# The Mechanistic Significance of the Si-O-Pd Bond in the Palladium Catalyzed Cross-Coupling Reactions of Arylsilanolates

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## SUPPORTING INFORMATION

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**General Experimental**

All reactions were performed in oven (140 °C) and/or flame dried glassware (including NMR tubes for kinetic experiments) under an atmosphere of dry nitrogen or argon, unless noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade) and diethyl ether (Fisher, BHT stabilized ACS grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexanes (Fisher, OPTIMA grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Reaction solvent dioxane was distilled over sodium prior to use. Benzene (Fisher, ACS grade) was distilled from sodium; benzotrifluoride (Aldrich, ACS grade) was distilled from $CaH_2$. Reaction solvent DMF was purchased from Acros containing 50 ppm water stored over 4 Å mol. sieves. Reaction solvent acetone (Aldrich) was dried over 4 Å molecular sieves prior to use. Solvents for filtration and chromatography were certified ACS grade. "Brine" refers to a saturated solution of sodium chloride. All reaction temperatures correspond to internal temperatures measured with Teflon coated thermocouples unless otherwise noted.

$^{1}$H and $^{13}$C NMR spectra were recorded on a Varian Unity 500 (500 MHz, $^{1}$H; 126 MHz, $^{13}$C) or a Varian VXR (500 MHz, 1H; 126 MHz, $^{13}$C) spectrometer. Spectra are referenced to residual chloroform (δ 7.26 ppm, $^{1}$H; δ 77.0 ppm, $^{13}$C), residual benzene (δ 7.16 ppm, $^{1}$H; δ 128.0 ppm, $^{13}$C), residual $CD_2Cl_2$ (5.32 ppm, $^{1}$H; 53.8 ppm, $^{13}$C), $CFCl_3$ (10% in $CDCl_3$) as an external reference for $^{19}$F NMR (δ 0.00 ppm $^{19}$F), and phosphoric acid (40% in $H_2O$) as an external reference for $^{31}$P NMR (δ 0.00 ppm $^{31}$P). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. All assignments are corroborated by 2D experiments (COSY, HETCOR). Spectra are available on request from sdenmark@illinois.edu. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Mass Spectrometry was performed by the University of Illinois Mass Spectrometer Center. Electron Impact (EI) spectra were performed on a Finnegan-MAT C5 spectrometer. Data are reported in the form of *m/z* (intensity relative to the base peak = 100). Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum BX spectrophotometer in

NaCl cells (film) or as a KBr plate. Peaks are reported in $cm^{-1}$ with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%), w (weak, 0-33%). Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr and boiling points correspond to uncorrected air bath temperatures (ABT). Melting points were obtained in a vacuum-sealed capillary tube using a Thomas Hoover melting point apparatus and are corrected. Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV (254). Column chromatography was performed using 230-400 mesh silica gel purchased from Silicycle.

Analytical gas chromatography (GC) was performed using a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a flame ionization detector ($H_2$ carrier gas, 1mL/min**)** Injections were made on a Hewlett-Packard HP-1 (30 meter) capillary column. The injector temperature was 250 °C, the detector temperature was 300 °C, with a split ratio of 100:1. Retention times ($t_R$) and integrated ratios were obtained using Agilent Chemstation Software.

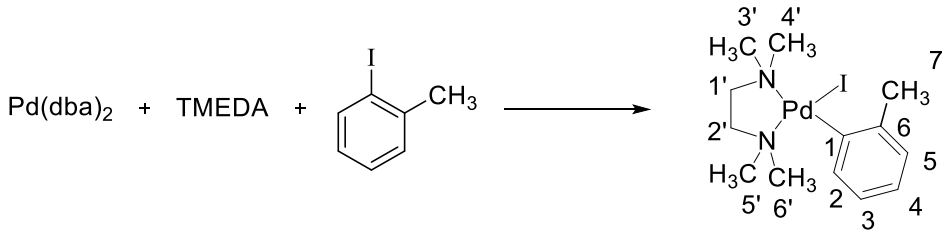
2-Bromotoluene, 2-iodotoluene, 1-bromo-4-fluorobenzene, TMEDA and 2-butanone were purchased from Aldrich and distilled prior to use. $Cs^0$ (Strem), CuTC (Aldrich), 2-(dimethylamino)ethanethiol hydrochloride (Aldrich), $Ph_3P$ (Aldrich), 1,3-diphenylphosphinopropane (Organometallics), 1,2-diphenylphosphinoethane (Organometallics), 1,2-diphenylphosphinobenzene (Organometallics), 1,1'-bis(diphenylphosphino)ferrocene (Organometallics), *t*-$Bu_3P$ (Strem), *t*-$Bu_3P{\cdot}HBF_4$ (Aldrich), and $(t\text{-}Bu_3P)_2Pd$ (Aldrich)[1] were used as received.

**Literature Procedures**

Allylpalladium(II)chloride dimer,[2] $Pd(dba)_2$,[3] 1,3-bis(diphenylphosphino)butane monoxide,[4] 1,3-bis(diphenylphosphino)butane dioxide,[5] KTC,[6] (4-methoxyphenyl)dimethylsilanol **5**,[7] **8**,[8] potassium (4-methoxyphenyl)dimethylsilanolate $K^+$**5**$^-$,[9] cesium (4-methoxyphenyl)dimethylsilanolate $Cs^+$**5**$^-$,[9] 4'-methoxy-2-methylbiphenyl **12**,[10] **13p**,[11] (4-methoxyphenyl)dimethylsilane **14**,[12] 4-methoxy-4'-fluorobiphenyl **16**,[13] potassium (4-*n*-butoxyphenyl)dimethylsilanolate $K^+$**21**$^-$,[14] 4-*n*-butoxy-4'-fluorobiphenyl **22**.[15]

## PREPARATION OF ARYL-DERIVED PALLADIUM(II) SILANOLATE COMPLEXES (SCHEME 1)

### Preparation of [Tetramethylethylenediamine]iodo(2-methylphenyl)palladium (4)[16]




**4**

In a drybox, a 35 mL, one-neck, round-bottom flask was charged with $Pd(dba)_2$ (1.15 g, 2.0 mmol), tetramethylethylenediamine (0.39 mL, 2.6 mmol, 1.3 equiv), benzene (10 mL) and 2-iodotoluene (0.36 mL, 2.8 mmol, 1.4 equiv). The flask was sealed with a septum, removed from the drybox, and heated in an oil bath at 50 $^0$C for 2 h. The flask was returned to the drybox and the reaction mixture was filtered through 2 g of diatomaceous earth. All solvents were then removed *in vacuo*. Ether (20 mL) was added to the resulting yellow solids and the mixture was stirred for 5 min. The supernatant was then removed by pipette. This washing process was repeated 3 times and the solids were collected on a glass fritted funnel, and were dried under vacuum (0.1 mm Hg) overnight to afford 362 mg (41%) of **4** as a pale orange powder.

Data for [Tetramethylethylenediamine]iodo(2-methylphenyl)palladium **(4):**

mp: 179-181 ˚C (dec)

$^1$H NMR: (500 MHz, $C_6H_6$)

7.43 (d, $J$ = 7.5, 1 H, HC(2)), 7.03 (d, $J$ = 7.5, 1 H, HC(5)), 6.91-6.98 (m, 2 H, HC(3 and 4)), 2.92 (s, 3 H, $H_3C$(3',4',5' or 6')), 2.25 (s, 3 H, $H_3C$(7), 2.16 (s, 3 H, $H_3C$(3',4',5' or 6')), 1.71 (s, 3 H, $H_3C$(3',4',5' or 6')), 1.64 (t, $J$ = 9.5, 1 H, $H_2C$(1' or 2')), 1.53 (t, $J$ = 9.5, 1 H, $H_2C$(1' or 2')), 1.45 (s, 3 H, $H_3C$(3',4',5' or 6')), 1.30 (t, $J$ = 9.5, 2 H, $H_2C$(1' or 2'))

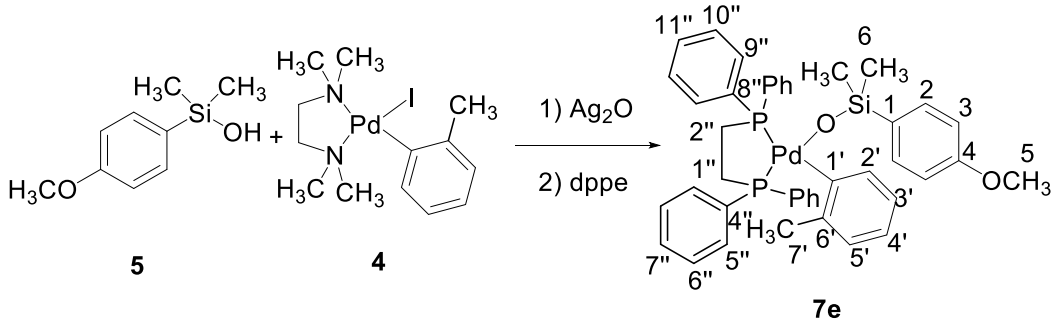
$^{13}$C NMR: (126 MHz, $C_6H_6$)

145.7 (C(1)), 142.2 (C(6)), 136.1 (C(4)), 127.3 (C(3)), 123.9 (C(5)), 123.0 (C(2)), 61.2 (C(1' or 2')), 57.4 (C(1' or 2')), 49.9 (C(3', 4', 5', or 6')), 49.4 (C(3', 4', 5', or 6')), 48.1 (C(3', 4', 5', or 6')), 47.9 (C(3', 4', 5', or 6')), 28.3 (C(7))

Analysis: $C_{17}H_{28}IN_2Pd$ (440.66)

| | | | | |
|---|---|---|---|---|
| Calcd: | C, 35.43; | H, 5.26% | N, 6.36% | I, 28.80% |
| Found: | C, 35.27; | H, 5.14% | N, 6.22% | I, 29.07% |

**Preparation of [1,2-Bis(diphenylphosphino)ethane](2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (7e)**




In a drybox, a 50-mL, one-necked flask equipped with a magnetic stir bar was charged with **4** (220 mg, 0.50 mmol), (4-methoxyphenyl)dimethylsilanol (100 mg, 0.55 mmol, 1.1 equiv) and THF (10 mL). While stirring, $Ag_2O$ (115 mg, 0.50 mmol, 1.0 equiv) was added and the resulting suspension was stirred in the drybox for 12 h. The solvents were removed *in vacuo* (0.1 mm Hg), then toluene (10 mL) was added, and the mixture was filtered through 2 g of diatomaceous earth. The solvents were removed *in vacuo* (0.1 mm Hg) for 4 h to afford a yellow wax. THF (5 mL) and dppe (199 mg, 0.50 mmol, 1.00 equiv) were added and the resulting solution was stirred for 16 h in the drybox. The solvent was removed in vacuo to afford an off-white foam. The foam was dissolved in a minimal amount of benzene (1 mL) and was layered with hexane (5 mL). The solution was allowed to sit at room temperature for 24 h then at -20 $^0$C for 24 h. The resulting solids were collected on a fritted glass funnel, then were washed with hexanes (5 mL), and dried under vacuum (0.1 mm Hg) for 12 h to afford 284 mg (73%) of **7e** as pale yellow needles.

Data for [1,2-bis(diphenylphosphino)ethane](2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (**7e**):

$^1$H NMR: (500 MHz, $C_6H_6$)

8.33 (t, $J$ = 9.5, 2 H, HC(6'' or 10'')), 8.06 (t, $J$ = 9.0, 2 H, HC(6'' or 10'')), 7.78 (d, $J$ = 8.0, 2 H, HC(2)), 7.60 (dd, $J$ = 8.0, 11.5, 2 H, HC(6'' or 10'')), 7.46 (t, $J$ = 7.5, 1 H, HC(2')), 6.87-7.15 (m, 14H, CH(5'', 7'', 9'', 11'', and 6''or 10'')), 6.73

(t, 8.0, 1 H, HC(2' or 5')), 6.72 (t, 8.0,1 H, HC(2' or 5')), 6.62 (t, $J$ = 9.5, 2 H, HC(3' and 4')), 3.40 (s, 3 H, $H_3C(5)$), 2.46 (s, 3 H, $H_3C(7')$), 1.80-2.2 (bm, 3 H, $H_2C(2''$ and 2 x 1''$)$), 1.20-1.40 (bs, 1 H, $H_2C(2'')$), 0.41 (s, 3 H, $H_3C(6)$), 0.39 (s, 3 H, $H_3C(6)$)

$^{31}$P NMR: (202 MHz, $C_6H_6CH_3$ )

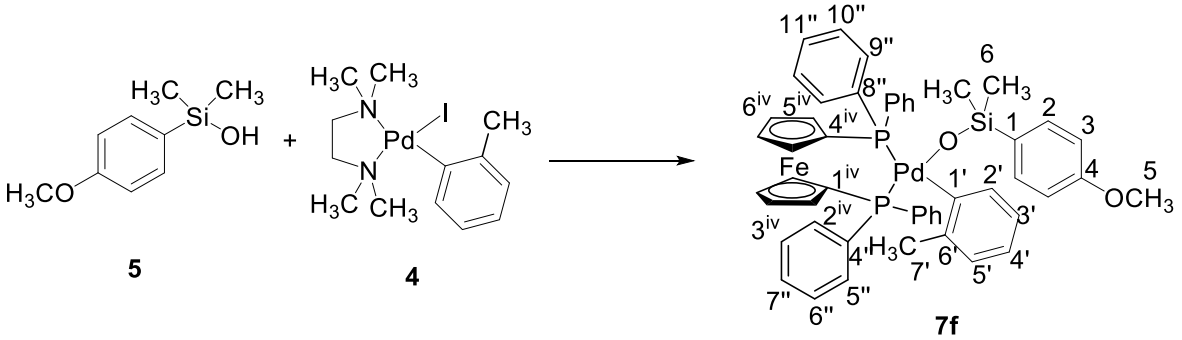
50.8 (d, $J$ = 46.1), 26.0 (d, $J$ = 46.1)

Analysis: $C_{42}H_{44}O_2P_2PdSi$ (777.25)

Calcd: C, 64.90; H, 5.71%

Found: C, 64.78 H, 5.65%

**Preparation of [1,1'-Bis(diphenylphosphino)ferrocene](2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (7f)**




In a drybox, a 50-mL, one-necked flask equipped with a magnetic stir bar was charged with **4** (220 mg, 0.50 mmol), (4-methoxyphenyl)dimethylsilanol (100 mg, 0.55 mmol, 1.1 equiv) and THF (10 mL). While stirring, $Ag_2O$ (115 mg, 0.50 mmol, 1.0 equiv) was added and the resulting suspension was stirred in the drybox for 12 h. The solvents were removed *in vacuo* (0.1 mm Hg), then toluene (10 mL) was added, and the mixture was filtered through 2 g of diatomaceous earth. The solvents were removed *in vacuo* (0.1 mm Hg) for 4 h to afford a yellow wax. THF (5 mL) and dppf (249 mg, 0.50 mmol, 1.00 equiv) were added and the resulting solution was stirred for 36 h in the drybox. The solvent was removed in vacuo to afford an off-white foam. The foam was dissolved in a minimal amount of benzene (1 mL) and was layered with hexane (5 mL). The solution was allowed to sit at room temperature for 24 h then at -20 $^0$C for 24 h. The resulting solids were collected on a fritted glass funnel, then were washed with hexanes (5 mL), and dried under vacuum (0.1 mm Hg) for 12 h to afford 268 mg (64%) of **7f** as

an organge powder.

Data for [1,1'-bis(diphenylphosphino)ferrocene](2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (**7f**):

$^1$H NMR: (500 MHz, $C_6H_6$)

8.42 (dd, *J* = 8.5, 9.5 8 H, HC(6'' and 10'')), 7.43 (t, *J* = 7.5, 1 H, HC(2')), 7.30 (d, *J* = 8.0, 2 H, HC(2)), 7.24 (t, *J* = 7.5, 2 H, HC(7'' or 11'')), 7.09-7.18 (m, 2H, CH(7'' or 11'')), 6.90 (d, *J* = 6.5, 1 H, HC(5')), 6.79 (d, *J* = 8.5, 2 H, HC(3)), 6.74-6.80 (m, 6H, HC( 3', 4', and 5'' or 9'')), 6.67 (t, *J* = 7.5, 4 H, HC(5'' or 9'')), 4.80 (s, 1 H, HC($3^{iv}$ or $6^{iv}$)), 4.36 (s, 1 H, HC($3^{iv}$ or $6^{iv}$)), 4.04 (s, 1 H, HC($3^{iv}$ or $6^{iv}$)), 3.96 (s, 1 H, HC($3^{iv}$ or $6^{iv}$)), 3.65 (s, 1 H, HC($2^{iv}$ or $5^{iv}$)), 3.63 (s, 2 H, HC($2^{iv}$ or $5^{iv}$)), 3.56 (s, 1 H, HC($2^{iv}$ or $5^{iv}$)), 3.37 (s, 3 H, $H_3C$(5)), 2.71 (s, 3 H, $H_3C$(7')), 0.19 (s, 3 H, $H_3C$(6)), 0.08 (s, 3 H, $H_3C$(6))

$^{31}$P NMR: (202 MHz, $C_6H_6CH_3$ )

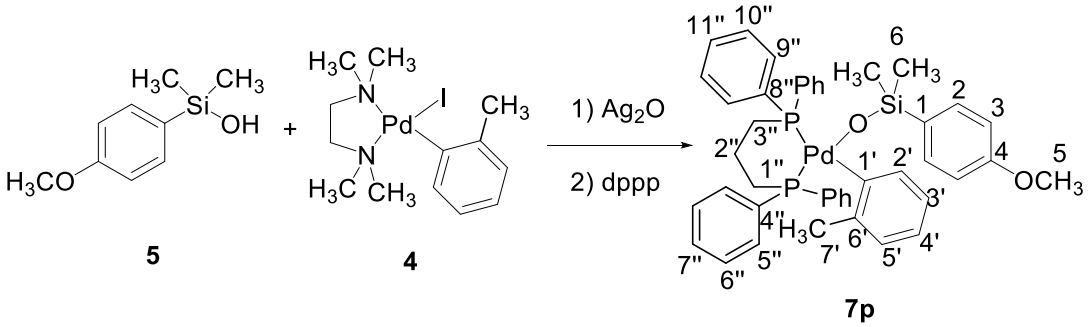
33.4 (d, *J* = 33.8), 9.2 (d, *J* = 33.8)

Analysis: $C_{50}H_{48}FeO_2P_2PdSi$ (933.21)

Calcd: C, 64.35; H, 5.18%

Found: C, 64.32 H, 5.14%

**Preparation of [1,3-Bis(diphenylphosphino)propane](2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (7p)**




In a drybox, a 50-mL, one-necked flask equipped with a magnetic stir bar was charged with **4** (620 mg, 1.40 mmol), (4-methoxyphenyl)dimethylsilanol (280 mg, 1.54 mmol, 1.1 equiv) and THF (25 mL). While stirring, $Ag_2O$ (323 mg, 1.40 mmol, 1.0 equiv) was added and the resulting suspension was stirred in the drybox for 24 h. The solvents were removed *in vacuo*

(0.1 mm Hg), then toluene (15 mL) was added, and the mixture was filtered through 2 g of diatomaceous earth. The solvents were removed *in vacuo* (0.1 mm Hg) for 4 h to afford a yellow wax. THF (20 mL) and dppp (606 mg, 1.47 mmol, 1.05 equiv) were added and the resulting solution was stirred for 12 h in the drybox. The solvent was removed in vacuo to afford an off-white foam. The foam was dissolved in a minimal amount of benzene (2 mL) and was layered with hexane (15 mL). The solution was allowed to sit at room temperature for 24 h then at -20 $^0$C for 24 h. The resulting solids were collected on a fritted glass funnel, then were washed with hexanes (5 mL), and dried under vacuum (0.1 mm Hg) for 12 h to afford 942 mg (74%) of **7p** as off-white needles.

Data for [1,3-bis(diphenylphosphino)propane](2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (**7p**):

mp: 103-104 ˚C (dec)

$^1$H NMR: (500 MHz, $C_6H_6$)

8.11 (t, *J* = 8.5, 2 H, HC(6'' or 10'')), 7.93 (t, *J* = 8.0, 2 H, HC(6'' or 10'')), 7.58 (t, *J* = 8.5, 2 H, HC(6'' or 10'')),7.40 (d, *J* = 9.0, 2 H, HC(2)), 7.30 (t, *J* = 7.5, 1 H, HC(2')), 6.92-7.11 (m, 6H, CH(5'', 6'', 9'', or 10'')), 6.90 (d, *J* = 8.0, 1 H, HC(5')), 6.80-6.87 (m, 3 H, HC(5'', 7'', 9'', or 11''), 6.79 (d, *J* = 8.5, 2 H, HC(3)), 6.73 (t, *J* = 6.5, 2 H, HC(3' and 4')), 6.48-6.68 (m, 5H, HC(5'', 7'', 9'' or 11'')), 3.35 (s, 3 H, $H_3C(5)$), 2.51 (s, 3 H, $H_3C(7')$), 2.08 (m, 1 H, $H_2C(1''$ or 3'')), 1.76 (m, 1 H, $H_2C(1''$ or 3'')), 1.66 (m, 1 H, $H_2C(1''$ or 3'')), 1.52 (m, 1 H, $H_2C(1''$ or 3'')), 1.30-1.40 (bs, 1 H, $H_2C(2'')$), 1.08 (m, 1 H, $H_2C(2'')$), 0.21 (s, 3 H, $H_3C(6)$), 0.13 (s, 3 H, $H_3C(6)$)

$^{13}$C NMR: (126 MHz, d$^8$ THF)

162.3 (C(1')), 161.2 (C(4)), 159.7 (C(6')), 144.1 (C(4')), 140.2 (C(1)), 136.9 (C(5')), 136.1, (d, *J* = 12, C(4' or 8')), 135.4 (C(2)), 135.2 (d, *J* = 12, C(4' or 8')), 134.3 (C(7' or 10'), 134.2 (d, *J* = 12, C(4' or 8')), 133.9 (C(7' or 11'), 133.0 (C(7' or 11'), 132.5 (d, *J* = 9, C(4' or 8')), 131.5 (C(7' or 11'), 130.4 (d, *J* = 14, C(5' or 9')), 129.6 (d, *J* = 3, C(6' or 10')), 129.3 (d, *J* = 9, C(5' or 9')), 129.1 (C(6' or 10')), 129.0 (d, *J* = 4, C(6' or 10')), 128.9 (d, *J* = 10, C(5' or 9')), 127.9 (d, *J* = 10, C(5' or 9')), 123.7 (d, *J* = 8, C(6' or 10')), 123.5 (C(3')), 113.9 (C(2')), 112.6 (C(3)), 54.8 (C(5)), 29.7 (d, *J* = 8, C(1'' or 3'')), 29.5 (d, *J* = 8, C(1'' or

3’’)), 27.0 (d, $J$ = 19, C(2’’)), 19.8 (C(7’)), 3.3 (C(6))

$^{31}$P NMR: (202 MHz, $C_6H_6CH_3$ )

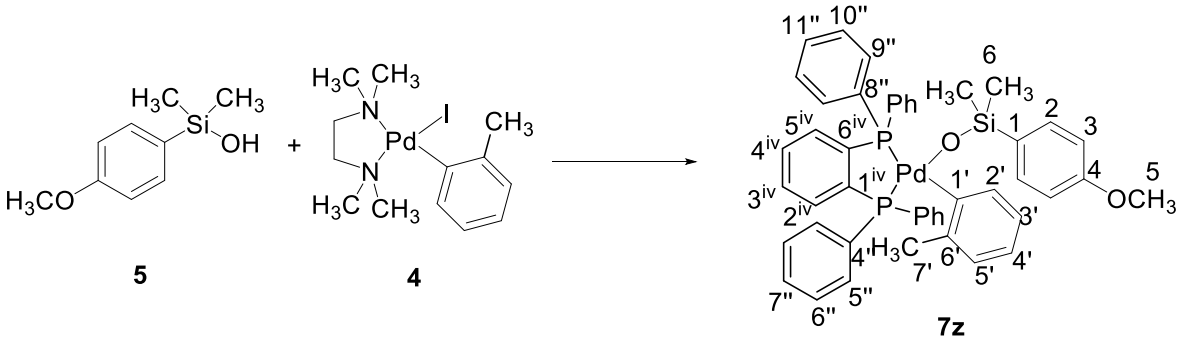
21.1 (d, $J$ = 48.8), -10.5 (d, $J$ = 48.7)

Analysis: $C_{43}H_{46}O_2P_2PdSi \cdot C_6H_6$ (869.39)

Calcd: C, 67.69; H, 6.03%

Found: C, 67.52; H, 5.81%

**Preparation of [1,2-Bis(diphenylphosphino)benzene](2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (7z)**




In a drybox, a 50-mL, one-necked flask equipped with a magnetic stir bar was charged with **4** (220 mg, 0.50 mmol), (4-methoxyphenyl)dimethylsilanol (100 mg, 0.55 mmol, 1.1 equiv) and THF (10 mL). While stirring, $Ag_2O$ (115 mg, 0.50 mmol, 1.0 equiv) was added and the resulting suspension was stirred in the drybox for 12 h. The solvents were removed *in vacuo* (0.1 mm Hg), then toluene (10 mL) was added, and the mixture was filtered through 2 g of diatomaceous earth. The solvents were removed *in vacuo* (0.1 mm Hg) for 4 h to afford a yellow wax. THF (5 mL) and 1,2-bis(diphenylphosphine)benzene (223 mg, 0.50 mmol, 1.00 equiv) were added and the resulting solution was stirred for 7 d in the drybox. The solvent was removed in vacuo to afford an off-white foam. The foam was dissolved in a minimal amount of benzene (1 mL) and was layered with hexane (5 mL). The solution was allowed to sit at room temperature for 24 h then at -20 $^0$C for 24 h. The resulting solids were collected on a fritted glass funnel, then were washed with hexanes (5 mL), and dried under vacuum (0.1 mm Hg) for 12 h to afford 347 mg (84%) of **7z** as pale yellow needles.

Data for [1,2-bis(diphenylphosphino)benzene](2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (**7z**):

$^{1}$H NMR: (500 MHz, $C_6H_6$)

8.29 (dd, *J* = 7.0, 9.5, 2 H, HC(6'' or 10'')), 7.65-7.74 (m, , 4 H, HC(6'' or 10'')), 7.58 (d, *J* = 8.5, 2 H, HC(2)), 7.47 (t, *J* = 7.5, 1 H, HC(2')), 7.25 (t, *J* = 7.5, 1 H, HC(5')), 6.68-7.20 (m, 22H, CH(3, 3', 4', 5'', 7'', 9'', 11'',2$^{iv}$, 3$^{iv}$, 4$^{iv}$, 5$^{iv}$ and 6''or 10'')), 3.42 (s, 3 H, $H_3C$(5)), 2.37 (s, 3 H, $H_3C$(7')), 0.33 (s, 3 H, $H_3C$(6)), 0.31 (s, 3 H, $H_3C$(6))

$^{31}$P NMR: (202 MHz, $C_6H_6CH_3$ )

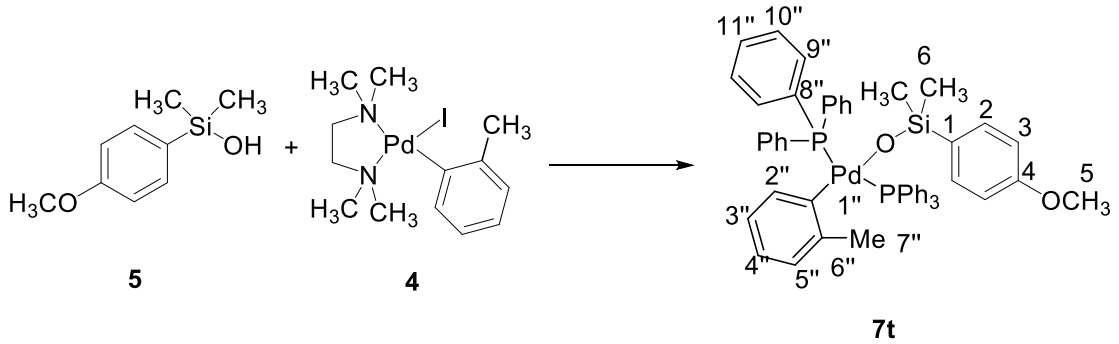
52.2 (d, *J* = 30.5), 35.9 (d, *J* = 30.5)

Analysis: $C_{46}H_{44}O_2P_2PdSi$ (825.29)

Calcd: C, 66.94; H, 5.37%

Found: C, 66.56 H, 5.13%

**Preparation of *trans*-Bis(triphenylphosphine)(2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (7t)**




In a drybox, a 50-mL, one-necked flask equipped with a magnetic stir bar was charged with **4** (440 mg, 1.00 mmol), (4-methoxyphenyl)dimethylsilanol (200 mg, 1.10 mmol, 1.1 equiv) and THF (10 mL). While stirring, $Ag_2O$ (230 mg, 1.0 mmol, 1.0 equiv) was added and the resulting suspension was stirred in the drybox for 12 h. The solvents were removed *in vacuo* (0.1 mm Hg), then toluene (20 mL) was added, and the mixture was filtered through 2 g of diatomaceous earth. The solvents were removed *in vacuo* (0.1 mm Hg) for 4 h to afford a yellow wax. THF (10 mL) and $Ph_3P$ (524 mg, 2.00 mmol, 2.00 equiv) were added and the resulting solution was stirred for 36 h in the drybox. The solvent was removed in vacuo to afford an off-white foam. The foam was dissolved in a minimal amount of THF (2 mL) and was layered with hexane (5 mL). The solution was allowed to sit at room temperature for 24 h then at -20 $^{0}$C for

24 h. The resulting solids were collected on a fritted glass funnel, then were washed with hexanes (5 mL), and dried under vacuum (0.1 mm Hg) for 12 h to afford 663 mg (73%) of **7t** as pale yellow plates.

Data for *trans*-bis(triphenylphosphine)(2-methylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (**7t**):

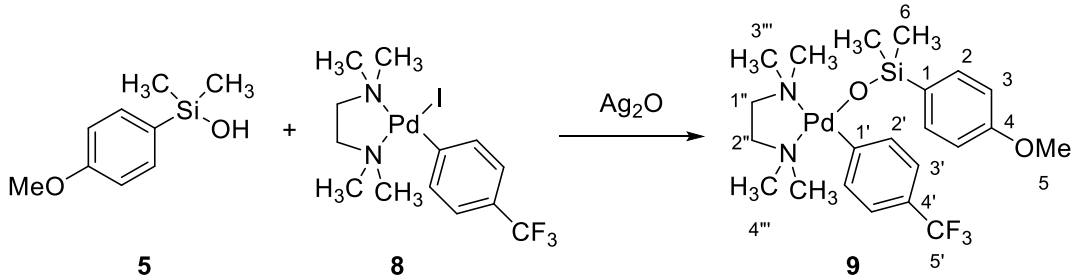
$^1$H NMR: (500 MHz, $C_6H_6$)
7.69-7.74 (m, 12 H, HC(10')), 7.38 (d, *J* = 8.0, 2 H, HC(2)), 6.98-7.04 (m, 19 H, HC(9', 11' and 2')), 6.84 (d, *J* = 8.0, 1H, HC(5')), 3.45 (s, 3H, $H_3$C(5)), 2.07 (s, 3H, $H_3$C(7)), -0.24 (s, 3H, HC(6))

$^{13}$C NMR: (126 MHz, $C_6H_6$)
159.5 (C(4)), 152.5 (C(6')), 145.3 (C(2')), 142.2 (C(4')), 140.2 (C(5')), 136.2 (C(1)), 135.3 (C(11')), 135.2 (C(10')), 130.2 (t, J = 21 C(8')), 129.9 (C(9')), 128.3 (C(2)), 123.8 (C(3')), 122.4 (C(1)), 112.8 (C(3)), 54.5 (C(5)), 26.6 (C(7')), 3.5 (C(6))

$^{31}$P NMR: (202 MHz, $C_6H_6CH_3$ )
22.6

Analysis: $C_{52}H_{50}OP_2PdSi$ (903.41)
Calcd: C, 69.13; H, 5.58%
Found: C, 69.06; H, 5.52%

**Preparation of [TMEDA](4-Trifluoromethylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (9)**




In a dry box, a 25 mL one-neck round-bottom flask containing a magnetic stir-bar and fitted with a stop-cock gas inlet was charged with **5** (182 mg, 1.0 mmol), THF (25 mL), and $Ag_2O$ (231 mg, 1.0 mmol, 1.0 equiv). To this solution was added **8** (495 mg, 1.0 mmol, 1.0

equiv). The resulting mixture was stirred for 12 h, and then the solvent was removed under vacuum (0.5 mm Hg) and replaced with toluene (25 mL). The suspension was filtered through a medium porosity glass frit covered with a plug of Celite (2 cm) into a pre-weighed one-neck flask fitted with a stop-cock gas adapter. The solvent was removed under vacuum (0.5 mm Hg) leaving 548 mg (99%) of **9** as an off-white solid residue. An analytical sample was obtained by recrystalization of 50 mg from 0.1 mL of THF and 5 mL of pentane. The crystals were isolated as colorless cubes.

Data for [TMEDA](4-Trifluoromethylphenyl)palladium 4-Methoxyphenyl dimethylsilanolate (**9**):

mp: 95-98 $^{o}$C (THF/pentane)

$^{1}$H NMR: (500 MHz, THF)

7.83 (d, $J$ = 8.5, 2 H, HC(2)), 7.63 (d, $J$ = 7.6, 2 H, HC(2')), 7.31 (d, $J$ = 7.6, 2 H, HC(3')), 6.99 (d, $J$ = 8.5, 2 H, HC(3)), 3.42 (s, 3 H, $H_3C(5)$), 2.13 (s, 6 H, $H_3C(3")$ or $H_3C(4")$), 1.55 (s, 6 H, $H_3C(4")$ or $H_3C(3")$), 1.40 (bs, 4 H, $H_2C(1")$ and $H_2C(2")$), 0.274 (s, 6 H, $H_3C(1''')$)

$^{13}$C NMR: (126 MHz, THF)

163.5 (C(4)), 161.2 (C(1), 140.5 (C(4')), 139.0 (C(2')), 136.5 (C(3')), 136.4 (C(2)), 126.2 (q, $J$ = 31.3, $F_3C(5')$), 122.8 (t, $J$ = 3.68, C(1'))) 114.0 (C(3), 64.8 (C(5)), 59.2 (C(1'') or C(2'')), 55.9 (C(1'') or C(2'')), 52.2 (C(3'') or C(4'')), 48.4 (C(3'') or C(4'')), 4.7 (C(6))

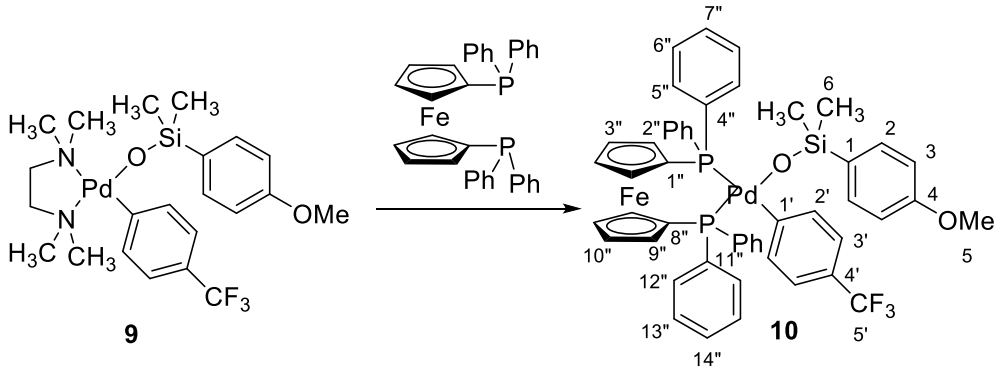
$^{19}$F NMR: (470 MHz, THF)

-61.46 (FC(5'))

Analysis: $C_{22}H_{33}F_3N_2O_2PdSi$ (549.01)

| | | | |
|---|---|---|---|
| Calcd: | C, 48.13; | H, 6.06; | N, 5.10 |
| Found: | C, 48.17; | H, 6.11; | N, 5.16 |

**Preparation of [1,1-Bis(diphenylphosphino)ferrocene](4-trifluoromethylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (10)**




In a dry box, a one-neck round-bottom flask containing magnetic stir-bar and fitted with a stop-cock gas adapter was charged with **9** (275 mg, 0.5 mmol), THF (25 mL), and dppf (277 mg, 0.5 mmol, 1.0 equiv). The resulting mixture was stirred for 1 h and then the solvent was removed under vacuum (0.5 mm Hg) until only ~1 mL remained. To the solution was added pentane (25 mL) and a precipitate was formed over a 30 min period. The suspended solid was filtered off through a fine porosity glass fritte then was dried to afford 363 mg, (73%) of **10** as a yellow/orange powder. An analytical sample was obtained by sacrificial recrystalization of 50 mg from 0.1 mL THF and 5 mL hexane where the initial solids formed were discarded and the remaining material allowed to crystallize. The crystals were isolated as small orange cubes.

Data for [1,1-bis(diphenylphosphino)ferrocene](4-trifluoromethylphenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*]palladium (**10**)

mp: 100-105 C (dec, THF/hexane)

$^1$H NMR: (500 MHz, $d_8$-THF)

9.01 (m, 4 H, HC(5”) or HC(12”)), 8.27 (d, *J* = 7.3, 2 H, HC(2)), 8.22-8.11 (m, 8 H, HC(6”) and HC(13”)), 8.11 (t, *J* = 6.4, 2 H, HC(7”) or HC(14”)), 7.96- 7.90 (m, 6 H, , HC(5”) or HC(12”), HC(7”) or HC(14”)), 7.65 (d, *J* = 8.4, 2 H, HC(2’)), 7.49 (d, *J* = 6.6, 2 H, HC(3’)), 7.31 (d, *J* = 8.4, 2 H, HC(3)), 5.66 (s, 2 H, HC(3'') or HC(10”)), 5.40 (bs, 2 H HC(3'') or HC(10”)), 5.04 (bs, 2 H, HC(2”) or HC(9”)), 4.48 (s, 3 H, H3C(5)), 4.41 (bs, 2 H, HC(2”) or HC(9”)), 0.28 (s, 6 H, H3C(6))

$^{13}$C NMR: (126 MHz, $d_8$-THF)

159.8 (C(4)), 139.3 (C(1)), 137.5 (d, *J* = 1.9, C(7“) or C(14“)), 136.4 (d, *J* = 12.9, C(4“) or C(12“)), 135.1 (C(7“) or C(14“)), 135.0 (d, *J* = 12.9, C(4“) or C(11“)), 134.8 (C(2)), 134.5 (C(4’)), 134.4 (C(2’)), 134.2 (C(3’)), 131.0 (d, *J* = 1.8 (C(6“) or C (14“)), 130.8 (d, *J* = 1.7, (C(6“) or C (13“)), 128.2 (d, *J* = 9.2, (C(5“) or C(12“)), 128.6 (d, *J* =11.0, C(5“) or C(12“)) 125.1 (q, *J* = 31.3, 282 C(5’)), 122.8 (q, *J* = 3.7, C(1’)), 112.6 (C(3)), 77.7 (*J* = 6.4, C(1“) or C(8“)), 77.3 (*J* = 6.4, C(1“) or C(8“)), 77.2 (*J* = 11.9, C(2“) or C(9“)), 75.3 (*J* = 8.3, C(2“) or C(9“)), 74.2 (*J* = 7.4, C(3“) or C(10“)), 73.0 (*J* = 3.7, C(3“) or C(10“)), 54.7 (C(5)), 3.2 (C(6))

$^{31}$P NMR: (162 MHz, $d_8$-THF)

34.9 (d, *J* = 32.0), 11.9 (d, *J* = 32.0)

(162 MHz, d8-toluene)

32.88 (d, *J* = 31.5), 10.71 (d, *J* = 31.7)

$^{19}$F NMR: (470 MHz, $d_8$-THF)

-61.07 (FC(5’))

Analysis: $C_{50}H_{45}F_3FeO_2P_2PdSi$ (987.18)

Calcd: C, 60.83; H, 4.59

Found: C, 60.49; H, 4.61

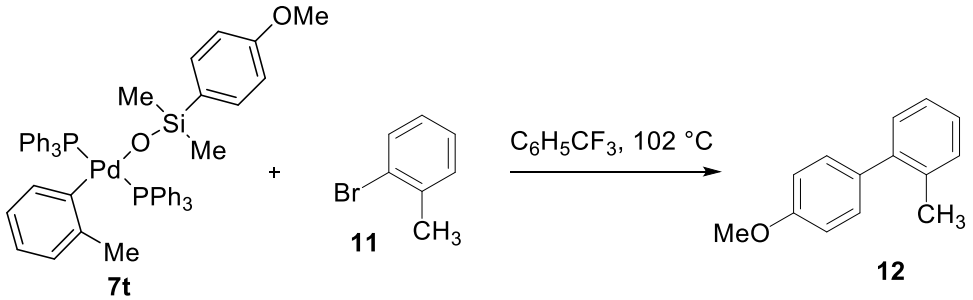
**KINETIC STUDIES OF THERMOLYLSIS OF ARYLPALLADIUM ARYLSILANOLATE COMPLEXES (TABLE 2)**

**Response Factors**

$$\text{Response factor for } \mathbf{12} = \frac{(\text{mmol } \mathbf{12} * \text{area internal standard})}{(\text{mmol internal standard} * \text{area } \mathbf{12})}$$

| naphthalene (mmol) | naphthalene (area) | product **12** (mmol) | product **12** (area) | response factor |
|---|---|---|---|---|
| 0.0998 | 4157580 | 0.0974 | 4184310 | 1.054 |
| 0.1001 | 5000900 | 0.0999 | 4698670 | 1.062 |
| 0.0983 | 4701810 | 0.1010 | 4518390 | 1.069 |

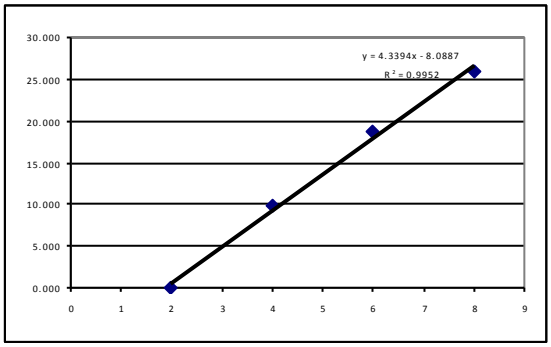
**Thermolysis of 7t (Table 2, entry 1)**




In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with naphthalene (15 mg), **7t** (45 mg, 0.05 mmol), 2-bromotoluene (20 μL, 0.167 mmol, 3.3 equiv), and dry benzotrifluoride (4.0 mL). The flask was removed from the drybox, purged with argon, and then was placed in a 105 $^{0}$C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 30 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.5 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC.

**Run 1**

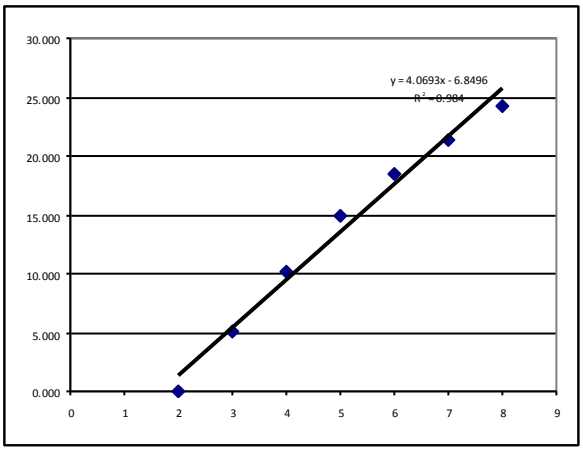
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 1 | 0 | 0.000 |
| 2 | 1 | 0 | 0.000 |
| 2 | 1 | 0 | 0.000 |
| 4 | 59059 | 4287 | 9.614 |
| 4 | 59524 | 4358 | 9.697 |
| 4 | 58847 | 4389 | 9.878 |
| 6 | 64418 | 9222 | 18.961 |
| 6 | 64634 | 9099 | 18.646 |
| 6 | 64901 | 9204 | 18.783 |
| 8 | 53716 | 10388 | 25.614 |
| 8 | 54206 | 10638 | 25.993 |
| 8 | 54147 | 10676 | 26.115 |




**rate = 0.0180 mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 1 | 0 | 0.000 |
| 2 | 1 | 0 | 0.000 |
| 2 | 1 | 0 | 0.000 |
| 3 | 46998 | 1895 | 5.007 |
| 3 | 46860 | 1910 | 5.061 |
| 3 | 46342 | 1906 | 5.107 |
| 4 | 48983 | 4011 | 10.168 |
| 4 | 48353 | 3967 | 10.187 |
| 4 | 48479 | 3983 | 10.202 |
| 5 | 51995 | 6221 | 14.857 |
| 5 | 51443 | 6199 | 14.963 |
| 5 | 52728 | 6428 | 15.138 |
| 6 | 44738 | 6689 | 18.565 |
| 6 | 45006 | 6771 | 18.681 |
| 6 | 45058 | 6679 | 18.406 |
| 7 | 44331 | 7556 | 21.164 |
| 7 | 44898 | 7870 | 21.765 |
| 7 | 44581 | 7640 | 21.280 |
| 8 | 48157 | 9470 | 24.418 |
| 8 | 48730 | 9439 | 24.052 |
| 8 | 48908 | 9617 | 24.416 |

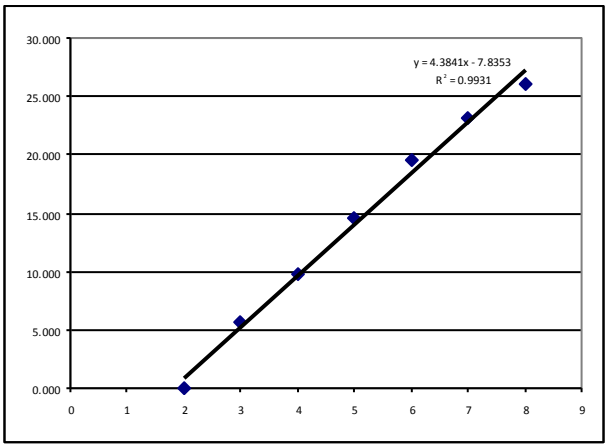



**rate = 0.0169 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 1 | 0 | 0.000 |
| 2 | 1 | 0 | 0.000 |
| 2 | 1 | 0 | 0.000 |
| 3 | 53875 | 2420 | 5.578 |
| 3 | 53537 | 2444 | 5.668 |

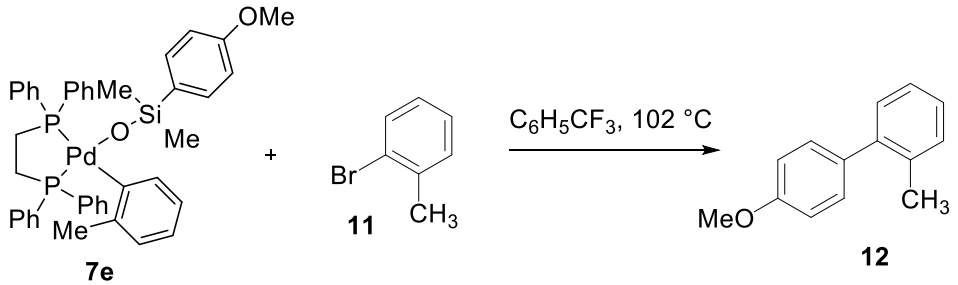
| | | | |
|---|---|---|---|
| 3 | 53228 | 2369 | 5.526 |
| 4 | 57807 | 4606 | 9.894 |
| 4 | 58271 | 4593 | 9.787 |
| 4 | 57980 | 4550 | 9.744 |
| 5 | 56711 | 6666 | 14.595 |
| 5 | 56649 | 6680 | 14.642 |
| 5 | 56077 | 6591 | 14.594 |
| 6 | 61895 | 9607 | 19.273 |
| 6 | 61769 | 9620 | 19.339 |
| 6 | 61492 | 9793 | 19.775 |
| 7 | 79437 | 14592 | 22.809 |
| 7 | 79719 | 14854 | 23.137 |
| 7 | 80549 | 15127 | 23.319 |
| 8 | 49516 | 10419 | 26.128 |
| 8 | 50163 | 10459 | 25.890 |
| 8 | 50300 | 10568 | 26.088 |




**rate = 0.0183 mM/sec**

**avg. rate = 1.77 x $10^{-2}$ mM/s**

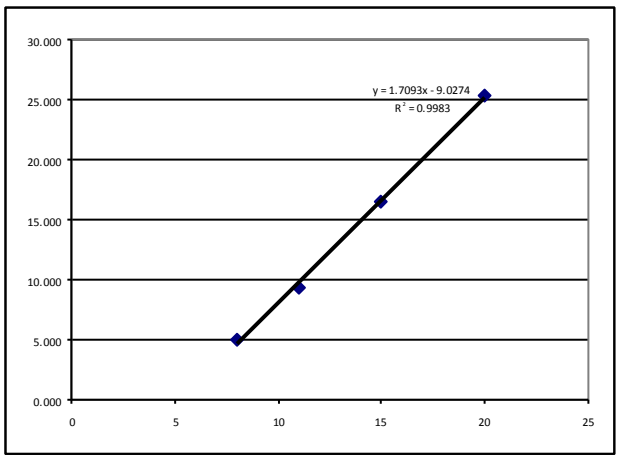
**Thermolysis of 7e (Table 2, entry 2)**




In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with naphthalene (15 mg), **7e** (39 mg, 0.05 mmol), 2-bromotoluene (20 μL, 0.167 mmol, 3.3 equiv), and dry benzotrifluoride (4.0 mL). The flask was removed from the drybox, purged with argon, and then was placed in a 105 $^{0}$C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 30 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.5 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC.

**Run 1**

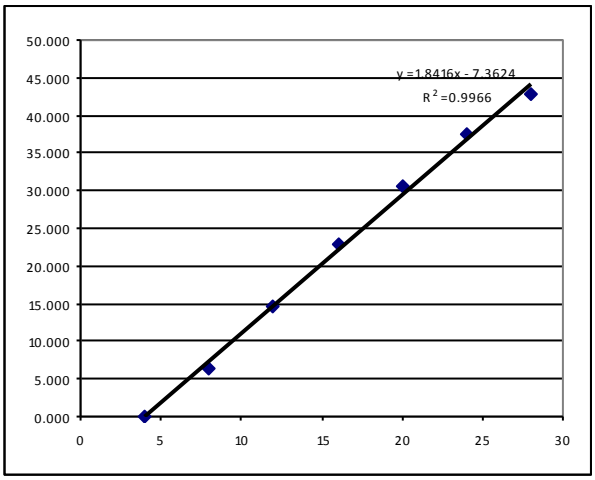
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 8 | 39213 | 1555 | 4.924 |
| 8 | 41046 | 1642 | 4.967 |
| 8 | 40905 | 1722 | 5.227 |
| 11 | 41668 | 3119 | 9.295 |
| 11 | 43423 | 3227 | 9.228 |
| 11 | 43752 | 3323 | 9.431 |
| 15 | 41585 | 5460 | 16.303 |
| 15 | 43147 | 5809 | 16.717 |
| 15 | 43990 | 5833 | 16.465 |
| 20 | 37354 | 7599 | 25.260 |
| 20 | 38795 | 7867 | 25.180 |
| 20 | 38415 | 7916 | 25.587 |
| 40 | 41532 | 15390 | 46.013 |
| 40 | 40984 | 15701 | 47.570 |
| 40 | 41100 | 15724 | 47.505 |




**rate = 0.00708 mM/sec**

**Run 2**

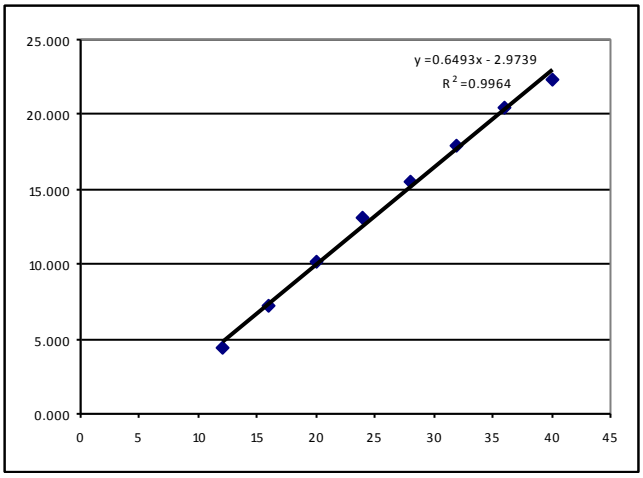
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 8 | 52787 | 1987 | 6.544 |
| 8 | 53276 | 1969 | 6.425 |
| 8 | 53855 | 1983 | 6.401 |
| 12 | 46810 | 3943 | 14.643 |
| 12 | 46852 | 3939 | 14.615 |
| 12 | 46814 | 3935 | 14.612 |
| 16 | 67557 | 8900 | 22.902 |
| 16 | 67821 | 8940 | 22.915 |
| 16 | 68719 | 8971 | 22.694 |
| 20 | 59846 | 10421 | 30.271 |
| 20 | 59939 | 10425 | 30.235 |
| 20 | 59658 | 10682 | 31.127 |
| 24 | 53035 | 11474 | 37.610 |
| 24 | 53361 | 11451 | 37.305 |
| 24 | 53357 | 11570 | 37.696 |
| 28 | 51488 | 12644 | 42.690 |
| 28 | 51522 | 12772 | 43.094 |
| 28 | 51681 | 12604 | 42.396 |




**rate = 0.00766 mM/sec**

**Run 3 (run at half scale vs Run 1 and 2)**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 12 | 65983 | 1672 | 4.405 |
| 12 | 67048 | 1690 | 4.382 |
| 12 | 66687 | 1677 | 4.372 |
| 16 | 53288 | 2212 | 7.216 |
| 16 | 54200 | 2256 | 7.236 |
| 16 | 53698 | 2225 | 7.203 |
| 20 | 47425 | 2724 | 9.985 |
| 20 | 46983 | 2762 | 10.220 |
| 20 | 47362 | 2796 | 10.263 |
| 24 | 54560 | 3985 | 12.697 |
| 24 | 32237 | 2541 | 13.702 |
| 24 | 54134 | 4048 | 12.999 |
| 28 | 50711 | 4448 | 15.248 |
| 28 | 50008 | 4519 | 15.709 |
| 28 | 49811 | 4482 | 15.642 |
| 32 | 50665 | 5106 | 17.519 |
| 32 | 50486 | 5199 | 17.902 |
| 32 | 50604 | 5383 | 18.492 |
| 36 | 55826 | 6495 | 20.225 |
| 36 | 33752 | 3937 | 20.277 |
| 36 | 33378 | 4022 | 20.947 |

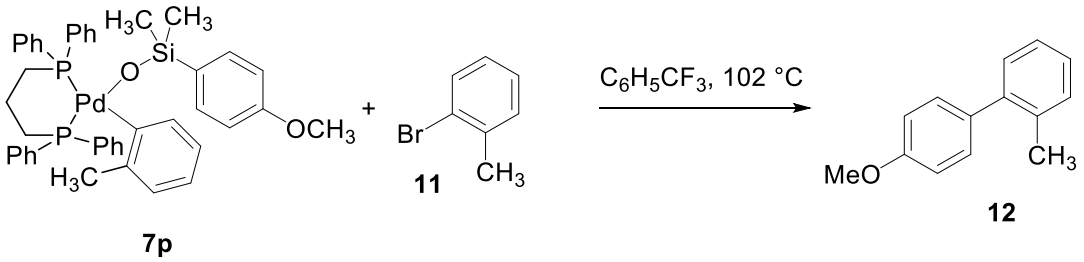



**rate = 0.00541 mM/sec**

| | | | |
|---|---|---|---|
| 40 | 51466 | 6533 | 22.067 |
| 40 | 51310 | 6625 | 22.446 |
| 40 | 50927 | 6634 | 22.645 |

**avg. rate = 0.671 x $10^{-2}$ mM/s**

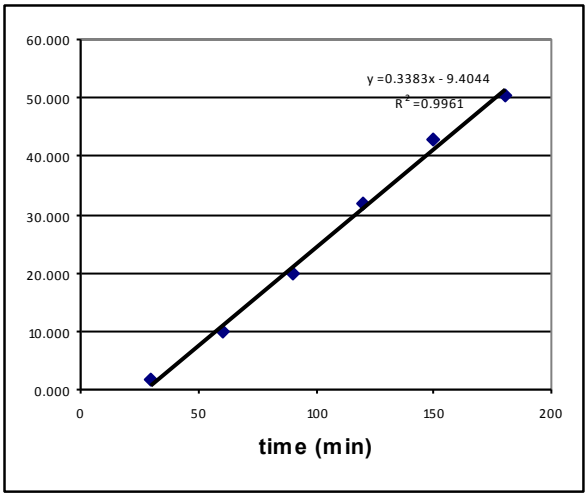
**Thermolysis of 7p (Table 2, entry 3)**




In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with naphthalene (20 mg), **7p** (45 mg, 0.05 mmol), 2-bromotoluene (20 μL, 0.167 mmol, 3.3 equiv), and dry benzotrifluoride (4.0 mL). The flask was removed from the drybox, purged with argon, and then was placed in a 105 $^{0}$C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 30 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.5 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 30 | 1 | 0 | 0.000 |
| 30 | 128110 | 1867 | 2.413 |
| 30 | 101636 | 1589 | 2.588 |
| 60 | 84983 | 5178 | 10.088 |
| 60 | 84995 | 5115 | 9.963 |
| 60 | 84319 | 5100 | 10.014 |
| 90 | 100224 | 12135 | 20.046 |
| 90 | 108641 | 12582 | 19.174 |
| 90 | 106269 | 12833 | 19.993 |
| 120 | 63258 | 12238 | 32.030 |
| 120 | 65740 | 12535 | 31.568 |
| 120 | 108358 | 20830 | 31.826 |
| 150 | 81771 | 21277 | 43.079 |
| 150 | 85072 | 22077 | 42.965 |
| 150 | 68956 | 17790 | 42.713 |
| 180 | 50224 | 15410 | 50.798 |

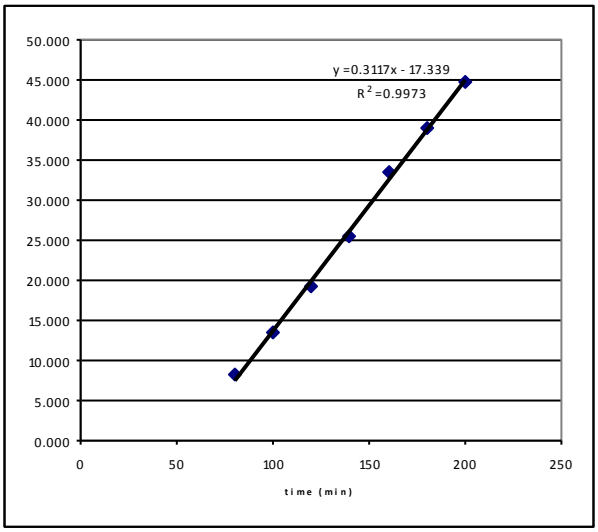



**rate = 0.00141 mM/sec**

| | | | |
|---|---|---|---|
| 180 | 51362 | 15752 | 50.775 |
| 180 | 68842 | 20837 | 50.112 |
| 240 | 83785 | 25161 | 49.719 |
| 240 | 83125 | 25151 | 50.094 |
| 240 | 50211 | 15420 | 50.845 |

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 60 | 66513 | 1793 | 4.463 |
| 60 | 67106 | 1818 | 4.485 |
| 60 | 66513 | 1793 | 4.463 |
| 80 | 67368 | 3362 | 8.262 |
| 80 | 66662 | 3345 | 8.308 |
| 80 | 66768 | 3401 | 8.433 |
| 100 | 64085 | 5221 | 13.488 |
| 100 | 64523 | 5241 | 13.448 |
| 100 | 64684 | 5377 | 13.763 |
| 120 | 97467 | 11326 | 19.239 |
| 120 | 98625 | 11456 | 19.231 |
| 120 | 97244 | 11455 | 19.503 |
| 140 | 107587 | 16470 | 25.345 |
| 140 | 107370 | 16500 | 25.443 |
| 140 | 107451 | 16644 | 25.645 |
| 160 | 81990 | 16355 | 33.025 |
| 160 | 83914 | 16855 | 33.255 |
| 160 | 47951 | 9903 | 34.192 |
| 180 | 71878 | 16732 | 38.540 |
| 180 | 72984 | 17194 | 39.004 |
| 180 | 42608 | 10240 | 39.789 |
| 200 | 78868 | 21500 | 45.133 |
| 200 | 78999 | 21239 | 44.511 |
| 200 | 80067 | 21588 | 44.639 |

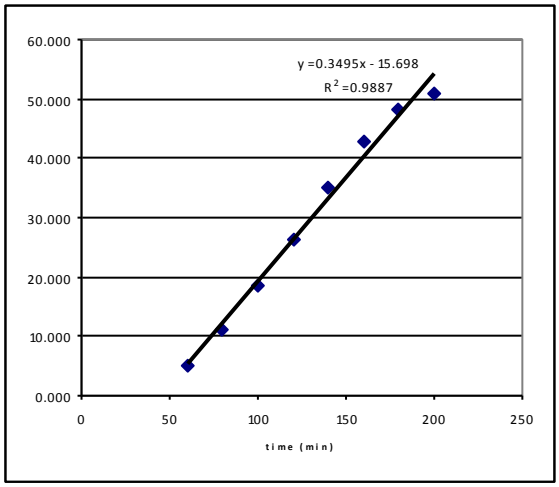



**rate = 0.00130 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 60 | 95078 | 2875 | 5.006 |
| 60 | 94825 | 2913 | 5.086 |
| 60 | 95101 | 2914 | 5.073 |
| 80 | 85479 | 5752 | 11.141 |
| 80 | 84735 | 5753 | 11.241 |
| 80 | 84482 | 5658 | 11.088 |
| 100 | 79383 | 8851 | 18.460 |
| 100 | 79433 | 8859 | 18.465 |
| 100 | 47003 | 5259 | 18.524 |
| 120 | 88977 | 14113 | 26.260 |
| 120 | 89942 | 14253 | 26.236 |

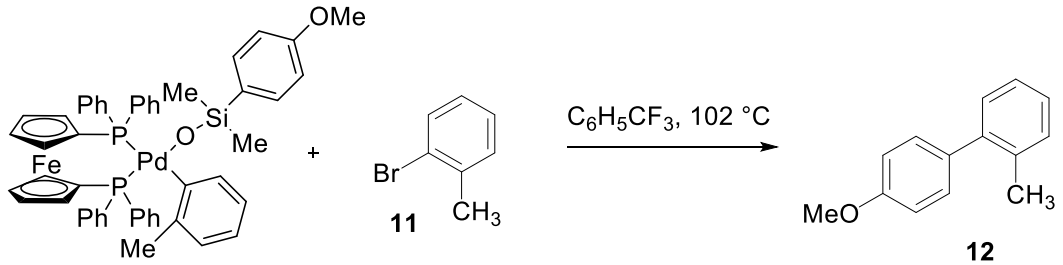
| | | | |
|---|---|---|---|
| 120 | 89940 | 14408 | 26.522 |
| 140 | 80924 | 17210 | 35.210 |
| 140 | 80974 | 17165 | 35.096 |
| 140 | 48287 | 10250 | 35.144 |
| 160 | 89260 | 22759 | 42.214 |
| 160 | 52710 | 13567 | 42.614 |
| 160 | 52956 | 13788 | 43.107 |
| 180 | 89344 | 25655 | 47.541 |
| 180 | 88844 | 25524 | 47.564 |
| 180 | 52275 | 15611 | 49.442 |
| 200 | 85287 | 25936 | 50.348 |
| 200 | 84991 | 26110 | 50.862 |
| 200 | 84273 | 26167 | 51.407 |




**rate = 0.00145 mM/sec**

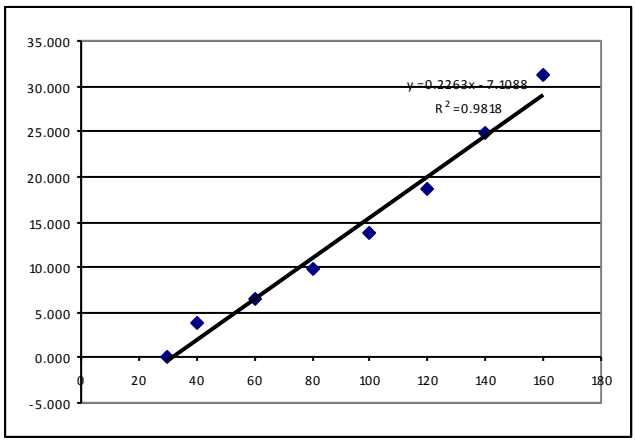
**avg. rate = 0.139 x $10^{-2}$ mM/s**

**Thermolysis of 7f (Table 2, entry 4)**




In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with naphthalene (15 mg), **7f** (47 mg, 0.05 mmol), 2-bromotoluene (20 μL, 0.167 mmol, 3.3 equiv), and dry benzotrifluoride (4.0 mL). The flask was removed from the drybox, purged with argon, and then was placed in a 105 $^{0}$C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 30 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.5 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC.

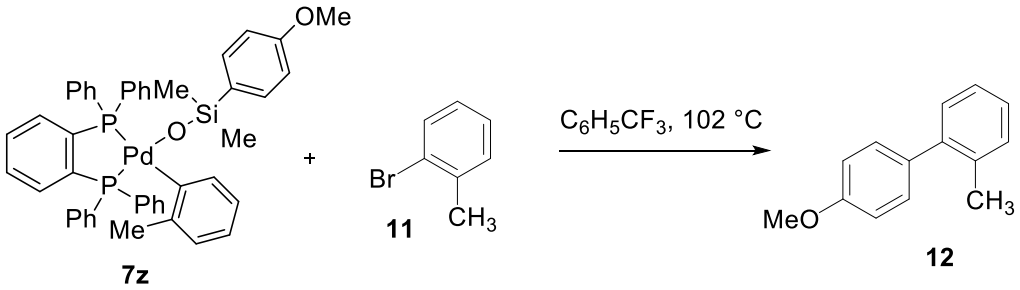
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 30 | 1 | 0 | 0.000 |
| 30 | 1 | 0 | 0.000 |
| 30 | 1 | 0 | 0.000 |
| 40 | 56858 | 1785 | 3.898 |
| 40 | 59669 | 1741 | 3.623 |
| 40 | 59289 | 1777 | 3.722 |
| 60 | 83950 | 4308 | 6.372 |
| 60 | 86727 | 4435 | 6.350 |
| 60 | 86326 | 4574 | 6.579 |
| 80 | 58836 | 4805 | 10.141 |
| 80 | 61975 | 4941 | 9.900 |
| 80 | 62027 | 4763 | 9.535 |
| 100 | 63283 | 7185 | 14.098 |
| 100 | 64909 | 7123 | 13.626 |
| 100 | 65933 | 7109 | 13.388 |
| 120 | 64131 | 9774 | 18.925 |
| 120 | 66297 | 9878 | 18.501 |




**rate = 9.41 x 10$^{-4}$ mM/sec**

| | | | |
|---|---|---|---|
| 120 | 65753 | 9722 | 18.359 |
| 140 | 55745 | 11206 | 24.961 |
| 140 | 57216 | 11388 | 24.714 |
| 140 | 32475 | 6428 | 24.578 |
| 160 | 55779 | 14823 | 32.998 |
| 160 | 57810 | 14407 | 30.945 |
| 160 | 33836 | 8114 | 29.777 |

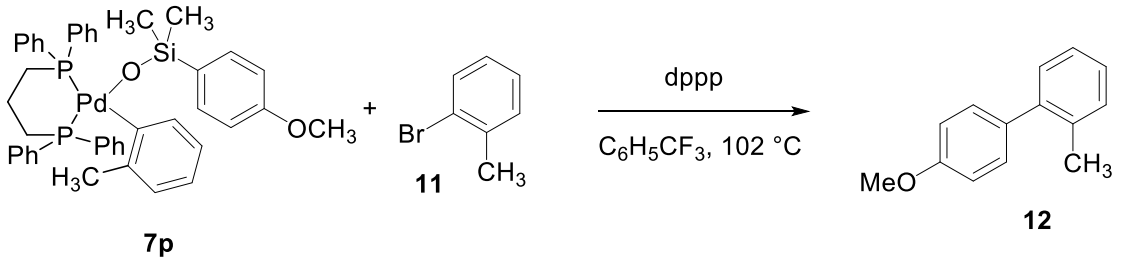
**Thermolysis of 7z (Table 2, entry 5)**




In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with naphthalene (15 mg), **7z** (41 mg, 0.05 mmol), 2-bromotoluene (20 μL, 0.167 mmol, 3.3 equiv), and dry benzotrifluoride (4.0 mL). The flask was removed from the drybox, purged with argon, and then was placed in a 105 $^{0}$C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 30 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.5 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC. No reaction was observed after 24h. The reaction was repeated twice with identical results.

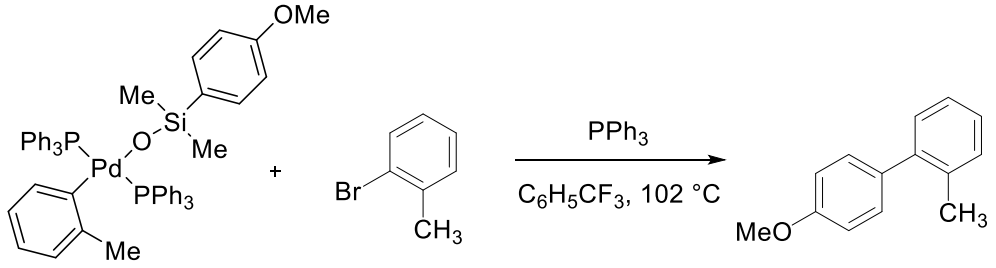
**EFFECT OF ADDED PHOSPHINE ON THE RATE OF THERMAL TRANSMETALATION OF 7p AND 7t (SCHEME 2)**

**Thermolysis of 7p in the presence of dppp**




In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with naphthalene (10 mg), **7p** (45 mg, 0.05 mmol), 2-bromotoluene (20 μL, 0.167 mmol, 3.3 equiv), dppp (10.3 mg , 0.025 mmol) and dry benzotrifluoride (4.0 mL). The flask was removed from the drybox, purged with argon, and then was placed in a 105 $^{0}$C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 30 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.5 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC. Cross-coupling product **12** was not observed after 2 h. The procedure was performed twice with identical results.

**Thermolysis of 14t in the presence of $Ph_3P$**

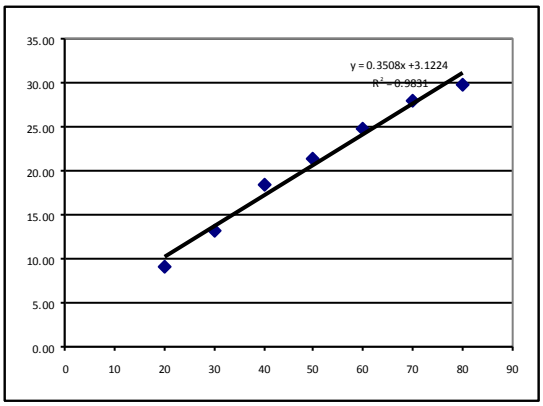



**7t** **11** **12**

In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with naphthalene (15 mg), **7t** (45 mg, 0.05 mmol), 2-bromotoluene (20 μL, 0.167 mmol, 3.3 equiv), $PPh_3$ (6.6 mg, 0.025 mmol, 0.5 equiv) and dry benzotrifluoride (4.0 mL). The flask was removed from the drybox, purged with argon, and then was placed in a 105 $^0$C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 30 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.5 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 20 | 6887 | 763 | 9.17 |
| 20 | 7261 | 805 | 9.18 |
| 20 | 7139 | 762 | 8.84 |
| 30 | 10084 | 1578 | 12.95 |
| 30 | 10191 | 1630 | 13.24 |
| 30 | 10358 | 1659 | 13.26 |
| 40 | 8377 | 1833 | 18.11 |
| 40 | 8440 | 1873 | 18.37 |
| 40 | 8517 | 1935 | 18.81 |
| 50 | 10938 | 2823 | 21.36 |
| 50 | 10912 | 2787 | 21.14 |
| 50 | 10664 | 2814 | 21.84 |
| 60 | 8212 | 2432 | 24.52 |
| 60 | 8118 | 2456 | 25.04 |
| 60 | 8232 | 2461 | 24.75 |

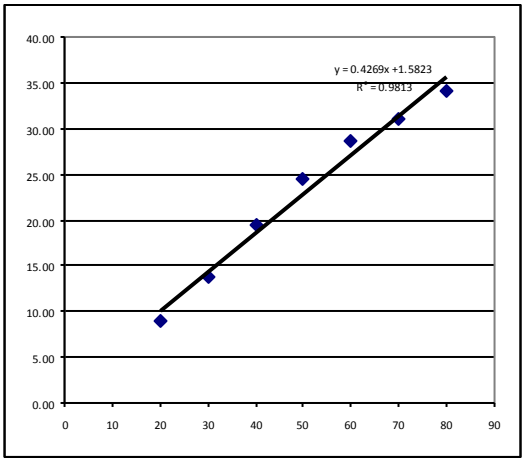


| | | | |
|---|---|---|---|
| 70 | 10294 | 3499 | 28.14 |
| 70 | 10790 | 3629 | 27.84 |
| 70 | 10883 | 3658 | 27.82 |
| 80 | 8340 | 3005 | 29.83 |
| 80 | 8031 | 2874 | 29.62 |
| 80 | 8180 | 2969 | 30.05 |

**rate = 1.45 x $10^{-3}$ mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 20 | 9724 | 1030 | 8.77 |
| 20 | 10134 | 1129 | 9.22 |
| 20 | 10468 | 1125 | 8.90 |
| 30 | 10492 | 1816 | 14.33 |
| 30 | 10408 | 1767 | 14.05 |
| 30 | 10826 | 1659 | 12.69 |
| 40 | 9074 | 2233 | 20.37 |
| 40 | 10020 | 2308 | 19.07 |
| 40 | 9889 | 2277 | 19.06 |
| 50 | 11147 | 3309 | 24.57 |
| 50 | 11324 | 3317 | 24.25 |
| 50 | 11177 | 3299 | 24.43 |
| 60 | 8547 | 2873 | 27.83 |
| 60 | 8458 | 2954 | 28.91 |
| 60 | 8158 | 2904 | 29.47 |
| 70 | 11695 | 4315 | 30.54 |
| 70 | 11519 | 4284 | 30.79 |
| 70 | 11558 | 4419 | 31.65 |
| 80 | 10718 | 4481 | 34.61 |
| 80 | 11000 | 4548 | 34.23 |
| 80 | 10999 | 4483 | 33.74 |

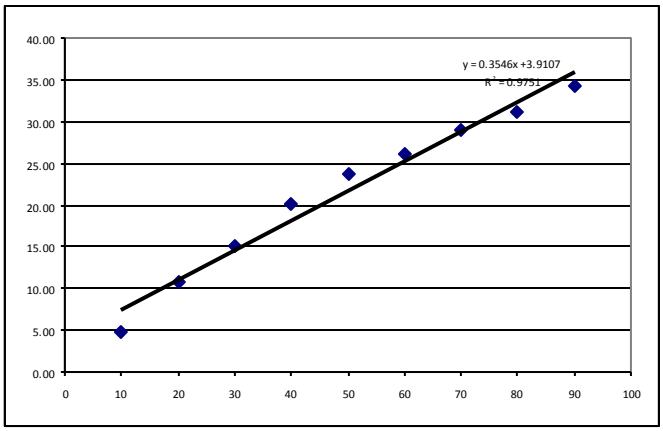



**rate = 1.77 x $10^{-3}$ mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 10 | 12385 | 756 | 5.05 |
| 10 | 12348 | 719 | 4.82 |
| 10 | 12775 | 741 | 4.80 |
| 20 | 10110 | 1230 | 10.07 |
| 20 | 9666 | 1290 | 11.05 |
| 20 | 9384 | 1236 | 10.90 |
| 30 | 10790 | 1919 | 14.72 |
| 30 | 10395 | 1948 | 15.51 |
| 30 | 10739 | 1952 | 15.05 |
| 40 | 9490 | 2276 | 19.85 |
| 40 | 9168 | 2371 | 21.41 |
| 40 | 10069 | 2284 | 18.78 |
| 50 | 9099 | 2679 | 24.37 |

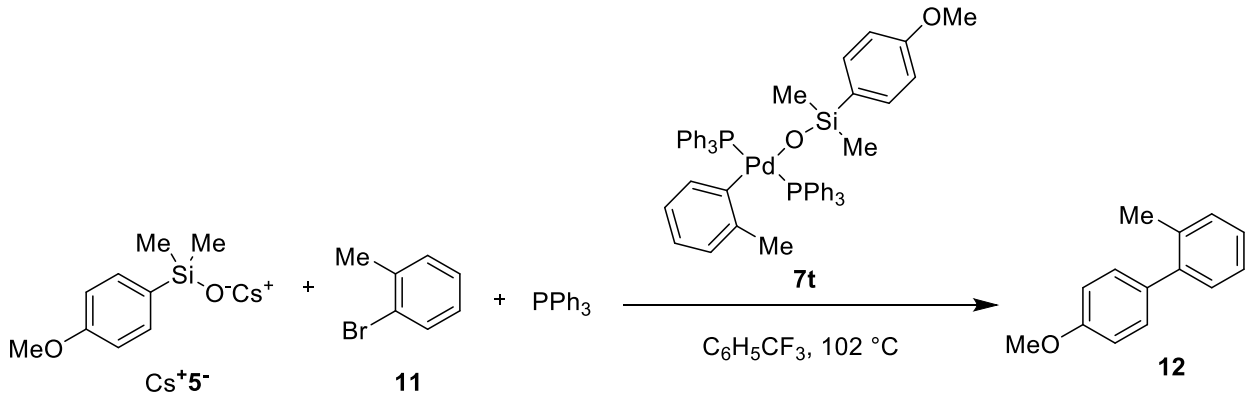
| | | | |
|---|---|---|---|
| 50 | 10258 | 2795 | 22.56 |
| 50 | 8809 | 2541 | 23.88 |
| 60 | 7772 | 2461 | 26.21 |
| 60 | 8037 | 2534 | 26.10 |
| 60 | 5824 | 1852 | 26.32 |
| 70 | 7110 | 2475 | 28.82 |
| 70 | 7327 | 2559 | 28.91 |
| 70 | 7186 | 2507 | 28.88 |
| 80 | 7805 | 2906 | 30.82 |
| 80 | 8083 | 3003 | 30.75 |
| 80 | 7927 | 3021 | 31.55 |
| 90 | 8256 | 3556 | 35.66 |
| 90 | 7913 | 3285 | 34.37 |
| 90 | 8189 | 3273 | 33.09 |




**rate = 1.47 x $10^{-3}$ mM/sec**

**avg. rate = 1.56 x $10^{-2}$ mM/s**

**General procedure I: Effect of Added Phosphine on the Rate of the Catalytic Cross-Coupling of $Cs^{+}\mathbf{5}^{-}$ (Footnote 12)**




**Order in $PPh_3$ (3.75 mM)**

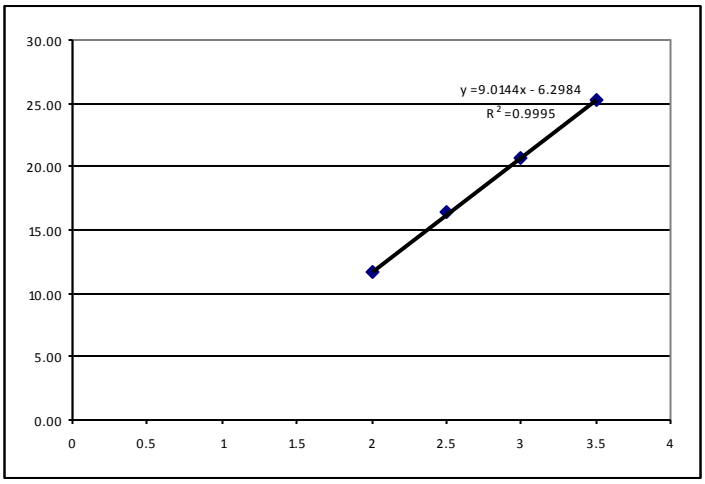
| | |
|---|---|
| $Cs^{+}\mathbf{5}^{-}$ | 62.5 mM |
| 2-Bromotoluene | 83 mM |
| **7t** | 7.5 mM |
| $PPh_3$ | 3.75 mM |

In a drybox, a one-necked, 5-mL round-bottomed flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with $Cs^{+}\mathbf{5}^{-}$ (39 mg, 0.125 mmol, 0.78 equiv), **7t** (13.5 mg, 0.015 mmol, 0.090 equiv), naphthalene (12 mg), $PPh_3$ (2.0 mg, 0.0075 mmol, 0.047 equiv), 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) and dry benzotrifluoride (2.0 mL). The flask was placed in a 105 °C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 50 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.0 mL of ethyl acetate and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 21798 | 2560 | 11.67 |
| 2 | 21145 | 2449 | 11.51 |

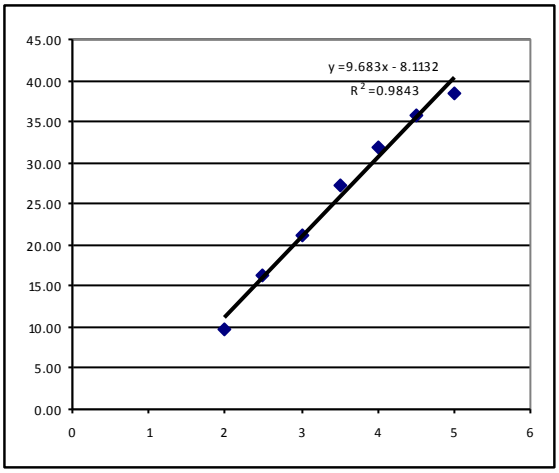
| | | | |
|---|---|---|---|
| 2 | 21173 | 2492 | 11.69 |
| 2.5 | 24839 | 4093 | 16.37 |
| 2.5 | 24598 | 4036 | 16.30 |
| 2.5 | 24706 | 4133 | 16.62 |
| 3 | 20886 | 4356 | 20.72 |
| 3 | 20922 | 4375 | 20.77 |
| 3 | 22037 | 4566 | 20.58 |
| 3.5 | 20344 | 5120 | 25.00 |
| 3.5 | 20258 | 5246 | 25.72 |
| 3.5 | 21533 | 5408 | 24.95 |
| 4 | 18764 | 5514 | 29.19 |
| 4 | 19319 | 5609 | 28.84 |
| 4 | 19665 | 5800 | 29.30 |




**rate = 0.0751 mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, µmol |
|---|---|---|---|
| 2 | 23965 | 2276 | 7.86 |
| 2 | 19465 | 2443 | 10.39 |
| 2 | 18725 | 2406 | 10.64 |
| 2.5 | 18458 | 3604 | 16.16 |
| 2.5 | 18389 | 3749 | 16.88 |
| 2.5 | 18733 | 3587 | 15.85 |
| 3 | 16781 | 4406 | 21.73 |
| 3 | 16373 | 4251 | 21.49 |
| 3 | 16573 | 4128 | 20.62 |
| 3.5 | 17289 | 5716 | 27.37 |
| 3.5 | 17280 | 5775 | 27.67 |
| 3.5 | 17513 | 5721 | 27.04 |
| 4 | 21898 | 8338 | 31.52 |
| 4 | 22659 | 8798 | 32.14 |
| 4 | 21473 | 8231 | 31.73 |
| 4.5 | 19223 | 8285 | 35.68 |
| 4.5 | 18863 | 8224 | 36.09 |
| 4.5 | 19703 | 8409 | 35.33 |
| 5 | 18849 | 8818 | 38.73 |
| 5 | 18611 | 8567 | 38.11 |
| 5 | 18743 | 8671 | 38.30 |

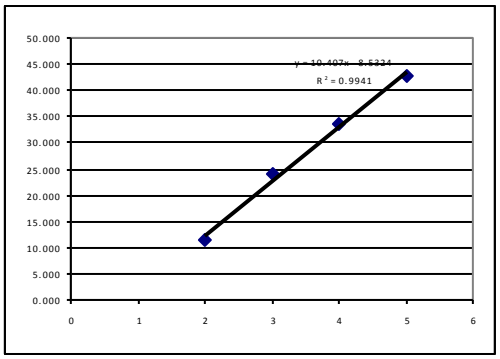



**rate = 0.0807 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, µmol |
|---|---|---|---|
| 2 | 93311 | 8576 | 11.412 |
| 2 | 93699 | 8455 | 11.205 |
| 2 | 95136 | 8663 | 11.307 |

| | | | |
|---|---|---|---|
| 3 | 89097 | 17178 | 23.940 |
| 3 | 88721 | 17109 | 23.945 |
| 3 | 87342 | 16726 | 23.779 |
| 4 | 81946 | 22610 | 34.260 |
| 4 | 80985 | 22046 | 33.802 |
| 4 | 84529 | 22312 | 32.776 |
| 5 | 81422 | 27452 | 41.865 |
| 5 | 78398 | 27549 | 43.634 |
| 5 | 79687 | 27446 | 42.767 |
| 6 | 75606 | 29791 | 48.927 |
| 6 | 75841 | 29538 | 48.361 |
| 6 | 75127 | 29876 | 49.379 |




**rate = 0.0867 mM/sec**

**avg. rate = 8.08 x $10^{-2}$ mM/s**

**Order in $PPh_3$ (7.5 mM)**

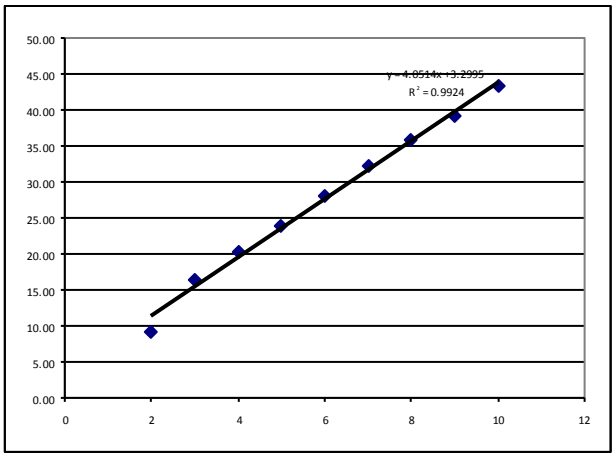
| | |
|---|---|
| $Cs^+$**12**$^-$ | 62.5 mM |
| 2-Bromotoluene | 83 mM |
| **7t** | 7.5 mM |
| $PPh_3$ | 7.50 mM |

Following the General Procedure I, a mixture of silanolate $Cs^+$**12**$^-$ (39 mg, 0.125 mmol), **7t** (13.5 mg, 0.015 mmol, 0.090 equiv), naphthalene (11 mg), $PPh_3$ (4.0 mg, 0.015 mmol) and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 15759 | 1609 | 9.30 |
| 2 | 16187 | 1688 | 9.50 |
| 2 | 8571 | 850 | 9.03 |
| 3 | 7799 | 1414 | 16.51 |
| 3 | 7613 | 1384 | 16.55 |
| 3 | 7799 | 1414 | 16.51 |
| 4 | 6764 | 1553 | 20.91 |
| 4 | 7309 | 1582 | 19.71 |
| 4 | 8347 | 1865 | 20.35 |
| 5 | 6960 | 1837 | 24.03 |
| 5 | 6453 | 1683 | 23.75 |

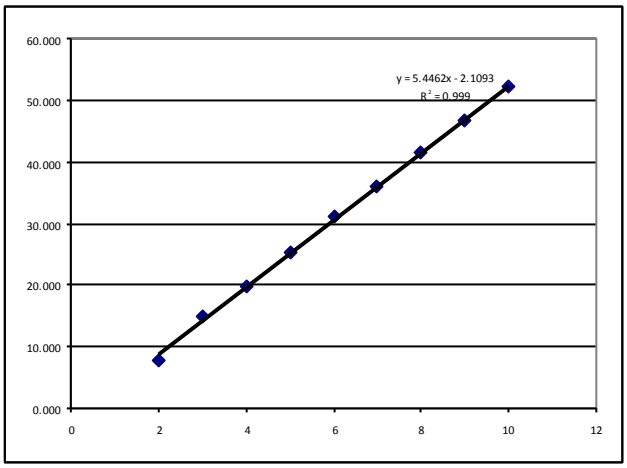
| | | | |
|---|---|---|---|
| 5 | 6960 | 1837 | 24.03 |
| 6 | 7151 | 2193 | 27.93 |
| 6 | 6493 | 1994 | 27.96 |
| 6 | 8180 | 2540 | 28.27 |
| 7 | 8376 | 2933 | 31.89 |
| 7 | 9165 | 3221 | 32.00 |
| 7 | 8134 | 2896 | 32.42 |
| 8 | 9487 | 3687 | 35.39 |
| 8 | 8729 | 3452 | 36.01 |
| 8 | 8961 | 3555 | 36.12 |
| 9 | 8388 | 3630 | 39.41 |
| 9 | 8943 | 3720 | 37.88 |
| 9 | 8663 | 3808 | 40.03 |
| 10 | 9524 | 4508 | 43.10 |
| 10 | 9777 | 4638 | 43.20 |
| 10 | 8728 | 4182 | 43.63 |




**rate = 0.0338 mM/sec**

**Run 2**

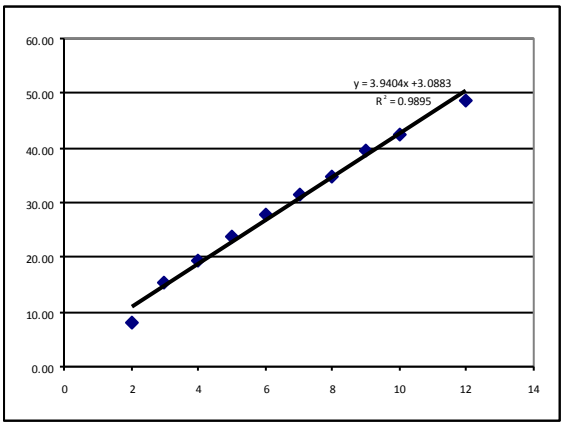
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 68147 | 4319 | 7.870 |
| 2 | 93227 | 5781 | 7.700 |
| 2 | 43836 | 2811 | 7.963 |
| 3 | 66193 | 8101 | 15.197 |
| 3 | 44073 | 5335 | 15.031 |
| 3 | 46200 | 5489 | 14.753 |
| 4 | 19012 | 2977 | 19.443 |
| 4 | 37975 | 5979 | 19.550 |
| 4 | 73901 | 11942 | 20.065 |
| 5 | 79537 | 16119 | 25.165 |
| 5 | 79245 | 16208 | 25.397 |
| 5 | 79372 | 16314 | 25.522 |
| 6 | 36003 | 9021 | 31.113 |
| 6 | 35745 | 8789 | 30.531 |
| 6 | 72104 | 18227 | 31.389 |
| 7 | 39346 | 11369 | 35.879 |
| 7 | 80292 | 23092 | 35.712 |
| 7 | 38841 | 11284 | 36.074 |
| 8 | 77781 | 26152 | 41.750 |
| 8 | 40458 | 13520 | 41.495 |
| 8 | 80453 | 26450 | 40.823 |
| 9 | 34049 | 13114 | 47.825 |
| 9 | 74228 | 27431 | 45.887 |
| 9 | 36009 | 13384 | 46.152 |
| 10 | 33433 | 14570 | 54.113 |
| 10 | 72102 | 30797 | 53.037 |
| 10 | 36465 | 14653 | 49.897 |




**rate = 0.0453 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 19898 | 1764 | 8.07 |
| 2 | 19543 | 1791 | 8.34 |
| 2 | 20124 | 1785 | 8.08 |
| 3 | 20826 | 3455 | 15.11 |
| 3 | 20842 | 3601 | 15.73 |
| 3 | 20698 | 3451 | 15.18 |
| 4 | 20173 | 4288 | 19.36 |
| 4 | 20741 | 4490 | 19.71 |
| 4 | 21314 | 4456 | 19.04 |
| 5 | 19625 | 5121 | 23.76 |
| 5 | 20327 | 5259 | 23.56 |
| 5 | 19782 | 5241 | 24.12 |
| 6 | 17618 | 5453 | 28.18 |
| 6 | 17240 | 5174 | 27.33 |
| 6 | 17584 | 5373 | 27.82 |
| 7 | 17394 | 5891 | 30.84 |
| 7 | 18553 | 6381 | 31.32 |
| 7 | 18198 | 6380 | 31.92 |
| 8 | 19562 | 7487 | 34.85 |
| 8 | 20464 | 7770 | 34.57 |
| 8 | 19970 | 7657 | 34.91 |
| 9 | 17502 | 7590 | 39.49 |
| 9 | 17946 | 7846 | 39.81 |
| 9 | 17601 | 7507 | 38.84 |
| 10 | 18206 | 8394 | 41.98 |
| 10 | 17628 | 8310 | 42.93 |
| 10 | 17847 | 8329 | 42.50 |




**rate = 0.0328 mM/sec**

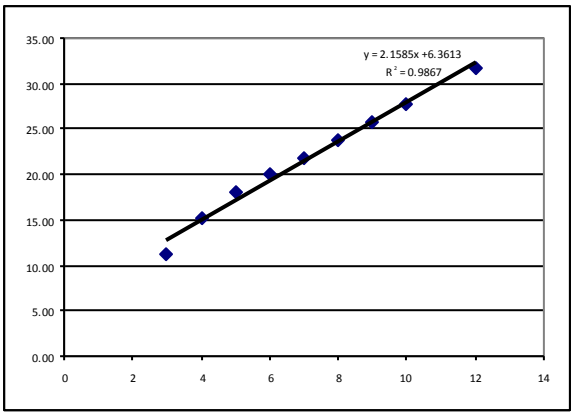
**Order in $PPh_3$ (15.0 mM)**

| | |
|---|---|
| $Cs^+$**5**$^-$ | 62.5 mM |
| 2-Bromotoluene | 83 mM |
| **7t** | 7.5 mM |
| $PPh_3$ | 15.0 mM |

Following the General Procedure I, a mixture of silanolate $Cs^+$**5**$^-$ (39 mg, 0.125 mmol), **7t** (13.5 mg, 0.015 mmol, 0.090 equiv), naphthalene (11 mg), $PPh_3$ (8.0 mg, 0.030 mmol) and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 3 | 19651 | 2423 | 11.23 |
| 3 | 19532 | 2407 | 11.22 |
| 3 | 19609 | 2439 | 11.33 |
| 4 | 19362 | 3205 | 15.07 |
| 4 | 19405 | 3249 | 15.25 |
| 4 | 19473 | 3286 | 15.37 |
| 5 | 15796 | 3098 | 17.86 |
| 5 | 15780 | 3190 | 18.41 |
| 5 | 15401 | 3045 | 18.00 |
| 6 | 24640 | 5376 | 19.87 |
| 6 | 24648 | 5355 | 19.78 |
| 6 | 24239 | 5408 | 20.32 |
| 7 | 18878 | 4389 | 21.17 |
| 7 | 18686 | 4576 | 22.30 |
| 7 | 18006 | 4375 | 22.12 |
| 8 | 18413 | 4838 | 23.93 |
| 8 | 18507 | 4871 | 23.97 |
| 8 | 18962 | 4861 | 23.34 |
| 9 | 17184 | 4952 | 26.24 |
| 9 | 17336 | 4862 | 25.54 |
| 9 | 17264 | 4782 | 25.22 |
| 10 | 19706 | 6077 | 28.08 |
| 10 | 19690 | 5886 | 27.22 |
| 10 | 19997 | 6149 | 28.00 |
| 12 | 22783 | 8033 | 32.11 |
| 12 | 23976 | 8250 | 31.33 |
| 12 | 23764 | 8327 | 31.91 |

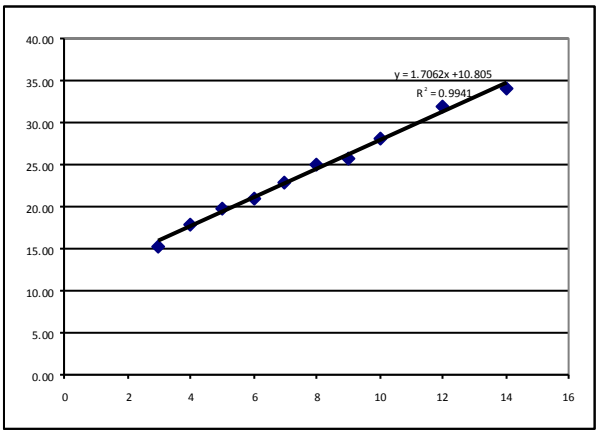



**rate = 0.0179 mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 3 | 7299 | 1243 | 15.51 |
| 3 | 6068 | 975 | 14.63 |
| 3 | 6629 | 1145 | 15.73 |
| 4 | 7067 | 1430 | 18.43 |
| 4 | 7769 | 1488 | 17.44 |
| 4 | 7027 | 1347 | 17.45 |
| 5 | 8284 | 1802 | 19.81 |
| 5 | 7938 | 1699 | 19.49 |
| 5 | 8734 | 1913 | 19.94 |
| 6 | 8180 | 1835 | 20.43 |
| 6 | 8906 | 2116 | 21.63 |
| 6 | 9073 | 2076 | 20.84 |
| 7 | 8237 | 2003 | 22.14 |
| 7 | 6740 | 1661 | 22.44 |

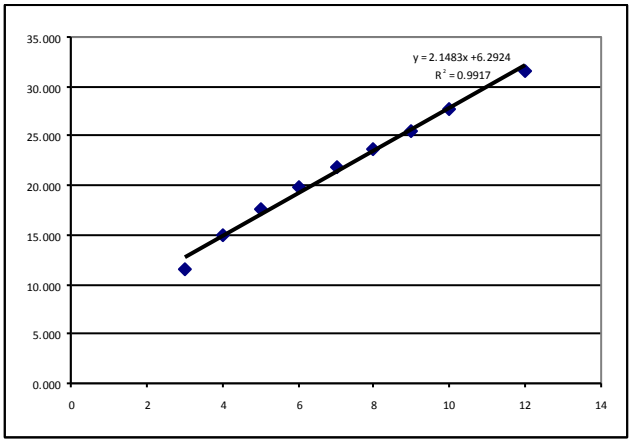
| | | | |
|---|---|---|---|
| 7 | 9064 | 2383 | 23.94 |
| 8 | 6528 | 1763 | 24.59 |
| 8 | 6224 | 1747 | 25.56 |
| 8 | 6765 | 1823 | 24.54 |
| 9 | 9251 | 2657 | 26.15 |
| 9 | 8762 | 2446 | 25.42 |
| 9 | 7043 | 1959 | 25.33 |
| 10 | 6459 | 2009 | 28.32 |
| 10 | 5860 | 1766 | 27.44 |
| 10 | 6037 | 1869 | 28.19 |
| 12 | 6343 | 2172 | 31.18 |
| 12 | 7241 | 2549 | 32.05 |
| 12 | 6866 | 2456 | 32.57 |
| 14 | 7962 | 2962 | 33.88 |
| 14 | 7607 | 2858 | 34.21 |
| 14 | 7763 | 2908 | 34.11 |




**rate = 0.0142 mM/sec**

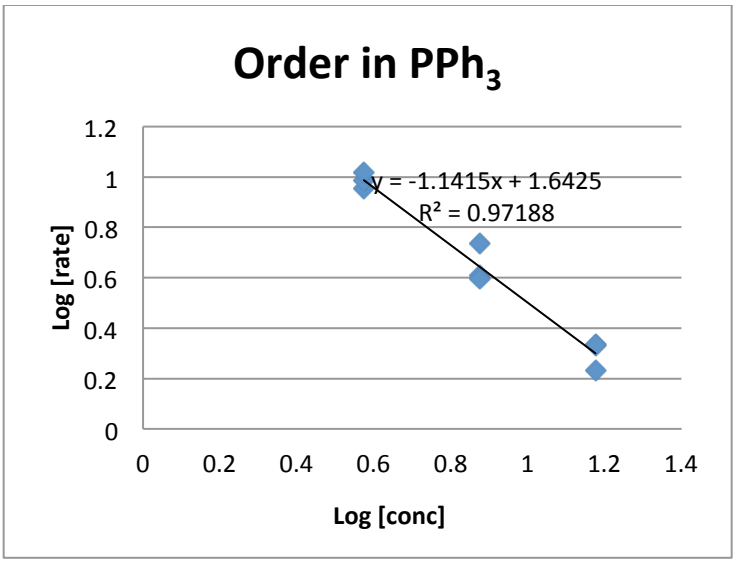
**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 3 | 84449 | 7737 | 11.376 |
| 3 | 84873 | 7908 | 11.570 |
| 3 | 84534 | 7962 | 11.695 |
| 4 | 80840 | 9585 | 14.723 |
| 4 | 80020 | 9728 | 15.095 |
| 4 | 81009 | 9828 | 15.064 |
| 5 | 82094 | 11450 | 17.319 |
| 5 | 81790 | 11577 | 17.576 |
| 5 | 82368 | 11754 | 17.719 |
| 6 | 73254 | 11664 | 19.771 |
| 6 | 73933 | 11803 | 19.823 |
| 6 | 74492 | 11901 | 19.838 |
| 7 | 77398 | 13464 | 21.601 |
| 7 | 78144 | 13674 | 21.728 |
| 7 | 56749 | 10133 | 22.172 |
| 8 | 75582 | 14570 | 23.937 |
| 8 | 37398 | 7057 | 23.431 |
| 8 | 76740 | 14583 | 23.596 |
| 9 | 78247 | 16082 | 25.521 |
| 9 | 59530 | 12094 | 25.226 |
| 9 | 79599 | 16628 | 25.939 |
| 10 | 79149 | 17686 | 27.746 |
| 10 | 78352 | 17604 | 27.899 |
| 10 | 60230 | 13280 | 27.378 |
| 12 | 79011 | 20051 | 31.511 |
| 12 | 81418 | 20486 | 31.243 |
| 12 | 78122 | 20056 | 31.878 |



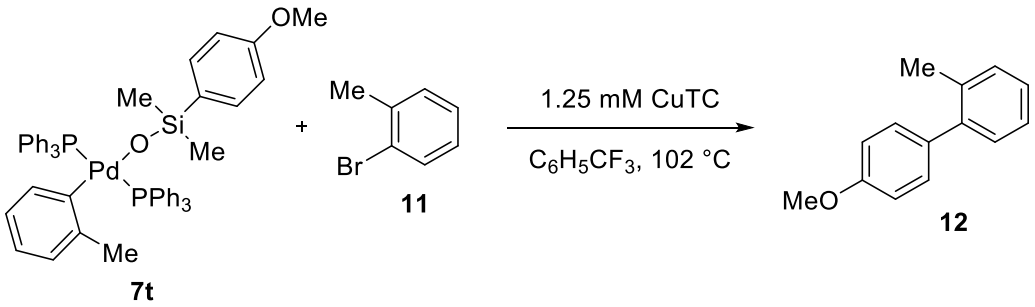

**rate = 0.0178 mM/sec**

**avg. rate = 1.66 x $10^{-2}$ mM/s**


Order in PPh3
y = -1.1415x + 1.6425
R² = 0.97188
Log [rate]
Log [conc]
1.2
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4

**GENERATION OF LIGANDLESS ARYLPALLADIUM(II) ARYLSILANOLATE SPECIES USING CuTC (Table 3)**

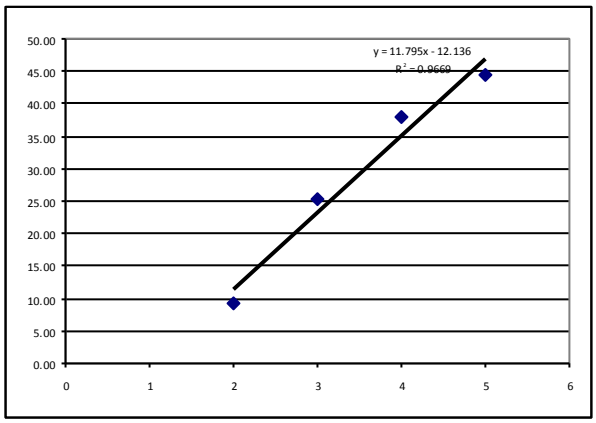
**General Procedure II: Thermolysis of 7t in the presence of CuTC (Table 3, entry 1)**




In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with naphthalene (10 mg), **7t** (45 mg, 0.05 mmol), 2-bromotoluene (20 μL, 0.167 mmol, 3.3 equiv), CuTC (0.95 mg, 0.005 mmol, 0.1 equiv) and dry benzotrifluoride (4.0 mL). The flask was removed from the drybox, purged with argon, and then was placed in a 105 °C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 30 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.5 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 9765 | 1093 | 9.27 |
| 2 | 9723 | 1114 | 9.48 |
| 2 | 10069 | 1060 | 8.71 |
| 3 | 13219 | 4069 | 25.48 |
| 3 | 13897 | 4273 | 25.45 |
| 3 | 14696 | 4432 | 24.96 |
| 4 | 10153 | 4654 | 37.95 |
| 4 | 10870 | 5005 | 38.12 |
| 4 | 10771 | 4874 | 37.46 |
| 5 | 11491 | 6087 | 43.85 |

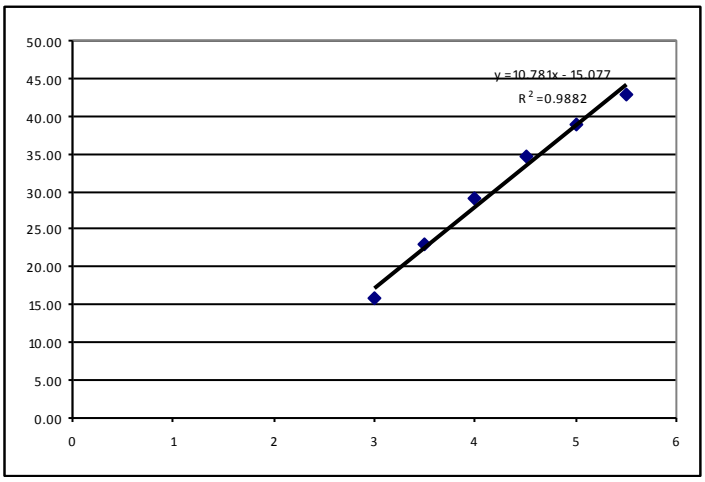


| | | | |
|---|---|---|---|
| 5 | 11422 | 6101 | 44.22 |
| 5 | 11358 | 6148 | 44.81 |
| 6 | 9271 | 5320 | 47.50 |
| 6 | 9304 | 5385 | 47.91 |
| 6 | 9457 | 5536 | 48.46 |

**rate 4.92 x $10^{-2}$ mM/sec**

**Run 2**

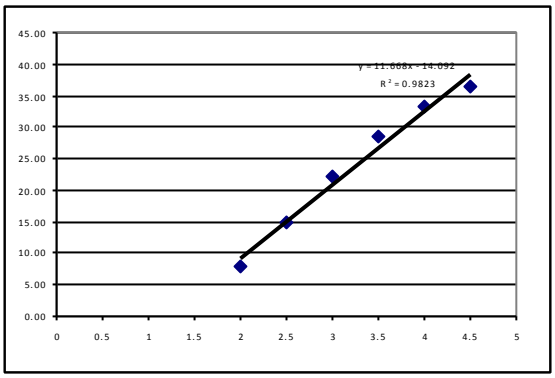
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 3 | 13778 | 2209 | 15.93 |
| 3 | 13323 | 2122 | 15.82 |
| 3 | 13872 | 2245 | 16.08 |
| 3.5 | 11203 | 2493 | 22.11 |
| 3.5 | 10548 | 2476 | 23.32 |
| 3.5 | 10698 | 2514 | 23.34 |
| 4 | 10143 | 2939 | 28.78 |
| 4 | 10389 | 3028 | 28.95 |
| 4 | 10124 | 2983 | 29.27 |
| 4.5 | 13298 | 4619 | 34.50 |
| 4.5 | 13722 | 4794 | 34.70 |
| 4.5 | 13571 | 4762 | 34.86 |
| 5 | 14896 | 5883 | 39.23 |
| 5 | 14263 | 5571 | 38.80 |
| 5 | 14624 | 5736 | 38.96 |
| 5.5 | 13568 | 5988 | 43.84 |
| 5.5 | 14216 | 6134 | 42.86 |
| 5.5 | 14346 | 6061 | 41.97 |
| 6 | 11228 | 5222 | 46.20 |
| 6 | 11481 | 5483 | 47.44 |
| 6 | 11703 | 5417 | 45.98 |




**rate 4.49 x $10^{-2}$ mM/sec**

**Run 3**

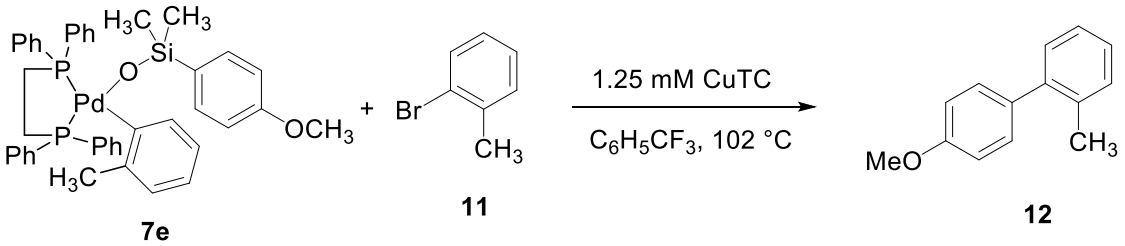
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 10366 | 1105 | 7.94 |
| 2 | 10925 | 1151 | 7.85 |
| 2 | 10873 | 1148 | 7.87 |
| 2.5 | 12027 | 2403 | 14.89 |
| 2.5 | 12119 | 2386 | 14.67 |
| 2.5 | 12190 | 2466 | 15.07 |
| 3 | 9978 | 2945 | 21.99 |
| 3 | 10466 | 3060 | 21.78 |
| 3 | 10221 | 3069 | 22.37 |
| 3.5 | 9593 | 3653 | 28.37 |
| 3.5 | 9279 | 3561 | 28.59 |



| | | | |
|---|---|---|---|
| 3.5 | 9740 | 3740 | 28.61 |
| 4 | 10177 | 4628 | 33.88 |
| 4 | 10082 | 4536 | 33.52 |
| 4 | 10454 | 4526 | 32.26 |
| 4.5 | 10556 | 5126 | 36.18 |
| 4.5 | 10667 | 5181 | 36.19 |
| 4.5 | 10791 | 5345 | 36.90 |
| 5 | 9016 | 4767 | 39.39 |
| 5 | 9348 | 4933 | 39.32 |
| 5 | 9440 | 5051 | 39.86 |

**rate 4.87 x $10^{-2}$ mM/sec**
**avg. rate = 4.76 x $10^{-2}$ mM/s**

**Thermolysis of 7e in the presence of CuTC (Table 3, entry 2)**

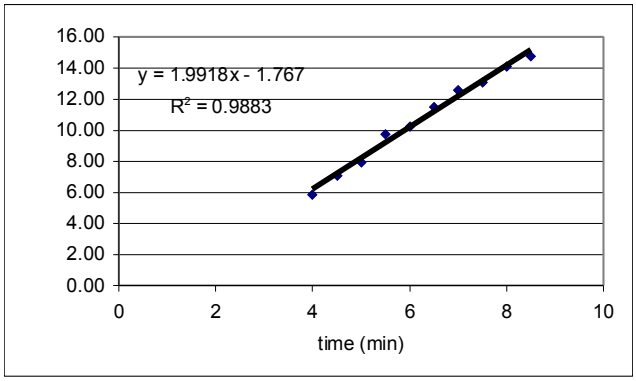



**Run 1**

Following General Procedure II, a mixture of **7e** (39 mg, 0.05 mmol, 1.0 equiv), naphthalene (10.8 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

| time, min | area naph | area **12** | mmol **12** |
|---|---|---|---|
| 1 | 13982 | 0 | 0.00 |
| 1 | 12629 | 0 | 0.00 |
| 1 | 13743 | 0 | 0.00 |
| 1.5 | 15342 | 0 | 0.00 |
| 1.5 | 14956 | 0 | 0.00 |
| 1.5 | 15337 | 0 | 0.00 |
| 2 | 15752 | 0 | 0.00 |
| 2 | 15691 | 0 | 0.00 |
| 2 | 16465 | 0 | 0.00 |
| 2.5 | 15891 | 0 | 0.00 |
| 2.5 | 16530 | 0 | 0.00 |
| 2.5 | 15498 | 0 | 0.00 |
| 3 | 16561 | 0 | 0.00 |
| 3 | 16078 | 0 | 0.00 |

| | | | |
|---|---|---|---|
| 3 | 15308 | 0 | 0.00 |
| 3.5 | 14274 | 0 | 0.00 |
| 3.5 | 13965 | 0 | 0.00 |
| 3.5 | 13767 | 0 | 0.00 |
| 4 | 14218 | 807 | 5.92 |
| 4 | 14989 | 822 | 5.72 |
| 4 | 14651 | 829 | 5.90 |
| 4.5 | 15307 | 992 | 6.76 |
| 4.5 | 15554 | 1147 | 7.69 |
| 4.5 | 15563 | 1017 | 6.82 |
| 5 | 15227 | 1194 | 8.18 |
| 5 | 15441 | 1154 | 7.80 |
| 5 | 15887 | 1196 | 7.85 |
| 5.5 | 14950 | 1354 | 9.45 |
| 5.5 | 14832 | 1377 | 9.68 |
| 5.5 | 14938 | 1449 | 10.12 |
| 6 | 11950 | 1165 | 10.17 |
| 6 | 12797 | 1241 | 10.11 |
| 6 | 11689 | 1167 | 10.41 |
| 6.5 | 13729 | 1537 | 11.68 |
| 6.5 | 14829 | 1582 | 11.13 |
| 6.5 | 13936 | 1570 | 11.75 |
| 7 | 10775 | 1303 | 12.61 |
| 7 | 10486 | 1281 | 12.74 |
| 7 | 10780 | 1273 | 12.32 |
| 7.5 | 16382 | 1997 | 12.71 |
| 7.5 | 15474 | 1958 | 13.20 |
| 7.5 | 15253 | 1937 | 13.25 |
| 8 | 12450 | 1667 | 13.97 |
| 8 | 12195 | 1658 | 14.18 |
| 8 | 12449 | 1684 | 14.11 |
| 8.5 | 16721 | 2288 | 14.27 |
| 8.5 | 14744 | 2175 | 15.39 |
| 8.5 | 16419 | 2295 | 14.58 |



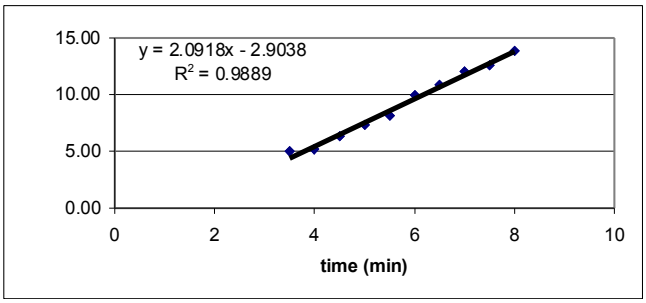

**rate = 8.29 x $10^{-3}$ mM/s**

**Run 2**

Following General Procedure II, a mixture of **7e** (39 mg, 0.05 mmol, 1.0 equiv),

naphthalene (9.4 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

| time, min | area naph | area **12** | umol **12** |
|---|---|---|---|
| 1 | 9987 | 0 | 0.00 |
| 1 | 9987 | 0 | 0.00 |
| 1 | 9987 | 0 | 0.00 |
| 1.5 | 10687 | 0 | 0.00 |
| 1.5 | 10687 | 0 | 0.00 |
| 1.5 | 10687 | 0 | 0.00 |
| 2 | 11730 | 0 | 0.00 |
| 2 | 11730 | 0 | 0.00 |
| 2 | 11730 | 0 | 0.00 |
| 2.5 | 11362 | 0 | 0.00 |
| 2.5 | 11362 | 0 | 0.00 |
| 2.5 | 11362 | 0 | 0.00 |
| 3 | 13764 | 0 | 0.00 |
| 3 | 13764 | 0 | 0.00 |
| 3 | 13764 | 0 | 0.00 |
| 3.5 | 12200 | 786 | 5.01 |
| 3.5 | 12200 | 786 | 5.01 |
| 3.5 | 12200 | 786 | 5.01 |
| 4 | 13444 | 899 | 5.20 |
| 4 | 13444 | 899 | 5.20 |
| 4 | 13444 | 899 | 5.20 |
| 4.5 | 13288 | 1078 | 6.31 |
| 4.5 | 13288 | 1078 | 6.31 |
| 4.5 | 13288 | 1078 | 6.31 |
| 5 | 12510 | 1173 | 7.30 |
| 5 | 12510 | 1173 | 7.30 |
| 5 | 12510 | 1173 | 7.30 |
| 5.5 | 15190 | 1584 | 8.11 |
| 5.5 | 15190 | 1584 | 8.11 |
| 5.5 | 15190 | 1584 | 8.11 |
| 6 | 12974 | 1656 | 9.93 |
| 6 | 12974 | 1656 | 9.93 |
| 6 | 12974 | 1656 | 9.93 |
| 6.5 | 14135 | 1977 | 10.88 |
| 6.5 | 14135 | 1977 | 10.88 |
| 6.5 | 14135 | 1977 | 10.88 |
| 7 | 13322 | 2059 | 12.03 |
| 7 | 13322 | 2059 | 12.03 |
| 7 | 13322 | 2059 | 12.03 |
| 7.5 | 13500 | 2181 | 12.57 |
| 7.5 | 13500 | 2181 | 12.57 |
| 7.5 | 13500 | 2181 | 12.57 |
| 8 | 13534 | 2415 | 13.89 |
| 8 | 13534 | 2415 | 13.89 |
| 8 | 13534 | 2415 | 13.89 |

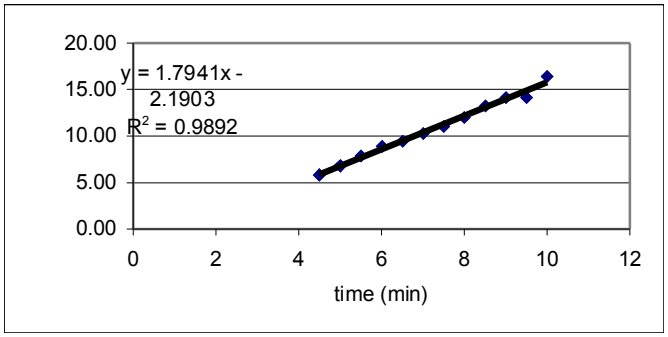



**rate = 8.70 x $10^{-3}$ mM/s**

**Run 3**

Following General Procedure II, a mixture of **7e** (39 mg, 0.05 mmol, 1.0 equiv), naphthalene (12.5 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

| time | area naph | area **12** | μmol **12** |
|---|---|---|---|
| 1 | 11884 | 0 | 0.00 |
| 1 | 11856 | 0 | 0.00 |
| 1 | 12754 | 0 | 0.00 |
| 1.5 | 14133 | 0 | 0.00 |
| 1.5 | 14060 | 0 | 0.00 |
| 1.5 | 13438 | 0 | 0.00 |
| 2 | 11943 | 0 | 0.00 |
| 2 | 12053 | 0 | 0.00 |
| 2 | 12700 | 0 | 0.00 |
| 2.5 | 14775 | 0 | 0.00 |
| 2.5 | 14223 | 0 | 0.00 |
| 2.5 | 12835 | 0 | 0.00 |
| 3 | 12953 | 0 | 0.00 |
| 3 | 12706 | 0 | 0.00 |
| 3 | 13666 | 0 | 0.00 |
| 3.5 | 14856 | 0 | 0.00 |
| 3.5 | 14319 | 0 | 0.00 |
| 3.5 | 13971 | 0 | 0.00 |
| 4 | 14531 | 0 | 0.00 |
| 4 | 13881 | 0 | 0.00 |
| 4 | 13108 | 0 | 0.00 |
| 4.5 | 14414 | 778 | 5.59 |
| 4.5 | 14368 | 747 | 5.38 |
| 4.5 | 12801 | 808 | 6.53 |
| 5 | 13924 | 882 | 6.55 |
| 5 | 13598 | 903 | 6.87 |
| 5 | 12839 | 868 | 7.00 |
| 5.5 | 11142 | 855 | 7.94 |
| 5.5 | 11559 | 892 | 7.99 |
| 5.5 | 11698 | 848 | 7.50 |
| 6 | 14108 | 1139 | 8.35 |
| 6 | 13380 | 1218 | 9.42 |
| 6 | 13350 | 1128 | 8.74 |
| 6.5 | 13874 | 1255 | 9.36 |
| 6.5 | 13281 | 1213 | 9.45 |
| 6.5 | 13071 | 1200 | 9.50 |
| 7 | 13096 | 1278 | 10.10 |
| 7 | 13186 | 1378 | 10.81 |
| 7 | 13266 | 1256 | 9.80 |
| 7.5 | 13680 | 1483 | 11.22 |
| 7.5 | 13744 | 1450 | 10.92 |

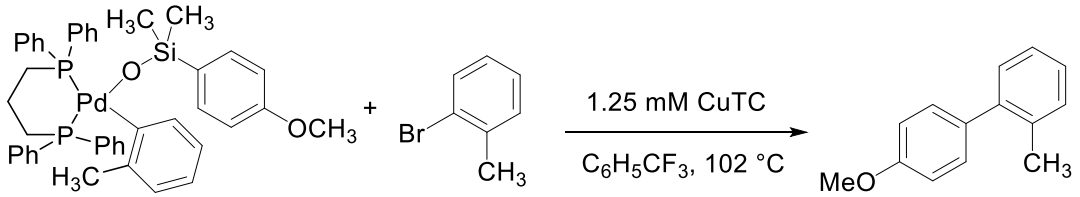


| | | | |
|---|---|---|---|
| 7.5 | 14110 | 1474 | 10.81 |
| 8 | 15048 | 1652 | 11.36 |
| 8 | 14406 | 1665 | 11.96 |
| 8 | 13130 | 1606 | 12.66 |
| 8.5 | 12996 | 1696 | 13.50 |
| 8.5 | 12773 | 1673 | 13.55 |
| 8.5 | 14610 | 1793 | 12.70 |
| 9 | 14361 | 1929 | 13.90 |
| 9 | 13733 | 1890 | 14.24 |
| 9 | 13576 | 1859 | 14.17 |
| 9.5 | 16056 | 2173 | 14.00 |
| 9.5 | 15258 | 2110 | 14.31 |
| 9.5 | 15439 | 2092 | 14.02 |
| 10 | 11778 | 1772 | 15.57 |
| 10 | 10675 | 1714 | 16.61 |
| 10 | 10264 | 1689 | 17.03 |

**rate = 7.46 x $10^{-3}$ mM/s**

**avg. rate = 8.15 x $10^{-3}$ mM/s**

**Thermolysis of 14p in the presence of CuTC (Table 3, entry 3)**



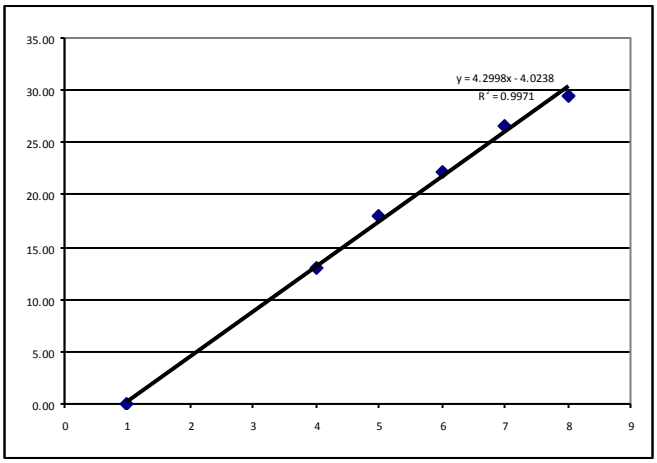

**7p** **11** **12**

Following General Procedure II, a mixture of **7p** (43 mg, 0.05 mmol, 1.0 equiv), naphthalene (9.4 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1 | 1 | 0 | 0.00 |
| 1 | 1 | 0 | 0.00 |
| 1 | 1 | 0 | 0.00 |
| 4 | 14848 | 2321 | 12.94 |
| 4 | 14848 | 2321 | 12.94 |

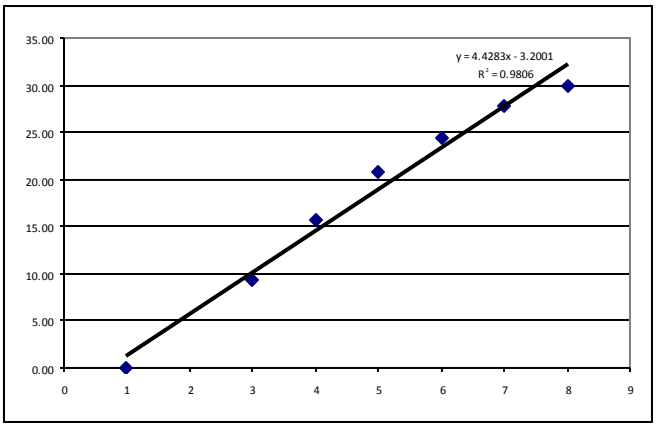
| | | | |
|---|---|---|---|
| 4 | 14848 | 2321 | 12.94 |
| 5 | 23038 | 4862 | 17.47 |
| 5 | 7610 | 1706 | 18.56 |
| 5 | 8010 | 1730 | 17.88 |
| 6 | 8377 | 2376 | 23.48 |
| 6 | 9810 | 2565 | 21.64 |
| 6 | 39135 | 10207 | 21.59 |
| 7 | 15304 | 5006 | 27.08 |
| 7 | 23342 | 7298 | 25.88 |
| 7 | 15565 | 5012 | 26.66 |
| 8 | 7678 | 2681 | 28.91 |
| 8 | 29806 | 10742 | 29.83 |
| 8 | 7677 | 2750 | 29.65 |




**rate = 1.79 x $10^{-2}$ mM/s**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1 | 1 | 0 | 0.00 |
| 1 | 1 | 0 | 0.00 |
| 1 | 1 | 0 | 0.00 |
| 3 | 42759 | 5958 | 9.23 |
| 3 | 42655 | 5911 | 9.18 |
| 3 | 43014 | 6097 | 9.39 |
| 4 | 41144 | 9475 | 15.25 |
| 4 | 37650 | 9462 | 16.64 |
| 4 | 41802 | 9498 | 15.05 |
| 5 | 37691 | 11542 | 20.28 |
| 5 | 37645 | 11798 | 20.75 |
| 5 | 36256 | 11847 | 21.64 |
| 6 | 36417 | 13417 | 24.40 |
| 6 | 37114 | 13621 | 24.30 |
| 6 | 36988 | 13839 | 24.78 |
| 7 | 39434 | 16576 | 27.84 |
| 7 | 39975 | 16798 | 27.83 |
| 7 | 41028 | 17308 | 27.94 |
| 8 | 39320 | 17788 | 29.96 |
| 8 | 29373 | 13396 | 30.20 |
| 8 | 39815 | 17936 | 29.83 |

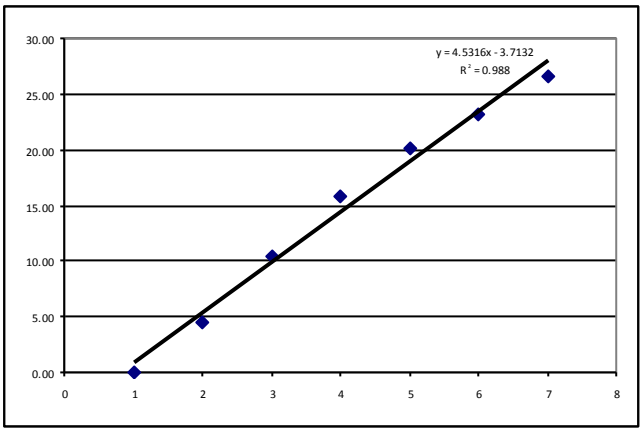



**rate = 1.84 x $10^{-2}$ mM/s**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1 | 1 | 0 | 0.00 |
| 1 | 1 | 0 | 0.00 |

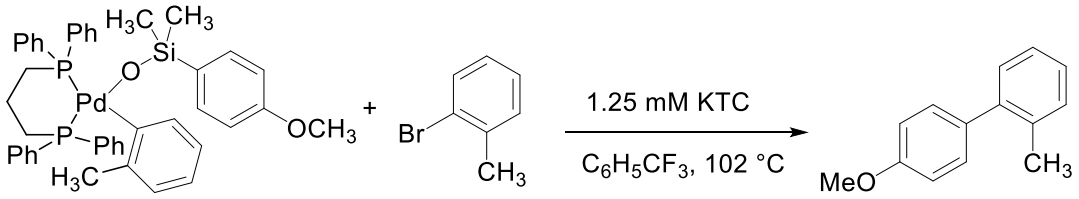
| | | | |
|---|---|---|---|
| 1 | 1 | 0 | 0.00 |
| 2 | 33849 | 1708 | 4.59 |
| 2 | 34312 | 1712 | 4.54 |
| 2 | 33849 | 1708 | 4.59 |
| 3 | 56720 | 6547 | 10.51 |
| 3 | 45725 | 5203 | 10.36 |
| 3 | 56720 | 6547 | 10.51 |
| 4 | 54966 | 9637 | 15.97 |
| 4 | 44183 | 7805 | 16.09 |
| 4 | 44394 | 7604 | 15.60 |
| 5 | 49869 | 10991 | 20.07 |
| 5 | 50264 | 11080 | 20.07 |
| 5 | 50263 | 11152 | 20.20 |
| 6 | 19723 | 4960 | 22.90 |
| 6 | 47495 | 12391 | 23.76 |
| 6 | 19723 | 4960 | 22.90 |
| 7 | 51994 | 15281 | 26.76 |
| 7 | 50784 | 14775 | 26.49 |
| 7 | 51994 | 15281 | 26.76 |




**rate = 1.88 x $10^{-2}$ mM/sec**

**avg. rate = 1.84 x $10^{-2}$ mM/s**

**Thermolysis of 7p in the presence of KTC (Footnote 14)**

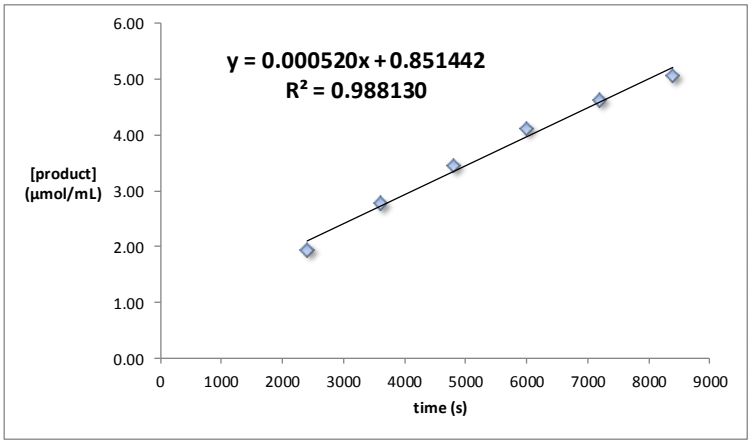



**14p** **20** **21**

**Run 1**

Following General Procedure II, a mixture of **14p** (43 mg, 0.05 mmol, 1.0 equiv), naphthalene (10.0 mg), KTC (0.8 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

| time (s) | naphthalene | | product | | | |
|---|---|---|---|---|---|---|
| | mmol | area | area | mmol | (%) | average mM |
| 2400 | 0.079 | 5.82E+03 | 7.23E+02 | 7.72E-03 | 15.4 | 1.94 |
| | 0.079 | 4.61E+03 | 5.82E+02 | 7.84E-03 | 15.7 | |
| | 0.079 | 6.42E+03 | 7.92E+02 | 7.67E-03 | 15.3 | |
| 3600 | 0.079 | 5.36E+03 | 9.37E+02 | 1.09E-02 | 21.7 | 2.78 |
| | 0.079 | 7.99E+03 | 1.45E+03 | 1.12E-02 | 22.5 | |
| | 0.079 | 5.21E+03 | 9.44E+02 | 1.13E-02 | 22.5 | |
| 4800 | 0.079 | 4.97E+03 | 9.95E+02 | 1.24E-02 | 24.9 | 3.45 |
| | 0.079 | 7.19E+03 | 1.70E+03 | 1.47E-02 | 29.4 | |
| | 0.079 | 6.61E+03 | 1.53E+03 | 1.43E-02 | 28.7 | |
| 6000 | 0.079 | 1.08E+04 | 2.76E+03 | 1.58E-02 | 31.6 | 4.11 |
| | 0.079 | 6.90E+03 | 1.84E+03 | 1.65E-02 | 33.1 | |
| | 0.079 | 9.85E+03 | 2.69E+03 | 1.69E-02 | 33.9 | |
| 7200 | 0.079 | 8.45E+03 | 2.43E+03 | 1.78E-02 | 35.7 | 4.62 |
| | 0.079 | 8.48E+03 | 2.54E+03 | 1.86E-02 | 37.2 | |
| | 0.079 | 8.05E+03 | 2.47E+03 | 1.90E-02 | 38.0 | |
| 8400 | 0.079 | 9.44E+03 | 3.01E+03 | 1.98E-02 | 39.6 | 5.07 |
| | 0.079 | 7.17E+03 | 2.37E+03 | 2.05E-02 | 41.1 | |
| | 0.079 | 7.71E+03 | 2.54E+03 | 2.05E-02 | 41.0 | |

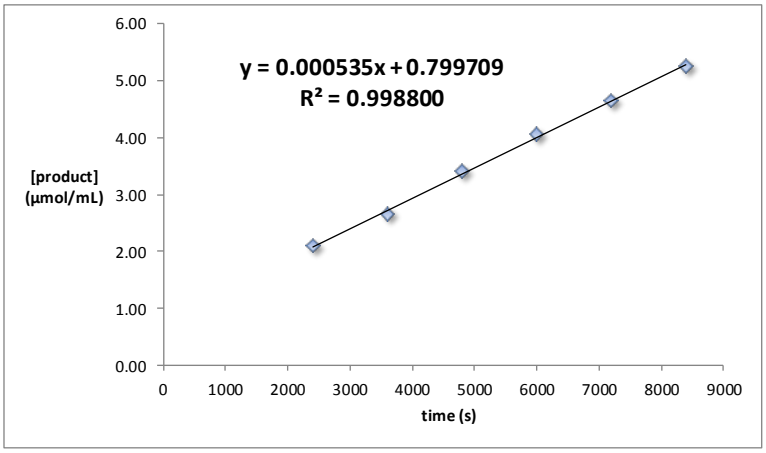



**rate = 5.20 x $10^{-4}$ mM/s**

**Run 2**

Following General Procedure II, a mixture of **14p** (43 mg, 0.05 mmol, 1.0 equiv), naphthalene (12.1 mg), KTC (0.8 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 µL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

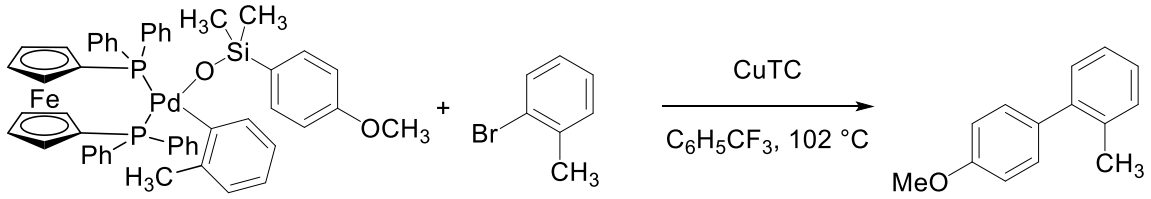
| time (s) | naphthalene | | product | | | |
|---|---|---|---|---|---|---|
| | mmol | area | area | mmol | (%) | average mM |
| 2400 | 0.094 | 1.28E+04 | 1.40E+03 | 8.10E-03 | 16.2 | 2.09 |
| | 0.094 | 8.72E+03 | 9.94E+02 | 8.42E-03 | 16.8 | |
| | 0.094 | 1.60E+04 | 1.85E+03 | 8.56E-03 | 17.1 | |
| 3600 | 0.094 | 9.43E+03 | 1.25E+03 | 9.81E-03 | 19.6 | 2.66 |
| | 0.094 | 7.35E+03 | 1.02E+03 | 1.03E-02 | 20.5 | |
| | 0.094 | 1.07E+04 | 1.73E+03 | 1.19E-02 | 23.8 | |
| 4800 | 0.094 | 1.48E+04 | 2.77E+03 | 1.38E-02 | 27.7 | 3.41 |
| | 0.094 | 1.14E+04 | 2.09E+03 | 1.36E-02 | 27.2 | |
| | 0.094 | 1.17E+04 | 2.12E+03 | 1.34E-02 | 26.8 | |
| 6000 | 0.094 | 1.18E+04 | 2.54E+03 | 1.60E-02 | 31.9 | 4.06 |
| | 0.094 | 1.51E+04 | 3.33E+03 | 1.64E-02 | 32.7 | |
| | 0.094 | 1.11E+04 | 2.46E+03 | 1.64E-02 | 32.8 | |
| 7200 | 0.094 | 1.16E+04 | 2.97E+03 | 1.88E-02 | 37.6 | 4.65 |
| | 0.094 | 8.71E+03 | 2.20E+03 | 1.87E-02 | 37.3 | |
| | 0.094 | 9.02E+03 | 2.23E+03 | 1.83E-02 | 36.6 | |
| 8400 | 0.094 | 1.25E+04 | 3.57E+03 | 2.10E-02 | 42.0 | 5.26 |
| | 0.094 | 1.22E+04 | 3.48E+03 | 2.12E-02 | 42.3 | |
| | 0.094 | 1.21E+04 | 3.42E+03 | 2.10E-02 | 42.0 | |




**rate = 5.35 x $10^{-4}$ mM/s**

**avg. rate = 5.28 x $10^{-4}$ mM/s**

**Thermolysis of 7f in the presence of CuTC (Table 3, entry 4)**

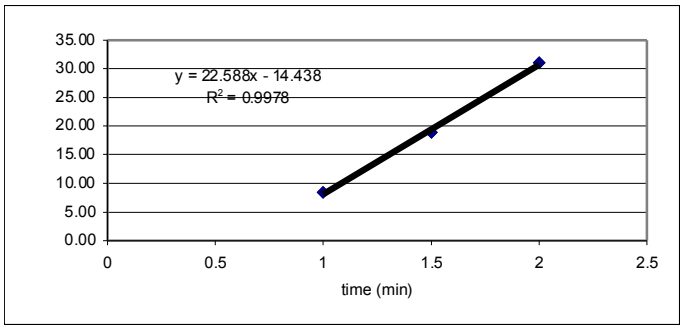



**7f** **11** **12**

**Run 1**

Following General Procedure II, a mixture of **7f** (47 mg, 0.05 mmol, 1.0 equiv), naphthalene (9.6 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

| time, min | area naph | area **12** | μmol **12** |
|---|---|---|---|
| 1 | 8703 | 901 | 8.23 |
| 1 | 8804 | 1005 | 9.07 |
| 1 | 8621 | 875 | 8.07 |
| 1.5 | 12133 | 2886 | 18.90 |
| 1.5 | 12211 | 2898 | 18.86 |
| 1.5 | 12280 | 2896 | 18.74 |
| 2 | 11164 | 4264 | 30.35 |
| 2 | 10464 | 4141 | 31.45 |
| 2 | 10852 | 4278 | 31.33 |

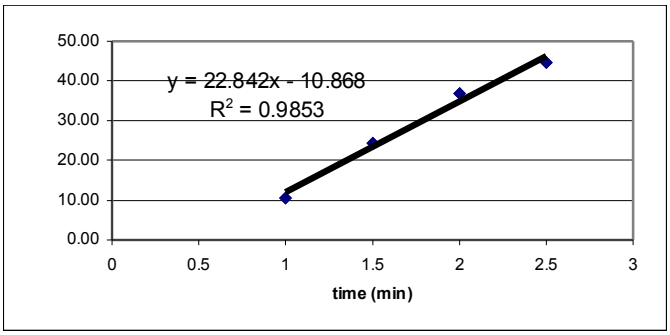



**rate = 9.42 x $10^{-2}$ mM/s**

**Run 2**

Following General Procedure II, a mixture of **7f** (47 mg, 0.05 mmol, 1.0 equiv), naphthalene (9.3 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

| time, min | area naph | area **12** | μmol **12** |
|---|---|---|---|
| 1 | 11121 | 1504 | 10.41 |
| 1 | 11049 | 1671 | 11.64 |
| 1 | 11176 | 1442 | 9.93 |
| 1.5 | 9784 | 3264 | 25.68 |
| 1.5 | 11020 | 3398 | 23.74 |
| 1.5 | 10511 | 3216 | 23.56 |
| 2 | 11524 | 5580 | 37.28 |
| 2 | 11378 | 5439 | 36.80 |
| 2 | 11581 | 5504 | 36.59 |
| 2.5 | 10959 | 6705 | 47.10 |
| 2.5 | 11810 | 6720 | 43.81 |
| 2.5 | 12496 | 6935 | 42.73 |



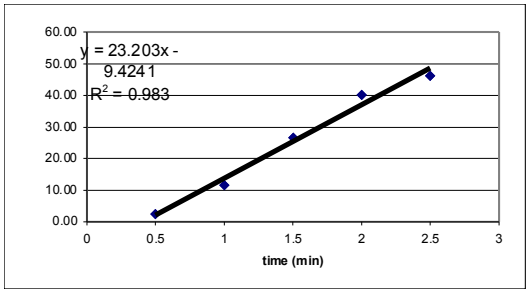

**rate = 9.50 x $10^{-2}$ mM/s**

**Run 3**

Following General Procedure II, a mixture of **7f** (47 mg, 0.05 mmol, 1.0 equiv), naphthalene (8.9 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis.

| time, min | area naph | area **12** | μmol **12** |
|---|---|---|---|
| 0.5 | 29670 | 1098 | 2.73 |
| 0.5 | 28296 | 890 | 2.32 |
| 0.5 | 28533 | 899 | 2.32 |
| 1 | 36631 | 5641 | 11.35 |
| 1 | 35237 | 5490 | 11.48 |
| 1 | 35263 | 5539 | 11.57 |
| 1.5 | 40480 | 14620 | 26.61 |
| 1.5 | 40140 | 14404 | 26.44 |
| 1.5 | 39716 | 14598 | 27.08 |
| 2 | 28674 | 15081 | 38.75 |
| 2 | 28328 | 15643 | 40.68 |
| 2 | 28665 | 15959 | 41.02 |
| 2.5 | 35983 | 22214 | 45.48 |

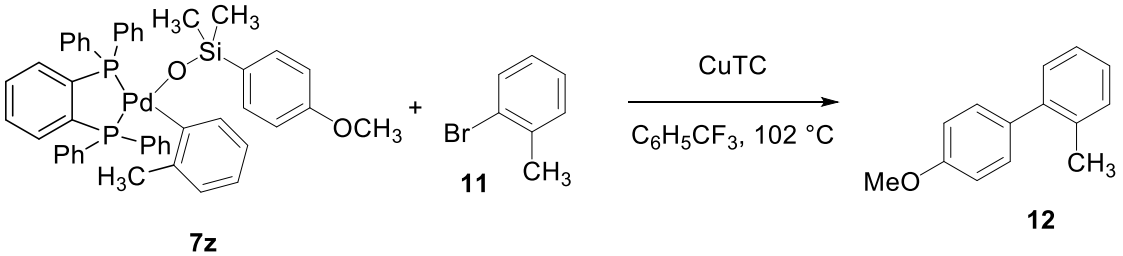
| | | | |
|---|---|---|---|
| 2.5 | 34904 | 22078 | 46.60 |
| 2.5 | 35568 | 22339 | 46.27 |




**rate = 9.67 x $10^{-2}$ mM/s**

**avg. rate = 9.21 x $10^{-2}$ mM/s**

**Thermolysis of 7z in the presence of CuTC (Table 3, entry 5)**




**Run 1**

Following General Procedure II, a mixture of **7z** (41 mg, 0.05 mmol, 1.0 equiv), naphthalene (8.7 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis. No product formation was observed after 3 h of heating.

**Run 2**

Following General Procedure II, a mixture of **7z** (41 mg, 0.05 mmol, 1.0 equiv), naphthalene (12.8 mg), CuTC (1 mg, 0.005 mmol, 0.1 equiv) and 2-bromotoluene (20 μL, 0.16 mmol, 3.3 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at 105 °C. Aliquots of the mixture were then taken for GC analysis. No product formation was observed after 3 h of heating.

**INDEX OF KINETIC EXPERIMENTS FOR THE CROSS-COUPLING OF CESIUM (4-METHOXYPHENYL)DIMETHYLSILANOLATE USING 1,3-BIS(DIPHENYLPHOSPHINO)PROPANE BIS-OXIDE AS A LIGAND (TABLE 4)**

**General Procedure III: Analysis and Kinetic Measurements for Cross-Coupling of $Cs^+$5$^-$ Initial Rates using Phosphine Oxide as the Ligand (Table 4)**

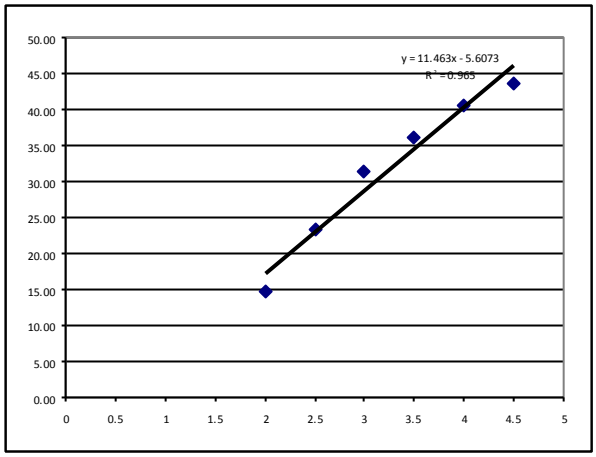
**Order in $Cs^+$5$^-$ with APC/dppp(O)$_2$ (Table 4, entry 1)**

| | |
|---|---|
| $Cs^+$**5**$^-$ | 62.5 mM |
| 2-Bromotoluene | 83 mM |
| APC | 3.75 mM |
| dppp(O)$_2$ | 7.5 mM |

In a drybox, a one-necked, 5-mL round-bottomed flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with $Cs^+$**5**$^-$ (39 mg, 0.125 mmol, 0.75 equiv), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), dppp(O)$_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (10 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) and dry benzotrifluoride (2.0 mL). The flask was placed in a 105 °C oil bath. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing 50 μL aliquots of the mixture by syringe and quenching the aliquots at regular intervals. The quench was performed as follows: the aliquot was injected into 100 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 1.0 mL of ethyl acetate and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 9039 | 1619 | 14.83 |
| 2 | 9540 | 1671 | 14.50 |
| 2 | 8910 | 1630 | 15.14 |
| 2.5 | 9429 | 2646 | 23.23 |
| 2.5 | 9426 | 2683 | 23.56 |
| 2.5 | 9443 | 2662 | 23.34 |
| 3 | 8404 | 3139 | 30.92 |
| 3 | 7872 | 3018 | 31.74 |
| 3 | 7938 | 3015 | 31.44 |
| 3.5 | 8016 | 3447 | 35.60 |
| 3.5 | 7943 | 3487 | 36.34 |
| 3.5 | 8850 | 3859 | 36.10 |
| 4 | 8357 | 4142 | 41.03 |

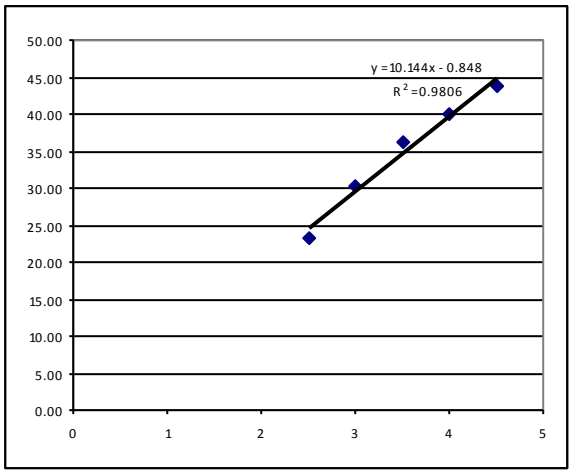


| | | | |
|---|---|---|---|
| 4 | 9292 | 4495 | 40.05 |
| 4 | 8931 | 4409 | 40.87 |
| 4.5 | 8012 | 4199 | 43.38 |
| 4.5 | 7901 | 4163 | 43.62 |
| 4.5 | 7741 | 4110 | 43.95 |

**rate = 0.0955 mM/sec**

**Run 2**

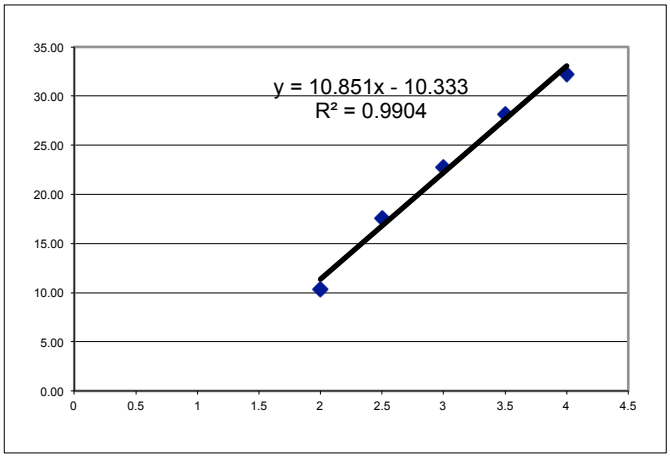
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2.5 | 7546 | 2034 | 24.54 |
| 2.5 | 8486 | 2134 | 22.90 |
| 2.5 | 7634 | 1880 | 22.42 |
| 3 | 8124 | 2685 | 30.10 |
| 3 | 8553 | 2875 | 30.61 |
| 3 | 8832 | 2892 | 29.82 |
| 3.5 | 7036 | 2810 | 36.37 |
| 3.5 | 7602 | 3010 | 36.05 |
| 3.5 | 6111 | 2418 | 36.03 |
| 4 | 8071 | 3544 | 39.98 |
| 4 | 8696 | 3837 | 40.18 |
| 4 | 9391 | 4069 | 39.45 |
| 4.5 | 7370 | 3559 | 43.97 |
| 4.5 | 7862 | 3751 | 43.44 |
| 4.5 | 7519 | 3632 | 43.99 |




**rate = 0.0845 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 17401 | 2190 | 10.42 |
| 2 | 17037 | 2154 | 10.47 |
| 2 | 17456 | 2163 | 10.26 |
| 2.5 | 18257 | 3875 | 17.57 |
| 2.5 | 18260 | 3832 | 17.37 |
| 2.5 | 18509 | 3978 | 17.79 |
| 3 | 21819 | 6022 | 22.85 |
| 3 | 21978 | 6055 | 22.81 |
| 3 | 22469 | 6148 | 22.65 |
| 3.5 | 18401 | 6292 | 28.31 |
| 3.5 | 17909 | 6047 | 27.95 |
| 3.5 | 18800 | 6400 | 28.18 |
| 4 | 18107 | 7005 | 32.03 |
| 4 | 18038 | 6988 | 32.07 |
| 4 | 17794 | 7002 | 32.57 |
| 4.5 | 18828 | 7990 | 35.13 |
| 4.5 | 18644 | 7951 | 35.30 |
| 4.5 | 17899 | 7639 | 35.33 |




**rate = 0.0905 mM/sec**

**avg. rate = 9.02 x $10^{-2}$ mM/s**

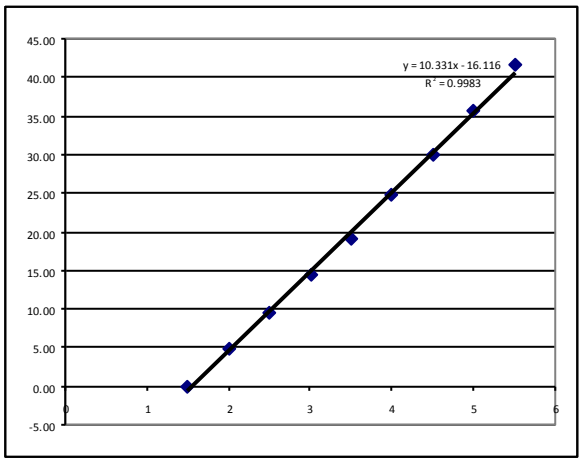
**Table 4, entry 2**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| APC | 3.75 mM |
| dppp$(O)_2$ | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (78 mg, 0.250 mmol, 1.5 equiv), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), dppp$(O)_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (10 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

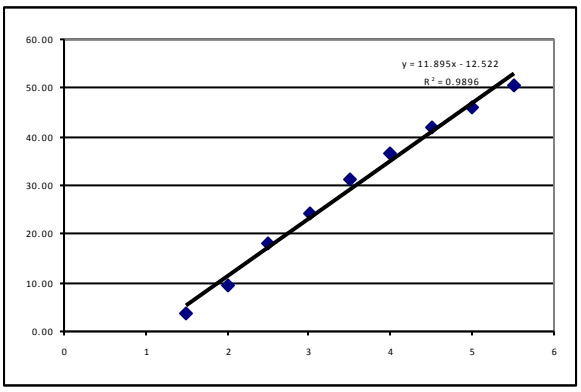
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 1 | 0 | 0.00 |
| 1.5 | 1 | 0 | 0.00 |
| 1.5 | 1 | 0 | 0.00 |
| 2 | 57759 | 3613 | 5.18 |
| 2 | 43602 | 2383 | 4.52 |
| 2 | 57759 | 3613 | 5.18 |
| 2.5 | 14242 | 1540 | 8.95 |
| 2.5 | 58344 | 6140 | 8.71 |
| 2.5 | 58941 | 7854 | 11.03 |
| 3 | 59989 | 11733 | 16.19 |
| 3 | 44769 | 7437 | 13.75 |
| 3 | 59805 | 9906 | 13.71 |
| 3.5 | 60961 | 14217 | 19.31 |
| 3.5 | 61510 | 14113 | 18.99 |
| 3.5 | 61459 | 14151 | 19.06 |
| 4 | 57100 | 17013 | 24.66 |
| 4 | 56481 | 17114 | 25.08 |
| 4 | 56573 | 16924 | 24.76 |
| 4.5 | 16301 | 5838 | 29.65 |
| 4.5 | 16248 | 6013 | 30.64 |
| 4.5 | 46728 | 16785 | 29.74 |
| 5 | 15976 | 6695 | 34.69 |
| 5 | 15420 | 6739 | 36.18 |
| 5 | 15745 | 6891 | 36.23 |
| 5.5 | 14179 | 7072 | 41.29 |
| 5.5 | 13234 | 6769 | 42.34 |
| 5.5 | 57590 | 28712 | 41.27 |




**rate = 0.0861 mM/sec**

**Run 2**

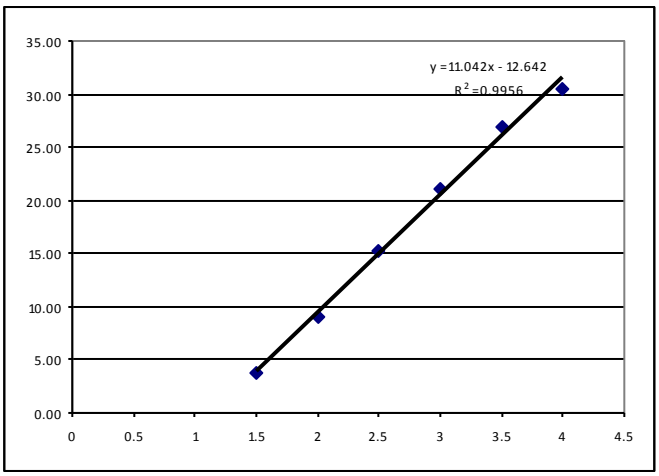
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 51699 | 2283 | 3.66 |
| 1.5 | 50502 | 2206 | 3.62 |
| 1.5 | 51699 | 2283 | 3.66 |
| 2 | 66484 | 7738 | 9.63 |
| 2 | 66489 | 7708 | 9.60 |
| 2 | 66278 | 7721 | 9.64 |
| 2.5 | 63901 | 14117 | 18.29 |
| 2.5 | 63363 | 13740 | 17.95 |
| 2.5 | 64165 | 13784 | 17.78 |
| 3 | 61905 | 18343 | 24.53 |
| 3 | 16797 | 4924 | 24.27 |
| 3 | 61630 | 18054 | 24.25 |
| 3.5 | 55118 | 20823 | 31.27 |
| 3.5 | 56083 | 20976 | 30.96 |
| 3.5 | 27825 | 10534 | 31.34 |
| 4 | 61868 | 27253 | 36.47 |
| 4 | 31213 | 13896 | 36.85 |
| 4 | 31627 | 14020 | 36.70 |
| 4.5 | 15611 | 7982 | 42.33 |
| 4.5 | 61972 | 31319 | 41.84 |
| 4.5 | 60808 | 30697 | 41.79 |
| 5 | 63762 | 35032 | 45.48 |
| 5 | 64313 | 36053 | 46.41 |
| 5 | 48599 | 27245 | 46.41 |
| 5.5 | 59569 | 36007 | 50.04 |
| 5.5 | 59196 | 36449 | 50.97 |
| 5.5 | 15862 | 9636 | 50.29 |




**rate = 0.0991 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 71276 | 2937 | 3.75 |
| 1.5 | 70946 | 2902 | 3.72 |
| 1.5 | 71276 | 2937 | 3.75 |
| 2 | 53080 | 5215 | 8.95 |
| 2 | 35434 | 3506 | 9.01 |
| 2 | 18085 | 1814 | 9.13 |
| 2.5 | 16559 | 2760 | 15.18 |
| 2.5 | 60532 | 10107 | 15.20 |
| 2.5 | 45349 | 7512 | 15.08 |
| 3 | 46905 | 10720 | 20.81 |
| 3 | 47953 | 11230 | 21.32 |
| 3 | 47469 | 10897 | 20.90 |
| 3.5 | 15274 | 4364 | 26.02 |
| 3.5 | 13887 | 4159 | 27.27 |



| | | | |
|---|---|---|---|
| 3.5 | 15899 | 4783 | 27.39 |
| 4 | 16387 | 5556 | 30.87 |
| 4 | 65024 | 21616 | 30.27 |
| 4 | 16575 | 5525 | 30.35 |

**rate = 0.0920 mM/sec**

**avg. rate = 9.24 x $10^{-2}$ mM/s**

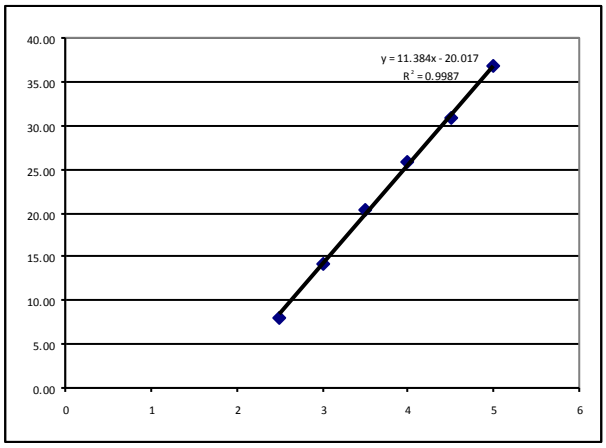
**Table 4, entry 3**

| | |
|---|---|
| $Cs^+$**5**$^-$ | 250 mM |
| 2-Bromotoluene | 83 mM |
| APC | 3.75 mM |
| dppp$(O)_2$ | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (157 mg, 0.500 mmol, 3.0 equiv), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), dppp$(O)_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (9 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

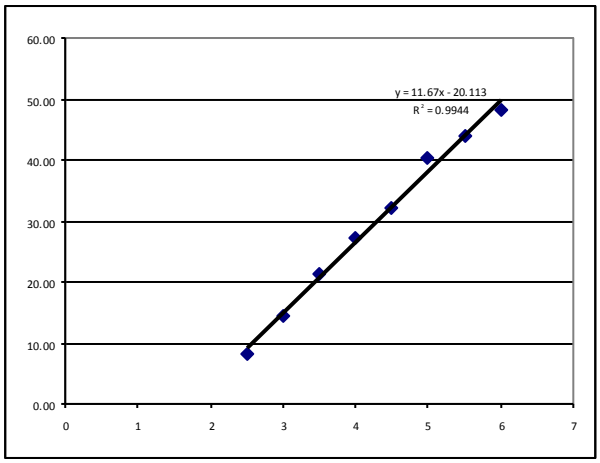
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2.5 | 16088 | 1743 | 8.07 |
| 2.5 | 16948 | 1824 | 8.02 |
| 2.5 | 16033 | 1752 | 8.14 |
| 3 | 17246 | 3240 | 14.00 |
| 3 | 16725 | 3208 | 14.29 |
| 3 | 16670 | 3110 | 13.90 |
| 3.5 | 16455 | 4444 | 20.12 |
| 3.5 | 16984 | 4660 | 20.44 |
| 3.5 | 17086 | 4714 | 20.56 |
| 4 | 19326 | 6710 | 25.87 |
| 4 | 18784 | 6480 | 25.70 |
| 4 | 19608 | 6903 | 26.23 |
| 4.5 | 19637 | 8107 | 30.76 |
| 4.5 | 19422 | 7983 | 30.62 |
| 4.5 | 18927 | 7950 | 31.29 |
| 5 | 18692 | 9275 | 36.97 |
| 5 | 18472 | 8993 | 36.27 |
| 5 | 18802 | 9312 | 36.90 |




**rate = 0.0948 mM/sec**

**Run 2**

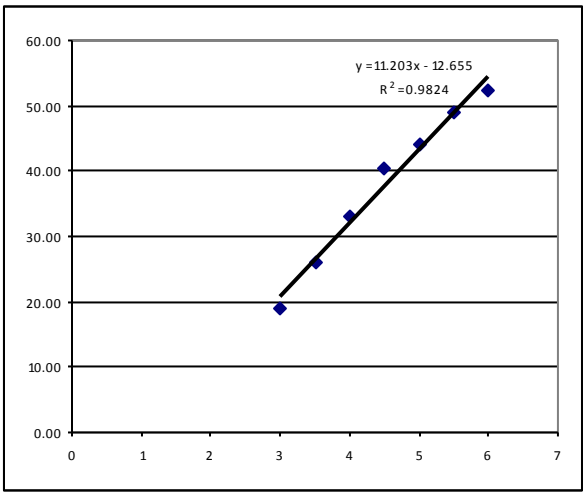
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2.5 | 18229 | 1992 | 8.14 |
| 2.5 | 17968 | 2000 | 8.29 |
| 2.5 | 17914 | 1972 | 8.20 |
| 3 | 10307 | 1975 | 14.28 |
| 3 | 9872 | 1984 | 14.97 |
| 3 | 10004 | 1932 | 14.39 |
| 3.5 | 8187 | 2400 | 21.84 |
| 3.5 | 7964 | 2270 | 21.24 |
| 3.5 | 8287 | 2279 | 20.49 |
| 4 | 8195 | 3020 | 27.46 |
| 4 | 8060 | 2893 | 26.74 |
| 4 | 8247 | 3015 | 27.24 |
| 4.5 | 8909 | 3843 | 32.14 |
| 4.5 | 8678 | 3788 | 32.52 |
| 4.5 | 8550 | 3675 | 32.02 |
| 5 | 6660 | 3671 | 41.07 |
| 5 | 7124 | 3761 | 39.33 |
| 5 | 6863 | 3712 | 40.30 |
| 5.5 | 8127 | 4781 | 43.83 |
| 5.5 | 8933 | 5372 | 44.80 |
| 5.5 | 8756 | 5121 | 43.57 |
| 6 | 8786 | 5605 | 47.53 |
| 6 | 9000 | 5819 | 48.17 |
| 6 | 9489 | 6250 | 49.07 |




**rate = 0.0973 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 3 | 8662 | 1976 | 18.88 |
| 3 | 8277 | 1904 | 19.04 |
| 3 | 8807 | 2062 | 19.38 |
| 3.5 | 7600 | 2404 | 26.18 |
| 3.5 | 8265 | 2623 | 26.27 |
| 3.5 | 8637 | 2716 | 26.03 |
| 4 | 7389 | 2955 | 33.11 |
| 4 | 6726 | 2752 | 33.87 |
| 4 | 7092 | 2780 | 32.45 |
| 4.5 | 8330 | 3981 | 39.56 |
| 4.5 | 7711 | 3797 | 40.76 |
| 4.5 | 8170 | 3997 | 40.50 |
| 5 | 9891 | 5277 | 44.16 |
| 5 | 9619 | 5138 | 44.22 |
| 5 | 9874 | 5256 | 44.06 |
| 5.5 | 8961 | 5367 | 49.58 |



| | | | |
|---|---|---|---|
| 5.5 | 8652 | 5039 | 48.21 |
| 5.5 | 9743 | 5789 | 49.19 |
| 6 | 8516 | 5424 | 52.72 |
| 6 | 8970 | 5682 | 52.44 |
| 6 | 9565 | 6046 | 52.33 |

**rate = 0.0933 mM/sec**

**avg. rate = 9.51 x $10^{-2}$ mM/sec**

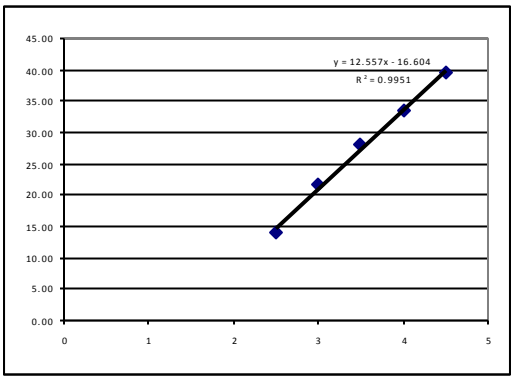
**Order in 2-bromotoluene with APC/dppp(O)$_2$ (Table 4, entry 4)**

| | |
|---|---|
| $Cs^+$**5**$^-$ | 125 mM |
| 2-Bromotoluene | 167 mM |
| APC | 3.75 mM |
| dppp(O)$_2$ | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (78 mg, 0.250 mmol, 1.5 equiv), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), dppp(O)$_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (10 mg), and 2-bromotoluene (40 μL, 0.33 mmol, 2.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

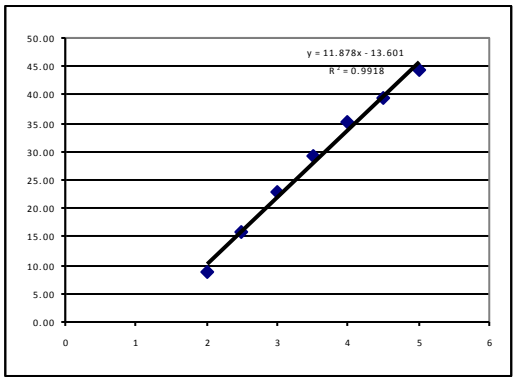
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2.5 | 5856 | 971 | 13.73 |
| 2.5 | 4338 | 734 | 14.01 |
| 2.5 | 5812 | 994 | 14.16 |
| 3 | 6153 | 1573 | 21.16 |
| 3 | 5917 | 1573 | 22.01 |
| 3 | 5769 | 1527 | 21.91 |
| 3.5 | 3978 | 1383 | 28.78 |
| 3.5 | 4491 | 1519 | 28.00 |
| 3.5 | 4093 | 1368 | 27.67 |
| 4 | 5885 | 2367 | 33.30 |
| 4 | 6151 | 2479 | 33.36 |
| 4 | 5123 | 2080 | 33.61 |
| 4.5 | 5519 | 2585 | 38.77 |
| 4.5 | 4334 | 2135 | 40.78 |
| 4.5 | 5677 | 2669 | 38.92 |




**rate = 0.105 mM/sec**

**Run 2**

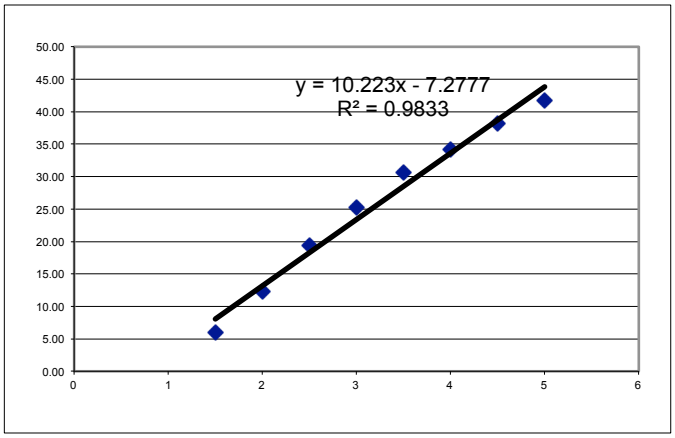
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 7909 | 910 | 8.57 |
| 2 | 7775 | 937 | 8.98 |
| 2 | 12272 | 1403 | 8.52 |
| 2.5 | 12923 | 2750 | 15.85 |
| 2.5 | 13321 | 2844 | 15.91 |
| 2.5 | 12785 | 2747 | 16.01 |
| 3 | 12888 | 4012 | 23.19 |
| 3 | 12461 | 3869 | 23.13 |
| 3 | 15864 | 4843 | 22.74 |
| 3.5 | 11297 | 4480 | 29.55 |
| 3.5 | 11158 | 4367 | 29.16 |
| 3.5 | 4109 | 1589 | 28.81 |
| 4 | 8806 | 4184 | 35.40 |
| 4 | 9374 | 4444 | 35.32 |
| 4 | 9270 | 4296 | 34.53 |
| 4.5 | 9063 | 4893 | 40.22 |
| 4.5 | 5181 | 2749 | 39.53 |
| 4.5 | 5426 | 2838 | 38.97 |
| 5 | 9824 | 5827 | 44.19 |
| 5 | 9107 | 5490 | 44.91 |
| 5 | 7990 | 4707 | 43.89 |




**rate = 0.0989 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 12622 | 730 | 5.75 |
| 1.5 | 12850 | 802 | 6.20 |
| 1.5 | 13783 | 879 | 6.34 |
| 2 | 13021 | 1511 | 11.53 |
| 2 | 13733 | 1748 | 12.64 |
| 2 | 13715 | 1733 | 12.55 |
| 2.5 | 16499 | 3247 | 19.55 |
| 2.5 | 17074 | 3305 | 19.23 |
| 2.5 | 16639 | 3210 | 19.16 |
| 3 | 14770 | 3843 | 25.85 |
| 3 | 13184 | 3323 | 25.04 |
| 3 | 14902 | 3680 | 24.53 |
| 3.5 | 15748 | 4864 | 30.68 |
| 3.5 | 15225 | 4748 | 30.98 |
| 3.5 | 15315 | 4705 | 30.52 |
| 4 | 15500 | 5290 | 33.90 |
| 4 | 15341 | 5320 | 34.45 |
| 4 | 15694 | 5375 | 34.02 |
| 4.5 | 12380 | 4785 | 38.39 |



| | | | |
|---|---|---|---|
| 4.5 | 14826 | 5704 | 38.22 |
| 4.5 | 13154 | 5024 | 37.94 |

**rate = 0.0852 mM/sec**

**avg. rate = 9.63 x $10^{-2}$ mM/s**

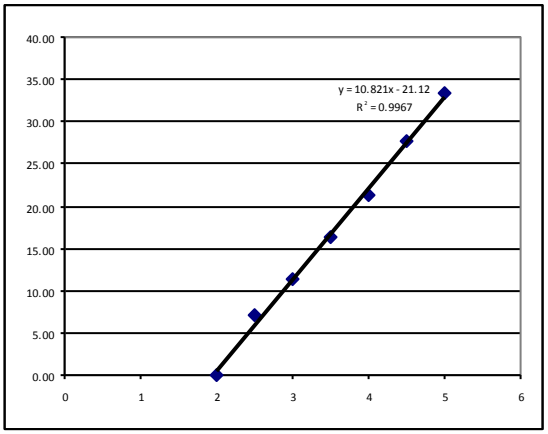
**Table 4, entry 5**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 125 mM |
| 2-Bromotoluene | 333 mM |
| APC | 3.75 mM |
| dppp$(O)_2$ | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (78 mg, 0.250 mmol, 1.5 equiv), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), dppp$(O)_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (11 mg), and 2-bromotoluene (80 μL, 0.66 mmol, 4.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 1 | 0 | 0.00 |
| 2 | 1 | 0 | 0.00 |
| 2 | 1 | 0 | 0.00 |
| 2.5 | 18321 | 1647 | 8.19 |
| 2.5 | 17823 | 1476 | 7.54 |
| 2.5 | 18708 | 1124 | 5.47 |
| 3 | 15745 | 2126 | 12.30 |
| 3 | 17707 | 2152 | 11.07 |
| 3 | 33522 | 4052 | 11.01 |
| 3.5 | 16388 | 2901 | 16.12 |
| 3.5 | 31045 | 5507 | 16.15 |
| 3.5 | 16215 | 2918 | 16.39 |
| 4 | 33510 | 7808 | 21.22 |
| 4 | 48626 | 11423 | 21.39 |
| 4 | 16795 | 3965 | 21.50 |
| 4.5 | 14022 | 4292 | 27.87 |
| 4.5 | 14330 | 4325 | 27.48 |
| 4.5 | 13947 | 4277 | 27.92 |
| 5 | 14843 | 5192 | 31.85 |
| 5 | 13256 | 5126 | 35.21 |

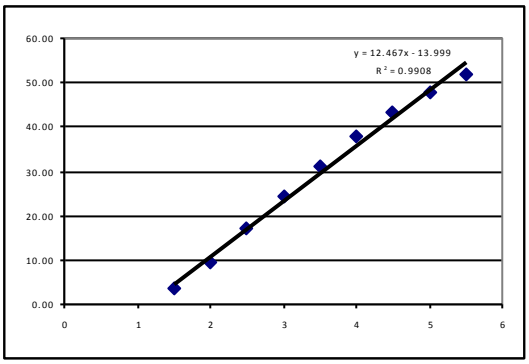


| | | | |
|---|---|---|---|
| 5 | 14350 | 5220 | 33.12 |

**rate = 0.0902 mM/sec**

**Run 2**

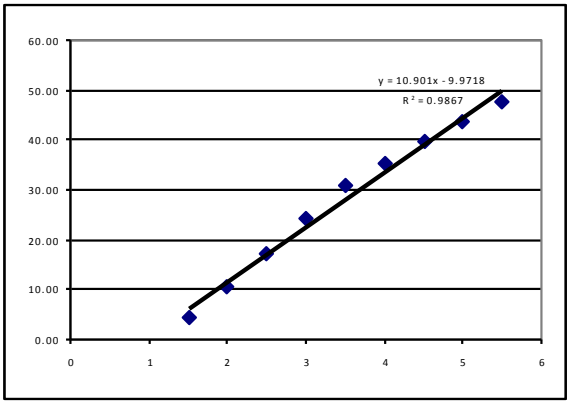
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 14973 | 748 | 3.72 |
| 1.5 | 14901 | 756 | 3.78 |
| 1.5 | 15322 | 736 | 3.58 |
| 2 | 14736 | 1783 | 9.01 |
| 2 | 13658 | 1770 | 9.66 |
| 2 | 14449 | 1795 | 9.26 |
| 2.5 | 14037 | 3154 | 16.74 |
| 2.5 | 17421 | 3984 | 17.04 |
| 2.5 | 54933 | 13125 | 17.80 |
| 3 | 17666 | 5840 | 24.63 |
| 3 | 17810 | 5842 | 24.44 |
| 3 | 17994 | 5811 | 24.06 |
| 3.5 | 17848 | 7509 | 31.34 |
| 3.5 | 18147 | 7540 | 30.96 |
| 3.5 | 17988 | 7444 | 30.83 |
| 4 | 16425 | 8504 | 38.57 |
| 4 | 16087 | 8143 | 37.71 |
| 4 | 16568 | 8410 | 37.82 |
| 4.5 | 18166 | 10513 | 43.12 |
| 4.5 | 18796 | 10730 | 42.53 |
| 4.5 | 17972 | 10826 | 44.88 |
| 5 | 18711 | 11987 | 47.73 |
| 5 | 18748 | 12093 | 48.06 |
| 5 | 19122 | 12270 | 47.81 |
| 5.5 | 16140 | 11212 | 51.75 |
| 5.5 | 15923 | 11011 | 51.52 |
| 5.5 | 16073 | 11187 | 51.85 |




**rate = 0.104 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 16906 | 970 | 4.75 |
| 1.5 | 17389 | 943 | 4.49 |
| 1.5 | 17355 | 963 | 4.59 |
| 2 | 19442 | 2420 | 10.30 |
| 2 | 19250 | 2505 | 10.77 |
| 2 | 19545 | 2418 | 10.24 |
| 2.5 | 21061 | 4408 | 17.33 |
| 2.5 | 20495 | 4264 | 17.22 |
| 2.5 | 20381 | 4364 | 17.73 |
| 3 | 19134 | 5662 | 24.50 |
| 3 | 19466 | 5640 | 23.98 |



| | | | |
|---|---|---|---|
| 3 | 19645 | 5721 | 24.11 |
| 3.5 | 20188 | 7598 | 31.16 |
| 3.5 | 19867 | 7337 | 30.57 |
| 3.5 | 20619 | 7548 | 30.30 |
| 4 | 16117 | 6801 | 34.93 |
| 4 | 15537 | 6713 | 35.77 |
| 4 | 15639 | 6722 | 35.58 |
| 4.5 | 21154 | 10223 | 40.01 |
| 4.5 | 21384 | 10162 | 39.34 |
| 4.5 | 22000 | 10565 | 39.75 |
| 5 | 19076 | 10065 | 43.68 |
| 5 | 18841 | 10092 | 44.34 |
| 5 | 19045 | 9892 | 43.00 |
| 5.5 | 17949 | 10321 | 47.60 |
| 5.5 | 17550 | 10100 | 47.64 |
| 5.5 | 18103 | 10336 | 47.26 |

**rate = 0.0908 mM/sec**

**avg. rate = 9.50 x $10^{-2}$ mM/s**

**Order in dppp(O)$_2$ with $Cs^+$**$\mathbf{5}^-$ **at (125 mM) (Table 4, entry 6)**

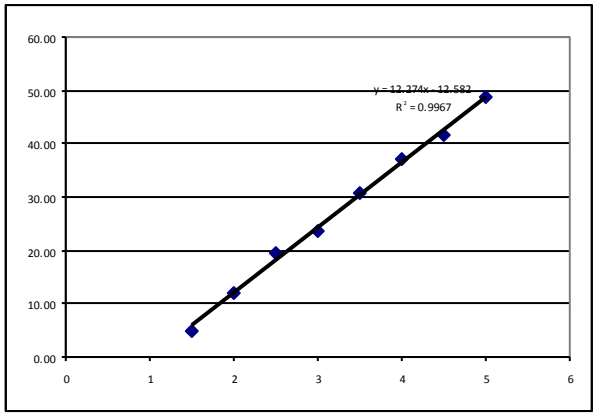
| | |
|---|---|
| $Cs^+$**5**$^-$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| APC | 3.75 mM |
| dppp(O)$_2$ | 15 mM |

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (78 mg, 0.250 mmol, 1.5 equiv), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), dppp(O)$_2$ (13.2 mg, 0.030 mmol, 0.180 equiv), naphthalene (10 mg), and 2-bromotoluene (20 μL, 0.167 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 19493 | 1138 | 4.83 |
| 1.5 | 19167 | 1118 | 4.83 |
| 1.5 | 19287 | 1165 | 5.00 |

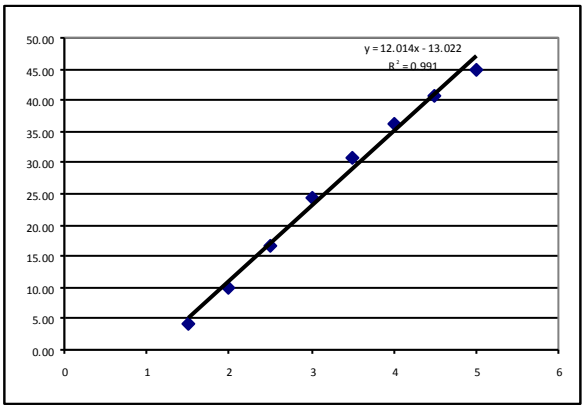
| | | | |
|---|---|---|---|
| 2 | 16823 | 2442 | 12.02 |
| 2 | 17199 | 2507 | 12.07 |
| 2 | 17521 | 2517 | 11.89 |
| 2.5 | 20646 | 5018 | 20.12 |
| 2.5 | 21106 | 5219 | 20.47 |
| 2.5 | 21815 | 4855 | 18.42 |
| 3 | 16178 | 4693 | 24.01 |
| 3 | 16148 | 4266 | 21.87 |
| 3 | 16426 | 4859 | 24.49 |
| 3.5 | 18989 | 7270 | 31.69 |
| 3.5 | 19609 | 7217 | 30.47 |
| 3.5 | 19959 | 7286 | 30.22 |
| 4 | 17076 | 7935 | 38.47 |
| 4 | 17248 | 7541 | 36.19 |
| 4 | 17194 | 7656 | 36.86 |
| 4.5 | 26131 | 13187 | 41.78 |
| 4.5 | 25624 | 12962 | 41.87 |
| 4.5 | 25718 | 12976 | 41.77 |
| 5 | 18615 | 11127 | 49.48 |
| 5 | 19403 | 11412 | 48.69 |
| 5 | 19410 | 11228 | 47.89 |




**rate = 0.102 mM/sec**

**Run 2**

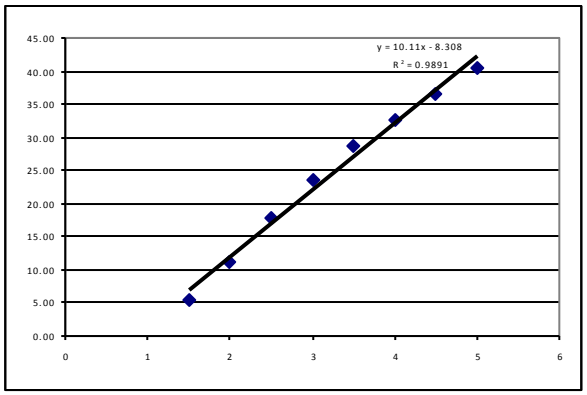
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 19405 | 834 | 4.63 |
| 1.5 | 19056 | 702 | 3.96 |
| 1.5 | 19338 | 732 | 4.07 |
| 2 | 23733 | 2225 | 10.09 |
| 2 | 25013 | 2254 | 9.70 |
| 2 | 25287 | 2265 | 9.64 |
| 2.5 | 20103 | 3288 | 17.60 |
| 2.5 | 20421 | 3015 | 15.89 |
| 2.5 | 20717 | 3254 | 16.90 |
| 3 | 22455 | 5083 | 24.36 |
| 3 | 21414 | 4910 | 24.67 |
| 3 | 22365 | 5096 | 24.52 |
| 3.5 | 25151 | 7247 | 31.01 |
| 3.5 | 25051 | 7178 | 30.84 |
| 3.5 | 25210 | 7218 | 30.81 |
| 4 | 21658 | 7288 | 36.21 |
| 4 | 21681 | 7364 | 36.55 |
| 4 | 21517 | 7207 | 36.05 |
| 4.5 | 23738 | 8997 | 40.79 |
| 4.5 | 23577 | 8931 | 40.76 |
| 4.5 | 23538 | 8887 | 40.63 |
| 5 | 25446 | 10546 | 44.60 |
| 5 | 25073 | 10460 | 44.89 |
| 5 | 25087 | 10584 | 45.40 |




**rate = 0.100 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 20061 | 1329 | 5.48 |
| 1.5 | 19989 | 1266 | 5.24 |
| 1.5 | 20464 | 1306 | 5.28 |
| 2 | 22297 | 3048 | 11.32 |
| 2 | 22875 | 3039 | 11.00 |
| 2 | 22725 | 3079 | 11.22 |
| 2.5 | 26268 | 5658 | 17.83 |
| 2.5 | 26051 | 5496 | 17.46 |
| 2.5 | 27117 | 5807 | 17.73 |
| 3 | 26012 | 7183 | 22.86 |
| 3 | 24908 | 7108 | 23.62 |
| 3 | 26016 | 7466 | 23.76 |
| 3.5 | 18417 | 6323 | 28.42 |
| 3.5 | 18223 | 6351 | 28.85 |
| 3.5 | 18161 | 6403 | 29.19 |
| 4 | 22283 | 8855 | 32.90 |
| 4 | 22693 | 8918 | 32.53 |
| 4 | 22875 | 9078 | 32.85 |
| 4.5 | 20533 | 8915 | 35.94 |
| 4.5 | 20902 | 9362 | 37.08 |
| 4.5 | 20522 | 9188 | 37.06 |
| 5 | 17621 | 8771 | 41.20 |
| 5 | 18462 | 9031 | 40.49 |
| 5 | 19003 | 9161 | 39.91 |




**rate = 0.0843 mM/sec**

**avg. rate = 9.54 x $10^{-2}$ mM/s**

**Order in $Cs^+$5$^-$ with APC/$Ph_3P(O)$ (15 mM) (Table 4, entry 7)**

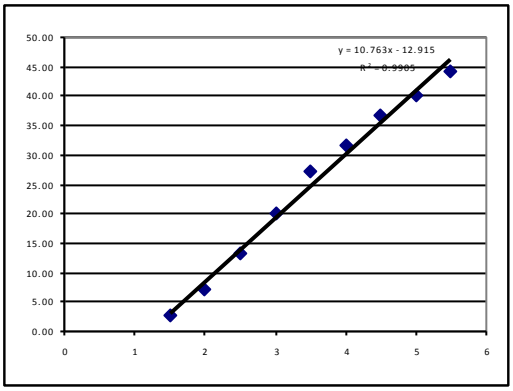
| | |
|---|---|
| $Cs^+$**5**$^-$ | 62.5 mM |
| 2-Bromotoluene | 83 mM |
| APC | 3.75 mM |
| $Ph_3P(O)$ | 15.0 mM |

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (39 mg, 0.125 mmol, 0.75 equiv), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), $Ph_3P(O)$ (8.3 mg, 0.030 mmol, 0.18 equiv), naphthalene (10 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the

mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, µmol |
|---|---|---|---|
| 1.5 | 105410 | 3236 | 2.54 |
| 1.5 | 109484 | 3472 | 2.63 |
| 1.5 | 110949 | 3605 | 2.69 |
| 2 | 59688 | 5262 | 7.30 |
| 2 | 80114 | 7009 | 7.24 |
| 2 | 79382 | 6932 | 7.23 |
| 2.5 | 69362 | 11158 | 13.32 |
| 2.5 | 36779 | 6023 | 13.56 |
| 2.5 | 52724 | 8459 | 13.28 |
| 3 | 15597 | 3667 | 19.46 |
| 3 | 43519 | 10684 | 20.32 |
| 3 | 43546 | 10596 | 20.14 |
| 3.5 | 31772 | 10117 | 26.36 |
| 3.5 | 62370 | 20912 | 27.76 |
| 3.5 | 31866 | 10404 | 27.03 |
| 4 | 41975 | 15736 | 31.03 |
| 4 | 55700 | 21238 | 31.56 |
| 4 | 42029 | 16316 | 32.14 |
| 4.5 | 78358 | 35582 | 37.59 |
| 4.5 | 55944 | 24662 | 36.49 |
| 4.5 | 38791 | 16799 | 35.85 |
| 5 | 20176 | 9827 | 40.32 |
| 5 | 23415 | 11079 | 39.17 |
| 5 | 64196 | 31854 | 41.08 |
| 5.5 | 23730 | 12428 | 43.35 |
| 5.5 | 21388 | 11363 | 43.98 |
| 5.5 | 22715 | 12350 | 45.01 |

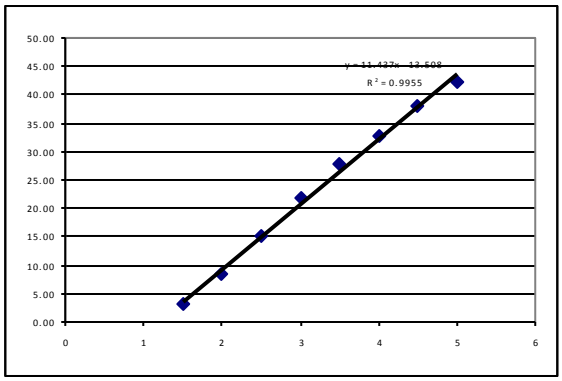



**rate = 0.0897 mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, µmol |
|---|---|---|---|
| 1.5 | 54408 | 2006 | 3.36 |
| 1.5 | 73503 | 2559 | 3.17 |
| 1.5 | 73532 | 2514 | 3.11 |
| 2 | 67041 | 6084 | 8.26 |
| 2 | 65872 | 6174 | 8.53 |
| 2 | 67179 | 6115 | 8.29 |
| 2.5 | 70837 | 11730 | 15.08 |
| 2.5 | 67516 | 11157 | 15.05 |
| 2.5 | 71189 | 12086 | 15.46 |
| 3 | 68116 | 16222 | 21.69 |
| 3 | 68485 | 16142 | 21.46 |
| 3 | 67694 | 16301 | 21.93 |

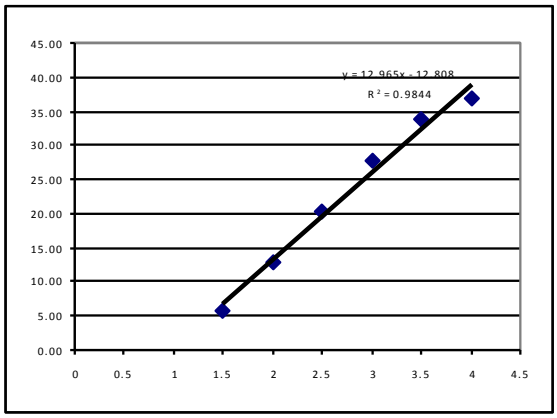
| | | | |
|---|---|---|---|
| 3.5 | 79310 | 23809 | 27.34 |
| 3.5 | 58461 | 17935 | 27.94 |
| 3.5 | 81849 | 24986 | 27.80 |
| 4 | 55807 | 20953 | 34.19 |
| 4 | 76660 | 26763 | 31.79 |
| 4 | 74217 | 26602 | 32.64 |
| 4.5 | 67046 | 27741 | 37.68 |
| 4.5 | 66874 | 27492 | 37.43 |
| 4.5 | 65015 | 28094 | 39.35 |
| 5 | 62238 | 28922 | 42.32 |
| 5 | 62444 | 28870 | 42.10 |
| 5 | 61915 | 28532 | 41.96 |
| 5.5 | 70446 | 35070 | 45.33 |
| 5.5 | 70756 | 34909 | 44.93 |
| 5.5 | 70895 | 35066 | 45.04 |




**rate = 0.0953 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 66027 | 4372 | 5.48 |
| 1.5 | 66912 | 4544 | 5.62 |
| 1.5 | 65412 | 4477 | 5.67 |
| 2 | 57943 | 9067 | 12.95 |
| 2 | 55534 | 8545 | 12.74 |
| 2 | 54735 | 8291 | 12.54 |
| 2.5 | 59683 | 14676 | 20.36 |
| 2.5 | 15454 | 3703 | 19.84 |
| 2.5 | 15354 | 3820 | 20.60 |
| 3 | 64778 | 21539 | 27.52 |
| 3 | 64205 | 21435 | 27.64 |
| 3 | 65032 | 22238 | 28.31 |
| 3.5 | 51457 | 21059 | 33.88 |
| 3.5 | 52292 | 21289 | 33.70 |
| 3.5 | 52594 | 21661 | 34.09 |
| 4 | 62573 | 27695 | 36.64 |
| 4 | 61985 | 27454 | 36.66 |
| 4 | 61169 | 27339 | 37.00 |




**rate = 0.108 mM/sec**

**avg. rate = 9.77 x $10^{-2}$ mM/s**

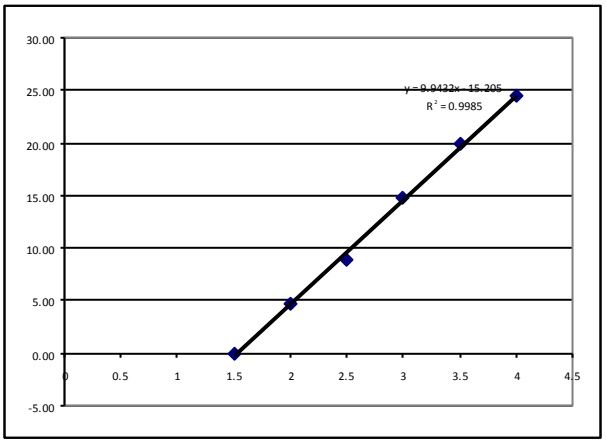
**Table 4, entry 8**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| APC | 3.75 mM |
| $Ph_3P(O)$ | 15.0 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (78 mg, 0.25 mmol), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), $Ph_3P(O)$ (8.3 mg, 0.030 mmol, 0.18 equiv), naphthalene (10 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

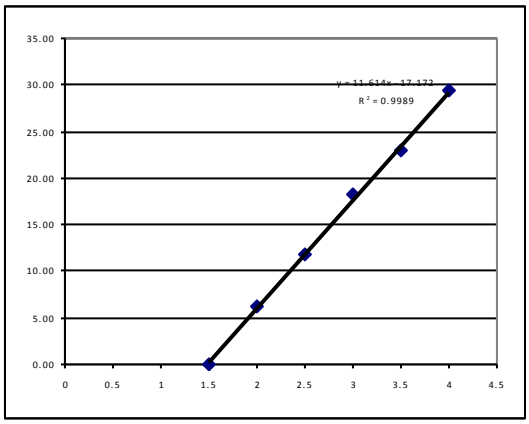
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 1 | 0 | 0.00 |
| 1.5 | 1 | 0 | 0.00 |
| 1.5 | 1 | 0 | 0.00 |
| 2 | 79559 | 3945 | 4.52 |
| 2 | 27890 | 1500 | 4.90 |
| 2 | 79559 | 3945 | 4.52 |
| 2.5 | 20989 | 2069 | 8.98 |
| 2.5 | 21455 | 2118 | 8.99 |
| 2.5 | 20989 | 2069 | 8.98 |
| 3 | 25142 | 3989 | 14.45 |
| 3 | 24340 | 3930 | 14.70 |
| 3 | 23100 | 3914 | 15.43 |
| 3.5 | 27294 | 5868 | 19.58 |
| 3.5 | 26257 | 5937 | 20.59 |
| 3.5 | 28979 | 6168 | 19.38 |
| 4 | 34248 | 8984 | 23.89 |
| 4 | 32323 | 8924 | 25.14 |
| 4 | 33158 | 8913 | 24.48 |
| 4.5 | 33652 | 10794 | 29.21 |
| 4.5 | 35470 | 11077 | 28.44 |
| 4.5 | 37301 | 11512 | 28.10 |




**rate = 0.0828 mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 1 | 0 | 0.00 |
| 1.5 | 1 | 0 | 0.00 |
| 1.5 | 1 | 0 | 0.00 |
| 2 | 29684 | 2264 | 6.31 |
| 2 | 29884 | 2249 | 6.23 |
| 2 | 30183 | 2306 | 6.32 |
| 2.5 | 25362 | 3603 | 11.76 |
| 2.5 | 24184 | 3509 | 12.01 |
| 2.5 | 26073 | 3648 | 11.58 |
| 3 | 16529 | 3567 | 17.86 |

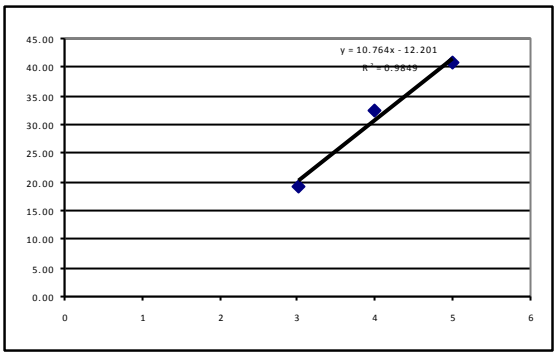


| | | | |
|---|---|---|---|
| 3 | 16055 | 3526 | 18.18 |
| 3 | 16289 | 3639 | 18.49 |
| 3.5 | 16848 | 4750 | 23.34 |
| 3.5 | 17485 | 4782 | 22.64 |
| 3.5 | 18200 | 5051 | 22.97 |
| 4 | 14734 | 5350 | 30.06 |
| 4 | 16846 | 5921 | 29.10 |
| 4 | 16547 | 5777 | 28.90 |
| 4.5 | 12763 | 5718 | 37.09 |
| 4.5 | 12719 | 5764 | 37.51 |
| 4.5 | 14570 | 6253 | 35.53 |

**rate = 0.0968 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 3 | 16154 | 3749 | 19.21 |
| 3 | 16447 | 3831 | 19.28 |
| 3 | 16073 | 3781 | 19.47 |
| 4 | 16039 | 6059 | 31.27 |
| 4 | 13742 | 5617 | 33.84 |
| 4 | 47781 | 18511 | 32.07 |
| 5 | 12763 | 6310 | 40.93 |
| 5 | 13252 | 6447 | 40.27 |
| 5 | 39732 | 19848 | 41.35 |
| 6 | 12583 | 7090 | 46.64 |
| 6 | 53789 | 31032 | 47.76 |
| 6 | 12434 | 7102 | 47.28 |




**rate = 0.0897 mM/sec**

**avg. rate = 8.98 x $10^{-2}$ mM/s**

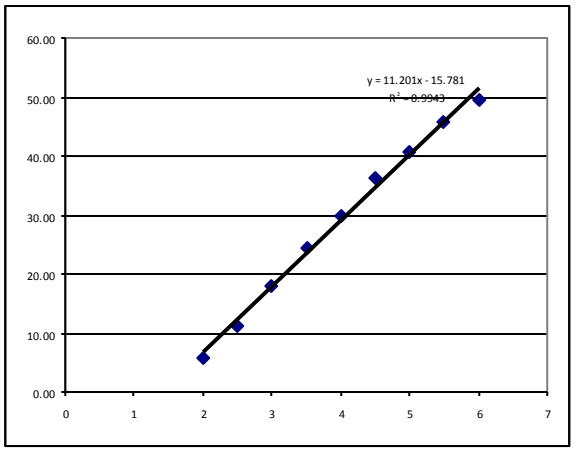
**Table 4, entry 9**

| | |
|---|---|
| $Cs^+$**5**$^-$ | 250 mM |
| 2-Bromotoluene | 83 mM |
| APC | 3.75 mM |
| $Ph_3P(O)$ | 15.0 mM |

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (157 mg, 0.50 mmol), APC (2.7 mg, 0.0075 mmol, 0.045 equiv), $Ph_3P(O)$ (8.3 mg, 0.030 mmol, 0.18 equiv), naphthalene (10 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

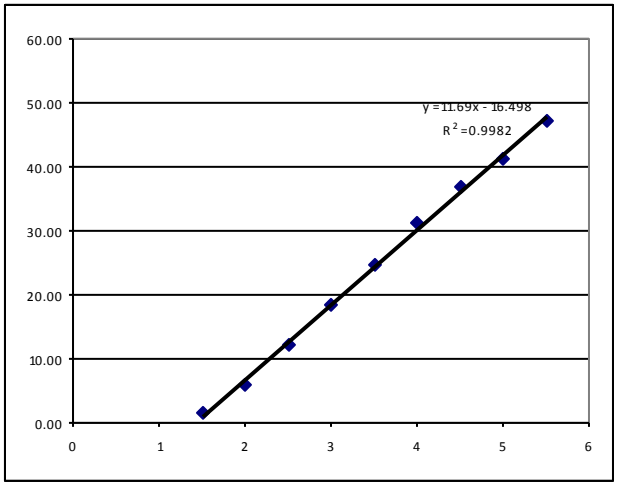
| Time | area, std | area, **12** | conv, µmol |
|---|---|---|---|
| 2 | 77524 | 5265 | 5.62 |
| 2 | 40009 | 2729 | 5.65 |
| 2 | 77524 | 5265 | 5.62 |
| 2.5 | 33247 | 4591 | 11.43 |
| 2.5 | 31590 | 4227 | 11.08 |
| 2.5 | 30299 | 4175 | 11.41 |
| 3 | 23363 | 5005 | 17.73 |
| 3 | 22495 | 5061 | 18.62 |
| 3 | 24141 | 5052 | 17.32 |
| 3.5 | 17884 | 5205 | 24.09 |
| 3.5 | 17613 | 5154 | 24.22 |
| 3.5 | 17639 | 5313 | 24.93 |
| 4 | 37263 | 13202 | 29.33 |
| 4 | 37162 | 13171 | 29.34 |
| 4 | 37578 | 13888 | 30.59 |
| 4.5 | 28395 | 12353 | 36.01 |
| 4.5 | 27569 | 12179 | 36.57 |
| 4.5 | 27878 | 12259 | 36.40 |
| 5 | 41637 | 20346 | 40.45 |
| 5 | 43205 | 21200 | 40.62 |
| 5 | 42773 | 21154 | 40.94 |
| 5.5 | 26892 | 14832 | 45.66 |
| 5.5 | 26887 | 15077 | 46.42 |
| 5.5 | 27348 | 15020 | 45.46 |
| 6 | 33779 | 20315 | 49.79 |
| 6 | 33799 | 20082 | 49.18 |
| 6 | 34110 | 20242 | 49.12 |




**rate = 0.0974 mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, µmol |
|---|---|---|---|
| 1.5 | 72888 | 2292 | 2.34 |
| 1.5 | 97031 | 3216 | 2.47 |
| 1.5 | 1 | 0 | 0.00 |
| 2 | 83816 | 6642 | 5.90 |
| 2 | 84393 | 6633 | 5.86 |
| 2 | 22194 | 1797 | 6.03 |
| 2.5 | 24682 | 4093 | 12.35 |
| 2.5 | 69704 | 11178 | 11.95 |
| 2.5 | 23648 | 3950 | 12.44 |
| 3 | 19824 | 5032 | 18.91 |
| 3 | 20396 | 5021 | 18.34 |
| 3 | 40382 | 9917 | 18.30 |
| 3.5 | 24112 | 7897 | 24.40 |
| 3.5 | 24839 | 8305 | 24.91 |
| 3.5 | 23942 | 8043 | 25.03 |

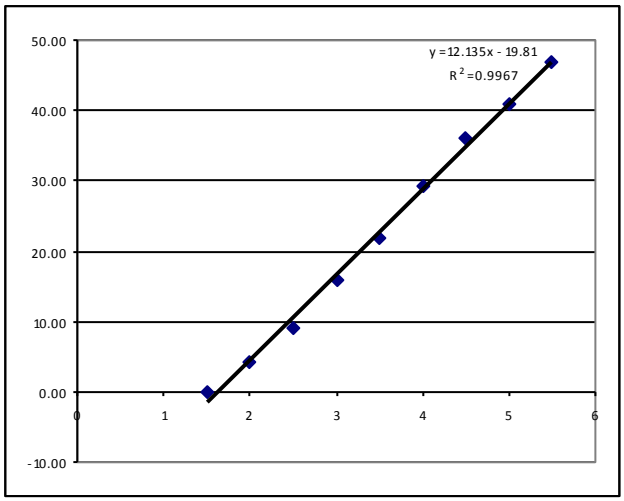


| | | | |
|---|---|---|---|
| 4 | 23375 | 9764 | 31.12 |
| 4 | 24278 | 10016 | 30.74 |
| 4 | 23086 | 9899 | 31.95 |
| 4.5 | 20600 | 10298 | 37.24 |
| 4.5 | 21464 | 10400 | 36.10 |
| 4.5 | 39720 | 19695 | 36.94 |
| 5 | 16690 | 9191 | 41.03 |
| 5 | 16573 | 9232 | 41.50 |
| 5 | 16406 | 9175 | 41.67 |
| 5.5 | 16469 | 10898 | 49.30 |
| 5.5 | 18577 | 11406 | 45.74 |
| 5.5 | 17264 | 10810 | 46.65 |

**rate = 0.0933 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 1.5 | 1 | 0 | 0.00 |
| 1.5 | 1 | 0 | 0.00 |
| 1.5 | 1 | 0 | 0.00 |
| 2 | 41893 | 2352 | 4.18 |
| 2 | 42152 | 2360 | 4.17 |
| 2 | 40580 | 2408 | 4.42 |
| 2.5 | 21090 | 2582 | 9.12 |
| 2.5 | 20880 | 2600 | 9.28 |
| 2.5 | 21868 | 2580 | 8.79 |
| 3 | 19609 | 4262 | 16.19 |
| 3 | 21364 | 4559 | 15.90 |
| 3 | 17483 | 3654 | 15.57 |
| 3.5 | 19130 | 5446 | 21.21 |
| 3.5 | 67894 | 20401 | 22.39 |
| 3.5 | 17952 | 5374 | 22.30 |
| 4 | 21986 | 8476 | 28.72 |
| 4 | 84417 | 33195 | 29.30 |
| 4 | 86865 | 34398 | 29.50 |
| 4.5 | 56701 | 28222 | 37.08 |
| 4.5 | 15402 | 7221 | 34.93 |
| 4.5 | 58066 | 27910 | 35.81 |
| 5 | 77488 | 43122 | 41.46 |
| 5 | 78275 | 42802 | 40.74 |
| 5 | 78001 | 42494 | 40.59 |
| 5.5 | 67725 | 42013 | 46.22 |
| 5.5 | 16899 | 10375 | 45.74 |
| 5.5 | 48791 | 31627 | 48.29 |




**rate = 0.101mM/sec**

**avg. rate = 9.72 x $10^{-2}$ mM/s**

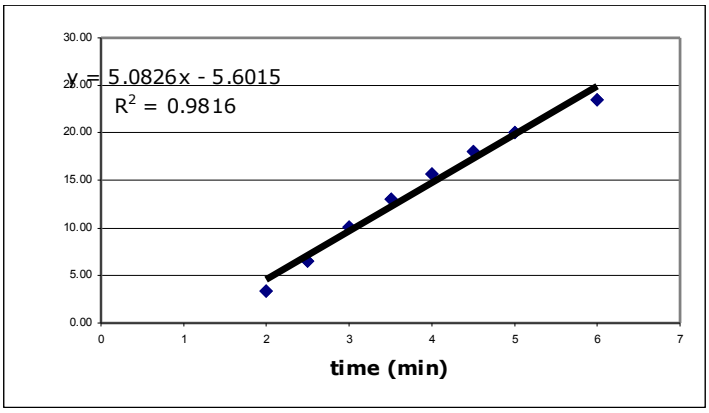
**Order in Pd with APC/dppp(O)$_2$ (Table 4, entry 10)**

| | |
|---|---|
| $Cs^+$**5**$^-$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| APC | 1.875 mM |
| dppp(O)$_2$ | 7.5 mM |

**Run 1**

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (78 mg, 0.250 mmol, 1.5 equiv), APC (1.3 mg, 0.00375 mmol, 0.0225 equiv), dppp(O)$_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (10 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 117421 | 4727 | 3.33 |
| 2 | 120660 | 4939 | 3.39 |
| 2 | 120909 | 5056 | 3.46 |
| 2.5 | 64562 | 5092 | 6.53 |
| 2.5 | 63760 | 5068 | 6.58 |
| 2.5 | 62291 | 4925 | 6.54 |
| 3 | 85025 | 10362 | 10.09 |
| 3 | 84853 | 10463 | 10.20 |
| 3 | 86138 | 10469 | 10.06 |
| 3.5 | 90882 | 14083 | 12.82 |
| 3.5 | 86204 | 13563 | 13.02 |
| 3.5 | 89079 | 14211 | 13.20 |
| 4 | 68920 | 13271 | 15.94 |
| 4 | 70608 | 13249 | 15.53 |
| 4 | 67878 | 12743 | 15.54 |
| 4.5 | 103628 | 22909 | 18.30 |
| 4.5 | 107005 | 22701 | 17.56 |
| 4.5 | 105908 | 23149 | 18.09 |
| 5 | 123690 | 30108 | 20.14 |
| 5 | 127691 | 31220 | 20.23 |
| 5 | 128222 | 30489 | 19.68 |
| 6 | 78902 | 22729 | 23.84 |
| 6 | 82348 | 22819 | 22.93 |
| 6 | 81171 | 23178 | 23.63 |

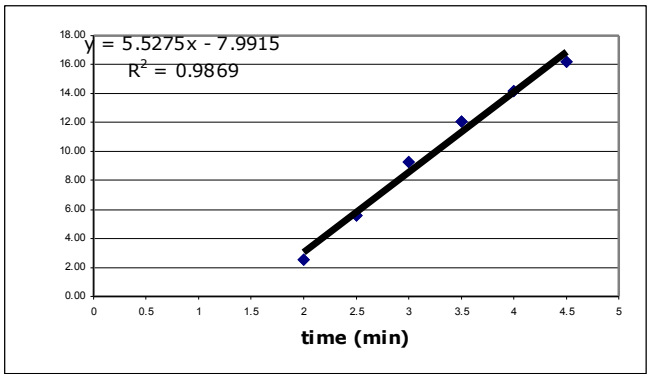



**rate = 0.0424 mM/sec**

**Run 2**

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (78 mg, 0.250 mmol, 1.5 equiv), APC (1.3 mg, 0.00375 mmol, 0.0225 equiv), dppp(O)$_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (8 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 84351 | 3219 | 2.53 |
| 2 | 84023 | 3252 | 2.56 |
| 2 | 83269 | 3193 | 2.54 |
| 2.5 | 60335 | 5106 | 5.60 |
| 2.5 | 59429 | 5101 | 5.68 |
| 2.5 | 60250 | 5019 | 5.52 |
| 3 | 59870 | 8416 | 9.31 |
| 3 | 59399 | 8340 | 9.30 |
| 3 | 59680 | 8302 | 9.21 |
| 3.5 | 84691 | 15580 | 12.18 |
| 3.5 | 84422 | 15303 | 12.00 |
| 3.5 | 82710 | 15021 | 12.02 |
| 4 | 154782 | 33515 | 14.34 |
| 4 | 157587 | 33048 | 13.88 |
| 4 | 158258 | 34137 | 14.28 |
| 4.5 | 74491 | 18459 | 16.41 |
| 4.5 | 74158 | 18352 | 16.38 |
| 4.5 | 74430 | 17738 | 15.78 |
| 5 | 57445 | 14862 | 17.13 |
| 5 | 57343 | 14749 | 17.03 |
| 5 | 58165 | 15021 | 17.10 |



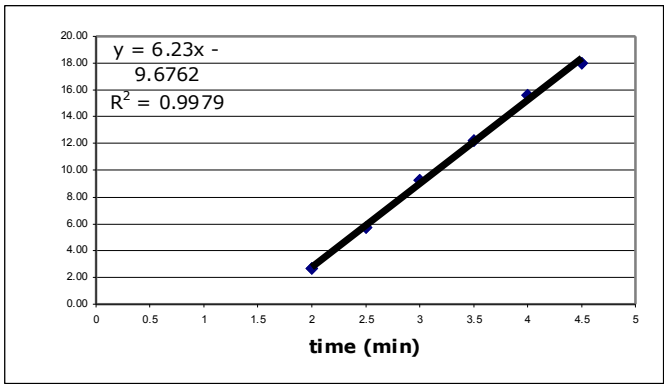

**rate = 0.0460 mM/sec**

**Run 3**

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (78 mg, 0.250 mmol, 1.5 equiv), APC (1.3 mg, 0.00375 mmol, 0.0225 equiv), dppp(O)$_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (8 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 21995 | 898 | 2.70 |
| 2 | 31435 | 1235 | 2.60 |

| | | | |
|---|---|---|---|
| 2 | 30740 | 1241 | 2.67 |
| 2.5 | 42915 | 3732 | 5.76 |
| 2.5 | 47683 | 4194 | 5.82 |
| 2.5 | 45901 | 3951 | 5.70 |
| 3 | 36456 | 5128 | 9.31 |
| 3 | 21505 | 3068 | 9.45 |
| 3 | 37688 | 5125 | 9.00 |
| 3.5 | 31164 | 5708 | 12.13 |
| 3.5 | 31931 | 5917 | 12.27 |
| 3.5 | 24672 | 4532 | 12.16 |
| 4 | 23559 | 5446 | 15.30 |
| 4 | 25441 | 6088 | 15.84 |
| 4 | 15749 | 3717 | 15.63 |
| 4.5 | 20739 | 5604 | 17.89 |
| 4.5 | 22753 | 6174 | 17.97 |
| 4.5 | 13837 | 3779 | 18.08 |
| 5 | 23279 | 7080 | 20.14 |
| 5 | 28262 | 8573 | 20.08 |
| 5 | 27780 | 8452 | 20.14 |




**rate = 0.0519 mM/sec**

**avg. rate = 4.68 x $10^{-2}$ mM/s**

**Table 4, entry 11**

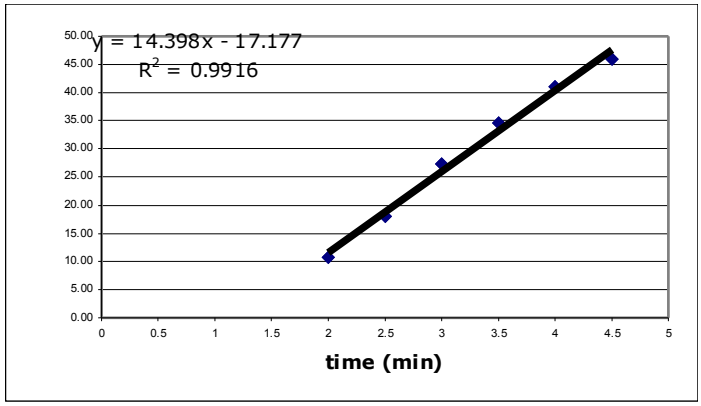
| | |
|---|---|
| $Cs^+$**5**$^-$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| APC | 5.625 mM |
| dppp$(O)_2$ | 7.5 mM |

**Run 1**

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (78 mg, 0.250 mmol, 1.5 equiv), APC (4.0 mg, 0.01125 mmol, 0.0675 equiv), dppp$(O)_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (13 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 29900 | 3012 | 10.79 |
| 2 | 31930 | 3207 | 10.76 |

| | | | |
|---|---|---|---|
| 2 | 20250 | 2027 | 10.73 |
| 2.5 | 24513 | 4125 | 18.03 |
| 2.5 | 17661 | 2932 | 17.79 |
| 2.5 | 20462 | 3533 | 18.50 |
| 3 | 33106 | 8415 | 27.24 |
| 3 | 31366 | 7928 | 27.09 |
| 3 | 31094 | 8003 | 27.58 |
| 3.5 | 32722 | 10585 | 34.66 |
| 3.5 | 32286 | 10394 | 34.50 |
| 3.5 | 20392 | 6572 | 34.54 |
| 4 | 29701 | 11342 | 40.92 |
| 4 | 29485 | 11303 | 41.08 |
| 4 | 18248 | 6968 | 40.92 |
| 4.5 | 36174 | 15585 | 46.17 |
| 4.5 | 36867 | 15698 | 45.63 |
| 4.5 | 36392 | 15672 | 46.15 |
| 5 | 23419 | 10715 | 49.03 |
| 5 | 13523 | 6097 | 48.31 |
| 5 | 13198 | 5966 | 48.44 |

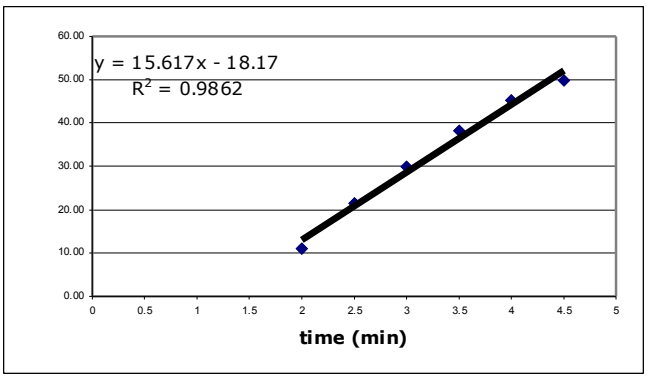



**rate = 0.120 mM/sec**

**Run 2**

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (78 mg, 0.250 mmol, 1.5 equiv), APC (4.0 mg, 0.01125 mmol, 0.0675 equiv), dppp(O)$_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (13 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 16137 | 1695 | 11.30 |
| 2 | 15140 | 1572 | 11.17 |
| 2 | 27750 | 2748 | 10.66 |
| 2.5 | 32610 | 6618 | 21.84 |
| 2.5 | 20900 | 4153 | 21.38 |
| 2.5 | 35367 | 7076 | 21.53 |
| 3 | 19796 | 5459 | 29.68 |
| 3 | 20488 | 5745 | 30.18 |
| 3 | 17231 | 4834 | 30.19 |
| 3.5 | 13030 | 4595 | 37.95 |
| 3.5 | 11177 | 3970 | 38.22 |
| 3.5 | 21990 | 7932 | 38.82 |
| 4 | 13173 | 5515 | 45.05 |
| 4 | 10985 | 4608 | 45.14 |
| 4 | 12600 | 5364 | 45.81 |
| 4.5 | 13008 | 6023 | 49.83 |
| 4.5 | 11263 | 5297 | 50.61 |
| 4.5 | 12709 | 5860 | 49.62 |



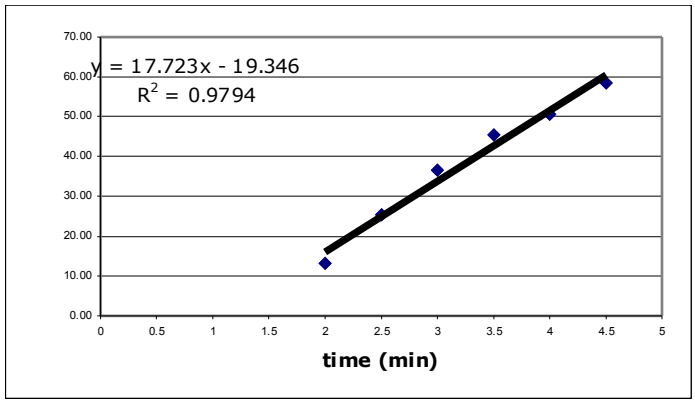
| | | | |
|---|---|---|---|
| 5 | 9175 | 4438 | 52.05 |
| 5 | 16610 | 8409 | 54.48 |
| 5 | 9464 | 4841 | 55.05 |

**rate = 0.130 mM/sec**

**Run 3**

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (78 mg, 0.250 mmol, 1.5 equiv), APC (4.0 mg, 0.01125 mmol, 0.0675 equiv), dppp(O)$_2$ (6.6 mg, 0.015 mmol, 0.090 equiv), naphthalene (13 mg), and 2-bromotoluene (20 μL, 0.16 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

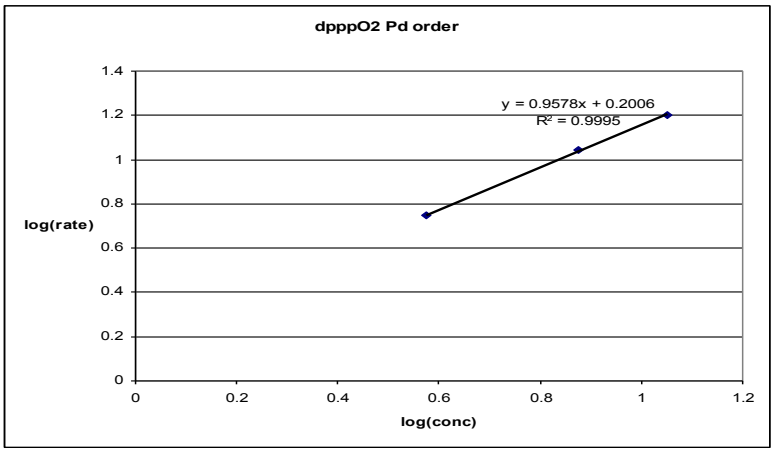
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 2 | 23509 | 2970 | 13.54 |
| 2 | 21619 | 2627 | 13.02 |
| 2 | 19721 | 2380 | 12.93 |
| 2.5 | 17261 | 4058 | 25.19 |
| 2.5 | 11917 | 2874 | 25.84 |
| 2.5 | 11538 | 2740 | 25.45 |
| 3 | 11917 | 4030 | 36.24 |
| 3 | 19322 | 6536 | 36.25 |
| 3 | 18870 | 6510 | 36.97 |
| 3.5 | 10893 | 4598 | 45.23 |
| 3.5 | 17178 | 7156 | 44.64 |
| 3.5 | 10170 | 4414 | 46.51 |
| 4 | 8982 | 4273 | 50.98 |
| 4 | 8524 | 3990 | 50.16 |
| 4 | 10521 | 4961 | 50.53 |
| 4.5 | 9121 | 4916 | 57.76 |
| 4.5 | 14204 | 7789 | 58.76 |
| 4.5 | 8402 | 4592 | 58.57 |
| 5 | 15002 | 9033 | 64.52 |
| 5 | 7814 | 4659 | 63.89 |
| 5 | 6775 | 3835 | 60.66 |




**rate = 0.148 mM/sec**

**avg. rate = 13.27 x $10^{-2}$ mM/s**

## Determination of Rate Order for Pd



**KINETICS STUDY FOR CATALYTIC CROSS-COUPLING EMPLOYING 13p AS CATALYST (Table 5)**

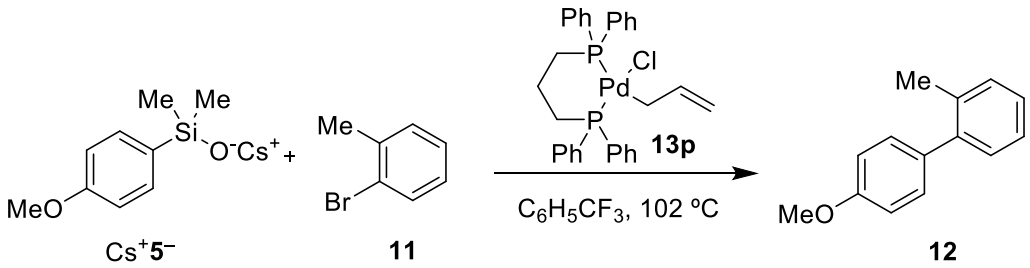



**Table 5, entry 1**

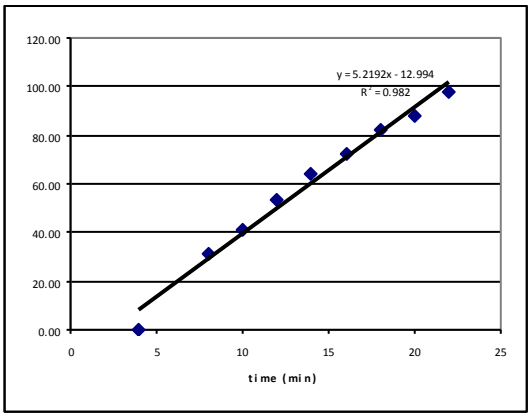
| | |
|---|---|
| $Cs^+$**5**$^-$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| **13p** | 7.5 mM |

Following General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (157 mg, 0.5 mmol, 1.5 equiv), **13p** (17.8 mg, 0.030 mmol, 0.090 equiv), naphthalene (30 mg), and 2-bromotoluene (40 μL, 0.33 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 8 | 18490 | 2337 | 31.39 |
| 8 | 17630 | 2294 | 32.31 |
| 8 | 18265 | 2292 | 31.16 |
| 10 | 21638 | 3550 | 40.74 |
| 10 | 21256 | 3596 | 42.01 |
| 10 | 21326 | 3551 | 41.35 |
| 12 | 18452 | 3891 | 52.37 |
| 12 | 17113 | 3682 | 53.43 |
| 12 | 18246 | 3951 | 53.78 |
| 14 | 17672 | 4550 | 63.94 |
| 14 | 18105 | 4647 | 63.74 |
| 14 | 18233 | 4670 | 63.61 |
| 16 | 16226 | 4765 | 72.93 |
| 16 | 16497 | 4732 | 71.23 |

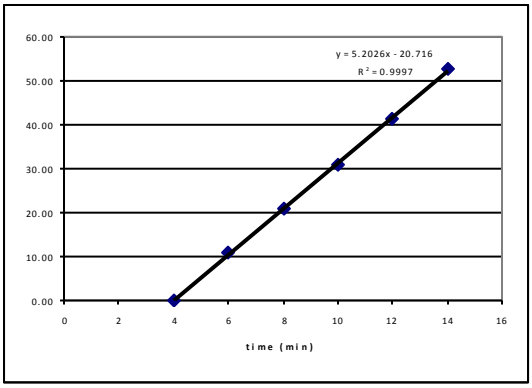
| | | | |
|---|---|---|---|
| 16 | 16086 | 4781 | 73.81 |
| 18 | 19848 | 6483 | 81.12 |
| 18 | 19963 | 6720 | 83.60 |
| 18 | 20677 | 6806 | 81.74 |
| 20 | 19753 | 6832 | 85.89 |
| 20 | 20282 | 7015 | 85.89 |
| 20 | 18993 | 7029 | 91.91 |
| 22 | 16392 | 6721 | 101.82 |
| 22 | 18035 | 6868 | 94.57 |
| 22 | 17602 | 6828 | 96.33 |




**rate = 0.0217mM/s**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 6 | 59105 | 2598 | 10.92 |
| 6 | 59105 | 2598 | 10.92 |
| 6 | 59105 | 2598 | 10.92 |
| 8 | 21886 | 1852 | 21.01 |
| 8 | 22582 | 1838 | 20.21 |
| 8 | 21493 | 1839 | 21.25 |
| 10 | 60569 | 7368 | 30.21 |
| 10 | 20146 | 2525 | 31.13 |
| 10 | 20492 | 2610 | 31.63 |
| 12 | 20602 | 3458 | 41.68 |
| 12 | 60751 | 10179 | 41.61 |
| 12 | 21260 | 3504 | 40.93 |
| 14 | 22089 | 4647 | 52.25 |
| 14 | 21337 | 4430 | 51.56 |
| 14 | 20757 | 4490 | 53.72 |

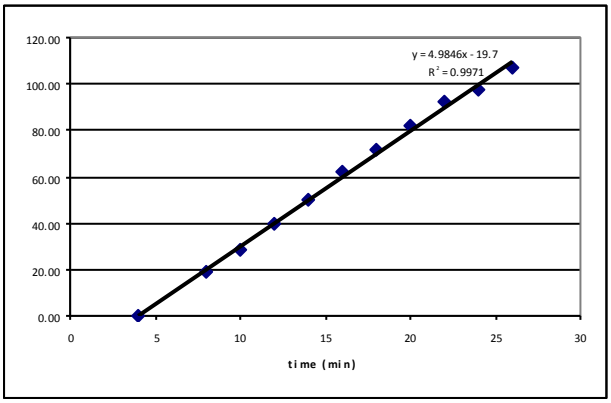



**rate = 0.0217 mM/s**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 8 | 17584 | 1216 | 18.32 |
| 8 | 18051 | 1264 | 18.55 |
| 8 | 17510 | 1247 | 18.87 |
| 10 | 17553 | 1898 | 28.64 |
| 10 | 17649 | 1914 | 28.73 |

| | | | |
|---|---|---|---|
| 10 | 17838 | 1951 | 28.97 |
| 12 | 19626 | 3021 | 40.78 |
| 12 | 19266 | 2886 | 39.68 |
| 12 | 20431 | 3064 | 39.73 |
| 14 | 20130 | 3861 | 50.81 |
| 14 | 21517 | 4203 | 51.74 |
| 14 | 21894 | 4036 | 48.83 |
| 16 | 17698 | 4165 | 62.34 |
| 16 | 18026 | 4291 | 63.06 |
| 16 | 18328 | 4278 | 61.83 |
| 18 | 19332 | 5300 | 72.62 |
| 18 | 18904 | 5129 | 71.87 |
| 18 | 20284 | 5368 | 70.10 |
| 20 | 19169 | 6107 | 84.39 |
| 20 | 19076 | 5848 | 81.21 |
| 20 | 20324 | 6204 | 80.86 |
| 22 | 19894 | 7008 | 93.31 |
| 22 | 20200 | 6740 | 88.39 |
| 22 | 19071 | 6789 | 94.30 |
| 24 | 21531 | 8266 | 101.70 |
| 24 | 22155 | 8100 | 96.85 |
| 24 | 22367 | 7947 | 94.12 |
| 26 | 18611 | 7624 | 108.52 |
| 26 | 17982 | 7392 | 108.89 |
| 26 | 20187 | 7912 | 103.82 |




**rate = 0.0208 mM/s**

**avg. rate = 2.14 x $10^{-2}$ mM/s**

**Table 5, entry 2**

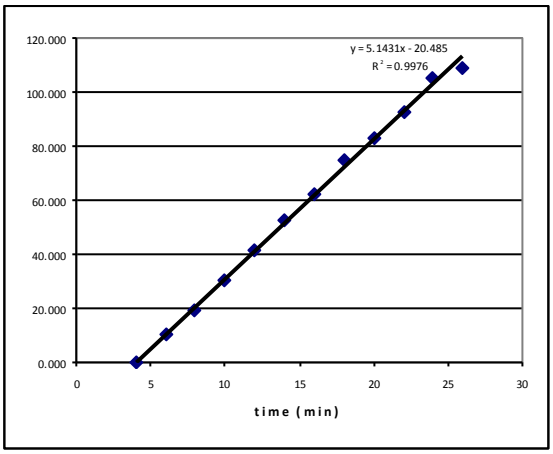
| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 250 mM |
| 2-Bromotoluene | 83 mM |
| **13p** | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (157 mg, 0.5 mmol, 3.0 equiv), **13p** (8.9 mg, 0.015 mmol, 0.09 equiv), naphthalene (20 mg), and 2-bromotoluene (20 μL, 0.165 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |

| | | | |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 6 | 71792 | 4368 | 10.073 |
| 6 | 23811 | 1513 | 10.520 |
| 6 | 71792 | 4368 | 10.073 |
| 8 | 21593 | 2485 | 19.053 |
| 8 | 41199 | 4800 | 19.289 |
| 8 | 20477 | 2280 | 18.434 |
| 10 | 20261 | 3933 | 32.138 |
| 10 | 22013 | 4017 | 30.212 |
| 10 | 22731 | 3977 | 28.967 |
| 12 | 21634 | 5350 | 40.943 |
| 12 | 21301 | 5323 | 41.373 |
| 12 | 20941 | 5267 | 41.641 |
| 14 | 20378 | 6436 | 52.289 |
| 14 | 20084 | 6434 | 53.038 |
| 14 | 20448 | 6342 | 51.349 |
| 16 | 20730 | 7625 | 60.898 |
| 16 | 19719 | 7579 | 63.634 |
| 16 | 60491 | 22648 | 61.987 |
| 18 | 19098 | 8753 | 75.880 |
| 18 | 20003 | 8896 | 73.631 |
| 18 | 19848 | 8964 | 74.773 |
| 20 | 22157 | 10669 | 79.721 |
| 20 | 20860 | 10270 | 81.511 |
| 20 | 19605 | 10463 | 88.359 |
| 22 | 19430 | 10461 | 89.137 |
| 22 | 18468 | 10198 | 91.423 |
| 22 | 17190 | 10130 | 97.565 |
| 24 | 19248 | 11421 | 98.238 |
| 24 | 16403 | 11240 | 113.449 |
| 24 | 18173 | 11398 | 103.839 |
| 26 | 24665 | 15513 | 104.129 |
| 26 | 22319 | 14762 | 109.504 |
| 26 | 21984 | 14971 | 112.747 |

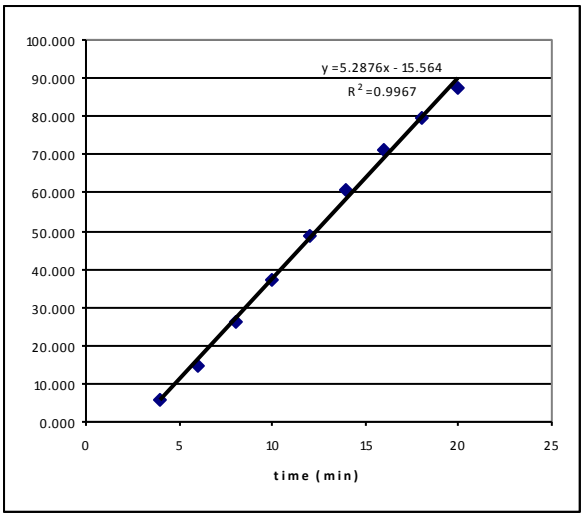



**rate = 0.0428mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 69333 | 2524 | 6.027 |
| 4 | 68716 | 2316 | 5.580 |
| 4 | 69019 | 2365 | 5.673 |
| 6 | 80187 | 7056 | 14.568 |
| 6 | 80633 | 7082 | 14.541 |
| 6 | 81031 | 7097 | 14.500 |
| 8 | 86604 | 13659 | 26.112 |
| 8 | 86955 | 13711 | 26.106 |
| 8 | 86936 | 13715 | 26.119 |
| 10 | 84746 | 19112 | 37.338 |
| 10 | 84239 | 19101 | 37.541 |

| | | | |
|---|---|---|---|
| 10 | 85286 | 19143 | 37.161 |
| 12 | 66306 | 19254 | 48.076 |
| 12 | 65443 | 19332 | 48.907 |
| 12 | 65808 | 19267 | 48.472 |
| 14 | 71468 | 26065 | 60.382 |
| 14 | 72004 | 26270 | 60.404 |
| 14 | 70381 | 26147 | 61.507 |
| 16 | 85199 | 36446 | 70.823 |
| 16 | 85120 | 36863 | 71.700 |
| 16 | 85462 | 36644 | 70.989 |
| 18 | 70584 | 33964 | 79.666 |
| 18 | 69372 | 33486 | 79.917 |
| 18 | 70209 | 33585 | 79.198 |
| 20 | 69459 | 36570 | 87.168 |
| 20 | 69805 | 36640 | 86.902 |
| 20 | 68859 | 36419 | 87.564 |

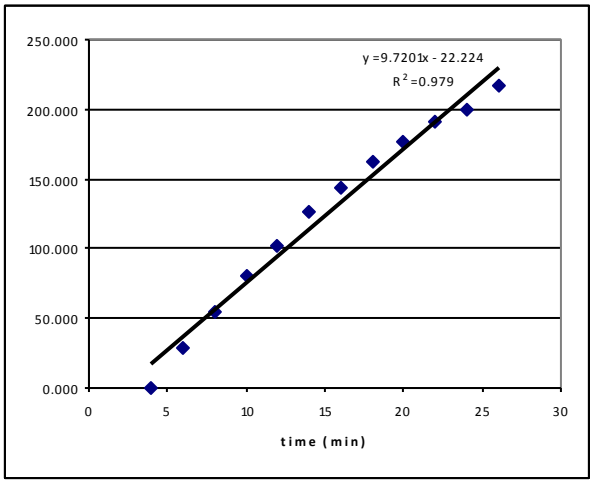



**rate = 0.0440mM/sec**

**Run 3**

The following experiment was run on 4-mL scale.

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.0000 |
| 4 | 1 | 0 | 0.0000 |
| 4 | 1 | 0 | 0.0000 |
| 6 | 23725 | 2780 | 29.0997 |
| 6 | 26188 | 2897 | 27.4724 |
| 6 | 49079 | 5442 | 27.5368 |
| 8 | 80720 | 17163 | 52.8035 |
| 8 | 27036 | 5725 | 52.5876 |
| 8 | 24727 | 5769 | 57.9401 |
| 10 | 21969 | 7324 | 82.7920 |
| 10 | 23559 | 7348 | 77.4573 |
| 10 | 21893 | 7323 | 83.0680 |
| 12 | 24522 | 10116 | 102.4479 |
| 12 | 73730 | 30164 | 101.6003 |
| 12 | 48306 | 20032 | 102.9849 |
| 14 | 49763 | 25673 | 128.1210 |
| 14 | 25630 | 13108 | 127.0100 |
| 14 | 26264 | 13157 | 124.4074 |
| 16 | 24301 | 13941 | 142.4689 |
| 16 | 23826 | 13625 | 142.0155 |
| 16 | 46992 | 27652 | 146.1345 |
| 18 | 22282 | 14850 | 165.5094 |
| 18 | 22819 | 14869 | 161.8212 |
| 18 | 68825 | 44438 | 160.3462 |
| 20 | 24707 | 17578 | 176.6850 |
| 20 | 24882 | 17659 | 176.2508 |
| 20 | 48088 | 34487 | 178.1021 |



| | | | |
|---|---|---|---|
| 22 | 21408 | 16163 | 187.4978 |
| 22 | 39795 | 31589 | 197.1322 |
| 22 | 63752 | 48737 | 189.8520 |
| 24 | 24484 | 19503 | 197.8196 |
| 24 | 23741 | 19351 | 202.4206 |
| 24 | 24119 | 19271 | 198.4245 |
| 26 | 17978 | 16149 | 223.0769 |
| 26 | 18905 | 16418 | 215.6720 |
| 26 | 19257 | 16304 | 210.2596 |

**rate = 0.0405mM/sec**

**avg. rate = 4.24 x $10^{-2}$ mM/s**

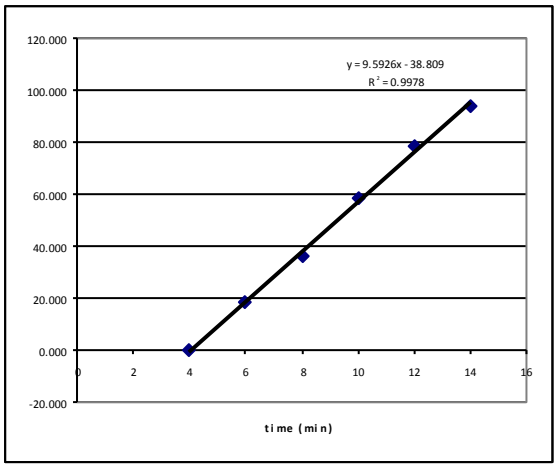
**Table 5, entry 3**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 500 mM |
| 2-Bromotoluene | 83 mM |
| **13p** | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (314 mg, 1.00 mmol, 6.0 equiv), **13p** (8.9 mg, 0.015 mmol, 0.09 equiv), naphthalene (20 mg), and 2-bromotoluene (20 μL, 0.165 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 6 | 27000 | 2973 | 18.230 |
| 6 | 27208 | 3008 | 18.304 |
| 6 | 83854 | 8999 | 17.768 |
| 8 | 25679 | 5652 | 36.440 |
| 8 | 25113 | 5500 | 36.260 |
| 8 | 25358 | 5526 | 36.079 |
| 10 | 21088 | 7494 | 58.835 |
| 10 | 44260 | 15460 | 57.831 |
| 10 | 21770 | 7833 | 59.570 |
| 12 | 25339 | 11923 | 77.903 |
| 12 | 25298 | 12059 | 78.919 |
| 12 | 25123 | 11915 | 78.520 |
| 14 | 24430 | 13402 | 90.825 |
| 14 | 22134 | 13453 | 100.628 |

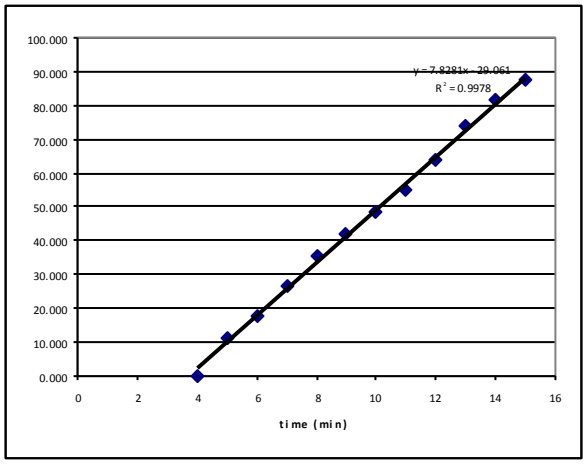


| | | | |
|---|---|---|---|
| 14 | 25183 | 13586 | 89.319 |

**rate = 0.0799mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 5 | 28589 | 1847 | 10.696 |
| 5 | 27608 | 1890 | 11.334 |
| 5 | 27011 | 1870 | 11.462 |
| 6 | 24997 | 2666 | 17.658 |
| 6 | 25433 | 2705 | 17.609 |
| 6 | 23937 | 2641 | 18.267 |
| 7 | 26362 | 4428 | 27.809 |
| 7 | 28165 | 4436 | 26.076 |
| 7 | 29537 | 4536 | 25.425 |
| 8 | 23370 | 5224 | 37.009 |
| 8 | 24602 | 5059 | 34.045 |
| 8 | 23599 | 5166 | 36.243 |
| 9 | 110358 | 28212 | 42.324 |
| 9 | 37001 | 9382 | 41.980 |
| 9 | 37888 | 9504 | 41.530 |
| 10 | 89093 | 26423 | 49.102 |
| 10 | 89093 | 26423 | 49.102 |
| 10 | 6464 | 1870 | 47.896 |
| 11 | 70699 | 24069 | 56.364 |
| 11 | 70442 | 23350 | 54.880 |
| 11 | 106538 | 34983 | 54.364 |
| 12 | 81883 | 31463 | 63.616 |
| 12 | 82641 | 32033 | 64.174 |
| 12 | 81324 | 31414 | 63.953 |
| 13 | 76733 | 33901 | 73.146 |
| 13 | 77632 | 34516 | 73.610 |
| 13 | 51955 | 23394 | 74.548 |
| 14 | 83445 | 40740 | 80.831 |
| 14 | 82683 | 40938 | 81.973 |
| 14 | 84233 | 41408 | 81.388 |
| 15 | 81707 | 43132 | 87.398 |
| 15 | 81325 | 43097 | 87.737 |
| 15 | 81967 | 43296 | 87.452 |

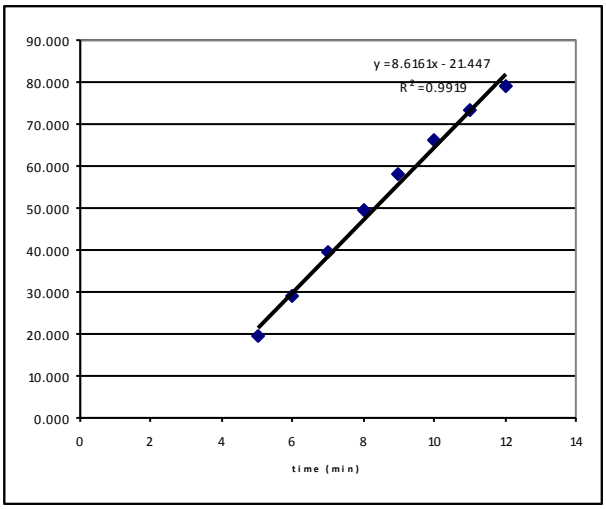



**rate = 0.0652mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 5 | 81116 | 9674 | 19.745 |
| 5 | 80889 | 9595 | 19.639 |
| 5 | 27440 | 3264 | 19.694 |

| | | | |
|---|---|---|---|
| 6 | 62869 | 11063 | 29.134 |
| 6 | 65573 | 11402 | 28.788 |
| 6 | 64751 | 11462 | 29.307 |
| 7 | 62006 | 14973 | 39.979 |
| 7 | 61578 | 14844 | 39.910 |
| 7 | 21474 | 5019 | 38.696 |
| 8 | 62712 | 18955 | 50.042 |
| 8 | 63437 | 18775 | 49.000 |
| 8 | 62921 | 18928 | 49.804 |
| 9 | 66144 | 23004 | 57.580 |
| 9 | 64996 | 22999 | 58.584 |
| 9 | 66433 | 23232 | 57.898 |
| 10 | 79458 | 31635 | 65.916 |
| 10 | 78068 | 31443 | 66.682 |
| 10 | 78489 | 31438 | 66.314 |
| 11 | 64921 | 28745 | 73.305 |
| 11 | 65823 | 29373 | 73.880 |
| 11 | 66337 | 28962 | 72.282 |
| 12 | 76937 | 36014 | 77.499 |
| 12 | 76405 | 36659 | 79.436 |
| 12 | 75792 | 36548 | 79.836 |




**rate = 0.0718mM/sec**

**avg. rate = 7.23 x $10^{-2}$ mM/s**

**Table 5, entry 4**

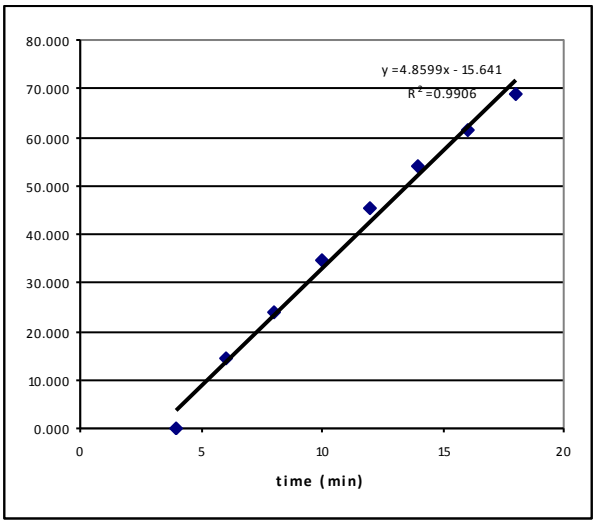
| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 250 mM |
| 2-Bromotoluene | 42 mM |
| **13p** | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (157 mg, 0.5 mmol, 6.0 equiv), **13p** (8.9 mg, 0.015 mmol, 0.18 equiv), naphthalene (20 mg), and 2-bromotoluene (10 μL, 0.083 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 6 | 20804 | 1824 | 14.516 |
| 6 | 21622 | 1767 | 13.530 |
| 6 | 19219 | 1784 | 15.368 |

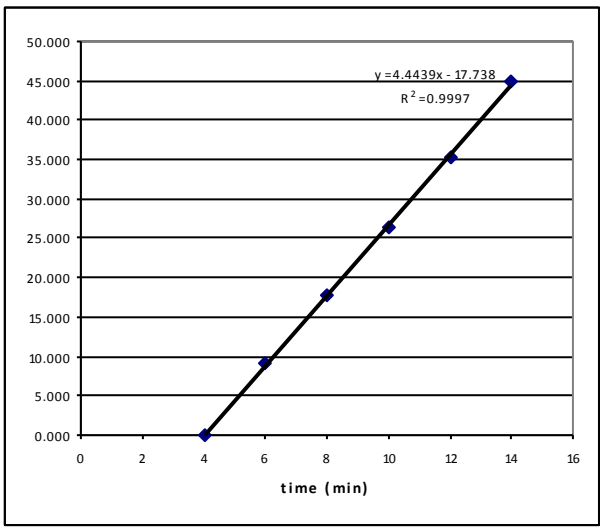
| | | | |
|---|---|---|---|
| 8 | 19327 | 2883 | 24.697 |
| 8 | 20651 | 2951 | 23.658 |
| 8 | 20651 | 2951 | 23.658 |
| 10 | 18777 | 3815 | 33.638 |
| 10 | 17560 | 3808 | 35.903 |
| 10 | 18331 | 3843 | 34.709 |
| 12 | 20748 | 5711 | 45.572 |
| 12 | 21150 | 5850 | 45.794 |
| 12 | 21725 | 5797 | 44.178 |
| 14 | 22320 | 7291 | 54.082 |
| 14 | 22759 | 7353 | 53.490 |
| 14 | 22161 | 7224 | 53.969 |
| 16 | 19266 | 7155 | 61.486 |
| 16 | 19320 | 7142 | 61.203 |
| 16 | 60491 | 22648 | 61.987 |
| 18 | 24273 | 10059 | 68.610 |
| 18 | 23272 | 9671 | 68.801 |
| 18 | 23441 | 9735 | 68.757 |




**rate = 0.0404mM/sec**

**Run 2**

| Time | area, std | area, **22** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 6 | 28488 | 1598 | 9.287 |
| 6 | 29122 | 1601 | 9.102 |
| 6 | 29436 | 1633 | 9.185 |
| 8 | 23457 | 2681 | 18.923 |
| 8 | 26700 | 2787 | 17.282 |
| 8 | 26638 | 2766 | 17.191 |
| 10 | 18932 | 3004 | 26.270 |
| 10 | 19140 | 3177 | 27.481 |
| 10 | 59077 | 9153 | 25.651 |
| 12 | 26697 | 5592 | 34.679 |
| 12 | 26428 | 5849 | 36.642 |
| 12 | 28159 | 5845 | 34.366 |
| 14 | 23842 | 6719 | 46.657 |
| 14 | 25507 | 6656 | 43.203 |
| 14 | 24744 | 6683 | 44.716 |

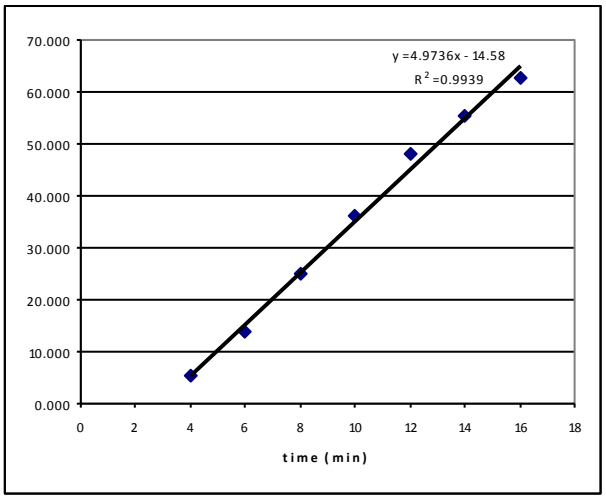



**rate = 0.0370mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 109341 | 3403 | 5.153 |
| 4 | 110412 | 3459 | 5.187 |
| 4 | 109974 | 3487 | 5.250 |

| | | | |
|---|---|---|---|
| 6 | 81721 | 6621 | 13.414 |
| 6 | 27468 | 2262 | 13.634 |
| 6 | 25362 | 2163 | 14.120 |
| 8 | 55925 | 8424 | 24.939 |
| 8 | 54871 | 8265 | 24.938 |
| 8 | 52712 | 8142 | 25.573 |
| 10 | 85763 | 18688 | 36.076 |
| 10 | 29334 | 6354 | 35.862 |
| 10 | 86663 | 18912 | 36.130 |
| 12 | 52735 | 14896 | 46.766 |
| 12 | 25539 | 7523 | 48.769 |
| 12 | 25175 | 7375 | 48.501 |
| 14 | 81858 | 26918 | 54.443 |
| 14 | 80594 | 26759 | 54.970 |
| 14 | 51746 | 17632 | 56.414 |
| 16 | 24660 | 9262 | 62.183 |
| 16 | 75462 | 28746 | 63.068 |
| 16 | 76149 | 28926 | 62.890 |




**rate = 0.0414mM/sec**

**avg. rate = 3.96 x $10^{-2}$ mM/s**

**Table 5, entry 5**

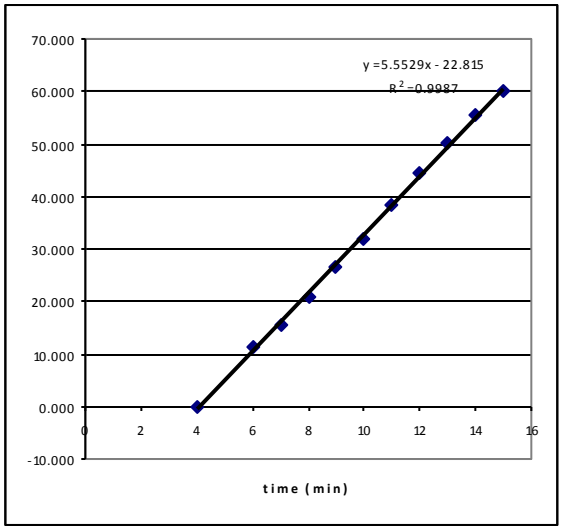
| | |
|---|---|
| $Cs^+$**5**$^-$ | 250 mM |
| 2-Bromotoluene | 167 mM |
| **13p** | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^+$**5**$^-$ (157 mg, 0.5 mmol, 1.5 equiv), **13p** (8.9 mg, 0.015 mmol, 0.045 equiv), naphthalene (20 mg), and 2-bromotoluene (30 μL, 0.33 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (2 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 6 | 23052 | 1562 | 11.218 |
| 6 | 41547 | 2892 | 11.524 |
| 6 | 23052 | 1562 | 11.218 |

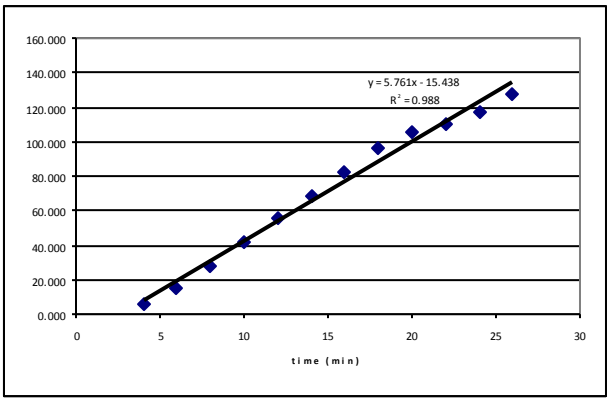
| | | | |
|---|---|---|---|
| 7 | 32819 | 3149 | 15.886 |
| 7 | 33630 | 3110 | 15.311 |
| 7 | 33668 | 3104 | 15.264 |
| 8 | 22289 | 2825 | 20.984 |
| 8 | 22709 | 2811 | 20.494 |
| 8 | 21979 | 2778 | 20.926 |
| 9 | 29192 | 4530 | 25.692 |
| 9 | 29366 | 4544 | 25.618 |
| 9 | 26565 | 4567 | 28.463 |
| 10 | 24633 | 4796 | 32.234 |
| 10 | 25102 | 4843 | 31.942 |
| 10 | 25776 | 4842 | 31.101 |
| 11 | 23817 | 5512 | 38.316 |
| 11 | 25099 | 5567 | 36.722 |
| 11 | 22710 | 5498 | 40.082 |
| 12 | 21768 | 5776 | 43.931 |
| 12 | 21317 | 5757 | 44.713 |
| 12 | 22010 | 5924 | 44.561 |
| 13 | 22132 | 6722 | 50.285 |
| 13 | 21882 | 6686 | 50.587 |
| 13 | 21957 | 6615 | 49.879 |
| 14 | 22268 | 7618 | 56.639 |
| 14 | 23367 | 7705 | 54.592 |
| 14 | 23605 | 7843 | 55.009 |
| 15 | 32159 | 11377 | 58.571 |
| 15 | 31871 | 11783 | 61.210 |
| 15 | 32005 | 11588 | 59.945 |




**rate = 0.0463mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 114908 | 4146 | 5.974 |
| 4 | 117524 | 4183 | 5.893 |
| 4 | 69019 | 2365 | 5.673 |
| 6 | 31447 | 2709 | 14.262 |
| 6 | 60359 | 5292 | 14.516 |
| 6 | 57104 | 5137 | 14.894 |
| 8 | 50912 | 8641 | 28.100 |
| 8 | 27162 | 4599 | 28.032 |
| 8 | 52381 | 8644 | 27.321 |
| 10 | 27656 | 7053 | 42.222 |
| 10 | 87542 | 21709 | 41.057 |
| 10 | 28407 | 7266 | 42.348 |
| 12 | 71771 | 23913 | 55.163 |
| 12 | 70050 | 23776 | 56.194 |
| 12 | 108610 | 35714 | 54.441 |
| 14 | 57591 | 23306 | 67.000 |
| 14 | 37642 | 15553 | 68.407 |
| 14 | 38130 | 15822 | 68.699 |

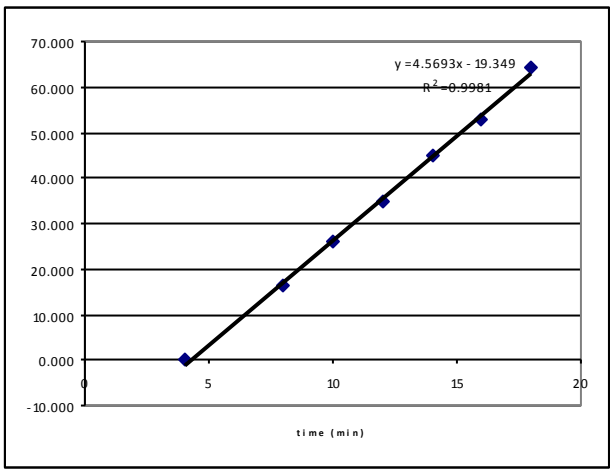


| | | | |
|---|---|---|---|
| 16 | 55365 | 27306 | 81.655 |
| 16 | 83031 | 40298 | 80.353 |
| 16 | 53149 | 27034 | 84.212 |
| 18 | 36762 | 21743 | 97.922 |
| 18 | 112486 | 63249 | 93.092 |
| 18 | 35780 | 20957 | 96.972 |
| 20 | 80587 | 50163 | 103.057 |
| 20 | 51165 | 33181 | 107.368 |
| 20 | 52487 | 33274 | 104.957 |
| 22 | 110745 | 71923 | 107.523 |
| 22 | 72892 | 48804 | 110.850 |
| 22 | 75554 | 50402 | 110.446 |
| 24 | 73933 | 51790 | 115.976 |
| 24 | 72631 | 51624 | 117.676 |
| 24 | 25090 | 18022 | 118.922 |
| 26 | 106379 | 80124 | 124.700 |
| 26 | 34658 | 28083 | 134.153 |
| 26 | 107205 | 81015 | 125.115 |

**rate = 0.0480mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 4 | 1 | 0 | 0.000 |
| 8 | 31563 | 3057 | 16.035 |
| 8 | 30150 | 3087 | 16.952 |
| 8 | 30435 | 2948 | 16.037 |
| 10 | 26857 | 4217 | 25.996 |
| 10 | 25500 | 4225 | 27.431 |
| 10 | 28972 | 4388 | 25.075 |
| 12 | 27659 | 5788 | 34.646 |
| 12 | 28349 | 5852 | 34.176 |
| 12 | 26804 | 5818 | 35.936 |
| 14 | 28425 | 7646 | 44.534 |
| 14 | 26536 | 7499 | 46.787 |
| 14 | 29275 | 7599 | 42.975 |
| 16 | 27074 | 8667 | 53.000 |
| 16 | 27871 | 8849 | 52.565 |
| 16 | 27522 | 8716 | 52.432 |
| 18 | 29336 | 11855 | 66.905 |
| 18 | 30154 | 11293 | 62.005 |
| 18 | 30230 | 11724 | 64.209 |




**rate = 0.0381mM/sec**

**avg. rate = 4.41 x $10^{-2}$ mM/s**

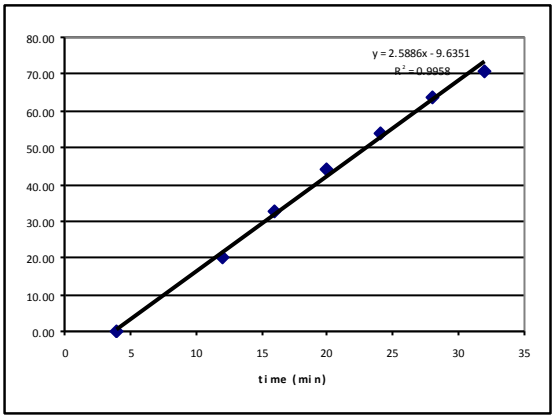
**Table 5, entry 6**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| **13p** | 3.75 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (157 mg, 0.5 mmol, 1.5 equiv), **13p** (8.9 mg, 0.015 mmol, 0.045 equiv), naphthalene (30 mg), and 2-bromotoluene (40 μL, 0.33 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 12 | 66000 | 5223 | 19.65 |
| 12 | 23443 | 1933 | 20.48 |
| 12 | 66700 | 5298 | 19.73 |
| 16 | 35606 | 4693 | 32.73 |
| 16 | 35095 | 4638 | 32.82 |
| 16 | 69727 | 9063 | 32.28 |
| 20 | 23098 | 4117 | 44.26 |
| 20 | 22163 | 3940 | 44.15 |
| 20 | 69286 | 12224 | 43.81 |
| 24 | 69279 | 14998 | 53.76 |
| 24 | 68733 | 14942 | 53.99 |
| 24 | 45583 | 9865 | 53.75 |
| 28 | 57839 | 14370 | 61.70 |
| 28 | 19275 | 4944 | 63.70 |
| 28 | 19041 | 4979 | 64.94 |
| 32 | 18547 | 5320 | 71.23 |
| 32 | 19432 | 5486 | 70.11 |
| 32 | 36814 | 10482 | 70.71 |

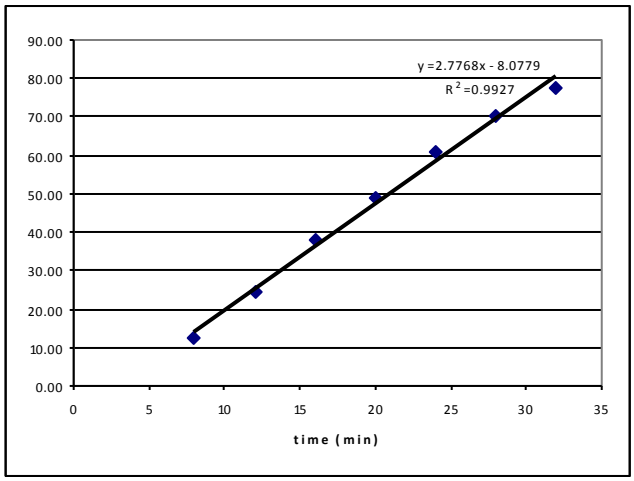



**rate = 0.0108mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 8 | 47352 | 2334 | 12.24 |
| 8 | 47352 | 2334 | 12.24 |
| 8 | 47352 | 2334 | 12.24 |
| 12 | 45702 | 4240 | 23.04 |
| 12 | 15935 | 1592 | 24.81 |
| 12 | 16058 | 1629 | 25.19 |

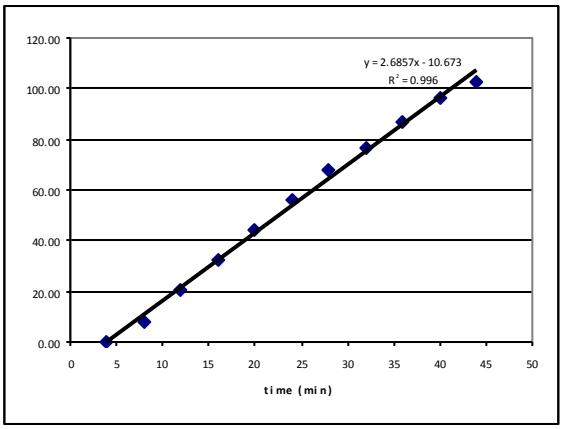
| | | | |
|---|---|---|---|
| 16 | 56991 | 8473 | 36.92 |
| 16 | 38113 | 5912 | 38.52 |
| 16 | 57556 | 8802 | 37.98 |
| 20 | 18184 | 3441 | 46.99 |
| 20 | 17173 | 3428 | 49.57 |
| 20 | 16875 | 3419 | 50.32 |
| 24 | 16397 | 3971 | 60.14 |
| 24 | 15371 | 3873 | 62.57 |
| 24 | 16185 | 3941 | 60.47 |
| 28 | 16984 | 4914 | 71.85 |
| 28 | 18505 | 5162 | 69.28 |
| 28 | 17864 | 4995 | 69.44 |
| 32 | 15392 | 4926 | 79.48 |
| 32 | 16258 | 5031 | 76.85 |
| 32 | 16390 | 5046 | 76.46 |




**rate = 0.0116mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 8 | 26260 | 837 | 7.92 |
| 8 | 27112 | 833 | 7.63 |
| 8 | 28326 | 899 | 7.88 |
| 12 | 22079 | 1800 | 20.25 |
| 12 | 21845 | 1863 | 21.18 |
| 12 | 21764 | 1766 | 20.15 |
| 16 | 27837 | 3496 | 31.19 |
| 16 | 26248 | 3586 | 33.93 |
| 16 | 27872 | 3527 | 31.43 |
| 20 | 20852 | 3687 | 43.91 |
| 20 | 21060 | 3713 | 43.78 |
| 20 | 19427 | 3496 | 44.69 |
| 24 | 21226 | 4741 | 55.47 |
| 24 | 20013 | 4641 | 57.59 |
| 24 | 20628 | 4526 | 54.49 |
| 28 | 22412 | 6327 | 70.11 |
| 28 | 23740 | 6301 | 65.91 |
| 28 | 22789 | 6208 | 67.65 |
| 32 | 19803 | 5979 | 74.98 |
| 32 | 18854 | 5848 | 77.03 |
| 32 | 18288 | 5780 | 78.49 |
| 36 | 24216 | 8616 | 88.36 |
| 36 | 23980 | 8411 | 87.11 |
| 36 | 24873 | 8613 | 86.00 |
| 40 | 19193 | 7095 | 91.80 |
| 40 | 17719 | 7241 | 101.49 |
| 40 | 18765 | 7212 | 95.45 |




**rate = 0.0112mM/sec**

**avg. rate = 1.12 x $10^{-2}$ mM/s**

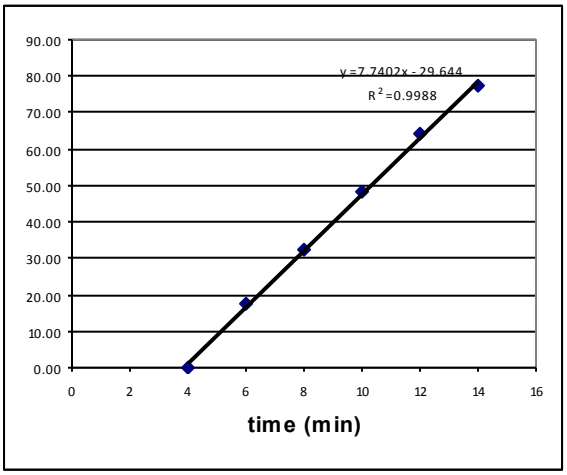
**Table 5, entry 7**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| **13p** | 11.25 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (157 mg, 0.5 mmol, 1.5 equiv), **13p** (26.7 mg, 0.045 mmol, 0.135 equiv), naphthalene (30 mg), and 2-bromotoluene (40 μL, 0.33 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 6 | 37067 | 2630 | 17.62 |
| 6 | 54886 | 3955 | 17.90 |
| 6 | 54886 | 3955 | 17.90 |
| 8 | 51368 | 6725 | 32.51 |
| 8 | 52487 | 6856 | 32.44 |
| 8 | 18021 | 2372 | 32.69 |
| 10 | 15923 | 3207 | 50.02 |
| 10 | 50250 | 9443 | 46.67 |
| 10 | 50719 | 9830 | 48.13 |
| 12 | 19392 | 5136 | 65.77 |
| 12 | 61708 | 15552 | 62.59 |
| 12 | 21074 | 5390 | 63.52 |
| 14 | 57702 | 17758 | 76.43 |
| 14 | 57886 | 17797 | 76.35 |
| 14 | 37153 | 11937 | 79.79 |

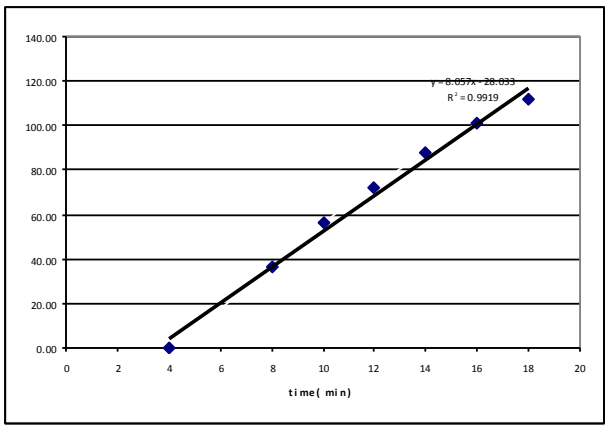



**rate = 0.0323mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 8 | 15755 | 2307 | 36.36 |
| 8 | 16058 | 2320 | 35.88 |
| 8 | 29975 | 4511 | 37.37 |
| 10 | 15102 | 3578 | 58.84 |
| 10 | 51299 | 10912 | 52.83 |

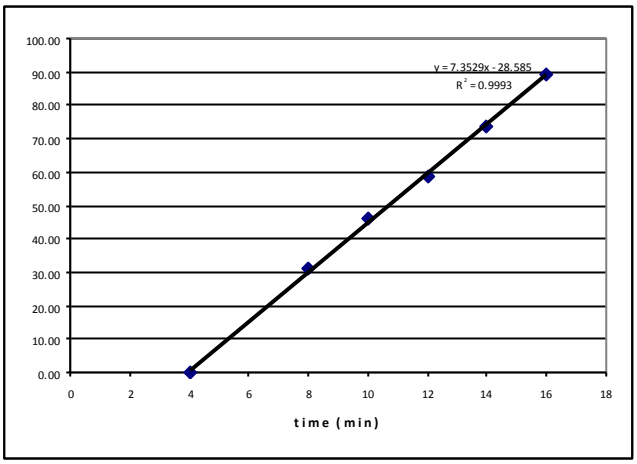
| | | | |
|---|---|---|---|
| 10 | 16213 | 3699 | 56.66 |
| 12 | 16990 | 4939 | 72.19 |
| 12 | 52319 | 15117 | 71.76 |
| 12 | 18162 | 5204 | 71.16 |
| 14 | 18237 | 6322 | 86.09 |
| 14 | 17769 | 6305 | 88.12 |
| 14 | 17089 | 6082 | 88.39 |
| 16 | 17139 | 6918 | 100.24 |
| 16 | 16810 | 6947 | 102.63 |
| 16 | 17785 | 7107 | 99.24 |
| 18 | 54511 | 24372 | 111.03 |
| 18 | 18866 | 8622 | 113.50 |
| 18 | 19631 | 8779 | 111.06 |




**rate = 0. 0336mM/sec**

**Run 3**

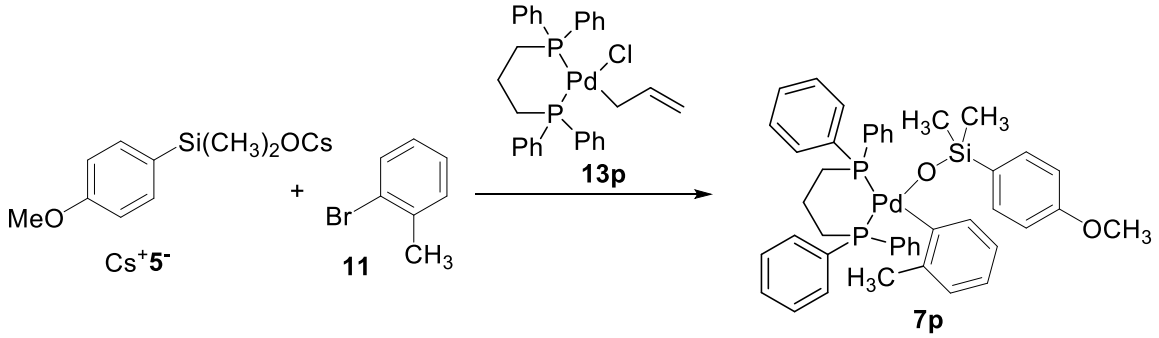
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 8 | 17233 | 2180 | 31.42 |
| 8 | 16536 | 2027 | 30.44 |
| 8 | 15126 | 1905 | 31.28 |
| 10 | 16225 | 3026 | 46.32 |
| 10 | 16745 | 3091 | 45.84 |
| 10 | 16102 | 3009 | 46.41 |
| 12 | 17341 | 4164 | 59.63 |
| 12 | 18159 | 4221 | 57.73 |
| 12 | 35062 | 8411 | 59.57 |
| 14 | 17471 | 5302 | 75.37 |
| 14 | 17399 | 5278 | 75.33 |
| 14 | 17406 | 4936 | 70.42 |
| 16 | 15316 | 5470 | 88.69 |
| 16 | 15668 | 5643 | 89.44 |
| 16 | 15869 | 5709 | 89.34 |




**rate = 0.0307mM/sec**

**avg. rate = 3.22 x $10^{-2}$ mM/s**

***In situ* detection of 7p by $^{31}$P NMR (Scheme 3)**




In a drybox, naphthalene (5 mg), **13p** (4.5 mg, 0.0075 mmol, 0.09 equiv), and 2-bromotoluene (10 μL, 0.082 mmol, 1.0 equiv) were dissolved in dry toluene-d$^8$ (1.0 mL) at room temperature in a 5mm NMR tube. To this solution was added $Cs^+$**5**$^-$ (40 mg, 0.125 mmol, 1.5 equiv) and the tube sealed with a septum. The tube was removed from the drybox, and was placed in a 90 $^0$C oil bath for 30 min. The tube was removed from the bath and analyzed by $^{31}$P NMR spectroscopy. A 100 μL aliquot of the solution was injected into 500 μL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride. This yellow solution was diluted with 3.0 mL of ether and the organic phase was filtered through a 0.5 x 1.0 cm plug of silica gel. The filtrate was analyzed by GC to determine reaction conversion.

$^{31}$P NMR (202 MHz, $C_6H_5CH_3$):

31.9 (s, dppp(O)$_2$), 21.6 (d, $J$ = 48.6), -9.9 (d, $J$ = 48.8)

**GC analysis**

| area, std | area, **12** | conv, μmol | conversion = 37 % |
|---|---|---|---|
| 238889 | 173007 | 29.98 | |

**KINETICS STUDY FOR CATALYTIC CROSS-COUPLING EMPLOYING ARYLSILANOLATE COMPLEX 7p AS CATALYST (Table 6)**

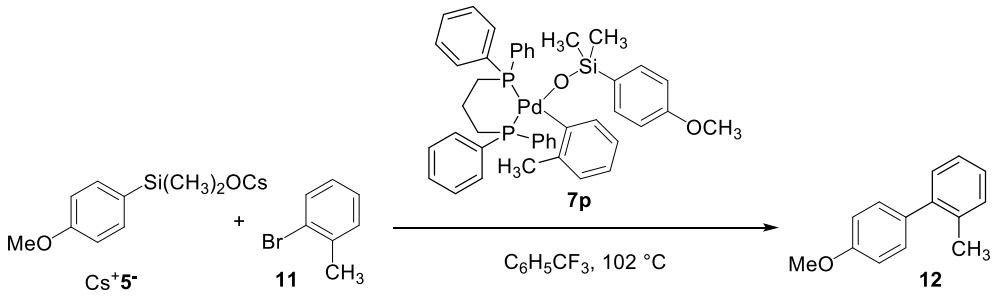


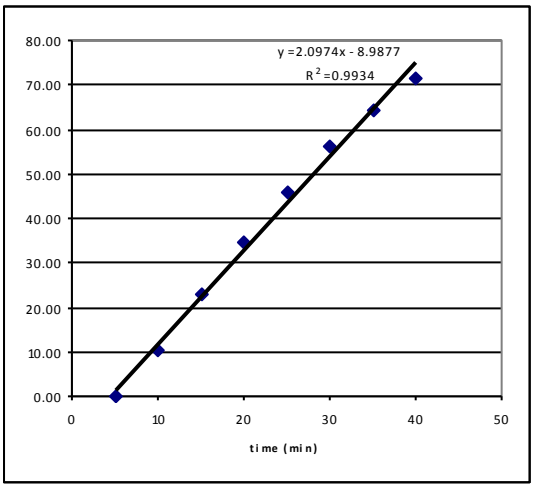

**Table 6, entry 1**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| **7p** | 1.875 mM |

Following General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (157 mg, 0.5 mmol, 1.5 equiv), **7p** (6.8 mg, 0.0075 mmol, 0.0225 equiv), naphthalene (30 mg), and 2-bromotoluene (40 μL, 0.33 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 5 | 1 | 0 | 0.00 |
| 5 | 1 | 0 | 0.00 |
| 5 | 1 | 0 | 0.00 |
| 10 | 26457 | 1108 | 10.40 |
| 10 | 26842 | 1072 | 9.92 |
| 10 | 26226 | 1138 | 10.78 |
| 15 | 23287 | 2118 | 22.59 |
| 15 | 23089 | 2107 | 22.66 |
| 15 | 23808 | 2250 | 23.47 |
| 20 | 30436 | 4163 | 33.97 |
| 20 | 29422 | 4279 | 36.12 |
| 20 | 32368 | 4351 | 33.38 |
| 25 | 26012 | 4814 | 45.96 |
| 25 | 25628 | 4716 | 45.70 |
| 25 | 25354 | 4745 | 46.48 |
| 30 | 23179 | 5272 | 56.48 |
| 30 | 22009 | 4835 | 54.56 |
| 30 | 22622 | 5214 | 57.24 |

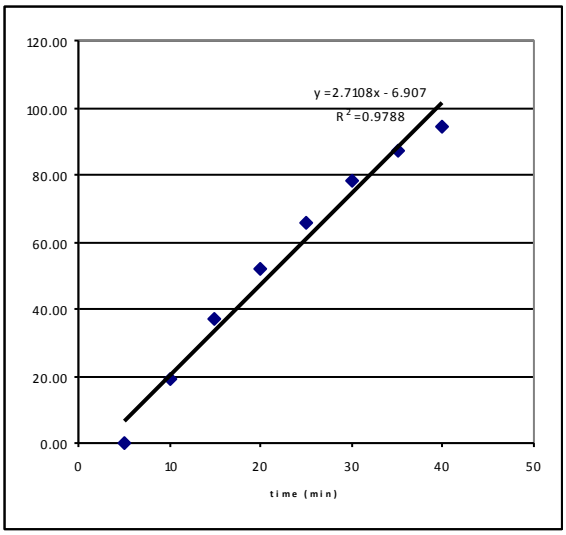


| | | | |
|---|---|---|---|
| 35 | 23295 | 6174 | 65.82 |
| 35 | 23414 | 6001 | 63.65 |
| 35 | 23176 | 5907 | 63.30 |
| 40 | 25007 | 7020 | 69.71 |
| 40 | 23514 | 6835 | 72.19 |
| 40 | 24481 | 7150 | 72.53 |

**rate = 0.00875 mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 5 | 1 | 0 | 0.00 |
| 5 | 1 | 0 | 0.00 |
| 5 | 1 | 0 | 0.00 |
| 10 | 22356 | 1510 | 16.77 |
| 10 | 29319 | 2771 | 23.47 |
| 10 | 22356 | 1510 | 16.77 |
| 15 | 25341 | 3642 | 35.69 |
| 15 | 23808 | 3576 | 37.30 |
| 15 | 22213 | 3331 | 37.24 |
| 20 | 25891 | 5444 | 52.22 |
| 20 | 26445 | 5452 | 51.20 |
| 20 | 27607 | 5762 | 51.83 |
| 25 | 23405 | 6255 | 66.37 |
| 25 | 24373 | 6280 | 63.99 |
| 25 | 23263 | 6179 | 65.96 |
| 30 | 20073 | 6552 | 81.06 |
| 30 | 19399 | 6076 | 77.78 |
| 30 | 20253 | 6222 | 76.29 |
| 35 | 20635 | 7353 | 88.49 |
| 35 | 21396 | 7539 | 87.50 |
| 35 | 21711 | 7509 | 85.89 |
| 40 | 20621 | 7792 | 93.84 |
| 40 | 20786 | 7788 | 93.05 |
| 40 | 20569 | 7895 | 95.32 |

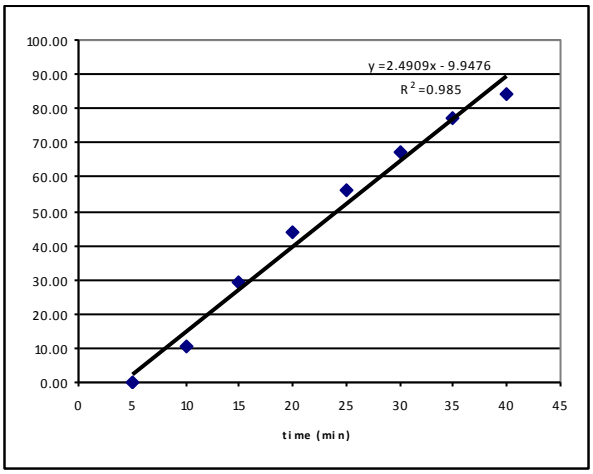



**rate = 0.0113 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 5 | 1 | 0 | 0.00 |
| 5 | 1 | 0 | 0.00 |
| 5 | 1 | 0 | 0.00 |
| 10 | 26188 | 1079 | 10.23 |
| 10 | 25415 | 1172 | 11.45 |
| 10 | 26164 | 1102 | 10.46 |
| 15 | 21601 | 2581 | 29.67 |
| 15 | 20954 | 2506 | 29.70 |
| 15 | 79336 | 9334 | 29.22 |
| 20 | 24680 | 4297 | 43.24 |

| | | | |
|---|---|---|---|
| 20 | 22026 | 4028 | 45.42 |
| 20 | 22437 | 3834 | 42.44 |
| 25 | 18221 | 4139 | 56.41 |
| 25 | 18967 | 4269 | 55.90 |
| 25 | 38078 | 8663 | 56.50 |
| 30 | 60207 | 16123 | 66.50 |
| 30 | 19447 | 5281 | 67.44 |
| 30 | 18978 | 5235 | 68.50 |
| 35 | 48932 | 14805 | 75.14 |
| 35 | 31510 | 10064 | 79.32 |
| 35 | 15721 | 4876 | 77.03 |
| 40 | 43882 | 14534 | 82.25 |
| 40 | 43969 | 14607 | 82.50 |
| 40 | 20162 | 7067 | 87.05 |




**rate = 0.0103 mM/sec**

**avg. rate = 1.01 x $10^{-2}$ mM/s**

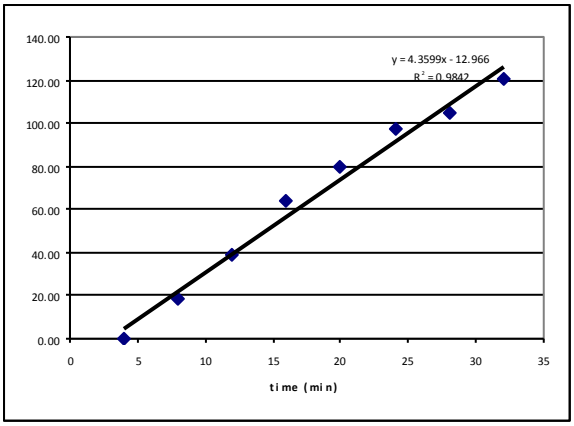
**Table 6, entry 2**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| **7p** | 3.75 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (157 mg, 0.5 mmol, 1.5 equiv), **7p** (13.6 mg, 0.015 mmol, 0.045 equiv), naphthalene (30 mg), and 2-bromotoluene (40 μL, 0.33 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 8 | 84481 | 6156 | 18.10 |
| 8 | 82451 | 6278 | 18.91 |
| 8 | 82449 | 6202 | 18.68 |
| 12 | 78409 | 11978 | 37.94 |
| 12 | 78709 | 12796 | 40.37 |
| 12 | 77810 | 12006 | 38.32 |
| 16 | 22784 | 5942 | 64.77 |
| 16 | 68141 | 17483 | 63.72 |
| 16 | 69287 | 18052 | 64.70 |
| 20 | 73123 | 23133 | 78.56 |

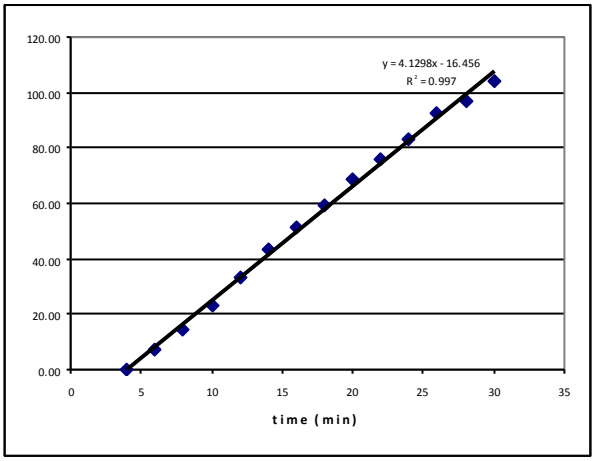


| | | | |
|---|---|---|---|
| 20 | 23719 | 7653 | 80.13 |
| 20 | 71795 | 23187 | 80.20 |
| 24 | 78012 | 30444 | 96.91 |
| 24 | 78796 | 30630 | 96.54 |
| 24 | 26487 | 10470 | 98.17 |
| 28 | 21998 | 9257 | 104.51 |
| 28 | 21699 | 9315 | 106.61 |
| 28 | 21557 | 9073 | 104.52 |
| 32 | 24013 | 11947 | 123.56 |
| 32 | 24971 | 12157 | 120.90 |
| 32 | 75187 | 35167 | 116.16 |

**rate = 0.0182 mM/sec**

**Run 2**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 6 | 62765 | 1753 | 6.94 |
| 6 | 62765 | 1753 | 6.94 |
| 6 | 62765 | 1753 | 6.94 |
| 8 | 57239 | 3373 | 14.63 |
| 8 | 57765 | 3351 | 14.41 |
| 8 | 57239 | 3373 | 14.63 |
| 10 | 62854 | 5721 | 22.60 |
| 10 | 66335 | 6097 | 22.83 |
| 10 | 44372 | 4192 | 23.46 |
| 12 | 22673 | 2986 | 32.71 |
| 12 | 22128 | 3055 | 34.29 |
| 12 | 23650 | 3173 | 33.32 |
| 14 | 59999 | 10347 | 42.83 |
| 14 | 23664 | 4030 | 42.29 |
| 14 | 44158 | 7862 | 44.22 |
| 16 | 22827 | 4645 | 50.53 |
| 16 | 25979 | 5215 | 49.85 |
| 16 | 49047 | 10472 | 53.02 |
| 18 | 20945 | 4970 | 58.93 |
| 18 | 20765 | 4883 | 58.40 |
| 18 | 20896 | 5168 | 61.42 |
| 20 | 16616 | 4559 | 68.14 |
| 20 | 16879 | 4757 | 69.99 |
| 20 | 50798 | 13949 | 68.19 |
| 22 | 64207 | 19579 | 75.73 |
| 22 | 23487 | 7015 | 74.17 |
| 22 | 23444 | 7315 | 77.49 |
| 24 | 20232 | 6671 | 81.88 |
| 24 | 56581 | 19460 | 85.41 |
| 24 | 59401 | 19630 | 82.07 |
| 26 | 60974 | 22494 | 91.62 |

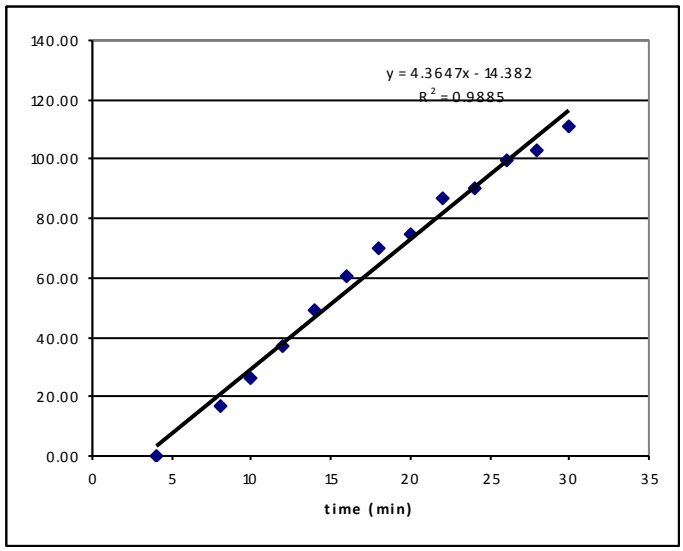


| | | | |
|---|---|---|---|
| 26 | 21777 | 8134 | 92.76 |
| 26 | 21159 | 7898 | 92.70 |
| 28 | 60919 | 23812 | 97.07 |
| 28 | 26499 | 10202 | 95.61 |
| 28 | 26085 | 10254 | 97.62 |
| 30 | 55231 | 22835 | 102.68 |
| 30 | 18831 | 8090 | 106.69 |
| 30 | 18914 | 7806 | 102.49 |

**rate = 0.0173 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 4 | 1 | 0 | 0.00 |
| 8 | 23965 | 1639 | 16.98 |
| 8 | 24264 | 1661 | 17.00 |
| 8 | 24770 | 1702 | 17.06 |
| 10 | 68886 | 7423 | 26.76 |
| 10 | 23791 | 2564 | 26.76 |
| 10 | 24239 | 2560 | 26.23 |
| 12 | 24093 | 3543 | 36.52 |
| 12 | 25329 | 3741 | 36.68 |
| 12 | 23647 | 3669 | 38.53 |
| 14 | 66762 | 13291 | 49.44 |
| 14 | 21827 | 4256 | 48.42 |
| 14 | 22919 | 4559 | 49.40 |
| 16 | 63840 | 15466 | 60.16 |
| 16 | 22403 | 5509 | 61.07 |
| 16 | 22693 | 5504 | 60.23 |
| 18 | 21135 | 5958 | 70.01 |
| 18 | 22835 | 6473 | 70.40 |
| 18 | 22799 | 6334 | 68.99 |
| 20 | 61798 | 18603 | 74.76 |
| 20 | 25603 | 7591 | 73.63 |
| 20 | 25502 | 7749 | 75.46 |
| 22 | 61418 | 21000 | 84.91 |
| 22 | 21473 | 7430 | 85.93 |
| 22 | 21266 | 7595 | 88.69 |
| 24 | 69078 | 25888 | 93.07 |
| 24 | 28347 | 9946 | 87.13 |
| 24 | 26831 | 9798 | 90.69 |
| 26 | 25305 | 10240 | 100.49 |
| 26 | 47311 | 19020 | 99.84 |
| 26 | 24615 | 9852 | 99.40 |
| 28 | 28164 | 11861 | 104.59 |



| | | | |
|---|---|---|---|
| 28 | 28350 | 11813 | 103.48 |
| 28 | 30328 | 12273 | 100.50 |
| 30 | 24289 | 10710 | 109.50 |
| 30 | 23132 | 10397 | 111.62 |
| 30 | 23774 | 10778 | 112.59 |

**rate = 0.0182 mM/sec**

**avg. rate = 1.79 x $10^{-2}$ mM/s**

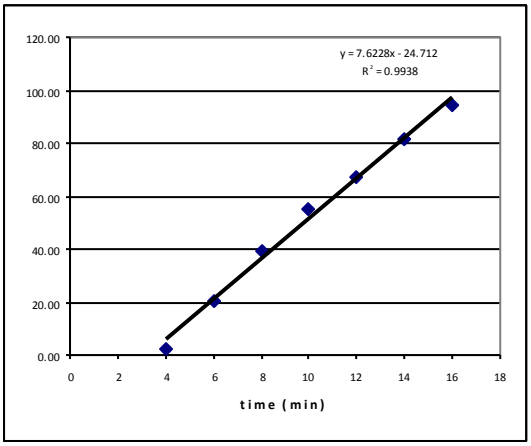
**Table 6, entry 3**

| | |
|---|---|
| $Cs^{+}$**5**$^{-}$ | 125 mM |
| 2-Bromotoluene | 83 mM |
| **7p** | 7.5 mM |

Following the General Procedure III, a mixture of silanolate $Cs^{+}$**5**$^{-}$ (157 mg, 0.5 mmol, 1.5 equiv), **7p** (27.2 mg, 0.030 mmol, 0.090 equiv), naphthalene (30 mg), and 2-bromotoluene (40 μL, 0.33 mmol, 1.0 equiv) were dissolved in dry benzotrifluoride (4 mL) at room temperature followed by stirring at reflux. Aliquots of the mixture were then taken for GC analysis.

**Run 1**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 1 | 0 | 0.00 |
| 4 | 74870 | 2173 | 7.21 |
| 4 | 1 | 0 | 0.00 |
| 6 | 20479 | 1779 | 21.57 |
| 6 | 63256 | 5081 | 19.95 |
| 6 | 63713 | 5143 | 20.05 |
| 8 | 60733 | 9249 | 37.82 |
| 8 | 63201 | 10081 | 39.61 |
| 8 | 62700 | 10017 | 39.68 |
| 10 | 59937 | 13322 | 55.20 |
| 10 | 61625 | 13699 | 55.21 |
| 10 | 61795 | 13703 | 55.07 |
| 12 | 62045 | 16811 | 67.29 |
| 12 | 65347 | 17787 | 67.60 |
| 12 | 66678 | 18072 | 67.31 |
| 14 | 64882 | 21519 | 82.37 |
| 14 | 69649 | 22249 | 79.33 |
| 14 | 23571 | 7866 | 82.88 |
| 16 | 57777 | 22014 | 94.62 |
| 16 | 21611 | 8017 | 92.13 |

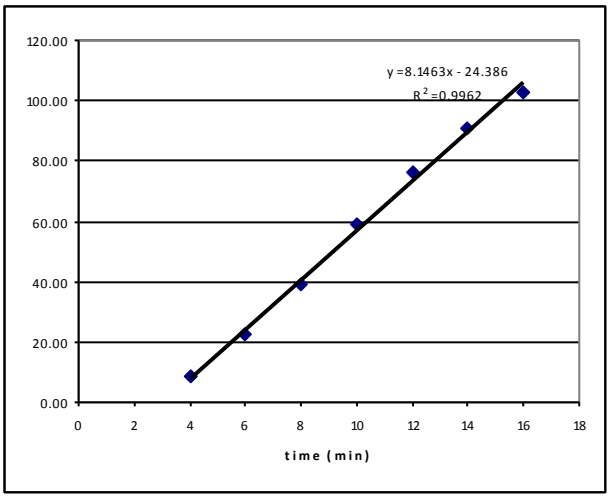


| | | | |
|---|---|---|---|
| 16 | 21182 | 8271 | 96.97 |

**rate = 0.0318 mM/sec**

**Run 2**

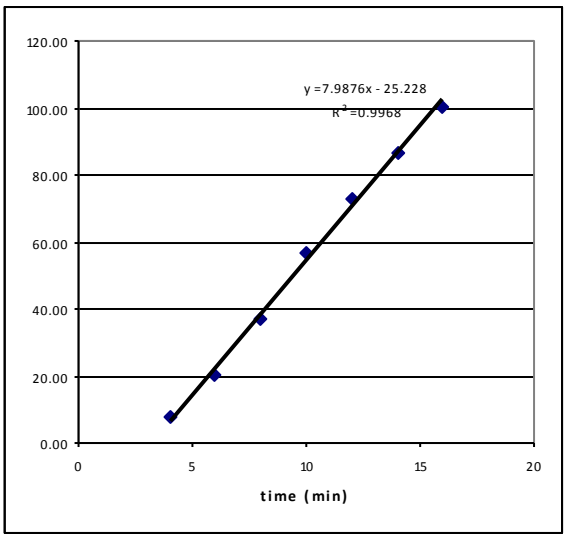
| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 49106 | 1746 | 8.83 |
| 4 | 49010 | 1697 | 8.60 |
| 4 | 49106 | 1746 | 8.83 |
| 6 | 67304 | 5980 | 22.07 |
| 6 | 70360 | 6359 | 22.44 |
| 6 | 72526 | 6672 | 22.85 |
| 8 | 22753 | 3613 | 39.43 |
| 8 | 69791 | 10884 | 38.73 |
| 8 | 70580 | 11326 | 39.85 |
| 10 | 26128 | 6257 | 59.47 |
| 10 | 81619 | 19277 | 58.65 |
| 10 | 81979 | 19461 | 58.95 |
| 12 | 65626 | 19880 | 75.23 |
| 12 | 69139 | 21486 | 77.18 |
| 12 | 68168 | 21013 | 76.55 |
| 14 | 62485 | 22745 | 90.40 |
| 14 | 69789 | 25418 | 90.45 |
| 14 | 69841 | 25558 | 90.88 |
| 16 | 63600 | 26083 | 101.85 |
| 16 | 67426 | 27886 | 102.71 |
| 16 | 66095 | 27857 | 104.67 |




**rate = 0.0339 mM/sec**

**Run 3**

| Time | area, std | area, **12** | conv, μmol |
|---|---|---|---|
| 4 | 101820 | 3118 | 7.60 |
| 4 | 98708 | 3167 | 7.97 |
| 4 | 103016 | 3143 | 7.58 |
| 6 | 97098 | 7836 | 20.04 |
| 6 | 96104 | 7873 | 20.34 |
| 6 | 95316 | 7970 | 20.77 |
| 8 | 72175 | 10978 | 37.77 |
| 8 | 73373 | 10812 | 36.59 |
| 8 | 71716 | 10765 | 37.28 |
| 10 | 76428 | 17651 | 57.35 |
| 10 | 77172 | 17729 | 57.05 |
| 10 | 79722 | 17987 | 56.03 |
| 12 | 78683 | 22973 | 72.51 |
| 12 | 78710 | 23128 | 72.97 |
| 12 | 78865 | 23308 | 73.40 |
| 14 | 69195 | 24388 | 87.53 |

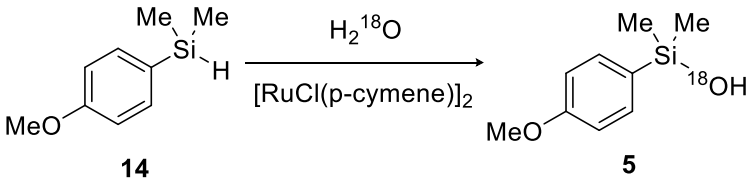


| | | | |
|---|---|---|---|
| 14 | 70832 | 24252 | 85.03 |
| 14 | 69242 | 24543 | 88.03 |
| 16 | 88670 | 35352 | 99.01 |
| 16 | 88169 | 36258 | 102.13 |
| 16 | 88822 | 35988 | 100.62 |

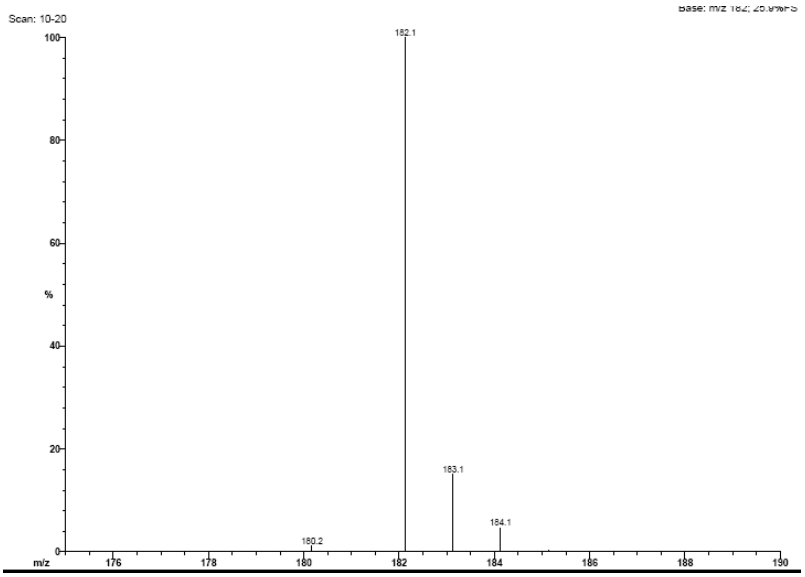
**rate = 0. 0333 mM/sec**

**avg. rate = 3.30 x $10^{-2}$ mM/s**

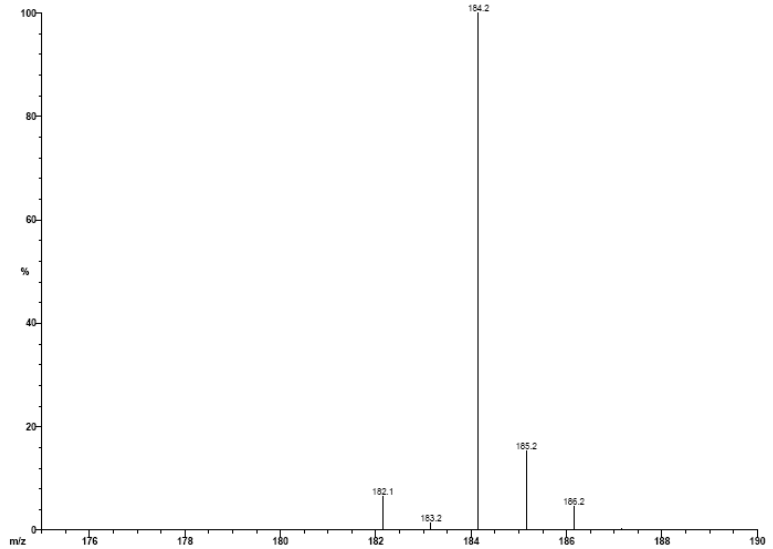
**Preparation of $^{18}$O-labeled (4-methoxyphenyl)dimethylsilanol (Scheme 4)**




To a 50-mL, round-bottom flask equipped with a magnetic stir bar was added (4-methoxyphenyl)dimethylsilane **14** (831 mg, 5.0 mmol), 15 mL of acetonitrile, and 95% $^{18}$O water (200 μL, 10.0 mmol, 2.0 equiv). To the resulting solution was added [$RuCl_2$(*p*-cymene)]$_2$ (61 mg, 0.10 mmol, 0.02 equiv). The solution was stirred at room temperature open to the atmosphere for 10 min. The volatile solvents were then was removed in vacuo to provide a red oil. The oil was taken up in 20 mL of hexanes and then was purified by silica gel chromatography (30 mm x 30 cm) using hexanes/ethyl acetate, 9/1 to afford 847 mg (92%) of **5** as a colorless oil. Label incorporation was determined by mass spectrometry (FI). Unlabeled standard- M/Z = 182.1. Labeled M/Z = 184.2. Incorporation = 94.4 %

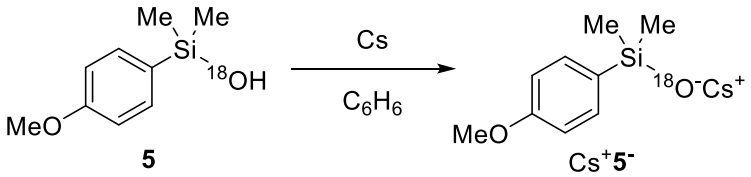



Standard



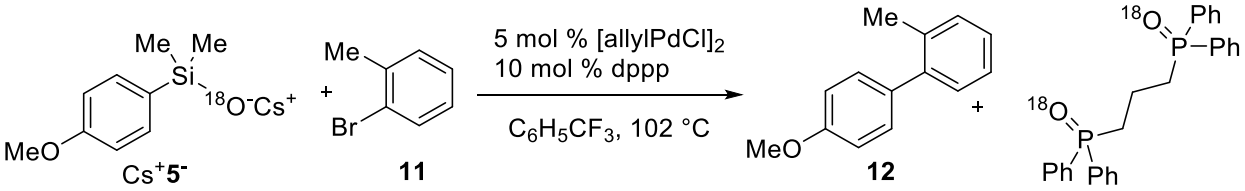

Labeled

**Preparation of $^{18}$O-labeled Cesium (4-methoxyphenyl)dimethylsilanolate (Scheme 4)**

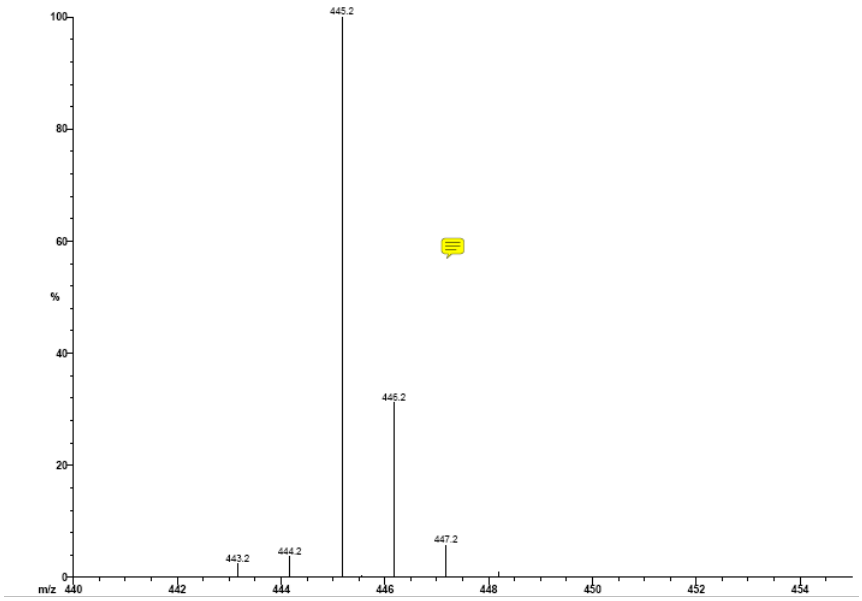



In the drybox, a 100-mL, one-necked flask equipped with a magnetic stir bar was charged with Cs (531 mg, 4.00 mmol, 1.0 equiv), and dry, degassed benzene (40 mL). While stirring, $^{18}$O-labeled (4-methoxyphenyl)dimethylsilanol **5** (737 mg, 4.0 mmol, 1.0 equiv) was added and the resulting suspension was stirred in the drybox for 20 min . The resulting solution was filtered through a medium glass frit. The solvents were removed *in vacuo* (0.1 mm Hg) for 4 h to afford a sticky white solid. Hexanes (25 mL) were added and the resulting suspension was stirred for 1 h in the drybox. The resulting solids were collected on a fritted glass funnel, then were washed with hexanes (5 mL), and dried under vacuum (0.1 mm Hg) for 12 h to afford 982 mg (79%) of $Cs^+$**5**$^-$ as a white powder.

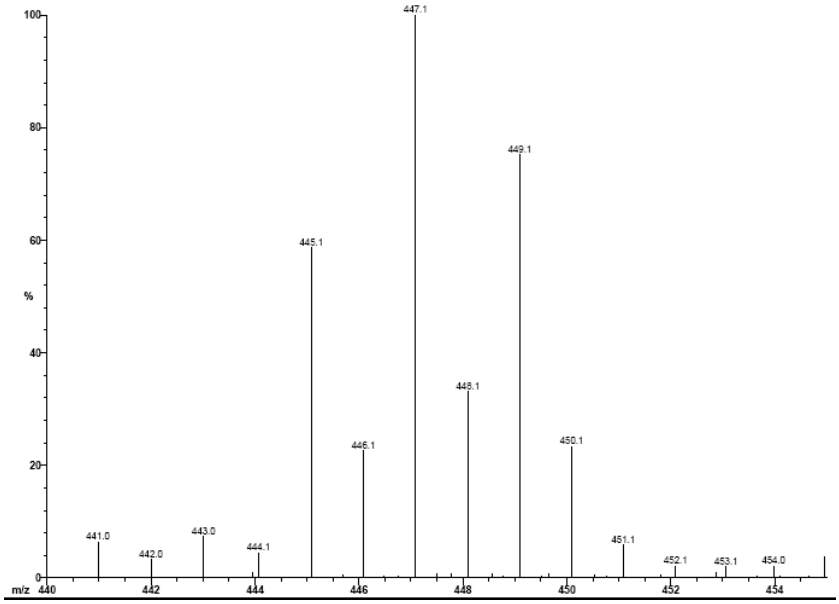
**Isolation of $^{18}$O labeled 1,3-bis(diphenylphosphino)propane dioxide (Scheme 4)**




In a drybox, a one-neck, 10-mL round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and three-way stop-cock (fitted with an argon inlet and a rubber septum) was charged with APC (9.1 mg, 0.025 mmol, 0.05 equiv), dppp (21.0 mg, 0.05 mmol, 0.1 equiv) 2-bromotoluene (63 μL, 0.50 mmol, 1.0 equiv), and dry benzotrifluoride (4.0 mL). To this solution was added $Cs^+$**5**$^-$ (190 mg, 0.60 mmol, 1.2 equiv). The flask was removed from the drybox, the stopcock purged with argon, and was placed in a 105 $^0$C oil bath for 3 h. The reaction was quenched by the addition of 2 mL of a 10% aqueous solution of 2-dimethylaminoethanethiol hydrochloride followed by stirring at rt for 30 min. The oganics were separated and purified by chromatography (silica gel, 30 mm x 30 cm, $CH_2Cl_2$) to afford 8 mg (30%) of dppp(O)$_2$ as a yellow oil and 140 mg of impure **12** as a colorless oil. Bulb-to-bulb distillation (120ºC, 0.5 mm Hg) provided 76 mg (67%) of **12** as a colorless oil. Label incorporation in the sample of dppp(O)$_2$ was determined by mass spectrometry (FAB). Unlabeled standard- M/Z = 445.1. Monolabeled M/Z = 447.1. Bislabeled M/Z = 449.1. Incorporation = 52.3 %




Standard



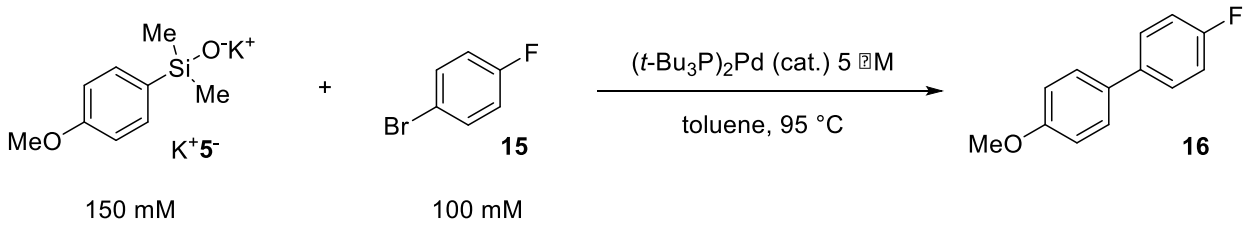

Labeled Sample

**INDEX OF KINETIC EXPERIMENTS FOR CATALYTIC CROSS-COUPLING OF ARYLSILANOLATES EMPLOYING (*t*-$Bu_3P)_2Pd$ (Scheme 6)**

**General Procedure IV: Kinetic Measurements for Catalytic Cross-Coupling of Arylsilanolates Employing ($t$-$Bu_3P)_2Pd$ (Scheme 11)**

Order in K+**5**$^-$

| | |
|---|---|
| K$^+$**5**$^-$ | 150 mM |
| **15** | 100 mM |
| Pd cat. | 5 mM |



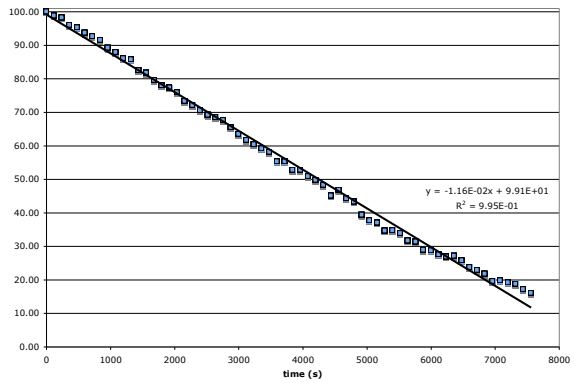

In a drybox, an oven-dried, 2.5-mL vial equipped with a magnetic stir bar was charged with ($t$-$Bu_3P)_2Pd$ (2.5 mg, 0.0049 mmol), toluene (0.8 mL), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) resulting in a colorless solution. K$^+$**5**$^-$ (33 mg, 0.15 mmol) was added as a solid and the sides of the vial were rinsed with additional toluene (0.2 mL). The mixture was stirred for 3 min to ensure complete dissolution was observed. The resulting solution was transferred into an oven-dried, 5-mm NMR tube. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and inserted into a preheated 95 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for 3 min prior to data collection.[17] The reaction progress was monitored by the disappearance of starting aryl halide ($^{19}$F NMR, -115.9 ppm) as compared to an internal reference ($PhCF_3$, $^{19}$F NMR, -63.2 ppm)) via $^{19}$F NMR spectroscopy using the following parameters: at = 0.328, d1 = 1, pw90 = 18.25, pw=pw90/2, nt=24, sampling every 120 s.[18] The rate of the reaction was determined by the slope of the linear plot[19]: **rate = 1.16 x 10$^{-2}$ mMs$^{-1}$**.

**Run 1**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalization (mM) |
|---|---|---|---|
| 0 | 1.086 | 1.435 | 100.03 |
| 120 | 1.076 | 1.417 | 98.77 |
| 240 | 1.098 | 1.409 | 98.20 |
| 360 | 1.095 | 1.377 | 95.99 |
| 480 | 1.083 | 1.368 | 95.30 |
| 600 | 1.058 | 1.345 | 93.70 |
| 720 | 1.077 | 1.329 | 92.61 |
| 840 | 1.056 | 1.313 | 91.51 |
| 960 | 1.099 | 1.280 | 89.20 |

| | | | |
|---|---|---|---|
| 1080 | 1.079 | 1.261 | 87.91 |
| 1200 | 1.067 | 1.235 | 86.08 |
| 1320 | 1.089 | 1.231 | 85.77 |
| 1440 | 1.042 | 1.183 | 82.47 |
| 1560 | 1.039 | 1.173 | 81.74 |
| 1680 | 1.053 | 1.143 | 79.63 |
| 1800 | 1.055 | 1.119 | 77.97 |
| 1920 | 1.040 | 1.109 | 77.31 |
| 2040 | 1.045 | 1.089 | 75.91 |
| 2160 | 1.059 | 1.052 | 73.32 |
| 2280 | 1.069 | 1.034 | 72.07 |
| 2400 | 1.062 | 1.012 | 70.55 |
| 2520 | 1.037 | 0.993 | 69.19 |
| 2640 | 1.045 | 0.982 | 68.44 |
| 2760 | 1.055 | 0.970 | 67.59 |
| 2880 | 1.027 | 0.940 | 65.52 |
| 3000 | 1.017 | 0.911 | 63.50 |
| 3120 | 1.031 | 0.886 | 61.71 |
| 3240 | 1.031 | 0.867 | 60.38 |
| 3360 | 1.040 | 0.849 | 59.14 |
| 3480 | 1.042 | 0.834 | 58.12 |
| 3600 | 1.003 | 0.793 | 55.29 |
| 3720 | 1.048 | 0.794 | 55.32 |
| 3840 | 1.022 | 0.757 | 52.75 |
| 3960 | 1.012 | 0.758 | 52.80 |
| 4080 | 1.002 | 0.730 | 50.86 |
| 4200 | 1.006 | 0.714 | 49.75 |
| 4320 | 1.052 | 0.693 | 48.29 |
| 4440 | 1.009 | 0.647 | 45.09 |
| 4560 | 1.029 | 0.672 | 46.83 |
| 4680 | 1.005 | 0.636 | 44.31 |
| 4800 | 1.024 | 0.621 | 43.29 |
| 4920 | 0.982 | 0.565 | 39.36 |
| 5040 | 0.999 | 0.541 | 37.72 |
| 5160 | 1.012 | 0.532 | 37.04 |
| 5280 | 0.990 | 0.497 | 34.65 |
| 5400 | 1.015 | 0.499 | 34.74 |
| 5520 | 0.978 | 0.486 | 33.86 |
| 5640 | 0.980 | 0.454 | 31.66 |
| 5760 | 0.976 | 0.450 | 31.37 |
| 5880 | 0.966 | 0.414 | 28.88 |
| 6000 | 0.973 | 0.412 | 28.70 |
| 6120 | 0.978 | 0.396 | 27.57 |
| 6240 | 0.970 | 0.385 | 26.86 |
| 6360 | 1.001 | 0.390 | 27.15 |
| 6480 | 0.985 | 0.370 | 25.80 |
| 6600 | 0.974 | 0.341 | 23.77 |
| 6720 | 0.985 | 0.328 | 22.86 |
| 6840 | 1.000 | 0.313 | 21.79 |
| 6960 | 0.965 | 0.281 | 19.57 |
| 7080 | 0.974 | 0.284 | 19.81 |
| 7200 | 0.971 | 0.275 | 19.18 |
| 7320 | 0.964 | 0.269 | 18.76 |
| 7440 | 1.001 | 0.246 | 17.15 |
| 7560 | 0.966 | 0.230 | 16.05 |
| 7680 | 0.964 | 0.232 | 16.17 |

| | | | |
|---|---|---|---|
| 7800 | 0.979 | 0.210 | 14.61 |
| 7920 | 0.988 | 0.208 | 14.49 |
| 8040 | 0.980 | 0.203 | 14.14 |
| 8160 | 1.001 | 0.190 | 13.22 |
| 8280 | 0.982 | 0.168 | 11.68 |
| 8400 | 0.978 | 0.161 | 11.18 |
| 8520 | 0.979 | 0.160 | 11.13 |
| 8640 | 0.924 | 0.151 | 10.55 |
| 8760 | 0.936 | 0.141 | 9.84 |
| 8880 | 0.952 | 0.137 | 9.51 |
| 9000 | 0.973 | 0.108 | 7.55 |
| 9120 | 0.957 | 0.128 | 8.91 |
| 9240 | 0.962 | 0.114 | 7.97 |




| | |
|---|---|
| $K^+$**5**$^-$ | 150 mM |
| **15** | 100 mM |
| Pd cat. | 5 mM |

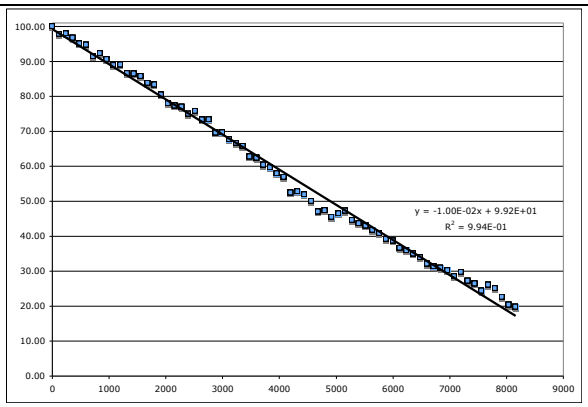
Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (2.7 mg, 0.0053 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 1.00 x $10^{-2}$ $s^{-1}$**.

**Run 2**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalization (mM) |
|---|---|---|---|
| 0 | 0.968 | 1.255 | 99.98 |
| 120 | 0.935 | 1.228 | 97.81 |
| 240 | 0.970 | 1.229 | 97.91 |
| 360 | 0.964 | 1.214 | 96.71 |
| 480 | 0.959 | 1.193 | 95.06 |
| 600 | 0.942 | 1.188 | 94.66 |
| 720 | 0.932 | 1.147 | 91.36 |
| 840 | 0.951 | 1.158 | 92.30 |

| | | | |
|---|---|---|---|
| 960 | 0.967 | 1.136 | 90.55 |
| 1080 | 0.962 | 1.115 | 88.88 |
| 1200 | 0.951 | 1.117 | 89.01 |
| 1320 | 0.964 | 1.087 | 86.58 |
| 1440 | 0.934 | 1.085 | 86.46 |
| 1560 | 0.958 | 1.076 | 85.75 |
| 1680 | 0.939 | 1.052 | 83.80 |
| 1800 | 0.980 | 1.045 | 83.30 |
| 1920 | 0.977 | 1.009 | 80.42 |
| 2040 | 0.945 | 0.978 | 77.94 |
| 2160 | 0.958 | 0.970 | 77.29 |
| 2280 | 0.972 | 0.966 | 76.95 |
| 2400 | 0.945 | 0.941 | 74.96 |
| 2520 | 0.917 | 0.951 | 75.75 |
| 2640 | 0.965 | 0.920 | 73.27 |
| 2760 | 0.926 | 0.920 | 73.33 |
| 2880 | 0.960 | 0.874 | 69.60 |
| 3000 | 0.973 | 0.874 | 69.63 |
| 3120 | 0.925 | 0.848 | 67.61 |
| 3240 | 0.929 | 0.836 | 66.64 |
| 3360 | 0.927 | 0.825 | 65.72 |
| 3480 | 0.932 | 0.787 | 62.72 |
| 3600 | 0.932 | 0.783 | 62.37 |
| 3720 | 0.964 | 0.758 | 60.40 |
| 3840 | 0.941 | 0.748 | 59.63 |
| 3960 | 0.961 | 0.727 | 57.89 |
| 4080 | 0.923 | 0.714 | 56.89 |
| 4200 | 0.958 | 0.658 | 52.42 |
| 4320 | 0.952 | 0.662 | 52.75 |
| 4440 | 0.922 | 0.651 | 51.91 |
| 4560 | 0.904 | 0.627 | 49.98 |
| 4680 | 0.946 | 0.590 | 47.01 |
| 4800 | 0.943 | 0.594 | 47.36 |
| 4920 | 0.946 | 0.570 | 45.45 |
| 5040 | 0.944 | 0.583 | 46.47 |
| 5160 | 0.963 | 0.593 | 47.25 |
| 5280 | 0.957 | 0.560 | 44.58 |
| 5400 | 0.946 | 0.547 | 43.61 |
| 5520 | 0.958 | 0.539 | 42.96 |
| 5640 | 0.956 | 0.524 | 41.74 |
| 5760 | 0.929 | 0.512 | 40.77 |
| 5880 | 0.942 | 0.492 | 39.16 |
| 6000 | 0.941 | 0.485 | 38.66 |
| 6120 | 0.931 | 0.459 | 36.59 |
| 6240 | 0.969 | 0.450 | 35.88 |
| 6360 | 0.965 | 0.439 | 34.95 |
| 6480 | 0.943 | 0.426 | 33.91 |
| 6600 | 0.959 | 0.403 | 32.10 |
| 6720 | 0.973 | 0.393 | 31.28 |
| 6840 | 0.955 | 0.388 | 30.90 |
| 6960 | 0.937 | 0.379 | 30.18 |
| 7080 | 0.970 | 0.357 | 28.46 |
| 7200 | 0.956 | 0.373 | 29.69 |
| 7320 | 0.978 | 0.341 | 27.17 |
| 7440 | 0.963 | 0.331 | 26.41 |
| 7560 | 0.961 | 0.306 | 24.37 |

| | | | |
|---|---|---|---|
| 7680 | 0.939 | 0.327 | 26.08 |
| 7800 | 0.952 | 0.314 | 25.04 |
| 7920 | 0.955 | 0.284 | 22.60 |
| 8040 | 0.924 | 0.256 | 20.36 |
| 8160 | 0.926 | 0.248 | 19.74 |
| 8280 | 0.919 | 0.224 | 17.89 |
| 8400 | 0.905 | 0.216 | 17.24 |
| 8520 | 0.914 | 0.229 | 18.29 |
| 8640 | 0.921 | 0.214 | 17.06 |
| 8760 | 0.952 | 0.197 | 15.71 |
| 8880 | 0.947 | 0.186 | 14.82 |
| 9000 | 0.936 | 0.166 | 13.23 |
| 9120 | 0.948 | 0.169 | 13.44 |
| 9240 | 0.934 | 0.162 | 12.90 |




**avg. rate = 1.08 x $10^{-2}$ $s^{-1}$ ± 1.1 x $10^{-3}$**

$K^+$**5**$^-$ 75 mM

**15** 100 mM

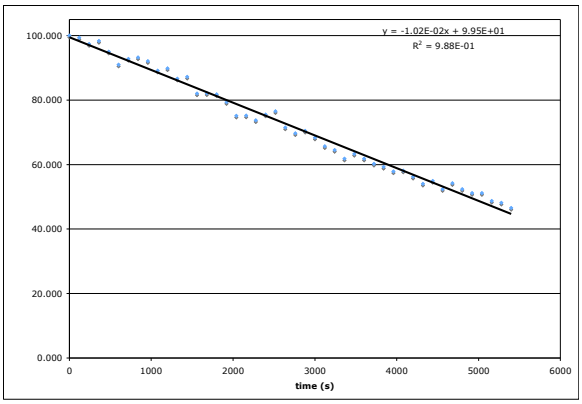
Pd cat. 5 mM

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (17 mg, 0.075 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 1.02 x $10^{-2}$ $mMs^{-1}$**.

**Run 1**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 1.335 | 1.744 | 99.99 |
| 120 | 1.320 | 1.712 | 98.18 |
| 240 | 1.342 | 1.707 | 97.88 |
| 360 | 1.305 | 1.676 | 96.11 |
| 480 | 1.314 | 1.630 | 93.47 |

| | | | |
|---|---|---|---|
| 600 | 1.336 | 1.587 | 91.01 |
| 720 | 1.292 | 1.566 | 89.77 |
| 840 | 1.275 | 1.553 | 89.04 |
| 960 | 1.264 | 1.520 | 87.14 |
| 1080 | 1.282 | 1.492 | 85.54 |
| 1200 | 1.244 | 1.459 | 83.66 |
| 1320 | 1.261 | 1.427 | 81.82 |
| 1440 | 1.240 | 1.413 | 81.00 |
| 1560 | 1.267 | 1.357 | 77.82 |
| 1680 | 1.243 | 1.332 | 76.40 |
| 1800 | 1.229 | 1.312 | 75.25 |
| 1920 | 1.235 | 1.279 | 73.34 |
| 2040 | 1.257 | 1.233 | 70.72 |
| 2160 | 1.240 | 1.218 | 69.82 |
| 2280 | 1.245 | 1.199 | 68.78 |
| 2400 | 1.201 | 1.184 | 67.92 |
| 2520 | 1.164 | 1.163 | 66.71 |
| 2640 | 1.204 | 1.124 | 64.46 |
| 2760 | 1.193 | 1.087 | 62.30 |
| 2880 | 1.172 | 1.079 | 61.85 |
| 3000 | 1.186 | 1.059 | 60.71 |
| 3120 | 1.209 | 1.036 | 59.42 |
| 3240 | 1.200 | 1.012 | 58.02 |
| 3360 | 1.210 | 0.977 | 56.03 |
| 3480 | 1.183 | 0.978 | 56.06 |
| 3600 | 1.154 | 0.932 | 53.44 |
| 3720 | 1.199 | 0.943 | 54.08 |
| 3840 | 1.168 | 0.904 | 51.85 |
| 3960 | 1.181 | 0.893 | 51.19 |
| 4080 | 1.164 | 0.883 | 50.66 |
| 4200 | 1.175 | 0.862 | 49.45 |
| 4320 | 1.165 | 0.823 | 47.16 |
| 4440 | 1.173 | 0.842 | 48.26 |
| 4560 | 1.169 | 0.800 | 45.85 |
| 4680 | 1.137 | 0.806 | 46.20 |
| 4800 | 1.154 | 0.789 | 45.25 |
| 4920 | 1.160 | 0.775 | 44.45 |
| 5040 | 1.135 | 0.758 | 43.48 |
| 5160 | 1.144 | 0.727 | 41.71 |
| 5280 | 1.154 | 0.726 | 41.61 |
| 5400 | 1.164 | 0.708 | 40.61 |
| 5520 | 1.150 | 0.706 | 40.47 |
| 5640 | 1.128 | 0.674 | 38.64 |
| 5760 | 1.169 | 0.693 | 39.74 |
| 5880 | 1.117 | 0.679 | 38.96 |
| 6000 | 1.150 | 0.668 | 38.31 |
| 6120 | 1.118 | 0.656 | 37.62 |
| 6240 | 1.139 | 0.637 | 36.52 |



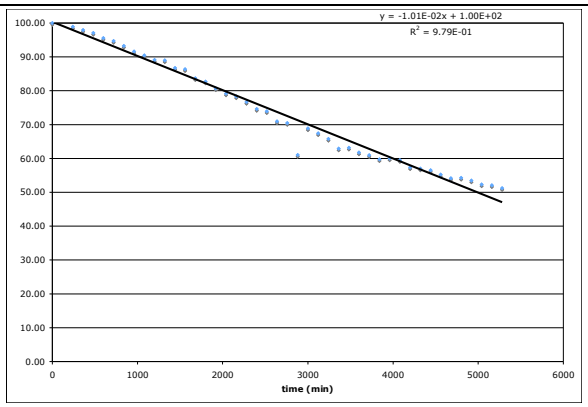

**Run 2**

| | |
|---|---|
| $K^+$**5**$^-$ | 75 mM |
| **15** | 100 mM |
| Pd cat. | 5 mM |

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (17 mg, 0.075 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by 19F NMR spectroscopy. **rate = 1.01 x $10^{-2}$ mMs$^{-1}$**.

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 1.335 | 1.744 | 100.00 |
| 120 | 1.320 | 1.712 | 100.74 |
| 240 | 1.342 | 1.707 | 98.93 |
| 360 | 1.305 | 1.676 | 97.93 |
| 480 | 1.314 | 1.630 | 97.06 |
| 600 | 1.336 | 1.587 | 95.57 |
| 720 | 1.292 | 1.566 | 94.67 |
| 840 | 1.275 | 1.553 | 93.23 |
| 960 | 1.264 | 1.520 | 91.58 |
| 1080 | 1.282 | 1.492 | 90.46 |
| 1200 | 1.244 | 1.459 | 89.07 |
| 1320 | 1.261 | 1.427 | 88.98 |
| 1440 | 1.240 | 1.413 | 86.75 |
| 1560 | 1.267 | 1.357 | 86.35 |
| 1680 | 1.243 | 1.332 | 83.68 |
| 1800 | 1.229 | 1.312 | 82.71 |
| 1920 | 1.235 | 1.279 | 80.72 |
| 2040 | 1.257 | 1.233 | 79.18 |
| 2160 | 1.240 | 1.218 | 78.30 |
| 2280 | 1.245 | 1.199 | 76.65 |

| | | | |
|---|---|---|---|
| 2400 | 1.201 | 1.184 | 74.62 |
| 2520 | 1.164 | 1.163 | 73.96 |
| 2640 | 1.204 | 1.124 | 70.94 |
| 2760 | 1.193 | 1.087 | 70.44 |
| 2880 | 1.172 | 1.079 | 61.01 |
| 3000 | 1.186 | 1.059 | 68.85 |
| 3120 | 1.209 | 1.036 | 67.44 |
| 3240 | 1.200 | 1.012 | 65.76 |
| 3360 | 1.210 | 0.977 | 62.92 |
| 3480 | 1.183 | 0.978 | 63.13 |
| 3600 | 1.154 | 0.932 | 61.73 |
| 3720 | 1.199 | 0.943 | 60.97 |
| 3840 | 1.168 | 0.904 | 59.72 |
| 3960 | 1.181 | 0.893 | 60.01 |
| 4080 | 1.164 | 0.883 | 59.48 |
| 4200 | 1.175 | 0.862 | 57.37 |
| 4320 | 1.165 | 0.823 | 57.02 |
| 4440 | 1.173 | 0.842 | 56.52 |
| 4560 | 1.169 | 0.800 | 55.26 |
| 4680 | 1.137 | 0.806 | 54.17 |
| 4800 | 1.154 | 0.789 | 54.28 |
| 4920 | 1.160 | 0.775 | 53.46 |
| 5040 | 1.135 | 0.758 | 52.34 |
| 5160 | 1.144 | 0.727 | 52.04 |
| 5280 | 1.154 | 0.726 | 51.24 |
| 5400 | 1.164 | 0.708 | 51.39 |
| 5520 | 1.150 | 0.706 | 48.93 |
| 5640 | 1.128 | 0.674 | 48.85 |
| 5760 | 1.169 | 0.693 | 47.38 |
| 5880 | 1.117 | 0.679 | 48.22 |
| 6000 | 1.150 | 0.668 | 100.00 |
| 6120 | 1.118 | 0.656 | 100.74 |
| 6240 | 1.139 | 0.637 | 98.93 |




**avg. rate = 1.02 x $10^{-2}$ $mMs^{-1}$ ± 7.1 x $10^{-5}$**

$K^+$**5**$^-$ 300 mM

**15** 100 mM

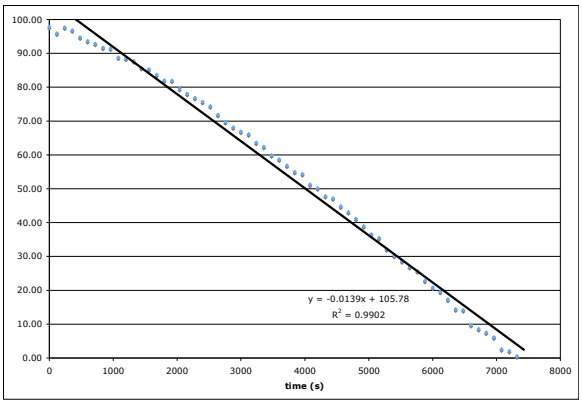
Pd cat. 5 mM

Following General Procedure IV, the following modifications were required for experiments involving >150 mM in $K^+$**5**$^-$ :[20] In a drybox, an oven-dried, 2.5-mL vial equipped with a magnetic stir bar was charged with ($t$-$Bu_3P)_2Pd$ (2.5 mg, 0.0049 mmol), toluene (0.8 mL), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) resulting in a colorless solution. Silanolate K+21$^-$ (33 mg, 0.15 mmol) was added as a solid and the sides of the vial were rinsed with toluene (0.2 mL). The mixture was stirred for 3 min to ensure complete dissolution. The remaining $K^+$**5**$^-$ (33 mg, 0.15 mmol) was added into an oven-dried, 5-mm NMR tube. The reaction solution was transferred into the NMR tube containing the excess silanolate and was shaken vigorously. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and inserted into a preheated 95 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for 3 min at which point the NMR tube was ejected and shaken to ensure complete homogeneity. The tube was returned to the heated probe and the reaction progress was monitored by the disappearance of starting aryl halide ($^{19}F$ NMR, -115.9 ppm) as compared to an internal reference ($PhCF_3$, $^{19}F$ NMR, -63.2 ppm)) via $^{19}F$ NMR spectroscopy using the following parameters: at = 0.328, d1 = 1, pw90 = 18.25, pw=pw90/2, nt=24, sampling every 120 s. **rate = 1.3 x $10^{-2}$ mMs$^{-1}$**.

**Run 1**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 2.465 | 1.992 | 97.86 |
| 120 | 2.486 | 1.982 | 95.89 |
| 240 | 2.478 | 1.982 | 97.70 |
| 360 | 2.501 | 1.967 | 96.85 |
| 480 | 2.489 | 1.954 | 94.75 |
| 600 | 2.486 | 1.960 | 93.69 |
| 720 | 2.494 | 1.978 | 92.89 |
| 840 | 2.528 | 1.931 | 91.72 |
| 960 | 2.516 | 1.927 | 91.44 |
| 1080 | 2.521 | 1.895 | 88.78 |
| 1200 | 2.550 | 1.915 | 88.50 |
| 1320 | 2.534 | 1.898 | 87.76 |
| 1440 | 2.501 | 1.872 | 85.77 |
| 1560 | 2.511 | 1.859 | 85.35 |
| 1680 | 2.534 | 1.822 | 83.67 |
| 1800 | 2.551 | 1.856 | 82.04 |

| | | | |
|---|---|---|---|
| 1920 | 2.528 | 1.840 | 81.97 |
| 2040 | 2.540 | 1.800 | 79.53 |
| 2160 | 2.538 | 1.780 | 78.11 |
| 2280 | 2.524 | 1.765 | 76.84 |
| 2400 | 2.531 | 1.743 | 75.70 |
| 2520 | 2.548 | 1.737 | 74.44 |
| 2640 | 2.536 | 1.687 | 71.88 |
| 2760 | 2.554 | 1.682 | 69.76 |
| 2880 | 2.529 | 1.667 | 68.16 |
| 3000 | 2.518 | 1.630 | 66.96 |
| 3120 | 2.559 | 1.622 | 66.16 |
| 3240 | 2.526 | 1.590 | 63.65 |
| 3360 | 2.548 | 1.559 | 62.45 |
| 3480 | 2.541 | 1.557 | 59.92 |
| 3600 | 2.554 | 1.511 | 58.68 |
| 3720 | 2.559 | 1.484 | 56.90 |
| 3840 | 2.579 | 1.460 | 54.99 |
| 3960 | 2.552 | 1.438 | 54.40 |
| 4080 | 2.548 | 1.414 | 51.29 |
| 4200 | 2.552 | 1.366 | 50.20 |
| 4320 | 2.551 | 1.325 | 47.89 |
| 4440 | 2.581 | 1.295 | 47.19 |
| 4560 | 2.554 | 1.272 | 44.82 |
| 4680 | 2.549 | 1.257 | 43.12 |
| 4800 | 2.549 | 1.209 | 41.19 |
| 4920 | 2.564 | 1.187 | 38.97 |
| 5040 | 2.579 | 1.138 | 36.60 |
| 5160 | 2.567 | 1.115 | 35.45 |
| 5280 | 2.548 | 1.081 | 32.16 |
| 5400 | 2.548 | 1.045 | 30.21 |
| 5520 | 2.555 | 1.034 | 28.60 |
| 5640 | 2.574 | 0.975 | 26.94 |
| 5760 | 2.553 | 0.954 | 25.73 |
| 5880 | 2.559 | 0.910 | 22.82 |
| 6000 | 2.557 | 0.897 | 20.83 |
| 6120 | 2.550 | 0.852 | 19.59 |
| 6240 | 2.569 | 0.819 | 17.27 |
| 6360 | 2.541 | 0.783 | 14.43 |
| 6480 | 2.577 | 0.740 | 14.17 |
| 6600 | 2.582 | 0.695 | 9.80 |
| 6720 | 2.575 | 0.674 | 8.61 |
| 6840 | 2.584 | 0.611 | 7.56 |
| 6960 | 2.589 | 0.574 | 6.14 |
| 7080 | 2.597 | 0.543 | 2.60 |
| 7200 | 2.558 | 0.512 | 2.07 |
| 7320 | 2.581 | 0.489 | 0.57 |



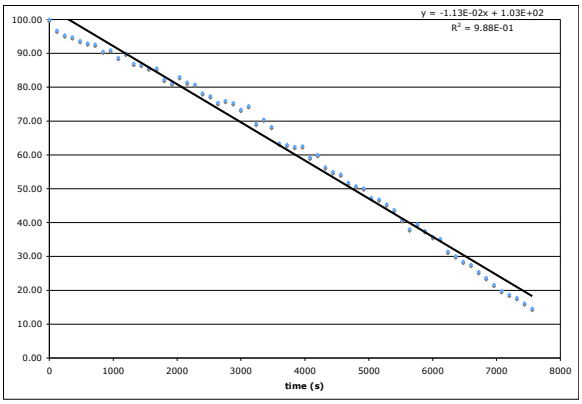

| | |
|---|---|
| $K^+$**5**$^-$ | 300 mM |
| **15** | 100 mM |
| Pd cat. | 5 mM |

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (66 mg, 0.30 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 1.13 x $10^{-2}$ mMs$^{-1}$**.

**Run 2**

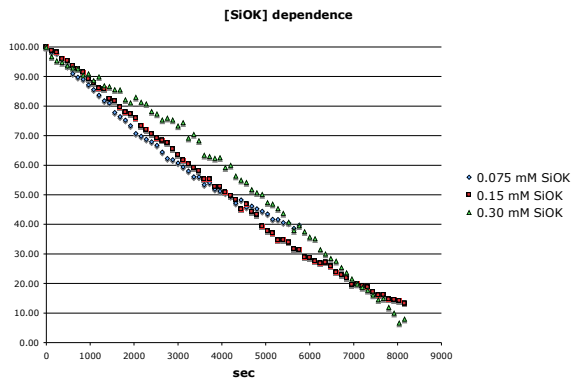
| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 0.997 | 1.135 | 100.00 |
| 120 | 0.959 | 1.254 | 96.78 |
| 240 | 0.961 | 1.214 | 95.40 |
| 360 | 0.966 | 1.196 | 94.81 |
| 480 | 0.966 | 1.189 | 93.75 |
| 600 | 0.948 | 1.176 | 92.99 |
| 720 | 0.943 | 1.166 | 92.66 |
| 840 | 0.987 | 1.162 | 90.59 |
| 960 | 0.997 | 1.136 | 91.00 |
| 1080 | 0.961 | 1.141 | 88.71 |
| 1200 | 0.974 | 1.112 | 89.92 |
| 1320 | 0.980 | 1.128 | 86.96 |
| 1440 | 0.954 | 1.091 | 86.66 |
| 1560 | 0.942 | 1.087 | 85.64 |
| 1680 | 0.951 | 1.074 | 85.56 |
| 1800 | 0.957 | 1.073 | 82.24 |
| 1920 | 0.959 | 1.031 | 81.19 |
| 2040 | 0.958 | 1.018 | 83.08 |
| 2160 | 0.973 | 1.042 | 81.40 |
| 2280 | 0.935 | 1.021 | 80.79 |
| 2400 | 0.939 | 1.013 | 78.26 |

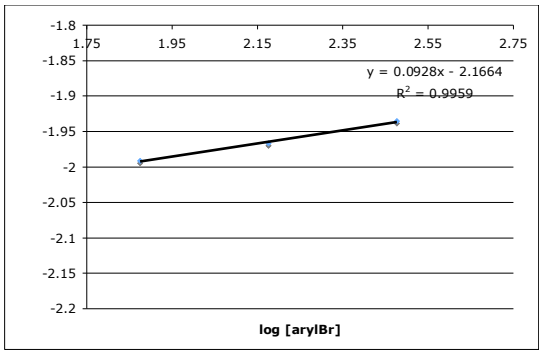
| | | | |
|---|---|---|---|
| 2520 | 0.963 | 0.981 | 77.42 |
| 2640 | 0.960 | 0.971 | 75.37 |
| 2760 | 0.963 | 0.945 | 76.00 |
| 2880 | 0.943 | 0.953 | 75.35 |
| 3000 | 0.954 | 0.945 | 73.37 |
| 3120 | 0.954 | 0.920 | 74.50 |
| 3240 | 0.954 | 0.934 | 69.22 |
| 3360 | 0.928 | 0.868 | 70.49 |
| 3480 | 0.962 | 0.884 | 68.36 |
| 3600 | 0.955 | 0.857 | 63.45 |
| 3720 | 0.968 | 0.796 | 63.01 |
| 3840 | 0.985 | 0.790 | 62.40 |
| 3960 | 0.939 | 0.782 | 62.59 |
| 4080 | 0.973 | 0.785 | 59.29 |
| 4200 | 0.926 | 0.743 | 60.03 |
| 4320 | 0.976 | 0.753 | 56.39 |
| 4440 | 0.947 | 0.707 | 54.99 |
| 4560 | 0.967 | 0.690 | 54.26 |
| 4680 | 0.949 | 0.680 | 51.83 |
| 4800 | 0.932 | 0.650 | 50.80 |
| 4920 | 0.971 | 0.637 | 50.19 |
| 5040 | 0.979 | 0.629 | 47.39 |
| 5160 | 0.946 | 0.594 | 46.92 |
| 5280 | 0.945 | 0.588 | 45.42 |
| 5400 | 0.921 | 0.570 | 43.77 |
| 5520 | 0.951 | 0.549 | 40.83 |
| 5640 | 0.958 | 0.512 | 38.04 |
| 5760 | 0.952 | 0.477 | 39.58 |
| 5880 | 0.963 | 0.496 | 37.59 |
| 6000 | 0.937 | 0.471 | 35.78 |
| 6120 | 0.936 | 0.449 | 35.25 |
| 6240 | 0.944 | 0.442 | 31.50 |
| 6360 | 0.936 | 0.395 | 30.06 |
| 6480 | 0.949 | 0.377 | 28.50 |
| 6600 | 0.970 | 0.357 | 27.58 |
| 6720 | 0.958 | 0.346 | 25.46 |
| 6840 | 0.970 | 0.319 | 23.72 |
| 6960 | 0.944 | 0.297 | 21.65 |
| 7080 | 0.935 | 0.272 | 19.84 |
| 7200 | 0.969 | 0.249 | 18.77 |
| 7320 | 0.935 | 0.235 | 17.78 |
| 7440 | 0.954 | 0.223 | 16.20 |
| 7560 | 0.942 | 0.203 | 14.60 |
| 7680 | 0.965 | 0.183 | 14.96 |
| 7800 | 0.917 | 0.188 | 12.02 |
| 7920 | 0.953 | 0.151 | 10.06 |
| 8040 | 0.982 | 0.126 | 6.70 |
| 8160 | 0.966 | 0.084 | 8.03 |
| 8280 | 0.934 | 0.101 | 7.37 |




**avg. rate = 1.22 x $10^{-2}$ $mMs^{-1}$ ± 1.2 x $10^{-3}$**

## Order in $K^{+}5^{-}$:



Order in **15**

$K^+$**5**$^-$ 150 mM

**15** 200 mM

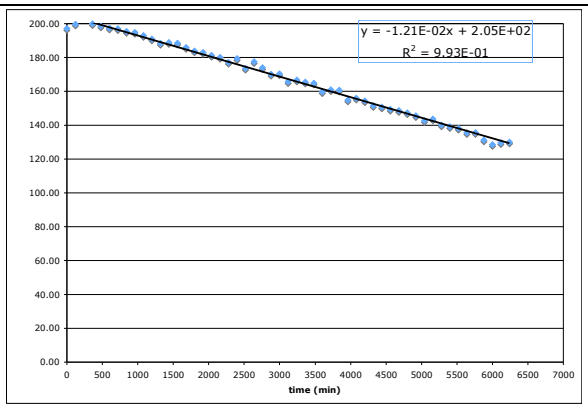
Pd cat. 5 mM

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **15** (22 μL, 35 mg, 0.20 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 1.12 x $10^{-2}$ mM$s^{-1}$**.

**Run 1**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 0.984 | 2.266 | 197.08 |
| 120 | 0.996 | 2.295 | 199.59 |
| 240 | 1.009 | 2.309 | 200.78 |
| 360 | 1.028 | 2.298 | 199.86 |
| 480 | 1.025 | 2.283 | 198.56 |
| 600 | 1.007 | 2.269 | 197.33 |
| 720 | 0.998 | 2.265 | 196.98 |
| 840 | 1.028 | 2.247 | 195.43 |
| 960 | 1.035 | 2.240 | 194.81 |
| 1080 | 1.029 | 2.219 | 192.97 |
| 1200 | 0.995 | 2.195 | 190.86 |
| 1320 | 0.982 | 2.166 | 188.33 |
| 1440 | 1.034 | 2.171 | 188.81 |
| 1560 | 1.017 | 2.167 | 188.39 |
| 1680 | 1.051 | 2.137 | 185.82 |
| 1800 | 1.030 | 2.113 | 183.78 |
| 1920 | 1.022 | 2.104 | 182.94 |
| 2040 | 1.008 | 2.084 | 181.19 |
| 2160 | 1.028 | 2.070 | 180.01 |
| 2280 | 1.035 | 2.037 | 177.09 |
| 2400 | 1.003 | 2.062 | 179.31 |
| 2520 | 1.023 | 1.996 | 173.59 |
| 2640 | 0.989 | 2.041 | 177.46 |
| 2760 | 1.034 | 2.000 | 173.92 |
| 2880 | 1.020 | 1.955 | 170.01 |
| 3000 | 1.001 | 1.959 | 170.32 |
| 3120 | 1.026 | 1.905 | 165.64 |
| 3240 | 1.009 | 1.917 | 166.66 |
| 3360 | 1.023 | 1.902 | 165.42 |
| 3480 | 1.004 | 1.896 | 164.83 |
| 3600 | 1.025 | 1.836 | 159.66 |
| 3720 | 0.991 | 1.850 | 160.87 |
| 3840 | 1.018 | 1.847 | 160.64 |
| 3960 | 1.040 | 1.780 | 154.82 |
| 4080 | 1.019 | 1.793 | 155.94 |

| | | | |
|---|---|---|---|
| 4200 | 0.999 | 1.775 | 154.36 |
| 4320 | 1.026 | 1.742 | 151.50 |
| 4440 | 1.017 | 1.732 | 150.63 |
| 4560 | 1.009 | 1.718 | 149.36 |
| 4680 | 0.998 | 1.709 | 148.64 |
| 4800 | 1.026 | 1.694 | 147.29 |
| 4920 | 1.019 | 1.674 | 145.54 |
| 5040 | 1.019 | 1.640 | 142.62 |
| 5160 | 0.994 | 1.651 | 143.57 |
| 5280 | 1.012 | 1.610 | 140.03 |
| 5400 | 1.039 | 1.599 | 139.08 |
| 5520 | 0.998 | 1.589 | 138.16 |
| 5640 | 0.995 | 1.559 | 135.53 |
| 5760 | 0.985 | 1.559 | 135.60 |
| 5880 | 1.004 | 1.508 | 131.13 |
| 6000 | 0.983 | 1.478 | 128.49 |
| 6120 | 1.007 | 1.490 | 129.54 |
| 6240 | 1.020 | 1.494 | 129.94 |
| 6360 | 1.033 | 1.463 | 127.23 |
| 6480 | 0.984 | 1.437 | 124.99 |
| 6600 | 0.991 | 1.379 | 119.89 |
| 6720 | 1.025 | 1.360 | 118.28 |
| 6840 | 1.050 | 1.345 | 116.99 |
| 6960 | 1.009 | 1.340 | 116.52 |
| 7080 | 1.032 | 1.320 | 114.79 |
| 7200 | 1.005 | 1.355 | 117.87 |
| 7320 | 1.003 | 1.329 | 115.59 |
| 7440 | 1.040 | 1.316 | 114.41 |
| 7560 | 0.993 | 1.314 | 114.26 |
| 7680 | 1.010 | 1.291 | 112.29 |
| 7800 | 1.012 | 1.264 | 109.91 |
| 7920 | 1.020 | 1.272 | 110.57 |
| 8040 | 1.019 | 1.269 | 110.34 |
| 8160 | 1.030 | 1.273 | 110.68 |
| 8280 | 1.008 | 1.235 | 107.43 |



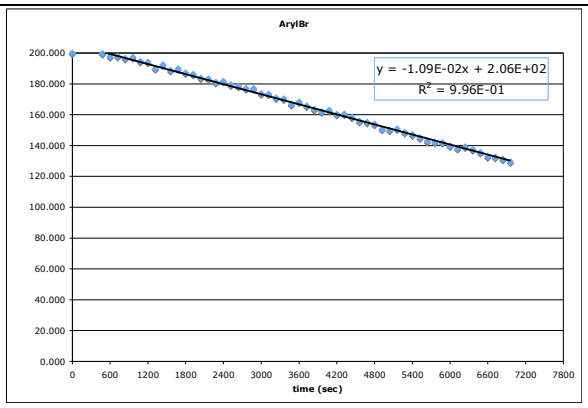

| | |
|---|---|
| $K^+$**5**$^-$ | 150 mM |
| **15** | 200 mM |
| Pd cat. | 5 mM |

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **15** (22 μL, 35 mg, 0.20 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 1.09 x $10^{-2}$ mM$s^{-1}$**.

**Run 2**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 4.745 | 7.762 | 100.00 |
| 120 | 4.728 | 7.791 | 100.37 |
| 240 | 4.714 | 7.745 | 99.78 |
| 360 | 4.669 | 7.762 | 100.00 |
| 480 | 4.657 | 7.610 | 98.04 |
| 600 | 4.672 | 7.555 | 97.34 |
| 720 | 4.726 | 7.648 | 98.53 |
| 840 | 4.689 | 7.541 | 97.15 |
| 960 | 4.715 | 7.605 | 97.98 |
| 1080 | 4.697 | 7.477 | 96.33 |
| 1200 | 4.715 | 7.487 | 96.46 |
| 1320 | 4.727 | 7.345 | 94.63 |
| 1440 | 4.730 | 7.441 | 95.87 |
| 1560 | 4.719 | 7.287 | 93.88 |
| 1680 | 4.756 | 7.388 | 95.18 |
| 1800 | 4.868 | 7.451 | 96.00 |
| 1920 | 4.810 | 7.327 | 94.40 |
| 2040 | 4.810 | 7.233 | 93.19 |
| 2160 | 4.847 | 7.265 | 93.60 |
| 2280 | 4.818 | 7.132 | 91.88 |
| 2400 | 4.774 | 7.097 | 91.43 |
| 2520 | 4.784 | 7.020 | 90.44 |
| 2640 | 4.844 | 7.073 | 91.13 |
| 2760 | 4.811 | 6.966 | 89.74 |
| 2880 | 4.758 | 6.890 | 88.77 |
| 3000 | 4.856 | 6.896 | 88.84 |
| 3120 | 4.811 | 6.827 | 87.95 |
| 3240 | 4.842 | 6.767 | 87.18 |
| 3360 | 4.832 | 6.732 | 86.73 |
| 3480 | 4.872 | 6.645 | 85.61 |
| 3600 | 4.821 | 6.638 | 85.52 |
| 3720 | 4.840 | 6.558 | 84.49 |
| 3840 | 4.870 | 6.512 | 83.90 |
| 3960 | 4.868 | 6.453 | 83.14 |
| 4080 | 4.848 | 6.463 | 83.27 |
| 4200 | 4.946 | 6.487 | 83.57 |
| 4320 | 4.871 | 6.391 | 82.33 |
| 4440 | 4.904 | 6.357 | 81.90 |
| 4560 | 4.950 | 6.307 | 81.26 |
| 4680 | 4.907 | 6.224 | 80.19 |
| 4800 | 4.922 | 6.195 | 79.81 |
| 4920 | 4.930 | 6.078 | 78.31 |
| 5040 | 4.979 | 6.109 | 78.70 |

| | | | |
|---|---|---|---|
| 5160 | 4.926 | 6.075 | 78.27 |
| 5280 | 4.948 | 6.012 | 77.46 |
| 5400 | 4.933 | 5.934 | 76.45 |
| 5520 | 4.906 | 5.823 | 75.02 |
| 5640 | 4.949 | 5.782 | 74.49 |
| 5760 | 4.992 | 5.804 | 74.78 |
| 5880 | 4.903 | 5.695 | 73.37 |
| 6000 | 4.896 | 5.601 | 72.16 |
| 6120 | 4.907 | 5.546 | 71.45 |
| 6240 | 4.869 | 5.541 | 71.38 |
| 6360 | 4.871 | 5.478 | 70.58 |
| 6480 | 4.894 | 5.425 | 69.89 |
| 6600 | 4.940 | 5.367 | 69.15 |
| 6720 | 4.971 | 5.387 | 69.40 |
| 6840 | 4.980 | 5.343 | 68.83 |
| 6960 | 4.926 | 5.215 | 67.19 |
| 7080 | 4.929 | 5.154 | 66.40 |
| 7200 | 4.913 | 5.177 | 66.70 |
| 7320 | 4.923 | 5.092 | 65.60 |




**avg. rate = 1.15 x $10^{-2}$ $s^{-1}$ ± 8.5 x $10^{-4}$**

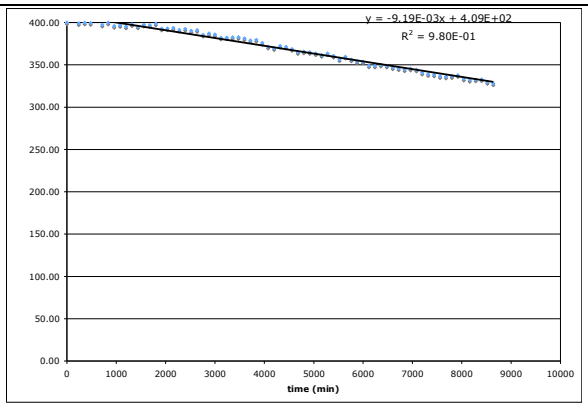
| | |
|---|---|
| $K^+$**5**$^-$ | 150 mM |
| **15** | 400 mM |
| Pd cat. | 5 mM |

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **15** (44 μL, 70 mg, 0.20 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 9.19 x $10^{-3}$ $mMs^{-1}$**.

**Run 1**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 2.424 | 8.506 | 400.02 |
| 120 | 2.445 | 8.559 | 402.47 |
| 240 | 2.466 | 8.484 | 398.96 |
| 360 | 2.464 | 8.500 | 399.70 |
| 480 | 2.491 | 8.492 | 399.35 |
| 600 | 2.486 | 8.511 | 400.23 |
| 720 | 2.502 | 8.450 | 397.37 |
| 840 | 2.483 | 8.501 | 399.77 |
| 960 | 2.511 | 8.420 | 395.95 |
| 1080 | 2.498 | 8.436 | 396.73 |
| 1200 | 2.506 | 8.405 | 395.24 |
| 1320 | 2.576 | 8.460 | 397.82 |
| 1440 | 2.556 | 8.403 | 395.15 |
| 1560 | 2.543 | 8.446 | 397.20 |
| 1680 | 2.535 | 8.440 | 396.87 |
| 1800 | 2.554 | 8.478 | 398.70 |
| 1920 | 2.555 | 8.350 | 392.68 |
| 2040 | 2.574 | 8.355 | 392.88 |
| 2160 | 2.558 | 8.369 | 393.55 |
| 2280 | 2.574 | 8.322 | 391.33 |
| 2400 | 2.575 | 8.346 | 392.50 |
| 2520 | 2.546 | 8.297 | 390.17 |
| 2640 | 2.578 | 8.315 | 391.00 |
| 2760 | 2.576 | 8.194 | 385.34 |
| 2880 | 2.584 | 8.234 | 387.21 |
| 3000 | 2.603 | 8.207 | 385.93 |
| 3120 | 2.583 | 8.124 | 382.03 |
| 3240 | 2.618 | 8.129 | 382.28 |
| 3360 | 2.631 | 8.131 | 382.35 |
| 3480 | 2.566 | 8.137 | 382.65 |
| 3600 | 2.610 | 8.107 | 381.25 |
| 3720 | 2.622 | 8.057 | 378.90 |
| 3840 | 2.619 | 8.069 | 379.44 |
| 3960 | 2.602 | 7.992 | 375.82 |
| 4080 | 2.626 | 7.896 | 371.33 |
| 4200 | 2.574 | 7.860 | 369.61 |
| 4320 | 2.634 | 7.918 | 372.34 |
| 4440 | 2.643 | 7.893 | 371.18 |
| 4560 | 2.639 | 7.836 | 368.51 |
| 4680 | 2.923 | 7.762 | 365.02 |
| 4800 | 2.606 | 7.778 | 365.77 |
| 4920 | 2.624 | 7.761 | 364.95 |
| 5040 | 2.620 | 7.730 | 363.51 |
| 5160 | 2.605 | 7.688 | 361.51 |
| 5280 | 2.618 | 7.728 | 363.40 |
| 5400 | 2.639 | 7.668 | 360.61 |
| 5520 | 2.628 | 7.580 | 356.46 |
| 5640 | 2.634 | 7.646 | 359.57 |
| 5760 | 2.631 | 7.576 | 356.26 |
| 5880 | 2.638 | 7.529 | 354.05 |
| 6000 | 2.657 | 7.522 | 353.75 |
| 6120 | 2.620 | 7.422 | 349.04 |

| | | | |
|---|---|---|---|
| 6240 | 2.623 | 7.419 | 348.87 |
| 6360 | 2.625 | 7.444 | 350.05 |
| 6480 | 2.634 | 7.420 | 348.93 |
| 6600 | 2.646 | 7.379 | 346.99 |
| 6720 | 2.637 | 7.351 | 345.68 |
| 6840 | 2.636 | 7.325 | 344.47 |
| 6960 | 2.646 | 7.347 | 345.52 |
| 7080 | 2.645 | 7.319 | 344.17 |
| 7200 | 2.650 | 7.242 | 340.58 |
| 7320 | 2.638 | 7.204 | 338.79 |
| 7440 | 2.680 | 7.198 | 338.47 |
| 7560 | 2.626 | 7.152 | 336.34 |
| 7680 | 2.611 | 7.144 | 335.93 |
| 7800 | 2.663 | 7.156 | 336.51 |
| 7920 | 2.671 | 7.178 | 337.56 |
| 8040 | 2.631 | 7.092 | 333.50 |
| 8160 | 2.645 | 7.062 | 332.09 |
| 8280 | 2.633 | 7.071 | 332.51 |
| 8400 | 2.631 | 7.078 | 332.85 |
| 8520 | 2.634 | 7.009 | 329.60 |
| 8640 | 2.647 | 6.973 | 327.90 |




**Run 3**

$K^+$**5**$^-$ 150 mM

**15** 400 mM

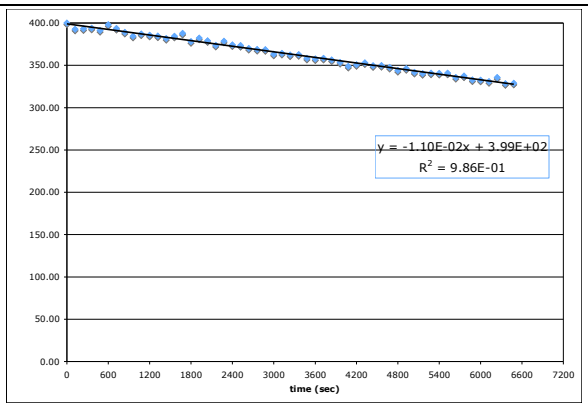
Pd cat. 5 mM

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **15** (44 μL, 70 mg, 0.20 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 1.10 x $10^{-2}$ mMs$^{-1}$**.

**Run 2**

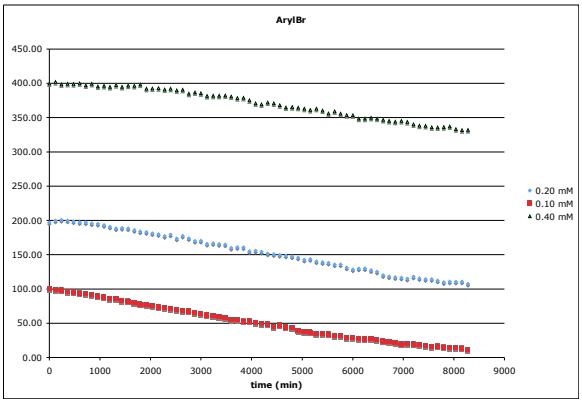
| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 5.088 | 16.116 | 400.01 |
| 120 | 5.087 | 15.823 | 392.72 |
| 240 | 5.061 | 15.839 | 393.12 |
| 360 | 5.124 | 15.868 | 393.85 |
| 480 | 5.136 | 15.762 | 391.22 |
| 600 | 5.129 | 16.033 | 397.93 |
| 720 | 5.114 | 15.862 | 393.69 |
| 840 | 5.119 | 15.671 | 388.97 |
| 960 | 5.122 | 15.492 | 384.52 |
| 1080 | 5.063 | 15.600 | 387.18 |
| 1200 | 5.072 | 15.535 | 385.59 |
| 1320 | 5.067 | 15.494 | 384.55 |
| 1440 | 5.102 | 15.384 | 381.82 |
| 1560 | 5.103 | 15.489 | 384.43 |
| 1680 | 5.092 | 15.630 | 387.93 |
| 1800 | 5.102 | 15.229 | 377.98 |
| 1920 | 5.108 | 15.395 | 382.12 |
| 2040 | 5.125 | 15.268 | 378.96 |
| 2160 | 5.129 | 15.058 | 373.73 |
| 2280 | 5.105 | 15.255 | 378.63 |
| 2400 | 5.125 | 15.073 | 374.11 |
| 2520 | 5.076 | 15.043 | 373.36 |
| 2640 | 5.117 | 14.913 | 370.15 |
| 2760 | 5.091 | 14.861 | 368.85 |
| 2880 | 5.144 | 14.846 | 368.48 |
| 3000 | 5.085 | 14.637 | 363.29 |
| 3120 | 5.105 | 14.670 | 364.12 |
| 3240 | 5.142 | 14.592 | 362.16 |
| 3360 | 5.106 | 14.611 | 362.66 |
| 3480 | 5.142 | 14.441 | 358.43 |
| 3600 | 5.098 | 14.412 | 357.71 |
| 3720 | 5.131 | 14.434 | 358.25 |
| 3840 | 5.113 | 14.359 | 356.39 |
| 3960 | 5.091 | 14.243 | 353.52 |
| 4080 | 5.087 | 14.059 | 348.94 |
| 4200 | 5.177 | 14.129 | 350.69 |
| 4320 | 5.171 | 14.225 | 353.07 |
| 4440 | 5.219 | 14.085 | 349.60 |
| 4560 | 5.177 | 14.099 | 349.93 |
| 4680 | 5.250 | 14.010 | 347.74 |
| 4800 | 5.132 | 13.857 | 343.93 |
| 4920 | 5.230 | 13.947 | 346.16 |
| 5040 | 5.190 | 13.766 | 341.67 |
| 5160 | 5.196 | 13.709 | 340.26 |
| 5280 | 5.208 | 13.726 | 340.69 |
| 5400 | 5.207 | 13.719 | 340.50 |
| 5520 | 5.235 | 13.729 | 340.76 |
| 5640 | 5.190 | 13.528 | 335.77 |
| 5760 | 5.186 | 13.597 | 337.47 |
| 5880 | 5.187 | 13.411 | 332.86 |
| 6000 | 5.161 | 13.400 | 332.59 |
| 6120 | 5.198 | 13.326 | 330.76 |

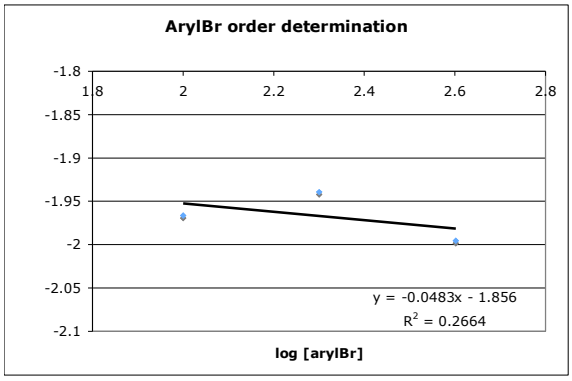
| | | | |
|---|---|---|---|
| 6240 | 5.255 | 13.530 | 335.81 |
| 6360 | 5.116 | 13.226 | 328.27 |
| 6480 | 5.179 | 13.245 | 328.75 |
| 6600 | 5.190 | 13.283 | 329.67 |




**avg. rate = 1.01 x $10^{-2}$ mM$s^{-1}$ ± 1.3 x $10^{-3}$**

## Order in 15 with (*t*-$Bu_3P)_2Pd$:



Order in Pd with ($t$-$Bu_3P)_2Pd$

$K^+$**5**$^-$ 150 mM

**15** 100 mM

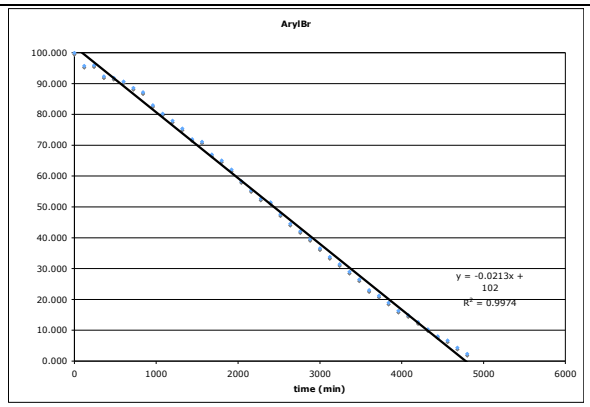
Pd cat. 10 mM

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (5.1 mg, 0.010 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 2.13 x $10^{-2}$ $mMs^{-1}$**.

**Run 1**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 2.881 | 2.434 | 99.959 |
| 120 | 2.925 | 2.366 | 95.725 |
| 240 | 2.930 | 2.375 | 95.921 |
| 360 | 2.925 | 2.282 | 92.340 |
| 480 | 2.941 | 2.282 | 91.820 |
| 600 | 2.927 | 2.241 | 90.621 |
| 720 | 2.946 | 2.205 | 88.589 |
| 840 | 2.927 | 2.157 | 87.199 |
| 960 | 2.948 | 2.066 | 82.945 |
| 1080 | 2.976 | 2.017 | 80.188 |
| 1200 | 2.970 | 1.956 | 77.924 |
| 1320 | 2.999 | 1.911 | 75.425 |
| 1440 | 3.014 | 1.832 | 71.905 |
| 1560 | 2.974 | 1.787 | 71.121 |
| 1680 | 3.016 | 1.707 | 66.966 |
| 1800 | 3.028 | 1.665 | 65.063 |
| 1920 | 3.015 | 1.582 | 62.103 |
| 2040 | 3.045 | 1.501 | 58.331 |
| 2160 | 3.062 | 1.434 | 55.410 |
| 2280 | 3.033 | 1.350 | 52.661 |
| 2400 | 3.040 | 1.321 | 51.444 |
| 2520 | 3.055 | 1.228 | 47.562 |
| 2640 | 3.056 | 1.149 | 44.488 |
| 2760 | 3.069 | 1.092 | 42.122 |
| 2880 | 3.054 | 1.021 | 39.575 |
| 3000 | 3.042 | 0.940 | 36.580 |
| 3120 | 3.045 | 0.869 | 33.776 |
| 3240 | 3.034 | 0.805 | 31.398 |
| 3360 | 3.053 | 0.747 | 28.939 |
| 3480 | 3.055 | 0.684 | 26.504 |
| 3600 | 3.069 | 0.596 | 22.992 |
| 3720 | 3.029 | 0.542 | 21.182 |
| 3840 | 3.079 | 0.492 | 18.913 |
| 3960 | 3.080 | 0.425 | 16.335 |
| 4080 | 3.074 | 0.388 | 14.931 |

| | | | |
|---|---|---|---|
| 4200 | 3.093 | 0.331 | 12.666 |
| 4320 | 3.036 | 0.264 | 10.283 |
| 4440 | 3.103 | 0.211 | 8.037 |
| 4560 | 3.085 | 0.174 | 6.677 |
| 4680 | 3.092 | 0.113 | 4.324 |
| 4800 | 3.084 | 0.061 | 2.327 |




$K^+$**5**$^-$ 150 mM

**15** 100 mM

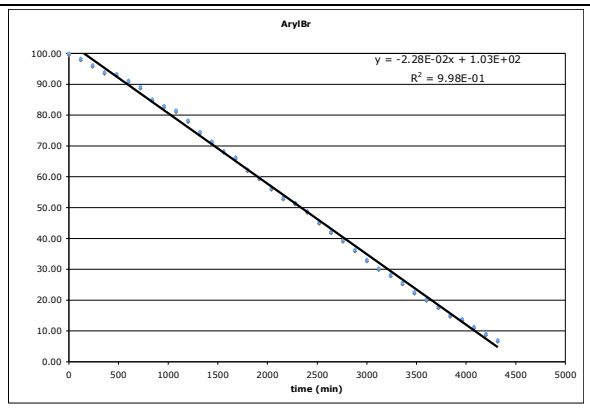
Pd cat. 10 mM

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (5.1 mg, 0.010 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 2.28 x $10^{-2}$ mMs$^{-1}$**.

**Run 2**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 3.160 | 2.534 | 100.01 |
| 120 | 3.175 | 2.491 | 98.31 |
| 240 | 3.149 | 2.439 | 96.26 |
| 360 | 3.161 | 2.382 | 94.01 |
| 480 | 3.139 | 2.366 | 93.37 |
| 600 | 3.150 | 2.312 | 91.22 |
| 720 | 3.158 | 2.260 | 89.19 |
| 840 | 3.145 | 2.157 | 85.13 |
| 960 | 3.171 | 2.103 | 83.00 |
| 1080 | 3.176 | 2.067 | 81.56 |
| 1200 | 3.154 | 1.985 | 78.32 |
| 1320 | 3.143 | 1.891 | 74.62 |
| 1440 | 3.155 | 1.813 | 71.55 |
| 1560 | 3.157 | 1.733 | 68.39 |
| 1680 | 3.132 | 1.680 | 66.28 |

| | | | |
|---|---|---|---|
| 1800 | 3.196 | 1.580 | 62.37 |
| 1920 | 3.165 | 1.514 | 59.76 |
| 2040 | 3.195 | 1.428 | 56.34 |
| 2160 | 3.169 | 1.348 | 53.21 |
| 2280 | 3.182 | 1.307 | 51.57 |
| 2400 | 3.176 | 1.239 | 48.88 |
| 2520 | 3.154 | 1.148 | 45.32 |
| 2640 | 3.172 | 1.071 | 42.28 |
| 2760 | 3.166 | 1.001 | 39.52 |
| 2880 | 3.124 | 0.922 | 36.39 |
| 3000 | 3.207 | 0.840 | 33.16 |
| 3120 | 3.150 | 0.770 | 30.37 |
| 3240 | 3.196 | 0.717 | 28.29 |
| 3360 | 3.195 | 0.650 | 25.65 |
| 3480 | 3.171 | 0.575 | 22.68 |
| 3600 | 3.191 | 0.515 | 20.32 |
| 3720 | 3.194 | 0.454 | 17.90 |
| 3840 | 3.178 | 0.385 | 15.18 |
| 3960 | 3.190 | 0.352 | 13.88 |
| 4080 | 3.192 | 0.290 | 11.44 |
| 4200 | 3.164 | 0.232 | 9.15 |
| 4320 | 3.138 | 0.179 | 7.06 |

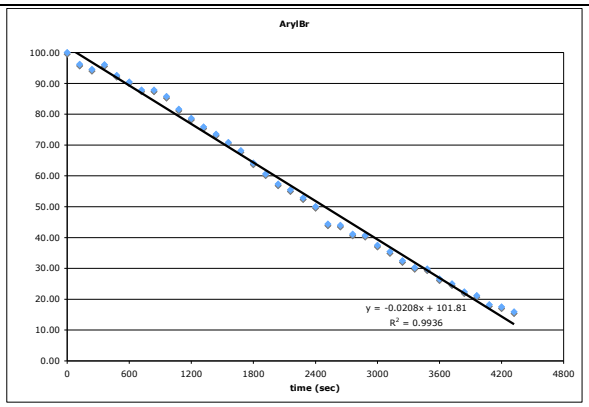



| | |
|---|---|
| $K^+$**5**$^-$ | 150 mM |
| **15** | 100 mM |
| Pd cat. | 10 mM |

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (5.1 mg, 0.010 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 2.08 x $10^{-2}$ mMs$^{-1}$**.

**Run 3**

| Time (s) | Integral IS (-63.2 ppm) | Integral **25** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 3.160 | 2.534 | 99.99 |
| 120 | 3.175 | 2.491 | 96.21 |
| 240 | 3.149 | 2.439 | 94.49 |
| 360 | 3.161 | 2.382 | 96.07 |
| 480 | 3.139 | 2.366 | 92.59 |
| 600 | 3.150 | 2.312 | 90.44 |
| 720 | 3.158 | 2.260 | 87.80 |
| 840 | 3.145 | 2.157 | 87.83 |
| 960 | 3.171 | 2.103 | 85.77 |
| 1080 | 3.176 | 2.067 | 81.60 |
| 1200 | 3.154 | 1.985 | 78.69 |
| 1320 | 3.143 | 1.891 | 75.84 |
| 1440 | 3.155 | 1.813 | 73.53 |
| 1560 | 3.157 | 1.733 | 70.86 |
| 1680 | 3.132 | 1.680 | 68.19 |
| 1800 | 3.196 | 1.580 | 64.16 |
| 1920 | 3.165 | 1.514 | 60.65 |
| 2040 | 3.195 | 1.428 | 57.37 |
| 2160 | 3.169 | 1.348 | 55.50 |
| 2280 | 3.182 | 1.307 | 52.85 |
| 2400 | 3.176 | 1.239 | 50.09 |
| 2520 | 3.154 | 1.148 | 44.38 |
| 2640 | 3.172 | 1.071 | 43.98 |
| 2760 | 3.166 | 1.001 | 41.12 |
| 2880 | 3.124 | 0.922 | 40.69 |
| 3000 | 3.207 | 0.840 | 37.52 |
| 3120 | 3.150 | 0.770 | 35.41 |
| 3240 | 3.196 | 0.717 | 32.49 |
| 3360 | 3.195 | 0.650 | 30.31 |
| 3480 | 3.171 | 0.575 | 29.83 |
| 3600 | 3.191 | 0.515 | 26.60 |
| 3720 | 3.194 | 0.454 | 25.01 |
| 3840 | 3.178 | 0.385 | 22.41 |
| 3960 | 3.190 | 0.352 | 21.17 |
| 4080 | 3.192 | 0.290 | 18.22 |
| 4200 | 3.164 | 0.232 | 17.55 |
| 4320 | 3.138 | 0.179 | 15.89 |




**avg. rate = 2.16 x $10^{-2}$ $mMs^{-1}$ ± 1.0 x $10^{-3}$**

$K^+$**5**$^-$ 150 mM

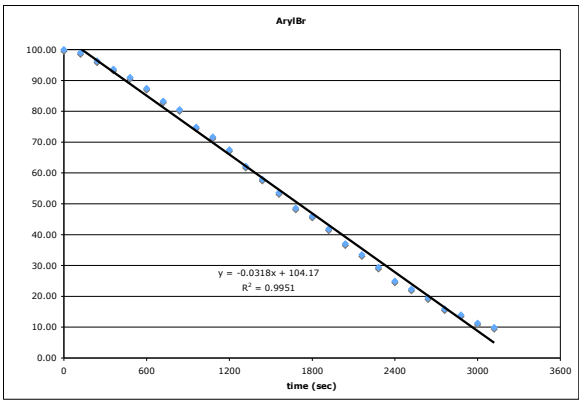
**15** 100 mM

Pd cat. 15 mM

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (7.6 mg, 0.015 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 3.18 x $10^{-2}$ mM$s^{-1}$**.

**Run 1**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 2.415 | 3.030 | 99.99 |
| 120 | 2.364 | 3.000 | 99.00 |
| 240 | 2.377 | 2.919 | 96.33 |
| 360 | 2.392 | 2.837 | 93.63 |
| 480 | 2.364 | 2.757 | 90.98 |
| 600 | 2.399 | 2.648 | 87.40 |
| 720 | 2.359 | 2.524 | 83.30 |
| 840 | 2.324 | 2.441 | 80.56 |
| 960 | 2.391 | 2.269 | 74.88 |
| 1080 | 2.323 | 2.171 | 71.65 |
| 1200 | 2.359 | 2.045 | 67.50 |
| 1320 | 2.384 | 1.883 | 62.14 |
| 1440 | 2.398 | 1.757 | 57.98 |
| 1560 | 2.372 | 1.625 | 53.63 |
| 1680 | 2.359 | 1.472 | 48.57 |
| 1800 | 2.381 | 1.392 | 45.96 |
| 1920 | 2.344 | 1.267 | 41.82 |
| 2040 | 2.347 | 1.122 | 37.04 |
| 2160 | 2.372 | 1.015 | 33.50 |
| 2280 | 2.346 | 0.891 | 29.39 |
| 2400 | 2.374 | 0.755 | 24.92 |
| 2520 | 2.305 | 0.676 | 22.31 |
| 2640 | 2.313 | 0.592 | 19.53 |
| 2760 | 2.314 | 0.482 | 15.90 |
| 2880 | 2.301 | 0.423 | 13.95 |
| 3000 | 2.304 | 0.343 | 11.31 |
| 3120 | 2.340 | 0.300 | 9.90 |
| 3240 | 2.347 | 0.257 | 8.47 |
| 3360 | 2.329 | 0.226 | 7.44 |



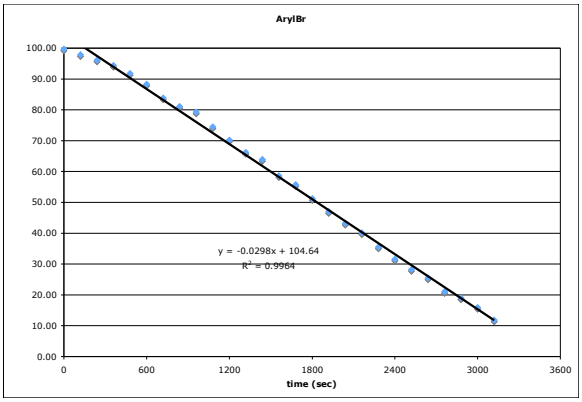

| | |
|---|---|
| $K^+$**5**$^-$ | 150 mM |
| **15** | 100 mM |
| Pd cat. | 15 mM |

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (7.6 mg, 0.015 mmol), benzotrifluoride (5 μL) and **24** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**12**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 2.98 x $10^{-2}$ mMs$^{-1}$**.

**Run 2**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 5.023 | 4.397 | 99.64 |
| 120 | 5.012 | 4.319 | 97.88 |
| 240 | 5.042 | 4.242 | 96.12 |
| 360 | 5.109 | 4.166 | 94.40 |
| 480 | 5.117 | 4.050 | 91.77 |
| 600 | 5.148 | 3.896 | 88.29 |
| 720 | 5.049 | 3.698 | 83.80 |
| 840 | 5.028 | 3.578 | 81.08 |
| 960 | 5.023 | 3.498 | 79.26 |
| 1080 | 5.006 | 3.286 | 74.47 |
| 1200 | 5.050 | 3.098 | 70.19 |
| 1320 | 5.041 | 2.920 | 66.17 |
| 1440 | 5.522 | 2.618 | 63.92 |
| 1560 | 5.045 | 2.587 | 58.63 |
| 1680 | 5.038 | 2.462 | 55.78 |
| 1800 | 5.081 | 2.259 | 51.19 |
| 1920 | 5.073 | 2.073 | 46.99 |
| 2040 | 5.080 | 1.906 | 43.20 |
| 2160 | 5.096 | 1.769 | 40.08 |
| 2280 | 5.090 | 1.566 | 35.47 |
| 2400 | 5.069 | 1.392 | 31.55 |

| | | | |
|---|---|---|---|
| 2520 | 5.053 | 1.244 | 28.19 |
| 2640 | 5.091 | 1.123 | 25.44 |
| 2760 | 5.097 | 0.931 | 21.09 |
| 2880 | 5.113 | 0.839 | 19.01 |
| 3000 | 5.101 | 0.703 | 15.93 |
| 3120 | 5.090 | 0.523 | 11.85 |
| 3240 | 5.060 | 0.471 | 10.67 |



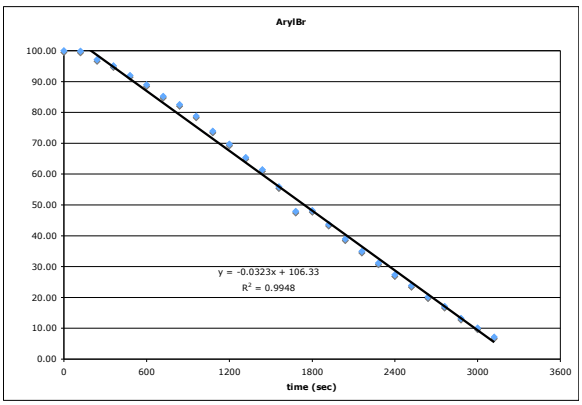

| | |
|---|---|
| $K^+$**5**$^-$ | 150 mM |
| **15** | 100 mM |
| Pd cat. | 15 mM |

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (7.6 mg, 0.015 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 3.23 x $10^{-2}$ mM$s^{-1}$**.

**Run 3**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 5.038 | 4.680 | 100.00 |
| 120 | 5.020 | 4.674 | 99.86 |
| 240 | 5.021 | 4.545 | 97.12 |
| 360 | 5.027 | 4.451 | 95.10 |
| 480 | 5.022 | 4.304 | 91.96 |
| 600 | 4.993 | 4.163 | 88.96 |
| 720 | 5.005 | 3.987 | 85.20 |
| 840 | 5.019 | 3.863 | 82.55 |
| 960 | 5.000 | 3.688 | 78.81 |
| 1080 | 5.085 | 3.461 | 73.95 |
| 1200 | 5.061 | 3.262 | 69.69 |
| 1320 | 5.040 | 3.061 | 65.40 |
| 1440 | 4.993 | 2.874 | 61.41 |
| 1560 | 4.999 | 2.614 | 55.85 |

| | | | |
|---|---|---|---|
| 1680 | 5.612 | 2.245 | 47.96 |
| 1800 | 4.983 | 2.254 | 48.17 |
| 1920 | 4.993 | 2.046 | 43.73 |
| 2040 | 5.017 | 1.823 | 38.96 |
| 2160 | 5.031 | 1.638 | 34.99 |
| 2280 | 5.062 | 1.458 | 31.15 |
| 2400 | 5.024 | 1.278 | 27.31 |
| 2520 | 5.016 | 1.116 | 23.86 |
| 2640 | 5.027 | 0.946 | 20.21 |
| 2760 | 5.009 | 0.801 | 17.11 |
| 2880 | 5.010 | 0.620 | 13.24 |
| 3000 | 5.055 | 0.472 | 10.09 |
| 3120 | 5.059 | 0.336 | 7.18 |
| 3240 | 5.020 | 0.274 | 5.85 |




**avg. rate = 3.13 x $10^{-2}$ mM$s^{-1}$ ± 1.3 x $10^{-3}$**

$K^+$**5**$^-$ 150 mM

**15** 100 mM

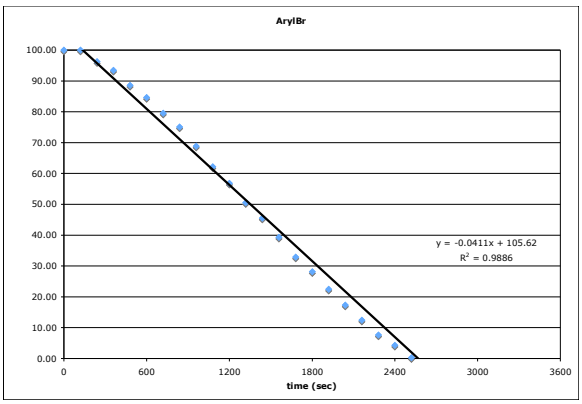
Pd cat. 20 mM

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (10.2 mg, 0.020 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 4.11 x $10^{-2}$ mM$s^{-1}$**.

**Run 1**

| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 2.813 | 2.571 | 100.00 |
| 120 | 2.757 | 2.570 | 99.98 |
| 240 | 2.806 | 2.474 | 96.23 |
| 360 | 2.818 | 2.403 | 93.45 |
| 480 | 2.800 | 2.277 | 88.55 |

| | | | |
|---|---|---|---|
| 600 | 2.790 | 2.176 | 84.62 |
| 720 | 2.788 | 2.044 | 79.51 |
| 840 | 2.780 | 1.929 | 75.04 |
| 960 | 2.799 | 1.770 | 68.86 |
| 1080 | 2.809 | 1.599 | 62.19 |
| 1200 | 2.777 | 1.460 | 56.81 |
| 1320 | 2.814 | 1.299 | 50.53 |
| 1440 | 2.771 | 1.171 | 45.54 |
| 1560 | 2.789 | 1.011 | 39.33 |
| 1680 | 2.811 | 0.845 | 32.87 |
| 1800 | 2.797 | 0.724 | 28.17 |
| 1920 | 2.759 | 0.577 | 22.43 |
| 2040 | 2.777 | 0.445 | 17.31 |
| 2160 | 2.765 | 0.319 | 12.40 |
| 2280 | 2.797 | 0.196 | 7.63 |
| 2400 | 2.821 | 0.109 | 4.25 |
| 2520 | 2.766 | 0.008 | 0.30 |




$K^+$**5**$^-$ 150 mM

**15** 100 mM

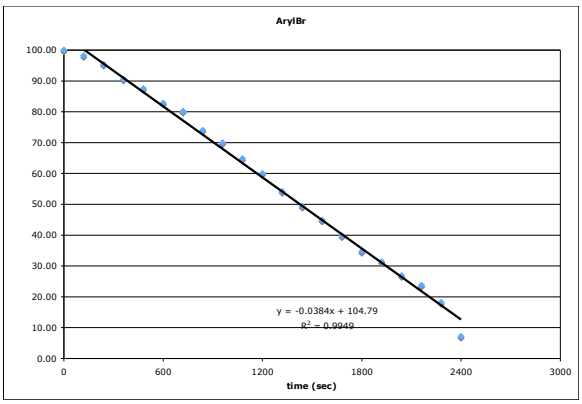
Pd cat. 20 mM

Following General Procedure IV, a mixture of ($t$-$Bu_3P)_2Pd$ (10.2 mg, 0.020 mmol), benzotrifluoride (5 μL) and **15** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+$**5**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by $^{19}F$ NMR spectroscopy. **rate = 3.84 x $10^{-2}$ mMs$^{-1}$**.

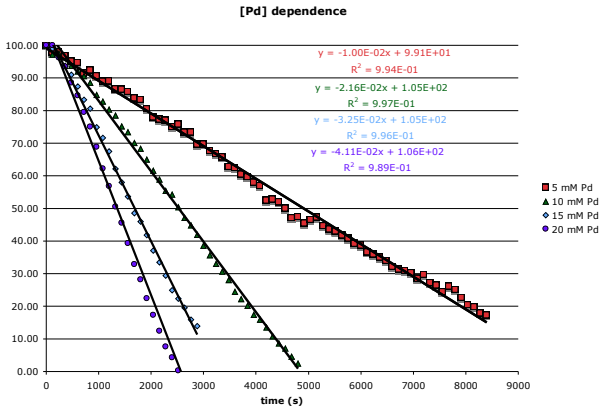
**Run 2**

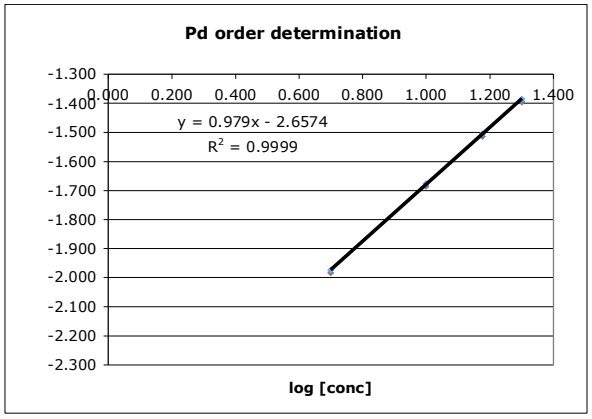
| Time (s) | Integral IS (-63.2 ppm) | Integral **15** (-115.9 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 2.661 | 3.132 | 100.00 |
| 120 | 2.633 | 3.076 | 98.21 |
| 240 | 2.610 | 2.988 | 95.40 |
| 360 | 2.569 | 2.837 | 90.59 |

| | | | |
|---|---|---|---|
| 480 | 2.591 | 2.741 | 87.52 |
| 600 | 2.537 | 2.594 | 82.82 |
| 720 | 2.509 | 2.509 | 80.12 |
| 840 | 2.508 | 2.317 | 73.97 |
| 960 | 2.492 | 2.189 | 69.90 |
| 1080 | 2.548 | 2.028 | 64.74 |
| 1200 | 2.462 | 1.878 | 59.96 |
| 1320 | 2.491 | 1.695 | 54.13 |
| 1440 | 2.517 | 1.544 | 49.31 |
| 1560 | 2.451 | 1.405 | 44.87 |
| 1680 | 2.446 | 1.246 | 39.77 |
| 1800 | 2.413 | 1.087 | 34.70 |
| 1920 | 2.435 | 0.981 | 31.34 |
| 2040 | 2.446 | 0.842 | 26.90 |
| 2160 | 2.390 | 0.742 | 23.70 |
| 2280 | 2.406 | 0.569 | 18.18 |
| 2400 | 2.397 | 0.223 | 7.12 |

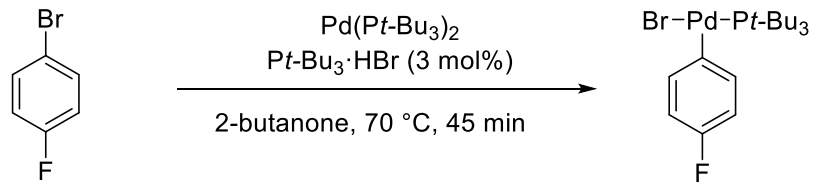



## Order in Pd with ($t$-$Bu_3P)_2Pd$:



**Preparation of Bromo(4-fluorophenyl)(tri-*tert*-butylphosphine)palladium (17) (Scheme 7)**




**17**

In a drybox, an oven-dried, 100-mL Schlenk flask was charged with Pd(*t*-$Bu_3P)_2$ (600 mg, 1.17 mmol, 1.0 equiv) and *t*-$Bu_3P$•HBr (10.0 mg, 0.035 mmol, 0.03 equiv) as solids. Degassed 2-butanone (24 mL) was then added, followed by 4-fluorobromobenzene (5.2 mL, 46.9 mmol, 40 equiv). The flask was sealed and removed from the drybox. The flask was then purged with Ar and submerged into a preheated 70 °C oil bath. After 45 min, the flask was removed from the oil bath and the reaction mixture was cooled to room temperature. The volatiles were removed *in vacuo* (0.1 mmHg) to afford an orange solid. The flask was again sealed and returned to a drybox. Toluene (10 mL) was added to the solid residue, resulting in a heterogeneous mixture. The mixture was added to vigorously stirring pentane (60 mL), which resulted in the precipitation of a yellow solid. The solid was collected on an oven-dried M porosity fritted funnel and washed with additional pentane (10 mL). The solid was dried *in vacuo* (0.1 mmHg) for 6 h to afford 465 mg (82%) of **17** as a yellow powder. The data for **17** matched those reported in the literature.[21]

Data for **17**:

$^1$H NMR: (500 MHz, $C_6D_6$)

7.25 (m, 2H), 6.65 (t, $J$ = 8.9 Hz, 2H), 1.05 (d, $J$ = 12.5 Hz, 27H)

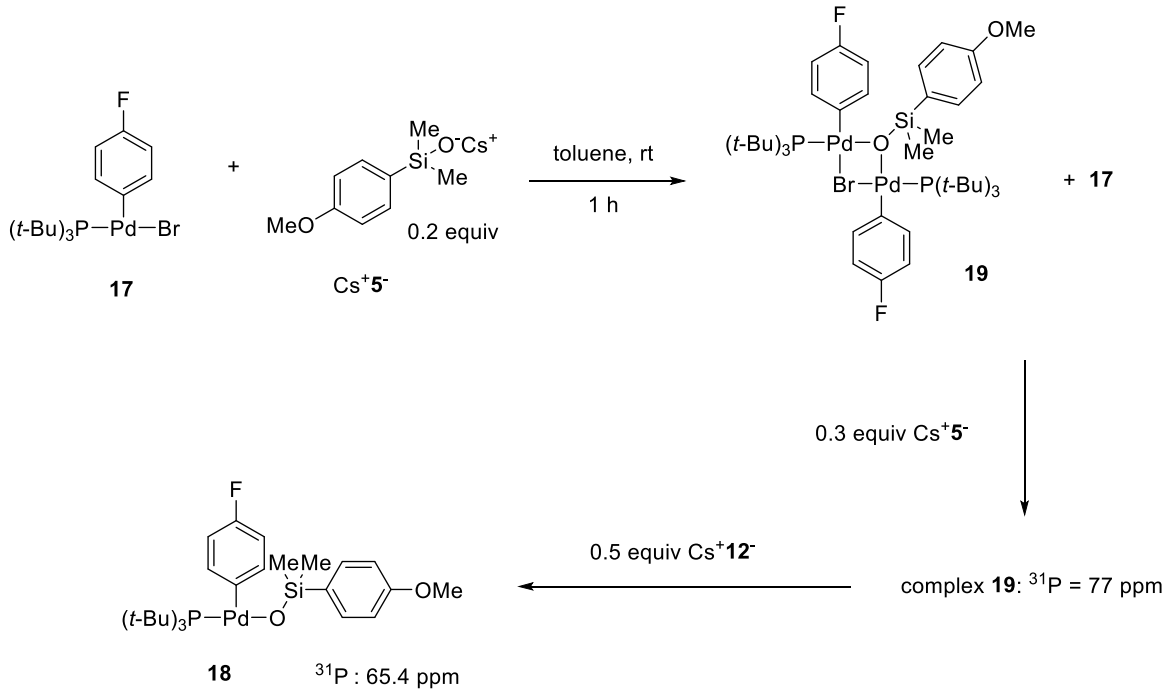
$^{19}$F NMR: (470 MHz, $C_6D_6$)

–122.4

$^{31}$P NMR: (202 MHz, $C_6D_6$)

66.5

**Study of Displacement Reaction: Arylpalladium(II) Bromide 17 with $Cs^{+}5^{-}$ (Scheme 8)**

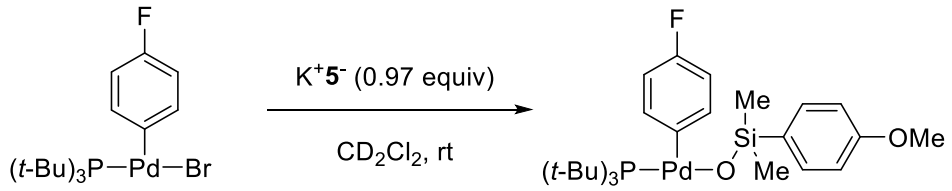



In a drybox, an oven-dried, 3-mL vial equipped with a magnetic stir bar was charged with **17** (5.2 mg, 0.011 mmol) and toluene (0.6 mL) resulting in an orange solution. Then, Cs+**5**$^{-}$ (0.8 mg, 0.002 mmol, 0.2 equiv) was added as a solid and the mixture was stirred until the mixture was completely homogeneous. The resulting solution was transferred into an oven-dried, 5-mm NMR tube using a syringe and the tube was sealed with a septum and Parafilm. The sample was analyzed by $^{31}$P NMR spectroscopy. The $^{31}$P NMR spectrum contained a resonance at 77.0 ppm in addition to that for **17** (64.5 ppm). The NMR tube was returned to the drybox and an additional 0.3 equiv of $Cs^{+}$**5**$^{-}$ (0.9 mg, 0.003 mmol, 0.3 equiv) was added. The mixture was shaken to ensure homogeneity and the sample again analyzed by $^{31}$P NMR spectroscopy. The signal for **17** completely vanished leaving a species (77.0 ppm) visible in the $^{31}$P NMR as the major constituent, with a visible signal at 65.4 ppm.[22] The stoichiometry of this experiment suggested that displacement occurs rapidly and the mutual coexistence of the bromide complex **17** and silanolate resulted in a dimerization (**19**). Subsequent addition of 0.5 equiv of $Cs^{+}$**5**$^{-}$ (1.5 mg, 0.006 mmol, 0.5 equiv) caused disappearance of the signal at 77.0 ppm with concomitant formation of a new signal at 65.4 ppm. This new species has been established as the expected palladium(II) silanolate complex **18.**

Interestingly, the chemical environments of the $^{31}$P nuclei in palladium(II) bromide **17**

and palladium(II) silanolate **18** were sufficiently similar to cause the coincidence of the $^{31}P$ resonances. This result was initially confusing because it appeared that no displacement took place even after 30 min. However, the titration study described above eliminated this possibility and allowed for the subsequent studies to be undertaken.

**Spectroscopic Identification and Crystallization of (4-Fluorophenyl)[1-(4-methoxyphenyl)-1,1,-dimethylsilanolato-κ-*O*](tris-*tert*-butylphosphine)]palladium (18)**




**17** **18**

In a drybox, an oven-dried, 3-mL vial was charged with **17** (12.2 mg, 0.0252 mmol) and $CD_2Cl_2$ (0.4 mL) resulting in an orange solution upon vigorous mixing using a magnetic stir bar. Then, $K^+\mathbf{5}^-$ (5.4 mg, 0.0244 mmol, 0.97 equiv) was added as a solid and the sides of the vial were rinsed with $CD_2Cl_2$ (0.4 mL). The mixture was vigorously mixed (Vortex) for ca. 5 min to ensure complete dissolution. As the mixture stirred, a precipitate formed on the sides of the vial. The supernatant solution was transferred into an oven-dried, 5 mM NMR tube using a 25 G needle to ensure none of the precipitate was transferred. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and placed into a $CO_2$/*i*-PrOH bath. The tube was then inserted into a cooled -70 °C NMR probe and the product was analyzed by NMR spectroscopy.

Data for **18**:

$^1$H NMR: (500 MHz, $CD_2Cl_2$)

7.51 (d, 2 H, $J$ = 7.3 Hz), 7.07 (br m, 2 H), 6.83 (d, 2 H, $J$ = 7.6 Hz), 6.65 (t, 2 H, $J$ = 8.5 Hz), 3.75 (s, 3 H), 1.24 (d, 9 H, $J_{PH}$ = 12.5 Hz), -0.16 (s, 6 H)

$^{13}$C NMR: (126 MHz, $CD_2Cl_2$)

160.2 (d, $J_{CF}$ = 235 Hz), 159.0, 136.2, 134.4, 134.2, 126.7, 113.0 (d, $J_{CF}$ = 19.8 Hz), 112.7, 112.3, 54.7, 39.1 (d, $J_{CP}$ = 13 Hz), 31.0, 1.6

$^{19}$F NMR: (470 MHz, $CD_2Cl_2$)
-123.5

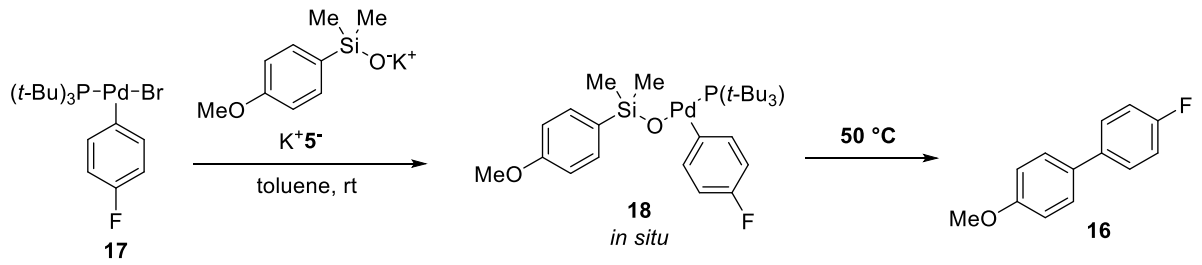
$^{31}$P NMR: (202 MHz, $CD_2Cl_2$)
61.4

X-ray quality crystals were obtained following an identical procedure as described above with the following modifications. After the reaction mixture was stirred for ca. 5 min, the supernatant solution was transferred to a separate oven-dried vial using a 25 G needle to ensure none of the inorganic salts were transferred. The volatiles were removed in vacuo (2 mm Hg) to afford a brown semi-solid. The residue was dissolved in a minimal amount of pentanes (1 mL) and the vial was sealed with a cap. The vial was thoroughly wrapped in Parafilm to exclude any oxygen or moisture and the vial removed from the drybox. The vial was then placed into a fitted Styrofoam container and inserted into a –80 °C freezer. Small yellow needles formed and were analyzed by X-ray diffraction.

**INDEX OF KINETIC EXPERIMENTS FOR CROSS-COUPLING OF IN-SITU GENERATED ARYLPALLADIUM ARYLSILANOLATE 18**

## KINETIC EXPERIMENTS FOR CROSS-COUPLING OF $K^+12^-$ WITH 27

### General Procedure V: Kinetic Measurements for Transmetalation Employing $K^+5^-$ at 50 °C (Table 7).

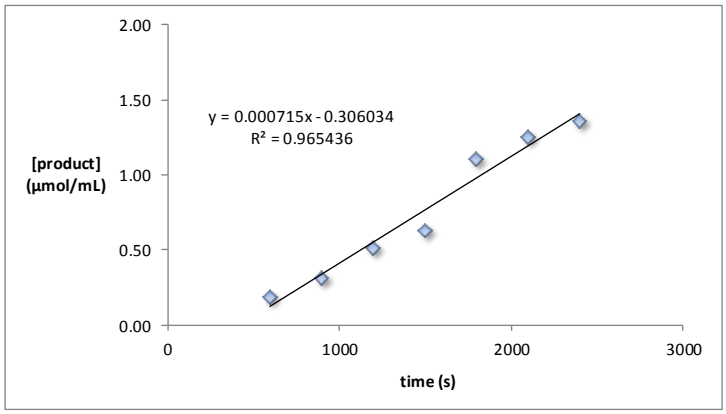



In a drybox, an oven-dried, 4-mL vial was charged with **17** (8.5 mg, 0.0175 mmol) and toluene, resulting in an orange solution. Then, a stock solution of $K^+\mathbf{5}^-$ and 1,4-difluorobenzene in toluene was added to a total volume of 0.7 mL (0.025 M in **17**) and the mixture was vigorously mixed. The resulting solution was transferred via syringe into an oven-dried, 5-mm NMR tube. The tube was sealed with a cap and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and inserted into a preheated 50 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for ca. 60 seconds prior to data collection. The reaction progress was monitored via $^{19}$F NMR spectroscopy by the appearance of the product **16** (δ = –117.2 ppm) as compared to an internal reference (1,4-difluorobenzene, δ = –119.9 ppm) using the following parameters: at = 0.5 s, d1 = 1 s, pw90 = 15 μs, pw = pw90/2, sw = –115 to –130 ppm, nt and sampling as specified in each individual experiment. Experiments were repeated in triplicate.

***<u>0.5 equivalents (Table 7, entry 1)</u>***

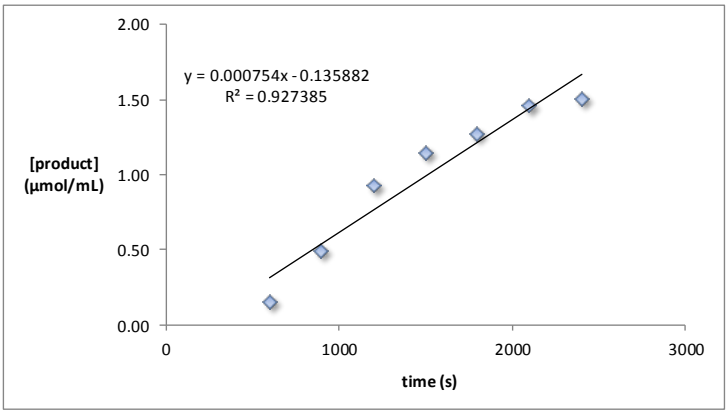
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.55 mL). A stock solution of $K^+\mathbf{5}^-$ (0.00875 mmol, 0.5 equiv) and 1,4-difluorobenzene (0.00875 mmol, 0.5 equiv) in toluene (0.15 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = $7.15 \cdot 10^{-4}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 600 | 59.0 | 7899.0 | 0.19 |
| 900 | 99.7 | 7966.5 | 0.31 |
| 1200 | 160.9 | 7829.2 | 0.51 |
| 1500 | 198.7 | 7933.3 | 0.63 |
| 1800 | 347.3 | 7859.8 | 1.10 |
| 2100 | 397.5 | 7946.9 | 1.25 |
| 2400 | 431.9 | 7906.8 | 1.37 |



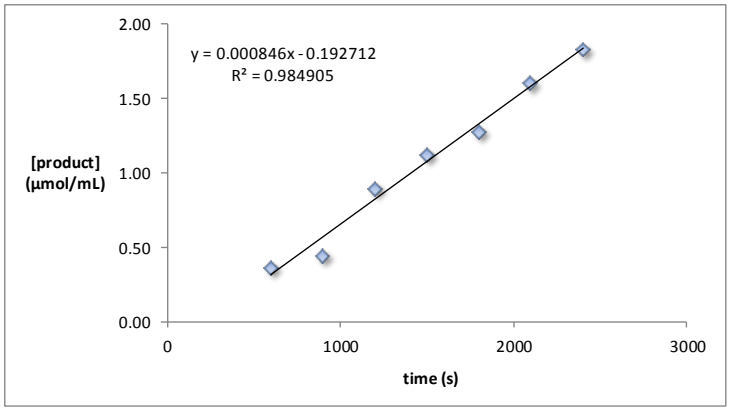

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.58 mL). A stock solution of $K^+$**5**$^-$ (0.00875 mmol, 0.5 equiv) and 1,4-difluorobenzene (0.00730 mmol, 0.42 equiv) in toluene (0.12 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 7.54 · 10$^{-4}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 600 | 102.6 | 14177.6 | 0.15 |
| 900 | 334.1 | 14094.4 | 0.49 |
| 1200 | 631.4 | 14110.1 | 0.93 |
| 1500 | 788.8 | 14293.8 | 1.15 |
| 1800 | 867.0 | 14161.5 | 1.28 |
| 2100 | 1000.3 | 14293.6 | 1.46 |
| 2400 | 1041.1 | 14417.1 | 1.50 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.58 mL). A stock solution of $K^+$**5**$^-$ (0.00875 mmol, 0.5 equiv) and 1,4-difluorobenzene (0.00730 mmol, 0.42 equiv) in toluene (0.12 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 8.46 · 10$^{-4}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 600 | 255.5 | 14532.6 | 0.37 |
| 900 | 314.8 | 14764.6 | 0.44 |
| 1200 | 617.6 | 14458.0 | 0.89 |
| 1500 | 783.0 | 14555.5 | 1.12 |
| 1800 | 895.5 | 14591.5 | 1.28 |
| 2100 | 1109.3 | 14424.9 | 1.60 |
| 2400 | 1268.6 | 14409.6 | 1.83 |

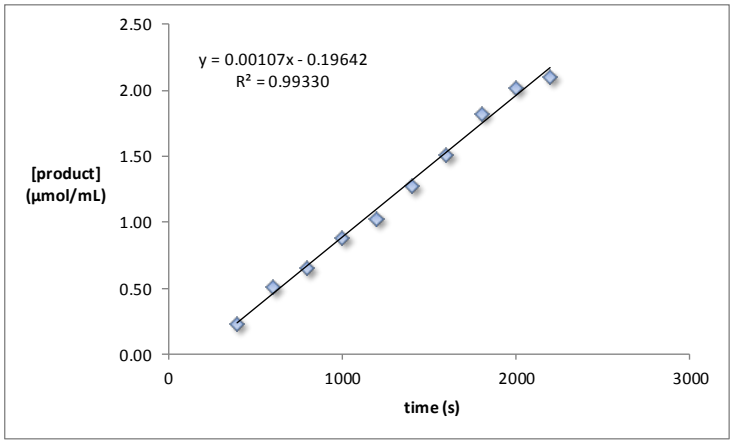



**avg. rate = 7.72 · $10^{-4}$ ± 6.73 · $10^{-5}$ mM/s**

***<u>0.6 equivalents (Table 7, entry 2)</u>***

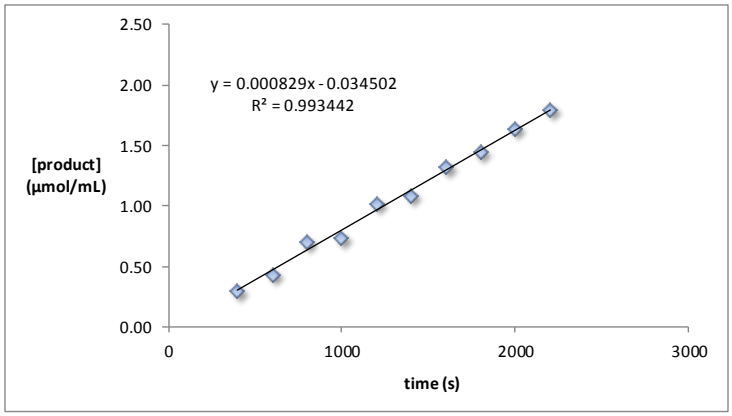
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0105 mmol, 0.6 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 200 s. **rate = 1.07 · $10^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 400 | 182.7 | 40901.4 | 0.22 |
| 600 | 418.3 | 41623.2 | 0.50 |
| 800 | 548.5 | 41909.7 | 0.65 |
| 1000 | 744.9 | 42188.0 | 0.88 |
| 1200 | 860.8 | 42290.1 | 1.02 |
| 1400 | 1082.6 | 42423.6 | 1.28 |
| 1600 | 1280.4 | 42381.0 | 1.51 |
| 1800 | 1543.4 | 42453.8 | 1.82 |
| 2000 | 1725.8 | 42716.9 | 2.02 |
| 2200 | 1809.6 | 43114.8 | 2.10 |



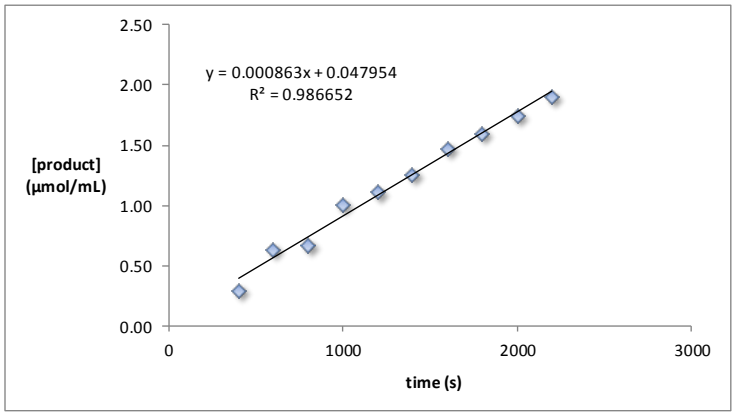

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0105 mmol, 0.6 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 200 s. **rate = 8.29 · $10^{-4}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 400 | 219.5 | 37101.6 | 0.30 |
| 600 | 322.0 | 37290.4 | 0.43 |
| 800 | 517.8 | 37115.9 | 0.70 |
| 1000 | 549.7 | 37343.0 | 0.74 |
| 1200 | 756.1 | 37306.8 | 1.01 |
| 1400 | 801.4 | 37049.9 | 1.08 |
| 1600 | 988.8 | 37495.5 | 1.32 |
| 1800 | 1090.7 | 37843.8 | 1.44 |
| 2000 | 1211.6 | 37135.3 | 1.63 |
| 2200 | 1333.0 | 37258.7 | 1.79 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0105 mmol, 0.6 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 200 s. **rate = 8.63 · 10$^{-4}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 400 | 221.7 | 37633.7 | 0.29 |
| 600 | 477.6 | 37596.4 | 0.64 |
| 800 | 505.9 | 37811.5 | 0.67 |
| 1000 | 755.0 | 37680.4 | 1.00 |
| 1200 | 838.6 | 37654.6 | 1.11 |
| 1400 | 943.2 | 37459.2 | 1.26 |
| 1600 | 1105.5 | 37456.8 | 1.48 |
| 1800 | 1198.2 | 37590.1 | 1.59 |
| 2000 | 1315.7 | 37703.2 | 1.74 |
| 2200 | 1443.6 | 37855.6 | 1.91 |

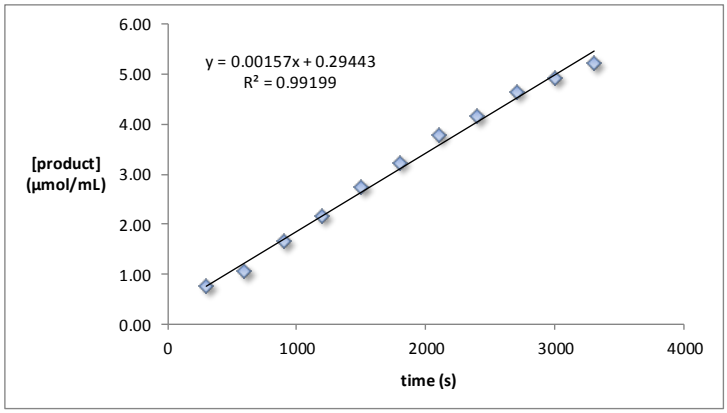



**avg. rate = 9.17 · 10$^{-4}$ ± 1.25 · 10$^{-4}$ mM/s**

***<u>0.75 equivalents (Table 7, entry 3)</u>***

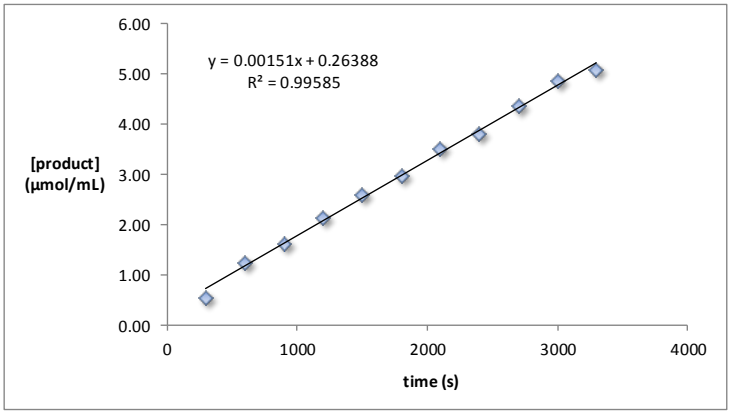
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^+$**5**$^-$ (0.0131 mmol, 0.75 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 1.57 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 506.2 | 33125.3 | 0.76 |
| 600 | 714.0 | 34233.5 | 1.04 |
| 900 | 1183.2 | 35837.1 | 1.65 |
| 1200 | 1589.1 | 36782.7 | 2.16 |
| 1500 | 2037.4 | 37108.5 | 2.75 |
| 1800 | 2391.3 | 37110.4 | 3.22 |
| 2100 | 2813.9 | 37213.5 | 3.78 |
| 2400 | 3118.2 | 37483.1 | 4.16 |
| 2700 | 3481.4 | 37378.4 | 4.66 |
| 3000 | 3650.7 | 37185.8 | 4.91 |
| 3300 | 3889.8 | 37279.0 | 5.22 |



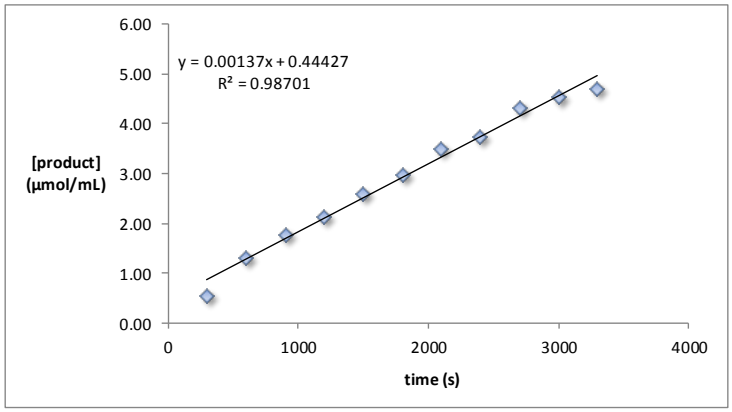

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^{+}\mathbf{5}^{-}$ (0.0131 mmol, 0.75 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 1.51 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 340.9 | 32395.1 | 0.53 |
| 600 | 788.6 | 31889.8 | 1.24 |
| 900 | 1030.4 | 31632.8 | 1.63 |
| 1200 | 1387.2 | 32326.3 | 2.15 |
| 1500 | 1710.1 | 32808.3 | 2.61 |
| 1800 | 2004.6 | 33804.8 | 2.96 |
| 2100 | 2476.3 | 35157.7 | 3.52 |
| 2400 | 2764.0 | 36349.2 | 3.80 |
| 2700 | 3214.9 | 36949.6 | 4.35 |
| 3000 | 3582.7 | 36881.0 | 4.86 |
| 3300 | 3756.5 | 36866.4 | 5.09 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^{+}\mathbf{5}^{-}$ (0.0131 mmol, 0.75 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 1.37 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 392.3 | 35774.8 | 0.55 |
| 600 | 950.6 | 36069.4 | 1.32 |
| 900 | 1287.5 | 36078.9 | 1.78 |
| 1200 | 1502.2 | 35472.6 | 2.12 |
| 1500 | 1860.4 | 35895.8 | 2.59 |
| 1800 | 2101.8 | 35346.7 | 2.97 |
| 2100 | 2495.8 | 35719.4 | 3.49 |
| 2400 | 2624.2 | 35181.5 | 3.73 |
| 2700 | 3065.9 | 35528.3 | 4.31 |
| 3000 | 3177.2 | 35063.6 | 4.53 |
| 3300 | 3355.3 | 35631.0 | 4.71 |

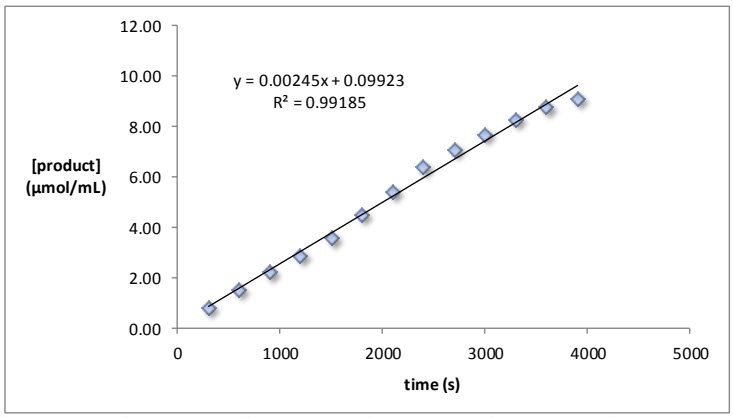



**avg. rate = 1.48 · $10^{-3}$ ± 1.03 · $10^{-4}$ mM/s**

***<u>1 equivalent (Table 7, entry 4)</u>***

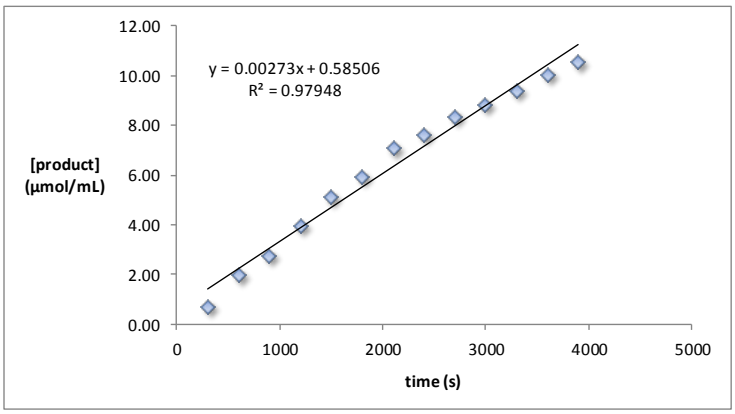
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^+$**5**$^-$ (0.0175 mmol, 1 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 2.45 · $10^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 585.0 | 35268.7 | 0.83 |
| 600 | 1093.2 | 36554.3 | 1.50 |
| 900 | 1611.3 | 36673.9 | 2.20 |
| 1200 | 2085.5 | 36313.3 | 2.87 |
| 1500 | 2563.1 | 35911.3 | 3.57 |
| 1800 | 3319.3 | 37187.5 | 4.46 |
| 2100 | 4004.4 | 37041.9 | 5.41 |
| 2400 | 4721.6 | 37079.1 | 6.37 |
| 2700 | 5247.0 | 37091.5 | 7.07 |
| 3000 | 5672.8 | 36970.9 | 7.67 |
| 3300 | 6110.2 | 36865.8 | 8.29 |
| 3600 | 6472.0 | 36842.4 | 8.78 |
| 3900 | 6648.4 | 36624.4 | 9.08 |



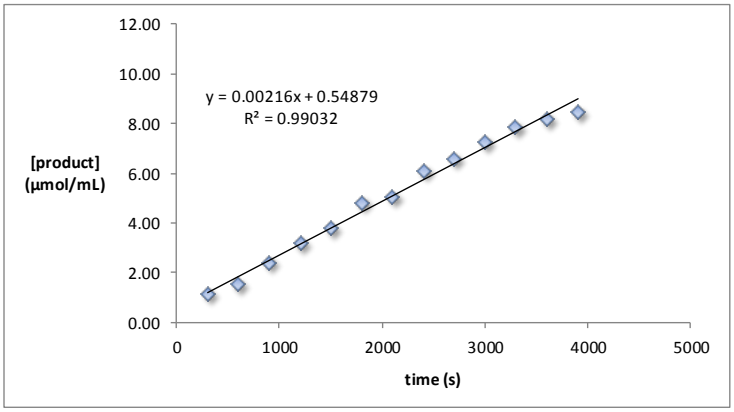

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^+$**5**$^-$ (0.0175 mmol, 1 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 2.73 · $10^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 223.3 | 15332.2 | 0.73 |
| 600 | 596.4 | 15308.3 | 1.95 |
| 900 | 838.9 | 15433.4 | 2.72 |
| 1200 | 1209.7 | 15441.8 | 3.92 |
| 1500 | 1530.2 | 15086.7 | 5.07 |
| 1800 | 1825.7 | 15454.1 | 5.91 |
| 2100 | 2181.0 | 15451.2 | 7.06 |
| 2400 | 2378.2 | 15581.3 | 7.63 |
| 2700 | 2594.3 | 15555.2 | 8.34 |
| 3000 | 2735.6 | 15472.1 | 8.84 |
| 3300 | 2885.3 | 15381.3 | 9.38 |
| 3600 | 3065.5 | 15301.2 | 10.02 |
| 3900 | 3184.2 | 15075.6 | 10.56 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^+$**5**$^-$ (0.0175 mmol, 1 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 2.16 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 342.2 | 15288.3 | 1.12 |
| 600 | 480.0 | 15539.0 | 1.54 |
| 900 | 734.7 | 15436.4 | 2.38 |
| 1200 | 965.7 | 15267.6 | 3.16 |
| 1500 | 1163.2 | 15411.7 | 3.77 |
| 1800 | 1483.5 | 15411.8 | 4.81 |
| 2100 | 1532.4 | 15142.0 | 5.06 |
| 2400 | 1840.3 | 15175.7 | 6.06 |
| 2700 | 2006.5 | 15249.5 | 6.58 |
| 3000 | 2200.6 | 15222.3 | 7.23 |
| 3300 | 2397.9 | 15295.6 | 7.84 |
| 3600 | 2508.9 | 15311.0 | 8.19 |
| 3900 | 2561.6 | 15148.1 | 8.46 |

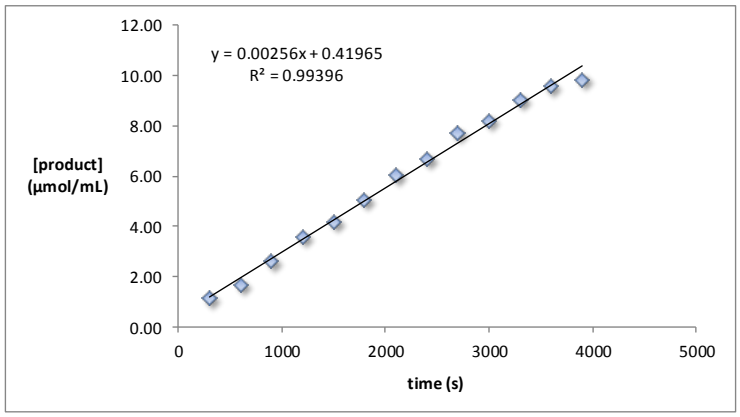



**avg. rate = 2.45 · 10$^{-3}$ ± 2.85 · 10$^{-4}$ mM/s**

***<u>1 equivalent - with added P(t-Bu)$_3$ (2 equivalents)</u>***

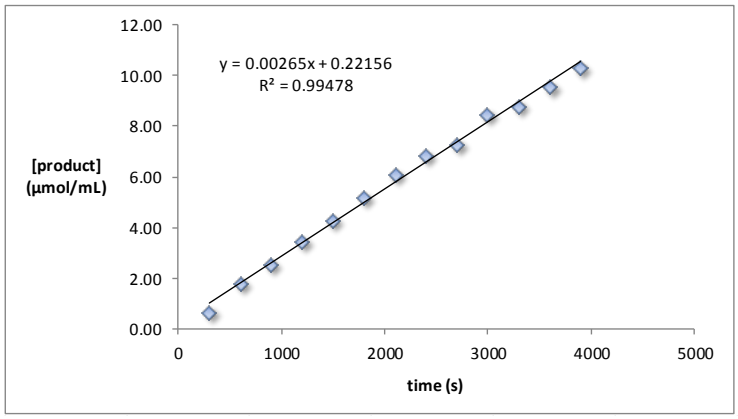
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^+$**5**$^-$ (0.0175 mmol, 1 equiv), P(*t*-Bu)$_3$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0289 mmol, 1.65 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 2.56 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 513.5 | 36786.5 | 1.15 |
| 600 | 753.7 | 36919.8 | 1.69 |
| 900 | 1167.3 | 37076.9 | 2.60 |
| 1200 | 1613.4 | 36981.7 | 3.60 |
| 1500 | 1880.8 | 37044.1 | 4.19 |
| 1800 | 2285.7 | 37294.1 | 5.06 |
| 2100 | 2746.7 | 37602.4 | 6.03 |
| 2400 | 3045.3 | 37733.2 | 6.66 |
| 2700 | 3519.5 | 37649.9 | 7.72 |
| 3000 | 3774.8 | 37994.7 | 8.20 |
| 3300 | 4125.6 | 37766.7 | 9.02 |
| 3600 | 4393.8 | 37928.2 | 9.57 |
| 3900 | 4538.5 | 37990.3 | 9.86 |



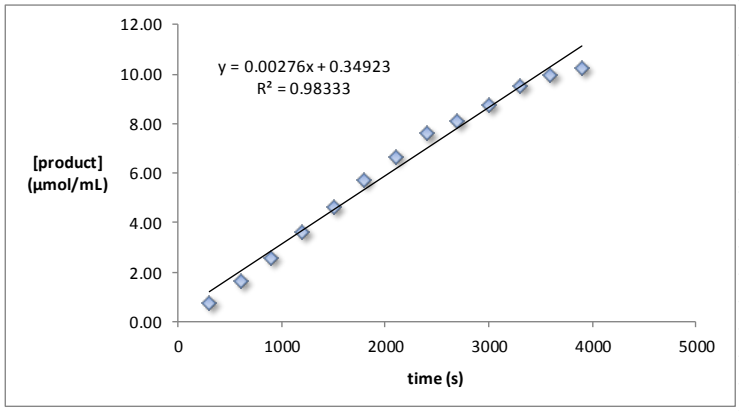

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^+\mathbf{5}^-$ (0.0175 mmol, 1 equiv), P(*t*-Bu)$_3$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0289 mmol, 1.65 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 2.65 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 307.4 | 39198.0 | 0.65 |
| 600 | 829.8 | 39050.9 | 1.75 |
| 900 | 1204.0 | 39172.5 | 2.54 |
| 1200 | 1621.8 | 38923.6 | 3.44 |
| 1500 | 2021.6 | 39023.1 | 4.28 |
| 1800 | 2446.0 | 39035.5 | 5.17 |
| 2100 | 2864.8 | 38972.4 | 6.07 |
| 2400 | 3231.8 | 38993.9 | 6.84 |
| 2700 | 3413.2 | 38672.1 | 7.29 |
| 3000 | 3932.7 | 38299.5 | 8.48 |
| 3300 | 4113.0 | 38703.3 | 8.77 |
| 3600 | 4431.6 | 38440.2 | 9.52 |
| 3900 | 4773.1 | 38300.6 | 10.29 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.4 mL). A stock solution of $K^+\mathbf{5}^-$ (0.0175 mmol, 1 equiv), P(*t*-Bu)$_3$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0289 mmol, 1.65 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = 2.76 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 454.4 | 49073.0 | 0.76 |
| 600 | 988.2 | 49325.2 | 1.65 |
| 900 | 1563.8 | 49560.7 | 2.61 |
| 1200 | 2160.1 | 49479.6 | 3.60 |
| 1500 | 2771.6 | 49579.2 | 4.62 |
| 1800 | 3443.7 | 49698.7 | 5.72 |
| 2100 | 4028.4 | 49826.9 | 6.68 |
| 2400 | 4550.2 | 49548.2 | 7.58 |
| 2700 | 4880.3 | 49615.2 | 8.12 |
| 3000 | 5243.7 | 49421.8 | 8.76 |
| 3300 | 5704.9 | 49420.1 | 9.53 |
| 3600 | 5973.9 | 49424.6 | 9.98 |
| 3900 | 6143.3 | 49403.9 | 10.27 |

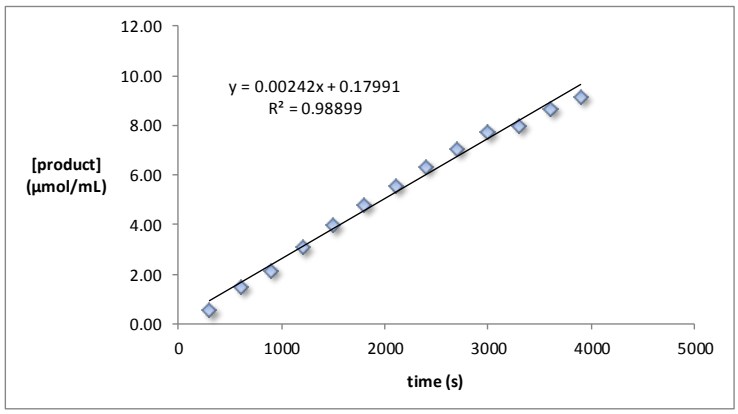



**avg. rate = $2.66 \cdot 10^{-3} \pm 1.00 \cdot 10^{-4}$ mM/s**

***<u>1 equivalent - with added P(t-Bu)$_3$ (5 equivalents)</u>***

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.3 mL). A stock solution of $K^+$**5**$^-$ (0.0175 mmol, 1 equiv), P(*t*-Bu)$_3$ (0.0875 mmol, 5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.3 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 64, sampling every 300 s. **rate = $2.42 \cdot 10^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 416.0 | 37751.5 | 0.55 |
| 600 | 1113.1 | 37573.6 | 1.48 |
| 900 | 1622.2 | 38065.5 | 2.13 |
| 1200 | 2334.0 | 37724.4 | 3.09 |
| 1500 | 2989.6 | 37602.8 | 3.98 |
| 1800 | 3620.4 | 37713.6 | 4.80 |
| 2100 | 4203.9 | 37678.7 | 5.58 |
| 2400 | 4799.8 | 37731.4 | 6.36 |
| 2700 | 5345.0 | 37809.6 | 7.07 |
| 3000 | 5810.3 | 37592.0 | 7.73 |
| 3300 | 6047.7 | 37741.1 | 8.01 |
| 3600 | 6499.5 | 37651.4 | 8.63 |
| 3900 | 6871.9 | 37630.5 | 9.13 |

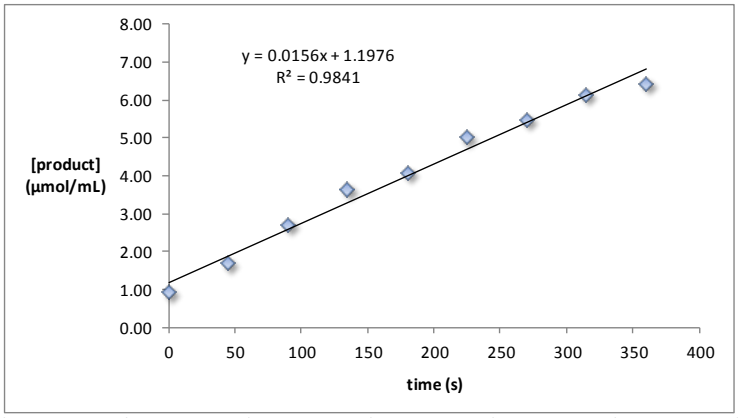



***<u>1.5 equivalents (Table 7, entry 5)</u>***

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0263 mmol, 1.5 equiv) and 1,4-difluorobenzene (0.0145 mmol, 0.83 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling

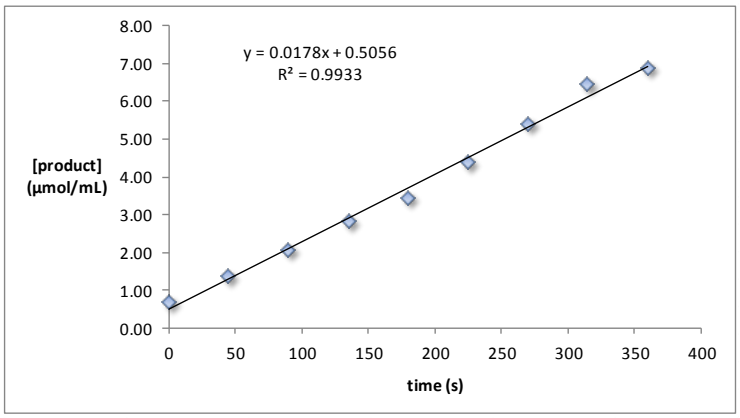
every 45 s. **rate = 1.56 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 108.2 | 4783.5 | 0.94 |
| 45 | 202.9 | 4998.0 | 1.69 |
| 90 | 313.6 | 4862.9 | 2.69 |
| 135 | 421.8 | 4844.8 | 3.63 |
| 180 | 472.8 | 4844.9 | 4.07 |
| 225 | 578.8 | 4831.3 | 5.00 |
| 270 | 640.2 | 4864.7 | 5.49 |
| 315 | 710.6 | 4844.6 | 6.12 |
| 360 | 749.8 | 4877.9 | 6.41 |



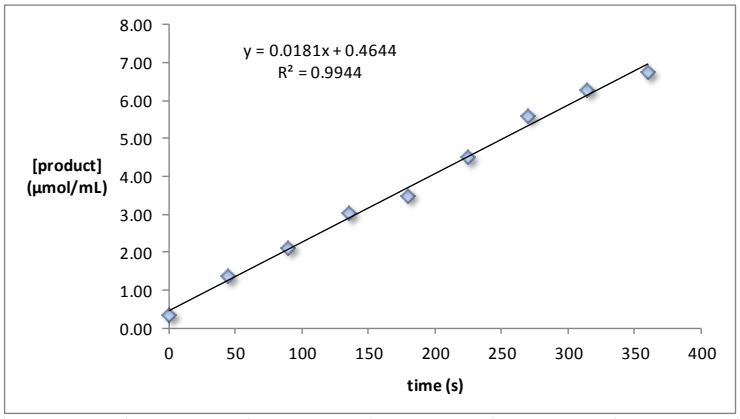

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0263 mmol, 1.5 equiv) and 1,4-difluorobenzene (0.0145 mmol, 0.83 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 1.78 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 85.3 | 5150.9 | 0.69 |
| 45 | 171.8 | 5200.6 | 1.38 |
| 90 | 250.5 | 5103.2 | 2.05 |
| 135 | 340.8 | 5041.9 | 2.82 |
| 180 | 416.8 | 5071.8 | 3.43 |
| 225 | 533.6 | 5085.0 | 4.38 |
| 270 | 660.2 | 5097.1 | 5.40 |
| 315 | 790.3 | 5124.6 | 6.43 |
| 360 | 840.2 | 5098.4 | 6.87 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0263 mmol, 1.5 equiv) and 1,4-difluorobenzene (0.0145 mmol, 0.83 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 1.81 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 39.6 | 4813.9 | 0.34 |
| 45 | 164.8 | 5052.9 | 1.36 |
| 90 | 252.6 | 4977.8 | 2.12 |
| 135 | 356.3 | 4912.6 | 3.02 |
| 180 | 410.5 | 4913.9 | 3.48 |
| 225 | 533.2 | 4927.4 | 4.51 |
| 270 | 664.3 | 4946.8 | 5.60 |
| 315 | 744.2 | 4942.9 | 6.28 |
| 360 | 798.4 | 4939.9 | 6.74 |

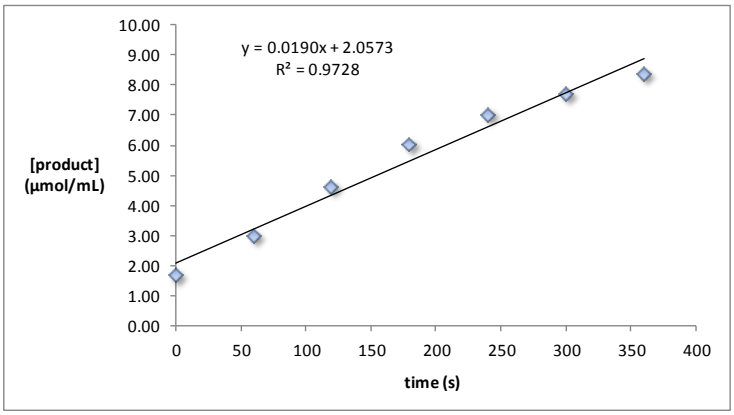



**avg. rate = $1.72 \cdot 10^{-2} \pm 1.37 \cdot 10^{-3}$ mM/s**

***<u>2 equivalents (Table 7, entry 6)</u>***

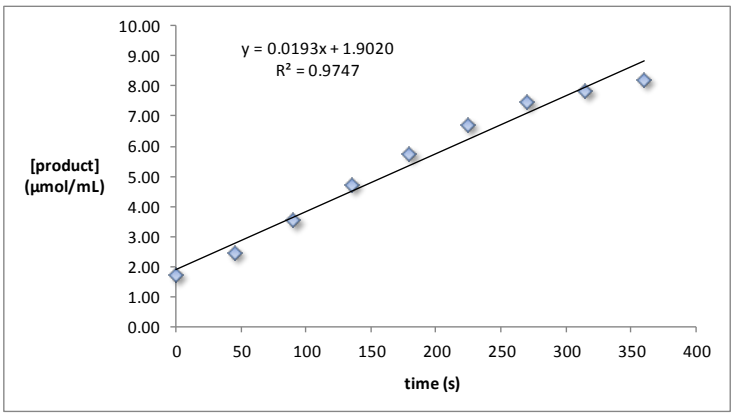
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0292 mmol, 1.67 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 60 s. **rate = $1.90 \cdot 10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 380.9 | 19209.5 | 1.65 |
| 60 | 665.0 | 18546.6 | 2.99 |
| 120 | 1008.2 | 18249.1 | 4.61 |
| 180 | 1309.5 | 18146.7 | 6.02 |
| 240 | 1528.4 | 18204.2 | 7.00 |
| 300 | 1677.0 | 18211.8 | 7.68 |
| 360 | 1818.6 | 18147.7 | 8.36 |



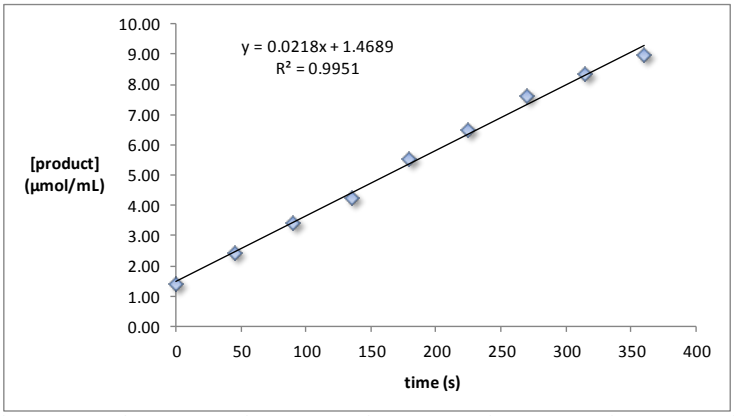

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0292 mmol, 1.67 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = $1.93 \cdot 10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 388.0 | 19101.6 | 1.69 |
| 45 | 523.9 | 17880.9 | 2.44 |
| 90 | 738.9 | 17534.6 | 3.52 |
| 135 | 997.6 | 17633.7 | 4.72 |
| 180 | 1203.2 | 17413.4 | 5.76 |
| 225 | 1409.3 | 17513.9 | 6.71 |
| 270 | 1573.5 | 17551.0 | 7.48 |
| 315 | 1653.1 | 17633.1 | 7.82 |
| 360 | 1732.2 | 17636.5 | 8.19 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0292 mmol, 1.67 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 2.18 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 328.8 | 19678.2 | 1.39 |
| 45 | 543.5 | 18834.1 | 2.41 |
| 90 | 753.2 | 18260.6 | 3.44 |
| 135 | 934.5 | 18427.2 | 4.23 |
| 180 | 1217.1 | 18244.6 | 5.57 |
| 225 | 1444.4 | 18600.6 | 6.48 |
| 270 | 1701.9 | 18602.9 | 7.63 |
| 315 | 1879.1 | 18754.0 | 8.36 |
| 360 | 1994.1 | 18568.2 | 8.96 |

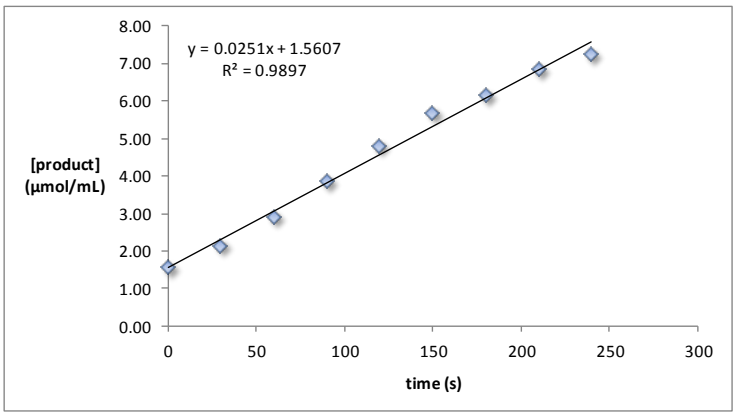



**avg. rate = 2.00 · $10^{-2}$ ± 1.54 · $10^{-3}$ mM/s**

***<u>3 equivalents (Table 7, entry 7)</u>***

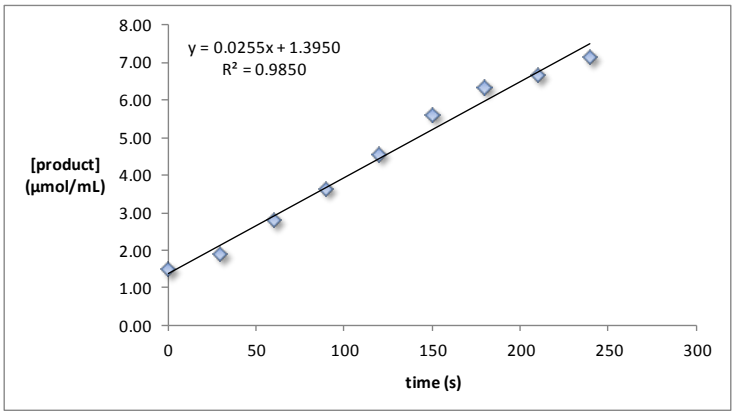
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0524 mmol, 3 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.51 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 216.5 | 6977.0 | 1.55 |
| 30 | 289.6 | 6727.1 | 2.15 |
| 60 | 374.3 | 6472.9 | 2.89 |
| 90 | 488.1 | 6344.0 | 3.85 |
| 120 | 612.2 | 6359.1 | 4.81 |
| 150 | 726.7 | 6410.5 | 5.67 |
| 180 | 787.9 | 6387.3 | 6.17 |
| 210 | 865.7 | 6329.2 | 6.84 |
| 240 | 919.8 | 6344.9 | 7.25 |



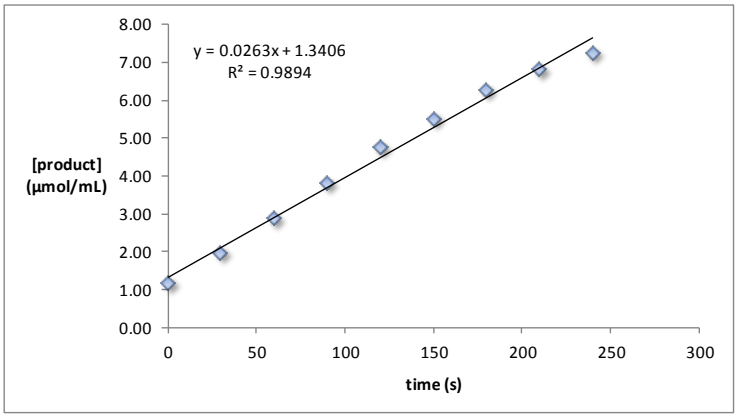

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0524 mmol, 3 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.55 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 201.4 | 6757.7 | 1.49 |
| 30 | 250.5 | 6612.9 | 1.89 |
| 60 | 353.5 | 6351.5 | 2.78 |
| 90 | 462.3 | 6324.7 | 3.65 |
| 120 | 571.6 | 6274.4 | 4.56 |
| 150 | 699.0 | 6249.8 | 5.59 |
| 180 | 788.0 | 6207.7 | 6.35 |
| 210 | 832.2 | 6258.4 | 6.65 |
| 240 | 896.0 | 6279.3 | 7.13 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0524 mmol, 3 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.63 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 155.0 | 6616.8 | 1.17 |
| 30 | 255.4 | 6477.6 | 1.97 |
| 60 | 361.8 | 6272.3 | 2.88 |
| 90 | 473.5 | 6199.7 | 3.82 |
| 120 | 587.2 | 6182.7 | 4.75 |
| 150 | 692.2 | 6254.7 | 5.53 |
| 180 | 780.5 | 6211.8 | 6.28 |
| 210 | 851.3 | 6255.9 | 6.80 |
| 240 | 899.8 | 6202.7 | 7.25 |

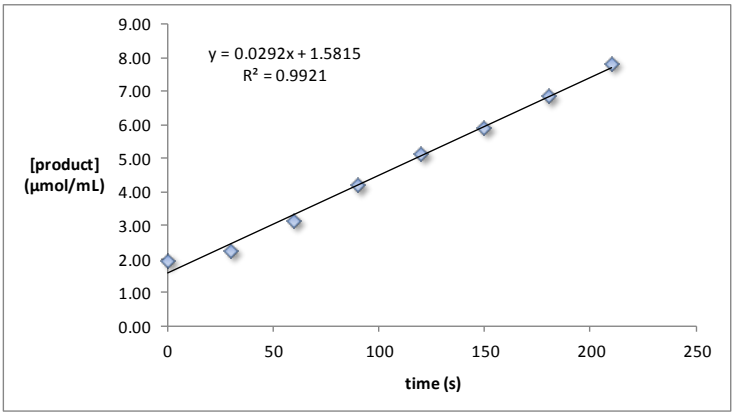



**avg. rate = 2.56 · $10^{-2}$ ± 6.11 · $10^{-4}$ mM/s**

***5 equivalents (Table 7, entry 8)***

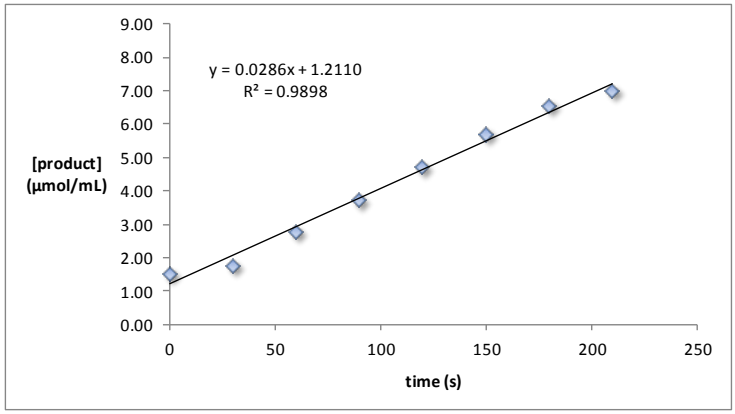
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0875 mmol, 5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.92 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 264.8 | 6784.2 | 1.95 |
| 30 | 297.1 | 6694.8 | 2.22 |
| 60 | 401.6 | 6439.2 | 3.12 |
| 90 | 527.9 | 6311.3 | 4.18 |
| 120 | 648.3 | 6305.7 | 5.14 |
| 150 | 749.2 | 6328.0 | 5.92 |
| 180 | 856.3 | 6236.8 | 6.86 |
| 210 | 979.7 | 6259.7 | 7.83 |



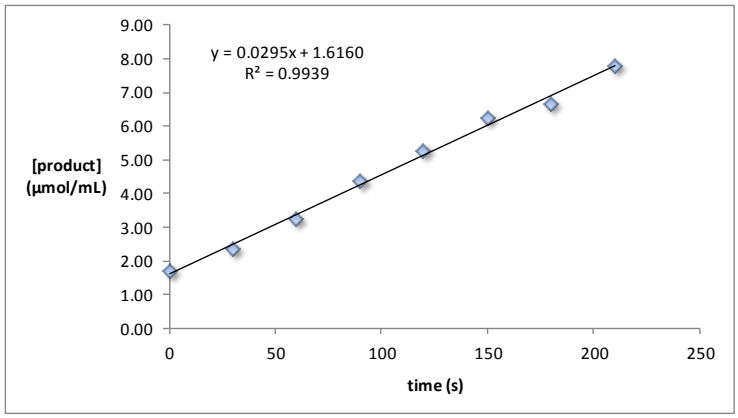

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0875 mmol, 5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.86 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 184.4 | 6143.2 | 1.50 |
| 30 | 231.6 | 6586.5 | 1.76 |
| 60 | 353.4 | 6324.4 | 2.79 |
| 90 | 466.8 | 6249.2 | 3.73 |
| 120 | 584.6 | 6207.2 | 4.71 |
| 150 | 712.6 | 6258.1 | 5.69 |
| 180 | 802.0 | 6127.8 | 6.54 |
| 210 | 877.1 | 6255.3 | 7.01 |




Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $K^+$**5**$^-$ (0.0875 mmol, 5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.95 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 231.2 | 6761.3 | 1.71 |
| 30 | 313.3 | 6710.2 | 2.33 |
| 60 | 418.8 | 6482.2 | 3.23 |
| 90 | 565.1 | 6426.5 | 4.40 |
| 120 | 678.5 | 6438.0 | 5.27 |
| 150 | 809.4 | 6460.6 | 6.26 |
| 180 | 862.0 | 6456.4 | 6.68 |
| 210 | 991.3 | 6365.0 | 7.79 |

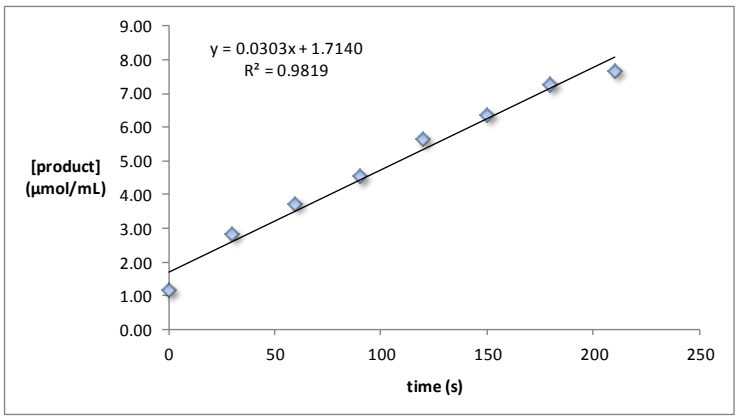



**avg. rate = 2.91 · 10$^{-2}$ ± 4.58 · 10$^{-4}$ mM/s**

***<u>7.5 equivalents (Table 7, entry 9)</u>***

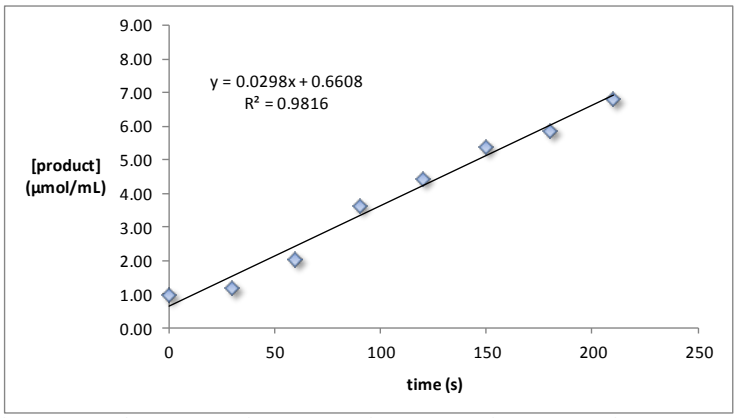
Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $K^+$**5**$^-$ (0.131 mmol, 7.5 equiv) and 1,4-difluorobenzene (0.021 mmol, 1.2 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 3.03 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 153.1 | 7712.0 | 1.19 |
| 30 | 349.0 | 7431.6 | 2.82 |
| 60 | 452.2 | 7255.1 | 3.74 |
| 90 | 542.9 | 7190.1 | 4.53 |
| 120 | 688.0 | 7333.6 | 5.63 |
| 150 | 773.1 | 7279.6 | 6.37 |
| 180 | 878.7 | 7264.8 | 7.26 |
| 210 | 934.0 | 7321.8 | 7.65 |



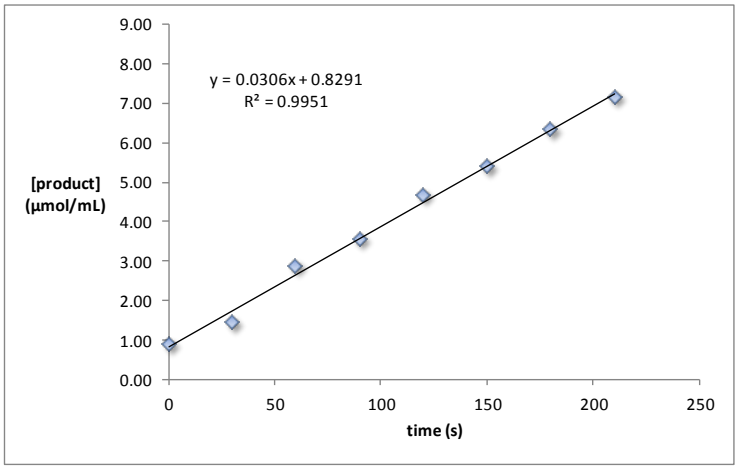

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $K^+$**5**$^-$ (0.131 mmol, 7.5 equiv) and 1,4-difluorobenzene (0.021 mmol, 1.2 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.98 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 51.2 | 3167.2 | 0.97 |
| 30 | 64.2 | 3276.1 | 1.18 |
| 60 | 108.2 | 3172.3 | 2.05 |
| 90 | 191.5 | 3156.0 | 3.64 |
| 120 | 234.0 | 3154.4 | 4.45 |
| 150 | 283.1 | 3154.1 | 5.39 |
| 180 | 306.4 | 3121.6 | 5.89 |
| 210 | 354.1 | 3124.0 | 6.80 |



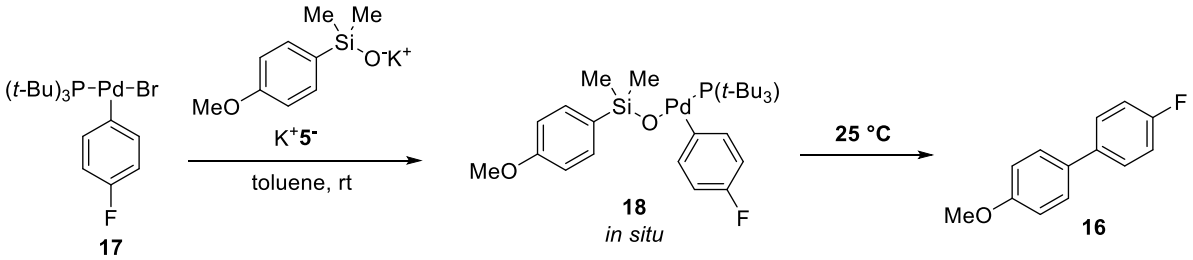

Following General Procedure V, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $K^+$**5**$^-$ (0.131 mmol, 7.5 equiv) and 1,4-difluorobenzene (0.021 mmol, 1.2 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 50 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 3.06 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 47.3 | 3166.7 | 0.90 |
| 30 | 79.1 | 3307.8 | 1.43 |
| 60 | 153.0 | 3208.7 | 2.86 |
| 90 | 188.8 | 3164.8 | 3.58 |
| 120 | 243.6 | 3133.1 | 4.66 |
| 150 | 283.4 | 3145.3 | 5.41 |
| 180 | 333.2 | 3149.8 | 6.35 |
| 210 | 377.2 | 3158.9 | 7.16 |




**avg. rate = $3.02 \cdot 10^{-2} \pm 4.04 \cdot 10^{-4}$ mM/s**

**General Procedure VI: Kinetic Measurements for Transmetalation of 18 at 25 °C Employing 7.5 Equiv of $K^+5^-$**

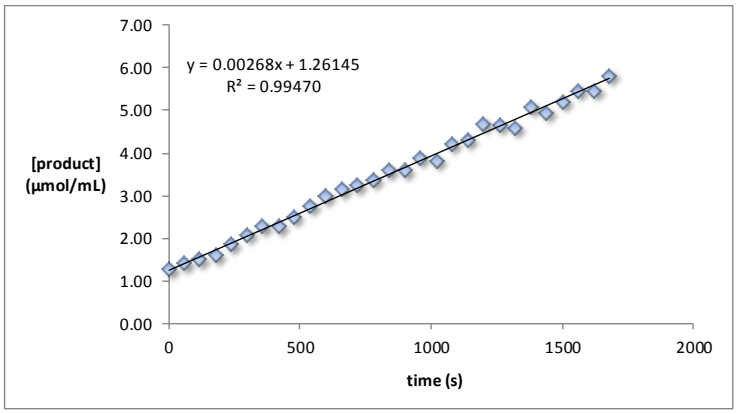



In a drybox, an oven-dried, 4-mL vial was charged with **17** (8.5 mg, 0.0175 mmol) and toluene, resulting in an orange solution. Then, a stock solution of $K^+\mathbf{5}^-$ and 1,4-difluorobenzene in toluene was added to a total volume of 0.7 mL (0.025 M in **17**) and the mixture was vigorously mixed. The resulting solution was transferred via syringe into an oven-dried, 5-mm NMR tube. The tube was sealed with a cap and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and inserted into a pre-warmed 25 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for ca. 60 seconds prior to data collection. The reaction progress was monitored via $^{19}$F NMR spectroscopy by the appearance of the product **16** (δ = –117.2 ppm) as compared to an internal reference (1,4-difluorobenzene, δ = –119.9 ppm) using the following parameters: at = 0.5 s, d1 = 1 s, pw90 = 15 μs, pw = pw90/2, sw = –115 to –130 ppm, nt and sampling as specified in each individual experiment. Experiments were repeated in triplicate.

***7.5 equivalents***

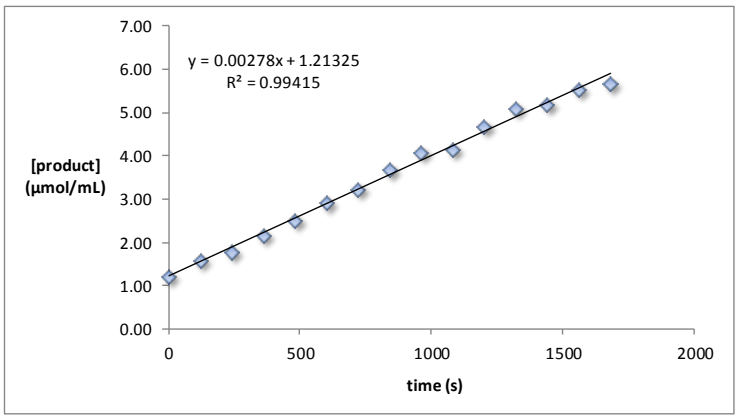
Following General Procedure VI, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $K^+$**5**$^-$ (0.131 mmol, 7.5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 60 s. **rate = 2.68 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 345.7 | 13627.8 | 1.27 |
| 60 | 381.3 | 13510.1 | 1.41 |
| 120 | 408.6 | 13489.6 | 1.51 |
| 180 | 436.1 | 13471.7 | 1.62 |
| 240 | 500.6 | 13449.0 | 1.86 |
| 300 | 564.1 | 13485.2 | 2.09 |
| 360 | 619.4 | 13503.4 | 2.29 |
| 420 | 615.5 | 13521.9 | 2.28 |
| 480 | 672.1 | 13414.4 | 2.51 |
| 540 | 747.2 | 13473.8 | 2.77 |
| 600 | 802.4 | 13451.7 | 2.98 |
| 660 | 852.7 | 13494.8 | 3.16 |
| 720 | 868.1 | 13399.5 | 3.24 |
| 780 | 907.5 | 13461.8 | 3.37 |
| 840 | 961.7 | 13412.9 | 3.59 |
| 900 | 973.5 | 13489.6 | 3.61 |
| 960 | 1044.0 | 13416.4 | 3.89 |
| 1020 | 1034.8 | 13576.8 | 3.81 |
| 1080 | 1139.5 | 13504.2 | 4.22 |
| 1140 | 1158.4 | 13464.4 | 4.30 |
| 1200 | 1252.3 | 13387.3 | 4.68 |
| 1260 | 1253.7 | 13418.4 | 4.67 |
| 1320 | 1236.0 | 13426.3 | 4.60 |
| 1380 | 1370.8 | 13469.0 | 5.09 |
| 1440 | 1331.0 | 13436.2 | 4.95 |
| 1500 | 1408.6 | 13532.9 | 5.20 |
| 1560 | 1467.2 | 13414.8 | 5.47 |
| 1620 | 1463.7 | 13360.0 | 5.48 |
| 1680 | 1569.9 | 13469.5 | 5.83 |



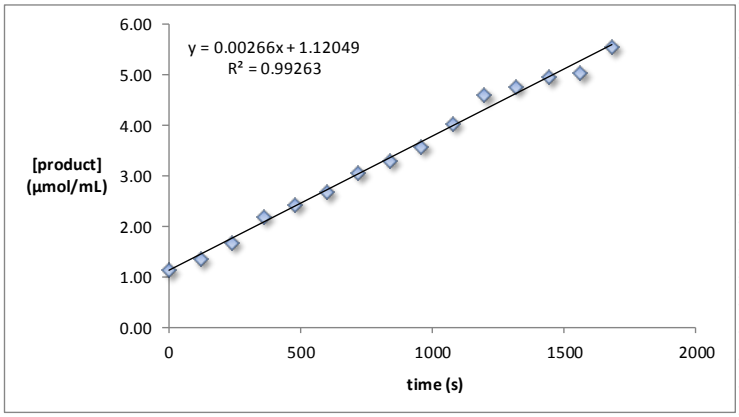

Following General Procedure VI, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $K^+$**5**$^-$ (0.131 mmol, 7.5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 120 s. **rate = 2.78 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 318.2 | 13324.9 | 1.19 |
| 120 | 444.2 | 14137.5 | 1.57 |
| 240 | 513.0 | 14417.8 | 1.78 |
| 360 | 610.7 | 14149.4 | 2.16 |
| 480 | 713.3 | 14354.6 | 2.48 |
| 600 | 822.3 | 14165.6 | 2.90 |
| 720 | 905.2 | 14102.3 | 3.21 |
| 840 | 1023.8 | 14024.5 | 3.65 |
| 960 | 1143.8 | 14035.7 | 4.07 |
| 1080 | 1156.7 | 14004.5 | 4.13 |
| 1200 | 1310.9 | 13997.0 | 4.68 |
| 1320 | 1424.2 | 14023.6 | 5.08 |
| 1440 | 1453.5 | 14068.4 | 5.17 |
| 1560 | 1544.6 | 13974.1 | 5.53 |
| 1680 | 1607.9 | 14211.4 | 5.66 |




Following General Procedure VI, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $K^+\mathbf{5}^-$ (0.131 mmol, 7.5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 120 s. **rate = 2.66 · $10^{-3}$ mM/s**

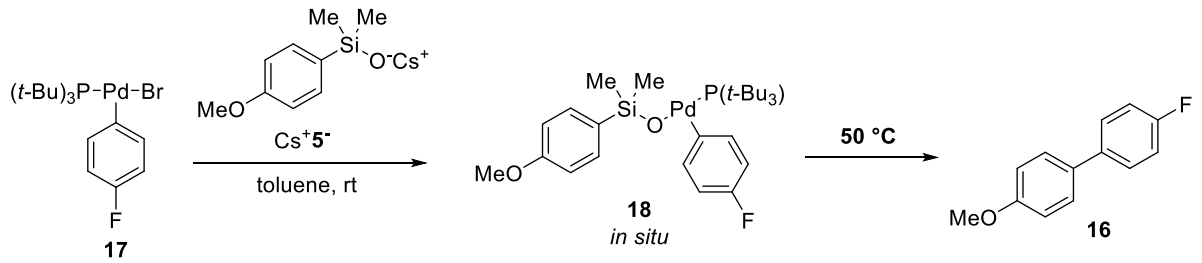
| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 0 | 318.5 | 13897.9 | 1.15 |
| 120 | 377.0 | 14101.8 | 1.34 |
| 240 | 475.7 | 14134.2 | 1.68 |
| 360 | 623.5 | 14187.6 | 2.20 |
| 480 | 687.8 | 14128.9 | 2.43 |
| 600 | 750.0 | 14049.8 | 2.67 |
| 720 | 866.4 | 14183.1 | 3.05 |
| 840 | 926.3 | 14054.8 | 3.30 |
| 960 | 1012.8 | 14174.1 | 3.57 |
| 1080 | 1138.6 | 14085.6 | 4.04 |
| 1200 | 1294.2 | 14073.0 | 4.60 |
| 1320 | 1342.0 | 14050.4 | 4.78 |
| 1440 | 1394.9 | 14088.7 | 4.95 |
| 1560 | 1413.6 | 14048.3 | 5.03 |
| 1680 | 1562.1 | 14067.2 | 5.55 |




**avg. rate = 2.71 · $10^{-3}$ ± 6.43 · $10^{-5}$ mM/s**

## KINETIC EXPERIMENTS FOR CROSS-COUPLING OF $Cs^+5^-$ WITH 17

### General Procedure VII: Kinetic Measurements for Transmetalation of 18 at 50 °C Starting with $Cs^+5^-$ (Table 8)

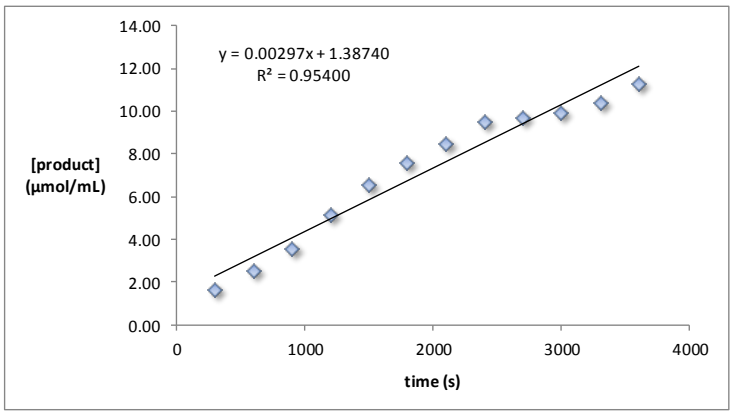



In a drybox, an oven-dried, 5-mm NMR tube was charged with **17** (9.4 mg, 0.0194 mmol), 1,4-difluorobenzene (1 μL, 0.00974 mmol, 0.5 equiv) and toluene (0.4 mL) resulting in an orange solution upon vigorous mixing. Then, $Cs^+\mathbf{5}^-$ (6.0 mg, 0.0192 mmol, 0.98 equiv) was added as a solid and the sides of the tube were rinsed with toluene (0.4 mL). The mixture was vigorously mixed using a vortex mixer for ca. 2 min to ensure complete dissolution. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and inserted into a preheated 50 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for ca. 90 s prior to data collection. The reaction progress was monitored via $^{19}$F NMR spectroscopy by the appearance of the product **16** (δ = –117.2 ppm) as compared to an internal reference (1,4-difluorobenzene, δ = –119.9 ppm) using the following parameters: at = 0.328, d1 = 0, pw90 = 8.85, pw = pw90/2, nt = 128, sampling every 300 s. Experiments were repeated in triplicate.

***<u>1 equivalent (Table 8, entry 1)</u>***

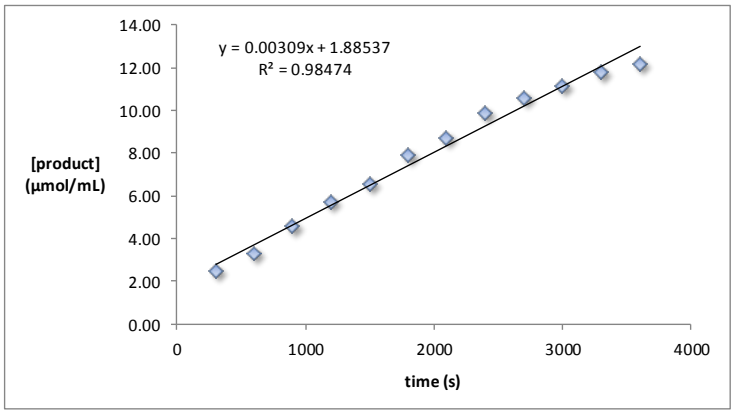
Following General Procedure VII, a mixture of **17** (9.4 mg, 0.0194 mmol) and 1,4-difluorobenzene (1 μL) was dissolved in toluene (0.4 mL), followed by the addition of $Cs^+\mathbf{5}^-$ (6.2 mg, 0.0192 mmol, 0.98 equiv) and toluene (0.4 mL) to afford an orange solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by $^{19}$F NMR spectroscopy. **rate = 2.97 · $10^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 493.4 | 7397.3 | 1.62 |
| 600 | 717.4 | 6934.6 | 2.51 |
| 900 | 981.3 | 6733.7 | 3.53 |
| 1200 | 1471.5 | 6950.8 | 5.13 |
| 1500 | 1876.7 | 6963.7 | 6.54 |
| 1800 | 2201.5 | 7049.4 | 7.57 |
| 2100 | 2406.6 | 6901.6 | 8.46 |
| 2400 | 2749.4 | 7003.2 | 9.52 |
| 2700 | 2848.2 | 7131.6 | 9.68 |
| 3000 | 2925.1 | 7136.3 | 9.94 |
| 3300 | 3062.9 | 7132.8 | 10.41 |
| 3600 | 3215.2 | 6900.0 | 11.30 |



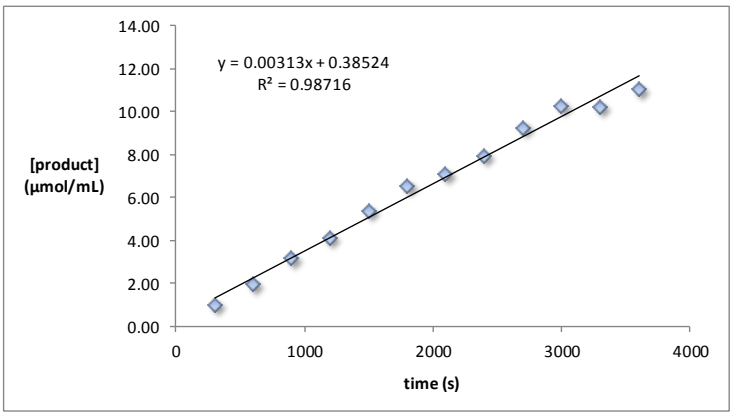

Following General Procedure VII, a mixture of **17** (9.4 mg, 0.0194 mmol) and 1,4-difluorobenzene (1 μL) was dissolved in toluene (0.4 mL), followed by the addition of $Cs^{+}$**5**$^{-}$ (6.2 mg, 0.0192 mmol, 0.98 equiv) and toluene (0.4 mL) to afford an orange solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by $^{19}$F NMR spectroscopy. **rate = 3.09 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 805.2 | 7863.9 | 2.48 |
| 600 | 1220.5 | 8997.9 | 3.29 |
| 900 | 1774.2 | 9456.3 | 4.55 |
| 1200 | 2171.5 | 9228.6 | 5.71 |
| 1500 | 2447.8 | 9020.8 | 6.58 |
| 1800 | 2832.9 | 8731.2 | 7.87 |
| 2100 | 3042.2 | 8431.4 | 8.75 |
| 2400 | 3334.1 | 8181.4 | 9.88 |
| 2700 | 3480.4 | 7965.8 | 10.60 |
| 3000 | 3656.3 | 7938.6 | 11.17 |
| 3300 | 3799.0 | 7802.5 | 11.81 |
| 3600 | 3872.4 | 7712.3 | 12.18 |



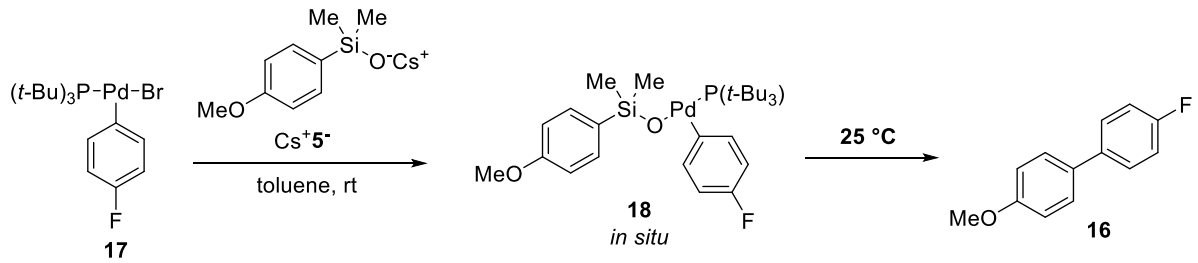

Following General Procedure VIII, a mixture of **17** (9.4 mg, 0.0194 mmol) and 1,4-difluorobenzene (1 μL) was dissolved in toluene (0.4 mL), followed by the addition of $Cs^{+}$**5**$^{-}$ (6.2 mg, 0.0192 mmol, 0.98 equiv) and toluene (0.4 mL) to afford an orange solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by $^{19}$F NMR spectroscopy. **rate = 3.13 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 300 | 480.2 | 11494.1 | 1.01 |
| 600 | 837.0 | 10369.9 | 1.96 |
| 900 | 1238.6 | 9564.7 | 3.14 |
| 1200 | 1587.1 | 9422.2 | 4.08 |
| 1500 | 2059.5 | 9275.3 | 5.38 |
| 1800 | 2461.0 | 9140.5 | 6.53 |
| 2100 | 2700.4 | 9201.7 | 7.12 |
| 2400 | 2983.0 | 9151.5 | 7.90 |
| 2700 | 3466.2 | 9062.0 | 9.28 |
| 3000 | 3834.8 | 9035.9 | 10.29 |
| 3300 | 3852.0 | 9153.4 | 10.21 |
| 3600 | 4140.2 | 9077.1 | 11.06 |




**avg. rate = $3.06 \cdot 10^{-3} \pm 8.24 \cdot 10^{-5}$ mM/s**

**General Procedure VIII: Kinetic Measurements for Transmetalation Employing $Cs^{+}5^{-}$ at 25 °C (Table 8)**

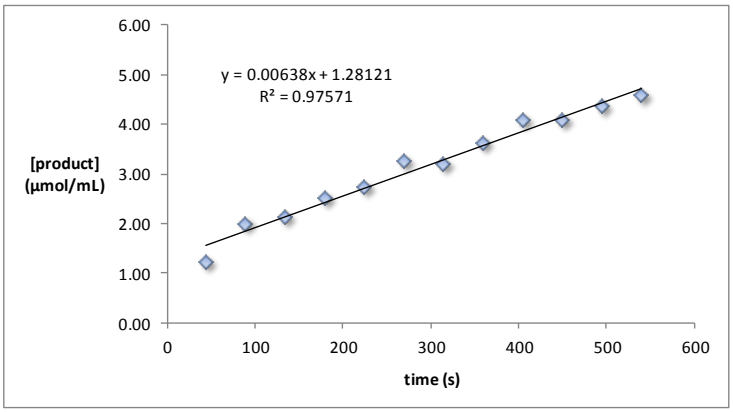



In a drybox, an oven-dried, 4-mL vial was charged with **17** (8.5 mg, 0.0175 mmol) and toluene, resulting in an orange solution. Then, a stock solution of $Cs^{+}$**5**$^{-}$ and 1,4-difluorobenzene in toluene was added to a total volume of 0.7 mL (0.025 M in **17**) and the mixture was vigorously mixed. The resulting solution was transferred via syringe into an oven-dried, 5-mm NMR tube. The tube was sealed with a cap and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and immediately inserted into a pre-warmed 25 °C NMR probe. The reaction progress was monitored via $^{19}$F NMR spectroscopy by the appearance of the product **16** (δ = –117.2 ppm) as compared to an internal reference (1,4-difluorobenzene, δ = –119.9 ppm) using the following parameters: at = 0.5 s, d1 = 1 s, pw90 = 15 μs, pw = pw90/2, sw = –115 to –130 ppm, nt and sampling as specified in each individual experiment. Experiments were repeated in triplicate.

***1.5 equivalents (Table 8, entry 2)***

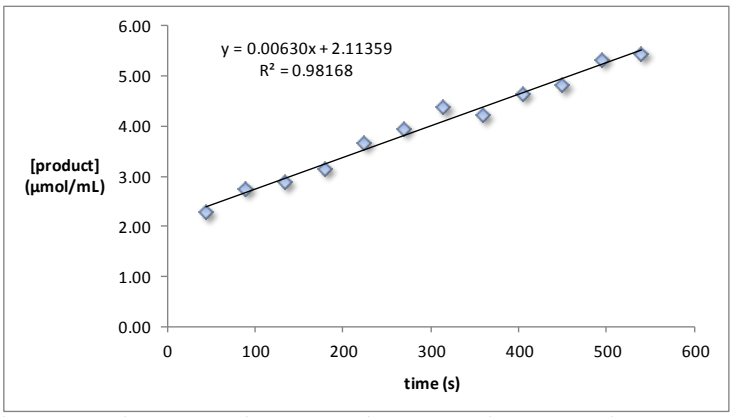
Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.0263 mmol, 1.5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 6.29 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 45 | 133.6 | 5445.5 | 1.23 |
| 90 | 215.1 | 5399.7 | 1.99 |
| 135 | 231.7 | 5411.0 | 2.14 |
| 180 | 271.1 | 5378.6 | 2.52 |
| 225 | 295.0 | 5401.2 | 2.73 |
| 270 | 351.0 | 5397.2 | 3.25 |
| 315 | 346.5 | 5409.8 | 3.20 |
| 360 | 389.8 | 5393.0 | 3.61 |
| 405 | 439.4 | 5386.7 | 4.08 |
| 450 | 438.8 | 5367.7 | 4.09 |
| 495 | 466.4 | 5346.6 | 4.36 |
| 540 | 492.7 | 5388.5 | 4.57 |




Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.0263 mmol, 1.5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 6.30 · 10$^{-3}$ mM/s**

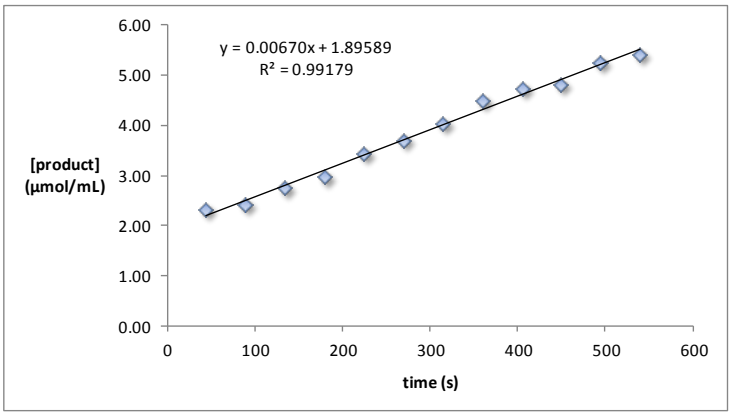
| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 45 | 257.3 | 5642.6 | 2.28 |
| 90 | 308.5 | 5596.6 | 2.76 |
| 135 | 320.3 | 5578.2 | 2.87 |
| 180 | 350.0 | 5554.6 | 3.15 |
| 225 | 408.2 | 5581.1 | 3.66 |
| 270 | 438.6 | 5562.4 | 3.94 |
| 315 | 487.2 | 5561.2 | 4.38 |
| 360 | 464.9 | 5533.2 | 4.20 |
| 405 | 516.7 | 5556.6 | 4.65 |
| 450 | 537.1 | 5572.1 | 4.82 |
| 495 | 595.2 | 5585.6 | 5.33 |
| 540 | 605.4 | 5567.9 | 5.44 |




Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.2 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.0263 mmol, 1.5 equiv) and 1,4-difluorobenzene (0.0175

mmol, 1 equiv) in toluene (0.5 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 6.70 · 10$^{-3}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 45 | 254.7 | 5490.0 | 2.32 |
| 90 | 264.9 | 5469.0 | 2.42 |
| 135 | 299.0 | 5442.5 | 2.75 |
| 180 | 323.8 | 5469.4 | 2.96 |
| 225 | 372.4 | 5444.6 | 3.42 |
| 270 | 402.3 | 5423.0 | 3.71 |
| 315 | 438.6 | 5458.0 | 4.02 |
| 360 | 483.4 | 5405.9 | 4.47 |
| 405 | 514.0 | 5432.3 | 4.73 |
| 450 | 523.8 | 5445.3 | 4.81 |
| 495 | 574.5 | 5470.1 | 5.25 |
| 540 | 590.1 | 5451.3 | 5.41 |

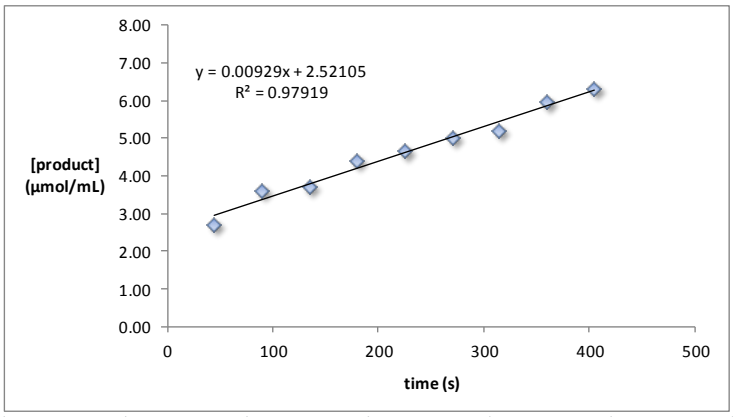



**avg. rate = 6.46 · 10$^{-3}$ ± 2.12 · 10$^{-4}$ mM/s**

***<u>2 equivalents (Table 8, entry 3)</u>***

Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of Cs$^{+}$**5**$^{-}$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 9.29 · 10$^{-3}$ mM/s**

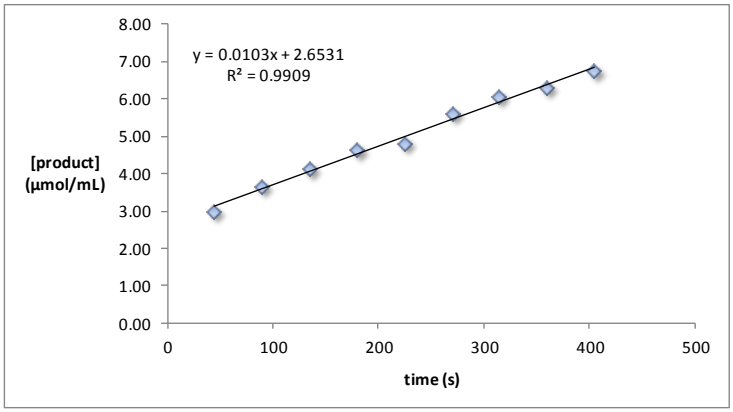
| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 45 | 302.3 | 5576.7 | 2.71 |
| 90 | 392.3 | 5452.6 | 3.60 |
| 135 | 402.8 | 5442.1 | 3.70 |
| 180 | 479.1 | 5459.9 | 4.39 |
| 225 | 504.5 | 5432.7 | 4.64 |
| 270 | 542.1 | 5422.8 | 5.00 |
| 315 | 567.6 | 5449.6 | 5.21 |
| 360 | 651.2 | 5457.5 | 5.97 |
| 405 | 686.6 | 5448.7 | 6.30 |




Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of Cs$^{+}$**5**$^{-}$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C

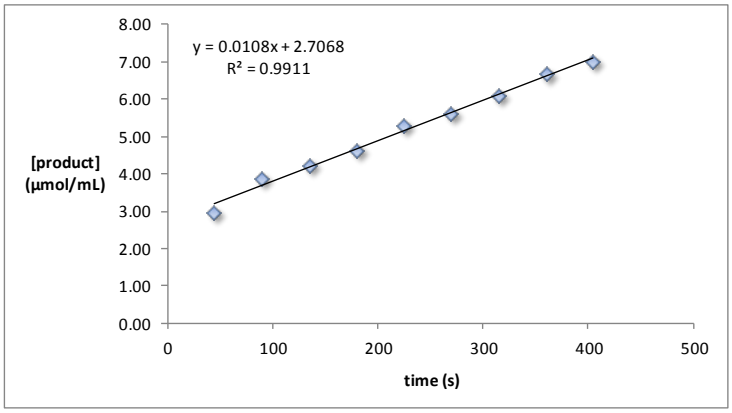
NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 1.03 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 45 | 328.7 | 5516.4 | 2.98 |
| 90 | 394.7 | 5445.7 | 3.62 |
| 135 | 446.5 | 5452.1 | 4.10 |
| 180 | 505.0 | 5451.8 | 4.63 |
| 225 | 525.9 | 5457.0 | 4.82 |
| 270 | 610.0 | 5452.5 | 5.59 |
| 315 | 649.6 | 5374.8 | 6.04 |
| 360 | 680.3 | 5403.4 | 6.29 |
| 405 | 726.9 | 5390.9 | 6.74 |




Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of Cs$^{+}$**5**$^{-}$ (0.035 mmol, 2 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16, sampling every 45 s. **rate = 1.08 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 45 | 327.6 | 5545.0 | 2.95 |
| 90 | 419.5 | 5449.4 | 3.85 |
| 135 | 462.0 | 5457.6 | 4.23 |
| 180 | 504.0 | 5435.8 | 4.64 |
| 225 | 573.9 | 5439.9 | 5.27 |
| 270 | 608.3 | 5426.0 | 5.61 |
| 315 | 662.0 | 5451.8 | 6.07 |
| 360 | 717.7 | 5380.3 | 6.67 |
| 405 | 760.6 | 5447.3 | 6.98 |



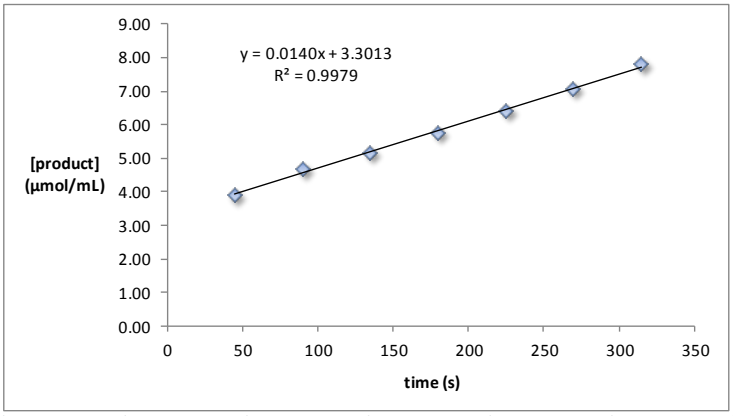

**avg. rate = 1.01 · 10$^{-2}$ ± 7.69 · 10$^{-4}$ mM/s**

***<u>3 equivalents (Table 8, entry 4)</u>***

Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of Cs$^{+}$**5**$^{-}$ (0.0525 mmol, 3 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 16,

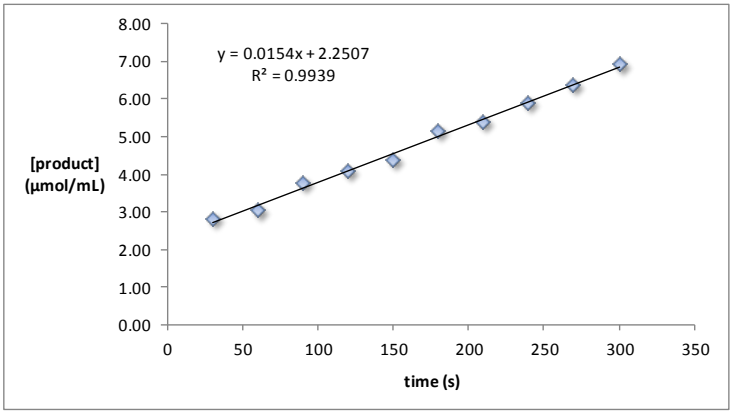
sampling every 45 s. **rate = 1.40 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 45 | 1033.4 | 13229.2 | 3.91 |
| 90 | 1210.3 | 12968.6 | 4.67 |
| 135 | 1337.3 | 12954.6 | 5.16 |
| 180 | 1511.5 | 13071.3 | 5.78 |
| 225 | 1665.9 | 13010.7 | 6.40 |
| 270 | 1842.5 | 13080.9 | 7.04 |
| 315 | 2031.2 | 13041.4 | 7.79 |



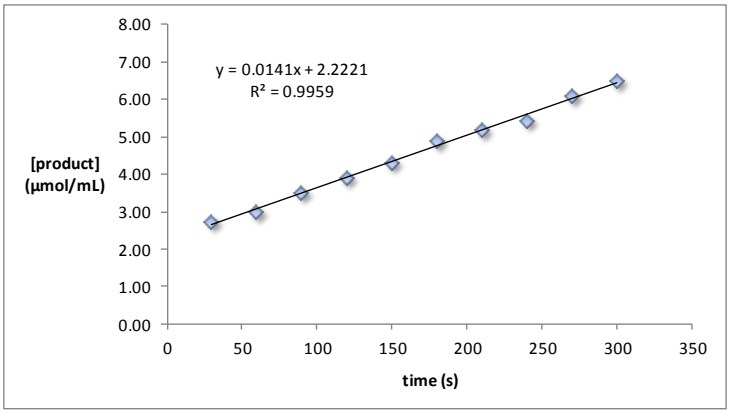

Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.0525 mmol, 3 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 1.54 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 30 | 441.6 | 7866.9 | 2.81 |
| 60 | 467.1 | 7706.8 | 3.03 |
| 90 | 575.0 | 7620.2 | 3.77 |
| 120 | 619.2 | 7590.5 | 4.08 |
| 150 | 665.3 | 7582.8 | 4.39 |
| 180 | 778.7 | 7561.5 | 5.15 |
| 210 | 827.8 | 7654.4 | 5.41 |
| 240 | 895.0 | 7573.2 | 5.91 |
| 270 | 970.2 | 7606.7 | 6.38 |
| 300 | 1051.7 | 7576.6 | 6.94 |




Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.0525 mmol, 3 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 1.41 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 30 | 424.6 | 7804.1 | 2.72 |
| 60 | 460.9 | 7703.9 | 2.99 |
| 90 | 529.7 | 7578.0 | 3.49 |
| 120 | 590.1 | 7604.8 | 3.88 |
| 150 | 651.6 | 7564.9 | 4.31 |
| 180 | 740.0 | 7576.9 | 4.88 |
| 210 | 786.5 | 7593.1 | 5.18 |
| 240 | 821.4 | 7549.2 | 5.44 |
| 270 | 919.8 | 7551.4 | 6.09 |
| 300 | 976.1 | 7530.7 | 6.48 |

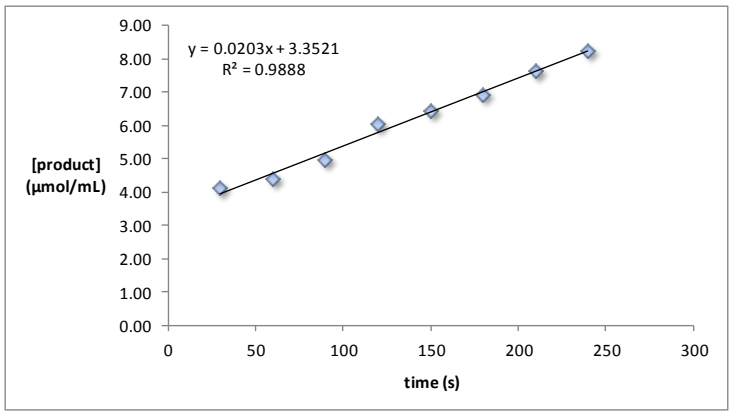



**avg. rate = 1.45 · $10^{-2}$ ± 7.81 · $10^{-4}$ mM/s**

***<u>5 equivalents (Table 8, entry 5)</u>***

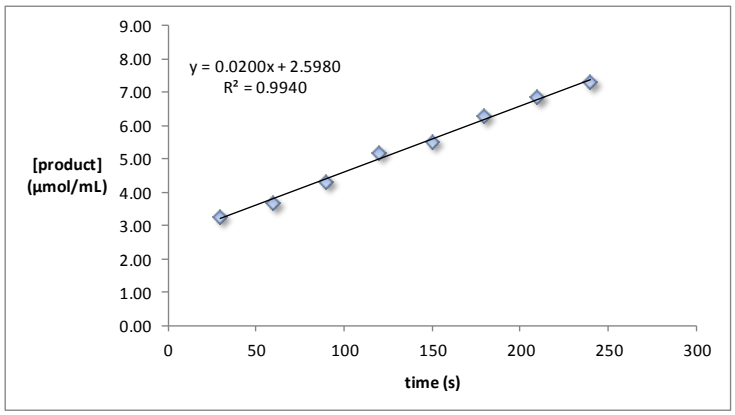
Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.0875 mmol, 5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.03 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 30 | 623.0 | 7574.0 | 4.11 |
| 60 | 654.1 | 7433.0 | 4.40 |
| 90 | 733.0 | 7375.4 | 4.97 |
| 120 | 888.9 | 7344.1 | 6.05 |
| 150 | 950.4 | 7377.7 | 6.44 |
| 180 | 1013.2 | 7324.2 | 6.92 |
| 210 | 1127.1 | 7374.0 | 7.64 |
| 240 | 1209.2 | 7356.0 | 8.22 |



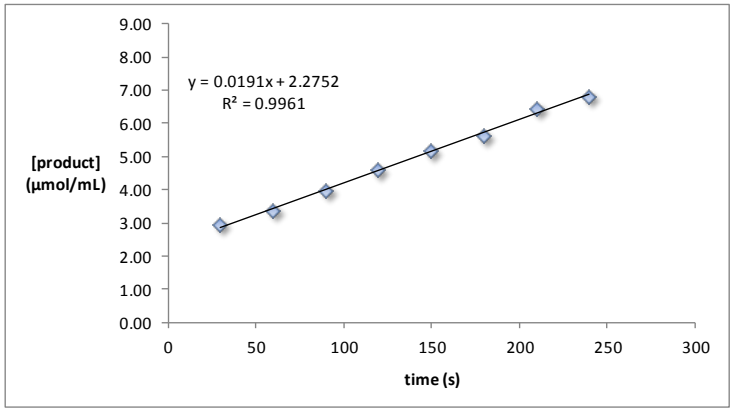

Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.0875 mmol, 5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.00 · $10^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 30 | 496.9 | 7587.7 | 3.27 |
| 60 | 550.8 | 7511.7 | 3.67 |
| 90 | 629.1 | 7295.0 | 4.31 |
| 120 | 752.6 | 7274.9 | 5.17 |
| 150 | 804.3 | 7319.7 | 5.49 |
| 180 | 920.1 | 7307.0 | 6.30 |
| 210 | 1002.0 | 7332.1 | 6.83 |
| 240 | 1069.9 | 7322.2 | 7.31 |




Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.0875 mmol, 5 equiv) and 1,4-difluorobenzene (0.0175 mmol, 1 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 1.91 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 30 | 445.3 | 7608.6 | 2.93 |
| 60 | 499.0 | 7467.8 | 3.34 |
| 90 | 592.8 | 7449.7 | 3.98 |
| 120 | 676.0 | 7398.8 | 4.57 |
| 150 | 765.5 | 7397.4 | 5.17 |
| 180 | 832.7 | 7438.7 | 5.60 |
| 210 | 957.2 | 7428.2 | 6.44 |
| 240 | 1000.3 | 7344.0 | 6.81 |

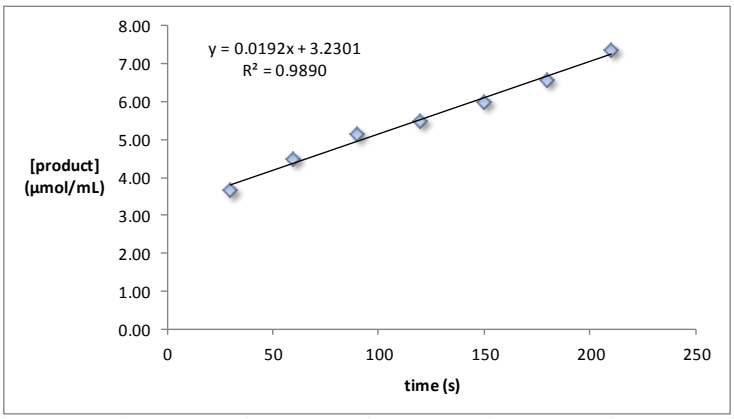



**avg. rate = 1.98 · 10$^{-2}$ ± 6.24 · 10$^{-4}$ mM/s**

***<u>7.5 equivalents (Table 8, entry 6)</u>***

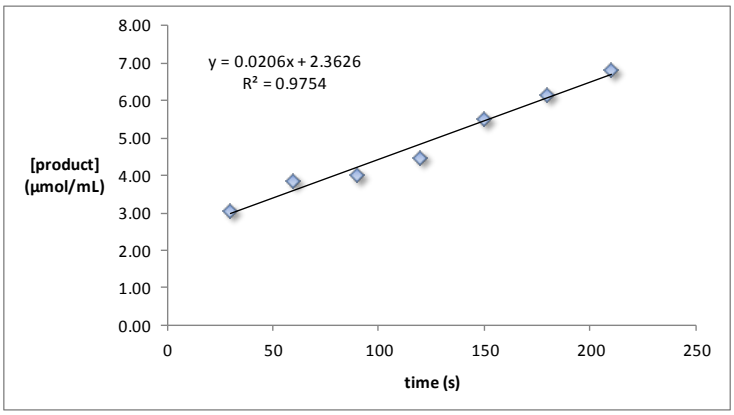
Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.131 mmol, 7 equiv) and 1,4-difluorobenzene (0.035 mmol, 2 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 1.92 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 30 | 559.3 | 15283.0 | 3.66 |
| 60 | 683.9 | 15208.7 | 4.50 |
| 90 | 773.6 | 15084.2 | 5.13 |
| 120 | 818.2 | 14867.6 | 5.50 |
| 150 | 897.3 | 14950.9 | 6.00 |
| 180 | 979.0 | 14933.0 | 6.56 |
| 210 | 1103.2 | 14986.0 | 7.36 |




Following General Procedure VIII, **17** (8.5 mg, 0.0175 mmol) was dissolved in toluene (0.1 mL). A stock solution of $Cs^{+}$**5**$^{-}$ (0.131 mmol, 7 equiv) and 1,4-difluorobenzene (0.035 mmol, 2 equiv) in toluene (0.6 mL) was added. The tube was inserted into a preheated 25 °C NMR probe and the reaction progress was monitored via $^{19}$F NMR spectroscopy; nt = 8, sampling every 30 s. **rate = 2.06 · 10$^{-2}$ mM/s**

| time (s) | product integral | standard integral | [product] (μmol/mL) |
|---|---|---|---|
| 30 | 380.6 | 12445.8 | 3.06 |
| 60 | 478.4 | 12374.0 | 3.87 |
| 90 | 493.9 | 12358.5 | 4.00 |
| 120 | 554.9 | 12368.0 | 4.49 |
| 150 | 680.7 | 12384.7 | 5.50 |
| 180 | 760.3 | 12372.1 | 6.15 |
| 210 | 847.7 | 12442.2 | 6.81 |



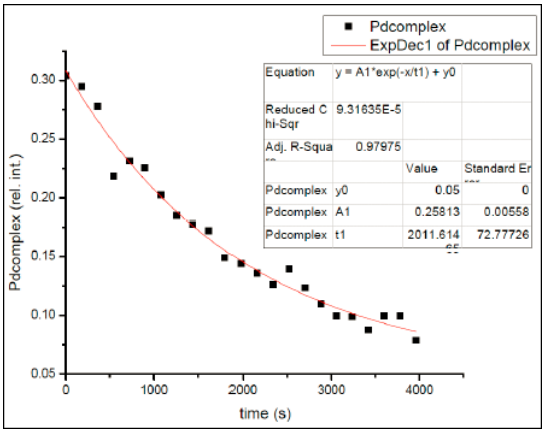

**avg. rate = 1.99 · 10$^{-2}$ ± 9.90 · 10$^{-4}$ mM/s**

**General Procedure IX: Kinetic Measurements for Thermal Transmetalation Employing $Cs^{+}$5$^{-}$ at 50 °C Removing the Inorganic Salts**

**Run 1**

The following modifications to General Procedure VII were made: the mixture was prepared in an oven-dried, 3-mL vial and the resulting reaction solution was transferred to the NMR tube using a 22G needle. A mixture of **17** (13.7 mg, 0.0283 mmol, 1.0 equiv) and 1,4-difluorobenzene (capillary) were dissolved in toluene (0.4 mL), followed by addition of $Cs^{+}$**5**$^{-}$ (8.7 mg, 0.0278 mmol, 0.98 equiv) and toluene (0.4 mL) to afford an orange solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by $^{19}$F NMR spectroscopy, sampling every 180 s. **rate = 4.97 x $10^{-4}$ $s^{-1}$**.

| Time (s) | Integral IS (-119.8 ppm) | Integral **18** (-121.7 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 1.252 | 0.381 | 35.38 |
| 180 | 1.251 | 0.369 | 34.33 |
| 360 | 1.192 | 0.331 | 32.34 |
| 540 | 1.202 | 0.263 | 25.42 |
| 720 | 1.381 | 0.320 | 26.93 |
| 900 | 1.299 | 0.293 | 26.24 |
| 1080 | 1.309 | 0.265 | 23.55 |
| 1260 | 1.333 | 0.246 | 21.51 |
| 1440 | 1.352 | 0.240 | 20.65 |
| 1620 | 1.291 | 0.222 | 20.04 |
| 1800 | 1.305 | 0.195 | 17.37 |
| 1980 | 1.363 | 0.197 | 16.80 |
| 2160 | 1.326 | 0.180 | 15.82 |
| 2340 | 1.306 | 0.165 | 14.68 |
| 2520 | 1.172 | 0.064 | 6.33 |
| 2700 | 1.211 | 0.049 | 4.73 |
| 2880 | 1.317 | 0.144 | 12.74 |
| 3060 | 1.313 | 0.130 | 11.56 |
| 3240 | 1.288 | 0.127 | 11.49 |
| 3420 | 1.433 | 0.125 | 10.17 |
| 3600 | 1.313 | 0.130 | 11.55 |
| 3780 | 1.333 | 0.133 | 11.59 |
| 3960 | 1.312 | 0.103 | 9.14 |

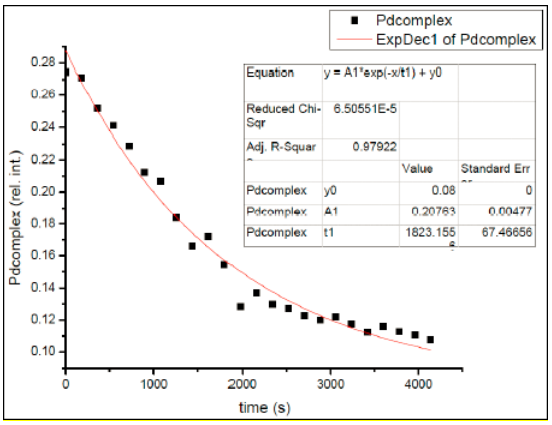



**Run 2**

Following General Procedure IX, the mixture was prepared in an oven-dried, 3-mL vial and the resulting reaction solution was transferred to the NMR tube using a 22G needle. A mixture of **17** (12.7 mg, 0.0263 mmol, 1.0 equiv) and 1,4-difluorobenzene (capillary) were dissolved in toluene (0.4 mL), followed by addition of $Cs^{+}$**5**$^{-}$ (8.1 mg, 0.0257 mmol, 0.98 equiv)

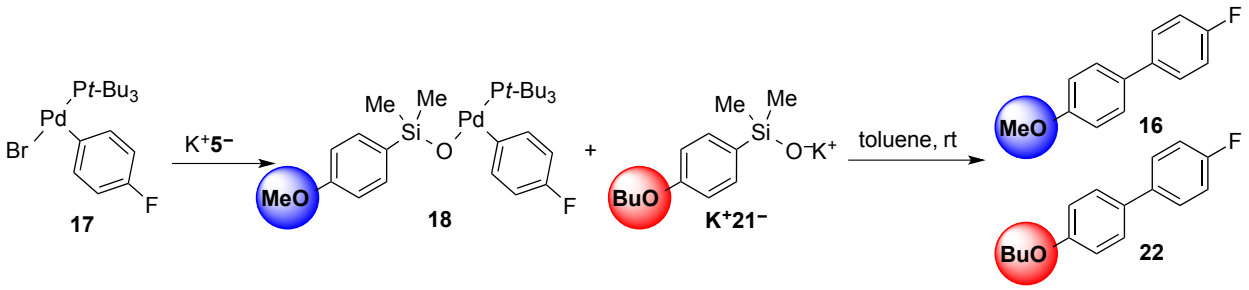
and toluene (0.4 mL) to afford an orange solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by $^{19}$F NMR spectroscopy, sampling every 180 s. **rate = 5.29 x 10$^{-4}$ s$^{-1}$**.

| Time (s) | Integral IS (-119.8 ppm) | Integral **18** (-121.7 ppm) | Normalized (mM) |
|---|---|---|---|
| 0 | 1.431 | 0.393 | 32.83 |
| 180 | 1.455 | 0.395 | 32.45 |
| 360 | 1.438 | 0.362 | 30.09 |
| 540 | 1.503 | 0.362 | 28.80 |
| 720 | 1.554 | 0.356 | 27.35 |
| 900 | 1.502 | 0.319 | 25.42 |
| 1080 | 1.452 | 0.300 | 24.74 |
| 1260 | 1.321 | 0.243 | 21.98 |
| 1440 | 1.349 | 0.224 | 19.85 |
| 1620 | 1.434 | 0.246 | 20.54 |
| 1800 | 1.368 | 0.211 | 18.47 |
| 1980 | 1.333 | 0.171 | 15.33 |
| 2160 | 1.402 | 0.192 | 16.40 |
| 2340 | 1.532 | 0.199 | 15.52 |
| 2520 | 1.496 | 0.190 | 15.22 |
| 2700 | 1.519 | 0.187 | 14.68 |
| 2880 | 1.485 | 0.178 | 14.35 |
| 3060 | 1.473 | 0.180 | 14.60 |
| 3240 | 1.467 | 0.172 | 14.03 |
| 3420 | 1.479 | 0.166 | 13.43 |
| 3600 | 1.475 | 0.171 | 13.87 |
| 3780 | 1.499 | 0.169 | 13.46 |
| 3960 | 1.471 | 0.163 | 13.25 |
| 4140 | 1.475 | 0.159 | 12.88 |
| 4320 | 1.491 | 0.161 | 12.93 |
| 4500 | 1.474 | 0.154 | 12.52 |
| 4680 | 1.489 | 0.157 | 12.60 |
| 4860 | 1.469 | 0.155 | 12.58 |
| 5040 | 1.391 | 0.147 | 12.60 |



**Analysis of Product Distribution for Cross-Coupling of 18 with Exogenous $K^+21^-$ as Activator (Scheme 11)**

**1.02 equiv $K^+21^-$**




To an oven dried 4-mL scintillation vial contained in a drybox was charged **17** (8.2 mg, 0.017 mmol) as an orange solid and biphenyl (6.8 mg, 0.044 mmol) as a white solid. Dry toluene (0.5 mL) was added affording an orange solution upon mixing. **$K^+5^-$** (3.7 mg, 0.017 mmol) was added as a solid and stirring resulted in complete dissolution. **$K^+21^-$** (4.5 mg, 0.017 mmol) was added in one portion as a solid and the sides of the vial were rinsed with additional toluene (0.2 mL). The resulting reaction mixture was allowed to stir in a drybox for 3 h. The reaction was then sampled by removing 100 μL of the reaction mixture and quenching onto water (0.5 mL). The organics were extracted with ethyl acetate (1.2 mL) and then passed through a pipet plug of $SiO_2$ to remove any insoluble material. The filtrate was analyzed by GC: Biphenyl, 3.84 min; $t_R$ 7.38 min, **16**, 0.0064 mmol (38%); $t_R$ 9.29 min, **23**, 0.0079 mmol (47%). Ratio of **16:22** based on biaryl product formation is 45/55.

**3.02 equiv $K^+21^-$**

To an oven dried 4-mL scintillation vial contained in a drybox was charged **17** (8.8 mg, 0.018 mmol) as an orange solid and biphenyl (4.8 mg, 0.031 mmol) as a white solid. Dry toluene (0.5 mL) was added affording an orange solution upon stirring. **$K^+5^-$** (3.9 mg, 0.018 mmol) was added as a solid and stirring resulted in complete dissolution. **$K^+21^-$** (14.4 mg, 0.055 mmol) was added in one portion as a solid and the sides of the vial were rinsed with additional toluene (0.2 mL). The resulting reaction mixture was allowed to stir in a drybox for 3h. The reaction was then sampled by removing 100 μL of the reaction mixture and quenching onto water (0.5 mL). The organics were extracted with ethyl acetate (1.2 mL) and then passed through a pipet plug of $SiO_2$ to remove any insoluble material. The filtrate was analyzed by GC:

Biphenyl, 3.84 min; $t_R$ 7.38 min, **16**, 0.0035 mmol (19%); $t_R$ 9.29 min, **22**, 0.015 mmol (83%). Ratio of **16:22** based on biaryl product formation is 19/81.

**GC Methods and Response Factors**

GC Method: Injections were made onto a Hewlett-Packard HP-1 50-m cross-linked 1%-phenyl methyl silicone gum phase column. The injector and detector temperature were 250 °C. The column oven temperature was as follows: GC: HP-1(manual) $T_0$ = 150 °C (5 min) Rate = 25 °C/min $T_f$ = 250 °C (5 min), total run time was 14 min. Retention times ($t_R$) and integrated ratios were obtained from reporting integrators.

Response factors ($R_f$) for quantitative GC analysis were obtained by the equation below:
Eq1: Response factor for A = (mmol A * area IS)/(area A * mmol IS)

| mmol of **22** | Area of **22** | mmol of IS | Area of IS | Response Factor |
|---|---|---|---|---|
| 0.0266 | 132408 | 0.0318 | 121727 | 0.769 |
| 0.0266 | 134283 | 0.0318 | 119941 | 0.747 |
| 0.0266 | 131848 | 0.0318 | 126715 | 0.804 |
| 0.027 | 150262 | 0.0441 | 178980 | 0.729 |
| 0.027 | 143526 | 0.0441 | 178802 | 0.763 |
| 0.027 | 151484 | 0.0441 | 183067 | 0.740 |
| 0.0221 | 123757 | 0.0447 | 189287 | 0.756 |
| 0.0221 | 121477 | 0.0447 | 186280 | 0.758 |
| 0.0221 | 118669 | 0.0447 | 182711 | 0.761 |
| | | | **AVG $R_f$** | 0.759 |

| mmol of **16** | Area of **16** | mmol of IS | Area of IS | Response Factor |
|---|---|---|---|---|
| 0.0321 | 108288 | 0.0422 | 129211 | 0.908 |
| 0.0321 | 105832 | 0.0422 | 129643 | 0.932 |
| 0.0321 | 104049 | 0.0422 | 130802 | 0.956 |
| 0.0371 | 154127 | 0.0363 | 145311 | 0.964 |
| 0.0371 | 154953 | 0.0363 | 149878 | 0.989 |
| 0.0371 | 153441 | 0.0363 | 145696 | 0.970 |
| 0.0277 | 123525 | 0.0455 | 185229 | 0.913 |
| 0.0277 | 124056 | 0.0455 | 181869 | 0.893 |
| 0.0277 | 120450 | 0.0455 | 176473 | 0.892 |
| | | | **AVG $R_f$** | 0.935 |

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(16) Procedure based upon: Yamashita, M.; Vicario, J.; Hartwig, J. *J. Am. Chem. Soc.* **2003**, *125*, 16347-16360.

(17) The time for temperature equilibration was independently confirmed by determining the time for 1 mL of ethylene glycol to reach a temperature that fluctuated by less than 0.2 °C

(18) The reaction progress was monitored through > 3 half lives to ensure consistency throughout the course of the reaction.

(19) The initial data points were normalized to the starting concentration of aryl halide. No product formation was observed at T = 0 min.

(20) The arylsilanolate $K^{+}\mathbf{5}^{-}$ proved to be insoluble at concentrations > 150 mM at room temperature. However independent solution studies showed that the silanolate was completely soluble up to a concentration of 600 mM at 90 °C.

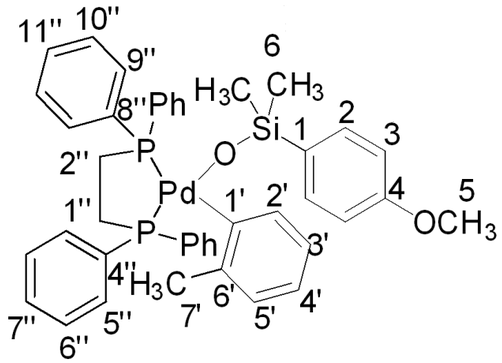
(21) Carrow, B. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 79.

(22) An independent experiment using 0.5 equiv of $Cs^{+}\mathbf{5}^{-}$ at the onset gave similar results whereby the peak at 77.0 ppm was the predominant species with small amount of **17** present. Attempts to isolate and fully characterize the proposed dimeric complex **19** were unsuccessful.

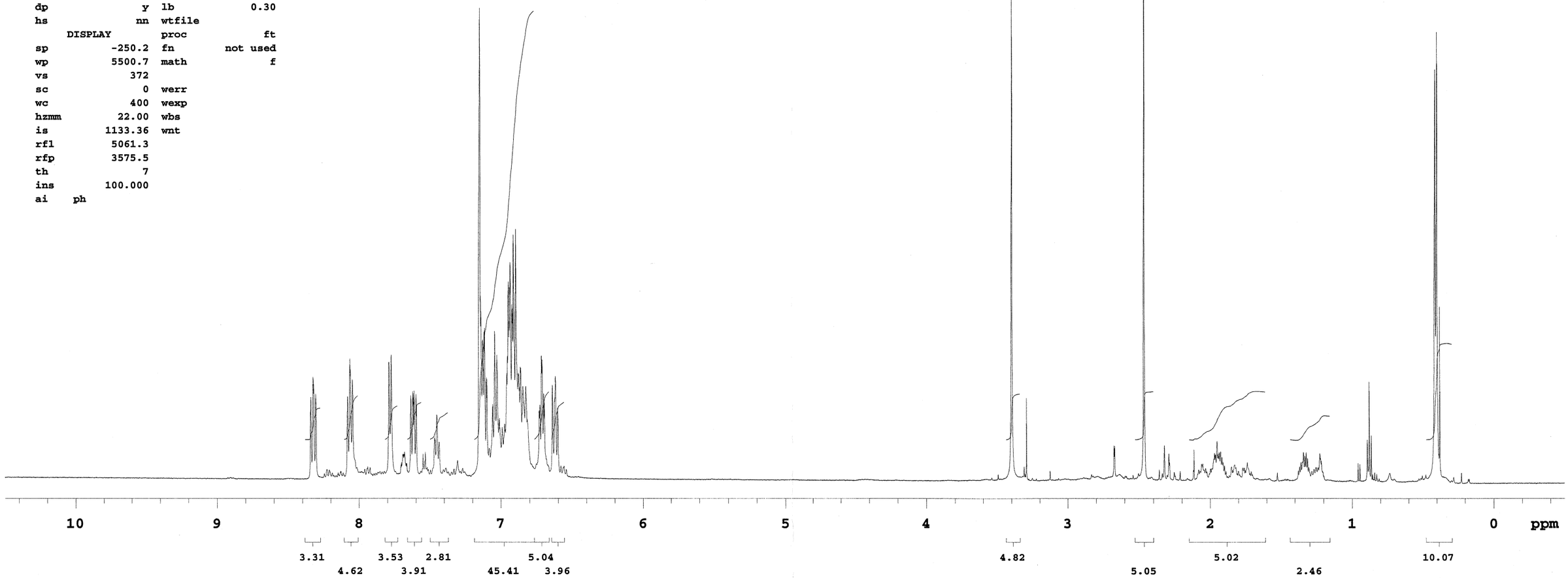
dppe complex

exp1 s2pul

| | | | |
|---|---|---|---|
| | SAMPLE | | DEC. & VT |
| date | Aug 29 2006 | dfrq | 500.076 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 18 |
| | ACQUISITION | dof | 0 |
| sfrq | 500.076 | dm | nnn |
| tn | H1 | dmm | c |
| at | 4.096 | dmf | 200 |
| np | 65536 | dseq | |
| sw | 8000.0 | dres | 1.0 |
| fb | not used | homo | n |
| bs | 16 | | DEC2 |
| tpwr | 55 | dfrq2 | 0 |
| pw | 7.7 | dn2 | |
| d1 | 5.000 | dpwr2 | 1 |
| tof | 0 | dof2 | 0 |
| nt | 8 | dm2 | n |
| ct | 8 | dmm2 | c |
| alock | n | dmf2 | 200 |
| gain | not used | dseq2 | |
| | FLAGS | dres2 | 1.0 |
| il | n | homo2 | n |
| in | n | | PROCESSING |
| dp | y | lb | 0.30 |
| hs | nn | wtfile | |
| | DISPLAY | proc | ft |
| sp | -250.2 | fn | not used |
| wp | 5500.7 | math | f |
| vs | 372 | | |
| sc | 0 | werr | |
| wc | 400 | wexp | |
| hzmm | 22.00 | wbs | |
| is | 1133.36 | wnt | |
| rf1 | 5061.3 | | |
| rfp | 3575.5 | | |
| th | 7 | | |
| ins | 100.000 | | |
| ai | ph | | |




**7e**



dppe complex

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
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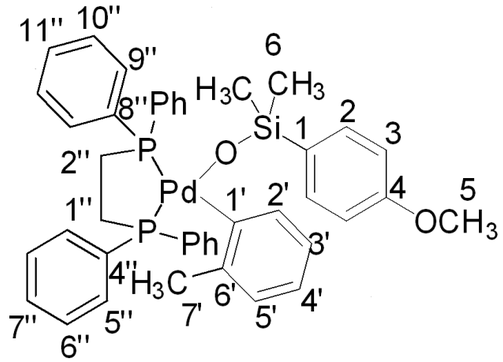
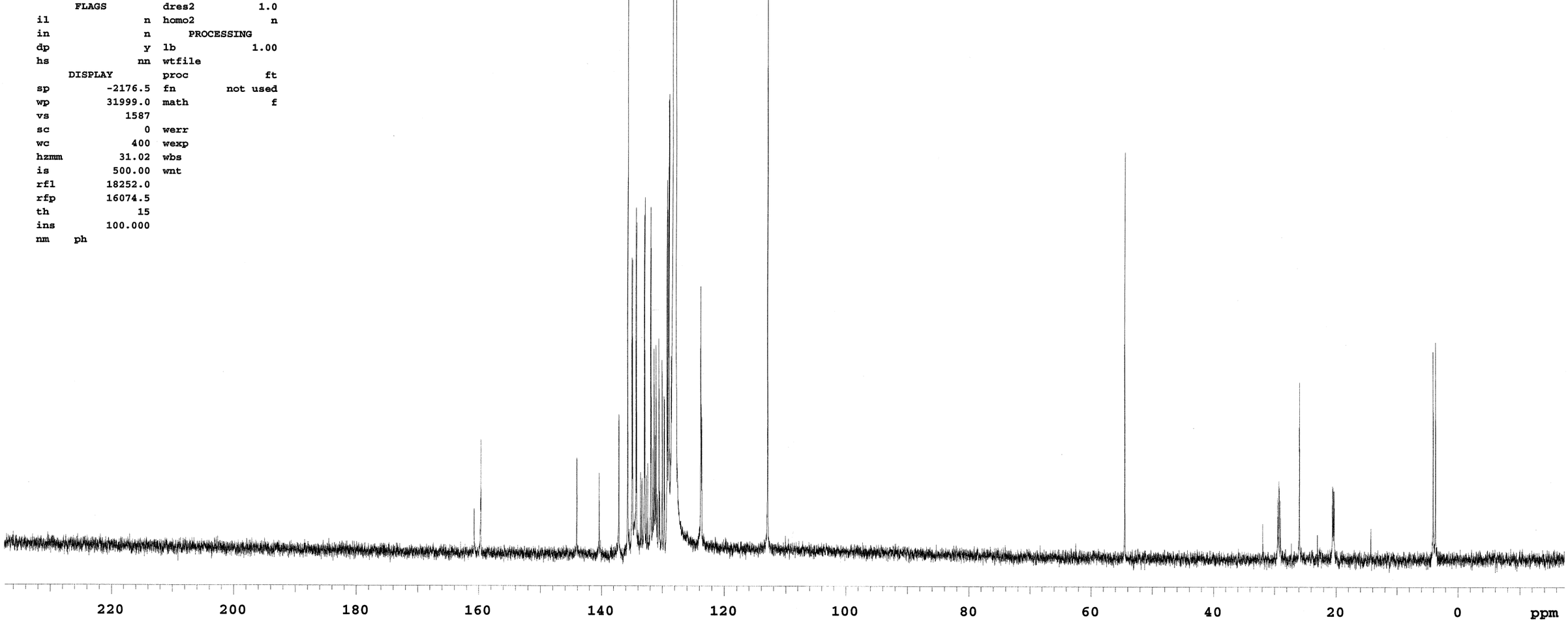
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 44 |
| ACQUISITION | | dof | -827.0 |
| sfrq | 125.596 | dm | yyy |
| tn | C13 | dmm | w |
| at | 1.024 | dmf | 19000 |
| np | 65536 | dseq | |
| sw | 32000.0 | dres | 1.0 |
| fb | 18000 | homo | n |
| bs | 16 | DEC2 | |
| tpwr | 63 | dfrq2 | 0 |
| pw | 4.0 | dn2 | |
| d1 | 1.000 | dpwr2 | 1 |
| tof | 1880.0 | dof2 | 0 |
| nt | 6000 | dm2 | n |
| ct | 3440 | dmm2 | c |
| alock | n | dmf2 | 18519 |
| gain | not used | dseq2 | |
| FLAGS | | dres2 | 1.0 |
| il | n | homo2 | n |
| in | n | PROCESSING | |
| dp | y | lb | 1.00 |
| hs | nn | wtfile | |
| DISPLAY | | proc | ft |
| sp | -2176.5 | fn | not used |
| wp | 31999.0 | math | f |
| vs | 1587 | | |
| sc | 0 | werr | |
| wc | 400 | wexp | |
| hzmm | 31.02 | wbs | |
| is | 500.00 | wnt | |
| rf1 | 18252.0 | | |
| rfp | 16074.5 | | |
| th | 15 | | |
| ins | 100.000 | | |
| nm | ph | | |



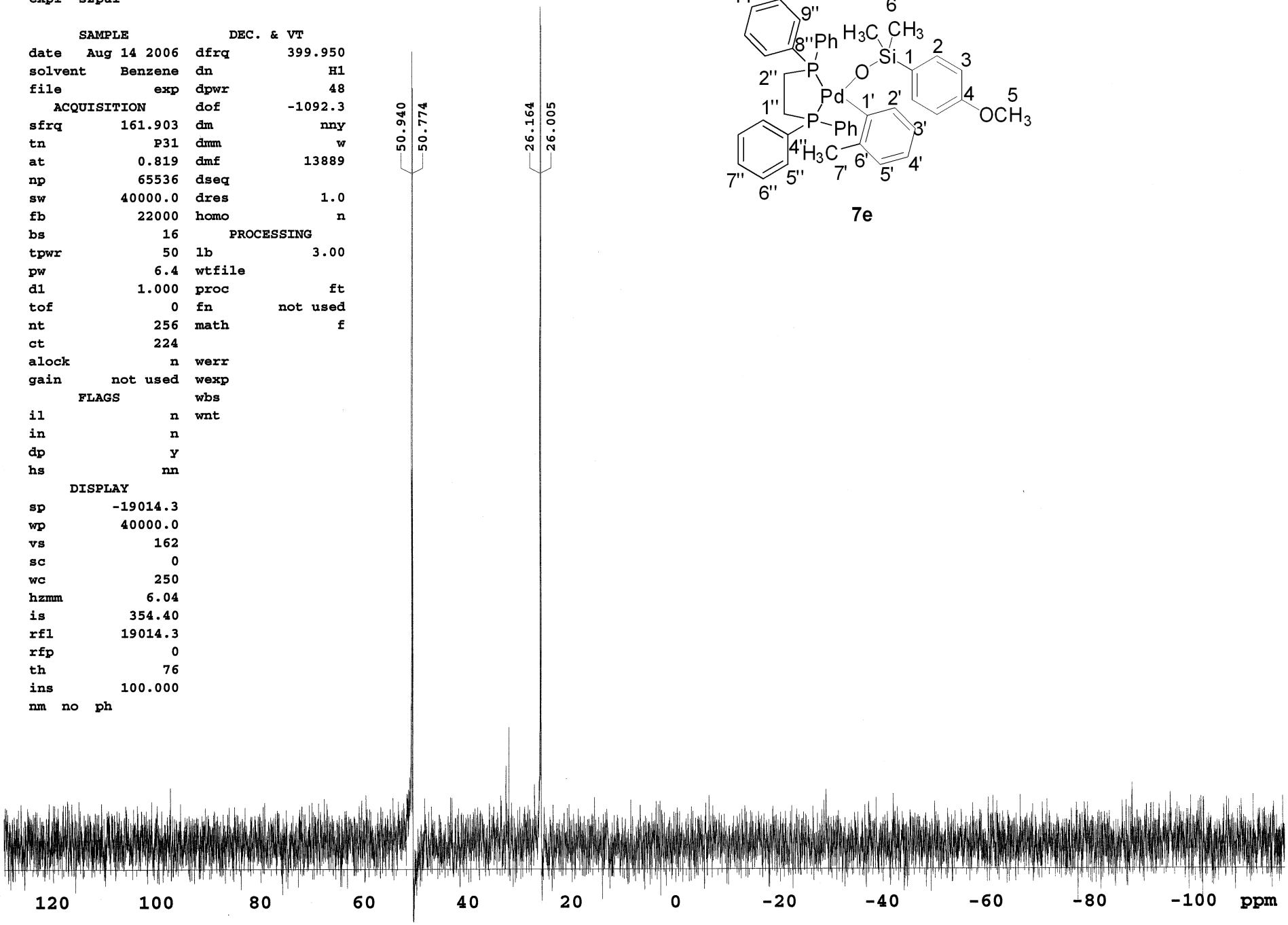

**7e**

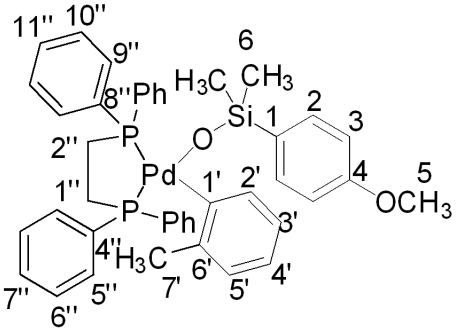


sat-xvii-19-31p

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Aug 14 2006 | dfrq | 399.950 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 48 |
| ACQUISITION | | dof | -1092.3 |
| sfrq | 161.903 | dm | nny |
| tn | P31 | dmm | w |
| at | 0.819 | dmf | 13889 |
| np | 65536 | dseq | |
| sw | 40000.0 | dres | 1.0 |
| fb | 22000 | homo | n |
| bs | 16 | PROCESSING | |
| tpwr | 50 | lb | 3.00 |
| pw | 6.4 | wtfile | |
| d1 | 1.000 | proc | ft |
| tof | 0 | fn | not used |
| nt | 256 | math | f |
| ct | 224 | | |
| alock | n | werr | |
| gain | not used | wexp | |
| FLAGS | | wbs | |
| il | n | wnt | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -19014.3 | | |
| wp | 40000.0 | | |
| vs | 162 | | |
| sc | 0 | | |
| wc | 250 | | |
| hzmm | 6.04 | | |
| is | 354.40 | | |
| rfl | 19014.3 | | |
| rfp | 0 | | |
| th | 76 | | |
| ins | 100.000 | | |
| nm no ph | | | |




**7e**

dppf complex

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
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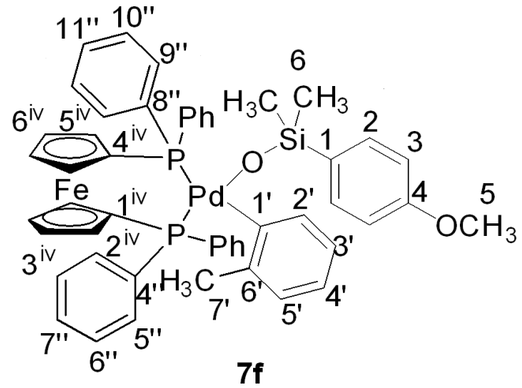
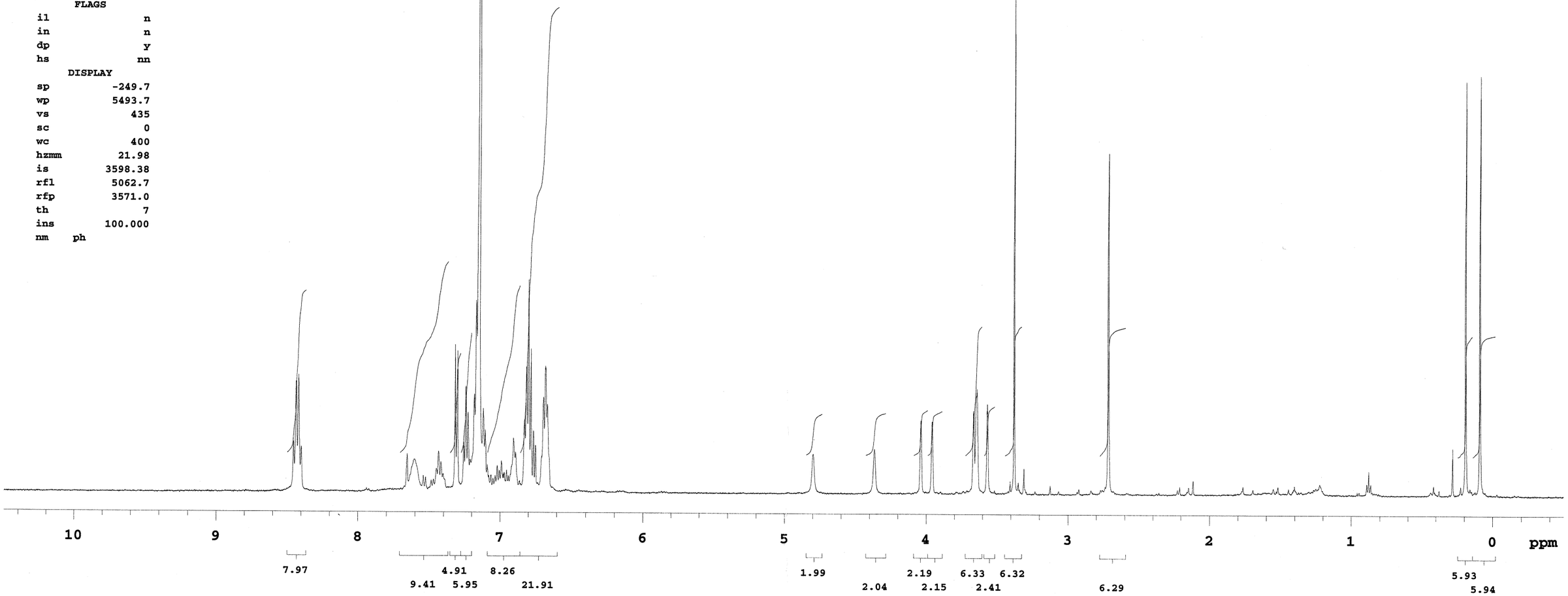
| solvent | Benzene | dn | H1 |
| file | /export/home/~ | dpwr | 25 |
| data/vxr500/tymonk~ | | dof | 0 |
| o/satxii31x.fid | | dm | nnn |
| ACQUISITION | | dmm | c |
| sfrq | 499.438 | dmf | 200 |
| tn | H1 | dseq | |
| at | 4.096 | dres | 1.0 |
| np | 65536 | homo | n |
| sw | 8000.0 | PROCESSING | |
| fb | 4400 | lb | 0.30 |
| bs | 4 | wtfile | |
| tpwr | 62 | proc | ft |
| pw | 5.0 | fn | not used |
| d1 | 4.000 | math | f |
| tof | 0 | | |
| nt | 8 | werr | |
| ct | 8 | wexp | |
| alock | n | wbs | |
| gain | not used | wnt | |
| FLAGS | | | |
| il | n | | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -249.7 | | |
| wp | 5493.7 | | |
| vs | 435 | | |
| sc | 0 | | |
| wc | 400 | | |
| hzmm | 21.98 | | |
| is | 3598.38 | | |
| rfl | 5062.7 | | |
| rfp | 3571.0 | | |
| th | 7 | | |
| ins | 100.000 | | |
| nm | ph | | |



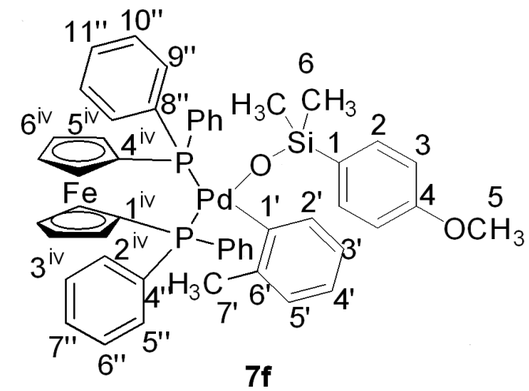

**7f**



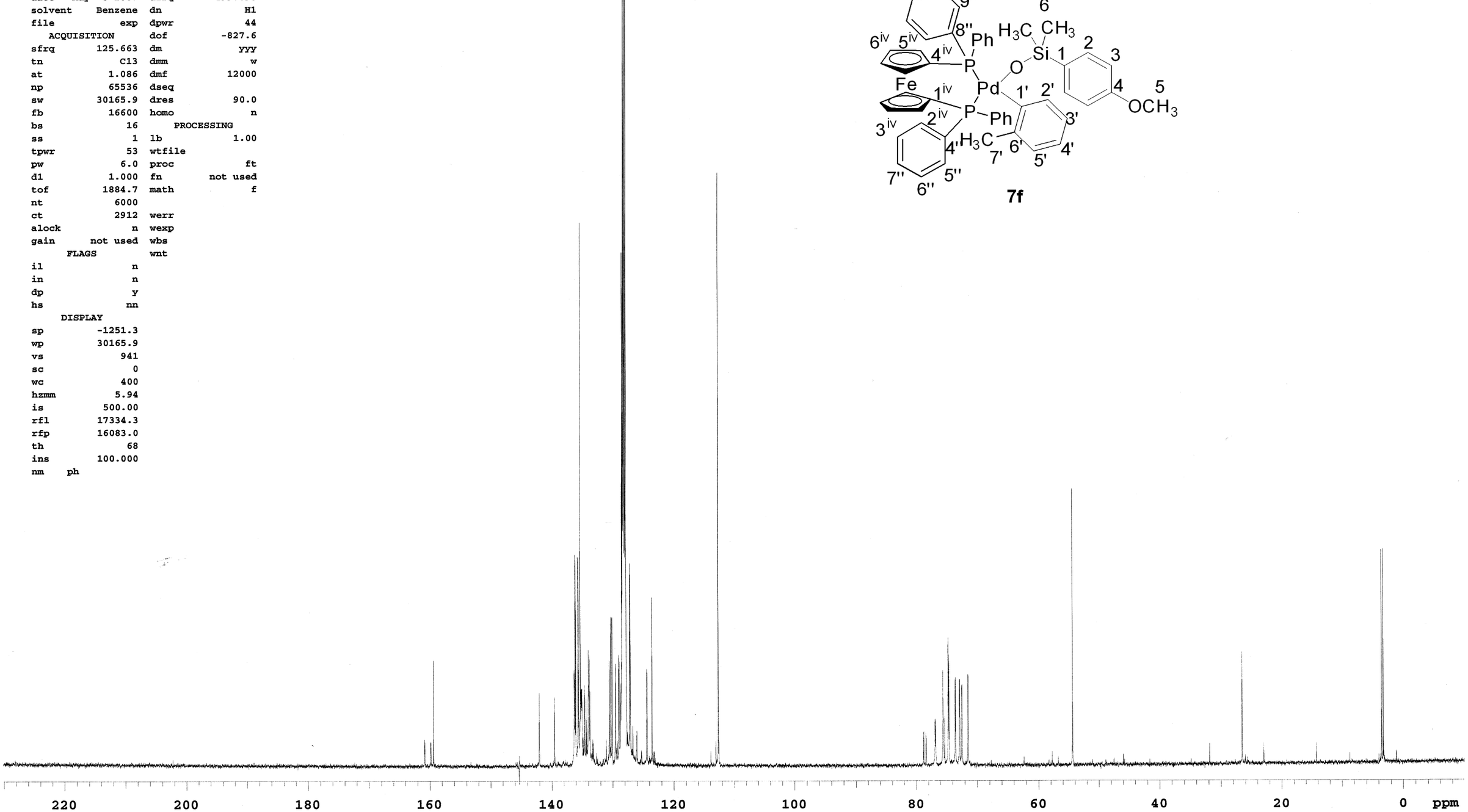
dppf complex

exp1 s2pul

| | | | |
|---|---|---|---|
| SAMPLE | | DEC. & VT | |
| date | May 8 2007 | dfrq | 499.698 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 44 |
| ACQUISITION | | dof | -827.6 |
| sfrq | 125.663 | dm | yyy |
| tn | C13 | dmm | w |
| at | 1.086 | dmf | 12000 |
| np | 65536 | dseq | |
| sw | 30165.9 | dres | 90.0 |
| fb | 16600 | homo | n |
| bs | 16 | PROCESSING | |
| ss | 1 | lb | 1.00 |
| tpwr | 53 | wtfile | |
| pw | 6.0 | proc | ft |
| d1 | 1.000 | fn | not used |
| tof | 1884.7 | math | f |
| nt | 6000 | | |
| ct | 2912 | werr | |
| alock | n | wexp | |
| gain | not used | wbs | |
| FLAGS | | wnt | |
| il | n | | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -1251.3 | | |
| wp | 30165.9 | | |
| vs | 941 | | |
| sc | 0 | | |
| wc | 400 | | |
| hzmm | 5.94 | | |
| is | 500.00 | | |
| rfl | 17334.3 | | |
| rfp | 16083.0 | | |
| th | 68 | | |
| ins | 100.000 | | |
| nm | ph | | |




**7f**

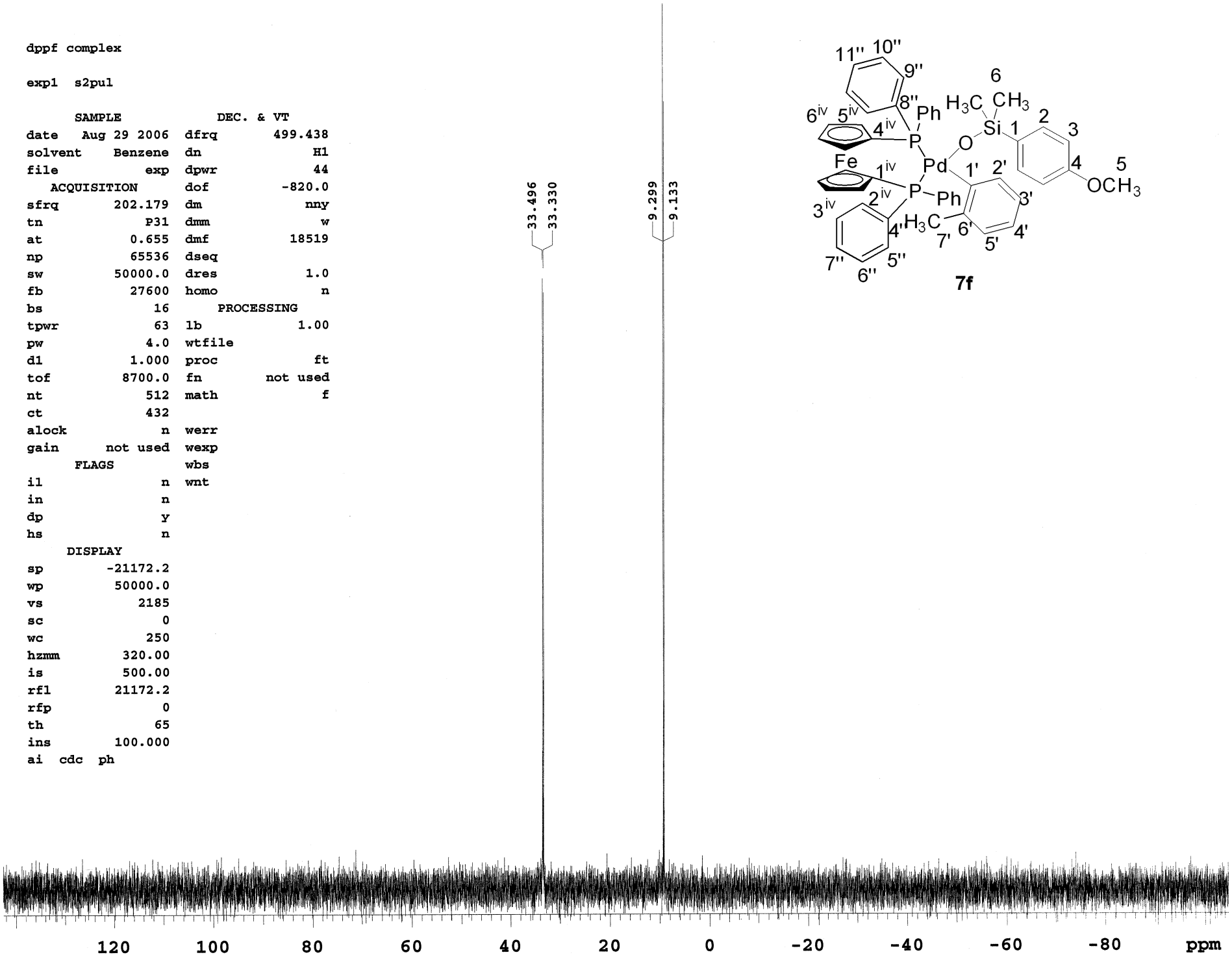


dppf complex

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Aug 29 2006 | dfrq | 499.438 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 44 |
| ACQUISITION | | dof | -820.0 |
| sfrq | 202.179 | dm | nny |
| tn | P31 | dmm | w |
| at | 0.655 | dmf | 18519 |
| np | 65536 | dseq | |
| sw | 50000.0 | dres | 1.0 |
| fb | 27600 | homo | n |
| bs | 16 | PROCESSING | |
| tpwr | 63 | lb | 1.00 |
| pw | 4.0 | wtfile | |
| d1 | 1.000 | proc | ft |
| tof | 8700.0 | fn | not used |
| nt | 512 | math | f |
| ct | 432 | | |
| alock | n | werr | |
| gain | not used | wexp | |
| FLAGS | | wbs | |
| il | n | wnt | |
| in | n | | |
| dp | y | | |
| hs | n | | |
| DISPLAY | | | |
| sp | -21172.2 | | |
| wp | 50000.0 | | |
| vs | 2185 | | |
| sc | 0 | | |
| wc | 250 | | |
| hzmm | 320.00 | | |
| is | 500.00 | | |
| rfl | 21172.2 | | |
| rfp | 0 | | |
| th | 65 | | |
| ins | 100.000 | | |

ai cdc ph



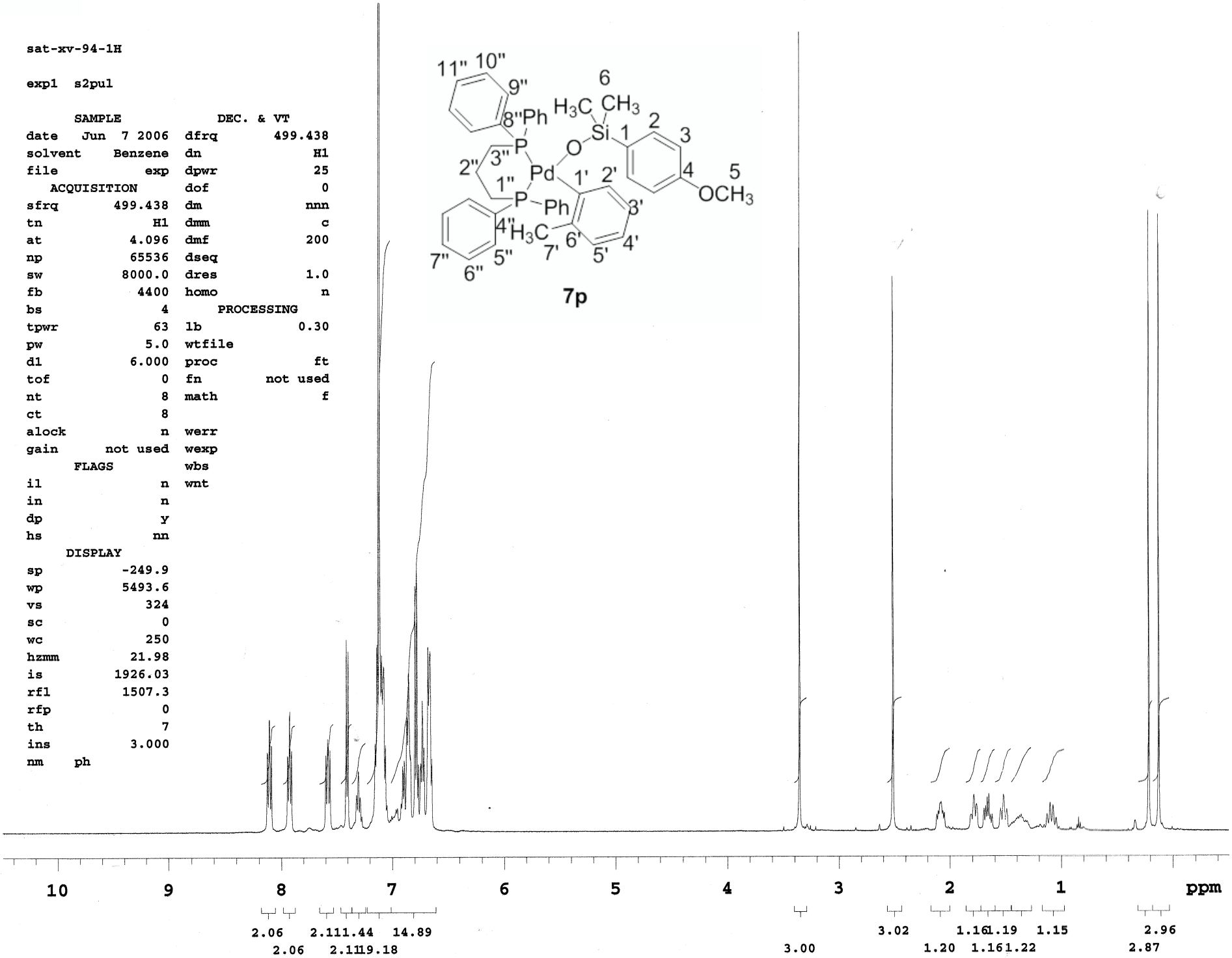
sat-xv-94-1H

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Jun 7 2006 | dfrq | 499.438 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 25 |
| ACQUISITION | | dof | 0 |
| sfrq | 499.438 | dm | nnn |
| tn | H1 | dmm | c |
| at | 4.096 | dmf | 200 |
| np | 65536 | dseq | |
| sw | 8000.0 | dres | 1.0 |
| fb | 4400 | homo | n |
| bs | 4 | PROCESSING | |
| tpwr | 63 | lb | 0.30 |
| pw | 5.0 | wtfile | |
| d1 | 6.000 | proc | ft |
| tof | 0 | fn | not used |
| nt | 8 | math | f |
| ct | 8 | | |
| alock | n | werr | |
| gain | not used | wexp | |
| FLAGS | | wbs | |
| il | n | wnt | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -249.9 | | |
| wp | 5493.6 | | |
| vs | 324 | | |
| sc | 0 | | |
| wc | 250 | | |
| hzmm | 21.98 | | |
| is | 1926.03 | | |
| rfl | 1507.3 | | |
| rfp | 0 | | |
| th | 7 | | |
| ins | 3.000 | | |
| nm | ph | | |




**7p**



sat-xv-94-13C

exp1 s2pul

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|---|---|---|---|
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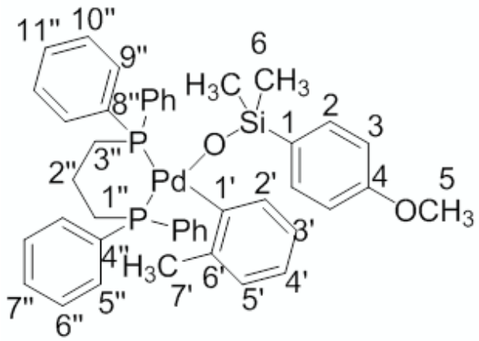
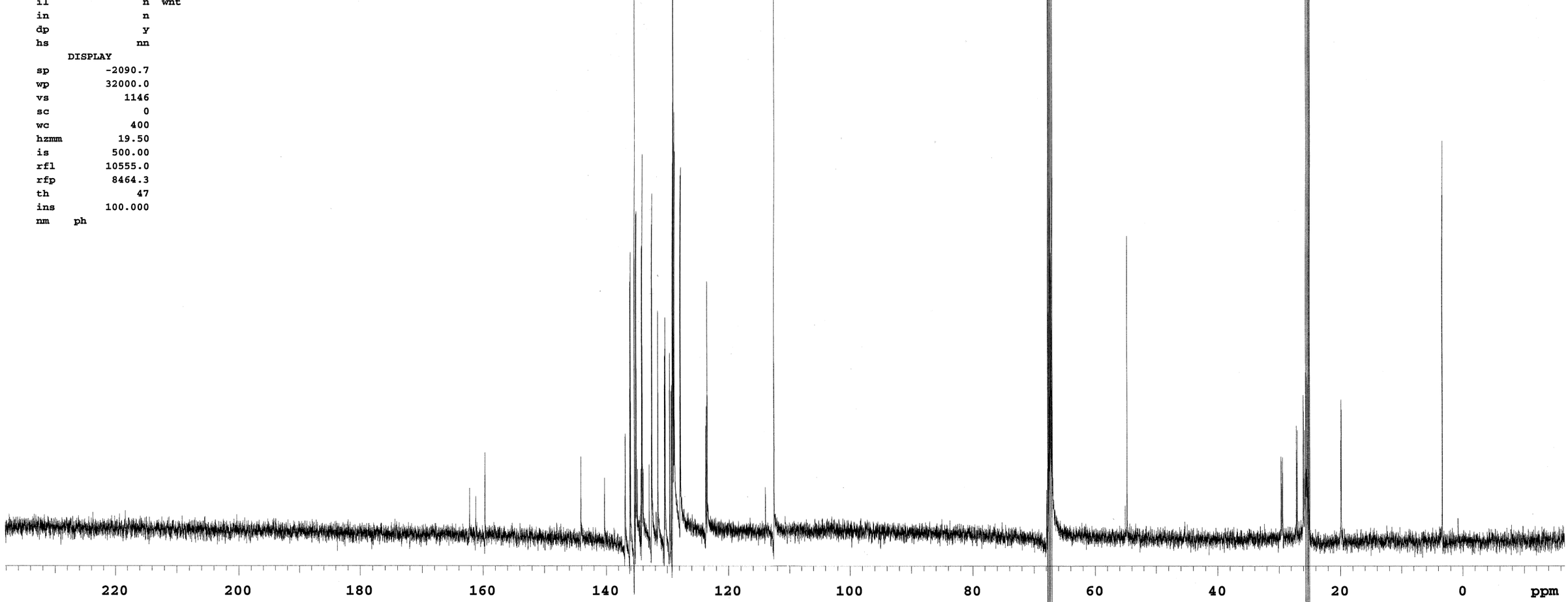
| solvent | THF | dn | H1 |
| file | exp | dpwr | 44 |
| ACQUISITION | | dof | -827.0 |
| sfrq | 125.597 | dm | yyy |
| tn | C13 | dmm | w |
| at | 1.024 | dmf | 18519 |
| np | 65536 | dseq | |
| sw | 32000.0 | dres | 1.0 |
| fb | 17600 | homo | n |
| bs | 16 | PROCESSING | |
| tpwr | 61 | lb | 1.00 |
| pw | 4.0 | wtfile | |
| d1 | 1.000 | proc | ft |
| tof | 1880.0 | fn | not used |
| nt | 4000 | math | f |
| ct | 2208 | | |
| alock | n | werr | |
| gain | not used | wexp | |
| FLAGS | | wbs | |
| il | n | wnt | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -2090.7 | | |
| wp | 32000.0 | | |
| vs | 1146 | | |
| sc | 0 | | |
| wc | 400 | | |
| hzmm | 19.50 | | |
| is | 500.00 | | |
| rfl | 10555.0 | | |
| rfp | 8464.3 | | |
| th | 47 | | |
| ins | 100.000 | | |
| nm | ph | | |



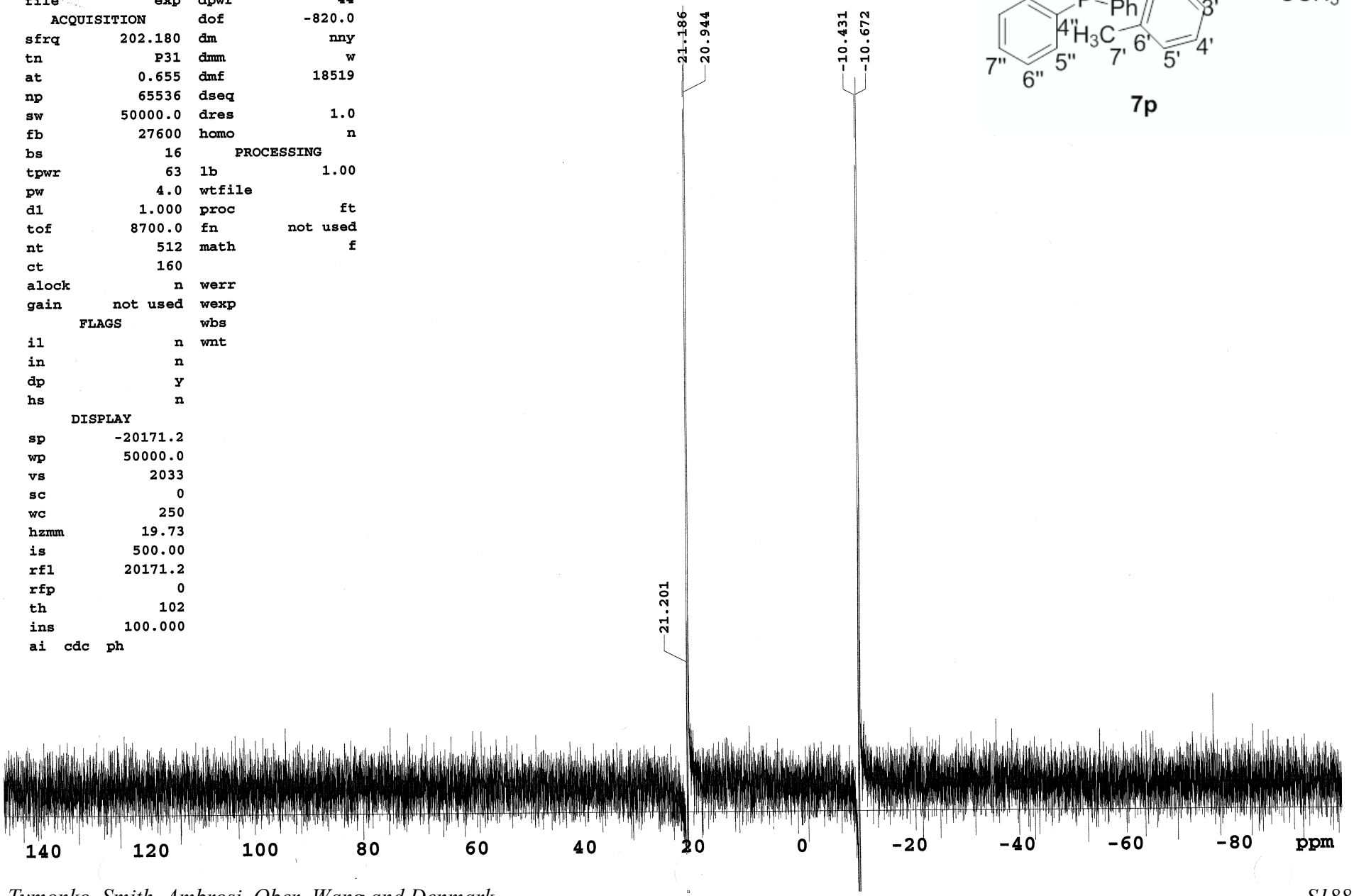

**7p**

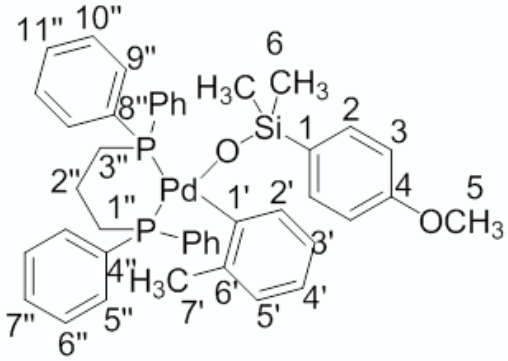


PdIIsilanolate

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Jun 12 2006 | dfrq | 499.440 |
| solvent | Toluene | dn | H1 |
| file | exp | dpwr | 44 |
| ACQUISITION | | dof | -820.0 |
| sfrq | 202.180 | dm | nny |
| tn | P31 | dmm | w |
| at | 0.655 | dmf | 18519 |
| np | 65536 | dseq | |
| sw | 50000.0 | dres | 1.0 |
| fb | 27600 | homo | n |
| bs | 16 | PROCESSING | |
| tpwr | 63 | lb | 1.00 |
| pw | 4.0 | wtfile | |
| d1 | 1.000 | proc | ft |
| tof | 8700.0 | fn | not used |
| nt | 512 | math | f |
| ct | 160 | | |
| alock | n | werr | |
| gain | not used | wexp | |
| FLAGS | | wbs | |
| il | n | wnt | |
| in | n | | |
| dp | y | | |
| hs | n | | |
| DISPLAY | | | |
| sp | -20171.2 | | |
| wp | 50000.0 | | |
| vs | 2033 | | |
| sc | 0 | | |
| wc | 250 | | |
| hzmm | 19.73 | | |
| is | 500.00 | | |
| rfl | 20171.2 | | |
| rfp | 0 | | |
| th | 102 | | |
| ins | 100.000 | | |
| ai cdc ph | | | |



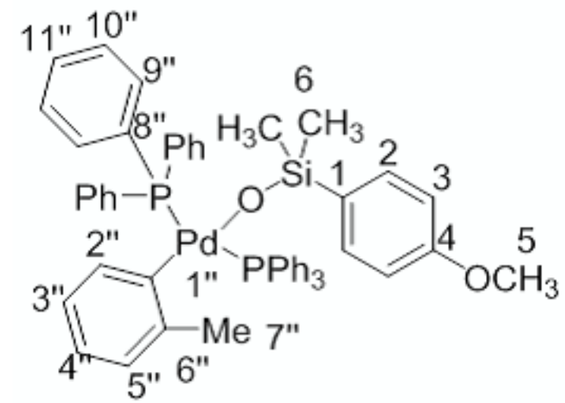




**7p**

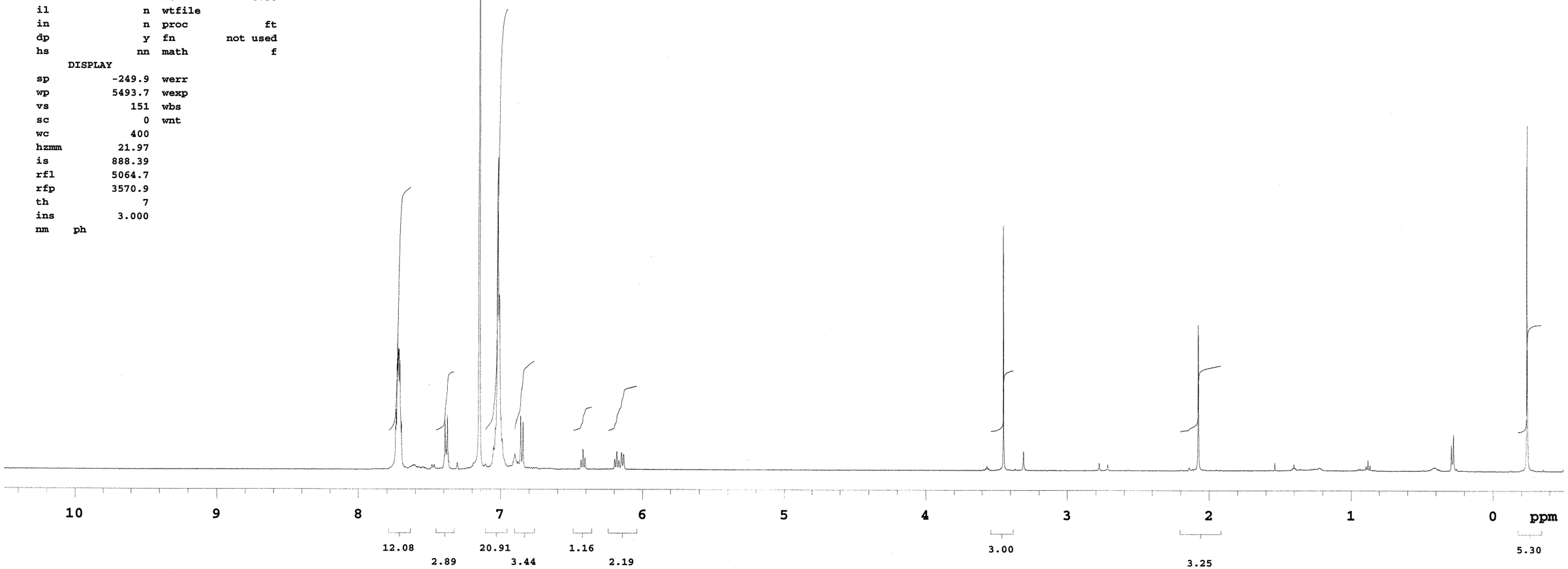
sat-xviii89x

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Feb 1 2007 | dfrq | 499.432 |
| solvent | Benzene | dn | H1 |
| file | /export/home/~ | dpwr | 25 |
| data/vxr500/Denmar~ | | dof | 0 |
| k/tymonko/satxviii~ | | dm | nnn |
| | 89x.fid | dmm | c |
| ACQUISITION | | dmf | 200 |
| sfrq | 499.432 | dseq | |
| tn | H1 | dres | 1.0 |
| at | 4.096 | homo | n |
| np | 65536 | DEC2 | |
| sw | 8000.0 | dfrq2 | 0 |
| fb | 4000 | dn2 | |
| bs | 4 | dpwr2 | 1 |
| tpwr | 62 | dof2 | 0 |
| pw | 5.0 | dm2 | n |
| d1 | 6.000 | dmm2 | c |
| tof | 0 | dmf2 | 200 |
| nt | 8 | dseq2 | |
| ct | 8 | dres2 | 1.0 |
| alock | n | homo2 | n |
| gain | not used | PROCESSING | |
| FLAGS | | lb | 0.30 |
| il | n | wtfile | |
| in | n | proc | ft |
| dp | y | fn | not used |
| hs | nn | math | f |
| DISPLAY | | | |
| sp | -249.9 | werr | |
| wp | 5493.7 | wexp | |
| vs | 151 | wbs | |
| sc | 0 | wnt | |
| wc | 400 | | |
| hzmm | 21.97 | | |
| is | 888.39 | | |
| rfl | 5064.7 | | |
| rfp | 3570.9 | | |
| th | 7 | | |
| ins | 3.000 | | |
| nm | ph | | |




**7t**



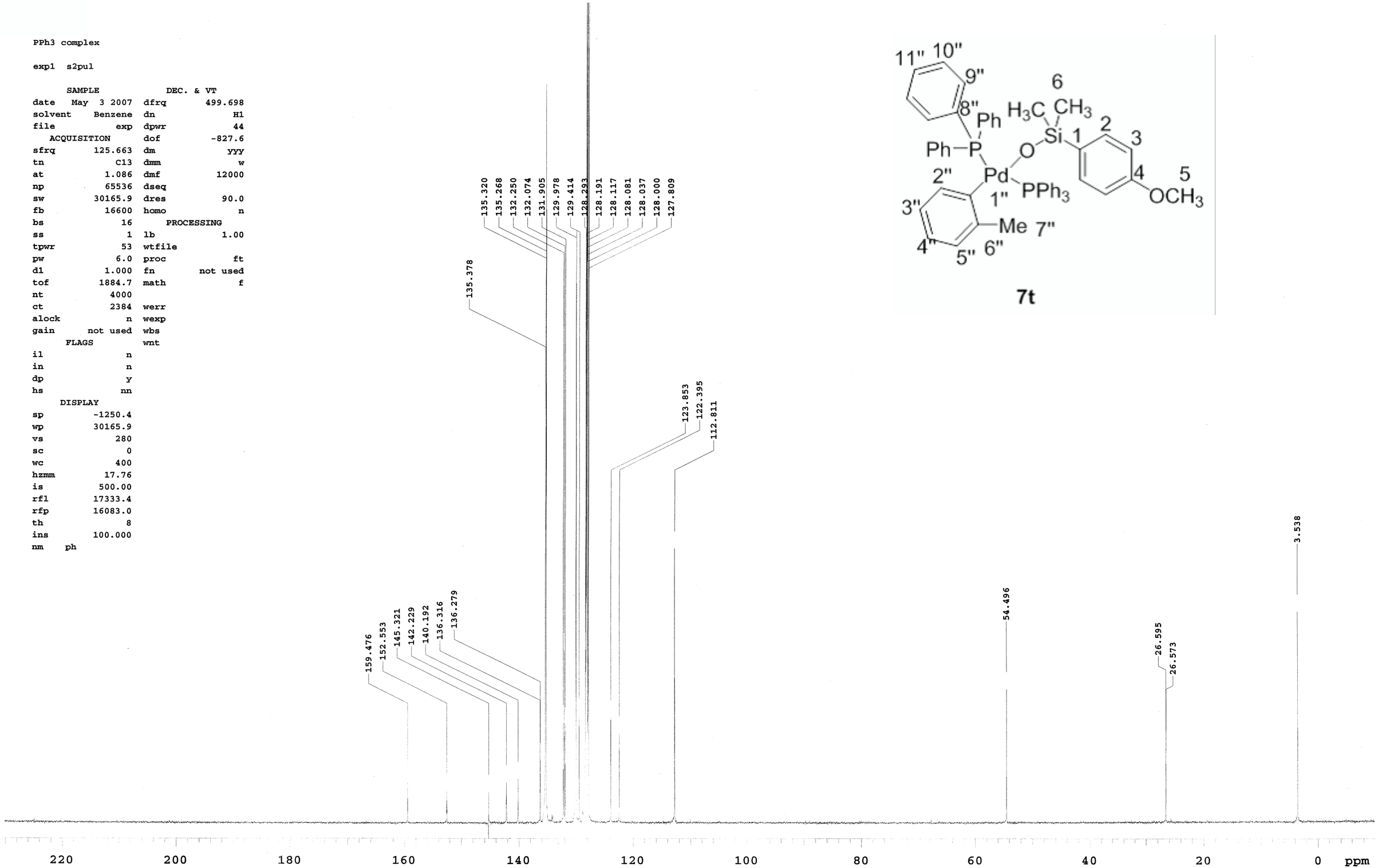
PPh3 complex

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | May 3 2007 | dfrq | 499.698 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 44 |
| ACQUISITION | | dof | -827.6 |
| sfrq | 125.663 | dm | yyy |
| tn | C13 | dmm | w |
| at | 1.086 | dmf | 12000 |
| np | 65536 | dseq | |
| sw | 30165.9 | dres | 90.0 |
| fb | 16600 | homo | n |
| bs | 16 | PROCESSING | |
| ss | 1 | lb | 1.00 |
| tpwr | 53 | wtfile | |
| pw | 6.0 | proc | ft |
| d1 | 1.000 | fn | not used |
| tof | 1884.7 | math | f |
| nt | 4000 | | |
| ct | 2384 | werr | |
| alock | n | wexp | |
| gain | not used | wbs | |
| FLAGS | | wnt | |
| il | n | | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -1250.4 | | |
| wp | 30165.9 | | |
| vs | 280 | | |
| sc | 0 | | |
| wc | 400 | | |
| hzmm | 17.76 | | |
| is | 500.00 | | |
| rfl | 17333.4 | | |
| rfp | 16083.0 | | |
| th | 8 | | |
| ins | 100.000 | | |
| nm | ph | | |



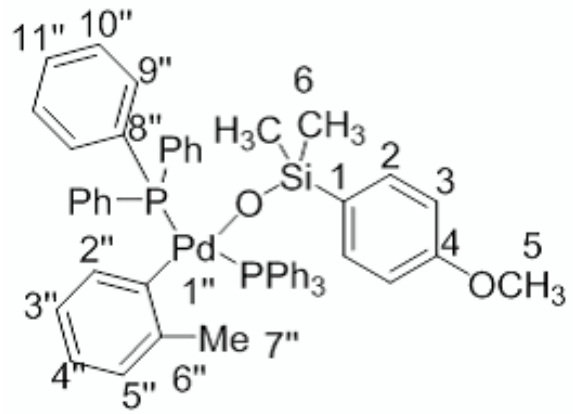

**7t**



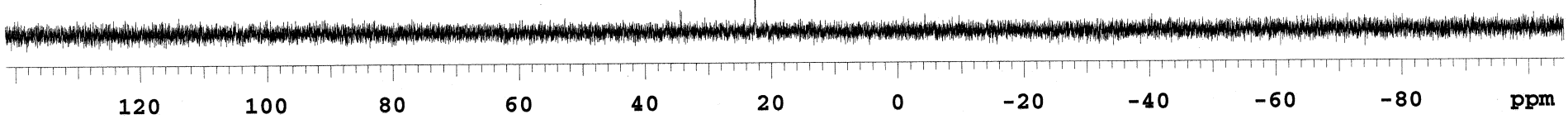
sat-xviii-89x

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Feb 1 2007 | dfrq | 499.432 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 44 |
| ACQUISITION | | dof | -820.0 |
| sfrq | 202.176 | dm | nny |
| tn | P31 | dmm | w |
| at | 0.655 | dmf | 19000 |
| np | 65536 | dseq | |
| sw | 50000.0 | dres | 1.0 |
| fb | 28000 | homo | n |
| bs | 16 | DEC2 | |
| tpwr | 63 | dfrq2 | 0 |
| pw | 4.0 | dn2 | |
| d1 | 1.000 | dpwr2 | 1 |
| tof | 8700.0 | dof2 | 0 |
| nt | 512 | dm2 | n |
| ct | 80 | dmm2 | c |
| alock | n | dmf2 | 18519 |
| gain | not used | dseq2 | |
| FLAGS | | dres2 | 1.0 |
| il | n | homo2 | n |
| in | n | PROCESSING | |
| dp | y | lb | 1.00 |
| hs | n | wtfile | |
| DISPLAY | | proc | ft |
| sp | -21364.2 | fn | not used |
| wp | 49998.5 | math | f |
| vs | 410 | | |
| sc | 0 | werr | |
| wc | 250 | wexp | |
| hzmm | 0.40 | wbs | |
| is | 500.00 | wnt | |
| rf1 | 21365.7 | | |
| rfp | 0 | | |
| th | 131 | | |
| ins | 100.000 | | |
| ai cdc ph | | | |



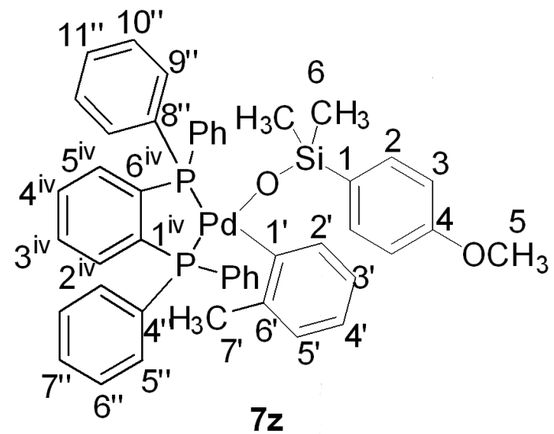

**7t**



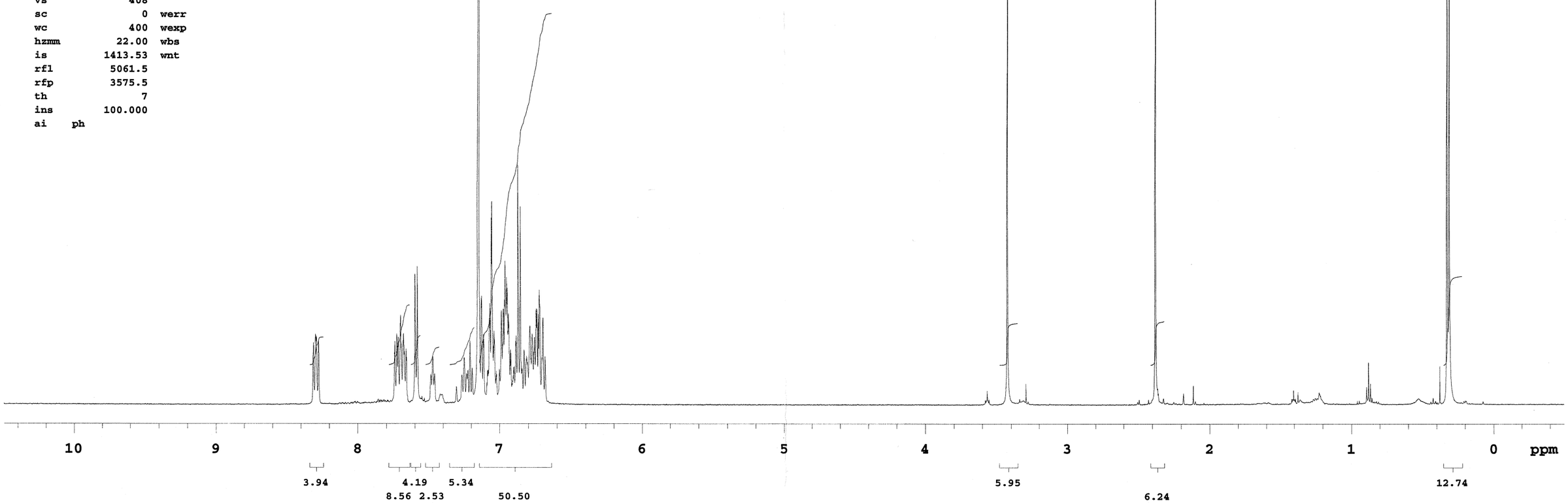
sat-xvii-33x

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Aug 30 2006 | dfrq | 500.076 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 18 |
| ACQUISITION | | dof | 0 |
| sfrq | 500.076 | dm | nnn |
| tn | H1 | dmm | c |
| at | 4.096 | dmf | 200 |
| np | 65536 | dseq | |
| sw | 8000.0 | dres | 1.0 |
| fb | not used | homo | n |
| bs | 16 | DEC2 | |
| tpwr | 55 | dfrq2 | 0 |
| pw | 7.7 | dn2 | |
| d1 | 5.000 | dpwr2 | 1 |
| tof | 0 | dof2 | 0 |
| nt | 8 | dm2 | n |
| ct | 8 | dmm2 | c |
| alock | n | dmf2 | 200 |
| gain | not used | dseq2 | |
| FLAGS | | dres2 | 1.0 |
| il | n | homo2 | n |
| in | n | PROCESSING | |
| dp | y | lb | 0.30 |
| hs | nn | wtfile | |
| DISPLAY | | proc | ft |
| sp | -250.2 | fn | not used |
| wp | 5500.7 | math | f |
| vs | 408 | | |
| sc | 0 | werr | |
| wc | 400 | wexp | |
| hzmm | 22.00 | wbs | |
| is | 1413.53 | wnt | |
| rf1 | 5061.5 | | |
| rfp | 3575.5 | | |
| th | 7 | | |
| ins | 100.000 | | |
| ai ph | | | |



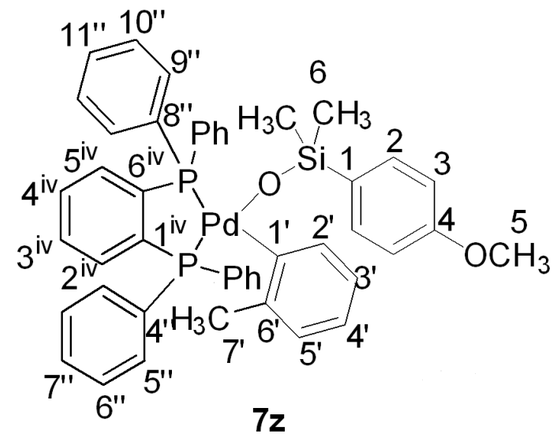

**7z**



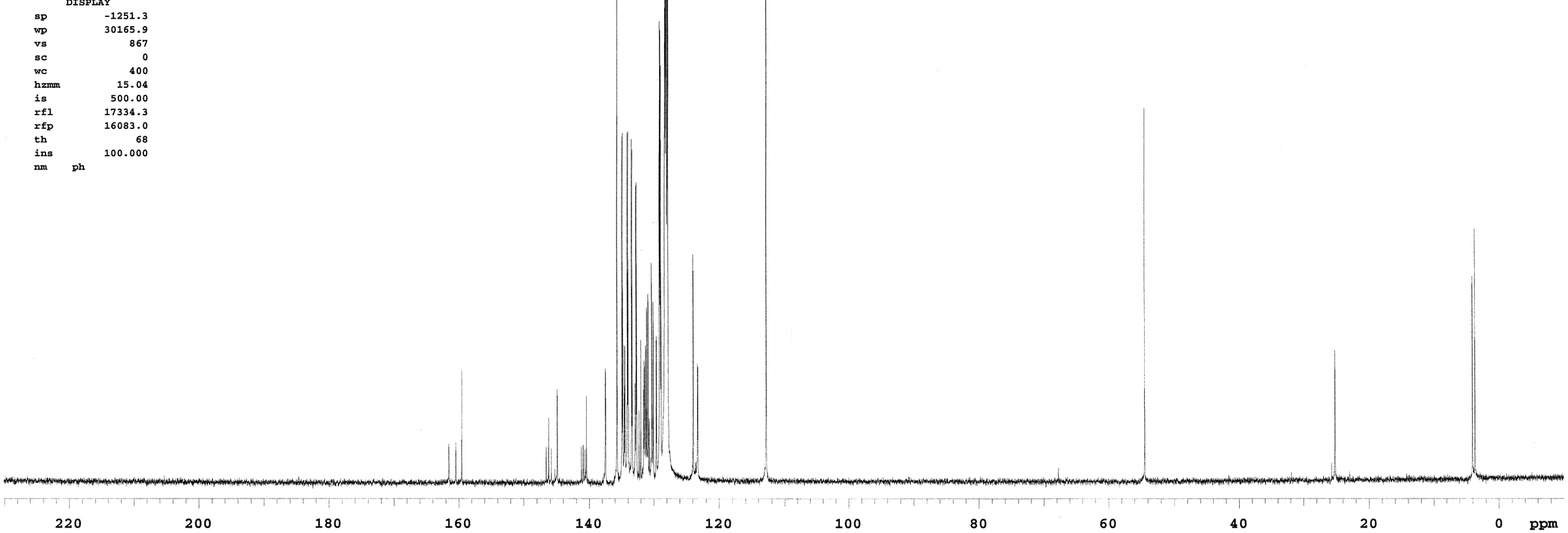
1,2phenyl complex

exp1 s2pul

| | | | |
|---|---|---|---|
| SAMPLE | | DEC. & VT | |
| date | May 6 2007 | dfrq | 499.698 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 44 |
| ACQUISITION | | dof | -827.6 |
| sfrq | 125.663 | dm | yyy |
| tn | C13 | dmm | w |
| at | 1.086 | dmf | 12000 |
| np | 65536 | dseq | |
| sw | 30165.9 | dres | 90.0 |
| fb | 16600 | homo | n |
| bs | 16 | PROCESSING | |
| ss | 1 | lb | 1.00 |
| tpwr | 53 | wtfile | |
| pw | 6.0 | proc | ft |
| d1 | 1.000 | fn | not used |
| tof | 1884.7 | math | f |
| nt | 9000 | | |
| ct | 4304 | werr | |
| alock | n | wexp | |
| gain | not used | wbs | |
| FLAGS | | wnt | |
| il | n | | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -1251.3 | | |
| wp | 30165.9 | | |
| vs | 867 | | |
| sc | 0 | | |
| wc | 400 | | |
| hzmm | 15.04 | | |
| is | 500.00 | | |
| rfl | 17334.3 | | |
| rfp | 16083.0 | | |
| th | 68 | | |
| ins | 100.000 | | |
| nm | ph | | |



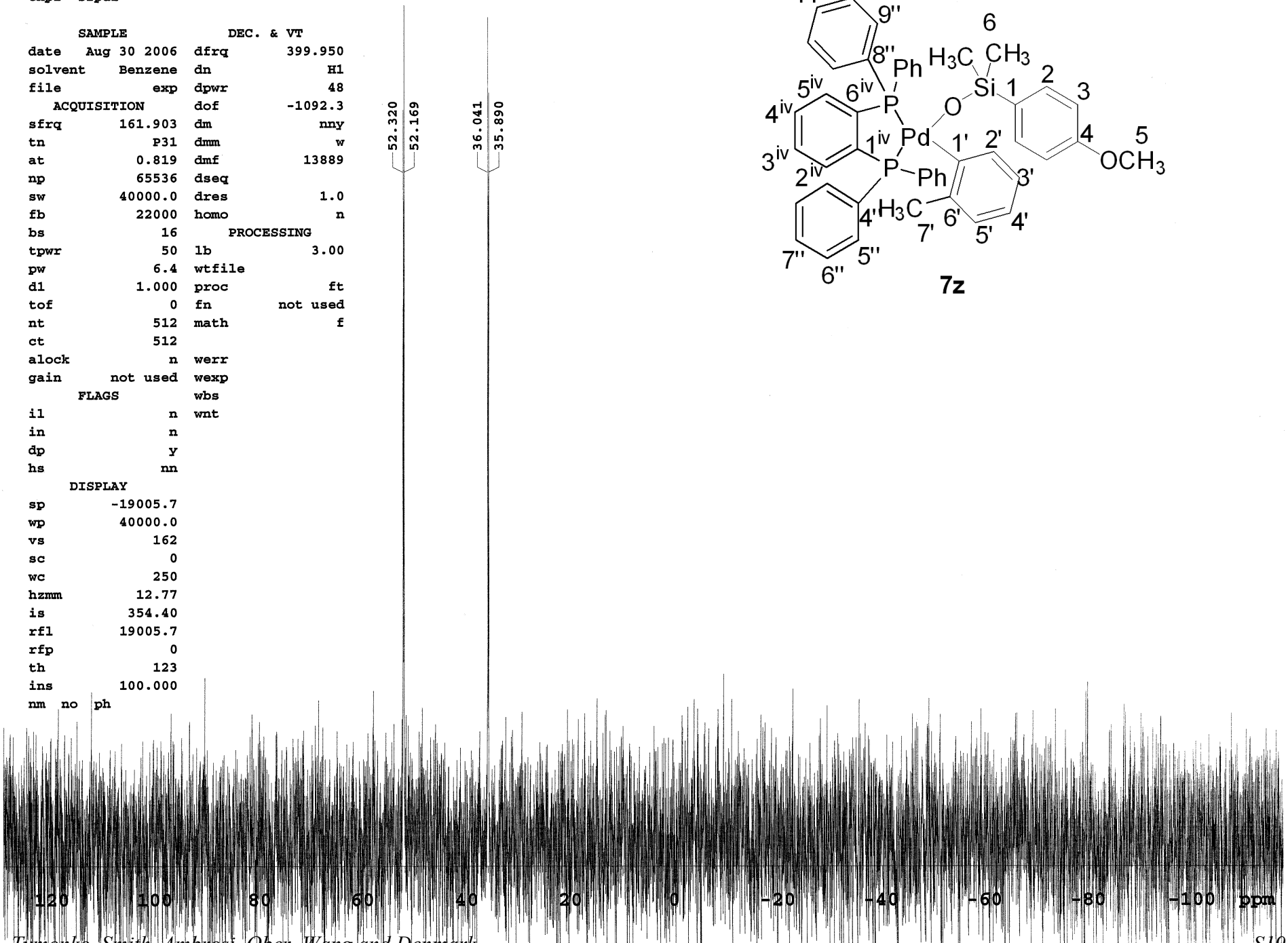

**7z**



satxvii33-31p

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Aug 30 2006 | dfrq | 399.950 |
| solvent | Benzene | dn | H1 |
| file | exp | dpwr | 48 |
| ACQUISITION | | dof | -1092.3 |
| sfrq | 161.903 | dm | nny |
| tn | P31 | dmm | w |
| at | 0.819 | dmf | 13889 |
| np | 65536 | dseq | |
| sw | 40000.0 | dres | 1.0 |
| fb | 22000 | homo | n |
| bs | 16 | PROCESSING | |
| tpwr | 50 | lb | 3.00 |
| pw | 6.4 | wtfile | |
| d1 | 1.000 | proc | ft |
| tof | 0 | fn | not used |
| nt | 512 | math | f |
| ct | 512 | | |
| alock | n | werr | |
| gain | not used | wexp | |
| FLAGS | | wbs | |
| il | n | wnt | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -19005.7 | | |
| wp | 40000.0 | | |
| vs | 162 | | |
| sc | 0 | | |
| wc | 250 | | |
| hzmm | 12.77 | | |
| is | 354.40 | | |
| rfl | 19005.7 | | |
| rfp | 0 | | |
| th | 123 | | |
| ins | 100.000 | | |
| nm no ph | | | |







**7z**

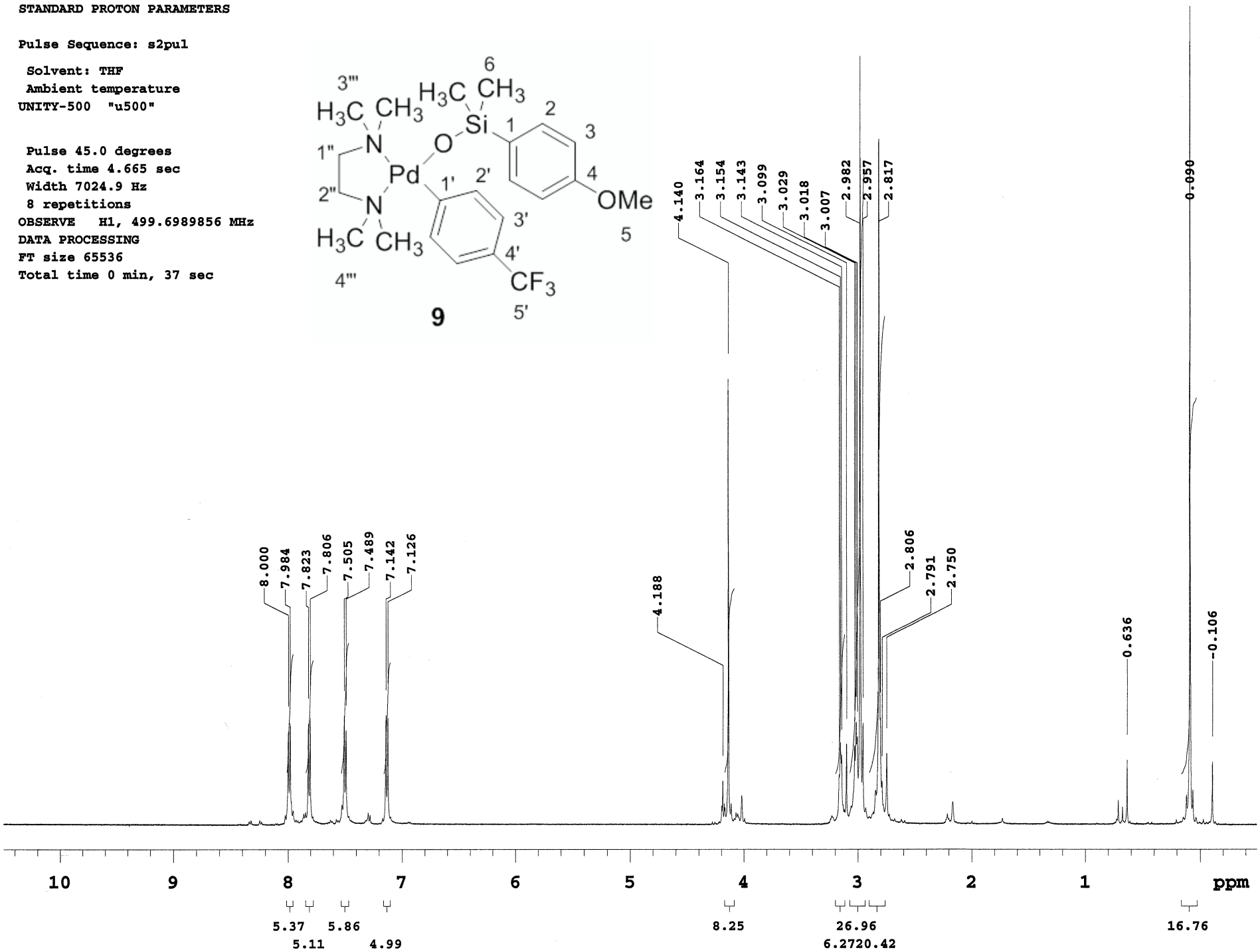
STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: THF
Ambient temperature
UNITY-500 "u500"

Pulse 45.0 degrees
Acq. time 4.665 sec
Width 7024.9 Hz
8 repetitions
OBSERVE H1, 499.6989856 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 37 sec



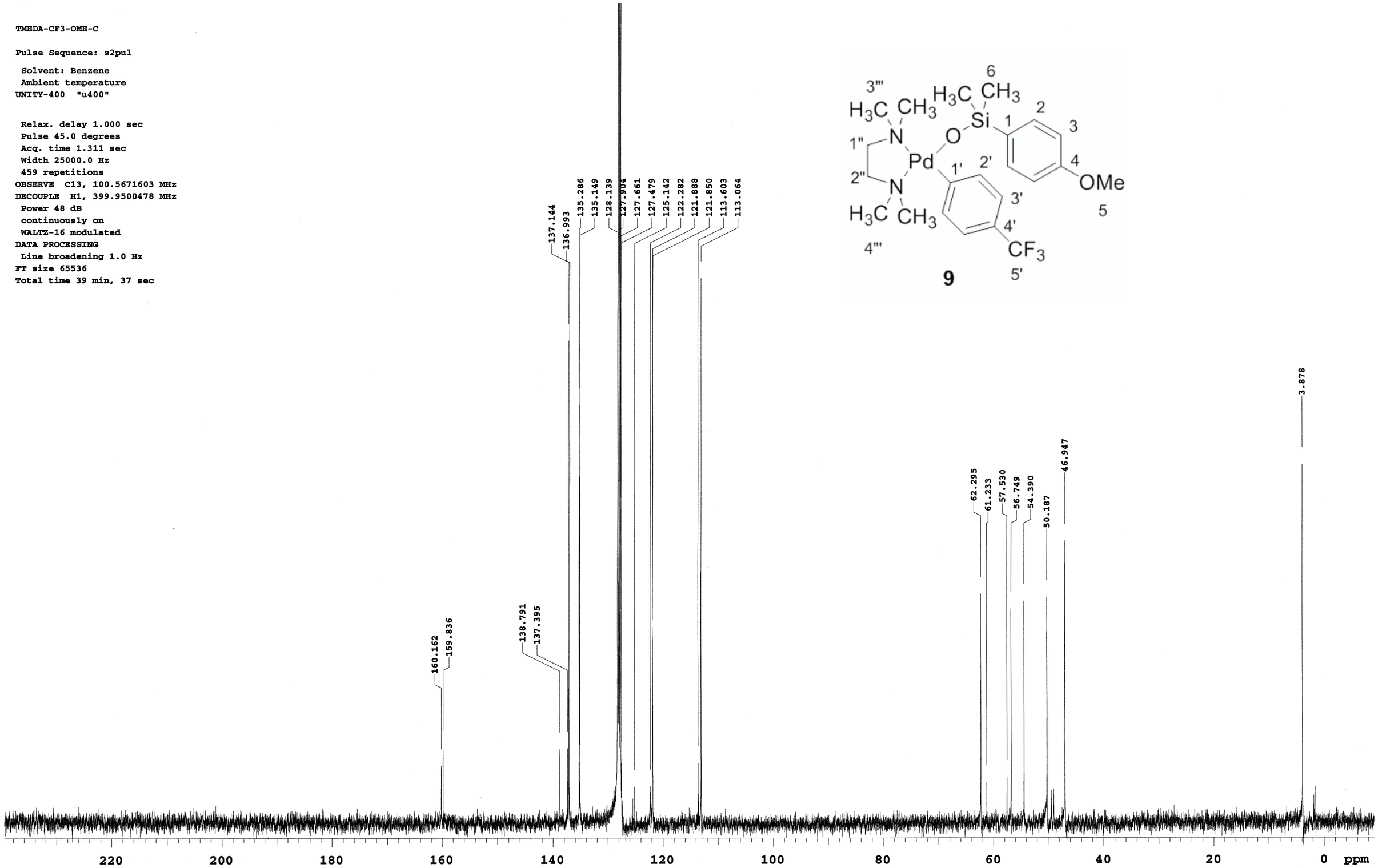



TMEDA-CF3-OME-C

Pulse Sequence: s2pul

Solvent: Benzene
Ambient temperature
UNITY-400 "u400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
459 repetitions
OBSERVE C13, 100.5671603 MHz
DECOUPLE H1, 399.9500478 MHz
Power 48 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 39 min, 37 sec







**9**

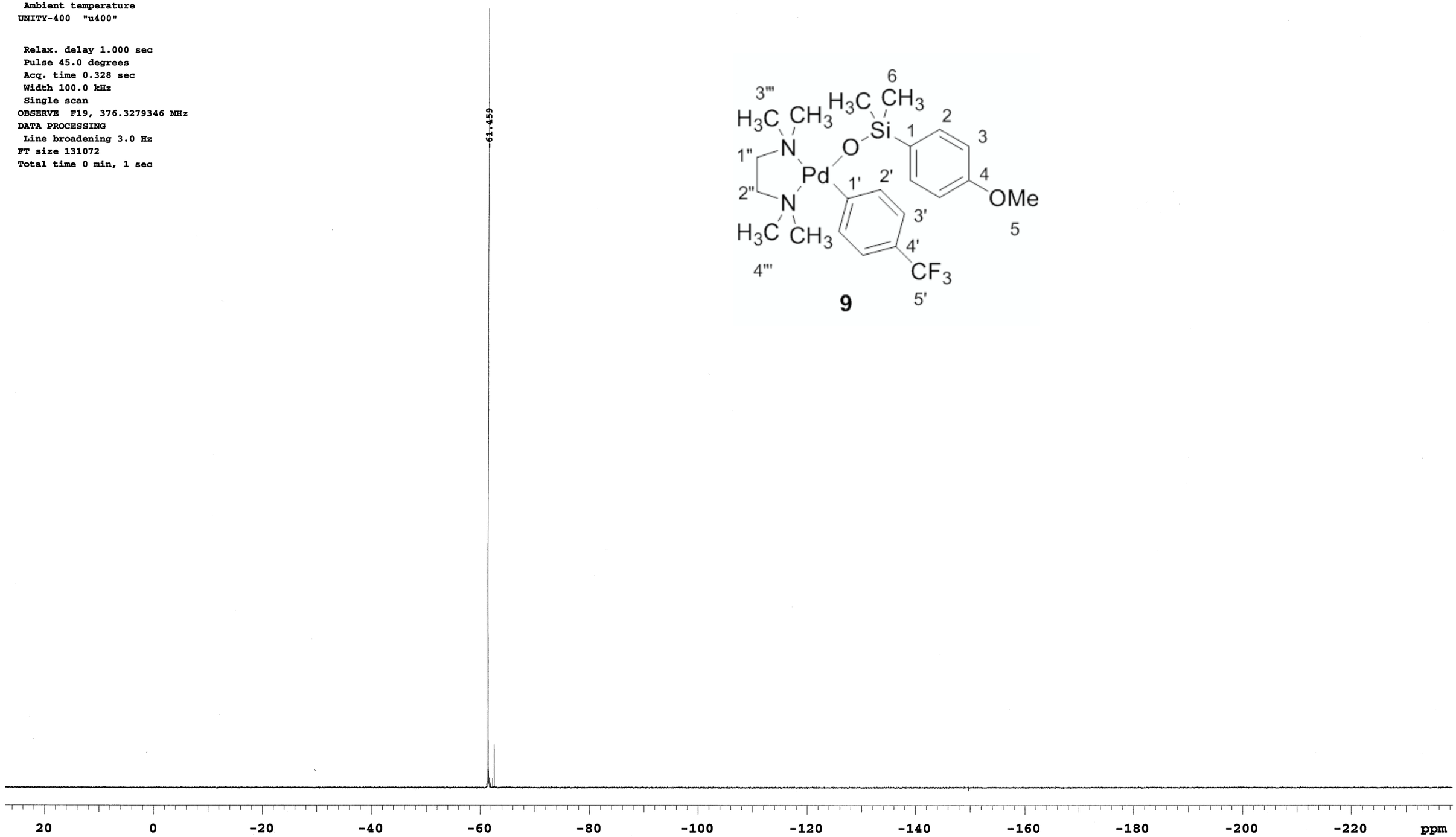
TMEDA-CF3-OME-F

Pulse Sequence: s2pul

Solvent: Benzene
Ambient temperature
UNITY-400 "u400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.328 sec
Width 100.0 kHz
Single scan
OBSERVE F19, 376.3279346 MHz
DATA PROCESSING
Line broadening 3.0 Hz
FT size 131072
Total time 0 min, 1 sec

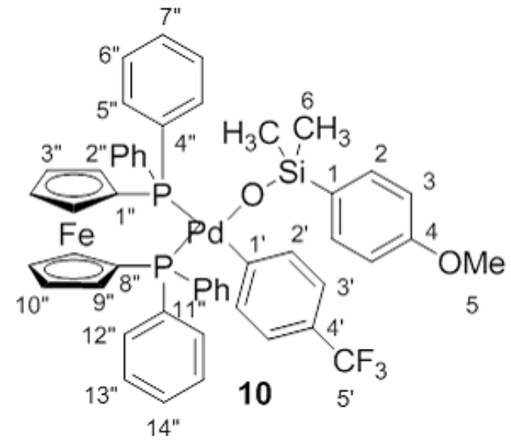


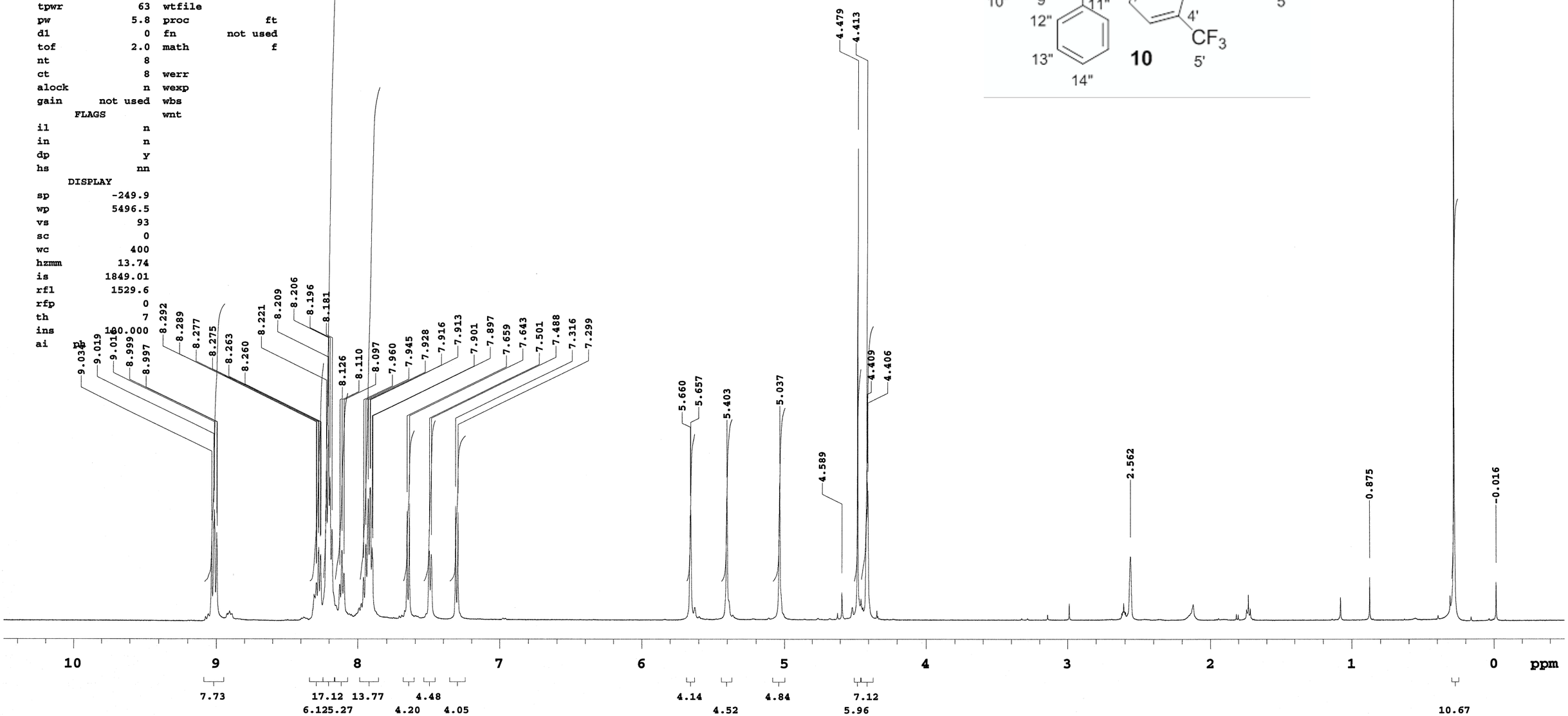



STANDARD PROTON PARAMETERS

exp1 s2pul

| SAMPLE | | DEC. & VT | |
|---|---|---|---|
| date | Jun 22 2005 | dfrq | 499.701 |
| solvent | THF | dn | H1 |
| file | exp | dpwr | 20 |
| ACQUISITION | | dof | 0 |
| sfrq | 499.701 | dm | nnn |
| tn | H1 | dmm | c |
| at | 4.665 | dmf | 200 |
| np | 65536 | dseq | |
| sw | 7024.9 | dres | 1.0 |
| fb | 4000 | homo | n |
| bs | 4 | PROCESSING | |
| tpwr | 63 | wtfile | |
| pw | 5.8 | proc | ft |
| d1 | 0 | fn | not used |
| tof | 2.0 | math | f |
| nt | 8 | | |
| ct | 8 | werr | |
| alock | n | wexp | |
| gain | not used | wbs | |
| FLAGS | | wnt | |
| il | n | | |
| in | n | | |
| dp | y | | |
| hs | nn | | |
| DISPLAY | | | |
| sp | -249.9 | | |
| wp | 5496.5 | | |
| vs | 93 | | |
| sc | 0 | | |
| wc | 400 | | |
| hzmm | 13.74 | | |
| is | 1849.01 | | |
| rfl | 1529.6 | | |
| rfp | 0 | | |
| th | 7 | | |
| ins | 100.000 | | |
| ai | pf | | |



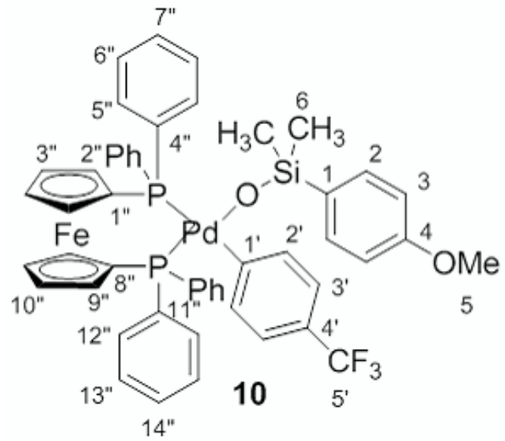



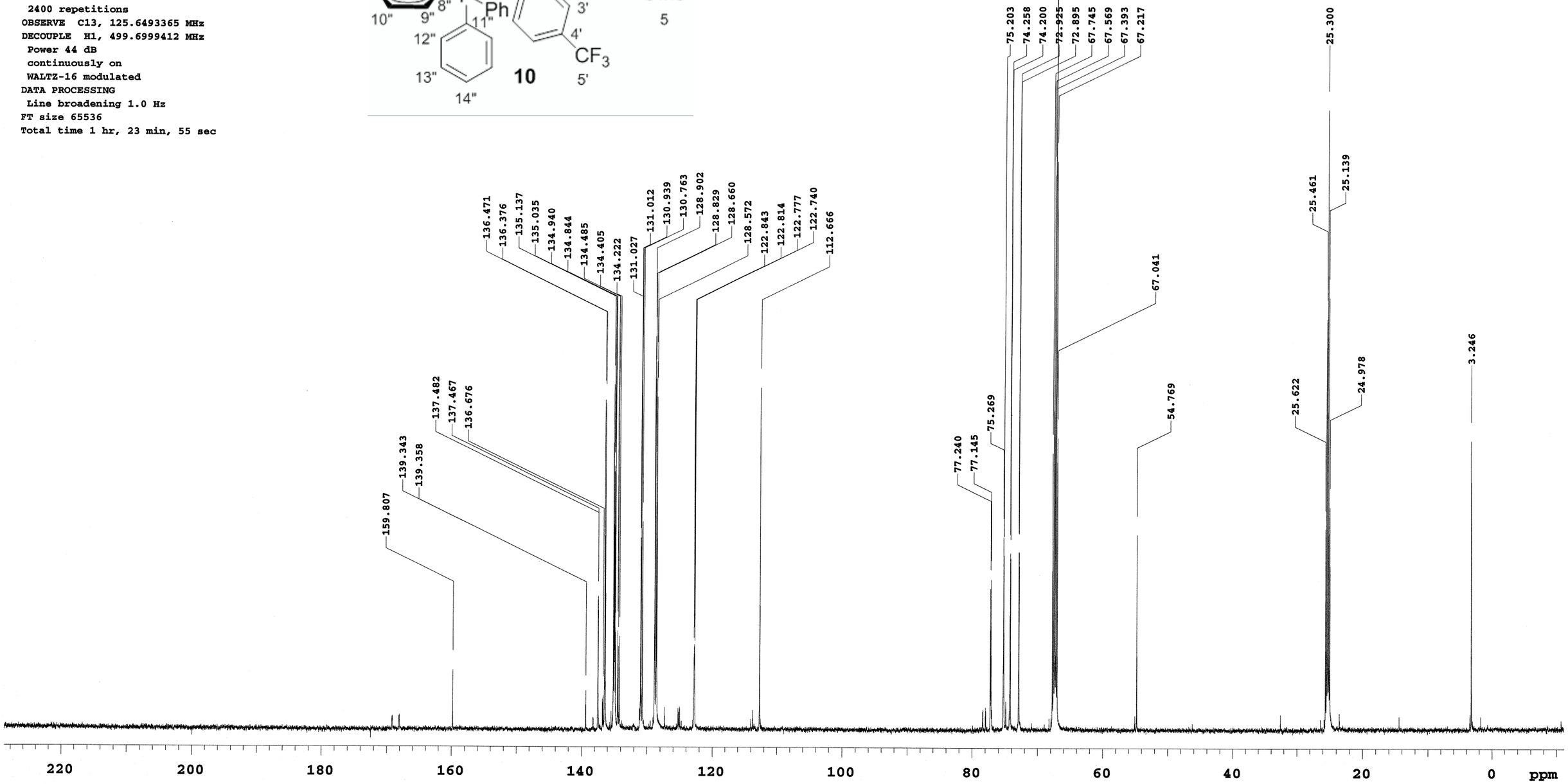
STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

Solvent: THF
Ambient temperature
User: 1-14-87
UNITY-500 "u500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.086 sec
Width 30165.9 Hz
2400 repetitions
OBSERVE C13, 125.6493365 MHz
DECOUPLE H1, 499.6999412 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 23 min, 55 sec



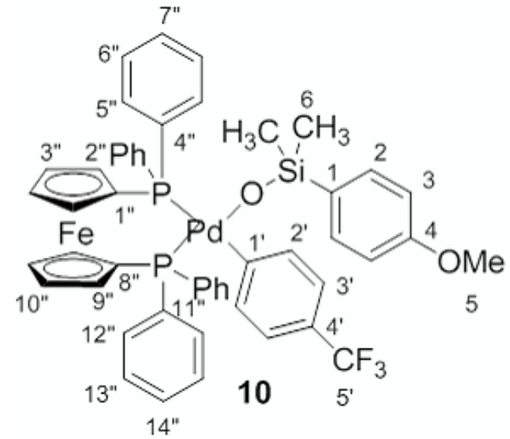



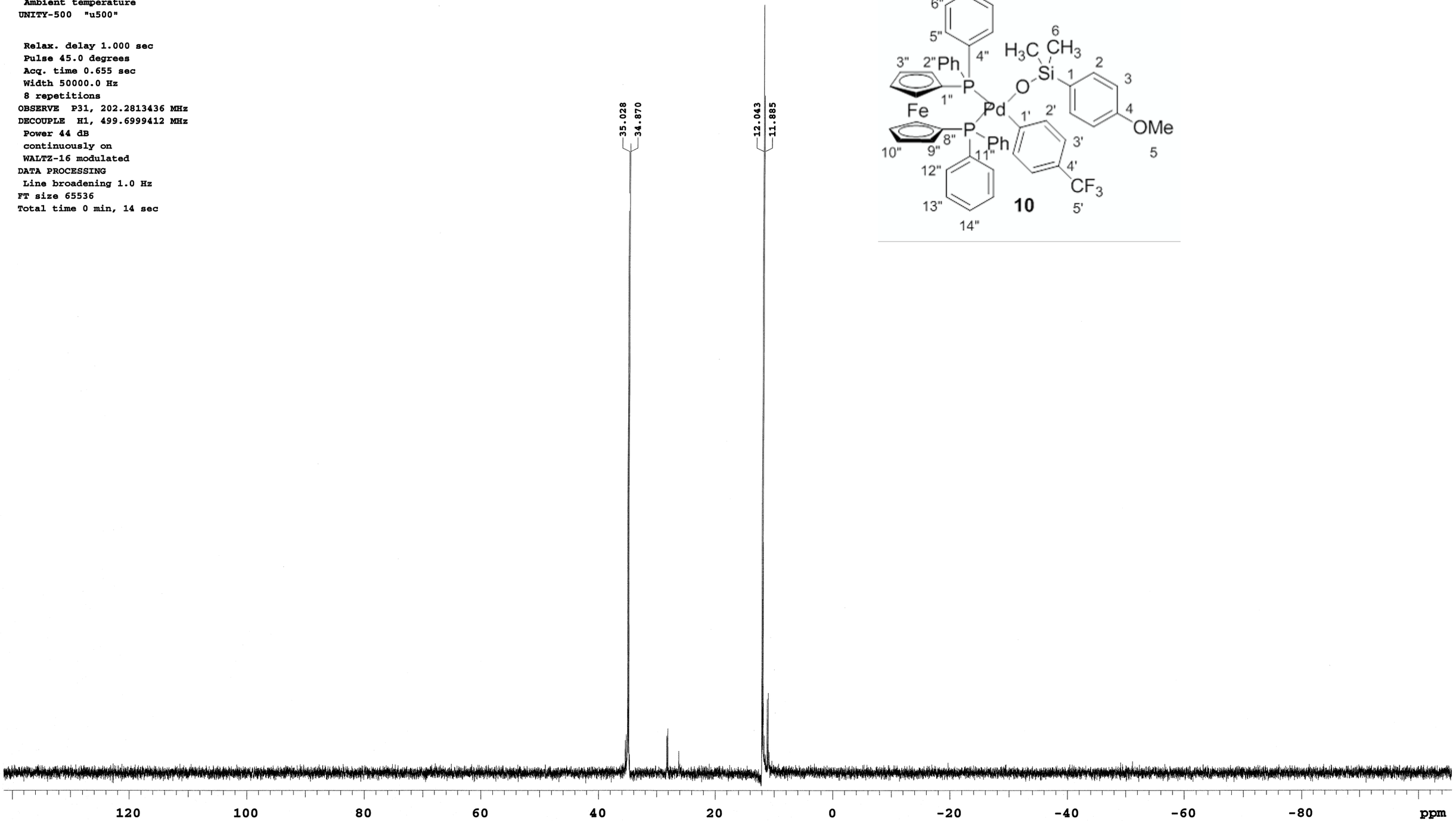
P31 TRIPHENYLPHOSPHATE PARAMETERS

Pulse Sequence: s2pul

Solvent: THF
Ambient temperature
UNITY-500 "u500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.655 sec
Width 50000.0 Hz
8 repetitions
OBSERVE P31, 202.2813436 MHz
DECOUPLE H1, 499.6999412 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 0 min, 14 sec



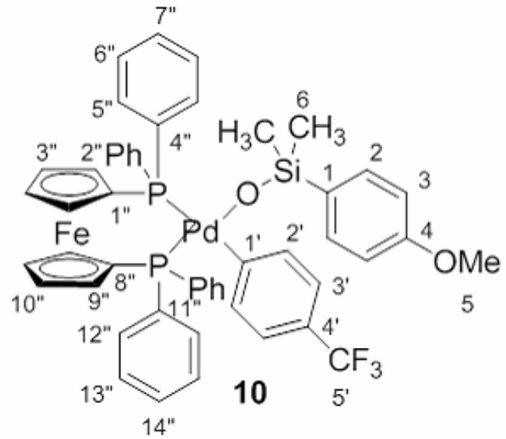
19F

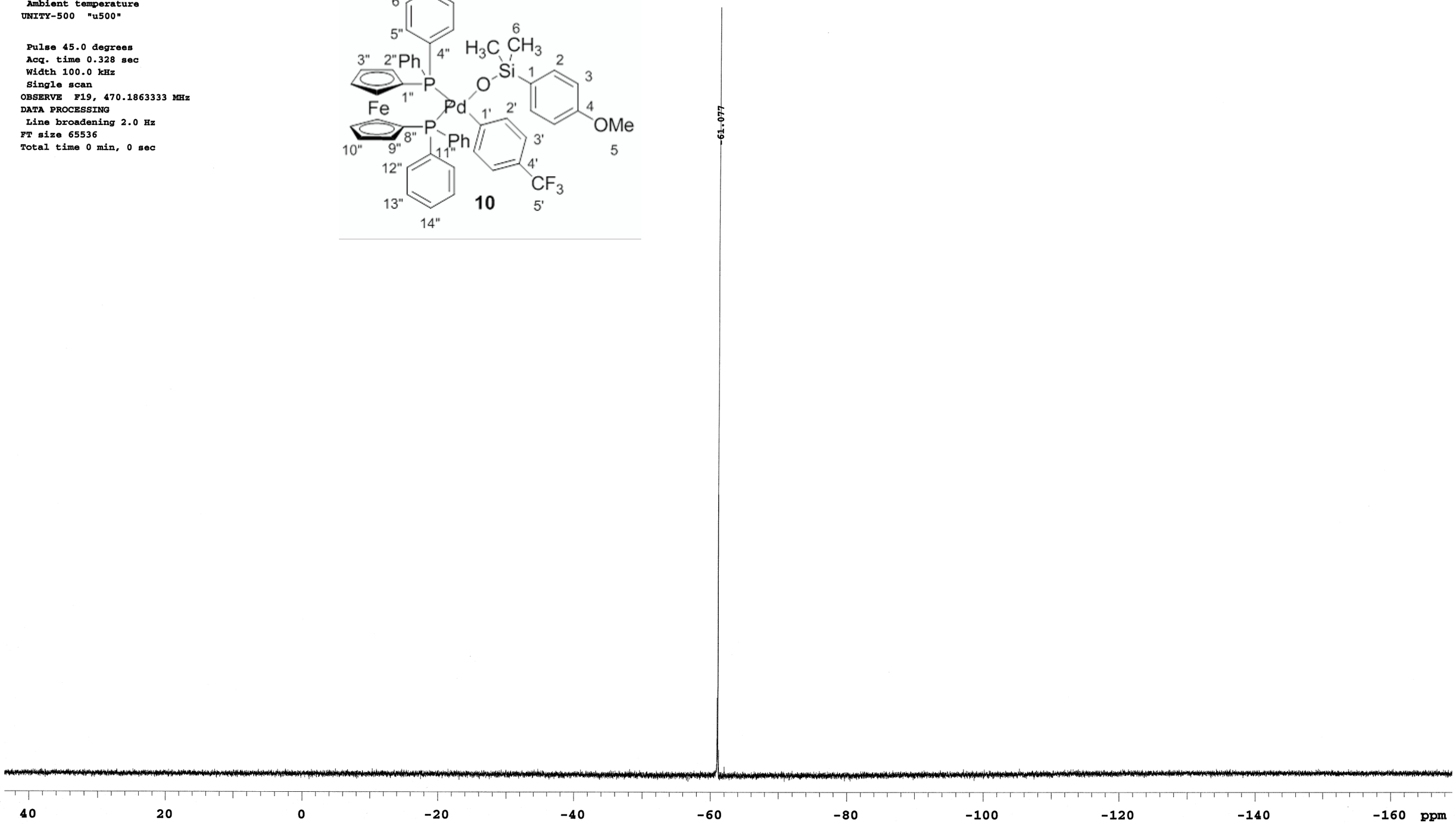
~~P31~~ TRIPHENYLPHOSPHATE PARAMETERS

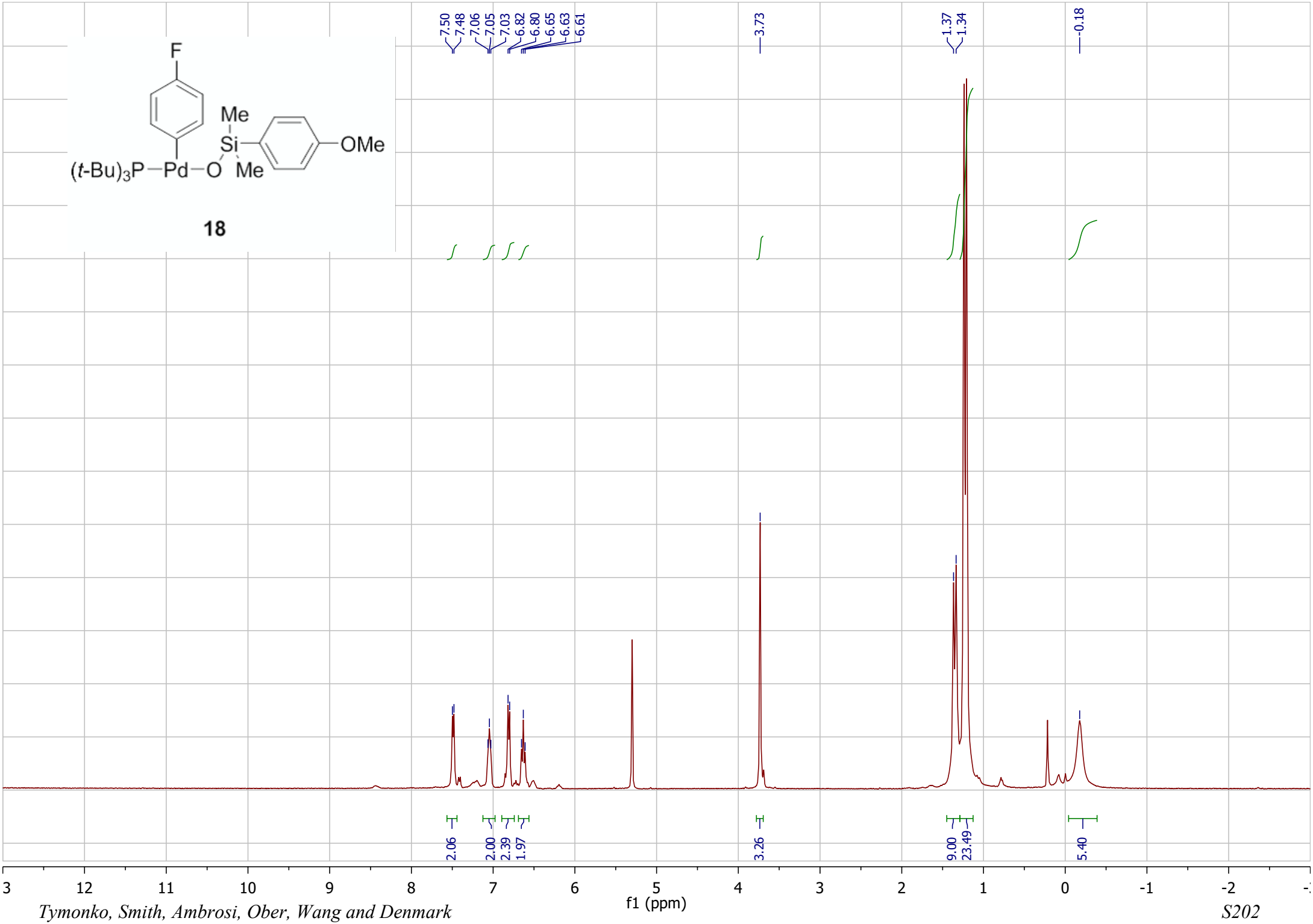
Pulse Sequence: s2pul

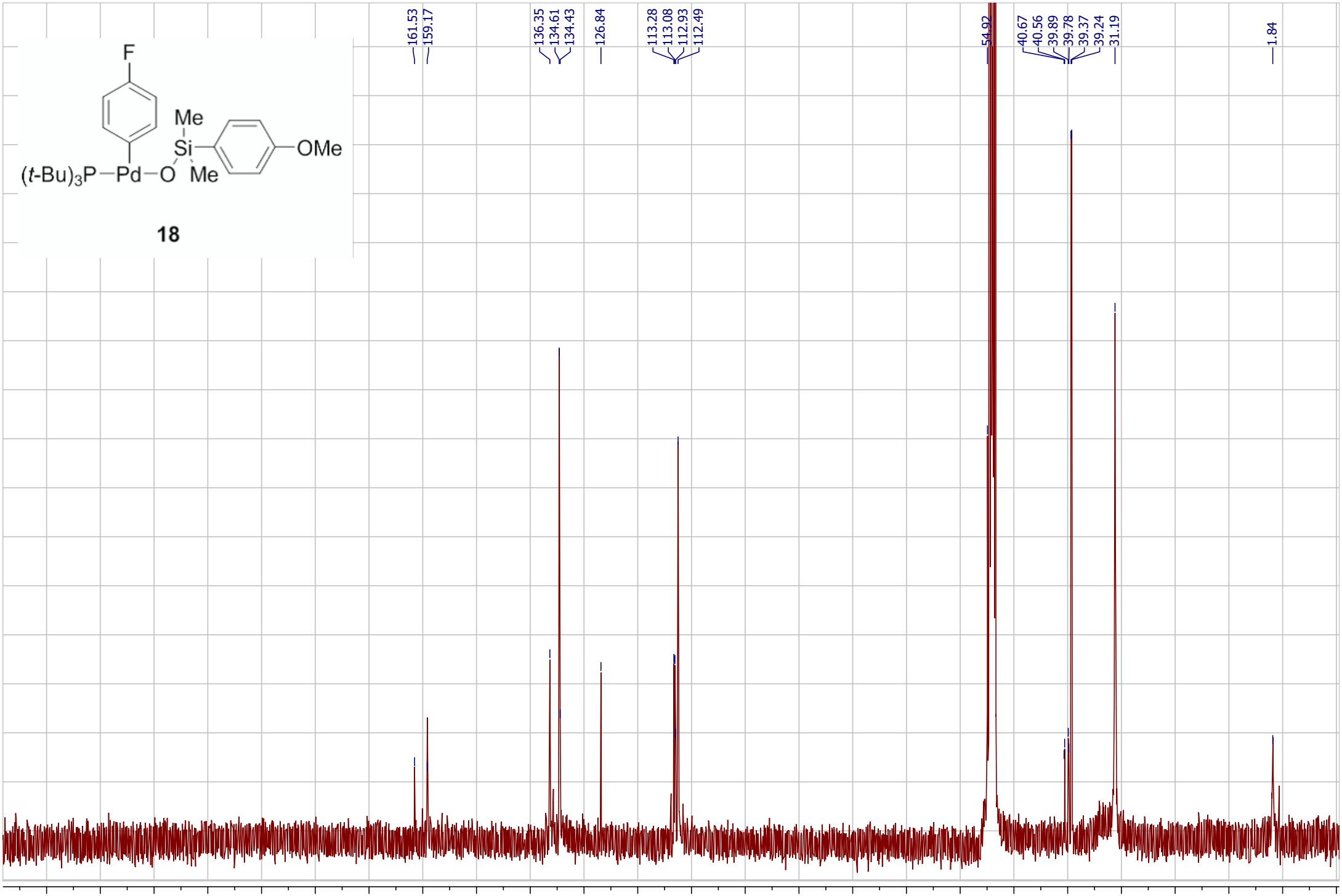
Solvent: THF
Ambient temperature
UNITY-500 "u500"

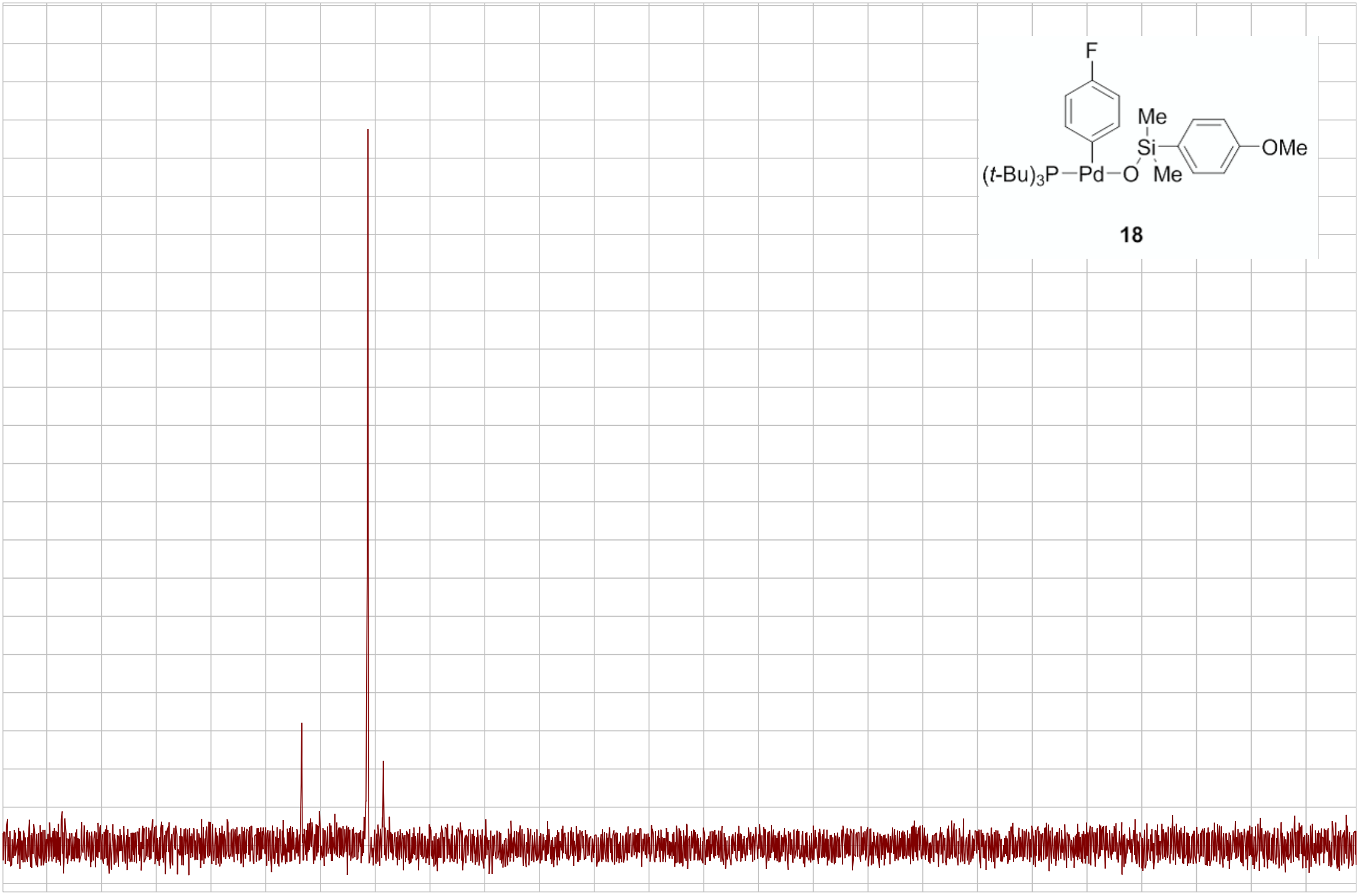
Pulse 45.0 degrees
Acq. time 0.328 sec
Width 100.0 kHz
Single scan
OBSERVE F19, 470.1863333 MHz
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 0 min, 0 sec

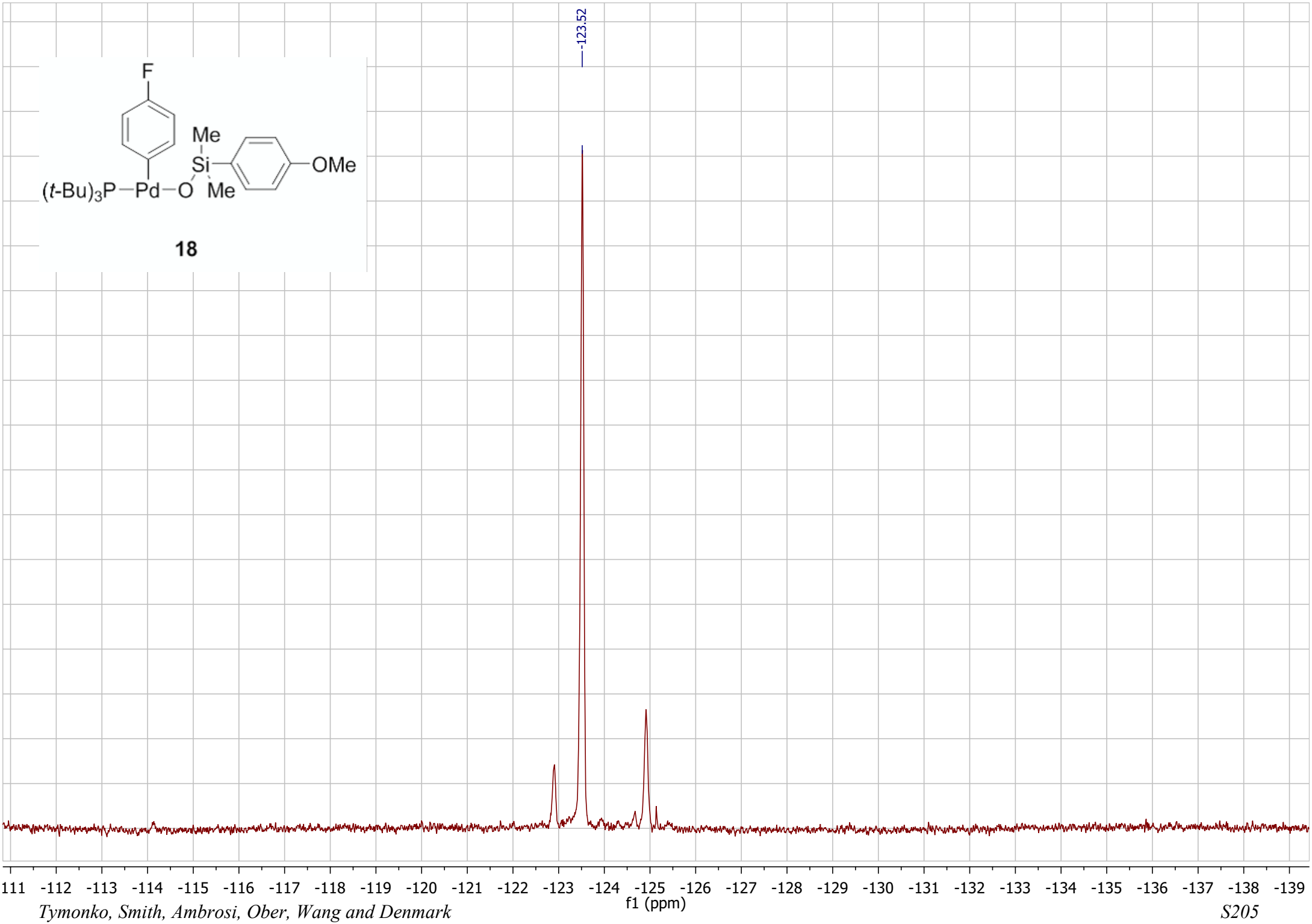


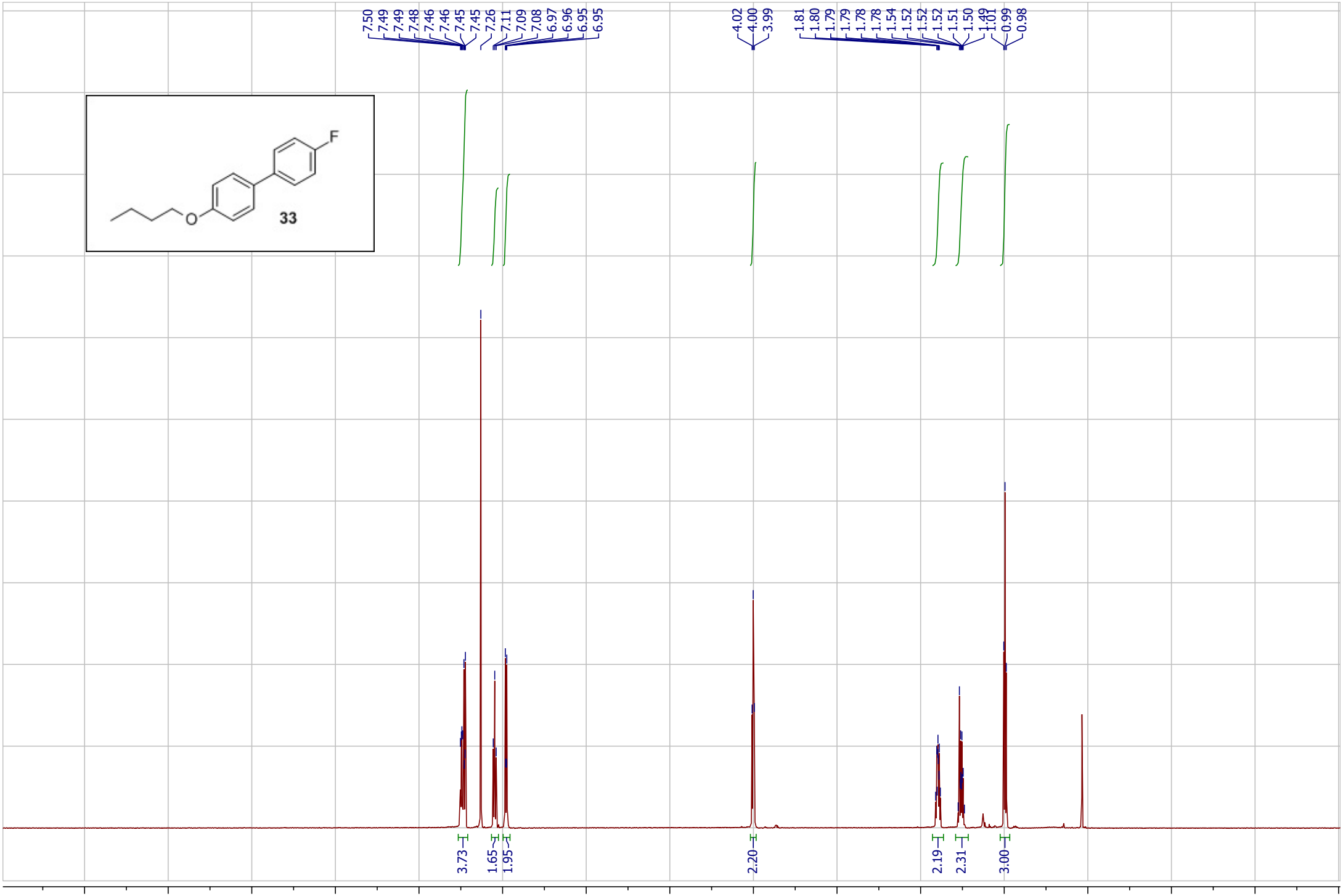




F
Me
Si
OMe
(t-Bu)3P—Pd—O Me
18
7.50
7.48
7.06
7.05
7.03
6.82
6.80
6.65
6.63
6.61
3.73
1.37
1.34
-0.18
2.06
2.00
2.39
1.97
3.26
9.00
23.49
5.40
f1 (ppm)


F
Me
Si
OMe
(t-Bu)3P—Pd—O
Me
18
161.53
159.17
136.35
134.61
134.43
126.84
113.28
113.08
112.93
112.49
54.92
40.67
40.56
39.89
39.78
39.37
39.24
31.19
1.84
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


F
Me
Si
OMe
(t-Bu)3P—Pd—O
Me
18
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)


-123.52
F
Me
Si
OMe
(t-Bu)3P—Pd—O
Me
18
111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127 -128 -129 -130 -131 -132 -133 -134 -135 -136 -137 -138 -139
f1 (ppm)


7.50
7.49
7.49
7.48
7.46
7.46
7.45
7.45
7.26
7.11
7.09
7.08
6.97
6.96
6.95
6.95
4.02
4.00
3.99
1.81
1.80
1.79
1.79
1.78
1.78
1.54
1.52
1.52
1.52
1.51
1.50
1.49
1.01
0.99
0.98
F
O
33
3.73
1.65
1.95
2.20
2.19
2.31
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)