Palladium Hydride-Enabled Hydroalkenylation of Strained Molecules

Ziyan Zhang and Vladimir Gevorgyan*

Department of Chemistry and Biochemistry, University of Texas at Dallas, 800 W Campbell RD, Richardson, Texas 75080, United States, Email: vlad@utdallas.edu

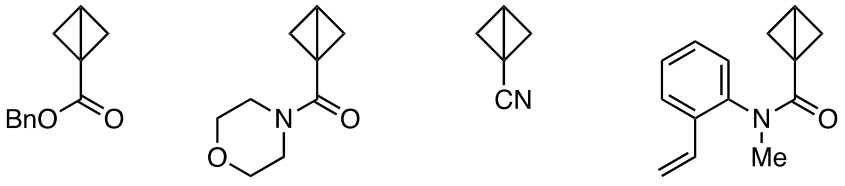
Table of Contents

1. General Information

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance III HD (600 MHz) instrument. ^{1}H signals are referenced to residual $CHCl_3$ at 7.26 ppm. ^{13}C signals are referenced to $CDCl_3$ at 77.16 ppm. ^{19}F NMR were obtained with ^{1}H decoupling. GC/MS analysis was performed on Agilent 7890A gas chromatograph coupled with Agilent 5975C mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out using Silicycle Silica-P flash silica gel (40-63 μm) and Acros Organics neutral aluminum oxide (Brockmann I, 40-300 μm, 60Å). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. HRMS analysis was performed on maXis plus quadrupole-time of flight mass spectrometer equipped with an electrospray ionization source or atmospheric pressure chemical ionization source (Bruker Daltonics). Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. All starting materials were purchased from Strem Chemicals, Aldrich, Gelest Inc., TCI America, Oakwood Chemical, AK Sci. or Alfa Aesar, or synthesized via known literature procedures. 34 W Blue LED lamps (Kessil KSH150B LED Grow Light) and 40 W LED lamp (Kessil PR160-427) were purchased from Kessil. Photoreactors (PhotoRedOx Box) were purchased from HepatoChem. All manipulations with transition metal catalysts were conducted in oven-dried glassware using a combination of glovebox and standard Schlenk techniques.

2. Preparation of Starting Materials

2.1 Synthesis of bicyclo[1.1.0]butanes (BCBs):

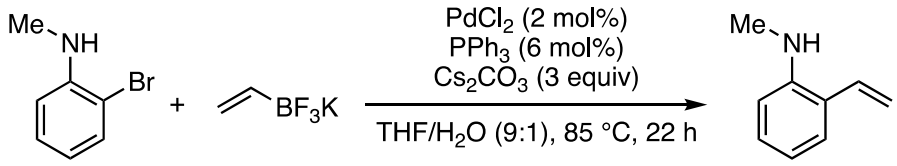


4a **4b** **4c** **4d**

BCBs **4a**-**4c** are known compounds and were prepared using reported procedures.[1]

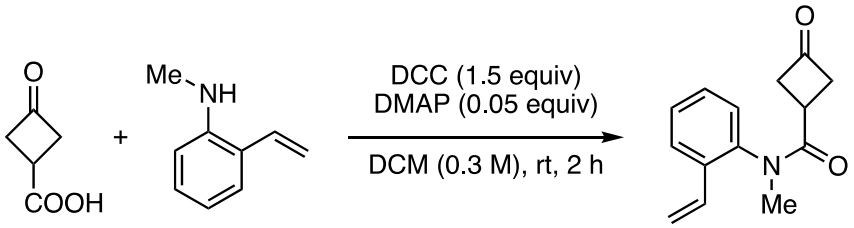
Starting material **4d** was synthesized according to the following modified literature procedures.[1]

Step 1:



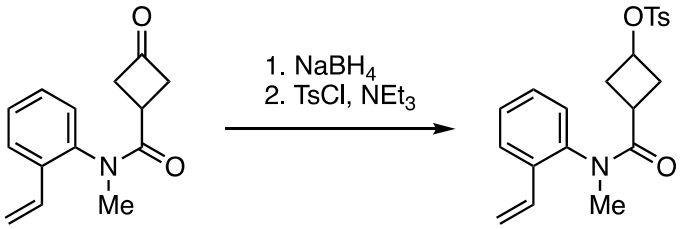
General procedure for Suzuki-Miyaura cross-coupling reactions[2]: A sealed tube was charged with aryl bromide (2.97 g, 16 mmol, 1.0 equiv), potassium vinyltrifluoroborate (0.669 g, 16 mmol, 1.0 equiv), $PdCl_2$ (0.017 g, 0.32 mmol, 0.02 equiv), and the tube was brought into a N_2-filled glovebox. PPh_3 (0.078 g, 0.96 mmol, 0.06 equiv), Cs_2CO_3 (15.63 g, 48 mmol, 3 equiv) and 28 mL THF were added, and the tube was sealed and removed from the glovebox. 3.2 mL H_2O was added, and the mixture was stirred at 85 °C for 22 h. The resulting dark brown mixture was allowed to cool to room temperature, diluted with DCM, and washed with H_2O. The aqueous layer was extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude alkenes were purified with column chromatography (silica, EtOAc/Hexanes) in 62% yield.

Step 2:



3-Oxocyclobutanecarboxylic acid (1.14 g, 9.5 mmol, 1.0 equiv) was dissolved in dry DCM (0.3 M) and amine (1.27 g, 9.5 mmol, 1 equiv), DMAP (58 mg, 0.47 mmol, 0.05 equiv) and DCC (2.94 g, 14.2 mmol, 1.5 equiv) were added. The reaction mixture was stirred under Ar atmosphere for 2 h (or until TLC indicated full conversion of the acid). Subsequently, the reaction mixture was filtrated, and the precipitate (dicyclohexylurea) was rinsed with small amount of DCM. The filtrate was concentrated in vacuo, and the crude amide was purified by column chromatography in 97% yield.

Step 3 and 4:

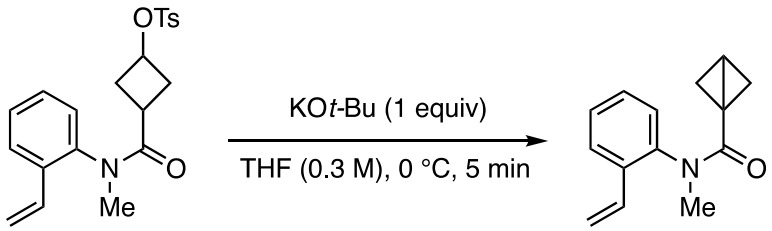


The ketone (2.10 g, 9.2 mmol, 1 equiv) was redissolved in MeOH (1.0 M), cooled to 0 °C and $NaBH_4$ (522 mg, 13.8 mmol, 1.5 equiv) was carefully added. The reaction mixture was stirred for 30 min at 0 °C. After this time, the reaction was quenched with water, and extracted with DCM. Combined organic fractions were dried over Na_2SO_4, filtrated and concentrated *in vacuo*.

The crude alcohol was redissolved in dry DCM (1.0 M), cooled to 0 °C and consecutively TsCl (2.28 g, 12 mmol, 1.3 equiv) and NEt_3 (1.67 ml, 12 mmol, 1.3 equiv) were added. The reaction mixture was warmed to rt and stirred under Ar atmosphere, until TLC indicated full conversion of the alcohol (usually within 2 h). Subsequently, the reaction mixture was washed with water and

brine. The organic layer was dried over Na_2SO_4, filtrated and concentrated in vacuo. The crude tosylate was purified by column chromatography in 60% over two steps.

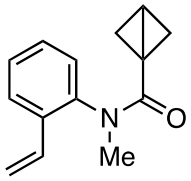
Step 5:



4d

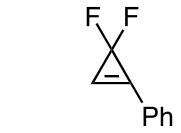
The solution of tosylate (2.15 g, 5.6 mmol, 1 equiv) in dry THF (0.15 M) was cooled to 0 °C, and KO*t*-Bu (1 M THF solution, 1 equiv) was added dropwise under Ar atmosphere. The reaction mixture was stirred for 5 min (if the TLC did not indicate full conversion of the substrate another portion (0.1 equiv.) of KO*t*Bu was added). Subsequently, the reaction was quenched with saturated NH_4Cl solution and extracted with DCM. Combined organic fractions were dried over Na_2SO_4, filtrated and concentrated in vacuo. The crude bicycle[1.1.0]butane **4d** was purified by column chromatography in 64% yield.

N-methyl-*N*-(2-vinylphenyl)bicyclo[1.1.0]butane-1-carboxamide **4d**

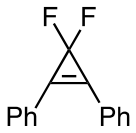


4d was prepared in 22% yield over 5 steps as colorless oil. R_f (hexanes/EtOAc = 2/1): 0.20. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 11.57 (s, 1H), 7.82 – 7.79 (m, 2H), 7.30 – 7.28 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.61 – 2.51 (m, 1H), 2.42 (s, 3H), 1.82 – 1.69 (m, 4H), 1.33 – 1.29 (m, 3H), 1.28 – 1.15 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 162.5, 144.6, 141.6, 138.8, 135.8, 129.9, 128.7, 128.2, 126.5, 126.4, 53.0, 28.0, 23.9, 21.9, 17.4. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{14}H_{16}NO$ 214.1226; found: 214.1230.

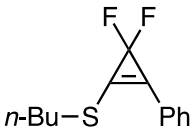
2.2 Synthesis of cyclopropenes:



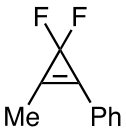
1a



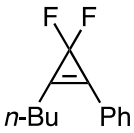
1b



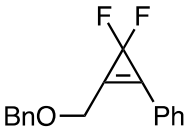
1c



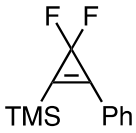
1d



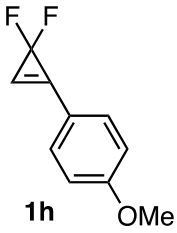
1e



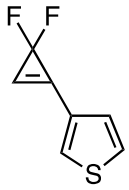
1f



1g

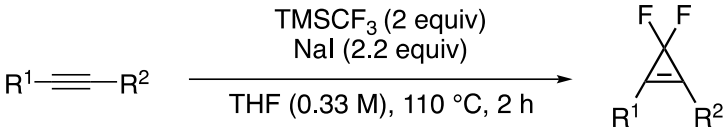


1h



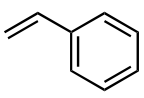
1i

gem-Difluorocyclopropenes **1a**-**1i** are known compounds and prepared using reported procedures.[3]

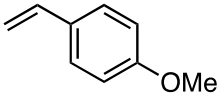


General Procedure A: Alkyne (5.0 mmol), $TMSCF_3$ (1.48 mL, 10.0 mmol), NaI (1.66 g, 11 mmol), and THF (15.0 mL) were mixed into a pressure tube at room temperature. Then the reaction mixture was heated at 110 °C for 2 h. The reaction was quenched by adding saturated Na_2CO_3 solution (15 mL), followed by extraction with Et_2O (50 mL) for two times. The organic phase was dried over anhydrous K_2CO_3. After the removal of solvent under vacuum, the residue was subjected to silica gel column chromatography using hexanes/Et_3N (40/1, v/v) as eluent. The column should be eluted previously with hexanes/Et_3N (10/1, v/v).

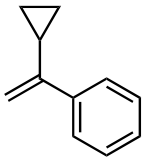
Synthesis of alkenes:



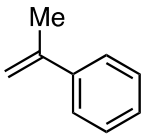
2a



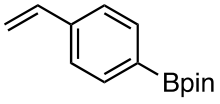
2b



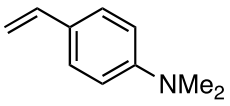
2c



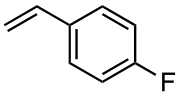
2d



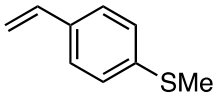
2e



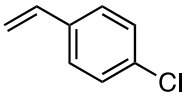
2f



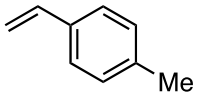
2g



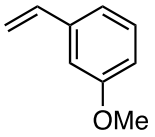
2h



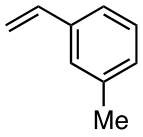
2i



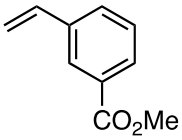
2j



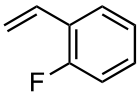
2k



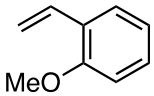
2l



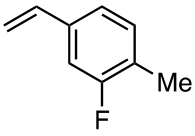
2m



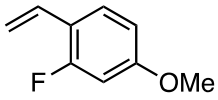
2n



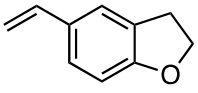
2o



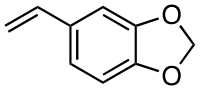
2p



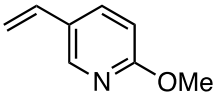
2q



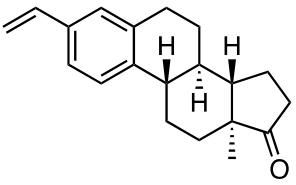
2r



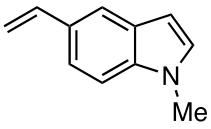
2s



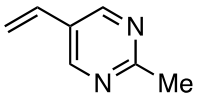
2t



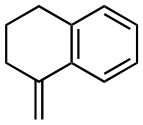
2u



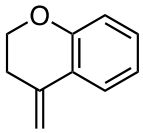
2v



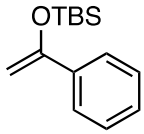
2w



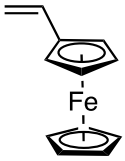
2x



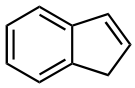
2y



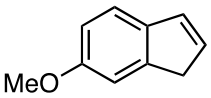
2z



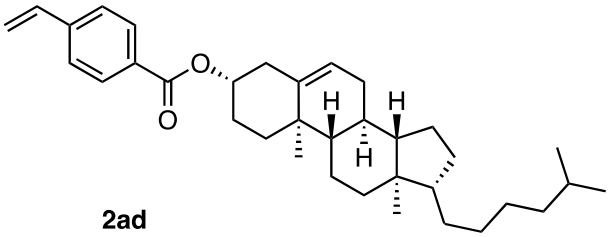
2aa



2ab



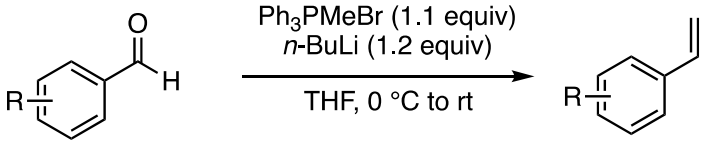
2ac



2ad

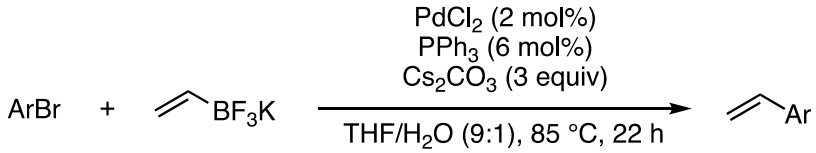
Alkenes **2c**, **2q**, **2t**, **2w**, **2x**, **2y**, and **2aa** were prepared using general procedure B. **2p**, **2r**, **2s**, and **2v** were prepared using general procedure C. **2e**,[4] **2u**,[5] **2z**,[6] **2ac**,[7] and **2ad**[8] were prepared using reported literature procedure. Other alkenes are commercially available.

General Procedure B:



General procedure for Wittig reaction: To a suspension of methyl triphenylphosphonium bromide (3.93 g, 11 mmol, 1.1 equiv) in THF (30 mL) at 0 ^{o}C was added *n*-butyllithium (1.6 M in hexanes) (7.5 mL, 12 mmol, 1.2 equiv) dropwise over 5 min under inert atmosphere. The resulting mixture was stirred at rt for 1 h. A solution of aldehyde or ketone (10 mmol, 1 equiv) in THF (5 mL) was then added dropwise. The reaction mixture was stirred at rt until the completion as monitored by TLC (2-4 h). The reaction was quenched with water (20 mL) and extracted with EtOAc (3 × 30 mL), the combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude alkenes were purified by flash chromatography (silica, EtOAc/Hexanes).

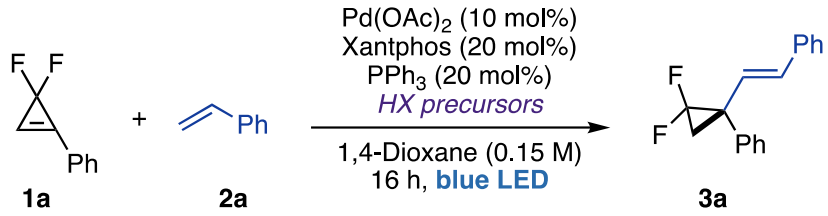
General Procedure C:



General procedure for Suzuki-Miyaura cross-coupling reactions[2]: A sealed tube was charged with arylbromide (5 mmol, 1.0 equiv), potassium vinyltrifluoroborate (0.669 g, 5 mmol, 1.0 equiv), $PdCl_2$ (0.017 g, 0.10 mmol, 0.02 equiv), and the tube was brought into a N_2-filled glovebox. PPh_3 (0.078 g, 0.30 mmol, 0.06 equiv), Cs_2CO_3 (4.88 g, 15 mmol, 3 equiv) and 9 mL THF were added, and the tube was sealed and removed from the glovebox. 1 mL H_2O was added, and the mixture was stirred at 85 °C for 22 h. The resulting dark brown mixture was allowed to cool to room temperature, diluted with DCM, and washed with H_2O. The aqueous layer was extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude alkenes were purified with column chromatography (silica, EtOAc/Hexanes).

3. Reaction Optimization for Hydroalkenylation of Cyclopropenes

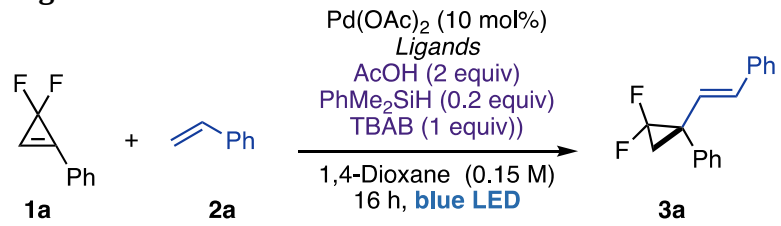
3.1 Screening of HX precursors



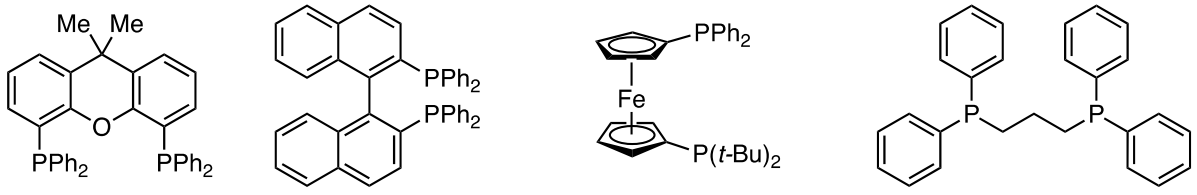
Entry	HX precursors			Yield[a] (%)
	Hydrosilane (0.2 equiv)	Acid (2 equiv)	Halide source (1 eqiuv)	
1	-	AcOH	NaI	22
2	$PhMe_2SiH$	AcOH	NaI	42
3	$PhMe_2SiH$	CF_3COOH	NaI	0
4	$PhMe_2SiH$	*p*-TsOH·H_2O	NaI	traces
5	$PhMe_2SiH$	PivOH	NaI	44
6	$PhMe_2SiH$	PhCOOH	NaI	31
7	$PhMe_2SiH$		Et_3N·HI	54
8	$PhMe_2SiH$		Et_3N·HBr	49
9	$PhMe_2SiH$		Et_3N·HCl	25
10	$PhMe_2SiH$		NH_4Cl	0
11	$PhMe_2SiH$	AcOH	TBAC	0
12	$PhMe_2SiH$	AcOH	TBAB	57
13	$PhMe_2SiH$	AcOH	TBAI	32
14	Ph_2SiH_2	AcOH	TBAB	48
15	$PhMeSiH_2$	AcOH	TBAB	55
16	Et_3SiH	AcOH	TBAB	52
17	$PhSiH_3$	AcOH	TBAB	40
18	PMHS	AcOH	TBAB	50
19	$(EtO)_3SiH$	AcOH	TBAB	0

[a]0.1 mmol scale, **1a**:**2a** = 1:2, blue LED (40 W, 427 nm). Yields were determined by ^1H NMR spectroscopy using dibromomethane as an internal standard.

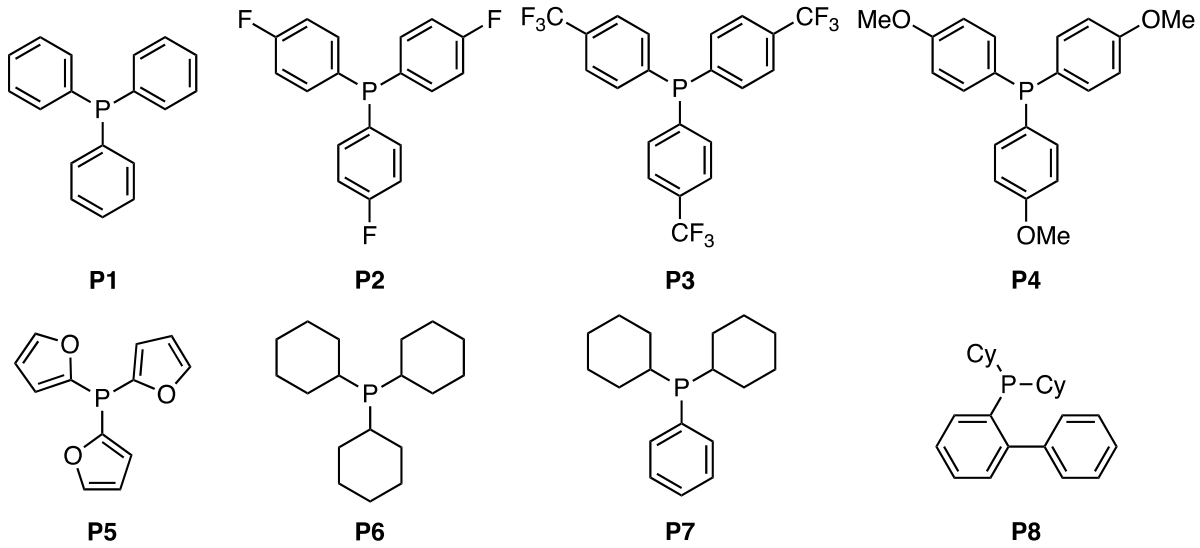
3.2 Screening of ligands



Bidentate phosphine ligands



Monodentate phosphine ligands

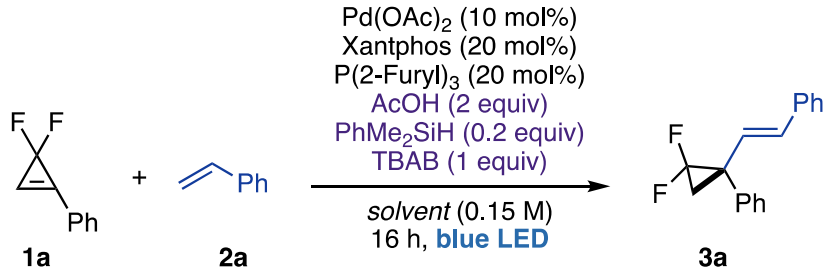


Entry	L_1 (20 mol%)	L_2 (20 mol%)	Yield[a] (%)
1	Xantphos	PPh_3	57
2	*rac*-BINAP	PPh_3	0
3	dtbdppf	PPh_3	0
4	dppp	PPh_3	0
5	Xantphos	$P(4\text{-F-Ph})_3$ **P2**	59
6	Xantphos	$P(4\text{-}CF_3\text{-Ph})_3$ **P3**	76

7	Xantphos	P(4-OMe-Ph)$_3$ **P4**	43
8	Xantphos	P(2-Furyl)$_3$ **P5**	80[b]
9	Xantphos	PCy$_3$ **P6**	72
10	Xantphos	PCy$_2$Ph **P7**	68
11	Xantphos	CyJohnPhos **P8**	61
12	Xantphos	P(*t*-Bu)$_3$	74

[a]0.1 mmol scale, **1a**:**2a** = 1:2, blue LED (40 W, 427 nm). Yields were determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. [b]0.15 mmol scale, isolated yields.

3.3 Screening of solvents



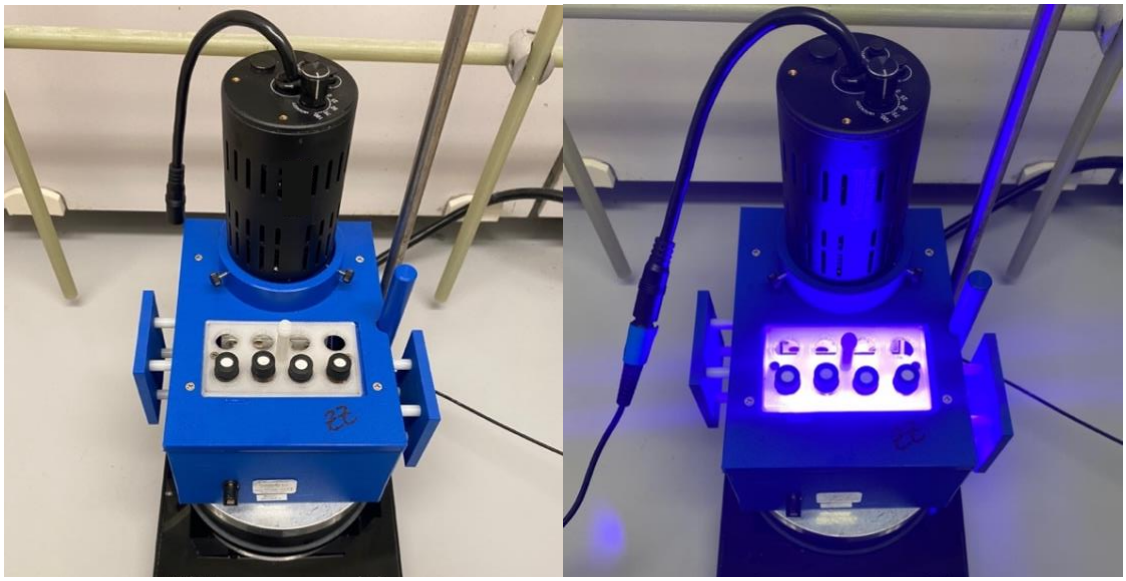
1a **2a** **3a**

Entry	Solvent	Yields[a] (%)
1	1,4-Dioxane	80[b]
2	DMA	0
3	DMF	traces
4	MeCN	0
5	THF	32
6	DCM	0
7	PhH	54
8	PhMe	57

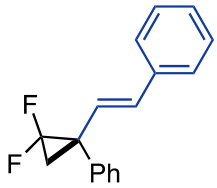
[a] 0.1 mmol scale, **1a**:**2a** = 1:2, blue LED (40 W, 427 nm). Yields were determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. [b]0.15 mmol scale, isolated yields.

4. General Procedures for Hydroalkenylation of Cyclopropenes

General Procedure D: An oven dried 2 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%), $P(2\text{-Furyl})_3$ (20 mol%), and TBAB (1 equiv) inside glovebox. Next, 1,4-dioxane (0.15 M), acetic acid (2 equiv), $PhMe_2SiH$ (0.2 equiv), styrene **2** (2 equiv) and cyclopropene **1** (0.15 mmol) were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was stirred for 16 h. The resulting mixture was filtered through a short plug of silica gel using hexanes/EtOAc as eluent. The filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography on neutral aluminum oxide in hexanes/EtOAc to afford the corresponding products **3**.

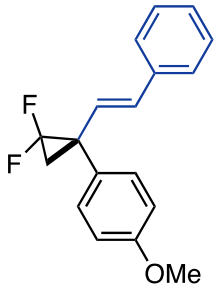


(*E*)-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)benzene **3a**



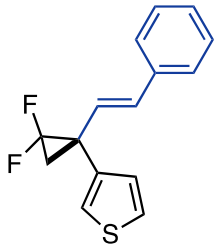
3a was prepared according to the general procedure in 80% yield (31 mg, 0.120 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.46 – 7.39 (m, 2H), 7.39 – 7.30 (m, 3H), 7.29 – 7.24 (m, 4H), 7.23 – 7.16 (m, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 6.01 (d, *J* = 15.9 Hz, 1H), 1.99 (ddd, *J* = 12.8, 7.7, 4.8 Hz, 1H), 1.88 (ddd, *J* = 12.7, 7.6, 4.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 136.4, 135.4, 132.0, 130.1 (d, *J* = 1.8 Hz), 128.4, 128.3, 128.3 (d, *J* = 3.5 Hz), 127.6, 127.4, 126.0, 113.7 (dd, *J* = 292.4, 289.6 Hz), 38.4 (t, *J* = 10.8 Hz), 24.0 (dd, *J* = 10.6, 8.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.7 (d, *J* = 149.7 Hz), -133.9 (d, *J* = 149.9 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{17}H_{14}F_2$ 256.1064, found: 256.1060.

(*E*)-1-(2,2-difluoro-1-styrylcyclopropyl)-4-methoxybenzene **3b**



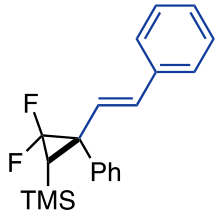
3b was prepared according to the general procedure in 46% yield (20 mg, 0.069 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 5H), 7.20 – 7.17 (m, 1H), 7.00 – 6.84 (m, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 6.01 (d, *J* = 15.9 Hz, 1H), 3.84 (s, 3H), 1.94 (ddd, *J* = 12.7, 7.5, 4.9 Hz, 1H), 1.89 – 1.77 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) 159.2, 136.8, 132.1, 131.5, 129.0 (dd, *J* = 6.7, 3.4 Hz), 128.6, 127.6, 126.2, 114.2 (dd, *J* = 292.6, 289.7 Hz), 114.1, 55.4, 38.1 (t, *J* = 10.7 Hz), 24.5 (dd, *J* = 10.6, 8.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -128.8 (d, *J* = 149.3 Hz), -134.0 (d, *J* = 149.4 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{16}F_2O$ 286.1164, found: 286.1164.

(*E*)-3-(2,2-difluoro-1-styrylcyclopropyl)thiophene **3c**



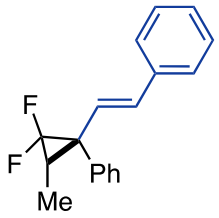
3c was prepared according to the general procedure in 66% yield (26 mg, 0.099 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.36. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.32 – 7.25 (m, 5H), 7.22 – 7.20 (m, 1H), 7.08 – 7.05 (m, 1H), 6.25 (d, *J* = 15.9 Hz, 1H), 6.18 (d, *J* = 15.9 Hz, 1H), 1.96 (ddd, *J* = 12.8, 7.6, 5.2 Hz, 1H), 1.88 (ddd, *J* = 12.7, 7.6, 4.7 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 136.6, 136.2, 132.4, 128.9, 128.7, 127.7, 127.4 (dd, *J* = 6.2, 3.4 Hz), 126.3, 126.0, 124.7, 113.8 (dd, *J* = 293.0, 289.3 Hz), 34.2 (t, *J* = 11.1 Hz), 24.9 (dd, *J* = 10.3, 8.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -130.1 (d, *J* = 150.0 Hz), -133.9 (d, *J* = 150.0 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{15}H_{12}F_2S$ 262.0622, found: 262.0621.

(*E*)-(2,2-difluoro-3-phenyl-3-styrylcyclopropyl)trimethylsilane **3d**



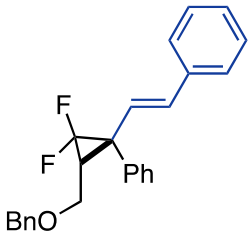
3d was prepared according to the general procedure in 68% yield (33 mg, 0.102 mmol) as colorless oil. One diastereomer. R_f (hexanes/EtOAc = 20/1): 0.48. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.42 – 7.32 (m, 5H), 7.28 – 7.24 (m, 4H), 7.19 (ddd, *J* = 6.2, 4.9, 3.4 Hz, 1H), 6.24 (dd, *J* = 15.9, 1.5 Hz, 1H), 5.92 (d, *J* = 15.9 Hz, 1H), 1.32 (dd, *J* = 18.7, 10.7 Hz, 1H), -0.11 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 136.7, 135.0, 131.8 (dd, *J* = 6.2, 3.9 Hz), 131.4, 131.0, 128.4, 128.2, 127.9 (d, *J* = 1.7 Hz), 127.5, 127.3, 126.0, 117.5 (dd, *J* = 291.8, 289.5 Hz), 41.9 – 41.5 (m), 28.6 (dd, *J* = 15.5, 3.2 Hz), -1.00. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -122.73 (d, *J* = 145.8 Hz), -126.65 (d, *J* = 145.6 Hz). HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{20}H_{23}F_2Si$ 329.1532, found: 329.1527.

(*E*)-(2-(2,2-difluoro-3-methyl-1-phenylcyclopropyl)vinyl)benzene **3e**



3e was prepared according to the general procedure in 69% yield (28 mg, 0.103 mmol), dr 9:1, as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.36. ^{1}H NMR data are provided only for the major diastereomer. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.44 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.34 (m, 2H), 7.33 – 7.26 (m, 6H), 7.23 – 7.17 (m, 1H), 6.23 (dd, *J* = 15.9, 1.7 Hz, 1H), 5.93 (d, *J* = 15.9 Hz, 1H), 2.10 – 1.96 (m, 1H), 1.06 (dd, *J* = 6.6, 2.3 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 137.1, 133.1, 131.8, 131.6, 130.9 (dd, *J* = 7.0, 3.2 Hz), 130.6, 128.8 (d, *J* = 3.1 Hz), 127.8, 127.7, 126.4 (d, *J* = 3.9 Hz), 116.2 (t, *J* = 295.2 Hz), 41.0 – 40.7 (m), 30.3 (t, *J* = 9.2 Hz), 9.2 (d, *J* = 5.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -126.2 (d, *J* = 148.2 Hz, minor), -130.0 (d, *J* = 150.8 Hz, major), -138.8 (d, *J* = 151.0 Hz, major), -144.3 (d, *J* = 148.5 Hz, minor). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{16}F_2$ 270.1215, found: 270.1211.

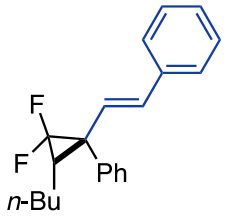
(*E*)-(2-(3-((benzyloxy)methyl)-2,2-difluoro-1-phenylcyclopropyl)vinyl)benzene **3f**



3f was prepared according to the general procedure in 40% yield (23 mg, 0.06 mmol), dr 6:1, as colorless oil. R_f (hexanes/EtOAc = 9/1): 0.32. ^{1}H NMR data are provided only for the major diastereomer. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.42 – 7.36 (m, 4H), 7.36 – 7.31 (m, 3H), 7.31 – 7.21 (m, 7H), 7.19 (dd, *J* = 10.9, 4.3 Hz, 1H), 6.19 (d, *J* = 15.8 Hz, 1H), 5.94 (d, *J* = 15.9 Hz, 1H), 4.48 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 3.45 (d, *J* = 7.0 Hz, 2H), 2.34 (dt, *J* = 14.5, 7.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 137.8, 136.6, 132.3, 132.1, 131.2, 129.5 (dd, *J* = 6.2, 2.9 Hz), 128.6, 128.5 (d, *J* = 4.1 Hz), 127.9, 127.8, 127.7, 127.5, 126.3, 126.2, 114.4 (t, *J* = 294.2 Hz), 73.2, 65.0 (d, *J* = 4.8 Hz), 41.6 (t, *J* = 10.3 Hz), 34.4 (dd, *J* = 9.5, 7.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -125.3 (d, *J* = 154.9 Hz, minor), -129.6 (d, *J* = 156.2 Hz, major),

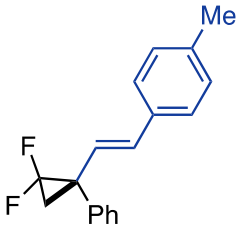
-136.7 (d, *J* = 156.1 Hz, major), -141.6 (d, *J* = 153.1 Hz, minor). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{25}H_{22}F_2O$ 312.1684, found: 312.1683.

(*E*)-(2-(3-butyl-2,2-difluoro-1-phenylcyclopropyl)vinyl)benzene **3g**



3g was prepared according to the general procedure in 50% yield (23 mg, 0.075mmol), dr 7:1, as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.41. ^{1}H NMR data are provided only for the major diastereomer. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.43 – 7.37 (m, 2H), 7.35 – 7.30 (m, 1H), 7.29 – 7.22 (m, 6H), 7.20 – 7.15 (m, 1H), 6.20 (dd, *J* = 15.9, 1.6 Hz, 1H), 5.89 (d, *J* = 15.9 Hz, 1H), 1.99 – 1.85 (m, 1H), 1.63 – 1.48 (m, 2H), 1.48 – 1.37 (m, 2H), 1.34 – 1.24 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 133.2, 131.5, 131.3, 130.8 (dd, *J* = 6.8, 3.3 Hz), 130.5, 128.6 (d, *J* = 4.6 Hz), 127.6, 127.4, 126.2 (d, *J* = 3.2 Hz), 116.0 (t, *J* = 295.1 Hz), 41.0 (dd, *J* = 11.3, 10.0 Hz), 35.5 (t, *J* = 8.6 Hz), 31.4, 24.5 (d, *J* = 3.5 Hz), 22.4, 14.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ -124.9 (d, *J* = 149.0 Hz, minor), -129.0 (d, *J* = 151.4 Hz, major), -138.6 (d, *J* = 151.3 Hz, major), -143.4 (d, *J* = 148.9 Hz, minor). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{21}H_{22}F_2$ 312.1684, found: 312.1683.

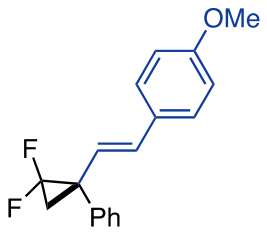
(*E*)-1-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-4-methylbenzene **3h**



3h was prepared according to the general procedure in 63% yield (25 mg, 0.094 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.44. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.46 – 7.30 (m, 5H), 7.16 – 7.13 (m, 2H), 7.07 – 7.05 (m, 2H), 6.21 (d, *J* = 15.9 Hz, 1H), 5.98 (d, *J* = 15.9 Hz, 1H), 2.31 (s, 3H), 2.01 – 1.94 (m, 1H), 1.86 (ddd, *J* = 12.7, 7.6, 4.9 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 137.5, 135.8, 133.9, 132.2, 130.4, 129.3, 128.7, 127.8, 127.5 (dd, *J* = 6.6, 3.4 Hz),

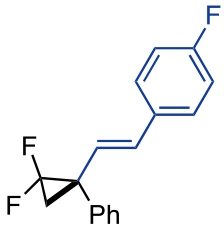
126.1, 114.0 (dd, *J* = 292.5, 289.7 Hz), 38.7 (t, *J* = 10.7 Hz), 24.2 (dd, *J* = 10.6, 8.3 Hz), 21.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.6 (d, *J* = 149.5 Hz), -134.0 (d, *J* = 149.7 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{16}F_2$ 270.1215, found: 270.1215.

(*E*)-1-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-4-methoxybenzene **3i**



3i was prepared according to the general procedure in 72% yield (31 mg, 0.108 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.32. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.45 – 7.31 (m, 5H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.13 (d, *J* = 15.9 Hz, 1H), 5.95 (d, *J* = 15.9 Hz, 1H), 3.78 (s, 3H), 2.00 – 1.92 (m, 1H), 1.85 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 158.7, 135.3, 131.1, 129.8 (d, *J* = 1.8 Hz), 128.9, 128.1, 127.2, 126.8, 125.8 (dd, *J* = 6.5, 3.4 Hz), 113.4, 113.4 (dd, *J* = 292.5, 289.4 Hz), 54.8, 38.0 (d, *J* = 10.6 Hz), 23.7 – 23.3 (m). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.7 (d, *J* = 149.6 Hz), -134.0 (d, *J* = 149.5 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{16}F_2O$ 286.1164, found: 286.1165.

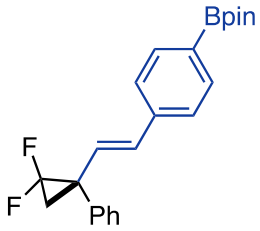
(*E*)-1-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-4-fluorobenzene **3j**



3j was prepared according to the general procedure in 73% yield (30 mg, 0.109 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.31. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.42 – 7.40 (m, 2H), 7.38 – 7.33 (m, 3H), 7.25 – 7.20 (m, 2H), 6.96 – 6.93 (m, 2H), 6.18 (d, *J* = 15.9 Hz, 1H), 5.97 (d, *J* = 15.9 Hz, 1H), 1.99 (ddd, *J* = 12.8, 7.6, 4.9 Hz, 1H), 1.87 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 163.5, 161.8, 135.8, 133.2 (d, *J* = 3.2 Hz), 131.5, 130.6, 129.1, 128.93 – 128.62 (m), 128.3, 128.1 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 21.6 Hz), 114.2 (dd, *J* = 292.5,

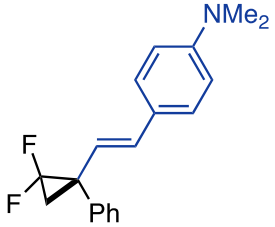
289.4 Hz), 38.9 (t, *J* = 10.7 Hz), 24.6 (dd, *J* = 10.2, 8.6 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -114.4 (s), -128.7 (d, *J* = 150.0 Hz), -133.9 (d, *J* = 150.0 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{17}H_{13}F_3$ 274.0964, found: 274.0965.

(*E*)-2-(4-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3k**



3k was prepared according to the general procedure in 31% yield (18 mg, 0.046 mmol) as yellow solid. R_f (hexanes/EtOAc = 10/1): 0.46. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.70 – 7.65 (m, 2H), 7.41 – 7.39 (m, 2H), 7.38 – 7.29 (m, 3H), 7.25 (s, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 5.99 (d, *J* = 15.9 Hz, 1H), 2.00 (ddd, *J* = 12.8, 7.6, 4.8 Hz, 1H), 1.89 (ddd, *J* = 12.7, 7.5, 4.8 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 139.4, 135.5, 135.1, 132.3, 130.4 (d, *J* = 1.6 Hz), 129.7 (dd, *J* = 6.4, 3.5 Hz), 128.7, 128.0, 125.5, 113.9 (dd, *J* = 292.5, 289.5 Hz), 83.9, 77.3, 77.2 – 77.0 (m), 76.9, 68.1, 38.8 (t, *J* = 10.9 Hz), 31.7, 25.7, 25.0, 24.4 (dd, *J* = 10.6, 8.2 Hz), 22.8, 14.2.^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.5 (d, *J* = 149.1 Hz), -133.8 (d, *J* = 150.4 Hz). HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{23}H_{26}BF_2O_2$ 383.1988, found: 383.1996.

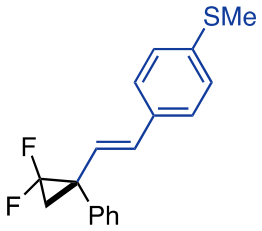
(*E*)-4-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-*N*,*N*-dimethylaniline **3l**



3l was prepared according to the general procedure in 34% yield (15 mg, 0.051 mmol) as colorless oil. R_f (hexanes/EtOAc = 4/1): 0.56. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.43 – 7.31 (m, 5H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.3 Hz, 2H), 6.06 (d, *J* = 15.9 Hz, 1H), 5.93 (d, *J* = 15.9 Hz, 1H), 2.97 – 2.89 (m, 6H), 1.98 – 1.91 (m, 1H), 1.82 (ddd, *J* = 10.4, 7.6, 3.8 Hz, 1H). ^{13}C NMR (151

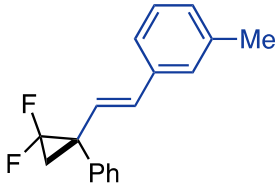
MHz, $CDCl_3$) δ ppm 150.4, 136.4, 132.4, 130.5 (d, *J* = 1.6 Hz), 128.8, 127.9, 127.4, 125.4, 124.3, 114.3 (dd, *J* = 292.6, 289.5 Hz), 112.7, 40.8, 39.0 (t, *J* = 10.6 Hz), 24.3 (dd, *J* = 10.4, 8.3 Hz).^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.6 (d, *J* = 149.0 Hz), -134.1 (d, *J* = 148.9 Hz). HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{19}H_{20}F_2N$ 300.1558, found: 300.1559.

(*E*)-(4-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)phenyl)(methyl)sulfane **3m**



3m was prepared according to the general procedure in 55% yield (25 mg, 0.082 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.22. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.41 – 7.40 (m, 2H), 7.39 – 7.31 (m, 3H), 7.20 – 7.18 (m, 2H), 7.17 – 7.12 (m, 2H), 6.23 (d, *J* = 15.9 Hz, 1H), 5.96 (d, *J* = 15.9 Hz, 1H), 2.46 (s, 3H), 1.99 (ddd, *J* = 12.8, 7.6, 4.8 Hz, 1H), 1.87 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 138.4, 136.2, 134.2, 132.2, 130.9 (d, *J* = 1.5 Hz), 130.4, 129.3, 128.6 (dd, *J* = 6.6, 3.4 Hz), 128.5, 127.2 (d, *J* = 2.5 Hz), 114.5 (dd, *J* = 292.7, 289.5 Hz), 39.3 (t, *J* = 10.7 Hz), 24.8 (dd, *J* = 10.5, 8.3 Hz), 16.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.6 (d, *J* = 149.9 Hz), -133.9 (d, *J* = 149.7 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{17}F_2S$ 303.1014; found: 303.1008.

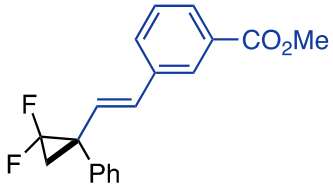
(*E*)-1-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-3-methylbenzene **3n**



3n was prepared according to the general procedure in 50% yield (20 mg, 0.075 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.47 – 7.26 (m, 5H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.04 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.25 (d, *J* = 15.9 Hz, 1H), 5.98 (d, *J* = 15.9 Hz, 1H), 2.30 (s, 3H), 1.99 (ddd, *J* = 12.8, 7.6, 4.8 Hz, 1H), 1.88 (ddd, *J* = 12.7, 7.6, 4.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 138.2, 136.6, 135.7, 132.4, 130.4 (d, *J* = 1.7

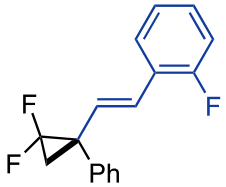
Hz), 128.7, 128.6 – 128.1 (m), 127.9, 127.0, 123.4, 114.0 (dd, *J* = 292.6, 289.6 Hz), 38.7 (t, *J* = 10.9 Hz), 24.2 (dd, *J* = 10.6, 8.3 Hz), 21.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.6 (d, *J* = 149.6 Hz), -133.9 (d, *J* = 149.6 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{16}F_2$ 270.1215, found: 270.1215.

Methyl (*E*)-3-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)benzoate **3o**



3o was prepared according to the general procedure in 40% yield (19 mg, 0.060 mmol) as colorless oil. R_f (hexanes/EtOAc = 10/1): 0.33. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.92 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.39 – 7.26 (m, 4H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 3.90 (s, 3H), 2.01 (ddd, *J* = 12.8, 7.7, 4.9 Hz, 1H), 1.91 (ddd, *J* = 12.8, 7.7, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 167.3, 137.2, 135.5, 131.6, 130.8, 130.7, 130.6 (d, *J* = 1.7 Hz), 130.2 (dd, *J* = 6.6, 3.4 Hz), 129.0, 128.9, 128.8, 128.3, 127.6, 114.1 (dd, *J* = 292.5, 289.3 Hz), 52.5, 39.0 – 38.7 (m), 24.6 (dd, *J* = 10.3, 8.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.6 (d, *J* = 150.1 Hz), -133.7 (d, *J* = 150.1 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{17}F_2O_2$ 315.1191, found: 315.1192.

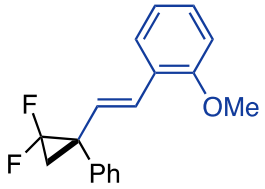
(*E*)-1-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-2-fluorobenzene **3p**



3p was prepared according to the general procedure in 38% yield (16 mg, 0.057 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.35. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.49 – 7.38 (m, 2H), 7.38 – 7.34 (m, 3H), 7.19 – 7.14 (m, 1H), 7.07 – 7.02 (m, 1H), 6.97 (ddd, *J* = 10.8, 8.2, 1.0 Hz, 1H), 6.36 (d, *J* = 16.1 Hz, 1H), 6.16 (d, *J* = 16.1 Hz, 1H), 2.01 (ddd, *J* = 12.8, 7.7, 4.9 Hz, 1H), 1.91 (ddd, *J* = 12.7, 7.7, 4.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 160.9, 159.2, 135.3, 131.2 (td, *J* = 6.2, 3.6 Hz), 130.3 (d, *J* = 1.8 Hz), 128.9 (d, *J* = 8.4 Hz), 128.8, 128.0, 127.5 (d, *J* =

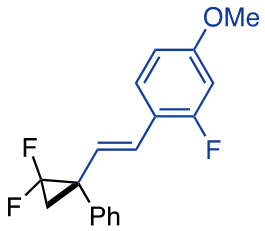
3.7 Hz), 125.0, 124.6 (d, *J* = 12.3 Hz), 124.1 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 22.2 Hz), 113.9 (dd, *J* = 292.6, 289.3 Hz), 39.0 (t, *J* = 10.8 Hz), 24.3 (dd, *J* = 10.6, 8.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -117.8 (s), -128.7 (d, *J* = 150.0 Hz), -133.9 (d, *J* = 150.0 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{17}H_{13}F_3$ 274.0964, found: 274.0961.

(*E*)-1-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-2-methoxybenzene **3q**



3q was prepared according to the general procedure in 43% yield (18 mg, 0.064 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 4H), 7.35 – 7.26 (m, 2H), 7.19 (td, *J* = 8.3, 1.6 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 6.33 (d, *J* = 16.1 Hz, 1H), 3.76 (s, 3H), 2.01 – 1.94 (m, 1H), 1.89 (ddd, *J* = 12.7, 7.6, 4.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 156.8, 136.2, 130.5 (d, *J* = 1.7 Hz), 129.4 (dd, *J* = 6.3, 3.3 Hz), 129.0, 128.9, 128.0, 127.7, 127.3, 126.0, 120.9, 114.2 (dd, *J* = 292.1, 289.5 Hz), 111.1, 55.7, 39.2 (t, *J* = 10.7 Hz), 24.2 (dd, *J* = 10.4, 8.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.7 (d, *J* = 149.1 Hz), -134.1 (d, *J* = 149.0 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{17}F_2O$ 287.1242, found: 287.1239.

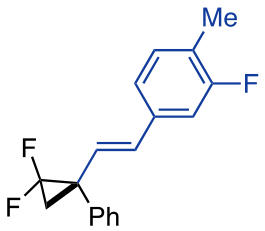
(*E*)-1-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-2-fluoro-4-methoxybenzene **3r**



3r was prepared according to the general procedure in 63% yield (29 mg, 0.094 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.36. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.38 – 7.32 (m, 5H), 7.24 (d, *J* = 8.7 Hz, 1H), 6.62 – 6.60 (m, 1H), 6.54 – 6.50 (m, 1H), 6.23 (d, *J* = 16.1 Hz, 1H), 6.08 (d, *J* = 16.1 Hz, 1H), 3.77 (s, 3H), 1.98 (ddd, *J* = 12.8, 7.6, 4.8 Hz, 1H), 1.88 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 161.9, 160.6 (d, *J* = 11.2 Hz), 160.2, 148.0 (d,

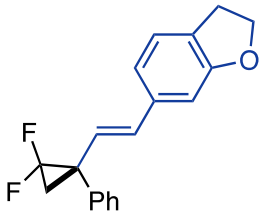
J = 2.8 Hz), 136.0, 130.7 (d, *J* = 1.6 Hz), 129.1, 128.4 (d, *J* = 5.7 Hz), 128.3, 125.1, 121.7, 121.6, 117.5 (d, *J* = 12.6 Hz), 114.3 (dd, *J* = 292.5, 289.5 Hz), 111.2 (d, *J* = 6.5 Hz), 110.7 (d, *J* = 3.0 Hz), 102.0, 101.9, 56.0, 39.3 (t, *J* = 10.7 Hz), 24.5 (dd, *J* = 10.5, 8.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -115.4 (s), -128.7 (d, *J* = 149.6 Hz), -134.0 (d, *J* = 149.5 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{15}F_3O$ 304.1070, found: 304.1070.

(*E*)-4-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-2-fluoro-1-methylbenzene **3s**



3s was prepared according to the general procedure in 64% yield (28 mg, 0.096 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.35. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.39 (m, 2H), 7.38 – 7.32 (m, 3H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.89 (t, *J* = 8.9 Hz, 1H), 6.16 (d, *J* = 15.9 Hz, 1H), 5.93 (d, *J* = 15.9 Hz, 1H), 2.22 (d, *J* = 1.6 Hz, 3H), 1.98 (ddd, *J* = 12.8, 7.6, 4.8 Hz, 1H), 1.87 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 161.8, 160.1, 135.6, 132.5 (d, *J* = 3.7 Hz), 131.3, 130.3 (d, *J* = 1.8 Hz), 129.3 (d, *J* = 5.2 Hz), 128.7, 128.2 – 127.9 (m), 125.0 (dd, *J* = 25.8, 12.8 Hz), 115.1 (d, *J* = 22.7 Hz), 113.9 (dd, *J* = 292.5, 289.4 Hz), 38.6 (t, *J* = 10.7 Hz), 24.2 (dd, *J* = 10.6, 8.2 Hz), 14.6 (d, *J* = 3.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -118.7 (s), -128.7 (d, *J* = 149.9 Hz), -133.9 (d, *J* = 149.9 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{15}F_3$ 288.1120, found: 288.1129.

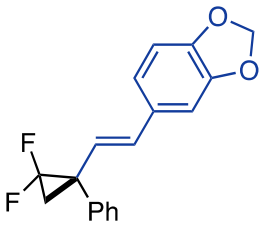
(*E*)-5-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-2,3-dihydrobenzofuran **3t**



3t was prepared according to the general procedure in 62% yield (28 mg, 0.093 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.30. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.55 – 7.28 (m, 5H), 7.16 (s, 1H), 6.99 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 6.09 (d, *J* = 15.9 Hz, 1H),

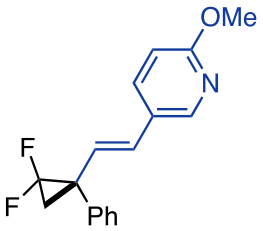
5.94 (d, *J* = 15.9 Hz, 1H), 4.55 (t, *J* = 8.7 Hz, 2H), 3.15 (t, *J* = 8.7 Hz, 2H), 1.99 – 1.92 (m, 1H), 1.84 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 160.1, 136.1, 132.3, 130.5, 129.8, 128.9, 128.0, 127.7, 127.0, 125.9 (dd, *J* = 6.5, 3.5 Hz), 122.7, 114.2 (dd, *J* = 292.4, 289.9 Hz), 109.5, 71.7, 38.9 (t, *J* = 10.6 Hz), 29.8, 24.3 (dd, *J* = 10.2, 8.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.7 (d, *J* = 149.4 Hz), -134.1 (d, *J* = 149.5 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{19}H_{16}F_2O$ 298.1164, found: 298.1167.

(*E*)-5-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)benzo[*d*][1,3]dioxole **3u**



3u was prepared according to the general procedure in 70% yield (31 mg, 0.105 mmol) as colorless oil. R_f (hexanes/EtOAc = 20/1): 0.27. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.37 – 7.26 (m, 3H), 6.83 (d, *J* = 1.5 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.09 (d, *J* = 15.9 Hz, 1H), 5.91 (d, *J* = 15.9 Hz, 1H), 5.91 (s, 2H), 1.97 (ddd, *J* = 12.8, 7.6, 4.8 Hz, 1H), 1.84 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 148.7, 147.8, 136.3, 132.5, 131.8, 130.9 (d, *J* = 1.8 Hz), 129.3, 128.5, 127.4 (dd, *J* = 6.6, 3.4 Hz), 121.5, 114.5 (dd, *J* = 292.8, 289.5 Hz), 108.9, 106.1, 101.7, 39.3 – 39.0 (m), 32.3, 24.8 (dd, *J* = 10.4, 8.3 Hz), 23.3, 14.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.7 (d, *J* = 149.7 Hz), -134.0 (d, *J* = 149.7 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{14}F_2O_2$ 300.0956, found: 300.0958.

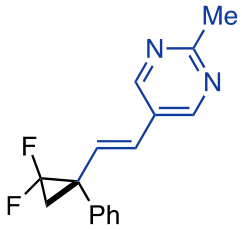
(*E*)-5-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-2-methoxypyridine **3v**



3v was prepared according to the general procedure in 58% yield (25 mg, 0.087 mmol) as colorless oil. R_f (hexanes/EtOAc = 5/1): 0.28. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.94 (d, *J* = 2.4 Hz, 1H), 7.58 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.42 (dd, *J* = 10.4, 4.4 Hz, 2H), 7.36 – 7.30 (m, 3H), 6.67 (d, *J* =

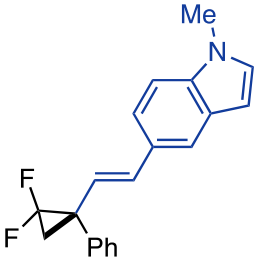
8.7 Hz, 1H), 6.14 (d, *J* = 15.9 Hz, 1H), 5.93 (d, *J* = 16.0 Hz, 1H), 3.91 (s, 3H), 1.99 (ddd, *J* = 12.8, 7.7, 4.9 Hz, 1H), 1.87 (ddd, *J* = 12.7, 7.7, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 163.9, 145.6, 135.7, 135.6, 130.5 (d, *J* = 1.7 Hz), 129.0, 128.7, 128.2, 128.1 (dd, *J* = 6.6, 3.4 Hz), 126.2, 114.0 (dd, *J* = 292.6, 289.3 Hz), 111.1, 53.8, 38.9 (t, *J* = 10.8 Hz), 24.5 (dd, *J* = 10.5, 8.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -128.7 (d, *J* = 150.0 Hz), -134.0 (d, *J* = 149.8 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{16}F_2NO$ 288.1194, found: 288.1194.

(*E*)-5-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-2-methylpyrimidine **3w**



3w was prepared according to the general procedure in 38% yield (15 mg, 0.057 mmol) as colorless oil. R_f (hexanes/EtOAc = 2/1): 0.29. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.51 (s, 2H), 7.48 – 7.39 (m, 2H), 7.39 – 7.29 (m, 3H), 6.33 (d, *J* = 16.1 Hz, 1H), 5.87 (d, *J* = 16.1 Hz, 1H), 2.68 (d, *J* = 8.1 Hz, 3H), 2.04 (ddd, *J* = 12.8, 7.7, 5.0 Hz, 1H), 1.94 (ddd, *J* = 12.8, 7.7, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 166.9, 156.4, 154.2, 134.7, 132.0 (dd, *J* = 6.8, 3.5 Hz), 130.4 (d, *J* = 1.6 Hz), 129.0, 128.9, 128.3, 127.8, 127.6, 127.1, 125.5, 113.6 (dd, *J* = 292.9, 289.1 Hz), 39.0 – 38.6 (m), 25.8 (s), 24.7 (dd, *J* = 10.7, 8.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -128.5 (d, *J* = 150.9 Hz), -133.5 (d, *J* = 151.0 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{16}H_{15}F_2N_2$ 273.1198, found: 273.1198.

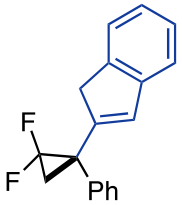
(*E*)-5-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-1-methyl-1*H*-indole **3x**



3x was prepared according to the general procedure in 64% yield (30 mg, 0.096 mmol) as white solid. R_f (hexanes/EtOAc = 10/1): 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.45 – 7.37

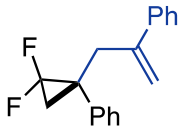
(m, 4H), 7.37 – 7.26 (m, 1H), 7.22 – 7.20 (m, 2H), 7.00 (d, *J* = 3.1 Hz, 1H), 6.40 (d, *J* = 3.1 Hz, 1H), 6.22 (d, *J* = 15.9 Hz, 1H), 6.13 (d, *J* = 15.9 Hz, 1H), 3.76 (s, 3H), 2.01 – 1.95 (m, 1H), 1.88 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 136.9, 136.5, 133.9, 130.8 (d, *J* = 1.6 Hz), 129.8, 129.1, 129.0, 128.7, 128.1, 125.8 (dd, *J* = 6.4, 3.4 Hz), 120.3, 119.7, 114.5 (dd, *J* = 292.7, 289.7 Hz), 109.7, 101.7, 39.2 (t, *J* = 10.8 Hz), 33.4, 24.5 (dd, *J* = 10.4, 8.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.6 (d, *J* = 149.1 Hz), -134.1 (d, *J* = 149.1 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{18}F_2N$ 310.1402, found: 310.1402.

2-(2,2-Difluoro-1-phenylcyclopropyl)-1*H*-indene **3y**



3y was prepared according to the general procedure in 61% yield (24 mg, 0.091 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.37. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.51 – 7.28 (m, 6H), 7.26 – 7.23 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.58 (s, 1H), 3.40 – 3.26 (m, 2H), 2.09 – 1.96 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 146.2, 144.5, 143.4, 137.6, 130.3, 129.9 (d, *J* = 1.8 Hz), 128.9, 128.0, 126.8, 124.9, 123.8, 121.1, 113.8 (t, *J* = 290.6 Hz), 40.2, 37.8 (t, *J* = 11.0 Hz), 24.3 (t, *J* = 9.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -127.3 (d, *J* = 148.4 Hz), -133.0 (d, *J* = 148.4 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{14}F_2$ 268.1058, found: 268.1058.

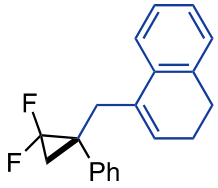
(2,2-Difluoro-1-(2-phenylallyl)cyclopropyl)benzene **3z**



3z was prepared according to the general procedure in 67% yield (26 mg, 0.100 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.29. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.35 – 7.19 (m, 8H), 7.19 – 7.04 (m, 2H), 5.17 (d, *J* = 0.7 Hz, 1H), 4.90 (s, 1H), 3.10 (d, *J* = 15.1 Hz, 1H), 2.98 (d, *J* = 15.0 Hz, 1H), 1.66 – 1.58 (m, 1H), 1.43 (ddd, *J* = 12.5, 7.9, 4.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 145.0, 141.7, 137.2, 129.7 (d, *J* = 1.8 Hz), 128.4 (d, *J* = 7.4 Hz), 127.7, 127.5, 126.9, 116.3, 116.1 – 112.2 (t, *J* = 290.6 Hz), 39.4 (dd, *J* = 5.3, 1.5 Hz), 35.3 (t, *J* = 9.9 Hz), 22.0 (t, *J* =

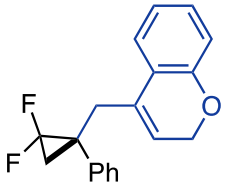
9.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -131.3 (d, *J* = 149.3 Hz), -135.8 (d, *J* = 149.3 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{18}H_{16}F_2$ 270.1215, found: 270.1216.

4-((2,2-Difluoro-1-phenylcyclopropyl)methyl)-1,2-dihydronaphthalene **3aa**



3aa was prepared according to the general procedure in 84% yield (37 mg, 0.126 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.33. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.28 – 7.22 (m, 2H), 7.22 – 7.13 (m, 3H), 7.12 – 7.05 (m, 3H), 7.04 (dd, *J* = 7.0, 2.1 Hz, 1H), 5.73 (t, *J* = 4.6 Hz, 1H), 3.03 (d, *J* = 15.3 Hz, 1H), 2.96 (d, *J* = 15.3 Hz, 1H), 2.60 (t, *J* = 7.9 Hz, 2H), 2.17 – 2.07 (m, 2H), 1.74 – 1.68 (m, 1H), 1.59 (ddd, *J* = 12.4, 7.8, 4.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 137.5, 136.7, 134.9, 132.8 (d, *J* = 1.6 Hz), 129.5 (d, *J* = 1.7 Hz), 128.3, 128.2, 127.5, 127.2, 126.7, 126.2, 122.9, 114.2 (t, *J* = 288.5 Hz), 35.9 (dd, *J* = 5.1, 1.5 Hz), 35.3 – 35.0 (m), 28.4, 23.1, 22.0 (t, *J* = 9.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -130.5 (d, *J* = 149.1 Hz), -135.7 (d, *J* = 149.1 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{20}H_{18}F_2$ 296.1371, found: 296.1373.

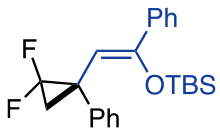
4-((2,2-Difluoro-1-phenylcyclopropyl)methyl)-2*H*-chromene **3ab**



3ab was prepared according to the general procedure in 72% yield (32 mg, 0.167 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.25. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.31 – 7.23 (m, 5H), 7.10 (td, *J* = 7.8, 1.4 Hz, 1H), 6.93 (d, *J* = 6.9 Hz, 1H), 6.79 (t, *J* = 7.3 Hz, 2H), 5.53 (t, *J* = 3.8 Hz, 1H), 4.65 (d, *J* = 3.8 Hz, 2H), 3.01 (d, *J* = 15.6 Hz, 1H), 2.92 (d, *J* = 15.6 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.62 (ddd, *J* = 12.5, 7.9, 4.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 154.1, 136.8, 130.4, 129.1 (d, *J* = 1.6 Hz), 128.8, 128.2, 127.2, 123.4, 123.2, 120.9, 120.7, 115.8, 113.8 (t, *J* = 288.6 Hz), 64.9, 34.4 (t, *J* = 9.9 Hz), 34.3 (dd, *J* = 5.6, 1.2 Hz), 21.7 (t, *J* = 10.0 Hz). ^{19}F NMR (565 MHz,

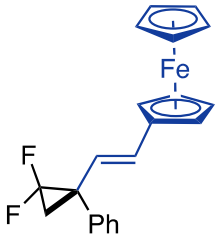
$CDCl_3$) δ ppm -131.1 (d, *J* = 149.8 Hz), -135.6 (d, *J* = 149.7 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{17}F_2O$ 299.1242, found: 299.1242.

tert-Butyl((2-(2,2-difluoro-1-phenylcyclopropyl)-1-phenylvinyl)oxy)dimethylsilane **3ac**



3ac was prepared according to the general procedure in 50% yield (29 mg, 0.075 mmol) as colorless oil. *E*/*Z* = 1.1:1. R_f (hexanes/EtOAc = 9/1): 0.22. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.43 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.30 (m, 4H), 7.31 – 7.28 (m, 4H), 7.28 – 7.22 (m, 8H), 5.56 (d, *J* = 1.4 Hz, 1H), 5.34 (d, *J* = 1.2 Hz, 1H), 2.12 (ddd, *J* = 12.8, 8.0, 4.5 Hz, 1H), 2.09 – 2.04 (m, 1H), 1.80 (ddd, *J* = 12.6, 8.3, 4.6 Hz, 1H), 1.17 (ddd, *J* = 13.6, 8.3, 5.7 Hz, 1H), 0.94 (s, 9H), 0.85 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H), -0.25 (s, 3H), -0.29 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 155.2, 154.8, 139.8, 137.7, 137.0, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.1, 126.8, 126.7, 114.2 (t, *J* = 288.7 Hz), 113.9 (t, *J* = 288.6 Hz), 106.2, 77.1, 33.1 (d, *J* = 10.5 Hz), 32.5 (t, *J* = 10.5 Hz), 31.7, 25.9, 25.8, 23.1 (t, *J* = 9.0 Hz), 22.8 – 21.8 (m), 18.3, 18.2, 14.2, -3.3, -3.7, -4.0, -4.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -133.0 (d, *J* = 145.5 Hz, major), -133.9 (d, *J* = 145.8 Hz, minor), -135.3 (d, *J* = 145.9 Hz, minor), -136.0 (d, *J* = 145.5 Hz, major). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{29}F_2OSi$ 387.1950, found: 387.1946.

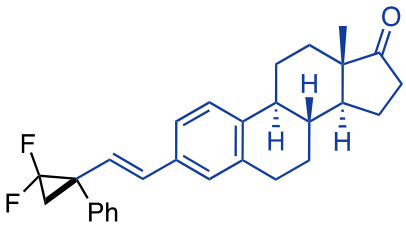
(*E*)-(2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)ferrocene **3ad**



3ad was prepared according to the general procedure in 60% yield (33 mg, 0.09 mmol) as orange solid. R_f (hexanes/EtOAc = 10/1): 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.49 – 7.40 (m, 2H), 7.40 – 7.27 (m, 3H), 5.86 (d, *J* = 15.7 Hz, 1H), 5.77 (d, *J* = 15.7 Hz, 1H), 4.25 (d, *J* = 21.9 Hz, 2H), 4.18 (s, 2H), 4.05 (s, 5H), 1.96 – 1.88 (m, 1H), 1.79 (ddd, *J* = 12.6, 7.5, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 136.4, 130.4 (d, *J* = 1.6 Hz), 130.3, 128.9, 127.9, 125.5 (dd, *J* = 6.2, 3.4

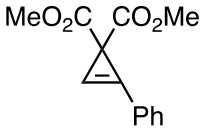
Hz), 114.0 (dd, *J* = 292.6, 289.4 Hz), 83.0, 69.5, 69.1 (d, *J* = 1.6 Hz), 67.1, 66.8, 38.9 (t, *J* = 10.5 Hz), 24.0 (dd, *J* = 10.2, 8.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.9 (d, *J* = 149.0 Hz), -134.1 (d, *J* = 148.9 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{21}H_{18}F_2Fe$ 364.0721, found: 364.0720.

(8*R*,9*S*,13*S*,14*S*)-3-((*E*)-2-(2,2-difluoro-1-phenylcyclopropyl)vinyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one **3ae**

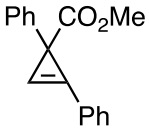


3ae was prepared according to the general procedure in 32% yield (21 mg, 0.048 mmol) as white solid. R_f (hexanes/EtOAc = 9/1): 0.35. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.48 – 7.37 (m, 2H), 7.37 – 7.26 (m, 3H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.00 (s, 1H), 6.22 (d, *J* = 15.9 Hz, 1H), 5.96 (d, *J* = 15.9 Hz, 1H), 2.86 (dd, *J* = 8.9, 4.1 Hz, 2H), 2.50 (dd, *J* = 19.1, 8.6 Hz, 1H), 2.40 (dt, *J* = 9.2, 3.6 Hz, 1H), 2.31 – 2.24 (m, 1H), 2.18 – 2.10 (m, 1H), 2.10 – 1.91 (m, 4H), 1.86 (ddd, *J* = 12.7, 7.6, 4.8 Hz, 1H), 1.64 – 1.40 (m, 6H), 0.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 139.6, 136.9, 135.9, 134.5, 132.2, 130.5, 128.9, 128.2 – 128.1 (m), 128.1, 127.1 (d, *J* = 3.2 Hz), 125.8, 123.8 (d, *J* = 3.3 Hz), 114.2 (dd, *J* = 292.4, 290.0 Hz), 50.8, 48.3, 44.7, 38.9 (t, *J* = 10.7 Hz), 38.4, 36.1, 31.9, 29.6, 26.8, 26.0, 24.4 (dd, *J* = 10.1, 8.4 Hz), 21.9, 14.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -128.6 (d, *J* = 149.6 Hz), -133.9 (dd, *J* = 149.7, 3.9 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{31}F_2O$ 433.2337, found: 433.2336.

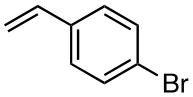
Failed substrates (decomposition or less than 20% yield):



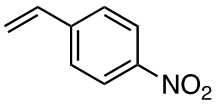
1j



1k



2ae

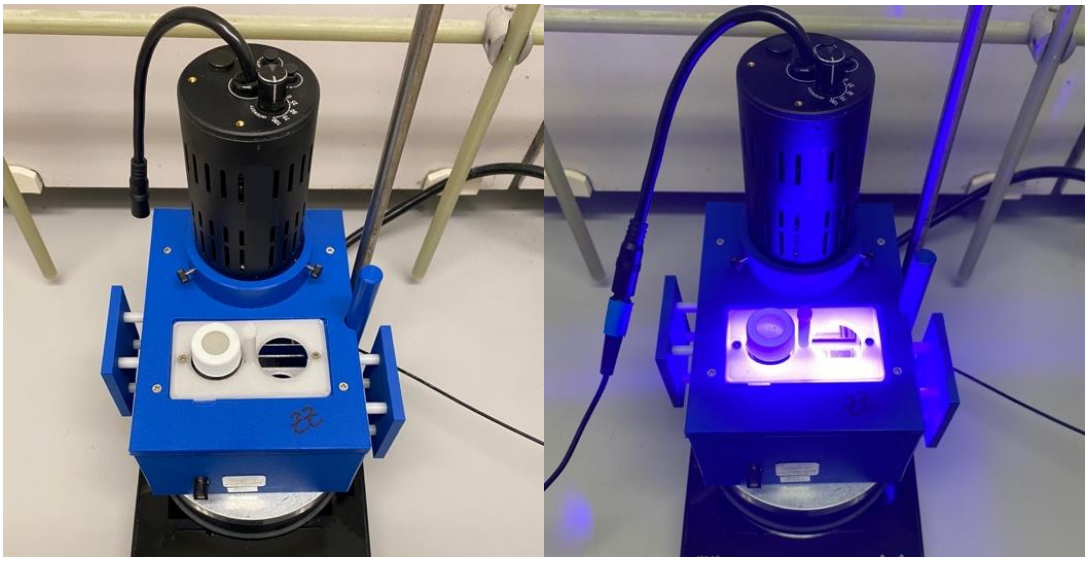


2af

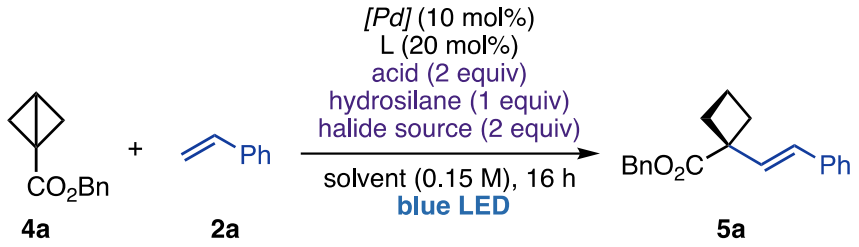
5. Procedure for 1 mmol Scale Preparation of Product 3a

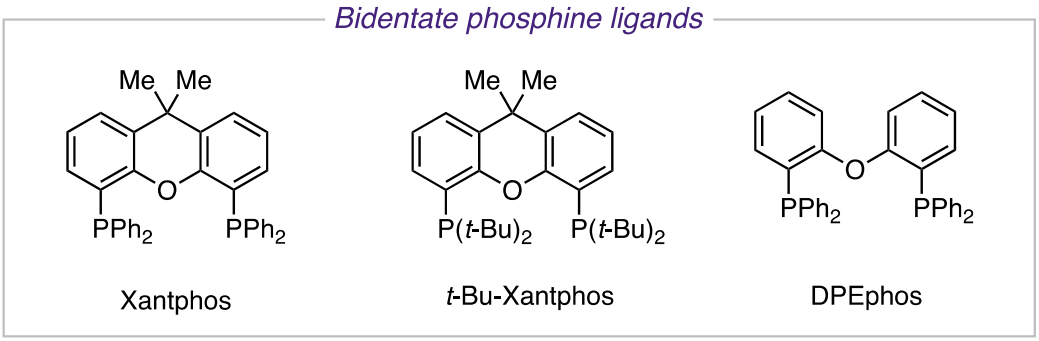
1a, 1mmol **2a**, 2 equiv **3a**, 73%

An oven dried 12 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%), $P(2\text{-Furyl})_3$ (20 mol%), and TBAB (1 equiv) inside glovebox. Next, 1,4-dioxane (0.15 M), acetic acid (2 equiv), $PhMe_2SiH$ (0.2 equiv) styrene **2a** (2 equiv) and cyclopropene **1a** (0.15 mmol) were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was stirred for 16 h. The resulting mixture was filtered through a short plug of silica gel using hexanes/EtOAc as eluent. The filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography on neutral aluminum oxide in hexanes/EtOAc to afford the product **3a** in 73% yield (205.0 mg, 0.80 mmol).



6. Reaction Optimization for Hydroalkenylation of BCBs

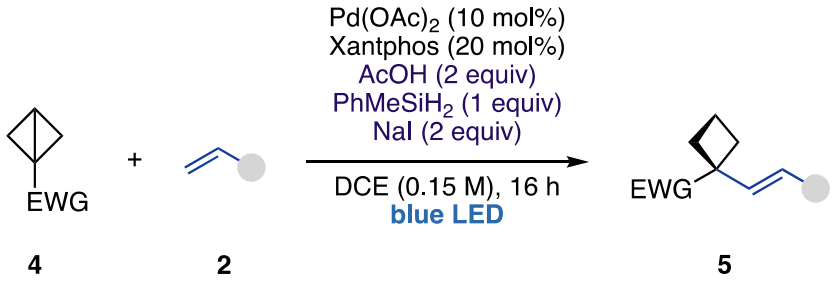




Entry	L	HX precursors			Solvent	Yields[a] (%)
		Acid	Hydrosilane	Halide source		
1	Xantphos	AcOH	$PhMeSiH_2$	NaI	PhH	55
2	Xantphos	-	$PhMeSiH_2$	NaI	PhH	33
3	Xantphos	AcOH	$PhMeSiH_2$	NaI	PhMe	27
4	Xantphos	AcOH	$PhMeSiH_2$	NaI	1,4-Dioxane	23
5	Xantphos	AcOH	$PhMeSiH_2$	NaI	DCM	51
6	Xantphos	AcOH	$PhMeSiH_2$	NaI	DCE	40[b]
7	Xantphos	AcOH	$PhMeSiH_2$	NaI	DCE	68
8	Xantphos	AcOH	$PhMeSiH_2$	NaI	$CHCl_3$	35
9	Xantphos	AcOH	$PhMeSiH_2$	NaI	DMA	traces
10	Xantphos	AcOH	$PhMeSiH_2$	TBAB	DCE	12
11	*t*-Bu-Xantphos	AcOH	$PhMeSiH_2$	NaI	DCE	0
12	DPEphos	AcOH	$PhMeSiH_2$	NaI	DCE	47
13	Xantphos	AcOH	$PhMeSiH_2$	NaI	DCE	75[c]

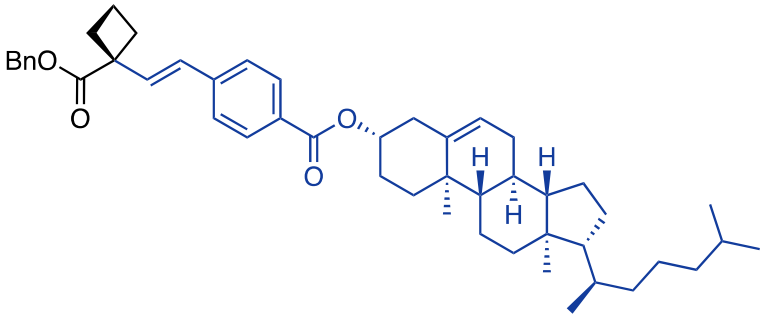
[a]0.1 mmol scale, **4a**:**2a** = 1:2. Yields were determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. [b]0.2 equivalent of $PhMeSiH_2$ was used. [c]Reaction was performed at 40 °C.

7. General Procedures for Hydroalkenylation of BCBs



General Procedures E: An oven dried 2 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%), and NaI (2 equiv) inside glovebox. Next, DCE (0.15 M), acetic acid (2 equiv), $PhMeSiH_2$ (1 equiv), styrene **2** (2 equiv) and BCB substrate **4** (0.15 mmol) were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was stirred for 16 h. The resulting mixture was filtered through a short plug of silica gel using hexanes/EtOAc as eluent. The filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel in hexanes/EtOAc to afford the corresponding products.

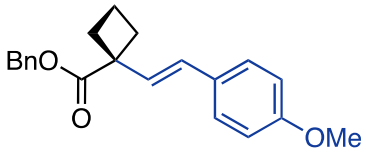
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*E*)-2-(1-((benzyloxy)carbonyl)cyclobutyl)vinyl)benzoate **5b**



5b was prepared according to the general procedure in 52% yield (55 mg, 0.078 mmol) as white solid. R_f (hexanes/EtOAc = 9/1): 0.33. ^1H NMR (600 MHz, $CDCl_3$): δ ppm 7.98 – 7.96 (m, 2H), 7.40 – 7.36 (m, 2H), 7.35 – 7.30 (m, 5H), 6.60 (d, *J* = 16.1 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 5.42 (d, *J* = 3.6 Hz, 1H), 5.18 (s, 2H), 4.85 (ddd, *J* = 11.7, 7.7, 4.0 Hz, 1H), 2.65 (dt, *J* = 12.1, 8.2

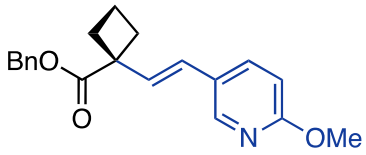
Hz, 2H), 2.47 (d, *J* = 7.7 Hz, 2H), 2.29 (dt, *J* = 12.1, 7.8 Hz, 2H), 2.05 – 1.90 (m, 7H), 1.86 – 1.82 (m, 1H), 1.75 – 1.71 (m, 1H), 1.63 – 1.42 (m, 9H), 1.42 – 1.27 (m, 5H), 1.30 – 0.95 (m, 19H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.8 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 175.3, 166.1, 141.6, 140.0, 136.4, 134.1, 130.2, 129.9, 128.9, 128.7, 128.5, 128.2, 126.4, 123.1, 74.9, 66.9, 57.0, 56.5, 50.5, 50.4, 42.6, 40.1, 39.8, 38.6, 37.4, 37.0, 36.5, 36.1, 32.3, 32.2, 31.3, 28.6, 28.3, 28.2, 24.6, 24.1, 23.1, 22.9, 21.4, 19.7, 19.0, 16.3, 12.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{48}H_{65}O_4$ 705.4877; found: 705.4880.

Benzyl (*E*)-1-(4-methoxystyryl)cyclobutane-1-carboxylate **5c**



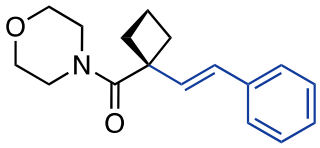
5c was prepared according to the general procedure in 78% yield (37 mg, 0.117 mmol) as colorless oil. R_f (hexanes/EtOAc = 9/1): 0.25. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.41 – 7.26 (m, 7H), 6.86 – 6.83 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.33 (d, *J* = 16.1 Hz, 1H), 5.17 (s, 2H), 3.81 (s, 3H), 2.62 (dt, *J* = 11.8, 8.6 Hz, 2H), 2.37 – 2.21 (m, 2H), 2.03 – 1.86 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 175.4, 159.0, 136.1, 129.6, 128.9, 128.5, 128.4, 127.9, 127.7, 127.4, 113.8, 66.3, 55.3, 49.9, 30.9, 15.9. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{23}O_3$ 323.1642; found: 323.1641.

(*E*)-1-(2-(6-methoxypyridin-3-yl)vinyl)cyclobutane-1-carboxylate **5d**



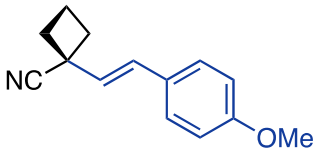
5d was prepared according to the general procedure in 63% yield (31 mg, 0.094 mmol) as colorless oil. R_f (hexanes/EtOAc = 3/1): 0.28. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 8.07 (d, *J* = 2.4 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.43 – 7.26 (m, 5H), 6.71 (d, *J* = 8.6 Hz, 1H), 6.41 (d, *J* = 16.1 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 5.17 (s, 2H), 3.94 (s, 3H), 2.63 (ddd, *J* = 12.3, 9.3, 5.4 Hz, 2H), 2.31 – 2.21 (m, 2H), 1.95 (p, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 175.4, 163.8, 145.6, 136.3, 135.7, 130.8, 128.7, 128.3, 128.1, 126.3, 125.5, 111.1, 66.7, 53.7, 50.2, 31.1, 16.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{22}NO_3$ 324.1594; found: 324.1599.

(*E*)-morpholino(1-styrylcyclobutyl)methanone **5e**



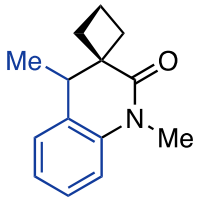
5e was prepared according to the general procedure in 40% yield (16 mg, 0.060 mmol) as colorless oil. R_f (EtOAc): 0.34. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.38 – 7.35 (m, 2H), 7.33 – 7.30 (m, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 16.2 Hz, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 3.67 (s, 4H), 3.53 (s, 2H), 3.25 (s, 2H), 2.74 – 2.68 (m, 2H), 2.21 (ddd, *J* = 9.3, 7.9, 4.0 Hz, 2H), 2.07 – 2.00 (m, 1H), 1.88 – 1.81 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 174.1, 137.0, 132.4, 129.0, 128.5, 128.0, 126.5, 67.3, 66.7, 50.4, 46.7, 42.8, 32.2, 15.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{22}NO_2$ 272.1645, found: 272.1647.

(*E*)-1-(4-methoxystyryl)cyclobutane-1-carbonitrile **5f**



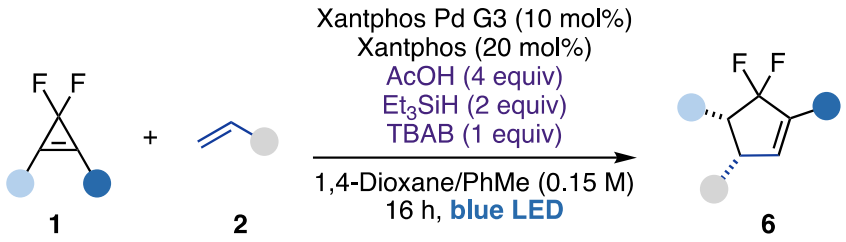
5f was prepared according to the general procedure in 55% yield (18 mg, 0.082 mmol) as white solid. R_f (hexanes/EtOAc = 9/1): 0.23. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.32 (m, 2H), 6.90 – 6.85 (m, 2H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.13 (d, *J* = 15.9 Hz, 1H), 3.82 (s, 3H), 2.71 – 2.66 (m, 2H), 2.40 – 2.34 (m, 2H), 2.31 – 2.23 (m, 1H), 2.12 – 2.04 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 159.7, 130.0, 128.6, 127.9, 125.9, 123.3, 114.2, 55.4, 38.3, 34.1, 17.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{14}H_{16}NO$ 214.1226, found: 214.1225.

1',4'-Dimethyl-1',4'-dihydro-2'*H*-spiro[cyclobutane-1,3'-quinolin]-2'-one **5g**



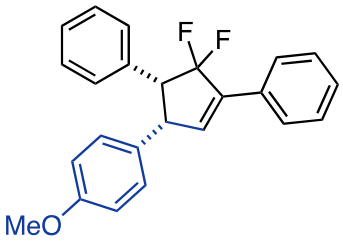
5g was prepared according to the general procedure without adding styrene in 54% yield (31 mg, 0.120 mmol) as colorless oil. R_f (hexanes/EtOAc = 4/1): 0.25. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.23 (td, *J* = 7.9, 1.5 Hz, 1H), 7.17 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.01 (td, *J* = 7.4, 1.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 3.38 (s, 3H), 2.98 (q, *J* = 7.1 Hz, 1H), 2.88 – 2.81 (m, 1H), 2.03 – 1.81 (m, 5H), 1.05 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 173.8, 139.4, 130.4, 128.5, 127.7, 123.2, 114.9, 47.8, 42.5, 31.3, 30.2, 25.4, 16.2, 15.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{14}H_{18}NO$ 216.1383; found: 216.1385.

8. General Procedures for Hydroalkenylation/Diastereoselective Rearrangement Cascade



General Procedures F: An oven dried 2 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with Xantphos Pd G3 (10 mol%), Xantphos (20 mol%), and TBAB (1 equiv) inside glovebox. Next, 1,4-dioxane/toluene (1/1 ratio in volume, 0.15 M), acetic acid (4 equiv), Et_3SiH (2 equiv), cyclopropene **1** (0.15 mmol) and styrene **2** (2 equiv) were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was stirred for 16 h. The resulting mixture was filtered through a short plug of silica gel using hexanes/EtOAc as eluent. The filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography on neutral aluminum oxide in hexanes/EtOAc to afford the corresponding products.

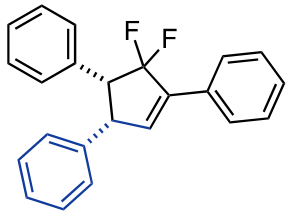
((1*R**,5*S**)-2,2-difluoro-5-(4-methoxyphenyl)cyclopent-3-ene-1,3-diyl)dibenzene **6a**



6a was prepared according to the general procedure in 53% yield (26 mg, 0.079 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.28. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.69 – 7.65 (m, 2H), 7.43 – 7.32 (m, 7H), 7.08 – 7.04 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.69 (s, 1H), 4.25 (d, *J* = 6.6 Hz, 1H), 3.78 (s, 3H), 3.61 (td, *J* = 16.4, 7.0 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 159.3, 138.7 – 138.3 (m), 135.0, 133.7, 131.6, 130.0, 129.1, 129.0, 128.8 (d, *J* = 12.3 Hz), 128.2, 127.1, 114.7, 62.8 (dd, *J* = 23.4, 22.0 Hz), 55.7, 52.2 (d, *J* = 6.2 Hz), 33.2 – 12.9 (m). ^{19}F NMR (565

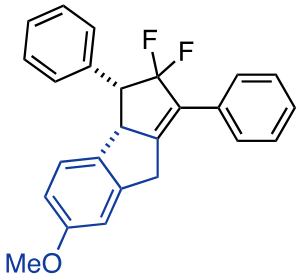
MHz, $CDCl_3$) δ ppm -90.3 (d, *J* = 248.8 Hz), -95.0 (d, *J* = 248.5 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{24}H_{20}F_2O$ 362.1477, found: 362.1477.

((1*R**,2*S**)-5,5-difluorocyclopent-3-ene-1,2,4-triyl)tribenzene **6b**



6b was prepared according to the general procedure in 70% yield (35 mg, 0.105 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.47. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.68 – 7.65 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.21 (m, 9H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.69 (s, 1H), 4.28 (s, 1H), 3.64 (td, *J* = 16.3, 6.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 141.5 (d, *J* = 3.4 Hz), 139.3 (dd, *J* = 26.0, 21.7 Hz), 138.5 – 137.4 (m), 134.7, 132.0, 131.4, 130.4, 129.9, 129.1, 128.9 (d, *J* = 12.7 Hz), 128.7, 128.1, 127.6, 127.0, 62.4 (t, *J* = 23.0 Hz), 52.7 (d, *J* = 6.4 Hz), 33.9 – 12.5 (m). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -90.3 (d, *J* = 248.8 Hz), -94.7 (d, *J* = 248.5 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{23}H_{18}F_2$ 332.1371, found: 332.1371.

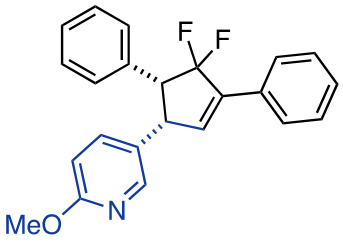
(3*R**,3a*R**)-2,2-difluoro-6-methoxy-1,3-diphenyl-2,3,3a,8-tetrahydrocyclopenta[*a*]indene **6c**



6c was prepared according to the general procedure in 54% yield (30 mg, 0.081 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.22. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.64 – 7.60 (m, 2H), 7.57 – 7.53 (m, 2H), 7.44 – 7.38 (m, 5H), 7.36 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 1.7 Hz, 1H), 6.70 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.56 (s, 1H), 3.93 – 3.81 (m, 2H), 3.78 (s, 3H), 3.73 – 3.65 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 159.6, 154.8 (t, *J* = 9.2 Hz), 143.9, 135.1, 134.4 (d, *J* = 2.1 Hz), 134.2, 132.5 (d, *J* = 4.5 Hz), 131.8 (d, *J* = 2.5 Hz), 130.8, 129.5, 128.7 (d, *J* = 7.8 Hz), 128.2 (d, *J* = 3.3 Hz), 128.1, 127.9, 124.5, 113.0, 110.7, 60.0 (dd, *J* = 26.5, 21.0 Hz),

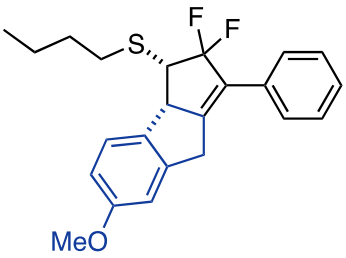
55.6, 53.8 (dd, *J* = 8.0, 1.5 Hz), 34.1, 31.9 – 12.6 (m). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -88.6 (d, *J* = 243.7 Hz), -94.5 (d, *J* = 243.8 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{25}H_{20}F_2O$ 374.1477, found: 374.1477.

5-((1*S**,5*R**)-4,4-difluoro-3,5-diphenylcyclopent-2-en-1-yl)-2-methoxypyridine **6d**



6d was prepared according to the general procedure in 41% yield (22 mg, 0.061 mmol) as white solid. R_f (hexanes/EtOAc = 9/1): 0.23. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.96 (d, *J* = 1.6 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.59 – 7.26 (m, 9H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.66 (s, 1H), 4.25 (d, *J* = 4.0 Hz, 1H), 3.90 (s, 3H), 3.58 (td, *J* = 16.1, 7.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 163.6, 145.5, 139.6 (dd, *J* = 26.6, 21.7 Hz), 137.3, 136.9 – 136.3 (m), 133.8, 130.8, 129.7, 129.5, 129.2 (d, *J* = 3.3 Hz), 128.8, 128.7, 128.5, 127.9, 126.7, 111.2, 62.1 (t, *J* = 23.1 Hz), 53.4, 49.3 (d, *J* = 6.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -90.7 (d, *J* = 249.4 Hz), -95.2 (d, *J* = 249.3 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{20}F_2NO$ 364.1507; found: 364.1507.

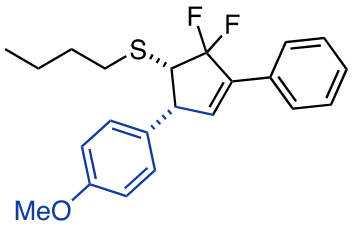
Butyl((3*S**,3a*R**)-2,2-difluoro-6-methoxy-1-phenyl-2,3,3a,8-tetrahydrocyclopenta[*a*]inden-3-yl)sulfane **6e**



6e was prepared according to the general procedure in 50% yield (29 mg, 0.075 mmol) as colorless oil. R_f (hexanes/EtOAc = 9/1): 0.26. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.56 – 7.53 (m, 2H), 7.49 (d, *J* = 8.9 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 1H), 6.85 – 6.77 (m, 2H), 3.97 (s, 1H), 3.84 – 3.72 (m, 5H), 3.54 – 3.48 (m, 1H), 2.91 – 2.86 (m, 1H), 2.83 – 2.78 (m, 1H), 1.74 – 1.66 (m, 2H), 1.51 – 1.47 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm

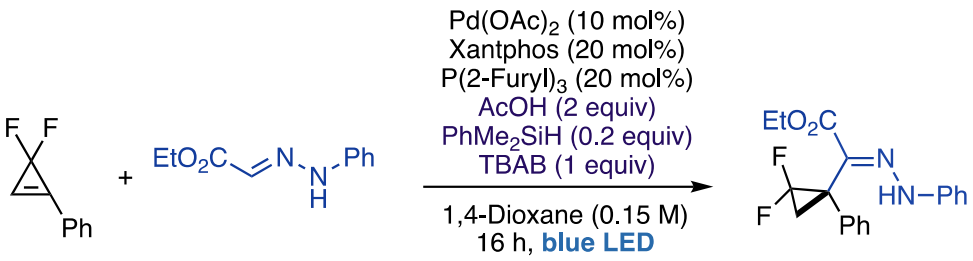
160.1, 144.0, 134.0, 132.0, 129.0, 128.6, 128.5 (d, J = 3.2 Hz), 125.0, 113.6, 111.0, 57.0, 56.0, 53.9 (d, J = 6.0 Hz), 34.4, 32.3, 32.0, 22.4, 14.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -87.6 (d, J = 242.1 Hz), -94.8 (d, J = 242.3 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{23}H_{24}F_2OS$ 386.1510, found: 386.1517.

Butyl((1*S**,5*R**)-2,2-difluoro-5-(4-methoxyphenyl)-3-phenylcyclopent-3-en-1-yl)sulfane **6f**



6f was prepared according to the general procedure in 46% yield (26 mg, 0.069 mmol) as colorless oil. R_f (hexanes/EtOAc = 4/1): 0.25. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.65 – 7.62 (m, 2H), 7.42 – 7.33 (m, 3H), 7.23 – 7.20 (m, 2H), 6.94 – 6.86 (m, 2H), 6.52 (t, J = 2.1 Hz, 1H), 3.82 (s, 3H), 3.73 (dt, J = 11.7, 6.1 Hz, 1H), 3.42 – 3.34 (m, 1H), 2.62 (t, J = 7.4 Hz, 2H), 1.53 – 1.44 (m, 2H), 1.38 – 1.30 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 158.8, 137.1 (t, J = 8.5 Hz), 132.3, 130.6, 128.9, 128.3, 128.3, 127.8 (d, J = 8.7 Hz), 126.3, 113.9, 60.0 – 57.9 (m), 55.0, 51.5 (d, J = 5.8 Hz), 31.5, 31.2, 21.5, 13.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -89.3 (d, J = 247.4 Hz), -94.7 (d, J = 247.4 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{25}F_2OS$ 375.1589; found: 375.1588.

9. Reaction of Cyclopropene with *α*-Ester Hydrazone

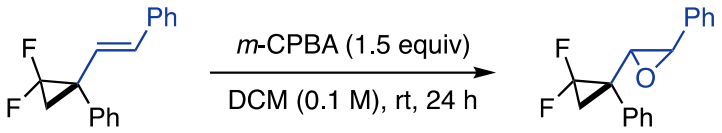


1a **7** **3af**, 62%

Following General Procedure D, *α*-ester hydrazone **7** (57.6 mg, 0.3 mmol) was used. The crude reaction mixture was purified by column chromatography in hexanes/EtOAc (10:1) to afford the product **3af** in 62% yield (32.0 mg, 0.093 mmol) as white solid. ^{1}H NMR (600 MHz, C_6D_6) δ ppm 8.26 (s, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.04 – 7.00 (m, 6H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.81 – 6.75 (m, 1H), 4.16 (pt, *J* = 10.8, 5.4 Hz, 2H), 1.73 (ddd, *J* = 12.0, 8.1, 5.4 Hz, 1H), 1.41 – 1.35 (m, 1H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, C_6D_6) δ ppm 164.2, 143.1, 133.4, 129.8 (d, *J* = 2.0 Hz), 129.7, 129.4, 128.7, 128.5, 128.4, 123.1, 114.7, 112.7 (t, *J* = 288.1 Hz), 61.3, 32.1, 31.7 (dd, *J* = 12.5, 10.9 Hz), 21.9 (t, *J* = 10.1 Hz), 14.5. ^{19}F NMR (565 MHz, C_6D_6) δ ppm -128.8 (d, *J* = 151.2 Hz), -134.8 (d, *J* = 151.1 Hz). HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{19}F_2N_2O_2$ 345.1414, found: 345.1402.

10. Post-functionalizations

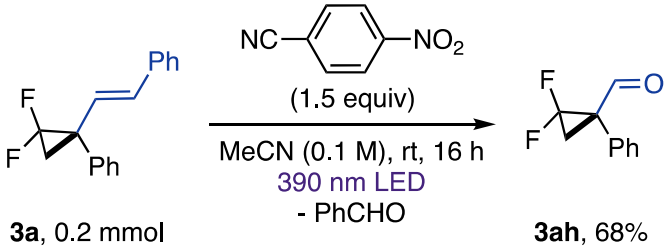
10.1 Epoxidation



3a, 0.2 mmol **3ag**, 89%, dr 2:1

To a stirred solution of **3a** (51.3 mg, 0.2 mmol) in DCM (2.0 mL, 0.1 M), *m*-CPBA (69 mg, 0.30 mmol, 1.5 equiv) was added at room temperature under Ar atmosphere. After being stirred for 24 h, the reaction mixture was poured into aq. $NaHCO_3$ (sat) with diethyl ether. The aqueous layer was extracted two times with diethyl ether. The combined extract was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on neutral aluminum oxide in hexanes/EtOAc to afford products **3ag** in 89% yield (49 mg, 0.18 mmol) as a colorless oil, dr 2:1. R_f (hexanes/EtOAc = 20/1): 0.22. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.46 – 7.32 (m, 7H), 7.29 (ddd, *J* = 17.3, 9.7, 1.0 Hz, 5H), 7.20 (dd, *J* = 8.6, 7.2 Hz, 3H), 3.56 (d, *J* = 1.5 Hz, 1H, major), 3.36 (d, *J* = 1.6 Hz, 1H, minor), 3.34 (s, 1H, major), 3.12 (s, 1H, minor), 1.99 – 1.93 (m, 1H), 1.88 – 1.79 (m, 1H), 1.66 (ddd, *J* = 12.4, 7.7, 4.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 136.4, 136.2, 133.8, 132.6, 130.4, 129.6, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 125.8, 125.7, 112.7 (t, *J* = 288.0 Hz), 112.5 (t, *J* = 288.2 Hz), 62.7 – 62.3 (m), 60.4 (d, *J* = 2.0 Hz), 56.5, 55.8, 35.9 (t, *J* = 9.9 Hz), 35.3 (t, *J* = 10.4 Hz), 19.9 (t, *J* = 10.2 Hz), 18.1 (t, *J* = 10.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -129.6 (d, *J* = 154.6 Hz, major), -130.4 (d, *J* = 155.4 Hz, minor), -136.0 (d, *J* = 154.6 Hz, major), -136.2 (d, *J* = 155.5 Hz, minor). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{17}H_{14}F_2O$ 272.1007, found: 272.1006.

10.2 Photoinduced oxidative cleavage

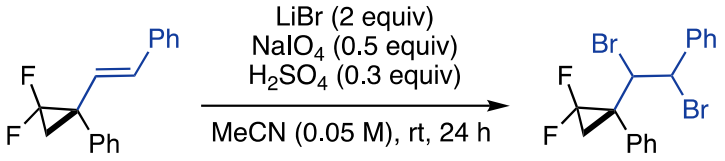


3a, 0.2 mmol **3ah**, 68%

3ah was prepared according to reported methods of photoinduced oxidative cleavage of alkenes.[9] An oven dried 4 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged

4-nitrobenzonitrile (44.4 mg, 0.3 mmol, 1.5 equiv) and **3a** (51.3 mg, 0.2 mmol). The reaction vial was purged with N_2 for 15 minutes followed by the addition of anhydrous MeCN (2 mL, 0.1 M). The reaction vial was placed 3 cm in front of a 390 nm lamp with cooling fan. The reaction was stirred under irradiation for 16 h to full conversion. Then, solvent was removed *in vacuo*. The resulting residue was purified by column chromatography on silica gel in hexanes/EtOAc to afford product **3ah** in 68% yield (25 mg, 0.136 mmol) as a colorless oil. R_f (hexanes/EtOAc = 20/1): 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 9.52 (s, 1H), 7.53 – 7.35 (m, 3H), 7.34 (d, *J* = 6.9 Hz, 2H), 2.70 – 2.63 (m, 1H), 2.13 (ddd, *J* = 11.5, 7.8, 5.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 194.0, 131.2, 130.7 (d, *J* = 2.0 Hz), 129.7, 129.6, 112.6 (dd, *J* = 290.7, 289.6 Hz), 47.3 (t, *J* = 10.6 Hz), 21.9 (dd, *J* = 11.2, 8.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -127.9 (d, *J* = 150.0 Hz), -133.7 (d, *J* = 150.0 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{10}H_8F_2O$ 182.0538, found: 182.0539.

10.3 Dibromination

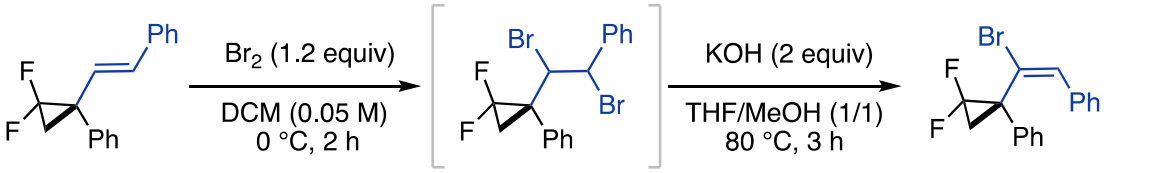


3a, 0.2 mmol **3ai**, 70%, dr 1.1:1

3ai was prepared according to reported procedure.[10] To a stirred solution of **3a** (51.3 mg, 0.2 mmol) in dry CH_3CN (4 mL, 0.05 M), anhydrous LiBr (34.8 mg, 0.4 mmol, 2 equiv), $NaIO_4$ (21.4 mg, 0.1 mmol, 0.5 equiv), and concentrated H_2SO_4 (5.8 mg, 0.06 mmol, 0.3 equiv) were added at rt. The resulting reaction mixture was stirred at rt for 24 hours (monitored by TLC or GC/MS). After completion, the reaction mixture was diluted with EtOAc (5 mL) and washed with water followed by saturated aqueous $Na_2S_2O_3$ solution (2x5 mL). The organic layer was dried over anhydrous $MgSO_4$, concentrated under pressure to afford crude product. The residue was purified by flash chromatography on neutral aluminum oxide in hexanes/EtOAc to afford compound **3ai** in 70% yield (58 mg, 0.139 mmol) as white solid, dr 1.1: 1. R_f (hexanes/EtOAc = 20/1): 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.88 – 7.79 (m, 3H), 7.48 – 7.40 (m, 5H), 7.35 – 7.26 (m, 6H), 7.25 (dd, *J* = 9.1, 3.4 Hz, 5H), 4.68 (dtd, *J* = 13.1, 11.7, 1.4 Hz, 3H), 4.51 (d, *J* = 11.6 Hz, 1H), 2.33 (ddd, *J* = 13.3, 8.7, 4.8 Hz, 1H), 2.22 (ddd, *J* = 11.4, 8.7, 5.9 Hz, 1H), 1.88 (ddd, *J* = 11.6, 8.2, 5.6 Hz, 1H), 1.78 (ddd, *J* = 12.8, 8.2, 4.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.6, 140.2, 129.0 (d,

J = 2.2 Hz), 129.0, 128.9, 128.7 (d, *J* = 4.8 Hz), 128.3, 127.7 (d, *J* = 8.2 Hz), 115.2 (dd, *J* = 290.7, 289.7 Hz), 112.3 (dd, *J* = 290.8, 289.3 Hz), 59.0, 56.6 (dd, *J* = 7.1, 2.8 Hz), 53.7 (d, *J* = 2.1 Hz), 52.9, 39.7 – 38.8 (m), 38.5 – 37.3 (m), 31.7, 29.8, 27.9 (t, *J* = 9.6 Hz), 27.3 (dd, *J* = 11.1, 8.7 Hz), 22.8, 14.2.^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -122.3 (d, *J* = 150.2 Hz), -128.5 (d, *J* = 150.2 Hz), -131.7 (d, *J* = 154.8 Hz), -138.9 (d, *J* = 154.8 Hz).

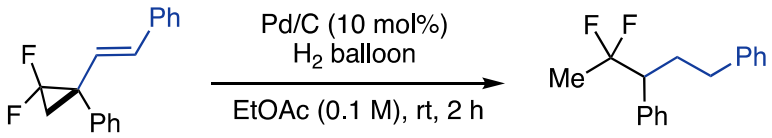
10.4 Semi one-pot dibromination and dehydrobromination



3a, 0.2 mmol *semi one-pot* **3aj**, 65%, over 2 steps

To a stirred solution of **3a** (51.3 mg, 0.2 mmol) in DCM (4 mL, 0.05 M), bromine (13 μL, 0.24 mmol, 1.2 equiv) was added dropwise under ice bath and stirred for 2 hours. After completion, the reaction mixture was concentrated under pressure to afford crude debromination product. Then, 1.2 mL of THF/ MeOH (1:1) was added, followed by KOH (0.4 mmol, 2 equiv) in one portion. The resulting solution was heated to 80 °C for 3 hours. After completion, the reaction mixture was quenched with saturated NH_4Cl, extracted three times by EtOAc. The combined organic layers were washed by saturated brine, dried over Na_2SO_4, then concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel in hexanes/EtOAc to afford compound **3aj** in 65% yield over two steps (44 mg, 0.131 mmol) as a colorless oil. R_f (hexanes/EtOAc = 20/1): 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.30 – 7.23 (m, 6H), 7.22 – 7.16 (m, 2H), 7.16 – 7.09 (m, 2H), 6.64 (s, 1H), 1.75 – 1.70 (m, 1H), 1.35 – 1.30 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 136.5, 129.6 – 129.5 (m), 129.3, 128.8, 128.6, 128.4, 127.6, 115.1 – 110.7 (m), 36.3 (t, *J* = 10.5 Hz), 35.0, 31.9, 23.0, 22.6 (t, *J* = 9.4 Hz), 14.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -133.3 (d, *J* = 147.3 Hz), -134.2 (d, *J* = 147.3 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{17}H_{13}BrF_2$ 334.0168, found: 334.0164.

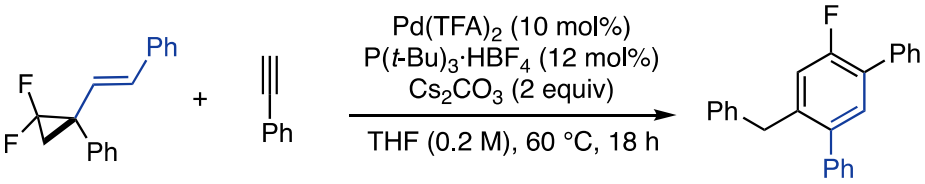
10.5 Hydrogenation



3a, 0.2 mmol **3ak**, 86%

To a solution of **3a** (51.3 mg, 0.2 mmol) in EtOAc (2 ml, 0.1 M) was added palladium on carbon (21.3 mg, 10 wt. % loading). After gas exchanging using hydrogen balloon for 10 min, the reaction mixture was stirred under hydrogen atmosphere at room temperature for 2 hours. Upon completion, the reaction was filtered through a pad of celite. The mixture was concentrated *in vacuo*. The residue was purified by flash chromatography on neutral aluminum oxide in hexanes/EtOAc to afford product **3ak** in 86% yield (45 mg, 0.173 mmol) as a colorless oil. R_f (hexanes/EtOAc = 20/1): 0.36. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.36 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.24 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 2.93 (ddd, *J* = 20.5, 11.6, 2.6 Hz, 1H), 2.51 (dt, *J* = 12.2, 8.7 Hz, 1H), 2.42 – 2.31 (m, 2H), 2.20 – 2.10 (m, 1H), 1.40 (t, *J* = 18.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 141.8, 138.2 (d, *J* = 5.7 Hz), 129.6, 128.9, 128.8, 128.7, 127.8, 126.2, 125.0 (dd, *J* = 290.8, 289.4 Hz), 53.0 (t, *J* = 23.9 Hz), 33.4, 30.2 (t, *J* = 3.8 Hz), 22.8 (t, *J* = 27.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -91.3 (d, *J* = 239.8 Hz), -98.0 (d, *J* = 239.8 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{17}H_{18}F_2$ 260.1371, found: 260.1375.

10.6 F-elimination/alkynylation/cycloisomerization cascade



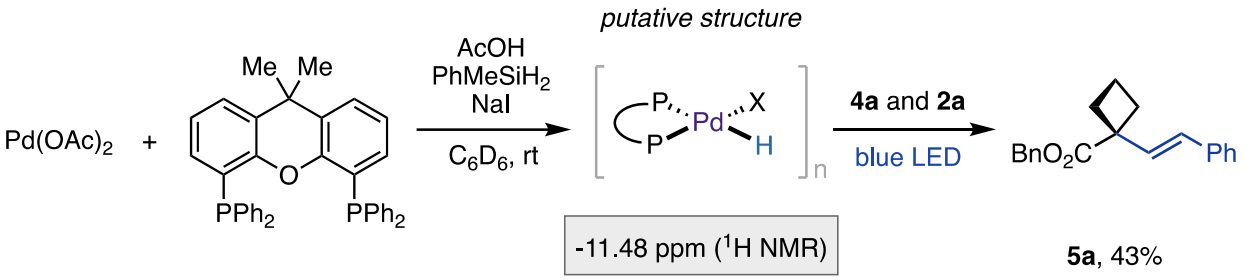
3a, 0.2 mmol 2 equiv **3al**, 41%

3al was prepared according to reported method.[11] An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with **3a** (51.3 mg, 0.2 mmol), $Pd(TFA)_2$ (6.6 mg, 10 mol%), P(*t*-Bu)$_3$·HBF_4 (8.3 mg, 12 mol%), Cs_2CO_3 (130 mg, 2 equiv) inside glovebox. Next, THF (1 mL, 0.2 M) and phenylacetylene (44 μL, 2 equiv) were added subsequently via syringe. The reaction vial was placed into an aluminum block, which was pre-heated to 60 °C. The resulting mixture was stirred for 18 hours. Upon completion, the reaction was cooled to room temperature, diluted with

EtOAc, and filtered under cotton column. The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on neutral aluminum oxide in hexanes/EtOAc to afford compound **3al** in 41% yield (28.0 mg, 0.083 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.58 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.37 – 7.32 (m, 3H), 7.31 – 7.28 (m, 2H), 7.27 – 7.25 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 11.7 Hz, 1H), 3.96 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 159.9, 158.2, 140.6 (d, *J* = 2.5 Hz), 139.9 (d, *J* = 7.6 Hz), 138.5 (d, *J* = 3.5 Hz), 135.6, 132.3 (d, *J* = 3.8 Hz), 129.5, 129.1 (d, *J* = 2.9 Hz), 129.0, 128.5 (d, *J* = 1.3 Hz), 128.3, 127.7, 127.3, 126.2, 117.5 (d, *J* = 23.1 Hz), 39.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -120.3 (s). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{25}H_{19}F$ 338.1465, found: 338.1471.

11. Mechanistic Studies

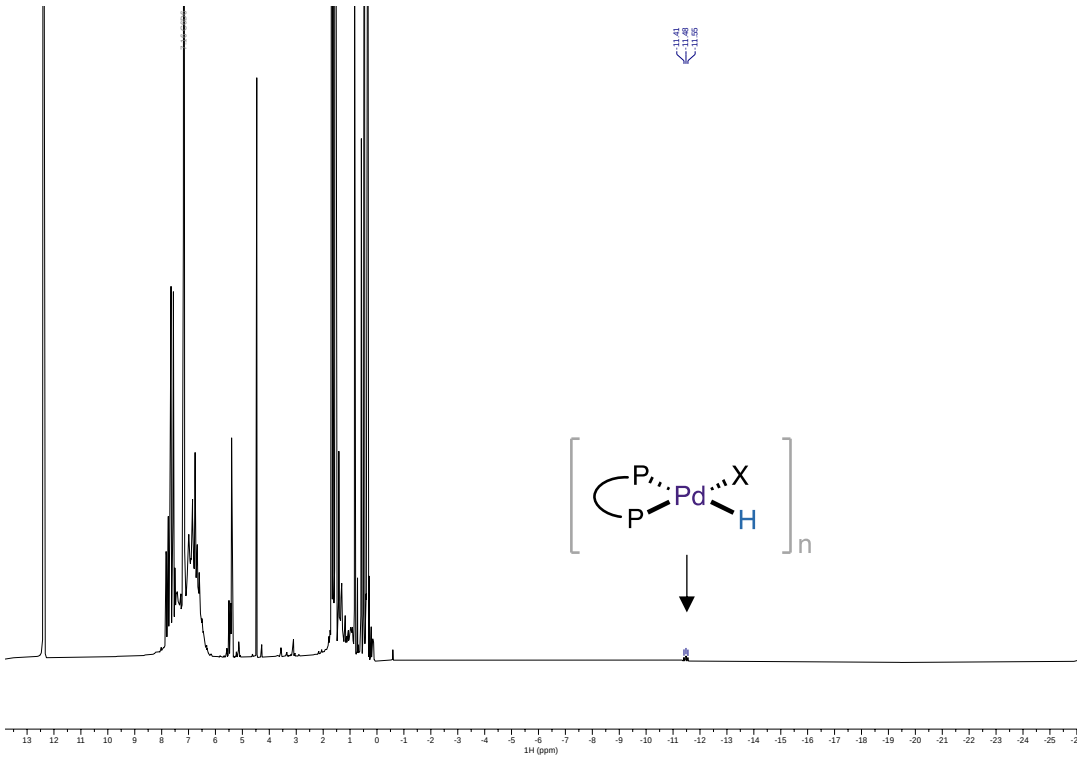
11.1 *In situ* generation of PdH species



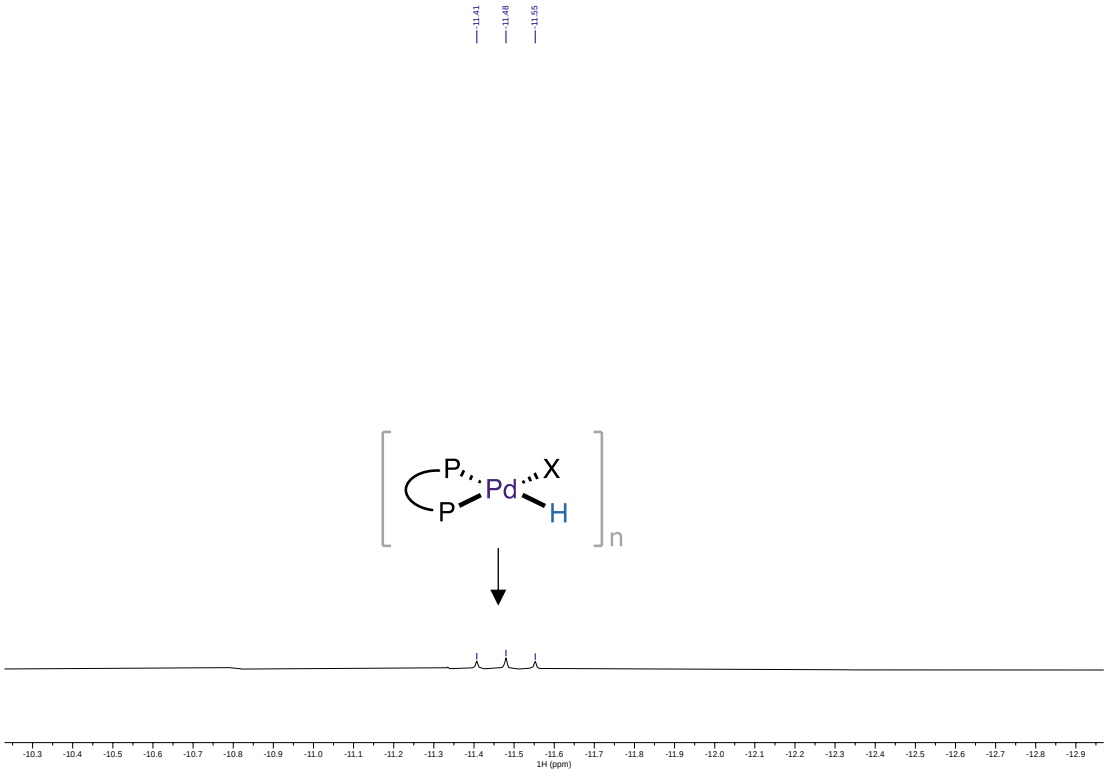
To a screw-cap NMR tube in glovebox, $Pd(OAc)_2$ (1.2 mg, 0.005 mmol, 0.1 equiv), Xantphos (5.8 mg, 0.01 mmol, 0.2 equiv) and NaI (15 mg, 0.1 mmol, 2 equiv) were added. Next, 0.5 mL of benzene-d_6, acetic acid (6 μL, 0.1 mmol, 2 equiv) and $PhMeSiH_2$ (7 μL, 0.05 mmol, 1 equiv) were added subsequently via syringe. After mixing at room temperature for 2 minutes, the reaction mixture quickly turned dark red and ^{1}H NMR analysis was performed. ^{1}H NMR spectra shows the formation of a small peak at -11.48 ppm that is attributed to the H−Pd(II)−X species.

Then, the reaction mixture was transferred to an over-dried 2 mL screw-cap vial equipped with a stir bar under inert atmosphere. BCB **4a** (0.05 mmol) and styrene **2a** (0.1 mmol, 2 equiv) was added. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was allowed to stir for 16 h. The resulting mixture was diluted using benzene-d_6 and analyzed by ^{1}H NMR using CH_2Br_2 (3.5 μL, 0.05 mmol, 1 equiv) as standard. NMR yield of hydroalkenylation product **5a** was found to be 43%.

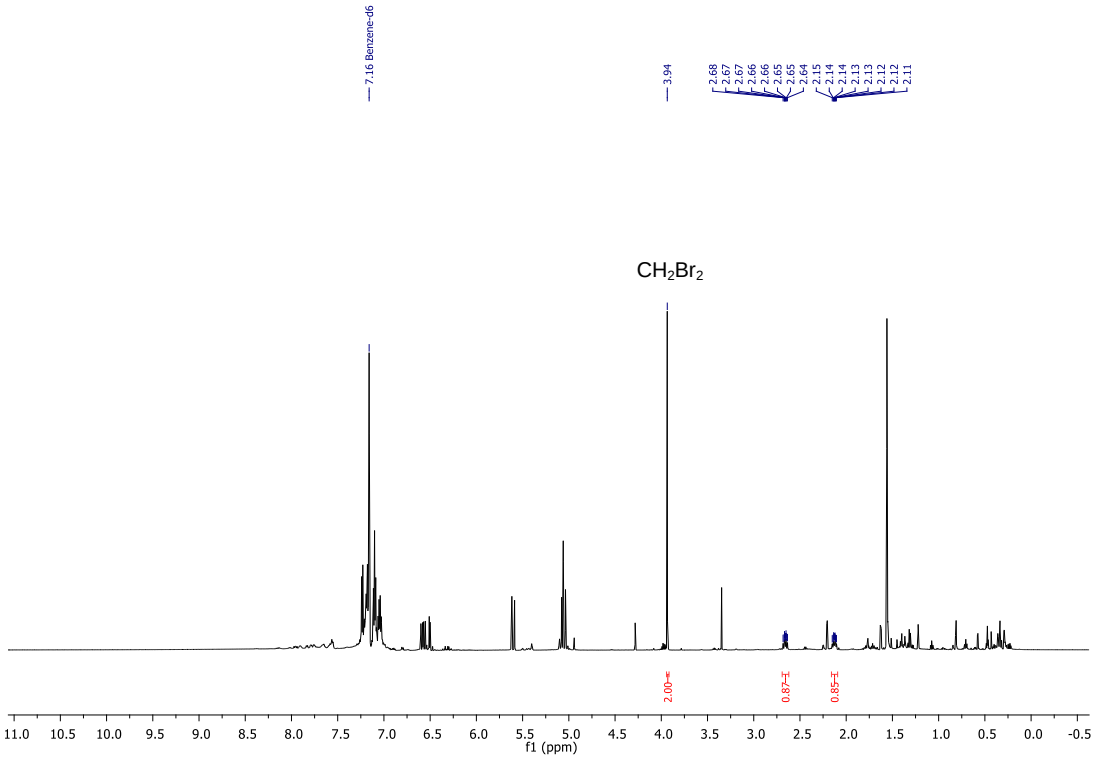
^{1}H NMR (600 MHz, C_6D_6) of $Pd(OAc)_2$, Xantphos and HX precusors mixture:



^{1}H NMR (600 MHz, C_6D_6) with expanded range (-10 to -13 ppm):

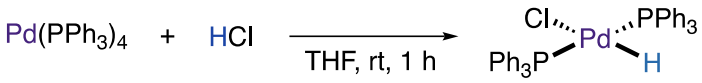


^{1}H NMR (600 MHz, C_6D_6) of reaction mixture:



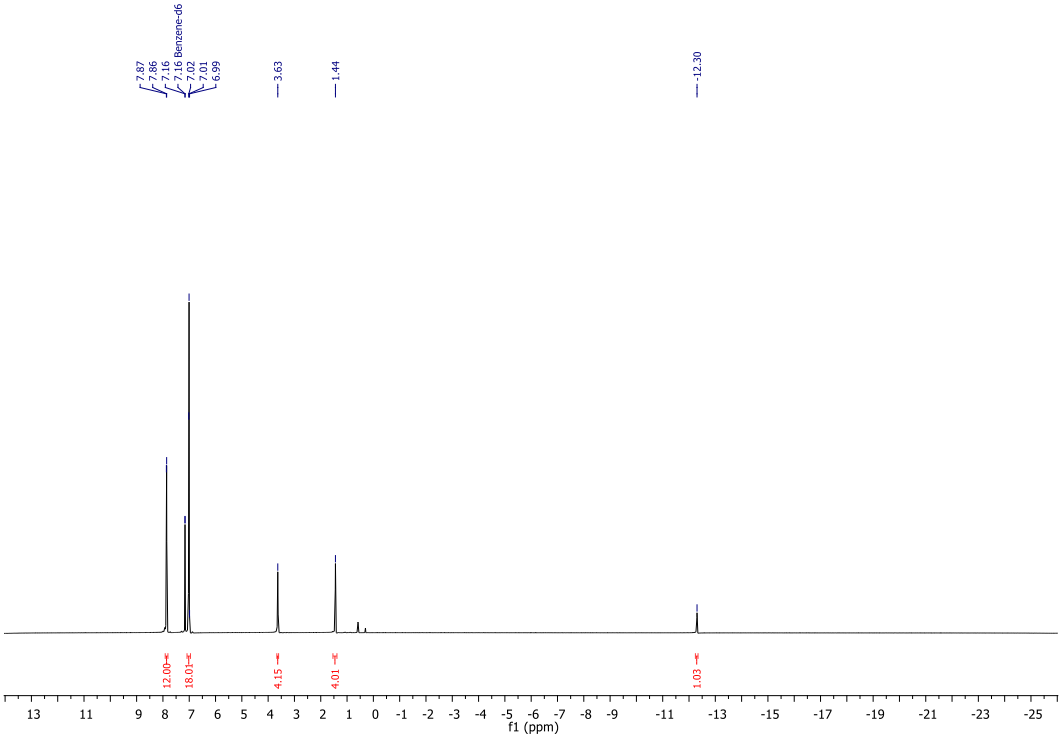
11.2 PdH complex as a catalyst

(a) Synthesis of $HPd(PPh_3)_2Cl$ complex

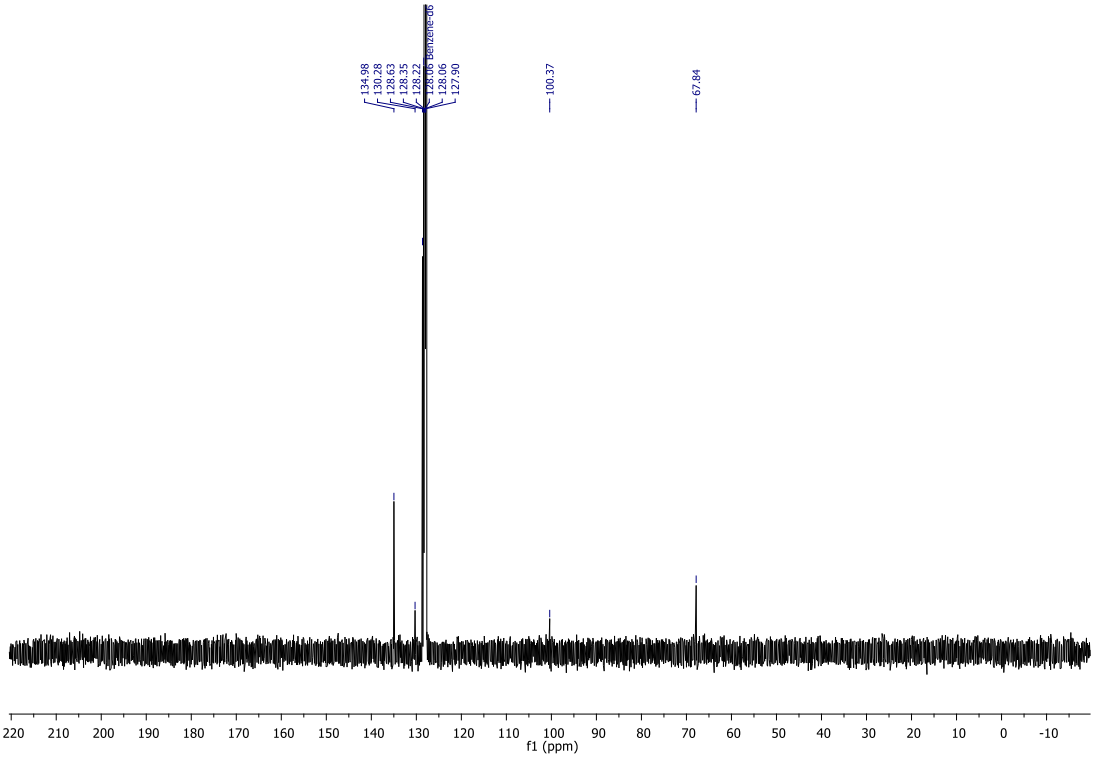


$HPd(PPh_3)_2Cl$ was synthesized according to modified literature procedure.[12] In a glove box, HCl (1.0 M in Et_2O, 0.22 mmol) was added dropwise into a stirring solution of $Pd(PPh_3)_4$ (232 mg, 0.2 mmol) in THF (2.5 mL) at room temperature for an hour. Then the solvent and excess HCl were removed under reduced pressure. The resulting solid was washed with pentane (5 mL x 3) and then dried under vacuum to afford the $HPd(PPh_3)_2Cl$ as off-white powder (76 mg, 51% yield). Compound was isolated as THF solvate (1 equiv THF, as observed by 1H NMR spectroscopy, remains after extensive vacuum drying of the isolated solid). **$HPd(PPh_3)_2Cl$**: ^{1}H NMR (600 MHz, C_6D_6) δ ppm 7.86 (d, J = 5.9 Hz, 12H), 7.00 (t, J = 8.4 Hz, 18H), -12.30 (s, 1H). ^{13}C NMR (151 MHz, C_6D_6) δ ppm 134.9, 130.2, 128.6, 128.3. ^{31}P NMR (243 MHz, C_6D_6) δ ppm 28.4.

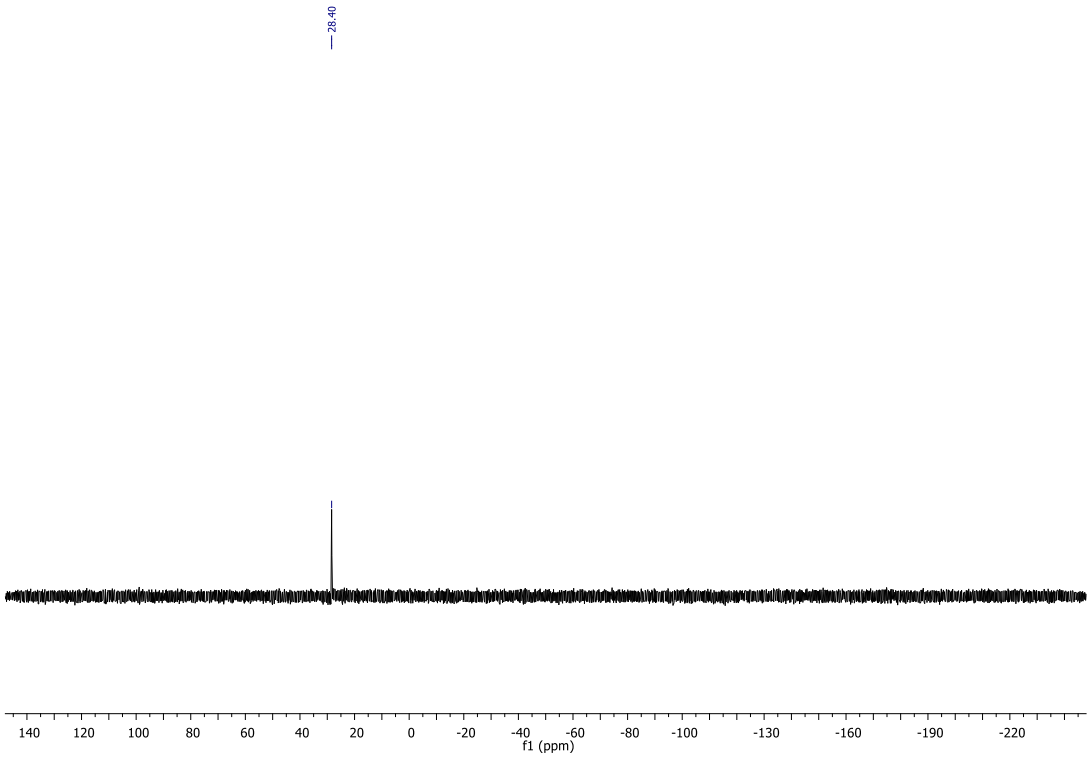
^{1}H NMR (600 MHz, C_6D_6) of **$HPd(PPh_3)_2Cl$**



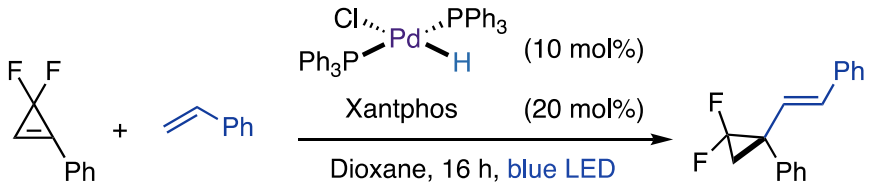
^{13}C NMR (151 MHz, C_6D_6) of **$HPd(PPh_3)_2Cl$**



^{31}P NMR (243 MHz, C_6D_6) of **HPd(PPh$_3$)$_2$Cl**



(b) Experiment using HPd(PPh$_3$)$_2$Cl as a catalyst

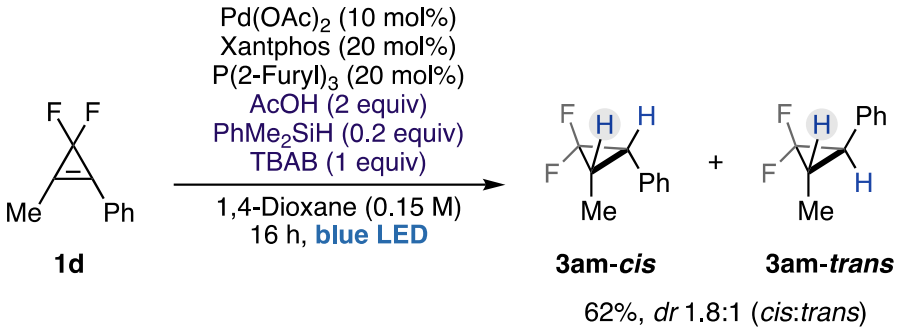


1a **2a** **3a**, 40%

An oven dried 2 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with HPd(PPh$_3$)$_2$Cl (10 mol%) and Xantphos (20 mol%) inside glovebox. Next, styrene (2 equiv) and cyclopropene **1a** (0.15 mmol) were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was stirred for 16 h. The resulting mixture was filter through a short plug of neutralized silica gel using hexanes/EtOAc as eluent. The filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography on neutral aluminum oxide in hexanes/EtOAc to afford the product **3a** in 40% yield (15.0 mg, 0.06 mmol).

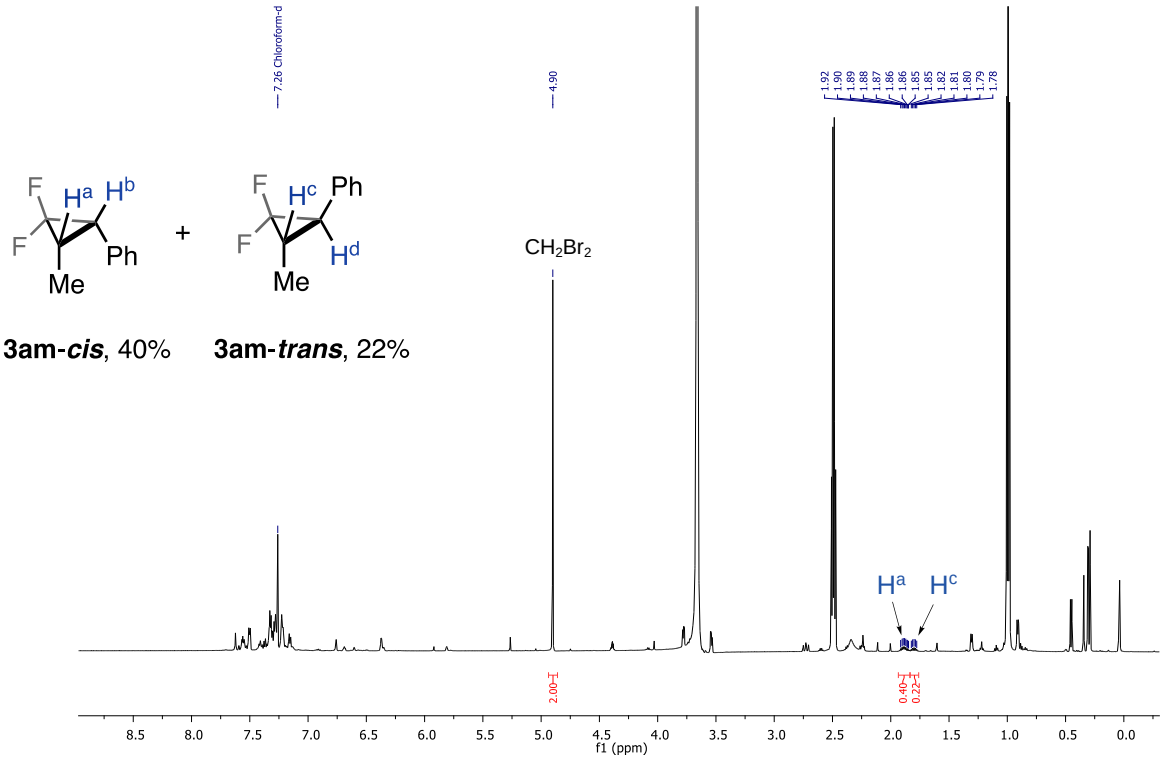
11.3 HAT of cyclopropyl and cyclobutyl radicals

(a) HAT of cyclopropyl radical



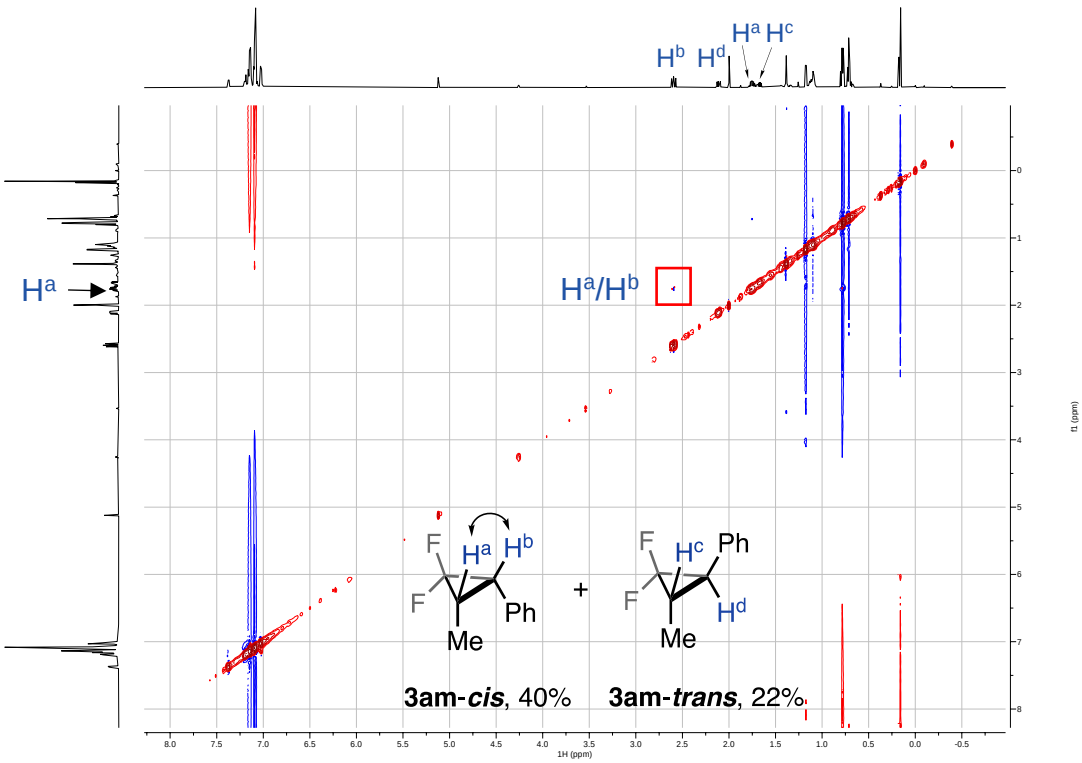
An oven dried 2 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%), $P(2\text{-Furyl})_3$ (20 mol%), and TBAB (1 equiv) inside glovebox. Next, 1,4-dioxane (0.15 M), acetic acid (2 equiv), $PhMe_2SiH$ (0.2 equiv), cyclopropene **1d** (0.15 mmol) were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was stirred for 16 h. The resulting mixture was filter through a short plug of neutralized silica gel using hexanes/EtOAc as eluent. The filtrate was concentrated *in vacuo*. The residue was diluted with $CDCl_3$ and analyzed by ^1H NMR using CH_2Br_2 (10.5 μL, 0.15 mmol, 1 equiv) as standard. NMR yield of cyclopropane **3am** was found to be 62% with dr 1.8:1 (*cis*:*trans*), compared with literature spectral data of **3am**.[13] The stereochemistry of major diastereomer was assigned via NOESY experiment.

^{1}H NMR (600 MHz, C_6D_6) of reaction mixture:

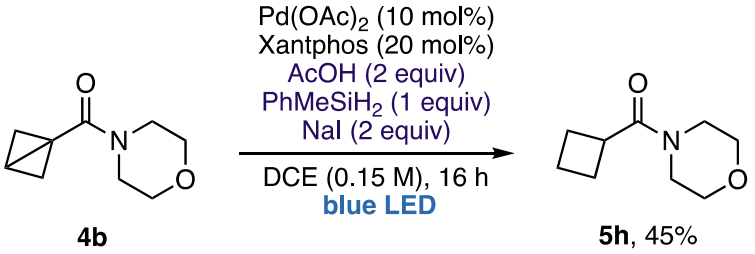


3am-*cis*, 40% **3am-*trans***, 22%

^{1}H-^{1}H NOESY of **3am**:

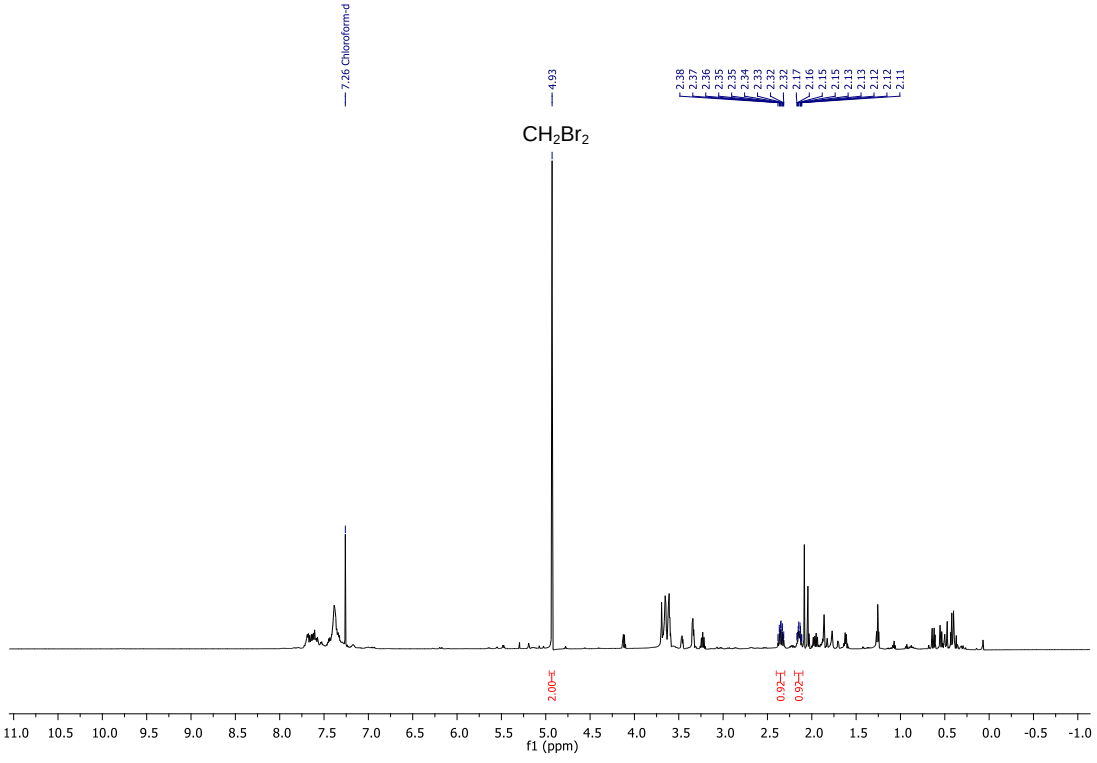


(b) HAT of cyclobutyl radical



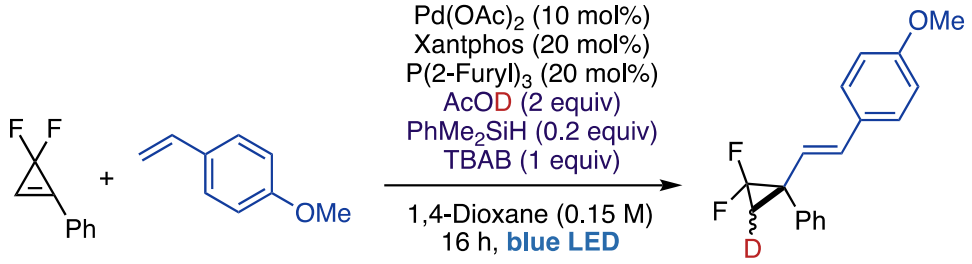
An oven dried 2 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with BCB **4b** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%), and NaI (2 equiv) inside glovebox. Next, DCE (0.15 M), acetic acid (2 equiv), and $PhMeSiH_2$ (1 equiv) were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was stirred for 16 h. The resulting mixture was filter through a short plug of silica gel using hexanes/EtOAc as eluent. The filtrate was concentrated *in vacuo*. The residue was diluted with $CDCl_3$ and analyzed by ^1H NMR using CH_2Br_2 (10.5 µL, 0.15 mmol, 1 equiv) as standard. NMR yield of cyclobutane **5h** was found to be 46%, compared with literature spectral data of **5h**.[14]

^1H NMR (600 MHz, $CDCl_3$) of reaction mixture:



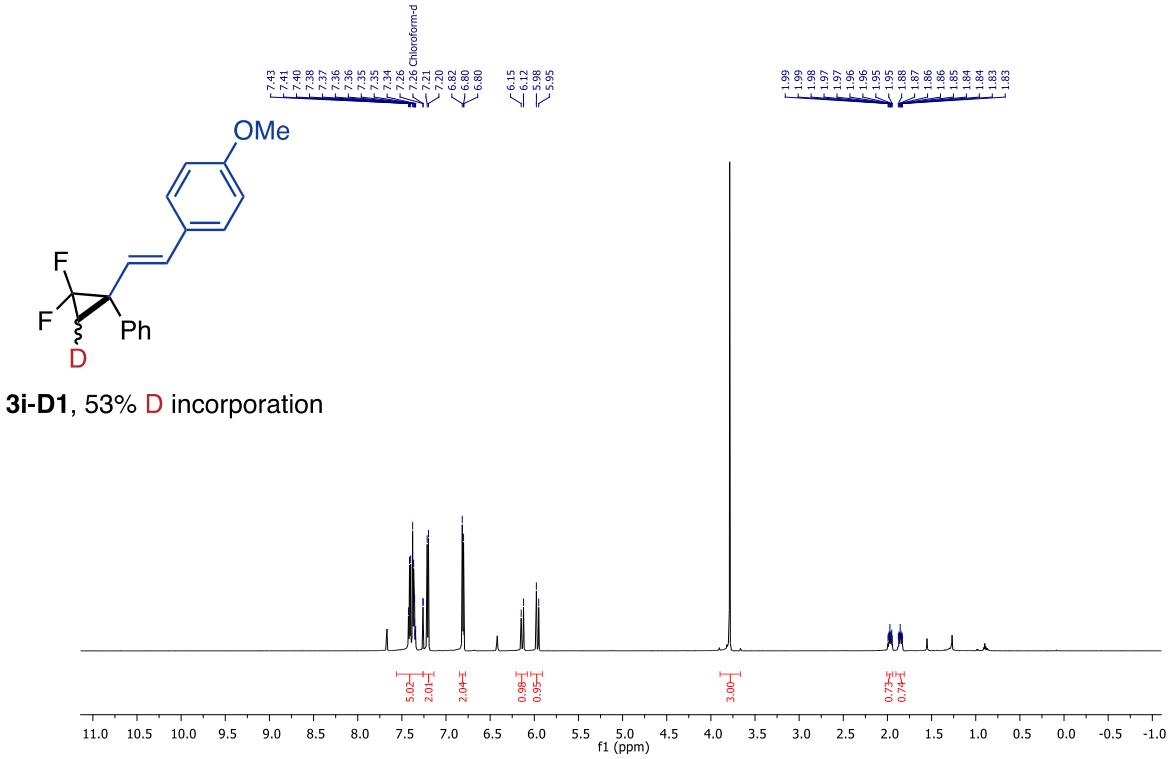
11.4 Deuterium-labeling studies:

(a) Reaction with acetic acid-d_4

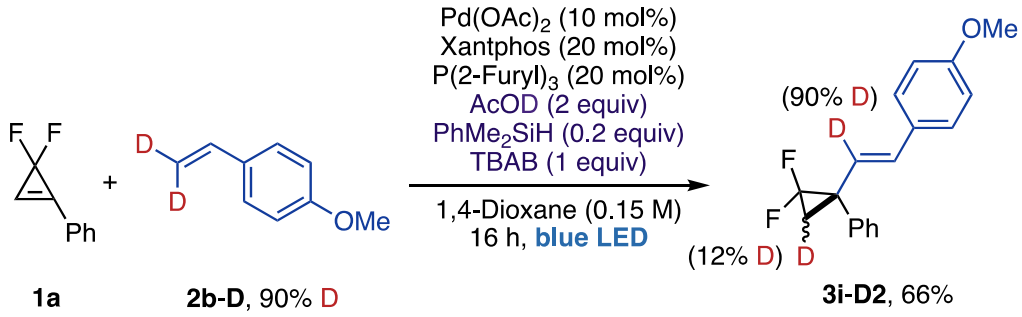


Following General Procedure D, acetic acid-d_4 (17 μL, 0.3 mmol, 2 equiv) was used. The crude reaction mixture was purified by column chromatography in hexanes/EtOAc (20:1) to afford the the product **3i-D1** in 63% yield with 53% D incorporation analyzed by ^{1}H NMR.

^{1}H NMR (600 MHz, $CDCl_3$) of **3i-D1**

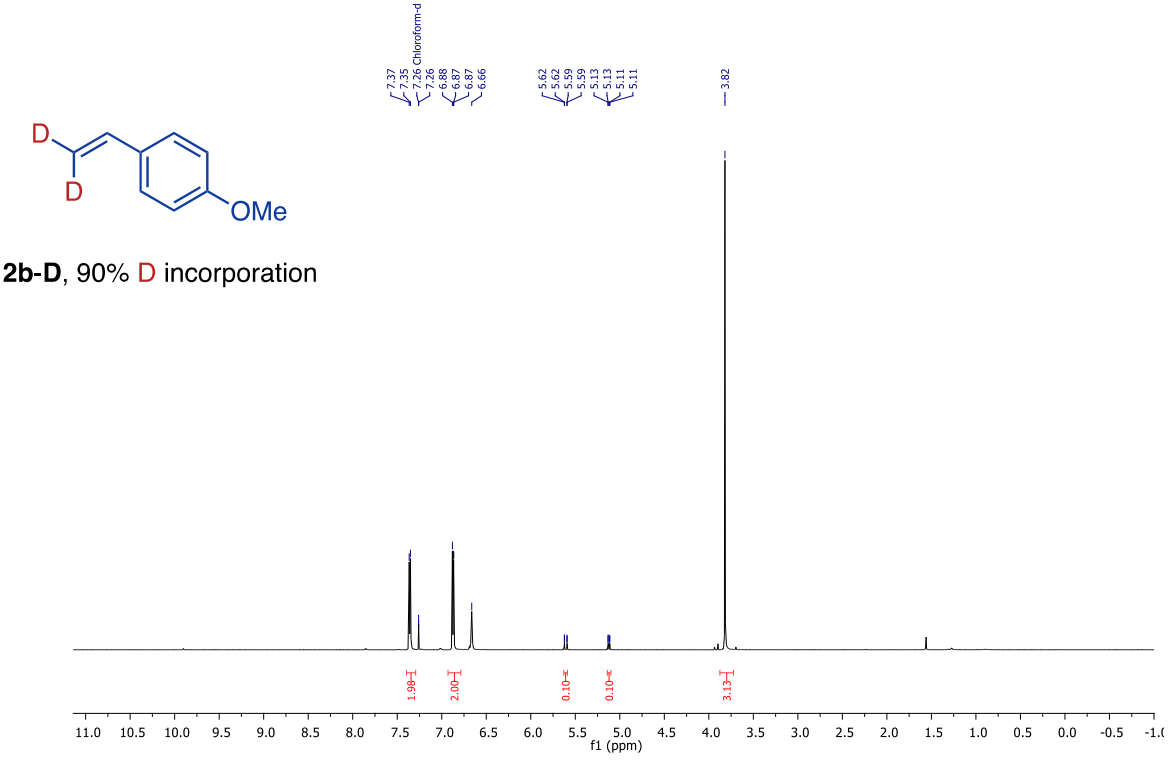


(b) Reaction with 4-vinylanisole-*d*$_2$

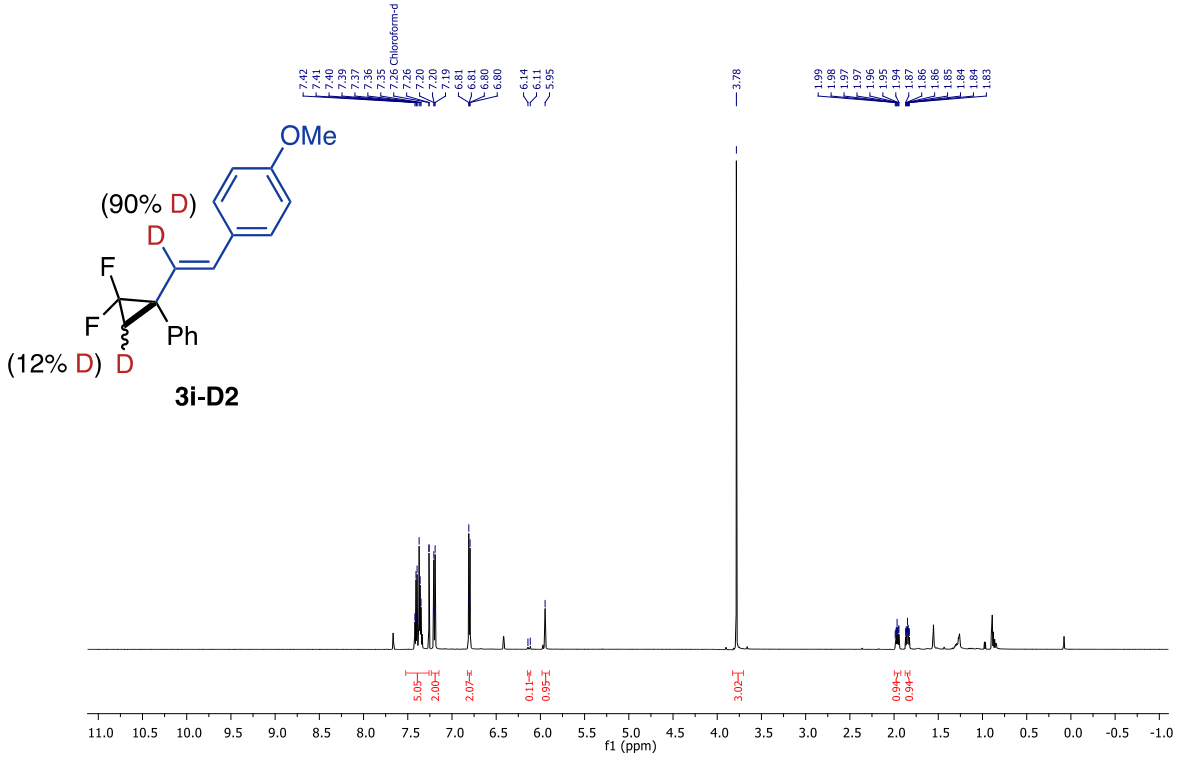


Reaction was performed according to the General Procedure E using **1a** (0.15 mmol), deuterated 4-vinylanisole[15] **2b-D** (0.3 mmol, 2.0 equiv) to afford the product **3i-D2** in 66% yield and deuterium incorporation was analyzed by ^{1}H NMR, *which indicates that H−Pd(II)−X species enters next catalytic cycle after β-H elimination.*

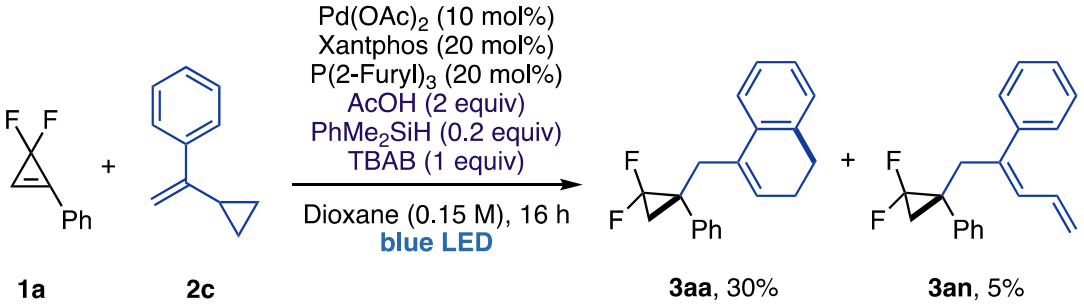
^{1}H NMR (600 MHz, $CDCl_3$) of **2b-D**



^{1}H NMR (600 MHz, $CDCl_3$) of **3i-D2**

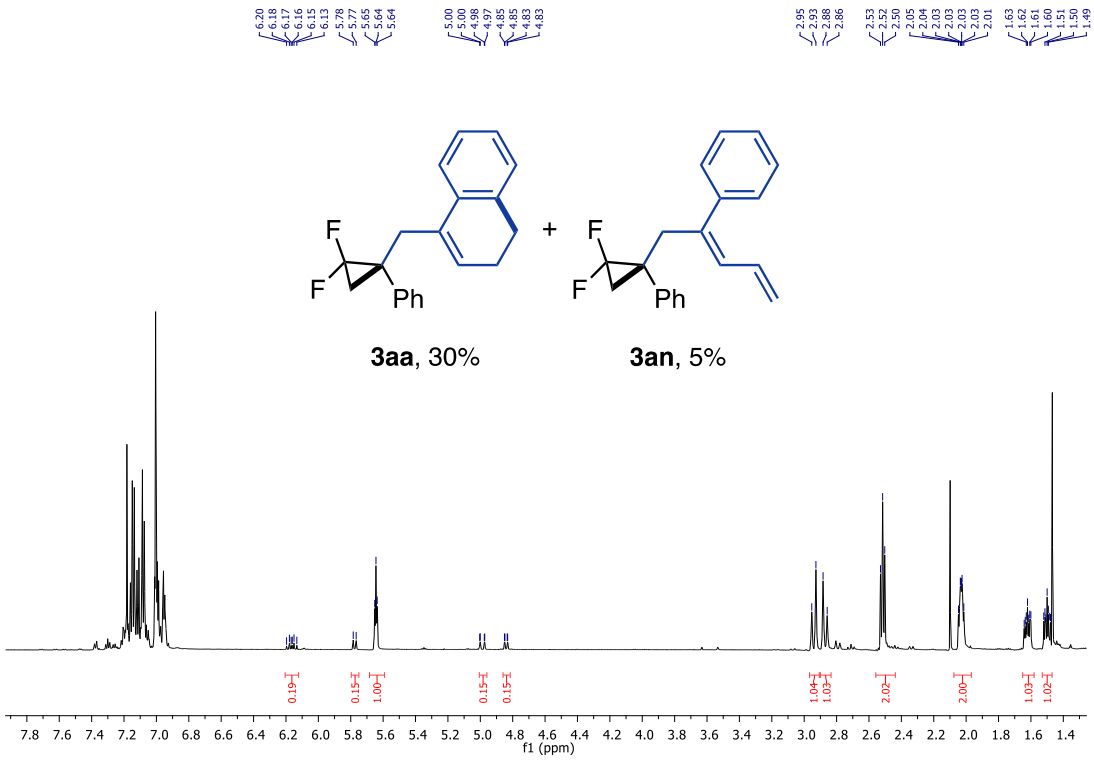


11.5 Radical probe experiments:



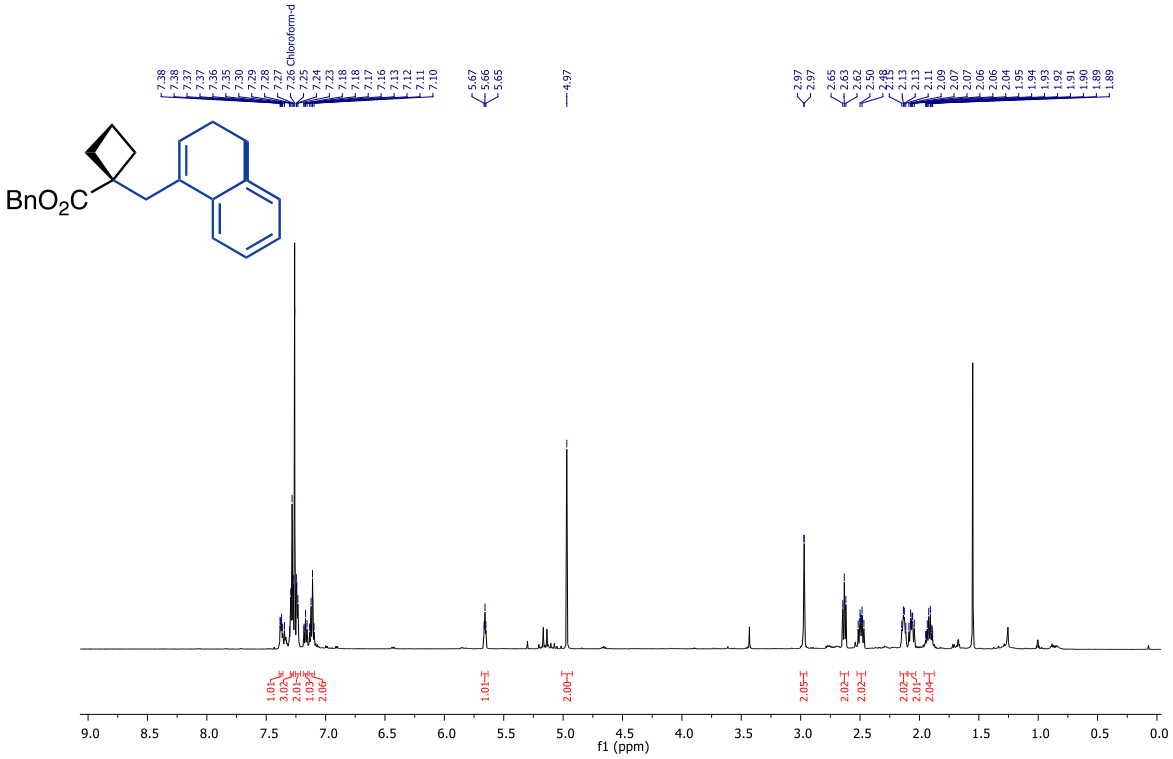
Following General Procedure D, cyclopropane **1a** (0.15 mmol) and (1-cyclopropylvinyl)benzene **2c** (43.5 mg, 0.3 mmol) were used. The crude reaction mixture was purified by column chromatography in hexanes/EtOAc (20:1) to afford the mixture of products **3aa** and **3an** in 35% yield (15.0 mg, 0.051 mmol). The ratio of **3aa** and **3an** was determined by ^{1}H NMR.

^{1}H NMR (600 MHz, $CDCl_3$) of isolated **3aa** and **3an**:

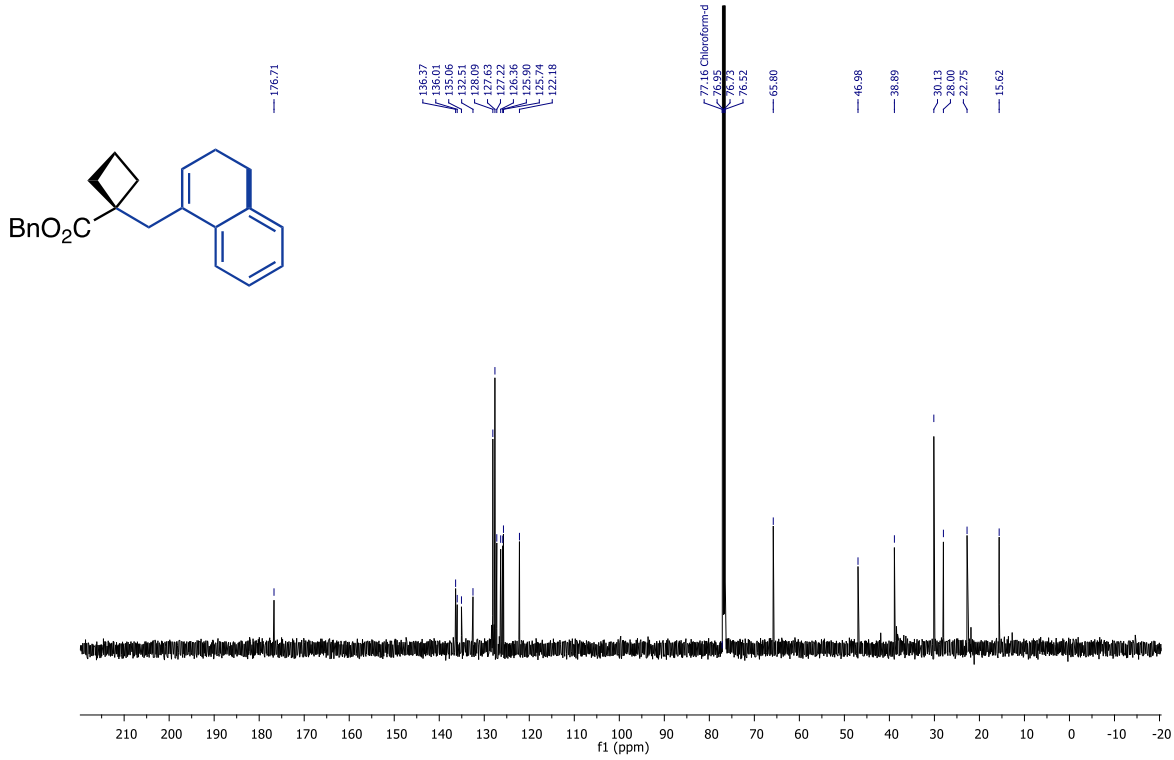


Following General Procedure E, BCB **4a** (0.15 mmol) and (1-cyclopropylvinyl)benzene **2c** (43.5 mg, 0.3 mmol) were used. The crude reaction mixture was purified by column chromatography in hexanes/EtOAc (10:1) to afford the product **5i** in 21% yield (10.0 mg, 0.031 mmol) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.39 – 7.36 (m, 1H), 7.28 (t, *J* = 6.6 Hz, 3H), 7.25 – 7.21 (m, 2H), 7.17 (dd, *J* = 11.7, 4.6 Hz, 1H), 7.12 (q, *J* = 7.4 Hz, 2H), 5.66 (t, *J* = 4.5 Hz, 1H), 4.97 (s, 2H), 2.97 (d, *J* = 1.1 Hz, 2H), 2.63 (t, *J* = 7.9 Hz, 2H), 2.53 – 2.45 (m, 2H), 2.13 (dd, *J* = 12.5, 7.9 Hz, 2H), 2.07 (dt, *J* = 11.8, 8.6 Hz, 2H), 1.96 – 1.87 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 176.7, 136.3, 136.0, 135.0, 132.5, 128.0, 127.6, 127.2, 126.3, 125.9, 125.7, 122.1, 65.8, 46.9, 38.8, 30.1, 28.0, 22.7, 15.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{25}O_2$ 333.1849, found: 333.1856.

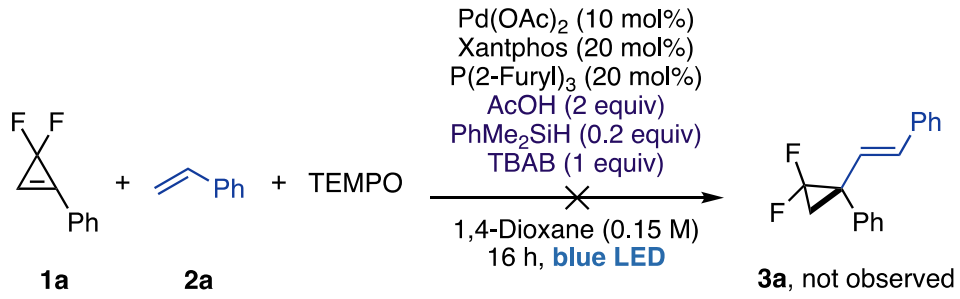
^{1}H NMR (600 MHz, $CDCl_3$) of **5i**:



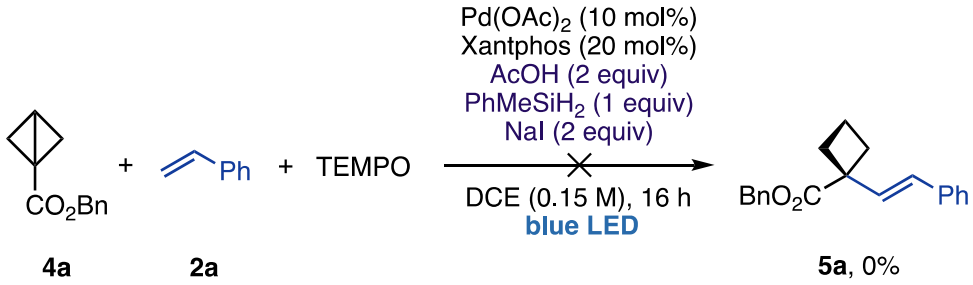
^{13}C NMR (151 MHz, $CDCl_3$) of **5i**:



11.6 Radical quenching experiments:

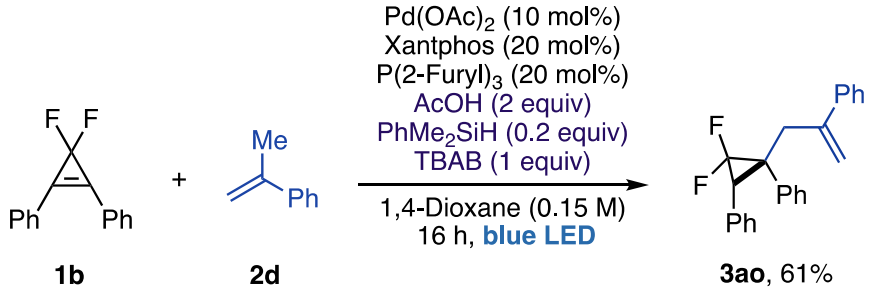


An oven dried 2 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%), $P(2\text{-Furyl})_3$ (20 mol%), TBAB (1 equiv) and TEMPO (2 equiv) inside glovebox. Next, 1,4-dioxane (0.15 M), acetic acid (2 equiv), $PhMe_2SiH$ (0.2 equiv), styrene **2a** (2 equiv) and cyclopropene **1a** (0.15 mmol) were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction was stirred for 16 h. The resulting reaction mixture was analyzed by GC-MS and ^{1}H NMR. Product **3a** was not detected and no radical trapping product with TEMPO was observed.



An oven dried 2 mL PTFE/silicone-lined septa screw cap vial containing a stirring bar was charged with $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%), NaI (2 equiv) and TEMPO (2 equiv) inside glovebox. Next, DCE (0.15 M), acetic acid (2 equiv), $PhMeSiH_2$ (1 equiv), styrene (2 equiv) and BCB **4a** (0.15 mmol), were added subsequently via syringe. The vial was placed in a photoreactor box equipped with 40 W LED lamp (Kessil PR160-427) without cooling fan (vial temperature reached 38 °C). The reaction mixture was stirred for 16 h. The resulting reaction mixture was analyzed by GC-MS and ^{1}H NMR. Product **5a** was not detected and no radical trapping product with TEMPO was observed.

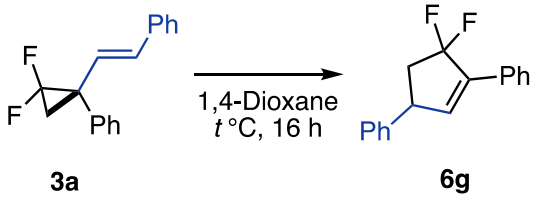
11.7 Reaction of cyclopropene with *α*-methyl styrene:



1b **2d** **3ao**, 61%

Following General Procedure F, *α*-methyl styrene **2d** (39 µL, 0.3 mmol) was used. The crude reaction mixture was purified by column chromatography in hexanes/EtOAc (10:1) to afford the product **3ao** in 61% yield (32.0 mg, 0.091 mmol) as white solid. One diastereomer. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.35 – 7.29 (m, 5H), 7.15 – 7.08 (m, 3H), 7.05 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 2H), 6.46 (d, *J* = 7.6 Hz, 2H), 5.13 (s, 1H), 4.81 (s, 1H), 3.25 (d, *J* = 14.5 Hz, 1H), 3.04 (d, *J* = 14.5 Hz, 1H), 2.73 (dd, *J* = 15.2, 2.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 145.1, 141.9, 133.2, 132.9, 131.8 (d, *J* = 1.0 Hz), 129.3 (d, *J* = 3.5 Hz), 128.7, 127.9 (d, *J* = 1.7 Hz), 127.3, 127.3, 126.7, 117.7, 117.3, 115.7, 42.5 (d, *J* = 5.2 Hz), 40.7 (dd, *J* = 10.5, 7.0 Hz), 38.5 (dd, *J* = 12.0, 9.1 Hz), 31.9, 23.0, 14.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -126.6 (d, *J* = 153.8 Hz), -138.7 (d, *J* = 153.6 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{24}H_{20}F_2$ 346.1533, found: 346.1528.

11.8 Thermal rearrangement:

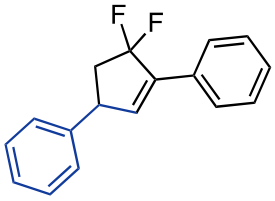


3a **6g**

t °C	conversion of **3a** (%)	yield of **6g** (%)
25	0	0
100	23	17
150	100	93

An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with vinyl cyclopropane **3a** (0.15 mmol) in 1,4-dioxane (0.1 M). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at indicated reaction temperature. The reaction mixture was allowed to stir for 16 h and then concentrated *in vacuo*. The resulting residue was purified by column chromatography on neutral aluminum oxide in hexanes/EtOAc to afford product **6g** and substrate **3a** was recovered.

(5,5-Difluorocyclopent-1-ene-1,3-diyl)dibenzene **6g**



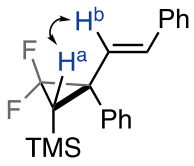
6g was obtained at 150 °C in 93% yield (36 mg, 0.139 mmol) as white solid. R_f (hexanes/EtOAc = 20/1): 0.26. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.59 – 7.55 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.20 – 7.15 (m, 3H), 6.46 (s, 1H), 4.06 – 3.96 (m, 1H), 2.97 (ddt, *J* = 17.9, 15.5, 7.9 Hz, 1H), 2.42 – 2.33 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 142.7 (d, *J* = 4.6 Hz), 139.2 (dd, *J* = 25.0, 23.6 Hz), 138.8 (t, *J* = 8.1 Hz), 134.5, 132.9, 131.2, 131.0, 129.0, 128.7, 128.6, 127.4, 127.2, 126.8, 45.7 – 45.3 (m), 44.6 (dd, *J* = 26.5, 23.6 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ ppm -83.5 (d, *J* = 250.1 Hz), -87.9 (d, *J* = 250.0 Hz). HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd. for $C_{17}H_{14}F_2$ 256.1058, found: 256.1060.

12. Assignment of Relative Configurations

12.1 Assignment of relative configurations for cyclopropanes

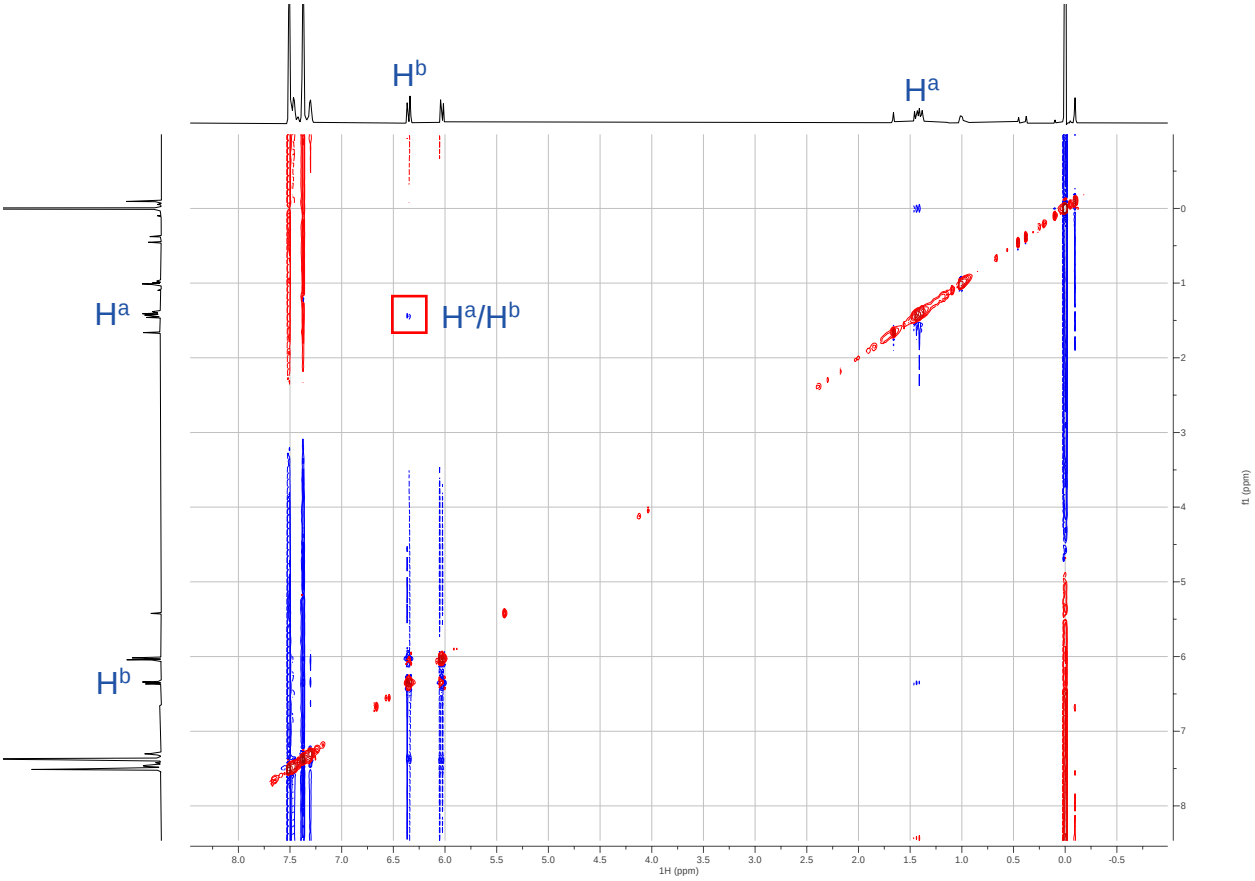
Relative configurations of cyclopropanes **3d**, **3ao** and major diastereomer of **3e**, **3f**, **3g** were assigned based on chemical shifts and ^{1}H-^{1}H NOESY experiments. Three representative examples of the structure elucidation performed for compounds **3d**, **3e**, and **3ao** are provided below. Relative configurations of other products were assigned by analogy.

(a) Stereochemistry of cyclopropanes 3d

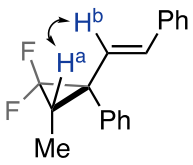


^{1}H-^{1}H NOESY spectrum showed that cyclopropyl H^{a} proton at 1.32 ppm has correlation with alkenyl H^{b} proton at 6.23 ppm, which means that H^{a} is *cis* to vinyl group in cyclopropane **3d**.

^{1}H-^{1}H NOESY of **3d**

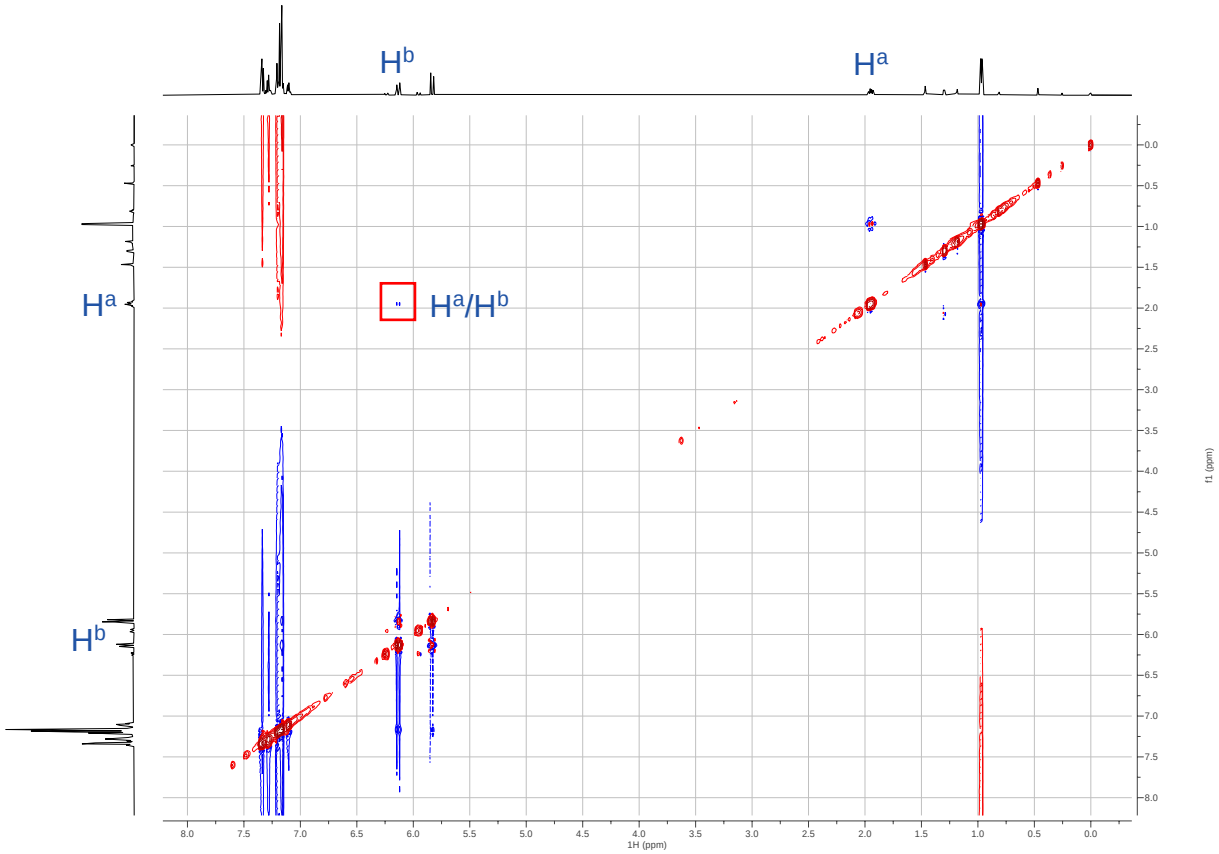


(b) Stereochemistry of cyclopropanes 3e (major diastereomer)

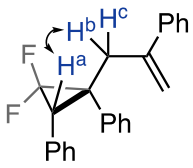


^{1}H-^{1}H NOESY spectrum showed that cyclopropyl H^a proton at 2.03 ppm has correlation with alkenyl H^b proton at 6.23 ppm, which means that H^a is *cis* to vinyl group in major diastereomer of cyclopropane **3e**.

^{1}H-^{1}H NOESY of **3e**

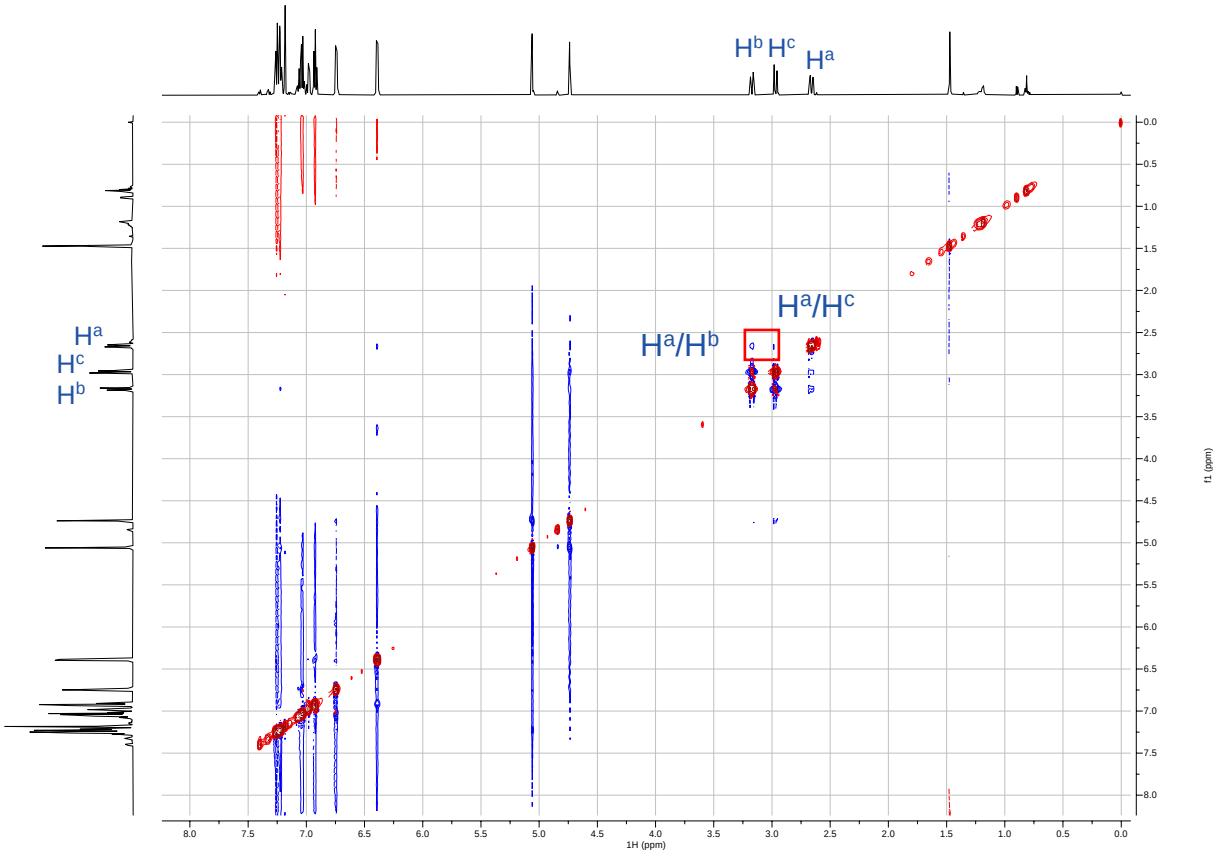


(b) Stereochemistry of cyclopropanes 3ao



^{1}H-^{1}H NOESY spectrum showed that cyclopropyl H^a proton at 2.73 ppm has correlation with both allylic H^b and H^c proton at 3.23 ppm and 3.03 ppm, which means that H^a is *cis* to allyl group in cyclopropane **3ao**.

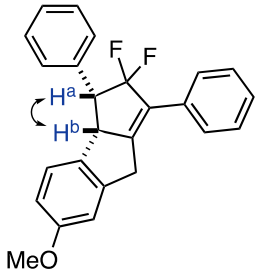
^{1}H-^{1}H NOESY of **3ao**



12.2 Assignment of relative configurations for cyclopentenes

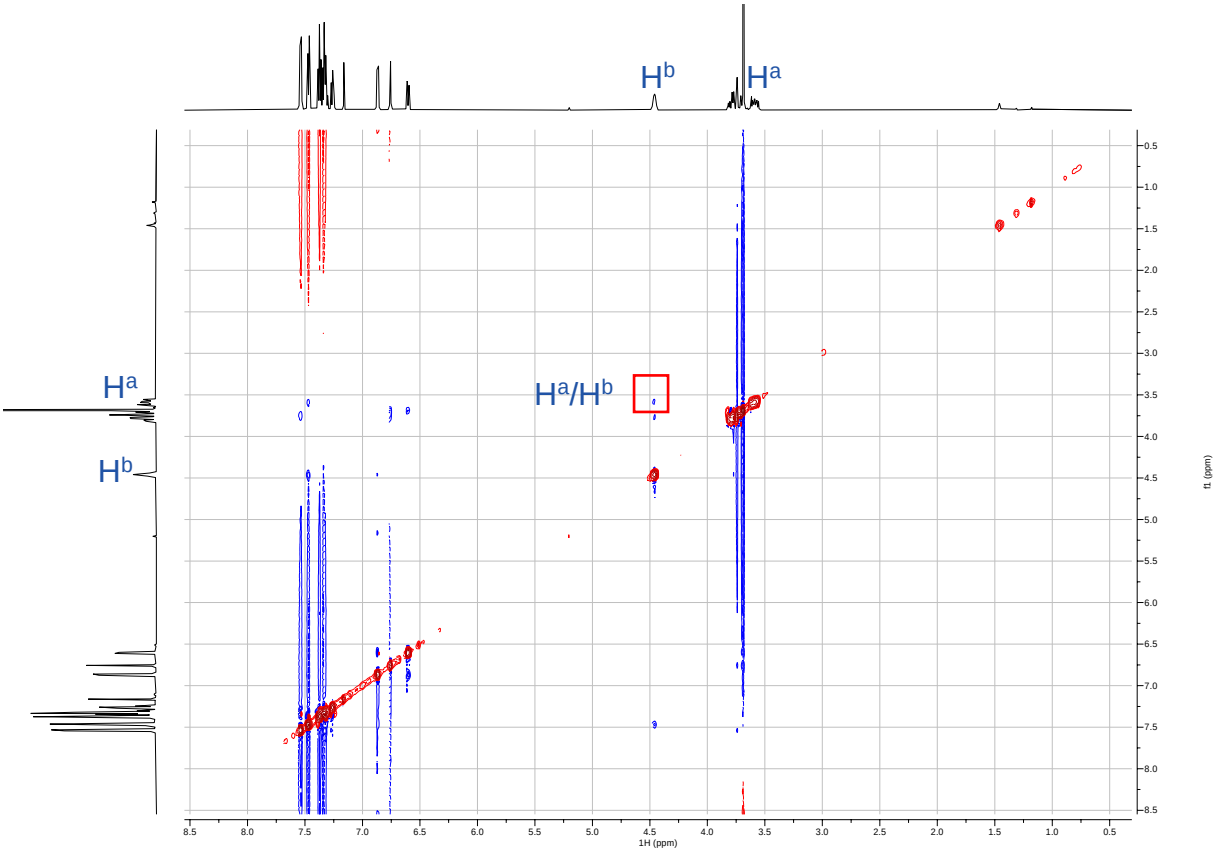
Relative configurations of cyclopentenes **6a**, **6b**, **6c**, **6d**, **6e**, **6f** were assigned based on chemical shifts and ^{1}H-^{1}H NOESY experiments. Three representative examples of the structure elucidation performed for compounds **6c**, **6d**, and **6f** are provided below. Relative configurations of other products were assigned by analogy.

(a) Stereochemistry of cyclopentene 6c

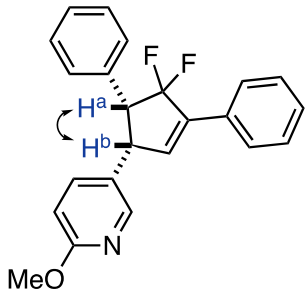


^{1}H-^{1}H NOESY spectrum showed that H^{a} proton at 3.70 ppm has correlation with H^{b} proton at 4.56 ppm, which means that H^{a} is *cis* to H^{b} in cyclopentene **6c**.

^{1}H-^{1}H NOESY of **6c**

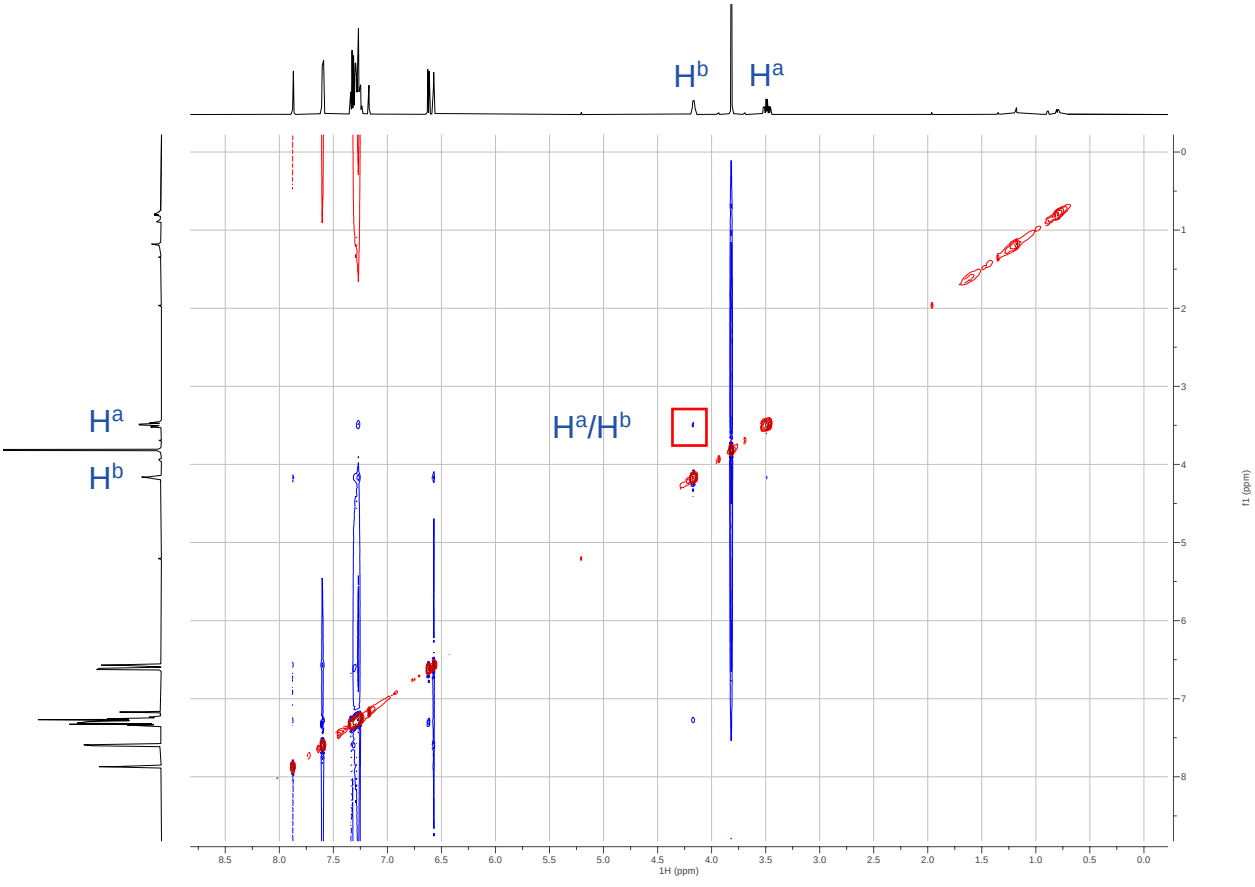


(b) Stereochemistry of cyclopentene 6d

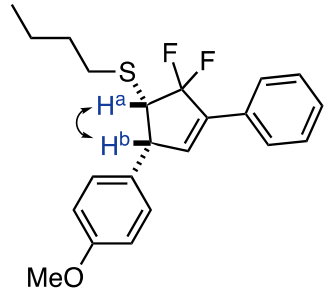


^{1}H-^{1}H NOESY spectrum showed that H^a proton at 3.60 ppm has correlation with H^b proton at 4.25 ppm, which means that H^a is *cis* to H^b. Thus, pyridyl group is *cis* to phenyl group in cyclopentene **6d**.

^{1}H-^{1}H NOESY of **6d**

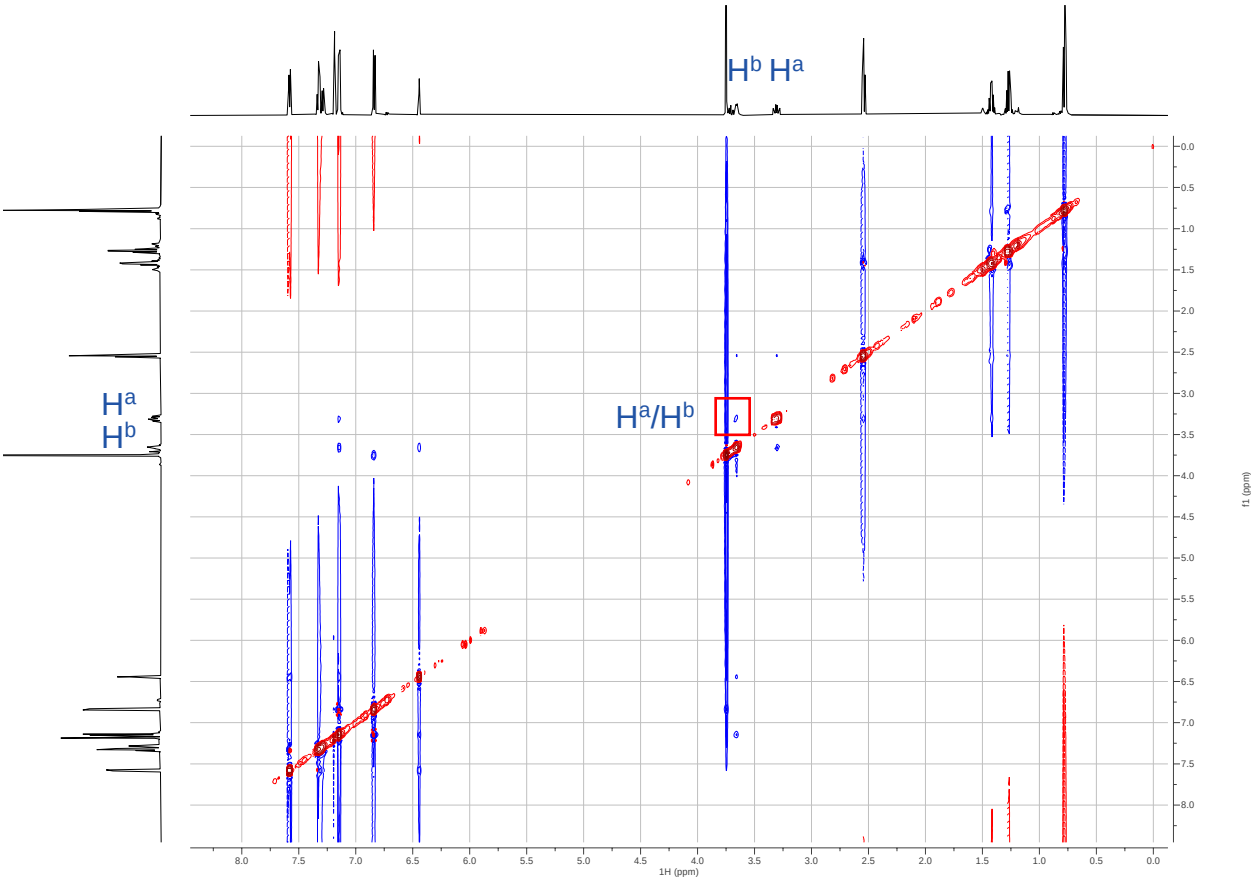


(c) Stereochemistry of cyclopentene 6f



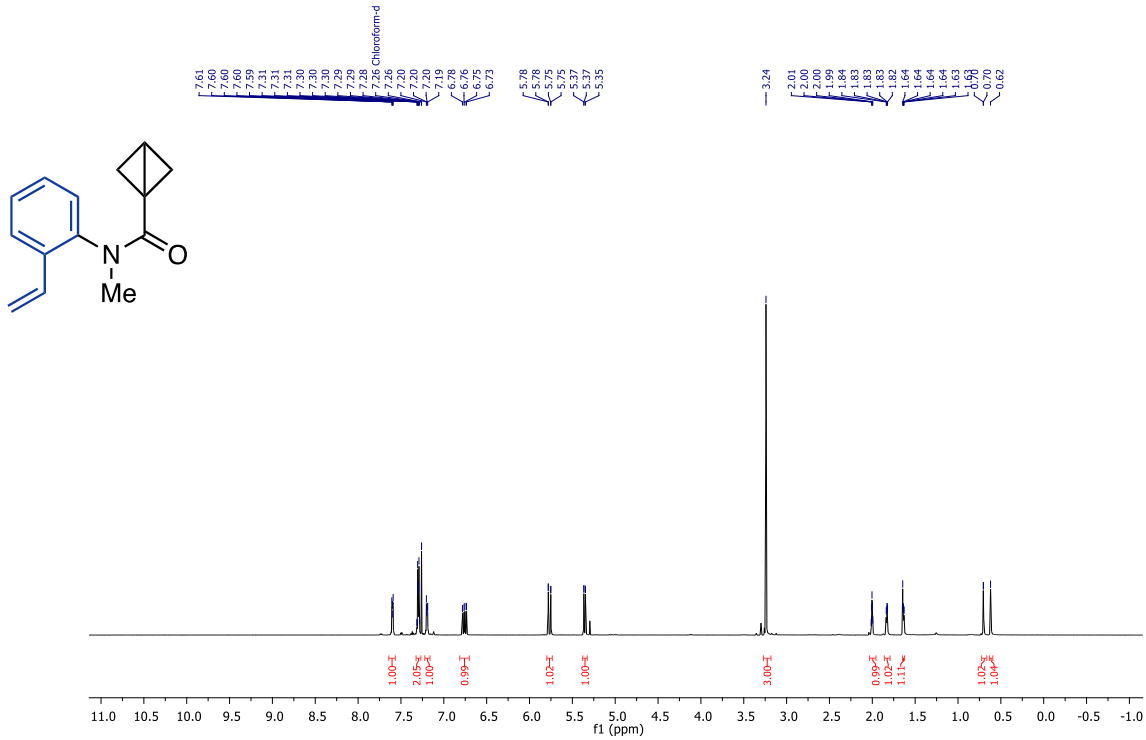
^{1}H-^{1}H NOESY spectrum showed that H^a proton at 3.37 ppm has correlation with H^b proton at 3.72 ppm, which means that H^a is *cis* to H^b.

^{1}H-^{1}H NOESY of **6f**

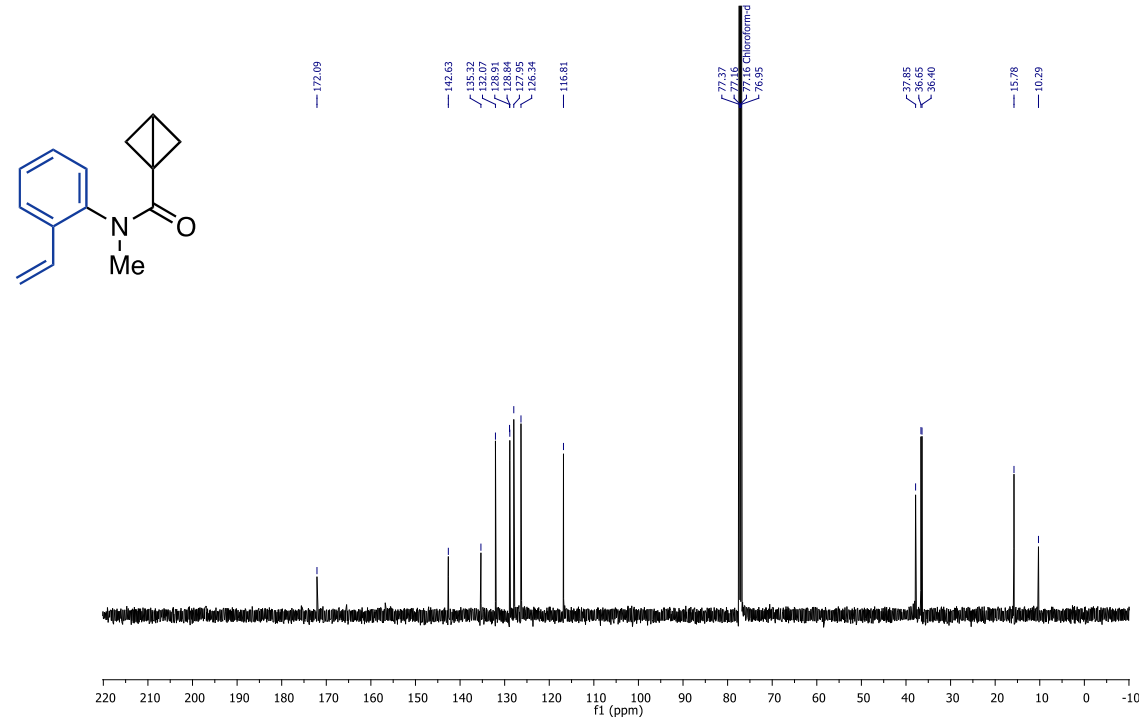


13. NMR Spectral Data

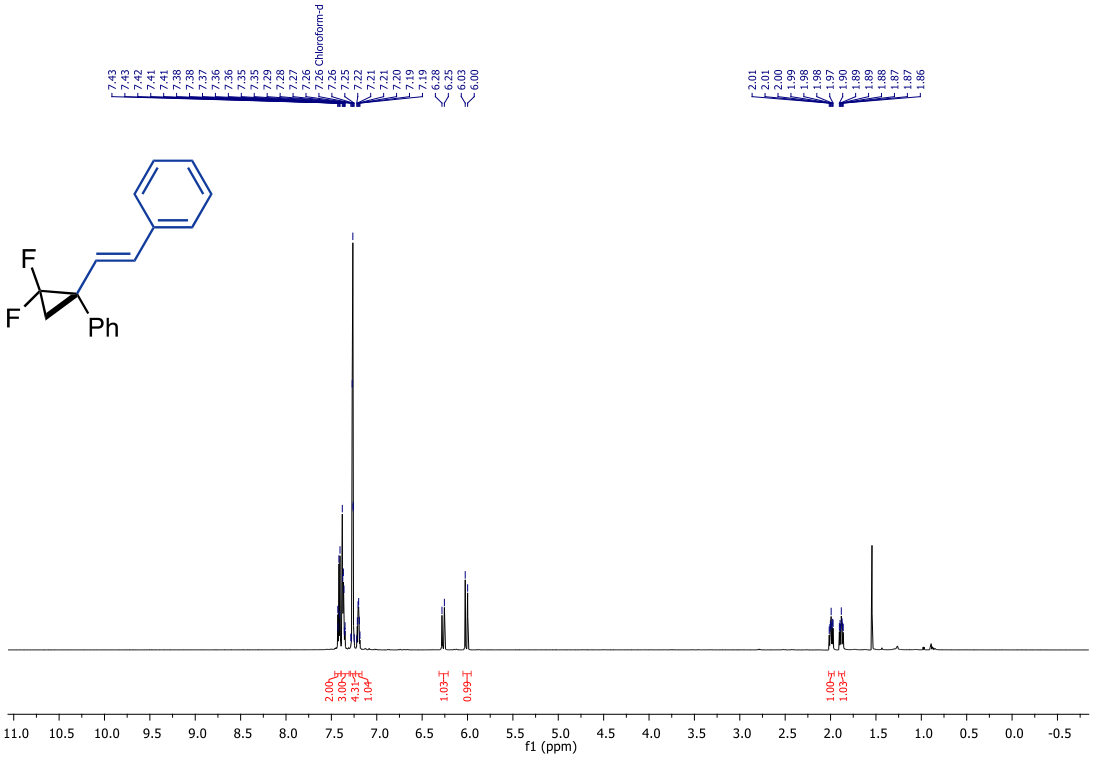
^{1}H NMR (600 MHz, $CDCl_3$) of **4d**



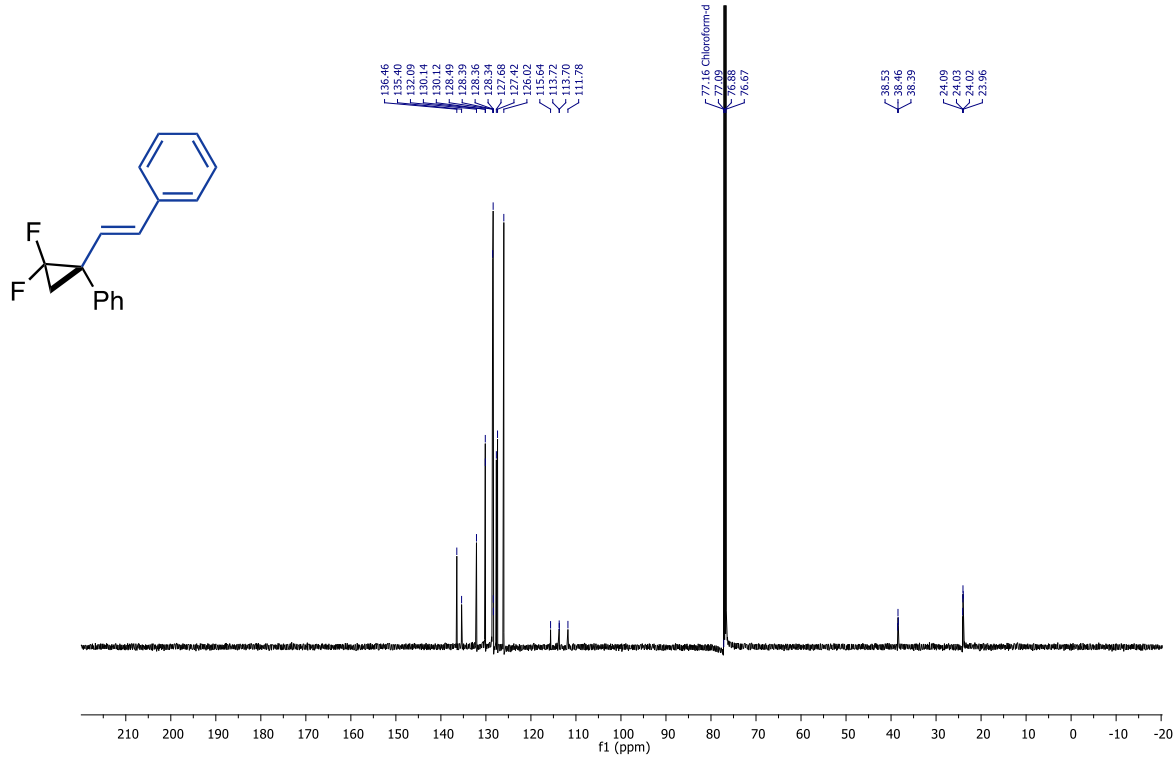
^{13}C NMR (151 MHz, $CDCl_3$) of **4d**



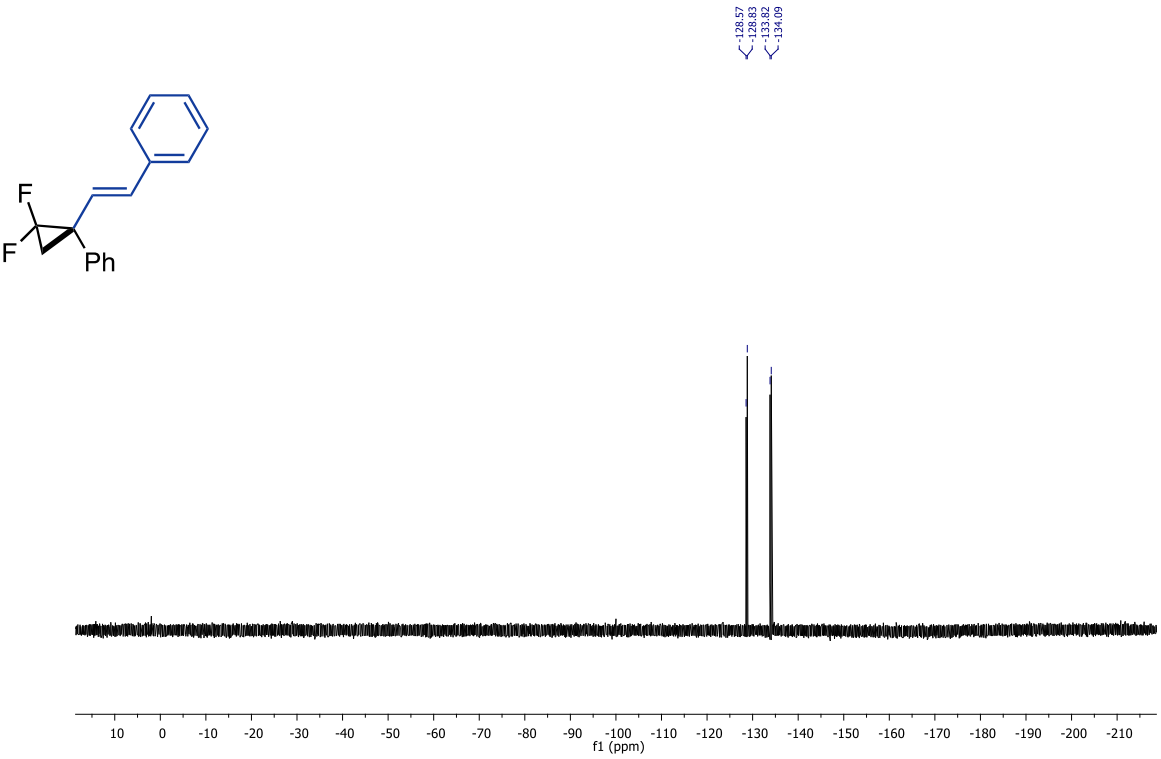
^{1}H NMR (600 MHz, $CDCl_3$) of **3a**



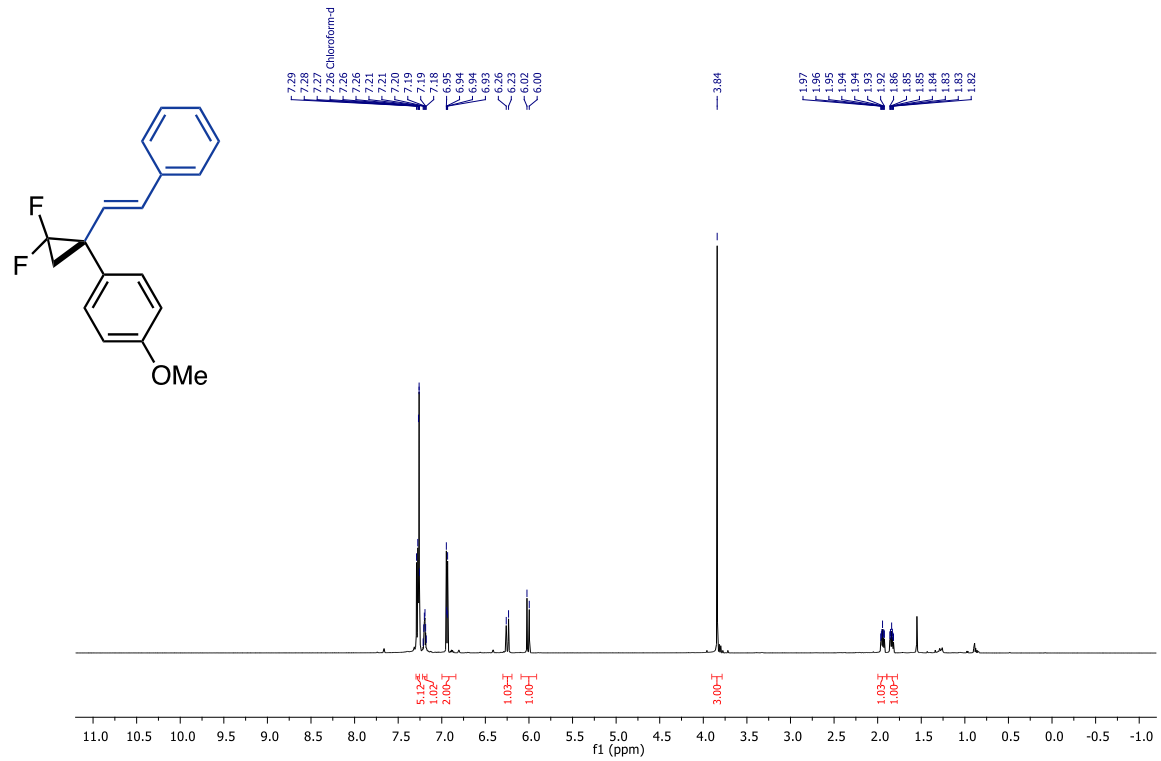
^{13}C NMR (151 MHz, $CDCl_3$) of **3a**



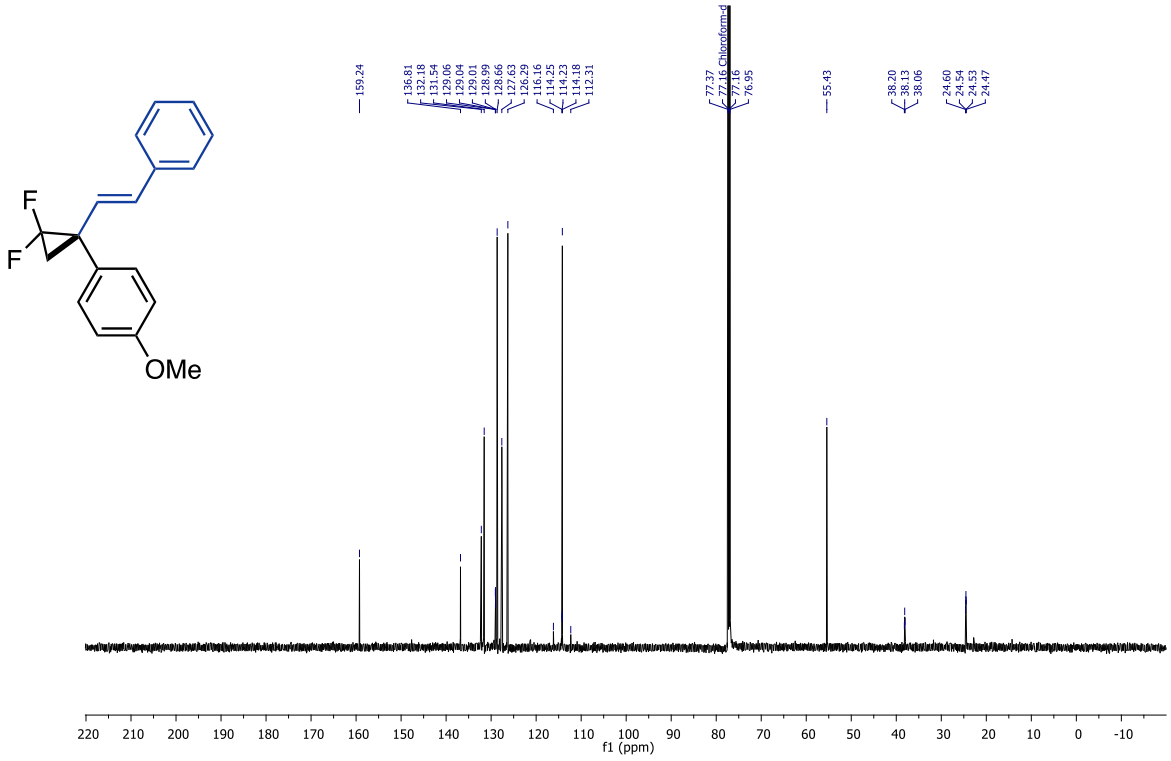
^{19}F NMR (565 MHz, $CDCl_3$) of **3a**



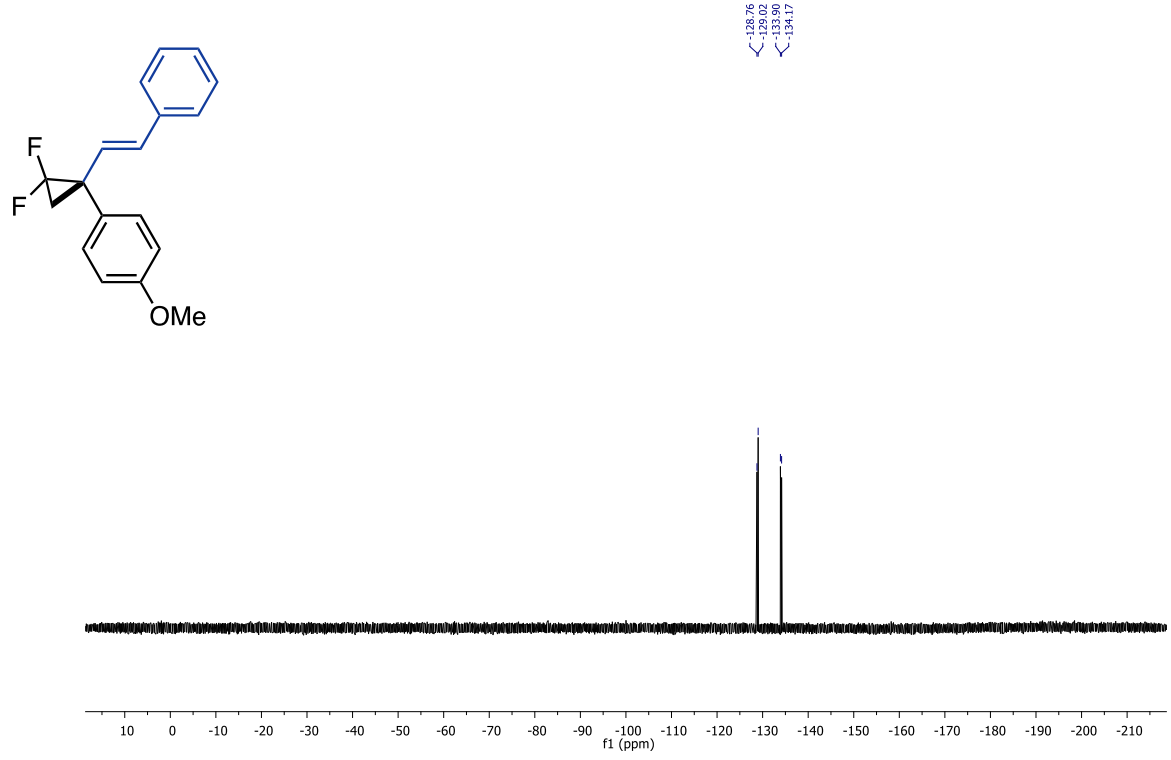
^{1}H NMR (600 MHz, $CDCl_3$) of **3b**



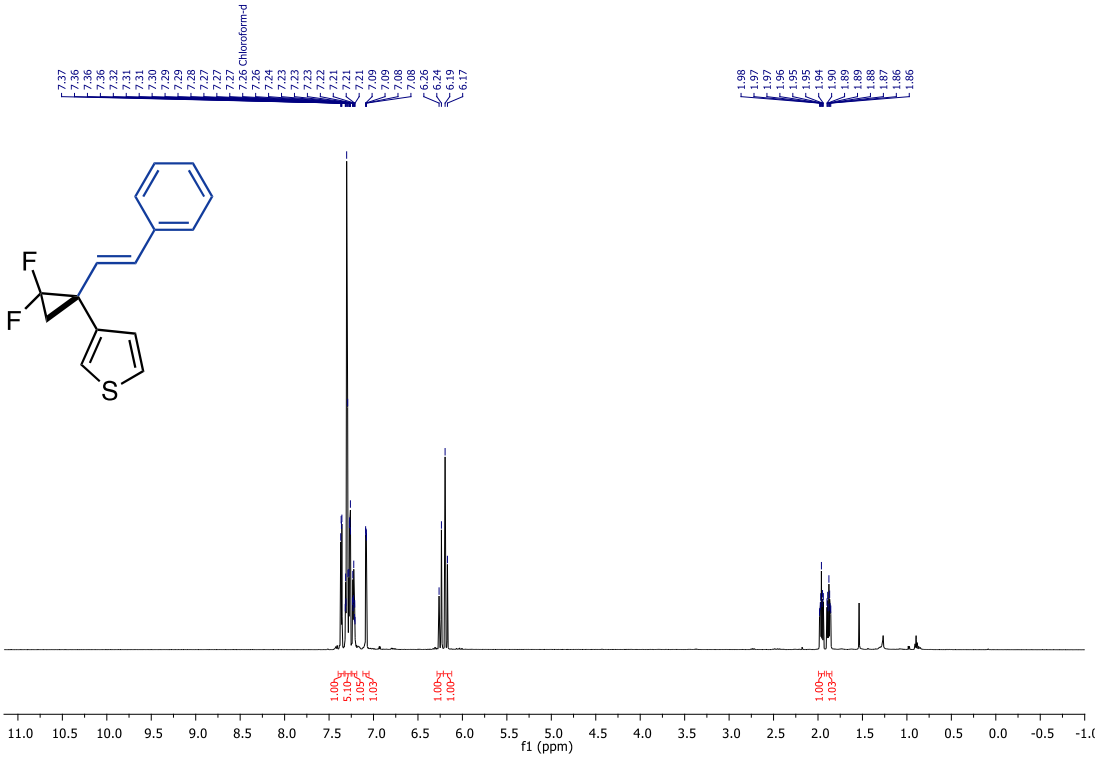
^{13}C NMR (151 MHz, $CDCl_3$) of **3b**



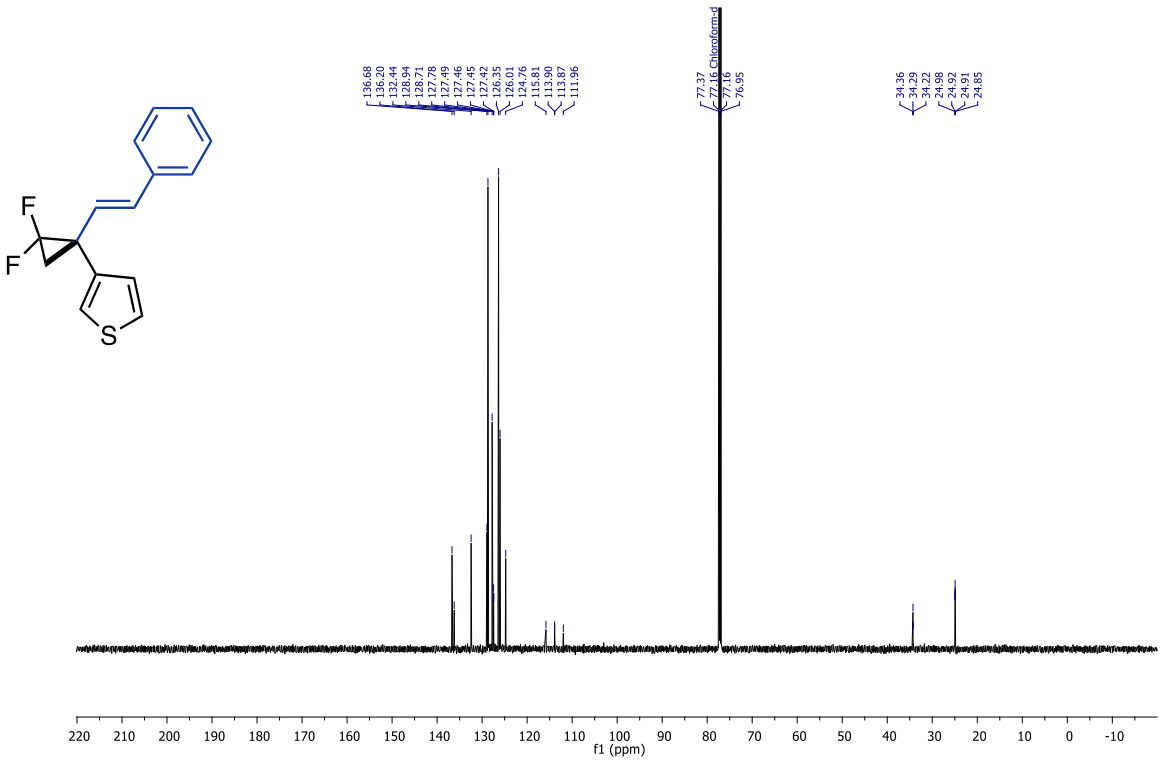
^{19}F NMR (565 MHz, $CDCl_3$) of **3b**



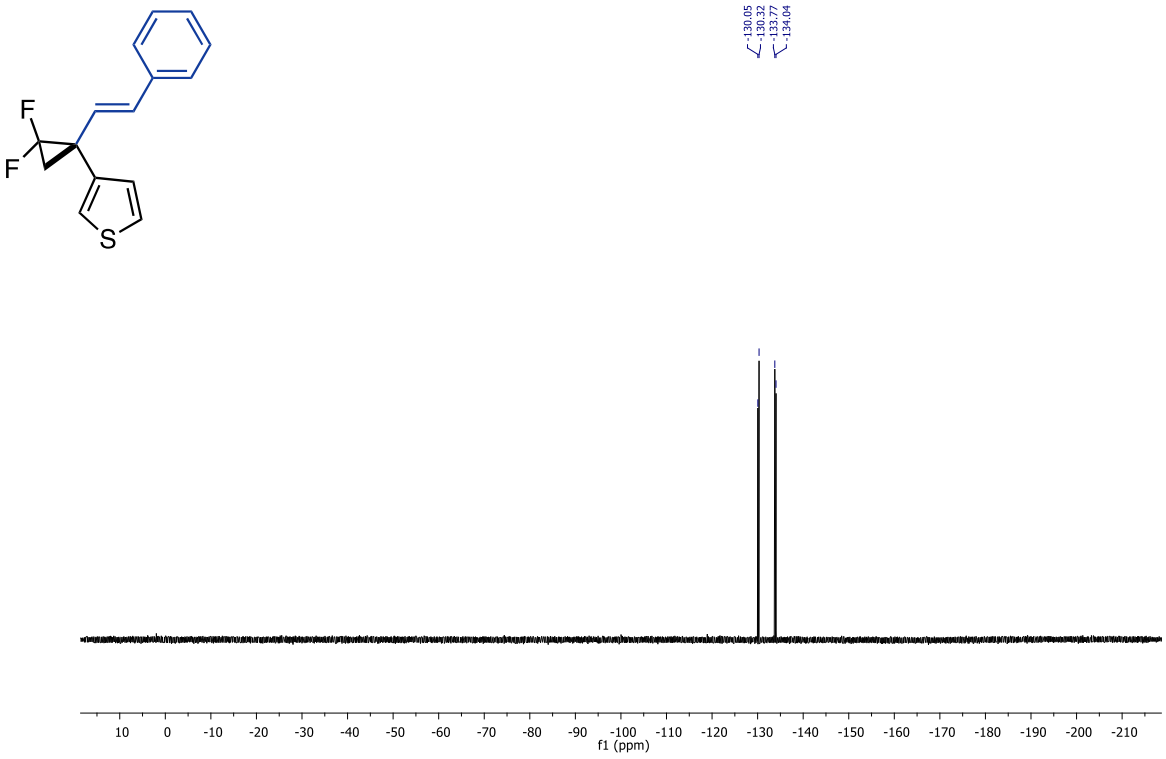
^{1}H NMR (600 MHz, $CDCl_3$) of **3c**



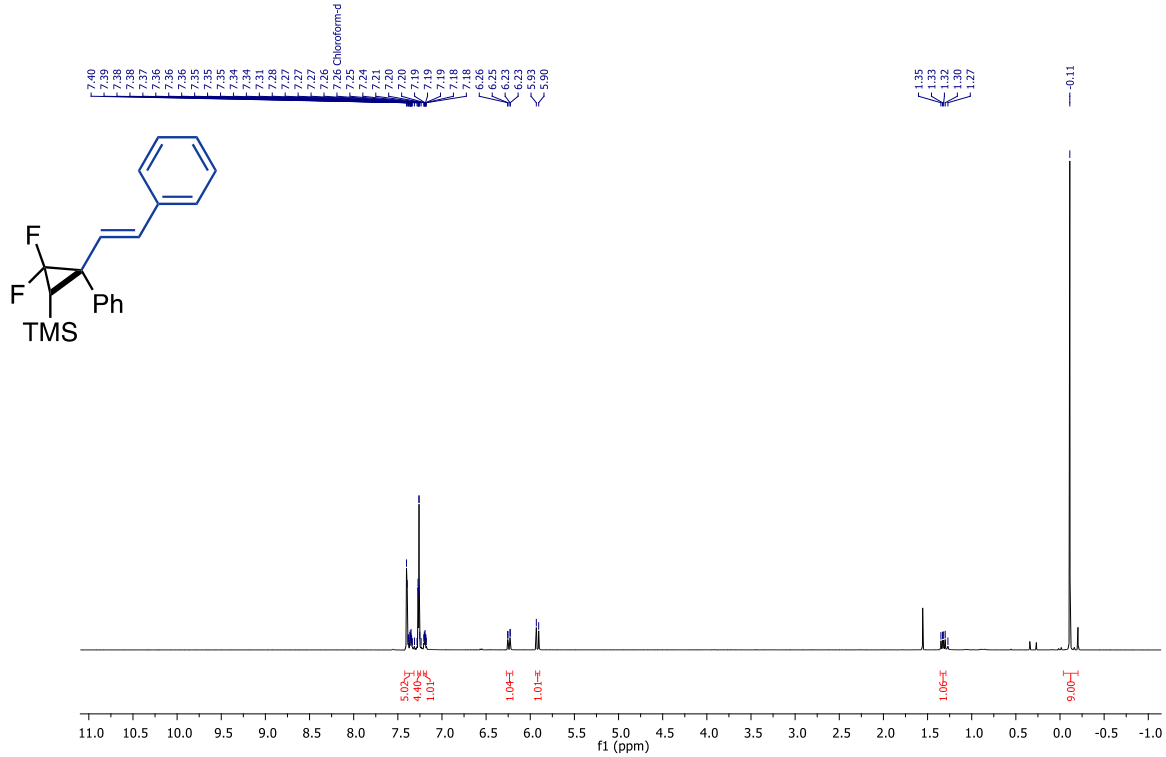
^{13}C NMR (151 MHz, $CDCl_3$) of **3c**



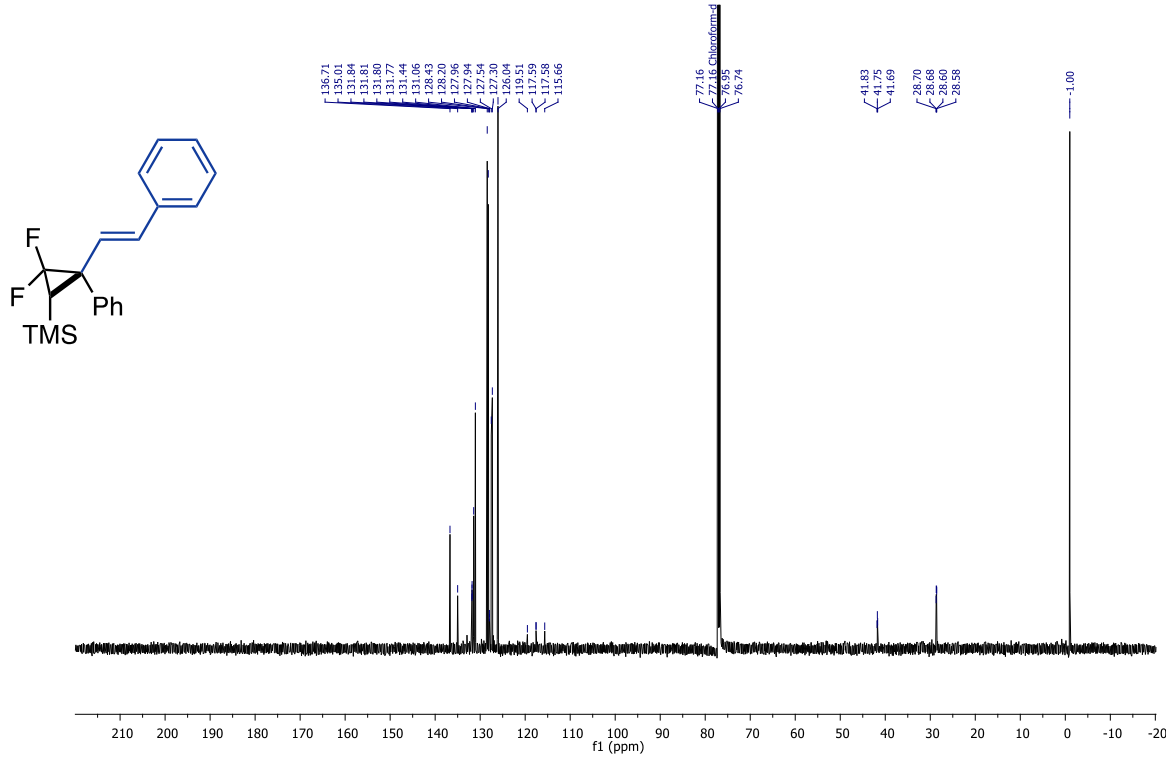
^{19}F NMR (565 MHz, $CDCl_3$) of **3c**



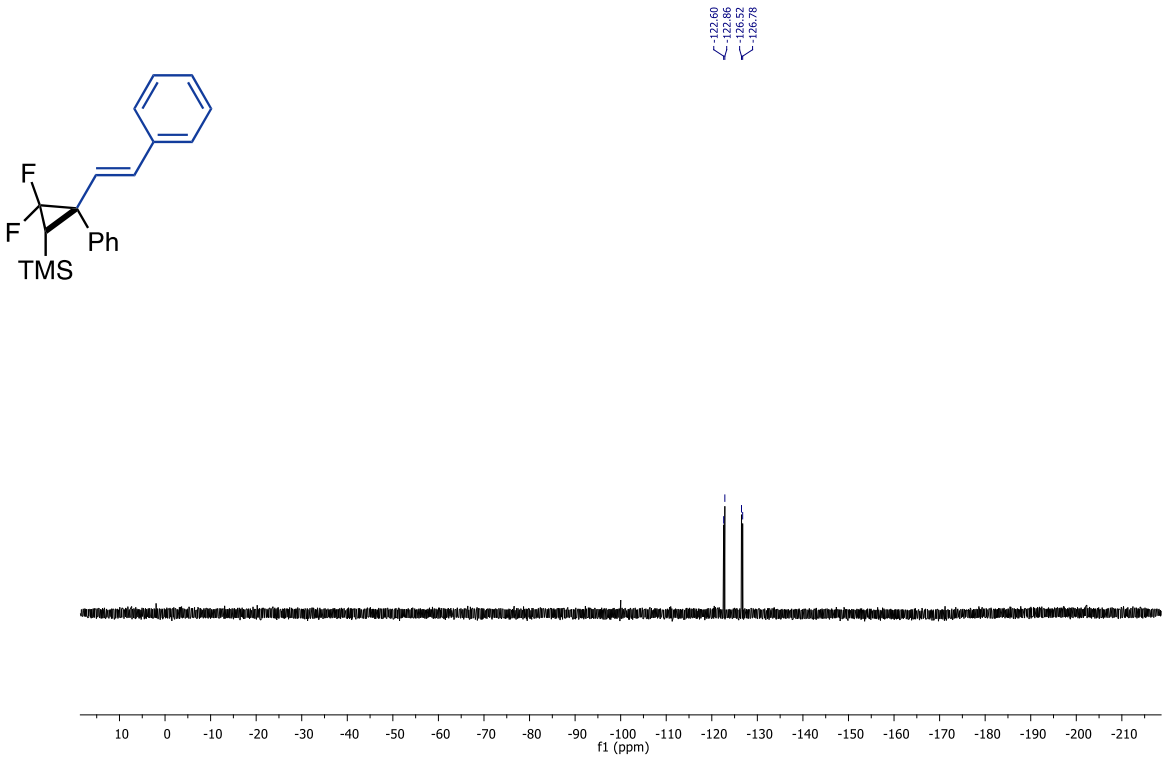
^{1}H NMR (600 MHz, $CDCl_3$) of **3d**



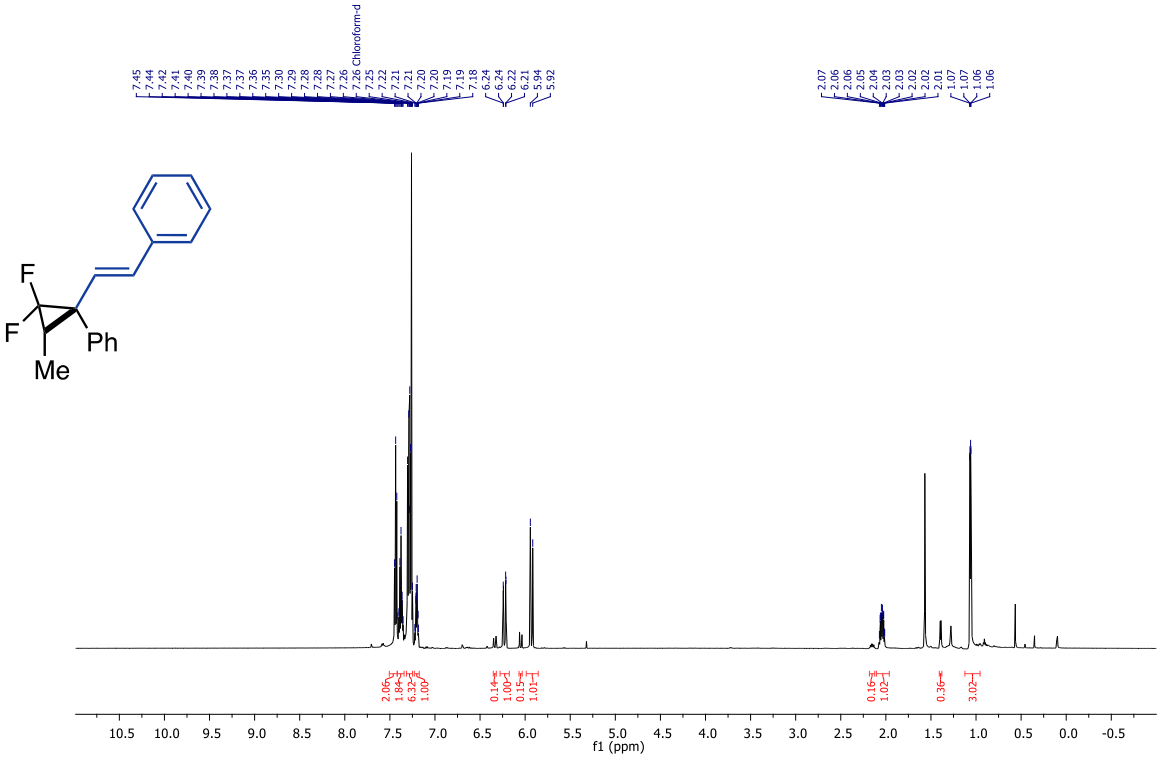
^{13}C NMR (151 MHz, $CDCl_3$) of **3d**



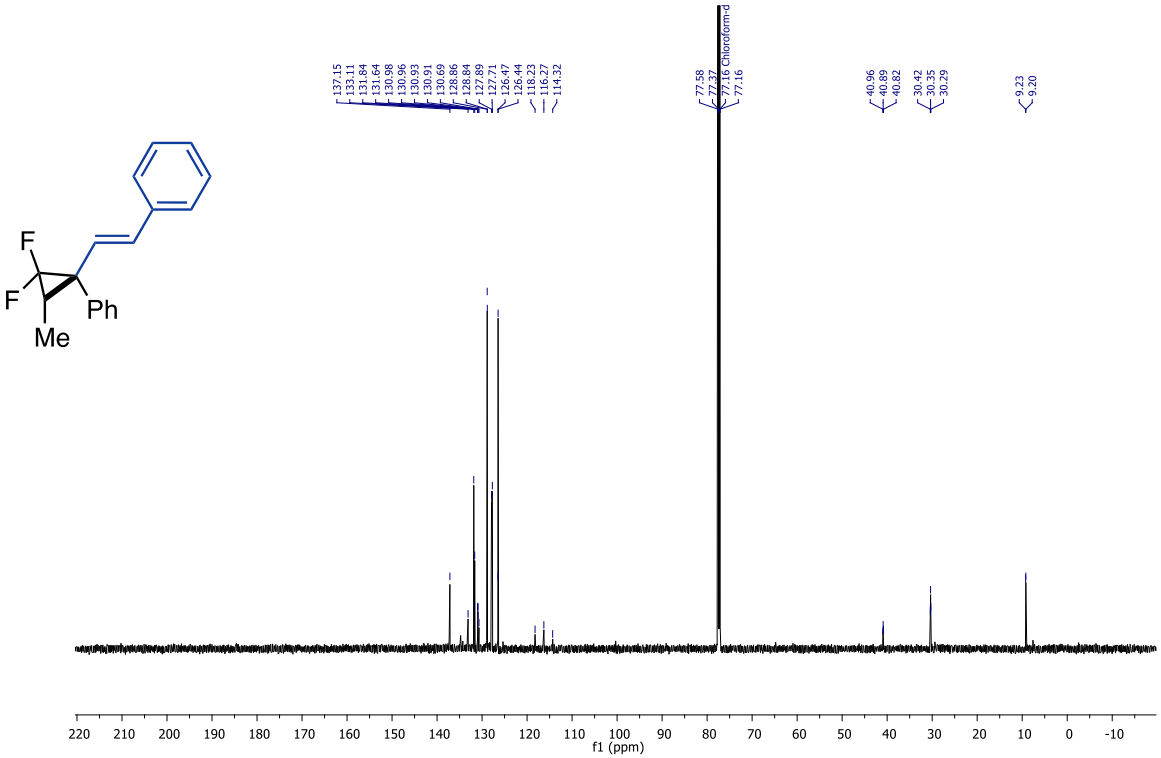
^{19}F NMR (565 MHz, $CDCl_3$) of **3d**



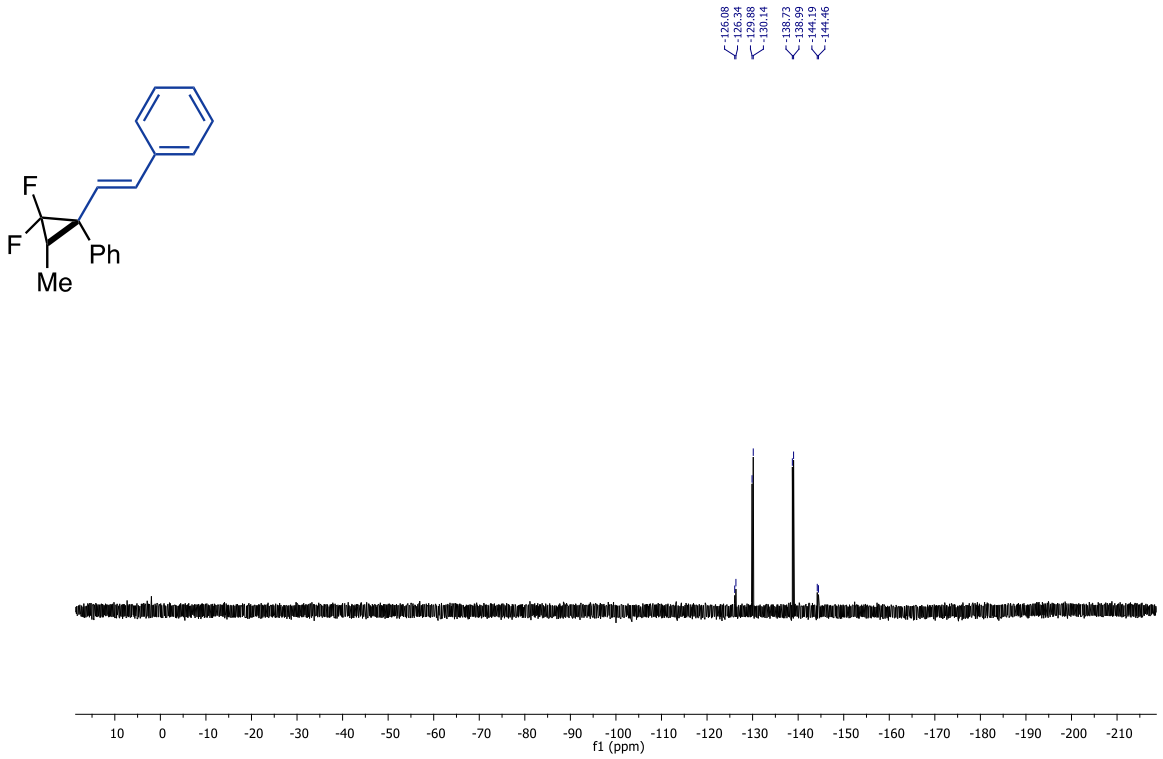
^{1}H NMR (600 MHz, $CDCl_3$) of **3e**



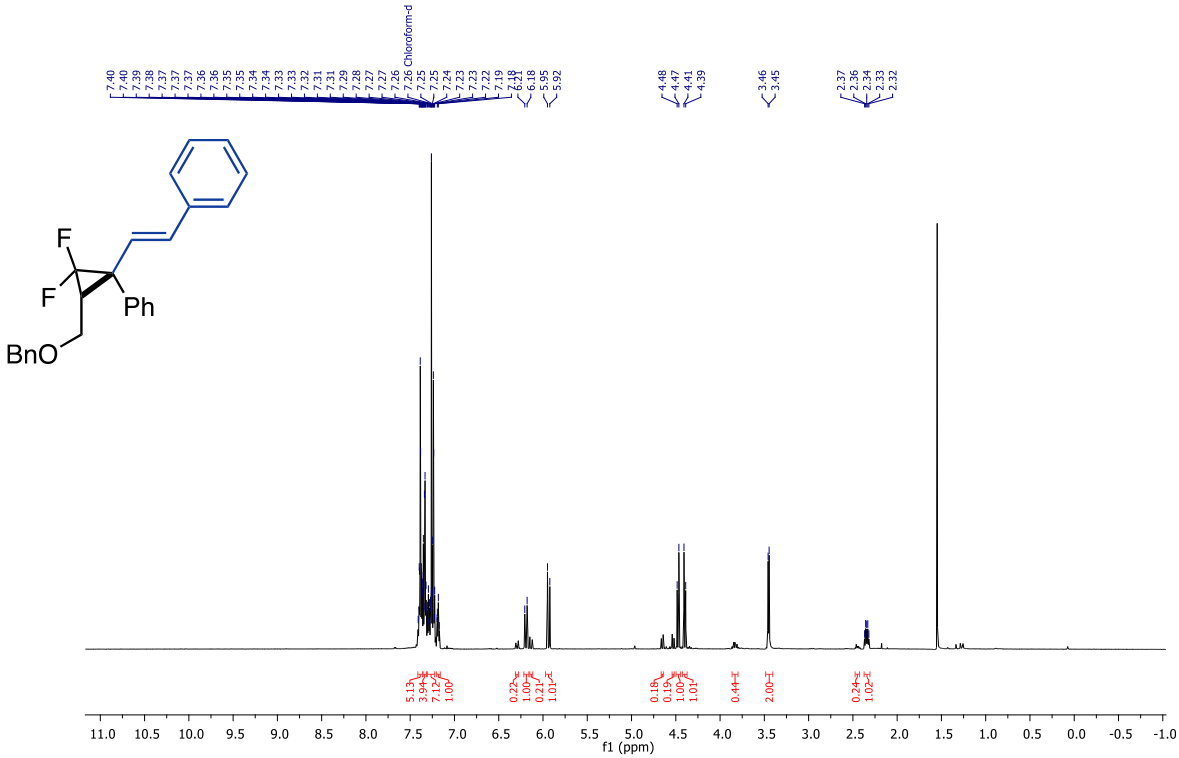
^{13}C NMR (151 MHz, $CDCl_3$) of **3e**



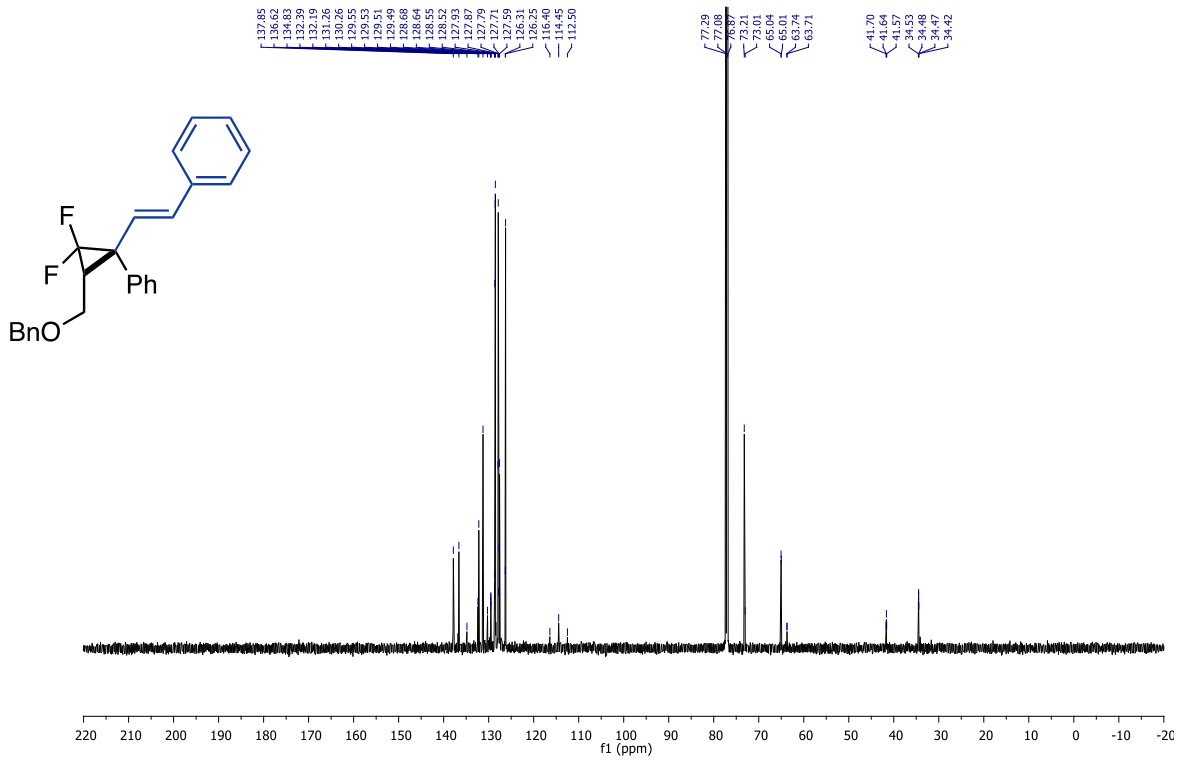
^{19}F NMR (565 MHz, $CDCl_3$) of **3e**



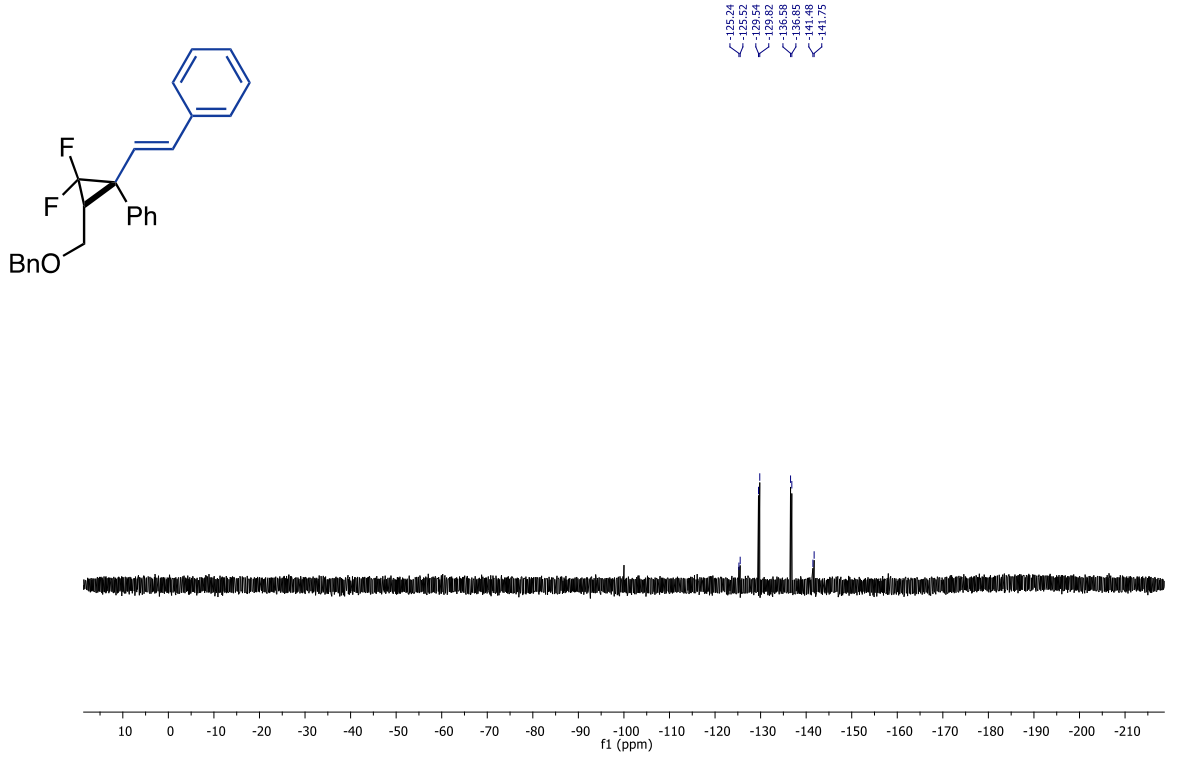
^{1}H NMR (600 MHz, $CDCl_3$) of **3f**



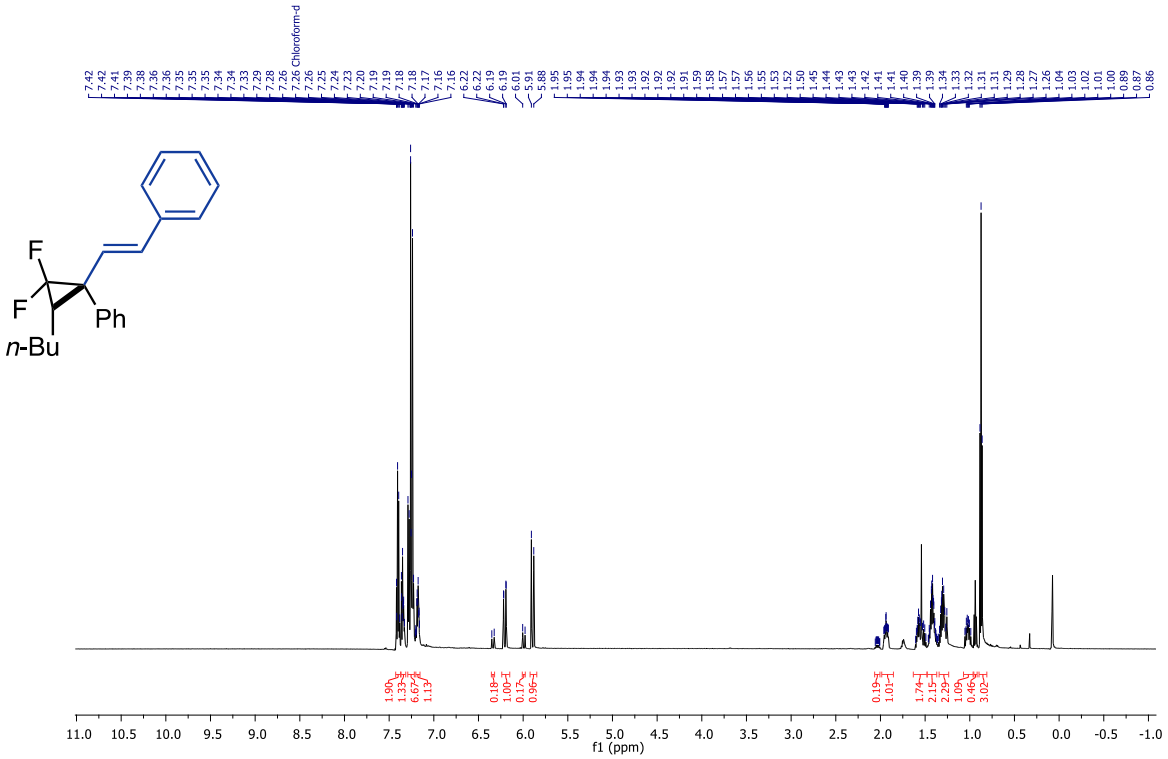
^{13}C NMR (151 MHz, $CDCl_3$) of **3f**



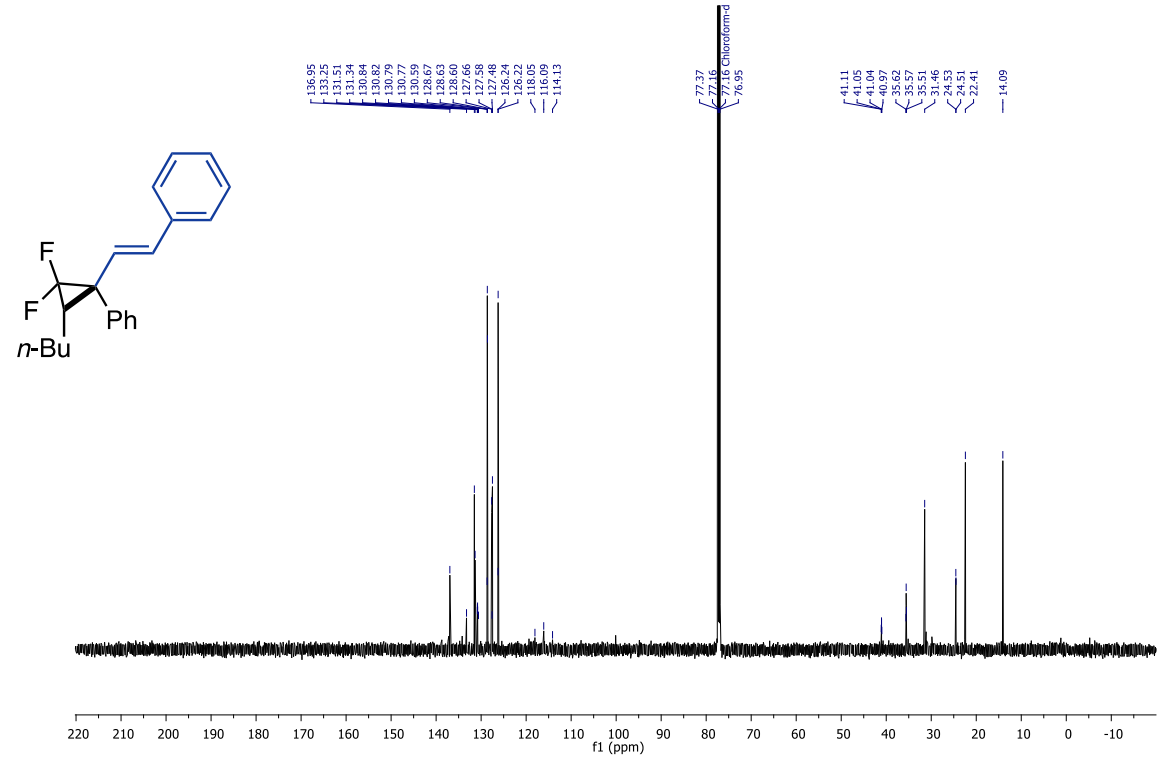
^{19}F NMR (565 MHz, $CDCl_3$) of **3f**



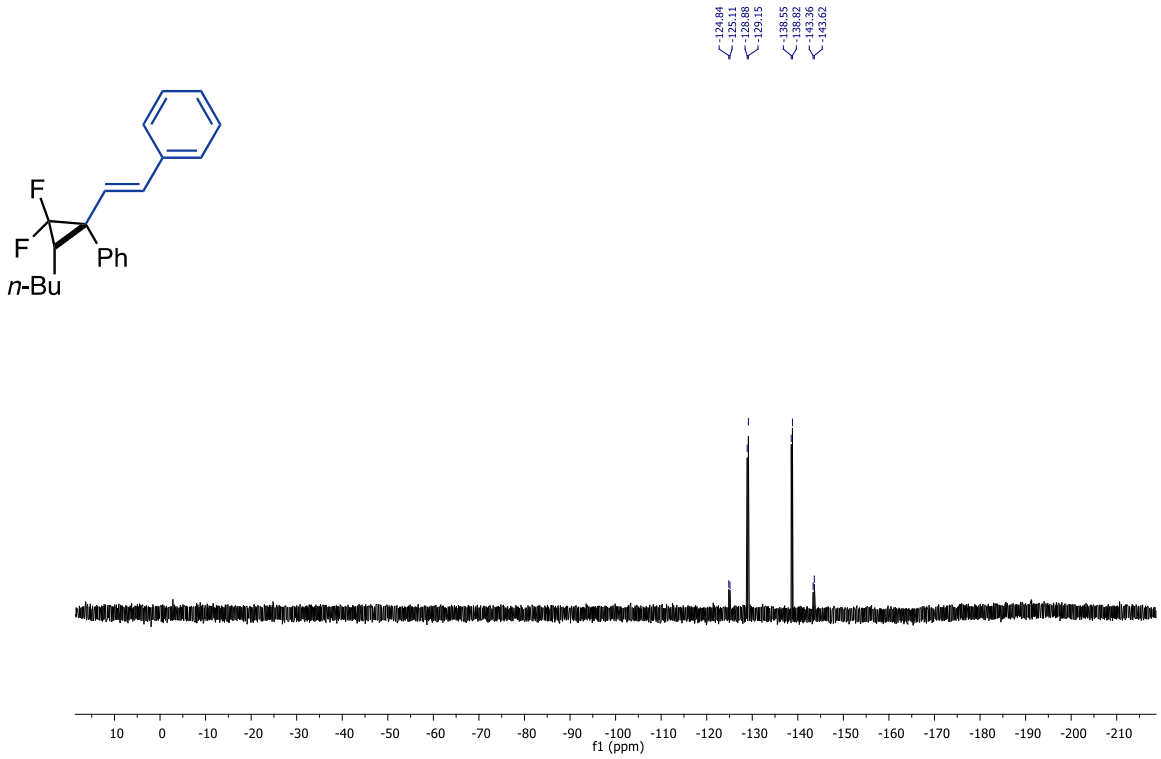
^{1}H NMR (600 MHz, $CDCl_3$) of **3g**



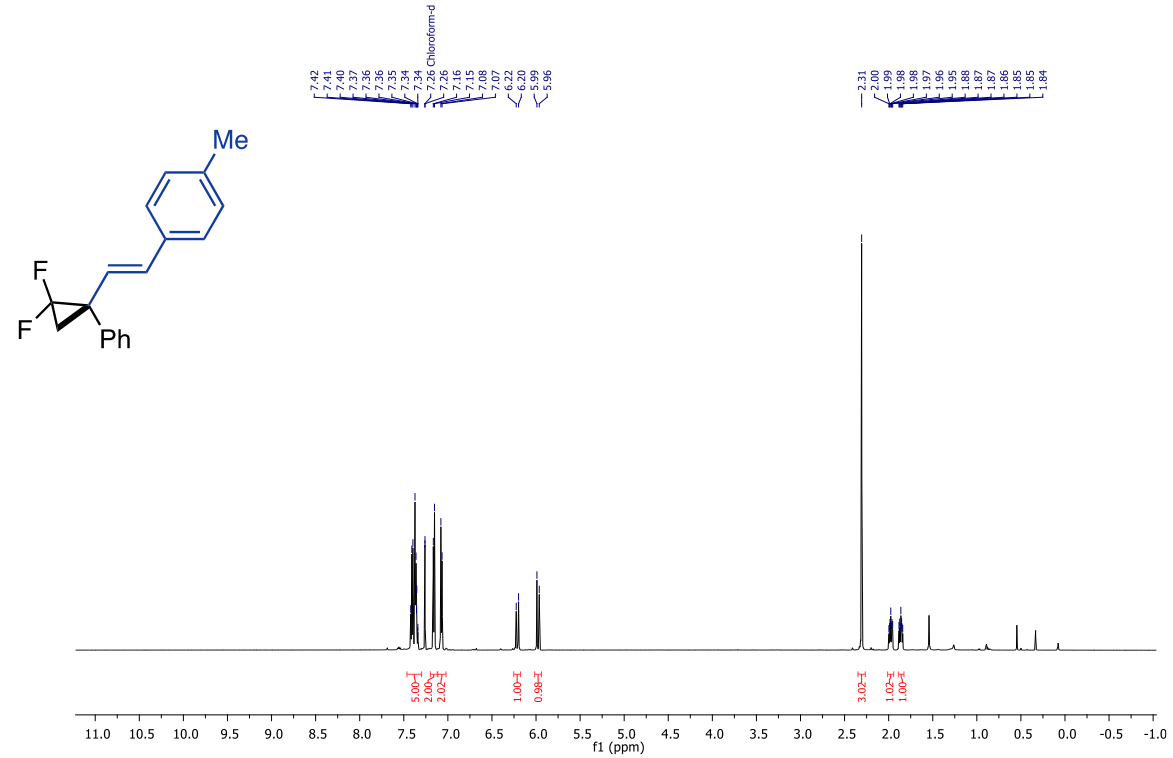
^{13}C NMR (151 MHz, $CDCl_3$) of **3g**



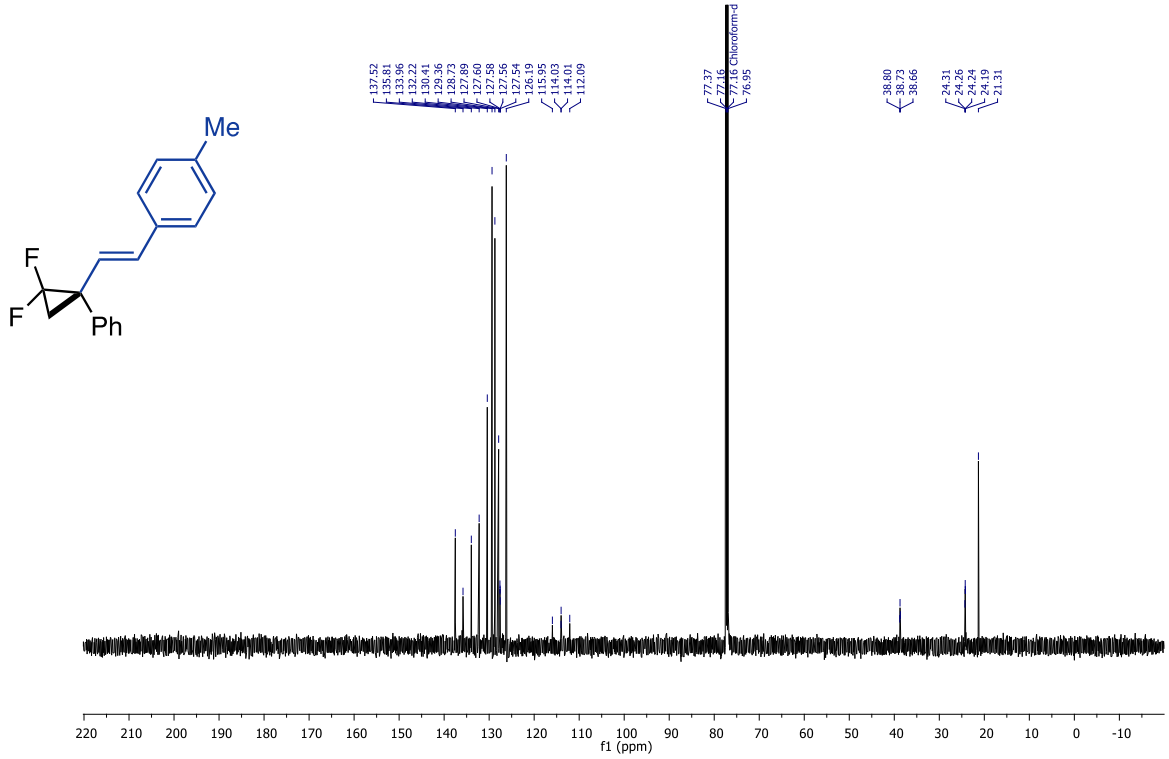
^{19}F NMR (565 MHz, $CDCl_3$) of **3g**



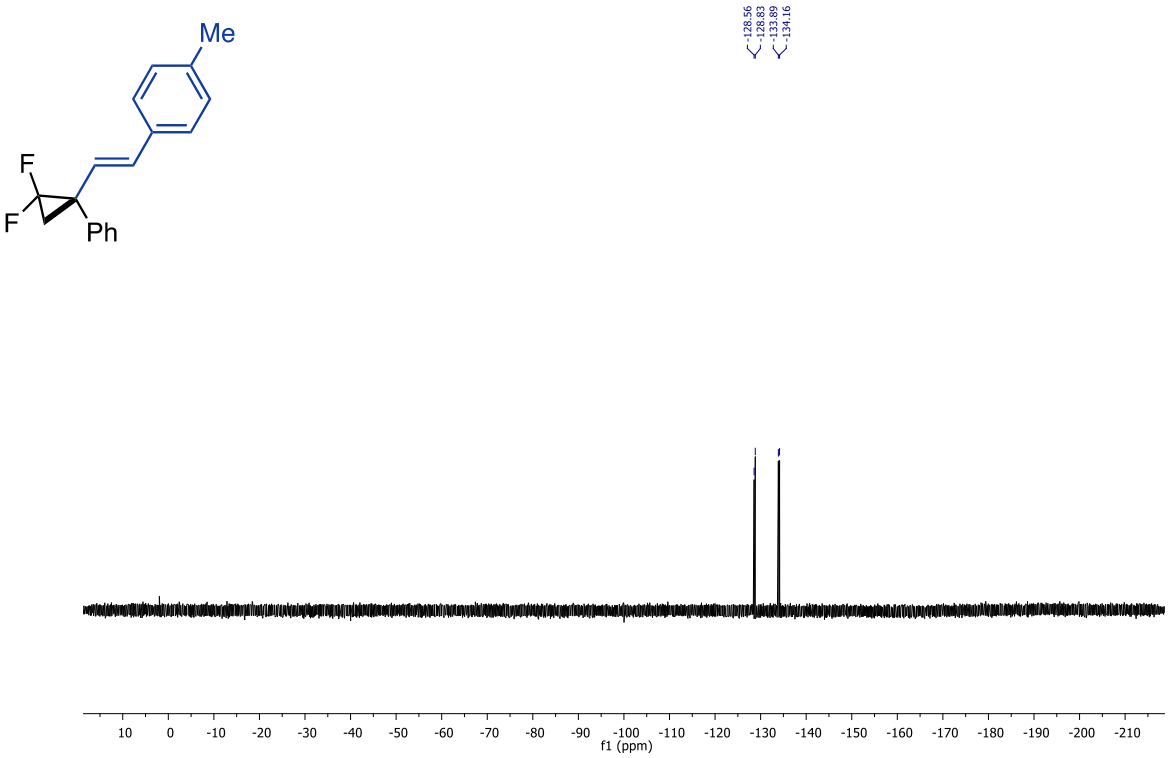
^{1}H NMR (600 MHz, $CDCl_3$) of **3h**



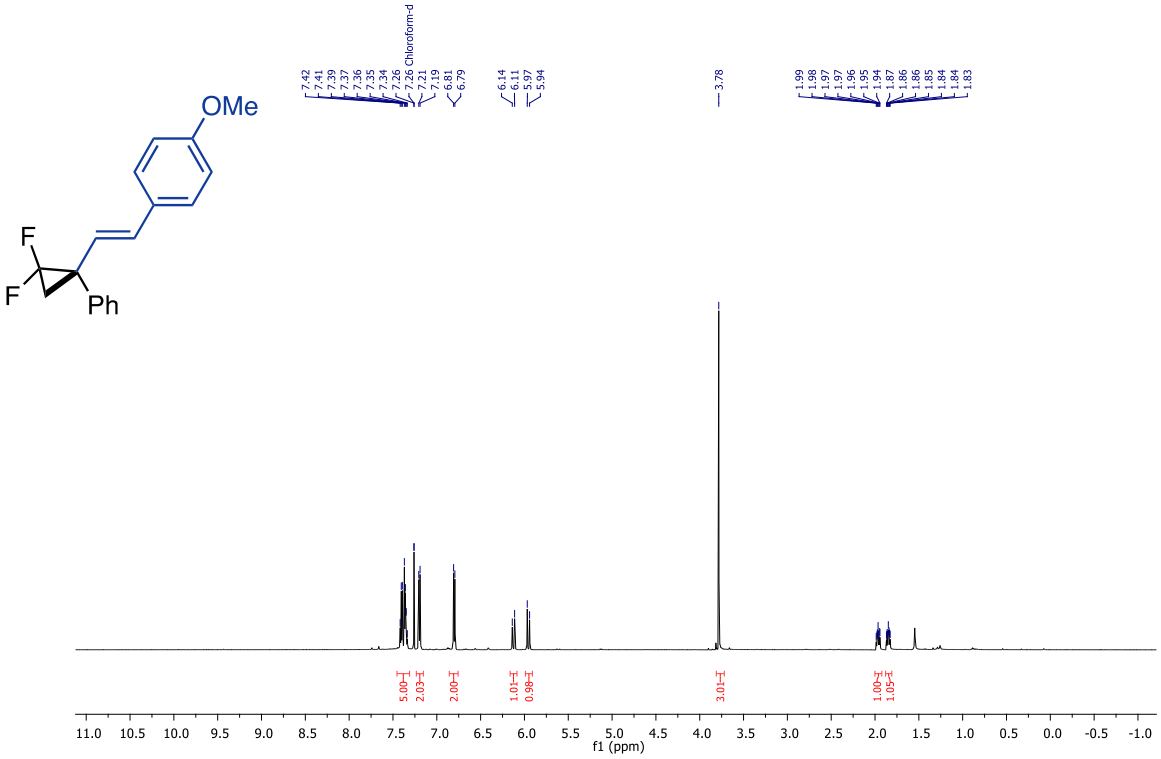
^{13}C NMR (151 MHz, $CDCl_3$) of **3h**



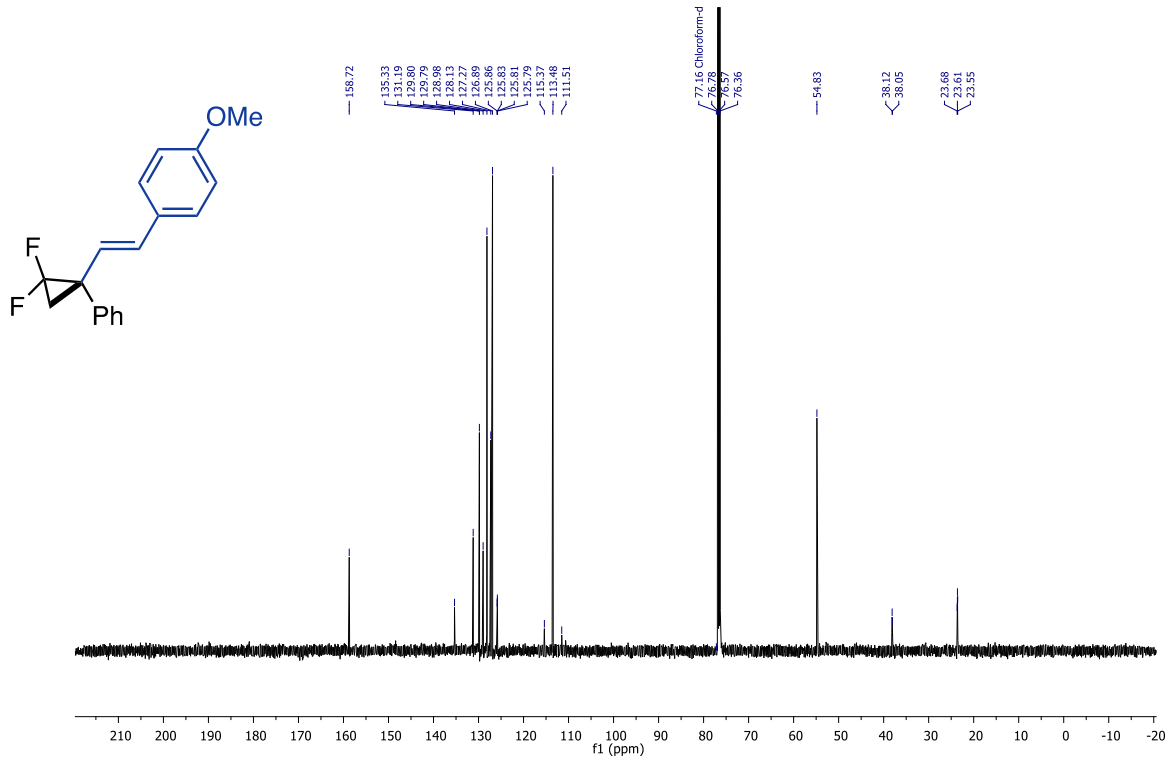
^{19}F NMR (565 MHz, $CDCl_3$) of **3h**



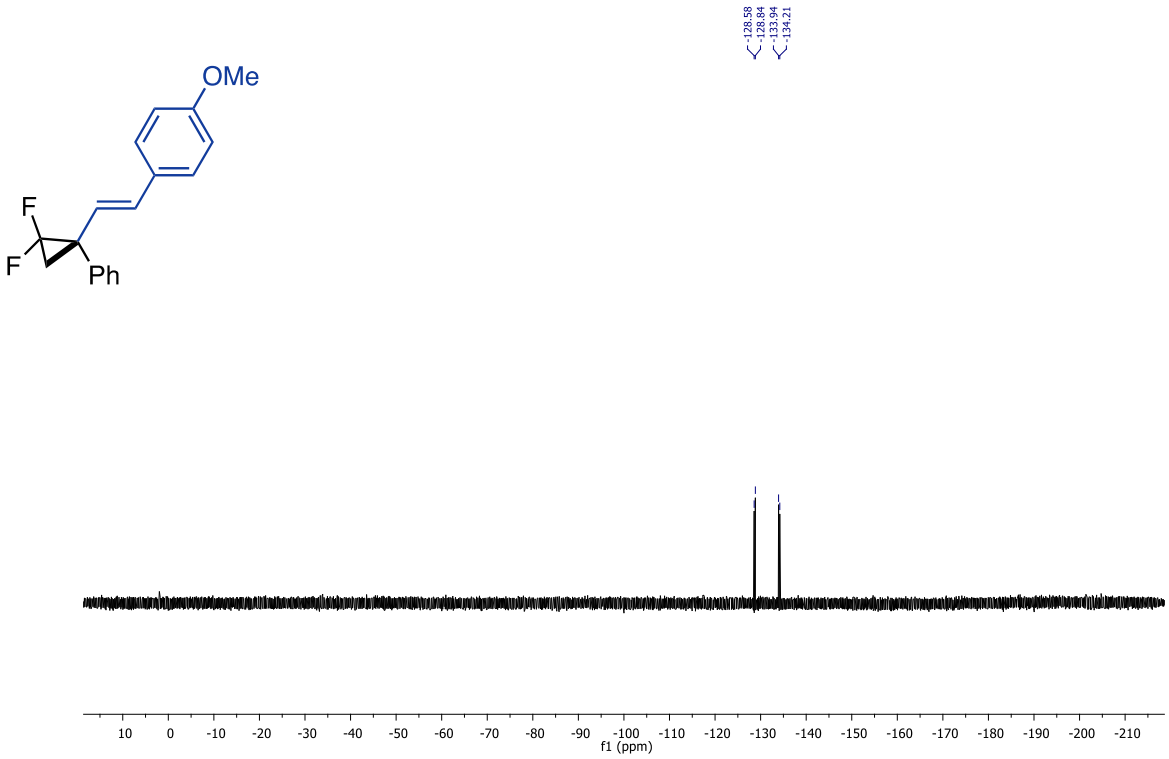
^{1}H NMR (600 MHz, $CDCl_3$) of **3i**



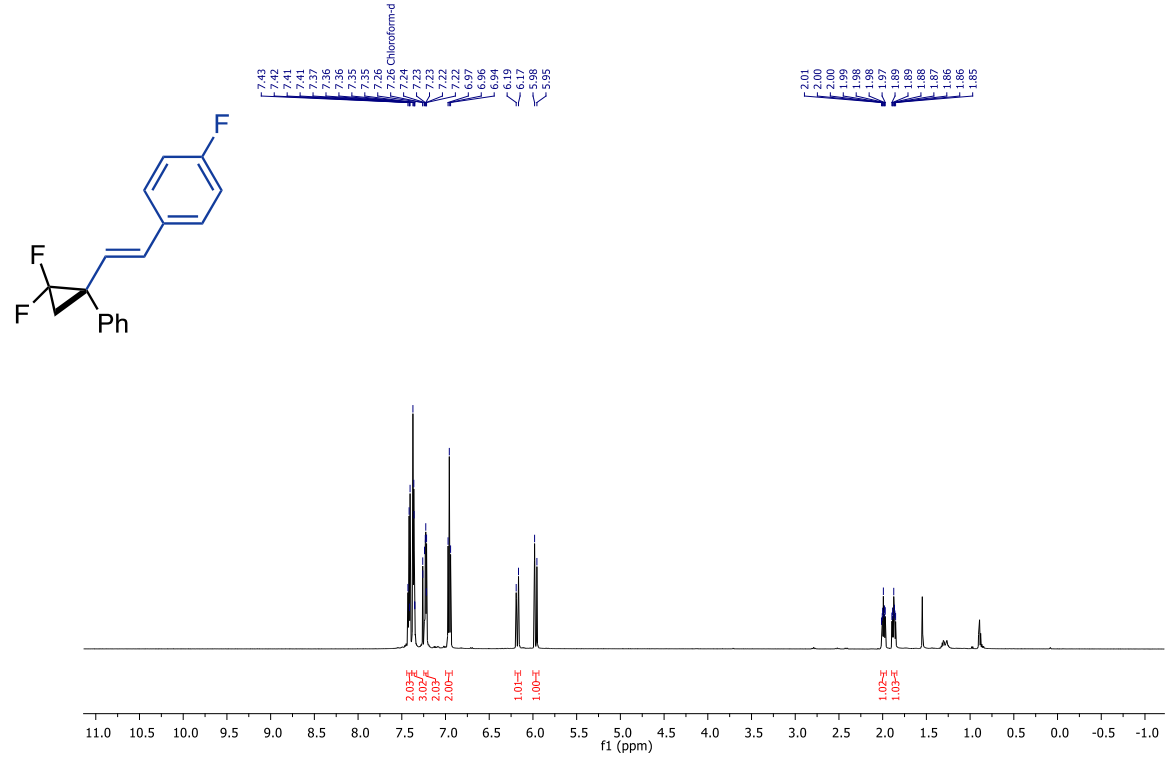
^{13}C NMR (151 MHz, $CDCl_3$) of **3i**



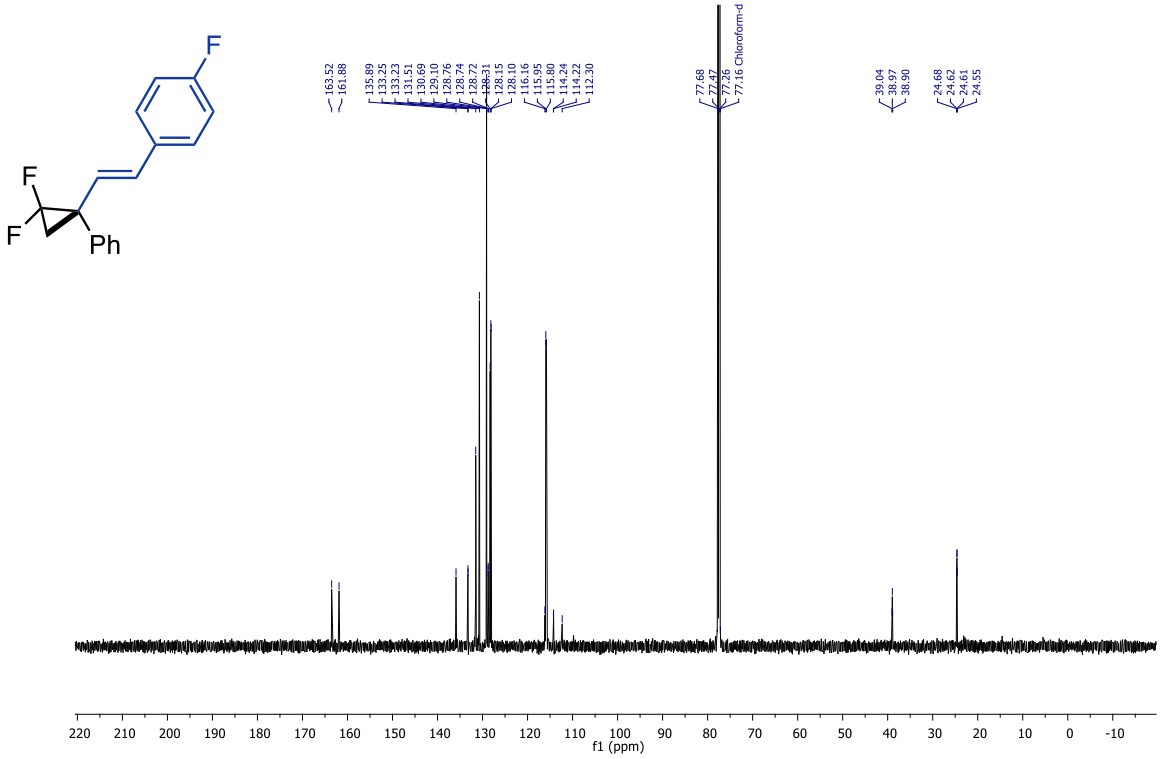
^{19}F NMR (565 MHz, $CDCl_3$) of **3i**



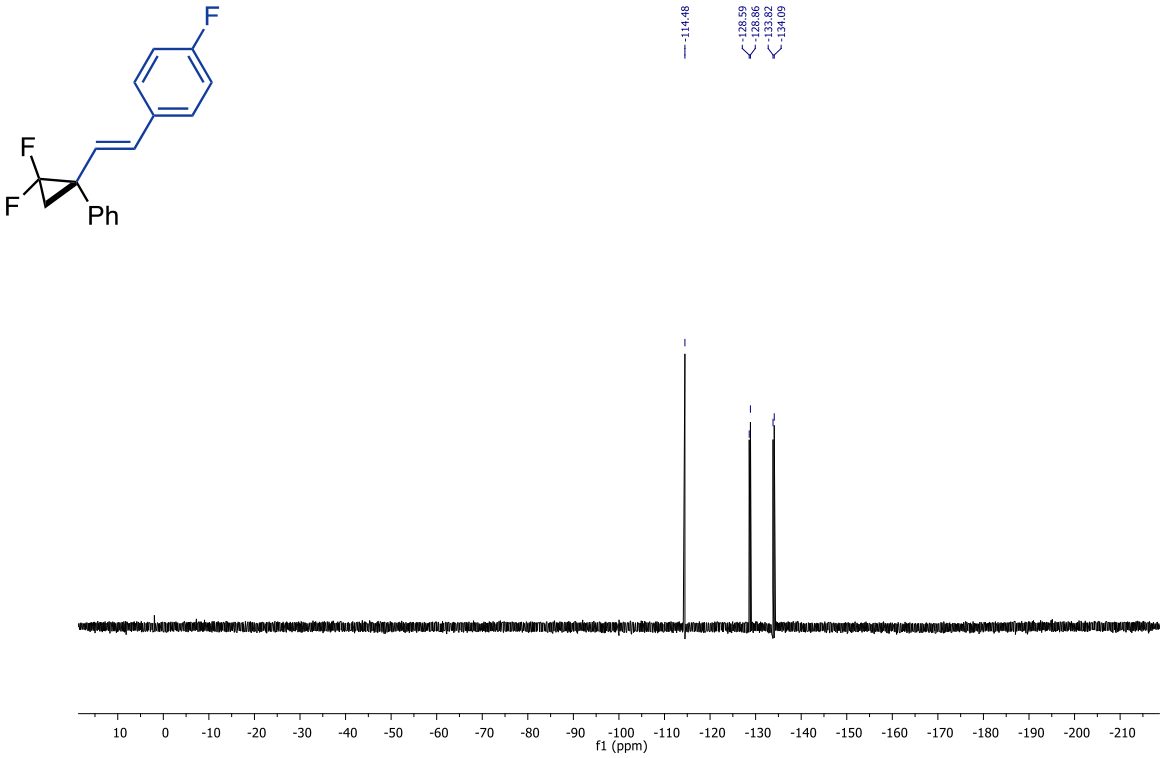
^{1}H NMR (600 MHz, $CDCl_3$) of **3j**



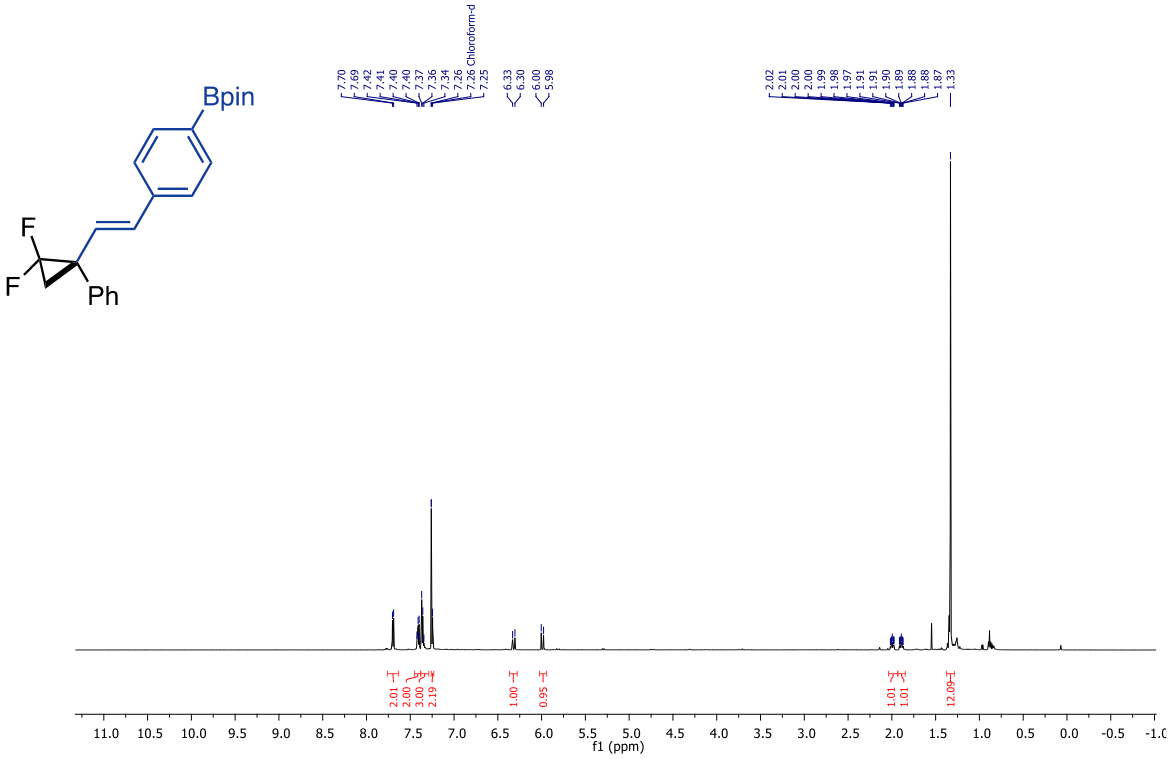
^{13}C NMR (151 MHz, $CDCl_3$) of **3j**



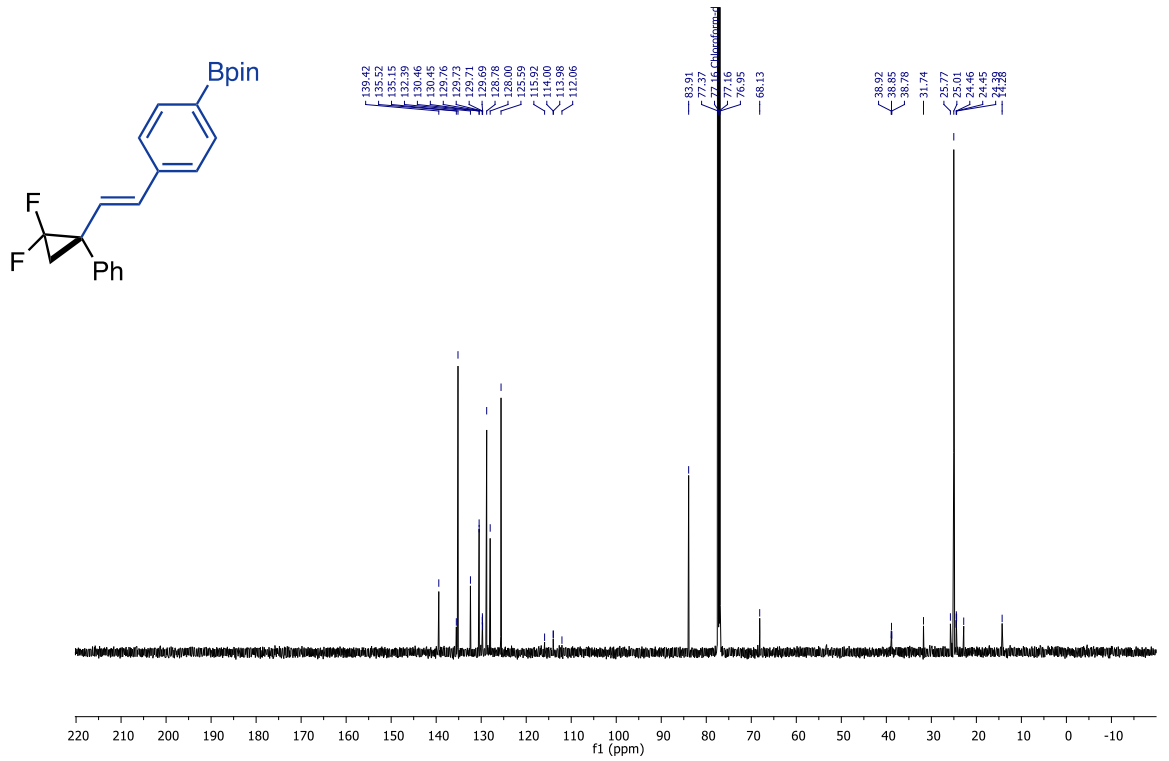
^{19}F NMR (565 MHz, $CDCl_3$) of **3j**



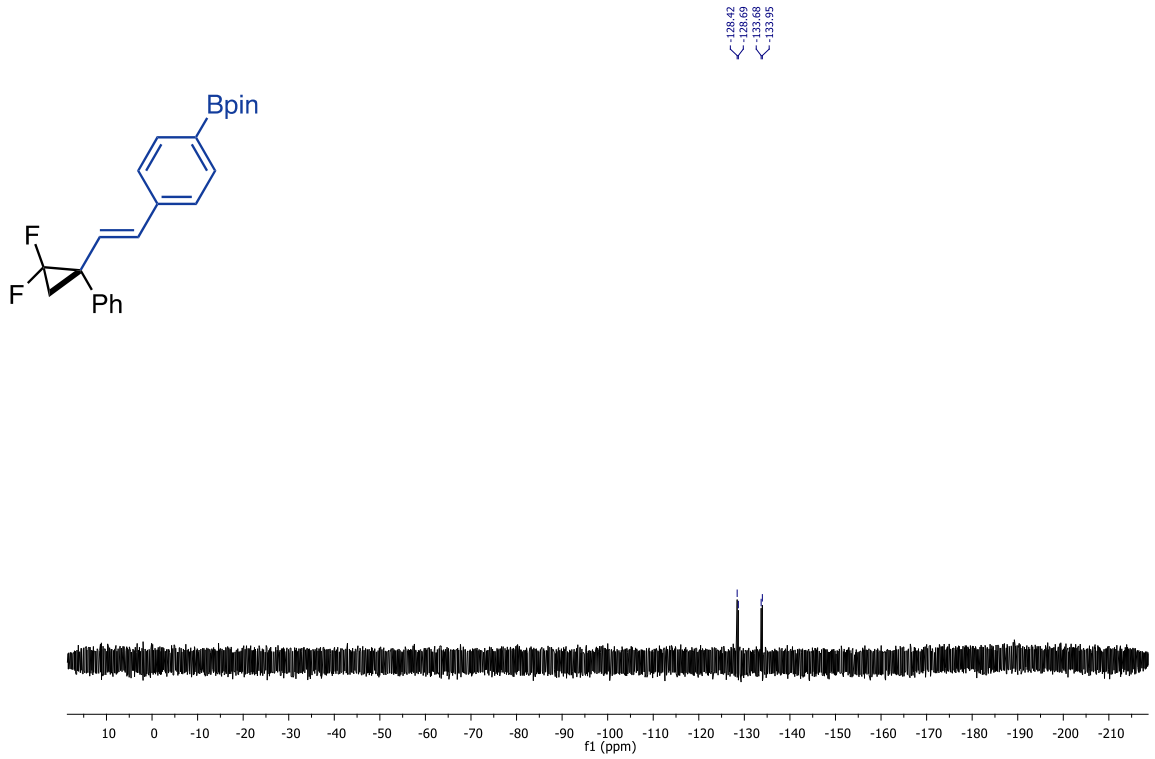
^{1}H NMR (600 MHz, $CDCl_3$) of **3k**



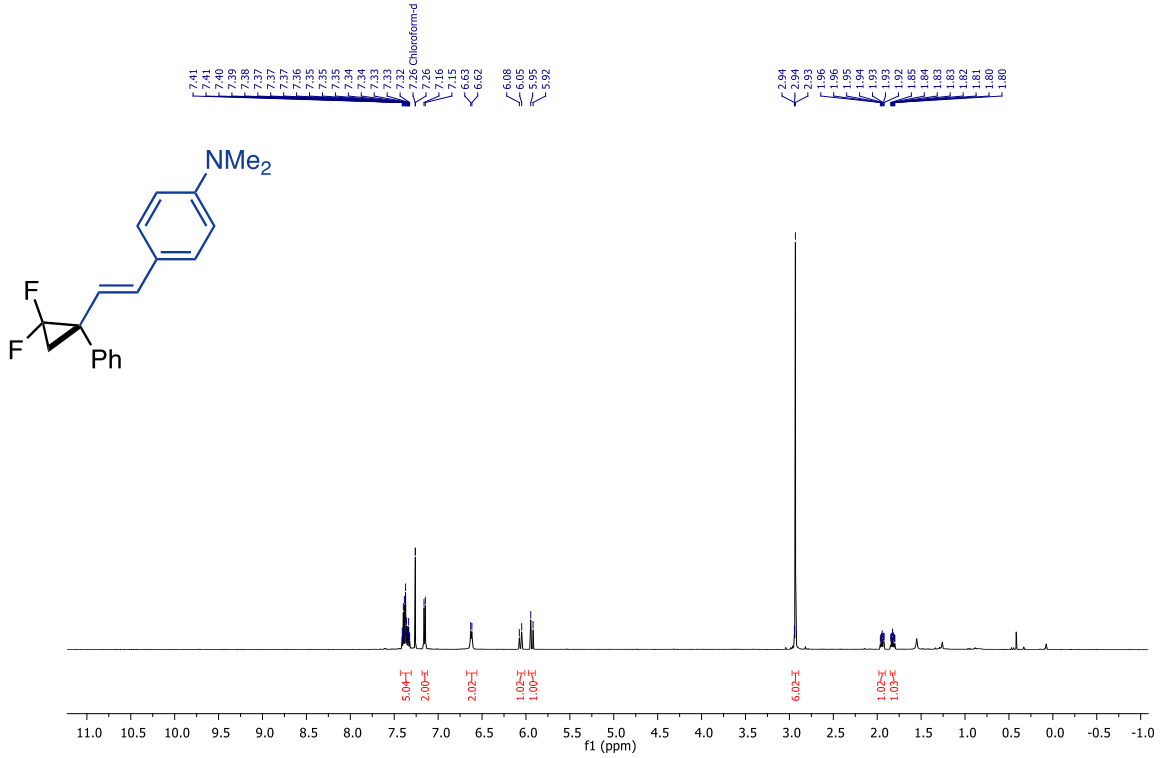
^{13}C NMR (151 MHz, $CDCl_3$) of **3k**



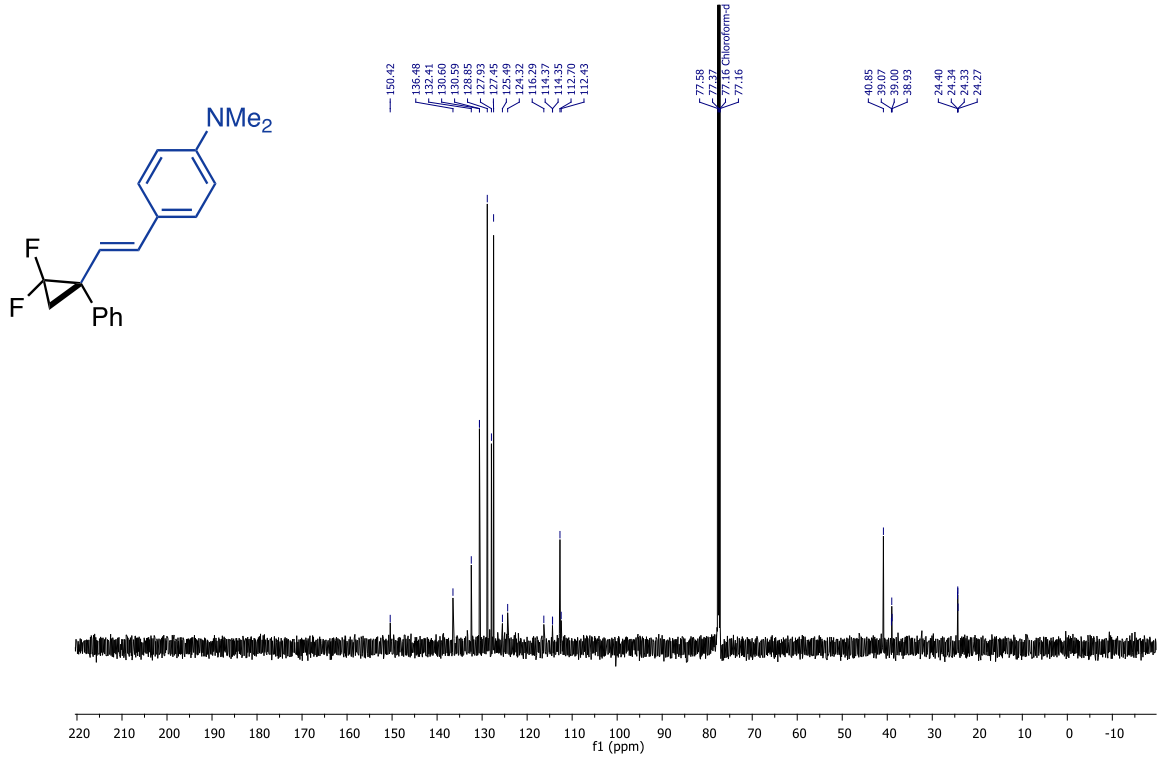
^{19}F NMR (565 MHz, $CDCl_3$) of **3k**



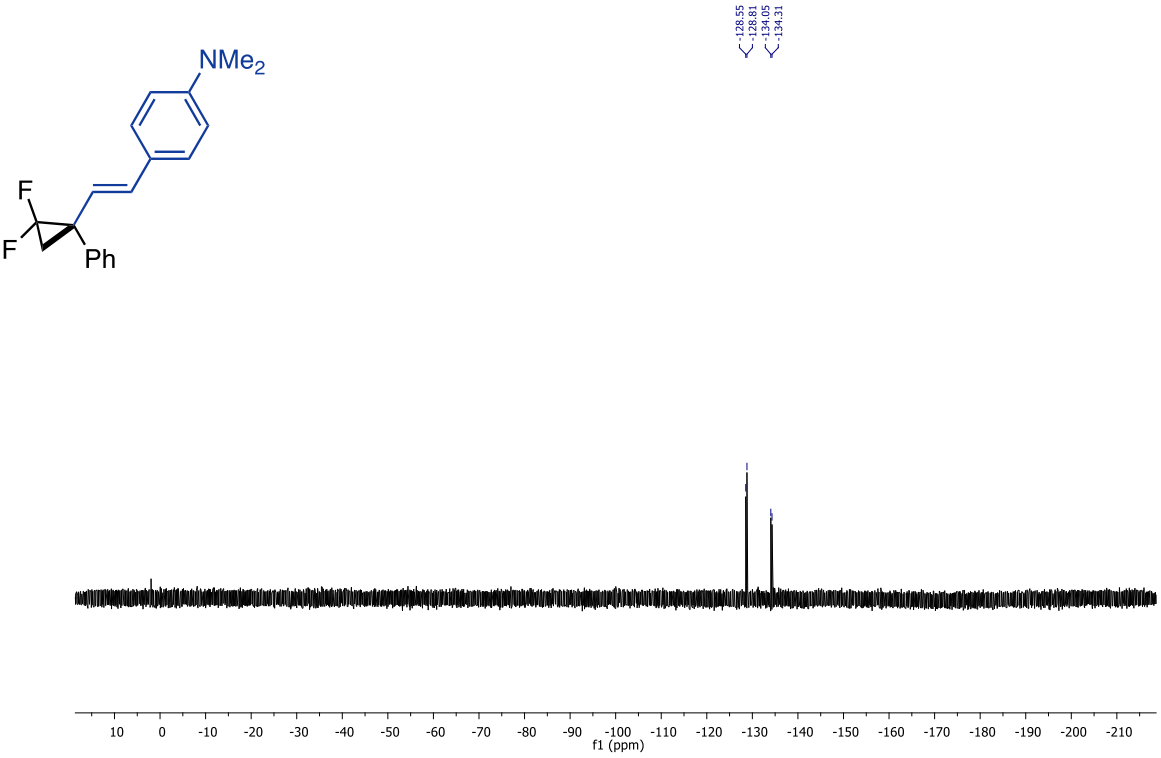
^{1}H NMR (600 MHz, $CDCl_3$) of **3l**



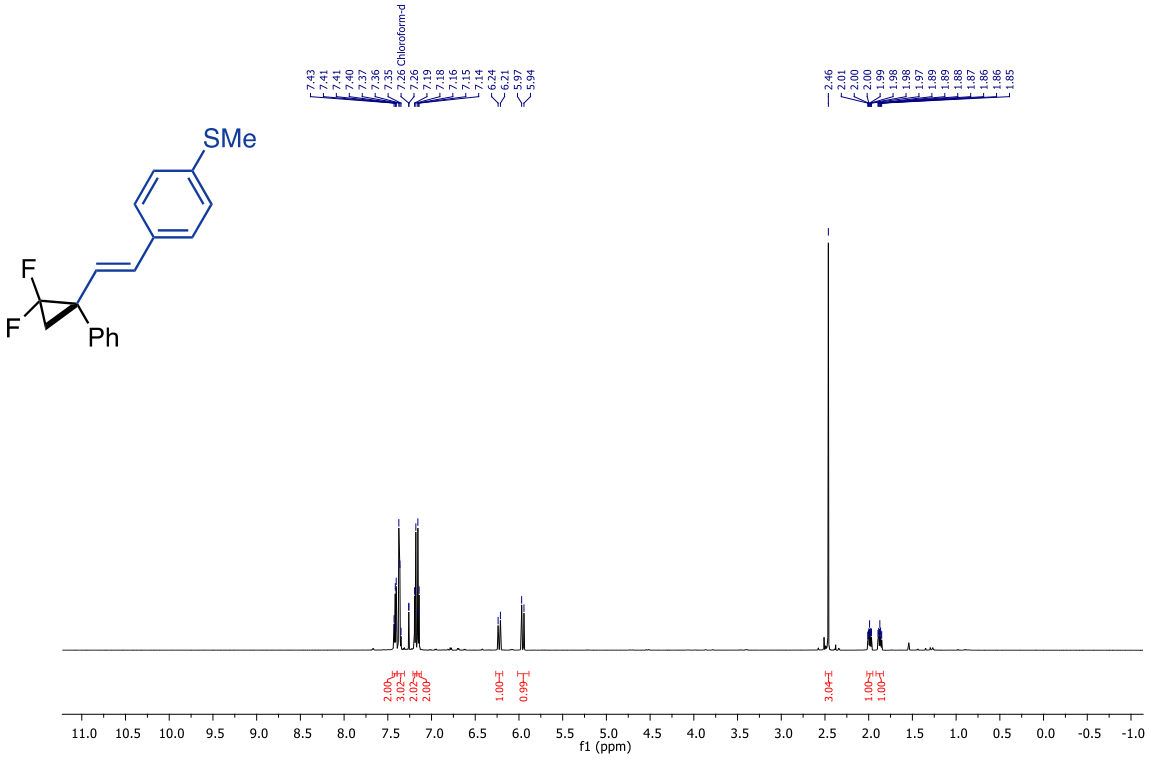
^{13}C NMR (151 MHz, $CDCl_3$) of **3l**



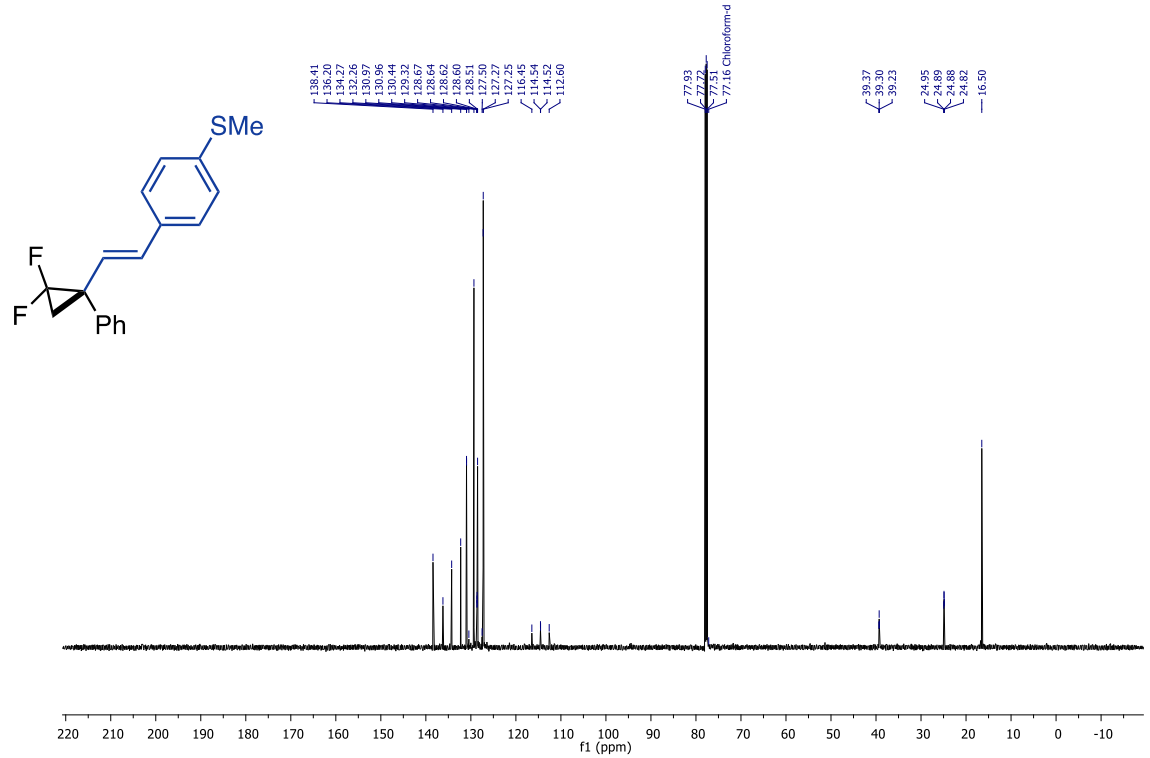
^{19}F NMR (565 MHz, $CDCl_3$) of **3l**



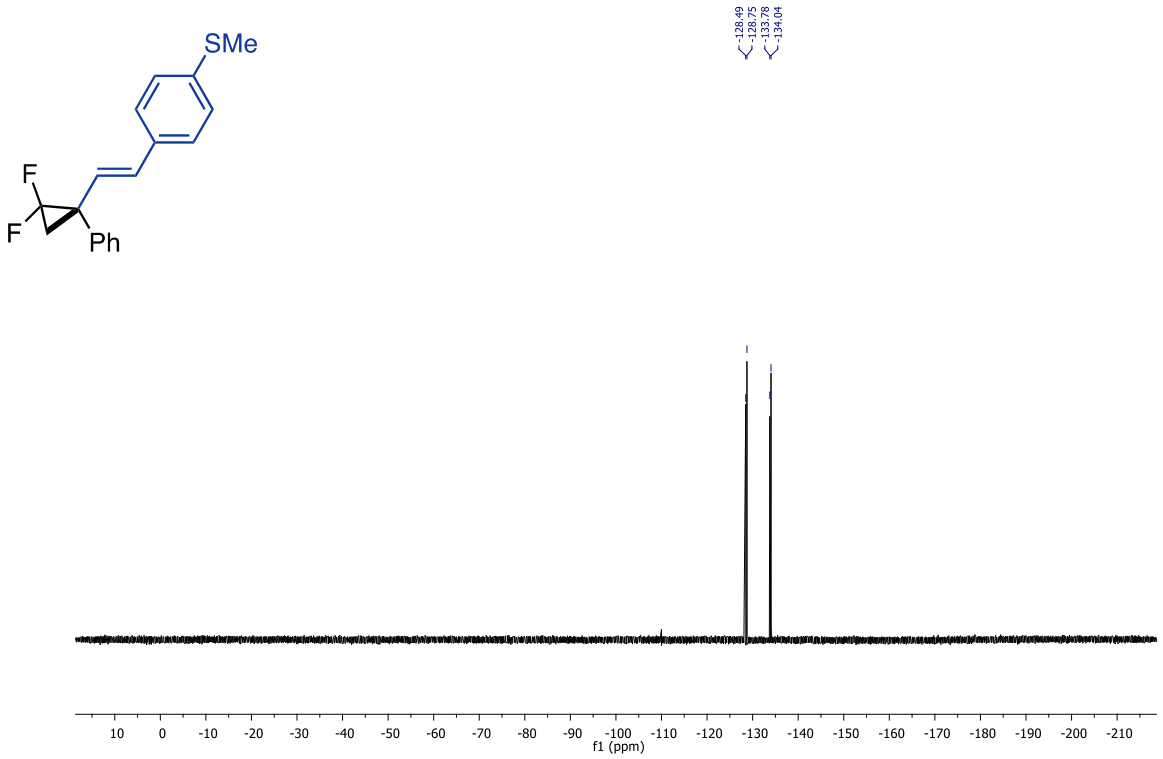
^{1}H NMR (600 MHz, $CDCl_3$) of **3m**



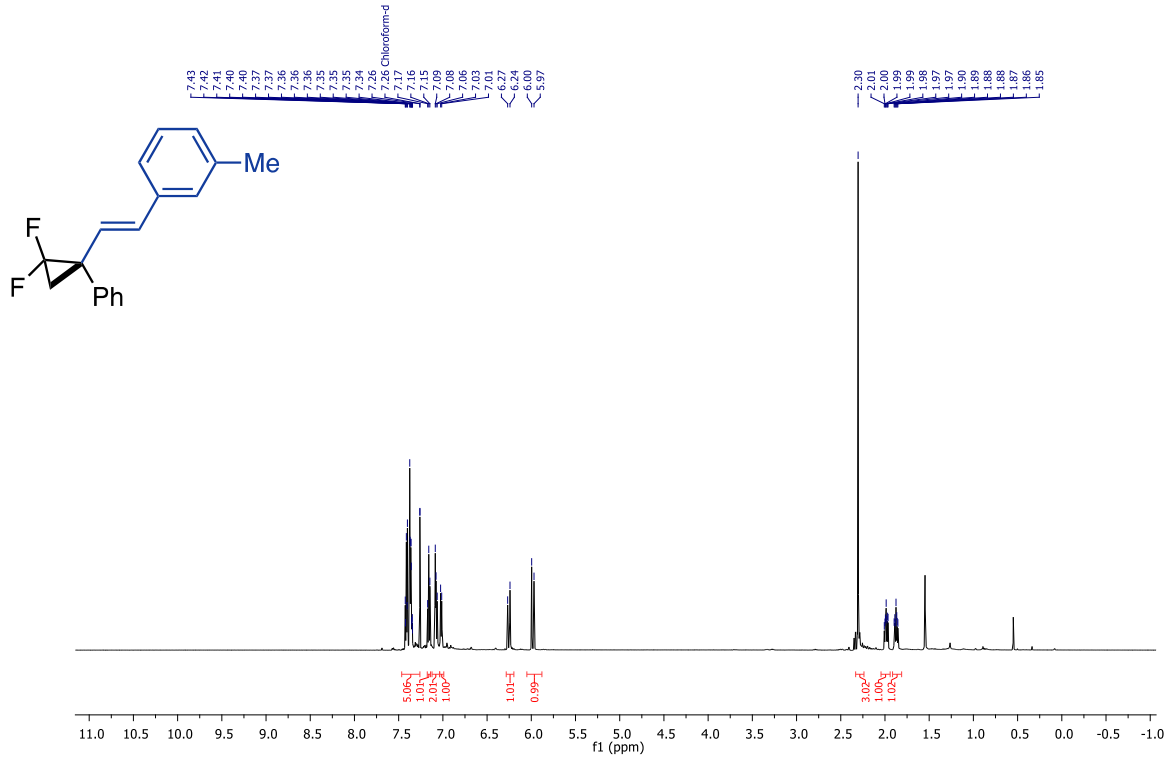
^{13}C NMR (151 MHz, $CDCl_3$) of **3m**



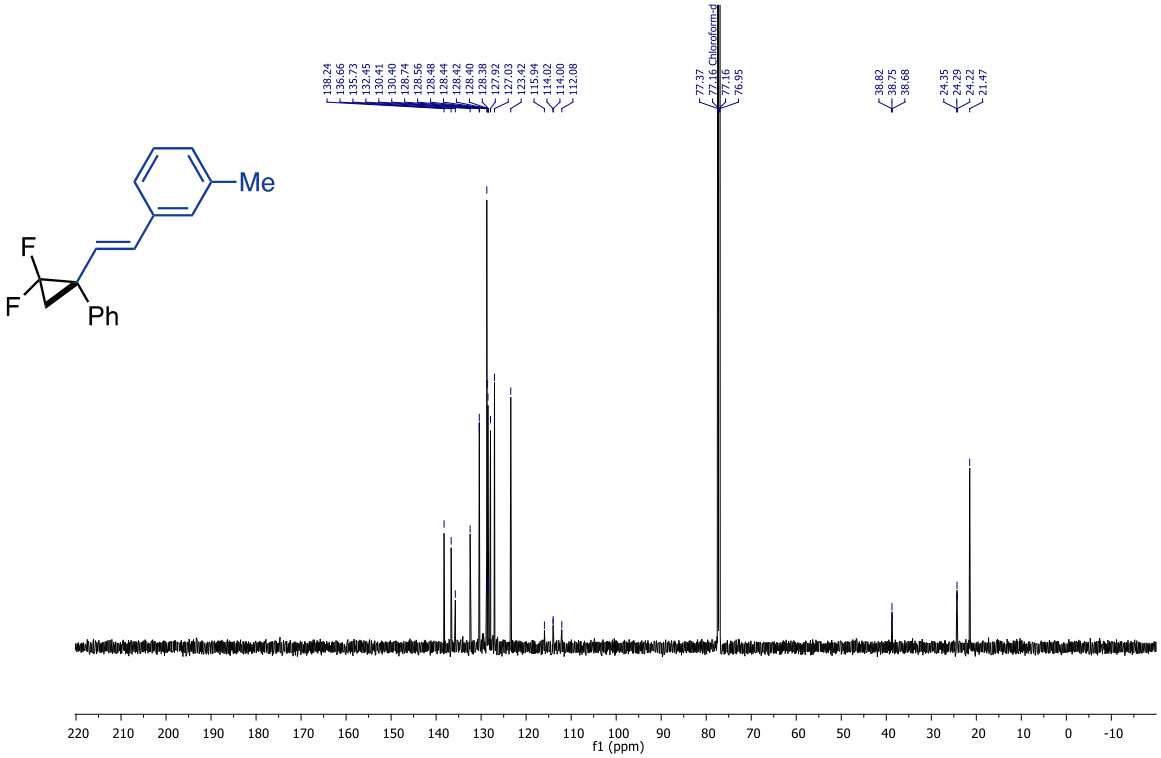
^{19}F NMR (565 MHz, $CDCl_3$) of **3m**



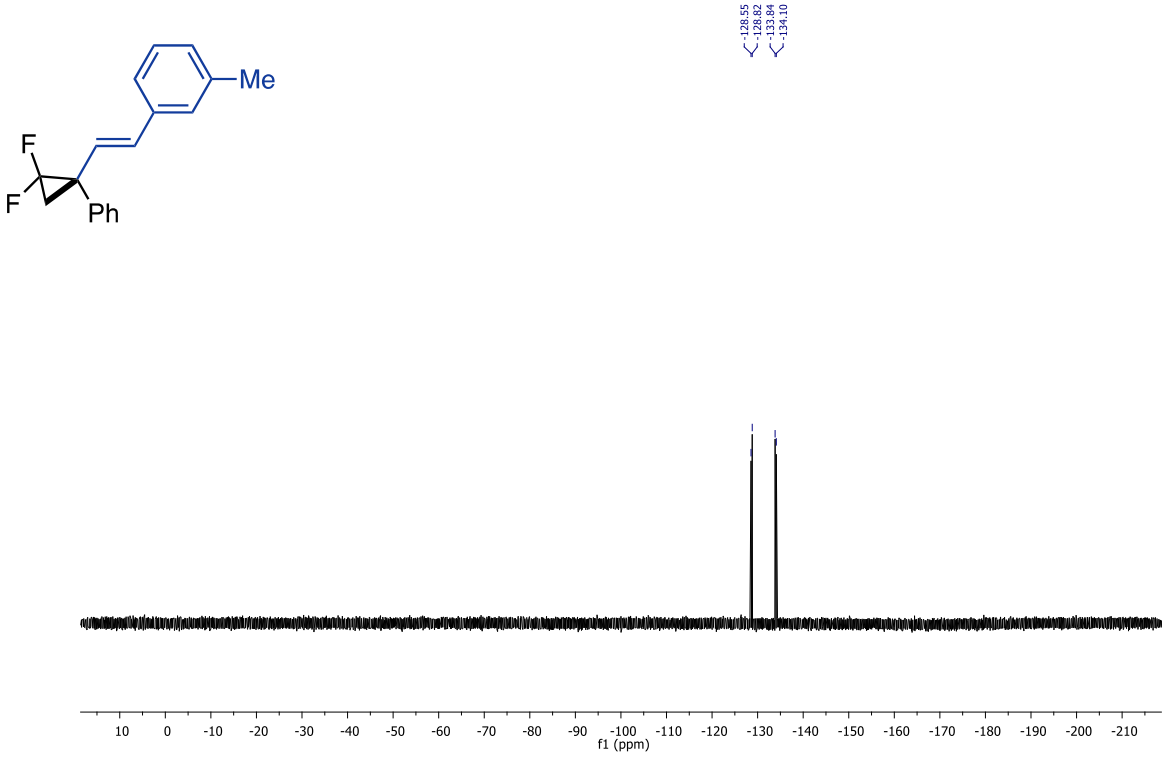
^{1}H NMR (600 MHz, $CDCl_3$) of **3n**



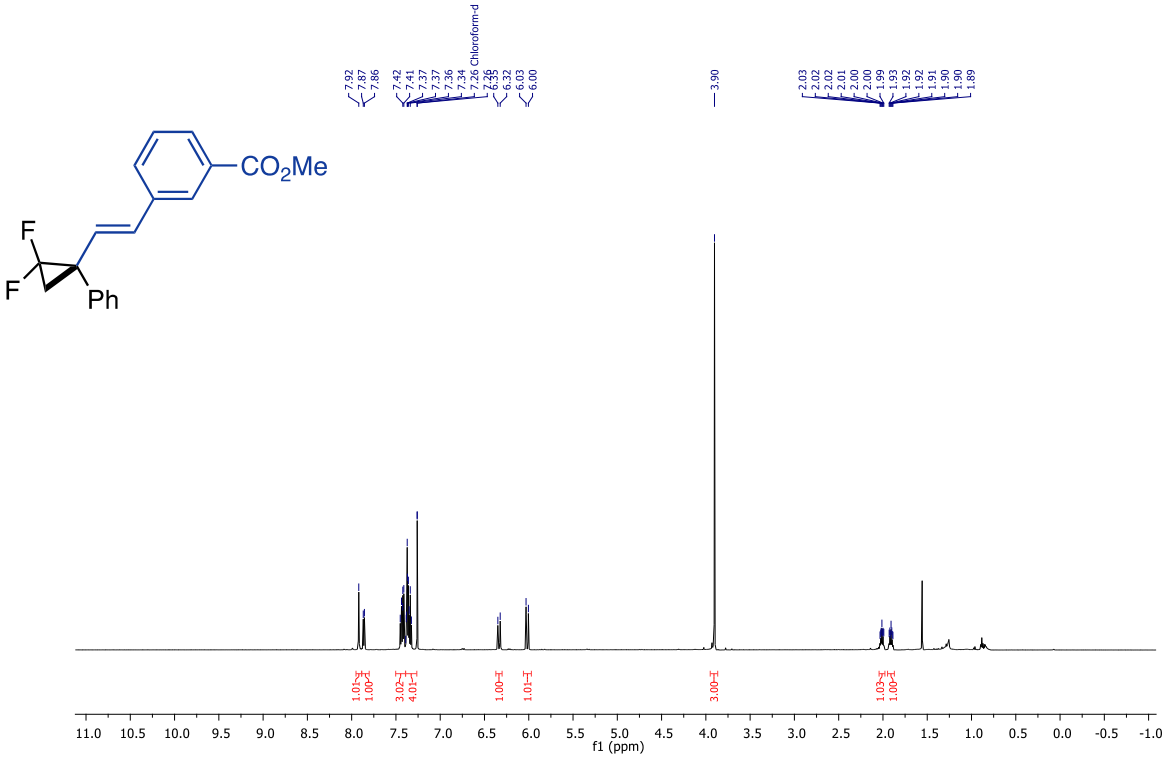
^{13}C NMR (151 MHz, $CDCl_3$) of **3n**



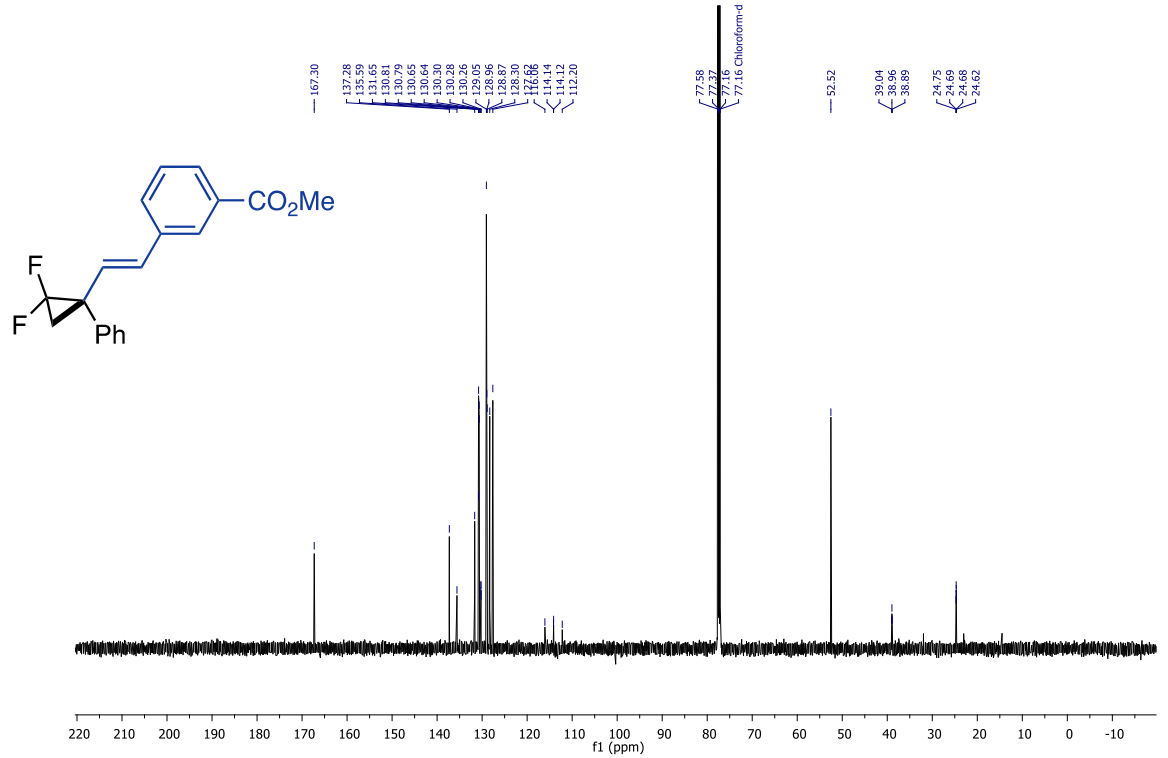
^{19}F NMR (565 MHz, $CDCl_3$) of **3n**



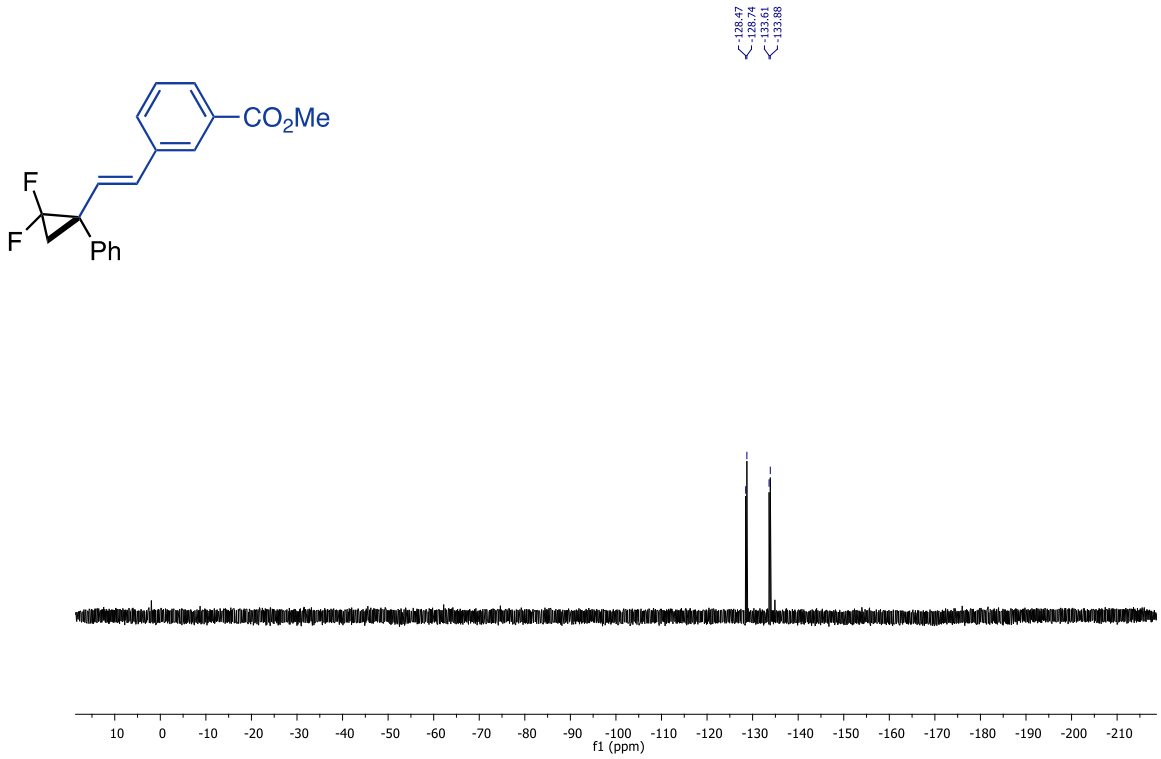
^{1}H NMR (600 MHz, $CDCl_3$) of **3o**



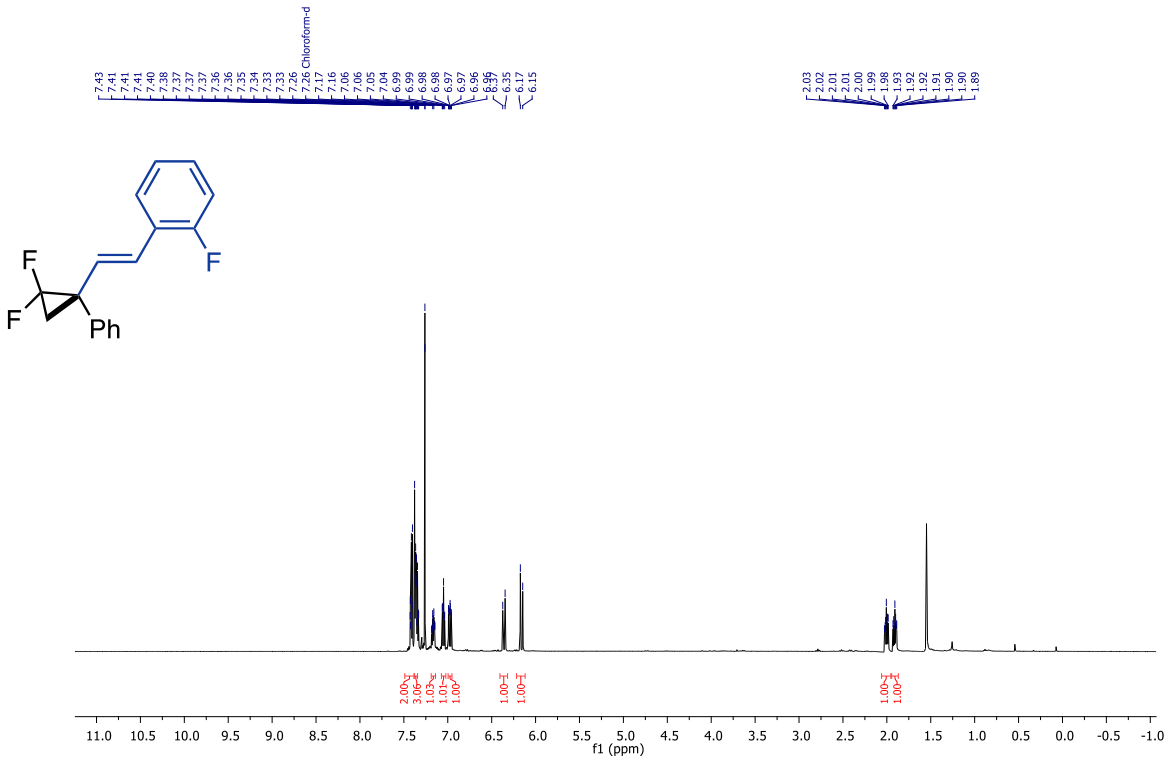
^{13}C NMR (151 MHz, $CDCl_3$) of **3o**



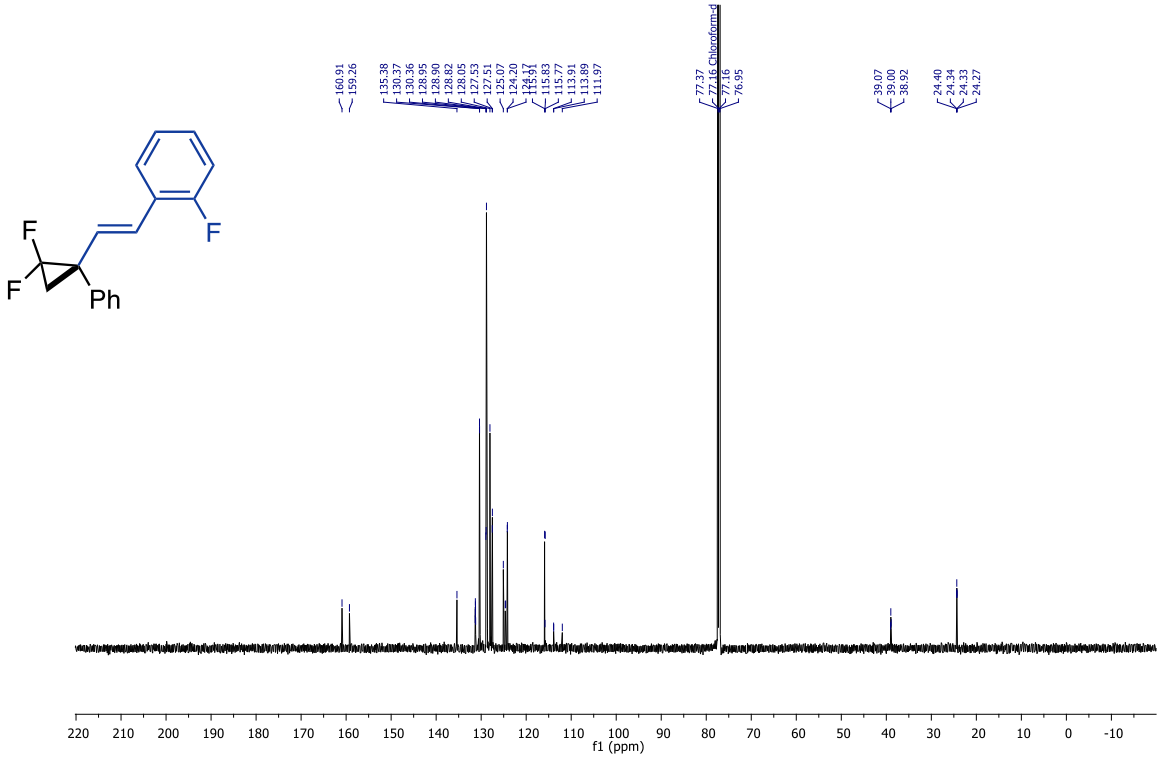
^{19}F NMR (565 MHz, $CDCl_3$) of **3o**



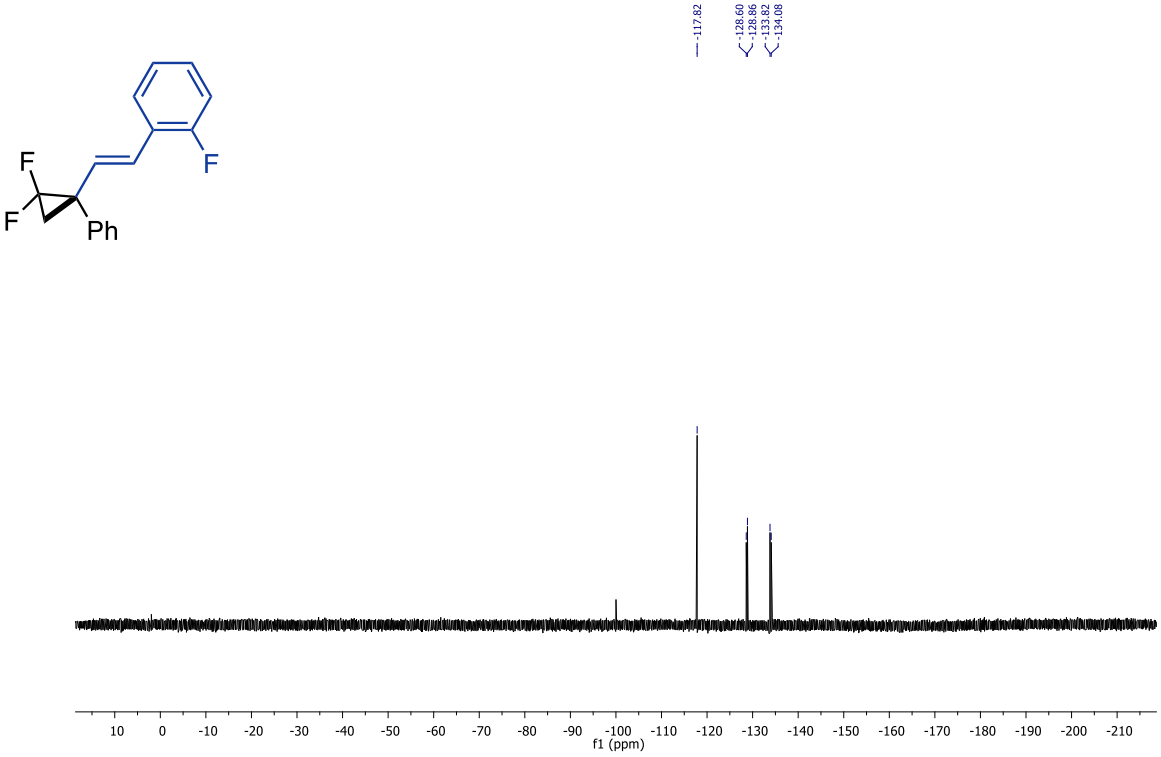
^{1}H NMR (600 MHz, $CDCl_3$) of **3p**



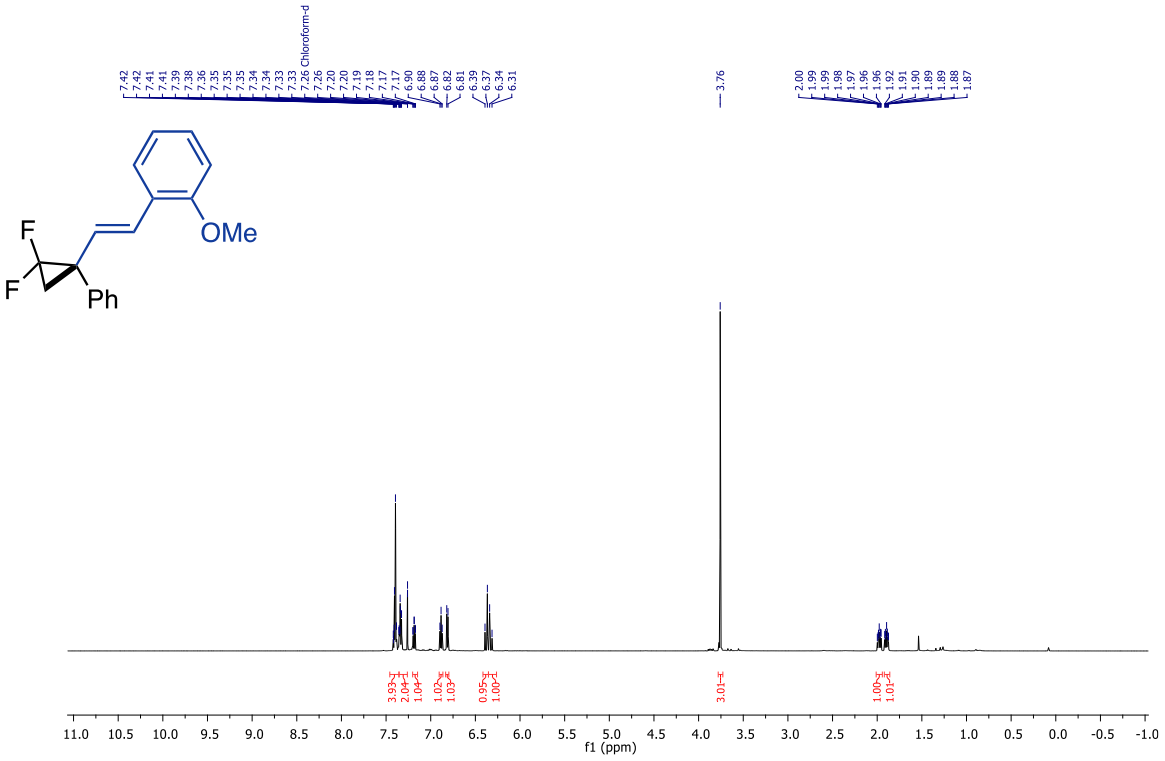
^{13}C NMR (151 MHz, $CDCl_3$) of **3p**



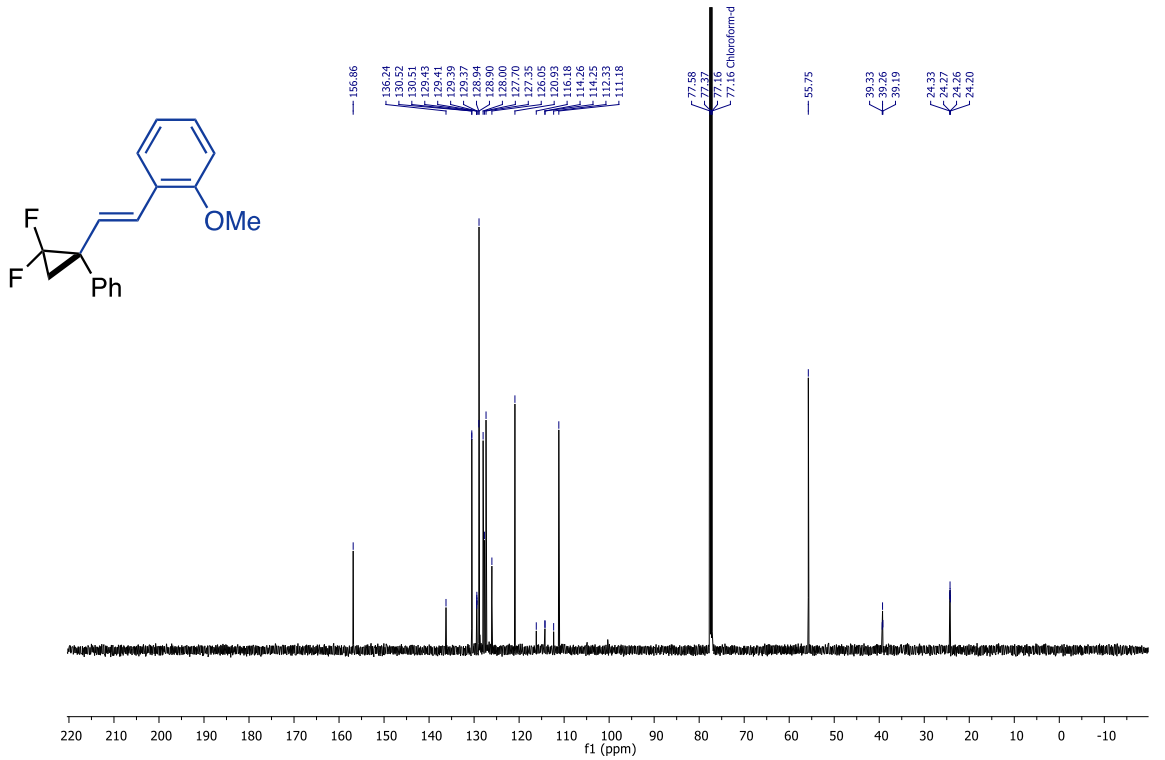
^{19}F NMR (565 MHz, $CDCl_3$) of **3p**



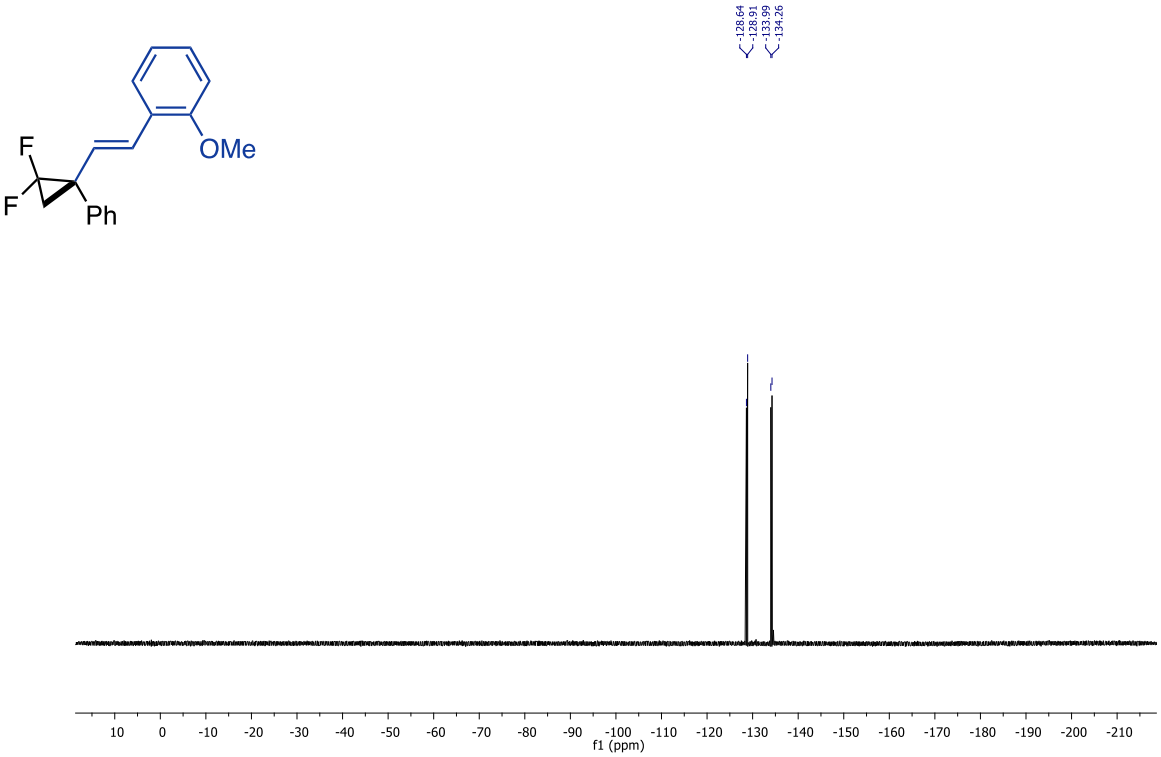
^{1}H NMR (600 MHz, $CDCl_3$) of **3q**



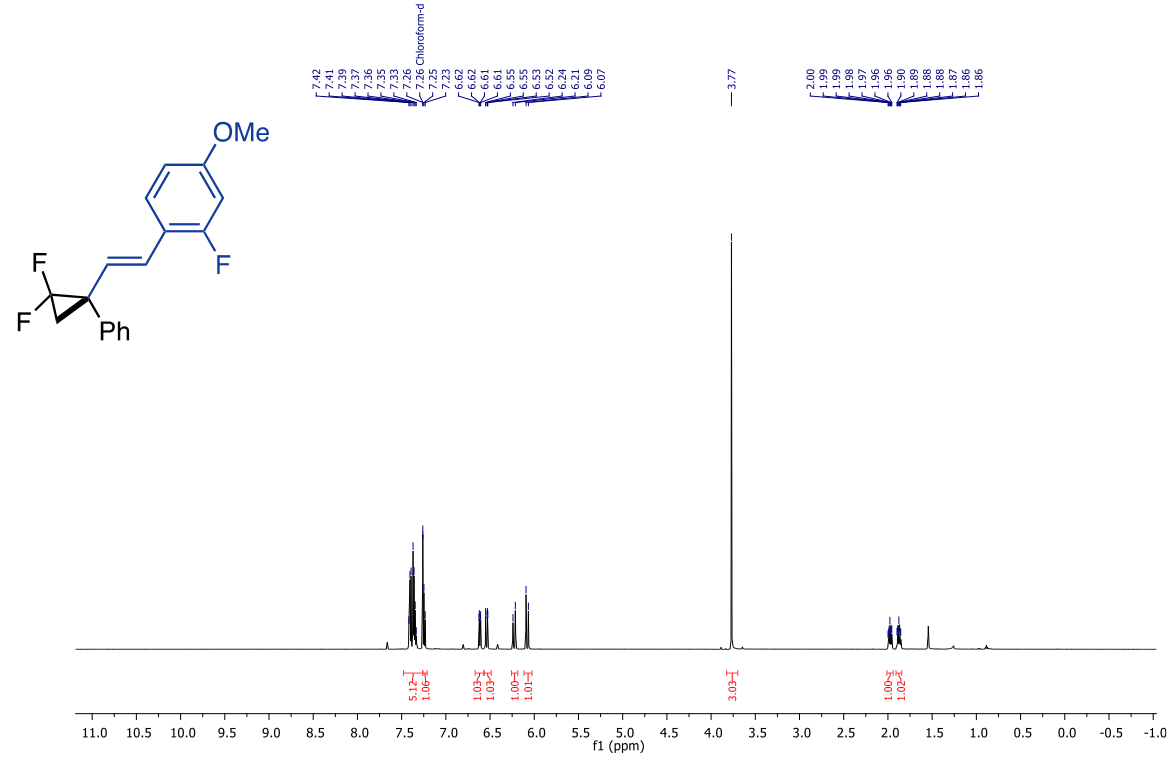
^{13}C NMR (151 MHz, $CDCl_3$) of **3q**



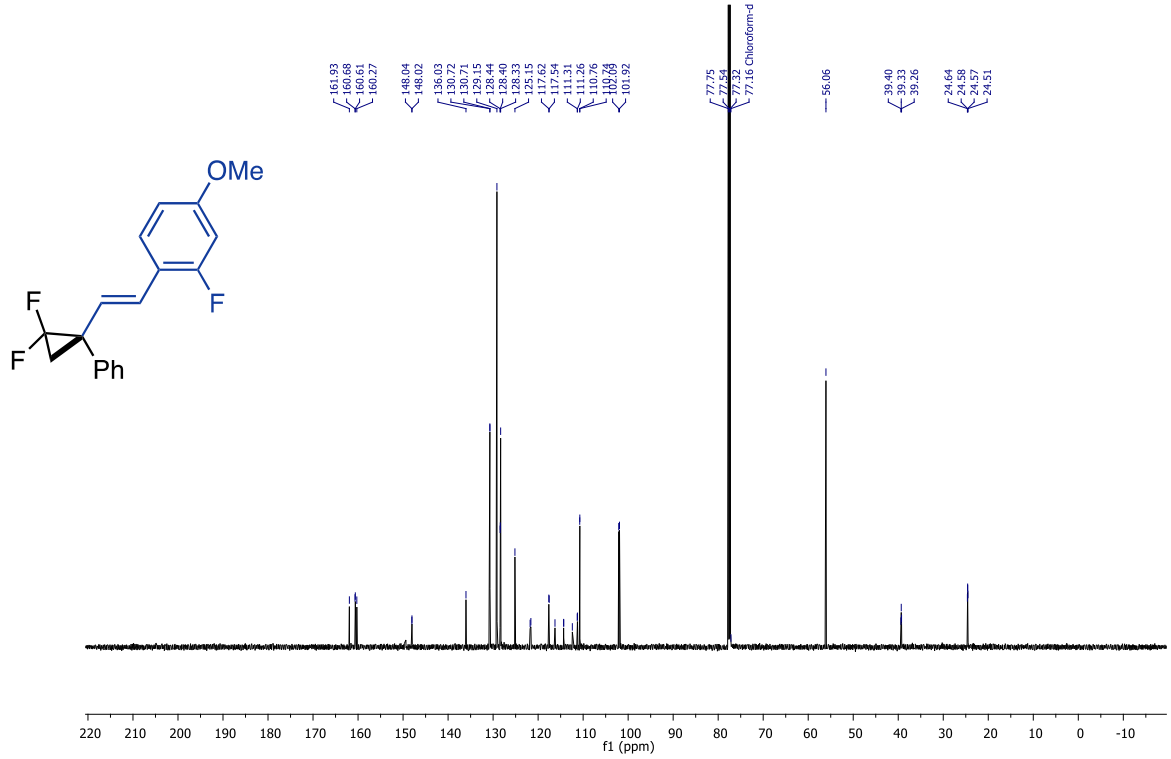
^{19}F NMR (565 MHz, $CDCl_3$) of **3q**



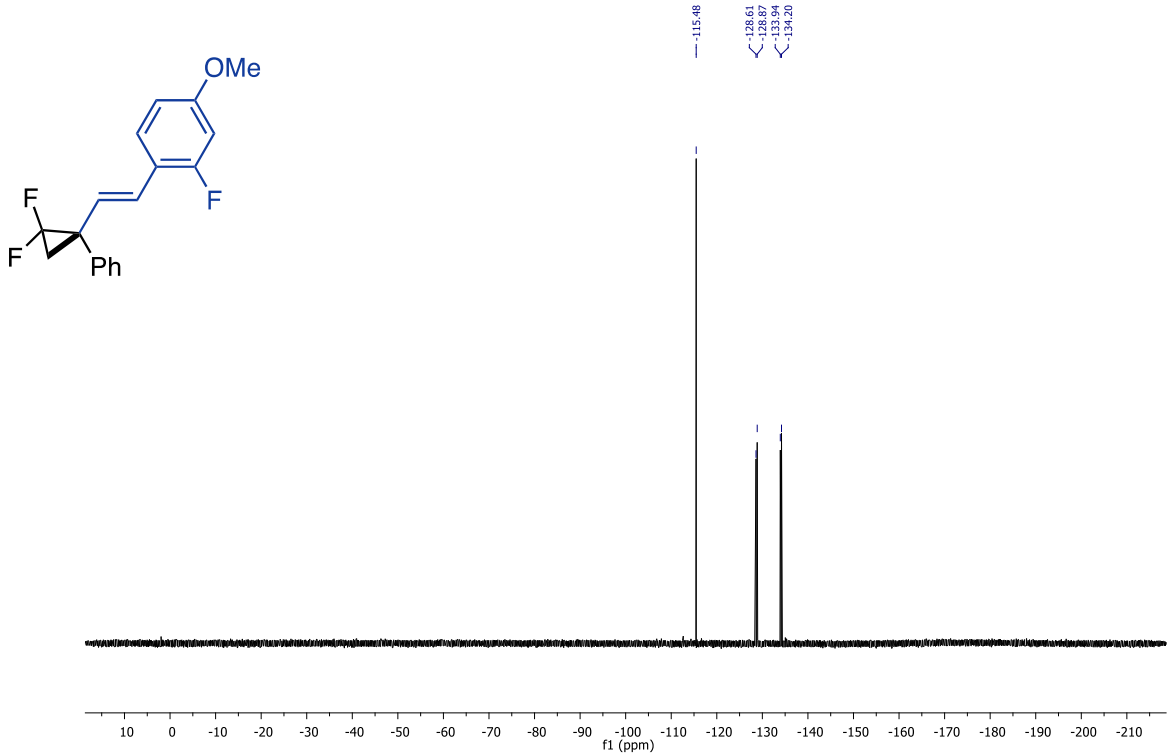
^{1}H NMR (600 MHz, $CDCl_3$) of **3r**



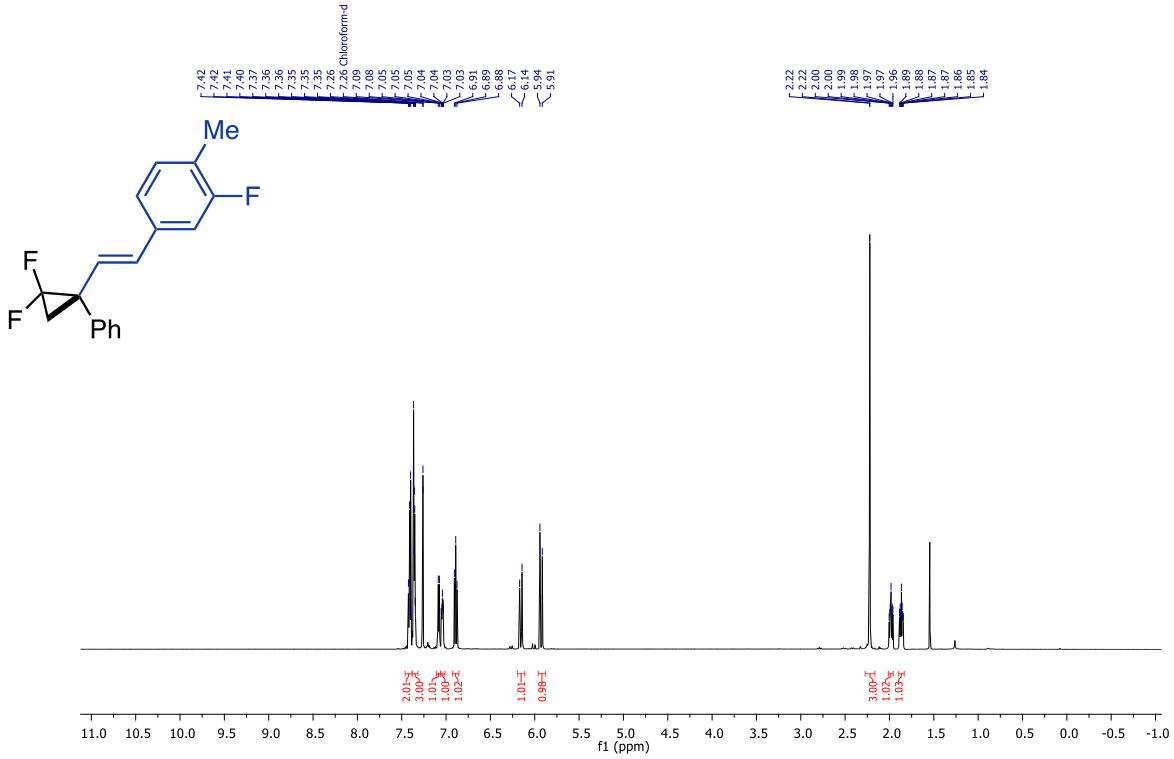
^{13}C NMR (151 MHz, $CDCl_3$) of **3r**



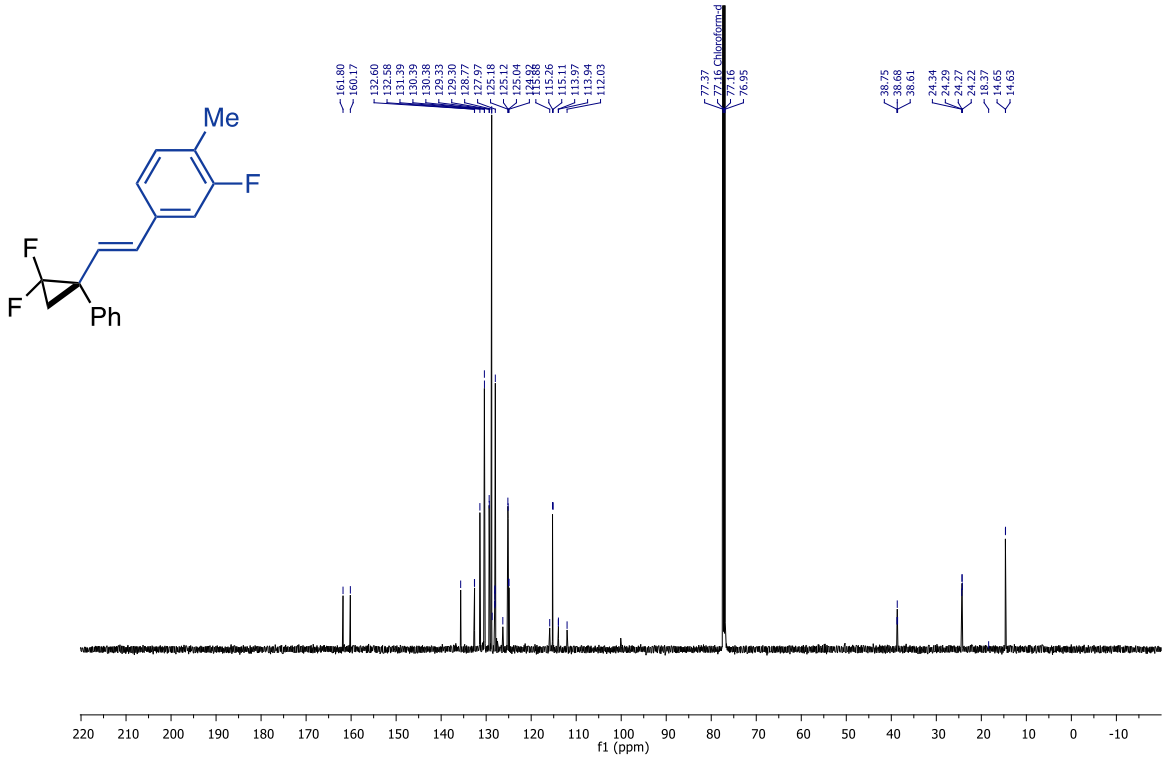
^{19}F NMR (565 MHz, $CDCl_3$) of **3r**



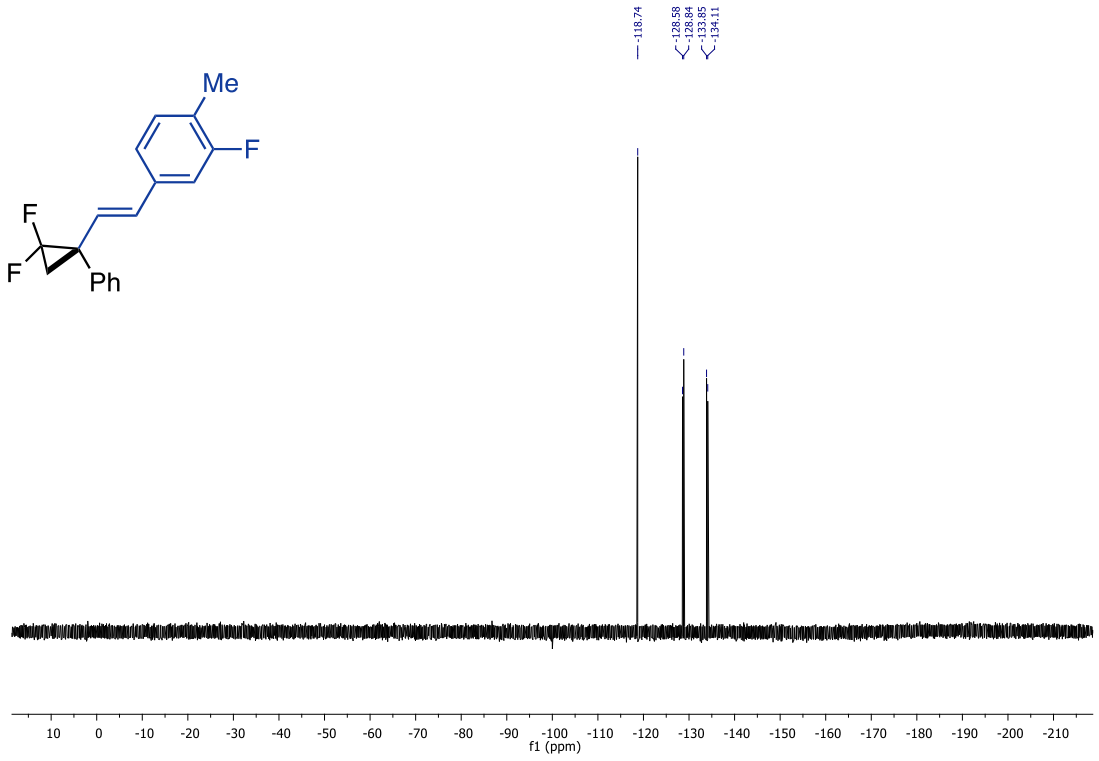
^{1}H NMR (600 MHz, $CDCl_3$) of **3s**



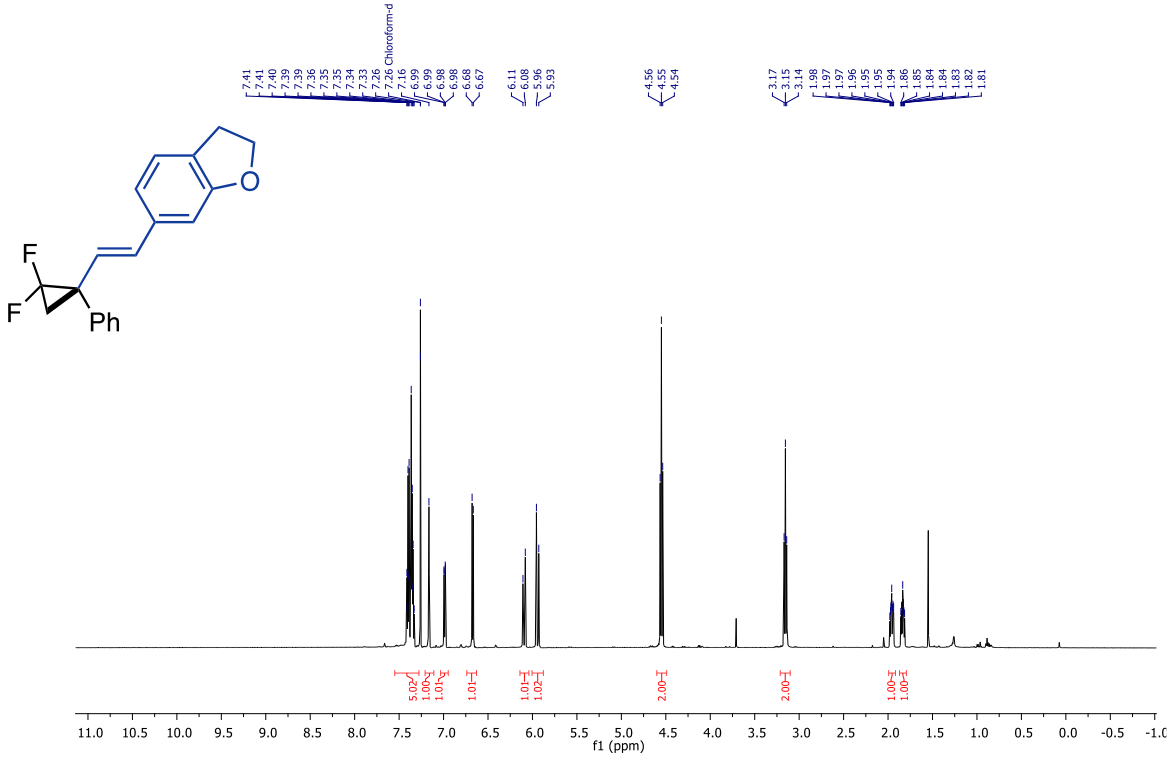
^{13}C NMR (151 MHz, $CDCl_3$) of **3s**



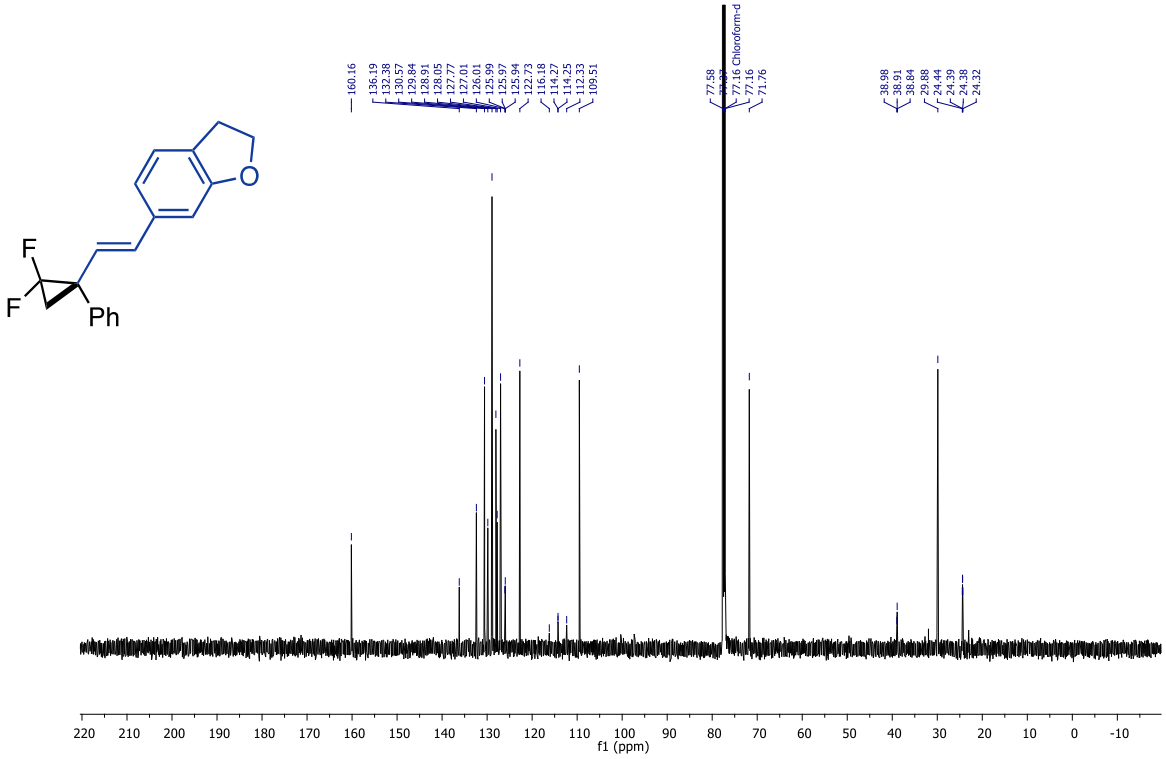
^{19}F NMR (565 MHz, $CDCl_3$) of **3s**



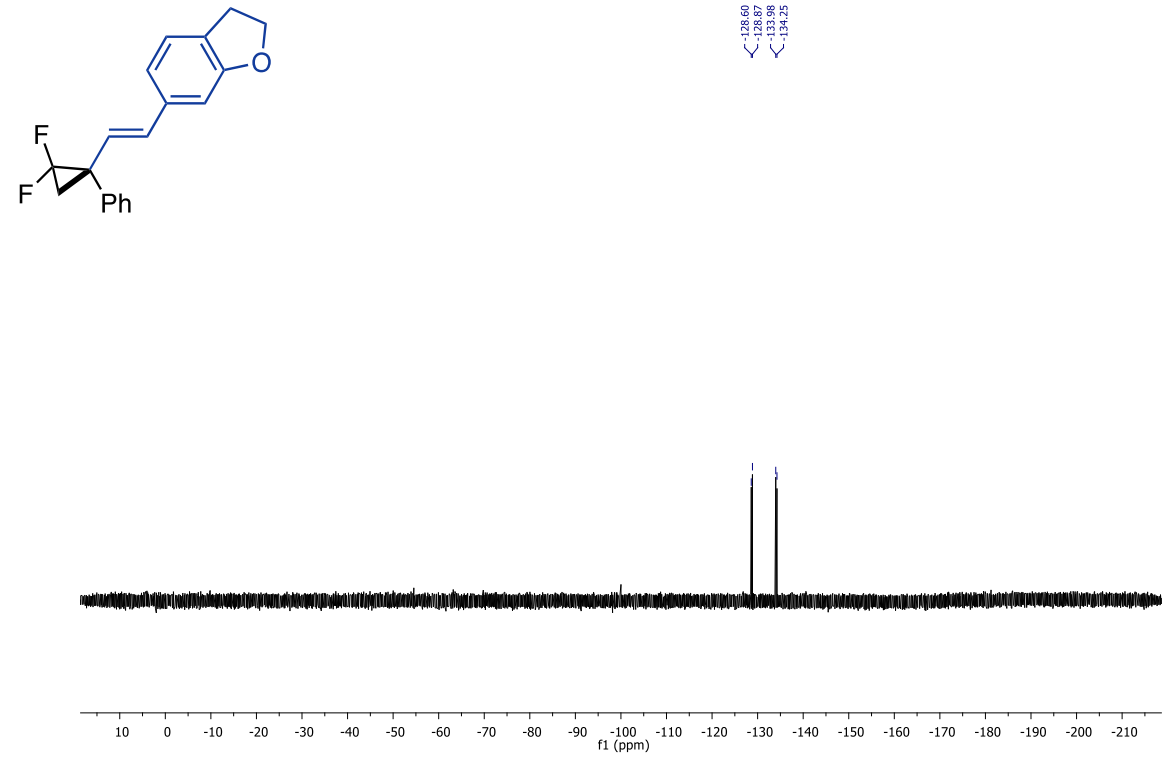
^{1}H NMR (600 MHz, $CDCl_3$) of **3t**



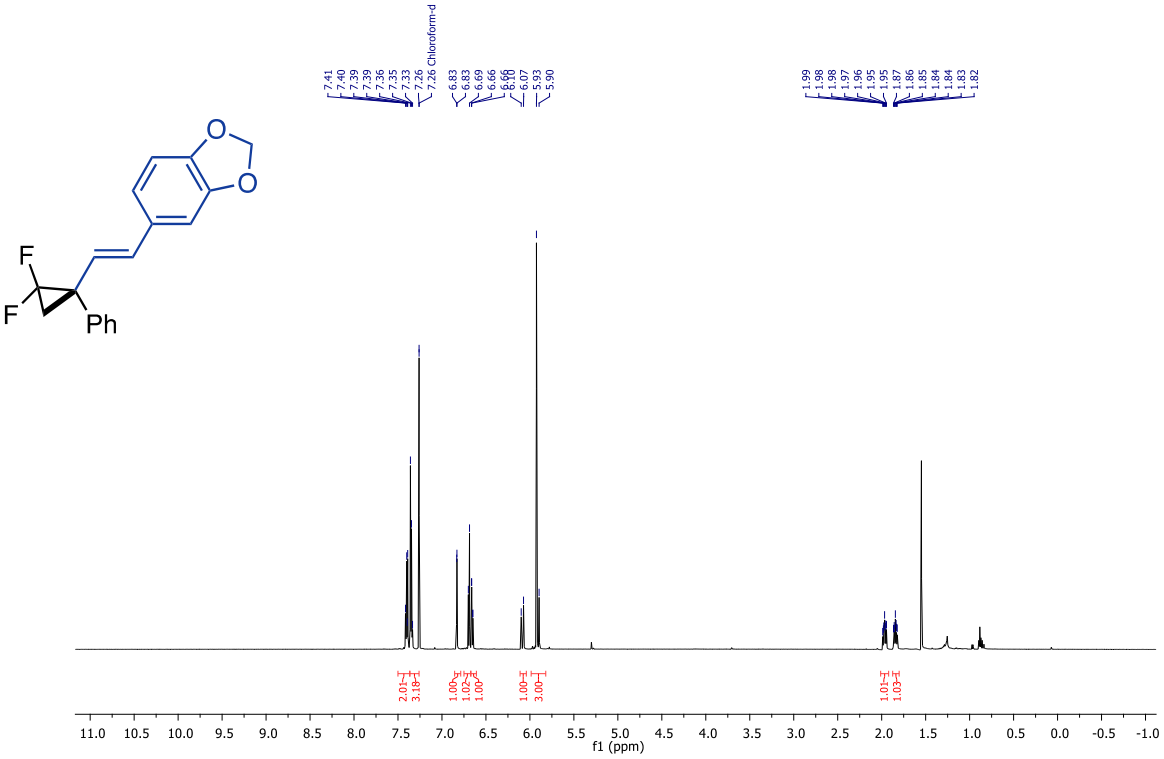
^{13}C NMR (151 MHz, $CDCl_3$) of **3t**



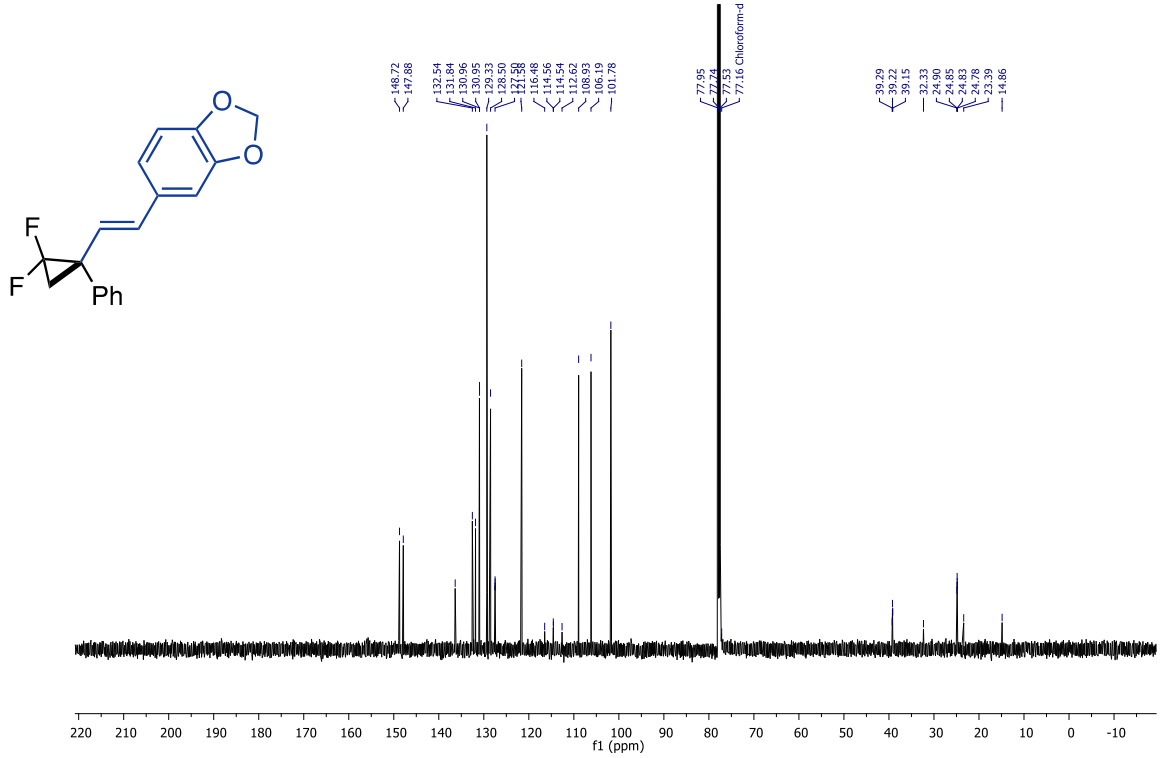
^{19}F NMR (565 MHz, $CDCl_3$) of **3t**



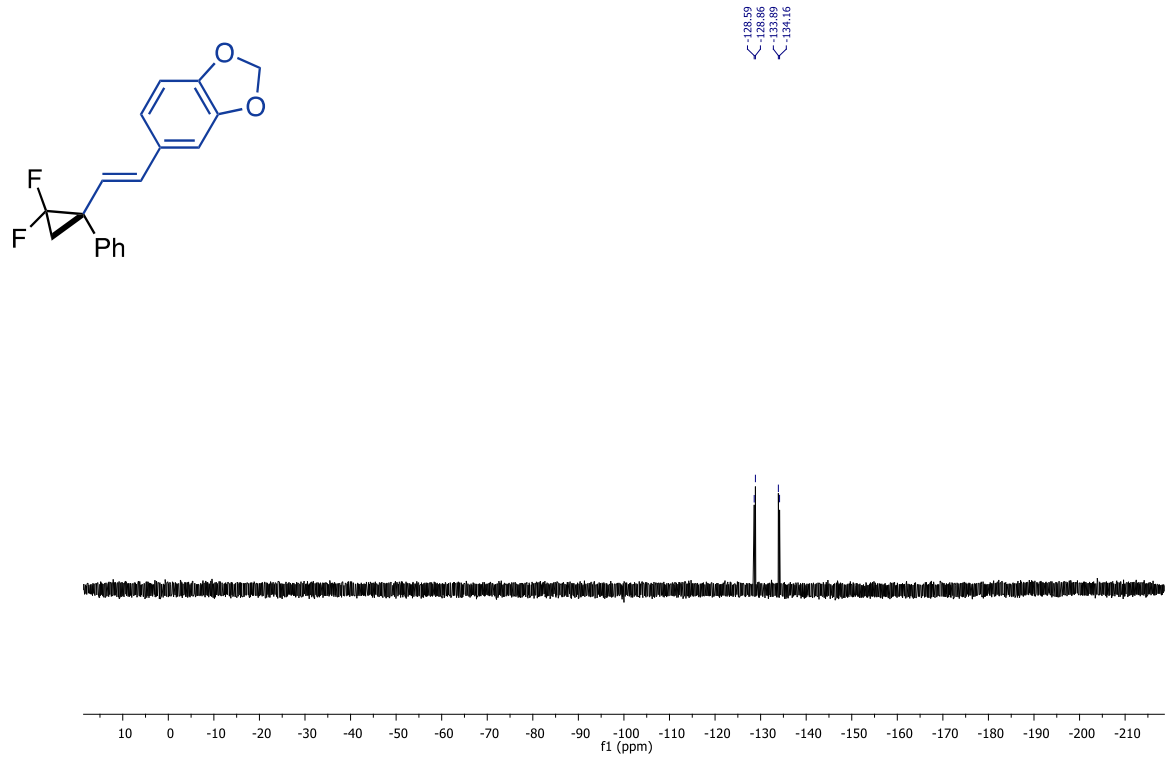
^{1}H NMR (600 MHz, $CDCl_3$) of **3u**



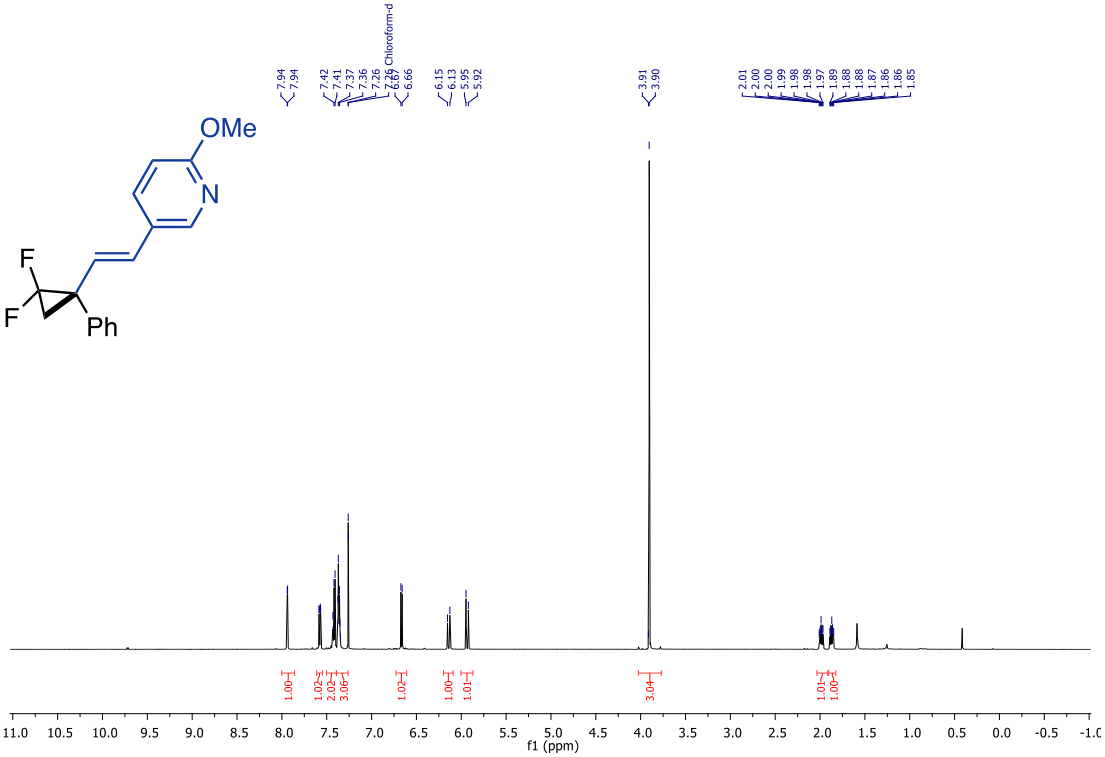
^{13}C NMR (151 MHz, $CDCl_3$) of **3u**



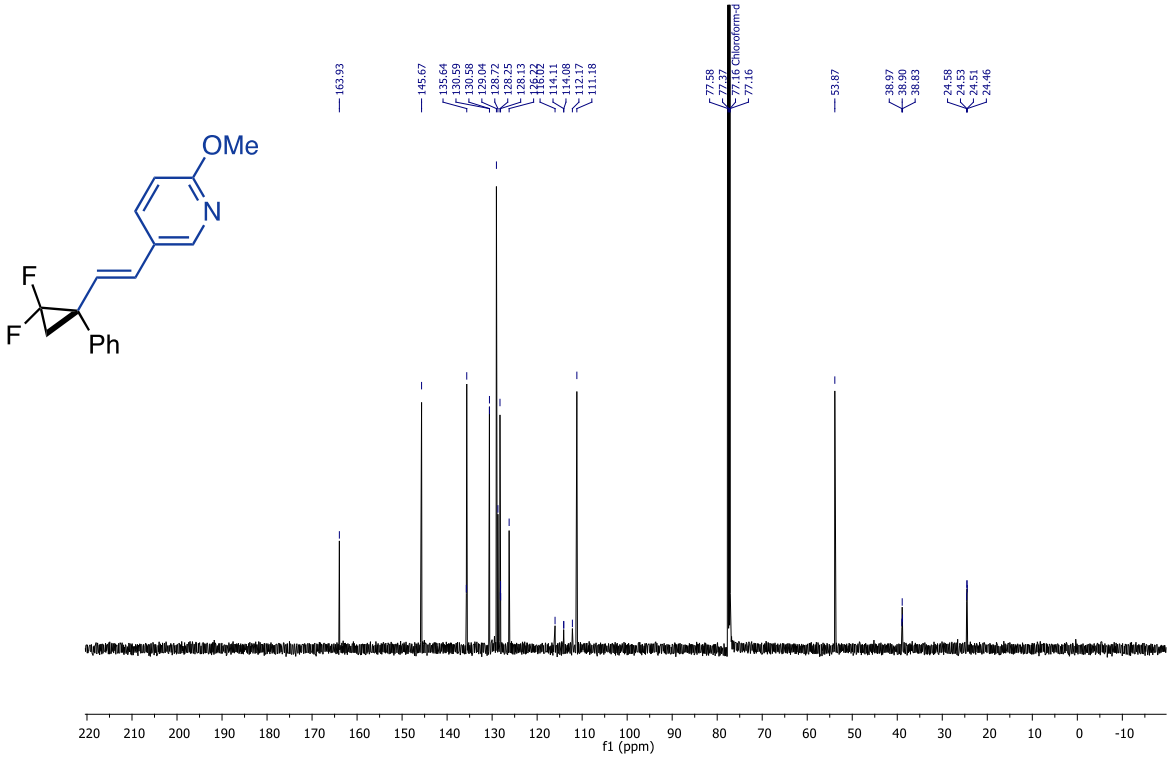
^{19}F NMR (565 MHz, $CDCl_3$) of **3u**



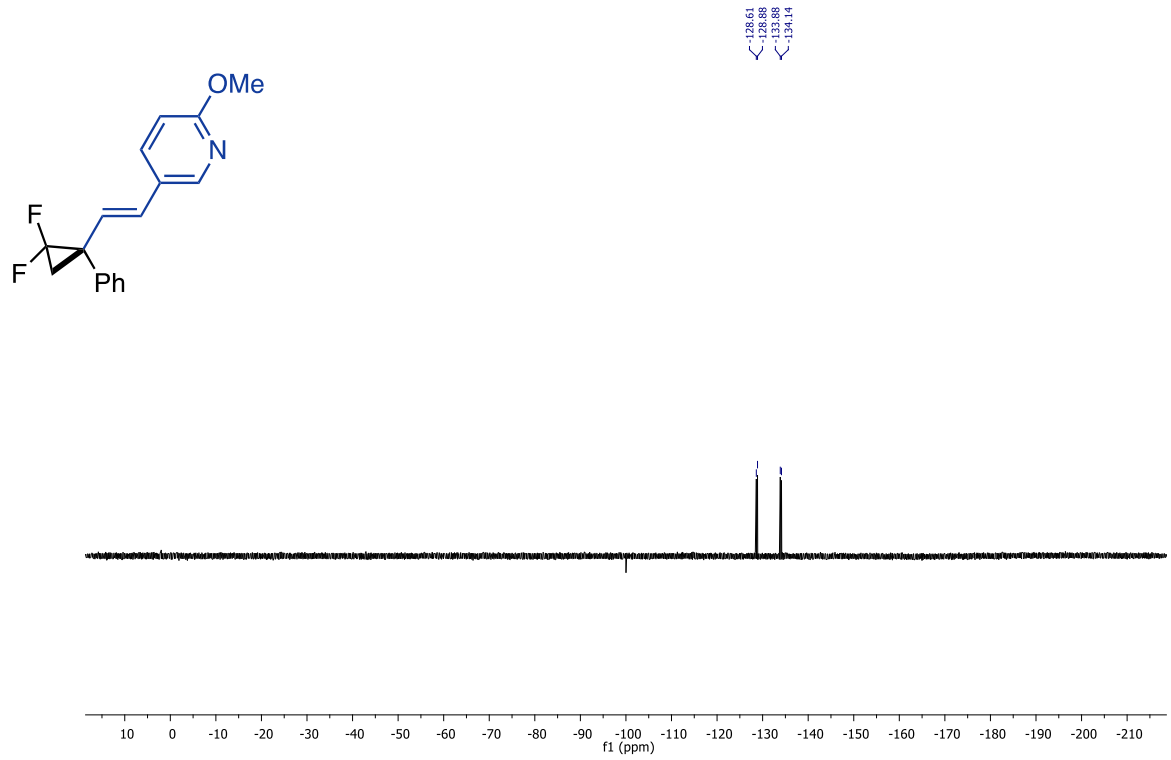
^{1}H NMR (600 MHz, $CDCl_3$) of **3v**



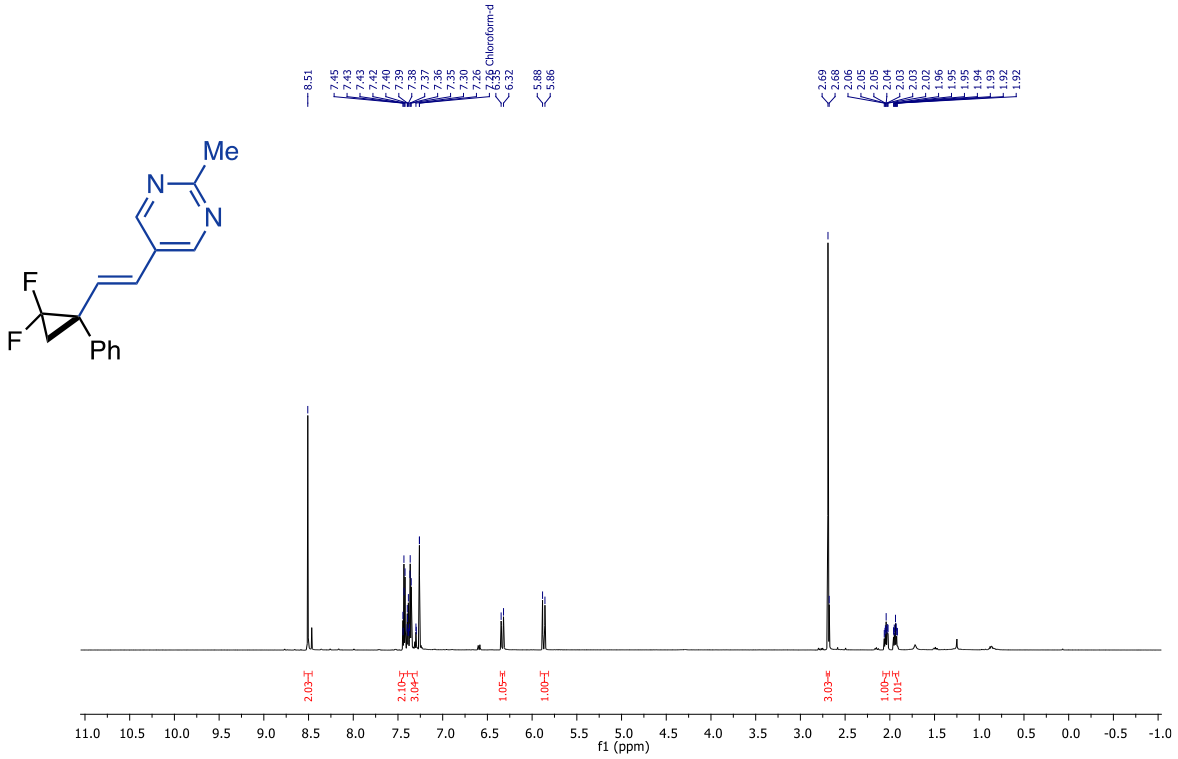
^{13}C NMR (151 MHz, $CDCl_3$) of **3v**



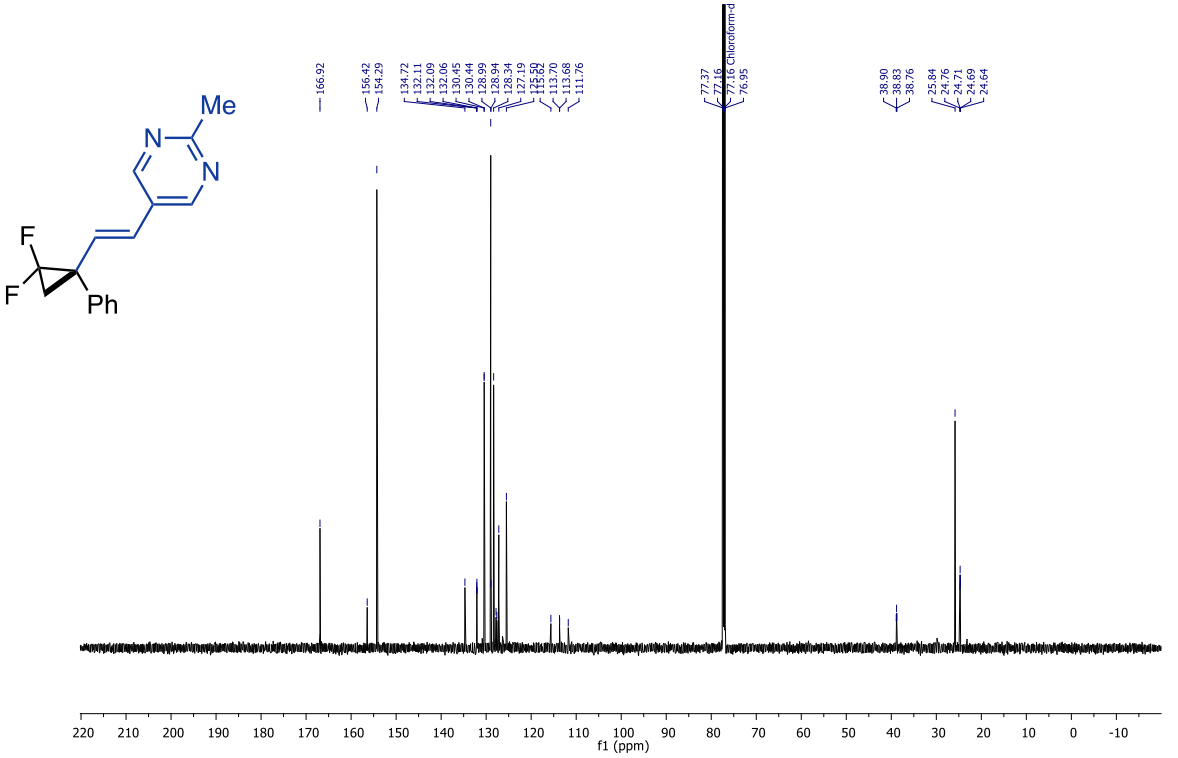
^{19}F NMR (565 MHz, $CDCl_3$) of **3v**



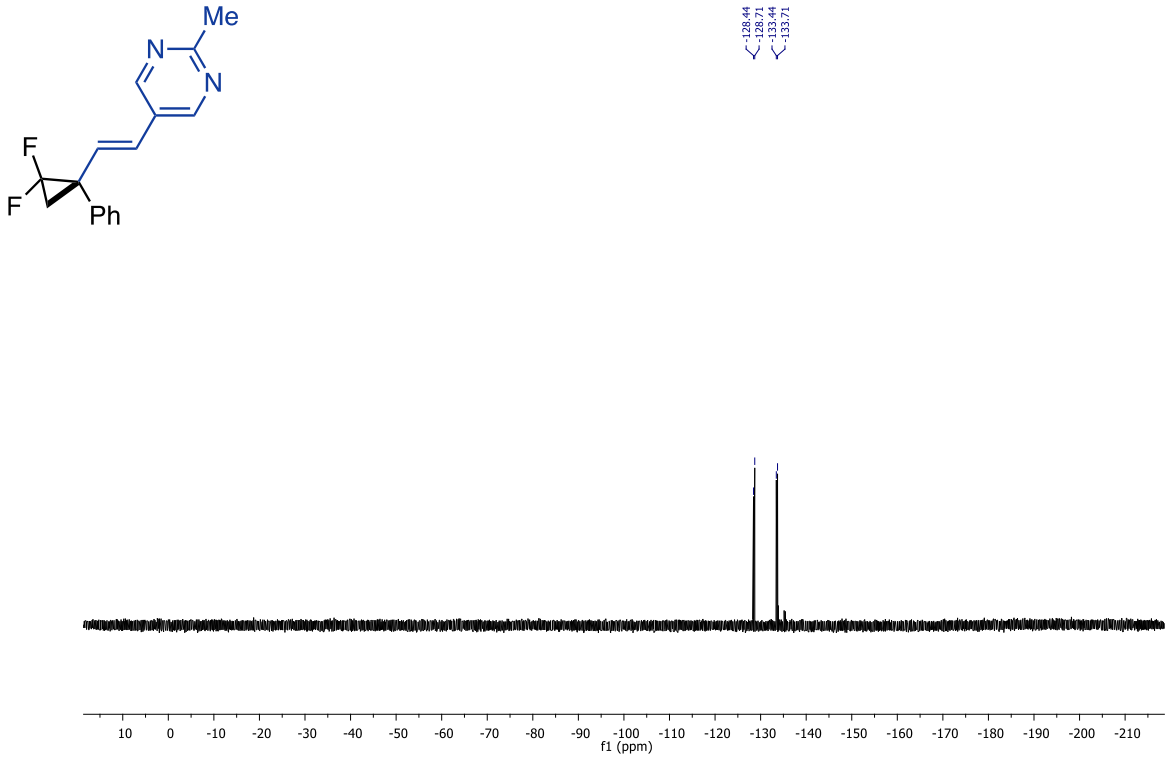
^{1}H NMR (600 MHz, $CDCl_3$) of **3w**



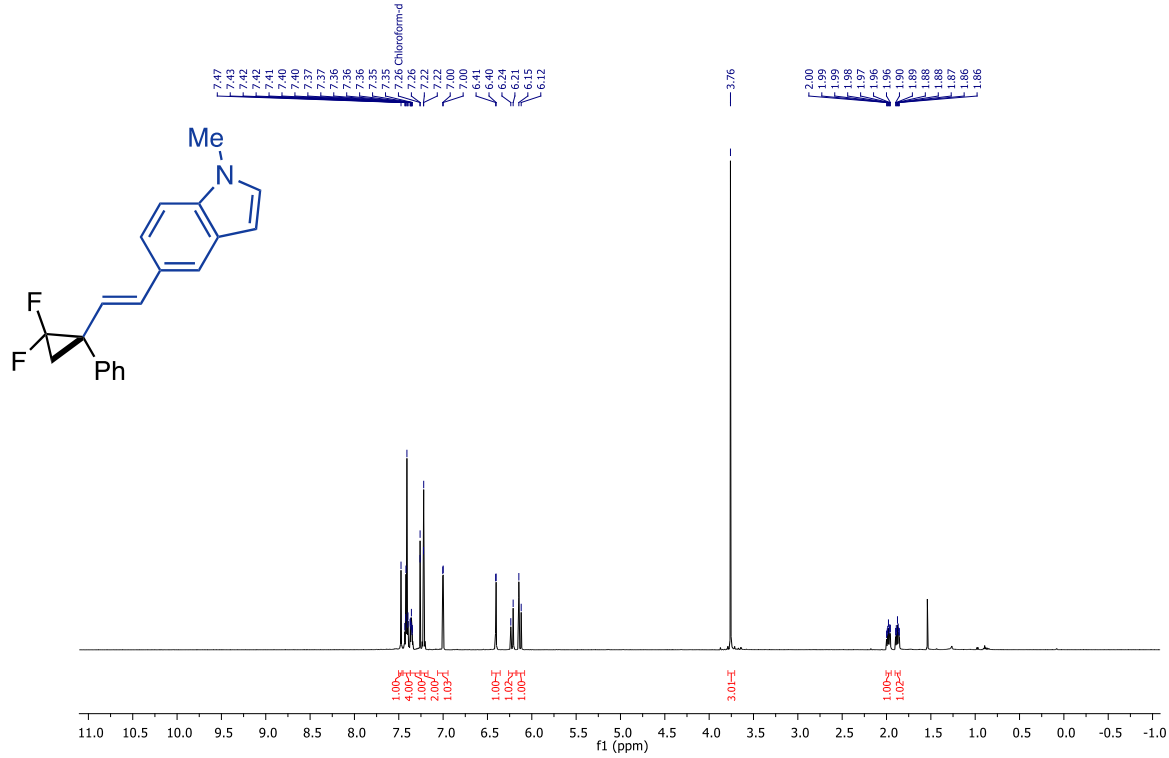
^{13}C NMR (151 MHz, $CDCl_3$) of **3w**



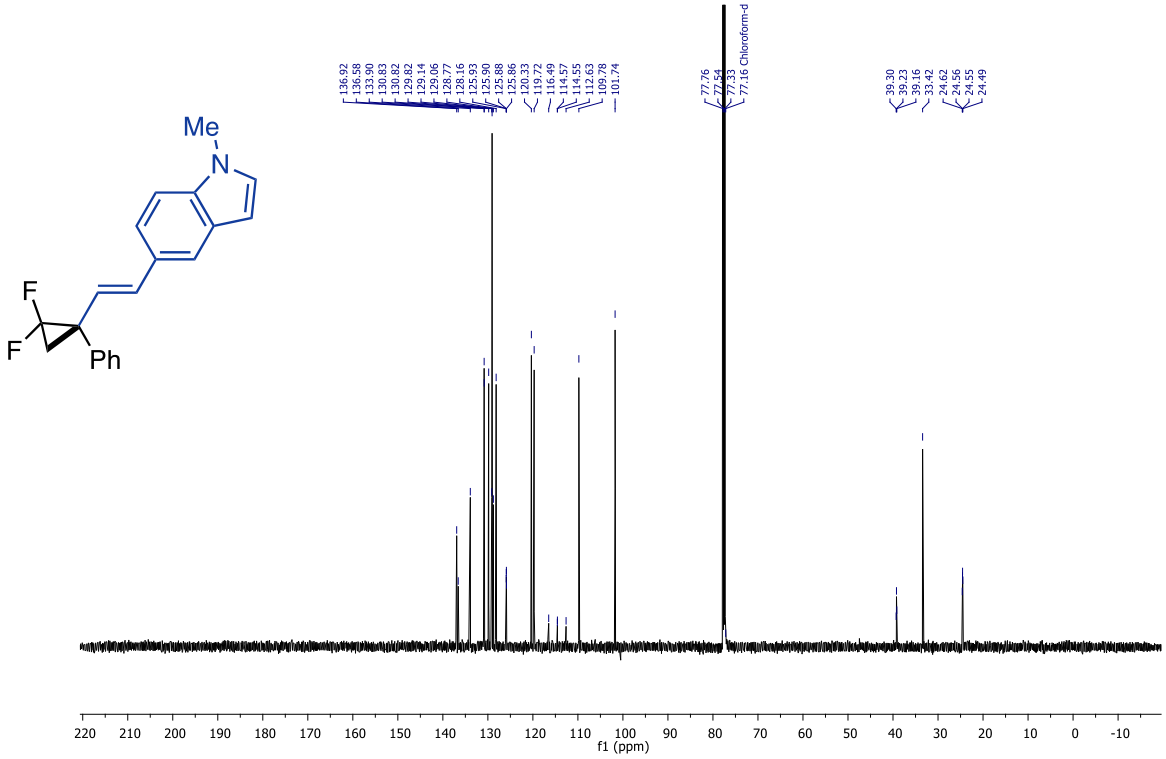
^{19}F NMR (565 MHz, $CDCl_3$) of **3w**



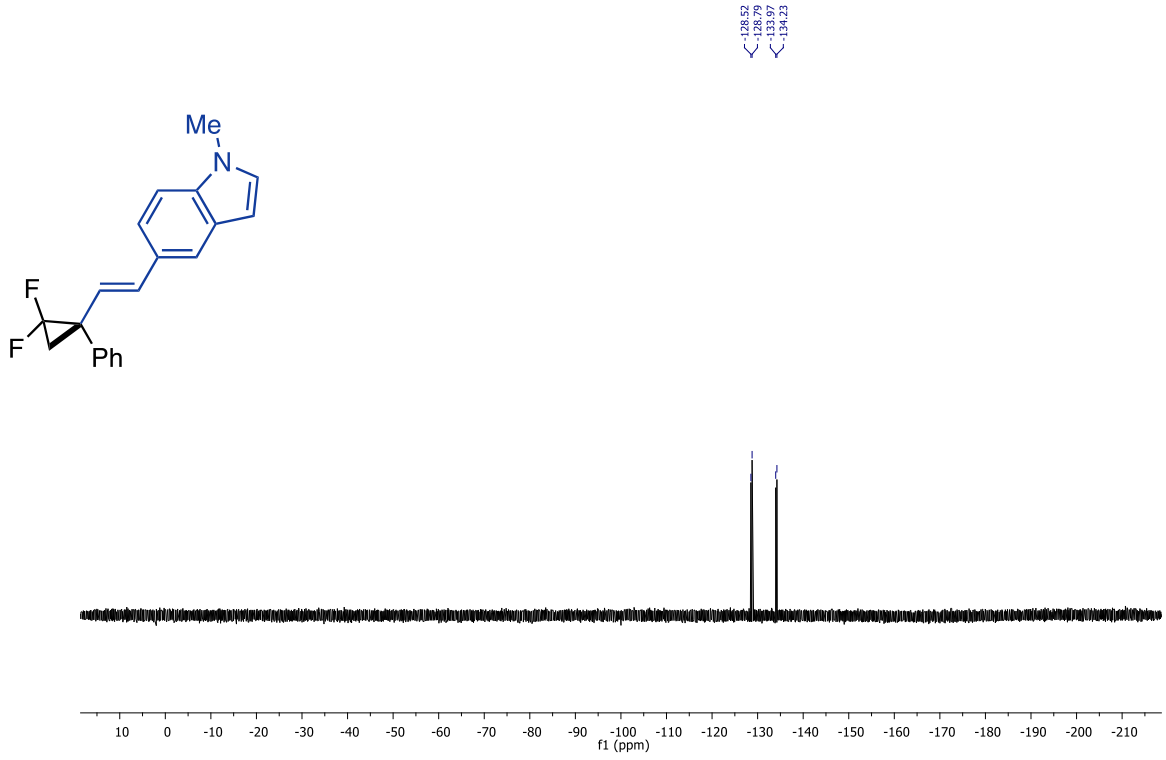
^{1}H NMR (600 MHz, $CDCl_3$) of **3x**



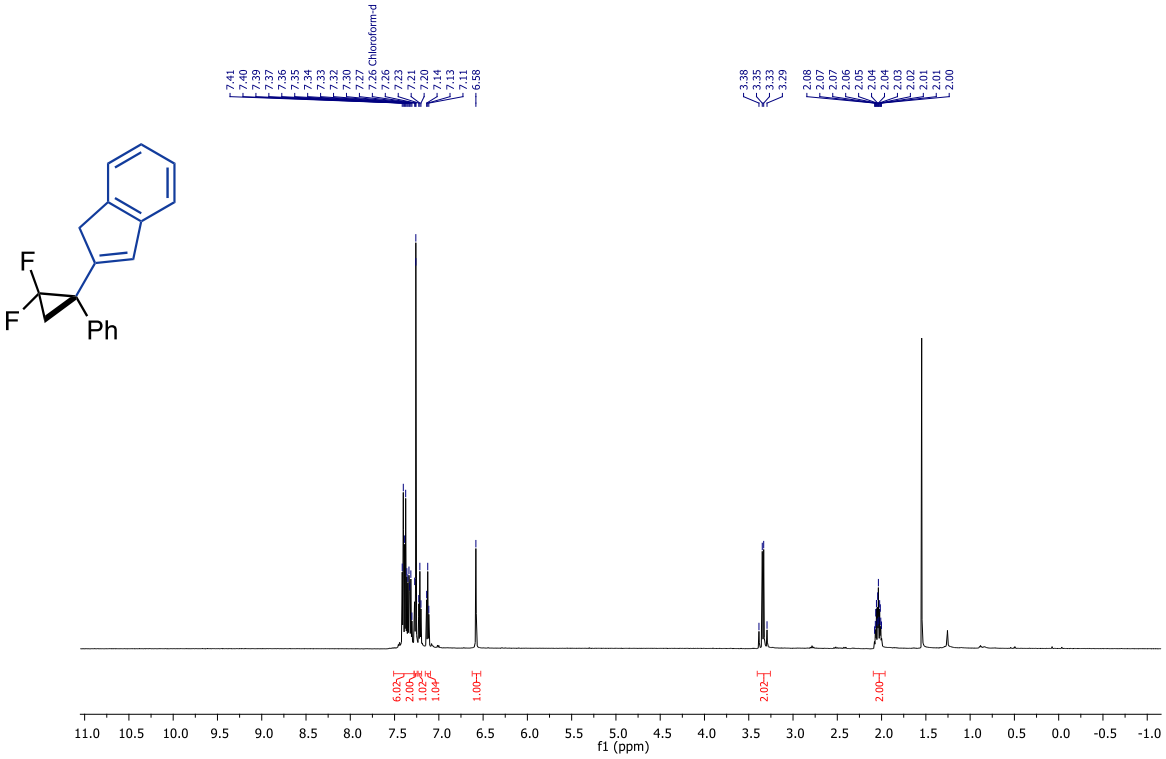
^{13}C NMR (151 MHz, $CDCl_3$) of **3x**



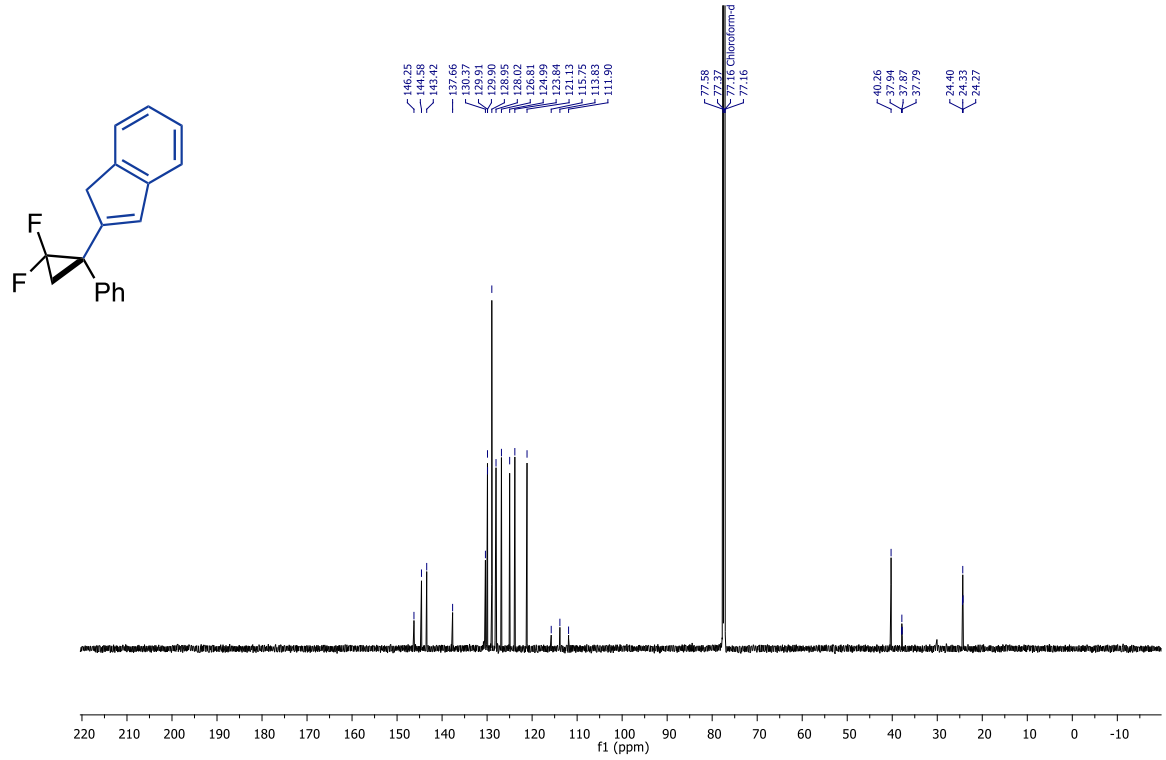
^{19}F NMR (565 MHz, $CDCl_3$) of **3x**



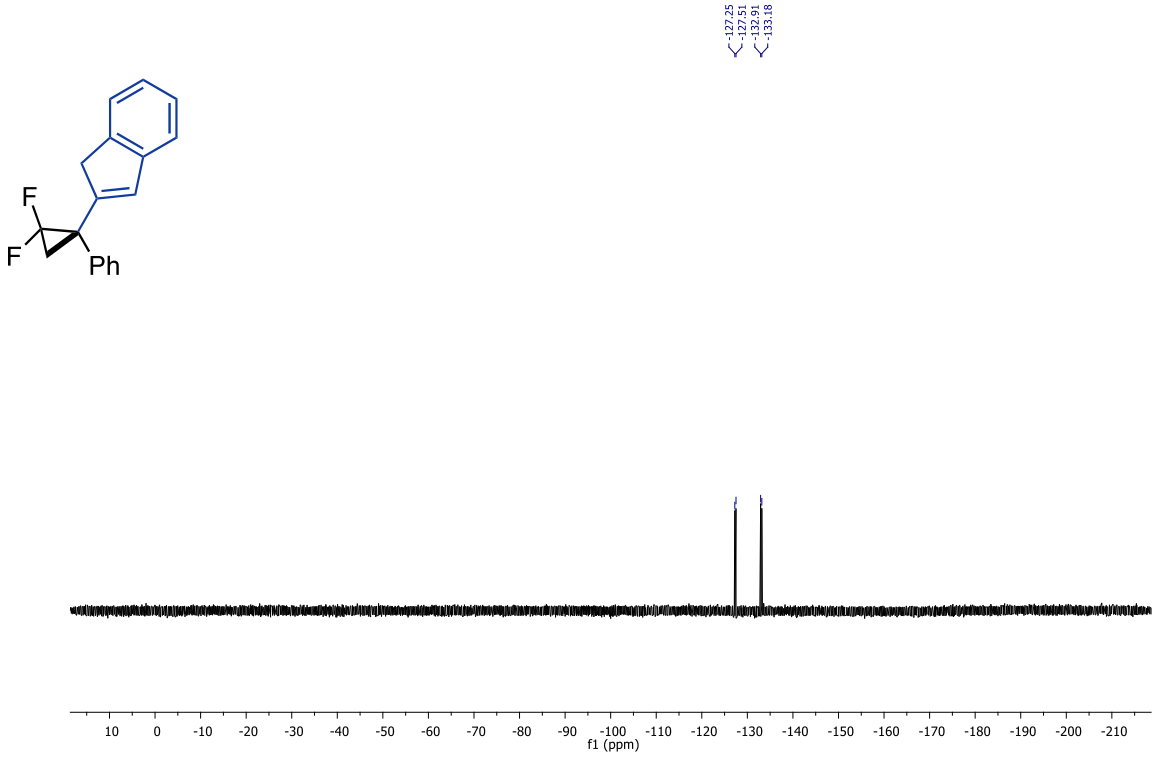
^{1}H NMR (600 MHz, $CDCl_3$) of **3y**



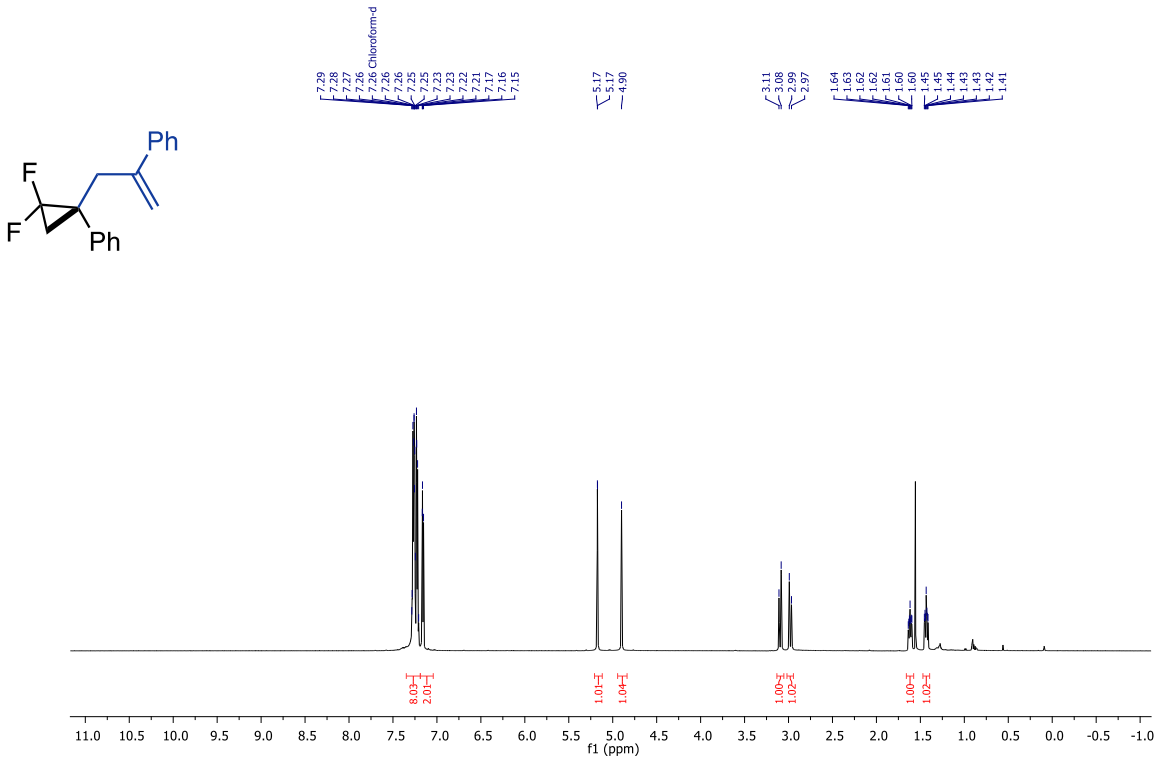
^{13}C NMR (151 MHz, $CDCl_3$) of **3y**



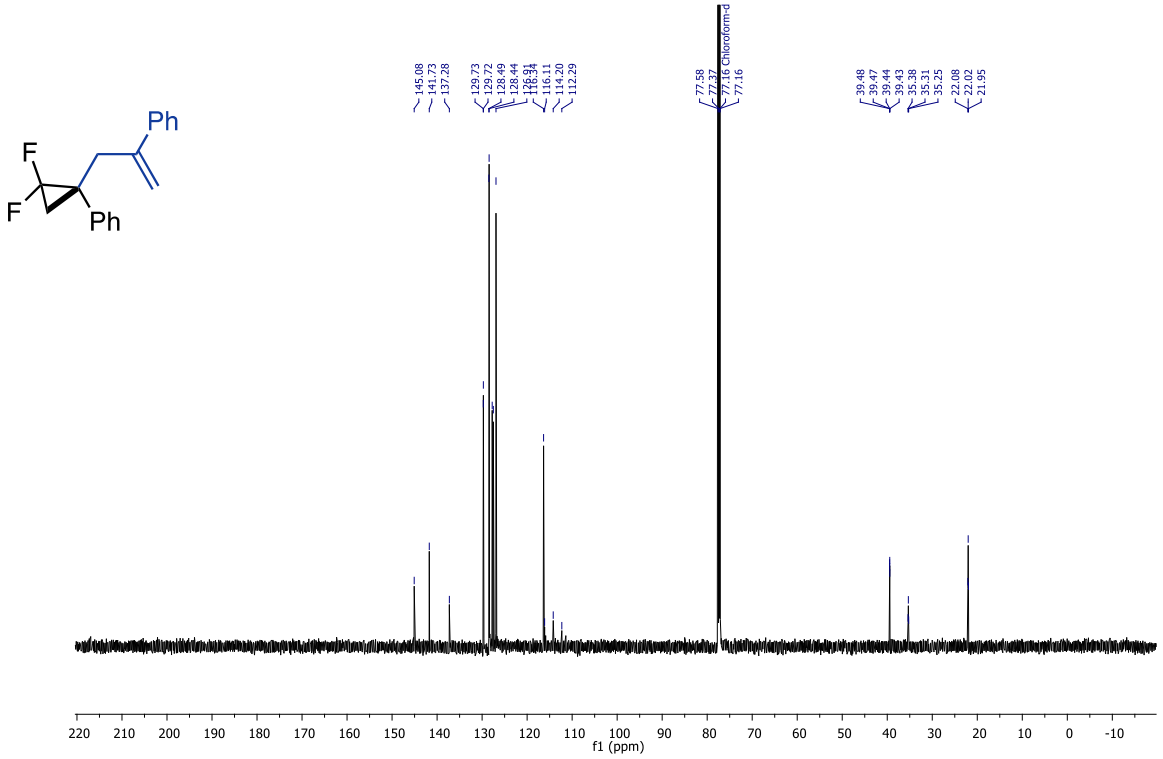
^{19}F NMR (565 MHz, $CDCl_3$) of **3y**



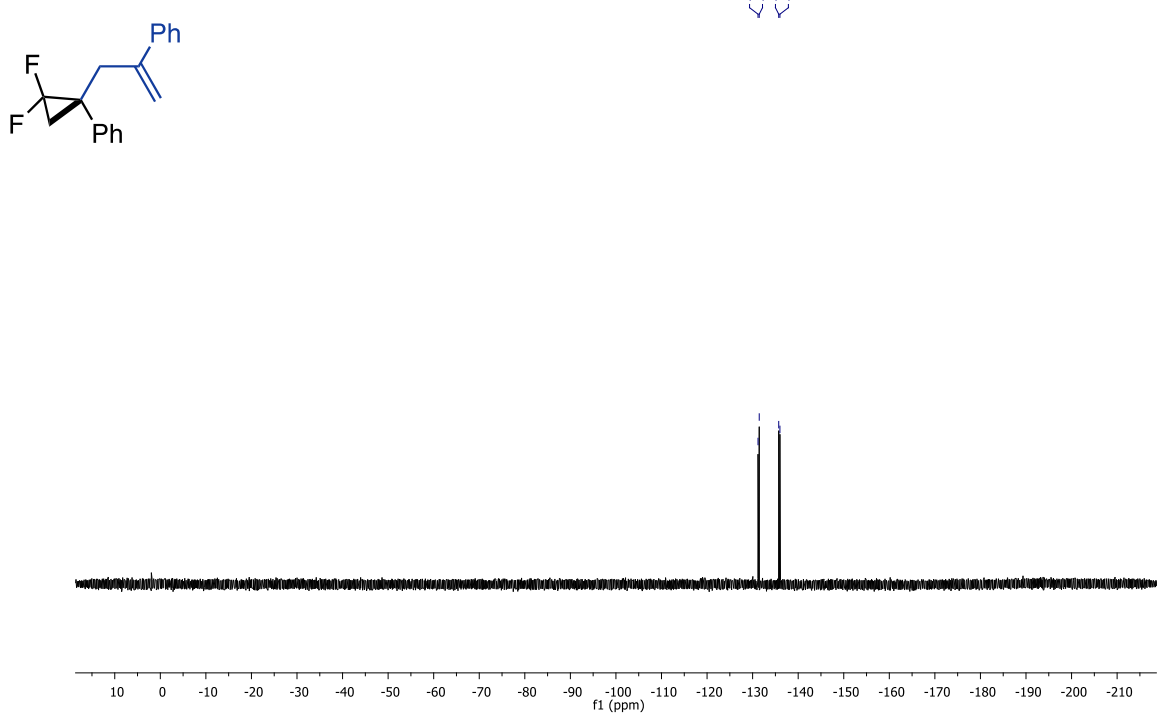
^{1}H NMR (600 MHz, $CDCl_3$) of **3z**



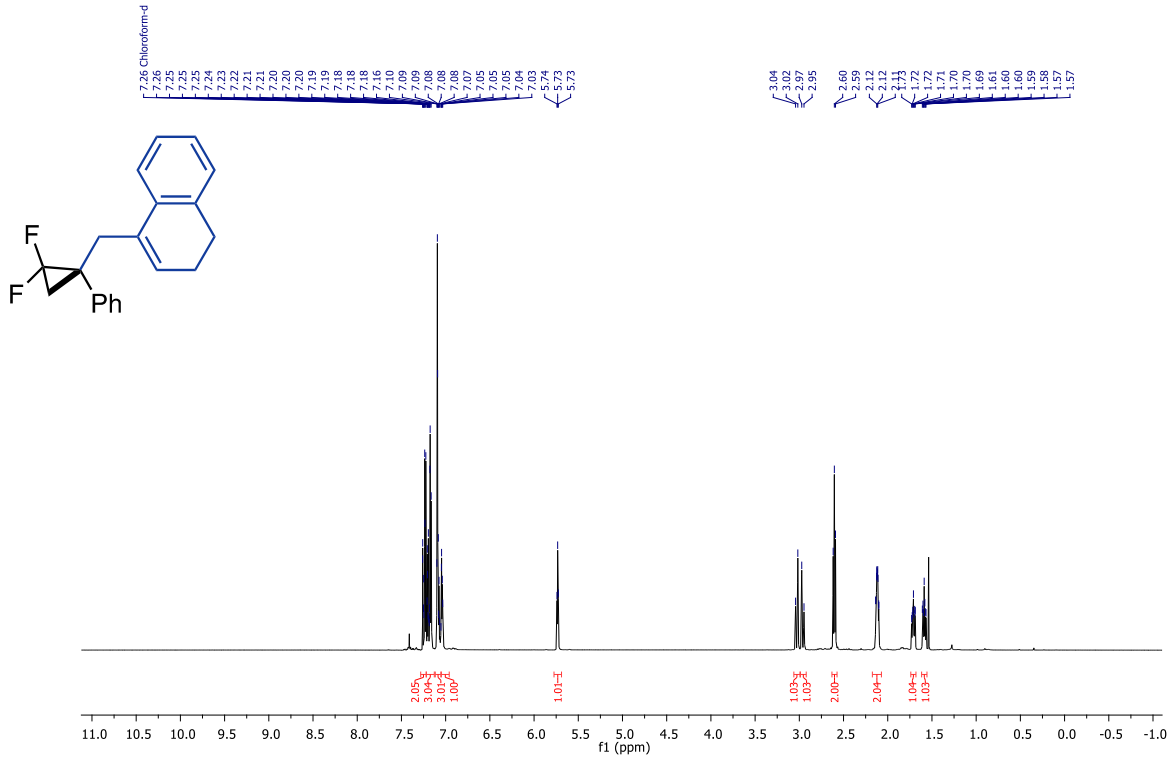
^{13}C NMR (151 MHz, $CDCl_3$) of **3z**



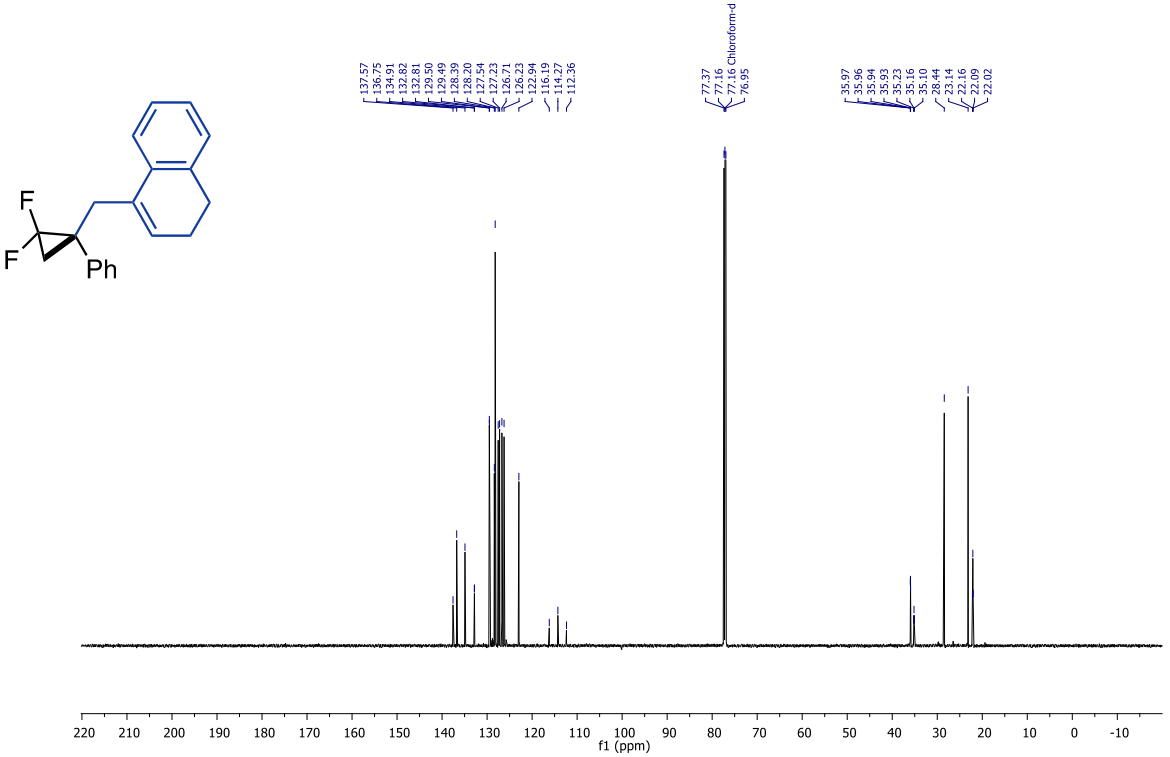
^{19}F NMR (565 MHz, $CDCl_3$) of **3z**



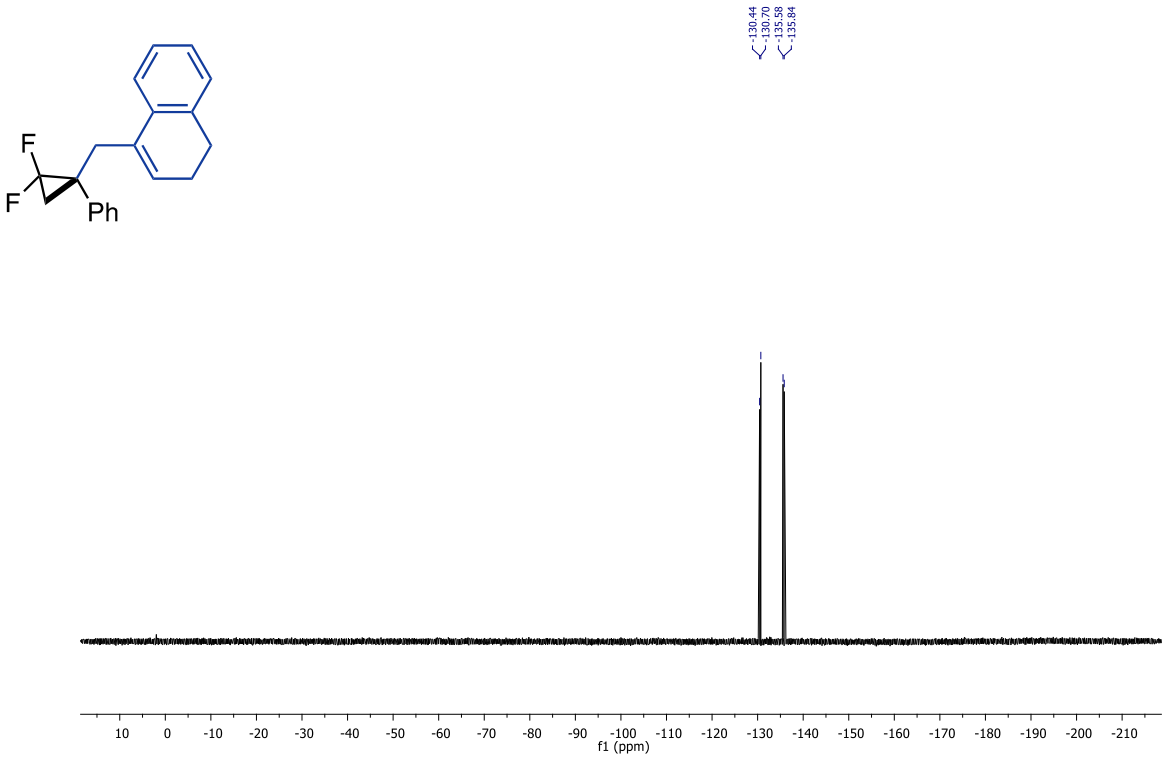
^{1}H NMR (600 MHz, $CDCl_3$) of **3aa**



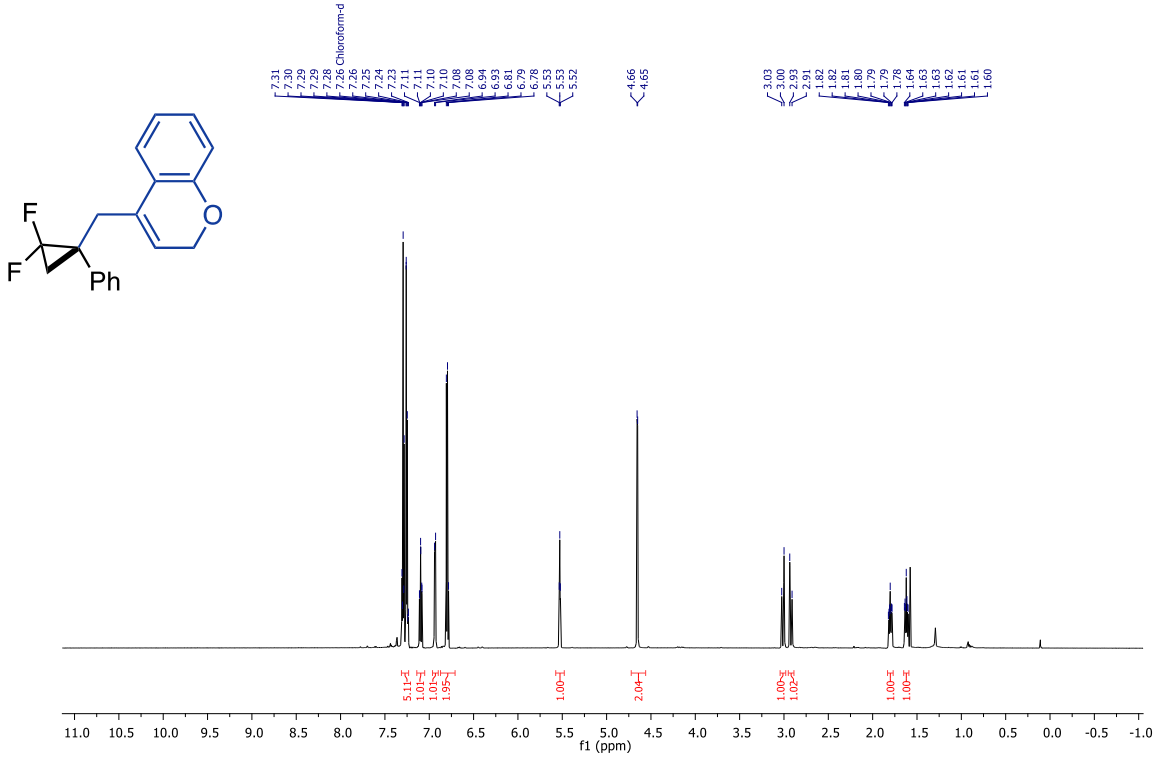
^{13}C NMR (151 MHz, $CDCl_3$) of **3aa**



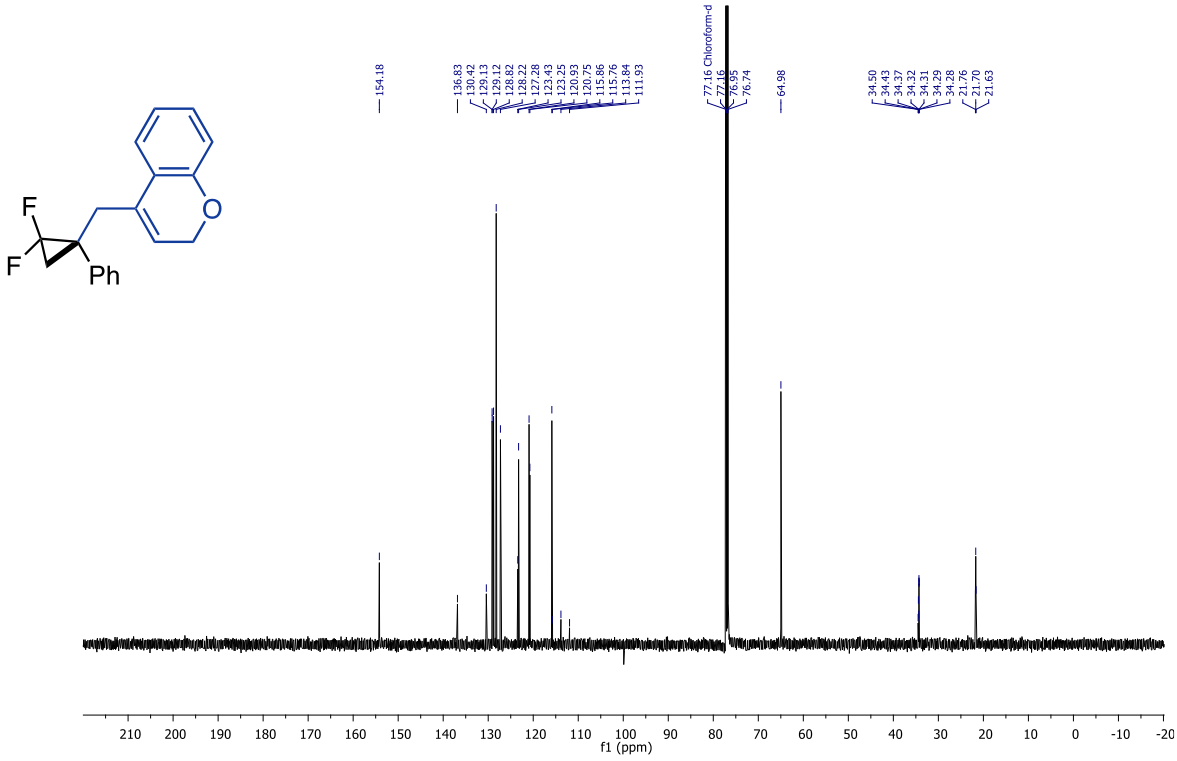
^{19}F NMR (565 MHz, $CDCl_3$) of **3aa**



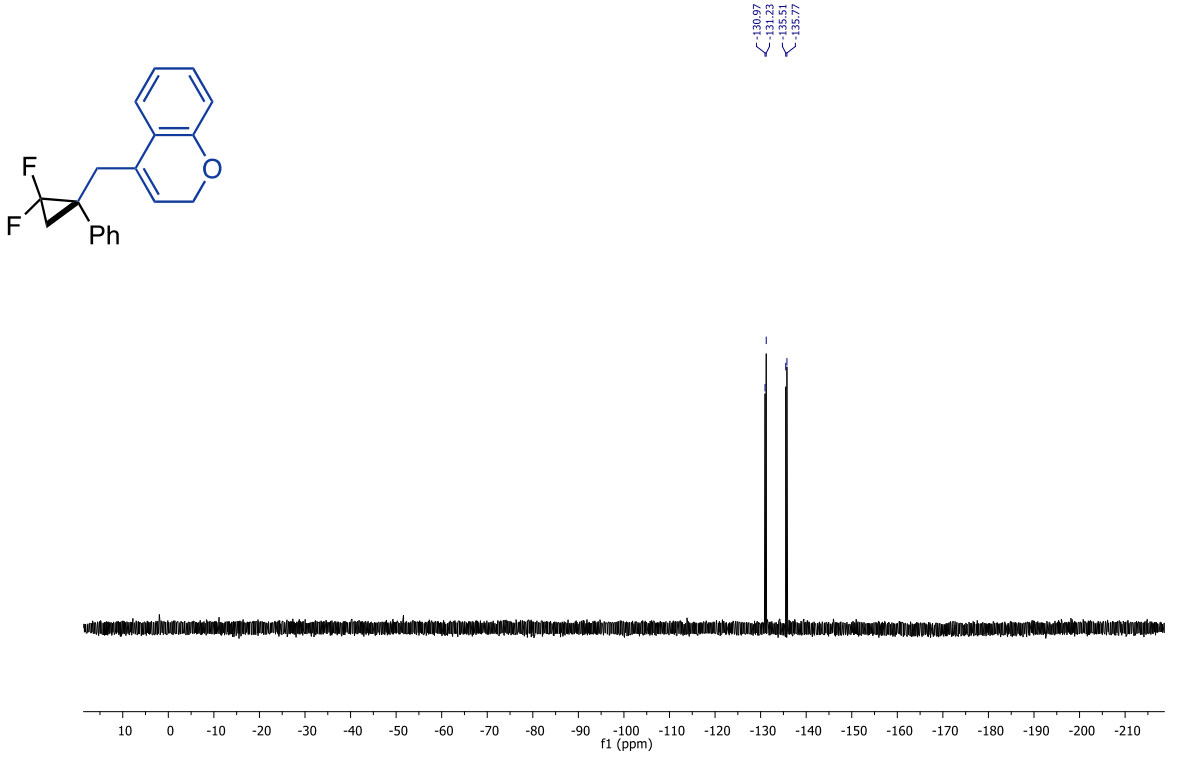
^{1}H NMR (600 MHz, $CDCl_3$) of **3ab**



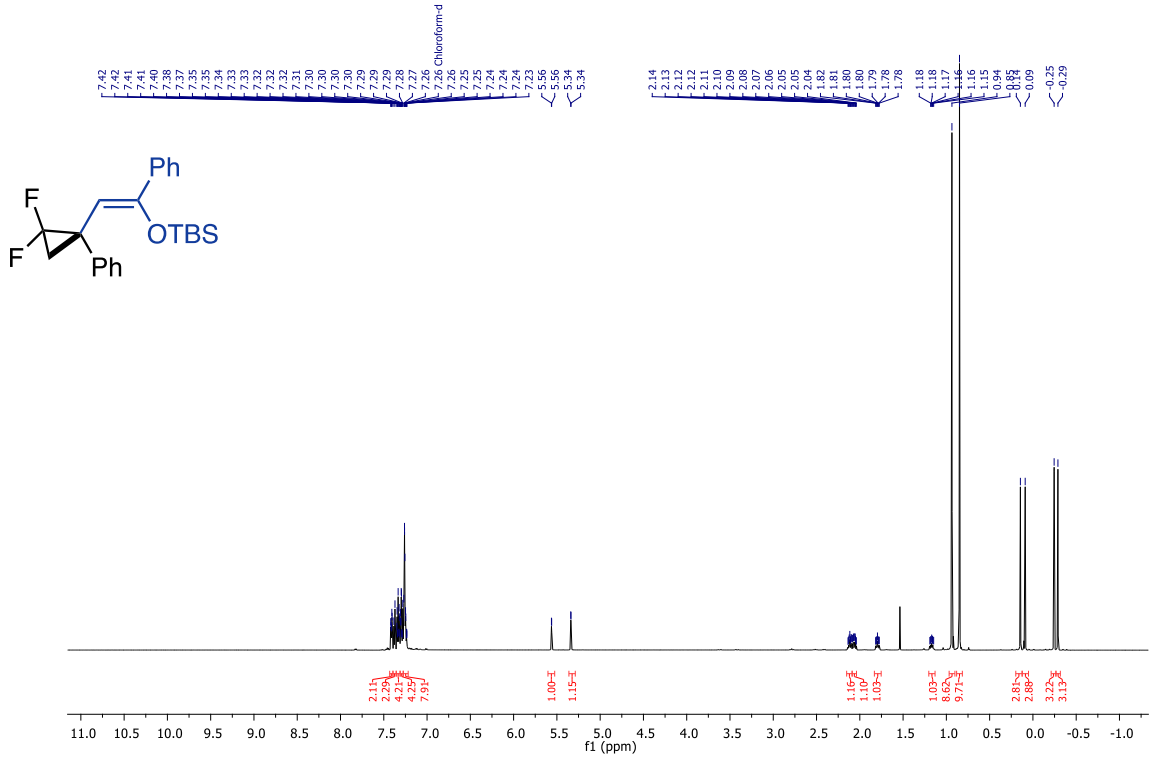
^{13}C NMR (151 MHz, $CDCl_3$) of **3ab**



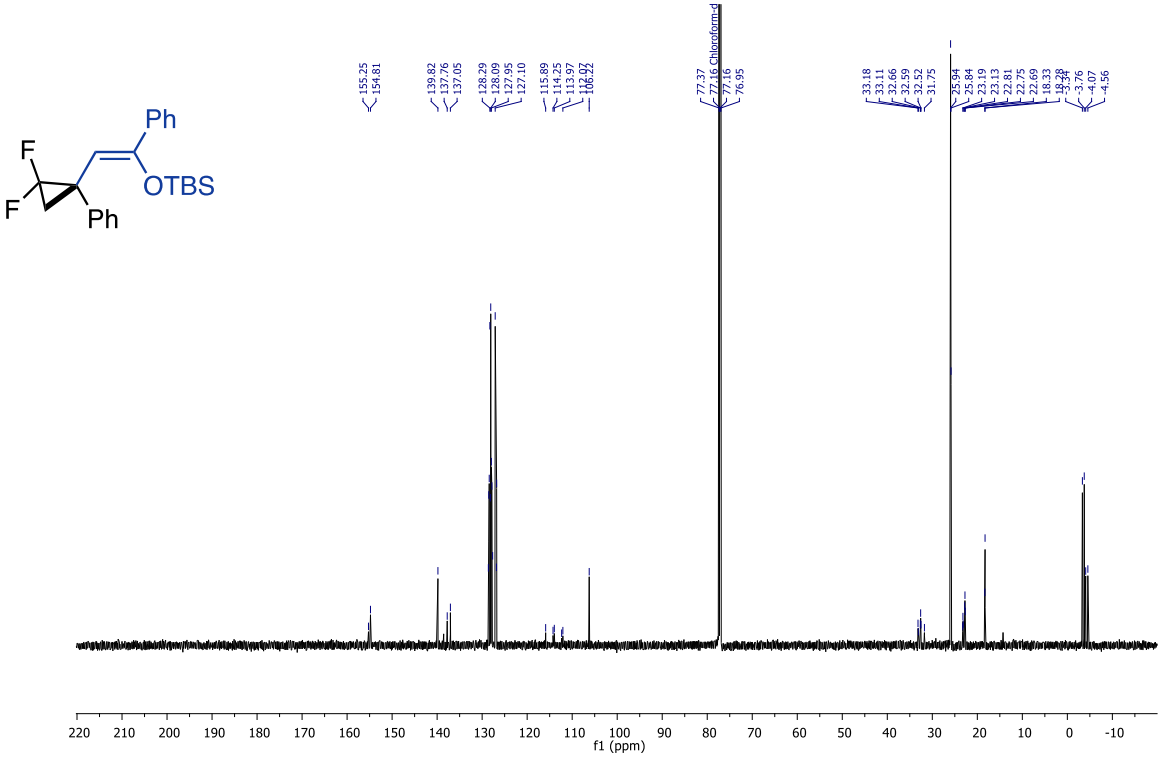
^{19}F NMR (565 MHz, $CDCl_3$) of **3ab**



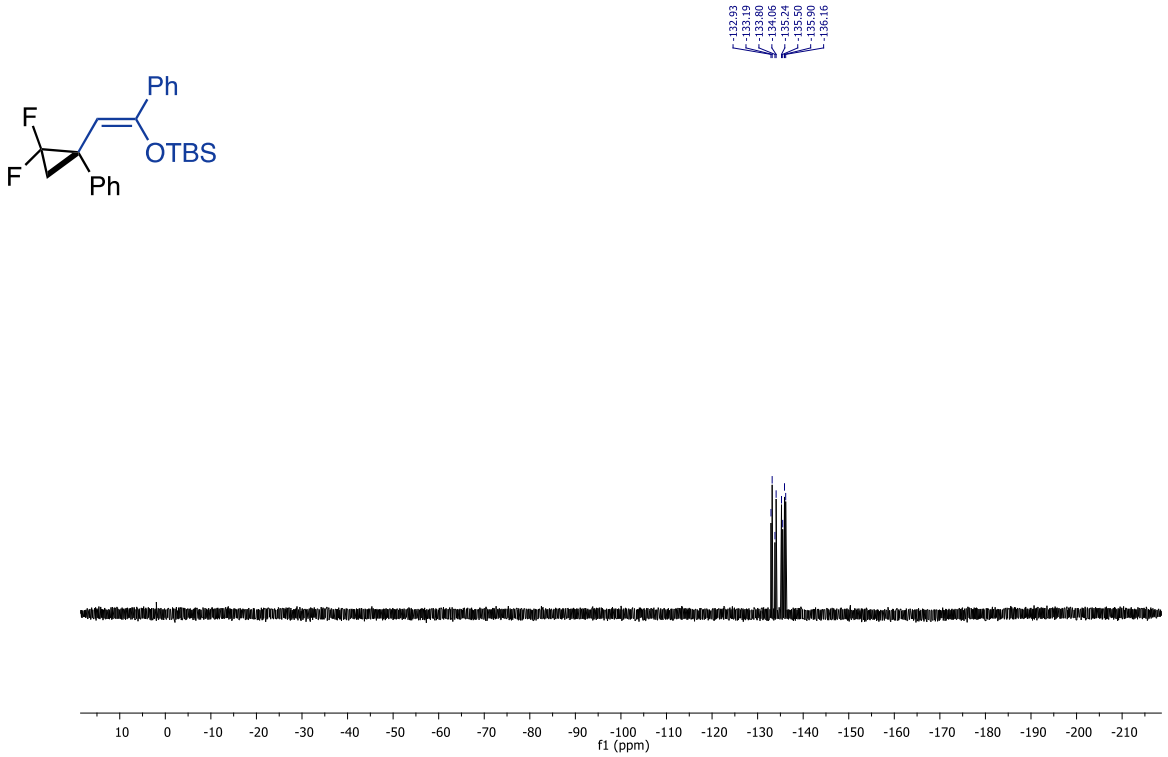
^{1}H NMR (600 MHz, $CDCl_3$) of **3ac**



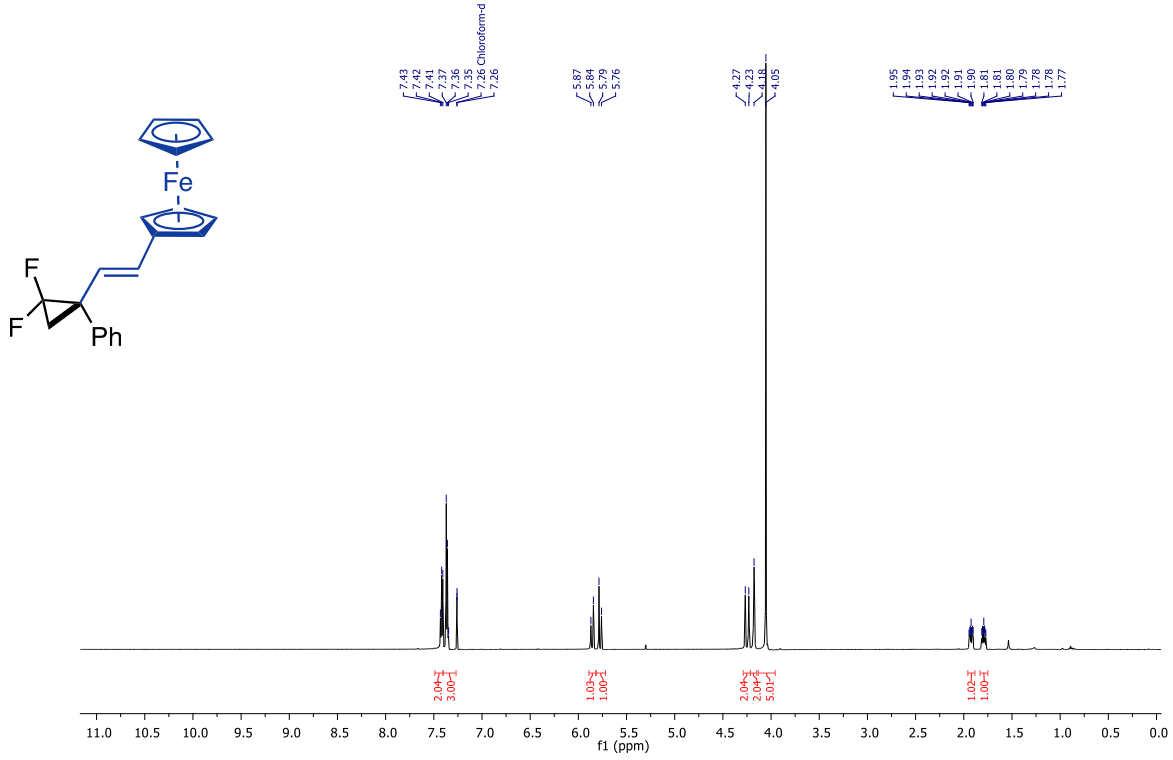
^{13}C NMR (151 MHz, $CDCl_3$) of **3ac**



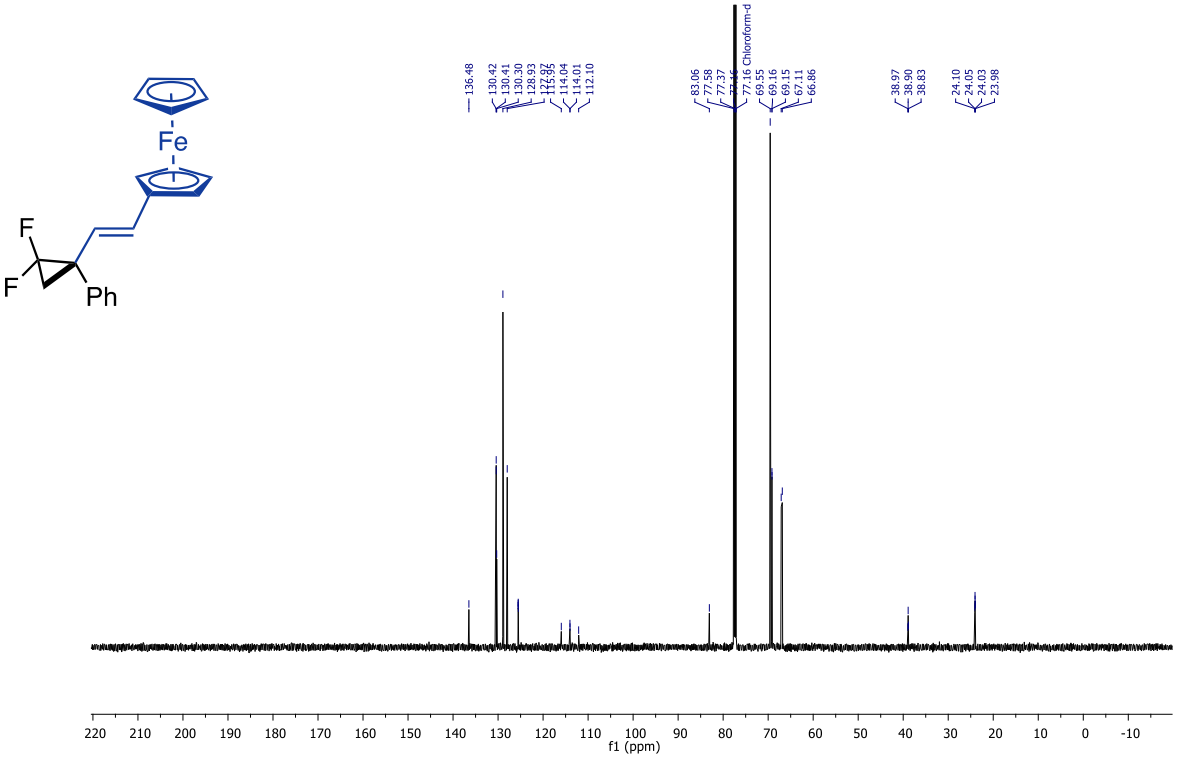
^{19}F NMR (565 MHz, $CDCl_3$) of **3ac**



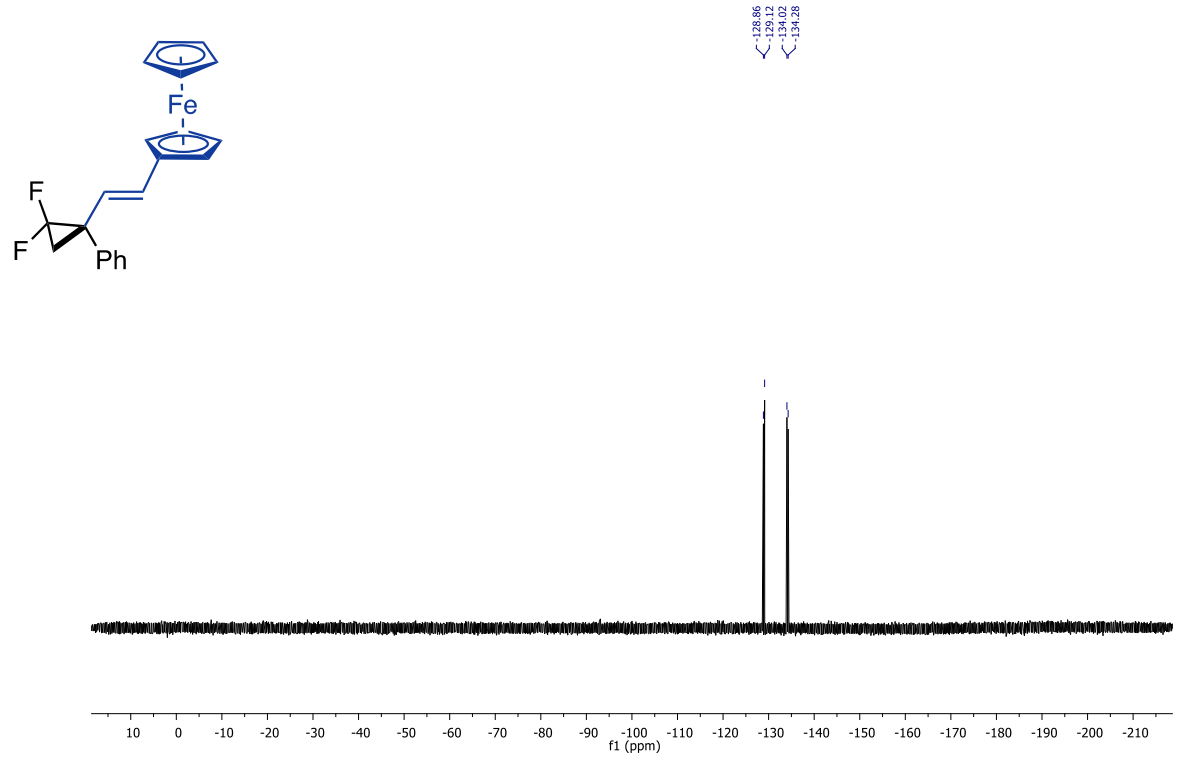
^{1}H NMR (600 MHz, $CDCl_3$) of **3ad**



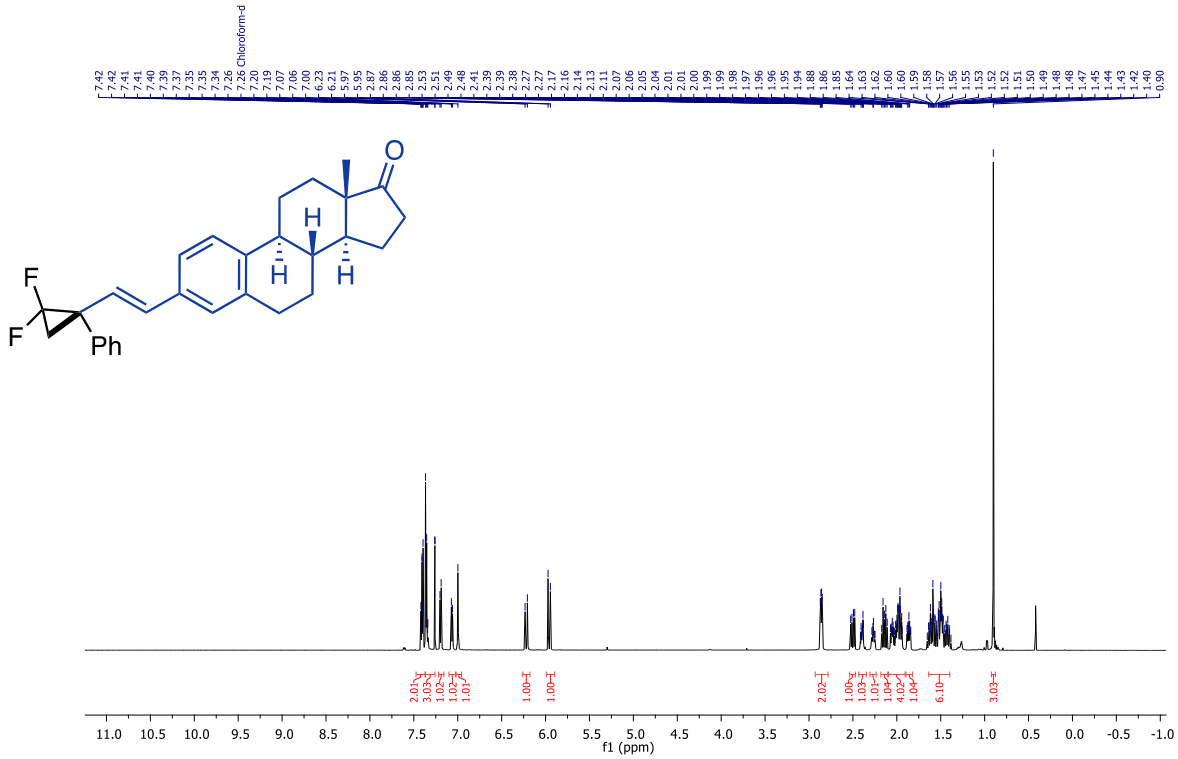
^{13}C NMR (151 MHz, $CDCl_3$) of **3ad**



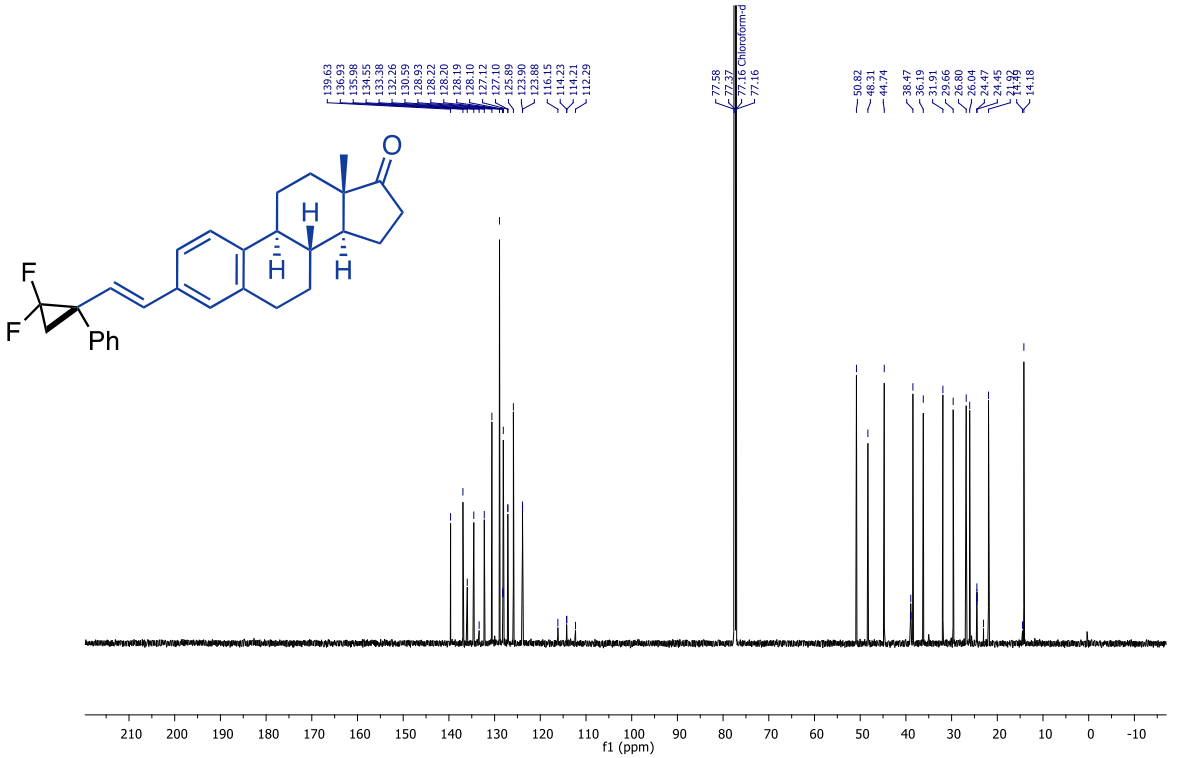
^{19}F NMR (565 MHz, $CDCl_3$) of **3ad**



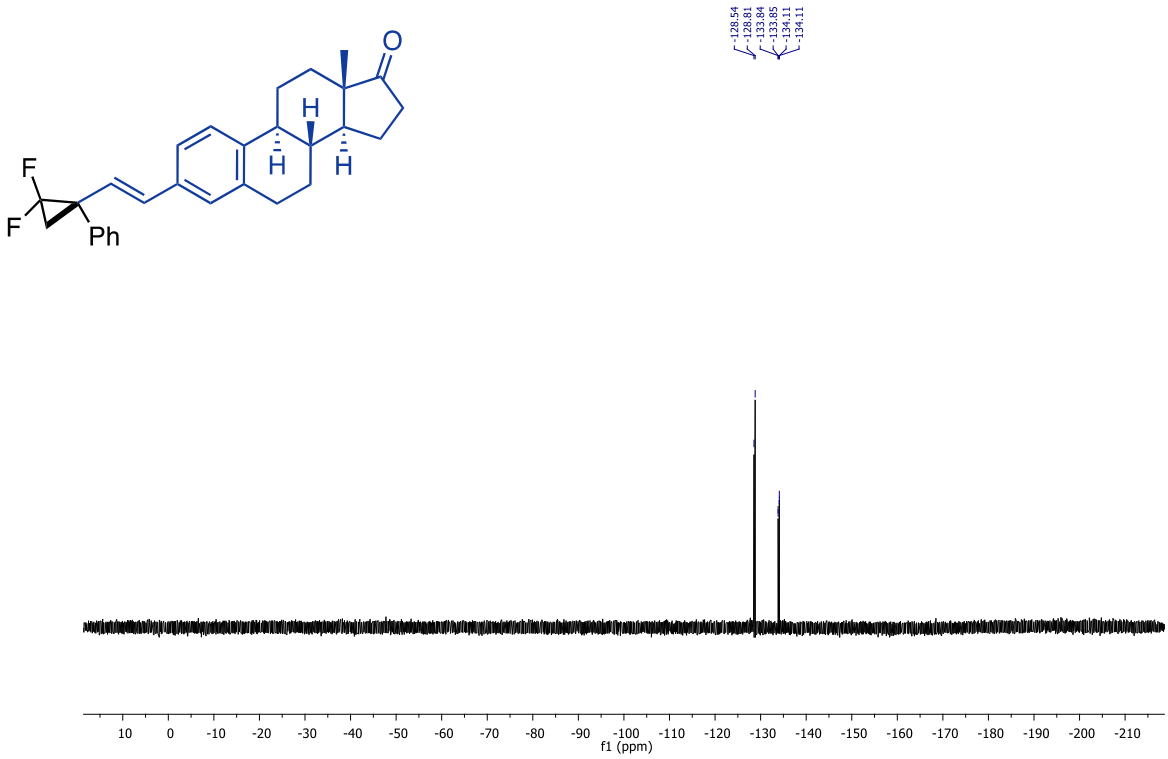
^{1}H NMR (600 MHz, $CDCl_3$) of **3ae**



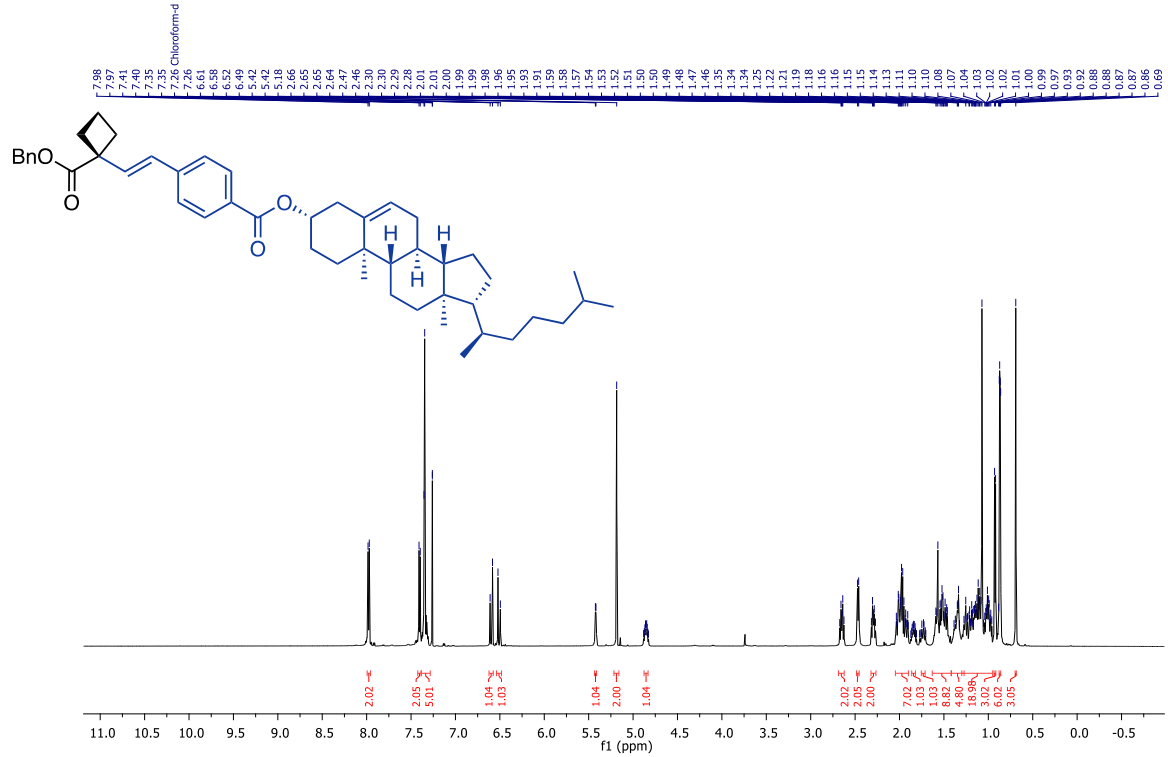
^{13}C NMR (151 MHz, $CDCl_3$) of **3ae**



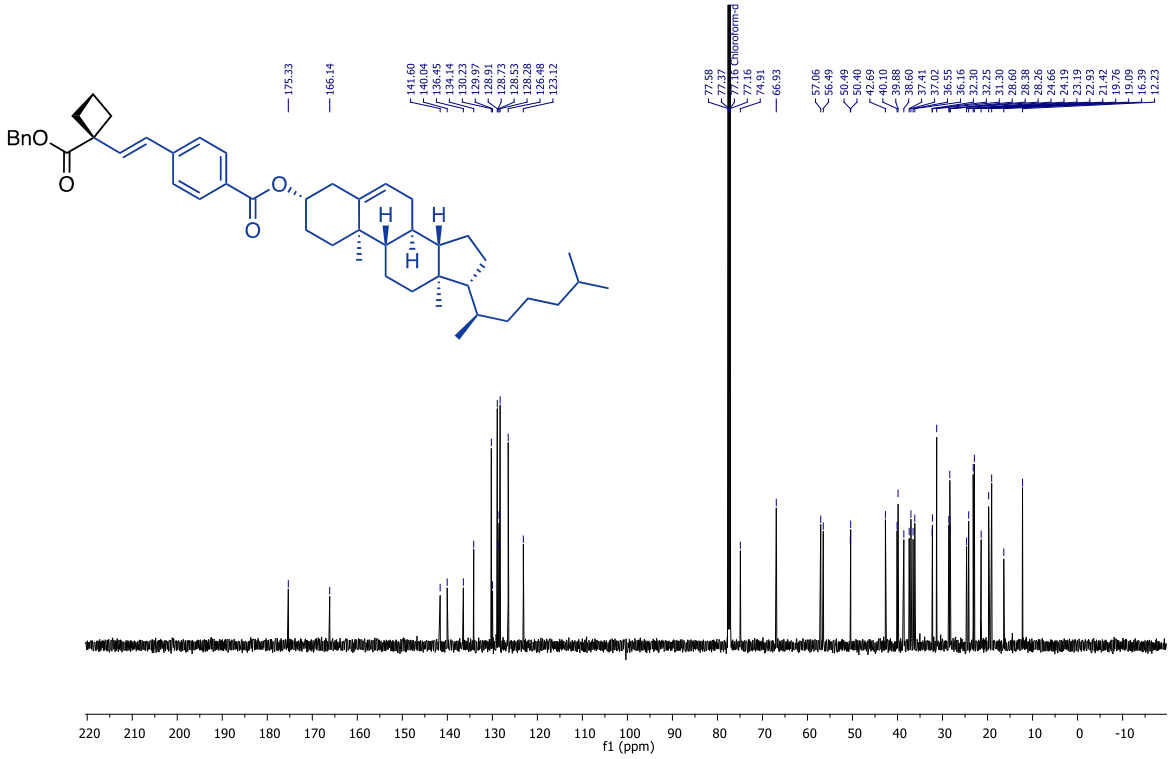
^{19}F NMR (565 MHz, $CDCl_3$) of **3ae**



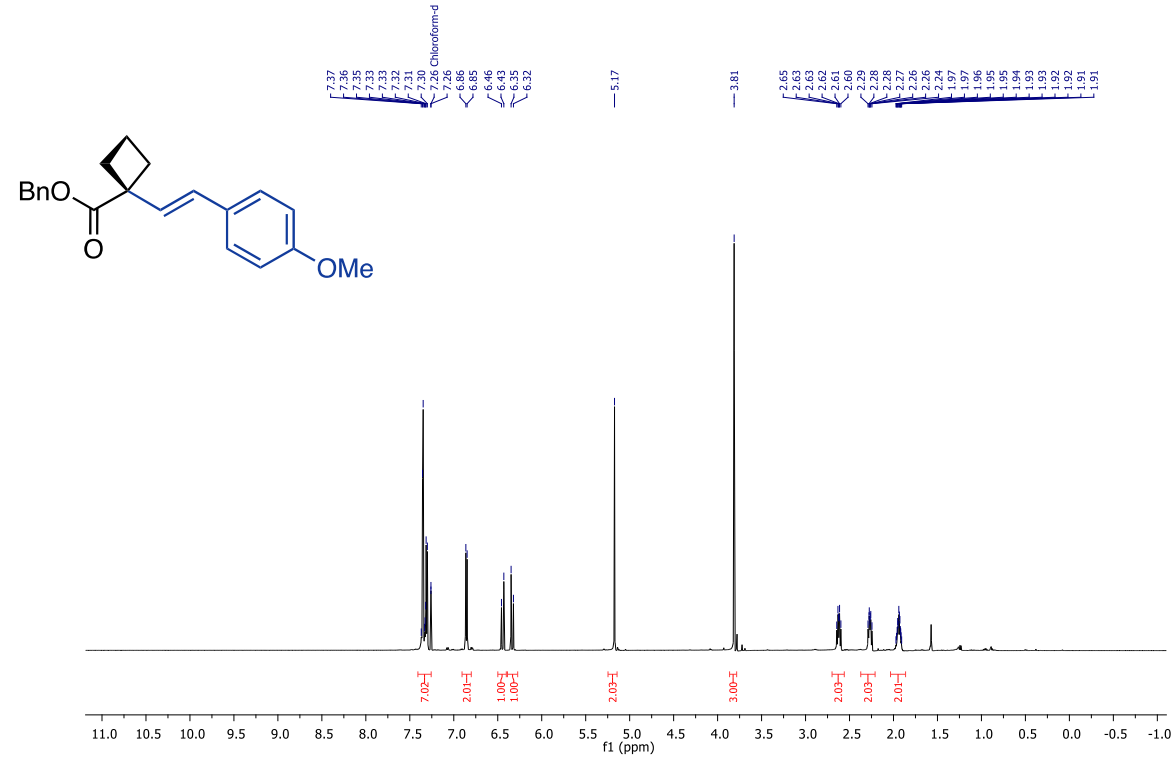
^{1}H NMR (600 MHz, $CDCl_3$) of **5b**



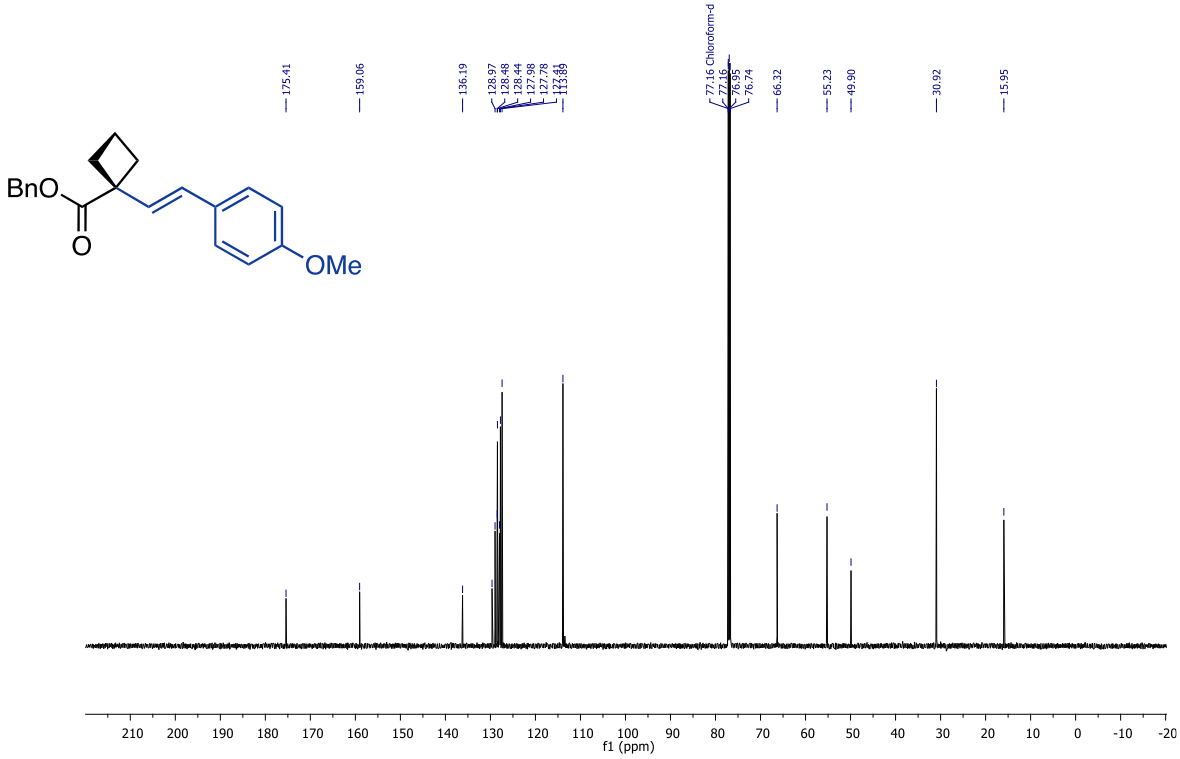
^{13}C NMR (151 MHz, $CDCl_3$) of **5b**



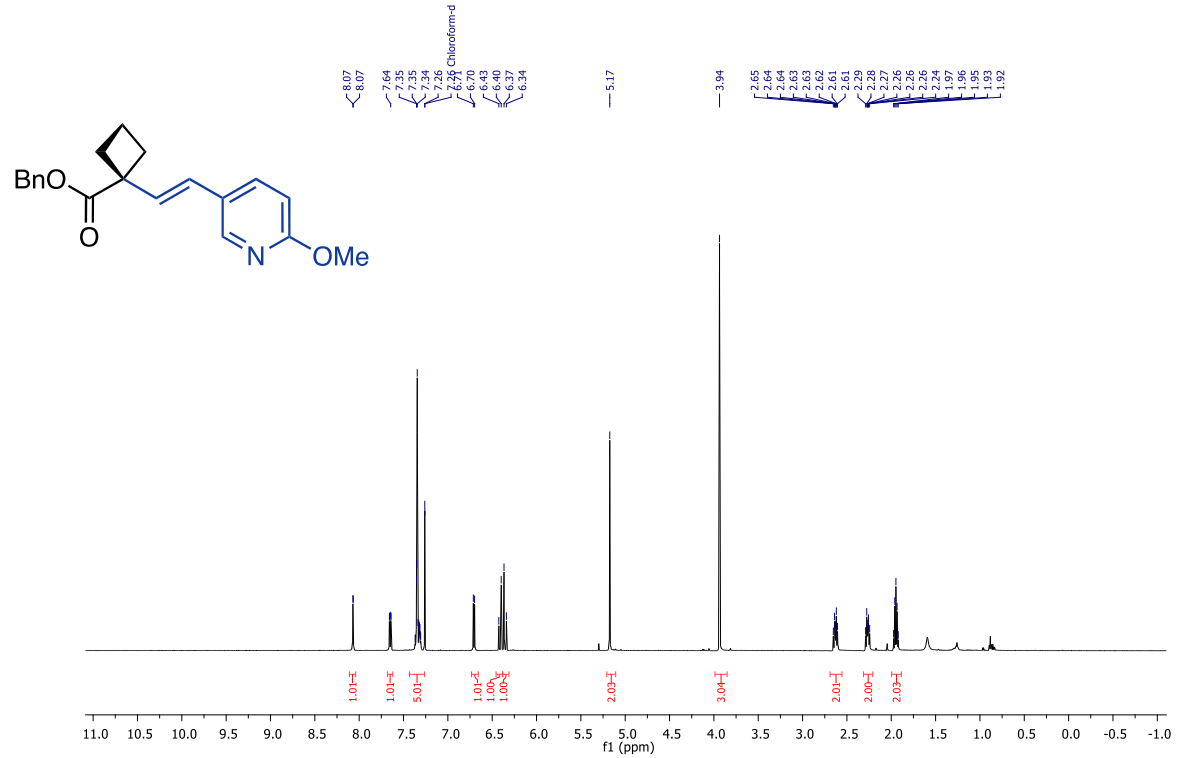
^{1}H NMR (600 MHz, $CDCl_3$) of **5c**



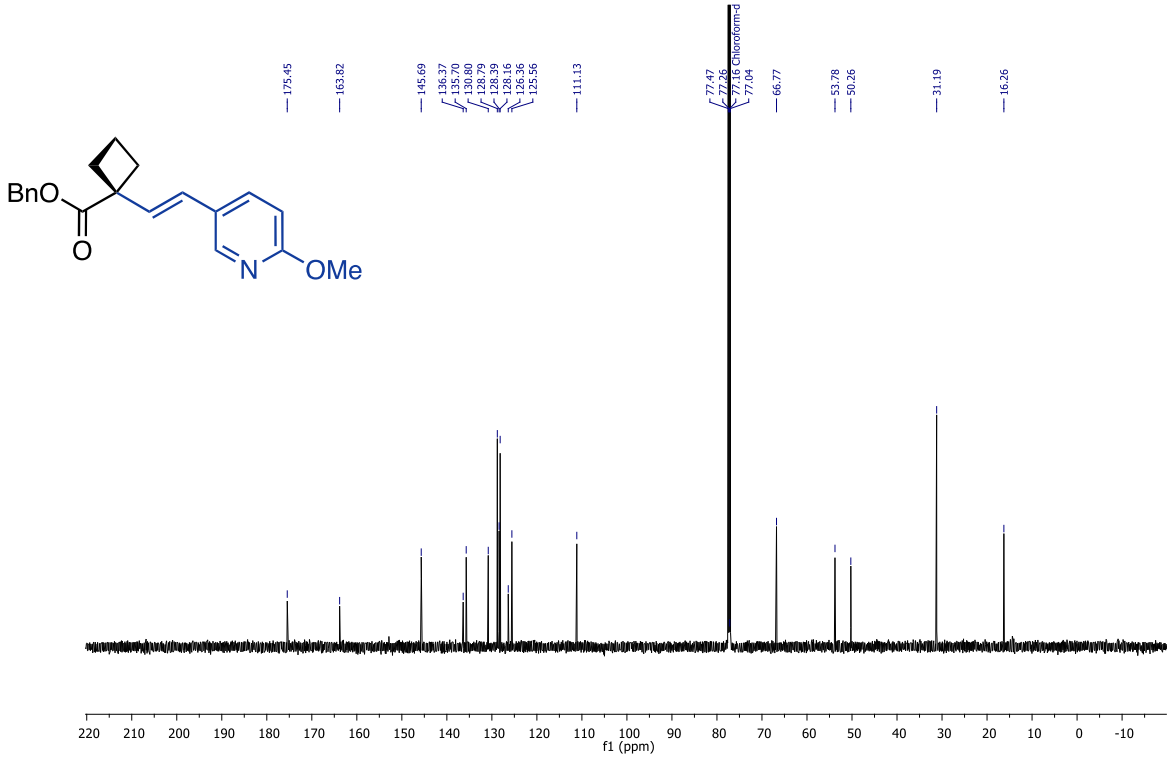
^{13}C NMR (151 MHz, $CDCl_3$) of **5c**



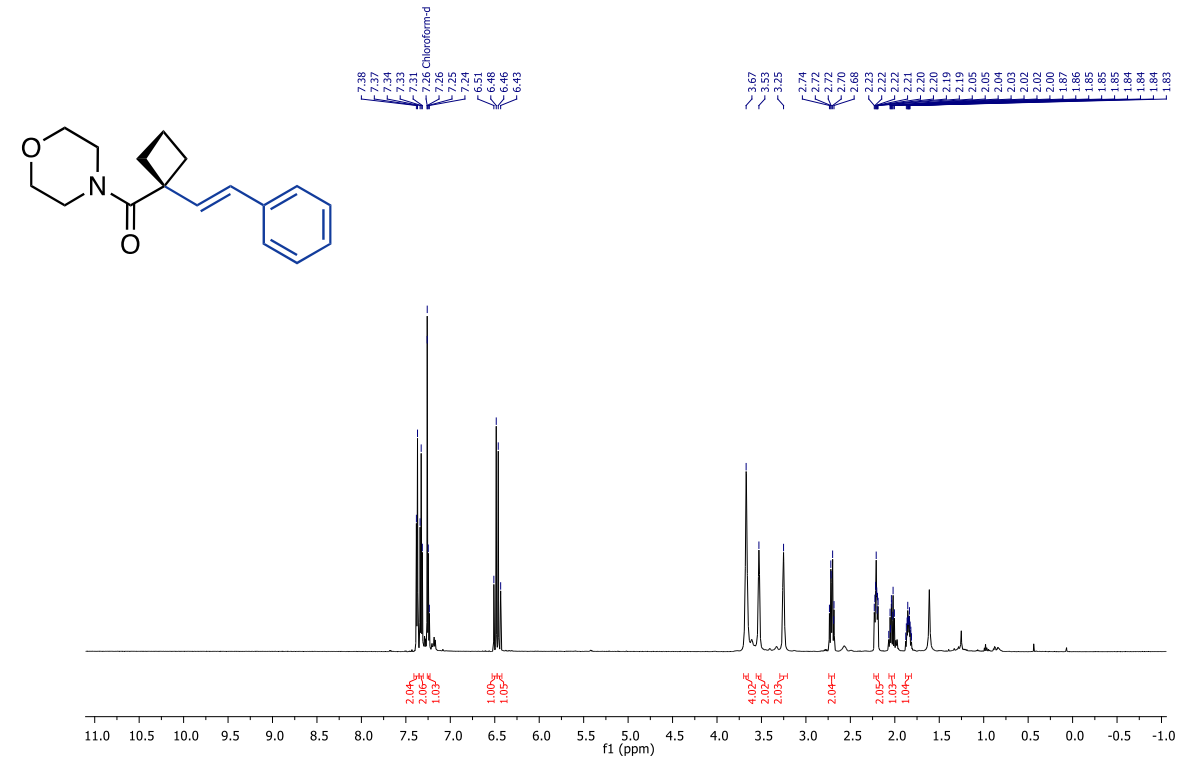
^{1}H NMR (600 MHz, $CDCl_3$) of **5d**



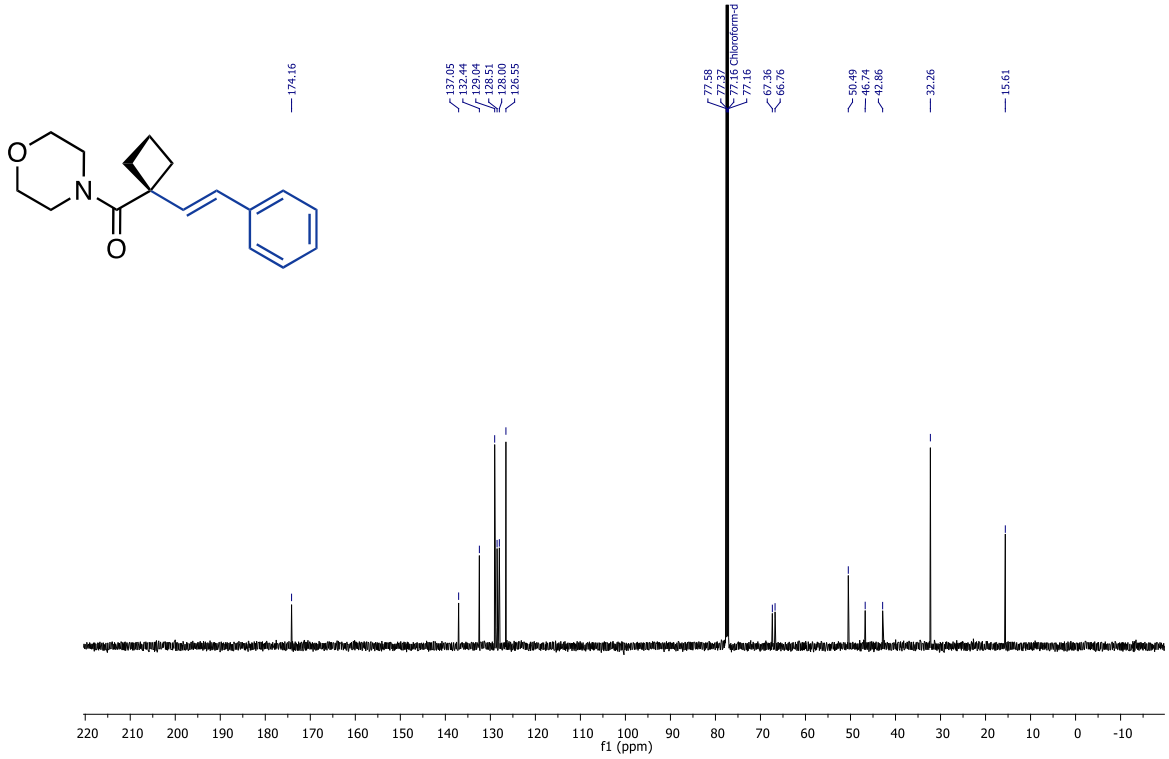
^{13}C NMR (151 MHz, $CDCl_3$) of **5d**



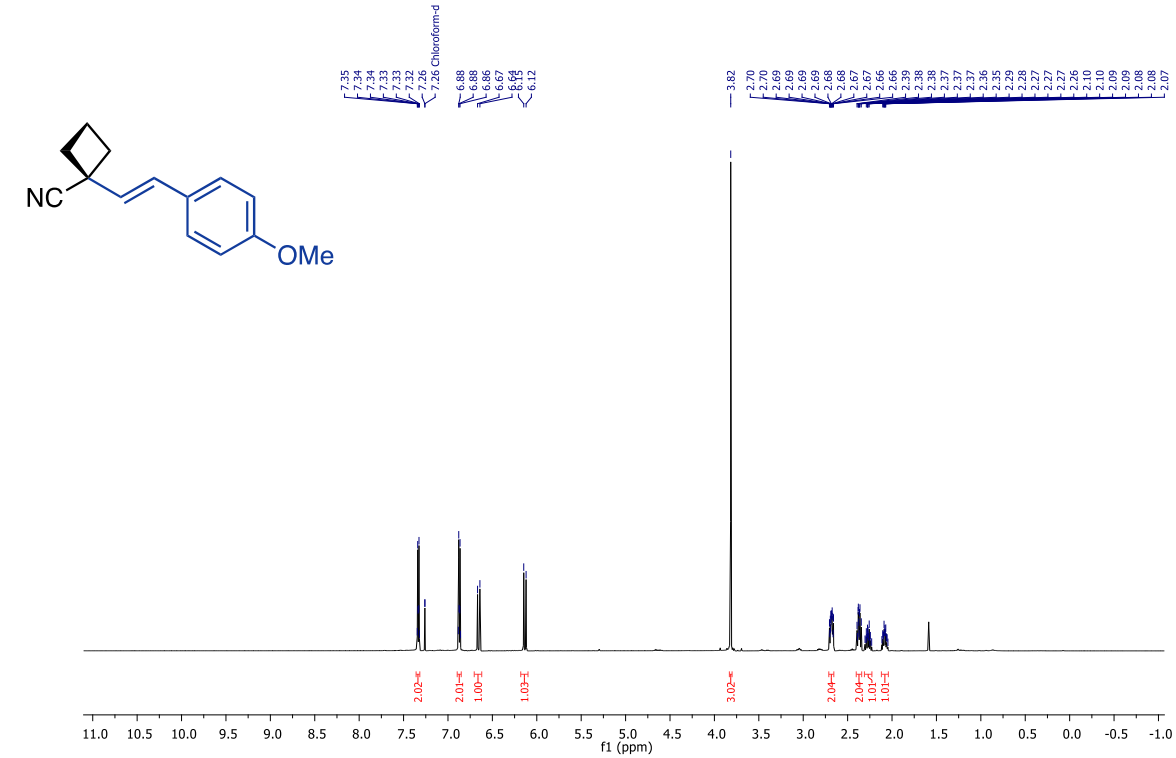
^{1}H NMR (600 MHz, $CDCl_3$) of **5e**



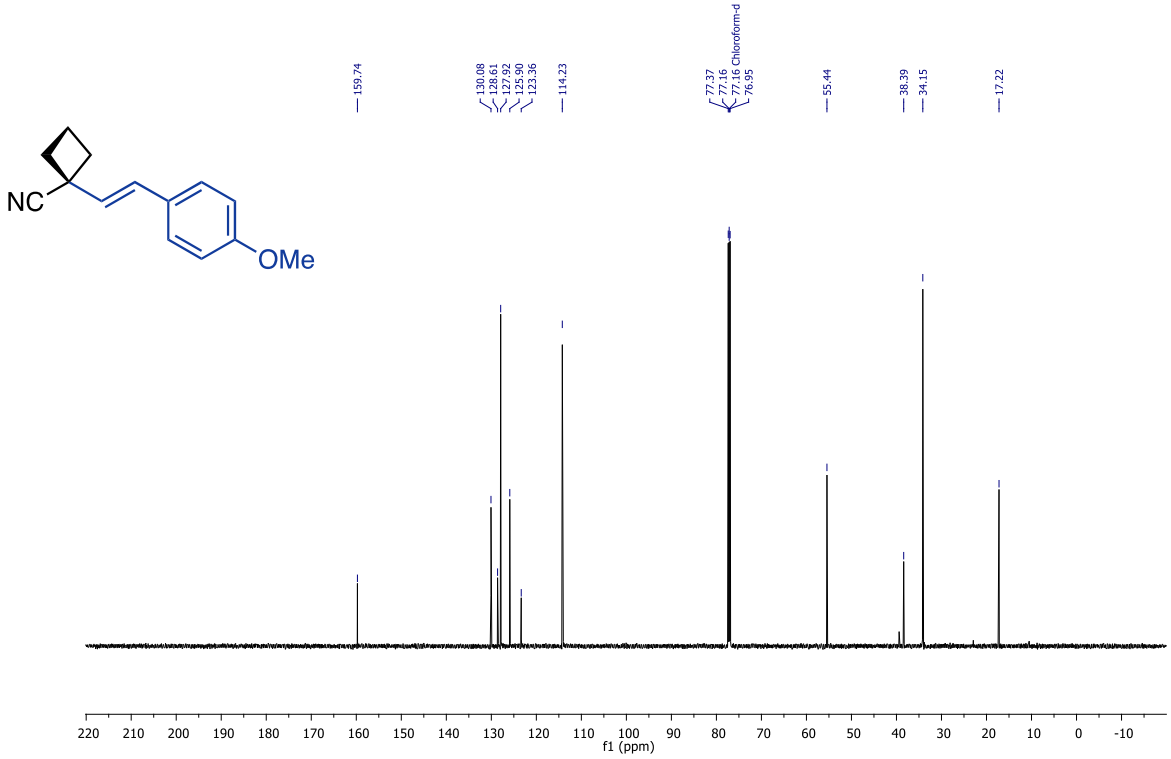
^{13}C NMR (151 MHz, $CDCl_3$) of **5e**



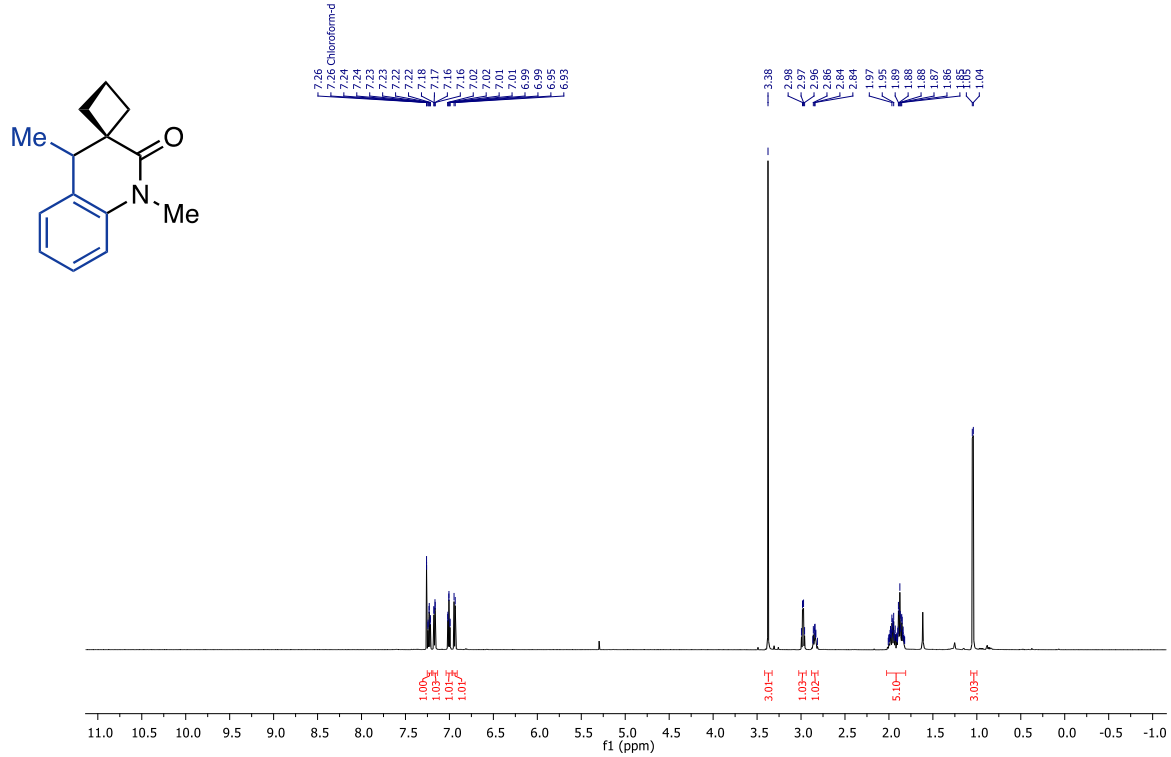
^{1}H NMR (600 MHz, $CDCl_3$) of **5f**



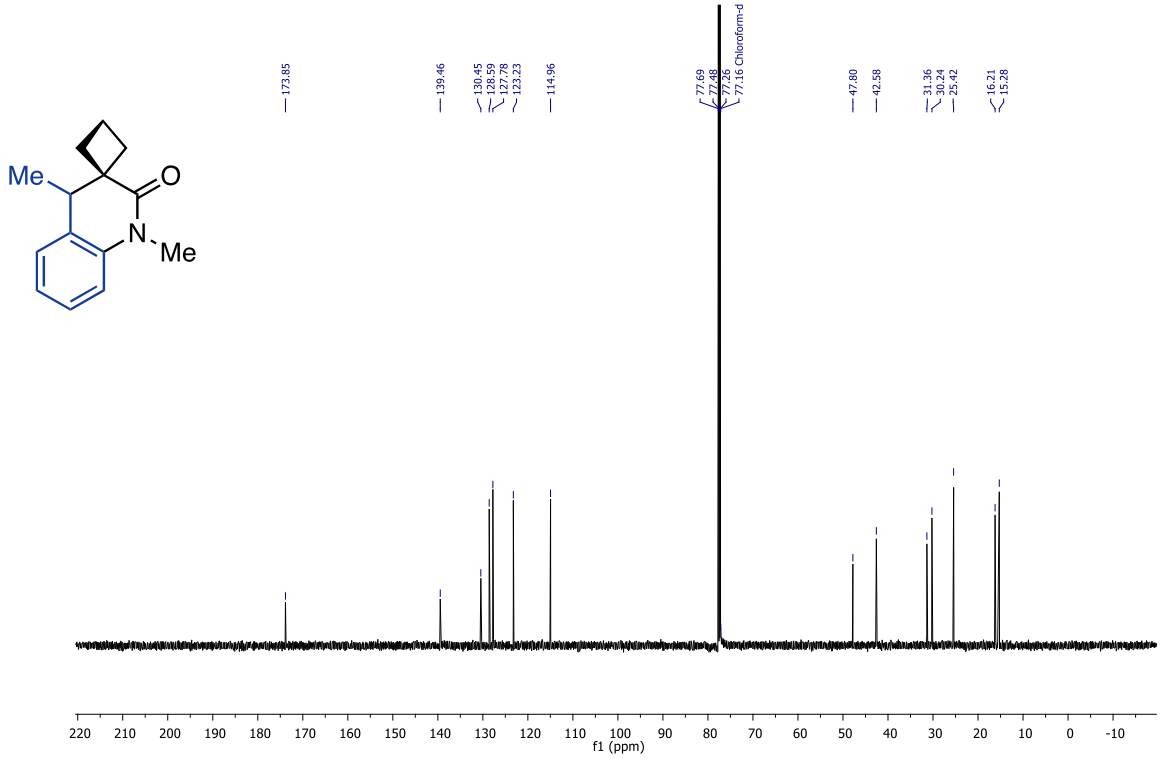
^{13}C NMR (151 MHz, $CDCl_3$) of **5f**



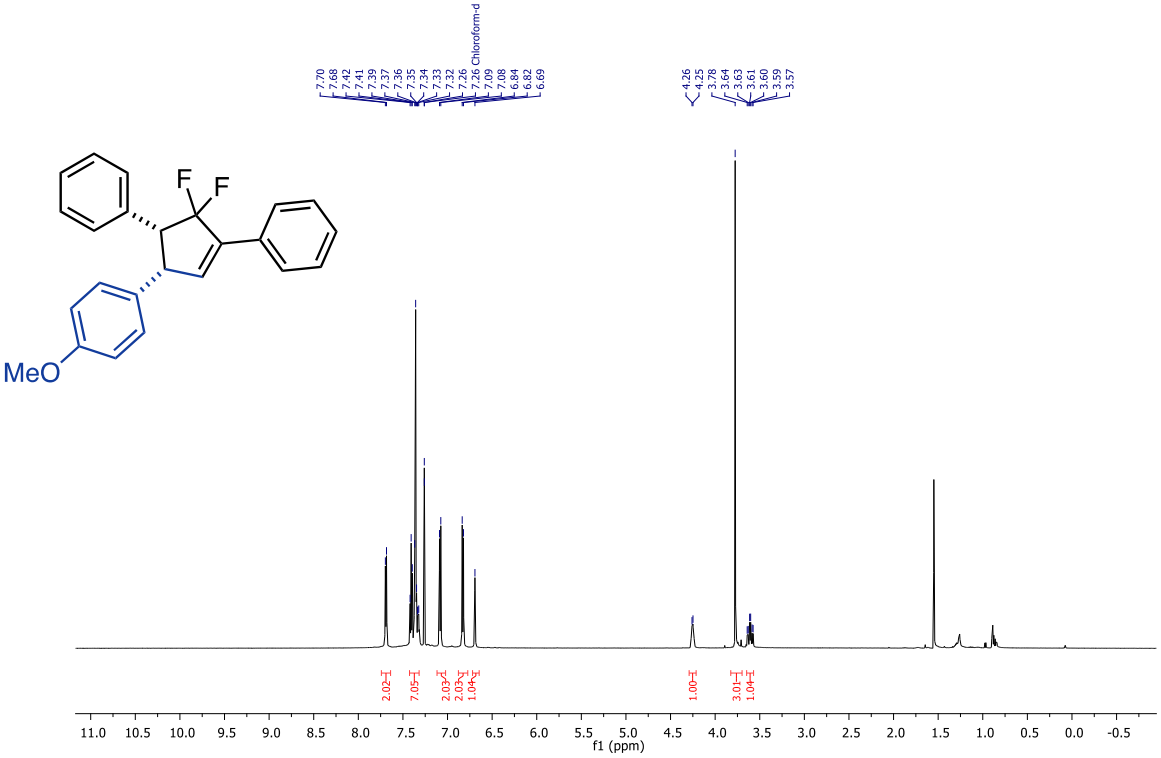
^{1}H NMR (600 MHz, $CDCl_3$) of **5g**



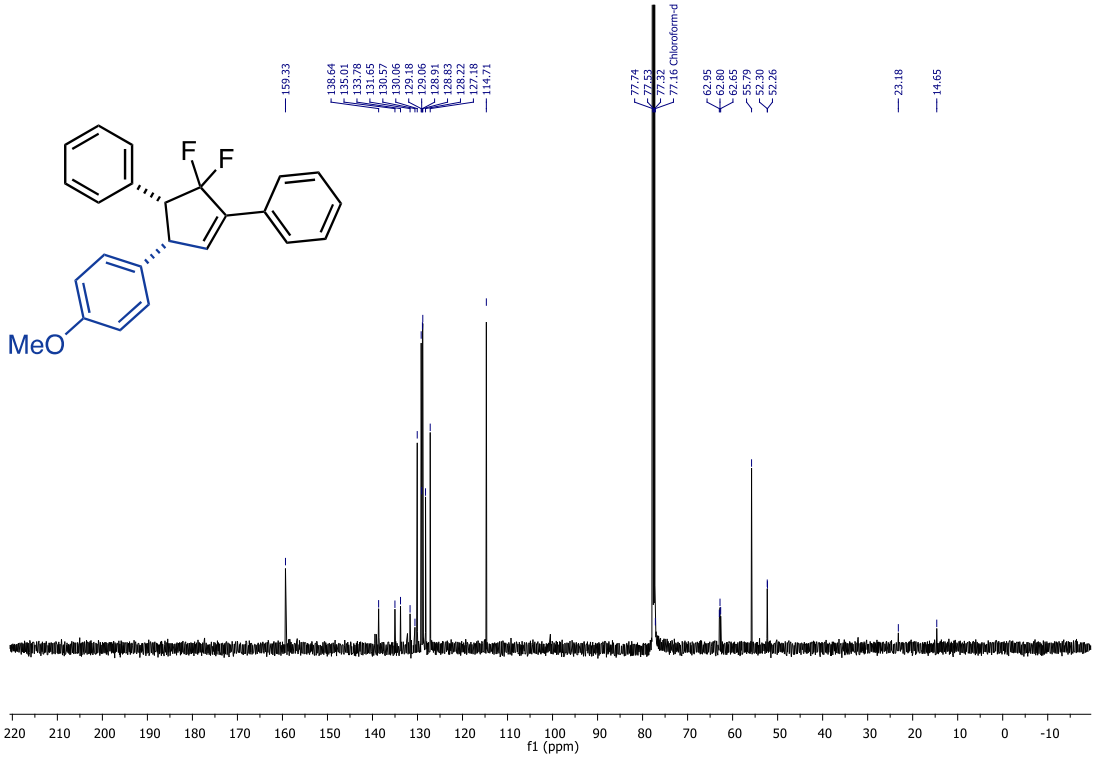
^{13}C NMR (151 MHz, $CDCl_3$) of **5g**



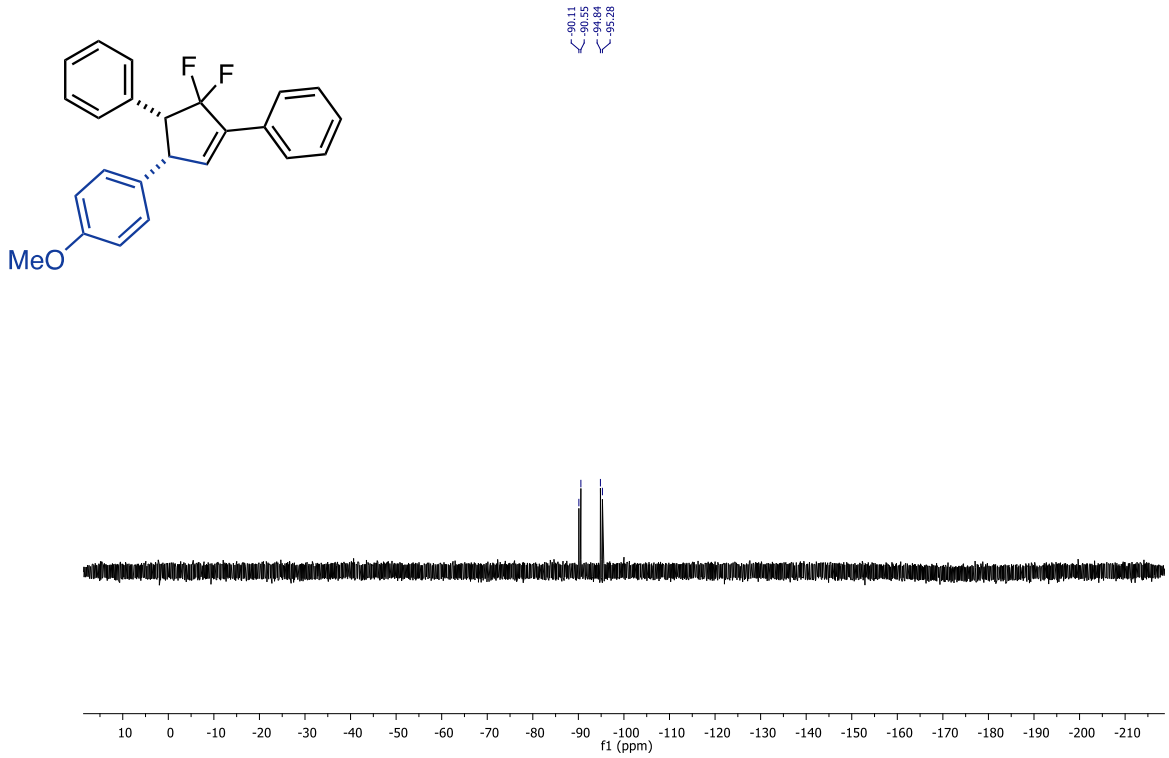
^{1}H NMR (600 MHz, $CDCl_3$) of **6a**



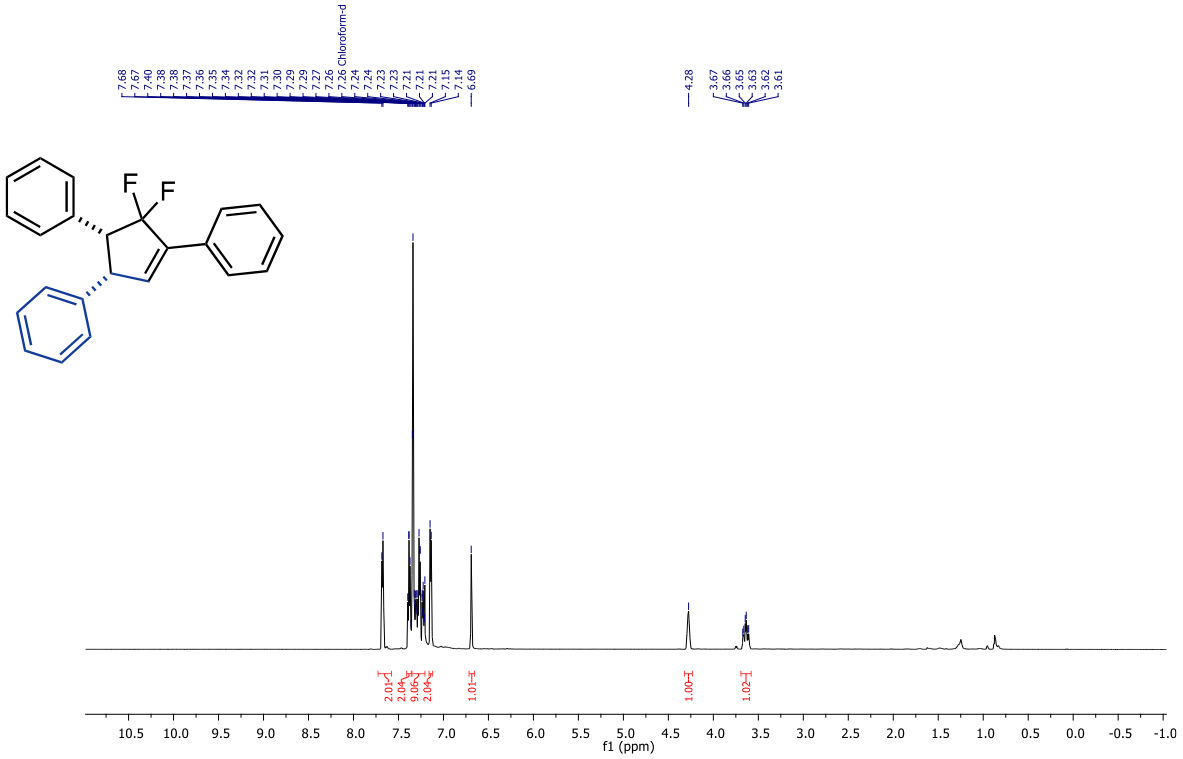
^{13}C NMR (151 MHz, $CDCl_3$) of **6a**



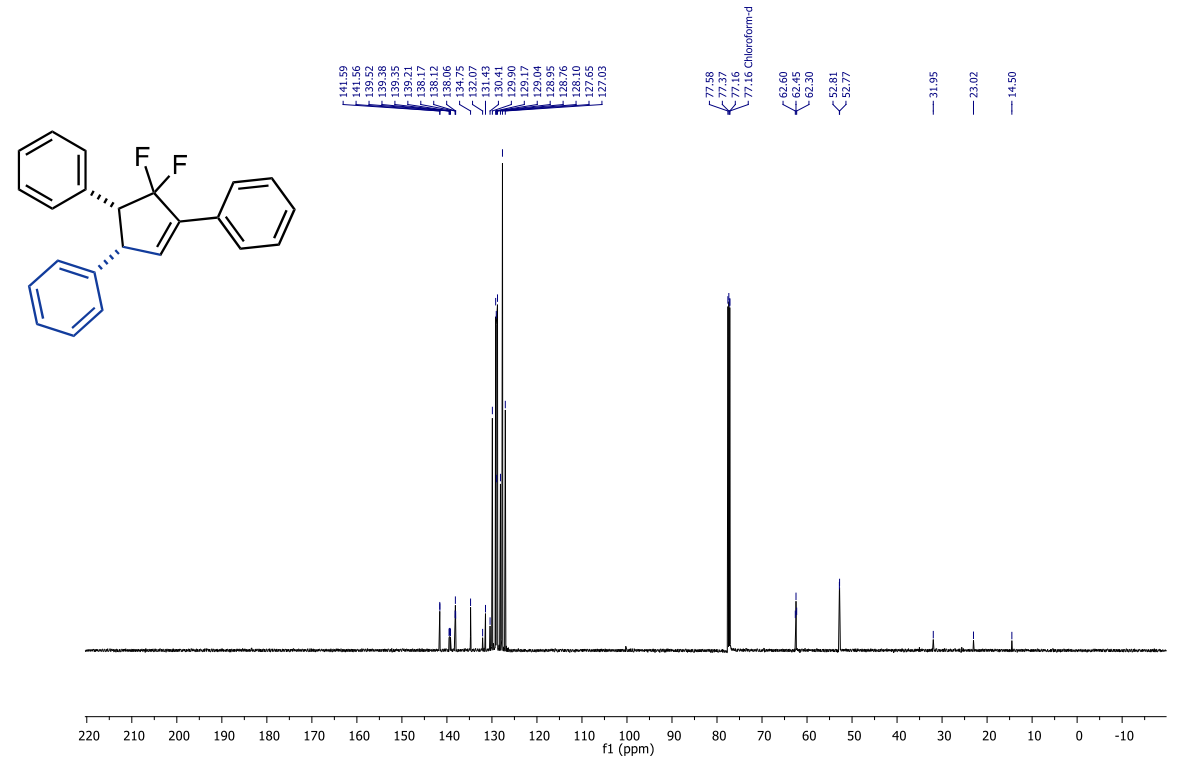
^{19}F NMR (565 MHz, $CDCl_3$) of **6a**



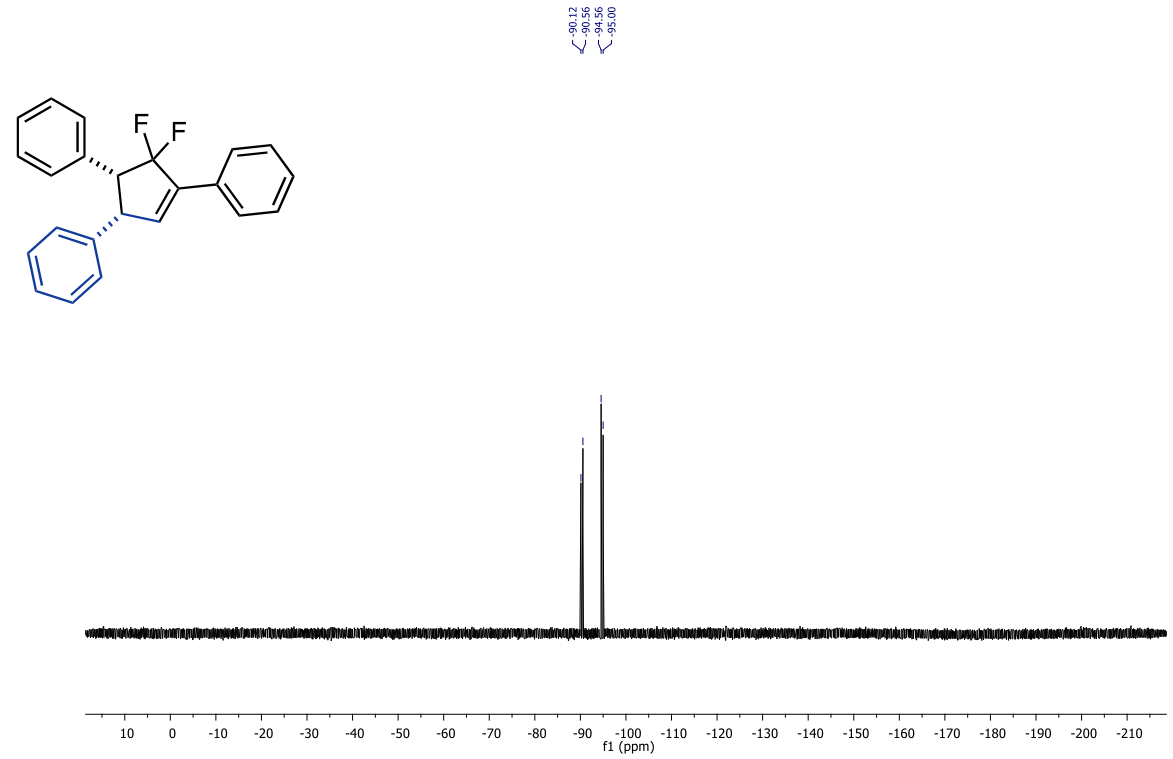
^{1}H NMR (600 MHz, $CDCl_3$) of **6b**



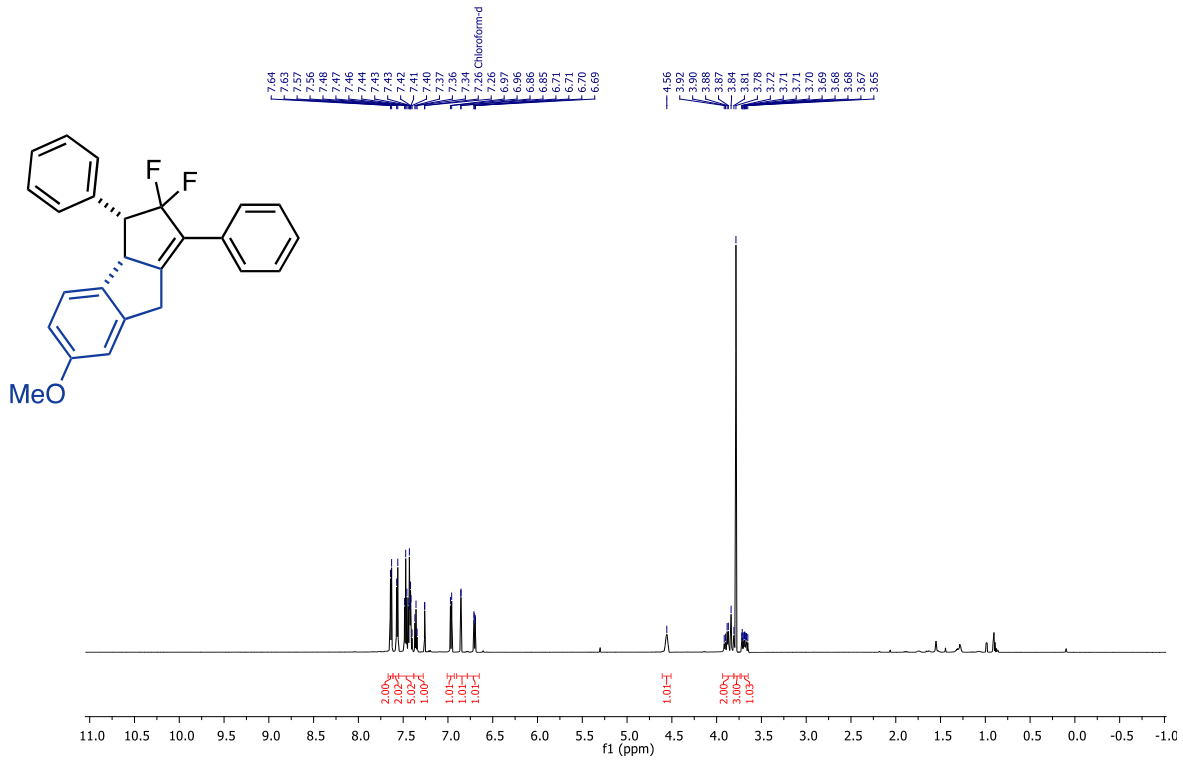
^{13}C NMR (151 MHz, $CDCl_3$) of **6b**



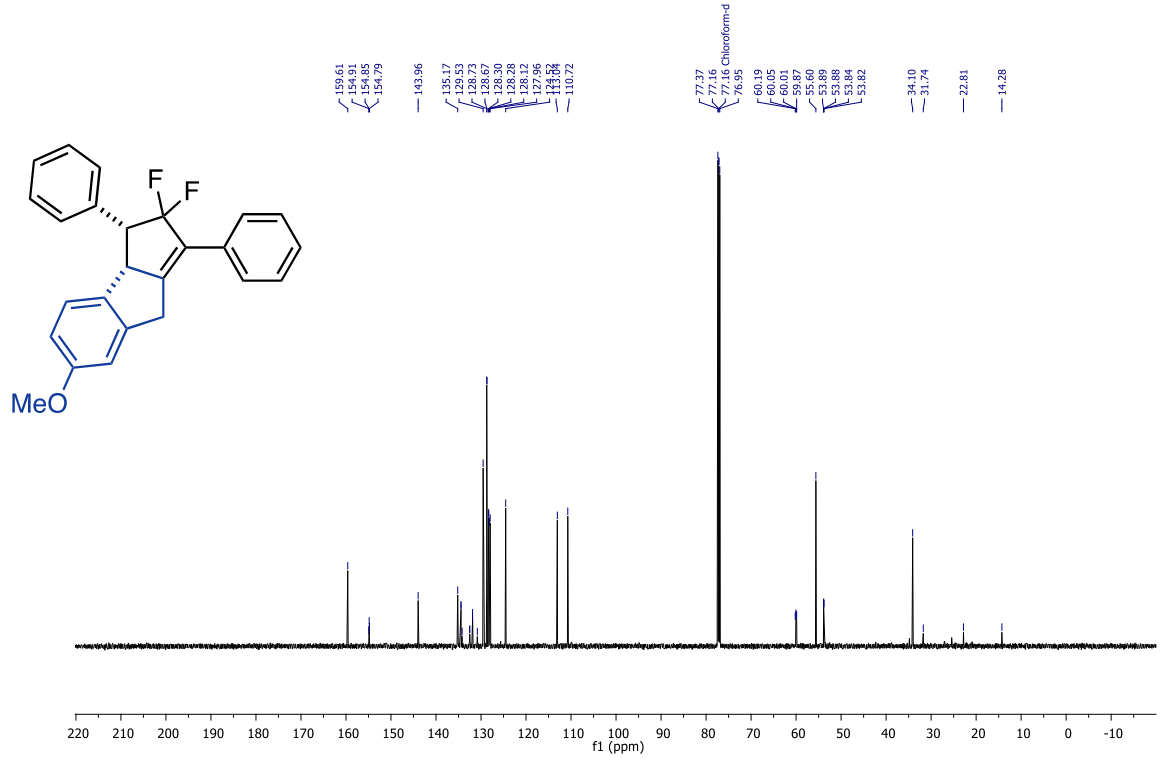
^{19}F NMR (565 MHz, $CDCl_3$) of **6b**



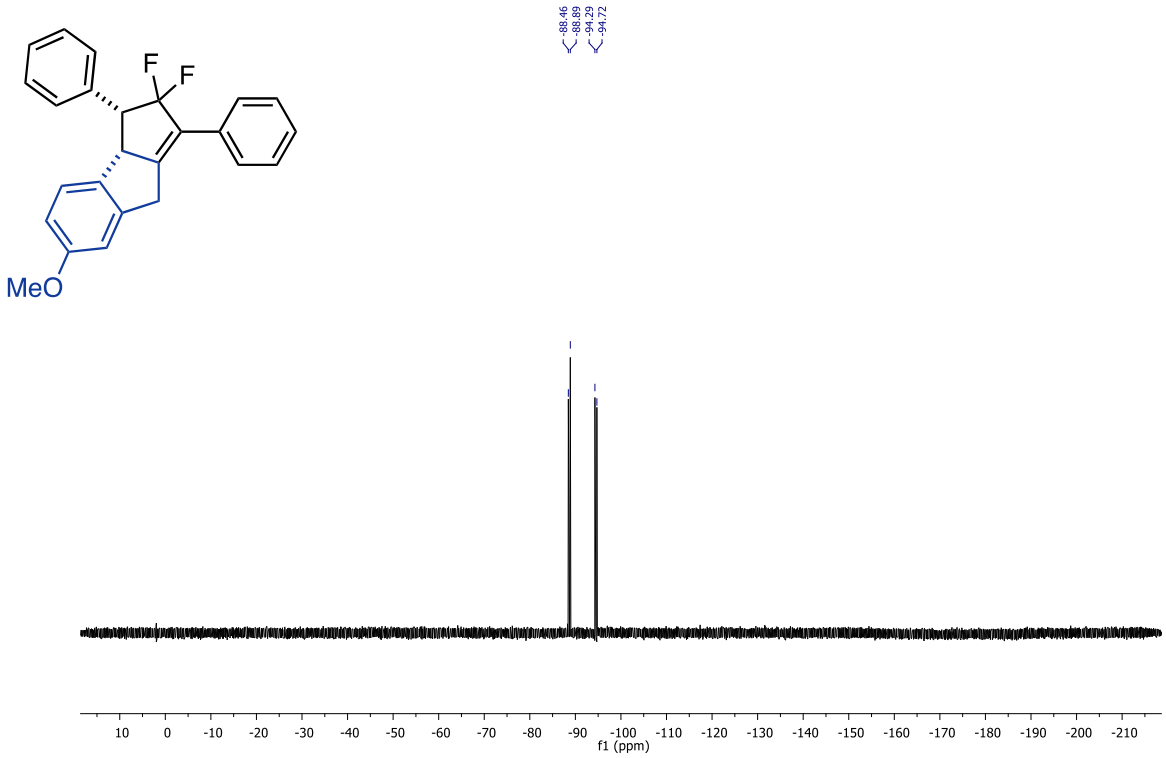
^{1}H NMR (600 MHz, $CDCl_3$) of **6c**



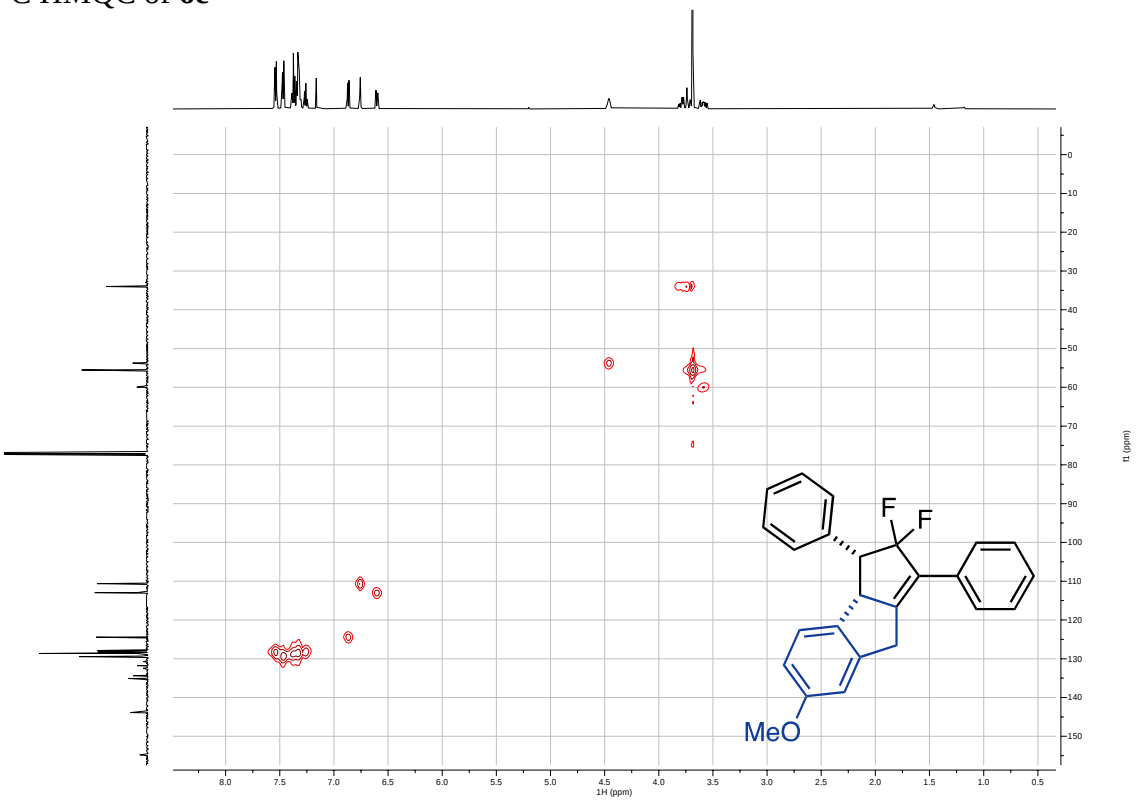
^{13}C NMR (151 MHz, $CDCl_3$) of **6c**



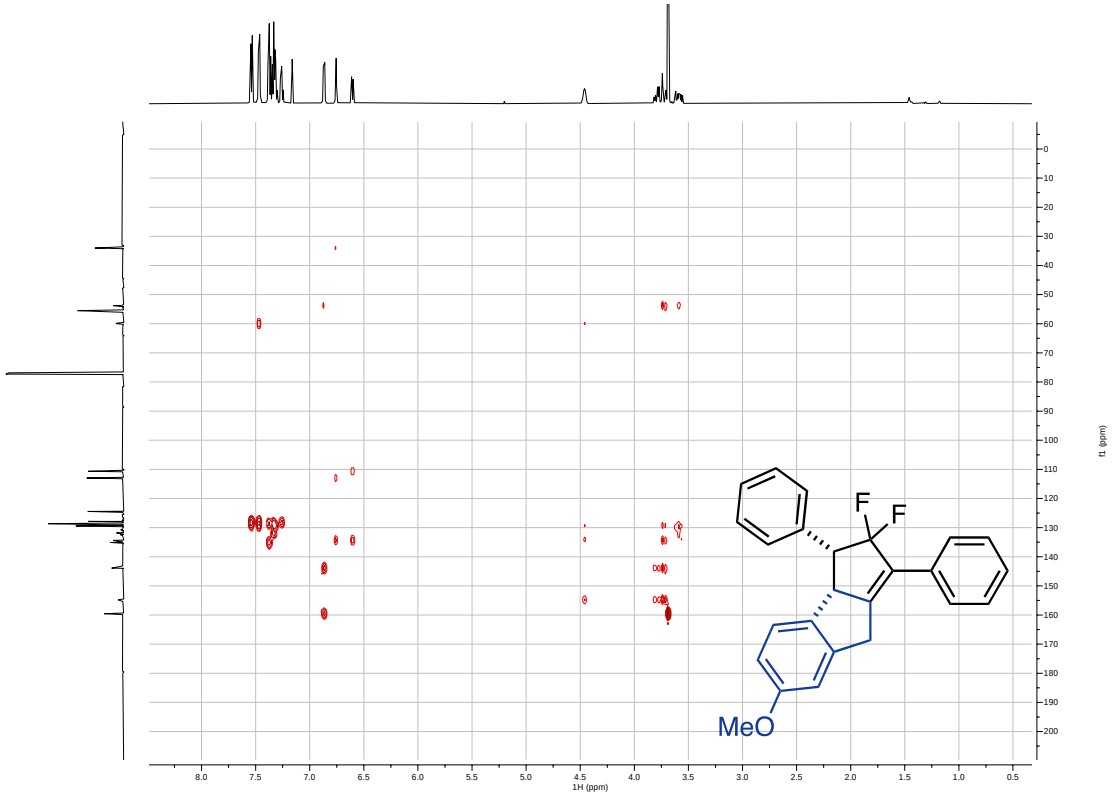
^{19}F NMR (565 MHz, $CDCl_3$) of **6c**



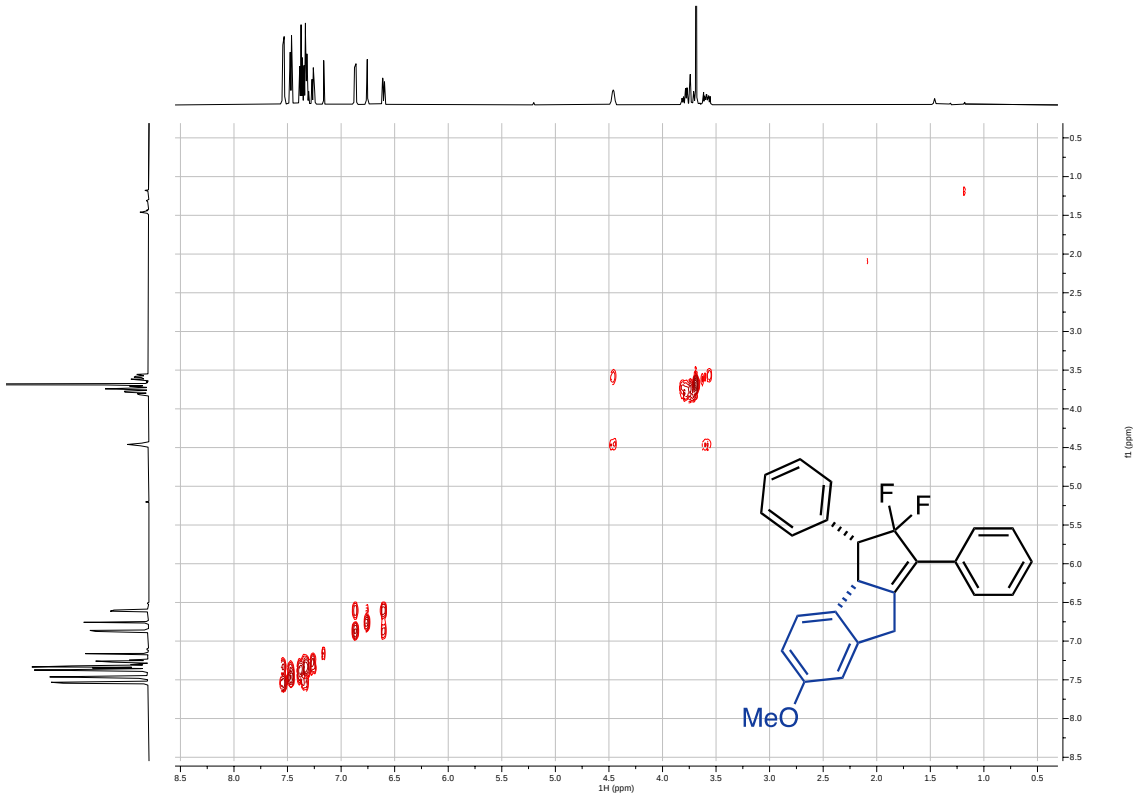
^{1}H-^{13}C HMQC of **6c**



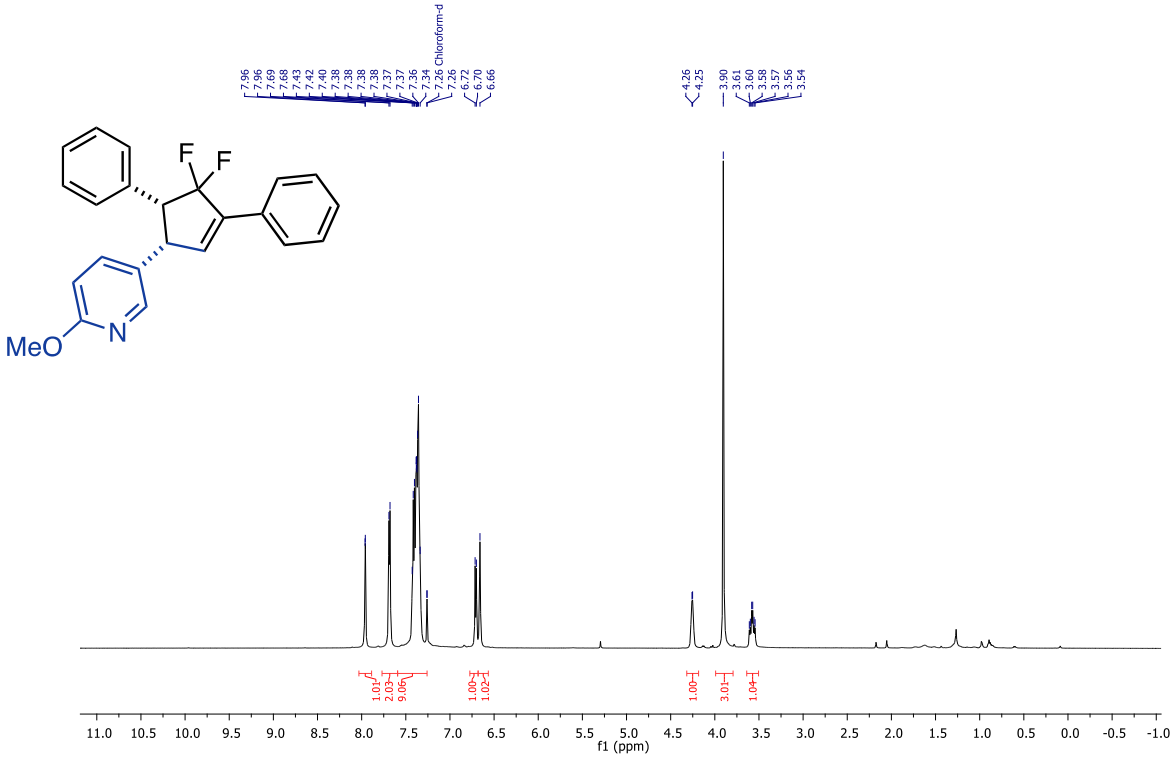
^{1}H-^{13}C HMBC of **6c**



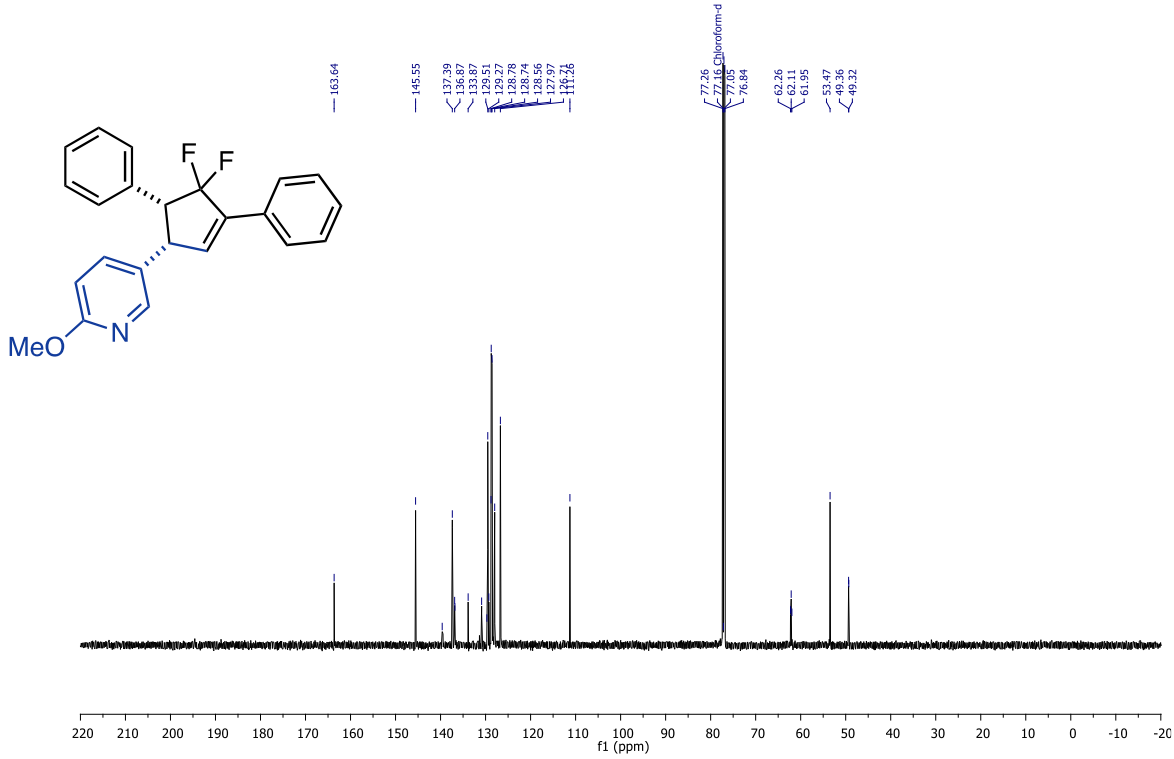
^{1}H-^{1}H COSY of **6c**



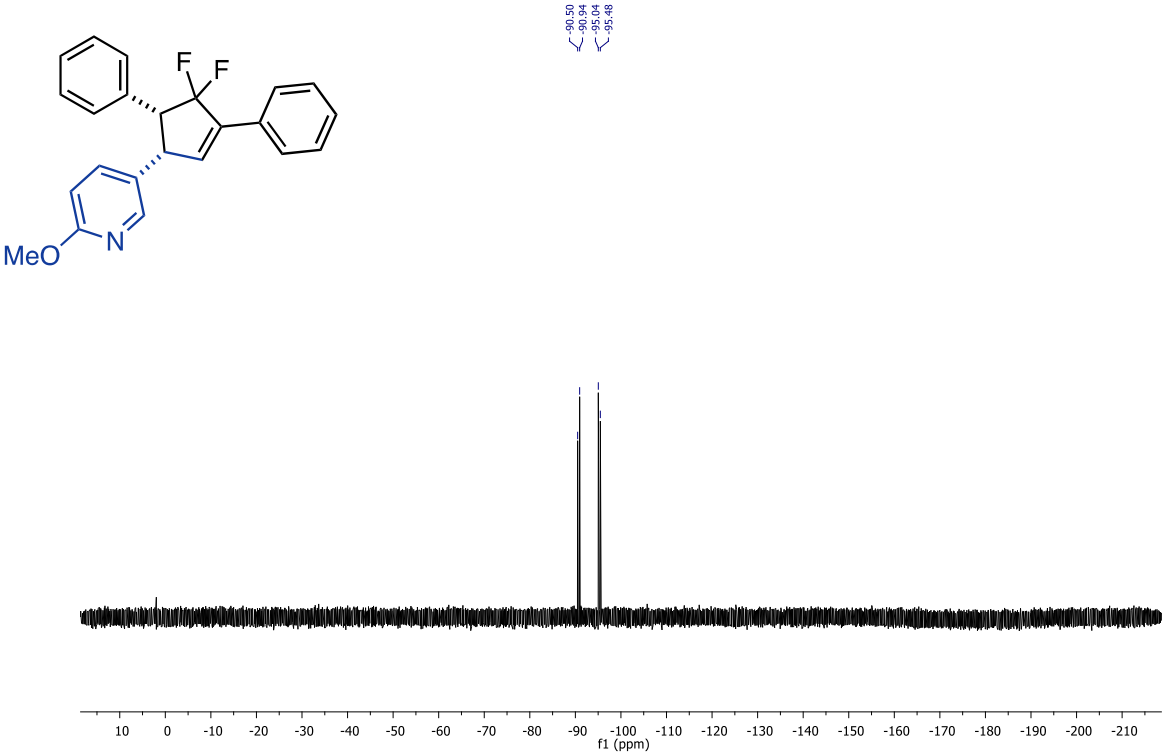
^{1}H NMR (600 MHz, $CDCl_3$) of **6d**



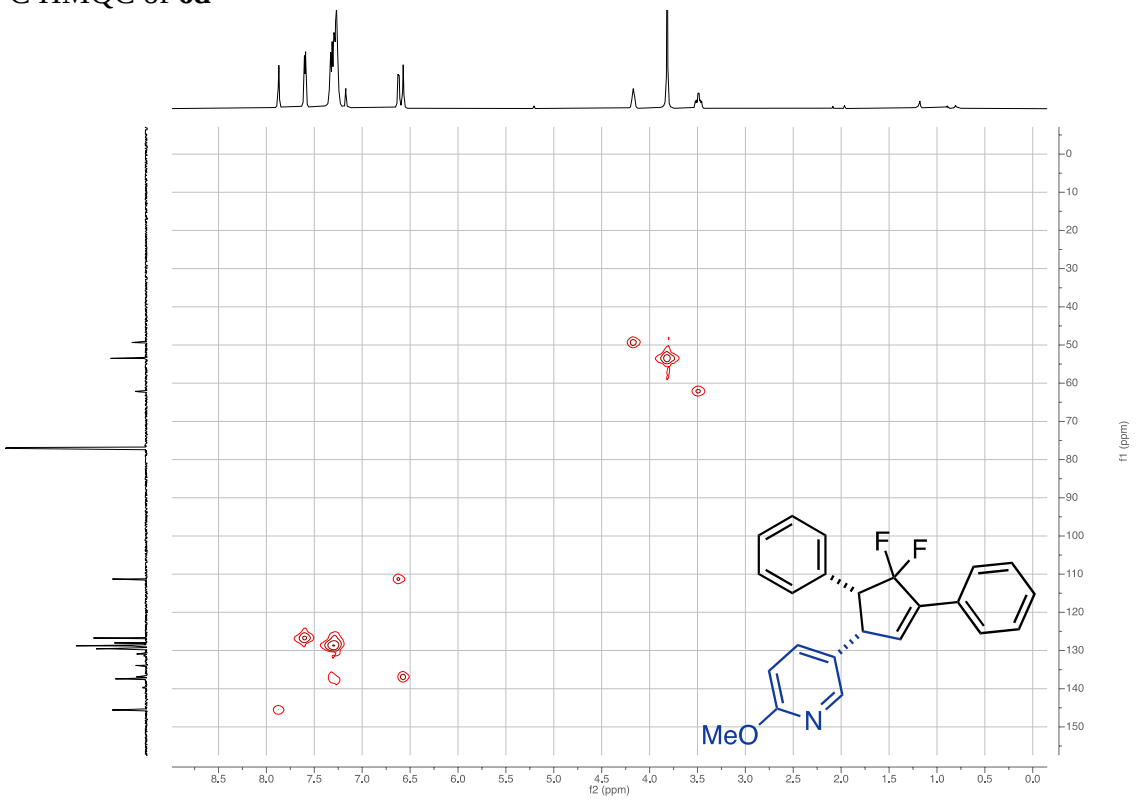
^{13}C NMR (151 MHz, $CDCl_3$) of **6d**



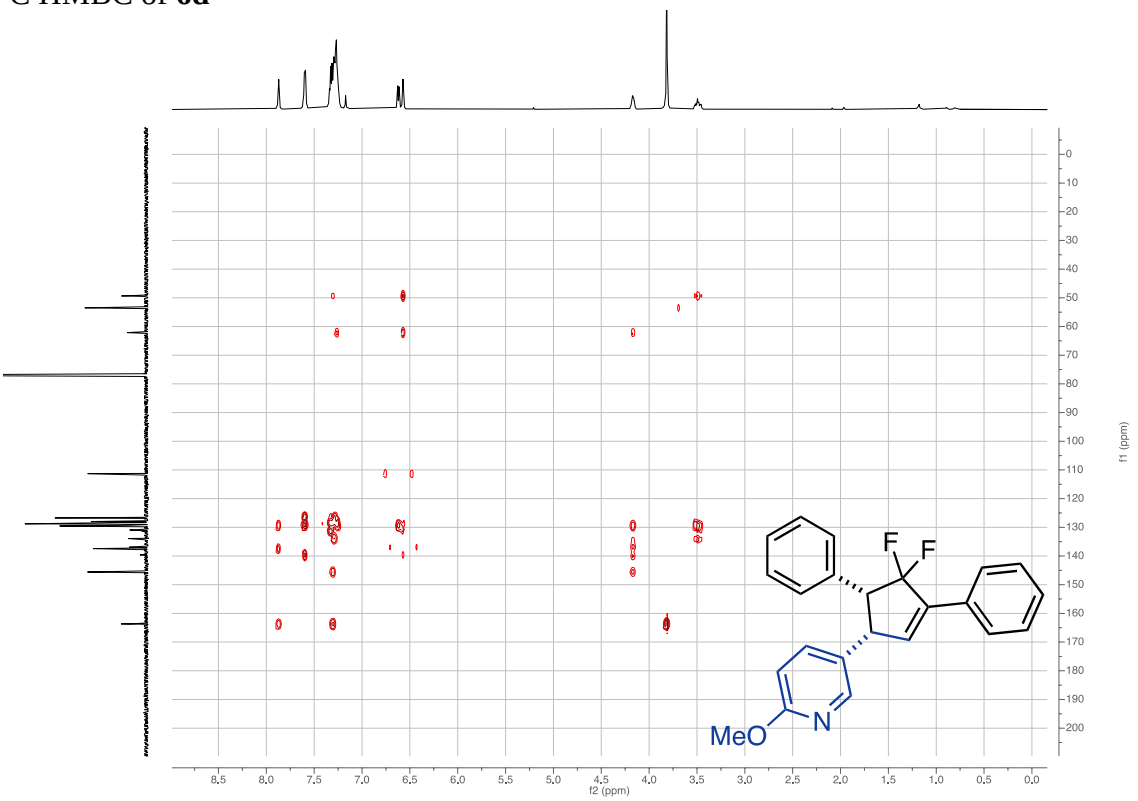
^{19}F NMR (565 MHz, $CDCl_3$) of **6d**



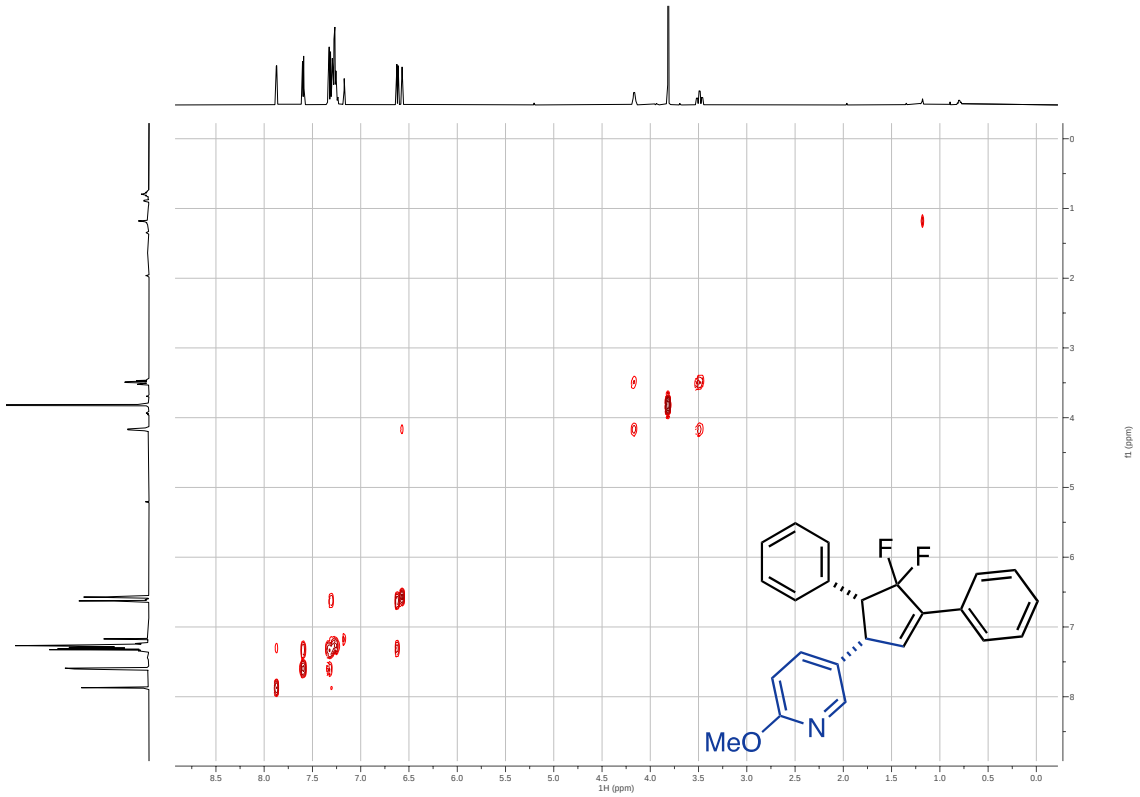
^{1}H-^{13}C HMQC of **6d**



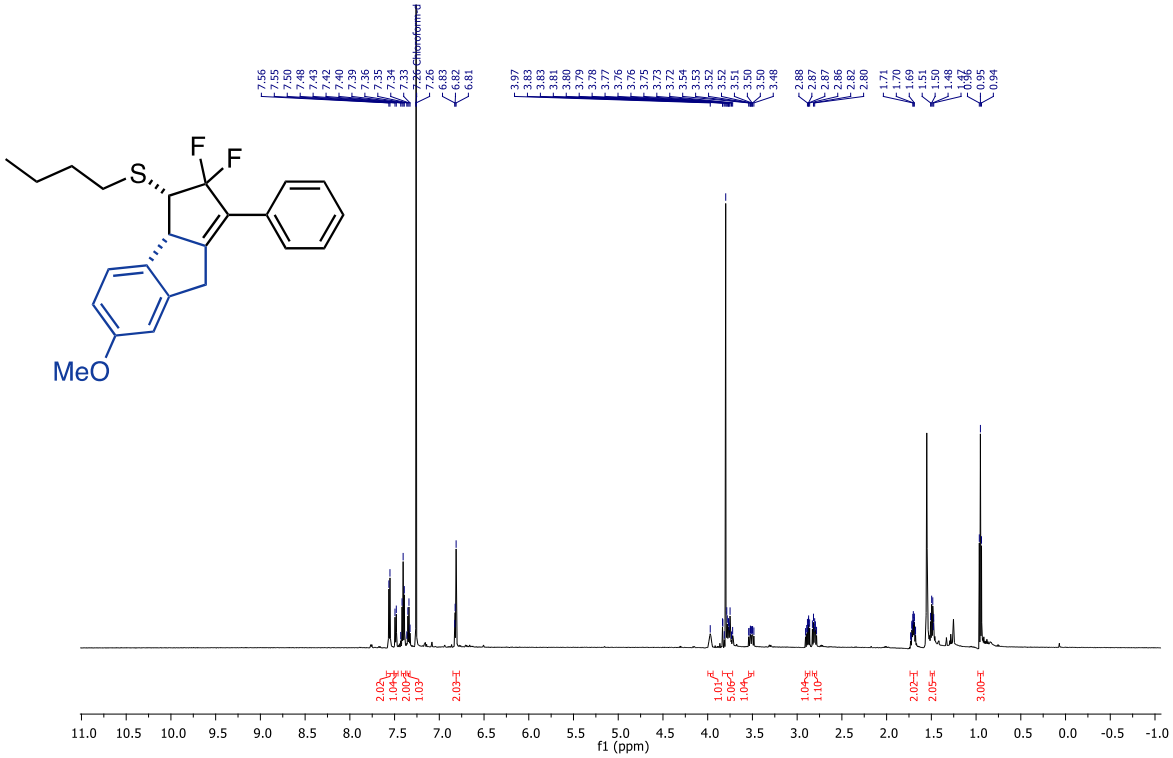
^{1}H-^{13}C HMBC of **6d**



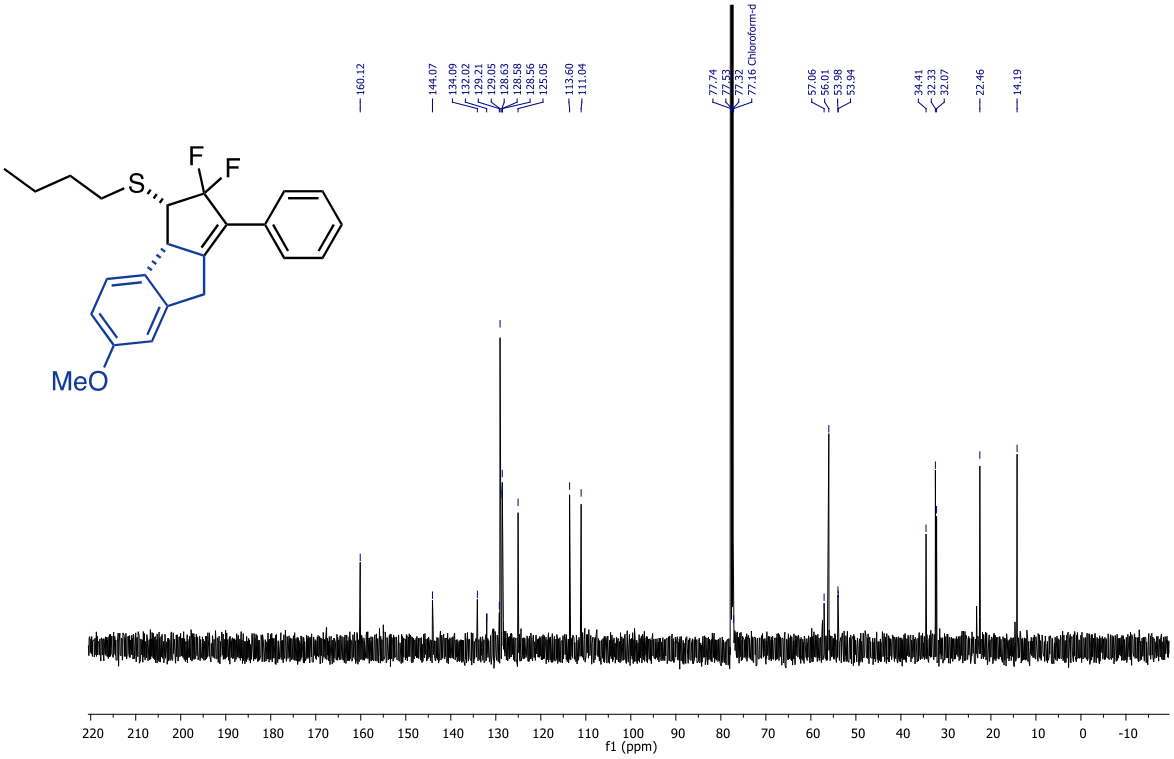
^{1}H-^{1}H COSY of **6d**



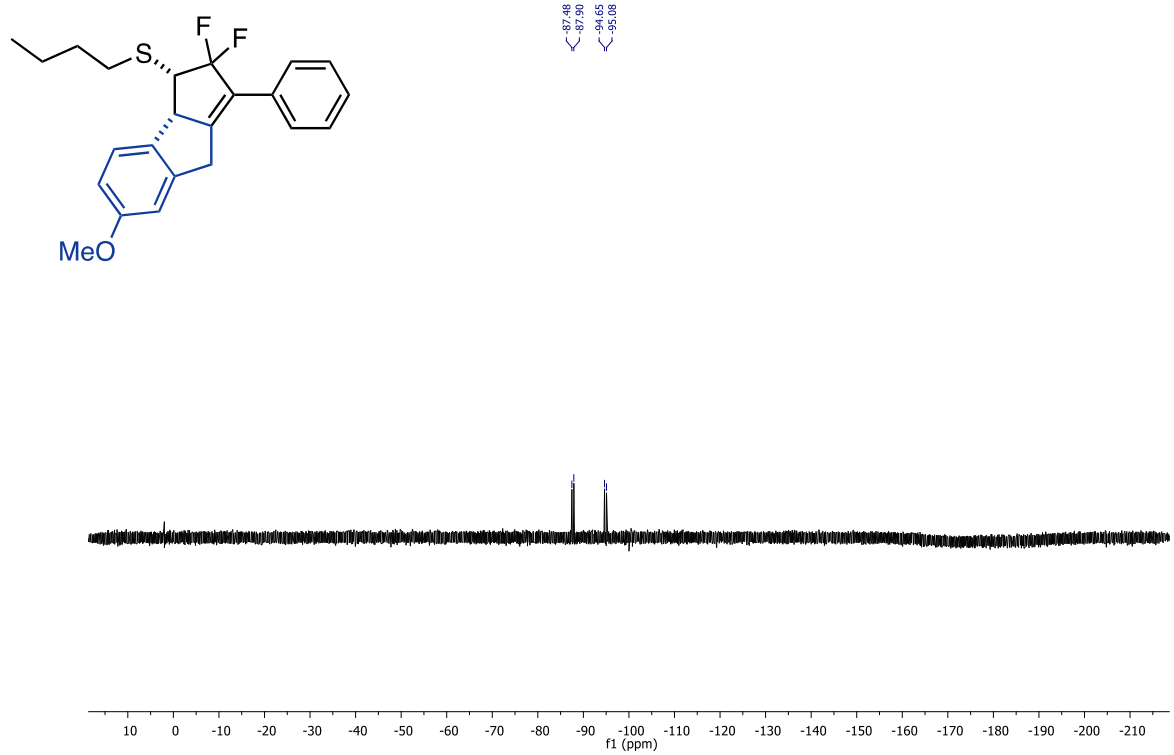
^{1}H NMR (600 MHz, $CDCl_3$) of **6e**



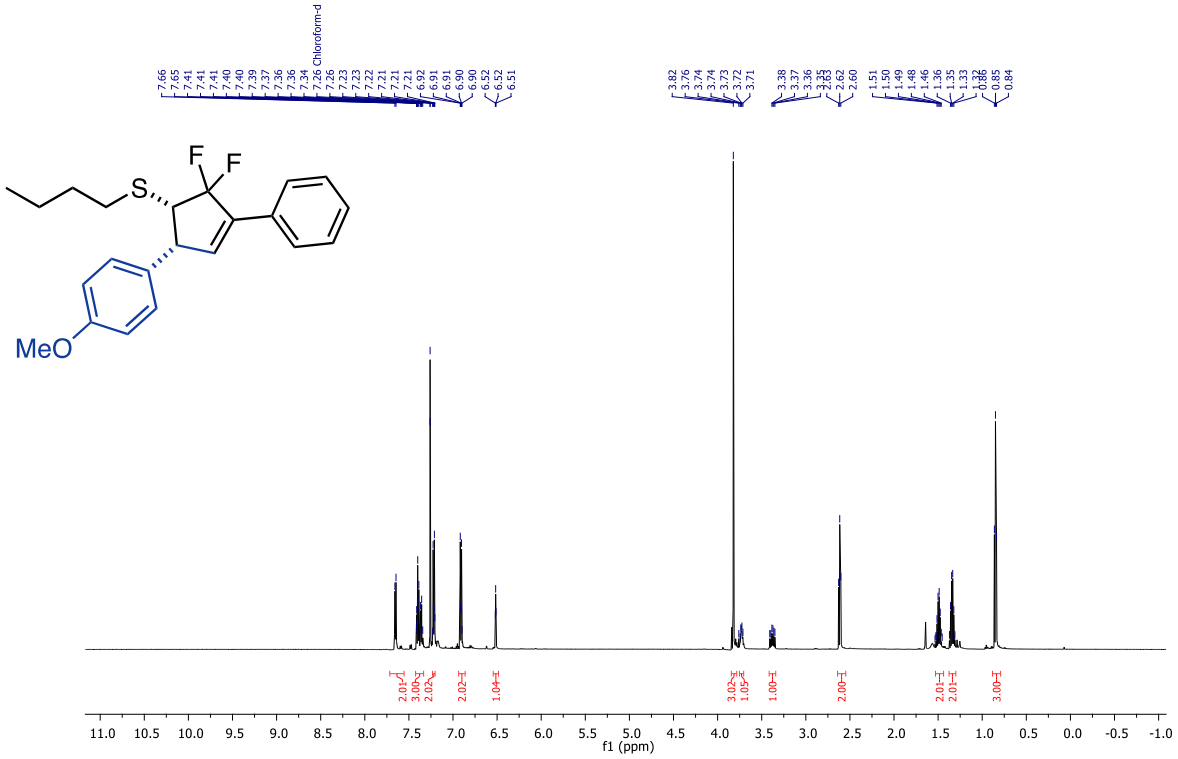
^{13}C NMR (151 MHz, $CDCl_3$) of **6e**



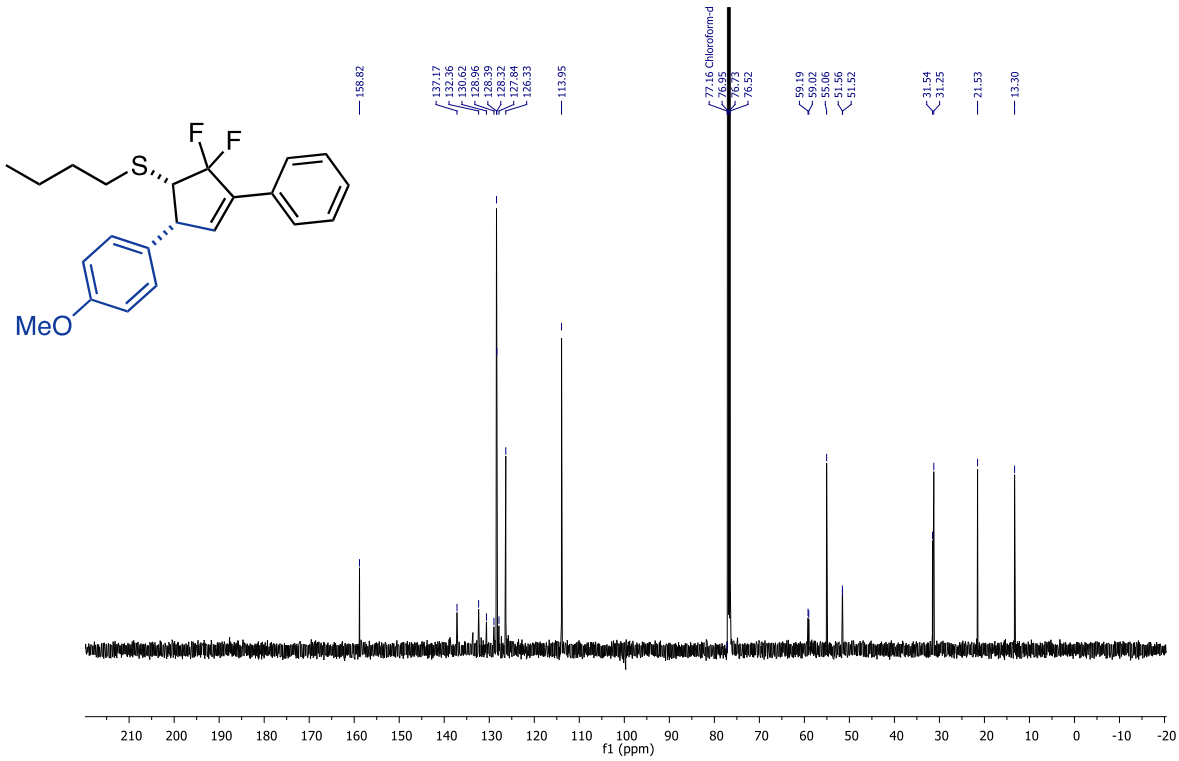
^{19}F NMR (565 MHz, $CDCl_3$) of **6e**



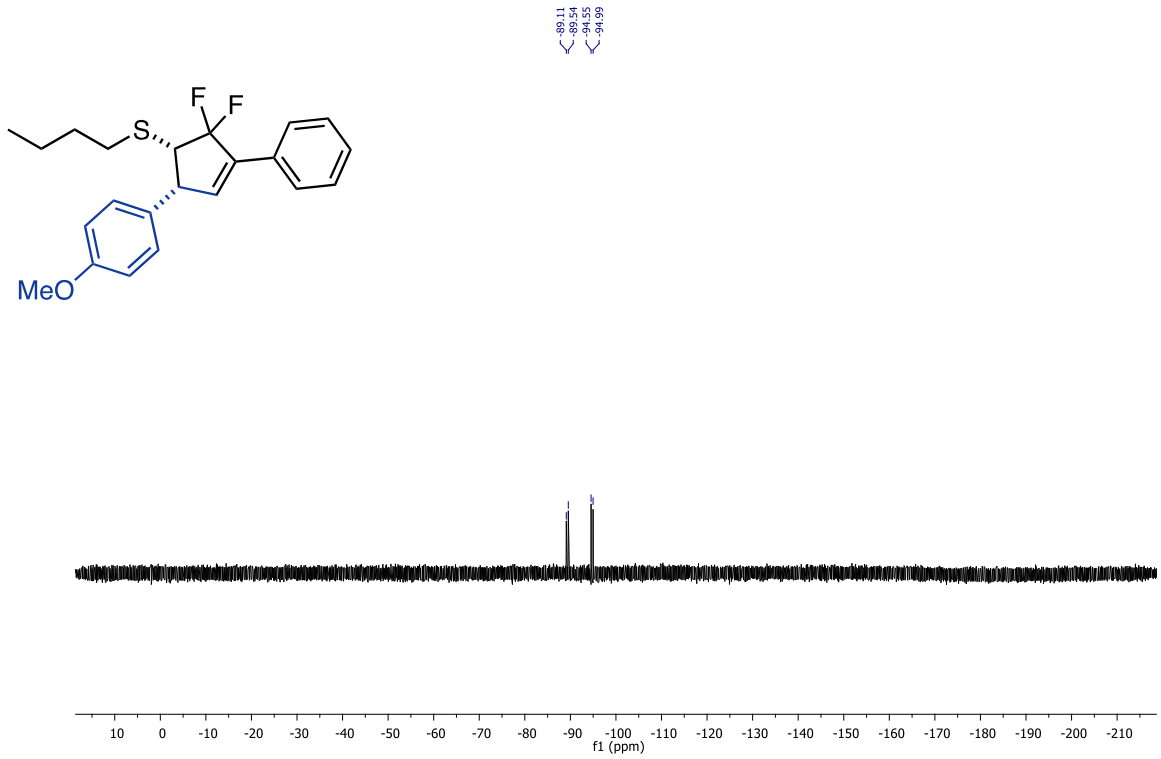
^{1}H NMR (600 MHz, $CDCl_3$) of **6f**



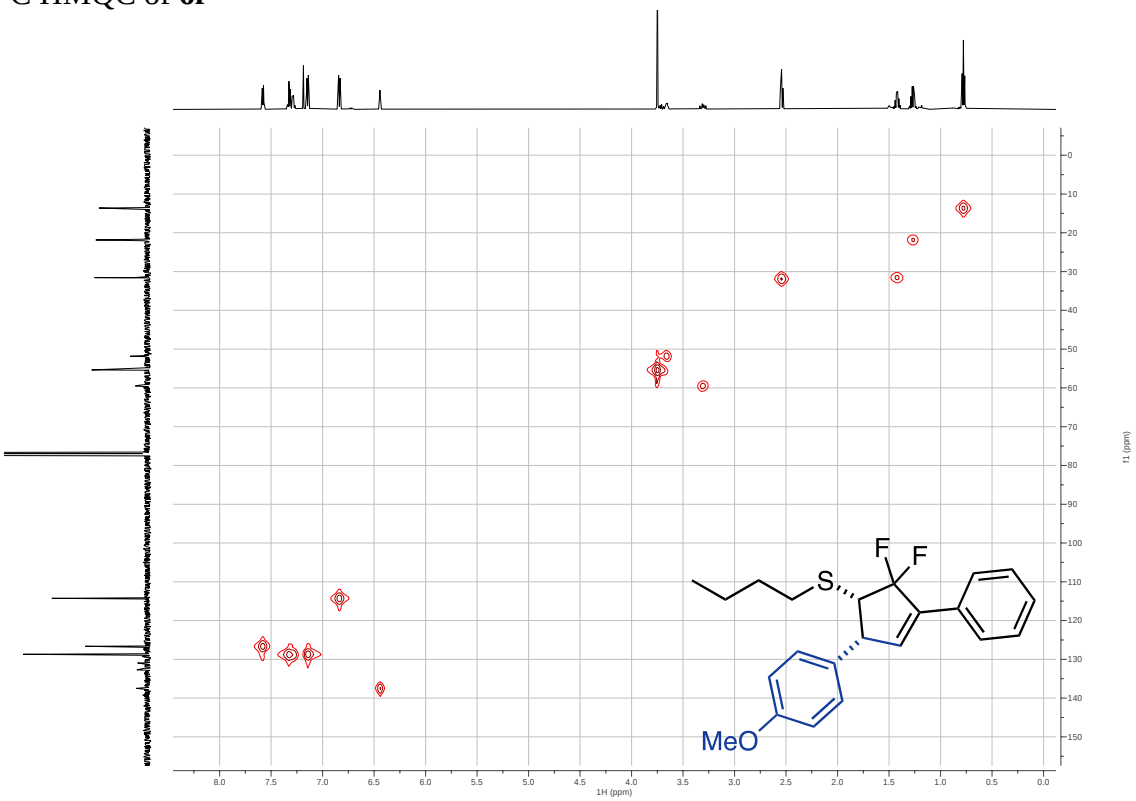
^{13}C NMR (151 MHz, $CDCl_3$) of **6f**



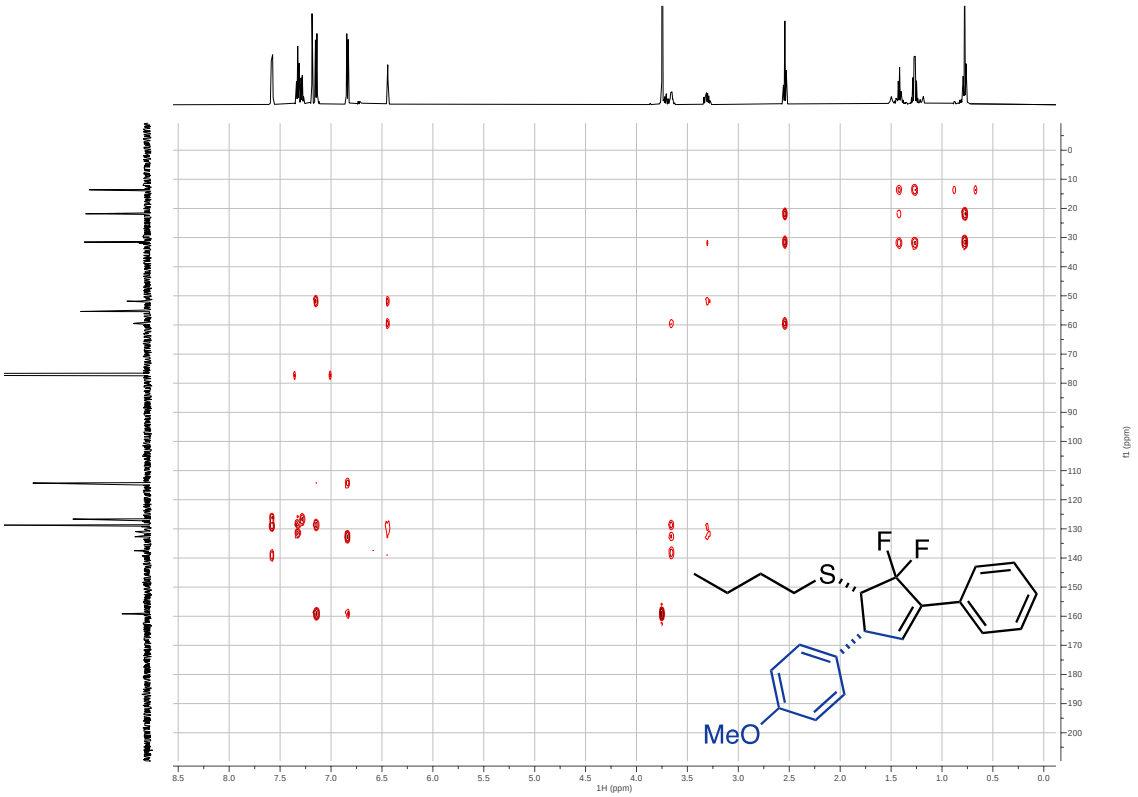
^{19}F NMR (565 MHz, $CDCl_3$) of **6f**



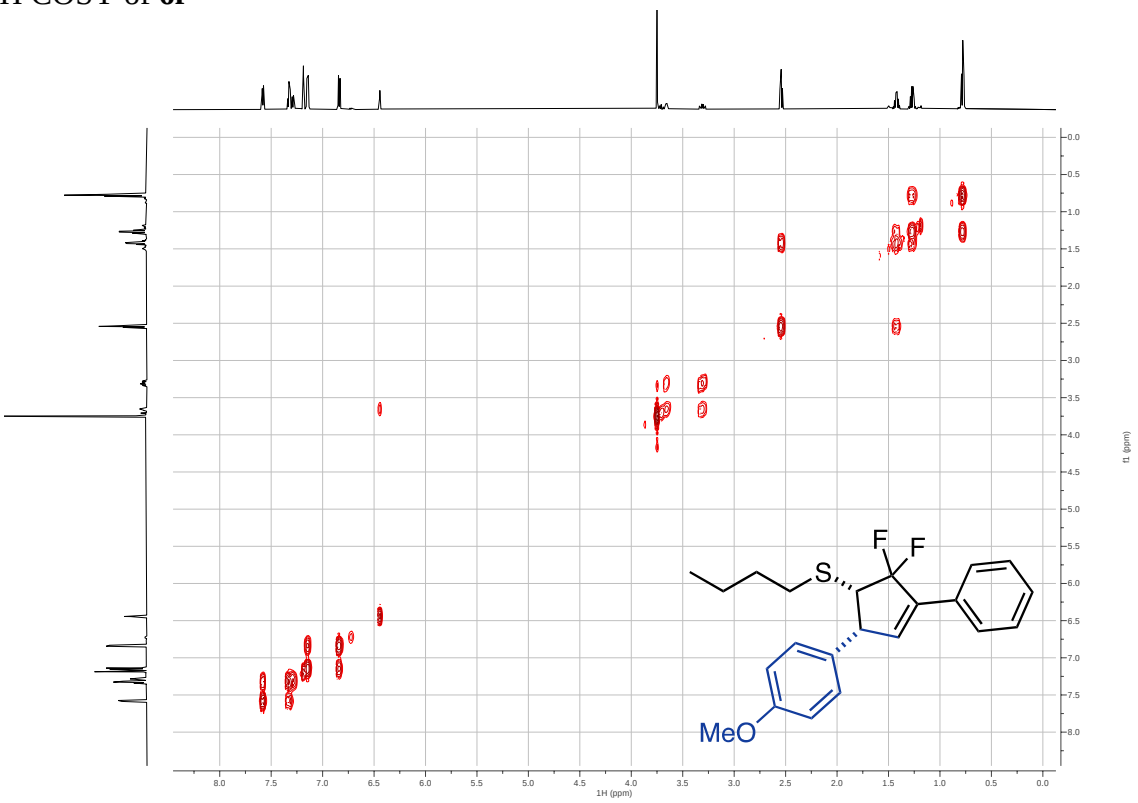
^{1}H-^{13}C HMQC of **6f**



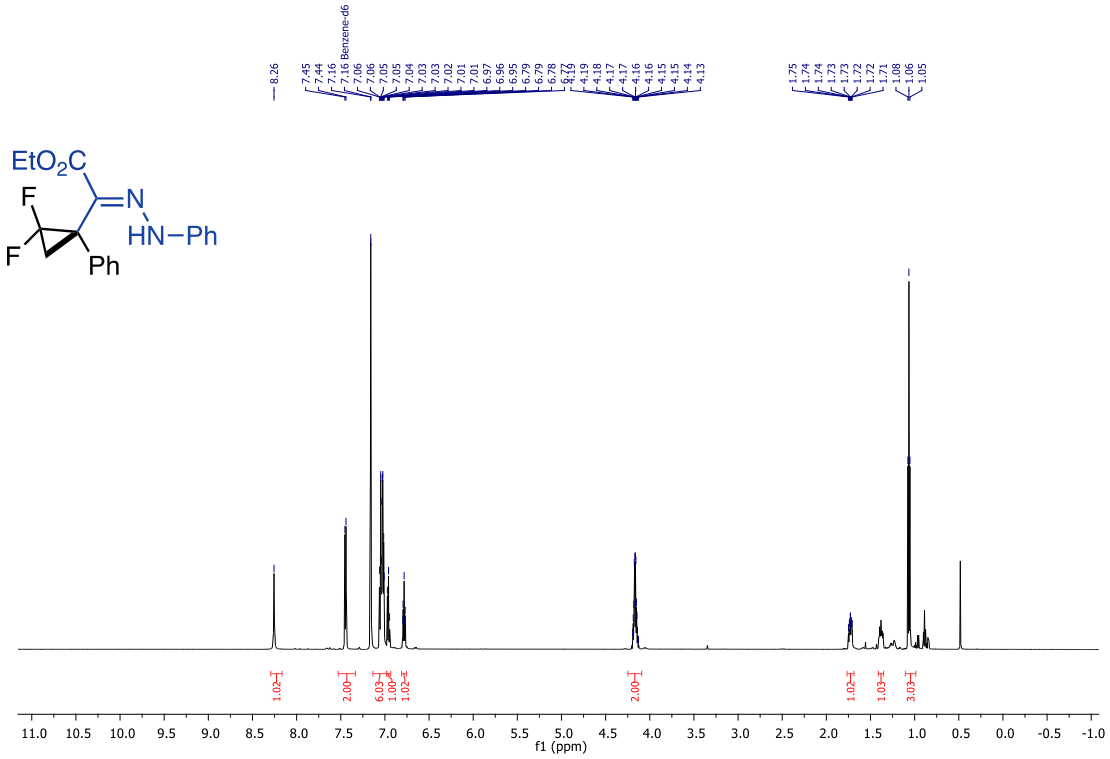
^{1}H-^{13}C HMBC of **6f**



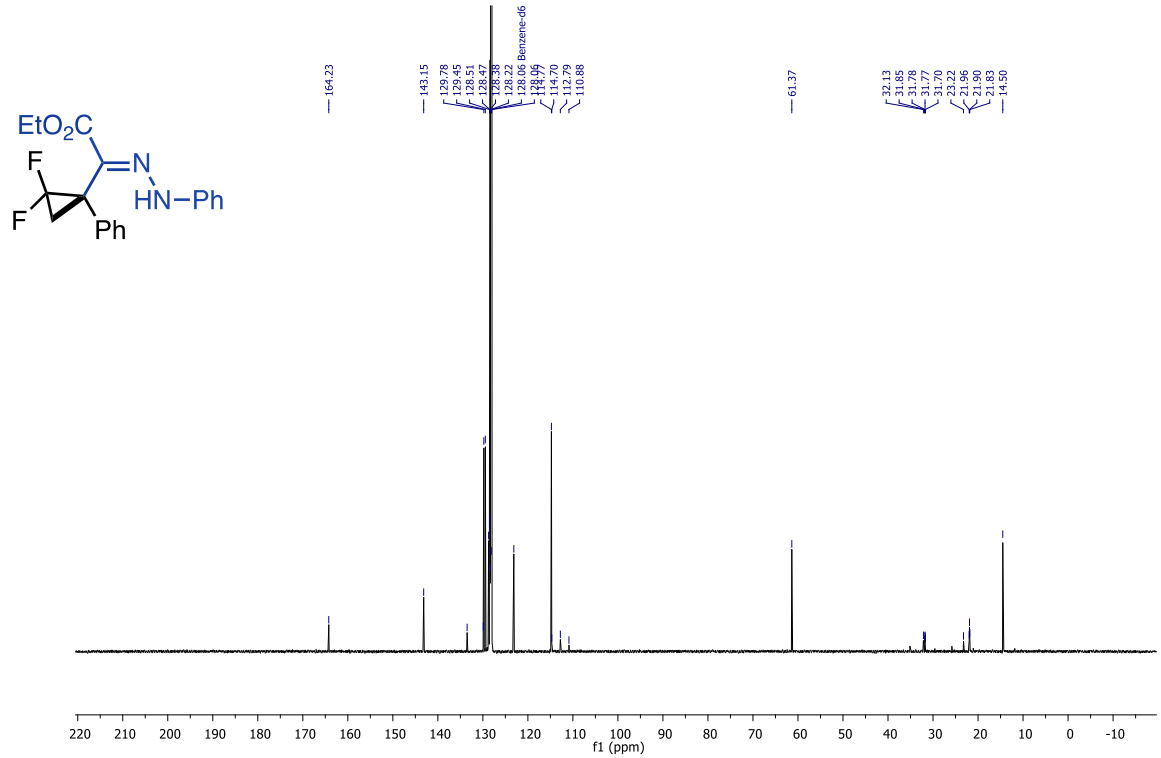
^{1}H-^{1}H COSY of **6f**



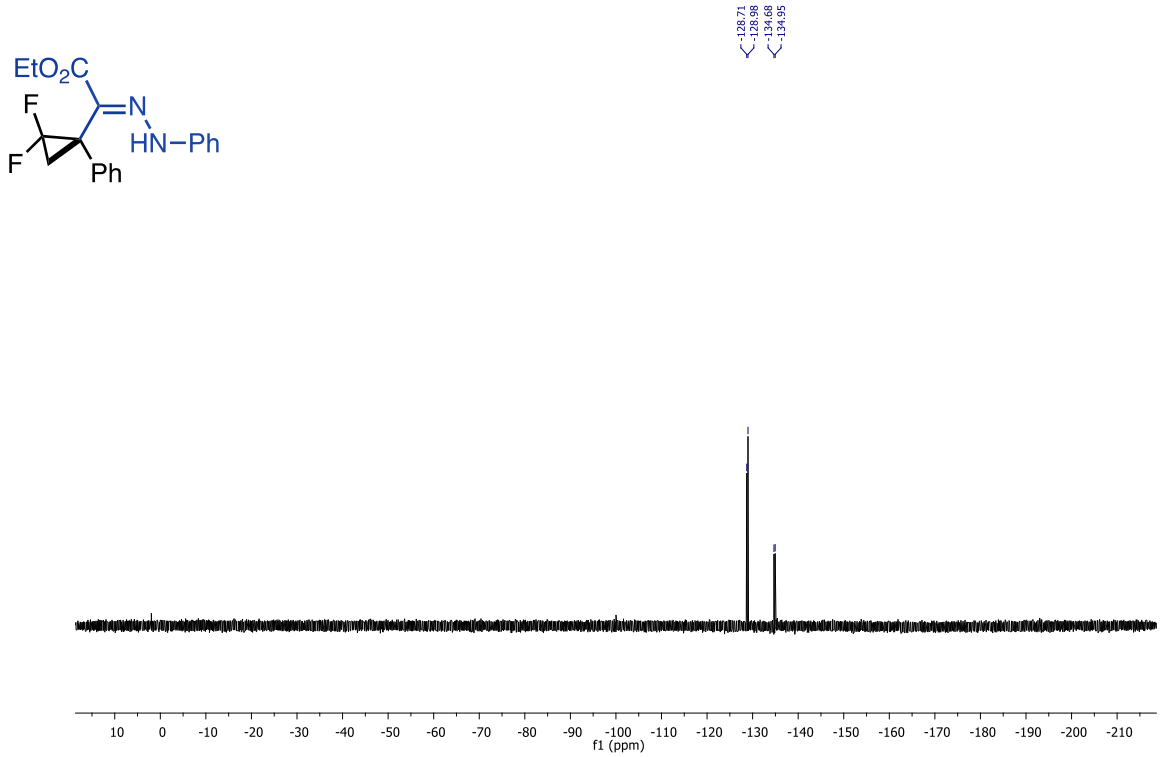
^{1}H NMR (600 MHz, C_6D_6) of **3af**



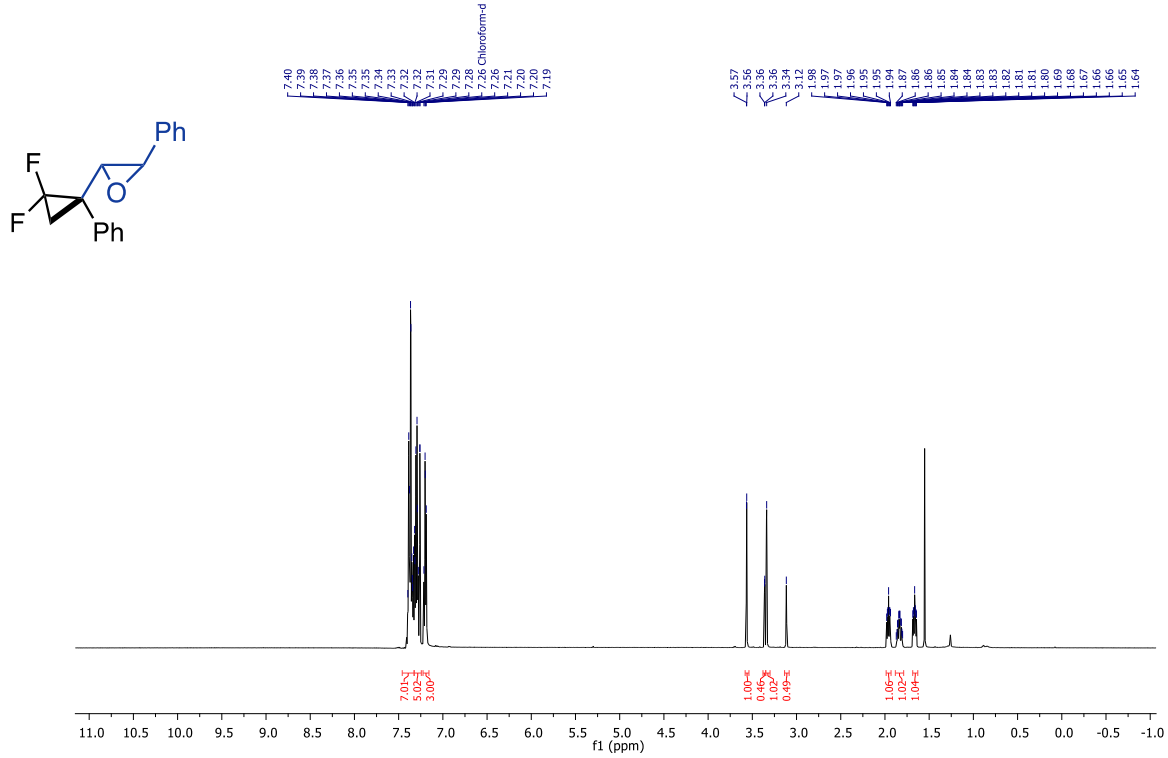
^{13}C NMR (151 MHz, C_6D_6) of **3af**



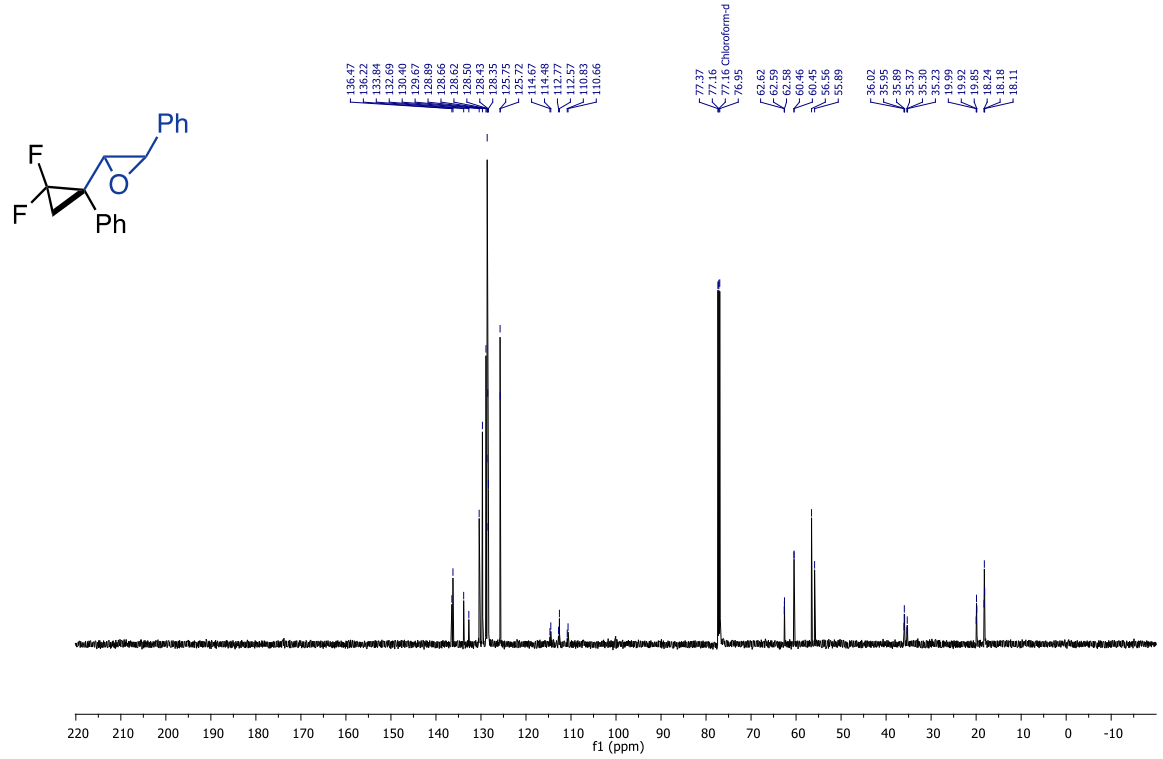
^{19}F NMR (565 MHz, C_6D_6) of **3af**



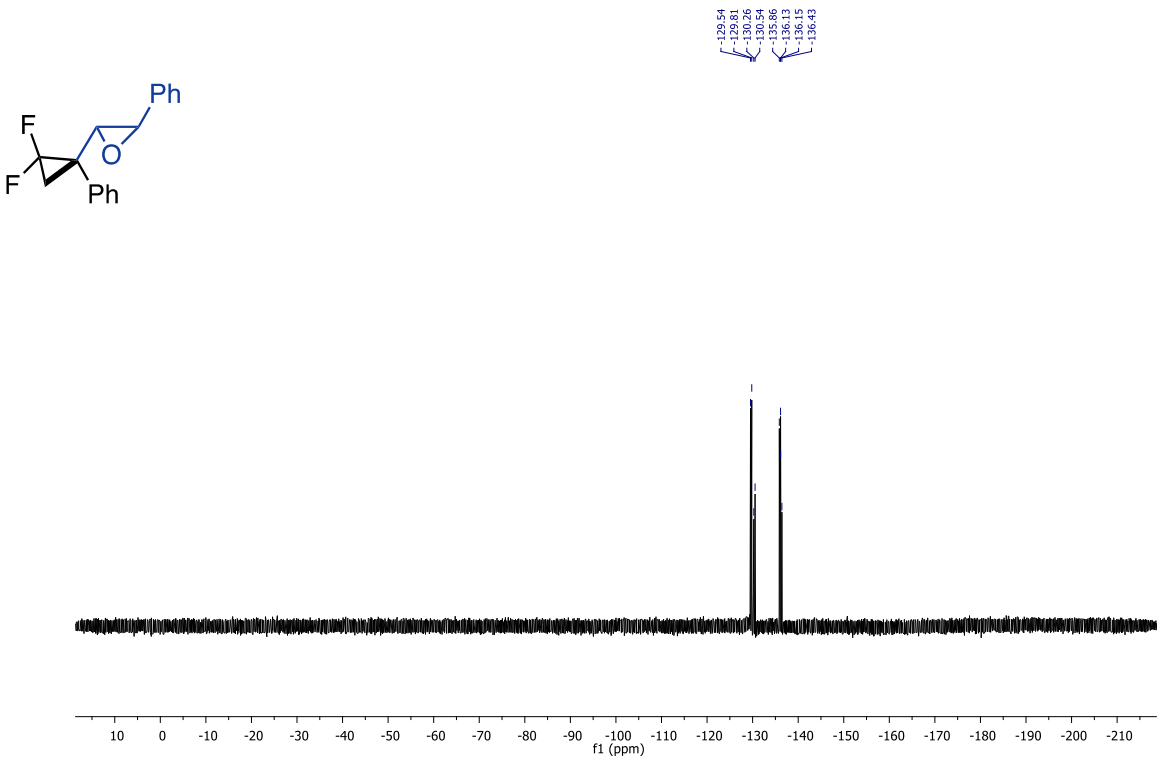
^{1}H NMR (600 MHz, C_6D_6) of **3ag**



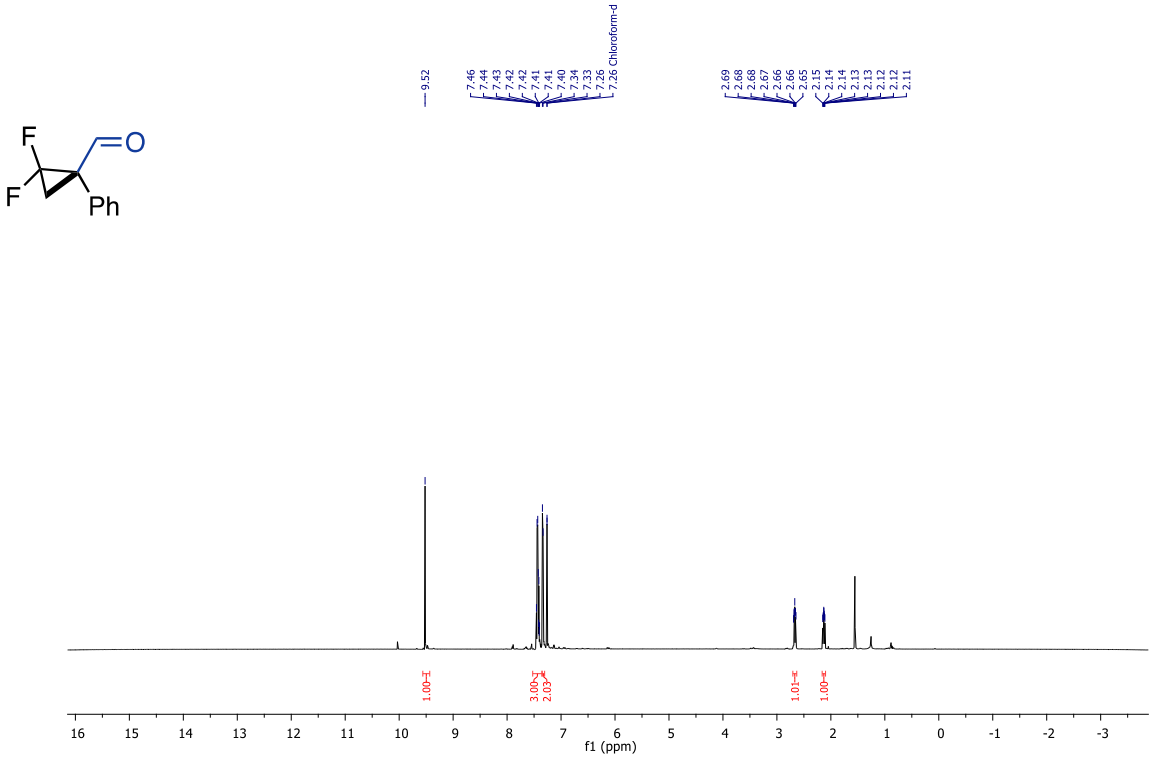
^{13}C NMR (151 MHz, C_6D_6) of **3ag**



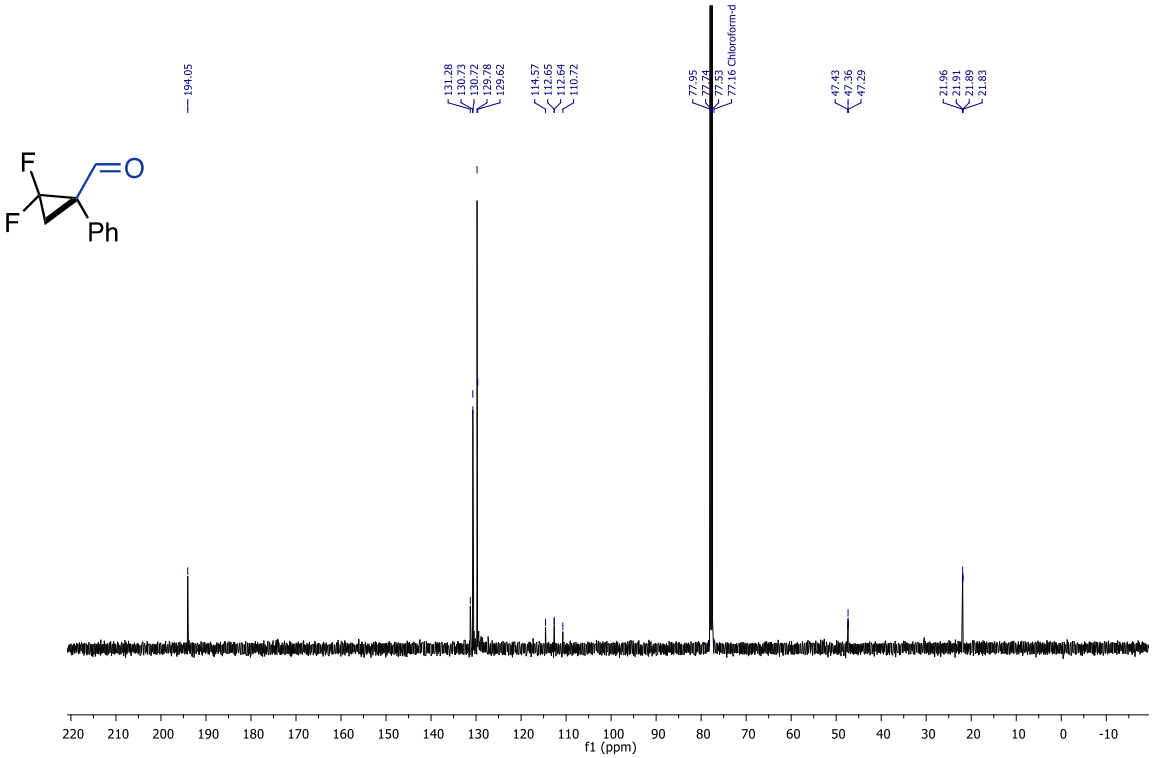
^{19}F NMR (565 MHz, C_6D_6) of **3ag**



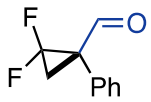
^{1}H NMR (600 MHz, C_6D_6) of **3ah**



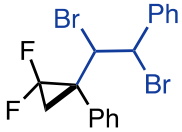
^{13}C NMR (151 MHz, C_6D_6) of **3ah**



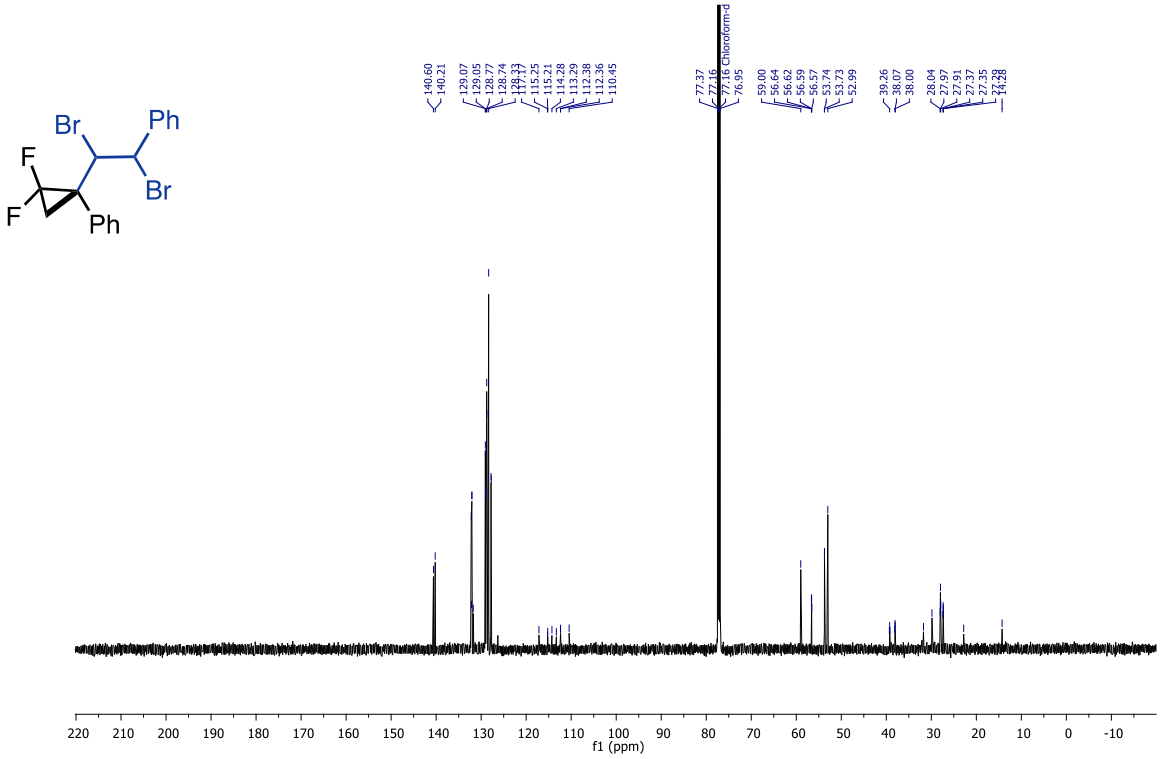
^{19}F NMR (565 MHz, C_6D_6) of **3ah**



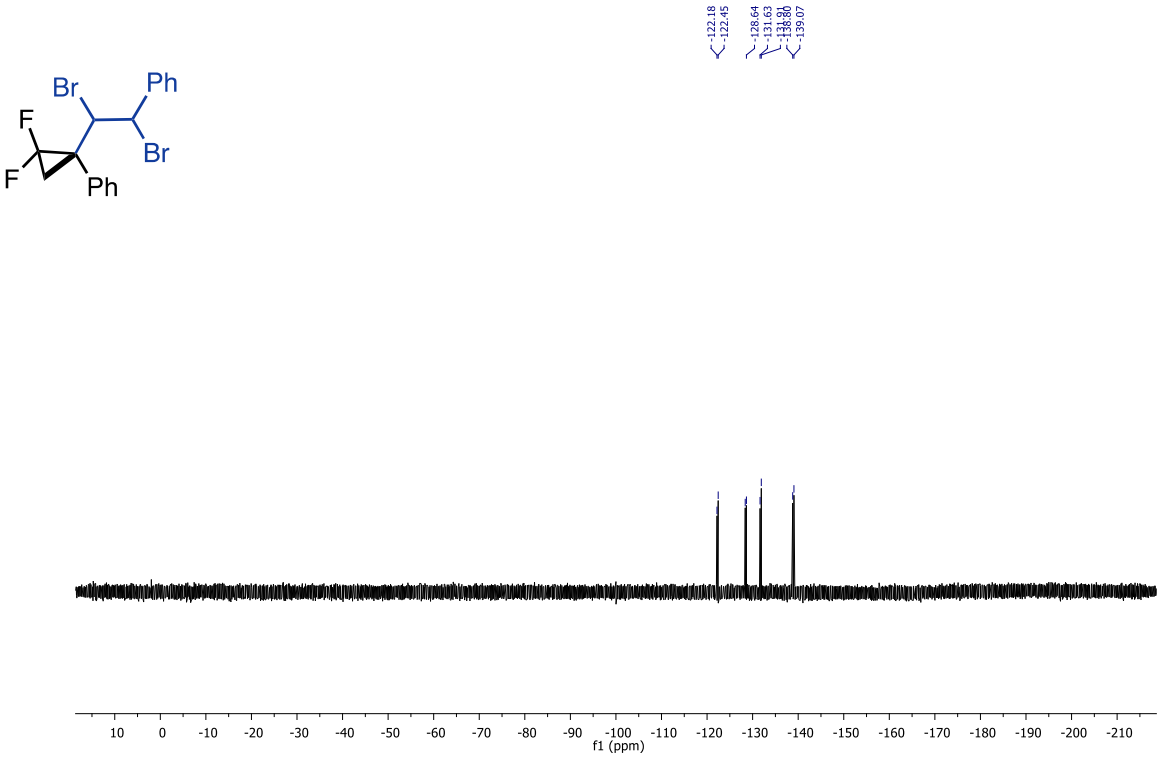
^{1}H NMR (600 MHz, C_6D_6) of **3ai**



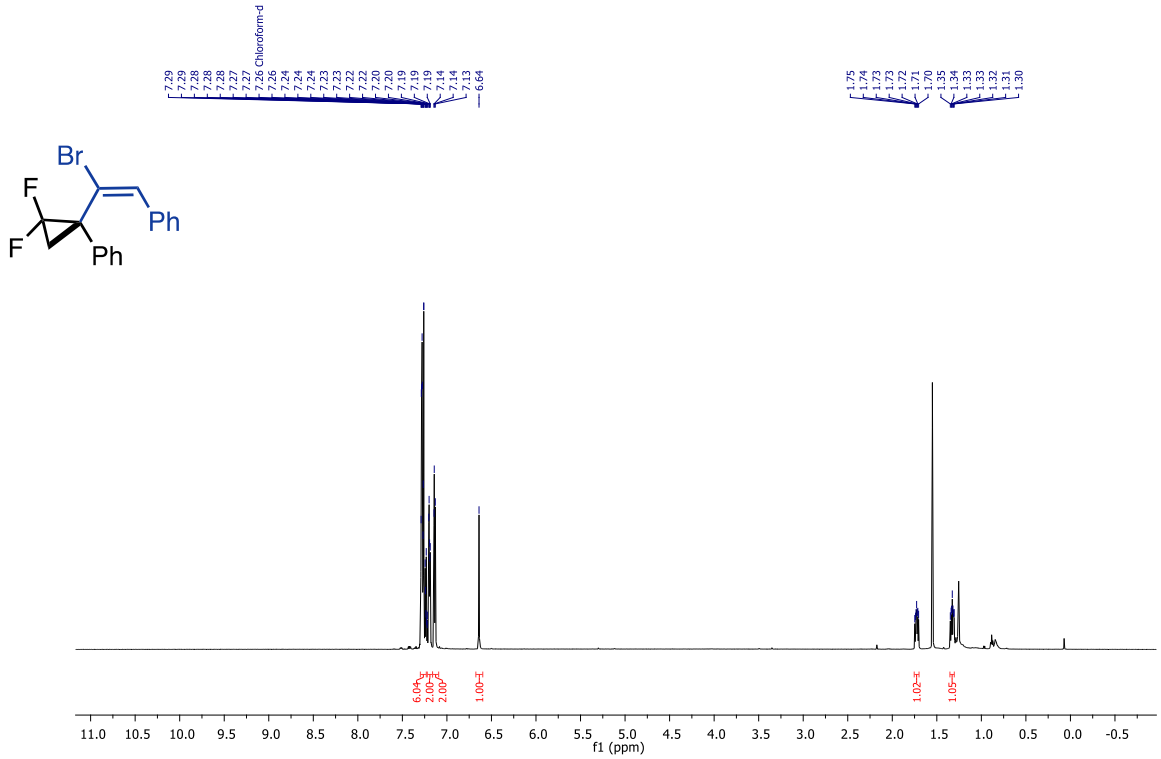
^{13}C NMR (151 MHz, C_6D_6) of **3ai**



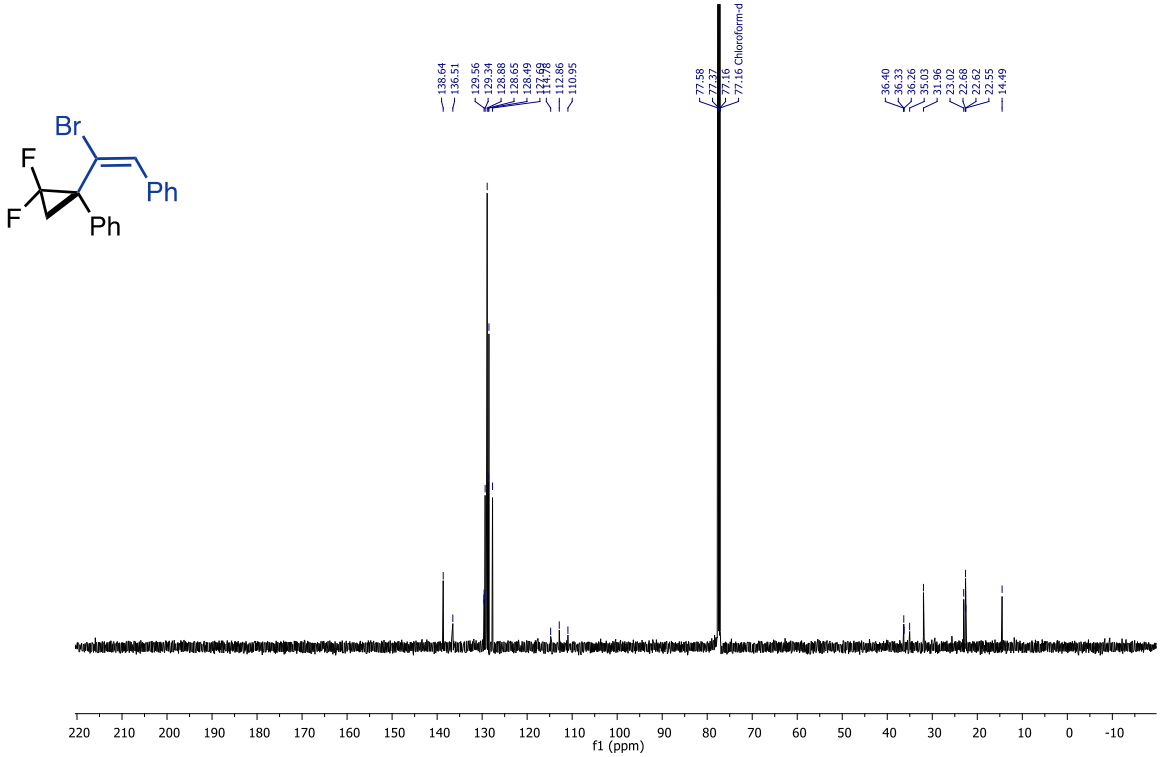
^{19}F NMR (565 MHz, C_6D_6) of **3ai**



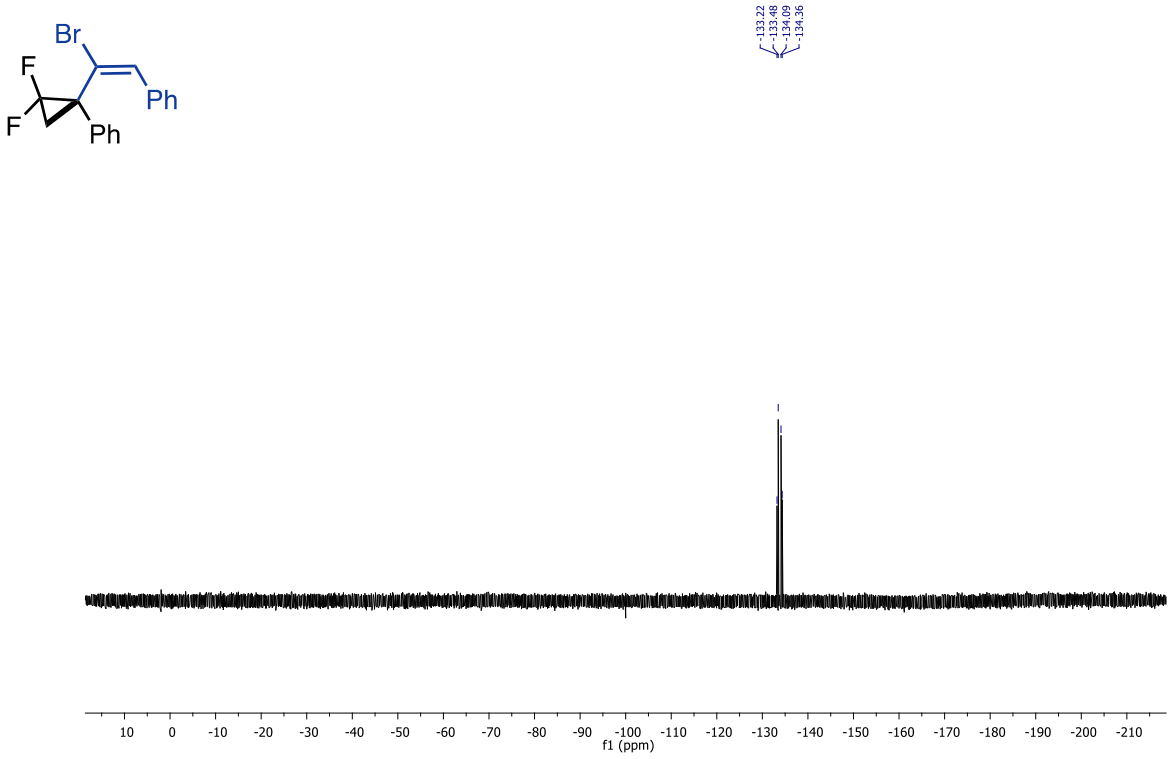
^{1}H NMR (600 MHz, C_6D_6) of **3aj**



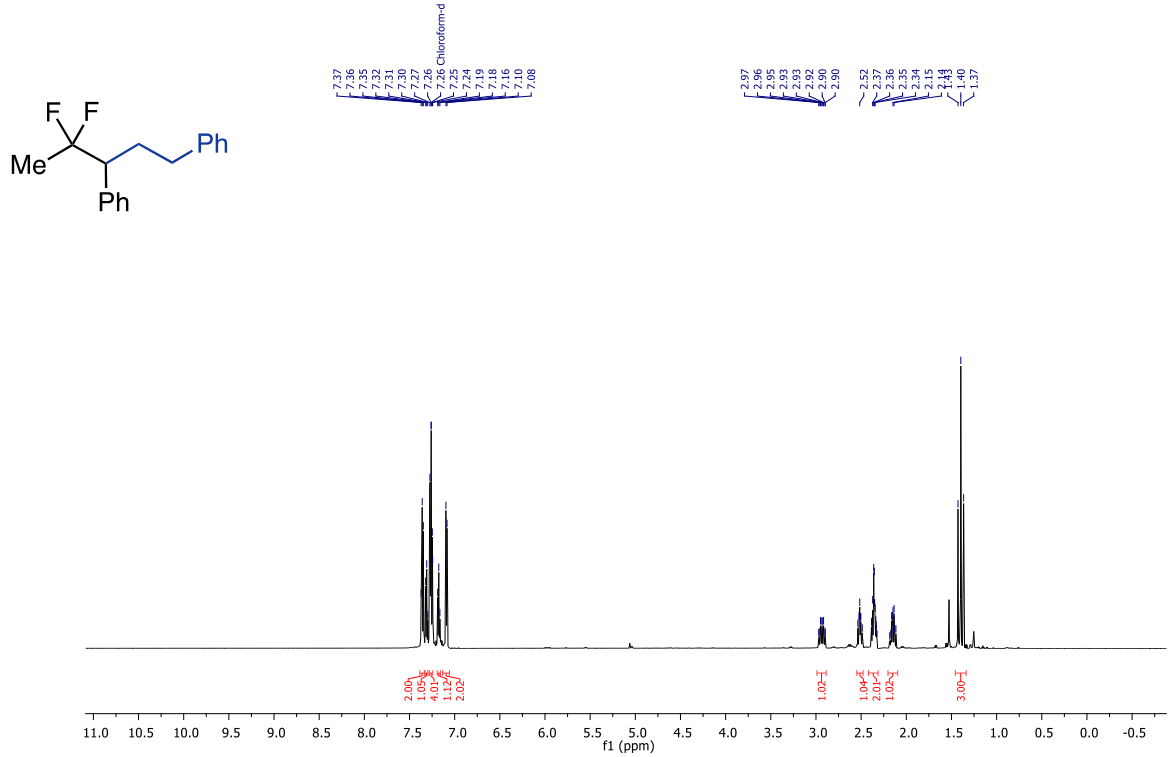
^{13}C NMR (151 MHz, C_6D_6) of **3aj**



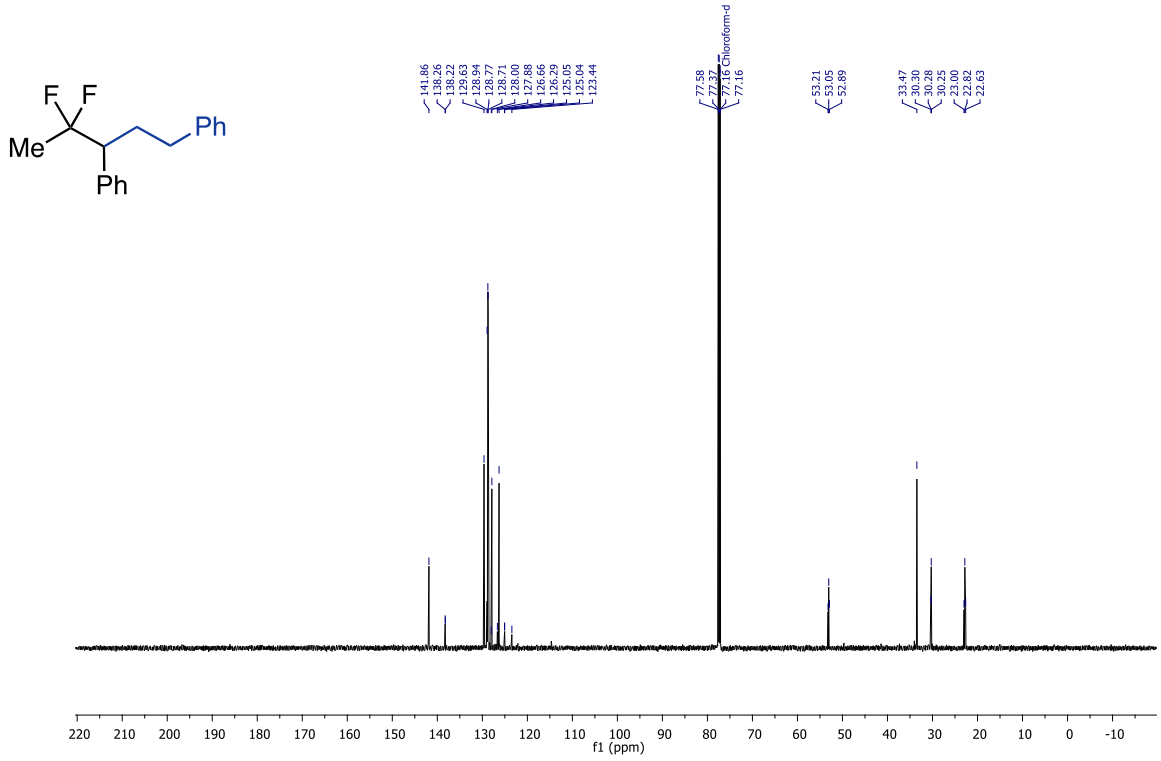
^{19}F NMR (565 MHz, C_6D_6) of **3aj**



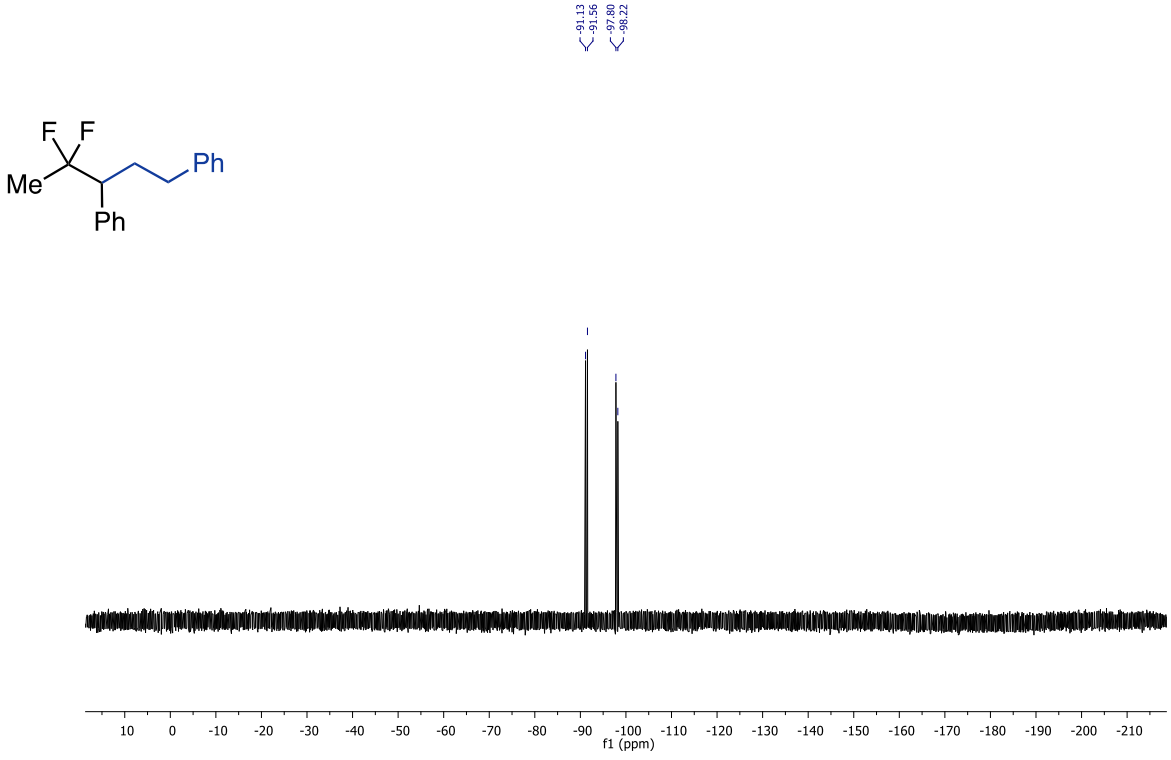
^{1}H NMR (600 MHz, C_6D_6) of **3ak**



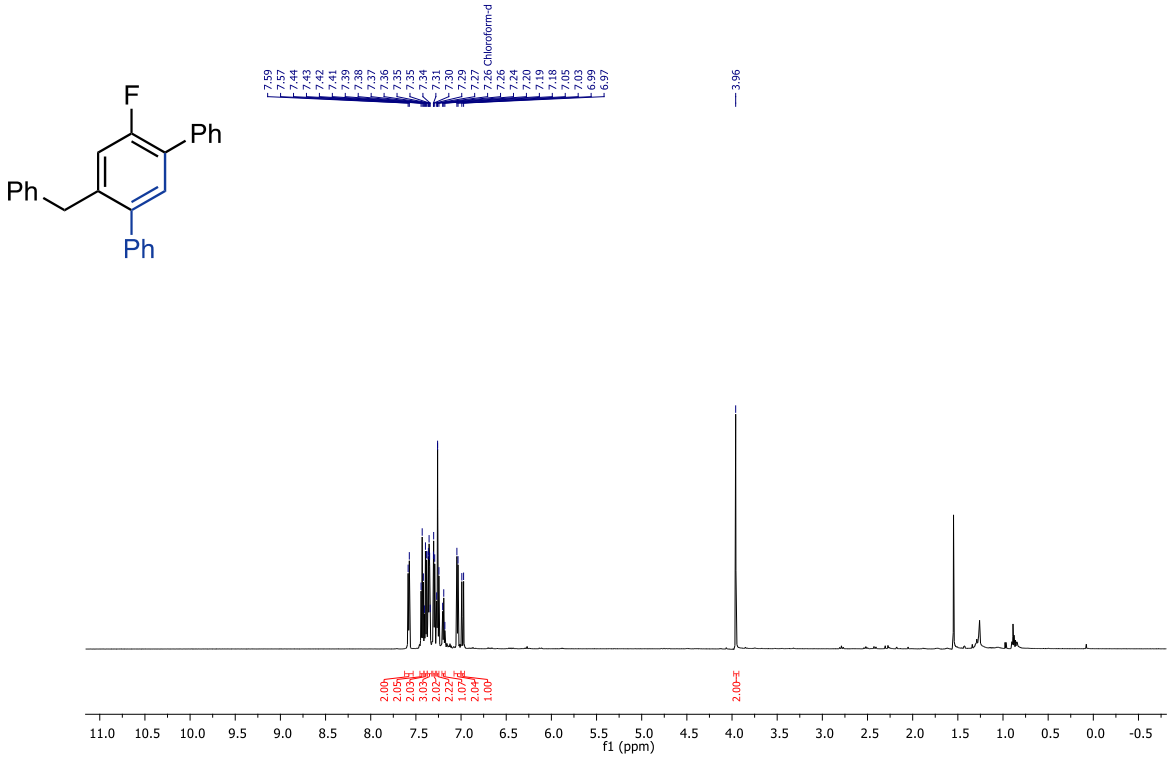
^{13}C NMR (151 MHz, C_6D_6) of **3ak**



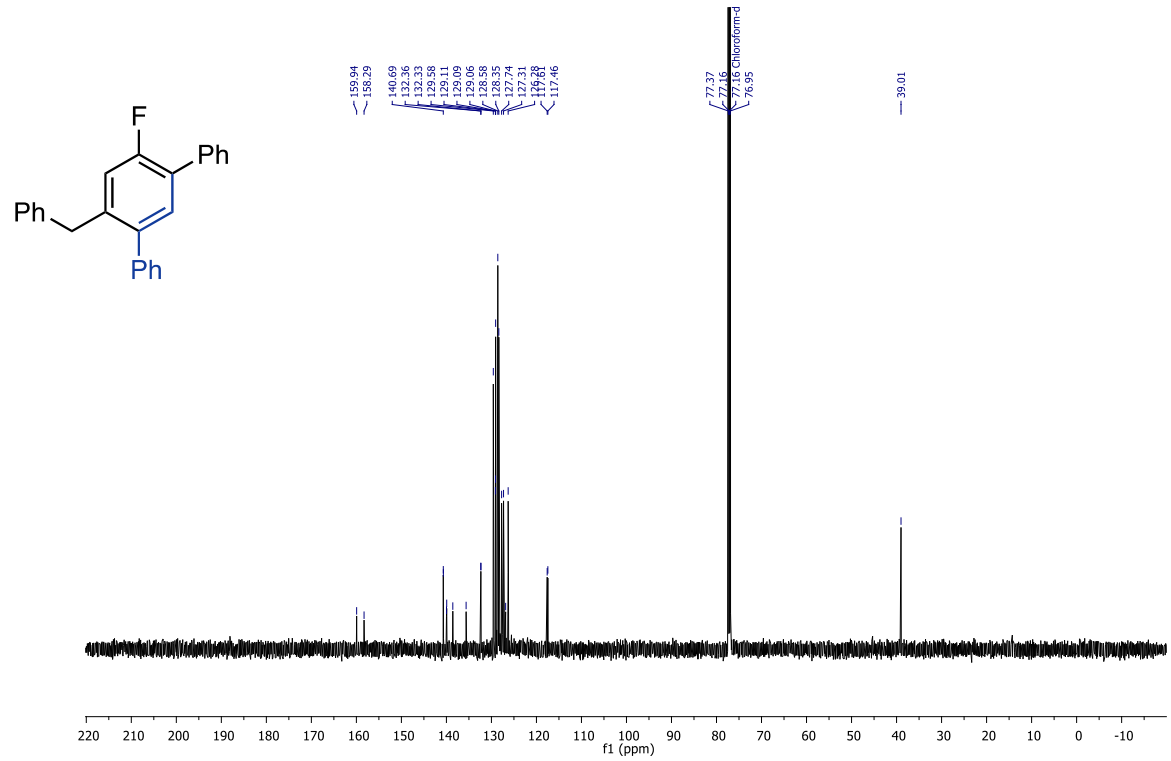
^{19}F NMR (565 MHz, C_6D_6) of **3ak**



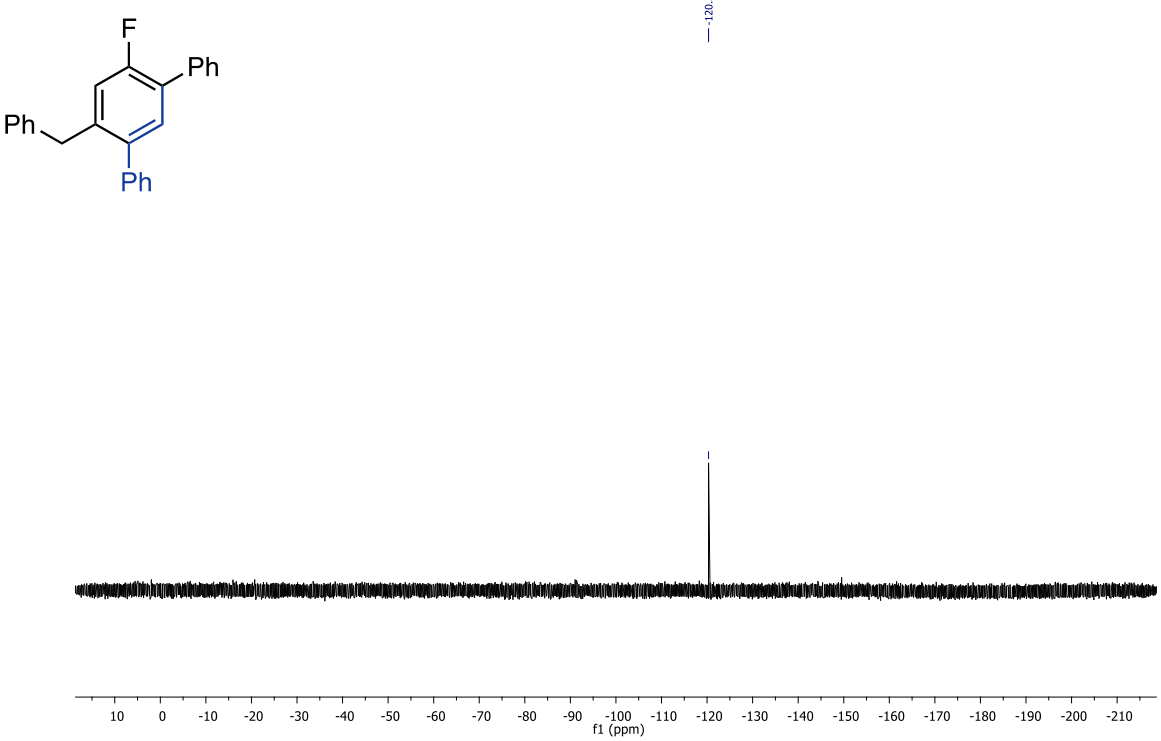
^{1}H NMR (600 MHz, C_6D_6) of **3al**



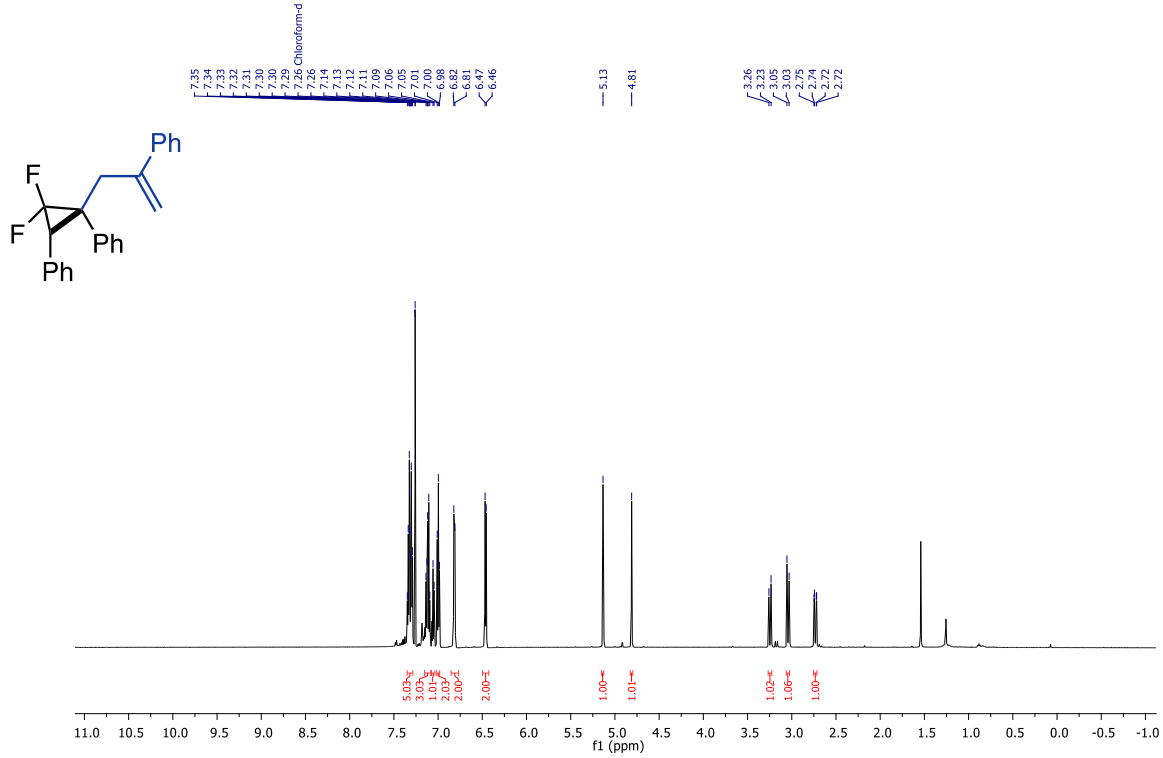
^{13}C NMR (151 MHz, C_6D_6) of **3al**



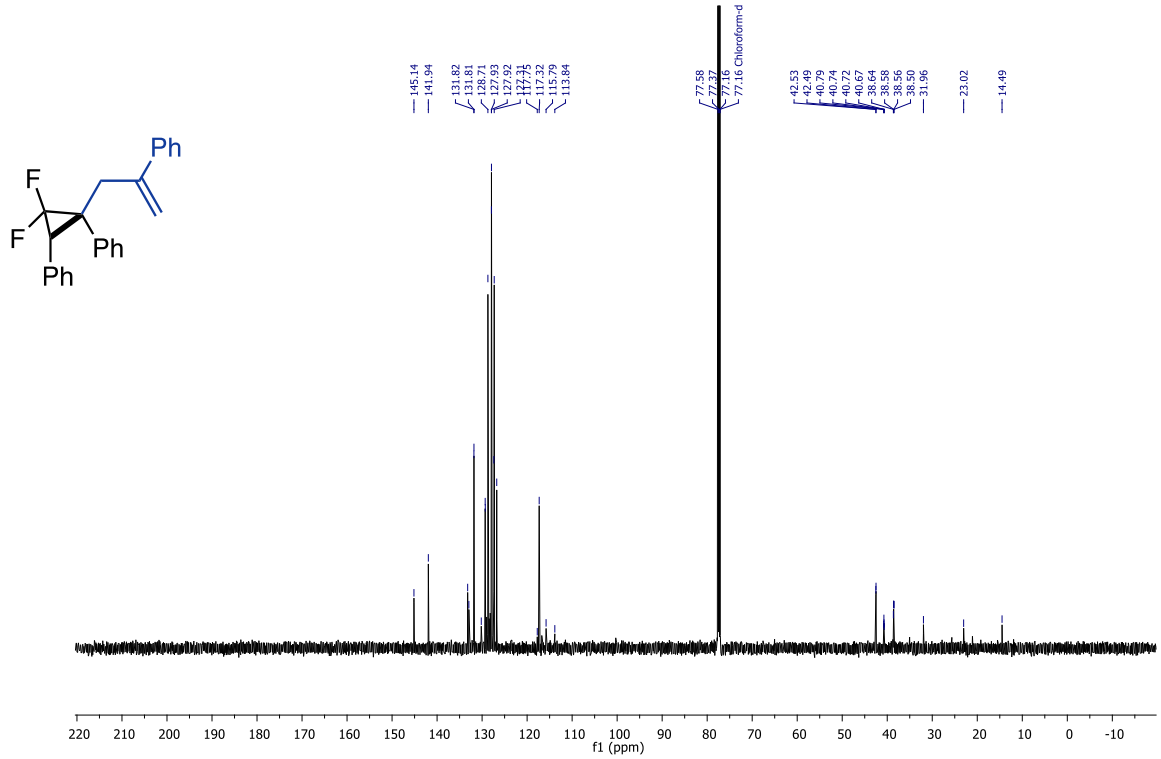
^{19}F NMR (565 MHz, C_6D_6) of **3al**



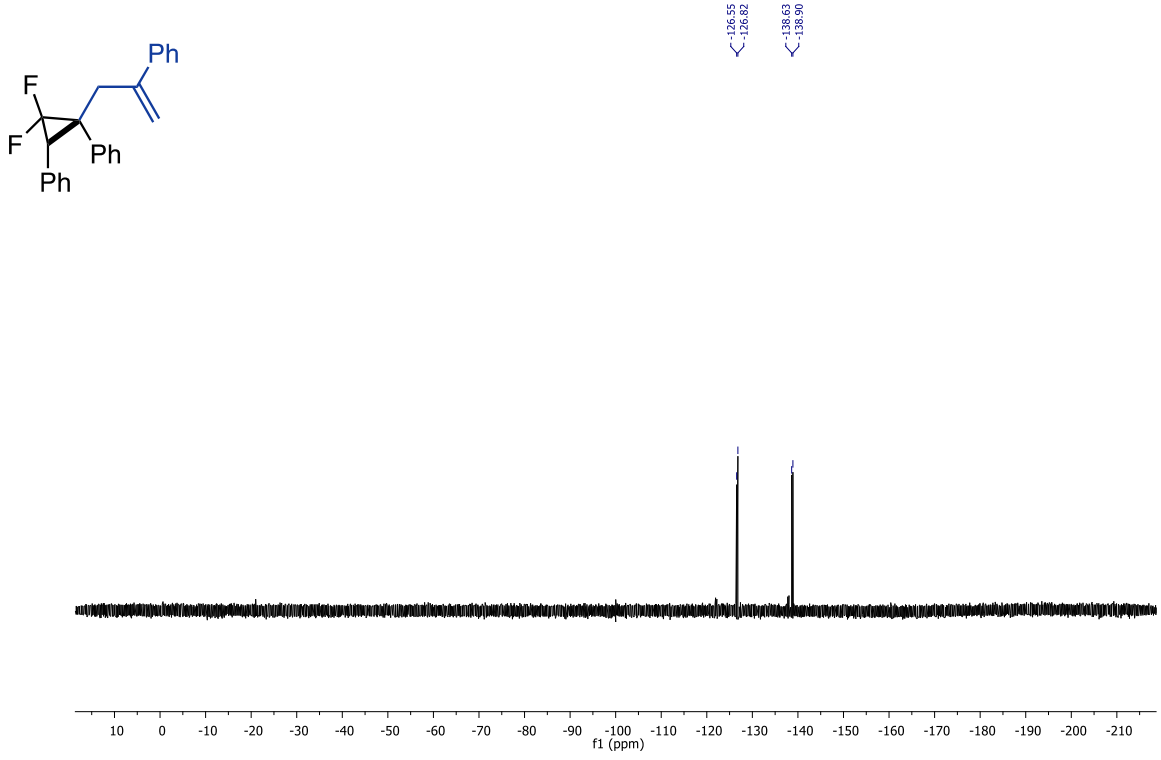
^{1}H NMR (600 MHz, $CDCl_3$) of **3ao**



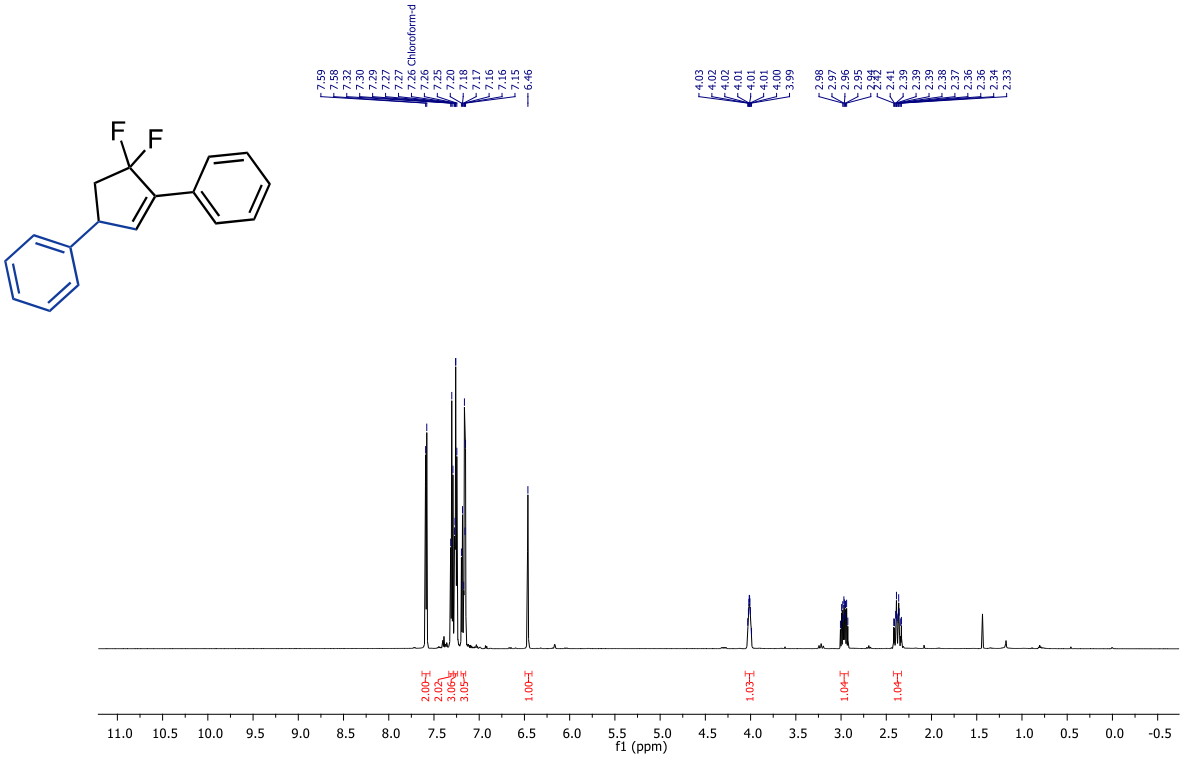
^{13}C NMR (151 MHz, $CDCl_3$) of **3ao**



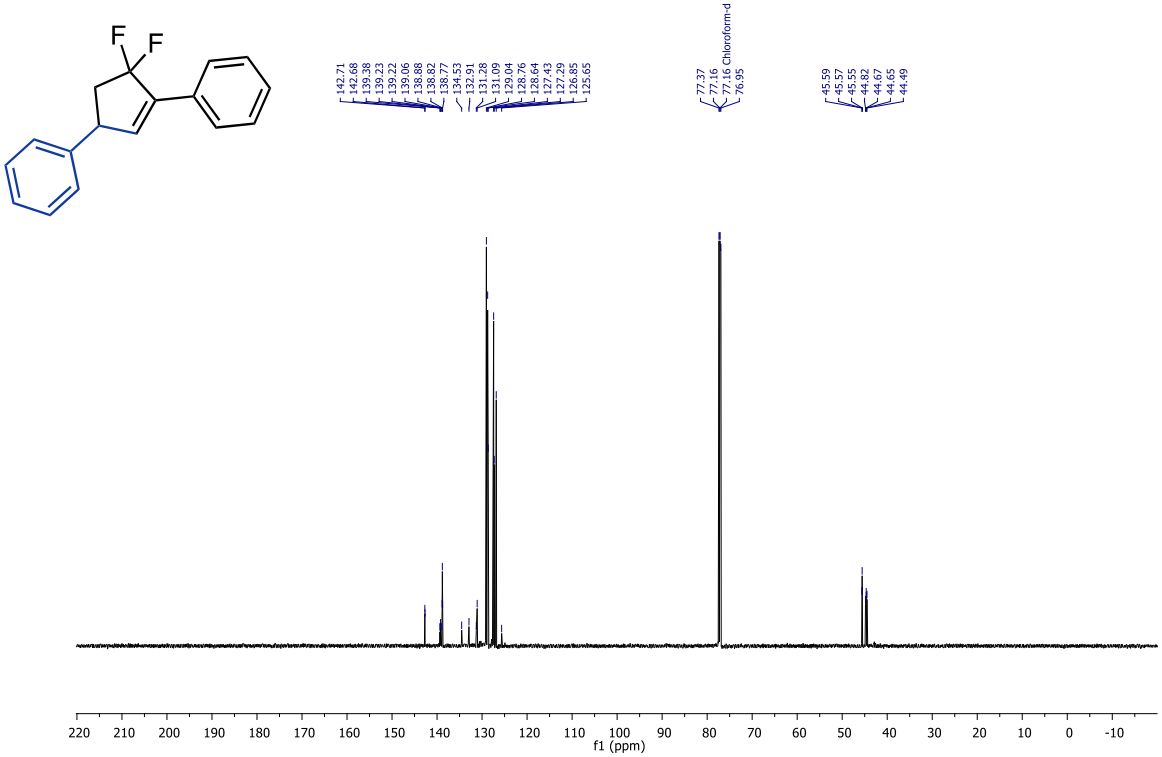
^{19}F NMR (565 MHz, $CDCl_3$) of **3ao**



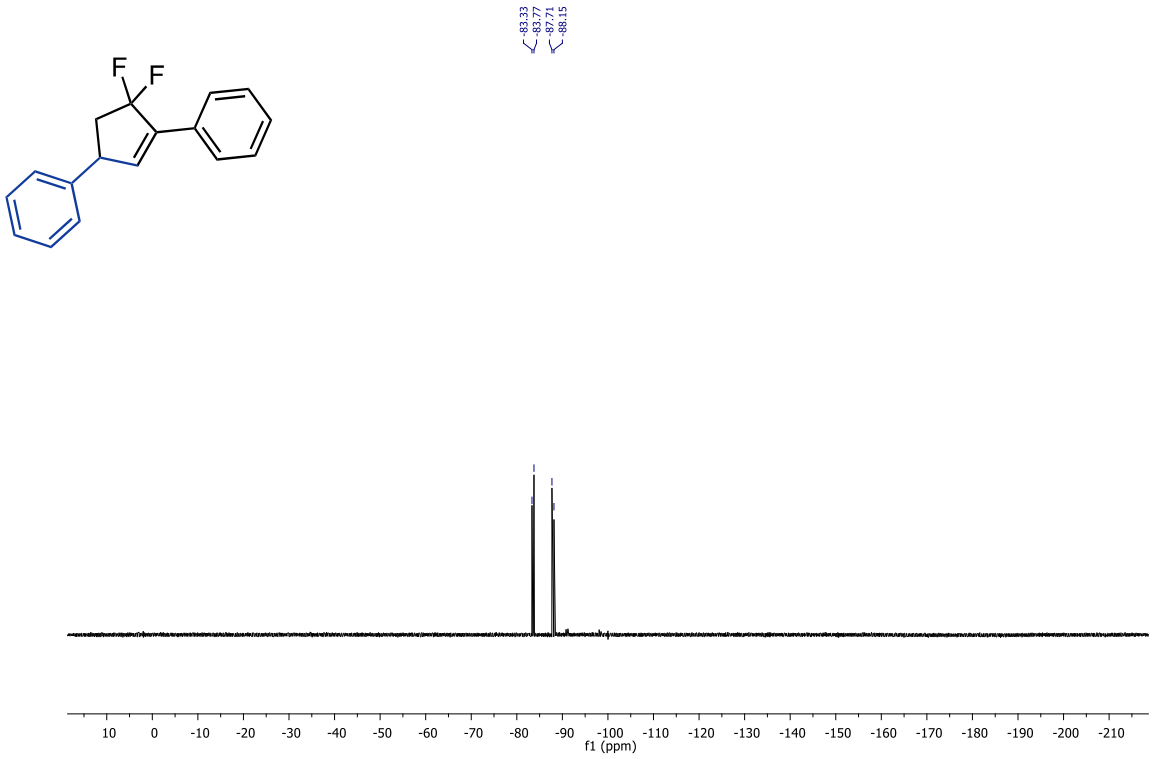
^{1}H NMR (600 MHz, $CDCl_3$) of **6g**



^{13}C NMR (151 MHz, $CDCl_3$) of **6g**



^{19}F NMR (565 MHz, $CDCl_3$) of **6g**



14. References

(1) (a) Ociepa, M.; Wierzba, A. J.; Turkowska, J.; Gryko, D. Polarity-Reversal Strategy for the Functionalization of Electrophilic Strained Molecules via Light-Driven Cobalt Catalysis. *J. Am. Chem. Soc.* **2020**, *142*, 5355-5361. (b) Schwartz, B. D.; Zhang, M. Y.; Attard, R. H.; Gardiner, M. G.; Malins, L. R. Structurally Diverse Acyl Bicyclobutanes: Valuable Strained Electrophiles. *Chem. Eur. J.* **2020**, *26*, 2808-2812.

(2) Molander, G. A.; Brown, A. R. Suzuki−Miyaura Cross-Coupling Reactions of Potassium Vinyltrifluoroborate with Aryl and Heteroaryl Electrophiles. *J. Org. Chem.* **2006**, *71*, 9681-9686.

(3) (a) Wang, F.; Luo, T.; Hu, J.; Wang, Y.; Krishnan, H. S.; Jog, P. V.; Ganesh, S. K.; Prakash, G. K. S.; Olah, G. A. Synthesis of *gem*-Difluorinated Cyclopropanes and Cyclopropenes: Trifluoromethyltrimethylsilane as a Difluorocarbene Source. *Angew. Chem., Int. Ed.* **2011**, *50*, 7153-7157. (b) Li, L.; Wang, F.; Ni, C.; Hu, J. Synthesis of *gem*-Difluorocyclopropa(e)nes and O-, S-, N-, and P-Difluoromethylated Compounds with $TMSCF_2Br$. *Angew. Chem., Int. Ed.* **2013**, *52*, 12390-12394.

(4) Qin, Y.; Sukul, V.; Pagakos, D.; Cui, C.; Jäkle, F. Preparation of Organoboron Block Copolymers via ATRP of Silicon and Boron-Functionalized Monomers. *Macromolecules* **2005**, *38*, 8987-8990.

(5) Huang, C.-Y.; Doyle, A. G. Nickel-Catalyzed Negishi Alkylations of Styrenyl Aziridines. *J. Am. Chem. Soc.* **2012**, *134*, 9541-9544.

(6) Schnell, S. D.; Schilling, M.; Sklyaruk, J.; Linden, A.; Luber, S.; Gademann, K. Nucleophilic Attack on Nitrogen in Tetrazines by Silyl-Enol Ethers. *Org. Lett.* **2021**, *23*, 2426-2430.

(7) Gui, J.; Xie, H.; Chen, F.; Liu, Z.; Zhang, X.; Jiang, F.; Zeng, W. Brønsted Acid/visible-light-promoted Markovnikov Hydroamination of Vinylarenes with Arylamines. *Org. Biomol. Chem.* **2020**, *18*, 956-963.

(8) Ye, Y.; Liu, J.; Xu, B.; Jiang, S.; Bai, R.; Li, S.; Xie, T.; Ye, X.-Y. Nickel-catalyzed Enantioselective 1,2-Vinylboration of Styrenes. *Chem. Sci.* **2021**, *12*, 13209-13215.

(9) (a) Wise, D. E.; Gogarnoiu, E. S.; Duke, A. D.; Paolillo, J. M.; Vacala, T. L.; Hussain, W. A.; Parasram, M. Photoinduced Oxygen Transfer Using Nitroarenes for the Anaerobic Cleavage of Alkenes. *J. Am. Chem. Soc.* **2022**, *144*, 15437-15442. (b) Ruffoni, A.; Hampton, C.; Simonetti,

M.; Leonori, D. Photoexcited Nitroarenes for the Oxidative Cleavage of Alkenes. *Nature* **2022**. DOI: 10.1038/s41586-022-05211-0.

(10) Karabal, P. U.; Chouthaiwale, P. V.; Shaikh, T. M.; Suryavanshi, G.; Sudalai, A. NaIO4/LiBr-Mediated Aziridination of Olefins Using Chloramine-T. *Tetrahedron Lett.* **2010**, *51*, 6460-6462.

(11) Ahmed, E.-A. M. A.; Suliman, A. M. Y.; Gong, T.-J.; Fu, Y. Access to Divergent Fluorinated Enynes and Arenes via Palladium-Catalyzed Ring-Opening Alkynylation of *gem*-Difluorinated Cyclopropanes. *Org. Lett.* **2020**, *22*, 1414-1419.

(12) (a) Hills, I. D.; Fu, G. C. Elucidating Reactivity Differences in Palladium-Catalyzed Coupling Processes: The Chemistry of Palladium Hydrides. *J. Am. Chem. Soc.* **2004**, *126*, 13178-13179. (b) Hu, Y.; Shen, Z.; Huang, H. Palladium-Catalyzed Intramolecular Hydroaminocarbonylation to Lactams: Additive-Free Protocol Initiated by Palladium Hydride. *ACS Catal.* **2016**, *6*, 6785-6789. (c) Tanase, T.; Ohizumi, T.; Kobayashi, K.; Yamamoto, Y. Spontaneous Multiple Insertion of a Bulky Aromatic Isocyanide into the Palladium−Hydride Bond of *trans*-[Pd(H)Cl(PPh_3)$_2$], Leading to Formation of Heterobicyclic and Pyrrole Compounds. *Organometallics* **1996**, *15*, 3404-3411.

(13) Dolbier, W. R.; Tian, F.; Duan, J.-X.; Li, A.-R.; Ait-Mohand, S.; Bautista, O.; Buathong, S.; Marshall Baker, J.; Crawford, J.; Anselme, P.; Cai, X. H.; Modzelewska, A.; Koroniak, H.; Battiste, M. A.; Chen, Q.-Y. Trimethylsilyl Fluorosulfonyldifluoroacetate (TFDA): A New, Highly Efficient Difluorocarbene Reagent. *J. Fluor. Chem.* **2004**, *125*, 459-469.

(14) Nicholson, W. I.; Barreteau, F.; Leitch, J. A.; Payne, R.; Priestley, I.; Godineau, E.; Battilocchio, C.; Browne, D. L. Direct Amidation of Esters by Ball Milling**. *Angew. Chem., Int. Ed.* **2021**, *60*, 21868-21874.

(15) Hu, F.; Chen, Z.; Tan, Y.; Xu, D.; Huang, S.; Jia, S.; Gong, X.; Qin, W.; Yan, H. Organocatalytic Enantioselective γ-Elimination: Applications in the Preparation of Chiral Peroxides and Epoxides. *Org. Lett.* **2020**, *22*, 1934-1940.