Supporting Information for

Copper-Catalyzed Defluorinative Borylation and Silylation of *gem*-Difluoroallyl Groups

Trevor W. Butcher,[‡] Jonathan L. Yang,[‡] and John F. Hartwig*

TABLE OF CONTENTS

[‡] These authors contributed equally.

GENERAL INFORMATION

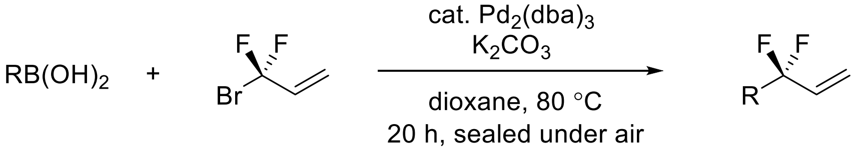
All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. Reactions conducted in vials (for example, the copper-catalyzed defluorinative borylations) were heated in a metal heating block, and reactions conducted in Schlenk flasks (for example, those for the synthesis of substrates) were heated in an oil bath. Unless stated otherwise, reagents and solvents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran was purified by passing it through a solvent column composed of activated A-1 alumina and degassed by the freeze-pump-thaw method.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on commercial instruments (300, 400, 500 and 600 MHz) at the NMR facility of the University of California, Berkeley. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 151 MHz. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were acquired at 565 MHz. Chemical shifts are reported relative to residual solvent peaks ($CDCl_3$ = 7.26 ppm, CD_2Cl_2 = 5.32 ppm, CD_3CN = 1.94 ppm, Acetone-d_6= 2.04 ppm, and C_6D_6 = 7.16 ppm for ^{1}H NMR spectra and $CDCl_3$ = 77.16 ppm, CD_2Cl_2 = 53.5 ppm, CD_3CN = 1.32 ppm (methyl resonance), Acetone-d_6 = 29.8 ppm (methyl resonance), and C_6D_6 = 128.1 ppm for ^{13}C NMR spectra). For ^{19}F NMR spectra, chemical shifts are reported relative to the δ –113.15 resonance of PhF used as an external reference. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; hept, heptet; AB, AB quartet; m, multiplet; br, broad.

High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer at the Micro Mass Analytical Facility operated by the College of Chemistry, University of California, Berkeley, or with an Agilent Time of Flight (Q-TOF) mass spectrometer in ESI mode. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and by staining with $KMnO_4$. Column chromatography was generally performed on a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold^{TM} columns.

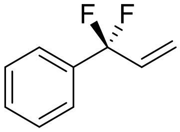
SYNTHESIS OF SUBSTRATES

Fluorinated allylic electrophiles **1a**–**1h** were prepared in one step from commercially-available arylboronic acids according to the protocol reported by Zhang and coworkers.[1] Fluorinated allylic electrophiles **1i**[2] and **1j**[3] were prepared by Barbier reaction of 3-bromo-3,3-difluoropropene and the appropriate carbonyl compound in one step according to the literature.



Allylic electrophiles **1a, 1c, 1d, 1f**–**1h** are known compounds as reported by Zhang and coworkers.[1] Allylic electrophiles **1b** and **1e** were reported in a recent report by us;[3] precise details of their synthesis are also given below.

(1,1-difluoroallyl)benzene (1b)



The title compound was prepared according to the following procedure. The reaction was conducted under air. Phenylboronic acid (365.8 mg, 3.000 mmol, 1 equiv) and K_2CO_3 (1.244 g, 9.000 mmol, 3.000 equiv) were weighed directly into a 50 mL Schlenk flask with a single opening sealed with a Teflon plug and containing a magnetic stir bar. $Pd_2(dba)_3$ (11.0 mg, 12.0 µmol, 0.400 mol %) was added, followed by dry dioxane (15.0 mL) and distilled water (27.0 µL, 1.50 mmol, 0.500 equiv). Lastly, 3-bromo-3,3-difluoropropene (495 µL, 4.50 mmol, 1.50 equiv) was added. The Schlenk flask was sealed, and the reaction mixture was stirred vigorously and heated at 80 °C in an oil bath for 20 h. After this time, the reaction mixture was cooled to ambient temperature, diluted with THF, and filtered through a pad of magnesium sulfate. Due to the volatility of the product, the crude reaction mixture was carefully concentrated under vacuum at 0 °C. The product was then purified by silica gel column chromatography (0/100 to 10/90 of ether/pentane) to provide (1,1-difluoroallyl)benzene (**1b**) as a clear, colorless liquid (188.5 mg, 1.223 mmol, 41%). *Note:* It is important that the reaction vessel has little headspace and that the entire vessel is submerged in the heating bath.

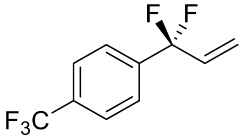
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.52 (ddt, *J* = 5.3, 3.1, 1.6 Hz, 2H), 7.44 (dd, *J* = 5.2, 2.0 Hz, 3H), 6.17 (ddt, *J* = 17.3, 11.0, 9.7 Hz, 1H), 5.58 (dt, *J* = 17.2, 2.8 Hz, 1H), 5.49 (d, *J* = 10.9 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 136.4 (t, *J* = 27.4 Hz), 134.0 (t, *J* = 30.2 Hz), 130.1 (t, *J* = 1.8 Hz), 128.6, 125.6 (t, *J* = 5.7 Hz), 119.9 (t, *J* = 9.3 Hz), 119.5 (t, *J* = 238.3 Hz).

^{19}F NMR (565 MHz, CDCl$_3$) δ -94.6 (dd, *J* = 9.7, 2.8 Hz).

HRMS (EI): *m/z* for $C_9H_8F_2$ $[M]^+$ calcd.: 154.0594, found: 154.0593

1-(1,1-difluoroallyl)-4-(trifluoromethyl)benzene (1e)



The title compound was prepared according to the following procedure. The reaction was conducted under air. 4-(Trifluoromethyl)phenylboronic acid (569.8 mg, 3.000 mmol, 1 equiv) and K_2CO_3 (1.244 g, 9.000 mmol, 3.000 equiv) were weighed directly into a 50 mL Schlenk flask with a single opening sealed with a Teflon plug and containing a magnetic stir bar. $Pd_2(dba)_3$ (11.0 mg, 12.0 µmol, 0.400 mol %) was added, followed by dry dioxane (15.0 mL) and distilled water (27.0 µL, 1.50 mmol, 0.500 equiv). Lastly, 3-bromo-3,3-difluoropropene (495 µL, 4.50 mmol, 1.50 equiv) was added. The Schlenk flask was sealed and the reaction mixture was stirred vigorously and heated at 80 °C in an oil bath for 20 h. After this time, the reaction mixture was cooled to ambient temperature, diluted with THF, and filtered through a pad of magnesium sulfate. Due to the volatility of the product, the crude reaction mixture was carefully concentrated under vacuum at 0 °C. The product was then purified by silica gel column chromatography (0/100 to 10/90 of ether/pentane) to provide difluoroallylarene **1e** as a clear, colorless liquid (261.5 mg, 1.177 mmol, 39%). *Note:* It is important that the reaction vessel has little headspace and that the entire vessel is submerged in the heating bath.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 6.15 (ddt, *J* = 17.3, 10.9, 9.8 Hz, 1H), 5.59 (dt, *J* = 17.3, 2.8 Hz, 1H), 5.53 (d, *J* = 10.9 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 140.1 (t, *J* = 27.8 Hz), 133.3 (t, *J* = 29.7 Hz), 132.3 (q, *J* = 32.7 Hz), 126.3 (t, *J* = 5.6 Hz), 125.7 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.4 Hz), 120.7 (t, *J* = 9.3 Hz), 118.8 (t, *J* = 239.2 Hz).

^{19}F NMR (565 MHz, CDCl$_3$) δ -63.9, -95.4 (dd, *J* = 9.7, 2.5 Hz).

HRMS (EI): *m/z* for $C_{10}H_7F_5$ $[M]^+$ calcd.: 222.0468, found: 222.0464.

DEFLUORINATIVE BORYLATION OF 3-SUBSTITUTED 3,3-DIFLUOROPROPENES

1) General Procedure for Investigation of Scope

Step 1: Defluorinative Borylation

In a nitrogen-filled glovebox, a stock solution of CuCl and PCy_3 in THF was prepared (20.0 mol %, 0.0400 mmol CuCl and 20.0 mol %, 0.0400 mmol PCy_3 per 400 µL THF). The solution was allowed to stir at room temperature for 20 minutes, at which time neat NaO*t*-Bu was added (40.0 mol %, 0.0800 mmol per 400 µL THF), and the subsequent solution was allowed to stir at room temperature for 1 hour. Separately, a 4 mL vial equipped with a stir bar was charged with the 3-substituted 3,3-difluoropropene (1.00 equiv, 0.200 mmol) and a 400 µL aliquot of the prepared catalyst solution. The resulting mixture was allowed to stir for 10 seconds, after which time neat bis(pinacolato)diboron (2.00 equiv, 0.400 mmol) was added. The the reaction mixture immediately turned a dark orange-brown. The reaction vial was then sealed with a PTFE cap and was heated at 45 °C in a metal heating block with stirring for 5 hours. After this time, the reaction was diluted with of $CDCl_3$ (1.00 mL) and fluorobenzene (internal standard, 80.0 µL) was added. The resulting mixture was thoroughly mixed, and an aliquot was analyzed via ^{1}H NMR and ^{19}F NMR spectroscopy. The NMR sample and bulk material were combined, and the reaction mixture was diluted with 30 mL of diethyl ether and washed with 1M HCl (3 x 30 mL), water (30 mL), and brine (30 mL). The organic layer was dried over sodium sulfate, and the solvent was evaporated under vacuum in a 100 mL round-bottomed flask to provide the crude allylic boronic ester.

Step 2: Oxidation to the Allylic Alcohol

The 100 mL round bottom flask containing the crude allylic boronic ester from Step 1 was equipped with a stir bar and charged with tetrahydrofuran (1.8 mL). The resulting solution was cooled to 0 °C with an ice bath, and aqueous 3 M NaOH (1.2 mL) was added dropwise, followed by immediate dropwise addition of aqueous hydrogen peroxide with a plastic syringe (950 µL, 34% by mass in H_2O). Following the addition of hydrogen peroxide, the reaction mixture turned dark brown. The reaction mixture was stirred in an ice bath, where it was allowed to slowly warm to room temperature overnight (14 h). After this time, the reaction mixture was again cooled to 0 °C and was quenched by dropwise addition of 2 M sodium thiosulfate. The mixture was extracted with dichloromethane (3 x 50 mL), the combined organic layers were dried over sodium sulfate, and the solvent was removed under vacuum. The resulting residue was subjected to silica-gel column chromatography to provide pure allylic alcohol **4**.

2) General Procedure for Investigation of Reaction Conditions

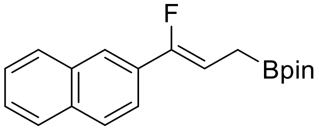
In a nitrogen-filled glovebox, a stock solution of CuCl and ligand or pre-formed copper catalyst in THF was prepared (1.0 mg, 20 mol %, 0.010 mmol CuCl and 20 mol %, 0.010 mmol ligand or 20 mol %, 0.010 mmol pre-ligated copper complex per 100 µL THF). The resulting solution was allowed to stir for 20 minutes, after which time a neat alkali metal *tert*-butoxide base was added (0.20 equiv–2.00 equiv, 0.010–0.100 mmol), and the subsequent solution was allowed to stir for 30 minutes. Separately, a 4 mL vial equipped with a stir bar was charged with 2-(1,1-difluoroallyl)naphthalene (**1a**) (10.2 mg, 1.00 equiv, 0.0500 mmol). A 100 µL aliquot of the prepared catalyst solution was added, and the resulting solution was allowed to stir for 10 seconds before adding neat bis(pinacolato)diboron (25.4 mg, 2.00 equiv, 0.100 mmol). The reaction vial was then sealed and heated at 45 °C in a metal heating block with stirring for 5 hours. After this time, the reaction was diluted with $CDCl_3$ (700 µL), and fluorobenzene (internal standard, 20.0 µL) was added. The resulting mixture was thoroughly mixed, and an aliquot was removed and analyzed via ^1H and ^{19}F NMR spectroscopy.

*3) Preparation of allylboronic ester **2a*** on a 1 mmol scale

In a nitrogen-filled glovebox, a solution of CuCl and PCy_3 in THF was prepared (19.8 mg, 0.200 mmol, 20.0 mol % CuCl and 58.9 mg, 0.200 mmol, 20.0 mol% PCy_3 in 2.0 mL THF). The resulting solution was allowed to stir at room temperature for 20 minutes, after which time neat NaO*t*-Bu was added (38.4 mg, 0.400 mmol, 40.0 mol), and the subsequent solution was allowed to stir at room temperature for 1 hour. Then, neat 2-(1,1-difluoroallyl)naphthalene (**1a**) (204.2 mg, 1.00 mmol, 1.00 equiv) was added to the catalyst solution. The resulting mixture was allowed to stir for 10 seconds, after which time neat bis(pinacolato)diboron (507.8 mg, 2.00 mmol, 2.00 equiv) was added. The reaction vial was then sealed with a PTFE cap and was heated at 45 °C in a metal heating block with stirring for 5 hours. After this time, the resulting mixture was diluted with 30 mL of diethyl ether and washed with 1M HCl (3 x 30 mL), water (30 mL), and brine (30 mL). The organic layer was dried over sodium sulfate, and the solvent was evaporated under vacuum in a 100 mL round-bottomed flask to provide the crude allylic boronic ester as a white powder (537.0 mg). This material was used for the subsequent diversitifications without further purification. ^1H NMR analysis of the crude material suggested the product was obtained as a 1.3:1 mixture of the desired product and B_2pin_2.

CHARACTERIZATION OF CRUDE ALLYLBORONIC ESTERS

(*Z*)-2-(3-fluoro-3-(naphthalen-2-yl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)

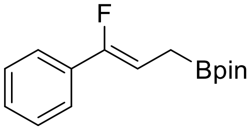


Prepared according to the general procedure. Crude allylboronic ester **2a** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum are reported only.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.95 (s, 1H), 7.87 – 7.74 (m, 3H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.50 – 7.43 (m, 2H), 5.67 (dt, *J* = 37.1, 7.9 Hz, 1H).

^{19}F NMR (565 MHz, CDCl$_3$) δ -103.4 (d, *J* = 22.3 Hz, minor *E*-isomer), -121.5 (d, *J* = 37.2 Hz, major *Z*-isomer).

(Z)-2-(3-fluoro-3-phenylallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)

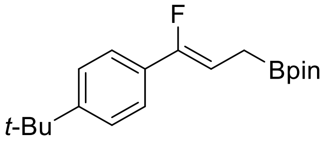


Prepared according to the general procedure. Crude allylboronic ester **2b** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum are reported only.

^{1}H NMR (600 MHz, CDCl$_3$) δ 5.51 (dt, *J* = 37.1, 7.9 Hz, 1H).

^{19}F NMR (565 MHz, CDCl$_3$) δ), -103.4 (d, *J* = 22.5 Hz, minor, *E*-isomer), -121.5 (d, *J* = 37.1 Hz, major, *Z*-isomer).

(*Z*)-2-(3-(4-(*tert*-butyl)phenyl)-3-fluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)

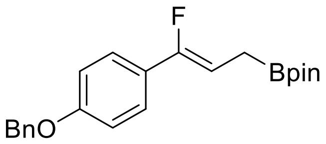


Prepared according to the general procedure. Crude allylboronic ester **2c** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum are reported only.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.46 (dt, *J* = 37.2, 8.0 Hz, 1H).

^{19}F NMR (565 MHz, $CDCl_3$) δ, -103.4 (d, *J* = 21.9 Hz, minor *E*-isomer), -121.4 (d, *J* = 37.3 Hz, major *Z*-isomer).

(*Z*)-2-(3-(4-(benzyloxy)phenyl)-3-fluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)

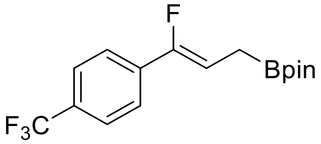


Prepared according to the general procedure. Crude allylboronic ester **2d** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum are reported only.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.33 (dt, *J* = 37.3, 7.9 Hz, 2H), 5.04 (s, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ, -120.5 (d, *J* = 37.2 Hz, major *Z*-isomer), -102.3 (d, *J* = 22.4 Hz, minor *E*-isomer).

(*Z*)-2-(3-fluoro-3-(4-(trifluoromethyl)phenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)

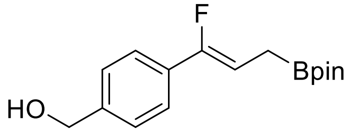


Prepared according to the general procedure. Crude allylboronic ester **2e** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum are reported only.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (s, 4H), 5.65 (dt, *J* = 36.6, 8.0 Hz, 1H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.7 (s, both isomers), -105.1 (d, *J* = 22.4 Hz, minor E-isomer), -122.2 (d, *J* = 36.6 Hz, major Z-isomer).

(*Z*)-(4-(1-fluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)phenyl)methanol (2f)

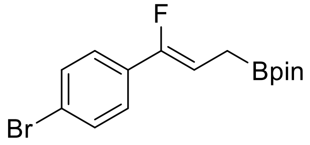


Prepared according to the general procedure. Crude allylboronic ester **2f** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum are reported only.

1H NMR (600 MHz, CDCl3) δ 5.48 (dt, *J* = 37.1, 7.9 Hz, 1H), 4.89 (s, 2H).

^{19}F NMR (565 MHz, CDCl$_3$) δ -103.5 (d, *J* = 22.5 Hz, minor *E*-isomer), -121.3 (d, *J* = 37.1 Hz, major *Z*-isomer).

(Z)-2-(3-(4-bromophenyl)-3-fluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)

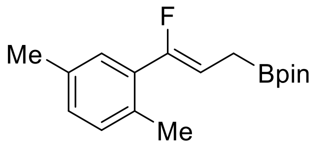


Prepared according to the general procedure. Crude allylboronic ester **2g** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum arereported only.

^{1}H NMR (600 MHz, CDCl$_3$) δ 5.50 (dt, *J* = 36.8, 7.9 Hz, 1H).

^{19}F NMR (565 MHz, CDCl$_3$) δ -104.2 (d, *J* = 22.2 Hz, minor *E*-isomer), -121.7 (d, *J* = 36.9 Hz, major *Z*-isomer).

(*Z*)-2-(3-(2,5-dimethylphenyl)-3-fluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)

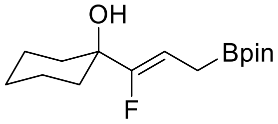


Prepared according to the general procedure. Crude allylboronic ester **2h** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum are reported only.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.08 (dt, *J* = 36.6, 7.9 Hz, 1H), 2.34 (d, *J* = 2.8 Hz, 3H), 2.30 (s, 3H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.7 (d, *J* = 36.5 Hz, major *Z*-isomer), -94.9 (d, *J* = 19.4 Hz, minor, *E*-isomer).

(*Z*)-1-(1-fluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)cyclohexan-1-ol (2i)

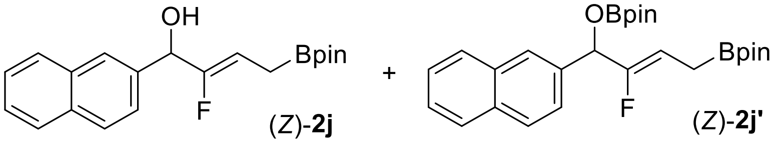


Prepared according to the general procedure with the following modifications: 25 mol% CuCl + PCy_3, 50 mol% NaO*t*-Bu RT, 20 h. Crude allylboronic ester **2i** was prepared according to the general procedure with the following modifications: 25 mol% catalyst (CuCl + PCy_3); 50 mol% NaO*t*-Bu, RT, 20 h. Crude allylboronic ester **2i** was characterized by ^{1}H and ^{19}F NMR spectroscopy after extraction with ethyl acetate. Only diagnostic resonances are reported in the ^{1}H NMR spectrum.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.21 (dt, *J* = 17.3, 3.7 Hz, minor *E*-isomer), 4.97 (dt, *J* = 38.4, 7.8 Hz, major *Z*-isomer).

^{19}F NMR (565 MHz, $CDCl_3$) δ -121.9 (d, *J* = 16.9 Hz, minor *E*-isomer), -125.7 (d, *J* = 38.4 Hz, major *Z*-isomer).

(*Z*)-2-fluoro-1-(naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-ol (2j)



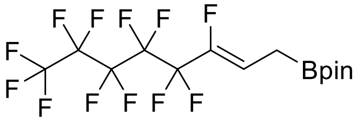
Prepared according to the general procedure with the following modifications: 25 mol% Cu(xantphos)Cl, 50 mol% NaO*t*-Bu RT, 20 h. Crude allylboronic ester **2j+2j'** was characterized by ^{1}H and ^{19}F NMR spectroscopy after extraction with ethyl acetate. The two species have similar

^{19}F NMR spectral features and together convert to the same diol (**4j**) upon oxidation. *Note:* Reactions conducted under standard conditions (with catalytic CuCl + PCy$_3$) produce product **2j** + **2j'** as a mixture of *Z* and *E* isomers in an 88:12 *Z:E* ratio. Reactions conducted with Cu(xantphos)Cl provided product **2j** + **2j'** each in >95:5 selectivity for the *Z* isomer (The *Z* isomers are not observed in crude ^{19}F NMR spectra but the corresponding diol formed after oxidation was isolated as a 98:2 mixture of *Z* and *E* isomers.) Only diagnostic resonances are reported in the ^{1}H NMR spectrum below.

^{1}H NMR (600 MHz, CDCl$_3$) δ major *Z*-isomers: 5.75 (d, *J* = 11.7 Hz 1H), 5.41 (d, *J* = 14.4 Hz, 1H), 5.14 (dt, *J* = 36.7, 7.9 Hz, 1H), 5.07 (dt, *J* = 36.0, 7.9 Hz, 1H).

^{19}F NMR (565 MHz, CDCl$_3$) δ major *Z*-isomers: -123.0 (dd, *J* = 36.0, 11.9 Hz), -123.8 (dd, *J* = 36.8, 14.2 Hz). minor *E*-isomers (only visible in crude reactions conducted with catalytic CuCl+PCy$_3$): -121.9 (dd, *J* = 25.6, 20.8 Hz), -122.7 (dd, *J* = 26.2, 20.4 Hz).

(*Z*)-2-(3,4,4,5,5,6,6,7,7,8,8,8-dodecafluorooct-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



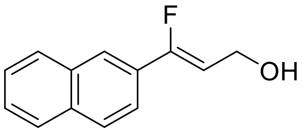
Prepared according to the general procedure. Crude allylboronic ester **2k** was characterized by ^{1}H and ^{19}F NMR spectroscopy. Diagnostic resonances in the ^{1}H NMR spectrum are reported only.

^{1}H NMR (600 MHz, CDCl$_3$) δ 5.71 (dt, *J* = 33.5, 8.4 Hz, 1H).

^{19}F NMR (565 MHz, CDCl$_3$) δ -80.9 (t, *J* = 10.1 Hz, 3F), -117.3 (q, *J* = 13.7 Hz, 2F), -122.9 – -123.1 (m, 2F), -123.4 – -123.6 (m, 2F), -126.2 – -126.3 (m, 2F), -134.1 – -134.3 (m, 1F).

CHARACTERIZATION OF PRODUCTS

(*Z*)-3-fluoro-3-(naphthalen-2-yl)prop-2-en-1-ol (4a)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale. The yield of the corresponding boronic ester was determined to be 91% by ^{19}F NMR analysis of the crude product with 99:1 *Z*:*E* selectivity. Oxidation conducted according to the general procedure and column chromatography (20/80 ethyl acetate/hexanes) of the crude product gave allylic alcohol **4a** as a white solid (32.8 mg, 0.162 mmol, 81%).

m.p. 86.5 – 88.0 °C

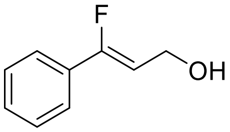
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.88 – 7.78 (m, 3H), 7.58 (dt, *J* = 8.7, 1.4 Hz, 1H), 7.54 – 7.48 (m, 2H), 5.79 (dt, *J* = 36.6, 7.1 Hz, 1H), 4.51 (dd, *J* = 7.1, 2.0 Hz, 2H), 1.71 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2 (d, *J* = 251.0 Hz), 133.7, 133.1, 129.0 (d, *J* = 27.8 Hz), 128.7, 128.5 (d, *J* = 2.4 Hz), 127.8, 127.0, 126.8, 124.0 (d, *J* = 7.6 Hz), 121.9 (d, *J* = 6.7 Hz), 105.5 (d, *J* = 15.4 Hz), 56.3 (d, *J* = 7.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.4 (d, *J* = 36.7 Hz).

HRMS (EI): *m/z* for $C_{13}H_{11}FO^+$ $[M]^+$ calcd.: 202.0794, found: 202.0796.

(*Z*)-3-fluoro-3-phenylprop-2-en-1-ol (4b)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale. The yield of the corresponding boronic ester was determined to be 97% by ^{19}F NMR analysis of the crude product with 98:2 *Z*:*E* selectivity. Oxidation according to the general procedure and column chromatography (20/80 ethyl acetate/hexanes) of the crude product gave allylic alcohol **4b** as a clear oil (28.1 mg, 0.185 mmol, 92%).

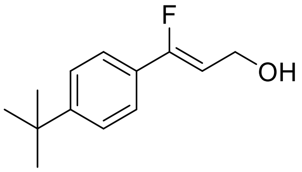
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.57 – 7.52 (m, 2H), 7.42 – 7.35 (m, 3H), 5.68 (dt, *J* = 37.0, 7.0 Hz, 1H), 4.41 (dd, *J* = 7.0, 2.2 Hz, 2H), 1.75 (br s, 1H).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 157.9 (d, *J* = 250.2 Hz), 131.9 (d, *J* = 28.7 Hz), 129.3, 128.6 (d, *J* = 2.1 Hz), 124.4 (d, *J* = 7.2 Hz), 105.3 (d, *J* = 15.3 Hz), 55.9 (d, *J* = 7.7 Hz).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -118.3 (d, *J* = 37.0 Hz).

NMR spectra are consistent with the literature.[4]

(*Z*)-3-(4-(tert-butyl)phenyl)-3-fluoroprop-2-en-1-ol (4c)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale. The yield of the corresponding boronic ester was determined to be 98% with 98:2 *Z*:*E* selectivity by ^{19}F NMR analysis of the crude product. Oxidation according to the general procedure and column chromatography (20/80 ethyl acetate/hexanes) of the crude product gave allylic alcohol **4c** as a white solid (39.9 mg, 0.192 mmol, 96%).

m.p. 59.0 – 60.0 ºC

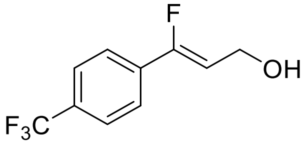
^{1}H NMR (600 MHz, C_6D_6) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.40 (dt, *J* = 37.3, 7.0 Hz, 1H), 4.22 (dd, *J* = 6.9, 2.1 Hz, 2H), 1.16 (s, 9H). *Note:* The OH proton was not observed.

^{13}C NMR (151 MHz, C_6D_6) δ 158.0 (d, *J* = 249.3 Hz), 152.4, 129.8 (d, *J* = 28.8 Hz), 125.8 (d, *J* = 2.1 Hz), 124.6 (d, *J* = 7.1 Hz), 105.6 (d, *J* = 15.2 Hz), 56.2 (d, *J* = 7.5 Hz), 34.7, 31.3.

^{19}F NMR (565 MHz, C_6D_6) δ -118.0 (d, *J* = 37.2 Hz).

HRMS (EI): *m/z* for $C_{13}H_{17}FO^+$ $[M]^+$ calcd.: 208.1263, found: 208.1264.

(*Z*)-3-fluoro-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (4e)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale. The yield of the corresponding boronic ester was determined to be 89% with 99:1 *Z*:*E* selectivity by ^{19}F NMR analysis of the crude product. Oxidation according to the general procedure and column chromatography (20/80 ethyl acetate/hexanes) of the crude product gave allylic alcohol **4e** as a clear oil (33.9 mg, 0.154 mmol, 77%).

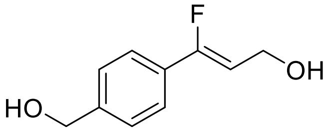
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 4H), 5.77 (dt, *J* = 36.3, 7.0 Hz, 1H), 4.48 (dd, *J* = 7.0, 2.2 Hz, 2H), 1.72 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7 (d, *J* = 251.1 Hz), 135.2 (d, *J* = 29.2 Hz), 131.3 (q, *J* = 32.6 Hz), 125.8 – 125.7 (m), 124.8 (d, *J* = 7.2 Hz), 124.0 (q, *J* = 272.1 Hz), 107.4 (d, *J* = 14.9 Hz), 56.2 (d, *J* = 7.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.9 (3F), -117.7 (d, *J* = 36.5 Hz, 1F).

NMR spectra are consistent with the literature.[4]

(*Z*)-3-fluoro-3-(4-(hydroxymethyl)phenyl)prop-2-en-1-ol (4f)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale. The yield of the corresponding boronic ester was determined to be 92% with 98:2 *Z*:*E* selectivity by ^{19}F NMR analysis of the crude product. Oxidation according to the general procedure and column chromatography (gradient from 20/80 to 50/50 ethyl acetate/hexanes) of the crude mixture gave allylic alcohol **4f** as a white solid (27.7 mg, 0.152 mmol, 76%).

m.p. 88.5 – 89.0 °C

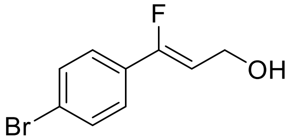
^{1}H NMR (600 MHz, Acetone-d_6) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.72 (dt, *J* = 38.1, 6.9 Hz, 1H), 4.65 (d, *J* = 5.8 Hz, 2H), 4.34 (ddd, *J* = 7.2, 5.8, 2.2 Hz, 2H), 4.27 (t, *J* = 5.8 Hz, 1H), 3.84 (t, *J* = 5.7 Hz, 1H).

^{13}C NMR (151 MHz, Acetone-d_6) δ 157.4 (d, *J* = 247.1 Hz), 144.6, 131.4 (d, *J* = 28.8 Hz), 127.5 (d, *J* = 2.1 Hz), 124.8 (d, *J* = 7.1 Hz), 107.0 (d, *J* = 15.4 Hz), 64.2, 55.7 (d, *J* = 7.8 Hz).

^{19}F NMR (565 MHz, Acetone-d_6) δ -120.4 (d, *J* = 37.9 Hz).

HRMS (EI): *m/z* for $C_{10}H_{11}FO_2^+$ $[M]^+$ calcd.: 182.0743, found: 182.0744.

(*Z*)-3-(4-bromophenyl)-3-fluoroprop-2-en-1-ol (4g)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale. The yield of the corresponding boronic ester was determined to be 99% with 99:1 *Z*:*E* selectivity by ^{19}F NMR analysis of the crude product. Oxidation according to the general procedure and column chromatography (20/80 ethyl acetate/hexanes) of the crude product gave allylic alcohol **4g** was isolated as a pale yellow gum (44.2 mg, 0.191 mmol, 96%).

Compound **4g** is known.[4]

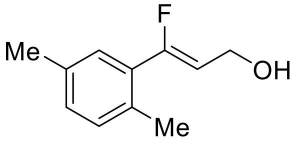
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 5.68 (dt, *J* = 36.4, 7.1 Hz, 1H), 4.46 (dd, *J* = 7.1, 2.1 Hz, 2H), 1.68 (br s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.3 (d, *J* = 251.0 Hz), 131.9 (d, *J* = 2.4 Hz), 130.8 (d, *J* = 29.3 Hz), 126.1 (d, *J* = 7.2 Hz), 123.7, 105.6 (d, *J* = 15.0 Hz), 56.2 (d, *J* = 7.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.4 (d, *J* = 36.4 Hz).

The NMR spectra are consistent with the literature.[4]

(*Z*)-3-(2,5-dimethylphenyl)-3-fluoroprop-2-en-1-ol (4h)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale. The yield of the corresponding boronic ester was determined to be 96% with 99:1 *Z*:*E* selectivity by ^{19}F NMR analysis of the crude product. Oxidation according to the general procedure and column chromatography (20/80 ethyl acetate/hexanes) of the crude product gave allylic alcohol **4h** as a clear oil (32.6 mg, 0.181 mmol, 91%).

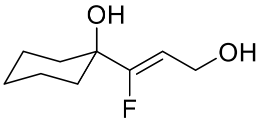
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.20 (s, 1H), 7.11 (s, 2H), 5.28 (dt, *J* = 36.1, 6.9 Hz, 1H), 4.40 (dd, *J* = 7.0, 2.2 Hz, 2H), 2.36 (d, *J* = 3.2 Hz, 3H), 2.32 (s, 3H), 1.76 (br s, 1H)

^{13}C NMR (151 MHz, CD_2Cl_2) δ 159.4 (d, *J* = 254.9 Hz), 135.4, 133.5, 132.0 (d, *J* = 25.6 Hz), 130.7, 130.3, 129.4 (d, *J* = 5.0 Hz), 109.2 (d, *J* = 15.9 Hz), 56.0 (d, *J* = 6.8 Hz), 20.6, 19.9 (d, *J* = 3.3 Hz).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -101.2 (d, *J* = 36.2 Hz).

HRMS (EI): *m/z* for $C_{11}H_{13}FO^+$ $[M]^+$ calcd.: 180.0950, found: 180.0951.

(*Z*)-1-(1-fluoro-3-hydroxyprop-1-en-1-yl)cyclohexan-1-ol (4i)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale with the following modifications: 25 mol% CuCl + PCy_3, 50 mol% NaO*t*-Bu RT, 20 h. The boronic ester intermediate was extracted with ethyl acetate prior to analysis by NMR spectroscopy. The yield of the corresponding boronic ester was determined to be 89% with 94:6 *Z*:*E* selectivity by ^{19}F NMR analysis of the crude product. Oxidation according to the general procedure and column chromatography (20/80 to 60/40 ethyl acetate/hexanes) of the crude product gave the pure *Z*-isomer of allylic alcohol **4i** as a white powder (27.5 mg, 0.158 mmol, 79%).

m.p. 69.0 – 70.0 °C

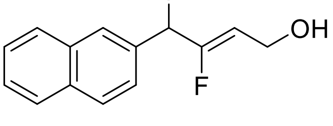
^{1}H NMR (600 MHz, CD_3CN) δ 5.13 (dt, *J* = 38.4, 7.0 Hz, 1H), 4.12 (d, *J* = 7.0 Hz, 2H), 2.97 (br s, 1H), 2.76 (br s, 1H), 1.71 – 1.49 (m, 9H), 1.33 – 1.22 (m, 1H).

^{13}C NMR (151 MHz, CD_3CN) δ 165.7 (d, *J* = 261.2 Hz), 104.7 (d, *J* = 12.9 Hz), 71.5 (d, *J* = 27.1 Hz), 55.3 (d, *J* = 8.7 Hz), 35.2, 26.1, 22.2.

^{19}F NMR (565 MHz, CD_3CN) δ -123.2 (d, *J* = 38.5 Hz).

HRMS (ESI negative): *m/z* for $C_9H_{14}FO_2^-$ $[M-H]^-$ calcd.: 173.0983, found: 173.0985.

(*Z*)-2-fluoro-1-(naphthalen-2-yl)but-2-ene-1,4-diol (4j)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale with the following modifications: 25 mol% Cu(xantphos)Cl, 50 mol% NaO*t*-Bu, RT, 20 h. The boronic ester intermediate was extracted with ethyl acetate prior to analysis by NMR spectroscopy. The yield of the corresponding boronic ester was determined to be 89% with >95:5 *Z*:*E* selectivity by ^{19}F NMR analysis of the crude product. Oxidation according to the general procedure and column chromatography (20/80 to 60/40 ethyl acetate/hexanes) of the crude product gave allylic alcohol **4j** as a white solid as a 98:2 mixture of *Z* and *E* isomers (36.4 mg, 0.157 mmol, 78%).

m.p. 108.5 – 110.0 °C

^{1}H NMR (600 MHz, CD_3CN) δ 7.95 – 7.86 (m, 4H), 7.57 – 7.47 (m, 3H), 5.36 (dd, *J* = 13.2, 4.7 Hz, 1H), 5.25 (dt, *J* = 37.3, 7.0 Hz, 1H), 4.14 (ddd, *J* = 7.4, 5.5, 2.0 Hz, 2H), 4.06 (d, *J* = 4.9 Hz, 1H), 2.84 (t, *J* = 5.7 Hz, 1H).

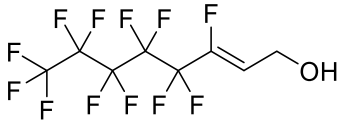
Note: Minor (2%) impurities corresponding to the E isomer were observed in the ^{1}H NMR spectrum. Diagnostic resonances: 5.81 (dd, *J* = 26.1, 4.6 Hz, 1H), 5.45 (dt, *J* = 21.2, 7.6 Hz, 1H).

^{13}C NMR (151 MHz, CD_3CN) δ 161.0 (d, *J* = 259.0 Hz), 138.9, 134.1, 134.1, 129.0, 128.9, 128.6, 127.3, 127.2, 126.5, 125.7, 108.0 (d, *J* = 11.5 Hz), 72.5 (d, *J* = 31.5 Hz), 55.1 (d, *J* = 7.2 Hz).

^{19}F NMR (565 MHz, CD_3CN) δ -121.20 (dd, *J* = 37.1, 13.2 Hz, 1F) Note: A minor (2%) impurity of the corresponding *E*-isomer was also observed in the ^{19}F NMR spectrum: -119.47 (t, *J* = 23.6 Hz).

HRMS (ESI negative): *m/z* for $C_{14}H_{12}FO_2^-$ [M-H]$^-$ calcd.: 231.0827, found: 231.0830.

(*Z*)-3,4,4,5,5,6,6,7,7,8,8,8-dodecafluorooct-2-en-1-ol (4k)



The title compound was prepared according to the general procedure for the defluorinative borylation of 3-substituted 3,3-difluoropropenes on a 0.200 mmol scale. The yield of the corresponding boronic ester was determined to be 98% with >98:2 *Z*:*E* selectivity by ^{19}F NMR analysis of the crude product (Although no diagnostic peaks for the corresponding *E* isomer could be identified, all impurities were present in <2% yield in the crude ^{19}F NMR spectrum). After oxidation according to the general procedure and column chromatography (gradient from 5/95 to 20/80 ethyl acetate/hexanes) of the crude reaction product, allylic alcohol **4i** was isolated under weak vacuum (15 torr) as a clear oil (46.0 mg, 0.134 mmol, 67%). After subjecting the sample to high vacuum (~0.5 torr, 10 minutes) the residual solvent was removed, but the isolated yield was significantly lower due to the volatility of the product (16.3 mg, 0.0474 mmol, 24%).

^{1}H NMR (600 MHz, CD_2Cl_2) δ 5.86 (dt, *J* = 34.1, 6.5 Hz, 1H), 4.44 – 4.38 (m, 2H), 1.79 (s, 1H).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 145.89 (dt, *J* = 261.5, 29.3 Hz), 115.95 (dt, *J* = 7.8, 4.2 Hz), 55.06 (d, *J* = 5.1 Hz) (all other signals were split by coupling to several fluorine atoms and could not be observed).

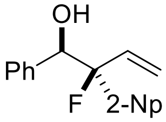
^{19}F NMR (565 MHz, CD_2Cl_2) δ -81.2 (t, *J* = 10.2 Hz, 3F), -118.1 (q, *J* = 13.8 Hz, 2F), -123.1 – -123.2 (m, 2F), -123.4 – -123.6 (m, 2F), -126.4 – -126.6 (m, 2F), -129.3 – -129.5 (m, 1F).

HRMS (EI): *m/z* for $C_8H_4F_{12}O^+$ $[M]^+$ calcd.: 344.0071, found: 344.0029.

Note: The error of the observed mass and predicted mass is 12 ppm. A second attempt to measure the HRMS was unsuccessful, as it is difficult to observe the molecular ion of compound **4k** by EI.

DERIVATIZATION OF DEFLUORINATIVE BORYLATION PRODUCTS

rac-(*1R,2S*)-2-fluoro-2-(naphthalen-2-yl)-1-phenylbut-3-en-1-ol (6a)



The following procedure was adapted from the literature.[5] In a nitrogen-filled glovebox, a 15 mL Schlenk flask with a single opening sealed with a Teflon plug was equipped with a stir bar was charged with 3-fluoro allyl boronic ester **2a** (45.7 mg of a 1.33:1 mole ratio of boronic ester **2a** to B_2pin_2, corresponding to 0.0900 mmol of **2a**) and tetrahydrofuran (0.90 mL). The flask was sealed with the Teflon plug, equipped with a rubber septum, and then removed from the glove box. The reaction mixture was and cooled to –78 °C with an acetone dry ice bath. Under N_2, a solution of *n*-butyllithium in hexanes (2.00 equiv, 1.6 M, 113 µL, 0.180 mmol) was added dropwise to the solution, and the reaction mixture was allowed to stir at –78 °C for 15 minutes. Trifluoroacetic anhydride (2.10 equiv, 39.7 µL, 0.189 mmol) was added dropwise, and the reaction mixture was allowed to stir at -78 °C for 30 minutes. Under N_2, benzaldehyde (0.27 mmol, 27.5 µL) was added dropwise, and the reaction stirred at -78º °C for 2 hours. The reaction was slowly warmed to room temperature and stirred overnight at the ambient temperature. After this time, the reaction was cooled to 0 ºC, quenched with 0.5 M NaOH (20 mL), extracted with dichloromethane (3 x 15 mL), and concentrated under vacuum. The crude material was subjected to purification by silica-gel column chromatography (gradient from 95/5 to 67/33 of hexanes/ethyl acetate) to provide pure homoallylic alcohol **6a** as a pale yellow solid (18.7 mg, 0.0640 mmol, 71%). The relative configuration was assigned based on a standard chair transition-state model and previous results.[5]

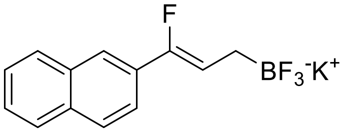
^{1}H NMR (600 MHz, Acetone-*d*$_6$) δ 7.90 – 7.83 (m, 4H), 7.58 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.31 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 6.68 (ddd, *J* = 21.1, 17.2, 11.3 Hz, 1H), 5.32 – 5.26 (m, 2H), 5.19 (dd, *J* = 14.3, 5.1 Hz, 1H), 4.83 (d, *J* = 5.0 Hz, 1H).

^{13}C NMR (151 MHz, Acetone-*d*$_6$) δ 140.9, 139.5 (d, *J* = 22.1 Hz), 137.7 (d, *J* = 19.7 Hz), 133.8, 133.7, 129.1, 129.1, 128.3, 128.2, 128.1, 128.0, 127.0, 127.0, 126.0 (d, *J* = 9.6 Hz), 125.0 (d, *J* = 8.0 Hz), 116.1 (d, *J* = 12.3 Hz), 99.7 (d, *J* = 184.0 Hz), 79.1 (d, *J* = 27.0 Hz).

^{19}F NMR (565 MHz, Acetone-*d*$_6$) δ -165.1 (t, *J* = 17.6 Hz).

HRMS (EI): *m/z* for $C_{20}H_{17}FO^+$ $[M]^+$ calcd.: 292.1263, found: 292.1262.

Potassium (*Z*)-trifluoro(3-fluoro-3-(naphthalen-2-yl)allyl)borate (5a)



A 20 mL polyethylene vial equipped with a magnetic stir bar was charged with 3-fluoro allyl boronic ester **2a** (30.2 mg of a 1.33:1 mole ratio of boronic ester **2a** and B_2pin_2, corresponding to 0.0600 mmol of **2a**) and KHF_2 (29.8 mg, 6.35 equiv, 0.381 mmol), and 670 µL of tetrahydrofuran and 670 µL of H_2O were added. The resulting suspension was then stirred for 1 hour at room temperature. The volatile materials were then evaporated under vacuum to provide a white powdery residue. Acetone (3 mL) was added to the resulting white solid, and the supernatant was filtered. The insoluble material was then washed with acetone (3 x 3 mL). The combined filtrate was dried under vacuum, and the resulting white powder was washed with diethyl ether (3 x 3 mL), which was again dried under vacuum to yield pure trifluoroborate **5a** as a white powder (16.6 mg, 0.0533 mmol, 89%).

m.p. >250 °C

^{1}H NMR (600 MHz, Acetone-*d*$_6$) δ 7.90 – 7.80 (m, 4H), 7.62 (dt, *J* = 8.7, 1.6 Hz, 1H), 7.47 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.43 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 5.88 (dt, *J* = 40.1, 8.6 Hz, 1H), 1.32 (br s, 2H).

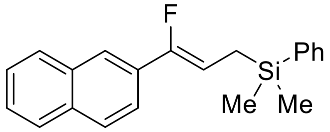
^{13}C NMR (151 MHz, Acetone-*d*$_6$) δ 154.3 (d, *J* = 235.2 Hz), 134.5, 133.4, 133.0 (d, *J* = 29.7 Hz), 128.9, 128.6 (d, *J* = 2.9 Hz), 128.4, 127.1, 126.4, 122.6 (d, *J* = 6.5 Hz), 121.3 (d, *J* = 7.1 Hz), 113.1 (d, *J* = 19.4 Hz), 18.4 (br s). The ^{13}C NMR resonance at 18.4 ppm has low intensity due to quadrupolar broadening.

^{19}F NMR (565 MHz, Acetone-*d*$_6$) δ -130.5 (d, *J* = 40.0 Hz, 1F), -140.2 – -140.7 (m, 3F).

HRMS (ESI negative): *m/z* for $C_{13}H_{10}{}^{11}BF_4^-$ $[M\text{-}Na]^-$ calcd.: 253.0817, found: 253.0818.

DEFLUORINATIVE SILYLATION OF 3-SUBSTITUTED 3,3-DIFLUOROPROPENES

(Z)-(3-fluoro-3-(naphthalen-2-yl)allyl)dimethyl(phenyl)silane (10a)



In a nitrogen-filled glovebox, a 4 mL vial equipped with a magnetic stir bar was charged with CuCl (2.0 mg, 0.020 mmol, 19 mol %), PCy_3 (5.6 mg, 0.020 mmol, 19 mol %), NaO*t*-Bu (3.9 mg, 0.041 mmol, 38 mol %), 2-(1,1-difluoroallyl)naphthalene **1a** (22.0 mg, 0.108 mmol, 1 equiv), and THF (500 µL). The resulting mixture was stirred at room temperature for five minutes. Then, neat pinB–$SiMe_2Ph$ was added with stirring (55.0 µL, 52.9 mg, 0.202 mmol, 1.87 equiv). The resulting suspension was stirred at room temperature for 24 h. After this time, the reaction mixture was diluted with saturated NH_4Cl (20 mL), extracted with DCM (3 x 20 mL), dried over sodium sulfate, and dried under vacuum. The resulting residue was subjected to silica-gel column chromatography (99/1 hexanes/ethyl acetate to 95/5 hexanes/ethyl acetate) to provide allyl silane **10a** as a white solid (33.9 mg, 0.106 mmol, 98%).

Note: This reaction was also conducted in an analogous fashion on a 0.661 mmol scale (135 mg of compound **1a**) to provide allyl silane **10a** in high yield and high *Z:E* selectivity (98:2 *Z:E*) (198.5 mg, 0.619 mmol, 94%).

m.p. 75.0 – 76.0 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.54 – 7.46 (m, 3H), 7.43 – 7.38 (m, 3H), 5.58 (dt, *J* = 36.8, 8.9 Hz, 1H), 2.00 (dd, *J* = 8.9, 1.5 Hz, 2H), 0.40 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0 (d, *J* = 242.8 Hz), 138.6, 133.7, 133.4, 133.0, 130.4 (d, *J* = 28.5 Hz), 129.3, 128.4, 128.2 (d, *J* = 2.7 Hz), 128.0, 127.7, 126.6, 126.3, 122.1 (d, *J* = 7.1 Hz), 121.7 (d, *J* = 6.5 Hz), 103.6 (d, *J* = 18.9 Hz), 14.6 (d, *J* = 4.1 Hz), -3.0.

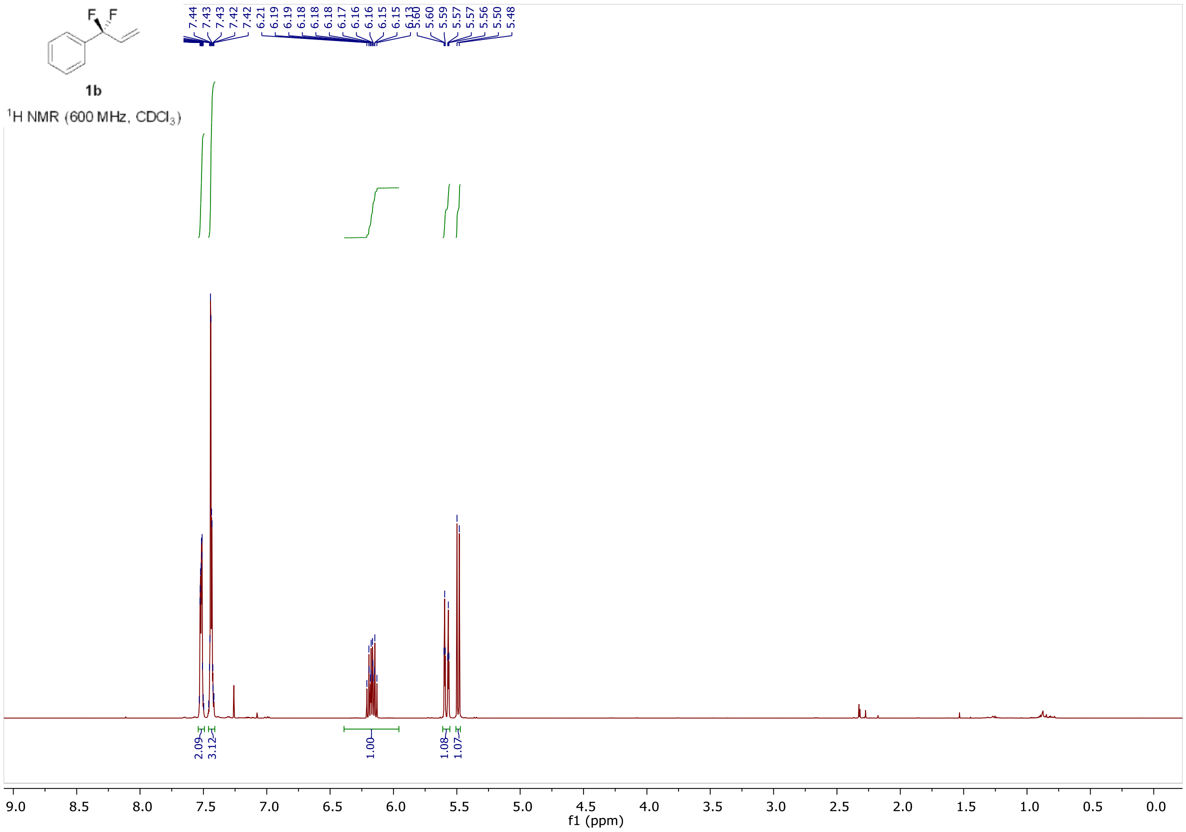
^{19}F NMR (565 MHz, $CDCl_3$) δ -122.7 (d, *J* = 36.8 Hz).

HRMS (EI): *m/z* for $C_{21}H_{21}SiF^+$ $[M]^+$ calcd.: 320.1397, found: 320.1398.

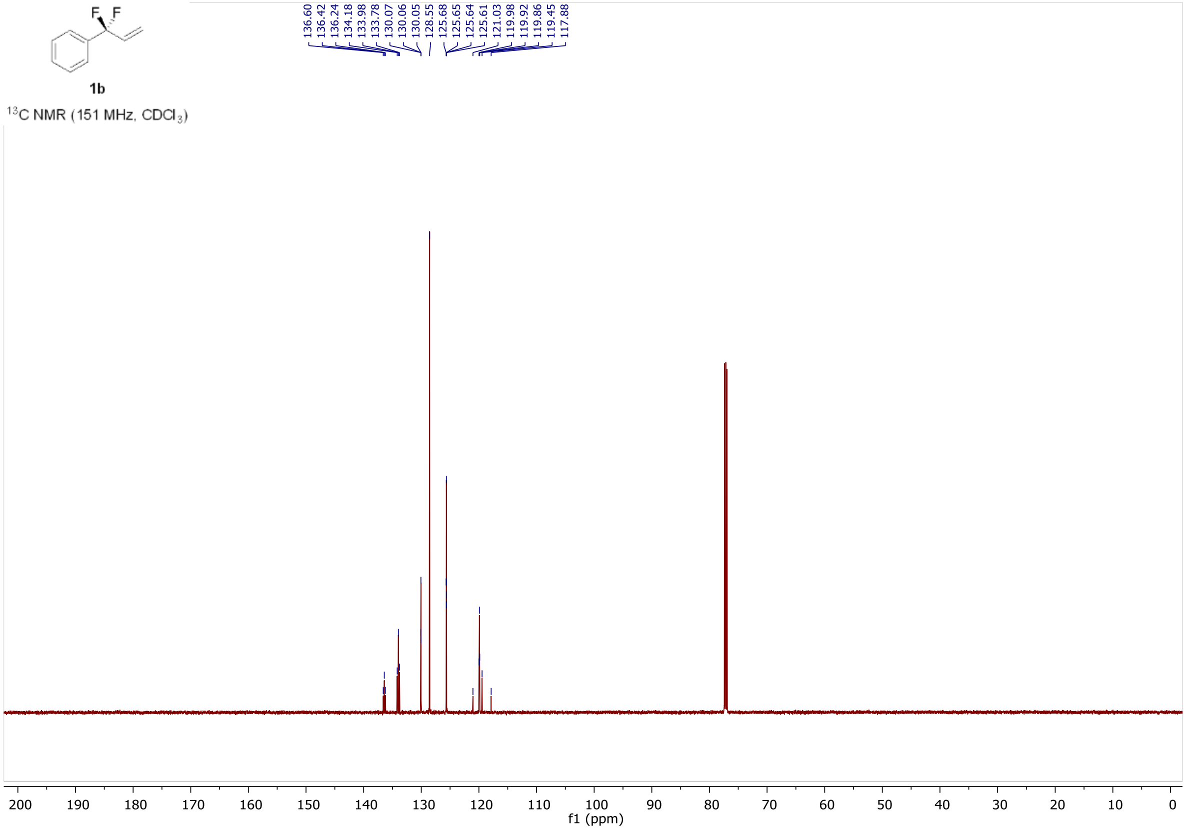
REFERENCES

1. Min, Q. Q.; Yin, Z. S.; Feng, Z.; Guo, W. H.; Zhang, X. G., Highly Selective *gem*-Difluoroallylation of Organoborons with Bromodifluoromethylated Alkenes Catalyzed by Palladium. *J. Am. Chem. Soc.* **2014,** *136*, 1230-1233.
2. Yang, Z.-Y.; J. Burton, D., A facile preparation of *gem*-difluorohomoallylic alcohols[1]. *Journal of Fluorine Chemistry* **1989,** *44*, 339-343.
3. Butcher, T. W.; Yang, J. L.; Amberg, W. M.; Watkins, N. B.; Wilkinson, N. D.; Hartwig, J. F., Desymmetrization of difluoromethylene groups by C–F bond activation. *Nature* **2020,** *583*, 548-553.
4. Kasten, K.; Slawin, A. M. Z.; Smith, A. D., Enantioselective Synthesis of β-Fluoro-β-aryl-α-aminopentenamides by Organocatalytic [2,3]-Sigmatropic Rearrangement. *Org. Lett.* **2017,** *19*, 5182-5185.
5. Akiyama, S.; Kubota, K.; Mikus, M. S.; Paioti, P. H. S.; Romiti, F.; Liu, Q.; Zhou, Y.; Hoveyda, A. H.; Ito, H., Catalytic Enantioselective Synthesis of Allylic Boronates Bearing a Trisubstituted Alkenyl Fluoride and Related Derivatives. *Angew. Chem. Int. Ed.* **2019,** *58*, 11998-12003.

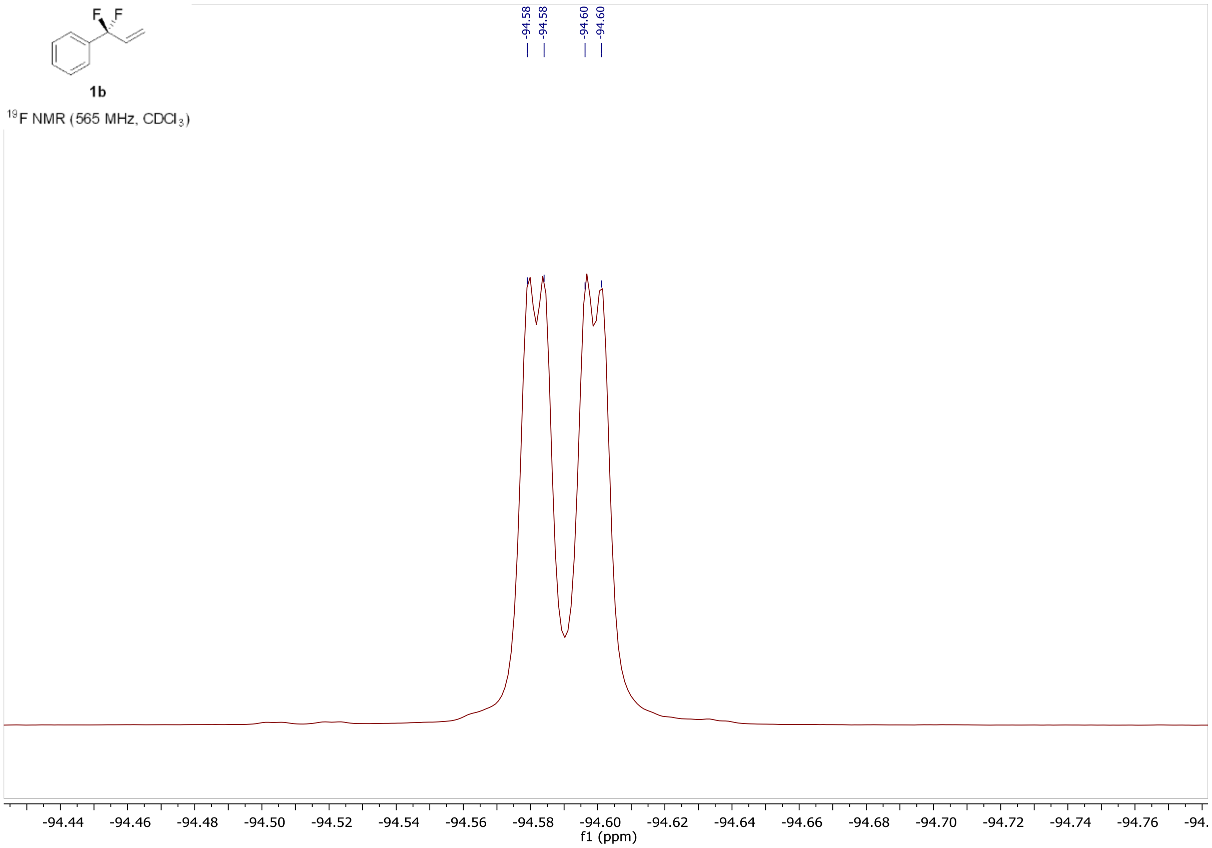
^{1}H, ^{13}C, AND ^{19}F NMR SPECTRA

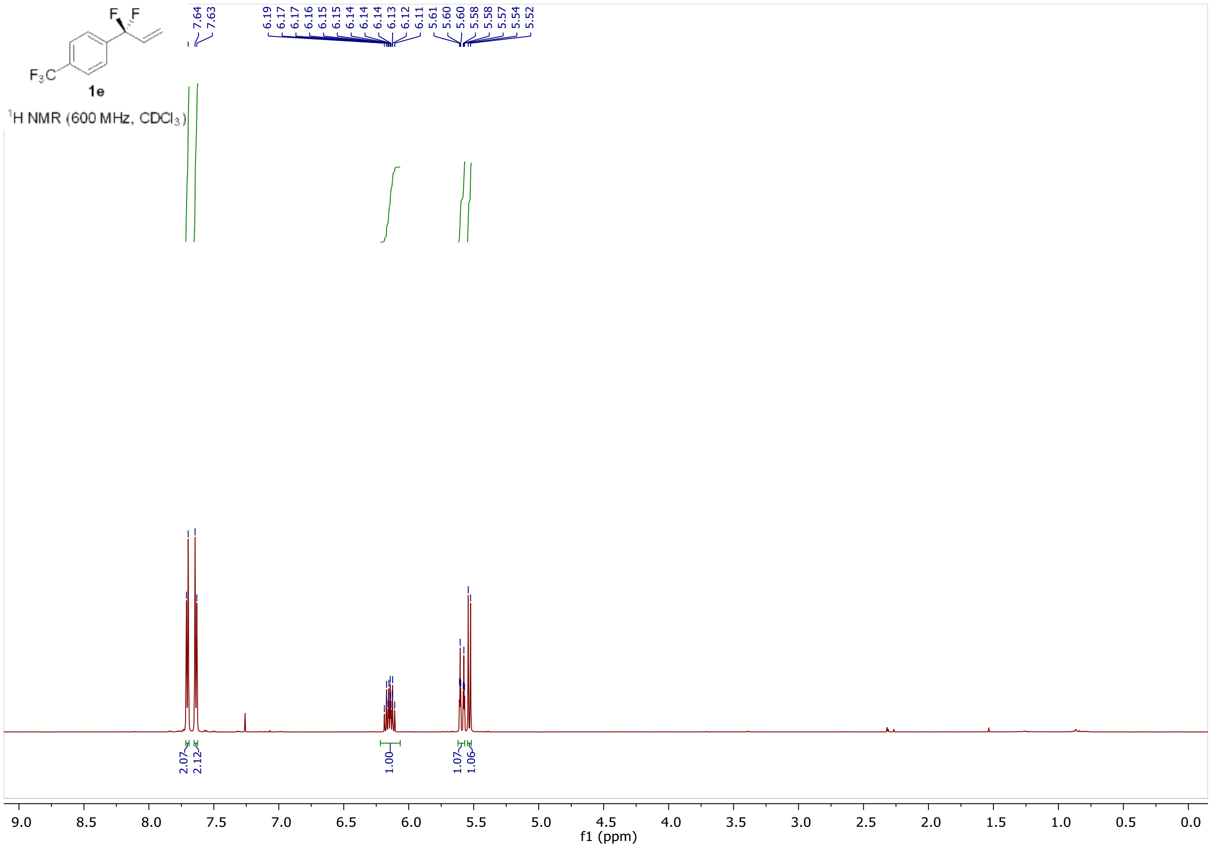

1b

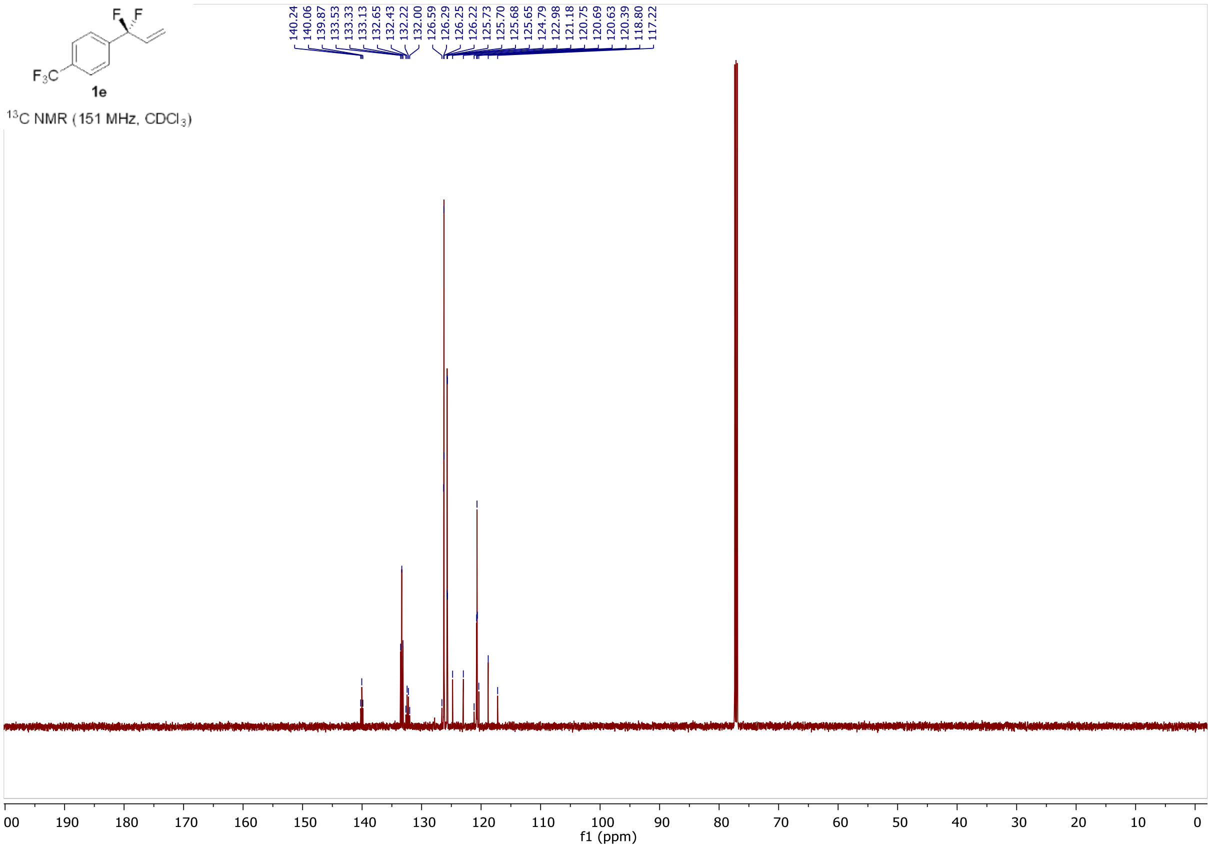
^{1}H NMR (600 MHz, $CDCl_3$)

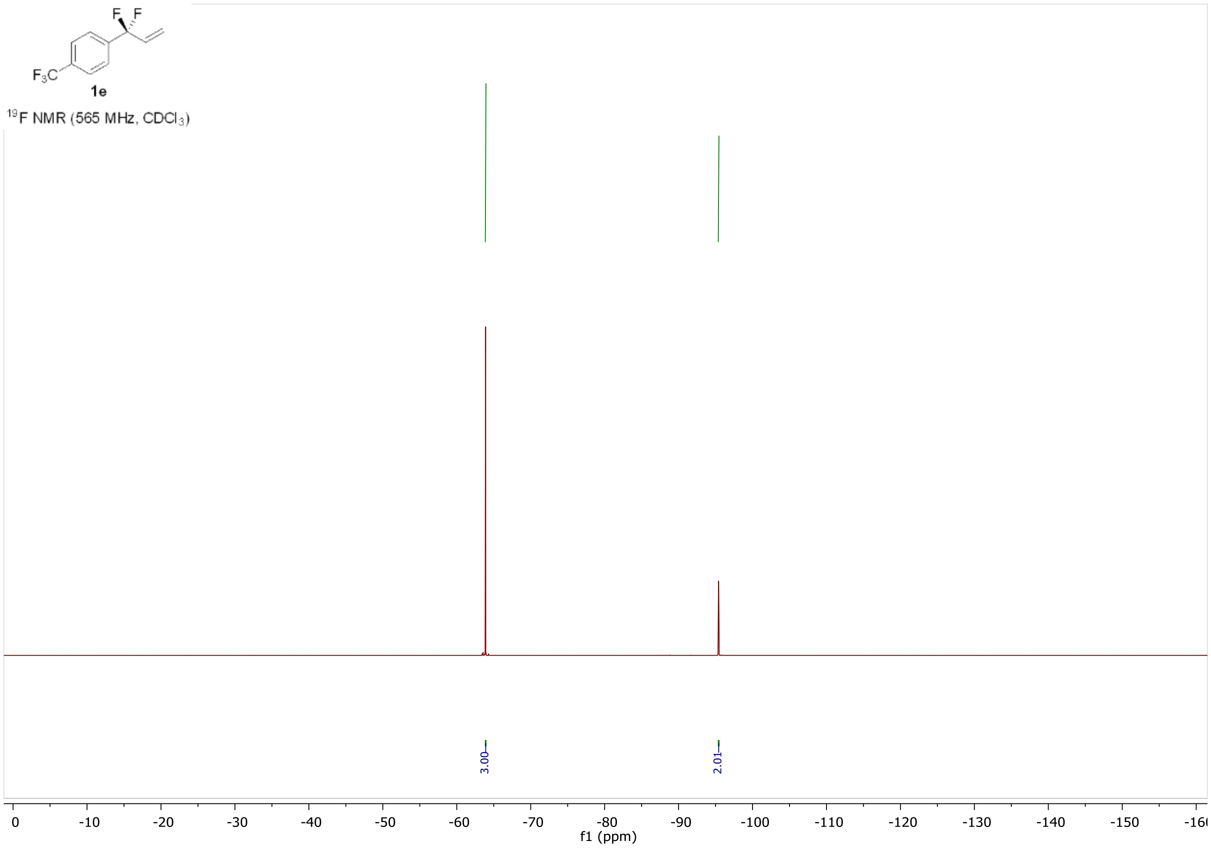

1b

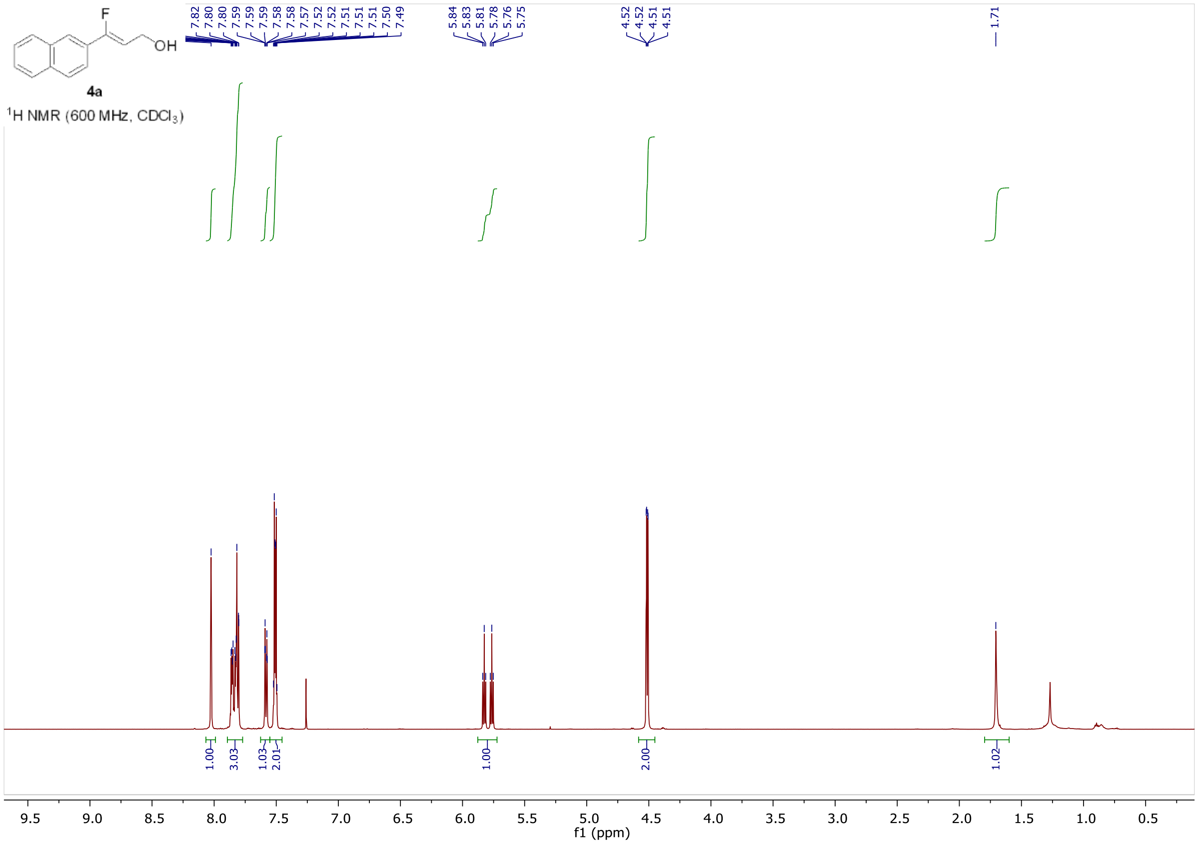
^{13}C NMR (151 MHz, $CDCl_3$)


1b
^{19}F NMR (565 MHz, CDCl$_3$)
-94.58
-94.58
-94.60
-94.60
-94.44
-94.46
-94.48
-94.50
-94.52
-94.54
-94.56
-94.58
-94.60
-94.62
-94.64
-94.66
-94.68
-94.70
-94.72
-94.74
-94.76
-94.
f1 (ppm)

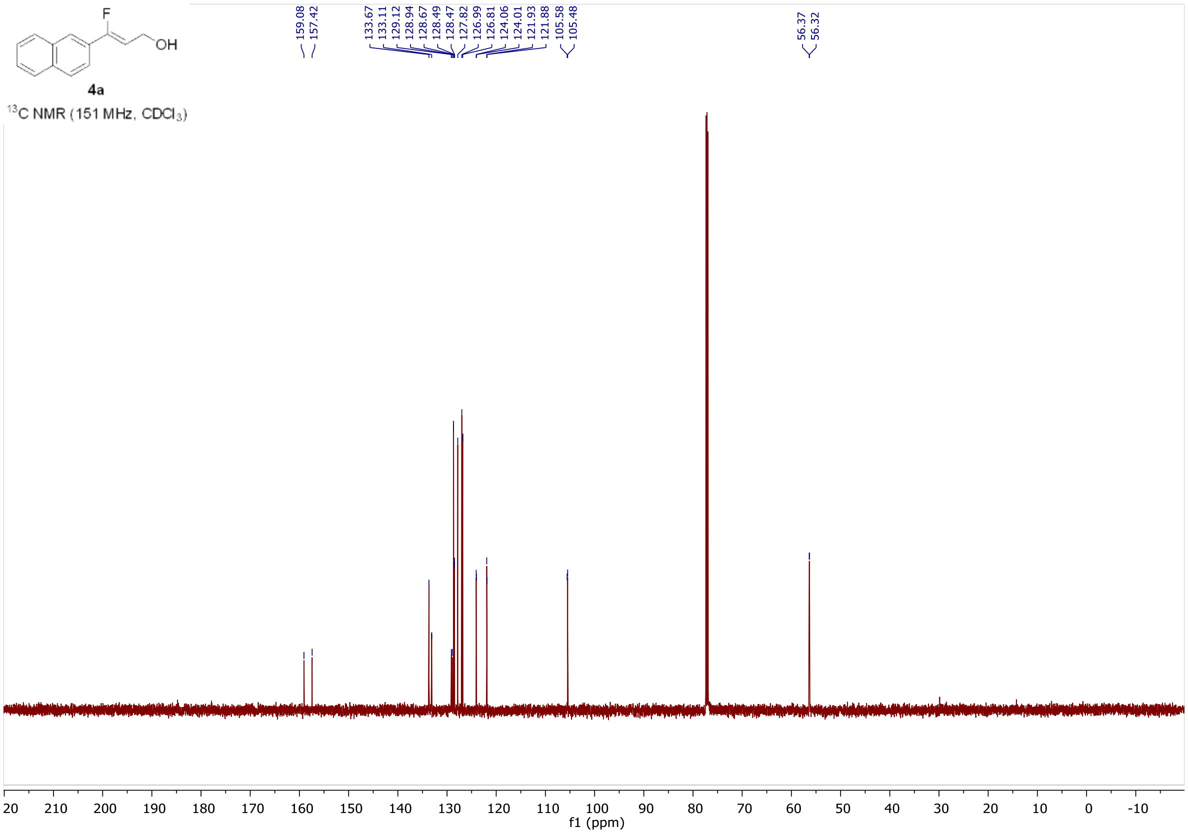

1e
^{1}H NMR (600 MHz, CDCl$_3$)
7.64
7.63
6.19
6.17
6.17
6.16
6.15
6.15
6.14
6.14
6.14
6.13
6.12
6.11
5.61
5.60
5.60
5.58
5.58
5.57
5.54
5.52
2.07
2.12
1.00
1.07
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


1e
^{13}C NMR (151 MHz, CDCl$_3$)
140.24
140.06
139.87
133.53
133.33
133.13
132.65
132.43
132.22
132.00
126.59
126.29
126.25
126.22
125.73
125.70
125.68
125.65
124.79
122.98
121.18
120.75
120.69
120.63
120.39
118.80
117.22
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

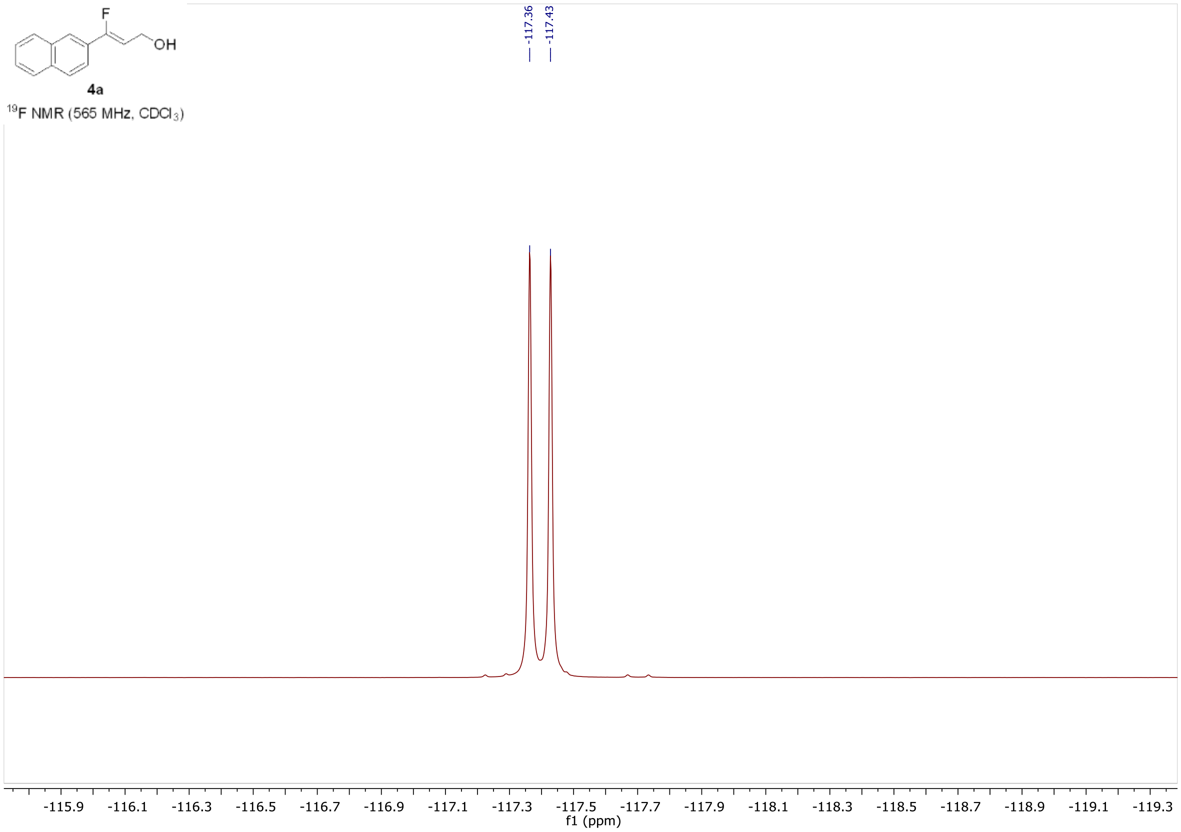

1e
^{19}F NMR (565 MHz, CDCl$_3$)
3.00
2.01
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-16
f1 (ppm)


4a

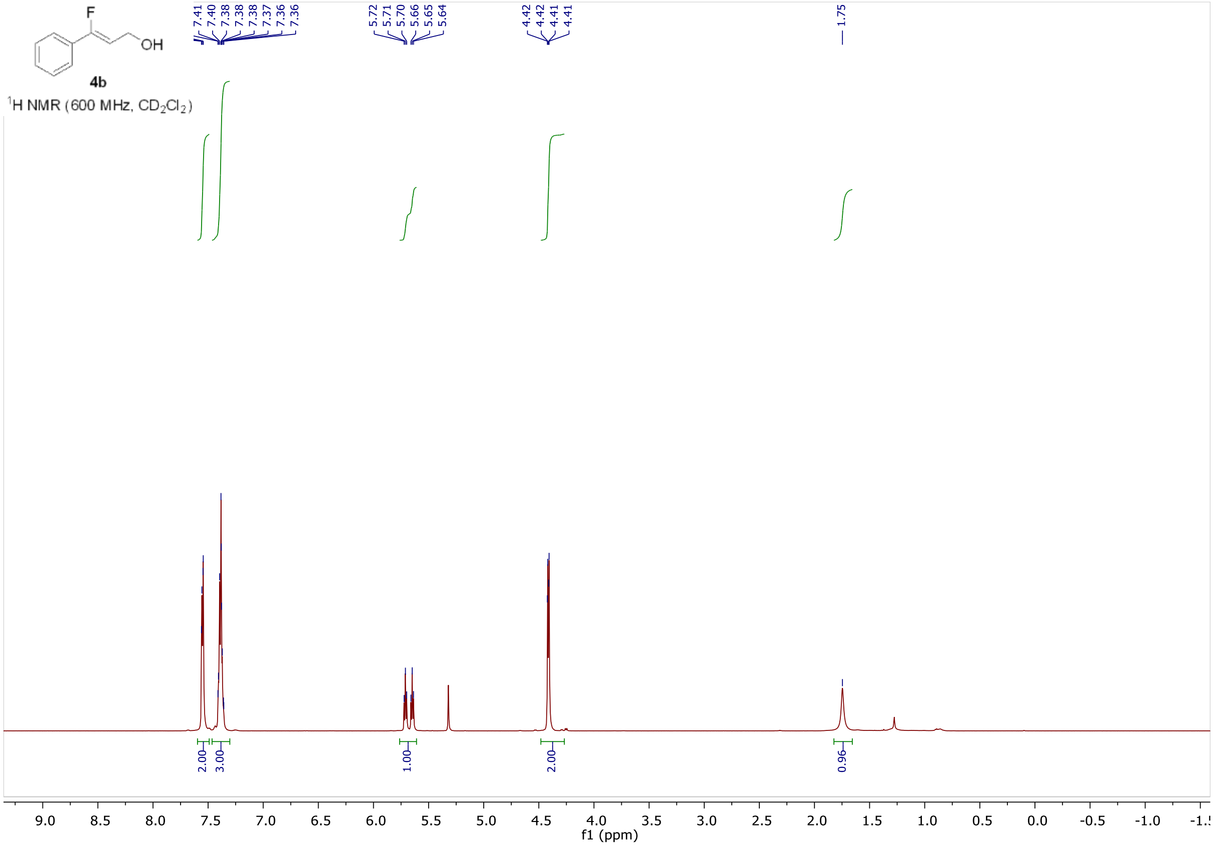
^{1}H NMR (600 MHz, CDCl$_3$)


4a

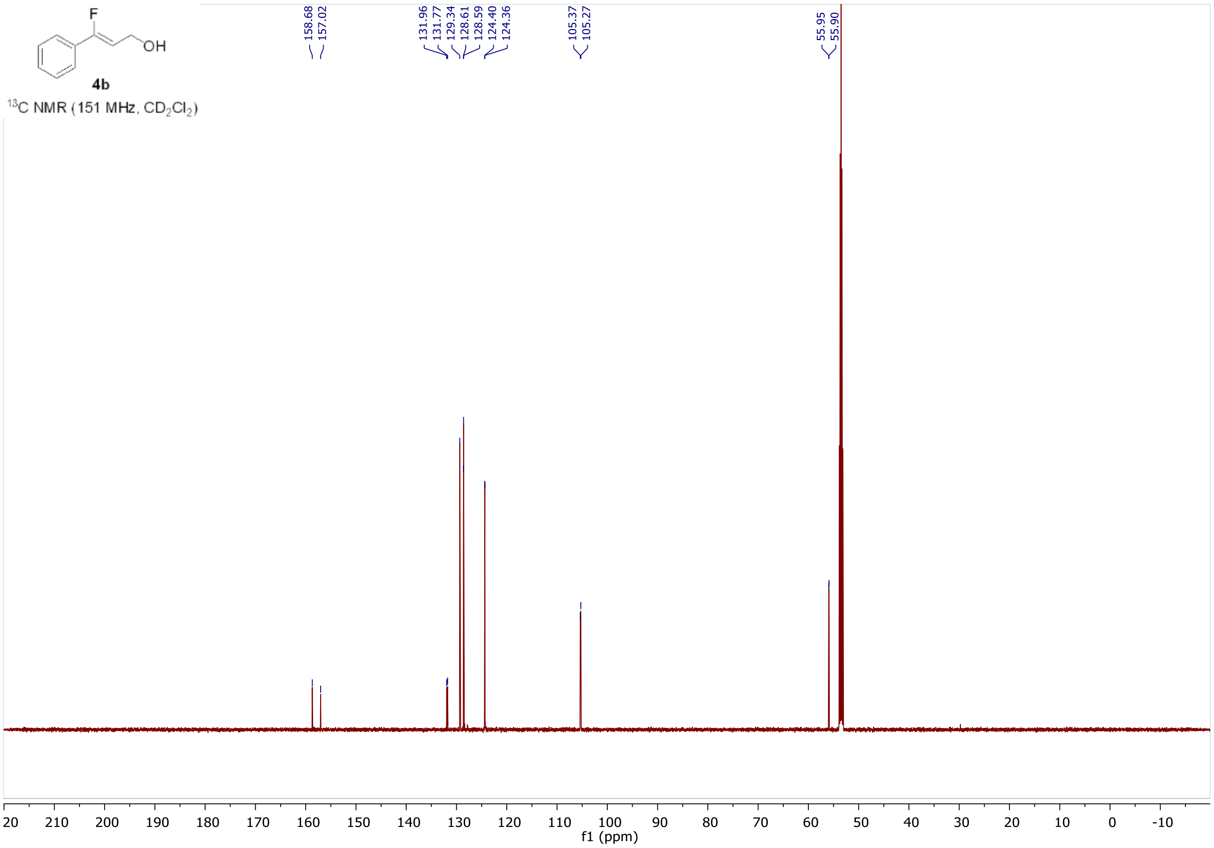
^{13}C NMR (151 MHz, CDCl$_3$)


4a

^{19}F NMR (565 MHz, $CDCl_3$)

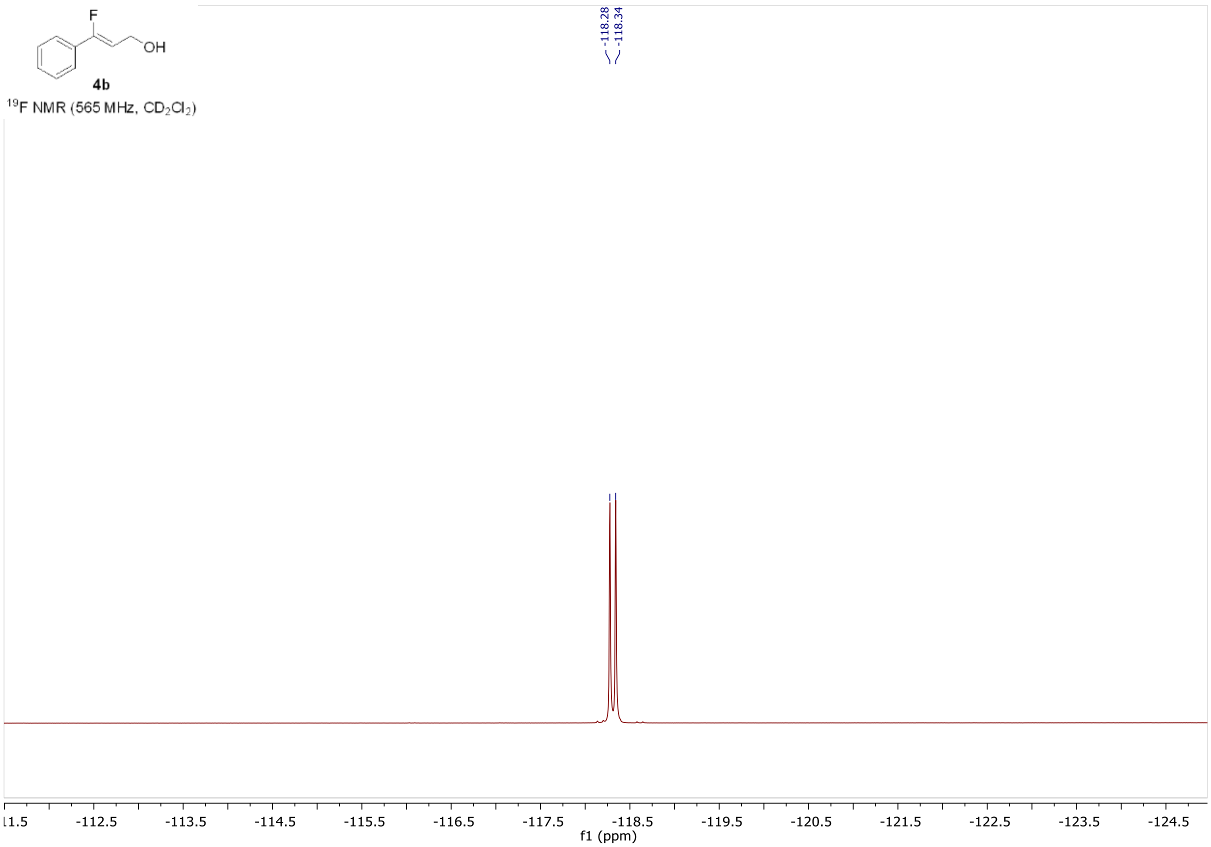

4b

^1H NMR (600 MHz, CD_2Cl_2)



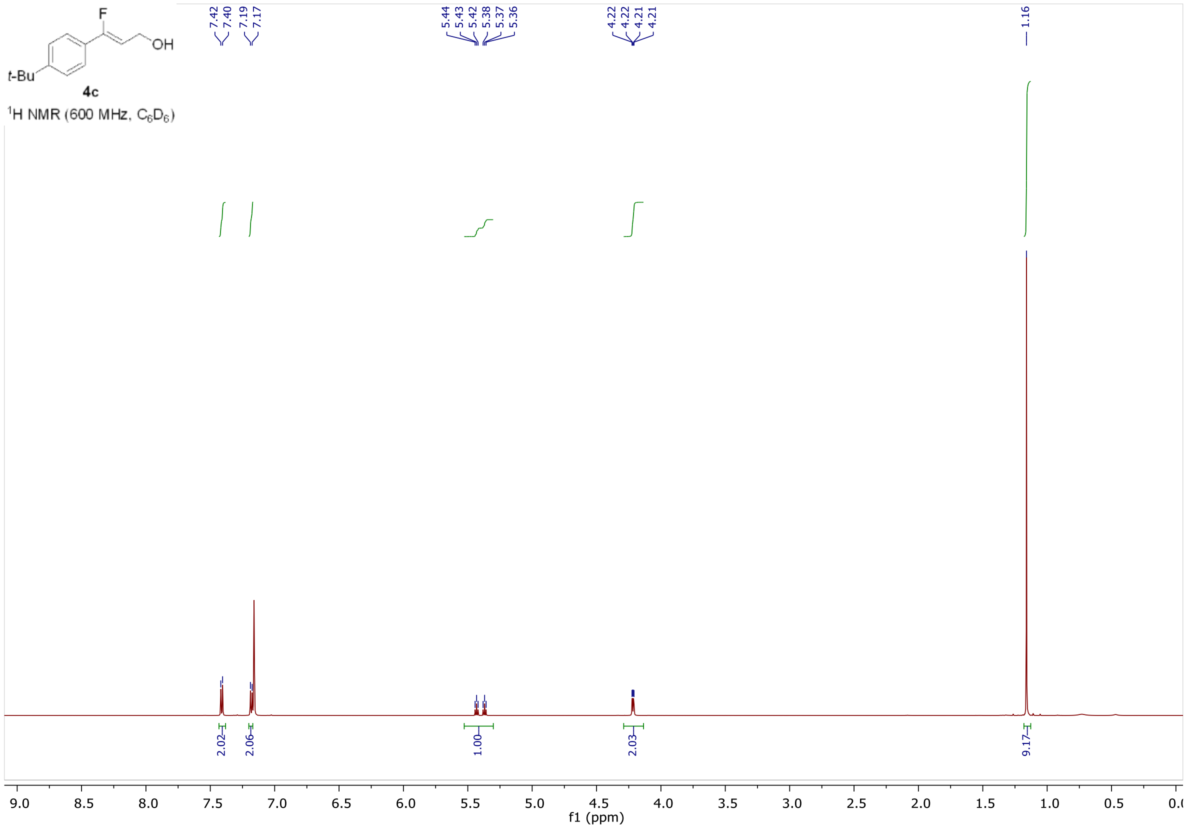
4b

^{13}C NMR (151 MHz, CD$_2$Cl$_2$)

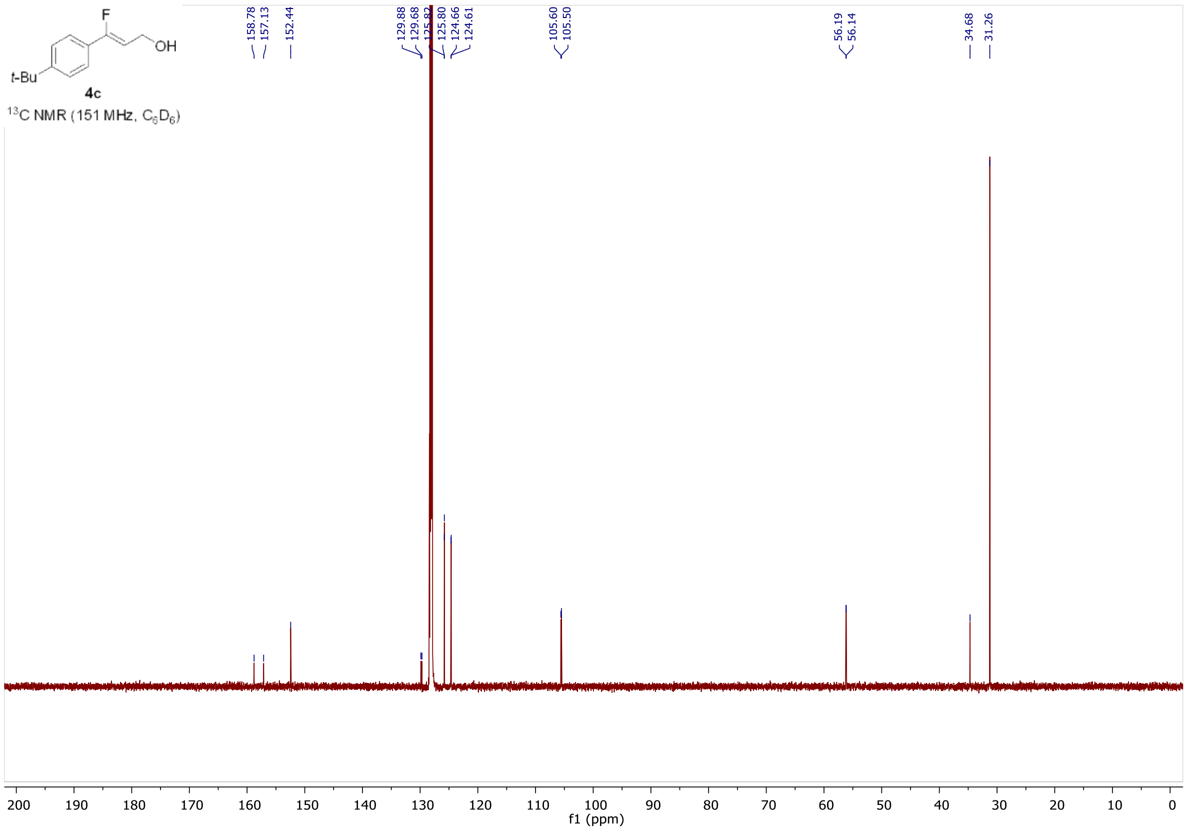


4b

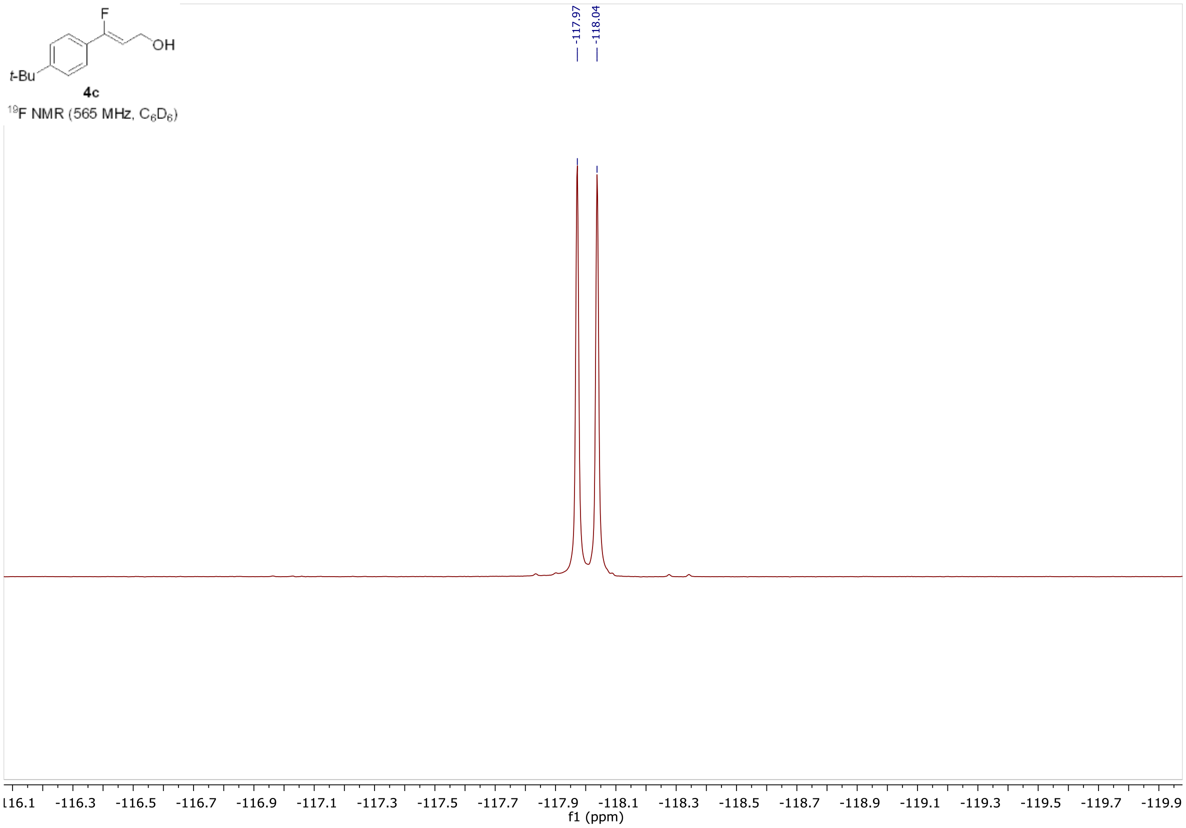
^{19}F NMR (565 MHz, CD$_2$Cl$_2$)

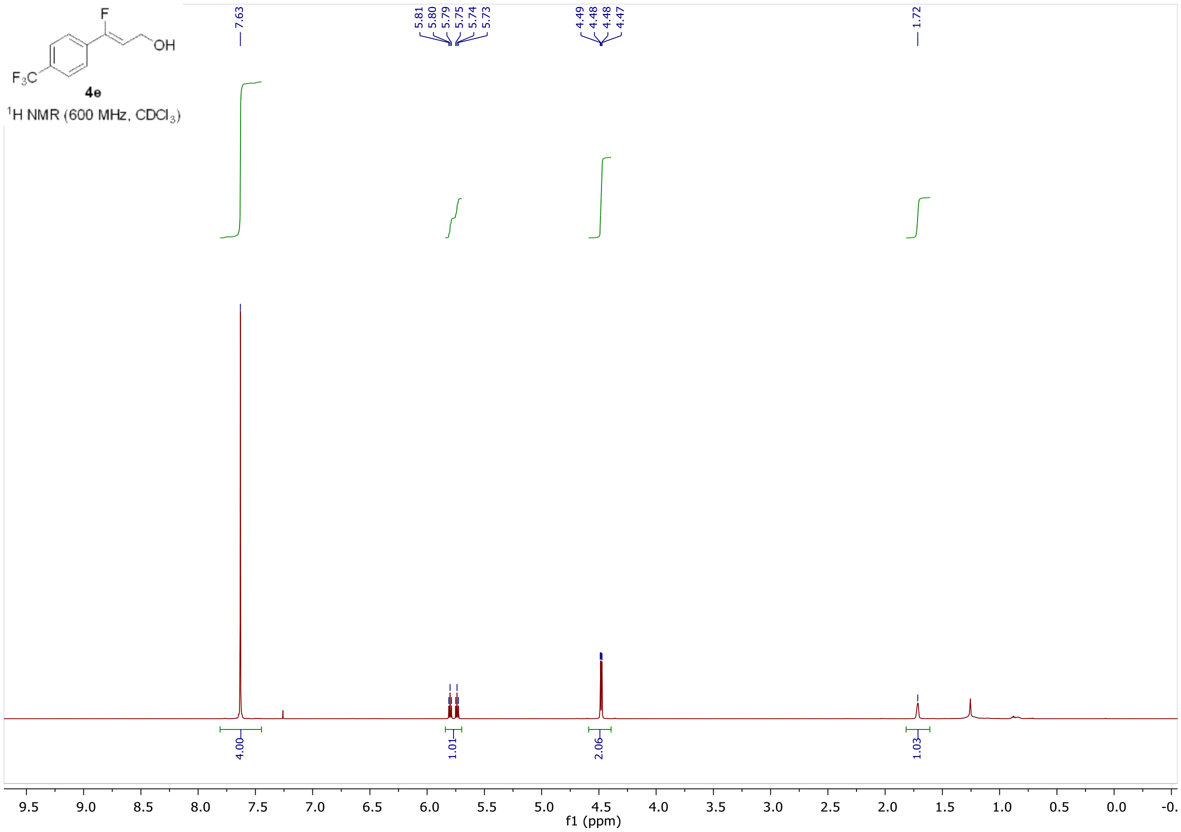

4c

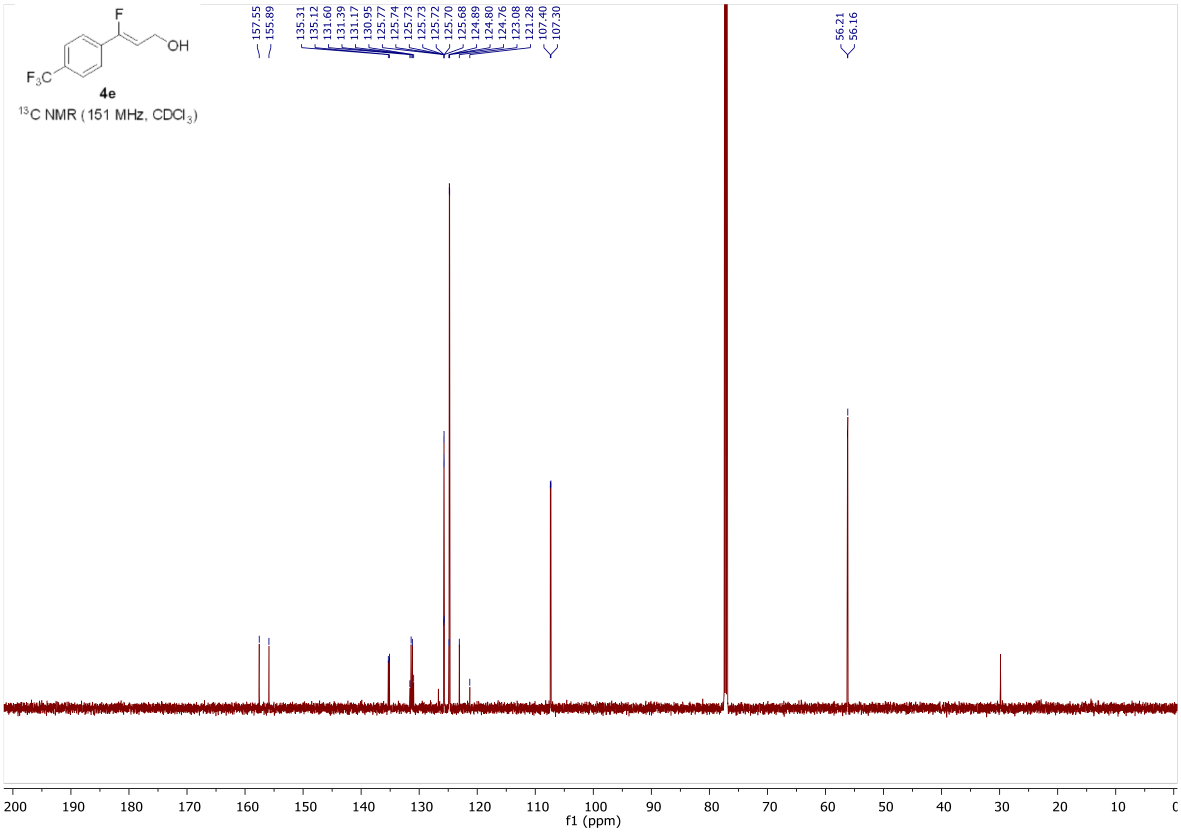
^{1}H NMR (600 MHz, C_6D_6)

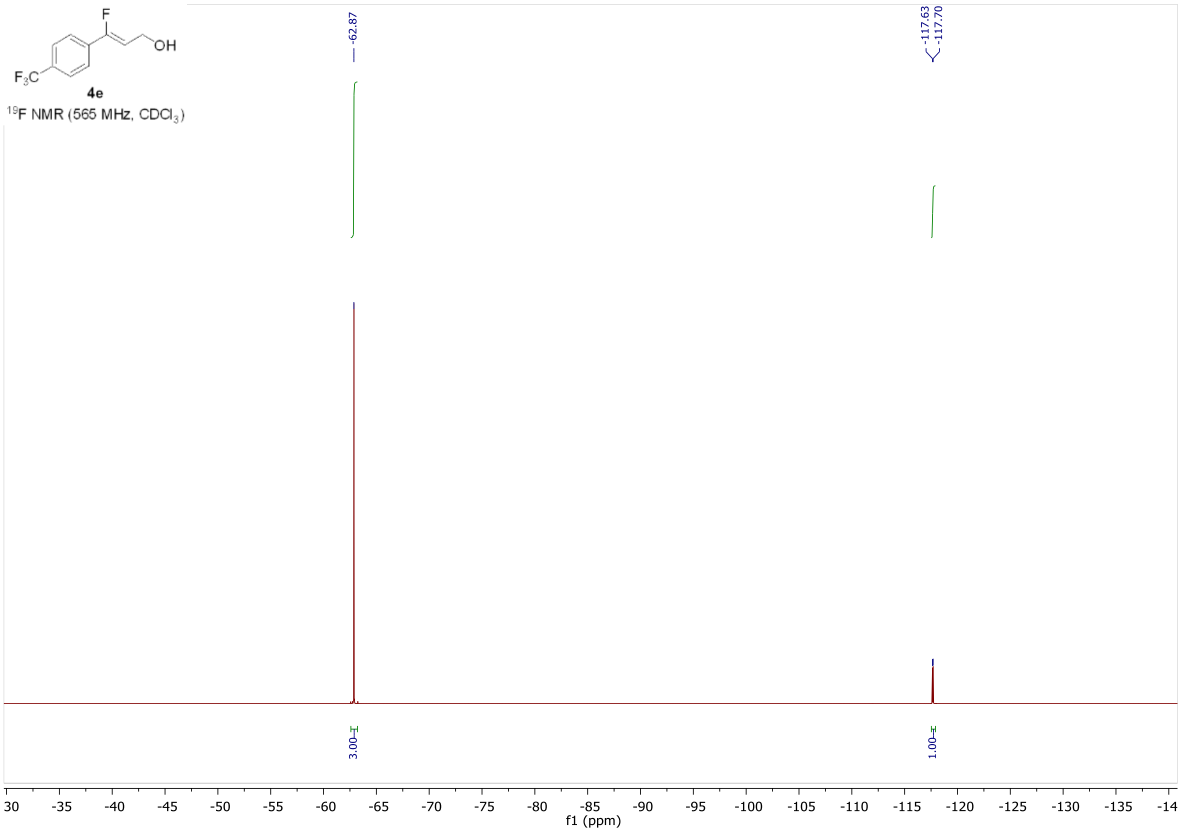

4c

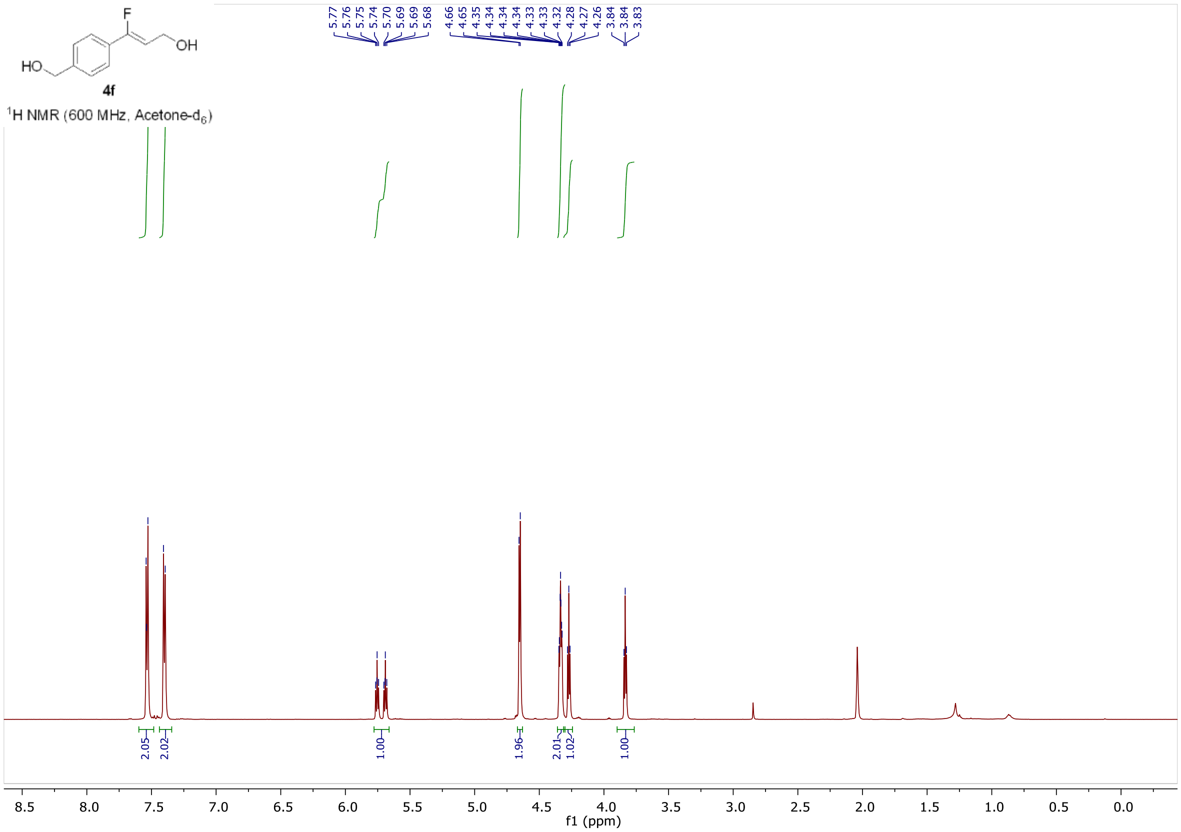
^{13}C NMR (151 MHz, C_6D_6)


F
OH
t-Bu
4c
^{19}F NMR (565 MHz, C_6D_6)
-117.97
-118.04
116.1
-116.3
-116.5
-116.7
-116.9
-117.1
-117.3
-117.5
-117.7
-117.9
-118.1
-118.3
-118.5
-118.7
-118.9
-119.1
-119.3
-119.5
-119.7
-119.9
f1 (ppm)


F
OH
F_3C
4e
^{1}H NMR (600 MHz, $CDCl_3$)
7.63
5.81
5.80
5.79
5.75
5.74
5.73
4.49
4.48
4.48
4.47
1.72
4.00
1.01
2.06
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

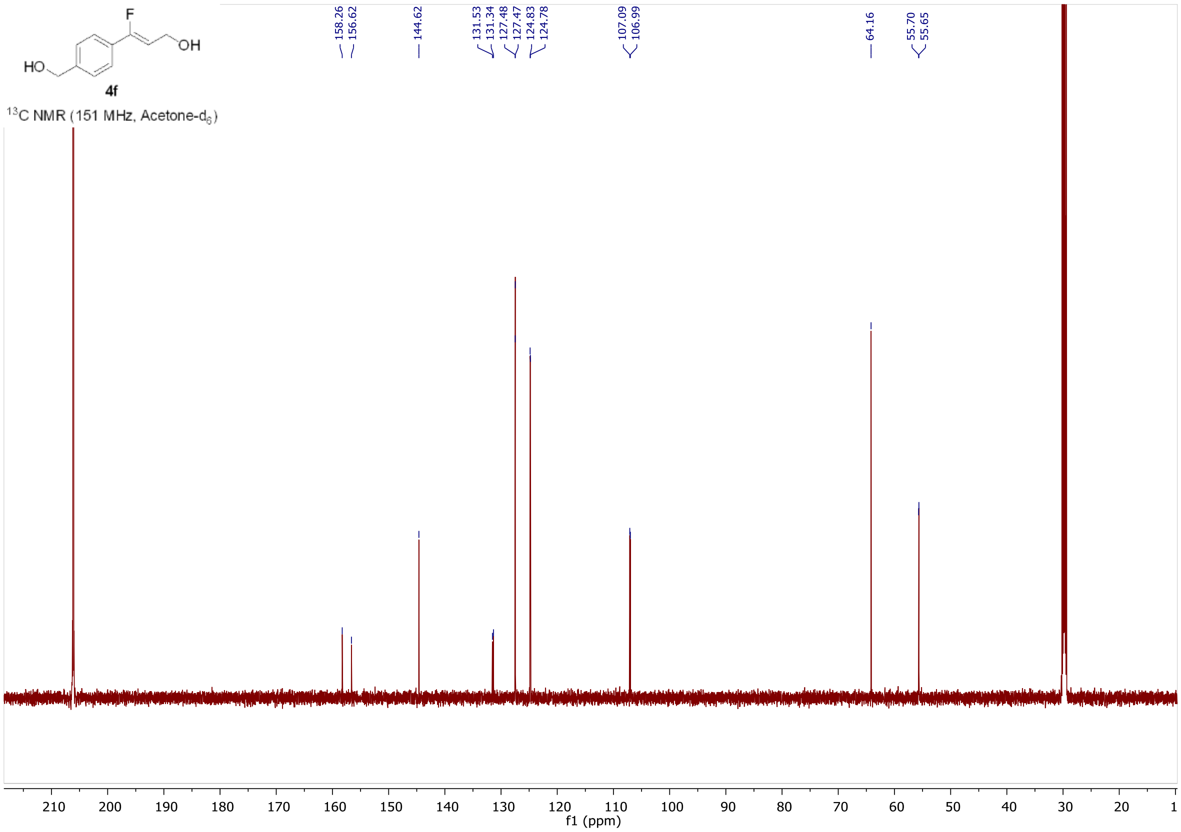

F
OH
F3C
4e
13C NMR (151 MHz, CDCl3)
157.55
155.89
135.31
135.12
131.60
131.39
131.17
130.95
125.77
125.74
125.73
125.73
125.72
125.70
125.68
124.89
124.80
124.76
123.08
121.28
107.40
107.30
56.21
56.16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
OH
F3C
4e
19F NMR (565 MHz, CDCl3)
-62.87
-117.63
-117.70
3.00
1.00
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
f1 (ppm)



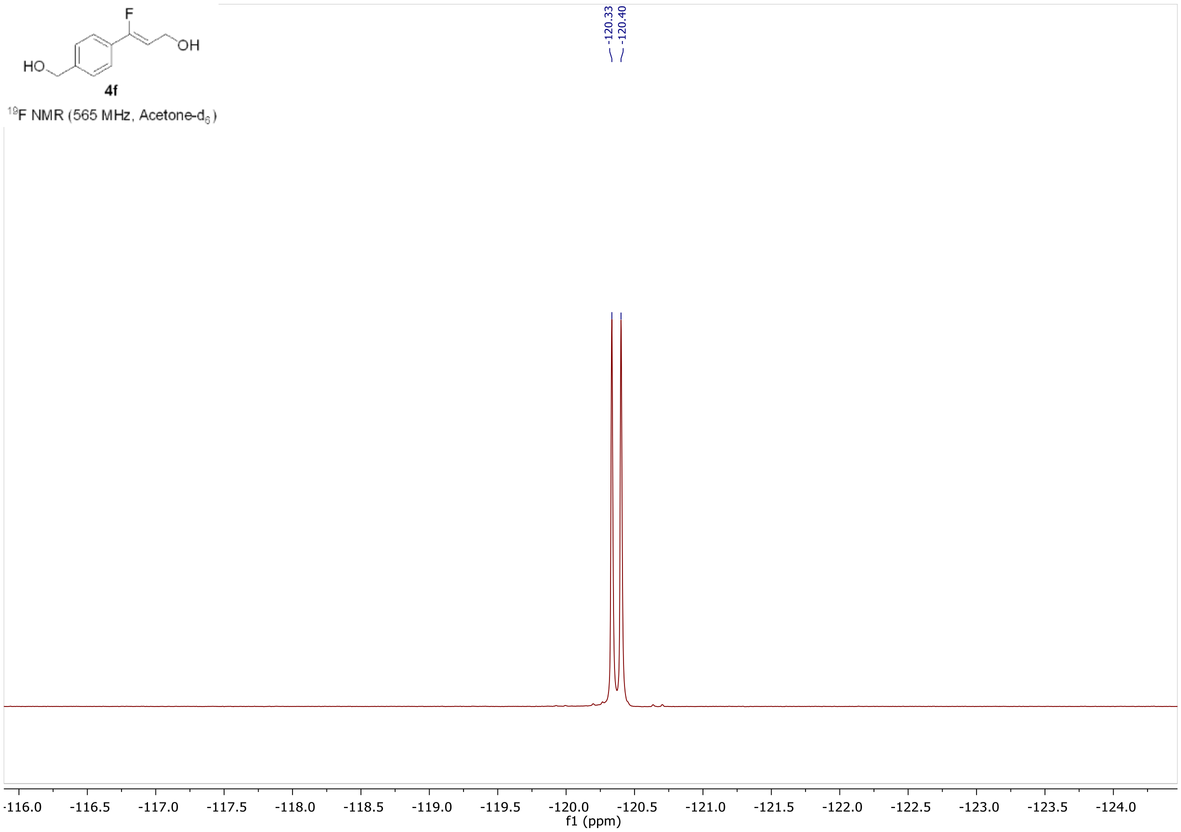
4f

^{1}H NMR (600 MHz, Acetone-d_6)



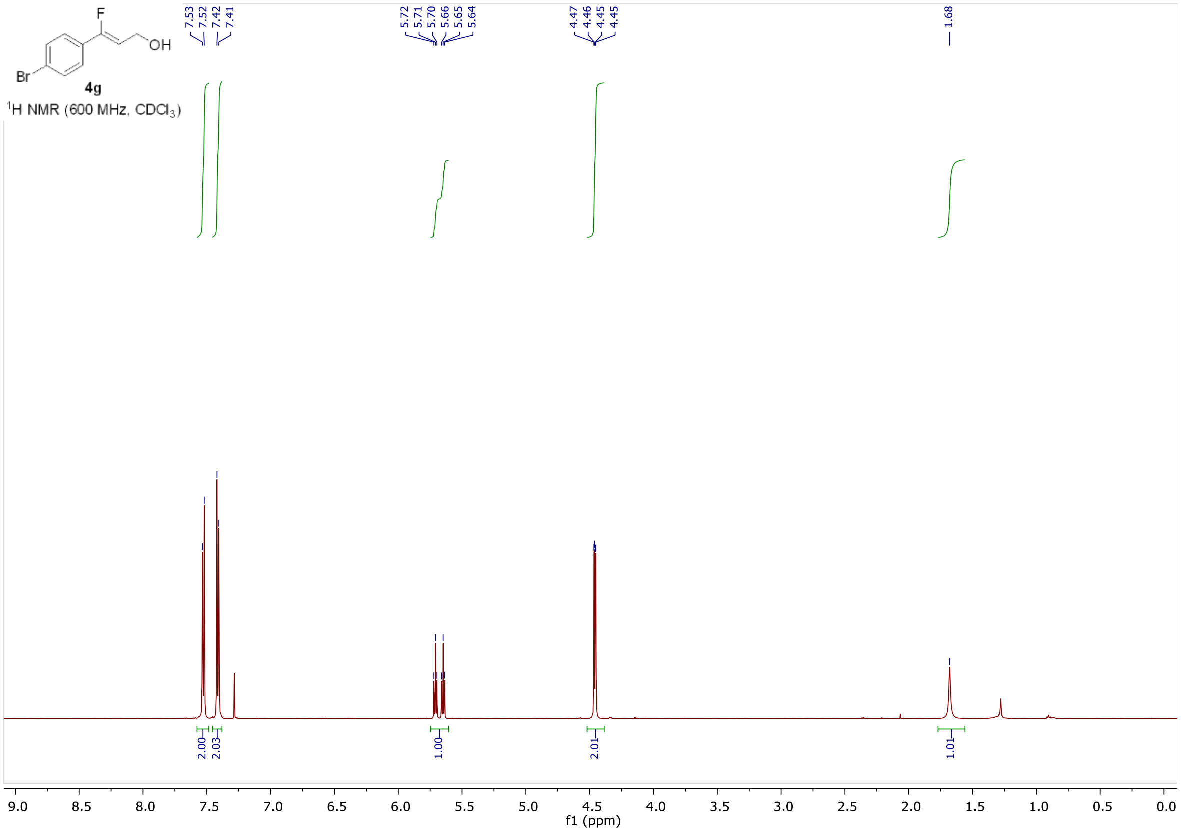
4f

^{13}C NMR (151 MHz, Acetone-d_6)



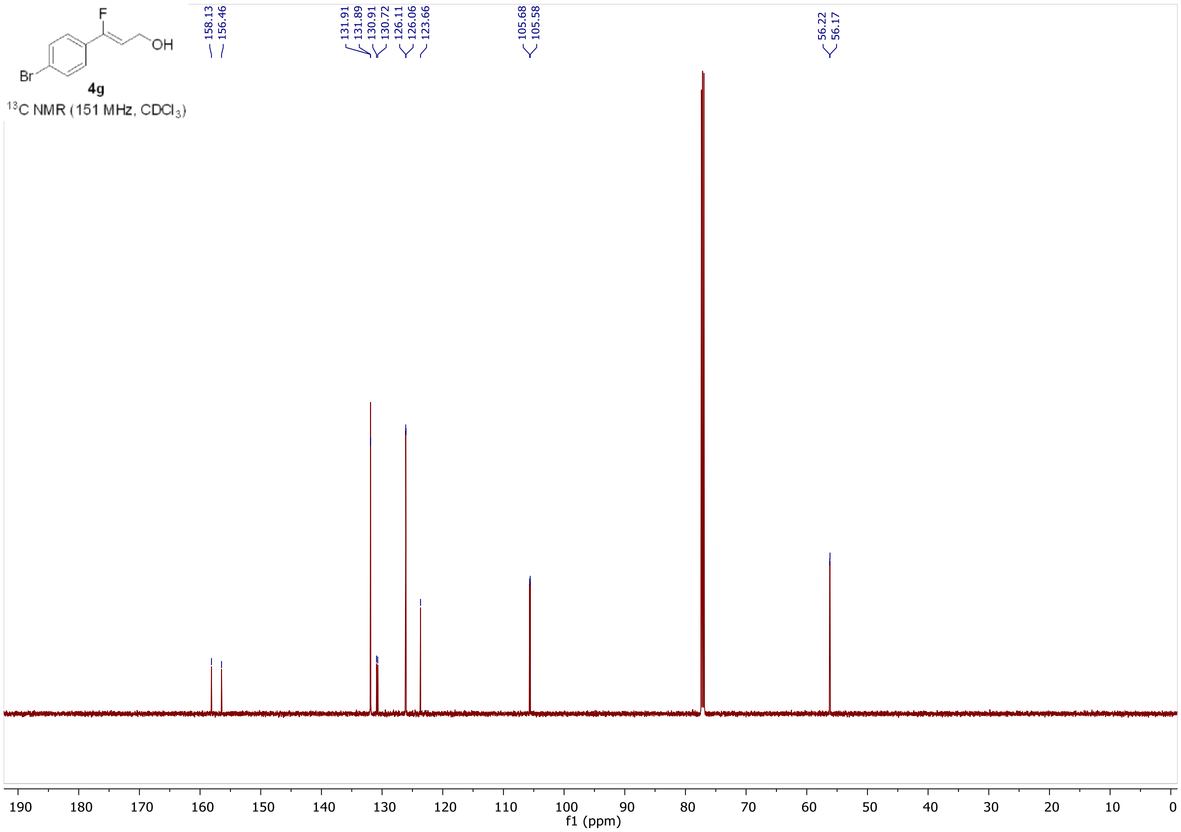
4f

^{19}F NMR (565 MHz, Acetone-d_6)



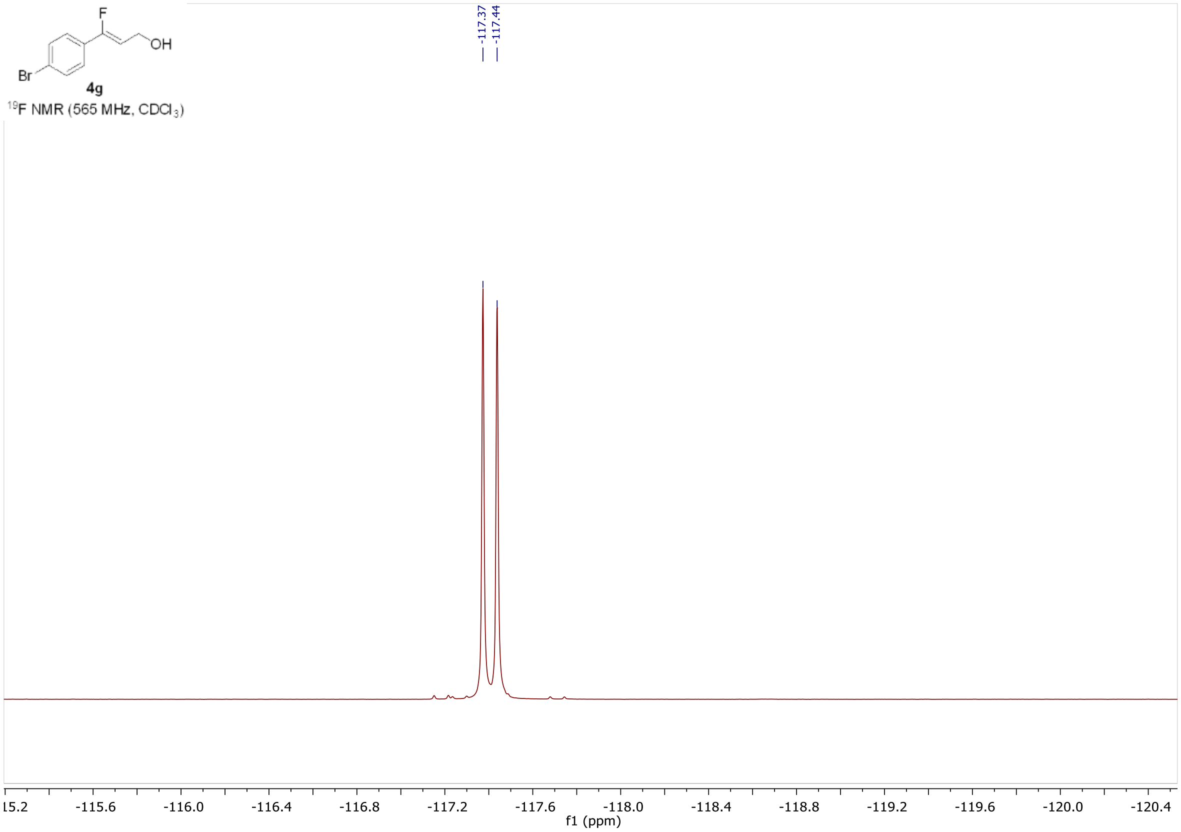
4g

^{1}H NMR (600 MHz, CDCl$_3$)



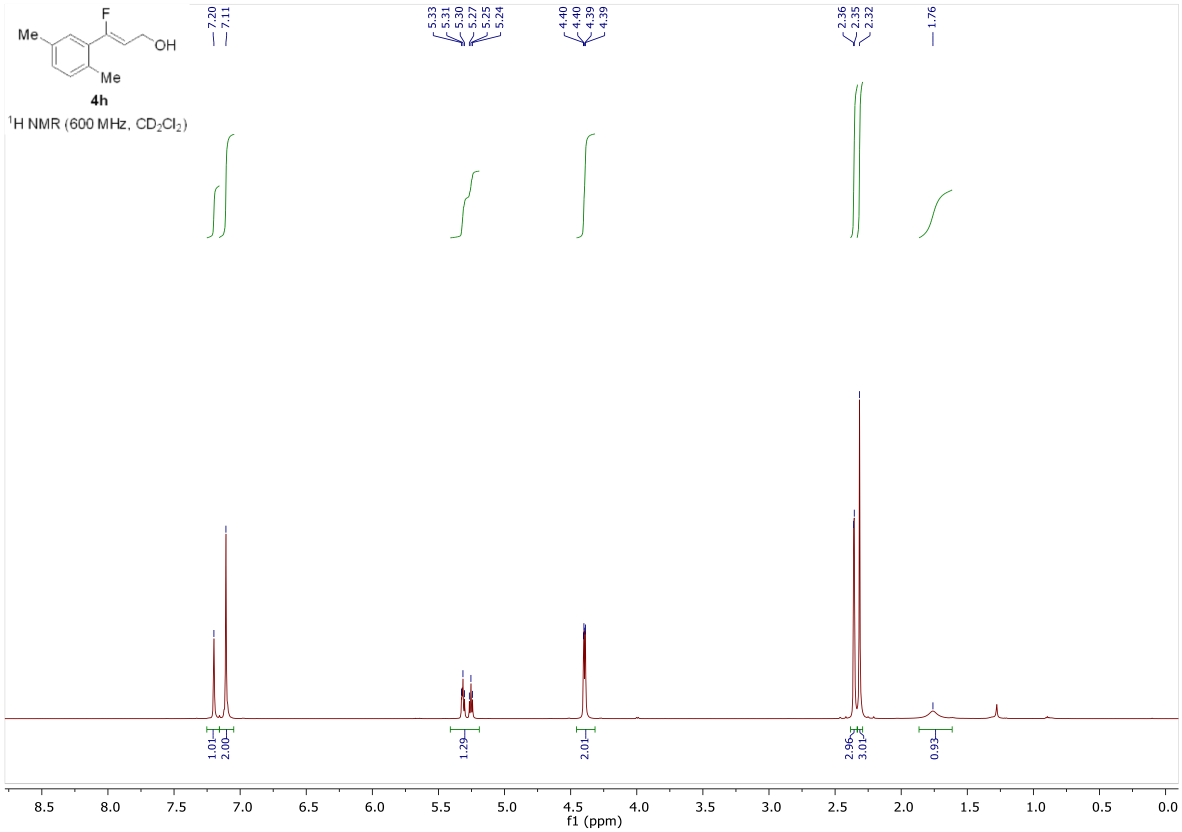
4g

^{13}C NMR (151 MHz, $CDCl_3$)



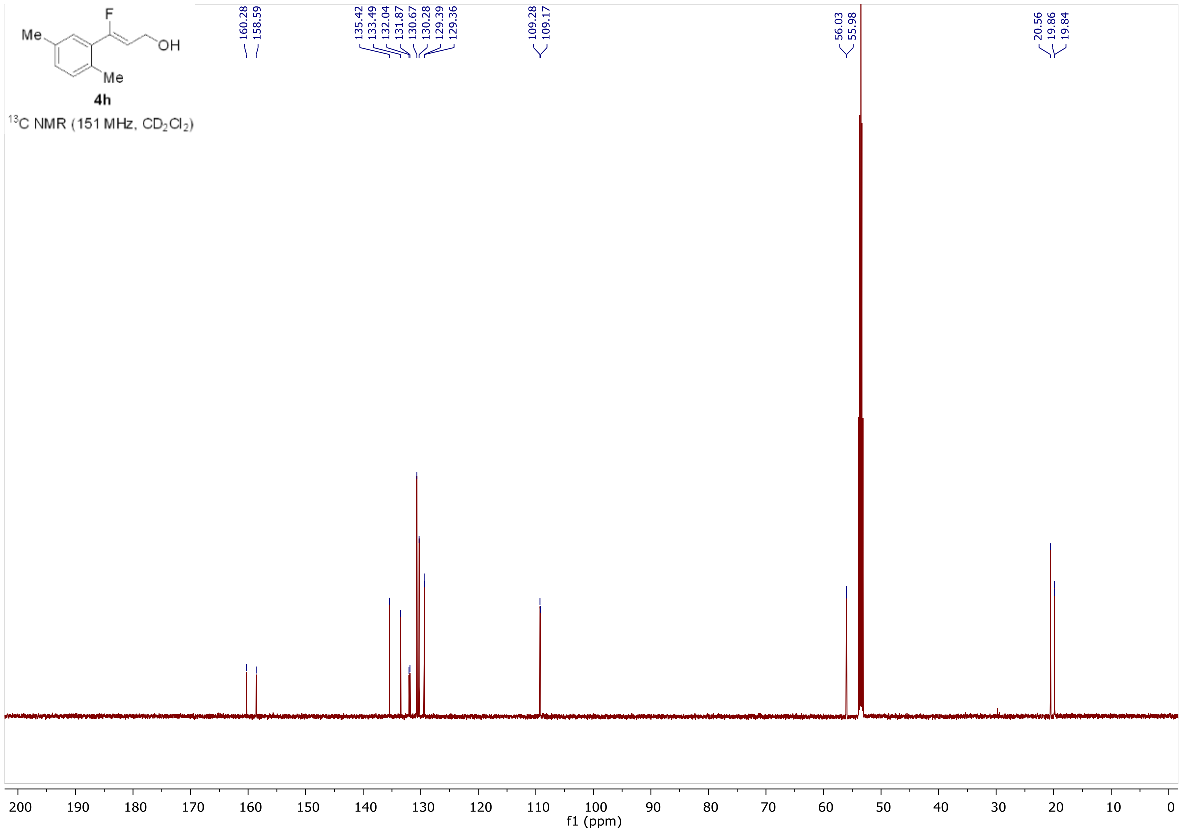
4g

^{19}F NMR (565 MHz, $CDCl_3$)



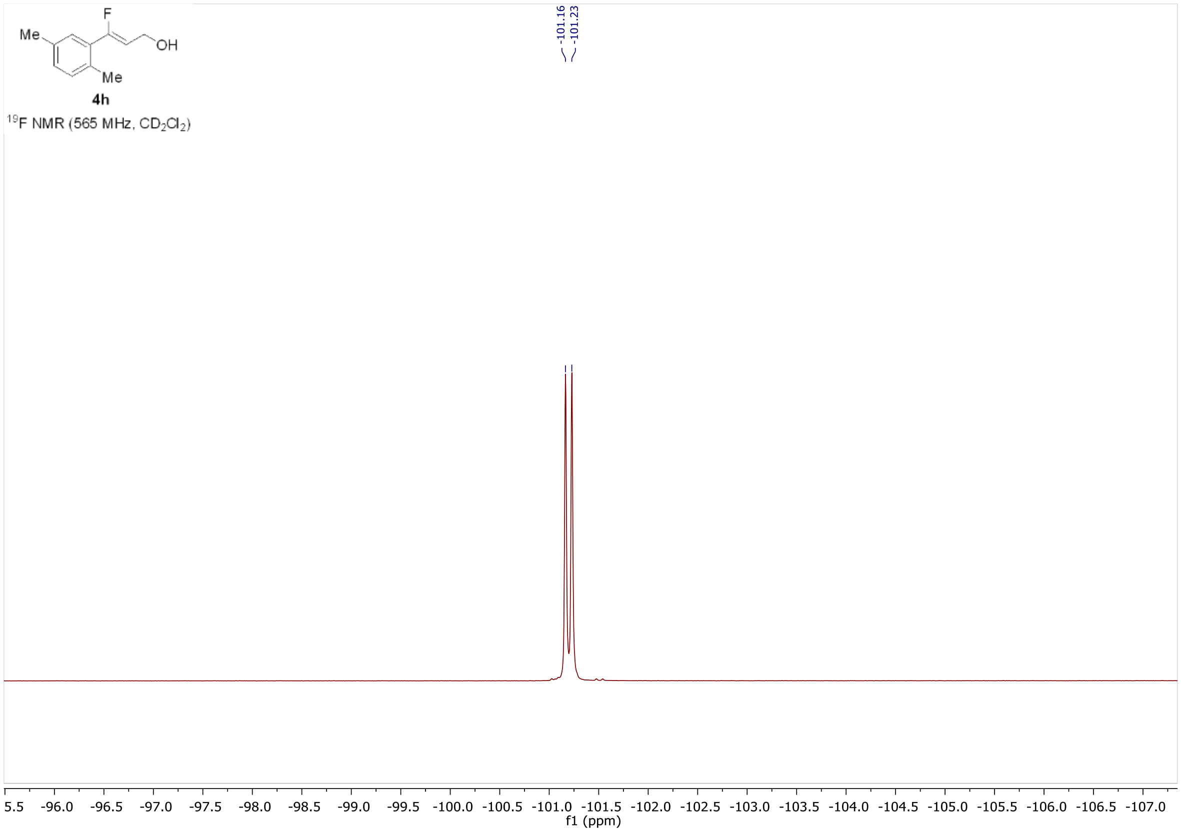
4h

^{1}H NMR (600 MHz, CD_2Cl_2)



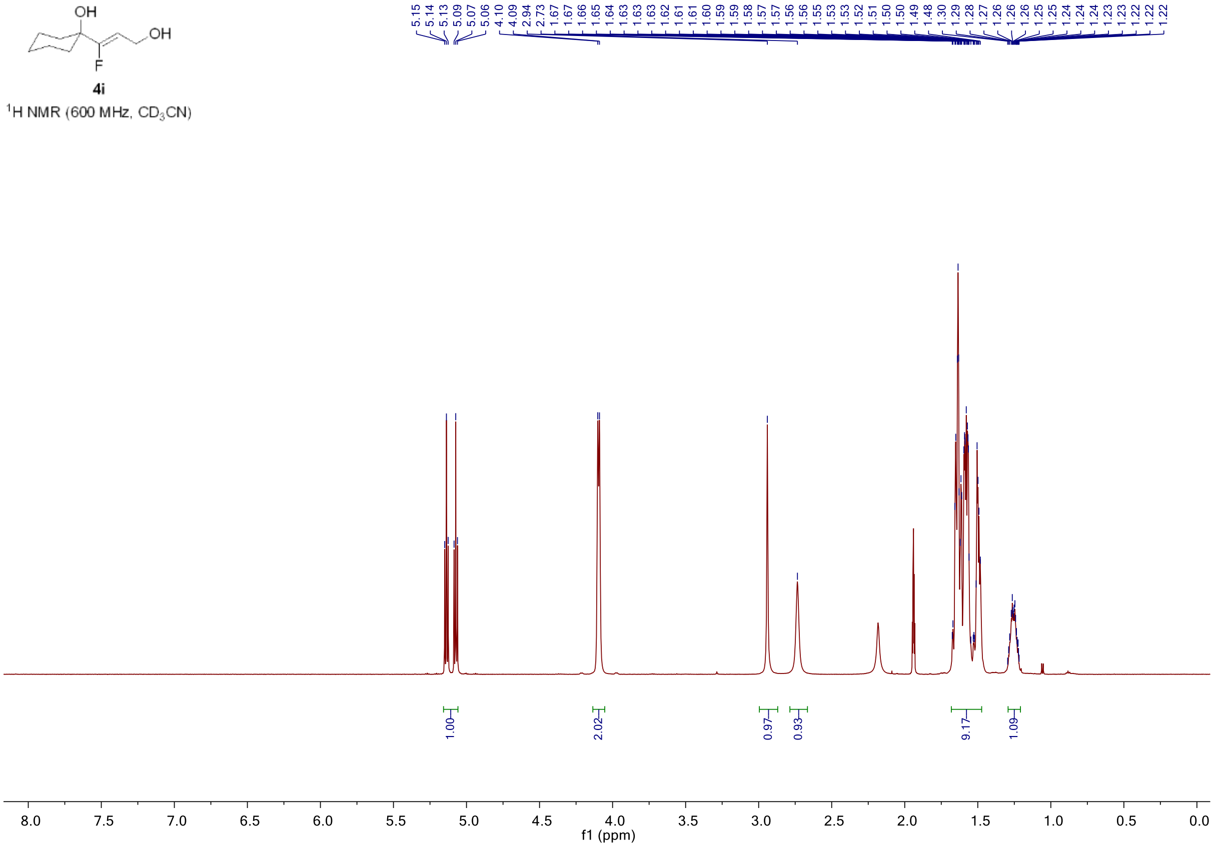
4h

^{13}C NMR (151 MHz, CD_2Cl_2)



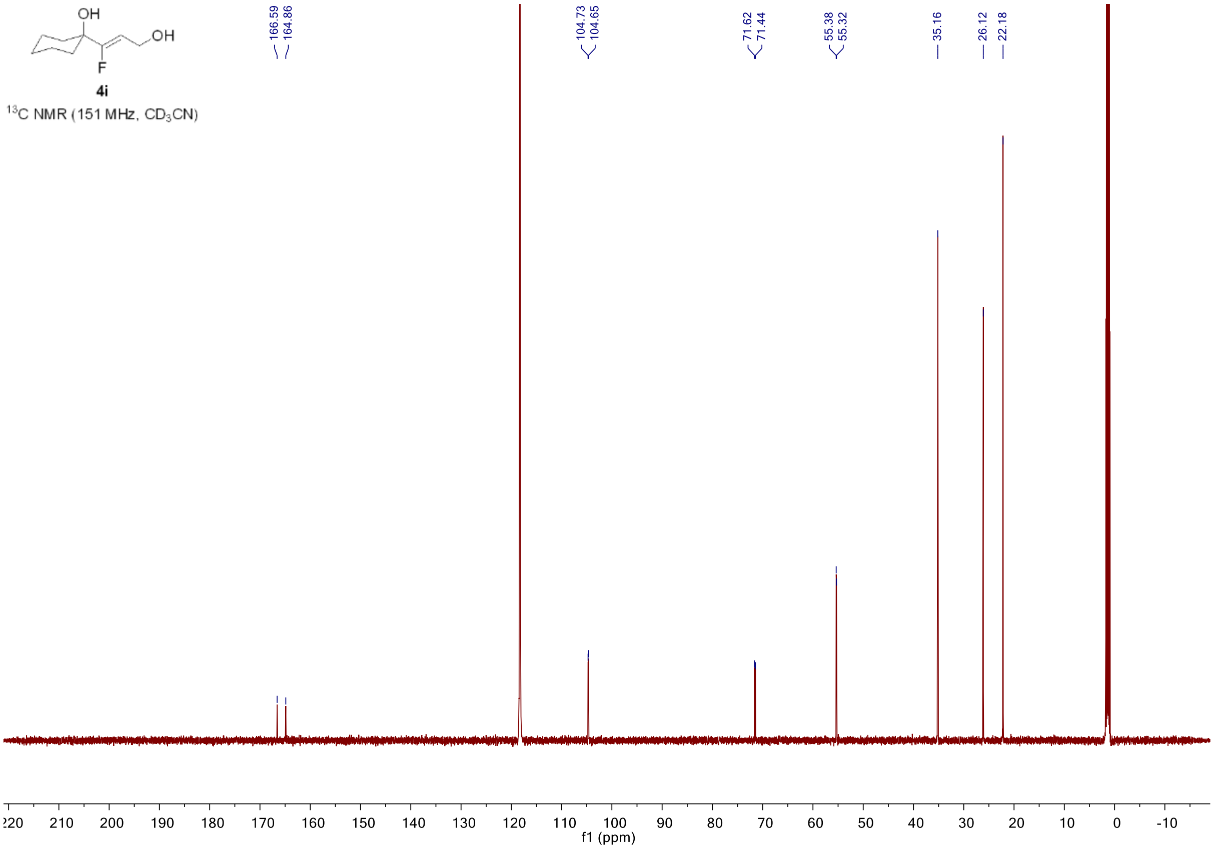
4h

^{19}F NMR (565 MHz, CD_2Cl_2)



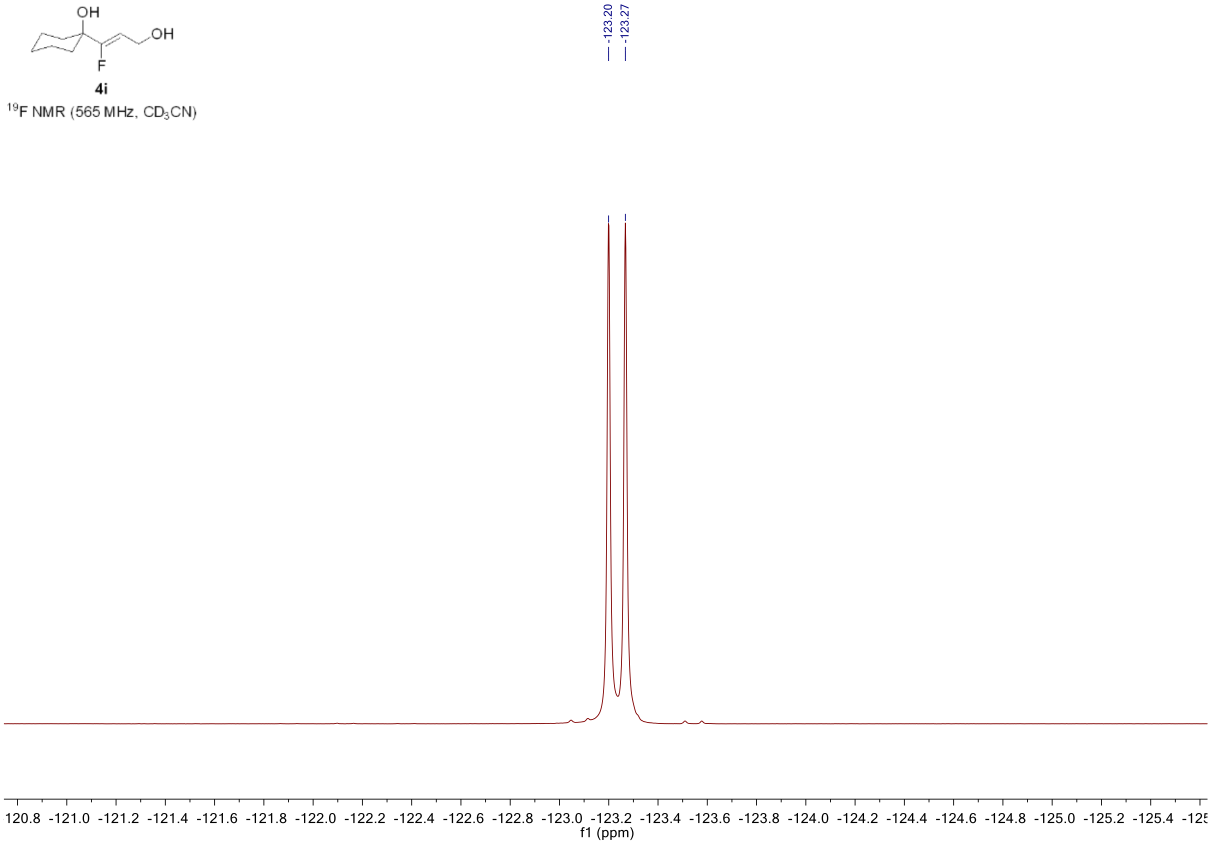
4i

^{1}H NMR (600 MHz, CD_3CN)



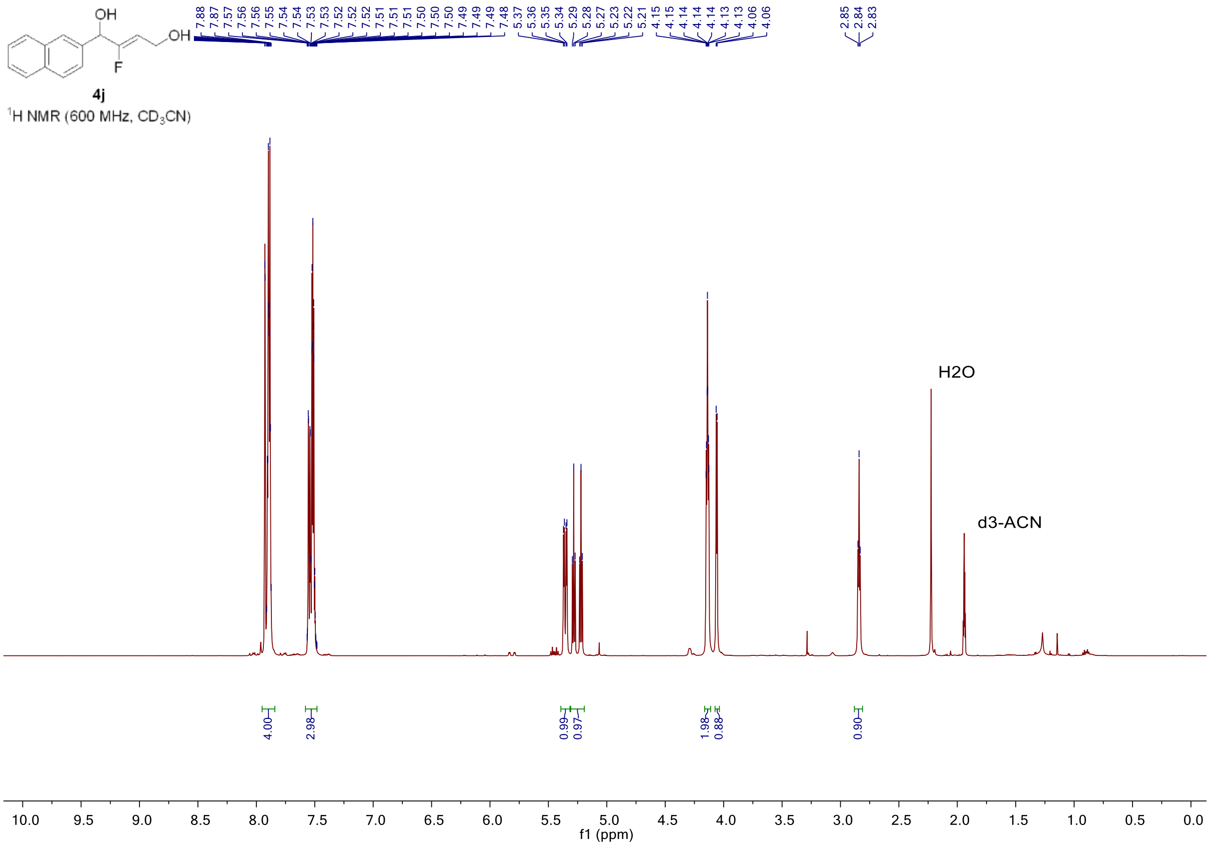
4i

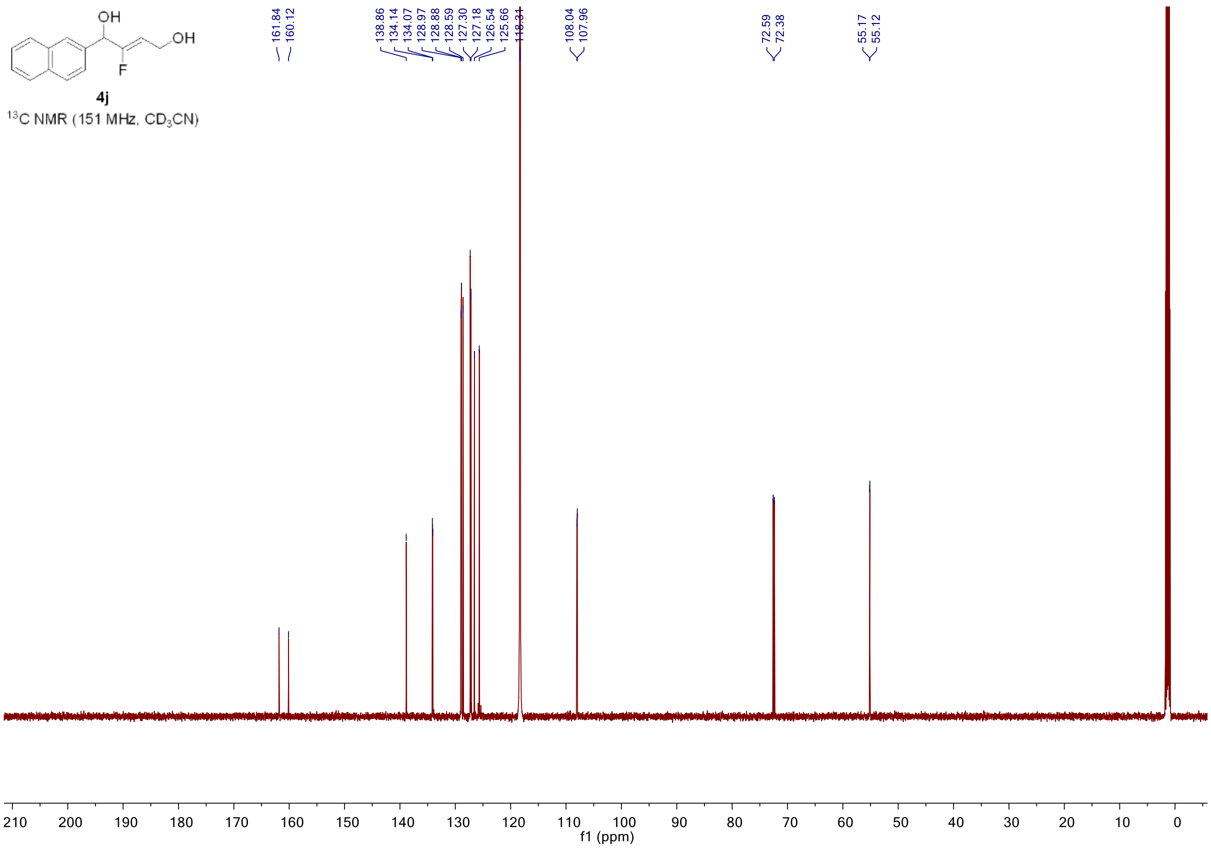
^{13}C NMR (151 MHz, CD_3CN)

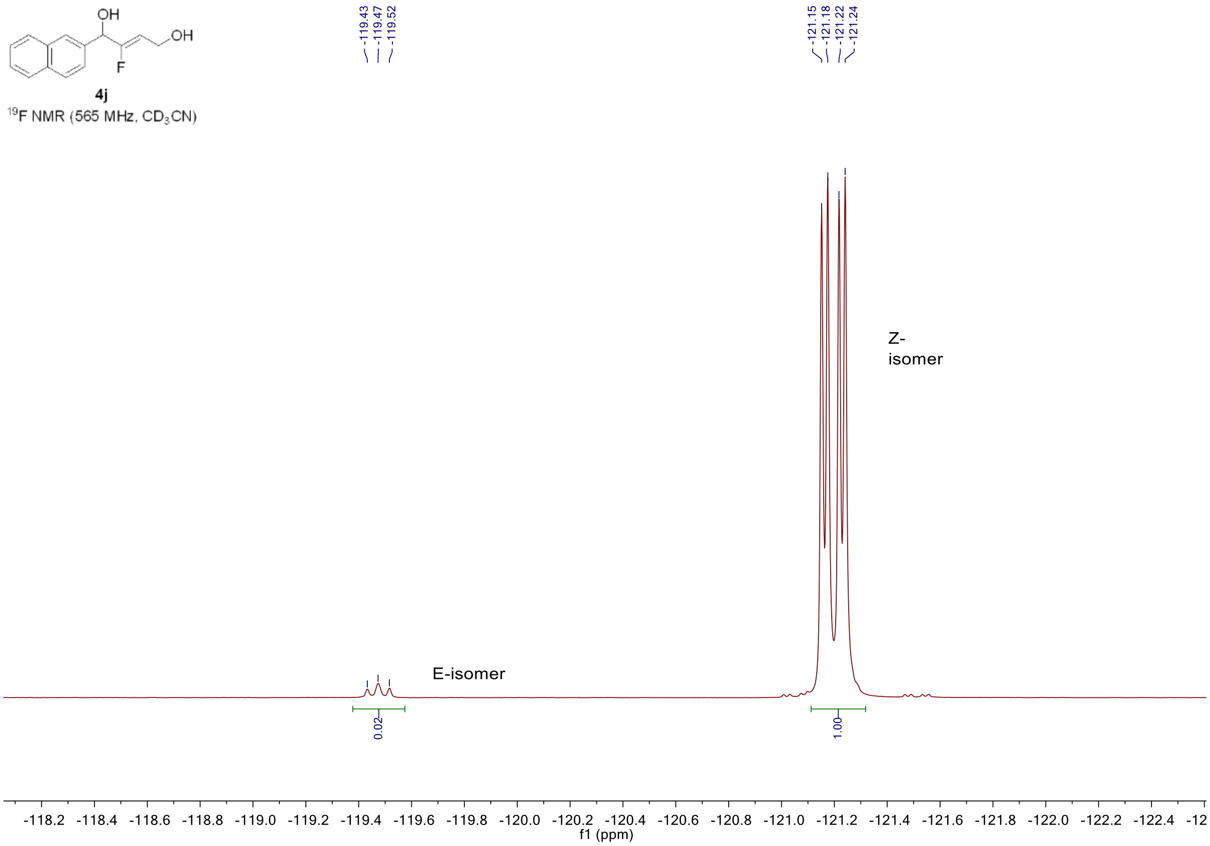


4i

^{19}F NMR (565 MHz, CD_3CN)

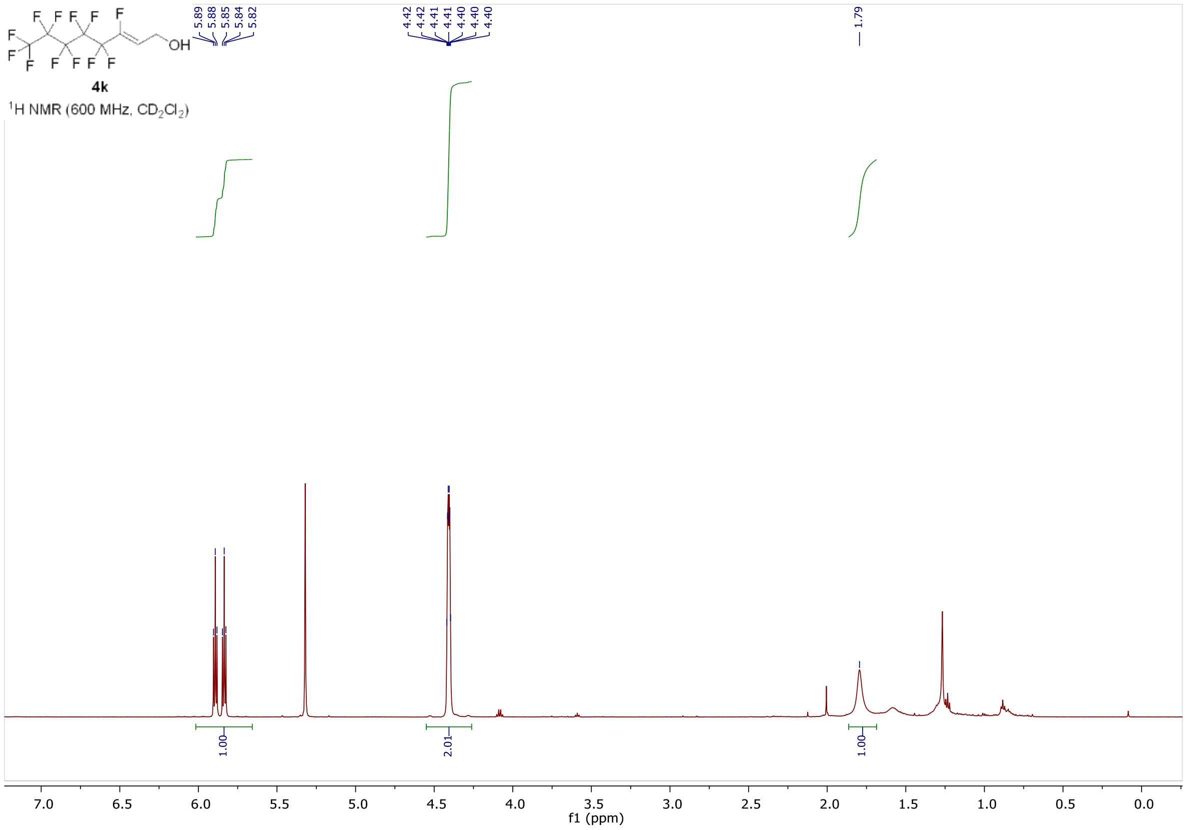

OH
OH
F
4j
1H NMR (600 MHz, CD3CN)
7.88
7.87
7.57
7.56
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.49
7.48
5.37
5.36
5.35
5.34
5.29
5.28
5.27
5.23
5.22
5.21
4.15
4.15
4.14
4.14
4.14
4.13
4.13
4.06
4.06
2.85
2.84
2.83
H2O
d3-ACN
4.00
2.98
0.99
0.97
1.98
0.88
0.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OH
OH
F
4j
13C NMR (151 MHz, CD3CN)
161.84
160.12
138.86
134.14
134.07
128.97
128.88
128.59
127.30
127.18
126.54
125.66
118.31
108.04
107.96
72.59
72.38
55.17
55.12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



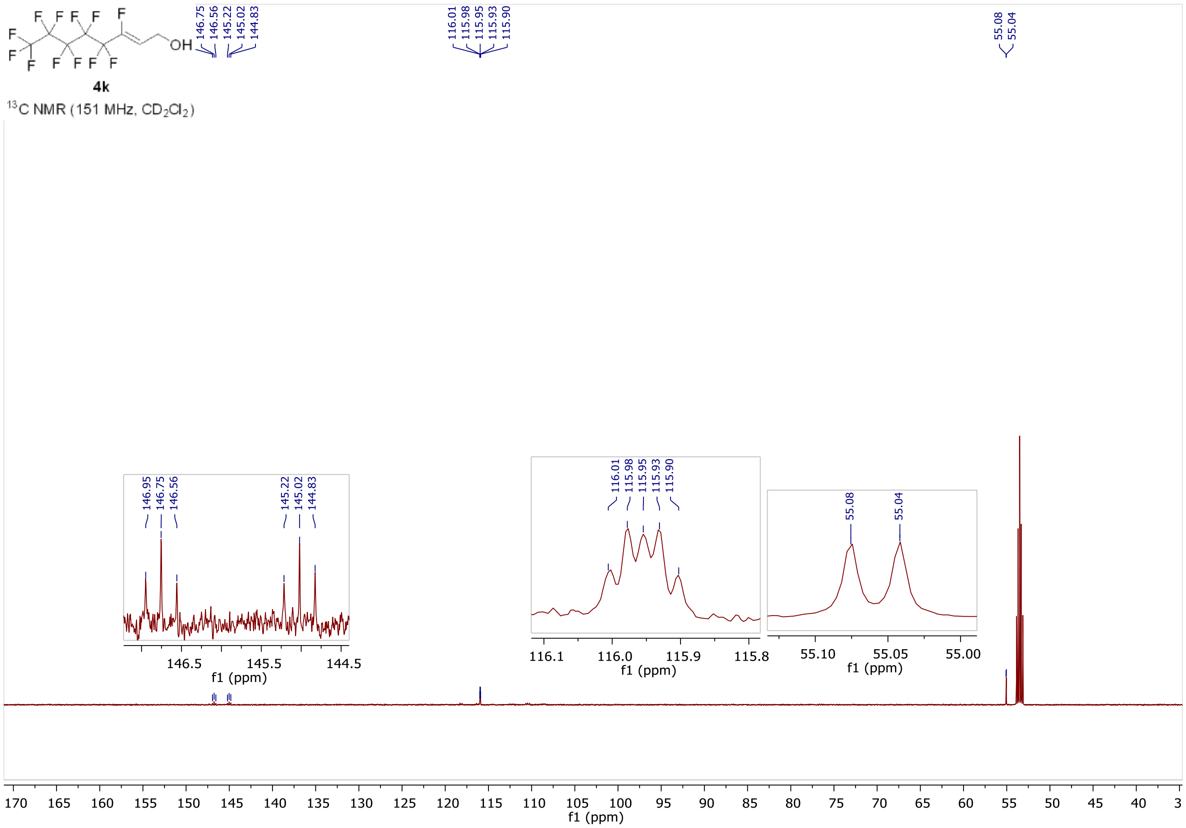
4j

^{19}F NMR (565 MHz, CD_3CN)

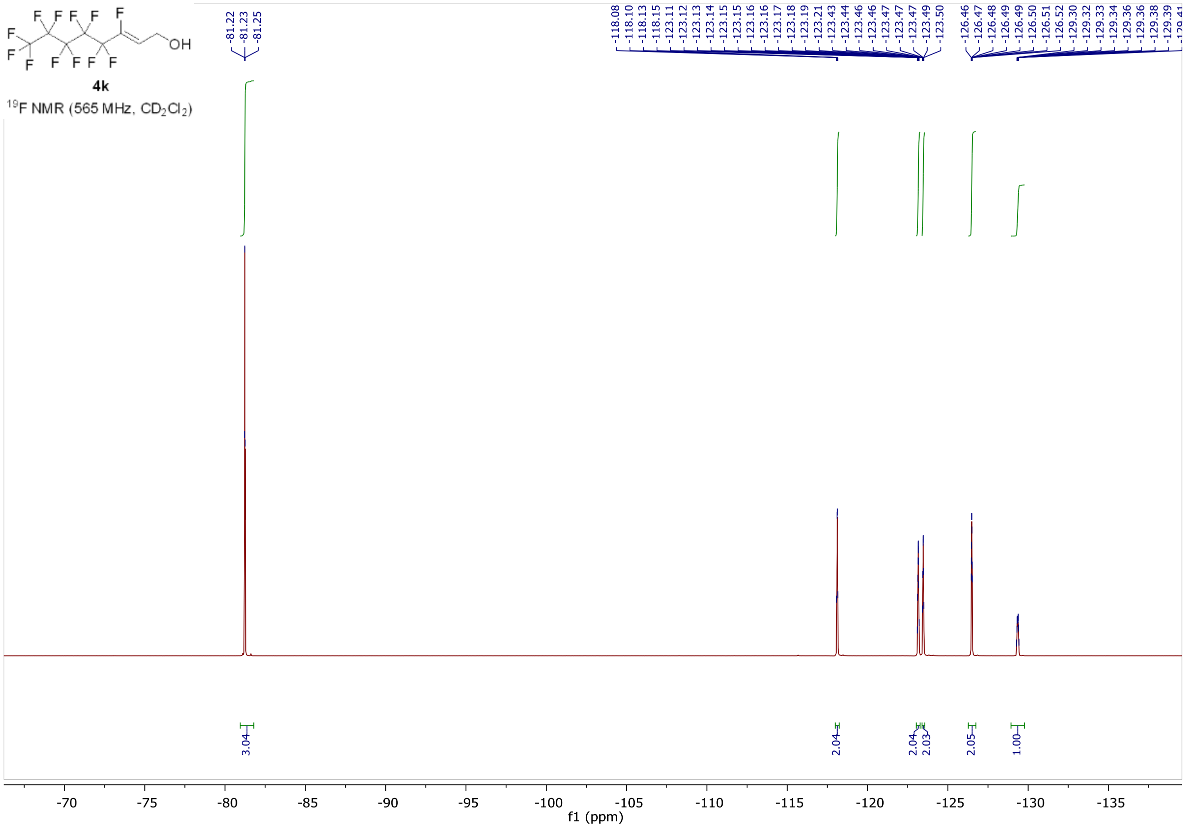


4k

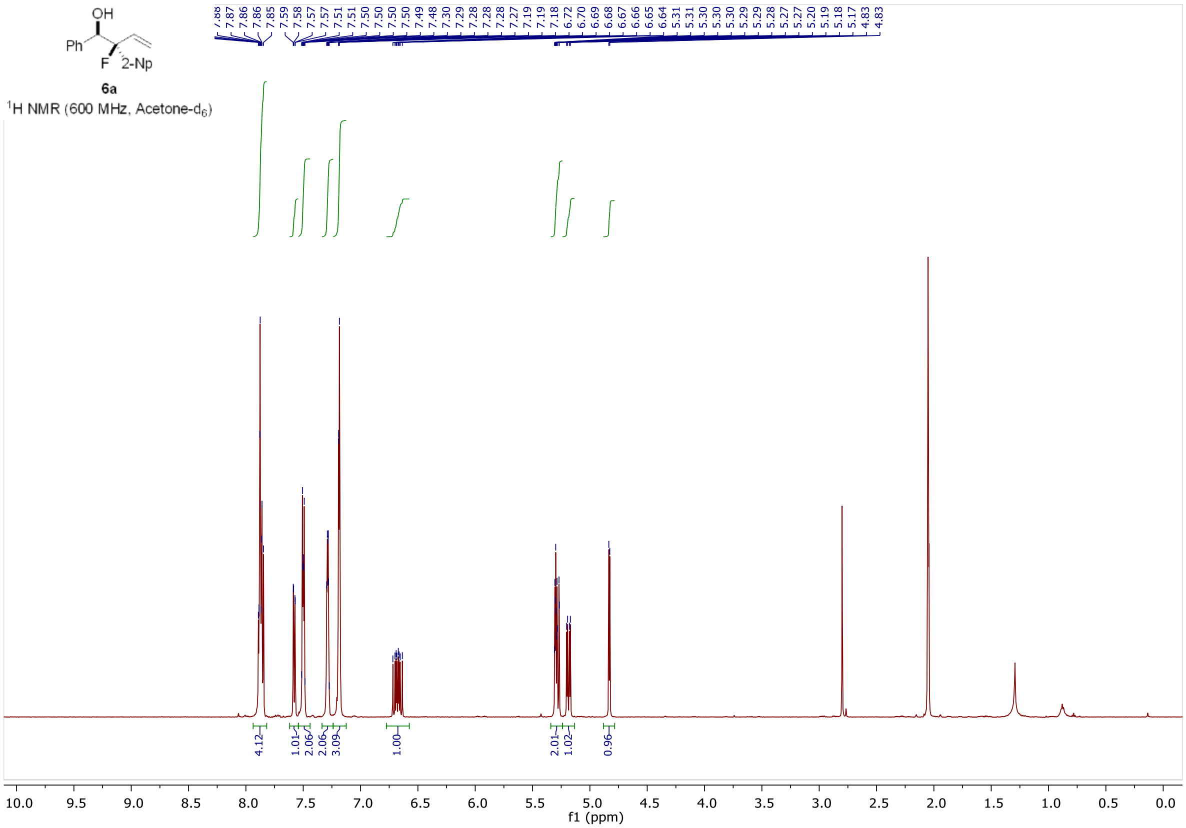
^{1}H NMR (600 MHz, CD_2Cl_2)


4k

^{13}C NMR (151 MHz, CD_2Cl_2)

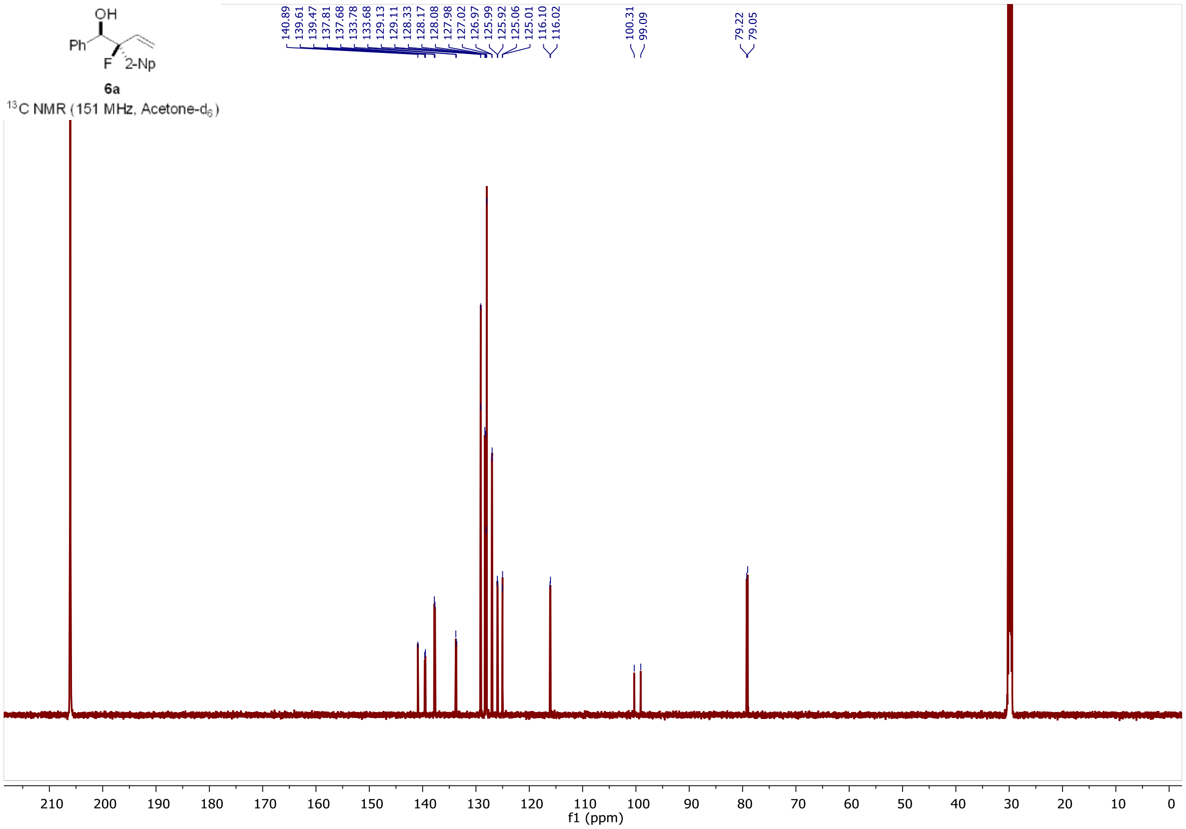

4k

^{19}F NMR (565 MHz, CD_2Cl_2)



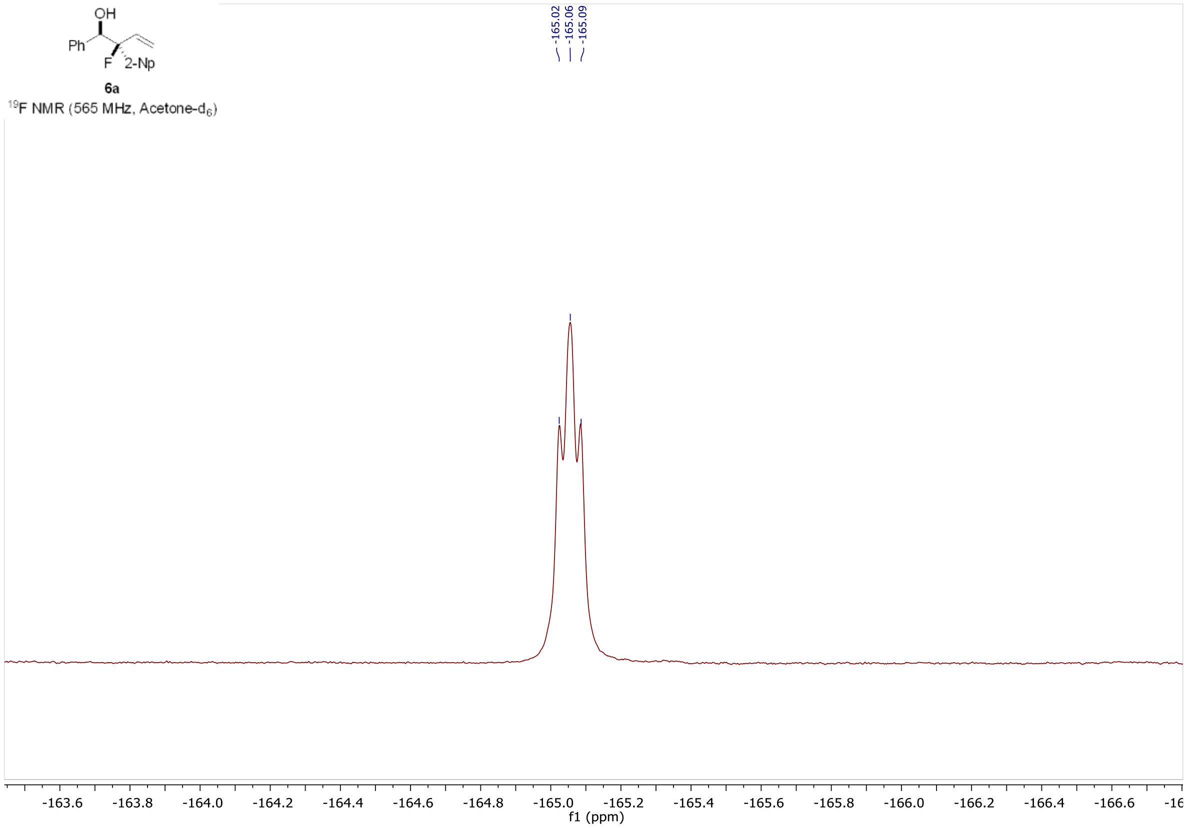
6a

^{1}H NMR (600 MHz, Acetone-d_6)



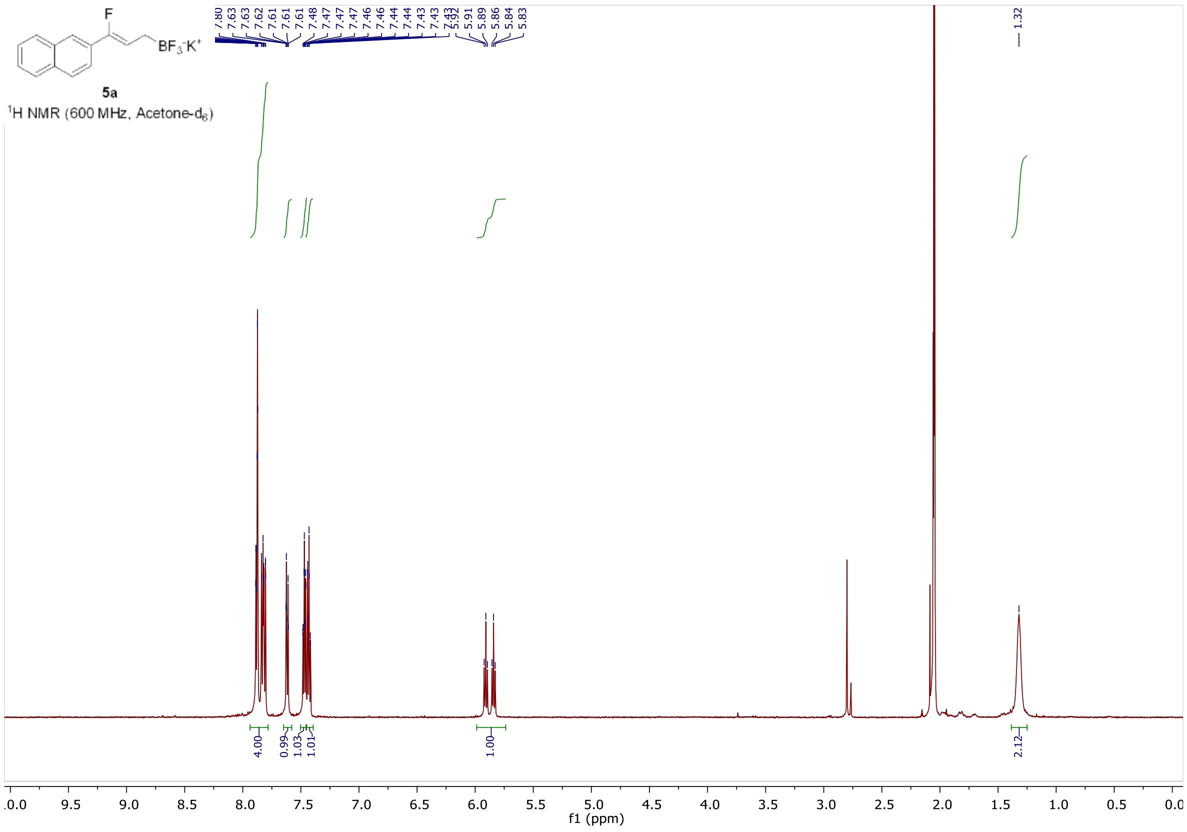
6a

^{13}C NMR (151 MHz, Acetone-d_6)



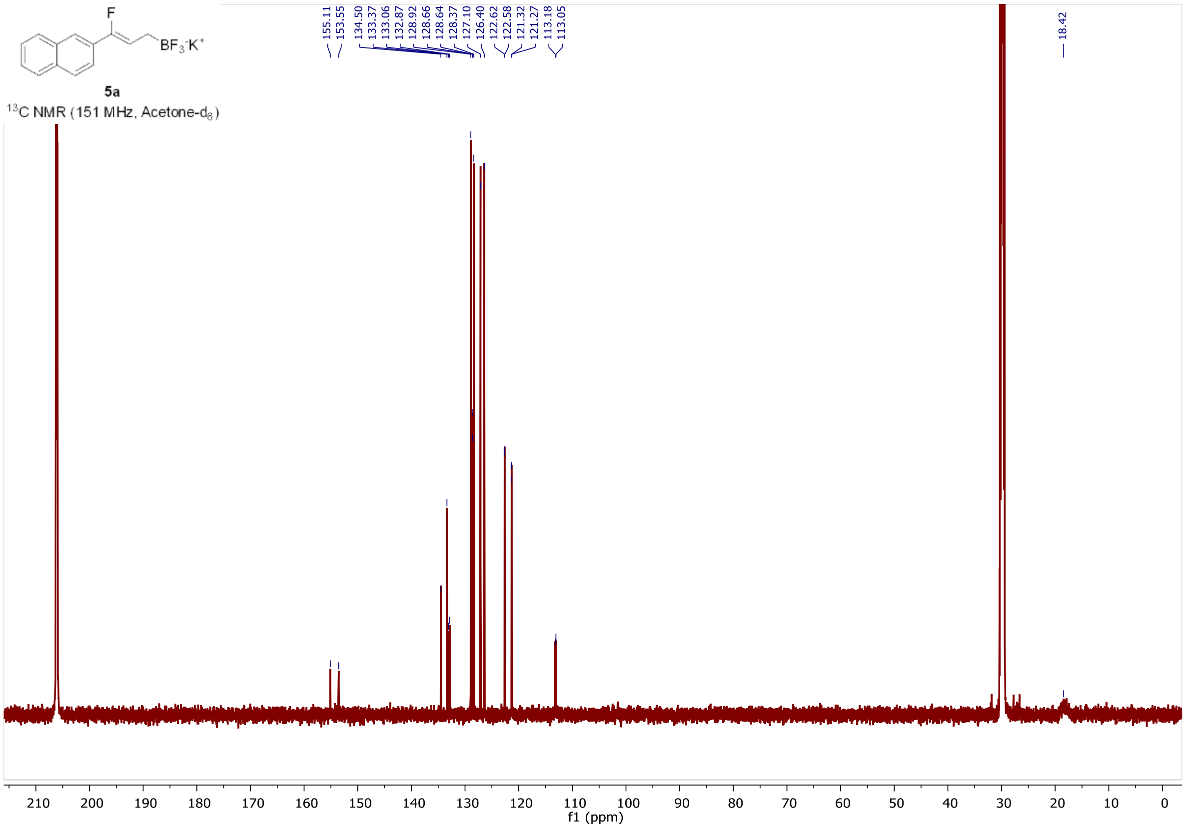
6a

^{19}F NMR (565 MHz, Acetone-d_6)



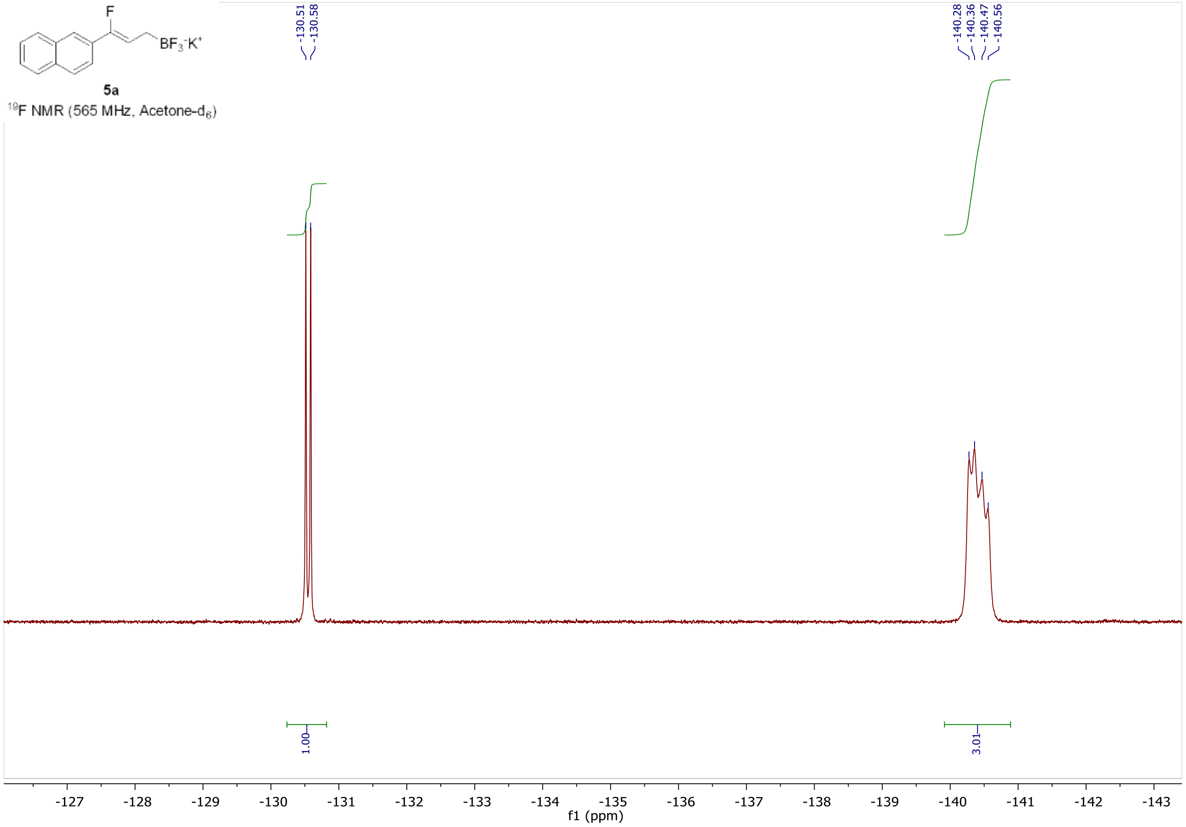
5a

^{1}H NMR (600 MHz, Acetone-d_6)



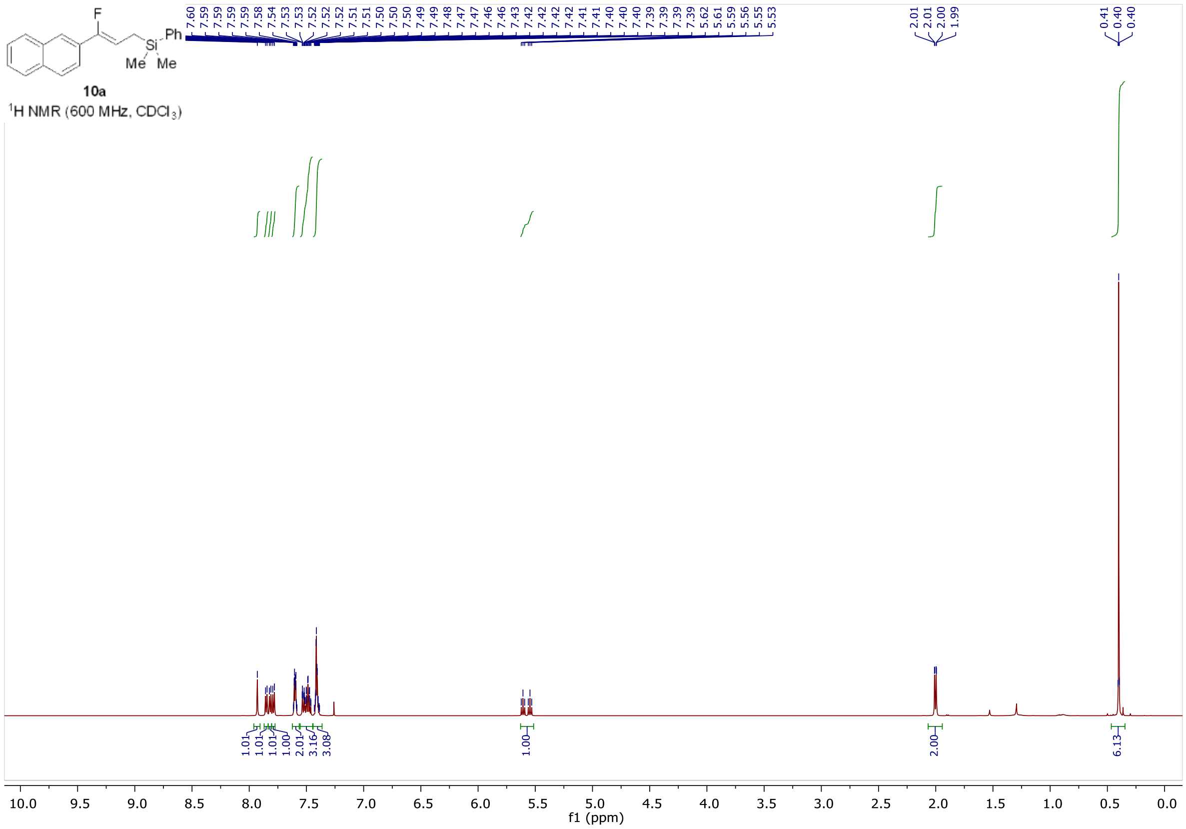
5a

^{13}C NMR (151 MHz, Acetone-d_6)



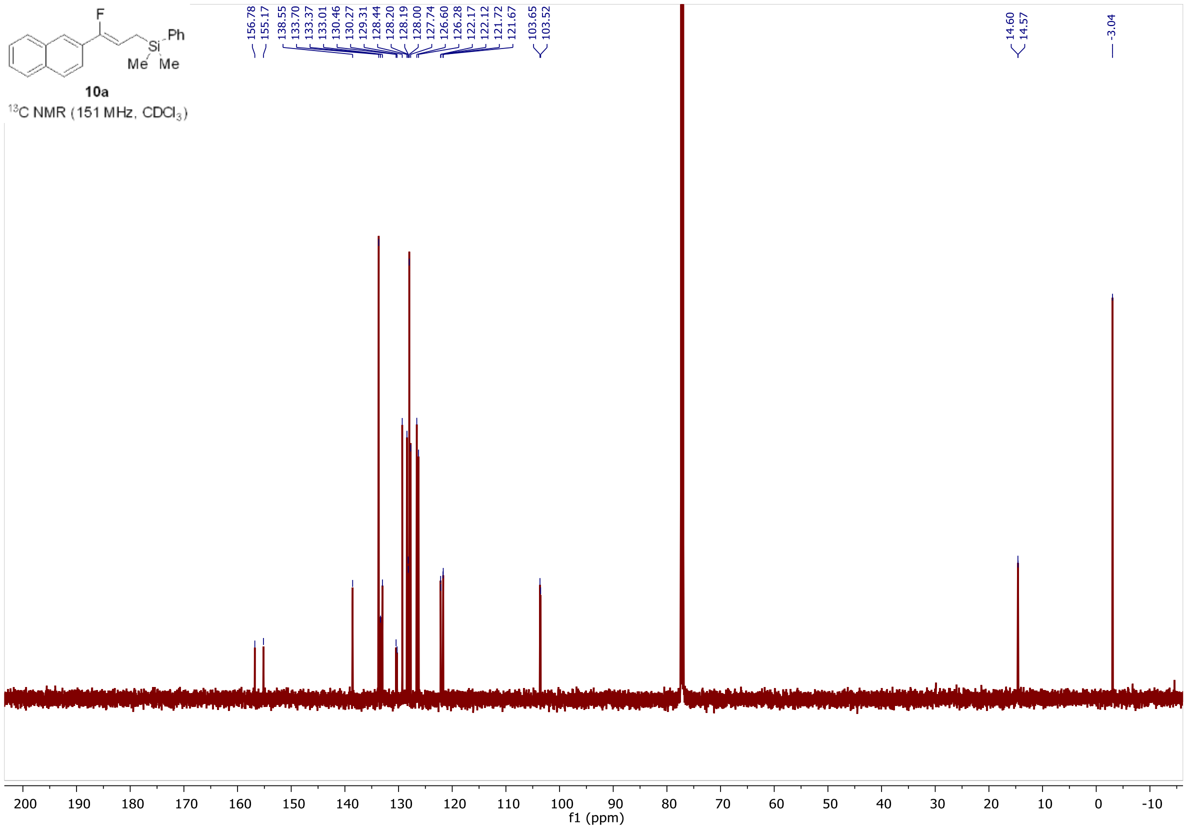
5a

^{19}F NMR (565 MHz, Acetone-d_6)



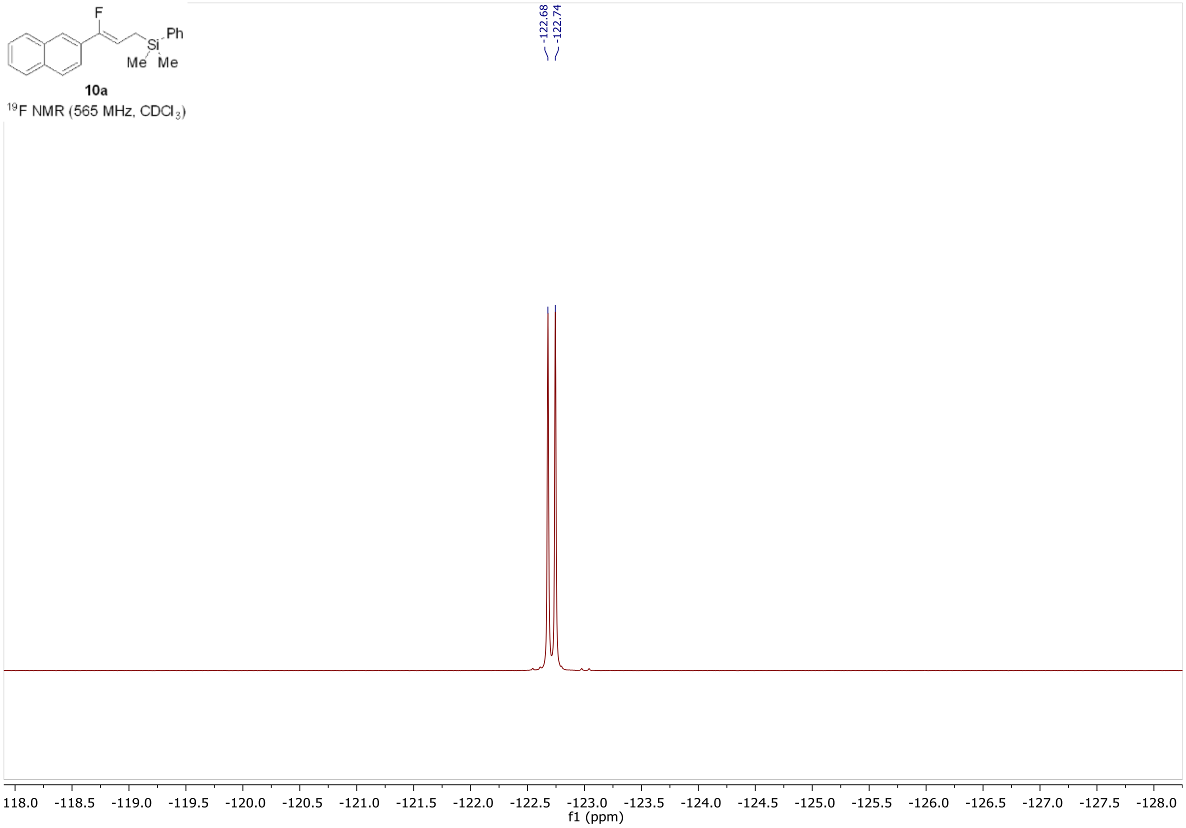
10a

^{1}H NMR (600 MHz, CDCl$_3$)



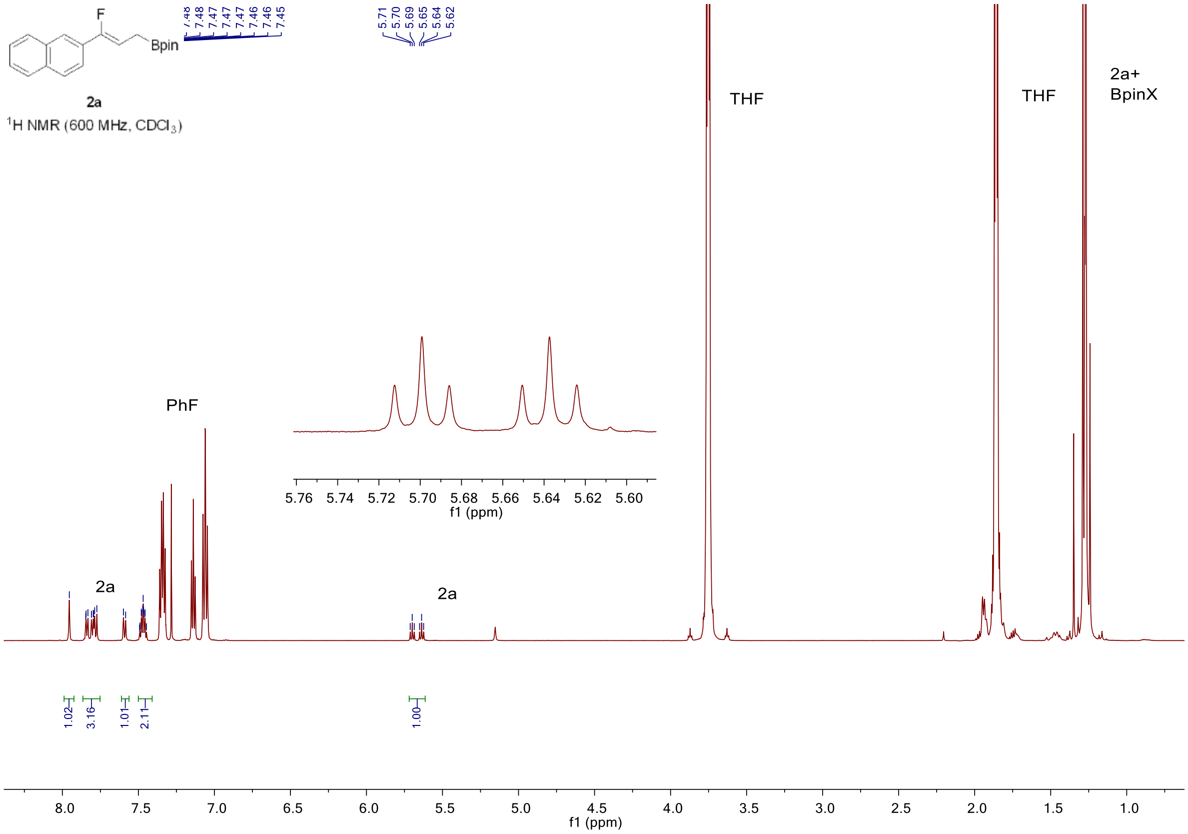
10a

^{13}C NMR (151 MHz, CDCl$_3$)


10a

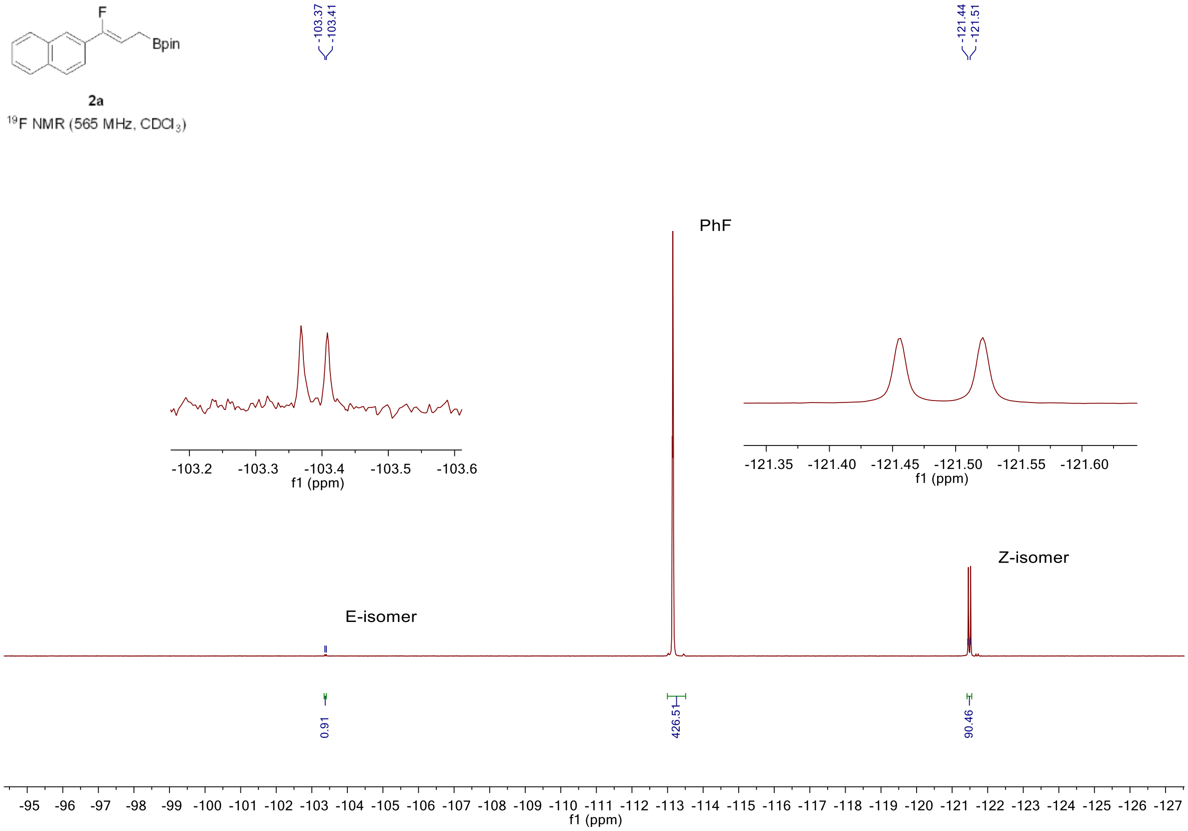
^{19}F NMR (565 MHz, $CDCl_3$)

CRUDE ^{1}H AND ^{19}F NMR SPECTRA



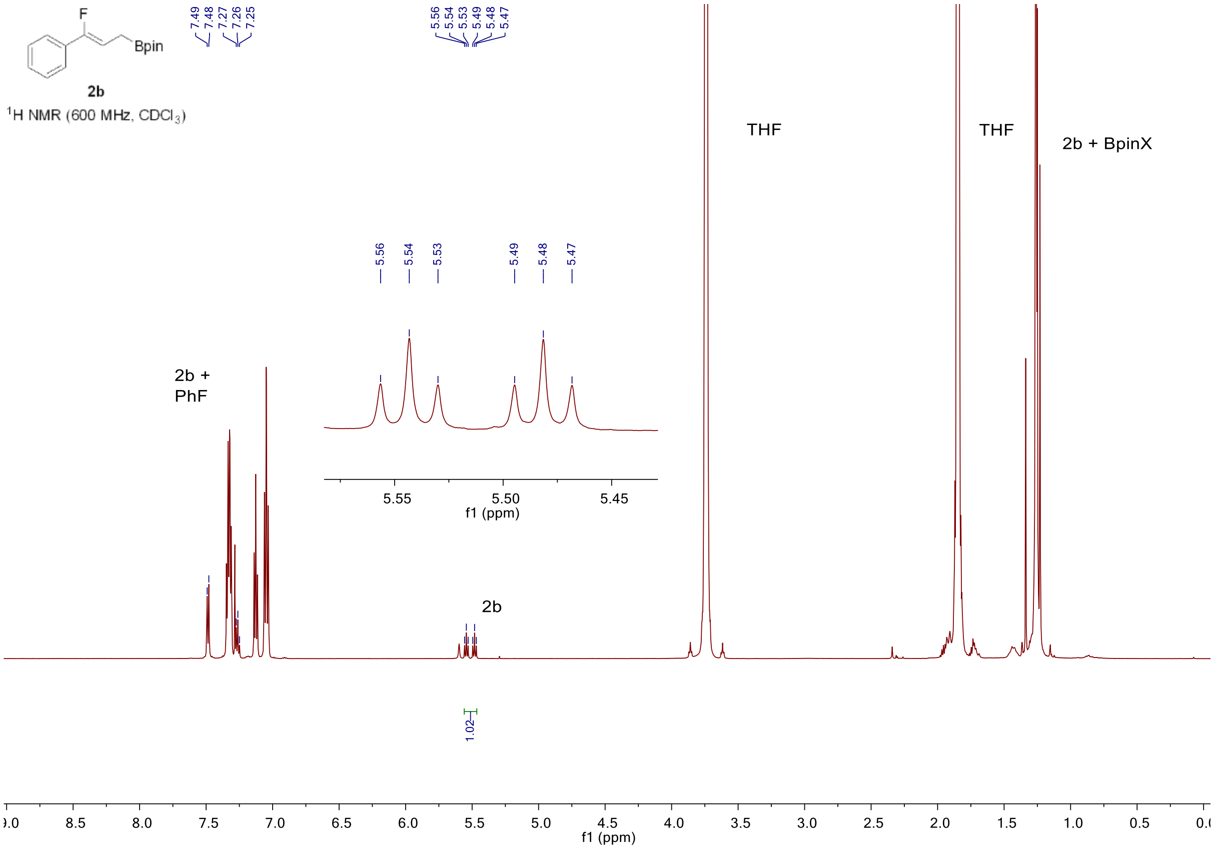
2a

^{1}H NMR (600 MHz, CDCl$_3$)

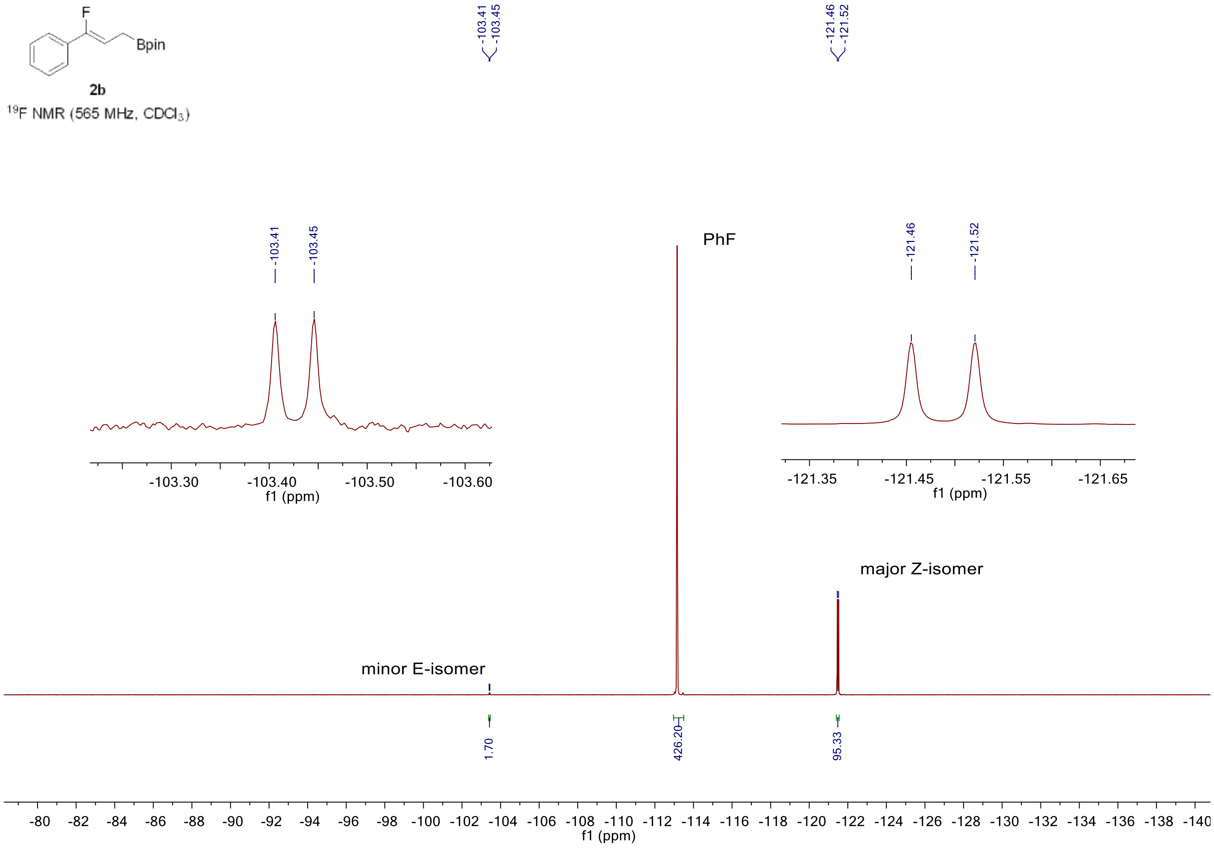


2a

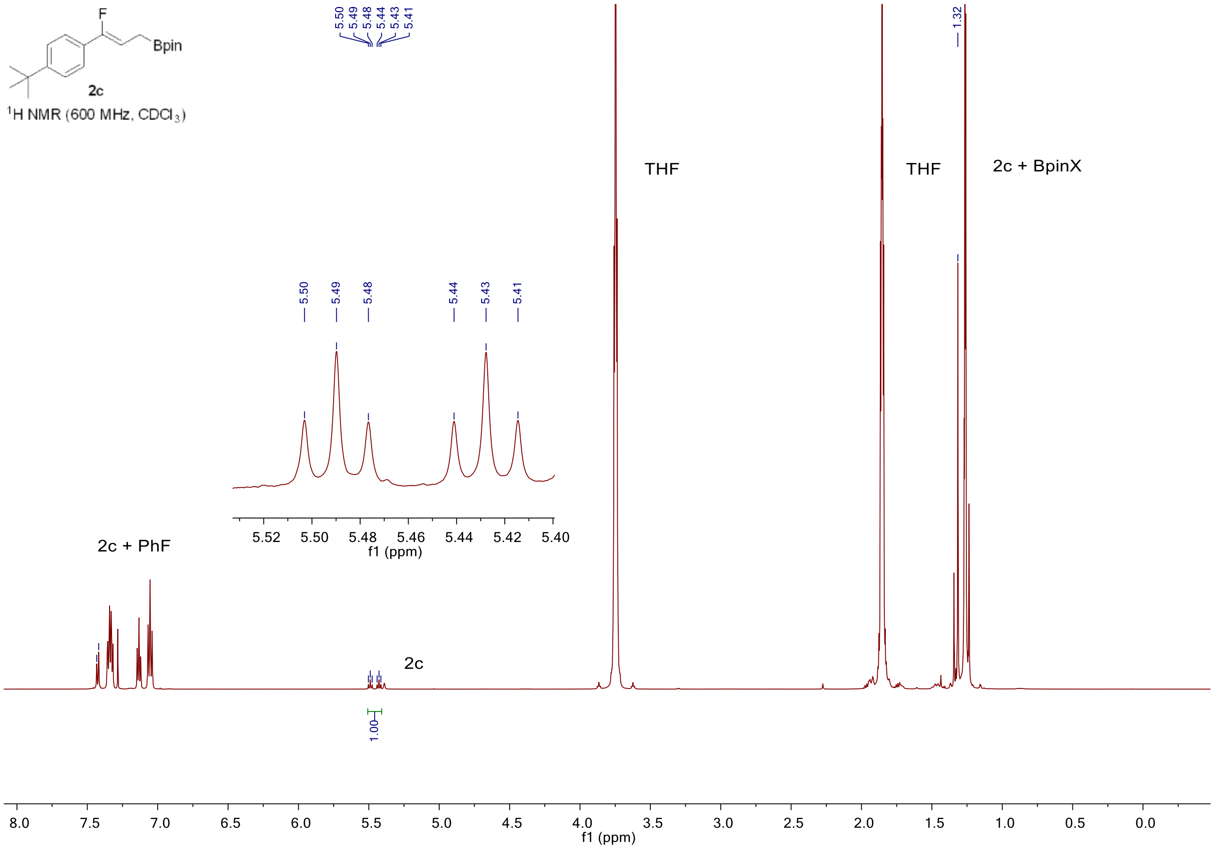
^{19}F NMR (565 MHz, CDCl$_3$)


2b

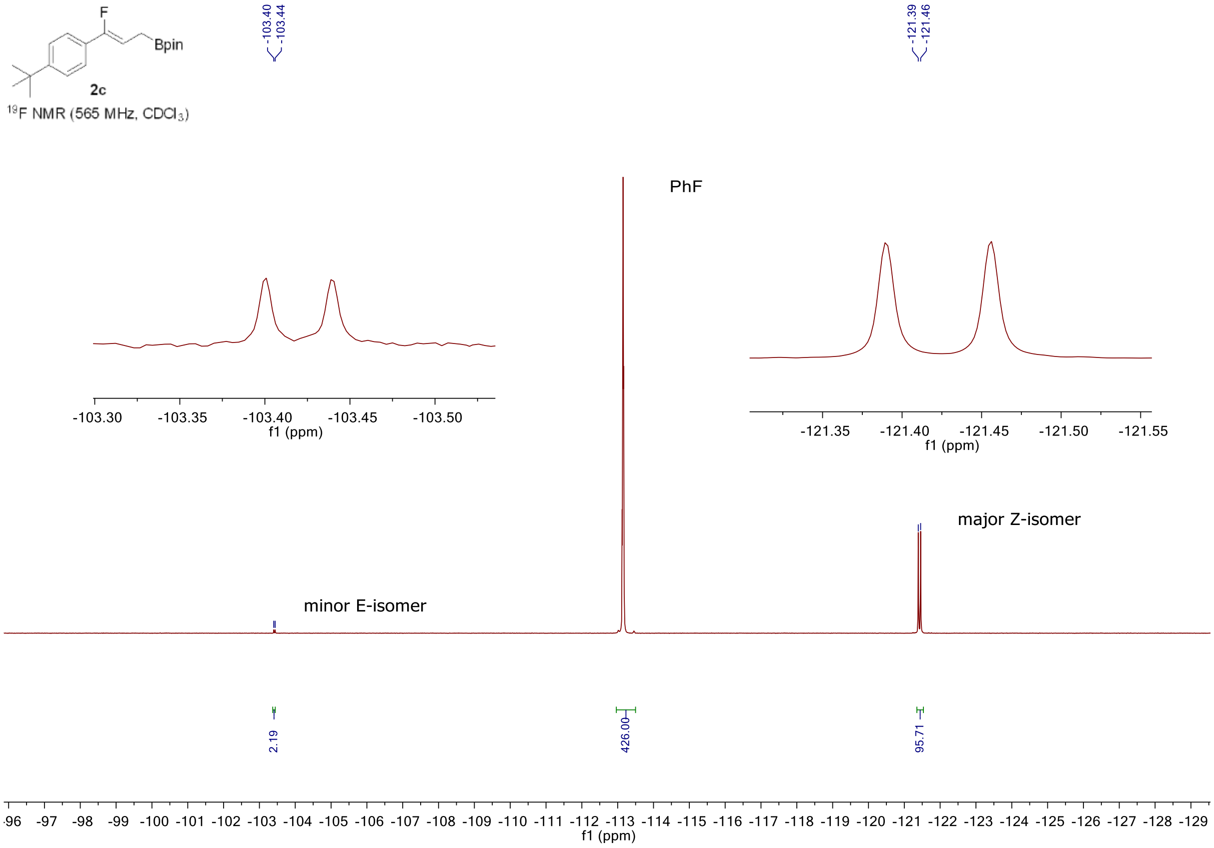
^{1}H NMR (600 MHz, CDCl$_3$)


2b

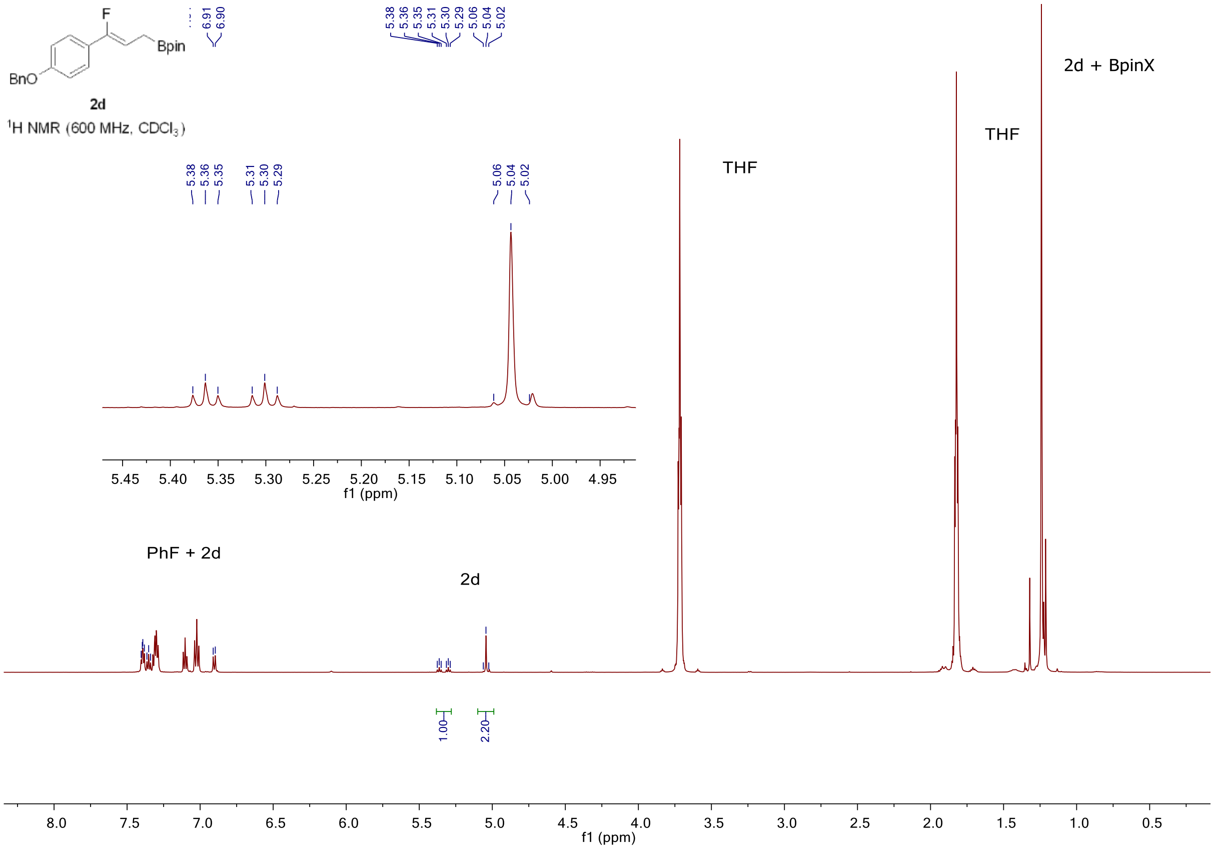
^{19}F NMR (565 MHz, CDCl$_3$)


2c

^{1}H NMR (600 MHz, $CDCl_3$)

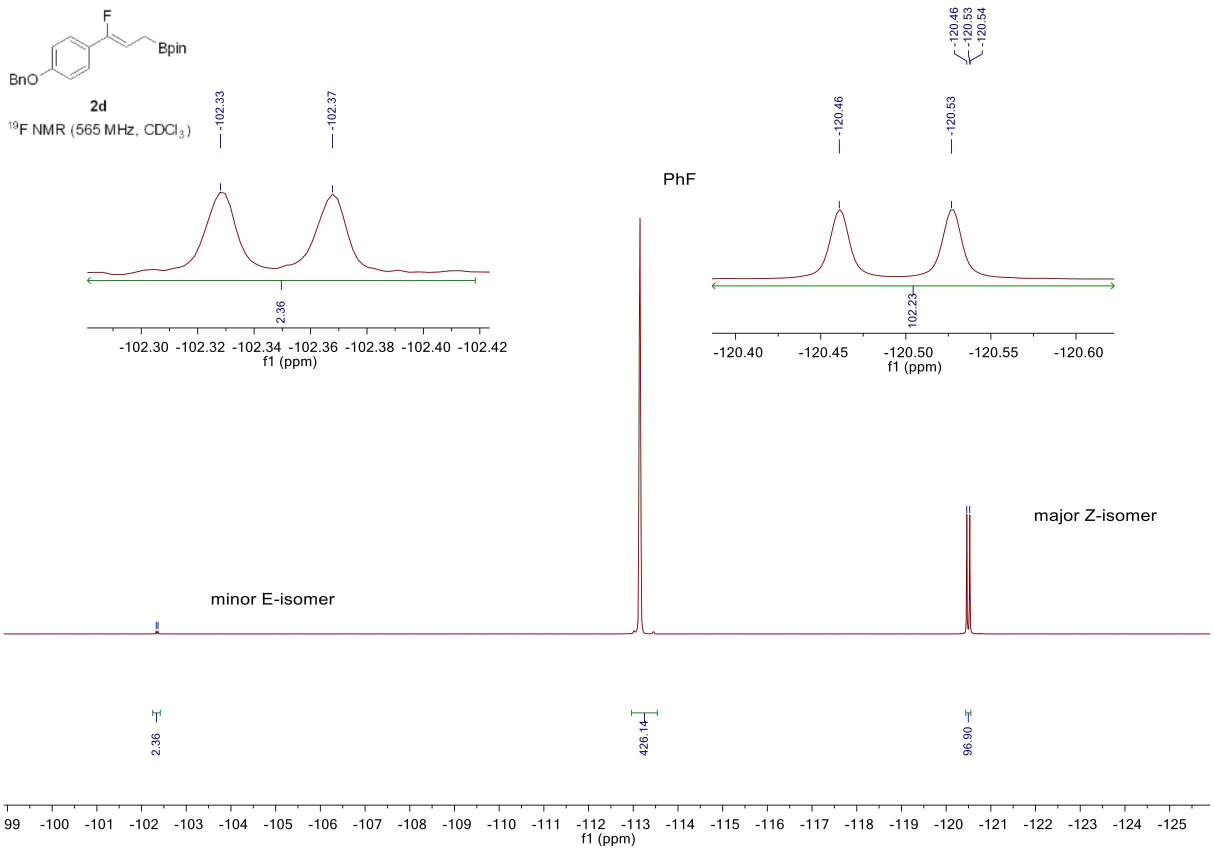

2c

^{19}F NMR (565 MHz, $CDCl_3$)



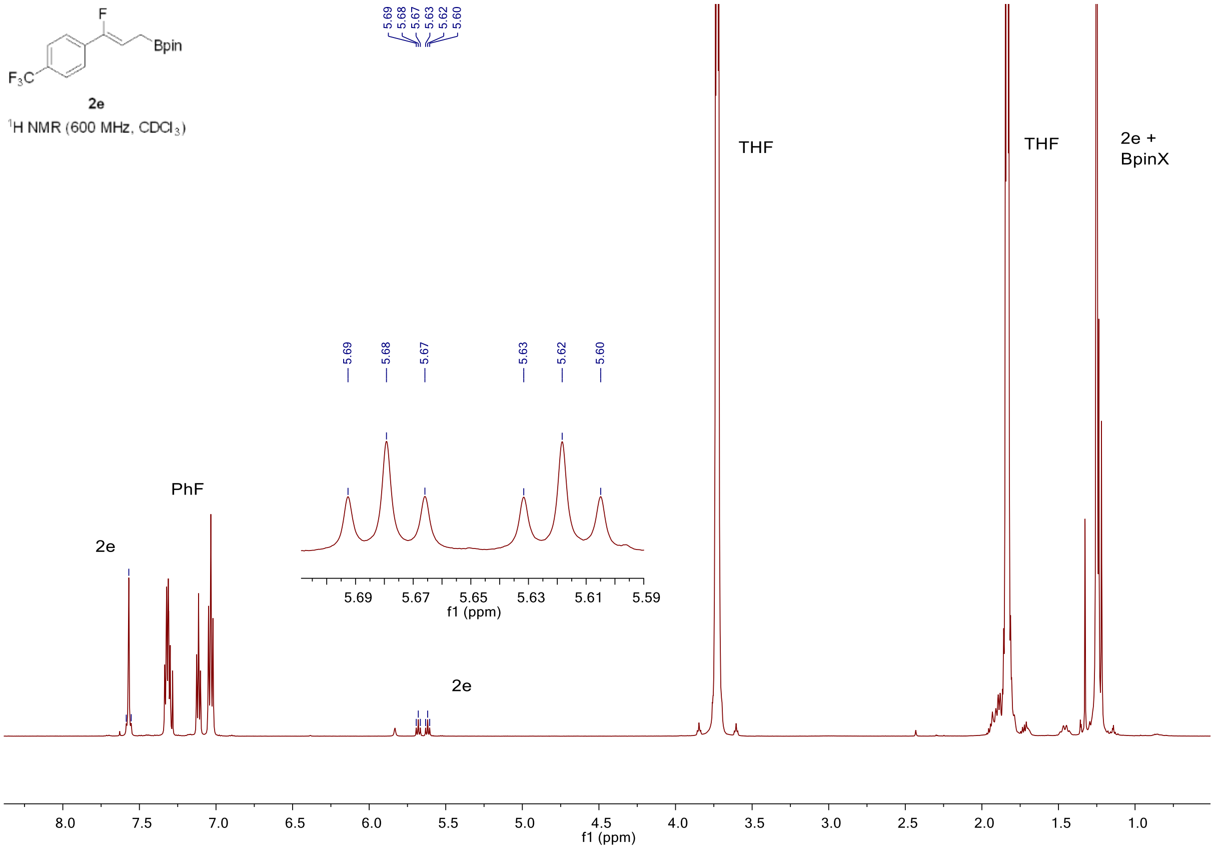
2d

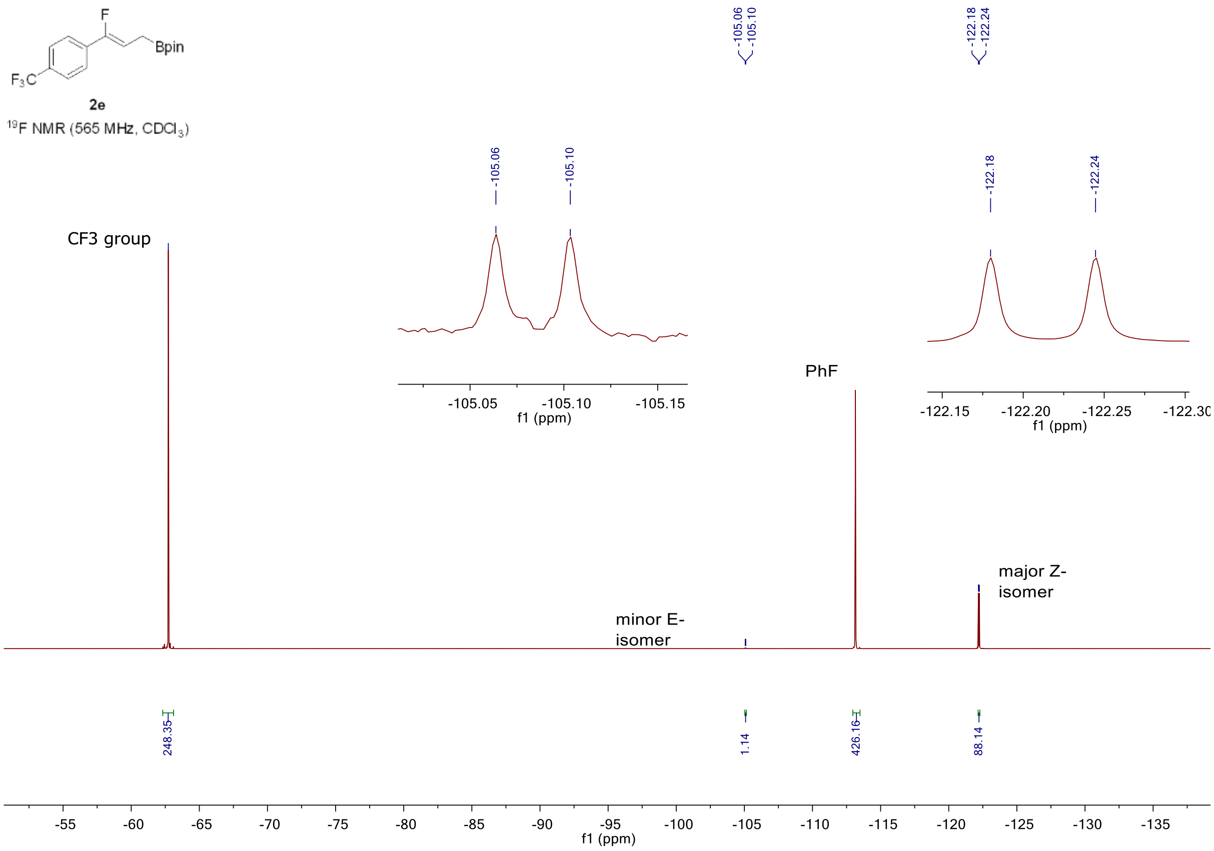
^{1}H NMR (600 MHz, CDCl$_3$)

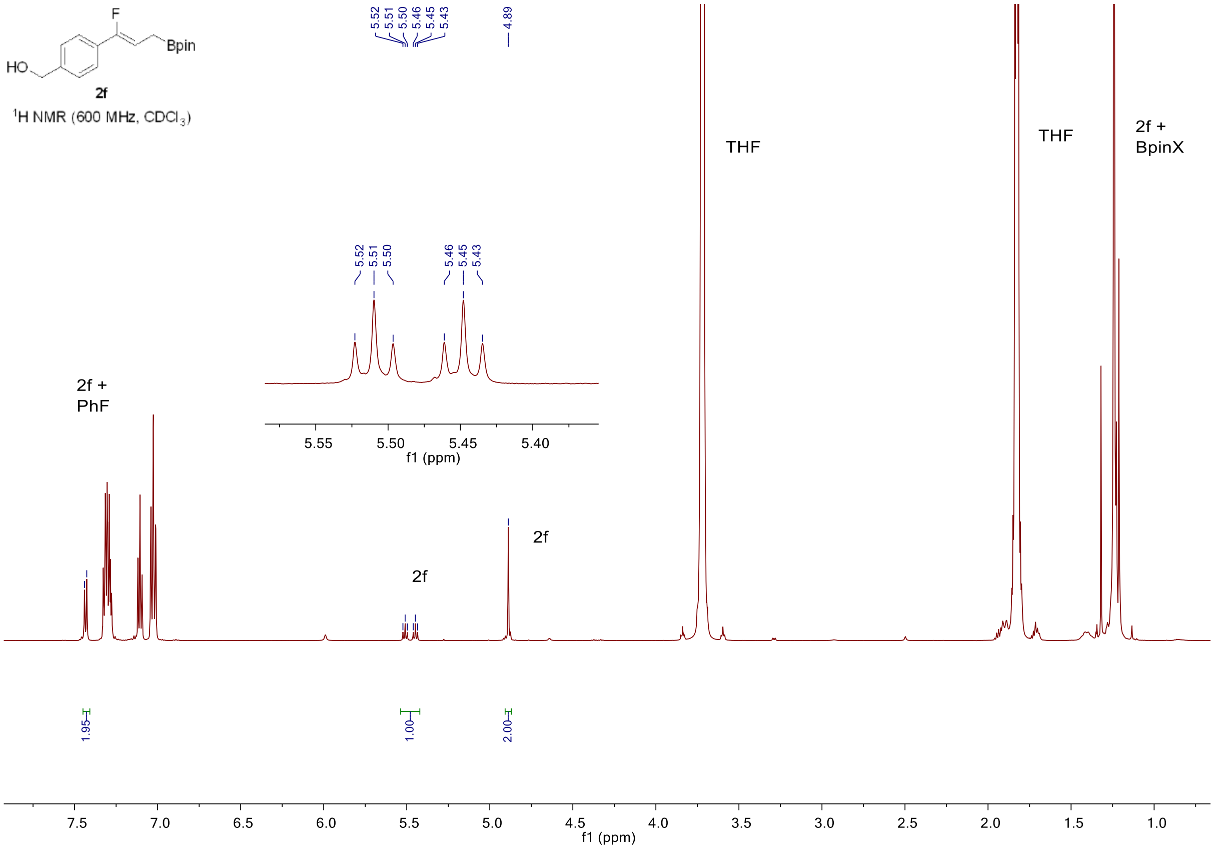


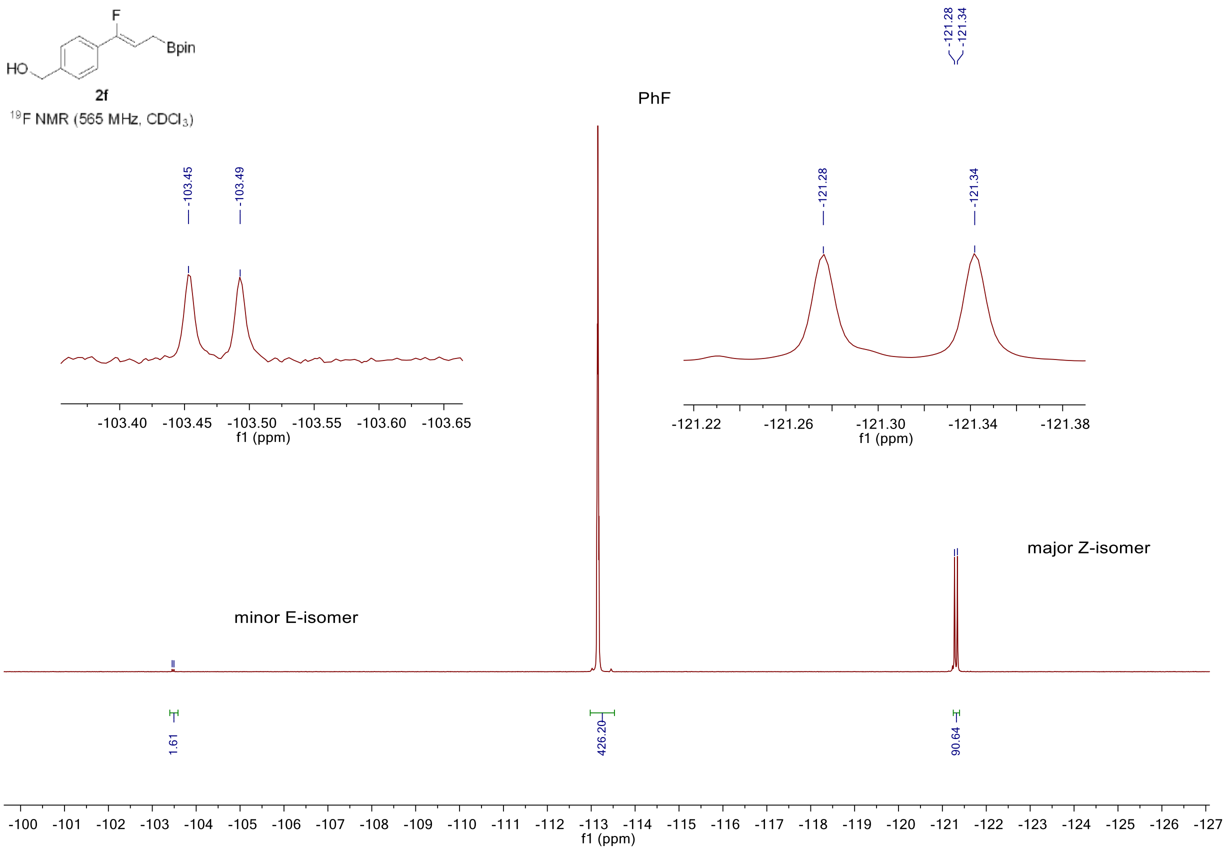
2d

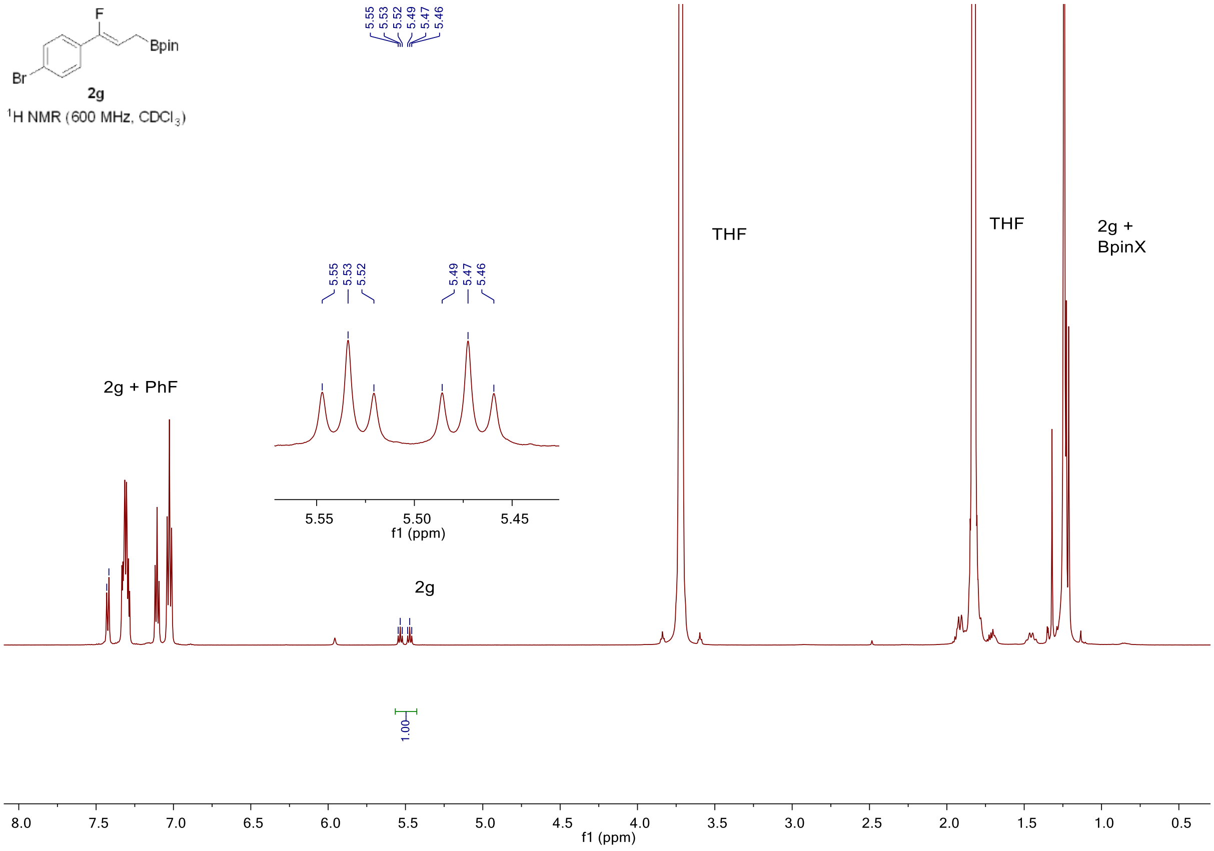
^{19}F NMR (565 MHz, CDCl$_3$)

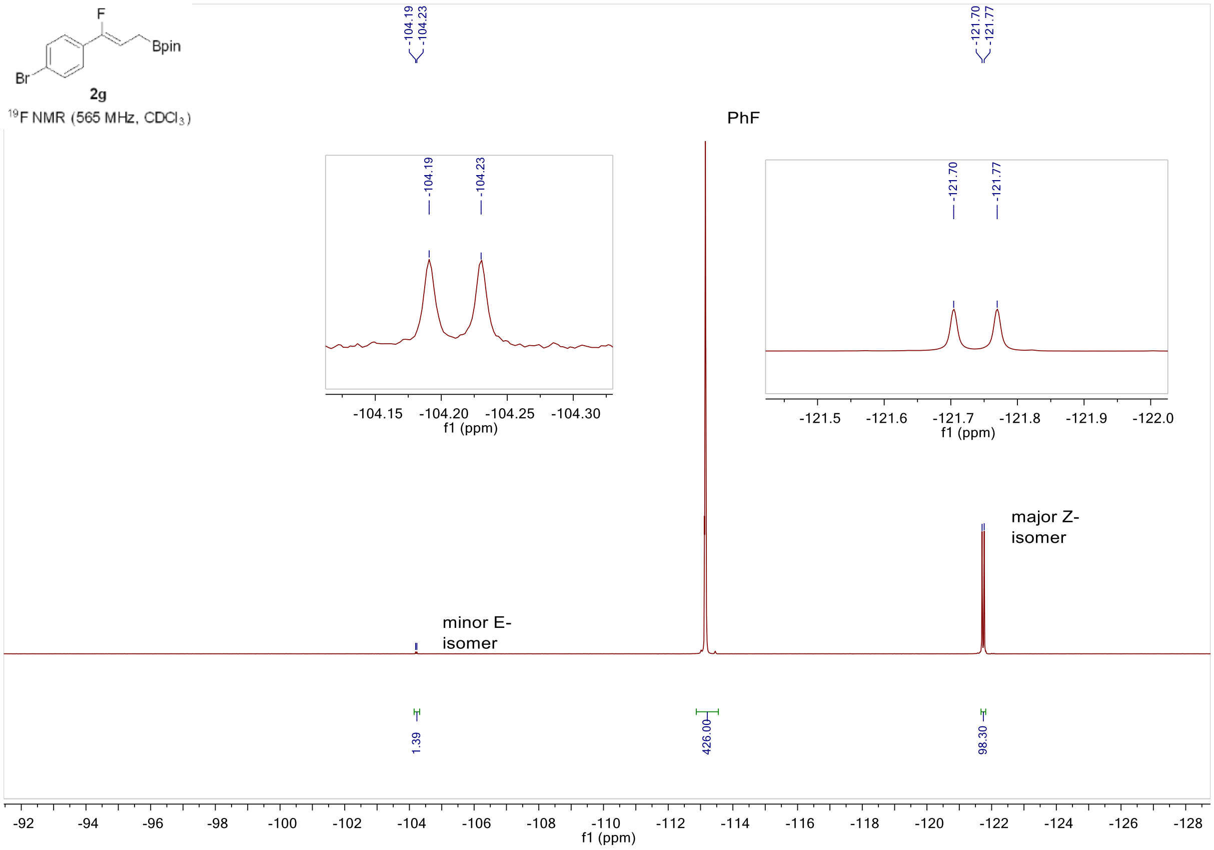

F
Bpin
F3C
2e
1H NMR (600 MHz, CDCl3)
5.69
5.68
5.67
5.63
5.62
5.60
THF
THF
2e +
BpinX
PhF
2e
2e
5.69
5.67
5.65
5.63
5.61
5.59
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

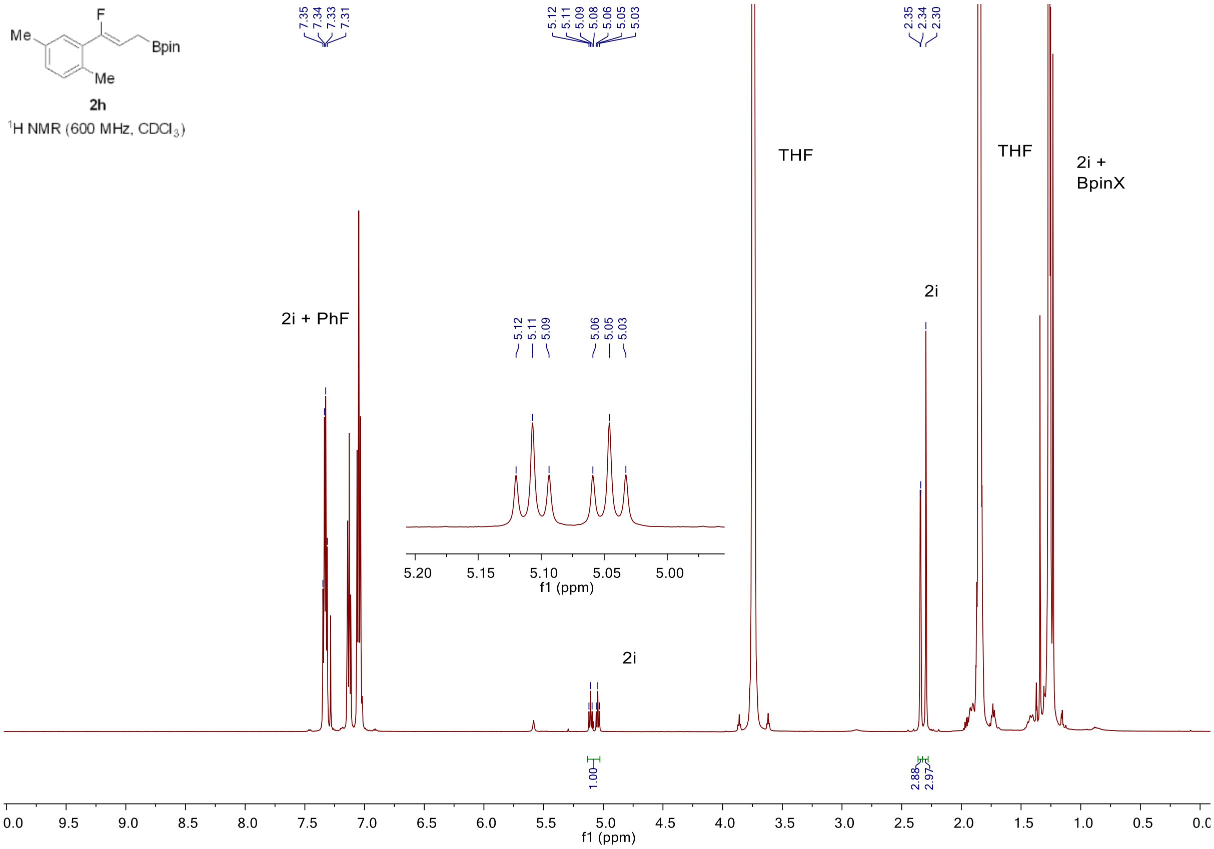

F
Bpin
F3C
2e
19F NMR (565 MHz, CDCl3)
-105.06
-105.10
-122.18
-122.24
CF3 group
-105.05
-105.10
-105.15
f1 (ppm)
PhF
-122.15
-122.20
-122.25
-122.30
f1 (ppm)
major Z-
isomer
minor E-
isomer
248.35
1.14
426.16
88.14
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
f1 (ppm)

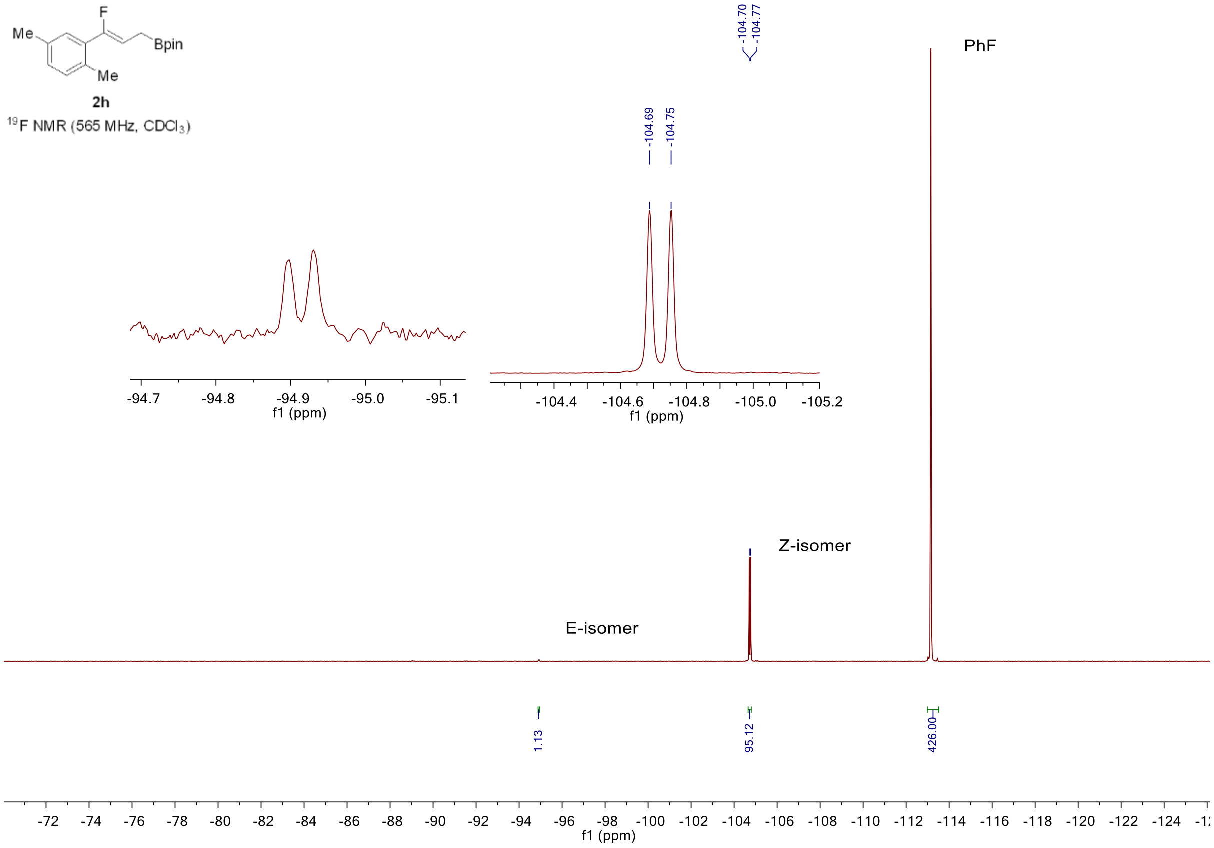

F
Bpin
HO
2f
1H NMR (600 MHz, CDCl3)
5.52 5.51 5.50 5.46 5.45 5.43
4.89
THF
THF
2f + BpinX
2f + PhF
2f
2f
5.52 5.51 5.50 5.46 5.45 5.43
5.55 5.50 5.45 5.40
f1 (ppm)
1.95
1.00
2.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

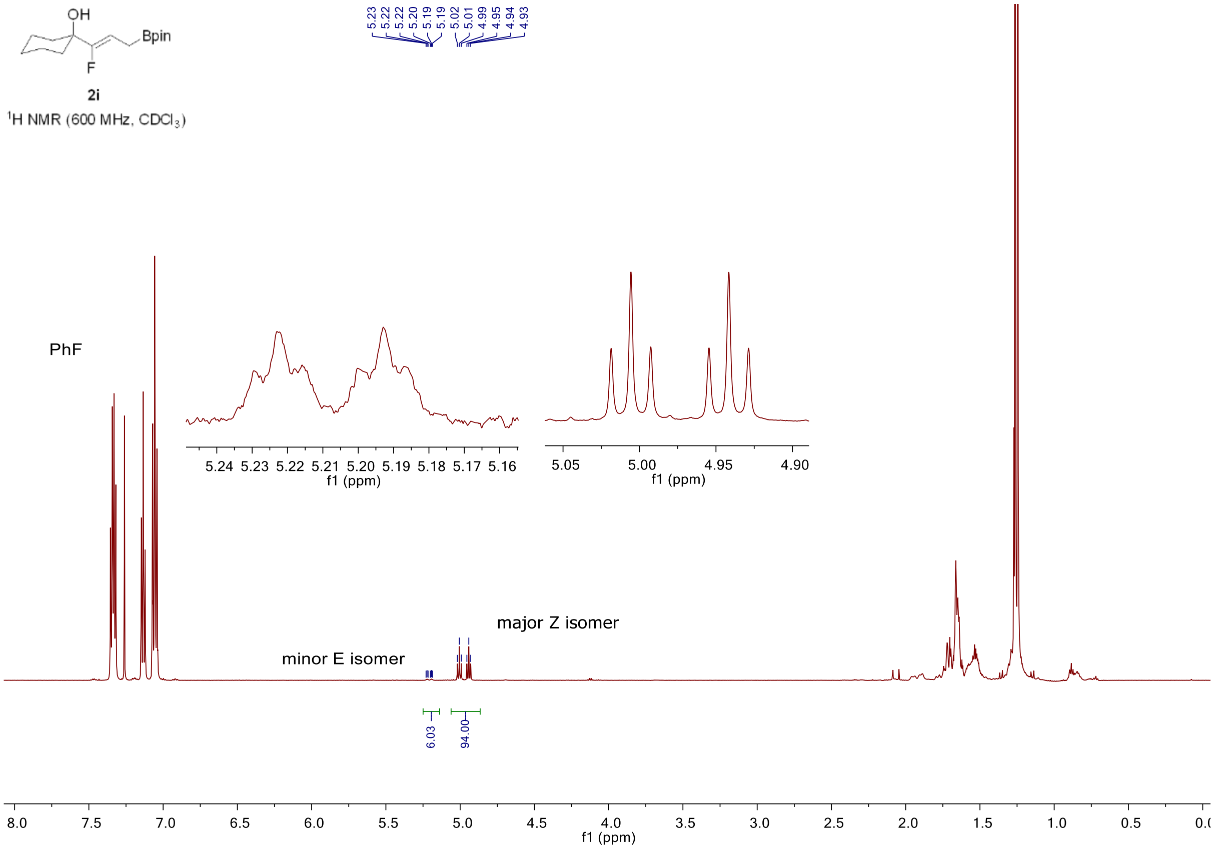

F
Bpin
HO
2f
19F NMR (565 MHz, CDCl3)
-121.28 -121.34
PhF
-103.45 -103.49
-103.40 -103.45 -103.50 -103.55 -103.60 -103.65
f1 (ppm)
-121.28 -121.34
-121.22 -121.26 -121.30 -121.34 -121.38
f1 (ppm)
major Z-isomer
minor E-isomer
1.61
426.20
90.64
-100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127
f1 (ppm)


2g
¹H NMR (600 MHz, CDCl₃)
Br
F
Bpin
5.55
5.53
5.52
5.49
5.47
5.46
THF
THF
2g + BpinX
2g + PhF
2g
1.00
5.55
5.50
5.45
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


2g
¹⁹F NMR (565 MHz, CDCl₃)
Br
F
Bpin
-104.19
-104.23
-121.70
-121.77
PhF
-104.15
-104.20
-104.25
-104.30
f1 (ppm)
-121.5
-121.6
-121.7
-121.8
-121.9
-122.0
f1 (ppm)
major Z-isomer
minor E-isomer
1.39
426.00
98.30
-92
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
f1 (ppm)

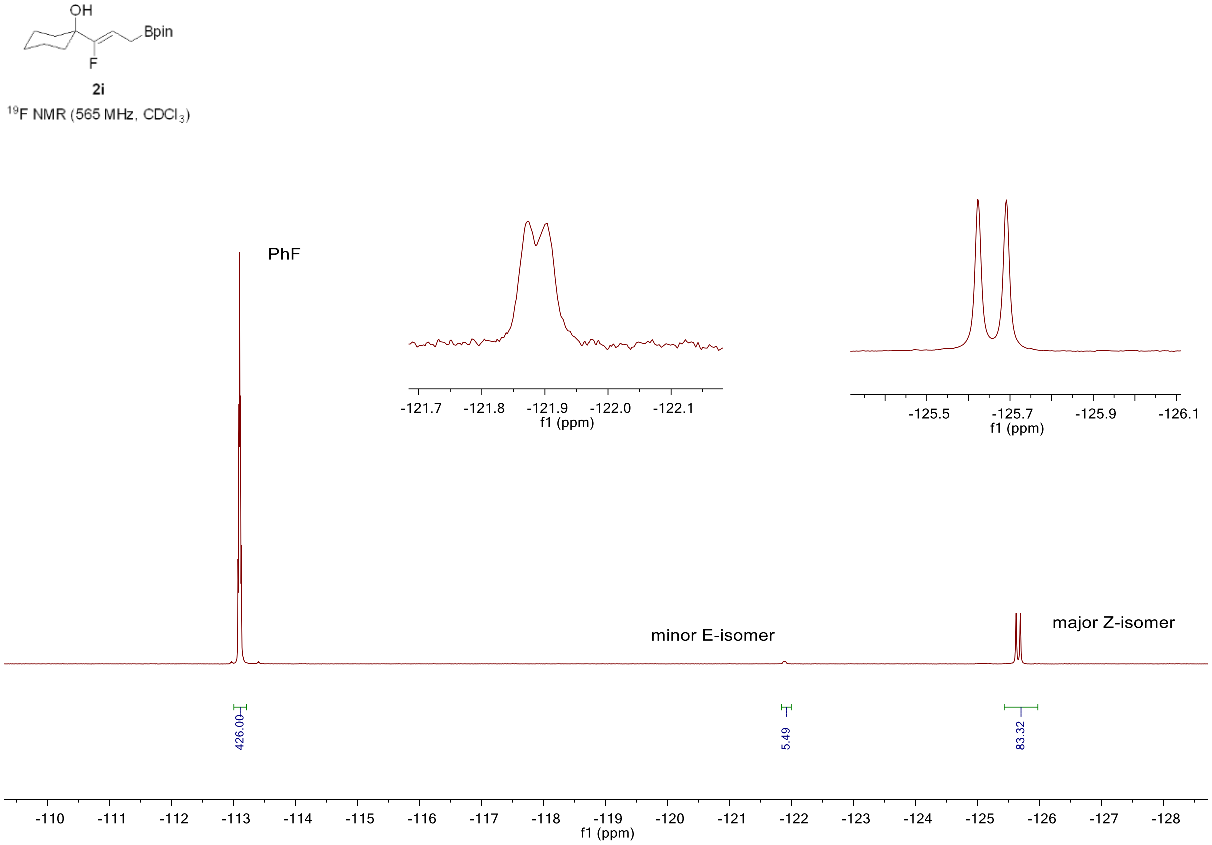

Me
F
Bpin
Me
2h
¹H NMR (600 MHz, CDCl₃)
7.35
7.34
7.33
7.31
5.12
5.11
5.09
5.08
5.06
5.05
5.03
2.35
2.34
2.30
THF
THF
2i +
BpinX
2i
2i + PhF
5.12
5.11
5.09
5.06
5.05
5.03
5.20
5.15
5.10
5.05
5.00
f1 (ppm)
2i
1.00
2.88
2.97
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
Me
Bpin
Me
2h
¹⁹F NMR (565 MHz, CDCl₃)
-104.70
-104.77
PhF
-104.69
-104.75
-94.7
-94.8
-94.9
-95.0
-95.1
f1 (ppm)
-104.4
-104.6
-104.8
-105.0
-105.2
f1 (ppm)
Z-isomer
E-isomer
1.13
95.12
426.00
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
f1 (ppm)



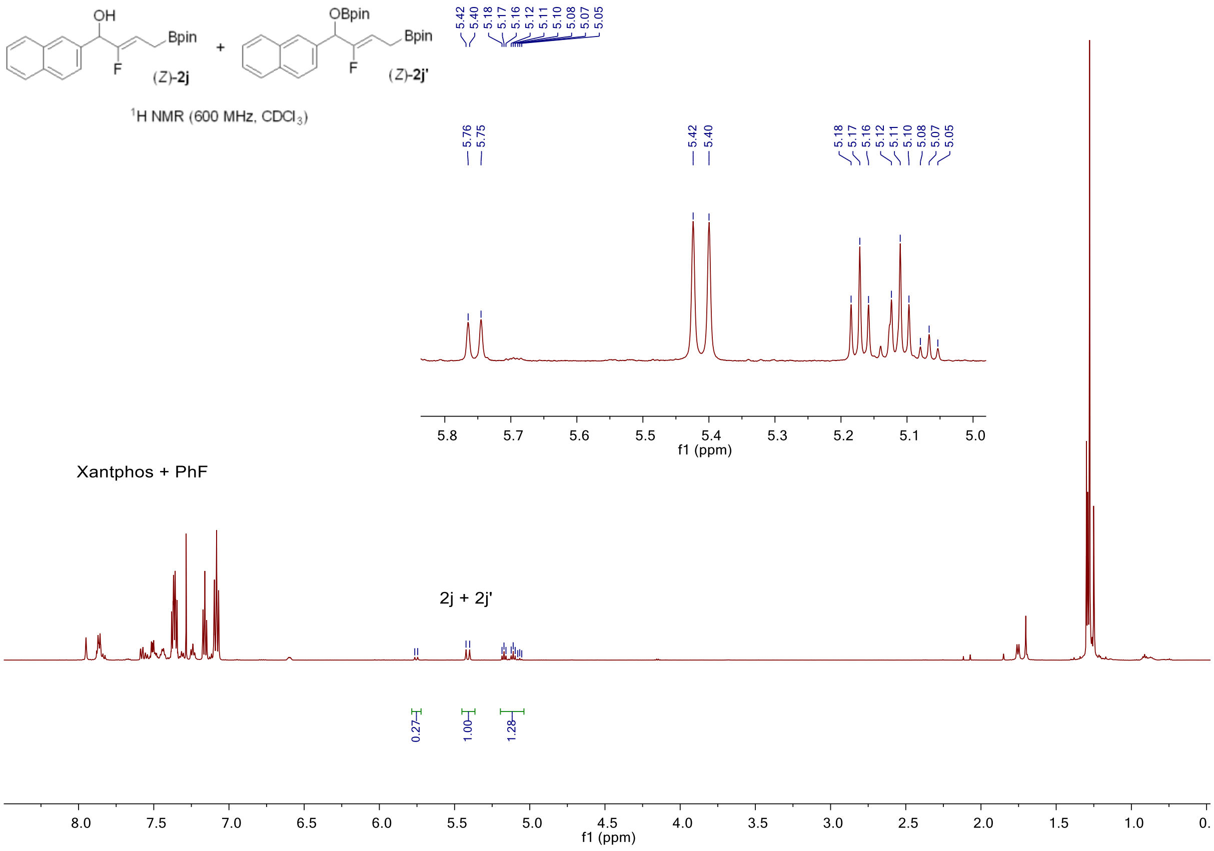
2i

^1H NMR (600 MHz, $CDCl_3$)

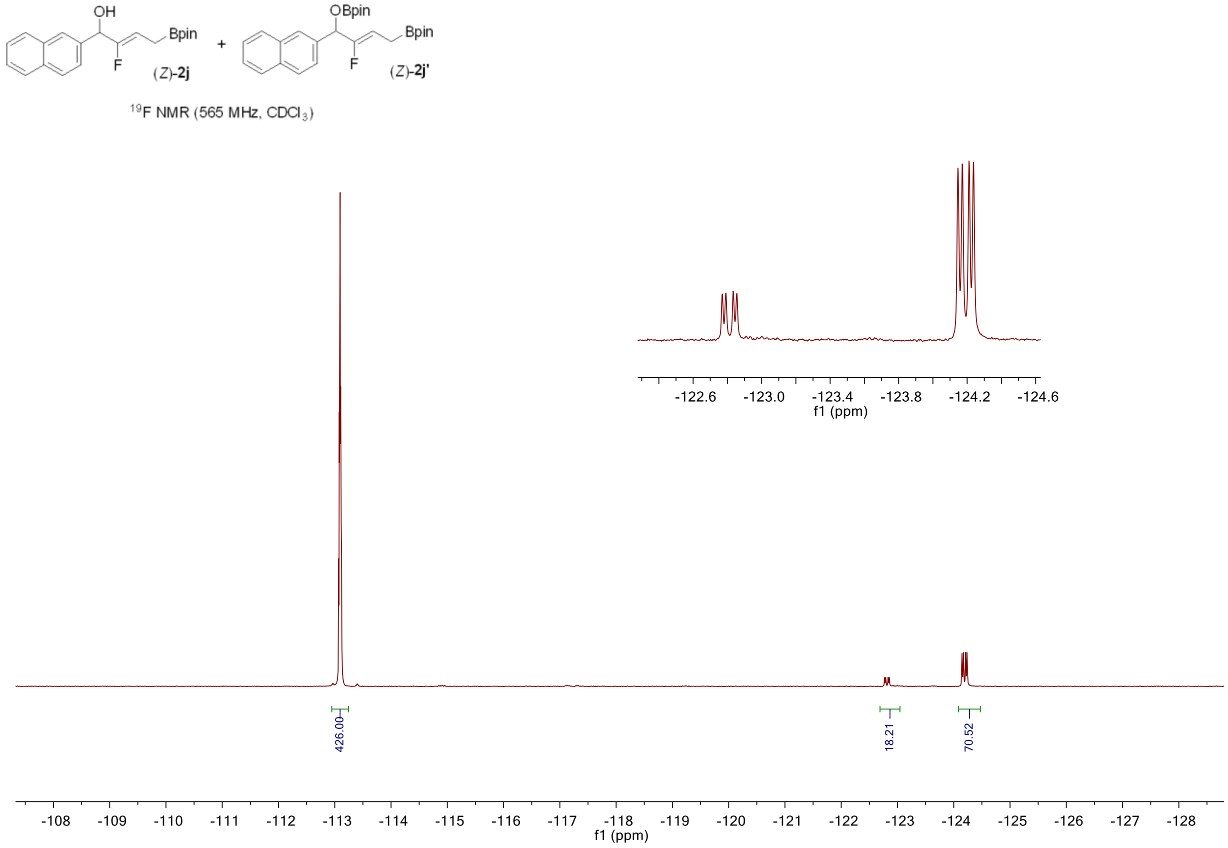


2i

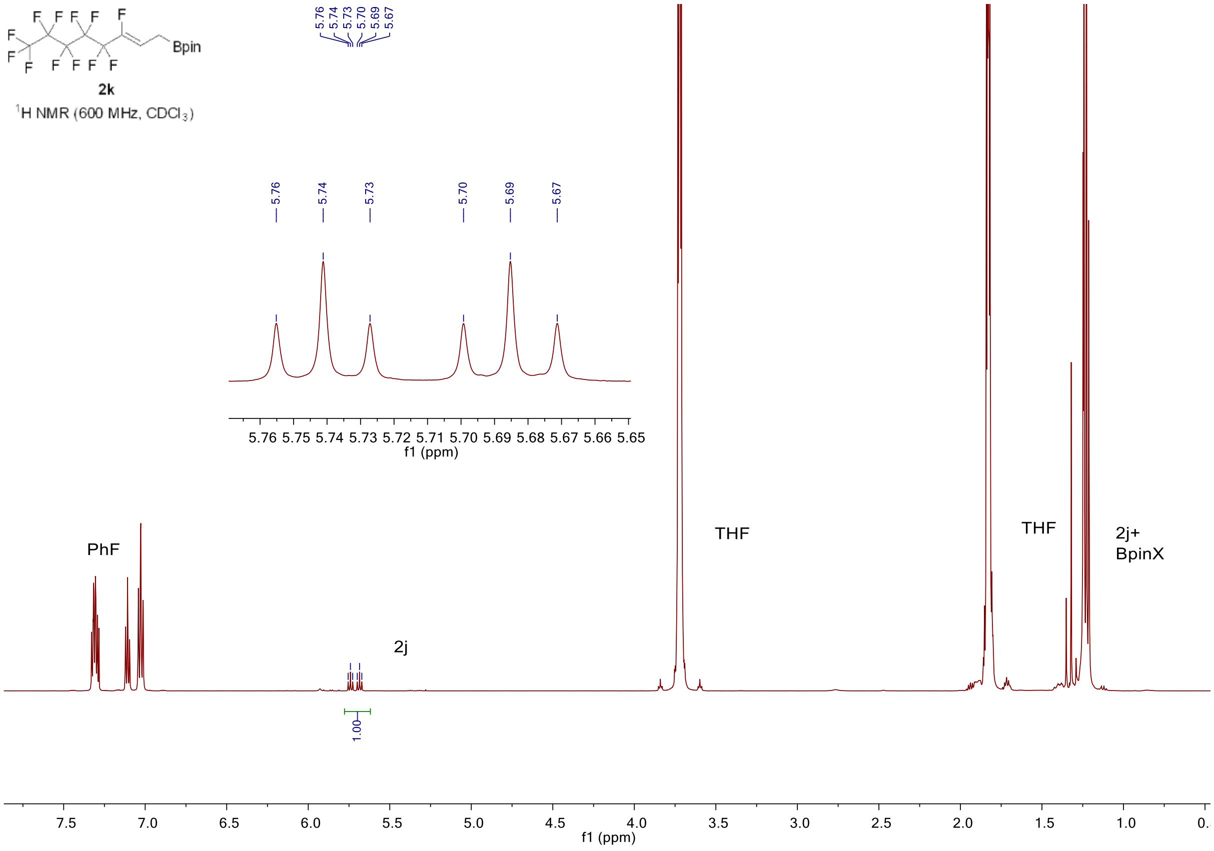
^{19}F NMR (565 MHz, $CDCl_3$)

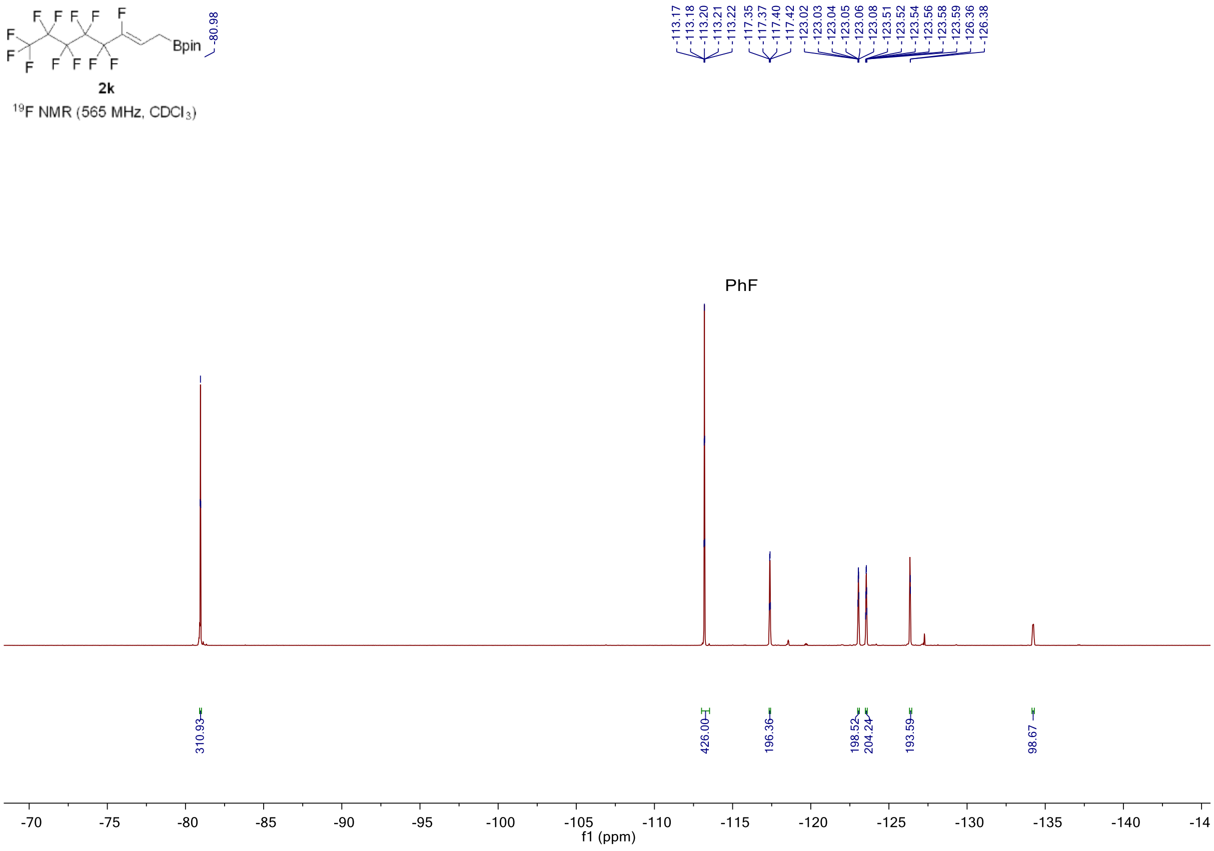

(Z)-**2j** + (Z)-**2j'**

^{1}H NMR (600 MHz, CDCl$_3$)


(Z)-**2j** + (Z)-**2j'**

^{19}F NMR (565 MHz, CDCl$_3$)


2k
^{1}H NMR (600 MHz, CDCl$_3$)
5.76
5.74
5.73
5.70
5.69
5.67
PhF
2j
THF
THF
2j+
BpinX
1.00
5.76 5.75 5.74 5.73 5.72 5.71 5.70 5.69 5.68 5.67 5.66 5.65
f1 (ppm)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.
f1 (ppm)


2k
^{19}F NMR (565 MHz, CDCl$_3$)
-80.98
-113.17
-113.18
-113.20
-113.21
-113.22
-117.35
-117.37
-117.40
-117.42
-123.02
-123.03
-123.04
-123.05
-123.06
-123.08
-123.51
-123.52
-123.54
-123.56
-123.58
-123.59
-126.36
-126.38
PhF
310.93
426.00
196.36
198.52
204.24
193.59
98.67
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -14
f1 (ppm)