Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

A metal-free strategy to construct fluoroalkyl-olefin linkages using fluoroalkanes.

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A) General Considerations:

Hexamethylborazine-CF_2Ph **1**; $[Me_6B_3N_3CF_2Ph]K(18\text{-c-}6)$[1], hexamethylborazine-$CF_2H$ **6a**; $[Me_6B_3N_3CF_2H]K(18\text{-c-}6)$[2] and Hexamethylborazine-CF_3; $[Me_6B_3N_3CF_3]K(18\text{-c-}6)$[3] were synthesized using previously described methods. THF, pentane and benzene were purified using a Glass Contour solvent purification system through percolation through a Cu catalyst, molecular sieves, and alumina and finally stored over activated molecular sieves for a minimum of 48 hours. (Trifluoromethoxy)benzene [$PhOCF_3$] and liquid difluoromethyl arenes ($ArCF_2H$) were dried over calcium hydride, distilled, and freeze-pump-thawed. Toluene was dried over sodium metal, then distilled, and freeze-pump-thawed. Methanol was dried over calcium hydride and then distilled and freeze-pump-thawed. All other reagents were used from commercial sources without further purification. Unless otherwise noted, all manipulations were performed under an inert nitrogen atmosphere.

NMR spectra were recorded on Varian Vnmrs 500, Varian MR400 and Bruker Advance Neo 500 spectrometer. ^1H, ^{13}C and ^{19}F shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F NMR spectra are referenced to (trifluoromethoxy)benzene or, in spectra lacking internal standard, on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^1H NMR spectrum. Peaks not listed in the peak assignment correspond to residual solvent. Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), double triplet (dt), triple doublet (td), quartet (q), pentet (p), septet (sp), and multiplet (m). Mass spectra were obtained on an electrospray a Micromass AutoSpec Ultima Magnetic Sector Mass Spectrometer electron ionization mass spectrometer, Shimadzu QP-2010 GCMS, Agilent 1290 Infinity II UPLC with Agilent 6230 LC/TOF for ESI or an Agilent GC 8860 with an Agilent mass spectrometer 5977B GC/MSD.

B) Experimental Procedures:

1) Procedure A: Zweifel olefination reaction of $[Me_6B_3N_3CF_2Ph]K(18\text{-c-}6)$ and vinyl-BPin derivatives.

$[Me_6B_3N_3CF_2Ph]K(18\text{-c-}6)$ (0.1 mmol), vinyl pinacol boronic ester (0.1 mmol) and $PhOCF_3$ (0.2 mmol) were dissolved in 1.6 mL of THF in a 20 mL vial. The reaction mixture was heated for 1 h at 50 °C and then cooled to -78 °C. Next, iodine (0.2 mmol, 0.2 mL solution in THF) was added at –78 °C and stirred for 30 min. Next, NaOMe (0.2 mmol, 0.2 mL solution in MeOH) was added to this mixture at –78 °C and stirred for 30 min. Finally, the contents were allowed to warm up at room temperature and mix for 2 h at 25 °C before the yield was assessed by ^{19}F NMR spectroscopy. The product was purified by column chromatography using hexane-dichloromethane as eluent.

2) Procedure B: One-pot Zweifel olefination reaction.

Vinyl-BPin derivatives (0.26 mmol) and difluoromethyl arenes ($ArCF_2H$) (0.26 mmol) were dissolved in 2.0 mL THF in a 20 mL vial and cooled to -78 °C. Then, $KN(^iPr)_2$ (0.39 mmol) was added as a solid to the mixture at -78 °C. The mixture was rapidly stirred at -78 °C for 10 minutes and allowed to warm to 25 °C. The

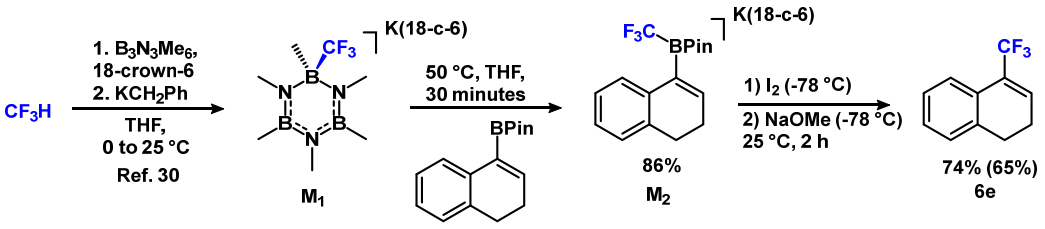
mixture was stirred at 25 °C for 20 minutes and 18-crown-6 (0.26 mmol) was added to this mixture. The mixture was again cooled to -78 °C. Iodine (0.52 mmol, 0.5 mL solution in THF) was added at the same temperature and stirred for 30 min. Next, NaOMe (0.52 mmol, 0.5 mL solution in MeOH) was added to this mixture at –78 °C and stirred for 30 min. The contents were allowed to warm to room temperature and mix for 2 h at 25 °C before the yield was assessed by ^{19}F NMR spectroscopy ($PhOCF_3$ (0.52 mmol) was added as internal standard). The product was purified by column chromatography using hexane-dichloromethane as eluent.

3) Procedure C: Zweifel olefination reaction of $[Me_6B_3N_3CF_2H]K(18\text{-}c\text{-}6)$ and vinyl-BPin derivatives.

$[Me_6B_3N_3CF_2H]K(18\text{-}c\text{-}6)$ (0.2 mmol), vinyl pinacol boronic ester (0.2 mmol) and $PhOCF_3$ (0.4 mmol) were dissolved in 3.0 mL of THF in a screw cap tube. The reaction mixture was heated for 20 h at 80 °C and then cooled to -78 °C. Next, iodine (0.4 mmol, 0.4 mL solution in THF) was added at –78 °C and stirred for 30 min. Next, NaOMe (0.4 mmol, 0.4 mL solution in MeOH) was added to this mixture at –78 °C and stirred for 30 min. Finally, the contents were allowed to warm up at room temperature and mix for 2 h at 25 °C before the yield was assessed by ^{19}F NMR spectroscopy. The product was purified by column chromatography using hexane as eluent.

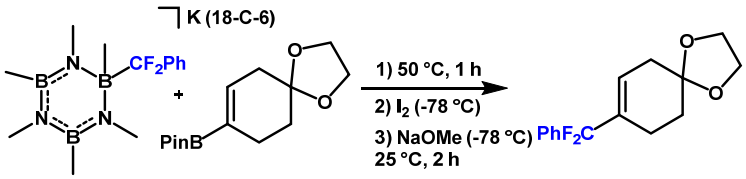
4) Procedure D: Zweifel olefination reaction of $[Me_6B_3N_3CF_3]K(18\text{-}c\text{-}6)$ and vinyl-BPin derivatives.

$[Me_6B_3N_3CF_3]K(18\text{-}c\text{-}6)$ (0.2 mmol), vinyl pinacol boronic ester (0.2 mmol) and $PhOCF_3$ (0.4 mmol) were dissolved in 3.0 mL of THF in a screw cap tube. The reaction mixture was heated for 30 minutes at 50 °C and then cooled to -78 °C. Next, iodine (0.4 mmol, 0.4 mL solution in THF) was added at –78 °C and stirred for 30 min. Next, NaOMe (0.4 mmol, 0.4 mL solution in MeOH) was added to this mixture at –78 °C and stirred for 30 min. Finally, the contents were allowed to warm up at room temperature and mix for 2 h at 25 °C before the yield was assessed by ^{19}F NMR spectroscopy. The product was purified by column chromatography using hexane as eluent.



C) Optimization tables:

Table S1. Optimization for the Zweifel olefination reaction.

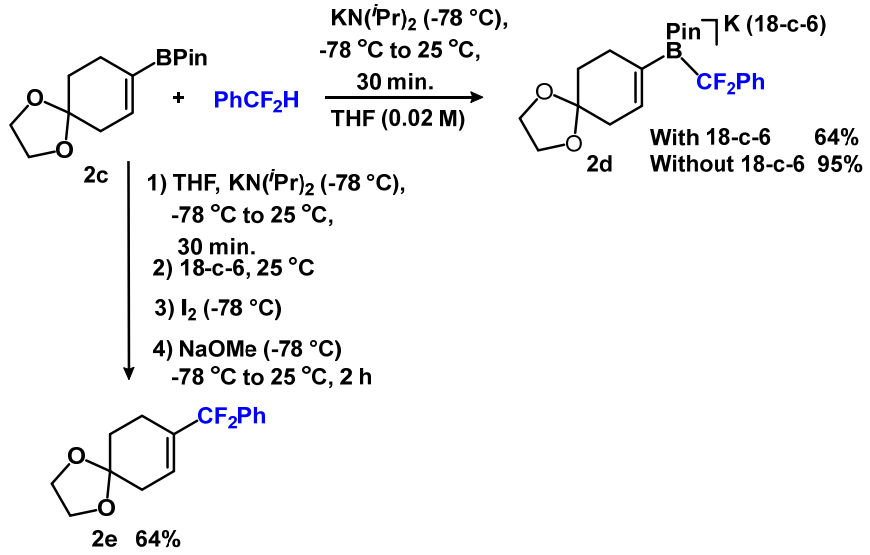


Entry	Base (equiv.)	I_2 (equiv.)	Yield
1[a]	NaOMe (1)	1	26%

2	NaOMe (1)	1	40%
3	NaOMe (1)	2	55%
4	NaOMe (2)	2	**94%**
5	NaOMe (4)	2	75%
6	NaOMe (2)	1.5	59%
7	NaOMe (2)	4	53%
8	KOMe (1)	1	34%
9	Na_2CO_3 (1)	1	22%

BPin derivatives (0.02 mmol), $[Me_6B_3N_3CF_2Ph]K(18\text{-c-}6)$ (0.02 mmol), I_2 (x mmol), NaOMe (x mmol). ^{19}F NMR yields are reported ($PhOCF_3$ used as internal standard). [a] I_2 and NaOMe addition at room temperature.

Table S2. Optimization of the one-pot Zweifel olefination reaction.

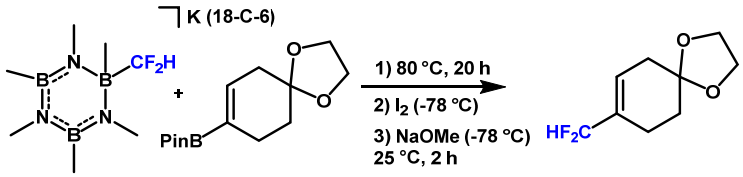


Entry	Base (equiv.)	Temperature	Adduct (%)
1	$KN(^iPr)_2$ (1.0)	-78°C	60% (47%)
2	$PhCH_2K$ (1.0)	-78°C	25%
3	$KN(^iPr)_2$ (1.5 equiv., as solution)	-78°C	25%
4	$KN(^iPr)_2$ (1.5 equiv., addition sequence reverse)	-78°C	<3%

5	$PhCH_2K$ (1.5 equiv., addition sequence reverse)	-78°C	27%
6	$KN(^iPr)_2$ (1.5)	0°C	32%
7	$PhCH_2K$ (1.5)	0°C	10%
8	LiHMDS (1.5)	-78°C	0%
9	^{n}BuLi (1.5)	-78°C	0%
10	$KN(^iPr)_2$ (1.5)	-78°C	64% (51%)
11	$KN(^iPr)_2$ (1.5), without 18-c-6	-78°C	95% (27%)
12.	$KN(^iPr)_2$ (1.5), 1.0 equiv. 18-c-6 added after deprotonation	-78 °C	95% (**64%**)
13.	$KN(^iPr)_2$ (1.5), 1.5 equiv. 18-c-6 added after deprotonation	-78 °C	95% (62%)

BPin derivatives (0.06 mmol), $KN(^iPr)_2$ (0.09 mmol), 18-c-6 (0.06 mmol) I_2 (0.12 mmol), NaOMe (0.12 mmol). ^{19}F NMR yields are reported ($PhOCF_3$ used as internal standard). Final step yields are in parentheses, and it was performed following one-pot strategy.

Table S3. Optimization of the vinyldifluoromethane molecules.

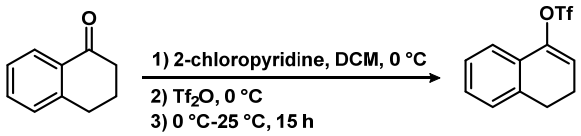


Entry	**Base (equiv.)**	**I_2 (equiv.), (temperature)**	**Yield**
1	NaOMe (1), RT	1.0, RT	52%
2	NaOMe (2.0), RT	1.5, RT	59%
3	NaOMe (2), -78 °C	1.5, -78°C	63-65%
4	NaOMe (2), -78 °C	2.0, -78 °C	**74%**
5	NaOMe (2), RT	2.0, -78 °C	49%
6	NaOMe (2), -78 °C	4.0, -78 °C	39%

BPin derivatives (0.02 mmol), $[Me_6B_3N_3CF_2H]K(18\text{-c-}6)$ (0.02 mmol), I_2 (x mmol), NaOMe (x mmol). ^{19}F NMR yields are reported ($PhOCF_3$ used as internal standard).

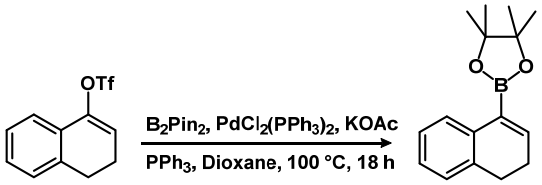
D) Procedure for the synthesis of vinyl-BPin derivatives: These compounds are prepared by modifying the known literature.[4, 5]

1) Synthesis of 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.



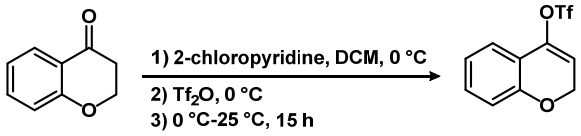
To a solution of 1-tetralone (3.4 mmol, 455 µL) in anhydrous dichloromethane (12 mL) was added 2-chloropyridine (3.74 mmol, 354 µL) at 0 °C under inert atmosphere. After stirring at 0 °C for 10 min trifluoromethanesulfonic anhydride (4.08 mmol, 686 µL) was added dropwise. The resulting solution was warmed to room temperature for 18 h. After the completion of the reaction (detected by TLC), the solution was concentrated under vacuum and the resulting vinyl triflates were purified by column chromatography (EtOAc/hexanes). Isolated as viscous liquid (751 mg, 79% isolated yield). Spectroscopic data are consistent with literature.[5] **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.32-7.29 (m, 1H), 7.23-7.21 (m, 2H), 7.16-7.13 (m, 1H), 5.98 (t, *J* = 4.8 Hz, 1H), 2.83 (t, *J* = 8.3 Hz, 2H), 2.50-2.45 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 146.37, 136.21, 129.18, 128.67, 127.75, 126.94, 121.14, 118.61 (q, $J_{C\text{-}F}$ = 370 Hz), 117.75, 26.86, 22.33. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -73.71 (s, 3F).

2) Synthesis of 2-(3,4-dihydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



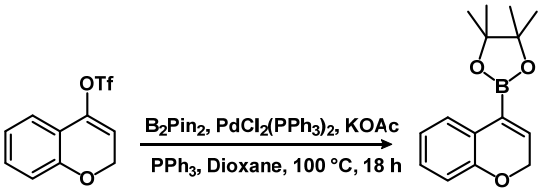
3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (2.66 mmol, 740 mg), bis(pinacolato)diboron (3.19 mmol, 810 mg) and KOAc (3.99 mmol, 392 mg) were taken into a two-necked flask under nitrogen. Dioxane (12 mL) was added to the mixture. Then, $Pd(PPh_3)_2Cl_2$ (5.0 mol%, 0.133 mmol, 94 mg) and PPh_3 (10 mol%, 0.265 mmol, 70 mg) were added to the reaction mixture and heated at 100°C for 18 hours. After that 20 mL water and 20 mL EtOAc were added to the reaction mixture. The organics were extracted with EtOAc and dried over Na_2SO_4. The mixture was filtered and concentrate in vacuo. The crude product was purified by column chromatography (CH_2Cl_2/hexane) to afford the product as white solid (421 mg, 62% isolated yield). Spectroscopic data are consistent with the known literature.[4] **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.17 (td, *J* = 7.4, 1.9 Hz, 1H), 7.11-7.05 (m, 2H), 6.92 (t, *J* = 4.6 Hz, 1H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.31-2.27 (m, 2H), 132 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 144.80, 135.51, 135.35, 127.42, 126.92, 126.58, 126.51, 83.39, 27.69, 24.87, 24.10. **^{11}B NMR** (128 MHz, $CDCl_3$, ppm) δ 30.23 (bs, 1B).

3) Synthesis of 2H-chromen-4-yl trifluoromethanesulfonate.



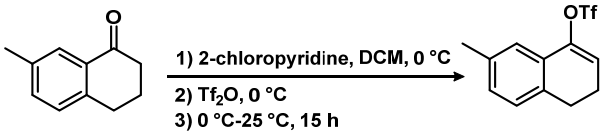
To a solution of 4-chromanone (3.37 mmol, 443 µL) in anhydrous dichloromethane (12 mL) was added 2-chloropyridine (3.71 mmol, 352 µL) at 0 °C under inert atmosphere. After stirring at 0 °C for 10 min trifluoromethanesulfonic anhydride (4.04 mmol, 681 µL) was added dropwise. The resulting solution was warmed to room temperature for overnight. After the completion of the reaction (detected by TLC), the solution was concentrated under vacuum and the resulting vinyl triflates were purified by column chromatography (EtOAc/hexane). Isolated as viscous liquid (670 mg, 70% isolated yield). Spectroscopic data are consistent with the known literature.[6] **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.24-7.21 (m, 2H), 6.95 (td, *J* = 7.6, 1.6 Hz, 1H), 6.82 (dd, *J* = 8.8, 1.4 Hz, 1H), 5.74 (t, *J* = 3.9 Hz, 1H), 4.96 (d, *J* = 3.9 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 155.00, 143.15, 131.55, 121.83, 121.71, 118.54 (q, J_{C-F} = 303.75 Hz), 117.35, 116.29, 110.02, 65.08. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -73.47 (s, 3F).

4) Synthesis of 2-(2H-chromen-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



2H-chromen-4-yl trifluoromethanesulfonate (2.32 mmol, 650 mg), bis(pinacolato)diboron (2.78 mmol, 707 mg) and KOAc (3.48 mmol, 342 mg) were taken into a two-necked flask under nitrogen. Dioxane (12 mL) was added to the mixture. Then, $Pd(PPh_3)_2Cl_2$ (5.0 mol%, 0.116 mmol, 82 mg) and PPh_3 (10 mol%, 0.232 mmol, 61 mg) were added to the reaction mixture and heated at 100°C for 18 hours. After that 20 mL water and 20 mL EtOAc were added to the reaction mixture. The organics were extracted with EtOAc and dried over Na_2SO_4. The mixture was filtered and concentrate in vacuo. The crude product was purified by column chromatography (CH_2Cl_2/hexane) to afford the product as white solid (398 mg, 66% isolated yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.66 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.07 (td, *J* = 7.8, 1.7 Hz, 1H), 6.87 (td, *J* = 7.5, 1.3 Hz, 1H), 6.75 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.55 (t, *J* = 3.8 Hz, 1H), 4.73 (d, *J* = 3.8 Hz, 2H), 1.31 (s, 12 H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 153.47, 136.59, 128.79, 127.67, 123.82, 121.45, 115.83, 83.75, 65.17, 24.85. **^{11}B NMR** (128 MHz, $CDCl_3$, ppm) δ 29.56 (bs, 1B). **ESI-MS**: calcd for $C_{15}H_{18}BO_3$ $(M-H)^-$: 257.1351, found: 257.1363.

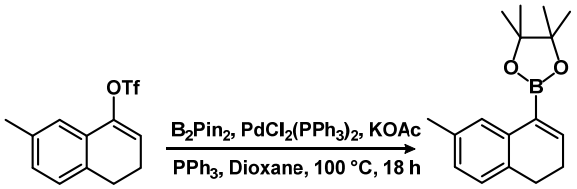
5) Synthesis of 7-methyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.



To a solution of 7-methyl-3,4-dihydronaphthalen-1(2H)-one (3.74 mmol, 546 µL) in anhydrous dichloromethane (15 mL) was added 2-chloropyridine (4.11 mmol, 390 µL) at 0 °C under inert atmosphere. After stirring at 0 °C for 10 min trifluoromethanesulfonic anhydride (4.49 mmol, 756 µL) was added dropwise. The resulting solution was warmed to room temperature for overnight. After the completion of the reaction (detected by TLC), the solution was concentrated under vacuum and the resulting vinyl triflates were purified by column chromatography (EtOAc/hexane). Isolated as viscous liquid (810 mg, 74% isolated yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.13 (s, 1H), 7.06-7.02 (m, 2H), 5.97 (t, *J* = 4.8 Hz, 1H), 2.80 (t, *J* = 8.3 Hz, 2H), 2.48-2.44 (m, 2H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm)

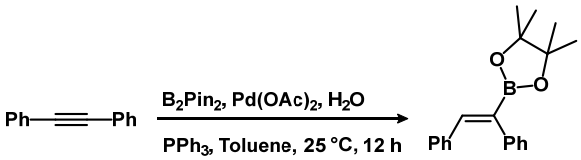
δ 146.54, 136.60, 133.22, 129.76, 128.50, 127.64, 121.89, 118.63 (q, $J_{C\text{-}F}$ = 268.8 Hz), 117.62, 26.46, 22.51, 21.25. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -73.65 (s, 3F).

6) Synthesis of 4,4,5,5-tetramethyl-2-(7-methyl-3,4-dihydronaphthalen-1-yl)-1,3,2-dioxaborolane.



7-methyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (2.74 mmol, 800 mg), bis(pinacolato)diboron (3.28 mmol, 834 mg) and KOAc (4.10 mmol, 403 mg) were taken into a two-necked flask under nitrogen. Dioxane (15 mL) was added to the mixture. Then, $Pd(PPh_3)_2Cl_2$ (5.0 mol%, 0.137 mmol, 96 mg) and PPh_3 (10 mol%, 0.274 mmol, 72 mg) were added to the reaction mixture and heated at 100°C for 18 hours. After that 20 mL water and 20 mL EtOAc were added to the reaction mixture. The organics were extracted with EtOAc and dried over Na_2SO_4. The mixture was filtered and concentrate in vacuo. The crude product was purified by column chromatography (CH_2Cl_2/hexane) to afford the product as white solid (437 mg, 59% isolated yield). Spectroscopic data are consistent with the known literature.[7] **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.50 (s, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.91-6.88 (m, 2H), 2.66 (t, *J* = 8.05 Hz, 2H), 2.30 (s, 3H), 2.28-2.24 (m, 2H), 1.32 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 144.73, 135.75, 135.17, 132.47, 127.66, 127.25, 127.14, 83.36, 27.31, 24.85, 24.29, 21.43. **^{11}B NMR** (128 MHz, $CDCl_3$, ppm) δ 29.97 (bs, 1B).

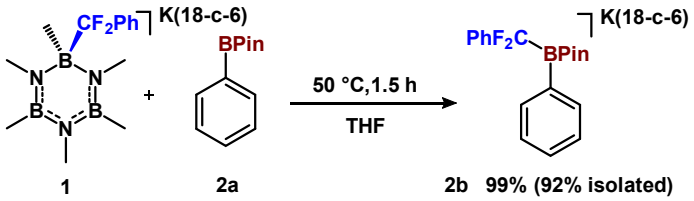
7) Synthesis of (2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



An oven dried, two-neck round bottom flask equipped with a magnetic stir bar was charged with diphenylacetylene (1.4 mmol, 250 mg), B_2pin_2 (1.68 mmol, 428 mg), PPh_3 (10 mol %, 0.14 mmol, 37 mg), H_2O (14.02 mmol, 28 mmol, 506 µL) and $Pd(OAc)_2$ (5 mol %, 0.07 mmol, 15.8 mg). The reaction mixture was then dissolved in toluene solvent (4.5 mL) and stirred at room temperature for 12 h. Crude mixture was then filtered through a short column with 230-400 mesh silica bed using Et_2O, concentrated and purified by column chromatography (CH_2Cl_2/hexane) to afford the product as white solid (272 mg, 63% isolated yield). Spectroscopic data are consistent with the known literature.[8] **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.35 (s, 1H), 7.27-7.24 (m, 2H), 7.21-7.17 (m, 1H), 7.16-7.14 (m, 2H), 7.11-7.09 (m, 3H), 7.05-7.03 (m, 2H), 1.29 (s, 12 H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 143.17, 140.43, 136.99, 129.96, 128.86, 128.24, 127.85, 127.58, 126.27, 83.79, 24.80. **^{11}B NMR** (128 MHz, $CDCl_3$, ppm) δ 29.76 (bs, 1B).

E) Procedure for the synthesis of [RBPin-CF_2Ph]$^-$ adducts:

A) Synthesis of 2b:



In a 20 mL vial, [K(18-c-6)($B_3N_3Me_6$-CF_2Ph)] (**1**) (45 mg, 0.076 mmol) and Ph-BPin (**2a**) (15.5 mg, 0.076 mmol) were mixed with 3 mL THF and heated for 1.5 h at 50 °C. After that the conversion was assessed by ^{19}F NMR ($PhOCF_3$ was added as internal standard). Next, the THF was removed, and the residue was washed with pentane to afford the title compound **2b** as an off-white solid (92%, 44 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 2H), 6.93 (tt, *J* = 7.2, 2.1 Hz, 1H), 3.41 (s, 24H), 0.85 (s, 6H), 0.76 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 143.27 (t, $J_{C\text{-}F}$ = 21.3 Hz), 133.10, 126.64 (t, $J_{C\text{-}F}$ = 7.5 Hz), 126.49, 126.41, 125.24, 123.14, 78.30, 69.75, 26.86, 26.23. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -104.21 (s, 2F). **^{11}B NMR** (128 MHz, $CDCl_3$, ppm) δ 3.95 (bs, 1B). **ESI-MS**: calcd for $C_{19}H_{22}BF_2O_2$ (M-K(18-c-6)): 331.1681, found: 331.1851.

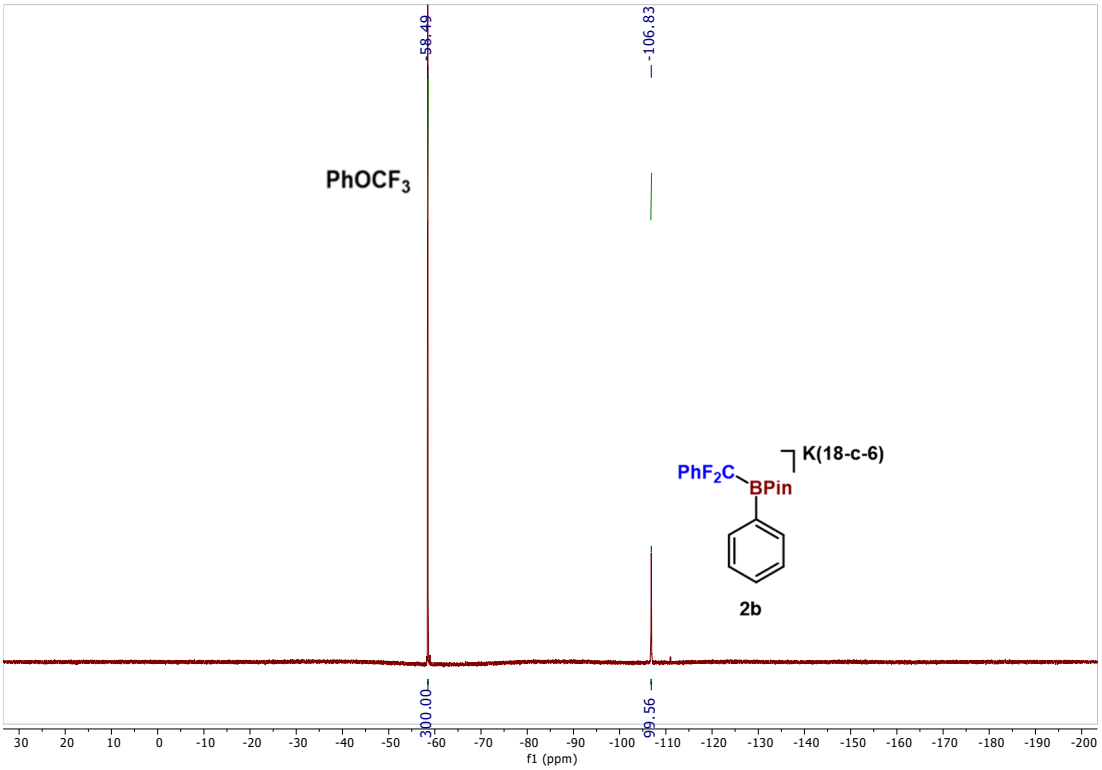


Fig. S1. ^{19}F NMR spectrum (THF-H_8, 25 °C) of reaction mixture of **2b**.

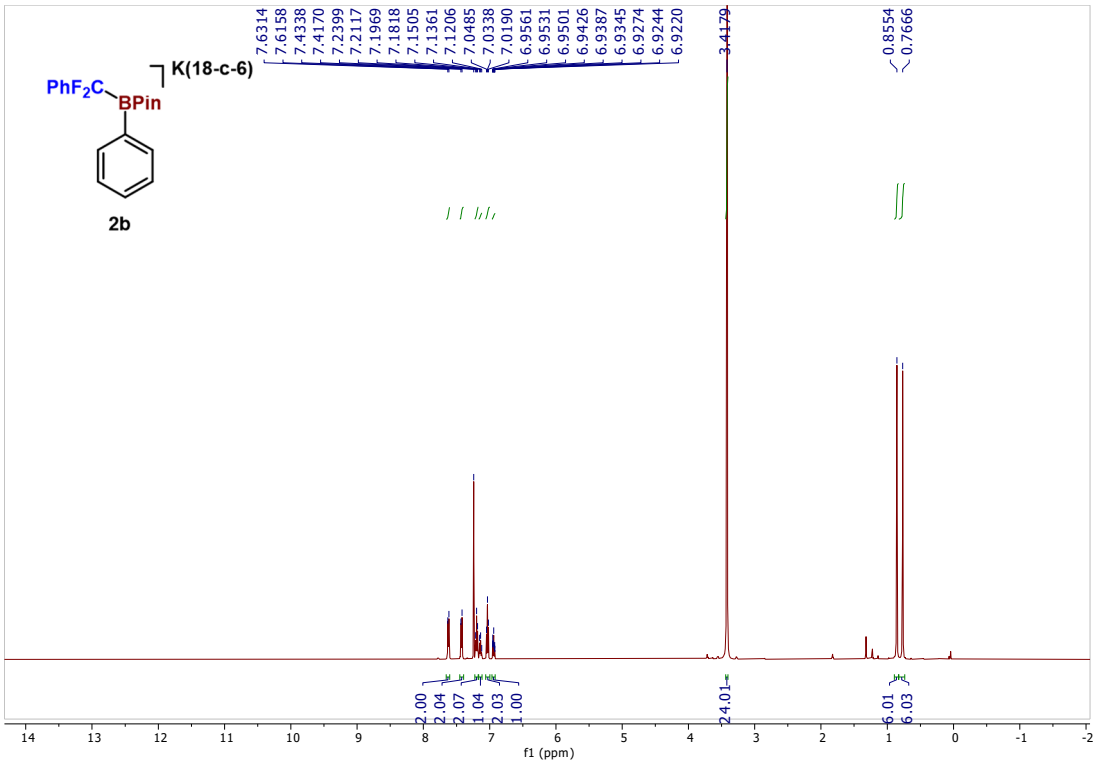


Fig. S2. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **2b**.

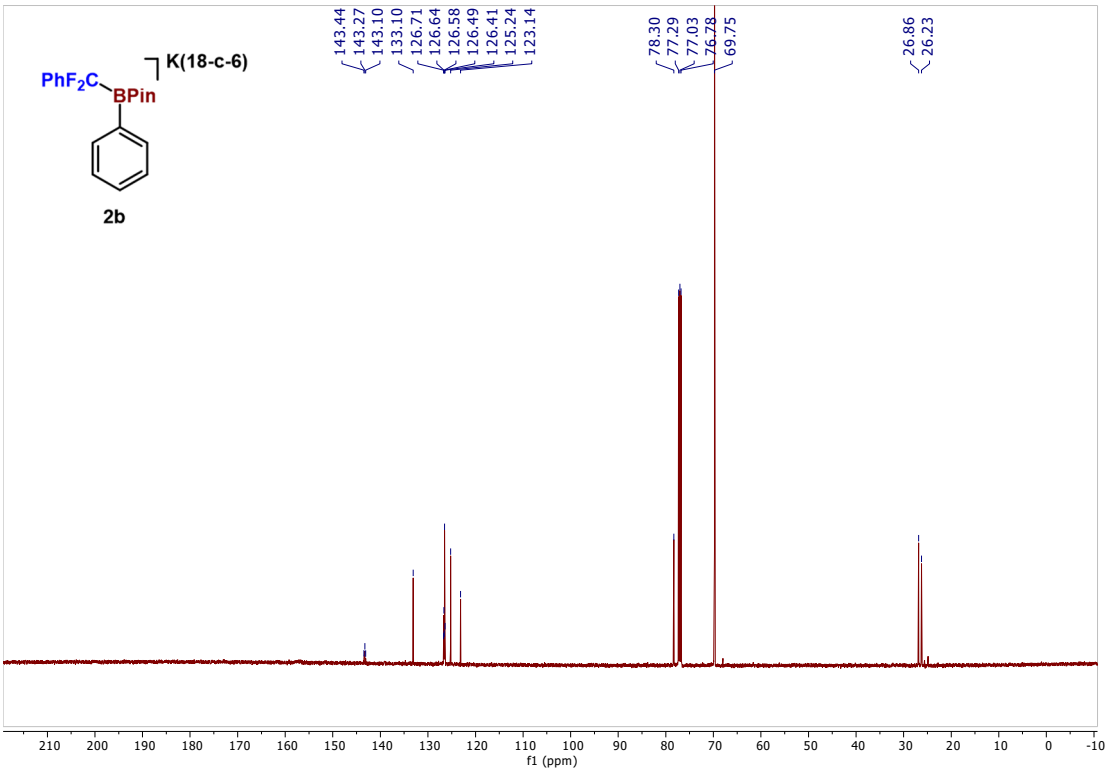


Fig. S3. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **2b**.

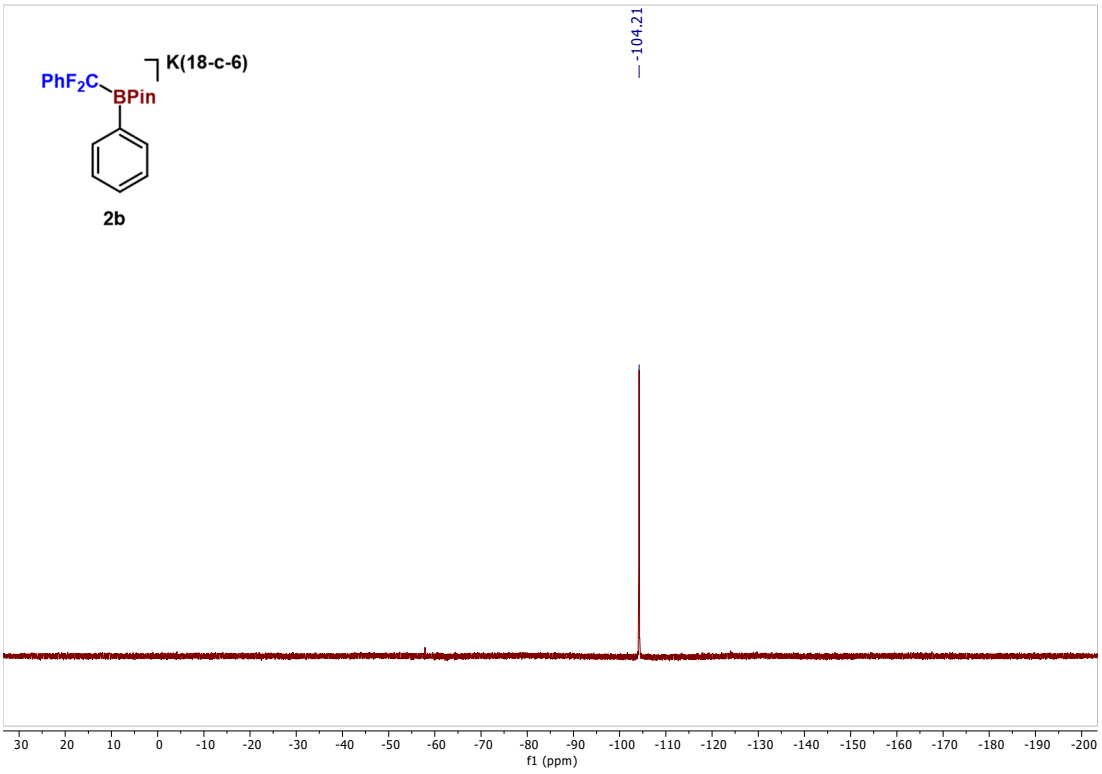


Fig. S4. ^{19}F NMR spectrum ($CDCl_3$, 25 °C) of **2b**.

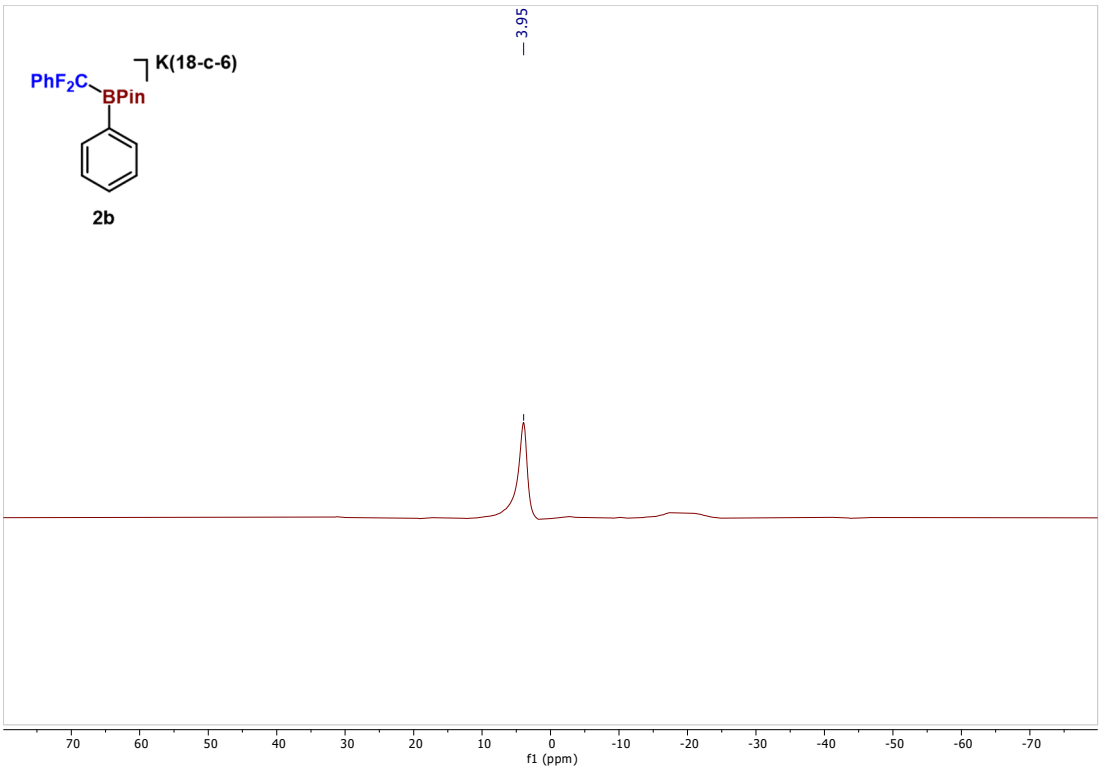
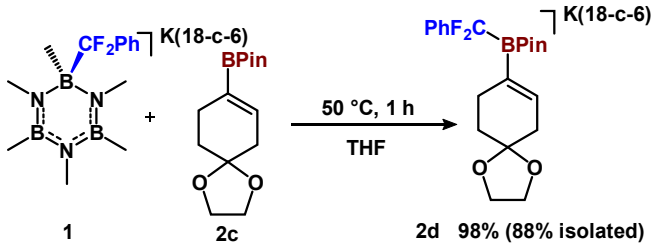


Fig. S5. ^{11}B NMR spectrum ($CDCl_3$, 25 °C) of **2b**.

B) Synthesis of 2d:



In a 20 mL vial, [K(18-c-6)($B_3N_3Me_6$-CF_2Ph)] (**1**) (45 mg, 0.076 mmol) and (1,4-Dioxa-spiro[4,5]dec-7-en-8-boronic acid, pinacol ester) (**2c**) (20.2 mg, 0.076 mmol) were mixed with 3 mL THF and heated for 1.0 h at 50 °C. After that the conversion was assessed by ^{19}F NMR ($PhOCF_3$ was added as internal standard). Next, the THF was removed, and the residue was washed with pentane to afford the title compound **2d** as an off-white solid (88%, 46 mg). **^{1}H NMR** (500 MHz, THF-d_8, ppm) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 5.17-5.16 (m, 1H), 3.76 (s, 4H), 3.63 (s, 24H), 1.99-1.96 (m, 4H), 1.36 (t, *J* = 6.3 Hz, 2H), 1.07 (s, 6H), 0.95 (s, 6H). **^{13}C NMR** (125 MHz, THF-d_8, ppm) δ 144.57 (t, J_{C-F} = 21.3 Hz), 126.29 (t, J_{C-F} = 7.5 Hz), 125.53, 125.18, 119.10, 109.67, 77.50, 69.68, 63.49, 37.05, 32.40, 27.46, 26.48, 26.30. **^{19}F NMR** (376 MHz, THF-d_8, ppm) δ -107.25 (s, 2F). **^{11}B NMR** (128 MHz, THF-d_8, ppm) δ 3.61 (bs, 1B). **ESI-MS**: calcd for $C_{21}H_{28}BF_2O_4$ (M-K(18-c-6)): 393.2049, found: 393.2109.

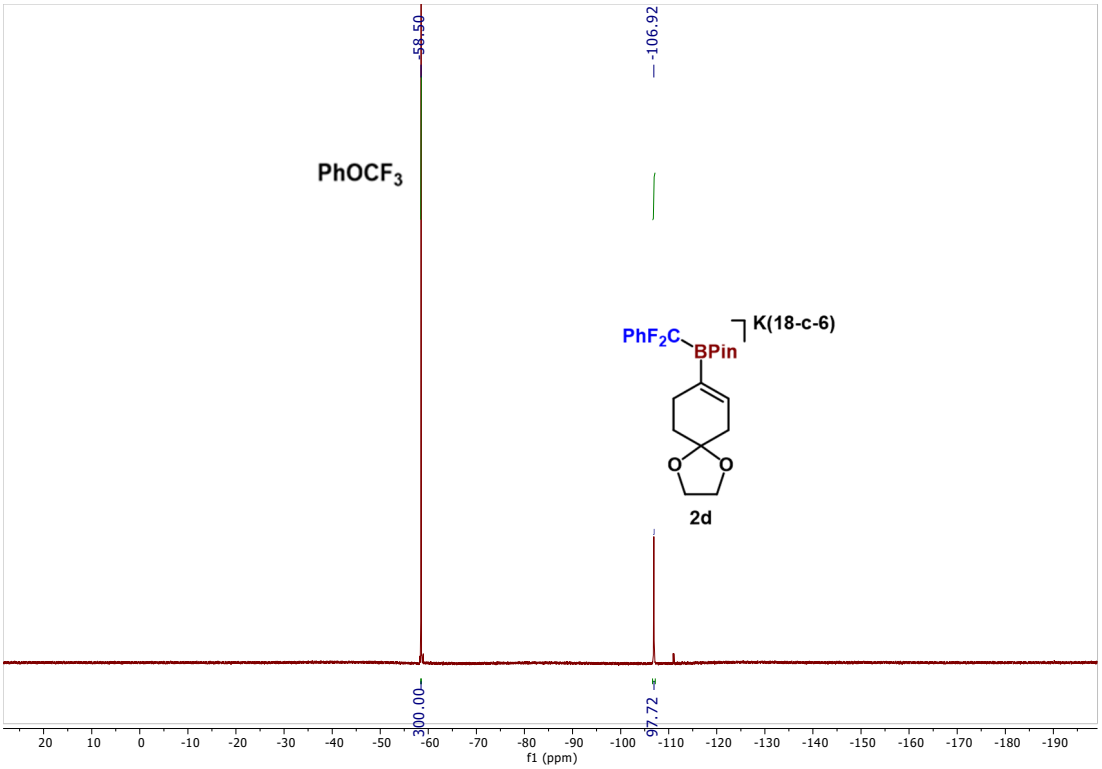


Fig. S6. ^{19}F NMR spectrum (THF-H_8, 25 °C) of reaction mixture of **2d**.

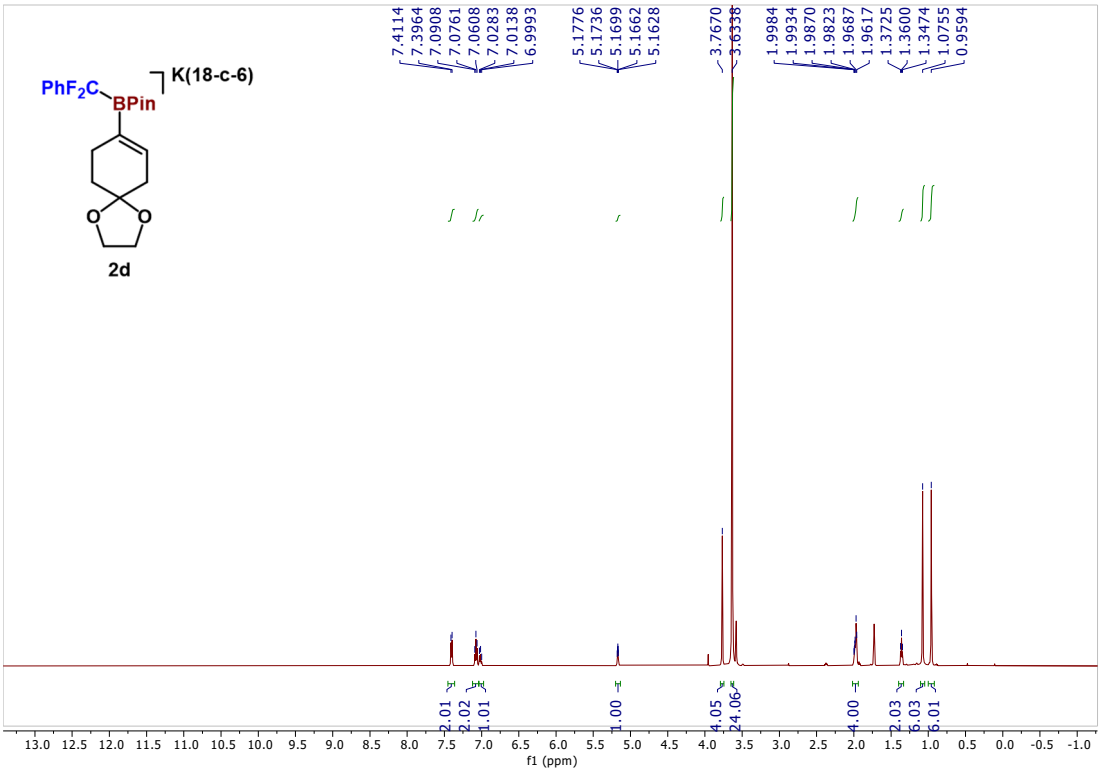


Fig. S7. ^{1}H NMR spectrum (THF-d_8, 25 °C) of **2d**.

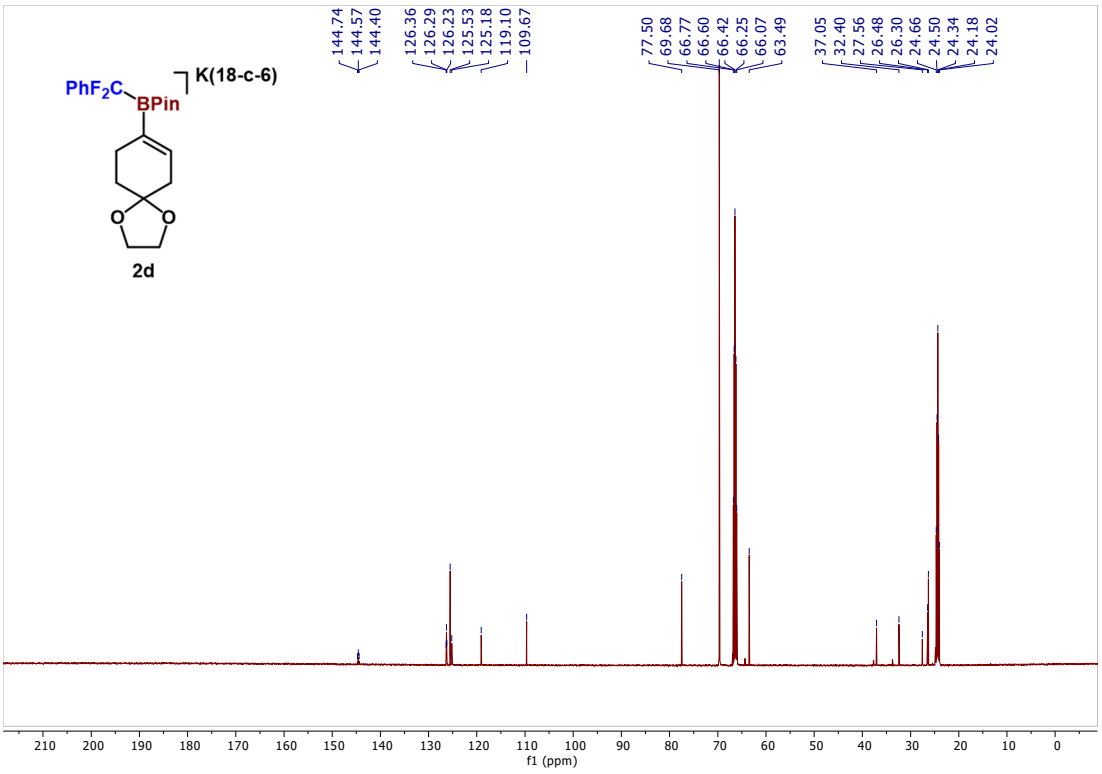


Fig. S8. ^{13}C NMR spectrum (THF-d_8, 25 °C) of **2d**.

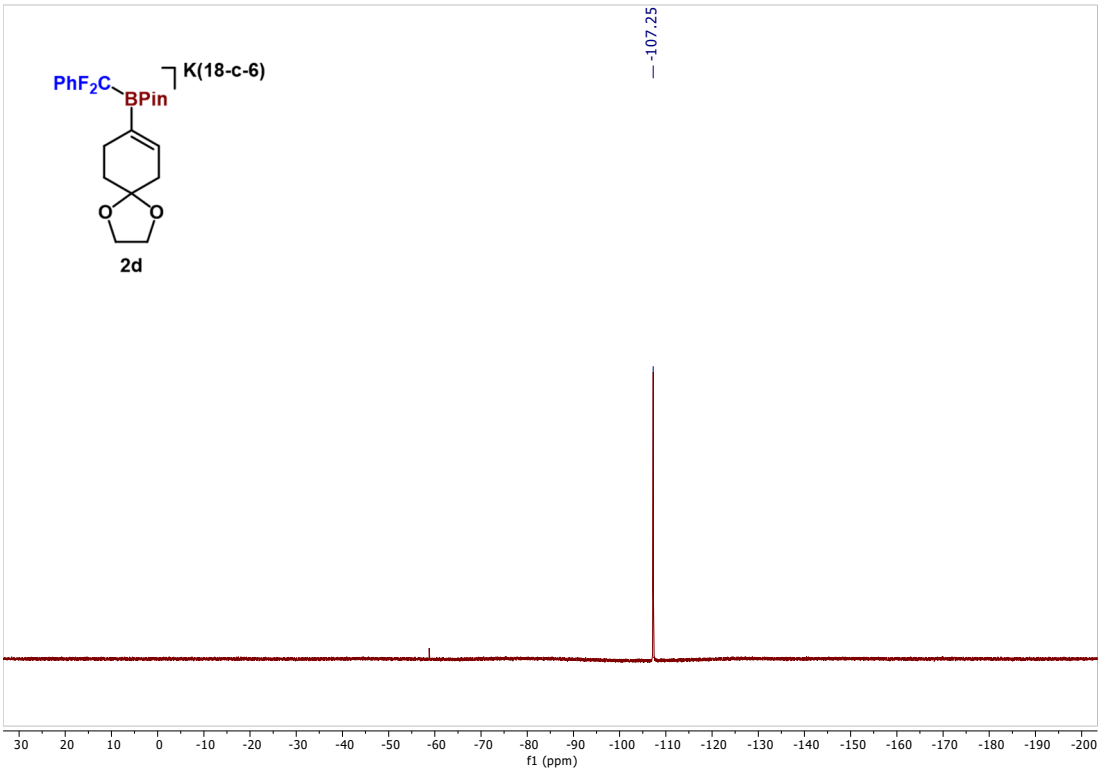


Fig. S9. ^{19}F NMR spectrum (THF-d_8, 25 °C) of **2d**.

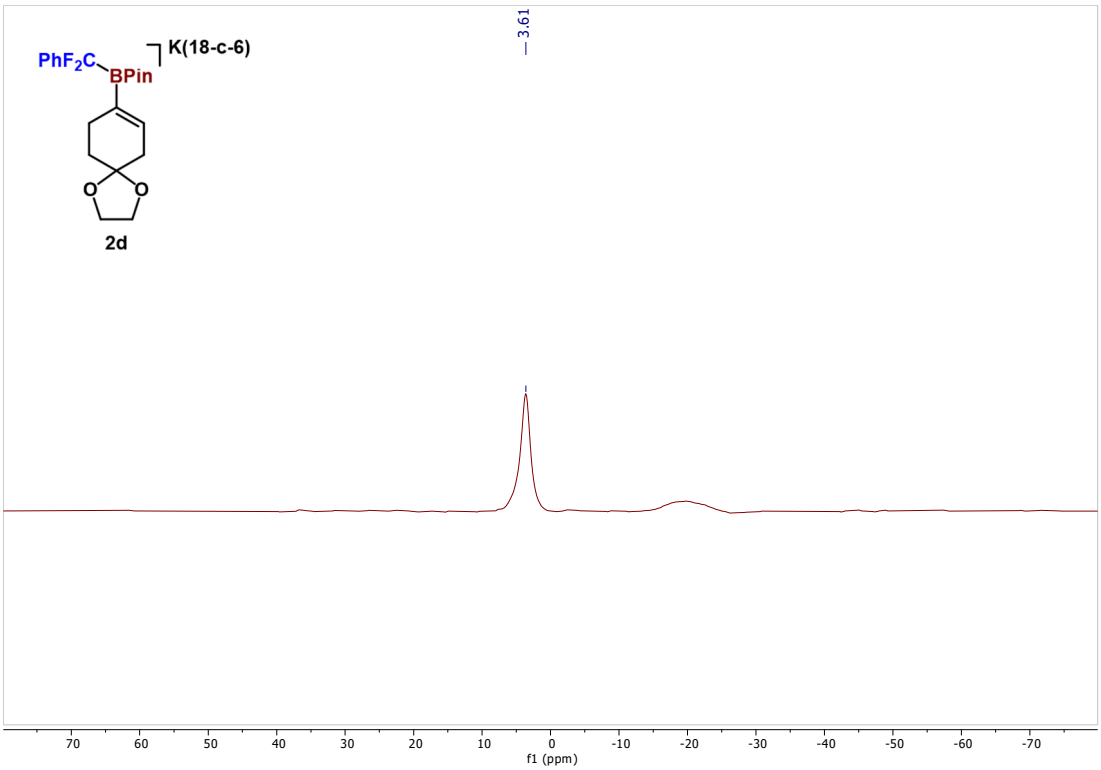
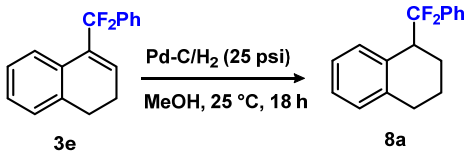


Fig. S10. ^{11}B NMR spectrum (THF-d_8, 25 °C) of **2d**.

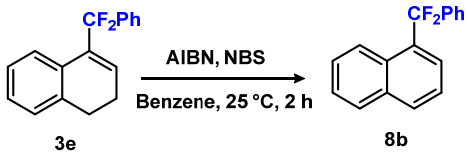
F) Procedure for the late-stage functionalization reactions:

1) Hydrogenation reaction:



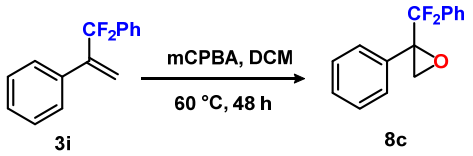
The preparation for compound **8a** is based on previously reported procedure.[9] In a Fisher-Porter tube (50 mL), 4-(difluoro(phenyl)methyl)-1,2-dihydronaphthalene (40 mg, 0.16 mmol) and 10% Pd on charcoal (12 wt%) were taken in methanol (4.0 mL). The solution was degassed with nitrogen for 5 minutes and then with H_2 for 5 minutes. Subsequently, the Fisher-Porter tube was pressurised with H_2 at 25 psi pressure and the reaction mixture was stirred for overnight at room temperature. Finally, the reaction was monitored by ^{19}F NMR using $PhOCF_3$ as internal standard. The reaction mixture was filtered through a pad of celite, washed with methanol and evaporated to dryness. The product **8a** was purified by column chromatography using hexane-DCM as eluent, white solid (34 mg, 84% isolated yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.33-7.26 (m, 3H), 7.23-7.17 (m, 3H), 7.12-7.09 (m, 1H), 7.04-6.99 (m, 2H), 3.56-3.47 (m, 1H), 2.61-2.49 (m, 2H), 1.83-1.68 (m, 3H), 1.50-1.43 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 139.42, 136.70 (t, $J_{C\text{-}F}$ = 26.3 Hz), 131.77 (t, $J_{C\text{-}F}$ = 2.5 Hz), 131.33 (t, $J_{C\text{-}F}$ = 2.5 Hz), 129.55 (t, $J_{C\text{-}F}$ = 1.3 Hz), 129.04, 128.11, 127.04, 125.82 (t, $J_{C\text{-}F}$ = 6.3 Hz), 125.23, 124.07 (dd, $J_{C\text{-}F}$ = 247.5, 2.5 Hz), 45.38 (t, $J_{C\text{-}F}$ = 25.0 Hz), 29.17, 23.77 (t, $J_{C\text{-}F}$ = 2.5 Hz), 19.69 (t, $J_{C\text{-}F}$ = 1.3 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -92.56 (dd, $J_{F\text{-}F}$ = 244.4 Hz, $J_{H\text{-}F}$ = 18.8 Hz, 1F), -96.85 (dd, $J_{F\text{-}F}$ = 244.4 Hz, $J_{H\text{-}F}$ = 18.8 Hz, 1F). **EI-MS**: 258.1229 (M^+).

2) Dehydrogenation reaction:



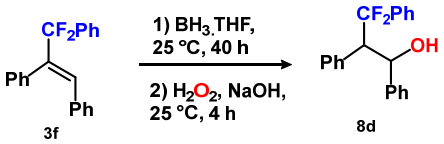
In a 20 mL vial, 4-(difluoro(phenyl)methyl)-1,2-dihydronaphthalene (40 mg, 0.16 mmol), AIBN(26.3 mg, 0.16 mmol), NBS (57 mg, 0.32 mmol) were taken in benzene (3.0 mL). The solution was degassed with nitrogen for 5 minutes was stirred for 2 h at room temperature. Finally, the reaction was monitored by ^{19}F NMR using $PhOCF_3$ as internal standard. The reaction mixture was quenched with sodium sulphite and the organics were extracted in dichloromethane. The dichloromethane layer was evaporated to dryness and the product **8b** was purified by column chromatography using hexane-DCM as eluent, white solid (28 mg, 72% isolated yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.98-7.94 (m, 2H), 7.87 (dd, J = 8.1, 1.5 Hz, 1H), 7.76 (dd, J = 7.4, 1.4 Hz, 1H), 7.52-7.44 (m, 4H), 7.42-7.37 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 137.74 (t, $J_{C\text{-}F}$ = 27.5 Hz), 134.16, 132.31 (t, $J_{C\text{-}F}$ = 25.0 Hz), 131.33 (t, $J_{C\text{-}F}$ = 2.5 Hz), 130.13 (t, $J_{C\text{-}F}$ = 1.9 Hz), 129.86 (t, $J_{C\text{-}F}$ = 2.0 Hz), 128.68, 128.48, 126.68, 126.23 (t, $J_{C\text{-}F}$ = 5.2 Hz), 125.98, 125.72 (t, $J_{C\text{-}F}$ = 3.0 Hz), 125.37 (t, $J_{C\text{-}F}$ = 8.5 Hz), 124.40, 121.70 (t, $J_{C\text{-}F}$ = 239.3 Hz).**^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -83.78 (s, 2F). **EI-MS**: 254.0899 (M^+).

3) Epoxidation reaction:



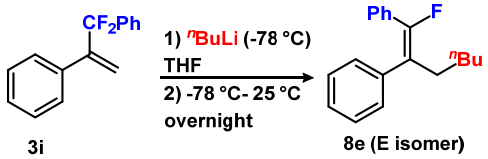
The preparation for compound **8c** is based on previously reported procedure.[10] In a screw cap tube, (1,1-difluoroprop-2-ene-1,2-diyl)dibenzene (30 mg, 0.13 mmol) and *meta*-chloroperbenzoic acid (mCPBA) (112 mg, 0.65 mmol) were taken in dichloromethane (3.0 mL). The solution was degassed with nitrogen for 5 minutes was stirred for 2 h at 60 °C. Finally, the reaction was monitored by ^{19}F NMR using $PhOCF_3$ as internal standard. The reaction mixture was quenched with sodium sulphite and the organics were extracted in dichloromethane. The dichloromethane layer was evaporated to dryness and the product **8c** was purified by column chromatography using hexane-DCM as eluent, viscous oil (24 mg, 74% isolated yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.39-7.24 (m, 10H), 3.32 (d, J = 5.5 Hz, 1H), 2.83 (d, J = 5.6 Hz, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 133.76 (t, J_{C-F} = 26.3 Hz), 133.68 (d, J_{C-F} = 1.3 Hz), 130.17 (t, J_{C-F} = 2.5 Hz), 128.68, 128.37 (t, J_{C-F} = 1.3 Hz), 127.98, 127.93, 126.16 (t, J_{C-F} = 6.3 Hz), 119.75 (q, J_{C-F} = 243.8, 3.8 Hz), 61.57 (q, J_{C-F} = 32.5, 3.8 Hz), 50.81 (q, J_{C-F} = 2.5, 2.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -102.63 (d, J_{F-F} = 255.7 Hz, 1F), -104.56 (d, J_{F-F} = 255.7 Hz, 1F). **EI-MS**: 246.0866 (M^+).

4) Hydroboration-oxidation reaction:



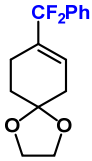
The preparation for compound **8d** is based on previously reported procedure.[11] In a screw cap tube, (3,3-difluoroprop-1-ene-1,2,3-triyl)tribenzene (35 mg, 0.12 mmol) and BH_3.THF (1M solution in THF, 0.29 mmol) were taken in tetrahydrofuran (3.0 mL) at 0 °C. The solution was stirred for overnight at room temperature. Then, the reaction mixture was quenched by addition of a 3 M aqueous solution of NaOH (1.0 mL), and a solution of H_2O_2 (30% in H_2O, 1.0 mL). The mixture was allowed to stir at room temperature for 5 h. Upon completion of the reaction, the reaction mixture was quenched with water and extracted with dichloromethane three times. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography (hexane/dichloromethane) to afford the product **8d** as a viscous oil (21 mg, 56% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.31-7.26 (m, 5H), 7.20-7.15 (m, 4H), 7.14-7.06 (m, 6H), 5.53 (t, J = 3.7 Hz, 1H), 3.55-3.48 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 142.06, 136.55 (t, J_{C-F} = 26.3 Hz), 132.81 (t, J_{C-F} = 5.0 Hz), 131.00, 129.55, 128.95 (t, J_{C-F} = 17.5 Hz), 128.05, 127.92, 127.63, 127.50, 126.23, 125.37 (t, J_{C-F} = 6.3 Hz), 120.34 (t, J_{C-F} = 250 Hz), 72.20, 61.52 (t, J_{C-F} = 25.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -93.22 (dd, J_{F-F} = 244.4, 11.3 Hz, 1F), -99.99 (dd, J_{F-F} = 244.4, 11.3 Hz, 1F). **GC-MS:** 324.1

5) S_N2' reaction with ^{n}BuLi:



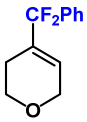
The preparation for compound **8e** is based on previously reported procedure.[12] In a 20 mL vial, (1,1-difluoroprop-2-ene-1,2-diyl)dibenzene (30 mg, 0.13 mmol) was taken in THF (2.5 mL) and cooled to -78 °C. Then, ^{n}BuLi (1.6 M in hexane, 0.19 mmol) was added dropwise to the solution. The mixture was allowed to warm to room temperature and further stirred overnight. Upon completion of the reaction, the reaction mixture was quenched by the addition of H_2O, Na_2CO_3, and extracted with DCM three times. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The product was purified by flash chromatography (hexane/dichloromethane), and the *E* isomer **8e** was isolated as viscous oil (26 mg 73%, ^{19}F NMR of the crude reaction mixture suggest 9:1 selectivity of *E* and *Z* isomer). Characterization for *E* isomer: **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.26-7.21 (m, 4H), 7.14-7.10 (m, 6H), 2.61-2.57 (m, 2H), 1.40-1.26 (m, 6H), 0.85 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 153.33 (d, $J_{C\text{-}F}$ = 241.3 Hz), 139.98 (d, $J_{C\text{-}F}$ = 8.8 Hz), 132.88 (d, $J_{C\text{-}F}$ = 30 Hz), 129.42 (d, $J_{C\text{-}F}$ = 2.5 Hz), 128.52, 128.06 (d, $J_{C\text{-}F}$ = 6.3 Hz), 128.00 (d, $J_{C\text{-}F}$ = 1.3 Hz), 127.70, 127.01, 121.97 (d, $J_{C\text{-}F}$ = 21.3 Hz), 31.59, 31.54 (d, $J_{C\text{-}F}$ = 6.3 Hz), 27.28 (d, $J_{C\text{-}F}$ = 2.5 Hz), 22.49, 14.08. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -107.53 (s, 1F). **EI-MS**: 268.1631 (M^+).

G) Characterization data of the vinyldifluoromethylene compounds:



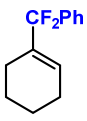
2e

Transparent oil (Procedure A: 0.1 mmol scale, 82% isolated, 22 mg), (Procedure B: 0.26 mmol scale, 56% isolated, 39 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.47-7.45 (m, 2H), 7.40-7.37 (m, 3H), 5.82-5.79 (m, 1H), 3.96-3.93 (m, 4H), 2.33-2.30 (m, 4H),1.75 (t, J = 6.55 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 136.22 (t, $J_{C\text{-}F}$ = 27.5 Hz), 134.67, 134.28 (t, $J_{C\text{-}F}$ = 26.3 Hz), 129.73 (t, $J_{C\text{-}F}$ = 2.5 Hz), 128.24, 125.91 (t, $J_{C\text{-}F}$ = 3.8 Hz), 128.87 (t, $J_{C\text{-}F}$ = 3.0 Hz), 120.93 (t, $J_{C\text{-}F}$ = 237.5 Hz), 107.32, 64.50, 35.35, 30.58, 22.4 (t, $J_{C\text{-}F}$ = 1.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -95.41 (s, 2F). **EI-MS**: 266.1118 (M^+).



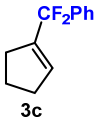
3a

Yellow oil (Procedure A: 0.1 mmol scale, 81% isolated, 17 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.48-7.44 (m, 2H), 7.43-7.38 (m, 3H), 5.95-5.93 (m, 1H), 4.20-4.16 (m, 2H), 3.77 (t, J = 5.4 Hz, 2H), 2.19-2.15 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 135.67 (t, $J_{C\text{-}F}$ = 27.5 Hz), 132.77 (t, $J_{C\text{-}F}$ = 27.5 Hz), 129.92 (t, $J_{C\text{-}F}$ = 2.5 Hz), 128.34, 126.66 (t, $J_{C\text{-}F}$ = 7.5 Hz), 125.79 (t, $J_{C\text{-}F}$ = 6.3 Hz), 120.14 (t, $J_{C\text{-}F}$ = 237.5 Hz), 64.75, 63.73, 23.15. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -97.52 (s, 2F). **EI-MS**: 208.0793 (M^+).



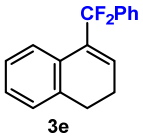
3b

Transparent oil (Procedure A: 0.1 mmol scale, 74% isolated, 16 mg), (Procedure B: 0.26 mmol scale, 40% isolated, 22 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.47-7.45 (m, 2H), 7.40-7.37 (m, 3H), 5.95-5.92 (m, 1H), 2.08-2.03 (m, 4H), 1.64-1.57 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 136.67 (t, $J_{C\text{-}F}$ = 28.8 Hz), 134.65 (t, $J_{C\text{-}F}$ = 26.3 Hz), 129.54 (t, $J_{C\text{-}F}$ = 2.5 Hz), 128.28, 128.21, 128.14, 125.83 (t, $J_{C\text{-}F}$ = 6.3 Hz), 121.81 (t, $J_{C\text{-}F}$ = 238.8 Hz), 24.70, 22.82 (t, $J_{C\text{-}F}$ = 2.5 Hz), 22.00, 21.72. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -96.52 (s, 2F). **EI-MS**: 208.1055 (M^+).



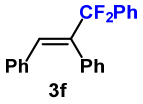
3c

Transparent oil (Procedure A: 0.1 mmol scale, 72% isolated, 14 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.48-7.46 (m, 2H), 7.40-7.37 (m, 3H), 5.83-5.81 (m, 1H), 2.45-2.36 (m, 4H), 1.93 (pent, J = 7.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 140.93 (t, $J_{C\text{-}F}$ = 28.8 Hz), 136.70 (t, $J_{C\text{-}F}$ = 27.5 Hz), 132.76 (t, $J_{C\text{-}F}$ = 7.5 Hz), 129.64 (t, $J_{C\text{-}F}$ = 1.3 Hz), 128.20, 125.46 (t, $J_{C\text{-}F}$ = 5.0 Hz), 119.66 (t, $J_{C\text{-}F}$ = 235 Hz), 32.65, 30.63, 23.28. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -93.62 (s, 2F). **EI-MS**: 194.0901 (M^+).



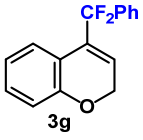
3e

White solid (Procedure A: 0.1 mmol scale, 89% isolated, 23 mg), (Procedure B: 0.26 mmol scale, 71% isolated, 47 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.58-7.56 (m, 2H), 7.41-7.39 (m, 3H), 7.28 (d, J = 7.8 Hz, 1H), 7.15-7.05 (m, 3H), 6.41-6.38 (m, 1H), 2.79 (t, J = 8.1 Hz, 2H), 2.41-2.36 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 136.87 (t, $J_{C\text{-}F}$ = 27.5 Hz), 136.84, 133.88 (t, $J_{C\text{-}F}$ = 26.3 Hz), 131.88 (t, $J_{C\text{-}F}$ = 8.8 Hz), 130.40, 130.01 (t, $J_{C\text{-}F}$ = 1.3 Hz), 128.42, 127.76, 127.39, 126.39, 126.19 (t, $J_{C\text{-}F}$ = 5 Hz), 125.47 (t, $J_{C\text{-}F}$ = 2.5 Hz), 121.09 (t, $J_{C\text{-}F}$ = 238.8 Hz), 27.85, 22.87. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -88.39 (s, 2F). **EI-MS**: 256.1059 (M^+).



3f

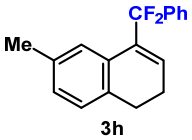
Viscous oil (Procedure A: 0.1 mmol scale, 83% isolated, 25 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.41 (t, J = 7.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.32-7.18 (m, 11H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 139.22 (t, $J_{C\text{-}F}$ = 2.1 Hz), 138.44 (t, $J_{C\text{-}F}$ = 26.3 Hz), 137.17 (t, $J_{C\text{-}F}$ = 27.5 Hz), 136.80 (t, $J_{C\text{-}F}$ = 5.0 Hz), 136.07, 130.39, 129.77, 129.04, 128.87 (t, $J_{C\text{-}F}$ = 2.5 Hz), 128.14, 128.03, 127.71, 127.40, 126.03 (t, $J_{C\text{-}F}$ = 5 Hz), 120.37 (t, $J_{C\text{-}F}$ = 241.3 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -80.93 (s, 2F). **EI-MS**: 306.1210 (M^+).



3g

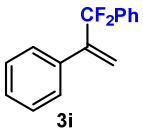
Pale yellow solid (Procedure A: 0.1 mmol scale, 84% isolated, 22 mg), (Procedure B: 0.26 mmol scale, 51% isolated, 34 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.58-7.56 (m, 2H), 7.45-7.39 (m, 3H), 7.21 (dd, J = 7.9,

1.8 Hz, 1H), 7.10 (td, *J* = 7.9, 1.6 Hz, 1H), 6.84-6.77 (m, 2H), 6.08-6.05 (m, 1H), 4.84-4.81 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 154.30, 135.79 (t, J_{C-F} = 26.3 Hz), 131.52 (t, J_{C-F} = 26.3 Hz), 130.33 (t, J_{C-F} = 1.3 Hz), 129.74, 128.54, 126.04 (t, J_{C-F} = 5.0 Hz), 125.86 (t, J_{C-F} = 2.5 Hz), 123.88 (t, J_{C-F} = 8.8 Hz), 121.45, 119.89 (t, J_{C-F} = 238.8 Hz), 118.99, 116.39, 64.56. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -90.16 (s, 2F). **EI-MS**: 258.0847 (M^+).



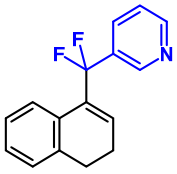
3h

White solid (Procedure A: 0.1 mmol scale, 85% isolated, 23 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.59-7.57 (m, 2H), 7.43-7.38 (m, 3H), 7.16 (s, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.94 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.36-6.33 (m, 1H), 2.74 (t, *J* = 8.1 Hz, 2H), 2.38-2.32 (m, 2H), 2.21 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 136.96 (t, J_{C-F} = 27.5 Hz), 135.76, 134.05 (t, J_{C-F} = 26.3 Hz), 133.43, 132.13 (t, J_{C-F} = 8.8 Hz), 130.26, 129.95 (t, J_{C-F} = 1.3 Hz), 128.37, 128.02, 127.58, 126.33 (t, J_{C-F} = 3.8 Hz), 126.19 (t, J_{C-F} = 6.3 Hz), 121.17 (t, J_{C-F} = 238.8 Hz), 27.47, 23.08, 21.37. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -88.28 (s, 2F). **EI-MS**: 270.1219 (M^+).



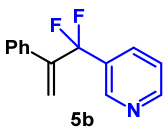
3i

Transparent oil (Procedure A: 0.1 mmol scale, 87% isolated, 20 mg), (Procedure B: 0.26 mmol scale, 72% isolated, 43 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.49 (dd, *J* = 7.7 Hz, 2H), 7.40-7.34 (m, 3H), 7.31-7.29 (m, 2H), 7.26-7.25 (m, 3H), 5.69 (s, 1H), 5.61 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 145.51 (t, J_{C-F} = 25.0 Hz), 136.45, 136.35 (t, J_{C-F} = 27.5 Hz), 129.89 (t, J_{C-F} = 1.3 Hz), 128.30, 128.21 (t, J_{C-F} = 1.3 Hz), 128.14, 128.12, 125.92 (t, J_{C-F} = 5.0 Hz), 120.48 (t, J_{C-F} = 241.3 Hz), 119.35 (t, J_{C-F} = 8.8 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -91.15 (s, 2F). **EI-MS**: 230.0901 (M^+).



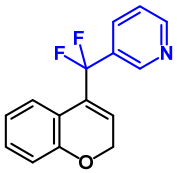
5a

Yellow solid (Procedure B: 0.26 mmol scale, 61% isolated, 41 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.81-8.79 (m, 1H), 8.66 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.86 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.35-7.32 (m, 1H), 7.24-7.22 (m, 1H), 7.15-7.11 (m, 2H), 7.08-7.05 (m, 1H), 6.44-6.41 (m, 1H), 2.79 (t, *J* = 8.1 Hz, 2H), 2.42-2.37 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 151.25 (t, J_{C-F} = 2.5 Hz), 147.89 (t, J_{C-F} = 6.3 Hz), 136.44, 133.89 (t, J_{C-F} = 5.0 Hz), 133.21 (t, J_{C-F} = 25.0 Hz), 132.69, 132.49 (t, J_{C-F} = 8.8 Hz), 129.87, 127.94, 127.70, 126.52, 125.21 (t, J_{C-F} = 2.5 Hz), 123.19, 120.16 (t, J_{C-F} = 238.8 Hz), 27.75, 22.84. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -89.03 (s, 2F). **EI-MS**: 257.1004 (M^+).



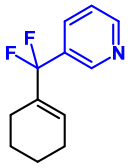
5b

Pale yellow oil (Procedure B: 0.26 mmol scale, 44% isolated, 26 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.71 (s, 1H), 8.62 (dd, *J* = 9.9, 1.6 Hz, 1H), 7.74 (d, *J* = 8.1Hz, 1H), 7.29-7.25 (m, 6H), 5.74 (s, 1H), 5.64 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 151.11 (t, J_{C-F} = 2.5 Hz), 147.52 (t, J_{C-F} = 6.3 Hz), 144.83 (t, J_{C-F} = 26.3 Hz), 135.80, 133.57 (t, J_{C-F} = 6.3 Hz), 132.18 (t, J_{C-F} = 27.5 Hz), 128.34 (t, J_{C-F} = 13.8 Hz), 124.73, 123.63, 121.43, 119.86 (t, J_{C-F} = 8.8 Hz), 119.50, 117.57. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -92.14 (s, 2F). **EI-MS**: 231.0851 (M^+).



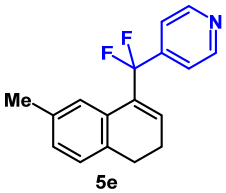
5c

White solid (Procedure B: 0.26 mmol scale, 57% isolated, 38 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.82 (d, *J* = 1.3 Hz, 1H), 8.67 (dd, *J* = 5.9, 1.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.34 (dd, *J* = 8.1, 4.9 Hz, 1H), 7.16-7.10 (m, 2H), 6.84 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.79 (td, *J* = 7.6, 1.3 Hz, 1H), 6.12-6.10 (m, 1H), 4.84-4.52 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 154.32, 151.58 (t, J_{C-F} = 1.3 Hz), 147.68 (t, J_{C-F} = 6.3 Hz), 133.81 (t, J_{C-F} = 5.0 Hz), 131.69 (t, J_{C-F} = 27.5 Hz), 130.87 (t, J_{C-F} = 27.5 Hz), 130.09, 125.54 (t, J_{C-F} = 2.5 Hz), 124.30 (t, J_{C-F} = 8.8 Hz), 123.27, 121.61, 119.00 (t, J_{C-F} = 238.6 Hz), 118.49, 116.61, 64.44. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -90.47 (s, 2F). **EI-MS**: 259.0799 (M^+).



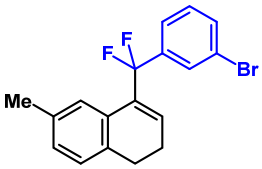
5d

Yellow oil (Procedure B: 0.26 mmol scale, 58% isolated, 32 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.70 (s, 1H), 8.65 (d, *J* = 5.6 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.33 (dd, *J* = 8.0, 4.9 Hz, 1H), 5.96-5.94 (m, 1H), 2.10-2.02 (m, 4H), 1.65-1.55 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 150.87 (t, J_{C-F} = 1.3 Hz), 147.55 (t, J_{C-F} = 6.3 Hz), 134.04 (t, J_{C-F} = 26.3 Hz), 133.59 (t, J_{C-F} = 6.3 Hz), 132.44 (t, J_{C-F} = 26.3 Hz), 129.22 (t, J_{C-F} = 7.5 Hz), 122.99, 120.34 (t, J_{C-F} = 253.8 Hz), 131.69 (t, J_{C-F} = 27.5 Hz), 130.87 (t, J_{C-F} = 27.5 Hz), 130.09, 125.54 (t, J_{C-F} = 2.5 Hz), 124.30 (t, J_{C-F} = 8.8 Hz), 24.70, 22.69 (t, J_{C-F} = 2.5 Hz), 21.87, 21.60. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -96.70 (s, 2F). **EI-MS**: 209.1000 (M^+).



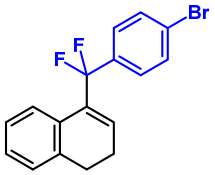
5e

Viscous oil (Procedure B: 0.26 mmol scale, 37% isolated, 26 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.69 (d, *J* = 6.2 Hz, 2H), 7.46 (d, *J* = 5.2 Hz, 2H), 7.07 (s, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.36-6.34 (m, 1H), 2.73 (t, *J* = 8.1 Hz, 2H), 2.38-2.32 (m, 2H), 2.20 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 150.32, 145.09 (t, J_{C-F} = 28.8 Hz), 135.94, 133.37, 132.97 (t, J_{C-F} = 23.8 Hz), 132.68 (t, J_{C-F} = 8.8 Hz), 129.57, 128.38, 127.78, 125.82 (t, J_{C-F} = 2.5 Hz), 120.63 (t, J_{C-F} = 5.0 Hz), 119.85 (t, J_{C-F} = 240.0 Hz), 27.31, 23.02, 21.35. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -91.34 (s, 2F). **EI-MS**: 271.1171 (M^+).



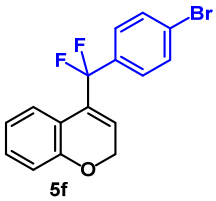
5f

White solid (Procedure B: 0.26 mmol scale, 48% isolated, 44 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.72 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 7.11 (s, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.33-6.30 (m, 1H), 2.73 (t, *J* = 3.05 Hz, 2H), 2.37-2.32 (m, 2H), 2.22 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 139.08 (t, $J_{C\text{-}F}$ = 27.5 Hz), 135.86, 133.59 (t, $J_{C\text{-}F}$ = 26.3 Hz), 133.40, 133.15 (t, $J_{C\text{-}F}$ = 1.3 Hz), 132.54 (t, $J_{C\text{-}F}$ = 8.8 Hz), 130.00, 129.89, 129.35 (t, $J_{C\text{-}F}$ = 5.0 Hz), 128.20, 127.87, 126.04 (t, $J_{C\text{-}F}$ = 3.8 Hz), 124.91 (t, $J_{C\text{-}F}$ = 5.0 Hz), 122.51, 120.39 (t, $J_{C\text{-}F}$ = 240.0 Hz), 27.37, 23.06, 21.38. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -88.56 (s, 2F). **EI-MS**: 258.0847 (M^+).



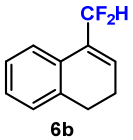
5g

White solid (Procedure B: 0.26 mmol scale, 35% isolated, 30 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.15-7.10 (m, 2H), 7.07-7.04 (m, 1H), 6.41-6.39 (m, 1H), 2.78 (t, *J* = 8.1 Hz, 2H), 2.41-2.35 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 136.41, 135.93 (t, $J_{C\text{-}F}$ = 28.8 Hz), 133.46 (t, $J_{C\text{-}F}$ = 25.0 Hz), 132.05 (t, $J_{C\text{-}F}$ = 8.8 Hz), 131.69, 130.09, 127.93 (t, $J_{C\text{-}F}$ = 5.0 Hz), 127.84, 127.55, 126.44, 125.30 (t, $J_{C\text{-}F}$ = 2.5 Hz), 124.47, 120.61 (t, $J_{C\text{-}F}$ = 235.0 Hz), 119.03, 27.78, 22.83. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -88.55 (s, 2F). **EI-MS**: 348.0312 (M^+).



5f

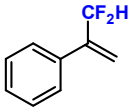
White solid (Procedure B: 0.26 mmol scale, 34% isolated, 30 mg). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.14-7.09 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 4.82 (dd, *J* = 6.9, 3.4 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 154.28, 134.84 (t, $J_{C\text{-}F}$ = 26.3 Hz), 131.84, 131.11 (t, $J_{C\text{-}F}$ = 27.5 Hz), 129.92, 127.79 (t, $J_{C\text{-}F}$ = 5.0 Hz), 125.67 (t, $J_{C\text{-}F}$ = 2.5 Hz), 124.85 (t, $J_{C\text{-}F}$ = 1.7 Hz), 123.99 (t, $J_{C\text{-}F}$ = 8.8 Hz), 121.53, 119.43 (t, $J_{C\text{-}F}$ = 238.8 Hz), 118.71, 116.50, 64.49. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -90.24 (s, 2F). **EI-MS**: 334.0153 (M^+).



6b

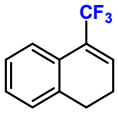
Transparent oil (Procedure C: 0.2 mmol scale, 63% isolated, 22 mg). Characterization data is consistent with the known literature.[13] **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.43 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.22-7.14 (m,

3H), 6.49-6.27 (m, 2H, CF_2-H and vinylic-H overlap), 2.78 (t, *J* = 8.2 Hz, 2H), 2.40-2.34 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 136.00, 131.82 (t, J_{C-F} = 10 Hz), 131.66, 129.61, 127.98, 127.88, 126.64, 1213.81, 116.11 (t, J_{C-F} = 472.5 Hz), 27.42, 22.62. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -113.78 (d, J_{C-F} = 52.64 Hz, 2F). **EI-MS**: 180.0744 (M^+).



6c

Procedure C: This product was eluted with hexane. But it is volatile and ^{1}H and ^{19}F NMR is consistent with the known literature.[14] **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.50-7.44 (m, 2H), 7.38-7.33 (m, 3H), 6.38 (t, *J* = 55.3 Hz, 1H), 5.71 (s, 1H), 5.65 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -113.28 (d, J_{C-F} = 56.4 Hz, 2F). **EI-MS**: 154.0664 (M^+).



6e

Transparent oil (Procedure C: 0.2 mmol scale, 65% isolated, 25 mg). Characterization data is consistent with the known literature.[15] **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.41-7.39 (m, 1H), 7.23-7.19 (m, 2H), 7.18-7.16 (m, 1H), 2.80 (t, *J* = 8.2 Hz, 2H), 2.43-2.37 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 135.90, 132.28 (q, J_{C-F} = 6.3 Hz), 128.67 (q, J_{C-F} = 30.0 Hz), 128.37, 128.18, 127.99, 126.80, 124.11 (q, J_{C-F} = 2.5 Hz), 123.67 (q, J_{C-F} = 233.8 Hz), 27.27, 22.48. **^{19}F NMR** (470 MHz, $CDCl_3$, ppm) δ -63.93 (s). **GC-MS:** 198.1.

H) X-ray Crystallographic data:

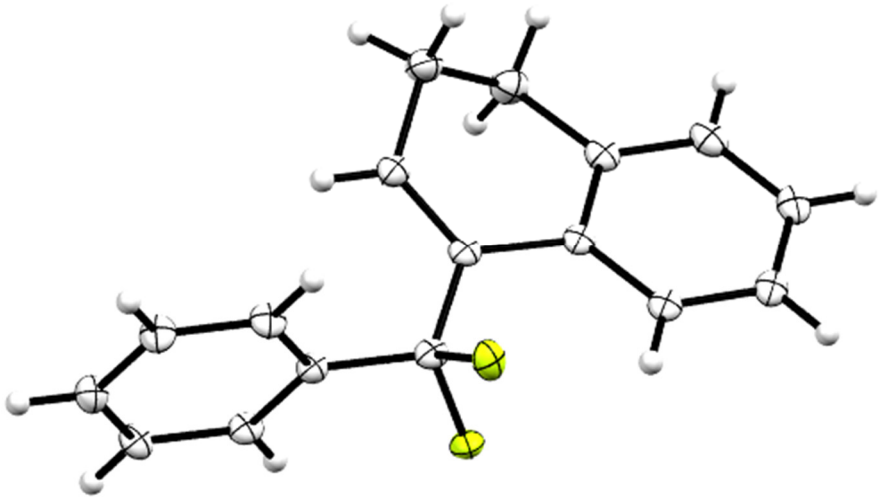


Fig. S11. X-ray crystal structure of **3e**. Colorless needles of KCRXN127 (**3e**) were grown from a concentrate solution of the compound in hexane at -30 °C. CCDC number: CCDC 2299679.

Table S4. Crystallographic parameters for **3e**.

KCRXN127	
Crystal data	
Chemical formula	$C_{17}H_{14}F_2$
M_r	256.28
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	293
a, b, c (Å)	8.6715 (1), 9.6510 (1), 15.2097 (2)
V (Å^3)	1272.88 (3)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.80
Crystal size (mm)	0.11 × 0.10 × 0.05
Data collection	
Diffractometer	Dtrek-*CrysAlis PRO*-abstract goniometer imported rigaku-*D*TREK* images
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.42.84a (Rigaku Oxford Diffraction, 2023) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.739, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18902, 2376, 2318
R_{int}	0.045
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.104, 1.08
No. of reflections	2376
No. of parameters	172
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.25
Absolute structure	Flack x determined using 924 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	−0.01 (9)

I) Spectroscopic data of the products:

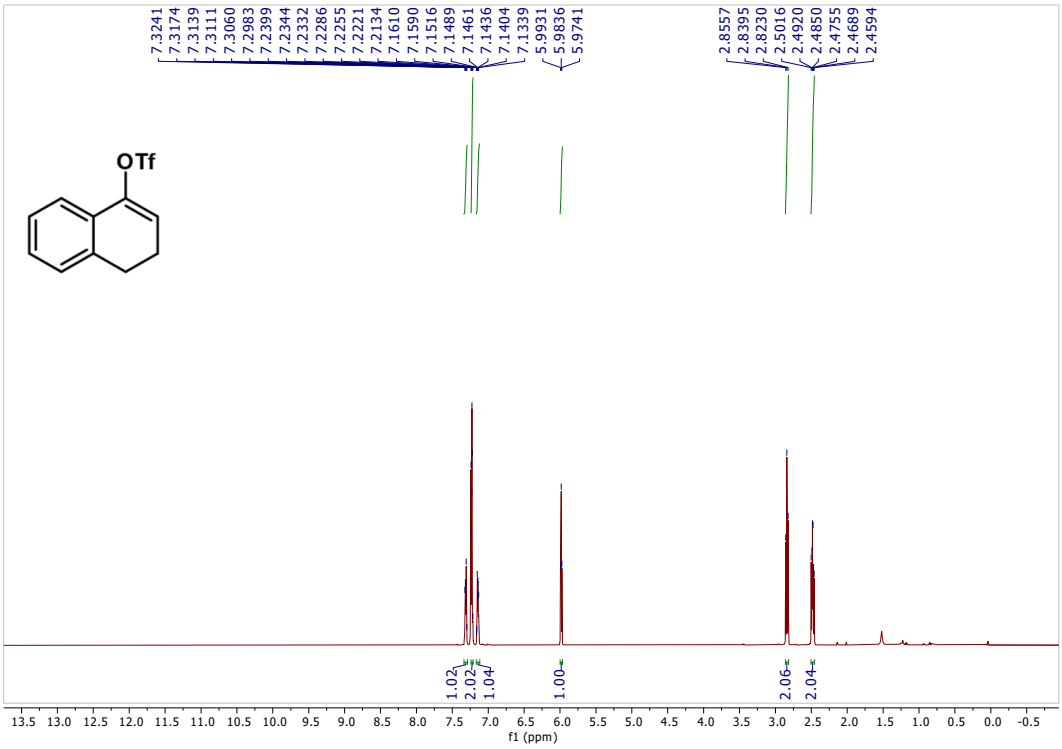


Fig. S12. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.

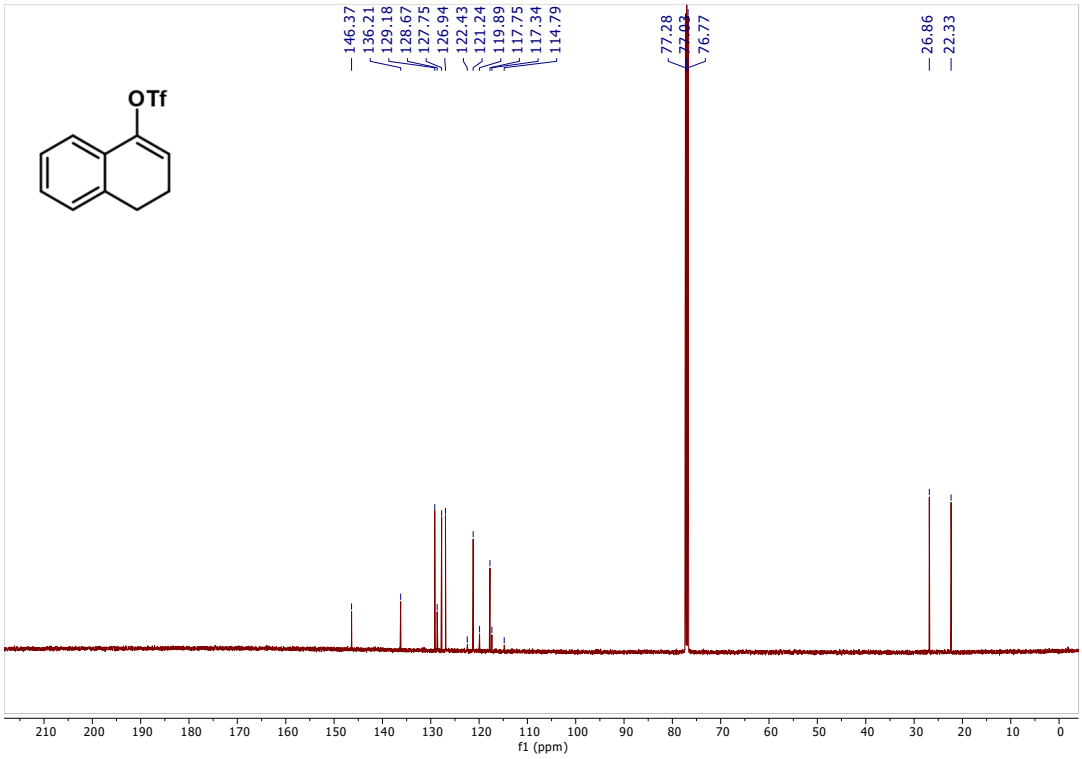


Fig. S13. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.

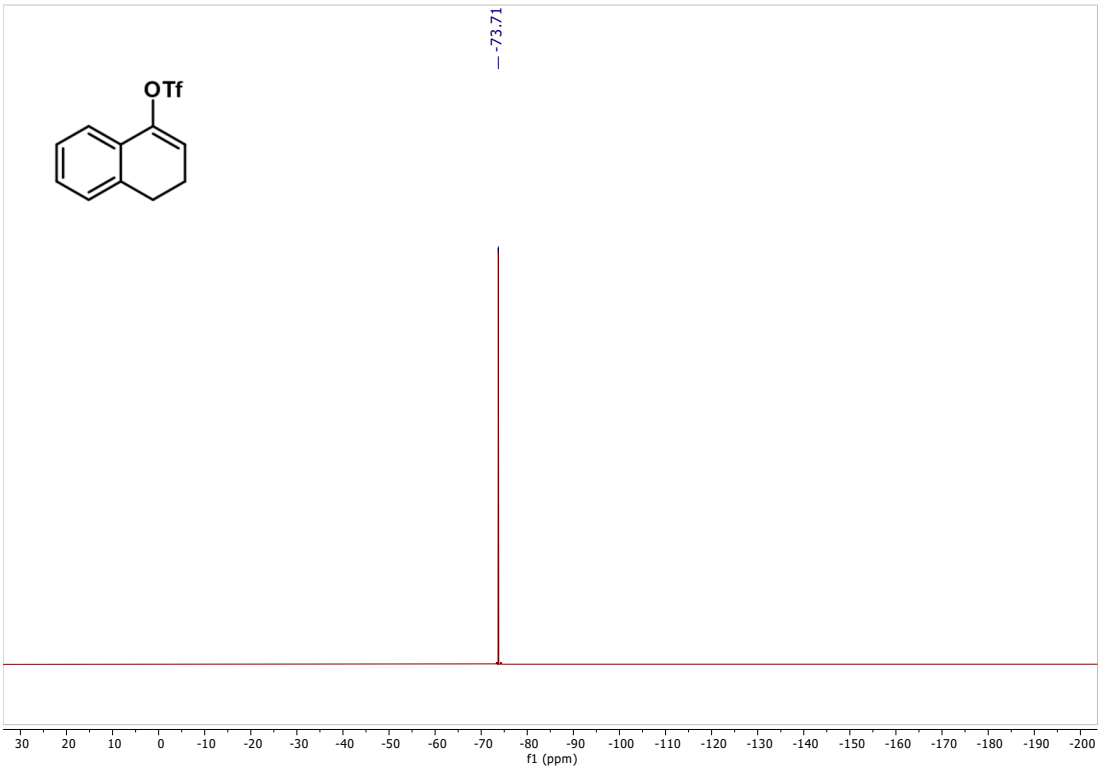


Fig. S14. ^{19}F NMR spectrum (**$CDCl_3$, 25** °C) of 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.

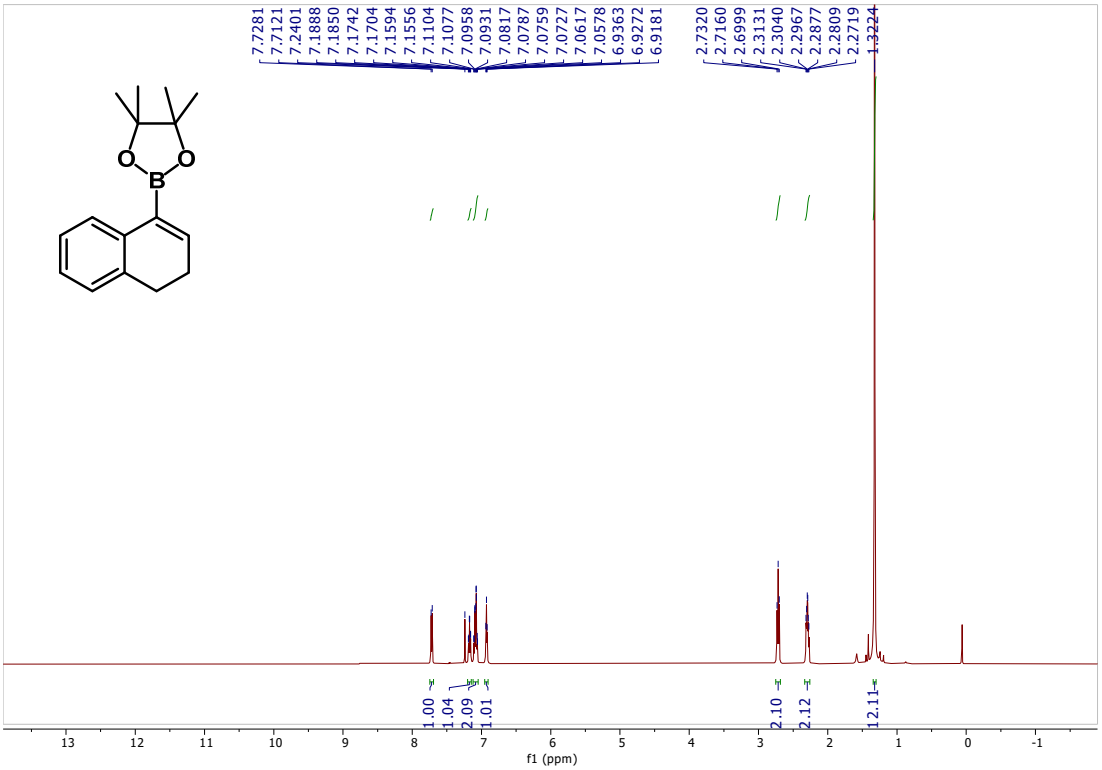


Fig. S15. ^{1}H NMR spectrum (**$CDCl_3$, 25** °C) of 2-(3,4-dihydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

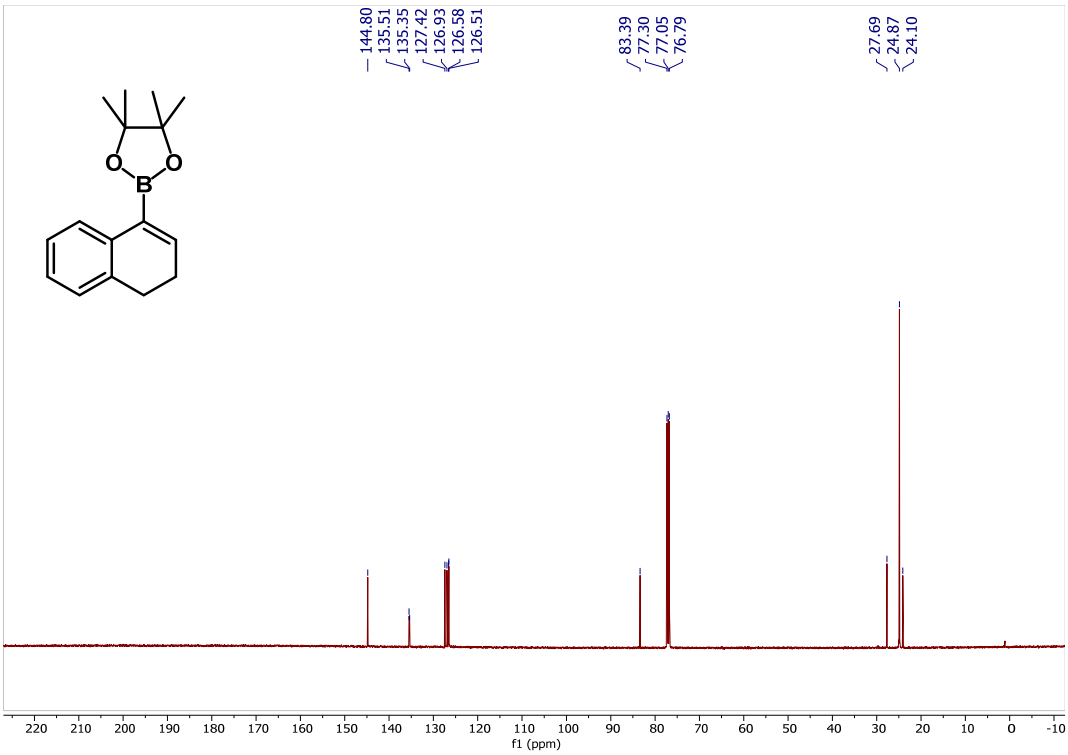


Fig. S16. ^{13}C NMR spectrum (**$CDCl_3$, 25** °C) of 2-(3,4-dihydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

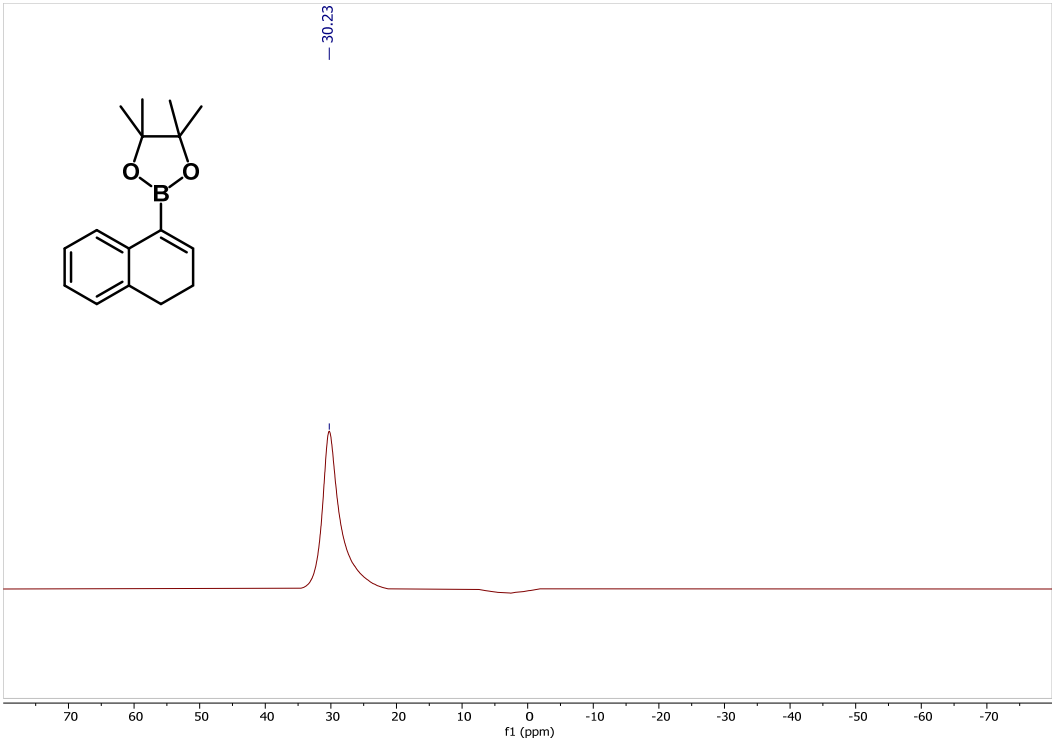


Fig. S17. ^{11}B NMR spectrum (**$CDCl_3$, 25** °C) of 2-(3,4-dihydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

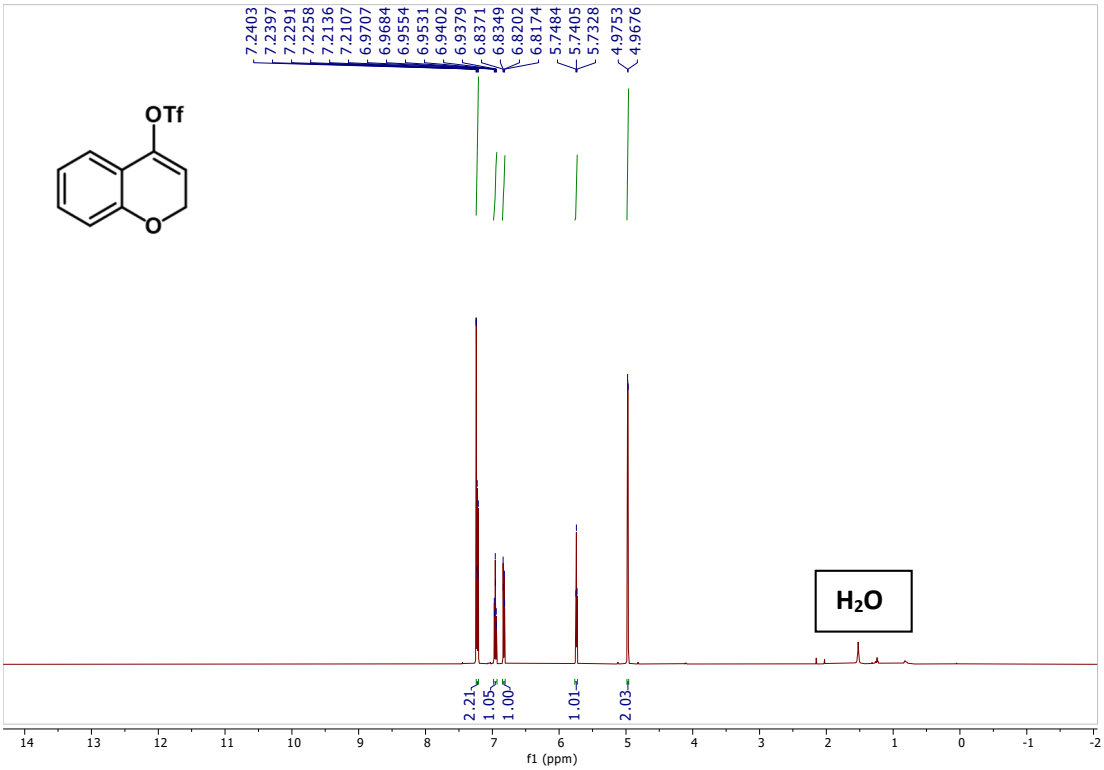


Fig. S18. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of 2H-chromen-4-yl trifluoromethanesulfonate.

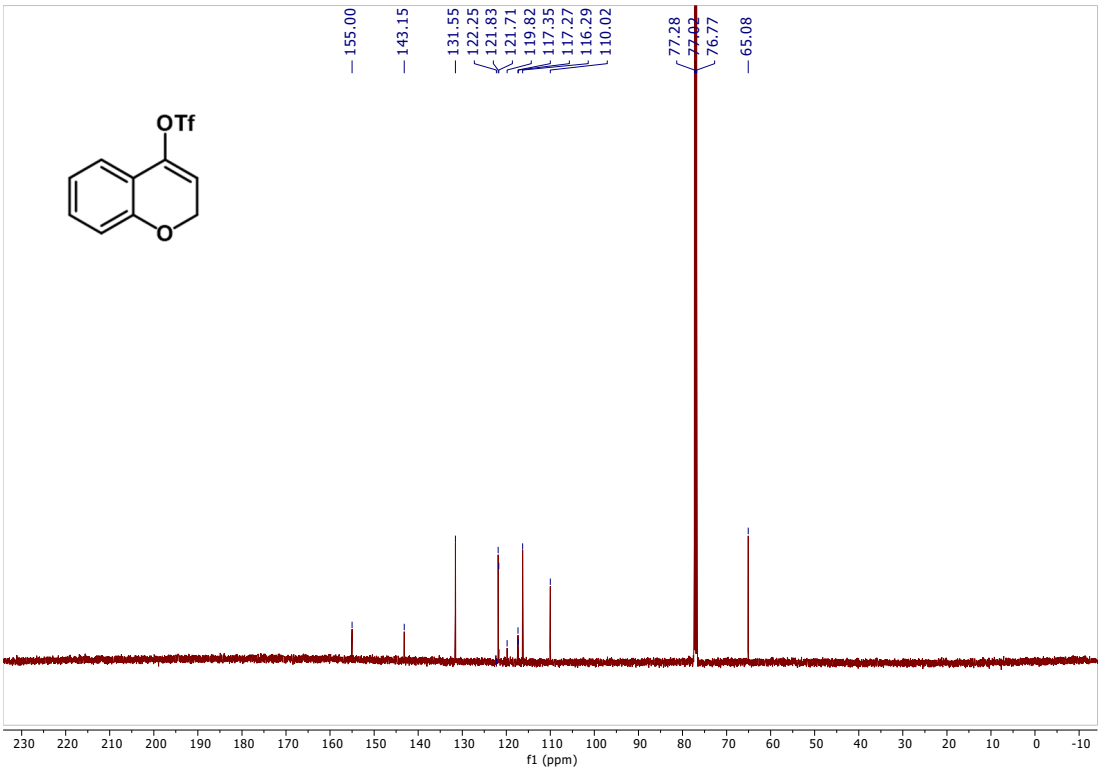


Fig. S19. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of 2H-chromen-4-yl trifluoromethanesulfonate.

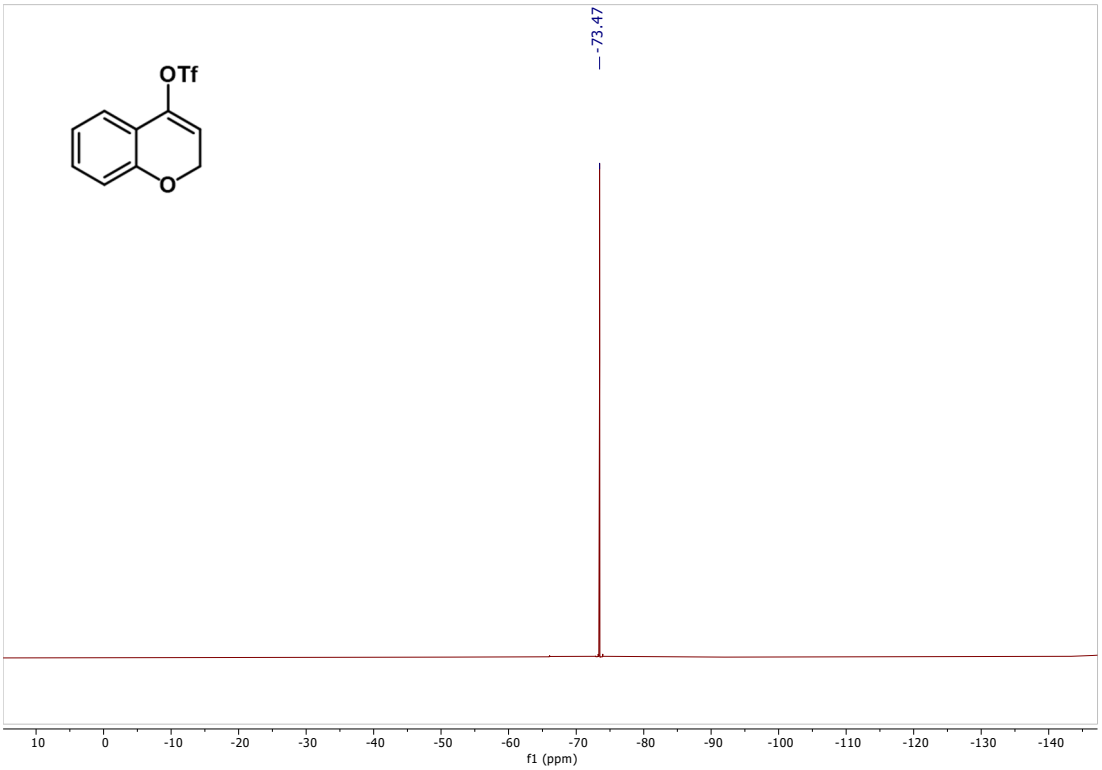


Fig. S20. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of 2H-chromen-4-yl trifluoromethanesulfonate.

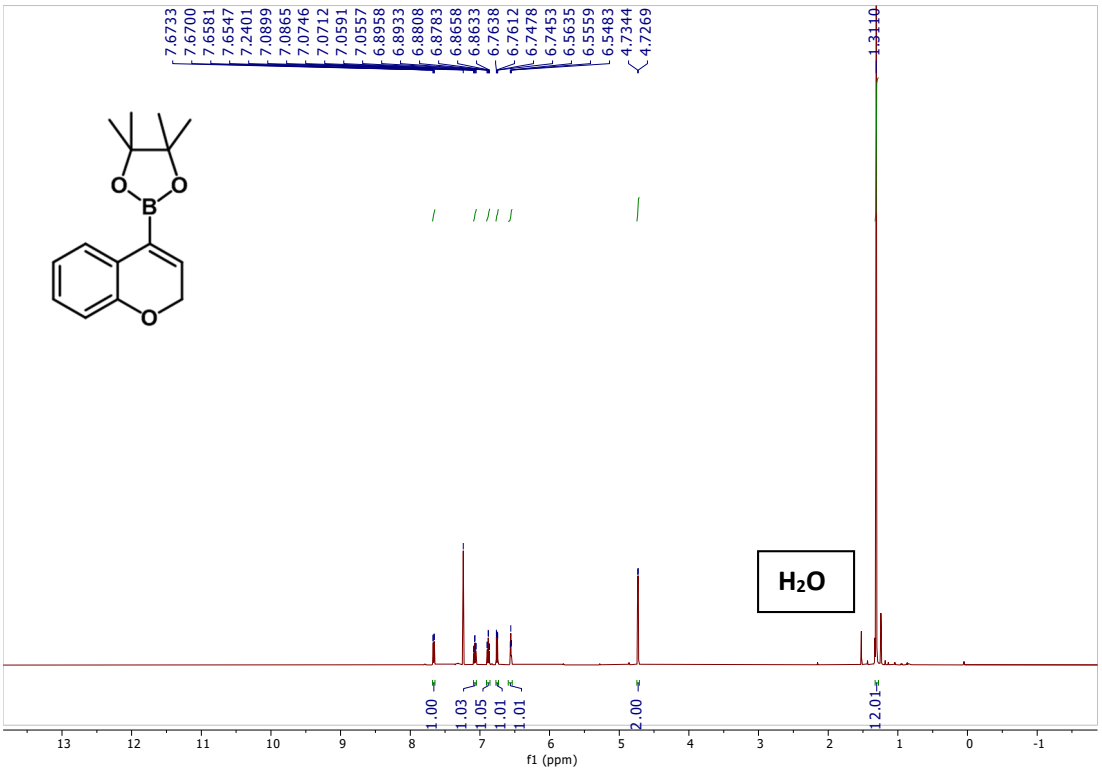


Fig. S21. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of 2-(2H-chromen-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

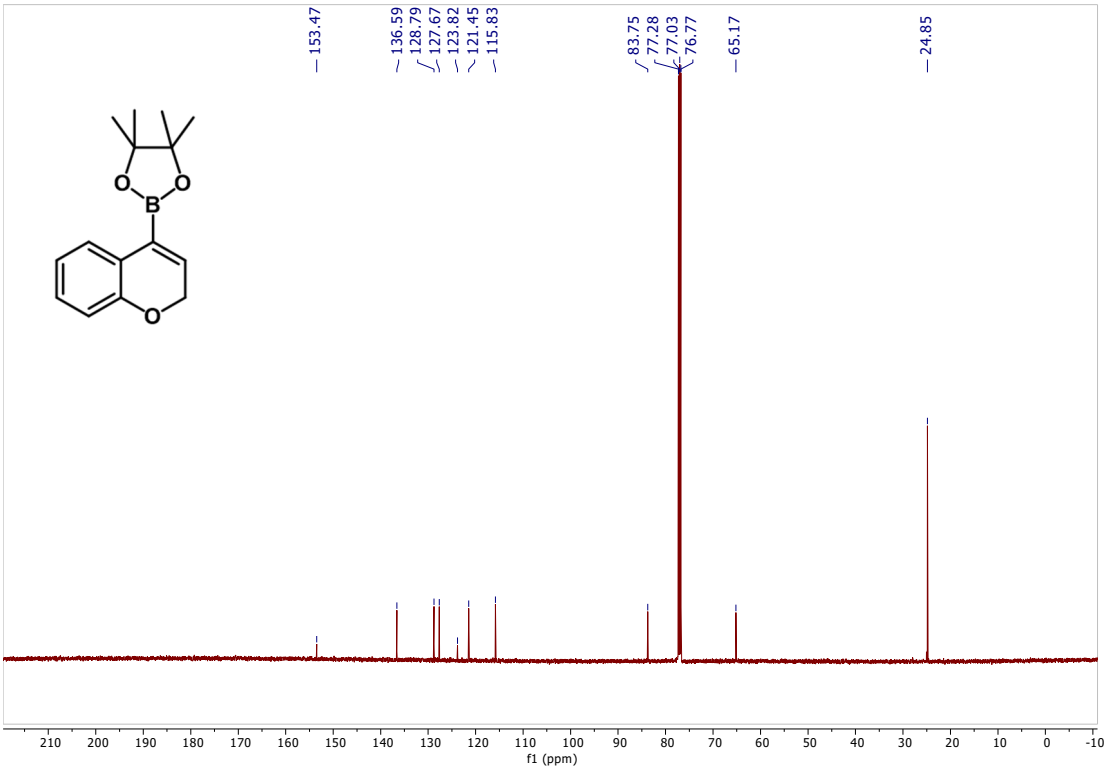


Fig. S22. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of 2-(2H-chromen-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

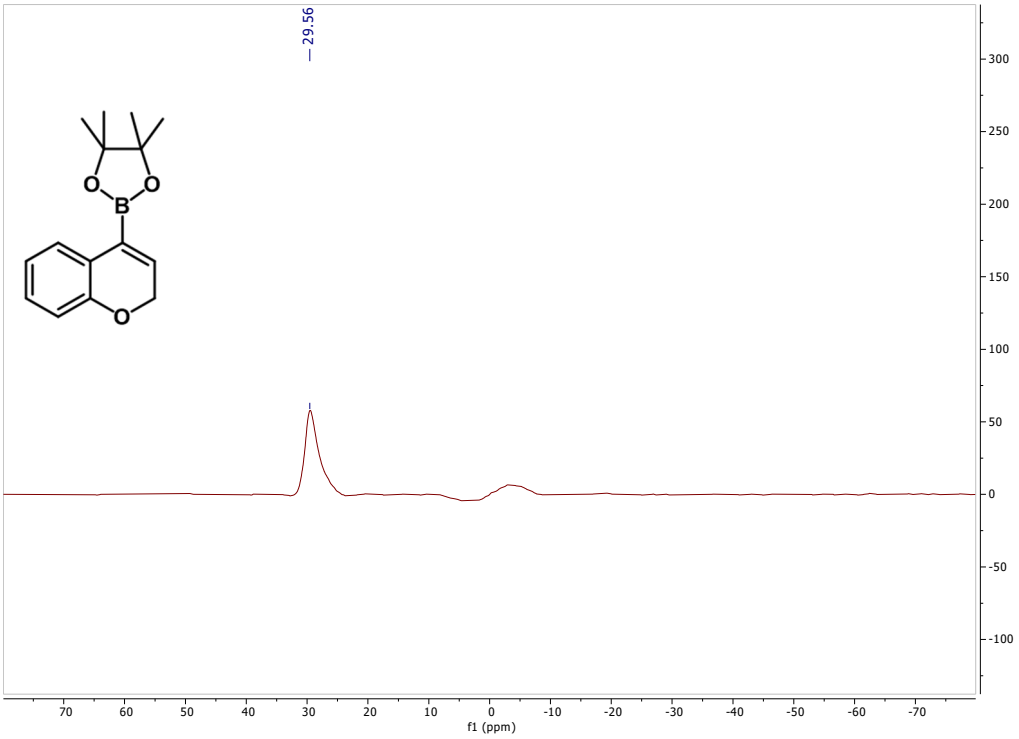


Fig. S23. ^{11}B NMR spectrum (**$CDCl_3$**, **25** °C) of 2-(2H-chromen-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

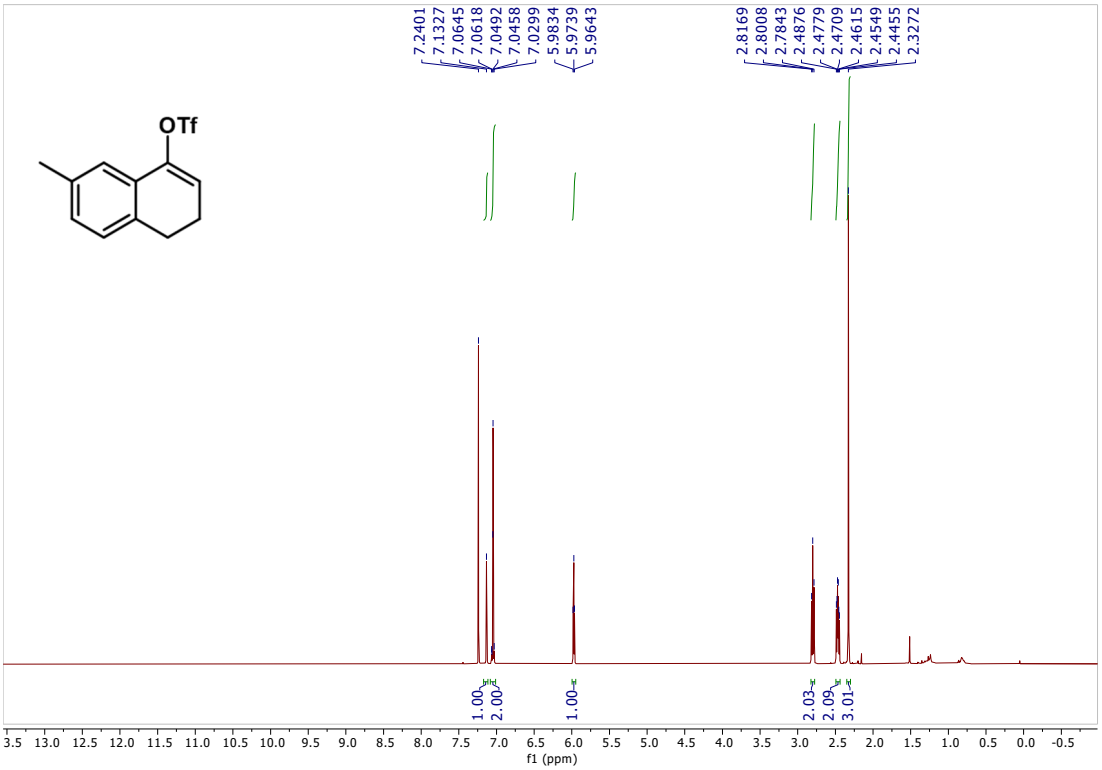


Fig. S24. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of 7-methyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.

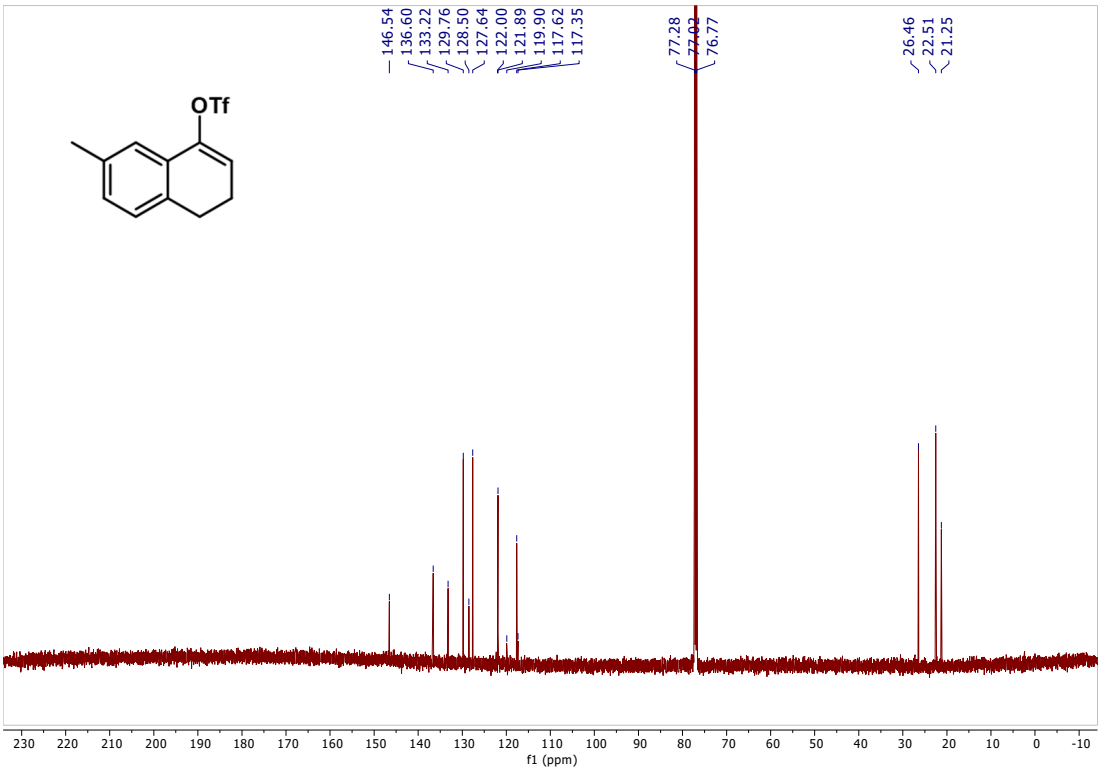


Fig. S25. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of 7-methyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.

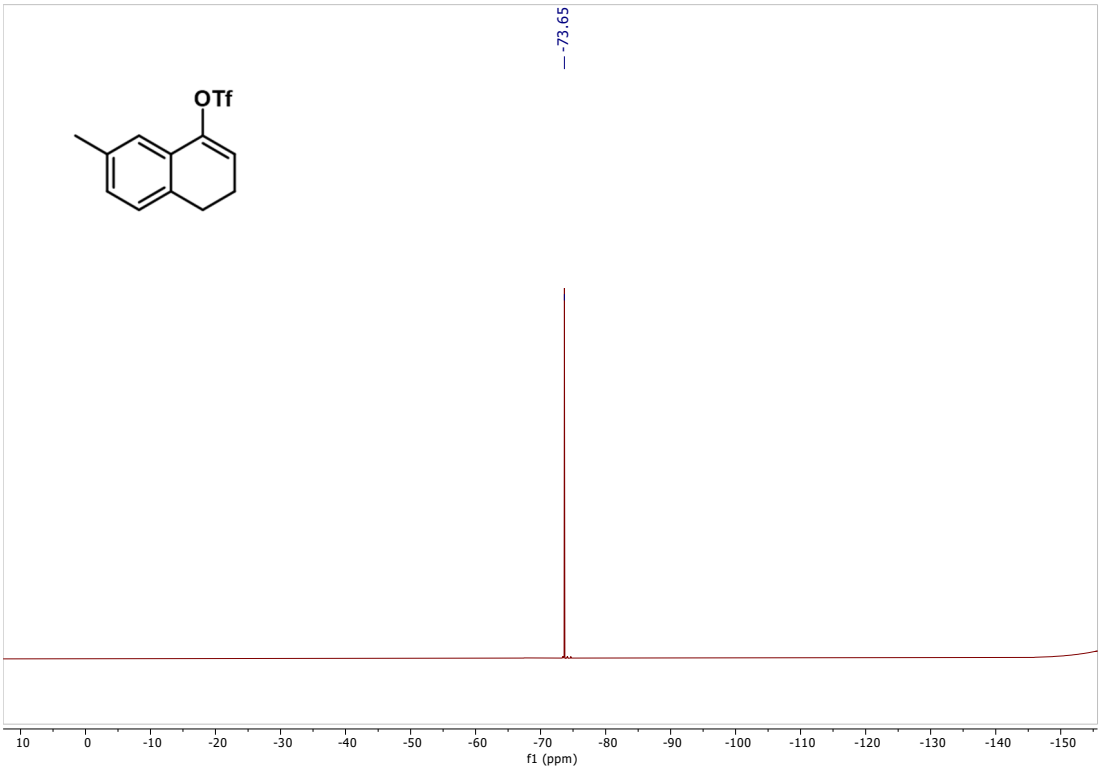


Fig. S26. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of 7-methyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.

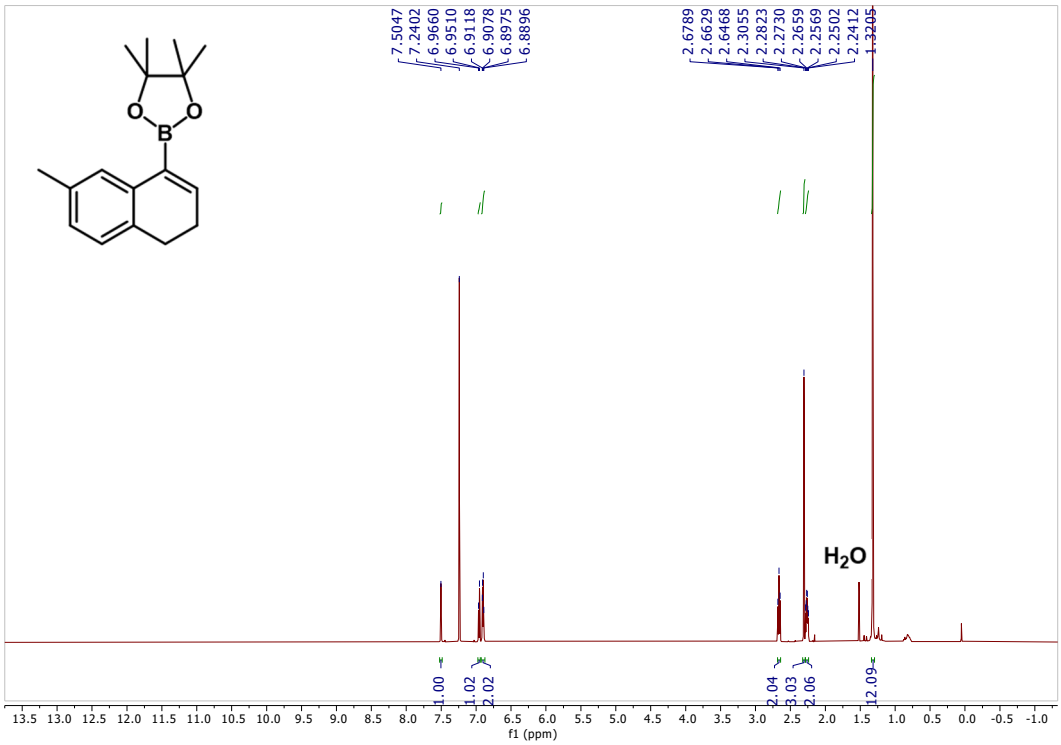


Fig. S27. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of 4,4,5,5-tetramethyl-2-(7-methyl-3,4-dihydronaphthalen-1-yl)-1,3,2-dioxaborolane.

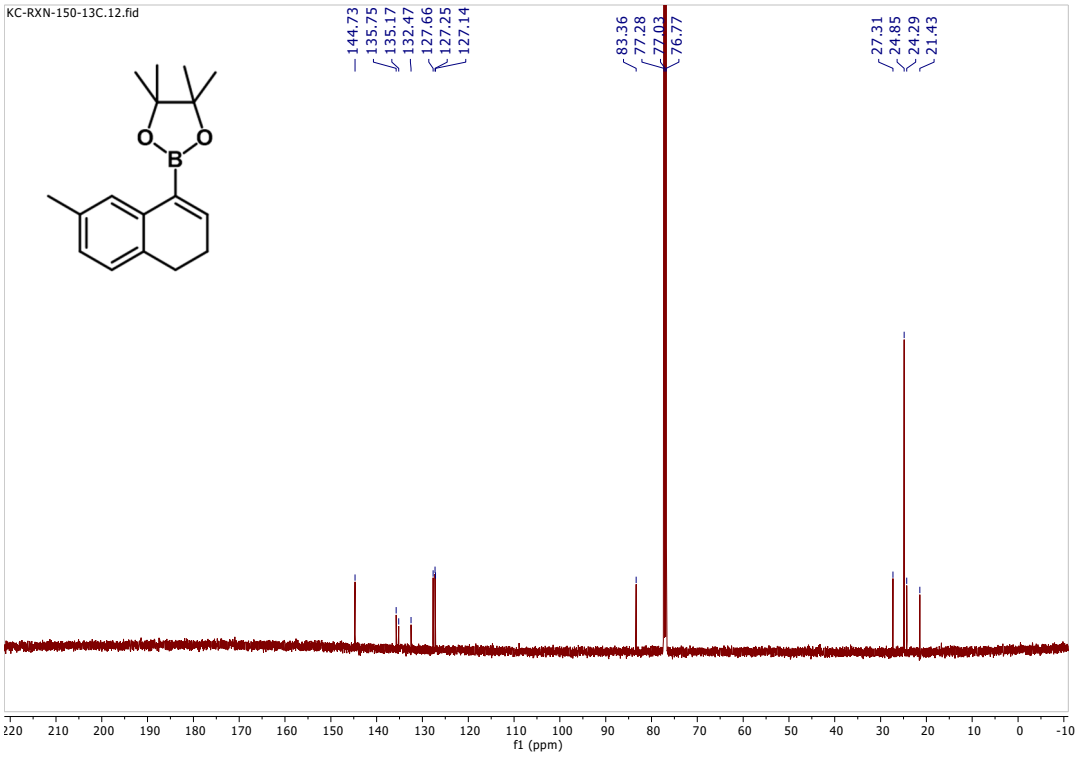


Fig. S28. ^{13}C NMR spectrum (**$CDCl_3$, 25** °C) of 4,4,5,5-tetramethyl-2-(7-methyl-3,4-dihydronaphthalen-1-yl)-1,3,2-dioxaborolane.

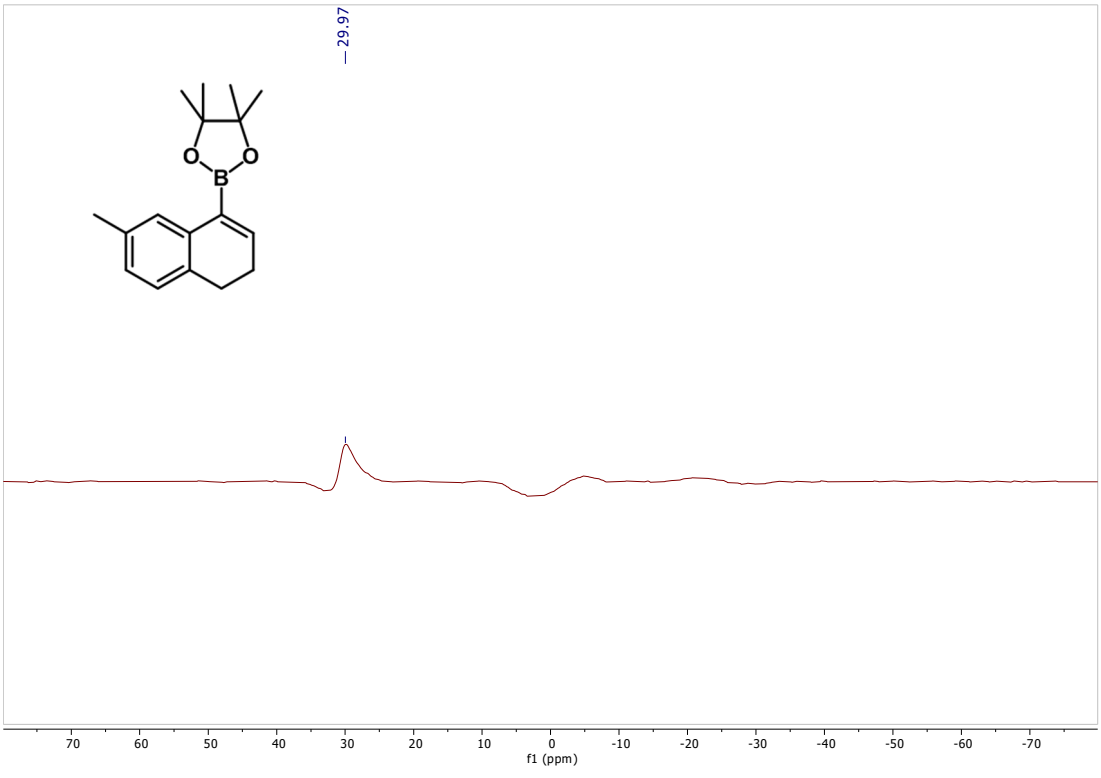


Fig. S29. ^{11}B NMR spectrum (**$CDCl_3$, 25** °C) of 4,4,5,5-tetramethyl-2-(7-methyl-3,4-dihydronaphthalen-1-yl)-1,3,2-dioxaborolane.

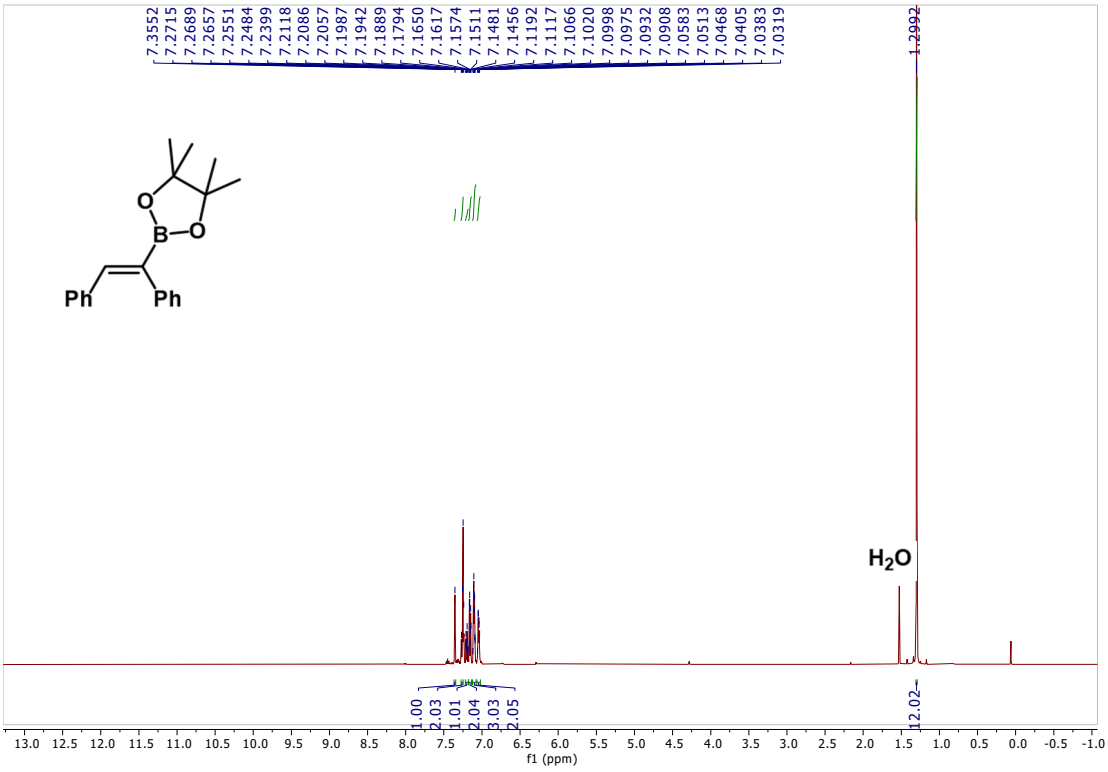


Fig. S30. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of (2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

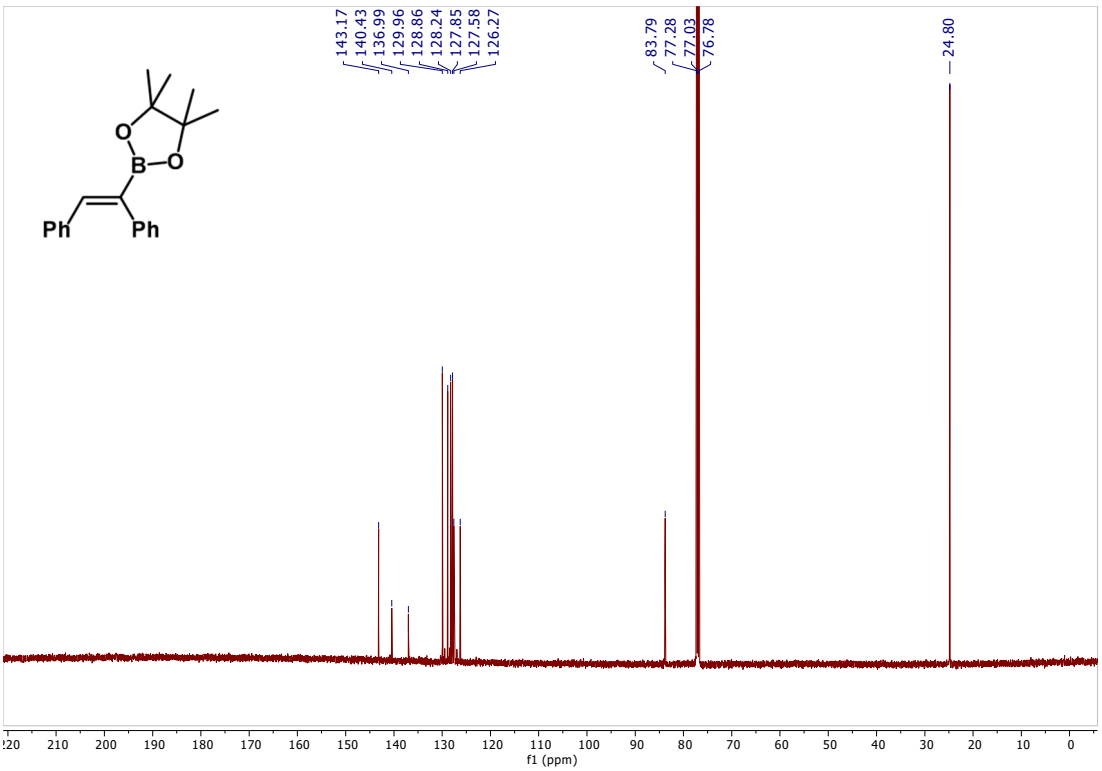


Fig. S31. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of (2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

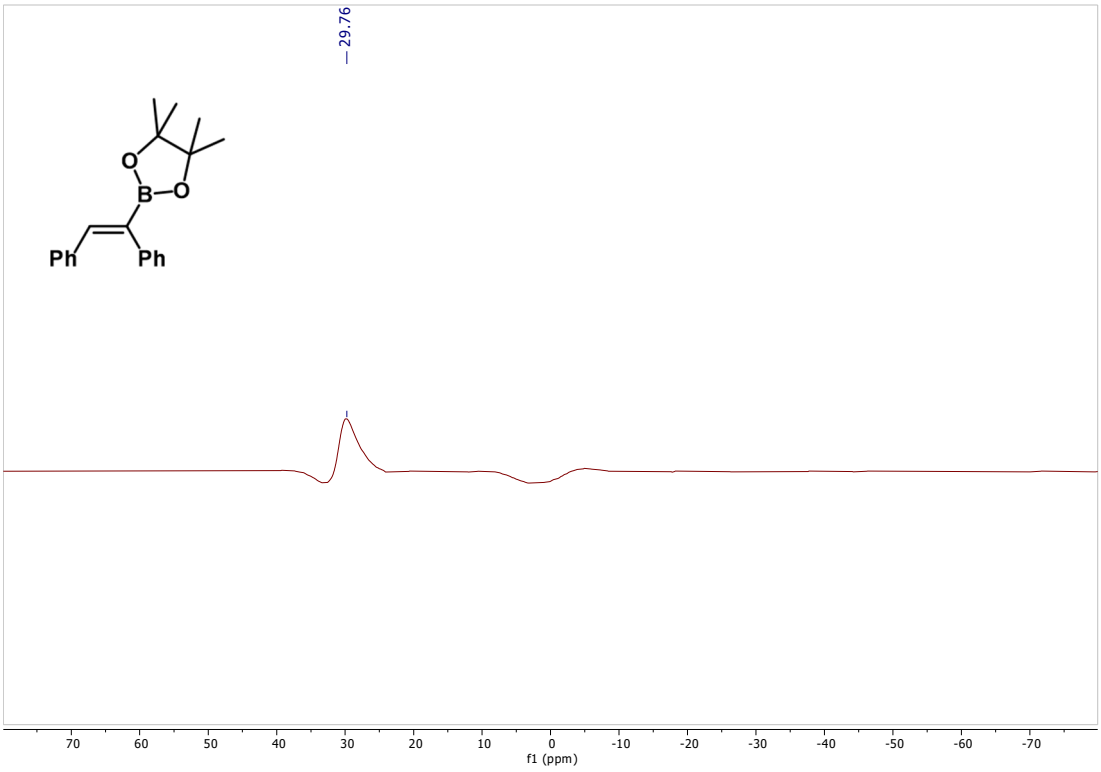


Fig. 32. ^{11}B NMR spectrum (**$CDCl_3$**, **25** °C) of (2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

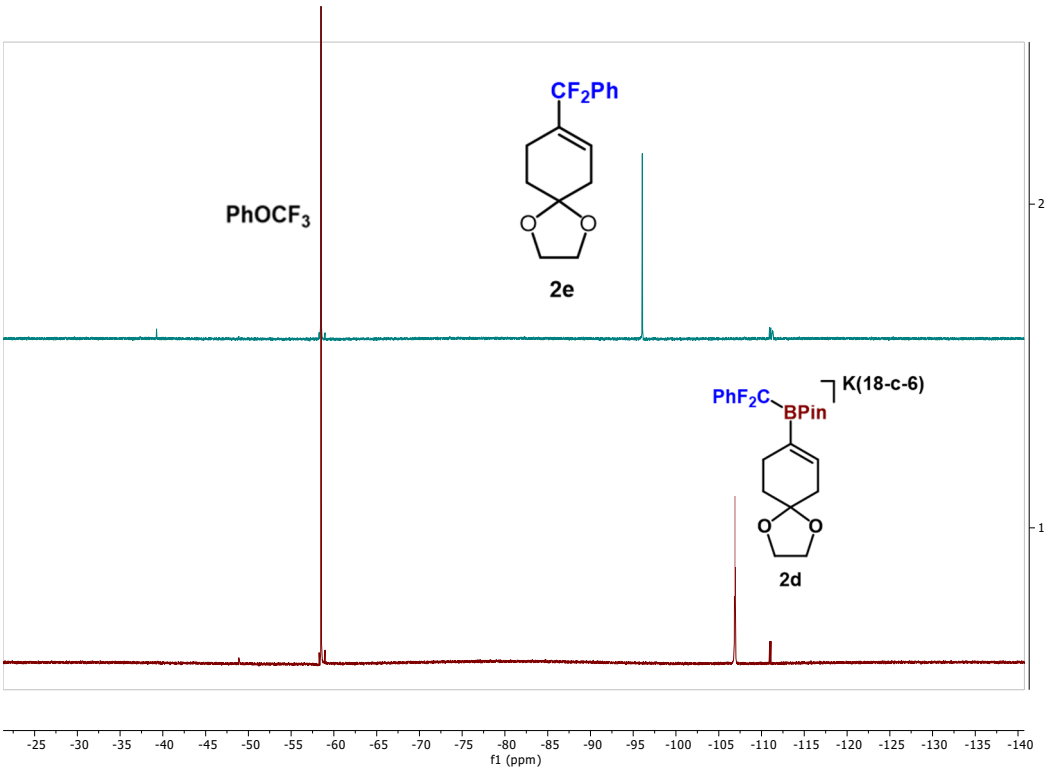


Fig. S33. Stacked ^{19}F NMR spectrum (**$THF\text{-}H_8$**, **25** °C) of the reaction mixture of **2e** and **2d**.

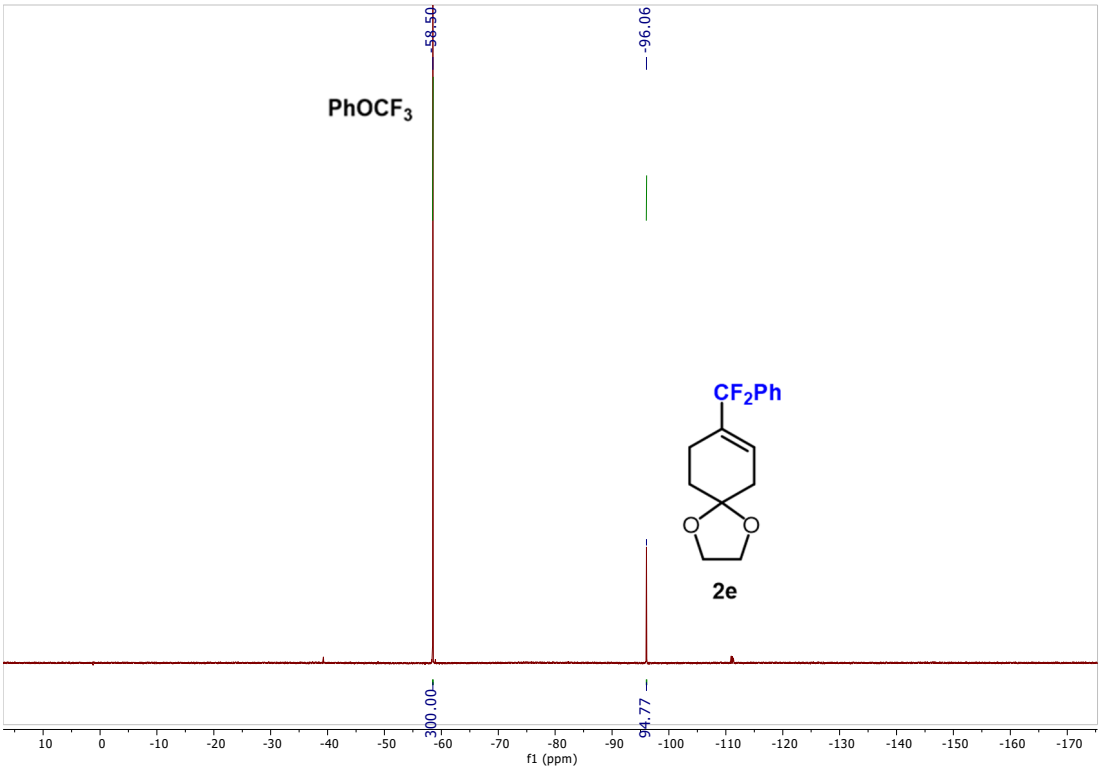


Fig. S34. ^{19}F NMR spectrum (**THF-H$_8$**, **25** °C) of the reaction mixture of **2e**.

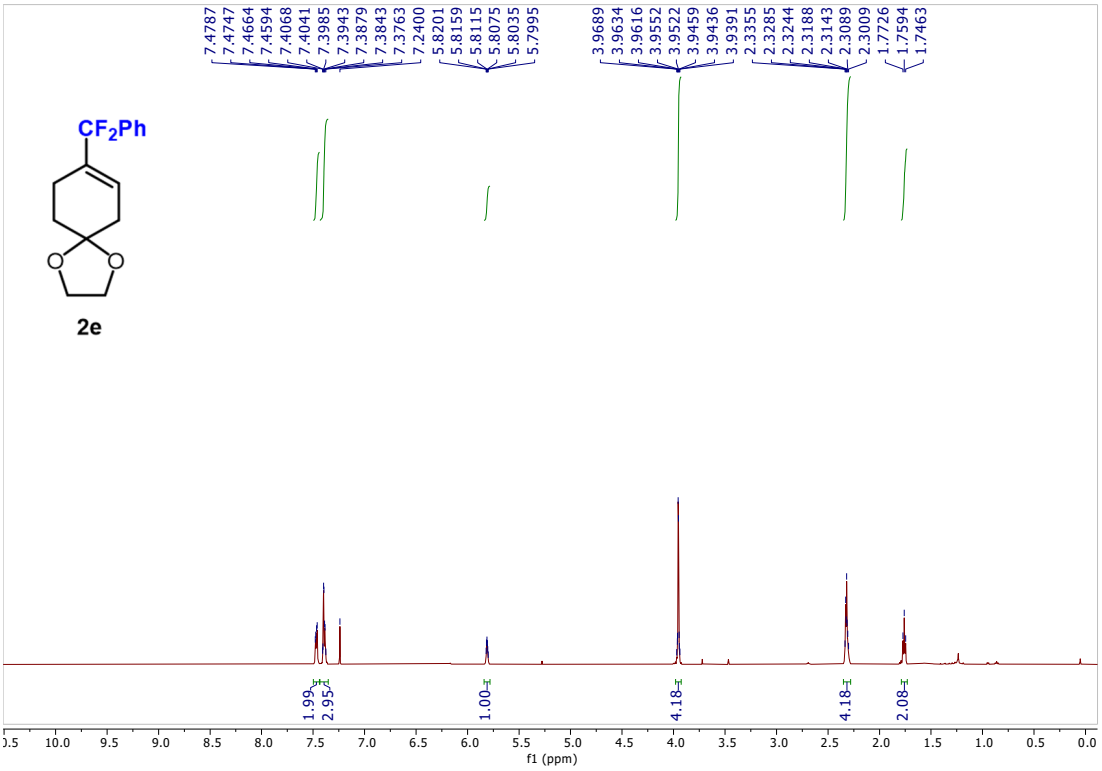


Fig. S35. ^{1}H NMR spectrum (**CDCl$_3$**, **25** °C) of **2e**.

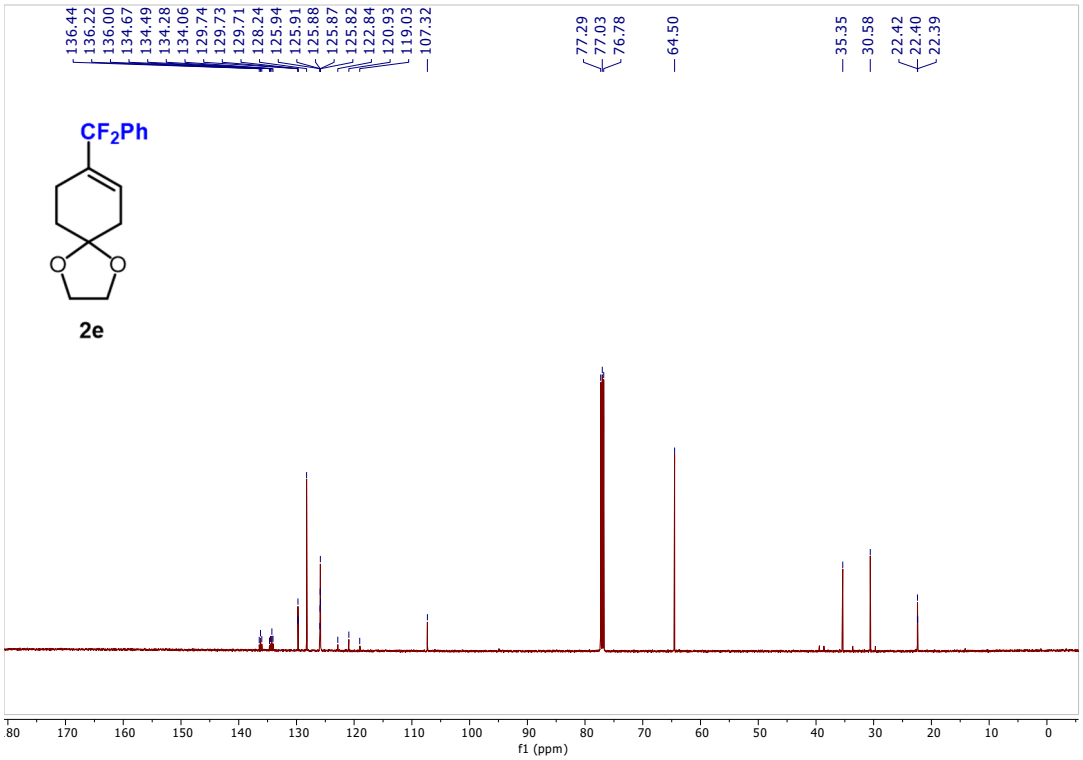


Fig. S36. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **2e**.

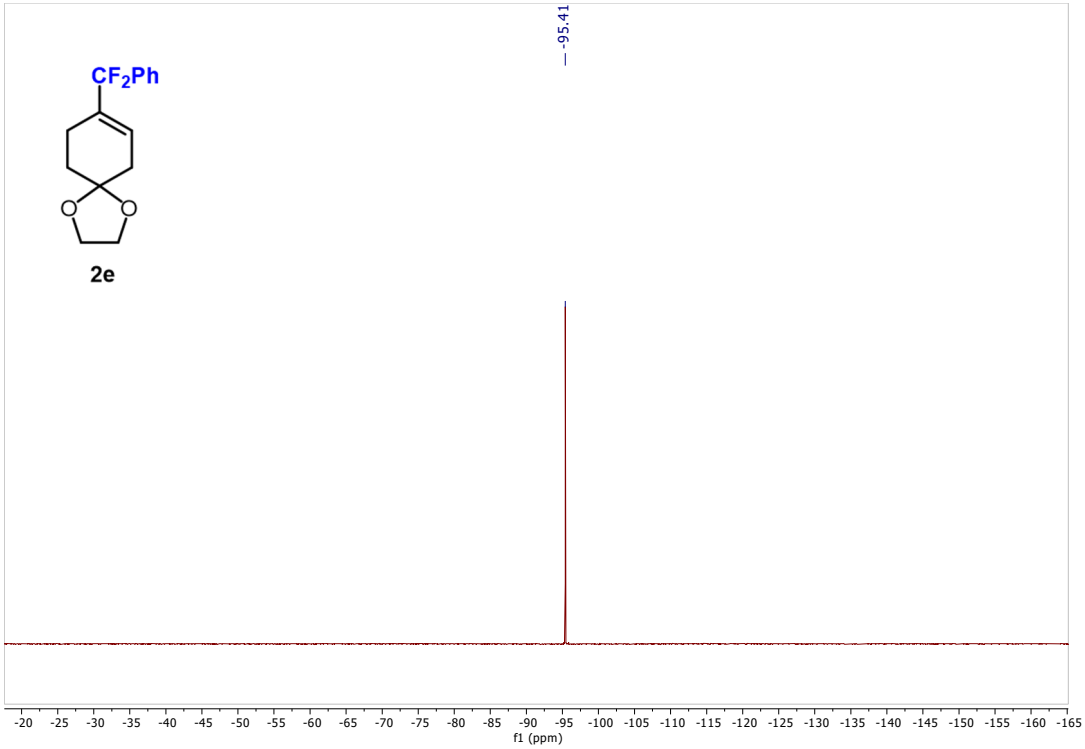


Fig. S37. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **2e**.

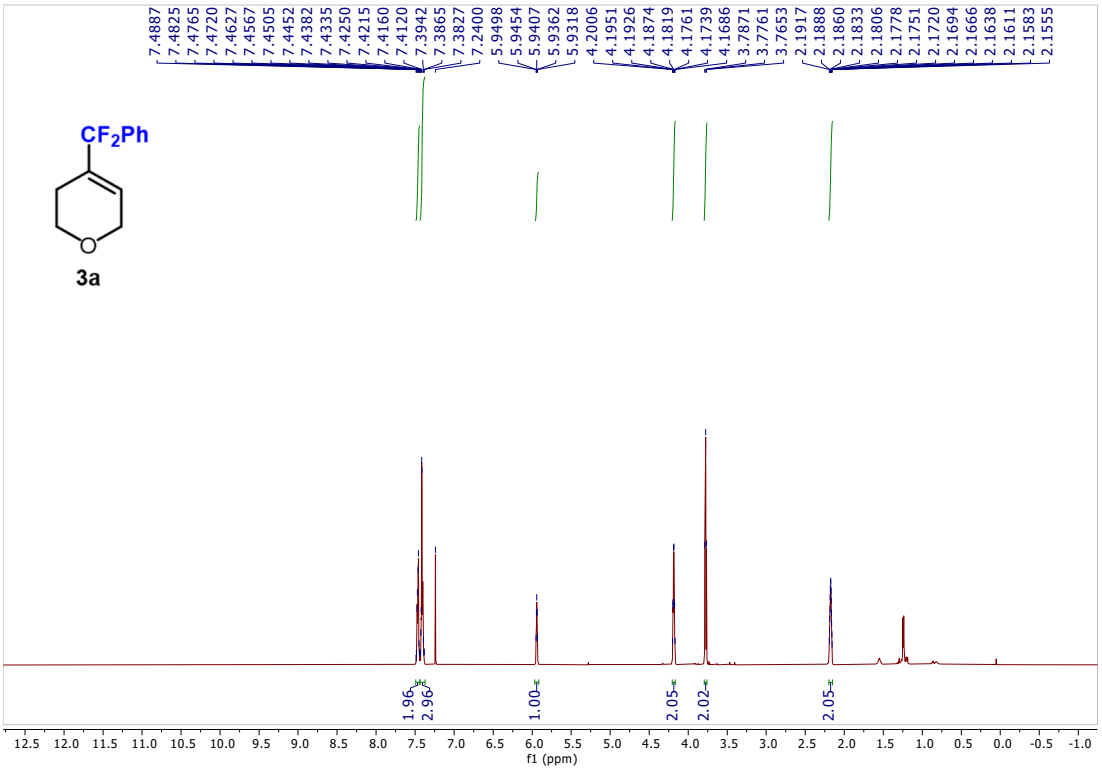


Fig. S38. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **3a**.

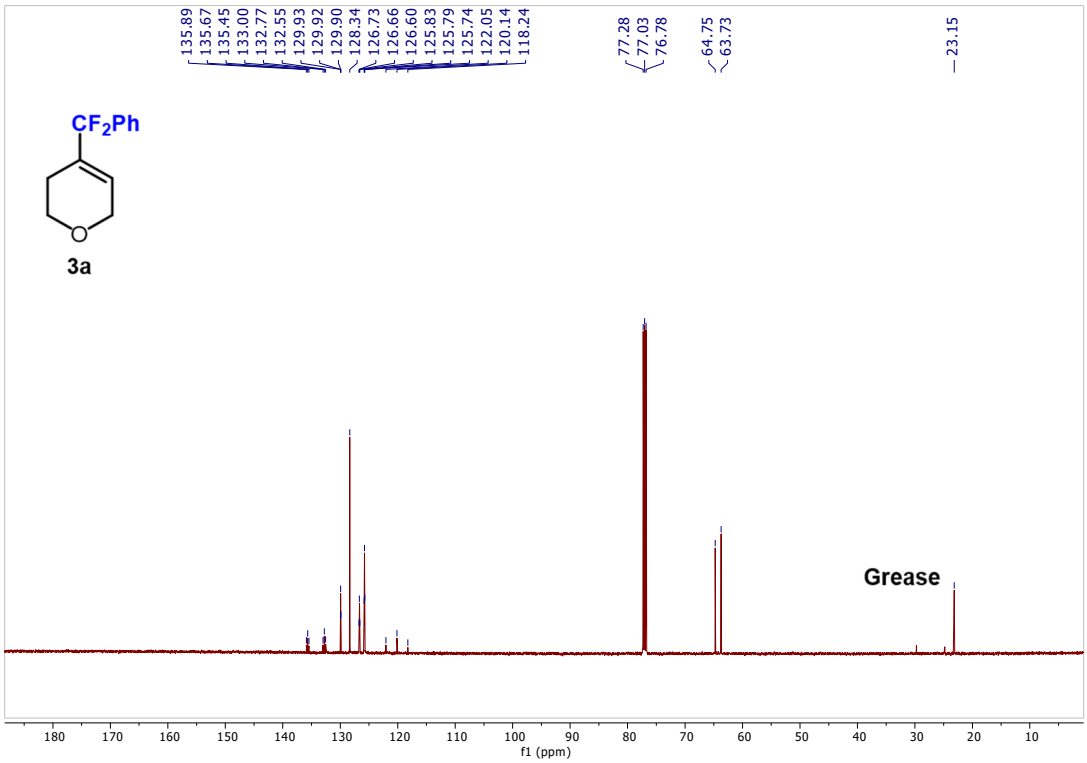


Fig. S39. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **3a**.

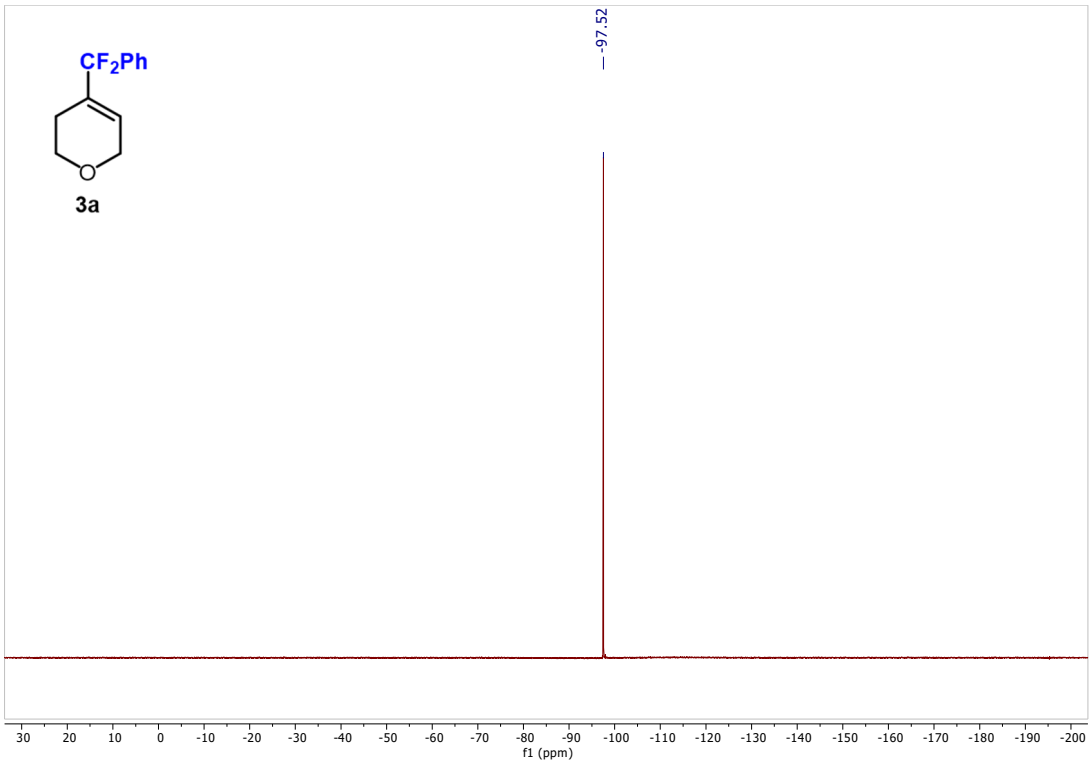


Fig. S40. ^{19}F NMR spectrum (**$CDCl_3$, 25** °C) of **3a**.

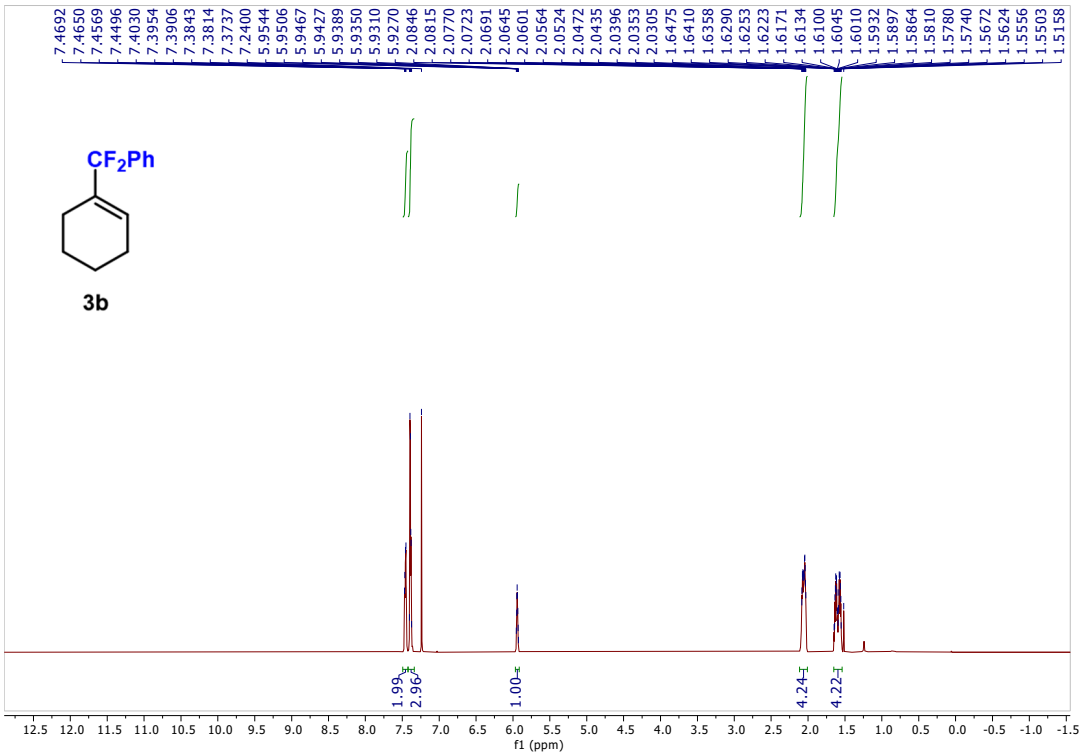


Fig. S41. ^{1}H NMR spectrum (**$CDCl_3$, 25** °C) of **3b**.

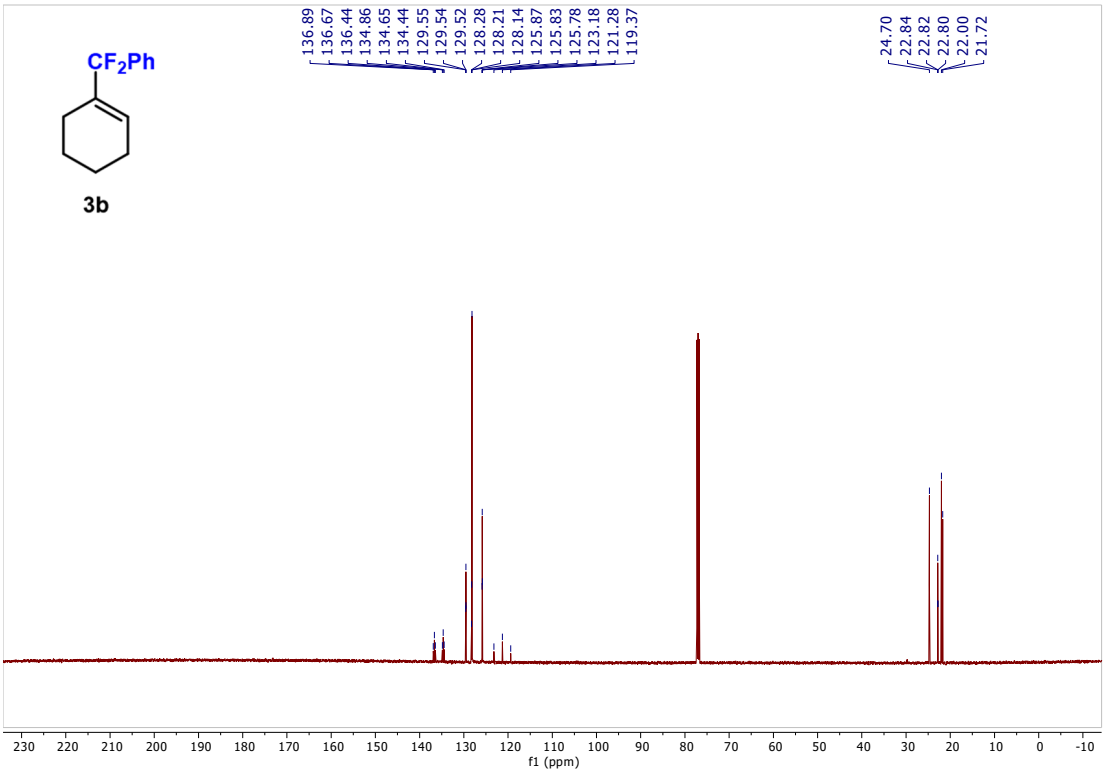


Fig. S42. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **3b**.

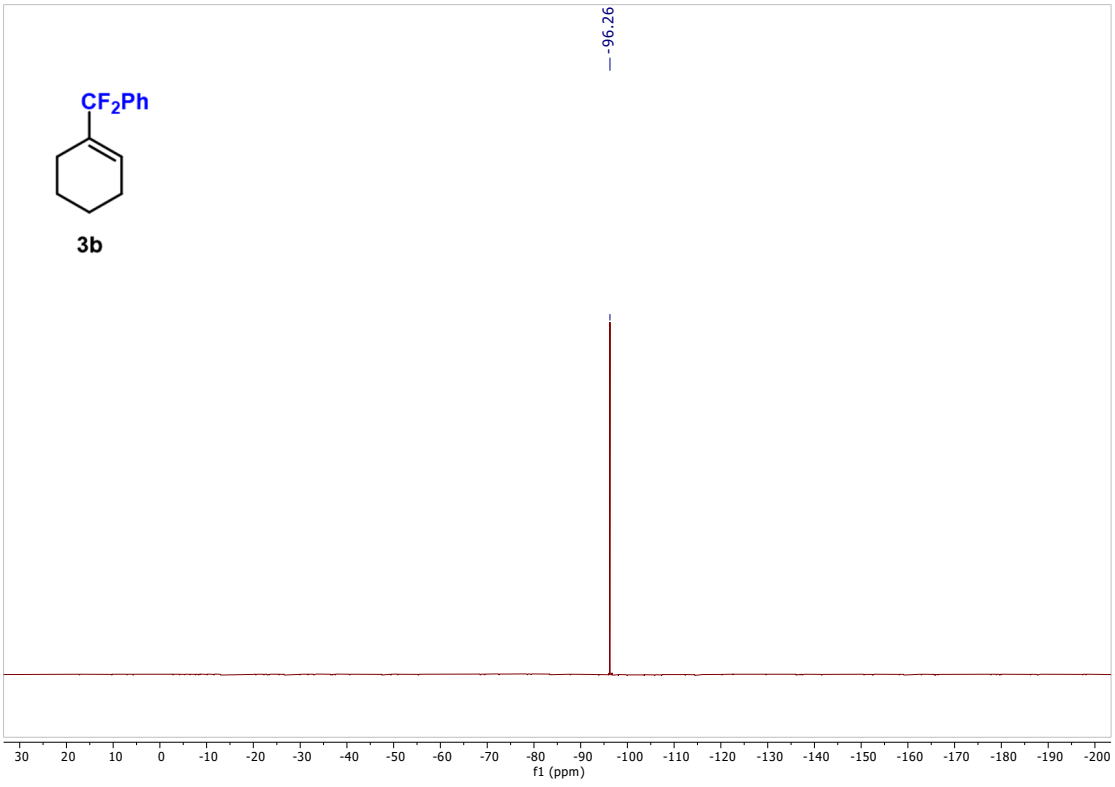


Fig. S43. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **3b**.

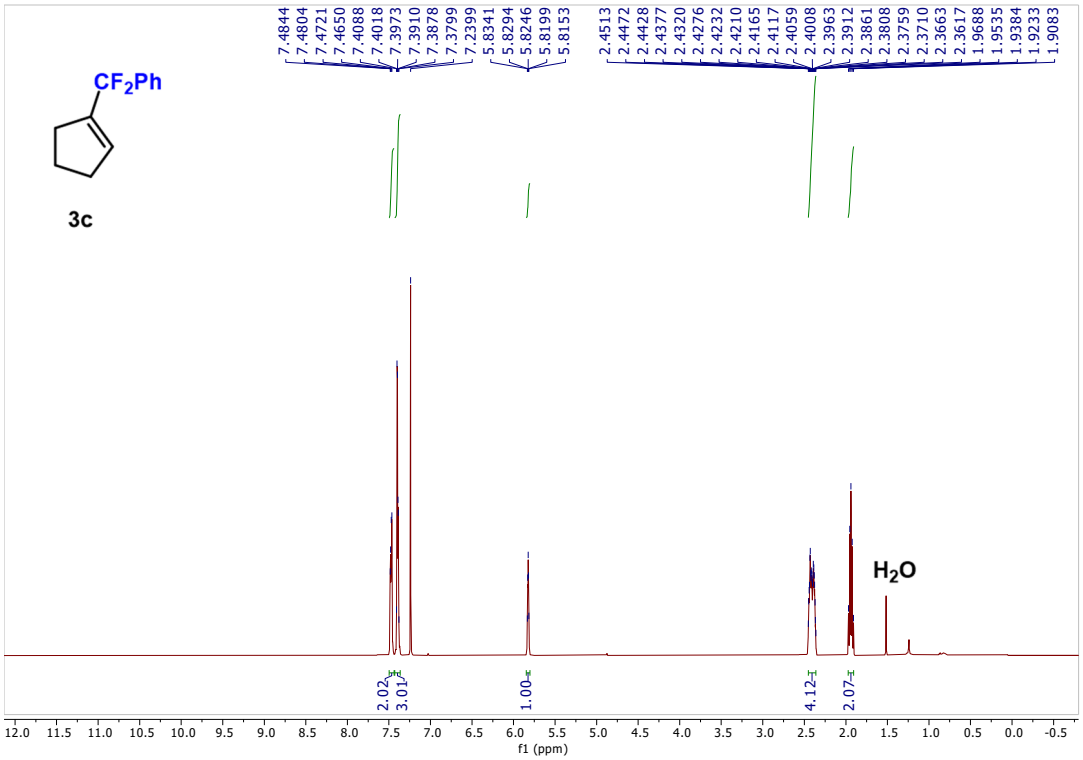


Fig. S44. ^{1}H NMR spectrum (**$CDCl_3$, 25** °C) of **3c**.

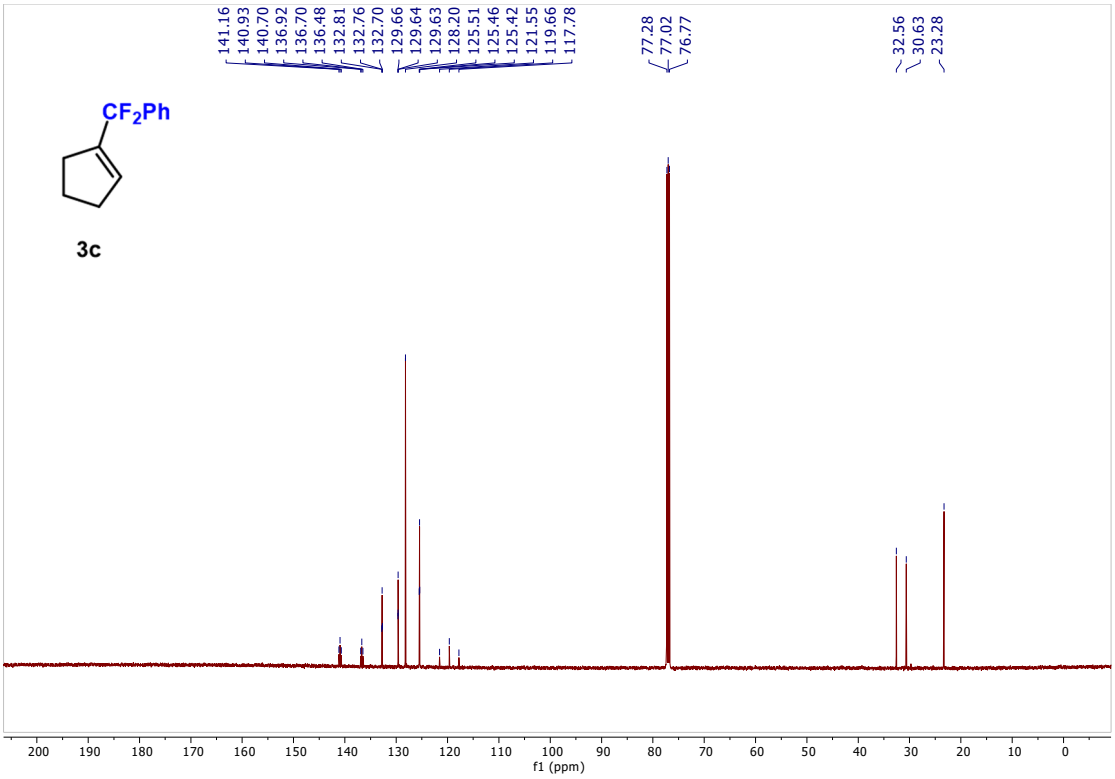


Fig. S45. ^{13}C NMR spectrum (**$CDCl_3$, 25** °C) of **3c**.

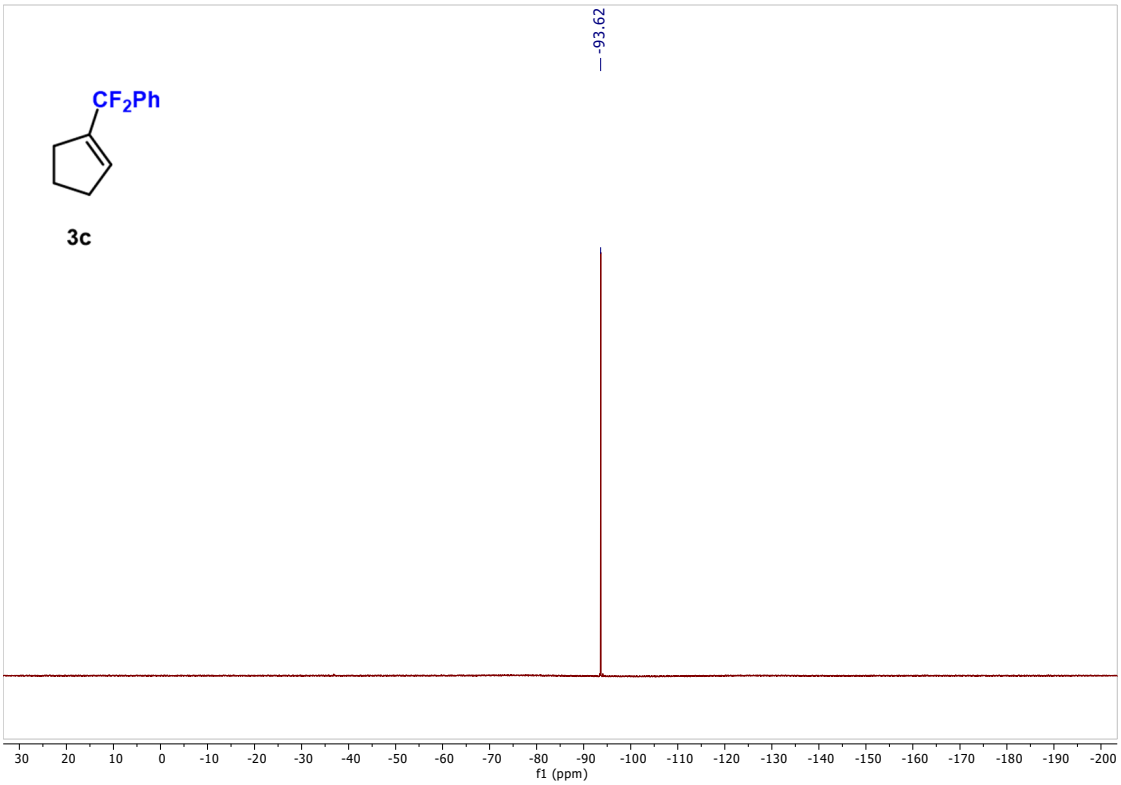


Fig. S46. ^{19}F NMR spectrum (**$CDCl_3$, 25** °C) of **3c**.

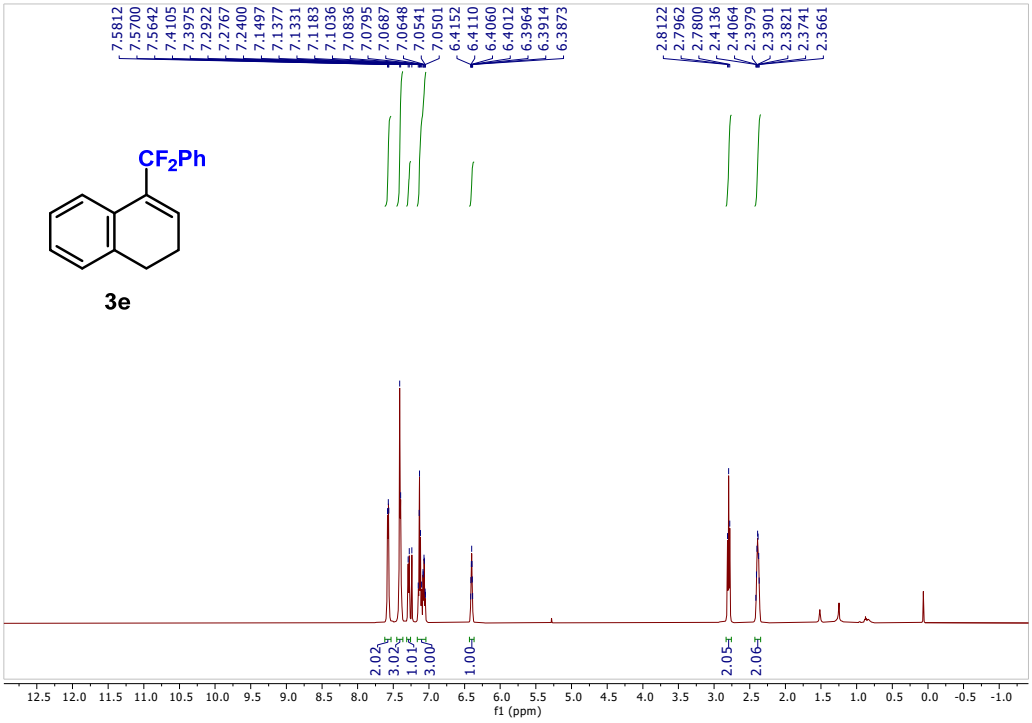


Fig. S47. ^{1}H NMR spectrum (**$CDCl_3$, 25** °C) of **3e**.

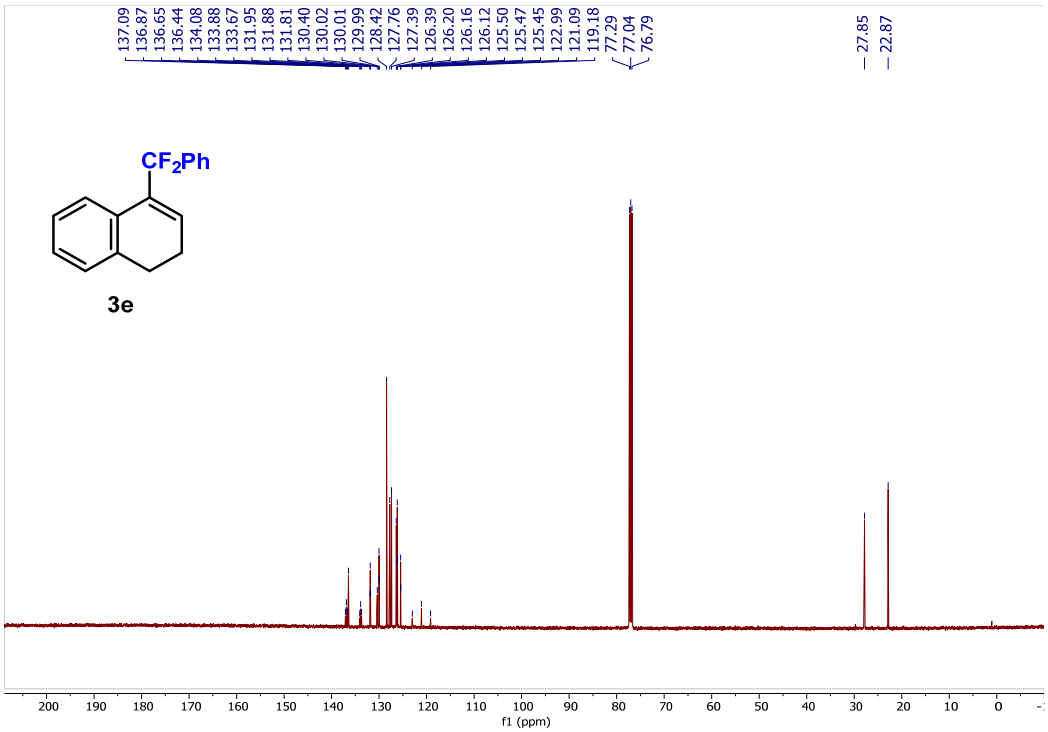


Fig. S48. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **3e**.

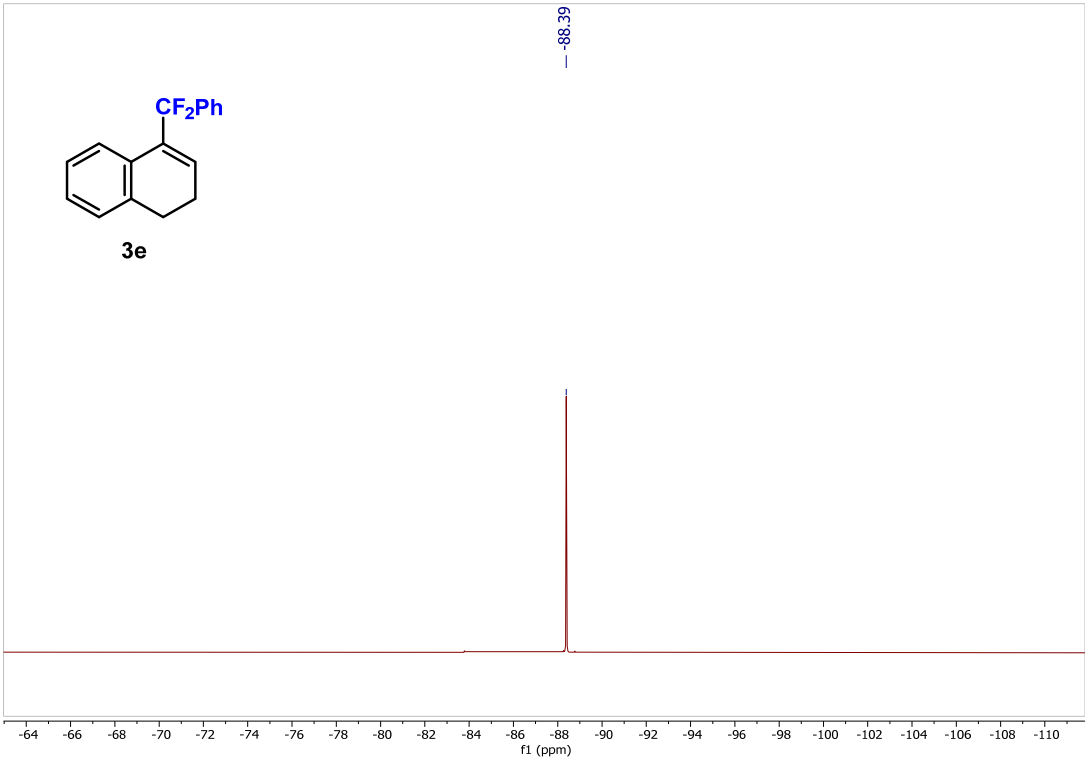


Fig. S49. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **3e**.

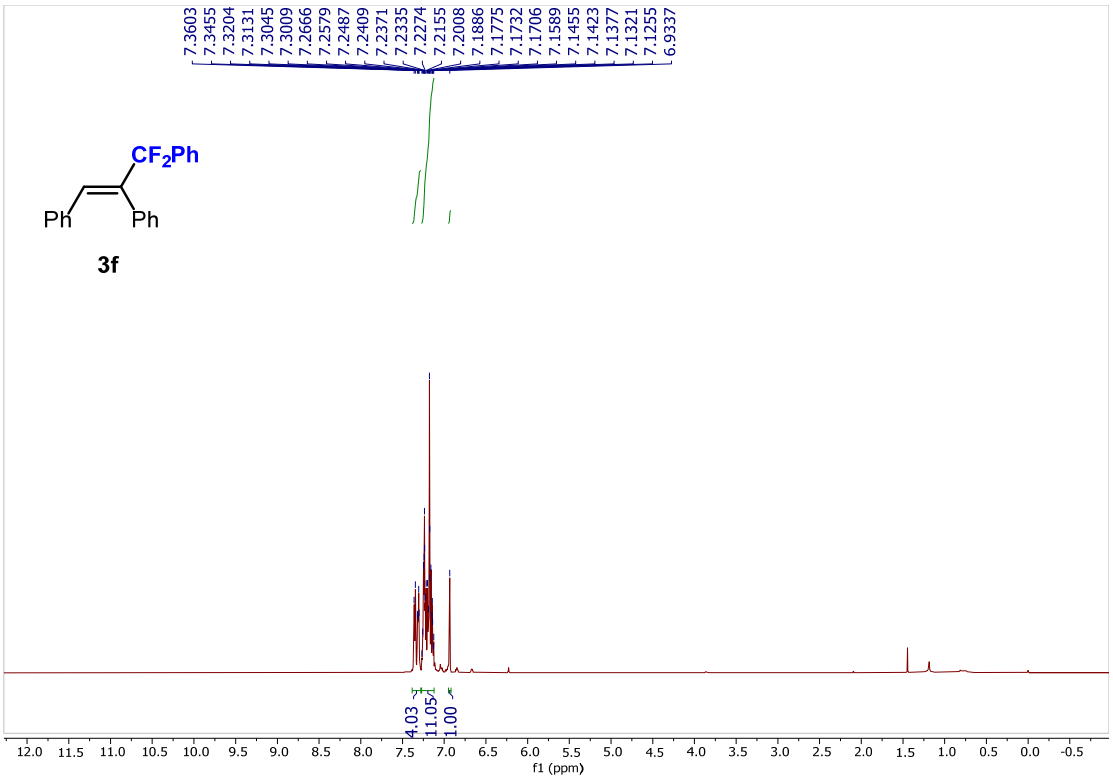


Fig. S50. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **3f**.

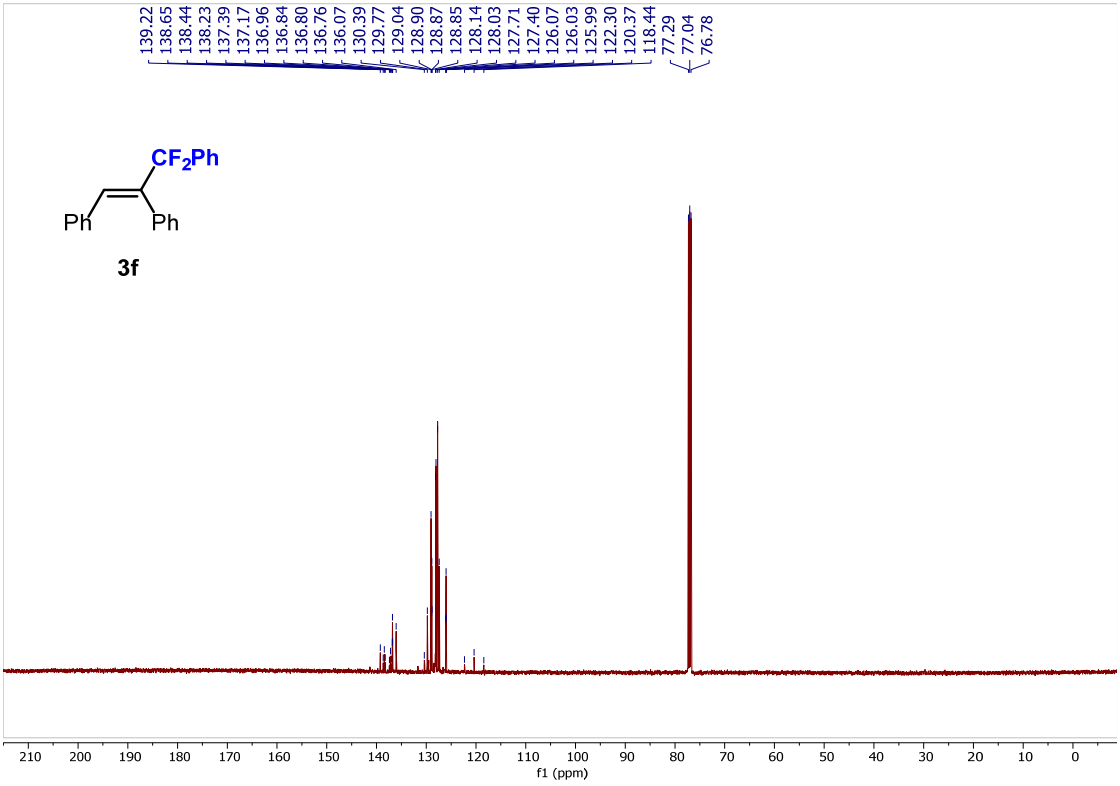


Fig. S51. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **3f**.

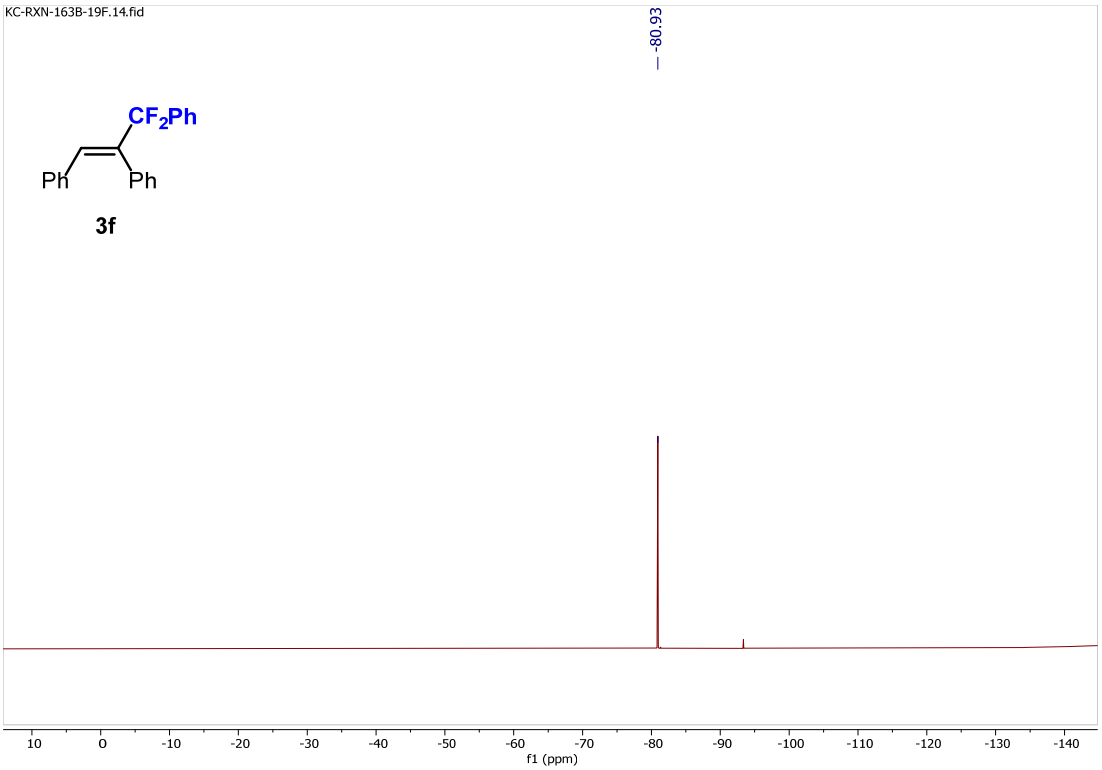


Fig. S52. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **3f**.

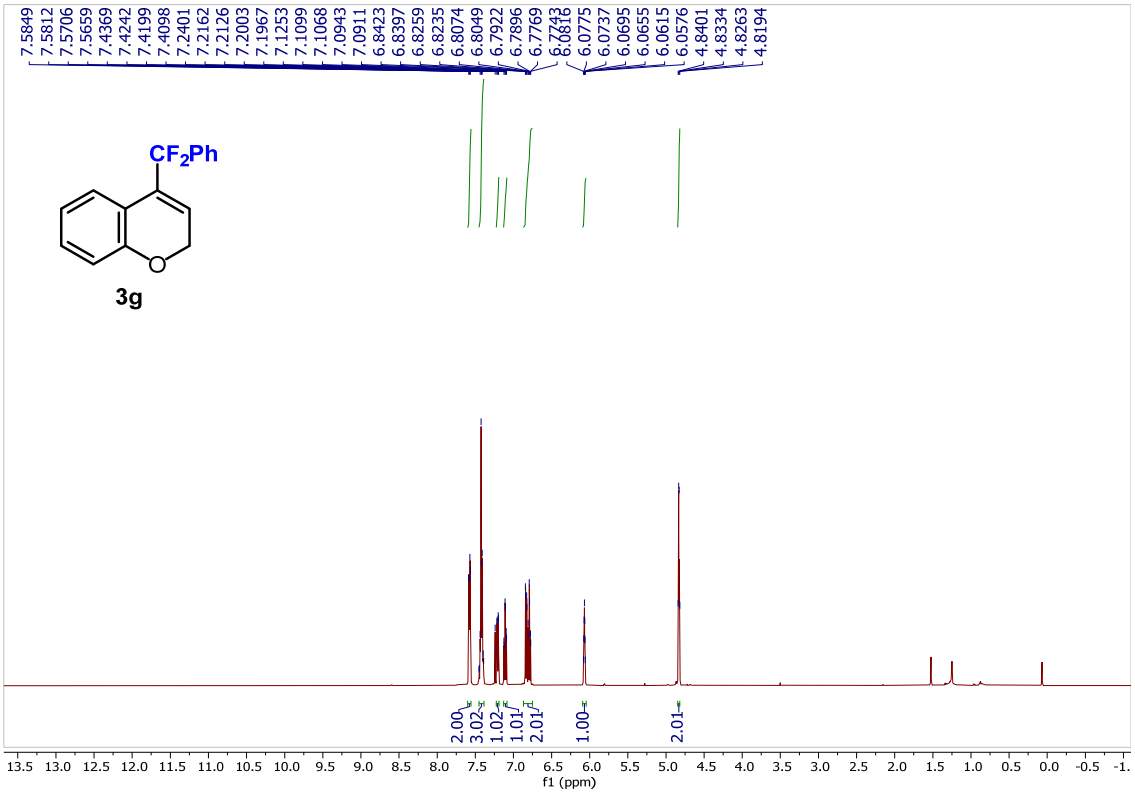


Fig. S53. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **3g**.

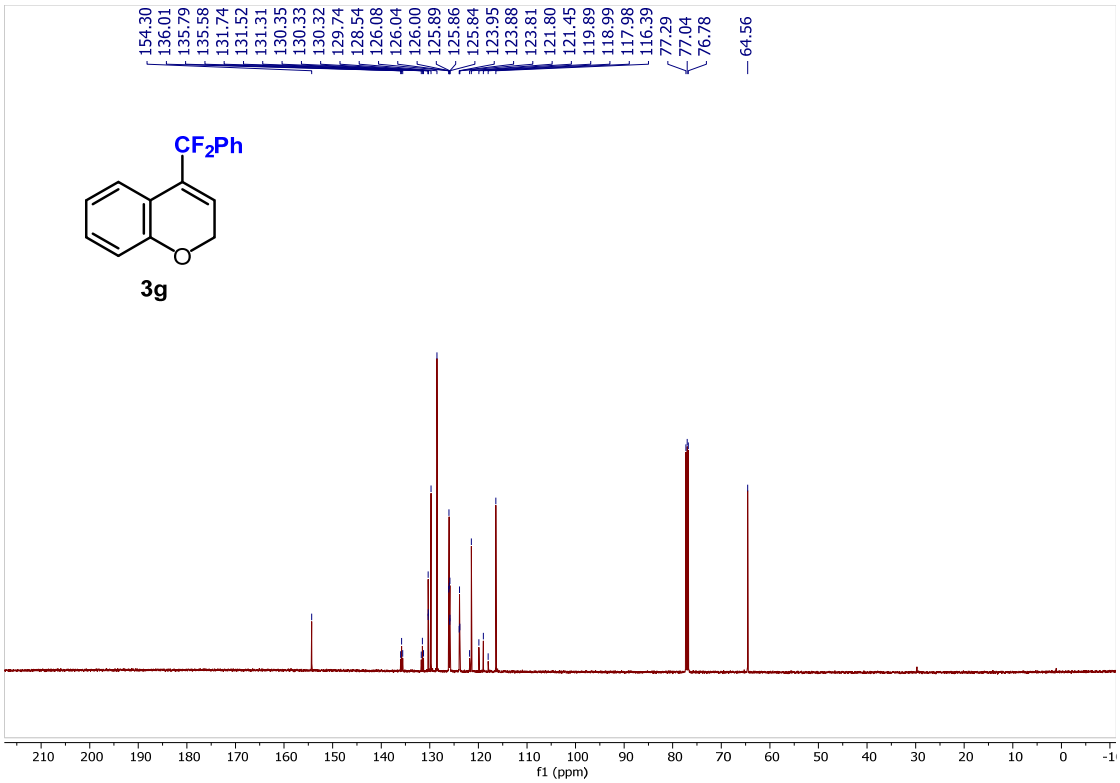


Fig. S54. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **3g**.

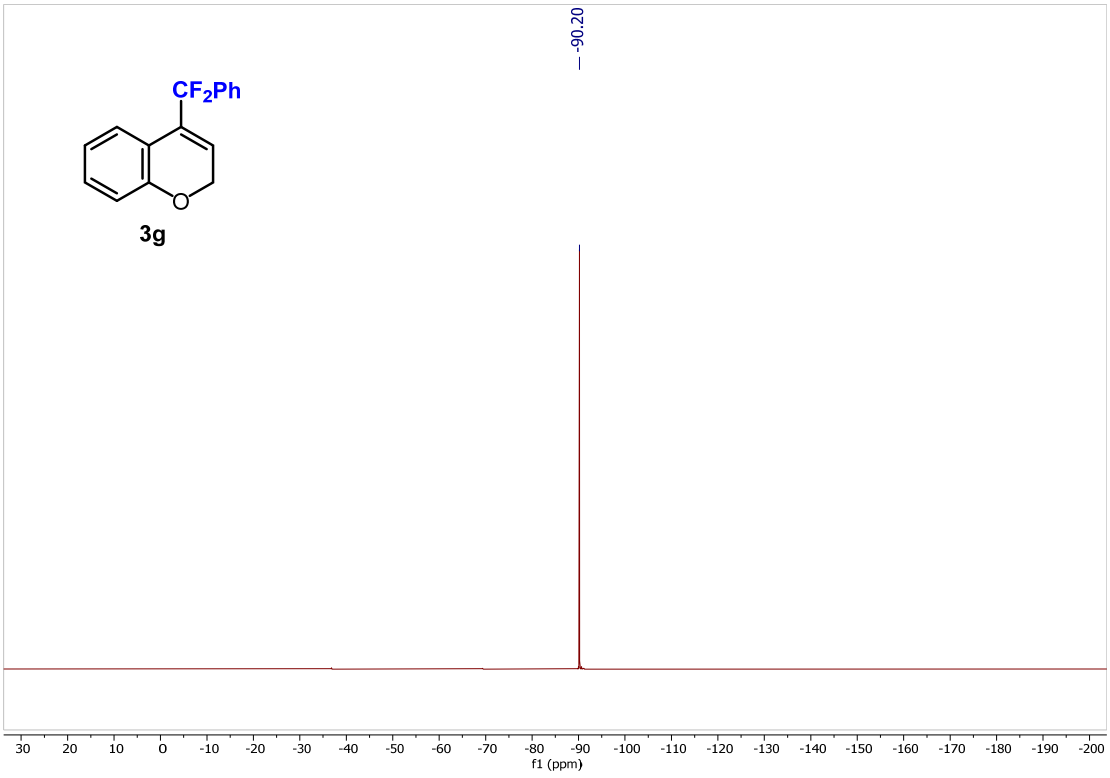


Fig. S55. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **3g**.

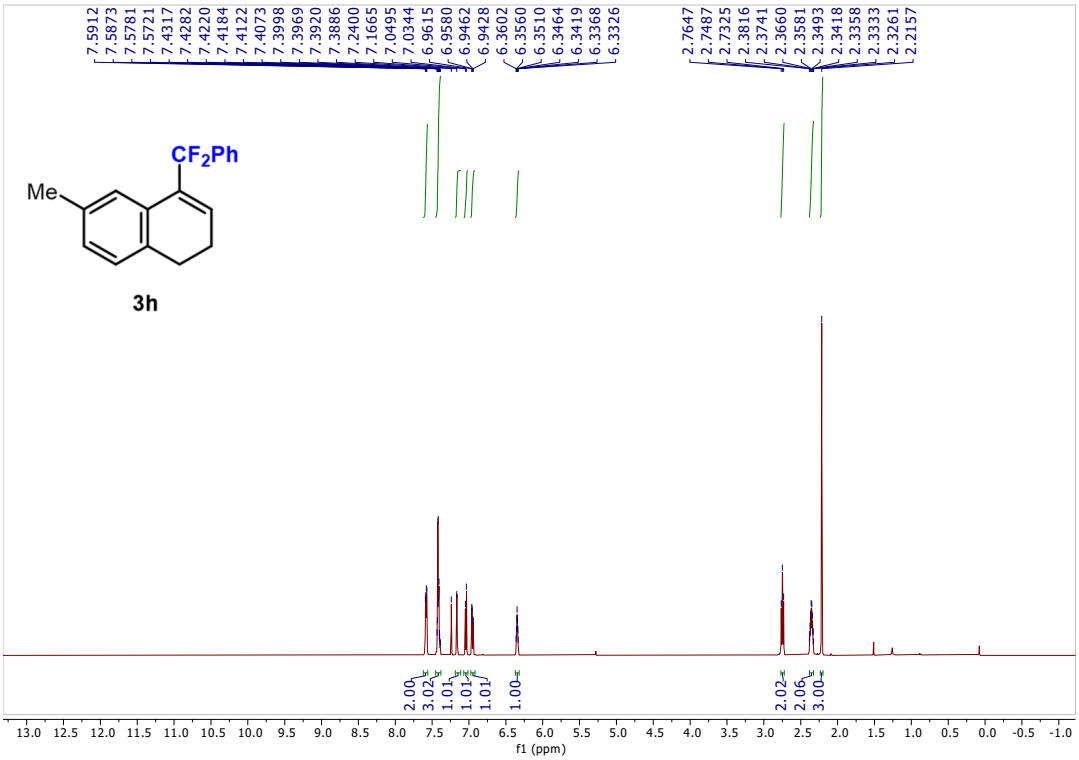


Fig. S56. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **3h**.

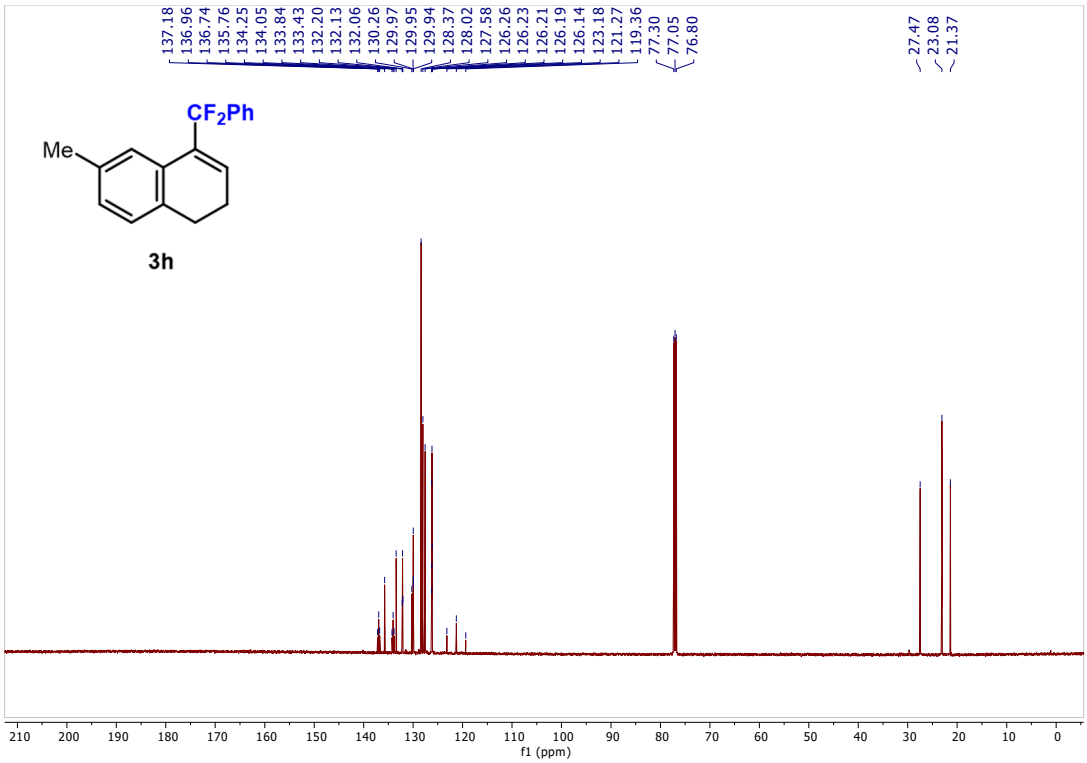


Fig. S57. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **3h**.

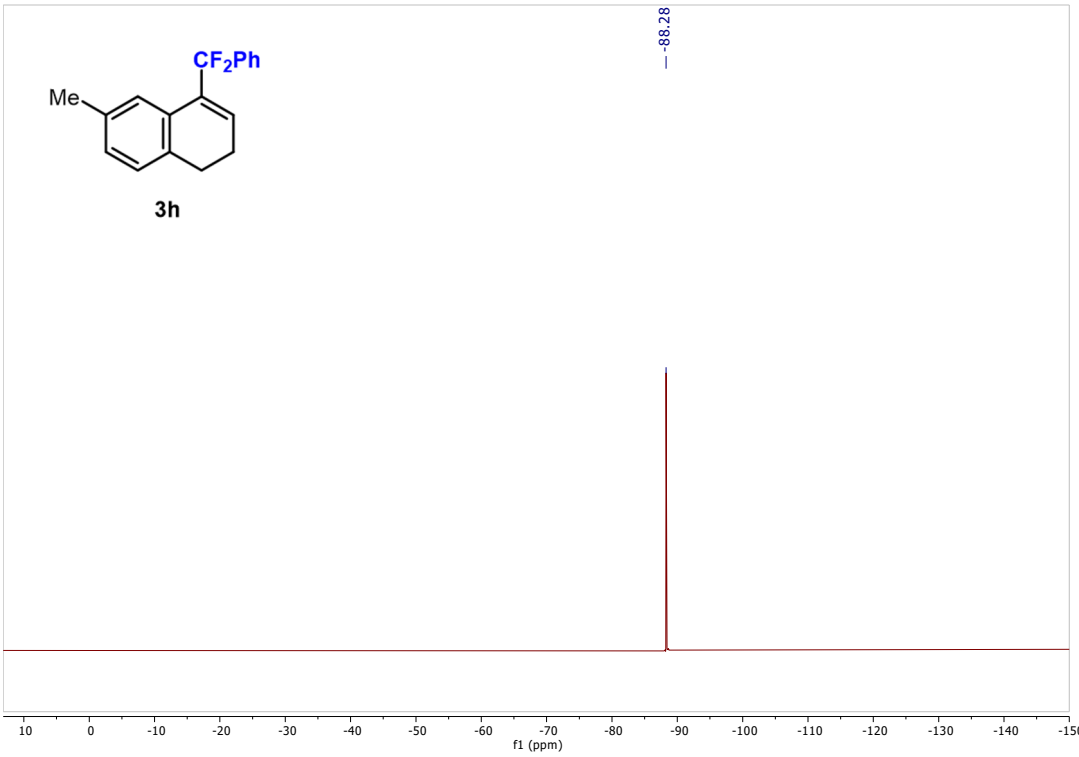


Fig. S58. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **3h**.

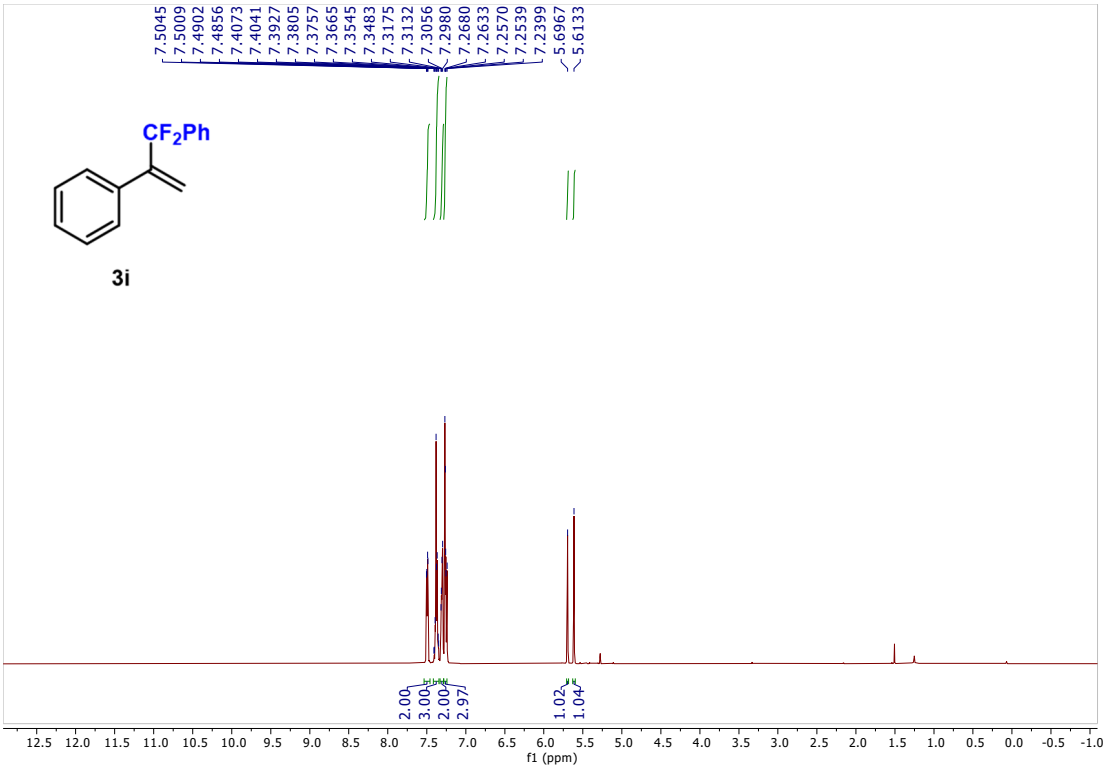


Fig. S59. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **3i**.

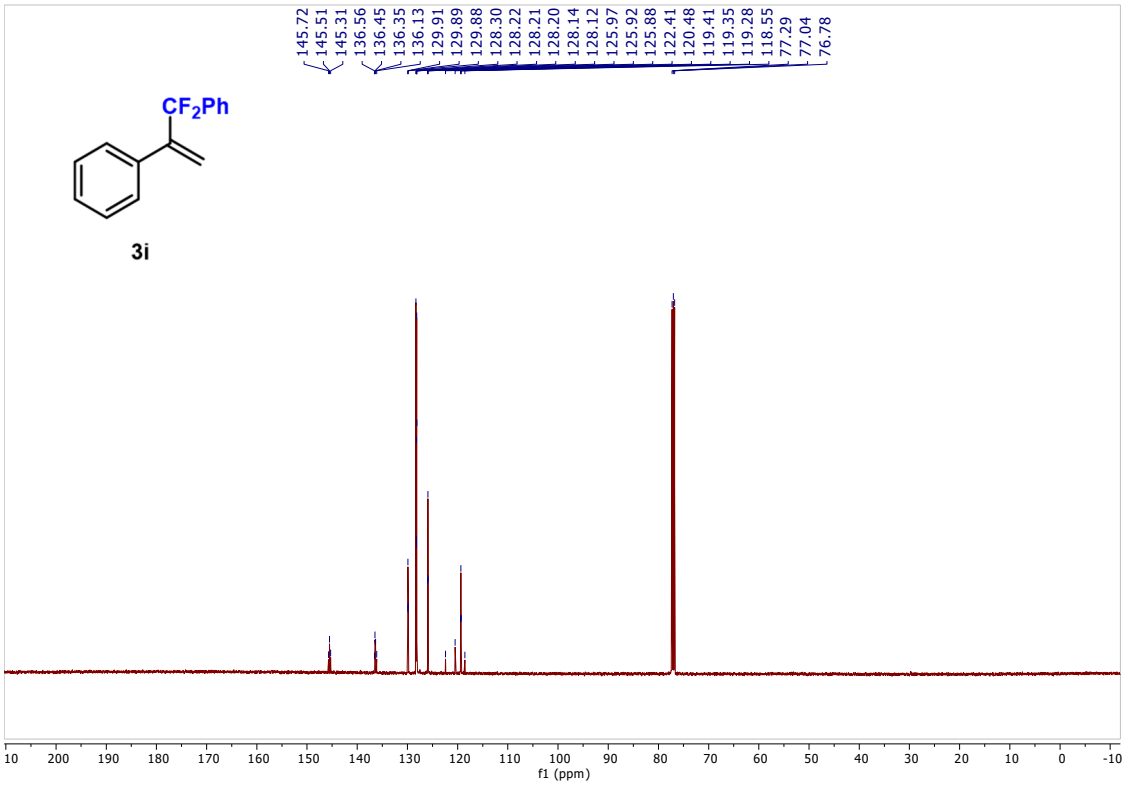


Fig. S60. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **3i**.

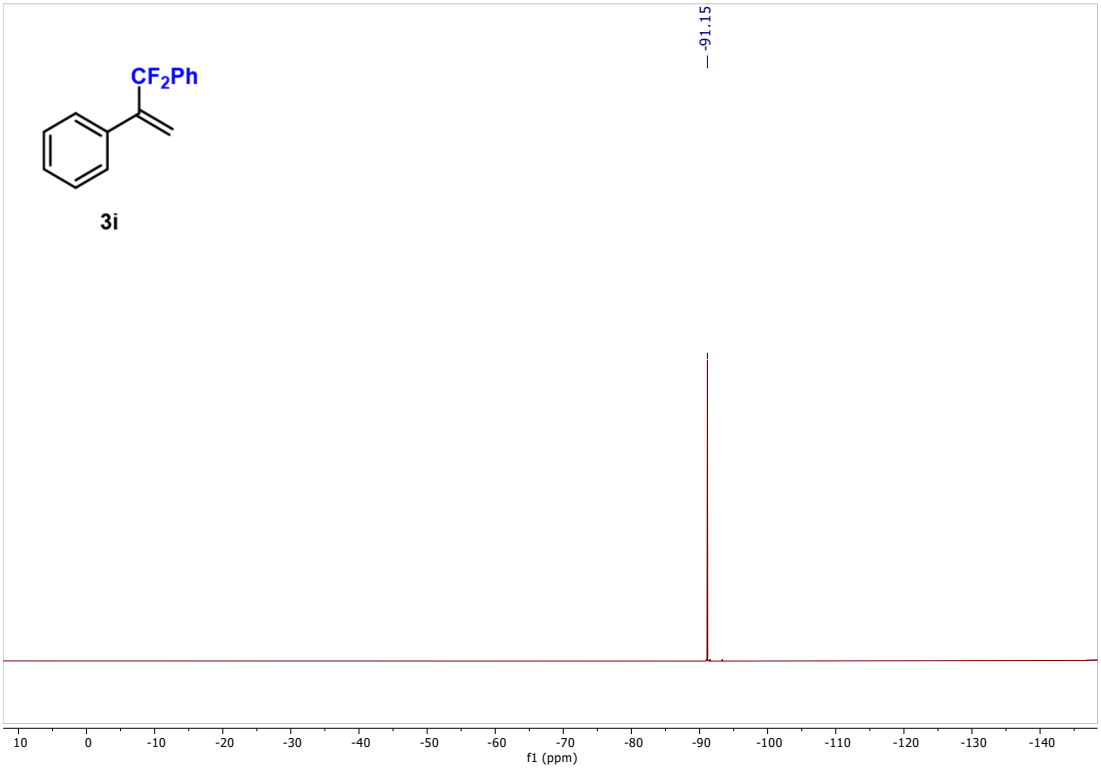


Fig. S61. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **3i**.

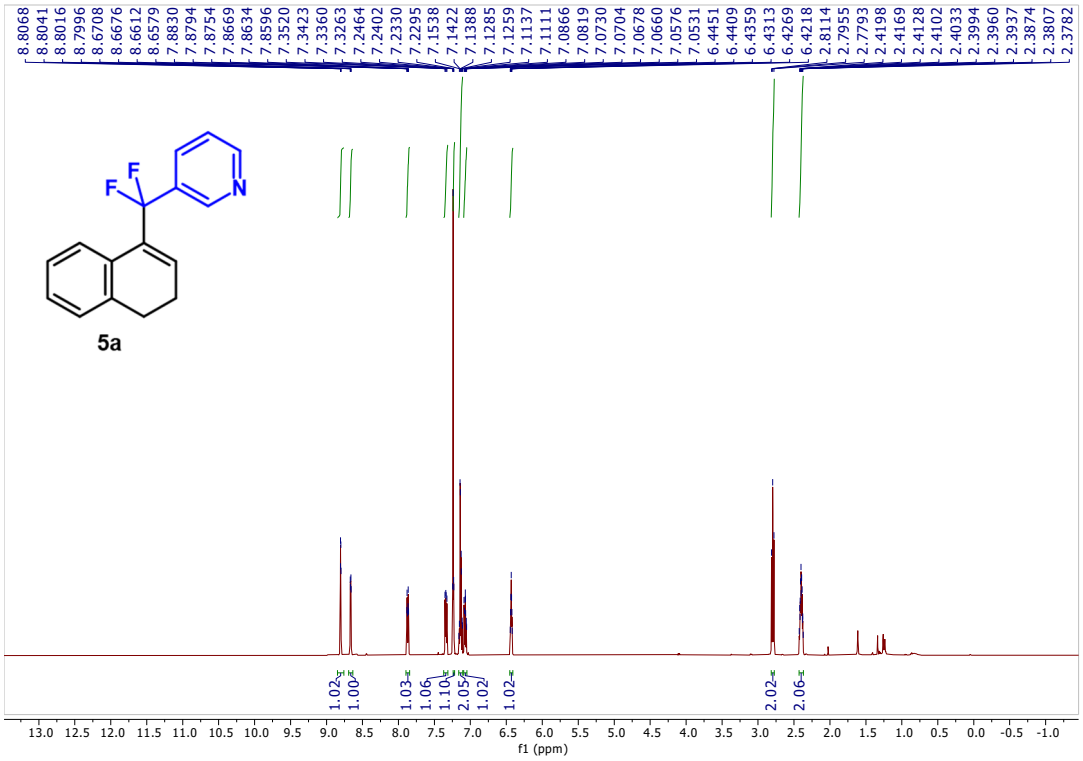


Fig. S62. ^{1}H NMR spectrum (**$CDCl_3$, 25** °C) of **5a**.

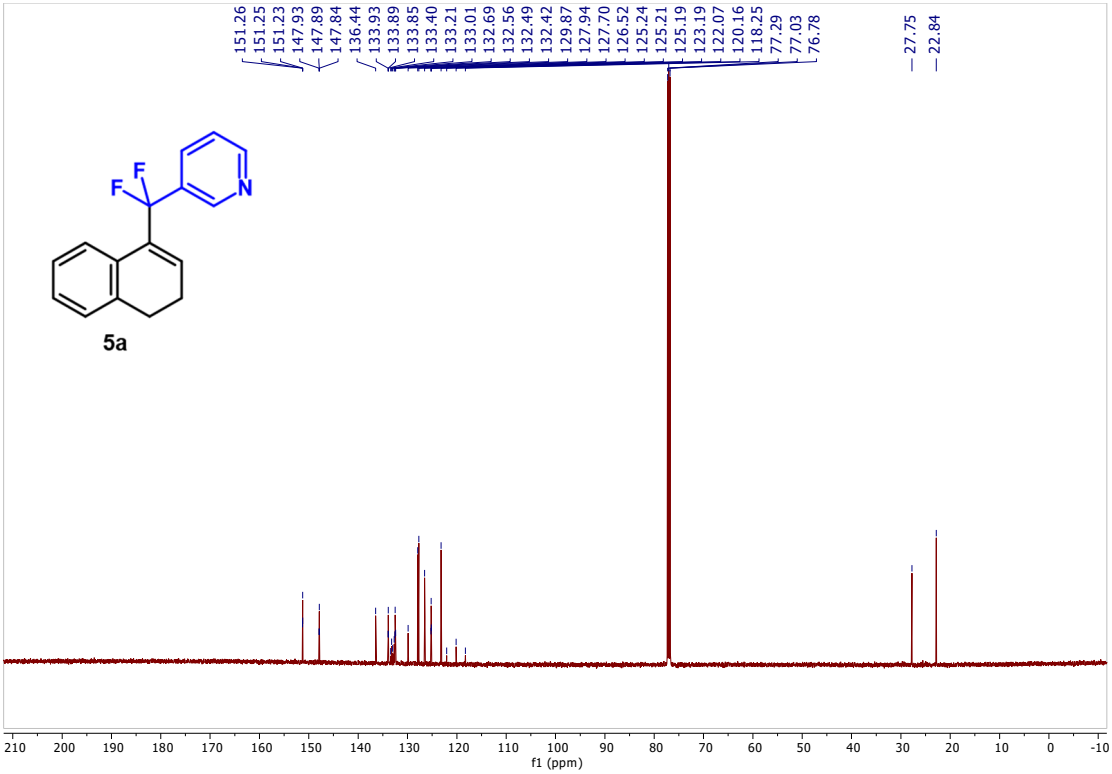


Fig. S63. ^{13}C NMR spectrum (**$CDCl_3$, 25** °C) of **5a**.

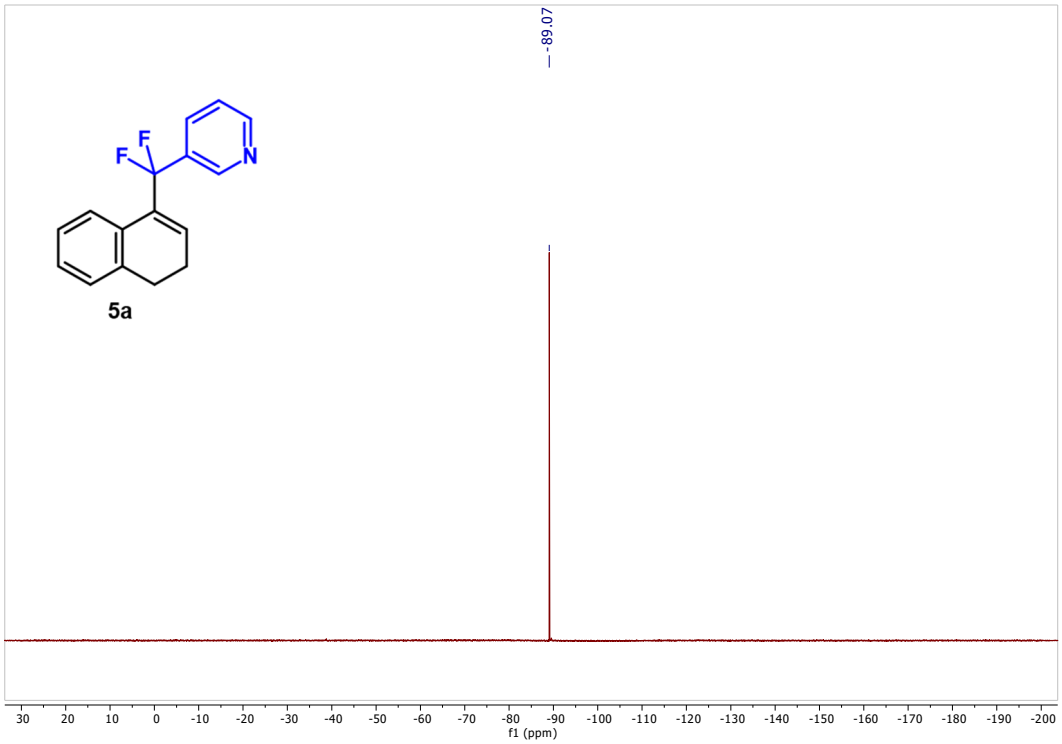


Fig. S64. ^{19}F NMR spectrum (**$CDCl_3$, 25** °C) of **5a**.

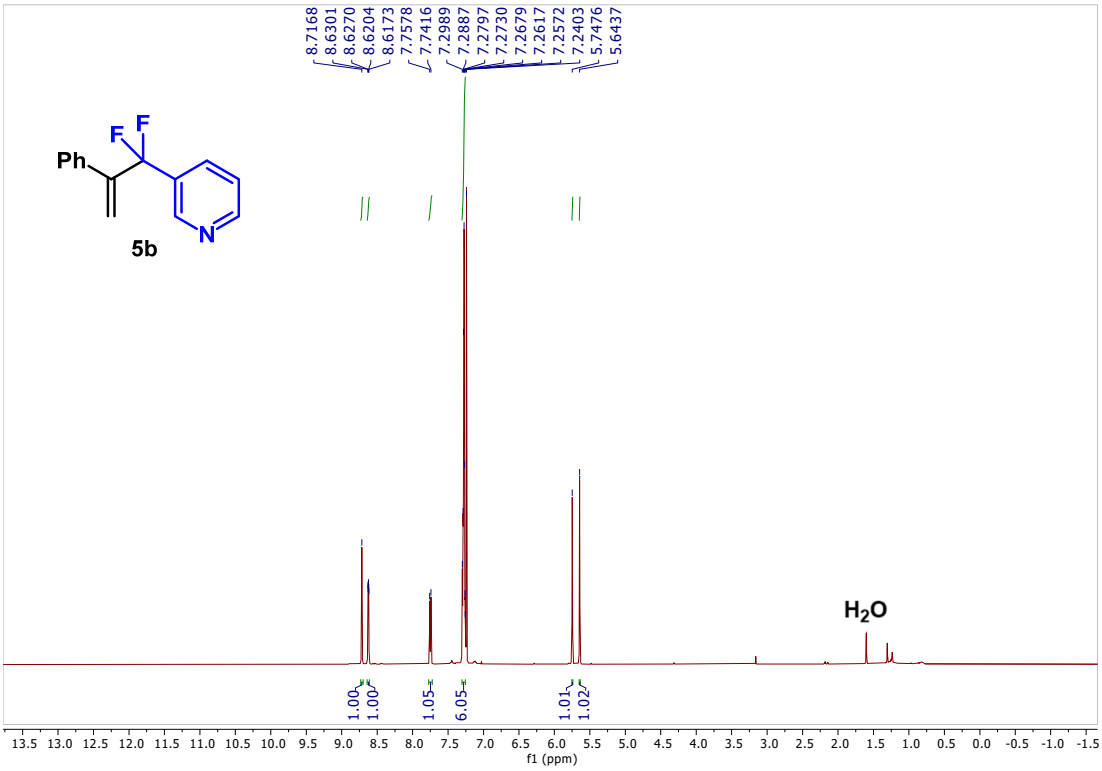


Fig. S65. ^{1}H NMR spectrum (**$CDCl_3$, 25** °C) of **5b**.

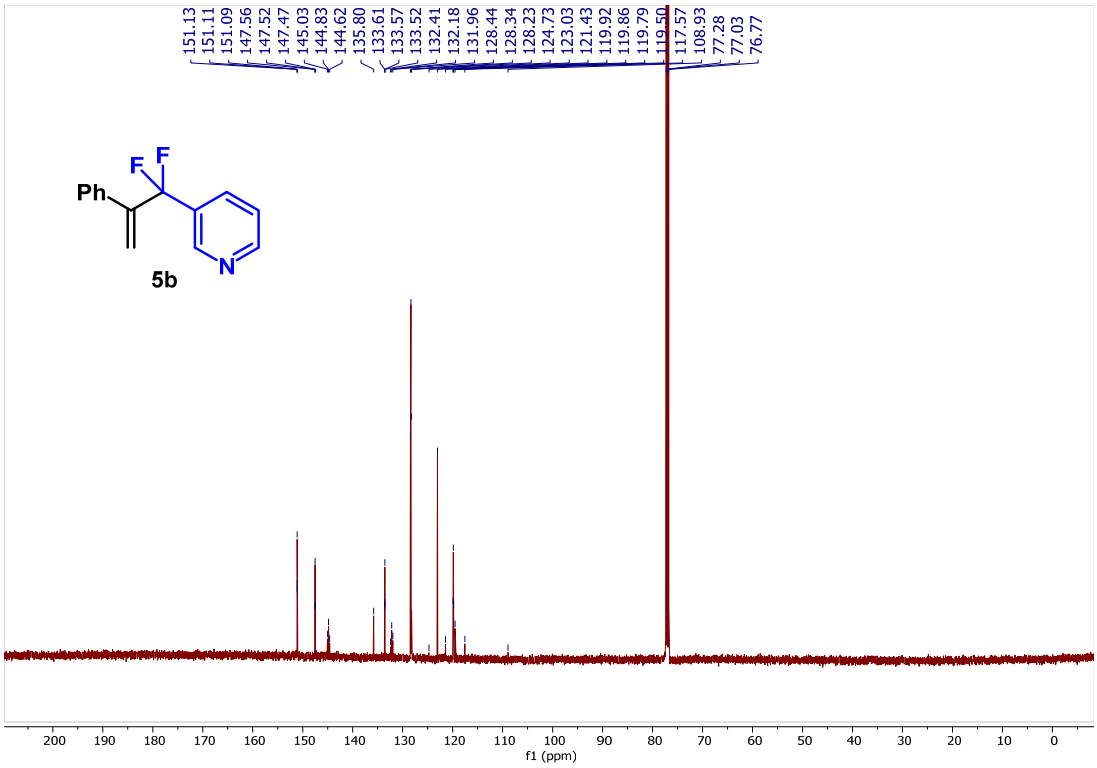


Fig. S66. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **5b**.

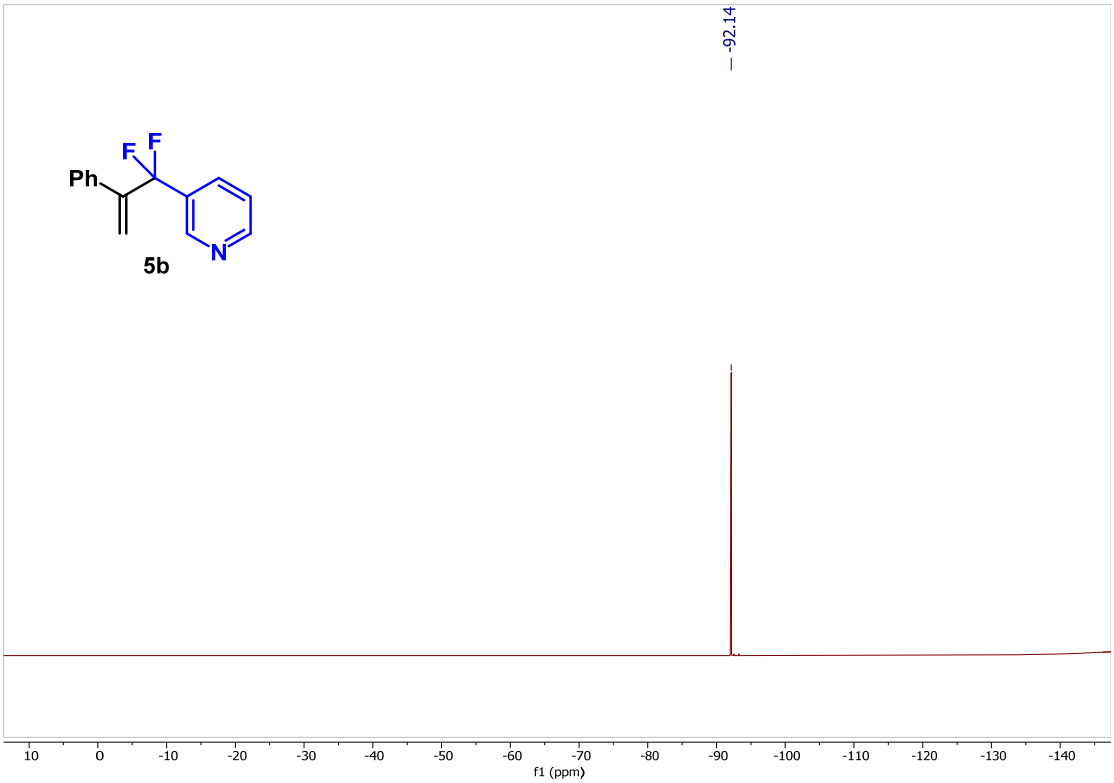


Fig. S67. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **5b**.

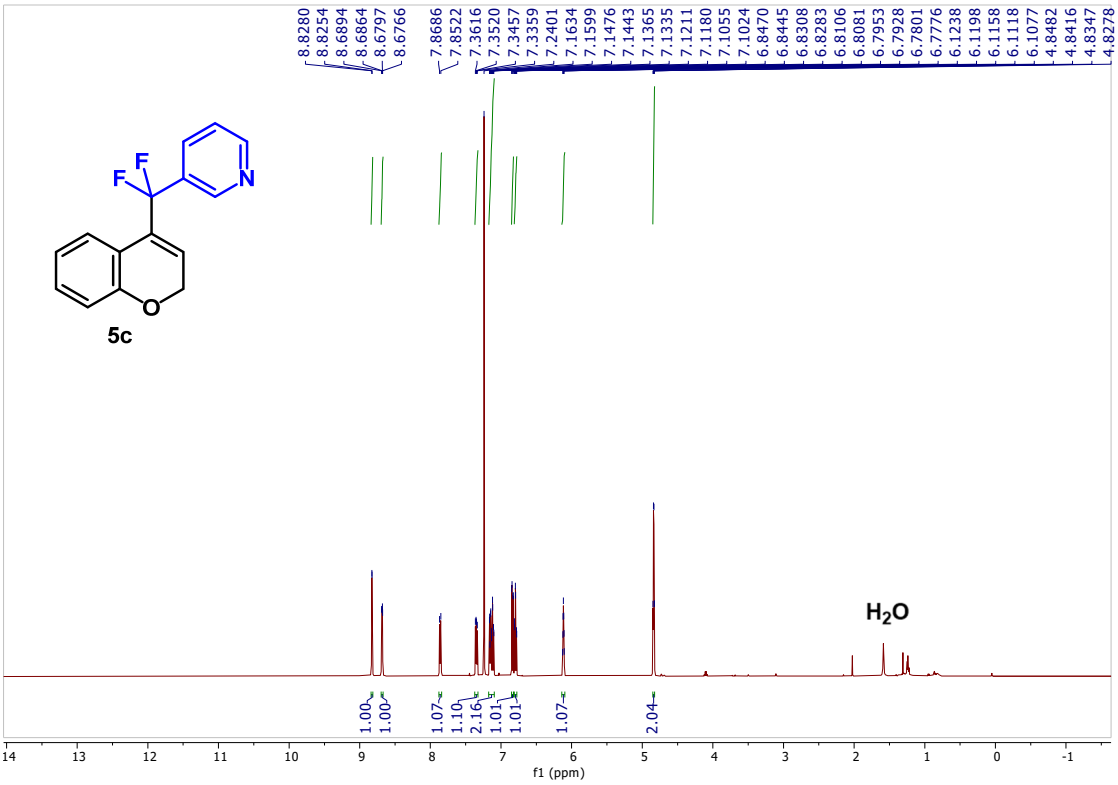


Fig. S68. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **5c**.

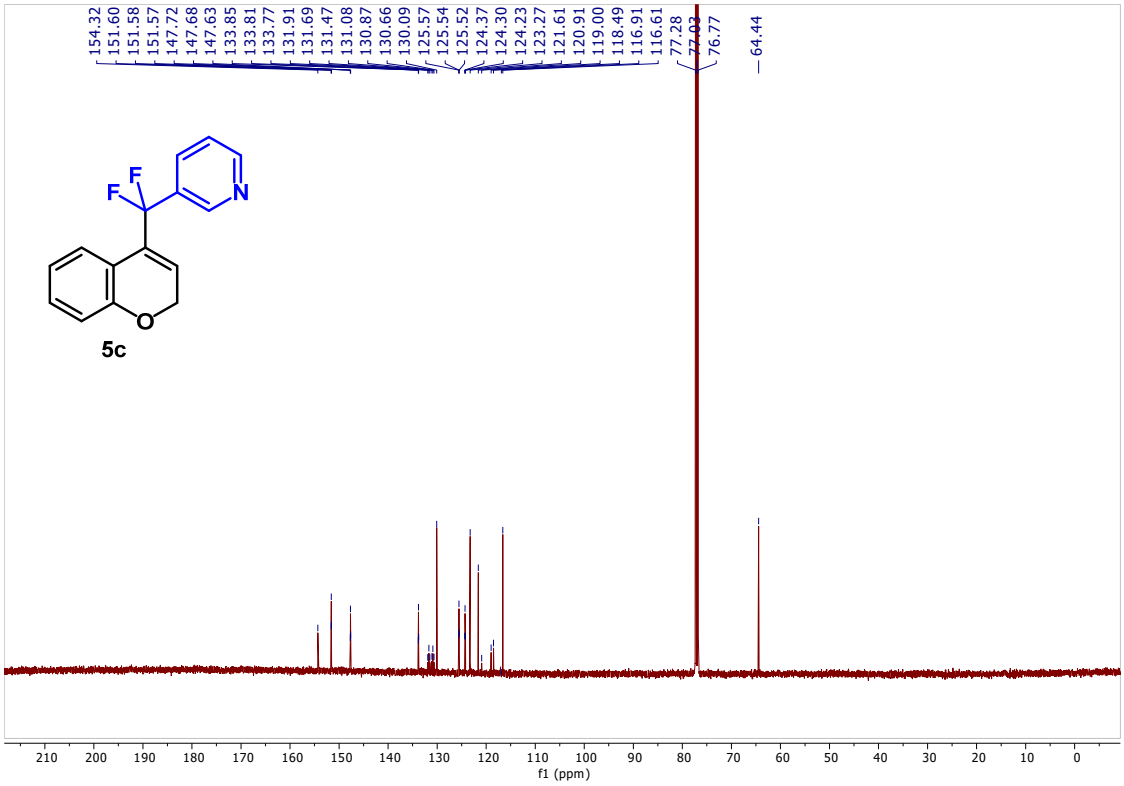


Fig. S69. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **5c**.

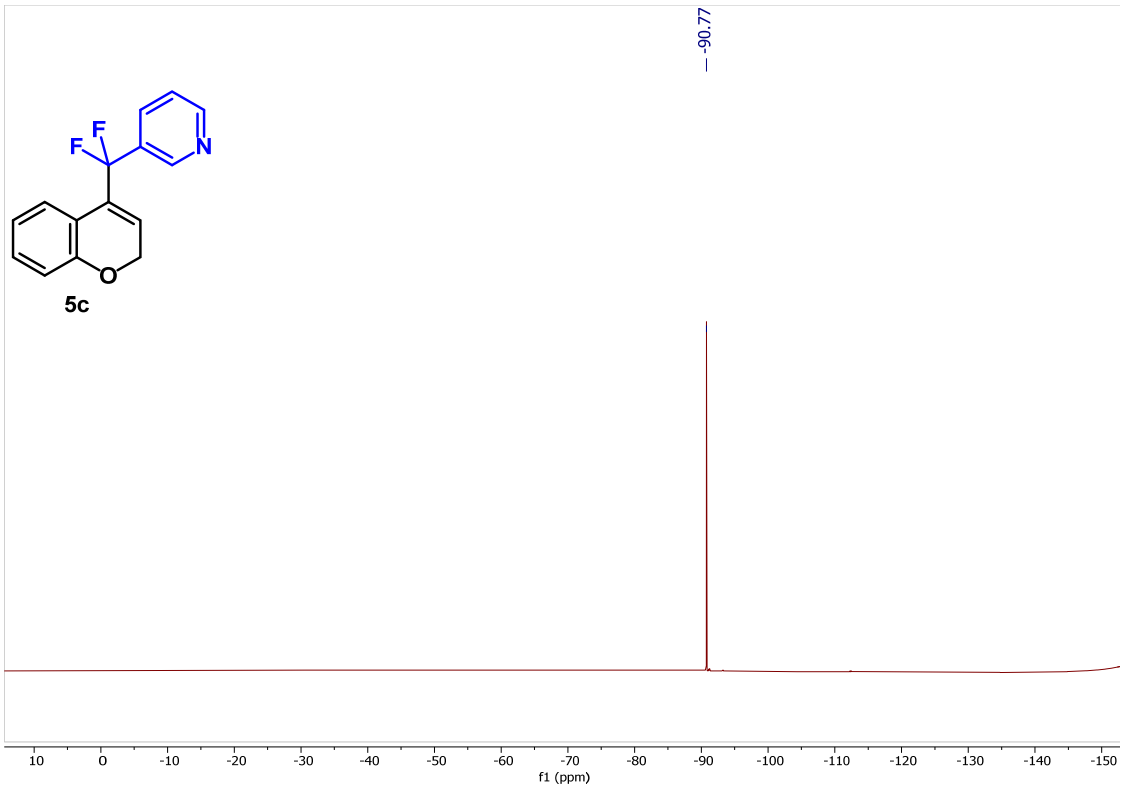


Fig. S70. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **5c**.

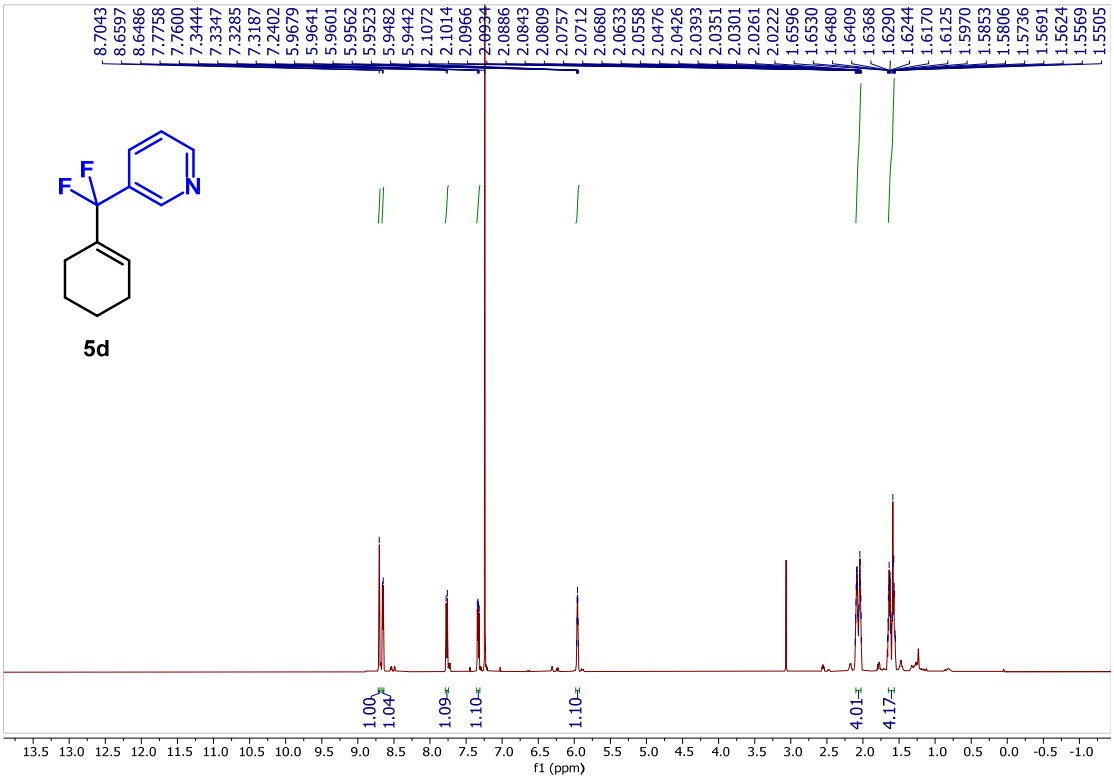


Fig. S71. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **5d**.

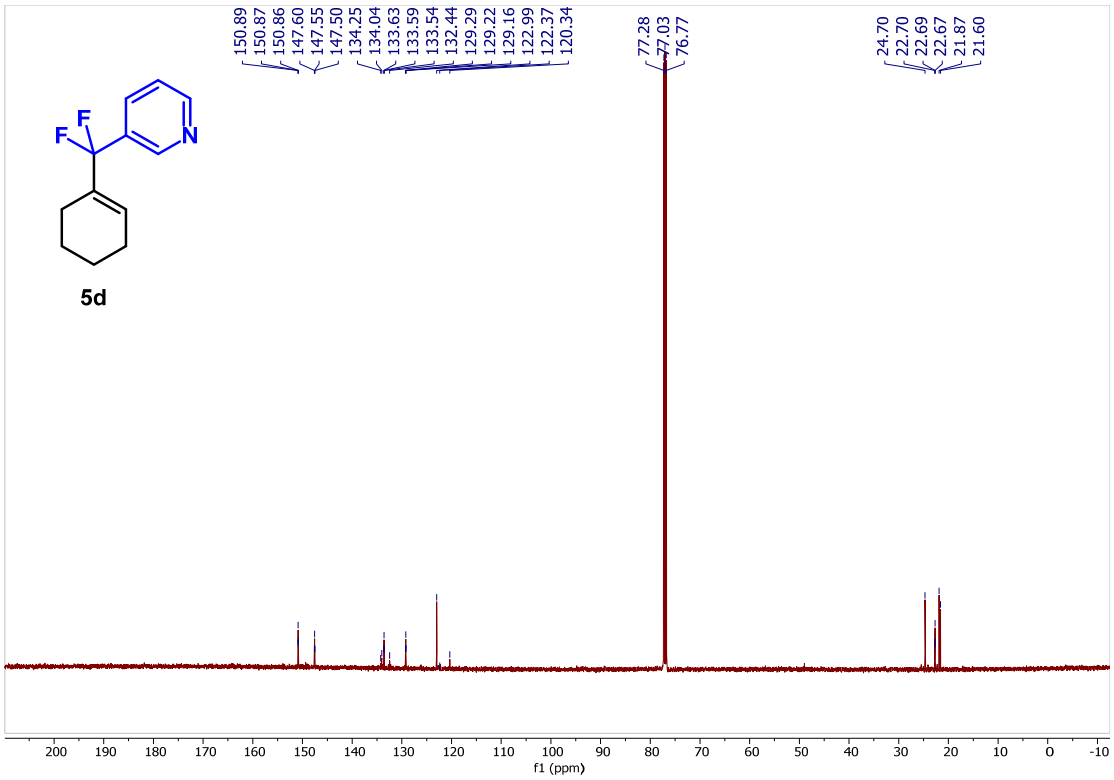


Fig. S72. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **5d**.

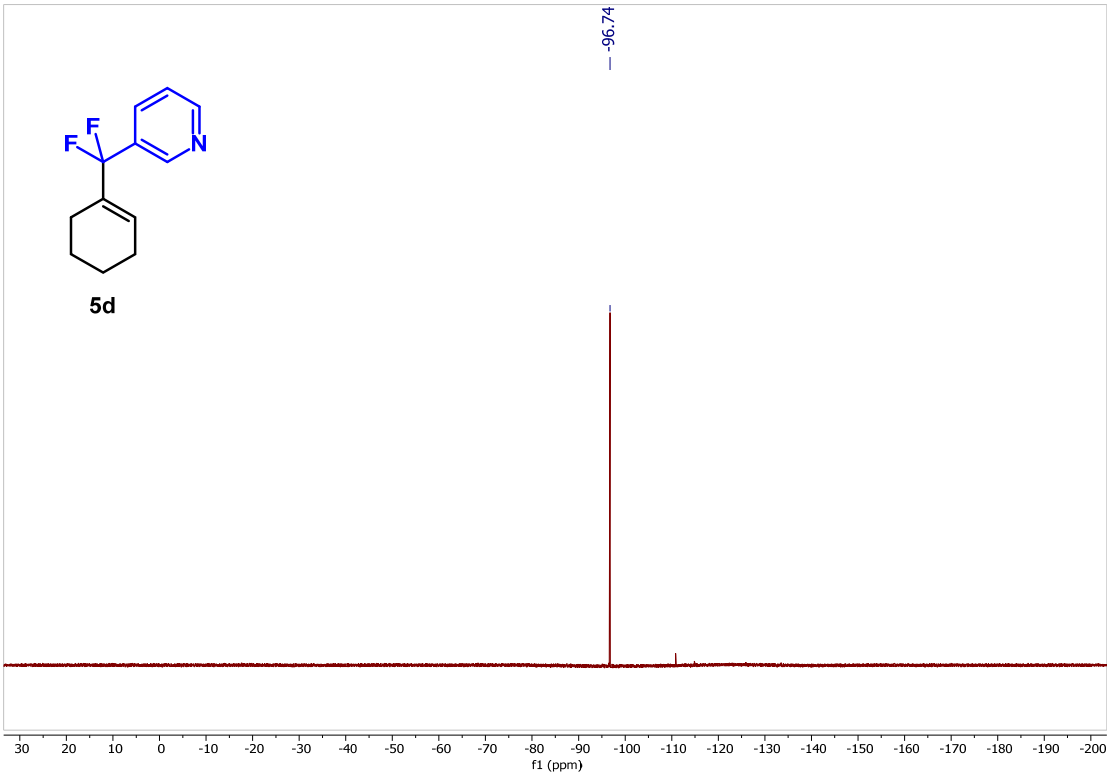


Fig. S73. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **5d**.

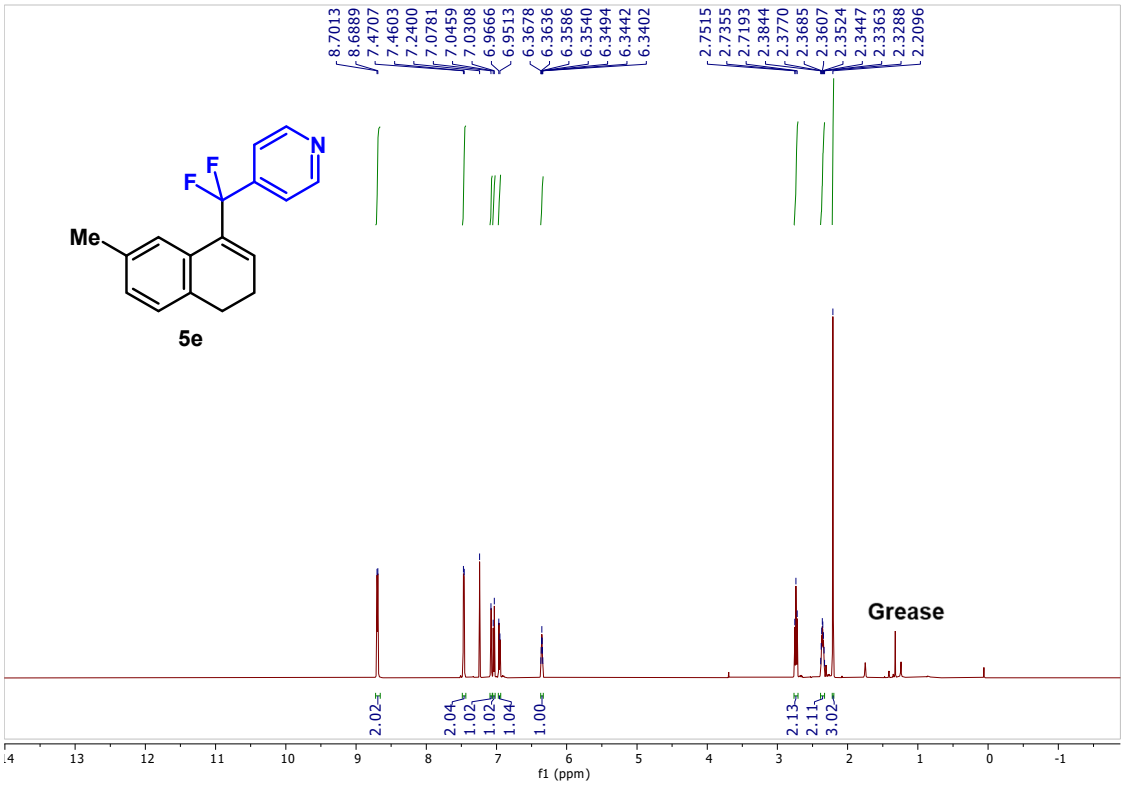


Fig. S74. ^{1}H NMR spectrum (**$CDCl_3$, 25** °C) of **5e**.

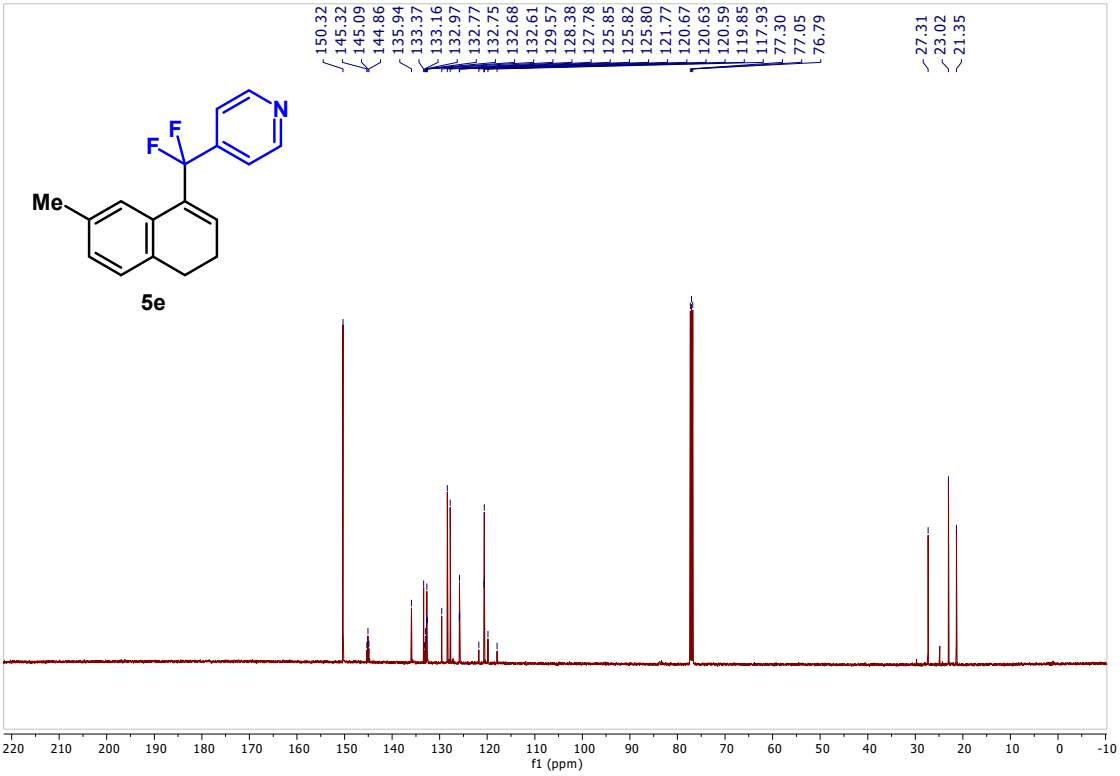


Fig. S75. ^{13}C NMR spectrum (**$CDCl_3$, 25** °C) of **5e**.

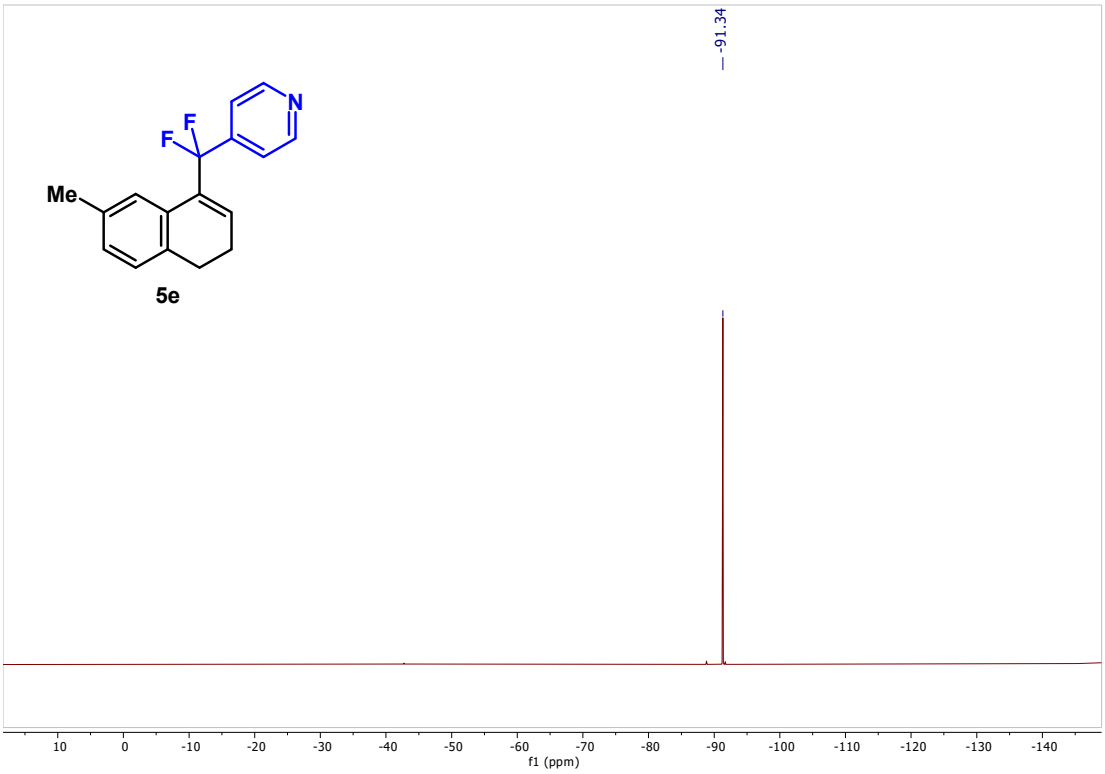


Fig. S76. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **5e**.

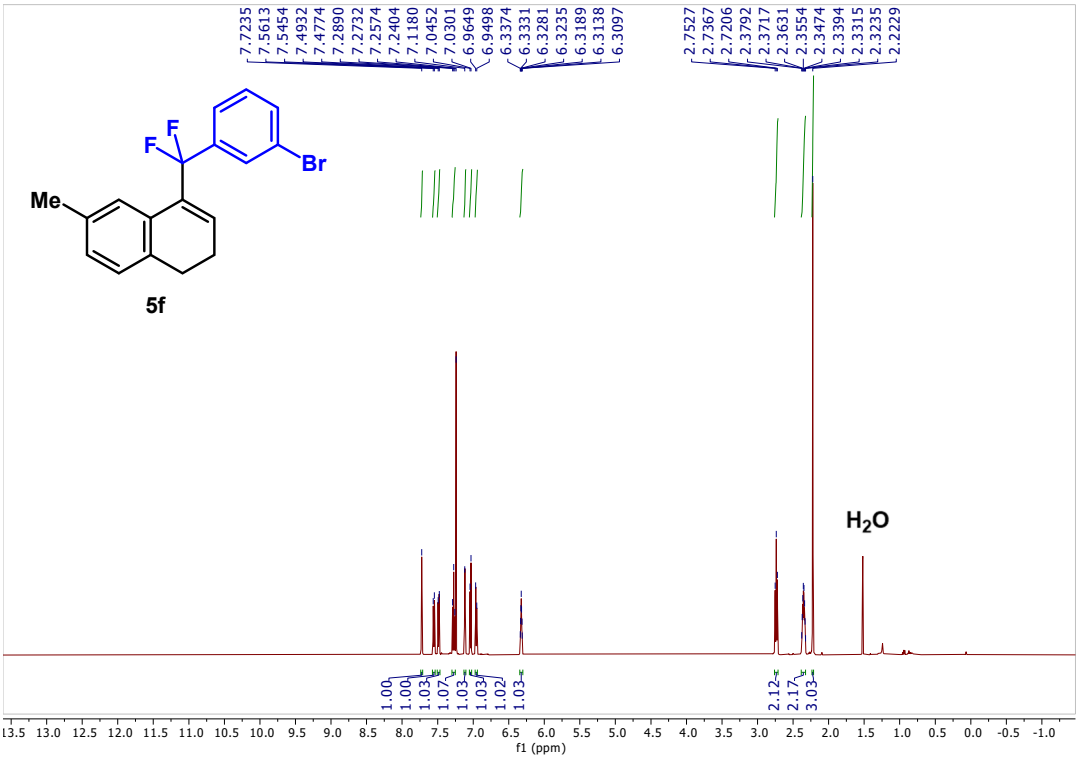


Fig. S77. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **5f**.

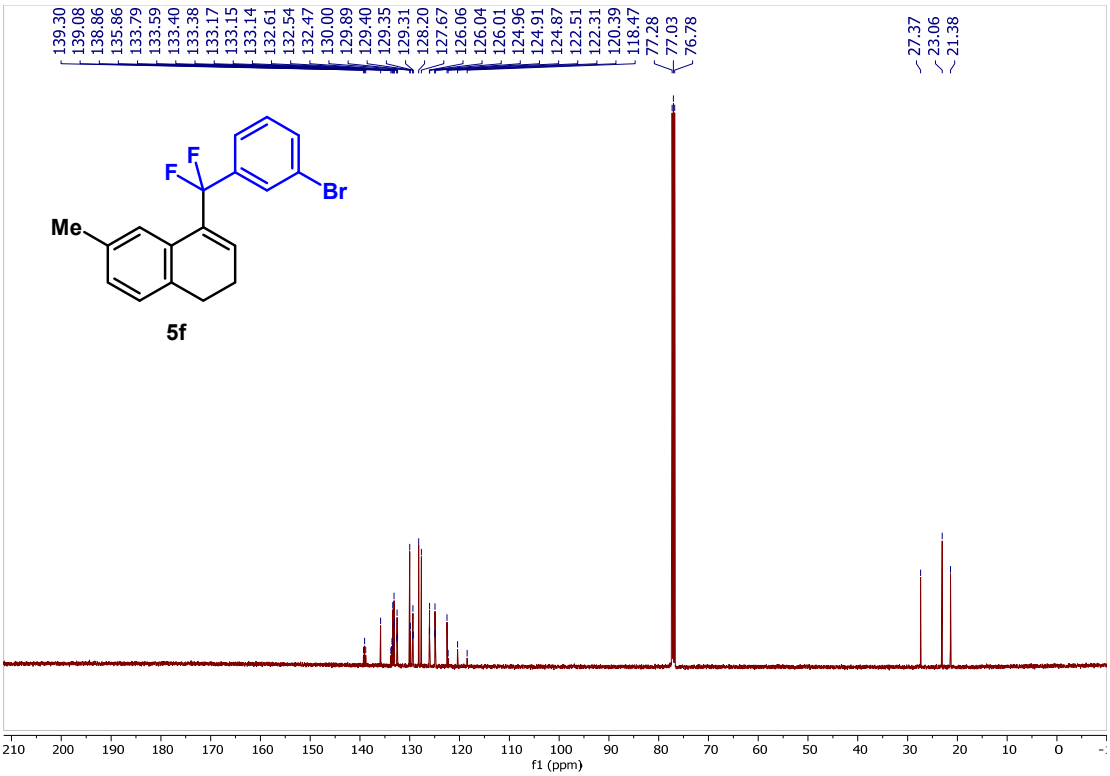


Fig. S78. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **5f**.

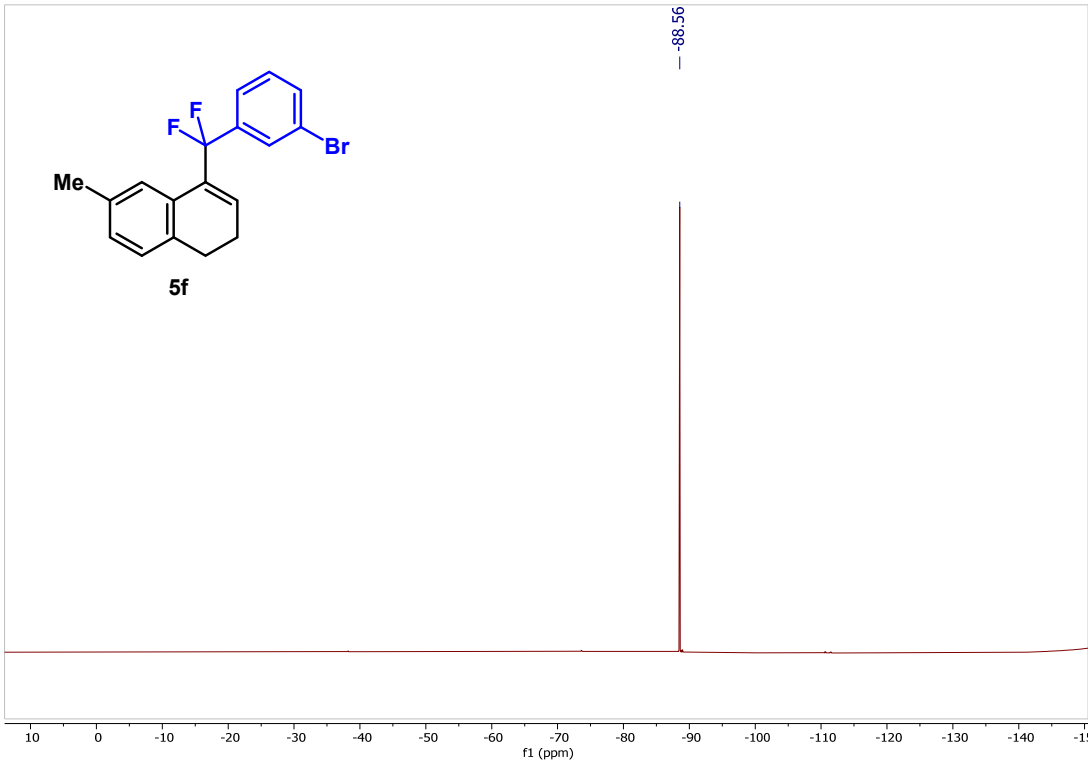


Fig. S79. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **5f**.

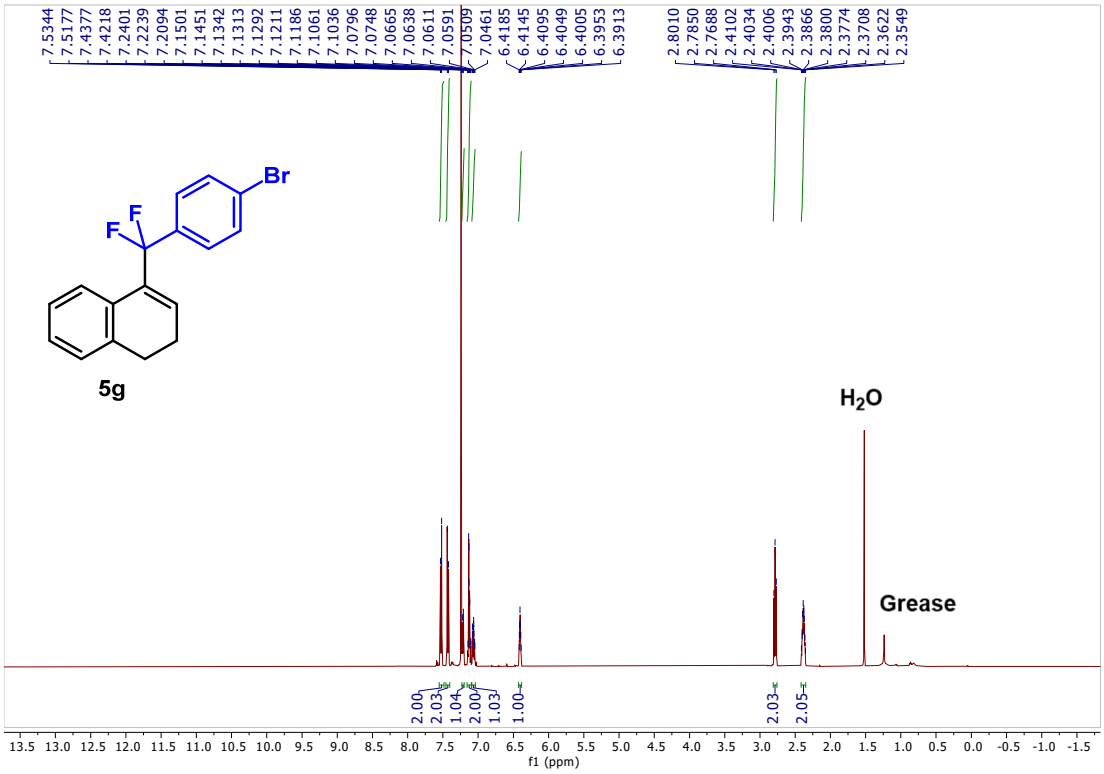


Fig. S80. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **5g**.

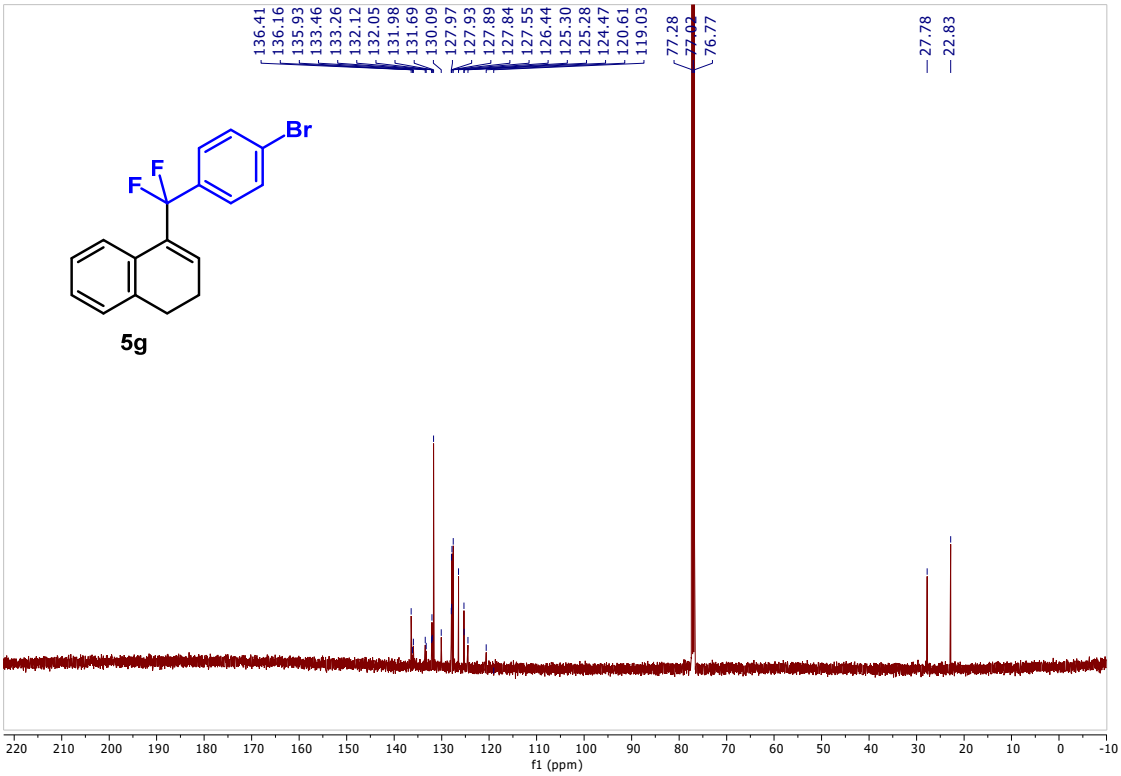


Fig. S81. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **5g**.

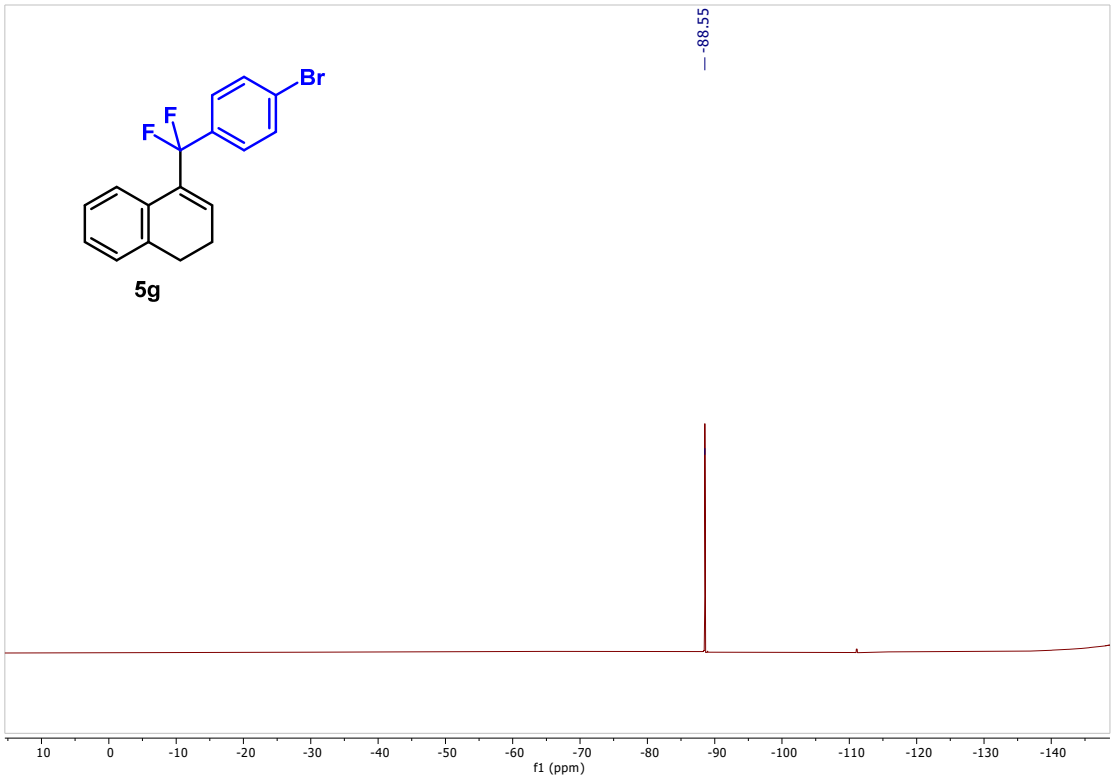


Fig. S82. ^{19}F NMR spectrum (**$CDCl_3$, 25** °C) of **5g**.

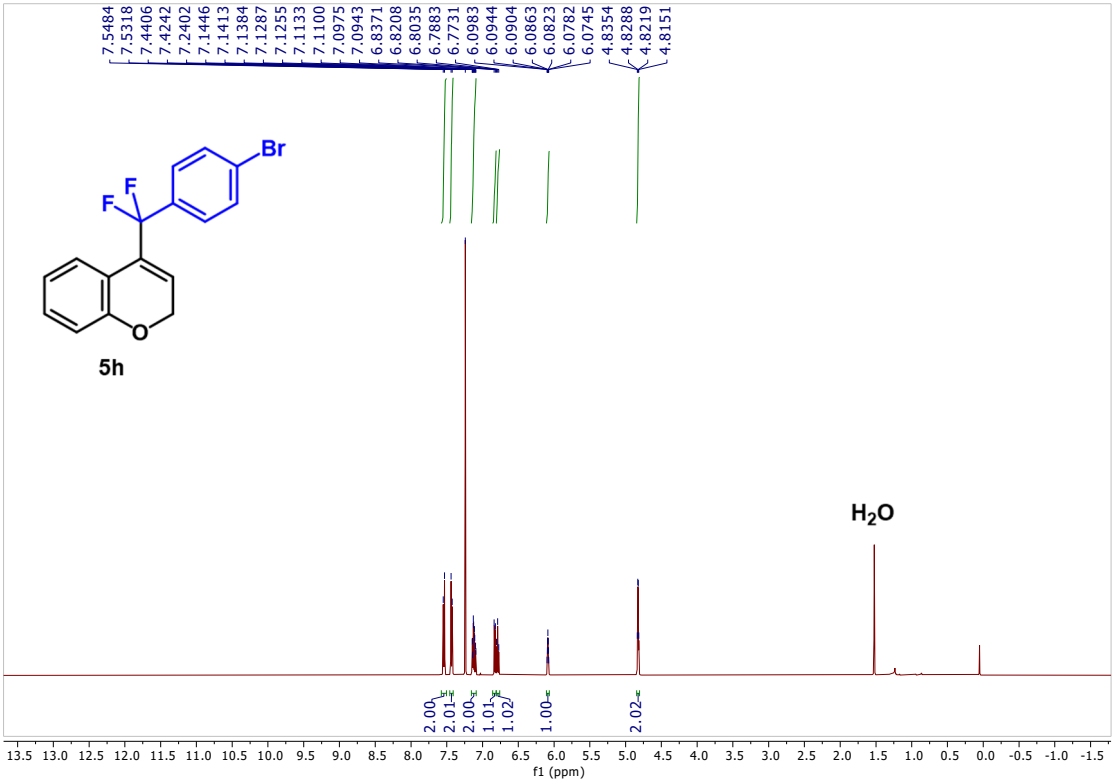


Fig. S83. ^{1}H NMR spectrum (**$CDCl_3$, 25** °C) of **5h**.

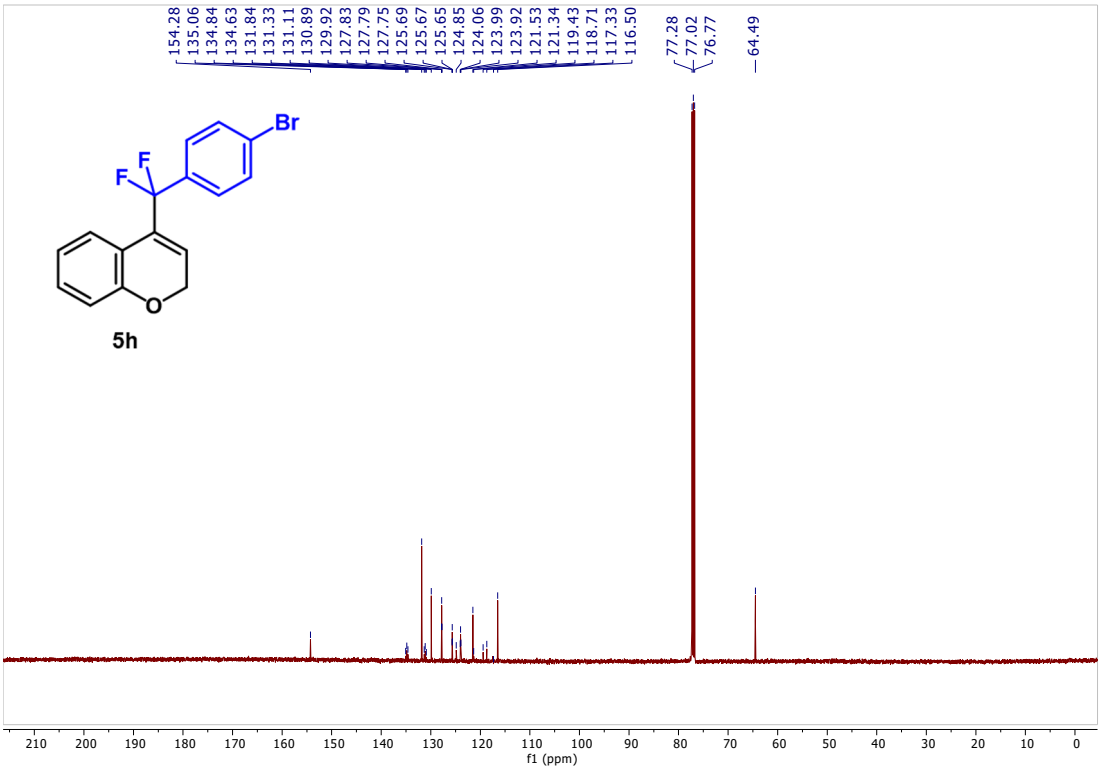


Fig. S84. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **5h**.

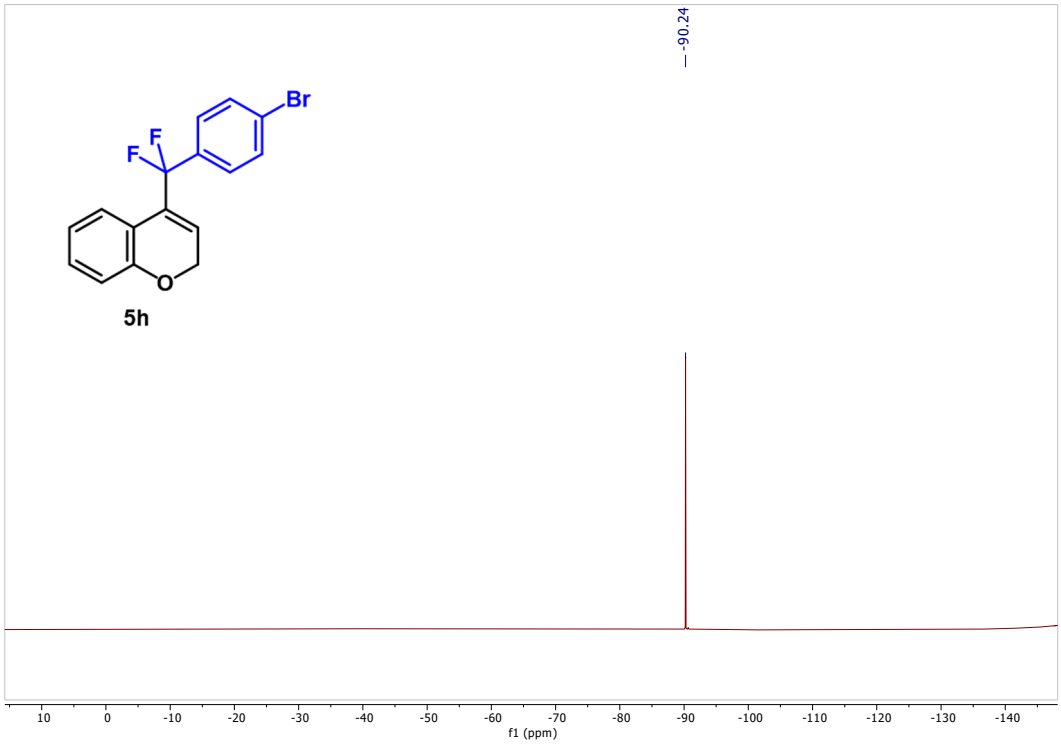


Fig. S85. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **5h**.

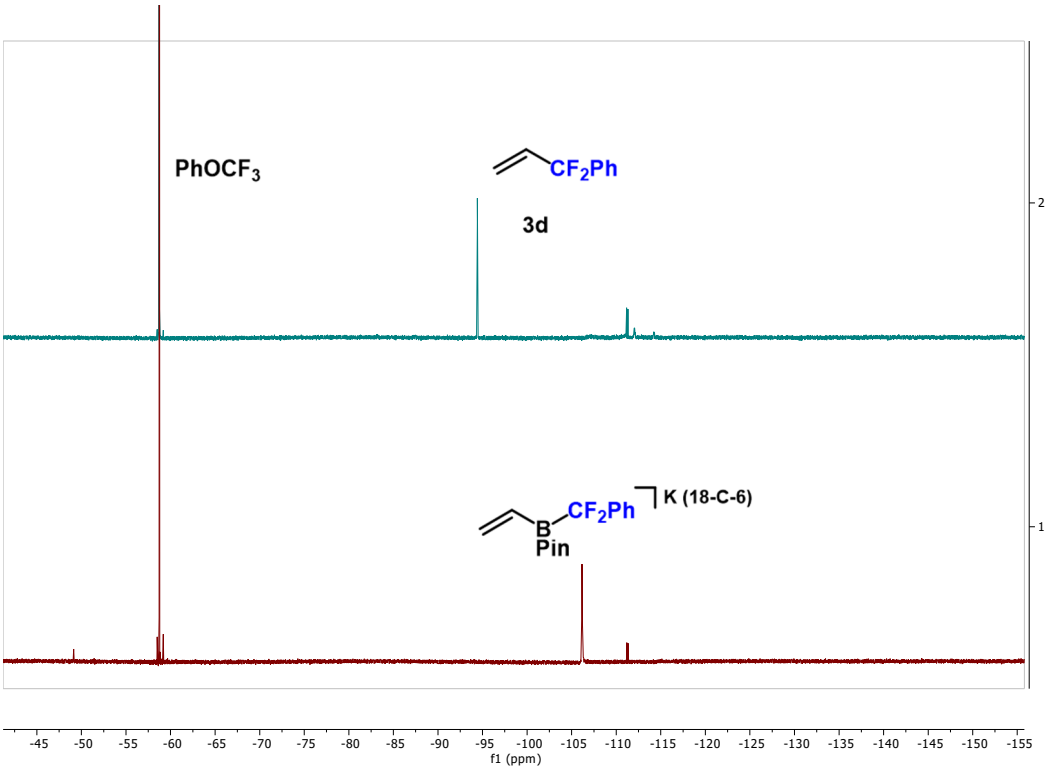


Fig. S86. ^{19}F NMR spectrum (**THF-H$_8$**, **25** °C) of **3d** and the **boronated intermediate**.

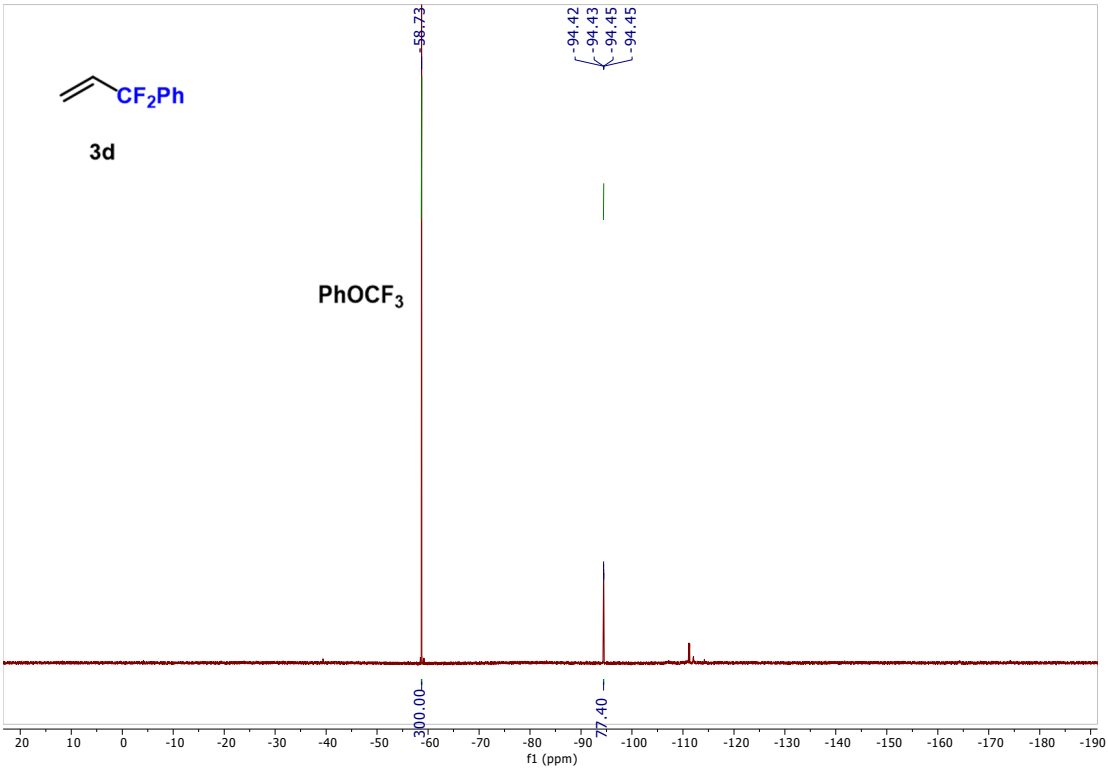


Fig. S87. ^{19}F NMR spectrum (**THF-H$_8$**, **25** °C) of **3d**.

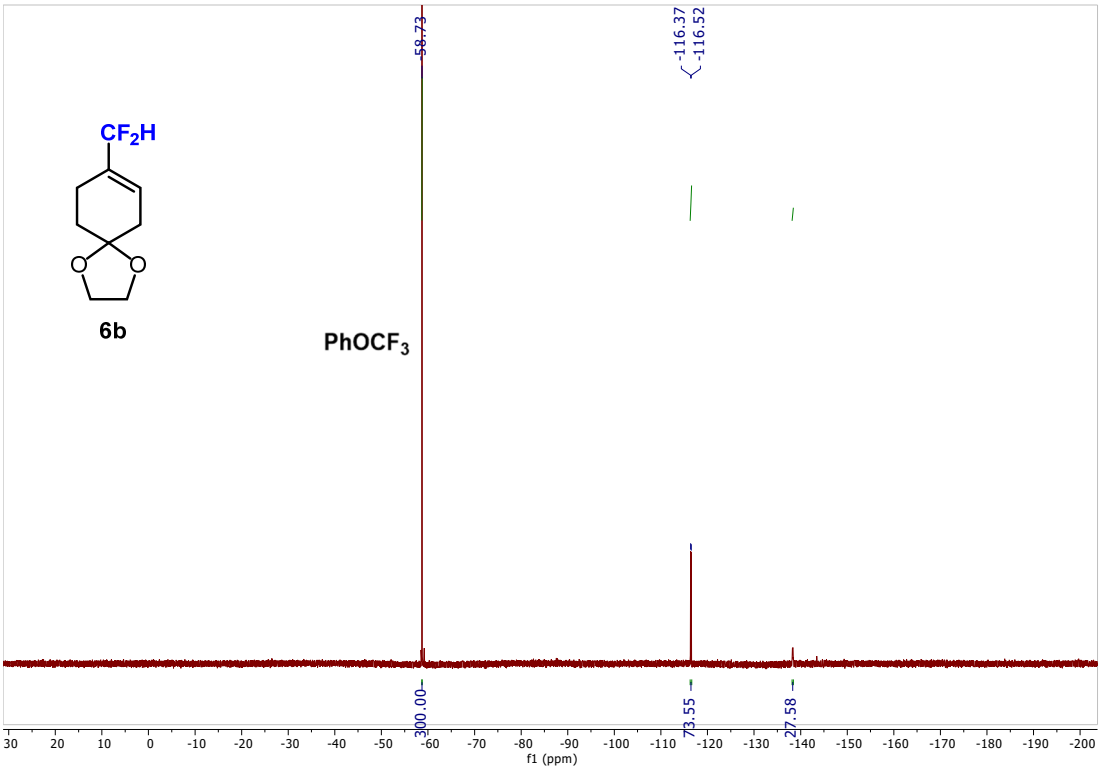


Fig. S88. ^{19}F NMR spectrum (**THF-H$_8$**, **25** °C) of **6b**.

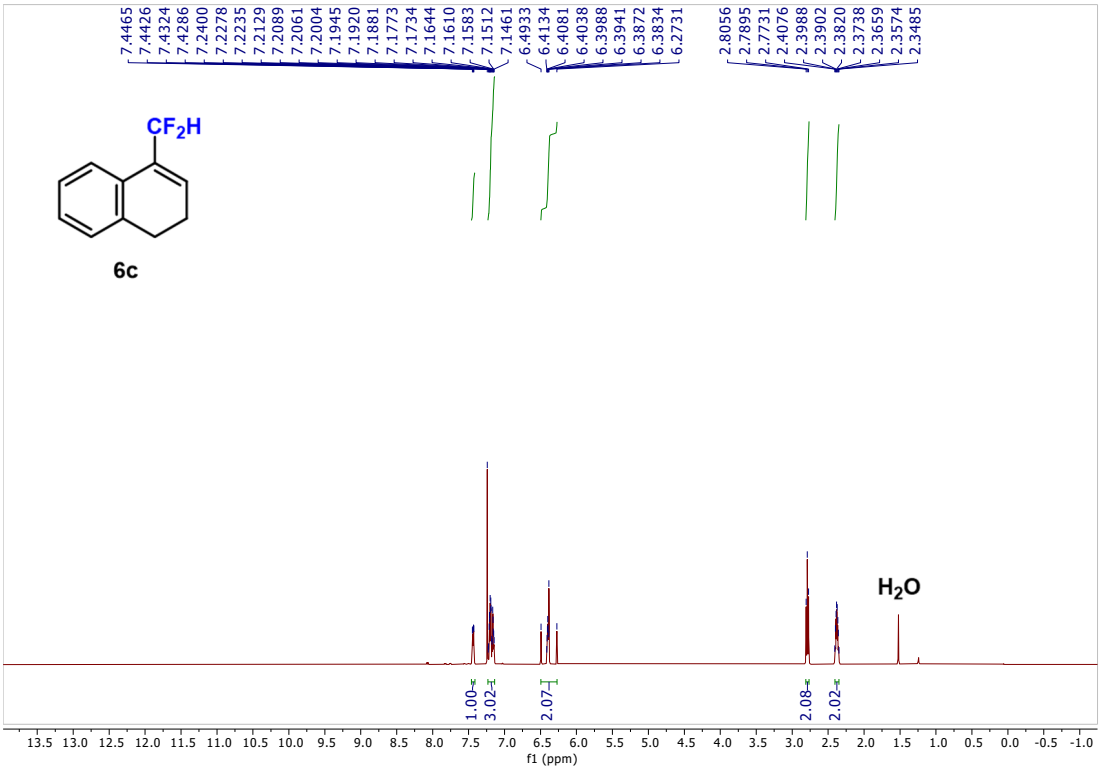


Fig. S89. ^{1}H NMR spectrum (**CDCl$_3$**, **25** °C) of **6c**.

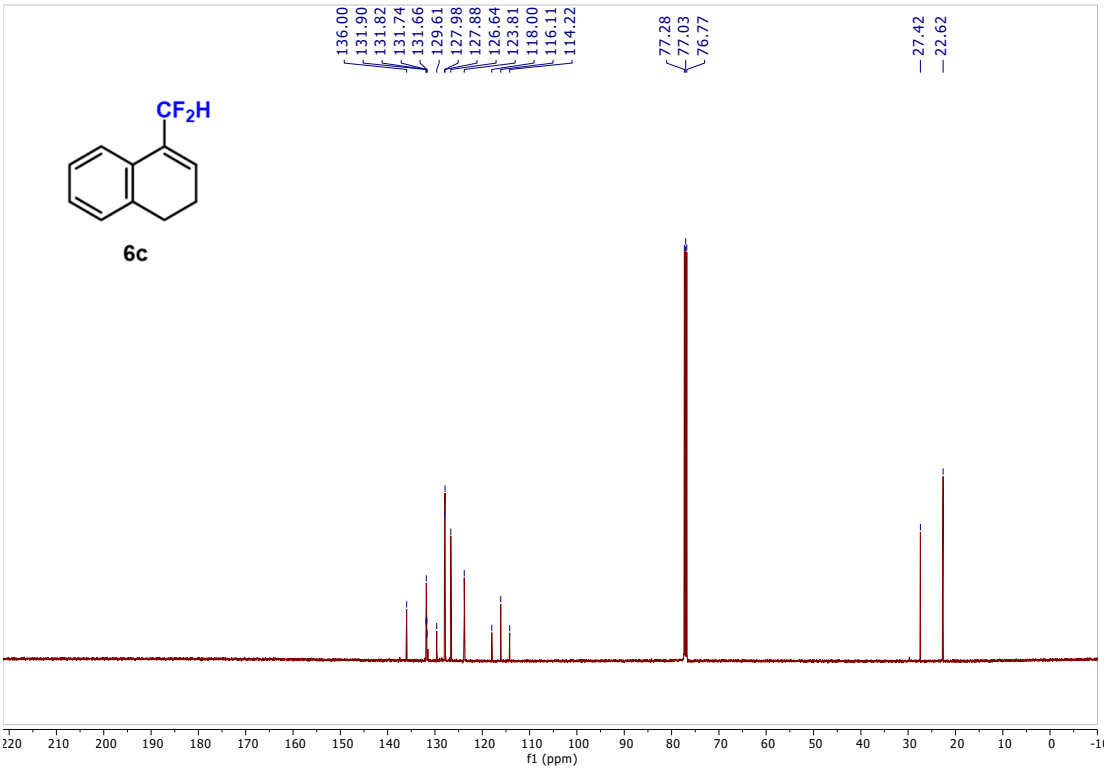


Fig. S90. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **6c**.

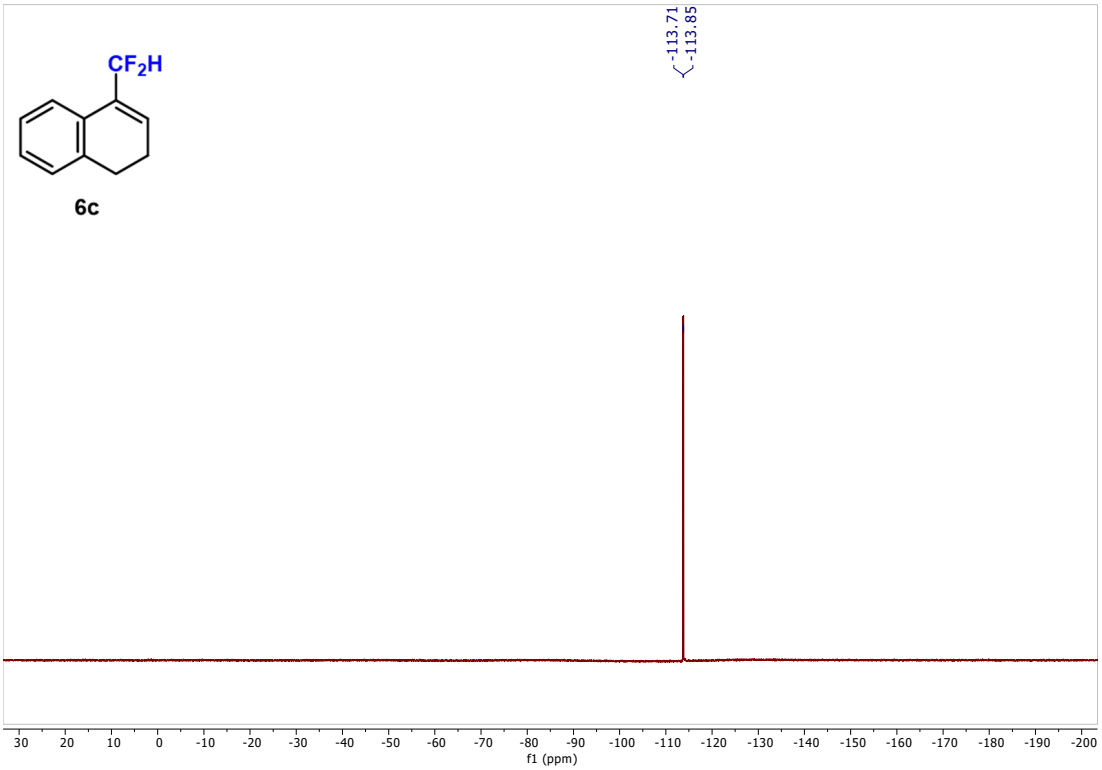


Fig. S91. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **6c**.

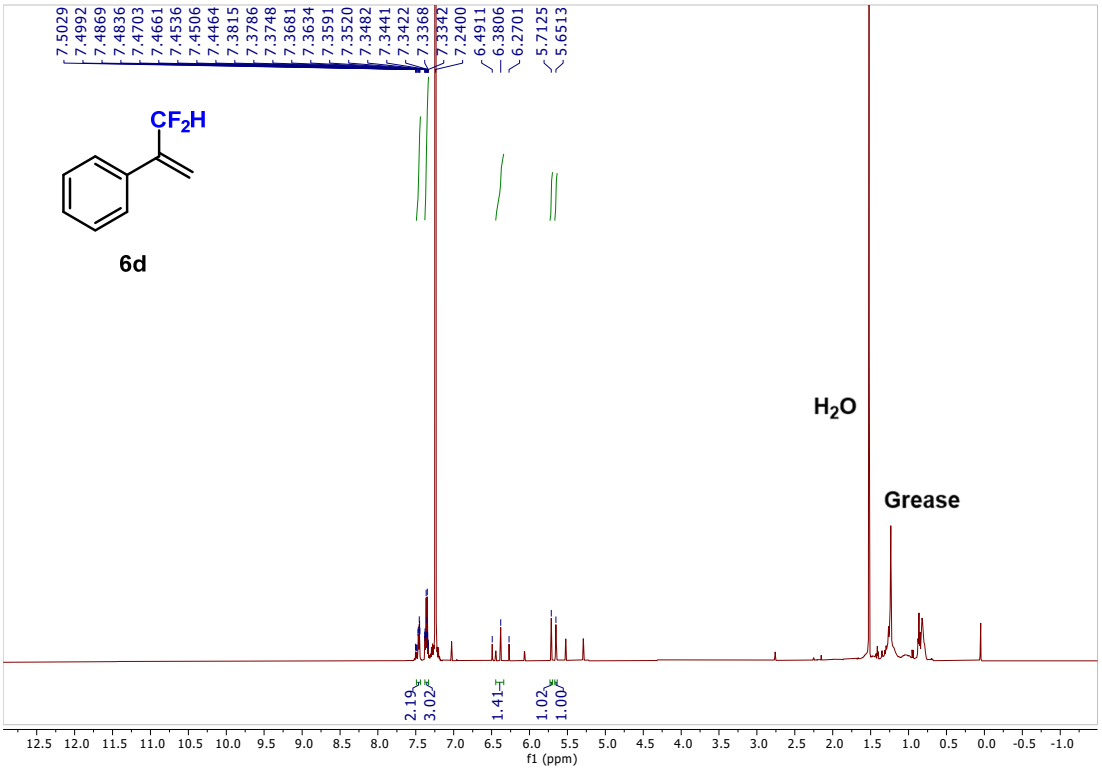


Fig. S92. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **6d**, hexane eluent.

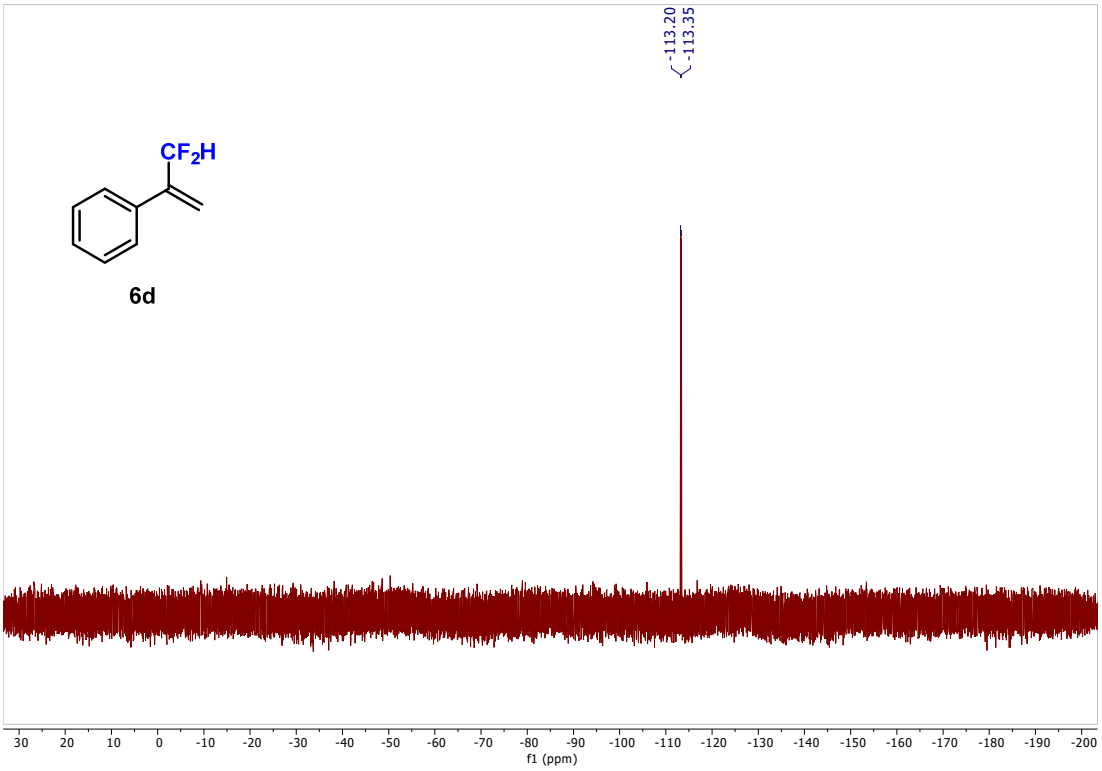


Fig. S93. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **6d**, hexane eluent.

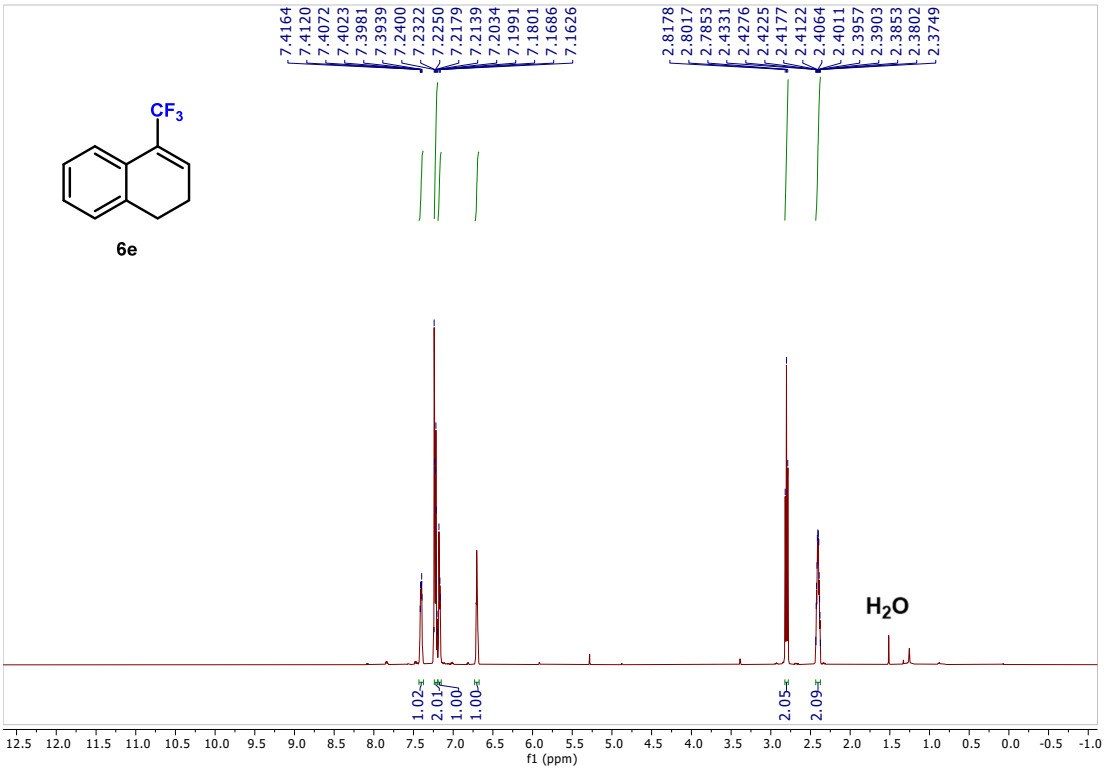


Fig. S94. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **6e**.

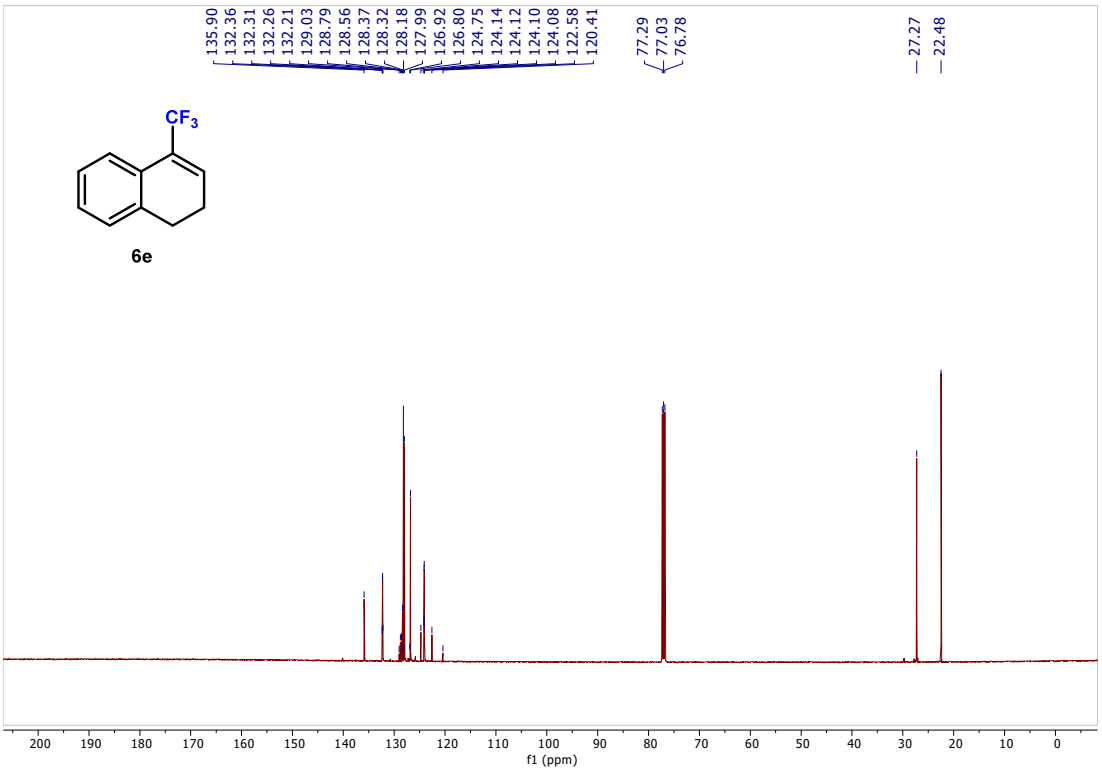


Fig. S95. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **6e**.

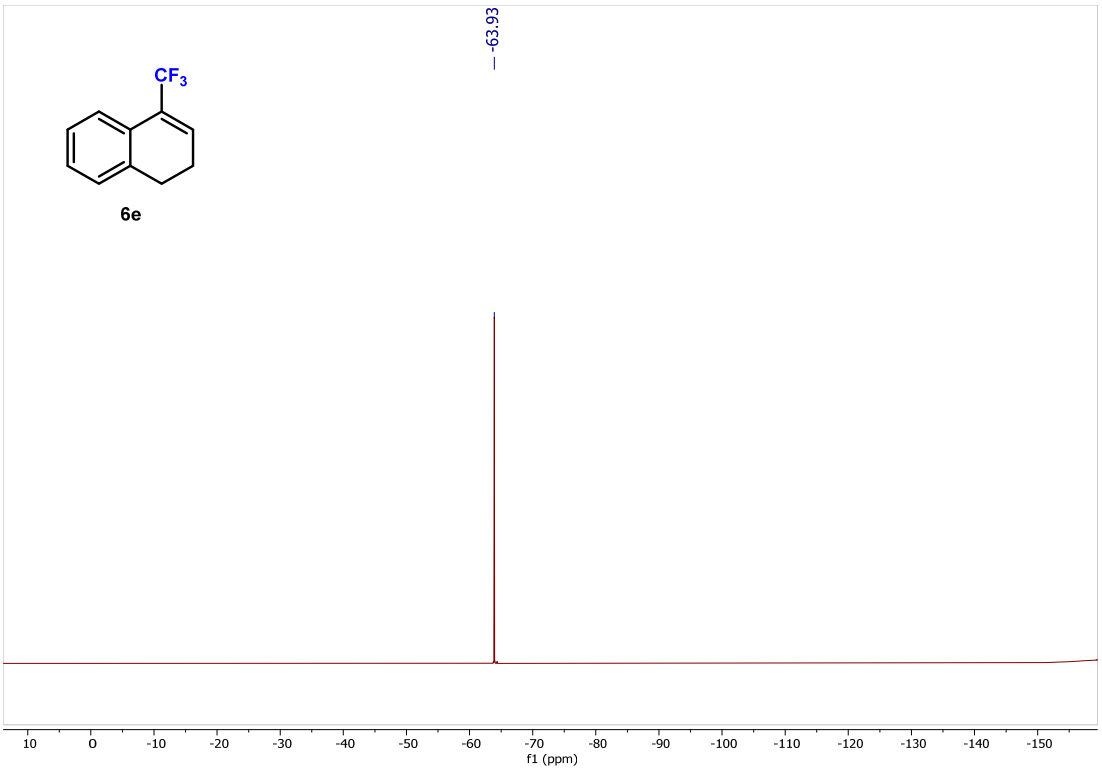


Fig. S96. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **6e**.

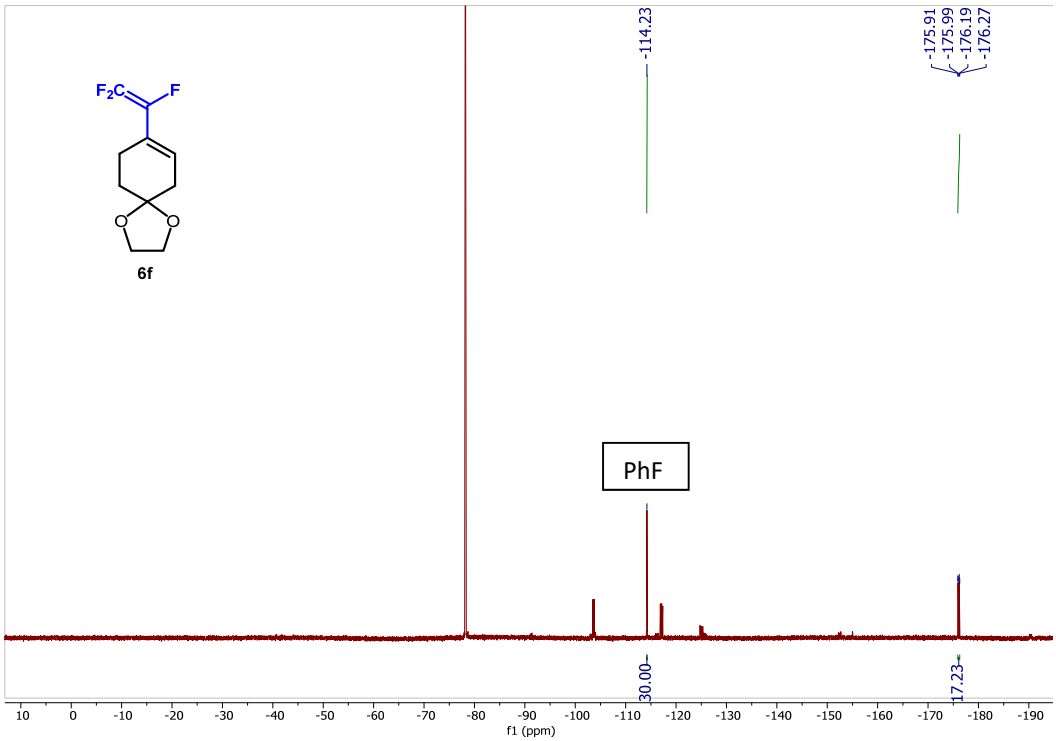


Fig. S97. ^{19}F NMR spectrum (**THF-H_8**, **25** °C) of **6f**.

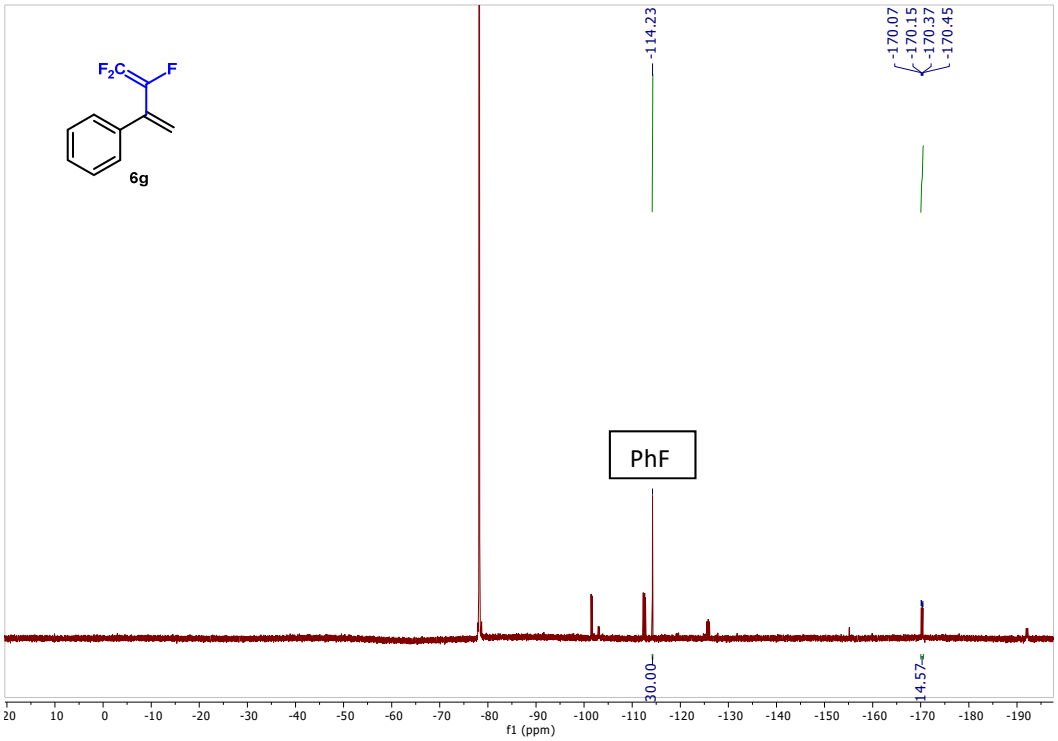


Fig. S98. ^{19}F NMR spectrum (**THF-H$_8$**, **25** °C) of **6g**.

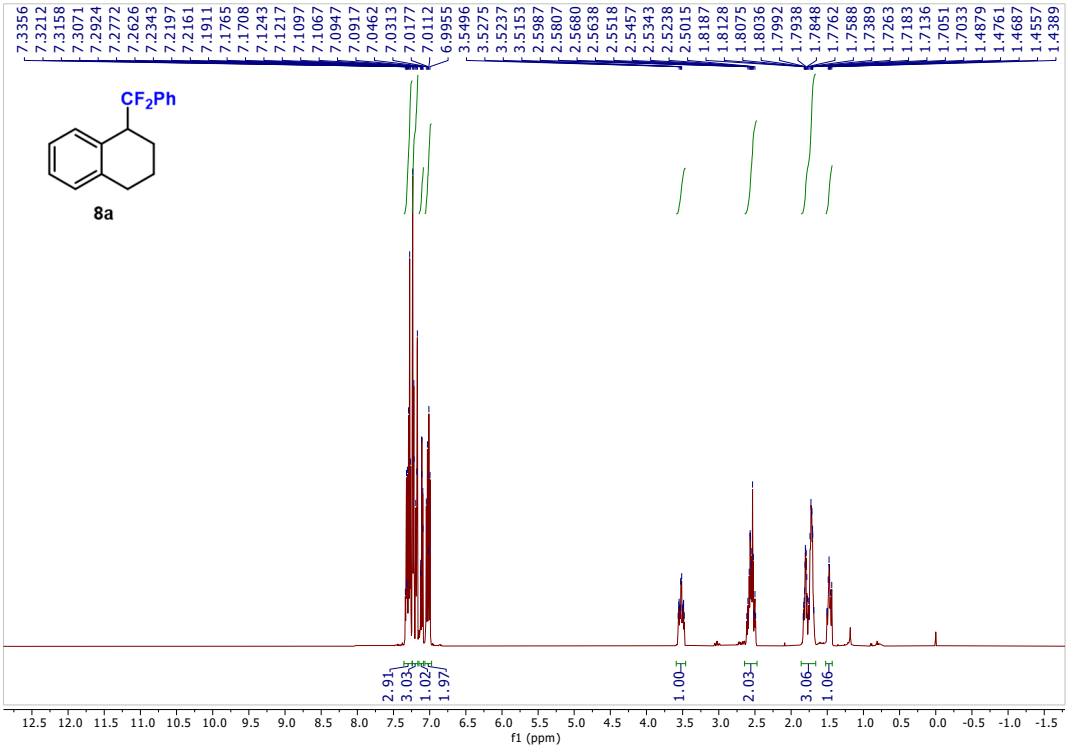


Fig. S99. ^{1}H NMR spectrum (**CDCl$_3$**, **25** °C) of **8a**.

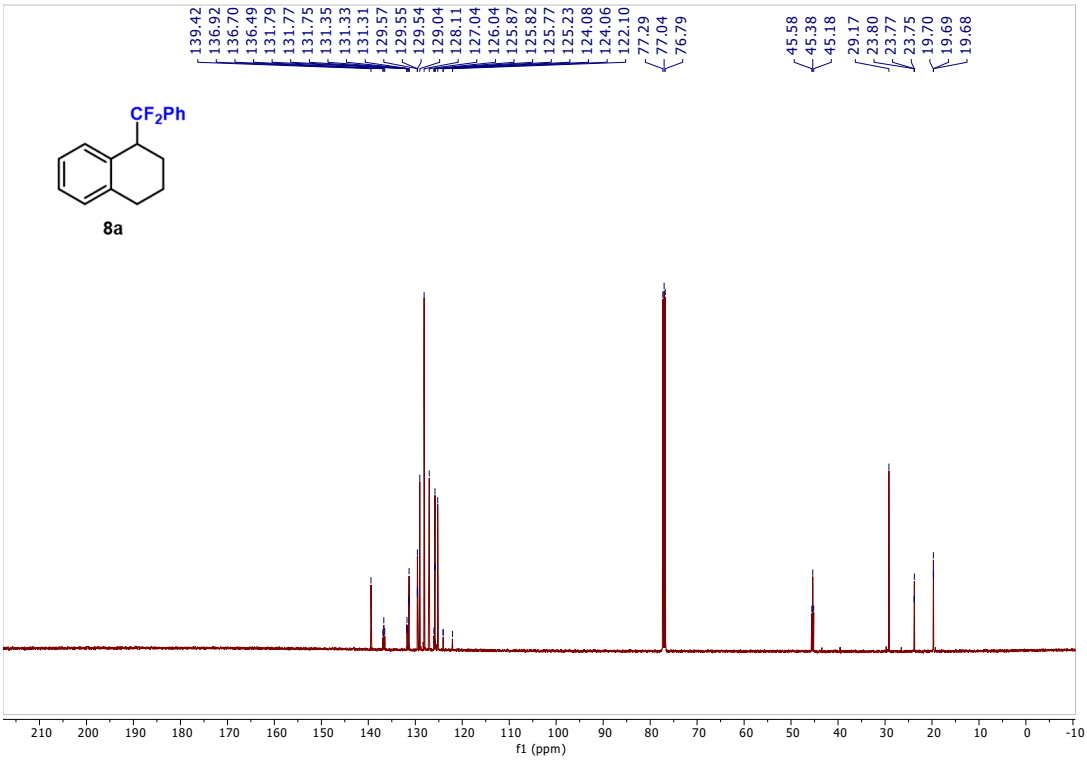


Fig. S100. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **8a**.

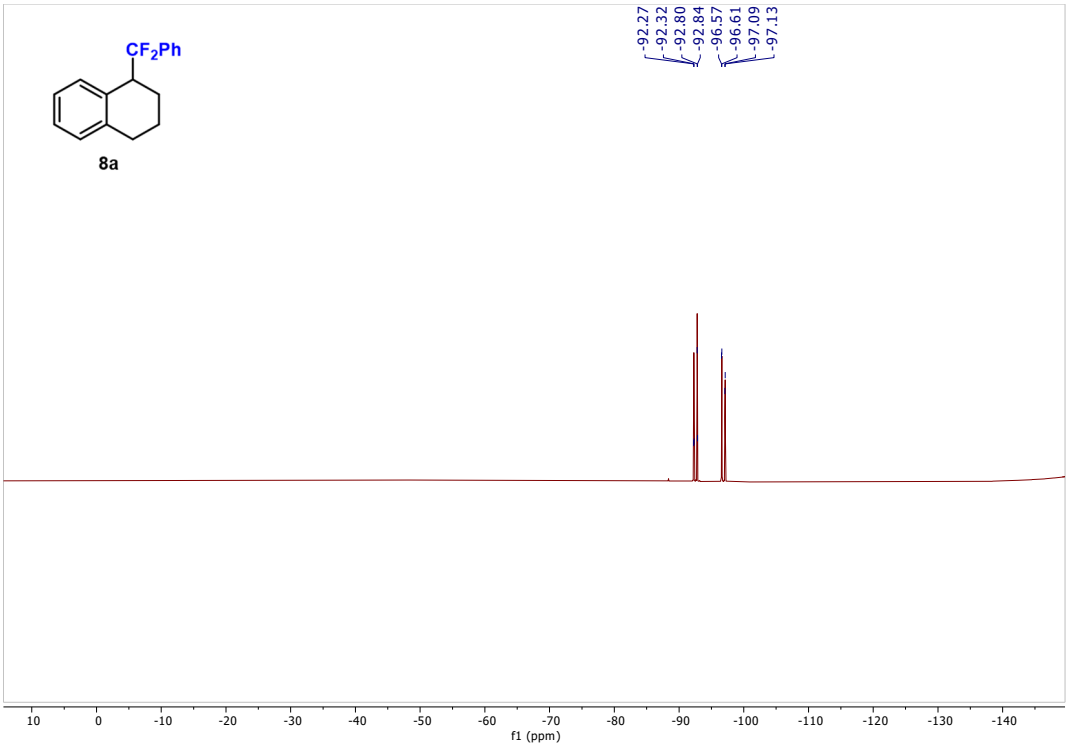


Fig. S101. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **8a**.

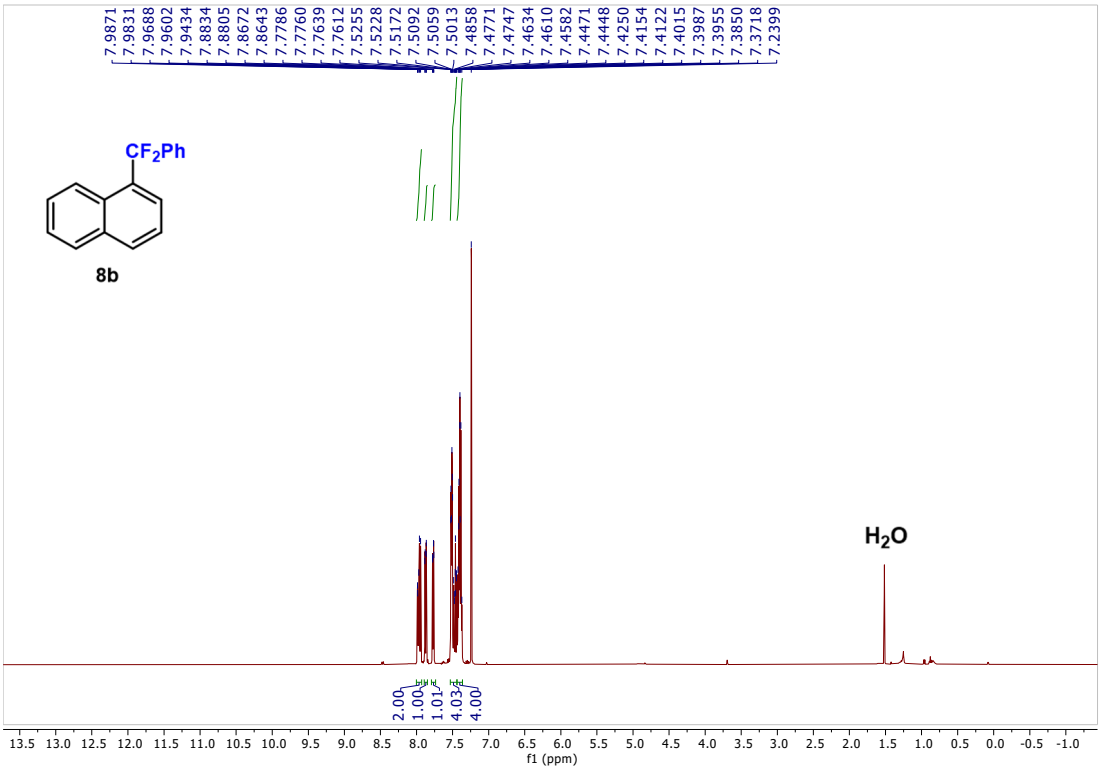


Fig. S102. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **8b**.

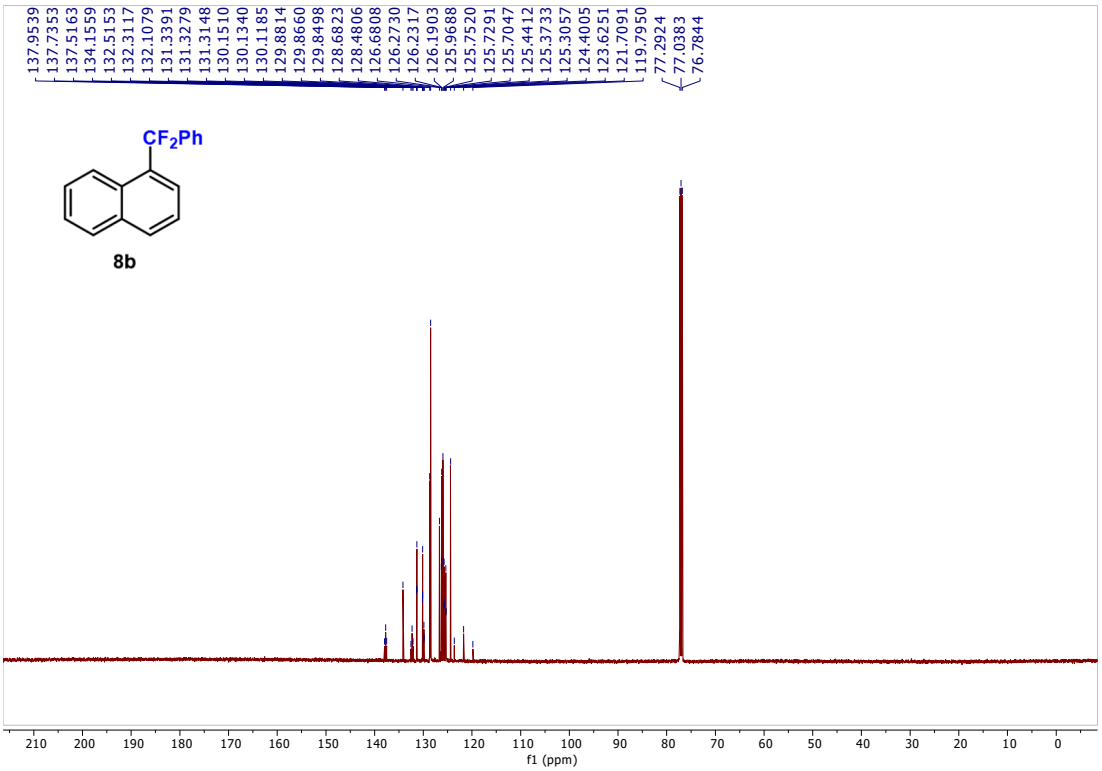


Fig. S103. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **8b**.

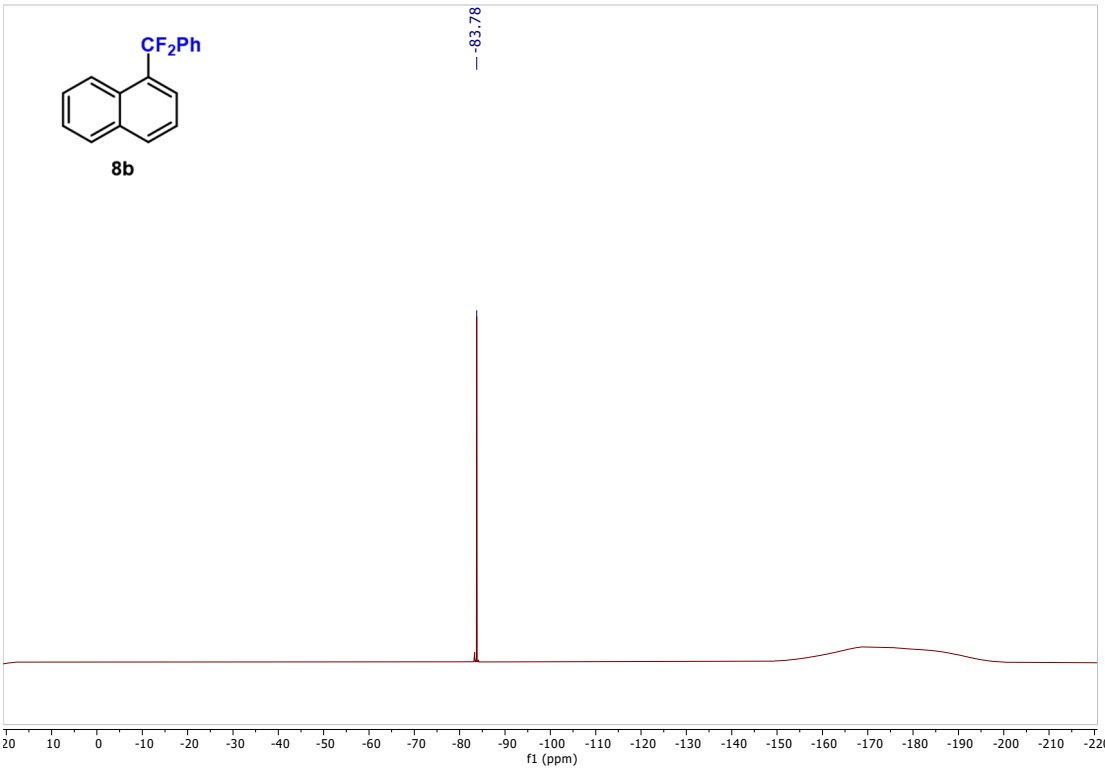


Fig. S104. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **8b**.

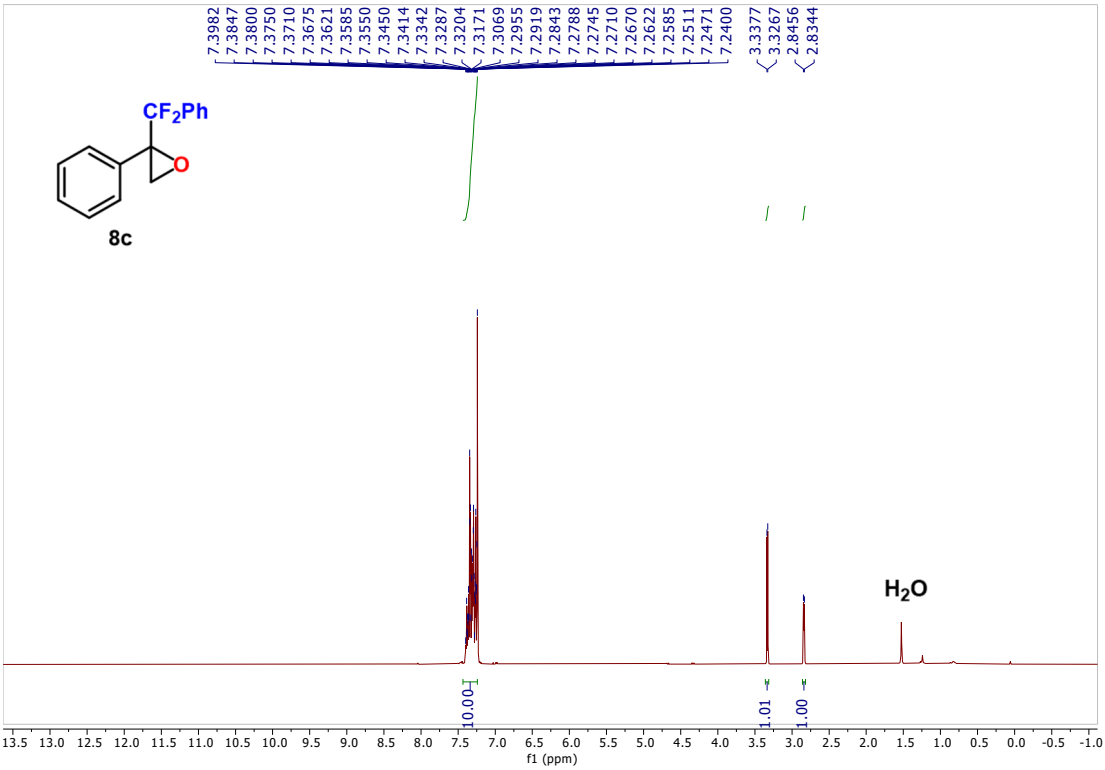


Fig. S105. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **8c**.

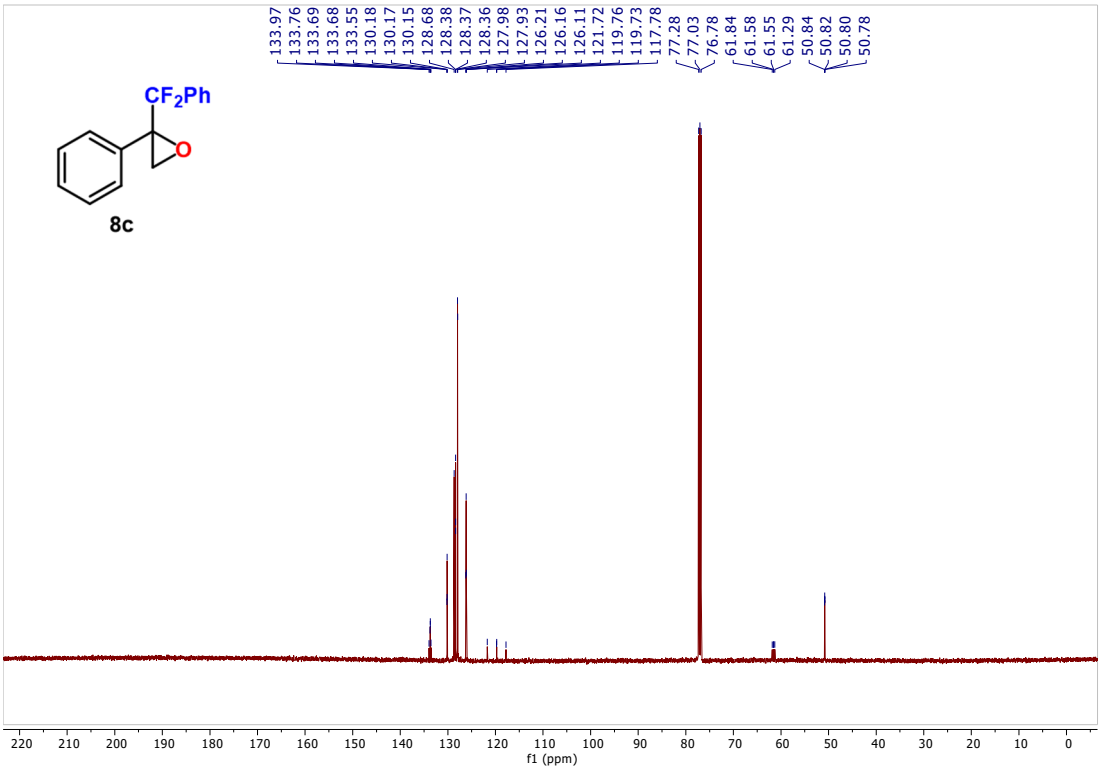


Fig. S106. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **8c**.

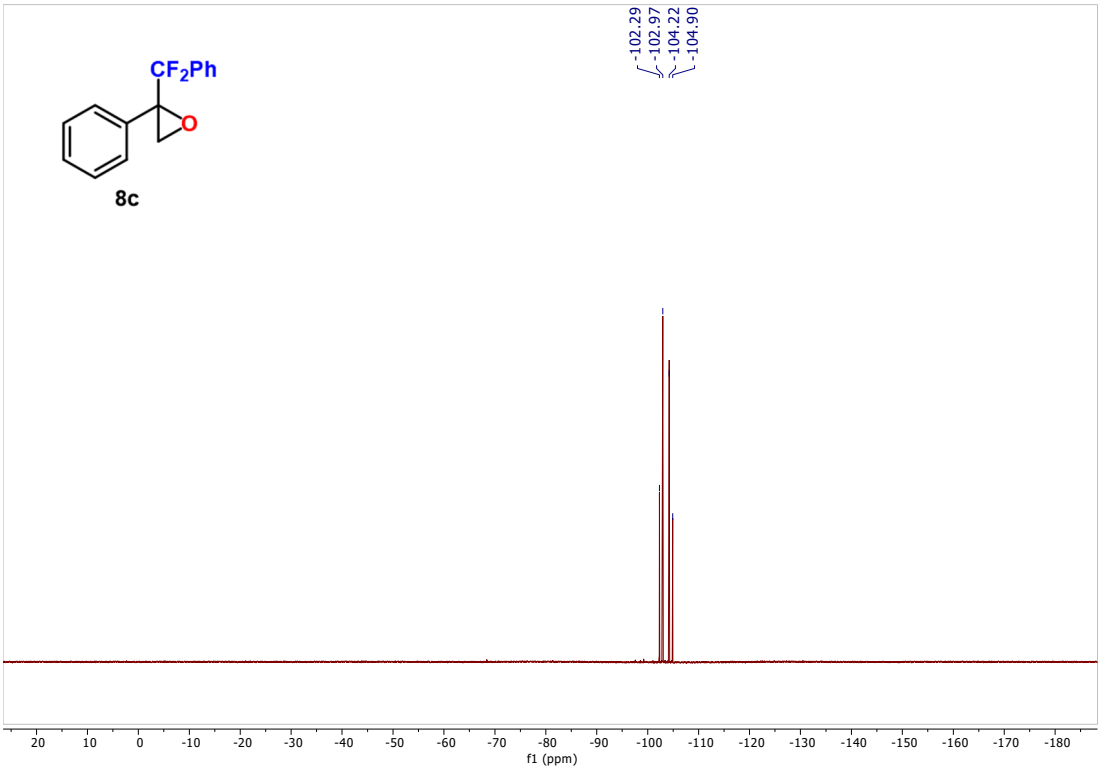


Fig. S107. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **8c**.

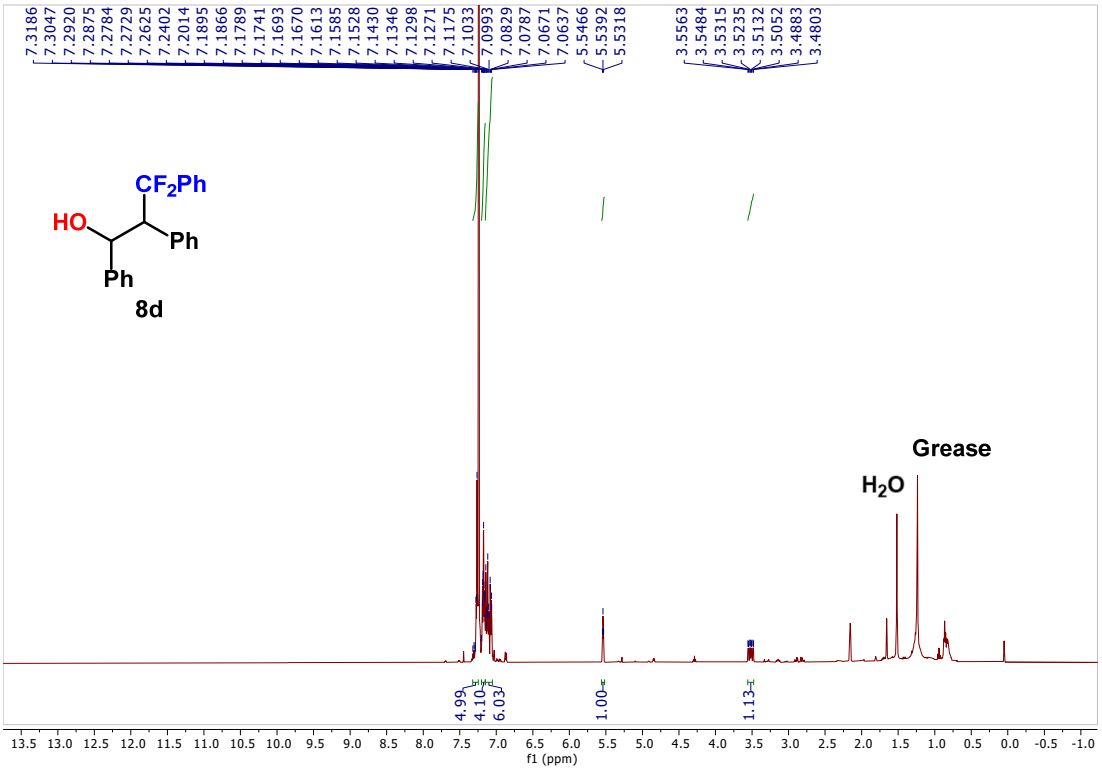


Fig. S108. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **8d**.

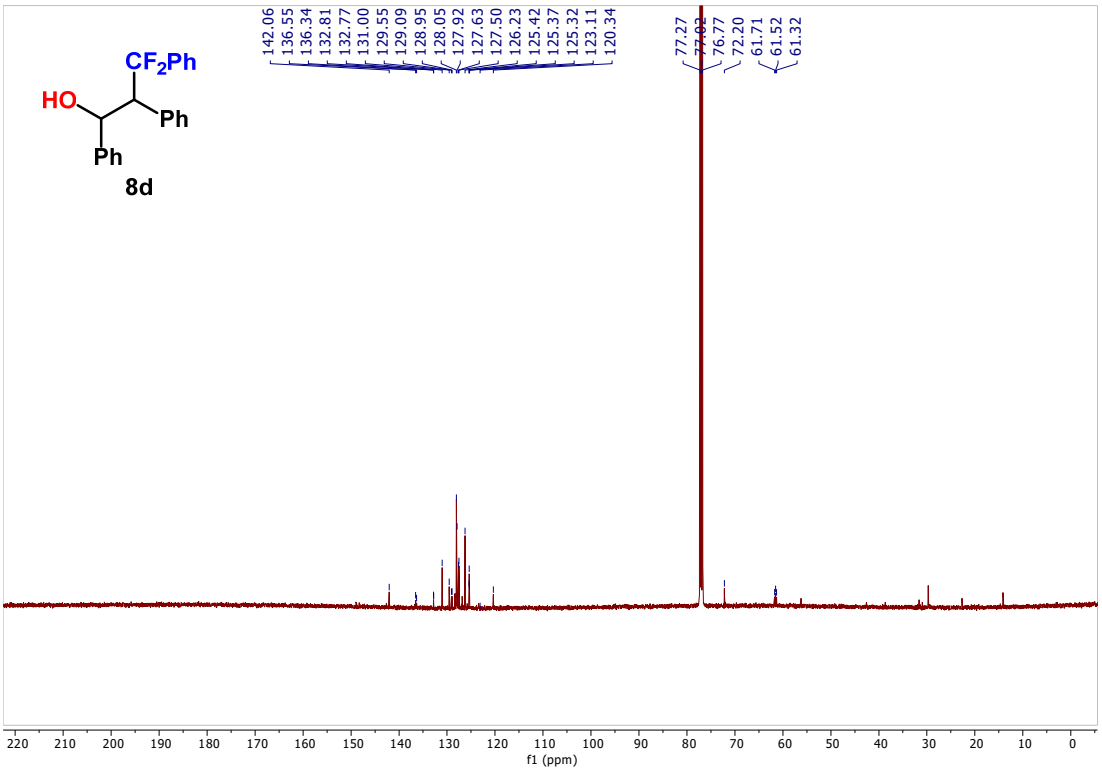


Fig. S109. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **8d**.

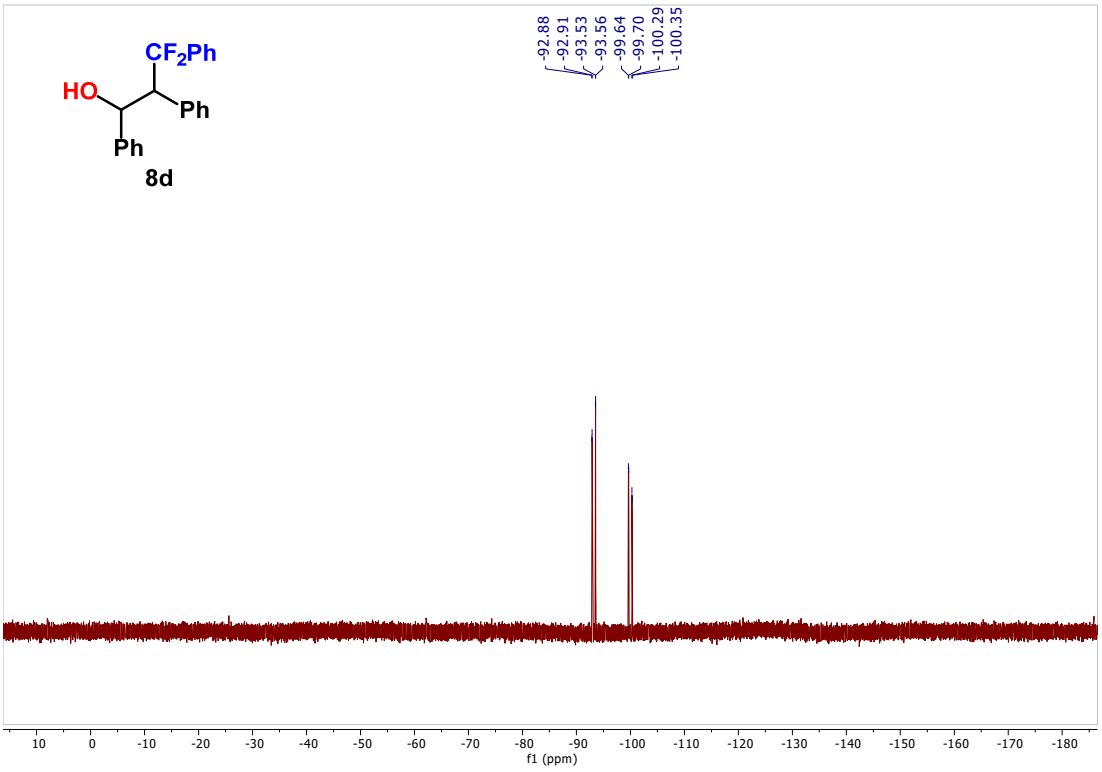


Fig. S110. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **8d**.

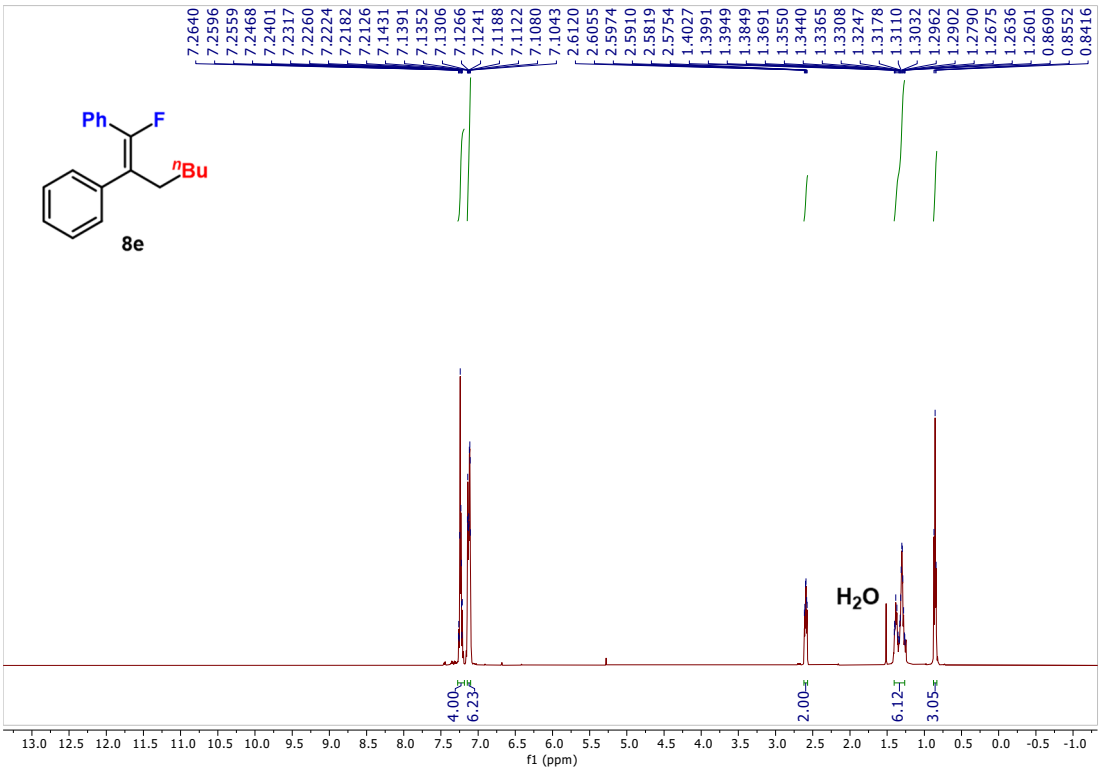


Fig. S111. ^{1}H NMR spectrum (**$CDCl_3$**, **25** °C) of **8e**.

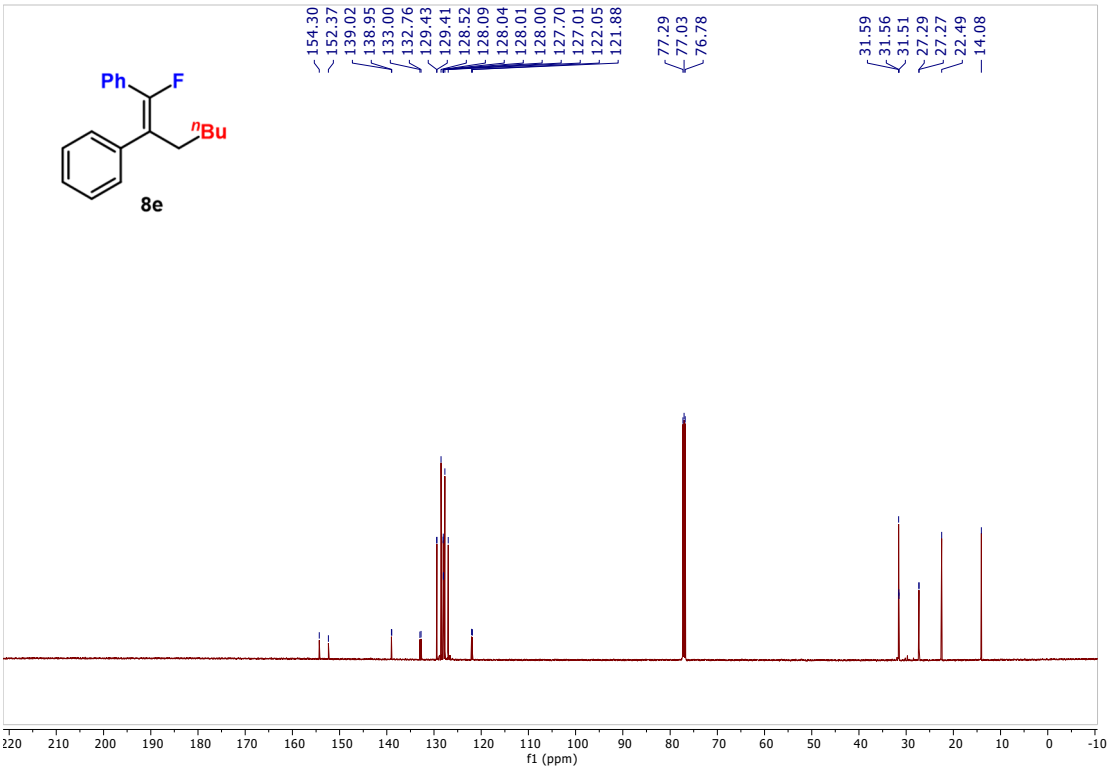


Fig. S112. ^{13}C NMR spectrum (**$CDCl_3$**, **25** °C) of **8e**.

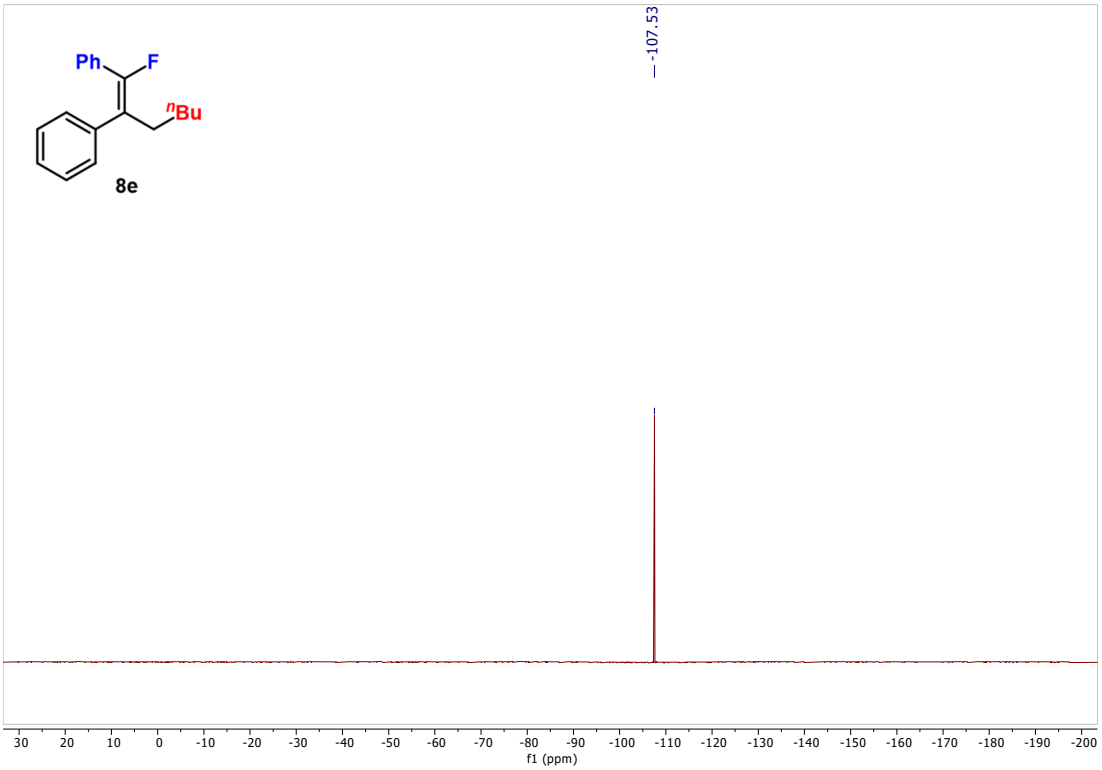
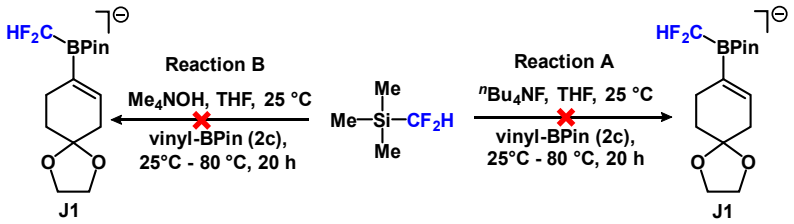


Fig. S113. ^{19}F NMR spectrum (**$CDCl_3$**, **25** °C) of **8e**.

J) Reaction of $Me_3Si\text{-}CF_2H$ with vinyl-BPin (2c):



$Me_3Si\text{-}CF_2H$ (0.1 mmol), $^nBu_4NF$ or Me_4NOH (0.12 mmol) and $PhOCF_3$ (0.2 mmol) were dissolved in 1.0 mL of THF in a screw cap tube. The reaction mixture was stirred for 30 minutes at 25 °C and then the change was observed by ^{19}F NMR spectroscopy. Next, vinyl-BPin (**2c**) (0.1 mmol) was added to the mixture. Finally, the mixture was stirred at 25 °C for 1 h and gradually increasing the temperature to 80 °C. The mixture was heated at 80 °C for 20 h and change was observed by ^{19}F NMR spectroscopy. ^{19}F NMR spectroscopy suggests that there is no conversion of the viny-BPin-CF_2H adduct even after 20 h at 80 °C.

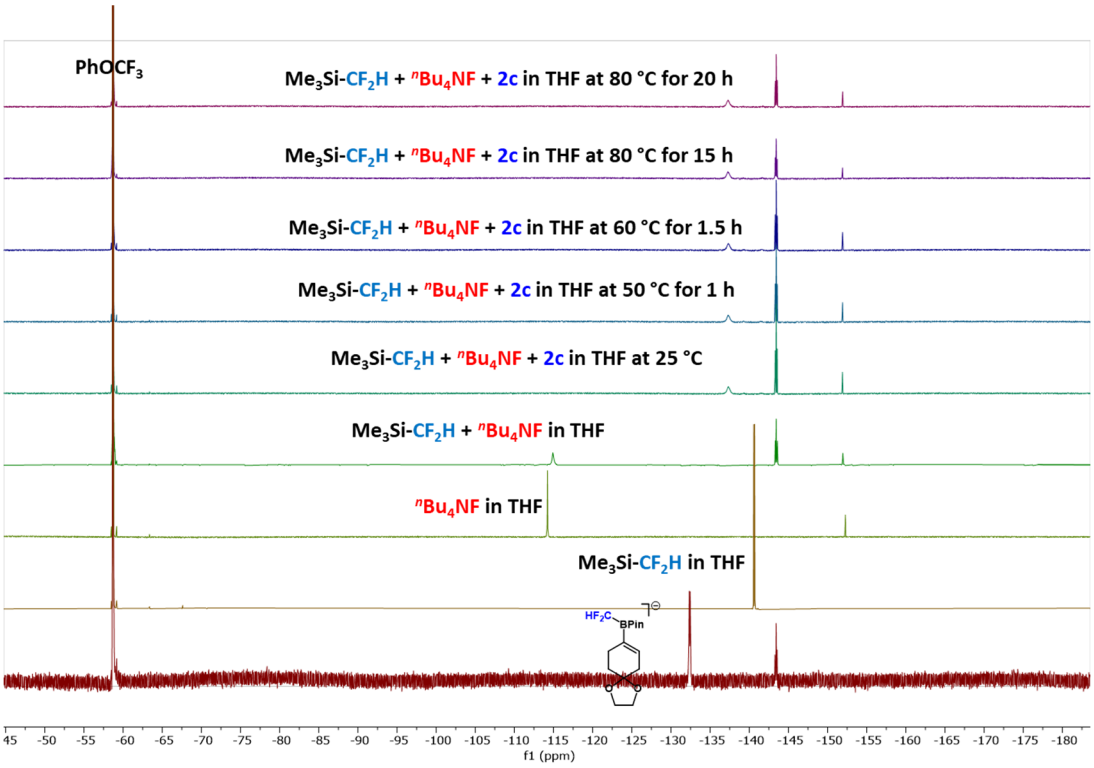


Fig. S114. Stacked ^{19}F NMR spectra (**THF-H_8, 25 °C**) of reaction **A**.

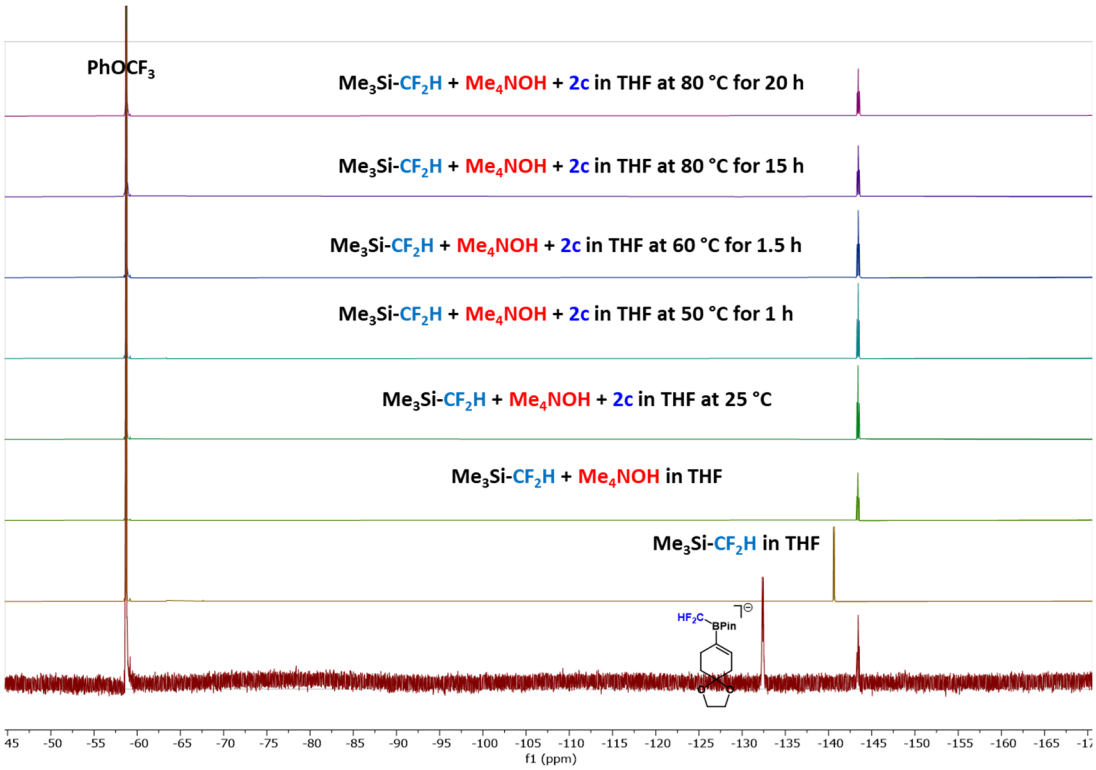
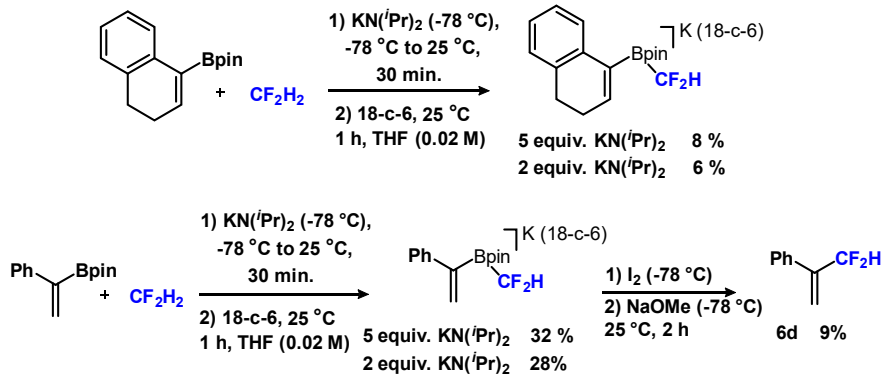


Fig. S115. Stacked ^{19}F NMR spectra (**THF-H$_8$, 25 °C**) of reaction **B**.

K) One-pot Zweifel olefination reaction with CH_2F_2:

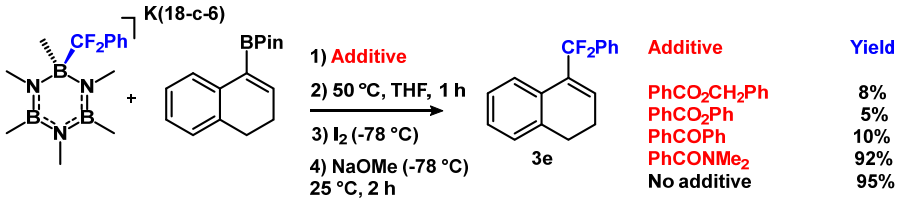


Vinyl-BPin derivatives (0.1 mmol) and KN(^{i}Pr)$_2$ (0.2 mmol or 0.5 mmol) were taken in a 20 mL vial and cooled to -78 °C. Then, 1.5 mL chilled THF (kept at -78 °C) was added to the solid mixture at -78 °C. The mixture was rapidly stirred at -78 °C for 10 minutes. Then, CH_2F_2 (0.4 mmol, 9 mL) was bubbled through the reaction mixture and stirred for 30 minutes. The mixture was allowed to warm at 25 °C and stirred for another 20 minutes. After that, 18-crown-6 (0.1 mmol) was added to this mixture and stirred for 1 hour. The yield of the adducts was assessed by ^{19}F NMR spectroscopy ($PhOCF_3$ (0. 2 mmol) was added as an internal standard).

For the Zweifel olefination sequence, the adduct mixture was again cooled to -78 °C. Iodine (0.2 mmol, 0.5 mL solution in THF) was added at the same temperature and stirred for 30 min. Next, NaOMe (0. 2 mmol, 0.5 mL solution in MeOH) was added to this mixture at –78 °C and stirred for 30 min. The contents

were allowed to warm to room temperature and mix for 2 h at 25 °C before the yield was assessed by ^{19}F NMR spectroscopy ($PhOCF_3$ (0.2 mmol) was added as internal standard).

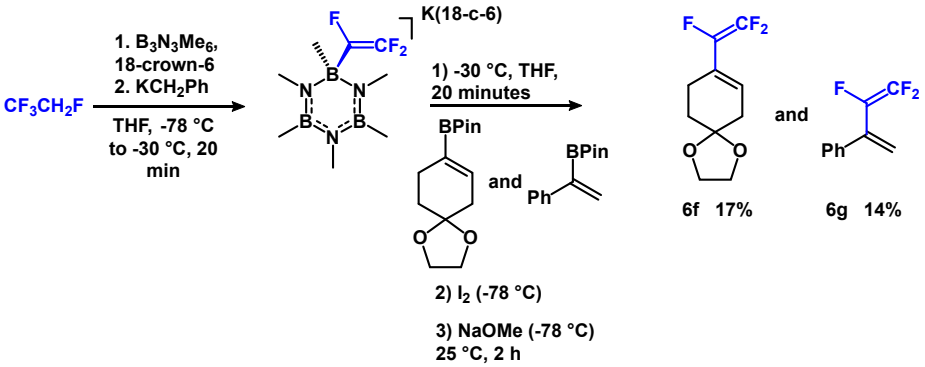
L) Electrophilic group tolerance in $PhCF_2^-$ anion transfer:



$[Me_6B_3N_3CF_2Ph]K(18\text{-c-}6)$ (0.1 mmol), 2-(3,4-dihydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.1 mmol), **additive (0.1 mmol)** and $PhOCF_3$ (0.2 mmol) were dissolved in 1.6 mL of THF in a 20 mL vial. The reaction mixture was heated for 1 h at 50 °C and then cooled to -78 °C. Next, iodine (0.2 mmol, 0.2 mL solution in THF) was added at –78 °C and stirred for 30 min. Next, NaOMe (0.2 mmol, 0.2 mL solution in MeOH) was added to this mixture at –78 °C and stirred for 30 min. Finally, the contents were allowed to warm up at room temperature and mix for 2 h at 25 °C before the yield was assessed by ^{19}F NMR spectroscopy ($PhOCF_3$ used as internal standard).

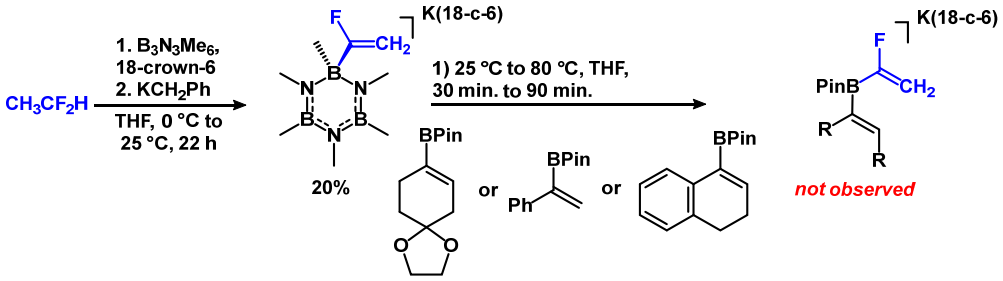
M) Zweifel olefination reaction with fluoroalkanes:

1) Reaction of 1,1,1,2-tetrafluoroethane (CF_3-CH_2F):



Hexamethylborazine, $B_3N_3Me_6$ (0.2 mmol) and 18-crown-6 (0.2 mmol) were dissolved in 1.4 mL of THF. The solution was cooled to -78 °C for 1 h and benzyl potassium (0.2 mmol) was added. After 10 minutes, 1,1,1,2-tetrafluoroethane gas (1.0 mmol) bubbled through the THF solution and the mixture was warmed to -30 °C. The reaction mixture was allowed to stir at -30 °C for 20 min. Then, vinyl-BPin was added to the mixture, and it was stirred at -30 °C for 20 min. Next, iodine (0.182 mmol in THF solution) was added at –78 °C and stirred for 30 min. After that, NaOMe (0.182 mmol in NaOMe solution) was added to this mixture at –78 °C and stirred it for 30 min (I_2 and NaOMe were added by assuming that the $[(B_3N_3Me_6\text{-}CF{=}CF_2)(K(18\text{-c-}6))]$ adduct formation is quantitative). Finally, the contents were allowed to mix for 2 hours at 25 °C and yield was determined by ^{19}F NMR (PhF was used as internal standard).

2) Reaction of 1,1-difluoroethane (CH_3-CF_2H):



Hexamethylborazine, $B_3N_3Me_6$ (0.61 mmol, 100 mg) and 18-crown-6 (0.61 mmol, 160 mg) were dissolved in 3 mL of THF. The solution was cooled to 0 °C in an ice bath and benzyl potassium (1.21 mmol, 158 mg) was added. After 10 minutes, 1,1-difluoroethane gas (0.74 mmol, 15 mL) bubbled through the THF solution and $PhOCF_3$ (0.061 mmol, 8.0 µL) were added. The reaction mixture was allowed to stir at 25 °C for 22 h and the in-situ yield was assessed by ^{19}F NMR (26%, $PhOCF_3$ was used as internal standard). The THF solution was removed and the crude solid was washed with pentane (3 x 5 mL). A pale pink powder was obtained after drying under vacuum (20% isolated yield).

[$(Me_6B_3N_3$-$CF=CH_2)$(K(18-crown-6))] (0.03 mmol), vinyl-BPin (0.03 mmol) were dissolved in 0.8 mL of THF in a screwcap NMR tube. The reaction mixture was heated for specified time at different temperatures (50 °C – 80 °C) and monitored through ^{19}F NMR spectroscopy ($PhOCF_3$ was used as internal standard). No reactivity was observed at 25 °C to 50 °C. However, all the higher temperature (60 °C and above) reactions decomposed to CH_2=CFH alkene.

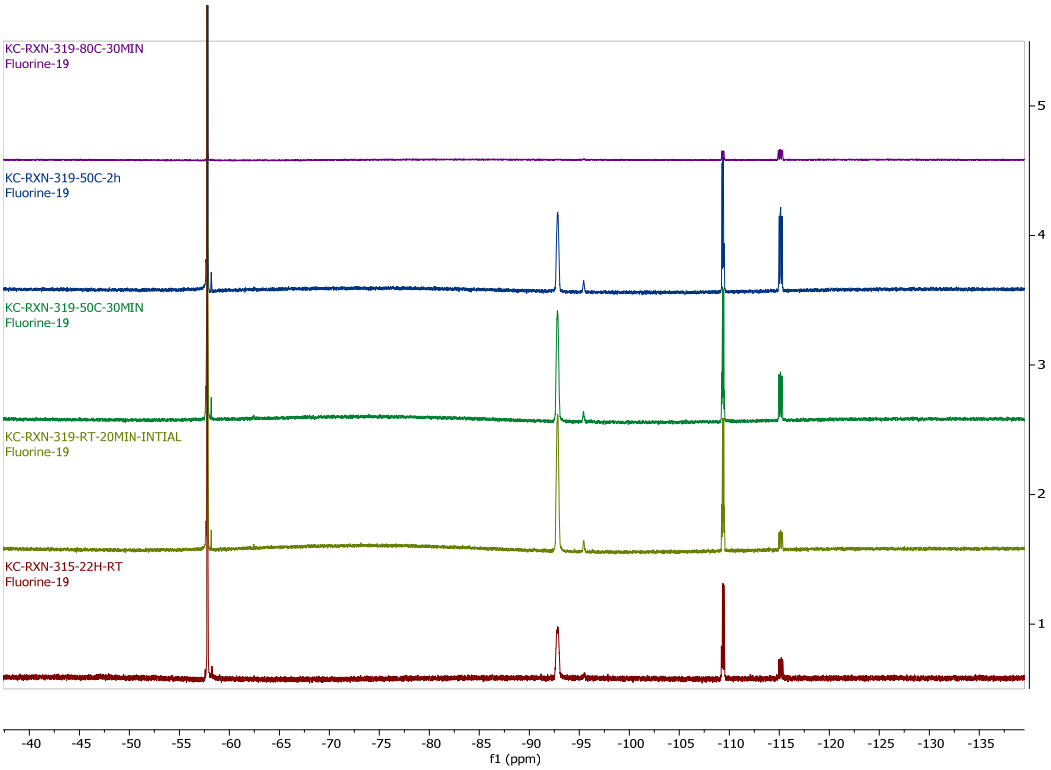
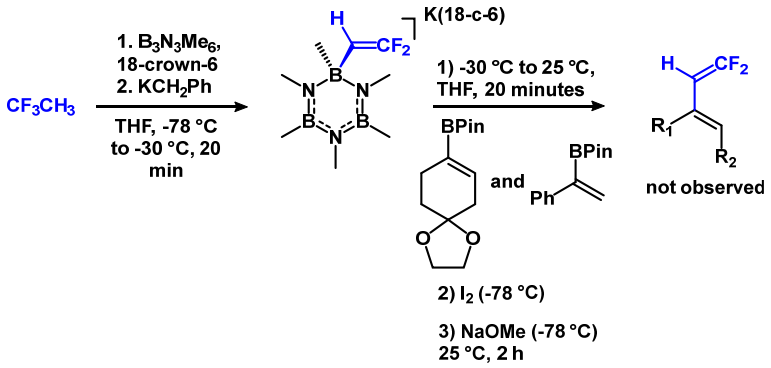


Fig. S116. Stacked ^{19}F NMR spectra (**THF-H_8, 25 °C**) of the reaction of [$Me_6B_3N_3$-$CF=CH_2$)(K(18-crown-6))] with 2-(3,4-dihydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

2) Reaction of 1,1,1-trifluoroethane (CH_3-CF_3):



Hexamethylborazine, $B_3N_3Me_6$ (0.2 mmol) and 18-crown-6 (0.2 mmol) were dissolved in 1.4 mL of THF. The solution was cooled to -78 °C for 1 h and benzyl potassium (0.2 mmol) was added. After 10 minutes, 1,1,1-tetrafluoroethane gas (1.0 mmol) bubbled through the THF solution and the mixture was warmed to -30 °C. The reaction mixture was allowed to stir at -30 °C for 20 min. Then, vinyl-BPin was added to the mixture, and it was stirred at -30 °C to 25 °C for 30 min. Next, iodine (0.182 mmol in THF solution) was added at –78 °C and stirred for 30 min. After that, NaOMe (0.182 mmol in NaOMe solution) was added to this mixture at –78 °C and stirred it for 30 min (I_2 and NaOMe were added by assuming that the [($B_3N_3Me_6$-$CF{=}CF_2$)(K(18-c-6))] adduct formation is quantitative). Finally, the contents were allowed to mix for 2 hours at 25 °C and yield was determined by ^{19}F NMR. We don't observe any peak related to the Zweifel olefination product in the spectrum ([($B_3N_3Me_6$-$CF{=}CF_2$)(K(18-c-6))] thermally unstable above -30 °C).

N) References:

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