Supporting Information

for

Solvent Coordination to Palladium Can Invert the Selectivity of Oxidative Addition

*Emily K. Elias, Steven M. Rehbein, Sharon R. Neufeldt**

Department of Chemistry and Biochemistry, Montana State University
Bozeman, MT 59717, USA

**Correspondence: sharon.neufeldt@montana.edu*

Table of Contents

I. Experimental Details

II. Computational Details

I. Experimental Details

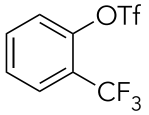
A. *General Materials and Methods*

NMR spectra were recorded at 298 K on Bruker DPX Avance I 300 MHz (300.130 MHz for ^{1}H, 75.468 MHz for ^{13}C, 282.404 MHz for ^{19}F, 121.495 MHz for ^{31}P), Bruker Ascend 400 MHz (400.130 MHz for ^{1}H NMR, 100.613 for ^{13}C, 376.498 for ^{19}F, 161.967 for ^{31}P), Bruker Ascend Avance III 500 MHz (500.130 for ^{1}H, 125.758 MHz for ^{13}C, 470.592 for ^{19}F, 202.478 MHz for ^{31}P), or Bruker Avance III 600 MHz (600.130 MHz for ^{1}H, 150.903 for ^{13}C) NMR spectrometers. ^{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); ^{13}C NMR: $CDCl_3$ (77.16 ppm).] ^{19}F chemical shifts are reported in ppm relative to fluorobenzene (–113.15 ppm). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), quartet of triplets (qt), triplet of triplets (tt), triplet of quintets (tqn), triplet of sextets of doublets (tsd), 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 on a Shimadzu GCMS-QP2020 NX gas chromatograph mass spectrometer. HRMS data were collected on a Bruker MicroTOF II in acetonitrile with NaCl doping. Purifications via flash chromatography were performed using a Biotage Selekt Flash Purification System. "Room temperature" reactions described herein are generally between 23–25 °C as measured by a temperature probe on the reaction stir plates.

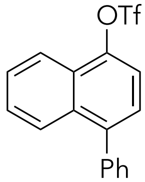
Unless otherwise noted, all commercially-obtained chemicals were used as received. Anisonitrile, dioxane, *N*,*N*-dimethylformamide, *p*-cresol, $PdCl_2$, KF, sulfolane, 4-(dimethylamino)benzonitrile, 4-chlorophenol, and 4-chlorotoluene were obtained from Acros Organics. Propylene carbonate was obtained from Aldrich Chemical. Acetonitrile, K_2CO_3, tetrahydrothiophene, P^tBu_3, and 4-methylbiphenyl were obtained from Alfa Aesar. Benzonitrile was obtained from Eastman Chemical. *p*-Xylene was obtained from Honeywell Fluka Research Chemicals. 4-Chloro-1,1′-biphenyl was obtained from Matrix Scientific. Biphenyl, methyl-4-cyanobenzoate, nitromethane, *o*-tolyl boronic acid, phenyl boronic acid, tetrabutylammonium bromide, tetrabutylammonium chloride, tetrabutylammonium fluoride hexahydrate, tetrabutylammonium trifluoromethanesulfonate, tetrabutylstannane, trifluoromethanesulfonic anhydride, 1-chloro-2-trifluoromethylbenzene, 1-naphthol, 18-crown-6, 2-bromobenzotrifluoride, 2-chlorobenzotrifluoride, 4-(trifluoromethyl)benzonitrile, 4-aminobenzonitrile, 4-ethoxybenzonitrile, 4-fluorobenzonitrile, 4-hydroxybenzonitrile, and 4-nitrobenzonitrile were obtained from Oakwood Chemical. The boronic acids were recrystallized from water prior to use. 1-Methylnaphthalene, $^n Bu_3SnOTf$, Me_3SnPh, and α, α, α-trifluorotoluene were obtained from Millipore Sigma. Bis(tri-t-butylphosphine)palladium(0), methanesulfonato(tri-*t*-butylphosphino)(2'-methylamino-1,1'-biphenyl-2-yl)palladium(II) (Buchwald's precatalyst P^tBu_3-Pd-G4), and Me_3SnBr were obtained from Strem Chemical. Fluoroacetonitrile, *N*-methyl-2-pyrrolidone, *p*-terphenyl, *p*-tolunitrile, 1-chloronaphthalene, 1,4-dimethylnaphthalene, 4-chlorobenzotrifluoride, 4-chloro-1-naphthol, 4-hydroxybenzotrifluoride, and 4-phenyl-1-bromonaphthalene were obtained from TCI America. KPF_6 was obtained from Alfa Aesar, Oakwood Chemical, or Millipore Sigma. $^n Bu_3SnPh$ was obtained from Alfa Aesar or Millipore Sigma. Tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) was obtained from Millipore Sigma or Strem Chemical. Compounds **1**,[1] **2a**,[1] **2b**,[1] **3a**,[1] **3b**,[1] **4b**,[2] $Pd(COD)(CH_2TMS)_2$,[3] $[Pd(P^tBu_3)(o\text{-}CF_3Ph)(Cl)]$ (**S10**),[4] and $P^tBu_3{\bullet}HCl$[5] were synthesized according to literature procedures.

Acetone, acetonitrile, chloroform, dichloromethane, diethyl ether, dimethyl formamide (DMF), dimethylsulfoxide (DMSO), ethanol, ethyl acetate, fluorobenzene, hexanes, isopropanol, methanol, pentane, tetrahydrofuran (THF), and toluene were obtained from Fisher Chemical. Benzene was obtained from TCI America. Solvents were used as received except for those that were used inside the glovebox. In these cases, MeCN, MeOH, DMF, toluene, and fluorobenzene were degassed and dried with a JC Meyer solvent system prior to use. The dried DMF, MeCN, toluene, and methanol were stored over molecular sieves in the glovebox. Deuterated solvents ($CDCl_3$, C_6D_6) were obtained from Cambridge Isotopes and stored over molecular sieves.

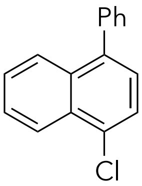
B. Synthesis and Characterization of Substrates and Authentic Samples of Products



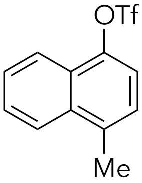
2-(Trifluoromethyl)phenyl triflate (3b): The title compound was prepared according to a modified literature procedure.[6] With cooling to 0 °C, a solution of trifluoromethanesulfonic anhydride (4.0 mL, 24.0 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) was added dropwise to a solution of 2-hydroxybenzotrifluoride (3.24 g, 20.0 mmol) and pyridine (3.23 mL, 40.0 mmol, 2 equiv) in CH_2Cl_2 (20 mL). The mixture was allowed to warm to room temperature and stirred for 1 h, after which the solution was diluted with Et_2O and acidified with aqueous 1 *M* HCl. The layers were separated, and the aqueous layer was washed with Et_2O (3 x 10 mL). The combined organic layers were washed with saturated $NaHCO_3$ and brine (aqueous NaCl), dried over $MgSO_4$, filtered, and concentrated to give a yellow oil that was purified through a short silica plug (100% hexanes) to afford **3b** as a clear, colorless oil (4.40 g, 75 % yield). Spectral data are consistent with those previously reported.[7]



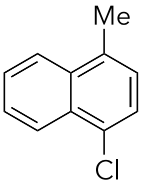
4-Phenylnaphthalen-1-yl triflate (9a). The title compound was prepared according to a modified literature procedure.[8] Pd-P^{t}Bu$_3$-G4 (7.0 mg, 0.012 mmol, 3 mol %), phenyl boronic acid (49.3 mg, 0.404 mmol, 1.01 equiv), and KF (69.7 mg, 1.20 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, 4-chloronaphthalen-1-yl triflate (**8**, 79 µL, 0.40 mmol), deionized water (7.2 µL, 0.40 mmol, 1 equiv), and THF (1.0 mL) were added to the vial and the mixture was immediately sparged with nitrogen for ~2 min. The vial was sealed with a PTFE-lined cap and the reaction was stirred at room temperature for 24 h. The reaction mixture was extracted with ethyl acetate, and the organic extract was filtered over a plug of celite. The filtrate was concentrated and then purified by flash column chromatography (100% hexanes) to afford **9a** as a colorless oil (40 mg, 28% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.17 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.5, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.51 (multiple overlapping signals, 8H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 145.2, 141.3, 139.4, 133.3, 130.1, 128.6, 128.0, 127.8, 127.6, 126.8, 126.7, 126.2, 121.1, 118.9 (q, $^1J_{CF}$ = 320 Hz), 117.4; ^{19}F (471 MHz, $CDCl_3$, δ): -73.3. HRMS (ESI/Q-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{17}H_{11}F_3NaO_3S^+$ 375.0273. Found 375.0261.



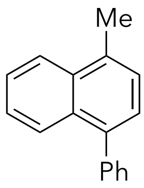
1-Chloro-4-phenylnaphthalene (9b). $PdCl_2$ (2.1 mg, 0.012 mmol, 3 mol %), phenyl boronic acid (48.8 mg, 0.40 mmol, 1 equiv), and KF (69.7 mg, 1.20 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, 4-chloronaphthalen-1-yl triflate (**8**, 79 µL, 0.40 mmol), deionized water (7.2 µL, 0.40 mmol, 1 equiv), and acetonitrile (750 µL) were added to the vial and the mixture was immediately sparged with nitrogen for ~2 min. The vial was sealed with a PTFE-lined cap and the reaction was stirred at room temperature for 22 h. The reaction mixture was extracted with ethyl acetate, and the organic extract was filtered over a plug of celite. The filtrate was concentrated and then purified by flash column chromatography (100% hexanes) to afford **9b** as a colorless oil (79 mg, 84% yield). Spectral data are consistent with those previously reported.[9]



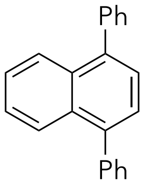
4-Methylnaphthalen-1-yl triflate (9c): In a nitrogen-filled glovebox, Pd_2dba_3 (6.9 mg, 0.0075 mmol 1.5 mol %), $Pd(P^tBu_3)_2$ (7.7 mg, 0.015 mmol, 3.0 mol %), and KPF_6 (276 mg, 1.50 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, 4-chloronaphthalen-1-yl triflate (**8**, 98 µL, 0.50 mmol), $PhSnMe_3$ (100 µL, 0.55 mmol, 1.1 equiv), and DMF (1.0 mL) were added. The vial was sealed with a PTFE-lined cap and the mixture was stirred at 100 °C for 24 h. The reaction mixture was extracted with ethyl acetate, and the organic extract was filtered over a plug of celite. The filtrate was concentrated and then purified by flash column chromatography (100% hexanes, dry-loaded on C18 silica gel) to afford **9c** as a white solid (52 mg, 36% yield).). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.21-8.01 (two overlapping signals, 2H), 7.68-7.60 (two overlapping signals, 2H), 7.38-7.30 (two overlapping signals 2H), 2.71 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$ δ): 144.4, 135.6, 133.9, 127.6, 127.3, 126.5, 125.7, 124.7, 122.7, 118.8 (q, $^1J_{CF}$ = 320 Hz), 117.5, 19.4; ^{19}F (471 MHz, $CDCl_3$, δ): -73.4. HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_9F_3NaO_3S^+$ 313.0117. Found 313.0123.



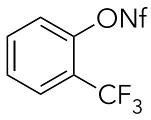
1-Chloro-4-methylnaphthalene (9d): In a nitrogen-filled glovebox, Pd_2dba_3 (6.9 mg, 0.0075 mmol 1.5 mol %), $Pd(P^tBu_3)_2$ (7.7 mg, 0.015 mmol, 3.0 mol %), and KPF_6 (276 mg, 1.50 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, 4-chloronaphthalen-1-yl triflate (**8**, 98 µL, 0.50 mmol), $PhSnMe_3$ (100 µL, 0.55 mmol, 1.1 equiv), and DMF (1.0 mL) were added. The vial was sealed with a PTFE-lined cap and the mixture was stirred at room temperature for 24 h. The reaction mixture was extracted with ethyl acetate, and the organic extract was filtered over a plug of celite. The filtrate was concentrated and then purified by flash column chromatography (100% hexanes, dry-loaded on C18 silica gel) to afford **9d** as a white solid (31 mg, 35% yield). Spectral data are consistent with those previously reported,[10] but higher resolution data are included here. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.30 (dd, *J* = 7.6 Hz, 1H), 8.0 (dd, 7.5 Hz, 1H), 7.70-7.57 (two overlapping signals, 2H), 7.46 (d, 7.7 Hz, 1H), 7.23 (d, 7.7 Hz, 1H, overlaps with solvent), 2.67 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$ δ): 133.8, 133.7, 130.8, 130.2, 130.0, 128.5, 126.8 (d, *J* = 7.2 Hz), 126.5, 125.9, 124.1, 124.7, 19.4.



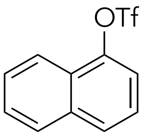
1-Methyl-4-phenylnaphthalene (9f): The title compound was prepared according to a modified literature procedure.[8] Pd-P^{t}Bu$_3$-G4 (7.0 mg, 0.012 mmol, 3 mol %), phenyl boronic acid (49.3 mg, 0.404 mmol, 1.01 equiv), and KF (69.7 mg, 1.20 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, 1-bromo-4-methylnaphthalene (63 µl, 0.40 mmol), deionized water (7.2 µL, 0.40 mmol, 1 equiv), and THF (1.0 mL) were added to the vial and the mixture was immediately sparged with nitrogen for ~ 2 min. The vial was sealed with a PTFE-lined cap and the reaction was stirred at room temperature for 24 h. The reaction mixture was extracted with ethyl acetate, and the organic extract was filtered over a plug of celite. The filtrate was concentrated and then purified by flash column chromatography (100% hexanes) to afford **9f** as a white solid (76 mg, 87% yield). Spectral data are consistent with those previously reported.[11]



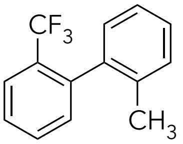
1,4-Diphenylnaphthalene (9g): The title compound was prepared according to a modified literature procedure.[8] Pd-P^{t}Bu$_3$-G4 (7.0 mg, 0.012 mmol, 3 mol %), phenyl boronic acid (49.3 mg, 0.404 mmol, 1.01 equiv), KF (69.7 mg, 1.20 mmol, 3 equiv), and 1-bromo-4-phenylnaphthalene (113.3 mg, 0.40 mmol) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, deionized water (7.2 µL, 0.40 mmol, 1 equiv) and THF (1.0 mL) were added to the vial and the mixture was immediately sparged with nitrogen for ~ 2 min. The vial was sealed with a PTFE-lined cap and the reaction was stirred at room temperature for 24 h. The reaction mixture was extracted with ethyl acetate, and the organic extract was filtered over a plug of celite. The filtrate was concentrated and then purified by flash column chromatography (100% hexanes) to afford **9g** as a white solid (45 mg, 40% yield). Spectral data are consistent with those previously reported.[11]



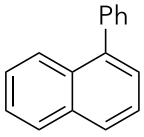
2-(Trifluoromethyl)phenyl nonaflate (S11). The title compound was prepared according to a modified literature procedure.[12] To an oven-dried 50 mL round bottom flask was added 2-(trifluoromethyl)phenol (0.68 g, 4.2 mmol, 1 equiv), K_2CO_3 (0.87 g, 6.3 mmol, 1.5 equiv), and acetonitrile (8.3 mL, 0.5 *M*). The resulting slurry was stirred rapidly while perfluorobutanesulfonyl fluoride (1.26 g, 5.0 mmol, 1.2 equiv) was added via Pasteur pipette. The solution was allowed to stir at room temperature for 16 h, after which the slurry was filtered over a pad of silica gel and rinsed thoroughly with hexanes. The filtrate was concentrated under vacuum to yield **S11** as a clear, colorless oil (1.39 g, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.77 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 146.4, 134.2, 128.4, 128.2 (q, *J* = 5.5 Hz), 123.6 (q, *J* = 33.1 Hz), 122.6, 122.2 (q, *J* = 272.7 Hz), 117.5, (qt, *J* = 295.6, 33.1 Hz), 114.7 (tt, *J* = 295.6, 33.1), 110.1 (tqn, *J* = 272.7, 31.8 Hz), 108.7 (tsd, *J* = 272.7, 31.8, 5.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$, δ): -60.9, -80.7, -109.3, -120.9, -125.9. HRMS (EI/Q-TOF) *m/z*: [M]$^+$ Calcd for $C_{11}H_4F_{12}O_3S^+$ 443.9690. Found 443.9686.



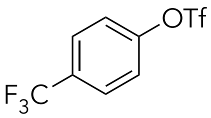
Naphthalen-1-yl triflate (S12): The title compound was prepared according to a modified literature procedure.[6] With cooling to 0 °C, trifluoromethanesulfonic anhydride (1.0 mL, 6.0 mmol, 1.2 equiv) was added dropwise to a solution of 1-naphthol (0.72 g, 5.0 mmol) and pyridine (0.81 mL, 10.0 mmol, 2 equiv) in CH_2Cl_2 (10 mL). The mixture was allowed to warm to room temperature and stirred for 1 h, after which the solution was diluted with Et_2O and acidified with aqueous 1 N HCl. The layers were separated, and the aqueous layer was washed with Et_2O (3 x 5 mL). and the combined organics washed with saturated $NaHCO_3$ and NaCl brine. The combined organic layers were washed with saturated $NaHCO_3$ and brine (aqueous NaCl), dried over $MgSO_4$, filtered, and concentrated to give a yellow oil that was purified through a short silica plug (100% hexanes) to afford **S12** as a clear, colorless oil (1.05 g, 76 % yield). Spectral data are consistent with those previously reported.[7]



2-Methyl-2'-(trifluoromethyl)biphenyl (S13). The title compound was prepared according to a modified literature procedure.[8] Pd-P^{t}Bu$_3$-G4 (7.0 mg, 0.012 mmol, 3 mol %), *ortho*-tolylboronic acid (54.9 mg, 0.404 mmol, 1.01 equiv), and KF (69.7 mg, 1.20 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, deionized water (7.2 µL, 0.40 mmol, 1 equiv), 2-chlorobenzotrifluoride (54 µL, 0.40 mmol), and toluene (1.0 mL) were added to the vial and the mixture was immediately sparged with nitrogen for ~2 min. The vial was sealed with a PTFE-lined cap and the reaction was stirred at room temperature for 24 h. The reaction mixture was extracted with ethyl acetate, and the organic extract was filtered over a plug of celite. The filtrate was concentrated and then purified by flash column chromatography (100% hexanes) to afford **S13** as a colorless oil (45 mg, 48 % yield).). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.79 (d, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.52 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.37-7.23 (multiple signals, 4H, overlaps with solvent), 7.16 (d, *J* = 7.5 Hz, 1H), 2.06 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$ δ): 140.8, 139.0, 136.1, 131.7, 131.4, 129.7, 129.6, 128.9 (q, $^2J_{CF}$ = 29 Hz), 128.0, 127.4, 126.1 (q, $^3J_{CF}$ = 5 Hz), 125.0, 124.1 (q, $^1J_{CF}$ = 276 Hz), 20.2. ^{19}F (471 MHz, $CDCl_3$, δ): -59.2. HRMS (ESI/Q-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{14}H_{11}F_3Na^+$ 259.0705. Found 259.0711 .



1-Phenylnaphthalene (S14): The title compound was prepared according to a modified literature procedure.[8] Pd-P^{t}Bu$_3$-G4 (7.0 mg, 0.012 mmol, 3 mol %), phenyl boronic acid (49.3 mg, 0.404 mmol, 1.01 equiv), and KF (69.7 mg, 1.20 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, deionized water (7.2 µL, 0.40 mmol, 1 equiv), 1-chloronaphthalene (55 µL, 0.40 mmol, 1 equiv), and THF (1.0 mL) were added to the vial and the mixture was immediately sparged with nitrogen for ~ 2 min.. The vial was sealed with a PTFE-lined cap and the reaction was stirred at room temperature for 24 h. The reaction mixture was extracted with ethyl acetate, and the organic extract was filtered over a plug of celite. The filtrate was concentrated and then purified by flash column chromatography (100% hexanes) to afford **S14** as a viscous, colorless oil (6 mg, 7% yield). Spectral data are consistent with those previously reported.[13]



4-(Trifluoromethyl)phenyl triflate (S15b): The title compound was prepared according to a modified literature procedure.[14] With cooling to 0 °C, a solution of trifluoromethanesulfonic anhydride (4.0 mL, 24.0 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) was added dropwise to a solution of 4-hydroxybenzotrifluoride (3.24 g, 20.0 mmol) and pyridine (3.25 mL, 40.3 mmol, 2 equiv) in CH_2Cl_2 (20 mL). The mixture was allowed to warm to room temperature and stirred for 1 h, after which the solution was diluted with Et_2O and acidified with aqueous 1 *M* HCl. The layers were separated, and the aqueous layer was washed with Et_2O (3 x 10 mL). The combined organic layers were washed with saturated $NaHCO_3$ and brine (aqueous NaCl), dried over $MgSO_4$, filtered, and concentrated to give a yellow oil that was purified through a short silica plug (100% hexanes) to afford **S15b** as a clear, colorless oil (4.53 g, 77% yield). Spectral data are consistent with those previously reported.[15]

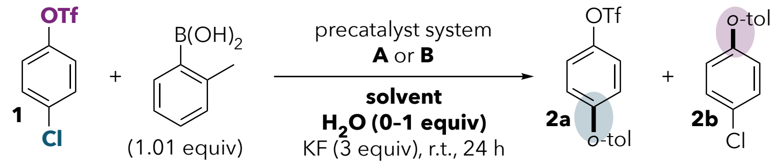
C. Catalytic Suzuki Couplings of 1

1. Evaluation of Precatalyst and Water Effect on Selectivity

General Procedure with Precatalyst System A: Without exclusion of air or moisture, P^tBu_3-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (0–1.4 µL, 0–0.08 mmol, 0–1 equiv), 4-chlorophenyl triflate (14 µL, 0.08 mmol, 1 equiv), and solvent (150 µL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at room temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

General Procedure for Precatalyst System B: In a nitrogen filled glovebox, Pd_2dba_3 (0.5 mg, 0.0006 mmol, 0.75 mol %), $Pd(PtBu_3)_2$ (0.6 mg, 0.0012 mmol, 1.5 mol %) , *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. The vial was sealed with a PTFE-lined cap and removed from the glovebox. Outside of the glovebox, the cap was removed and, in rapid succession, water (0–1.4 µL, 0–0.08 mmol, 0–1 equiv), 4-chlorophenyl triflate (14 µL, 0.08 mmol, 1 equiv), and solvent (150 µL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum cap was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at room temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S1. Effect of Precatalyst and Water on Selectivity[a]



precatalyst system **A**: P^{t}Bu$_3$-Pd-G4 (3 mol %)
precatalyst system **B**: Pd$_2$(dba)$_3$ (0.75 mol %), Pd(P^{t}Bu$_3$)$_2$ (1.5 mol %)

entry	solvent	precatalyst	H_2O (equiv)	trial	**1** (%)	**2a** (%)	**2b** (%)
1	THF	**A**	0	1	25	79	1
2	THF	**A**	0	2	21	79	1
3	THF	**A**	0	Average	23	79	1
4	THF	**A**	1	1	5	63	<1
5	THF	**A**	1	2	23	72	<1
6	THF	**A**	1	3	26	68	1
7	THF	**A**	1	4	25	71	1
8	THF	**A**	1	5	27	75	1
9	THF	**A**	1	6	24	79	1
10	THF	**A**	1	7	20	78	1
11	THF	**A**	1	8	18	79	1
12	THF	**A**	1	Average	20	74	<1
13	THF	**B**	1	1	28	72	1
14	THF	**B**	1	2	19	75	1
15	THF	**B**	1	Average	24	74	1
16	MeOH	**A**	1	1	0	68	3
17	MeOH	**A**	1	2	0	65	2
18	MeOH	**A**	1	Average	0	67	2
19	MeOH	**B**	1	1	35	19	2
20	MeOH	**B**	1	2	36	21	2
21	MeOH	**B**	1	Average	35	19	2
22	DMF	**A**	0	1	65	6	30
23	DMF	**A**	0	2	63	7	31
24	DMF	**A**	0	Average	64	7	30
25	DMF	**A**	1	1	16	9	58
26	DMF	**A**	1	2	19	9	61
27	DMF	**A**	1	3	24	11	59
28	DMF	**A**	1	4	26	11	59
29	DMF	**A**	1	5	16	12	66
30	DMF	**A**	1	6	20	11	62
31	DMF	**A**	1	7	18	9	66
32	DMF	**A**	1	8	46	7	46
33	DMF	**A**	1	Average	23	10	60
34	DMF	**B**	1	1	49	7	42
35	DMF	**B**	1	2	23	10	62
36	DMF	**B**	1	Average	36	9	52
37	MeCN	**A**	1	1	8	2	75
38	MeCN	**A**	1	2	8	2	78
39	MeCN	**A**	1	Average	8	2	77
40	MeCN	**B**	1	1	16	4	72
41	MeCN	**B**	1	2	19	4	71
42	MeCN	**B**	1	Average	17	4	72
43	propylene carbonate	**A**	1	1	9	57	6

44	propylene carbonate	**A**	1	2	23	68	6
45	propylene carbonate	**A**	1	3	12	75	5
46	propylene carbonate	**A**	1	4	19	68	6
47	propylene carbonate	**A**	1	Average	16	67	6
48	propylene carbonate	**B**	1	1	22	52	6
49	propylene carbonate	**B**	1	2	20	55	5
50	propylene carbonate	**B**	1	Average	21	53	6

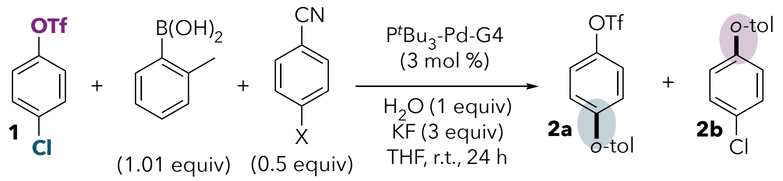
[a] GC yields calibrated against undecane as an internal standard. Diarylated product observed in ≤5% yield in all cases.

Discussion: The addition of 1 equiv water does not significantly impact selectivity (compare entries 3 vs 12, and 24 vs 33). Precatalyst systems **A** and **B** provide very similar selectivity in all solvents examined, although in some cases precatalyst **A** affords somewhat higher yields. Precatalyst **A** has the added advantage that it can be handled open to air.

2. *Benzonitrile Additives (Table 1 and Figure 1)*

General Procedure: Without exclusion of air or moisture, P^{t}Bu$_3$-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (1.4 μL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 μL, 0.08 mmol, 1 equiv), benzonitrile additive (0.04 mmol, 0.5 equiv, if applicable), and solvent (usually THF, 150 μL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at room temperature for 24 h. Undecane (7.5 μL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S2. Effect of Benzonitrile Additives on Selectivity[a]



entry	X	σ_p	σ_p^+	trial	**1** (%)	**2a** (%)	**2b** (%)	log (**2a**/**2b**)	std. dev.[b]
1[c]	--	--	--	1	5	63	<1	>1.80	
2[c]	--	--	--	2	23	72	<1	>1.86	
3[c]	--	--	--	3	26	68	1	1.83	
4[c]	--	--	--	4	25	71	1	1.85	
5[c]	--	--	--	5	27	75	1	1.88	
6[c]	--	--	--	6	24	79	1	1.90	
7[c]	--	--	--	7	20	78	1	1.89	
8[c]	--	--	--	8	18	79	1	1.90	
9[c]	--	--	--	Average	20	74	<1	>1.87	0.03
10	NMe2	-0.83	-1.70	1	46	28	15	0.27	
11	NMe2	-0.83	-1.70	2	47	29	20	0.16	
12	NMe2	-0.83	-1.70	3	37	36	21	0.23	

13	NMe2	-0.83	-1.70	Average	44	31	18	0.24	0.06
14	NH2	-0.66	-1.30	1	29	46	19	0.38	
15	NH2	-0.66	-1.30	2	29	45	20	0.35	
16	NH2	-0.66	-1.30	3	36	43	17	0.40	
17	NH2	-0.66	-1.30	Average	31	45	19	0.37	0.03
18	OH	-0.37	-0.92	1	38	50	16	0.49	
19	OH	-0.37	-0.92	2	28	53	14	0.58	
20	OH	-0.37	-0.92	3	33	46	16	0.46	
21	OH	-0.37	-0.92	Average	33	50	15	0.52	0.06
22	OEt	-0.24	-0.81	1	35	47	10	0.67	
23	OEt	-0.24	-0.81	2	41	45	8	0.75	
24	OEt	-0.24	-0.81	3	48	42	10	0.62	
25	OEt	-0.24	-0.81	Average	42	45	10	0.65	0.06
26	OMe	-0.27	-0.73	1	72	26	3	0.94	
27	OMe	-0.27	-0.73	2	56	18	2	0.95	
28	OMe	-0.27	-0.73	3	62	32	4	0.90	
29	OMe	-0.27	-0.73	Average	63	26	3	0.94	0.03
30	Me	-0.17	-0.31	1	65	35	2	1.24	
31	Me	-0.17	-0.31	2	66	25	2	1.10	
32	Me	-0.17	-0.31	3	69	28	2	1.15	
33	Me	-0.17	-0.31	Average	67	29	2	1.16	0.07
34	F	0.06	-0.07	1	40	51	5	1.01	
35	F	0.06	-0.07	2	71	30	2	1.18	
36	F	0.06	-0.07	3	46	50	5	1.00	
37	F	0.06	-0.07	Average	52	44	4	1.04	0.10
38	H	0	0	1	37	53	3	1.25	
39	H	0	0	2	43	53	6	0.95	
40	H	0	0	3	38	59	3	1.29	
41	H	0	0	Average	39	55	4	1.14	0.19
42	COOMe	0.45	0.49	1	56	41	3	1.14	
43	COOMe	0.45	0.49	2	55	44	3	1.17	
44	COOMe	0.45	0.49	3	55	41	3	1.14	
45	COOMe	0.45	0.49	Average	55	42	3	1.15	0.02
46	CF3	0.54	0.61	1	44	45	3	1.18	
47	CF3	0.54	0.61	2	46	49	3	1.21	
48	CF3	0.54	0.61	3	49	44	3	1.17	
49	CF3	0.54	0.61	Average	46	46	3	1.19	0.02
50	NO2	0.78	0.79	1	63	32	8	0.60	
51	NO2	0.78	0.79	2	49	38	8	0.68	
52	NO2	0.78	0.79	3	59	35	6	0.77	
53	NO2	0.78	0.79	Average	57	35	7	0.70	0.08
54[d]	--	--	--	1	27	7	54	-0.89	
55[d]	--	--	--	2	26	7	53	-0.88	
56[d]	--	--	--	Average	27	7	53	-0.88	0.01

[a]GC yields calibrated against undecane as an internal standard. Diarylated product observed in ≤5% yield in all cases. Sigma values from reference 16. [b]Standard deviation of the log(**2a**/**2b**) values. [b]No benzonitrile derivatives were added. [c]PhCN was used as the reaction solvent (no additional benzonitrile derivatives were added).

<u>Discussion</u>: Table S2 entries 10-49 were used to create Figure 1 in the manuscript, which shows a good correlation between σ_p^+ and log(**2a**/**2b**), with an R^2 value of 0.8639. The correlation to σ_p is not quite as strong (Figure S1). Unusual results were observed with 4-nitrobenzonitrile (entry 53). With this additive, the **2a**/**2b** ratio was much smaller than expected based on the trend with all of the other substituted benzonitriles (Figure S2). This particularly electron-poor nitrile is expected to coordinate to Pd(0) as a π-acceptor, and we speculate that the increased reaction

at OTf may be due to this coordination mode. There is no evidence that nitro groups in isolation promote reaction at triflate. For example, high selectivity for reaction at chloride is observed in the catalytic Suzuki coupling using 3-nitrophenylboronic acid in MeOH and THF,[8] and running the reaction shown in Table S2 with $PhNO_2$ as the solvent leads exclusively to product **2a** from reaction at chloride.

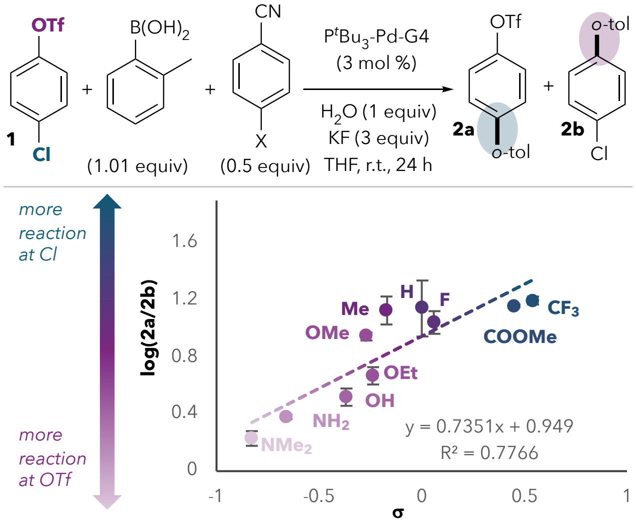


Figure S1. Hammett-type plot using σ shows slightly worse correlation than the plot using σ+.

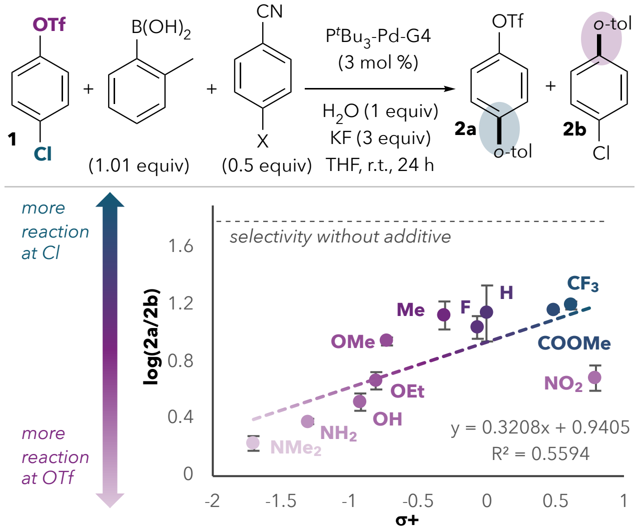
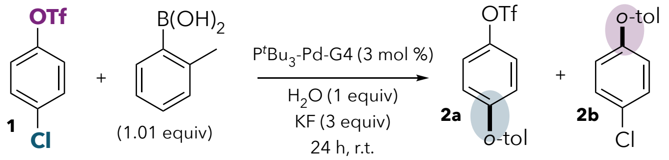


Figure S2. NO_2 is an outlier in the Hammett-type plot correlating benzonitrile donor ability and increased reaction at triflate.

3. Mixed THF/Benzonitrile Solvent

General Procedure: Without exclusion of air or moisture, P^tBu_3-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (1.4 μL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 μL, 0.08 mmol, 1 equiv), and solvent(s) (total of 150 μL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at room temperature for 24 h. Undecane (7.5 μL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S3. Effect of Mixed PhCN/THF Solvent on Selectivity[a]



PhCN (% of total solvent volume)	THF (% of total solvent volume)	trial	**1** (%)	**2a** (%)	**2b** (%)	total yield **2a** + **2b**	ratio **2a** : **2b**
0	100	1	5	63	<1	63	>63 : 1
0	100	2	23	72	<1	72	>72 : 1
0	100	3	26	68	1	69	68 : 1
0	100	4	25	71	1	72	71 : 1
0	100	5	27	75	1	76	75 : 1
0	100	6	24	79	1	80	79 : 1
0	100	7	20	78	1	79	78 : 1
0	100	8	18	79	1	80	79 : 1
0	100	average	21	74	1	75	74 : 1
1	99	1	33	56	2	58	28 : 1
1	99	2	19	74	2	76	37 : 1
1	99	average	26	65	2	67	33 : 1
5	95	1	58	30	6	36	5 : 1
5	95	2	45	41	9	50	5 : 1
5	95	average	51	35	7	43	5 : 1
10	90	1	39	33	17	50	2 : 1
10	90	2	38	36	19	55	2 : 1
10	90	average	39	35	18	53	2 : 1
25	75	1	26	25	38	63	1 : 2
25	75	2	21	26	38	64	1 : 2
25	75	average	24	25	38	63	1 : 2
50	50	1	13	15	48	63	1 : 3
50	50	2	17	13	52	65	1 : 4
50	50	average	15	14	50	64	1 : 4
75	25	1	18	12	56	68	1: 5
75	25	2	27	10	44	54	1 : 4
75	25	average	22	11	50	61	1 : 5
100	0	1	27	7	54	61	1 : 8
100	0	2	26	7	53	60	1 : 8
100	0	average	27	7	53	60	1 : 8

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

Discussion: The data in Table S3 show that selectivity inverts between 10-25% PhCN, as illustrated in Figure S3. Interestingly, small amounts of PhCN (5% and 10% of total volume) lead to lower conversion than observed in neat THF or with larger amounts of PhCN (≥25% of total volume). This phenomenon is illustrated in Figure S4. The unusual shape of the curve in Figure S4 may relate to solvent polarity. Small quantities of PhCN begin to suppress reaction at chloride because Pd is more likely to be bisligated. Reaction at triflate increases with small quantities of PhCN, but it increases even more with larger quantities of PhCN because of increased polarity of the reaction medium. Aryl triflates are known to undergo faster oxidative addition at bisligated palladium in more polar media.[17]

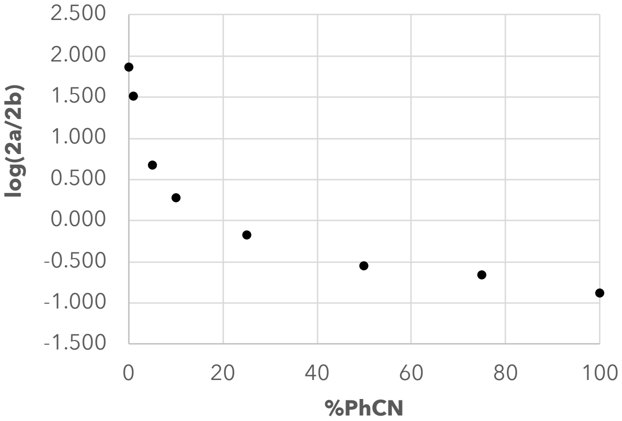


Figure S3. Effect of PhCN/THF ratio on product ratio.

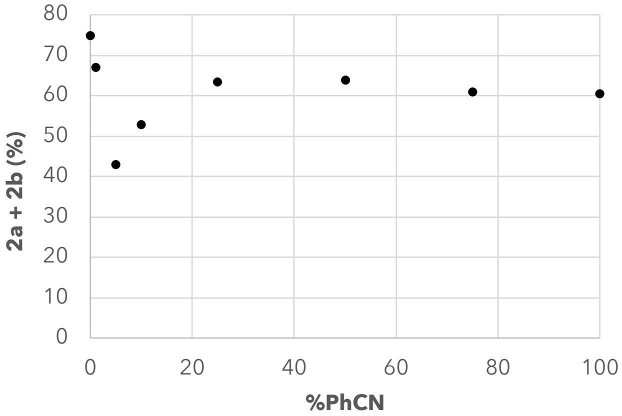
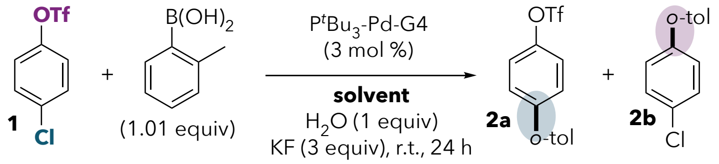


Figure S4. Effect of PhCN/THF ratio on the total yield of **2a** + **2b**.

4. Results with Fluoroacetonitrile, Sulfolane (Table 2), and Tetrahydrothiophene

General Procedure: Without exclusion of air or moisture, P^tBu_3-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (1.4 µL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 µL, 0.08 mmol, 1 equiv), and solvent (150 µL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at room temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S4. Modifying the Coordinating Ability of Common Solvents Leads to Changes in Selectivity[a]



entry	solvent	ε[b]	trial	**1** (%)	**2a** (%)	**2b** (%)
1	CH_3CN	36.6	1	8	2	75
2	CH_3CN	36.6	2	8	2	78
3	CH_3CN	36.6	Average	8	2	77
4	CH_2FCN	~36	1	85	4	10
5	CH_2FCN	~36	2	88	3	9
6	CH_2FCN	~36	Average	86	4	10
7	DMSO	47.2	1	61	1	26
8	DMSO	47.2	2	25	1	64
9	DMSO	47.2	Average	43	1	45
10	sulfolane	42.2	1	41	44	12
11	sulfolane	42.2	2	41	43	10
12	sulfolane	42.2	Average	41	44	11
13	THF	7.5	1	5	63	<1
14	THF	7.5	2	23	72	<1
15	THF	7.5	3	26	68	1
16	THF	7.5	4	25	71	1
17	THF	7.5	5	27	75	1
18	THF	7.5	6	24	79	1
19	THF	7.5	7	20	78	1
20	THF	7.5	8	18	79	1
21	THF	7.5	Average	20	74	<1
22	tetrahydrothiophene	8.6	1	92	0	2
23	tetrahydrothiophene	8.6	2	105	0	1
24	tetrahydrothiophene	8.6	Average	99	0	2

[a]GC yields calibrated against undecane as an internal standard. Results are the average of at least two trials. Diarylated product observed in ≤3% yield in all cases. [b]Dielectric constants from references 18 and 19.

Discussion: Although reaction in THF provides **2a** as the major product (Table S4, entry 21), the only product observed in tetrahydrothiophene (THT) is **2b** (entry 24). This is consistent with THT acting as a coordinating ligand during oxidative addition. However the yield is so low that selectivity cannot be reliably interpreted. The low yield is likely due to the strong coordinating ability of sulfides to palladium, effectively poisoning it as a catalyst. For a discussion of entries 1-12, see the manuscript.

5. Effect of Temperature (Table 4)

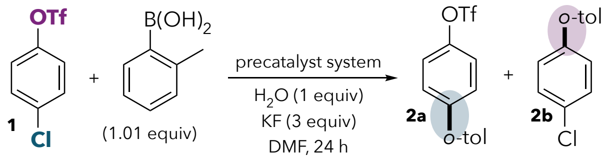
General Procedure with Precatalyst System A: Without exclusion of air or moisture, P^tBu_3-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (1.4 µL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 µL, 0.08 mmol, 1 equiv), and solvent (150 µL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at the indicated temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

General Procedure for Precatalyst Systems B-E: In a nitrogen filled glovebox, the following reagents were combined with *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv) and KF (13.9 mg, 0.24 mmol, 3 equiv) in a 1-dram vial equipped with a magnetic stir bar:

Precatalyst System B: Pd_2dba_3 (0.5 mg, 0.0006 mmol, 0.75 mol %), $Pd(PtBu_3)_2$ (0.6 mg, 0.0012 mmol, 1.5 mol %)
Precatalyst System C: Pd_2dba_3 (1.1 mg, 0.0012 mmol, 1.5 mol %), $PtBu_3$ (0.5 mg, 0.0024 mmol, 3.0 mol %)
Precatalyst System D: $Pd(OAc)_2$ (0.7 mg, 0.0024 mmol, 3.0 mol %), $PtBu_3$ (0.5 mg, 0.0024 mmol, 3.0 mol %)
Precatalyst System E: $Pd(COD)(CH_2TMS)_2$ (0.9 mg, 0.0024 mmol, 3.0 mol %), $PtBu_3$ (0.5 mg, 0.0024 mmol, 3.0 mol %)

The vial was sealed with a PTFE-lined cap and removed from the glovebox. Outside of the glovebox, the cap was removed and, in rapid succession, water (1.4 µL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 µL, 0.08 mmol, 1 equiv), and solvent (150 µL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at the indicated temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S5. Effect of Reaction Temperature of Suzuki Selectivity[a]



precatalyst system **A**: P^tBu_3-Pd-G4 (3 mol %)
precatalyst system **B**: $Pd_2(dba)_3$ (0.75 mol %), $Pd(P^tBu_3)_2$ (1.5 mol %)
precatalyst system **C**: $Pd_2(dba)_3$ (1.5 mol %), P^tBu_3 (3 mol %)
precatalyst system **D**: $Pd(OAc)_2$ (3 mol %), P^tBu_3 (3 mol %)
precatalyst system **E**: $Pd(COD)(CH_2TMS)_2$ (3 mol %), P^tBu_3 (3 mol %)

entry	solvent	precatalyst	temperature	trial	**1** (%)	**2a** (%)	**2b** (%)	ΔΔG‡
1	THF	**A**	r.t.	1	5	63	<1	>2.4
2	THF	**A**	r.t.	2	23	72	<1	>2.5
3	THF	**A**	r.t.	3	26	68	1	2.5
4	THF	**A**	r.t.	4	25	71	1	2.5
5	THF	**A**	r.t.	5	27	75	1	2.6
6	THF	**A**	r.t.	6	24	79	1	2.6
7	THF	**A**	r.t.	7	20	78	1	2.6
8	THF	**A**	r.t.	8	18	79	1	2.6
9	THF	**A**	r.t.	Average	20	74	<1	>2.5
10	THF	**A**	100 °C	1	9	77	0	>2.6
11	THF	**A**	100 °C	2	10	87	1	2.6
12	THF	**A**	100 °C	Average	10	82	<1	>2.6
13	THF	**B**	r.t.	1	17	79	1	2.6
14	THF	**B**	r.t.	2	16	78	0	2.6
15	THF	**B**	r.t.	Average	17	79	1	2.6
16	THF	**B**	100 °C	1	7	75	<1	>2.6
17	THF	**B**	100 °C	2	5	72	<1	>2.5
18	THF	**B**	100 °C	Average	6	73	<1	>2.5
19	DMF	**A**	r.t.	1	16	9	58	-1.1
20	DMF	**A**	r.t.	2	19	9	61	-1.1
21	DMF	**A**	r.t.	3	24	11	59	-1.0
22	DMF	**A**	r.t.	4	26	11	59	-1.0
23	DMF	**A**	r.t.	5	16	12	66	-1.0
24	DMF	**A**	r.t.	6	20	11	62	-1.0
25	DMF	**A**	r.t.	7	18	9	66	-1.2
26	DMF	**A**	r.t.	8	46	7	46	-1.1
27	DMF	**A**	r.t.	Average	23	10	60	-1.1
28	DMF	**A**	100 °C	1	2	24	29	-0.1
29	DMF	**A**	100 °C	2	3	19	31	-0.3
30	DMF	**A**	100 °C	Average	2	21	30	-0.2
31	DMF	**B**	r.t.	1	17	11	67	-1.1
32	DMF	**B**	r.t.	2	17	11	67	-1.1
33	DMF	**B**	r.t.	Average	17	11	67	-1.1
34	DMF	**B**	100 °C	1	6	33	24	0.2
35	DMF	**B**	100 °C	2	9	34	22	0.3
36	DMF	**B**	100 °C	Average	7	33	23	0.2
37	DMF	**C**	r.t.	1	101	0	1	--
38	DMF	**C**	r.t.	2	75	3	23	-1.2

39	DMF	**C**	r.t.	Average	88	2	12	-1.1
40	DMF	**C**	100 °C	1	10	38	19	0.4
41	DMF	**C**	100 °C	2	42	30	19	0.3
42	DMF	**C**	100 °C	Average	26	34	19	0.3
43	DMF	**D**	r.t.	1	48	1	42	-2.2
44	DMF	**D**	r.t.	2	39	7	44	-1.1
45	DMF	**D**	r.t.	Average	44	4	43	-1.4
46	DMF	**D**	100 °C	1	12	20	18	0.1
47	DMF	**D**	100 °C	2	11	8	14	-0.3
48	DMF	**D**	100 °C	Average	11	14	16	-0.1
49	DMF	**E**	r.t.	1	60	4	33	-1.2
50	DMF	**E**	r.t.	2	39	6	47	-1.2
51	DMF	**E**	r.t.	Average	50	5	40	-1.2
52	DMF	**E**	100 °C	1	9	26	20	0.2
53	DMF	**E**	100 °C	2	9	38	20	0.4
54	DMF	**E**	100 °C	Average	9	32	20	0.3

[a]GC yields calibrated against undecane as an internal standard. [b]Calculated difference in activation barriers to forming products (**2b** – **2a**) based on $\Delta\Delta G^{\ddagger} = RT\ln(\mathbf{2a}/\mathbf{2b})$.

Discussion: In DMF, more reaction at chloride is observed at 100 °C compared to room temperature. However, the 100 °C product ratios vary somewhat depending on precatalyst source. This difference is most prominent for precatalyst system **A** compared to the other precatalyst systems. As shown in Table S6, the change in $\Delta\Delta G^{\ddagger}$ when going from room temperature to 100 °C is smaller for this system than for the other systems.

Table S6. Effect of Reaction Temperature of Suzuki Selectivity[a]

precatalyst	$\Delta\Delta G_{(\mathbf{2b}\text{-}\mathbf{2a})}^{\ddagger}$ at r.t.	$\Delta\Delta G_{(\mathbf{2b}\text{-}\mathbf{2a})}^{\ddagger}$ at 100 °C	change in $\Delta\Delta G^{\ddagger}$ from r.t. to 100 °C
A	-1.1	-0.2	0.9
B	-1.1	+0.2	1.3
C	-1.1	+0.3	1.4
D	-1.4	-0.1	1.3
E	-1.2	+0.3	1.5

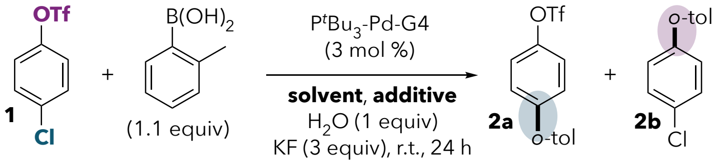
[a]Data are taken from Table S5.

The difference in selectivity between different precatalyst systems at 100 °C is inconsistent with hypotheses that (a) the temperature effect is solely due to entropy (where higher temperature disfavors a bisligated oxidative addition transition state) or (b) that oxidative addition is reversible at this temperature and selectivity is based on thermodynamics or on the rate of a subsequent step of the catalytic cycle. Instead, these observations are consistent with catalyst decomposition at 100 °C leading to a species that favors chloride activation. Different precatalysts may decompose at different rates. However, further study is needed to generate higher quality data to support or refute this hypothesis. In THF, no significant temperature effect is observed with either precatalyst system, and the reaction is selective for chloride at both temperatures.

6. Effect of Additives (Table 6)

General Procedure: Without exclusion of air or moisture, P^tBu_3-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), KF (13.9 mg, 0.24 mmol, 3 equiv), and other additives (0–3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (1.4 μL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 μL, 0.08 mmol, 1 equiv), and solvent (150 μL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at room temperature for 24 h. Undecane (7.5 μL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S7. Additive Effects[a]



entry	solvent	additive (equiv)	trial	**1** (%)	**2a** (%)	**2b** (%)
1	THF	--	1	5	63	<1
2	THF	--	2	23	72	<1
3	THF	--	3	26	68	1
4	THF	--	4	25	71	1
5	THF	--	5	27	75	1
6	THF	--	6	24	79	1
7	THF	--	7	20	78	1
8	THF	--	8	18	79	1
9	THF	--	Average	20	74	<1
10	THF	18-crown-6 (3)	1	0	2	77
11	THF	18-crown-6 (3)	2	0	1	76
12	THF	18-crown-6 (3)	Average	0	1	76
13[b]	THF	NBu_4F (3)	1	<1	<1	17
14[b]	THF	NBu_4F (3)	2	<1	<1	9
15[b]	THF	NBu_4F (3)	Average	<1	<1	13
16	THF	NBu_4Cl (1)	1	20	4	70
17	THF	NBu_4Cl (1)	2	21	4	69
18	THF	NBu_4Cl (1)	Average	20	4	69
19	THF	NBu_4Br (1)	1	1	4	90
20	THF	NBu_4Br (1)	2	5	1	91
21	THF	NBu_4Br (1)	Average	3	2	91
22	THF	NBu_4OTf (1)	1	27	72	3
23	THF	NBu_4OTf (1)	2	26	67	3
24	THF	NBu_4OTf (1)	Average	26	70	3
25	^{i}PrOH	--	1	4	79	1
26	^{i}PrOH	--	2	1	95	1
27	^{i}PrOH	--	Average	2	87	1
28	^{i}PrOH	18-crown-6 (3)	1	0	0	5
29	^{i}PrOH	18-crown-6 (3)	2	0	0	1
30	^{i}PrOH	18-crown-6 (3)	Average	0	0	3

31	PC	--	1	12	75	5
32	PC	--	2	19	68	6
33	PC	--	Average	15	71	5
34	PC	18-crown-6 (3)	1	5	2	14
35	PC	18-crown-6 (3)	2	5	1	8
36	PC	18-crown-6 (3)	Average	5	1	11
37	DMF	--	1	16	9	58
38	DMF	--	2	19	9	61
39	DMF	--	3	24	11	59
40	DMF	--	4	26	11	59
41	DMF	--	5	16	12	66
42	DMF	--	6	20	11	62
43	DMF	--	7	18	9	66
44	DMF	--	8	46	7	46
45	DMF	--	Average	23	10	60
46	DMF	18-crown-6 (3)	1	0	0	45
47	DMF	18-crown-6 (3)	2	0	0	50
48	DMF	18-crown-6 (3)	Average	0	0	47

[a] GC yields calibrated against undecane as an internal standard. Diarylated product observed in ≤4% yield in all cases except entry 12 (8%). [b] KF was omitted from the reaction mixture.

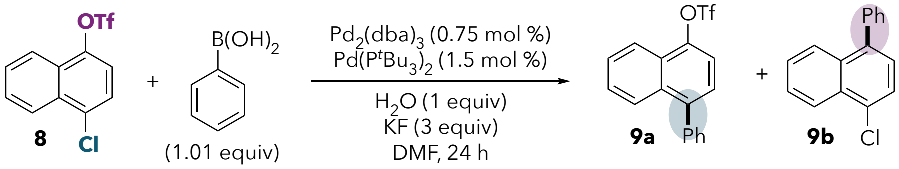
7. Recycling "Decomposed" Catalyst

Hypothesis: The results in Tables 3-5 of the manuscript show that heating either the Stille or Suzuki coupling in DMF leads to increased reaction at chloride. One hypothesis is that, upon heating, the catalyst decomposes to a new catalytically active species that preferentially reacts at chloride. If this is the case, then we would expect that the 'decomposed' catalyst would continue to demonstrate chloride-selectivity when it is recycled. To test this hypothesis, we conducted a Suzuki coupling of **1** at 100 °C for 4 h, then added a second substrate (**8**) and a second boronic acid and stirred for an additional 100 °C at either room temperature or 100 °C (Table S9). In order to interpret the results, it was necessary to establish the baseline selectivity of the Suzuki cross-coupling of **8** at both room temperature and 100 °C (Table S8).

General Procedure for Table S8: In a nitrogen filled glovebox, Pd_2dba_3 (0.5 mg, 0.0006 mmol, 0.75 mol %), $Pd(Pt\text{-}Bu_3)_2$ (0.6 mg, 0.0012 mmol, 1.5 mol %) , and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. The vial was sealed with a PTFE-lined cap and removed from the glovebox. Outside of the glovebox, the cap was removed and, in rapid succession, water (1.4 µL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 µL, 0.08 mmol, 1 equiv), phenylboronic acid (9.9 mg, 0.081 mmol, 1.01 equiv), and DMF (150 µL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes, then resealed with a PTFE-lined cap. The reaction was stirred vigorously at the indicated temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

General Procedure for Table S9: In a nitrogen filled glovebox, Pd_2dba_3 (0.5 mg, 0.0006 mmol, 0.75 mol %), Pd(Pt-Bu$_3$)$_2$ (0.6 mg, 0.0012 mmol, 1.5 mol %) , *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. The vial was sealed with a PTFE-lined cap and removed from the glovebox. Outside of the glovebox, the cap was removed and, in rapid succession, water (1.4 µL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 µL, 0.08 mmol, 1 equiv), and DMF (150 µL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes, then resealed with a PTFE-lined cap and the reaction stirred vigorously at 100 °C for 4 h. The reaction was allowed to cool to room temperature, then briefly uncapped (~10 seconds) and phenylboronic acid (9.9 mg, 0.081 mmol, 1.01 equiv) and 4-chloronaphthyl triflate (16 µL, 0.08 mmol) were quickly added. The reaction mixture was immediately sparged with nitrogen for two minutes through a septum cap. The sparging needle and septum cap were quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at the indicated temperature for an additional 24 h. Undecane (7.5 µL) and dodecane (8.0 µL) were added to the reaction mixture as internal standards, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

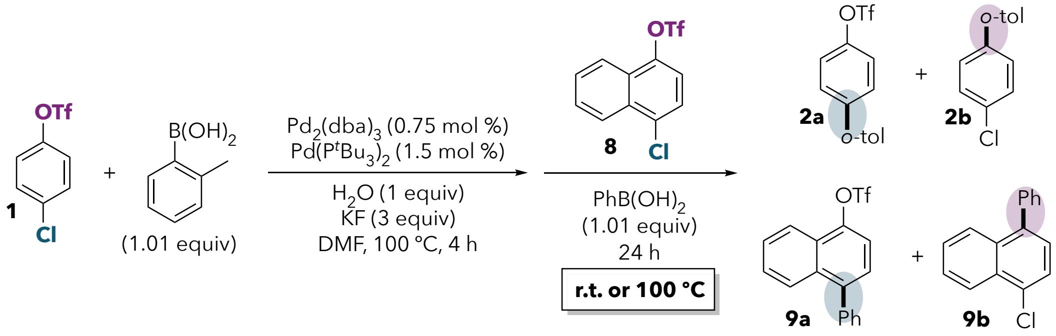
Table S8. Effect of Temperature on Selectivity of Suzuki Coupling of Substrate **8**[a]



entry	temperature	trial	**8** (%)	**9a** (%)	**9b** (%)
1	r.t.	1	7	3	52
2	r.t.	2	16	4	43
3	r.t.	Average	11	4	47
4	100 °C	1	0	1	31
5	100 °C	2	0	2	30
6	100 °C	Average	0	1	30

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

Table S9. Recycling Thermally Decomposed Catalyst[a]



entry	temperature	trial	**1** (%)	**2a** (%)	**2b** (%)	**8** (%)	**9a** (%)	**9b** (%)
1	r.t.	1	19	44	22	87	1	7
2	r.t.	2	25	40	21	89	1	4
3	r.t.	Average	22	42	21	88	1	5
4	100 °C	1	17	29	17	24	22	13
5	100 °C	2	17	40	20	25	29	20
6	100 °C	Average	17	35	18	25	26	17

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

Discussion: As shown in Table S8, substrate **8** does *not* exhibit the same switch in selectivity at 100 °C as seen for substrate **1** in Table 4 of the manuscript. The major product of Suzuki coupling of **8** is **9b**, from reaction at triflate, at both room temperature and at 100 °C. This observation may be rationalized by the higher reactivity of substrate **8**. If Suzuki coupling is fast, then it can outcompete slower decomposition of catalyst. Notably, the mass balance is poor at both temperatures, suggesting that this substrate is prone to decomposition (e.g., by hydrolysis of the triflate).

When the catalyst is recycled, very poor conversion of **8** is observed at room temperature (Table S9, entry 3). Under these conditions, the major product remains the one resulting from triflate activation (**9b**), albeit in only 5% yield. On the other hand, the use of recycled catalyst at 100 °C leads to preferential reaction at chloride, giving **9a** as the major product in 26% yield (entry 6). Critically, this chloride selectivity is different from the triflate-selectivity observed in the high-temperature Suzuki reaction of **8** using fresh catalyst (Table S8, entry 6). A comparison of Table S8, entry 6 and Table S9, entry 6 demonstrates that high temperature alone is *not* sufficient to cause chloride-selective cross-coupling of **8**. Instead, prior heat treatment of the catalyst (hypothesized to cause decomposition) is necessary before chloride-selectivity can be observed.

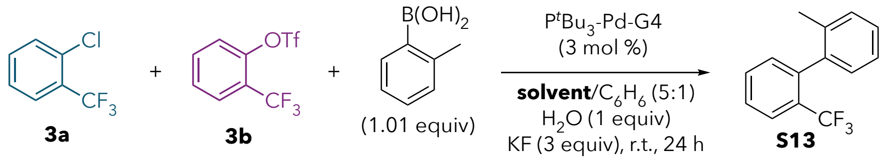
These results are consistent with the following scenario: Using fresh catalyst, the Suzuki reaction of **8** is fast enough at 100 °C to outcompete catalyst decomposition. Thus, Suzuki coupling of **8** using fresh catalyst favors triflate activation at both room temperature and 100 °C (Table S8). The active catalytic species is expected to be [Pd(P^{t}Bu$_3$)(DMF)] prior to decomposition. Heating to 100 °C for 4 h in the presence of Suzuki coupling reagents (including **1**) leads to decomposition of most of the catalyst to an unidentified species that exhibits chloride selectivity. When this decomposed catalyst is recycled at room-temperature for the reaction of **8**, poor yield is observed because the decomposed catalyst is not active at low temperature (i.e., the barrier to one or more steps of the catalytic cycle with this catalytic species is too high to be overcome at room temperature). Instead, the small amount of cross-coupling that does occur at room temperature is catalyzed by residual [Pd(P^{t}Bu$_3$)(DMF)]. However, the decomposed catalyst *is* active at 100 °C, and leads primarily to chloride activation (Table S9, entry 2).

D. Reactions with 3a and 3b

1. Catalytic Suzuki Couplings

<u>General Procedure</u>: Without exclusion of air or moisture, P^{t}Bu$_3$-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (1.4 µL, 0.08 mmol, 1 equiv), 1-chloro-2-trifluoromethylbenzene (6.5 µL, 0.08 mmol, 1 equiv), 2-trifluoromethylphenyl triflate (14.8 µL, 0.08 mmol, 1 equiv), and a 5:1 mixture of solvent:benzene (150 µL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at room temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S10. Intermolecular Competition Between **3a** and **3b** in the Catalytic Suzuki Coupling[a]



entry	solvent	trial	**3a** (%)	**3b** (%)	**S13**(%)
1	toluene	1	11	88	91
2	toluene	2	13	92	90
3	toluene	Average	12	90	91
4	THF	1	20	90	86
5	THF	2	20	90	84
6	THF	Average	20	90	85
7	acetone	1	22	82	84
8	acetone	2	13	78	92
9	acetone	Average	17	80	88
10	MeOH	1	3	52	94
11	MeOH	2	2	43	88
12	MeOH	Average	3	48	91
13	MeCN	1	92	18	67
14	MeCN	2	93	17	66
15	MeCN	Average	92	18	66
16	DMF	1	77	11	88
17	DMF	2	79	15	81
18	DMF	Average	78	13	84
19	sulfolane	1	55	61	50
20	sulfolane	2	64	58	37
21	sulfolane	Average	59	60	43
22	PC	1	30	80	75
23	PC	2	26	77	84
24	PC	Average	28	78	79

[a] GC yield calibrated against undecane as an internal standard.

Discussion: The catalytic cross-coupling selectivity shown in Table S10 qualitatively matches the selectivity observed in the stoichiometric oxidative addition studies (Table 3). However, the mass balance is poor in polar solvents. For example, 91% yield of **S13** is observed in MeOH, but 149% of the starting material is consumed (97% of **3a** and 52% of **3b**). The poor mass balance in polar solvents is likely due to hydrolysis of the electron-deficient aryl triflate **3b**.

2. Stoichiometric Oxidative Addition Studies (Table 3)

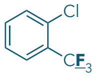
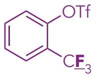
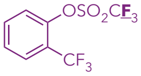
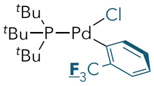
a. 19F NMR Calibrations

Representative Procedure: Inside a nitrogen-filled glovebox, P^tBu_3 (5.5 mg, 0.027 mmol, 1 equiv) was measured into a 1-dram scintillation vial. In a separate vial, a solution was prepared of **3a** (3.6 μL, 0.027 mmol, 1 equiv), **3b** (5.0 μL, 0.027 mmol, 1 equiv), and C_6H_5F (7.6 μL, 0.081 mmol, 3 equiv) in C_6D_6 (100 μL). 500 μL of the indicated solvent was added to the vial containing P^tBu_3, followed by the entire volume of the substrate solution. The vial was capped and shaken briefly, and then the solution was transferred via Pasteur pipette into an NMR tube. The tube was capped tightly, removed from the glovebox, and the sample was immediately analyzed by ^{19}F NMR. The observed ratio of substrate to C_6H_5F signals at this "time=0" was used to define the expected ratios for 100% calibrated yield of recovered substrates in the subsequent intermolecular competition reactions run for 6 h. For **3b**, yields were calculated separately based on each of its two fluorine signals and then averaged together.

b. ^{19}F NMR Chemical Shifts

Peaks corresponding to **3a**, **3b**, and 'free' triflate were assigned by comparison to the spectra of authentic samples of **3a**, **3b**, and NBu_4OTf in 600 μL of a mixture of solvent:C_6D_6 (5:1 v/v). Chemical shifts were referenced to fluorobenzene (set to -113.15 ppm regardless of solvent). The ^{19}F NMR signals corresponding to **S10** were assigned by comparison to the spectra of an authentic sample prepared by a literature procedure and/or by analogy to the published spectral data for this compound and the spectra in other solvents.[4] Relevant chemical shifts in the different solvent mixtures are assigned as follows:

Table S11. ^{19}F Chemical Shifts of Relevant Species by Solvent: *ortho*-CF_3 Substrates

	 **3a**	 **3b**	 **3b**	OTf^- anion (NBu_4OTf)	 **S10**
toluene	-62.9	-61.2	-74.7	-78.4	-55.3[b]
THF	-62.2	-60.3	-74.0	-78.1	-54.7[c]
acetone	-61.6	-59.7	-73.5	-77.4	-54.1[c]
MeOH[a]	-61.9	-60.0	-73.6	-78.0	-54.3[b]
MeCN	-61.5	-59.5	-73.1	-77.5	-54.1[b]
DMF	-61.1	-59.4	-73.3	-77.4	-53.9[b]
sulfolane	-59.8	-61.7	-73.5	-80.0	*n.d.*[d]
PC	-59.5	-61.1	-73.1	-77.7	-54.1[c]

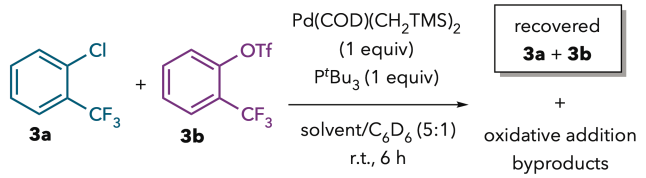
[a] In a control reaction in this solvent in the absence of palladium, a small amount of decomposition of **3b** to form 2-$CF_3C_6H_4OH$ and free OTf was observed. [b] Chemical shift was identified by analysis of the authentic material, prepared by a literature

procedure,[4] in the indicated solvent. [c]Chemical shift was identified in the oxidative addition reactions by analogy to the chemical shift observed of this compound in other solvents. [d]n.d. = not determined.

c. Oxidative Addition Reactions

Representative Procedure: Inside a nitrogen-filled glovebox, P^{t}Bu$_3$ (5.5 mg, 0.027 mmol, 1 equiv) and Pd(COD)(CH$_2$TMS)$_2$ (10.5 mg, 0.027 mmol, 1 equiv) were combined in a 1-dram vial equipped with a stir bar. In a separate vial, a solution was prepared of **3a** (3.6 µL, 0.027 mmol, 1 equiv), **3b** (5.0 µL, 0.027 mmol, 1 equiv), and C_6H_5F (7.6 µL, 0.081 mmol, 3 equiv) in C_6D_6 (100 µL). 500 µL of the indicated solvent was added to the vial containing P^{t}Bu$_3$ and Pd(COD)(CH$_2$TMS)$_2$, followed by the entire volume of the substrate solution. The vial was sealed with a PTFE-lined cap and the reaction was allowed to stir for 6 h at room temperature. The reaction mixture was transferred via Pasteur pipette into an NMR tube. The tube was capped tightly, removed from the glovebox, and immediately analyzed by ^{19}F NMR.

Table S12. Stoichiometric oxidative addition reactions of **3a** and **3b**.

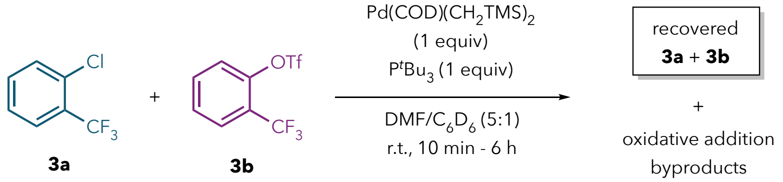


entry	solvent	trial	recovered (%)[a] **3a**	**3b**	reacted **3a** : **3b**
1	toluene	1	90	≥99	≥ 10 : 1
2	toluene	2	89	≥99	≥ 11 : 1
3	toluene	Average	89	≥99	≥ 11 : 1
4[b]	toluene	1	64	≥99	≥ 36 : 1
5[b]	toluene	2	40	91	7 : 1
6[b]	toluene	Average	52	98	24 : 1
7	THF	1	61	≥99	≥39 : 1
8	THF	2	52	≥99	≥48 : 1
9	THF	3	51	92	6 : 1
10	THF	Average	55	97	15 : 1
11	acetone	1	69	91	3 : 1
12	acetone	2	73	≥99	≥27 : 1
13	acetone	Average	71	98	15 : 1
14	MeOH	1	66	≥99	≥36 : 1
15	MeOH	2	74	≥99	≥26 : 1
16	MeOH	Average	70	≥99	≥30 : 1
17	MeCN	1	94	0	1 : 16
18	MeCN	2	96	3	1 : 24
19	MeCN	3	≥99	0	≤1 : 100
20	MeCN	4	≥99	0	≤1 : 100
21	MeCN	Average	97	1	1 : 33
22	DMF	1	88	57	1 : 4
23	DMF	2	87	57	1 : 3
24	DMF	3	76	33	1 : 3
25	DMF	4	63	29	1 : 2
26	DMF	Average	78	44	1 : 3

27	sulfolane	1	82	93	3 : 1
28	sulfolane	2	90	98	5 : 1
29	sulfolane	Average	86	95	3 : 1
30	PC[c]	1	74	93	4 : 1
31	PC[c]	2	79	95	4 : 1
32	PC[c]	3	98	97	1 : 2
33	PC[c]	4	80	92	3 : 1
34	PC[c]	Average	83	94	3 : 1
35[d]	MeCN	1	>99	≥99	--
36[d]	DMF	1	>99	≥99	--
37[e]	MeCN	1	n.a.	5	--
38[e]	MeCN	2	n.a.	3	--
39[e]	MeCN	3	n.a.	0	--
40[e]	MeCN	Average	n.a.	3	--
41[e]	DMF	1	n.a.	23	--
42[e]	DMF	2	n.a.	25	--
43[e]	DMF	3	n.a.	36	--
44[e]	DMF	Average	n.a.	28	--
45	Toluene-d_8	1	74	97	9 : 1
46	Toluene-d_8	2	85	≥99	≥15 : 1
47	Toluene-d_8	Average	79	98	11 : 1
48	MeCN-d_3	1	87	0	1 : 8
49	MeCN-d_3	2	87	1	1 : 8
50	MeCN-d_3	Average	87	1	1 : 8
51	DMF-d_7	1	91	40	1 : 7
52	DMF-d_7	2	93	52	1 : 7
53	DMF-d_7	Average	92	46	1 : 7
54[f]	DMF	1	36	34	1 : 1
55[f]	DMF	2	47	45	1 : 1
56[f]	DMF	Average	42	39	1 : 1
57[g]	DMF	1	94	86	1 : 2
58[g]	DMF	2	98	83	1 : 8
59[g]	DMF	Average	96	83	1 : 4

[a] ^{19}F NMR yields calibrated against C_6H_5F as an internal standard. [b] Heated to 80 °C for 2 h. [c] PC = propylene carbonate. [d] $Pd(COD)(CH_2TMS)_2$ was omitted from the reaction mixture. [e] **3a** was omitted from the reaction mixture (n.a. = not applicable). [f] Heated at 100°C. [g] Cooled to 0 °C.

Table S13. Stoichiometric oxidative addition reactions of **3a** and **3b** in DMF tracked over time.[a]



entry	time	recovered (%)[b] **3a**	**3b**	reacted **3a : 3b**
1	10 min	99	94	1 : 3
2	20 min	≥99	95	<1 : 5
3	30 min	99	93	1 : 7
4	1 h	98	88	1 : 6
5	3 h	98	82	1 : 9
6	6 h	97	74	1 : 9

[a] The reaction setup differed from the Representative Procedure in that the reaction was run in an NMR tube (without stirring) instead of in a vial with a stir bar. [b] ^{19}F NMR yields calibrated against C_6H_5F as an internal standard.

Analysis of Variable Temperature and Time Studies for the Reaction in DMF

Three main signals are observed in the ^{31}P NMR spectrum of the DMF reaction after 6 h at room temperature: 85 ppm [assigned to $Pd(P^tBu_3)_2$], ~75 ppm, and 53 ppm (assigned to cationic HP^tBu_3). At 0 °C, the phosphonium signal is absent, but there is an additional signal at ~64 ppm. Finally, at 100 °C there are around a dozen signals. One small signal corresponds to $Pd(P^tBu_3)_2$, but none of the other signals match those seen at r.t. or 0 °C. Figure S5 illustrates the ^{31}P NMR spectra of these reactions, which correspond to entries 26, 56, and 59 in Table S12. The signals at ~74 and ~64 are tentatively assigned as products resulting from oxidative addition of aryl triflate **3b**. The following observations are worth noting:

- The signal at 64 ppm is observable within 10 minutes at room temperature (Table S13 and Figure S6), but is slowly replaced by the signal at 74 ppm. By 3 h reaction time, the 64 ppm signal is gone but the 74 ppm signal remains at 6 h.
- The signal at 64 ppm is detected even at 6 h when the reaction is run at cold temperature (0 °C).
- The signal at 74 ppm is detected even in the absence of **3a**, so it is not derived from **3a**.

Two signals in the ^{19}F NMR spectra for the time studies in DMF display a pattern of growth and disappearance that matches those of the signals in the ^{31}P NMR spectra. These are labeled in Figure S7 with the same labels used in Figure S6.

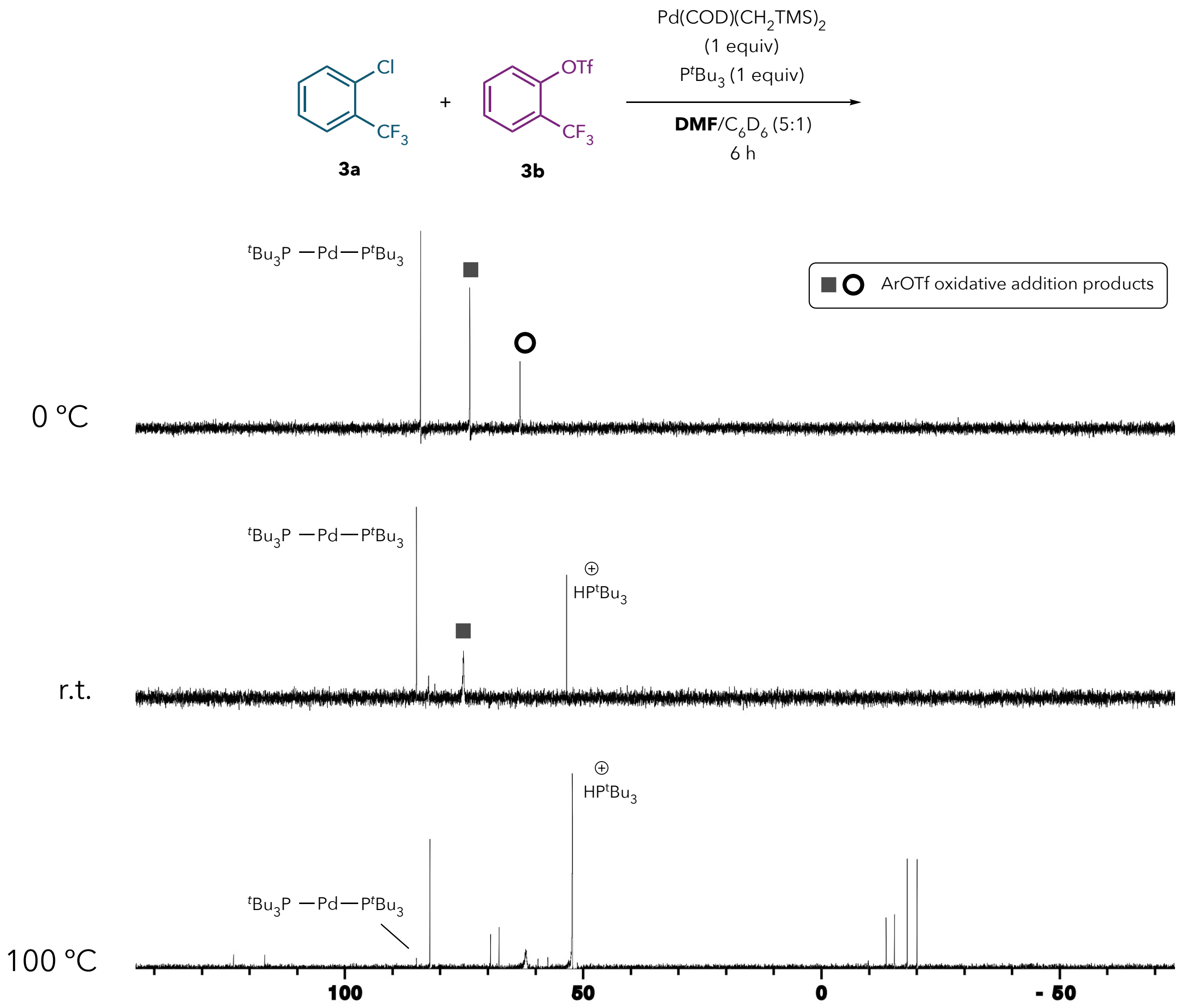


Figure S5. Stacked ^{31}P NMR spectra for the reaction of **3a** and **3b** in DMF at three temperatures.

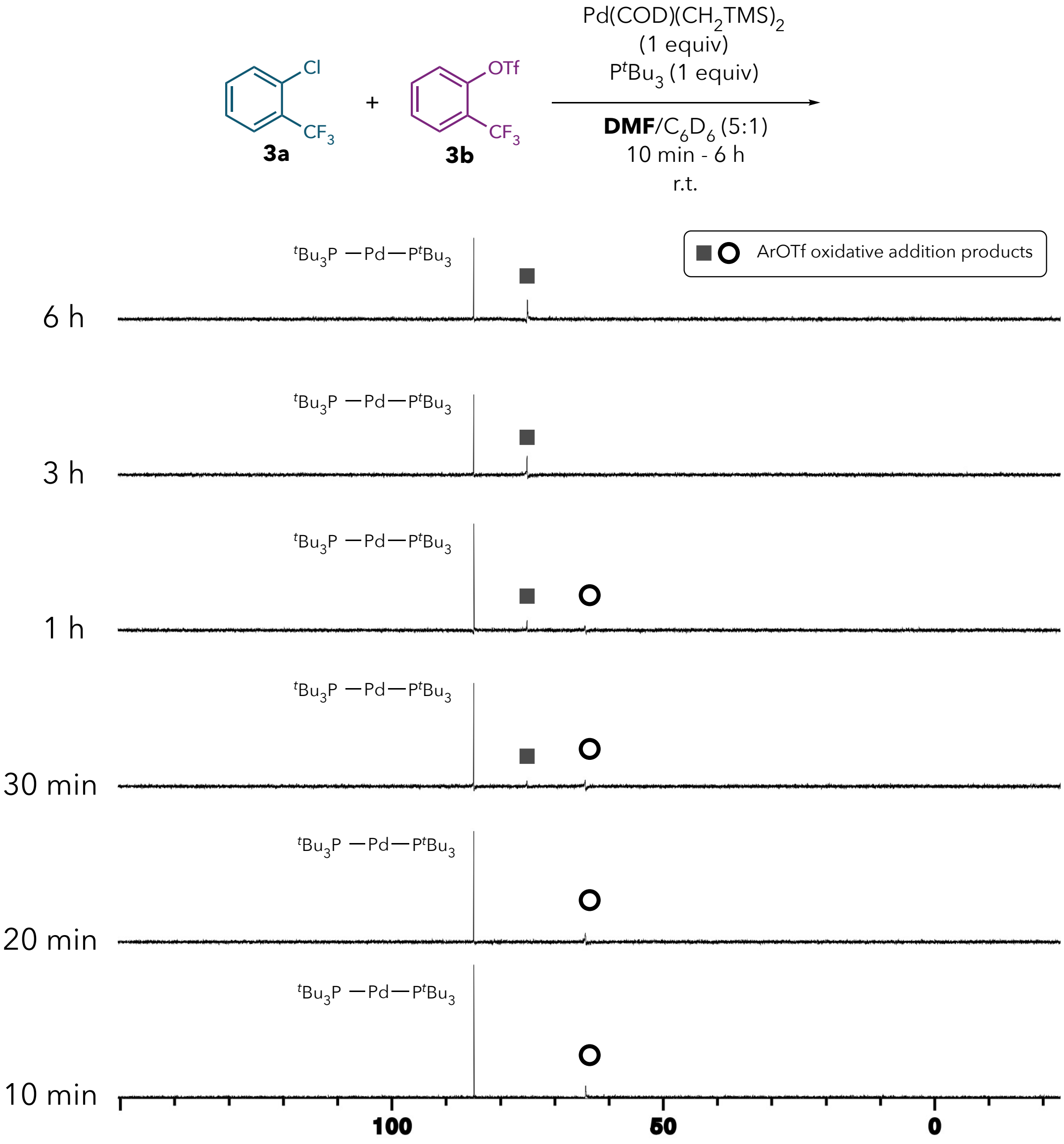


Figure S6. Stacked ^{31}P NMR spectra for the reaction of **3a** and **3b** tracked over time.

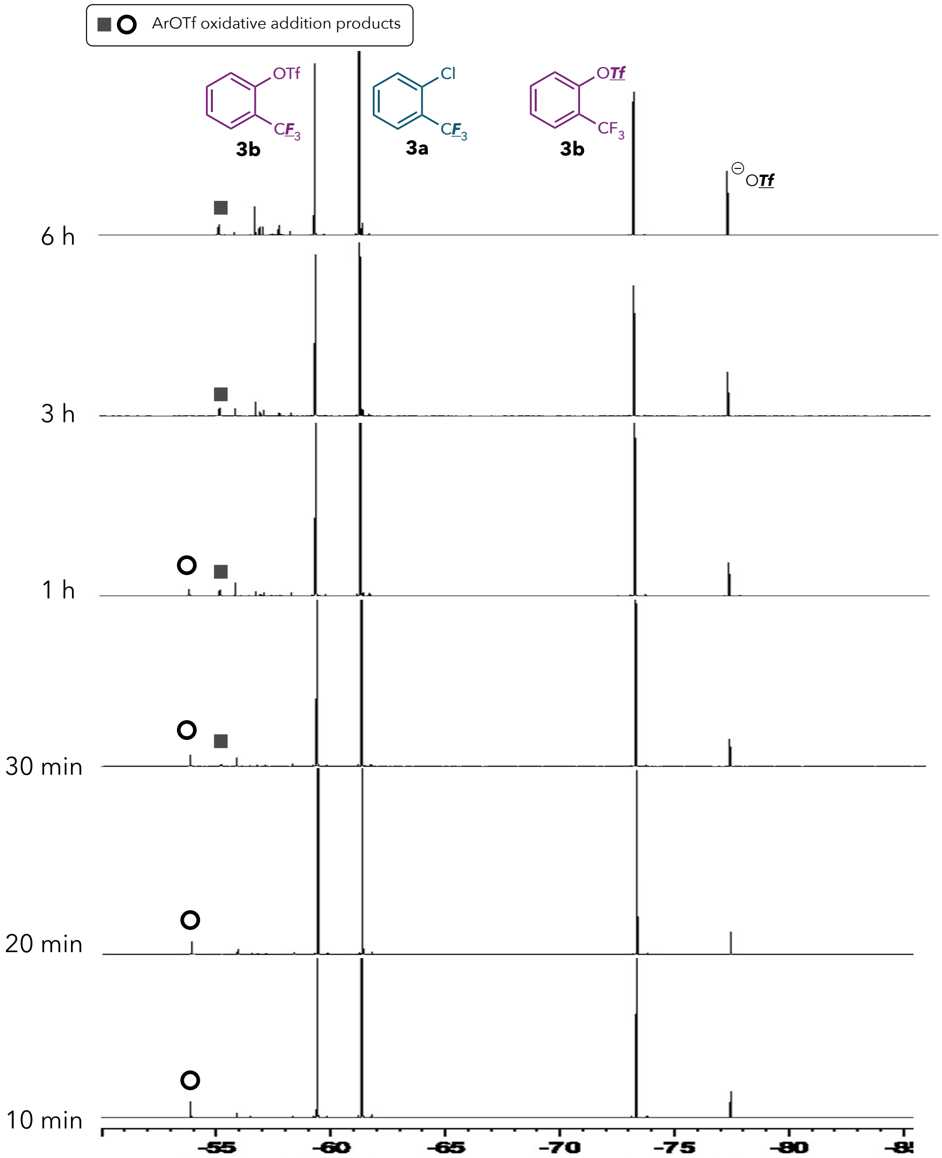
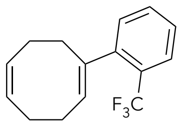


Figure S7. Stacked ^{19}F NMR spectra for the reaction of **3a** and **3b** tracked over time.

See pages S91-S135 for additional representative NMR spectra corresponding to the stoichiometric experiments with **3a** and **3b** (spectra are provided for a single replicate of each experiment, although most experiments were repeated multiple times).

Analysis of Decomposition Products of Oxidative Addition Adducts

The stoichiometric reaction of **3a** and **3b** was repeated in deuterated toluene, acetonitrile, and DMF (i.e., repeats of entries 3, 21, and 26 of Table S12 using deutero instead of protio solvents). The results were analyzed by ^{1}H NMR as well as by GCMS. The primary compounds detected by GCMS have m/z = 252, which is consistent with Heck coupling products resulting from reaction of Pd(Ar) oxidative addition adducts with COD. Indeed, ^{1}H NMR reveals the presence of alkene signals that do not correspond to COD itself (see S92, S102, and S107).



and isomers
Exact Mass: 252.11

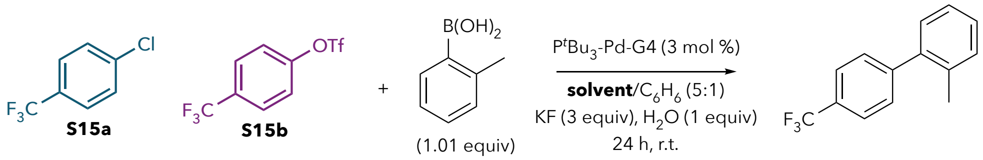
GCMS was also used to analyze the reactions of the stoichiometric oxidative additions performed in THF and propylene carbonate (PC). Heck products were detected in THF but not in PC.

E. Reactions with S15a and S15b

1. Catalytic Suzuki Couplings

General Procedure: Without exclusion of air or moisture, P^tBu_3-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (1.4 μL, 0.08 mmol, 1 equiv), 1-chloro-4-trifluoromethylbenzene (10.8 μL, 0.08 mmol, 1 equiv), 4-trifluoromethylphenyl triflate (14.8 μL, 0.08 mmol, 1 equiv), and a 5:1 mixture of solvent:benzene (150 μL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at room temperature for 24 h. Undecane (7.5 μL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S14. Intermolecular Competition Between **S15a** and **S15b** in the Catalytic Suzuki Coupling[a]



entry	trial	solvent	recovered **S15a** (%)	recovered **S15b** (%)	total conversion **S15a** + **S15b** (%)	reacted **S15a** : **S15b**
1	1	THF	18	89	92	7.7 : 1
2	2	THF	2	88	110	8.3 : 1
3	average	THF	10	89	101	8.0 : 1
4	1	MeCN	68	1	131	1 : 3.1
5	2	MeCN	53	1	147	1 : 2.1
6	average	MeCN	60	1	139	1 : 2.5
7	1	DMF	60	48	92	1 : 1.3
8	2	DMF	58	52	90	1 : 1.2
9	average	DMF	59	50	91	1 : 1.2
10	1	PC	4	61	135	2.4 : 1
11	2	PC	7	64	129	2.6 : 1
12	average	PC	6	62	132	2.5 : 1

[a] GC yield calibrated against undecane as an internal standard.

Discussion: The catalytic cross-coupling selectivities shown in Table S14 qualitatively match the selectivity observed in the stoichiometric oxidative additions and catalytic couplings of **3a/3b** and **1**. However, it is clear that one or both of the substrates is decomposing in a non-productive pathway based on the >100% conversion observed in some cases. Hydrolysis of the electron-deficient aryl triflate **S15b** is likely taking place.

2. *Stoichiometric Oxidative Addition Studies*

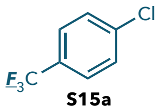
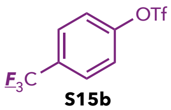
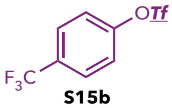
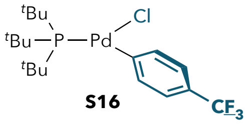
a. ^{19}F NMR Calibrations

Representative Procedure: Inside a nitrogen-filled glovebox, P^{t}Bu$_3$ (5.5 mg, 0.027 mmol, 1 equiv) was measured into a 1-dram scintillation vial. In a separate vial, a solution was prepared of **S15a** (3.6 µL, 0.027 mmol, 1 equiv), **S15b** (5.0 µL, 0.027 mmol, 1 equiv), and C_6H_5F (7.6 µL, 0.081 mmol, 3 equiv) in C_6D_6 (100 µL). 500 µL of the indicated solvent was added to the vial containing P^{t}Bu$_3$, followed by the entire volume of the substrate solution. The vial was capped and shaken briefly, and then the solution was transferred via Pasteur pipette into an NMR tube. The tube was capped tightly, removed from the glovebox, and the sample was immediately analyzed by ^{19}F NMR. The observed ratio of substrate to C_6H_5F signals at this "time=0" was used to define the expected ratios for 100% calibrated yield of recovered substrates in the subsequent intermolecular competition reactions run for 6 h. For **S15b**, yields were calculated separately based on each of its two fluorine signals and then averaged together.

b. ^{19}F NMR Chemical Shifts

Peaks corresponding to **S15a**, **S15b**, and unbound triflate were assigned by comparison to the spectra of authentic samples of **S15a**, **S15b**, and NBu_4OTf in 600 µL of a mixture of solvent:C_6D_6 (5:1 v/v). Chemical shifts were referenced to fluorobenzene (set to -113.15 ppm regardless of solvent). The ^{19}F NMR signals corresponding to the putative complex **S16** were assigned by comparison to the spectra obtained by reacting **S15a** in the absence of **S15b** in THF. Relevant chemical shifts in the different solvent mixtures are assigned as follows:

Table S15. ^{19}F Chemical Shifts of Relevant Species by Solvent: *para*-CF_3 Substrates [a]

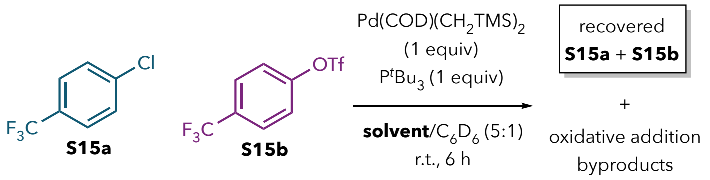
	 **S15a**	 **S15b**	 **S15b**	OTf⁻ anion (NBu_4OTf)	 **S16**
THF	-62.3	-62.3	-73.2	-78.2	-62.8[b]
MeCN	-61.5	-61.6	-72.2	-77.6	-60.9[b]
DMF	-61.4	-61.4	-72.6	-77.4	n.d.
PC	-61.4	-61.5	-72.3	-77.7	-60.7[b]

[a]The chemical shifts of the Ar-CF_3 groups of **S15a** and **S15b** are very close. In each of the 4 solvents examined, the ^{19}F signal for **S15a** is slightly further downfield than **S15b**. n.d. = not determined. [b]Tentative assignment; the chemical shift of **S16** was assigned by analogy to **S10** and by corroboration with ^{31}P NMR.

c. Oxidative Addition Reactions

Representative Procedure: Inside a nitrogen-filled glovebox, P^{t}Bu$_3$ (5.5 mg, 0.027 mmol, 1 equiv) and Pd(COD)(CH_2TMS)$_2$ (10.5 mg, 0.027 mmol, 1 equiv) were combined in a 1-dram vial equipped with a stir bar. In a separate vial, a solution was prepared of **S15a** (3.6 µL, 0.027 mmol, 1 equiv), **S15b** (5.0 µL, 0.027 mmol, 1 equiv), and C_6H_5F (7.6 µL, 0.081 mmol, 3 equiv) in C_6D_6 (100 µL). 500 µL of the indicated solvent was added to the vial containing P^tBu_3 and $Pd(COD)(CH_2TMS)_2$, followed by the entire volume of the substrate solution. The vial was sealed with a PTFE-lined cap and the reaction was allowed to stir for 6 h at room temperature. The reaction mixture was transferred via Pasteur pipette into an NMR tube. The tube was capped tightly, removed from the glovebox, and immediately analyzed by ^{19}F NMR.

Table S16. Solvent effect on selective of stochiometric oxidative addition



entry	trial	solvent	recovered (%)[a] **S15a**	 **S15b**	total conversion **S15a** + **S15b** (%)	reacted **S15a** : **S15b**
1	1	THF	50	>99	50	> 50 : 1
2	2	THF	28	99	72	>72 : 1
3	Average	THF	39	>99	61	>61 : 1
4	1	MeCN	71	7	122	1 : 3
5	2	MeCN	51	9	140	1 : 2
6	Average	MeCN	61	8	131	1 : 2
7	1	DMF	62	14	124	1 : 2
8	2	DMF	50	11	139	1 : 2
9	Average	DMF	56	13	131	1 : 2
10	1	PC[b]	52	98	50	24 : 1
11	2	PC[b]	51	91	60	6 : 1
12	Average	PC[b]	51	95	54	10 : 1
13[c]	1	DMF	>99	>99	<1	--
14[c]	1	MeCN	89	>99	11	>11 : 1
15[c]	2	MeCN	93	95	12	1 : 1
16[c]	Average	MeCN	91	>99	9	> 9 : 1
17[c,d]	1	MeCN	97	96	7	1 : 1
18[c,d]	2	MeCN	85	97	18	5 : 1
19[c,d]	Average	MeCN	91	97	12	3 : 1
20[d]	1	MeCN	89	35	76	1 : 6
21[d]	2	MeCN	87	18	95	1 : 6
22[d]	Average	MeCN	88	27	85	1 : 6

[a] ^{19}F NMR yields calibrated against C_6H_5F as an internal standard. [b]PC = propylene carbonate. [c]$Pd(COD)(CH_2TMS)_2$ was omitted from the reaction mixture. [d]Reaction time = 1 h.

Discussion: The selectivities shown in Table S16 qualitatively match the selectivity observed in the stoichiometric oxidative additions of **3a**/**3b** and **1**. However, more reaction of chloride (**S15a**) is observed in MeCN (entry 6) than expected based on the results with **3a**/**3b** (i.e., the selectivity in MeCN appears much worse for the *p*-CF_3 substrates compared to the *o*-CF_3 substrates). The selectivity is better at shorter reaction time (1 h, entry 22). On closer examination it appears that the substrates, especially **S15a**, undergo a background reaction in the absence of palladium (see entries 14-19). The ^{31}P NMR spectra reveals at least 2 new signals (Figure S8), suggesting that the substrate(s) can react with P^{t}Bu$_3$, a process that is apparently hindered by *ortho* substituents in **3a** and **3b** (comparable signals are never detected in the reactions of **3a** and **3b**).

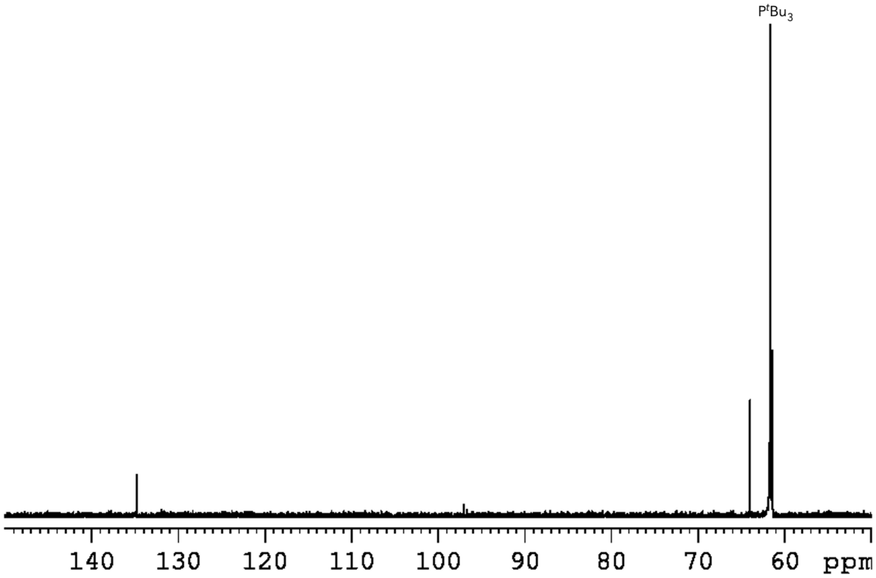


Figure S8. ^{31}P NMR spectrum of Pd-free control reaction of **S15a** + **S15b** with P^{t}Bu$_3$ in MeCN.

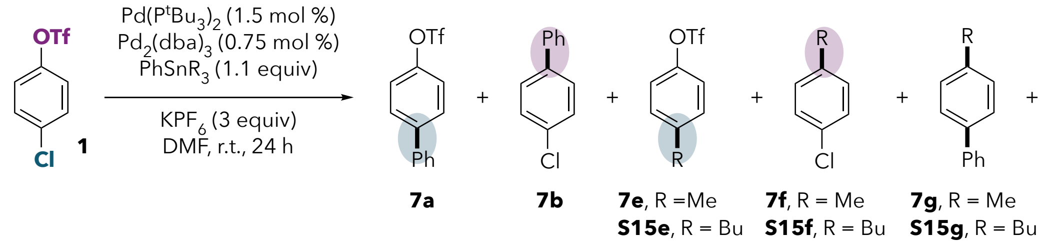
See pages S144-S153 for the NMR spectra corresponding to the experiments in Table S16.

F. Stille Cross-Couplings

1. Reactions of 1 (Scheme 3)

In a nitrogen filled glovebox, Pd$_2$dba$_3$ (0.5 mg, 0.0006 mmol, 0.75 mol %), Pd(PtBu$_3$)$_2$ (0.6 mg, 0.0012 mmol, 1.5 mol %), and KPF$_6$ (44.2 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. Trialkylphenyl stannane (0.088 mmol, 1.1 equiv), **1** (14 μL, 0.08 mmol, 1 equiv), and DMF (150 μL) were added. The vial was immediately sealed with a PTFE-lined cap and removed from the glovebox, and the reaction was stirred at the indicated temperature for 24 h. Dodecane (8.0 μL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography. (Safety Note: Organostannanes and their byproducts are toxic and should be handled in a fumehood or glovebox. For reactions utilizing fluoride bases, quenching crude reaction mixtures via acidification[20] prior to disposal is undesirable due to the additional hazard of generating hydrogen fluoride.)

Table S17. Base-Free Stille Coupling of **1**[a]



***S15g** was identified based on MS but has not been isolated. **S15e** and **S15f** are hypothetical and were not detected.*

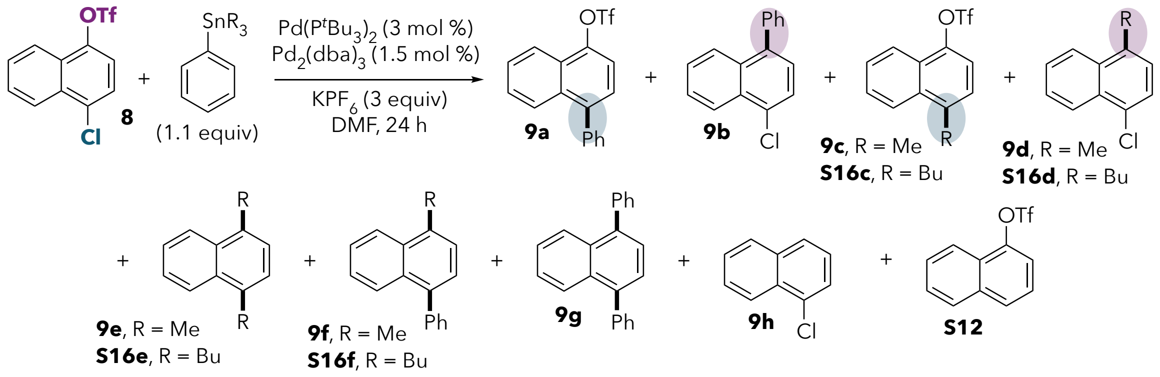
entry	Trial	R	temperature	**1** (%)	**7a** (%)	**7b** (%)	**e** (%)	**f** (%)	**g** (%)	**7h** (%)
1	1	*n*-Bu	r.t.	86	5	4	n.d.	n.d.	trace	0
2	2	*n*-Bu	r.t.	80	4	4	n.d.	n.d.	trace	0
3	Average	*n*-Bu	r.t.	83	5	4	n.d.	n.d.	trace	0
4	1	*n*-Bu	100 °C	71	14	2	n.d.	n.d.	trace	0
5	2	*n*-Bu	100 °C	76	14	2	n.d.	n.d.	trace	0
6	Average	*n*-Bu	100 °C	74	14	2	n.d.	n.d.	trace	0
7	1	Me	r.t.	87	2	4	2	2	2	0
8	2	Me	r.t.	80	3	4	2	3	2	0
9	Average	Me	r.t.	83	2	4	2	3	2	0
10	1	Me	100 °C	7	42	5	20	4	4	5
11	2	Me	100 °C	1	36	4	21	4	6	7
12	Average	Me	100 °C	4	39	3	20	4	5	6

[a] GC yields calibrated against dodecane as an internal standard. Trace = a minor signal with the expected mass for this compound was detected by GCMS, although no authentic material was available for calibration. n.d. = not detected by GCMS.

2. Reactions of 8 (Table 5)

General Procedure: In a nitrogen filled glovebox, Pd_2dba_3 (1.1 mg, 0.0012 mmol, 1.5 mol %), $Pd(P^tBu_3)_2$ (1.2 mg, 0.0024 mmol, 3.0 mol %), and KPF_6 (44.2 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. Trialkylphenyl stannane (0.088 mmol, 1.1 equiv), **8** (16 µL, 0.08 mmol, 1 equiv), and DMF (150 µL) were added. The vial was immediately sealed with a PTFE-lined cap and removed from the glovebox, and the reaction was stirred at the indicated temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S18. Base-Free Stille Coupling of **8**[a]



S16c *and* ***S16f*** *were identified based on MS but have not been isolated.* ***S16d*** *and* ***S16e*** *are hypothetical and were not detected.*

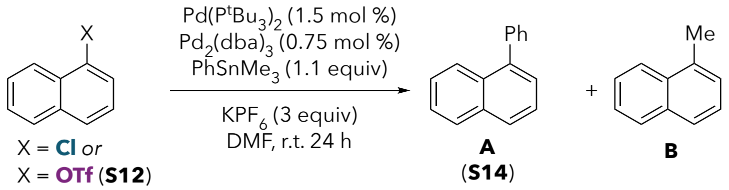
entry	trial	R	temperature	**8** (%)	**9a** (%)	**9b** (%)	**c** (%)	**d** (%)	**e** (%)	**f** (%)	**9g** (%)	**9h** (%)	**S12** (%)
1	1	*n*-Bu	r.t.	79	4	5	trace	n.d.	n.d.	trace	1	1	<1
2	2	*n*-Bu	r.t.	80	4	5	trace	n.d.	n.d.	trace	1	1	<1
3	Average	*n*-Bu	r.t.	80	4	5	trace	n.d.	n.d.	trace	1	1	<1
4	1	*n*-Bu	100 °C	15	19	11	trace	n.d.	n.d.	trace	10	1	<1
5	2	*n*-Bu	100 °C	39	30	8	trace	n.d.	n.d.	trace	4	1	<1
6	Average	*n*-Bu	100 °C	27	25	10	trace	n.d.	n.d.	trace	7	1	<1
7	1	Me	r.t.	24	1	10	3	39	1	1	1	1	<1
8	2	Me	r.t.	24	1	9	3	37	1	1	1	1	<1
9	Average	Me	r.t.	24	1	9	3	42	1	1	1	1	<1
10	1	Me	100 °C	2	14	5	31	12	2	8	8	1	<1
11	2	Me	100 °C	1	13	4	35	12	1	9	9	1	<1
12	Average	Me	100 °C	1	13	4	33	12	1	8	9	1	<1
13[b]	1	Me	r.t.	11	1	12	4	54	12	1	1	8	<1
14[b]	2	Me	r.t.	11	2	12	4	50	13	1	1	4	<1
15[b]	Average	Me	r.t.	11	1	12	4	52	12	1	1	6	<1

[a] GC yields calibrated against undecane as an internal standard. Average of two runs. Trace = a minor signal with the expected mass for this compound was detected by GCMS, although no authentic material was available for calibration. n.d. = not detected by GCMS. [b] KPF_6 was omitted from the reaction mixture.

3. Independent Reactions of an Aryl Chloride and an Aryl Triflate

General Procedure: In a nitrogen filled glovebox, Pd_2dba_3 (0.5 mg, 0.0006 mmol, 0.75 mol %), $Pd(P^tBu_3)_2$ (0.6 mg, 0.0012 mmol, 1.5 mol %), and KPF_6 (44.2 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. Trimethylphenyl stannane (16 µL, 0.088 mmol, 1.1 equiv), 1-substituted naphthalene substrate (0.08 mmol, 1 equiv), and DMF (150 µL) were added. The vial was immediately sealed with a PTFE-lined cap and removed from the glovebox, and the reaction was stirred at the indicated temperature for 24 h. Undecane (7.5 µL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S19. Stille Cross-Couplings of 1-Chloronaphthalene and **S12** Tracked Over Time[a]



entry	X	temp (°C)	time (h)	**A** (%)	**B** (%)	**ratio A/B**	**total product (A+B)**
1	**Cl**	r.t.	2	2	0	--	2
2	**Cl**	r.t.	4	2	0	--	2
3	**Cl**	r.t.	8	2	1	2.0	3
4	**Cl**	r.t.	16	3	2	1.5	5
5	**Cl**	r.t.	24	3	3	1.0	6
6	**Cl**	100	2	35	31	1.1	66
7	**Cl**	100	4	42	34	1.2	76
8	**Cl**	100	8	36	35	1.0	71
9	**Cl**	100	16	42	31	1.4	73
10	**Cl**	100	24	45	37	1.2	82
11	**OTf**	r.t.	2	3	2	1.5	5
12	**OTf**	r.t.	4	3	3	1.0	6
13	**OTf**	r.t.	8	5	6	0.8	11
14	**OTf**	r.t.	16	9	11	0.8	20
15	**OTf**	r.t.	24	10	11	0.9	21
16	**OTf**	100	2	44	38	1.2	82
17	**OTf**	100	4	44	37	1.2	81
18	**OTf**	100	8	51	40	1.3	91
19	**OTf**	100	16	50	39	1.3	89
20	**OTf**	100	24	47	42	1.1	89

[a] GC yields calibrated against undecane as an internal standard. Results of a single trial.

Discussion: The results suggest that an aryl triflate reacts with faster initial rate than an aryl chloride at both room temperature and at 100 °C in the base-free Stille cross-coupling in DMF. There is no clear trend in the ratio of phenylation versus methylation.

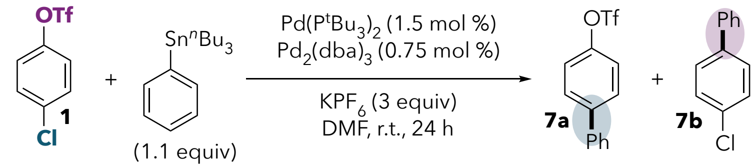
4. *Efforts to Reproduce Literature[21] Results for the Base-Free Stille Coupling of 1*

For the room-temperature base-free coupling of **1** with $PhSnBu_3$ catalyzed by $Pd_2(dba)_3/P^tBu_3$, the literature reports a **1**:**7a**:**7b** ratio of 45:47:8. We have been unable to reproduce this ratio. In an effort to control for possible variables, we evaluated different sources of most reagents (Table S20). Additionally, six different chemists across three different labs, including our own, set up the reaction using the exact conditions reported (e.g., same scale, same Pd and ligand source, same reaction time; Table S21). As shown below, none of these efforts enabled us to reproduce the literature report.

<u>Procedure for Table S20</u>: In a nitrogen filled glovebox, Pd_2dba_3 (0.5 mg, 0.0006 mmol, 0.75 mol %), $Pd(P^tBu_3)_2$ (0.6 mg, 0.0012 mmol, 1.5 mol %), and KPF_6 (44.2 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. Tributylphenyl stannane (28μL, 0.088 mmol, 1.1 equiv), **1** (14 μL, 0.08 mmol), and DMF (150 μL) were added. The vial was immediately sealed with a PTFE-lined cap and removed from the glovebox, and the reaction was stirred at room temperature for 24 h. Dodecane (8.0 μL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

<u>Procedure for Table S21</u>: Six chemists in three organometallic chemistry research groups were recruited to attempt to reproduce the literature results of the base-free Stille coupling of **1** by following the procedure described in Table 3, entry 1 of reference 21, on the same scale described in the literature (0.65 mmol of **1**). The only alterations to the reported procedure are as follows: (1) an aqueous workup was not performed for entries 1 and 4-8 in Table S14 below, and (2) dodecane was used as the internal standard for calibrated GC yields instead of mesitylene, the standard reported in the literature. Dodecane was added to the reaction mixture after the 38-hour reaction time. For the table entries without an aqueous workup, the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography. The preparation method for **1** is noted below. The chemists outside of our own laboratory ordered new bottles of all commercial reagents for use in these studies.

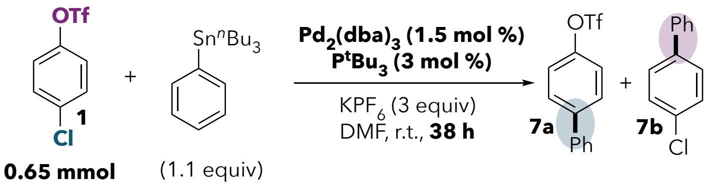
Table S20. Varying Material Sources in Stille Cross-Coupling of **1**[a]



entry	Pd_2dba_3 source	Pd_2dba_3 purity[b]	KPF_6 source	Bu_3SnPh source	literature procedure used to prepare **1**	DMF source	trial	**1**	**7a**	**7b**
1	Aldrich	31%	Oakwood	Aldrich	ref. 6	solvent system	1	84	4	3
2	Aldrich	31%	Oakwood	Aldrich	ref. 6	solvent system	2	88	3	3
3	Aldrich	31%	Oakwood	Aldrich	ref. 6	solvent system	Average	86	4	3
4	Aldrich	30%	Oakwood	Aldrich	ref. 6	solvent system	1	88	4	3
5	Aldrich	30%	Oakwood	Aldrich	ref. 6	solvent system	2	88	4	4
6	Aldrich	30%	Oakwood	Aldrich	ref. 6	solvent system	Average	88	4	3
7	Aldrich	30 %	Oakwood	Alfa Aesar	ref. 6	solvent system	1	88	3	3
8	Aldrich	30 %	Oakwood	Alfa Aesar	ref. 6	solvent system	2	88	4	3
9	Aldrich	30 %	Oakwood	Alfa Aesar	ref. 6	solvent system	Average	88	3	3
10	Aldrich	69%	Oakwood	Alfa Aesar	ref. 6	solvent system	1	87	4	3
11	Aldrich	69%	Oakwood	Alfa Aesar	ref. 6	solvent system	2	89	3	3
12	Aldrich	69%	Oakwood	Alfa Aesar	ref. 6	solvent system	Average	89	4	3
13	Strem	63%	Oakwood	Alfa Aesar	ref. 6	solvent system	1	88	3	3
14	Strem	63%	Oakwood	Alfa Aesar	ref. 6	solvent system	2	88	3	3
15	Strem	63%	Oakwood	Alfa Aesar	ref. 6	solvent system	Average	88	3	3
16	prepared in-house (ref. 22)	27%	Oakwood	Alfa Aesar	ref. 6	solvent system	1	88	3	3
17	prepared in-house (ref.22)	27%	Oakwood	Alfa Aesar	ref. 6	solvent system	2	88	4	3
18	prepared in-house (ref.22)	27%	Oakwood	Alfa Aesar	ref. 6	solvent system	Average	88	3	3
19	Aldrich	30%	Aldrich[c]	Alfa Aesar	ref. 6	solvent system	1	92	3	3
20	Aldrich	30%	Aldrich[c]	Alfa Aesar	ref. 6	solvent system	2	88	3	3
21	Aldrich	30%	Aldrich[c]	Alfa Aesar	ref. 6	solvent system	Average	90	3	3
22	Aldrich	30%	Alfa Aesar	Alfa Aesar	ref. 6	solvent system	1	92	3	3
23	Aldrich	30%	Alfa Aesar	Alfa Aesar	ref. 6	solvent system	2	89	3	3
24	Aldrich	30%	Alfa Aesar	Alfa Aesar	ref. 6	solvent system	Average	90	3	3
25	Aldrich	30%	Oakwood	Alfa Aesar	ref. 6	new, sealed[d]	1	89	4	4
26	Aldrich	30%	Oakwood	Alfa Aesar	ref. 6	new, sealed[d]	2	89	4	4
27	Aldrich	30%	Oakwood	Alfa Aesar	ref. 6	new, sealed[d]	Average	89	4	4
28	Aldrich	30%	Oakwood	Alfa Aesar	ref. 21	solvent system	1	89	1	2
29	Aldrich	30%	Oakwood	Alfa Aesar	ref. 21	solvent system	2	90	2	2
30	Aldrich	30%	Oakwood	Alfa Aesar	ref. 21	solvent system	Average	89	1	2

[a] GC yields calibrated against undecane as an internal standard. Average of two runs. [b] Purity was determined by ^1H NMR in $CDCl_3$ by the method in reference 23. [c] 99.5 % trace metals basis KPF_6. [d] Newly-opened bottle of DMF in an AcroSeal bottle from Acros Organics was used.

Table S21. Impact of Chemist and Workup Procedure in Stille Cross-Coupling of **1**[a]



entry	chemist	literature procedure used to prepare **1**	workup chemist	aqueous workup?[b]	extra additive?	**1**	**7a**	**7b**
1	A	ref. 21	A	no	no	89	2	2
2	A	ref. 21	A	yes	no	76	3	2
3	A	ref. 21	A	yes	mesitylene (1 equiv)[c]	84	3	2
4	B	ref. 6	B	no	no	85	6	3
5	C	ref. 6	C	no	no	94	2	2
6	D	ref. 21	D	no	no	86	6	3
7	E	ref. 21	A	no	no	77	10	6
8	F	ref. 21	A	no	no	89	3	3

[a]GC yields calibrated against dodecane as an internal standard. Results of a single run. [b]When indicated, the aqueous workup was performed after adding internal standard (dodecane) and followed the procedure described in reference 21. [c]Mesitylene, which is the internal GCMS standard used in reference 21, was added with the other liquid reagents prior to the start of the reaction.

Discussion: As shown in Table S20, the Pd source and its purity, the KPF$_6$ source, the Bu$_3$SnPh source, the DMF source, and the preparation method for **1** did not have a significant effect on the reaction yields in our hands. Furthermore, there was little variation among the different chemists (Table S21). The total yield of products **7a** + **7b** ranged from 4–16% yield, and the remaining starting material ranged from 77–94% based on calibrated GC.

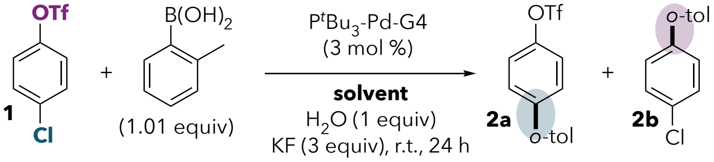
G. Evaluation of Alternative Hypotheses

1. Alternative Hypothesis: Is Solvent Effect Related to KF Solubility?

Hypothesis: We evaluated an alternative hypothesis for the observed solvent effect wherein better solubility of KF promotes formation of anionic bisligated [Pd(P^{t}Bu$_3$)(F)]$^-$, which in turn favors reaction at triflate.

General Procedure: Without exclusion of air or moisture, P^{t}Bu$_3$-Pd-G4 (1.5 mg, 0.0026 mmol, 3 mol %), *o*-tolyl boronic acid (11.0 mg, 0.081 mmol, 1.01 equiv), and KF (13.9 mg, 0.24 mmol, 3 equiv) were combined in a 1-dram vial equipped with a magnetic stir bar. In rapid succession, water (1.4 μL, 0.08 mmol, 1 equiv), 4-chlorophenyl triflate (14 μL, 0.08 mmol, 1 equiv), and solvent (150 μL) were added to the vial and the mixture was immediately sparged with nitrogen for two minutes. The sparging needle and septum was quickly replaced with a PTFE-lined cap and the reaction was stirred vigorously at the indicated temperature for 24 h. Undecane (7.5 μL) was added to the reaction mixture as an internal standard, and the mixture was diluted with EtOAc. A small aliquot was removed and filtered through celite, and the celite was washed with additional EtOAc. The filtrate was analyzed by gas chromatography.

Table S22. Comparing Selectivity to KF Solubility.[a]



entry	solvent	KF solubility (g KF/100 g solvent, 20-25 °C)[b]	reference for solubility data	trial	**1** (%)	**2a** (%)	**2b** (%)
1	H_2O	102	24	1	22	55	0
2	H_2O	102	24	2	35	64	0
3	H_2O	102	24	Average	28	59	0
4	THF	0.85	25	1	5	63	<1
5	THF	0.85	25	2	23	72	<1
6	THF	0.85	25	3	26	68	1
7	THF	0.85	25	4	25	71	1
8	THF	0.85	25	5	27	75	1
9	THF	0.85	25	6	24	79	1
10	THF	0.85	25	7	20	78	1
11	THF	0.85	25	8	18	79	1
12	THF	0.85	25	Average	20	74	<1
13	DMF	7.0 x 10^{-3}	24	1	16	9	58
14	DMF	7.0 x 10^{-3}	24	2	19	9	61
15	DMF	7.0 x 10^{-3}	24	3	24	11	59
16	DMF	7.0 x 10^{-3}	24	4	26	11	59
17	DMF	7.0 x 10^{-3}	24	5	16	12	66
18	DMF	7.0 x 10^{-3}	24	6	20	11	62
19	DMF	7.0 x 10^{-3}	24	Average	23	10	60
20	MeCN	3.6 x 10^{-3}	24	1	8	2	75
21	MeCN	3.6 x 10^{-3}	24	2	8	2	78
22	MeCN	3.6 x 10^{-3}	24	Average	8	2	77
23	acetone	2.2 x 10^{-5}	24	1	16	72	3
24	acetone	2.2 x 10^{-5}	24	2	26	63	4
25	acetone	2.2 x 10^{-5}	24	Average	21	68	4
26	propylene carbonate (PC)	2.0 x 10^{-7}	26	1	9	57	6
27	propylene carbonate (PC)	2.0 x 10^{-7}	26	2	23	68	6
28	propylene carbonate (PC)	2.0 x 10^{-7}	26	3	12	75	5
29	propylene carbonate (PC)	2.0 x 10^{-7}	26	4	19	68	6
30	propylene carbonate (PC)	2.0 x 10^{-7}	26	Average	16	67	6

[a] GC yields calibrated against undecane as an internal standard. Diarylated product observed in ≤4% yield in all cases.

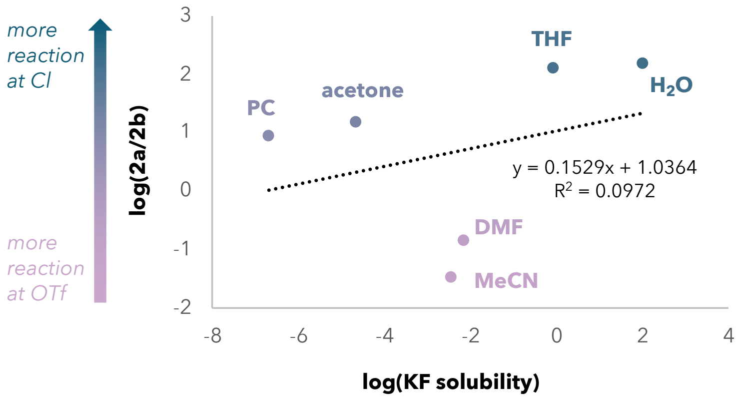
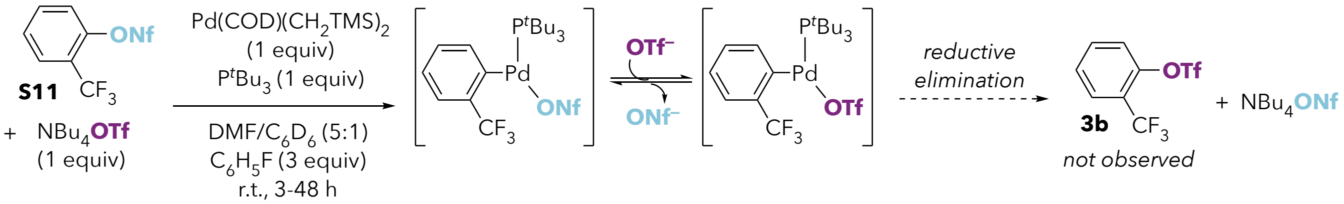


Figure S9. No correlation between KF solubility and selectivity is observed in six representative solvents.

Discussion: Solubility data and selectivity were plotted on a linear free energy relationship diagram (Table S22 and Figure S9). For six representative solvents, in which KF solubility is known, there is no trend between solubility and selectivity. As such, it does not appear that fluoride availability is responsible for the observed solvent effects.

2. Alternative Hypothesis: Is Oxidative Addition Reversible (Curtin-Hammett)?

Hypothesis: We considered a scenario in which the previously reported difference between the Suzuki and Stille selectivities[21] relates to reversible oxidative addition. If transmetallation with organostannane reagents is sufficiently slow, and oxidative addition is reversible, then the Stille reaction kinetics would fall into a Curtin-Hammett regime wherein transmetallation would actually be the selectivity-determining step. For this scenario to serve as an explanation for why chloride-selectivity was reported in the base-free Stille coupling in DMF, despite the observation that stoichiometric oxidative addition occurs preferentially at C—OTf in this solvent, oxidative addition of triflate must be reversible and transmetallation at $P^tBu_3Pd(Ar)Cl$ must be faster than at a putative $P^tBu_3Pd(Ar)OTf$ intermediate. To evaluate this hypothesis, we conducted an experiment using an aryl nonaflate in the presence of triflate anion designed to look for reversible oxidative addition of fluorinated sulfonates. Successful oxidative addition of **S11**, followed by exchange of $^-$ONf for $^-$OTf at palladium and C—O bond-forming reductive elimination would result in product **3b**. We hypothesized that this process could be tracked by ^{19}F NMR, since NBu_4OTf (-77.4 ppm) would be consumed and peaks corresponding to product **3b** (diagnostic signal at -73.3 ppm) would appear.



Procedure: Inside a nitrogen-filled glovebox, P^{t}Bu$_3$ (5.5 mg, 0.027 mmol, 1 equiv), Pd(COD)(CH$_2$TMS)$_2$ (10.5 mg, 0.027 mmol, 1 equiv), and NBu$_4$OTf (10.6 mg, 0.027 mmol, 1 equiv) were combined in a 1-dram vial equipped with a stir bar. In a separate vial, a solution was prepared of **S11** (0.027 mmol, 1 equiv), C$_6$H$_5$F (7.6 µL, 0.081 mmol, 3 equiv) in C$_6$D$_6$ (100 µL). DMF (500 µL) was added to the vial containing Pd, followed by the entire volume of the substrate solution. The vial was sealed with a PTFE-lined cap and the reaction was allowed to stir for 3-48 h at room temperature. The reaction mixture was transferred via Pasteur pipette into an NMR tube. The tube was capped tightly, removed from the glovebox, and immediately analyzed by ^{19}F NMR.

Results and Discussion: The NMR spectra from these experiments show evidence of oxidative addition of **S11** based on decrease in the signals corresponding to this compound, but **3b** is not detected after 3 hours, nor after extended reaction time (up to 48 h). We conclude from these results that reductive elimination of C—OTf is unlikely to occur in polar coordinating solvent at room temperature. As such, a Curtin-Hammett scenario involving rapid equilibrium between oxidative addition adducts [Pd(P^{t}Bu$_3$)(Ar)(Cl)] and [Pd(P^{t}Bu$_3$)(Ar)(OTf)] is not feasible. This conclusion is consistent with the dearth of literature examples of C$_{(sp2)}$—O reductive elimination from Pd(II). Furthermore, DFT calculations suggest that oxidative addition of both C—OTf and C—Cl at [Pd(P^{t}Bu$_3$)] is highly exergonic and unlikely to be reversible based on the calculated free energy barriers for the reverse reaction (see Figure 2 of the manuscript).

See pages S154-S155 for the ^{19}F NMR spectra corresponding to these experiments.

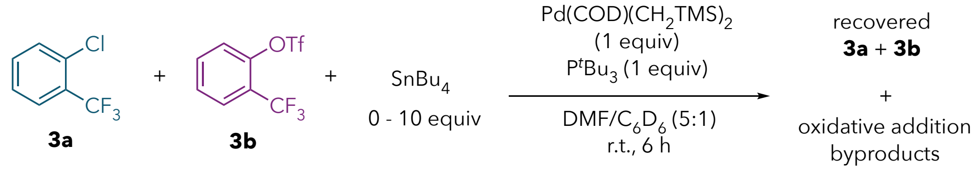
3. *Alternative Hypothesis: "Greasy Tin Hypothesis"*

<u>Hypothesis</u>: We considered an alternative hypothesis to explain the previously-reported anomalous solvent effects in the Stille coupling. In this hypothesis, we envisioned that the greasy organostannane reagents could modulate the polarity of the reaction medium (for example, oxidative addition could take place within nonpolar micelles rather than within the bulk reaction medium). To test this hypothesis, stoichiometric oxidative addition studies were conducted in DMF at room temperature in the presence of $SnBu_4$ (a reagent that is structurally similar to Bu_3SnPh but is unlikely to undergo transmetallation).

<u>Procedure</u>: Inside a nitrogen-filled glovebox, P^tBu_3 (5.5 mg, 0.027 mmol, 1 equiv) and $Pd(COD)(CH_2TMS)_2$ (10.5 mg, 0.027 mmol, 1 equiv) were combined in a 1-dram vial equipped with a stir bar. In a separate vial, a solution was prepared of **3a** (3.6 µL, 0.027 mmol, 1 equiv), **3b** (5.0 µL, 0.027 mmol, 1 equiv), C_6H_5F (7.6 µL, 0.081 mmol, 3 equiv), and $SnBu_4$ (8.9 µL – 88.9 µL, 0.027 – 0.27 mmol, 1-10 equiv) in C_6D_6 (100 µL). DMF (500 µL) was added to the vial containing Pd, followed by the entire volume of the substrate solution. The vial was sealed with a PTFE-lined cap and the reaction was allowed to stir for 6 h at room temperature. The reaction mixture was transferred via Pasteur pipette into an NMR tube. The tube was capped tightly, removed from the glovebox, and immediately analyzed by ^{19}F NMR.

<u>Results</u>:

Table S23. Effect of $SnBu_4$ on Stoichiometric Selectivity[a]



entry	additive (equiv)	recovered (%) **3a**	**3b**	reacted **3a** : **3b**
1	(none)	87	57	1 : 3
2	$SnBu_4$ (1 equiv)	86	26	1 : 5
3	$SnBu_4$ (2 equiv)	73	16	1 : 3
4	$SnBu_4$ (10 equiv)	76	23	1 : 3

<u>Discussion:</u> $SnBu_4$ did not have a significant effect on the selectivity of oxidative addition, even when used in large excess. C—OTf oxidative addition continues to occur preferentially.

See pages S136-S138 for the ^{19}F NMR spectra corresponding to these experiments.

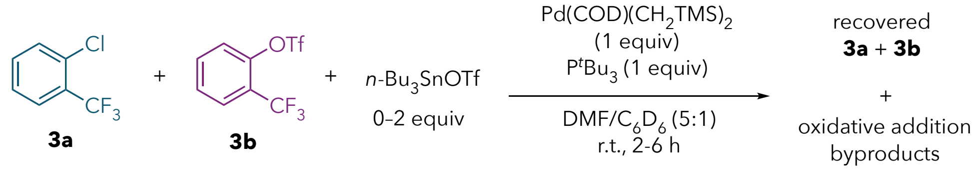
4. Alternative Hypothesis: Effect of n-Bu_3SnOTf

Hypothesis: We speculated that the byproduct of transmetallation with organotin reagents might influence the selectivity of oxidative addition in subsequent catalyst turnovers. In a coordinating solvent like DMF, which favors oxidative addition at triflate, the formal byproduct of transmetallation with $PhSnR_3$ would be R_3SnOTf (R = ^{n}Bu or Me). In this compound, tin has Lewis acidic character, and we envisioned that the Lewis acidic tin might activate an Ar—Cl bond toward oxidative addition through interaction with lone pairs on Cl. We evaluated this hypothesis through stoichiometric oxidative addition studies in DMF in the presence of added Bu_3SnOTf.

Procedure: Inside a nitrogen-filled glovebox, P^tBu_3 (5.5 mg, 0.027 mmol, 1 equiv) and $Pd(COD)(CH_2TMS)_2$ (10.5 mg, 0.027 mmol, 1 equiv) were combined in a 1-dram vial equipped with a stir bar. In a separate vial, a solution was prepared of **3a** (3.6 µL, 0.027 mmol, 1 equiv), **3b** (5.0 µL, 0.027 mmol, 1 equiv), C_6H_5F (7.6 µL, 0.081 mmol, 3 equiv), and *n*-Bu_3SnOTf (0.027–0.054 mmol, 1-2 equiv) in C_6D_6 (100 µL). DMF (500 µL) was added to the vial containing Pd, followed by the entire volume of the substrate solution. The vial was sealed with a PTFE-lined cap and the reaction was allowed to stir for 2-6 h at room temperature. The reaction mixture was transferred via Pasteur pipette into an NMR tube. The tube was capped tightly, removed from the glovebox, and immediately analyzed by ^{19}F NMR.

Results:

Table S24. Effect of *n*-Bu_3SnOTf on Stoichiometric Selectivity[a]



entry	Bu_3SnOTf (equiv)	recovered (%) **3a**	**3b**	reacted **3a** : **3b**
1	0	87	57	1 : 3
2	1	88	64	1 : 3
3	2	86	65	1 : 3

[a] ^{19}F NMR yields calibrated against C_6H_5F as an internal standard.

Discussion: The addition of *n*-Bu_3SnOTf does not influence the observed selectivity. Thus the previously reported difference between Stille and Suzuki selectivity in DMF should not be attributed to the formation of the byproduct *n*-Bu_3SnOTf.

See pages S139-S140 for the ^{19}F NMR spectra corresponding to these experiments.

5. Alternative Hypothesis: Autocatalysis in Stoichiometric Oxidative Addition?

Hypothesis: Hartwig has previously observed autocatalytic oxidative addition of PhBr to Pd(P^tBu_3)$_2$ through the proposed mechanism illustrated below in Figure S10.[27] In this mechanism, a side product of the initial reaction is (P^tBu_3)$_2$Pd(H)(Br) (the proton is derived from C—H activation of a phosphine ligand). This complex undergoes reductive elimination to form [H—P^tBu_3][Pd(P^tBu_3)(Br)], which contains anionic Pd(0). The anionic Pd(0) is believed to undergo much more rapid oxidative addition into PhBr than the original neutral Pd(P^tBu_3)$_n$ species.

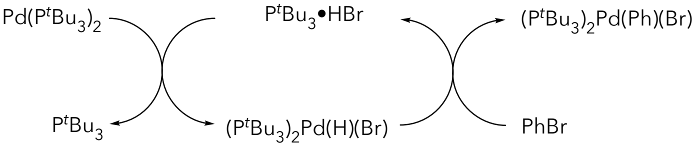
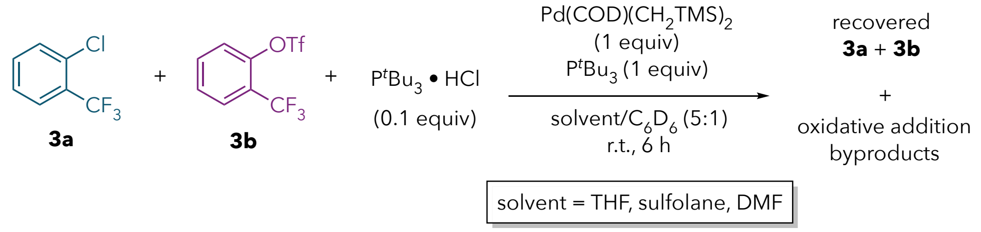


Figure S10. Previously reported autocatalytic oxidative addition of PhBr mediated by phosphonium salt.[27]

We considered the possibility that, in our stoichiometric oxidative addition reactions between [Pd(P^tBu_3)] and **3a/3b**, an analogous process could occur that would generate highly reactive [Pd(P^tBu_3)(Cl)]$^-$. This anionic bisligated Pd(0) species would be expected to preferentially react at C—OTf, as proposed by Proutiere and Schoenebeck.[21] Because the envisioned autocatalytic cycle would be mediated by P^tBu_3•HCl, by analogy to Figure S4, we evaluated this hypothesis by using P^tBu_3•HCl as an additive in our stoichiometric studies. If this species promotes a catalytic cycle involving anionic bisligated [Pd(P^tBu_3)(Cl)]$^-$, we would expect to see a change in selectivity toward increased reaction at triflate.

Procedure: Inside a nitrogen-filled glovebox, P^tBu_3 (5.5 mg, 0.027 mmol, 1 equiv), Pd(COD)(CH_2TMS)$_2$ (10.5 mg, 0.027 mmol, 1 equiv), and P^tBu_3•HCl (0.7 mg, 0.0027 mmol, 0.1 equiv) were combined in a 1-dram vial equipped with a stir bar. In a separate vial, a solution was prepared of **3a** (3.6 μL, 0.027 mmol, 1 equiv), **3b** (5.0 μL, 0.027 mmol, 1 equiv), and C_6H_5F (7.6 μL, 0.081 mmol, 3 equiv) in C_6D_6 (100 μL). 500 μL of the indicated solvent was added to the vial containing Pd, followed by the entire volume of the substrate solution. The vial was sealed with a PTFE-lined cap and the reaction was allowed to stir for 6 h at room temperature. The reaction mixture was transferred via Pasteur pipette into an NMR tube. The tube was capped tightly, removed from the glovebox, and immediately analyzed by ^{19}F NMR.

Table S25. Effect of Phosphonium Chloride on Stoichiometric Selectivity



entry	solvent	P^tBu_3·HCl (equiv)	trial	recovered (%)[a] **3a**	**3b**	reacted **3a : 3b**
1	THF	0	1	61	≥99	≥39 : 1
2	THF	0	2	52	≥99	≥48 : 1
3	THF	0	3	51	92	6 : 1
4	THF	0	Average	55	97	15 : 1
5	THF	0.1	1	60	94	7 : 1
6	THF	0.1	2	62	96	10 : 1
7	THF	0.1	Average	61	95	8 : 1
8	sulfolane	0	1	82	93	3 : 1
9	sulfolane	0	2	90	98	5 : 1
10	sulfolane	0	Average	86	95	3 : 1
11	sulfolane	0.1	1	91	96	2 : 1
12	sulfolane	0.1	2	90	94	2 : 1
13	sulfolane	0.1	Average	90	95	2 : 1
14	DMF	0	1	88	57	1 : 4
15	DMF	0	2	87	57	1 : 3
16	DMF	0	3	76	33	1 : 3
17	DMF	0	4	63	29	1 : 2
18	DMF	0	Average	78	44	1 : 3
19	DMF	0.1	1	76	31	1 : 3
20	DMF	0.1	2	81	44	1 : 3
21	DMF	0.1	Average	79	37	1 : 3

[a] ^{19}F NMR yields calibrated against C_6H_5F as an internal standard.

Discussion: The addition of 10 mol % of P^tBu_3•HCl led to some selectivity deterioration in THF and sulfolane. However, addition of this quantity of phosphonium salt was insufficient to result in an inversion of selectivity in these solvents. There was no change to the observed selectivity in DMF. These results suggest that, under the standard stoichiometric conditions in the absence of added P^tBu_3•HCl, it is unlikely that bisligated anionic $[Pd(P^tBu_3)(Cl)]^-$ is primarily responsible for the preferential triflate selectivity that is observed in coordinating solvents.

Additionally, there are other observations that contradict the hypothesis that triflate selectivity in DMF/MeCN is due to the involvement of $[Pd(P^tBu_3)(Cl)]^-$ under the stoichiometric conditions. (1) While it makes sense to consider that this anionic species would be better stabilized in polar solvents, preferential reaction at triflate is *not* observed in polar noncoordinating solvents like sulfolane and propylene carbonate (see Table 3 of the manuscript, entries 8-9). (2) Hartwig observed autocatalysis in the oxidative addition of PhBr in the nonpolar solvents toluene and THF, in addition to the polar non-coordinating solvent 2-butanone. If a similar mechanism occurred in our stoichiometric studies, we would expect to see preferential reaction at triflate (via $[Pd(P^tBu_3)(Cl)]^-$) in toluene, THF, and acetone, but instead we see preferential selectivity for reaction of chloride in these solvents (Table 3, entries 1-4). (3) Control studies show that the presence of a **3a** as a chloride source is not necessary to observe reaction of **3b** in MeCN and DMF (Table 3, entries 12-13).

See pages S141-S143 for the ^{19}F NMR spectra corresponding to these experiments.

H. Error Analysis

Possible sources of error in GC yields include measurements of reagents and internal standard (typically undecane) and instrument error. To analyze measurement error, substrate **1** and undecane were measured out by volume in the same manner used for reaction set up, and the masses of the measured volumes were weighed by injecting the volume into an empty tared vial. In particular, 7.5 µL of undecane was measured with a 10 µL syringe (marked with 0.2 µL gradations), and 14 µL of **1** was measured with a 25 µL syringe (marked with 0.5 µL gradations). This process was repeated 5x for each compound. The results are summarized in Tables S26 and S27 below. To analyze error in GC analysis, the same reaction sample was analyzed by GC 5x (Table S28).

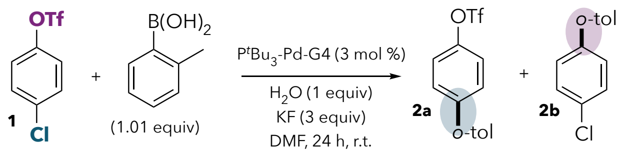
Table S26. Undecane measurement error.

trial	mass
1	5.8 mg
2	5.7 mg
3	5.5 mg
4	5.6 mg
5	5.7 mg
Average	5.66 mg
Std. dev.	0.11 mg
Std. dev. as % of avg	±1.9%

Table S27. Substrate **1** measurement error.

trial	mass
1	21.8 mg
2	21.9 mg
3	21.6 mg
4	21.9 mg
5	21.7 mg
Average	21.78 mg
Std. dev.	0.13 mg
Std. dev. as % of avg	±0.6%

Table S28. Instrument error: GC yields based on 5 GC runs of the same sample.



trial	**1** (%)	**2a** (%)	**2b** (%)
1	21.018	9.039	60.442
2	21.151	9.168	60.546
3	21.225	9.399	60.106
4	20.917	9.390	60.323
5	21.449	9.655	60.716
Average (%)	21.152	9.330	60.427
Std. dev. (%)	0.204	0.237	0.230

Discussion:

The standard deviation of the measured quantity of undecane is ±1.9% of the average. The standard deviation of the measured quantity of substrate is ±0.6% of the average. The standard deviation of the yields of **2a** and **2b** determined by GC analysis is ±0.2% of the average. As such, measurement error of both substrate and (especially) standard are expected to contribute to the most error in calculated yields. Instrument variation is associated with only a small amount of error. Overall, the estimated error in the total mass balance throughout the manuscript is about ±3% based on the standard deviations of the measurements in this error analysis. Importantly, this error is expected to influence the yields of the two products in the same direction (e.g., under-measuring undecane would increase the yield of both **2a** and **2b**, leading to a relatively minor effect on calculated ratio). Additional variation in yields can be attributed to factors including other measurement errors (e.g., of precatalyst), minor variations in room temperature, heterogeneity of particle size of solid reagents, and variations in the amount of residual O_2 in the reaction vessel.

II. Computational Details

A. General Methods

Calculations were performed with Gaussian 16.[28] An ultrafine integration grid and the keyword 5d were used for all calculations. Geometry optimizations of stationary points were carried out in implicit solvent using the CPCM continuum solvation model[29] with the indicated functional (B3LYP or MN15L[30]) and basis sets (either LANL2DZ[31] or SDD for Pd and 6-31+G(d) for all other atoms). Frequency analyses were carried out at the same level to evaluate the zero-point vibrational energy and thermal corrections at 298.15 K. Unless otherwise indicated, Gibbs free energy values are reported after applying Cramer and Truhlar's quasi-harmonic approximation to vibrational entropy[32] and Head-Gordon's quasi-harmonic approximation to vibrational enthalpy[33] to frequencies that are less than 100 cm^{-1}. All thermodynamic quantities were computed with the GoodVibes code.[34] The nature of the stationary points was determined in each case according to the appropriate number of negative eigenvalues of the Hessian matrix. Forward and reverse intrinsic reaction coordinate (IRC) calculations were carried out on the optimized transition structures to ensure that the TSs indeed connect the appropriate reactants and products.[35] Multiple conformations were considered for all structures, and the lowest energy conformations are reported. It is worth noting that the lowest-energy π-complexes are not necessarily directly connected to the oxidative addition transition structures on the potential energy surfaces (i.e., in some cases the IRC calculations lead to different higher-energy π complexes than the lowest-energy structures reported). This factor is unimportant to the overall energetics, assuming that the barrier to interconverting π-complexes is low (e.g., by palladium ring-walking or by rotation of the triflate group). 3D images of optimized structures were generated with CYLview.[36] Where indicated, Grimme's D3(BJ) empirical dispersion correction with Becke-Johnson damping was added to the B3LYP energies using the empiricaldispersion=GD3BJ keyword.[37]

B. Reaction Free Energy Diagram Using DMF Calculated with B3LYP-D3(BJ)

CPCM(DMF)-**B3LYP-D3BJ**/6-31+G(d)/**SDD**(Pd)

free energies are corrected for concentration and reported after applying Truhlar and Head-Gordon's quasi-harmonic approximations to entropy and enthalpy

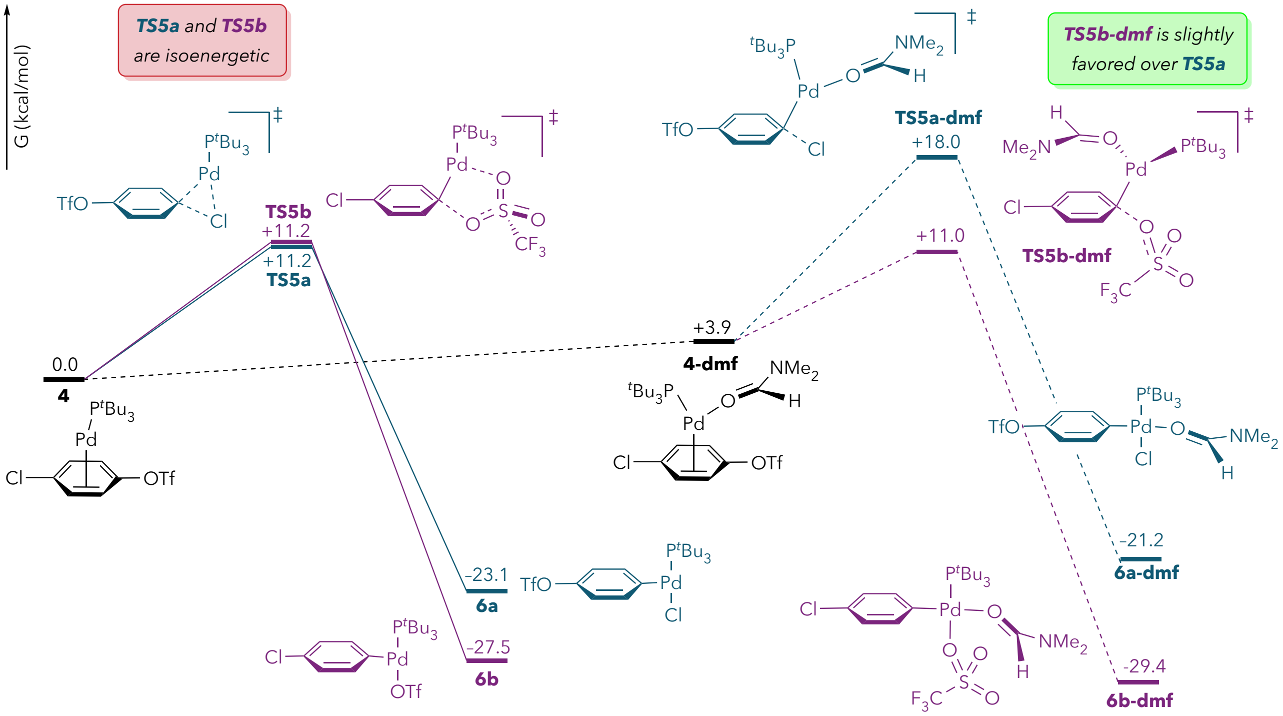
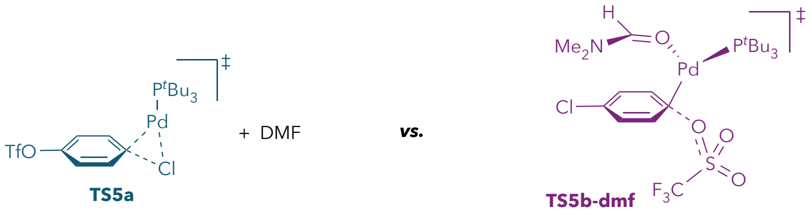


Figure S11. Reaction free energy diagrams in DMF calculated with B3LYP-D3(BJ).

Discussion: Although the functional B3LYP does not consider London dispersion forces, dispersion corrections can be added. Here we applied Grimme's D3(BJ) empirical dispersion correction with Becke-Johnson damping to the DFT energies using the empiricaldispersion=GD3BJ keyword.[38] The results are similar to those obtained using MN15L in that **TS5b-dmf** becomes much more favorable than it appears without dispersion. However, this level of theory also predicts that **TS5b** and **TS5a** should be isoenergetic, which contradicts the well-established preference for monoligated Pd to react at chloride.[1,39,40,41] As such, MN15L appears to perform better than B3LYP-D3BJ for these calculations. This observation is consistent with prior benchmarking studies with transition metals.[42]

C. DFT Predictions at 100 °C

Applying thermal corrections at 373.15 K to the calculations performed at the CPCM(DMF)-MN15L/6-31+G(d)/SDD(Pd) level of theory predicts lower selectivity for triflate, (Figure S12). This is expected because **TS5b-dmf** is less entropically favorable than **TS5a**.



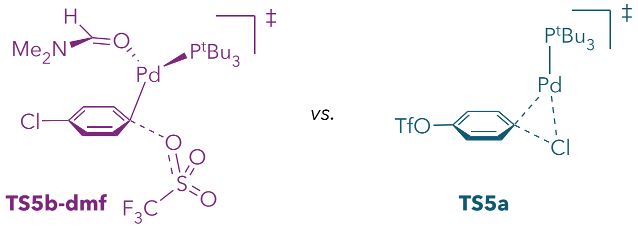
25 °C: $\Delta G_{qh}^{\ddagger}$ = –2.9 kcal/mol
100 °C: $\Delta G_{qh}^{\ddagger}$ = -0.6 kcal/mol

Figure S12. DFT predictions at 100 °C using CPCM(DMF)-MN15L/6-31+G(d)/SDD(Pd).

D. Discussion of DFT Shortcomings

Our DFT calculations, at minimum, suggest that solvent coordination should not be ruled out on the basis of dispersion-free DFT calculations. In particular, they show that the energy of **TS5b-dmf** is similar in energy to **TS5a**. However, even when dispersion is included, the DFT methods used in this work fall short of being able to reproduce the expected coordinating ability trends of different solvents to palladium. For example, the expected order of solvent cordinating ability is MeCN > DMF > THF > benzene, but DFT predicts different trends that vary with method. These results are summarized in Tables S29-S31.

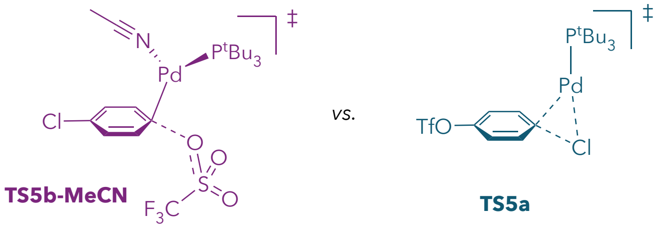
Table S29. Differences in energy between **TS5b-dmf** and **TS5a** calculated in implicit DMF[a]



	TS5b–dmf — TS5a			
Method	ΔE	ΔH_{qh}	ΔG	ΔG_{qh}
CPCM(DMF)-B3LYP/6-31+G(d)/LANL2DZ(Pd)	+6.3	+6.3	+16.2	+16.4
CPCM(DMF)-B3LYP-D3(BJ)/6-31+G(d)/LANL2DZ(Pd)	−9.3	−8.2	+0.9	+0.7
CPCM(DMF)-B3LYP-D3(BJ)/6-31+G(d)/SDD(Pd)	−10.6	−10.3	−0.1	−0.1
CPCM(DMF)-MN15L/6-31+G(d)/LANL2DZ(Pd)	−13.0	−12.7	−1.7	−2.4
CPCM(DMF)-MN15L/6-31+G(d)/SDD(Pd)	−13.7	−12.7	−2.0[c]	−2.9

[a] Thermal corrections at 298.15 K. All energies reported in kcal/mol. Free energies are corrected for concentration (ratio of DMF:Pd = 765:1). Enthalpy (ΔH_{qh}) is reported after applying Head-Gordon's quasi-harmonic approximation to vibrational enthalpy. The free energy value labeled with ΔG_{qh} is reported after applying Cramer and Truhlar's and Head-Gordon's quasi-harmonic approximations to vibrational entropy and enthalpy, while the value labeled as ΔG does not include the quasi-harmonic approximations.

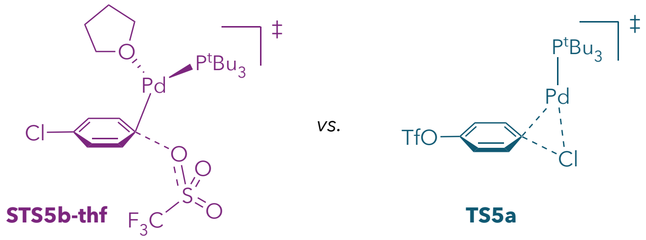
Table S30. Differences in energy between **TS5b-MeCN** and **TS5a** calculated in implicit MeCN[a]



Method	TS5b–dmf — TS5a ΔE	 ΔH	 ΔG	 $\Delta G_{corrected}$
CPCM(MeCN)-MN15L/6-31+G(d)/LANL2DZ(Pd)	−7.2	−7.3	+0.3	+0.1
CPCM(MeCN)-MN15L/6-31+G(d)/SDD(Pd)	−7.4	−7.4	+0.3	0.0

[a] Thermal corrections at 298.15 K. All energies reported in kcal/mol. Free energies are corrected for concentration (ratio of DMF:Pd = 1,118:1). Enthalpy (ΔH_{qh}) is reported after applying Head-Gordon's quasi-harmonic approximation to vibrational enthalpy. The free energy value labeled with ΔG_{qh} is reported after applying Cramer and Truhlar's and Head-Gordon's quasi-harmonic approximations to vibrational entropy and enthalpy, while the value labeled as ΔG does not include the quasi-harmonic approximations.

Table S31. Differences in energy between **TS5b-thf** and **TS5a** calculated in implicit THF[a]

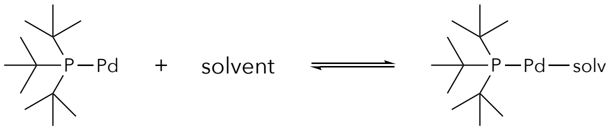


Method	TS5b–dmf — TS5a ΔE	 ΔH	 ΔG	 $\Delta G_{corrected}$
CPCM(THF)-B3LYP-D3(BJ)/6-31+G(d)/LANL2DZ(Pd)	−9.1	−8.8	+0.8	+1.4
CPCM(MeCN)-MN15L/6-31+G(d)/SDD(Pd)	−11.2	−10.9	0.0	−1.0

[a] Thermal corrections at 298.15 K. All energies reported in kcal/mol. Free energies are corrected for concentration (ratio of DMF:Pd = 718:1). Enthalpy (ΔH_{qh}) is reported after applying Head-Gordon's quasi-harmonic approximation to vibrational enthalpy. The free energy value labeled with ΔG_{qh} is reported after applying Cramer and Truhlar's and Head-Gordon's quasi-harmonic approximations to vibrational entropy and enthalpy, while the value labeled as ΔG does not include the quasi-harmonic approximations.

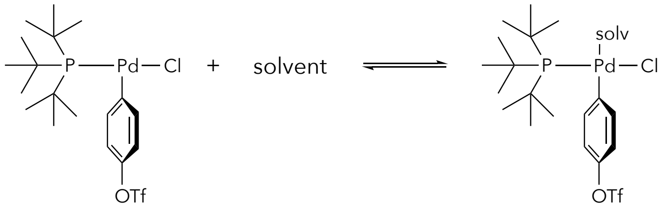
Using CPCM(solvent)-MN15L/6-31+G(d)/LANL2DZ(Pd), we also attempted to evaluate coordinating strength of several different solvents at both Pd(0) and Pd(II) by calculating the energies of the species depicted in Schemes S1 and S2. The free energy values in these schemes are reported after applying a standard state concentration assuming that Pd is 0.017 *M* in solvent, and with quasi-harmonic approximations to vibrational enthalpy and entropy. However, as shown, DFT at this level of theory suggests that the order of coordinating ability to 12 e^- Pd(0) should be benzene > MeCN > DMF > THF, which does not match the expected order of MeCN > DMF > THF > benzene. When considering coordination to 14 e^- Pd(II), the calculations indicate that solvent coordination is unfavorable in all cases, and the energetics suggest the following order of coordinating ability to Pd(II): benzene > DMF ≈ MeCN > THF. Moreover, in the optimized structures of the solvato complexes with THF and benzene, the solvent molecule is very far away from Pd (≥3.65 Å). The failure of DFT to discriminate between coordinating ability of these solvents indicates that this level of theory is not adequate for describing the strength of weak dative bonds. It is possible that more useful information may be gleaned using different functionals or larger basis sets; alternatively, molecular dynamics simulations may contribute to a more accurate representation of solvent coordination.

Scheme S1. Calculating favorability of solvent coordination to 12 *e*⁻ Pd(0).



MeCN (σ-type): -9.2 kcal/mol
MeCN (π-type): -9.0 kcal/mol
DMF: -6.9 kcal/mol
THF: -6.2 kcal/mol
benzene: -13.1 kcal/mol

Scheme S2. Calculating favorability of solvent coordination to 14 *e*⁻ Pd(II).



MeCN (σ-type): +3.9 kcal/mol
DMF: +4.0 kcal/mol
THF: +3.4 kcal/mol
benzene: +0.9 kcal/mol

E. Energies, Entropies, and Lowest Frequencies of Minimum Energy Structures

Table S32. Calculations at the CPCM(DMF)-B3LYP/6-31+G(d)/LANL2DZ(Pd) level of theory.[a]

Structure	**E_{elec} (Hartree)**	**ZPE (Hartree)**	**H_{qh} (Hartree)[c]**	**G[d] (Hartree)**	**G_{qh}[e] (Hartree)**	**Imaginary Freq[f]**
4	-2594.348615	0.479968	-2593.838126	-2593.939812	-2593.935128	
TS5a	-2594.33273	0.478858	-2593.823409	-2593.925542	-2593.920232	-206.2301
TS5b	-2594.325045	0.47793	-2593.816619	-2593.916959	-2593.913175	-259.9956
6a	-2594.380785	0.481617	-2593.868329	-2593.967968	-2593.965253	
6b	-2594.388147	0.481944	-2593.875515	-2593.97488	-2593.97189	
(4-dmf)[b]	-2842.870244	0.583401	-2842.251221	-2842.367065	-2842.362175	-14.5954
(TS5a-dmf)[b]	-2842.851507	0.583269	-2842.232268	-2842.350003	-2842.34438	-179.6848
TS5b-dmf	-2842.853054	0.582742	-2842.234138	-2842.351143	-2842.345837	-260.8251
6a-dmf	-2842.911073	0.586476	-2842.28799	-2842.404586	-2842.39992	
6b-dmf	-2842.919852	0.586244	-2842.297336	-2842.41364	-2842.409048	
DMF	-248.530317	0.102799	-248.420798	-248.45138	-248.451688	

[a] 1 Hartree = 627.51 kcal mol^{-1}. Thermal corrections at 298.15 K, with concentration = 13 *M* for DMF and 0.017 *M* for all other species. [b] Optimized with a constrained Pd—O distance; so these are unlikely to represent a true minimum-energy structure at this level of theory. [c] Enthalpy reported after application of Head-Gordon's quasi-harmonic approximation to vibrational enthalpy. [d] Solvent-corrected free energy given by $G = E_{elec} + G_{corr}$, where G_{corr} is the thermal correction to Gibbs free energy. [e] Solvent-corrected free energy given by $G_{qh} = E_{elec} + G_{corr^*}$, where G_{corr^*} is the thermal correction to Gibbs free energy obtained after applying Cramer and Truhlar's and Head-Gordon's quasi-harmonic approximations. [f] The single imaginary frequency is reported for the structures that have one (i.e., the transition structures; and **4-dmf** (optimized with constrained Pd-O distance) also has one imaginary frequency).

Table S33. Calculations at the CPCM(DMF)-MN15L/6-31+G(d)/SDD(Pd) level of theory.[a]

Structure	**E_{elec} (Hartree)**	**ZPE (Hartree)**	**H_{qh} (Hartree)[b]**	**G[c] (Hartree)**	**G_{qh}[d] (Hartree)**	**Imaginary Freq[e]**
4	-2593.644346	0.481345	-2593.133222	-2593.228452	-2593.227671	
TS5a	-2593.625463	0.480954	-2593.114724	-2593.210282	-2593.2083	-171.5502
TS5b	-2593.616729	0.478692	-2593.108203	-2593.205818	-2593.202853	-228.3686
6a	-2593.675812	0.483879	-2593.161958	-2593.257676	-2593.255789	
6b	-2593.685169	0.483386	-2593.17171	-2593.266324	-2593.265437	
4-dmf	-2841.934404	0.586643	-2841.312338	-2841.419651	-2841.419805	
TS5a-dmf	-2841.902557	0.585601	-2841.281456	-2841.391212	-2841.389741	-137.2208
TS5b-dmf	-2841.914925	0.585201	-2841.294157	-2841.402029	-2841.401882	-246.0247
6a-dmf	-2841.959897	0.588859	-2841.33526	-2841.446021	-2841.443004	
6b-dmf	-2841.974739	0.588358	-2841.350582	-2841.459279	-2841.45836	
DMF	-248.26759	0.10276	-248.158125	-248.188622	-248.188946	

[a] 1 Hartree = 627.51 kcal mol^{-1}. Thermal corrections at 298.15 K, with concentration = 13 *M* for DMF and 0.017 *M* for all other species. [b] Enthalpy reported after application of Head-Gordon's quasi-harmonic approximation to vibrational enthalpy. [c] Solvent-corrected free energy given by $G = E_{elec} + G_{corr}$, where G_{corr} is the thermal correction to Gibbs free energy. [d] Solvent-corrected free energy given by $G_{qh} = E_{elec} + G_{corr^*}$, where G_{corr^*} is the thermal correction to Gibbs free energy obtained after applying Cramer and Truhlar's and Head-Gordon's quasi-harmonic approximations. [e] The single imaginary frequency is reported for the structures that have one (i.e., the transition structures).

Table S34. Calculations at the CPCM(DMF)-B3LYP-D3BJ/6-31+G(d)/SDD(Pd) level of theory.[a]

Structure	**E_{elec} (Hartree)**	**ZPE (Hartree)**	**H_{qh} (Hartree)[b]**	**G[c] (Hartree)**	**G_{qh}[d] (Hartree)**	**Imaginary Freq[e]**
4	-2595.688612	0.481727	-2595.176572	-2595.276064	-2595.272339	
TS5a	-2595.670641	0.481266	-2595.159196	-2595.257293	-2595.254542	-143.4386
TS5b	-2595.66856	0.479359	-2595.158894	-2595.258514	-2595.254518	-291.4703
6a	-2595.728252	0.48407	-2595.213709	-2595.311295	-2595.309183	
6b	-2595.735645	0.484165	-2595.221073	-2595.318547	-2595.316219	
4-dmf	-2844.243619	0.586633	-2843.621117	-2843.734454	-2843.731391	
TS5a-dmf	-2844.220638	0.586291	-2843.598437	-2843.71181	-2843.708974	-101.0273
TS5b-dmf	-2844.231449	0.585406	-2843.610018	-2843.722351	-2843.720012	-320.8933
6a-dmf	-2844.286863	0.589193	-2843.661374	-2843.775281	-2843.771396	
6b-dmf	-2844.298688	0.588445	-2843.674178	-2843.788233	-2843.784421	
DMF	-248.543978	0.10288	-248.434389	-248.464973	-248.46527	

[a] 1 Hartree = 627.51 kcal mol^{-1}. Thermal corrections at 298.15 K, with concentration = 13 *M* for DMF and 0.017 *M* for all other species. [b] Enthalpy reported after application of Head-Gordon's quasi-harmonic approximation to vibrational enthalpy. [c] Solvent-corrected free energy given by $G = E_{elec} + G_{corr}$, where G_{corr} is the thermal correction to Gibbs free energy. [d] Solvent-corrected free energy given by $G_{qh} = E_{elec} + G_{corr*}$, where G_{corr*} is the thermal correction to Gibbs free energy obtained after applying Cramer and Truhlar's and Head-Gordon's quasi-harmonic approximations. [e] The single imaginary frequency is reported for the structures that have one (i.e., the transition structures).

III. References

1. Reeves, E. K.; Humke, J. N.; Neufeldt, S. R. *J. Org. Chem.* **2019**, *84*, 11789-11812.
2. Gill, D.; Hester, A. J.; Lloyd-Jones, G. C. *Org. Biomol. Chem.* **2004**, *2*, 2547-2548.
3. Andersen, T. L.; Kramer, S.; Overgaard, J.; Skrydstrup, T. *Organometallics* **2017**, *36*, 2058-2066.
4. Barrios-Landeros, F.; Carrow, B. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 8141-8154.
5. Morozova, V.; Mayer, P.; Berionni, G. *Angew. Chem. Int. Ed.* **2015**, *54*, 14508-14512.
6. Gooβen, L.J.; Rodríguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248-15249.
7. Onodera, S.; Kochi, T.; Kakiuchi, F. *J. Org. Chem.* **2019**, *84*, 6508-6515
8. Reeves, E.K.; Bauman, O.R.; Mitchem, G.B.; Neufeldt, S.R. *Isr. J. Chem.* **2020**, *60*, 406-409.
9. Entz, E. D.; Russell, J. E. A.; Hooker, L. V. *J. Am. Chem. Soc.* **2020**, *142*, 15454-15463.
10. Bartoli, G.; Bosco, M. *Synthesis* **1980**, *8*, 616-617.
11. Viswanathan, G.S.; Wang, M.; Li, C.J. *Angew. Chem. Int. Ed.* **2002**, *41*, 2138-2141.
12. Shekhar, S.; Dunn, T. B.; Kotecki, B. J.; Montavon, D. K.; Cullen, S. C. *J. Org. Chem.* **2011**, *76*, 4552-4563.
13. Zhang, Z.; Wang, Z. *J. Am. Chem. Soc.* **2006**, *71*, 7485-7487.
14. Gooβen, L.J.; Rodríguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248-15249.
15. Gill, D.; Hester, A.J.; Lloyd-Jones, G.C. *Org. & Biomol. Chem.* **2004**, *2*, 2547-2548.
16. Hansch, C.; Leo, A.; Taft, R.W. *Chem. Rev.* **1991**, *91*, 165-195.
17. Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 194-202.
18. Wohlfarth, C. "Permittivity (Dielectric Constant) of Liquids" in CRC Handbook of Chemistry and Physics, Rumble, Jr., J. R.; Lide, D. R.; Bruno, T. J., eds. CRC Press, Boca Raton, FL, 2020.
19. Suzuki, K.; Shin-ya, M.; Ono, Y.; Matsumoto, T.; Nanbu, N.; Takehara, M.; Ue, M.; Sasaki, Y. *Electrochemistry* **2007**, *75*, 611-614.
20. Salmon, C. J.; Danelon, G. O.; Mascaretti, O. A. *J. Org. Chem.* **2000**, *65*, 9220-9222.
21. Proutiere, F.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2011**, *50*, 8192-9195.
22. Fairlamb, I.J.S.; Kapdi, A.R.; Lee, A.F. *J. Am. Chem. Soc.* **2004**, *6*, 4435-4438,
23. Zalesskiy, S.S.; Ananikov, V.P. *Organometallics* **2012**, *13*, 2302-2309.
24. National Institute of Health PubChem. Potassium fluoride. https://pubchem.ncbi.nlm.nih.gov/compound/522689 (accessed Sep 30, 2020).
25. Wynn, D. A.; Roth, M. M.; Pollard, B. D. Talanta **1984**, *31*, 1036-1040.
26. Peruzzi, N.; Lo Nostro, P.; Ninham, B. W.; Baglioni, P. *J. Solution Chem.* **2015**, *44*, 1224-1239.
27. Barrios-Landeros, F.; Carrow, B. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 5842-5843
28. Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.;

Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016

29. Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669.

30. Yu, H. S.; He, X.; Truhlar, D. G. *J. Chem. Theory Comput.* **2016**, *12*, 1280.

31. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

32. Ribeiro, R.F.; Marenich, A.V.; Cramer, C.J.; Truhlar, D.G. *J. Phys. Chem. B.* **2011**, *115*, 14556.

33. Li, Y.-P.; Gomes, J.; Sharada, S. M.; Bell, A.T.; Head-Gordon, M. *J. Phys. Chem. C* **2015**, *119*, 1840

34. Luchini, G.; Alegre-Requena, J. V.; Funes-Ardoiz, I.; Paton, R. S. GoodVibes: Automated Thermochemistry for Heterogeneous Computational Chemistry Data. *F1000Research*, **2020**, *9*, 291.

35. (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154; (b) Gonzalez, C.; Schlegel, H.B. *J. Phys. Chem.* **1990**, *94*, 5523; (c) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

36. CYLview, 1.0b; Legault CY, Université de Sherbrooke, 2009 (http://www.cylview.org)

37 (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, 132, 154104-154119. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456-1465.

38 (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, 132, 154104-154119. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456-1465.

39. Schoenebeck, F.; Houk, K. N. *J. Am. Chem. Soc.* **2010**, 1*32*, 2496.

40. Niemeyer, Z. L.; Milo, A.; Hickey, D. P.; Sigman, M. S. *Nat. Chem.* **2016**, *8*, 610.

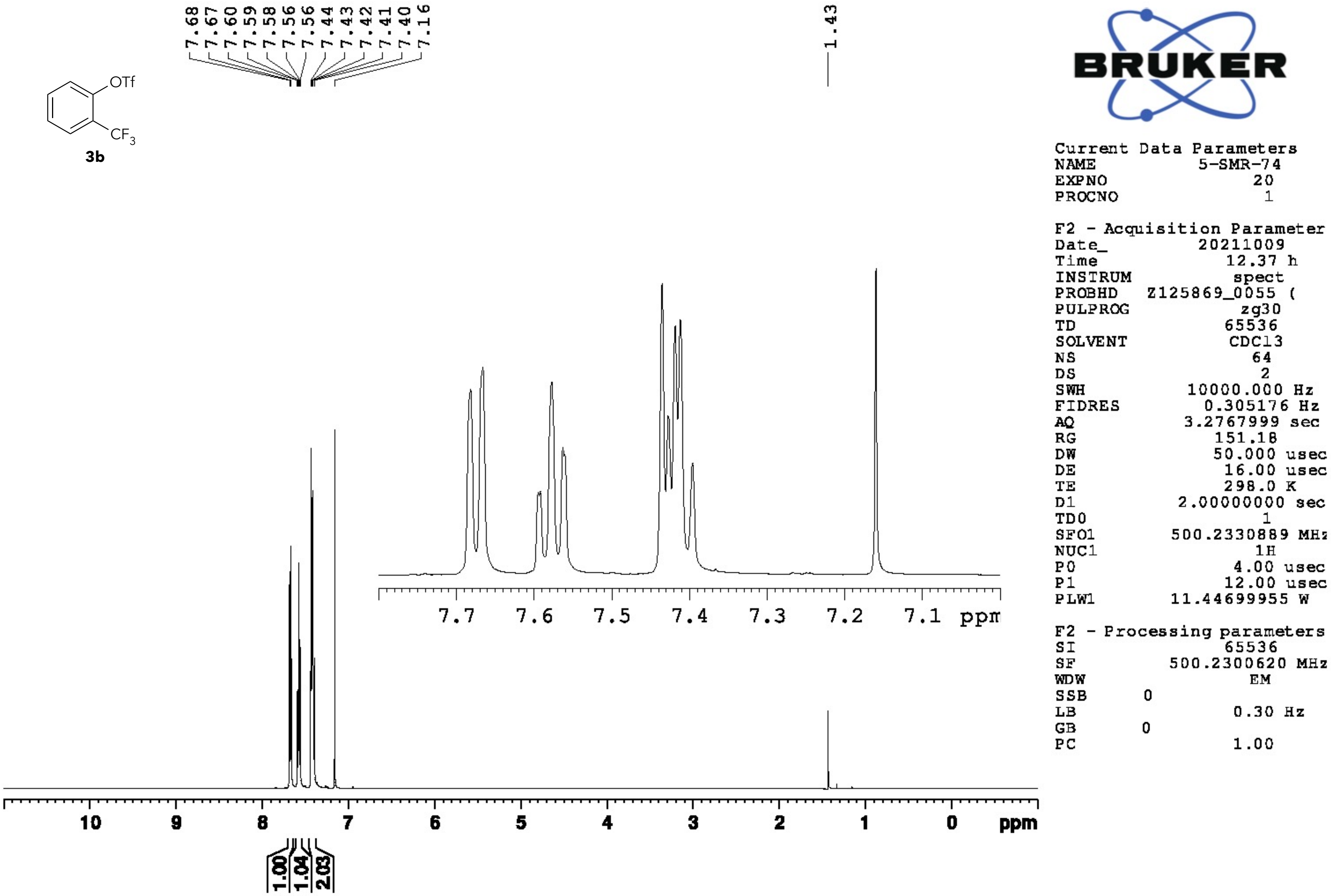
41. So, C. M.; Yuen, O. Y.; Ng, S. S.; Chen, Z. *ACS Catal.* **2021**, *11*, 7820/

42. Moltved, K. A.; Kepp, K. P. *J. Chem. Theory Comput.* **2018**, *14*, 3479.

IV. NMR Spectra

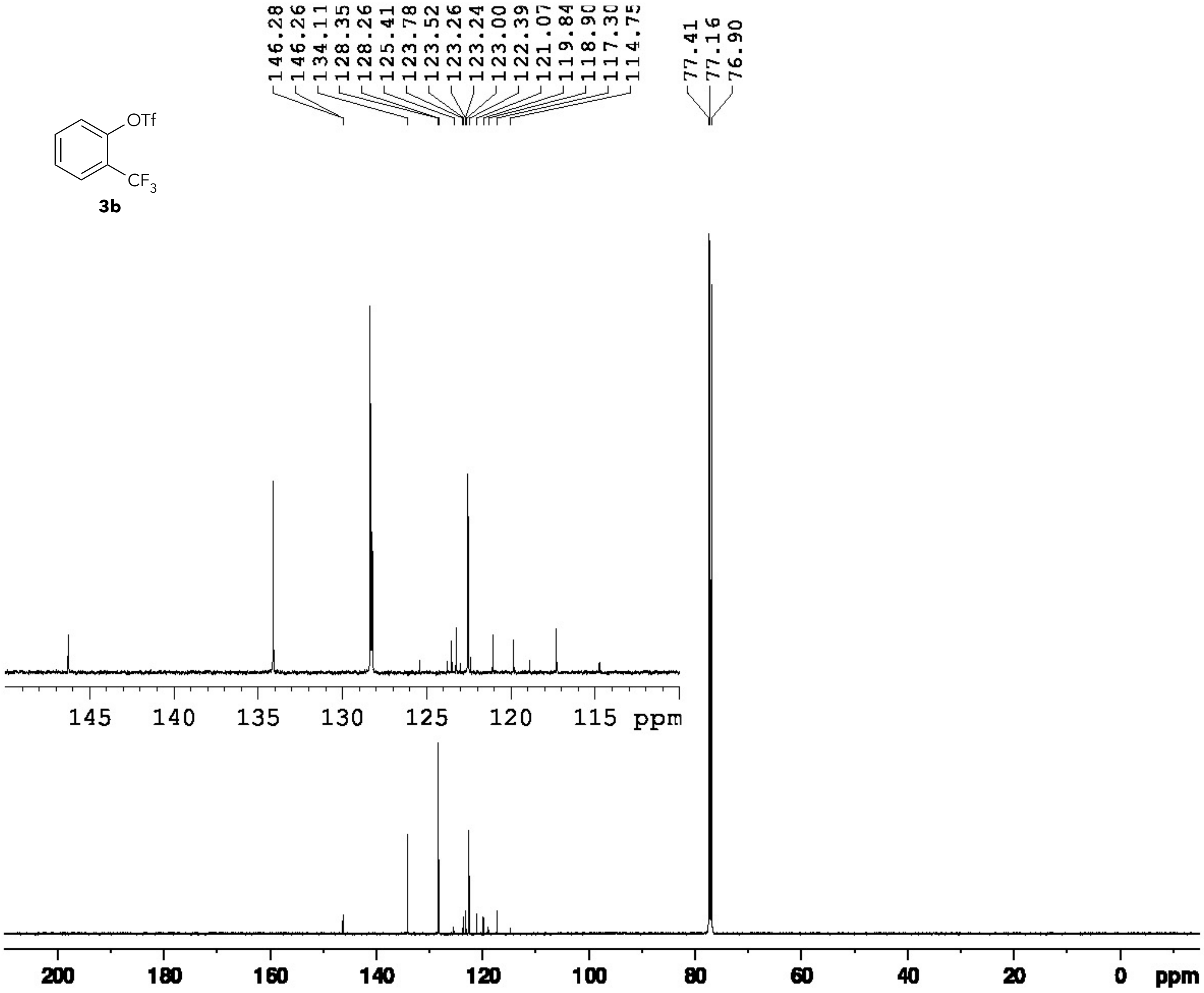
A. Compound Characterization

3b



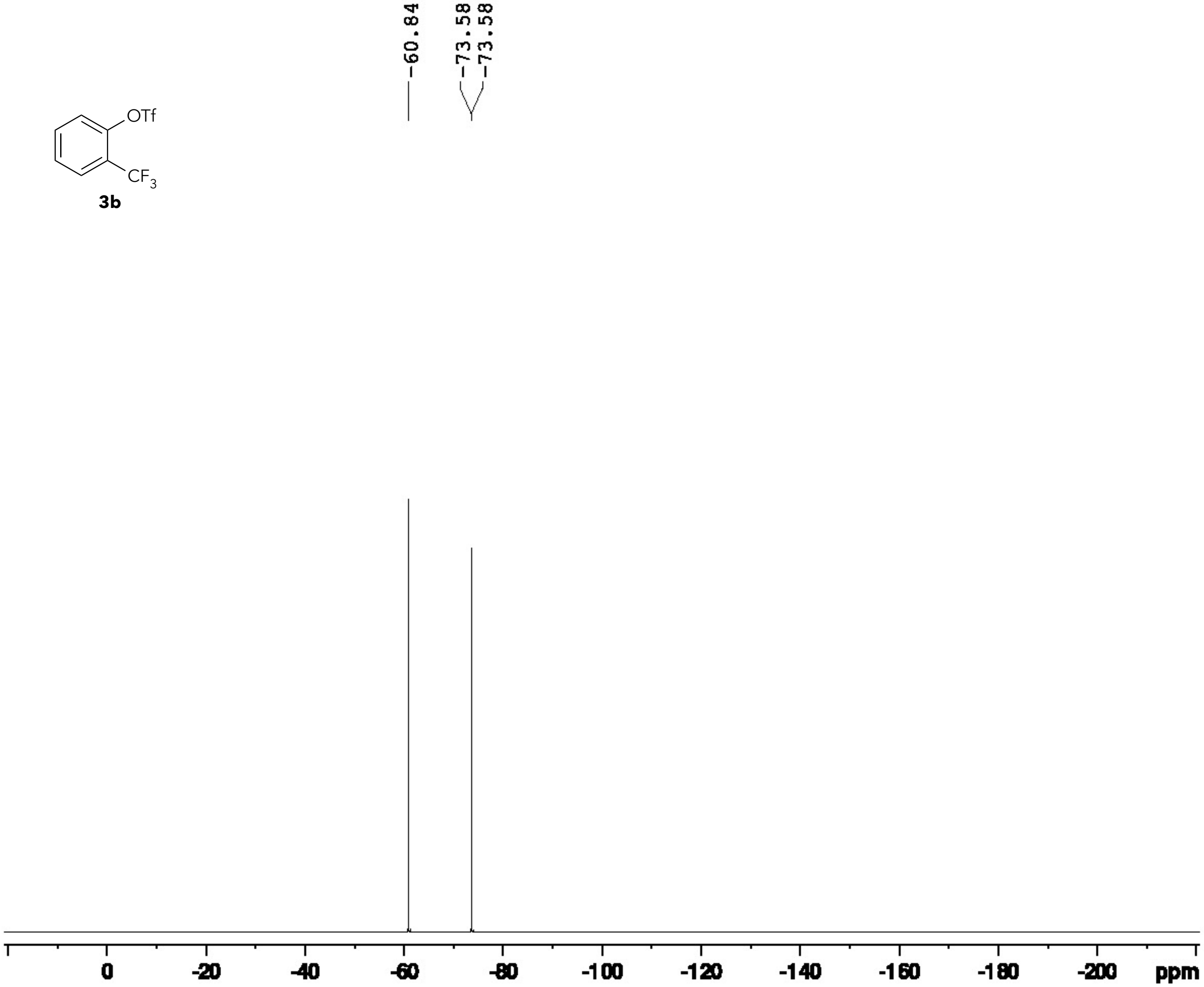
```
Current Data Parameters
NAME              5-SMR-74
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameter
Date_             20211009
Time               12.37 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                  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          500.2300620 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```

3b



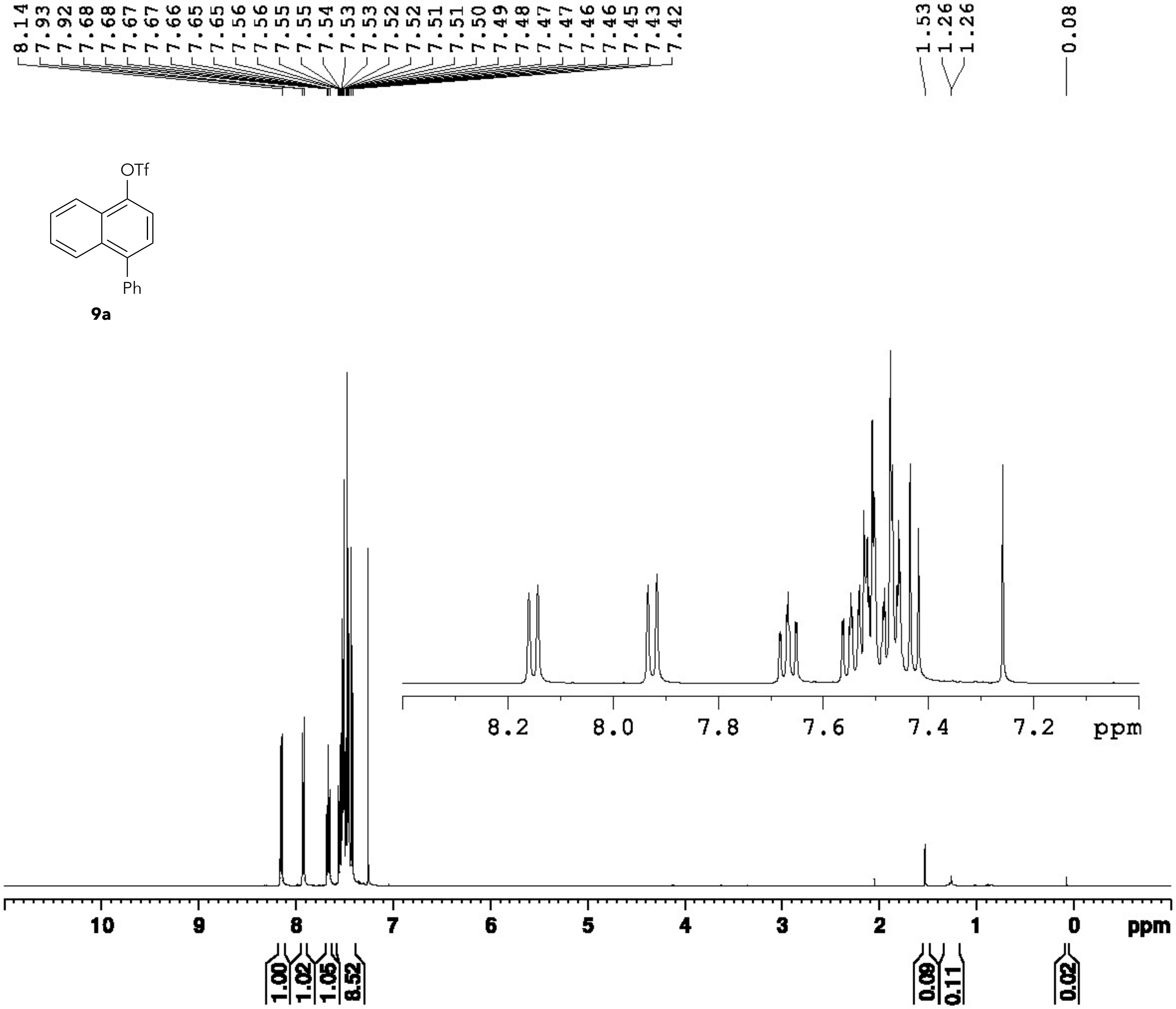
```
Current Data Parameters
NAME               5-SMR-74
EXPNO                    22
PROCNO                    1

F2 - Acquisition Parameter
Date_              20211009
Time                13.35 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             125.7829153 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

3b



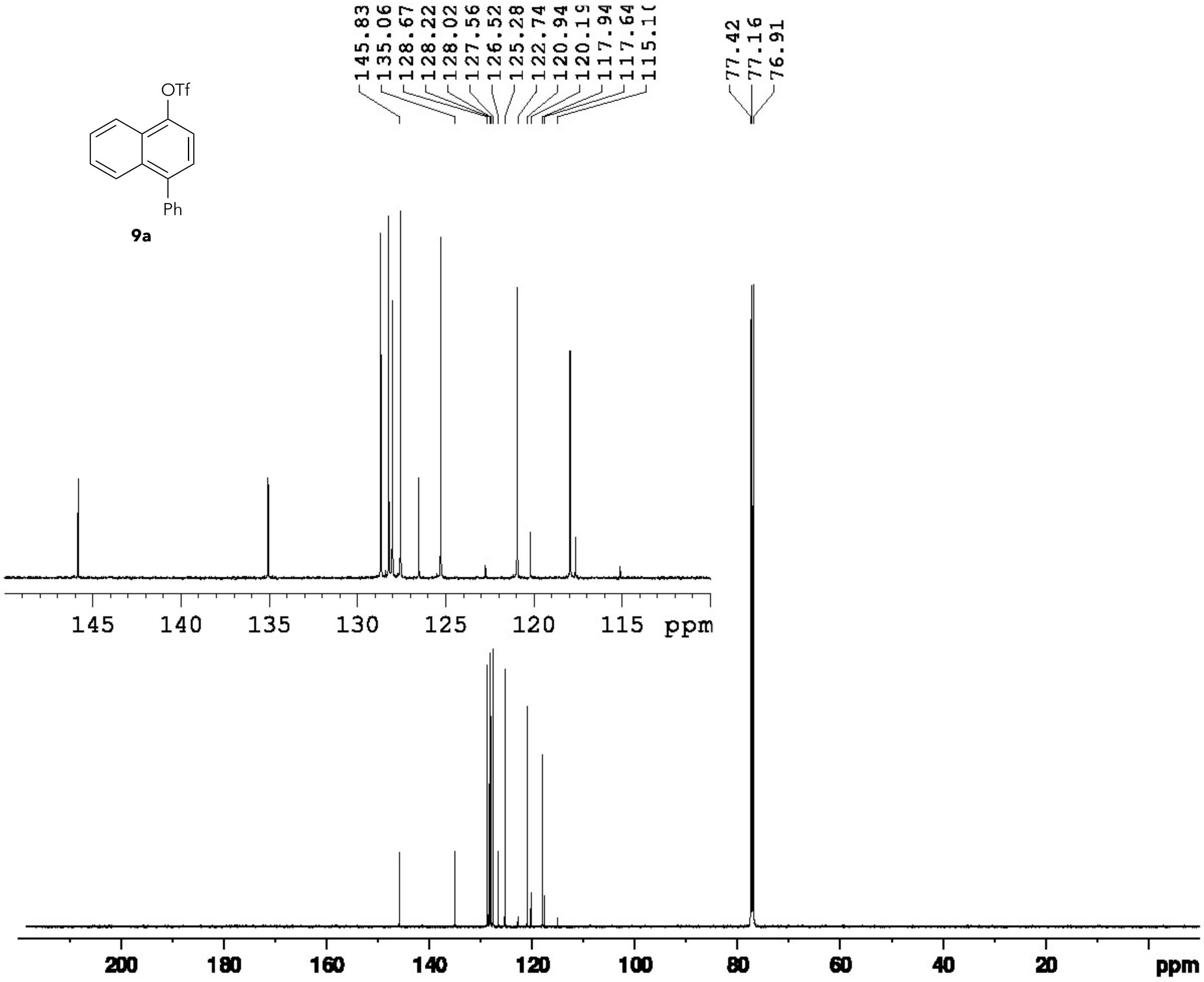
```
Current Data Parameters
NAME             5-SMR-74
EXPNO                  21
PROCNO                  2

F2 - Acquisition Parameter
Date_            20211009
Time              12.39 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG           zgflqn
TD                130892
SOLVENT            CDCl3
NS                     16
DS                      4
SWH           113636.367 Hz
FIDRES          1.736338 Hz
AQ             0.5759248 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
```

9a

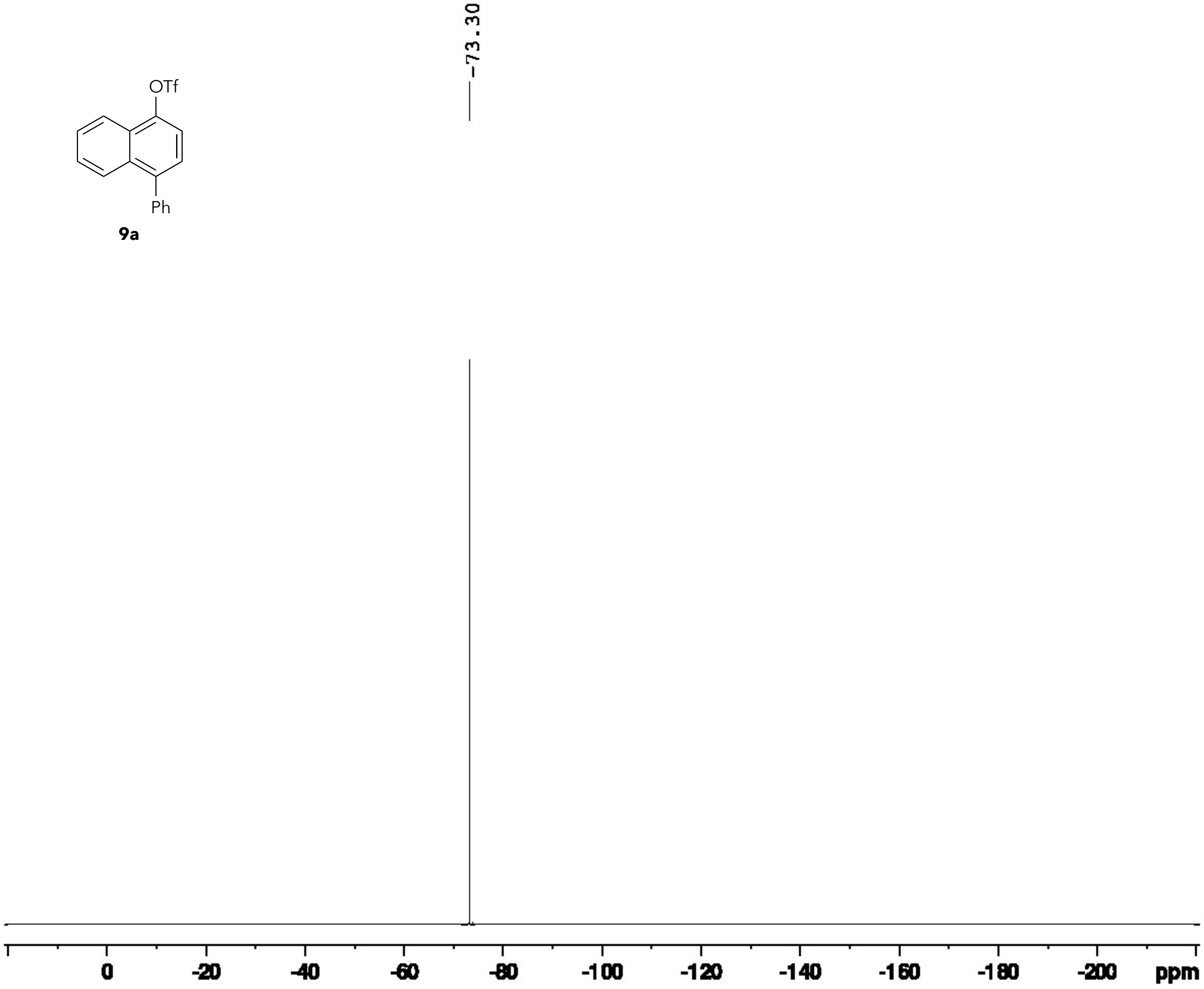


```
Current Data Parameters
NAME             EKB-1-188
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameter
Date_             20211006
Time               15.56 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                  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            500.2300126 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

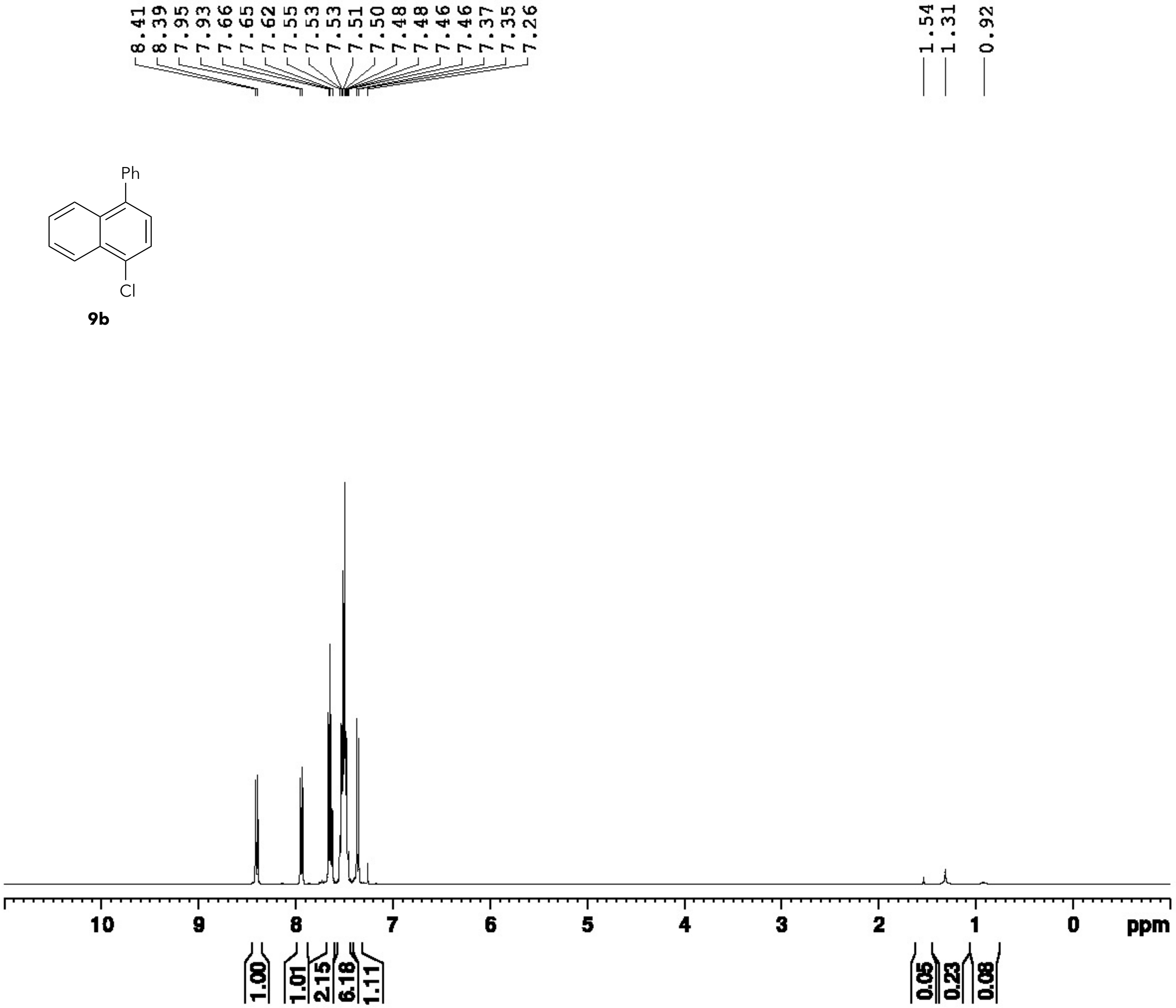
9a



```
Current Data Parameters
NAME            EKB-1-184
EXPNO                  22
PROCNO                  1

F2 - Acquisition Parameter
Date_           20211007
Time              12.53 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           125.7829156 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

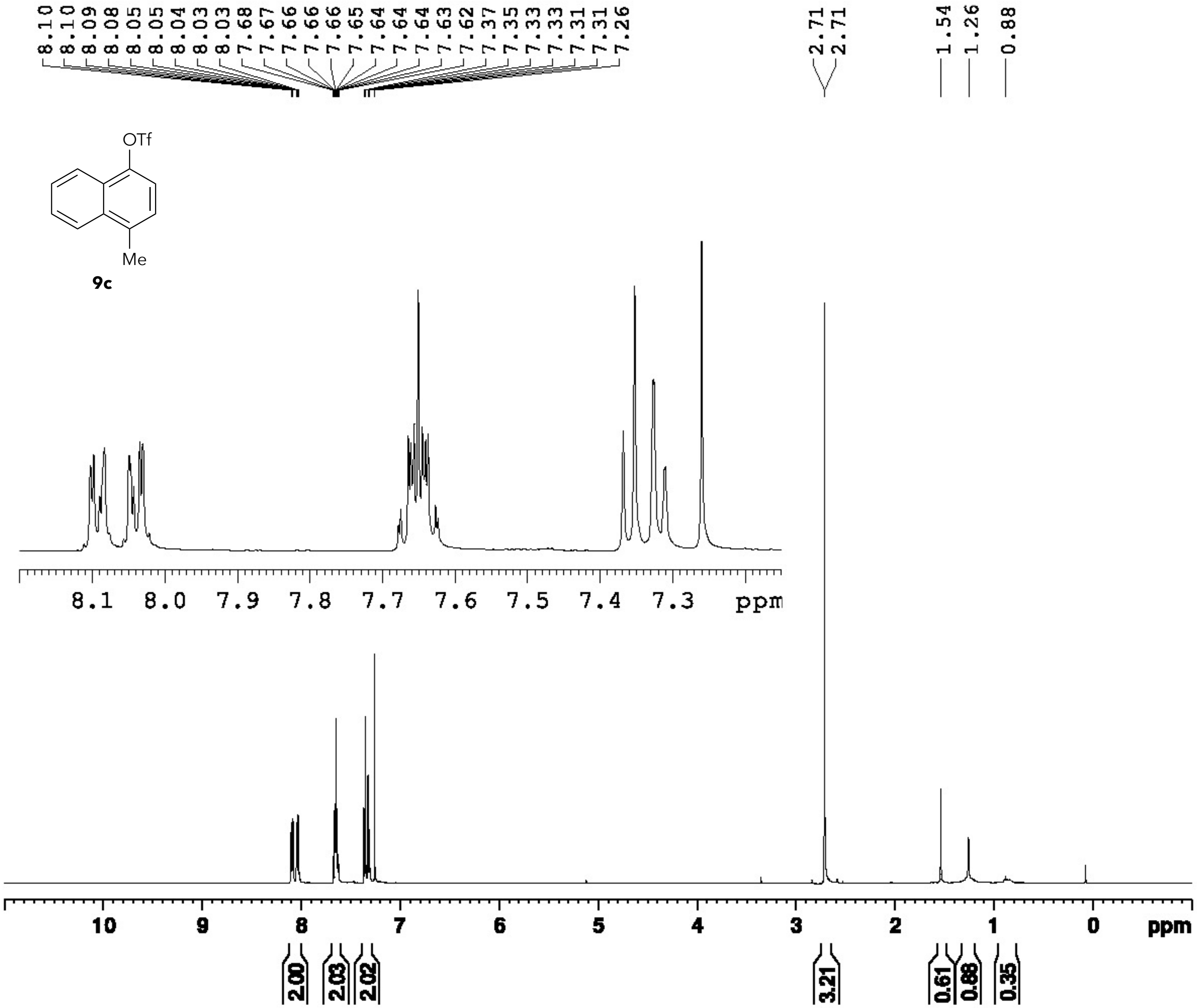


```
Current Data Parameters
NAME             EKB-1-188
EXPNO                   21
PROCNO                   2

F2 - Acquisition Parameter
Date_             20211006
Time               15.59 h
INSTRUM              spect
PROBHD   Z125869_0055 (
PULPROG             zgflqn
TD                  130892
SOLVENT              CDCl3
NS                      16
DS                       4
SWH          113636.367 Hz
FIDRES         1.736338 Hz
AQ           0.5759248 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
```



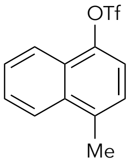
9b

```
Current Data Parameters
NAME      5-SMR-147-final
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameter
Date_          20210902
Time             16.06 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              79.9054
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
SI                65536
SF       400.1300097 MHz
WDW                  EM
SSB      0
LB               0.30 Hz
GB       0
PC                 1.00
```

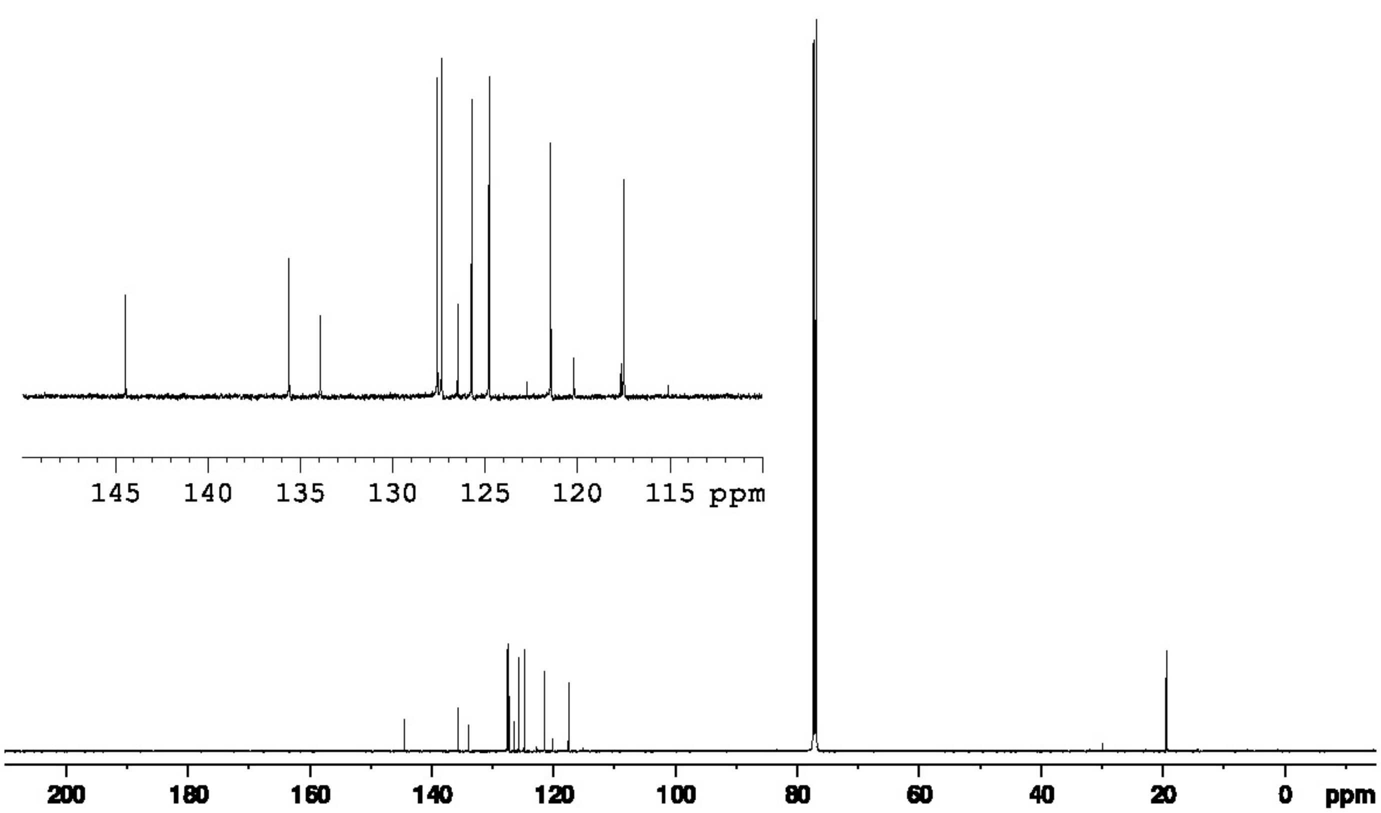


9c

```
Current Data Parameters
NAME             5-SMR-181
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameter
Date_             20211007
Time               18.30 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                  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             500.2300124 MHz
WDW                     EM
SSB        0
LB                    0.30 Hz
GB         0
PC                    1.00
```

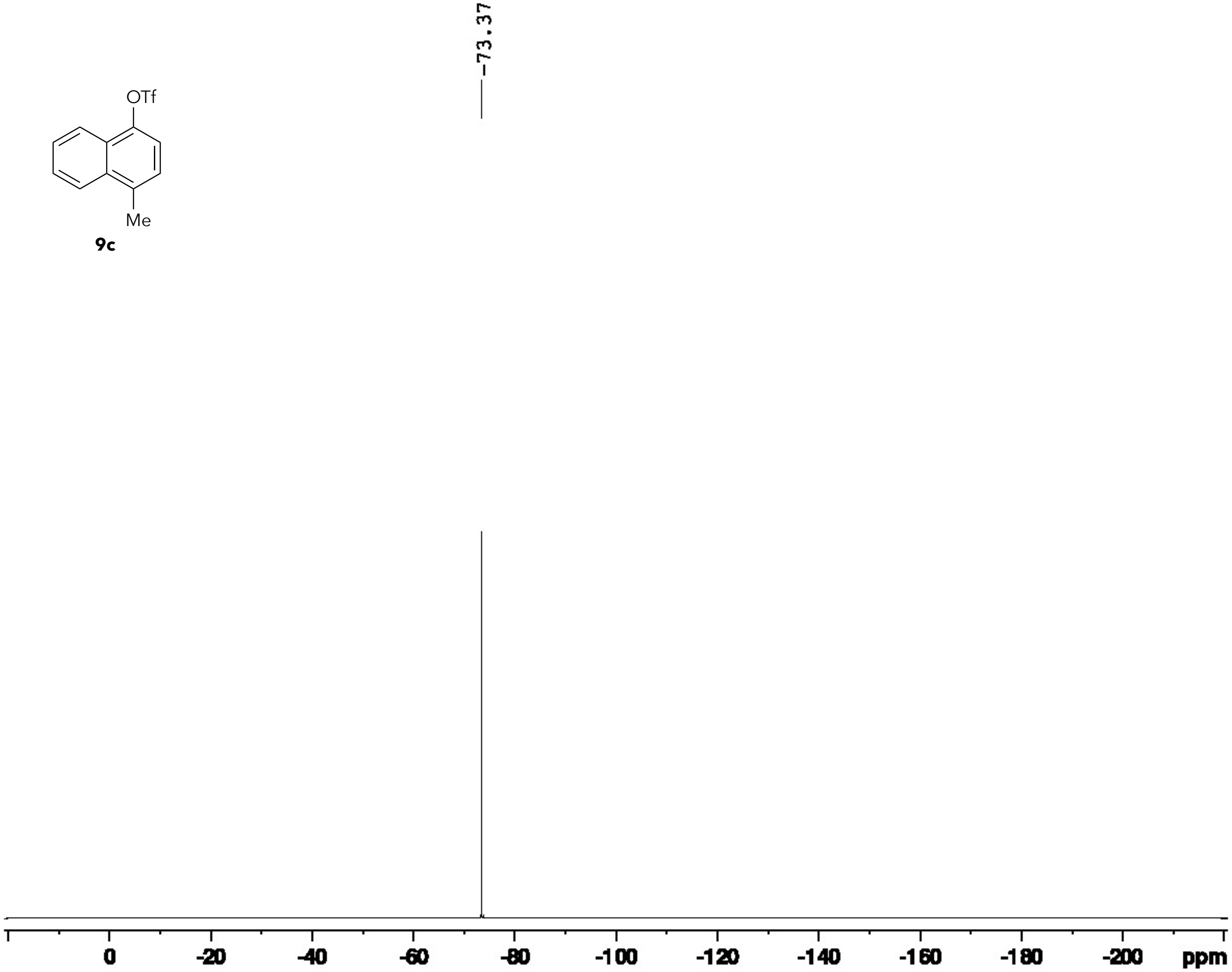


9c

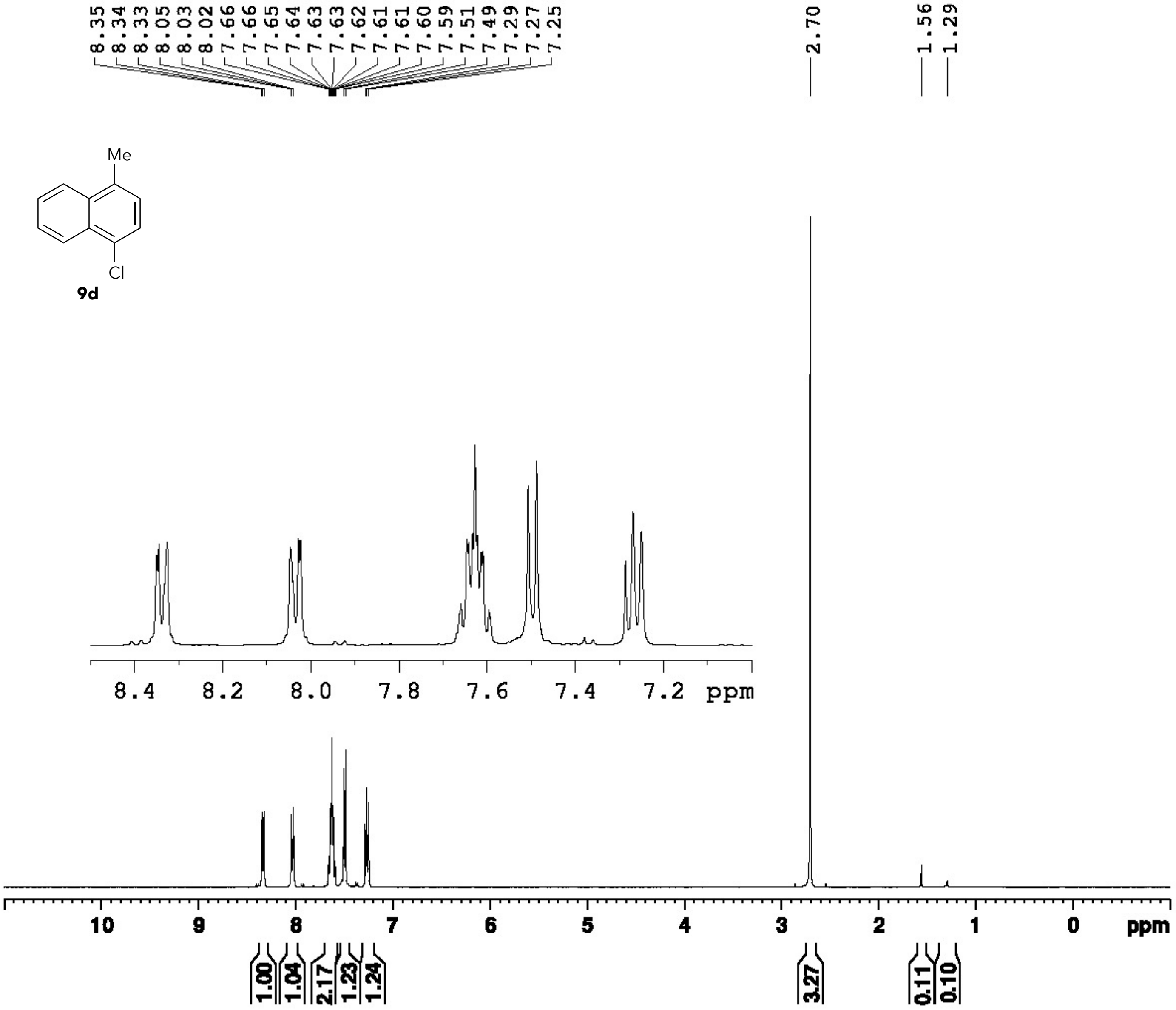


```
Current Data Parameters
NAME              5-SMR-181
EXPNO                    21
PROCNO                    1

F2 - Acquisition Parameter
Date_              20211007
Time                20.21 h
INSTRUM               spect
PROBHD   Z125869_0055 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2048
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             125.7829158 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

9c



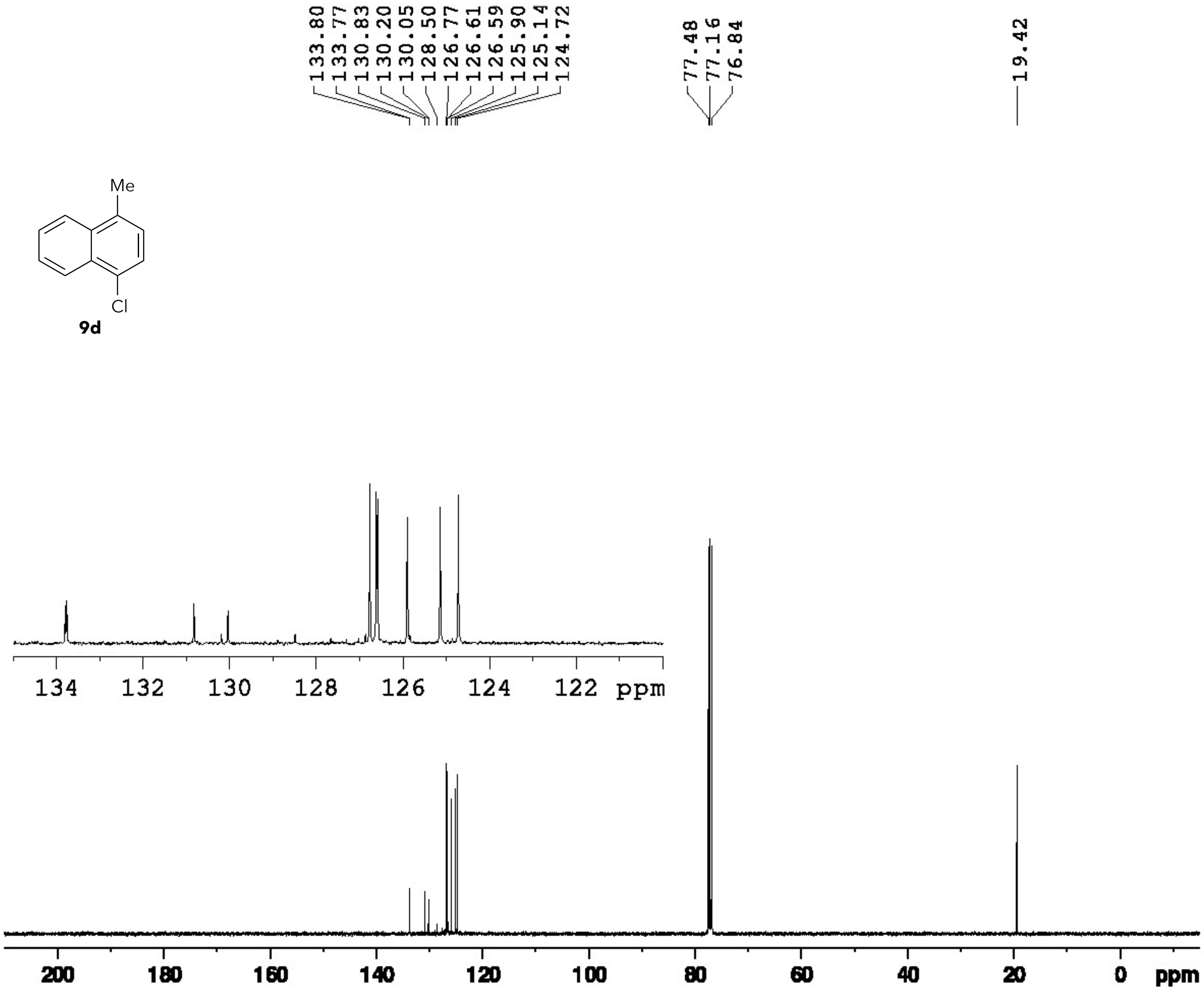
```
Current Data Parameters
NAME            5-SMR-181
EXPNO                  22
PROCNO                  2

F2 - Acquisition Parameter
Date_            20211007
Time              20.23 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG            zgflqn
TD                 130892
SOLVENT             CDCl3
NS                     16
DS                      4
SWH           113636.367 Hz
FIDRES          1.736338 Hz
AQ             0.5759248 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
```



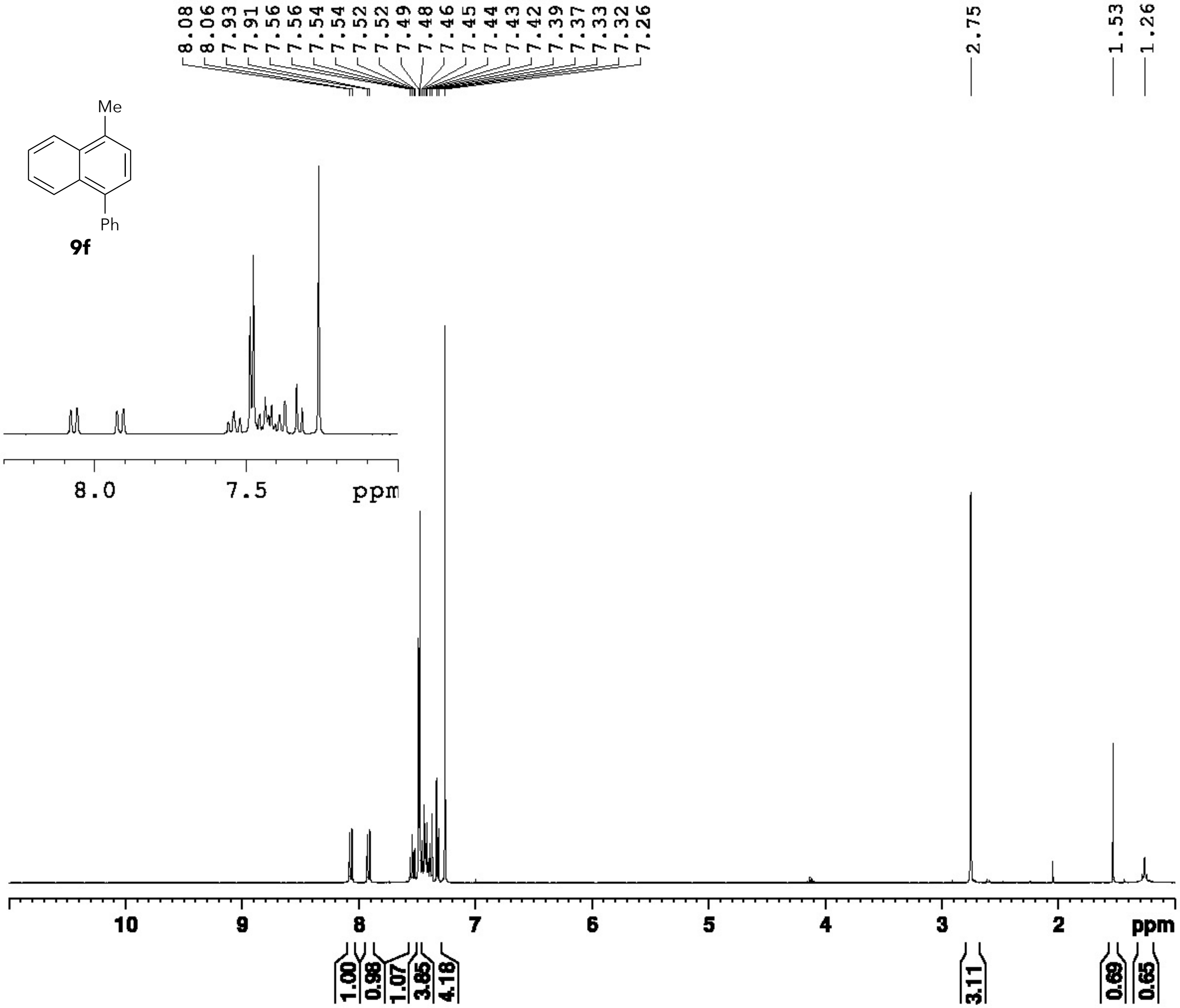
9d

```
Current Data Parameters
NAME      5-SMR-156-final
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameter
Date_            20210902
Time              17.12 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                298.2 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
SI                  65536
SF          400.1299991 MHz
WDW                    EM
SSB      0
LB                0.30 Hz
GB       0
PC                   1.00
```

9d

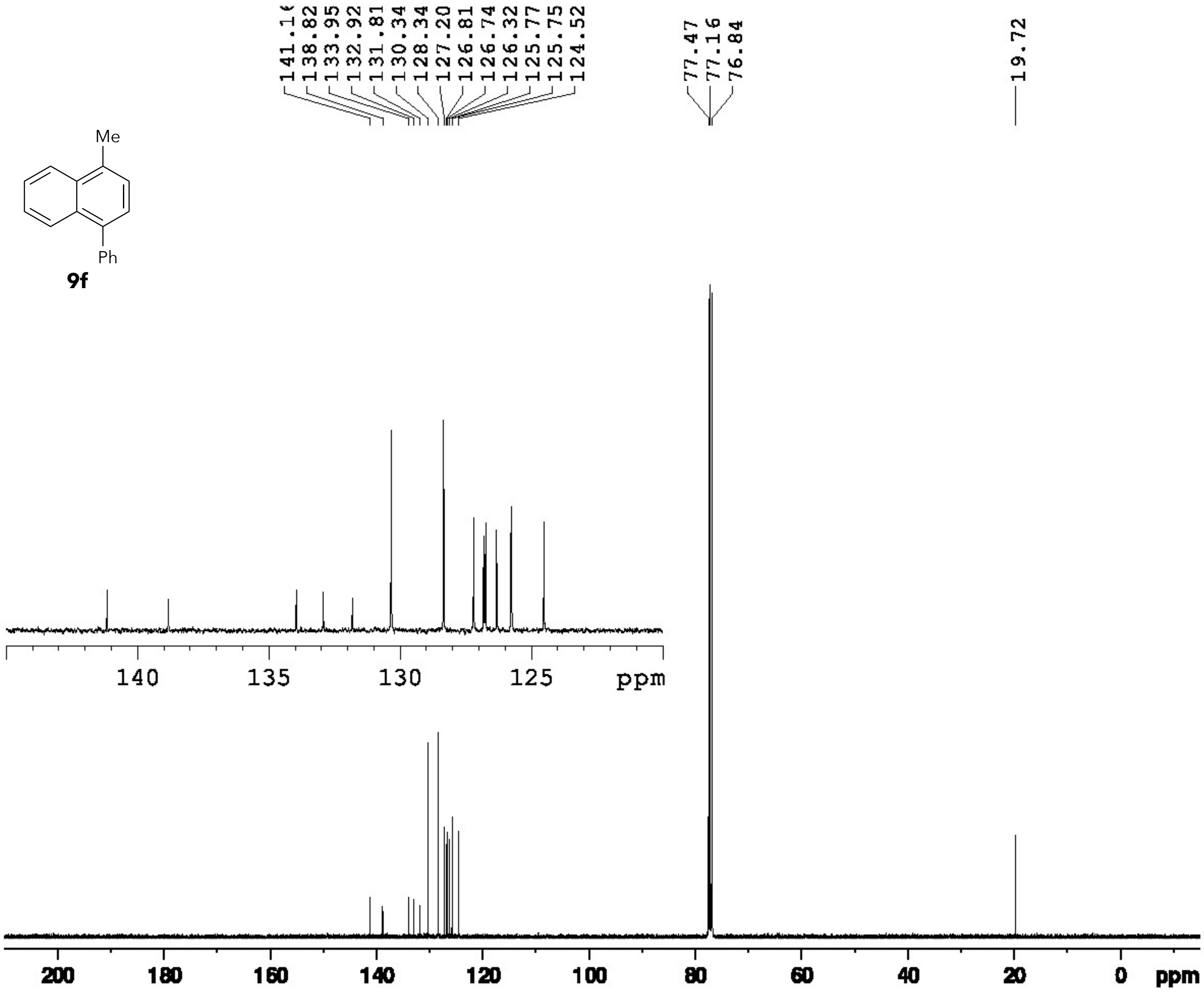


```
Current Data Parameters
NAME      5-SMR-156-final
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_          20210902
Time              18.12 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                298.2 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          100.6127555 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

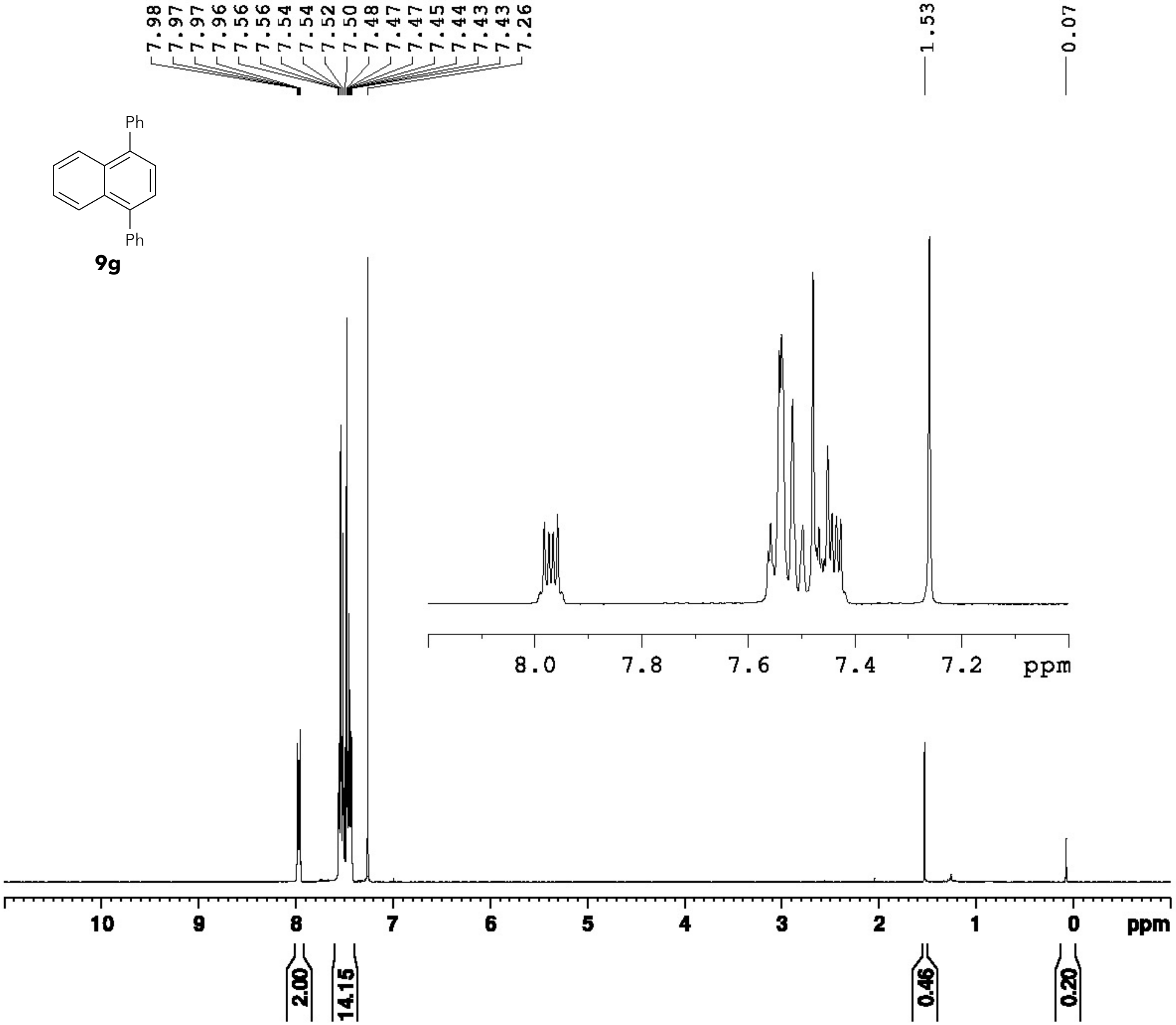


```
Current Data Parameters
NAME              5-SMR-149
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameter
Date_              20210803
Time                14.52 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           400.1300093 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.00
```

9f



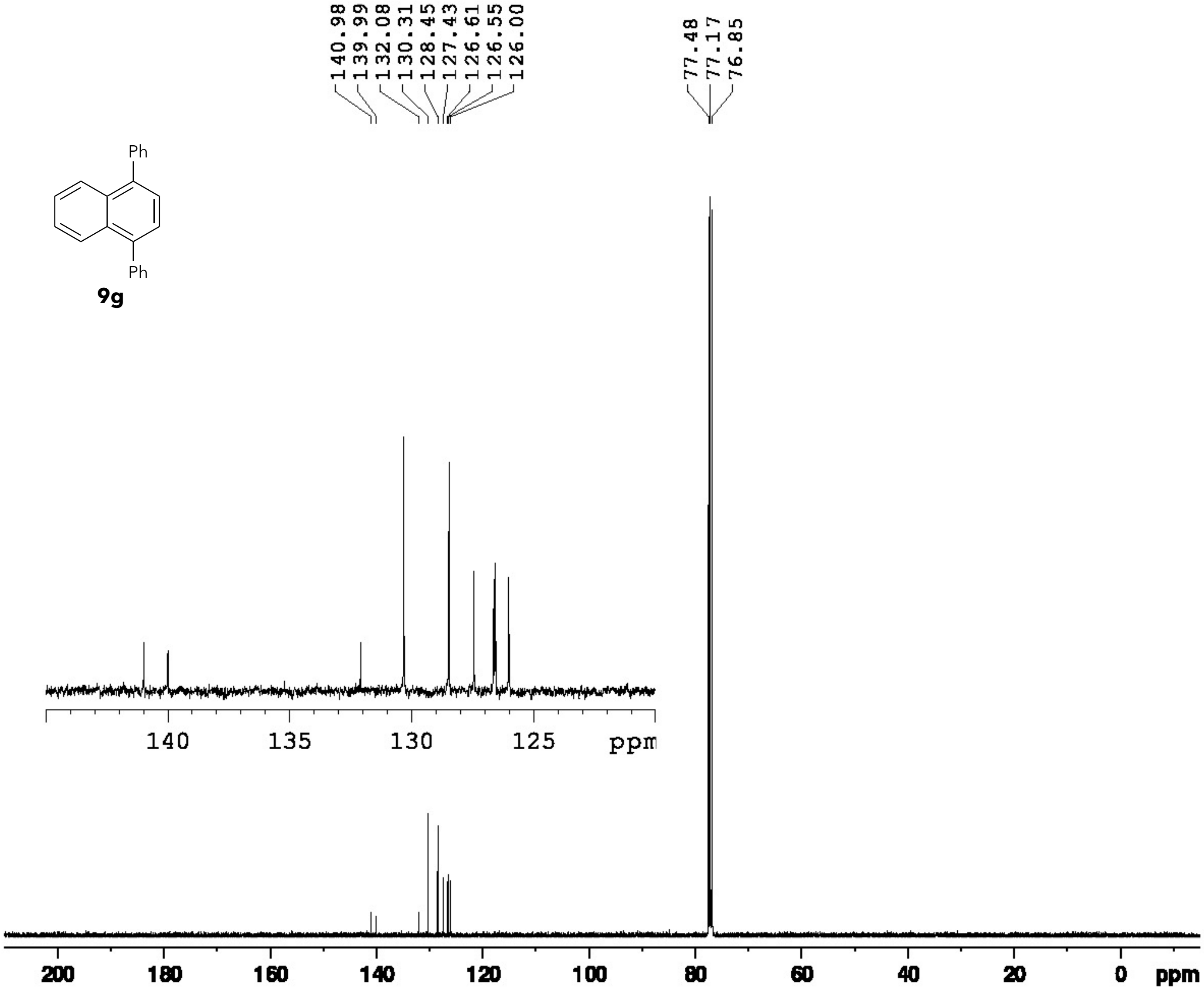
```
Current Data Parameters
NAME            5-SMR-149
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameter
Date_            20210906
Time              14.20 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                298.2 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          100.6127551 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



9g

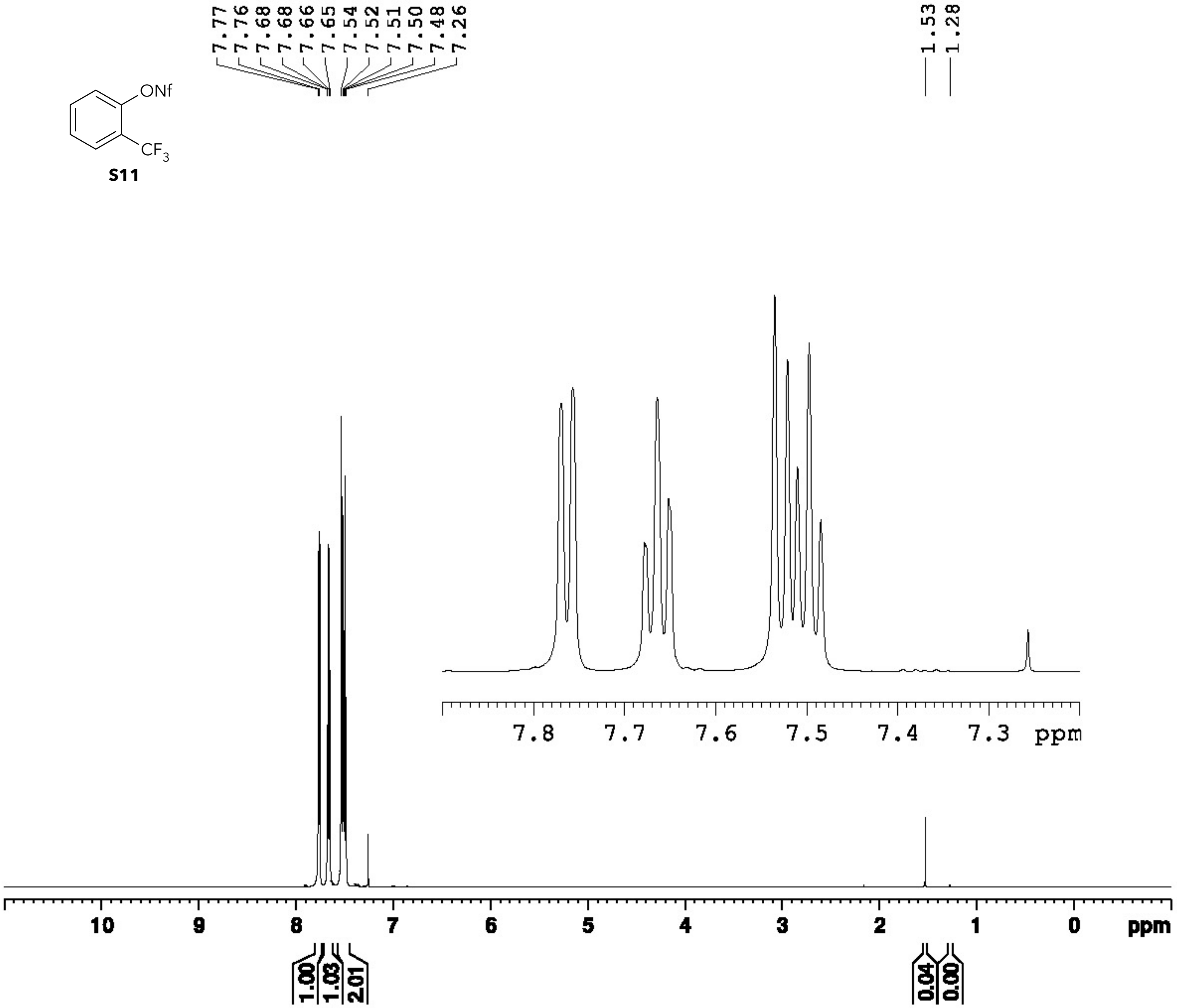
```
Current Data Parameters
NAME      5-SMR-163-full
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameter
Date_           20210906
Time             14.26 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               298.2 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
SI                 65536
SF       400.1300095 MHz
WDW                   EM
SSB       0
LB               0.30 Hz
GB        0
PC                  1.00
```

9g



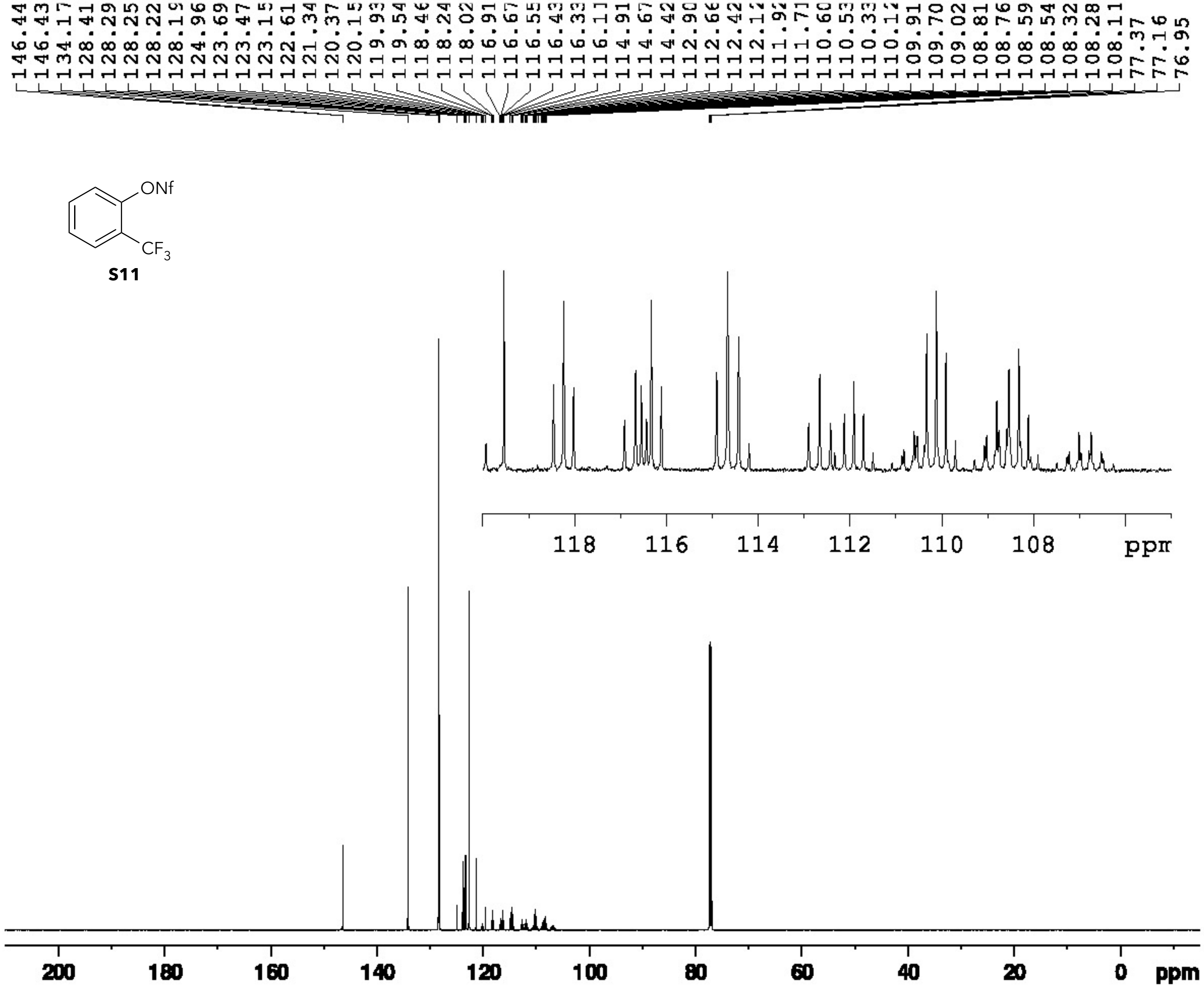
```
Current Data Parameters
NAME      5-SMR-163-full
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameter
Date_           20210906
Time               15.27 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                298.2 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          100.6127534 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

S11



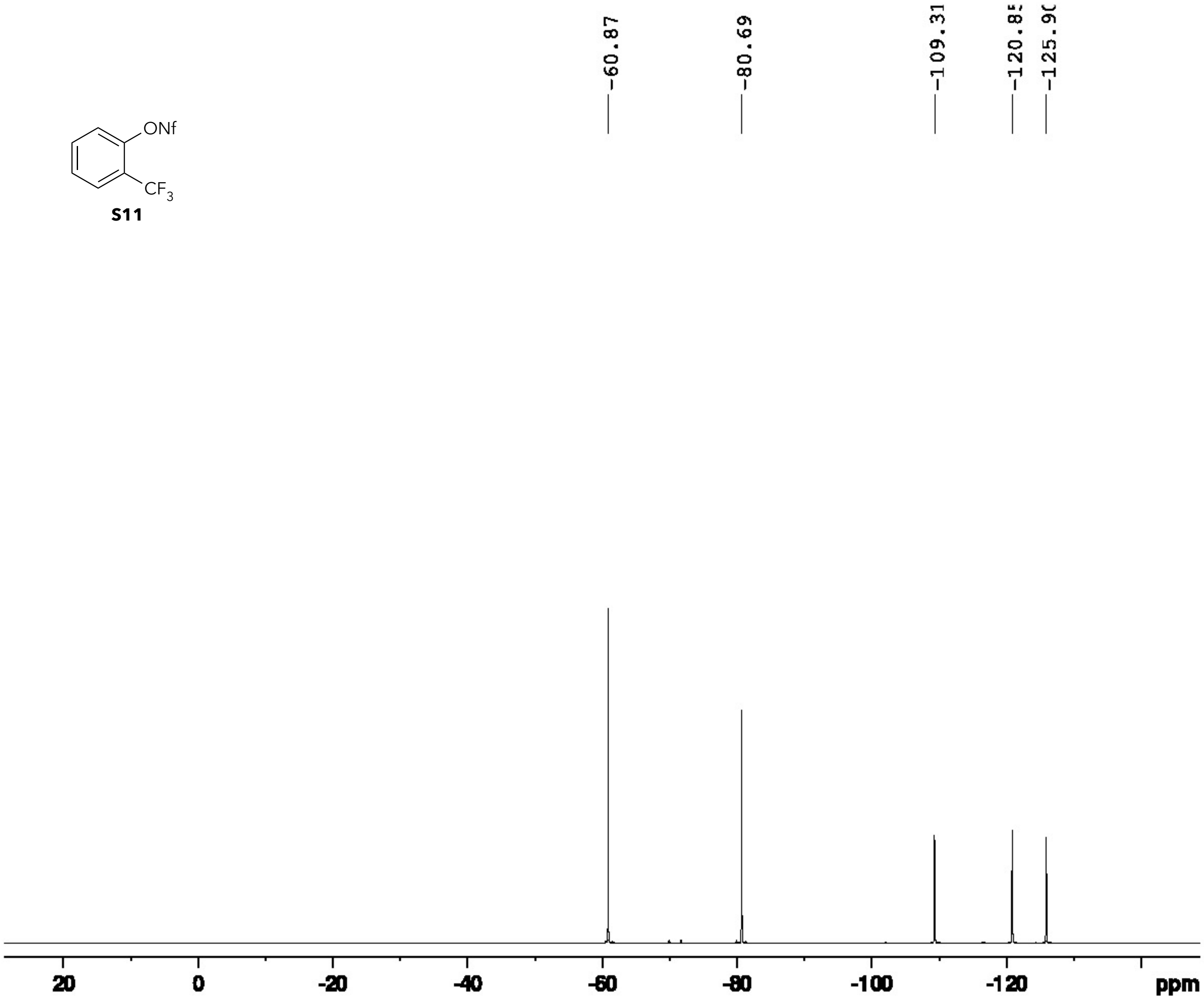
```
Current Data Parameters
NAME      ER-6-CF3PhONf
EXPNO                10
PROCNO                1

F2 - Acquisition Parameter
Date_          20200709
Time              15.43 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         600.1300162 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

S11

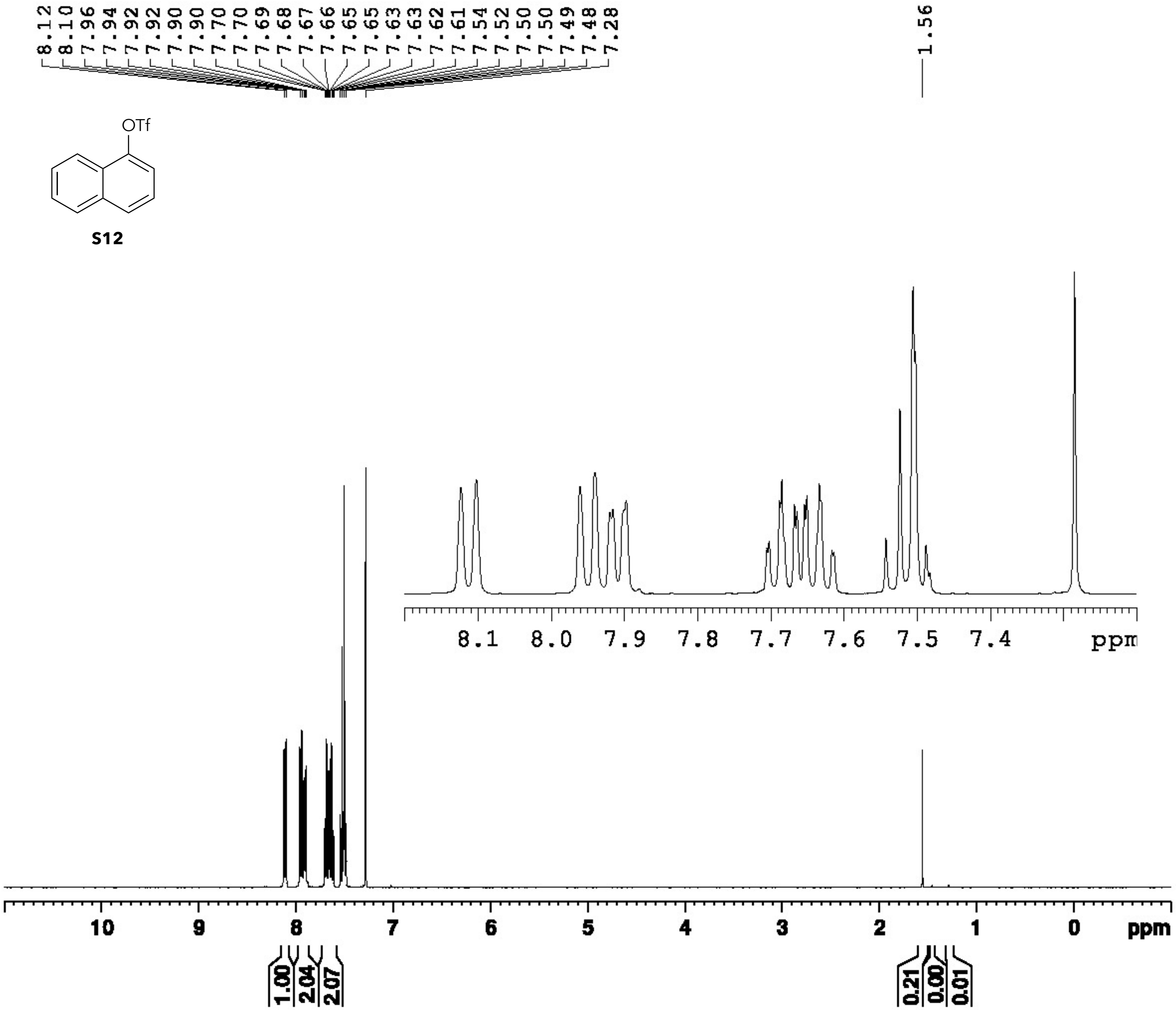


```
Current Data Parameters
NAME       ER-6-CF3PhONf
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameter
Date_           20200709
Time             16.35 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          150.9027731 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                  1.40
```

S11



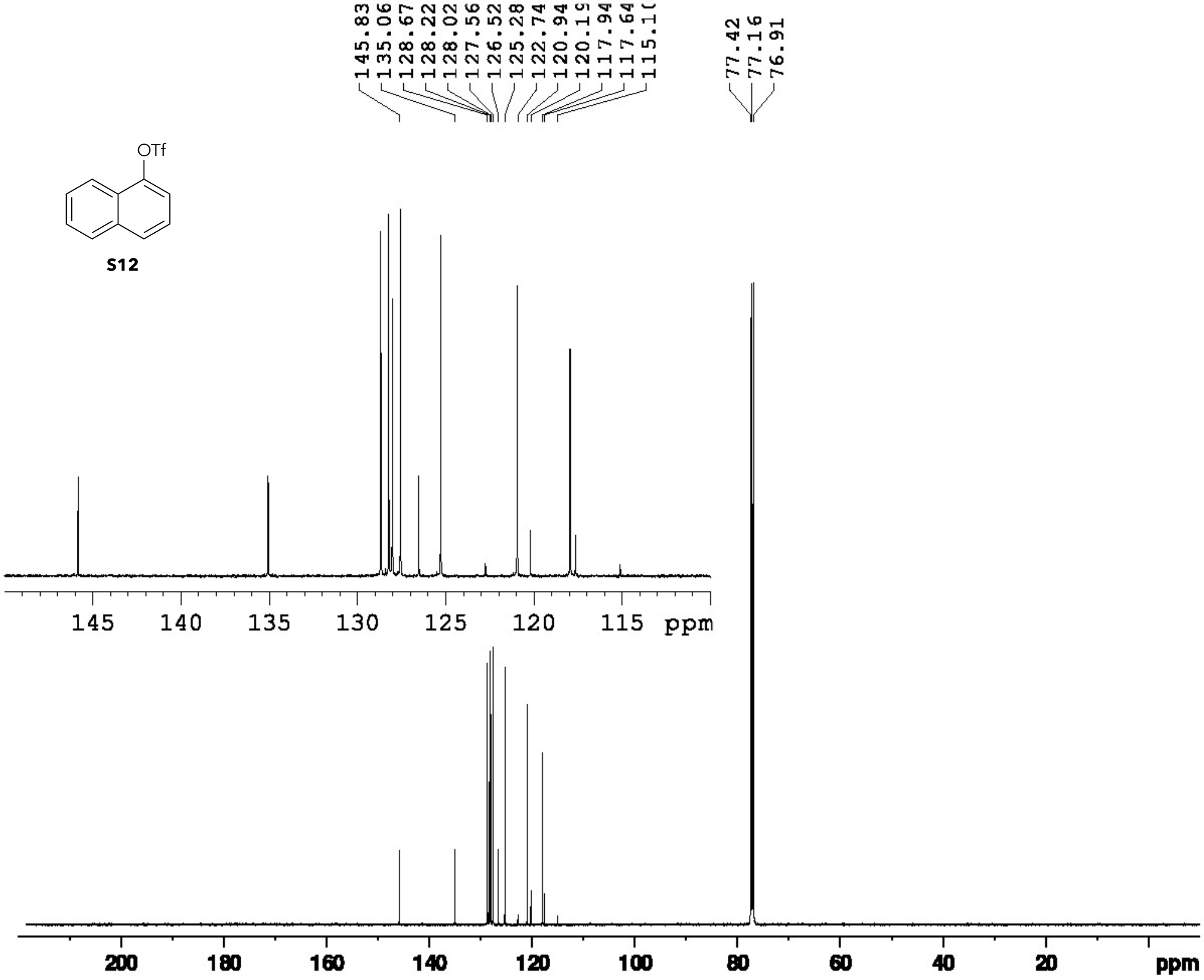
```
Current Data Parameters
NAME      ER-6-CF3PhONf
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameter
Date_          20201005
Time               7.13
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgflqn
TD                32768
SOLVENT            C6D6
NS                   64
DS                    0
SWH          50125.312 Hz
FIDRES        1.529703 Hz
AQ           0.3268608 sec
RG                645.1
DW                9.975 usec
DE                 6.00 usec
TE                683.2 K
D1           1.50000000 sec
TD0                   1

======= CHANNEL f1 =======
NUC1                19F
P1                 9.00 usec
PL1       0 dB
SFO1        282.4250465 MHz

F2 - Processing parameters
SI                65536
SF          282.4419930 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



S12

```
Current Data Parameters
NAME             EKB-1-184
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameter
Date_            20210702
Time              12.05 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         400.1300000 MHz
WDW                    EM
SSB      0
LB                0.30 Hz
GB       0
PC                   1.00
```

S12



Current Data Parameters

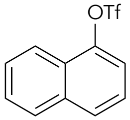
NAME	EKB-1-184
EXPNO	22
PROCNO	1

F2 - Acquisition Parameter

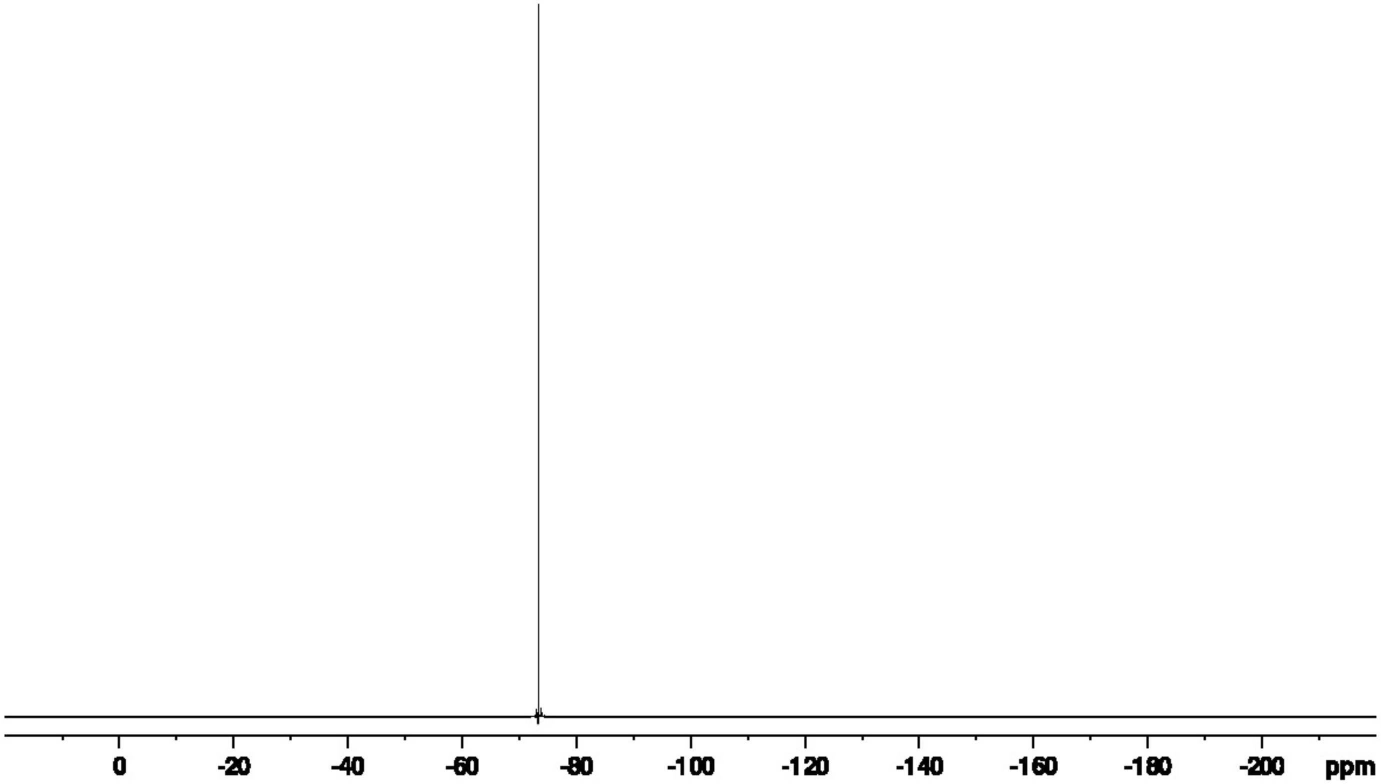
Date_	20211007
Time	12.53 h
INSTRUM	spect
PROBHD	Z125869_0055 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	29761.904 Hz
FIDRES	0.908261 Hz
AQ	1.1010048 sec
RG	190.44
DW	16.800 usec
DE	18.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.7955118 MHz
NUC1	13C
P0	3.33 usec
P1	10.00 usec
PLW1	56.90299988 W
SFO2	500.2320009 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 use
PLW2	11.44699955 W
PLW12	0.25756001 W
PLW13	0.12955000 W

F2 - Processing parameters

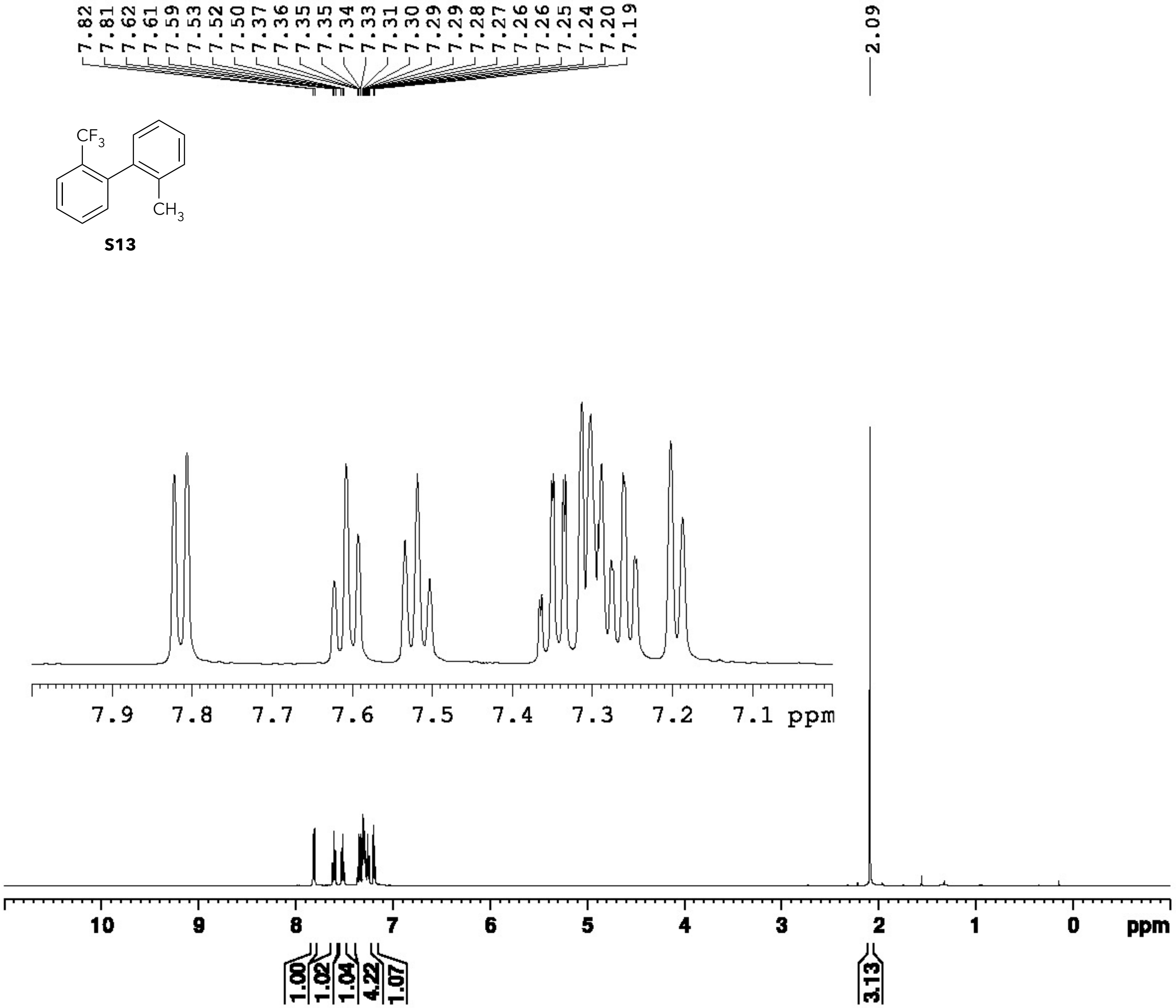
SI	32768
SF	125.7829156 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



S12



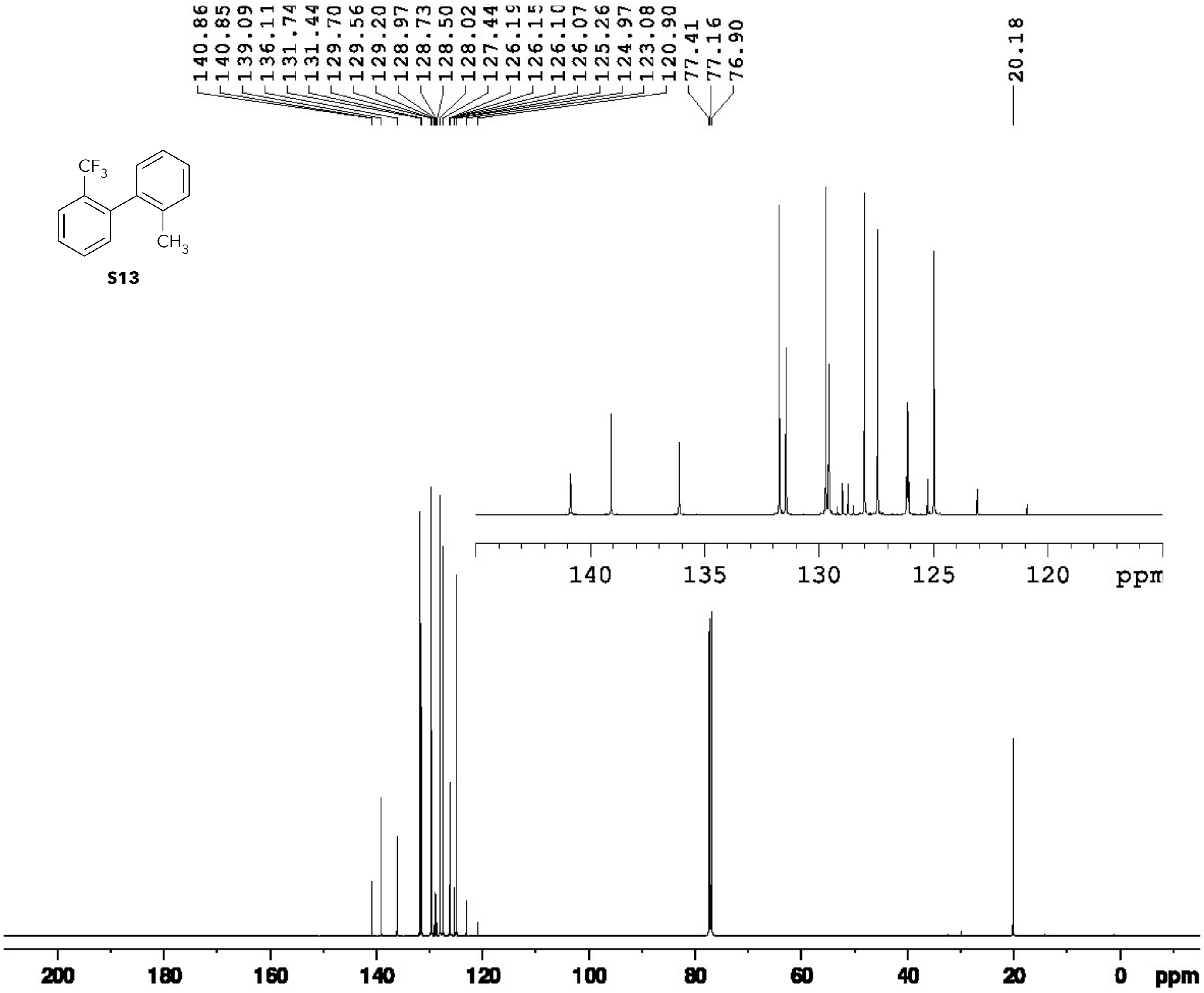
```
Current Data Parameters
NAME            EKB-1-184
EXPNO                  11
PROCNO                  2

F2 - Acquisition Parameter
Date_            20210702
Time              12.13 h
INSTRUM         Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zgig
TD                130892
SOLVENT            CDCl3
NS                    16
DS                     4
SWH          90909.094 Hz
FIDRES        1.389070 Hz
AQ           0.7199060 sec
RG                   101
DW              5.500 usec
DE               6.50 usec
TE               298.1 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                    1
SFO1       376.4607164 MHz
NUC1                 19F
P1              12.00 usec
PLW1       31.08900070 W
SFO2       400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2           90.00 usec
PLW2       24.03499985 W
PLW12       0.18990999 W

F2 - Processing parameters
SI                 65536
SF           376.4983662 MHz
WDW                   EM
SSB      0
LB                0.30 Hz
GB       0
PC                  1.00
```



Current Data Parameters
NAME 6-SMR-4
EXPNO 30
PROCNO 1

F2 - Acquisition Parameter
Date_ 20211008
Time 15.37 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 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 500.2299955 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



S13

Current Data Parameters

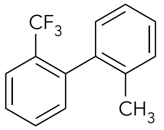
NAME	6-SMR-4
EXPNO	32
PROCNO	1

F2 - Acquisition Parameter

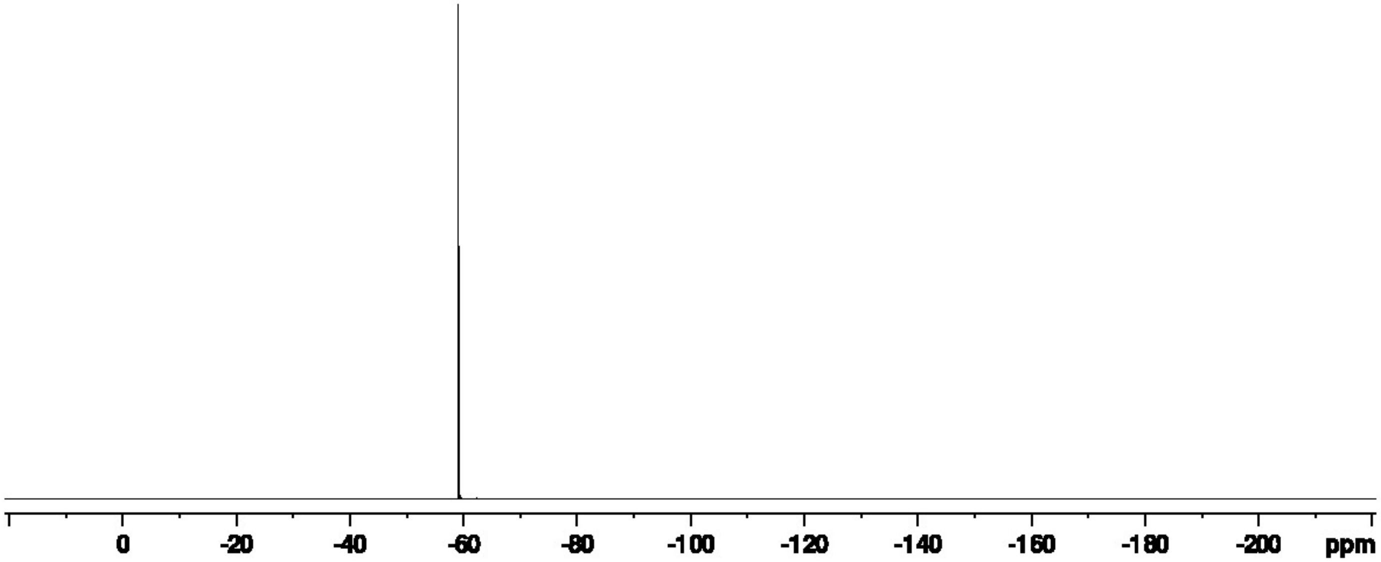
Date_	20211008
Time	17.31 h
INSTRUM	spect
PROBHD	Z125869_0055 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2048
DS	4
SWH	29761.904 Hz
FIDRES	0.908261 Hz
AQ	1.1010048 sec
RG	190.44
DW	16.800 usec
DE	18.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.7955118 MHz
NUC1	13C
P0	3.33 usec
P1	10.00 usec
PLW1	56.90299988 W
SFO2	500.2320009 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 use
PLW2	11.44699955 W
PLW12	0.25756001 W
PLW13	0.12955000 W

F2 - Processing parameters

SI	32768
SF	125.7829185 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

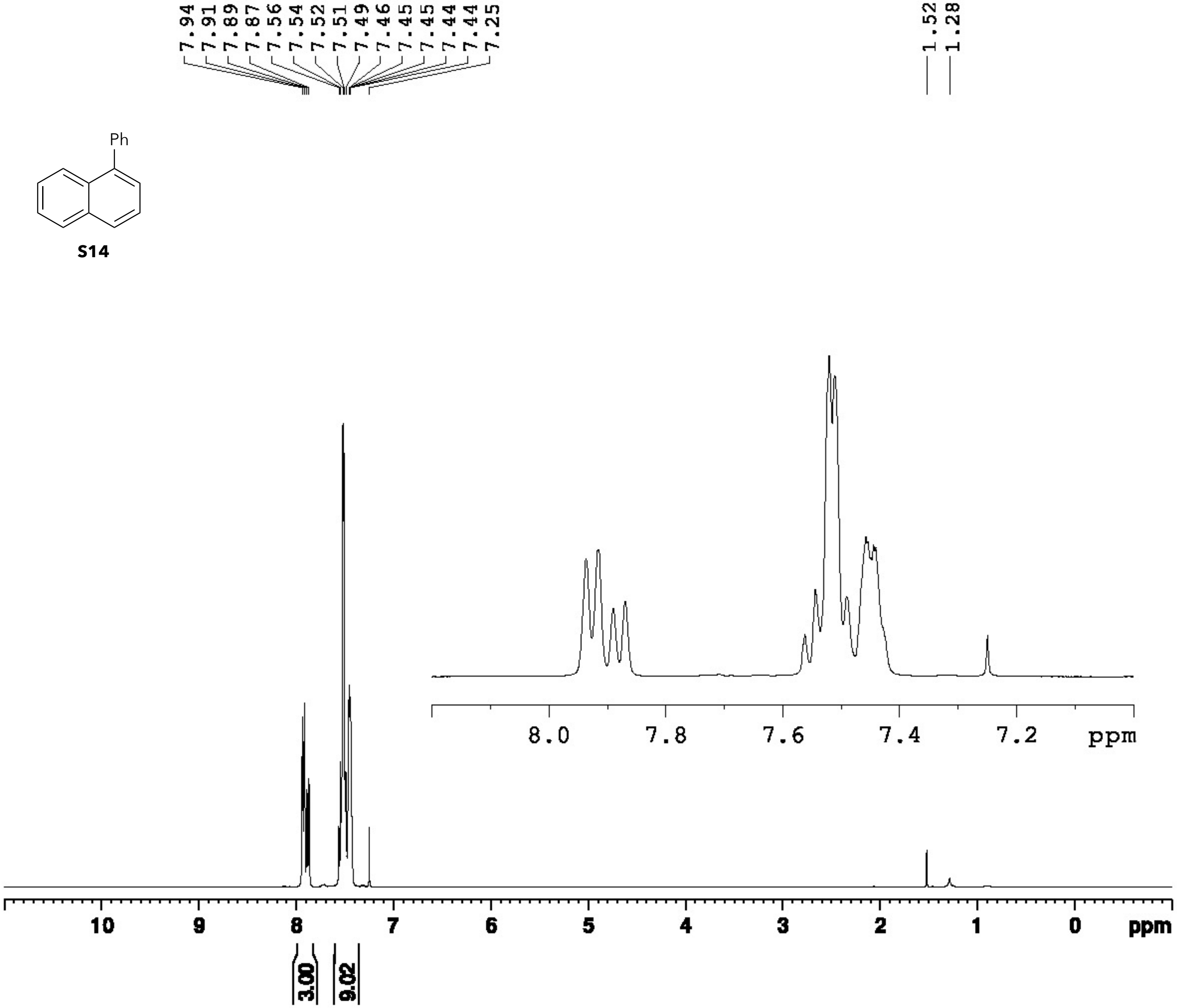


S13

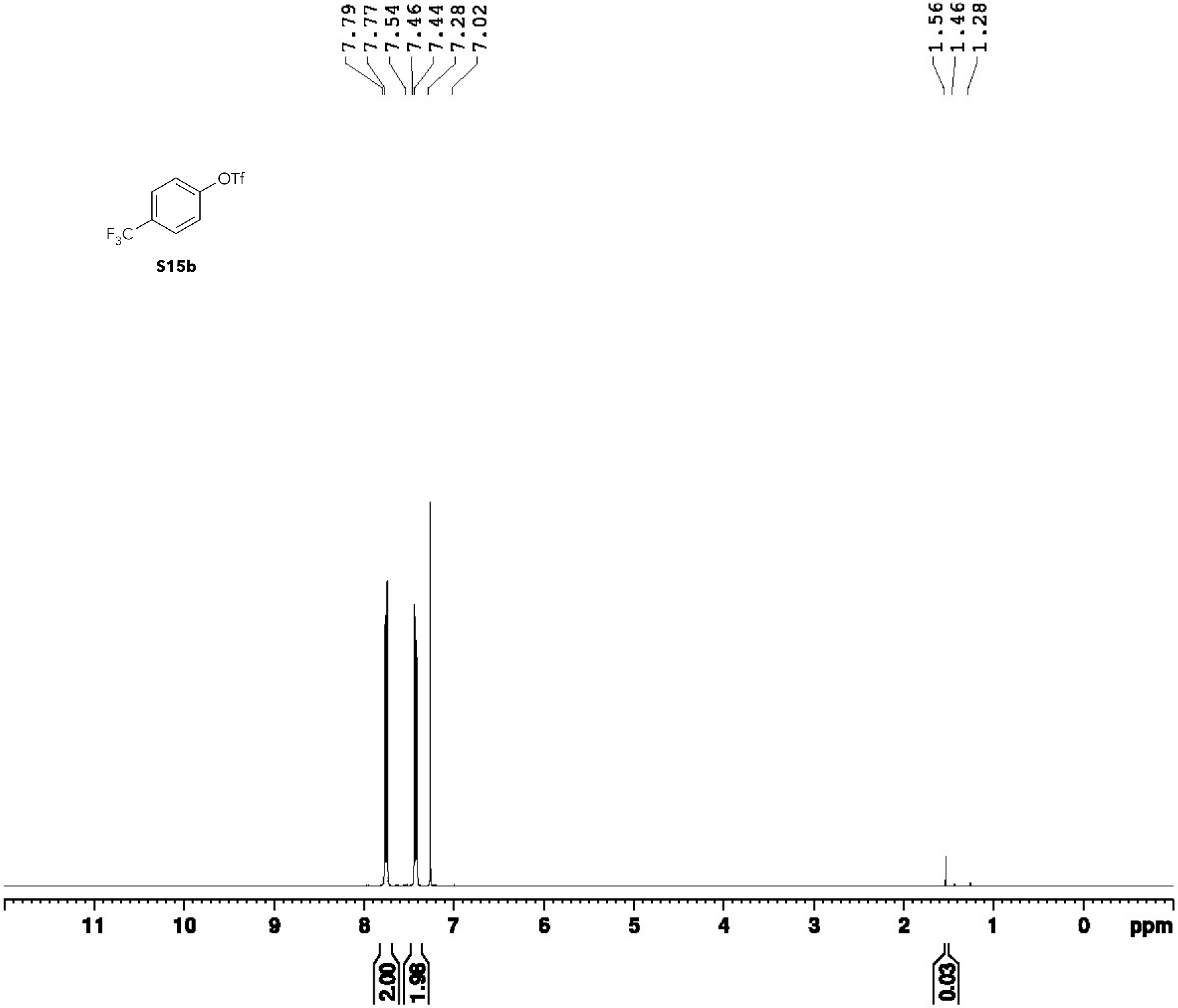


```
Current Data Parameters
NAME             6-SMR-4
EXPNO                 31
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211008
Time             15.39 h
INSTRUM            spect
PROBHD    Z125869_0055 (
PULPROG           zgflqn
TD                130892
SOLVENT            CDCl3
NS                    16
DS                     4
SWH          113636.367 Hz
FIDRES         1.736338 Hz
AQ            0.5759248 sec
RG                 17.98
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
```

S14

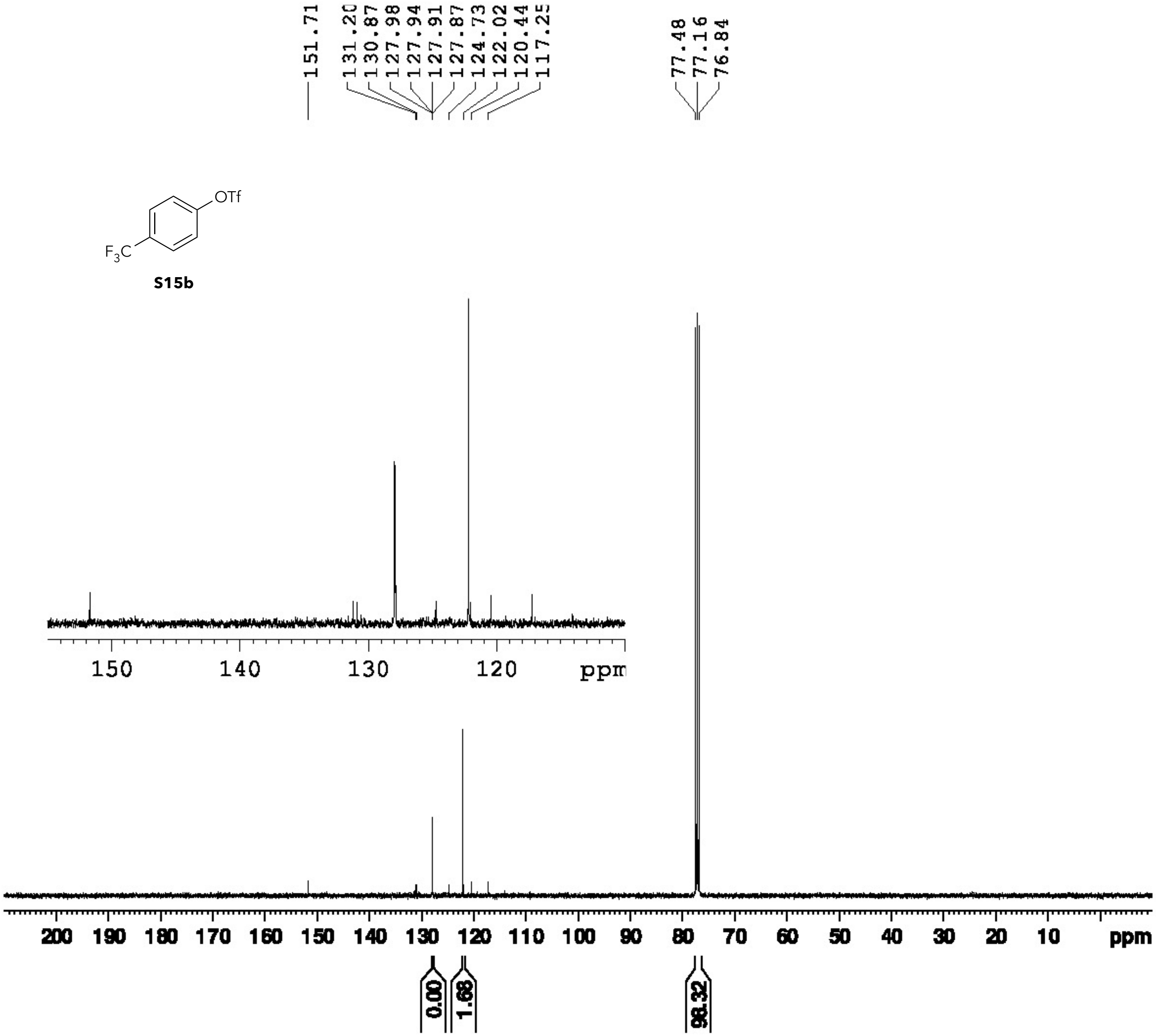


```
Current Data Parameters
NAME              5-SMR-153
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameter
Date_              20210802
Time                12.33 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                  298.2 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
SI                    65536
SF           400.1300138 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.00
```



S15b

```
Current Data Parameters
NAME              6-SMR-25
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameter
Date_             20211105
Time               20.28 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           400.1300097 MHz
WDW                     EM
SSB       0
LB                 0.30 Hz
GB        0
PC                    1.00
```



S15b

Current Data Parameters

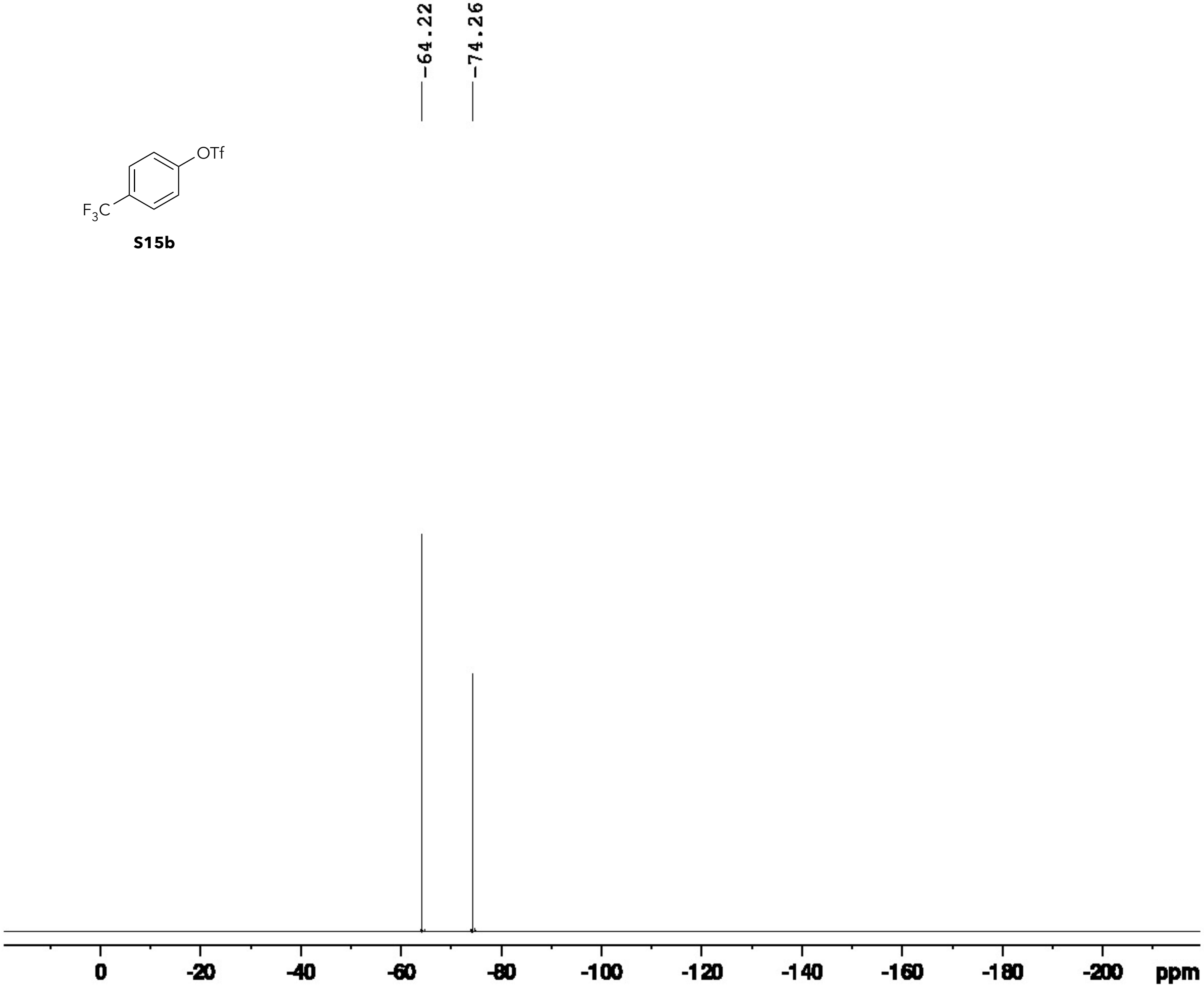
NAME	6-SMR-25
EXPNO	11
PROCNO	1

F2 - Acquisition Parameter

Date_	20211105
Time	21.29 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	100.6127535 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

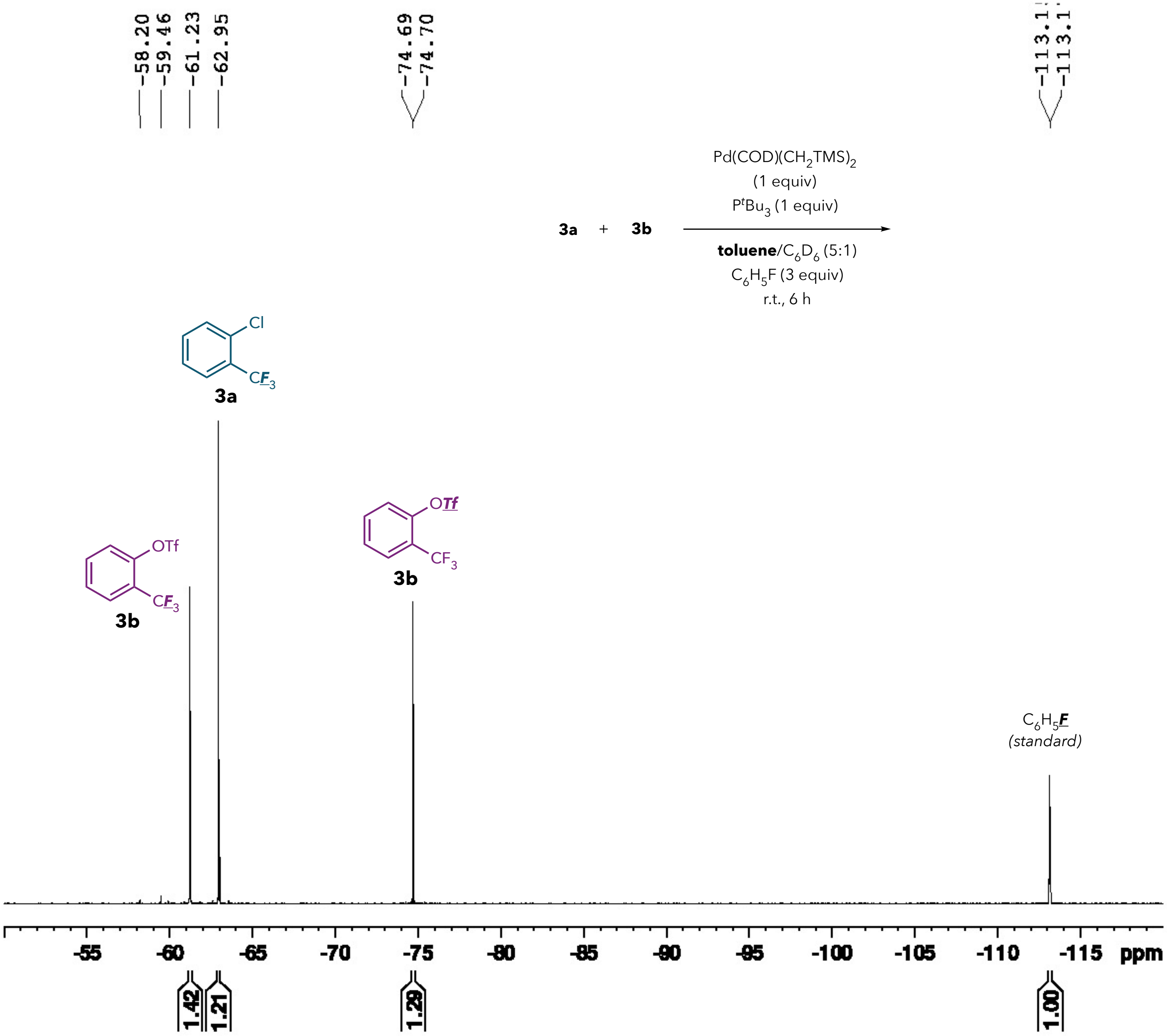


S15b

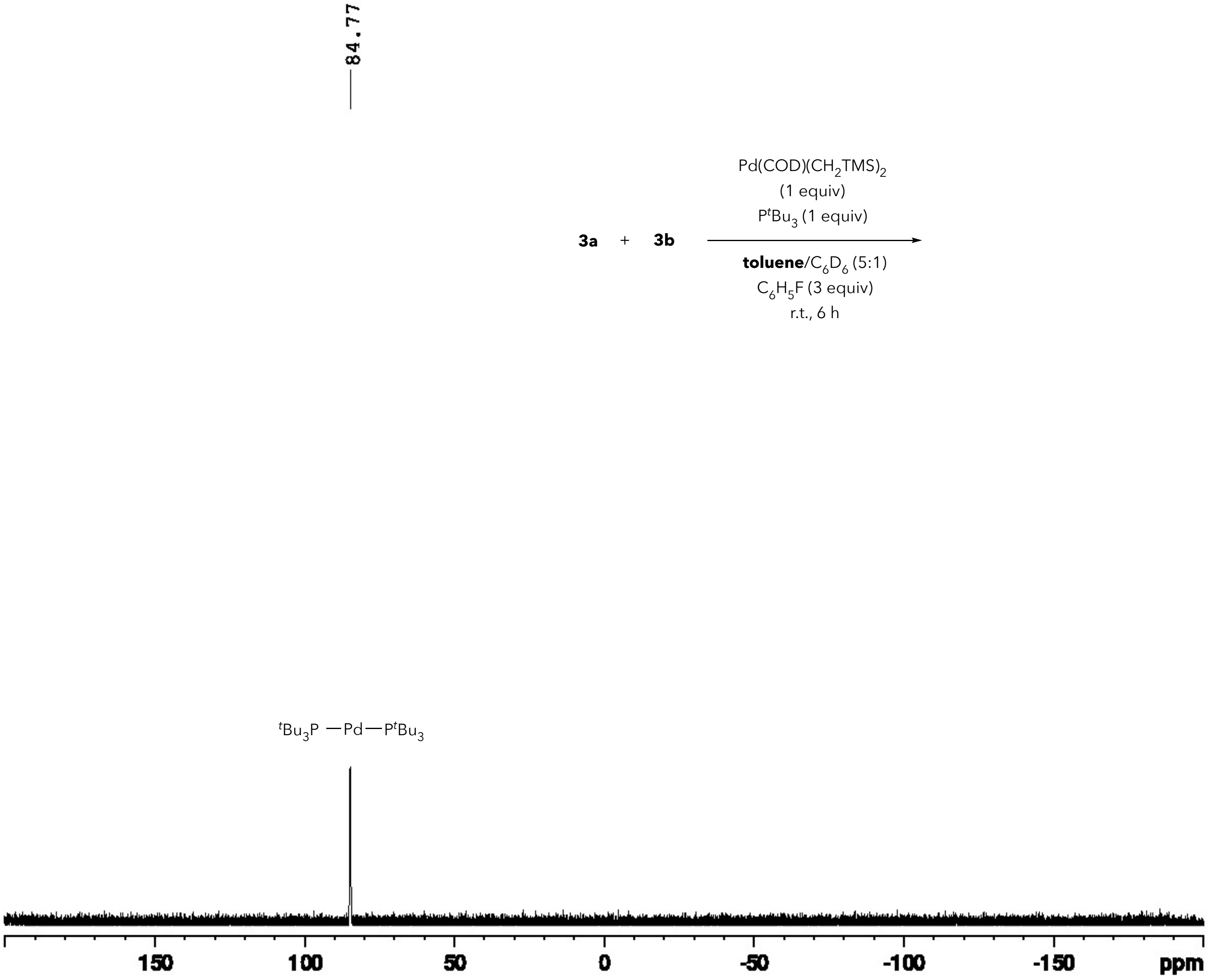
```
Current Data Parameters
NAME              6-SMR-25
EXPNO                   12
PROCNO                   1

F2 - Acquisition Parameter
Date_             20211105
Time               21.32 h
INSTRUM          Avance Neo
PROBHD    Z152088_0031 (
PULPROG                 zg
TD                  131072
SOLVENT              CDCl3
NS                      16
DS                       4
SWH            90909.094 Hz
FIDRES          1.387163 Hz
AQ             0.7208960 sec
RG                     101
DW                5.500 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                      1
SFO1         376.4607164 MHz
NUC1                   19F
P1                12.00 usec
PLW1         31.08900070 W

F2 - Processing parameters
SI                   65536
SF           376.4989587 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```

B. Stoichiometric Oxidative Addition Studies with 3a and 3b

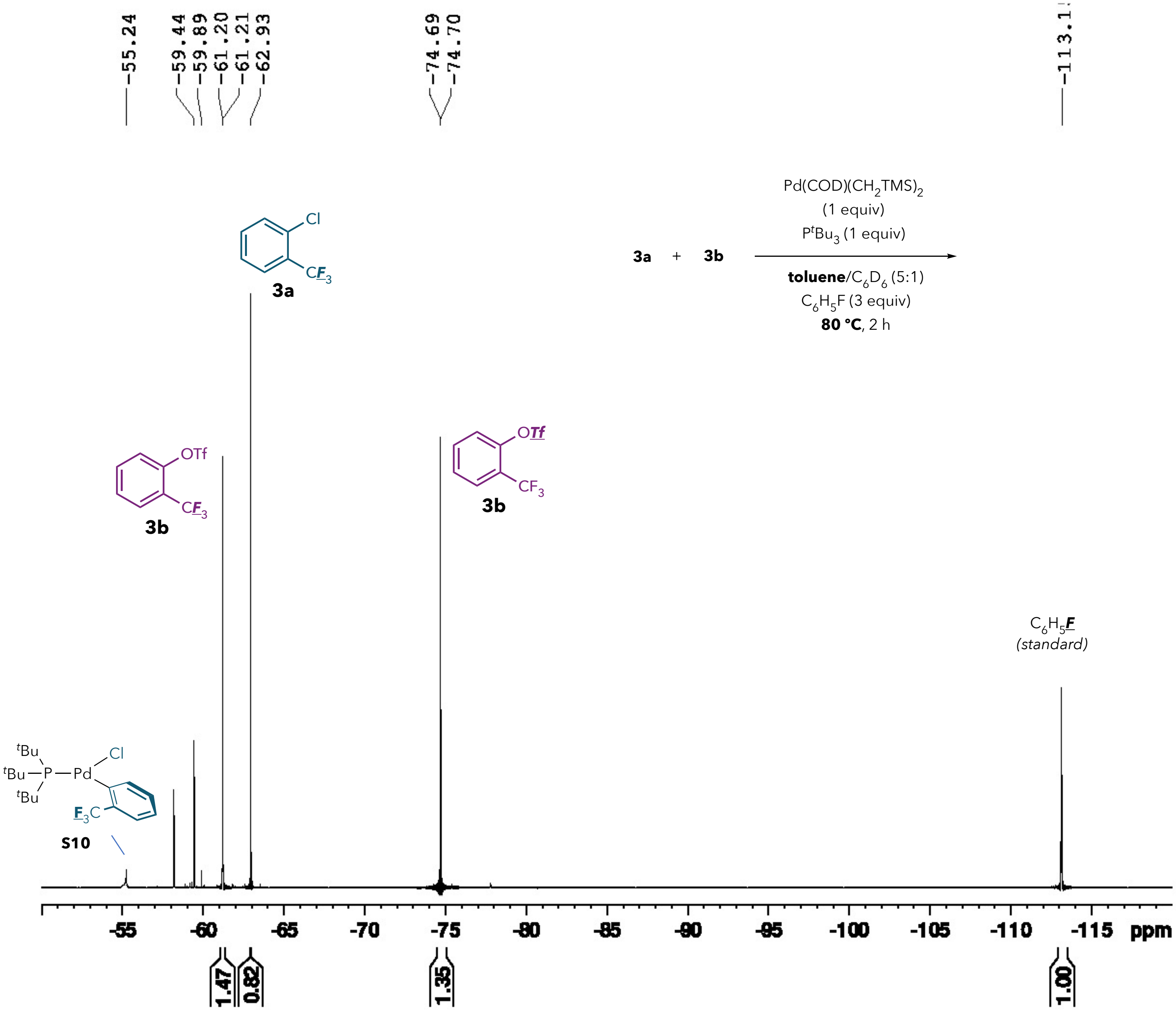
1. Experiments from Table 3 and with Deuterated Solvents



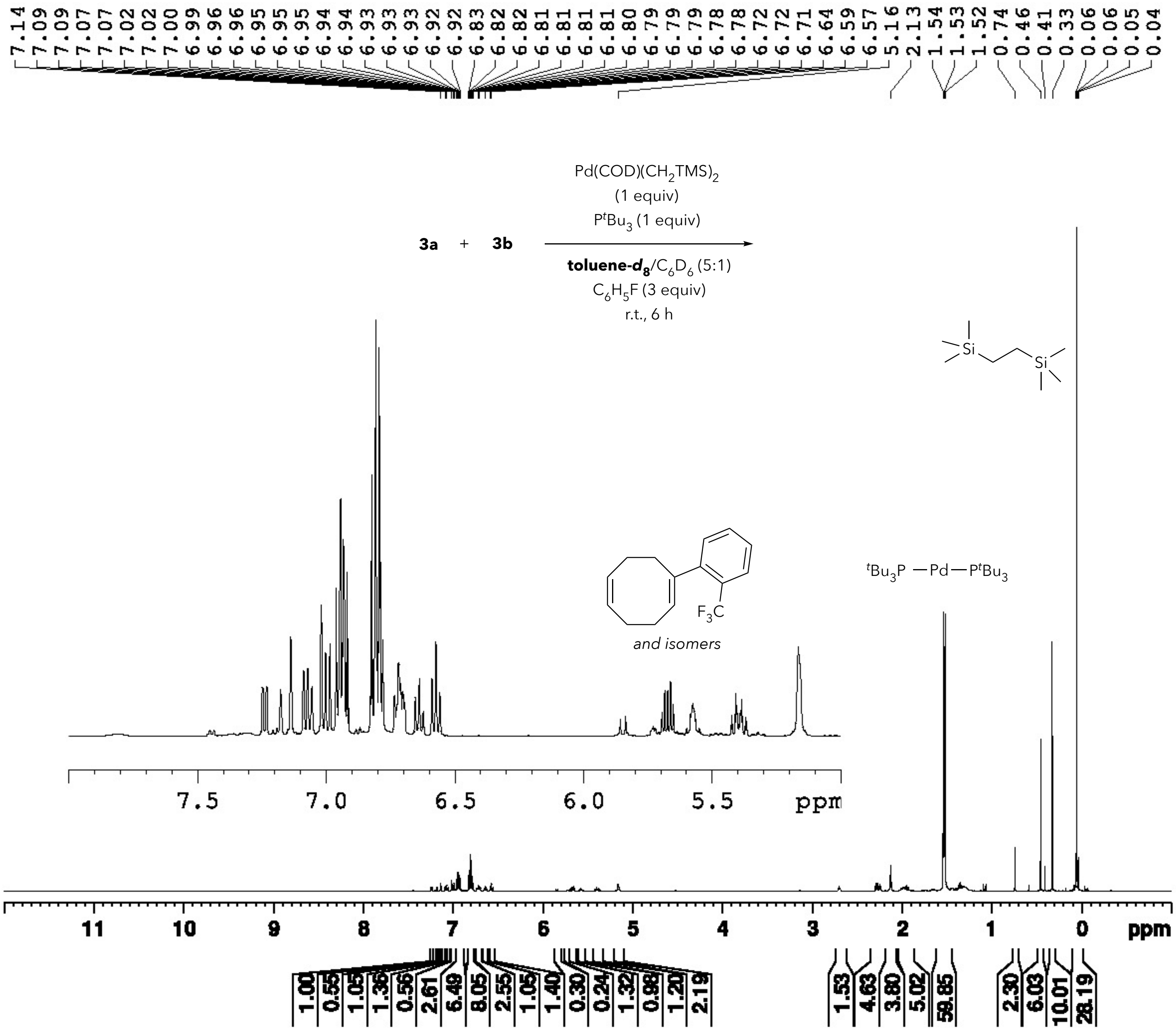
```
Current Data Parameters
NAME         ER-6-52-1_tol
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameter
Date_             20200618
Time                 15.39
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgflqn
TD                   32768
SOLVENT               C6D6
NS                      64
DS                       0
SWH           50125.312 Hz
FIDRES         1.529703 Hz
AQ           0.3268608 sec
RG                  1290.2
DW               9.975 usec
DE                6.00 usec
TE                 683.2 K
D1          1.50000000 sec
TD0                      1

====== CHANNEL f1 ======
NUC1                   19F
P1                9.00 usec
PL1        0 dB
SFO1        282.4250465 MHz

F2 - Processing parameters
SI                   65536
SF          282.4421181 MHz
WDW                     EM
SSB        0
LB                 0.30 Hz
GB         0
PC                    1.00
```



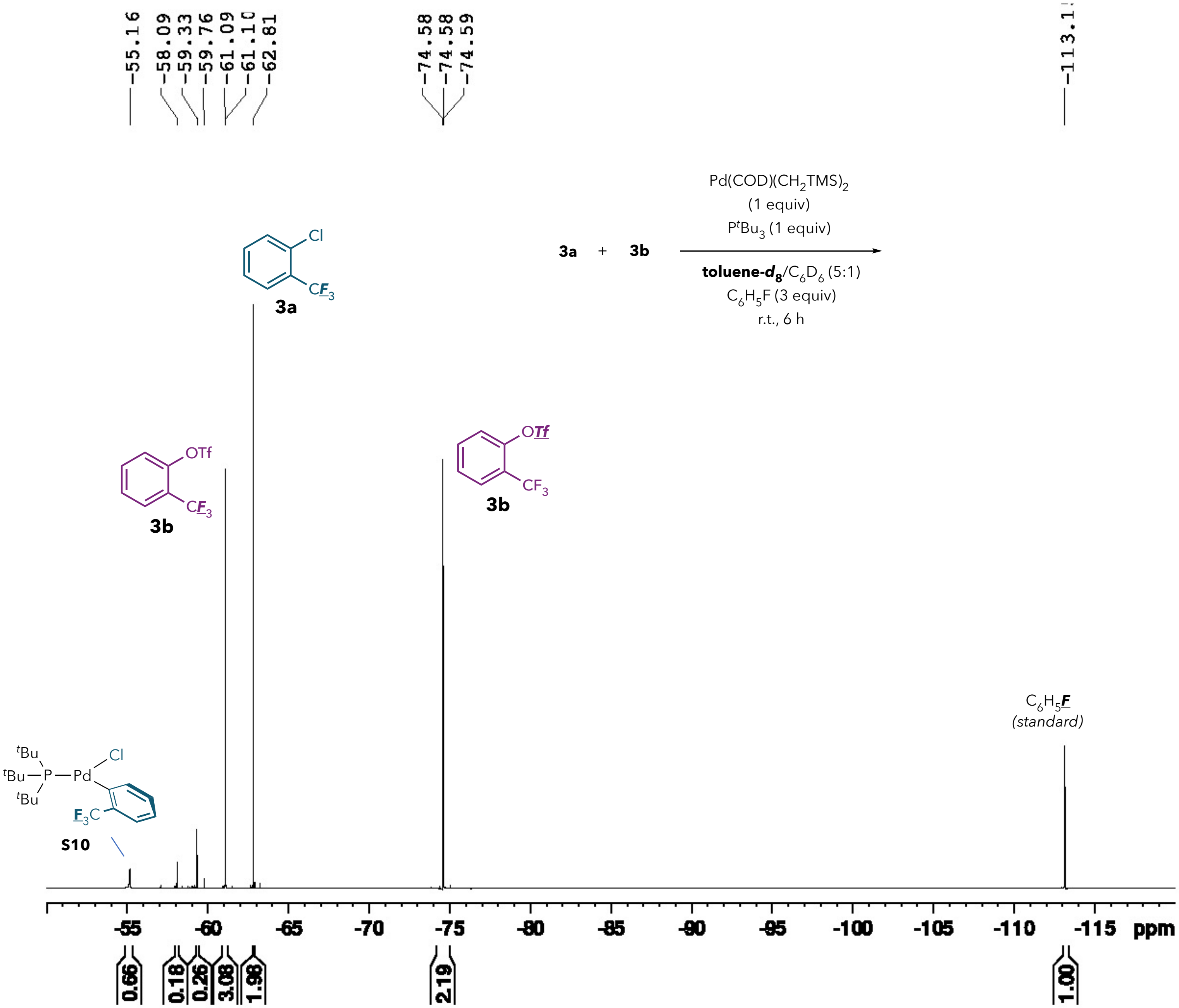
```
Current Data Parameters
NAME      ER-6-55-1_toluene
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameter
Date_             20200513
Time                  7.30
INSTRUM              spect
PROBHD    5 mm QNP 1H/13
PULPROG                 zg
TD                   32768
SOLVENT            Acetone
NS                      32
DS                       0
SWH           48661.801 Hz
FIDRES         1.485040 Hz
AQ           0.3366912 sec
RG                 14596.5
DW              10.275 usec
DE                6.00 usec
TE                 683.2 K
D1           2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   31P
P1                8.00 usec
PL1       0 dB
SFO1         121.5110430 MHz

F2 - Processing parameters
SI                   32768
SF           121.5110430 MHz
WDW                     EM
SSB       0
LB                 1.00 Hz
GB        0
PC                    1.40
```



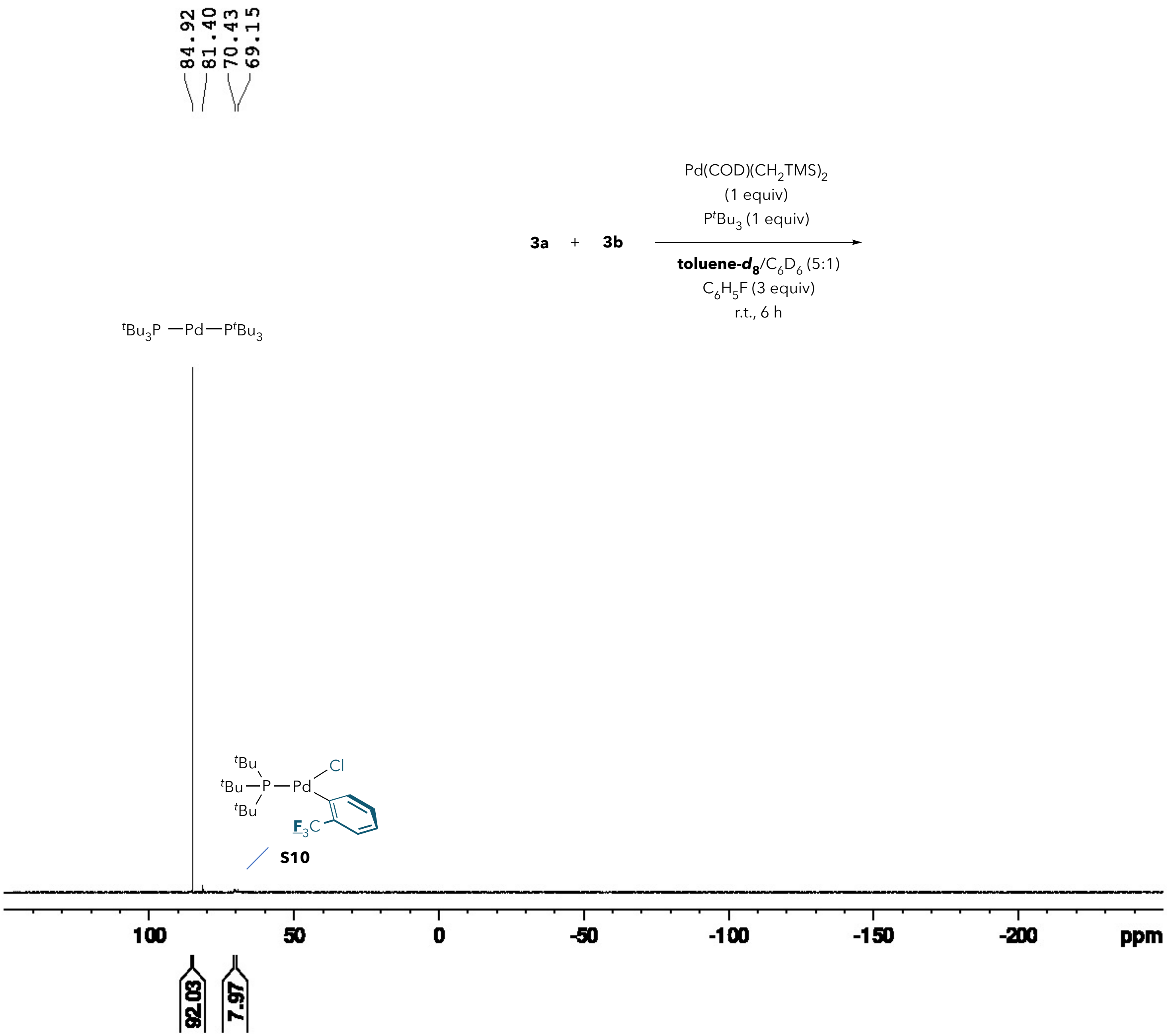
```
Current Data Parameters
NAME      ER-6-55-1_toluene_80
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20200707
Time                   7.51
INSTRUM               spect
PROBHD     5 mm QNP 1H/13
PULPROG             zgflqn
TD                    32768
SOLVENT                C6D6
NS                       64
DS                        0
SWH              50125.312 Hz
FIDRES            1.529703 Hz
AQ               0.3268608 sec
RG                   1625.5
DW                    9.975 usec
DE                     6.00 usec
TE                    683.2 K
D1               1.50000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    19F
P1                     9.00 usec
PL1         0 dB
SFO1          282.4250465 MHz

F2 - Processing parameters
SI                    65536
SF            282.4421250 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



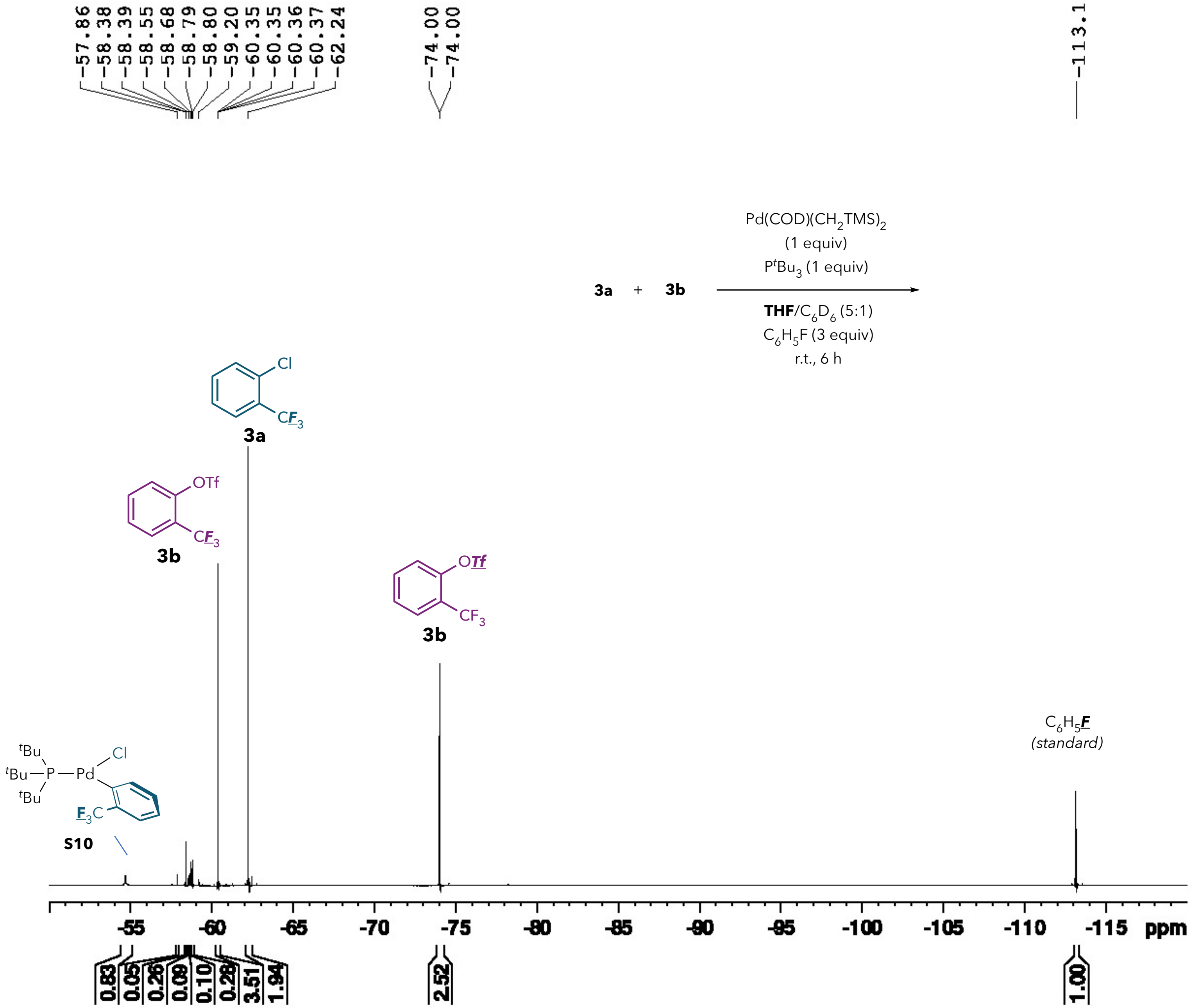
```
Current Data Parameters
NAME           6-SMR-41-3
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211116
Time              15.16 h
INSTRUM             spect
PROBHD   Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT               Tol
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         500.2300000 MHz
WDW                    EM
SSB      0
LB                0.30 Hz
GB       0
PC                   1.00
```



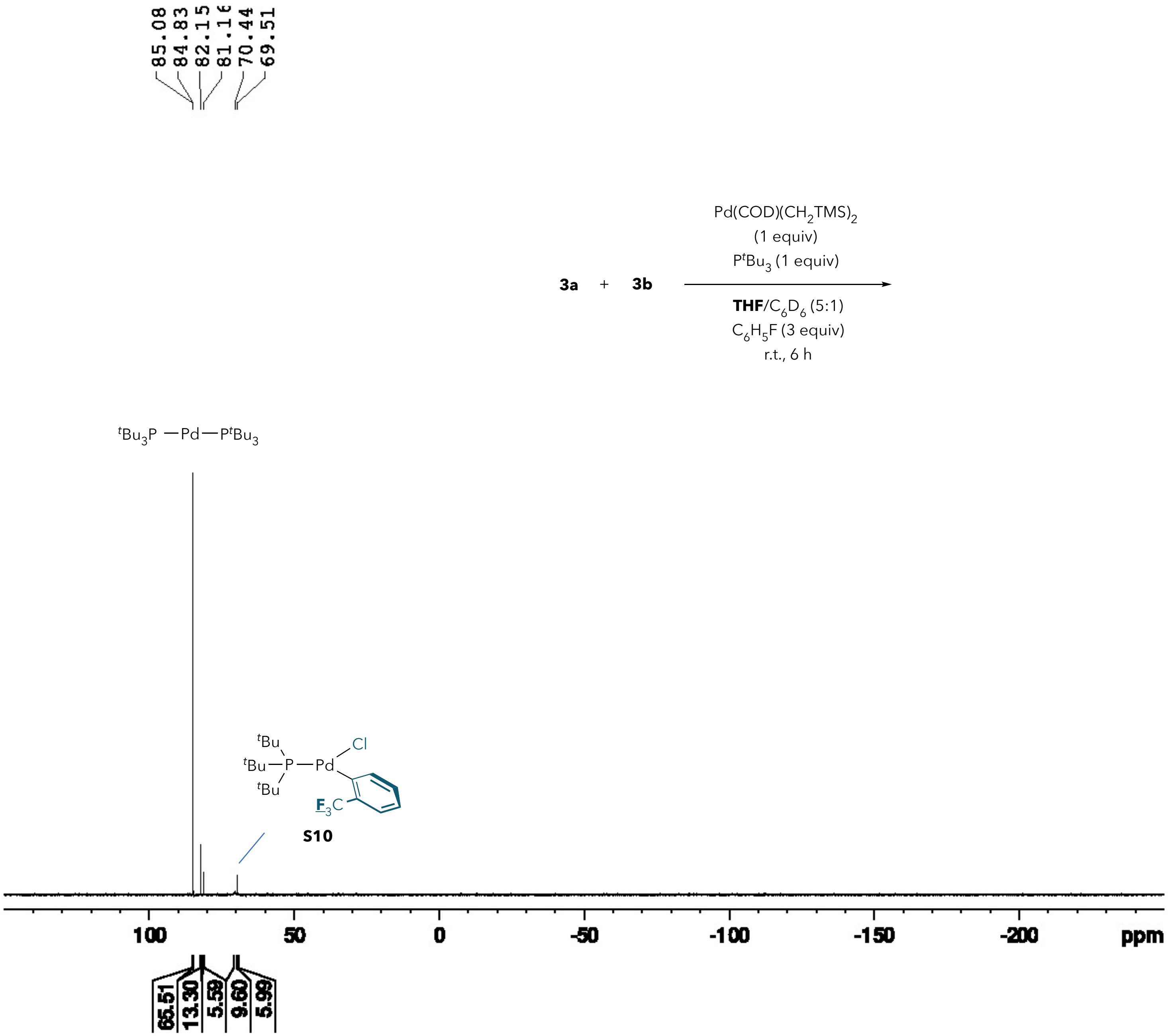
```
Current Data Parameters
NAME             6-SMR-41-3
EXPNO                    11
PROCNO                    2

F2 - Acquisition Parameter
Date_             20211116
Time                 15.18 h
INSTRUM              spect
PROBHD   Z125869_0055 (
PULPROG             zgflqn
TD                  131072
SOLVENT                Tol
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            470.6866398 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



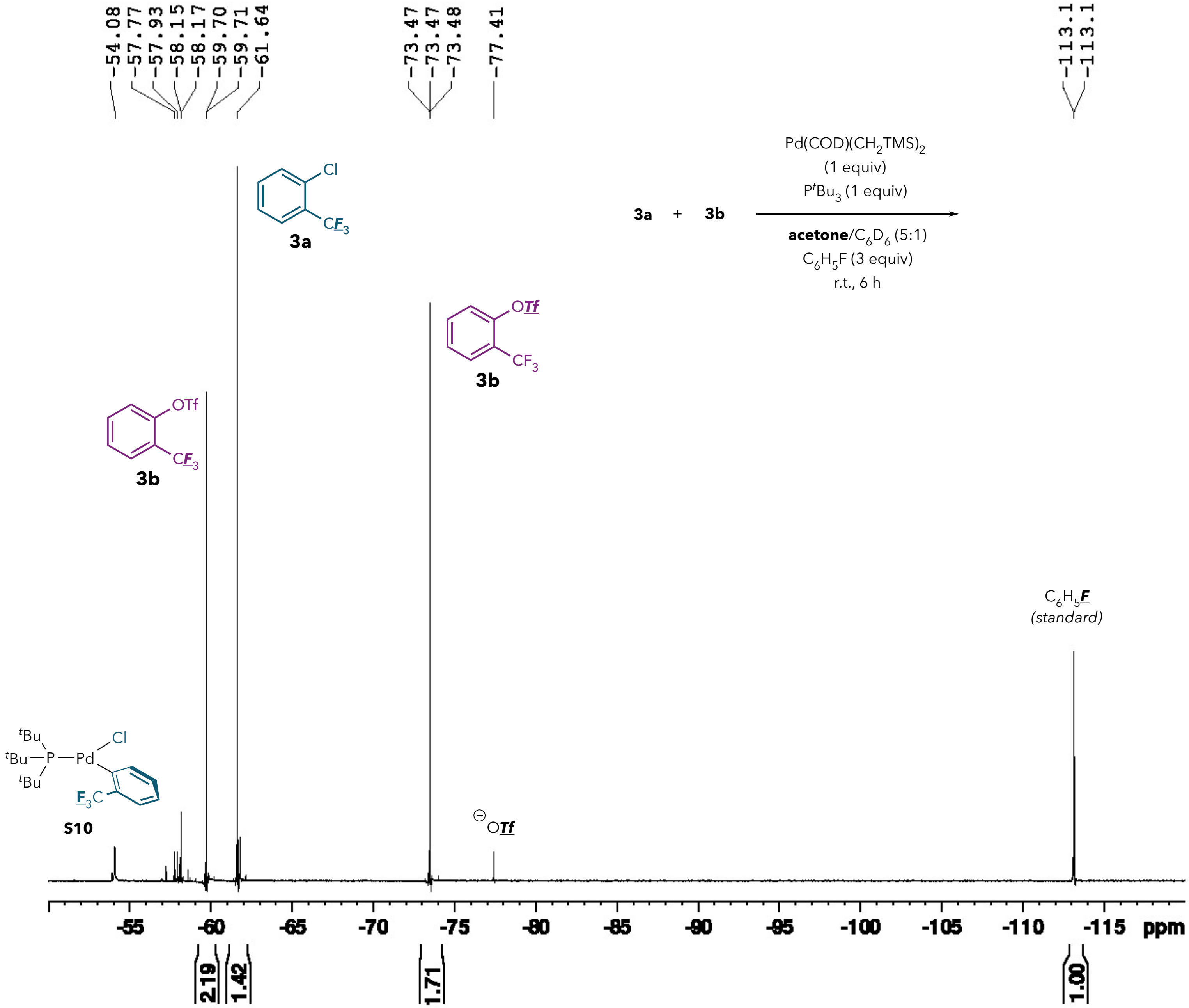
```
Current Data Parameters
NAME          6-SMR-41-3
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameter
Date_           20211116
Time               15.21 h
INSTRUM            spect
PROBHD     Z125869_0055 (
PULPROG           zgpg30
TD                 65536
SOLVENT              Tol
NS                    16
DS                     4
SWH           81521.742 Hz
FIDRES         2.487846 Hz
AQ            0.4019541 sec
RG                190.44
DW                 6.133 usec
DE                 18.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         202.4866909 MHz
NUC1                 31P
P0                  4.00 usec
P1                 12.00 usec
PLW1         40.26200104 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           202.4968157 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



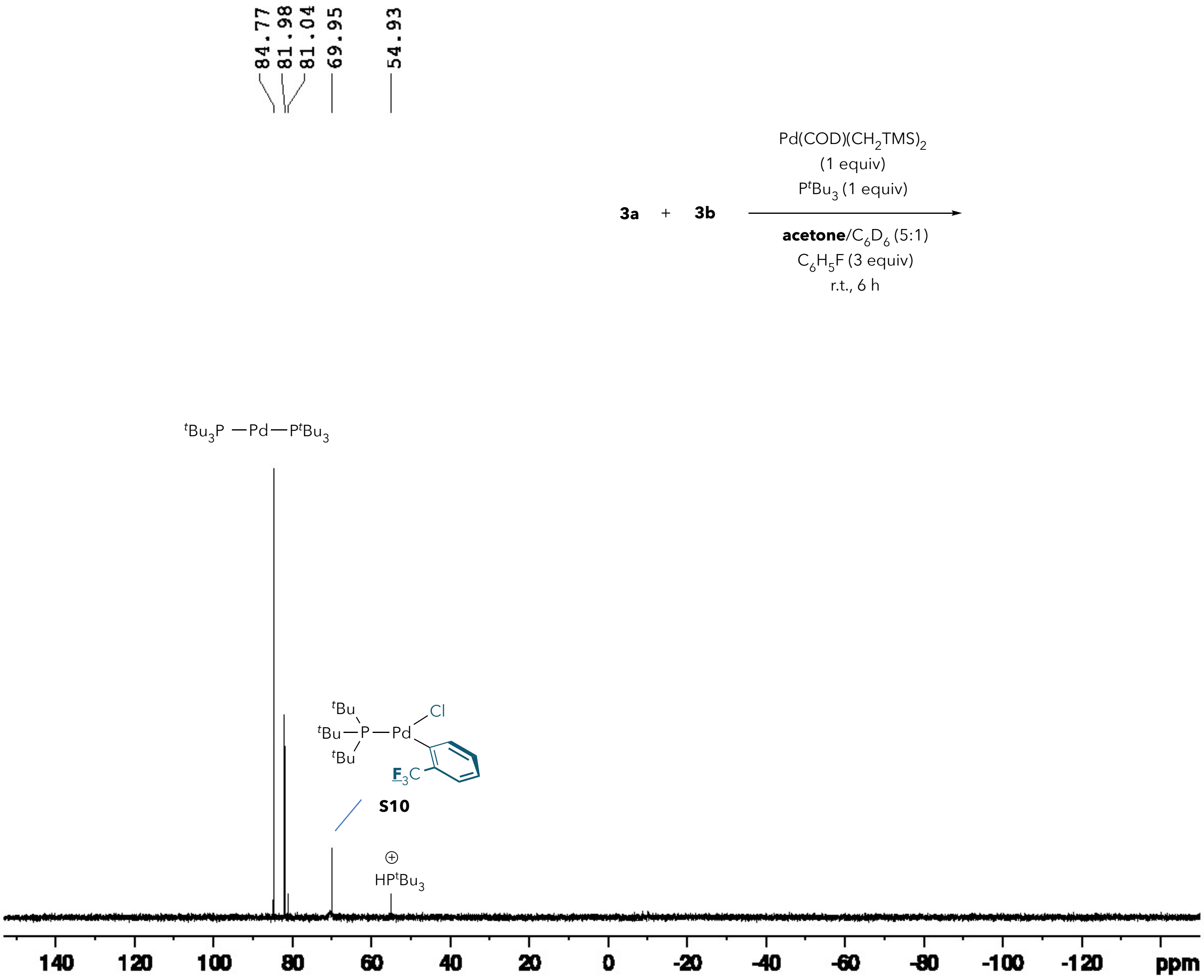
```
Current Data Parameters
NAME          6-SMR-39-3
EXPNO                 10
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211115
Time               15.47 h
INSTRUM        Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zgig
TD                131072
SOLVENT             C6D6
NS                    16
DS                     4
SWH          90909.094 Hz
FIDRES        1.387163 Hz
AQ           0.7208960 sec
RG                   101
DW                 5.500 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         376.4607164 MHz
NUC1                 19F
P1                 12.00 usec
PLW1         31.08900070 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W

F2 - Processing parameters
SI                 65536
SF           376.4979704 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



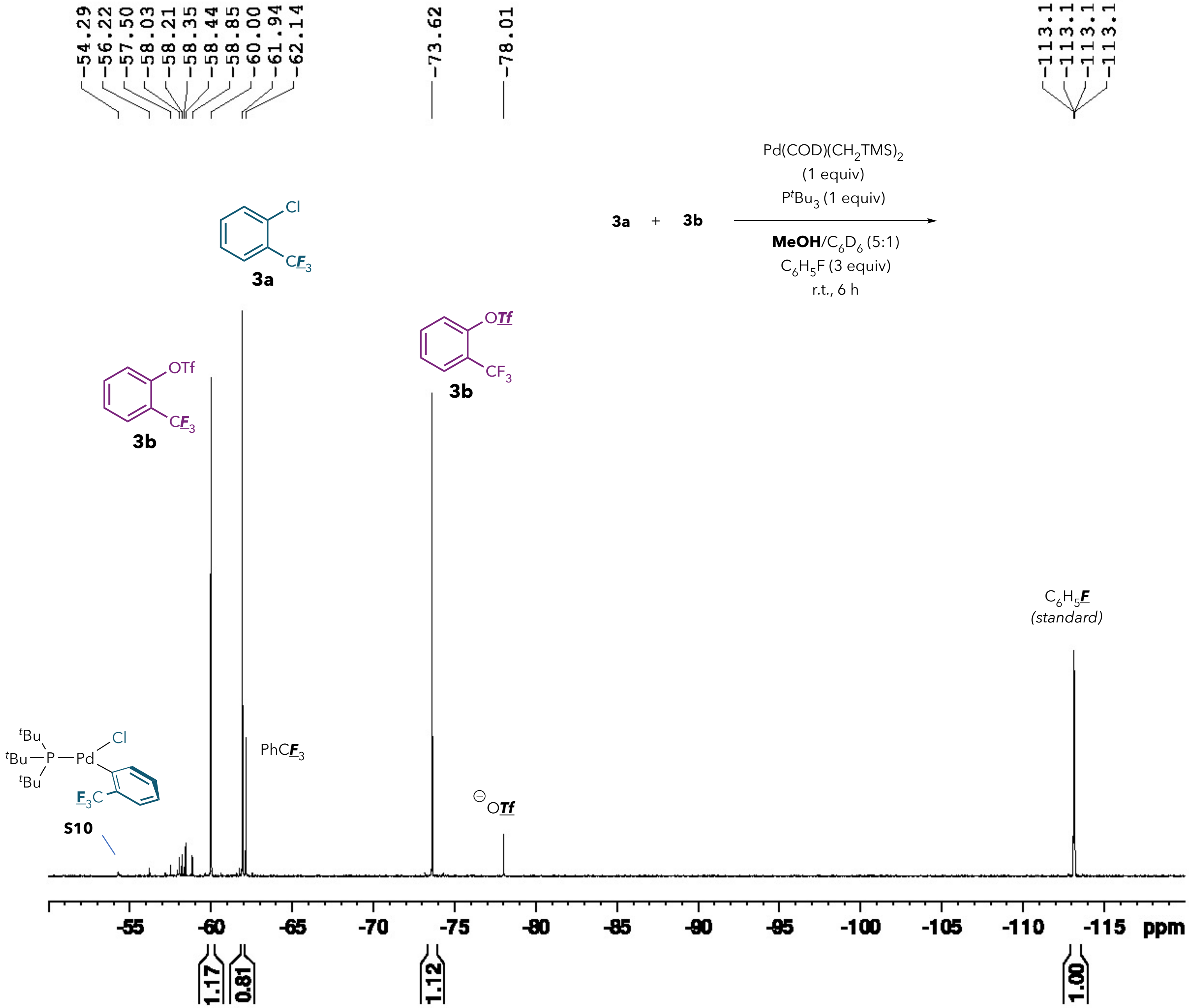
```
Current Data Parameters
NAME           6-SMR-39-3
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211115
Time              15.50 h
INSTRUM        Avance Neo
PROBHD      Z152088_0031 (
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     4
SWH          65789.477 Hz
FIDRES        2.007735 Hz
AQ           0.4980736 sec
RG                   101
DW              7.600 usec
DE               6.50 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                    1
SFO1        161.9674942 MHz
NUC1                 31P
P0               2.67 usec
P1               8.00 usec
PLW1         45.86100006 W
SFO2        400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2           90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                 32768
SF          161.9755930 MHz
WDW                   EM
SSB      0
LB               1.00 Hz
GB       0
PC                  1.40
```



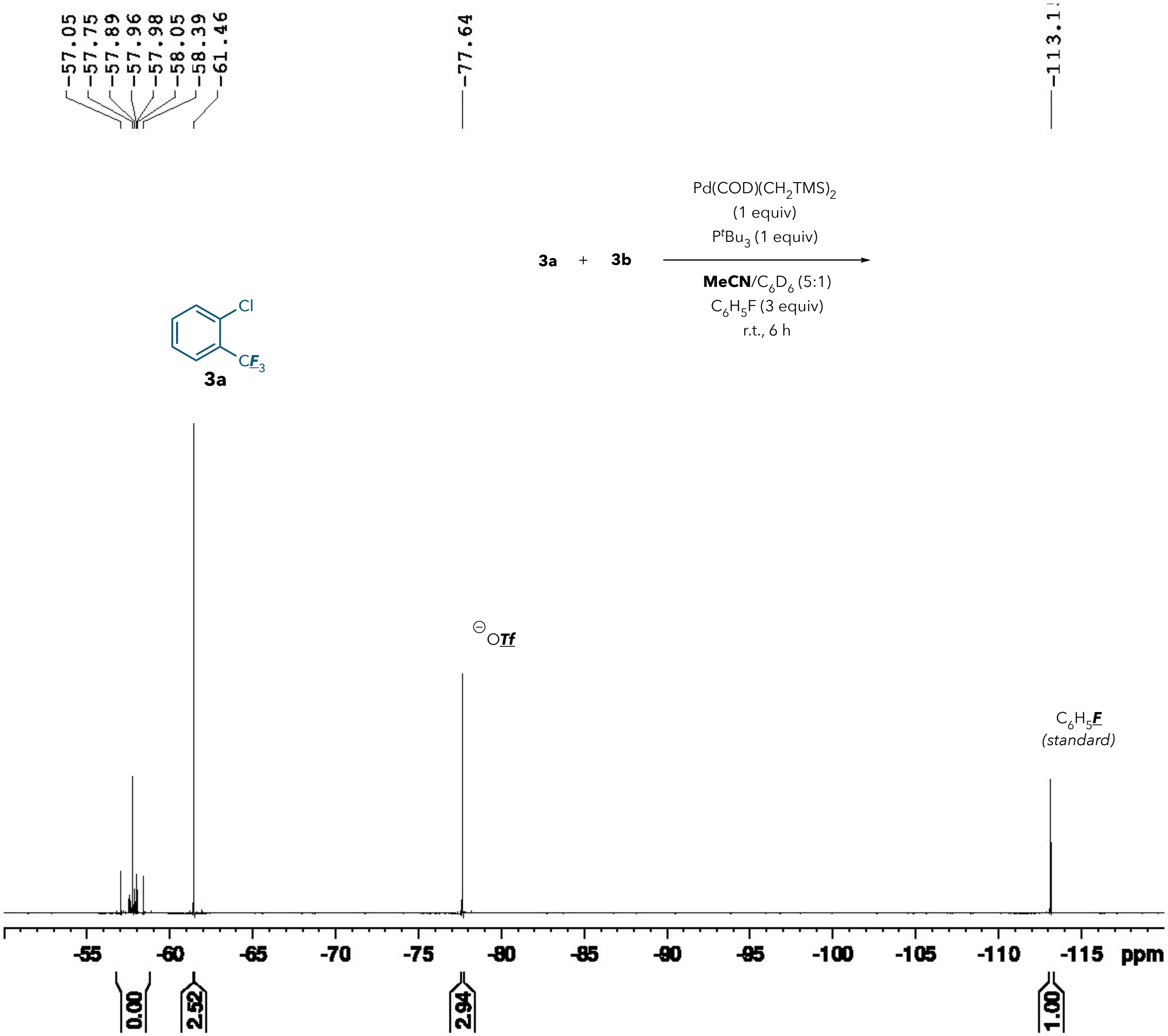
```
Current Data Parameters
NAME             6-SMR-5-7
EXPNO                   12
PROCNO                   2

F2 - Acquisition Parameter
Date_             20210911
Time               22.06 h
INSTRUM          Avance Neo
PROBHD    Z152088_0031 (
PULPROG                 zg
TD                  130892
SOLVENT               C6D6
NS                      16
DS                       4
SWH           90909.094 Hz
FIDRES         1.389070 Hz
AQ            0.7199060 sec
RG                     101
DW               5.500 usec
DE                6.50 usec
TE                 298.0 K
D1           1.00000000 sec
TD0                      1
SFO1        376.4607164 MHz
NUC1                   19F
P1               12.00 usec
PLW1        31.08900070 W

F2 - Processing parameters
SI                   65536
SF          376.4978043 MHz
WDW                     EM
SSB       0
LB                 0.30 Hz
GB        0
PC                    1.00
```



```
Current Data Parameters
NAME             6-SMR-5-7
EXPNO                   13
PROCNO                   2

F2 - Acquisition Parameter
Date_             20210911
Time               22.10 h
INSTRUM          Avance Neo
PROBHD    Z152088_0031 (
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                     32
DS                      4
SWH            65789.477 Hz
FIDRES          2.007735 Hz
AQ             0.4980736 sec
RG                    101
DW                 7.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1
SFO1         161.9674942 MHz
NUC1                  31P
P0                  2.67 usec
P1                  8.00 usec
PLW1         45.86100006 W
SFO2         400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                  32768
SF           161.9755930 MHz
WDW                    EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



```
Current Data Parameters
NAME        ER-6-52-2_MeOH_new
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameter
Date_             20200618
Time                 15.46
INSTRUM              spect
PROBHD    5 mm QNP 1H/13
PULPROG             zgflqn
TD                   32768
SOLVENT               C6D6
NS                      64
DS                       0
SWH           50125.312 Hz
FIDRES         1.529703 Hz
AQ            0.3268608 sec
RG                  2580.3
DW               9.975 usec
DE                6.00 usec
TE                 683.2 K
D1           1.50000000 sec
TD0                      1

======= CHANNEL f1 =======
NUC1                   19F
P1                9.00 usec
PL1        0 dB
SFO1        282.4250465 MHz

F2 - Processing parameters
SI                   65536
SF          282.4414859 MHz
WDW                     EM
SSB        0
LB                 0.30 Hz
GB         0
PC                    1.00
```



Current Data Parameters

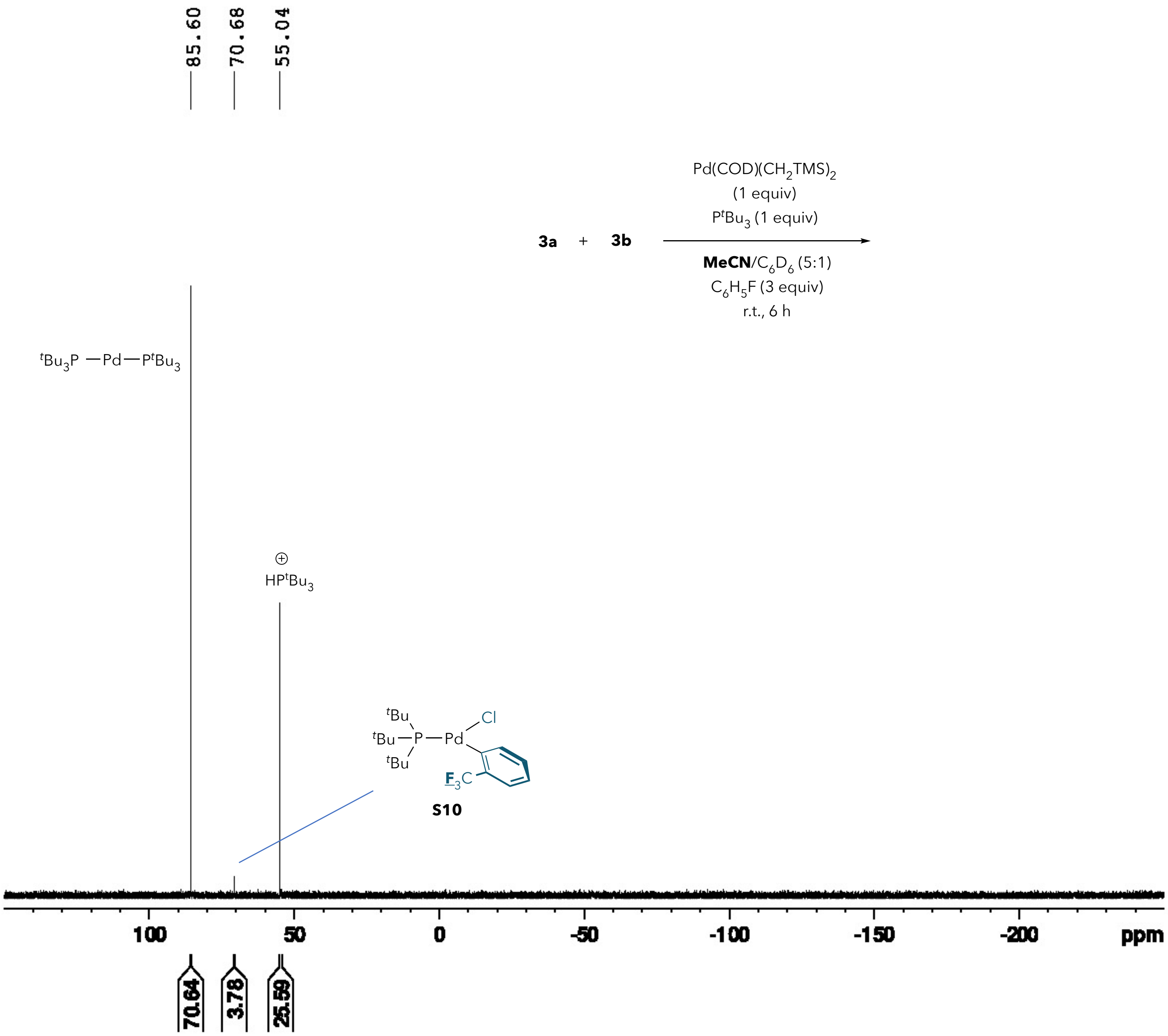
NAME	6-SMR-39-7
EXPNO	10
PROCNO	2

F2 - Acquisition Parameter

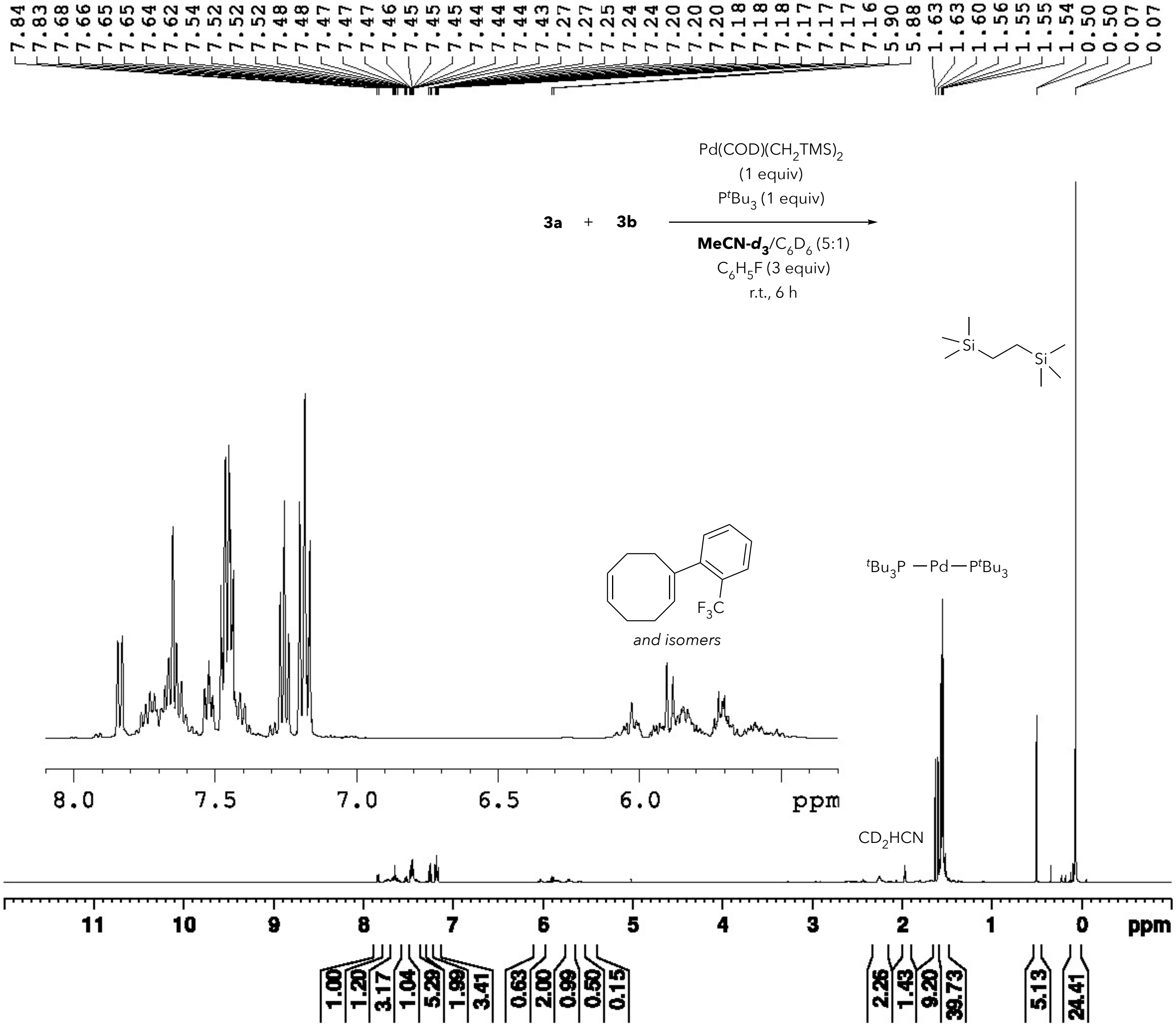
Date_	20211115
Time	16.20 h
INSTRUM	Avance Neo
PROBHD	Z152088_0031 (
PULPROG	zgig
TD	131072
SOLVENT	C6D6
NS	16
DS	4
SWH	90909.094 Hz
FIDRES	1.387163 Hz
AQ	0.7208960 sec
RG	101
DW	5.500 usec
DE	6.50 usec
TE	298.1 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	376.4607164 MHz
NUC1	19F
P1	12.00 usec
PLW1	31.08900070 W
SFO2	400.1316005 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	90.00 usec
PLW2	24.03499985 W
PLW12	0.18990999 W

F2 - Processing parameters

SI	65536
SF	376.4977327 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



```
Current Data Parameters
NAME           6-SMR-39-7
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211115
Time                16.23 h
INSTRUM         Avance Neo
PROBHD      Z152088_0031 (
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     4
SWH          65789.477 Hz
FIDRES        2.007735 Hz
AQ           0.4980736 sec
RG                   101
DW                 7.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         161.9674942 MHz
NUC1                 31P
P0                  2.67 usec
P1                  8.00 usec
PLW1         45.86100006 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                 32768
SF           161.9755930 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```



Current Data Parameters

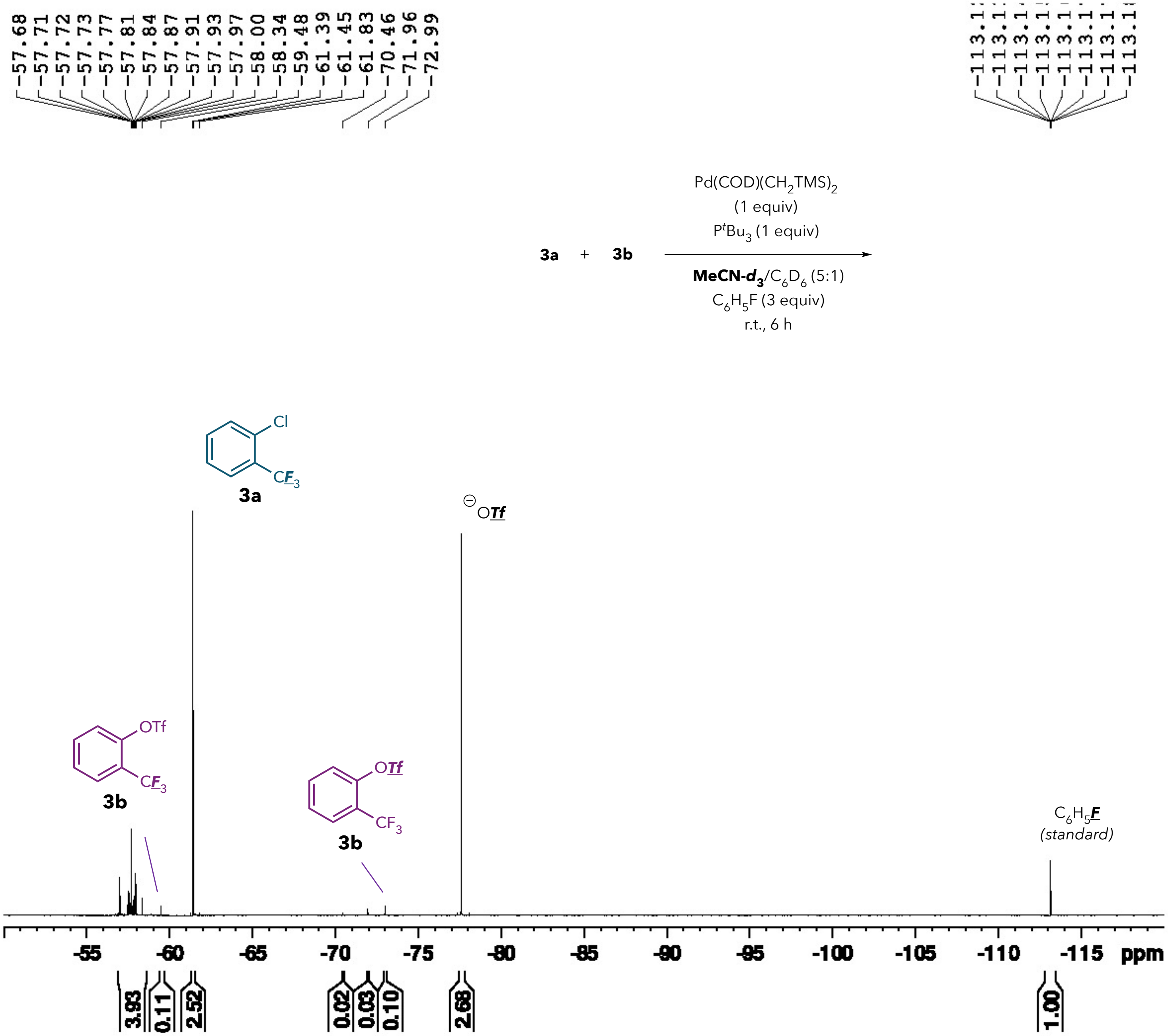
NAME	6-SMR-41-6
EXPNO	10
PROCNO	1

F2 - Acquisition Parameter

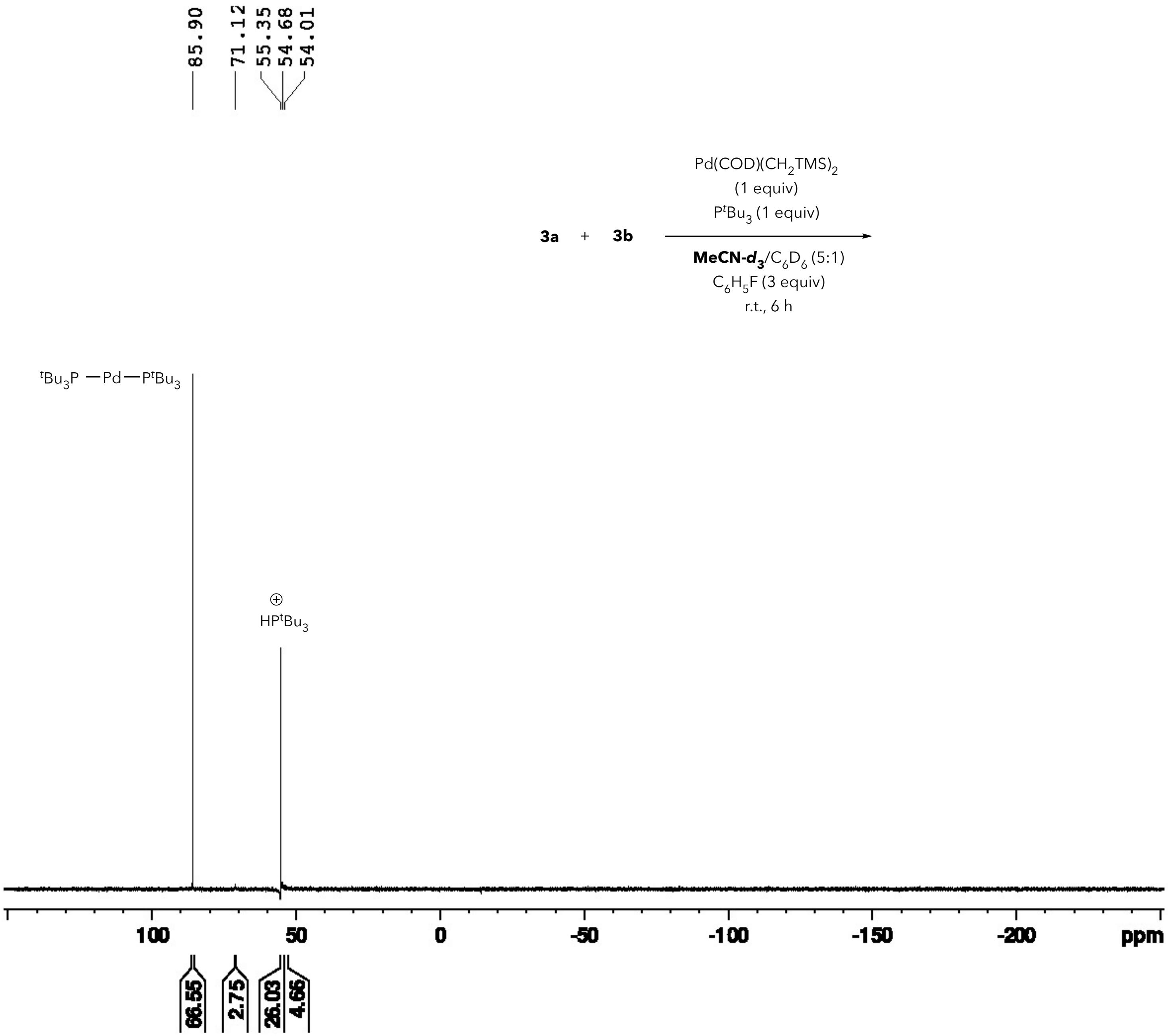
Date_	20211116
Time	15.46 h
INSTRUM	spect
PROBHD	Z125869_0055 (
PULPROG	zg30
TD	65536
SOLVENT	CD3CN
NS	64
DS	2
SWH	10000.000 Hz
FIDRES	0.305176 Hz
AQ	3.2767999 sec
RG	35.18
DW	50.000 usec
DE	16.00 usec
TE	298.0 K
D1	2.00000000 sec
TD0	1
SFO1	500.2330889 MHz
NUC1	1H
P0	4.00 usec
P1	12.00 usec
PLW1	11.44699955 W

F2 - Processing parameters

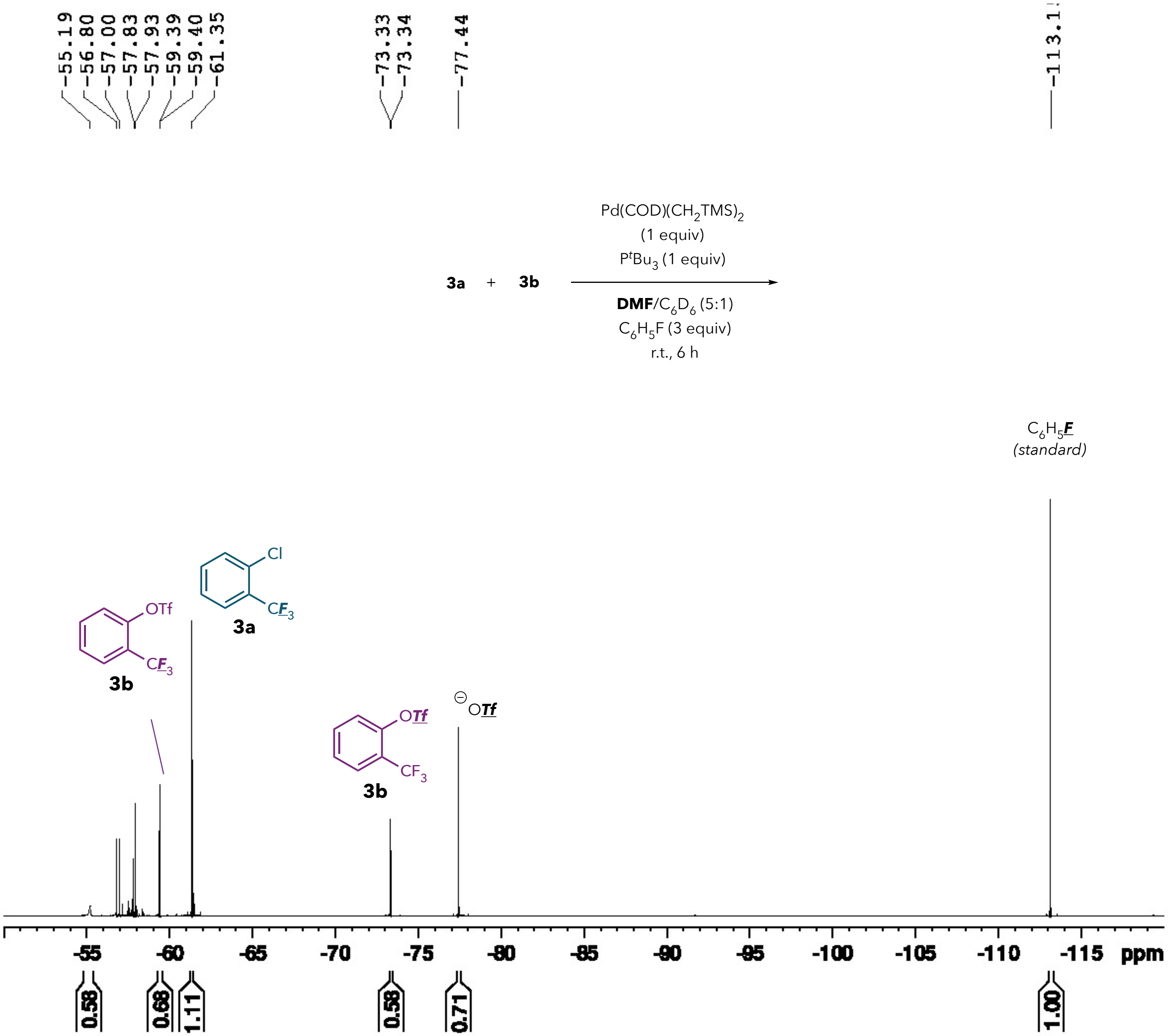
SI		65536
SF		500.2300000 MHz
WDW		EM
SSB	0	
LB		0.30 Hz
GB	0	
PC		1.00


$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\mathbf{MeCN\text{-}}\boldsymbol{d_3}/C_6D_6\ (5{:}1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t., 6 h}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

```
Current Data Parameters
NAME          6-SMR-41-6
EXPNO                 11
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211116
Time             15.48 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG           zgflqn
TD                131072
SOLVENT            CD3CN
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           470.6857814 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

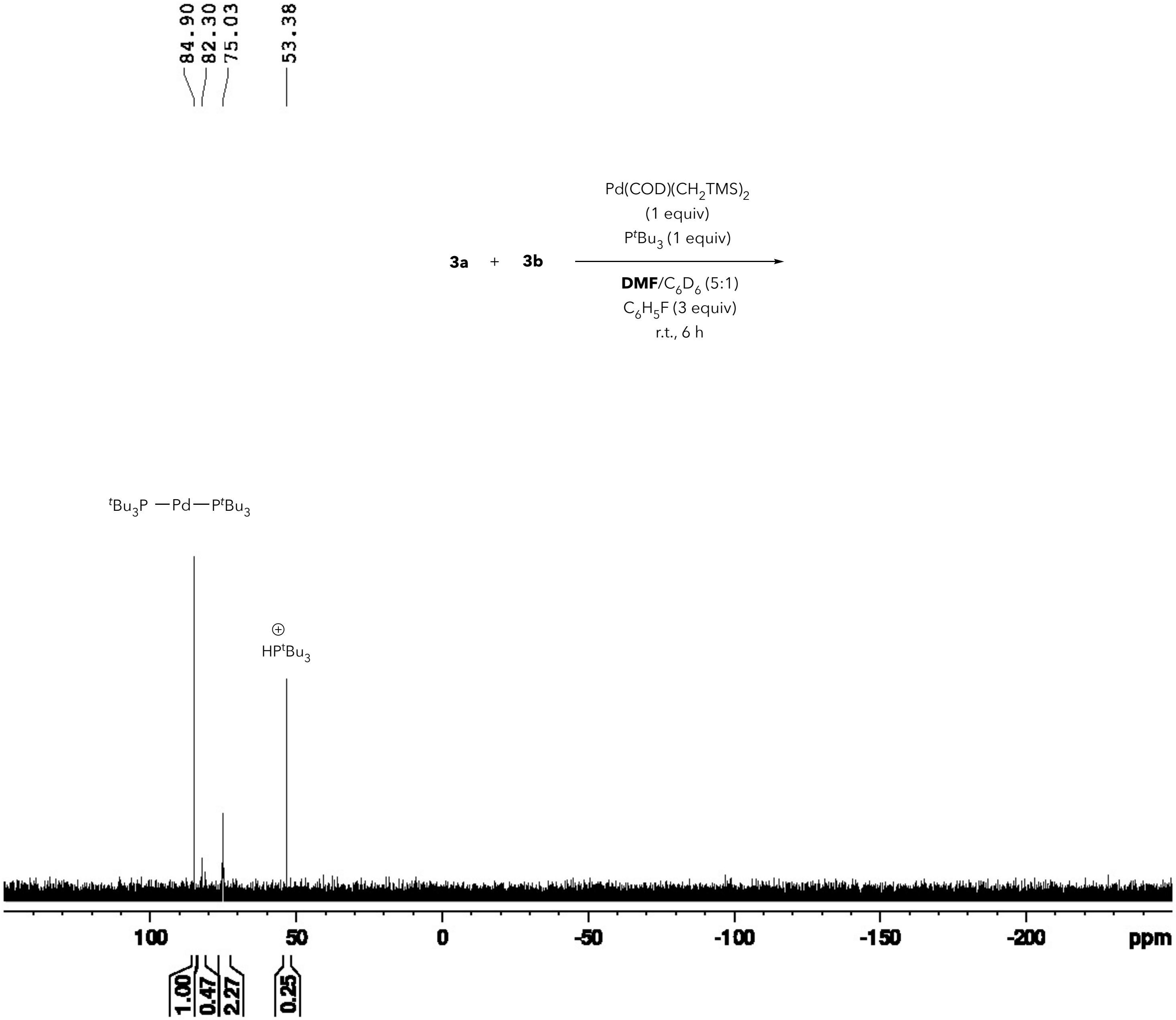


```
Current Data Parameters
NAME          6-SMR-41-6
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameter
Date_           20211116
Time               15.51 h
INSTRUM            spect
PROBHD      Z125869_0055 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CD3CN
NS                    16
DS                     4
SWH            81521.742 Hz
FIDRES          2.487846 Hz
AQ             0.4019541 sec
RG                190.44
DW                 6.133 usec
DE                 18.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         202.4866909 MHz
NUC1                 31P
P0                  4.00 usec
P1                 12.00 usec
PLW1         40.26200104 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           202.4968157 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

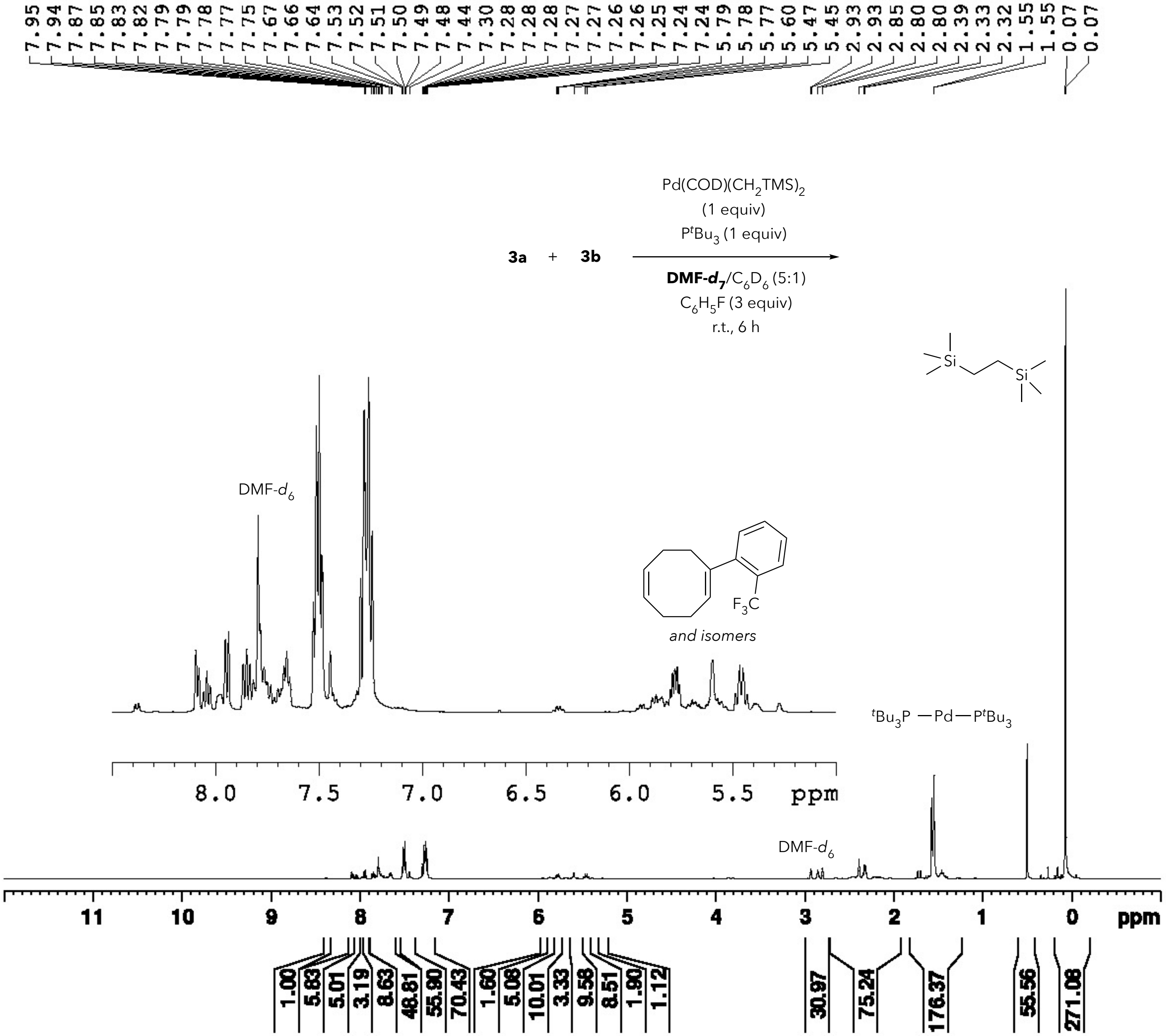


```
Current Data Parameters
NAME        6-SMR-39-11
EXPNO                10
PROCNO                2

F2 - Acquisition Parameter
Date_          20211115
Time              16.46 h
INSTRUM      Avance Neo
PROBHD   Z152088_0031 (
PULPROG            zgig
TD               131072
SOLVENT            C6D6
NS                   16
DS                    4
SWH          90909.094 Hz
FIDRES        1.387163 Hz
AQ           0.7208960 sec
RG                  101
DW                5.500 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        376.4607164 MHz
NUC1                19F
P1                12.00 usec
PLW1        31.08900070 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W

F2 - Processing parameters
SI                65536
SF          376.4978850 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

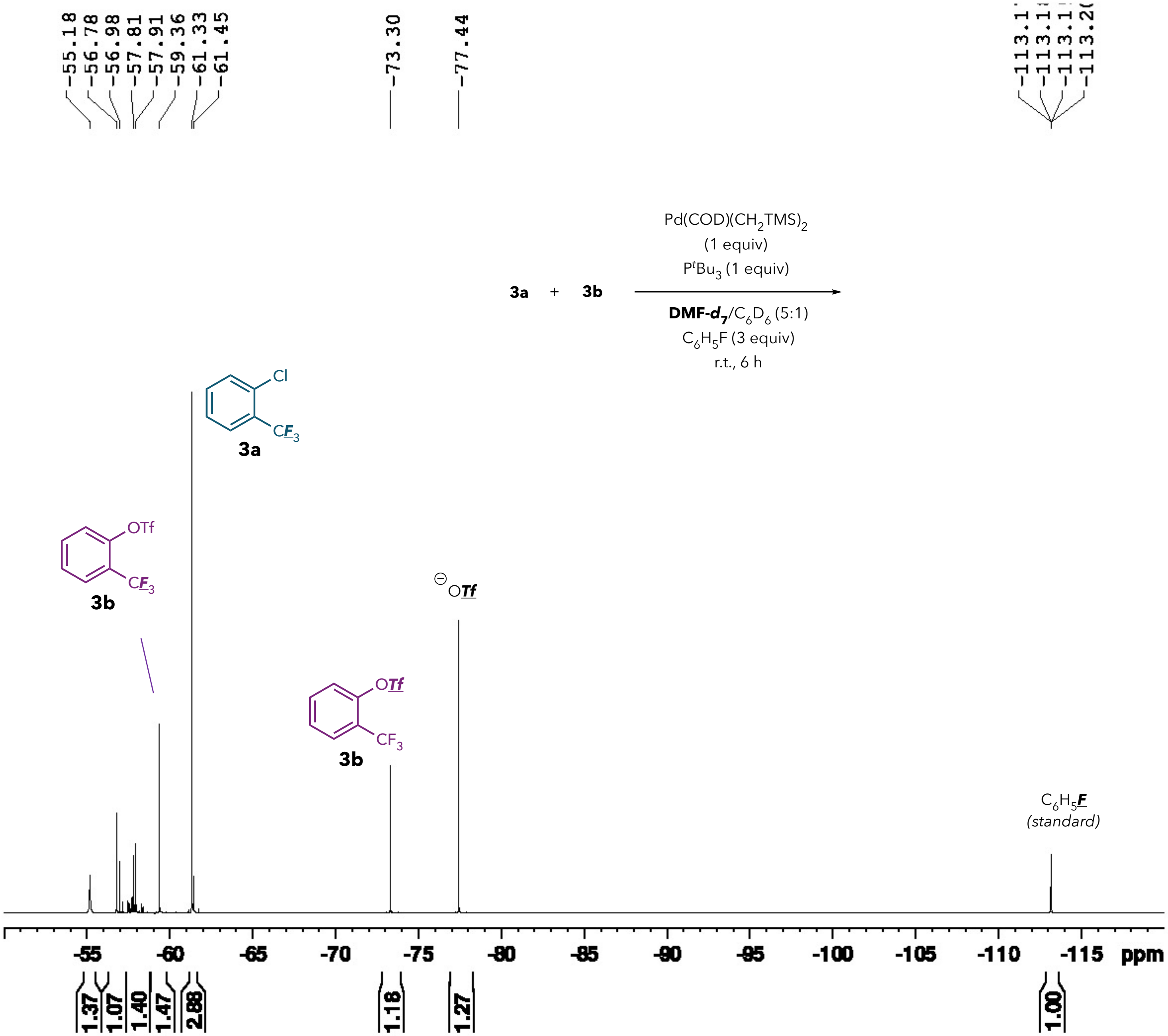
$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\mathbf{DMF}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t., 6 h}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$



```
Current Data Parameters
NAME          6-SMR-39-11
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211115
Time              16.50 h
INSTRUM        Avance Neo
PROBHD     Z152088_0031 (
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     4
SWH          65789.477 Hz
FIDRES        2.007735 Hz
AQ           0.4980736 sec
RG                   101
DW             7.600 usec
DE              6.50 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                    1
SFO1      161.9674942 MHz
NUC1                 31P
P0              2.67 usec
P1              8.00 usec
PLW1      45.86100006 W
SFO2      400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2          90.00 usec
PLW2      24.03499985 W
PLW12      0.18990999 W
PLW13      0.09552100 W

F2 - Processing parameters
SI                 32768
SF        161.9755930 MHz
WDW                   EM
SSB      0
LB               1.00 Hz
GB       0
PC                  1.40
```

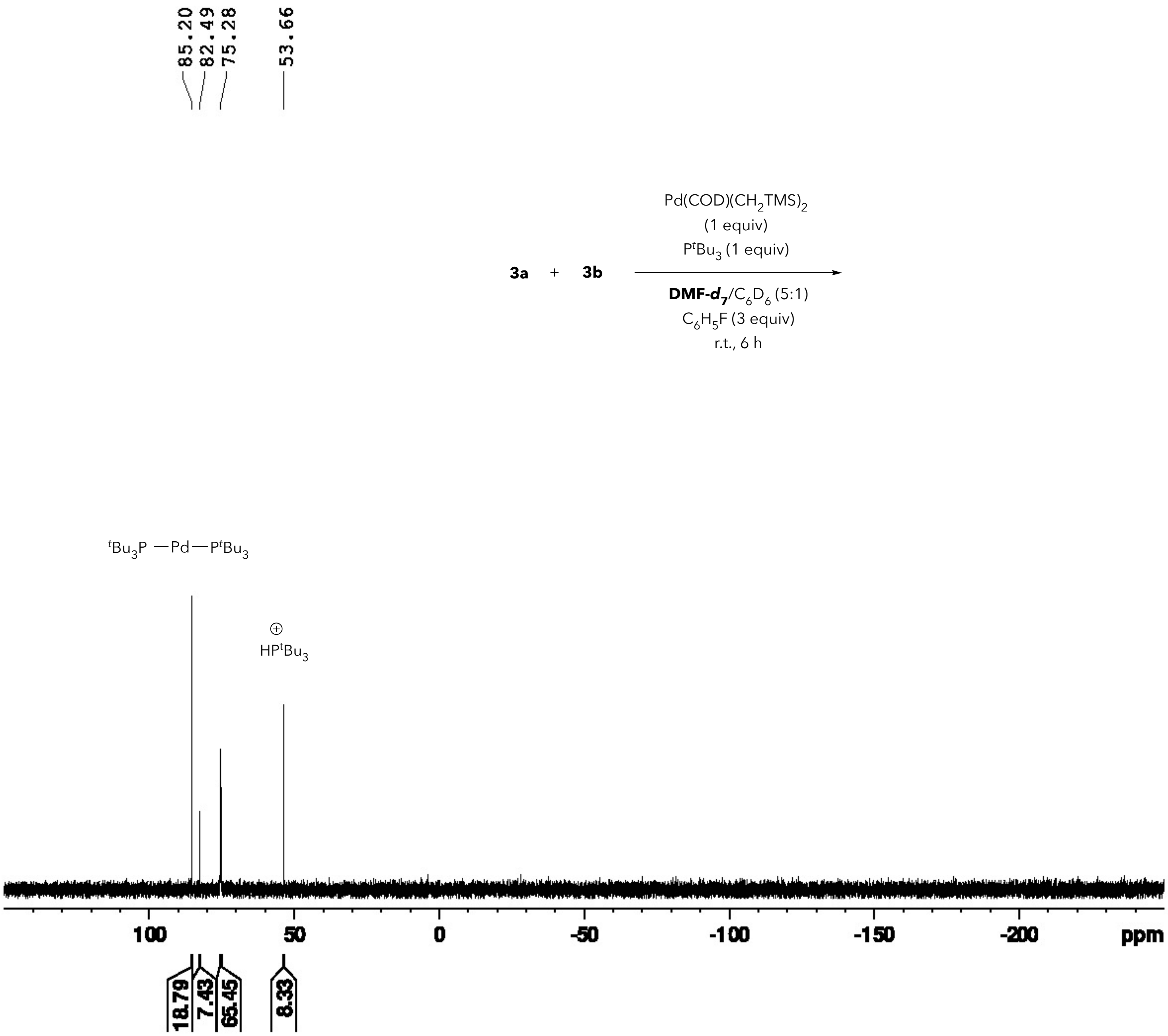


```
Current Data Parameters
NAME          6-SMR-41-11
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211116
Time              16.15 h
INSTRUM             spect
PROBHD     Z125869_0055 (
PULPROG              zg30
TD                  65536
SOLVENT               DMF
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          500.2300000 MHz
WDW                    EM
SSB      0
LB                 0.30 Hz
GB       0
PC                   1.00
```

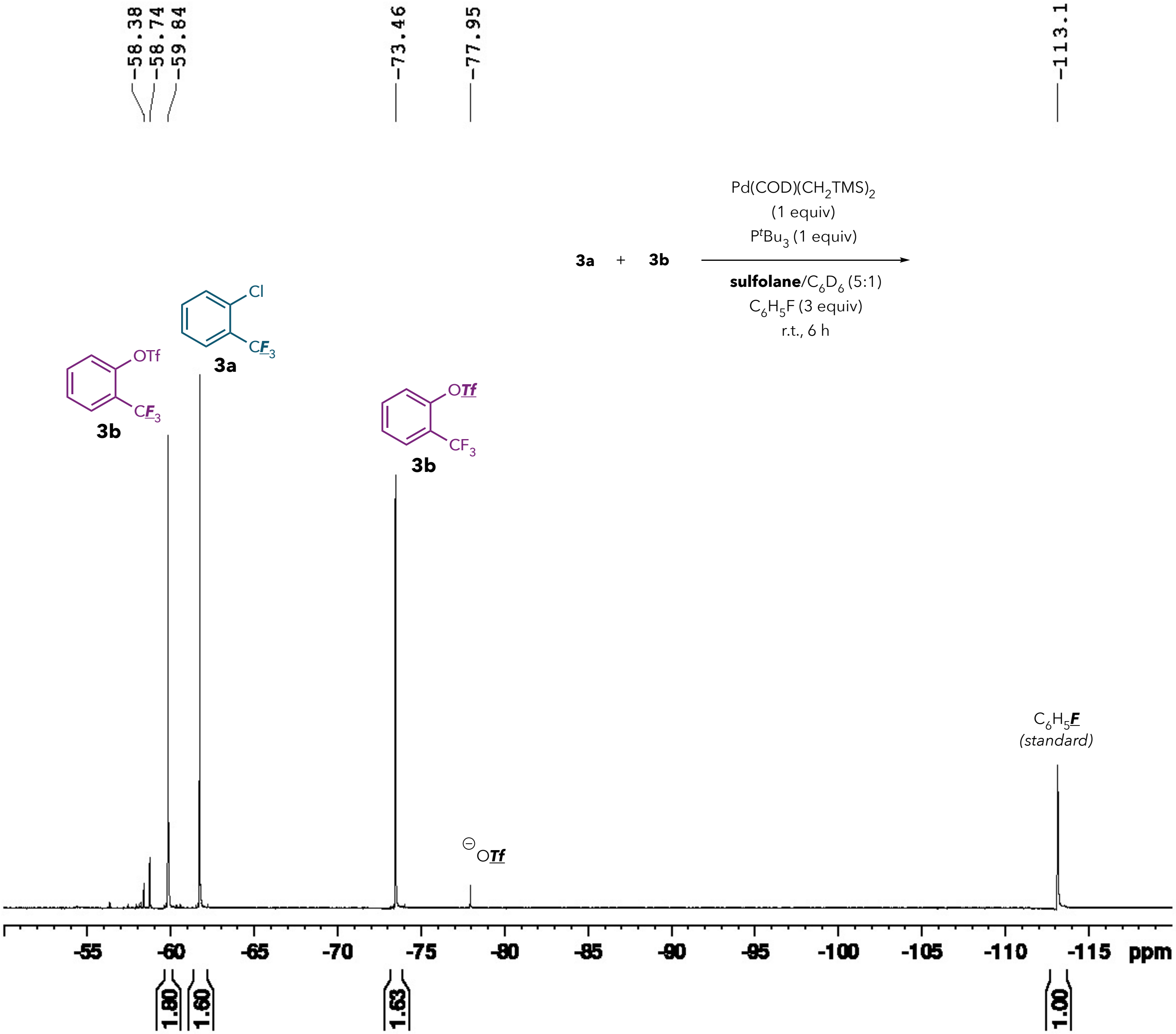


```
Current Data Parameters
NAME         6-SMR-41-11
EXPNO                 11
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211116
Time               16.17 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG           zgflqn
TD                131072
SOLVENT              DMF
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           470.6859888 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

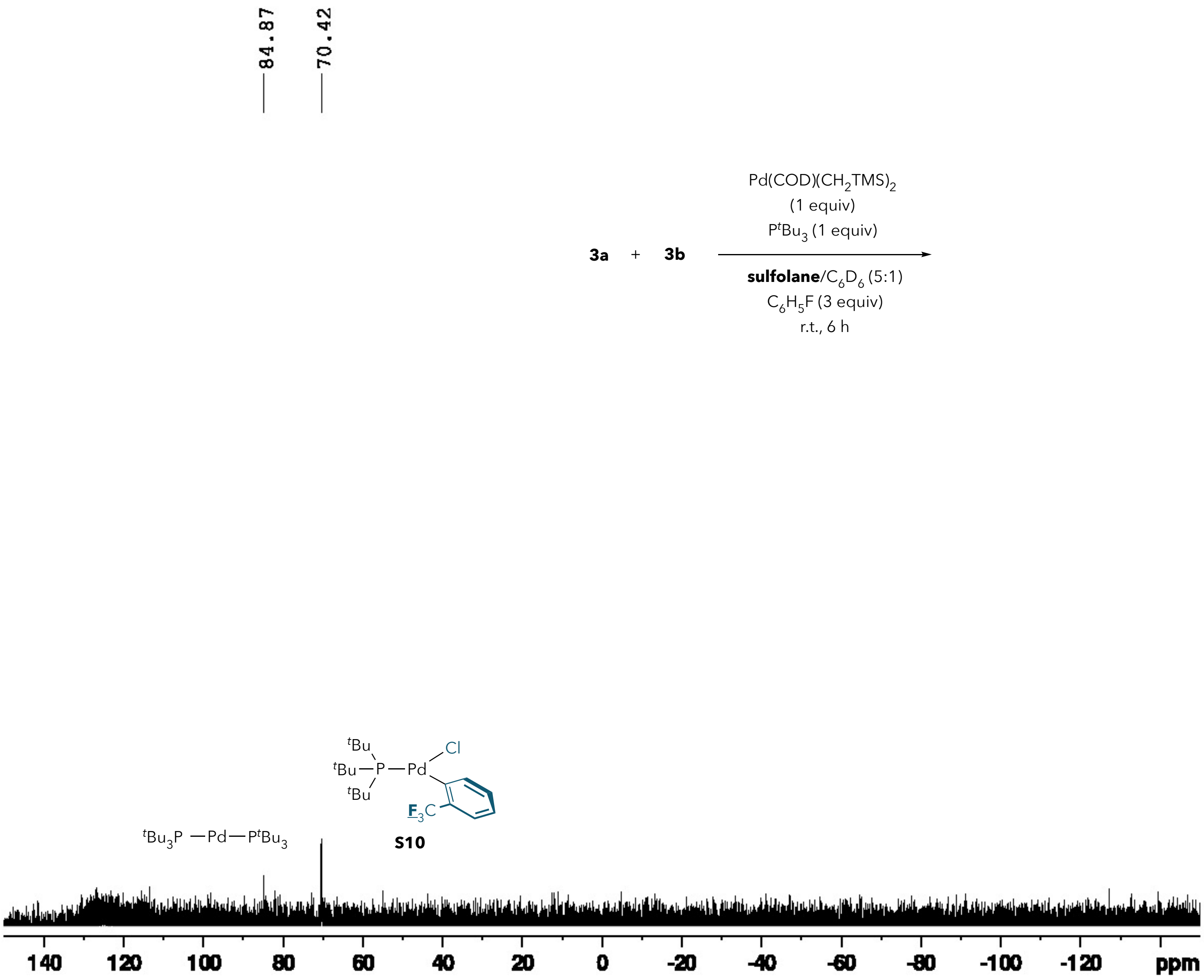
$$\textbf{3a} + \textbf{3b} \xrightarrow[\substack{\textbf{DMF-}\boldsymbol{d_7}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t., 6 h}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$



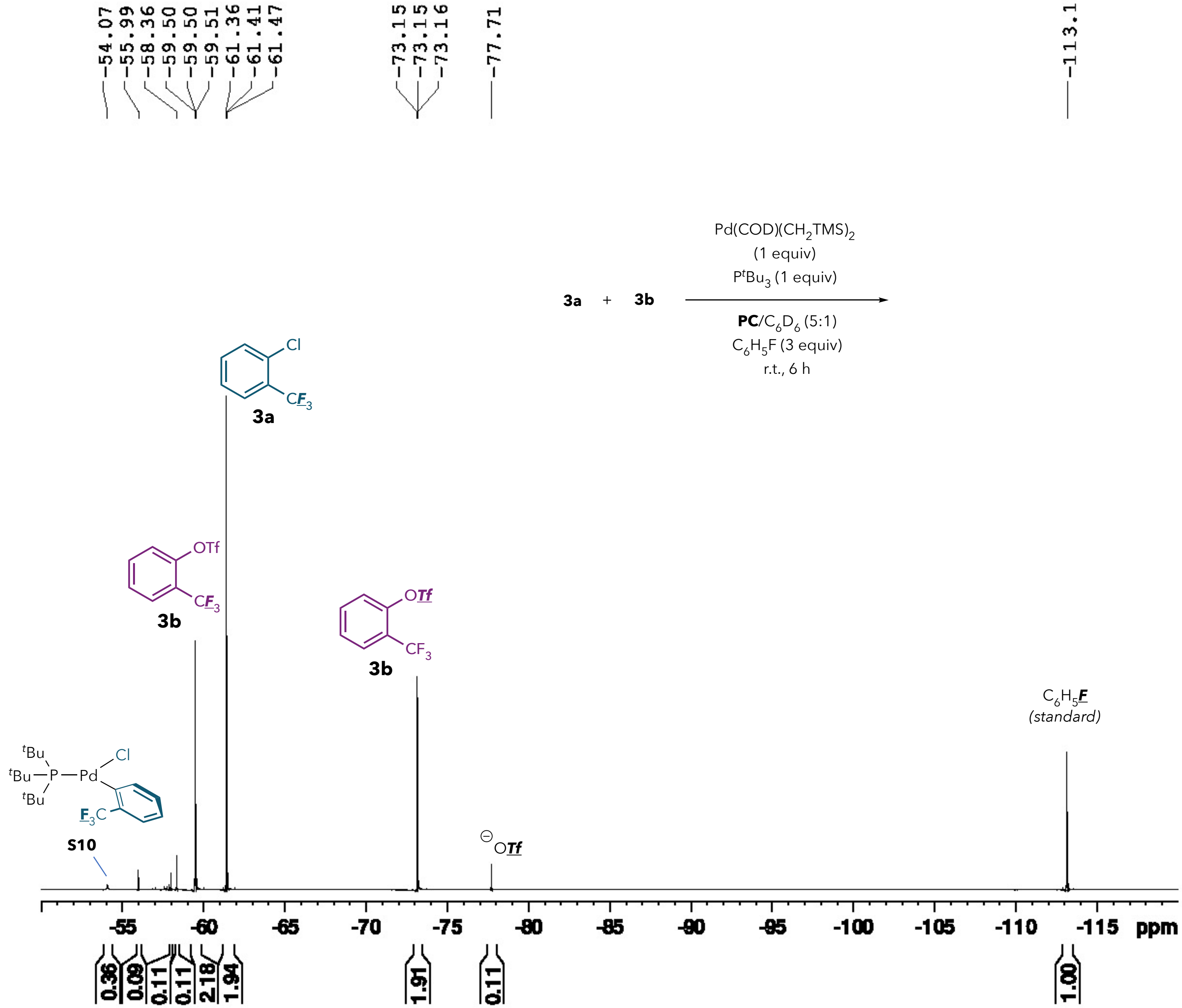
```
Current Data Parameters
NAME        6-SMR-41-11
EXPNO                12
PROCNO                1

F2 - Acquisition Parameter
Date_          20211116
Time              16.19 h
INSTRUM           spect
PROBHD     Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT             DMF
NS                   16
DS                    4
SWH           81521.742 Hz
FIDRES         2.487846 Hz
AQ            0.4019541 sec
RG               190.44
DW                6.133 usec
DE                18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        202.4866909 MHz
NUC1                31P
P0                 4.00 usec
P1                12.00 usec
PLW1        40.26200104 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          202.4968157 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



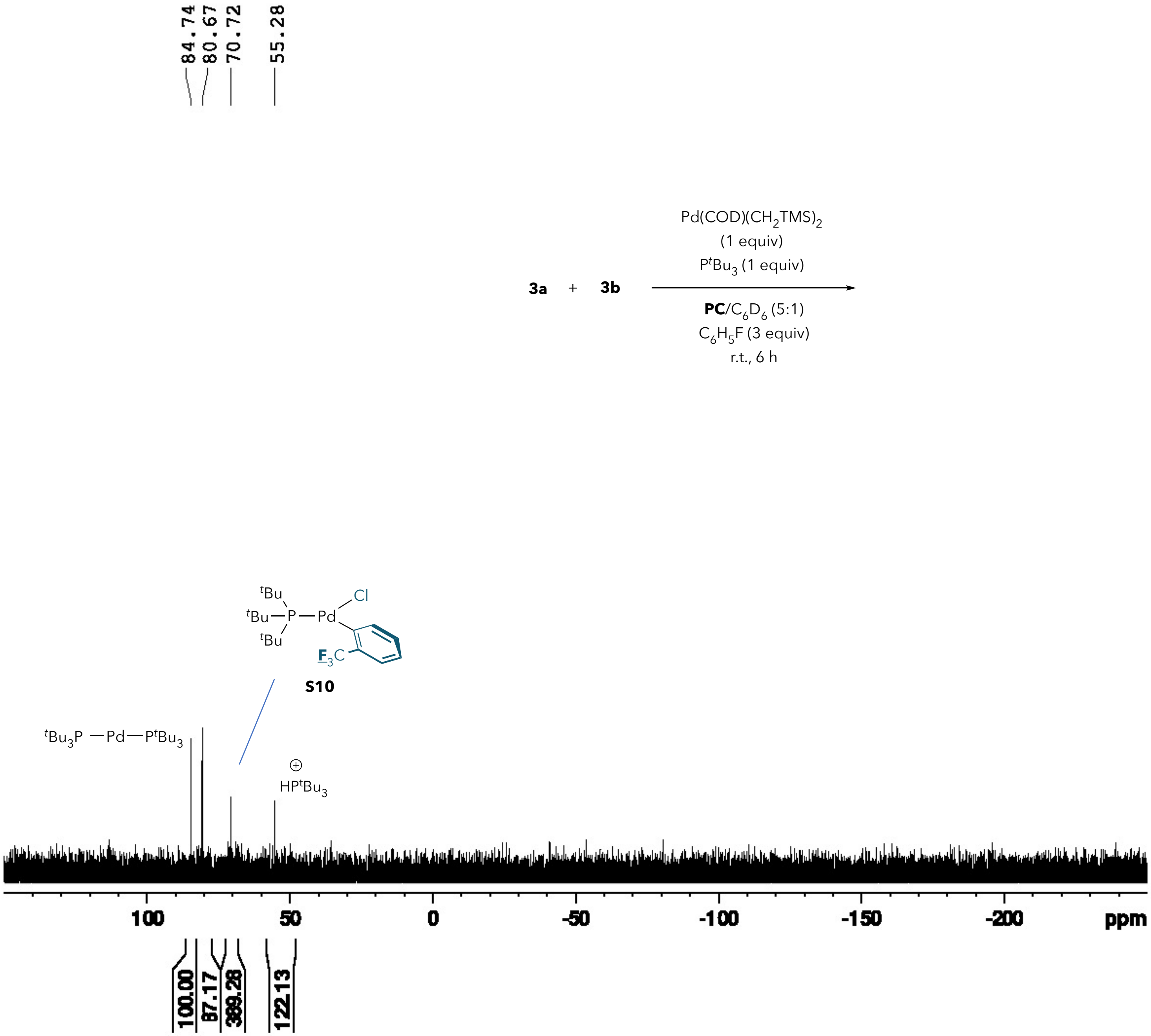
```
Current Data Parameters
NAME          6-SMR-5-15
EXPNO                 10
PROCNO                 2

F2 - Acquisition Parameter
Date_           20210911
Time             20.34 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG               zg
TD                130892
SOLVENT             C6D6
NS                    16
DS                     4
SWH         90909.094 Hz
FIDRES       1.389070 Hz
AQ          0.7199060 sec
RG                   101
DW             5.500 usec
DE              6.50 usec
TE               298.0 K
D1        1.00000000 sec
TD0                    1
SFO1      376.4607164 MHz
NUC1                 19F
P1             12.00 usec
PLW1      31.08900070 W

F2 - Processing parameters
SI                 65536
SF        376.4982209 MHz
WDW                   EM
SSB      0
LB               0.30 Hz
GB       0
PC                  1.00
```



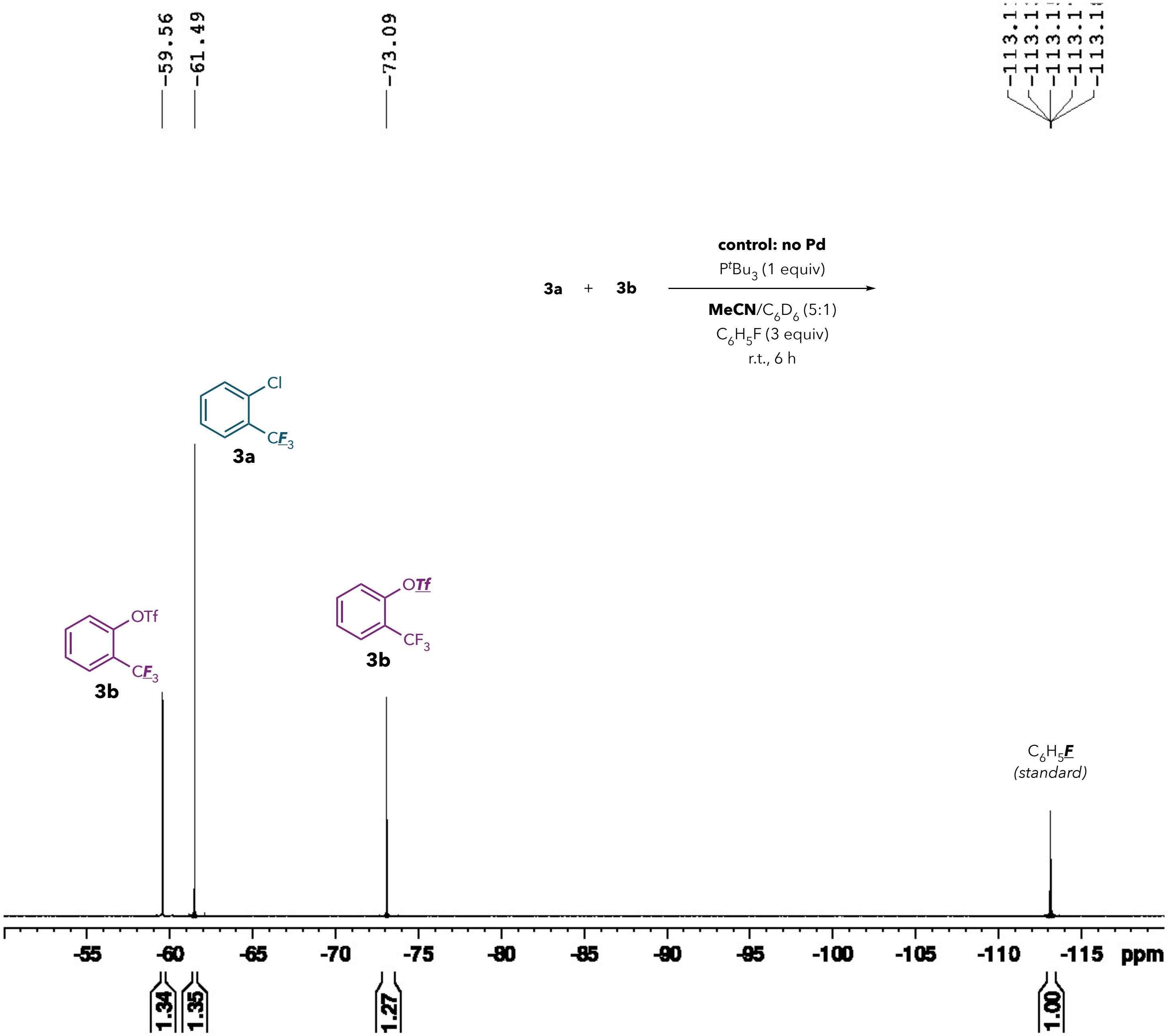
```
Current Data Parameters
NAME          6-SMR-5-15
EXPNO                 11
PROCNO                 2

F2 - Acquisition Parameter
Date_           20210911
Time             20.38 h
INSTRUM        Avance Neo
PROBHD    Z152088_0031 (
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     4
SWH          65789.477 Hz
FIDRES        2.007735 Hz
AQ           0.4980736 sec
RG                   101
DW             7.600 usec
DE              6.50 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                    1
SFO1       161.9674942 MHz
NUC1                 31P
P0              2.67 usec
P1              8.00 usec
PLW1        45.86100006 W
SFO2       400.1316005 MHz
NUC2                  1H
CPDPRG[2        waltz16
PCPD2          90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                 32768
SF         161.9755930 MHz
WDW                   EM
SSB      0
LB               1.00 Hz
GB       0
PC                  1.40
```



```
Current Data Parameters
NAME         6-SMR-39-15
EXPNO                 10
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211115
Time               17.06 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zgig
TD                131072
SOLVENT             C6D6
NS                    16
DS                     4
SWH         90909.094 Hz
FIDRES       1.387163 Hz
AQ         0.7208960 sec
RG                   101
DW             5.500 usec
DE              6.50 usec
TE               298.1 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0                    1
SFO1     376.4607164 MHz
NUC1                 19F
P1             12.00 usec
PLW1     31.08900070 W
SFO2     400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2          90.00 usec
PLW2     24.03499985 W
PLW12     0.18990999 W

F2 - Processing parameters
SI                 65536
SF       376.4979014 MHz
WDW                   EM
SSB      0
LB                0.30 Hz
GB       0
PC                  1.00
```

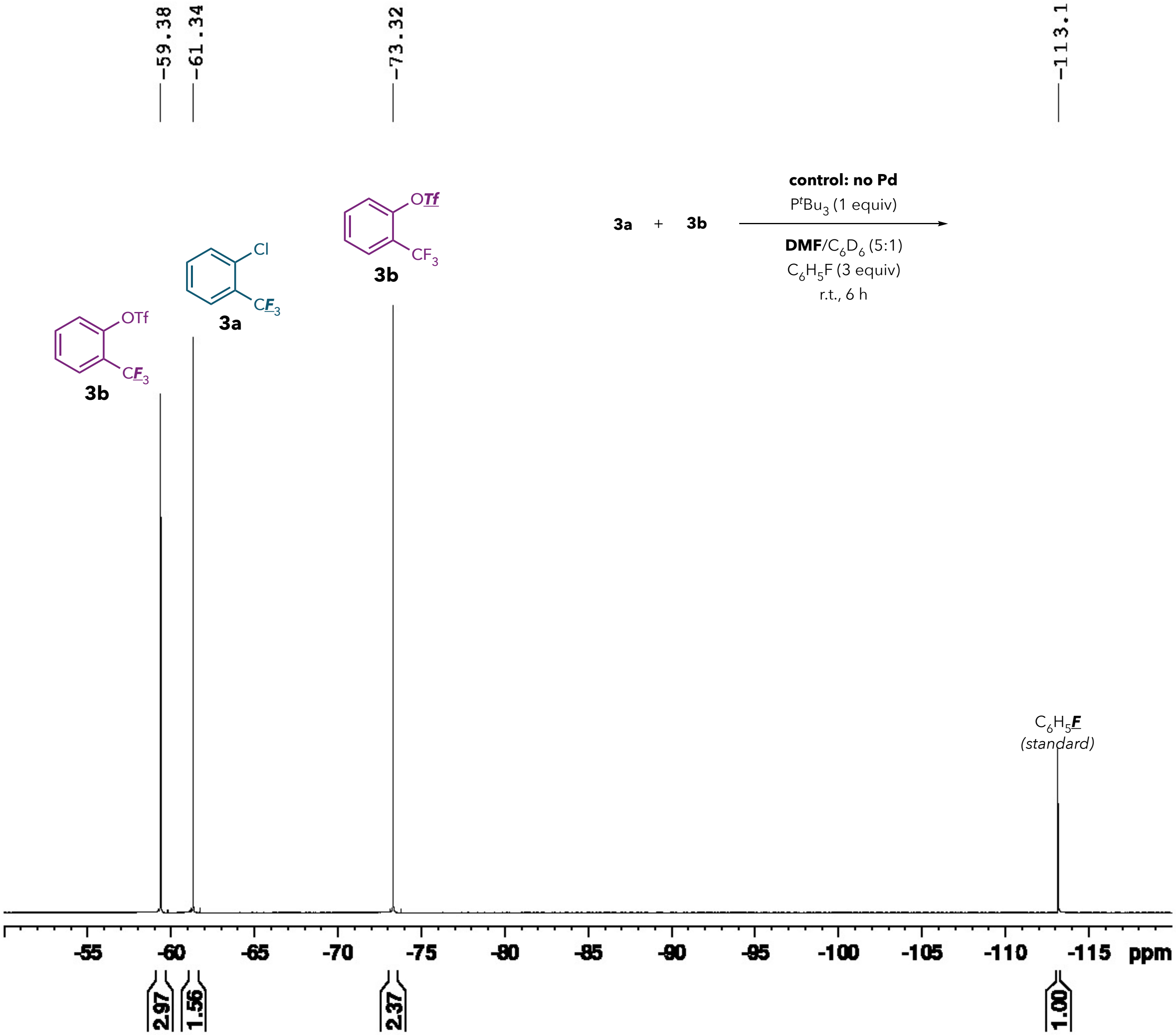


```
Current Data Parameters
NAME          6-SMR-39-15
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211115
Time              17.09 h
INSTRUM        Avance Neo
PROBHD   Z152088_0031 (
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     4
SWH         65789.477 Hz
FIDRES       2.007735 Hz
AQ          0.4980736 sec
RG                   101
DW             7.600 usec
DE              6.50 usec
TE               298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                    1
SFO1      161.9674942 MHz
NUC1                 31P
P0              2.67 usec
P1              8.00 usec
PLW1       45.86100006 W
SFO2      400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2            90.00 use
PLW2       24.03499985 W
PLW12       0.18990999 W
PLW13       0.09552100 W

F2 - Processing parameters
SI                 32768
SF        161.9755930 MHz
WDW                   EM
SSB      0
LB               1.00 Hz
GB       0
PC                  1.40
```

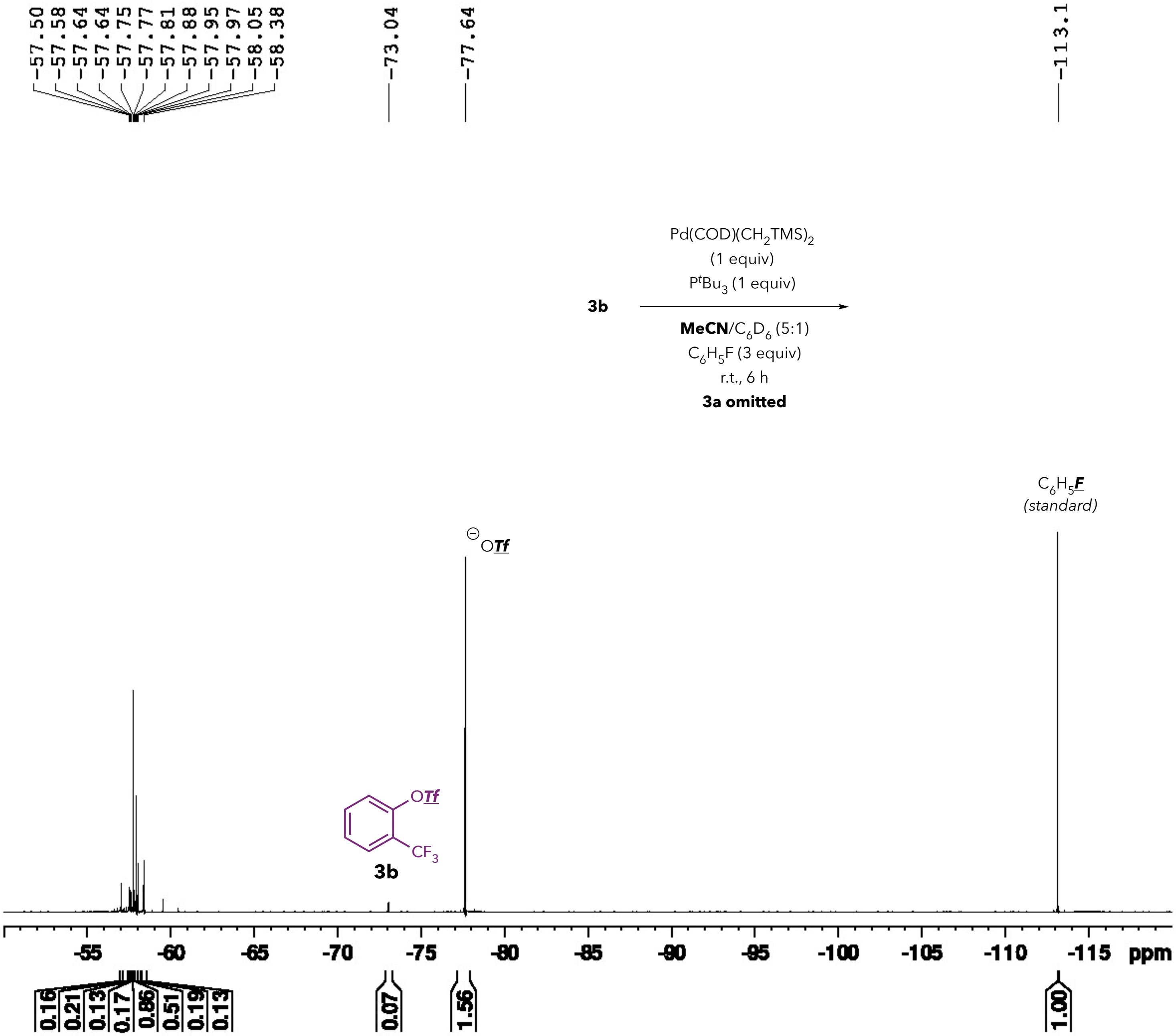


3a + **3b** $\xrightarrow[\substack{\textbf{MeCN}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t., 6 h}}]{\substack{\textbf{control: no Pd} \\ P^tBu_3\ (1\ \text{equiv})}}$

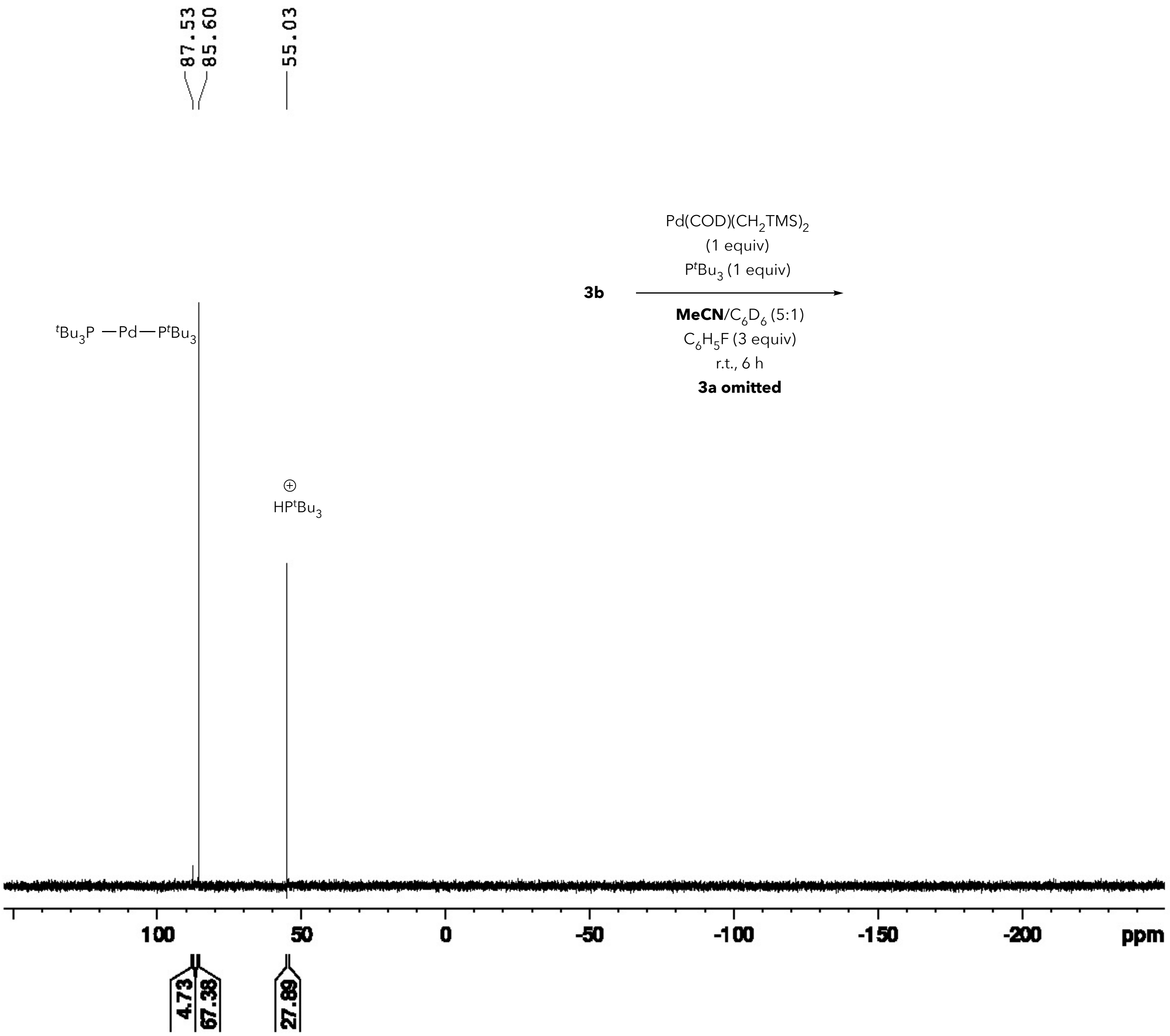
```
Current Data Parameters
NAME      ER-6-55-2control_Pdfree_
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200707
Time                 10.25
INSTRUM              spect
PROBHD    5 mm QNP 1H/13
PULPROG             zgflqn
TD                   32768
SOLVENT               C6D6
NS                      64
DS                       0
SWH          50125.312 Hz
FIDRES        1.529703 Hz
AQ           0.3268608 sec
RG                  2896.3
DW               9.975 usec
DE                6.00 usec
TE                 683.2 K
D1          1.50000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   19F
P1                9.00 usec
PL1          0 dB
SFO1      282.4250465 MHz

F2 - Processing parameters
SI                   65536
SF         282.4415558 MHz
WDW                     EM
SSB          0
LB                 0.30 Hz
GB           0
PC                    1.00
```



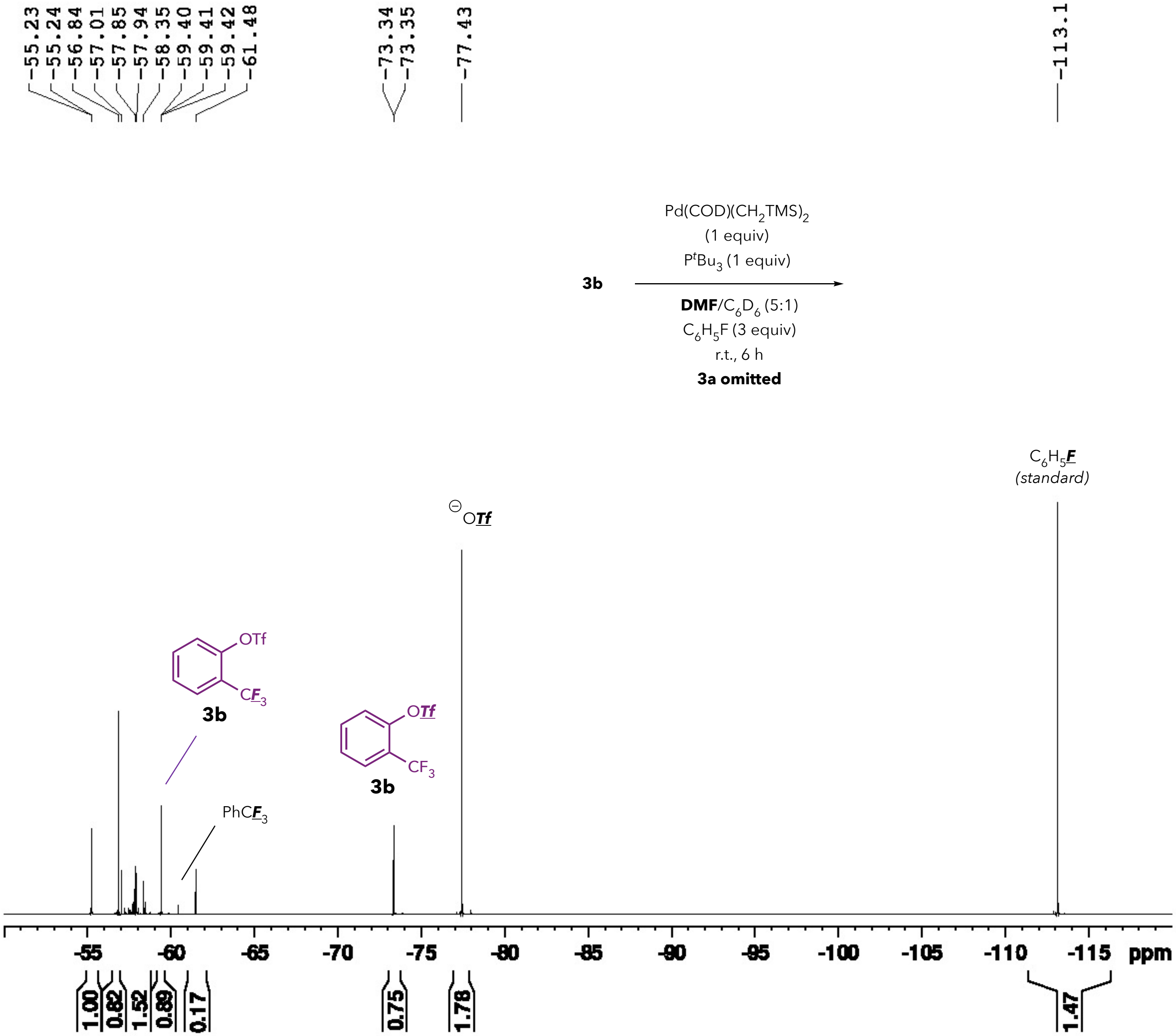
```
Current Data Parameters
NAME          5-SMR-95-1
EXPNO                 10
PROCNO                 2

F2 - Acquisition Parameter
Date_           20210519
Time             17.06 h
INSTRUM            spect
PROBHD    Z125869_0055 (
PULPROG           zgflqn
TD                130892
SOLVENT             C6D6
NS                    16
DS                     4
SWH        113636.367 Hz
FIDRES       1.736338 Hz
AQ          0.5759248 sec
RG                 15.61
DW             4.400 usec
DE             18.00 usec
TE               300.0 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        470.6858616 MHz
WDW                   EM
SSB      0
LB               0.30 Hz
GB       0
PC                  1.00
```



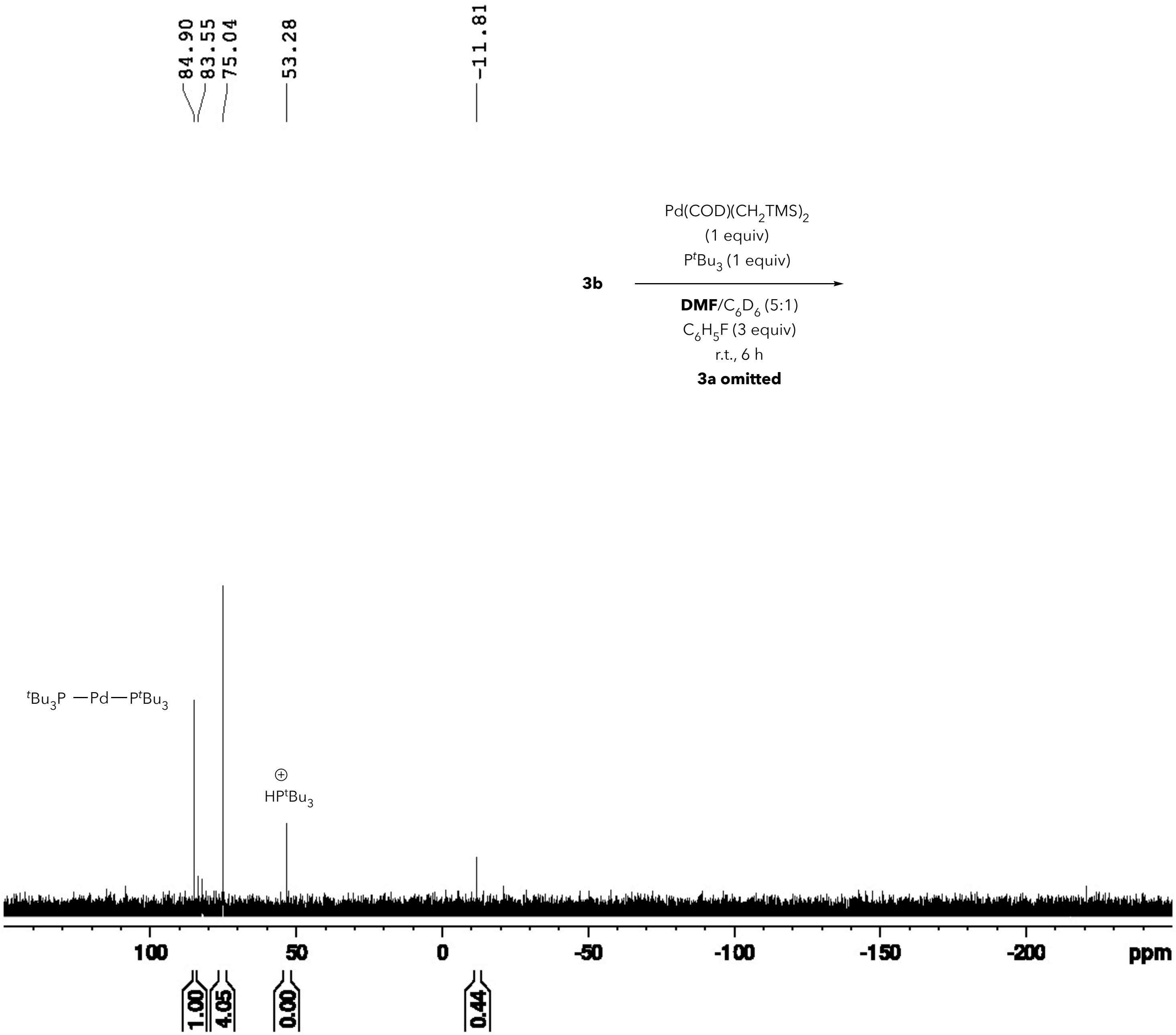
```
Current Data Parameters
NAME           6-SMR-40-4
EXPNO                  10
PROCNO                  2

F2 - Acquisition Parameter
Date_            20211115
Time              17.49 h
INSTRUM         Avance Neo
PROBHD     Z152088_0031 (
PULPROG              zgig
TD                 131072
SOLVENT              C6D6
NS                     16
DS                      4
SWH          90909.094 Hz
FIDRES        1.387163 Hz
AQ          0.7208960 sec
RG                    101
DW              5.500 usec
DE               6.50 usec
TE                298.1 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                     1
SFO1       376.4607164 MHz
NUC1                  19F
P1              12.00 usec
PLW1        31.08900070 W
SFO2       400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2           90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W

F2 - Processing parameters
SI                  65536
SF         376.4977310 MHz
WDW                    EM
SSB      0
LB                0.30 Hz
GB       0
PC                   1.00
```



```
Current Data Parameters
NAME          6-SMR-40-4
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameter
Date_           20211115
Time             17.52 h
INSTRUM       Avance Neo
PROBHD     Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT            C6D6
NS                   32
DS                    4
SWH          65789.477 Hz
FIDRES        2.007735 Hz
AQ           0.4980736 sec
RG                  101
DW               7.600 usec
DE                6.50 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1
SFO1        161.9674942 MHz
NUC1                31P
P0                2.67 usec
P1                8.00 usec
PLW1       45.86100006 W
SFO2       400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2       24.03499985 W
PLW12       0.18990999 W
PLW13       0.09552100 W

F2 - Processing parameters
SI                32768
SF          161.9755930 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



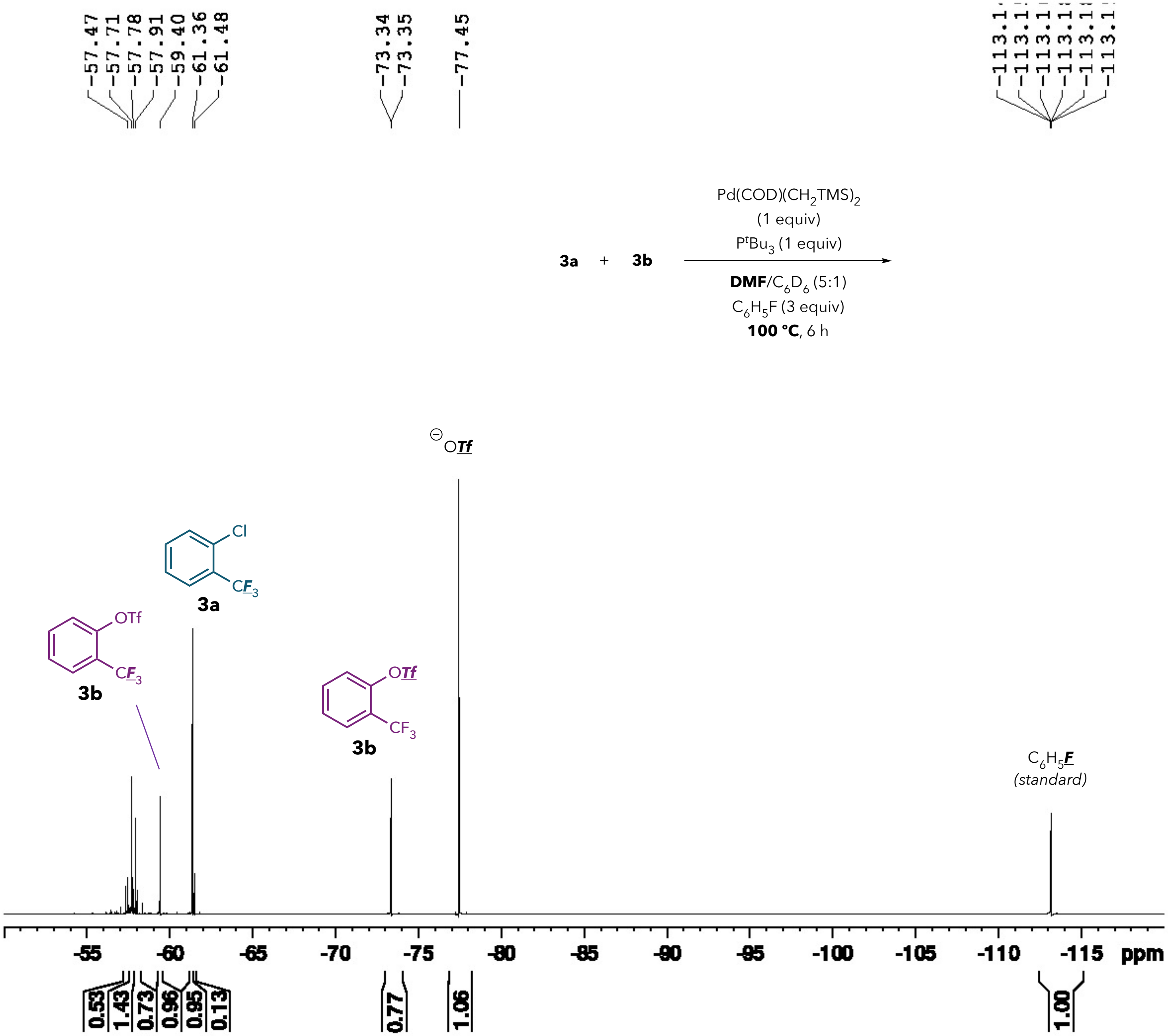
```
Current Data Parameters
NAME          6-SMR-40-7
EXPNO                 10
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211115
Time             18.00 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zgig
TD                131072
SOLVENT             C6D6
NS                    16
DS                     4
SWH         90909.094 Hz
FIDRES       1.387163 Hz
AQ          0.7208960 sec
RG                   101
DW            5.500 usec
DE             6.50 usec
TE               298.1 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0                    1
SFO1     376.4607164 MHz
NUC1                 19F
P1            12.00 usec
PLW1      31.08900070 W
SFO2     400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2         90.00 usec
PLW2      24.03499985 W
PLW12      0.18990999 W

F2 - Processing parameters
SI                 65536
SF       376.4978961 MHz
WDW                   EM
SSB      0
LB               0.30 Hz
GB       0
PC                  1.00
```



$$\mathbf{3b} \xrightarrow[\substack{\mathbf{DMF}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t., 6 h} \\ \mathbf{3a\ omitted}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

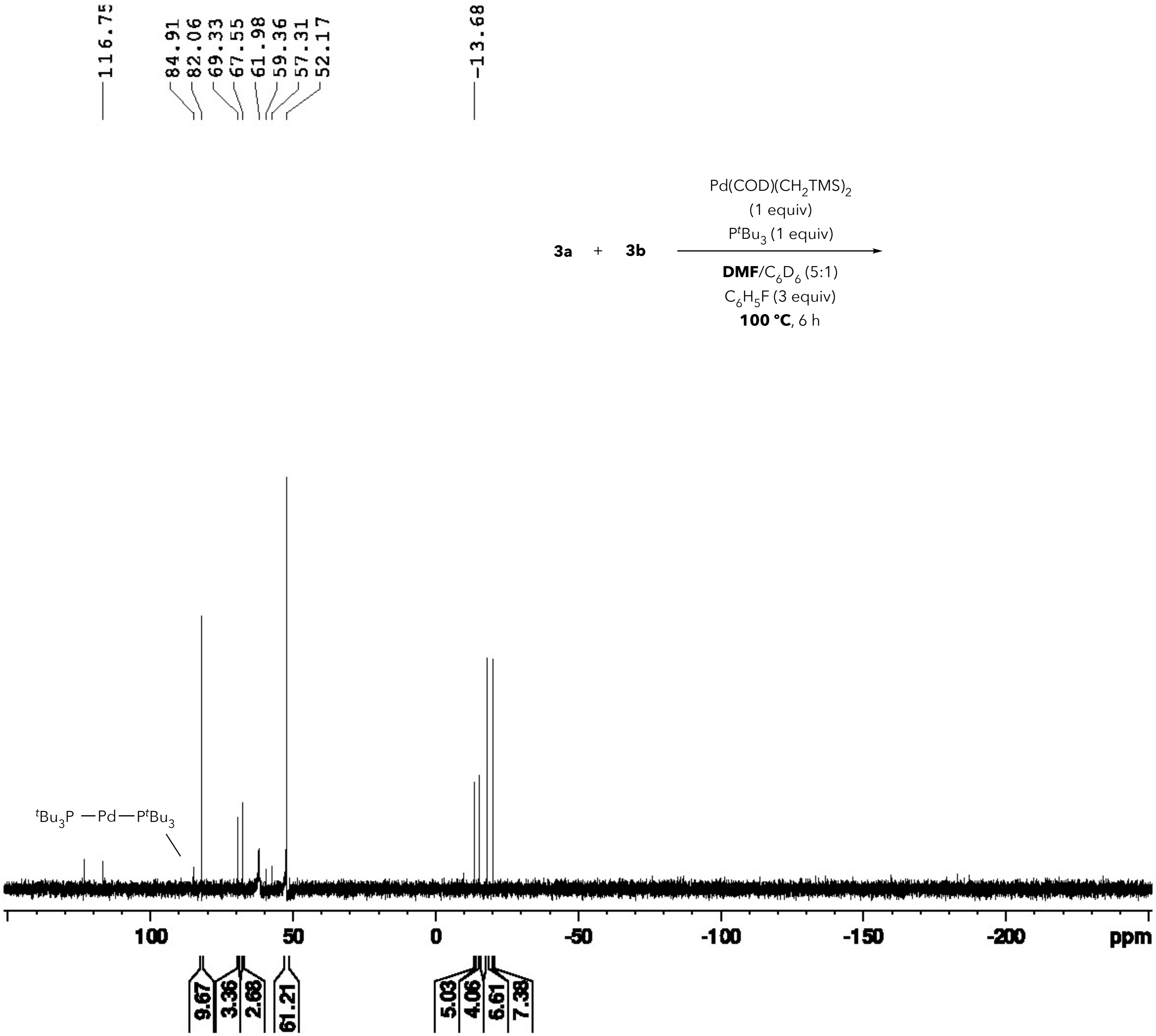
```
Current Data Parameters
NAME            6-SMR-40-7
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameter
Date_             20211115
Time               18.04 h
INSTRUM          Avance Neo
PROBHD     Z152088_0031 (
PULPROG             zgpg30
TD                   65536
SOLVENT               C6D6
NS                      32
DS                       4
SWH           65789.477 Hz
FIDRES         2.007735 Hz
AQ            0.4980736 sec
RG                     101
DW               7.600 usec
DE                6.50 usec
TE                 298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                      1
SFO1        161.9674942 MHz
NUC1                   31P
P0                2.67 usec
P1                8.00 usec
PLW1        45.86100006 W
SFO2        400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2            90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                   32768
SF          161.9755930 MHz
WDW                     EM
SSB      0
LB                 1.00 Hz
GB       0
PC                    1.40
```

2. Experiments in DMF at 100 and 0 ºC

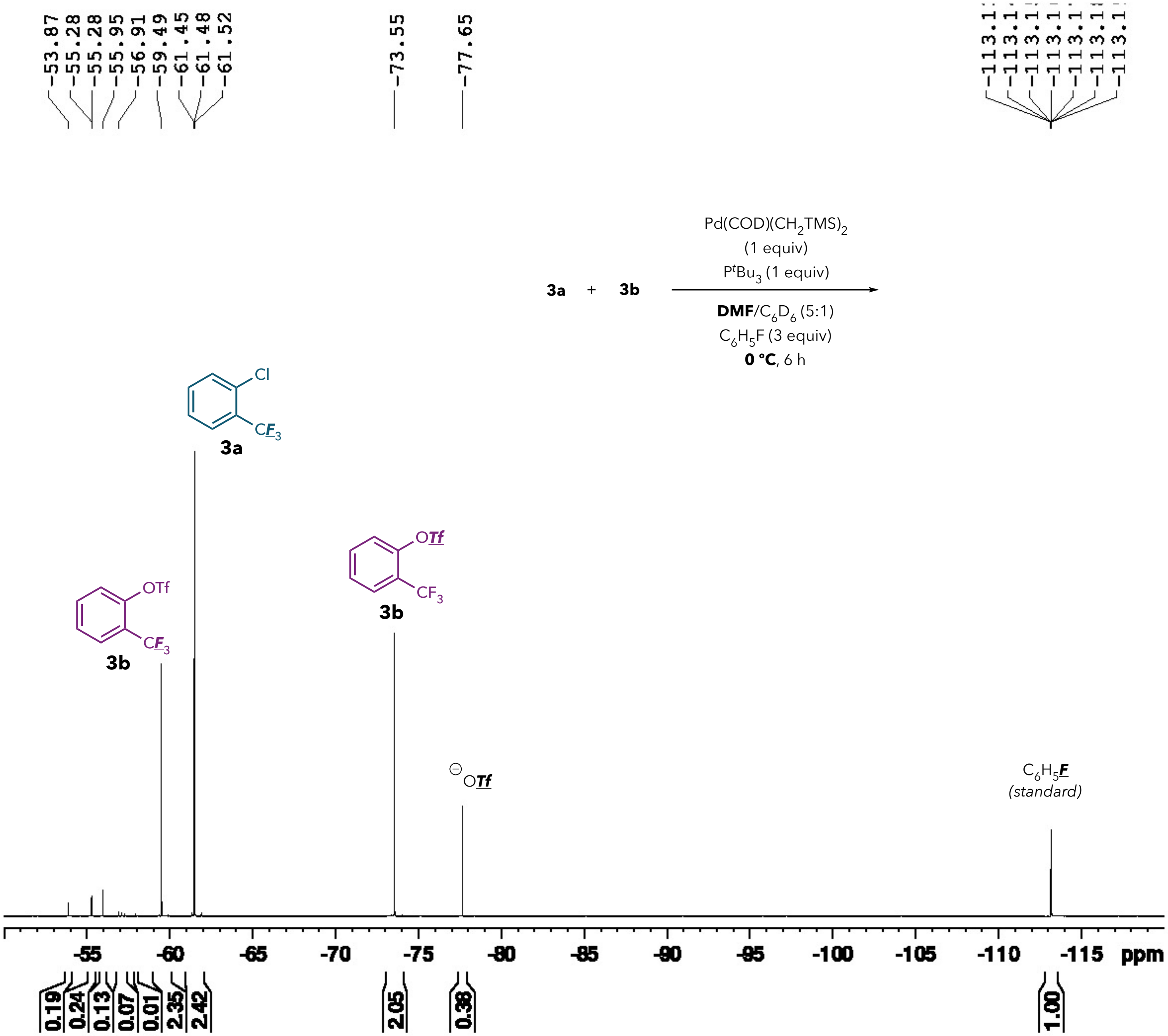


```
Current Data Parameters
NAME          6-SMR-42-3
EXPNO                 11
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211116
Time               16.56 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG           zgflqn
TD                131072
SOLVENT             C6D6
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           470.6858765 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\mathbf{DMF}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \mathbf{100\ °C},\ 6\ \text{h}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

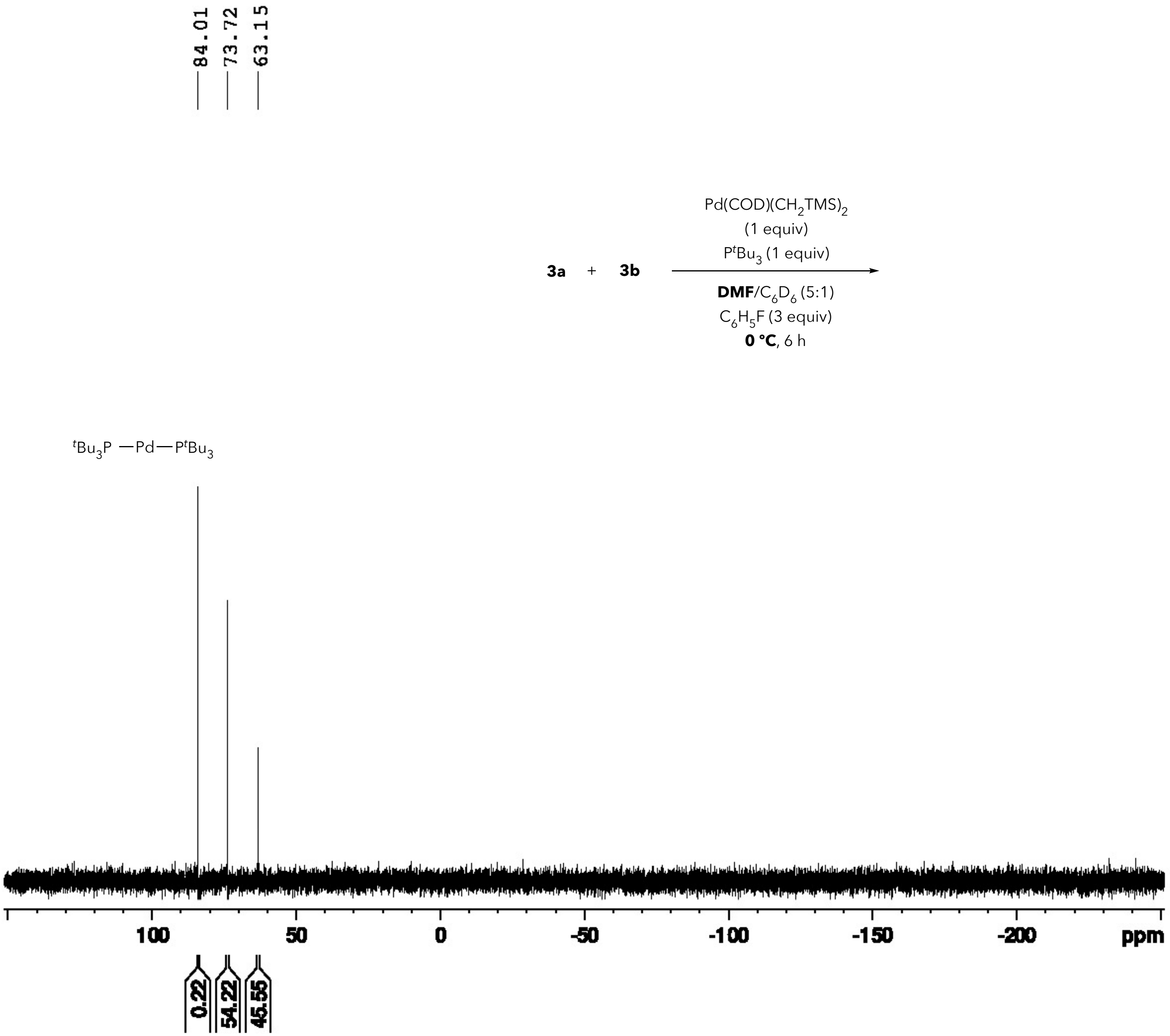


```
Current Data Parameters
NAME          6-SMR-42-3
EXPNO                 12
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211116
Time              16.58 h
INSTRUM            spect
PROBHD     Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT            C6D6
NS                   16
DS                    4
SWH          81521.742 Hz
FIDRES        2.487846 Hz
AQ           0.4019541 sec
RG              190.44
DW               6.133 usec
DE               18.00 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1
SFO1       202.4866909 MHz
NUC1                31P
P0                4.00 usec
P1               12.00 usec
PLW1       40.26200104 W
SFO2       500.2320009 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2            80.00 use
PLW2       11.44699955 W
PLW12       0.25756001 W
PLW13       0.12955000 W

F2 - Processing parameters
SI                32768
SF         202.4968157 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



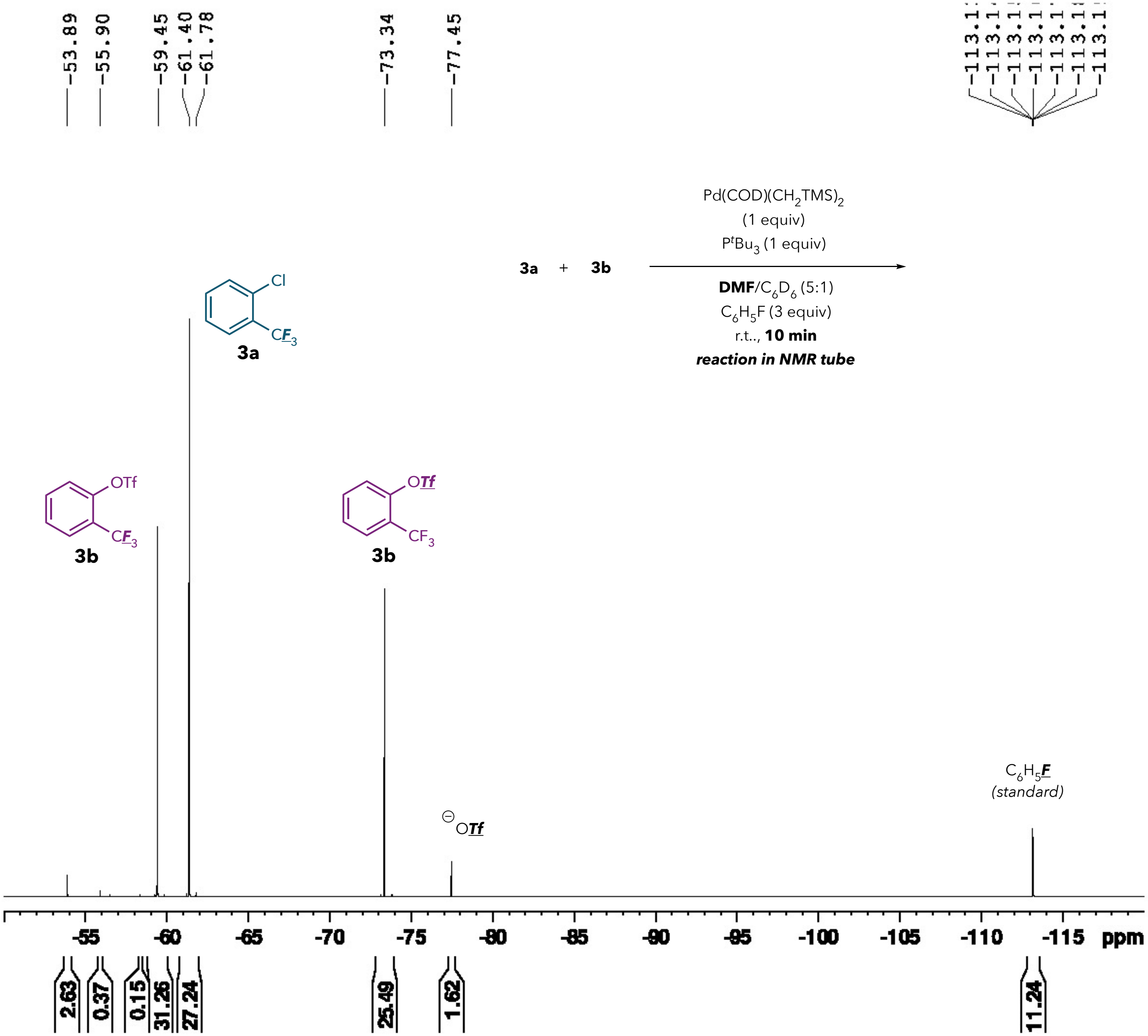
```
Current Data Parameters
NAME          6-SMR-42-8
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameter
Date_           20211117
Time             15.39 h
INSTRUM            spect
PROBHD   Z125869_0055 (
PULPROG          zgflqn
TD               131072
SOLVENT            C6D6
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                273.0 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          470.6859023 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\mathbf{DMF}/C_6D_6\ (5{:}1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \mathbf{0\ °C},\ 6\ \text{h}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

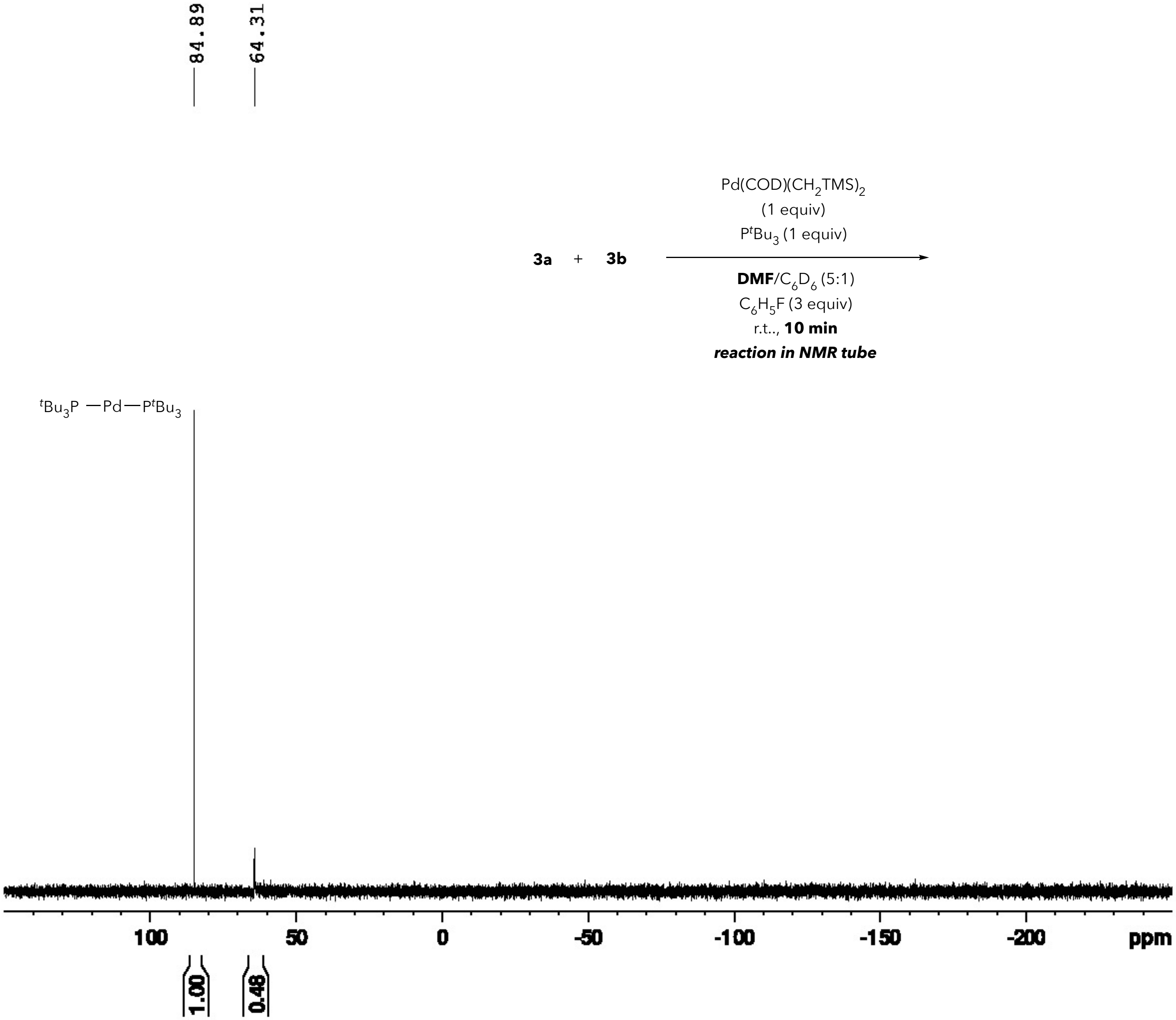


```
Current Data Parameters
NAME          6-SMR-42-8
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameter
Date_           20211117
Time               15.37 h
INSTRUM            spect
PROBHD    Z125869_0055 (
PULPROG          zgpg30
TD                65536
SOLVENT            C6D6
NS                   16
DS                    4
SWH          81521.742 Hz
FIDRES        2.487846 Hz
AQ           0.4019541 sec
RG              190.44
DW               6.133 usec
DE               18.00 usec
TE               273.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1
SFO1       202.4866909 MHz
NUC1                31P
P0                 4.00 usec
P1                12.00 usec
PLW1        40.26200104 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         202.4968157 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

3. Monitoring the Reaction in DMF over Time

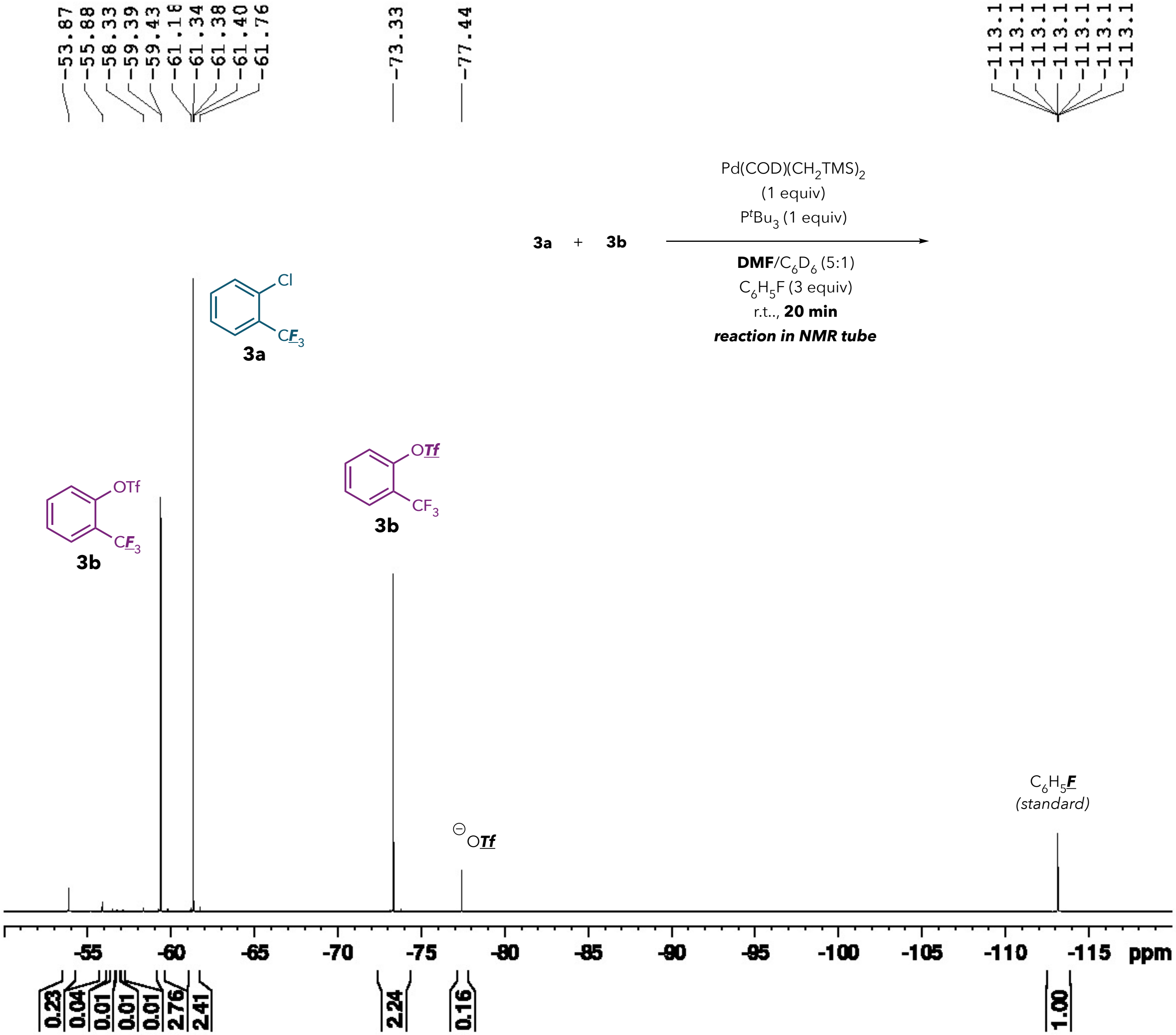


```
Current Data Parameters
NAME        6-SMR-43-5min
EXPNO                  10
PROCNO                  2

F2 - Acquisition Parameter
Date_            20211117
Time               9.05 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG            zgflqn
TD                 131072
SOLVENT              C6D6
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            470.6858694 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



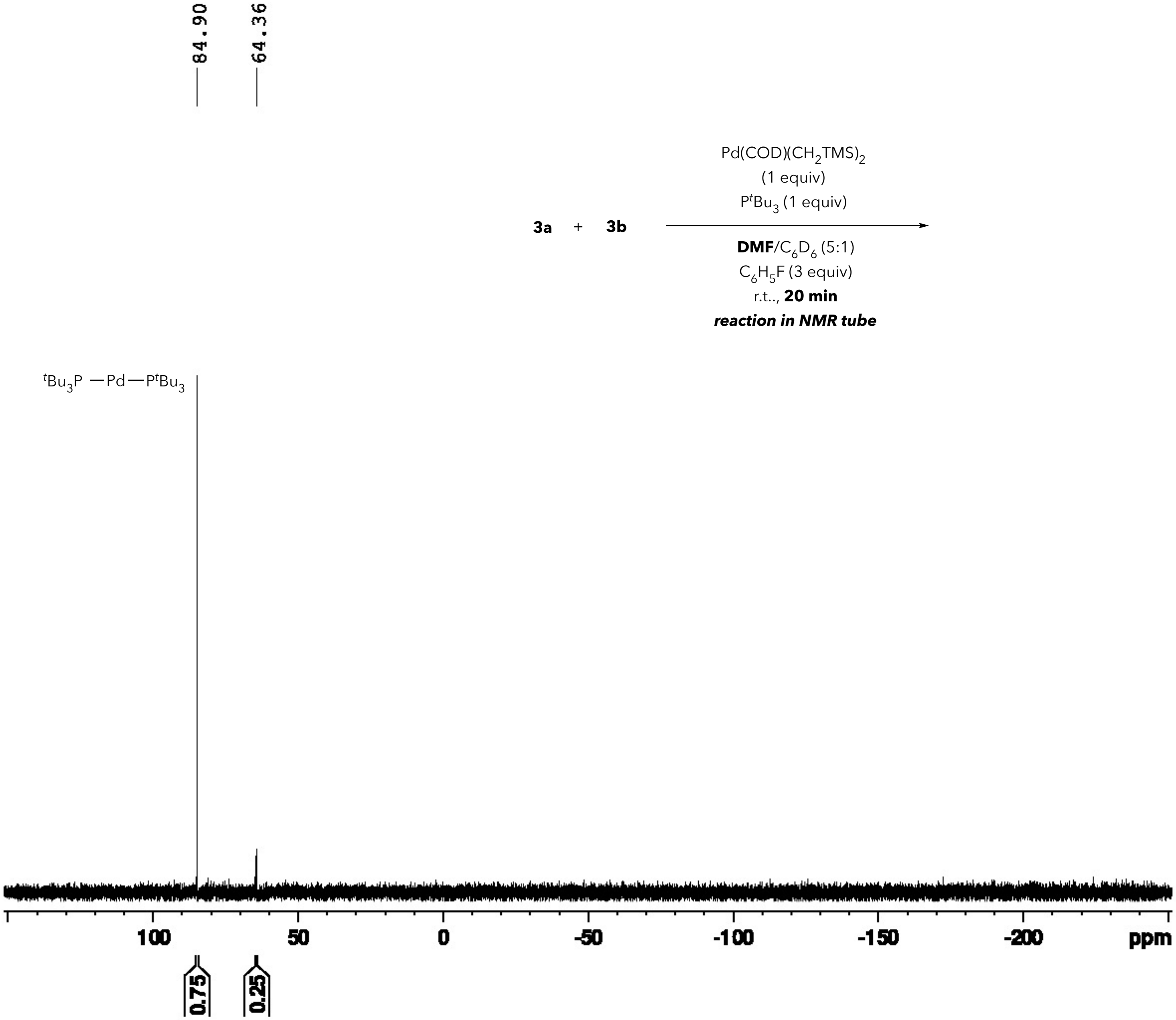
$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\textbf{DMF}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t.., } \textbf{10 min} \\ \textbf{\textit{reaction in NMR tube}}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^{t}Bu_3\ (1\ \text{equiv})}}$$

```
Current Data Parameters
NAME         6-SMR-43-5min
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameter
Date_             20211117
Time                9.09 h
INSTRUM              spect
PROBHD     Z125869_0055 (
PULPROG            zgpg30
TD                   65536
SOLVENT               C6D6
NS                      16
DS                       4
SWH           81521.742 Hz
FIDRES         2.487846 Hz
AQ            0.4019541 sec
RG                  190.44
DW               6.133 usec
DE               18.00 usec
TE                 298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                      1
SFO1        202.4866909 MHz
NUC1                   31P
P0                4.00 usec
P1               12.00 usec
PLW1         40.26200104 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          202.4968157 MHz
WDW                     EM
SSB      0
LB                 1.00 Hz
GB       0
PC                    1.40
```

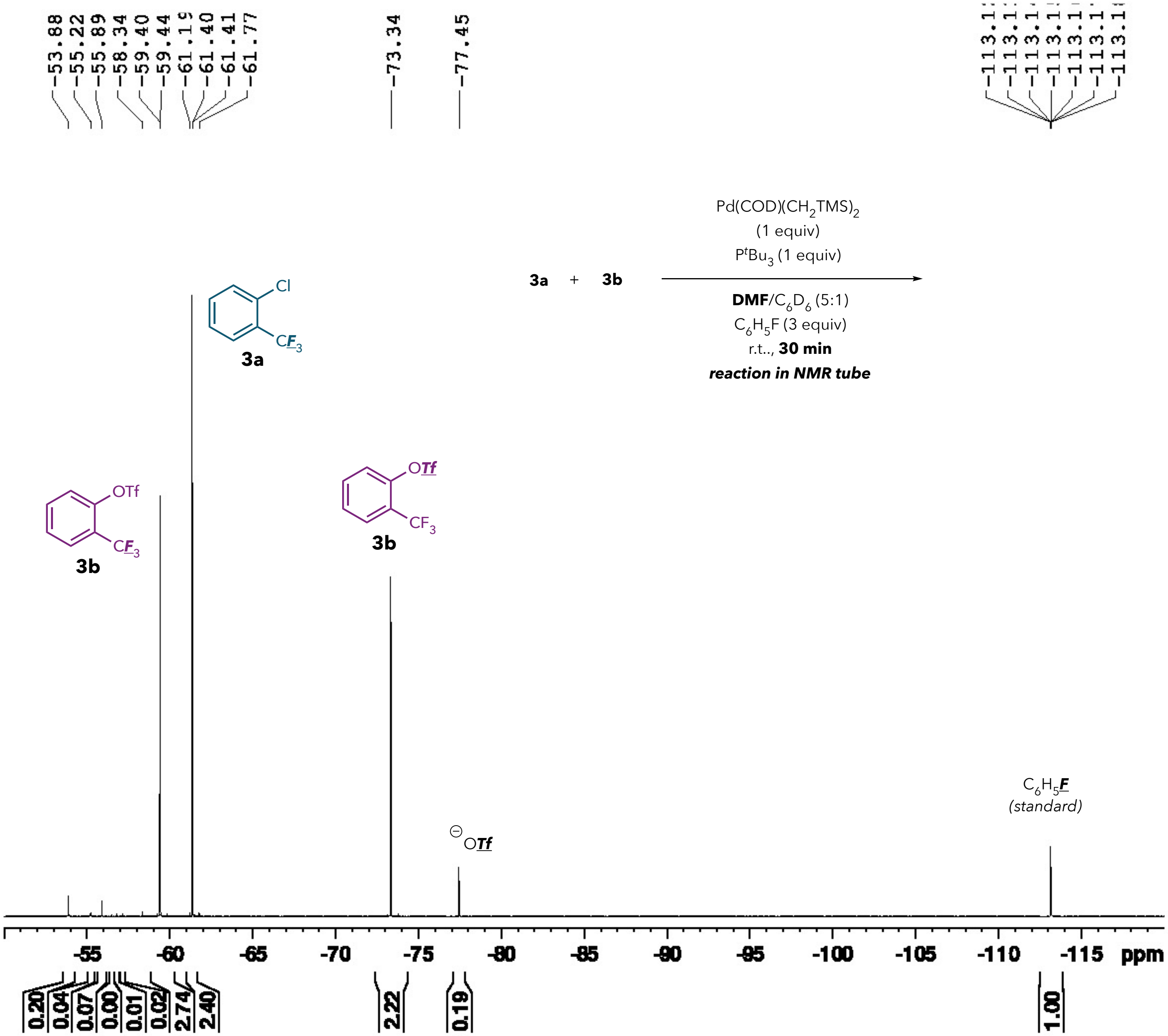


```
Current Data Parameters
NAME        6-SMR-43-10min
EXPNO                   10
PROCNO                   2

F2 - Acquisition Parameter
Date_             20211117
Time                9.12 h
INSTRUM              spect
PROBHD   Z125869_0055 (
PULPROG             zgflqn
TD                  131072
SOLVENT               C6D6
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             470.6858608 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\mathbf{DMF}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t., } \mathbf{20\ min} \\ \textbf{\textit{reaction in NMR tube}}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

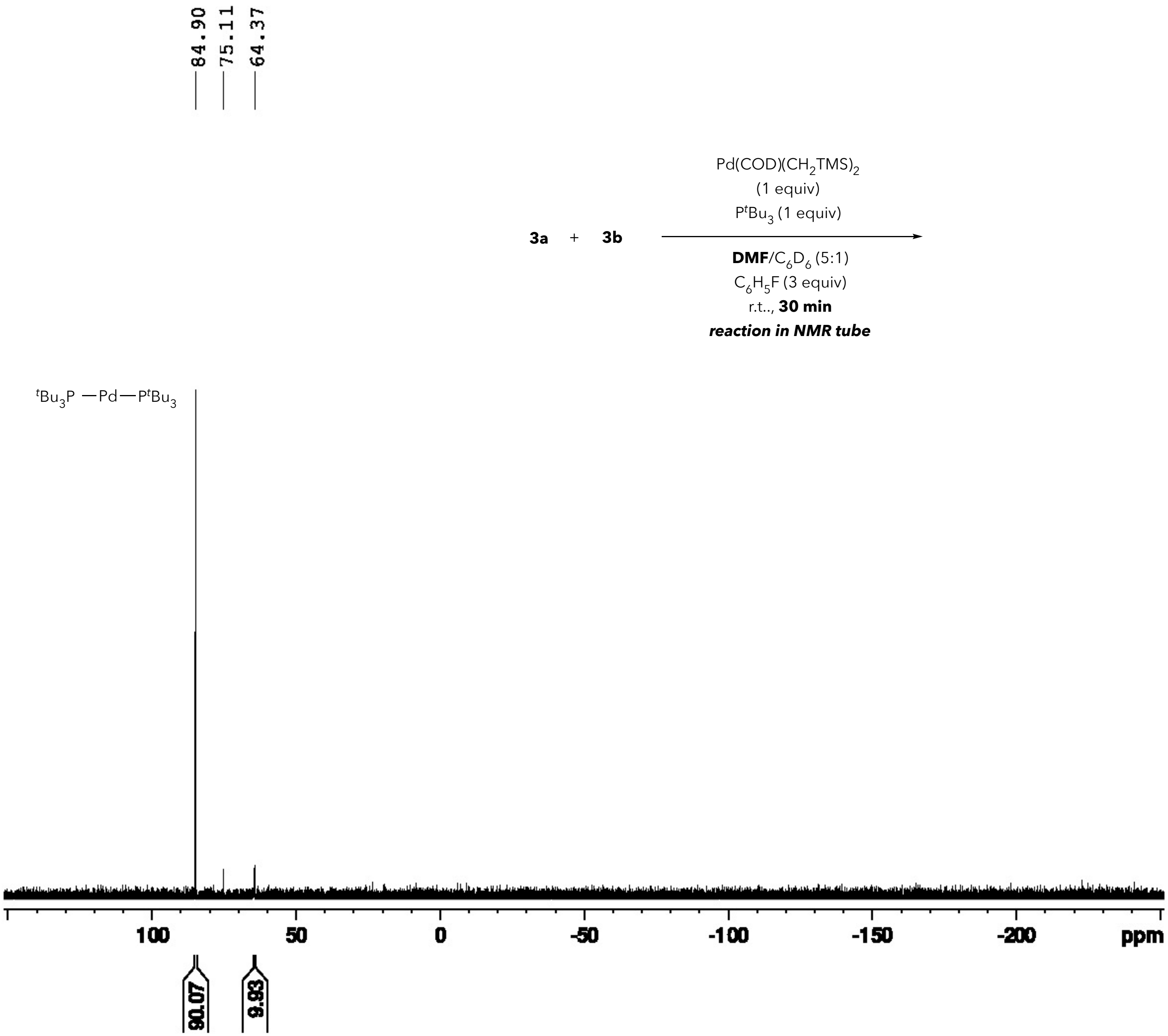


```
Current Data Parameters
NAME        6-SMR-43-10min
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameter
Date_             20211117
Time                9.17 h
INSTRUM              spect
PROBHD    Z125869_0055 (
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                     16
DS                      4
SWH          81521.742 Hz
FIDRES        2.487846 Hz
AQ           0.4019541 sec
RG                 190.44
DW              6.133 usec
DE              18.00 usec
TE                298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                     1
SFO1       202.4866909 MHz
NUC1                  31P
P0               4.00 usec
P1              12.00 usec
PLW1        40.26200104 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         202.4968157 MHz
WDW                    EM
SSB      0
LB                1.00 Hz
GB       0
PC                   1.40
```

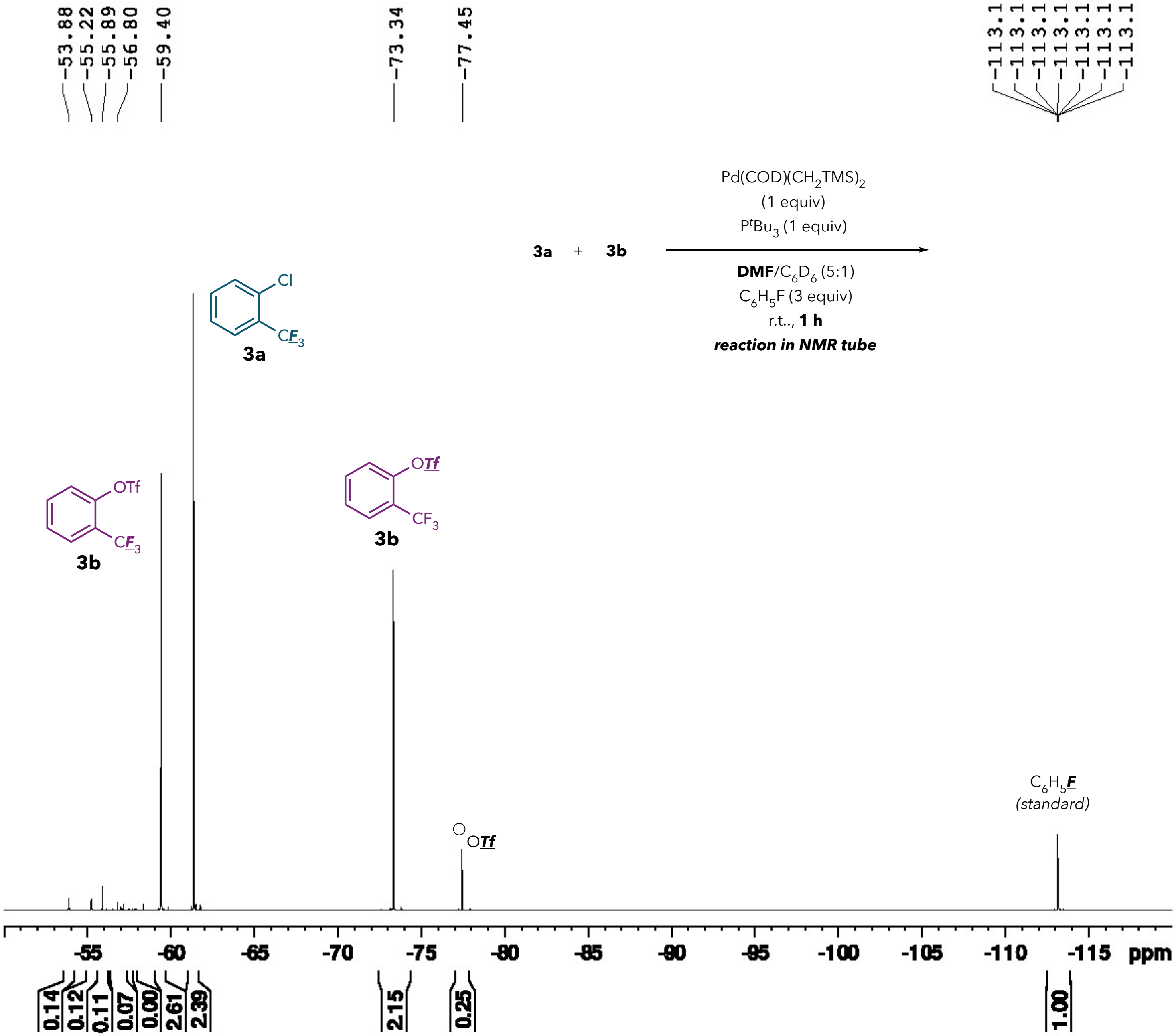


```
Current Data Parameters
NAME     6-SMR-43-30min
EXPNO              10
PROCNO              2

F2 - Acquisition Parameter
Date_          20211117
Time               9.26 h
INSTRUM           spect
PROBHD   Z125869_0055 (
PULPROG          zgflqn
TD               131072
SOLVENT            C6D6
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          470.6858658 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

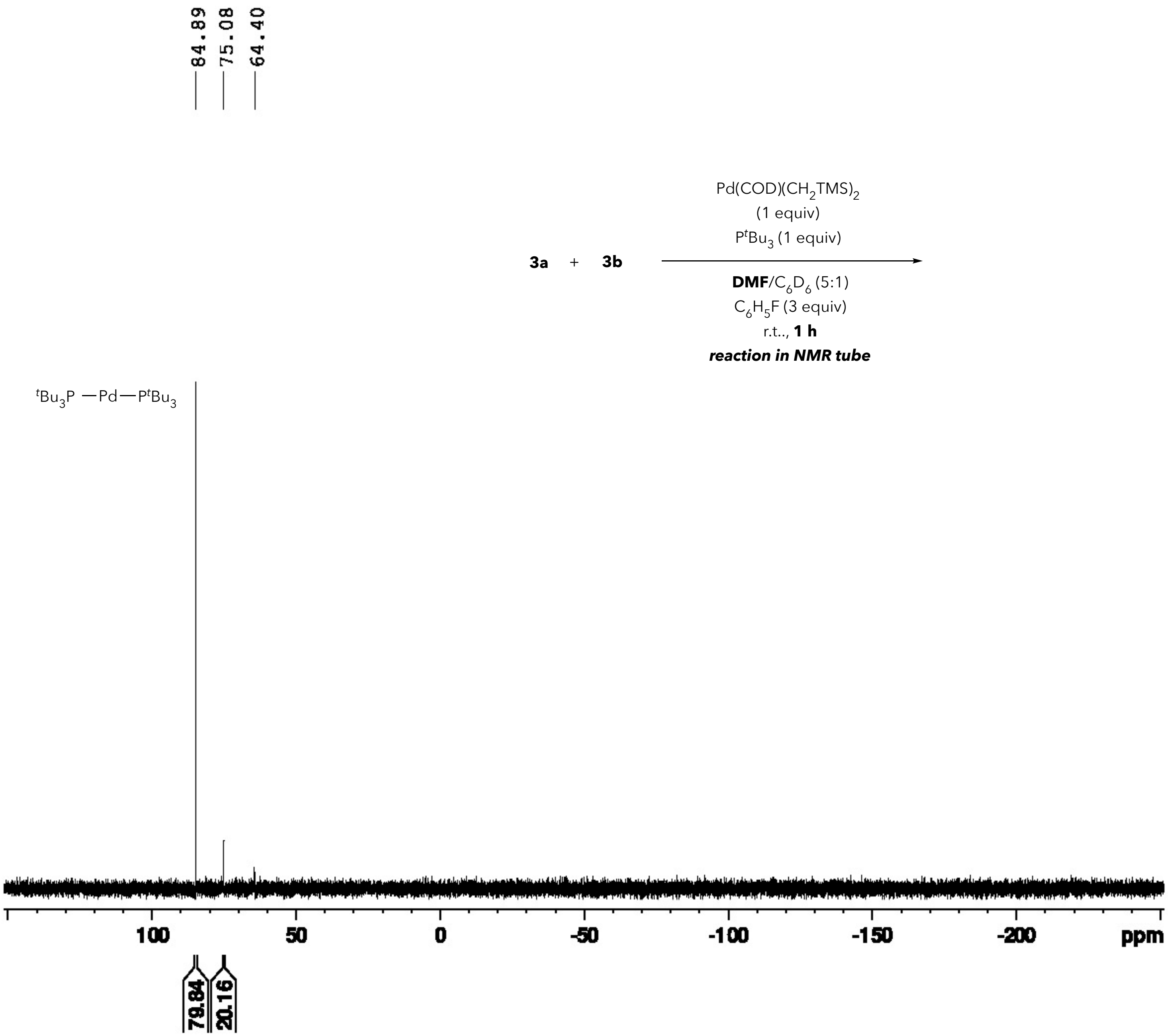
$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\mathbf{DMF}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t.},\ \mathbf{30\ min} \\ \textit{reaction in NMR tube}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$



```
Current Data Parameters
NAME       6-SMR-43-30min
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211117
Time                 9.29 h
INSTRUM              spect
PROBHD       Z125869_0055 (
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                     16
DS                      4
SWH            81521.742 Hz
FIDRES          2.487846 Hz
AQ             0.4019541 sec
RG                 190.44
DW                  6.133 usec
DE                  18.00 usec
TE                  298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1
SFO1         202.4866909 MHz
NUC1                  31P
P0                   4.00 usec
P1                  12.00 usec
PLW1         40.26200104 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           202.4968157 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



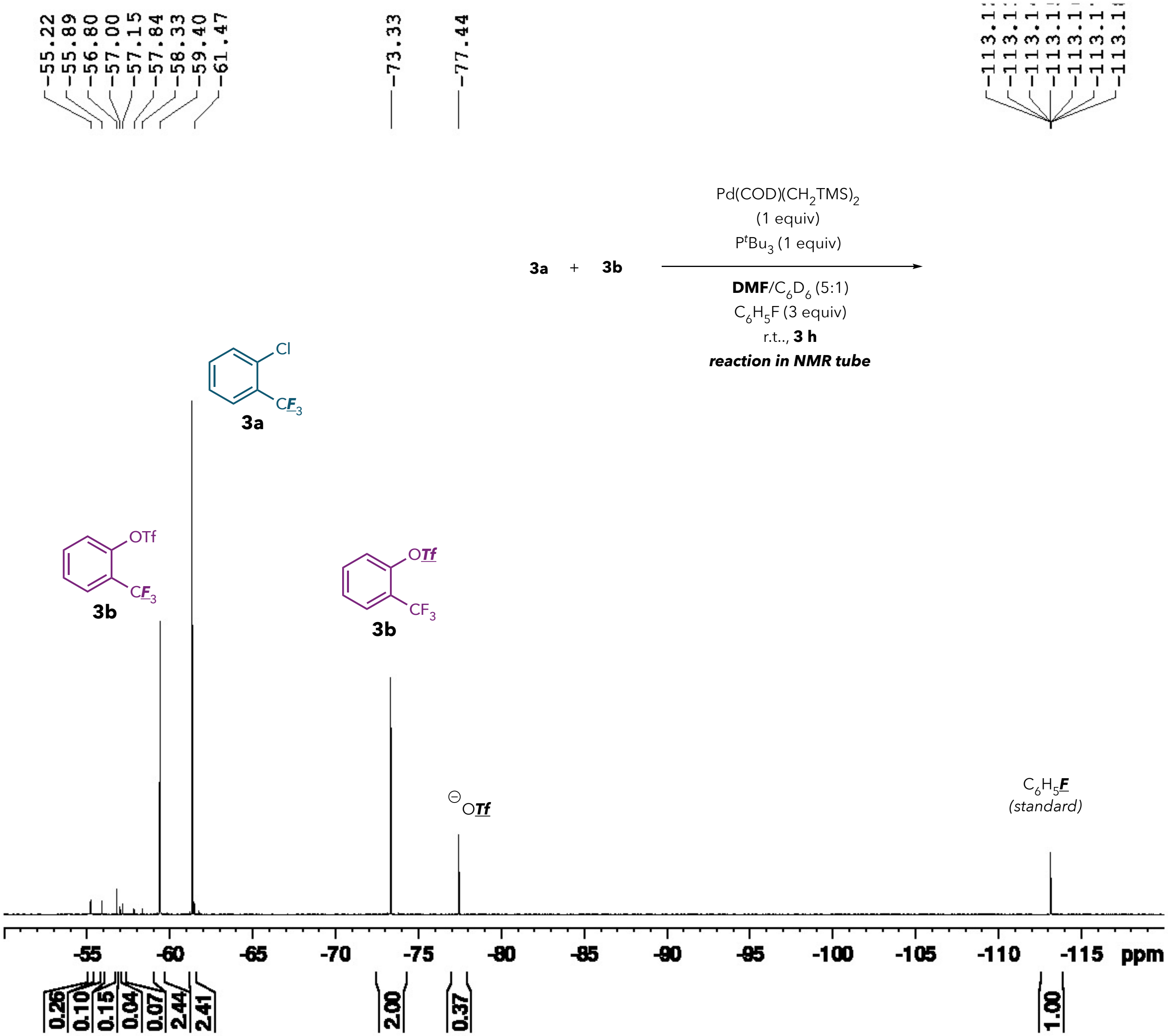
```
Current Data Parameters
NAME        6-SMR-43-1h
EXPNO                10
PROCNO                2

F2 - Acquisition Parameter
Date_          20211117
Time             9.56 h
INSTRUM           spect
PROBHD   Z125869_0055 (
PULPROG          zgflqn
TD               131072
SOLVENT            C6D6
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          470.6858656 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



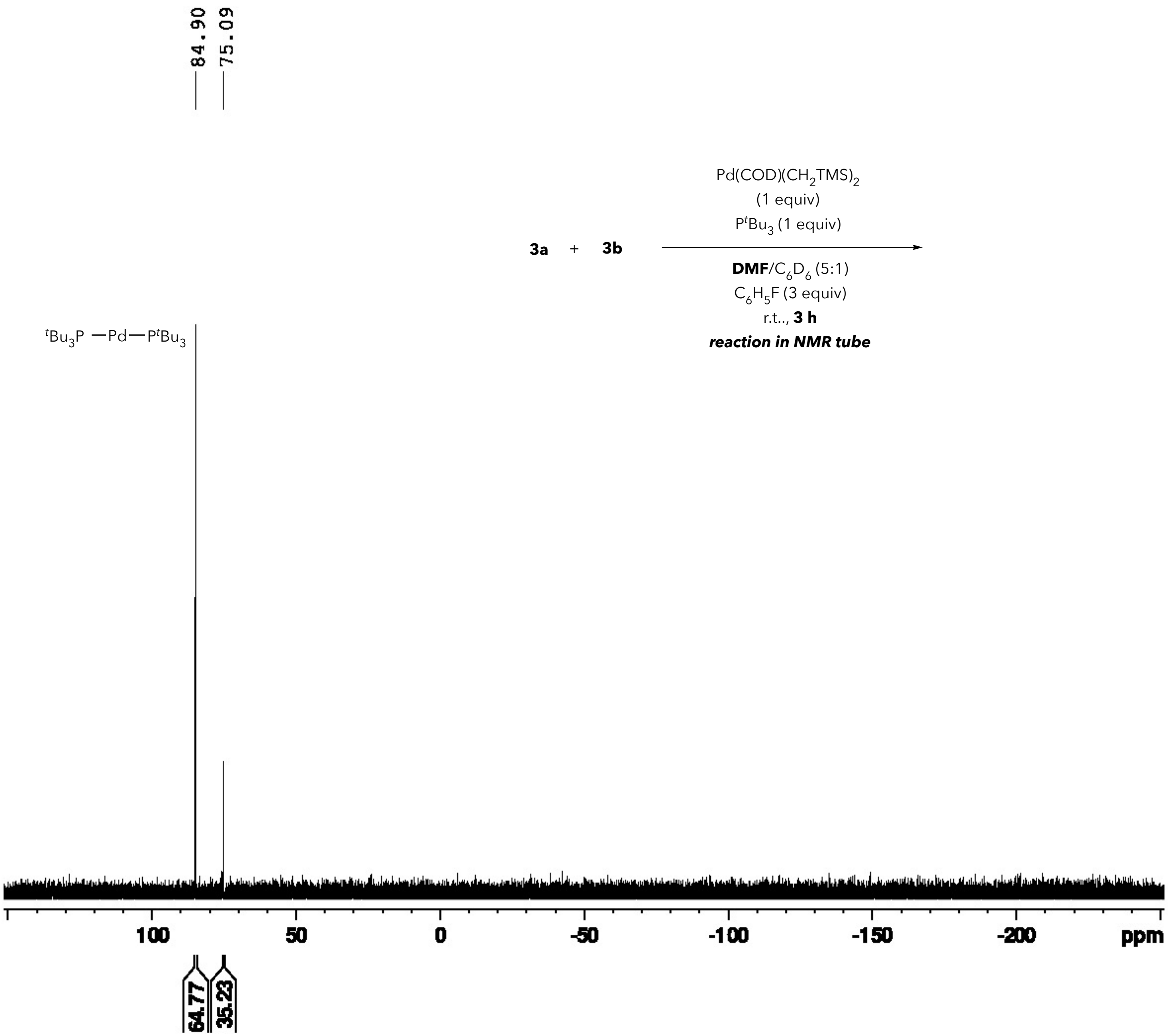
$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\mathbf{DMF}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t.., } \mathbf{1\ h} \\ \textit{\textbf{reaction in NMR tube}}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

$^tBu_3P—Pd—P^tBu_3$

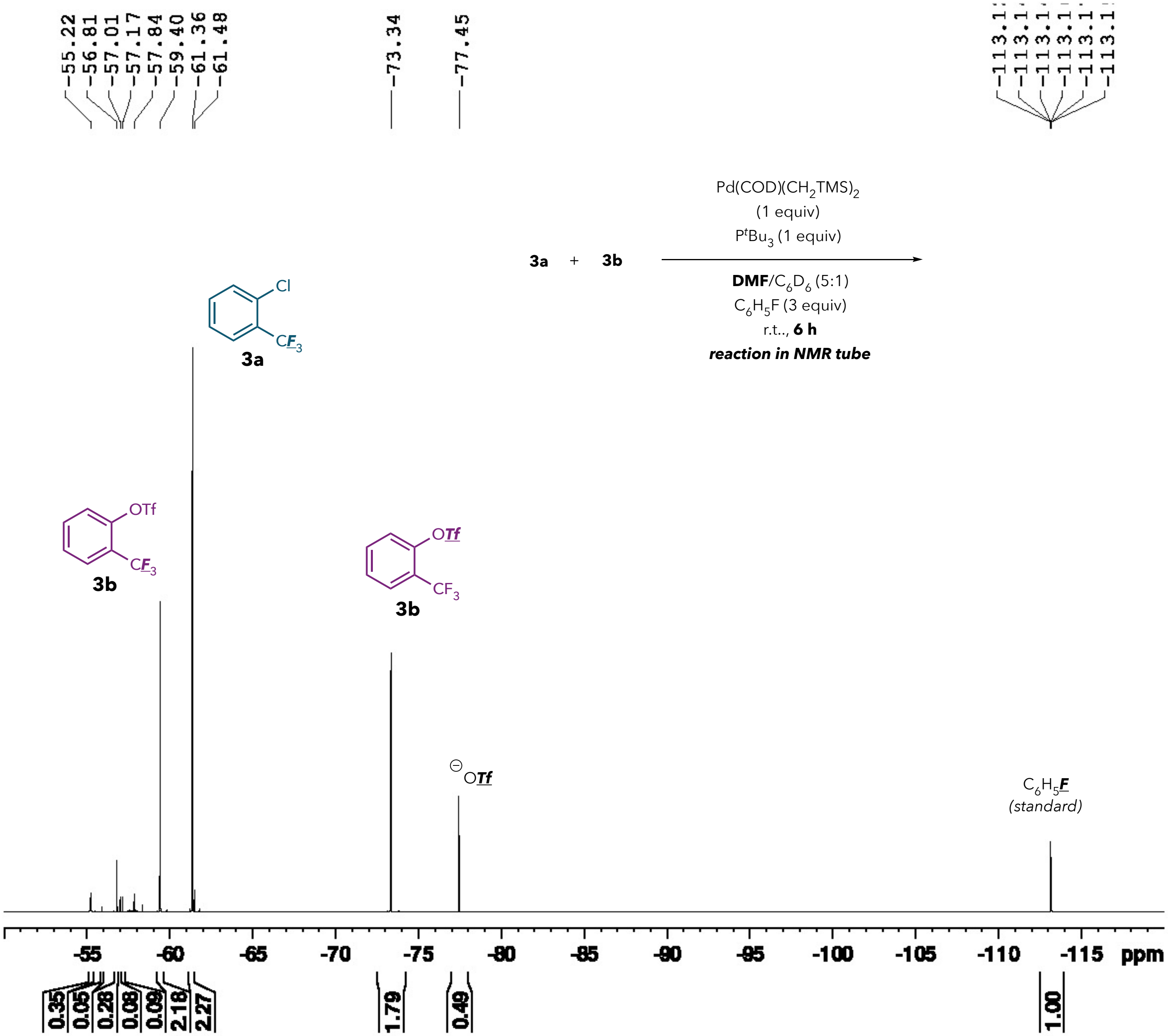
```
Current Data Parameters
NAME        6-SMR-43-1h
EXPNO                11
PROCNO                1

F2 - Acquisition Parameter
Date_          20211117
Time             9.59 h
INSTRUM           spect
PROBHD   Z125869_0055 (
PULPROG         zgpg30
TD               65536
SOLVENT           C6D6
NS                  16
DS                   4
SWH         81521.742 Hz
FIDRES       2.487846 Hz
AQ          0.4019541 sec
RG              190.44
DW               6.133 usec
DE               18.00 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1
SFO1       202.4866909 MHz
NUC1               31P
P0                4.00 usec
P1               12.00 usec
PLW1       40.26200104 W
SFO2       500.2320009 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            80.00 use
PLW2       11.44699955 W
PLW12       0.25756001 W
PLW13       0.12955000 W

F2 - Processing parameters
SI               32768
SF         202.4968157 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```



```
Current Data Parameters
NAME          6-SMR-43-3h
EXPNO                  10
PROCNO                  2

F2 - Acquisition Parameter
Date_            20211117
Time                11.59 h
INSTRUM             spect
PROBHD    Z125869_0055 (
PULPROG            zgflqn
TD                 131072
SOLVENT              C6D6
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           470.6858650 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



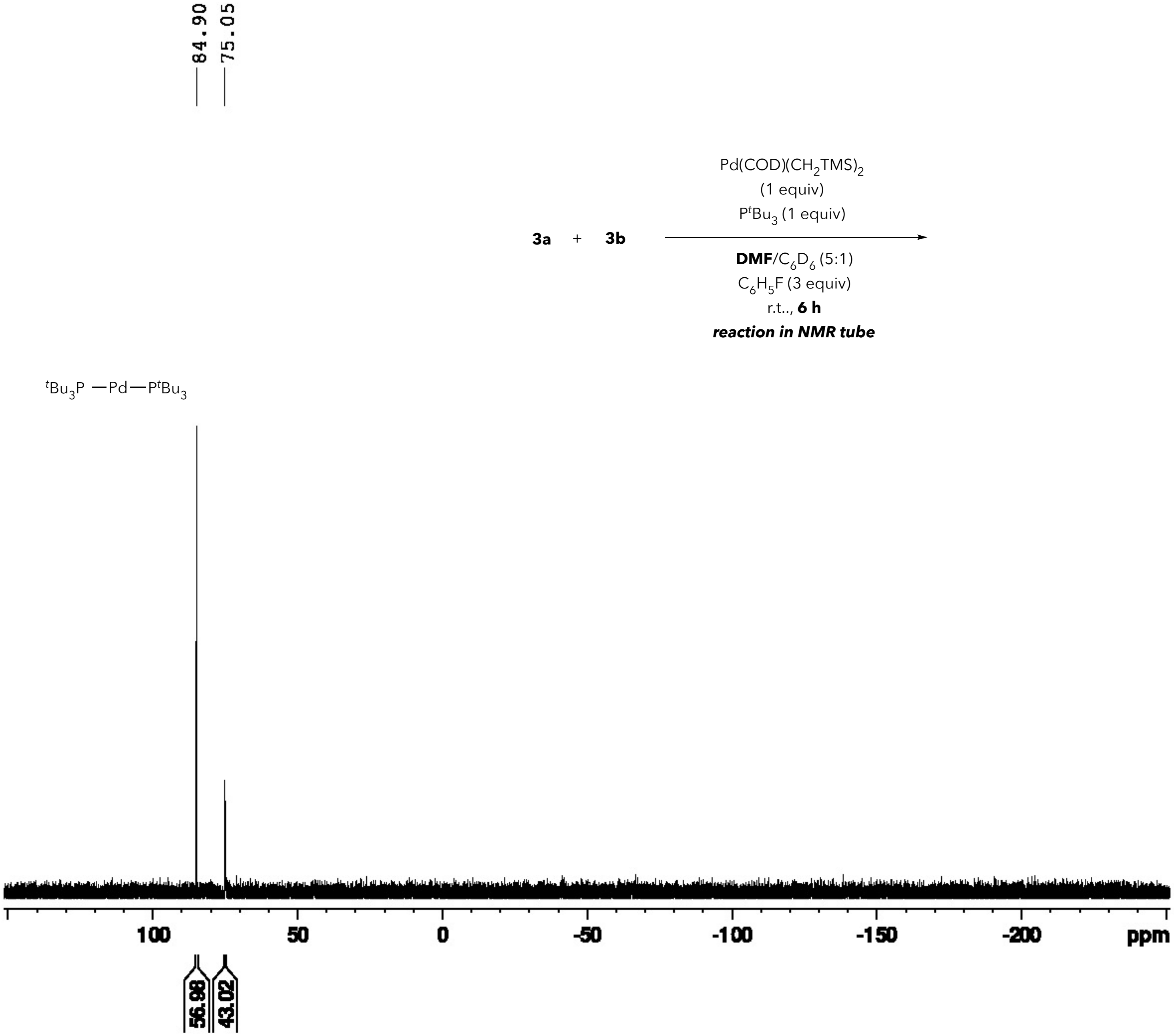
```
Current Data Parameters
NAME          6-SMR-43-3h
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211117
Time                12.03 h
INSTRUM              spect
PROBHD      Z125869_0055 (
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                     16
DS                      4
SWH           81521.742 Hz
FIDRES         2.487846 Hz
AQ            0.4019541 sec
RG                 190.44
DW                 6.133 usec
DE                 18.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1
SFO1         202.4866909 MHz
NUC1                  31P
P0                  4.00 usec
P1                 12.00 usec
PLW1         40.26200104 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           202.4968157 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



```
Current Data Parameters
NAME         6-SMR-43-65
EXPNO                 10
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211117
Time               15.03 h
INSTRUM            spect
PROBHD    Z125869_0055 (
PULPROG           zgflqn
TD                131072
SOLVENT             C6D6
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           470.6858683 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

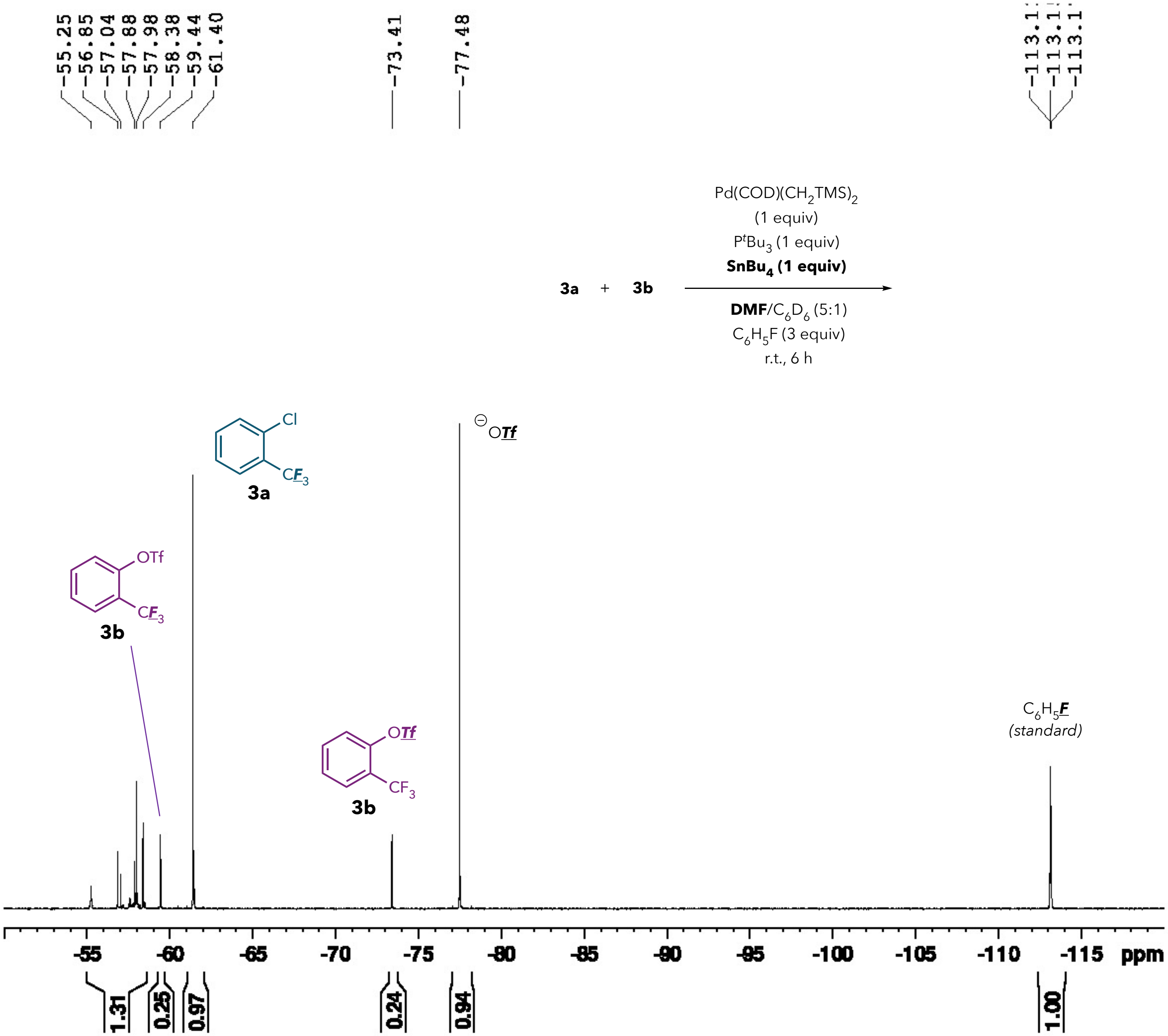
$$\mathbf{3a} + \mathbf{3b} \xrightarrow[\substack{\textbf{DMF}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t.., } \mathbf{6\ h} \\ \textbf{\textit{reaction in NMR tube}}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

$^tBu_3P$ —Pd— P^tBu_3

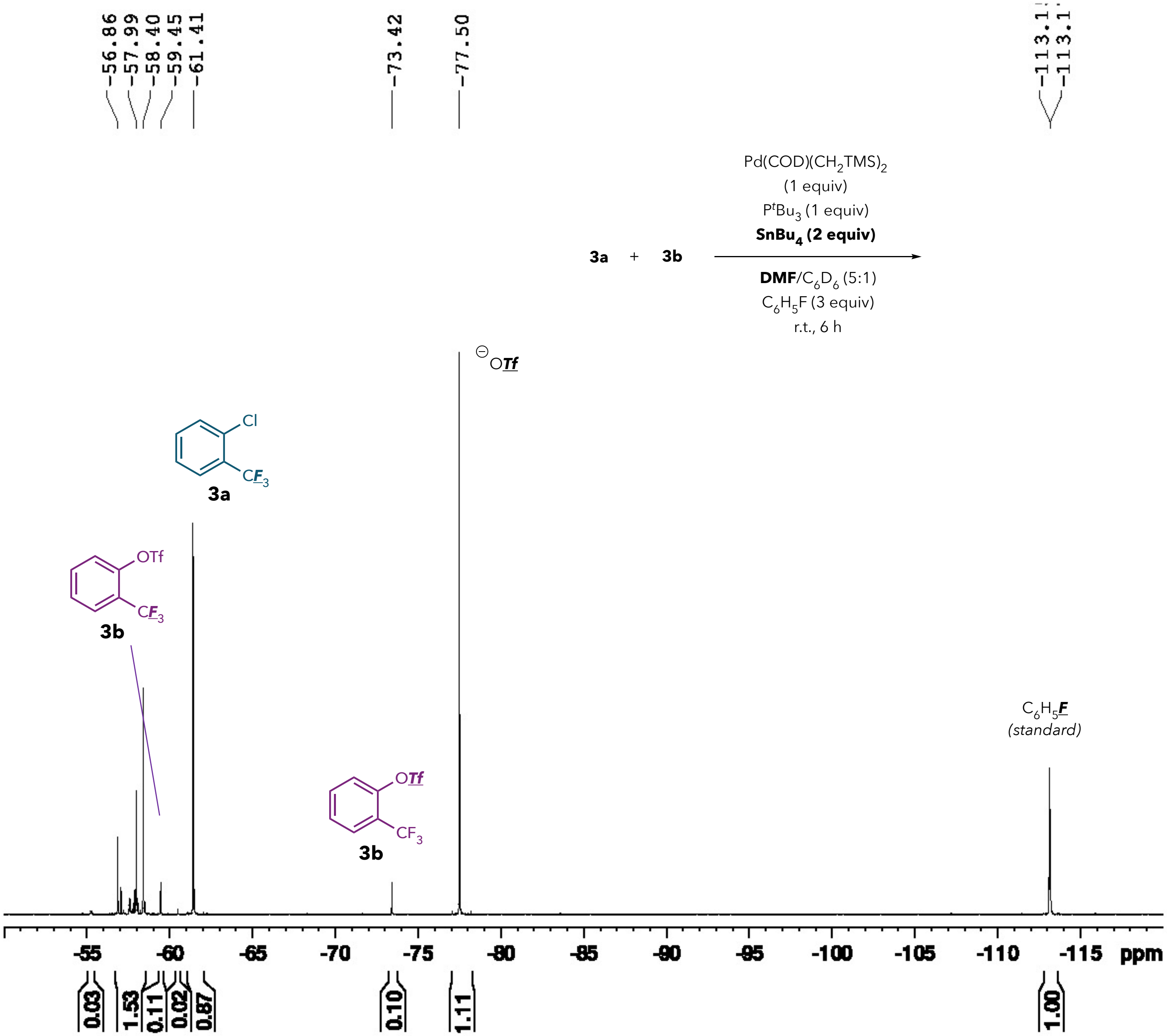


```
Current Data Parameters
NAME          6-SMR-43-65
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_          20211117
Time              15.06 h
INSTRUM             spect
PROBHD     Z125869_0055 (
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                     16
DS                      4
SWH          81521.742 Hz
FIDRES        2.487846 Hz
AQ           0.4019541 sec
RG                 190.44
DW              6.133 usec
DE              18.00 usec
TE                298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                     1
SFO1       202.4866909 MHz
NUC1                  31P
P0               4.00 usec
P1              12.00 usec
PLW1        40.26200104 W
SFO2       500.2320009 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2           80.00 use
PLW2        11.44699955 W
PLW12        0.25756001 W
PLW13        0.12955000 W

F2 - Processing parameters
SI                  32768
SF         202.4968157 MHz
WDW                    EM
SSB      0
LB                1.00 Hz
GB       0
PC                   1.40
```

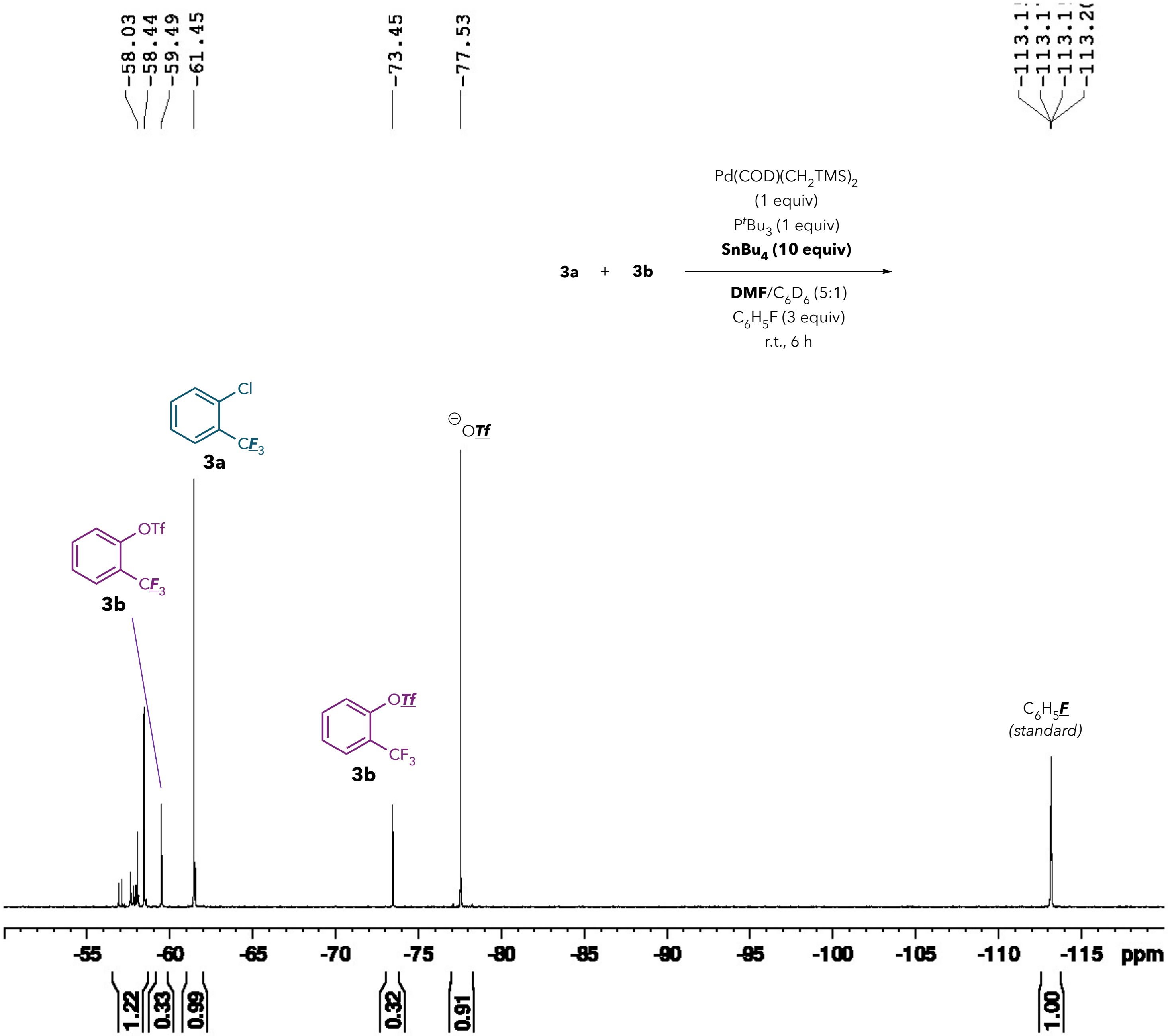
4. Reactions in the Presence of Additives



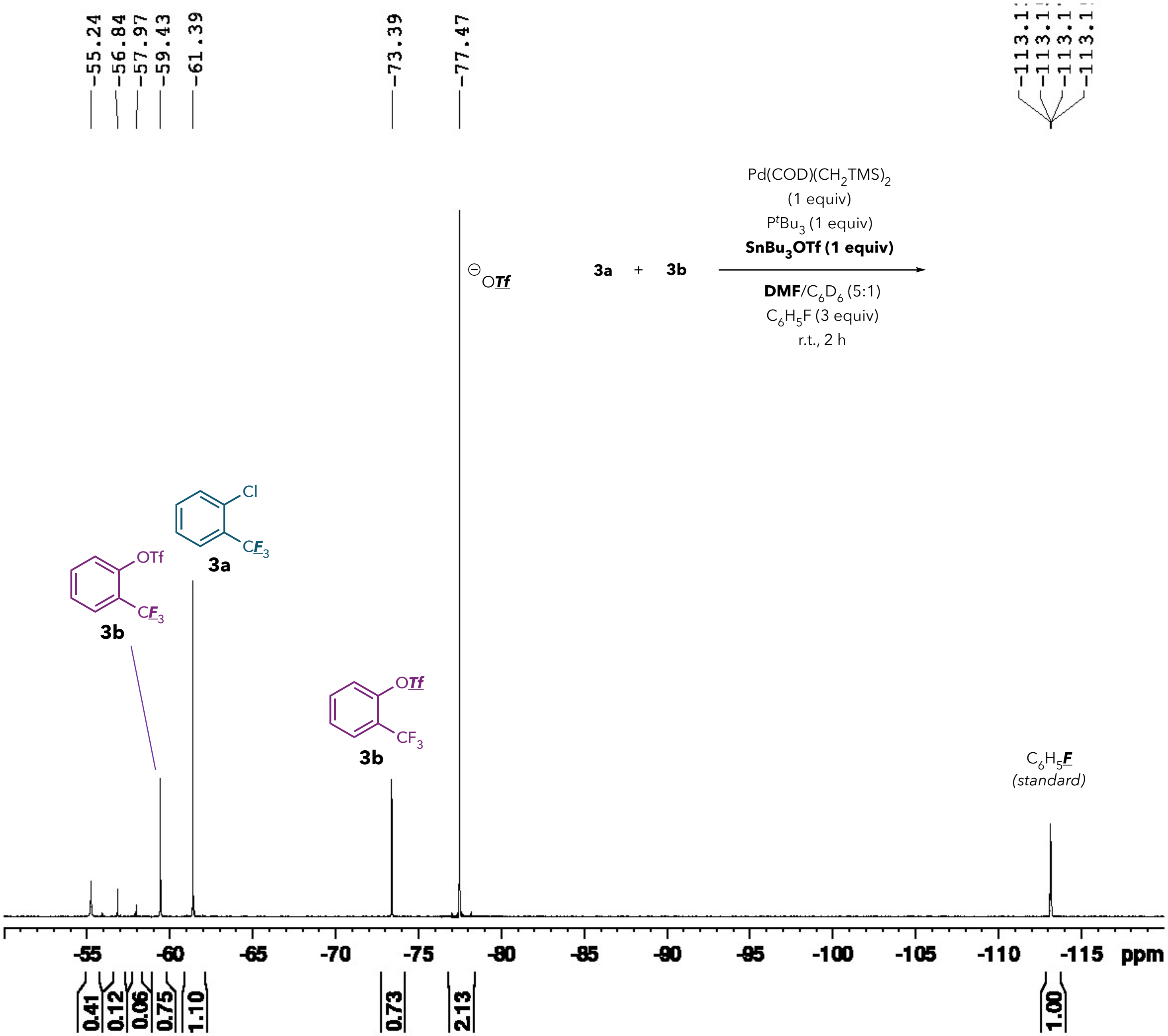
```
Current Data Parameters
NAME      ER-6-70-1_1SnBu4
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameter
Date_            20200831
Time                 7.31
INSTRUM             spect
PROBHD    5 mm QNP 1H/13
PULPROG            zgflqn
TD                  32768
SOLVENT              C6D6
NS                     64
DS                      0
SWH          50125.312 Hz
FIDRES        1.529703 Hz
AQ          0.3268608 sec
RG                 3649.1
DW            9.975 usec
DE             6.00 usec
TE                683.2 K
D1         1.50000000 sec
TD0                     1

======= CHANNEL f1 =======
NUC1                  19F
P1             9.00 usec
PL1       0 dB
SFO1      282.4250465 MHz

F2 - Processing parameters
SI                  65536
SF         282.4416810 MHz
WDW                    EM
SSB       0
LB                0.30 Hz
GB        0
PC                   1.00
```



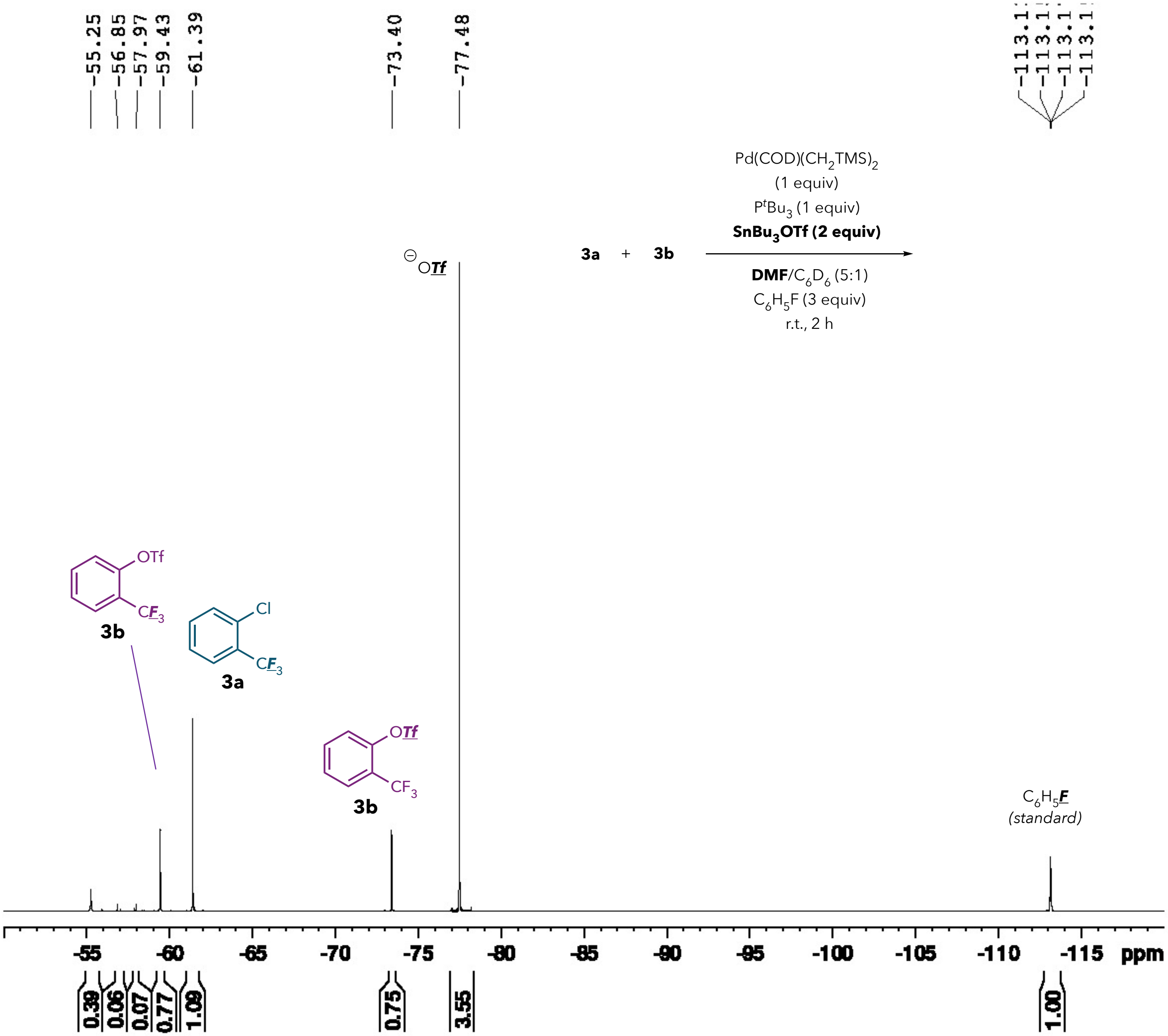
```
Current Data Parameters
NAME      ER-6-70-3_2SnBu4
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameter
Date_             20200831
Time                  7.37
INSTRUM              spect
PROBHD     5 mm QNP 1H/13
PULPROG             zgflqn
TD                   32768
SOLVENT               C6D6
NS                      64
DS                       0
SWH           50125.312 Hz
FIDRES         1.529703 Hz
AQ           0.3268608 sec
RG                  3649.1
DW               9.975 usec
DE                6.00 usec
TE                 683.2 K
D1          1.50000000 sec
TD0                      1

======= CHANNEL f1 =======
NUC1                   19F
P1                9.00 usec
PL1       0 dB
SFO1        282.4250465 MHz

F2 - Processing parameters
SI                   65536
SF          282.4416834 MHz
WDW                     EM
SSB       0
LB                 0.30 Hz
GB        0
PC                    1.00
```



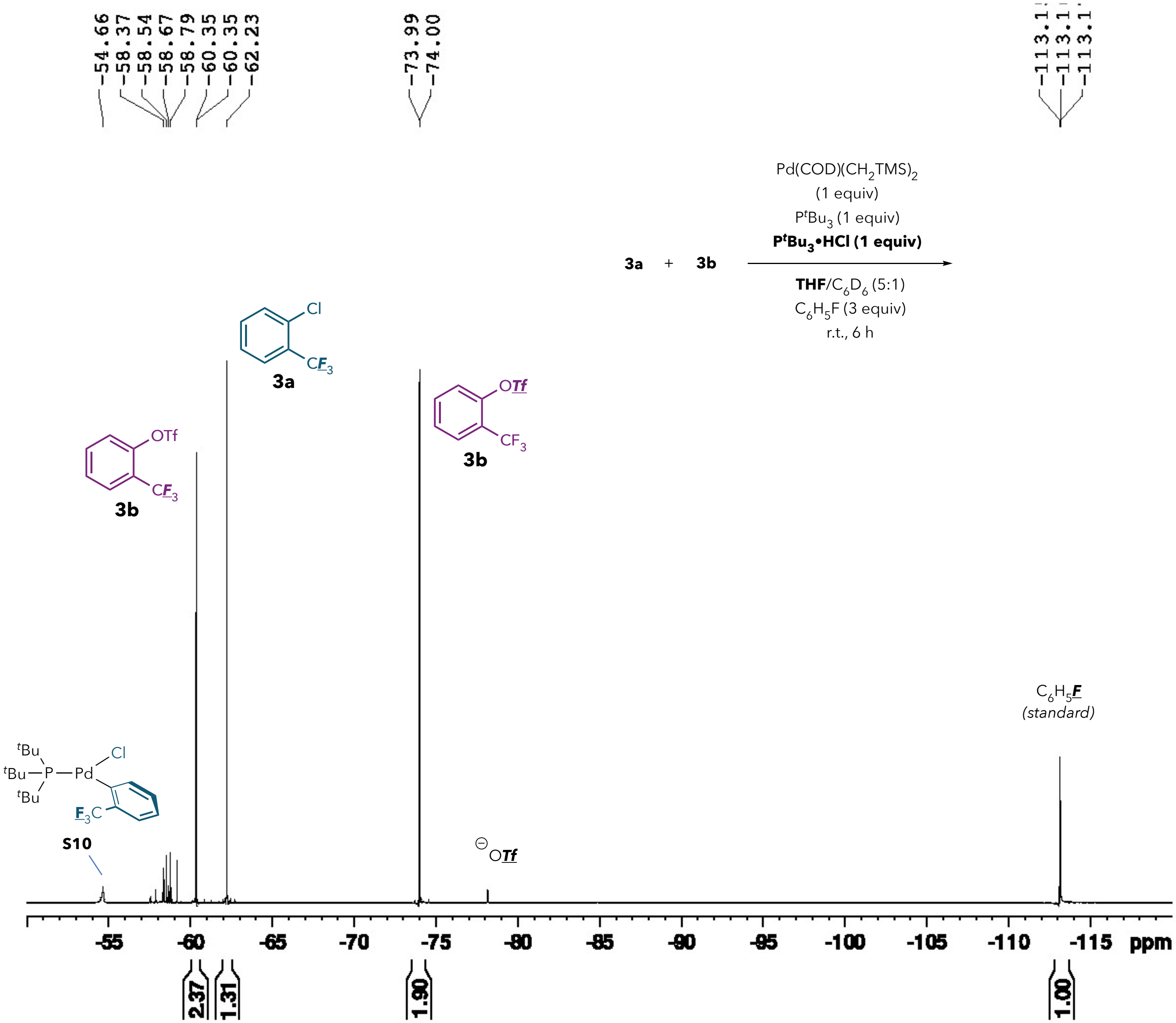
```
Current Data Parameters
NAME        ER-6-70-5_10SnBu4
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameter
Date_              20200831
Time                   7.43
INSTRUM               spect
PROBHD     5 mm QNP 1H/13
PULPROG              zgflqn
TD                    32768
SOLVENT                C6D6
NS                       64
DS                        0
SWH            50125.312 Hz
FIDRES          1.529703 Hz
AQ            0.3268608 sec
RG                   2580.3
DW                9.975 usec
DE                 6.00 usec
TE                  683.2 K
D1            1.50000000 sec
TD0                       1

======= CHANNEL f1 =======
NUC1                    19F
P1                 9.00 usec
PL1         0 dB
SFO1          282.4250465 MHz

F2 - Processing parameters
SI                    65536
SF            282.4416899 MHz
WDW                      EM
SSB         0
LB                  0.30 Hz
GB          0
PC                     1.00
```



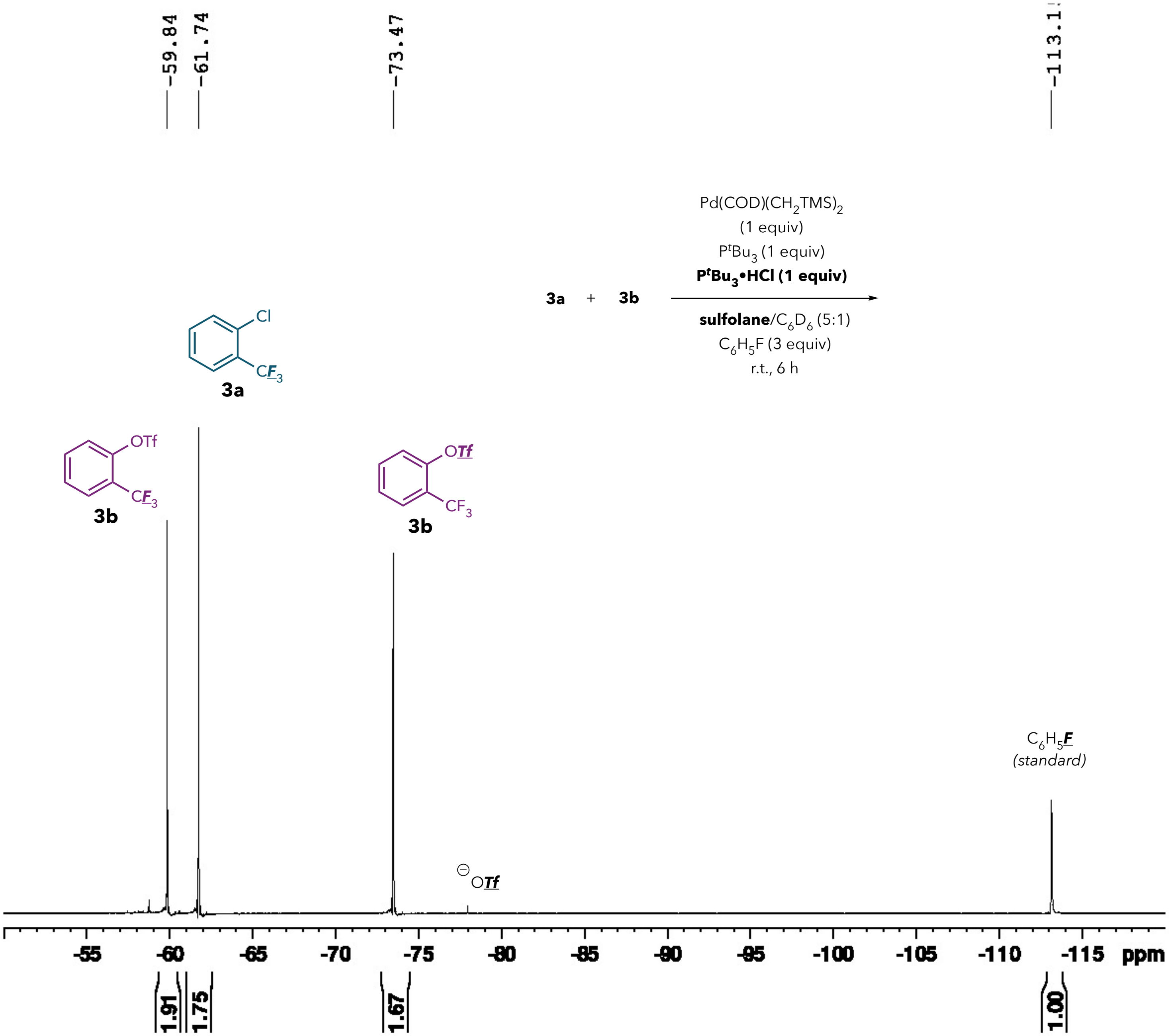
```
Current Data Parameters
NAME        ER-6-81_OA_1SnBu3OTf
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20201026
Time                    7.51
INSTRUM                spect
PROBHD     5 mm QNP 1H/13
PULPROG              zgflqn
TD                     32768
SOLVENT                C6D6
NS                        64
DS                         0
SWH             50125.312 Hz
FIDRES           1.529703 Hz
AQ              0.3268608 sec
RG                    2580.3
DW                 9.975 usec
DE                  6.00 usec
TE                   683.2 K
D1             1.50000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     19F
P1                 9.00 usec
PL1           0 dB
SFO1          282.4250465 MHz

F2 - Processing parameters
SI                     65536
SF            282.4416787 MHz
WDW                       EM
SSB           0
LB                   0.30 Hz
GB            0
PC                      1.00
```



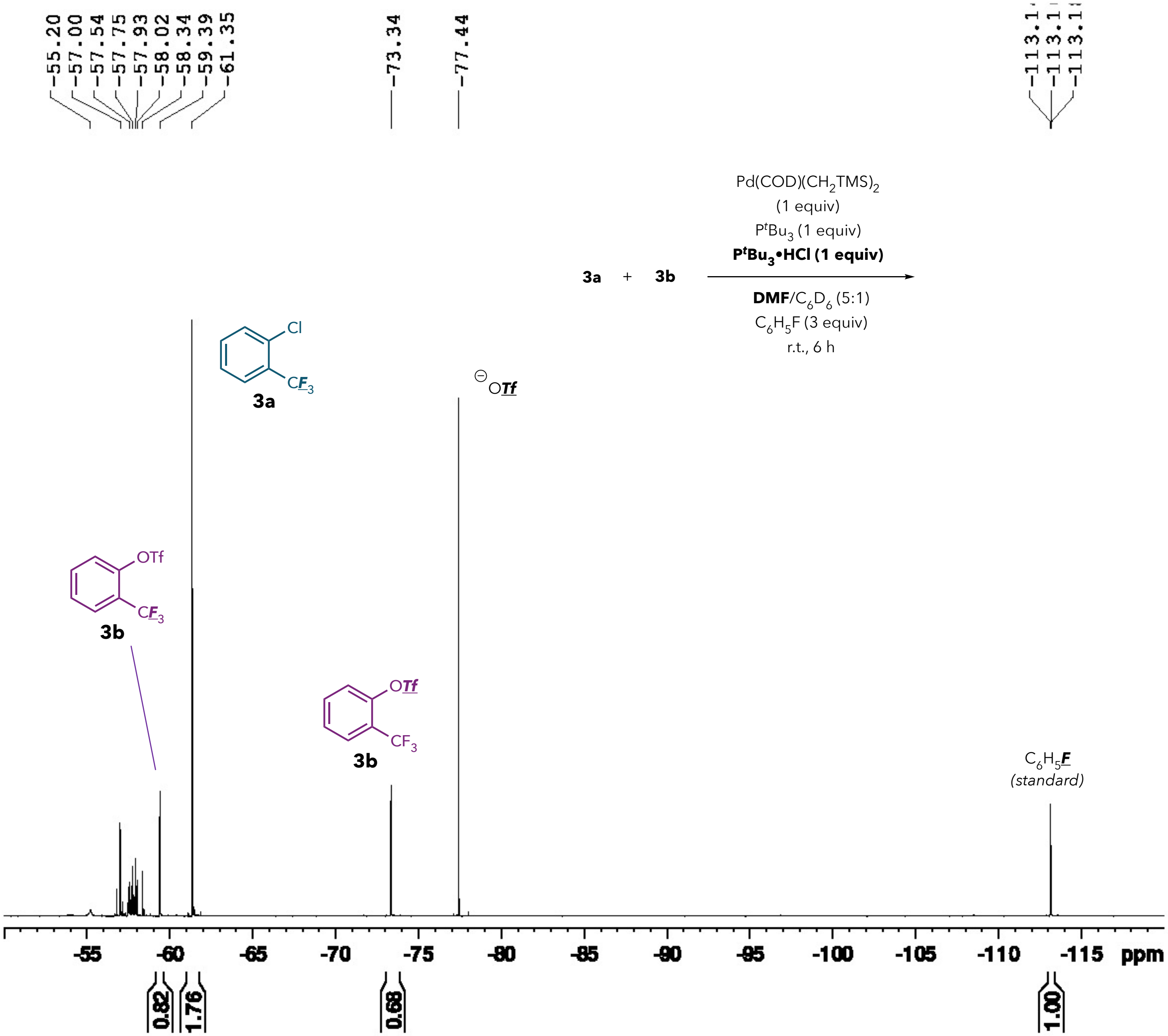
```
Current Data Parameters
NAME      ER-6-81_OA_2SnBu3OTf
EXPNO                        3
PROCNO                       1

F2 - Acquisition Parameters
Date_               20201026
Time                    7.55
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG               zgflqn
TD                     32768
SOLVENT                 C6D6
NS                        64
DS                         0
SWH             50125.312 Hz
FIDRES           1.529703 Hz
AQ             0.3268608 sec
RG                    2580.3
DW                 9.975 usec
DE                  6.00 usec
TE                   683.2 K
D1            1.50000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     19F
P1                 9.00 usec
PL1        0 dB
SFO1         282.4250465 MHz

F2 - Processing parameters
SI                     65536
SF           282.4416809 MHz
WDW                       EM
SSB        0
LB                   0.30 Hz
GB         0
PC                      1.00
```



```
Current Data Parameters
NAME             6-SMR-6-3
EXPNO                   10
PROCNO                   2

F2 - Acquisition Parameter
Date_             20210912
Time               17.49 h
INSTRUM          Avance Neo
PROBHD   Z152088_0031 (
PULPROG                 zg
TD                  130892
SOLVENT               C6D6
NS                      16
DS                       4
SWH            90909.094 Hz
FIDRES          1.389070 Hz
AQ             0.7199060 sec
RG                     101
DW                5.500 usec
DE                 6.50 usec
TE                  298.0 K
D1            1.00000000 sec
TD0                      1
SFO1         376.4607164 MHz
NUC1                   19F
P1                12.00 usec
PLW1         31.08900070 W

F2 - Processing parameters
SI                   65536
SF           376.4979689 MHz
WDW                     EM
SSB       0
LB                 0.30 Hz
GB        0
PC                    1.00
```

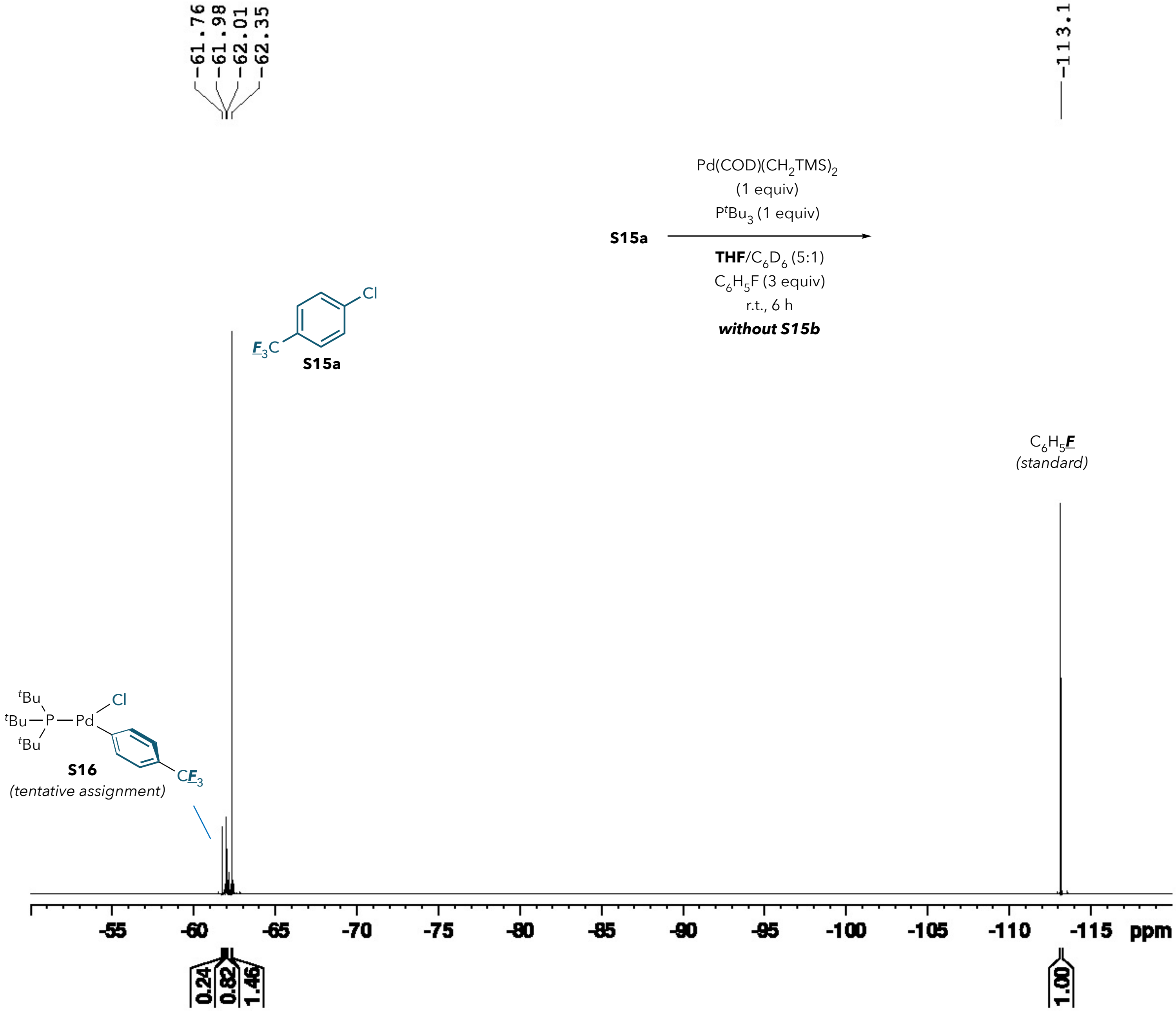


```
Current Data Parameters
NAME              6-SMR-6-7
EXPNO                    10
PROCNO                    2

F2 - Acquisition Parameter
Date_            20210912
Time                18.08 h
INSTRUM          Avance Neo
PROBHD    Z152088_0031 (
PULPROG                  zg
TD                   130892
SOLVENT                C6D6
NS                       16
DS                        4
SWH            90909.094 Hz
FIDRES          1.389070 Hz
AQ             0.7199060 sec
RG                      101
DW                5.500 usec
DE                 6.50 usec
TE                  298.0 K
D1          1.00000000 sec
TD0                       1
SFO1        376.4607164 MHz
NUC1                    19F
P1                12.00 usec
PLW1         31.08900070 W

F2 - Processing parameters
SI                    65536
SF          376.4982233 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.00
```

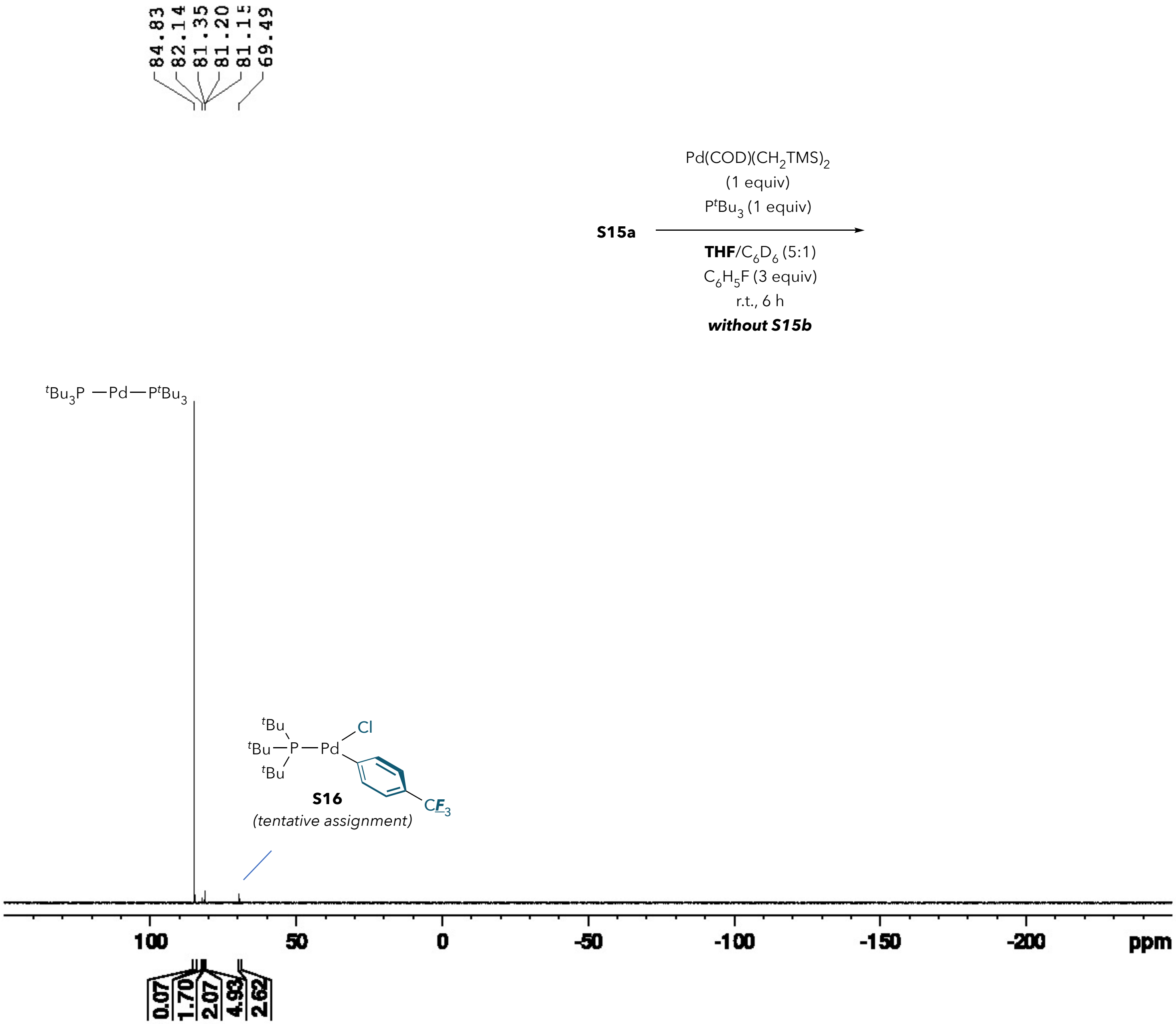


```
Current Data Parameters
NAME           6-SMR-6-11
EXPNO                  10
PROCNO                  2

F2 - Acquisition Parameter
Date_            20210912
Time              18.27 h
INSTRUM        Avance Neo
PROBHD   Z152088_0031 (
PULPROG                zg
TD                 130892
SOLVENT              C6D6
NS                     16
DS                      4
SWH          90909.094 Hz
FIDRES        1.389070 Hz
AQ          0.7199060 sec
RG                    101
DW              5.500 usec
DE               6.50 usec
TE                298.0 K
D1         1.00000000 sec
TD0                     1
SFO1       376.4607164 MHz
NUC1                  19F
P1              12.00 usec
PLW1        31.08900070 W

F2 - Processing parameters
SI                  65536
SF         376.4978866 MHz
WDW                    EM
SSB      0
LB                0.30 Hz
GB       0
PC                   1.00
```

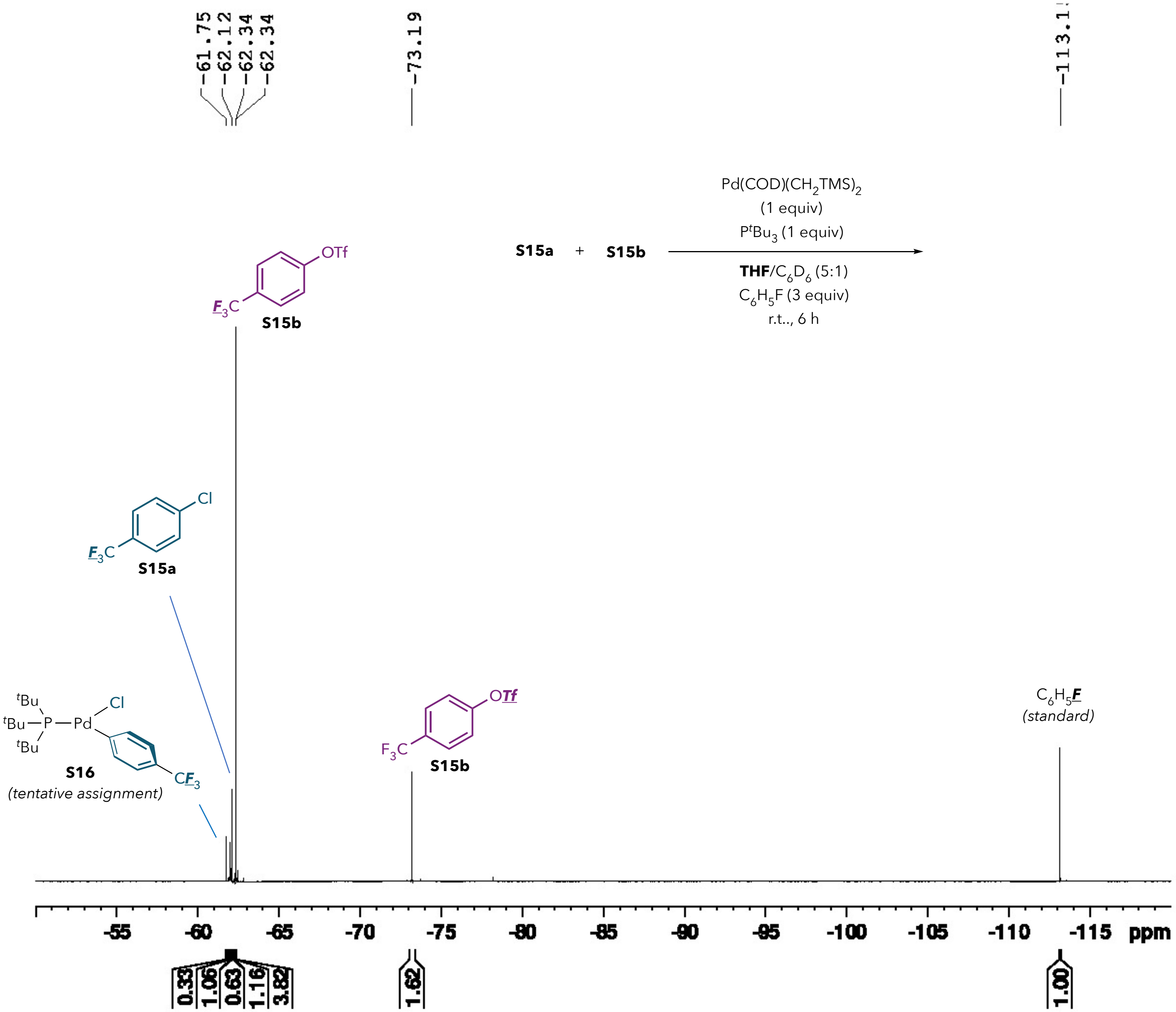
C. Stoichiometric Oxidative Addition Studies with S15a and S15b



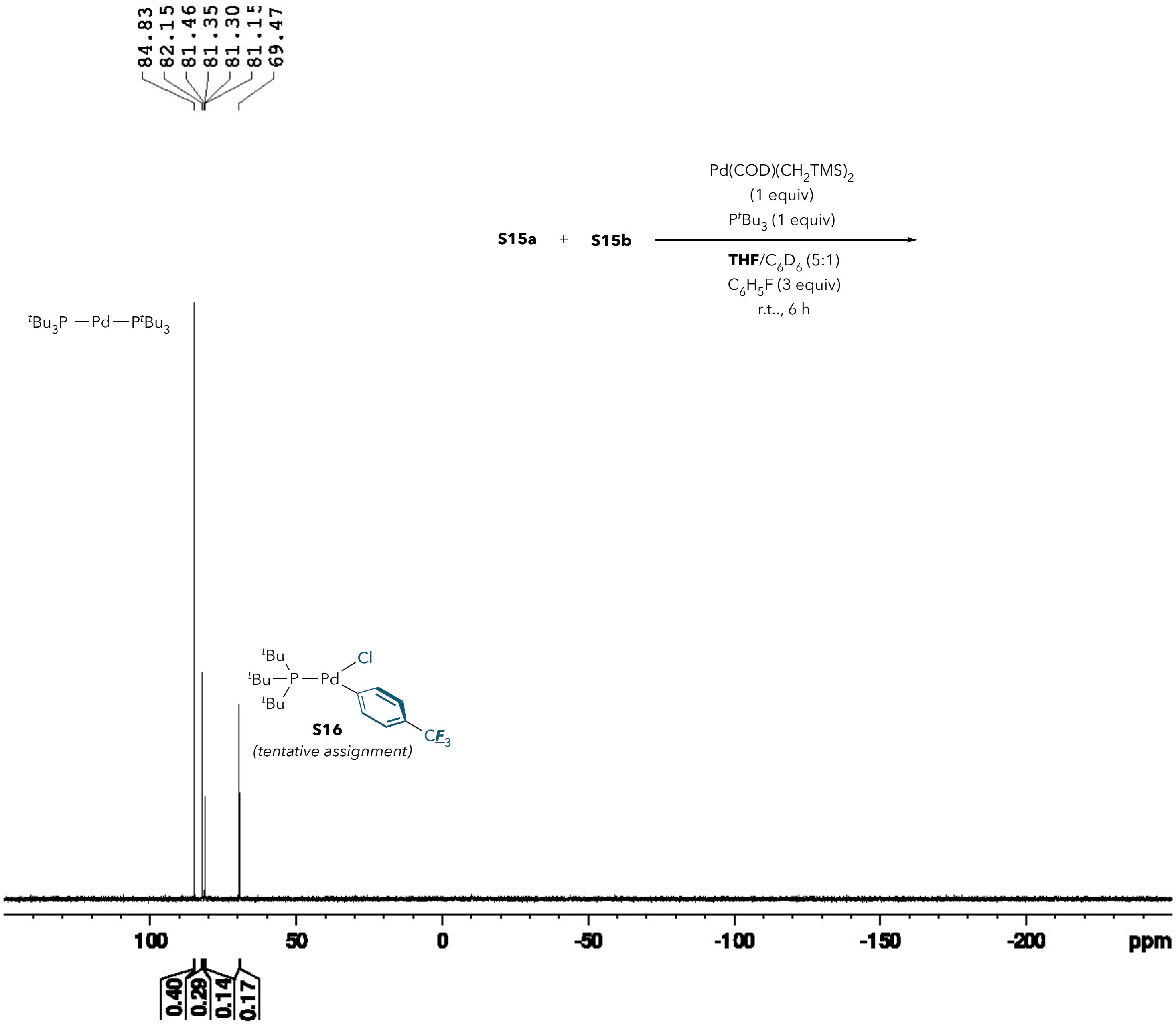
```
Current Data Parameters
NAME          6-SMR-37-3
EXPNO                 10
PROCNO                 2

F2 - Acquisition Parameter
Date_           20211112
Time             15.41 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG             zgig
TD                130892
SOLVENT             C6D6
NS                    16
DS                     4
SWH         90909.094 Hz
FIDRES       1.389070 Hz
AQ          0.7199060 sec
RG                   101
DW             5.500 usec
DE              6.50 usec
TE               298.1 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0                    1
SFO1      376.4607164 MHz
NUC1                 19F
P1             12.00 usec
PLW1       31.08900070 W
SFO2      400.1316005 MHz
NUC2                  1H
CPDPRG[2        waltz16
PCPD2          90.00 usec
PLW2       24.03499985 W
PLW12       0.18990999 W

F2 - Processing parameters
SI                 65536
SF        376.4979782 MHz
WDW                   EM
SSB       0
LB               0.30 Hz
GB        0
PC                  1.00
```



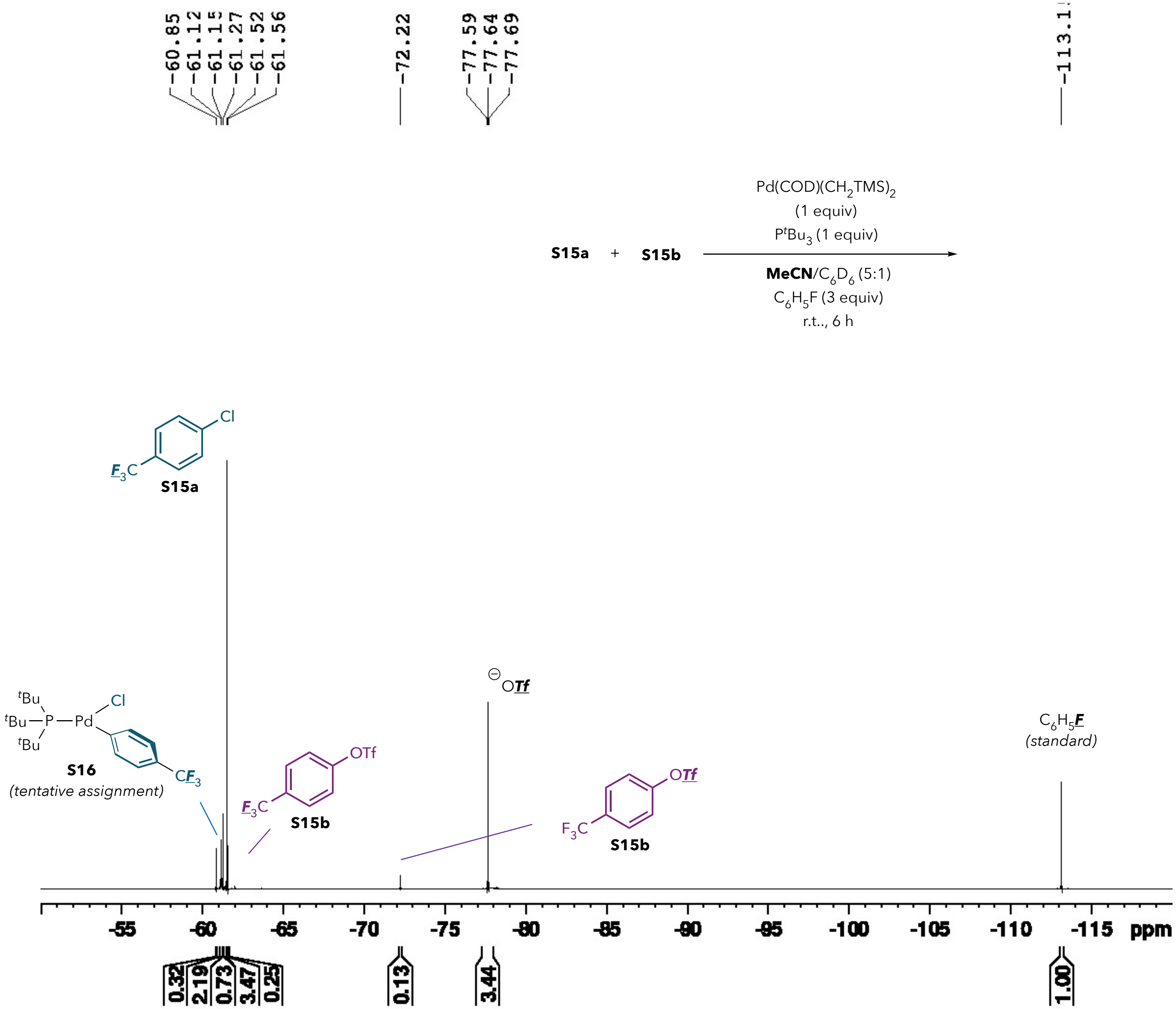
```
Current Data Parameters
NAME          6-SMR-37-4
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameter
Date_           20211112
Time             15.56 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zgpg30
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     4
SWH          65789.477 Hz
FIDRES        2.007735 Hz
AQ           0.4980736 sec
RG                   101
DW               7.600 usec
DE                6.50 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                    1
SFO1       161.9674942 MHz
NUC1                 31P
P0                2.67 usec
P1                8.00 usec
PLW1       45.86100006 W
SFO2       400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2            90.00 use
PLW2       24.03499985 W
PLW12       0.18990999 W
PLW13       0.09552100 W

F2 - Processing parameters
SI                 32768
SF         161.9755930 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



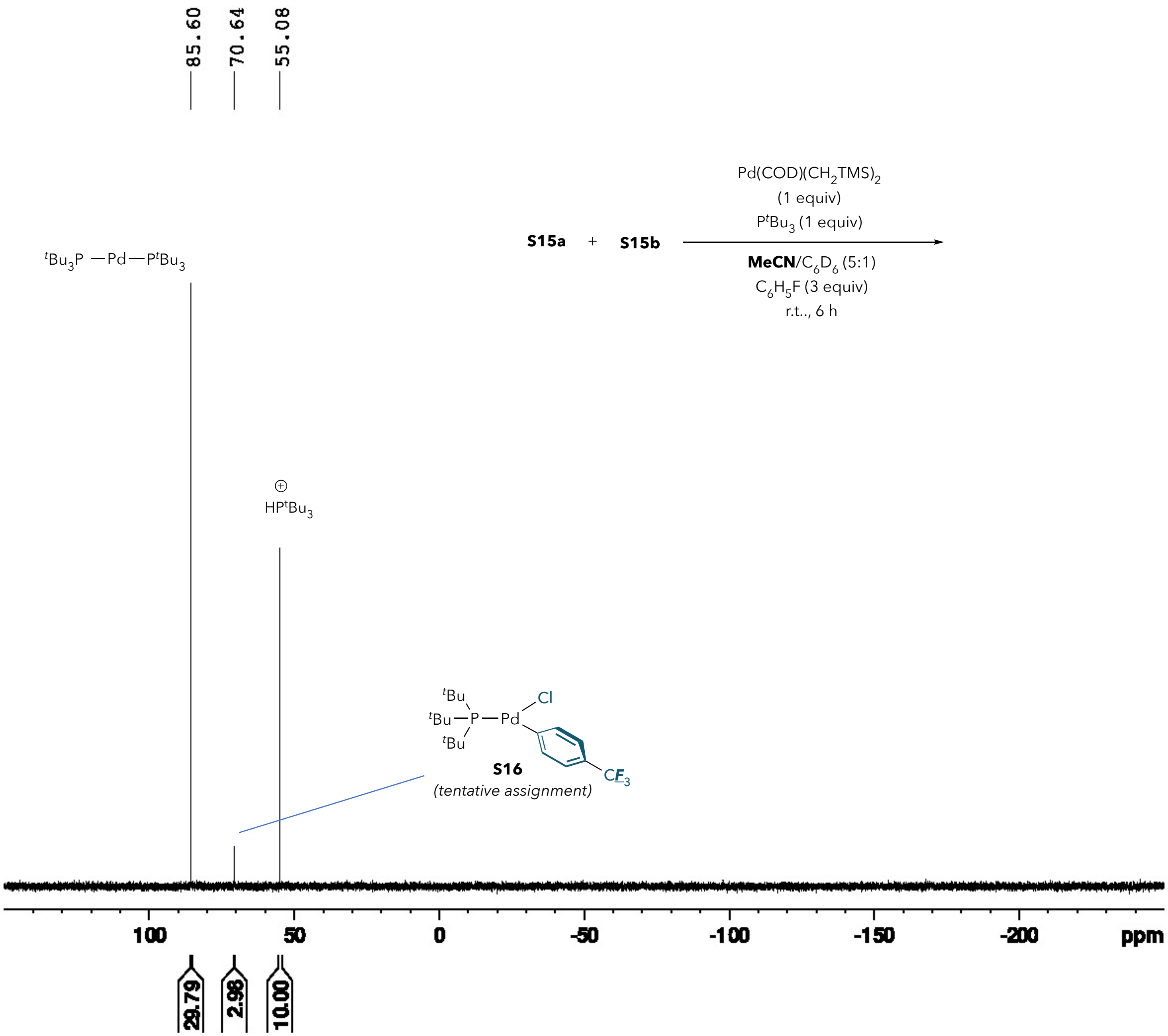
```
Current Data Parameters
NAME             6-SMR-38-4
EXPNO                    10
PROCNO                    2

F2 - Acquisition Parameter
Date_              20211113
Time                16.28 h
INSTRUM          Avance Neo
PROBHD     Z152088_0031 (
PULPROG                zgig
TD                   131072
SOLVENT                C6D6
NS                       16
DS                        4
SWH            90909.094 Hz
FIDRES          1.387163 Hz
AQ            0.7208960 sec
RG                      101
DW                5.500 usec
DE                 6.50 usec
TE                  298.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                       1
SFO1         376.4607164 MHz
NUC1                    19F
P1                12.00 usec
PLW1           31.08900070 W
SFO2         400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2              90.00 usec
PLW2           24.03499985 W
PLW12           0.18990999 W

F2 - Processing parameters
SI                    65536
SF           376.4979697 MHz
WDW                      EM
SSB        0
LB                  0.30 Hz
GB         0
PC                     1.00
```



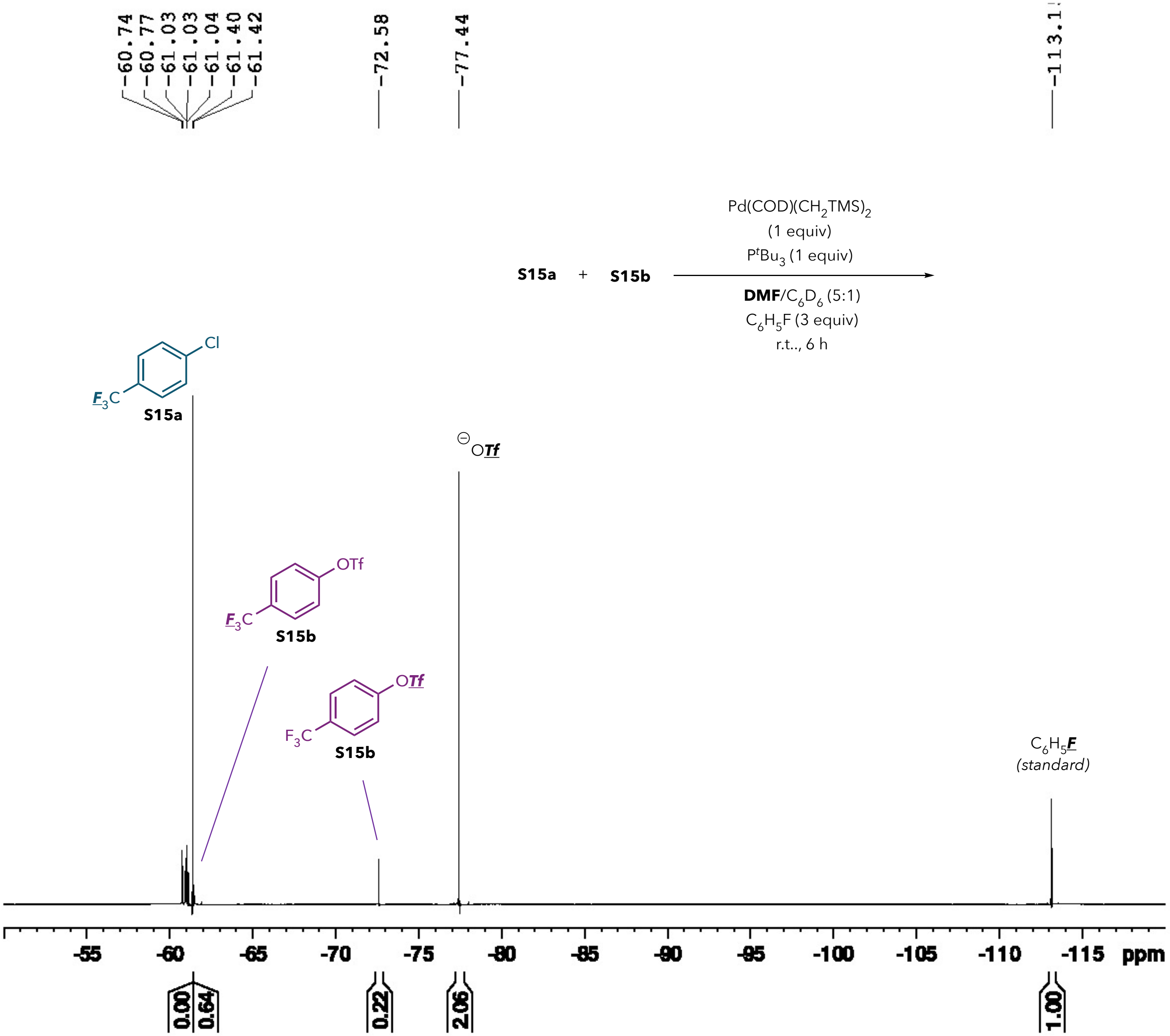
```
Current Data Parameters
NAME           6-SMR-38-4
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_            20211113
Time              16.32 h
INSTRUM         Avance Neo
PROBHD      Z152088_0031 (
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                     32
DS                      4
SWH          65789.477 Hz
FIDRES        2.007735 Hz
AQ          0.4980736 sec
RG                    101
DW              7.600 usec
DE               6.50 usec
TE                298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                     1
SFO1       161.9674942 MHz
NUC1                  31P
P0               2.67 usec
P1               8.00 usec
PLW1        45.86100006 W
SFO2       400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2           90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                  32768
SF         161.9755930 MHz
WDW                    EM
SSB        0
LB                1.00 Hz
GB         0
PC                   1.40
```



```
Current Data Parameters
NAME             6-SMR-38-7
EXPNO                    10
PROCNO                    2

F2 - Acquisition Parameter
Date_              20211113
Time                16.49 h
INSTRUM           Avance Neo
PROBHD     Z152088_0031 (
PULPROG                zgig
TD                   131072
SOLVENT                C6D6
NS                       16
DS                        4
SWH            90909.094 Hz
FIDRES          1.387163 Hz
AQ            0.7208960 sec
RG                      101
DW                5.500 usec
DE                 6.50 usec
TE                  298.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                       1
SFO1         376.4607164 MHz
NUC1                    19F
P1                12.00 usec
PLW1         31.08900070 W
SFO2         400.1316005 MHz
NUC2                     1H
CPDPRG[2           waltz16
PCPD2              90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W

F2 - Processing parameters
SI                    65536
SF          376.4977288 MHz
WDW                      EM
SSB        0
LB                  0.30 Hz
GB         0
PC                     1.00
```

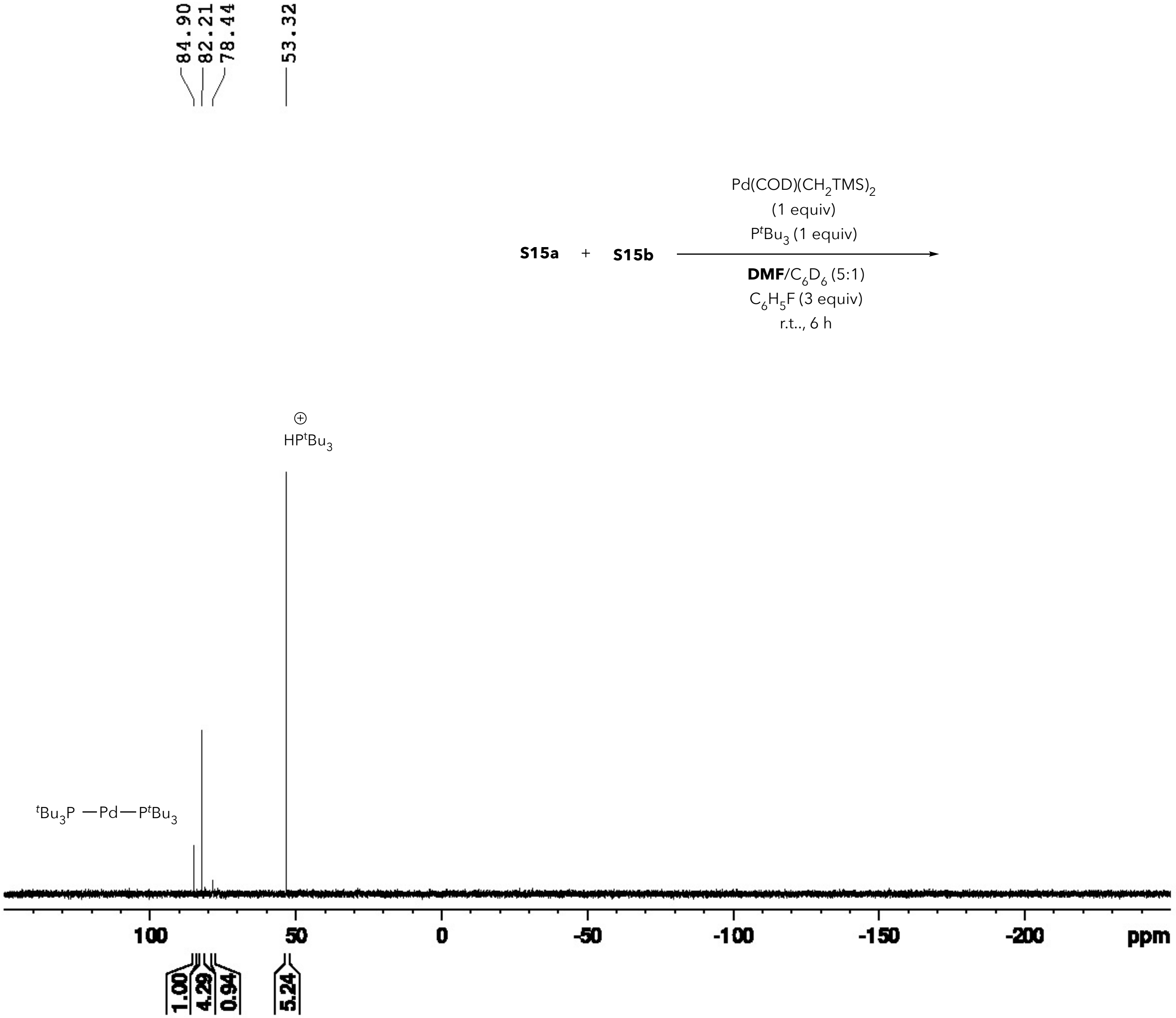


```
Current Data Parameters
NAME          6-SMR-38-7
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameter
Date_           20211113
Time             16.52 h
INSTRUM        Avance Neo
PROBHD     Z152088_0031 (
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     4
SWH            65789.477 Hz
FIDRES          2.007735 Hz
AQ             0.4980736 sec
RG                   101
DW                 7.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         161.9674942 MHz
NUC1                 31P
P0                  2.67 usec
P1                  8.00 usec
PLW1         45.86100006 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                 32768
SF           161.9755930 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

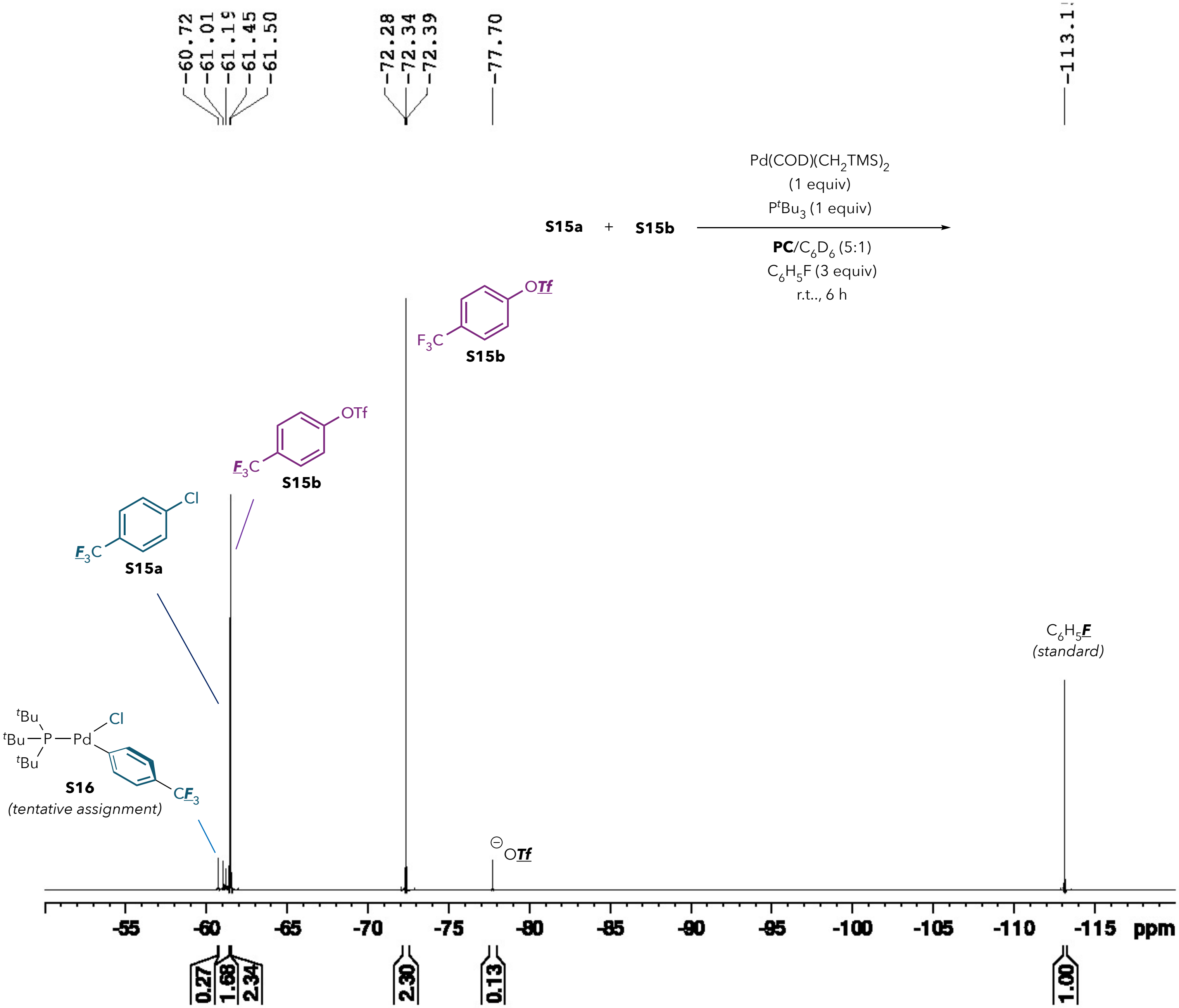


```
Current Data Parameters
NAME          6-SMR-38-11
EXPNO                  10
PROCNO                  2

F2 - Acquisition Parameter
Date_            20211113
Time              17.21 h
INSTRUM        Avance Neo
PROBHD   Z152088_0031 (
PULPROG              zgig
TD                 131072
SOLVENT              C6D6
NS                     16
DS                      4
SWH          90909.094 Hz
FIDRES        1.387163 Hz
AQ           0.7208960 sec
RG                    101
DW              5.500 usec
DE               6.50 usec
TE                298.1 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                     1
SFO1       376.4607164 MHz
NUC1                  19F
P1              12.00 usec
PLW1       31.08900070 W
SFO2       400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2           90.00 usec
PLW2       24.03499985 W
PLW12       0.18990999 W

F2 - Processing parameters
SI                  65536
SF         376.4978876 MHz
WDW                    EM
SSB      0
LB                0.30 Hz
GB       0
PC                   1.00
```

$$\textbf{S15a} + \textbf{S15b} \xrightarrow[\substack{\textbf{DMF}/C_6D_6\ (5{:}1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t.., 6 h}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

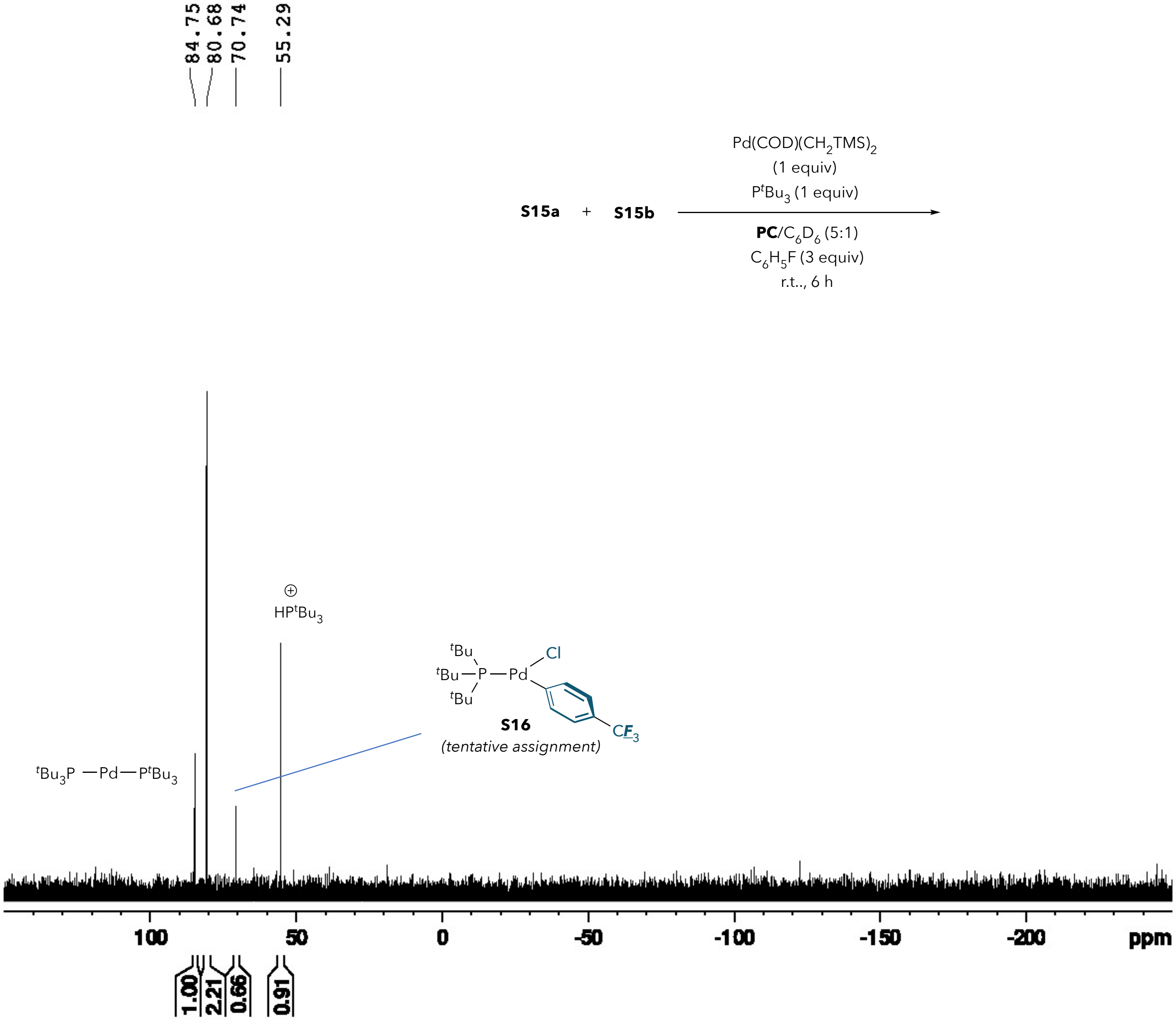


```
Current Data Parameters
NAME        6-SMR-38-11
EXPNO                11
PROCNO                1

F2 - Acquisition Parameter
Date_          20211113
Time              17.24 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT            C6D6
NS                   32
DS                    4
SWH           65789.477 Hz
FIDRES         2.007735 Hz
AQ            0.4980736 sec
RG                  101
DW                7.600 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        161.9674942 MHz
NUC1                31P
P0                 2.67 usec
P1                 8.00 usec
PLW1        45.86100006 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                32768
SF          161.9755930 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



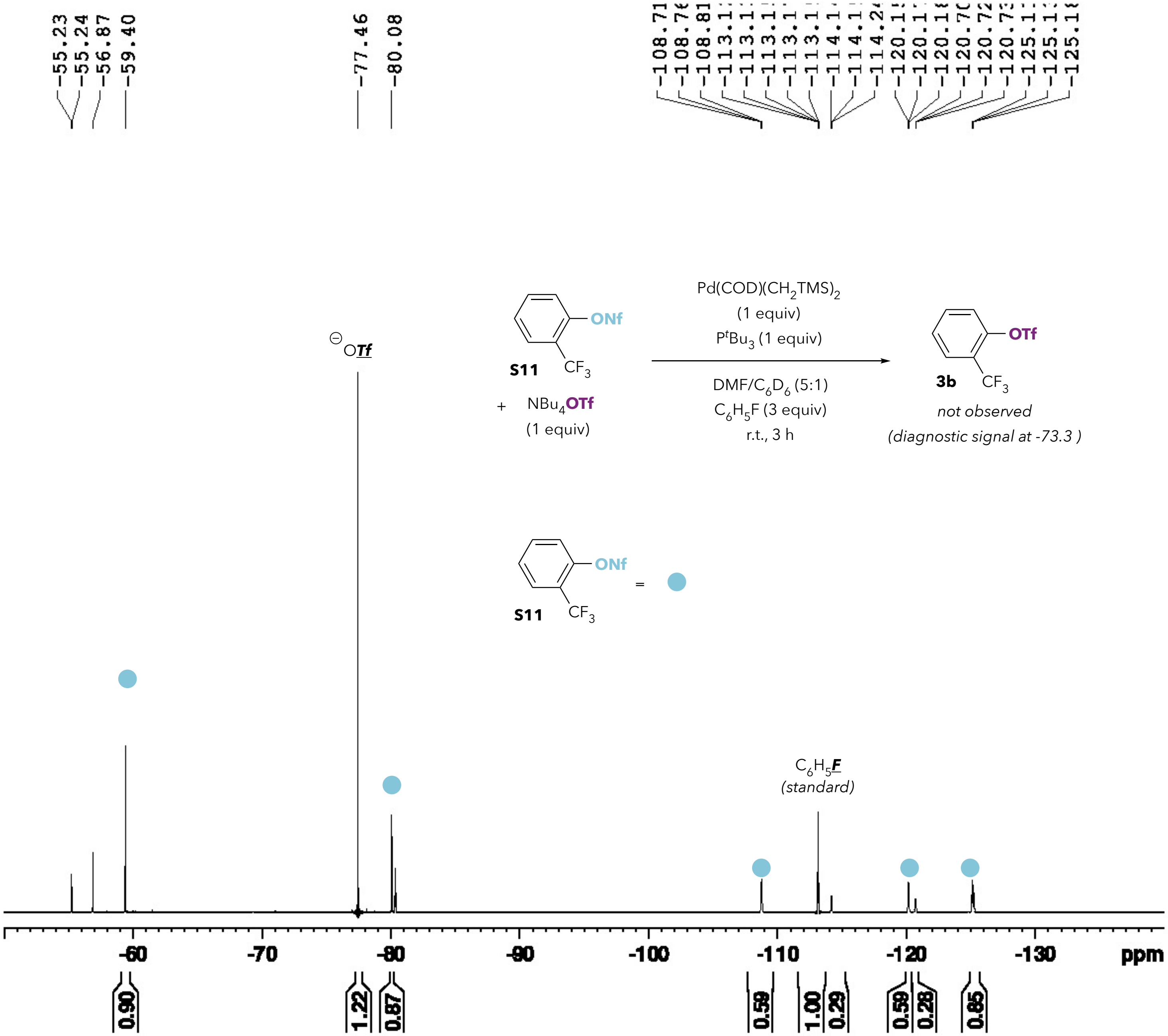
```
Current Data Parameters
NAME          6-SMR-38-15
EXPNO                  10
PROCNO                  2

F2 - Acquisition Parameter
Date_            20211113
Time              17.40 h
INSTRUM         Avance Neo
PROBHD    Z152088_0031 (
PULPROG              zgig
TD                 131072
SOLVENT              C6D6
NS                     16
DS                      4
SWH           90909.094 Hz
FIDRES         1.387163 Hz
AQ            0.7208960 sec
RG                    101
DW                5.500 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                     1
SFO1        376.4607164 MHz
NUC1                  19F
P1                12.00 usec
PLW1        31.08900070 W
SFO2        400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2             90.00 use
PLW2        24.03499985 W
PLW12        0.18990999 W

F2 - Processing parameters
SI                  65536
SF          376.4978968 MHz
WDW                    EM
SSB          0
LB                   0.30 Hz
GB           0
PC                   1.00
```

$$\mathbf{S15a} + \mathbf{S15b} \xrightarrow[\substack{\mathbf{PC}/C_6D_6\ (5:1) \\ C_6H_5F\ (3\ \text{equiv}) \\ \text{r.t.., 6 h}}]{\substack{Pd(COD)(CH_2TMS)_2 \\ (1\ \text{equiv}) \\ P^tBu_3\ (1\ \text{equiv})}}$$

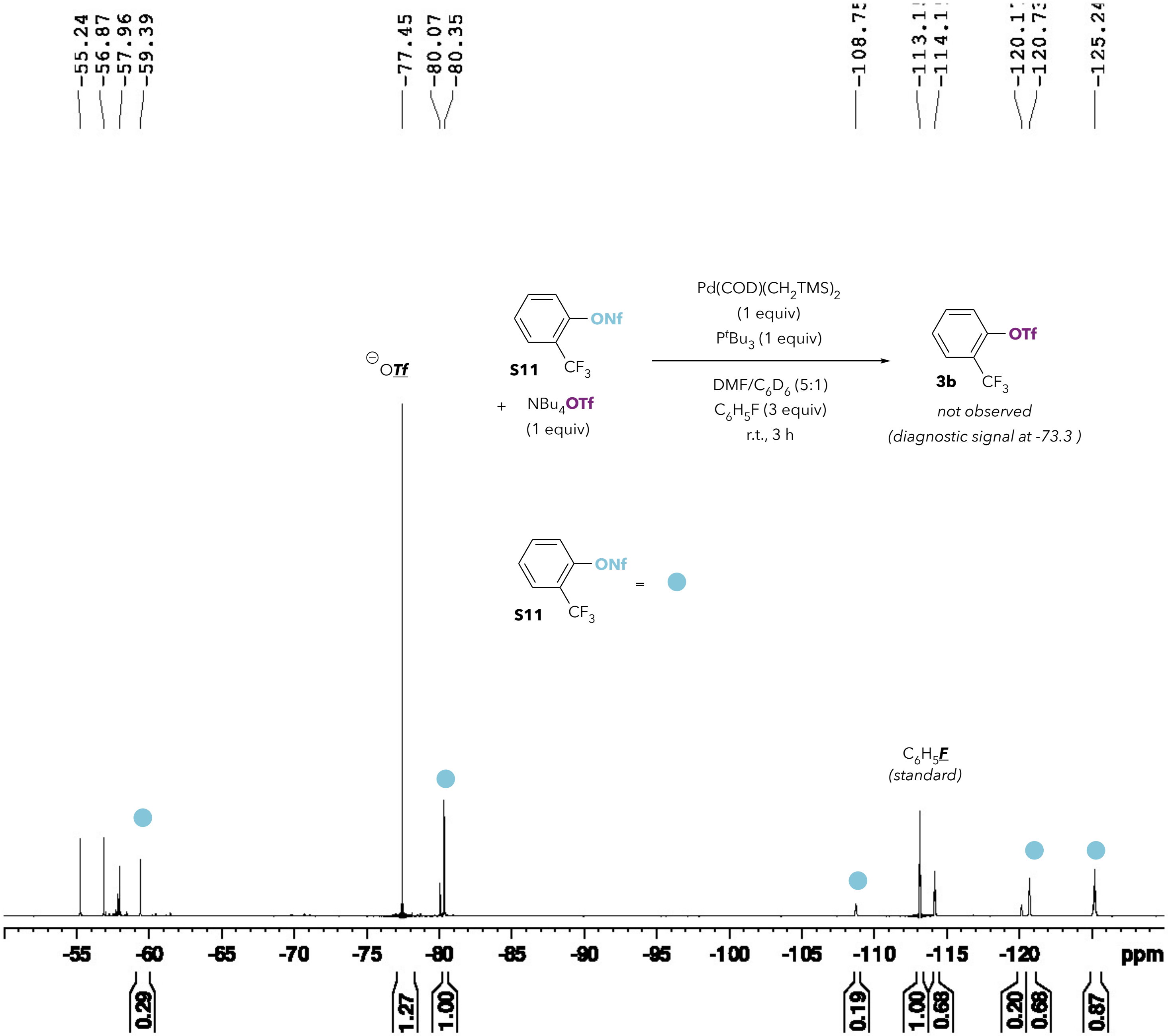


```
Current Data Parameters
NAME          6-SMR-38-15
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameter
Date_           20211113
Time               17.44 h
INSTRUM         Avance Neo
PROBHD    Z152088_0031 (
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                     32
DS                      4
SWH           65789.477 Hz
FIDRES         2.007735 Hz
AQ            0.4980736 sec
RG                    101
DW                7.600 usec
DE                 6.50 usec
TE                298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                     1
SFO1       161.9674942 MHz
NUC1                  31P
P0                 2.67 usec
P1                 8.00 usec
PLW1        45.86100006 W
SFO2       400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                  32768
SF         161.9755930 MHz
WDW                    EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

D. Reaction with S11 and NBu$_4$OTf



```
Current Data Parameters
NAME       ER-6-57_ONftoOTf_1
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameter
Date_              20200707
Time                  10.36
INSTRUM               spect
PROBHD    5 mm QNP 1H/13
PULPROG              zgflqn
TD                    32768
SOLVENT                C6D6
NS                       64
DS                        0
SWH            50125.312 Hz
FIDRES          1.529703 Hz
AQ            0.3268608 sec
RG                   2896.3
DW                9.975 usec
DE                 6.00 usec
TE                  683.2 K
D1           1.50000000 sec
TD0                       1

======= CHANNEL f1 =======
NUC1                    19F
P1                 9.00 usec
PL1        0 dB
SFO1          282.4250465 MHz

F2 - Processing parameters
SI                    65536
SF            282.4416726 MHz
WDW                      EM
SSB        0
LB                  0.30 Hz
GB         0
PC                     1.00
```



```
Current Data Parameters
NAME         ER-6-57_ONftoOTf_1
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameter
Date_              20200709
Time                   9.09
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgflqn
TD                    32768
SOLVENT               C6D6
NS                       64
DS                        0
SWH            50125.312 Hz
FIDRES          1.529703 Hz
AQ             0.3268608 sec
RG                   2896.3
DW                9.975 usec
DE                 6.00 usec
TE                  683.2 K
D1            1.50000000 sec
TD0                       1

======= CHANNEL f1 =======
NUC1                    19F
P1                 9.00 usec
PL1        0 dB
SFO1          282.4250465 MHz

F2 - Processing parameters
SI                    65536
SF            282.4416743 MHz
WDW                      EM
SSB        0
LB                   0.30 Hz
GB         0
PC                     1.00
```