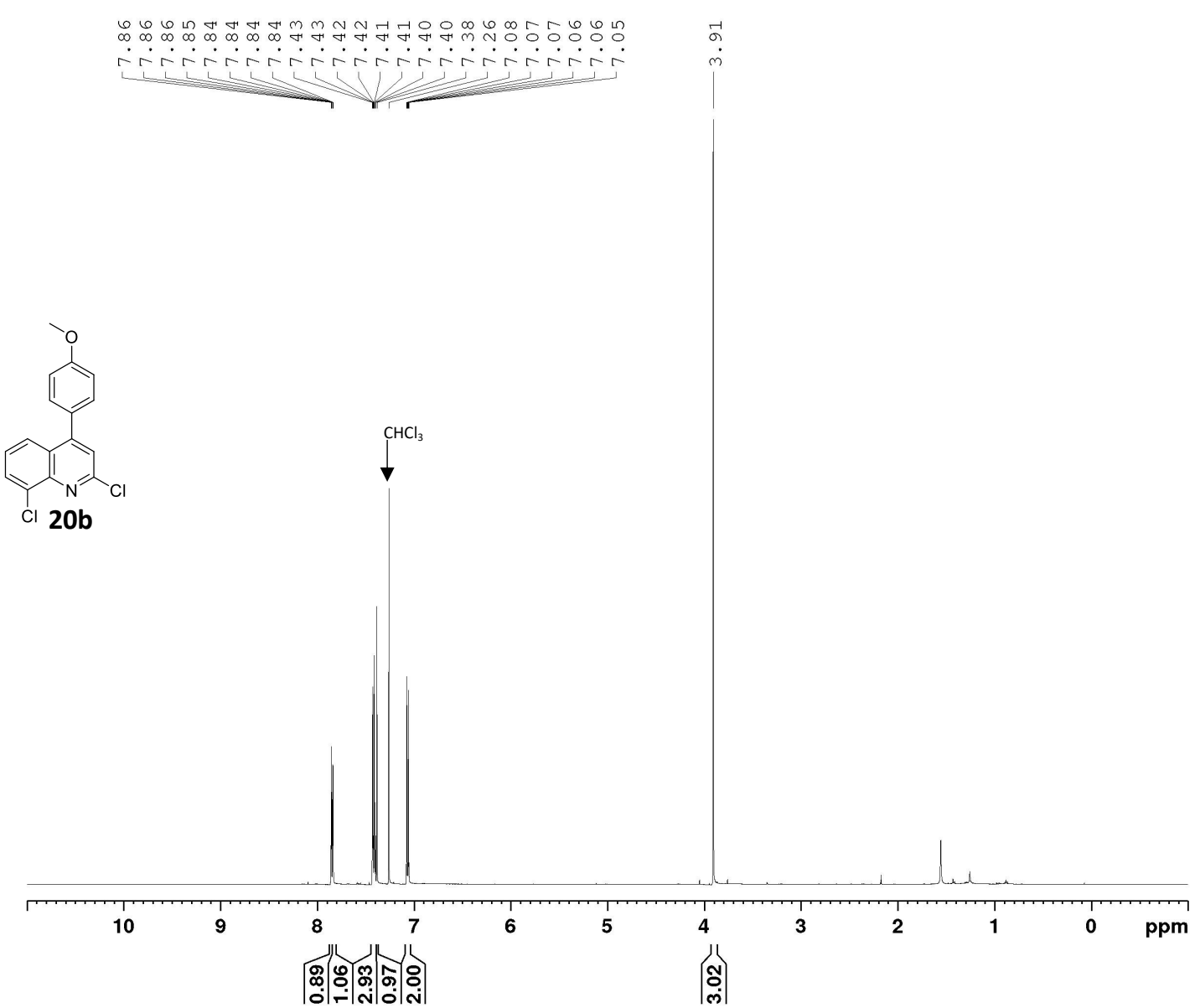
F2 - Processing parameters
SI                 65536
SF           500.2300121 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

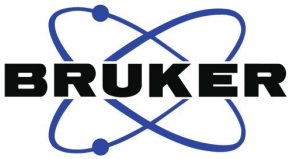



```
Current Data Parameters
NAME      JPN-2-42-3_(2)
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20211128
Time             21.42 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                1024
DS                   4
SWH          29761.904 Hz
FIDRES        0.908261 Hz
AQ           1.1010048 sec
RG              190.44
DW              16.800 usec
DE              18.00 usec
TE              298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1
SFO1        125.7955118 MHz
NUC1               13C
P0                3.33 usec
P1               10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2            80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

F2 - Processing parameters
SI                32768
SF          125.7829163 MHz
WDW                  EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```

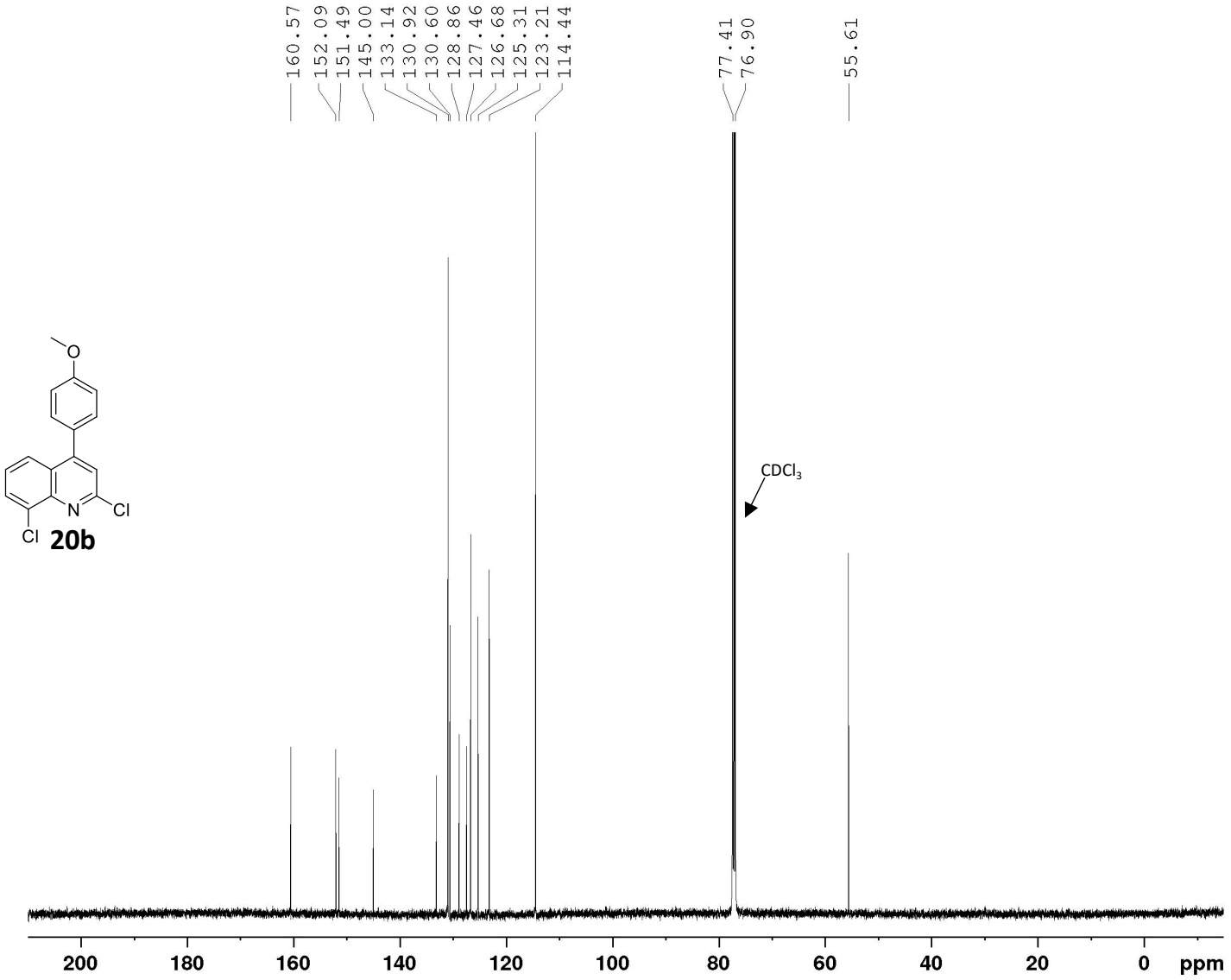





```
Current Data Parameters
NAME      JPN-2-47-3_20-Nov-2021
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211120
Time               21.51 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                 151.18
DW                 50.000 usec
DE                 16.00 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1
SFO1         500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1         11.44699955 W

F2 - Processing parameters
SI                  65536
SF           500.2300121 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

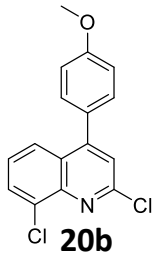



```
Current Data Parameters
NAME      JPN-2-47-3_20-Nov-2021
EXPNO                 11
PROCNO                 1

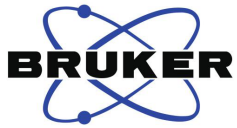
F2 - Acquisition Parameters
Date_           20211120
Time              22.47 h
INSTRUM           spect
PROBHD   Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.44
DW               16.800 usec
DE               18.00 usec
TE               298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1         125.7955118 MHz
NUC1                 13C
P0                3.33 usec
P1               10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2            80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

F2 - Processing parameters
SI                32768
SF           125.7829164 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

HSQC



20b




```
Current Data Parameters
NAME                  JPN-2-47-3
EXPNO                         13
PROCNO                         1

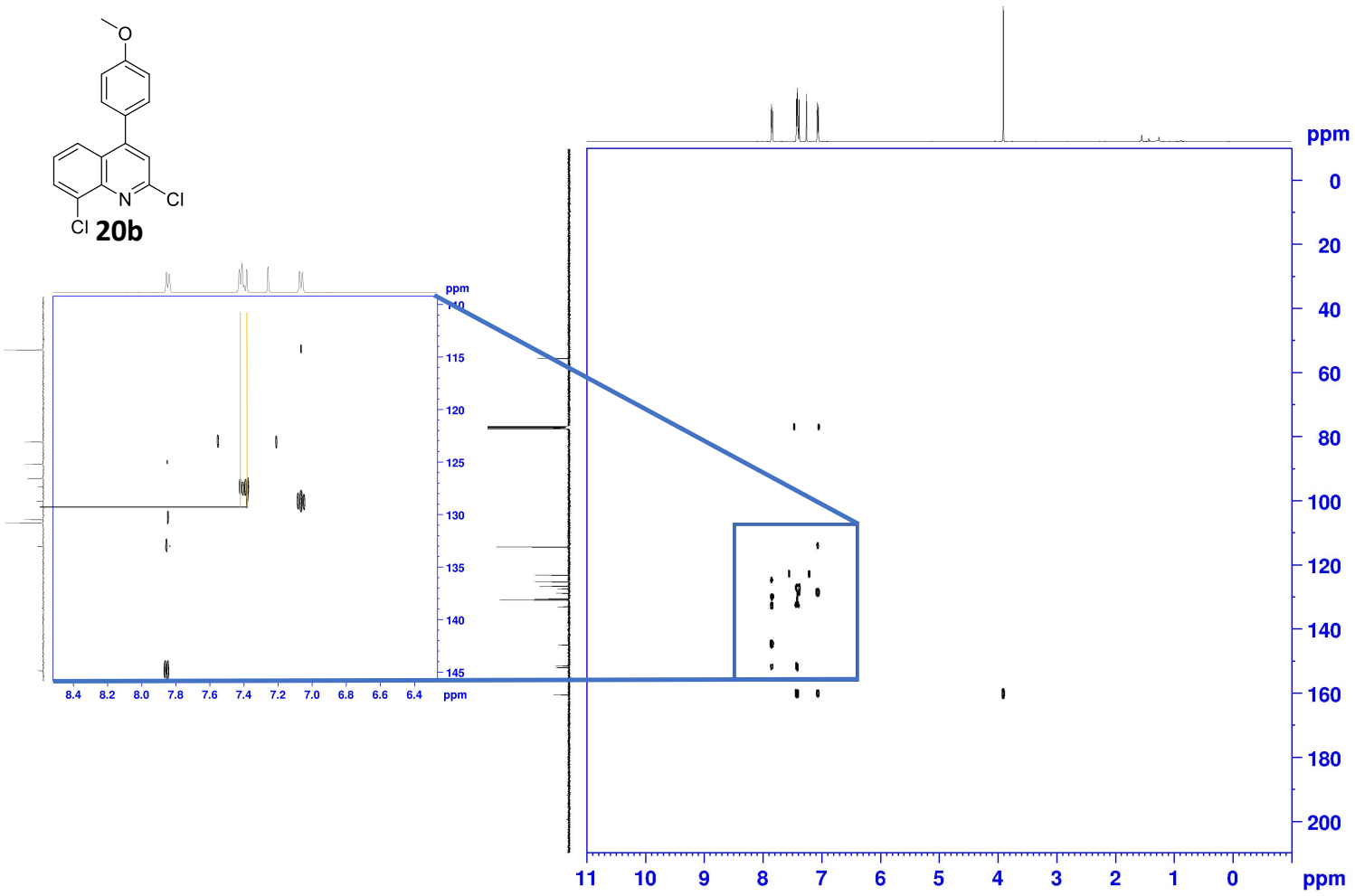
F2 - Acquisition Parameters
Date_                  20211103
Time                      18.57 h
INSTRUM                    spect
PROBHD    2125869_0055 (
PULPROG                hsqcetgp
TD                         1024
SOLVENT                   CDCl3
NS                            8
DS                           16
SWH                    7002.801 Hz
FIDRES                13.677346 Hz
AQ                     0.0731136 sec
RG                        190.44
DW                        71.400 usec
DE                        16.00 usec
TE                        298.0 K
CNST2                145.0000000
D0                    0.00000300 sec
D1                    1.50000000 sec
D4                    0.00172414 sec
D11                   0.03000000 sec
D16                   0.00020000 sec
IN0                   0.00001990 sec
TDav                          1
ZGOPTNS
SFO1                500.2330889 MHz
NUC1                        1H
P1                        12.00 usec
P2                        24.00 usec
PLW1               11.44699955 W
SFO2                125.7948829 MHz
NUC2                        13C
CPDPRG[2                  garp
P3                        10.00 usec
P4                        20.00 usec
PCPD2                     70.00 usec
PLW2               56.90299988 W
PLW12               1.16129994 W
GPNAM[1]            SMSQ10.100
GPZ1                      80.00 %
GPNAM[2]            SMSQ10.100
GPZ2                      20.10 %
P16                     1000.00 usec

F1 - Acquisition parameters
TD                          256
SFO1                125.7949 MHz
FIDRES              196.293976 Hz
SW                     199.735 ppm
FnMODE          Echo-Antiecho

F2 - Processing parameters
SI                         1024
SF                  500.2300122 MHz
WDW                       QSINE
SSB                           2
LB                            0 Hz
GB                            0
PC                         1.40

F1 - Processing parameters
SI                         1024
MC2               echo-antiecho
SF                  125.7829335 MHz
WDW                       QSINE
SSB                           2
LB                            0 Hz
GB                            0
```

HMBC




```
Current Data Parameters
NAME                  JPN-2-47-3
EXPNO                         11
PROCNO                         1

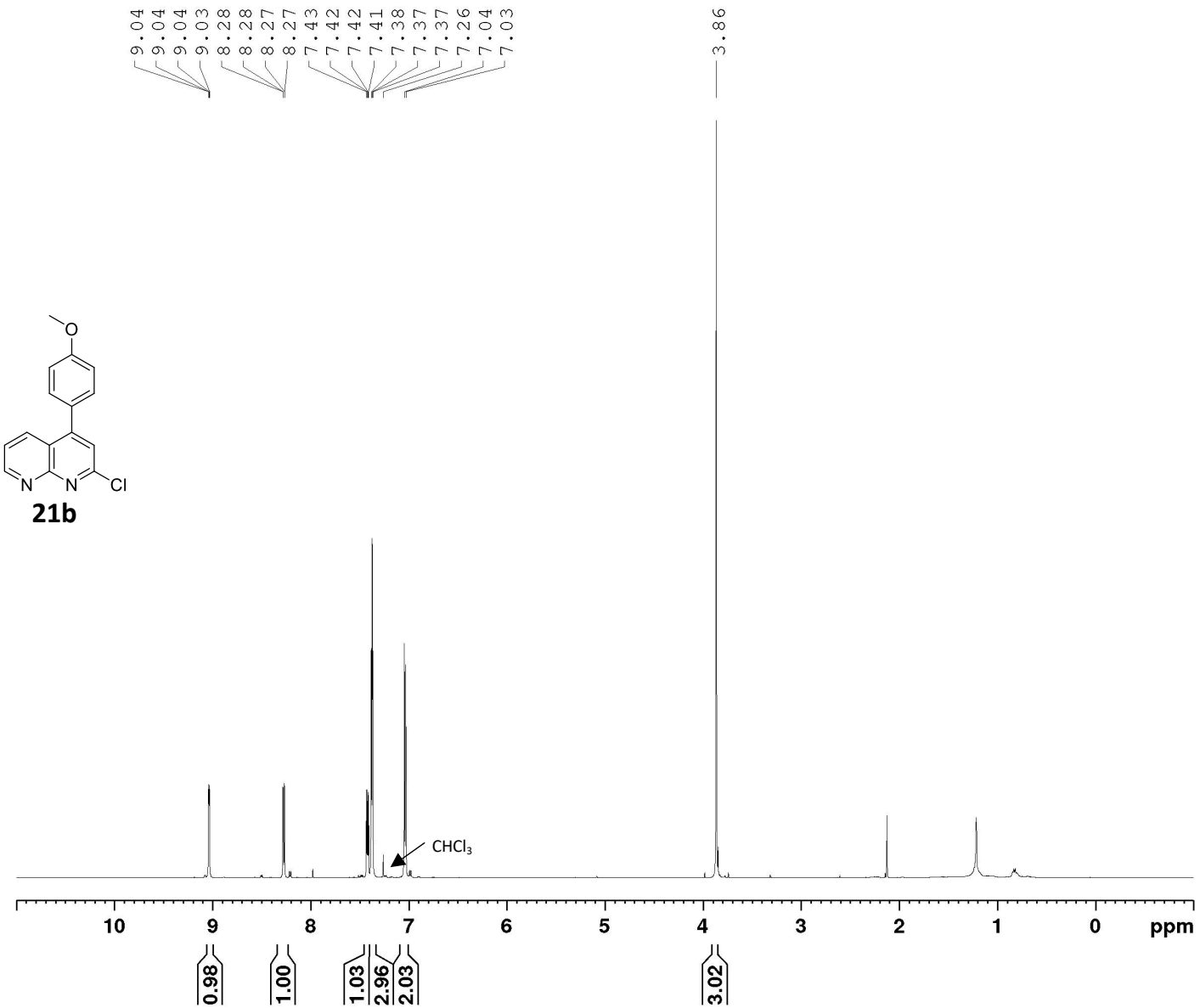
F2 - Acquisition Parameters
Date_               20211103
Time                      18.01 h
INSTRUM                   spect
PROBHD     Z125869_0055 (
PULPROG       hmbcgplpndqf
TD                        4096
SOLVENT                   CDCl3
NS                           4
DS                          16
SWH                   4201.681 Hz
FIDRES                2.051602 Hz
AQ                    0.4874240 sec
RG                       190.44
DW                      119.000 usec
DE                       16.00 usec
TE                       298.0 K
CNST2               145.0000000
CNST13               10.0000000
D0                    0.00000300 sec
D1                    1.50000000 sec
D2                    0.00344828 sec
D6                    0.05000000 sec
D16                   0.00020000 sec
IN0                   0.00001810 sec
TDav                         1
SFO1                500.2321971 MHz
NUC1                        1H
P1                       12.00 usec
P2                       24.00 usec
PLW1                11.44699955 W
SFO2                125.7955118 MHz
NUC2                        13C
P3                       10.00 usec
PLW2                56.90299988 W
GPNAM[1]             SMSQ10.100
GPZ1                     50.00 %
GPNAM[2]             SMSQ10.100
GPZ2                     30.00 %
GPNAM[3]             SMSQ10.100
GPZ3                     40.10 %
P16                    1000.00 usec

F1 - Acquisition parameters
TD                         128
SFO1                125.7955 MHz
FIDRES               431.629822 Hz
SW                    219.597 ppm
FnMODE                      QF

F2 - Processing parameters
SI                        4096
SF                  500.2300126 MHz
WDW                      QSINE
SSB                         0
LB                          0 Hz
GB                          0
PC                       1.40

F1 - Processing parameters
SI                        1024
MC2                         QF
SF                  125.7829432 MHz
WDW                      QSINE
SSB                         0
LB                          0 Hz
GB                          0
```

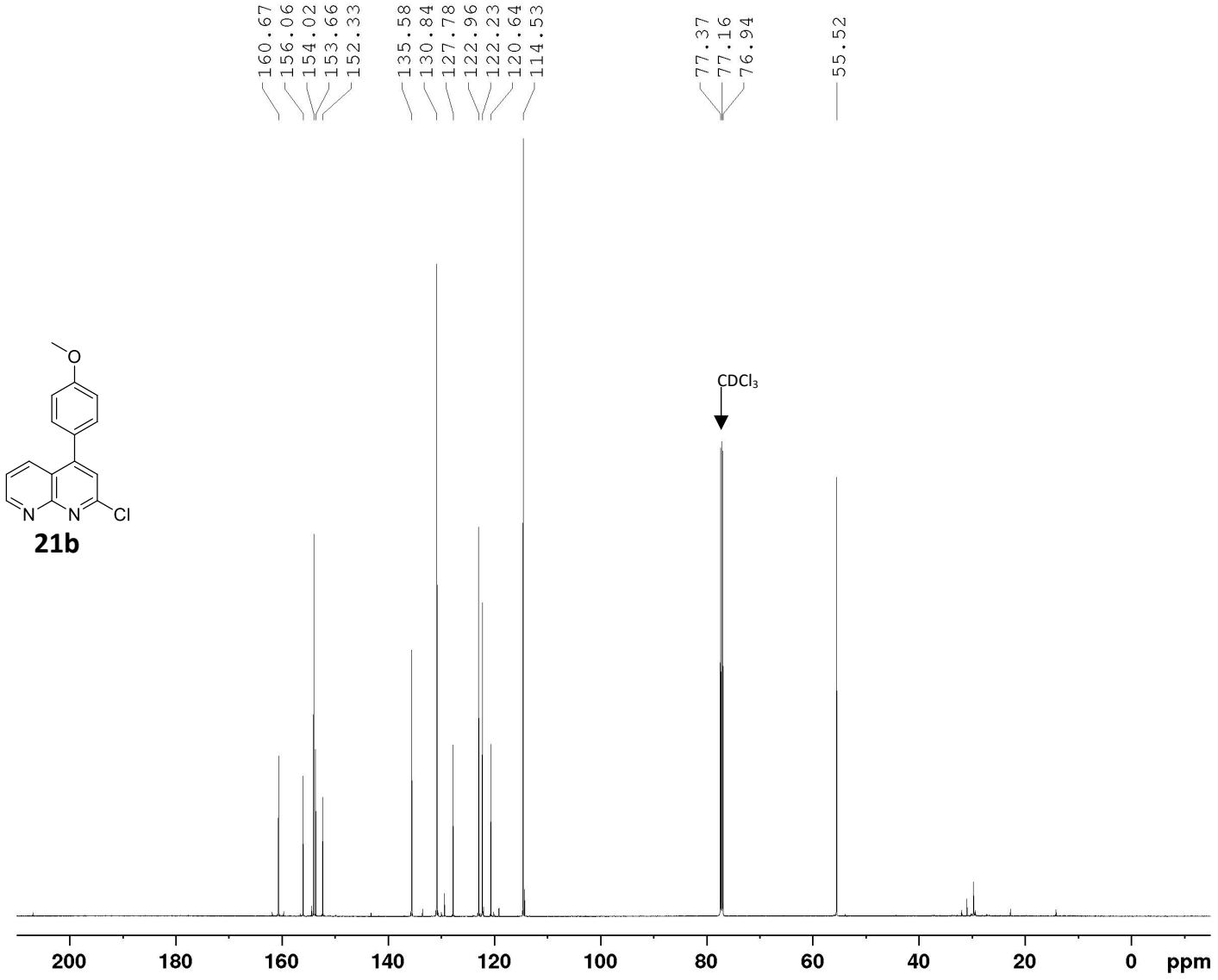
C9 correlation to *meta* C-H and C3-H

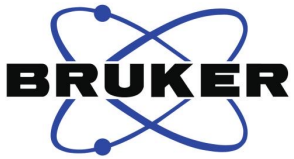



```
Current Data Parameters
NAME      JPN-1-169-2_C4-monoaryl
EXPNO                 22
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200527
Time              10.24 h
INSTRUM            spect
PROBHD    Z127277_0002 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           12019.230 Hz
FIDRES         0.366798 Hz
AQ             2.7262976 sec
RG                  4.41
DW                41.600 usec
DE                10.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                    1
SFO1         600.1337060 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1          5.59999990 W

F2 - Processing parameters
SI                 65536
SF           600.1300147 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

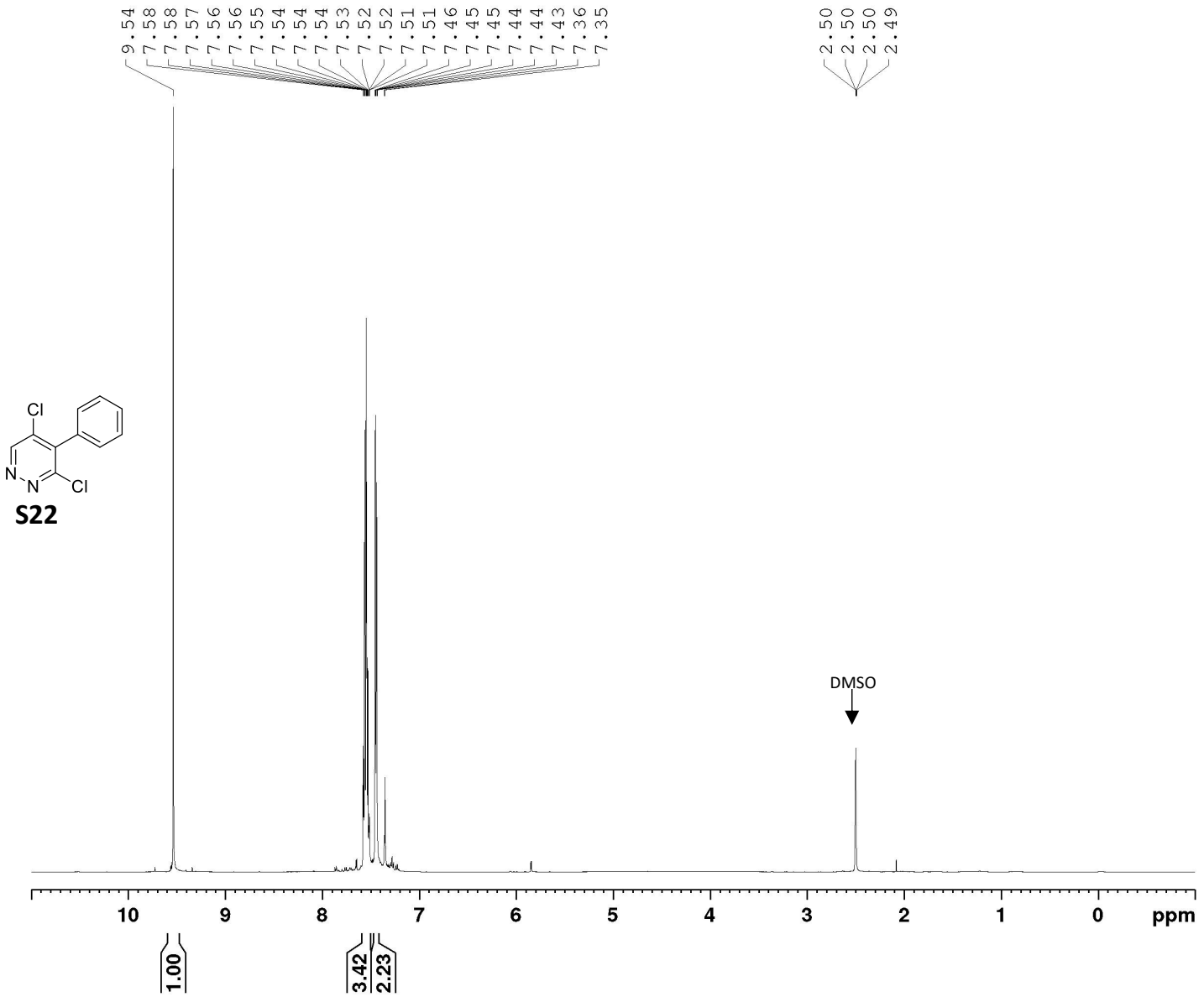





```
Current Data Parameters
NAME      JPN-1-169-2_C4-monoaryl
EXPNO                 23
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200527
Time               11.16 h
INSTRUM            spect
PROBHD   Z127277_0002 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.9087659 sec
RG                184.4
DW               13.867 usec
DE                18.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        150.9178981 MHz
NUC1               13C
P0                4.00 usec
P1               12.00 usec
PLW1        91.00000000 W
SFO2        600.1324005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2             70.00 usec
PLW2         5.59999990 W
PLW12        0.07314300 W
PLW13        0.03679000 W

F2 - Processing parameters
SI                32768
SF          150.9028026 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

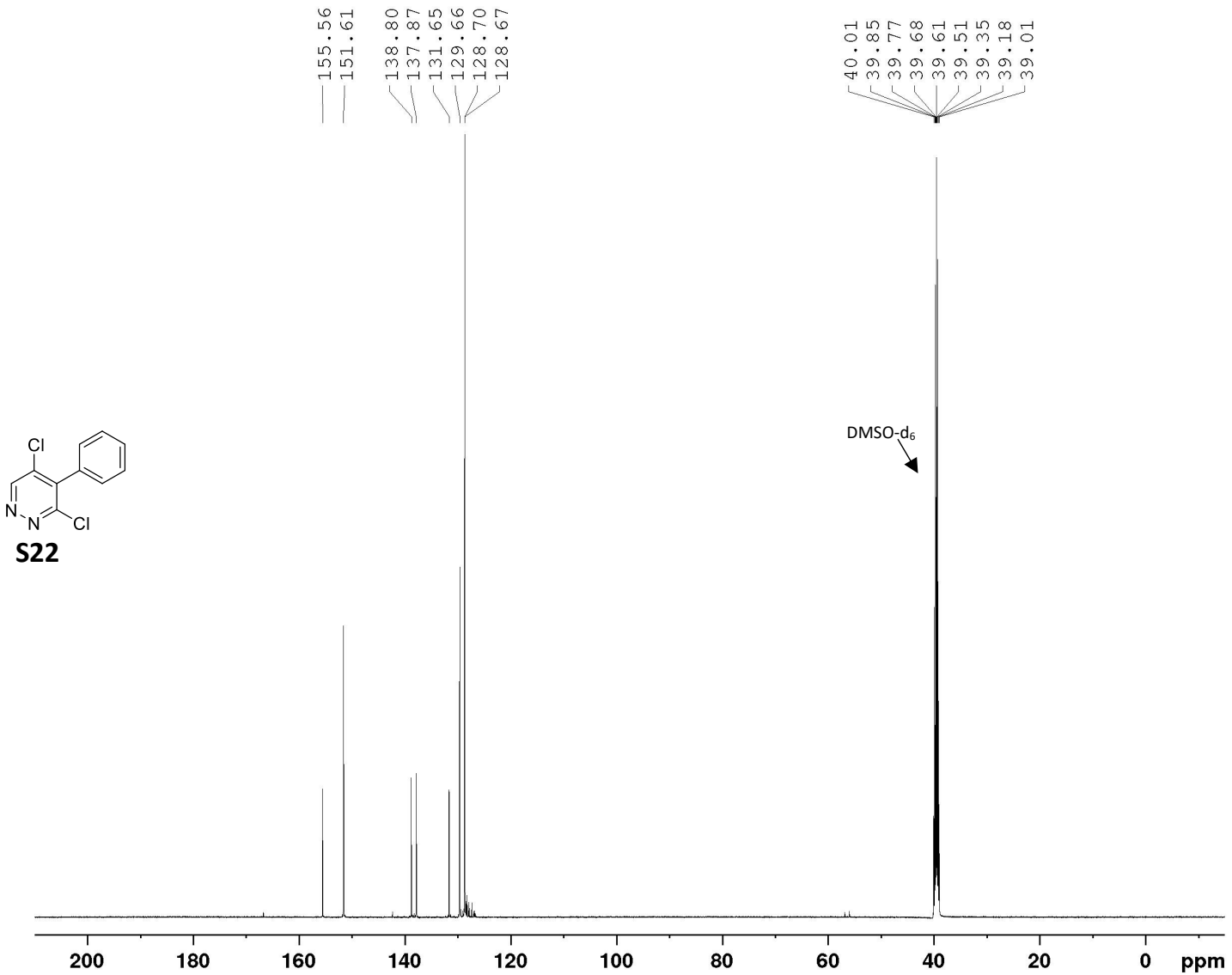


BRUKER

```
Current Data Parameters
NAME      JPN-2-22-2_dried
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20201010
Time                10.30 h
INSTRUM              spect
PROBHD   Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     64
DS                      2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                  69.97
DW                 50.000 usec
DE                 16.00 usec
TE                 300.0 K
D1            2.00000000 sec
TD0                     1
SFO1         500.2330889 MHz
NUC1                   1H
P0                  4.00 usec
P1                 12.00 usec
PLW1         11.44699955 W

F2 - Processing parameters
SI                  65536
SF           500.2300035 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

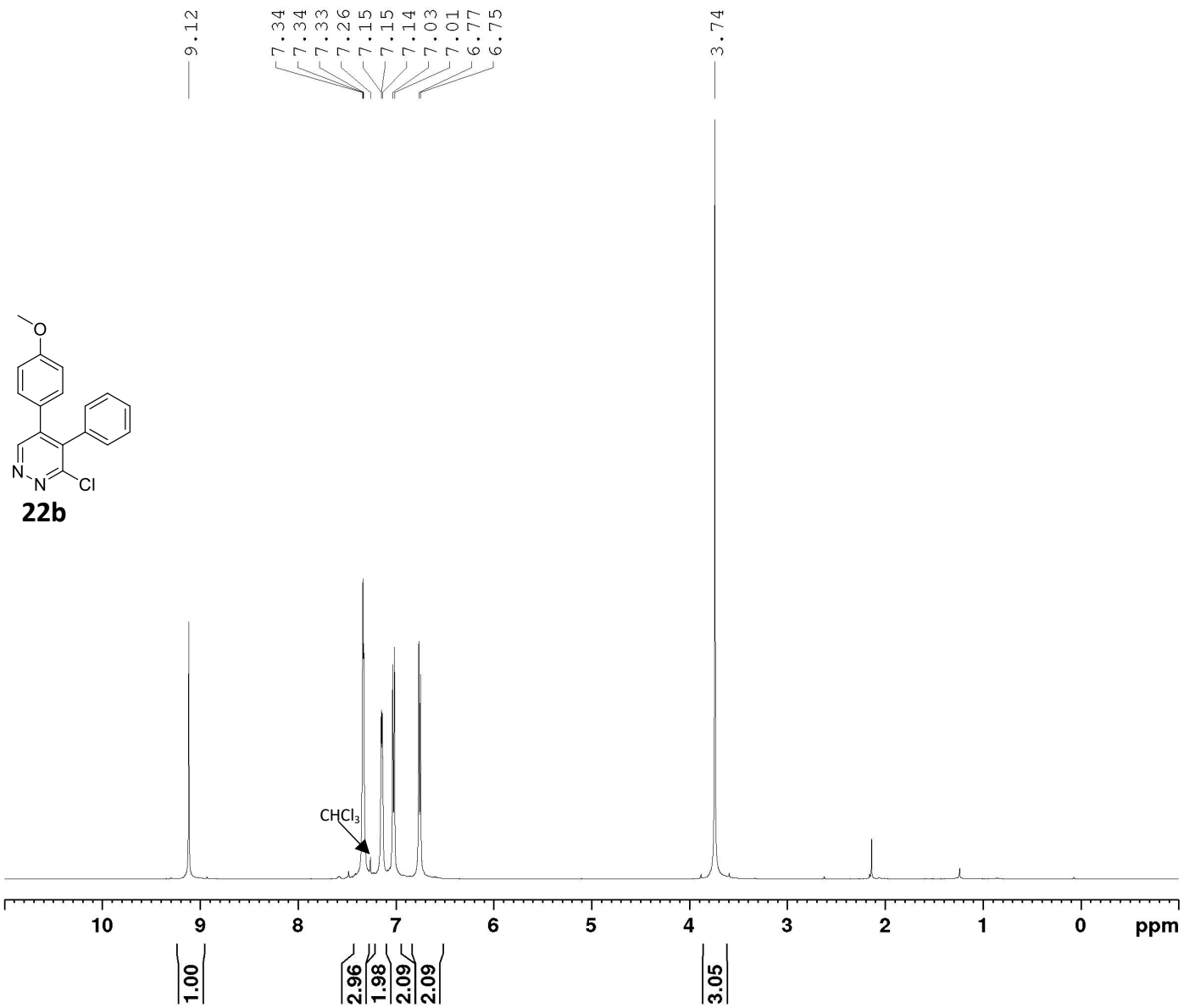


S22

```
Current Data Parameters
NAME      JPN-2-22-2_dried
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_           20201010
Time               12.37 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG           zgpg30
TD                 65536
SOLVENT              DMSO
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         125.7955118 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

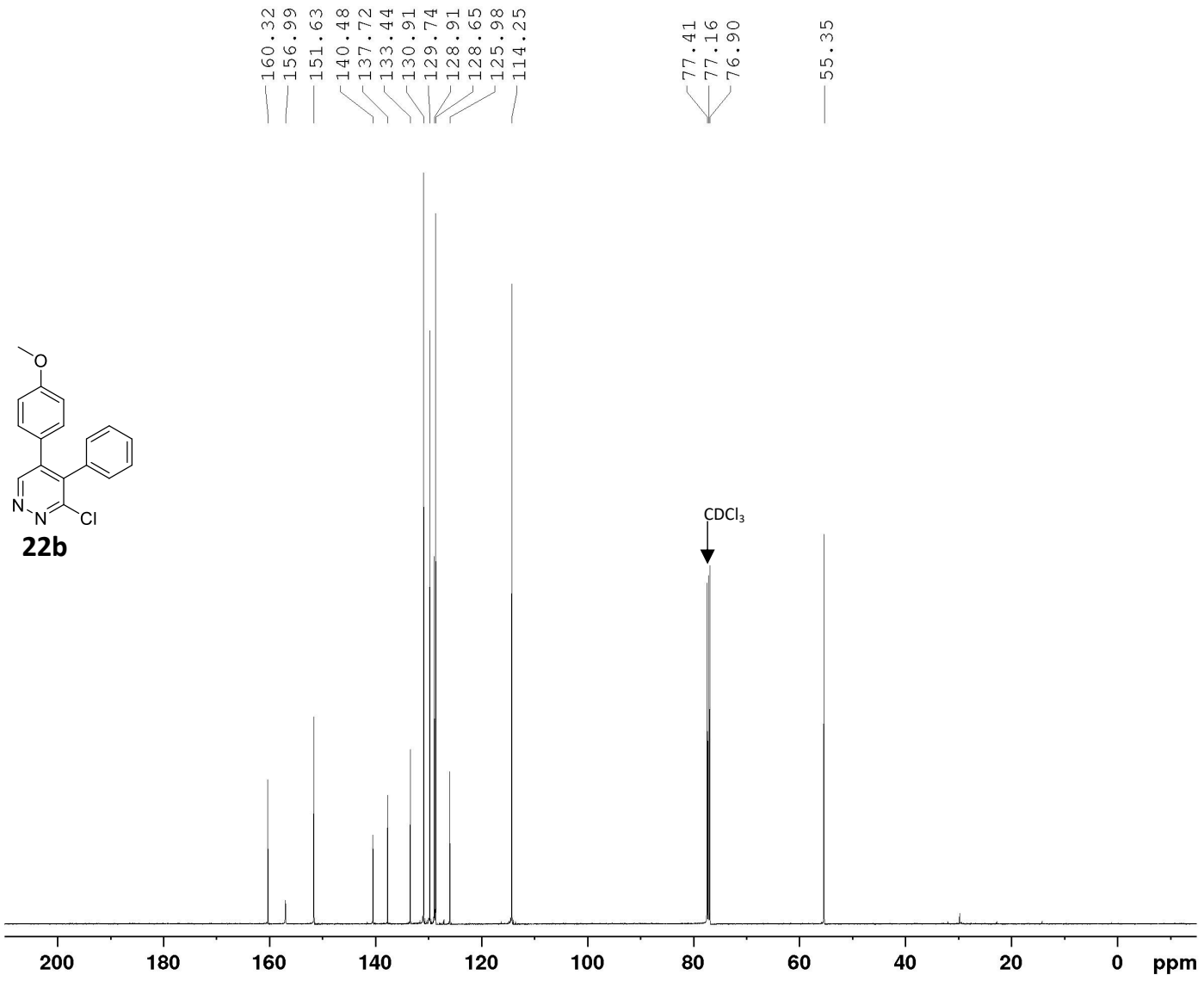
F2 - Processing parameters
SI                 32768
SF           125.7829976 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```




```
Current Data Parameters
NAME      JPN-2-27-1_repeat_C5-mono
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201130
Time              17.40 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ             3.2767999 sec
RG                 22.16
DW                50.000 usec
DE                16.00 usec
TE                300.0 K
D1             2.00000000 sec
TD0                    1
SFO1         500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1         11.44699955 W

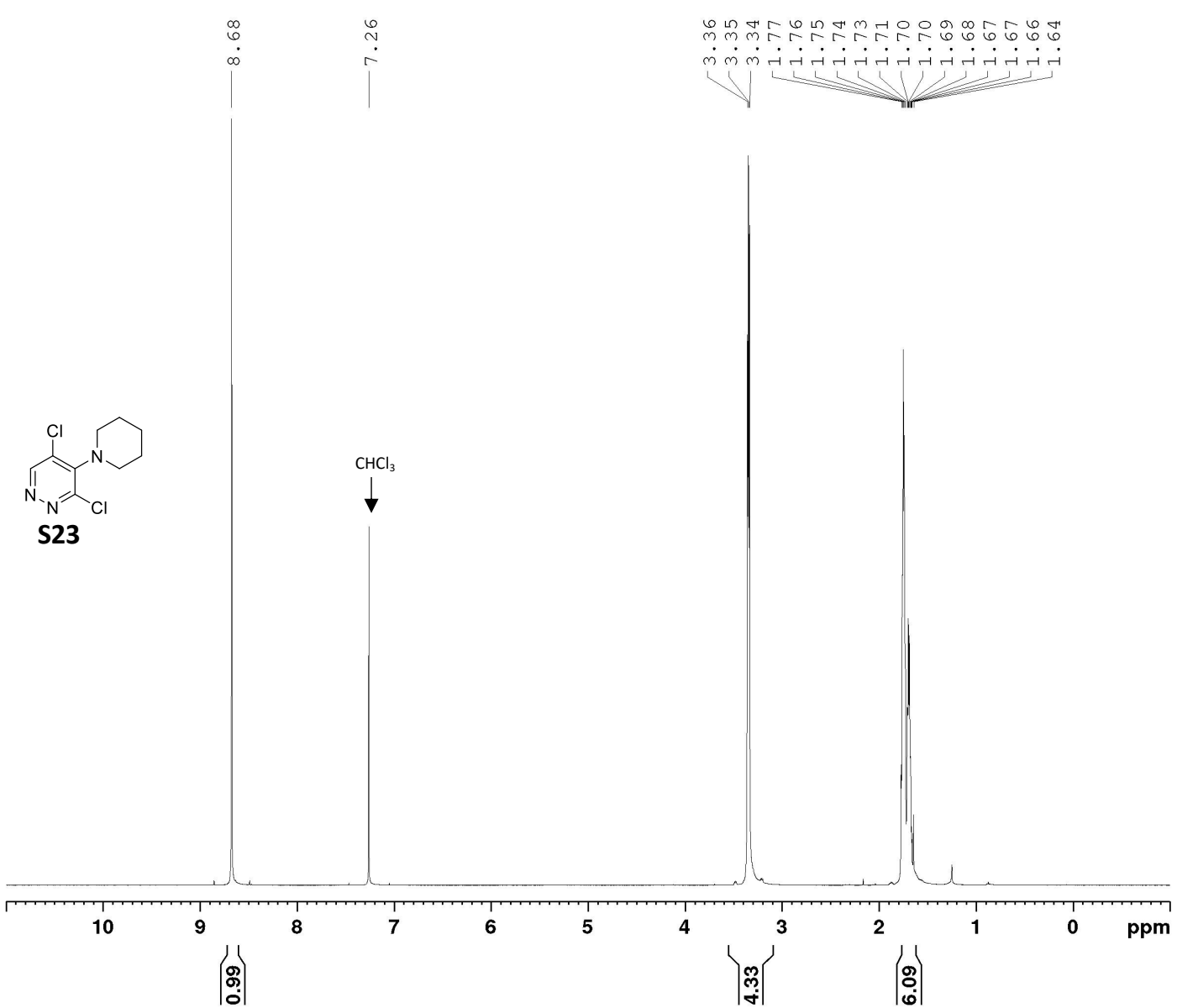
F2 - Processing parameters
SI                 65536
SF           500.2300118 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME      JPN-2-27-1_repeat
EXPNO                   17
PROCNO                   1

F2 - Acquisition Parameters
Date_           20211119
Time                4.28 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.44
DW               16.800 usec
DE               18.00 usec
TE               298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7955118 MHz
NUC1                13C
P0                3.33 usec
P1               10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

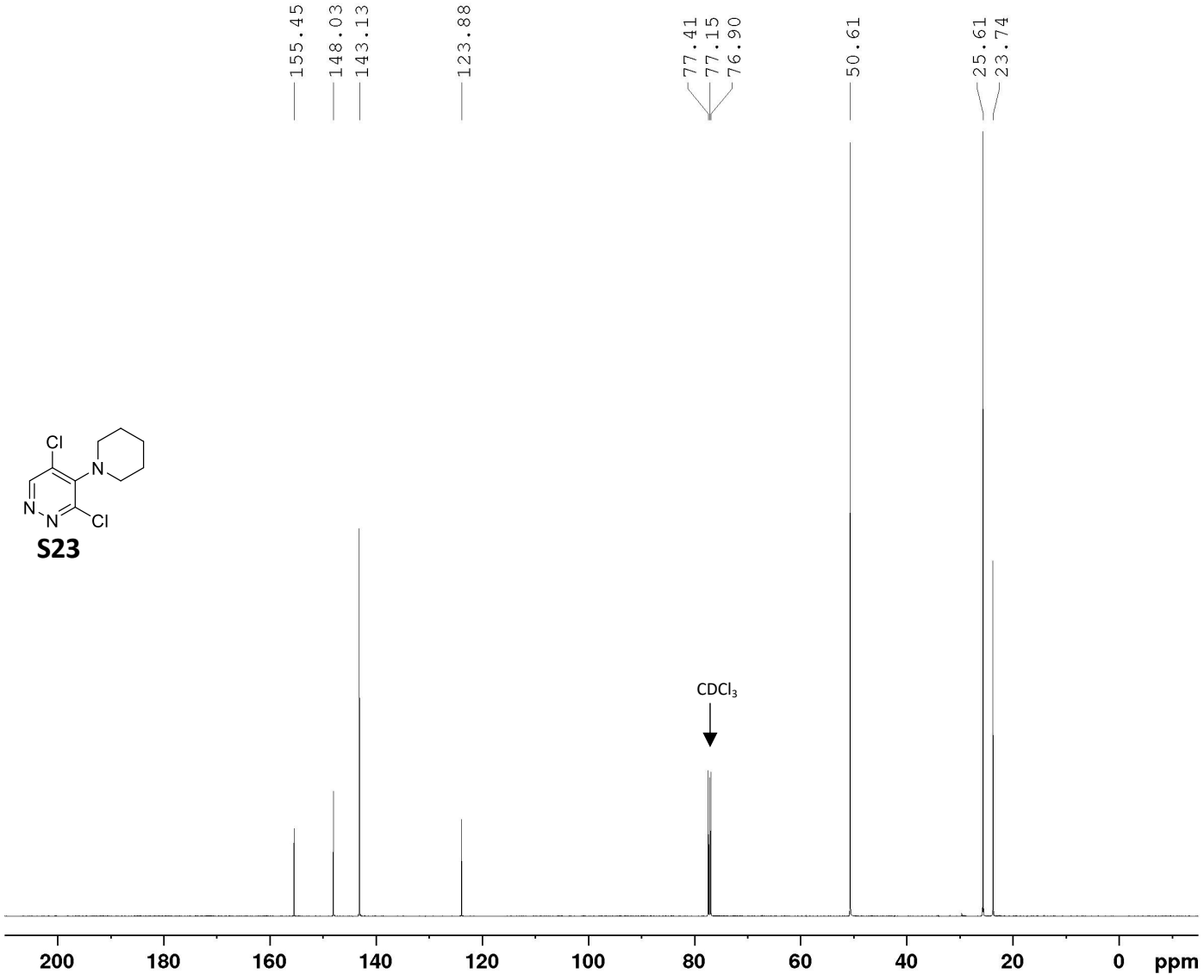
F2 - Processing parameters
SI                32768
SF          125.7829267 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```




```
Current Data Parameters
NAME      JPN-2-14-1_C4-subst%2E
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200914
Time                3.42 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10000.000 Hz
FIDRES            0.305176 Hz
AQ                3.2767999 sec
RG                  122.05
DW                 50.000 usec
DE                 16.00 usec
TE                 300.0 K
D1              2.00000000 sec
TD0                    1
SFO1          500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1          11.44699955 W

F2 - Processing parameters
SI                 65536
SF            500.2300122 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

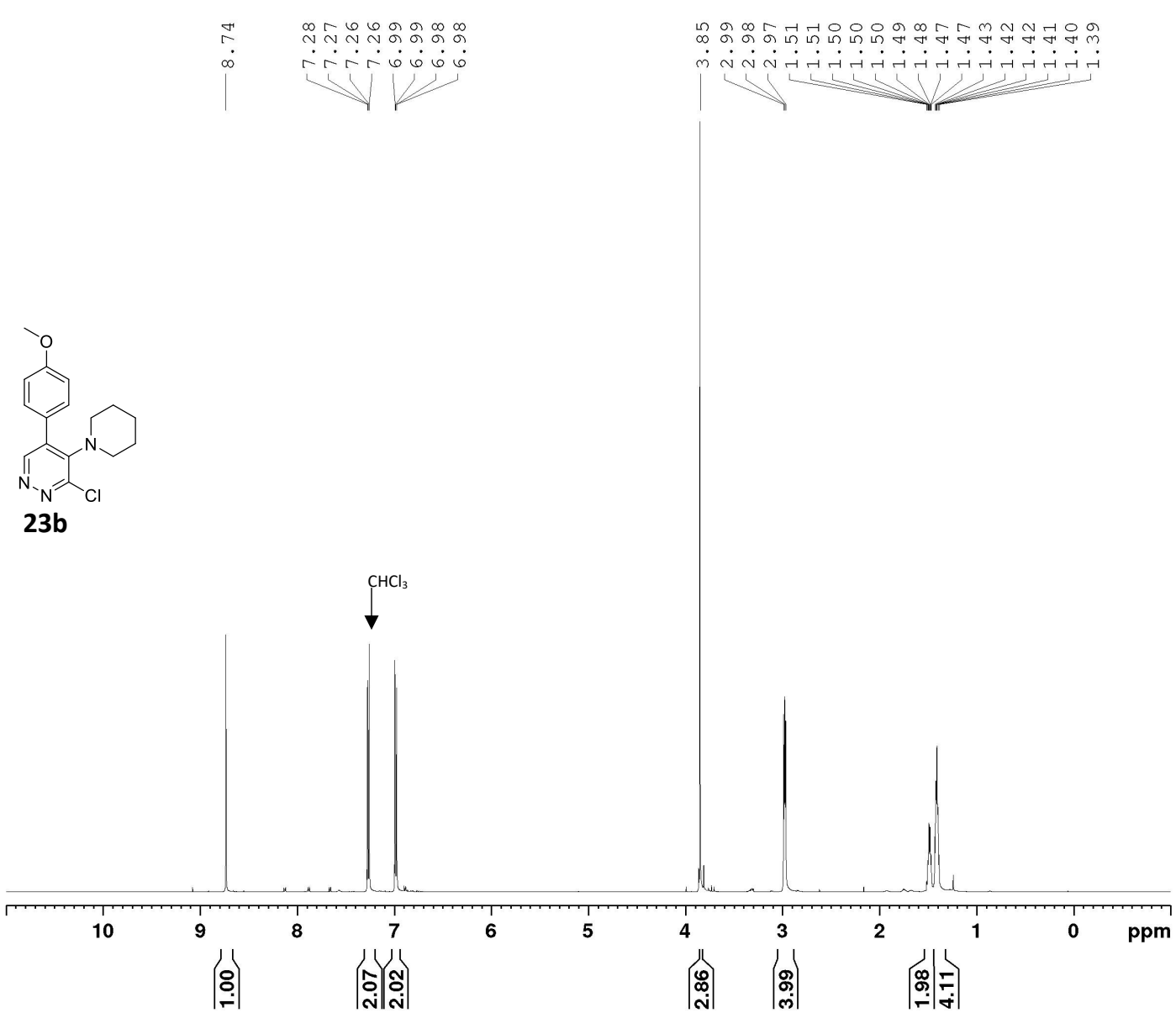


S23

```
Current Data Parameters
NAME      JPN-2-14-1_(C4-subst.)
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211127
Time              20.52 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.44
DW               16.800 usec
DE               18.00 usec
TE               298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         125.7955118 MHz
NUC1                 13C
P0                3.33 usec
P1               10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

F2 - Processing parameters
SI                32768
SF           125.7829371 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

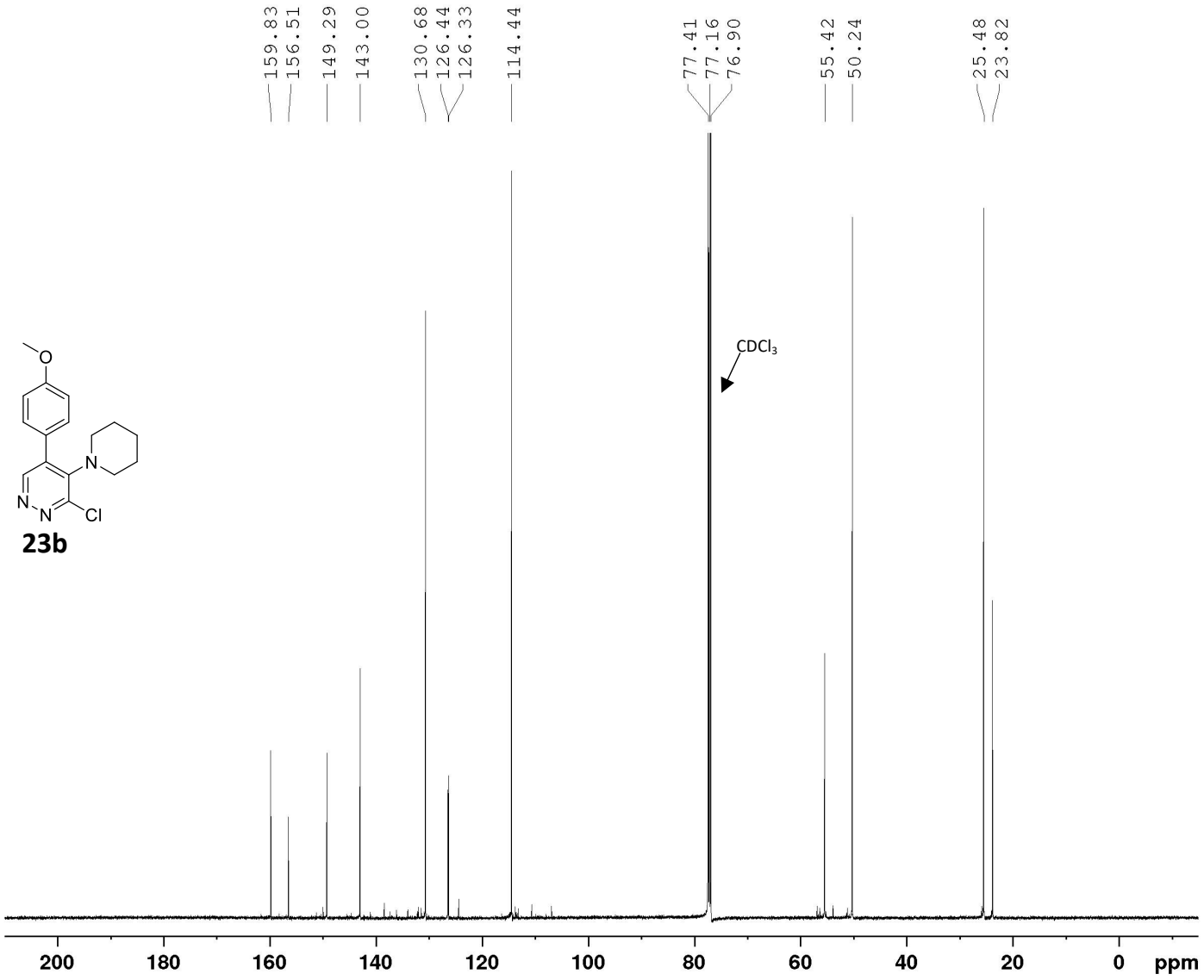


23b

Current Data Parameters
NAME JPN-2-27-2_C5-mono
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201130
Time 18.00 h
INSTRUM spect
PROBHD Z125869_0055 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 35.18
DW 50.000 usec
DE 16.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.2330889 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 11.44699955 W

F2 - Processing parameters
SI 65536
SF 500.2300119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

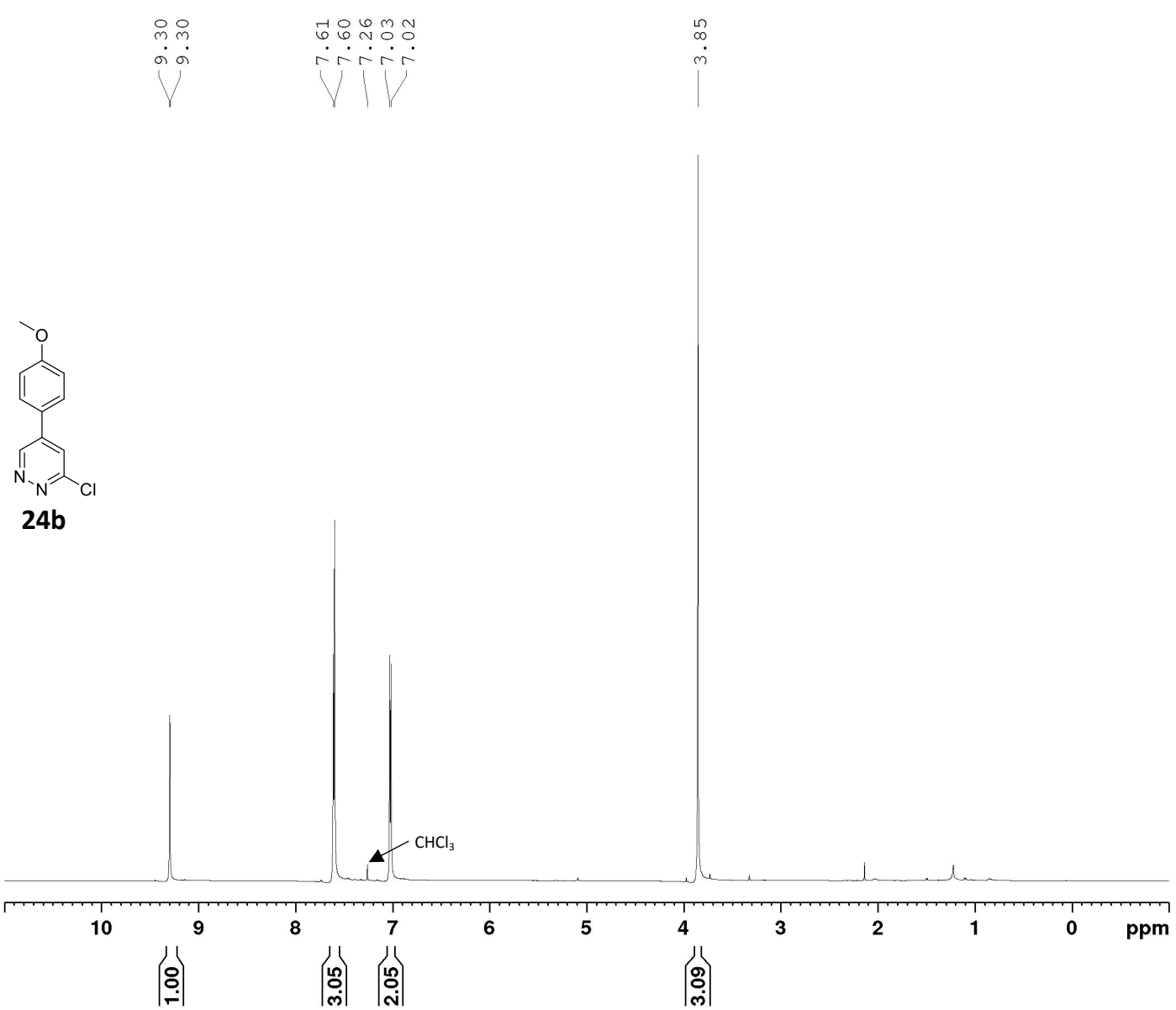


23b

```
Current Data Parameters
NAME          JPN-2-27-2
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211119
Time                5.26 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ              1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1         125.7955118 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

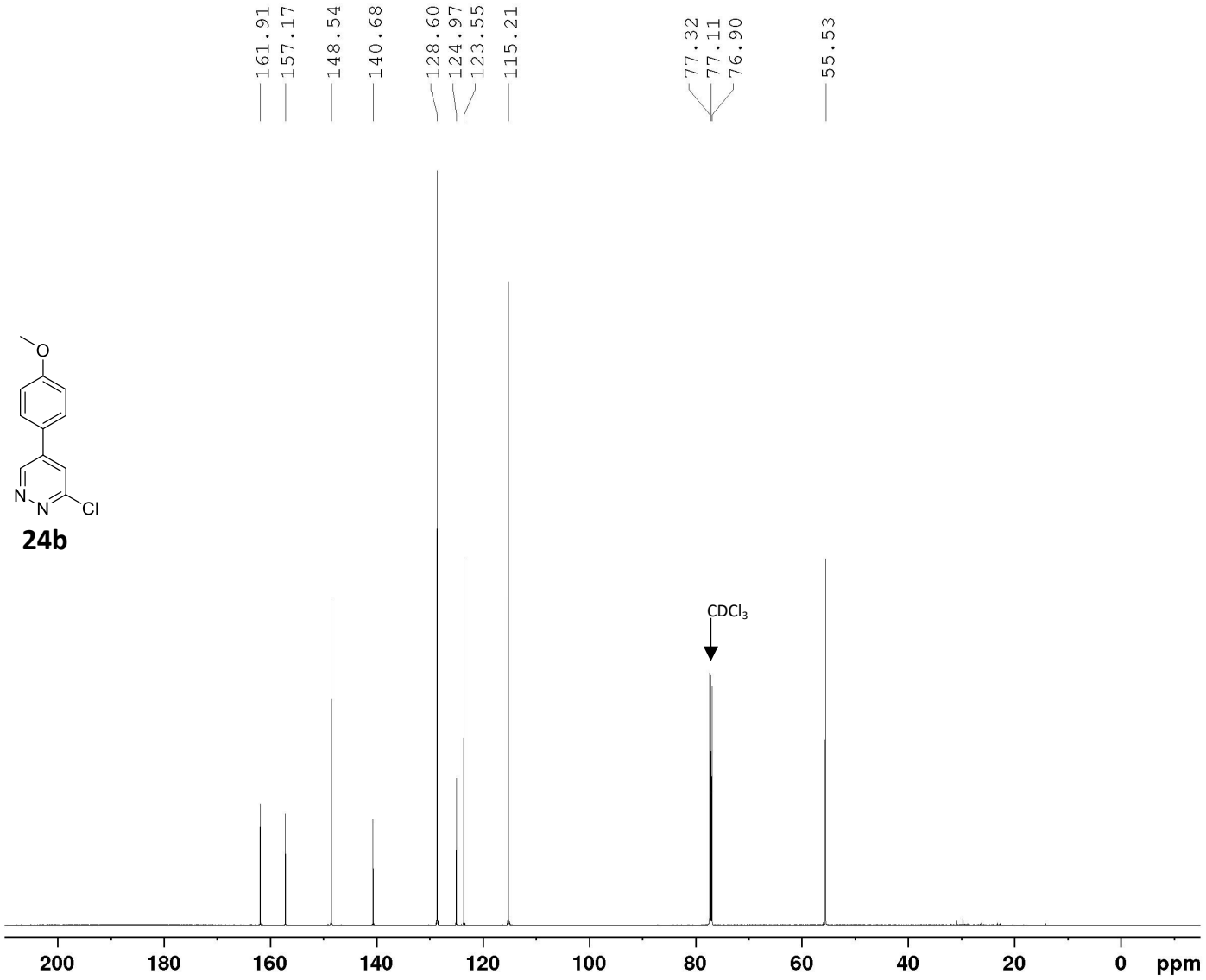
F2 - Processing parameters
SI                 32768
SF           125.7829191 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



Current Data Parameters
NAME JPN-1-166-2_C5-Mono
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200519
Time 13.52 h
INSTRUM spect
PROBHD Z127277_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 2.7262976 sec
RG 4.41
DW 41.600 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337060 MHz
NUC1 1H
P0 2.67 usec
P1 8.00 usec
PLW1 5.59999990 W

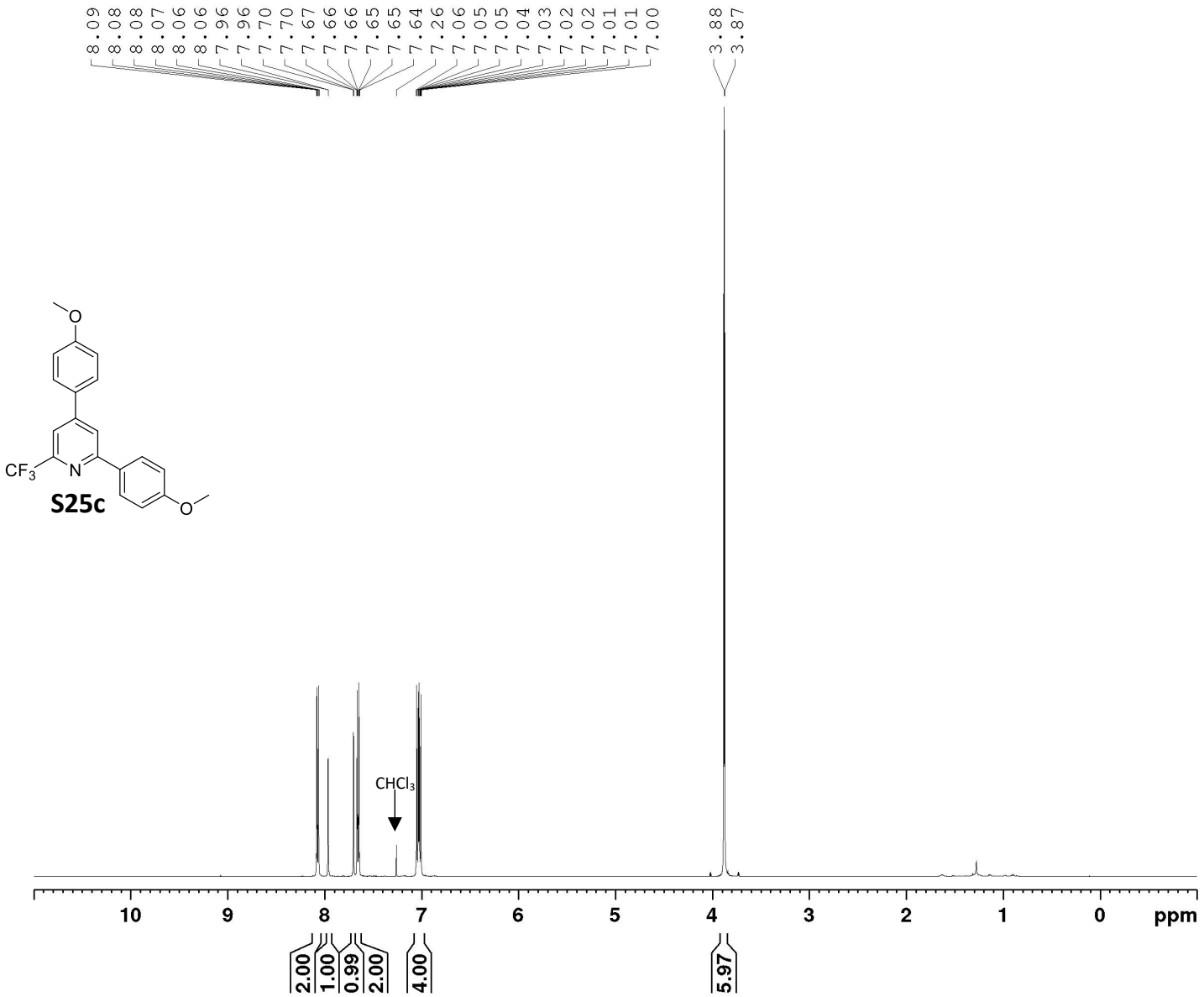
F2 - Processing parameters
SI 65536
SF 600.1300144 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

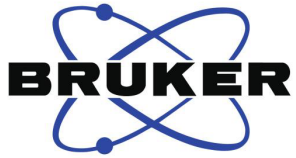



```
Current Data Parameters
NAME      JPN-1-166-2_C5-Mono
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_            20200519
Time                15.36 h
INSTRUM             spect
PROBHD    Z127277_0002 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            36057.691 Hz
FIDRES          1.100393 Hz
AQ             0.9087659 sec
RG                 184.4
DW                13.867 usec
DE                18.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         150.9178981 MHz
NUC1                13C
P0                 4.00 usec
P1                12.00 usec
PLW1         91.00000000 W
SFO2         600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2          5.59999990 W
PLW12         0.07314300 W
PLW13         0.03679000 W

F2 - Processing parameters
SI                 32768
SF           150.9028090 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

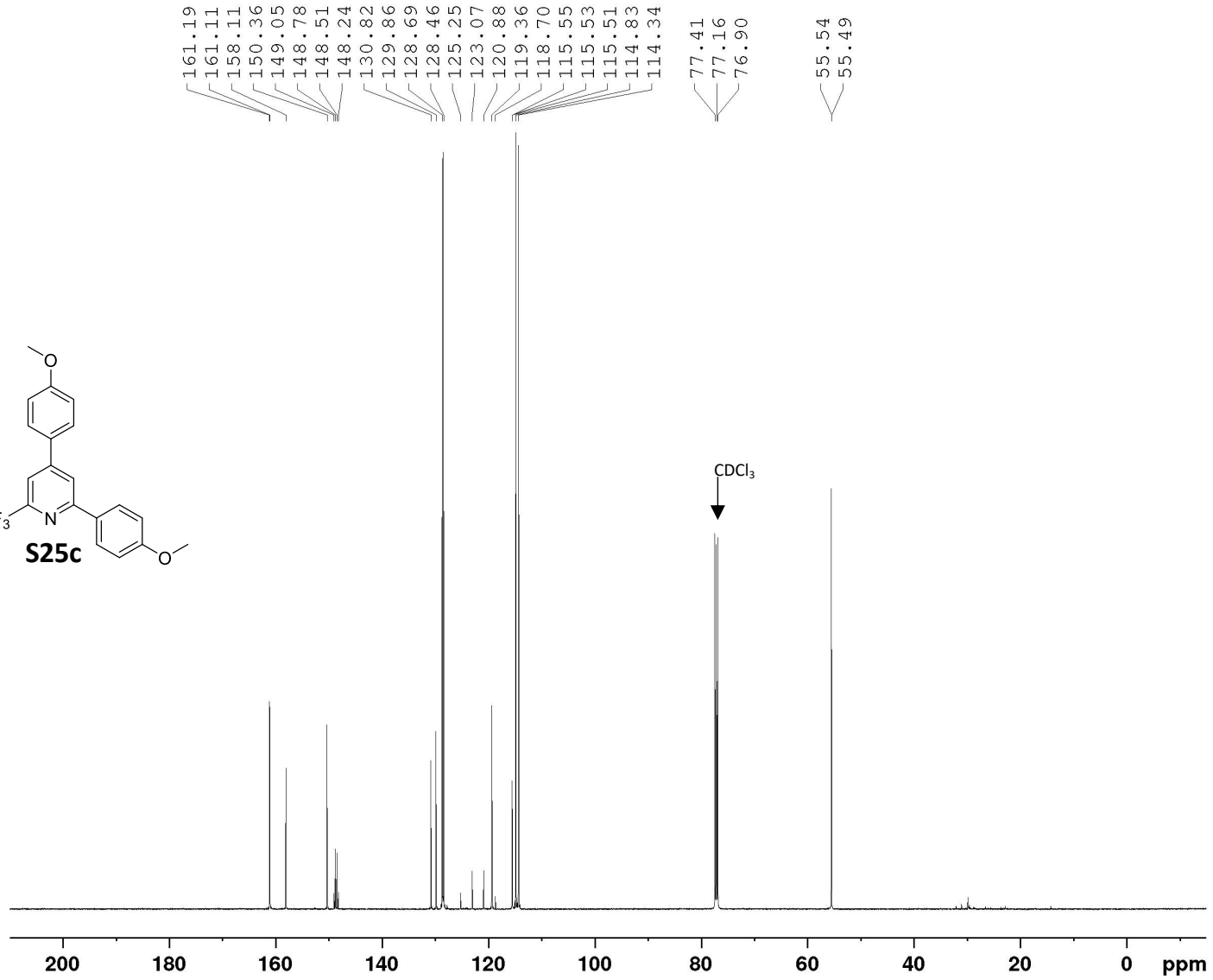





```
Current Data Parameters
NAME      JPN-1-187-2_20-Nov-2021
EXPNO                  20
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211121
Time                1.37 h
INSTRUM            spect
PROBHD    Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                 30.54
DW                50.000 usec
DE                16.00 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1         500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1         11.44699955 W

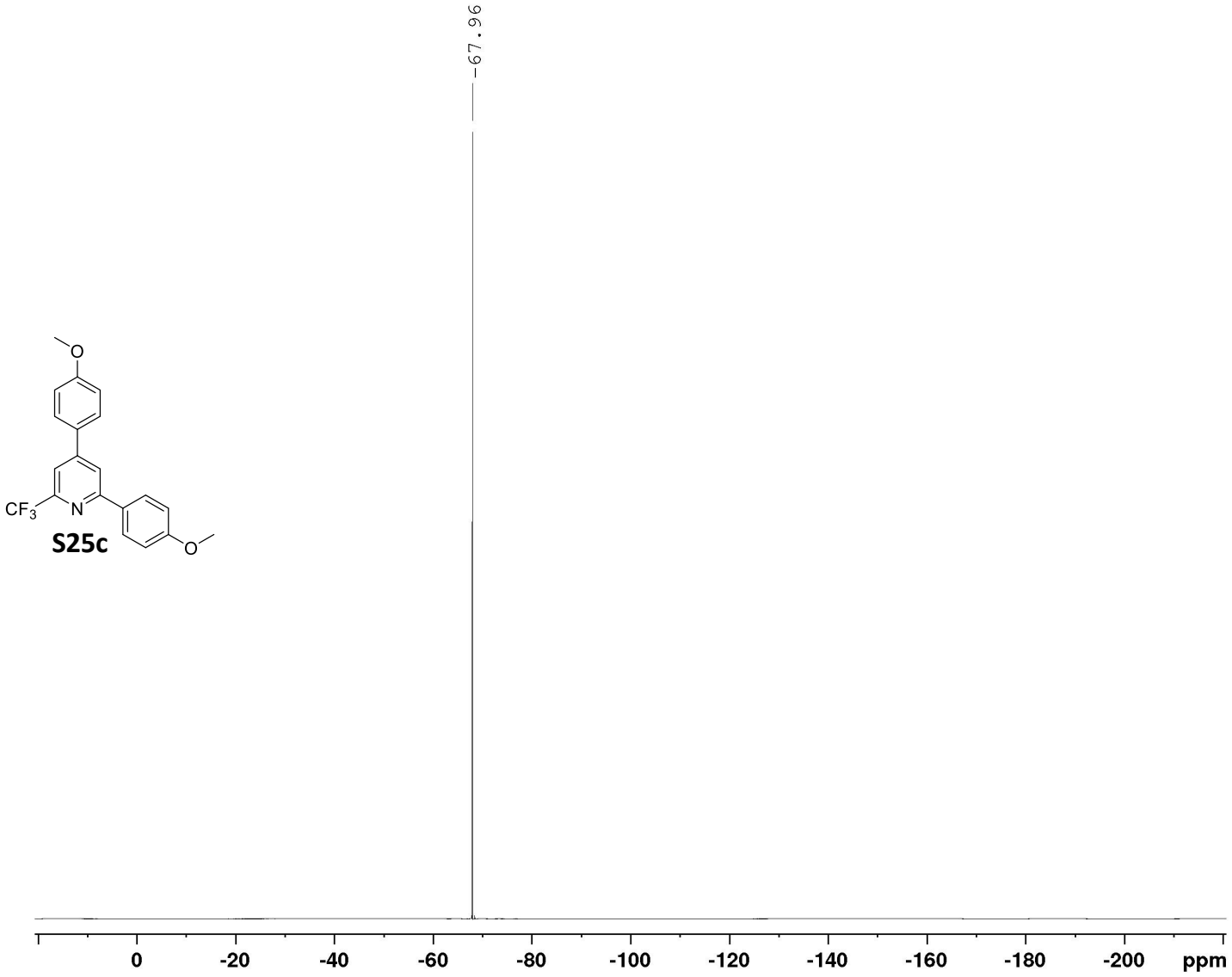
F2 - Processing parameters
SI                 65536
SF           500.2300119 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME      JPN-1-187-2_DA
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20200812
Time               3.15 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.44
DW               16.800 usec
DE               18.00 usec
TE               300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7955118 MHz
NUC1                13C
P0                3.33 usec
P1               10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

F2 - Processing parameters
SI                32768
SF          125.7829205 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

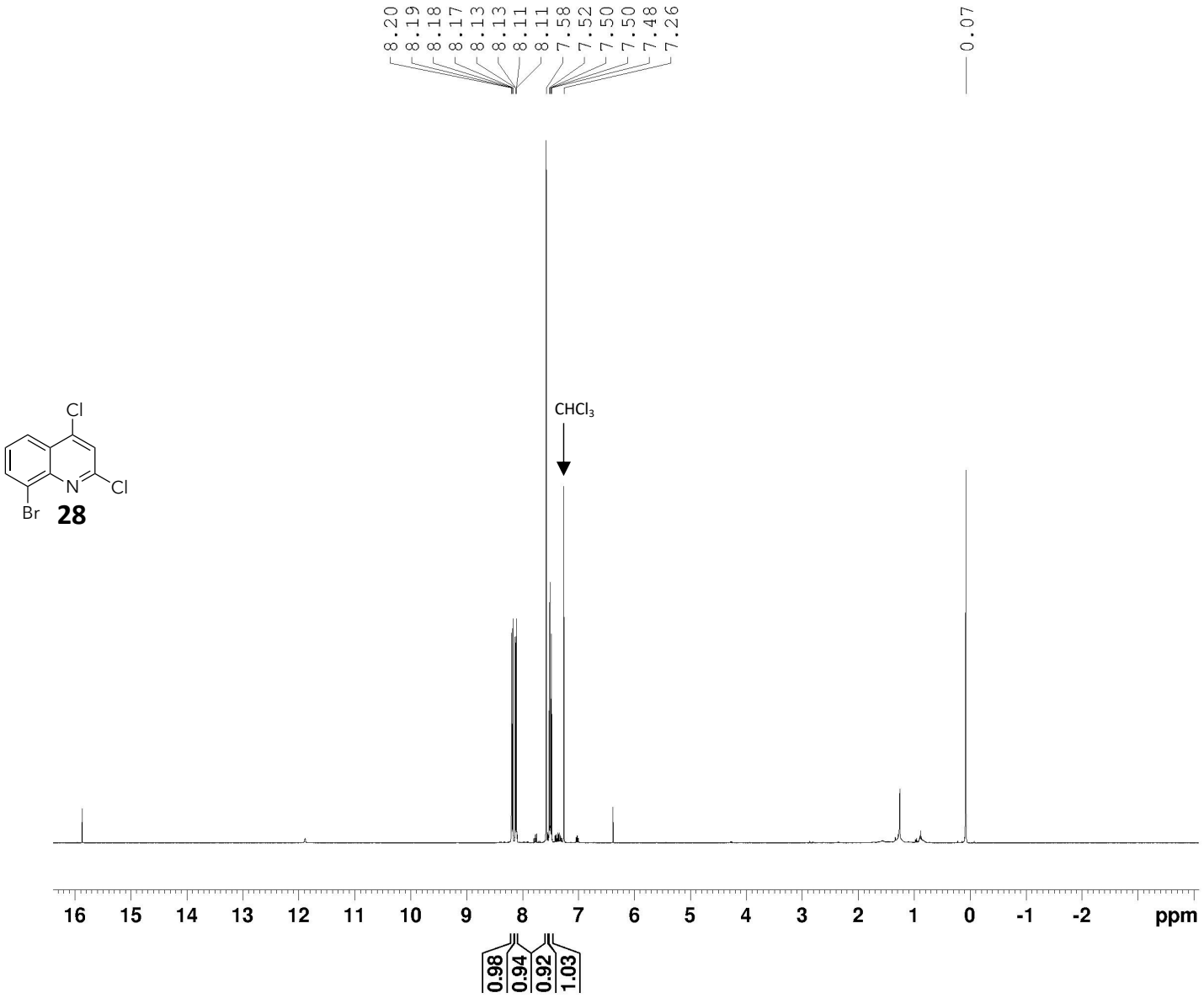


S25c

```
Current Data Parameters
NAME         JPN-1-187-2
EXPNO                 18
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211120
Time                3.44 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG           zgflqn
TD                131072
SOLVENT             CDCl3
NS                     16
DS                      4
SWH          113636.367 Hz
FIDRES         1.733953 Hz
AQ            0.5767168 sec
RG                 15.61
DW                 4.400 usec
DE                 18.00 usec
TE                 298.0 K
D1           1.00000000 sec
TD0                    1
SFO1         470.6394024 MHz
NUC1                19F
P1                 15.00 usec
PLW1        11.70800018 W

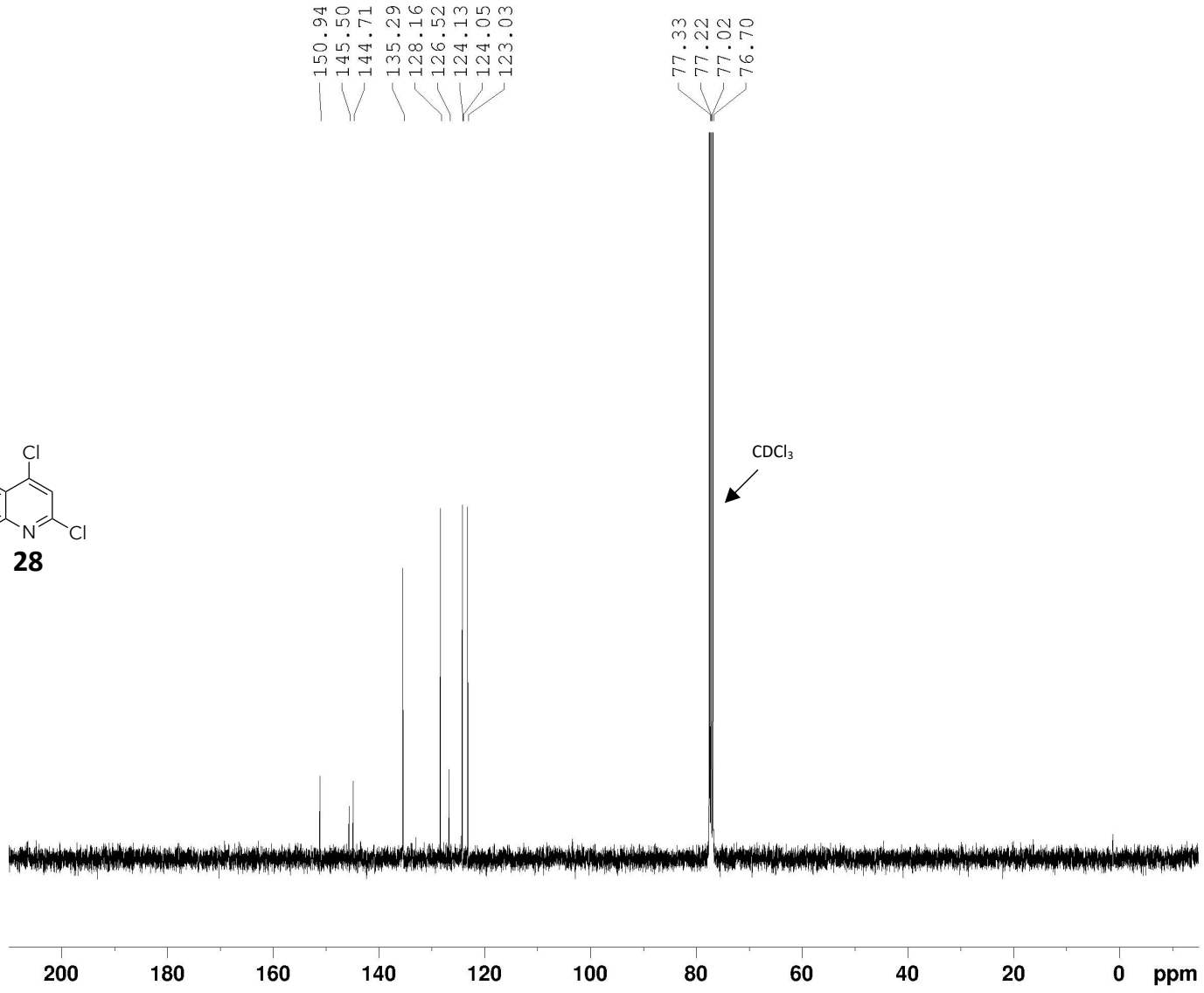
F2 - Processing parameters
SI                 65536
SF           470.6864712 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME          NL-1-117-1H
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211208
Time               14.16 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9976959 sec
RG                   101
DW                61.000 usec
DE                13.89 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1          24.03499985 W

F2 - Processing parameters
SI                 65536
SF            400.1300098 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



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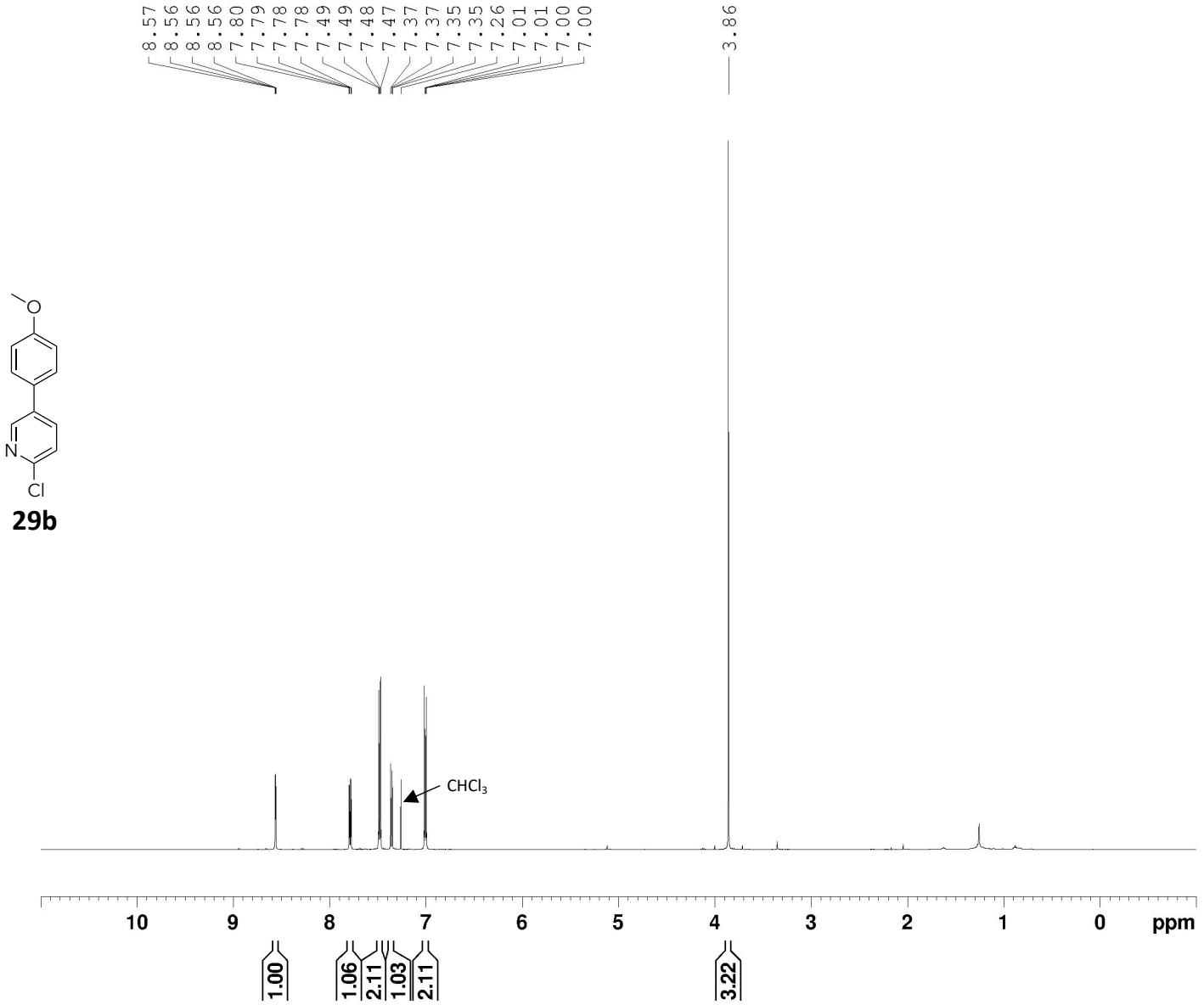
```
Current Data Parameters
NAME                  NL-1-117
EXPNO                       14
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20211127
Time                     14.39 h
INSTRUM              Avance Neo
PROBHD    Z152088_0031 (
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                 23809.523 Hz
FIDRES               0.726609 Hz
AQ                   1.3762560 sec
RG                       8.125
DW                      21.000 usec
DE                       6.50 usec
TE                      298.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                         1
SFO1               100.6228298 MHz
NUC1                       13C
P0                       2.67 usec
P1                       8.00 usec
PLW1                86.55400085 W
SFO2               400.1316005 MHz
NUC2                       1H
CPDPRG[2                waltz65
PCPD2                   90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                         32768
SF                 100.6127505 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                          1.40
```

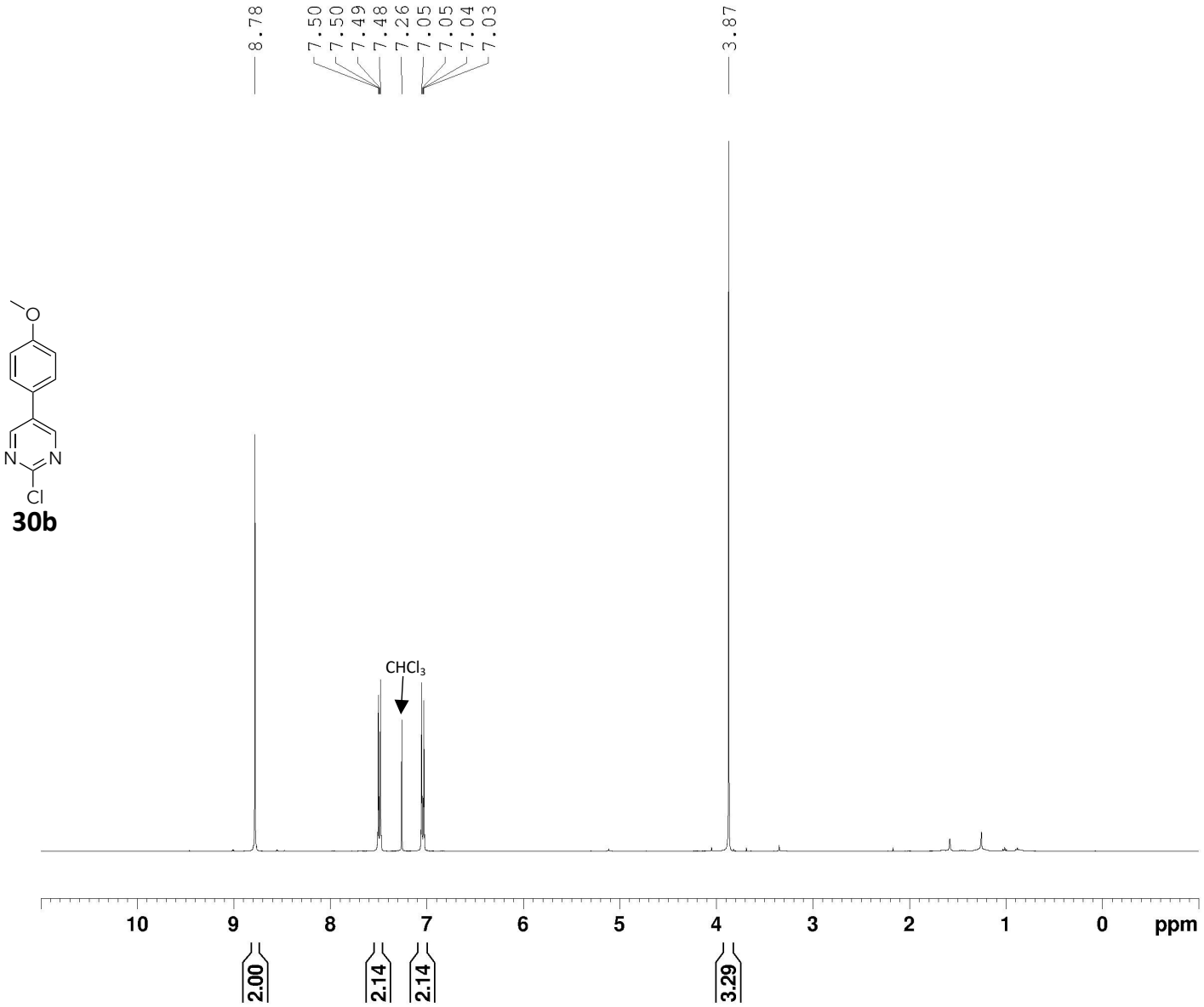


29b

Current Data Parameters
NAME NL-1-189-1-C5
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220317
Time 11.49 h
INSTRUM spect
PROBHD Z125869_0055 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 94.51
DW 50.000 usec
DE 16.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.2330889 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 11.44699955 W

F2 - Processing parameters
SI 65536
SF 500.2300120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

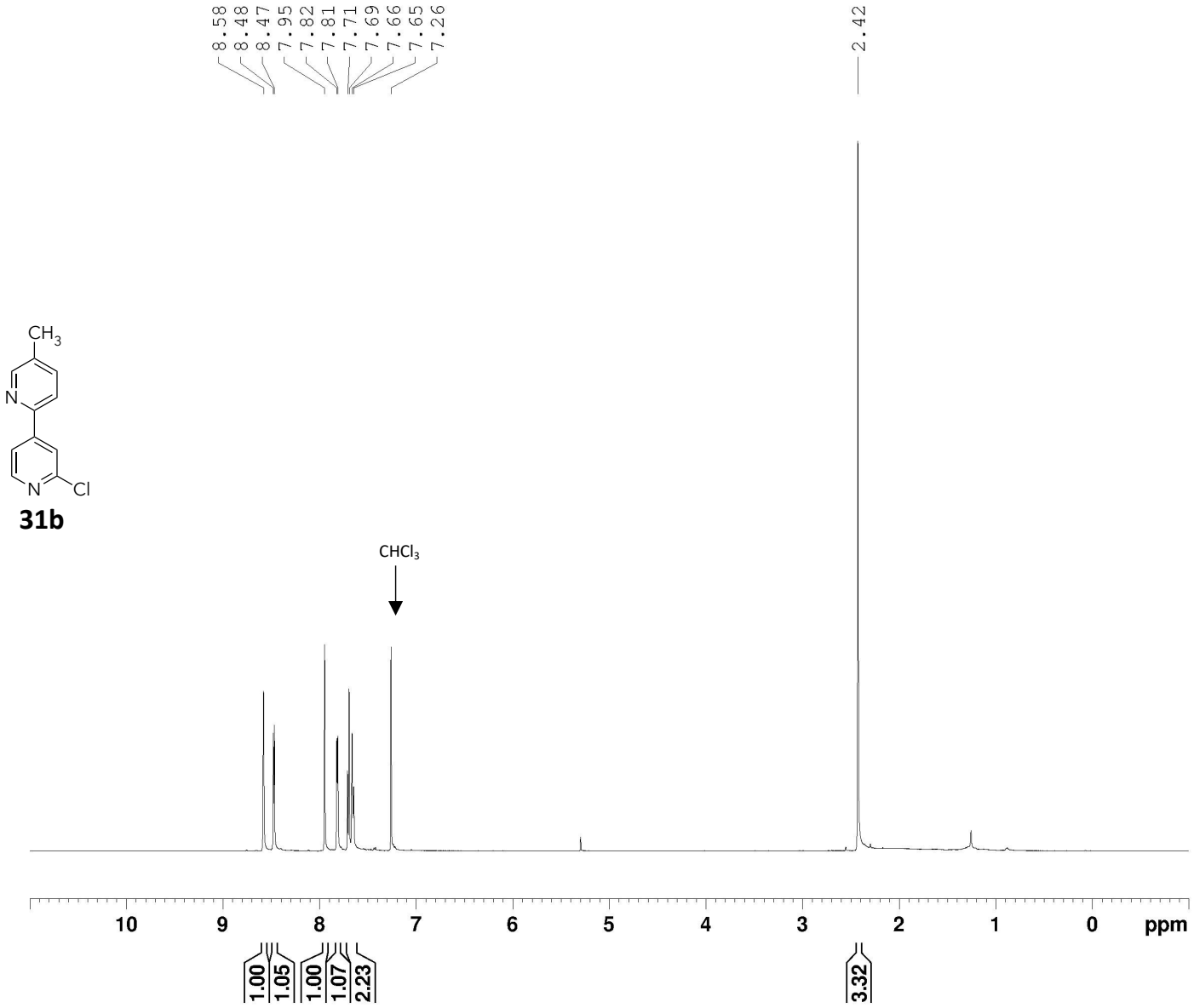


30b

Current Data Parameters
NAME NL-1-190-2-C5
EXPNO 14
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220319
Time 12.27 h
INSTRUM Avance Neo
PROBHD Z152088_0031 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8196.722 Hz
FIDRES 0.250144 Hz
AQ 3.9976959 sec
RG 101
DW 61.000 usec
DE 13.89 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P0 2.67 usec
P1 8.00 usec
PLW1 24.03499985 W

F2 - Processing parameters
SI 65536
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

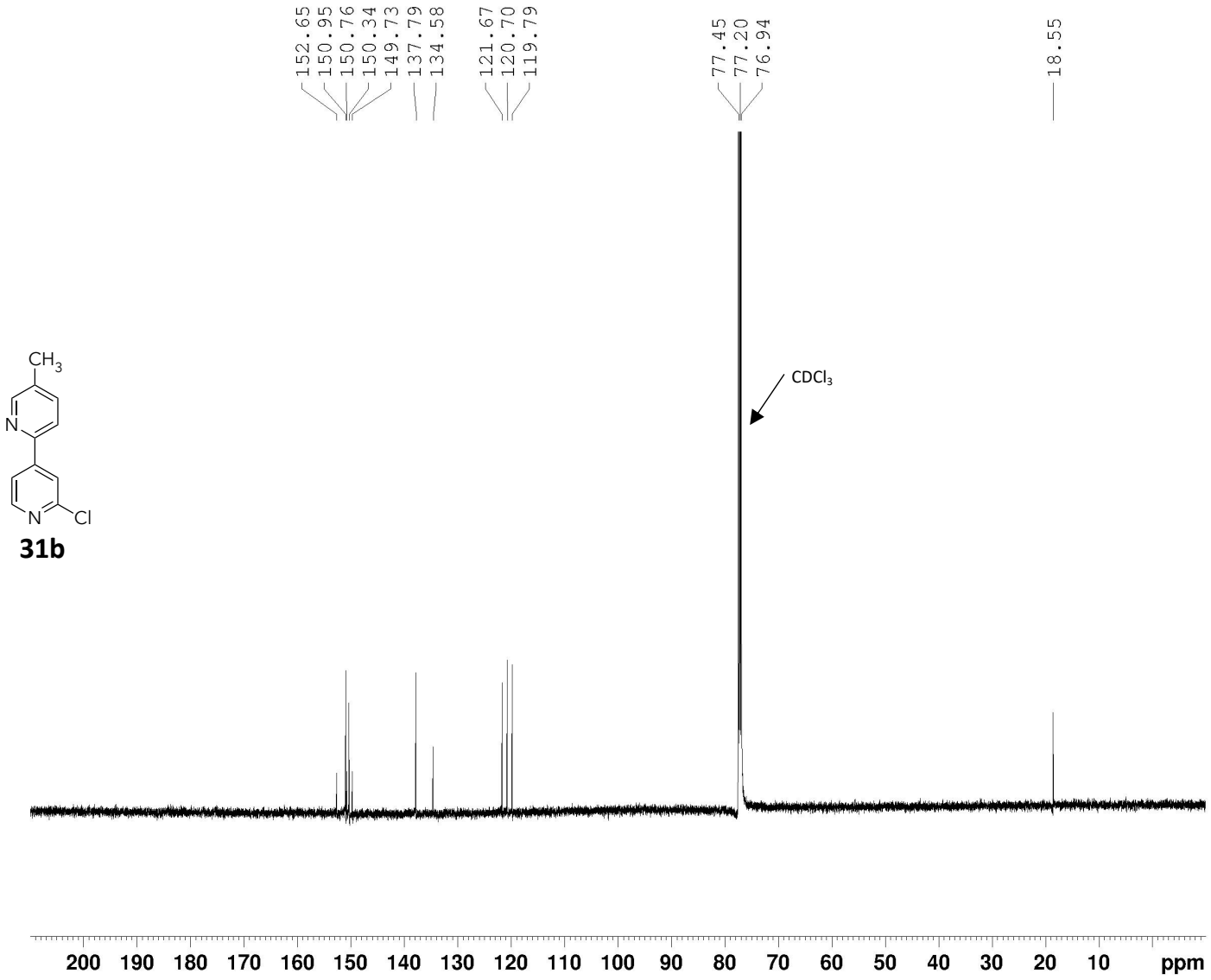


BRUKER

```
Current Data Parameters
NAME                  NL-1-6-2d
EXPNO                        11
PROCNO                        1

F2 - Acquisition Parameters
Date_                 20210701
Time                      17.05 h
INSTRUM                   spect
PROBHD    Z125869_0055 (
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  10000.000 Hz
FIDRES                0.305176 Hz
AQ                    3.2767999 sec
RG                       137.36
DW                       50.000 usec
DE                       16.00 usec
TE                       300.0 K
D1                    1.00000000 sec
TD0                          1
SFO1                500.2330889 MHz
NUC1                        1H
P0                       4.00 usec
P1                      12.00 usec
PLW1                11.44699955 W

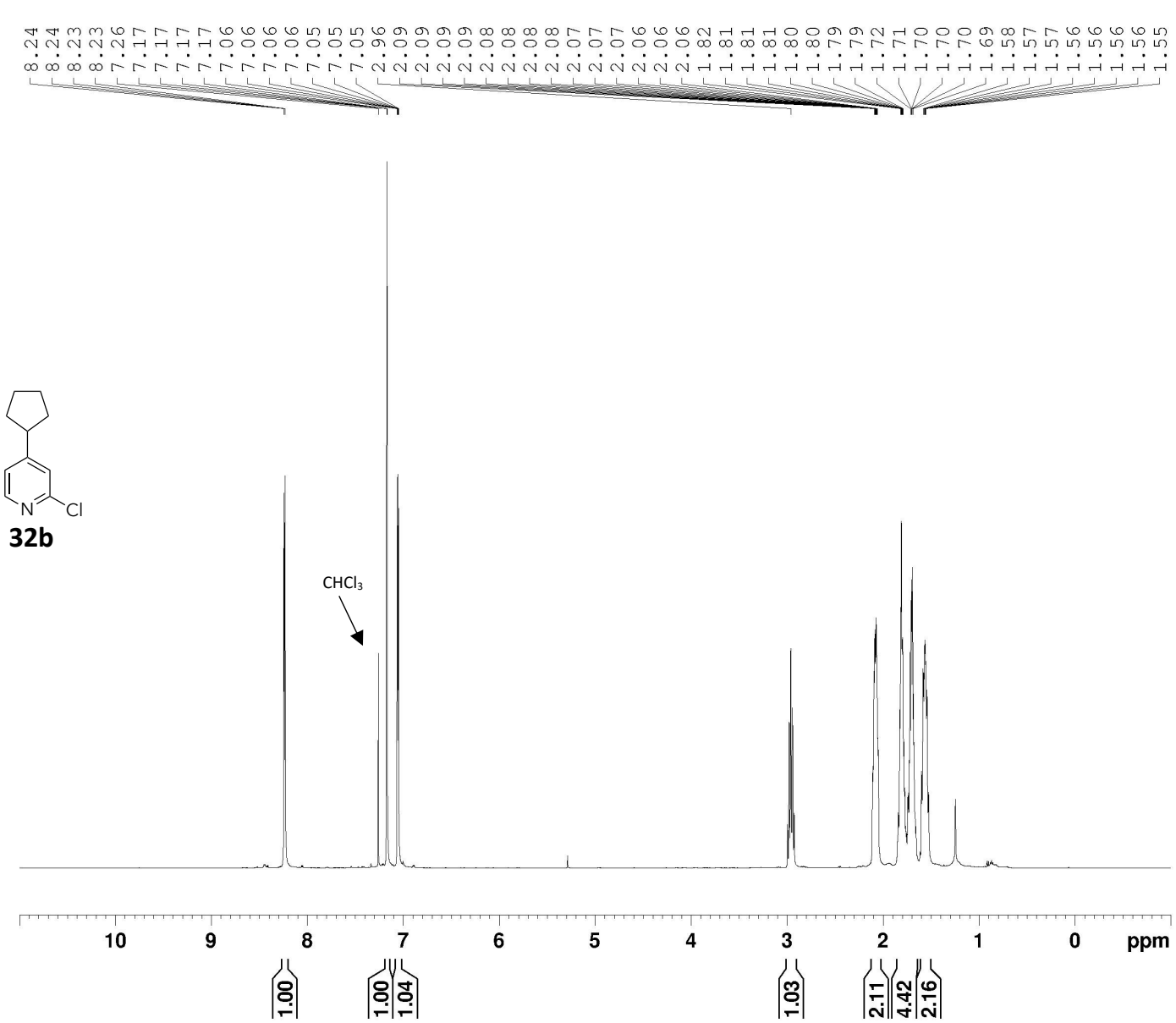
F2 - Processing parameters
SI                       65536
SF                  500.2300121 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```




```
Current Data Parameters
NAME        NL-1-6-13Cx2
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211028
Time               23.54 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.44
DW               16.800 usec
DE               18.00 usec
TE               298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7955118 MHz
NUC1                13C
P0                3.33 usec
P1               10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

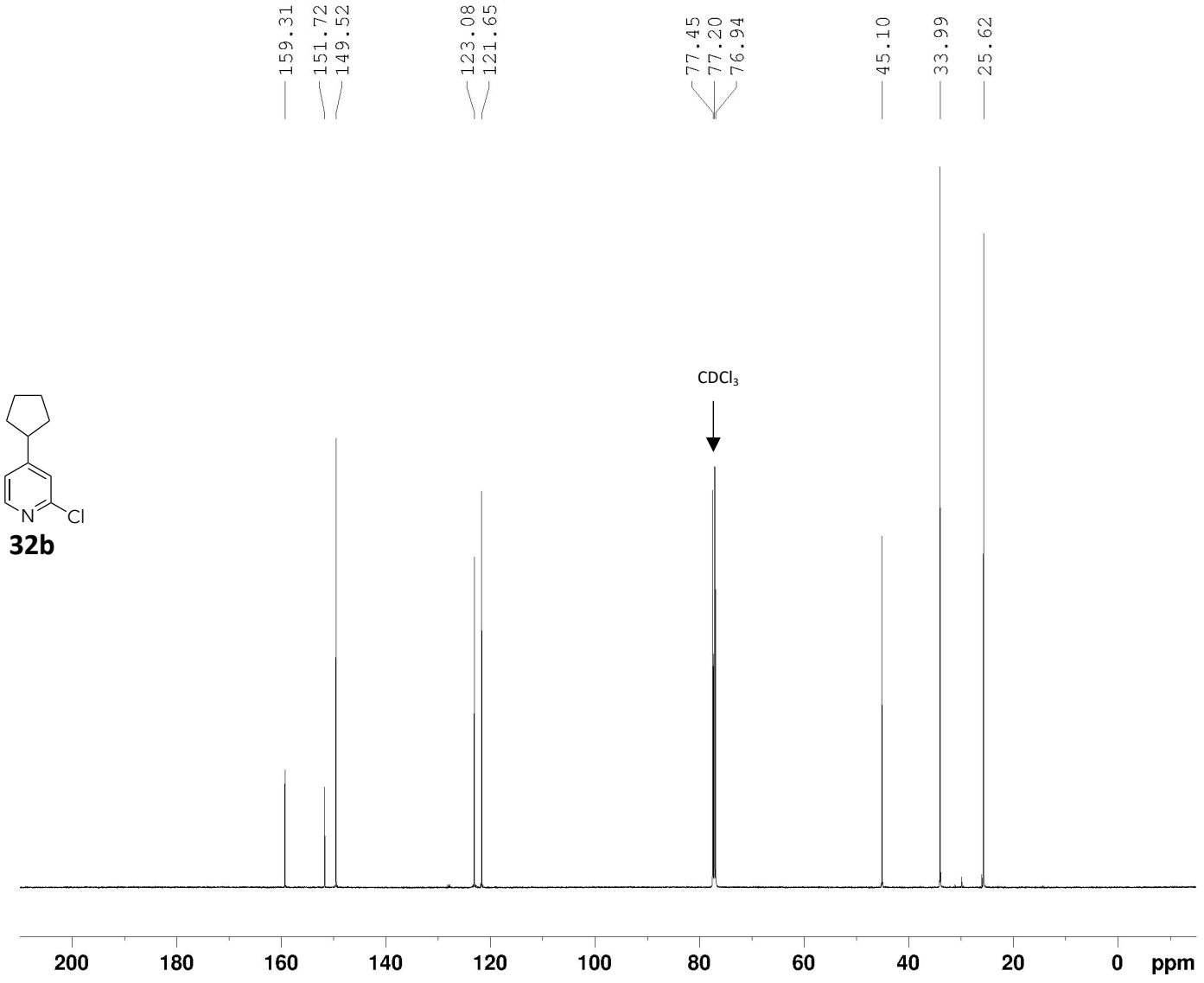
F2 - Processing parameters
SI                32768
SF          125.7829104 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



Current Data Parameters
NAME NL-1-73-C4-1H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210621
Time 13.29 h
INSTRUM spect
PROBHD Z125869_0055 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 37.93
DW 50.000 usec
DE 16.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.2330889 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 11.44699955 W

F2 - Processing parameters
SI 65536
SF 500.2300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 5.00

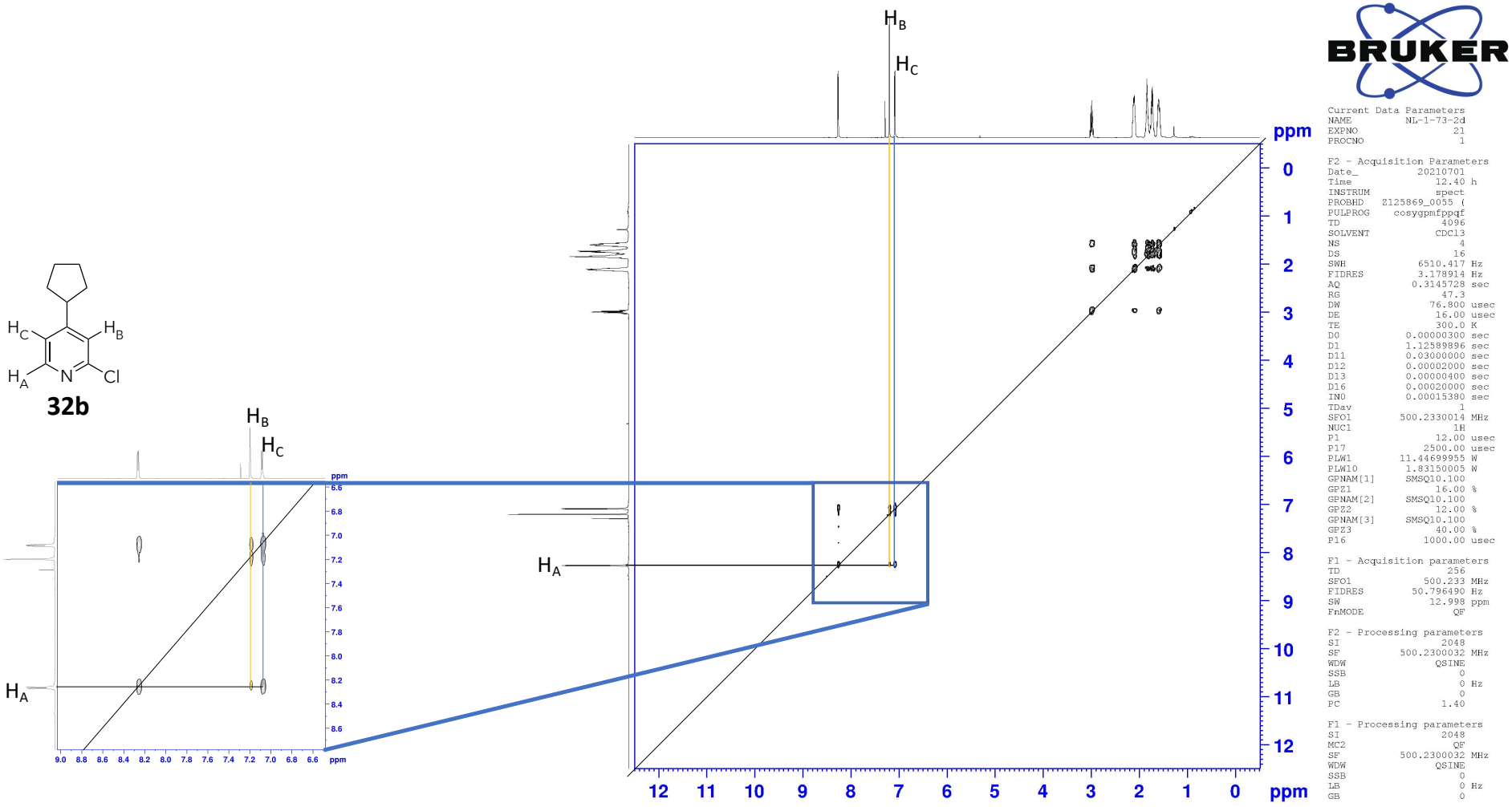



```
Current Data Parameters
NAME          NL-1-73-2d
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210701
Time               12.39 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1         125.7955118 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

F2 - Processing parameters
SI                 32768
SF           125.7829141 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

COSY



32b


```
Current Data Parameters
NAME                  NL-1-73-2d
EXPNO                         21
PROCNO                         1

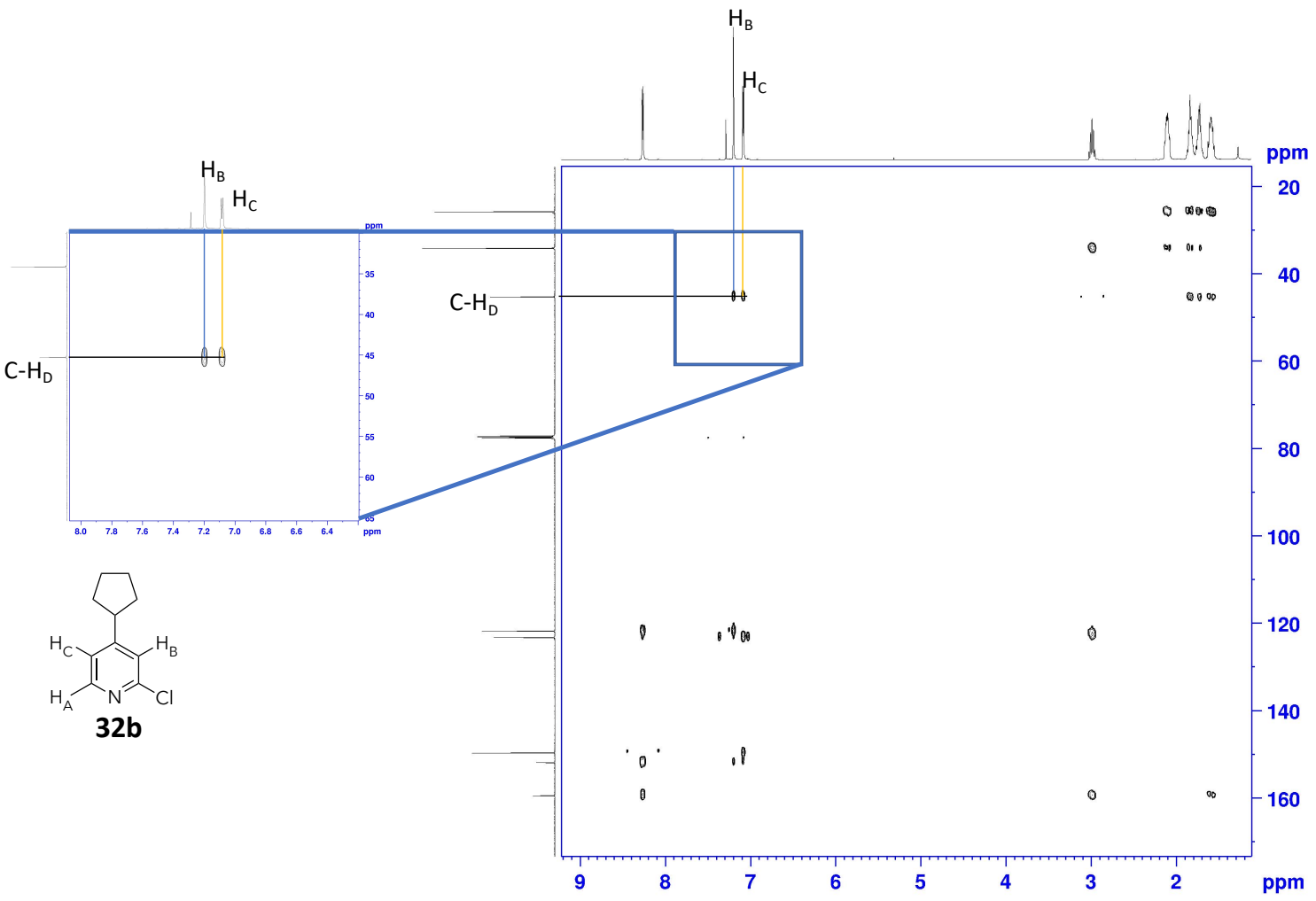
F2 - Acquisition Parameters
Date_                   20210701
Time                       12.40 h
INSTRUM                    spect
PROBHD     Z125869_0055 (
PULPROG      cosygpmfppqf
TD                         4096
SOLVENT                  CDCl3
NS                             4
DS                            16
SWH                    6510.417 Hz
FIDRES                 3.178914 Hz
AQ                     0.3145728 sec
RG                          47.3
DW                        76.800 usec
DE                        16.00 usec
TE                        300.0 K
D0                     0.00000300 sec
D1                     1.12589896 sec
D11                    0.03000000 sec
D12                    0.00002000 sec
D13                    0.00000400 sec
D16                    0.00020000 sec
IN0                    0.00015380 sec
TDav                           1
SFO1                500.2330014 MHz
NUC1                        1H
P1                        12.00 usec
P17                     2500.00 usec
PLW1                11.44699955 W
PLW10                1.83150005 W
GPNAM[1]              SMSQ10.100
GPZ1                      16.00 %
GPNAM[2]              SMSQ10.100
GPZ2                      12.00 %
GPNAM[3]              SMSQ10.100
GPZ3                      40.00 %
P16                     1000.00 usec

F1 - Acquisition parameters
TD                           256
SFO1                 500.233 MHz
FIDRES              50.796490 Hz
SW                      12.998 ppm
FnMODE                      QF

F2 - Processing parameters
SI                          2048
SF                500.2300032 MHz
WDW                       QSINE
SSB                           0
LB                            0 Hz
GB                            0
PC                         1.40

F1 - Processing parameters
SI                          2048
MC2                         QF
SF                500.2300032 MHz
WDW                       QSINE
SSB                           0
LB                            0 Hz
GB                            0
```

HMBC



32b

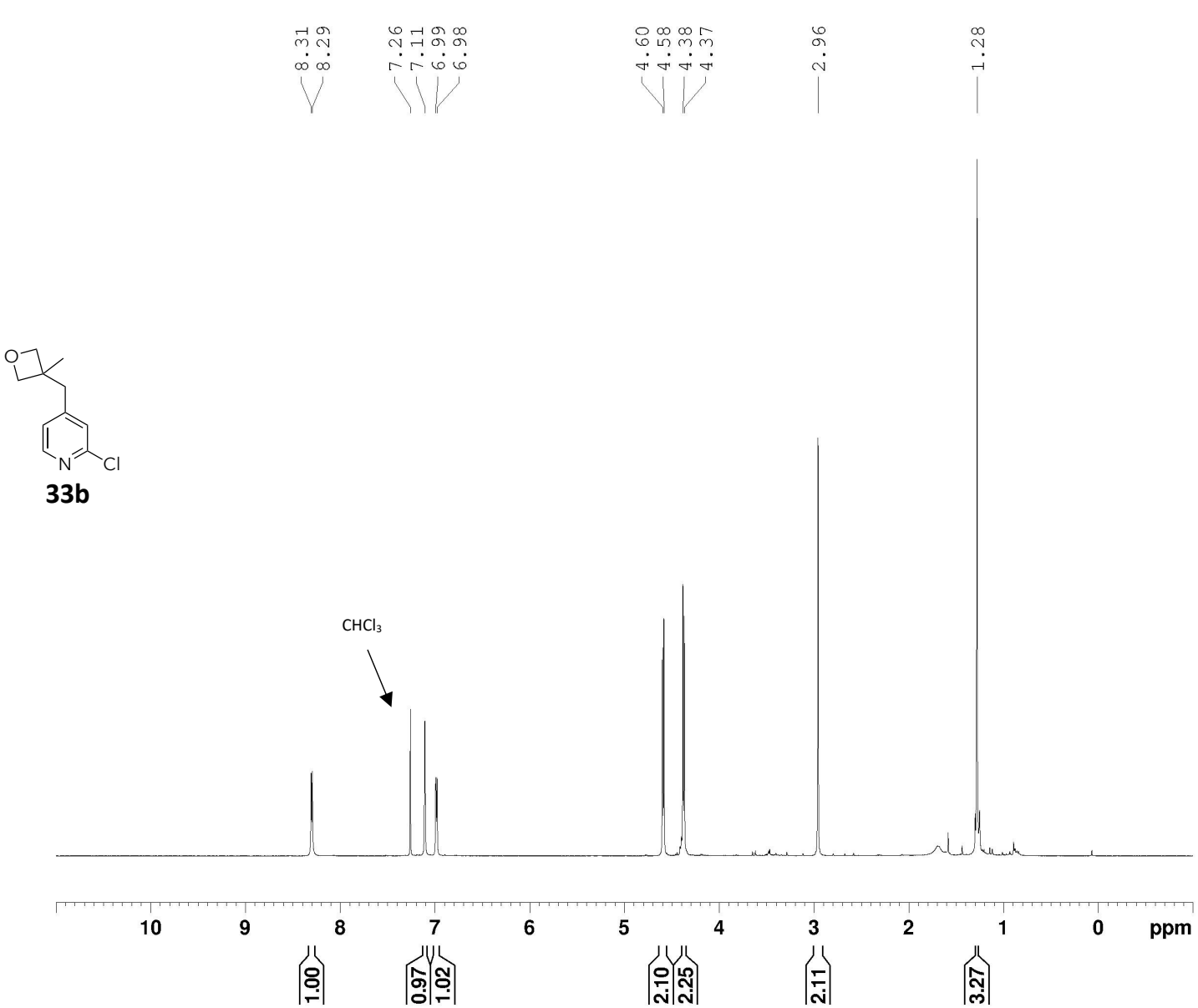
```
Current Data Parameters
NAME                  NL-1-73-2d
EXPNO                         23
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210701
Time                       13.09 h
INSTRUM                     spect
PROBHD    Z125869_0055 (
PULPROG      hmbcgplpndqf
TD                          2048
SOLVENT                   CDCl3
NS                             4
DS                            16
SWH                     4716.981 Hz
FIDRES                  4.606427 Hz
AQ                      0.2170880 sec
RG                        190.44
DW                        106.000 usec
DE                         16.00 usec
TE                         300.0 K
CNST2                145.0000000
CNST13                10.0000000
D0                     0.00000300 sec
D1                     1.50000000 sec
D2                     0.00344828 sec
D6                     0.05000000 sec
D16                    0.00020000 sec
IN0                    0.00001810 sec
TDav                           1
SFO1                500.2322599 MHz
NUC1                         1H
P1                         12.00 usec
P2                         24.00 usec
PLW1                11.44699955 W
SFO2                125.7955118 MHz
NUC2                        13C
P3                         10.00 usec
PLW2                56.90299988 W
GPNAM[1]             SMSQ10.100
GPZ1                       50.00 %
GPNAM[2]             SMSQ10.100
GPZ2                       30.00 %
GPNAM[3]             SMSQ10.100
GPZ3                       40.10 %
P16                      1000.00 usec

F1 - Acquisition parameters
TD                           128
SFO1                125.7955 MHz
FIDRES              431.629822 Hz
SW                      219.597 ppm
FnMODE                      QF

F2 - Processing parameters
SI                          2048
SF                  500.2299980 MHz
WDW                        SINE
SSB                           0
LB                            0 Hz
GB                            0
PC                         1.40

F1 - Processing parameters
SI                          1024
MC2                         QF
SF                  125.7828890 MHz
WDW                        SINE
SSB                           0
LB                            0 Hz
GB                            0
```

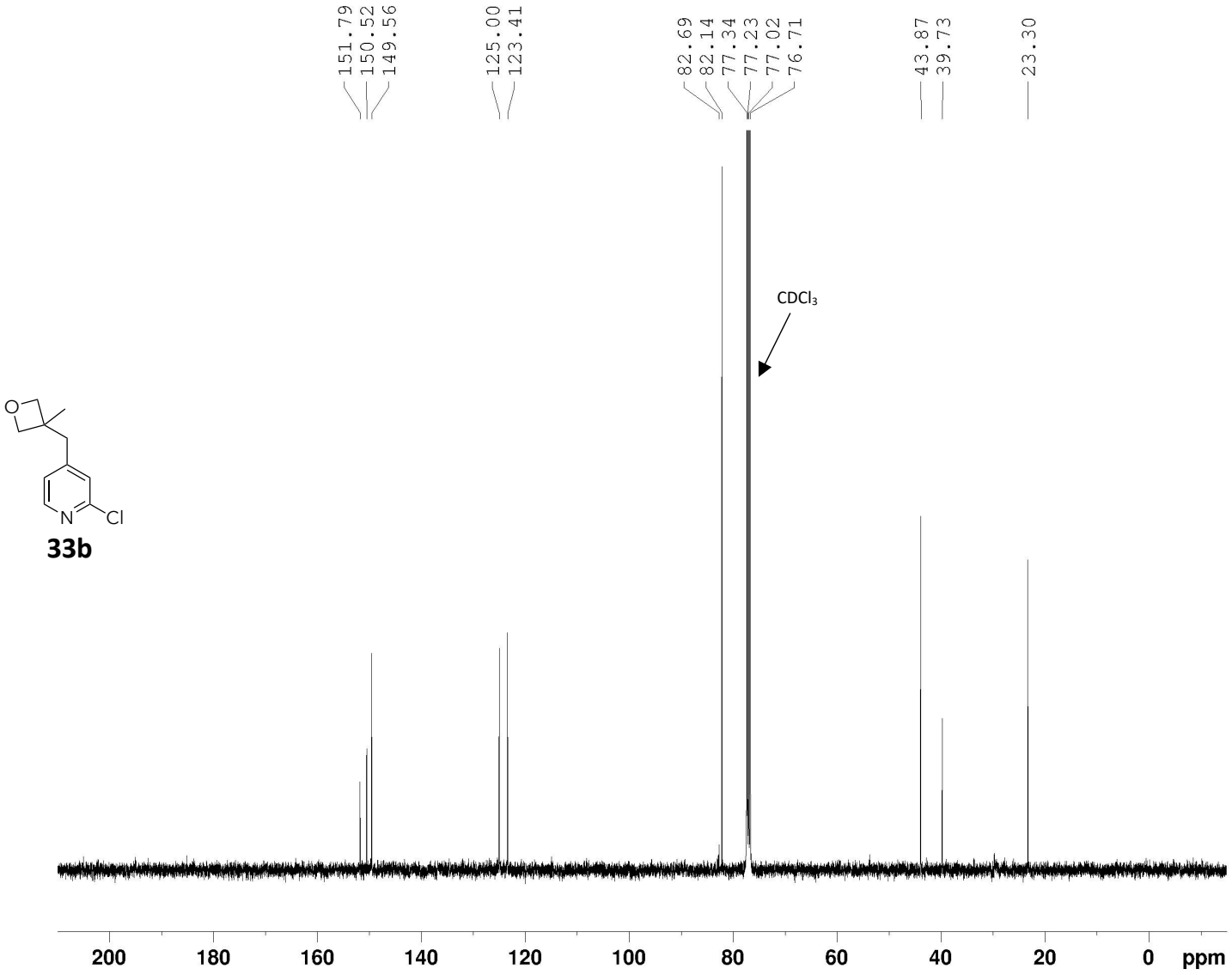


33b

```
Current Data Parameters
NAME      NL-1-89-incconc
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210729
Time               18.10 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9976959 sec
RG                   101
DW                61.000 usec
DE                13.89 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1
SFO1        400.1324708 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1        24.03499985 W

F2 - Processing parameters
SI                 65536
SF          400.1300099 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

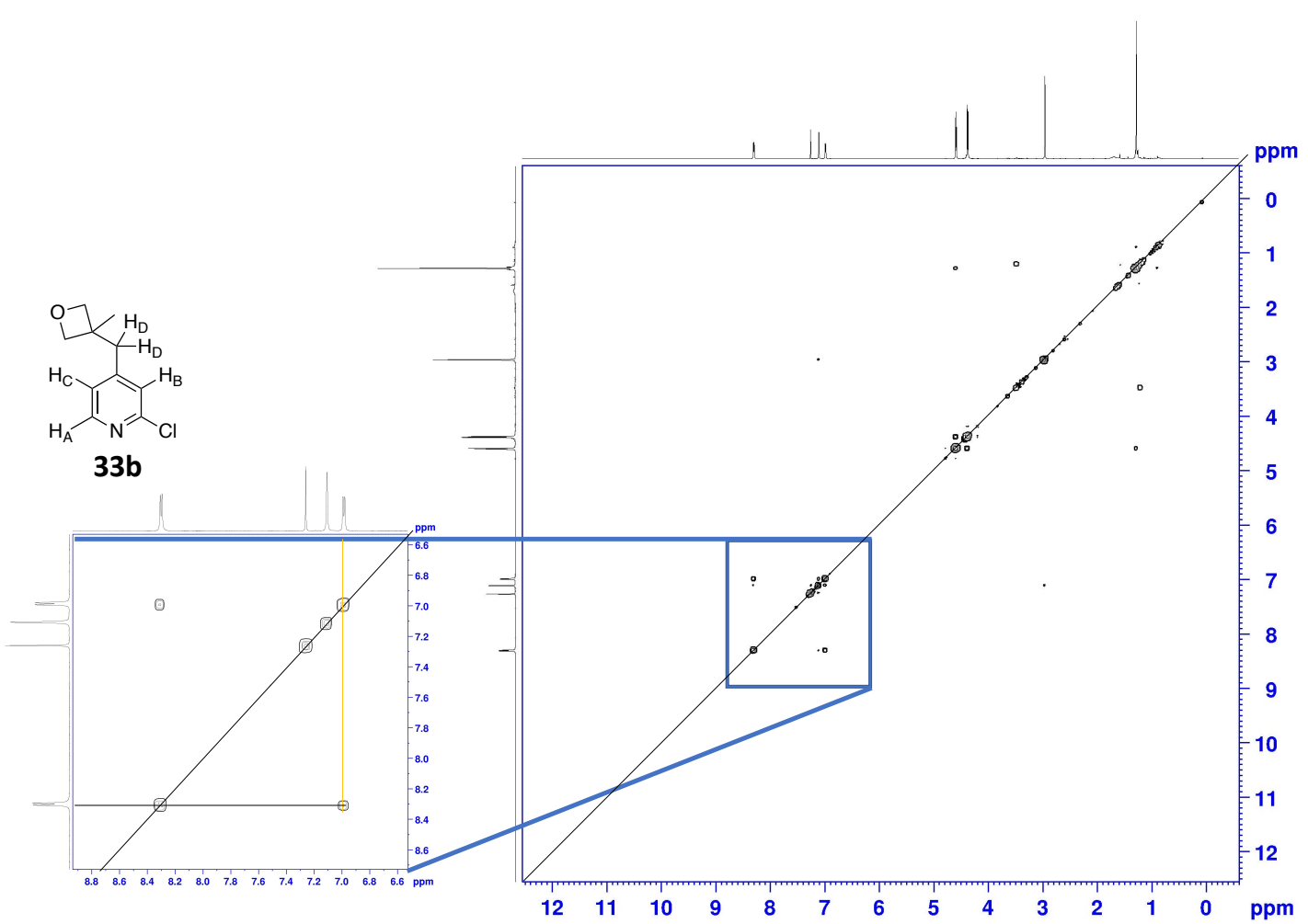


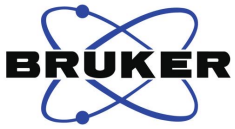
Current Data Parameters
NAME NL-1-89-incconc
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210729
Time 19.12 h
INSTRUM Avance Neo
PROBHD Z152088_0031 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 1.3762560 sec
RG 8.125
DW 21.000 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 86.55400085 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 90.00 usec
PLW2 24.03499985 W
PLW12 0.18990999 W
PLW13 0.09552100 W

F2 - Processing parameters
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

COSY






```
Current Data Parameters
NAME                  NL-1-89d-1H
EXPNO                          13
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20210727
Time                        19.20 h
INSTRUM                Avance Neo
PROBHD    Z152088_0031 (
PULPROG                cosygpppqf
TD                            2048
SOLVENT                    CDCl3
NS                               8
DS                              16
SWH                      5263.158 Hz
FIDRES                   5.139802 Hz
AQ                       0.1945600 sec
RG                             101
DW                          95.000 usec
DE                           6.50 usec
TE                          298.1 K
D0                    0.00000300 sec
D1                    2.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec
D13                   0.00000400 sec
D16                   0.00020000 sec
IN0                   0.00019000 sec
TDav                            1
SFO1                400.1324008 MHz
NUC1                           1H
P0                           8.00 usec
P1                           8.00 usec
P17                       2500.00 usec
PLW1                24.03499985 W
PLW10                1.70920002 W
GPNAM[1]            SMSQ10.100
GPZ1                        10.00 %
P16                       1000.00 usec

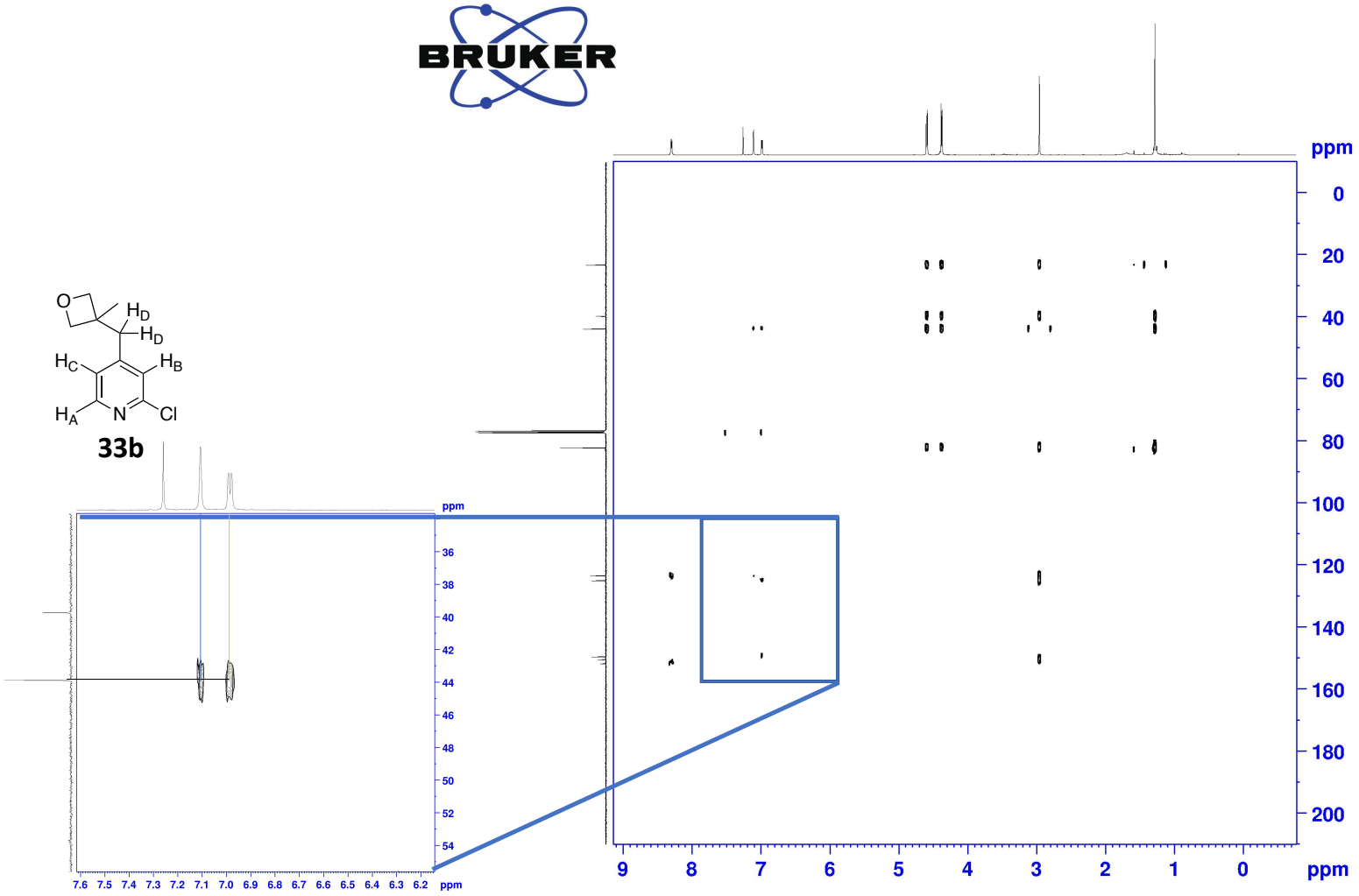
======== F1 INDIRECT DIMENSION ========
td1             128
sw_F1       13.153541

F1 - Acquisition parameters
TD                            128
SFO1                    400.1324 MHz
FIDRES                 82.236839 Hz
SW                         13.154 ppm
FnMODE                          QF

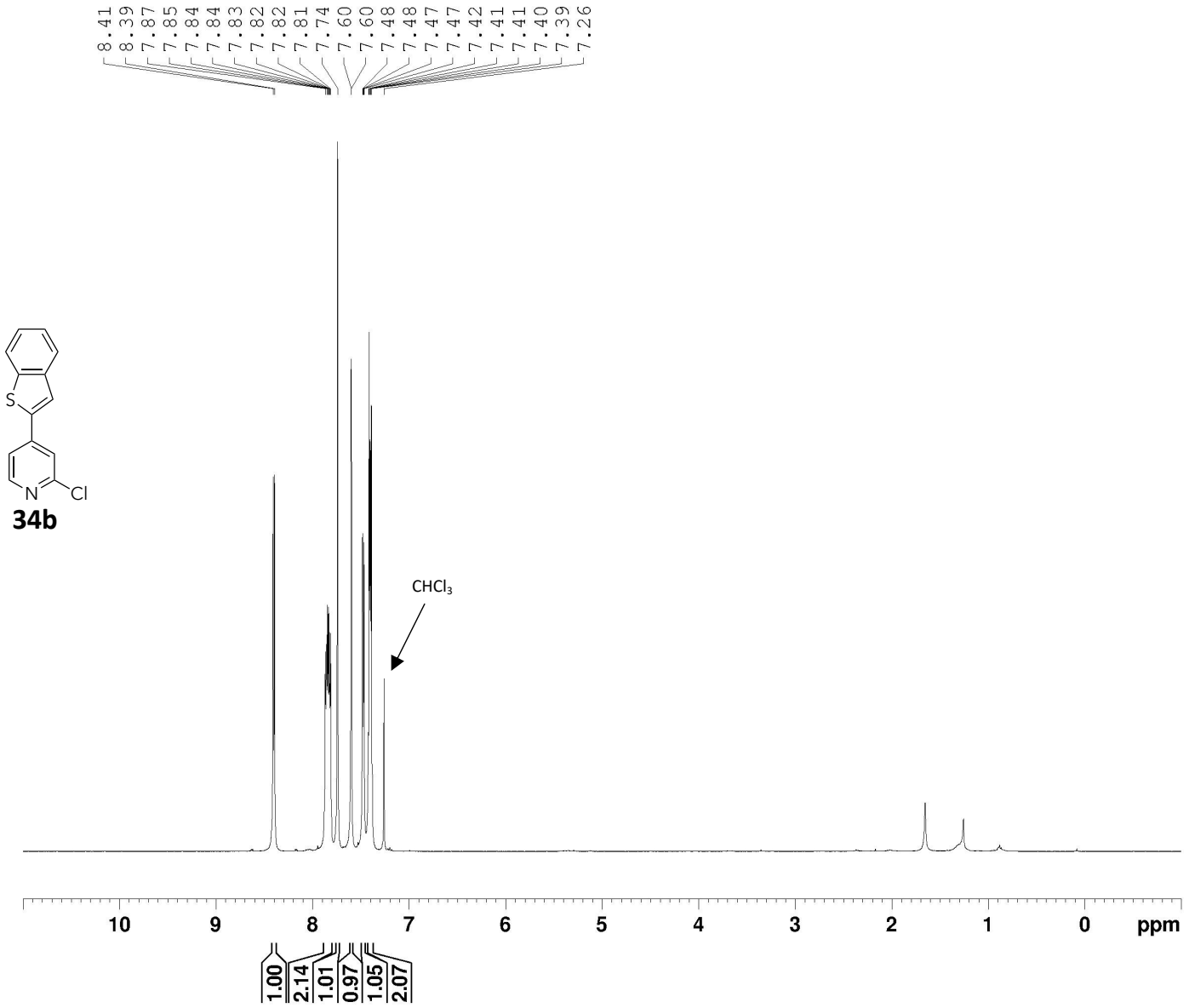
F2 - Processing parameters
SI                            1024
SF                  400.1300096 MHz
WDW                        QSINE
SSB                             0
LB                              0 Hz
GB                              0
PC                           1.40

F1 - Processing parameters
SI                            1024
MC2                             QF
SF                  400.1300099 MHz
WDW                        QSINE
SSB                             0
LB                              0 Hz
GB                              0
```

HMBC




```
Current Data Parameters
NAME      NL-1-89-incconc
F2 - Acquisition Parameters
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG     hmbcgplpndqf
TD                  4096
SOLVENT             CDCl3
NS                     4
DS                    16
SWH             3968.254 Hz
FIDRES          1.937624 Hz
AQ             0.5160960 sec
RG                   101
DW               126.000 usec
DE                 6.50 usec
TE                298.2 K
CNST2         145.0000000
CNST13         10.0000000
D0              0.00000300 sec
D1              1.50000000 sec
D2              0.00344828 sec
D6              0.05000000 sec
D16             0.00020000 sec
IN0             0.00002259 sec
TDav                    1
SFO1          400.1316847 MHz
NUC1                   1H
P1                  8.00 usec
P2                 16.00 usec
PLW1          24.03499985 W
SFO2          100.6228298 MHz
NUC2                  13C
P3                  8.00 usec
PLW2          86.55400085 W
GPNAM[1]       SMSQ10.100
GPZ1                50.00 %
GPNAM[2]       SMSQ10.100
GPZ2                30.00 %
GPNAM[3]       SMSQ10.100
GPZ3                40.10 %
P16               1000.00 usec
======== F1 INDIRECT DIMENSION =
td1       128
sw_F1     220.000000
F1 - Acquisition parameters
TD                  128
SFO1            100.6228 MHz
FIDRES        345.877136 Hz
SW              219.991 ppm
FnMODE                QF
```

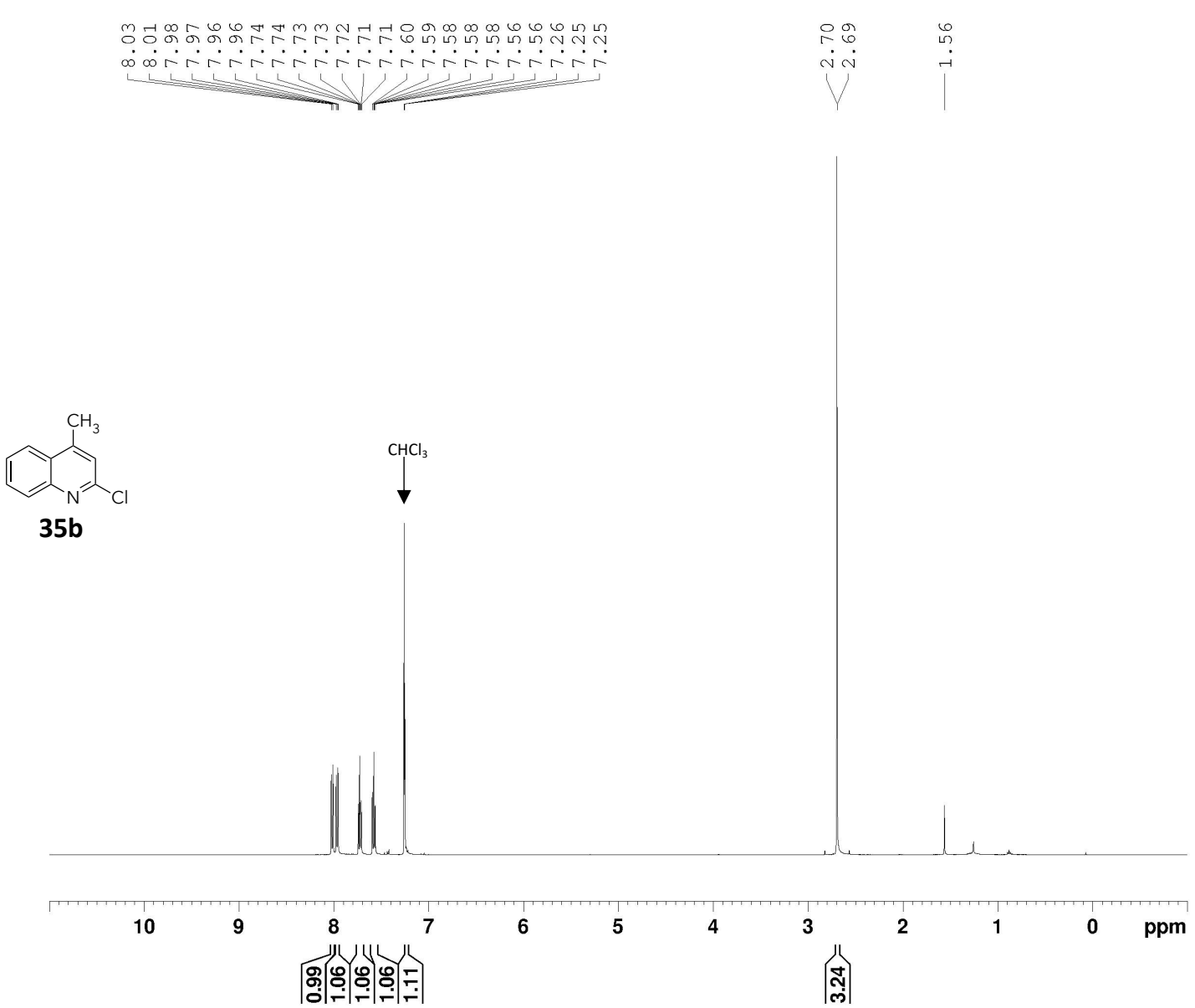


BRUKER

```
Current Data Parameters
NAME          NL-1-38-C4+
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210501
Time               14.01 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9976959 sec
RG                   101
DW                61.000 usec
DE                13.89 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1          24.03499985 W

F2 - Processing parameters
SI                 65536
SF          400.1300100 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                 10.00
```

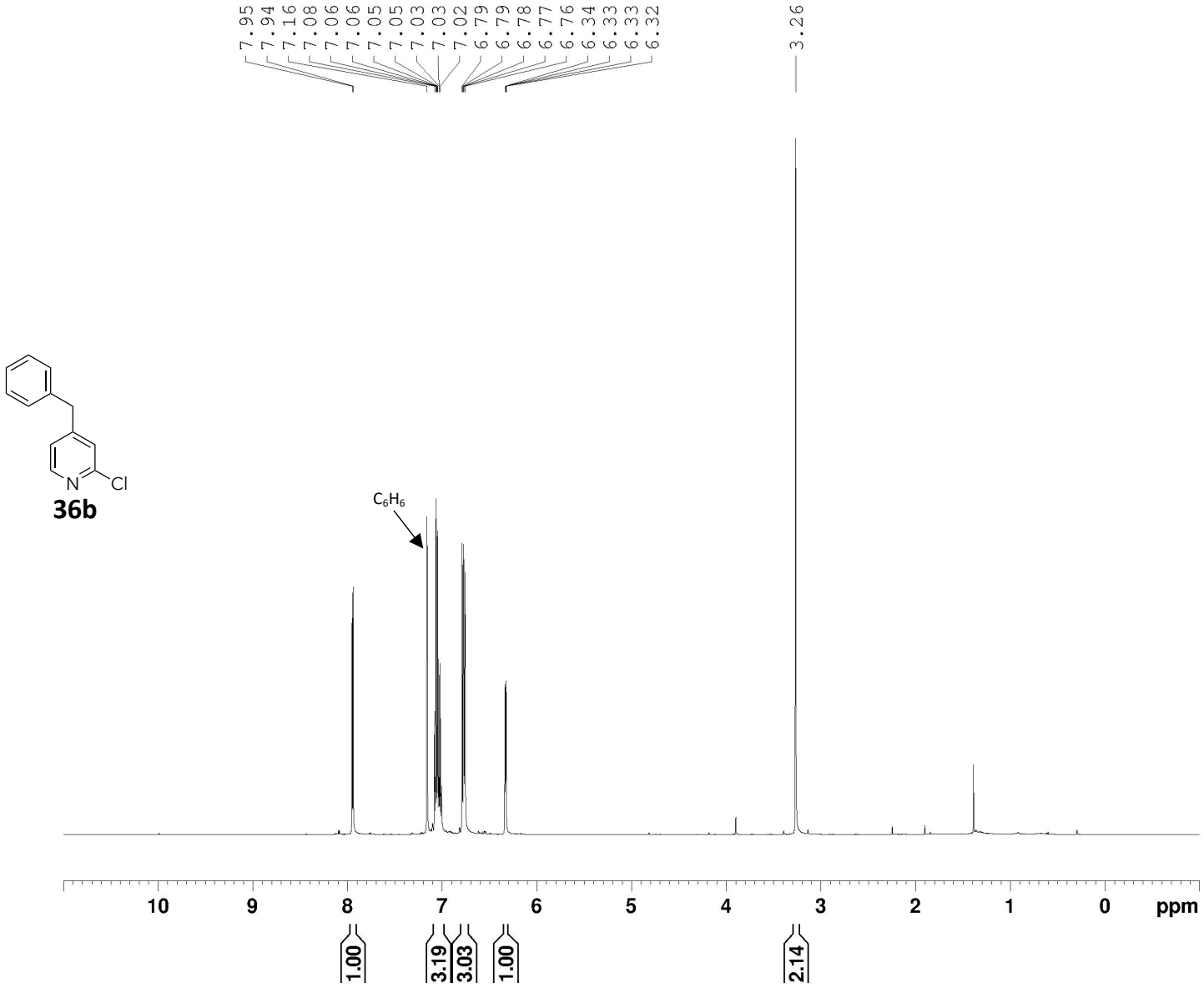


BRUKER

```
Current Data Parameters
NAME          NL-1-75-1H
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211028
Time               14.50 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            10000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                151.18
DW                 50.000 usec
DE                 16.00 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1         500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                 12.00 usec
PLW1         11.44699955 W

F2 - Processing parameters
SI                 65536
SF           500.2300122 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```

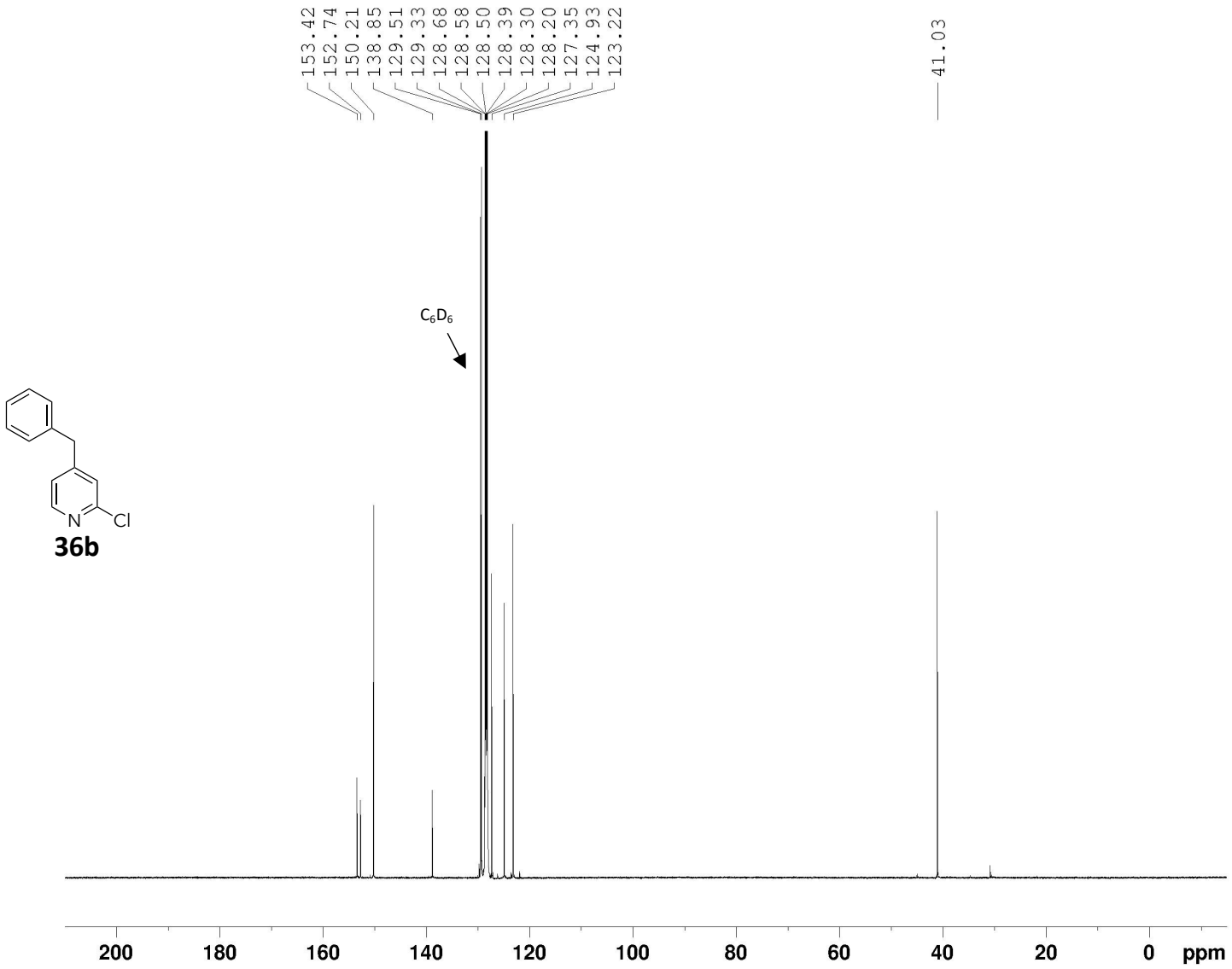


BRUKER

```
Current Data Parameters
NAME      NL-1-61-C4-1H-benzene
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameters
Date_              20210624
Time                 14.01 h
INSTRUM              spect
PROBHD    Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                     64
DS                      2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                  43.72
DW                 50.000 usec
DE                 16.00 usec
TE                 300.0 K
D1             2.00000000 sec
TD0                     1
SFO1          500.2330889 MHz
NUC1                   1H
P0                  4.00 usec
P1                 12.00 usec
PLW1          11.44699955 W

F2 - Processing parameters
SI                  65536
SF            500.2299949 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



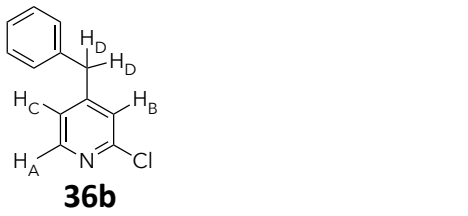
BRUKER

```
Current Data Parameters
NAME       NL-1-61-C4-2d
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210701
Time              18.21 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT            C6D6
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.44
DW               16.800 usec
DE               18.00 usec
TE               300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7955118 MHz
NUC1                13C
P0                3.33 usec
P1               10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

F2 - Processing parameters
SI                32768
SF          125.7828447 MHz
WDW                EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```

COSY



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```
Current Data Parameters
NAME          NL-1-61-C4-2d
EXPNO                    13
PROCNO                    1

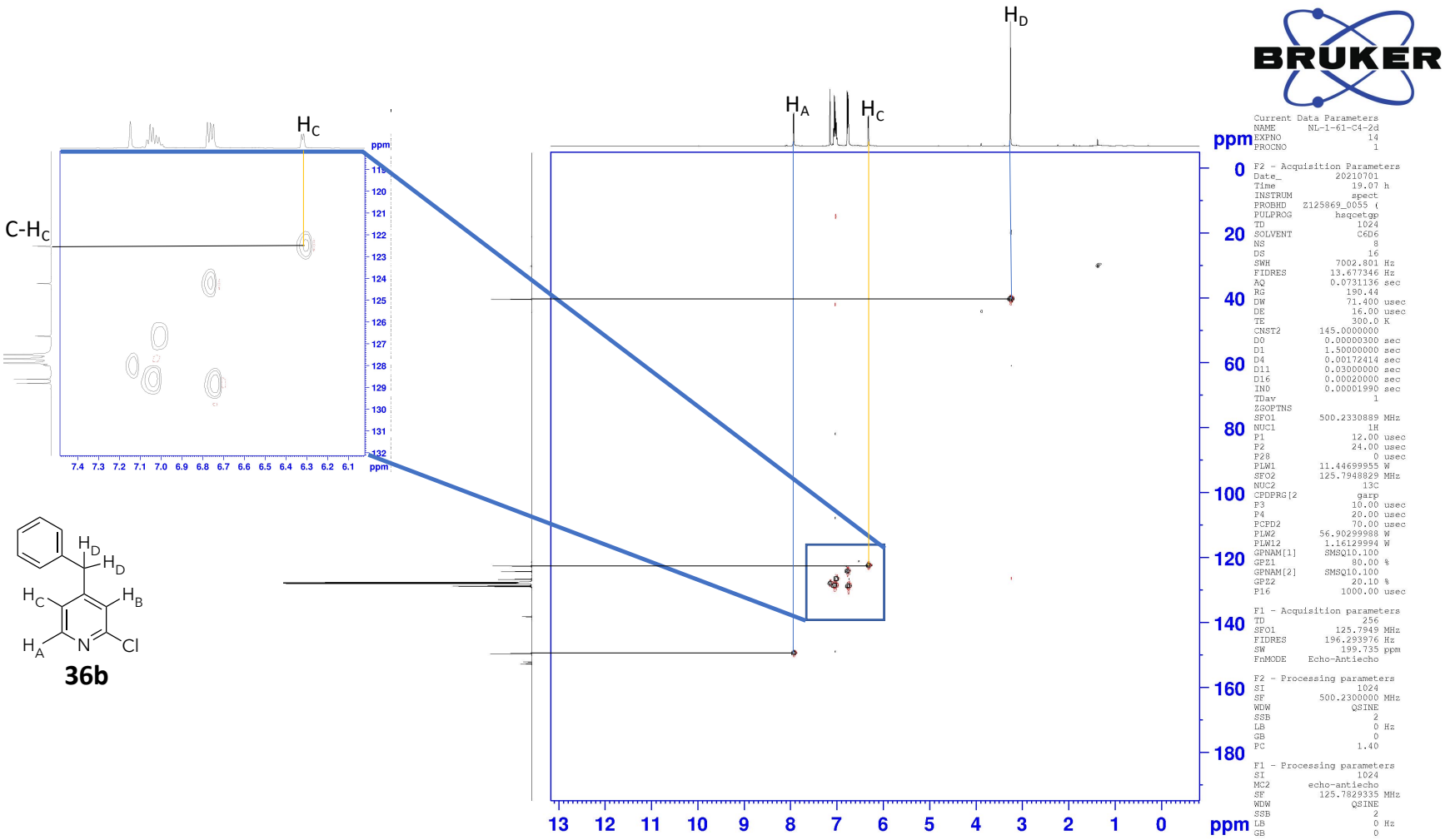
F2 - Acquisition Parameters
Date_              20210701
Time                 18.40 h
INSTRUM              spect
PROBHD    Z125869_0055 (
PULPROG     cosygpmfppqf
TD                   4096
SOLVENT              C6D6
NS                      4
DS                     16
SWH               6510.417 Hz
FIDRES            3.178914 Hz
AQ                0.3145728 sec
RG                    53.13
DW                  76.800 usec
DE                  16.00 usec
TE                  300.0 K
D0                0.00000300 sec
D1                1.12589896 sec
D11               0.03000000 sec
D12               0.00002000 sec
D13               0.00000400 sec
D16               0.00020000 sec
IN0               0.00015380 sec
TDav                     1
SFO1          500.2330014 MHz
NUC1                    1H
P1                  12.00 usec
P17               2500.00 usec
PLW1          11.44699955 W
PLW10          1.83150005 W
GPNAM[1]       SMSQ10.100
GPZ1                16.00 %
GPNAM[2]       SMSQ10.100
GPZ2                12.00 %
GPNAM[3]       SMSQ10.100
GPZ3                40.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                     256
SFO1            500.233 MHz
FIDRES         50.796490 Hz
SW                12.998 ppm
FnMODE                 QF

F2 - Processing parameters
SI                    2048
SF            500.2299911 MHz
WDW                 QSINE
SSB                     0
LB                      0 Hz
GB                      0
PC                   1.40

F1 - Processing parameters
SI                    2048
MC2                    QF
SF            500.2299933 MHz
WDW                 QSINE
SSB                     0
LB                      0 Hz
GB                      0
```

HSQC



BRUKER

```
Current Data Parameters
NAME        NL-1-61-C4-2d
EXPNO                 14
PROCNO                 1

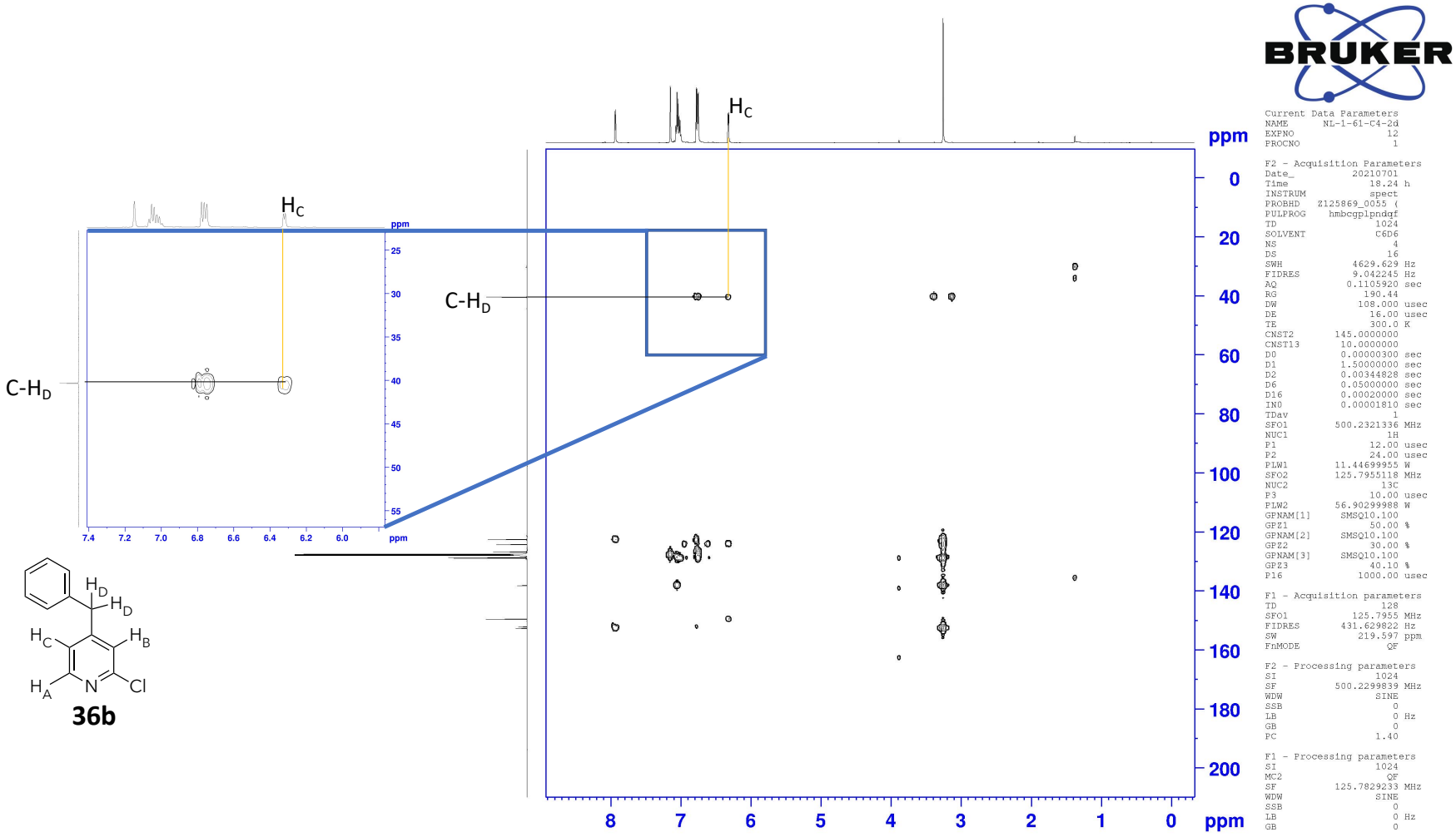
F2 - Acquisition Parameters
Date_           20210701
Time              19.07 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG         hsqcetgp
TD                 1024
SOLVENT             C6D6
NS                     8
DS                    16
SWH             7002.801 Hz
FIDRES         13.677346 Hz
AQ              0.0731136 sec
RG                190.44
DW                71.400 usec
DE                16.00 usec
TE                300.0 K
CNST2         145.0000000
D0             0.00000300 sec
D1             1.50000000 sec
D4             0.00172414 sec
D11            0.03000000 sec
D16            0.00020000 sec
IN0            0.00001990 sec
TDav                   1
ZGOPTNS
SFO1          500.2330889 MHz
NUC1                  1H
P1                12.00 usec
P2                24.00 usec
P28                0 usec
PLW1         11.44699955 W
SFO2         125.7948829 MHz
NUC2                 13C
CPDPRG[2            garp
P3                10.00 usec
P4                20.00 usec
PCPD2             70.00 usec
PLW2         56.90299988 W
PLW12         1.16129994 W
GPNAM[1]     SMSQ10.100
GPZ1              80.00 %
GPNAM[2]     SMSQ10.100
GPZ2              20.10 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1          125.7949 MHz
FIDRES        196.293976 Hz
SW              199.735 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                 1024
SF          500.2300000 MHz
WDW                QSINE
SSB                    2
LB                     0 Hz
GB                     0
PC                  1.40

F1 - Processing parameters
SI                 1024
MC2        echo-antiecho
SF          125.7829335 MHz
WDW                QSINE
SSB                    2
LB                     0 Hz
GB                     0
```

HMBC



36b

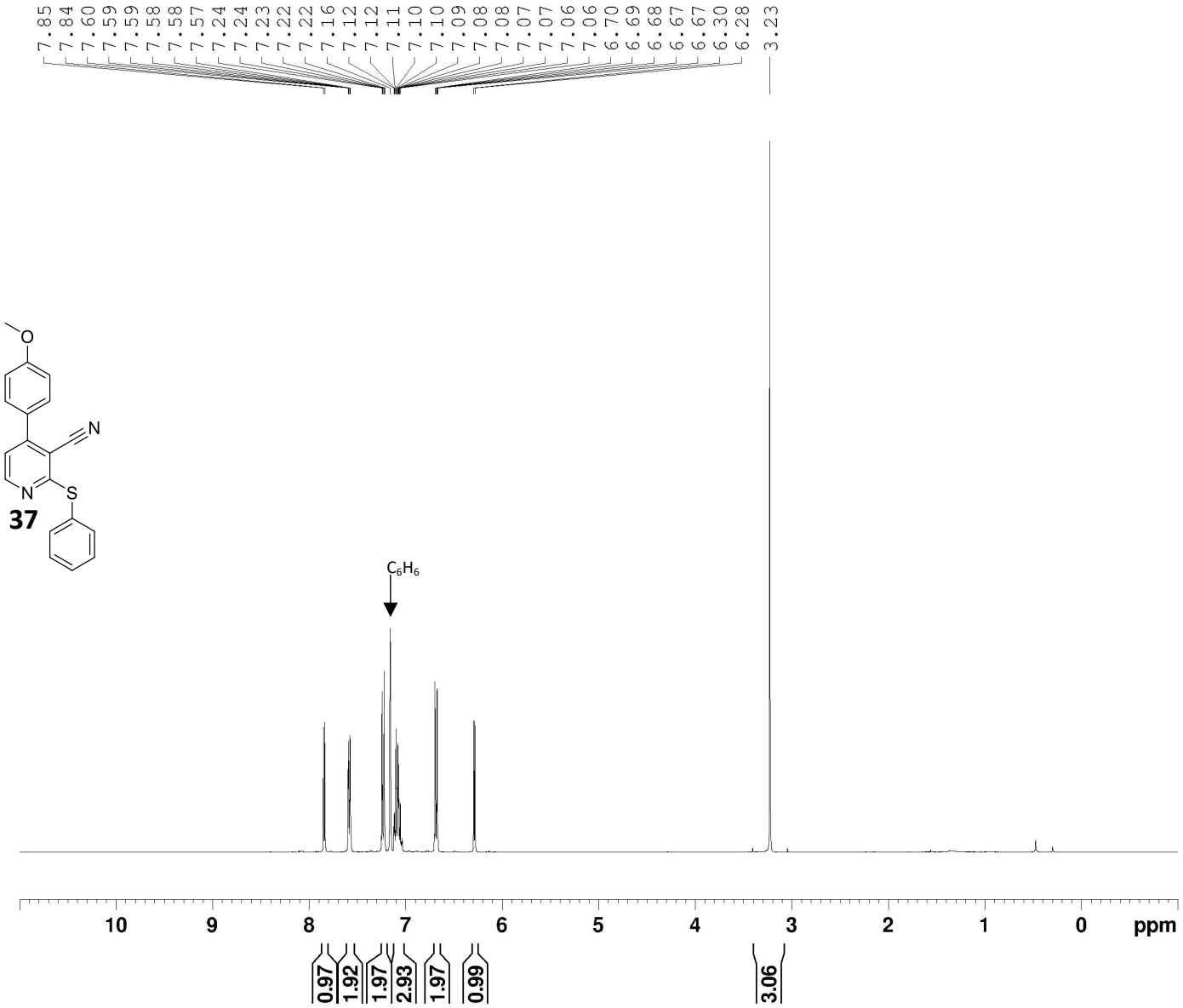
Current Data Parameters
NAME NL-1-61-C4-2d
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210701
Time 18.24 h
INSTRUM spect
PROBHD Z125869_0055 (
PULPROG hmbcgplpndqf
TD 1024
SOLVENT C6D6
NS 4
DS 16
SWH 4629.629 Hz
FIDRES 9.042245 Hz
AQ 0.1105920 sec
RG 190.44
DW 108.000 usec
DE 16.00 usec
TE 300.0 K
CNST2 145.0000000
CNST13 10.0000000
D0 0.00000300 sec
D1 1.50000000 sec
D2 0.00344828 sec
D6 0.05000000 sec
D16 0.00020000 sec
IN0 0.00001810 sec
TDav 1
SFO1 500.2321336 MHz
NUC1 1H
P1 12.00 usec
P2 24.00 usec
PLW1 11.44699955 W
SFO2 125.7955118 MHz
NUC2 13C
P3 10.00 usec
PLW2 56.90299988 W
GPNAM[1] SMSQ10.100
GPZ1 50.00 %
GPNAM[2] SMSQ10.100
GPZ2 30.00 %
GPNAM[3] SMSQ10.100
GPZ3 40.10 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 128
SFO1 125.7955 MHz
FIDRES 431.629822 Hz
SW 219.597 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 500.2299839 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 125.7829233 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0



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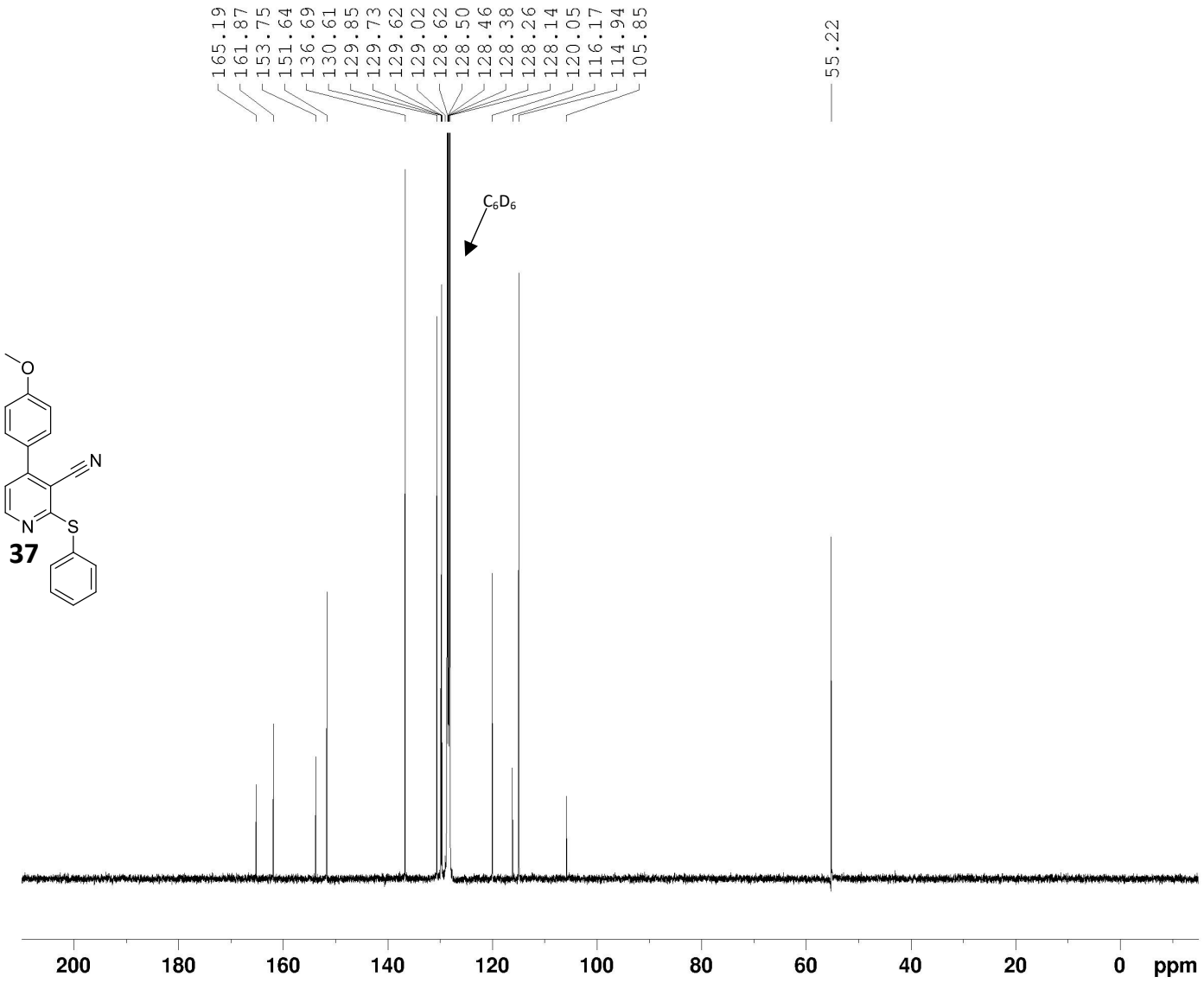
```
Current Data Parameters
NAME          JPN-1-189-1
EXPNO                  15
PROCNO                  1

F2 - Acquisition Parameters
Date_            20211107
Time                20.23 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                    16
DS                     2
SWH              8196.722 Hz
FIDRES           0.250144 Hz
AQ               3.9976959 sec
RG                   101
DW                61.000 usec
DE                13.89 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1          24.03499985 W

F2 - Processing parameters
SI                 65536
SF            400.1299968 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                  1.00
```

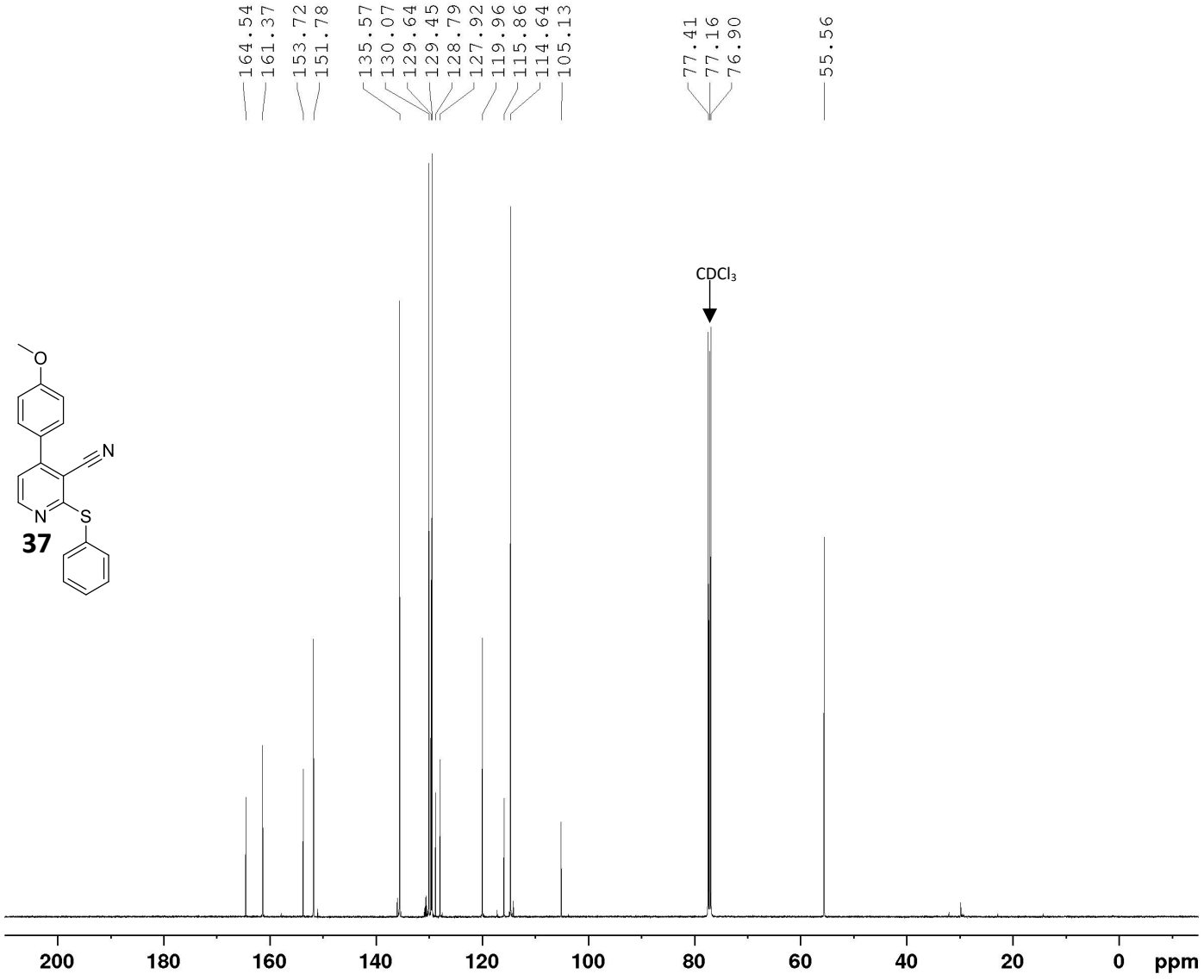


BRUKER

```
Current Data Parameters
NAME          JPN-1-189-1
EXPNO                  14
PROCNO                  1

F2 - Acquisition Parameters
Date_            20211107
Time                20.21 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                   1024
DS                      4
SWH             23809.523 Hz
FIDRES           0.726609 Hz
AQ               1.3762560 sec
RG                   8.125
DW                  21.000 usec
DE                   6.50 usec
TE                  298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          100.6228298 MHz
NUC1                  13C
P0                   2.67 usec
P1                   8.00 usec
PLW1          86.55400085 W
SFO2          400.1316005 MHz
NUC2                  1H
CPDPRG[2          waltz65
PCPD2                90.00 usec
PLW2          24.03499985 W
PLW12          0.18990999 W
PLW13          0.09552100 W

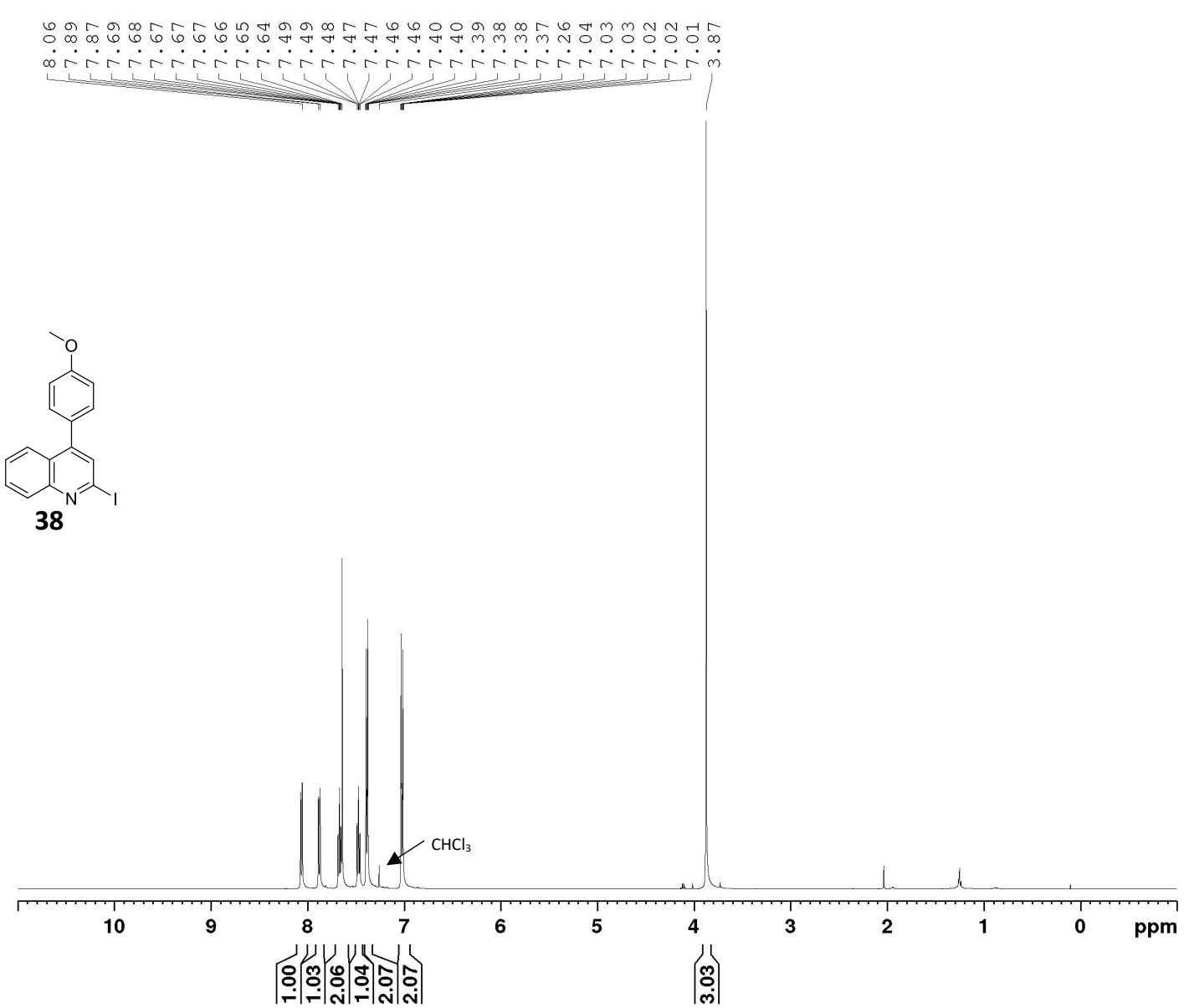
F2 - Processing parameters
SI                   32768
SF            100.6126995 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```




```
Current Data Parameters
NAME      JPN-1-189-1_CDCl3
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_            20211209
Time                0.37 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         125.7955118 MHz
NUC1                 13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

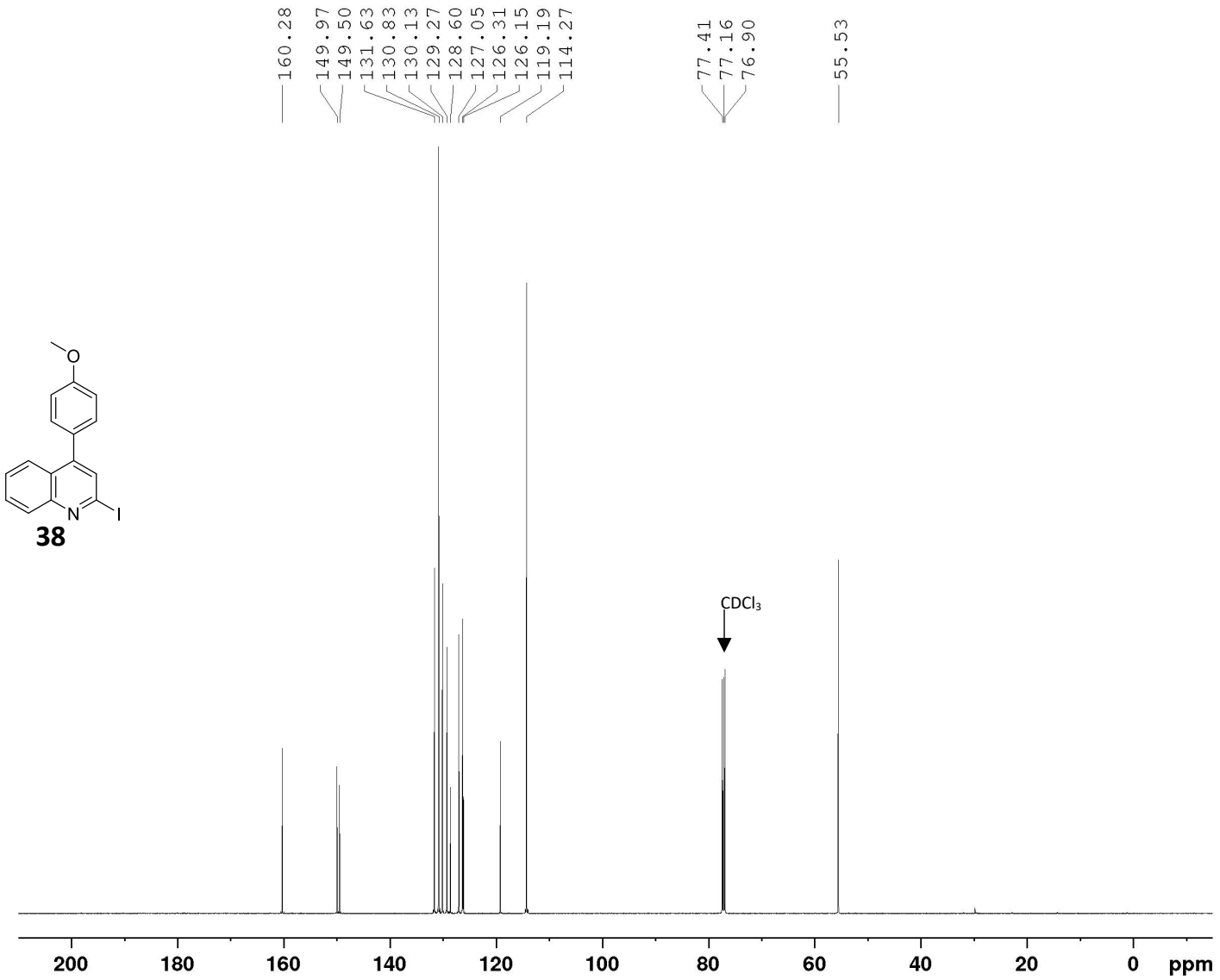
F2 - Processing parameters
SI                32768
SF           125.7829231 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```




```
Current Data Parameters
NAME            JPN-2-25
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201019
Time               18.36 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10000.000 Hz
FIDRES            0.305176 Hz
AQ                3.2767999 sec
RG                   22.16
DW                 50.000 usec
DE                 16.00 usec
TE                 300.0 K
D1              2.00000000 sec
TD0                    1
SFO1         500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1         11.44699955 W

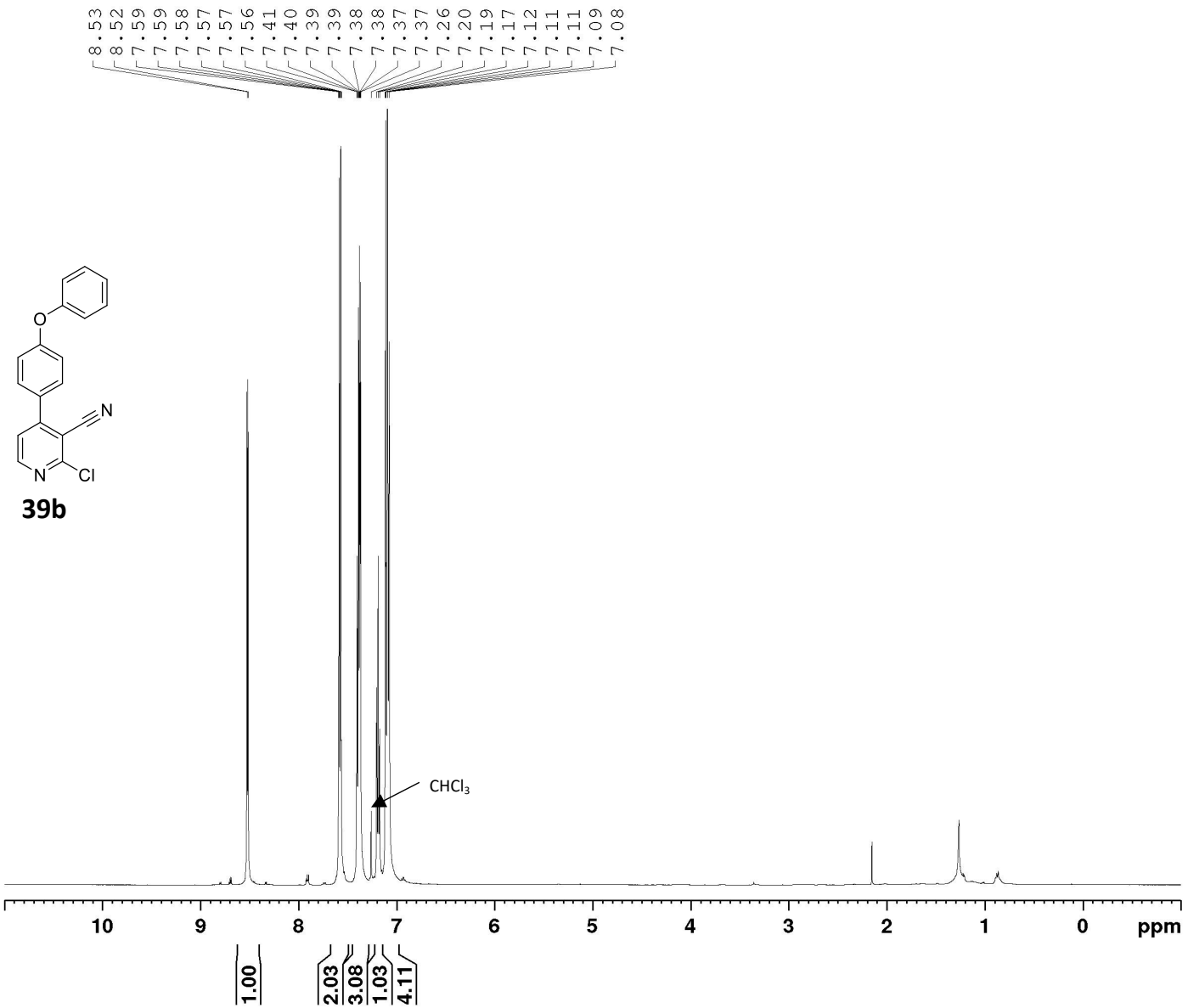
F2 - Processing parameters
SI                 65536
SF           500.2300124 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME          JPN-2-25-1
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211120
Time                4.43 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ              1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1         125.7955118 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

F2 - Processing parameters
SI                 32768
SF           125.7829267 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

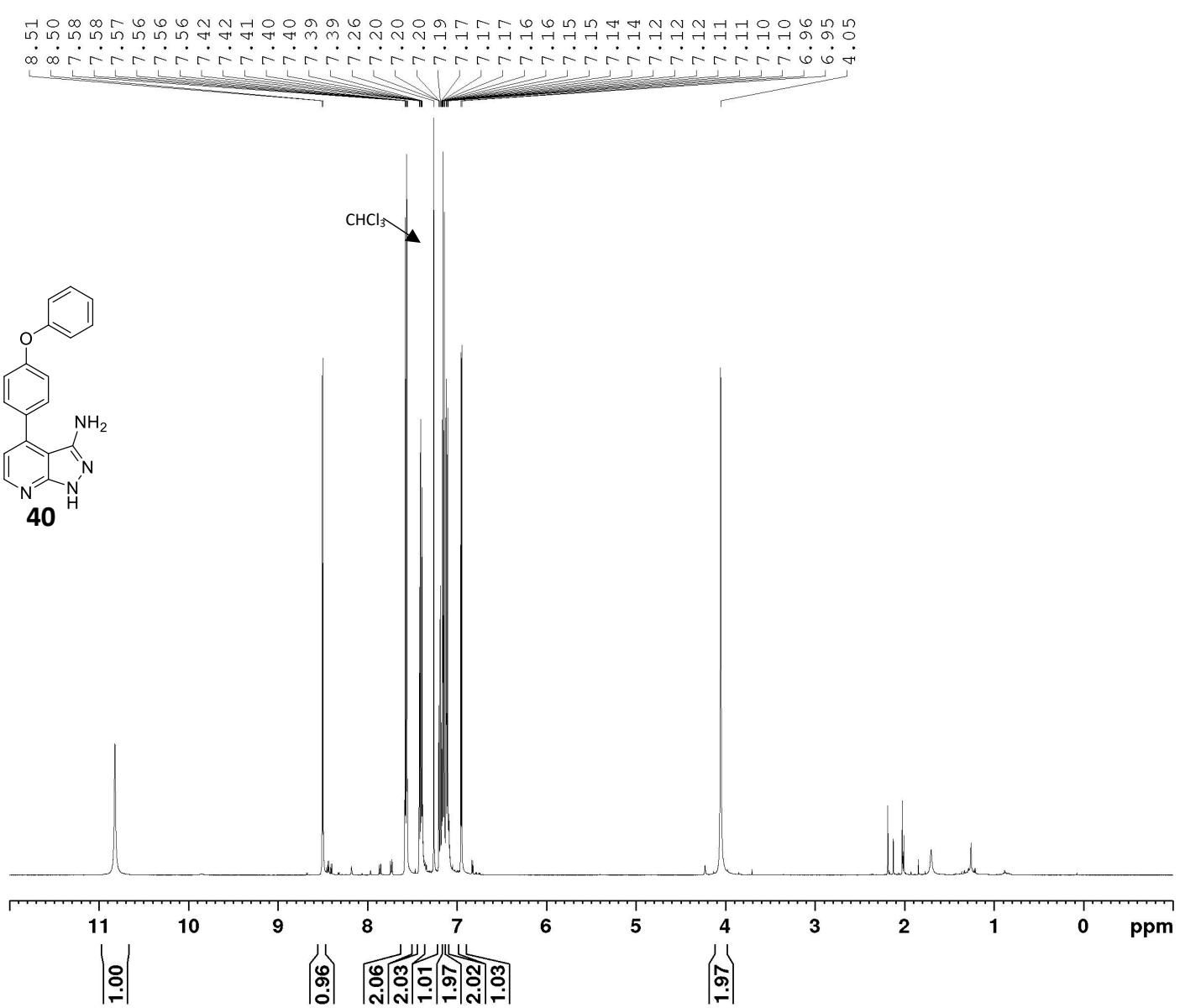


BRUKER

```
Current Data Parameters
NAME      JPN-2-6-C4-mono_dried
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_            20200823
Time                  8.03 h
INSTRUM              spect
PROBHD    Z125869_0055 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      64
DS                       2
SWH             10000.000 Hz
FIDRES              0.305176 Hz
AQ                3.2767999 sec
RG                   19.46
DW                  50.000 usec
DE                  16.00 usec
TE                  300.0 K
D1               2.00000000 sec
TD0                      1
SFO1           500.2330889 MHz
NUC1                    1H
P0                  4.00 usec
P1                  12.00 usec
PLW1           11.44699955 W

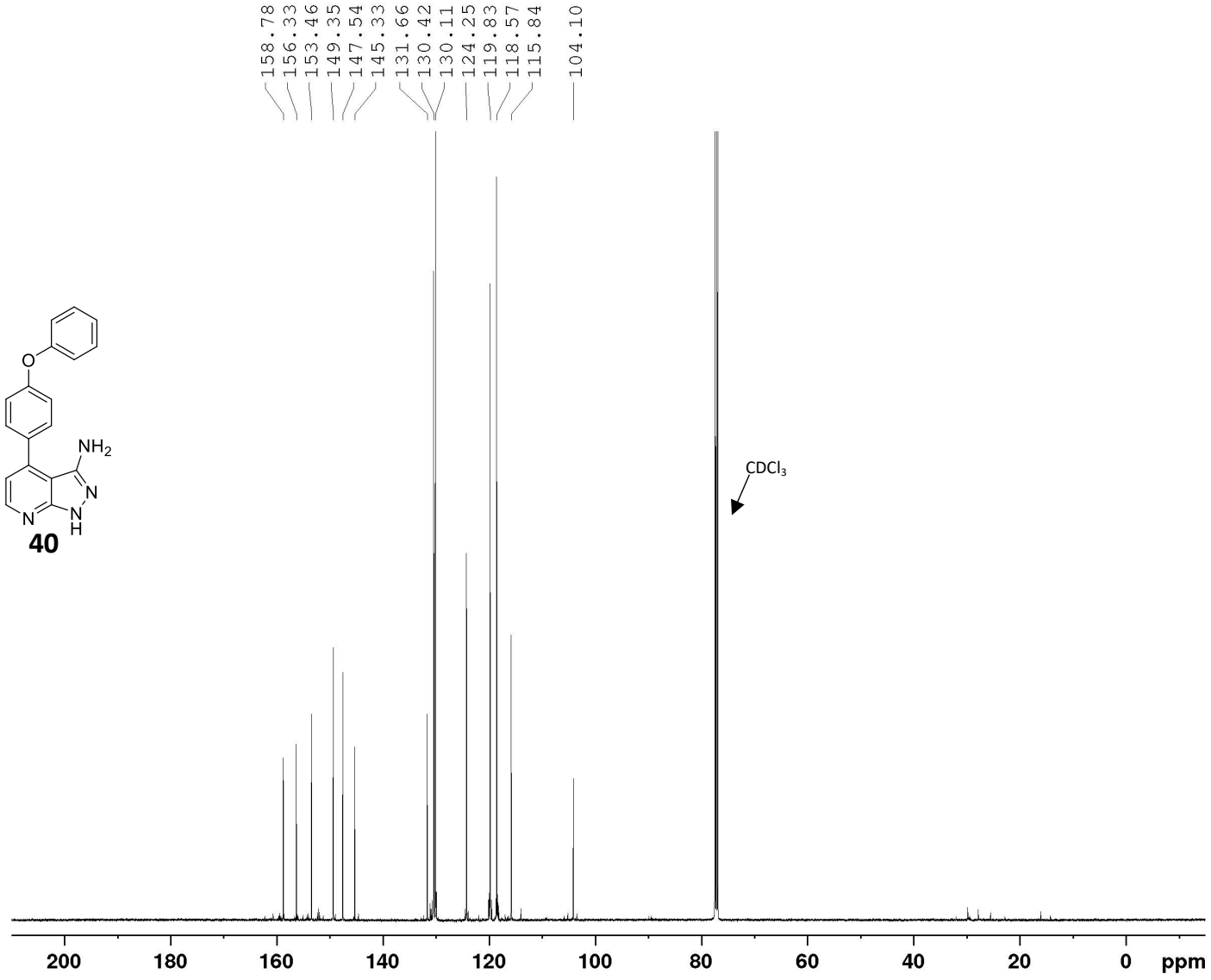
F2 - Processing parameters
SI                   65536
SF             500.2300120 MHz
WDW                     EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```




```
Current Data Parameters
NAME      JPN-2-6-2_repeat
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_            20201019
Time                18.27 h
INSTRUM              spect
PROBHD   Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH             10000.000 Hz
FIDRES              0.305176 Hz
AQ                3.2767999 sec
RG                   151.18
DW                  50.000 usec
DE                  16.00 usec
TE                  300.0 K
D1               2.00000000 sec
TD0                     1
SFO1           500.2330889 MHz
NUC1                   1H
P0                   4.00 usec
P1                  12.00 usec
PLW1          11.44699955 W

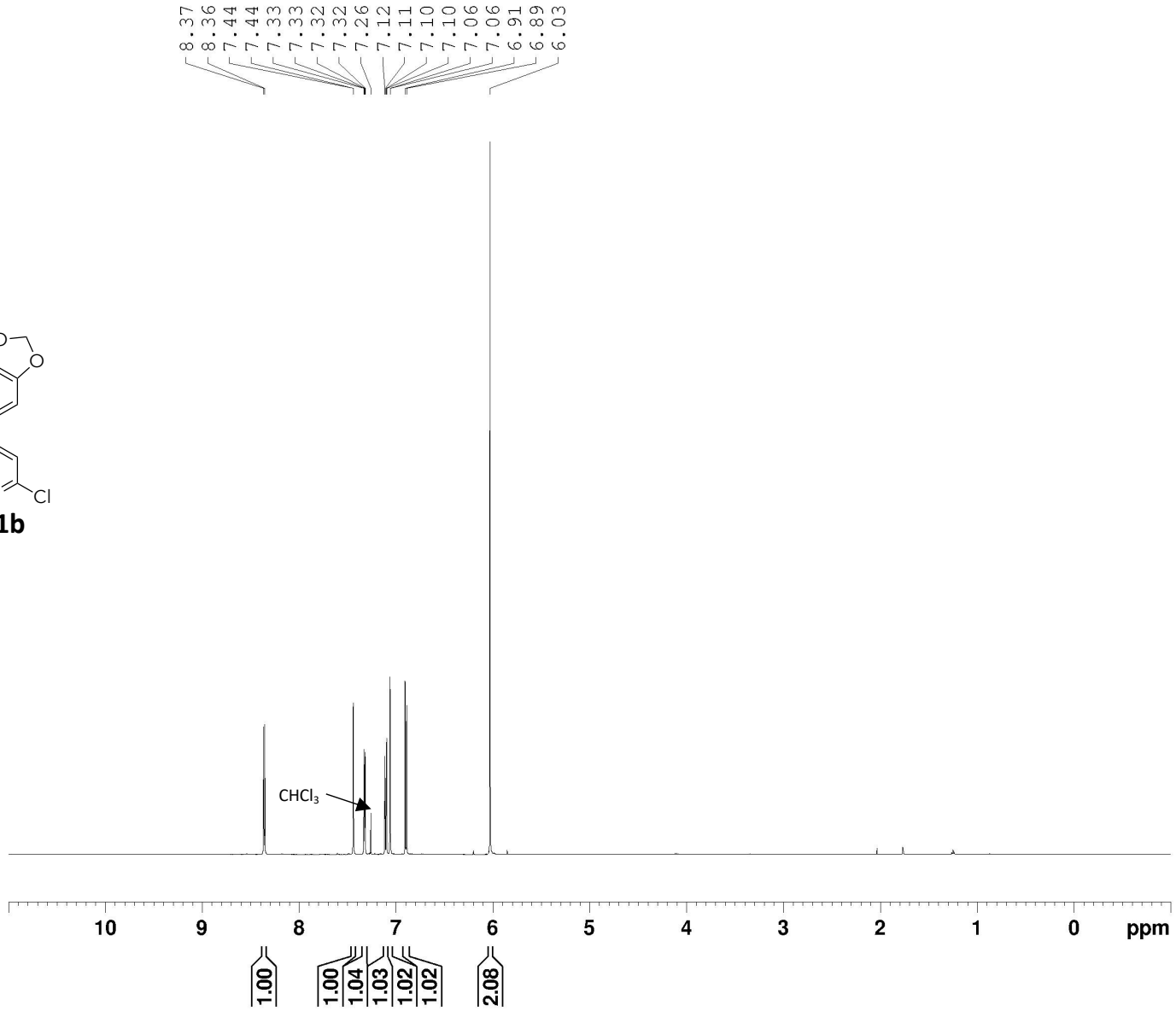
F2 - Processing parameters
SI                  65536
SF             500.2300122 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```




```
Current Data Parameters
NAME           JPN-2-6-2
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211120
Time                5.41 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7955118 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

F2 - Processing parameters
SI                32768
SF          125.7829211 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

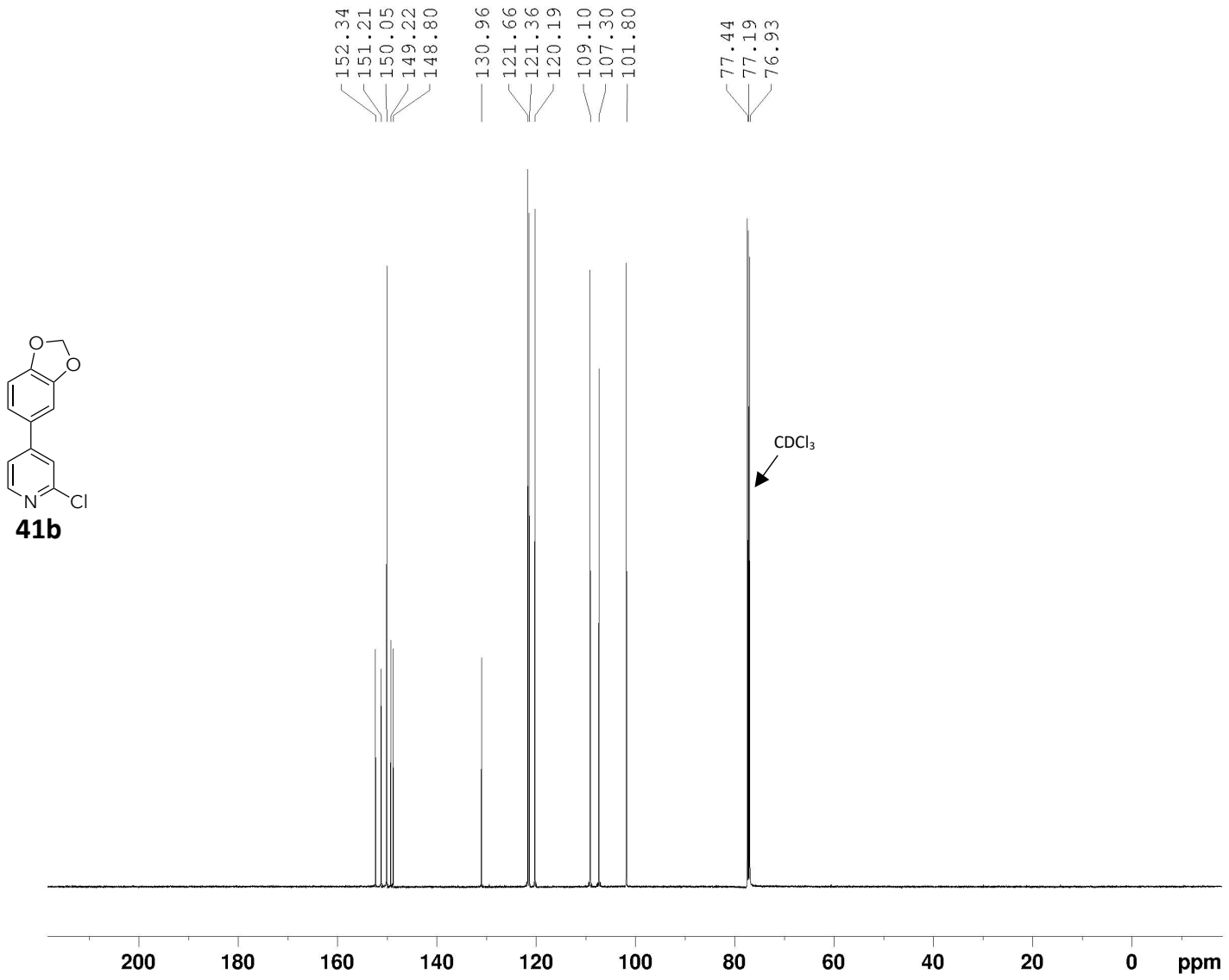


41b

Current Data Parameters
NAME JPN-2-153-3
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220228
Time 14.24 h
INSTRUM spect
PROBHD Z125869_0055 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 43.72
DW 50.000 usec
DE 16.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.2330889 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 11.44699955 W

F2 - Processing parameters
SI 65536
SF 500.2300120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

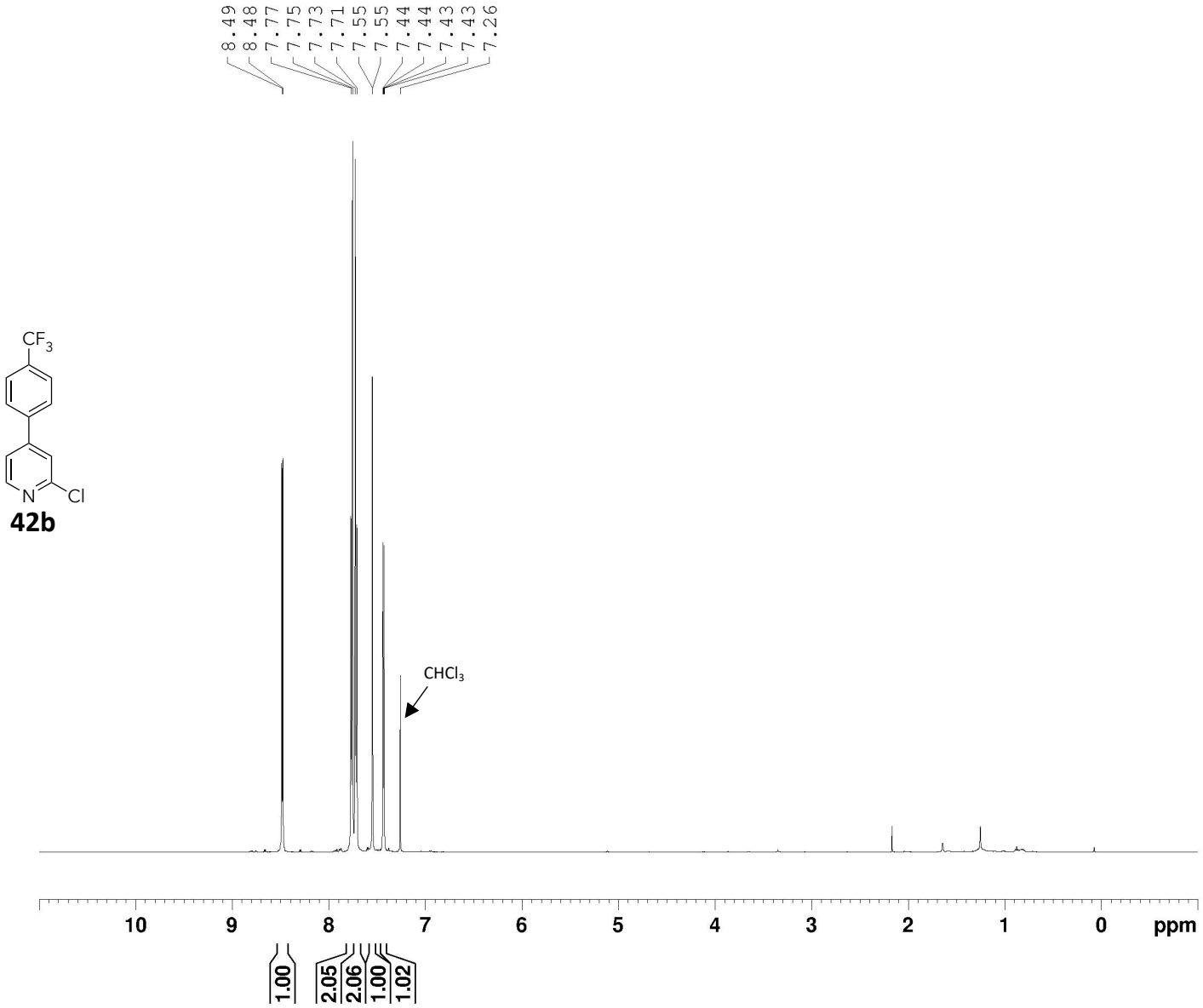


41b

```
Current Data Parameters
NAME         JPN-2-153-3
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220301
Time                0.04 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         125.7955118 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

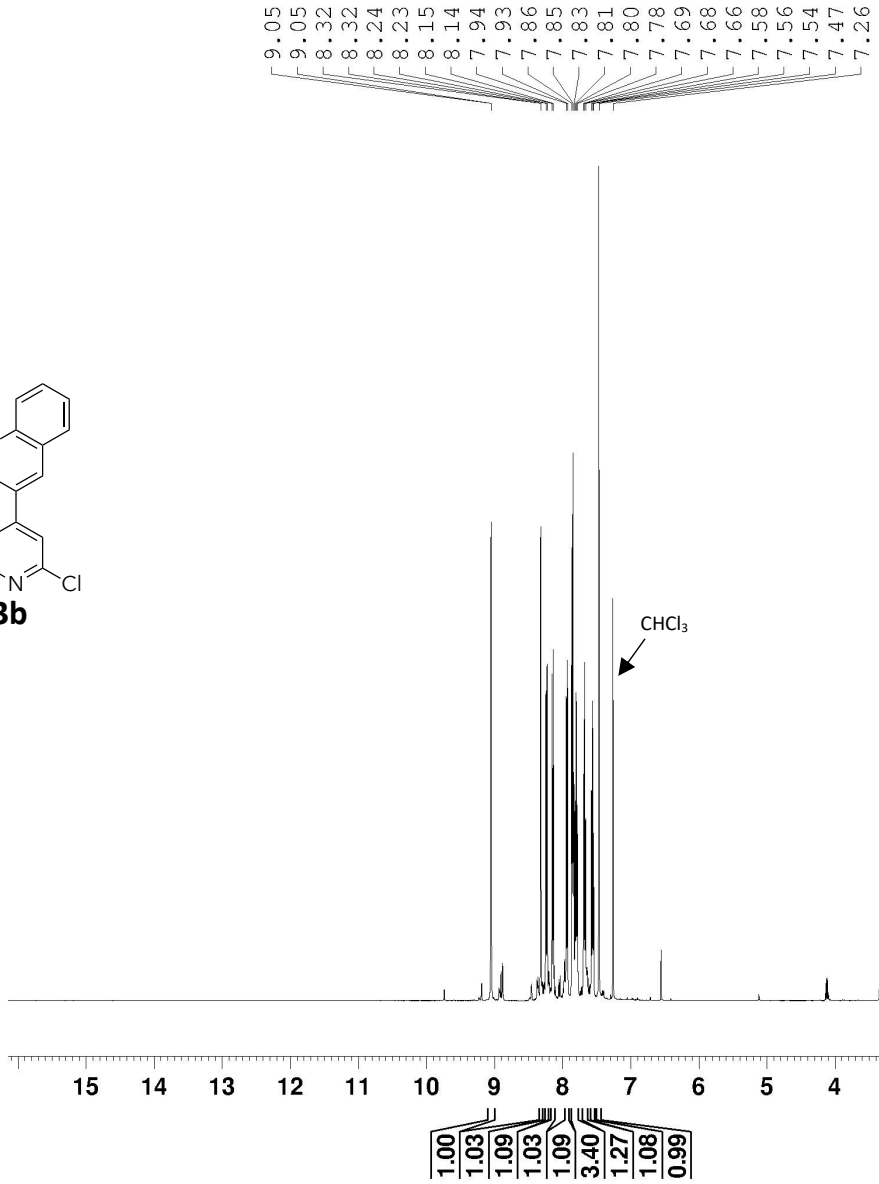
F2 - Processing parameters
SI                 32768
SF           125.7829176 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



Current Data Parameters
NAME NL-1-186-1-F1
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220317
Time 12.09 h
INSTRUM spect
PROBHD Z125869_0055 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 94.51
DW 50.000 usec
DE 16.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.2330889 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 11.44699955 W

F2 - Processing parameters
SI 65536
SF 500.2300120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

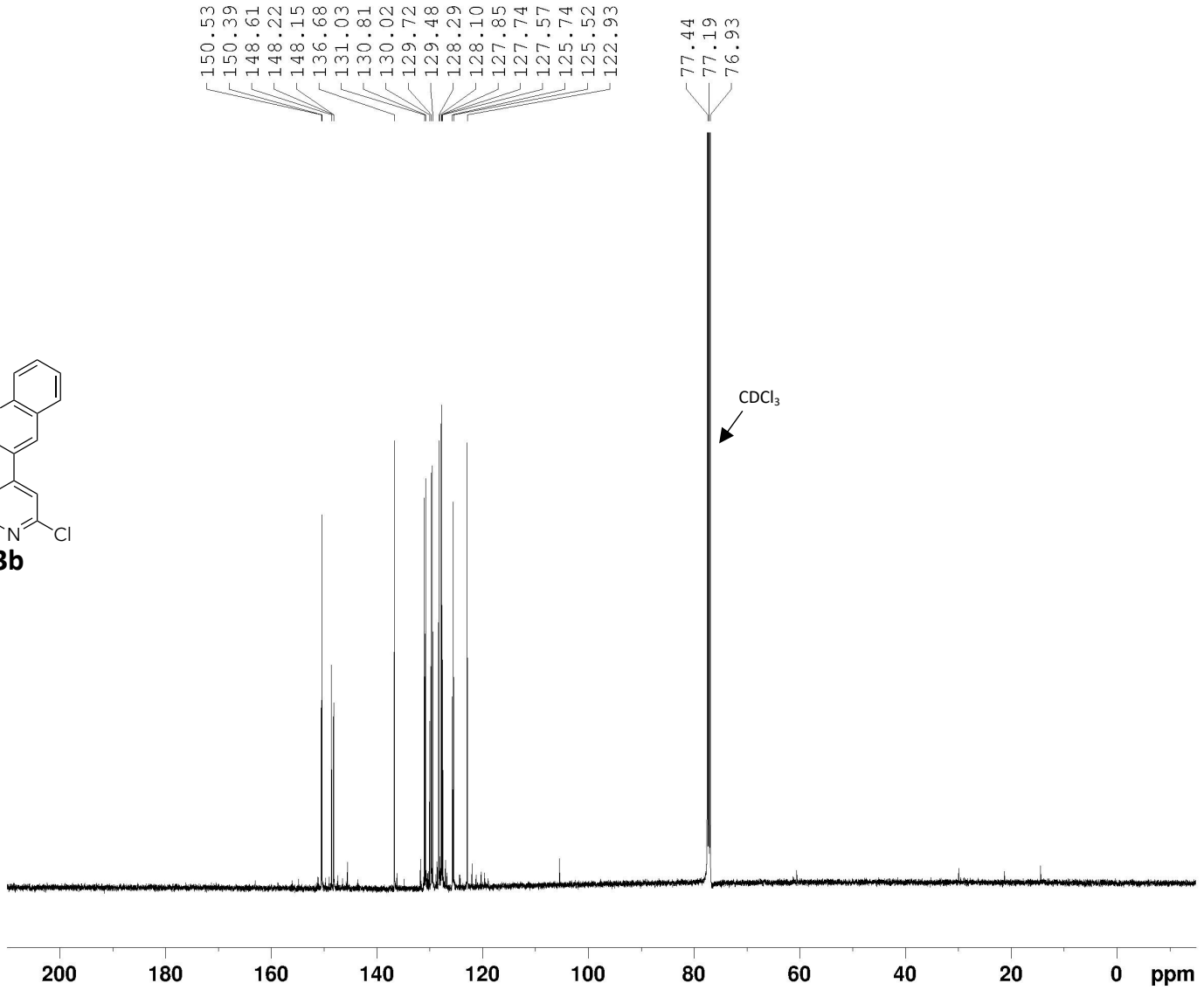


43b

```
Current Data Parameters
NAME         JPN-2-156-2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220317
Time               11.59 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ              3.2767999 sec
RG                151.18
DW                50.000 usec
DE                16.00 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1          500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1          11.44699955 W

F2 - Processing parameters
SI                 65536
SF            500.2300120 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

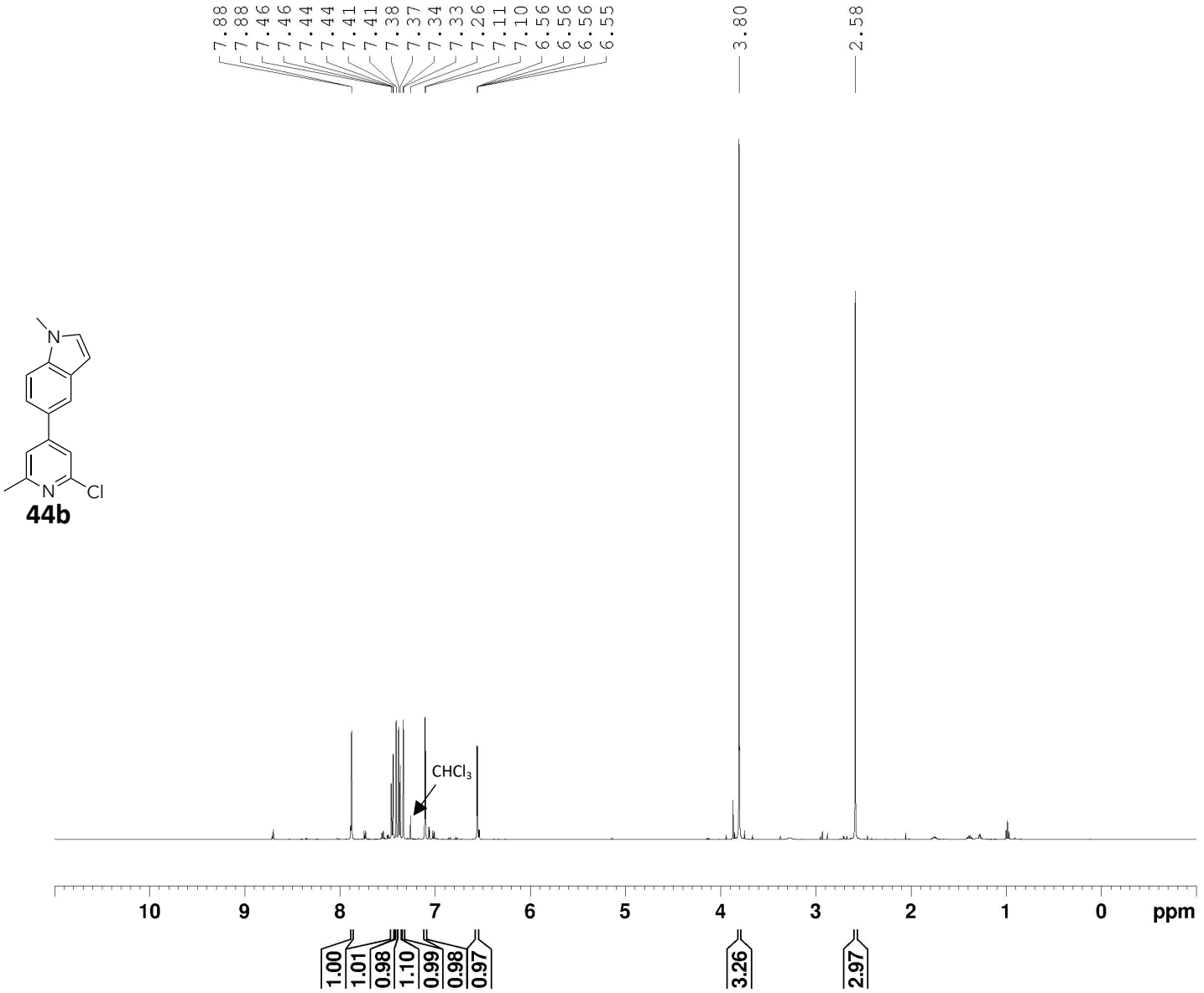


43b

```
Current Data Parameters
NAME         JPN-1-156-2
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220317
Time              17.59 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ             1.1010048 sec
RG                190.44
DW                16.800 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         125.7955118 MHz
NUC1                 13C
P0                 3.33 usec
P1                10.00 usec
PLW1         56.90299988 W
SFO2         500.2320009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         11.44699955 W
PLW12         0.25756001 W
PLW13         0.12955000 W

F2 - Processing parameters
SI                32768
SF         125.7829137 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

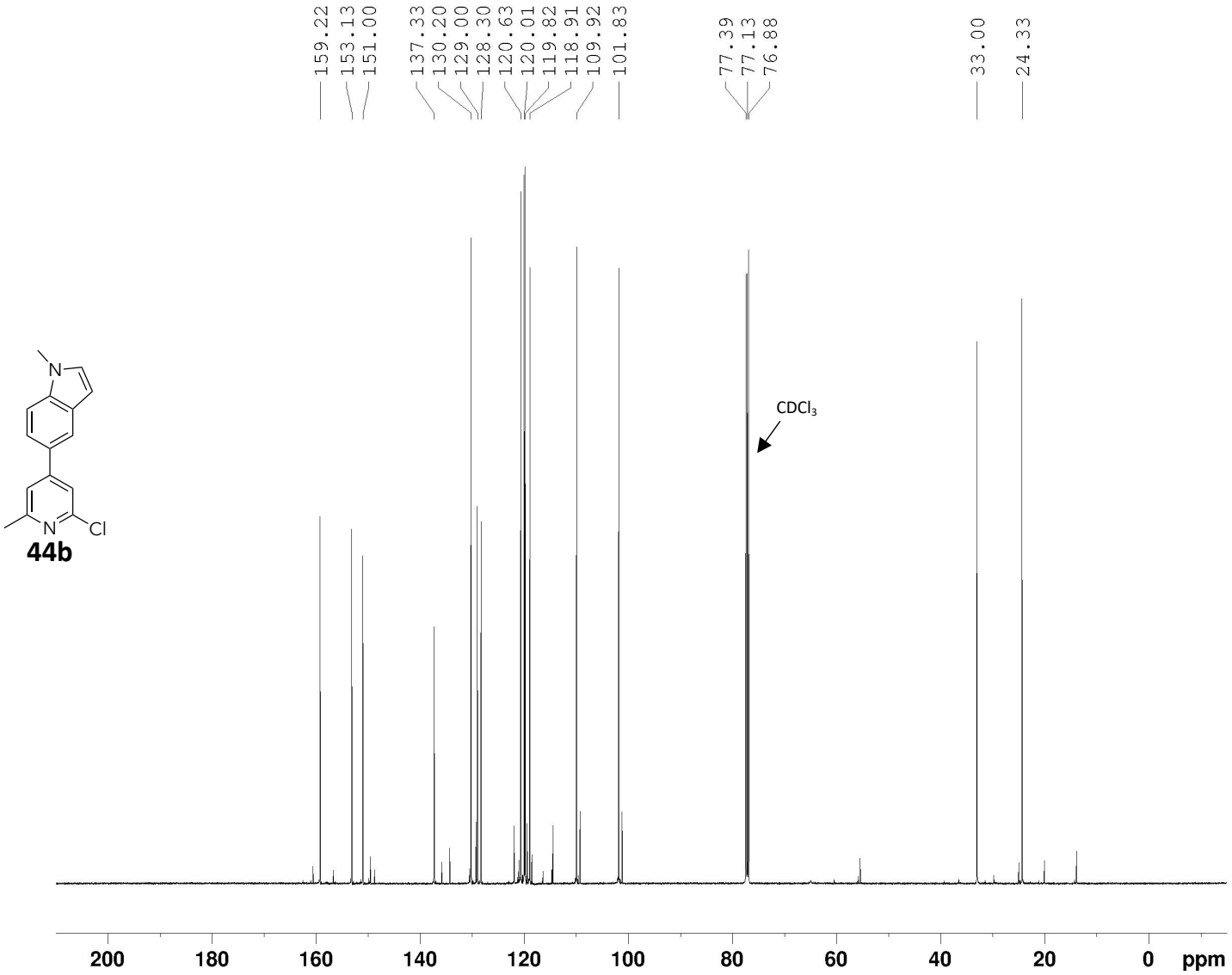


44b

```
Current Data Parameters
NAME         JPN-2-156-3
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220316
Time                3.15 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            10000.000 Hz
FIDRES             0.305176 Hz
AQ             3.2767999 sec
RG                  26.9
DW                50.000 usec
DE                16.00 usec
TE                298.0 K
D1           2.00000000 sec
TD0                    1
SFO1         500.2330889 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1         11.44699955 W

F2 - Processing parameters
SI                 65536
SF           500.2300119 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

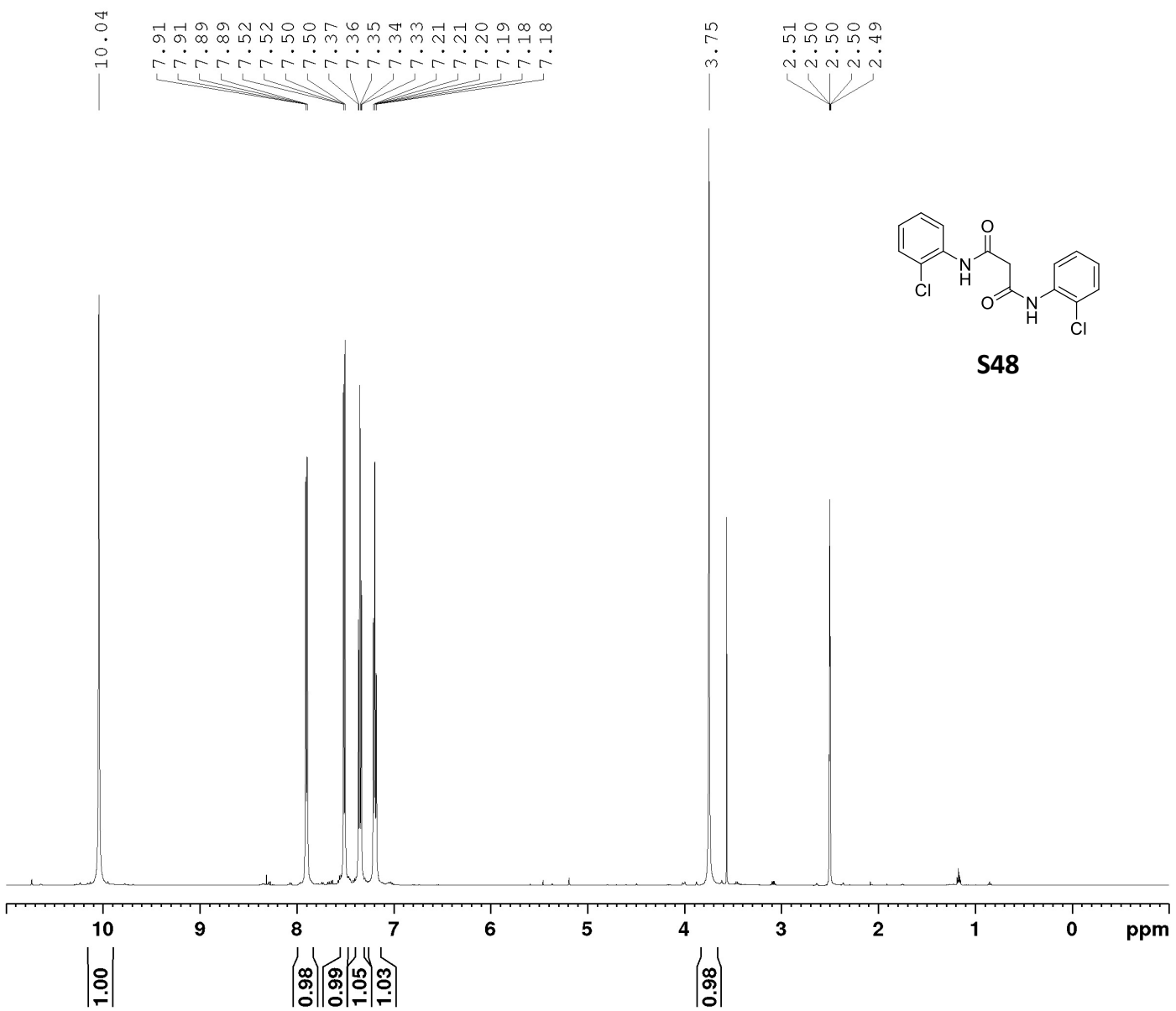


44b

```
Current Data Parameters
NAME          JPN-2-156-3
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220316
Time                4.13 h
INSTRUM            spect
PROBHD    Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.44
DW               16.800 usec
DE               18.00 usec
TE               298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7955118 MHz
NUC1               13C
P0                3.33 usec
P1               10.00 usec
PLW1        56.90299988 W
SFO2        500.2320009 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

F2 - Processing parameters
SI                32768
SF          125.7829335 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



S48

```
Current Data Parameters
NAME      JPN-2-143_DMSO-D6
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_            20220211
Time                14.25 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     32
DS                      2
SWH             10000.000 Hz
FIDRES              0.305176 Hz
AQ                3.2767999 sec
RG                   86.13
DW                  50.000 usec
DE                  16.00 usec
TE                  298.0 K
D1             2.00000000 sec
TD0                     1
SFO1          500.2330889 MHz
NUC1                   1H
P0                  4.00 usec
P1                 12.00 usec
PLW1          11.44699955 W

F2 - Processing parameters
SI                  65536
SF            500.2300032 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```