Supporting Information for:

Stoichiometric and Catalytic Aryl-Perfluoroalkyl Coupling at Tri-*tert*-butylphosphine Palladium(II) Complexes

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1. General Information

NMR spectra were obtained on a Varian MR400 (400.52 MHz for ^{1}H, 376.87 MHz for ^{19}F), Varian VNMRS 500 (470.47 MHz for ^{19}F), Varian Inova 500 (499.91 MHz for ^{1}H), or a Varian VNMRS 700 (699.75 MHz for ^{1}H, 175.97 MHz for ^{13}C, 283.28 MHz for ^{31}P) spectrometer. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS), with the residual NMR solvent peak used as an internal reference. ^{19}F and ^{31}P NMR chemical shifts are reported in ppm and are referenced to the solvent lock. Abbreviations used to report the NMR data: app, apparent; br, broad; s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; td, triplet of doublets; dt, doublet of triplets; tt, triplet of triplets; dq, doublet of quartets; qd, quartet of doublets; qt, quartet of triplets; tq, triplet of quartets; m, multiplet. ^{19}F NMR yields for stoichiometric reductive elimination reactions were obtained on a Varian VNMRS 500 spectrometer (470.47 MHz for ^{19}F) using (trifluoromethoxy)benzene (–58.3 ppm) as an internal standard with one scan used for data acquisition. Formation of the desired reductive elimination product was confirmed by spiking the reaction mixture with an authentic sample of product. ^{19}F NMR yields for catalytic trifluoromethylation and pentafluoroethylation reactions were obtained on a Varian MR400 (376.87 MHz for ^{19}F) spectrometer using 1,3,5-trifluorobenzene (–108.33 ppm) for trifluoromethylation and (trifluoromethoxy)benzene or benzotrifluoride for pentafluoroethylation as internal standards with a relaxation delay of five seconds. GC-MS analysis was performed on a Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer. The products were separated on a 30 m length by 0.25 mm id RESTEK XTI-5 column coated with a 0.25 μm film. Helium was employed as the carrier gas with a constant column flow of 1.5 mL/min. The injector temperature was held constant at 250 °C. Two GC oven temperature methods were used: (1) 40 °C hold for 4 min, ramp at 15 °C/min to 300 °C, and hold at 300 °C for 1 min; (2) 60 °C, ramp at 15 °C/min to 300 °C, and hold at 300 °C for 8 min. High-resolution mass spectra were recorded on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer. Elemental analyses were performed by Midwest Microlab, Inc. located in Indianapolis, Indiana. X-ray crystallographic data were obtained on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer.

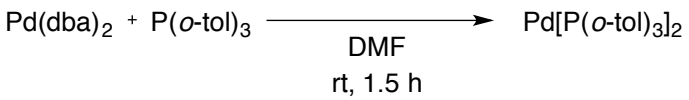
2. Materials and Methods

All commercial reagents were used as received unless stated otherwise. $Pd(P^tBu_3)_2$ was synthesized according to a literature procedure.[1] $Pd(dba)_2$ was purchased from Frontier Scientific. Tri-*tert*-butylphosphine (P^tBu_3), 1-bromonaphthalene (sparged and stored over activated 3 Å molecular sieves), 4-bromobenzonitrile, and ethyl 4-bromobenzoate were purchased from Aldrich. Trimethyl(trifluoromethyl)silane ($TMSCF_3$), (pentafluoroethyl)benzene, and tri(*o*-tolyl)phosphine ($P(o\text{-tol})_3$) were purchased from Oakwood Products, Inc. CsF was obtained from Chemetall. Spray-dried KF was obtained from the Dow Chemical Company and was further dried by heating at 160 °C under vacuum for 31 h. Trifluoroacetic anhydride (TFAA), 1-butyl-4-chlorobenzene (sparged and stored over activated 3 Å molecular sieves), 1-butyl-4-bromobenzene (sparged and stored over activated 3 Å molecular sieves), 4-bromodiphenyl ether (sparged), 3-bromo-*N,N*-dimethylaniline (sparged), and 3-bromo-9-phenylcarbazole were purchased from Alfa Aesar. 1-Bromo-4-*tert*-butylbenzene (sparged) was purchased from Lancaster Synthesis, Inc. 1,4-Dioxane (99.5% Extra Dry in an AcroSeal® bottle) was purchased from Acros Organics, was further dried by distillation from sodium benzophenone ketyl, and was stored over activated 3 Å molecular sieves. 4-Bromobiphenyl, 2-bromodibenzo[b,d]furan, and 2-bromodibenzo[b,d]thiophene, 4-bromo-8-methyl-2-(trifluoromethyl)quionoline, 1-BOC-4-(3-Bromophenyl)piperazine were purchased from Ark Pharm, Inc. 1-(4-Bromophenyl)pyrrole was purchased from Arkpharm and was purified by flash chromatography before use. 2-(4-Bromophenyl)-1,3-dioxolane was purchased from Acros and was purified by flash chromatography before use. 1-(4-Bromobenzoyl)piperidine was made according to the literature.[2] Diphenylzinc was purchased from Strem Chemicals. Triethyl(trifluoromethyl)silane ($TESCF_3$), trimethyl(pentafluoroethyl)silane ($TMSCF_2CF_3$), and pentafluoropropionic anhydride (PFPA) were purchased from Synquest Laboratories, Inc. (Trifluoromethoxy)benzene was purchased from Matrix Scientific and was deaerated using three freeze-pump-thaw cycles before being stored over activated molecular sieves under an atmosphere of N_2. The solvents Et_2O (Alfa Aesar), pentane (Fisher Scientific), THF (Alfa Aesar), and toluene (VWR) used in the glovebox were deaerated by sparging with N_2 and were dried using an Innovative Technology, Inc. (now rebranded to Inert) solvent purification system. Anhydrous *N,N*-dimethylformamide (*N,N*-DMF) was purchased from Acros Organics in an AcroSeal® bottle. Anhydrous benzene was purchased from Alfa Aesar. C_6D_6 was purchased from Cambridge Isotope Laboratories, deaerated using three freeze-pump-thaw cycles, and stored over activated 3 Å molecular sieves under an atmosphere of N_2. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, Inc and stored over activated 3 Å molecular sieves. All solvents used in the glovebox were stored over activated 3 Å molecular sieves. Celite used in the glovebox was purchased from Aqua Solutions, Inc. and dried under vacuum at 150 °C for 24 h. All glassware used in the glovebox was dried in an oven at 150 °C for at least 3 h and cooled under an inert atmosphere. DCM (Fisher Scientific), Et_2O (EMD Millipore), pentane (Fisher Scientific), and hexanes

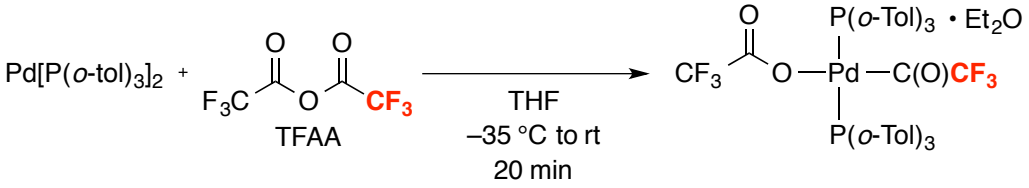
(Fisher Scientific) used on the bench top were used as received. Celite used on the bench top was purchased from Aqua Solutions, Inc. and used as received.

3. Synthesis of Palladium Complexes

i. *$[P(o\text{-tol})_3]_2Pd(CF_3)(OC(O)CF_3)$*

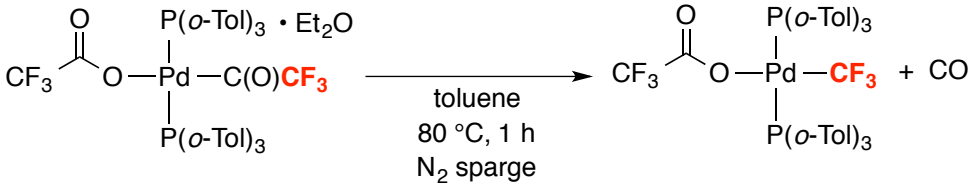


$Pd[P(o\text{-tol})_3]_2$ was synthesized via a modified literature procedure.[3] In a glovebox under N_2 atmosphere, a 250 mL round bottom flask equipped with an oven-dried magnetic stir bar was charged with $Pd(dba)_2$ (4.00 g, 6.96 mmol, 1.00 equiv), $P(o\text{-tol})_3$ (4.24 g, 13.9 mmol, 2.00 equiv), and *N,N*-DMF (124 mL, 0.0561 M). The flask was capped with a rubber septum, and the dark mixture was stirred at room temperature for 1.5 h in the glovebox. A yellow precipitate formed, and this grey, green-yellow solid was collected via filtration. The solid was washed with Et_2O (100 mL) and dried under vacuum to yield the desired product as a grey, green-yellow solid (4.226 g, 85% yield). The grey color is believed to be a Pd black impurity that does not appear to affect subsequent steps of the synthesis. The product was carried on to the next step without further purification or characterization.



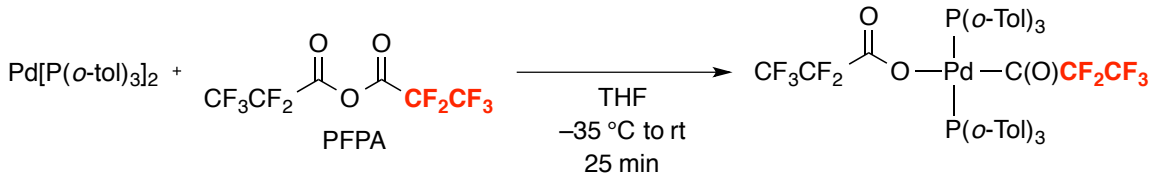
$[P(o\text{-tol})_3]_2Pd(C(O)CF_3)(OC(O)CF_3)$ was synthesized via a modified literature procedure.[4] In a glovebox under N_2 atmosphere, a 100 mL round bottom flask equipped with an oven-dried magnetic stir bar was charged with $Pd[P(o\text{-tol})_3]_2$ (2.10 g, 2.94 mmol, 1.00 equiv) and THF (42 mL, 0.070 M). The flask was capped with a rubber septum and placed in the glovebox freezer (–35 °C) for 15 min. The flask was removed from the glovebox freezer and TFAA (0.49 mL, 3.5 mmol, 1.2 equiv) was added dropwise with stirring. The reaction was allowed to warm to room temperature with stirring. The reaction was then stirred for 20 min. The reaction turned from a grey, green heterogeneous mixture to a black solution. The crude mixture was filtered through a pad of celite using THF. Pd black was trapped on top of the celite pad, and the filtrate was a yellow solution. The filtrate was concentrated to a yellow residue. This residue was dissolved in Et_2O, and a pale yellow solid began to precipitate after ~2 min. This mixture was allowed to stand in the drybox for at least 1 h, and then the yellow solid was collected via filtration, washed with Et_2O (50 mL), and dried under vacuum to

afford the desired product as a pale yellow solid (2.294 g, 78% yield). The compound is reported to have 1 equiv of co-crystallized Et_2O. This was taken into consideration in the determination of the yield and in the stoichiometry for the next step. The compound was taken on to the next step without further characterization.

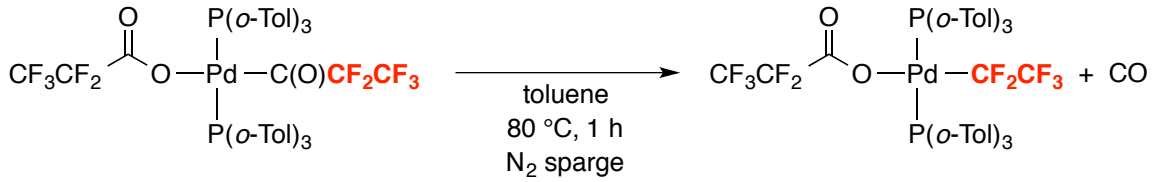


$[P(o\text{-tol})_3]_2Pd(CF_3)(OC(O)CF_3)$ was synthesized via a modified literature procedure.[4] In a glovebox under N_2 atmosphere, a 250 mL 3-neck round bottom flask equipped with an oven-dried magnetic stir bar was charged with $[P(o\text{-tol})_3]_2Pd(C(O)CF_3)(OC(O)CF_3)\bullet Et_2O$ (2.294 g, 2.29 mmol, 1.00 equiv) and toluene (128 mL, 0.0179 M), resulting in a heterogeneous yellow mixture. A Vigreux column was attached to the center neck of the flask and was sealed with a rubber septum. The two necks flanking the center neck were also sealed with rubber septa. This assembly was removed from the glovebox and attached to a N_2 line via a needle inserted into one of the side necks of the flask. The needle was placed into the reaction mixture, and a vent needle was placed in the septum at the top of the Vigreux column. The N_2 pressure was adjusted until light bubbling was observed in the reaction mixture. This served to sparge the reaction and displace carbon monoxide as it was formed. The reaction was placed in an oil bath preheated at 80 °C. After ~5 min of heating, the reaction turned from a yellow heterogeneous mixture to an orange homogeneous solution. After 1 h, the reaction was removed from the oil bath and cooled to room temperature. The brown-orange solution was filtered in air through a pad of celite using toluene (50 mL), affording an orange solution. The solution was concentrated, resulting in an orange residue. The residue was dissolved in 30 mL $^{i}Pr_2O$ and cooled to –10 °C. After 1 h, a beige solid formed, and the flask was briefly sonicated to precipitate additional product. The solid was collected via filtration, washed with pentane (50 mL), and dried under vacuum to afford the desired product as beige solid (1.656 g, 81% yield). The compound is reported to have 1 equiv of co-crystallized $^{i}Pr_2O$; however, this was not consistent. This attempt afforded a negligible amount of $^{i}Pr_2O$. A second attempt afforded 0.91 equiv of $^{i}Pr_2O$ as judged by ^{1}H NMR spectroscopic analysis with 1,3,5-trimethoxybenzene as an internal standard. Prolonged drying under vacuum did not appear to have an impact on the amount of $^{i}Pr_2O$ trapped in the product. This was taken into consideration in the stoichiometry of subsequent steps, and the presence or absence of $^{i}Pr_2O$ did not have a noticeable effect on subsequent syntheses. ^{1}H, ^{19}F, and ^{31}P NMR spectroscopic data for this complex were consistent with those reported in the literature.[4] ^{1}H, ^{19}F, and ^{31}P NMR spectra were all acquired in $CDCl_3$ at 23 °C and contained broad resonances.

ii. *[P(o-tol)$_3$]$_2$Pd(CF$_2$CF$_3$)(OC(O)CF$_2$CF$_3$)*



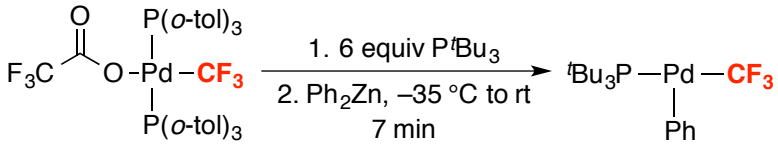
In a glovebox under N_2 atmosphere, a 100 mL round bottom flask equipped with an oven-dried magnetic stir bar was charged with Pd[P(*o*-tol)$_3$]$_2$ (2.42 g, 3.38 mmol, 1.00 equiv) and THF (49 mL, 0.069 M). The flask was sealed with a rubber septum and placed into the glovebox freezer (–35 °C) for 15 min. The flask was removed from the glovebox freezer, and PFPA (0.77 mL, 3.9 mmol, 1.2 equiv) was added dropwise with stirring. After addition, the reaction was warmed to room temperature with stirring. The reaction was stirred for 25 min. The crude mixture was filtered through a pad of celite. The yellow filtrate was concentrated, yielding a yellow oil. Et_2O (30 mL) was added, resulting in a pale yellow solid. The Et_2O was removed under vacuum, and the solid was collected via filtration to yield the desired product as a pale yellow solid (3.211 g, 93% yield). The compound was taken on to the next step without further characterization.



In a glovebox under N_2 atmosphere, a 250 mL 3-neck round bottom flask equipped with an oven-dried magnetic stir bar was charged with [P(*o*-tol)$_3$]$_2$Pd(C(O)CF$_2$CF$_3$)(OC(O)CF$_2$CF$_3$) (3.19 g, 3.11 mmol, 1.00 equiv) and toluene (173 mL, 0.0180 M), resulting in a heterogeneous yellow mixture. A Vigreux column was attached to the center neck of the flask and was sealed with a rubber septum. The two necks flanking the center neck were also sealed with rubber septa. The assembly was removed from the glovebox and attached to a N_2 line via a long needle inserted into one of the side necks of the flask. The needle was placed into the reaction mixture, and a vent needle was placed in the septum at the top of the Vigreux column. The N_2 pressure was adjusted until light bubbling was observed in the reaction mixture. This served to sparge the reaction to displace carbon monoxide as it was formed. The setup was lowered into an oil bath preheated at 80 °C. The reaction went from a yellow heterogeneous mixture to a solution with slight Pd black formation. After 1 h, the reaction was removed from the oil bath and allowed to cool to room temperature. The solution was filtered in air through a pad of celite using toluene (50 mL), affording a yellow solution. The solution was concentrated, resulting in a yellow solid. The solid was collected via filtration and washed with $^{i}Pr_2O$ (3 x 30 mL). A significant amount of product was lost with each wash. The desired product was

collected as a yellow solid (1.001 g, 30% yield). The compound was found to contain 0.62 equiv of $^{i}Pr_2O$ as determined by ^{1}H NMR spectroscopic analysis with 1,3,5-trimethoxybenzene as internal standard. This was taken into consideration in the stoichiometry of subsequent steps. ^{1}H, ^{19}F, and ^{31}P NMR were all acquired in $CDCl_3$ at 23 °C and contained broad resonances.

iii. ***(P^{t}Bu$_3$)Pd(Ph)(CF$_3$) (1-CF$_3$)***



(1-CF$_3$)

In a glovebox, a 20 mL scintillation vial was charged with [P(*o*-tol)$_3$]$_2$Pd(CF$_3$)(OC(O)CF$_3$) (150 mg, 0.167 mmol, 1.00 equiv), P^{t}Bu$_3$ (203 mg, 1.00, 6.00 equiv), and THF (8.8 mL, 0.019 M), affording a yellow solution. The vial was sealed with a Teflon-lined screw cap and allowed to sit in the glovebox freezer at –35 °C for 15 min. During this time, a 4 mL scintillation vial was charged with Ph_2Zn (20.2 mg, 0.0920 mmol, 0.550 equiv). After cooling for 15 min, the reaction vial was removed from the glovebox freezer, and the preweighed Ph_2Zn was added, resulting in an immediate color change from pale yellow to vibrant yellow. The reaction was homogeneous. The vial containing the Ph_2Zn was washed once with the reaction solution. This wash was combined with the reaction mixture. The reaction was allowed to stand at room temperature for 7 min. The reaction was concentrated under vacuum to yield a yellow oil. Pentane (2 mL) was added, and the vial was shaken. After ~2 min a yellow solid precipitated, and the pentane layer was removed by decantation. If product did not precipitate, the vial was placed in the glovebox freezer at –35 °C for ~1 min (or until yellow solid began to form). The resulting yellow solid was washed with pentane (3 x 2 mL) and Et_2O (0.5 mL) and dried under vacuum for 25 min to afford the desired product as a yellow solid (28-48 mg, 37-63% yield).

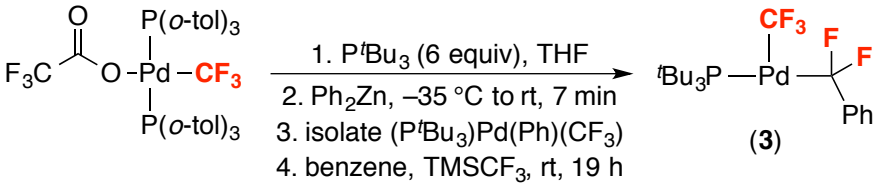
^{1}H NMR (400.52 MHz, C_6D_6, 23 °C): δ 7.66 (app d, J = 7.6 Hz, 2H), 6.98 (app t, J = 7.5 Hz, 2H), 6.88 (app t, J = 7.1 Hz, 1H), 0.94 (d, J = 12.1 Hz, 27H).

^{19}F NMR (470.47 MHz, C_6D_6, 23 °C): δ –28.34 (d, J = 39.6 Hz, 3F).

^{31}P NMR (283.28 MHz, C_6D_6, 23 °C): δ 54.60 (q, J = 39.6 Hz, 1P).

Elemental analysis calculated for $C_{19}H_{32}F_3PPd$, C: 50.17, H: 7.09; found, C: 49.98, H: 6.89

iv. *(P^tBu_3)Pd(CF_2Ph)(CF_3) (**3**)*



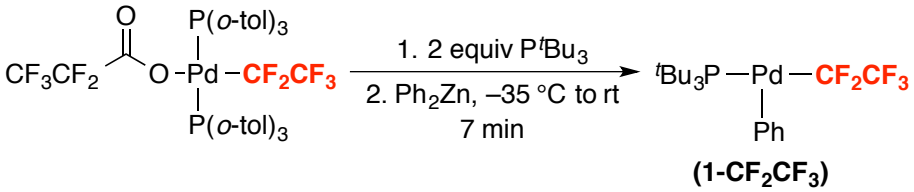
In a glovebox, a 20 mL scintillation vial was charged with [P(*o*-tol)$_3$]$_2$Pd(CF_3)(OC(O)CF_3) (150 mg, 0.167 mmol, 1.00 equiv), P^tBu_3 (203 mg, 1.00, 6.00 equiv), and THF (8.8 mL, 0.019 M), affording a yellow solution. The vial was sealed with a Teflon-lined screw cap and allowed to stand in the glovebox freezer at –35 °C for 15 min. A 4 mL scintillation vial was charged with Ph_2Zn (20.2 mg, 0.0920 mmol, 0.550 equiv). After cooling for 15 min, the reaction vial was removed from the glovebox freezer, and the preweighed Ph_2Zn was immediately added. The vial containing the Ph_2Zn was washed once with the reaction solution. This wash was combined with the reaction mixture. The reaction was allowed to stand at room temperature for 7 min. The reaction was concentrated under vacuum to afford a yellow oil, pentane (2 mL) was added, and the vial was placed in the freezer for ~1 min, resulting in the formation of a yellow solid. The vial was removed from the freezer and was shaken, resulting in precipitation of the yellow product. The pentane was removed by decantation, and the resulting yellow solid was dried under vacuum for 10 min, affording (P^tBu_3)Pd(Ph)(CF_3) (24 mg, 0.053 mmol). Benzene (4.4 mL, 0.012 M based on isolated (P^tBu_3)Pd(Ph)(CF_3)) and $TMSCF_3$ (0.39 mL, 2.6 mmol, 50 equiv based on (P^tBu_3)Pd(Ph)(CF_3)) were added to the vial containing (P^tBu_3)Pd(Ph)(CF_3). The solution was allowed to stand at room temperature in the glovebox for 19 h. During this time, the solution changed color from yellow to brown. The reaction mixture was then filtered through a pipette plug of celite, and the resulting solution was concentrated to afford a brown residue. The brown residue was washed with pentane until the washes were colorless (total volume of pentane ~5 mL). The washes were combined, resulting in an orange pentane solution which was concentrated to afford a yellow-orange solid. The solid was washed carefully with pentane (the desired product is very soluble in pentane) until the pentane washes went from orange to yellow in color (6 x 0.1 mL) affording the desired product as a yellow solid (5 mg, 6% yield over entire sequence, 19% yield based on isolated (P^tBu_3)Pd(Ph)(CF_3)).

^{1}H NMR (499.91 MHz, C_6D_6, 23 °C): δ 7.80 (m, 2H), 7.08-7.01 (multiple peaks, 3H), 0.98 (d, J = 12.1 Hz, 27H).

^{19}F NMR (470.47 MHz, C_6D_6, 23 °C): δ –18.15 (dt, J = 20.9, 9.1 Hz, 3F), –64.16 (dq, J = 43.5, 9.1 Hz, 2F).

^{31}P NMR (283.28 MHz, C_6D_6, 23 °C): δ 66.15 (tq, J = 43.5, 20.9 Hz, 1P).

v. ***(P^{t}Bu$_3$)Pd(Ph)(CF$_2$CF$_3$) (1-CF$_2$CF$_3$)***



(1-CF$_2$CF$_3$)

In the glovebox, a 20 mL scintillation vial was charged with [P(*o*-tol)$_3$]$_2$Pd(CF$_2$CF$_3$)(OC(O)CF$_2$CF$_3$) • 0.62 ^{i}Pr$_2$O (177 mg, 0.167 mmol, 1.00 equiv), P^{t}Bu$_3$ (67.6 mg, 0.334 mmol, 2.00 equiv), and THF (8.8 mL, 0.019 M), affording a yellow solution. The vial was capped with a Teflon-lined screw cap and allowed to stand in the glovebox freezer at –35 °C for 15 min. A 4 mL scintillation vial was charged with Ph$_2$Zn (20.2 mg, 0.0920 mmol, 0.550 equiv). After cooling for 15 min, the reaction was removed from the glovebox freezer, and the preweighed Ph$_2$Zn was added. The reaction remained yellow and homogeneous. The vial containing the Ph$_2$Zn was washed once with the reaction solution. This wash was combined with the reaction mixture. The reaction was allowed to stand at room temperature for 7 min. The reaction was concentrated under vacuum to afford a yellow oil, and pentane (5 mL) was added. The vial was placed in the glovebox freezer at –35 °C for 2 min, at which time a yellow solid began to form. The vial was placed back in the freezer for 1 min, and a significant amount of additional yellow solid formed. The pentane was removed by decantation, and the resulting solid was dried under vacuum for 25 min to afford the desired product as a yellow solid (62 mg, 74% yield). ^{1}H and ^{31}P NMR spectroscopic analysis show the presence of 2-4% of P(*o*-tol)$_3$ as an impurity.

^{1}H NMR (499.91 MHz, C$_6$D$_6$, 23 °C): δ 7.58 (app d, J = 7.8 Hz, 2H), 6.94 (app t, J = 7.6 Hz, 2H), 6.85 (app t, J = 7.2 Hz, 1H), 0.96 (d, J = 12.1 Hz, 27H).

^{19}F NMR (470.47 MHz, C$_6$D$_6$, 23 °C): δ –80.14 (m, 3F), –103.47 (d, J = 21.6 Hz, 2F).

^{31}P NMR (283.28 MHz, C$_6$D$_6$, 23 °C): δ 54.26 (t, J = 21.6 Hz, 1P).

Elemental analysis calculated for C$_{20}$H$_{32}$F$_5$PPd, C: 47.58, H: 6.39; found, C: 47.38, H: 6.33

4. Representative Procedure for Thermolysis of (P^tBu_3)Pd(Ph)(CF_3) (**1-CF_3**) and (P^tBu_3)Pd(Ph)(CF_2CF_3) (**1-CF_2CF_3**) Complexes

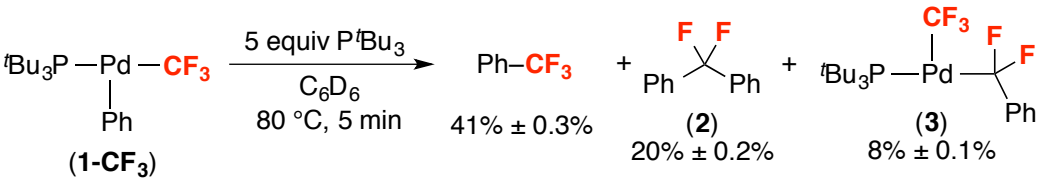
In a glovebox, a J. Young NMR tube was charged with **1-CF_3** (0.25 mL of 0.024 M stock solution in C_6D_6), P^tBu_3 (0.20 mL of 0.15 M stock solution in C_6D_6), and (trifluoromethoxy)benzene (50 μL of 0.12 M stock solution in C_6D_6). The NMR tube was sealed, removed from the glovebox, and immediately placed in a liquid N_2 bath. The reaction was removed from the liquid N_2 bath and allowed to warm to room temperature, and then a ^{19}F NMR spectrum was acquired prior to heating to obtain the starting material to internal standard ratio. Immediately after the this initial spectrum was acquired, the reaction was placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, allowed to warm to room temperature, placed in a preheated oil bath at 80 °C, and allowed to stand for 5 min. Upon completion, the NMR tube was removed from the oil bath and immediately placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, and a ^{19}F NMR spectrum was acquired to determine the conversion of starting material and the yield of benzotrifluoride. The same procedure was followed for **1-CF_2CF_3**. The experiments were performed in triplicate.

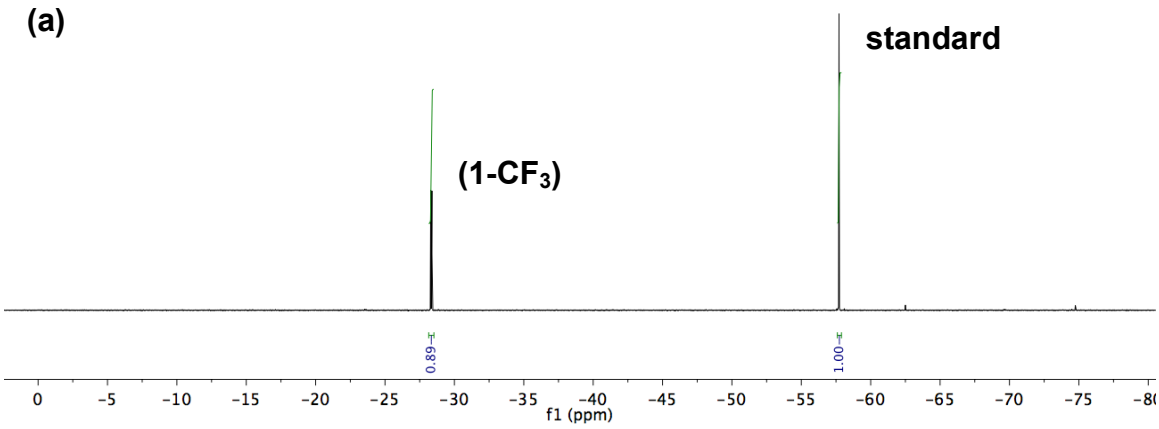
NMR Setup for **1-CF_3**: spectral window: +2.5 to –80.6 ppm; number of scans: 1

NMR Setup for **1-CF_2CF_3**: spectral window: –41.6 to –130.2 ppm; number of scans: 1

i. Data

*a. (P^tBu_3)Pd(Ph)(CF_3) (**1-CF_3**)*





(b)

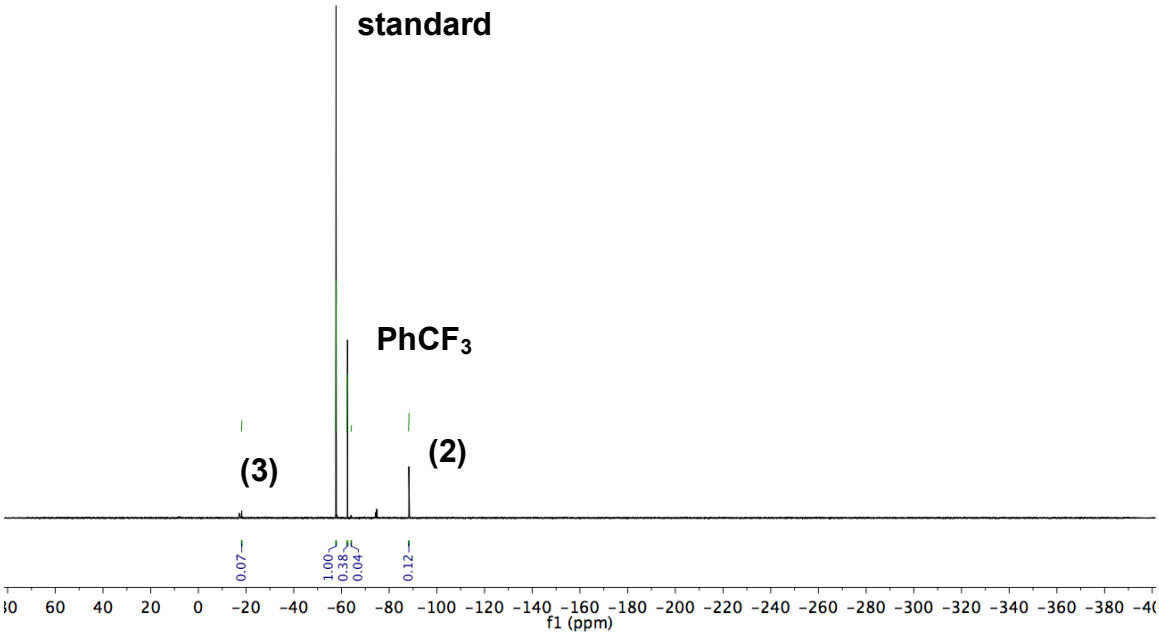


Figure S1. ^{19}F NMR spectra of: (a) **1-CF_3** and internal standard prior to thermolysis; (b) Reaction mixture after heating at 80 °C for 5 min.

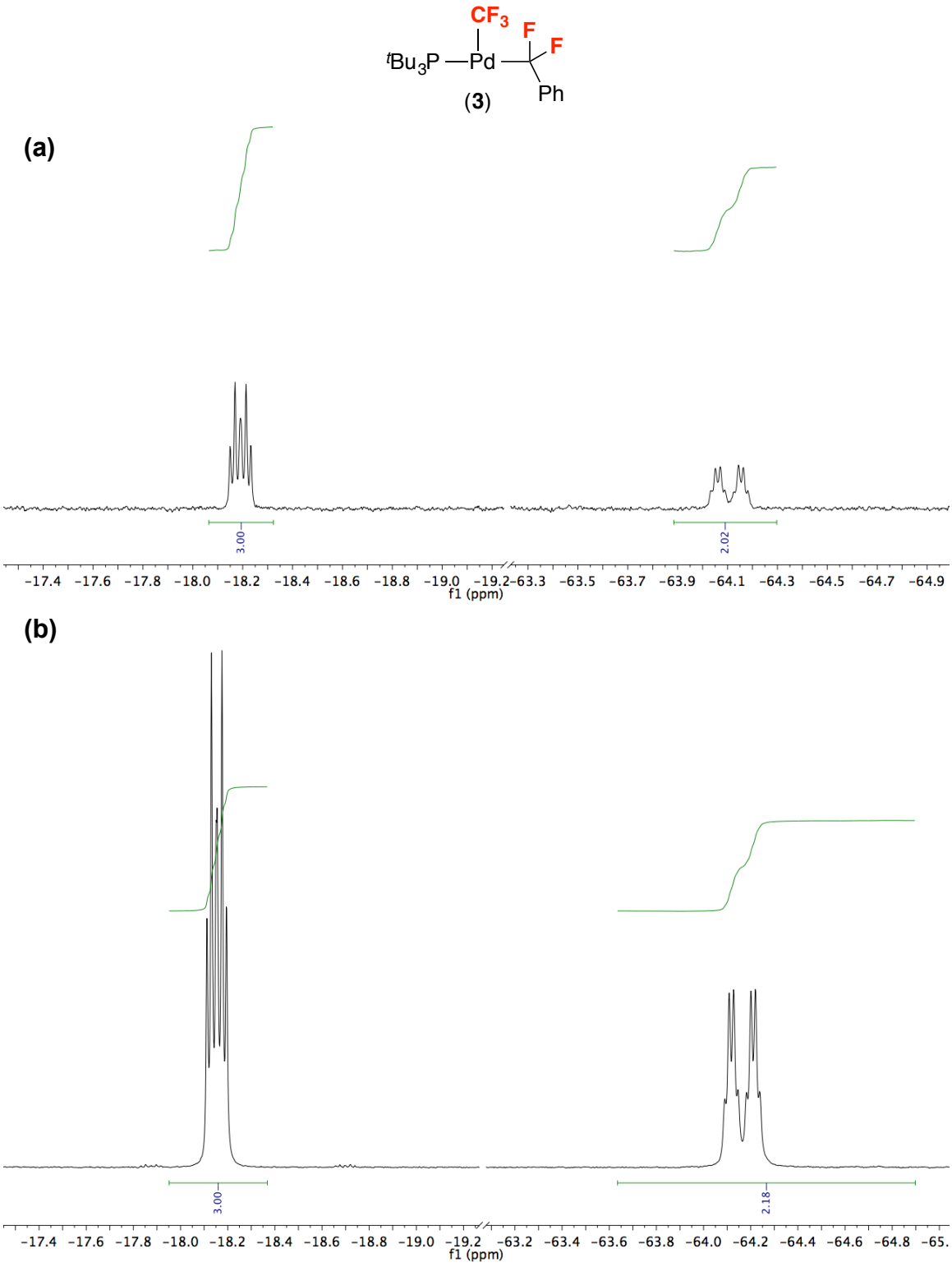
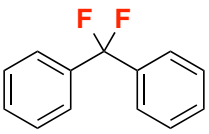


Figure S2. ^{19}F NMR spectra of: (a) **3** generated as a side product in the thermolysis of **1-CF$_3$**; (b) Authentic sample of **3**.



(2)

Exact Mass = 204.0751

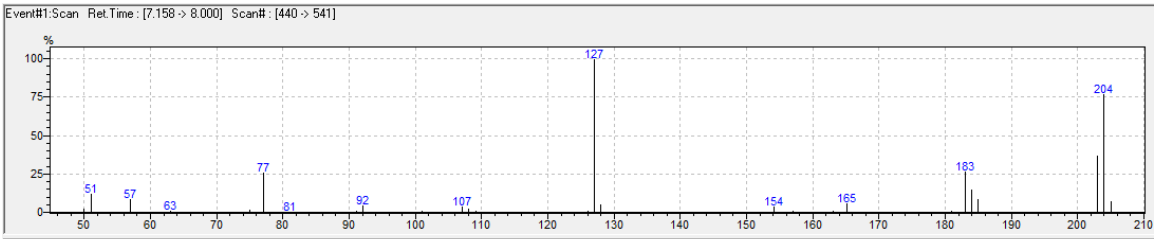


Figure S3. Mass spectrum of **2**.

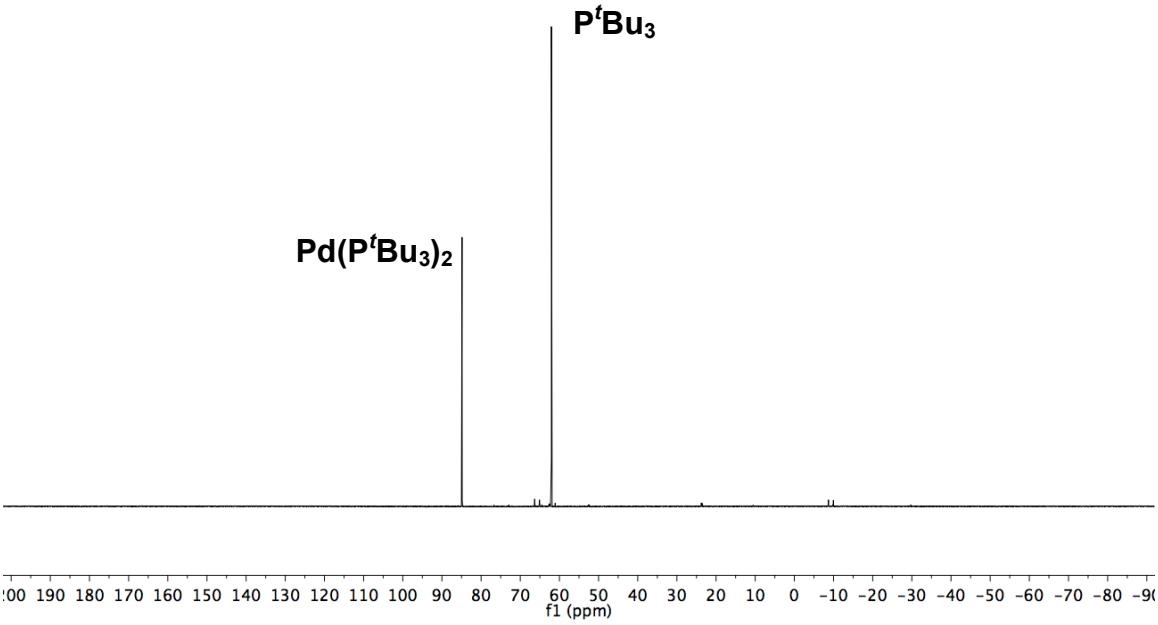
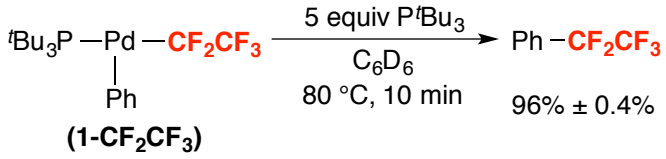


Figure S4. ^{31}P NMR spectrum of reaction mixture after heating at 80 °C for 5 min.

Note: The products that we can confidently identify by ^{19}F NMR spectroscopy account for 66% of the fluorine mass balance. If we assign the broad doublet at –17 ppm as a Pd(CF_3) species (unconfirmed, but a reasonable assumption based on the chemical shift of related species), the mass balance for fluorine is 76%. We do not observe (P^tBu_3)Pd(Ph)(F), (P^tBu_3)Pd(CF_3)(F), Ph–F, or CF_4. We also looked for products associated with P–F bond formation and these were not observed.

*b. (P^tBu_3)Pd(Ph)(CF_2CF_3) (**1-CF_2CF_3**)*



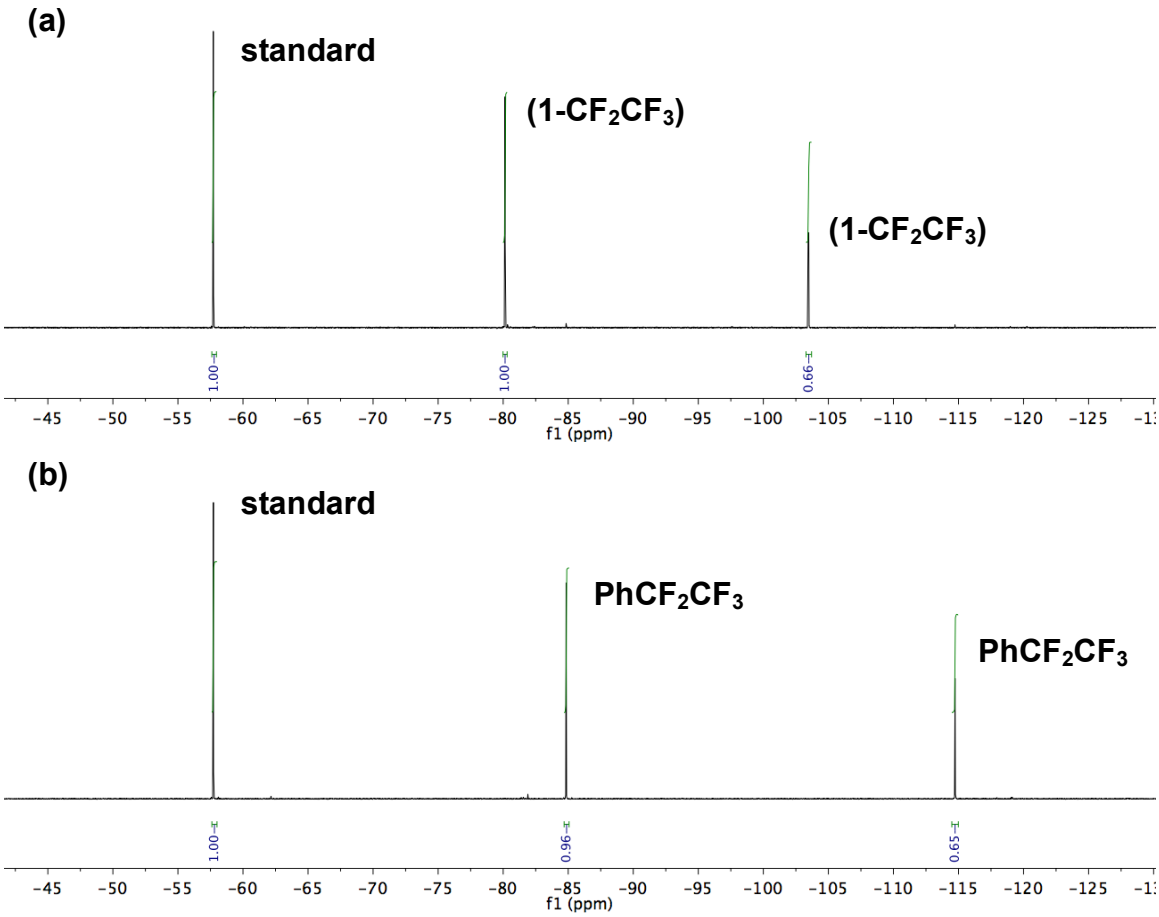


Figure S5. ^{19}F NMR spectra of: (a) **1-CF_2CF_3** and internal standard prior to thermolysis; (b) Reaction mixture after heating at 80 °C for 10 min.

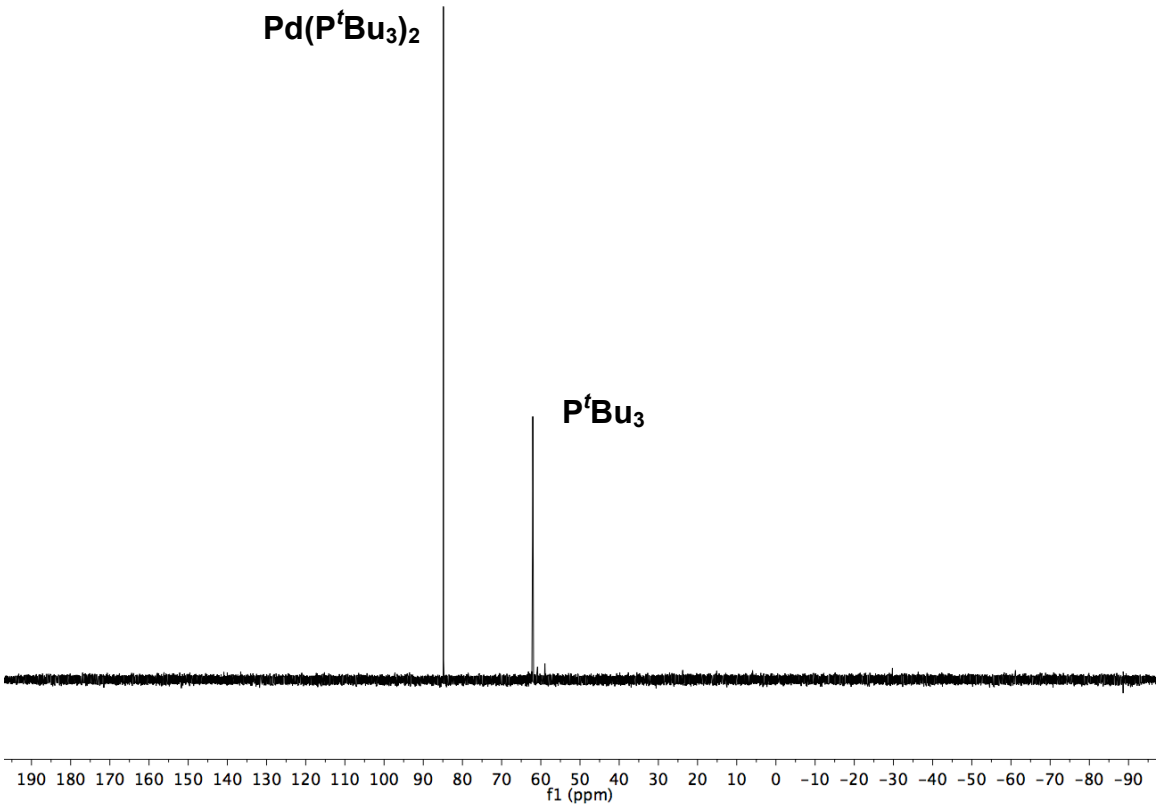
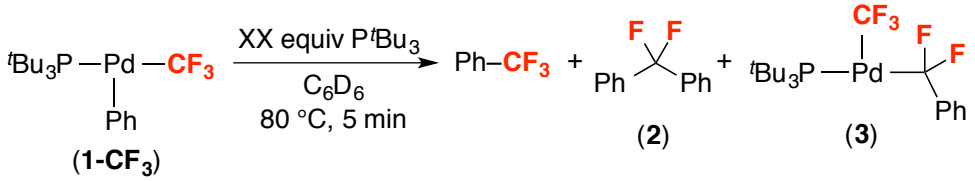


Figure S6. ^{31}P NMR spectrum of reaction mixture after heating at 80 °C for 10 min.

*ii. Effect of Equiv of P^{t}Bu$_3$ on Reductive Elimination from **1-CF$_3$** and **1-CF$_2$CF$_3$***

*a. Reductive Elimination from **1-CF$_3$***

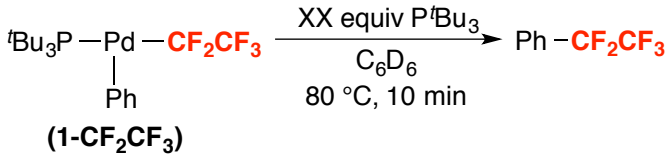


Equiv P^{t}Bu$_3$	Yield Ph–CF$_3$ (%)	Yield (2) (%)	Yield (3) (%)
1[a]	16	14	16
2[a]	23	22	8
5	41	20	8

[a]2 min reaction time (>98% conversion)

Table S1. Effect of equiv of added P^{t}Bu$_3$ on reductive elimination from **1-CF$_3$**.

b. Reductive Elimination from ***1-CF$_2$CF$_3$***



Equiv P^{t}Bu$_3$	Yield Ph–CF$_2$CF$_3$
1	84
2	89
5	96

Table S2. Effect of equiv of added P^{t}Bu$_3$ on reductive elimination from **1-CF$_2$CF$_3$**.

5. Reductive Elimination from 1-CF$_3$ Under Catalytically Relevant Conditions

i. Data

Catalytic conditions are quite different than the stoichiometric conditions. As shown in Figure S7, under catalytic conditions it is likely that [Pd-F] intermediates such as **A** will competitively transmetallate with TESCF$_3$ (which is at high concentration under catalytic conditions) over a [Pd-Ar] species (which is expected to be at low concentration under catalytic conditions). Thus, less of side product **5** is expected during catalysis (vs in the stoichiometric reactions).

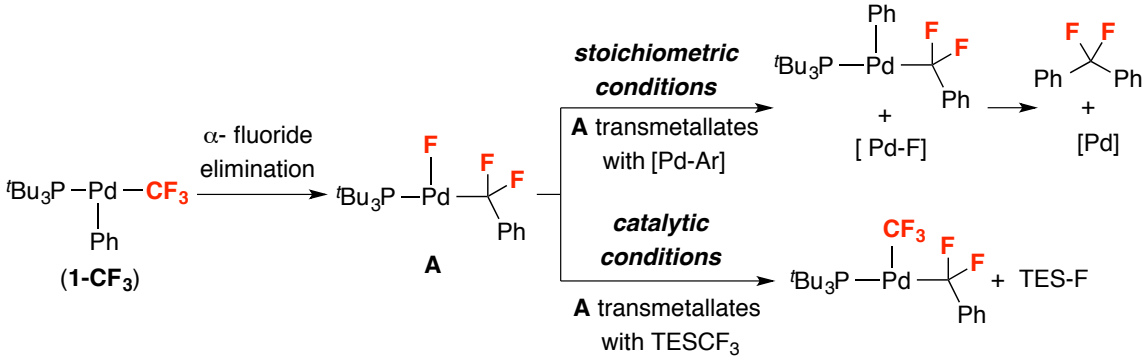


Figure S7. Potential pathways for the decomposition of **A** under stoichiometric and catalytic conditions

To test this hypothesis, we explored the reactivity of **1-CF$_3$** in the presence of 20 equiv of TESCF$_3$. As it can be seen in Figure S8, we observed a decrease in the amount of side product **2**. This is consistent with the proposal above. In addition, it is noted that TES–F was observed suggesting the formation of free F$^-$ or a Pd–F species.

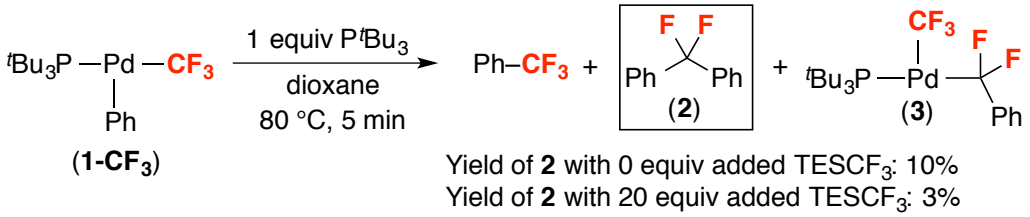


Figure S8. Effect of added $TESCF_3$ on the yield of side product **2**.

We also explored the effect of added F^- (in the form of KF) on the stoichiometric reductive elimination. A reviewer suggested that this might lead to an increase in α-F elimination products due to the presence of Lewis acidic K^+ ions or due to the presence of F^- ions assisting in the α-F elimination step. As shown in Figure S9, the presence of 20 equiv of KF had a minimal effect on the yields of any of the products, suggesting that α-F elimination is not accelerated by KF.

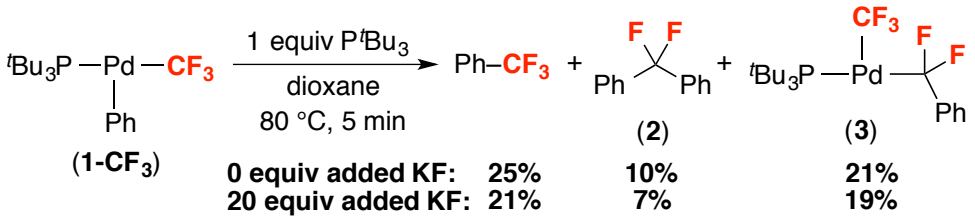


Figure S9. Effect of added KF on the thermolysis of **1-CF$_3$**.

ii. Procedure

In a glovebox, a J. Young NMR tube was charged with **1-CF$_3$** (0.25 mL of 0.070 M stock solution in dioxane), P^tBu_3 (0.10 mL of 0.174 M stock solution in dioxane), (trifluoromethoxy)benzene (0.10 mL of 0.174 M stock solution in dioxane), and dioxane (0.13 mL).

Three reactions were setup. The first reaction (#1) was a control reaction that did not include any additional additives. To the second reaction (#2) was added $TESCF_3$ (65 µL, 20 equiv). To the third reaction (#3) was added KF (20.2 mg, 20 equiv). The third reaction was not carried out in a J. Young NMR tube due to the heterogeneous nature of the reaction mixture. Instead, the reaction was performed in a sealed 4 mL vial containing a magnetic stir bar.

For reactions #1 and #2, the NMR tubes were sealed, removed from the glovebox, and immediately placed in a liquid N_2 bath. The reaction was removed from the liquid N_2 bath and allowed to warm to room temperature, and then a ^{19}F NMR spectrum was acquired prior to heating to obtain the starting material to internal standard ratio. Immediately after this initial spectrum was acquired, the reaction was placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, allowed to warm to room temperature, placed in a preheated oil

bath at 80 °C, and allowed to stand for 5 min. Upon completion, the NMR tube was removed from the oil bath and immediately placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, and a ^{19}F NMR spectrum was acquired to determine the conversion of starting material and the yield of benzotrifluoride.

For reaction #3, the vial was removed from the glovebox, placed on a preheated aluminum block at 80 °C, and allowed to stir vigorously for 5 min. Upon completion, the vial was removed from the heating block and immediately placed in a liquid N_2 bath. The vial was removed from the liquid N_2 bath, allowed to warm to room temperature, and brought into a glovebox. The solution was transferred to a J. Young NMR tube, which was sealed, brought out of the glovebox, and immediately placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, and a ^{19}F NMR spectrum was acquired to determine the conversion of starting material and the yield of benzotrifluoride.

NMR Setup for **1-CF_3**: spectral window: +2.5 to –80.6 ppm; number of scans: 1

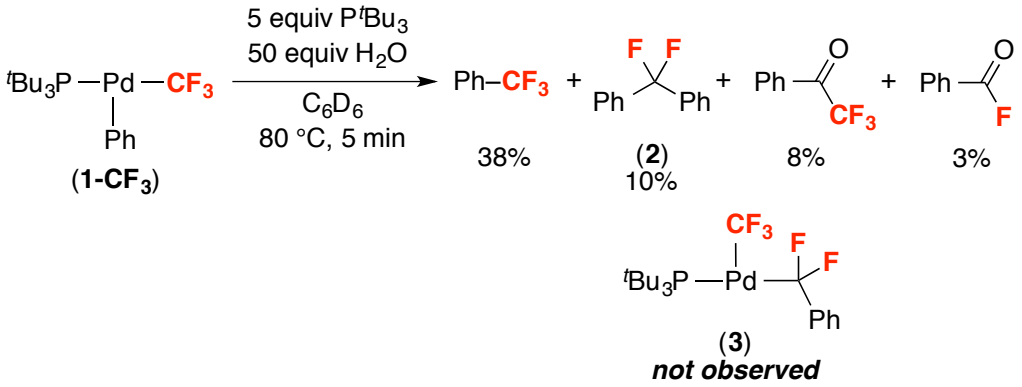
6. Thermolysis of 1-CF_3, 1-CF_2CF_3, and 3 in the Presence of Water

i. Data

Grushin has proposed that Pd-difluorocarbene intermediates are readily hydrolyzed by H_2O to afford carbon monoxide and subsequently yield carbonyl-containing products.[5] Thus, he has proposed that the addition of exogenous water to aryl–CF_3 coupling reactions can be used to test whether this mechanism is operating. Specifically, he proposes that if Pd=CF_2 are formed, the addition of water will lead to the appearance of Ar-C(O)X derivatives as well as potential decreases in the yields of Pd=CF_2-derived products.

Thermolysis of **1-CF_3** in the presence of 50 equiv water afforded Ph–CF_3 in a slightly reduced yield relative to anhydrous conditions (38% versus 41%) (Figure S10). Additionally, we observed the carbonyl-containing organic products PhC(O)CF_3 and PhC(O)F. To probe the possibility that PhC(O)CF_3 and PhC(O)F result from the hydrolysis of a Pd-difluorobenzyl species such as side product **3** or intermediate **B**, we heated **3** in the presence of 50 equiv of H_2O. Indeed, PhC(O)CF_3 was generated in 97% yield suggesting that Pd-difluorobenzyl species also undergo hydrolysis to form carbonyl-containing products (Table S3). Notably, the presence of water did not affect the yield in the thermolysis of **1-CF_2CF_3** and no PhC(O)X products were detected in this system (Figure S11). Overall, these results indicate that intermediates susceptible to hydrolysis are generated in the thermolysis of **1-CF_3**. However, we cannot definitively determine whether hydrolysis is occurring at a Pd=CF_2 species or whether Ph–CF_3 coupling is proceeding via the difluorocarbene pathway.

a. ***1-CF$_3$***



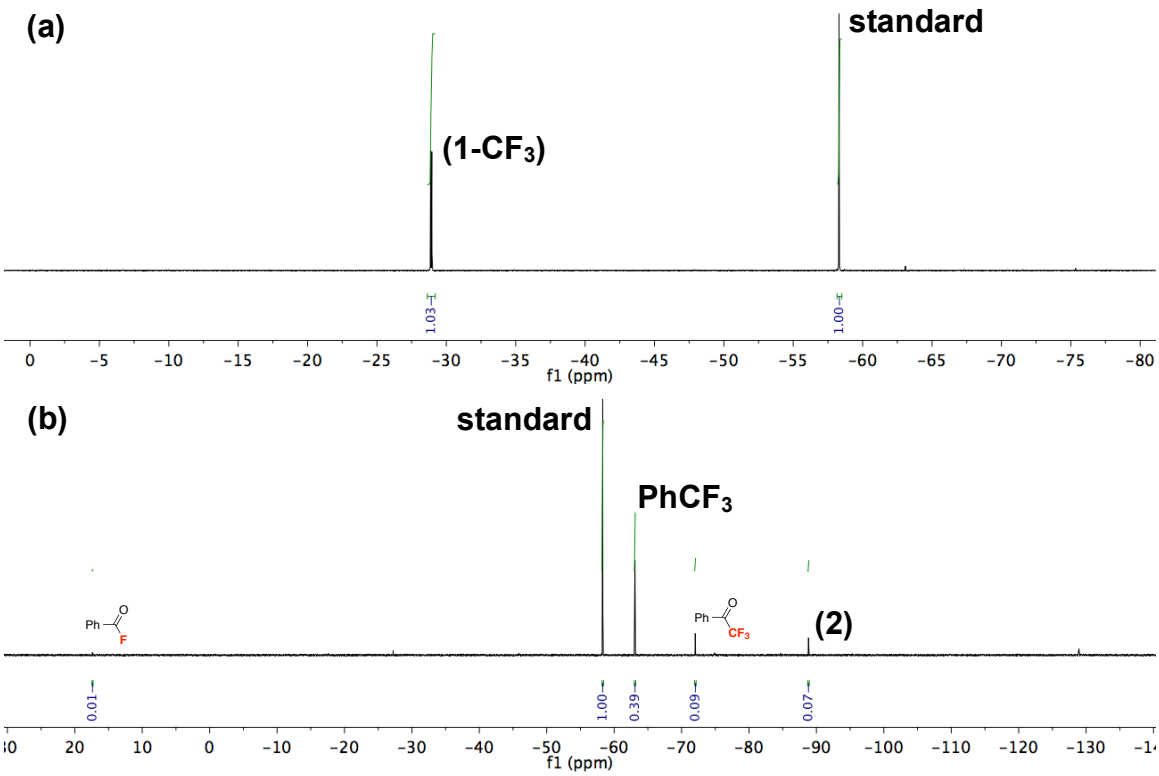
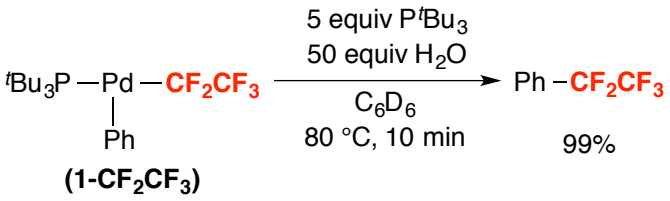


Figure S10. ^{19}F NMR spectra of: (a) **1-CF$_3$** and internal standard prior to thermolysis; (b) Reaction mixture after heating at 80 °C for 5 min.

b. ***1-CF$_2$CF$_3$***



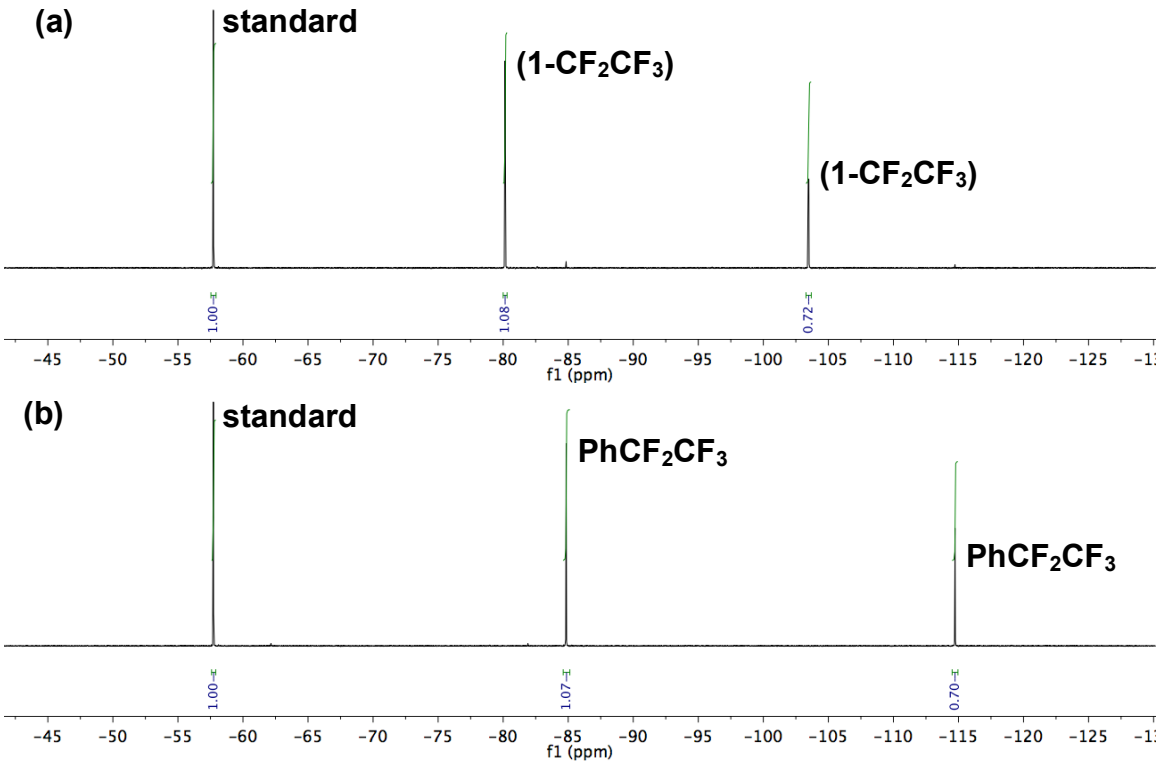
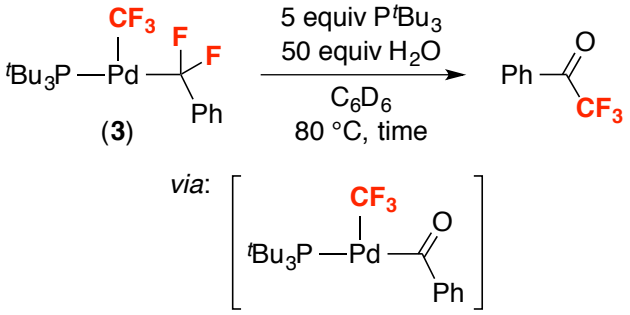


Figure S11. ^{19}F NMR spectra of: (a) **1-CF_2CF_3** and internal standard prior to thermolysis; (b) Reaction mixture after heating at 80 °C for 10 min.

c. ***Complex 3***



Time (min)	(3) Conversion (%)	Intermediate Yield (%)	PhC(O)CF_3 Yield (%)
0[a]	12	12	0
1	80	69	12
2	quant.	68	33
5	quant.	23	78
10	quant.	quant.	97

[a]temperature was room temperature, approx. 5 min.

Table S3. Hydrolysis of **3**.

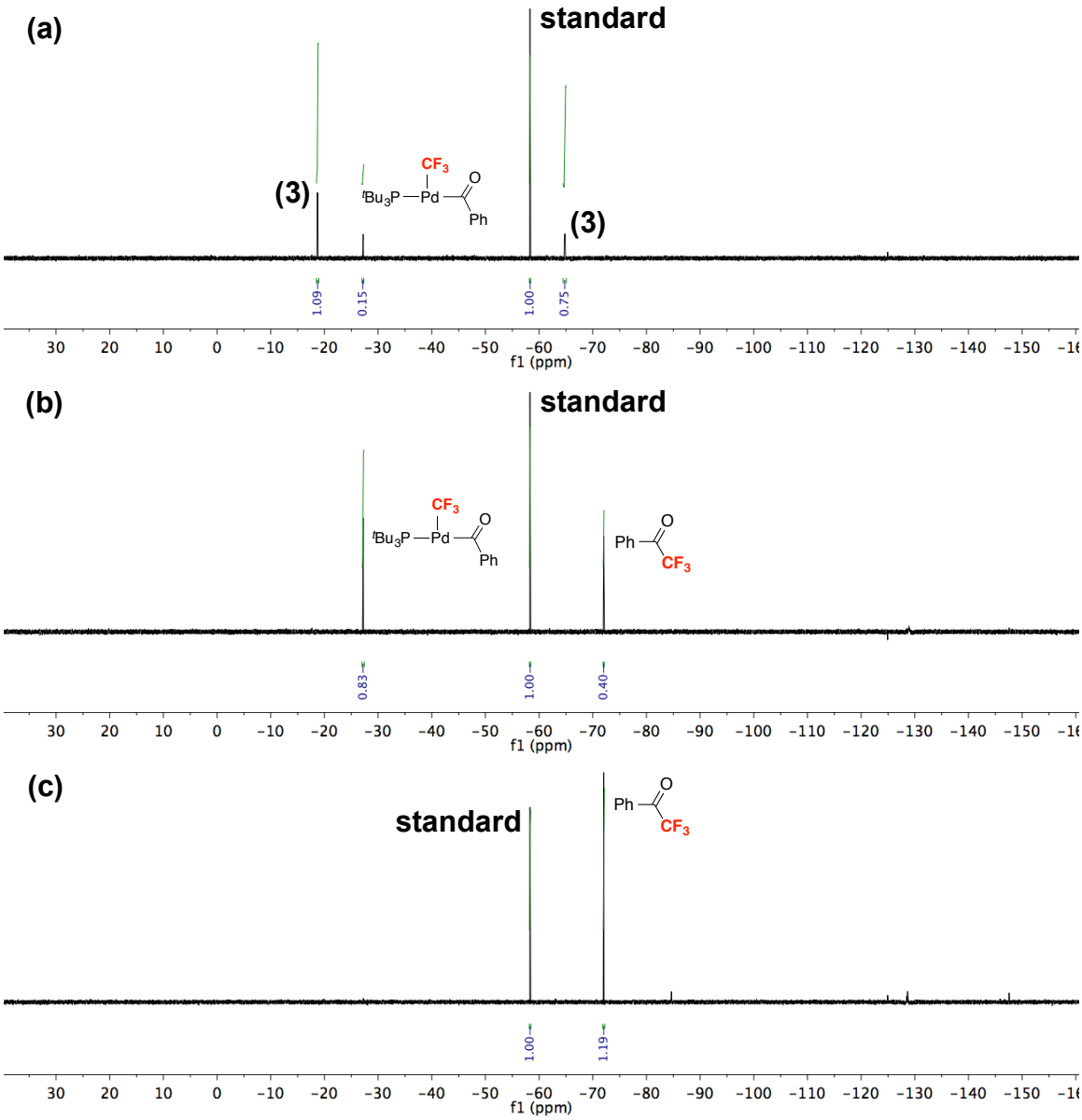


Figure S12. ^{19}F NMR spectra of: (a) **3**, hydrolysis intermediate, and internal standard prior to thermolysis; (b) Reaction mixture after heating at 80 °C for 2 min; (c) Reaction mixture after heating at 80 °C for 10 min.

ii. Procedure

Procedure for 1-CF_3

To a 4 mL vial was added **1-CF_3** (2.7 mg, 0.0060 mmol), P^{t}Bu$_3$ (0.20 mL of 0.15 M stock solution in C_6D_6), C_6D_6 (0.25 mL), and (trifluoromethoxy)benzene (50 µL of 0.12 M stock solution in C_6D_6). The solution was mixed with a pipette and transferred to a J. Young NMR tube. Next, sparged, deionized water (5 µL, 0.3

mmol) was added via microsyringe, and the NMR tube was sealed, removed from the glovebox, and immediately placed in a liquid N_2 bath. The reaction was removed from the liquid N_2 bath and allowed to warm to room temperature, and then a ^{19}F NMR spectrum was acquired prior to heating to obtain the starting material to internal standard ratio. Immediately after this initial spectrum was acquired, the reaction was placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, allowed to warm to room temperature, placed in a preheated oil bath at 80 °C, and allowed to stand for 5 min. Upon completion, the NMR tube was removed from the oil bath and immediately placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, and a ^{19}F NMR spectrum was acquired to determine the conversion of starting material and the yield of benzotrifluoride.

Procedure for 1-CF_2CF_3

To a J. Young NMR tube was added **1-CF_2CF_3** (0.25 mL of 0.024 M solution in C_6D_6), P^{t}Bu$_3$ (0.20 mL of 0.15 M stock solution in C_6D_6), (trifluoromethoxy)benzene (50 µL of 0.12 M stock solution in C_6D_6), and sparged, deionized water (5 µL, 0.3 mmol). The NMR tube was sealed, removed from the glovebox, and immediately placed in a liquid N_2 bath. The reaction was removed from the liquid N_2 bath and allowed to warm to room temperature, and then a ^{19}F NMR spectrum was acquired prior to heating to obtain the starting material to internal standard ratio. Immediately after this initial spectrum was acquired, the reaction was placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, allowed to warm to room temperature, placed in a preheated oil bath at 80 °C, and allowed to stand for 10 min. Upon completion, the NMR tube was removed from the oil bath and immediately placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, and a ^{19}F NMR spectrum was acquired to determine the conversion of starting material and the yield of (pentafluoroethyl)benzene.

Procedure for 3

To a 4 mL vial was added **3** (3.0 mg, 0.0060 mmol, 1.0 equiv), P^{t}Bu$_3$ (6.1 mg, 0.030 mmol, 5.0 equiv), C_6D_6 (0.45 mL), and (trifluoromethoxy)benzene (50 µL of 0.12 M stock solution in C_6D_6). The solution was mixed with a pipette and transferred to a J. Young NMR tube. Next, sparged, deionized water (5 µL, 0.3 mmol) was added via microsyringe and the NMR tube was sealed, removed from the glovebox, and immediately placed in a liquid N_2 bath. The reaction was removed from the liquid N_2 bath and allowed to warm to room temperature, and then a ^{19}F NMR spectrum was acquired prior to heating to obtain the starting material to internal standard ratio. Immediately after this initial spectrum was acquired, the reaction was placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, allowed to warm to room temperature, placed in a preheated oil bath at 80 °C, and allowed to stand for the appropriate amount of time. Upon completion, the NMR tube was removed from the oil bath and

immediately placed in a liquid N_2 bath. The NMR tube was removed from the liquid N_2 bath, and a ^{19}F NMR spectrum was acquired to determine the conversion of starting material and the yield of $PhC(O)CF_3$. This process was repeated for each time point.

7. Catalytic competency of (P^tBu_3)Pd(CF_2Ph)(CF_3) (3)

To probe the possibility of **3** decomposing into a catalytically inactive Pd species, we carried out the palladium-catalyzed trifluoromethylation of 1-butyl-4-chlorobenzene using **3** as the Pd source. As shown in Figure S13, this complex was not a competent catalyst for the trifluoromethylation reaction. This suggests that it may serve as a sink for Pd during catalysis.

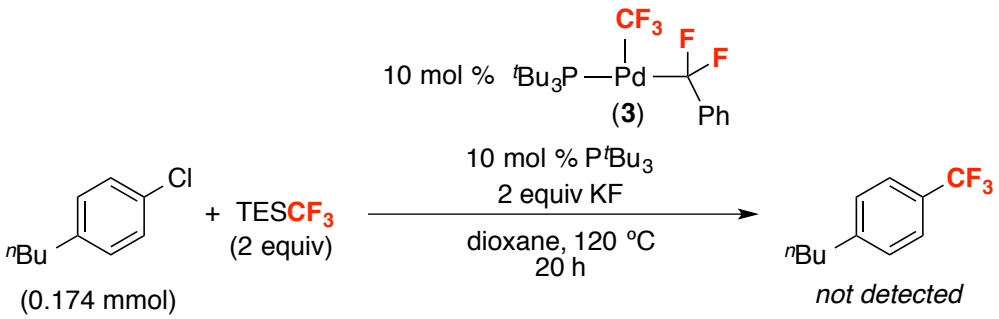
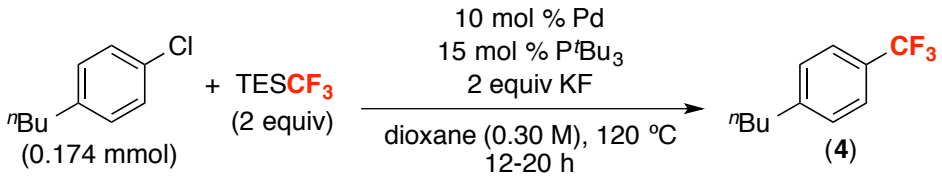


Figure S13. Catalytic competency of **3**.

8. Catalytic Studies

i. Trifluoromethylation

a. Optimization of Pd catalyst



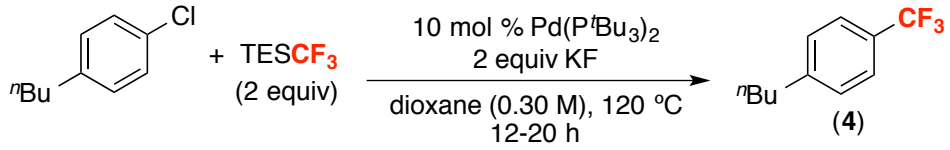
Entry	Pd Source	Yield of Ar–CF_3 (%)[a]
1	$[(allyl)PdCl]_2$	<1
2	$[(cinnamyl)PdCl]_2$	<1
3	$Pd(dba)_2$[b]	2
4	$Pd(dba)_2$[c]	6
5	Buchwald G4-P^tBu_3[d]	1
6	$Pd(P^tBu_3)_2$[d]	22
7	$Pd(P^tBu_3)_2$[e]	4

8	$Pd(P^tBu_3)_2$[f]	15

[a]^{19}F NMR yields against 1,3,5-trifluorobenzene as internal standard; [b]11 mol % P^tBu_3; [c]20 mol % P^tBu_3; [d]no added P^tBu_3; [e]5 mol % $Pd(P^tBu_3)_2$ with 5 mol % added $Pd(dba)_2$ and no additional P^tBu_3; [f]10 mol % P^tBu_3 added.

Table S4. Optimization of palladium catalyst for the trifluoromethylation of 1-butyl-4-chlorobenzene

b. Optimization of reaction conditions with $Pd(P^tBu_3)_2$



Entry	Deviation from Above	Yield of Ar–CF_3 (%)[a]
1	none	22
2	2 equiv $TMSCF_3$	5
3	dioxane (0.60 M)	15
4	2 equiv CsF	4
5	2 equiv CsF, 100 °C	<1
6	2 equiv NaO^tBu, 100 °C	<1
7	5 equiv $TESCF_3$	13
8	4 equiv KF	16
9	4 equiv KF, 4 equiv $TESCF_3$	14
10	4 equiv KF, 8 equiv $TESCF_3$	10
11	3:1 dioxane:toluene (0.30 M)	17
12	1:1 dioxane:toluene (0.30 M)	14
13	1:3 dioxane:toluene (0.30 M)	5
14	2 equiv CsF, 3:1 dioxane:toluene (0.30 M)	4
15	2 equiv CsF, 1:1 dioxane:toluene (0.30 M)	5
16	2 equiv CsF, 1:3 dioxane:toluene (0.30 M)	5
17	2 equiv CsF, toluene	5
18	0.5 mmol scale	15
19	20 mol % $Pd(P^tBu_3)_2$	19

[a]^{19}F NMR yields against 1,3,5-trifluorobenzene as internal standard.

Table S5. Optimization of reaction conditions for the catalytic trifluoromethylation of 1-butyl-4-chlorobenzene with $Pd(P^tBu_3)_2$.

c. Effect of temperature on catalytic trifluoromethylation

Our stoichiometric results with **1-CF$_3$** suggest that catalysis could potentially occur at lower temperature (<120 °C). As such, we carried out catalytic aryl trifluoromethylation at 80 °C for 20 h and 40 h (Figure S14). Benzotrifluoride was observed, albeit in diminished yield (2%) relative to the standard conditions (22%). The lower yield appears to be due, at least in part, to competing decomposition of $TESCF_3$, as no $TESCF_3$ remained after 20 or 40 h.

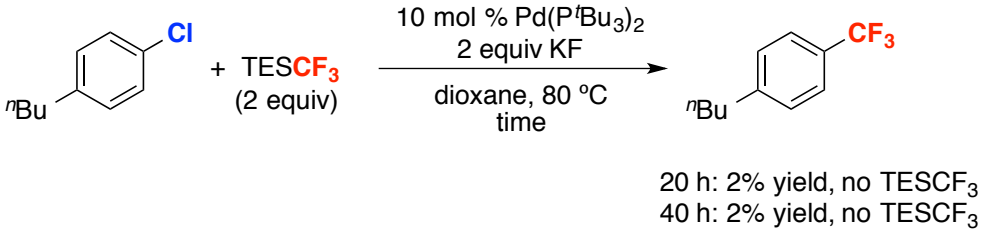


Figure S14. Effect of temperature on catalytic aryl trifluoromethylation.

d. Survey of substrates under optimal conditions

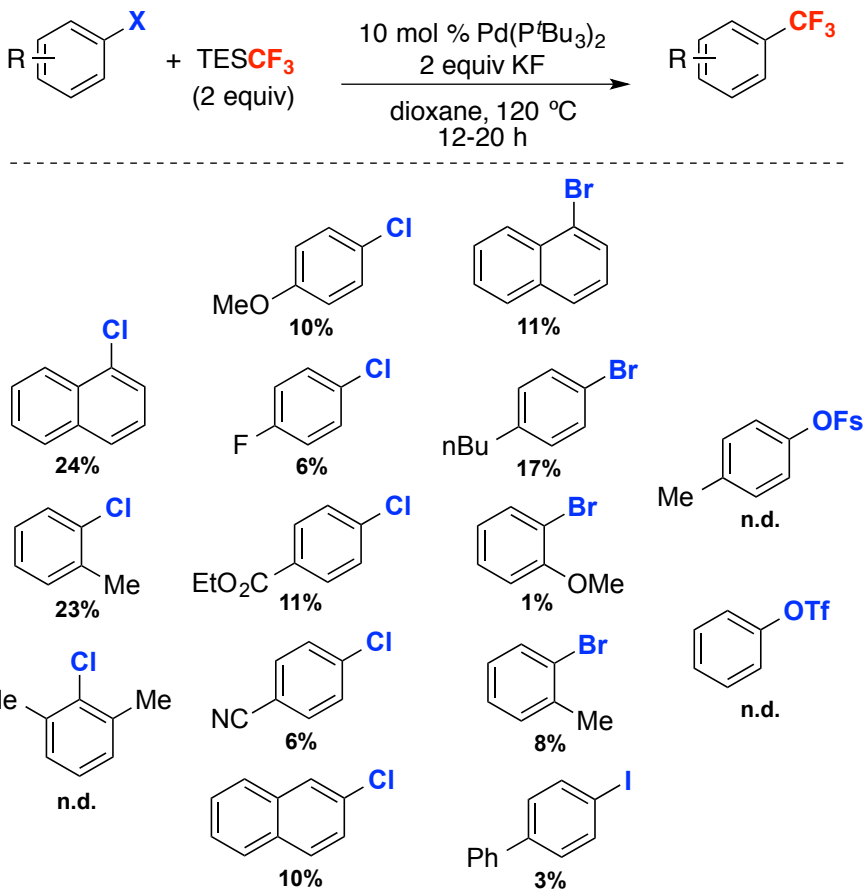
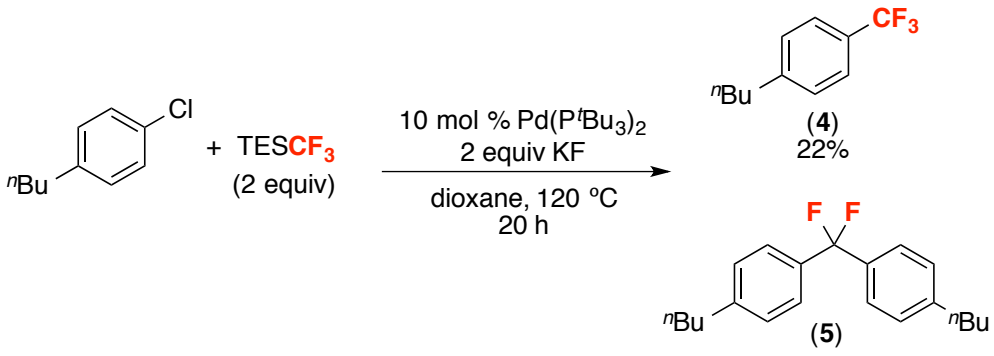


Table S6. Survey of aryl electrophiles for catalytic trifluoromethylation with $Pd(P^tBu_3)_2$.

e. Catalytic trifluoromethylation of 1-butyl-4-chlorobenzene under optimal conditions



In the glovebox, a 4 mL scintillation vial was charged with $Pd(P^tBu_3)_2$ (8.9 mg, 0.017 mmol, 0.10 equiv), KF (20.2 mg, 0.348 mmol, 2.00 equiv), 1-butyl-4-chlorobenzene (29.3 mg, 0.174 mmol, 1.00 equiv) as a solution in 1,4-dioxane (0.58 mL, 0.30 M), and $TESCF_3$ (65 µL, 0.35 mmol, 2.0 equiv). The vial was sealed with a Teflon-lined screw cap, removed from the glovebox, placed on an

aluminum heating block preheated to 120 °C, and the reaction was allowed to stir vigorously for 20 h. The reaction was then allowed to cool to room temperature, opened to air, and diluted with 1.5 mL THF. 1,3,5-trifluorobenzene (0.20 mL, 0.87 M solution in THF, 1.0 equiv) was added as internal standard, and a ^{19}F NMR spectrum was acquired using a 5 s relaxation delay. The yield of **4** was determined by ^{19}F NMR spectroscopy as an average of two runs (21% and 22%). This product was also confirmed by GC-MS. The difluorodiarylmethane side product was observed by ^{19}F NMR spectroscopy, GC-MS, and HRMS EI.

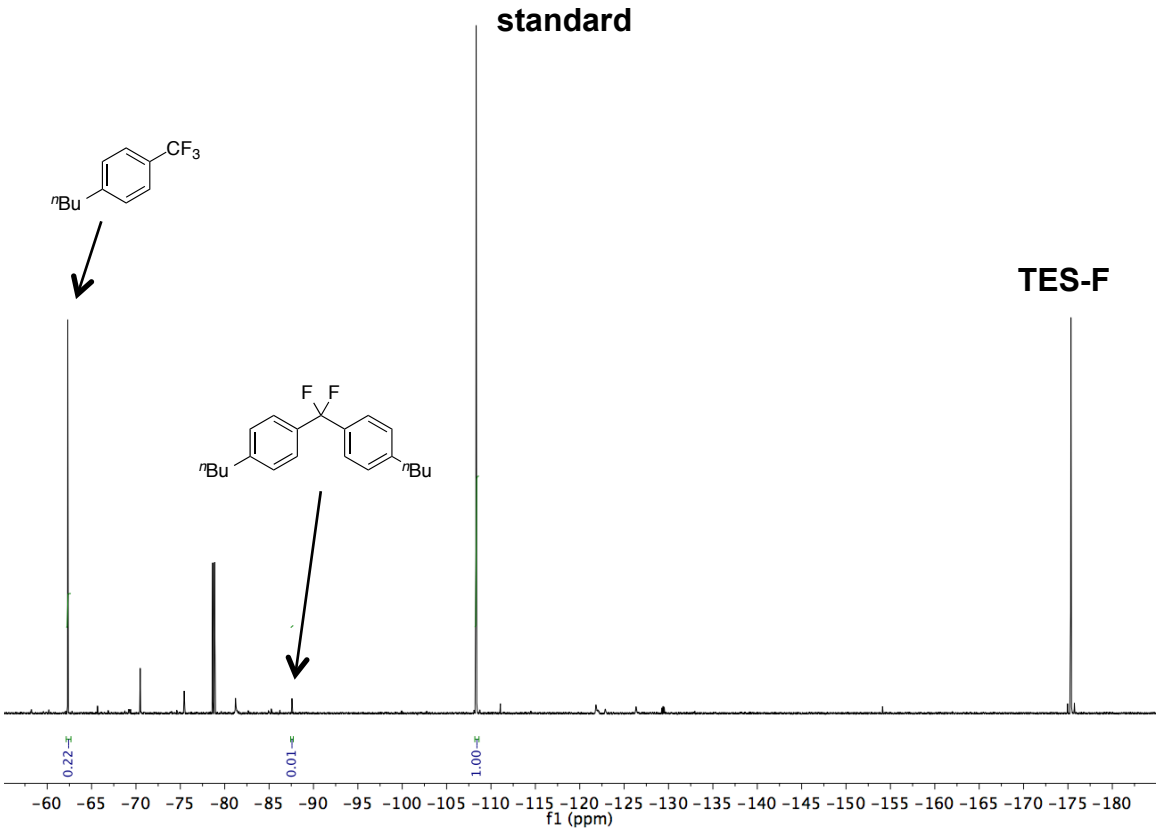
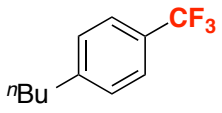


Figure S15. ^{19}F NMR spectrum of crude reaction mixture.



(**4**)

Exact Mass = 202.0969

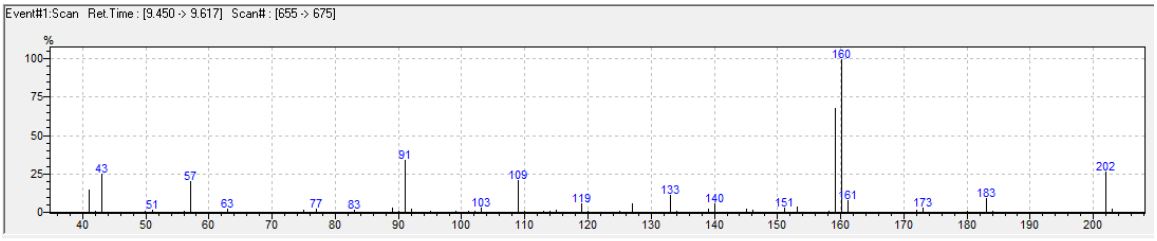
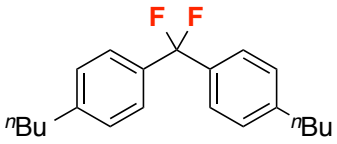


Figure S16. Mass spectrum of product **4**.



(**5**)

Exact Mass = 316.2003

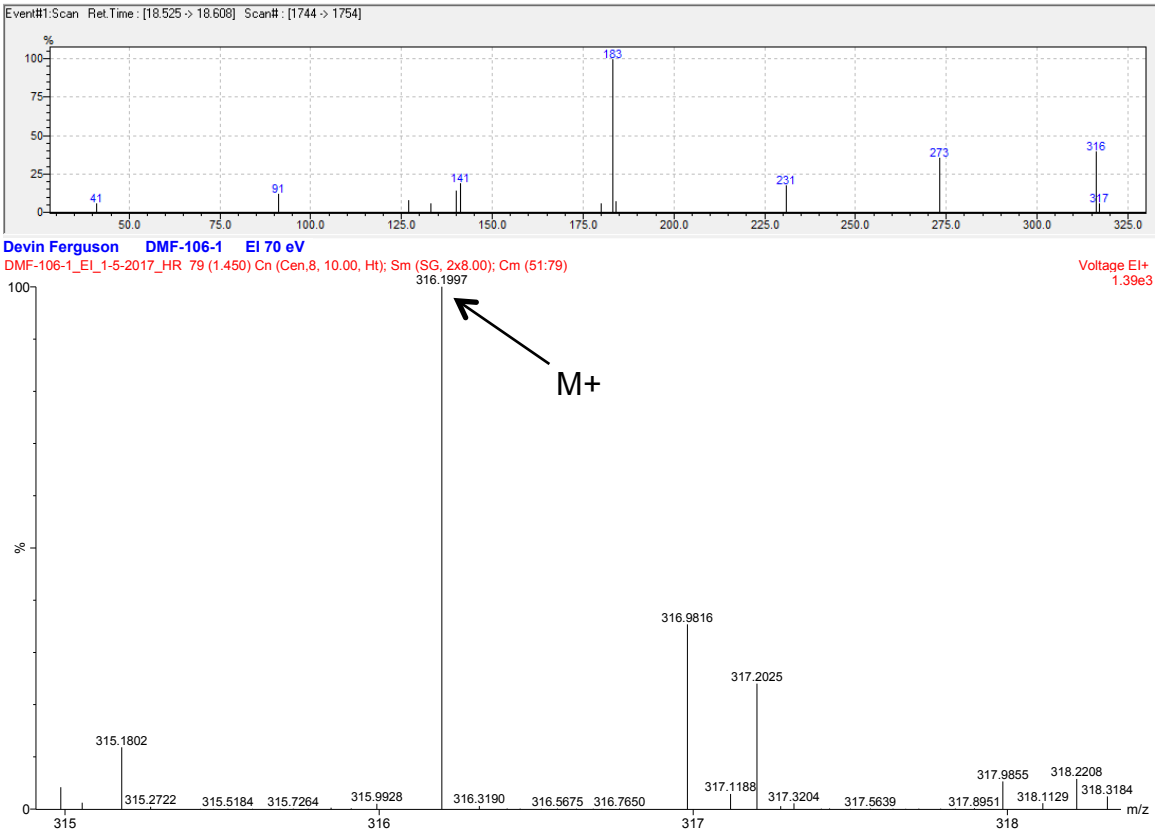
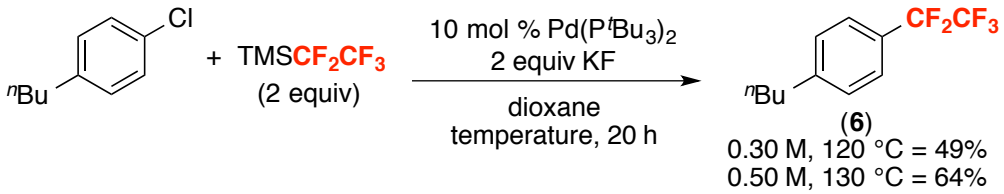


Figure S17. (Top) Mass spectrum of diaryldifluoromethane side product **5**. (Bottom) High resolution mass spectrum of diaryldifluoromethane side product **5**.

f. Other potential challenges for Pd(P^tBu_3)$_2$-catalyzed aryl trifluoromethylation

Although side reactions that derive from α-F elimination appear to be a significant challenge to developing a Pd(P^tBu_3)$_2$-catalyzed aryl trifluoromethylation method, other challenges may also be important. For instance, it has been noted that CF_3^- equivalents can readily displace phosphine ligands on Pd to form catalytically inactive $Pd(CF_3)_n$ species.[5b,6] We did not observe any evidence for these species by ^{19}F NMR spectroscopy; however, their stability under our reaction conditions is unknown. Additionally, transmetallation of CF_3^- onto Pd may be a significant challenge, and this has not been thoroughly investigated. It is not immediately clear why such high reaction temperatures are required for catalytic aryl trifluoromethylation. Both oxidative addition and reductive elimination are known to occur at much lower temperatures (≤80 °C) than the temperature required for catalysis (120 °C).[7] This may be due to a challenging transmetallation step, or the need to speed up the catalytic reaction to avoid problems with competing decomposition of the CF_3 source (e.g. CF_3^- formation). Our efforts in optimizing the Pd(P^tBu_3)$_2$-catalyzed aryl trifluoromethylation allude to transmetallation being a challenge under some conditions (see Table S5 above). For example, attempts to change reaction conditions to increase or decrease the amount "CF_3^-" equivalents available for transmetallation (e.g. base activator, CF_3 source, solvent, concentration, etc.) proved deleterious to the reaction. Additionally, as shown on p. S24, background decomposition of the CF_3 source could be a challenge under some conditions. Potentially, another way to address the challenge that is $Pd^{0/II}$-catalyzed aryl trifluoromethylation is to identify a CF_3 source that is highly reactive towards transmetallation, yet stable to unproductive decomposition.

ii. Pentafluoroethylation of 1-butyl-4-chlorobenzene



Optimization of temperature and concentration resulted in an increase in yield.

In the glovebox, a 4 mL scintillation vial was charged with Pd(P^tBu_3)$_2$ (8.9 mg, 0.017 mmol, 0.10 equiv), KF (20.2 mg, 0.348 mmol, 2.00 equiv), 1-butyl-4-chlorobenzene (29.3 mg, 0.174 mmol, 1.00 equiv) as a solution in 1,4-dioxane (0.35 mL, 0.50 M), and $TMSCF_2CF_3$ (60 µL, 0.35 mmol, 2.0 equiv). The vial was sealed with a Teflon-lined screw cap, removed from the glovebox, placed on an aluminum heating block preheated to 120 °C, and the reaction was allowed to stir

vigorously for 20 h. The reaction was then allowed to cool to room temperature, opened to air, and diluted with 1.5 mL THF. (Trifluoromethoxy)benzene (0.20 mL, 0.87 M solution in THF, 1.0 equiv) was added as internal standard, and a ^{19}F NMR spectrum was acquired using a 5 s relaxation delay. The yield of **6** was obtained by ^{19}F NMR spectroscopy. This product was also confirmed by GC-MS.

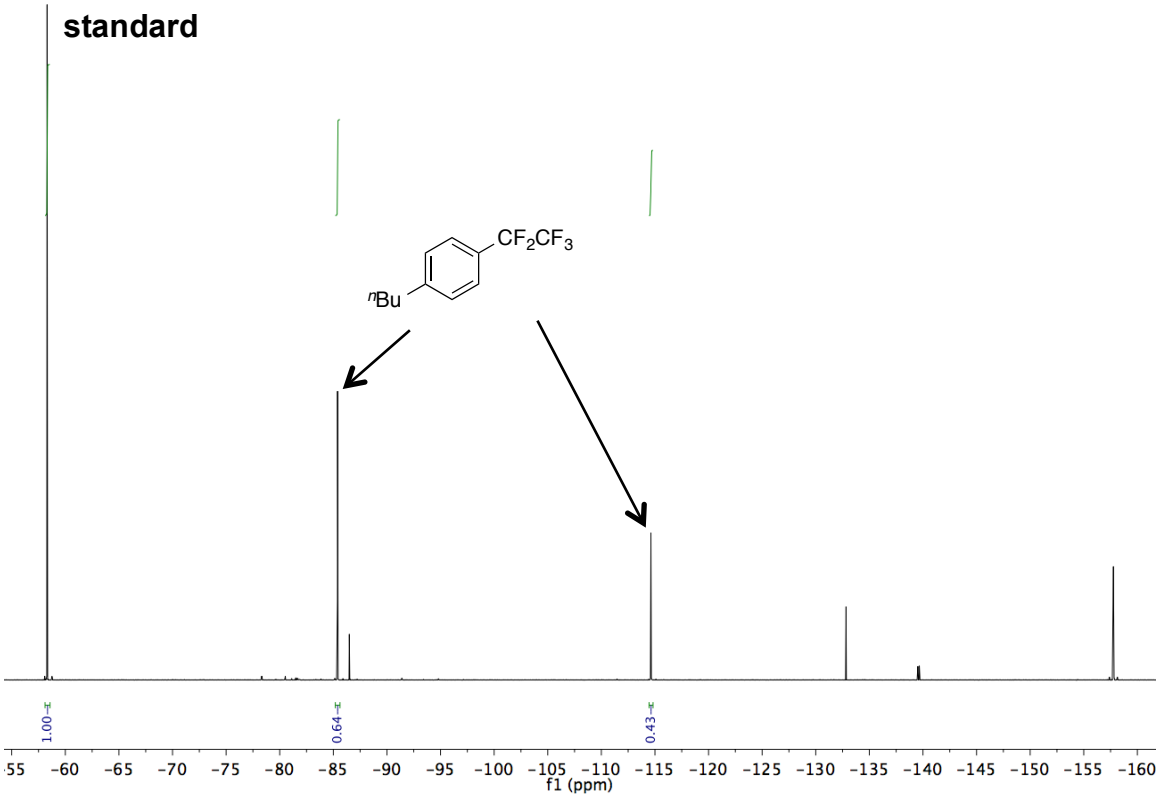
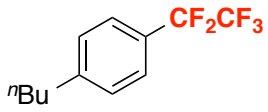


Figure S18. ^{19}F NMR spectrum of crude reaction mixture.



(**6**)

Exact Mass = 252.0937

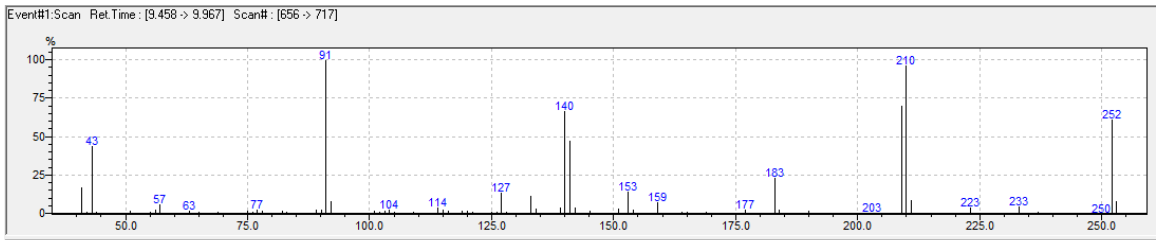
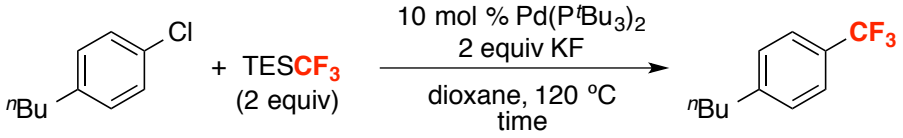


Figure S19. Mass spectrum of product **6**.

a. Comparison of trifluoromethylation and pentafluoroethylation of 1-butyl-4-chlorobenzene

In an attempt to gain insight into the success of pentafluoroethylation under catalytic conditions, we compared the catalytic trifluoromethylation and pentafluoroethylation of 1-butyl-4-chlorobenzene. Under catalytic trifluoromethylation conditions, aryl halide remains (as determined by GC-MS) after 20 h and $TESCF_3$ is fully consumed (as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture). When the reaction time is cut in half (11 h), we observe the same amount of product (22%), but 52% of the $TESCF_3$ remains (Figure S20). This suggests that, under these conditions, the reaction does not stop due to consumption of $TESCF_3$. Instead, it appears that the trifluoromethylation reaction is impeded by catalyst deactivation. In contrast, under catalytic pentafluoroethylation conditions, $TMSCF_2CF_3$ is fully consumed after 8 h. This observation suggests that $TESCF_3$ is more stable than $TMSCF_2CF_3$ under catalytic conditions.



20 h: 22% yield, no $TESCF_3$
11 h: 22% yield, 52% $TESCF_3$

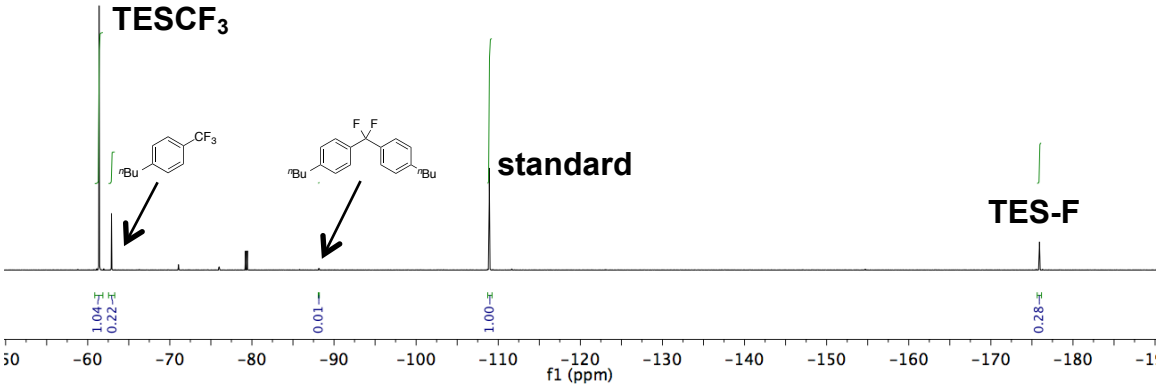
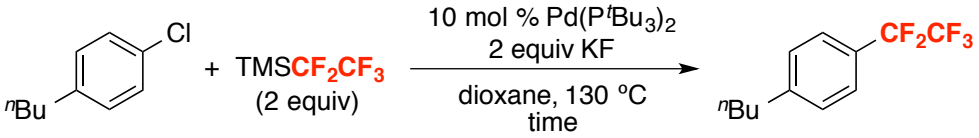


Figure S20. Effect of time on catalytic trifluoromethylation and ^{19}F NMR spectrum of crude reaction mixture for aryl trifluoromethylation after 11 h.

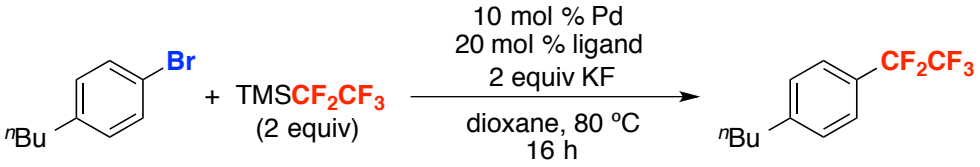


16 h: 64% yield, no $TMSCF_2CF_3$
8 h: 66% yield, no $TMSCF_2CF_3$

Figure S21. Effect of time on catalytic aryl pentafluoroethylation.

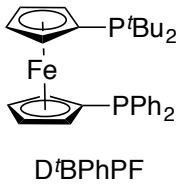
iii. Pentafluoroethylation of aryl bromides

a. Optimization of Pd source and ligand

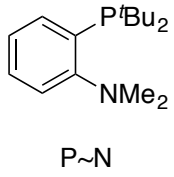


Pd Source	Ligand	Yield Ar–CF_2CF_3 (%)
$Pd(P^tBu_3)_2$	-	85
$Pd[P(o\text{-tol})_3]_2$	-	1
$Pd(dba)_2$	P^tBu_3	26
$Pd(dba)_2$	$P(o\text{-tol})_3$	nd
$Pd(dba)_2$	PCy_3	nd
$Pd(dba)_2$	D^tBPhPF	1
$Pd(dba)_2$	P~N[a]	nd
$Pd(dba)_2$	IPr*OMe[a]	nd
$Pd(dba)_2$	BrettPhos[a]	4

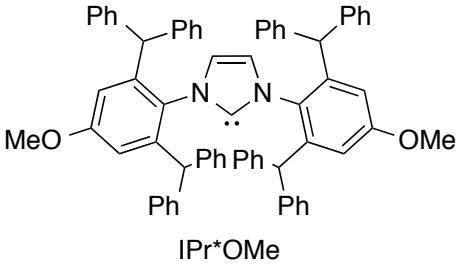
[a]15 mol % ligand



D^tBPhPF



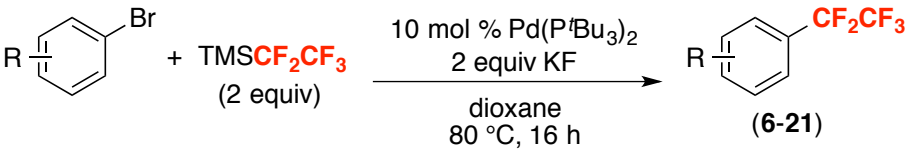
P~N



IPr*OMe

Table S7. Optimization of Pd source and ligand for the Pd-catalyzed pentafluoroethylation of aryl bromides.

b. General procedure for $Pd(P^tBu_3)_2$-catalyzed aryl pentafluoroethylation



(**6-21**)

Procedure A: For solid aryl bromides

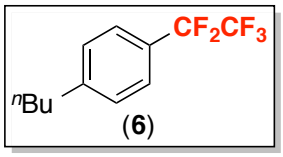
In a glovebox, a 4 mL scintillation vial was charged with $Pd(P^tBu_3)_2$ (8.9 mg, 0.017 mmol, 0.10 equiv), aryl bromide (0.174 mmol, 1.00 equiv), KF (20.2 mg, 0.348 mmol, 2.00 equiv), 1,4-dioxane (0.35 mL, 0.50 M), and $TMSCF_2CF_3$ (60 µL, 0.35 mmol, 2.0 equiv). The vial was sealed with a Teflon-lined screw cap, removed from the glovebox, placed on an aluminum heating block preheated to 120 °C, and the reaction was allowed to stir vigorously for 16 h. The reaction was allowed to cool to room temperature, opened to air, and diluted with 1.5 mL Et_2O.

Benzotrifluoride (21 μL, 0.17 mmol, 1.0 equiv) was added as an internal standard, and a ^{19}F NMR yield was obtained using a 5 s relaxation delay. The NMR sample was combined with the reaction mixture, and the reaction mixture was filtered through a plug of celite, eluting with Et_2O (3 mL). The resulting solution was concentrated, and the crude product was purified by silica gel chromatography.

Procedure B: For liquid aryl bromides

In the glovebox, a 4 mL scintillation vial was charged with $Pd(P^tBu_3)_2$ (8.9 mg, 0.017 mmol, 0.10 equiv) and KF (20.2 mg, 0.348 mmol, 2.00 equiv). A separate 4 mL scintillation vial was charged with the appropriate aryl bromide (0.174 mmol, 1.00 equiv), and the substrate was transferred to the vial containing $Pd(P^tBu_3)_2$ and KF using 1,4-dioxane (0.35 mL, 0.50 M). Finally, $TMSCF_2CF_3$ (60 μL, 0.35 mmol, 2.0 equiv) was added. The vial was sealed with a Teflon-lined screw cap, removed from the glovebox, placed on an aluminum heating block preheated to 120 °C, and the reaction was allowed to stir vigorously for 16 h. The reaction was allowed to cool to room temperature, opened to air, and diluted with Et_2O (1.5 mL). Benzotrifluoride (21 μL, 0.17 mmol, 1.0 equiv) was added as internal standard, and a ^{19}F NMR yield was obtained using a 5 s relaxation delay. The NMR sample was combined with the reaction mixture, and the reaction mixture was filtered through a plug of celite, eluting with Et_2O (3 mL). The resulting solution was concentrated, and the crude product was purified by silica gel chromatography.

c. Data



(**6**)

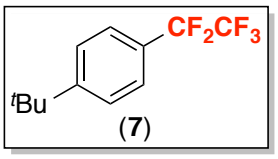
Procedure B was followed. Column chromatography using 100% pentane (R_F = 0.73) afforded **6** as a colorless oil (32 mg, 73% yield). ^{19}F NMR yield: 85%. Spectral data were consistent with those reported in the literature.[8]

^{1}H NMR (499.91 MHz, $CDCl_3$, 23 °C): δ 7.49 (d, J_{HH} = 7.9 Hz, 2H), 7.30 (d, J_{HH} = 7.9 Hz, 2H), 2.67 (t, J_{HH} = 7.7 Hz, 2H), 1.65-1.59 (m, 2H), 1.41-1.33 (m, 2H), 0.94 (t, J_{HH} = 7.3 Hz, 3H).

^{19}F NMR (470.47 MHz, $CDCl_3$, 23 °C): δ –84.88 (s, 3F), –114.53 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 147.32 (t, J_{CF} = 1.6 Hz), 128.86, 126.47 (t, J_{CF}= 6.3 Hz), 126.13 (t, J_{CF} = 24.1 Hz), 35.64, 33.44, 22.46, 14.04. The peaks corresponding to the CF_2CF_3 group were poorly resolved and are in the region of 122-108 ppm.

HRMS calcd. for $C_{12}H_{13}F_5$: 252.0937; Found: 252.0929



(**7**)

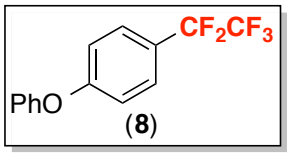
Procedure B was followed. Column chromatography using 100% pentane (R_F = 0.77) afforded **7** as a colorless oil (29 mg, 66% yield). ^{19}F NMR yield: 82%. Spectral data were consistent with those reported in the literature.[9]

^{1}H NMR (499.91 MHz, $CDCl_3$, 23 °C): δ 7.53-7.49 (multiple peaks, 4H), 1.35 (s, 9H).

^{19}F NMR (470.47 MHz, $CDCl_3$, 23 °C): δ –84.84 (s, 3F), –114.56 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 155.43 (t, J_{CF} = 1.3 Hz), 126.32 (t, J_{CF} = 6.3 Hz), 125.81, 35.10, 31.28. The peaks corresponding to the CF_2CF_3 group were poorly resolved and are in the region of 122-108 ppm. A peak corresponding to an aromatic carbon appears to be overlapping with the peak at 125.81.

HRMS calcd. for $C_{12}H_{13}F_5$: 252.0937; Found: 252.0928



(**8**)

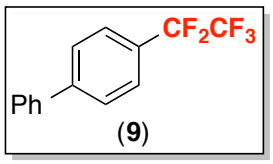
Procedure B was followed. Column chromatography using 100% pentane (R_F = 0.50) afforded **8** as a colorless oil (36 mg, 72% yield). ^{19}F NMR yield: 77%.

^{1}H NMR (499.91 MHz, $CDCl_3$, 23 °C): δ 7.54 (d, J_{HH} = 8.5 Hz, 2H), 7.42-7.39 (m, 2H), 7.20 (tt, J_{HH} = 7.5, 1.2 Hz, 1H), 7.07 (t, J_{HH} = 8.0 Hz, 4H).

^{19}F NMR (470.47 MHz, $CDCl_3$, 23 °C): δ –84.91 (s, 3F), –114.05 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 160.97 (t, J_{CF} = 1.5 Hz), 155.68, 130.23, 128.42 (t, J_{CF} = 6.3 Hz), 124.76, 122.79 (t, J_{CF} = 24.5 Hz), 120.23, 117.89. The peaks corresponding to the CF_2CF_3 group were poorly resolved and are in the region of 122-108 ppm.

HRMS calcd. for $C_{14}H_9F_5O$: 288.0574; Found: 288.0562



(**9**)

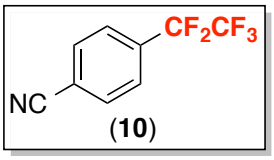
Procedure A was followed. Column chromatography using 100% pentane (R_F = 0.57) afforded **9** as a white solid (36 mg, 76% yield). ^{19}F NMR yield: 85%. Spectral data were consistent with those reported in the literature.[10]

^{1}H NMR (499.91 MHz, $CDCl_3$, 23 °C): δ 7.71 (d, J_{HH} = 8.3 Hz, 2H), 7.67 (d, J_{HH} = 8.3 Hz, 2H), 7.62-7.60 (m, 2H), 7.50-7.47 (m, 2H), 7.43-7.40 (m, 1H).

^{19}F NMR (470.47 MHz, $CDCl_3$, 23 °C): δ –84.73 (s, 3F), –114.70 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 145.02 (t, J_{CF} = 1.7 Hz), 139.83, 129.14, 128.38, 127.56, 127.44, 127.05 (t, J_{CF} = 6.3 Hz). The peaks corresponding to the CF_2CF_3 group were poorly resolved and are in the region of 122-108 ppm. A peak corresponding to an aromatic carbon appears to be overlapping with the peak at 127.44.

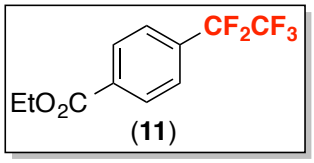
HRMS calcd. for $C_{14}H_9F_5$: 272.0624; Found: 272.0627



(**10**)

Procedure A was followed. ^{19}F NMR yield: 41%. Spectral data were consistent with those reported in the literature (^{19}F NMR: –85.64 (s, 3F), –116.42 (s, 2F)).[11]

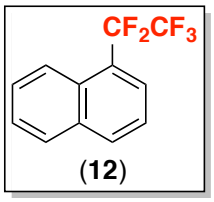
HRMS calcd. for $C_9H_4F_5N$: 221.0264; Found: 221.0262



(**11**)

Procedure B was followed. ^{19}F NMR yield: 56%. Spectral data were consistent with those reported in the literature (^{19}F NMR: –85.91 (s, 3F), –116.17 (s, 2F)).[11]

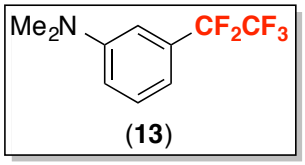
HRMS calcd. for $C_{11}H_9F_5O_2$: 268.0523; Found: 268.0530



(**12**)

Procedure B was followed. ^{19}F NMR yield: 67%. Spectral data were consistent with those reported in the literature (^{19}F NMR: –84.36 (s, 3F), –108.88 (s, 2F)).[11]

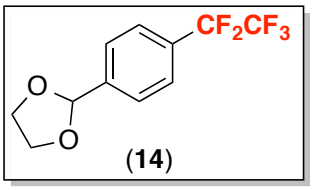
HRMS calcd. for $C_{12}H_7F_5$: 246.0468; Found: 246.0461



(**13**)

Procedure B was followed. ^{19}F NMR yield: 77%. Spectral data were consistent with those reported in the literature (^{19}F NMR: –85.64 (s, 3F), –115.46 (s, 2F)).[12]

HRMS calcd. for $C_{10}H_{10}F_5N$ $[M+H]^+$: 240.0806; Found: 240.0809



(**14**)

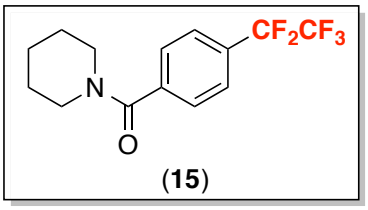
Procedure B was followed. Column chromatography using 4:1 hexane:ethyl acetate (R_F = 0.43, 2:1 hexanes:ethyl acetate) afforded **14** as a colorless oil (33 mg, 70% yield). ^{19}F NMR yield: 87%.

^{1}H NMR (699.75 MHz, $CDCl_3$, 23 °C): δ 7.68-7.60 (multiple peaks, 4H), 5.87 (s, 1H), 4.18 – 3.98 (multiple peaks, 4H).

^{19}F NMR (376.87 MHz, $CDCl_3$, 23 °C): -84.61 (s, 3F), -114.99 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 142.03 (t, J_{CF}= 1.7 Hz), 129.38 (t, J_{CF}= 23.9 Hz), 128.35 , 126.57 (t, J_{CF}=5.7 hz), 118.97 (qt, J = 285.9, 39.3 Hz) ,113.29 (tq, J_{CF} = 253.44, 38.4 Hz). 102.72 , 65.40.

HRMS calcd. for $C_{11}H_9F_2O_2$: 268.0523; Found: 268.0511



(**15**)

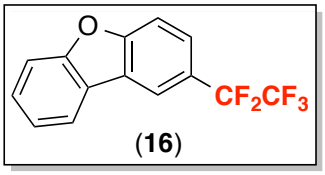
Procedure A was followed. Column chromatography using 9:1 hexane:ethyl acetate (R_F = 0.25, 4:1 hexanes:ethyl acetate) afforded **15** as a colorless oil (42 mg, 80% yield). ^{19}F NMR yield: 85%.

^{1}H NMR (699.75 MHz, $CDCl_3$, 23 °C): δ 7.64 (d, J_{HH}= 8.1 Hz, 2H), 7.51 (d, J_{HH}= 8.1 Hz, 2H), 3.72 (bs, 2H), 3.30 (bs,1H), 1.87 – 1.61 (overlapping peaks, 4H), 1.51 (bs, 2H).

^{19}F NMR (376.87 MHz, $CDCl_3$, 23 °C): -84.74 (s, 3F), -115.12 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 168.70, 140.21,129.53 (t, J_{CF}= 24.1 Hz), 126.77 (t, J_{CF}= 6.3 Hz), 118.86 (qt, J_{CF}= 286.0, 38.7 Hz),113.13 (tq, J_{CF}= 255.5 38.7 Hz), 48.66 , 43.12 , 26.53 , 25.52 , 24.46.

HRMS calcd. for $C_{14}H_{14}F_5NO$: 308.1068; Found: 308.1071



(**16**)

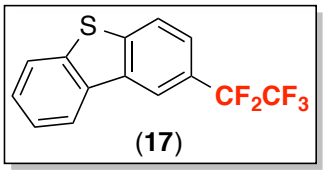
Procedure A was followed. Column chromatography using 100% hexane (R_F = 0.54) afforded **16** as a white solid (29 mg, 58% yield). ^{19}F NMR yield: 68%.

^{1}H NMR (699.75 MHz, $CDCl_3$, 23 °C): δ 8.20 (d, J_{HH} = 1.8 Hz, 1H), 8.01 (d, J_{HH} = 7.7 Hz, 1H), 7.72-7.66 (multiple peaks, 2H), 7.62 (d, J = 8.3, Hz, 1H), 7.53 (dd, J_{HH} = 8.3, 7.4 Hz, 1H), 7.41 (t, J_{HH} = 7.4 Hz, 1H).

^{19}F NMR (376.87 MHz, $CDCl_3$, 23 °C): δ –84.72 (s, 3F), –113.08 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 157.78 (t, J_{CF} = 1.8 Hz), 156.78, 128.23, 125.25 (t, J_{CF} = 6.3 Hz), 124.72, 123.37, 123.22, 123.17, 120.95, 120.02 (qt, J_{CF} = 285.3, 40.0 Hz), 119.50 (t, J_{CF} = 6.7 Hz), 113.80 (qt, J_{CF} = 285.3, 38.2 Hz), 112.06 , 111.95 .

HRMS calcd. for $C_{14}H_7OF_5$: 286.0417; Found: 286.0410



(**17**)

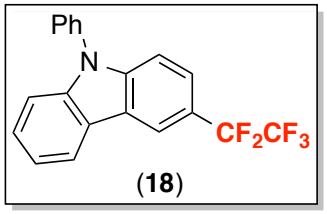
Procedure A was followed. Column chromatography using 100% hexane (R_F = 0.65) afforded **17** as a white solid (33 mg, 62% yield). ^{19}F NMR yield: 68%.

^{1}H NMR (699.75 MHz, $CDCl_3$, 23 °C): δ 8.37 (s, 1H), 8.22 (d, J_{HH} = 8.4 Hz, 1H), 7.96 (d, J_{HH} = 8.4 Hz, 1H), 7.88 (d, J_{HH} = 6.7, 1H), 7.66 (d, J_{HH} = 8.4 Hz, 1H), 7.56-7.49 (multiple peaks, 2H).

^{19}F NMR (376.87 MHz, $CDCl_3$, 23 °C): δ –84.64 (s, 3F), –113.77 (s, 2F)

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 143.18, 139.79, 135.62, 134.62, 127.63, 126.67, 124.89, 123.98 (t, J_{CF} = 6.2 Hz), 123.18, 122.91, 121.90, 119.80 (t, J_{CF} = 6.8 Hz), 118.40 (qt, J_{CF} =254.4, 39.4 Hz), 113.81 (qt, J_{CF} =254.4, 38.0 Hz).

HRMS calcd. for $C_{14}H_7F_5S$: 302.0189; Found: 302.0193



(**18**)

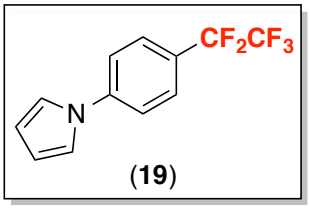
Procedure A was followed. Column chromatography using 100% hexane (R_F = 0.39) afforded **18** as a colorless oil (33 mg, 53% yield). ^{19}F NMR yield: 67%. Spectral data were consistent with those reported in the literature.[13]

^{1}H NMR (699.75 MHz, $CDCl_3$, 23 °C): δ 8.39 (s, 1H), 8.20 (d, J_{HH} = 7.7 Hz, 1H), 7.64 (t, J = 7.7 Hz, 2H), 7.60 (dd, J_{HH} = 8.7, 1.8 Hz, 1H), 7.57-7.54 (multiple peaks, 3H), 7.52 (td, J_{HH} = 7.4, 1.3 Hz, 1H), 7.49-7.45 (m, 2H), 7.42 (d, J_{HH} = 8.2 Hz, 1H), 7.36 (t, J_{HH} = 7.4 Hz, 1H).

^{19}F NMR (376.87 MHz, $CDCl_3$, 23 °C): δ –84.70 (s, 3F), –112.54 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 142.47, 141.60, 136.91, 130.07, 128.10, 127.14, 126.92, 123.71 (t, J_{CF} = 6.3 Hz), 123.18, 122.71, 120.75, 120.56, 119.85 (t, J_{CF} = 24.5 Hz), 119.13 (t, J_{CF} = 6.7 Hz), 110.18, 109.91. The peaks corresponding to the CF_2CF_3 group were poorly resolved and are in the region of 122-108 ppm.

HRMS calcd. for $C_{20}H_{12}NF_5$: 361.0890; Found: 361.0890



(**19**)

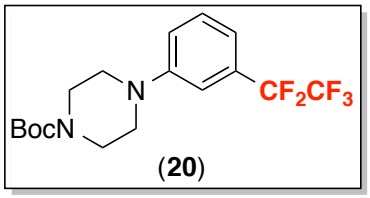
Procedure B was followed. Column chromatography using 9:1 hexane:ethyl acetate (R_F = 0.79, 4:1 hexane:ethyl acetate) afforded **19** as a microcrystalline white powder (32 mg, 68% yield). ^{19}F NMR yield: 76%.

^{1}H NMR (699.75 MHz, $CDCl_3$, 23 °C): δ 7.66 (d, J_{HH} = 8.5 Hz, 2H), 7.51 (d, J_{HH}= 8.5 Hz, 2H), 7.15 (t, J_{HH}= 2.2 Hz, 2H), 6.40 (t, J_{HH}= 2.2 Hz, 2H).

^{19}F NMR (376.87 MHz, $CDCl_3$, 23 °C): -84.78 (s, 3F), -112.62 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 143.34, 128.05 (t, J = 6.3 Hz), 125.37 (t, J = 24.5 Hz), 119.94 , 119.29 (qt, J_{CF}= 289.3 Hz, 39.6 Hz)119.05 , 113.24 (tq, J_{CF}= 248.2, 39.6 Hz) 111.55.

HRMS calcd. for $C_{12}H_8F_5N$: 261.0577; Found: 261.0580



(**20**)

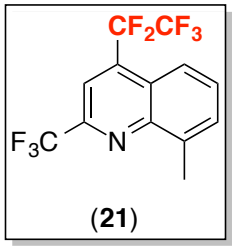
Procedure A was followed. Column chromatography using 20:1 hexane:ethyl acetate (R_F = 0.51, 4:1 hexane:ethyl acetate) afforded **20** as a colorless oil (51 mg, 77% yield). ^{19}F NMR yield: 84%.

^{1}H NMR (699.75 MHz, $CDCl_3$, 23 °C): δ 7.38 (app t, J_{HH}= 7.0 Hz, 2H), 7.15-7.01 (multiple peaks, 3H), 3.59 (t, J_{HH}= 5.2 Hz, 4H), 3.18 (bs, 4H), 1.48 (s, 9H).

^{19}F NMR (376.87 MHz, $CDCl_3$, 23 °C): -84.71 (s, 3F), -114.85 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 154.61, 151.35 , 129.58 (t, J_{CF} = 6.2 Hz), 119.41 (t, J_{CF}= 7.2 Hz), 118.95 (qt, J_{CF} = 285.9, 39.7 Hz) 117.66 (t, J_{CF}= 6.3 Hz), 113.88 (t, J-7.0 Hz), 113.43 (tq, , 254.3, 39.7), 80.04 , 48.91 , 43.88, 42.89, 28.39.

HRMS calcd. for $C_{17}H_{21}F_5N_2O_2$ [M+H]: 381.1596; Found: 381.1597



(**21**)

Procedure A was followed. Column chromatography using 9:1 hexane:ethyl acetate (R_F = 0.83, 4:1 hexane:ethyl acetate) afforded **21** as a colorless oil (41 mg, 70% yield). ^{19}F NMR yield: 77%.

^{1}H NMR (699.75 MHz, $CDCl_3$, 23 °C): δ 8.10 (d, J_{HH} = 8.7 Hz, 1H), 7.98 (s, 1H), 7.76 (d, J_{HH} = 7.0 Hz, 1H), 7.69 (dd, J_{HH} = 8.7, 7.0 Hz, 1H), 2.88 (s, 3H).

^{19}F NMR (376.87 MHz, $CDCl_3$, 23 °C): -67.60 (s, 3F), -83.07 (s, 3F) , -110.36 (s, 2F).

^{13}C NMR (175.97 MHz, $CDCl_3$, 23 °C): δ 147.38, 145.82 (q, J_{CF}= 35.8 Hz), 139.73, 135.29 (t, J_{CF}= 23.0 Hz), 131.37 , 130.13 , 124.89 , 122.04 (d, J_{CF}= 57.5 Hz), 122.21-112.22 (multiple peaks, 3C) 116.12 , 18.33.

HRMS calcd. for $C_{13}H_7F_8N$ [M+H]: 330.0524; Found: 330.0526

d. Comparison of Pd(P^tBu_3)$_2$ catalyzed pentafluoroethylation of aryl bromides with copper mediated pentafluoroethylation of aryl bromides

Currently, there are no copper-catalyzed methods for the pentafluoroethylation of aryl bromides. There is one copper-catalyzed method for the pentafluoroethylation of aryl iodides that employs $(DMPU)_2Zn(CF_2CF_3)_2$ as the pentafluoroethyl source[14] A few methods have also been developed that use stoichiometric Cu–CF_2CF_3.[15] In general, the substrate scope for the copper mediated methods is broader than for our method developed with Pd(P^tBu_3)$_2$. A variety of heteroarenes with varying electronics and functional groups are tolerated. In contrast, the method developed with Pd(P^tBu_3)$_2$ shows modest tolerance with N-heteroarenes that are not N-protected or hindered around nitrogen. This is likely due to competing binding of the substrate to Pd, which generates catalytically inactive Pd species that are susceptible to unproductive reactivity. In addition, the copper-mediated methods generally show good reactivity with substrates bearing acidic protons and/or electrophilic carbonyl groups. The method developed with Pd(P^tBu_3)$_2$ shows modest tolerance of these substrates. We attribute this to the CF_2CF_3 source. Under our reaction conditions, it is likely that nucleophilic/basic $^-CF_2CF_3$ is generated, and this can deprotonate acidic protons or attack electrophilic carbon centers. The preformed Cu–CF_2CF_3 likely circumvents the generation of $^-CF_2CF_3$.

9. Computational Details

The calculations were conducted using Gaussian 09[16] at the M06[17] level of density functional theory for geometry optimization. Palladium was described by the Stuttgart/Dresden ECP (SDD),[18] and the other atoms were described by 6-31G(d) (basis set denoted BS1). The computations were carried out using benzene as the solvent employing the IEFPCM (SCRF) model. Energy refinements were performed by carrying out single point energy calculations at the B3LYP-D3 level of theory.[19] A larger basis set was employed that used the quadrupole-ξ valence polarized def2-QZVP basis set[20] on Pd along with the corresponding ECP and the 6-311+G(2d,p) basis set on the other atoms (basis set BS2).

*i. Gaussview and reaction profiles for isomerization and concerted reductive elimination for **1-CF$_3$** and **1-CF$_2$CF$_3$***

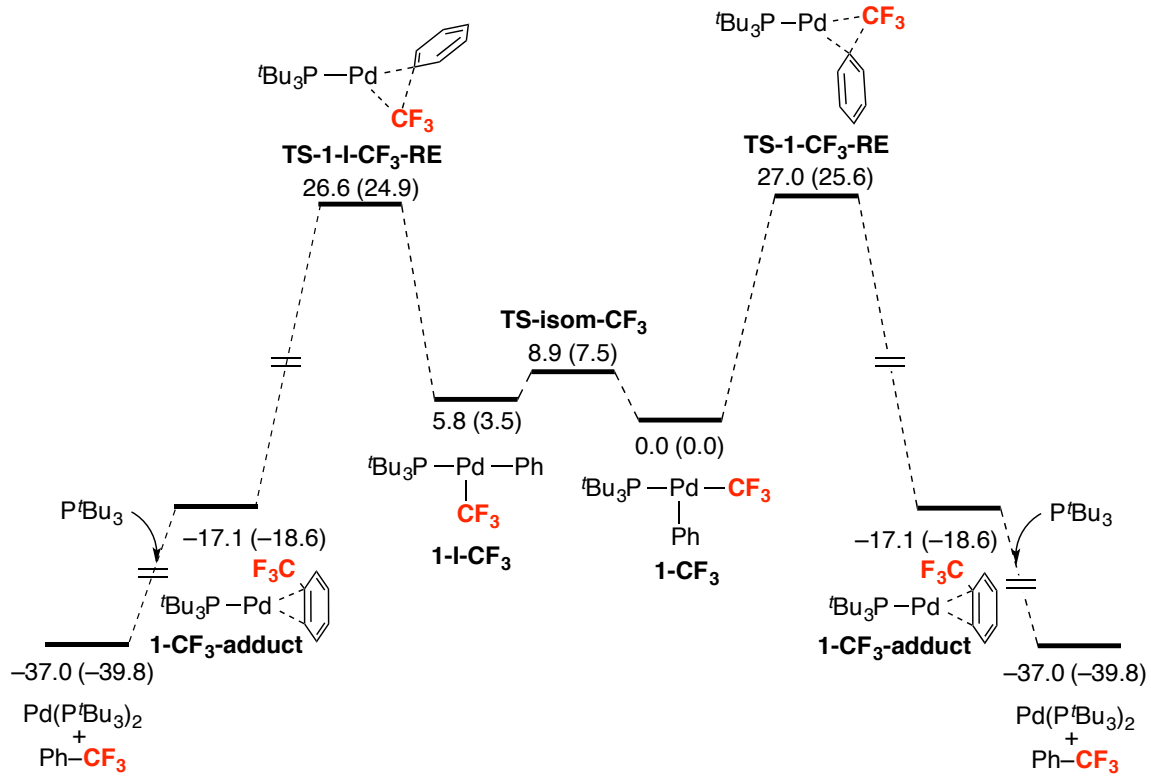


Figure S22. Isomerization and concerted reductive elimination profile for **1-CF$_3$**. Energies ΔG (ΔH) in kcal/mol.

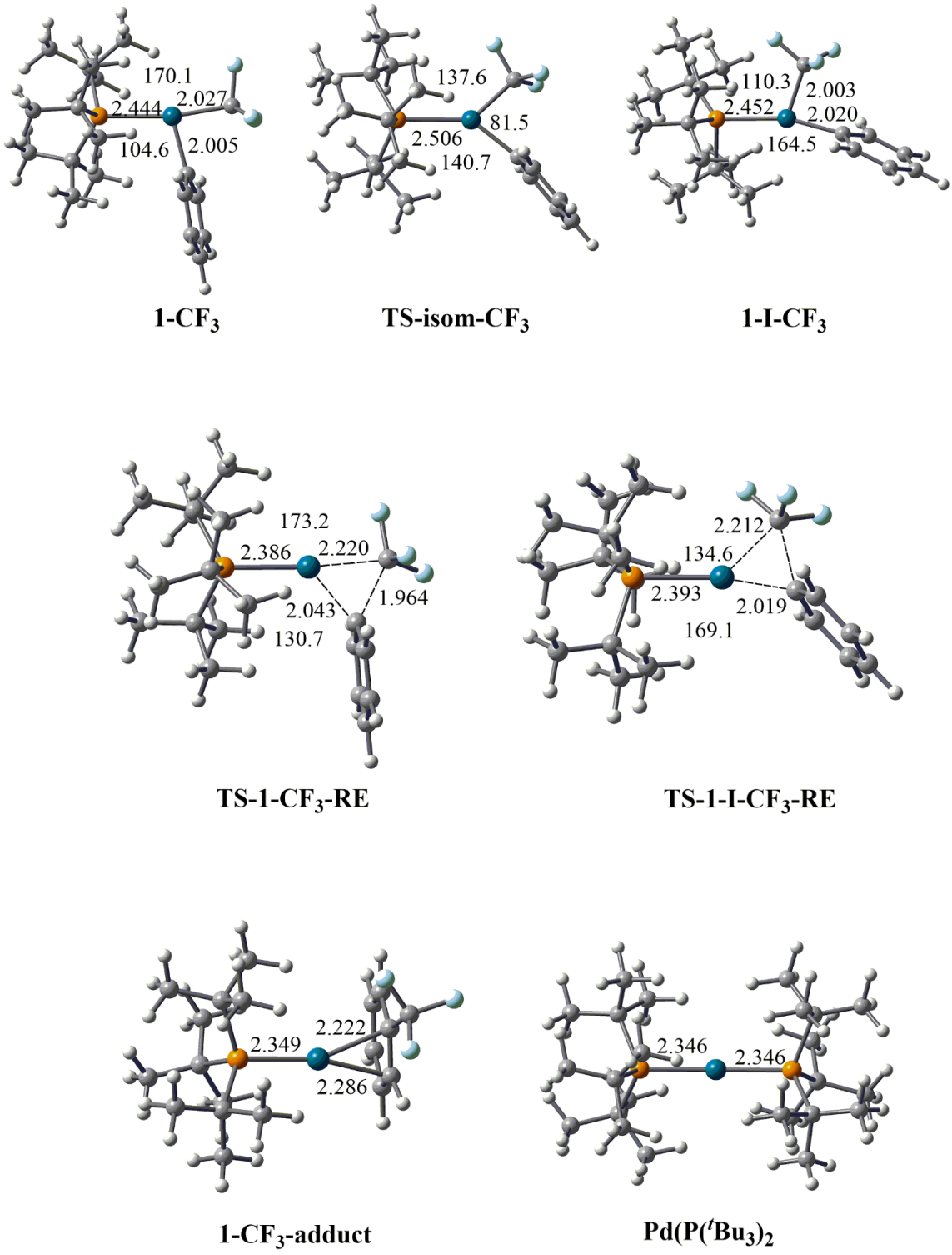


Figure S23. Gaussview diagrams for palladium-containing species in Figure S22 showing selected distances (Å) and angles (°).

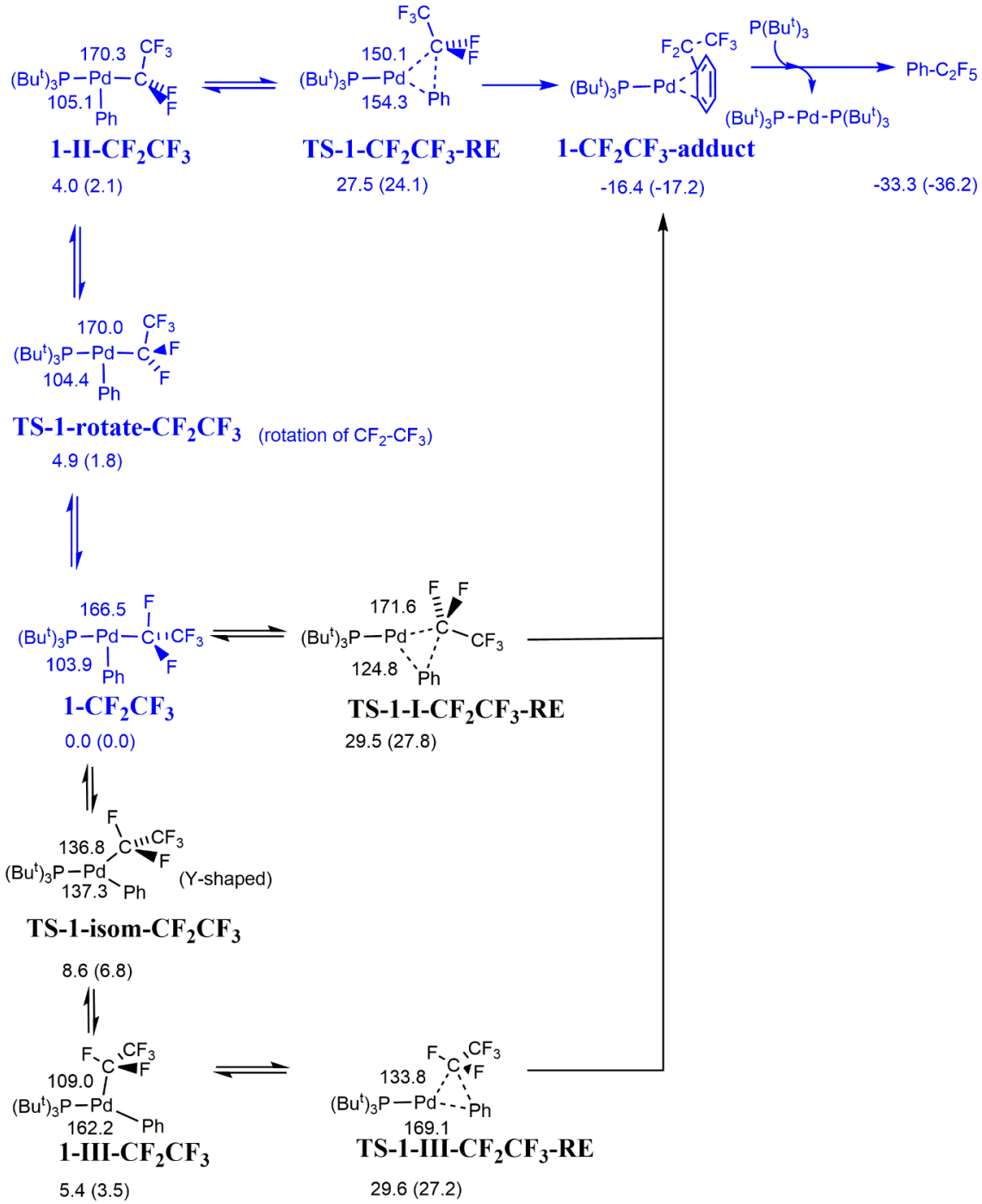


Figure S24. Equilibria and concerted reductive elimination profile for **1-CF_2CF_3**, illustrating conformational and isomerization processes between T-shaped isomers. Energies ΔG (ΔH) in kcal/mol.

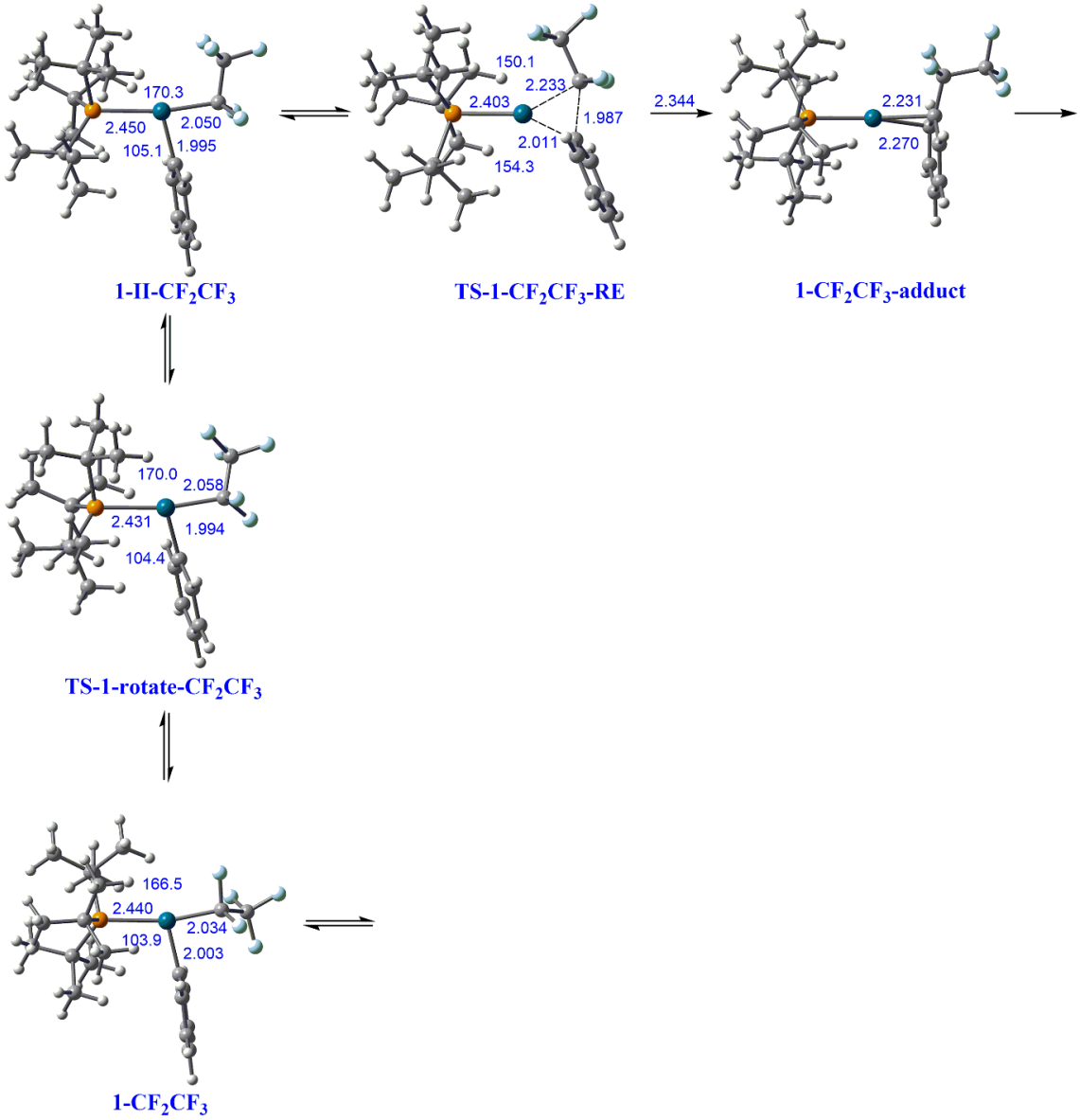


Figure S25. Gaussview diagrams for the low energy pathway for concerted reductive elimination from **1-CF_2CF_3** showing selected distances (Å) and angles (°).

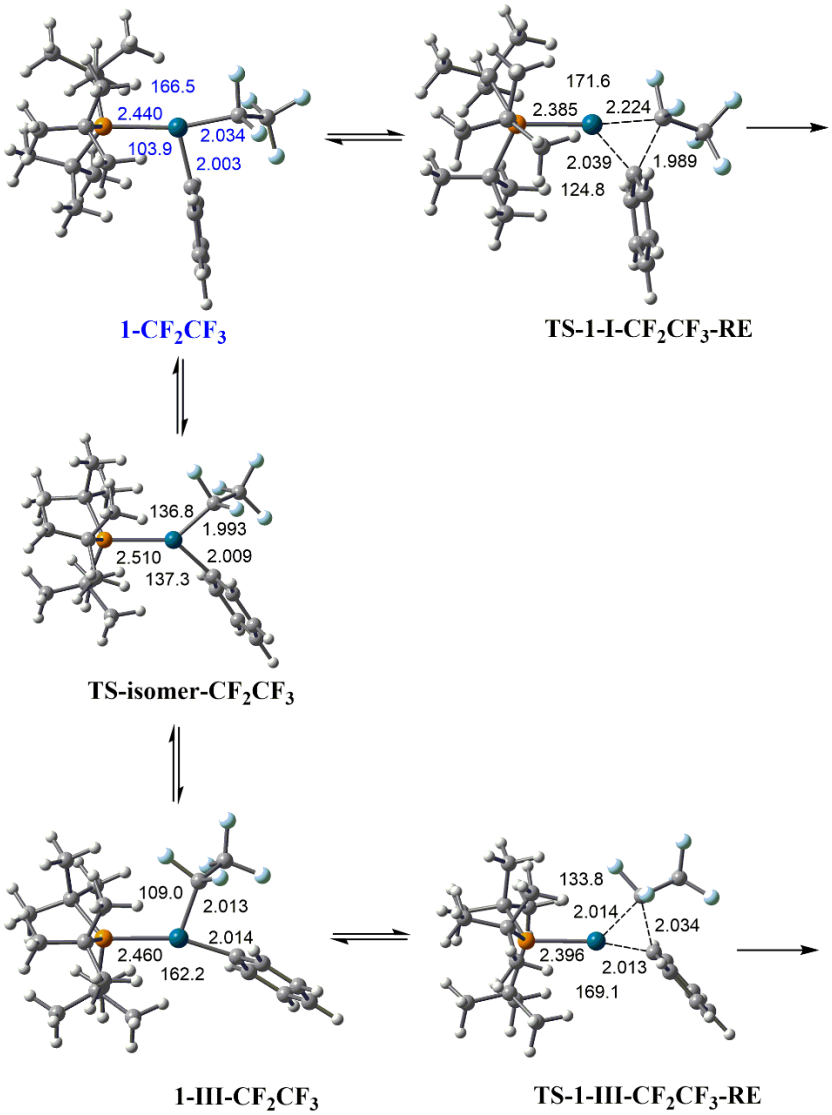
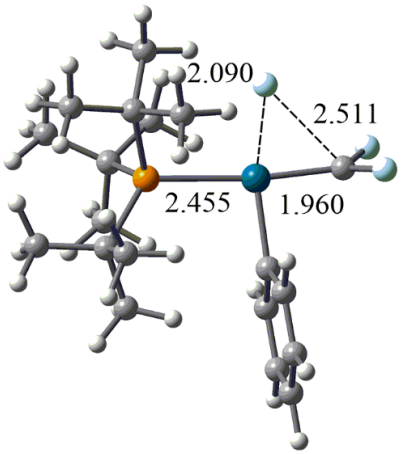
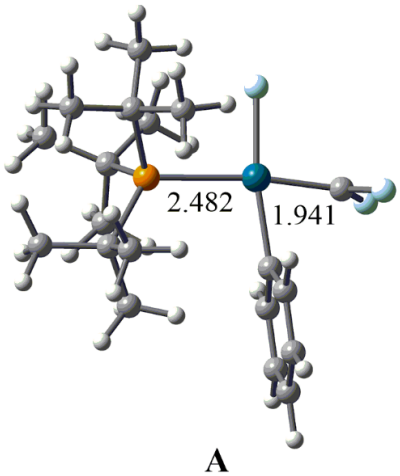


Figure S26. Gaussview diagrams for higher energy pathways for concerted reductive elimination from **1-CF_2CF_3** showing selected distances (Å) and angles (°).

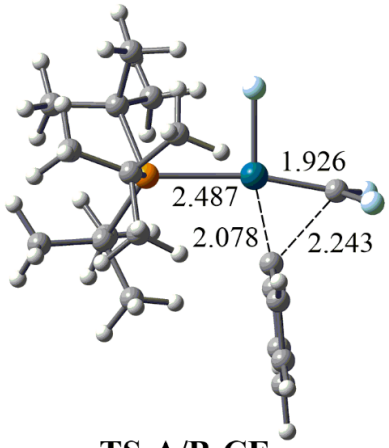
*ii. Gaussview for α-F elimination and reductive elimination for **1-CF_3** and **1-CF_2CF_3***



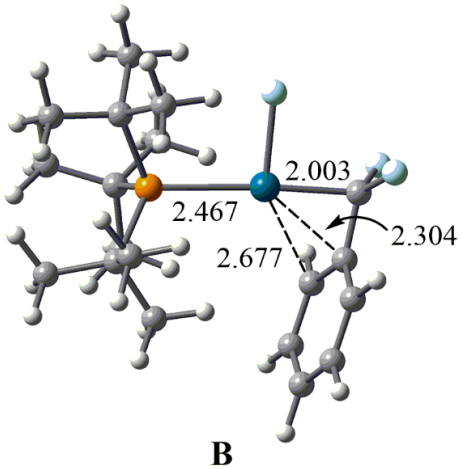
TS-1/A-CF_3



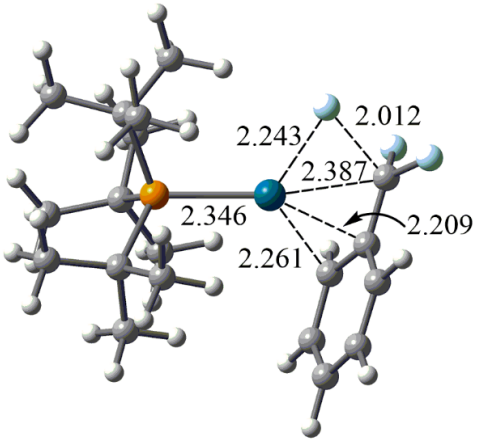
A



TS-A/B-CF_3

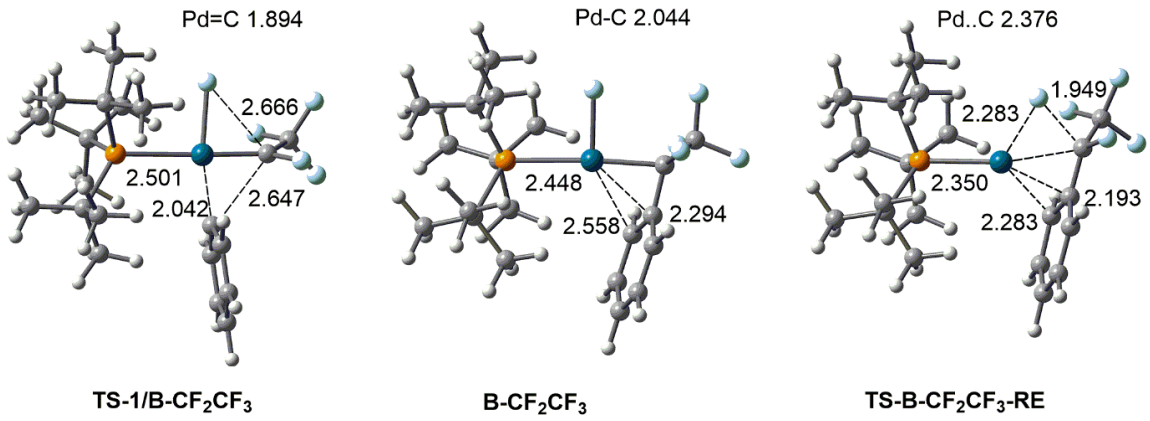


B



TS-B-CF_3-RE

Figure S27. Gaussview diagrams for α-F elimination with **1-CF_3**.



TS-1/B-CF_2CF_3 **B-CF_2CF_3** **TS-B-CF_2CF_3-RE**

Figure S28. Gaussview diagrams for α-F elimination with **1-CF_2CF_3**.

iii. Energies of calculated species and Cartesian coordinates

Figure S22 and direct reductive elimination in Figure 2

1-CF_3

```
 Zero-point correction=                           0.474091 (Hartree/Particle)
 Thermal correction to Energy=                    0.503643
 Thermal correction to Enthalpy=                  0.504587
 Thermal correction to Gibbs Free Energy=         0.415234
 Sum of electronic and zero-point Energies=          -1510.893740
 Sum of electronic and thermal Energies=             -1510.864189
 Sum of electronic and thermal Enthalpies=           -1510.863244
 Sum of electronic and thermal Free Energies=        -1510.952597
 E(RB3LYP) =  -1512.58028391

56
1-CF3
P     1.494309    0.169245    0.005265
C    -1.997237    0.692351   -0.017296
C    -2.510487    1.168006   -1.224614
C    -2.309063    1.348439    1.173273
C    -3.277505    2.332729   -1.244678
H    -2.312684    0.635461   -2.155075
C    -3.082179    2.509857    1.145305
H    -1.952518    0.965327    2.129173
C    -3.558620    3.011047   -0.062495
H    -3.663970    2.703488   -2.193837
H    -3.315635    3.019614    2.079896
H    -4.160628    3.918195   -0.080151
C    -2.392142   -2.008235   -0.042049
F    -3.166208   -1.970792   -1.147707
F    -3.237084   -1.906294    1.004905
F    -1.907247   -3.293501    0.010462
Pd   -0.724274   -0.856301   -0.030309
C     1.758372    1.869051   -0.832498
C     2.512464   -1.167082   -0.919588
C     2.100879    0.258186    1.823502
C     0.992925    0.920438    2.653576
H     0.761512    1.947504    2.357291
H     0.065050    0.335899    2.593020
H     1.309392    0.942807    3.707588
C     2.235169   -1.156626    2.399188
H     2.423891   -1.069042    3.479641
```

```
H     1.310229   -1.739061    2.282279
H     3.069407   -1.727099    1.976621
C     3.419313    0.999150    2.045102
H     3.695938    0.920798    3.107758
H     4.246824    0.577415    1.460793
H     3.346123    2.068806    1.814558
C     1.872340   -2.519482   -0.564808
H     2.372675   -3.317565   -1.134903
H     1.938744   -2.786486    0.493036
H     0.807422   -2.554115   -0.866725
C     2.328061   -1.013712   -2.432530
H     2.759883   -1.899412   -2.922368
H     1.268818   -0.965773   -2.720643
H     2.845810   -0.138859   -2.841306
C     4.011295   -1.203744   -0.625058
H     4.238670   -1.422812    0.424172
H     4.475985   -1.999597   -1.227675
H     4.509730   -0.262982   -0.890599
C     3.213033    2.208086   -1.160542
H     3.644378    1.525169   -1.903262
H     3.250041    3.218560   -1.596084
H     3.864128    2.208387   -0.278778
C     0.931636    1.912735   -2.123861
H     0.999187    2.928933   -2.541318
H     1.285266    1.224845   -2.895308
H    -0.127709    1.703920   -1.929055
C     1.174643    2.963235    0.067561
H     1.749990    3.117924    0.986780
H     1.195497    3.913054   -0.487283
H     0.125964    2.760007    0.330764
```

TS-1-CF_3-RE

```
 Zero-point correction=                           0.473928 (Hartree/Particle)
 Thermal correction to Energy=                    0.502711
 Thermal correction to Enthalpy=                  0.503655
 Thermal correction to Gibbs Free Energy=         0.416471
 Sum of electronic and zero-point Energies=         -1510.867452
 Sum of electronic and thermal Energies=            -1510.838669
 Sum of electronic and thermal Enthalpies=          -1510.837725
 Sum of electronic and thermal Free Energies=       -1510.924909
 E(RB3LYP) =  -1512.53857321

56
TS-1-CF3-RE
P     1.584880    0.073176    0.025506
C    -2.437341    0.294932   -0.025841
C    -2.794249    0.824426   -1.272390
C    -2.753817    0.988021    1.145084
C    -3.370801    2.087008   -1.344928
H    -2.606155    0.249961   -2.179016
C    -3.341146    2.249312    1.059436
H    -2.526007    0.555869    2.117733
C    -3.640959    2.805180   -0.180649
H    -3.622204    2.507926   -2.317566
H    -3.568860    2.796832    1.973211
H    -4.103608    3.788715   -0.241764
C    -2.677790   -1.648218    0.125314
F    -3.842675   -1.643857   -0.541873
F    -2.961783   -1.841714    1.422309
F    -2.100749   -2.822896   -0.295701
Pd   -0.665301   -0.720881   -0.007807
C     1.702791    1.734825   -0.934516
C     2.768810   -1.198561   -0.790707
```

C	2.151998	0.365660	1.838123
C	0.975250	0.975474	2.611938
H	0.669297	1.962042	2.252747
H	0.096248	0.316998	2.567265
H	1.268450	1.084995	3.667621
C	2.421825	-0.984017	2.511359
H	2.568788	-0.809429	3.587929
H	1.571631	-1.672003	2.405405
H	3.327011	-1.480032	2.143023
C	3.389447	1.245619	2.012500
H	3.647232	1.291789	3.082110
H	4.264486	0.848277	1.483858
H	3.226350	2.277195	1.679005
C	2.346819	-2.600771	-0.328931
H	2.937883	-3.347019	-0.881975
H	2.511366	-2.782298	0.736227
H	1.284011	-2.789695	-0.543749
C	2.552029	-1.185756	-2.306622
H	3.090530	-2.040841	-2.742222
H	1.490781	-1.297655	-2.569523
H	2.943331	-0.283332	-2.789085
C	4.259627	-1.000742	-0.514236
H	4.518106	-1.139731	0.542375
H	4.829985	-1.751551	-1.083152
H	4.620887	-0.012730	-0.824537
C	3.117110	2.191360	-1.296960
H	3.606552	1.518252	-2.011817
H	3.057615	3.179239	-1.780002
H	3.771883	2.296187	-0.423543
C	0.872018	1.614293	-2.219593
H	0.852049	2.597382	-2.714850
H	1.273944	0.896512	-2.939923
H	-0.164111	1.328158	-1.993081
C	1.023886	2.836731	-0.113495
H	1.589324	3.124764	0.780343
H	0.946839	3.735881	-0.743335
H	0.002780	2.557443	0.184634

1-CF_3-adduct

Zero-point correction=	0.477369	(Hartree/Particle)
Thermal correction to Energy=	0.506059	
Thermal correction to Enthalpy=	0.507003	
Thermal correction to Gibbs Free Energy=	0.419967	
Sum of electronic and zero-point Energies=	-1510.946192	
Sum of electronic and thermal Energies=	-1510.917502	
Sum of electronic and thermal Enthalpies=	-1510.916558	
Sum of electronic and thermal Free Energies=	-1511.003594	

E(RB3LYP) = -1512.61231257

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1-CF3-adduct

P	-1.618702	-0.037396	-0.025412
C	2.865601	0.054537	0.050460
C	2.983503	0.769420	1.267683
C	2.734474	0.766113	-1.166720
C	2.981700	2.152476	1.266116
H	3.107893	0.213907	2.196443
C	2.701283	2.176835	-1.134742
H	2.804382	0.245400	-2.120792
C	2.841190	2.859627	0.063086
H	3.089236	2.691447	2.205429
H	2.604458	2.721057	-2.072392
H	2.842992	3.947888	0.070333

C	3.228524	-1.398841	0.058892
F	4.553414	-1.557858	0.224563
F	2.904206	-2.025773	-1.077925
F	2.639396	-2.059202	1.066394
Pd	0.683748	0.196472	-0.409346
C	-2.526395	-0.793634	-1.543856
C	-2.388195	1.686501	0.350701
C	-1.920113	-1.178035	1.496758
C	-1.651730	-1.927860	-2.096268
H	-0.626584	-1.578832	-2.287114
H	-1.590771	-2.795268	-1.433527
H	-2.081686	-2.274123	-3.049245
C	-2.584807	0.257805	-2.656006
H	-1.596590	0.696909	-2.853077
H	-2.920484	-0.232233	-3.582571
H	-3.295214	1.065864	-2.447225
C	-3.940675	-1.322385	-1.303482
H	-4.621070	-0.557593	-0.909616
H	-4.358611	-1.669024	-2.261849
H	-3.961336	-2.180246	-0.621152
C	-3.913489	1.772046	0.282702
H	-4.410208	1.057805	0.950263
H	-4.230203	2.781511	0.589157
H	-4.299464	1.614329	-0.732387
C	-1.787317	2.705874	-0.628230
H	-2.077287	2.538675	-1.669293
H	-2.139609	3.711172	-0.348490
H	-0.688479	2.700188	-0.578527
C	-1.931579	2.146053	1.739312
H	-0.838609	2.083551	1.847473
H	-2.215976	3.201694	1.867036
H	-2.400712	1.589215	2.558411
C	-3.316005	-1.109396	2.116736
H	-4.109333	-1.344199	1.396842
H	-3.382916	-1.849044	2.930096
H	-3.536059	-0.129910	2.558967
C	-0.874610	-0.845308	2.571910
H	-0.977816	0.158958	2.992794
H	-0.988613	-1.561334	3.400840
H	0.145669	-0.942479	2.173802
C	-1.639364	-2.630464	1.098339
H	-2.403618	-3.052807	0.436338
H	-0.654936	-2.740831	0.621663
H	-1.633364	-3.245909	2.010825

Pd(P^tBu_3)$_2$

Zero-point correction=	0.742351	(Hartree/Particle)
Thermal correction to Energy=	0.780329	
Thermal correction to Enthalpy=	0.781273	
Thermal correction to Gibbs Free Energy=	0.679202	
Sum of electronic and zero-point Energies=	-1756.164582	
Sum of electronic and thermal Energies=	-1756.126605	
Sum of electronic and thermal Enthalpies=	-1756.125661	
Sum of electronic and thermal Free Energies=	-1756.227732	
E(RB3LYP) = -1758.25602039		

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Pd(PtBu3)2

P	-1.518713	0.205552	0.234486
Pd	0.786525	0.355256	-0.175331
C	-2.434668	-0.577238	-1.270661
C	-2.284510	1.944981	0.555517
C	-1.870382	-0.886341	1.783749

C	-1.572138	-1.735305	-1.792466
H	-0.547572	-1.395481	-2.005578
H	-1.504855	-2.578108	-1.099308
H	-2.014920	-2.114457	-2.727416
C	-2.472726	0.443365	-2.412498
H	-1.478219	0.868592	-2.610518
H	-2.802883	-0.069775	-3.328934
H	-3.178102	1.263188	-2.234878
C	-3.856816	-1.082615	-1.027342
H	-4.527492	-0.302050	-0.648518
H	-4.277405	-1.440918	-1.980571
H	-3.891355	-1.927507	-0.329497
C	-3.807883	2.048150	0.467809
H	-4.321257	1.358832	1.149456
H	-4.114563	3.069979	0.743030
H	-4.186229	1.868214	-0.546315
C	-1.658961	2.929821	-0.443678
H	-1.948989	2.743197	-1.481461
H	-1.990161	3.949479	-0.190229
H	-0.560281	2.898786	-0.392948
C	-1.844853	2.439682	1.937557
H	-0.755199	2.369557	2.067166
H	-2.121083	3.501234	2.031983
H	-2.332326	1.909844	2.764040
C	-3.270042	-0.786726	2.390806
H	-4.059503	-1.046495	1.675090
H	-3.346916	-1.493111	3.232867
H	-3.489357	0.210310	2.792199
C	-0.830222	-0.531705	2.857599
H	-0.952666	0.472924	3.272621
H	-0.927483	-1.244142	3.692121
H	0.190795	-0.605564	2.453984
C	-1.603914	-2.353937	1.433487
H	-2.363290	-2.785542	0.771820
H	-0.615239	-2.489444	0.972567
H	-1.619427	-2.943086	2.363374
P	3.094187	0.498135	-0.570709
C	3.467779	0.996349	-2.395877
C	3.906481	1.814864	0.581822
C	3.954639	-1.191176	-0.228548
C	5.471979	-1.156631	-0.046555
H	5.842615	-2.185854	0.083876
H	5.991897	-0.730933	-0.912732
H	5.779383	-0.593303	0.843169
C	3.311256	-1.797493	1.027349
H	3.493877	-1.218795	1.937369
H	2.222447	-1.887503	0.900400
H	3.728616	-2.804490	1.187529
C	3.624820	-2.169678	-1.360305
H	2.543186	-2.220600	-1.551870
H	4.139782	-1.936106	-2.299214
H	3.953885	-3.175835	-1.057364
C	5.314150	2.277633	0.204028
H	5.679642	2.978825	0.971237
H	6.033734	1.451077	0.148829
H	5.340218	2.814043	-0.752345
C	3.944247	1.275034	2.015577
H	4.679847	0.475634	2.160420
H	4.230651	2.097868	2.688833
H	2.958774	0.911490	2.340550
C	2.973431	3.033274	0.634903
H	1.959566	2.737111	0.942188
H	3.366465	3.748709	1.374732

```
H     2.889869    3.562978   -0.318152
C     4.897476    0.774317   -2.891573
H     5.174253   -0.286343   -2.930404
H     4.984625    1.163125   -3.918778
H     5.643747    1.297616   -2.281684
C     3.114553    2.474386   -2.593253
H     3.822809    3.157577   -2.110596
H     3.139647    2.698163   -3.671055
H     2.100976    2.701945   -2.232883
C     2.495913    0.225971   -3.301557
H     2.619731    0.583047   -4.336411
H     2.663581   -0.854684   -3.307576
H     1.453933    0.402494   -2.996258
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TS-isom-CF_3

```
 Zero-point correction=                           0.474095 (Hartree/Particle)
 Thermal correction to Energy=                    0.502821
 Thermal correction to Enthalpy=                  0.503765
 Thermal correction to Gibbs Free Energy=         0.416731
 Sum of electronic and zero-point Energies=          -1510.885206
 Sum of electronic and thermal Energies=             -1510.856480
 Sum of electronic and thermal Enthalpies=           -1510.855536
 Sum of electronic and thermal Free Energies=        -1510.942570
 E(RB3LYP) =  -1512.56754286

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TS-isom-CF3
P    -1.647480   -0.227905    0.009770
C     2.589648   -0.419857   -0.052957
C     3.071556   -1.004905    1.119425
C     3.251793   -0.627787   -1.263204
C     4.190829   -1.835950    1.068095
H     2.578691   -0.812758    2.074345
C     4.368224   -1.462463   -1.305386
H     2.900432   -0.139130   -2.172272
C     4.838382   -2.067285   -0.142622
H     4.562703   -2.294588    1.984078
H     4.877618   -1.631018   -2.253946
H     5.716055   -2.710964   -0.177529
C     1.869464    2.079730    0.154226
F     2.680906    2.395120   -0.869676
F     0.944587    3.080377    0.205723
F     2.596389    2.206502    1.277995
Pd    0.776016    0.409545   -0.023563
C    -2.077140   -0.836158    1.776928
C    -1.891902   -1.665251   -1.237257
C    -2.797012    1.233134   -0.461011
C    -0.666449   -2.586931   -1.138626
H    -0.745288   -3.360023   -1.918137
H     0.269137   -2.032905   -1.315306
H    -0.573981   -3.102801   -0.179197
C    -1.865667   -1.108414   -2.664121
H    -0.975582   -0.489921   -2.846217
H    -1.821768   -1.957081   -3.363004
H    -2.759551   -0.530290   -2.923493
C    -3.167545   -2.486377   -1.055489
H    -3.222955   -3.242475   -1.853861
H    -3.191910   -3.027108   -0.101941
H    -4.074646   -1.873707   -1.122311
C    -2.145175    1.994045   -1.623335
H    -2.065651    1.409969   -2.543304
H    -2.760759    2.877847   -1.850936
H    -1.140452    2.348884   -1.356163
```

C	-4.226666	0.845824	-0.838941
H	-4.802103	1.763801	-1.034829
H	-4.274654	0.240009	-1.751572
H	-4.744325	0.301204	-0.039671
C	-2.849348	2.228377	0.701550
H	-1.845292	2.533248	1.027134
H	-3.369094	3.134155	0.355020
H	-3.405080	1.852694	1.567634
C	-3.569346	-0.969018	2.080838
H	-3.693869	-1.385727	3.092285
H	-4.092292	-0.004979	2.067400
H	-4.082342	-1.642916	1.384551
C	-1.434111	0.132315	2.780456
H	-1.857655	1.139844	2.755675
H	-1.589142	-0.262563	3.796211
H	-0.350390	0.219015	2.612360
C	-1.404061	-2.189729	2.027323
H	-1.513830	-2.435668	3.094094
H	-1.858503	-3.012356	1.463641
H	-0.326033	-2.163244	1.809952

1-I-CF_3

Zero-point correction=	0.475645 (Hartree/Particle)
Thermal correction to Energy=	0.504465
Thermal correction to Enthalpy=	0.505409
Thermal correction to Gibbs Free Energy=	0.418662
Sum of electronic and zero-point Energies=	-1510.889243
Sum of electronic and thermal Energies=	-1510.860423
Sum of electronic and thermal Enthalpies=	-1510.859479
Sum of electronic and thermal Free Energies=	-1510.946226

E(RB3LYP) = -1512.56754286

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1-I-CF3

P	1.626369	0.190264	-0.007459
C	-2.803961	0.282694	-0.022045
C	-3.506247	0.628419	-1.180959
C	-3.438549	0.414017	1.217617
C	-4.803617	1.133050	-1.097898
H	-3.041516	0.500616	-2.160641
C	-4.735966	0.919372	1.300076
H	-2.917529	0.115184	2.130032
C	-5.419477	1.281181	0.142355
H	-5.338850	1.404109	-2.008057
H	-5.216507	1.022494	2.273117
H	-6.434812	1.670477	0.205968
C	-1.315671	-1.981191	-0.248245
F	-2.104264	-2.281258	-1.295237
F	-1.921994	-2.471448	0.850279
F	-0.204581	-2.745441	-0.412844
Pd	-0.812673	-0.048769	-0.084859
C	2.272896	-0.118464	1.767087
C	1.630534	2.079855	-0.361795
C	2.771859	-0.685541	-1.267241
C	1.838903	-1.532137	2.180013
H	0.751134	-1.657701	2.090603
H	2.318328	-2.327302	1.603404
H	2.109583	-1.686619	3.235559
C	1.564834	0.826501	2.744031
H	0.470451	0.765087	2.653805
H	1.823658	0.519682	3.768432
H	1.872687	1.873251	2.640349
C	3.782696	0.034370	1.953764

H	4.142017	1.035362	1.683164
H	4.029356	-0.126166	3.014764
H	4.358469	-0.700853	1.378964
C	2.849333	2.866667	0.116238
H	3.783000	2.502348	-0.330123
H	2.735702	3.921622	-0.178505
H	2.964598	2.850516	1.206427
C	0.363527	2.650926	0.297173
H	0.340940	2.565067	1.385841
H	0.278510	3.720464	0.049410
H	-0.566282	2.193609	-0.104280
C	1.447398	2.329733	-1.862903
H	0.575814	1.796814	-2.267717
H	1.270658	3.405311	-2.014383
H	2.327232	2.064738	-2.457692
C	4.090195	0.038612	-1.545054
H	4.690085	0.175012	-0.636660
H	4.687546	-0.567983	-2.243060
H	3.953805	1.020937	-2.012547
C	1.977969	-0.853239	-2.569992
H	1.725490	0.093850	-3.055032
H	2.586837	-1.431982	-3.281188
H	1.046074	-1.407694	-2.396668
C	3.101846	-2.105027	-0.792993
H	3.771320	-2.126554	0.074286
H	2.201677	-2.685743	-0.561490
H	3.624449	-2.622686	-1.611291

TS-1-I-CF_3

Zero-point correction=	0.473959 (Hartree/Particle)
Thermal correction to Energy=	0.502582
Thermal correction to Enthalpy=	0.503526
Thermal correction to Gibbs Free Energy=	0.416945
Sum of electronic and zero-point Energies=	-1510.867633
Sum of electronic and thermal Energies=	-1510.839010
Sum of electronic and thermal Enthalpies=	-1510.838066
Sum of electronic and thermal Free Energies=	-1510.924648

E(RB3LYP) = -1512.53953828

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TS-1-I-CF3

P	1.649061	0.160875	-0.017236
C	-2.744621	0.151111	-0.010914
C	-3.285943	0.663546	-1.194717
C	-3.262887	0.525157	1.230291
C	-4.298160	1.614915	-1.126432
H	-2.913925	0.313953	-2.157701
C	-4.280904	1.476552	1.285009
H	-2.866931	0.085173	2.144339
C	-4.794023	2.021831	0.111998
H	-4.710050	2.032422	-2.044173
H	-4.677230	1.787449	2.250640
H	-5.595105	2.757542	0.160679
C	-2.133932	-1.756731	-0.093008
F	-3.251095	-2.117975	-0.754701
F	-2.278130	-2.181300	1.174635
F	-1.194120	-2.584915	-0.648059
Pd	-0.734986	-0.044149	-0.051827
C	2.392478	-0.624443	1.569056
C	2.058690	2.038801	-0.024026
C	2.469499	-0.650644	-1.552896
C	1.701235	-1.975904	1.799764
H	0.610403	-1.857107	1.865510

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H     1.908991   -2.716796    1.023320
H     2.057104   -2.393320    2.754441
C     2.016649    0.236113    2.779520
H     0.937339    0.440929    2.817772
H     2.277737   -0.319263    3.693084
H     2.559527    1.187165    2.820001
C     3.908910   -0.818354    1.568233
H     4.453605    0.118336    1.396611
H     4.220313   -1.203581    2.551739
H     4.243002   -1.548133    0.821527
C     3.484017    2.420867    0.373225
H     4.243333    1.951466   -0.264036
H     3.602098    3.511234    0.274360
H     3.712016    2.169431    1.415838
C     1.067380    2.745320    0.913539
H     1.217152    2.508884    1.970401
H     1.190901    3.833726    0.802228
H     0.024805    2.498553    0.657991
C     1.772546    2.607003   -1.418336
H     0.759154    2.355073   -1.762151
H     1.838767    3.704278   -1.366581
H     2.493536    2.279711   -2.175721
C     3.899182   -0.202859   -1.856071
H     4.586485   -0.387447   -1.021526
H     4.274789   -0.772056   -2.720747
H     3.963241    0.859315   -2.120841
C     1.577763   -0.369153   -2.770910
H     1.512593    0.689617   -3.036270
H     1.995627   -0.899617   -3.640601
H     0.556066   -0.740608   -2.606414
C     2.456999   -2.173665   -1.386775
H     3.174613   -2.536029   -0.641874
H     1.456933   -2.547099   -1.128927
H     2.740416   -2.628024   -2.348181
```

Species in carbene mechanism of Figure 2

TS-1/A-CF_3

```
 Zero-point correction=                           0.472963 (Hartree/Particle)
 Thermal correction to Energy=                    0.502322
 Thermal correction to Enthalpy=                  0.503266
 Thermal correction to Gibbs Free Energy=         0.415718
 Sum of electronic and zero-point Energies=          -1510.854470
 Sum of electronic and thermal Energies=             -1510.825110
 Sum of electronic and thermal Enthalpies=           -1510.824166
 Sum of electronic and thermal Free Energies=        -1510.911715
 E(RB3LYP) =  -1512.54762752

56
TS-1/A-CF3
P     1.368386    0.153724    0.211005
C    -1.883896    0.749227   -0.307544
C    -2.244668    0.644419   -1.653242
C    -2.326058    1.852495    0.427562
C    -2.982123    1.655179   -2.268627
H    -1.935729   -0.226240   -2.235234
C    -3.061794    2.864933   -0.189800
H    -2.083620    1.932756    1.489934
C    -3.384060    2.773062   -1.541269
H    -3.244320    1.567201   -3.322877
H    -3.385806    3.727937    0.391717
H    -3.955534    3.564558   -2.023666
C    -2.579638   -1.595337    1.093989
```

```
F    -2.960109   -2.761647    0.715162
F    -3.383002   -1.206240    2.023620
F    -0.289452   -2.414622    1.719385
Pd   -0.881838   -0.735602    0.624492
C     1.633405    1.980024   -0.361156
C     2.164581   -1.008490   -1.089917
C     2.272246   -0.058816    1.902088
C     1.311993    0.441688    2.992358
H     1.050289    1.500599    2.898624
H     0.383357   -0.145171    3.001154
H     1.797017    0.308228    3.971568
C     2.515530   -1.543186    2.198883
H     2.897657   -1.615626    3.229044
H     1.584808   -2.118914    2.136223
H     3.277223   -1.989077    1.548835
C     3.612740    0.664051    2.032732
H     4.029941    0.427042    3.023255
H     4.343834    0.326261    1.287718
H     3.535347    1.754826    1.973260
C     1.614451   -2.424229   -0.868891
H     2.099074   -3.097316   -1.593129
H     1.786966   -2.820345    0.134558
H     0.530817   -2.462168   -1.048475
C     1.712027   -0.597644   -2.493711
H     2.004688   -1.394266   -3.194187
H     0.620279   -0.488708   -2.561315
H     2.182360    0.327213   -2.846729
C     3.694036   -1.055658   -1.070710
H     4.094484   -1.479783   -0.143395
H     4.031974   -1.705679   -1.892461
H     4.154689   -0.073872   -1.224281
C     3.061297    2.277755   -0.835316
H     3.284312    1.794033   -1.795057
H     3.146970    3.362659   -1.001173
H     3.841577    1.998320   -0.120186
C     0.684936    2.372248   -1.503726
H     0.980613    3.375827   -1.846048
H     0.722791    1.711221   -2.372741
H    -0.352810    2.432101   -1.168121
C     1.278272    2.924500    0.792899
H     1.992863    2.897820    1.621874
H     1.274111    3.954102    0.404704
H     0.272325    2.722724    1.185449
```

A

```
 Zero-point correction=                           0.473801 (Hartree/Particle)
 Thermal correction to Energy=                    0.503720
 Thermal correction to Enthalpy=                  0.504664
 Thermal correction to Gibbs Free Energy=         0.415693
 Sum of electronic and zero-point Energies=          -1510.854260
 Sum of electronic and thermal Energies=             -1510.824341
 Sum of electronic and thermal Enthalpies=           -1510.823397
 Sum of electronic and thermal Free Energies=        -1510.912368
 E(RB3LYP) =  -1512.54873926
```

56

A

```
P     1.350851    0.133416    0.232016
C    -1.956813    0.801298   -0.302873
C    -2.308762    0.698487   -1.652215
C    -2.358094    1.933970    0.413584
C    -2.973382    1.742506   -2.293041
H    -2.046835   -0.199488   -2.215752
```

C	-3.021416	2.979510	-0.227060
H	-2.135944	2.007644	1.480619
C	-3.321437	2.890068	-1.584390
H	-3.223866	1.656936	-3.350019
H	-3.310005	3.864663	0.339169
H	-3.839976	3.706231	-2.085069
C	-2.818508	-1.191318	0.820521
F	-3.508335	-1.875049	-0.030516
F	-3.632869	-0.781311	1.734413
F	-0.217213	-2.327845	1.661417
Pd	-0.945611	-0.712363	0.644162
C	1.615683	1.961582	-0.337359
C	2.135885	-1.022094	-1.080099
C	2.281321	-0.080412	1.911657
C	1.314689	0.385624	3.010847
H	1.005866	1.432016	2.914553
H	0.416067	-0.245275	3.025507
H	1.814959	0.278080	3.985709
C	2.570444	-1.558053	2.202580
H	2.978221	-1.618771	3.223632
H	1.651904	-2.150904	2.159196
H	3.325719	-1.987136	1.534629
C	3.606346	0.672127	2.035761
H	4.032412	0.443807	3.024580
H	4.341450	0.347608	1.288496
H	3.509090	1.760952	1.976895
C	1.588743	-2.438078	-0.853888
H	2.106263	-3.121171	-1.545319
H	1.713410	-2.810688	0.165193
H	0.514124	-2.483280	-1.078814
C	1.672743	-0.612579	-2.480703
H	1.954192	-1.413621	-3.180944
H	0.581137	-0.497604	-2.538816
H	2.146160	0.308131	-2.840897
C	3.666050	-1.064026	-1.076919
H	4.080068	-1.487124	-0.155376
H	3.996347	-1.712056	-1.903409
H	4.121287	-0.080562	-1.235442
C	3.040118	2.264653	-0.819221
H	3.253786	1.788230	-1.784929
H	3.123878	3.350865	-0.977820
H	3.827370	1.979808	-0.114621
C	0.665964	2.355064	-1.478403
H	0.959714	3.359822	-1.819052
H	0.705117	1.695979	-2.348757
H	-0.371351	2.414192	-1.142898
C	1.258777	2.902843	0.819298
H	1.971216	2.875842	1.649991
H	1.252108	3.933792	0.434430
H	0.253222	2.697323	1.211231

TS-A/B-CF_3

Zero-point correction=	0.473754 (Hartree/Particle)
Thermal correction to Energy=	0.502655
Thermal correction to Enthalpy=	0.503599
Thermal correction to Gibbs Free Energy=	0.417948
Sum of electronic and zero-point Energies=	-1510.854022
Sum of electronic and thermal Energies=	-1510.825121
Sum of electronic and thermal Enthalpies=	-1510.824177
Sum of electronic and thermal Free Energies=	-1510.909828

E(RB3LYP) = -1512.54833708

56

TS-A/B-CF3

P	1.340865	0.163578	-0.286125
C	-2.073647	0.820550	0.435105
C	-2.279070	0.628221	1.806057
C	-2.542766	1.998407	-0.158995
C	-2.860867	1.627560	2.581496
H	-1.972704	-0.308816	2.275941
C	-3.129289	2.996919	0.615212
H	-2.437365	2.140525	-1.236082
C	-3.279136	2.816803	1.988390
H	-2.996820	1.473940	3.651352
H	-3.476065	3.915700	0.143801
H	-3.740085	3.595744	2.593487
C	-2.898507	-0.909003	-0.731125
F	-3.741146	-0.421038	-1.586931
F	-0.308873	-2.097394	-1.821254
Pd	-1.002593	-0.574976	-0.671032
C	1.633690	2.006091	0.207688
C	2.043938	-0.954415	1.102517
C	2.322652	-0.163795	-1.916563
C	1.410819	0.263045	-3.077016
H	1.097178	1.311528	-3.032357
H	0.520763	-0.378212	-3.105951
H	1.960266	0.124693	-4.021213
C	2.582821	-1.661933	-2.118887
H	3.011472	-1.787565	-3.125505
H	1.647516	-2.227620	-2.071121
H	3.313126	-2.071019	-1.412324
C	3.670514	0.549104	-2.023528
H	4.133134	0.254459	-2.977844
H	4.365106	0.253968	-1.226479
H	3.595144	1.641492	-2.031594
C	1.457112	-2.358815	0.913615
H	1.848489	-3.009120	1.711309
H	1.702691	-2.813413	-0.049373
H	0.360731	-2.343011	0.993754
C	1.545020	-0.462146	2.463874
H	1.765943	-1.236962	3.213550
H	0.459221	-0.294370	2.474159
H	2.046513	0.455407	2.793707
C	3.570632	-1.042731	1.165408
H	4.009567	-1.520690	0.283245
H	3.848634	-1.657975	2.035349
H	4.047780	-0.064556	1.294576
C	3.045981	2.317379	0.715134
H	3.234341	1.863408	1.696896
H	3.132108	3.406900	0.849109
H	3.847642	2.010291	0.036948
C	0.655807	2.455078	1.301982
H	0.906856	3.494076	1.565528
H	0.709023	1.866795	2.220978
H	-0.378088	2.445933	0.949600
C	1.313131	2.892177	-1.001852
H	2.040292	2.811485	-1.816664
H	1.313904	3.942251	-0.672633
H	0.312197	2.677466	-1.403225
F	-3.575776	-1.633391	0.104158

B

Zero-point correction=	0.476290	(Hartree/Particle)
Thermal correction to Energy=	0.505219	
Thermal correction to Enthalpy=	0.506164	
Thermal correction to Gibbs Free Energy=	0.420333	

```
 Sum of electronic and zero-point Energies=          -1510.906104
 Sum of electronic and thermal Energies=             -1510.877174
 Sum of electronic and thermal Enthalpies=           -1510.876230
 Sum of electronic and thermal Free Energies=        -1510.962061
 E(RB3LYP) =  -1512.59375307

56
B
P     1.381767    0.266609    0.286360
C    -3.018931    0.448139   -0.296078
C    -2.498279    0.195348   -1.586738
C    -3.341267    1.774319    0.075555
C    -2.384925    1.242309   -2.505350
H    -2.288411   -0.830386   -1.889301
C    -3.228470    2.791805   -0.850576
H    -3.710827    1.967017    1.080329
C    -2.756140    2.527120   -2.144163
H    -2.008854    1.039126   -3.506305
H    -3.508725    3.806129   -0.573978
H    -2.674488    3.338307   -2.865103
C    -2.975854   -0.630509    0.683860
F    -3.579417   -0.410673    1.851863
F    -0.719548   -1.560511    2.123699
Pd   -1.011284   -0.250392    0.594052
C     1.712936    2.112926   -0.131101
C     2.012113   -0.818290   -1.165713
C     2.371360   -0.181937    1.868644
C     1.568868    0.316462    3.080363
H     1.437687    1.401473    3.113427
H     0.586935   -0.171857    3.099640
H     2.113838    0.028051    3.992923
C     2.425092   -1.706596    2.027743
H     2.854600   -1.923340    3.018001
H     1.416786   -2.137999    2.002186
H     3.068916   -2.200062    1.290877
C     3.797734    0.366841    1.927779
H     4.278707   -0.016973    2.840970
H     4.415588    0.049822    1.077810
H     3.834673    1.461390    1.988568
C     1.334339   -2.189945   -1.041296
H     1.630858   -2.809736   -1.901813
H     1.602008   -2.733518   -0.132050
H     0.237964   -2.096172   -1.052544
C     1.529654   -0.238844   -2.499076
H     1.732867   -0.976238   -3.290594
H     0.446992   -0.049419   -2.497466
H     2.048418    0.684429   -2.782026
C     3.528539   -0.996616   -1.248830
H     3.940588   -1.534208   -0.387400
H     3.770619   -1.590348   -2.144244
H     4.058069   -0.039415   -1.337839
C     3.090548    2.427413   -0.715193
H     3.248145    1.958949   -1.694455
H     3.173893    3.515471   -0.864627
H     3.914041    2.125715   -0.057401
C     0.634101    2.585910   -1.111608
H     0.747856    3.670509   -1.264762
H     0.692072    2.112541   -2.095562
H    -0.372529    2.409193   -0.707867
C     1.507173    2.959176    1.129179
H     2.286686    2.812460    1.883610
H     1.532205    4.021323    0.841855
H     0.529151    2.767861    1.594168
```

F -3.286614 -1.862152 0.259345

TS-B-CF_3-RE

Zero-point correction= 0.475604 (Hartree/Particle)
Thermal correction to Energy= 0.503883
Thermal correction to Enthalpy= 0.504827
Thermal correction to Gibbs Free Energy= 0.420697
Sum of electronic and zero-point Energies= -1510.876136
Sum of electronic and thermal Energies= -1510.847857
Sum of electronic and thermal Enthalpies= -1510.846912
Sum of electronic and thermal Free Energies= -1510.931043
E(RB3LYP) = -1512.55490080

56
TS-B-CF3-RE

Pd	0.038740	-1.518773	-0.614137
P	-1.375727	-0.185014	0.698138
F	1.251305	-1.917086	-3.252540
F	1.245065	-3.995529	-2.663649
F	-0.755696	-2.897138	-2.195697
C	1.250474	-2.759369	-2.254236
C	1.982320	-2.466320	-1.066995
C	2.259879	-1.105411	-0.697156
H	2.202005	-0.319184	-1.450894
C	2.996800	-0.865783	0.487748
H	3.269054	0.160463	0.731035
C	3.357116	-1.900956	1.317807
H	3.918551	-1.700010	2.228245
C	3.000343	-3.230921	0.995518
H	3.282958	-4.040898	1.665136
C	2.312642	-3.517255	-0.155021
H	2.042831	-4.539850	-0.408178
C	-3.171704	-0.717408	0.268363
C	-1.065827	-0.523487	2.564528
C	-1.200360	1.700760	0.376954
C	-0.742204	-2.015985	2.728437
H	-1.568353	-2.680572	2.458798
H	0.131612	-2.296770	2.121987
H	-0.498968	-2.207765	3.785378
C	0.199126	0.214940	3.010643
H	0.473011	-0.141640	4.015519
H	1.045143	0.001322	2.343357
H	0.067375	1.300441	3.085048
C	-2.206375	-0.145164	3.510643
H	-1.884004	-0.329860	4.547463
H	-2.481804	0.914503	3.439499
H	-3.111405	-0.742962	3.347906
C	-3.413078	-2.122948	0.827936
H	-3.499013	-2.147026	1.919925
H	-4.365933	-2.497680	0.424451
H	-2.629672	-2.827511	0.514910
C	-4.284095	0.205051	0.765756
H	-5.257680	-0.248434	0.522108
H	-4.257852	0.357943	1.851885
H	-4.262903	1.189165	0.281506
C	-3.275712	-0.865914	-1.257963
H	-3.186789	0.081806	-1.795818
H	-2.523211	-1.561944	-1.658403
H	-4.269920	-1.276543	-1.494503
C	0.292840	2.044402	0.296933
H	0.799435	1.427508	-0.457668
H	0.395690	3.099519	0.000418
H	0.822830	1.921626	1.245741

```
C    -1.871514    2.613411    1.404215
H    -1.419663    2.536355    2.400600
H    -1.756384    3.659785    1.080611
H    -2.946210    2.419016    1.501926
C    -1.771654    2.026119   -1.006748
H    -2.865501    1.974253   -1.043264
H    -1.493191    3.059012   -1.265744
H    -1.361842    1.368251   -1.785898
```

Species in Figure 3 and Figure S24

1-CF_2CF_3

```
 Zero-point correction=                           0.486733 (Hartree/Particle)
 Thermal correction to Energy=                    0.519147
 Thermal correction to Enthalpy=                  0.520091
 Thermal correction to Gibbs Free Energy=         0.424177
 Sum of electronic and zero-point Energies=          -1748.591775
 Sum of electronic and thermal Energies=             -1748.559361
 Sum of electronic and thermal Enthalpies=           -1748.558417
 Sum of electronic and thermal Free Energies=        -1748.654331
 E(RB3LYP) =  -1750.45233648

59
1-CF2CF3
P     1.434924    0.216984    0.010690
C    -2.042784    0.683256    0.022837
C    -2.476867    1.144340   -1.221005
C    -2.436087    1.349725    1.182477
C    -3.246269    2.303921   -1.304226
H    -2.218423    0.601449   -2.131247
C    -3.206989    2.509751    1.091523
H    -2.148998    0.971382    2.163291
C    -3.604247    2.995907   -0.150279
H    -3.574357    2.660915   -2.280219
H    -3.501247    3.029747    2.002980
H    -4.204971    3.901541   -0.217509
C    -2.334362   -2.105311    0.387797
F    -3.122973   -1.907922    1.477486
F    -1.648872   -3.289708    0.618113
Pd   -0.756916   -0.849954    0.118888
C     1.677986    1.867136   -0.925856
C     2.461307   -1.160985   -0.842163
C     2.048451    0.416143    1.819427
C     0.944371    1.114941    2.624086
H     0.697831    2.120376    2.272970
H     0.021748    0.519738    2.614399
H     1.277819    1.202310    3.669432
C     2.196191   -0.965433    2.467195
H     2.388217   -0.821031    3.540992
H     1.275298   -1.559985    2.382863
H     3.033127   -1.549798    2.070288
C     3.363608    1.175439    1.991989
H     3.646960    1.154474    3.055630
H     4.190013    0.726712    1.426494
H     3.282342    2.231441    1.707088
C     1.844751   -2.500771   -0.407668
H     2.371226   -3.322031   -0.918123
H     1.899624   -2.699438    0.665891
H     0.787010   -2.576410   -0.722873
C     2.258907   -1.096799   -2.359040
H     2.686708   -2.008742   -2.802191
H     1.195552   -1.068844   -2.635122
H     2.768959   -0.245997   -2.824194
```

C	3.963083	-1.158856	-0.562099
H	4.204443	-1.318208	0.494852
H	4.433991	-1.978540	-1.126666
H	4.443466	-0.225884	-0.882671
C	3.129765	2.210247	-1.263405
H	3.574161	1.493368	-1.965654
H	3.152786	3.194992	-1.755293
H	3.778054	2.271224	-0.382070
C	0.868204	1.830183	-2.228454
H	0.923796	2.826238	-2.693427
H	1.244718	1.113267	-2.962068
H	-0.189397	1.614377	-2.037912
C	1.067568	2.998675	-0.091768
H	1.636303	3.217770	0.818941
H	1.072137	3.915843	-0.699378
H	0.021515	2.789659	0.179266
C	-3.267660	-2.415391	-0.774659
F	-2.556523	-2.604656	-1.894500
F	-4.118300	-1.415343	-0.983747
F	-3.986026	-3.521449	-0.560276

TS-1-rotate-CF_2CF_3

Zero-point correction=	0.488129 (Hartree/Particle)
Thermal correction to Energy=	0.519096
Thermal correction to Enthalpy=	0.520040
Thermal correction to Gibbs Free Energy=	0.429027
Sum of electronic and zero-point Energies=	-1748.587800
Sum of electronic and thermal Energies=	-1748.556833
Sum of electronic and thermal Enthalpies=	-1748.555889
Sum of electronic and thermal Free Energies=	-1748.646902

E(RB3LYP) = -1750.44944572

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TS-1-rotate-CF2CF3

P	1.371946	0.211772	-0.060059
C	-2.058574	0.790491	0.418195
C	-2.320448	1.921974	-0.351179
C	-2.588565	0.680087	1.703761
C	-3.071908	2.966874	0.190145
H	-1.951432	2.003575	-1.374117
C	-3.335970	1.730212	2.236001
H	-2.420416	-0.221668	2.294544
C	-3.574538	2.877768	1.484140
H	-3.271225	3.851076	-0.415024
H	-3.742124	1.641454	3.243289
H	-4.162010	3.694147	1.900997
C	-2.640898	-1.693788	-0.614878
F	-3.857286	-1.088280	-0.646888
F	-2.747434	-2.710996	0.307522
Pd	-0.888664	-0.670889	-0.269636
C	1.730995	1.638468	-1.291167
C	2.358053	-1.344665	-0.603076
C	1.932673	0.726466	1.697667
C	0.870475	1.652034	2.305534
H	0.742202	2.597148	1.772243
H	-0.110489	1.163886	2.355343
H	1.177051	1.897722	3.333735
C	1.958517	-0.510192	2.601739
H	2.121546	-0.175340	3.636963
H	1.001233	-1.050558	2.582073
H	2.767679	-1.209479	2.362399
C	3.299488	1.409238	1.762548
H	3.547447	1.606390	2.816974

H	4.102409	0.788137	1.347411
H	3.313307	2.376798	1.246233
C	1.698776	-2.566607	0.056804
H	2.223696	-3.474133	-0.279029
H	1.727547	-2.556017	1.148775
H	0.644866	-2.688961	-0.247109
C	2.182589	-1.554559	-2.111660
H	2.565112	-2.553831	-2.368264
H	1.126464	-1.523070	-2.416762
H	2.744445	-0.833533	-2.715365
C	3.852465	-1.346245	-0.285816
H	4.060152	-1.360944	0.790699
H	4.304620	-2.256253	-0.710221
H	4.375883	-0.487568	-0.722968
C	3.198917	1.819357	-1.680033
H	3.606960	0.953266	-2.214346
H	3.279355	2.680962	-2.360844
H	3.845427	2.025138	-0.818352
C	0.898596	1.401209	-2.558957
H	0.926011	2.312849	-3.174665
H	1.273537	0.583914	-3.180104
H	-0.152221	1.184537	-2.320410
C	1.221715	2.953972	-0.690471
H	1.814904	3.293144	0.166223
H	1.298551	3.735958	-1.460700
H	0.166765	2.890669	-0.388471
C	-2.502877	-2.384156	-1.969153
F	-1.351506	-3.080593	-2.008681
F	-2.463993	-1.480240	-2.951705
F	-3.495146	-3.232142	-2.229724

1-II-CF_2CF_3

Zero-point correction=	0.487999	(Hartree/Particle)
Thermal correction to Energy=	0.519830	
Thermal correction to Enthalpy=	0.520774	
Thermal correction to Gibbs Free Energy=	0.427902	
Sum of electronic and zero-point Energies=	-1748.589813	
Sum of electronic and thermal Energies=	-1748.557982	
Sum of electronic and thermal Enthalpies=	-1748.557038	
Sum of electronic and thermal Free Energies=	-1748.649909	

E(RB3LYP) = -1750.44964853

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1-II-CF2CF3

P	1.403581	0.351599	0.271365
C	-2.060770	0.480011	-0.437422
C	-2.196361	0.021694	-1.746260
C	-2.693590	1.653309	-0.031352
C	-2.925730	0.774829	-2.666518
H	-1.741486	-0.920722	-2.054579
C	-3.423146	2.397696	-0.959332
H	-2.618462	1.992680	1.001937
C	-3.532497	1.966155	-2.278453
H	-3.024705	0.418748	-3.691691
H	-3.911137	3.319117	-0.642481
H	-4.102309	2.550113	-2.999430
C	-2.549201	-1.428833	1.416284
F	-3.176874	-2.170345	0.456107
Pd	-0.838474	-0.467505	0.822508
C	1.662323	2.143620	-0.359909
C	2.166912	-0.877280	-0.991272
C	2.310291	0.153267	1.958581
C	1.428931	0.772451	3.055454

```
H     1.288358    1.851636    2.955157
H     0.430838    0.308980    3.091853
H     1.908115    0.593359    4.030128
C     2.402656   -1.336406    2.306983
H     2.746213   -1.428718    3.348102
H     1.428250   -1.844640    2.248028
H     3.116944   -1.886021    1.684630
C     3.710199    0.759509    2.041737
H     4.142646    0.523314    3.026400
H     4.392631    0.360748    1.281178
H     3.699502    1.852199    1.951611
C     1.574931   -2.269822   -0.723775
H     1.942866   -2.961537   -1.496993
H     1.854118   -2.691612    0.245536
H     0.475740   -2.256749   -0.782023
C     1.704015   -0.501160   -2.402282
H     1.976903   -1.320632   -3.083963
H     0.613530   -0.376244   -2.459368
H     2.184602    0.404957   -2.787523
C     3.693188   -0.967462   -0.984974
H     4.090170   -1.368731   -0.044653
H     4.012624   -1.652664   -1.785396
H     4.174415    0.000062   -1.172183
C     3.066541    2.444201   -0.886930
H     3.296405    1.892258   -1.806719
H     3.126142    3.515095   -1.135414
H     3.855779    2.233999   -0.155243
C     0.640260    2.453414   -1.462547
H     0.777653    3.503036   -1.764273
H     0.756555    1.843646   -2.361768
H    -0.390417    2.340582   -1.105142
C     1.340042    3.115632    0.779004
H     2.094940    3.116947    1.572905
H     1.308083    4.134875    0.366314
H     0.354526    2.911516    1.222034
C    -2.108167   -2.438435    2.475864
F    -3.513664   -0.670468    2.014029
F    -3.103364   -3.186230    2.942184
F    -1.549663   -1.800045    3.514181
F    -1.178519   -3.260301    1.963491
```

TS-1-CF_2CF_3-RE

```
 Zero-point correction=                           0.488182 (Hartree/Particle)
 Thermal correction to Energy=                    0.519034
 Thermal correction to Enthalpy=                  0.519978
 Thermal correction to Gibbs Free Energy=         0.429502
 Sum of electronic and zero-point Energies=          -1748.567044
 Sum of electronic and thermal Energies=             -1748.536192
 Sum of electronic and thermal Enthalpies=           -1748.535248
 Sum of electronic and thermal Free Energies=        -1748.625724
 E(RB3LYP) =  -1551.87141658

59
TS-1-CF2CF3_RE
P     1.262990    0.009738    0.485196
C    -2.942748   -0.846347    0.809903
C    -3.401791   -1.198167   -0.461322
C    -3.546092    0.191653    1.526165
C    -4.424838   -0.453808   -1.044989
H    -2.953109   -2.034995   -0.994092
C    -4.566157    0.927306    0.930337
H    -3.212190    0.422555    2.536744
C    -5.003057    0.607936   -0.353911
```

H	-4.774365	-0.711064	-2.043841
H	-5.028487	1.748579	1.476083
H	-5.808045	1.179866	-0.812276
C	-2.265294	-2.349692	1.917861
F	-2.774189	-3.350857	1.152221
Pd	-0.936587	-0.838256	0.949834
C	1.000954	1.780802	-0.213852
C	2.150300	-1.050917	-0.847617
C	2.373470	0.112796	2.049220
C	1.505631	0.592414	3.220999
H	1.174167	1.629877	3.125337
H	0.616046	-0.040209	3.339368
H	2.098494	0.523254	4.146130
C	2.817844	-1.305875	2.420448
H	3.295971	-1.271951	3.410976
H	1.964195	-1.995070	2.490413
H	3.554950	-1.722010	1.724425
C	3.607957	1.007640	1.937182
H	4.192854	0.923880	2.866449
H	4.268180	0.723686	1.108906
H	3.350703	2.067650	1.819207
C	1.937720	-2.530595	-0.498450
H	2.383308	-3.144535	-1.296483
H	2.401708	-2.833888	0.444271
H	0.867981	-2.773378	-0.437960
C	1.453854	-0.851679	-2.196955
H	1.852127	-1.593324	-2.905758
H	0.369735	-1.019148	-2.121863
H	1.628409	0.136496	-2.637149
C	3.645528	-0.782756	-1.021157
H	4.225868	-1.043303	-0.127275
H	4.026818	-1.407618	-1.843697
H	3.862635	0.261691	-1.277117
C	2.192287	2.371379	-0.969530
H	2.417063	1.833398	-1.898216
H	1.958101	3.410016	-1.250656
H	3.105422	2.396282	-0.363658
C	-0.226788	1.763478	-1.138971
H	-0.401760	2.787470	-1.504342
H	-0.113232	1.119860	-2.015399
H	-1.131942	1.441370	-0.601058
C	0.635152	2.732209	0.928308
H	1.480380	2.955639	1.589280
H	0.308976	3.687723	0.490482
H	-0.198772	2.347781	1.532824
C	-1.114178	-3.064895	2.682216
F	-3.141170	-2.102257	2.931399
F	-1.616742	-4.098806	3.360553
F	-0.529956	-2.257144	3.569194
F	-0.179871	-3.551336	1.865898

1-CF_2CF_3-adduct

Zero-point correction=	0.490218 (Hartree/Particle)
Thermal correction to Energy=	0.521752
Thermal correction to Enthalpy=	0.522696
Thermal correction to Gibbs Free Energy=	0.428062
Sum of electronic and zero-point Energies=	-1748.639359
Sum of electronic and thermal Energies=	-1748.607826
Sum of electronic and thermal Enthalpies=	-1748.606881
Sum of electronic and thermal Free Energies=	-1748.701515

E(RB3LYP) = -1750.48230309

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1-CF2CF3-adduct

P	1.581513	0.400971	-0.103151
C	-2.883100	-0.343520	0.002539
C	-2.789919	0.174222	-1.313698
C	-3.177668	0.536653	1.074381
C	-2.984990	1.554465	-1.526391
H	-2.716442	-0.501886	-2.164367
C	-3.394759	1.881976	0.832203
H	-3.264573	0.135765	2.082413
C	-3.304046	2.393020	-0.469671
H	-2.917773	1.945047	-2.540298
H	-3.636793	2.543362	1.661751
H	-3.483035	3.451142	-0.651203
C	-2.989942	-1.821915	0.227507
F	-2.479198	-2.178050	1.429320
F	-2.344511	-2.527747	-0.729976
Pd	-0.726767	0.093431	-0.369973
C	2.116658	2.066209	-0.909998
C	2.592878	-1.021658	-0.911447
C	2.023021	0.470143	1.770512
C	0.932371	1.274824	2.492616
H	0.901678	2.329954	2.207254
H	-0.063391	0.847588	2.303268
H	1.125782	1.233215	3.576045
C	1.941489	-0.941663	2.359286
H	2.005256	-0.864027	3.455302
H	0.987292	-1.431938	2.118722
H	2.763721	-1.590880	2.038741
C	3.391731	1.059623	2.114328
H	3.550255	0.985522	3.201824
H	4.217272	0.526134	1.627684
H	3.472279	2.121536	1.852335
C	1.879787	-2.345216	-0.600218
H	2.381115	-3.154599	-1.153852
H	1.898838	-2.615529	0.459232
H	0.827534	-2.311865	-0.918284
C	2.534320	-0.873118	-2.434728
H	2.947606	-1.786046	-2.889935
H	1.501506	-0.764013	-2.794543
H	3.129289	-0.032456	-2.809246
C	4.059470	-1.126227	-0.491407
H	4.177269	-1.383053	0.568242
H	4.541779	-1.929934	-1.069747
H	4.622730	-0.203816	-0.681232
C	3.618475	2.259678	-1.124235
H	4.038638	1.542992	-1.840690
H	3.793574	3.264665	-1.539847
H	4.194862	2.188391	-0.193691
C	1.397641	2.198367	-2.259691
H	1.602719	3.199089	-2.671265
H	1.725811	1.466939	-3.002980
H	0.309782	2.091017	-2.138599
C	1.590913	3.223087	-0.054422
H	2.123764	3.333235	0.896758
H	1.731449	4.162201	-0.611030
H	0.515502	3.117978	0.152025
C	-4.440103	-2.334974	0.209496
F	-5.000685	-2.060699	-0.966071
F	-5.150312	-1.747696	1.168448
F	-4.475715	-3.648125	0.401374

TS-1-I-CF_2CF_3-RE

Zero-point correction= 0.486611 (Hartree/Particle)

```
 Thermal correction to Energy=                  0.518113
 Thermal correction to Enthalpy=                0.519058
 Thermal correction to Gibbs Free Energy=       0.425926
 Sum of electronic and zero-point Energies=         -1748.560620
 Sum of electronic and thermal Energies=            -1748.529117
 Sum of electronic and thermal Enthalpies=          -1748.528172
 Sum of electronic and thermal Free Energies=       -1748.621304
 E(RB3LYP) =  -1750.40701671

59
TS-1-I-CF2CF3-RE
P     1.588706    0.078131   -0.000970
C    -2.411841    0.327618   -0.085811
C    -2.731892    0.886426   -1.330340
C    -2.758999    1.000170    1.090625
C    -3.328500    2.141756   -1.388999
H    -2.498062    0.349663   -2.248213
C    -3.361291    2.252804    1.017284
H    -2.554216    0.547203    2.059070
C    -3.644901    2.828064   -0.218866
H    -3.552769    2.582987   -2.359316
H    -3.615479    2.779659    1.936181
H    -4.124494    3.803897   -0.271224
C    -2.677092   -1.630382    0.139093
F    -2.811094   -1.819458    1.473952
F    -2.114648   -2.799249   -0.361585
Pd   -0.659885   -0.715344   -0.064316
C     1.727886    1.750356   -0.938841
C     2.784356   -1.186673   -0.810151
C     2.123853    0.346703    1.825423
C     0.934854    0.949362    2.586189
H     0.634633    1.939723    2.232509
H     0.056691    0.291461    2.520510
H     1.211036    1.047817    3.647539
C     2.378587   -1.011702    2.487370
H     2.505964   -0.850211    3.568484
H     1.529364   -1.696884    2.358063
H     3.289668   -1.505109    2.130295
C     3.360071    1.220955    2.034105
H     3.599269    1.249946    3.108639
H     4.243538    0.830153    1.514602
H     3.204676    2.258028    1.714514
C     2.351738   -2.593288   -0.372670
H     2.949042   -3.334466   -0.925815
H     2.500020   -2.788022    0.692523
H     1.291875   -2.777150   -0.605657
C     2.594346   -1.154917   -2.329385
H     3.137939   -2.006241   -2.765984
H     1.537510   -1.260034   -2.612040
H     2.996573   -0.247830   -2.793832
C     4.270145   -0.994229   -0.504527
H     4.509134   -1.146821    0.554763
H     4.850192   -1.738151   -1.072631
H     4.637166   -0.002458   -0.795630
C     3.149328    2.207328   -1.271777
H     3.652908    1.536211   -1.978623
H     3.099329    3.196682   -1.752860
H     3.786977    2.309949   -0.385598
C     0.919987    1.647645   -2.239974
H     0.903019    2.638972   -2.718533
H     1.338697    0.944729   -2.965419
H    -0.118048    1.351697   -2.036764
C     1.038853    2.844830   -0.116163
```

H	1.588390	3.116582	0.792419
H	0.980244	3.753204	-0.734689
H	0.010267	2.568938	0.158273
C	-4.107794	-1.732587	-0.435906
F	-4.079089	-1.634980	-1.764275
F	-4.926541	-0.808041	0.048733
F	-4.619145	-2.923333	-0.121452

TS-1-isom-CF_2CF_3

Zero-point correction=	0.487291 (Hartree/Particle)
Thermal correction to Energy=	0.518703
Thermal correction to Enthalpy=	0.519647
Thermal correction to Gibbs Free Energy=	0.426653
Sum of electronic and zero-point Energies=	-1748.582697
Sum of electronic and thermal Energies=	-1748.551285
Sum of electronic and thermal Enthalpies=	-1748.550341
Sum of electronic and thermal Free Energies=	-1748.643336

E(RB3LYP) = -1750.44110870

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TS-1-isom-CF2CF3

P	1.627649	0.182247	0.016374
C	-2.425540	1.221810	0.363827
C	-2.681925	2.150592	-0.647889
C	-3.054914	1.342413	1.601731
C	-3.542966	3.219394	-0.402699
H	-2.214555	2.040982	-1.628574
C	-3.909735	2.419555	1.839613
H	-2.885556	0.600192	2.381436
C	-4.154723	3.357655	0.841021
H	-3.738844	3.944578	-1.192331
H	-4.390955	2.518521	2.812434
H	-4.828803	4.192045	1.028468
C	-2.241532	-1.463674	-0.069059
F	-2.958989	-1.751742	1.042400
F	-1.434359	-2.555754	-0.294854
Pd	-0.874322	-0.000111	0.090604
C	2.380493	-0.487085	1.647048
C	2.099129	2.031452	-0.192024
C	2.315130	-0.821648	-1.467441
C	1.622540	-1.769710	2.019636
H	0.541191	-1.584826	2.100981
H	1.771032	-2.591788	1.314897
H	1.978427	-2.115567	3.002205
C	2.094932	0.499921	2.783415
H	1.027828	0.756082	2.848779
H	2.373458	0.019320	3.733199
H	2.677472	1.425471	2.712059
C	3.882352	-0.770346	1.612817
H	4.474656	0.115823	1.351850
H	4.206512	-1.098901	2.612380
H	4.144649	-1.573161	0.913790
C	3.556357	2.369015	0.118626
H	4.263939	1.804635	-0.501140
H	3.724832	3.438420	-0.081785
H	3.811945	2.197950	1.171051
C	1.178482	2.864082	0.712000
H	1.318577	2.674737	1.779203
H	1.392574	3.929982	0.539639
H	0.116769	2.698795	0.475448
C	1.784816	2.480023	-1.622483
H	0.754134	2.233594	-1.915504
H	1.883906	3.574797	-1.669365

H	2.473140	2.065959	-2.367922
C	3.752634	-0.493009	-1.868616
H	4.465315	-0.646288	-1.048732
H	4.053119	-1.158320	-2.692758
H	3.865611	0.535272	-2.232458
C	1.383504	-0.597147	-2.666963
H	1.383880	0.430302	-3.039602
H	1.717305	-1.242598	-3.493645
H	0.345669	-0.870115	-2.426652
C	2.222827	-2.318502	-1.155179
H	2.937005	-2.647833	-0.392367
H	1.209762	-2.612214	-0.847772
H	2.459179	-2.875455	-2.074197
C	-3.225559	-1.449048	-1.240589
F	-3.756716	-2.659977	-1.427123
F	-4.220609	-0.597750	-1.027392
F	-2.600848	-1.098678	-2.368309

1-III-CF_2CF_3

Zero-point correction=	0.488174	(Hartree/Particle)
Thermal correction to Energy=	0.519861	
Thermal correction to Enthalpy=	0.520805	
Thermal correction to Gibbs Free Energy=	0.427892	
Sum of electronic and zero-point Energies=	-1748.587016	
Sum of electronic and thermal Energies=	-1748.555329	
Sum of electronic and thermal Enthalpies=	-1748.554385	
Sum of electronic and thermal Free Energies=	-1748.647298	

E(RB3LYP) = -1750.44743378

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1-III-CF2CF3

P	1.590263	-0.020577	-0.076939
C	-2.745206	0.770620	0.266528
C	-3.191521	1.695873	-0.684693
C	-3.473295	0.605207	1.447200
C	-4.325545	2.469841	-0.440146
H	-2.654006	1.815409	-1.629489
C	-4.604548	1.383627	1.691710
H	-3.159239	-0.139812	2.180002
C	-5.031351	2.316989	0.750491
H	-4.662915	3.188895	-1.186727
H	-5.158636	1.254573	2.621508
H	-5.918581	2.919074	0.941716
C	-1.614696	-1.760421	-0.239821
F	-2.229955	-2.263366	0.860940
F	-0.572752	-2.608314	-0.503868
Pd	-0.864893	0.087841	0.033300
C	2.325426	-0.590650	1.595973
C	1.856768	1.873154	-0.274497
C	2.498673	-0.922466	-1.504945
C	1.702226	-1.956036	1.920538
H	0.606830	-1.888988	1.969106
H	1.957699	-2.741972	1.204891
H	2.063301	-2.280790	2.908452
C	1.863730	0.344392	2.717932
H	0.770064	0.453085	2.740628
H	2.163993	-0.100342	3.678619
H	2.320580	1.339466	2.672360
C	3.850268	-0.688150	1.648030
H	4.339224	0.271282	1.437990
H	4.152772	-0.994497	2.661325
H	4.253953	-1.435725	0.955348
C	3.220879	2.415787	0.146667

H	4.042641	1.952077	-0.411893
H	3.257757	3.498118	-0.053280
H	3.418245	2.281914	1.216909
C	0.756038	2.559389	0.550187
H	0.805374	2.363926	1.624172
H	0.826122	3.649373	0.409417
H	-0.260933	2.289573	0.197020
C	1.587592	2.292978	-1.724193
H	0.609224	1.940779	-2.082323
H	1.571835	3.392487	-1.766601
H	2.357697	1.959231	-2.427511
C	3.881448	-0.358130	-1.838217
H	4.564907	-0.383006	-0.980076
H	4.331797	-0.975034	-2.631123
H	3.848205	0.669822	-2.216858
C	1.593773	-0.856469	-2.742694
H	1.407926	0.160436	-3.100465
H	2.081062	-1.405836	-3.562790
H	0.623554	-1.332996	-2.551533
C	2.662184	-2.412746	-1.188489
H	3.390844	-2.610050	-0.394386
H	1.710779	-2.886626	-0.924698
H	3.036801	-2.911612	-2.094804
C	-2.576287	-1.968668	-1.416308
F	-2.732318	-3.273091	-1.660523
F	-3.776581	-1.458110	-1.181041
F	-2.082105	-1.403473	-2.522422

TS-1-III-CF_2CF_3-RE

Zero-point correction=	0.487320	(Hartree/Particle)
Thermal correction to Energy=	0.518475	
Thermal correction to Enthalpy=	0.519419	
Thermal correction to Gibbs Free Energy=	0.427410	
Sum of electronic and zero-point Energies=	-1748.560210	
Sum of electronic and thermal Energies=	-1748.529056	
Sum of electronic and thermal Enthalpies=	-1748.528112	
Sum of electronic and thermal Free Energies=	-1748.620121	
E(RB3LYP) = -1750.40833954		

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TS-1-III-CF2CF3-RE

P	1.644674	0.165543	-0.014929
C	-2.745049	0.192267	-0.045736
C	-3.225782	0.771776	-1.225700
C	-3.308197	0.522435	1.190138
C	-4.239571	1.723245	-1.153735
H	-2.808943	0.483370	-2.189625
C	-4.321372	1.475795	1.247240
H	-2.954136	0.034083	2.096775
C	-4.788243	2.072248	0.078506
H	-4.607120	2.188847	-2.067137
H	-4.753585	1.747166	2.209328
H	-5.590798	2.806319	0.127036
C	-2.148075	-1.752535	-0.063216
F	-2.262152	-2.132322	1.233228
F	-1.173260	-2.568811	-0.616926
Pd	-0.743606	-0.027152	-0.053116
C	2.394806	-0.629188	1.563389
C	2.059874	2.042240	-0.013870
C	2.455715	-0.639937	-1.559306
C	1.697903	-1.977760	1.792198
H	0.609933	-1.849676	1.879621
H	1.884280	-2.712890	1.004890

H	2.066860	-2.407228	2.736509
C	2.030604	0.226576	2.780852
H	0.953002	0.438667	2.825575
H	2.291979	-0.336482	3.689661
H	2.580362	1.173474	2.824928
C	3.910260	-0.829750	1.551779
H	4.457858	0.105416	1.381001
H	4.226358	-1.220950	2.531430
H	4.236345	-1.557268	0.799456
C	3.488372	2.418422	0.377809
H	4.243012	1.952952	-0.267911
H	3.607788	3.509347	0.287063
H	3.722307	2.158172	1.416864
C	1.074938	2.745469	0.932736
H	1.230826	2.504578	1.987673
H	1.198125	3.834303	0.825347
H	0.031030	2.499355	0.682185
C	1.767757	2.619557	-1.403153
H	0.751122	2.373827	-1.741903
H	1.838928	3.716231	-1.345482
H	2.482534	2.293643	-2.166927
C	3.884272	-0.192249	-1.868062
H	4.576112	-0.385207	-1.039129
H	4.253459	-0.755247	-2.739521
H	3.949140	0.871868	-2.124430
C	1.556806	-0.350813	-2.770430
H	1.493076	0.709372	-3.030760
H	1.967310	-0.878635	-3.645212
H	0.534629	-0.719845	-2.601304
C	2.444085	-2.163931	-1.402279
H	3.162805	-2.530977	-0.660796
H	1.445035	-2.540149	-1.145577
H	2.726118	-2.612172	-2.366959
C	-3.403184	-2.313440	-0.770287
F	-3.420346	-3.641149	-0.650725
F	-4.541420	-1.859061	-0.260190
F	-3.362464	-2.016473	-2.069279

Carbene species of Figure 3

TS-1/B-CF_2CF_3

Zero-point correction=	0.486421 (Hartree/Particle)
Thermal correction to Energy=	0.518351
Thermal correction to Enthalpy=	0.519295
Thermal correction to Gibbs Free Energy=	0.426044
Sum of electronic and zero-point Energies=	-1748.530460
Sum of electronic and thermal Energies=	-1748.498530
Sum of electronic and thermal Enthalpies=	-1748.497586
Sum of electronic and thermal Free Energies=	-1748.590837

E(RB3LYP) = -1750.39888420

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TS-1/B-CF2CF3

P	1.327562	0.202185	0.198703
C	-1.988622	0.829285	-0.366082
C	-2.350898	0.705389	-1.710081
C	-2.402081	1.956094	0.348296
C	-3.049645	1.728921	-2.349528
H	-2.068223	-0.187189	-2.273090
C	-3.097268	2.981174	-0.293796
H	-2.165483	2.045755	1.411004
C	-3.415071	2.873499	-1.645540
H	-3.312693	1.627929	-3.402156

H	-3.395078	3.865828	0.268633
H	-3.958149	3.673976	-2.145439
C	-2.706883	-1.412567	0.845025
F	-3.648027	-0.997313	1.628465
F	-0.341957	-2.325562	1.671961
Pd	-0.983866	-0.665601	0.595728
C	1.606967	2.011431	-0.413083
C	2.138816	-0.995786	-1.057247
C	2.202608	0.027667	1.909928
C	1.218679	0.550726	2.968035
H	0.943472	1.602122	2.835024
H	0.297937	-0.048909	2.981775
H	1.688228	0.455465	3.959215
C	2.441982	-1.448851	2.248333
H	2.801358	-1.494864	3.288214
H	1.514124	-2.027681	2.178806
H	3.217568	-1.910716	1.626681
C	3.539157	0.756119	2.050055
H	3.942563	0.535515	3.050151
H	4.281588	0.409191	1.320660
H	3.460915	1.845977	1.973139
C	1.565122	-2.399380	-0.816535
H	2.091862	-3.103129	-1.479687
H	1.655919	-2.757586	0.211531
H	0.496545	-2.435044	-1.072875
C	1.722456	-0.617077	-2.481168
H	2.021295	-1.435677	-3.153309
H	0.633444	-0.499419	-2.575738
H	2.211543	0.292671	-2.847500
C	3.666836	-1.051647	-1.002721
H	4.043341	-1.459472	-0.058484
H	4.020761	-1.718522	-1.804012
H	4.135255	-0.074228	-1.163348
C	3.040879	2.307410	-0.867168
H	3.292184	1.788702	-1.801439
H	3.118903	3.385900	-1.074256
H	3.806614	2.065503	-0.123073
C	0.676355	2.363487	-1.582043
H	0.927732	3.384170	-1.908685
H	0.780008	1.712995	-2.453540
H	-0.372881	2.363287	-1.278487
C	1.219417	2.982521	0.707846
H	1.906548	2.971685	1.559524
H	1.230480	4.003667	0.298168
H	0.200902	2.791255	1.072646
C	-3.184479	-2.727055	0.209383
F	-2.285336	-3.199864	-0.633318
F	-4.308077	-2.472276	-0.462513
F	-3.428559	-3.626099	1.151137

B-CF_2CF_3

Zero-point correction=	0.489705 (Hartree/Particle)
Thermal correction to Energy=	0.521233
Thermal correction to Enthalpy=	0.522177
Thermal correction to Gibbs Free Energy=	0.430207
Sum of electronic and zero-point Energies=	-1748.614491
Sum of electronic and thermal Energies=	-1748.582963
Sum of electronic and thermal Enthalpies=	-1748.582019
Sum of electronic and thermal Free Energies=	-1748.673989

E(RB3LYP) = -1750.47859557

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B-CF2CF3

P	1.374105	0.257520	0.292417
C	-2.999269	0.427426	-0.330422
C	-2.322517	0.263773	-1.569016
C	-3.466456	1.721035	0.025420
C	-2.211825	1.350678	-2.450614
H	-2.039594	-0.728484	-1.912847
C	-3.338475	2.769169	-0.856520
H	-3.950917	1.855055	0.989226
C	-2.719445	2.586229	-2.105935
H	-1.732381	1.202056	-3.416848
H	-3.728263	3.748574	-0.586042
H	-2.640470	3.422296	-2.797994
C	-3.008452	-0.655539	0.634985
F	-3.607205	-0.352727	1.814754
F	-0.680765	-1.484200	2.135184
Pd	-1.002129	-0.270531	0.555419
C	1.703878	2.103103	-0.130688
C	1.988934	-0.837304	-1.160613
C	2.378627	-0.182228	1.868823
C	1.601719	0.333108	3.089443
H	1.496874	1.420639	3.123581
H	0.609823	-0.131534	3.122389
H	2.152608	0.033503	3.994611
C	2.435521	-1.705385	2.037435
H	2.875157	-1.915453	3.024446
H	1.428992	-2.139039	2.023064
H	3.072844	-2.201767	1.296981
C	3.807609	0.363941	1.899464
H	4.301478	-0.019144	2.805894
H	4.411634	0.042834	1.041476
H	3.848682	1.458222	1.957794
C	1.324960	-2.214753	-1.019313
H	1.619857	-2.835918	-1.879208
H	1.611436	-2.749362	-0.110411
H	0.227356	-2.139681	-1.018220
C	1.492363	-0.267194	-2.493222
H	1.693633	-1.008019	-3.281837
H	0.409271	-0.082745	-2.485879
H	2.004733	0.656974	-2.785043
C	3.505789	-1.008299	-1.257437
H	3.927885	-1.545635	-0.400838
H	3.740400	-1.601088	-2.155272
H	4.031088	-0.049516	-1.351894
C	3.074190	2.407554	-0.736780
H	3.208565	1.945207	-1.722119
H	3.163193	3.495763	-0.880274
H	3.907776	2.095001	-0.097517
C	0.613764	2.579391	-1.094317
H	0.747552	3.657744	-1.272689
H	0.634943	2.084327	-2.069055
H	-0.384809	2.432886	-0.661532
C	1.519016	2.954666	1.129356
H	2.312106	2.814889	1.870349
H	1.536790	4.014861	0.834819
H	0.549347	2.764857	1.611785
C	-3.426113	-2.058945	0.263533
F	-2.726242	-2.536937	-0.775796
F	-4.720645	-2.082338	-0.092655
F	-3.275956	-2.894590	1.279236

TS-B-CF_2CF_3-RE

Zero-point correction= 0.488844 (Hartree/Particle)
Thermal correction to Energy= 0.519553

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 Thermal correction to Enthalpy=                0.520497
 Thermal correction to Gibbs Free Energy=       0.431583
 Sum of electronic and zero-point Energies=          -1748.576344
 Sum of electronic and thermal Energies=             -1748.545635
 Sum of electronic and thermal Enthalpies=           -1748.544691
 Sum of electronic and thermal Free Energies=        -1748.633605
 E(RB3LYP) =  -1750.43020172

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TS-B-CF2CF3-RE
P     1.398068    0.346266    0.127188
C    -3.023235    0.323349   -0.063791
C    -2.363757    0.069263   -1.316839
C    -3.466903    1.656444    0.213932
C    -2.331628    1.092886   -2.290966
H    -2.173569   -0.955606   -1.636553
C    -3.381991    2.628333   -0.749276
H    -3.904417    1.872020    1.185009
C    -2.827259    2.346074   -2.017627
H    -1.904682    0.870585   -3.267653
H    -3.757914    3.627183   -0.536160
H    -2.791318    3.125345   -2.776384
C    -3.118368   -0.677611    0.954487
F    -3.964117   -0.381582    1.927788
F    -1.753209   -0.964268    2.315403
Pd   -0.909095    0.031662    0.441857
C     1.850984    2.181705   -0.206013
C     2.087208   -0.729845   -1.307063
C     2.223997   -0.211331    1.772352
C     1.346957    0.301340    2.925748
H     1.311368    1.391724    2.998156
H     0.314706   -0.074072    2.850360
H     1.766834   -0.074106    3.872220
C     2.167314   -1.739115    1.871239
H     2.462546   -2.028786    2.890982
H     1.150867   -2.124281    1.708383
H     2.856542   -2.243145    1.184404
C     3.669521    0.235148    1.990769
H     4.034053   -0.193331    2.937568
H     4.345858   -0.108223    1.197896
H     3.770995    1.323998    2.077219
C     1.360375   -2.081755   -1.282631
H     1.713445   -2.684699   -2.133784
H     1.535132   -2.663600   -0.374043
H     0.275517   -1.948070   -1.393169
C     1.709402   -0.093896   -2.646960
H     1.930750   -0.813878   -3.449365
H     0.635325    0.133305   -2.693208
H     2.273410    0.818395   -2.871689
C     3.597324   -0.968557   -1.284583
H     3.918062   -1.556385   -0.416100
H     3.881406   -1.541471   -2.181157
H     4.174388   -0.035946   -1.296753
C     3.279661    2.427793   -0.691683
H     3.471436    1.990075   -1.679321
H     3.444006    3.512667   -0.785579
H     4.034675    2.042256    0.003906
C     0.859053    2.742462   -1.233593
H     1.043655    3.822257   -1.344889
H     0.952507    2.294237   -2.227191
H    -0.178204    2.604815   -0.897748
C     1.618077    2.999320    1.067884
H     2.346785    2.789893    1.858222
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H	1.716100	4.066328	0.817105
H	0.606008	2.848686	1.469650
C	-3.189808	-2.170739	0.632664
F	-2.059934	-2.660253	0.124915
F	-4.146450	-2.348382	-0.295004
F	-3.525884	-2.877953	1.692509

Other species

$PhCF_3$

```
 Zero-point correction=                           0.105711 (Hartree/Particle)
 Thermal correction to Energy=                    0.113509
 Thermal correction to Enthalpy=                  0.114453
 Thermal correction to Gibbs Free Energy=         0.072195
 Sum of electronic and zero-point Energies=           -568.883030
 Sum of electronic and thermal Energies=              -568.875232
 Sum of electronic and thermal Enthalpies=            -568.874288
 Sum of electronic and thermal Free Energies=         -568.916546
 E(RB3LYP) =  -569.486232937
```

15

PhCF3

C	0.758996	1.226327	-0.009425
C	2.150148	1.196546	0.000595
C	2.821991	-0.021286	0.005922
C	2.104945	-1.216204	0.000560
C	0.717263	-1.191334	-0.010199
C	0.047806	0.031830	-0.016044
H	0.227788	2.174829	-0.014093
H	2.710170	2.129578	0.003714
H	3.910206	-0.041835	0.013718
H	2.630373	-2.169151	0.003583
H	0.143889	-2.117333	-0.018094
C	-1.447742	0.013178	-0.001256
F	-1.937829	-0.757891	-0.983065
F	-1.916821	-0.495609	1.148185
F	-1.981213	1.230098	-0.143825

PhC_2F_5

```
 Zero-point correction=                           0.118827 (Hartree/Particle)
 Thermal correction to Energy=                    0.129351
 Thermal correction to Enthalpy=                  0.130296
 Thermal correction to Gibbs Free Energy=         0.081608
 Sum of electronic and zero-point Energies=           -806.571230
 Sum of electronic and thermal Energies=              -806.560706
 Sum of electronic and thermal Enthalpies=            -806.559762
 Sum of electronic and thermal Free Energies=         -806.608450
 E(RB3LYP) =  -807.352877066
```

18

PhC2F5

C	-0.060667	-0.132042	-0.108163
C	1.322627	-0.182524	0.082557
C	2.057347	0.989898	0.179001
C	1.413831	2.222127	0.085265
C	0.037488	2.273727	-0.100383
C	-0.704729	1.100114	-0.195120
H	1.817915	-1.149831	0.150772
H	3.134639	0.943183	0.324685
H	1.988635	3.143686	0.156142
H	-0.468175	3.234413	-0.174132
H	-1.779623	1.166594	-0.337572
C	-0.760998	-1.456586	-0.182464

F	-0.139199	-2.257729	-1.082595
F	-0.695248	-2.090980	1.014047
C	-2.241521	-1.455016	-0.581591
F	-2.969656	-0.790810	0.314446
F	-2.400213	-0.885187	-1.772864
F	-2.694073	-2.700224	-0.644199

$PtBu_3$

Zero-point correction= 0.369100 (Hartree/Particle)
Thermal correction to Energy= 0.386627
Thermal correction to Enthalpy= 0.387571
Thermal correction to Gibbs Free Energy= 0.328128
Sum of electronic and zero-point Energies= -814.078302
Sum of electronic and thermal Energies= -814.060775
Sum of electronic and thermal Enthalpies= -814.059831
Sum of electronic and thermal Free Energies= -814.119274
E(RB3LYP) = -815.094980997

40

PtBu3

P	-0.002243	0.001202	-0.723292
C	-1.739251	0.439842	0.001392
C	1.246613	1.285132	-0.004367
C	0.490472	-1.723972	-0.008011
C	-2.777396	-0.294250	-0.860440
H	-2.638919	-0.068952	-1.926847
H	-2.755412	-1.380981	-0.741154
H	-3.786449	0.042529	-0.574471
C	-2.013416	1.929787	-0.228872
H	-1.832083	2.221393	-1.273209
H	-3.074108	2.131803	-0.012624
H	-1.425199	2.586288	0.422699
C	-1.994405	0.124026	1.474082
H	-1.284790	0.628116	2.141691
H	-3.005451	0.465277	1.751033
H	-1.952743	-0.951200	1.688151
C	1.091059	1.680829	1.463629
H	1.154164	0.819105	2.139722
H	1.899973	2.376613	1.740914
H	0.144923	2.198456	1.663896
C	1.142785	2.541899	-0.881431
H	0.182495	3.057037	-0.796358
H	1.923633	3.257667	-0.579238
H	1.302669	2.300007	-1.941184
C	2.675383	0.773836	-0.214417
H	2.849327	0.458295	-1.252828
H	3.377666	1.594602	-0.000747
H	2.941971	-0.054237	0.451895
C	0.901819	-1.801810	1.461512
H	0.112076	-1.453344	2.137835
H	1.118288	-2.850839	1.722233
H	1.809745	-1.227523	1.679883
C	1.639018	-2.248599	-0.883430
H	2.566567	-1.678100	-0.779562
H	1.864041	-3.288596	-0.598213
H	1.359879	-2.246319	-1.946103
C	-0.663579	-2.706441	-0.231983
H	-1.513434	-2.532510	0.437815
H	-1.025592	-2.686371	-1.269607
H	-0.301749	-3.726937	-0.030938

10. References

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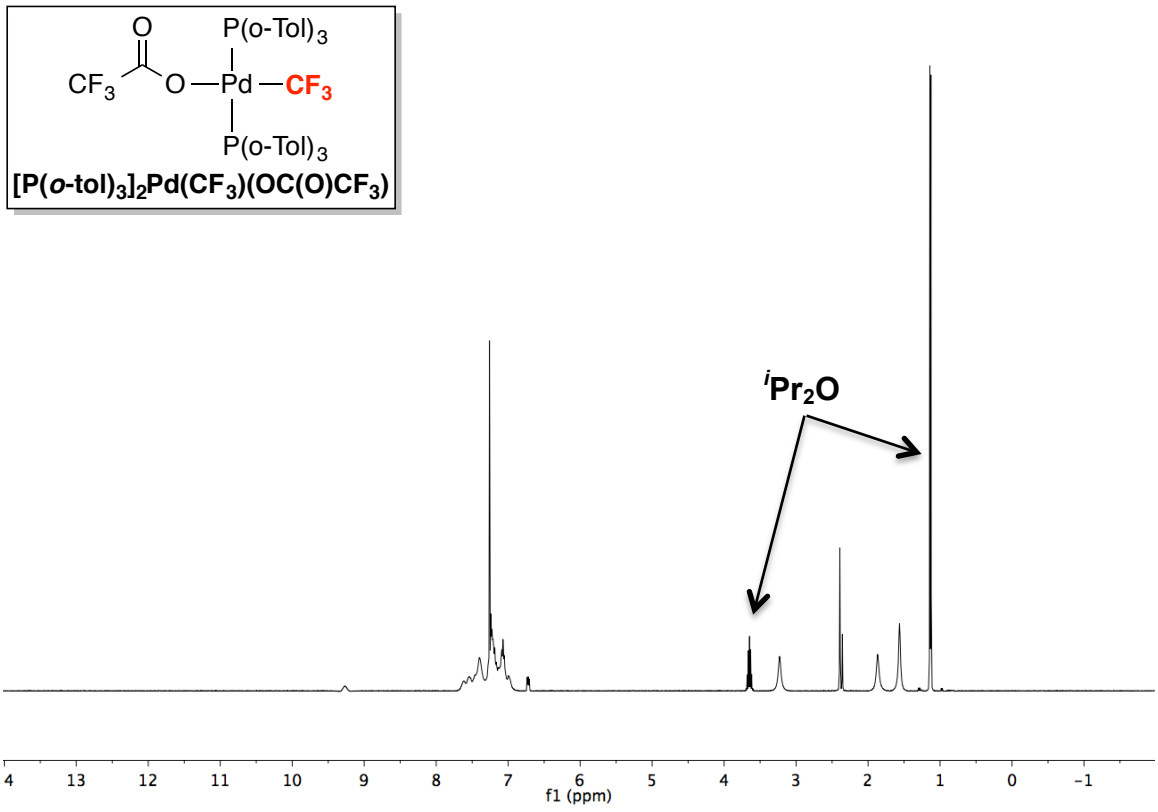
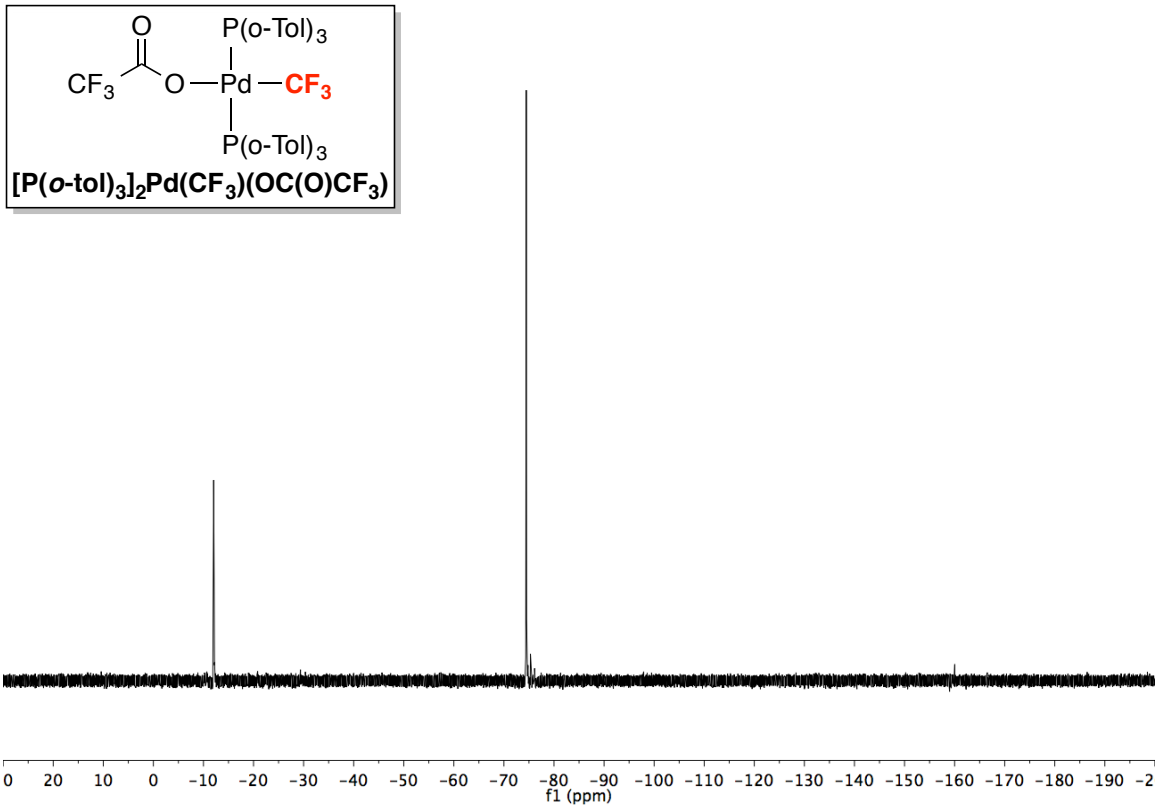
11. NMR Spectra

i. *[P(o-tol)$_3$]$_2$Pd(CF$_3$)(OC(O)CF$_3$)*

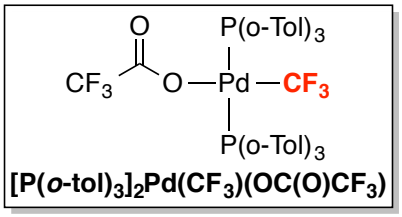
^{1}H NMR at 23 ºC ($CDCl_3$)



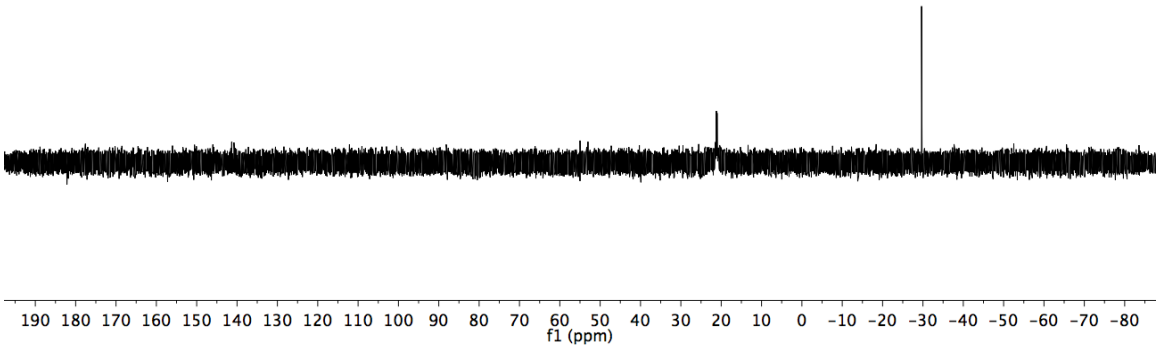
^{19}F NMR at 23 ºC ($CDCl_3$)



^{31}P NMR at 23 °C ($CDCl_3$)

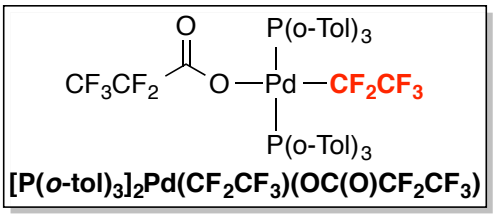


[P(*o*-tol)$_3$]$_2$Pd(CF$_3$)(OC(O)CF$_3$)

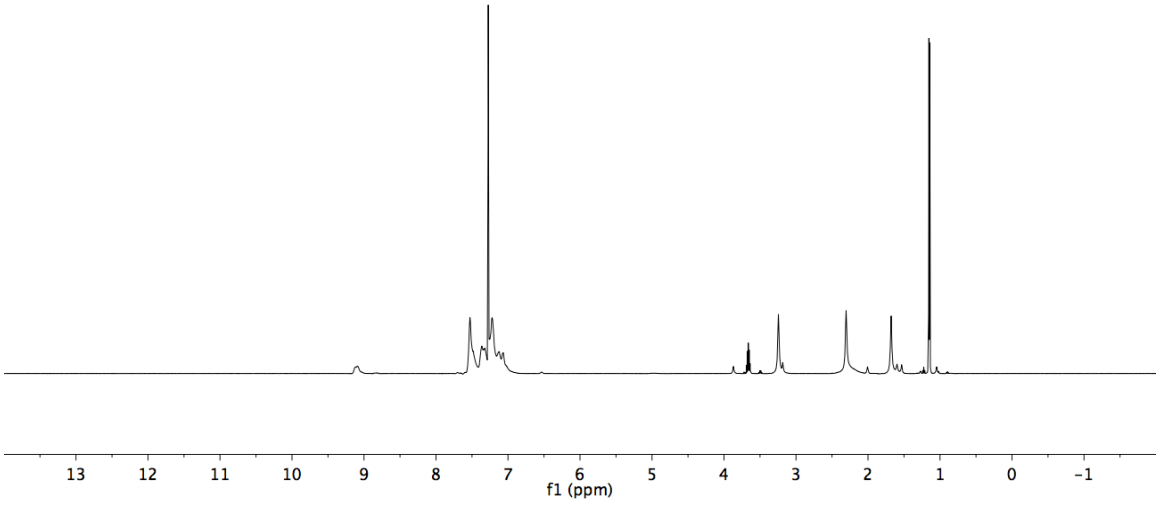


ii. [P(o-tol)$_3$]$_2$Pd(CF$_2$CF$_3$)(OC(O)CF$_2$CF$_3$)

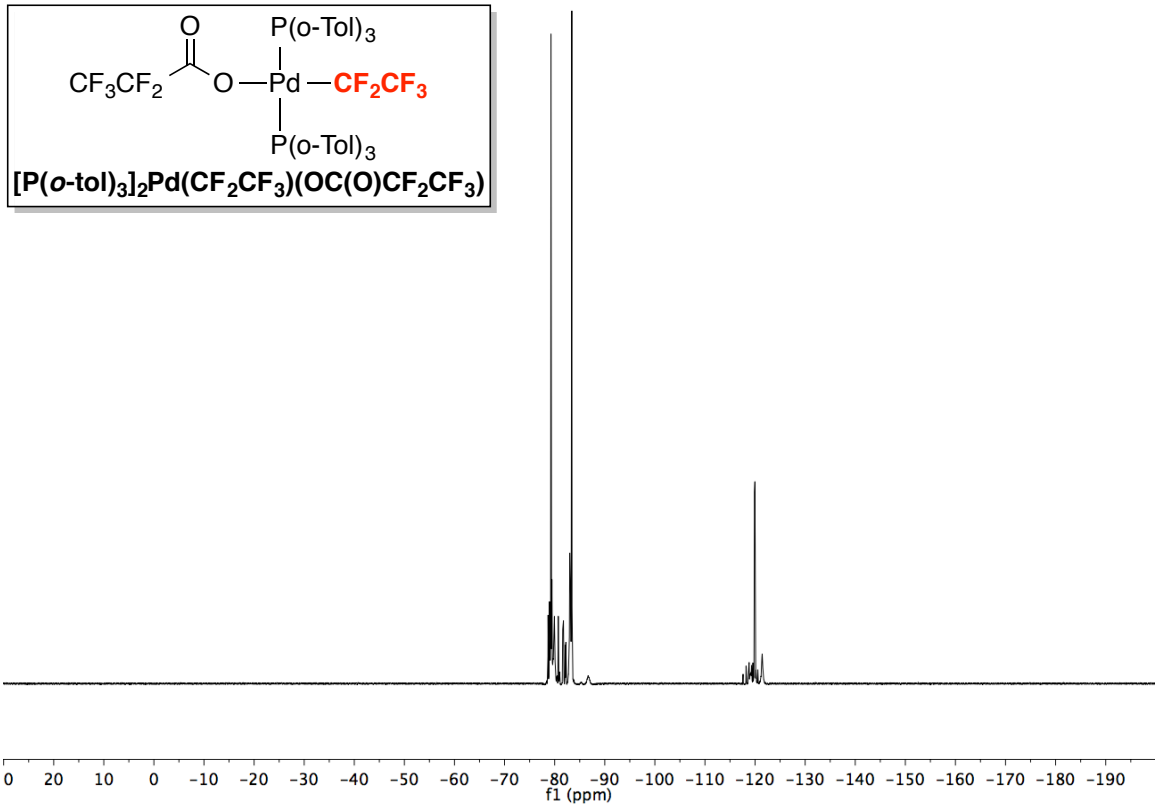
^{1}H NMR at 23 ºC (CDCl$_3$)



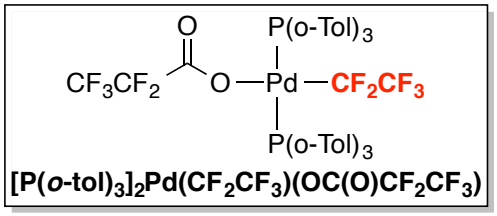
[P(*o*-tol)$_3$]$_2$Pd(CF$_2$CF$_3$)(OC(O)CF$_2$CF$_3$)



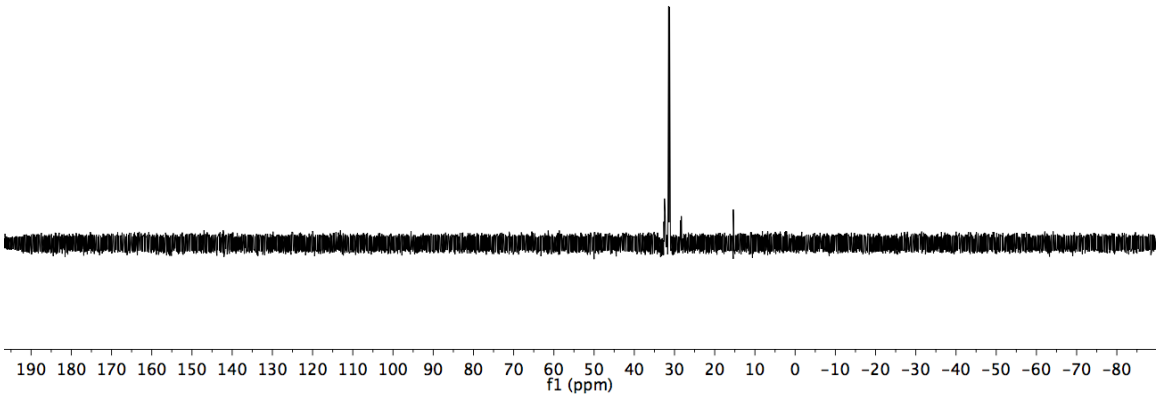
^{19}F NMR at 23 ºC ($CDCl_3$)



^{31}P NMR at 23 ºC ($CDCl_3$)

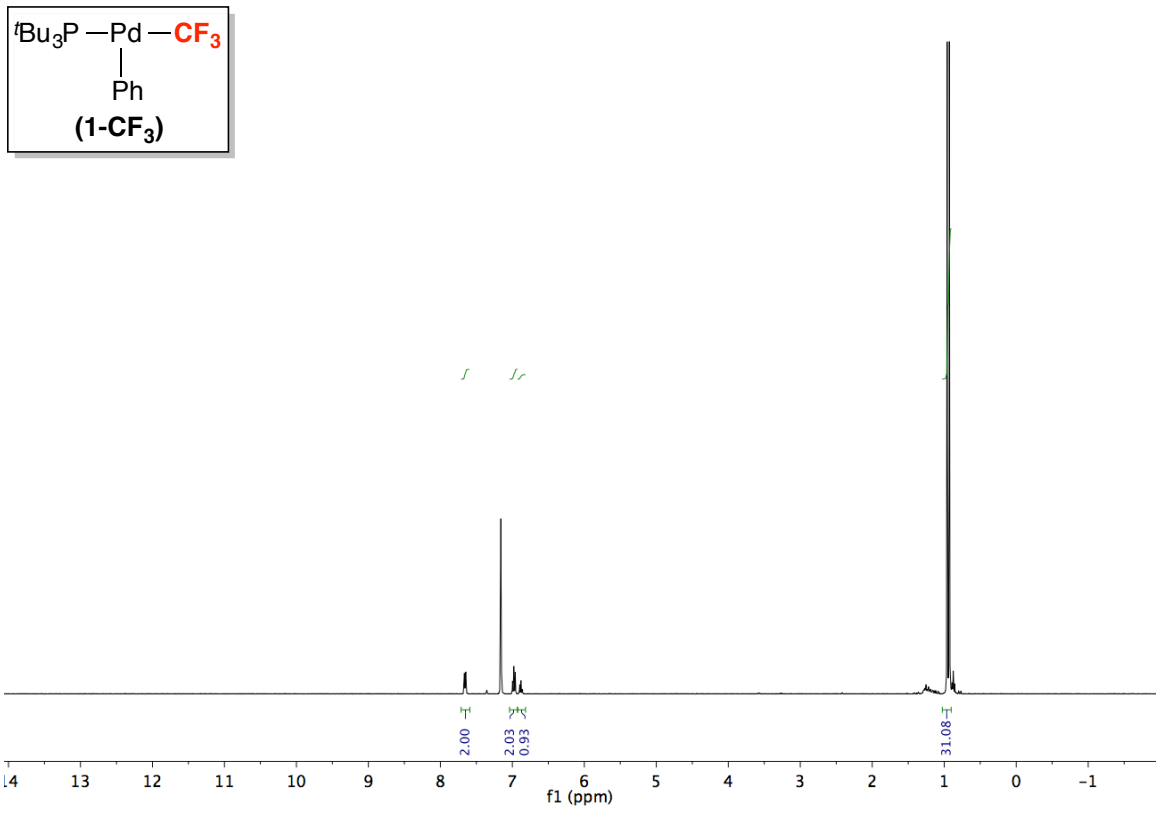


[P(*o*-tol)$_3$]$_2$Pd(CF_2CF_3)(OC(O)CF_2CF_3)

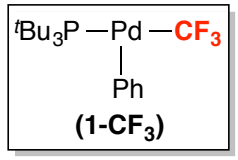


iii. *(P^tBu_3)Pd(Ph)(CF_3)* (***1-CF_3***)

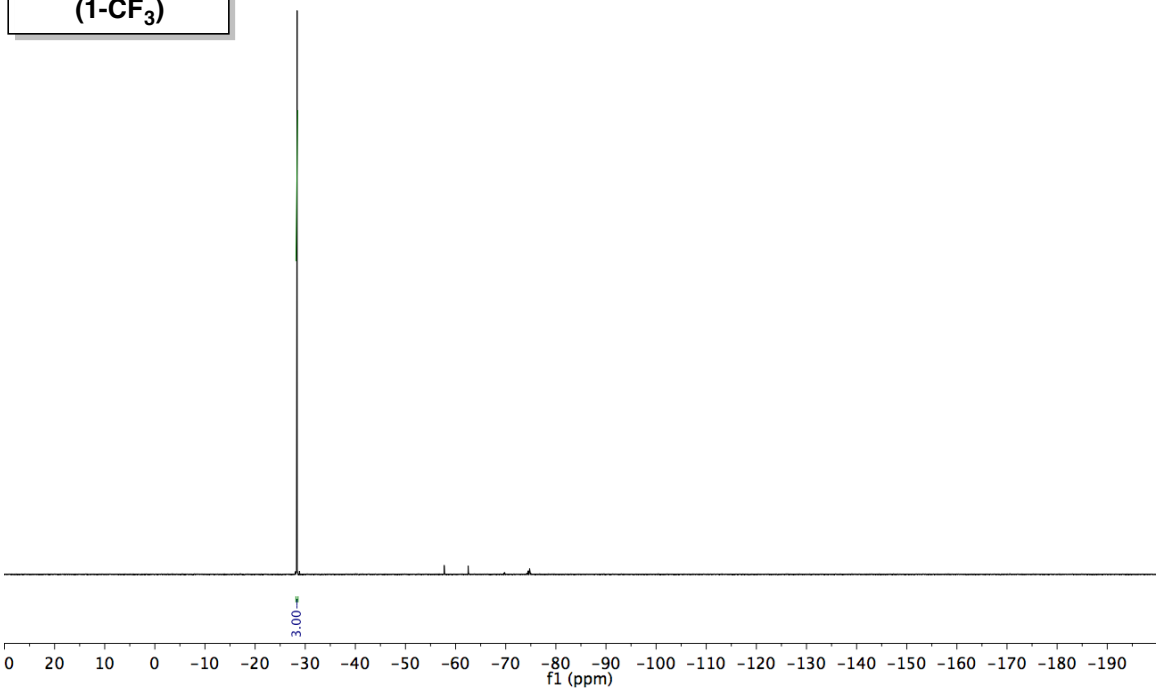
^{1}H NMR at 23 ºC (C_6D_6)

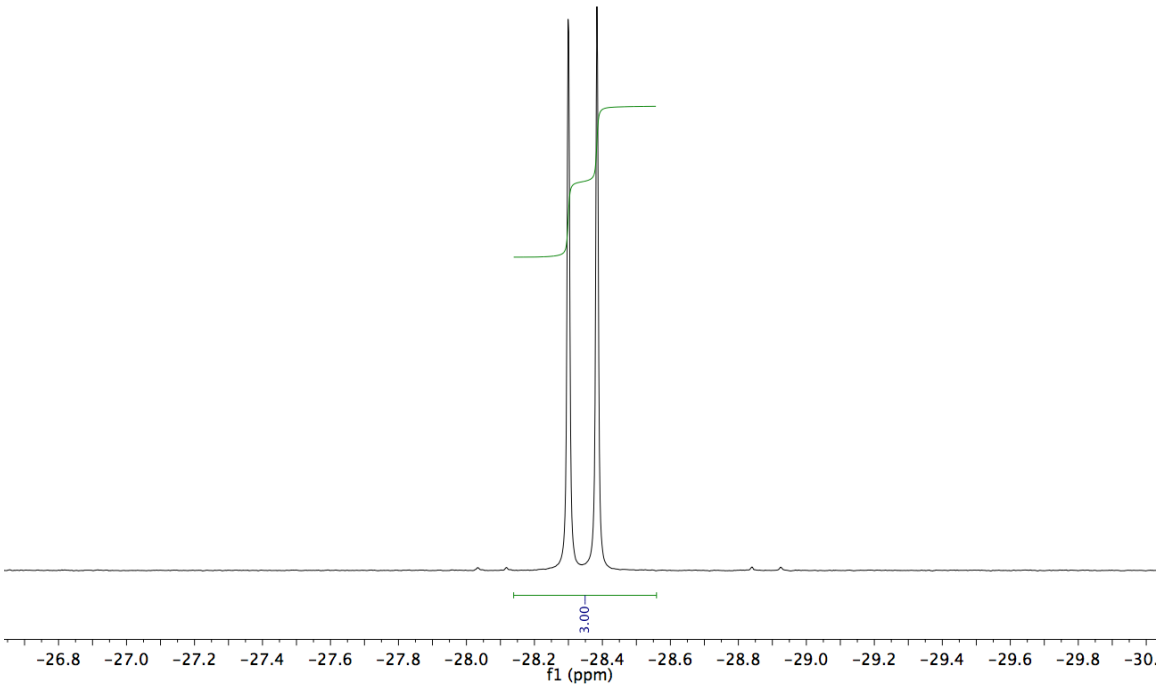


^{19}F NMR at 23 ºC (C_6D_6)

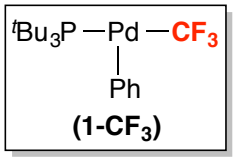


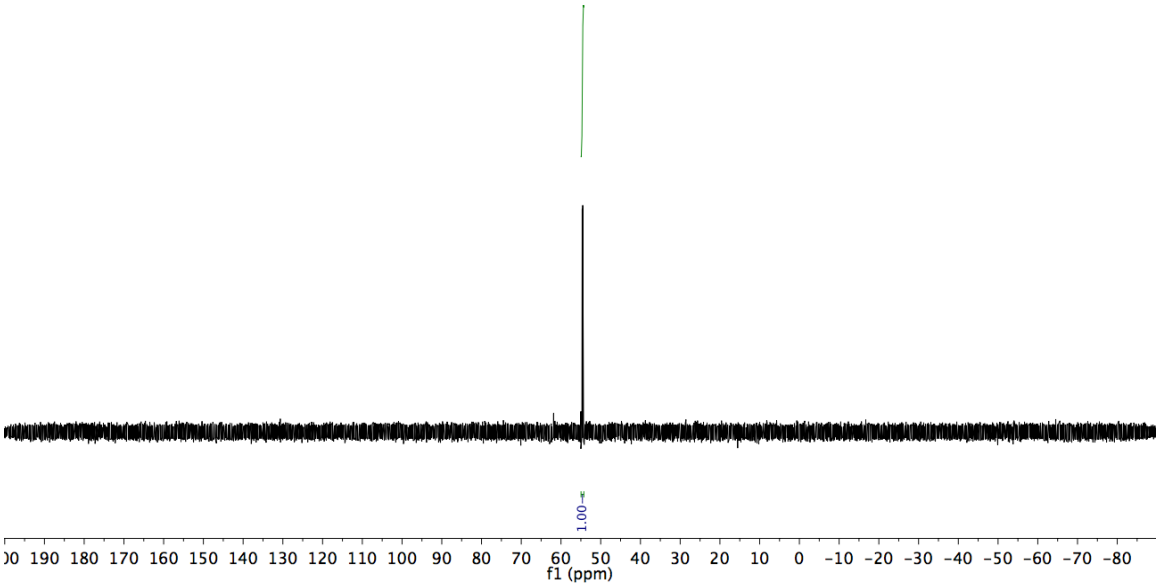
(1-CF_3)

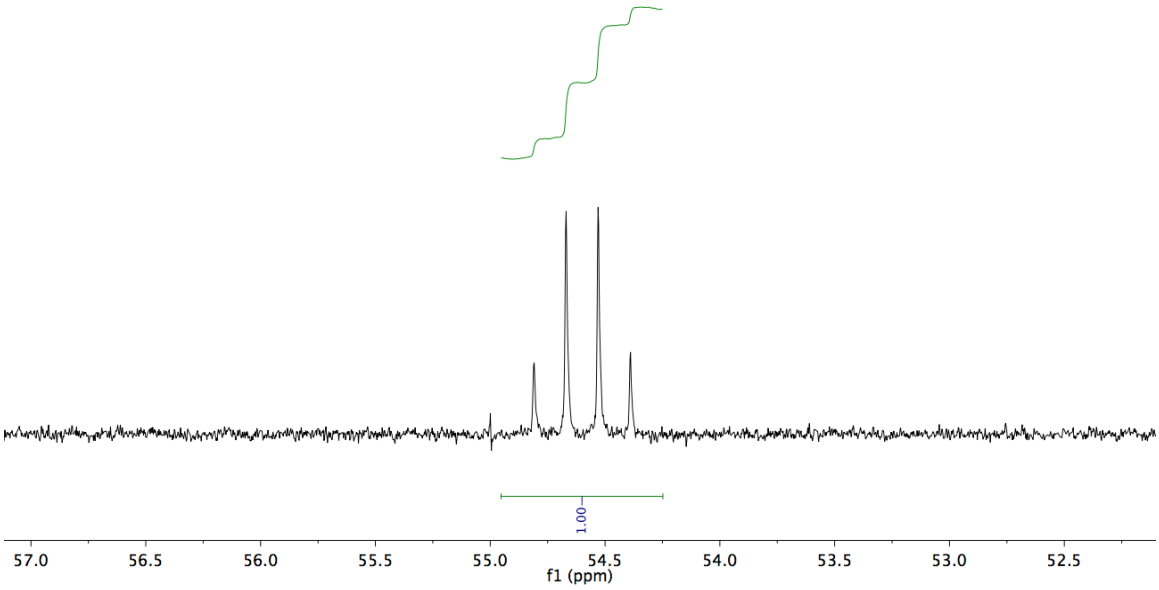




^{31}P NMR at 23 ºC (C_6D_6)

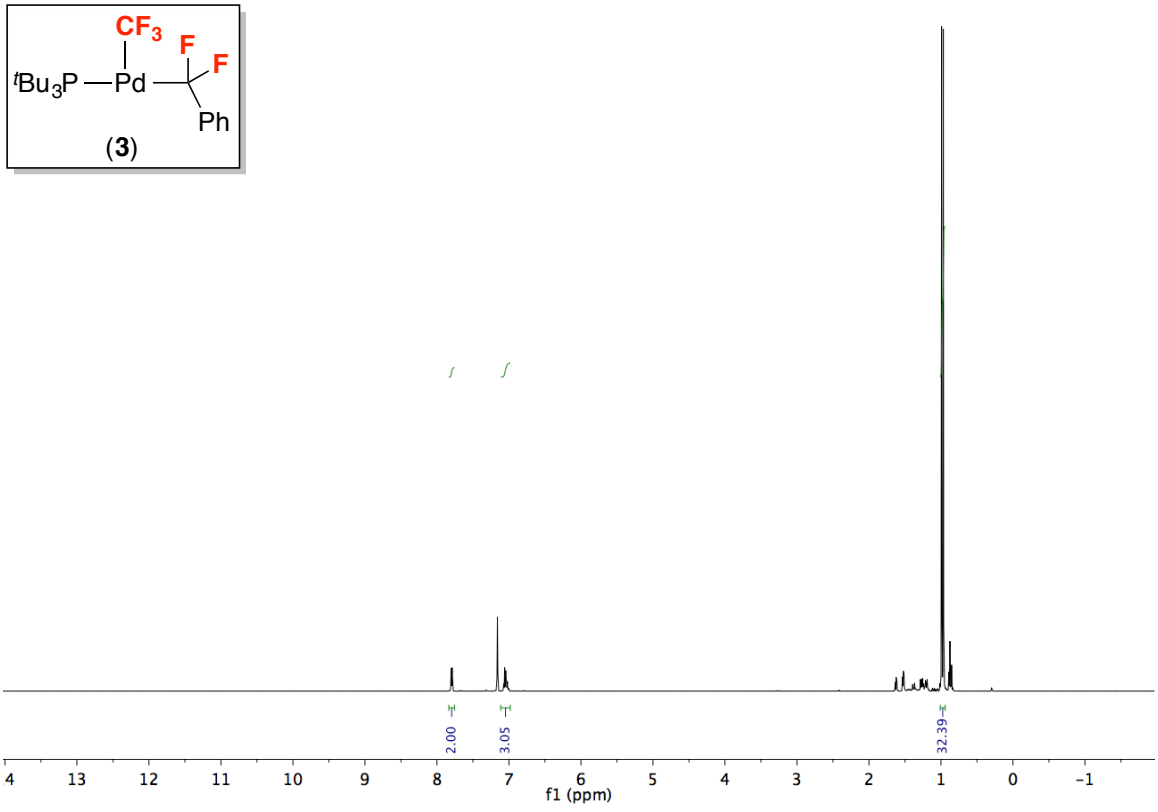




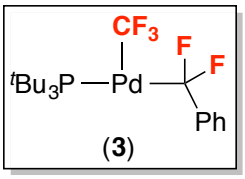


iv. *(P^tBu_3)Pd(CF_2Ph)(CF_3)* (***3***)

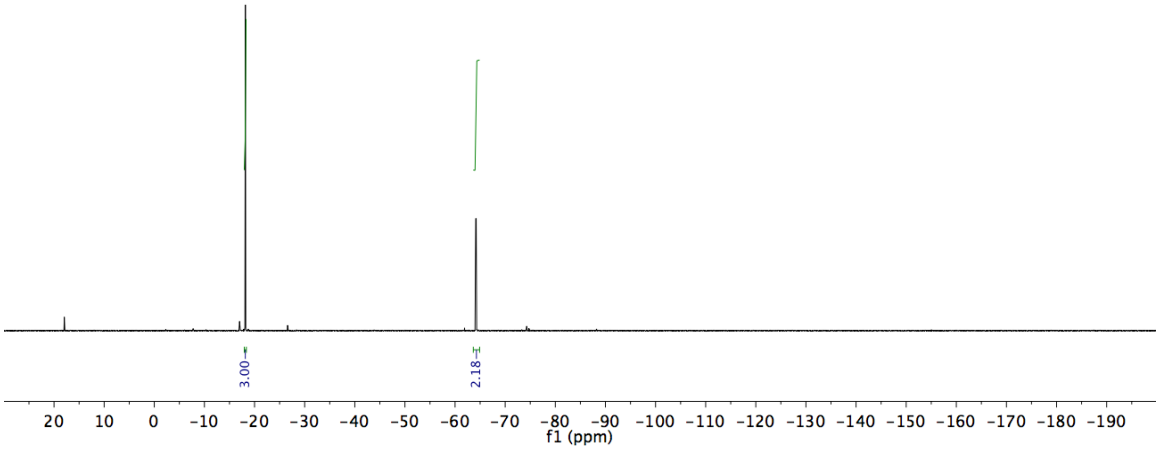
^{1}H NMR at 23 ºC (C_6D_6)

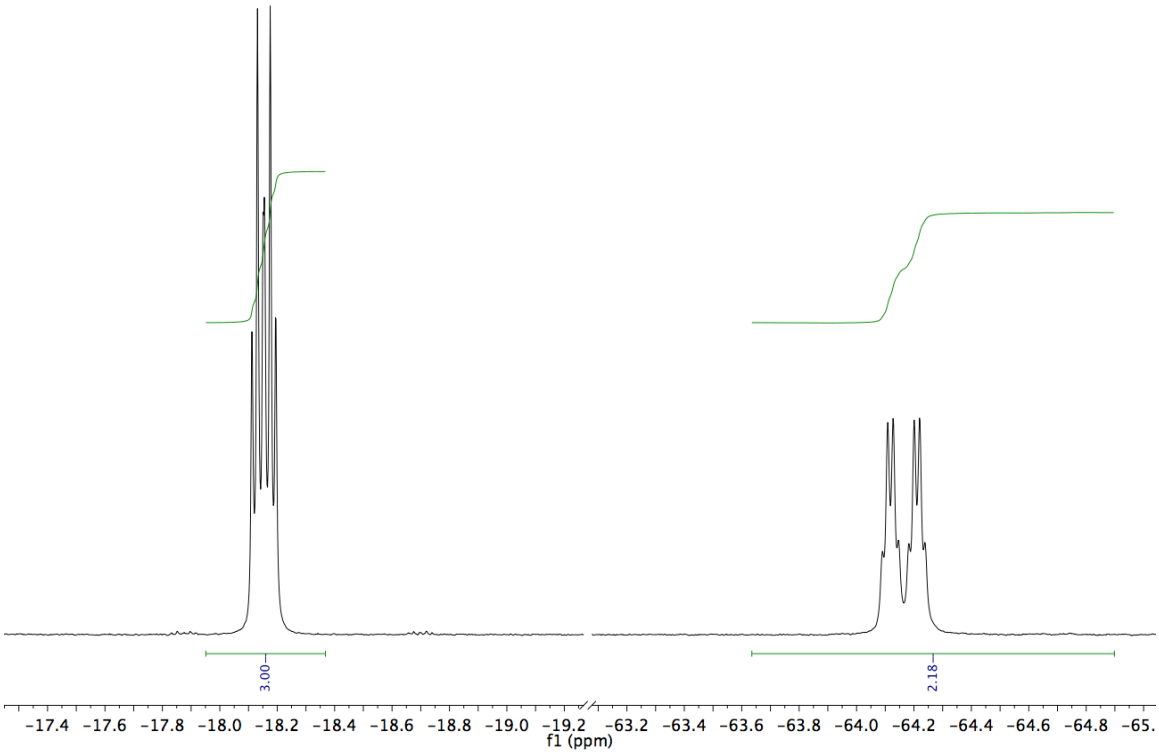


^{19}F NMR at 23 ºC (C_6D_6)

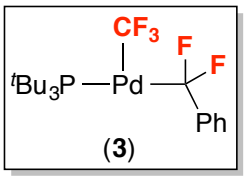


(**3**)

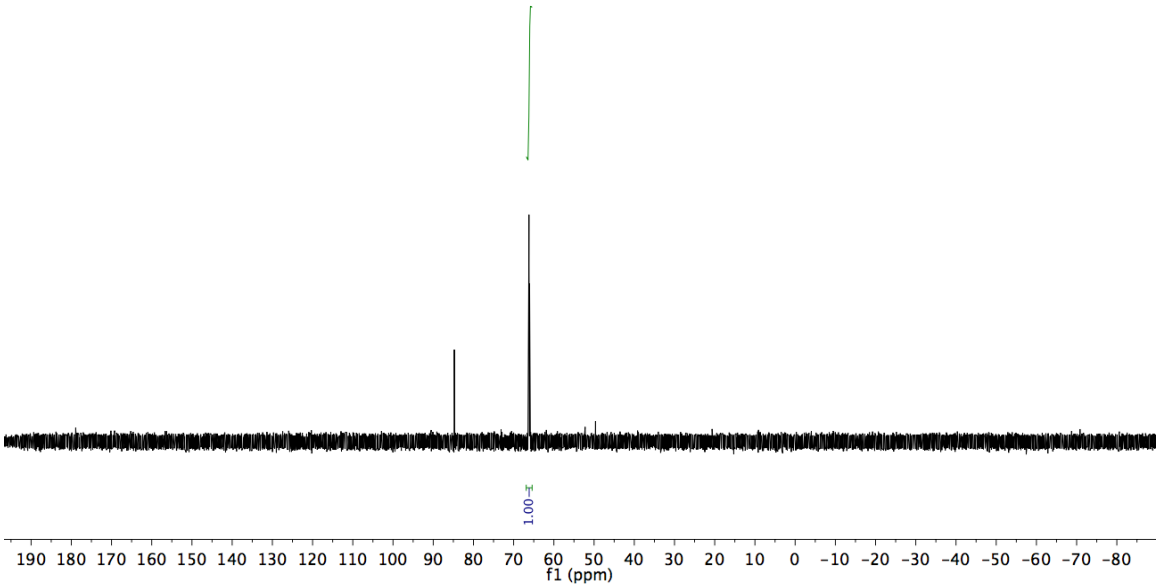


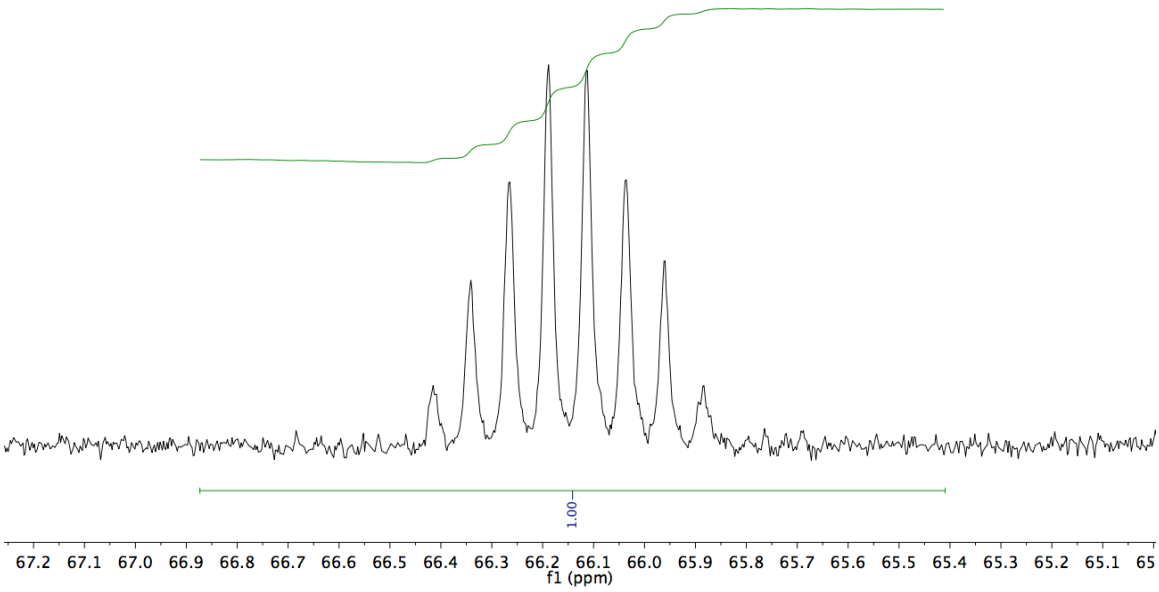


^{31}P NMR at 23 ºC (C_6D_6)



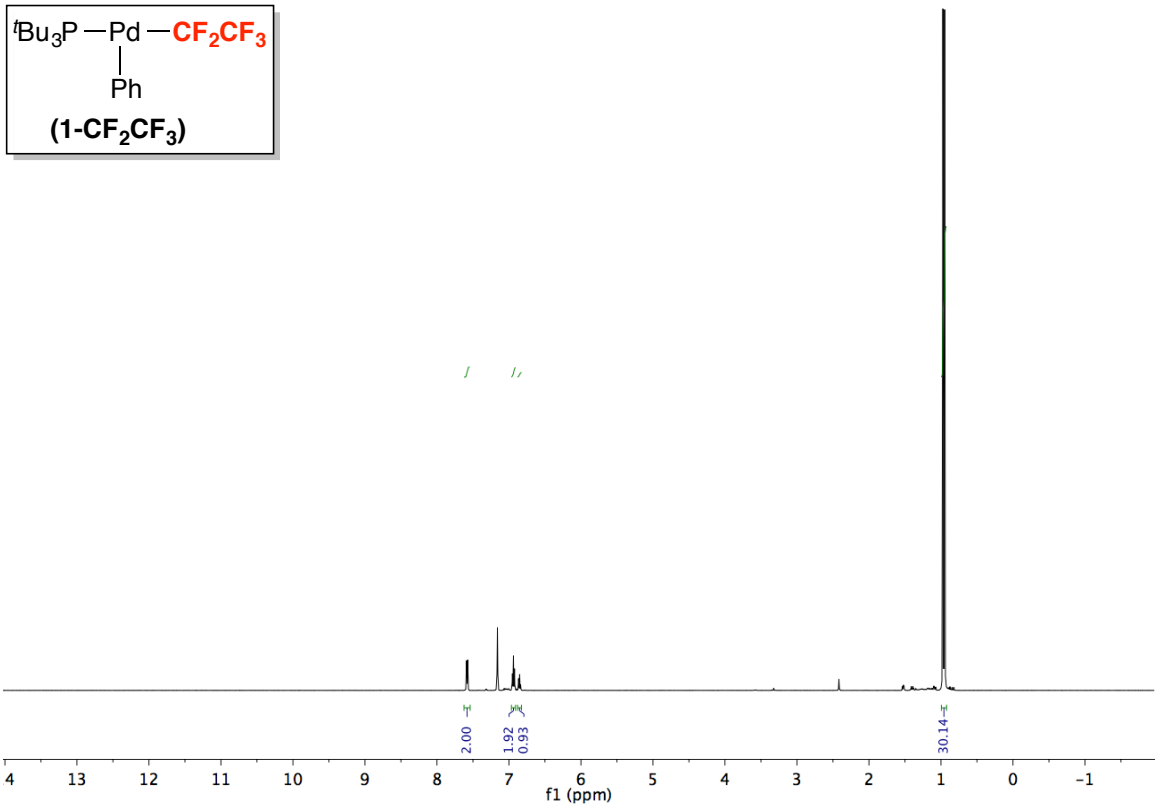
(**3**)



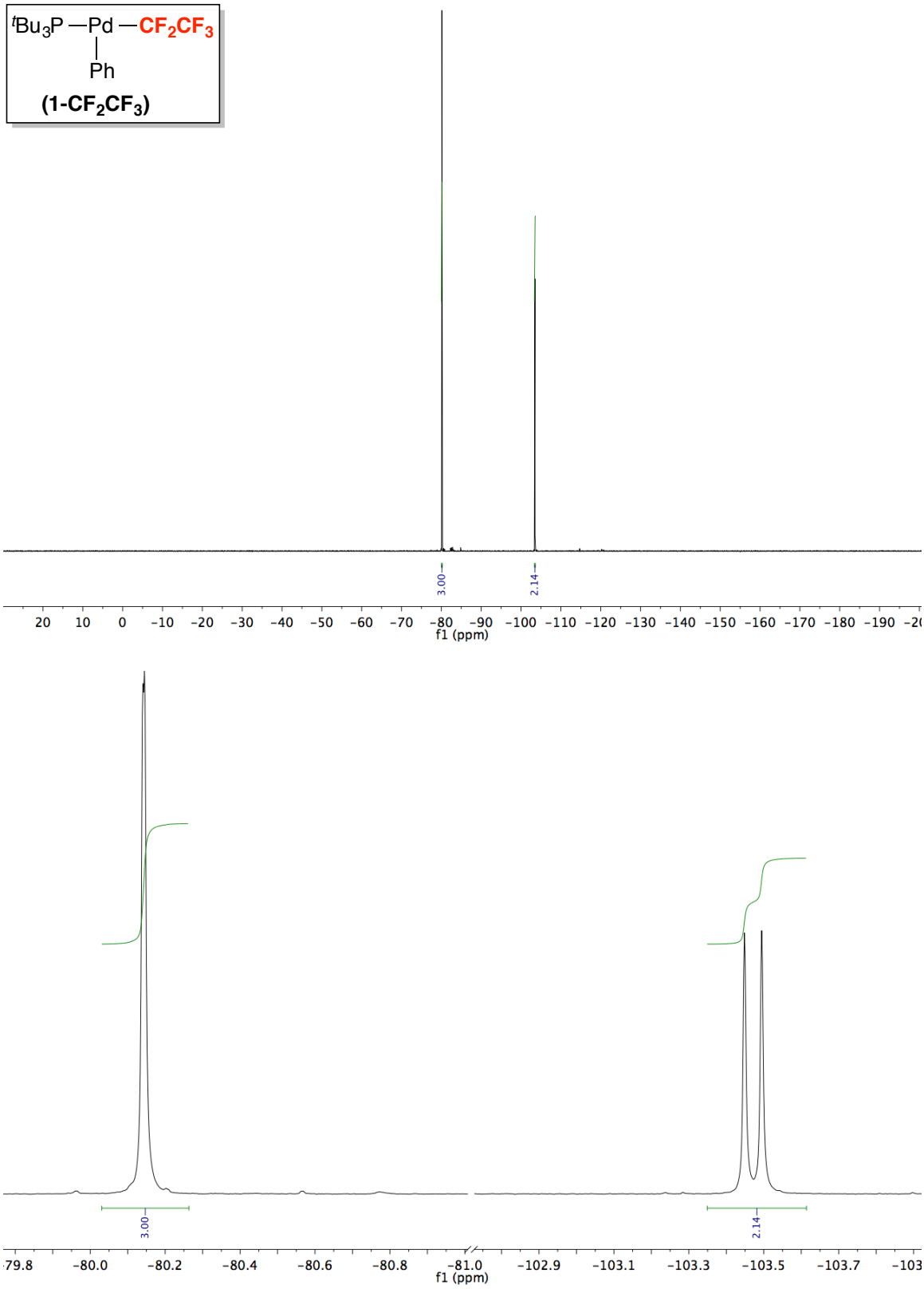


v. *(P^tBu_3)Pd(Ph)(CF_2CF_3)* (***1-CF_2CF_3***)

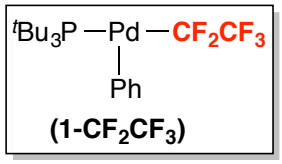
^{1}H NMR at 23 ºC (C_6D_6)



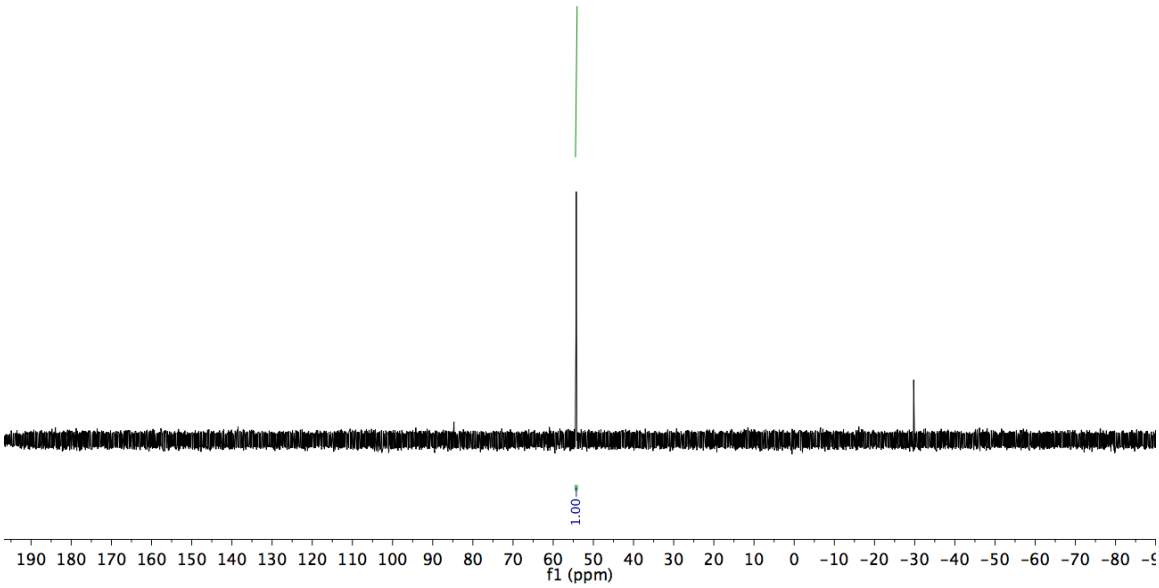
^{19}F NMR at 23 ºC (C_6D_6)

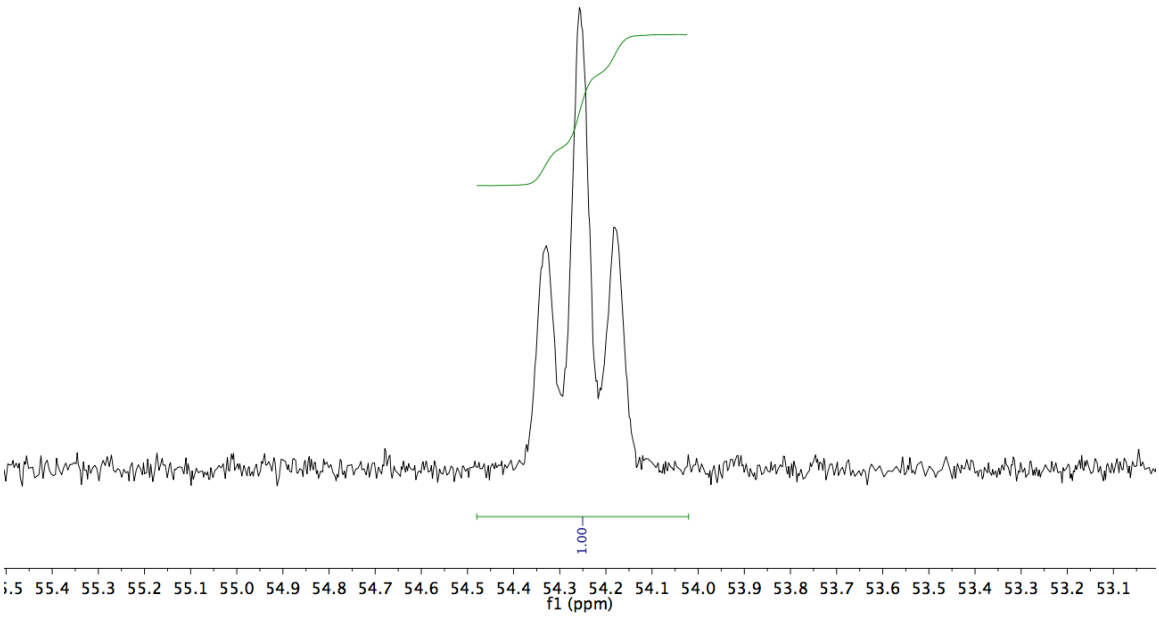


^{31}P NMR at 23 ºC (C_6D_6)



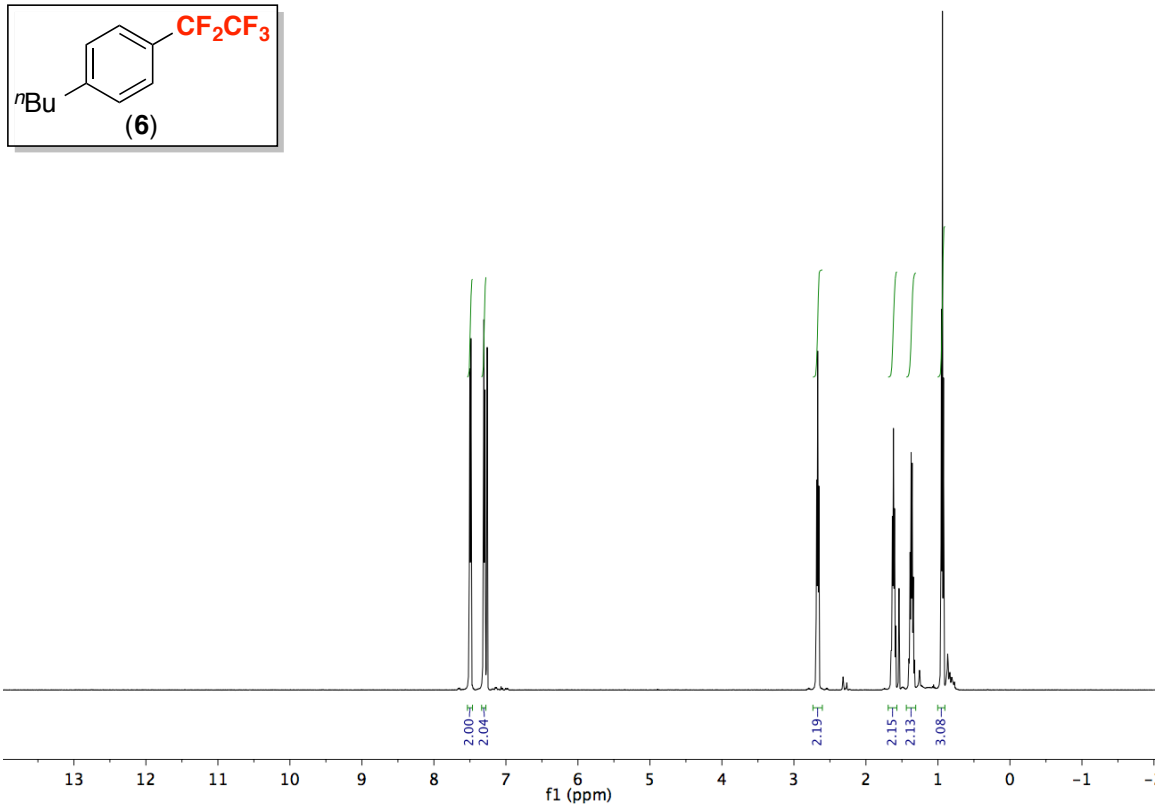
(1-CF_2CF_3)



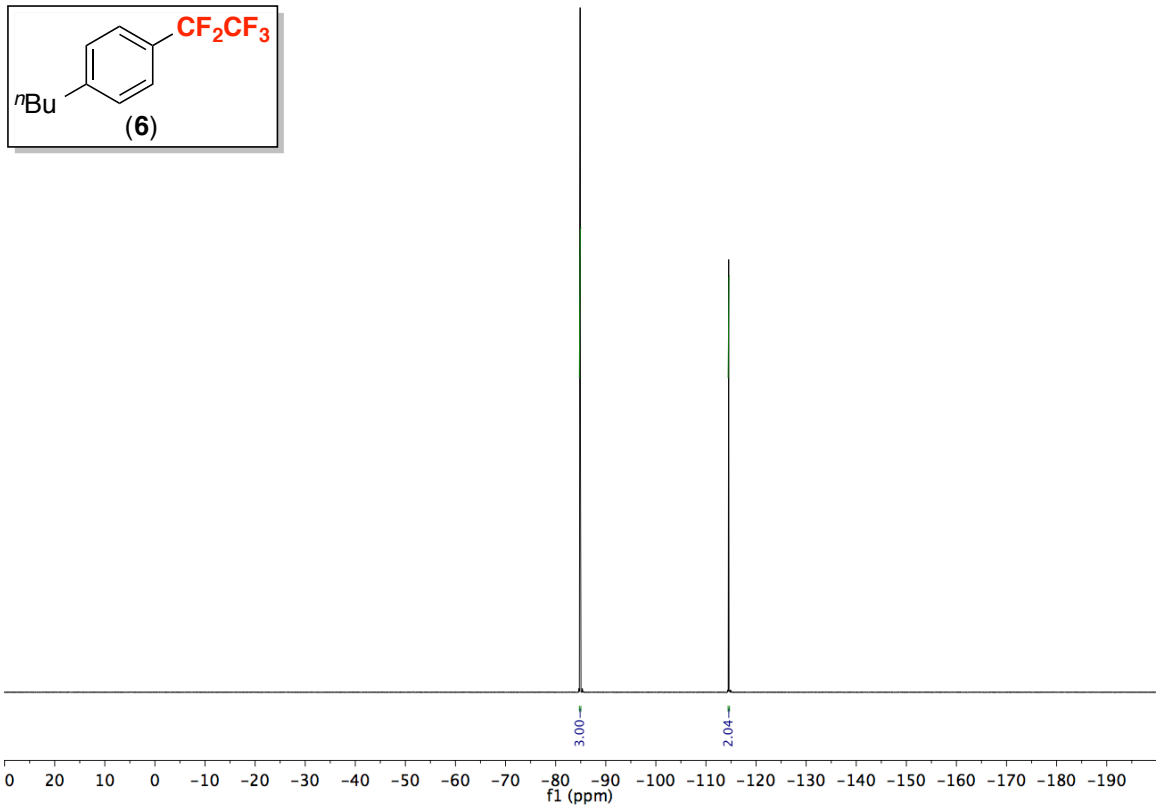


*vi. (**6**)*

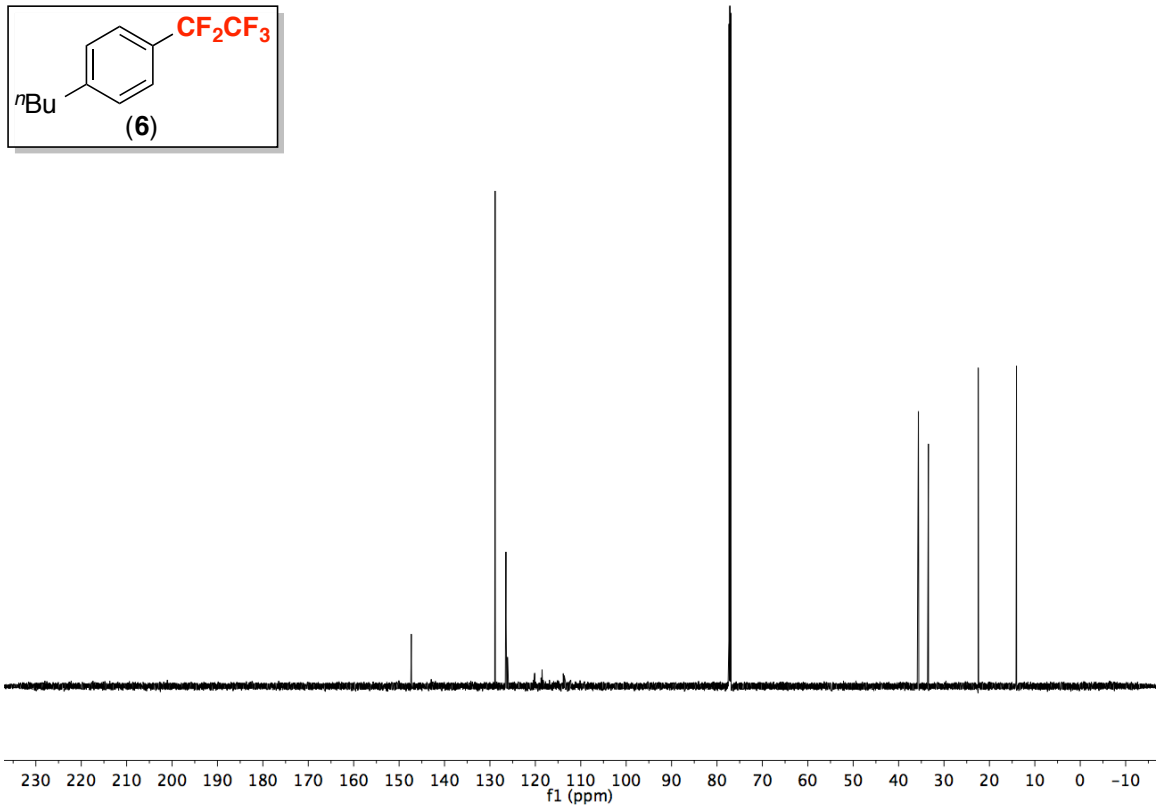
^{1}H NMR at 23 ºC ($CDCl_3$)



^{19}F NMR at 23 ºC ($CDCl_3$)

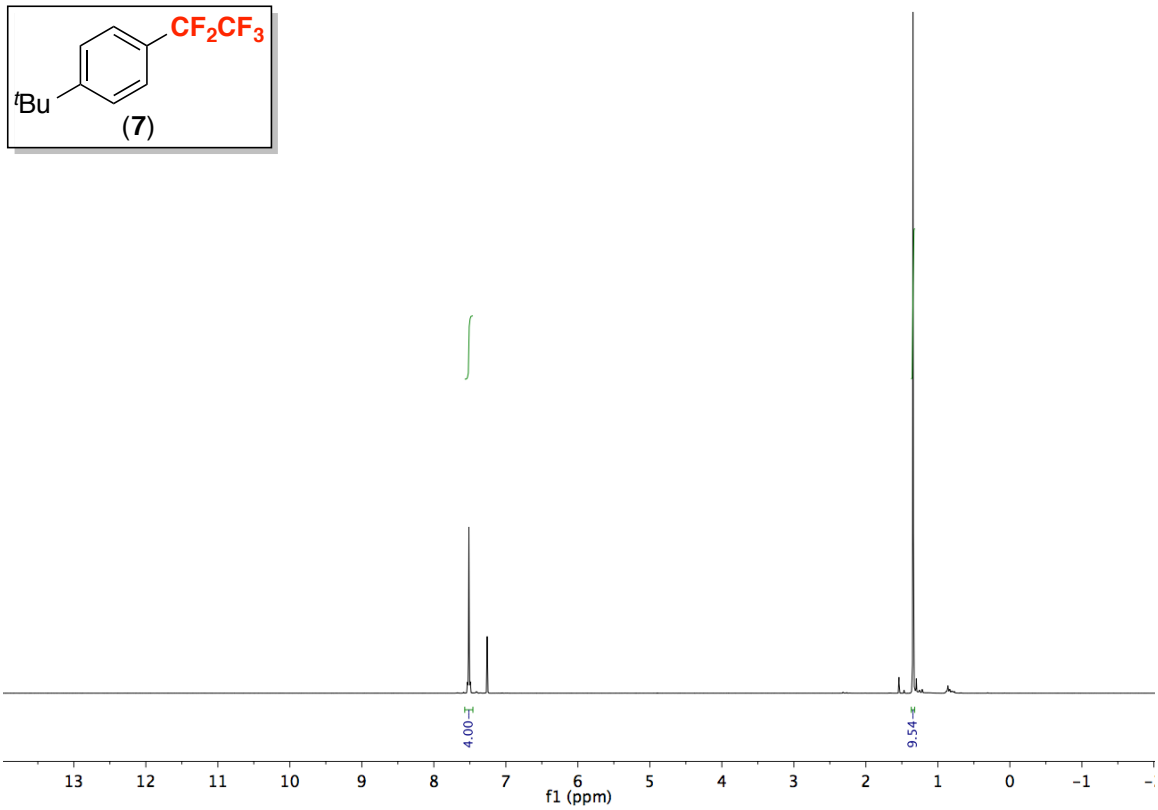


^{13}C NMR at 23 ºC ($CDCl_3$)

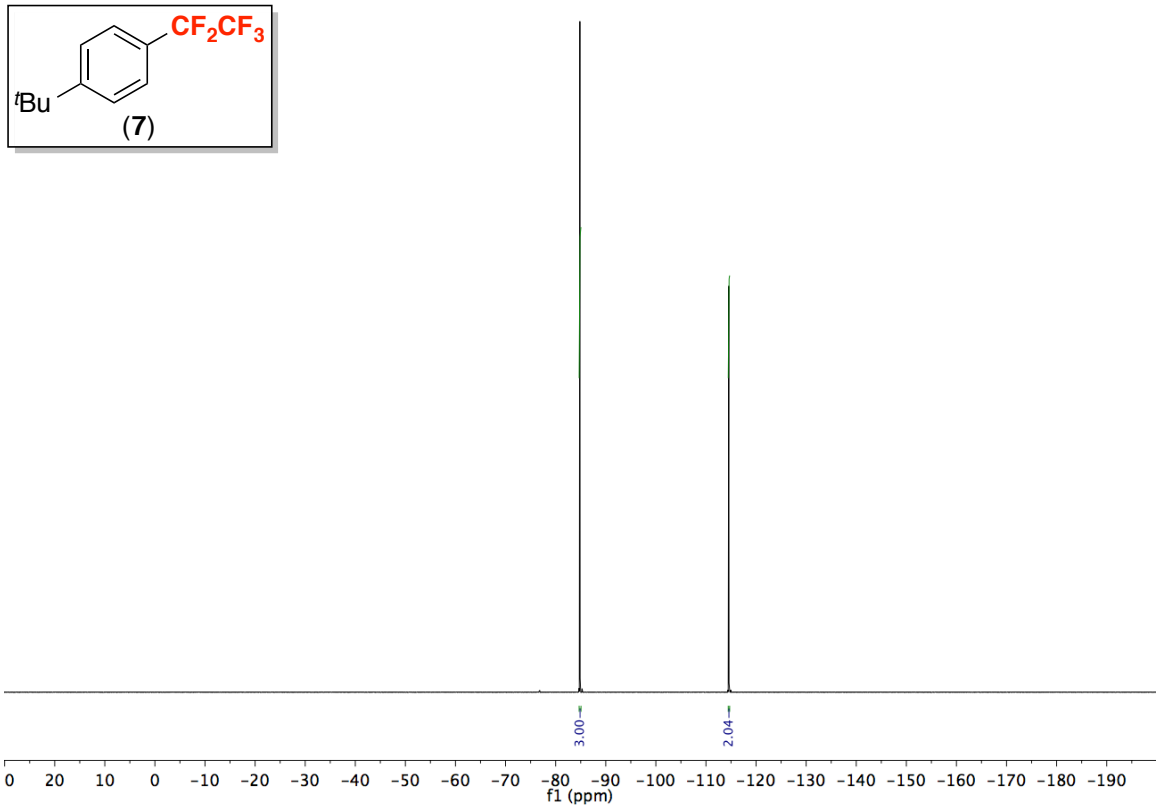


*vii. (**7**)*

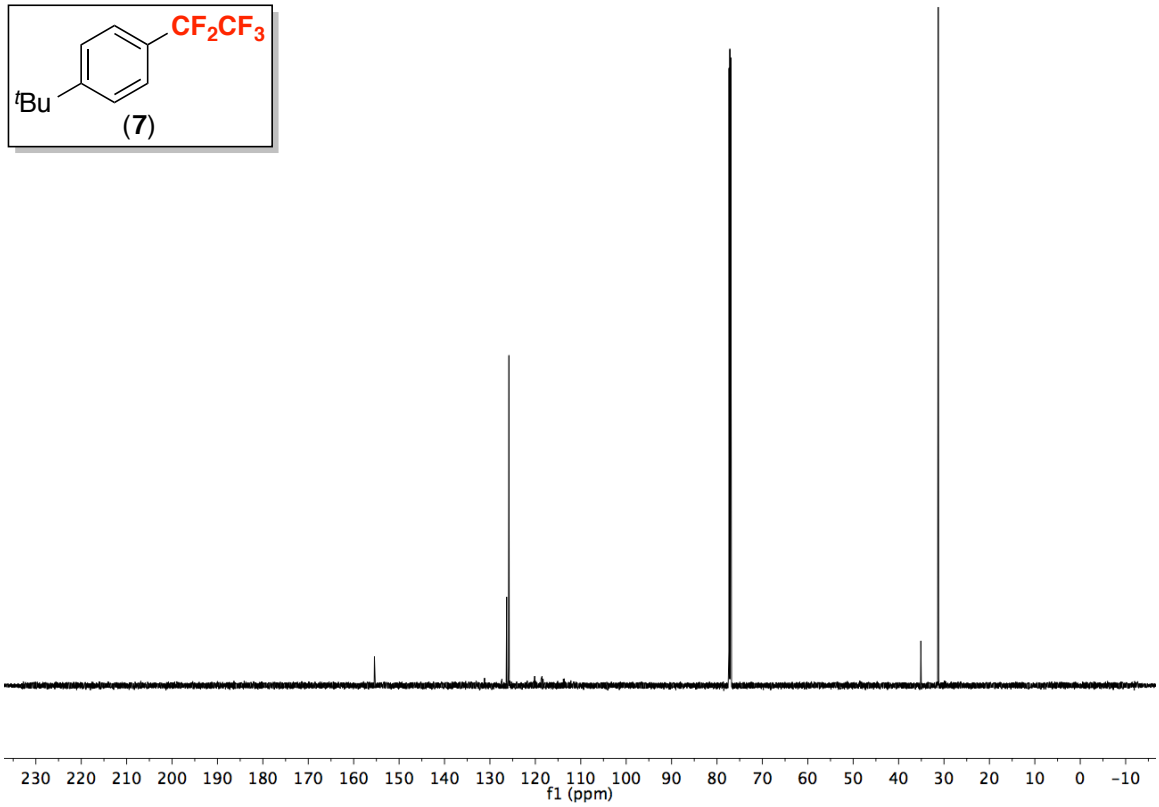
^{1}H NMR at 23 ºC ($CDCl_3$)



^{19}F NMR at 23 °C ($CDCl_3$)

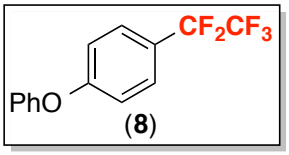


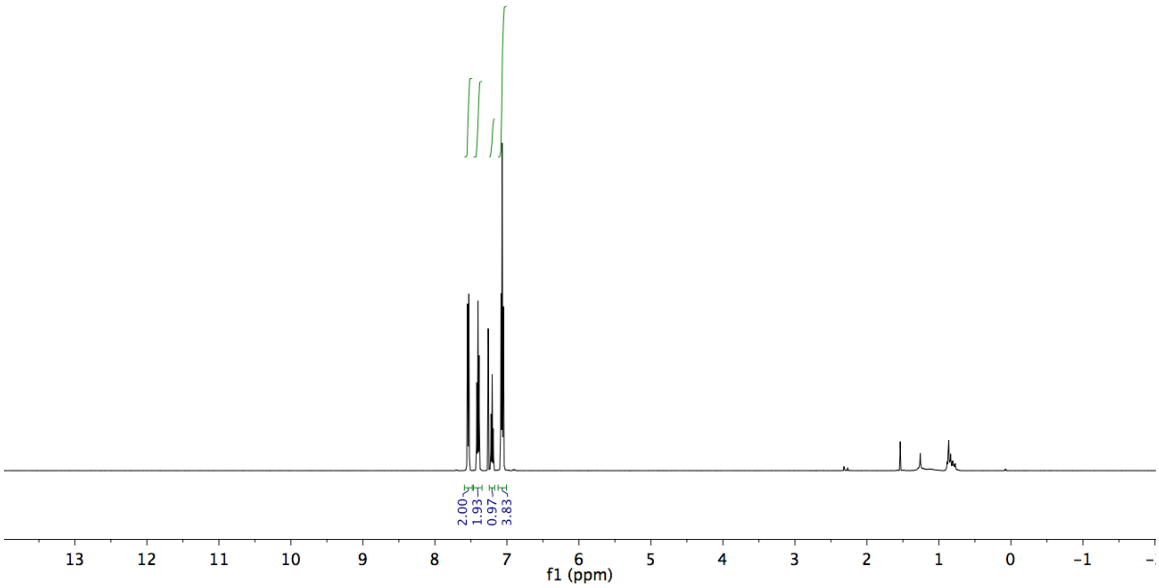
^{13}C NMR at 23 ºC ($CDCl_3$)



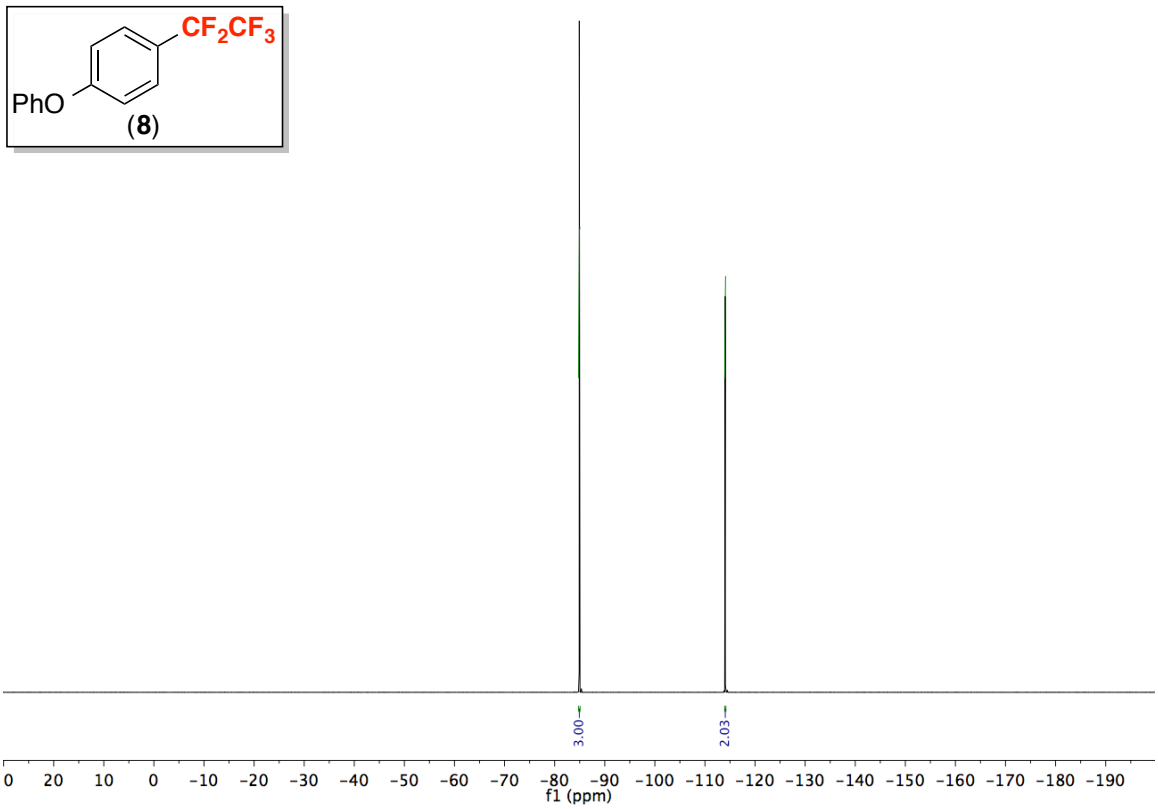
*viii.(**8**)*

^{1}H NMR at 23 ºC ($CDCl_3$)

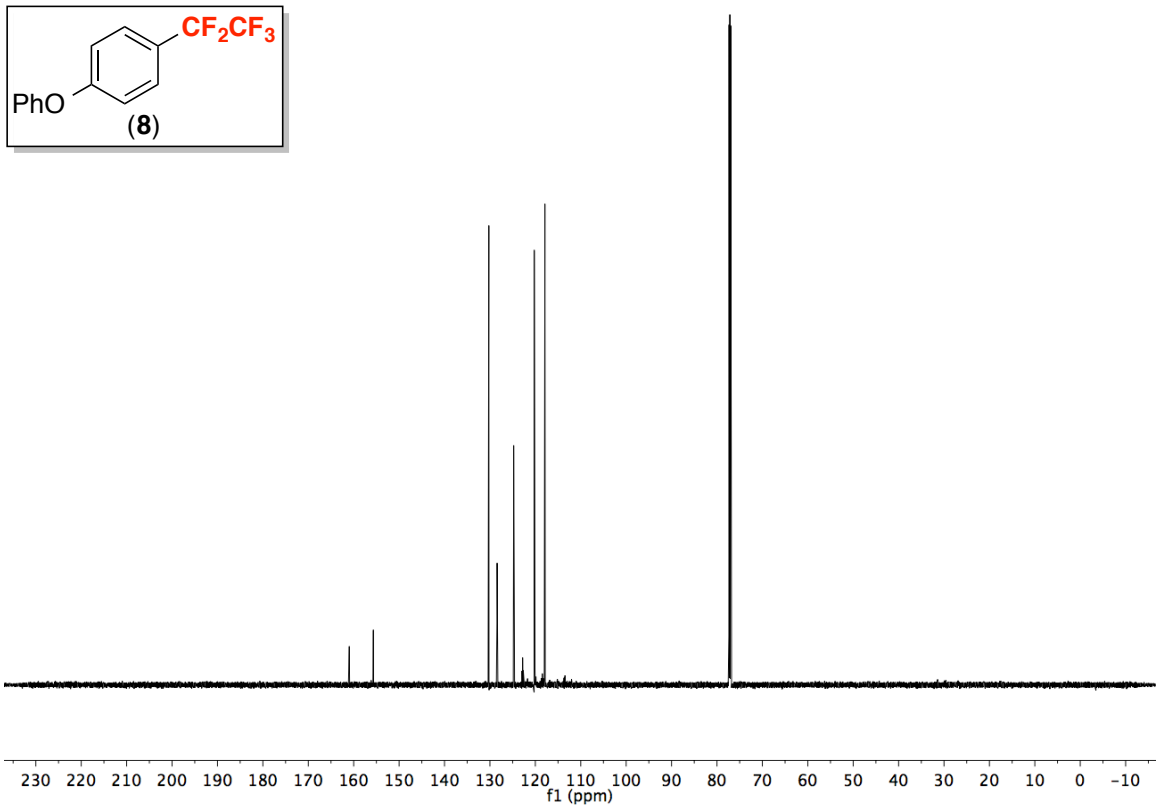




^{19}F NMR at 23 ºC ($CDCl_3$)

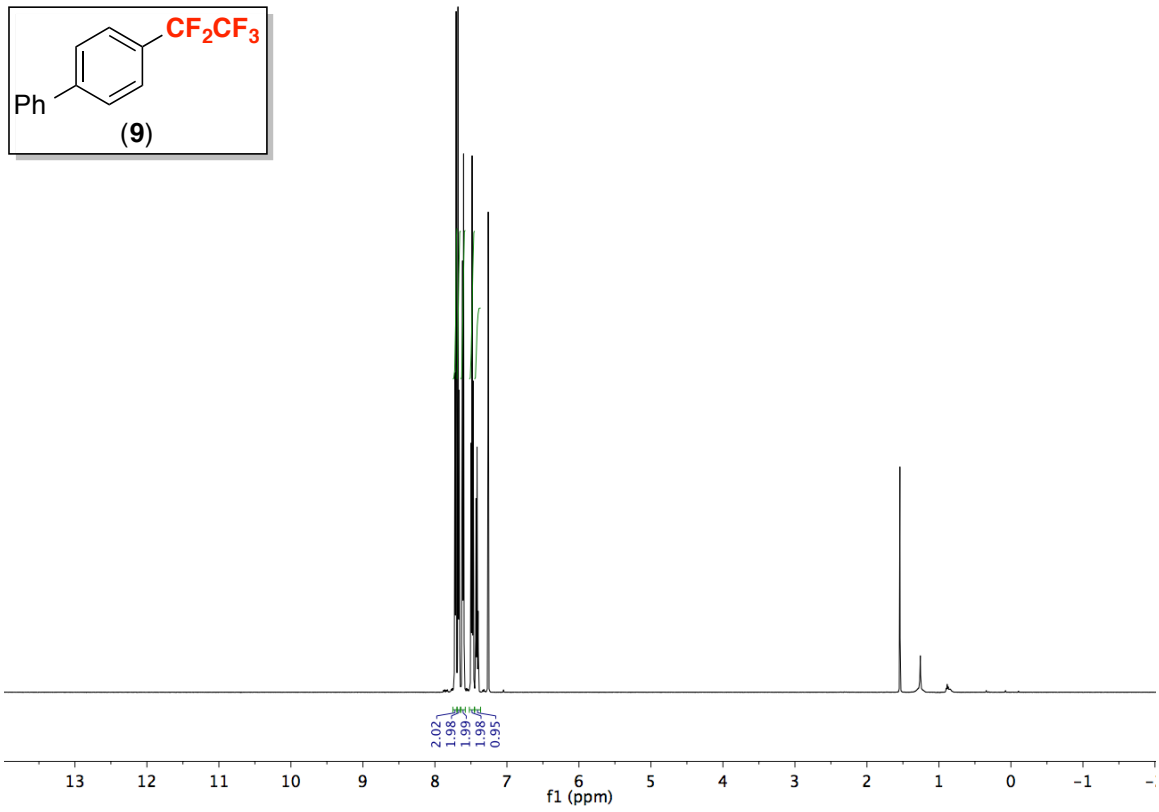


^{13}C NMR at 23 ºC ($CDCl_3$)

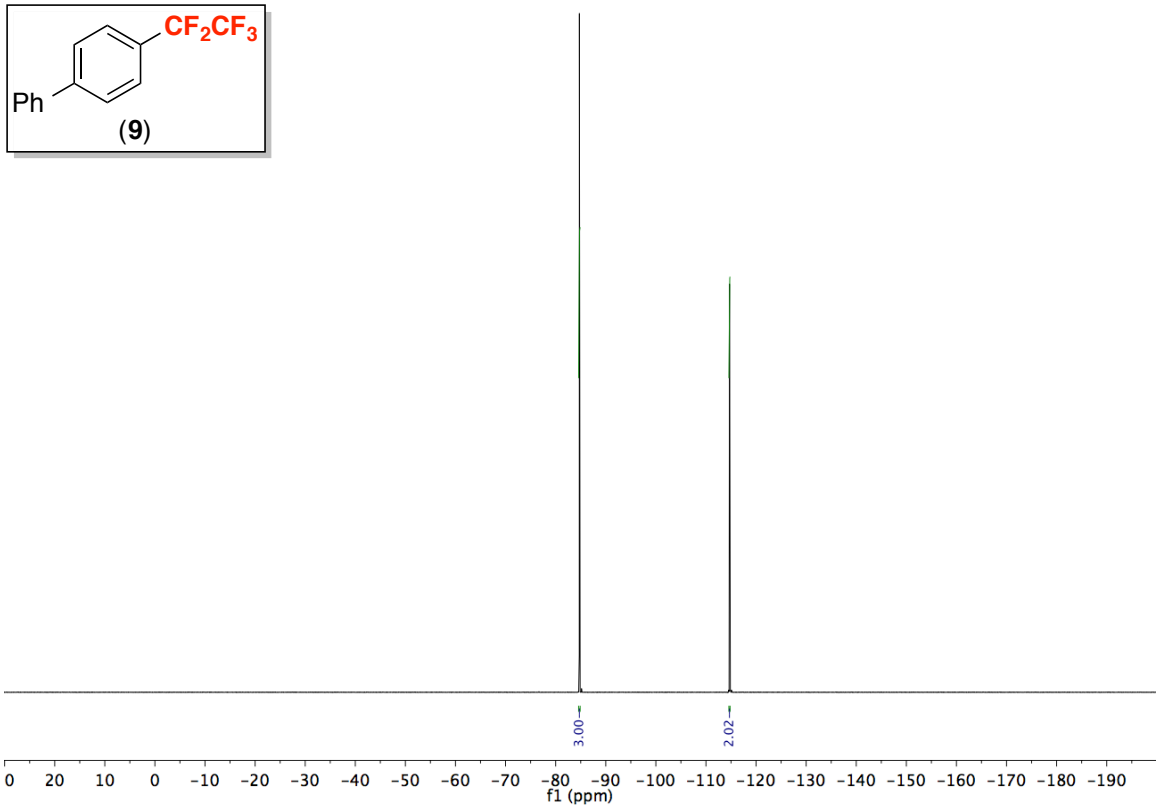


*ix. (**9**)*

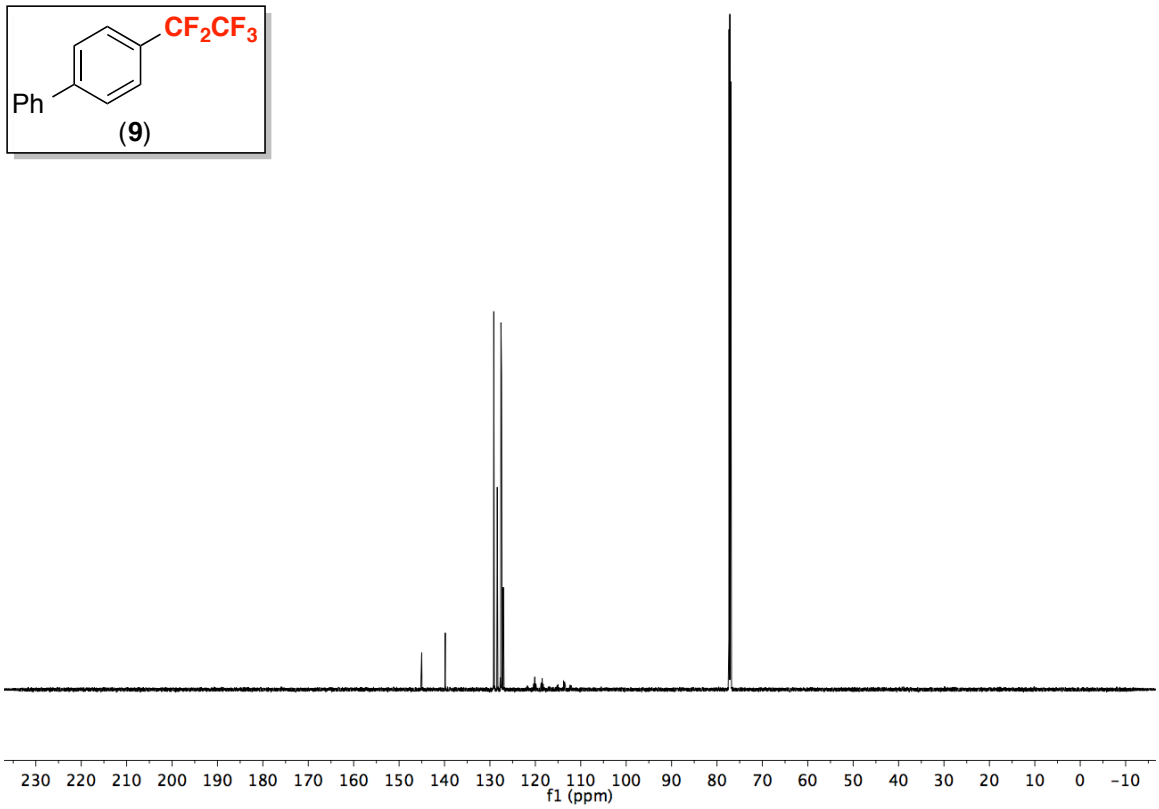
^{1}H NMR at 23 ºC ($CDCl_3$)



^{19}F NMR at 23 ºC ($CDCl_3$)

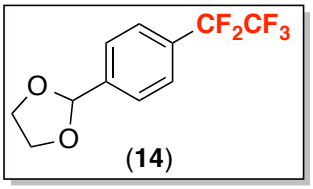


^{13}C NMR at 23 ºC ($CDCl_3$)

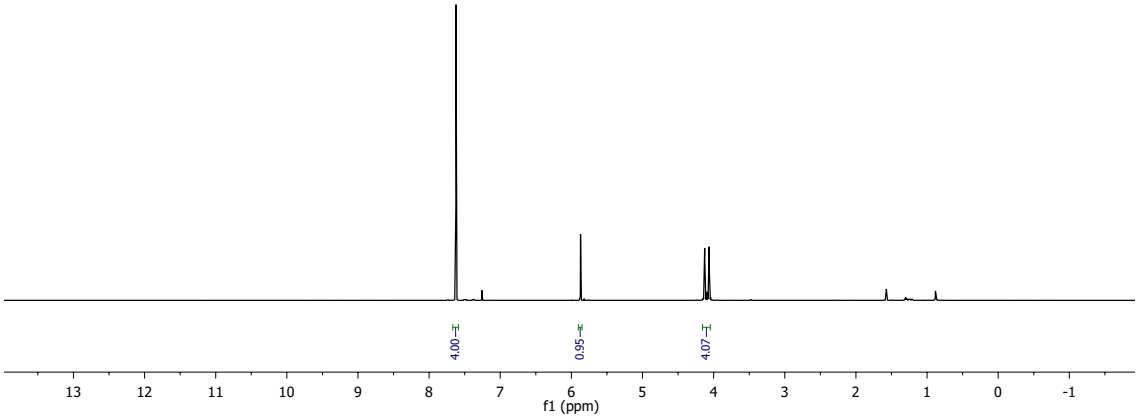


x. ***(14)***

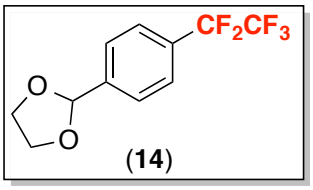
^{1}H NMR at 23 ºC ($CDCl_3$)



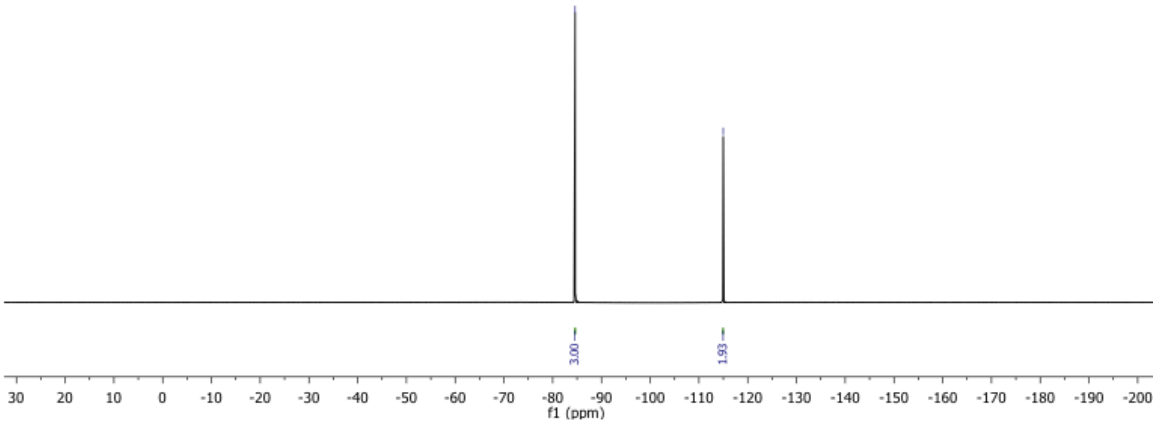
(**14**)



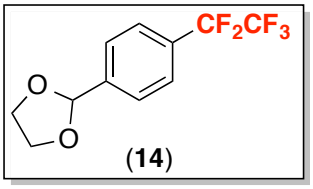
^{19}F NMR at 23 ºC ($CDCl_3$)



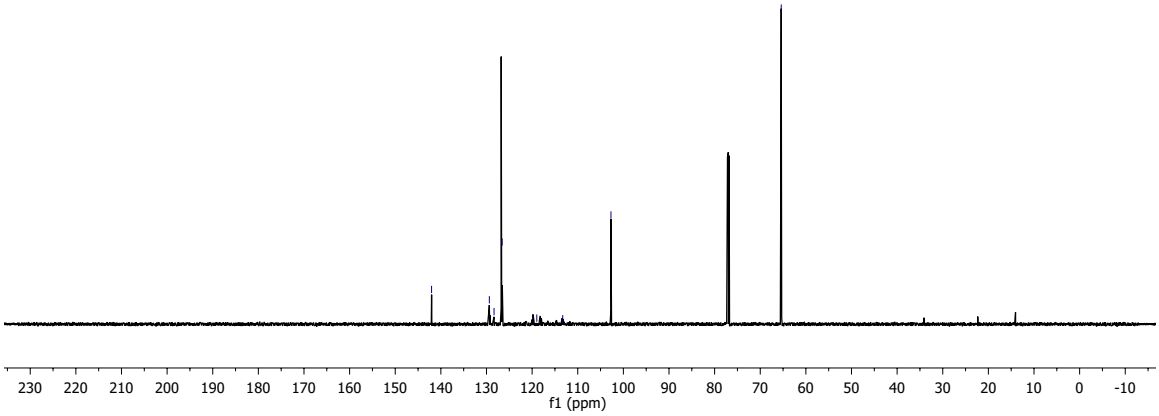
(**14**)



^{13}C NMR at 23 ºC ($CDCl_3$)

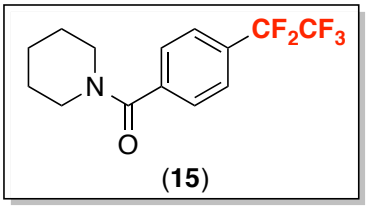


(**14**)

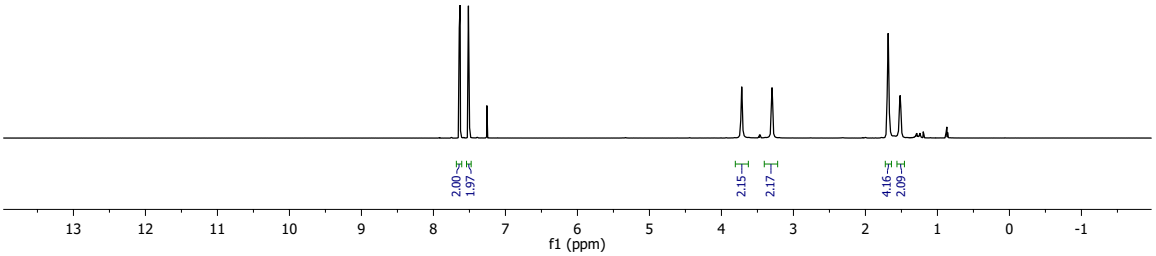


*xi. (**15**)*

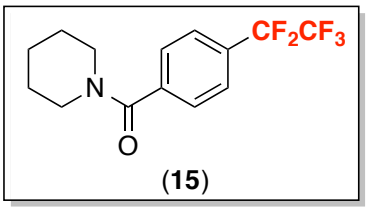
^{1}H NMR at 23 ºC ($CDCl_3$)



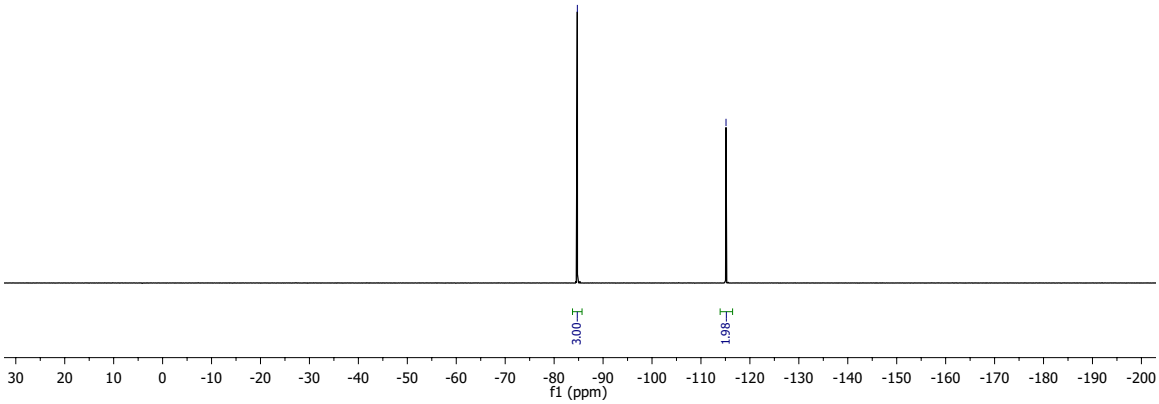
(**15**)



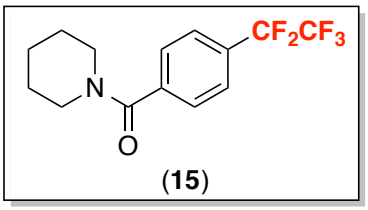
^{19}F NMR at 23 ºC ($CDCl_3$)



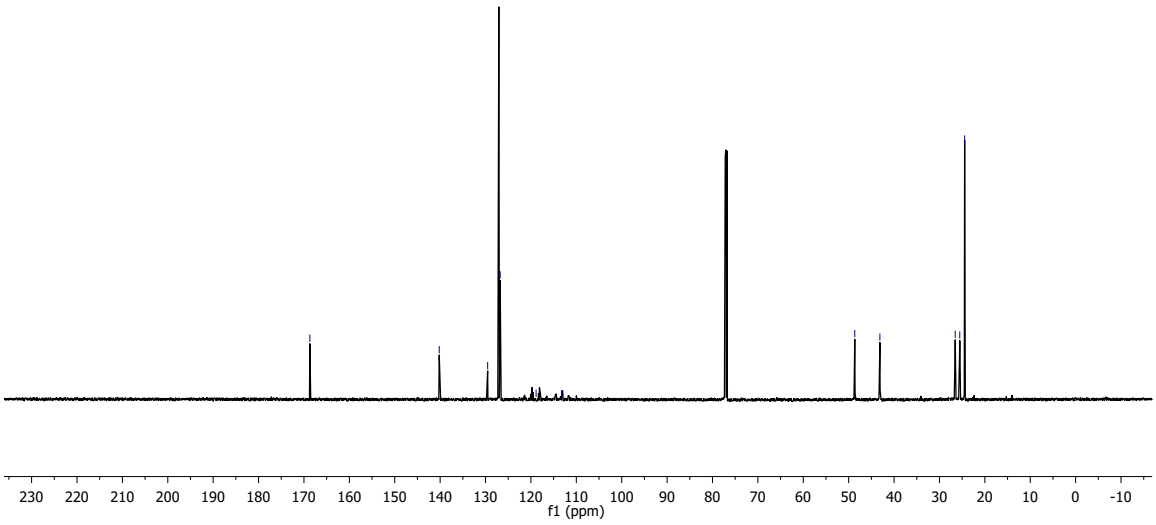
(**15**)



^{13}C NMR at 23 ºC ($CDCl_3$)

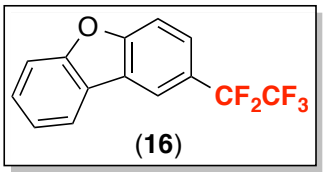


(**15**)



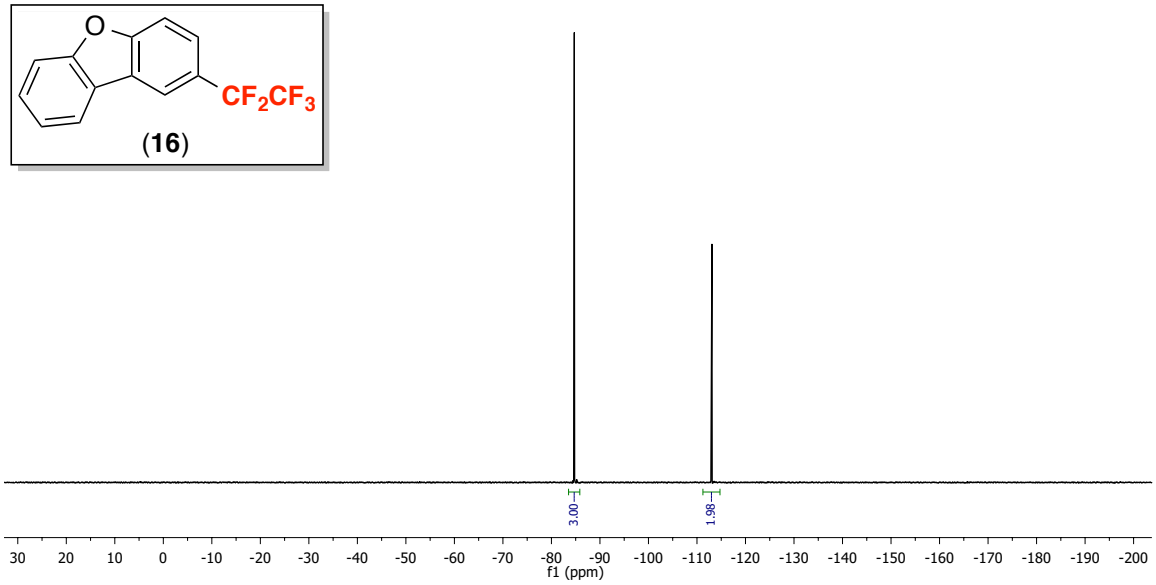
*xii. (**16**)*

^{1}H NMR at 23 ºC ($CDCl_3$)

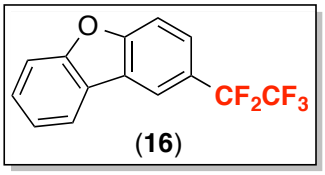


(**16**)

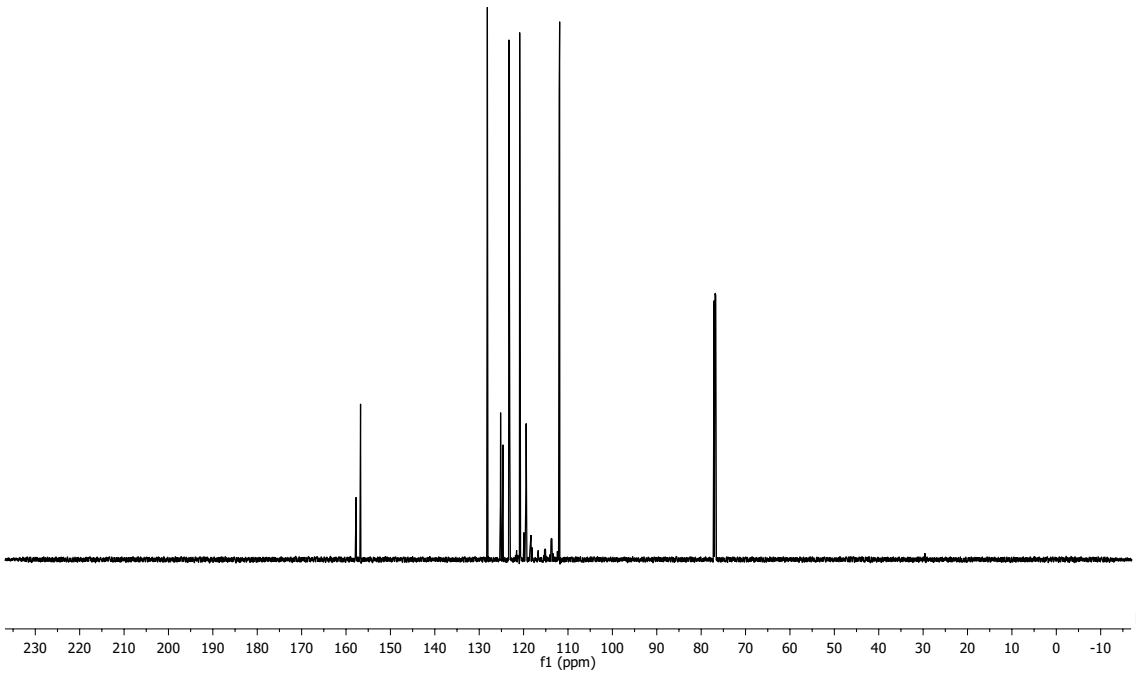
^{19}F NMR at 23 ºC ($CDCl_3$)



^{13}C NMR at 23 ºC ($CDCl_3$)

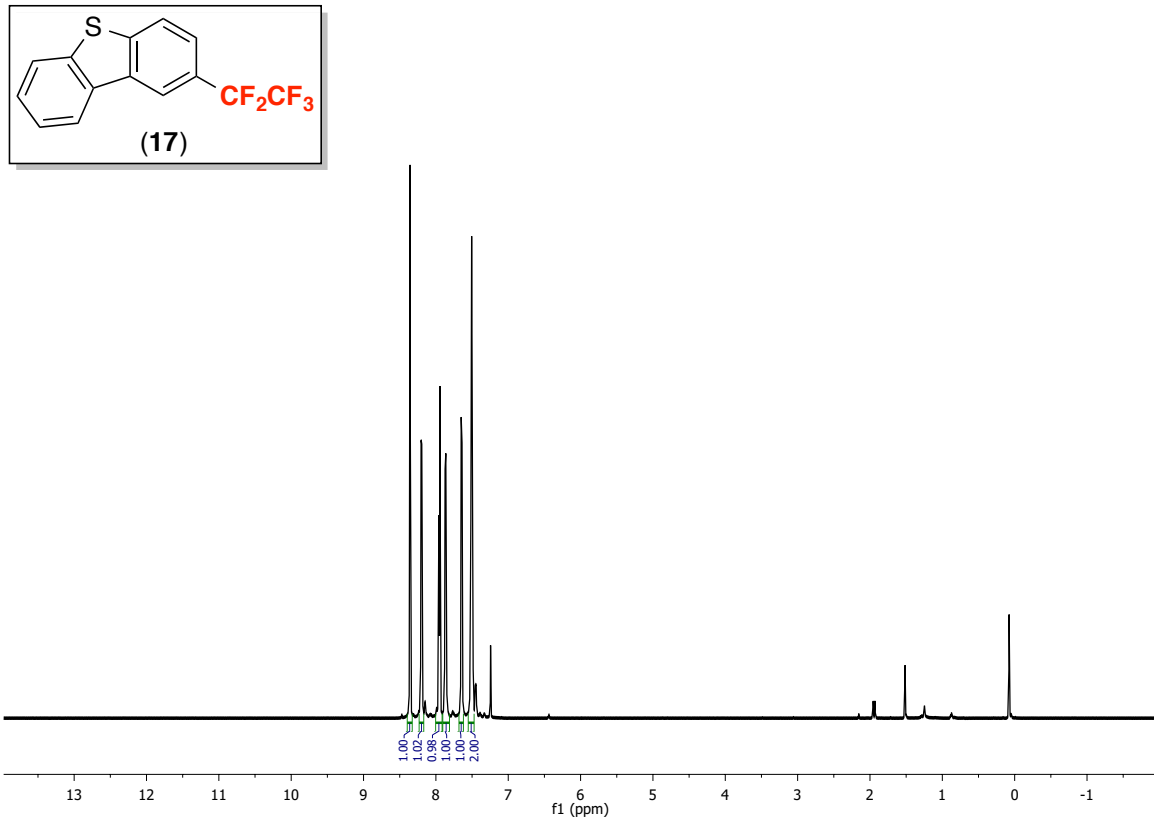


(**16**)

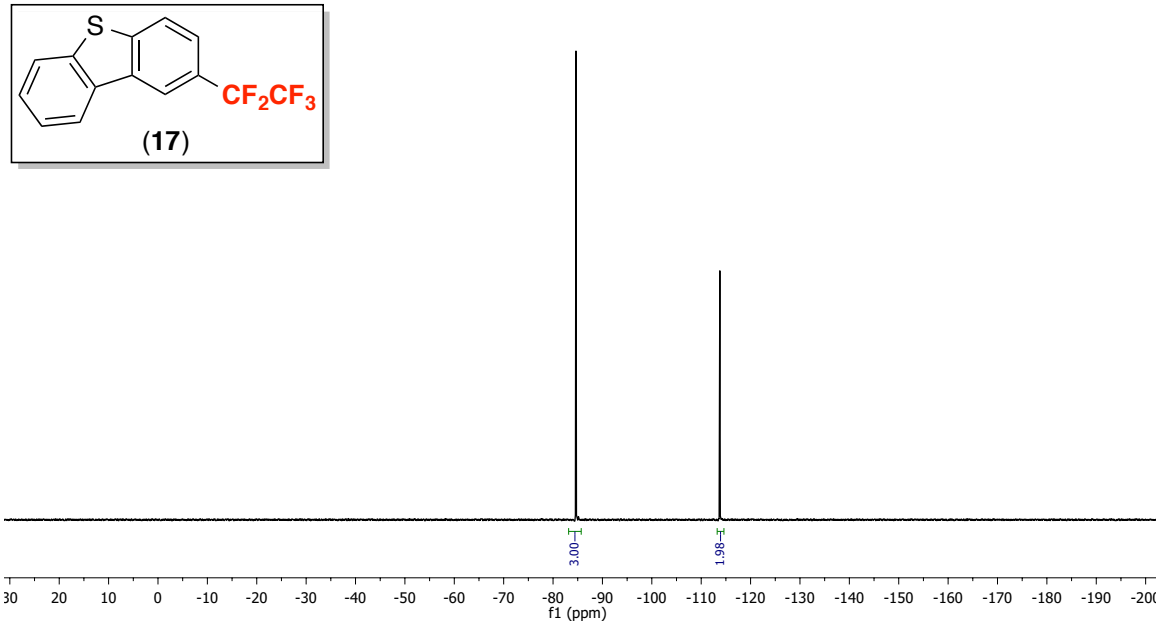


*xiii.(**17**)*

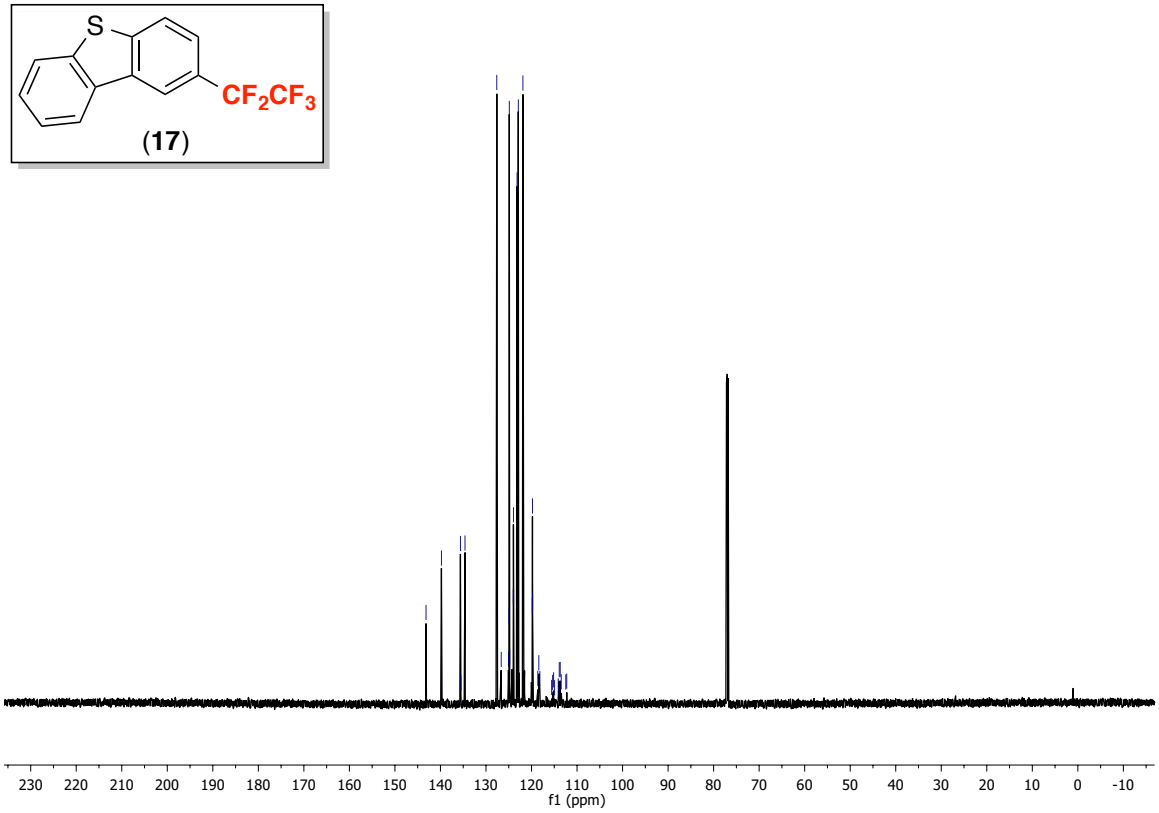
^{1}H NMR at 23 ºC ($CDCl_3$)



^{19}F NMR at 23 ºC ($CDCl_3$)

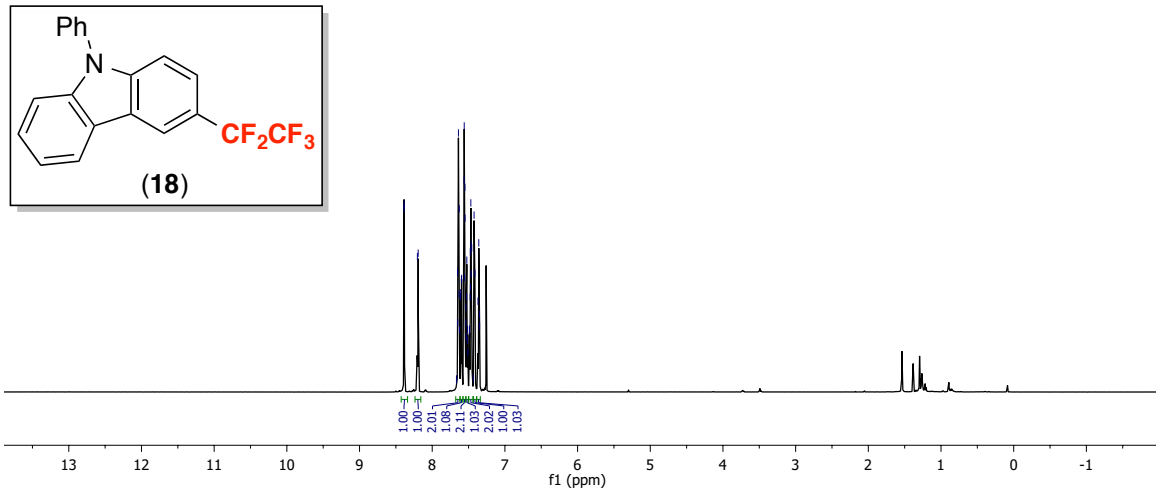


^{13}C NMR at 23 ºC ($CDCl_3$)

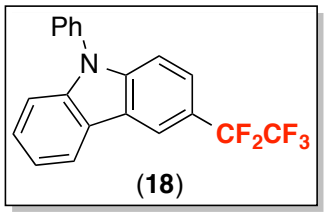


*xiv.(**18**)*

^{1}H NMR at 23 ºC ($CDCl_3$)

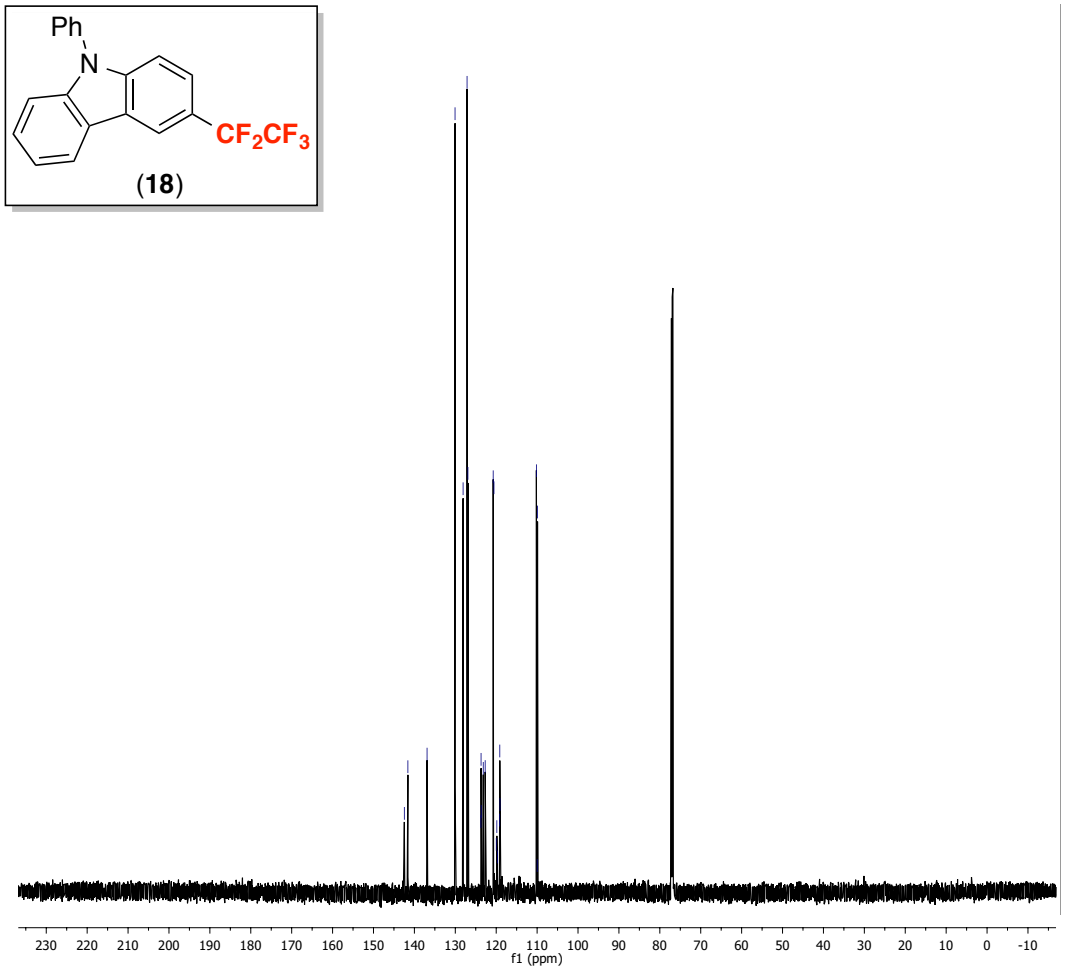


^{19}F NMR at 23 ºC ($CDCl_3$)



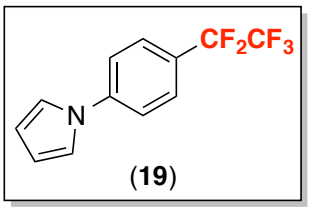
(**18**)

^{13}C NMR at 23 ºC ($CDCl_3$)

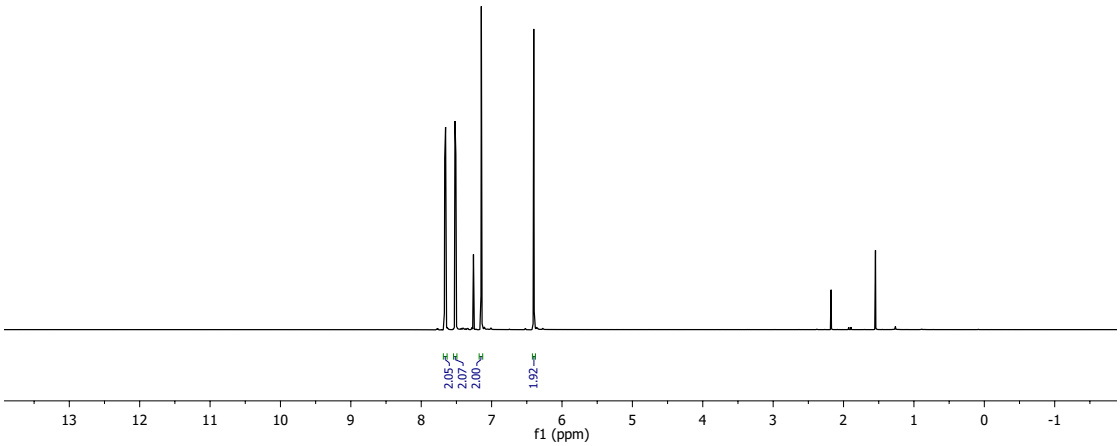


*xv. (**19**)*

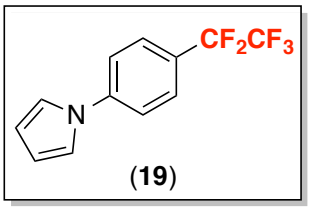
^{1}H NMR at 23 ºC ($CDCl_3$)



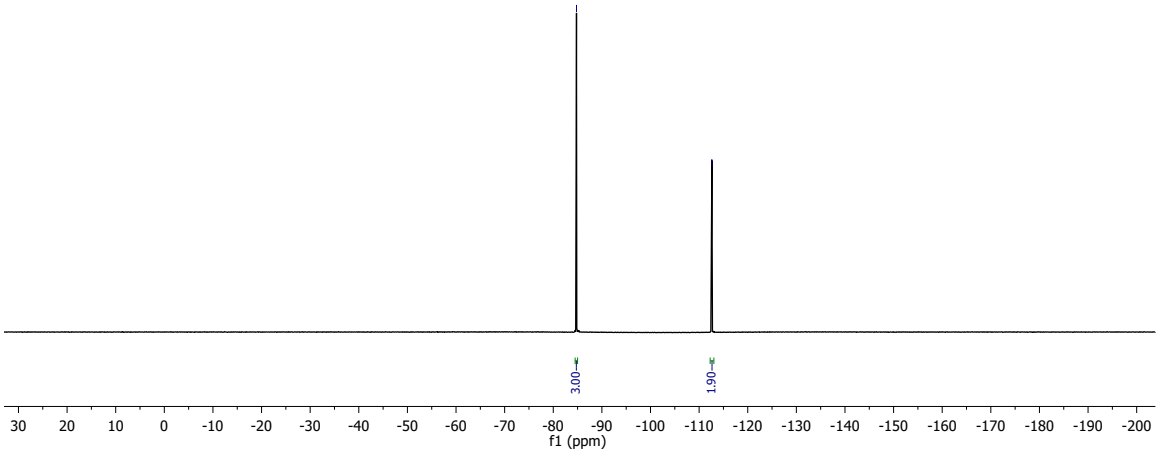
(**19**)



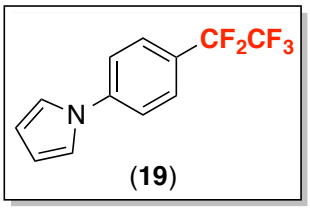
^{19}F NMR at 23 ºC ($CDCl_3$)



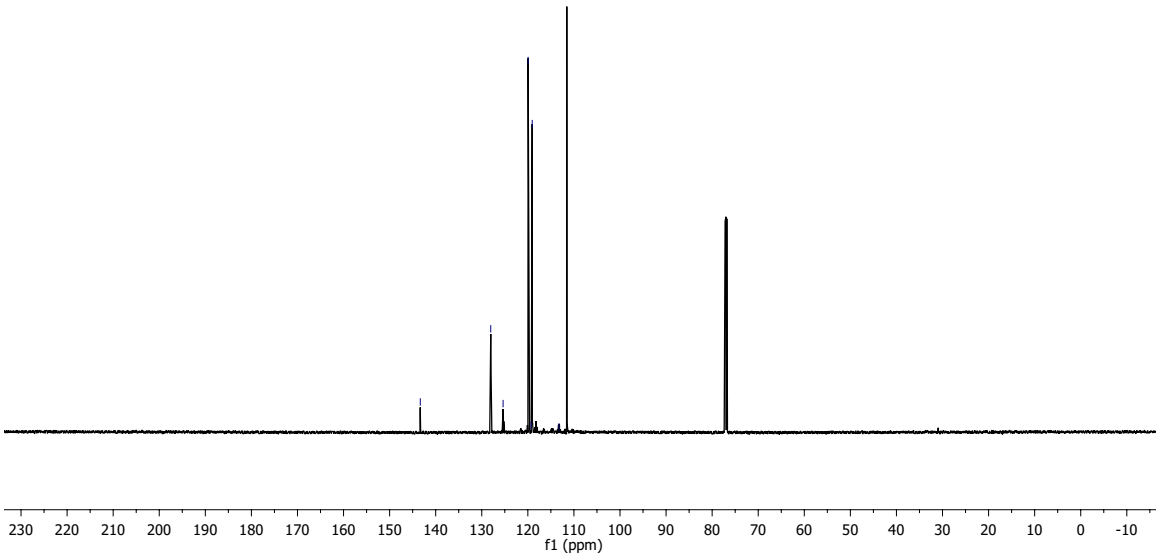
(**19**)



^{13}C NMR at 23 ºC ($CDCl_3$)

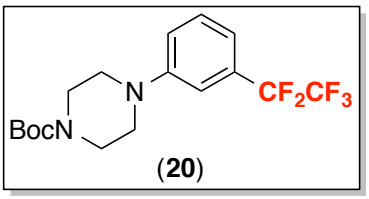


(**19**)

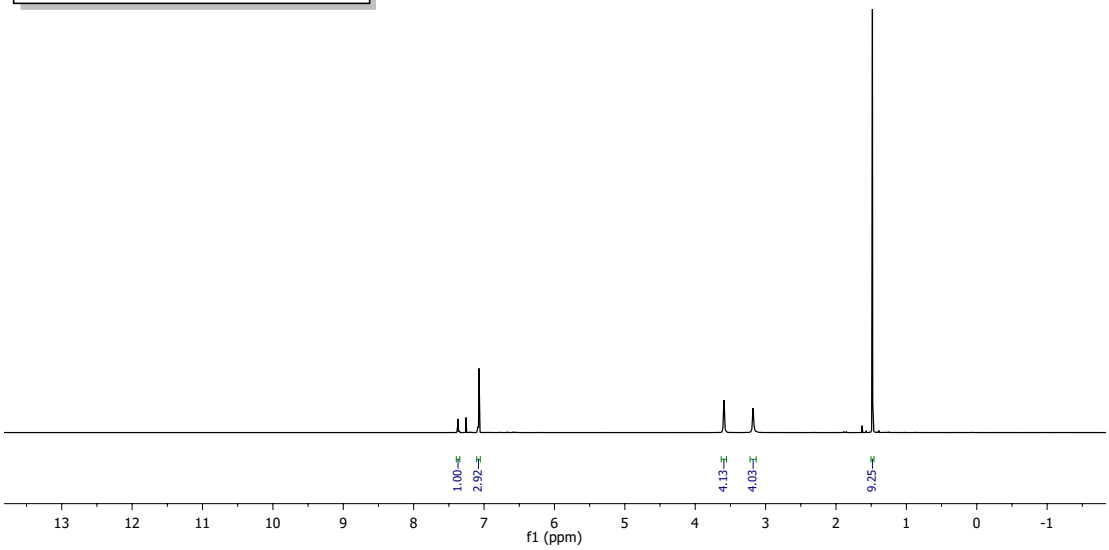


*xvi. (**20**)*

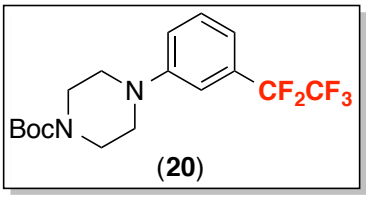
^{1}H NMR at 23 ºC ($CDCl_3$)



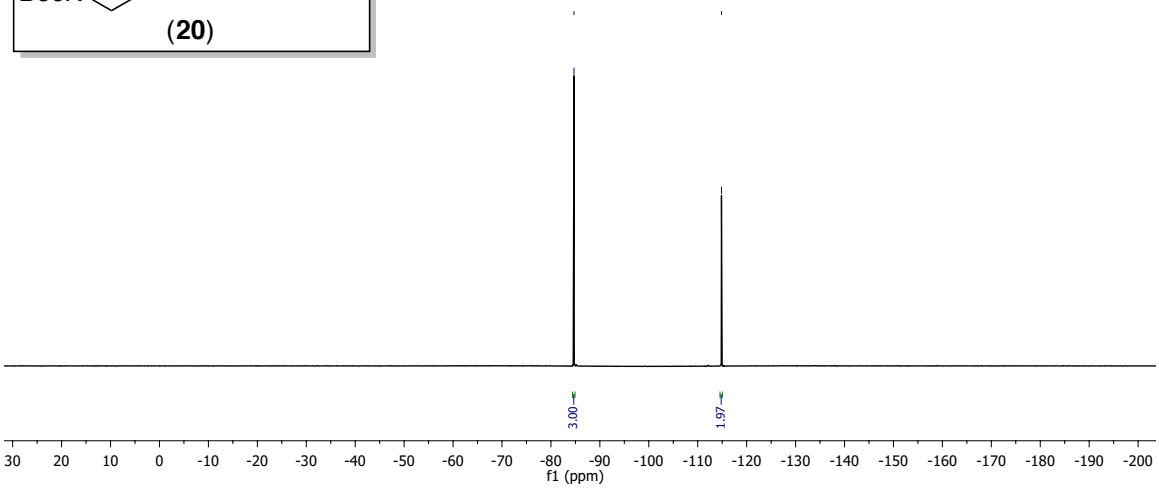
(**20**)



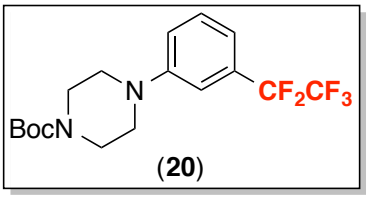
^{19}F NMR at 23 ºC ($CDCl_3$)



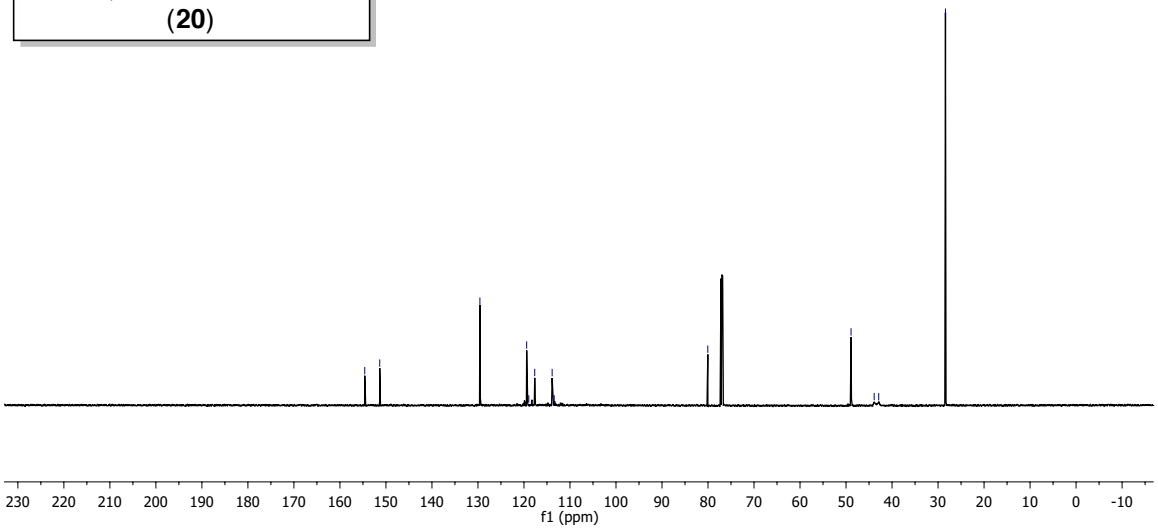
(**20**)



^{13}C NMR at 23 ºC ($CDCl_3$)

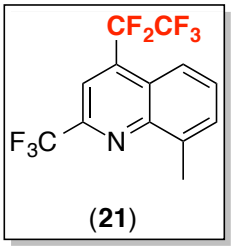


(**20**)

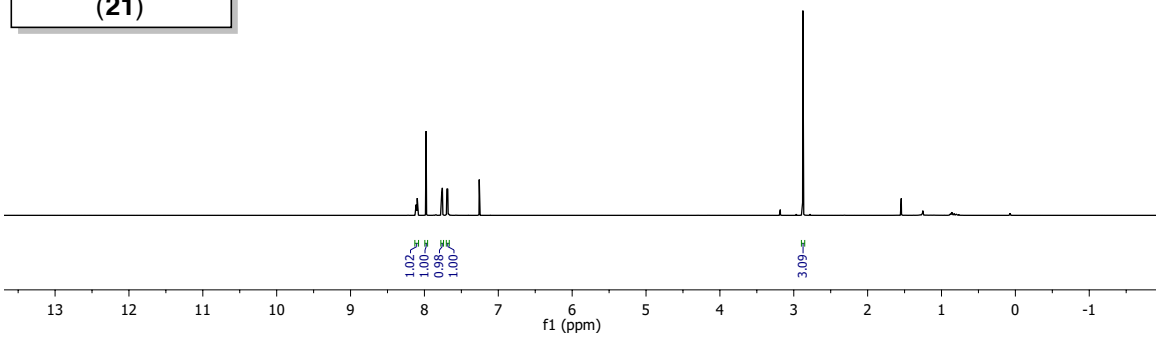


xvii. ***(21)***

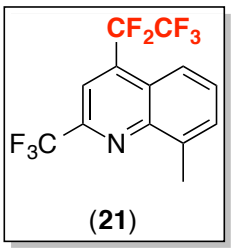
^{1}H NMR at 23 ºC ($CDCl_3$)



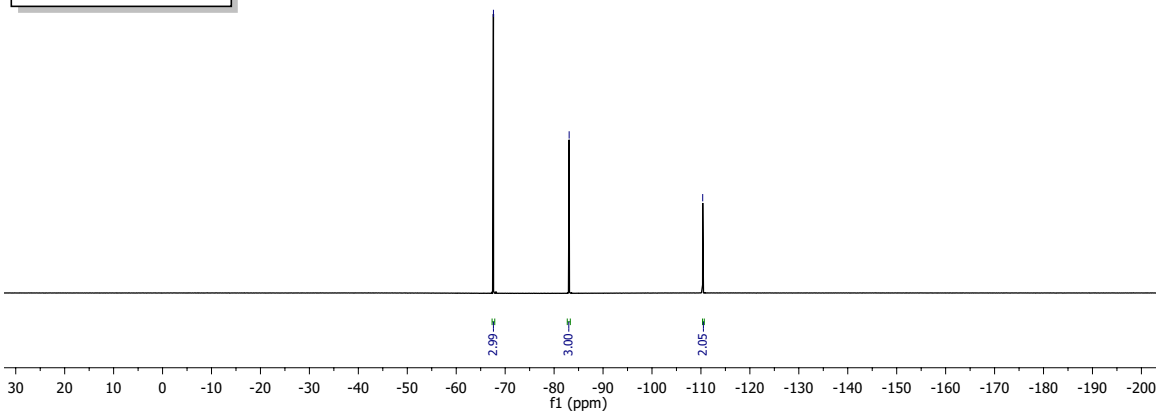
(**21**)



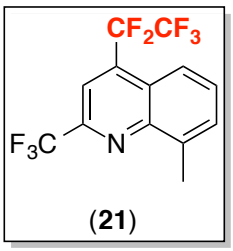
^{19}F NMR at 23 ºC ($CDCl_3$)



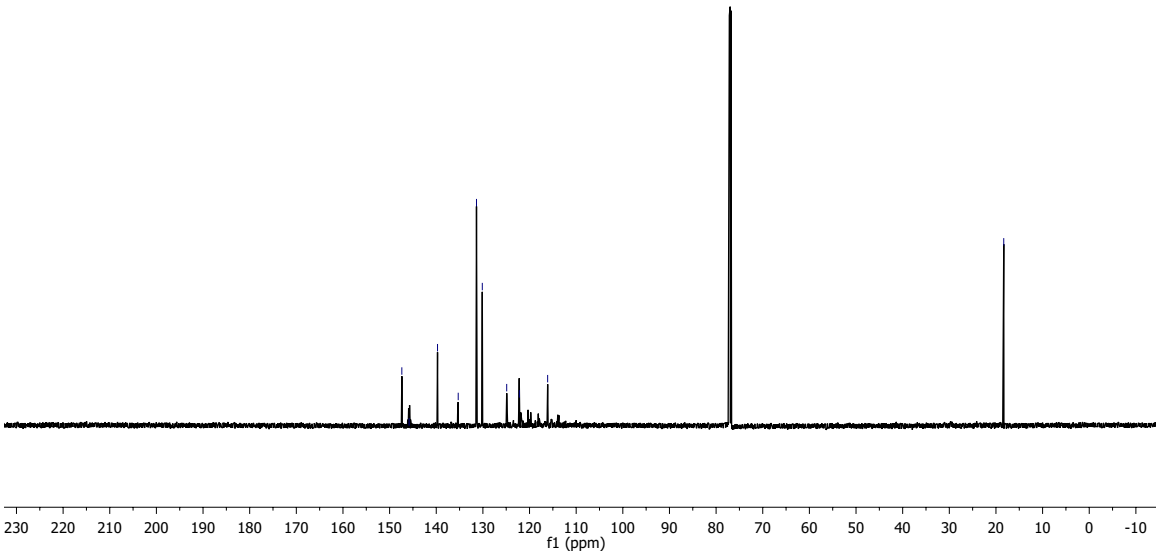
(**21**)



^{13}C NMR at 23 ºC ($CDCl_3$)

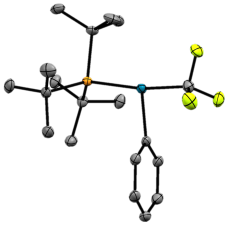


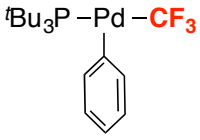
(**21**)



12. X-Ray Crystallography Experimental Data

*i. Structure determination of **1-CF$_3$***





Yellow block-like crystals of **1-CF$_3$** were grown from a diethyl ether solution of the compound at -35 ºC. A crystal of dimensions 0.25 x 0.12 x 0.10 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ùω The exposure times were 1 sec. for the low angle images, 5 sec. for high angle. Rigaku

d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 29861 reflections to a maximum 2è value of 138.50° of which 3785 were independent and 3772 were greater than 2ó(I). The final cell constants (Table S8) were based on the xyz centroids 22377 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/n with Z = 4 for the formula $C_{19}H_{32}F_3PPd$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0385 and wR2 = 0.1051 [based on I > 2sigma(I)], R1 = 0.0385 and wR2 = 0.1051 for all data. Additional details are presented in Table S8 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

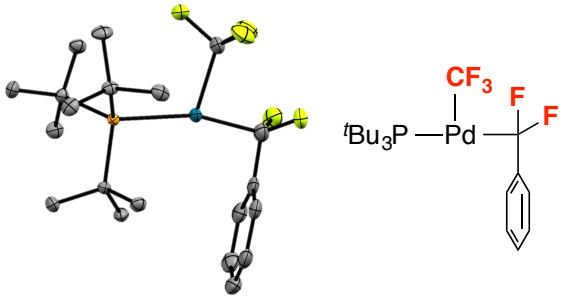
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015)

Empirical Formula	$C_{19}H_{32}F_3PPd$
Formula Weight	454.81
Temperature	85K
Wavelength	1.54184 Å
Crystal System	Monoclinic
Space Group	P2(1)/n
Unit Cell Dimensions	a = 9.97560 Å alpha = 90.00º b =15.5846 Å beta = 101.8610º c = 13.3924 Å gamma = 90.00 º
Volume	2037.60 $Å^3$
Z	4
Calculated Density	1.483 Mg/m^3
Absorption Coefficient	8.304 mm^{-1}
F(000)	936
Crystal Size	0.250 x 0.120 x 0.100 mm
Theta Range for Data Collection	4.408 to 69.251 º
Limiting Indices	-12≤h≤12, -18≤k≤18, -16≤l≤16
Reflections Collected	29863
Independent Reflections	3785 [R(int) =0.0954]

Completeness to Theta	67.684 (100.0%)
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.0000. and 0.25793
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	3785/ 0 / 227
Goodness-of-Fit on F^2	1.125
Final R Indices [I>2σ(I)]	R1 = 0.0385, wR2 = 0.1051
R indices (all data)	R1 = 0.0387, wR2 = 0.1052
Largest Difference Peak and Hole	1.850 and -1.192 e. $Å^{-3}$

Table S8. Crystallographic information for **1-CF_3**.

*ii. Structure determination of **3***



Yellow block-like crystals of **3** were grown from a diethyl ether/pentane solution of the compound at -35 ºC. A crystal of dimensions 0.14 x 0.08 x 0.07 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 5 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 64632 reflections to a maximum 2θ value of 138.86° of which 4073 were independent and 4057 were greater than 2σ(I). The final cell constants (Table S9) were based on the xyz centroids 44062 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group Pbca with Z = 8 for the formula $C_{20}H_{32}F_5PPd$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0235 and wR2 = 0.0598 [based on I > 2sigma(I)], R1 = 0.0235 and wR2 = 0.0598 for all data. Additional details are presented in Table S9 and are given as Supporting

Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014. CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Empirical Formula	$C_{20}H_{32}F_5PPd$
Formula Weight	504.82
Temperature	85K
Wavelength	1.54184 Å
Crystal System	Orthorhombic
Space Group	Pbca
Unit Cell Dimensions	a = 16.80637 Å alpha = 90.00º b =14.39046 Å beta = 90.00º c = 18.03556 Å gamma = 90.00 º
Volume	4361.93 $Å^3$
Z	8
Calculated Density	1.537 Mg/m^3
Absorption Coefficient	7.958 mm^{-1}
F(000)	2064
Crystal Size	0.140 x 0.080 x 0.07 mm
Theta Range for Data Collection	4.730 to 69.434 º
Limiting Indices	-20≤h≤20, -17≤k≤17, -20≤l≤21
Reflections Collected	64362
Independent Reflections	4073[R(int) =0.0512]
Completeness to Theta	67.684 (100.0%)
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.0000. and 0.55148
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	4073/ 0 / 254
Goodness-of-Fit on F^2	1.089
Final R Indices [I>2σ(I)]	R1 = 0.0235, wR2 = 0.0598
R indices (all data)	R1 = 0.0235, wR2 = 0.0598
Largest Difference Peak and Hole	0.897 and -0.787 e. $Å^{-3}$

Table S9. Crystallographic information for **3**.