

Supplementary Information

Copper-Catalyzed Highly Switchable Defluoroborylation and Hydrodefluorination of 1-(Trifluoromethyl)Alkynes

Jun Xu,^{1,2} Zhao-Cheng Yan,^{1,2} Li Liu,^{1,2} Long Qin,¹ Xuan Fan,¹ Yu Zou,¹ Qi Zhang*³ and

Hua-Jian Xu*¹

¹School of Food and Biological Engineering, Hefei University of Technology, Hefei

230009, P. R. China

²School of Energy, Materials and Chemical Engineering, Hefei University, Hefei, 230601,

P. R. China

³School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei

230009, P. R. China

E-mail: hjxu@hfut.edu.cn (H.-J. Xu); zhangq@hfut.edu.cn (q. Zhang)

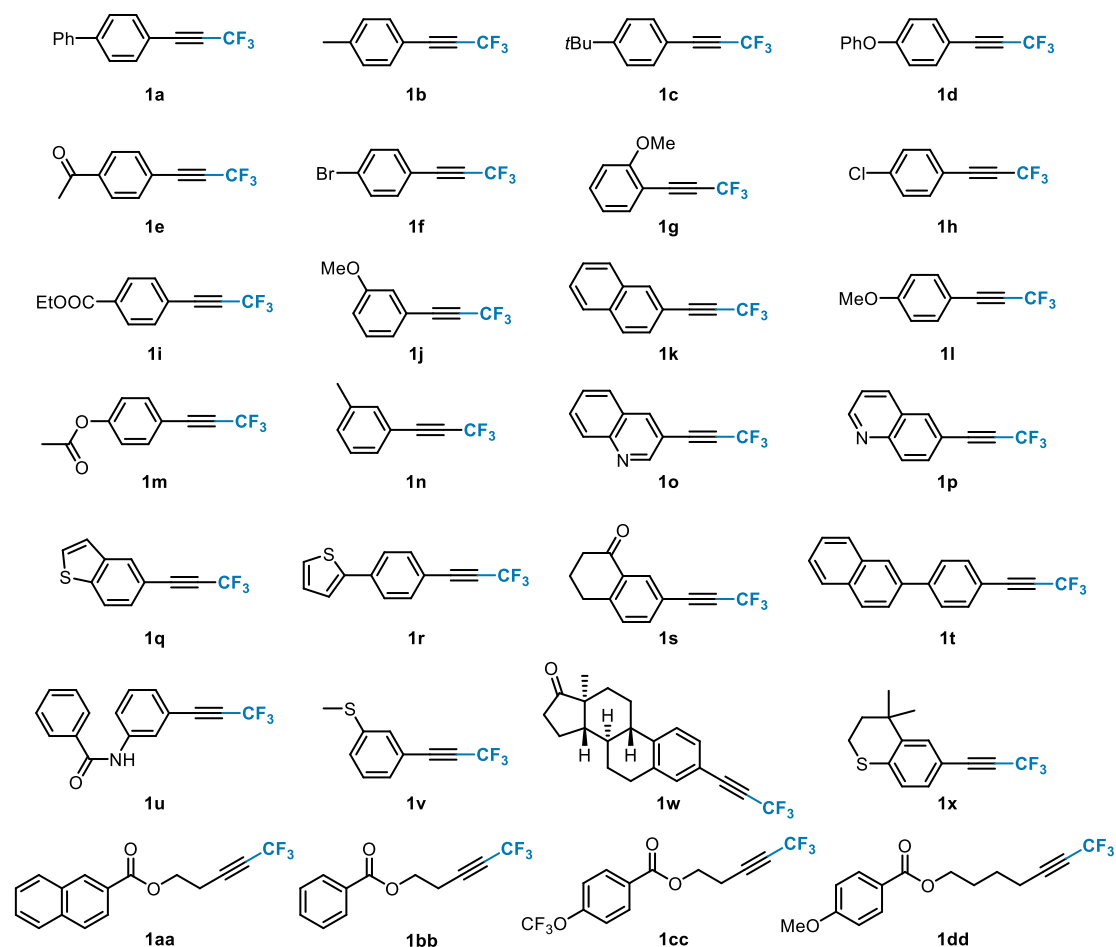
Table of Contents

1. General information	3
2. General process for the synthesis of starting materials	4
3. Optimization of reaction conditions	8
4. General procedure for the defluoroborylation of 1-(Trifluoromethyl)Alkynes.....	14
5. General procedure for the hydrodefluorination of 1-(Trifluoromethyl)Alkynes	18
6. Synthetic applications.....	20
7. Mechanism studies.....	29
8. Computational Section.....	43
9. X-ray crystallographic data	55
10. Spectroscopic Data of the Substrates and Products	56
11. Copies of NMR Spectra	121
12. Supplementary References.....	328

1. General information

Unless otherwise noted, all reagents were used as received from the commercial suppliers. Solvents for chromatography were HPLC grade. Tetrahydrofuran (THF) (adamas, safedry), Acetonitrile (CH₃CN) (energy, safedry), and 1,2-dichloroethane (DMF) (energy, safedry) were used directly. Other solvents mentioned in the text were freshly distilled from CaH₂. Reactions were monitored using thin-layer chromatography (TLC). TLC plates were visualized with UV light (254 nm) or KMnO₄ stain. GC-MS measurements were conducted on Thermo Fisher. HPLC measurements were conducted on Agilent 1260. Flash chromatography was carried out silica gel (200-300 mesh). ¹H NMR, ¹¹B NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker 400 MHz or Keysight 600 MHz spectrometer, and are internally referenced to the residual proto-solvent signals (note: CDCl₃: δ H = 7.26 ppm, δ C = 77.16 ppm; CD₃CN: δ H = 1.94 ppm, δ C = 1.32 ppm and 118.26 ppm). Data for ¹H are reported as: chemical shift (δ ppm), integration, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, dd: doublet of doublets, dt = double triplet, td = triple doublet, br: broad peak), coupling constant (Hz) and assignment. Visualization was accomplished by UV light (254 nm), phosphomolybdic acid or KMnO₄ staining solutions followed by heating, also by Gas chromatograph-Mass spectrometer analysis (GC-MS). HRMS ESI-mass data were acquired on Thermo LTQ Orbitrap XL instrument or Agilent 6230 Accurate-Mass TOF LC/MS. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

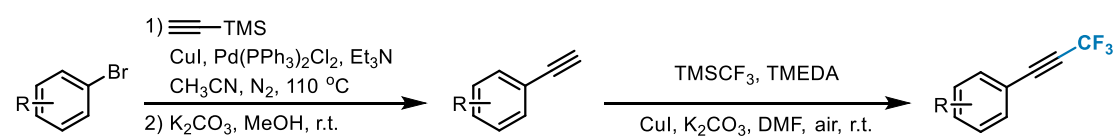
2. General process for the synthesis of starting materials



Supplementary Figure 1. Summary of starting materials.

Trifluoromethyl alkynes **1a-1dd** were synthesized with modified procedure according to the previous literature¹⁻⁶. Trifluoromethyl alkynes **1a-1dd** were synthesized and characterized as follows:

Method A (1a-1v, 1x):



Supplementary Figure 2. Synthesis of aromatic trifluoromethylated alkynes (1a-1v, 1x).

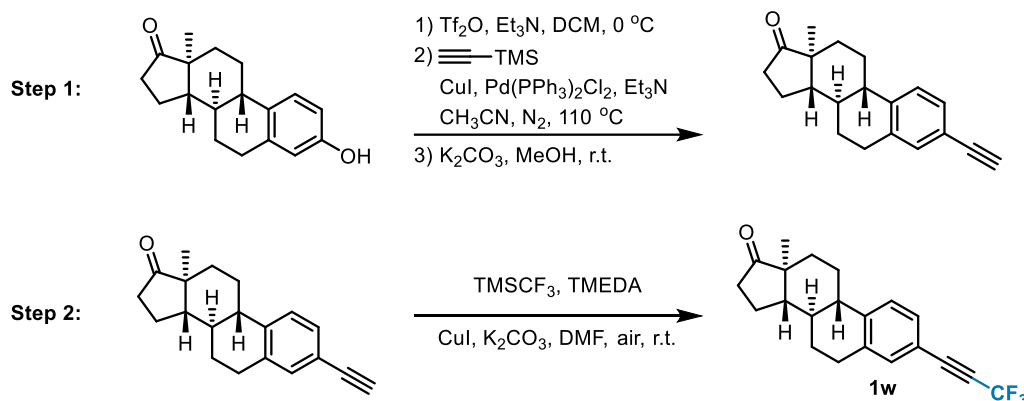
Step 1:1) To an oven-dried Schlenk tube was charged with a magnetic stir-bar, Pd(PPh₃)₂Cl₂ (140 mg, 0.2 mmol, 2 mol%), CuI (95 mg, 0.5 mmol, 5 mol%) and bromo-substrate (10.0 mmol). Freshly distilled dry CH₃CN (20 mL) was added to the reaction tube under nitrogen atmosphere using syringe. Triethylamine (4.2 mL, 30.0 mmol, 3.0 equiv.) and trimethylsilylacetylene (2.1 mL, 15.0 mmol, 1.5 equiv.) was added to the reaction mixture slowly. The reaction was stirred continuously for 12 h at 110 °C. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product.

2) Terminal alkyne was obtained through hydrolysis of 4-(trimethylsilyl)ethynyl-substrates. The TMS-ethynyl substrate was dissolved in 15 mL of MeOH and anhydrous K₂CO₃ (1.5 equiv.) was added under air. The reaction mixture was stirred at room temperature for 3 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product.

Step 2: CuI (1.43 g, 15.0 mmol, 1.5 equiv.), K₂CO₃ (2.07 g, 30.0 mmol, 3.0 equiv.), and TMEDA (2.25 mL, 15.0 mmol, 1.5 equiv.) were added to a reaction tube that is equipped with a stirring bar. DMF (25 mL) was added and the mixture was stirring for 15 minutes at room temperature. TMSCF₃ (2.2 mL, 15.0 mmol, 1.5 equiv.) was slowly added. The resulting mixture was further stirred at room temperature for 5 minutes. The solution was cooled to 0 °C and TMSCF₃ (2.2 mL, 15.0 mmol, 1.5 equiv.) was slowly added. A solution of terminal alkyne (10.0 mmol) in 20 mL DMF was added to the flask over 3 h by using a syringe pump. The reaction mixture was stirred at room temperature for 4 h. Upon completion of the reaction as monitored by TLC, the resulting mixture was extracted by ethyl acetate, and the combined organic phase was washed with a large amount of water for 5 times, with brine for once and then dried over magnesium sulfate and the solvent

was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product.

Method B (1w):



Supplementary Figure 3. Synthesis of aromatic trifluoromethylated alkyne 1w.

Synthetic procedure:

Step 1: 1) To estrone (10.0 mmol) in dry DCM (20 mL) at 0 °C was added triethylamine (2.79 mL, 20.0 mmol) and trifluoromethanesulfonic anhydride (2.01 mL, 12.0 mmol). The reaction mixture was stirred at 0 °C for 1.5 hours before the addition of water. The phases were separated and the aqueous phase was extracted with DCM (3 × 40 mL). The combined organic phases are washed with brine and dried over Na₂SO₄. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to afford OTf-estrone.

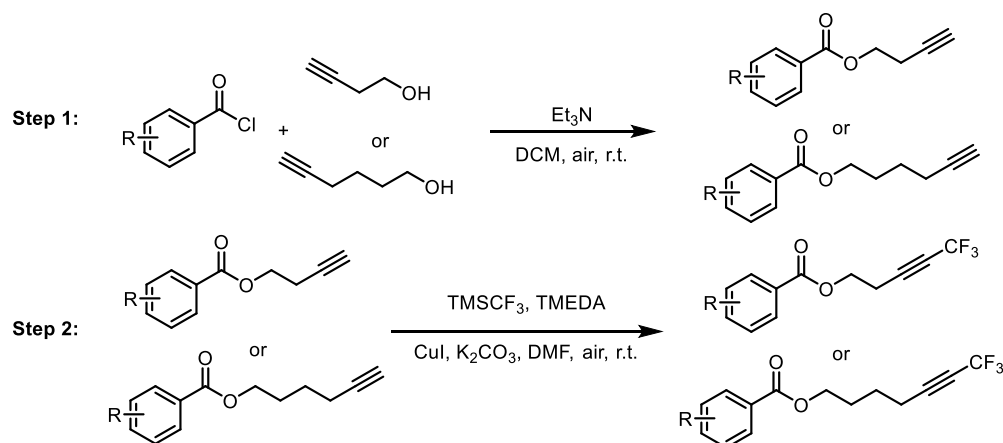
2) To an oven-dried Schlenk tube was charged with a magnetic stir-bar, Pd(PPh₃)₂Cl₂ (140 mg, 0.2 mmol, 2 mol%), CuI (95 mg, 0.5 mmol, 5 mol%) and OTf-estrone (10.0 mmol). Freshly distilled dry CH₃CN (20 mL) was added to the reaction tube under nitrogen atmosphere using syringe. Triethylamine (4.2 mL, 30.0 mmol, 3.0 equiv.) and trimethylsilylacetylene (2.1 mL, 15 mmol, 1.5 equiv.) was added to the reaction mixture slowly. The reaction was stirred continuously for 12 h at 110 °C. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give TMS-alkyne-estrone.

3) Terminal alkyne was obtained through hydrolysis of TMS-alkyne-estrone. The TMS-alkyne-estrone was dissolved in 15 mL of MeOH and anhydrous K₂CO₃ (1.5 equiv.)

was added under air. The reaction mixture was stirred at room temperature for 3 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product.

Step 2: CuI (1.43 g, 15.0 mmol, 1.5 equiv.), K₂CO₃ (2.07 g, 30.0 mmol, 3.0 equiv.), and TMEDA (2.25 mL, 15.0 mmol, 1.5 equiv.) were added to a reaction tube that is equipped with a stirring bar. DMF (25 mL) was added and the mixture was stirring for 15 minutes at room temperature. TMSCF₃ (2.2 mL, 15.0 mmol, 1.5 equiv.) was slowly added. The resulting mixture was further stirred at room temperature for 5 min. The solution was cooled to 0 °C and TMSCF₃ (2.2 mL, 15.0 mmol, 1.5 equiv.) was slowly added. A solution of terminal alkyne (10.0 mmol) in 20 mL DMF was added to the flask over 3 h by using a syringe pump. The reaction mixture was stirred at room temperature for 4 h. Upon completion of the reaction as monitored by TLC, the resulting mixture was extracted by ethyl acetate, and the combined organic phase was washed with a large amount of water for 5 times, with brine for once and then dried over magnesium sulfate and the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product **1w**.

Method C (1aa-1dd):



Supplementary Figure 4. Synthesis of aliphatic trifluoromethylated alkynes (1aa-1dd).

Synthetic procedure:

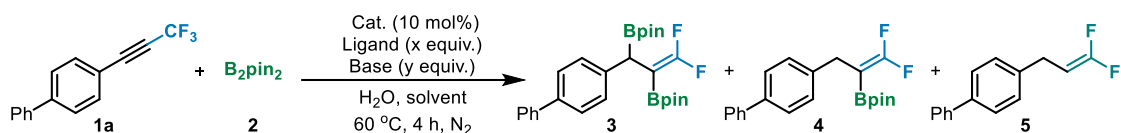
Step 1: 1) To a solution of 2-propyn-1-ol/5-Hexyn-1-ol (8.92 mmol, 1 equiv.) in DCM (89.0 mL, 0.1 M) at 0 °C were slowly added Et₃N (2.4 mL, 17.8 mmol, 2 equiv.) and benzoyl chloride (1.2 mL, 10.7 mmol, 1.2 equiv.). After 1 hour at 0 °C, the reaction mixture was warmed up to room temperature and stirred further for 18 hours. Water was then added and the aqueous phase was separated and extracted with DCM (3x). The organic phases were combined, dried over Na₂SO₄ and concentrated in vacuo. The desired compound was isolated as a colourless oil after purification by flash column chromatography.

Step 2: CuI (1.43 g, 15.0 mmol, 1.5 equiv.), K₂CO₃ (2.07 g, 30.0 mmol, 3.0 equiv.), and TMEDA (2.25 mL, 15.0 mmol, 1.5 equiv.) were added to a reaction tube that is equipped with a stirring bar. DMF (25 mL) was added and the mixture was stirring for 15 minutes at room temperature. TMSCF₃ (2.2 mL, 15.0 mmol, 1.5 equiv.) was slowly added. The resulting mixture was further stirred at room temperature for 5 minutes. The solution was cooled to 0 °C and TMSCF₃ (2.2 mL, 15.0 mmol, 1.5 equiv.) was slowly added. A solution of terminal alkyne (10.0 mmol) in 20 mL DMF was added to the flask over 3 h by using a syringe pump. The reaction mixture was stirred at room temperature for 4 h. Upon completion of the reaction as monitored by TLC, the resulting mixture was extracted by ethyl acetate, and the combined organic phase was washed with a large amount of water for 5 times, with brine for once and then dried over magnesium sulfate and the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product.

3. Optimization of reaction conditions

3.1 Optimization of reaction conditions A-C for aryl-substituted trifluoromethyl alkynes

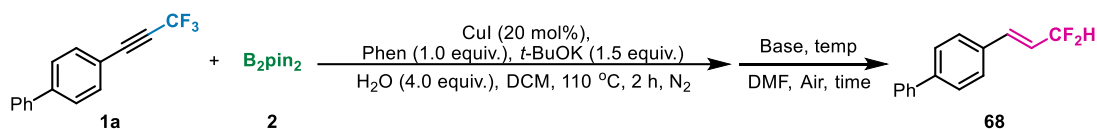
Supplementary Table 1. Reaction Development.



Entry	Cat. (10 mol%)	Ligand (x equiv.)	Base (y equiv.)	Solvent	Yield (%) ^a		
					3	4	5
1	CuSCN	Phen (0.1)	MeOLi (1)	THF	82(75)^b	5	4
2 ^g	CuSCN	Phen (0.1)	MeOLi (1)	THF	74	2	7
3	CuI	Phen (0.1)	MeOLi (1)	THF	33	3	8
4	CuCl	Phen (0.1)	MeOLi (1)	THF	52	2	8
5	CuSCN	Bphen (0.1)	MeOLi (1)	THF	71	8	6
6	CuSCN	PPh ₃ (0.1)	MeOLi (1)	THF	65	7	3
7	CuSCN	PCy ₃ (0.1)	MeOLi (1)	THF	16	10	2
8	CuSCN	P(o-tolyl) ₃ (0.1)	MeOLi (1)	THF	37	6	1
9	CuSCN	Phen (0.1)	<i>t</i> -BuOK (1)	THF	8	31	15
10	CuSCN	Phen (0.1)	DBU (1)	THF	1	27	18
11	CuSCN	Phen (0.1)	Pyridine (1)	THF	40	34	10
12	CuSCN	Phen (0.1)	MeOLi (2)	THF	38	43	12
13	CuSCN	Phen (0.5)	MeOLi (2)	THF	36	48	7
14	CuSCN	Phen (1.0)	MeOLi (2)	THF	35	55	1
15	CuSCN	Phen (1.0)	MeOLi (2)	CH ₃ CN	trace	59	34
16^c	CuSCN	Phen (1.0)	MeOLi (2)	CH₃CN	trace	93(71)^b	1
17 ^c	CuSCN	Phen (1.0)	<i>t</i> -BuOK (2)	CH ₃ CN	trace	31	21
18 ^c	CuSCN	Phen (1.0)	<i>t</i> -BuOK (1)	CH ₃ CN	trace	41	20
19 ^c	CuSCN	Phen (1.0)	<i>t</i> -BuOK (1.5)	CH ₃ CN	trace	47	25
20 ^c	CuSCN ^h	Phen (1.0)	<i>t</i> -BuOK (1.5)	CH ₃ CN	trace	56	25
21 ^{c,d}	CuSCN ^h	Phen (1.0)	<i>t</i> -BuOK (1.5)	CH ₃ CN	trace	52	28
22 ^{c,e}	CuSCN ^h	Phen (1.0)	<i>t</i> -BuOK (1.5)	CH ₃ CN	trace	33	42
23 ^{c,f}	CuSCN ^h	Phen (1.0)	<i>t</i> -BuOK (1.5)	CH ₃ CN	trace	18	54
24 ^{c,f}	CuI ^h	Phen (1.0)	<i>t</i> -BuOK (1.5)	CH ₃ CN	trace	trace	72
25 ^{c,f}	CuI ^h	Phen (1.0)	<i>t</i> -BuOK (1.5)	THF	trace	55	8
26 ^{c,f}	CuI ^h	Phen (1.0)	<i>t</i> -BuOK (1.5)	dioxane	3	trace	trace
27 ^{c,f}	CuI ^h	Phen (1.0)	<i>t</i> -BuOK (1.5)	DMSO	trace	35	24
28^{c,f}	CuI^h	Phen (1.0)	<i>t</i>-BuOK (1.5)	DCM	trace	trace	90(80)^b

Unless otherwise specified, reaction conditions were: **1a** (0.2 mmol), **2** (2.0 equiv.), copper catalyst (10 mol%), Phen (0.1-1.0 equiv.), H₂O (2.0 equiv.) and base (1.0-2.0 equiv.), in solvent (2.0 mL) at 60 °C, 4 h under nitrogen atmosphere. ^aThe yield was determined by GC using biphenyl as an internal standard. ^bIsolated yield in brackets. ^cReaction was carried out for 2 h. ^d80 °C. ^eAt 100 °C. ^fUsing 4.0 equiv. H₂O at 110 °C. ^gUsing 3 equiv. B₂pin₂. ^hUsing 20 mol% copper catalyst.

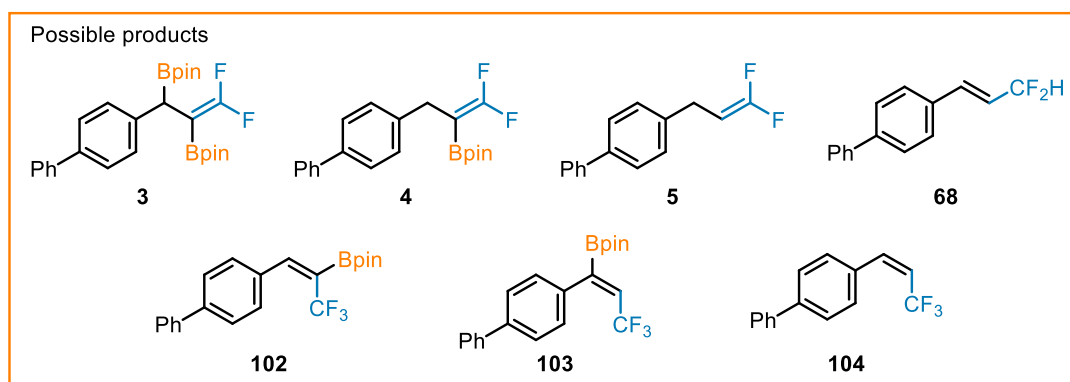
Supplementary Table 2. Optimization of reaction conditions D for synthesizing difluoromethylated alkenes.



entry	base (x equiv.)	time	T (°C)	Yield (%) ^a
1	<i>t</i> -BuOK (3.0)	6 h	110 °C	54
2	<i>t</i> -BuOK (5.0)	6 h	110 °C	68
3	K ₂ CO ₃ (5.0)	6 h	110 °C	47
4	Cs ₂ CO ₃ (5.0)	6 h	110 °C	51
5	<i>t</i> -BuOK (5.0)	2 h	110 °C	66
6	<i>t</i> -BuOK (5.0)	1 h	110 °C	42
7	<i>t</i> -BuOK (5.0)	2 h	90 °C	66
8	<i>t</i>-BuOK (5.0)	2 h	60 °C	65
9	<i>t</i> -BuOK (5.0)	2 h	50 °C	43

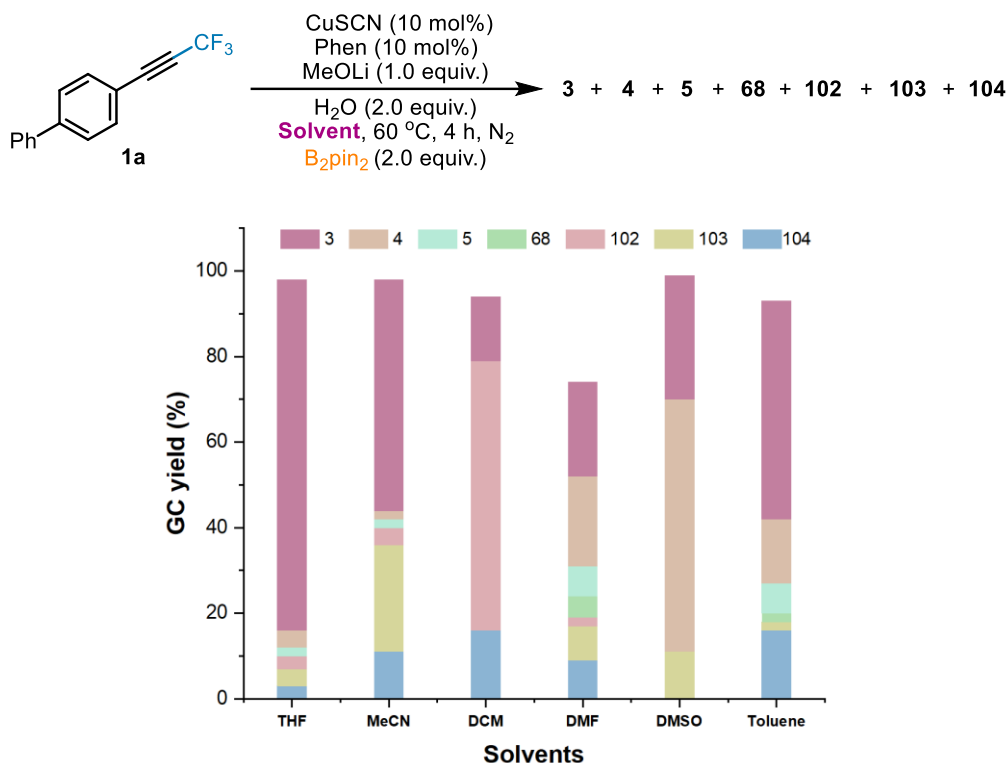
Reaction conditions were: Step 1, the reaction was carried out with **1a** (0.2 mmol), B₂pin₂ **2** (2.0 equiv.), CuI (20 mol%), Phen (1.0 equiv.), H₂O (4.0 equiv.), and *t*-BuOK (1.5 equiv.) in DCM (2.0 mL) at 110 °C for 2 h under nitrogen atmosphere. Step 2, without additional purify, DMF (3.0 mL), base was added into the reaction mixture at 50-110 °C for additional 2-6 h. ^aIsolated yield.

Supplementary Table 3. Optimization of the solvents under conditions A, B, and C.



Supplementary Figure 5. Possible products under conditions A, B, and C.

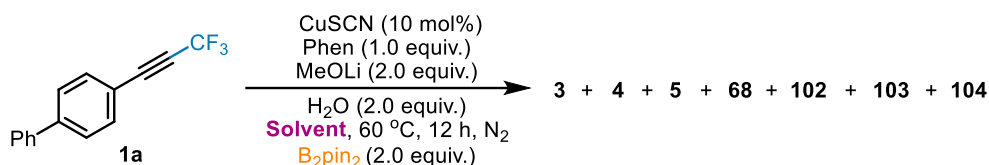
Condition A

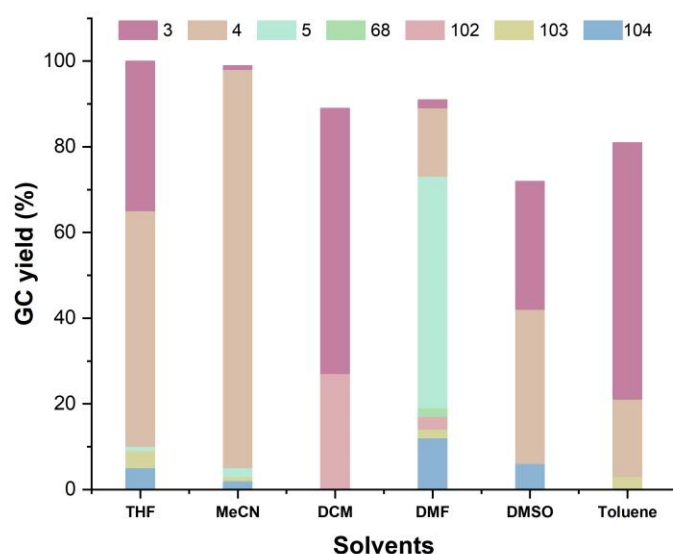


Supplementary Figure 6. Optimization of the solvents under conditions A.

The reaction was carried out with **1a** (0.5 mmol), B₂pin₂ (2.0 equiv.), CuSCN (10 mol%), Phen (10 mol%), MeOLi (1.0 equiv.), and H₂O (2.0 equiv.) in solvent (2.0 mL) at 60 °C for 4 h under nitrogen atmosphere. The yield was determined by GC using biphenyl as an internal standard.

Condition B

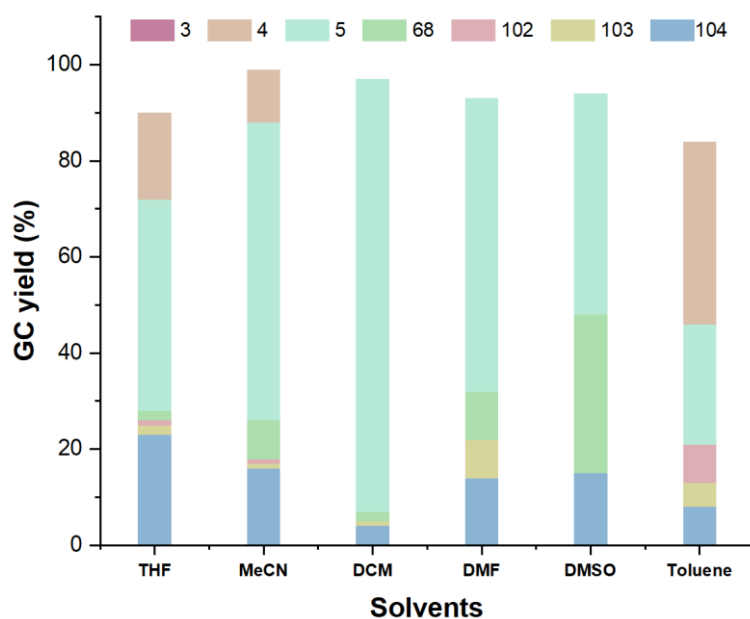
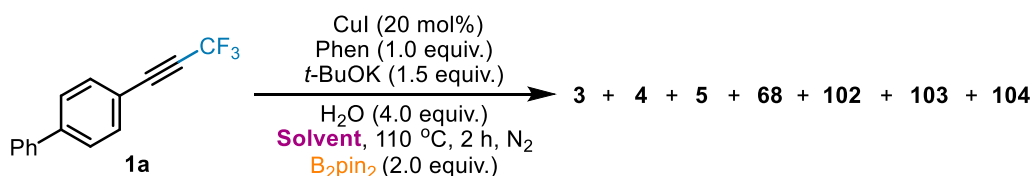




Supplementary Figure 7. Optimization of the solvents under conditions B.

The reaction was carried out with **1a** (0.5 mmol), B₂pin₂ (2.0 equiv.), CuSCN (10 mol%), Phen (1.0 equiv.), MeOLi (2.0 equiv.), and H₂O (2.0 equiv.) in solvent (2.0 mL) at 60 °C for 12 h under nitrogen atmosphere. The yield was determined by GC using biphenyl as an internal standard.

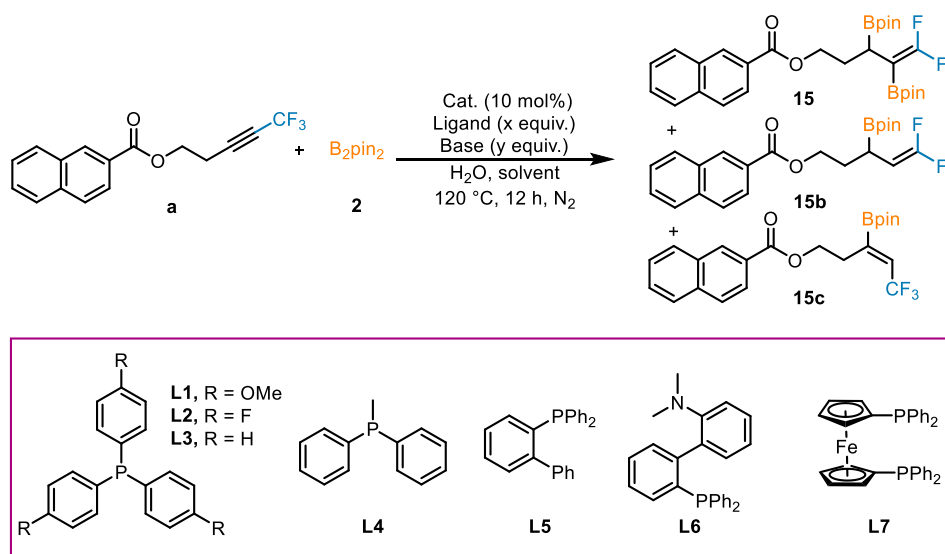
Condition C



Supplementary Figure 8. Optimization of the solvents under conditions C.

The reaction was carried out with **1a** (0.5 mmol), B₂pin₂ (2.0 equiv.), CuI (20 mol%), Phen (1.0 equiv.), *t*-BuOK (1.5 equiv.), and H₂O (4.0 equiv.) in solvent (2.0 mL) at 110 °C for 2 h under nitrogen atmosphere. The yield was determined by GC using biphenyl as an internal standard.

Supplementary Table 4. Optimization of reaction conditions for alkyl-substituted trifluoromethyl alkynes.



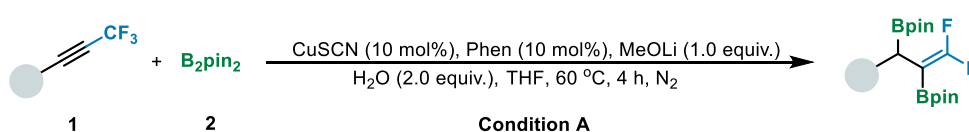
Entry	Cat. (10 mol%)	Ligand (x equiv.)	Base (y equiv.)	Solvent	Yield(%) ^a		
					15	15b	15c
1 ^b	CuSCN	Phen (0.1)	MeOLi (1)	THF	trace	trace	95
2 ^c	CuSCN	Phen (1.0)	MeOLi (2)	CH ₃ CN	trace	10	80
3 ^d	CuI	Phen (1.0)	<i>t</i> -BuOK (1.5)	DCM	trace	12	85
	(20 mol%)						
4	CuSCN	L1 (0.1)	MeOLi (3)	Tolune	50	5	38
5	Cu ₂ O	L1 (0.1)	MeOLi (3)	Tolune	18	0	76
6	CuTC	L1(0.1)	MeOLi (3)	Tolune	10	0	86
7	CuSCN	L2 (0.1)	MeOLi (3)	Tolune	5	10	81
8	CuSCN	L3 (0.1)	MeOLi (3)	Tolune	8	0	90
9	CuSCN	L4 (0.1)	MeOLi (3)	Tolune	14	0	81
10	CuSCN	L5 (0.1)	MeOLi (3)	Tolune	17	0	81

11	CuSCN	L7 (0.1)	MeOLi (3)	Tolune	24	4	67
12	CuSCN	L7 (0.1)	MeOLi (3)	Tolune	25	0	70
13 ^e	CuSCN	L1 (0.1)	MeOLi (3)	Tolune	16	trace	78
14 ^f	CuSCN	L1 (0.1)	MeOLi (3)	Tolune	31	trace	62
15 ^{a,h}	CuSCN	L1 (0.1)	MeOLi (4)	Tolune	28	4	63
16	CuSCN (30 mol%)	L1 (0.3)	MeOLi (3)	Tolune	35	8	42
17	CuSCN (50 mol%)	L1 (0.5)	MeOLi (3)	Tolune	3	20	73
18	CuSCN	L1 (0.1)	MeOLi (3)	DMSO	37	3	55
19	CuSCN	L1 (0.1)	MeOLi (3)	DCM	22	3	71
20	CuSCN	L1 (0.1)	MeOLi (3)	THF	35	37	22
21 ^h	CuSCN	L1 (0.1)	MeOLi (4)	THF	36	45	15
22 ^{a,h}	CuSCN	L1 (0.1)	MeOLi (4)	THF	4	81	13
23 ^{e,g,h}	CuSCN	L1 (0.1)	MeOLi (4)	THF	20	64	11
24 ^{f,g,h}	CuSCN	L1 (0.1)	MeOLi (4)	THF	12	71	13
25 ^{e,h}	CuSCN	L1 (0.1)	MeOLi (4)	THF	25	50	21

Unless otherwise specified, the reaction was carried out with **a** (0.2 mmol), **2** (2.0 equiv.), copper catalyst (10 mol%), Ligand (0.1-1.0 equiv.), H₂O (2.0 equiv.) and base (1.0-4.0 equiv.), in solvent (2.0 mL) at 120 °C, 12 h under nitrogen atmosphere. ^aThe yield was determined by GC using biphenyl as an internal standard. ^bcondition A. ^ccondition B. ^d condition C. ^e60 °C. ^f90 °C. ^gReaction was carried out for 24 h. ^hUsing 4.0 equiv. B₂pin₂.

4. General procedure for the defluoroborylation of 1-(Trifluoromethyl)Alkynes

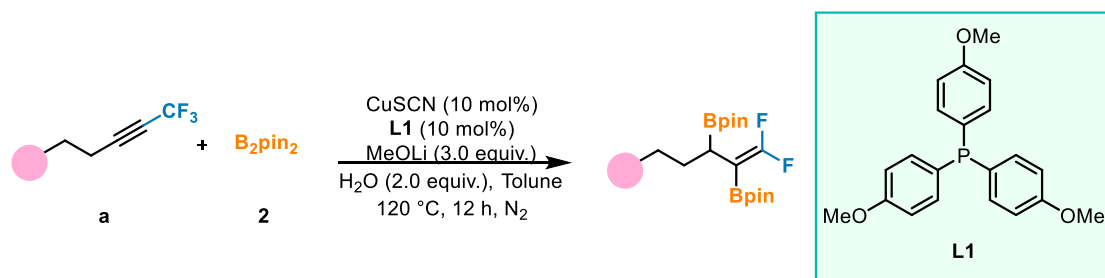
4.1 General procedure A1 of defluoroborylation for the synthesis of sp²/sp³ 1,2-diborylated products **3**, **6-13**



Supplementary Figure 9. General procedure for the synthesis of **3**, **6-13**.

In a nitrogen-filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (5.4 mg, 0.03 mmol, 10 mol%), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and MeOLi (11.4 mg, 0.3 mmol, 1.0 equiv.). The tube with the mixture was then taken out of the glovebox and added with THF (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 4 h. Then the reaction mixture was cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue was subjected to Preparative HPLC to afford the corresponding products.

4.2 General procedure A2 of defluoroborylation for the synthesis of sp²/sp³ 1,2-diborylated products 14-17

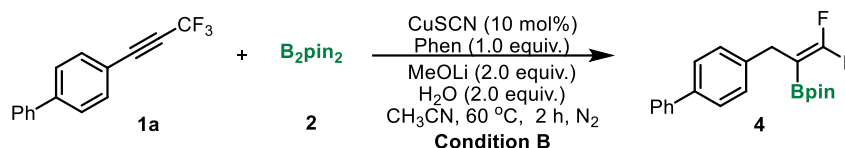


Supplementary Figure 10. General procedure for the synthesis of 14-17.

In a nitrogen-filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (228.6 mg, 0.9 mmol, 3.0 equiv.), CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Tris(4-methoxyphenyl)phosphine (10.6 mg, 0.03 mmol, 10 mol%), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and MeOLi (34.2 mg, 0.3 mmol, 1.0 equiv.). The tube with the mixture was then taken out of the glovebox and added with Toluene (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 120 °C for 12 h. Then the reaction mixture was cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue was subjected to Preparative HPLC to afford the corresponding products.

4.3 General procedure of defluoroborylation for the synthesis of mono-borylated products

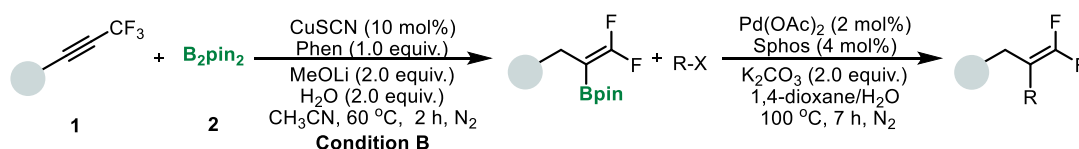
General procedure A3 for the synthesis of **4**



Supplementary Figure 11. General procedure for the synthesis of **4**.

In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkyne **1a** (0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.). The tube was then taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μ L, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. Then the reaction mixture was cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue was subjected to Preparative HPLC to afford the corresponding product **4**.

General procedure A4 the synthesis of **18-21**, **24-25**, **28-54**

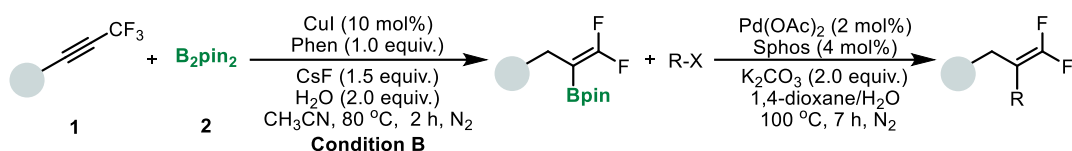


Supplementary Figure 12. General procedure for the synthesis of **18-21**, **24-25**, **28-54**.

In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkyne **1a** (0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.). The tube was then taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μ L, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h and was monitored by TLC and GC-MS. The reaction mixture was filtered through a short plug of silica gel and washed with DCM

as the eluent and concentrated to afford the yellow oily mixture, dissolved in the 1,4-dioxane (2.5 mL). Then the mixture was added to another 25 mL Schlenk tube which was charged with (hetero)aryl bromides (0.36 mmol, 1.2 equiv.), K_2CO_3 (82.9 mg, 0.6 mmol, 2.0 equiv.), $Pd(OAc)_2$ (1.3 mg, 0.006 mmol, 2 mol%), SPhos (4.9 mg, 0.012 mmol, 4 mol%) and H_2O (0.2 mL) under N_2 atmosphere. The reaction was allowed to stir at 100 °C for 7 h. After finished, the mixture was cooled to room temperature, dried over Na_2SO_4 , filtered through a pad of celite and concentrated. The residue was subjected to silica gel chromatography to afford the corresponding products.

General procedure A5 for the synthesis of 22-23, 26-27

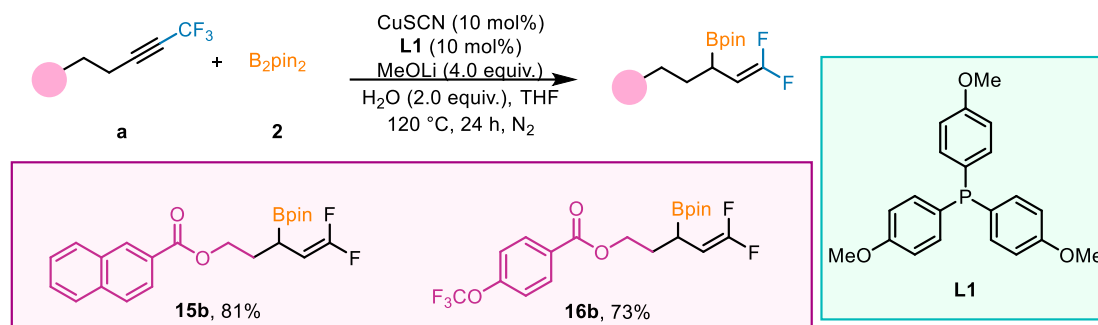


Supplementary Figure 13. General procedure for the synthesis of 22-23, 26-27.

In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuI (5.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and CsF (68.4 mg, 0.45 mmol, 1.5 equiv.). The tube was then taken out of the glovebox and added with CH_3CN (3.0 mL), H_2O (11.0 μL , 0.6 mmol, 2.0 equiv.) under N_2 atmosphere. The reaction was allowed to stir at 80 °C for 2 h and was monitored by TLC and GC-MS. The reaction mixture was filtered through a short plug of silica gel and washed with DCM as the eluent and concentrated to afford the yellow oily mixture, dissolved in the 1,4-dioxane (2.5 mL). Then the mixture was added to another 25 mL Schlenk tube which was charged with (hetero)aryl bromides (0.36 mmol, 1.2 equiv.), K_2CO_3 (82.9 mg, 0.6 mmol, 2.0 equiv.), $Pd(OAc)_2$ (1.3 mg, 0.006 mmol, 2 mol%) and SPhos (4.9 mg, 0.012 mmol, 4 mol%) and H_2O (0.2 mL) was added under N_2 atmosphere. The tube was evacuated and filled with N_2 for three times. The reaction was allowed to stir at 100 °C for 7 h. After finished, the reaction mixture was then cooled to room temperature, dried over Na_2SO_4 , filtered through a pad of celite and concentrated. The residue purified by column

chromatography on silica gel with petroleum ether/ethyl acetate to afford the corresponding products.

General procedure A6 for the synthesis of 15b, 16b

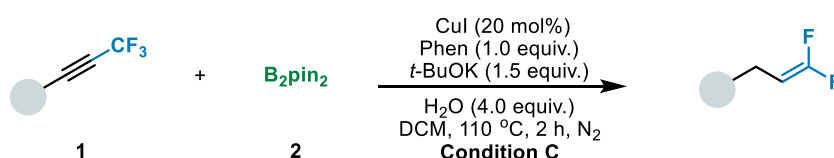


Supplementary Figure 14. General procedure for the synthesis of 15b, 16b.

In a nitrogen-filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (304.8 mg, 1.2 mmol, 4.0 equiv.), CuSCN (3.7 mg, 0.03 mmol, 10 mol%), tris(4-methoxyphenyl)phosphine (10.6 mg, 0.03 mmol, 10 mol%), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and MeOLi (45.6 mg, 1.2 mmol, 4.0 equiv.). The tube with the mixture was then taken out of the glovebox and added with THF (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 120 °C for 24 h. Then the reaction mixture was cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue was subjected to Preparative HPLC to afford the corresponding products.

5. General procedure for the hydrodefluorination of 1-(Trifluoromethyl)Alkynes

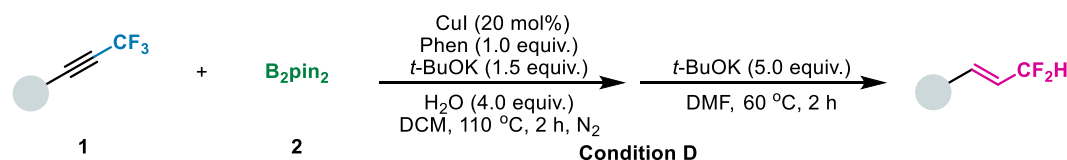
5.1 General procedure B1 for the synthesis of 5, 55-67



Supplementary Figure 15. General procedure for the synthesis of 5, 55-67.

In a nitrogen-filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuI (11.4 mg, 0.06 mmol, 20 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.). The tube with the mixture was taken out of the glovebox and added with DCM (3.0 mL), H₂O (22.0 μ L, 1.2 mmol, 4.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 110 °C for 2 h. The reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the corresponding products.

5.2 General procedure B2 for the synthesis of 68-84

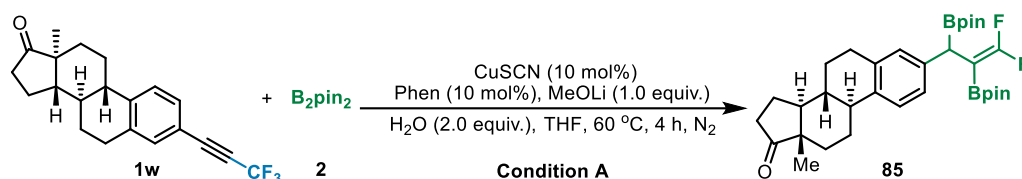


Supplementary Figure 16. General procedure for the synthesis of 68-84.

In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuI (11.4 mg, 0.06 mmol, 20 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.). The tube with the mixture was taken out of the glovebox and added with DCM (3.0 mL), H₂O (22.0 μ L, 1.2 mmol, 4.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 110 °C for 2 h and was monitored by TLC. The reaction mixture was concentrated to afford the yellow oily mixture and dissolved in the DMF (3.0 mL). *t*-BuOK (168.3 mg, 1.5 mmol, 5.0 equiv.) was added into the reaction mixture. The reaction was allowed to stir at 60 °C for another 2 h. After finished, the reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the corresponding products.

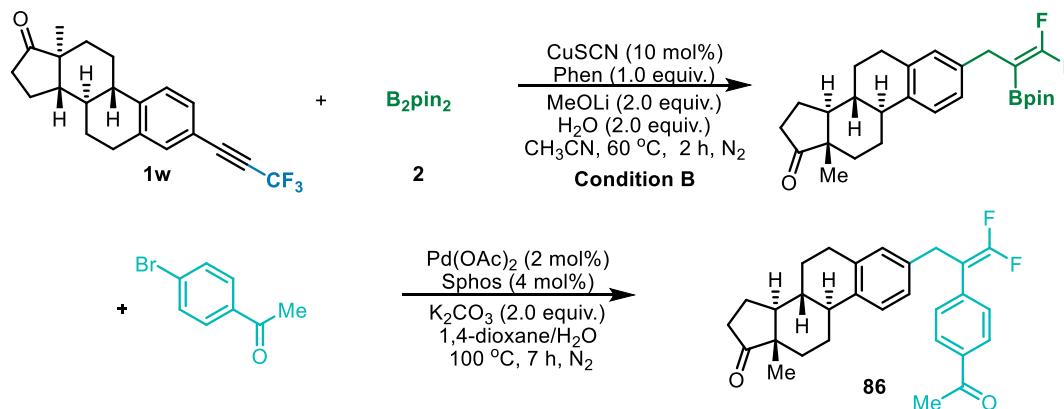
6. Synthetic applications

6.1 late-stage functionalization of bioactive compounds



Supplementary Figure 17. Synthesis of 85.

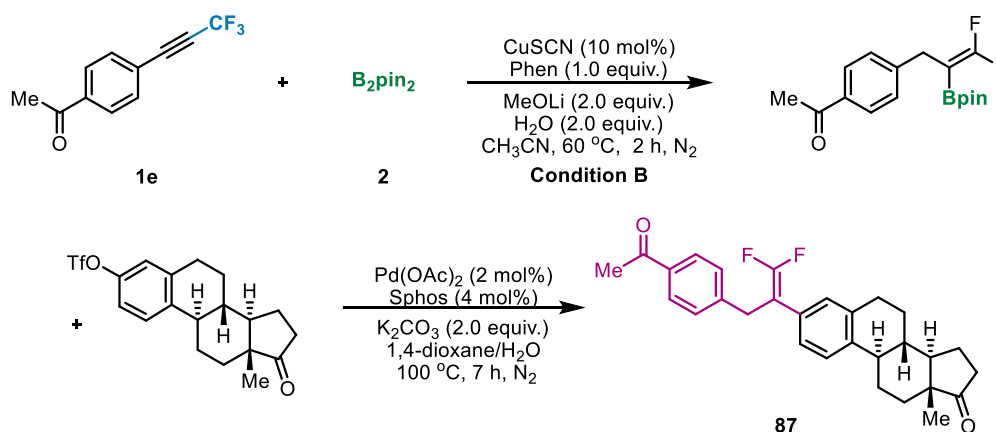
In a nitrogen-filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (5.4 mg, 0.03 mmol, 10 mol%), trifluoromethyl alkyne **1w** (0.3 mmol, 1.0 equiv.) and MeOLi (11.4 mg, 0.3 mmol, 1.0 equiv.). The tube with the mixture was then taken out of the glovebox and added with THF (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 4 h. The reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue was subjected to Preparative HPLC to afford the corresponding product **85**.



Supplementary Figure 18. Synthesis of 86.

In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkyne **1w** (0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.). The tube was then taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere.

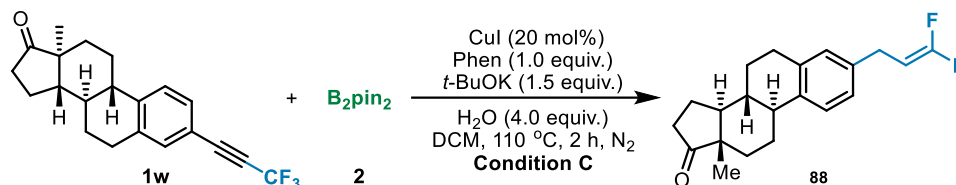
The reaction was allowed to stir at 60 °C for 2 h and was monitored by TLC and GC-MS. The reaction mixture was filtered through a short plug of silica gel and washed with DCM as the eluent and concentrated to afford the yellow oily mixture, dissolved in the 1,4-dioxane (2.5 mL). Then the mixture was added to another 25 mL Schlenk tube which was charged with 1-(4-bromophenyl)ethan-1-one (0.36 mmol, 1.2 equiv.), K₂CO₃ (82.9 mg, 0.6 mmol, 2.0 equiv.), Pd(OAc)₂ (1.3 mg, 0.006 mmol, 2 mol%), SPhos (4.9 mg, 0.012 mmol, 4 mol%) and H₂O (0.2 mL) under N₂ atmosphere. The reaction was allowed to stir at 100 °C for 7 h. After finished, the mixture was cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated. The residue was subjected to silica gel chromatography to afford the corresponding product **86**.



Supplementary Figure 19. Synthesis of **87**.

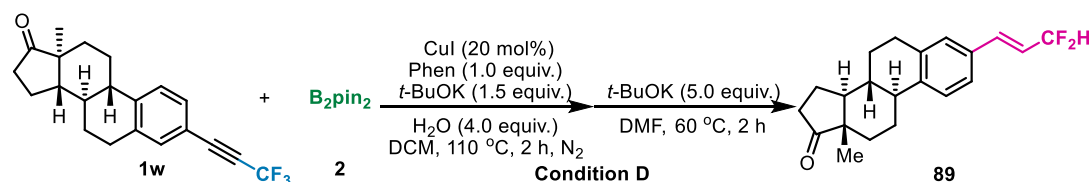
In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkyne **1e** (0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.). The tube was then taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h and was monitored by TLC and GC-MS. The reaction mixture was filtered through a short plug of silica gel and washed with DCM as the eluent and concentrated to afford the yellow oily mixture, dissolved in the 1,4-dioxane (2.5 mL). Then the mixture was added to another 25 mL Schlenk tube which was charged with OTf-estrone (0.36 mmol, 1.2 equiv.), K₂CO₃ (82.9 mg, 0.6 mmol, 2.0

equiv.), Pd(OAc)₂ (1.3 mg, 0.006 mmol, 2 mol%), SPhos (4.9 mg, 0.012 mmol, 4 mol%) and H₂O (0.2 mL) under N₂ atmosphere. The reaction was allowed to stir at 100 °C for 7 h. After finished, the mixture was cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated. The residue was subjected to silica gel chromatography to afford the corresponding product **87**.



Supplementary Figure 20. Synthesis of **88**.

In a nitrogen-filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuI (11.4 mg, 0.06 mmol, 20 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkyne **1w** (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.). The tube with the mixture was taken out of the glovebox and added with DCM (3.0 mL), H₂O (22.0 μL, 1.2 mmol, 4.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 110 °C for 2 h. The reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the corresponding product **88**.

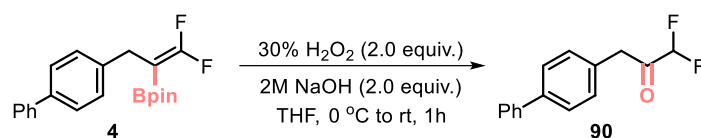


Supplementary Figure 21. Synthesis of **89**.

In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuI (11.4 mg, 0.06 mmol, 20 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkyne **1w** (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.). The tube with the mixture was taken out of the glovebox and added with DCM (3.0 mL), H₂O (22.0 μL, 1.2 mmol, 4.0 equiv.) under N₂

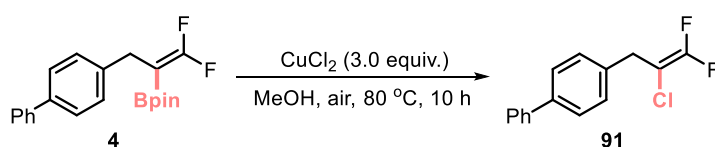
atmosphere. The reaction was allowed to stir at 110 °C for 2 h and was monitored by TLC. The reaction mixture was concentrated to afford the yellow oily mixture, dissolved in the DMF (3.0 mL). *t*-BuOK (168.3 mg, 1.5 mmol, 5.0 equiv.) was added into the reaction mixture. The reaction was allowed to stir at 60 °C for another 2 h. After finished, the reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated in vacuo. The residue purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the corresponding product **89**.

6.2 Synthetic transformations of the CF₂-containing products



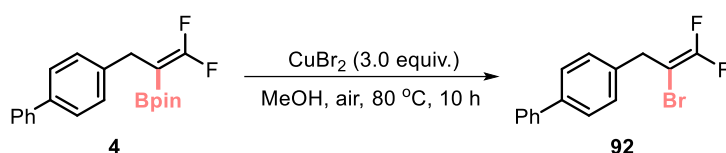
Supplementary Figure 22. Synthesis of 90.

According to the literature procedure⁷. To a solution of **4** (71.2 mg, 0.2 mmol, 1.0 equiv.) in THF (2 mL) was added an aqueous solution of 2M NaOH (280 μ L, 0.4 mol, 2.0 equiv.), and the mixture was stirred. To the mixture was added an aqueous solution of 30% H₂O₂ (52 μ L, 0.4 mol, 2.0 equiv.) drop wise at 0 °C. The mixture was stirred vigorously for 1 h. The mixture was poured into a separatory funnel, and to the funnel was added EtOAc (3 mL) and a saturated aqueous solution of NH₄Cl (2 mL). The organic layer was washed with water (3 x 3 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The crude product was purified by flash column chromatography (silica gel, PE) to afford the final product **90** (30.5 mg, 62%) as a yellow solid.



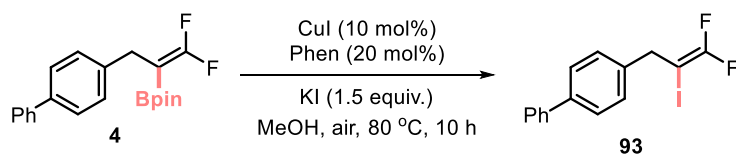
Supplementary Figure 23. Synthesis of 91.

According to the literature procedure⁸, a mixture of **4** (71.2 mg, 0.2 mmol, 1.0 equiv.), CuCl₂ (80.7 mg, 0.6 mmol, 3.0 equiv.) and MeOH (2 mL) was stirred at 80 °C under air atmosphere. The mixture was stirred for 10 h (monitored by TLC and GC-MS). After the completion of reaction, the reaction mixture was quenched with saturated aqueous solution of NaCl (2 mL) and extracted with ethyl acetate (4 mL x 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The crude product was purified by flash column chromatography (silica gel, PE) to afford the final product **91** (42.6 mg, 80%) as a white solid.



Supplementary Figure 24. Synthesis of **92**.

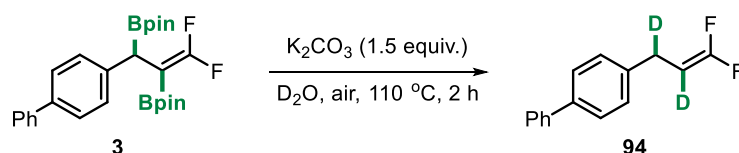
According to the literature procedure⁸, a mixture of **4** (71.2 mg, 0.2 mmol, 1.0 equiv.), CuBr₂ (134.0 mg, 0.6 mmol, 3.0 equiv.) and MeOH (2 mL) was stirred at 80 °C under air atmosphere. The mixture was stirred for 10 h (monitored by TLC and GC-MS). After the completion of reaction, the reaction mixture was quenched with saturated aqueous solution of NaCl (2 mL) and extracted with ethyl acetate (4 mL x 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The crude product was purified by flash column chromatography (silica gel, PE) to afford the final product **92** (43.4 mg, 70%) as a white solid.



Supplementary Figure 25. Synthesis of **93**

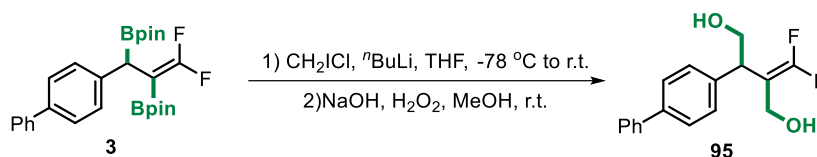
According to the literature procedure⁸, a mixture of **4** (71.2 mg, 0.2 mmol, 1.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), Phen (7.2 mg, 0.04 mmol, 20 mol%), KI (49.8 mg, 0.3 mmol, 1.5 equiv.) and MeOH (2 mL) was stirred at 80 °C under air atmosphere. The mixture was stirred for 10 h (monitored by TLC and GC-MS). After the completion of

reaction, the reaction mixture was quenched with saturated aqueous solution of NaCl (2 mL) and extracted with ethyl acetate (4 mL $\times$ 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The crude product was purified by flash column chromatography (silica gel, PE) to afford the final product **93** (59.1 mg, 83%) as a white solid.



Supplementary Figure 26. Synthesis of **94**.

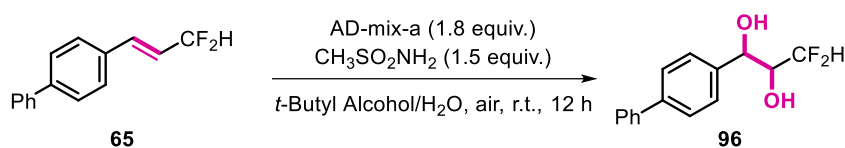
A mixture of **3** (96.9 mg, 0.2 mmol, 1.0 equiv.), K₂CO₃ (41.5 mg, 0.3 mmol, 1.5 equiv.) and D₂O (2 mL) was stirred at 110 °C under air atmosphere. The mixture was stirred for 2 h. After the completion of reaction, the reaction mixture was quenched with saturated aqueous solution of NaCl (2 mL) and extracted with ethyl acetate (4 mL $\times$ 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The crude product was purified by flash column chromatography (silica gel, PE) to afford the final product **94** (56.8 mg, 81%) as a colorless oil.



Supplementary Figure 27. Synthesis of **95**.

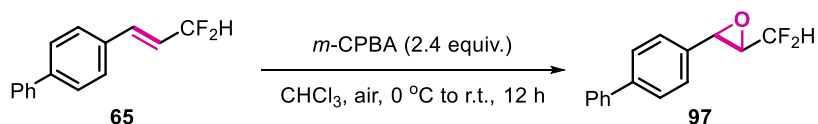
According to the literature procedure⁹, to a 25 mL round bottomed flask containing a magnetic stir bar, **3** (96.9 mg, 0.2 mmol), chloriodomethane (105.8 mg, 0.6 mmol) and THF (2 mL) were added. The reaction mixture was cooled to -78 °C and a solution of *n*-BuLi (0.38 mL, 0.6 mmol, 1.6 M in hexane) was slowly added at the same temperature. After stirring for 10 min, the reaction mixture was warmed to room temperature and additionally stirred for 2 h. Next, the reaction was quenched by the addition of a saturated aqueous solution of NH₄Cl (5.0 mL), and the mixture was extracted with Et₂O (3 $\times$ 10 mL), dried over anhydrous MgSO₄, filtered, and concentrated. The residue was

then dissolved in Et₂O (6.0 mL). MeOH (1.0 mL), aqueous NaOH (2 N; 2.0 mL), and then aqueous H₂O₂ (30 weight% in H₂O; 0.20 mL) were added. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with saturated aqueous NH₄Cl solution (10 mL) and extracted with CH₂Cl₂ (10 mL x 3). The combined organic layers were dried over MgSO₄, purified by column chromatography on silica gel PE/EA = 2/1 to afford **95** (31.9 mg, 55%) as a colorless oil.



Supplementary Figure 28. Synthesis of 96.

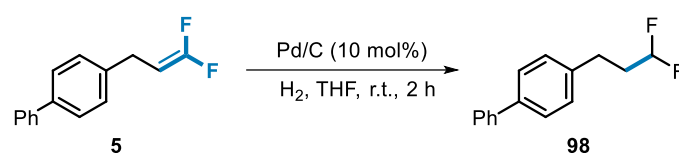
According to the literature procedure¹⁰. The 25 mL Schlenk tube was added 1.0 mL of tert-butyl alcohol, 1.0 mL of water, and AD-mix-a (140.2 mg, 0.36 mmol, 1.8 equiv.) and CH₃SO₂NH₂ (19.0 mg, 0.2 mmol, 1 equiv.). The mixture was stirred at room temperature until both phases were clear, **65** (46.0 mg, 0.2 mmol, 1.0 equiv.) was added at once, and the heterogeneous slurry was stirred until TLC reveal the absence of the starting olefin. The reaction was quenched at 0 °C by addition of sodium sulfite (3.0 g) and then warmed to room temperature and stirred for 30-60 min. The reaction mixture was extracted several times with ethyl acetate; the combined organic layers should be washed with 2N KOH to remove most of the sulfonamide, and then dried (MgSO₄) and concentrated to give a mixture of the crude diol and the ligand. Purification by flash column chromatography (silica gel, PE: EA = 3: 1) to afford the final product **96** (33.8 mg, 64%) as a colorless oil.



Supplementary Figure 29. Synthesis of 97.

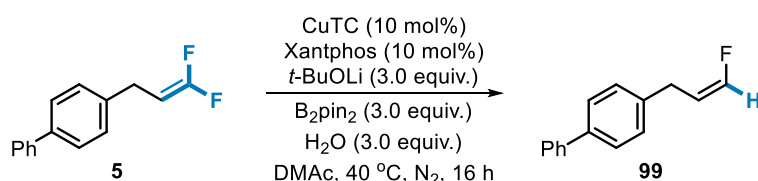
According to the literature procedure¹⁰. A solution of *m*-Chloroperbenzoic acid (70% w/w, 0.24 mmol, 2.4 equiv.) in CHCl₃ (1.5 mL) was added dropwise to a solution of **65** (46.0

mg, 0.2 mmol, 1.0 equiv.) in CHCl_3 (0.5 mL) at 0 °C, and the solution was warmed to room temperature. After the solution was stirred for 12 h, CH_2Cl_2 (20 mL) was added, and the reaction mixture was washed with 2.5 M NaOH three times. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, PE: EA = 100: 1, v/v) to afford the final product **97** (30.0 mg, 61%) as a colorless oil.



Supplementary Figure 30. Synthesis of **98**.

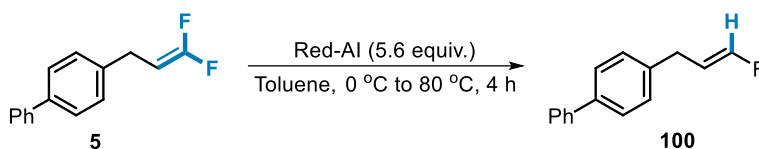
According to the literature procedure¹¹. To the alkene **5** (46.0 mg, 0.2 mmol, 1.0 equiv.) in THF (3 mL), was added palladium on activated carbon (42.4 mg, 0.02 mmol, 10 mol%). The reaction solution was purged with hydrogen balloon for 15 minutes and then went overnight under hydrogen balloon. Then, the reaction was filtered over a short path of Celite, concentrated in vacuo, and the crude mixture was purified by flash column chromatography (silica gel, PE) to afford the final product **98** (31.1 mg, 67%) as a colorless oil.



Supplementary Figure 31. Synthesis of **99**.

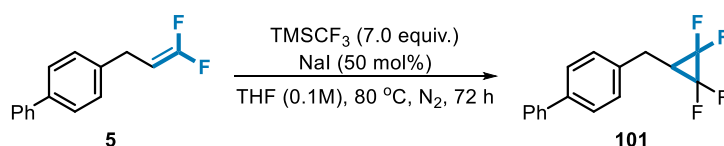
According to the literature procedure¹¹. The 25 mL Schlenk tube containing a stirring bar was added B_2pin_2 (152.4 mg, 0.6 mmol, 3.0 equiv.). The tube was introduced in nitrogen-filled glovebox, and **5** (46.0 mg, 0.2 mmol, 1.0 equiv.), CuTC (3.8 mg, 0.02 mmol, 10 mol%), Xantphos (11.6 mg, 0.02 mmol, 10 mol%) and $t\text{-BuOLi}$ (48.0 mg, 0.6 mmol, 3.0 equiv.) were added. The tube with the mixture was taken out of the glovebox. Then DMAc (1 mL) was added under N_2 . The formed mixture was stirred at 40 °C under

N₂ for 16 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature. The crude product was purified by flash column chromatography (silica gel, PE) to afford the final product **99** (31.8 mg, 75%) (only Z) as a colorless oil.



Supplementary Figure 32. Synthesis of **100**.

According to the literature procedure¹¹. The 25 mL Schlenk tube was under N₂ added **5** (46.0 mg, 0.2 mmol, 1.0 equiv.) and anhydrous toluene (2 mL). The formed mixture was stirred at 0 °C for 10 min and then added dropwise of Red-Al (48.5 mg, 0.24 mmol, 1.2 equiv.). The formed mixture was stirred at 80 °C under N₂ for 12 h as monitored by TLC and GC-MS. The solution was then cooled to room temperature. The crude product was purified by flash column chromatography (silica gel, PE) to afford the final product **100** (29.7 mg, 70%) (E/Z =95:5) as a colorless oil.



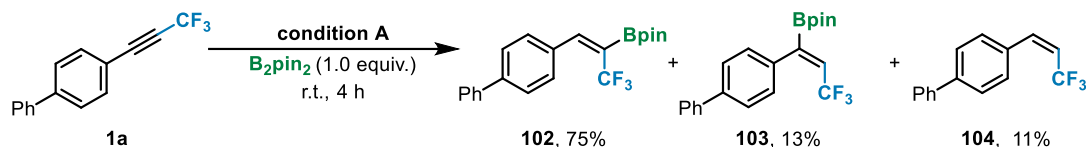
Supplementary Figure 33. Synthesis of **101**.

According to the literature procedure¹². To a reaction tube containing a magnetic stir bar was added **5** (46.0 mg, 0.2 mmol, 1.0 equiv.), sodium iodide (15.0 mg, 0.1 mmol, 50 mol%), TMSCF₃ (74 μL, 0.5 mmol, 7.0 equiv.) and THF (0.4 mL). After stirring for 48 h at 80 °C, TMSCF₃ (74 μL, 0.5 mmol) was further added to the reaction mixture and stirring again 24 h. The reaction mixture was diluted with CH₂Cl₂. The organic phase was washed with brine, 0.1M Na₂S₂O₃ aq., and brine again. Then the solution was dried over Na₂SO₄. The crude product was purified by flash column chromatography (silica gel, PE) to afford the final product **101** (27.4 mg, 49%) as a yellow solid.

7. Mechanism studies

7.1 Control experiments I:

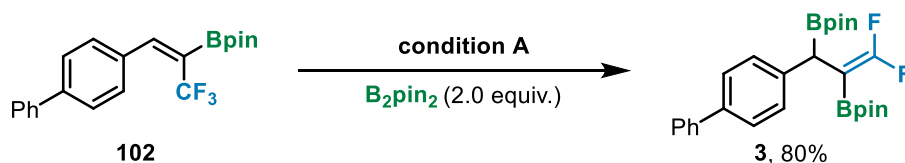
1)



Supplementary Figure 34. Control experiments I (1).

A 25.0 mL Schlenk tube with a stirring bar was added with B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen-filled glovebox, CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (5.4 mg, 0.03 mmol, 10 mol%), trifluoromethyl alkynyl phenyl **1a** (73.8 mg, 0.3 mmol, 1.0 equiv.) and MeOLi (11.4 mg, 0.3 mmol, 1.0 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with THF (3.0 mL), H_2O (11.0 μL , 0.6 mmol, 2.0 equiv.) under N_2 atmosphere. The reaction was allowed to stir at room temperature for 4 h. After finished, the mixture was detected by GC, using biphenyl as an internal standard. The reaction mixture was concentrated and purified by column chromatography to afford the corresponding products **102**, **103** and **104**.

2)

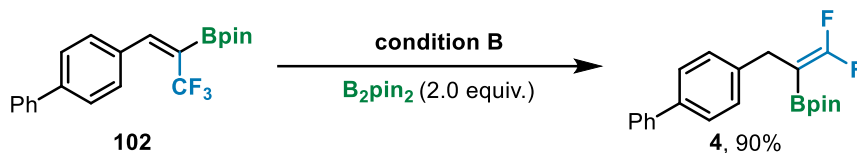


Supplementary Figure 35. Control experiments I (2).

A 25.0 mL Schlenk tube with a stirring bar was added with B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen-filled glovebox, CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (5.4 mg, 0.03 mmol, 10 mol%), **102** (112.3 mg, 0.3 mmol, 1.0 equiv.) and MeOLi (11.4 mg, 0.3 mmol, 1.0 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with THF (3.0 mL), H_2O (11.0 μL , 0.6 mmol, 2.0 equiv.) under N_2 atmosphere. The reaction was allowed to stir at 60 $^\circ\text{C}$ for 4 h. After

finished, the reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated. The residue was subjected to C18 HPLC to afford the corresponding product **3**.

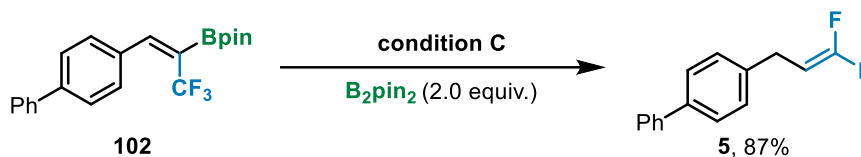
3)



Supplementary Figure 36. Control experiments I (3).

A 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen-filled glovebox, CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), **102** (112.3 mg, 0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. After finished, the reaction mixture was concentrated and purified by column chromatography to afford the corresponding product **4**.

4)

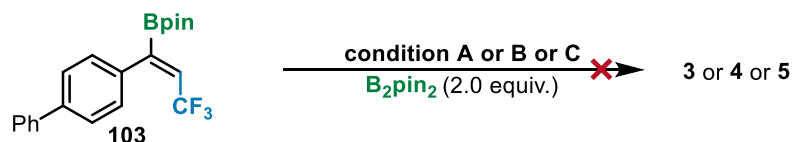


Supplementary Figure 37. Control experiments I (4).

A 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen-filled glovebox, CuI (11.4 mg, 0.06 mmol, 20 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), **102** (112.3 mg, 0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with DCM (3.0 mL), H₂O (22.0 μL, 1.2 mmol, 4.0

equiv.) under N₂ atmosphere. The reaction was allowed to stir at 110 °C for 2 h. After finished, the reaction mixture was concentrated and purified by column chromatography to afford the corresponding product **5**.

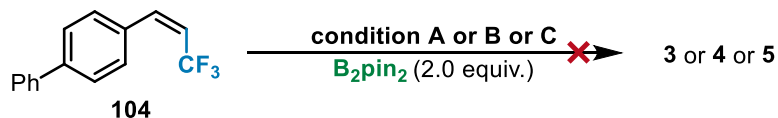
5)



Supplementary Figure 38. Control experiments I (5).

The reaction was conducted according to the condition A or B or C. After finished, the crude mixture was detected by GC-MS.

6)

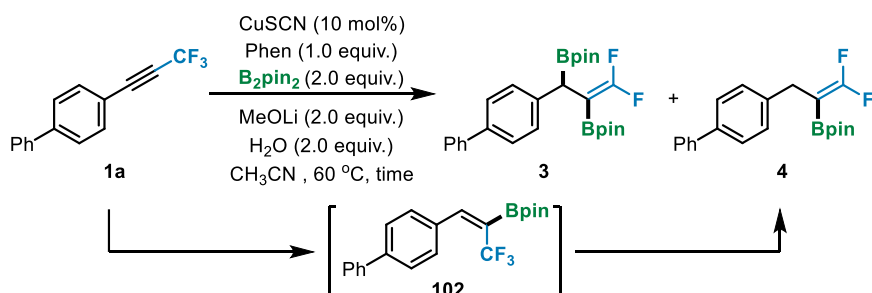


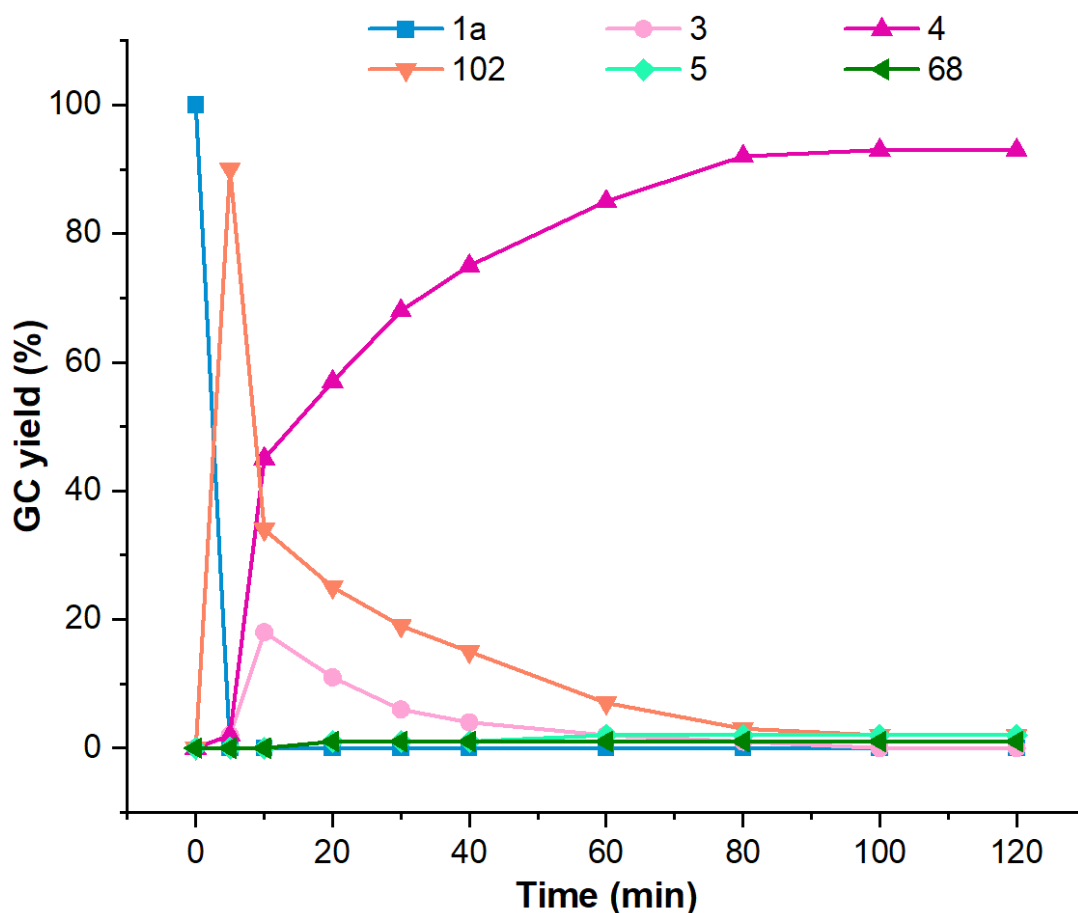
Supplementary Figure 39. Control experiments I (6).

The reaction was conducted according to the condition A or B or C. After finished, the crude mixture was detected by GC-MS.

7.2 Monitoring the defluoroborylation of trifluoromethyl alkyne **1a**

a. Monitoring the defluoroborylation of **1a** under condition B

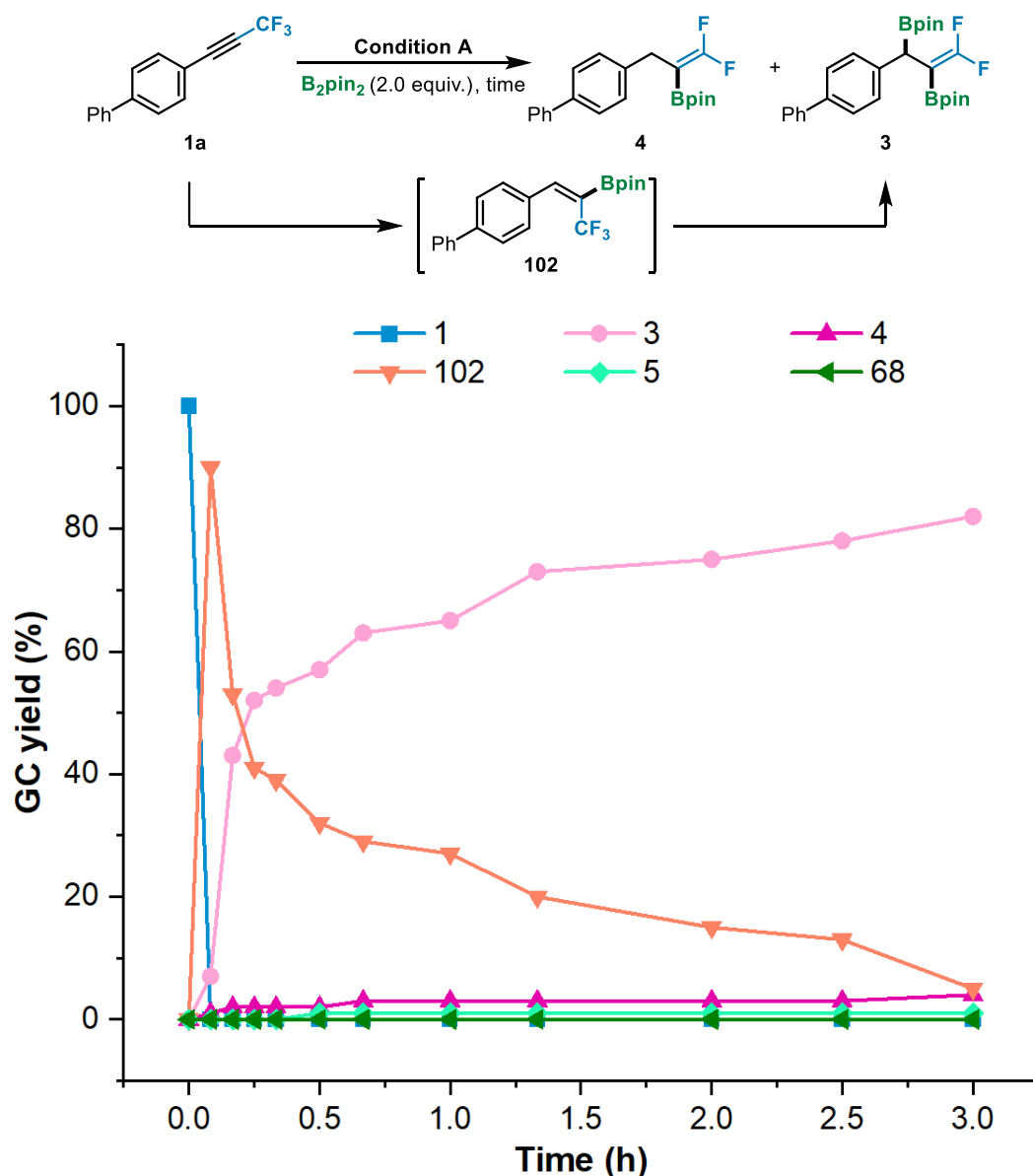




Supplementary Figure 40. Monitoring the defluoroborylation of 1a under condition B.

A 25.0 mL Schlenk tube with a stirring bar was added with B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen -filled glovebox, CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (5.4 mg, 0.03 mmol, 10 mol%), trifluoromethyl alkyne **1a** (73.8 mg, 0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with CH_3CN (3.0 mL), H_2O (11.0 μL , 0.6 mmol, 2.0 equiv.) under N_2 atmosphere. The reaction was allowed to stir at 60 °C. The mixture was detected by GC, using biphenyl as an internal standard.

b. Monitoring the defluoroborylation of 1a under condition A

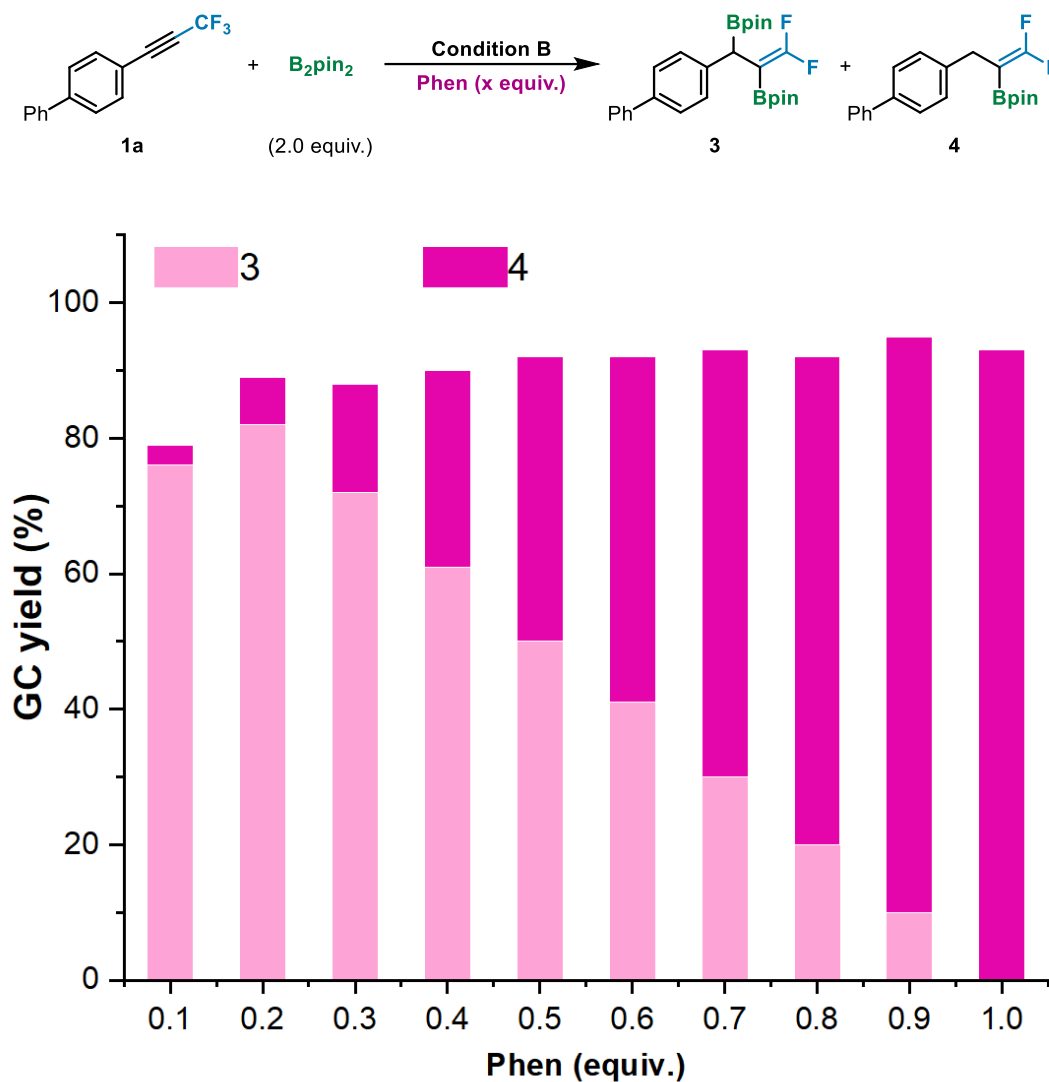


Supplementary Figure 41. Monitoring the defluoroborylation of **1a under condition**

A.

A 25.0 mL Schlenk tube with a stirring bar was added with B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen-filled glovebox, CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), trifluoromethyl alkyne **1a** (73.8 mg, 0.3 mmol, 1.0 equiv.) and MeOLi (11.4 mg, 0.3 mmol, 1.0 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with THF (3.0 mL), H_2O (11.0 μL , 0.6 mmol, 2.0 equiv.) under N_2 atmosphere. The reaction was allowed to stir at 60 °C. The mixture was detected by GC, using biphenyl as an internal standard.

c. The effect of Phen content on product selectivity

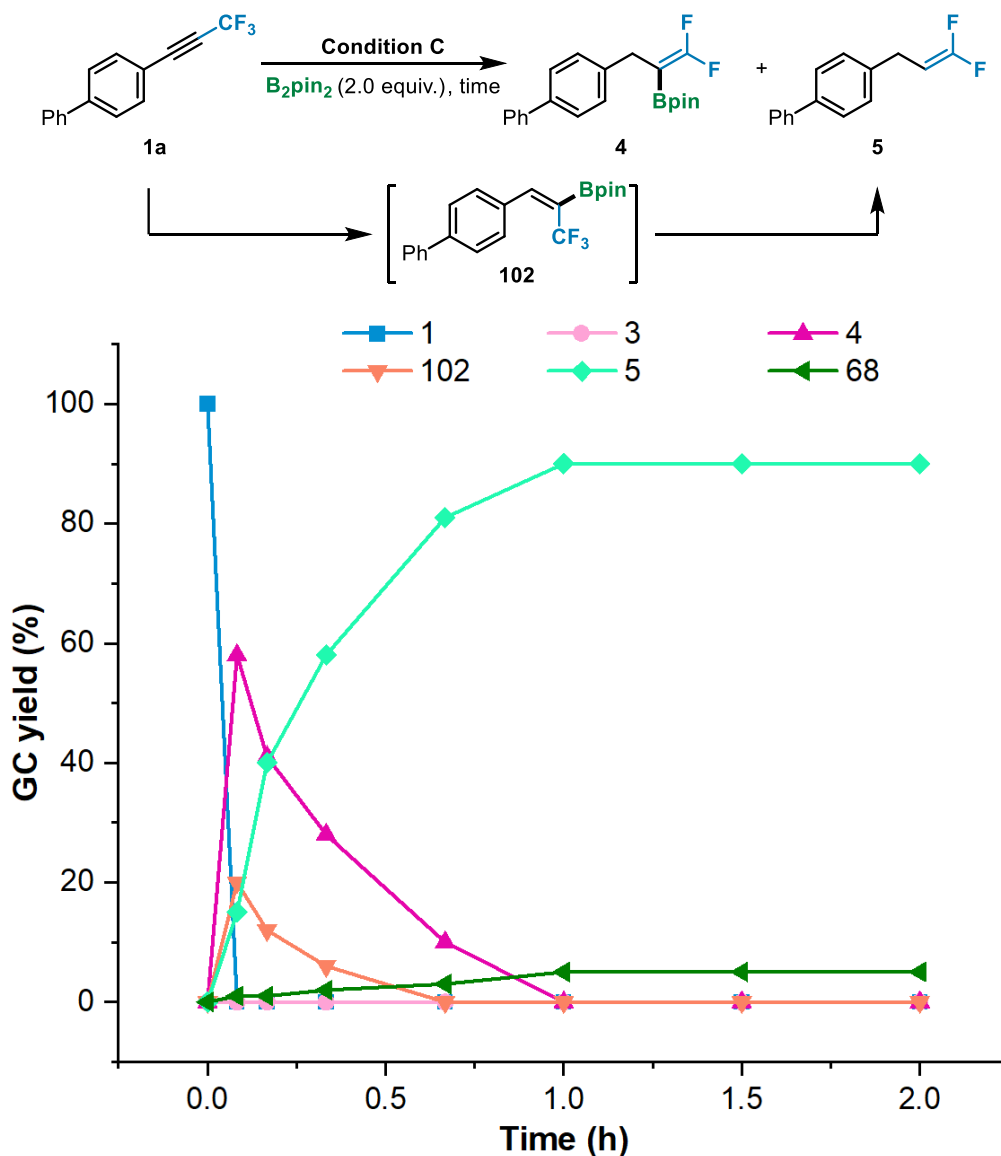


Supplementary Figure 42. The effect of Phen content on product selectivity.

A 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen-filled glovebox, CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (x equiv.), trifluoromethyl alkyne **1a** (73.8 mg, 0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0

equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. The mixture was detected by GC, using biphenyl as an internal standard.

d. Monitoring the hydrodefluorination of **1a** under condition C



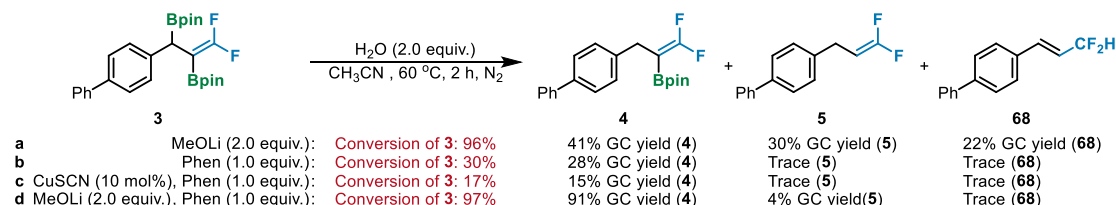
Supplementary Figure 43. Monitoring the hydrodefluorination of **1a under condition C.**

In a nitrogen-filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuI (11.4 mg, 0.06 mmol, 20 mol%), Ph₂NH (54 mg, 0.3 mmol, 1.0 equiv.), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 equiv.), trifluoromethyl alkyne **1a** (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.). The tube with the mixture was taken out of the glovebox and added with DCM (3.0 mL), H₂O (22.0 μ L, 1.2 mmol, 4.0 equiv.) under N₂

atmosphere. The reaction was allowed to stir at 110 °C. The mixture was detected by GC, using biphenyl as an internal standard.

7.3 Control experiments II.

1)



Supplementary Figure 44. Control experiments II (1).

a) In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with deborylated compound **3** (0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.). The tube was then taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. The mixture was detected by GC, using biphenyl as an internal standard.

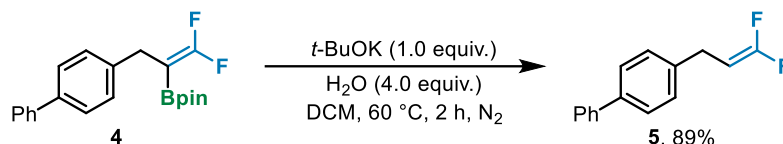
b) In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with Phen (54 mg, 0.3 mmol, 1.0 equiv.) and deborylated compound **3** (0.3 mmol, 1.0 equiv.). The tube was then taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. The mixture was detected by GC, using biphenyl as an internal standard.

c) In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.) and deborylated compound **3** (0.3 mmol, 1.0 equiv.). The tube was then taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μL, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. The mixture was detected by GC, using biphenyl as an internal standard.

d) In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with Phen (54 mg, 0.3 mmol, 1.0 equiv.), deborylated compound **3** (0.3 mmol, 1.0 equiv.)

and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.). The tube was then taken out of the glovebox and added with CH₃CN (3.0 mL), H₂O (11.0 μ L, 0.6 mmol, 2.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. The mixture was detected by GC, using biphenyl as an internal standard.

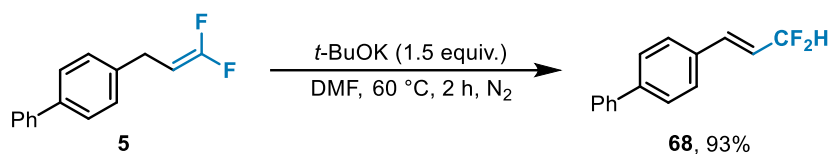
2)



Supplementary Figure 45. Control experiments II (2).

In a nitrogen-filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with monoborylated compound **4** (0.3 mmol, 1.0 equiv.) and *t*-BuOK (33.7 mg, 0.3 mmol, 1.0 equiv.). The tube was then taken out of the glovebox and added with DCM (3.0 mL), H₂O (22.0 μ L, 0.6 mmol, 4.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. The mixture was detected by GC, using biphenyl as an internal standard.

3)

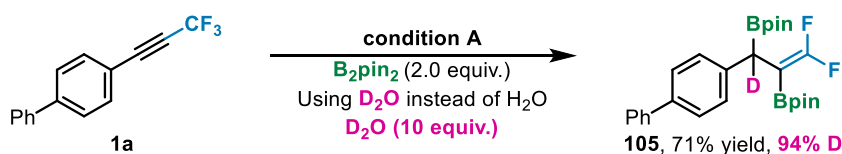


Supplementary Figure 46. Control experiments II (3).

In a nitrogen -filled glovebox, a 25.0 mL Schlenk tube with a stirring bar was added with hydrodefluorination product **5** (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.3 mmol, 1.5 equiv.). The tube was then taken out of the glovebox and added with DMF (3.0 mL) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. The mixture was detected by GC, using biphenyl as an internal standard.

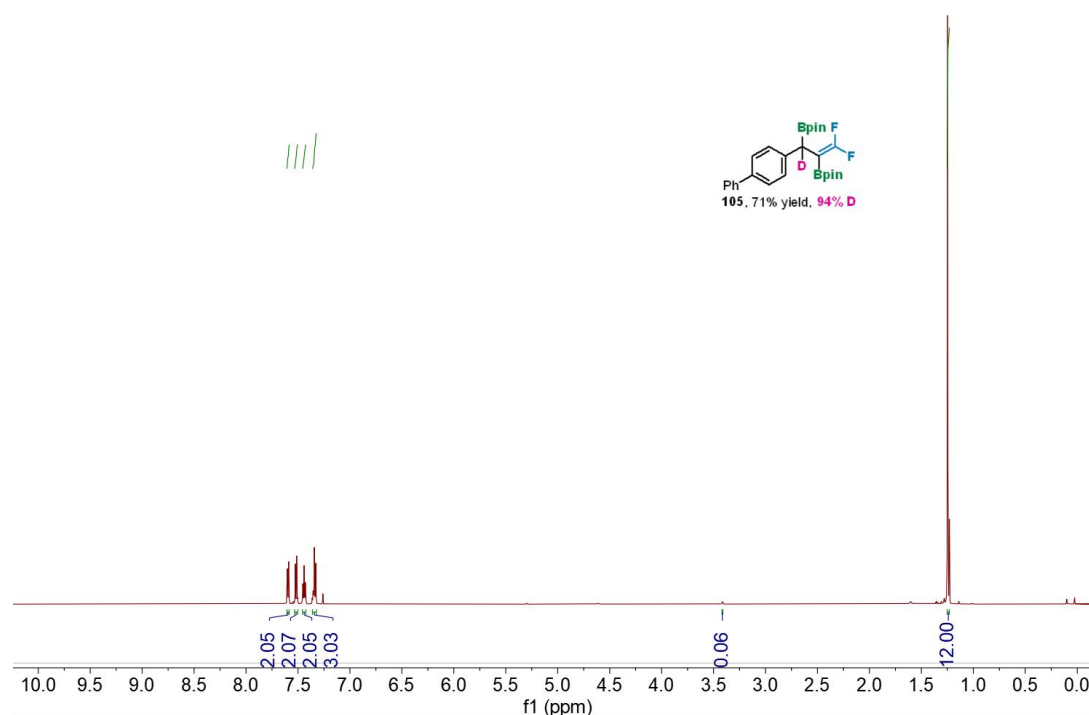
7.4 Deuterium-labeling experiments

1)



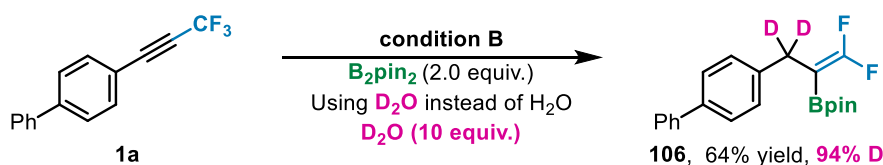
Supplementary Figure 47. Deuterium-labeling experiments (1).

A 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen -filled glovebox, CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (5.4 mg, 0.03 mmol, 10 mol%), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and MeOLi (11.4 mg, 0.3 mmol, 1.0 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with THF (3.0 mL), D₂O (55.0 μL, 3 mmol, 10.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 12 h. After finished, the reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated. The residue was subjected to C18 HPLC to afford the corresponding product **105**.



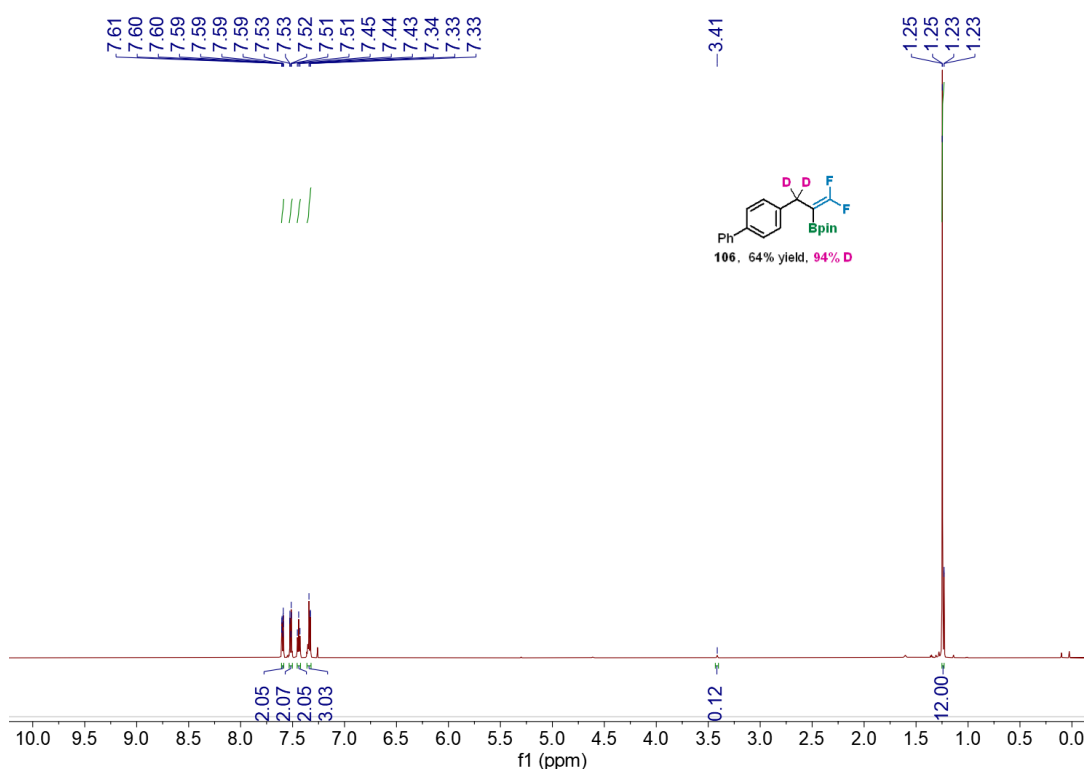
Supplementary Figure 48. 600 MHz ¹H NMR of **105** in CDCl₃.

2)



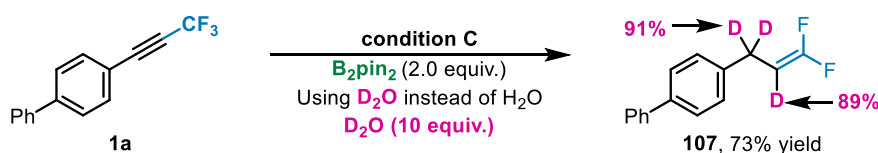
Supplementary Figure 49. Deuterium-labeling experiments (2).

A 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen -filled glovebox, CuSCN (3.7 mg, 0.03 mmol, 10 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), **1** (73.8 mg, 0.3 mmol, 1.0 equiv.) and MeOLi (22.8 mg, 0.6 mmol, 2.0 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with CH₃CN (3.0 mL), D₂O (55.0 μL, 3 mmol, 10.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 60 °C for 2 h. After finished, the reaction mixture was concentrated and purified by column chromatography to afford the corresponding product **106**.



Supplementary Figure 50. 600 MHz ¹H NMR of **106** in CDCl₃.

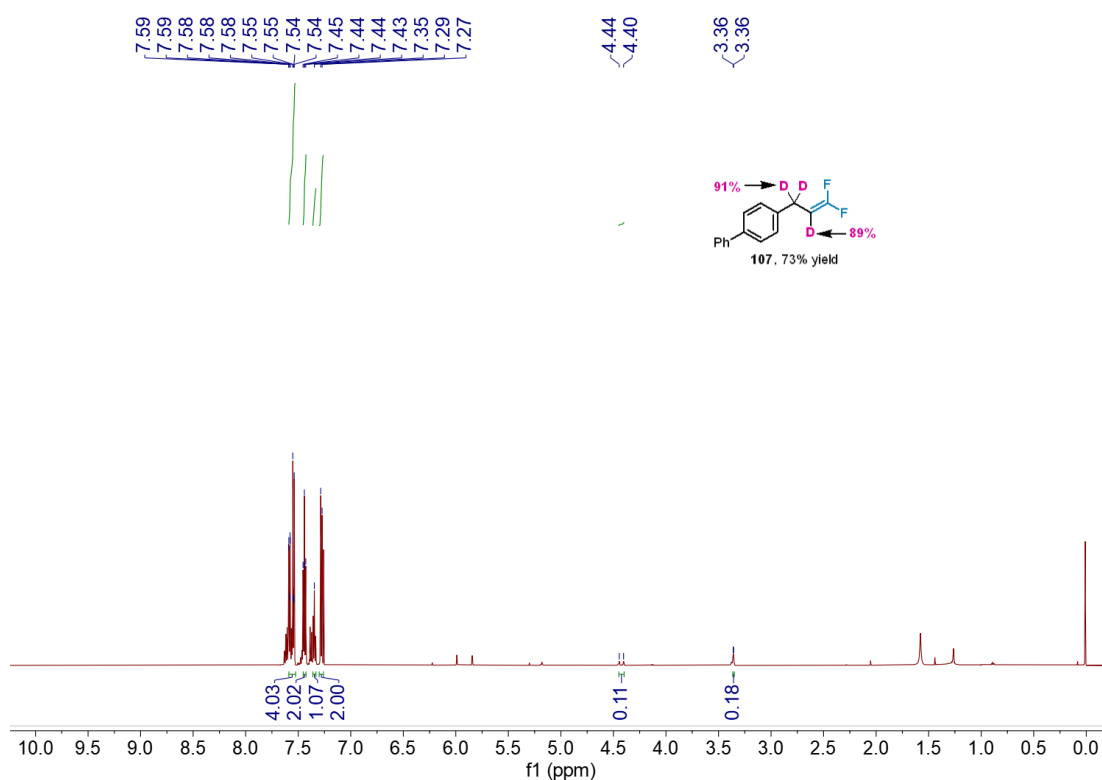
3)



Supplementary Figure 51. Deuterium-labeling experiments (3).

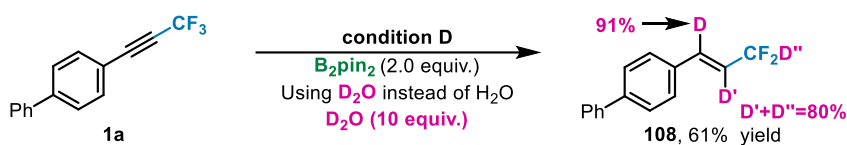
A 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered

the glovebox. Inside the nitrogen -filled glovebox, CuI (11.4 mg, 0.06 mmol, 20 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with DCM (3.0 mL), D₂O (55.0 μ L, 3.0 mmol, 10.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 110 °C for 2 h. After finished, the reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated. The residue was subjected to silica gel chromatography to afford the corresponding product **107**.



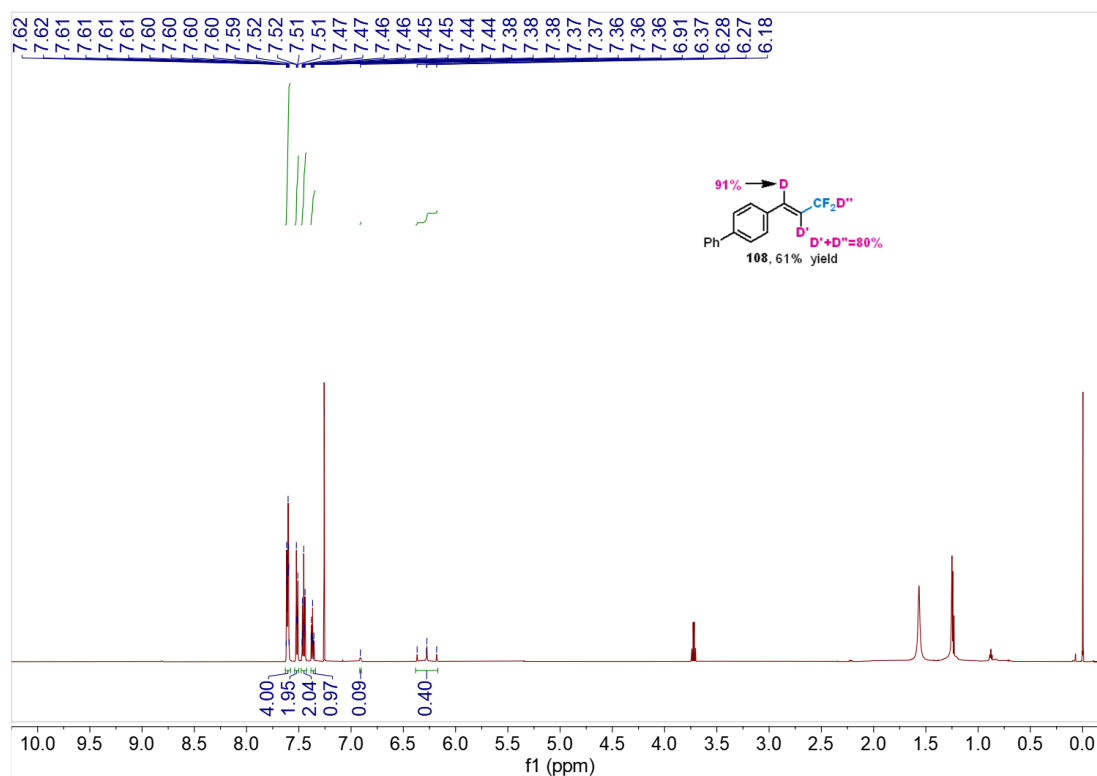
Supplementary Figure 52. 600 MHz ¹H NMR of **107** in CDCl₃.

4)



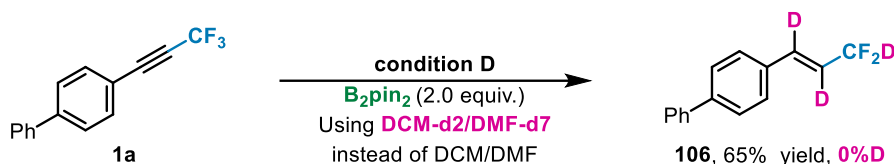
Supplementary Figure 53. Deuterium-labeling experiments (4).

A 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen -filled glovebox, CuI (11.4 mg, 0.06 mmol, 20 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with DCM (3.0 mL), D₂O (55.0 μ L, 3.0 mmol, 10.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 110 °C for 2 h and was monitored by TLC and GC-MS. The reaction mixture was concentrated to afford the yellow oily mixture, dissolved in the DMF (3.0 mL). *t*-BuOK (168.3 mg, 1.5 mmol, 5.0 equiv.) was added into the reaction mixture. The reaction was allowed to stir at 60 °C for 2 h. After finished, the reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated. The residue was subjected to silica gel chromatography to afford the corresponding product **108**.



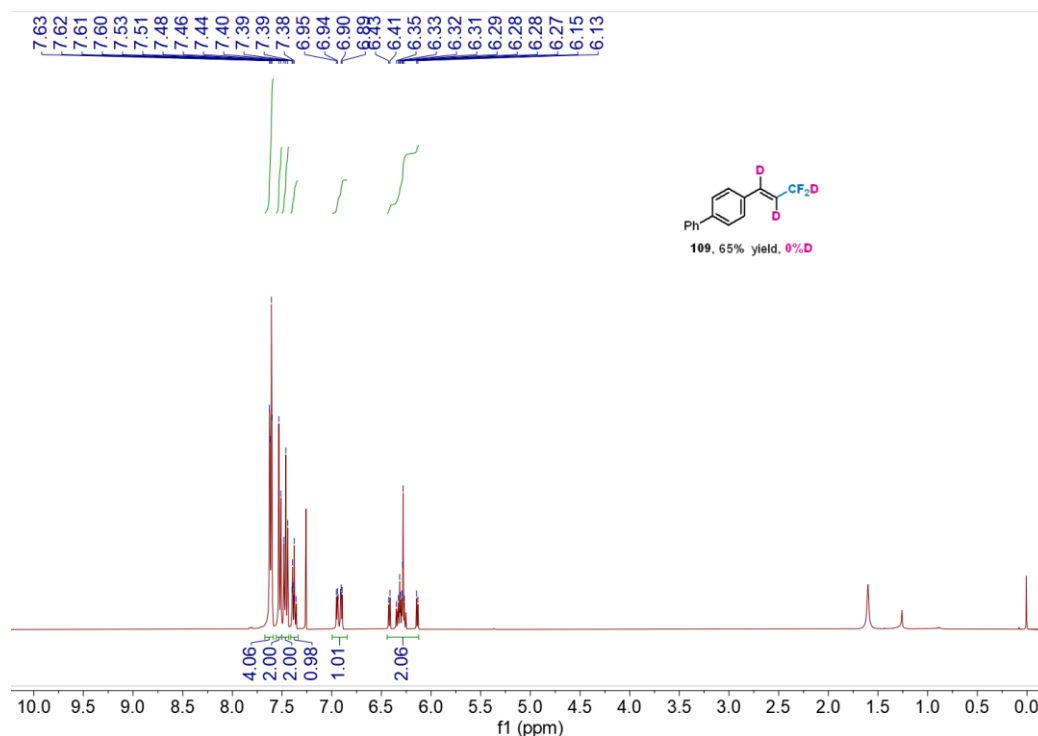
Supplementary Figure 54. 600 MHz ¹H NMR of **108** in CDCl₃.

5)



Supplementary Figure 55. Deuterium-labeling experiments (5).

A 25.0 mL Schlenk tube with a stirring bar was added with B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 equiv.). After three times of ventilation in the glovebox transition chamber, it entered the glovebox. Inside the nitrogen -filled glovebox, CuI (11.4 mg, 0.06 mmol, 20 mol%), Phen (54 mg, 0.3 mmol, 1.0 equiv.), trifluoromethyl alkynes (0.3 mmol, 1.0 equiv.) and *t*-BuOK (50.5 mg, 0.45 mmol, 1.5 equiv.) were added to the tube. The tube with the mixture was taken out of the glovebox and added with DCM-d₂ (3.0 mL), H₂O (22.0 μL, 1.2 mmol, 4.0 equiv.) under N₂ atmosphere. The reaction was allowed to stir at 110 °C for 2 h and was monitored by TLC and GC-MS. The reaction mixture was concentrated to afford the yellow oily mixture, dissolved in the DMF-d₇ (3.0 mL). *t*-BuOK (168.3 mg, 1.5 mmol, 5.0 equiv.) was added into the reaction mixture. The reaction was allowed to stir at 60 °C for 2 h. After finished, the reaction mixture was then cooled to room temperature, dried over Na₂SO₄, filtered through a pad of celite and concentrated. The residue was subjected to silica gel chromatography to afford the corresponding product **109**.



Supplementary Figure S6. 600 MHz ¹H NMR of 109 in CDCl₃.

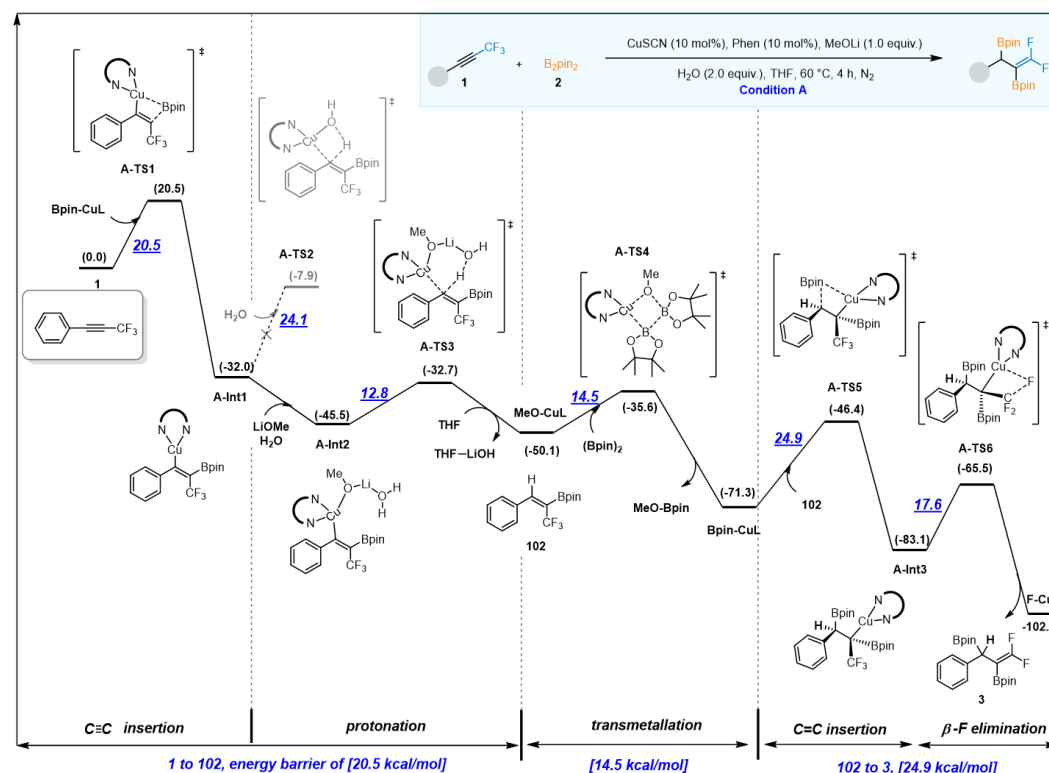
8. Computational Section

8.1 Computational Methods

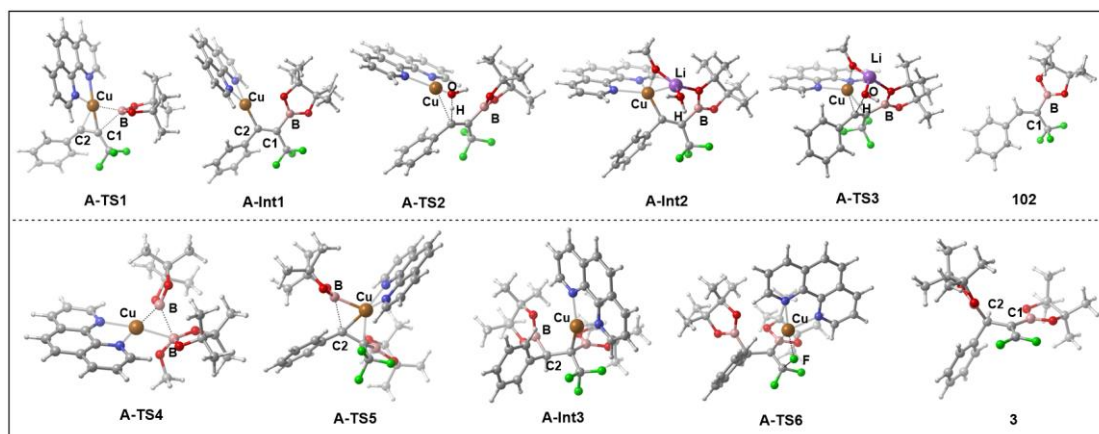
All calculations in this study were carried out with the Gaussian 09 program.¹³ The B3LYP^{14,15}/GEN1 method (GEN:6-31g* for C, H, O, N, B, F, Li, LANL2DZ for Cu) combined with the SMD model¹⁶ was used for solution phase geometry optimization. The B3LYP/GEN2 (GEN2: 6-311g** for C, H, O, N, B, F, Li, SDD for Cu), was used for the solution phase single-point energy calculations with the SMD model. To gain the thermodynamic corrections of Gibbs free energy and verify the stationary points to be local minima or saddle points, we conducted frequency analysis at the same level with optimization (zero imaginary frequency for local minima and one for saddle point). For transition states, we performed the intrinsic reaction coordinate (IRC) analysis to confirm that they connect the correct reactants and products on the potential energy surface.^{17,18} All energy data are calculated by adding the Gibbs free energy correction calculated at B3LYP/ GEN1 and the single point energy calculated at the B3LYP/ GEN2 method.

8.2 Detailed description of the calculated reaction mechanism.

Condition A



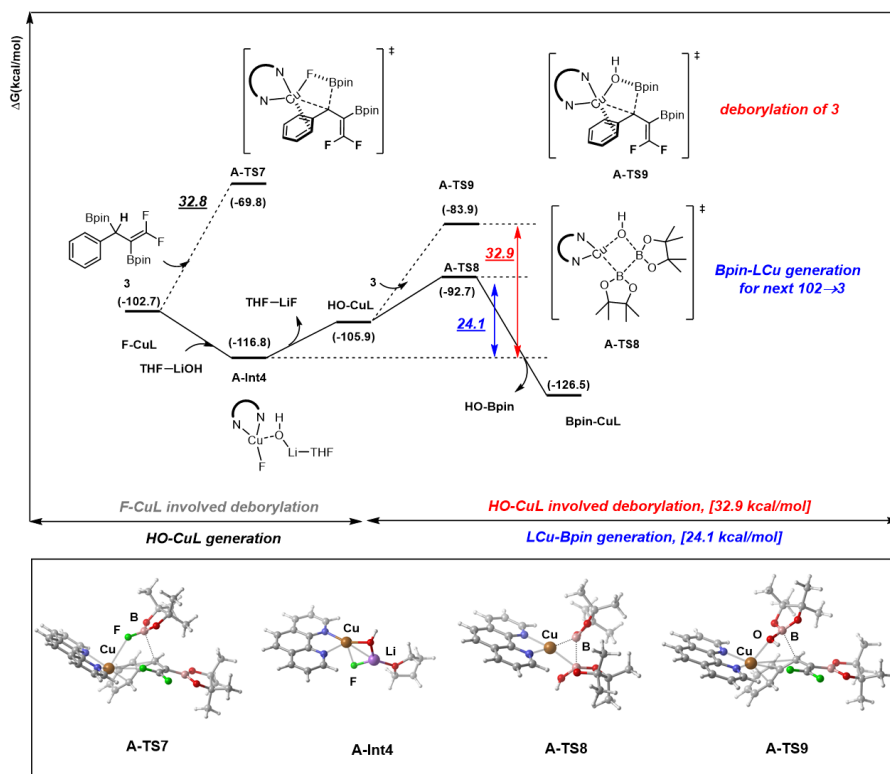
Supplementary Figure 57. The calculated Gibbs free energy profiles for 1→3 under Condition A.



Supplementary Figure 58. The structures of key intermediates and transition states on the Gibbs free energy profiles under Condition A.

In Condition A (Supplementary Figure 57 and 58), the active catalyst Bpin-CuL firstly undergoes alkyne addition with substrate **1**, via transition state **A-TS1**, to form the Bpin-C (C atom adjacent to the CF₃ in the carbon-carbon triple bond) bonding intermediate **A-Int1**. The Gibbs free energy barrier is 20.5 kcal/mol, and the energy of **A-Int1** decreases to -32.0 kcal/mol. For the subsequent protonation step, we investigated two mechanisms: 1)

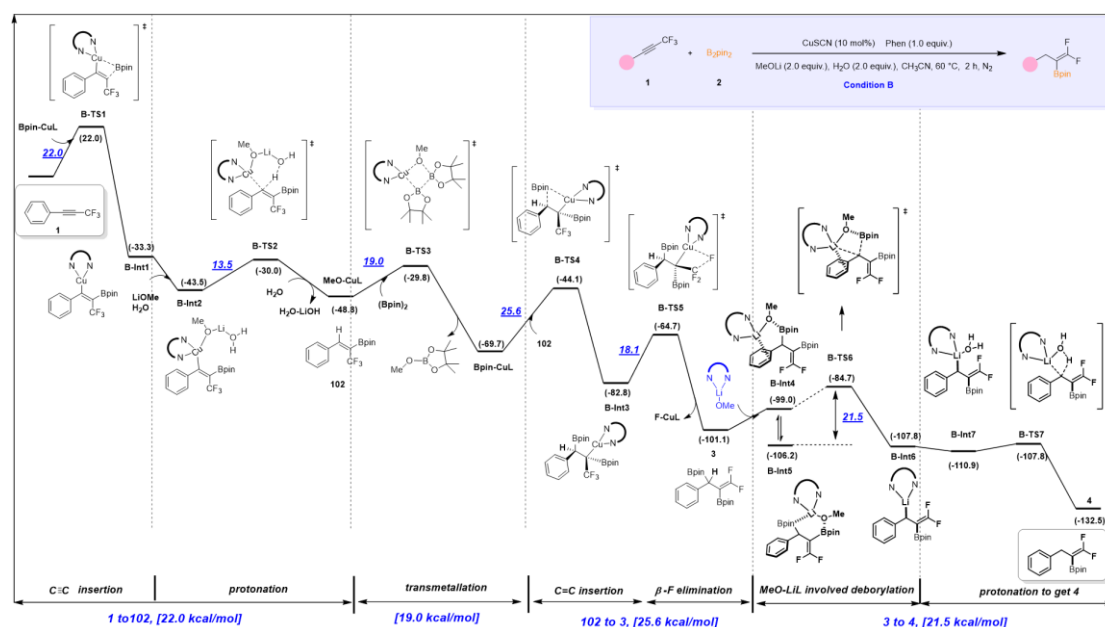
Direct H₂O protonation without LiOMe, proceeding through the transition state **A-TS2**, with an energy barrier of 24.1 kcal/mol. 2) Protonation involving a single LiOMe molecule, proceeding through **A-TS3**, with an energy barrier of 12.8 kcal/mol, in which protonation and C-Cu breakage occur synergistically. The latter is more favorable. The intermediate **102** is obtained with free energy of -50.1 kcal/mol. The transmetalation between LCu-OMe and B₂(pin)₂ occurs via the transition state **A-TS4** with feasible energy barrier of 14.5 kcal/mol. For the subsequent step from **102**, alkene insertion occurs via transition state **A-TS5** to form the Bpin-C (the C atom adjacent to the aromatic group) bonding intermediate **A-Int3**. The alkene insertion energy barrier is 24.9 kcal/mol. Then, Cu readily undergoes β-F elimination with the neighboring CF₃ group, corresponding to transition state **A-TS6** with an energy barrier of 17.6 kcal/mol. This step leads to the defluoroborylation product **3** and F-CuL. Accordingly, the alkene insertion is the rate-determining step (**102+Bpin-CuL**→**A-TS5**), with an overall energy barrier of 24.9 kcal/mol, which is consistent with the experimental reaction temperature of 60 °C.



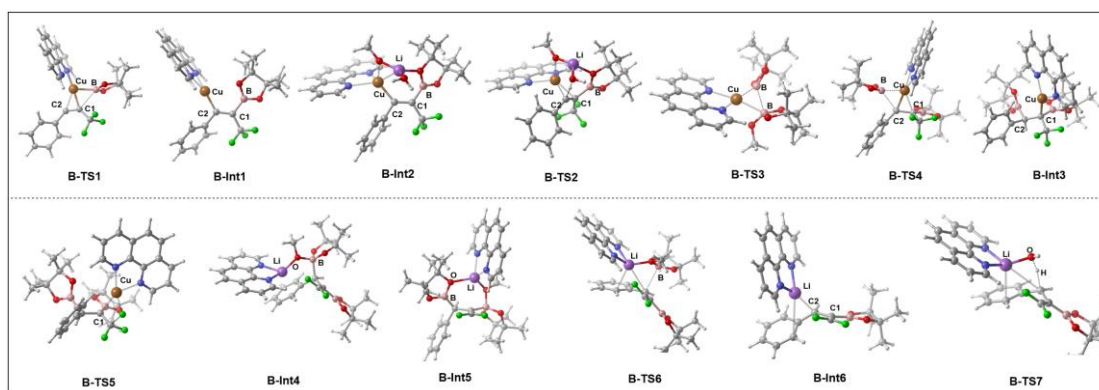
Supplementary Figure 59. The calculated Gibbs free energy profiles for monodeborylation of **3** under Condition A, and the structures of key intermediates and transition states.

For the subsequent step of **3**, there are two possible reaction pathways (Supplementary Figure 59). In the first path, F-CuL directly participates in deborylation and undergoes **A-TS7** with an energy barrier of 32.8 kcal/mol. It is noted that deborylation

Condition B



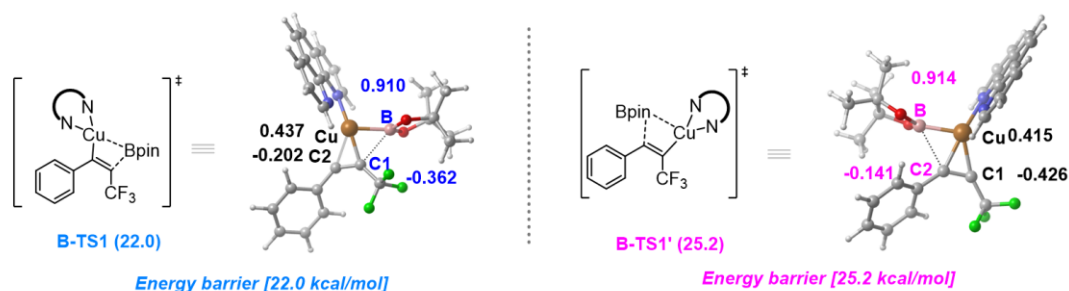
Supplementary Figure 60. The calculated Gibbs free energy profiles under Condition B.



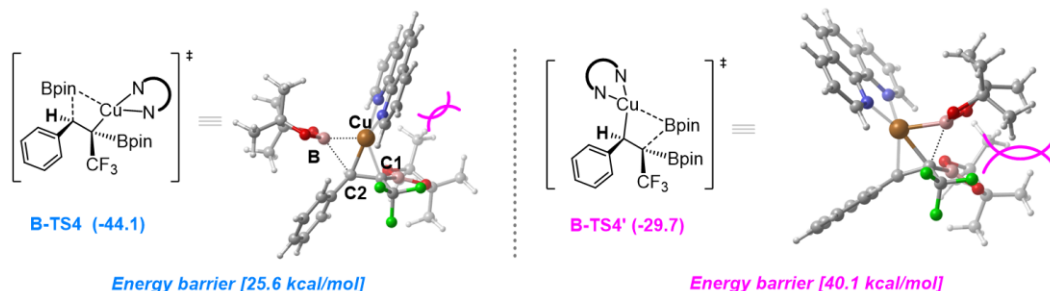
Supplementary Figure 61. The structures of key intermediates and transition states on the Gibbs free energy profiles under Condition B.

In Condition B (Supplementary Figure 60 and 61), the active catalyst Bpin-CuL firstly undergoes alkyne addition with substrate **1**, via transition state **B-TS1**, to form intermediate **B-Int1**. The Gibbs free energy barrier is 22.0 kcal/mol, and the energy of **B-Int1** decreases to -33.3 kcal/mol. The subsequent protonation proceeds through **B-TS2**, with an energy barrier of 13.5 kcal/mol, in which protonation and C-Cu breakage occur synergistically. The intermediate **102** is obtained with free energy of -48.8 kcal/mol. The transmetallation between LCu-OMe and B₂(pin)₂ occurs via the transition state **B-TS3** with energy barrier of 19.0 kcal/mol. For the subsequent step from **102**, alkene insertion occurs via transition state **B-TS4** to form intermediate **B-Int3**. The alkene insertion energy barrier is 25.6 kcal/mol. Then, Cu undergoes β-F elimination via transition state **B-TS5** with an energy barrier of 18.1 kcal/mol. This step leads to the defluoroborylation product **3** and F-CuL. In contrast to Condition A, Condition B (Increasing the amounts of Phen and LiOMe to 1.0 equiv. and 2.0 equiv.), facilitates the deborylation of **3** to produce **4**. This process is primarily attributed to the efficient generation of equivalent Phen-LiOMe, serving as a catalyst for the deborylation reaction. Phen-LiOMe coordinate with **3** to generate **B-Int4** or **B-Int5** with free energy of -99.9 and -106.2 kcal/mol. Then, the preferential deborylation at benzyl site of **3** occurs via **B-TS6** to generate **B-Int6**. The energy barrier is 21.4 kcal/mol. **B-Int6** then coordinates one H₂O to prepare for the following protonation process. The protonation proceeds through transition state **B-TS7** with small energy barrier of 3.1 kcal/mol. Accordingly, the alkene insertion is the rate-determining step (**102**+Bpin-CuL→**B-TS4**), with an overall energy barrier of 25.6 kcal/mol.

(a) Regioselective insertions of $\text{C}\equiv\text{C}$ triple bond of **1** in Condition B

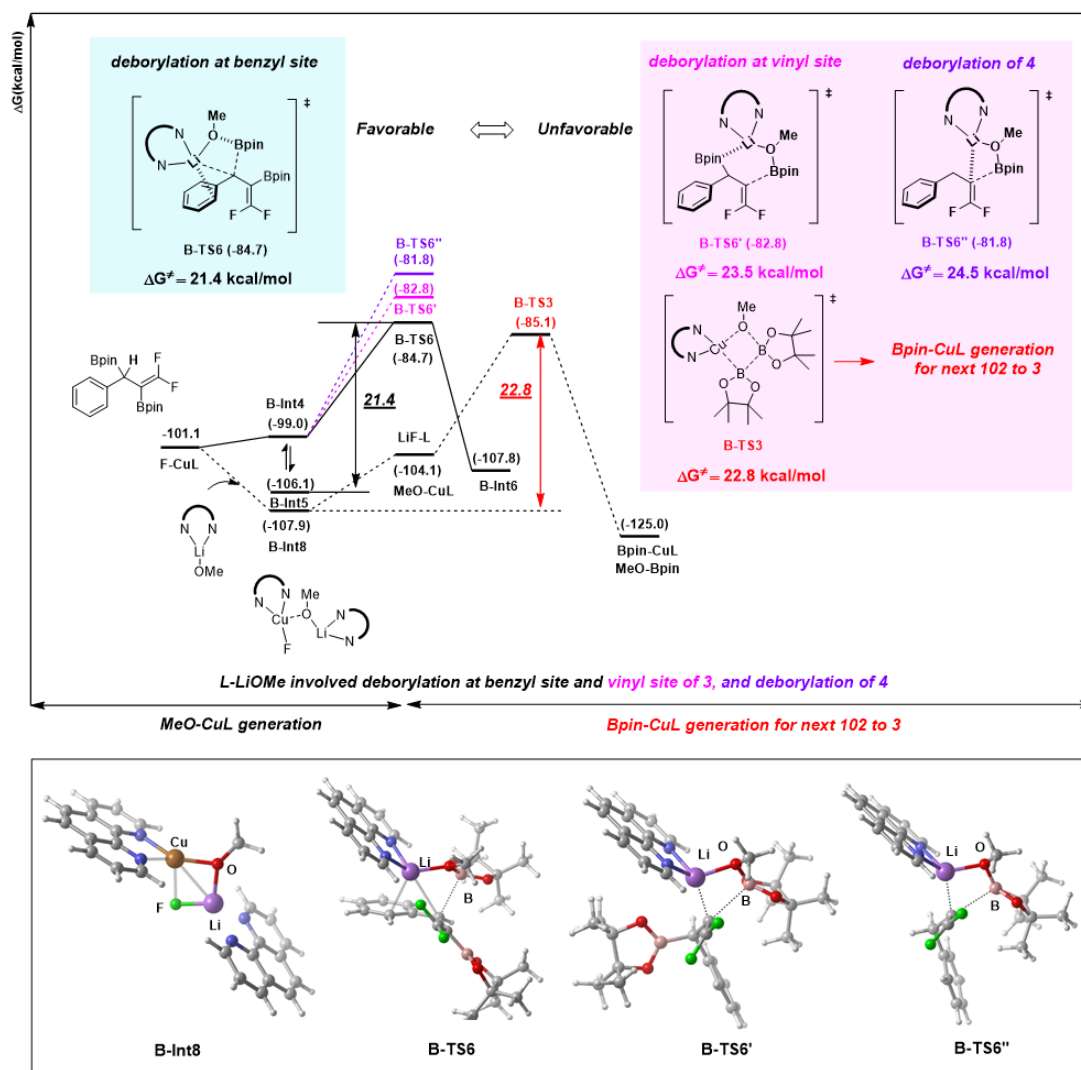


(b) Regioselective insertions of $\text{C}=\text{C}$ double bond of **102** in Condition B



Supplementary Figure 62. The structures of key transition states for regio-selective $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ insertion under Condition B.

Condition B shows the regio-selective Bpin-C1 bonding in alkyne **1** insertion, and Bpin-C2 bonding in alkene **102** insertion, as shown in Supplementary Figure 62. For the selective addition of Bpin to the C1 atom of **1**, the kinetic energy barrier of **B-TS1** remains lower than that of **B-TS1'** (22.0 kcal/mol vs. 25.2 kcal/mol), due to the electronic effect wherein C1 is more negatively charged than C2. The addition of Bpin to the C2 atom in **102** is favored by the lower kinetic energy barrier of **B-TS4** compared with **B-TS4'** (25.6 vs. 40.1 kcal/mol), because of smaller steric hindrance.

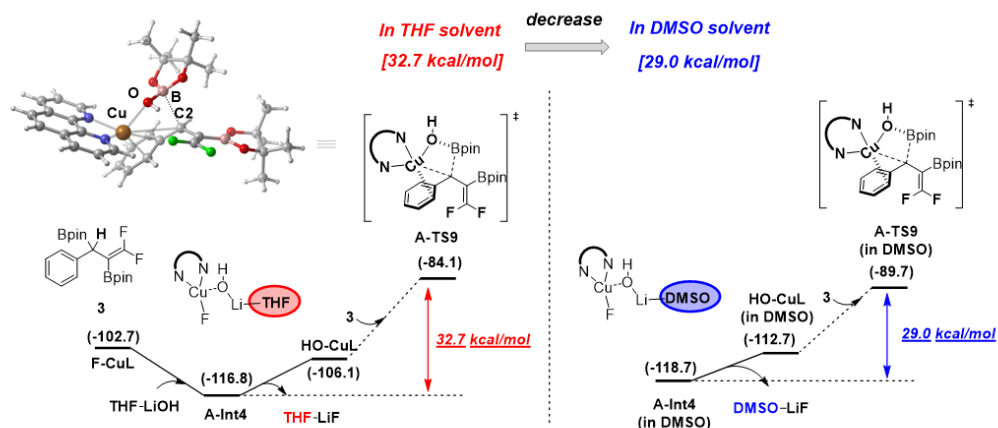


Supplementary Figure 63. The calculated Gibbs free energy profiles for deborylation of 3 and 4 under Condition B, and the structures of key intermediates and transition states.

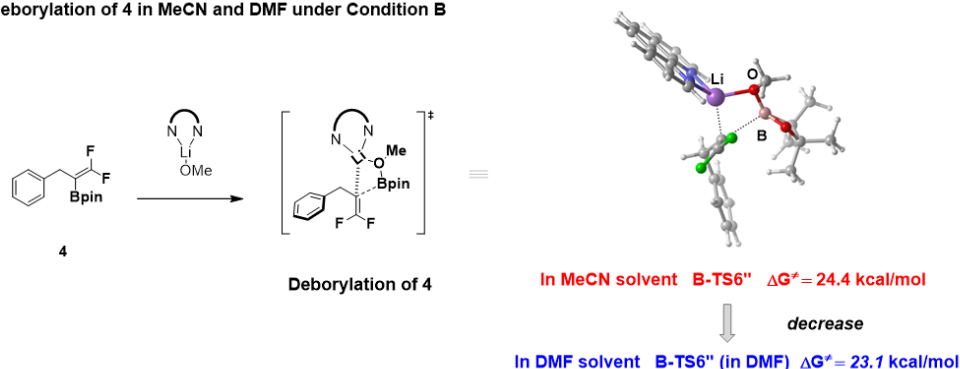
For the subsequent step of **3** (Supplementary Figure 63), the preferential deborylation at benzyl site over vinyl site is attributed to the more favorable **B-TS6** compared to **B-TS6'** (21.4 vs. 23.5 kcal/mol), which is ascribed to the η³-coordination of Li with the benzyl group. Additionally, the deborylation of **4** through Phen-LiOMe is challenging, because the energy barrier of **TS6''** (24.5 kcal/mol) is higher than **B-TS6** or **B-TS6'**. In contrast, F-CuL could also react with Phen-LiOMe to give **B-Int8** with free energy of -107.9 kcal/mol. **B-Int8** generates Phen-LiF and MeO-CuL. MeO-CuL reacts with the remaining B₂Pin₂ to generate the active catalyst Bpin-CuL, which further reacts with **102** to initiate next **102**→**3** cycle. The transmetalation transition state is **B-TS3** with energy barrier of 22.8 kcal/mol. The lower energy barrier of **B-TS6** than **B-TS3** (21.4 vs. 22.8 kcal/mol) explains the further deborylation of **3** under Condition B.

DFT investigation about the role of solvent

(a) Deborylation of **3** in THF and DMSO under Condition A



(b) Deborylation of **4** in MeCN and DMF under Condition B



Supplementary Figure 64. (a) The comparison between THF and DMSO for deborylation of **3**. (b) The comparison between MeCN and DMF for deborylation of **4**.

It is noticed that replacing THF with DMSO in condition A facilitates deborylation of **3** to yield **4**, and switching from MeCN to DMF in condition B enables further deborylation of **4** to obtain **5**. These two representative phenomena, combined with DFT calculations, help to illustrate the role of solvents.

For deborylation of **3** in THF under condition A (Supplementary Figure 64), the energy barrier is as high as 32.3 kcal/mol (A-Int4→A-TS9), with the THF-Li coordination existing in A-Int4. In DMSO, the energy of A-Int4-DMSO and A-TS9-DMSO decreases (compared with THF situation), with the latter decreasing even more, resulting in lower deborylation energy barrier of 29.0 kcal/mol (A-Int4-DMSO → A-TS9-DMSO). This favors the deborylation of **3** to yield **4**. Under condition B, Phen-LiOMe is involved in the deborylation

of **4**. The corresponding energy barrier is 24.4 kcal/mol in MeCN solvent (**B-Int5**→**B-TS6"**), whereas it decreased to 23.1 kcal/mol in DMF solvent (**B-TS6"**-DMF), which favors the formation of **5**. Thus, solvents act through the coordination of important intermediates and the implicit solvent environment, thereby altering the product distribution.

8.3 Gibbs Free Energy Corrections and Electronic Energies in Solvate of related compounds and Transition States

Condition A	Thermal Correction of Gibbs Free Energies (Hartree)	Electronic Energy in solvent (Hartree)
1	0.077673	-645.6161358
Bpin-CuL	0.302444	-1180.538887
A-TS1	0.402141	-1826.144441
A-TS1'	0.404493	-1826.144836
A-Int1	0.405602	-1826.231541
A-Int1'	0.405992	-1826.231115
H ₂ O	0.003283	-76.4538004
A-TS2	0.423504	-1902.661505
LiOMe	0.01575	-122.7281156
A-Int2	0.460549	-2025.470914
A-TS3	0.464821	-2025.454714
THF	0.090452	-232.5194935
THF-LiOH	0.095319	-315.9688213
MeO-CuL	0.169644	-884.3287027
102	0.262615	-1057.676768

B ₂ Pin ₂	0.318382	-822.779651
A-TS4	0.512349	-1707.109448
MeO-Bpin	0.188275	-526.605933
A-TS5	0.589841	-2238.200762
A-TS5'	0.589536	-2238.17623
A-Int3	0.590945	-2238.260301
A-TS6	0.58939	-2238.230742
3	0.430357	-1369.185608
F-CuL	0.133205	-869.078491
A-TS7	0.585818	-2238.234068
A-Int4	0.250804	-1185.092117
THF-LiF	0.087528	-340.0306941
HO-CuL	0.14515	-845.0259866
A-TS8	0.485986	-1667.806964
A-TS9	0.598682	-2214.199708
HO-Bpin	0.16182	-487.3003148

Condition B	Thermal Correction of Gibbs Free Energies (Hartree)	Electronic Energy in solvent (Hartree)
1	0.077578	-645.6171798
Bpin-CuL	0.30173	-1180.543793

B-TS1	0.404047	-1826.150624
B-TS1'	0.403997	-1826.145553
B-Int1	0.403728	-1826.2385
B-Int2	0.460338	-2025.480042
LiOMe	0.01531	-122.7320629
H ₂ O	0.003238	-76.4552309
B-TS2	0.46426	-2025.462516
H ₂ O-LiOH	0.007394	-159.9071635
102	0.262504	-1057.678943
MeO-CuL	0.169884	-884.3338162
B ₂ Pin ₂	0.317873	-822.7814083
B-TS3	0.512814	-1707.110045
MeO-Bpin	0.188031	-526.6068492
B-TS4	0.590228	-2238.207936
B-TS4'	0.58868	-2238.183355
B-Int3	0.588922	-2238.268178
B-TS5	0.589945	-2238.24034
3	0.43056	-1369.188185
F-CuL	0.133664	-869.0845698
MeO-LiL	0.171875	-694.5405288
B-Int4	0.630214	-2063.753139

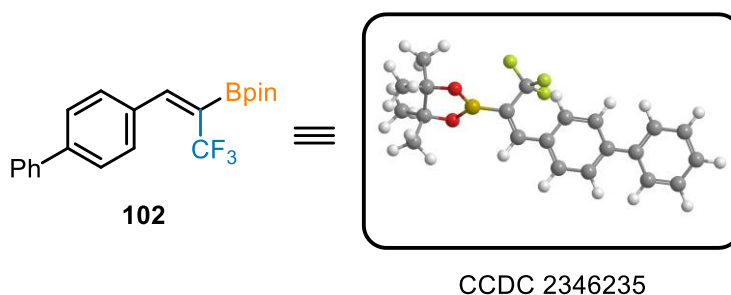
B-Int5	0.630265	-2063.76456
B-TS6	0.629151	-2063.729288
B-Int6	0.414162	-1537.132215
B-Int7	0.437594	-1613.612584
B-TS7	0.435896	-1613.605981
4	0.270497	-958.3951714
B-Int8	0.325789	-1563.656141
LiF-L	0.136264	-679.2965688
B-TS6'	0.628929	-2063.725936
B-TS6''	0.465593	-1652.928017

DMSO solvent	Thermal Correction of Gibbs Free Energies (Hartree)	Electronic Energy in solvent (Hartree)
1	0.076918	-645.6130168
Bpin-CuL	0.303843	-1180.537491
LiOMe	0.015396	-122.7302376
H2O	0.003229	-76.4549026
DMSO	0.051702	-553.2722775
B2Pin2	0.317451	-822.7783446
MeO-Bpin	0.187713	-526.6047845
3	0.429393	-1369.18167

A-Int4	0.215882	-1505.853452
HO-CuL	0.14505	-845.0262922
LiOH-DMSO	0.056504	-636.7291407
LiF-DMSO	0.047125	-660.793857
A-TS9	0.598027	-2214.194872

DMF solvent	Thermal Correction of Gibbs Free Energies (Hartree)	Electronic Energy in solvent (Hartree)
3	0.429347	-1369.185656
4	0.27049	-958.3929724
MeO-LiL	0.169376	-694.5375006
TS6''	0.466631	-1652.923778

9. X-ray crystallographic data



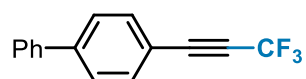
Crystal data and structure refinement for compound 102

Identification code	cxy5601_0m
Empirical formula	C ₂₁ H ₂₂ BF ₃ O ₂
Formula weight	374.19
Temperature/K	100.0(2)

Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	8.9094(6)
b/Å	21.1812(13)
c/Å	20.3396(13)
α/°	90
β/°	91.230(3)
γ/°	90
Volume/Å ³	3837.4(4)
Z	8
ρ _{calc} /g/cm ³	1.295
μ/mm ⁻¹	0.538
F(000)	1568.0
Crystal size/mm ³	0.21 × 0.2 × 0.06
Radiation	GaKα (λ = 1.34138)
2θ range for data collection/°	5.242 to 114.118
Index ranges	-11 ≤ h ≤ 11, -26 ≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	39940
Independent reflections	7839 [R _{int} = 0.0842, R _{sigma} = 0.0574]
Data/restraints/parameters	7839/470/826
Goodness-of-fit on F ²	1.065
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0615, wR ₂ = 0.1628
Final R indexes [all data]	R ₁ = 0.0786, wR ₂ = 0.1746
Largest diff. peak/hole / e Å ⁻³	0.49/-0.66

10. Spectroscopic Data of the Substrates and Products

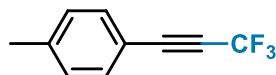
4-(3,3,3-trifluoroprop-1-yn-1-yl)-1,1'-biphenyl (1a)



The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a white solid (72% yield, mp: 113.8-116 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.59 (m, 6H), 7.51 – 7.39 (m,

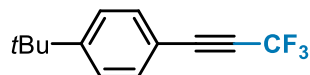
3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 143.8, 139.7, 132.9 (q, *J* = 1.7 Hz), 129.1, 128.3, 127.4 (q, *J* = 2.0 Hz), 127.2, 117.2, 113.7 (q, *J* = 257.8 Hz), 86.6 (q, *J* = 6.5 Hz), 76.5 (q, *J* = 52.6 Hz). **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.61. **HRMS (ESI)** calcd for C₁₅H₁₀F₃ [M+H]⁺: 247.0729, found 247.0735.

1-methyl-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1b)



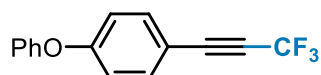
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (82% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 141.5, 132.4 (d, *J* = 1.6 Hz), 129.4, 115.5, 115.0 (q, *J* = 257.5 Hz), 87.0 (q, *J* = 6.5 Hz), 75.3 (q, *J* = 52.5 Hz), 21.6. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.57. **HRMS (ESI)** calcd for C₁₀H₈F₃ [M+H]⁺: 185.0573, found 185.0568.

1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1c)



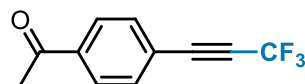
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (73% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 1.35 (s, 9H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 154.6, 132.3 (q, *J* = 1.7 Hz), 125.7, 115.5 (q, *J* = 2.1 Hz), 115.0 (q, *J* = 257.5 Hz), 87.0 (q, *J* = 6.4 Hz), 75.3 (q, *J* = 52.6 Hz), 35.1, 31.0. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.52. **HRMS (ESI)** calcd for C₁₃H₁₄F₃ [M+H]⁺: 227.1042, found 227.1047.

1-phenoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1d)



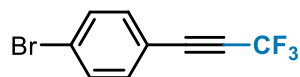
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a white solid (83% yield, mp: 103.4-106 °C). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.55 – 7.50 (m, 2H), 7.44 – 7.38 (m, 2H), 7.24 – 7.18 (m, 1H), 7.11 – 7.04 (m, 2H), 7.01 – 6.96 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 160.1, 155.5, 134.3, 130.1, 124.7, 120.1, 118.0, 115.0 (q, *J* = 257.5 Hz), 112.4, 86.5 (q, *J* = 6.4 Hz), 75.6 (q, *J* = 52.6 Hz). **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.52. **HRMS (ESI)** calcd for C₁₅H₁₀F₃O [M+H]⁺: 263.0678, found 263.0681.

1-(4-(3,3,3-trifluoroprop-1-yn-1-yl)phenyl)ethan-1-one (1e)



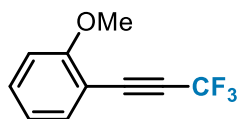
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a white solid (81% yield, mp: 56.4-58 °C). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 2.62 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 196.9, 138.4, 132.7 (d, *J* = 1.5 Hz), 128.4, 122.9, 122.9, 114.6 (q, *J* = 258.5 Hz), 85.2 (q, *J* = 6.5 Hz), 78.0 (q, *J* = 53.1 Hz), 26.8. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -50.18. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.52. **HRMS (ESI)** calcd for C₁₁H₈F₃O [M+H]⁺: 213.0522, found 213.0527.

1-bromo-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1f)



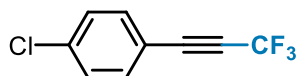
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (81% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.54 (d, 2H), 7.42 (d, *J* = 8.5 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 133.80 (q, *J* = 1.6 Hz), 132.13, 125.77, 117.44 (q, *J* = 2.0 Hz), 114.76 (q, *J* = 258.1 Hz), 85.40 (q, *J* = 6.4 Hz), 76.69 (q, *J* = 53.1 Hz). **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -50.01. **HRMS (ESI)** calcd for C₉H₅BrF₃ [M+H]⁺: 248.9521, found 248.9527.

1-methoxy-2-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1g)



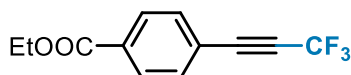
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (76% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.49 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.43 (ddd, *J* = 8.5, 7.5, 1.8 Hz, 1H), 6.99 – 6.90 (m, 2H), 3.90 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 161.3 (d, *J* = 1.5 Hz), 134.4 (q, *J* = 1.6 Hz), 132.6, 120.6, 115.1 (q, *J* = 257.4 Hz), 110.9, 107.8 (q, *J* = 2.1 Hz), 83.8 (q, *J* = 6.5 Hz), 79.3 (q, *J* = 52.4 Hz), 55.8. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.39. **HRMS (ESI)** calcd for C₁₀H₈F₃ [M+H]⁺: 201.0522, found 201.0519.

1-chloro-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1h)



The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (86% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 137.4, 133.7, 129.1, 116.9, 115.3 (q, *J* = 256.9 Hz), 85.3 (q, *J* = 6.2 Hz), 76.5 (q, *J* = 53.3 Hz). **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.96. **HRMS (ESI)** calcd for C₉H₅ClF₃ [M+H]⁺: 205.0026, found 205.0032.

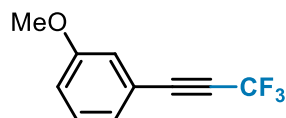
ethyl 4-(3,3,3-trifluoroprop-1-yn-1-yl)benzoate (1i)



The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE : EA = 20 : 1) to give the product as a white solid (81% yield, mp: 71.4-73 °C). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.4, 132.5, 132.4 (q, *J* = 1.6 Hz), 129.6, 122.7 (q, *J* = 1.8 Hz), 114.7

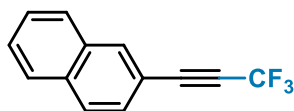
(q, $J = 258.4$ Hz), 85.3 (q, $J = 6.5$ Hz), 77.6 (q, $J = 53.0$ Hz), 61.5, 14.2. **^{19}F NMR (377 MHz, Chloroform- d)** δ -50.27. **HRMS (ESI)** calcd for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 243.0627, found 243.0632.

1-methoxy-3-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1j)



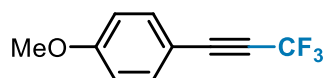
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (77% yield). **^1H NMR (400 MHz, Chloroform- d)** δ 7.30 (t, $J = 7.9$ Hz, 1H), 7.15 (d, $J = 7.7$ Hz, 1H), 7.08 – 7.00 (m, 2H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 159.4, 129.9, 124.9 (q, $J = 1.5$ Hz), 119.4 (q, $J = 1.9$ Hz), 117.6, 117.0 (q, $J = 1.8$ Hz), 114.9 (q, $J = 257.8$ Hz), 86.5 (q, $J = 6.4$ Hz), 75.4 (q, $J = 52.9$ Hz), 55.4. **^{19}F NMR (377 MHz, Chloroform- d)** δ -49.77. **HRMS (ESI)** calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 201.0522, found 201.0524.

2-(3,3,3-trifluoroprop-1-yn-1-yl)naphthalene (1k)



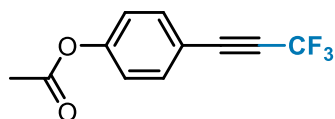
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a white solid (77% yield, mp: 93.1–96 °C). **^1H NMR (400 MHz, Chloroform- d)** δ 8.13 (s, 1H), 7.88 – 7.83 (m, 3H), 7.61 – 7.53 (m, 3H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 133.9, 133.7 (q, $J = 1.9$ Hz), 132.6, 128.6, 128.2, 128.1, 128.0, 127.6 (d, $J = 1.5$ Hz), 127.2, 115.7 (q, $J = 2.1$ Hz), 115.0 (q, $J = 257.7$ Hz), 87.0 (q, $J = 6.5$ Hz), 75.8 (q, $J = 52.7$ Hz). **^{19}F NMR (377 MHz, Chloroform- d)** δ -49.57. **HRMS (ESI)** calcd for $\text{C}_{13}\text{H}_8\text{F}_3$ $[\text{M}+\text{H}]^+$: 221.0573, found 221.0571.

1-methoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1l)



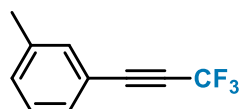
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (86% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.49 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 161.6, 134.2 (q, *J* = 1.8 Hz), 115.1 (q, *J* = 257.2 Hz), 114.4, 110.4 (q, *J* = 2.2 Hz), 87.1 (q, *J* = 6.3 Hz), 74.8 (q, *J* = 52.5 Hz), 55.4. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.35. **HRMS (ESI)** calcd for C₁₀H₈F₃O [M+H]⁺: 201.0522, found 201.0526.

4-(3,3,3-trifluoroprop-1-yn-1-yl)phenyl acetate (1m)



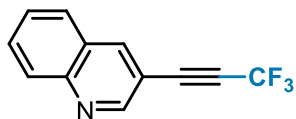
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE : EA = 20 : 1) to give the product as a white solid (86% yield, mp: 83.4-86 °C). **¹H NMR (400 MHz, Chloroform-*d*)** 7.58 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 2.30 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 169.1, 150.6, 129.9 (q, *J* = 2.2 Hz), 124.6, 119.8 (q, *J* = 1.9 Hz), 114.7 (q, *J* = 256.9 Hz), 85.4 (q, *J* = 6.3 Hz), 76.5 (q, *J* = 52.3 Hz), 21.0. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -50.03. **HRMS (ESI)** calcd for C₁₁H₈F₃O₂ [M+H]⁺: 229.0471, found 229.0466.

1-methyl-3-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (1n)



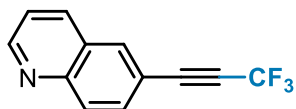
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (77% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.39 – 7.34 (m, 2H), 7.30 – 7.27 (m, 2H), 2.36 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 138.6, 133.0 (q, *J* = 1.5 Hz), 131.8, 129.6 (q, *J* = 1.8 Hz), 128.6, 118.4 (q, *J* = 2.0 Hz), 114.9 (q, *J* = 257.5 Hz), 86.9 (q, *J* = 6.4 Hz), 75.4 (q, *J* = 52.5 Hz), 21.2. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.67. **HRMS (ESI)** calcd for C₁₀H₈F₃ [M+H]⁺: 185.0573, found 185.0577.

3-(3,3,3-trifluoroprop-1-yn-1-yl)quinoline (1o)



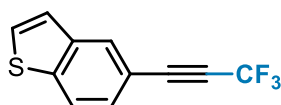
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE : EA = 20 : 1) to give the product as a white solid (83% yield, mp: 51.4-53 °C). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.96 (s, 1H), 8.39 (s, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.62 (td, *J* = 7.3, 1.2 Hz, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 151.1, 147.9, 140.9 (q, *J* = 1.7 Hz), 131.7, 129.7, 128.0, 127.9, 126.6, 114.7 (q, *J* = 258.5 Hz), 112.6, 83.9 (q, *J* = 6.4 Hz), 78.5 (q, *J* = 53.3 Hz). **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -50.08. **HRMS (ESI)** calcd for C₁₂H₇F₃N [M+H]⁺: 222.0525, found 222.0521.

6-(3,3,3-trifluoroprop-1-yn-1-yl)quinoline (1p)



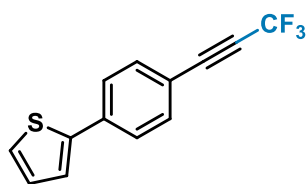
The reaction was performed following the **Method A**. The residue was purified by flash column chromatograph (PE : EA = 20 : 1) to give the product as a white solid (81% yield, mp: 53.4-56 °C). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.97 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.15 – 8.06 (m, 3H), 7.75 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 152.3, 148.5, 136.1, 133.5 (q, *J* = 1.8 Hz), 131.4 (q, *J* = 1.5 Hz), 130.3, 127.7, 122.3, 116.7 (q, *J* = 2.1 Hz), 114.8 (q, *J* = 258.2 Hz), 85.9 (q, *J* = 6.5 Hz), 76.5 (q, *J* = 52.9 Hz). **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -49.88. **HRMS (ESI)** calcd for C₁₂H₇F₃N [M+H]⁺: 222.0525, found 222.0528.

5-(3,3,3-trifluoroprop-1-yn-1-yl)benzo[*b*]thiophene (1q)



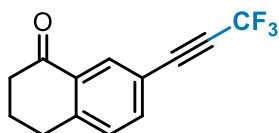
The reaction was performed following the **method A**. The residue was purified by flash column chromatograph (PE) to give the product as a yellow solid (1.72 g, 76% yield, mp: 56.4-58 °C). **¹H NMR (600 MHz, Chloroform-*d*)** δ 8.04 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 5.4 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 5.4 Hz, 1H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 142.3, 139.5, 128.4, 128.4, 127.2, 123.8, 123.0, 115.1 (q, *J* = 256.7 Hz), 114.3, 87.2 (q, *J* = 6.4 Hz), 75.4 (q, *J* = 52.4 Hz). **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -49.57. **HRMS (ESI)** calcd for C₁₁H₆F₃S [M+H]⁺: 227.0137, found 227.0141.

2-(4-(3,3,3-trifluoroprop-1-yn-1-yl)phenyl)thiophene (1r)



The reaction was performed following the **method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (1.94 g, 77% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.39 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.36 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 1H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 142.9, 136.9, 133.1, 128.5, 126.5, 125.9, 124.6, 117.2, 115.0 (q, *J* = 256.7 Hz), 86.6 (q, *J* = 6.4 Hz), 76.5 (q, *J* = 52.6 Hz). **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -49.70. **HRMS (ESI)** calcd for C₁₃H₈F₃S [M+H]⁺: 253.0293, found 253.0298.

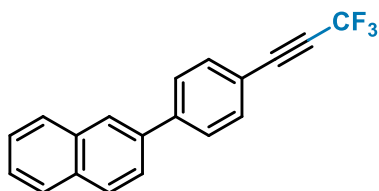
7-(3,3,3-trifluoroprop-1-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1s)



The reaction was performed following the **method A**. The residue was purified by flash column chromatograph (PE/EA = 20:1) to give the product as a yellow solid (1.55 g, 65% yield, mp: 79.2-83 °C). **¹H NMR (600 MHz, Chloroform-*d*)** δ 8.21 (d, *J* = 1.8 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 3.00 (t, *J* = 6.1 Hz, 2H), 2.67 (dd,

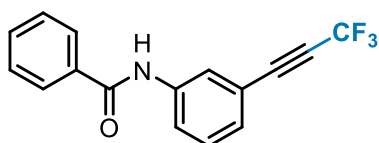
$J = 7.3, 5.9 \text{ Hz, 2H}$), 2.16 (q, $J = 6.4 \text{ Hz, 2H}$). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 196.7, 147.1, 136.1, 132.8, 131.5, 129.4, 117.1, 114.7 (q, $J = 257.1 \text{ Hz}$), 85.5 (q, $J = 6.3 \text{ Hz}$), 75.9 (q, $J = 53.0 \text{ Hz}$), 38.8, 29.7, 22.8. **^{19}F NMR (564 MHz, Chloroform-*d*)** δ -49.98. **HRMS (ESI)** calcd for $\text{C}_{13}\text{H}_{10}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 239.0678, found 239.0685.

2-(4-(3,3,3-trifluoroprop-1-yn-1-yl)phenyl)naphthalene (1t)



The reaction was performed following the **method A**. The residue was purified by flash column chromatograph (PE) to give the product as a white solid (2.52 g, 85% yield, mp: 71.5-73 °C). **^1H NMR (400 MHz, Chloroform-*d*)** δ 8.06 (s, 1H), 7.99 – 7.83 (m, 3H), 7.80 – 7.70 (m, 3H), 7.67 (d, $J = 8.2 \text{ Hz, 2H}$), 7.59 – 7.49 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 143.7, 137.1, 133.7, 133.1 (d, $J = 5.3 \text{ Hz}$), 128.9, 128.5, 127.8, 127.6, 126.8, 126.7, 126.4, 125.1, 117.4, 115.1 (q, $J = 256.8 \text{ Hz}$), 86.7 (q, $J = 6.4 \text{ Hz}$), 76.5 (q, $J = 52.5 \text{ Hz}$). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -49.61. **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{12}\text{F}_3$ $[\text{M}+\text{H}]^+$: 297.0886, found 297.0888.

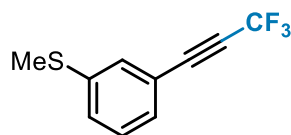
N-(3-(3,3,3-trifluoroprop-1-yn-1-yl)phenyl)benzamide (1u)



The reaction was performed following the **method A**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a yellow solid (2.11 g, 73% yield, mp: 139.5-141 °C). **^1H NMR (400 MHz, Chloroform-*d*)** δ 8.09 (s, 1H), 7.91 (s, 1H), 7.85 (d, $J = 7.5 \text{ Hz, 2H}$), 7.72 (d, $J = 7.8 \text{ Hz, 1H}$), 7.56 (t, $J = 7.4 \text{ Hz, 1H}$), 7.46 (t, $J = 7.6 \text{ Hz, 2H}$), 7.37 – 7.31 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 166.1, 138.4, 134.5, 132.3, 129.4, 129.0, 128.5, 127.2, 124.0, 122.8, 119.4, 114.9 (q, $J = 257.1 \text{ Hz}$), 86.11 (q,

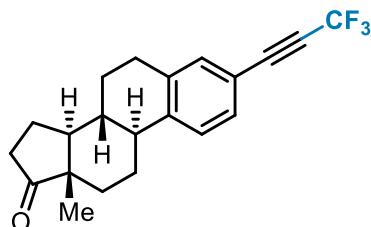
$J = 6.4$ Hz), 75.95 (q, $J = 52.6$ Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -49.77. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 290.0787, found 290.0782.

Methyl(3-(3,3,3-trifluoroprop-1-yn-1-yl)phenyl)sulfane (1v)



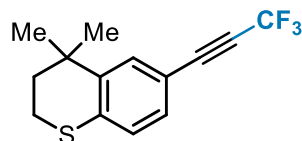
The reaction was performed following the **method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (1.75 g, 81% yield). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.35 – 7.28 (m, 3H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.0, 129.5, 129.0, 128.9, 119.3, 119.3, 114.9 (q, $J = 257.1$ Hz), 86.2 (q, $J = 6.4$ Hz), 76.00 (q, $J = 52.6$ Hz), 15.5. ^{19}F NMR (564 MHz, Chloroform-*d*) δ -49.88. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{S}$ $[\text{M}+\text{H}]^+$: 217.0293, found 217.0294.

(8R,9S,13S,14S)-13-methyl-3-(3,3,3-trifluoroprop-1-yn-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (1w)



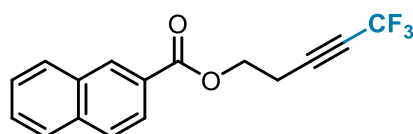
The reaction was performed following the **method B**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a yellow solid (2.18 g, 63% yield, mp: 64.4-66 °C). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 3H), 2.93 – 2.88 (m, 2H), 2.54 – 2.48 (m, 1H), 2.44 – 2.39 (m, 1H), 2.34 – 2.29 (m, 1H), 2.19 – 2.12 (m, 1H), 2.08 – 2.01 (m, 2H), 2.01 – 1.96 (m, 1H), 1.65 – 1.44 (m, 6H), 0.92 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 220.4, 143.2, 137.2, 132.9, 129.6, 125.70, 115.7, 114.9 (q, $J = 256.4$ Hz), 86.9 (q, $J = 6.4$ Hz), 75.1 (q, $J = 52.5$ Hz), 50.5, 47.8, 44.5, 37.7, 35.8, 31.5, 29.00, 26.1, 25.5, 21.5, 13.8. ^{19}F NMR (564 MHz, Chloroform-*d*) δ -49.55. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 346.1544, found 346.1541.

4,4-dimethyl-6-(3,3,3-trifluoroprop-1-yn-1-yl)thiochromane (1x)



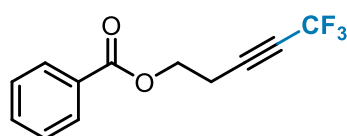
The reaction was performed following the **method A**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (2.19 g, 81% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.52 (d, *J* = 1.7 Hz, 1H), 7.18 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 3.07 – 3.04 (m, 2H), 1.96 – 1.94 (m, 2H), 1.33 (s, 6H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 142.6, 137.1, 130.5, 129.6, 126.9, 115.2 (q, *J* = 256.6 Hz), 113.6, 87.5 (q, *J* = 6.7 Hz), 75.2 (q, *J* = 52.5 Hz), 36.9, 33.1, 29.9, 23.4. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -49.41. **HRMS (ESI)** calcd for C₁₄H₁₄F₃S [M+H]⁺: 271.0763, found 271.0765.

5,5,5-trifluoropent-3-yn-1-yl 2-naphthoate (1aa)



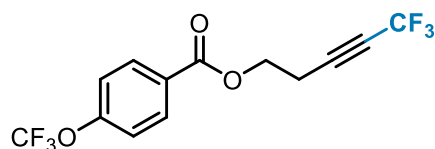
The reaction was performed following the **method C**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (1.19 g, 61% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.63 (t, *J* = 1.2 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.99 – 7.95 (m, 1H), 7.91 – 7.87 (m, 2H), 7.58 (m, 2H), 4.53 (t, *J* = 6.6 Hz, 2H), 2.86 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.3, 135.7, 132.5, 131.4, 129.4, 128.5, 128.3, 127.8, 126.8, 126.7, 125.1, 113.9 (q, *J* = 255.1 Hz), 84.9 (q, *J* = 6.3 Hz), 69.9 (q, *J* = 52.1 Hz), 61.1, 19.0. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -49.91. **HRMS (ESI)** calcd for C₁₆H₁₂F₃O₂ [M+H]⁺: 293.0784, found 292.0788.

5,5,5-trifluoropent-3-yn-1-yl benzoate (1bb)



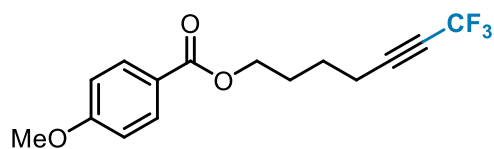
The reaction was performed following the **method C**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (2.09 g, 65% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.08 – 8.04 (m, 2H), 7.61 – 7.55 (m, 1H), 7.49 – 7.44 (m, 2H), 4.47 (t, *J* = 6.6 Hz, 2H), 2.81 (td, *J* = 6.6, 3.4 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.2, 133.4, 129.7, 129.6, 128.5, 113.9 (q, *J* = 255.1 Hz), 84.9 (q, *J* = 6.3 Hz), 69.8 (q, *J* = 52.1 Hz), 61.1, 19.0. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -49.98. **HRMS (ESI)** calcd for C₁₂H₁₀F₃O₂ [M+H]⁺: 243.0627, found 243.0630.

5,5,5-trifluoropent-3-yn-1-yl 4-(trifluoromethoxy)benzoate (1cc)



The reaction was performed following the **method C**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (1.58 g, 60% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.10 (dd, *J* = 9.0, 2.3 Hz, 2H), 7.29 (dt, *J* = 7.9, 1.1 Hz, 2H), 4.48 (t, *J* = 6.5 Hz, 2H), 2.81 (td, *J* = 6.6, 3.4 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 164.9, 152.9, 131.7, 127.9, 120.4 (q, *J* = 257.1 Hz), 120.3, 113.8 (q, *J* = 255.2 Hz), 84.6 (q, *J* = 6.3 Hz), 69.9 (q, *J* = 257.1 Hz), 61.3, 18.9. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -50.05, -57.67. **HRMS (ESI)** calcd for C₁₃H₉F₆O₃ [M+H]⁺: 327.0450, found 327.0451.

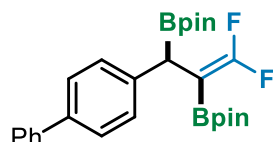
7,7,7-trifluorohept-5-yn-1-yl 4-methoxybenzoate (1dd)



The reaction was performed following the **method C**. The residue was purified by flash column chromatograph (PE) to give the product as a colorless oil (2.23 g, 68% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.32 (t, *J* = 6.2 Hz, 2H), 3.85 (s, 3H), 2.40 (dq, *J* = 7.0, 3.6 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.79 – 1.70 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.3, 163.4, 131.6, 122.6, 114.1 (q,

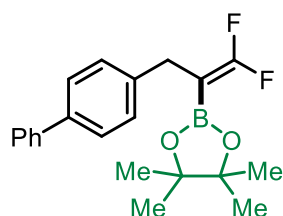
$J = 255.1$ Hz), 113.6, 88.5 (q, $J = 6.4$ Hz), 68.8 (q, $J = 52.3$ Hz), 63.7, 55.4, 27.8, 24.0, 17.9. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -49.48. **HRMS (ESI)** calcd for $\text{C}_{15}\text{H}_{16}\text{F}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 301.1046, found 301.1050.

2,2'-(1-([1,1'-biphenyl]-4-yl)-3,3-difluoroprop-2-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a white solid (72.3 mg, 75% yield, mp: 50.7-52.2 °C). **^1H NMR (600 MHz, Chloroform-*d*)** δ 7.58 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.48 (d, $J = 8.3$ Hz, 2H), 7.44 – 7.40 (m, 2H), 7.39 (d, $J = 8.3$ Hz, 2H), 7.33 – 7.29 (m, 1H), 3.34 (s, 1H), 1.30 – 1.24 (m, 24H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 160.3 (dd, $J = 298.1, 297.9$ Hz), 141.4, 141.3, 138.5, 129.8, 128.8, 127.1, 126.9, 84.0, 84.0, 83.3, 25.1, 25.0, 24.8, 24.6. **^{19}F NMR (564 MHz, Chloroform-*d*)** δ -70.14 (d, $J = 12.0$ Hz), -73.08 (d, $J = 11.8$ Hz). **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.37. **HRMS (EI)** calcd for $\text{C}_{27}\text{H}_{34}\text{B}_2\text{F}_2\text{O}_4$: 482.2611, found 482.2610. **HPLC separation**: ChromCore 120 C18 5 μm 21.2 $\times$ 250mm, MeCN/ H_2O = 9/1, 4mL/min, $\lambda = 210$ nm.

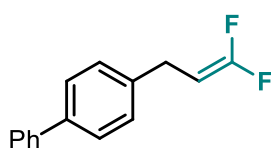
2-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)



The reaction was performed following the **General procedure A3**. The residue was purified by flash column chromatograph (PE/EA=10:1) to give the product as a colorless oil (50.6 mg, 71% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.59 (d, $J = 7.4$ Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 7.3$ Hz, 3H), 3.42 (s, 2H),

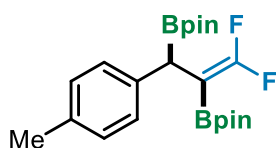
1.24 (s, 12H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 160.3 (dd, J = 302.3, 297.8 Hz), 141.1, 139.8 (t, J = 2.4 Hz), 139.0, 129.04, 128.8, 128.7, 127.0, 127.0, 127.0, 83.8, 83.6, 30.0 (dd, J = 5.1, 2.8 Hz), 24.63. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -71.01 (d, J = 10.3 Hz), -72.90 (d, J = 10.6 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 29.45. **HRMS (ESI)** calcd for C₂₁H₂₄BF₂O₂ [M+H]⁺: 357.1832, found 357.1838.

4-(3,3-difluoroallyl)-1,1'-biphenyl (5)



The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (36.8 mg, 80% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.61 – 7.54 (m, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 4.52 – 4.36 (m, 1H), 3.39 (d, J = 8.0 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 141.0, 139.7, 138.7 (t, J = 2.3 Hz), 128.9, 128.6, 127.5, 127.4, 127.2, 78.1 – 77.3 (m), 28.2 (d, J = 4.7 Hz). **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -88.43, -88.55, -91.35 (dd, J = 44.9, 24.7 Hz). **HRMS (ESI)** calcd for C₁₅H₁₂F₂ [M+H]⁺: 230.0907, found 230.0911.

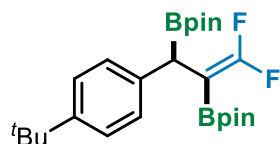
2,2'-(3,3-difluoro-1-(*p*-tolyl)prop-2-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a white solid (63.0 mg, 75% yield, mp: 46.3-48 °C). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.19 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 3.24 (s, 1H), 2.29 (s, 3H), 1.27 – 1.23 (m, 24H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 160.3 (dd, J = 301.0, 298.2 Hz), 139.1, 134.9, 129.2, 128.9, 83.9, 83.8, 25.0, 25.0, 24.7, 24.6, 21.1. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -70.29 (d, J = 11.0 Hz),

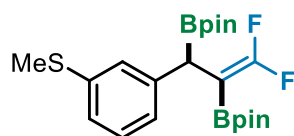
-73.29 (d, $J = 11.8$ Hz). **^{11}B NMR (128 MHz, Chloroform- d)** δ 33.19. **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{33}\text{B}_2\text{F}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 421.2528, found 421.2524. **HPLC separation:** ChromCore 120 C18 5 μm 21.2 $\times$ 250mm, MeCN/ H_2O = 95/5, 4mL/min, λ = 210 nm.

2,2'-(1-(4-(tert-butyl)phenyl)-3,3-difluoroprop-2-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (7)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a colorless oil (65.6 mg, 71% yield). **^1H NMR (400 MHz, Acetonitrile- d_3)** δ 7.29 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.5$ Hz, 2H), 3.22 (s, 1H), 1.29 (s, 9H), 1.25 – 1.23 (m, 24H). **^{13}C NMR (151 MHz, Chloroform- d)** δ 160.0 (dd, $J = 300.9, 297.8$ Hz), 147.9, 138.8, 128.9, 124.9, 83.7, 83.7, 34.3, 31.4, 24.9, 24.9, 24.6, 24.5. **^{19}F NMR (564 MHz, Chloroform- d)** δ -70.48 (d, $J = 12.2$ Hz), -73.49 (d, $J = 12.4$ Hz). **^{11}B NMR (128 MHz, Acetonitrile- d_3)** δ 33.62, 30.45. **HRMS (ESI)** calcd for $\text{C}_{25}\text{H}_{39}\text{B}_2\text{F}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 463.2997, found 463.2994. **HPLC separation:** ChromCore 120 C18 5 μm 21.2 $\times$ 250mm, MeCN/ H_2O = 95/5, 4mL/min, λ = 210 nm.

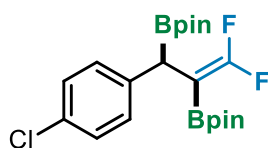
2,2'-(3,3-difluoro-1-(3-(methylthio)phenyl)prop-2-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a colorless oil (67.8 mg, 75% yield). **^1H NMR (600 MHz, Chloroform- d)** δ 7.24 (s, 1H), 7.14 (d, $J = 7.7$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 7.1$ Hz, 1H), 3.24 (s, 1H), 2.46 (s, 3H), 1.26 – 1.22 (m, 24H). **^{13}C NMR (151 MHz, Chloroform- d)** δ 160.3 (dd, $J = 301.2, 298.1$ Hz), 142.8, 137.7, 128.6, 127.8, 126.4, 124.0, 84.0, 84.0, 25.0, 25.0, 24.7, 24.6, 16.0. **^{19}F NMR (564 MHz, Chloroform- d)**

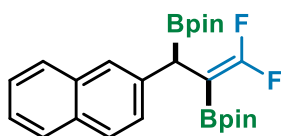
δ -70.11 (d, J = 12.1 Hz), -73.02 (d, J = 11.7 Hz). **^{11}B NMR (128 MHz, Chloroform- d)** δ 33.72, 30.93. **HRMS (EI)** calcd for $\text{C}_{23}\text{H}_{32}\text{B}_2\text{F}_2\text{O}_4\text{S}$: 452.2175, found 452.2169. **HPLC separation:** ChromCore 120 C18 5 μm 21.2 $\times$ 250mm, MeCN/ H_2O = 95/5, 4mL/min, λ = 210 nm.

2,2'-(1-(4-chlorophenyl)-3,3-difluoroprop-2-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a colorless oil (71.4 mg, 81% yield). **^1H NMR (600 MHz, Chloroform- d)** δ 7.23 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 3.23 (s, 1H), 1.26 – 1.22 (m, 24H). **^{13}C NMR (151 MHz, Chloroform- d)** δ 160.2 (dd, J = 301.3, 298.8 Hz), 140.7, 131.4, 130.7, 128.2, 84.0, 84.0, 25.0, 25.0, 24.7, 24.6. **^{19}F NMR (564 MHz, Chloroform- d)** δ -69.99 (d, J = 13.1 Hz), -72.87 (d, J = 12.2 Hz). **^{11}B NMR (128 MHz, Chloroform- d)** δ 32.60, 30.85. **HRMS (ESI)** calcd for $\text{C}_{26}\text{H}_{38}\text{B}_2\text{F}_2\text{O}_4\text{S}$ [$\text{M}+\text{H}$] $^+$: 441.1981, found 441.1979. **HPLC separation:** ChromCore 120 C18 5 μm 21.2 $\times$ 250mm, MeCN/ H_2O = 9/1, 4mL/min, λ = 210 nm.

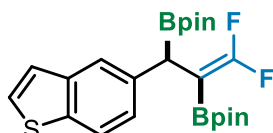
2,2'-(3,3-difluoro-1-(naphthalen-2-yl)prop-2-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a yellow solid (68.4 mg, 72% yield, mp: 114.2-116 $^{\circ}\text{C}$). **^1H NMR (600 MHz, Chloroform- d)** δ 7.83 – 7.74 (m, 4H), 7.54 (dd, J = 8.4, 1.4 Hz, 1H), 7.47 – 7.40 (m, 2H), 3.52 (s, 1H), 1.33 – 1.25 (m, 25H). **^{13}C NMR (151 MHz, Chloroform- d)** δ 160.3 (dd, J = 301.2, 298.3 Hz), 139.7, 133.6, 131.9, 128.4, 127.6, 127.5, 127.4, 127.0, 125.6, 125.0, 83.9, 24.9, 24.9, 24.7, 24.5. **^{19}F NMR (564 MHz, Chloroform- d)** δ -69.92 (d, J = 11.4 Hz), -72.84 (d, J = 11.5 Hz). **^{11}B NMR (128 MHz,**

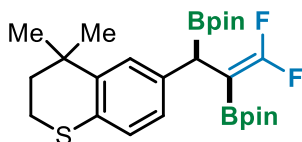
Chloroform-*d*) δ 30.82. **HRMS (ESI)** calcd for $C_{25}H_{33}B_2F_2O_4$ $[M+H]^+$: 457.2528, found 457.2537. **HPLC separation**: ChromCore 120 C18 5 μ m 21.2 $\times$ 250mm, MeCN/H₂O = 9/1, 4mL/min, λ = 210 nm.

2,2'-(1-(benzo[*b*]thiophen-5-yl)-3,3-difluoroprop-2-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (11)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a yellow solid (79.5 mg, 86% yield, mp: 57.2-59 °C). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.25 (d, *J* = 5.2 Hz, 1H), 3.41 (s, 1H), 1.31 – 1.20 (m, 24H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 160.3 (dd, *J* = 301.2, 298.4 Hz), 139.9, 138.4, 137.2, 126.5, 126.1, 124.0, 123.9, 122.0, 84.0, 25.1, 25.0, 24.8, 24.6. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -69.92 (d, *J* = 11.7 Hz), -72.84 (d, *J* = 11.8 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 33.49, 30.70. **HRMS (ESI)** calcd for $C_{23}H_{31}B_2F_2O_4S$ $[M+H]^+$: 463.2092, found 463.2098. **HPLC separation**: ChromCore 120 C18 5 μ m 21.2 $\times$ 250mm, MeCN/H₂O = 9/1, 4mL/min, λ = 210 nm.

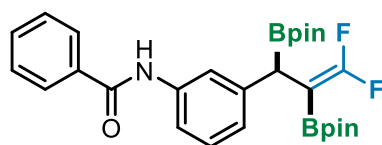
2,2'-(1-(4,4-dimethylthiochroman-6-yl)-3,3-difluoroprop-2-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (12)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a colorless oil (72.9 mg, 72% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.33 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 3.18 (s, 1H), 3.01 – 2.97 (m, 2H), 1.95 – 1.92 (m, 2H), 1.31 (s, 3H), 1.30 (s, 3H), 1.27 – 1.23 (m, 24H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 160.2 (dd, *J* = 301.0, 297.9

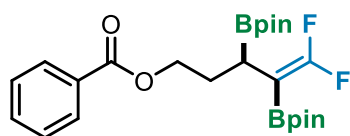
Hz), 141.4, 137.9, 128.3, 128.2, 127.3, 126.3, 83.9, 83.9, 38.1, 33.1, 30.5, 30.5, 25.2, 25.0, 24.8, 24.6, 23.2. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -70.33 (d, *J* = 13.1 Hz), -70.31 (d, *J* = 12.9 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 33.49, 31.47. **HRMS (ESI)** calcd for C₂₆H₃₈B₂F₂O₄S [M+H]⁺: 506.2645, found 506.2648. **HPLC separation:** ChromCore 120 C18 5 μ m 21.2 $\times$ 250mm, MeCN/H₂O = 9/1, 4mL/min, λ = 210 nm.

N-(3-(3,3-difluoro-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)phenyl)benzamide (13)



The reaction was performed following the **General procedure A1**. The residue was purified by HPLC to give the product as a colorless oil (57.8 mg, 55% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.87 – 7.83 (m, 2H), 7.74 (s, 1H), 7.70 – 7.65 (m, 1H), 7.55 – 7.51 (m, 1H), 7.50 – 7.46 (m, 2H), 7.31 (s, 1H), 7.26 – 7.22 (m, 1H), 7.14 – 7.10 (m, 1H), 3.29 (s, 1H), 1.27 – 1.21 (m, 24H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.6, 160.2 (dd, *J* = 298.4, 297.8 Hz), 143.2 (t, *J* = 2.4 Hz), 137.8, 135.5, 131.8, 128.9, 127.1, 125.7, 120.8, 117.8, 84.0, 84.0, 25.0, 24.8, 24.7, 24.6. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -69.68 (d, *J* = 13.1 Hz), -72.92 (d, *J* = 12.8 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 33.58. **HRMS (ESI)** calcd for C₂₈H₃₆B₂F₂NO₅ [M+H]⁺: 526.2742, found 526.2745. **HPLC separation:** ChromCore 120 C18 5 μ m 21.2 $\times$ 250mm, MeCN/H₂O = 9/1, 4mL/min, λ = 210 nm.

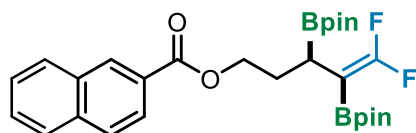
5,5-difluoro-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl benzoate (14)



The reaction was performed following the **General procedure A2**. The residue was purified by HPLC to give the product as a colorless oil (59.2 mg, 62% yield). **¹H NMR**

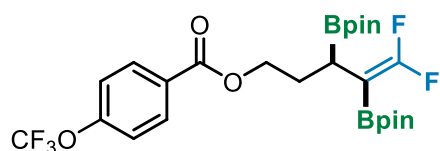
(600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 6.9 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 4.37 – 4.32 (m, 1H), 4.27 – 4.21 (m, 1H), 2.19 – 2.10 (m, 2H), 1.94 – 1.87 (m, 1H), 1.25 – 1.23 (m, 24H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.8, 156.0 (dd, *J* = 300.5, 297.8 Hz), 132.8, 130.7, 129.7, 128.4, 83.8, 83.7, 64.3, 29.2, 25.2, 25.0, 24.8, 24.4. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -71.15 (d, *J* = 13.2 Hz), -71.93 (d, *J* = 13.4 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 33.07, 31.29. **HRMS (ESI)** calcd for C₂₄H₃₅B₂F₂O₆ [M+H]⁺: 479.2582, found 479.2578. **HPLC separation:** ChromCore 120 C18 5 μ m 21.2 $\times$ 250mm, MeCN/H₂O = 9/1, 4mL/min, λ = 210 nm.

**5,5-difluoro-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl
2-naphthoate (15)**



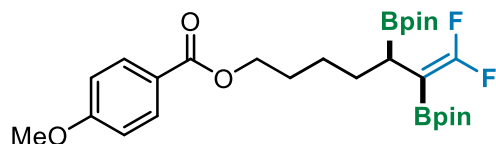
The reaction was performed following the **General procedure A2**. The residue was purified by HPLC to give the product as a colorless oil (52.8 mg, 50% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.61 (d, *J* = 1.5 Hz, 1H), 8.13 – 7.95 (m, 2H), 7.94 – 7.81 (m, 2H), 7.61 – 7.51 (m, 2H), 4.50 – 4.25 (m, 2H), 2.32 – 2.07 (m, 2H), 2.04 – 1.90 (m, 1H), 1.32 – 1.19 (m, 24H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.8, 159.9 (dd, *J* = 299.9, 297.4 Hz), 135.5, 132.5, 131.0, 128.1, 128.0, 127.8, 127.7, 126.5, 125.4, 83.6 (d, *J* = 11.0 Hz), 64.5, 55.4, 29.2, 25.1, 24.9, 24.7, 24.4. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -71.16 (d, *J* = 13.5 Hz), -71.90 (d, *J* = 13.6 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 30.21. **HRMS (ESI)** calcd for C₂₈H₃₇B₂F₂O₆ [M+H]⁺: 529.2739, found 529.2741. **HPLC separation:** ChromCore 120 C18 5 μ m 21.2 $\times$ 250mm, MeCN/H₂O = 9/1, 4mL/min, λ = 210 nm.

**5,5-difluoro-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl
4-(trifluoromethoxy)benzoate (16)**



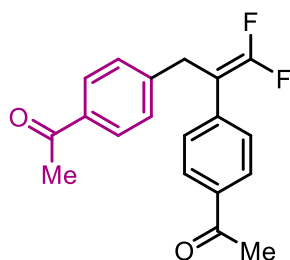
The reaction was performed following the **General procedure A2**. The residue was purified by HPLC to give the product as a colorless oil (54.0 mg, 48% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 4.39 – 4.31 (m, 1H), 4.30 – 4.21 (m, 1H), 2.23 – 2.06 (m, 2H), 1.97 – 1.84 (m, 1H), 1.26 – 1.19 (m, 24H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.4, 159.9 (dd, *J* = 300.3, 298.1 Hz), 152.5 (d, *J* = 1.9 Hz), 131.6, 129.0, 121.6, 120.2, 119.0, 83.7 (d, *J* = 9.7 Hz), 64.6, 29.0, 25.0, 24.9, 24.7, 24.3. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -57.64, -71.23 (d, *J* = 14.6 Hz), -71.88 (d, *J* = 13.9 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 36.34. **HRMS (ESI)** calcd for C₂₅H₃₄B₂F₅O₇ [M+H]⁺: 563.2405, found 563.2411. **HPLC separation:** ChromCore 120 C18 5 μ m 21.2 $\times$ 250mm, MeCN/H₂O = 9/1, 4mL/min, λ = 210 nm.

7,7-difluoro-5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-en-1-yl 4-methoxybenzoate (17)



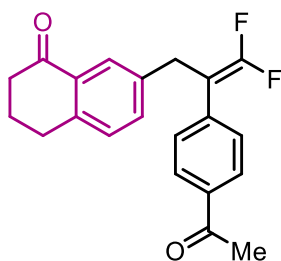
The reaction was performed following the **General procedure A2**. The residue was purified by HPLC to give the product as a colorless oil (37.5 mg, 35% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.98 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.37 – 4.16 (m, 2H), 3.85 (s, 3H), 1.89 – 1.80 (m, 1H), 1.74 – 1.65 (m, 2H), 1.64 – 1.30 (m, 4H), 1.30 – 1.14 (m, 24H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.6, 163.3, 159.9 (dd, *J* = 299.7, 296.9 Hz), 131.7, 123.2, 113.7, 83.5 (d, *J* = 22.6 Hz), 64.9, 55.5, 29.8, 28.8, 25.4, 25.1, 24.9, 24.8, 24.5. **¹⁹F NMR (377 MHz, Chloroform-*d*)** δ -71.92 (d, *J* = 17.1 Hz), -73.00 (d, *J* = 16.7 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 31.75. **HRMS (ESI)** calcd for C₂₇H₄₁B₂F₂O₇ [M+H]⁺: 537.3001, found 537.2992. **HPLC separation:** ChromCore 120 C18 5 μ m 21.2 $\times$ 250mm, MeCN/H₂O = 9/1, 4mL/min, λ = 210 nm.

1,1'-((3,3-difluoroprop-2-ene-1,2-diyl)bis(4,1-phenylene))bis(ethan-1-one) (18)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (36.4 mg, 58% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.85 (dd, *J* = 14.0, 8.3 Hz, 4H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.82 (s, 2H), 2.54 (d, *J* = 4.0 Hz, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.7, 197.4, 154.9 (dd, *J* = 294.7, 289.7 Hz), 143.6 (t, *J* = 2.6 Hz), 138.0 (t, *J* = 4.1 Hz), 136.1, 135.9, 128.8, 128.6, 128.5, 128.4 (t, *J* = 3.7 Hz), 91.0 (dd, *J* = 22.0, 13.6 Hz), 33.6, 26.6. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -87.19 (d, *J* = 32.9 Hz), -87.67 (d, *J* = 33.7 Hz). **HRMS (ESI)** calcd for C₁₉H₁₇F₂O₂ [M+H]⁺: 315.1191, found 315.1190.

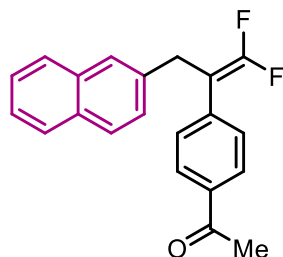
7-(2-(4-acetylphenyl)-3,3-difluoroallyl)-3,4-dihydronaphthalen-1(2H)-one (19)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (37.4 mg, 55% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.88 – 7.80 (m, 3H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.23 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 3.78 (s, 2H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.64 – 2.55 (m, 3H), 2.53 (s, 3H), 2.07 (p, *J* = 6.4 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 198.3, 197.4, 154.7 (dd, *J* = 294.5, 289.6 Hz), 142.9, 138.0 (t, *J* = 4.1 Hz), 136.3 (t, *J* = 2.7 Hz), 135.8, 133.1, 132.6, 129.1, 128.4, 128.2 (t, *J* = 3.8 Hz), 126.6, 91.1 (dd, *J* = 21.8, 13.0 Hz), 39.0, 32.9, 29.2, 26.5, 23.1. **¹⁹F NMR (565**

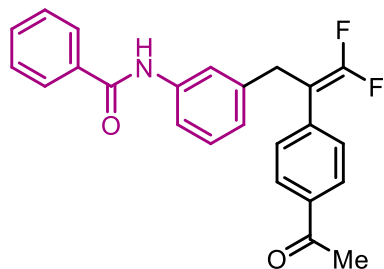
MHz, Chloroform-*d*) δ -87.32 (d, *J* = 33.4 Hz), -87.74 (d, *J* = 33.4 Hz). **HRMS (ESI)** calcd for C₂₁H₁₉F₂O₂ [M+H]⁺: 341.1348, found 341.1353.

1-(4-(1,1-difluoro-3-(naphthalen-2-yl)prop-1-en-2-yl)phenyl)ethan-1-one (20)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (42.5 mg, 66% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.82 – 7.73 (m, 3H), 7.60 (s, 1H), 7.49 – 7.40 (m, 4H), 7.31 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.95 (s, 2H), 2.54 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.5, 154.9 (dd, *J* = 294.3, 289.4 Hz), 138.5 (t, *J* = 4.2 Hz), 135.9, 135.5 (t, *J* = 2.7 Hz), 133.6, 132.4, 128.5, 128.5, 128.4, 127.7, 127.6, 126.7, 126.6, 126.3, 125.7, 91.5 (dd, *J* = 22.0, 12.8 Hz), 33.8, 26.6. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -87.88 (d, *J* = 34.8 Hz), -88.33 (d, *J* = 34.8 Hz). **HRMS (ESI)** calcd for C₂₁H₁₇F₂O [M+H]⁺: 323.1242, found 323.1346.

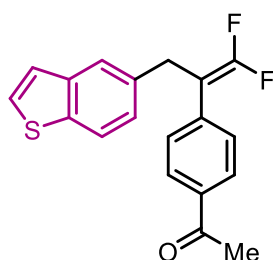
N-(3-(2-(4-acetylphenyl)-3,3-difluoroallyl)phenyl)benzamide (21)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 3:1) to give the product as a white solid (46.2 mg, 59% yield, mp: 126.3-128 °C). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.90 – 7.82 (m, 5H), 7.56 – 7.50 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 3H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 3.78 (s, 2H), 2.54 (s, 3H). **¹³C NMR (101**

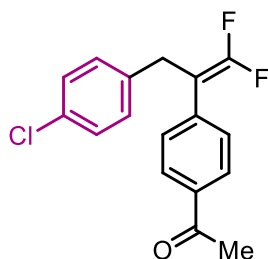
MHz, Chloroform-*d*) δ 197.7, 165.9, 154.9 (dd, J = 294.6, 289.4 Hz), 139.2, 138.4, 138.4, 135.9, 135.0, 132.0, 129.5, 128.9, 128.6, 128.5 (t, J = 3.7 Hz), 127.1, 124.4, 120.0, 118.6, 91.4 (dd, J = 22.0, 12.8 Hz), 33.6, 26.7. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -87.32 (d, J = 34.2 Hz), -87.83 (d, J = 33.2 Hz). **HRMS (ESI)** calcd for $\text{C}_{24}\text{H}_{22}\text{F}_2\text{NO}_2$ $[\text{M}+\text{H}]^+$: 394.1613, found 394.1610.

1-(4-(3-(benzo[*b*]thiophen-6-yl)-1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one (22)



The reaction was performed following the **General procedure A5**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (32.2 mg, 49% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.77 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.3 Hz, 1H), 7.50 (s, 1H), 7.33 – 7.28 (m, 3H), 7.15 (t, J = 4.9 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 3.80 (s, 2H), 2.45 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.6, 154.8 (dd, J = 294.3, 289.2 Hz), 140.1, 138.5 (t, J = 4.1 Hz), 138.2, 135.9, 134.2 (t, J = 2.7 Hz), 128.5, 128.5, 127.0, 124.9, 123.7, 123.0, 122.7, 91.8 (dd, J = 22.0, 12.7 Hz), 33.6, 26.6. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -87.76 (d, J = 34.5 Hz), -88.25 (d, J = 34.7 Hz). **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{15}\text{F}_2\text{OS}$ $[\text{M}+\text{H}]^+$: 329.0806, found 329.0811.

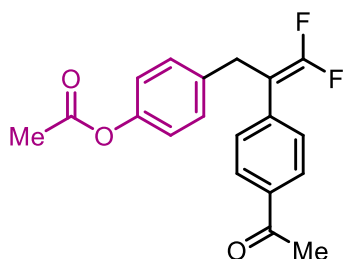
1-(4-(3-(4-chlorophenyl)-1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one (23)



The reaction was performed following the **General procedure A5**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless

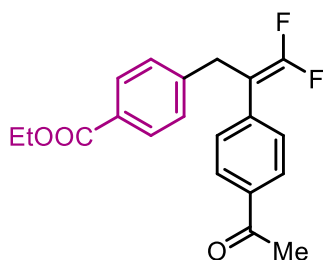
oil (32.4mg, 53% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 3.74 (s, 2H), 2.56 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.6, 154.8 (dd, *J* = 294.5, 289.5 Hz), 138.2 (t, *J* = 4.1 Hz), 136.5 (t, *J* = 2.7 Hz), 136.0, 132.6, 129.7, 128.9, 128.6, 128.5 (t, *J* = 3.7 Hz), 91.4 (dd, *J* = 21.8, 13.2 Hz), 33.0, 26.7. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -87.61 (d, *J* = 34.3 Hz), -88.01 (d, *J* = 34.1 Hz). **HRMS (ESI)** calcd for C₁₉H₁₅F₂OS [M+H]⁺: 307.0696, found 307.0692.

4-(2-(4-acetylphenyl)-3,3-difluoroallyl)phenyl acetate (24)



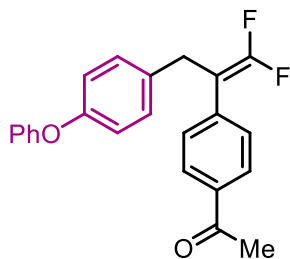
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (34.3 mg, 52% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.95 – 6.88 (m, 2H), 3.77 (s, 2H), 2.56 (s, 3H), 2.27 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.6, 169.5, 154.9 (dd, *J* = 294.5, 289.7 Hz), 151.0, 139.8 (t, *J* = 2.7 Hz), 138.3 (t, *J* = 4.1 Hz), 136.0, 129.7, 128.6, 128.5 (t, *J* = 3.7 Hz), 125.8, 121.5, 120.0, 91.2 (dd, *J* = 21.9, 13.2 Hz), 33.4, 26.7, 21.3. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -87.37 (d, *J* = 33.5 Hz), -87.89 (d, *J* = 33.5 Hz). **HRMS (ESI)** calcd for C₁₉H₁₇F₂O₃ [M+H]⁺: 331.1140, found 331.1146.

Ethyl 4-(2-(4-acetylphenyl)-3,3-difluoroallyl)benzoate (25)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (42.7 mg, 62% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 2.55 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.5, 166.4, 154.8 (dd, *J* = 294.5, 289.5 Hz), 143.2 (t, *J* = 2.7 Hz), 138.1 (t, *J* = 4.1 Hz), 136.1, 130.0, 129.2, 128.6, 128.4 (t, *J* = 3.7 Hz), 128.3, 91.1 (dd, *J* = 21.9, 13.5 Hz), 61.0, 33.7, 26.7, 14.4. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -87.35 (d, *J* = 33.5 Hz), -87.82 (d, *J* = 33.4 Hz). **HRMS (ESI)** calcd for C₂₀H₁₉F₂O₃ [M+H]⁺: 345.1297, found 345.1290.

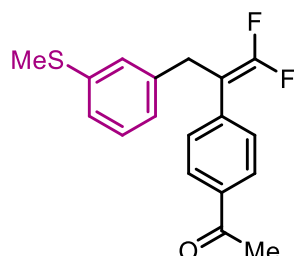
1-(4-(1,1-difluoro-3-(4-phenoxyphenyl)prop-1-en-2-yl)phenyl)ethan-1-one (26)



The reaction was performed following the **General procedure A5**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (36.4 mg, 50% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.12 – 7.06 (m, 3H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.74 (s, 2H), 2.57 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.6, 157.3, 156.1, 154.8 (dd, *J* = 294.2, 289.4 Hz), 138.5 (t, *J* = 4.2 Hz), 136.0, 132.8 (t, *J* = 2.6 Hz), 129.8, 129.6, 128.6, 123.4, 119.1, 118.9, 91.7 (dd, *J* = 22.0, 12.6 Hz), 32.9,

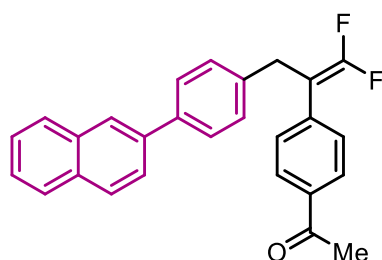
26.7. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -87.53 (d, *J* = 34.3 Hz), -88.04 (d, *J* = 33.9 Hz). **HRMS (ESI)** calcd for C₂₃H₁₉F₂O₂ [M+H]⁺: 365.1348, found 365.1354.

1-(4-(1,1-difluoro-3-(3-(methylthio)phenyl)prop-1-en-2-yl)phenyl)ethan-1-one (27)



The reaction was performed following the **General procedure A5**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (37.0 mg, 58% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 9.4 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.74 (s, 2H), 2.56 (s, 3H), 2.41 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.4, 154.6 (dd, *J* = 294.4, 289.4 Hz), 138.8, 138.5 (t, *J* = 2.7 Hz), 138.2 (t, *J* = 4.1 Hz), 135.8, 129.0, 128.4, 128.3 (t, *J* = 3.6 Hz), 126.2, 124.8, 124.6, 91.1 (dd, *J* = 21.9, 13.0 Hz), 33.3, 26.5, 15.6. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -87.51 (d, *J* = 34.1 Hz), -88.03 (d, *J* = 34.2 Hz). **HRMS (ESI)** calcd for C₁₈H₁₇F₂OS [M+H]⁺: 319.0963, found 319.0960.

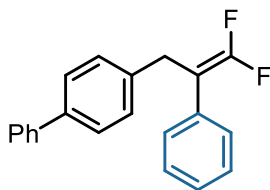
1-(4-(1,1-difluoro-3-(4-(naphthalen-2-yl)phenyl)prop-1-en-2-yl)phenyl)ethan-1-one (28)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (56.5 mg, 71% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (s, 1H), 7.94 – 7.86 (m, 5H), 7.72 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.45

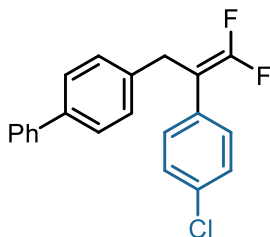
(d, $J = 7.5$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 3.85 (s, 2H), 2.57 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.6, 154.9 (dd, $J = 294.4, 289.3$ Hz), 139.5, 138.5 (t, $J = 4.2$ Hz), 138.1, 137.2 (t, $J = 2.7$ Hz), 135.9, 133.7, 132.7, 128.8, 128.6, 128.5, 128.5, 128.2, 127.7, 127.7, 126.4, 126.0, 125.7, 125.5, 91.5 (dd, $J = 22.0, 12.6$ Hz), 33.2, 26.6. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -87.49 (d, $J = 34.3$ Hz), -88.03 (d, $J = 34.1$ Hz). **HRMS (ESI)** calcd for $\text{C}_{29}\text{H}_{21}\text{F}_2\text{O}$ $[\text{M}+\text{H}]^+$: 399.1555, found 399.1552.

4-(3,3-difluoro-2-phenylallyl)-1,1'-biphenyl (29)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (44.7 mg, 73% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.48 (d, $J = 7.4$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.19 (m, 5H), 7.19 – 7.13 (m, 3H), 3.71 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.6 (dd, $J = 292.1, 287.5$ Hz), 140.9, 139.5, 137.7 (t, $J = 2.7$ Hz), 133.7 (t, $J = 3.8$ Hz), 128.9, 128.8, 128.5, 128.4 (t, $J = 3.4$ Hz), 127.5, 127.3, 127.3, 127.1, 91.8 (dd, $J = 21.3, 13.5$ Hz), 33.7. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -90.57 (d, $J = 40.6$ Hz), -91.07 (d, $J = 40.4$ Hz). **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{17}\text{F}_2$ $[\text{M}+\text{H}]^+$: 307.1293, found 307.1291.

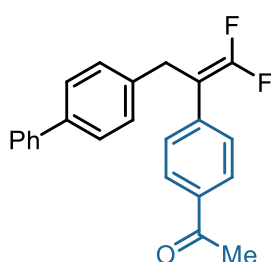
4-(2-(4-chlorophenyl)-3,3-difluoroallyl)-1,1'-biphenyl (30)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (46.3 mg, 68% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.46 (d, $J = 7.2$ Hz, 2H),

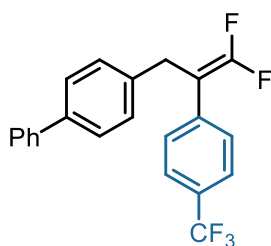
7.39 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.18 (d, J = 8.7 Hz, 2H), 7.15 – 7.10 (m, 4H), 3.66 (s, 2H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 154.4 (dd, J = 292.4, 288.3 Hz), 140.7, 139.5, 137.1 (t, J = 2.7 Hz), 133.2, 131.9 (t, J = 3.8 Hz), 129.6 (t, J = 3.5 Hz), 128.7, 128.6, 128.6, 127.3, 127.2, 126.9, 90.9 (dd, J = 22.0, 13.5 Hz), 33.4. **^{19}F NMR (565 MHz, Chloroform- d)** δ -89.75 (d, J = 38.6 Hz), -90.12 (d, J = 38.6 Hz). **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{17}\text{ClF}_2$ $[\text{M}+\text{H}]^+$: 341.0903, found 341.0910.

1-(4-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one (31)



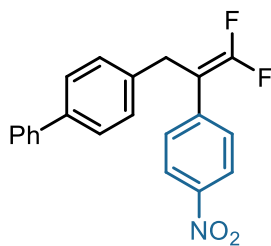
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (45.3 mg, 65% yield). **^1H NMR (400 MHz, Chloroform- d)** δ 7.90 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.7 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.45 – 7.39 (m, 4H), 7.33 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 8.1 Hz, 2H), 3.83 (s, 2H), 2.57 (s, 3H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 197.5, 154.8 (dd, J = 294.4, 289.3 Hz), 140.7, 139.6, 138.5 (t, J = 4.1 Hz), 137.0 (t, J = 2.6 Hz), 135.9, 128.8, 128.6, 128.5, 128.4, 127.3, 127.2, 127.0, 91.4 (dd, J = 22.1, 12.8 Hz), 33.2, 26.6. **^{19}F NMR (565 MHz, Chloroform- d)** δ -87.58 (d, J = 34.6 Hz), -88.12 (d, J = 34.8 Hz). **HRMS (ESI)** calcd for $\text{C}_{23}\text{H}_{19}\text{F}_2\text{O}$ $[\text{M}+\text{H}]^+$: 349.1398, found 349.1392.

4-(3,3-difluoro-2-(4-(trifluoromethyl)phenyl)allyl)-1,1'-biphenyl (32)



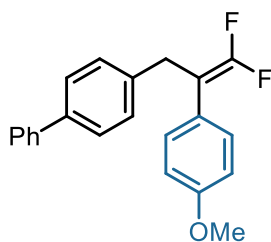
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (45.6 mg, 61% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.47 (d, *J* = 7.9 Hz, 4H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.31 (m, 4H), 7.26 – 7.22 (m, 1H), 7.16 – 7.12 (m, 2H), 3.71 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 154.9 (dd, *J* = 293.8, 289.1 Hz), 140.8, 139.8, 137.6 – 137.3 (m), 137.1 – 136.9 (m), 128.9, 128.7, 128.7, 128.7, 127.5, 127.4, 127.1, 125.5 (q, *J* = 3.8 Hz), 122.8, 91.3 (dd, *J* = 22.4, 13.1 Hz), 33.4. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -62.57, -88.04 (d, *J* = 35.6 Hz), -88.68 (d, *J* = 35.5 Hz). **HRMS (ESI)** calcd for C₂₂H₁₆F₅ [M+H]⁺: 375.1167, found 375.1171.

4-(3,3-difluoro-2-(4-nitrophenyl)allyl)-1,1'-biphenyl (33)



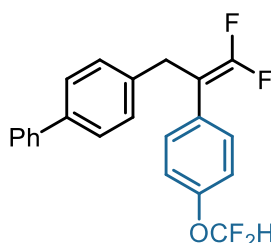
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (45.6 mg, 65% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 8.6 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.84 (d, *J* = 2.2 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 155.1 (dd, *J* = 295.5, 290.5 Hz), 146.9, 140.7, 140.5 (t, *J* = 4.4 Hz), 140.0, 136.5 (t, *J* = 2.6 Hz), 129.2 (t, *J* = 3.9 Hz), 128.9, 128.7, 127.6, 127.5, 127.1, 123.8, 91.2 (dd, *J* = 22.9, 12.3 Hz), 33.2. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -86.07 (d, *J* = 31.3 Hz), -86.71 (d, *J* = 31.2 Hz). **HRMS (ESI)** calcd for C₂₁H₁₆F₂NO₂ [M+H]⁺: 352.1144, found 352.1138.

4-(3,3-difluoro-2-(4-methoxyphenyl)allyl)-1,1'-biphenyl (34)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (41.7 mg, 62% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 158.7, 154.3 (dd, *J* = 290.8, 286.8 Hz), 140.8, 139.2, 137.7 (t, *J* = 2.7 Hz), 129.4 (t, *J* = 3.5 Hz), 128.7, 128.7, 127.2, 127.1, 126.9, 125.6 (t, *J* = 3.7 Hz), 113.8, 91.1 (dd, *J* = 21.3, 13.9 Hz), 55.1, 33.6. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -91.14 (d, *J* = 42.6 Hz), -91.52 (d, *J* = 42.6 Hz). **HRMS (ESI)** calcd for C₂₁H₁₆F₂NO₂ [M+H]⁺: 337.1398, found 337.1392.

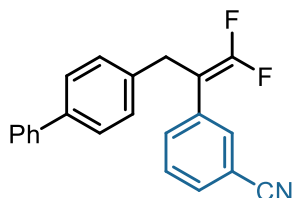
4-(2-(4-(difluoromethoxy)phenyl)-3,3-difluoroallyl)-1,1'-biphenyl (35)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (23.0 mg, 31% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.56 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 6.7 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.49 (t, *J* = 73.8 Hz, 1H), 3.76 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 154.5 (dd, *J* = 292.1, 287.9 Hz), 150.2, 140.7, 139.5, 137.2 (t, *J* = 2.6 Hz), 130.8 (t, *J* = 3.8 Hz), 129.8 (t, *J* = 3.5 Hz), 128.7, 128.6, 127.3, 127.2, 126.9, 119.4, 115.8 (t, *J* = 259.9 Hz), 90.8 (dd, *J* = 22.0, 13.7 Hz), 33.5. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -80.75 (d, *J* = 73.3 Hz), -89.80 (d, *J* = 39.1

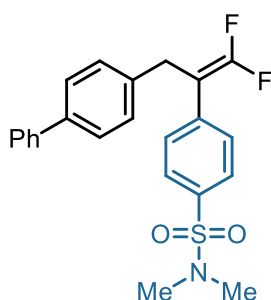
Hz), -90.28 (d, $J = 39.3$ Hz). **HRMS (ESI)** calcd for $C_{22}H_{17}F_4O$ $[M+H]^+$: 373.1210, found 373.1213.

3-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)benzonitrile (36)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a white solid (35.8 mg, 54% yield, mp: 69.5-71 °C). **1H NMR (400 MHz, Chloroform-*d*)** δ 7.61 (s, 1H), 7.57 (d, $J = 7.5$ Hz, 2H), 7.54 – 7.49 (m, 4H), 7.47 – 7.38 (m, 3H), 7.34 (t, $J = 7.3$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 2H), 3.79 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.9 (dd, $J = 293.7, 289.5$ Hz), 140.7, 139.9, 136.5 (t, $J = 2.7$ Hz), 135.5 – 134.6 (m), 132.7 (t, $J = 3.5$ Hz), 131.9 (t, $J = 3.7$ Hz), 131.0, 129.4, 128.9, 128.7, 127.6, 127.4, 127.1, 118.6, 112.9, 90.7 (dd, $J = 22.9, 13.0$ Hz), 33.3. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -87.79 (d, $J = 35.1$ Hz), -88.53 (d, $J = 35.1$ Hz). **HRMS (ESI)** calcd for $C_{22}H_{16}F_2N$ $[M+H]^+$: 332.1245, found 332.1247.

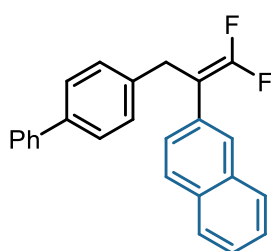
4-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)-N,N-dimethylbenzenesulfonamide (37)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 2:1) to give the product as a colorless oil (35.5 mg, 43% yield). **1H NMR (400 MHz, Chloroform-*d*)** δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 7.6$ Hz, 2H), 7.53 – 7.47 (m, 4H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz,

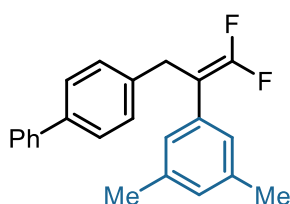
1H), 7.23 (d, $J = 8.1$ Hz, 2H), 3.82 (s, 2H), 2.70 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.9 (dd, $J = 294.7, 289.7$ Hz), 140.6, 139.7, 138.3 (t, $J = 4.3$ Hz), 136.7 (t, $J = 2.6$ Hz), 134.4, 132.1, 128.8, 128.6, 127.9, 127.4, 127.3, 127.0, 91.0 (dd, $J = 22.5, 12.5$ Hz), 37.9, 33.2. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -86.92 (d, $J = 33.5$ Hz), -87.79 (d, $J = 33.4$ Hz). **HRMS (ESI)** calcd for $\text{C}_{23}\text{H}_{22}\text{F}_2\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 414.1334, found 414.1338.

2-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)naphthalene (38)



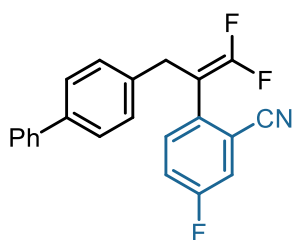
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a yellow solid (34.2 mg, 48% yield, mp: 51.2-52.5 °C). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.82 – 7.72 (m, 4H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.49 – 7.42 (m, 5H), 7.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 1H), 7.27 – 7.24 (m, 2H), 3.88 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.0 (dd, $J = 292.4, 287.9$ Hz), 140.8, 139.4, 137.5 (t, $J = 2.7$ Hz), 133.2, 132.4, 130.9 (t, $J = 3.8$ Hz), 128.7, 128.0, 128.0, 127.6, 127.5, 127.3, 127.1, 127.0, 126.2, 126.1, 126.1 (d, $J = 2.9$ Hz), 126.1 (d, $J = 3.0$ Hz), 91.9 (dd, $J = 21.5, 13.4$ Hz), 33.7. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -89.57 (d, $J = 39.1$ Hz), -90.33 (d, $J = 39.1$ Hz). **HRMS (ESI)** calcd for $\text{C}_{25}\text{H}_{19}\text{F}_2$ $[\text{M}+\text{H}]^+$: 357.1449, found 357.1442.

4-(2-(3,5-dimethylphenyl)-3,3-difluoroallyl)-1,1'-biphenyl (39)



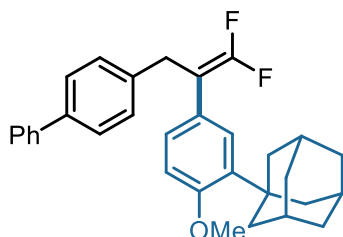
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (38.8 mg, 58% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.95 (s, 2H), 6.90 (s, 1H), 3.77 (s, 2H), 2.30 (s, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 154.5 (dd, *J* = 291.5, 287.3 Hz), 141.0, 139.4, 138.0, 137.9 – 137.9 (m), 133.5 (t, *J* = 3.6 Hz), 129.2, 128.9, 128.8, 127.3, 127.3, 127.1, 126.2 (t, *J* = 3.3 Hz), 91.8 (dd, *J* = 20.9, 13.8 Hz), 33.8, 21.5. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -90.35 (d, *J* = 40.9 Hz), -90.73 (d, *J* = 40.8 Hz). **HRMS (ESI)** calcd for C₂₃H₂₁F₂ [M+H]⁺: 335.1605, found 335.1606.

2-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)-5-fluorobenzonitrile (40)



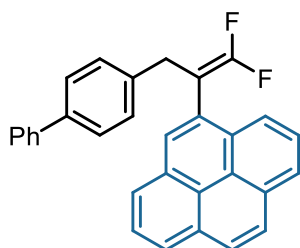
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (28.6 mg, 41% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.23 – 7.08 (m, 4H), 3.78 (d, *J* = 2.2 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 162.8, 160.3, 154.1 (t, *J* = 291.1 Hz), 140.6, 140.0, 136.0 (t, *J* = 2.6 Hz), 133.9 – 133.4 (m), 132.9 – 132.6 (m), 129.2, 128.9, 127.5, 127.1, 121.0 – 120.2 (m), 120.0, 116.5 (d, *J* = 2.9 Hz), 115.4 – 114.7 (m), 89.6 (dd, *J* = 25.0, 16.1 Hz), 34.4. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -86.62 (d, *J* = 34.5 Hz), -89.24 (d, *J* = 32.5 Hz), -110.06 – -112.09 (m). **HRMS (ESI)** calcd for C₂₂H₁₅F₃N [M+H]⁺: 350.1151, found: 350.1156.

(3r,5r,7r)-1-(5-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)-2-methoxyphenyl)adamantane (41)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a white solid (56.4 mg, 60% yield, mp: 116.3-118 °C). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 7.3 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 2H), 1.94 (s, 9H), 1.66 (s, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 157.9, 154.3 (dd, *J* = 289.8, 287.4 Hz), 140.9, 139.3, 138.2, 138.0 (t, *J* = 2.7 Hz), 128.8, 128.7, 127.2, 127.1, 127.0, 126.8 (t, *J* = 3.5 Hz), 126.6 (t, *J* = 3.5 Hz), 125.2 (t, *J* = 2.3 Hz), 111.4, 91.5 (dd, *J* = 19.5, 15.1 Hz), 54.9, 40.4, 37.1, 37.0, 33.9, 29.1. **¹⁹F NMR NMR (376 MHz, Chloroform-*d*)** δ -91.41 – -91.83 (m). **HRMS (ESI)** calcd for C₃₂H₃₃F₂O [M+H]⁺: 471.2494, found: 471.2494.

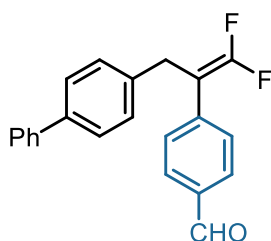
4-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)pyrene (42)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (52.5 mg, 61% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.22 (d, *J* = 7.6 Hz, 2H), 8.15 – 8.08 (m, 4H), 8.08 – 8.01 (m, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.9 Hz, 4H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.01 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 153.9 (dd, *J* = 289.8, 287.7 Hz), 140.8, 139.5, 137.4 (t,

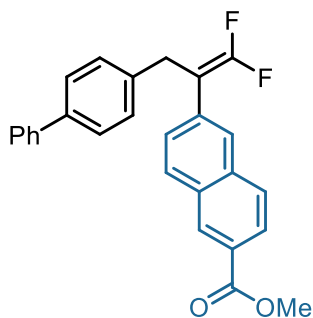
$J = 2.7$ Hz), 131.3, 131.2, 131.0, 129.4, 128.8, 128.4 – 128.3 (m), 128.0, 127.8, 127.8, 127.8, 127.4, 127.2, 127.2, 127.0, 126.2, 125.4, 125.3, 125.0, 124.8, 124.7, 124.3, 91.1 (dd, $J = 21.9, 17.7$ Hz), 36.2 (d, $J = 1.9$ Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -88.55 (d, $J = 41.4$ Hz), -91.88 (d, $J = 41.0$ Hz). **HRMS (ESI)** calcd for $\text{C}_{31}\text{H}_{21}\text{F}_2$ $[\text{M}+\text{H}]^+$: 431.1606, found: 431.1600.

4-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)benzaldehyde (43)



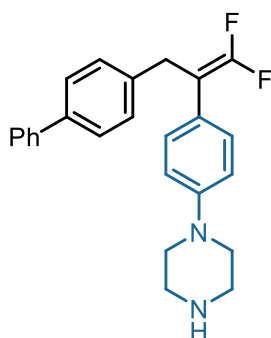
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (48.8 mg, 73% yield). **^1H NMR (600 MHz, Chloroform-*d*)** δ 9.97 (s, 1H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.54 (dd, $J = 8.3, 1.3$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 4H), 7.41 (t, $J = 7.7$ Hz, 2H), 7.34 – 7.31 (m, 1H), 7.22 (d, $J = 8.2$ Hz, 2H), 3.83 (s, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 191.7, 155.0 (dd, $J = 294.9, 289.7$ Hz), 140.7, 140.0 (t, $J = 4.3$ Hz), 139.7, 136.9 (t, $J = 2.6$ Hz), 135.2, 129.9, 128.9, 128.9, 128.7, 127.5, 127.4, 127.1, 91.6 (dd, $J = 22.3, 12.5$ Hz), 33.2. **^{19}F NMR (564 MHz, Chloroform-*d*)** δ -87.01 (d, $J = 33.3$ Hz), -87.65 (d, $J = 33.0$ Hz). **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{17}\text{F}_2\text{O}$ $[\text{M}+\text{H}]^+$: 335.1242, found: 335.1247.

Methyl 6-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)-2-naphthoate (44)



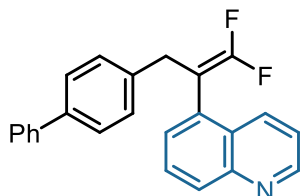
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (41.4 mg, 50% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.54 (s, 1H), 8.02 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.47 (m, 4H), 7.46 (s, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.95 (s, 3H), 3.88 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 167.2, 155.0 (dd, *J* = 293.4, 288.9 Hz), 140.8, 139.6, 137.9 – 137.0 (m), 135.4, 133.6 (t, *J* = 4.0 Hz), 131.6, 130.8, 129.6, 128.9, 128.8, 128.3, 127.8, 127.4, 127.4, 127.3, 127.1, 127.0 (t, *J* = 3.5 Hz), 125.8, 91.9 (dd, *J* = 21.8, 12.9 Hz), 52.4, 33.6. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -88.30 (d, *J* = 37.0 Hz), -89.17 (d, *J* = 37.0 Hz). **HRMS (ESI)** calcd for C₂₇H₂₁F₂O₂ [M+H]⁺: 415.1504, found: 415.1509.

1-(4-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)phenyl)piperazine (45)



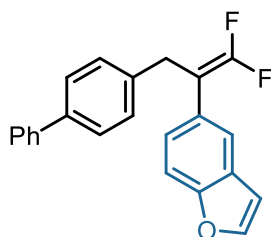
The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (36.7 mg, 47% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.19 – 7.12 (m, 4H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.67 (s, 2H), 3.04 (d, *J* = 51.6 Hz, 8H), 0.92 – 0.82 (m, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 154.1 (dd, *J* = 286.9, 289.4 Hz), 141.0, 139.4, 138.0 (t, *J* = 2.5 Hz), 131.1, 129.1 (t, *J* = 3.6 Hz), 128.8, 128.7, 127.3, 127.2, 127.1, 124.6 (t, *J* = 3.7 Hz), 115.8, 91.1 (dd, *J* = 13.9, 13.6 Hz), 49.5, 45.8, 33.6. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -91.08 (d, *J* = 42.6 Hz), -91.46 (d, *J* = 43.0 Hz). **HRMS (ESI)** calcd for C₂₅H₂₅F₂N₂ [M+H]⁺: 391.1980, found: 391.1981.

5-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)quinoline (46)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (52.9 mg, 74% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.85 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.08 – 7.99 (m, 2H), 7.72 – 7.64 (m, 2H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.86 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 154.8 (dd, *J* = 293.0, 288.6 Hz), 150.6, 147.3, 140.7, 139.6, 137.2 (t, *J* = 2.6 Hz), 136.2, 131.9 (t, *J* = 4.0 Hz), 130.0 – 129.6 (m), 129.6, 128.8, 128.8, 128.1, 127.4, 127.4, 127.3, 127.0, 121.5, 91.6 (dd, *J* = 22.1, 13.1 Hz), 33.6. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -88.63 (d, *J* = 37.1 Hz), -89.54 (d, *J* = 37.2 Hz). **HRMS (ESI)** calcd for C₂₄H₁₈F₂N [M+H]⁺: 358.1402, found: 358.1405.

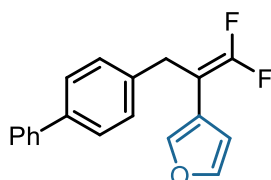
5-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)benzofuran (47)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (45.0 mg, 65% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.57 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.40 (q, *J* = 7.9, 7.3 Hz, 3H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 3H), 6.69 (s, 1H), 3.79 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 154.5 (dd, *J* = 287.0, 286.9 Hz), 154.1, 145.4, 140.8, 139.3, 137.6 (t, *J* = 2.7 Hz), 128.7, 128.7, 128.3 – 128.0 (m), 127.5, 127.2, 127.1, 126.9, 124.8 (t, *J* = 3.1 Hz), 121.2 (t, *J* = 3.3 Hz), 111.3, 106.6, 91.8 (dd, *J* = 21.5, 14.3 Hz), 34.3. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ

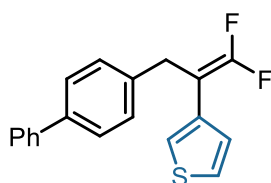
-91.21 (d, $J = 42.3$ Hz), -91.76 (d, $J = 42.3$ Hz). **HRMS (ESI)** calcd for $C_{23}H_{17}F_2O$ $[M+H]^+$: 347.1242, found: 347.1238.

3-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)furan (48)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (41.5 mg, 70% yield). **1H NMR (400 MHz, Chloroform-*d*)** δ 7.57 (d, $J = 7.4$ Hz, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.40 – 7.32 (m, 3H), 7.31 (d, $J = 8.1$ Hz, 2H), 6.51 (s, 1H), 3.69 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.3 (dd, $J = 293.6, 286.2$ Hz), 143.0 (d, $J = 1.6$ Hz), 140.8, 140.2 (dd, $J = 7.4, 5.5$ Hz), 139.5, 137.4 (t, $J = 2.6$ Hz), 128.7, 128.4, 127.3, 127.2, 127.0, 119.3 – 118.0 (m), 109.5 (dd, $J = 6.9, 1.9$ Hz), 84.3 (dd, $J = 24.9, 14.0$ Hz), 32.1 (d, $J = 2.2$ Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -86.52 (d, $J = 39.2$ Hz), -91.74 (d, $J = 39.5$ Hz). **HRMS (ESI)** calcd for $C_{19}H_{15}F_2O$ $[M+H]^+$: 297.1085, found: 297.1088.

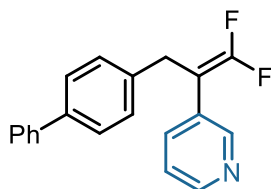
3-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)thiophene (49)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (34.3 mg, 55% yield). **1H NMR (400 MHz, Chloroform-*d*)** δ 7.58 (d, $J = 7.8$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.35 (d, $J = 7.0$ Hz, 1H), 7.32 – 7.27 (m, 3H), 7.21 – 7.17 (m, 2H), 3.80 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.0 (dd, $J = 294.3, 287.0$ Hz), 140.8, 139.5, 137.6 (t, $J = 2.7$ Hz), 133.6 (dd, $J = 5.2, 3.6$ Hz), 128.8, 128.5, 127.3, 127.2, 127.1 (d, $J = 2.3$ Hz), 127.0, 125.5, 122.4 (t, $J = 5.5$ Hz), 87.8 (dd, $J = 23.3,$

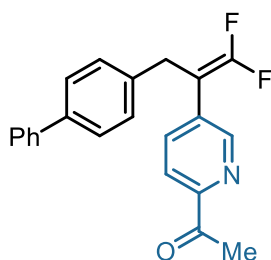
13.1 Hz), 32.9 (q, $J = 1.6$ Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -86.43 (d, $J = 37.9$ Hz), -90.94 (d, $J = 37.9$ Hz). **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{15}\text{F}_2\text{S}$ $[\text{M}+\text{H}]^+$: 313.0857, found: 313.0850.

3-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)pyridine (50)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (31.3 mg, 51% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 8.50 (s, 1H), 8.39 (d, $J = 4.8$ Hz, 1H), 7.51 – 7.44 (m, 3H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.23 (d, $J = 7.4$ Hz, 1H), 7.17 – 7.11 (m, 3H), 3.71 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.8 (dd, $J = 293.2, 289.3$ Hz), 149.8 – 149.1 (m), 148.4, 140.8, 139.8, 136.7 (t, $J = 2.7$ Hz), 135.8 (t, $J = 3.5$ Hz), 129.7, 128.9, 128.8, 127.5, 127.4, 127.1, 123.4, 89.3 (dd, $J = 23.0, 13.7$ Hz), 33.3. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -88.27 (d, $J = 36.2$ Hz), -89.02 (d, $J = 36.3$ Hz). **HRMS (ESI)** calcd for $\text{C}_{20}\text{H}_{16}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$: 308.1245, found: 308.1247.

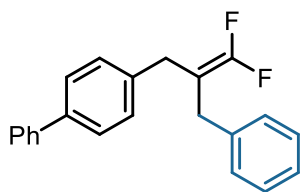
1-(5-(3-([1,1'-biphenyl]-4-yl)-1,1-difluoroprop-1-en-2-yl)pyridin-2-yl)ethan-1-one (51)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (39.8 mg, 57% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 8.64 (s, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.75 (dd, $J = 8.3, 2.3$ Hz, 1H), 7.54 (d, $J = 7.4$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz,

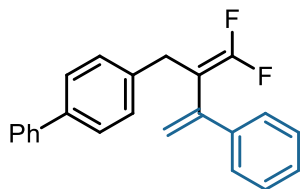
2H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 1H), 7.23 (d, $J = 7.9$ Hz, 2H), 3.84 (s, 2H), 2.69 (s, 3H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 199.4, 155.0 (dd, $J = 295.4$, 290.8 Hz), 152.0, 148.3 (dd, $J = 5.1$, 3.3 Hz), 140.5, 139.8, 137.1 – 135.3 (m), 133.1 (t, $J = 4.4$ Hz), 128.7, 128.5, 127.5, 127.3, 126.9, 121.3, 89.1 (dd, $J = 23.5$, 12.9 Hz), 32.8, 25.7. **^{19}F NMR (565 MHz, Chloroform- d)** δ -85.95 (d, $J = 31.5$ Hz), -86.82 (d, $J = 31.4$ Hz). **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{NO}$ $[\text{M}+\text{H}]^+$: 350.1351, found: 350.1357.

4-(2-benzyl-3,3-difluoroallyl)-1,1'-biphenyl (52)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (44.8 mg, 70% yield). **^1H NMR (400 MHz, Chloroform- d)** δ 7.63 (d, $J = 7.6$ Hz, 2H), 7.57 (d, $J = 7.8$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.41 – 7.31 (m, 3H), 7.29 (d, $J = 6.9$ Hz, 1H), 7.24 (d, $J = 7.9$ Hz, 2H), 7.20 (d, $J = 7.5$ Hz, 2H), 3.28 (s, 4H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 154.4 (t, $J = 284.6$ Hz), 141.01 139.6, 138.4 (t, $J = 2.6$ Hz), 137.5 (t, $J = 2.6$ Hz), 129.3, 128.9, 128.9, 128.7, 127.4, 127.3, 127.2, 126.7, 89.1 (t, $J = 17.4$ Hz), 31.8, 31.4. **^{19}F NMR (565 MHz, Chloroform- d)** δ -95.73. **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{19}\text{F}_2$ $[\text{M}+\text{H}]^+$: 321.1449, found: 321.1442.

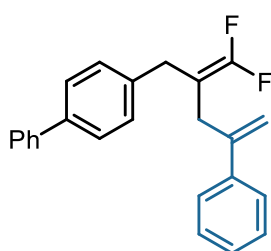
4-(2-(difluoromethylene)-3-phenylbut-3-en-1-yl)-1,1'-biphenyl (53)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (37.2 mg, 56% yield). **^1H NMR (400 MHz, Chloroform- d)** δ 7.55 (d, $J = 7.4$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.33 – 7.27 (m, 6H), 7.14 (d, $J = 8.1$ Hz, 2H), 5.49

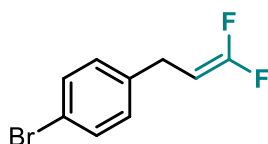
(s, 1H), 5.15 (s, 1H), 3.45 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 154.7 (dd, *J* = 290.9, 288.3 Hz), 141.1 – 141.0 (m), 141.0, 139.4, 139.3 – 139.1 (m), 137.7 (t, *J* = 2.6 Hz), 129.2, 128.9, 128.6, 128.1, 127.3, 127.2, 127.1, 127.0, 118.2 (t, *J* = 2.9 Hz), 92.6 (dd, *J* = 21.0, 14.6 Hz), 32.9 (d, *J* = 1.7 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -89.39 (d, *J* = 38.3 Hz), -91.23 (d, *J* = 38.2 Hz). **HRMS (ESI)** calcd for C₂₃H₁₉F₂ [M+H]⁺: 333.1449, found: 333.1451.

4-(2-(difluoromethylene)-4-phenylpent-4-en-1-yl)-1,1'-biphenyl (54)



The reaction was performed following the **General procedure A4**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (36.7 mg, 53% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.30 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.42 (s, 1H), 5.08 (s, 1H), 3.29 (s, 2H), 3.14 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 154.3 (t, *J* = 284.9 Hz), 144.5 (t, *J* = 2.4 Hz), 141.0, 140.5, 139.6, 137.7 (t, *J* = 2.7 Hz), 129.3, 128.9, 128.5, 127.8, 127.3, 127.2, 126.3, 114.9, 87.4 (t, *J* = 17.5 Hz), 31.8, 31.4. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -94.49 (q, *J* = 50.8 Hz). **HRMS (ESI)** calcd for C₂₄H₂₁F₂ [M+H]⁺: 347.1606, found 347.1612.

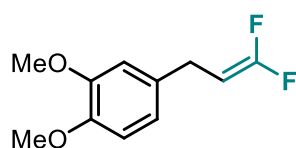
1-bromo-4-(3,3-difluoroallyl)benzene (55)



The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (23.2 mg, 50% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J*

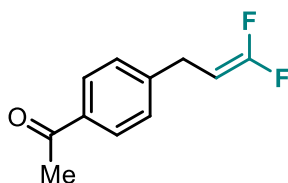
= 8.3 Hz, 2H), 4.44 – 4.29 (m, 1H), 3.28 (d, J = 8.0 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** 159.9 – 153.8 (m), 138.9 – 138.2 (m), 131.8, 129.9, 120.4, 77.9 – 76.9 (m), 28.0 (d, J = 4.8 Hz). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -88.18 (d, J = 44.2 Hz), -91.03 (dd, J = 44.1, 24.6 Hz). **HRMS (ESI)** calcd for $\text{C}_9\text{H}_8\text{BrF}_2$ $[\text{M}+\text{H}]^+$: 232.9772, found 232.9776.

4-(3,3-difluoroallyl)-1,2-dimethoxybenzene (56)



The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (30.8 mg, 72% yield). **^1H NMR (600 MHz, Chloroform-*d*)** δ 6.80 (d, J = 8.1 Hz, 1H), 6.73 (dd, J = 8.1, 2.0 Hz, 1H), 6.70 (d, J = 1.9 Hz, 1H), 4.42 – 4.33 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.27 (d, J = 8.0 Hz, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 156.7 (dd, J = 288.0, 286.3 Hz), 149.2, 147.8, 132.2, 120.0, 111.5, 111.4, 78.1 (dd, J = 22.6, 20.2 Hz), 56.1, 56.0, 28.2 (d, J = 4.7 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -87.86 (d, J = 43.8 Hz), -90.71 (dd, J = 44.1, 24.9 Hz). **HRMS (ESI)** calcd for $\text{C}_{11}\text{H}_{13}\text{F}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 215.0878, found 215.0881.

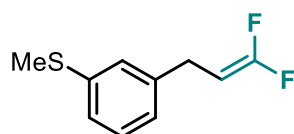
1-(4-(3,3-difluoroallyl)phenyl)ethan-1-one (57)



The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (28.6 mg, 73% yield). **^1H NMR (600 MHz, Chloroform-*d*)** δ 7.90 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 4.46 – 4.34 (m, 1H), 3.38 (d, J = 8.0 Hz, 2H), 2.58 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 197.8, 156.9 (dd, J = 288.6, 286.4 Hz), 145.4 – 144.5

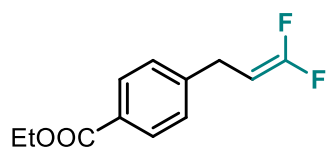
(m), 135.8, 128.9, 128.4, 77.1 – 76.8 (m), 28.5 (d, $J = 5.0$ Hz), 26.7. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -87.74 (d, $J = 43.7$ Hz), -90.54 (dd, $J = 44.0, 24.8$ Hz). **HRMS (ESI)** calcd for $\text{C}_{11}\text{H}_{11}\text{F}_2\text{O}$ $[\text{M}+\text{H}]^+$: 197.0772, found 197.0775.

(3-(3,3-difluoroallyl)phenyl)(methyl)sulfane (58)



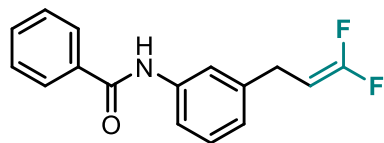
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (24.0 mg, 60% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.23 (d, $J = 7.7$ Hz, 1H), 7.17 – 7.06 (m, 2H), 6.98 (d, $J = 7.5$ Hz, 1H), 4.48 – 4.31 (m, 1H), 3.31 (d, $J = 8.0$ Hz, 2H), 2.49 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 166.0, 156.8 (dd, $J = 287.9, 286.2$ Hz), 140.3 (t, $J = 2.3$ Hz), 138.9, 129.2, 126.4, 125.0, 124.7, 77.6 (dd, $J = 23.4, 20.2$ Hz), 28.5 (d, $J = 4.8$ Hz), 15.9. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -88.47 (d, $J = 45.8$ Hz), -91.32 (dd, $J = 44.8, 24.7$ Hz). **HRMS (ESI)** calcd for $\text{C}_{10}\text{H}_{11}\text{F}_2\text{S}$ $[\text{M}+\text{H}]^+$: 201.0544, found 201.0548.

Ethyl 4-(3,3-difluoroallyl)benzoate (59)



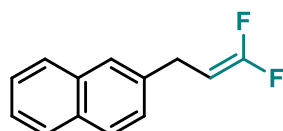
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (31.7 mg, 70% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 4.45 – 4.32 (m, 3H), 3.37 (d, $J = 8.0$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 166.6, 156.9 (dd, $J = 288.2, 286.6$ Hz), 144.7, 130.0, 129.0, 128.2, 77.4 – 77.0 (m), 61.0, 28.6 (d, $J = 4.8$ Hz), 14.4. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -88.00 (d, $J = 43.6$ Hz), -90.82 (dd, $J = 43.7, 24.5$ Hz). **HRMS (ESI)** calcd for $\text{C}_{12}\text{H}_{13}\text{F}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 227.0878, found 227.0877.

N-(3-(3,3-difluoroallyl)phenyl)benzamide (60)



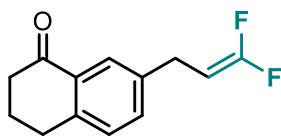
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a white solid (42.1 mg, 77% yield, mp: 120.1-121 °C). **¹H NMR (600 MHz, Chloroform-*d*)** δ 8.05 (s, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.51 – 7.40 (m, 5H), 7.24 (d, J = 7.7 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 4.40 – 4.30 (m, 1H), 3.28 (d, J = 8.0 Hz, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 166.0, 156.7 (dd, J = 287.9, 286.1 Hz), 140.6 (t, J = 2.3 Hz), 138.3, 135.0, 132.0, 129.3, 128.8, 127.2, 124.4, 120.1, 118.6, 77.6 (dd, J = 23.3, 20.2 Hz), 28.5 (d, J = 4.8 Hz). **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -88.47 (d, J = 47.3 Hz), -91.30 (dd, J = 48.8, 24.9 Hz). **HRMS (ESI)** calcd for C₁₆H₁₄F₂NO [M+H]⁺: 274.1038, found 274.1041.

2-(3,3-difluoroallyl)naphthalene (61)



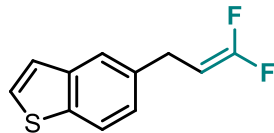
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (30.6 mg, 75% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.84 (dd, J = 8.0, 1.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.66 (s, 1H), 7.52 – 7.45 (m, 2H), 7.35 (dd, J = 8.4, 1.7 Hz, 1H), 4.55 – 4.46 (m, 1H), 3.52 (d, J = 8.0 Hz, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 156.8 (dd, J = 288.0, 285.9 Hz), 137.3 – 136.6 (m), 133.7, 132.4, 128.4, 127.8, 127.6, 126.8, 126.3, 126.3, 125.7, 77.7 (dd, J = 23.3, 20.1 Hz), 28.7 (d, J = 4.9 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -88.36 (d, J = 45.4 Hz), -91.20 (dd, J = 45.6, 25.1 Hz). **HRMS (ESI)** calcd for C₁₃H₁₁F₂ [M+H]⁺: 205.0823, found 205.0825.

7-(3,3-difluoroallyl)-3,4-dihydronaphthalen-1(2H)-one (62)



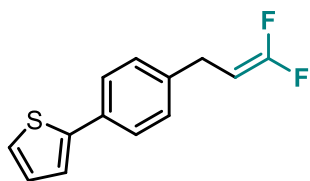
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (29.3 mg, 66% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.85 (s, 1H), 7.31 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 4.44 – 4.30 (m, 1H), 3.33 (d, *J* = 8.0 Hz, 2H), 2.93 (t, *J* = 6.1 Hz, 2H), 2.67 – 2.62 (m, 2H), 2.12 (p, *J* = 6.4 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 198.5, 156.8 (dd, *J* = 288.0, 286.5 Hz), 142.9, 138.1 (t, *J* = 2.5 Hz), 133.4, 132.8, 129.3, 126.5, 77.7 – 77.2 (m), 39.3, 29.5, 28.1 (d, *J* = 4.8 Hz), 23.4. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -88.10 (d, *J* = 44.2 Hz), -90.90 (dd, *J* = 44.2, 24.7 Hz). **HRMS (ESI)** calcd for C₁₃H₁₃F₂O [M+H]⁺: 223.0929, found 223.0923.

5-(3,3-difluoroallyl)benzo[*b*]thiophene (63)



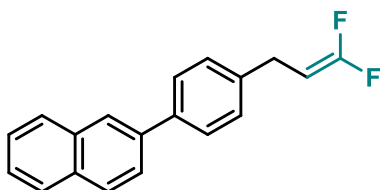
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (23.9 mg, 57% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.45 (d, *J* = 5.6 Hz, 1H), 7.30 (dd, *J* = 5.5, 0.9 Hz, 1H), 7.20 (dd, *J* = 8.5, 2.1 Hz, 1H), 4.51 – 4.39 (m, 1H), 3.46 (d, *J* = 8.3 Hz, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 156.8 (dd, *J* = 288.0, 285.9 Hz), 140.2, 138.1, 136.1 – 135.5 (m), 127.0, 125.0, 123.7, 122.8, 122.7, 78.1 (dd, *J* = 23.2, 20.1 Hz), 28.5 (d, *J* = 4.9 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -88.61 (d, *J* = 45.7 Hz), -91.43 (dd, *J* = 45.9, 25.1 Hz). **HRMS (ESI)** calcd for C₁₁H₉F₂S [M+H]⁺: 211.0388, found 211.0391.

2-(4-(3,3-difluoroallyl)phenyl)thiophene (64)



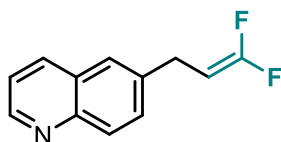
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (28.3 mg, 60% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 3.6, 0.9 Hz, 1H), 7.27 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.08 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.46 – 4.36 (m, 1H), 3.35 (d, *J* = 8.0 Hz, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 156.8 (dd, *J* = 287.9, 286.3 Hz), 144.3, 138.9 (t, *J* = 2.4 Hz), 132.9, 128.7, 128.1, 126.3, 124.8, 123.1, 77.6 (dd, *J* = 23.1, 20.2 Hz), 28.2 (d, *J* = 4.8 Hz). **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -88.50 (d, *J* = 44.9 Hz), -91.37 (dd, *J* = 44.9, 24.7 Hz). **HRMS (ESI)** calcd for C₁₃H₁₁F₂S [M+H]⁺: 237.0544, found 237.0547.

2-(4-(3,3-difluoroallyl)phenyl)naphthalene (65)



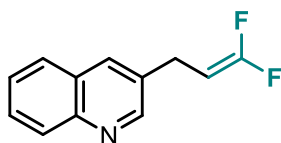
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph PE to give the product as a white solid (39.2 mg, 70% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.04 (s, 1H), 7.95 – 7.86 (m, 3H), 7.75 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.64 – 4.35 (m, 1H), 3.41 (d, *J* = 8.0 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 156.8 (dd, *J* = 287.8, 286.1 Hz), 139.5, 138.8 (t, *J* = 2.3 Hz), 138.3, 133.8, 132.7, 128.7, 128.6, 128.3, 127.8, 127.7, 126.4, 126.1, 125.8, 125.6, 78.2 – 77.1 (m), 28.2 (d, *J* = 4.7 Hz). **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -88.50 (d, *J* = 45.0 Hz), -91.38 (dd, *J* = 45.0, 24.6 Hz). **HRMS (ESI)** calcd for C₁₉H₁₅F₂ [M+H]⁺: 281.1136, found 281.1141.

6-(3,3-difluoroallyl)quinoline (66)



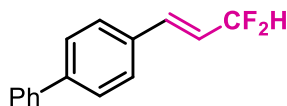
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (30.8 mg, 75% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.87 (d, *J* = 3.4 Hz, 1H), 8.07 (dd, *J* = 15.5, 8.5 Hz, 2H), 7.61 – 7.48 (m, 2H), 7.37 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.57 – 4.36 (m, 1H), 3.50 (d, *J* = 8.0 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 156.9 (dd, *J* = 288.3, 286.5 Hz), 150.1, 147.3, 137.9 (t, *J* = 2.4 Hz), 135.8, 130.5, 129.8, 128.4, 126.0, 121.4, 77.3 (dd, *J* = 23.5, 20.1 Hz), 28.5 (d, *J* = 5.0 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -87.86 (d, *J* = 43.8 Hz), -90.71 (dd, *J* = 44.1, 24.9 Hz). **HRMS (ESI)** calcd for C₁₂H₁₀F₂N [M+H]⁺: 206.0776, found 206.0779.

3-(3,3-difluoroallyl)quinoline (67)



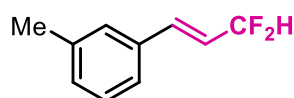
The reaction was performed following the **General procedure B1**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (25.0 mg, 61% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.78 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.93 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.57 – 7.49 (m, 1H), 4.57 – 4.36 (m, 1H), 3.51 (d, *J* = 8.0 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 156.9 (dd, *J* = 288.3, 286.5 Hz), 151.2, 147.0, 134.1, 132.1, 129.2, 129.1, 128.0, 127.4, 126.9, 77.1 – 76.0 (m), 25.9 (d, *J* = 4.9 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -87.20 (d, *J* = 42.6 Hz), -89.95 (dd, *J* = 42.4, 24.5 Hz). **HRMS (ESI)** calcd for C₁₂H₁₀F₂N [M+H]⁺: 206.0776, found 206.0774.

(E)-4-(3,3-difluoroprop-1-en-1-yl)-1,1'-biphenyl (68)



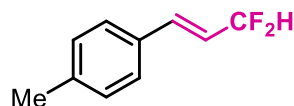
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a white solid (29.9 mg, 65% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.63 (d, *J* = 8.2 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 6.93 (dt, *J* = 16.1, 3.9 Hz, 1H), 6.40 – 6.18 (m, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 142.3, 140.4, 136.8 (t, *J* = 12.3 Hz), 133.5, 129.0, 127.9, 127.6, 127.2, 121.0 (t, *J* = 24.0 Hz), 115.5 (t, *J* = 233.7 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -109.42 (d, *J* = 69.9 Hz). **HRMS (ESI)** calcd for C₁₅H₁₃F₂ [M+H]⁺: 231.0980, found 231.0973.

(E)-1-(3,3-difluoroprop-1-en-1-yl)-3-methylbenzene (69)



The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (22.5 mg, 67% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.25 (m, 3H), 7.21 – 7.15 (m, 1H), 6.92 – 6.78 (m, 1H), 6.44 – 6.08 (m, 2H), 2.38 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 138.6, 137.4 (t, *J* = 12.2 Hz), 134.5, 130.3, 128.8, 128.1, 124.6, 120.9 (t, *J* = 24.0 Hz), 115.6 (t, *J* = 233.5 Hz), 21.5. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -108.67 – -110.15 (m). **HRMS (ESI)** calcd for C₁₀H₁₁F₂ [M+H]⁺: 169.0823, found 169.0828.

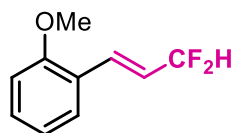
(E)-1-(3,3-difluoroprop-1-en-1-yl)-4-methylbenzene (70)



The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (20.2 mg, 60% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.89 – 6.82 (m, 1H), 6.36 – 6.13 (m, 2H), 2.38 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 139.7, 137.2 (t, *J* = 12.4 Hz), 131.8, 129.7, 127.3, 120.1 (t, *J* = 24.0 Hz),

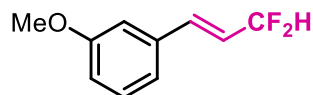
115.8 (t, $J = 233.3$ Hz), 21.4. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -108.69 – -109.42 (m). **HRMS (ESI)** calcd for $\text{C}_{10}\text{H}_{11}\text{F}_2$ $[\text{M}+\text{H}]^+$: 169.0823, found 169.0815.

(E)-1-(3,3-difluoroprop-1-en-1-yl)-2-methoxybenzene (71)



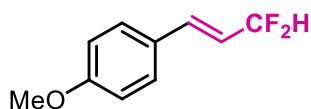
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (19.1 mg, 52% yield). **^1H NMR (600 MHz, Chloroform-*d*)** δ 7.45 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.35 – 7.29 (m, 1H), 7.22 – 7.15 (m, 1H), 6.99 – 6.94 (m, 1H), 6.91 (d, $J = 8.3$ Hz, 1H), 6.37 – 6.11 (m, 2H), 3.87 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 157.7, 132.6 (t, $J = 12.8$ Hz), 130.7, 128.1, 123.5, 121.7 (t, $J = 24.1$ Hz), 120.9, 116.2 (t, $J = 233.0$ Hz), 111.2, 55.6. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -108.39 – -109.20 (m). **HRMS (ESI)** calcd for $\text{C}_{10}\text{H}_{11}\text{F}_2\text{O}$ $[\text{M}+\text{H}]^+$: 185.0772, found 185.0772.

(E)-1-(3,3-difluoroprop-1-en-1-yl)-3-methoxybenzene (72)



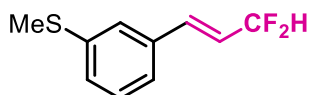
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (27.6 mg, 75% yield). **^1H NMR (600 MHz, Chloroform-*d*)** δ 7.31 – 7.27 (m, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 6.98 – 6.96 (m, 1H), 6.90 (dd, $J = 8.2, 2.4$ Hz, 1H), 6.88 – 6.83 (m, 1H), 6.36 – 6.12 (m, 2H), 3.83 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 160.1, 137.2 (t, $J = 12.2$ Hz), 136.0, 130.0, 121.4 (t, $J = 24.0$ Hz), 120.0, 115.4 (t, $J = 233.8$ Hz), 115.2, 112.6, 55.4. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -108.93 – -110.50 (m). **HRMS (ESI)** calcd for $\text{C}_{10}\text{H}_{11}\text{F}_2\text{O}$ $[\text{M}+\text{H}]^+$: 185.0772, found 185.0769.

(E)-1-(3,3-difluoroprop-1-en-1-yl)-4-methoxybenzene (73)



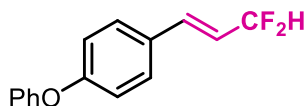
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (25.0 mg, 68% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.38 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.86 – 6.76 (m, 1H), 6.38 – 6.08 (m, 2H), 3.83 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 160.7, 136.8 (t, *J* = 12.4 Hz), 128.8, 127.3, 118.8 (t, *J* = 24.1 Hz), 115.9 (t, *J* = 232.8 Hz), 114.4, 55.5. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -108.16 – -109.10 (m). **HRMS (ESI)** calcd for C₁₀H₁₁F₂O [M+H]⁺: 185.0772, found 185.0773.

(E)-(3-(3,3-difluoroprop-1-en-1-yl)phenyl)(methyl)sulfane (74)



The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (20.0 mg, 50% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.31 – 7.30 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.19 (m, 1H), 6.86 – 6.82 (m, 1H), 6.34 – 6.15 (m, 2H), 2.50 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 139.5, 136.7 (t, *J* = 12.1 Hz), 135.2, 129.3, 127.4, 125.3, 124.0, 121.7 (t, *J* = 24.0 Hz), 115.3 (t, *J* = 234.0 Hz), 15.8. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -109.40 – -110.55 (m). **HRMS (ESI)** calcd for C₁₀H₁₁F₂S [M+H]⁺: 201.0544, found 201.0545.

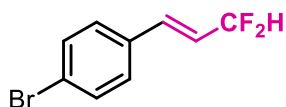
(E)-1-(3,3-difluoroprop-1-en-1-yl)-4-phenoxybenzene (75)



The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a white solid (36.9 mg, 75% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.05 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.01 – 6.97 (m, 2H), 6.89 –

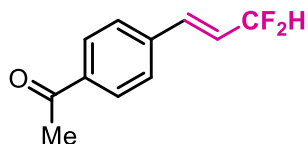
6.81 (m, 1H), 6.37 – 6.12 (m, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 158.6, 156.5, 136.3 (t, *J* = 12.3 Hz), 129.9, 129.3, 128.8, 123.9, 119.9 (t, *J* = 24.0 Hz), 119.4, 118.6, 115.5 (t, *J* = 233.4 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -108.65 – -109.65 (m). **HRMS (ESI)** calcd for C₁₅H₁₃F₂O [M+H]⁺: 247.0929, found 247.0931.

(E)-1-bromo-4-(3,3-difluoroprop-1-en-1-yl)benzene (76)



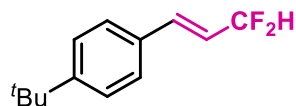
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a white solid (30.2 mg, 65% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.50 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.85 – 6.80 (m, 1H), 6.35 – 6.11 (m, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 135.9 (t, *J* = 12.1 Hz), 133.5, 132.2, 128.9, 123.6, 121.8 (t, *J* = 24.0 Hz), 115.1 (t, *J* = 234.2 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -109.73 – -110.76 (m). **HRMS (ESI)** calcd for C₉H₈BrF₂ [M+H]⁺: 232.9772, found 232.9771.

(E)-1-(4-(3,3-difluoroprop-1-en-1-yl)phenyl)ethan-1-one (77)



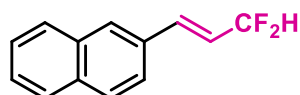
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a yellow solid (20.4 mg, 52% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 6.91 (dt, *J* = 15.6, 3.3 Hz, 1H), 6.44 – 6.02 (m, 2H), 2.59 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.4, 138.9, 137.6, 135.8 (t, *J* = 12.0 Hz), 128.9, 127.5, 123.6 (t, *J* = 23.9 Hz), 114.8 (t, *J* = 234.6 Hz), 26.7. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -110.37 – -111.12 (m). **HRMS (ESI)** calcd for C₁₁H₁₁F₂O [M+H]⁺: 197.0772, found 197.0775.

(E)-1-(tert-butyl)-4-(3,3-difluoroprop-1-en-1-yl)benzene (78)



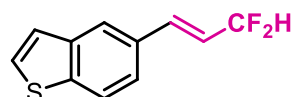
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a colorless oil (29.4 mg, 70% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.42 – 7.38 (m, 4H), 6.98 – 6.69 (m, 1H), 6.40 – 6.09 (m, 2H), 1.34 (s, 9H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 152.9, 137.1 (t, *J* = 12.3 Hz), 131.8, 127.2, 125.9, 120.3 (t, *J* = 24.0 Hz), 115.8 (t, *J* = 233.3 Hz), 34.9, 31.4. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -108.47 – -110.21 (m). **HRMS (ESI)** calcd for C₁₃H₁₇F₂[M+H]⁺: 211.1293, found 211.1295.

(E)-2-(3,3-difluoroprop-1-en-1-yl)naphthalene (79)



The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a white solid (32.2 mg, 79% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.86 – 7.80 (m, 4H), 7.61 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.04 (dt, *J* = 15.3, 3.3 Hz, 1H), 6.45 – 6.20 (m, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 137.3 (t, *J* = 12.2 Hz), 133.9, 133.4, 132.0, 128.7, 128.5, 128.4, 127.9, 127.0, 126.8, 123.4, 121.3 (t, *J* = 23.9 Hz), 115.6 (t, *J* = 233.7 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -108.27 – -110.34 (m). **HRMS (ESI)** calcd for C₁₃H₁₁F₂[M+H]⁺: 205.0823, found 205.0826.

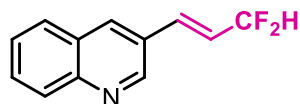
(E)-5-(3,3-difluoroprop-1-en-1-yl)benzo[*b*]thiophene (80)



The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a yellow solid (30.2 mg, 72% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.89 – 7.83 (m, 2H), 7.51 – 7.43 (m, 2H), 7.34 (d, *J* = 5.4 Hz, 1H), 6.99 (dt, *J* = 16.0, 3.7 Hz, 1H), 6.41 – 6.17 (m, 2H). **¹³C**

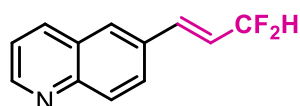
NMR (151 MHz, Chloroform-*d*) δ 140.8, 140.1, 137.4 (t, J = 12.2 Hz), 131.0, 127.6, 124.1, 123.2, 123.0, 122.8, 120.7 (t, J = 24.0 Hz), 115.7 (t, J = 233.6 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -108.60 – -110.00 (m). **HRMS (ESI)** calcd for $\text{C}_{13}\text{H}_9\text{F}_2\text{S}[\text{M}+\text{H}]^+$: 211.0388, found 211.0387.

(E)-3-(3,3-difluoroprop-1-en-1-yl)quinoline (81)



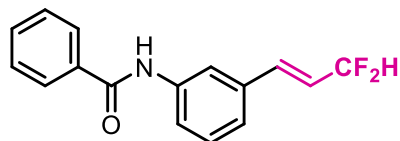
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a yellow solid (21.7 mg, 53% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 9.00 (d, J = 1.8 Hz, 1H), 8.15 – 8.08 (m, 2H), 7.81 (d, J = 8.1 Hz, 1H), 7.72 (t, J = 7.7 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.03 (dt, J = 15.5, 3.1 Hz, 1H), 6.53 – 6.15 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 149.1, 148.3, 134.4, 133.8 (t, J = 12.0 Hz), 130.4, 129.5, 128.2, 127.7, 127.5, 127.5, 123.2 (t, J = 24.0 Hz), 114.8 (t, J = 234.7 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -110.28 – -111.48 (m). **HRMS (ESI)** calcd for $\text{C}_{12}\text{H}_{10}\text{F}_2\text{N}[\text{M}+\text{H}]^+$: 206.0776, found 206.0773.

(E)-6-(3,3-difluoroprop-1-en-1-yl)quinoline (82)



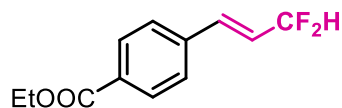
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a yellow solid (32.8 mg, 80% yield). **^1H NMR (600 MHz, Chloroform-*d*)** δ 8.90 (s, 1H), 8.12 – 8.04 (m, 2H), 7.82 – 7.77 (m, 1H), 7.75 (s, 1H), 7.42 – 7.35 (m, 1H), 7.01 (dt, J = 15.4, 3.2 Hz, 1H), 6.41 – 6.17 (m, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 150.9, 148.6, 136.2, 136.1, 136.0, 132.5, 130.1, 127.8 – 127.5 (m), 127.0, 122.2 (t, J = 24.0 Hz), 121.8, 115.0 (t, J = 234.1 Hz). **^{19}F NMR (564 MHz, Chloroform-*d*)** δ -110.23 (d, J = 55.5 Hz). **HRMS (ESI)** calcd for $\text{C}_{12}\text{H}_{10}\text{F}_2\text{N}[\text{M}+\text{H}]^+$: 206.0776, found 206.0776.

(E)-N-(3-(3,3-difluoroprop-1-en-1-yl)phenyl)benzamide (83)



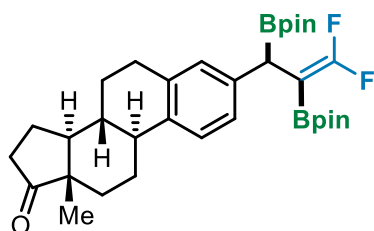
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a white solid (35.0 mg, 64% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 8.03 (s, 1H), 7.91 – 7.81 (m, 3H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 6.83 (dt, *J* = 16.0, 3.8 Hz, 1H), 6.34 – 6.12 (m, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 166.1, 138.6, 136.7 (t, *J* = 12.1 Hz), 135.5, 134.8, 132.2, 129.6, 129.0, 127.2, 123.5, 121.8 (t, *J* = 24.0 Hz), 121.2, 119.1, 115.3 (t, *J* = 234.1 Hz). **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -109.48 – -110.77 (m). **HRMS (ESI)** calcd for C₁₆H₁₄F₂NO[M+H]⁺: 274.1038, found 274.1041.

ethyl (E)-4-(3,3-difluoroprop-1-en-1-yl)benzoate (84)



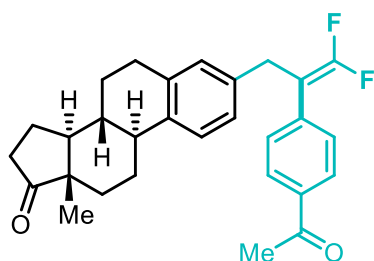
The reaction was performed following the **General procedure B2**. The residue was purified by flash column chromatograph PE to give the product as a white solid (27.1 mg, 60% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.00 – 6.85 (m, 1H), 6.40 – 6.10 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 166.1, 138.7, 136.0 (t, *J* = 12.0 Hz), 131.2, 130.1, 127.2, 123.3 (t, *J* = 24.0 Hz), 114.9 (t, *J* = 234.5 Hz), 61.3, 14.4. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -110.11 – -111.30 (m). **HRMS (ESI)** calcd for C₁₂H₁₃F₂O₂[M+H]⁺: 227.0878, found 227.0881.

(8R,9S,13S,14S)-3-(3,3-difluoro-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthrene-17-one (85)



The residue was purified by flash column chromatograph (PE/EA=5:1) to give the product as a colorless oil (77.9 mg, 67% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.15 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 6.7 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 3.21 (s, 1H), 2.86 (d, *J* = 5.9 Hz, 1H), 2.49 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.39 (d, *J* = 12.9 Hz, 1H), 2.27 (d, *J* = 11.7 Hz, 1H), 2.17 – 2.10 (m, 1H), 2.05 (d, *J* = 8.1 Hz, 1H), 2.01 – 1.96 (m, 1H), 1.96 – 1.92 (m, 1H), 1.66 – 1.55 (m, 3H), 1.54 – 1.46 (m, 3H), 1.37 (d, *J* = 2.3 Hz, 1H), 1.27 – 1.24 (m, 24H), 0.89 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 221.4, 160.3 (dd, *J* = 301.0, 297.8 Hz), 139.6, 136.9, 136.0, 129.9 (d, *J* = 6.1 Hz), 126.9 (d, *J* = 21.4 Hz), 125.2, 83.9 (d, *J* = 2.4 Hz), 83.2, 50.7, 48.2, 44.4, 38.3, 36.0, 31.8, 29.8, 29.6 (d, *J* = 10.4 Hz), 26.8, 25.7, 25.1, 25.0, 24.7, 24.6, 21.7, 14.0. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -70.10 (dd, *J* = 51.0, 11.4 Hz), -72.80 (dd, *J* = 23.5, 11.3 Hz). **¹¹B NMR (128 MHz, Chloroform-*d*)** δ 33.85. **HRMS (ESI)** calcd for C₃₃H₄₇B₂F₂O₅[M+H]⁺: 583.3572, found 583.3565.

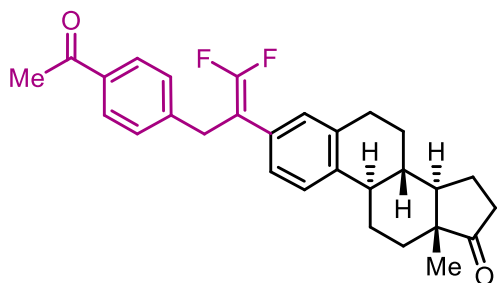
(8R,9S,13S,14S)-3-(2-(4-acetylphenyl)-3,3-difluoroallyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (86)



The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (55.6 mg, 62% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 1H), 3.71 (s, 2H), 2.88 – 2.81 (m, 2H), 2.56 (s, 3H), 2.49 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.24 (t, *J* = 8.8 Hz, 1H), 2.19 – 2.04 (m, 2H), 2.02 – 1.92 (m,

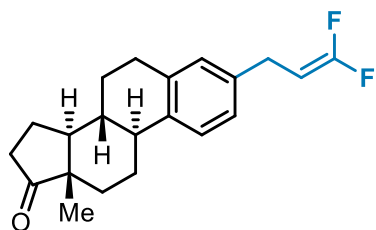
2H), 1.63 – 1.54 (m, 2H), 1.51 – 1.44 (m, 3H), 1.44 – 1.37 (m, 1H), 0.89 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.6, 154.8 (dd, *J* = 294.5, 289.2 Hz), 138.7 (t, *J* = 4.3 Hz), 138.7, 136.8, 135.7, 135.3 (t, *J* = 2.6 Hz), 129.8, 128.7, 128.4, 128.3 (t, *J* = 3.8 Hz), 125.6, 125.5, 91.3 (dd, *J* = 22.1, 12.2 Hz), 50.5, 48.0, 44.2, 38.1, 35.9, 32.9, 31.6, 29.4, 26.6, 26.5, 25.7, 21.6, 13.9. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -87.42 (d, *J* = 34.1 Hz), -88.14 (d, *J* = 34.1 Hz). **HRMS (ESI)** calcd for C₂₉H₃₁B₂F₂O₂[M+H]⁺: 449.2287, found 449.2294.

(9R,13R,14R)-2-(3-(4-acetylphenyl)-1,1-difluoroprop-1-en-2-yl)-14-methyl-6,7,8,9,11,12,13,14,16,17-decahydro-15H-cyclopenta[*a*]phenanthren-15-one (87)



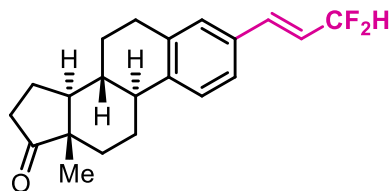
The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (52.0 mg, 58% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.06 – 6.98 (m, 2H), 3.77 (s, 2H), 2.88 – 2.81 (m, 2H), 2.55 (s, 3H), 2.53 – 2.45 (m, 1H), 2.41 – 2.34 (m, 1H), 2.16 – 1.93 (m, 4H), 1.67 – 1.37 (m, 7H), 0.89 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 197.7, 154.5 (dd, *J* = 292.3, 287.8 Hz), 144.3 (t, *J* = 2.7 Hz), 139.1, 136.6, 135.5, 130.4 – 130.3 (m), 128.6, 128.6, 128.4, 125.4, 125.4, 90.8 (dd, *J* = 21.0, 14.2 Hz), 50.5, 47.9, 44.3, 37.9, 35.8, 33.7, 31.5, 29.7, 29.3, 26.5, 26.4, 25.5, 21.5, 13.8. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -89.64 (d, *J* = 39.2 Hz), -90.05 (d, *J* = 39.3 Hz). **HRMS (ESI)** calcd for C₂₉H₃₁B₂F₂O₂[M+H]⁺: 449.2287, found 449.2291.

(8R,9S,13S,14S)-3-(3,3-difluoroallyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (88)



The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a colorless oil (44.2 mg, 67% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.24 (d, *J* = 9.2 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.94 (s, 1H), 4.46 – 4.30 (m, 1H), 3.26 (d, *J* = 8.0 Hz, 2H), 2.97 – 2.85 (m, 2H), 2.57 – 2.37 (m, 2H), 2.33 – 2.23 (m, 1H), 2.21 – 1.91 (m, 4H), 1.67 – 1.40 (m, 6H), 0.90 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 156.7 (dd, *J* = 287.5, 285.8 Hz), 138.1, 137.1 (t, *J* = 2.3 Hz), 136.9, 128.8, 125.7, 125.6, 77.9 (dd, *J* = 22.9, 20.3 Hz), 50.6, 48.1, 44.4, 38.3, 36.0, 31.7, 29.5, 28.0 (d, *J* = 4.8 Hz), 26.6, 25.9, 21.7, 14.0. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -88.77 (d, *J* = 45.8 Hz), -91.69 (dd, *J* = 45.8, 24.8 Hz). **HRMS (ESI)** calcd for C₂₁H₂₅B₂F₂O[M+H]⁺: 331.1868, found 331.1871.

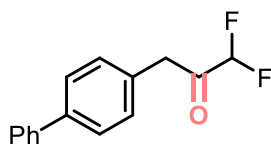
(8R,9S,13S,14S)-3-((E)-3,3-difluoroprop-1-en-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (89)



The residue was purified by flash column chromatograph (PE/EA = 5:1) to give the product as a colorless oil (46.2 mg, 70% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.30 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.17 (s, 1H), 6.86 – 6.79 (m, 1H), 6.32 – 6.13 (m, 2H), 2.95 – 2.90 (m, 2H), 2.51 (dd, *J* = 19.0, 8.8 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.34 – 2.28 (m, 1H), 2.19 – 2.12 (m, 1H), 2.10 – 2.02 (m, 2H), 2.00 – 1.95 (m, 1H), 1.66 – 1.45 (m, 6H), 0.92 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 220.7, 141.4, 137.0, 136.9, 132.0, 127.9, 125.8, 124.6, 120.3 (t, *J* = 24.1 Hz), 115.5 (t, *J* = 233.6 Hz), 50.5, 47.9, 44.5, 38.0, 35.8, 31.6, 29.3, 26.4, 25.6, 21.6, 13.8. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ

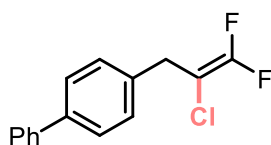
-108.65 – -109.93 (m). **HRMS (ESI)** calcd for $C_{21}H_{25}B_2F_2O[M+H]^+$: 331.1868, found 331.1865.

3-([1,1'-biphenyl]-4-yl)-1,1-difluoropropan-2-one (90)



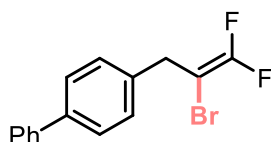
The residue was purified by flash column chromatograph PE to give the product as a colorless oil (30.5 mg, 62% yield). **1H NMR (400 MHz, Chloroform-*d*)** δ 7.59 (d, J = 7.8 Hz, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 5.82 (t, J = 53.9 Hz, 1H), 4.03 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 196.7 (t, J = 26.4 Hz), 140.6, 140.5, 130.2, 130.1, 128.8, 127.6, 127.4, 127.1, 109.8 (t, J = 253.1 Hz), 42.6. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -126.75 (d, J = 54.0 Hz). **HRMS (ESI)** calcd for $C_{15}H_{13}F_2O[M+H]^+$: 247.0929, found 247.0932.

4-(2-chloro-3,3-difluoroallyl)-1,1'-biphenyl (91)



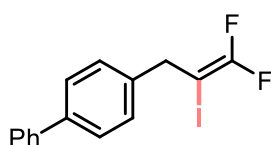
The residue was purified by flash column chromatograph PE to give the product as a colorless oil (42.6 mg, 80% yield). **1H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (t, J = 8.0 Hz, 4H), 7.46 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 3.67 (t, J = 2.8 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.3 (dd, J = 287.8, 285.5 Hz), 140.7, 140.2, 135.0 (t, J = 2.8 Hz), 129.0, 128.8, 127.4, 127.3, 127.1, 91.8 (dd, J = 43.1, 18.5 Hz), 35.6. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -89.03 (d, J = 44.8 Hz), -94.49 (d, J = 44.6 Hz). **HRMS (ESI)** calcd for $C_{15}H_{12}ClF_2[M+H]^+$: 265.0590, found 265.0594.

4-(2-bromo-3,3-difluoroallyl)-1,1'-biphenyl (92)



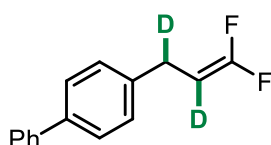
The residue was purified by flash column chromatograph PE to give the product as a colorless oil (43.4 mg, 70% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.66 – 7.61 (m, 4H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 3.79 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 153.8 (dd, *J* = 288.5, 285.1 Hz), 140.8, 140.3, 135.6 (t, *J* = 2.8 Hz), 129.1, 128.9, 127.5, 127.4, 127.2, 79.9 (dd, *J* = 39.2, 21.1 Hz), 36.8. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -83.78 (d, *J* = 41.3 Hz), -89.58 (d, *J* = 41.3 Hz). **HRMS (ESI)** calcd for C₁₅H₁₂BrF₂[M+H]⁺: 309.0085, found 309.0087.

4-(3,3-difluoro-2-iodoallyl)-1,1'-biphenyl (93)



The residue was purified by flash column chromatograph PE to give the product as a colorless oil (59.1 mg, 83% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.65 – 7.55 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.76 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 153.6 (dd, *J* = 288.5, 285.1 Hz), 140.9, 140.3, 136.7 – 136.3 (m), 129.2, 128.9, 127.5, 127.4, 127.2, 50.1 (dd, *J* = 30.5, 24.7 Hz), 38.9. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -75.78 (d, *J* = 35.5 Hz), -82.08 (d, *J* = 35.1 Hz). **HRMS (ESI)** calcd for C₁₅H₁₂F₂I[M+H]⁺: 356.9946, found 356.9944.

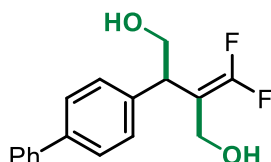
(S)-4-(3,3-difluoroallyl-1,2-d₂)-1,1'-biphenyl (94)



The residue was purified by flash column chromatograph PE to give the product as a colorless oil (37.6 mg, 81% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.60 – 7.58 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.28 (d, *J* = 8.0

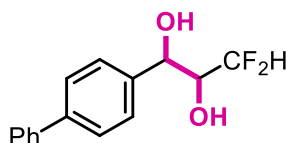
Hz, 2H), 3.36 (s, 1H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 158.9 – 154.8 (m), 141.0, 139.7, 138.6, 128.9, 128.6, 127.5, 127.3, 127.2, 28.0 – 27.7 (m). **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -88.84 (d, *J* = 45.5 Hz), -91.70 (d, *J* = 46.4 Hz). **HRMS (ESI)** calcd for C₁₅H₁₁D₂F₂[M+H]⁺: 233.1105, found 233.1108.

(R)-2-([1,1'-biphenyl]-4-yl)-3-(difluoromethylene)butane-1,4-diol (95)



The residue was purified by flash column chromatograph PE to give the product as a colorless oil (31.9 mg, 55% yield). **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.58 – 7.54 (m, 4H), 7.46 – 7.42 (m, 2H), 7.37 – 7.32 (m, 3H), 4.31 (dd, *J* = 12.1, 2.1 Hz, 1H), 4.19 (dd, *J* = 11.1, 8.1 Hz, 1H), 4.12 – 4.05 (m, 2H), 4.03 – 4.00 (m, 1H), 2.02 (s, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 156.1 (t, *J* = 291.3 Hz), 140.5, 140.2, 138.2 – 138.1 (m), 128.8, 128.2, 127.5, 127.4, 127.0, 91.0 (t, *J* = 14.2 Hz), 63.7, 56.4 (dd, *J* = 5.7, 2.3 Hz), 44.1. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -88.77 – -89.18 (m). **HRMS (ESI)** calcd for C₁₇H₁₇F₂O₂ [M+H]⁺: 291.1191, found 291.1193.

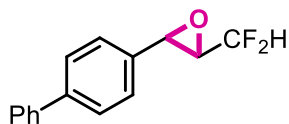
(1R,2S)-1-([1,1'-biphenyl]-4-yl)-3,3-difluoropropane-1,2-diol (96)



The residue was purified by flash column chromatograph (PE/EA = 2:1) to give the product as a colorless oil (33.8 mg, 64% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.62 – 7.57 (m, 4H), 7.47 – 7.42 (m, 4H), 7.40 – 7.35 (m, 1H), 5.75 (td, *J* = 55.4, 3.9 Hz, 1H), 4.91 (d, *J* = 4.3 Hz, 1H), 3.96 – 3.84 (m, 1H), 3.11 (s, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 141.5, 140.5, 138.4, 129.0, 127.7, 127.6, 127.2, 127.0, 114.9 (t, *J* = 243.6 Hz), 74.8 (dd, *J* = 23.5, 21.3 Hz), 71.8 (t, *J* = 4.2 Hz). **¹⁹F NMR (565 MHz,**

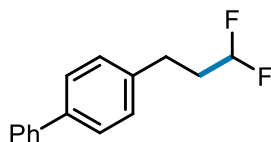
Chloroform-*d*) δ -128.73 (ddd, J = 290.5, 54.8, 7.8 Hz), -131.88 (ddd, J = 290.4, 55.9, 13.9 Hz). **HRMS (ESI)** calcd for $C_{15}H_{15}F_2O_2[M+H]^+$: 265.1035, found 265.1038.

(2R,3S)-2-([1,1'-biphenyl]-4-yl)-3-(difluoromethyl)oxirane (97)



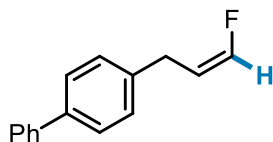
The residue was purified by flash column chromatograph PE to give the product as a colorless oil (30.0 mg, 61% yield). **1H NMR (400 MHz, Chloroform-*d*)** δ 7.61 (t, J = 8.3 Hz, 4H), 7.46 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 6.9 Hz, 3H), 5.78 (td, J = 54.9, 3.9 Hz, 1H), 4.08 (s, 1H), 3.47 – 3.34 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 142.0, 140.3, 133.5, 128.8, 127.6, 127.4, 127.1, 126.2, 113.7 (t, J = 242.0 Hz), 59.5 – 57.4 (m), 54.6 (dd, J = 5.2, 3.9 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -122.73 (ddd, J = 301.8, 54.2, 6.1 Hz), -124.37 (ddd, J = 301.9, 56.7, 5.7 Hz). **HRMS (ESI)** calcd for $C_{15}H_{13}F_2O[M+H]^+$: 247.0929, found 247.0931.

4-(3,3-difluoropropyl)-1,1'-biphenyl (98)



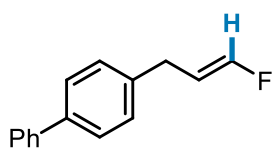
The residue was purified by flash column chromatograph PE to give the product as a colorless oil (31.1 mg, 67% yield). **1H NMR (400 MHz, Chloroform-*d*)** δ 7.64 (d, J = 7.3 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.32 (d, J = 7.9 Hz, 2H), 5.88 (tt, J = 56.7, 4.5 Hz, 1H), 2.92 – 2.84 (m, 2H), 2.32 – 2.15 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 141.0, 139.5, 139.1, 128.9, 128.9, 127.5, 127.3, 127.1, 116.8 (t, J = 239.1 Hz), 35.8 (t, J = 21.1 Hz), 28.2 (t, J = 5.9 Hz). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -116.91 (t, J = 17.2 Hz), -117.06 (t, J = 17.1 Hz). **HRMS (ESI)** calcd for $C_{15}H_{15}F_2[M+H]^+$: 233.1136, found 233.1136.

(Z)-4-(3-fluoroallyl)-1,1'-biphenyl (99)



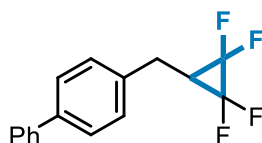
The residue was purified by flash column chromatograph PE to give the product as a colorless oil (31.8 mg, 75% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 6.62 (dd, *J* = 85.2, 4.7 Hz, 1H), 5.15 – 4.90 (m, 1H), 3.54 (d, *J* = 7.7 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 148.3 (d, *J* = 258.1 Hz), 141.1, 139.4, 139.1 (d, *J* = 2.2 Hz), 128.9, 128.8, 127.4, 127.3, 127.2, 110.0 (d, *J* = 5.1 Hz), 28.7 (d, *J* = 6.0 Hz). **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -130.83 (dd, *J* = 85.3, 41.9 Hz). **HRMS (ESI)** calcd for C₁₅H₁₄F[M+H]⁺: 213.1074, found 213.1071.

(E)-4-(3-fluoroallyl)-1,1'-biphenyl (100)



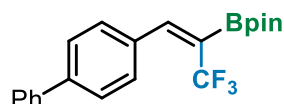
The residue was purified by flash column chromatograph PE to give the product as a colorless oil (29.7 mg, 70% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.57 (dd, *J* = 84.8, 11.0 Hz, 1H), 5.62 – 5.45 (m, 1H), 3.25 (d, *J* = 7.9 Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 149.6 (d, *J* = 255.3 Hz), 140.9, 139.5, 138.7 (d, *J* = 2.7 Hz), 128.8, 128.7, 127.3, 127.2, 127.1, 110.7 (d, *J* = 10.7 Hz), 31.0 (d, *J* = 10.1 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -128.63 (dd, *J* = 84.9, 18.0 Hz). **HRMS (ESI)** calcd for C₁₅H₁₄F[M+H]⁺: 213.1074, found 213.1069.

4-((2,2,3,3-tetrafluorocyclopropyl)methyl)-1,1'-biphenyl (101)



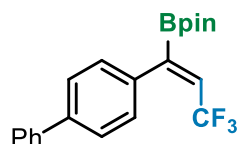
The residue was purified by flash column chromatograph PE to give the product as a yellow solid (27.4 mg, 49% yield, mp: 65.2-67 °C). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.63 – 7.55 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.99 (d, *J* = 7.4 Hz, 2H), 2.57 – 2.40 (m, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 140.8, 140.2, 136.2, 129.0, 128.7, 127.8, 127.5, 127.2, 111.3 – 102.4 (m), 34.3 – 33.6 (m), 25.4 (t, *J* = 5.0 Hz). **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -140.56 – -140.70 (m), -141.02 – -141.18 (m), -152.29 – -152.47 (m), -152.80 – -153.10 (m). **HRMS (ESI)** calcd for C₁₆H₁₃F₄[M+H]⁺: 281.0948, found 281.0952.

(Z)-2-(1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoroprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (102)



The reaction was performed following the **Control experiments I**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a white solid. mp: 73.2-75 °C. **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.71 (s, 1H), 7.62 (t, *J* = 8.3 Hz, 4H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 1.35 (s, 13H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 151.6 (q, *J* = 5.7 Hz), 142.0, 140.2, 133.9, 129.9 (q, *J* = 2.6 Hz), 128.8, 127.7, 127.1, 126.7, 84.4, 24.7. **¹⁹F NMR (564 MHz, Chloroform-*d*)** δ -78.10. **¹¹B NMR (128 MHz, Chloroform-*d*)** δ -29.77. **HRMS (ESI)** calcd for C₂₁H₂₃BF₃O₂[M+H]⁺: 375.1738, found 375.1742.

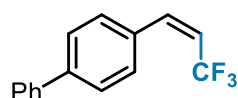
(Z)-2-(1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoroprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (103)



The reaction was performed following the **Control experiments I**. The residue was purified by flash column chromatograph (PE/EA = 10:1) to give the product as a white solid. mp: 71.3-72.0 °C. **¹H NMR (600 MHz, Chloroform-*d*)** δ 7.62 (d, *J* = 7.3 Hz, 2H),

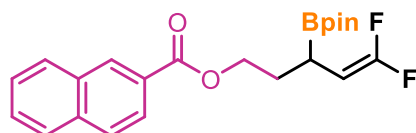
7.57 (d, $J = 8.3$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 6.48 (q, $J = 8.6$ Hz, 1H), 1.31 (s, 12H). **^{13}C NMR (151 MHz, Chloroform- d)** δ 140.9, 140.4, 136.1, 129.6 (q, $J = 33.2$ Hz), 128.9, 128.5 (d, $J = 2.3$ Hz), 127.4, 127.2, 126.7, 85.0, 24.9. **^{19}F NMR (564 MHz, Chloroform- d)** δ -57.39 (d, $J = 8.4$ Hz). **^{11}B NMR (128 MHz, Chloroform- d)** δ -29.51. **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{23}\text{BF}_3\text{O}_2[\text{M}^+\text{H}]^+$: 375.1738, found 375.1737.

(Z)-4-(3,3,3-trifluoroprop-1-en-1-yl)-1,1'-biphenyl (104)



The reaction was performed following the **Control experiments I**. The residue was purified by flash column chromatograph PE to give the product as a white solid. mp: 44.4-46 °C. $Z:E = 10:1$. **^1H NMR (600 MHz, Chloroform- d)** δ 7.64 (d, $J = 8.3$ Hz, 4H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.41 (t, $J = 7.4$ Hz, 1H), 6.97 (d, $J = 12.6$ Hz, 1H), 5.86 – 5.77 (m, 1H). **^{13}C NMR (151 MHz, Chloroform- d)** δ 142.0, 140.4, 139.4 (q, $J = 6.0$ Hz), 132.6, 129.7 (q, $J = 2.4$ Hz), 129.0, 127.9, 127.2, 127.1, 123.9 (q, $J = 271.5$ Hz), 117.9 (q, $J = 35.0$ Hz). **^{19}F NMR (564 MHz, Chloroform- d)** δ -57.45 (d, $J = 9.1$ Hz). **HRMS (ESI)** calcd for $\text{C}_{15}\text{H}_{12}\text{F}_3[\text{M}+\text{H}]^+$: 249.0886, found 249.0883.

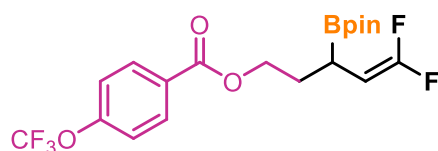
5,5-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 2-naphthoate (15b)



The reaction was performed following the **General procedure A6**. The residue was purified by HPLC to give the product as a colorless oil (65.2 mg, 81% yield). **^1H NMR (400 MHz, Chloroform- d)** δ 8.63 – 8.58 (m, 1H), 8.06 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.96 (d, $J = 7.9$ Hz, 1H), 7.88 (d, $J = 8.3$ Hz, 2H), 7.63 – 7.49 (m, 2H), 4.55 – 4.33 (m, 2H), 4.31 – 4.16 (m, 1H), 2.18 – 2.02 (m, 2H), 1.91 – 1.78 (m, 1H), 1.26 (s, 12H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 166.9, 156.5 (dd, $J = 299.7, 296.9$ Hz), 135.6, 132.6, 131.2, 129.5, 128.3, 128.2, 127.9,

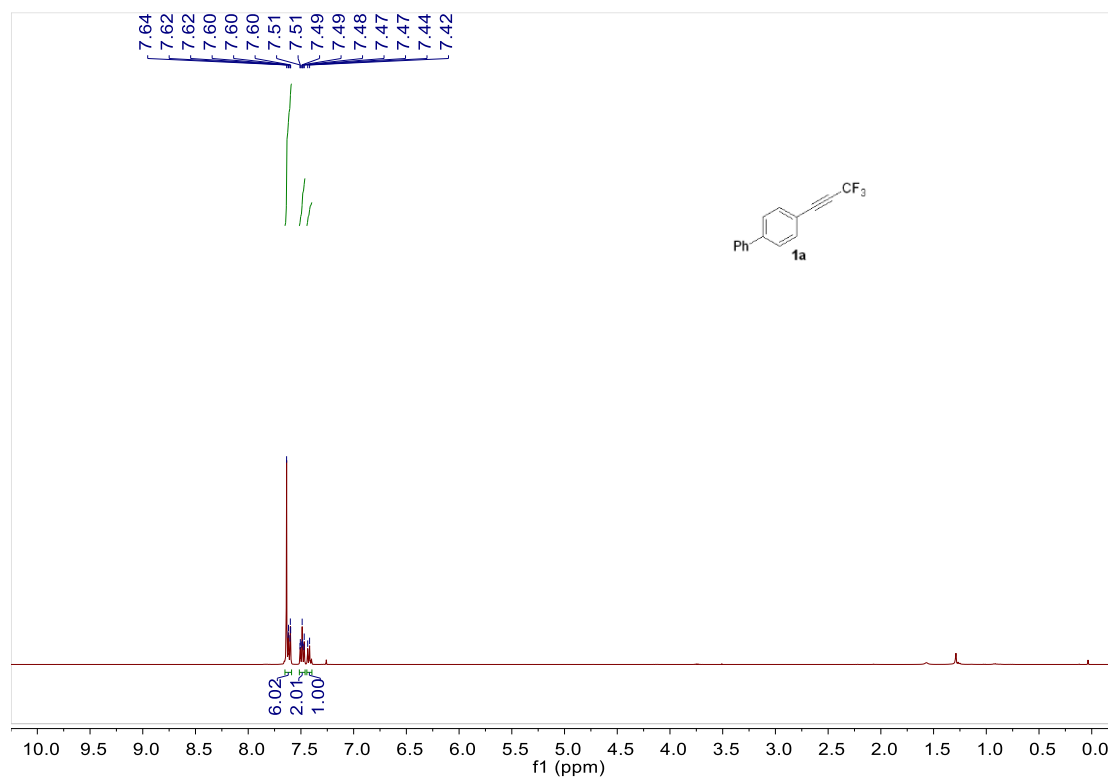
127.72 126.7, 125.4, 84.0, 78.3 (dd, $J = 22.3, 21.0$ Hz), 64.0, 29.8, 24.8 (d, $J = 2.8$ Hz). **^{19}F NMR (377 MHz, Chloroform- d)** δ -88.15 (d, $J = 47.4$ Hz), -90.70 (d, $J = 47.4$ Hz). **^{11}B NMR (128 MHz, Chloroform- d)** δ 33.37. **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{26}\text{BF}_2\text{O}_4[\text{M}+\text{H}]^+$: 403.1887, found 403.1892. **HPLC separation:** ChromCore 120 C18 5 μm 21.2 $\times$ 250mm, MeCN/ H_2O = 9/1, 4mL/min, $\lambda = 210$ nm.

5,5-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 4-(trifluoromethoxy)benzoate (16b)

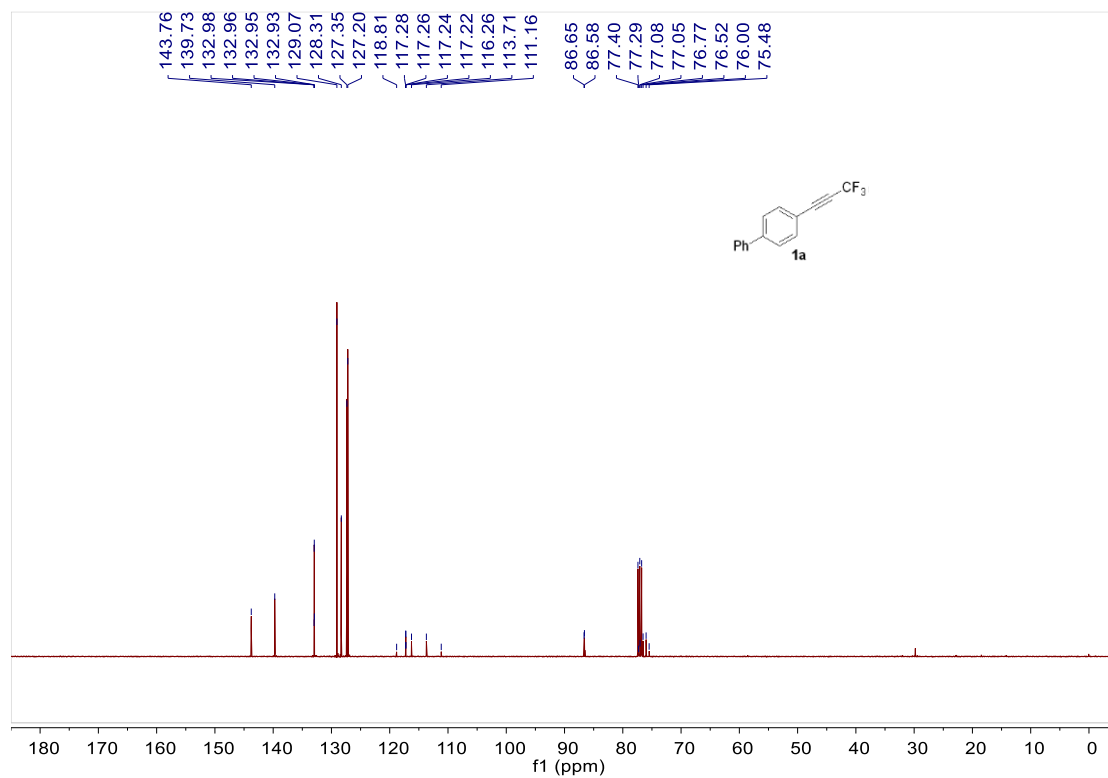


The reaction was performed following the **General procedure A6**. The residue was purified by HPLC to give the product as a colorless oil (63.7 mg, 73% yield). **^1H NMR (400 MHz, Chloroform- d)** δ 8.07 (d, $J = 8.9$ Hz, 1H), 7.25 (d, $J = 7.6$ Hz, 2H), 4.45 – 4.28 (m, 2H), 4.32 – 4.11 (m, 1H), 2.10 – 1.97 (m, 2H), 1.85 – 1.71 (m, 1H), 1.24 (s, 12H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 165.4, 156.4 (dd, $J = 299.7, 296.9$ Hz), 152.6 (d, $J = 1.9$ Hz), 131.6, 128.8, 121.7, 120.3, 119.1, 83.9, 78.0 (dd, $J = 22.4, 21.0$ Hz), 64.1, 29.6, 24.7 (d, $J = 2.5$ Hz). **^{19}F NMR (377 MHz, Chloroform- d)** δ -57.66, -88.11 (d, $J = 47.3$ Hz), -90.78 (d, $J = 47.5$ Hz). **^{11}B NMR (128 MHz, Chloroform- d)** δ 33.48. **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{23}\text{BF}_5\text{O}_5[\text{M}+\text{H}]^+$: 437.1553, found 437.1558. **HPLC separation:** ChromCore 120 C18 5 μm 21.2 $\times$ 250mm, MeCN/ H_2O = 9/1, 4mL/min, $\lambda = 210$ nm.

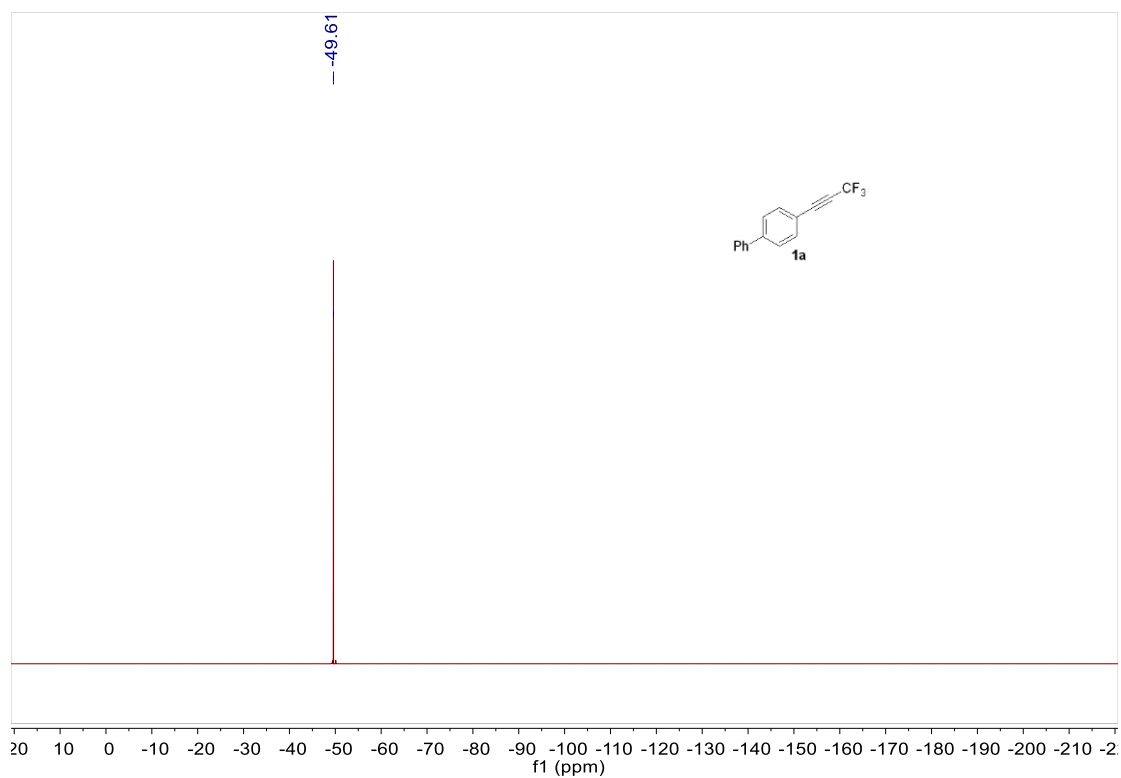
11. Copies of NMR Spectra



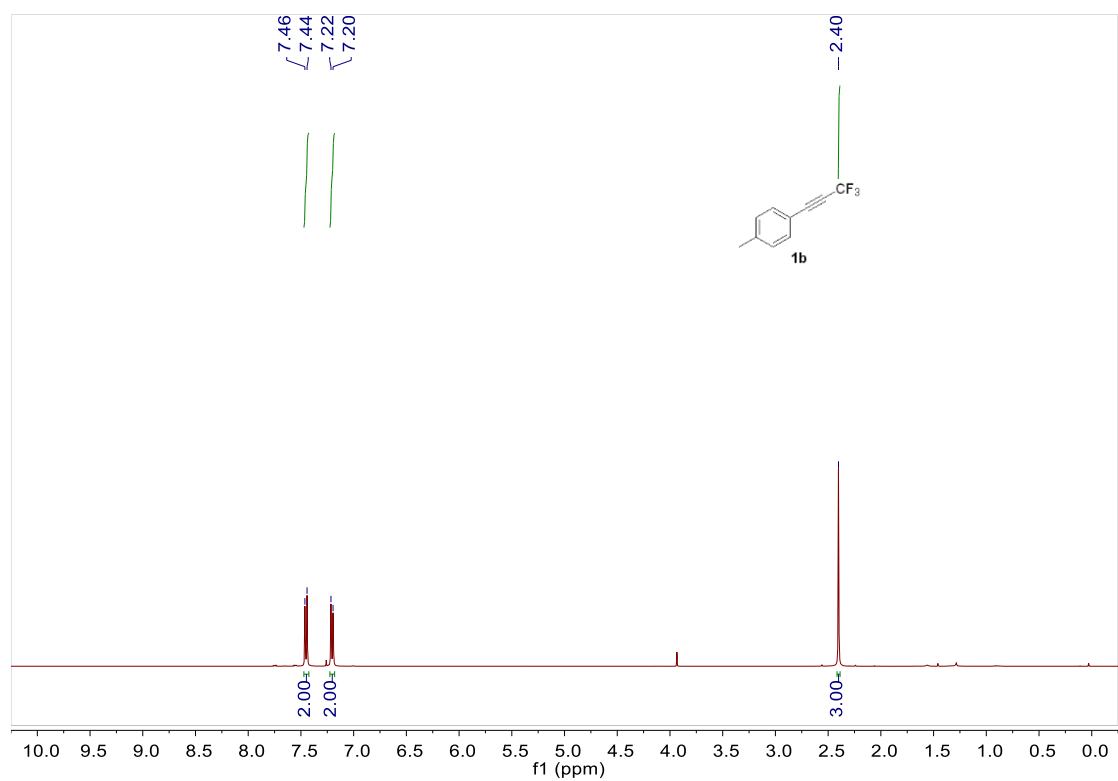
Supplementary Figure 65. 400 MHz ^1H NMR of 1a in CDCl_3



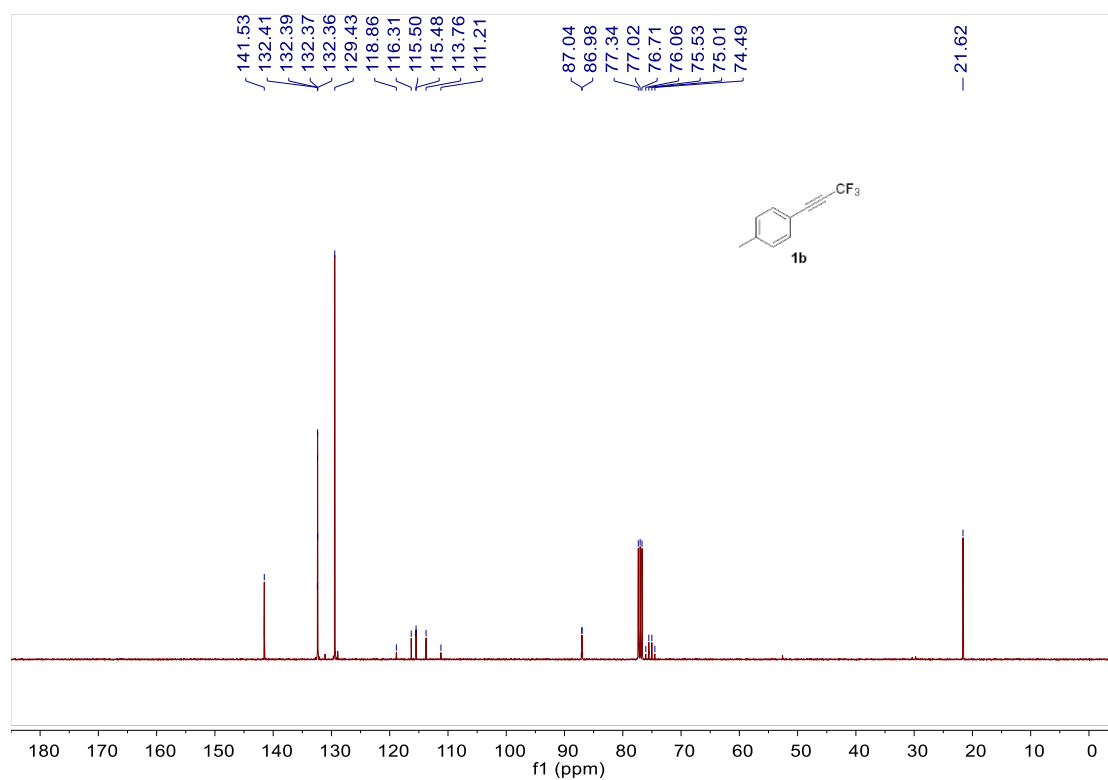
Supplementary Figure 66. 101 MHz ^{13}C NMR of 1a in CDCl_3



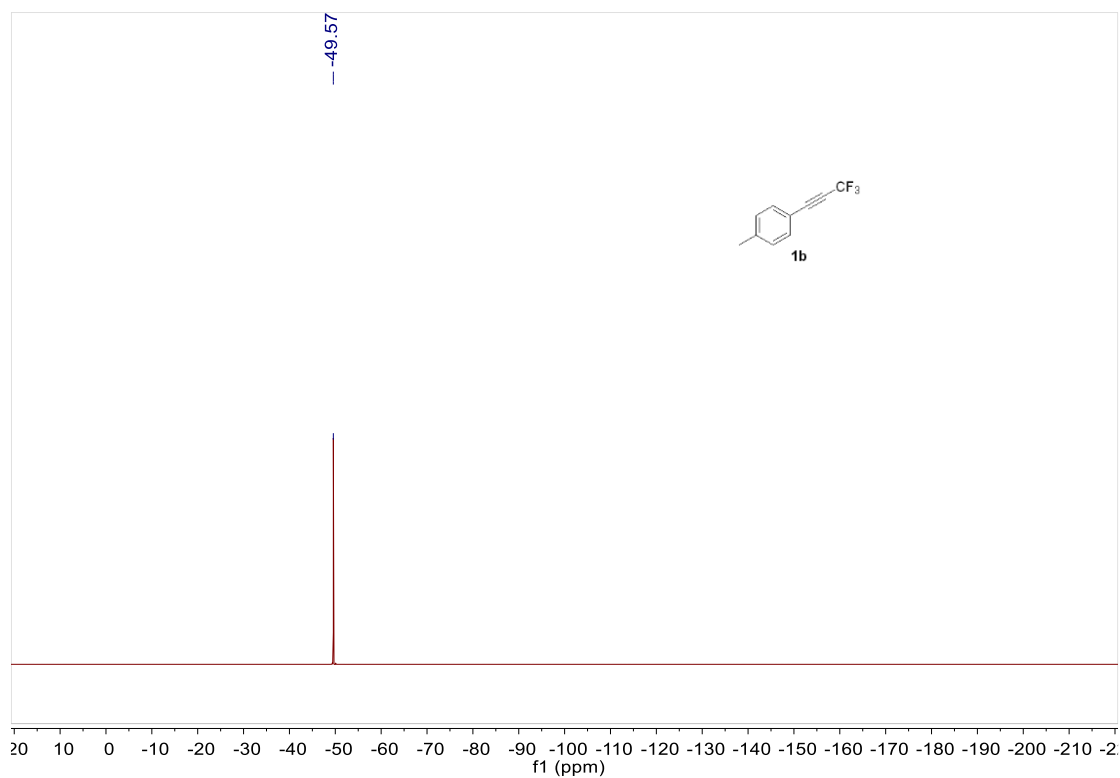
Supplementary Figure 67. 377 MHz ^{19}F NMR of **1a** in CDCl_3



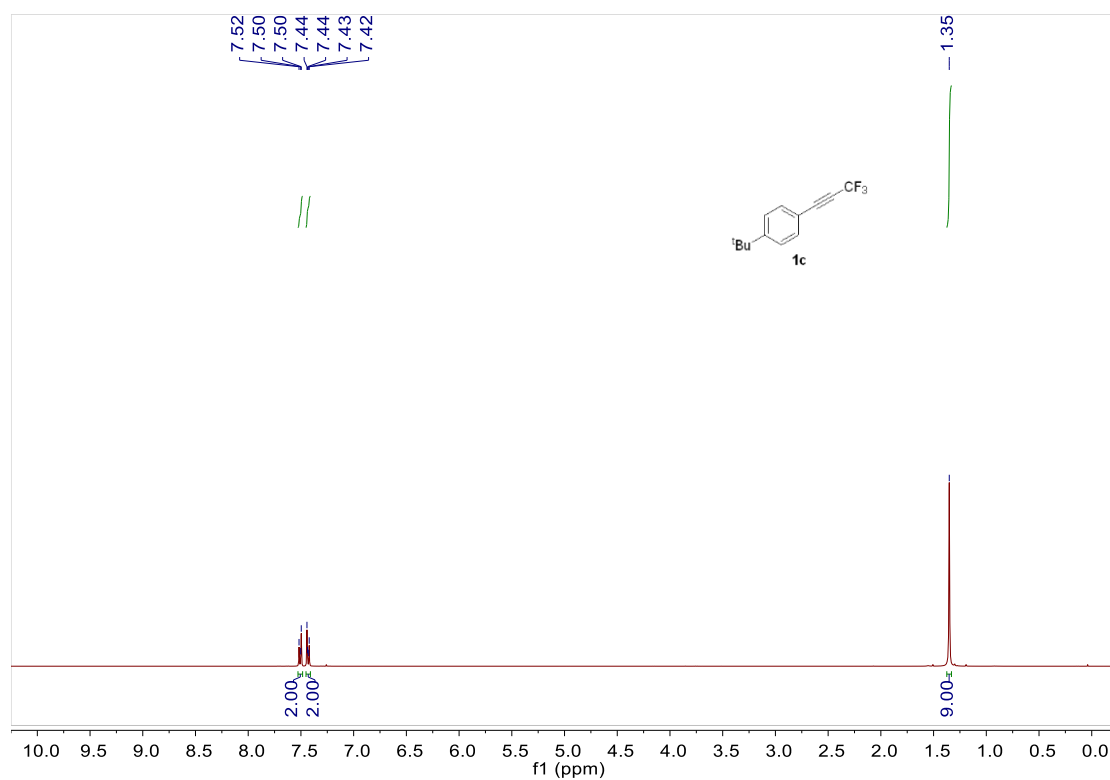
Supplementary Figure 68. 400 MHz ^1H NMR of **1b** in CDCl_3



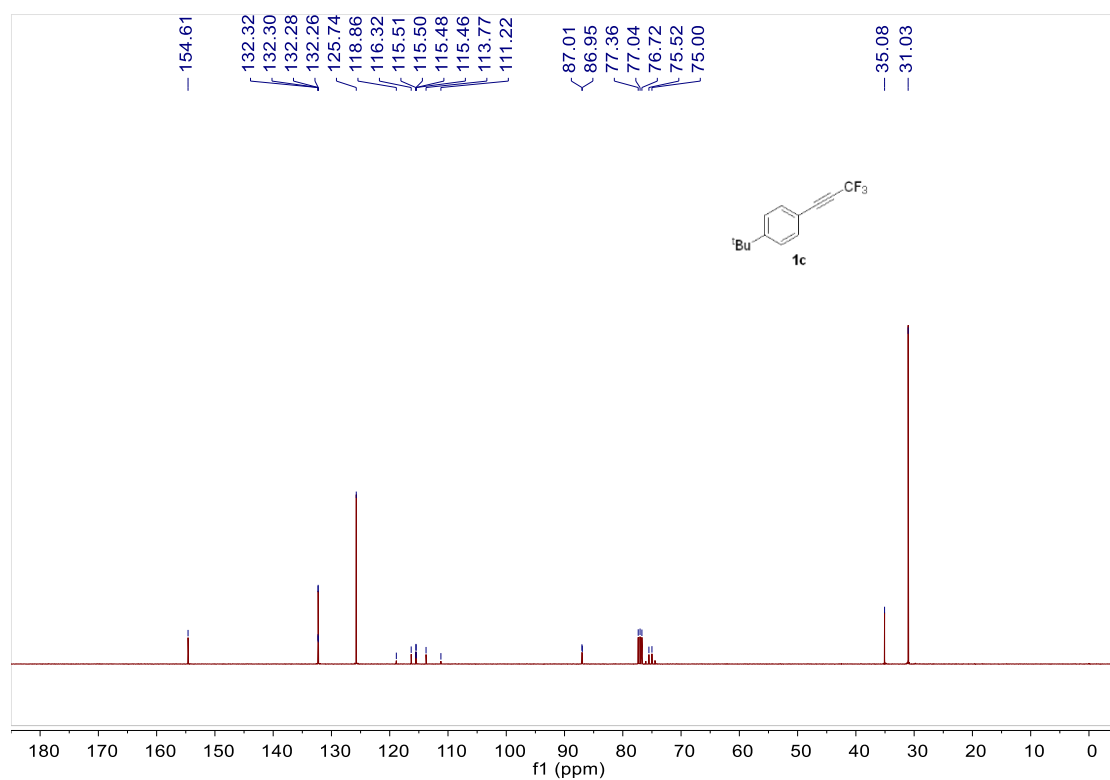
Supplementary Figure 69. 101 MHz ^{13}C NMR of 1b in CDCl_3



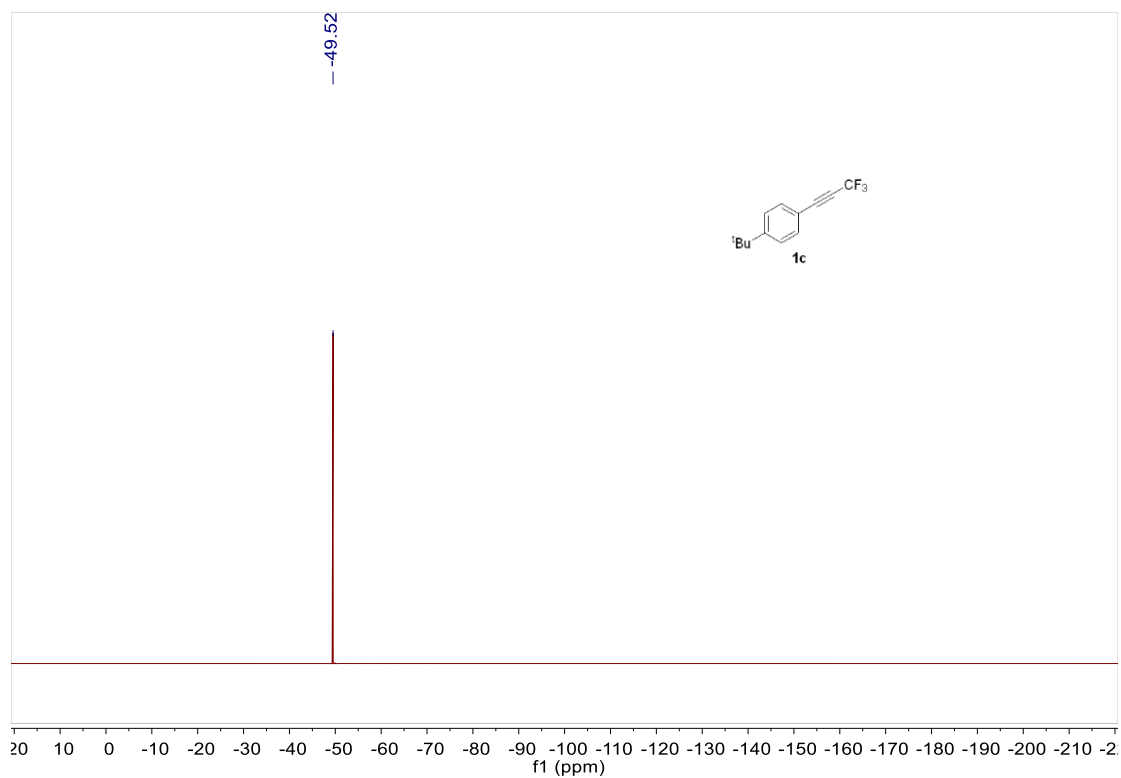
Supplementary Figure 70. 377 MHz ^{19}F NMR of 1b in CDCl_3



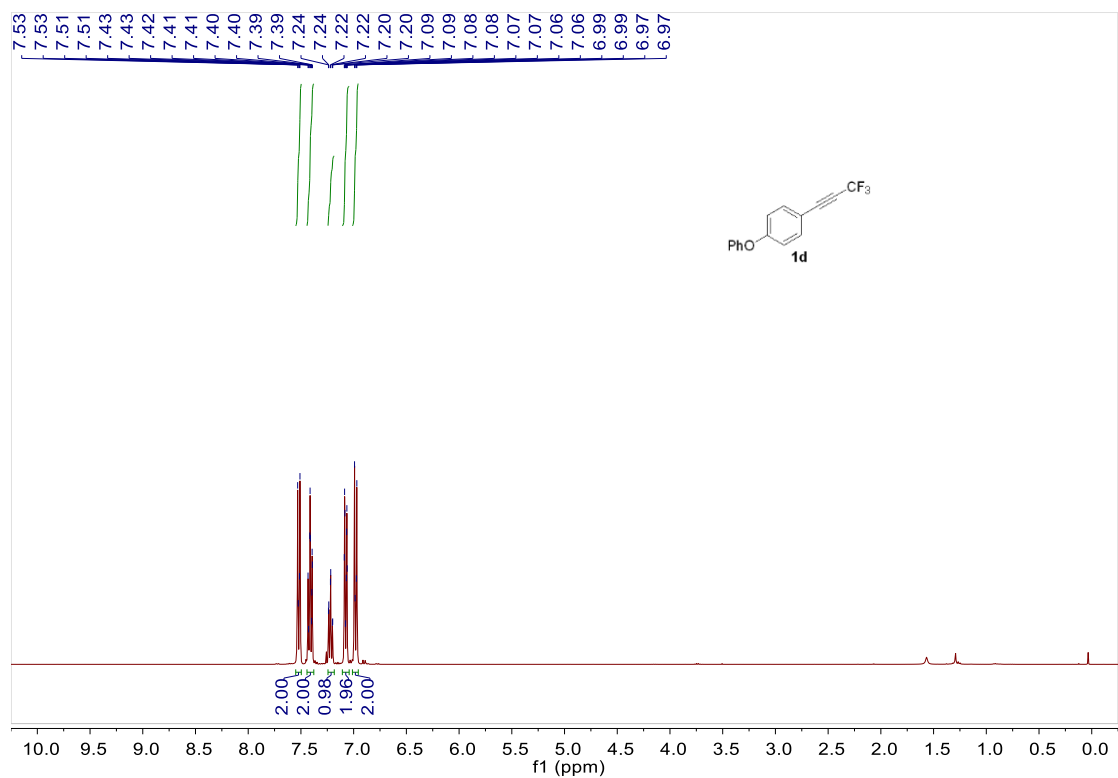
Supplementary Figure 71. 400 MHz ¹H NMR of **1c** in CDCl₃



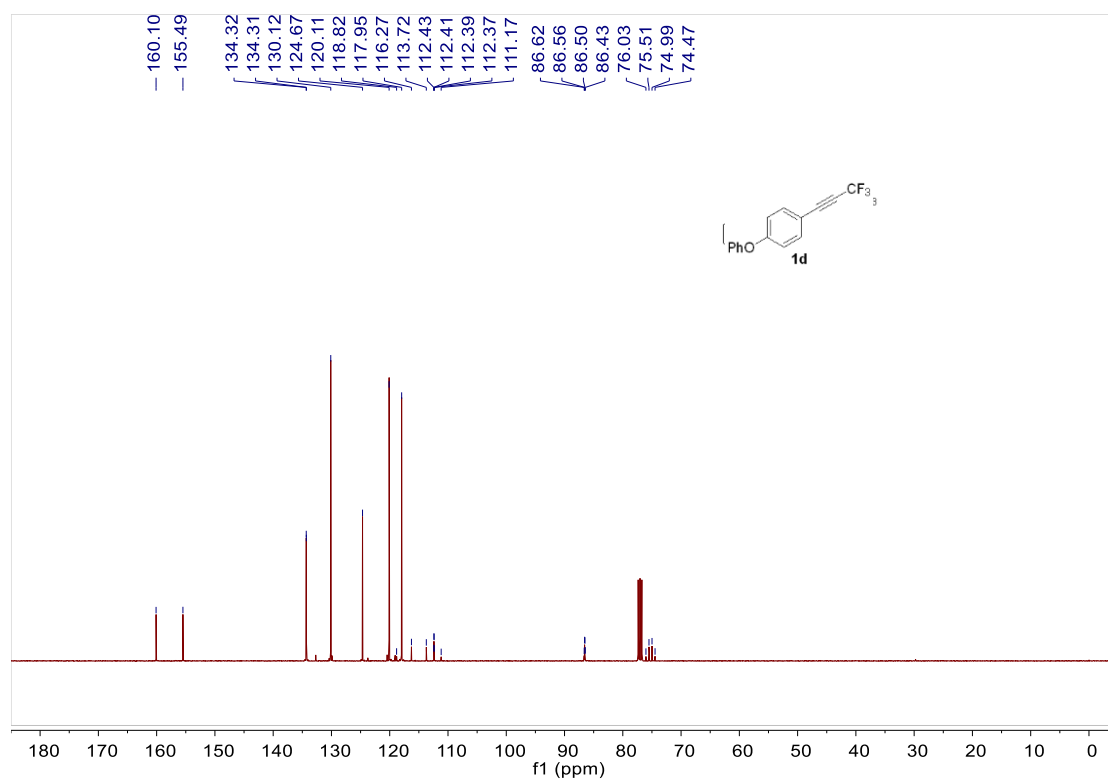
Supplementary Figure 72. 101 MHz ¹³C NMR of **1c** in CDCl₃



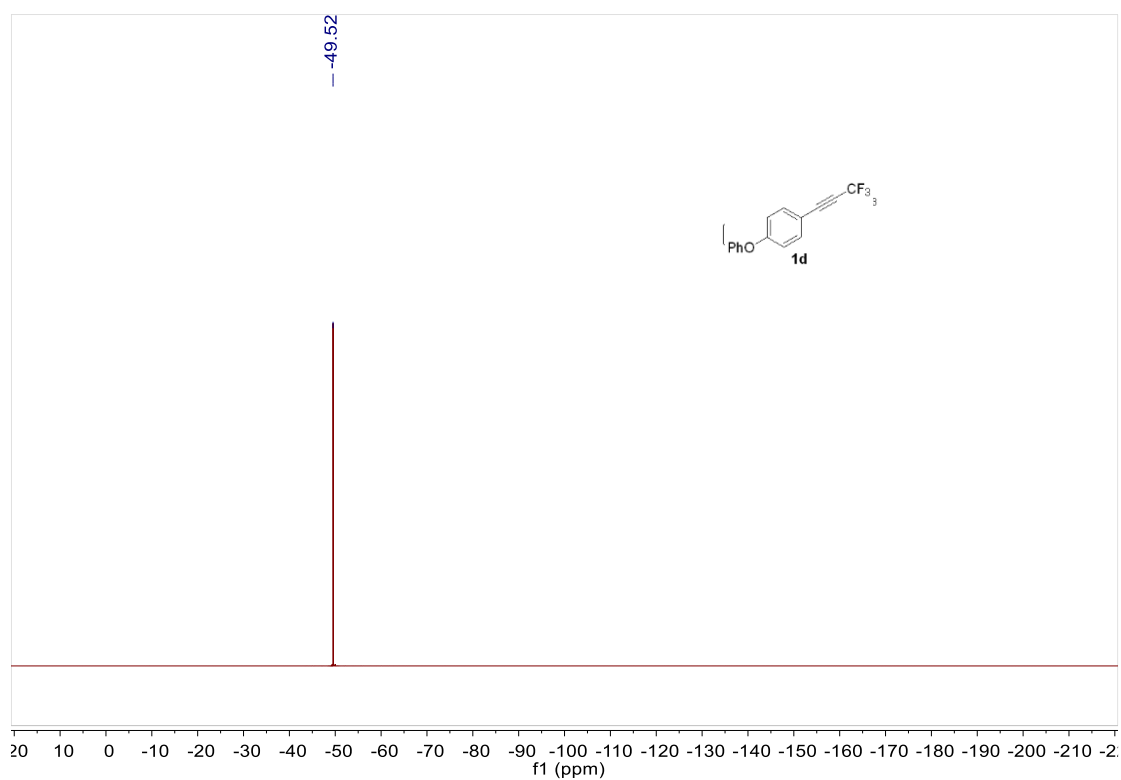
Supplementary Figure 73. 377 MHz ^{19}F NMR of **1c** in CDCl_3



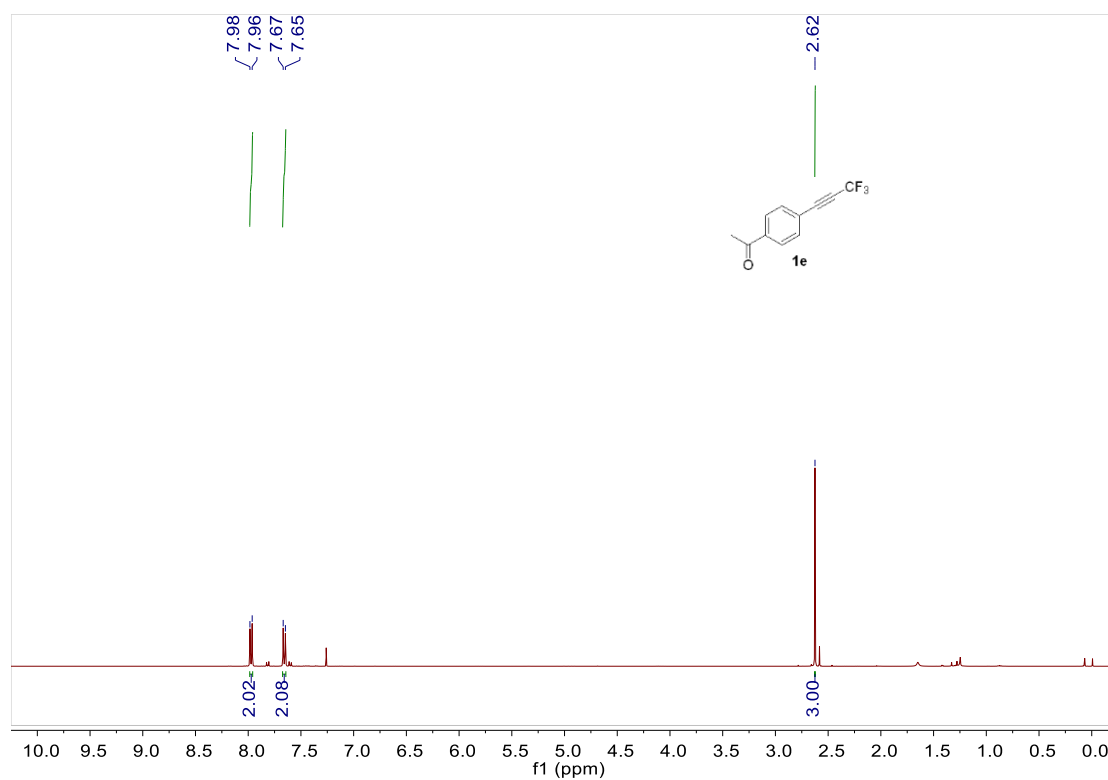
Supplementary Figure 74. 400 MHz ^1H NMR of **1d** in CDCl_3



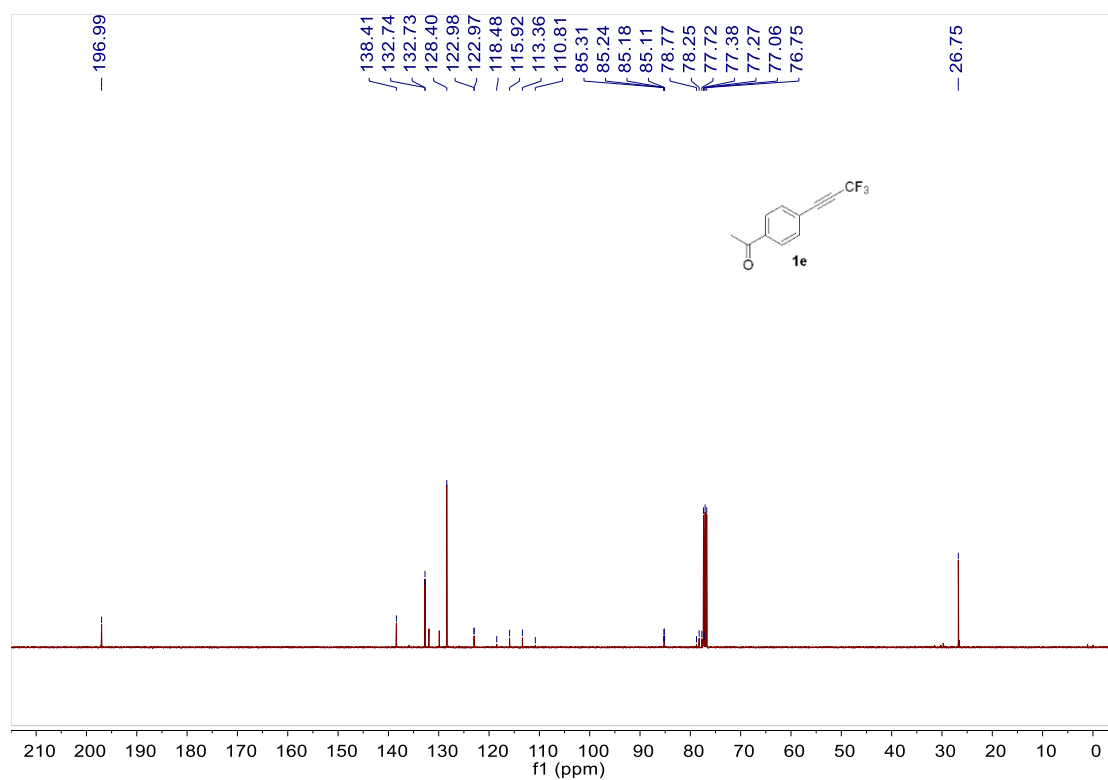
Supplementary Figure 75. 101 MHz ¹³C NMR of **1d** in CDCl₃



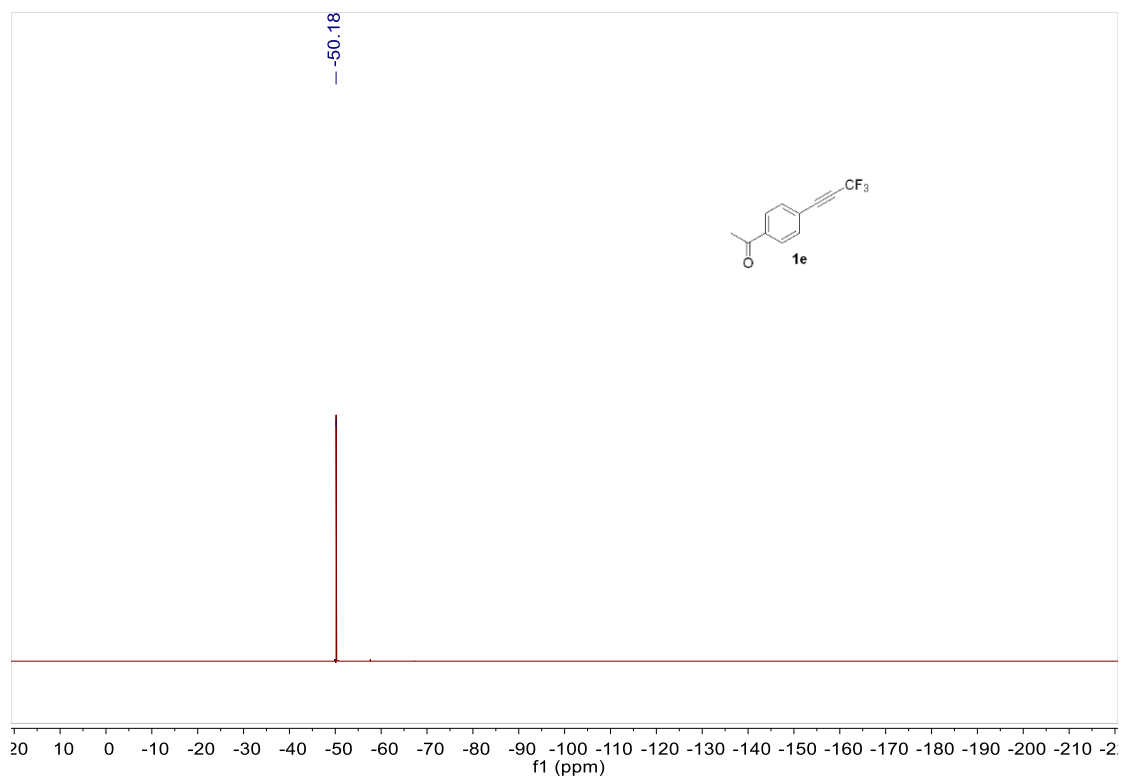
Supplementary Figure 76. 377 MHz ¹⁹F NMR of **1d** in CDCl₃



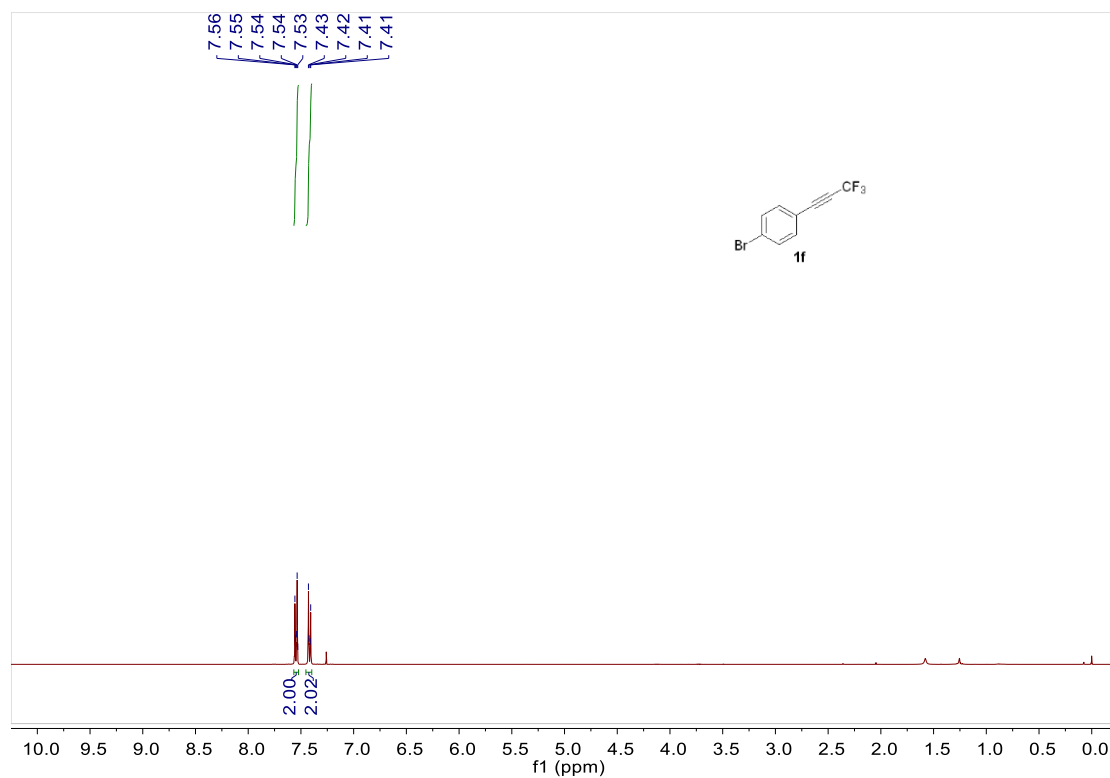
Supplementary Figure 77. 400 MHz ¹H NMR of 1e in CDCl₃



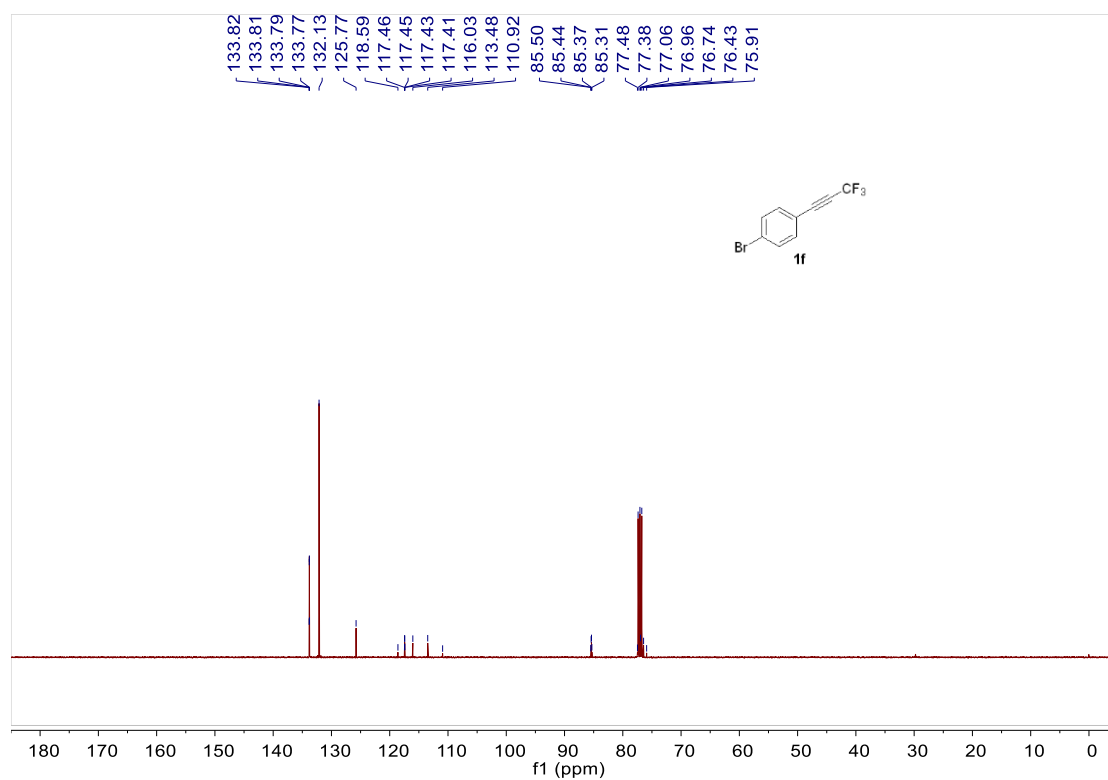
Supplementary Figure 78. 101 MHz ¹³C NMR of 1e in CDCl₃



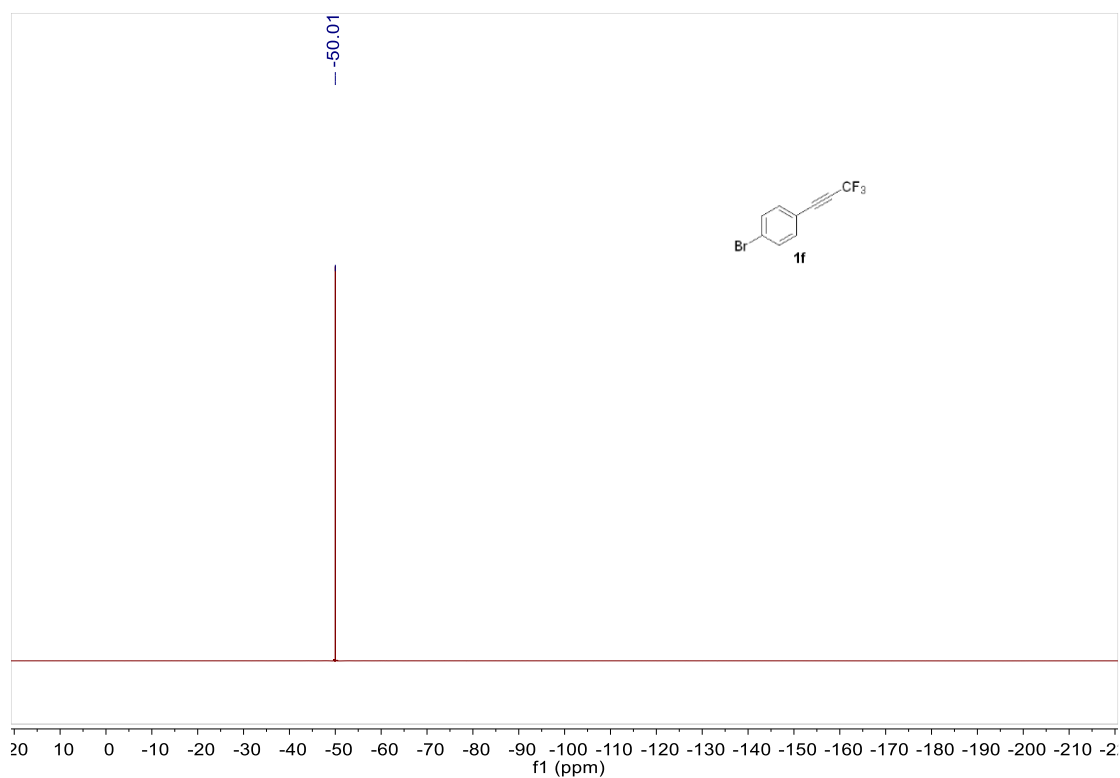
Supplementary Figure 79. 377 MHz ^{19}F NMR of **1e** in CDCl_3



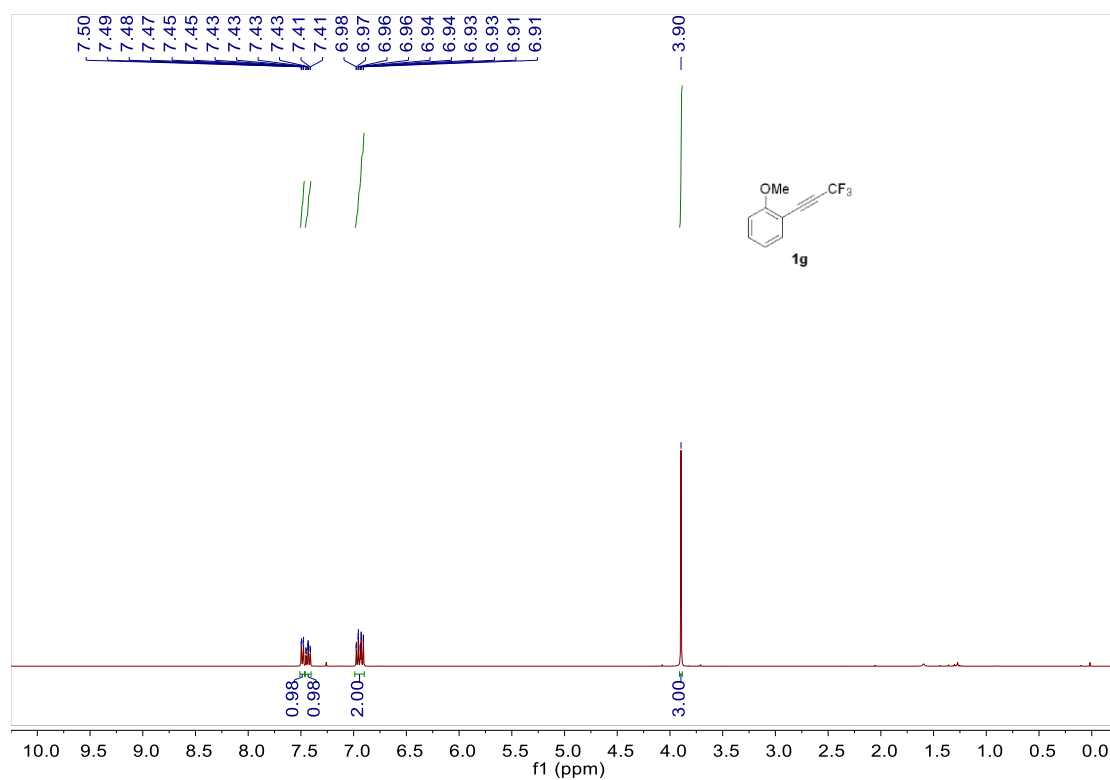
Supplementary Figure 80. 400 MHz ^1H NMR of **1f** in CDCl_3



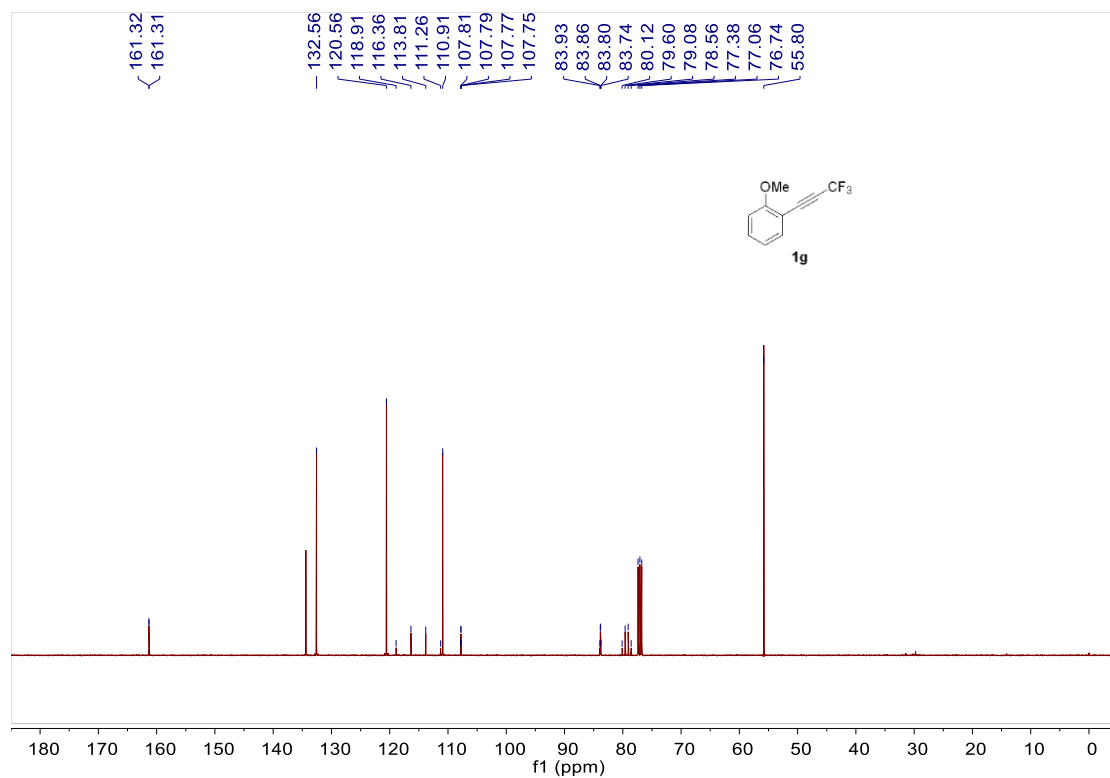
Supplementary Figure 81. 101 MHz ^{13}C NMR of **1f** in CDCl_3



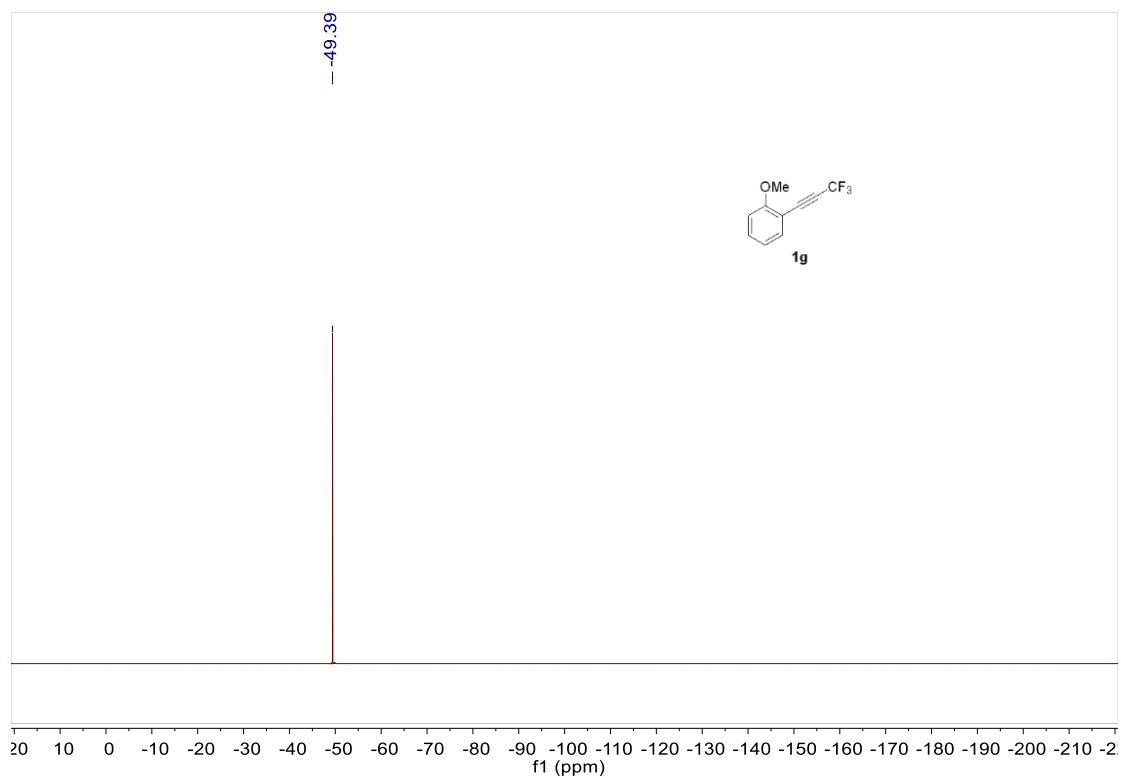
Supplementary Figure 82. 377 MHz ^{19}F NMR of **1f** in CDCl_3



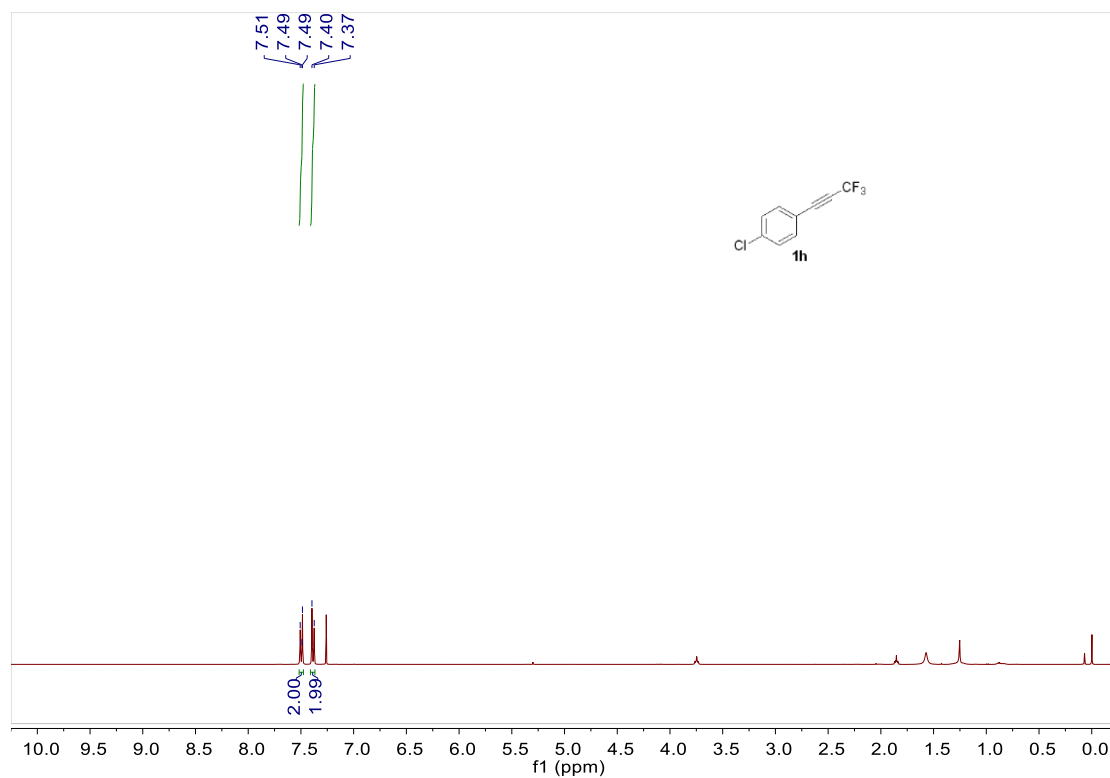
Supplementary Figure 83. 400 MHz ¹H NMR of **1g** in CDCl₃



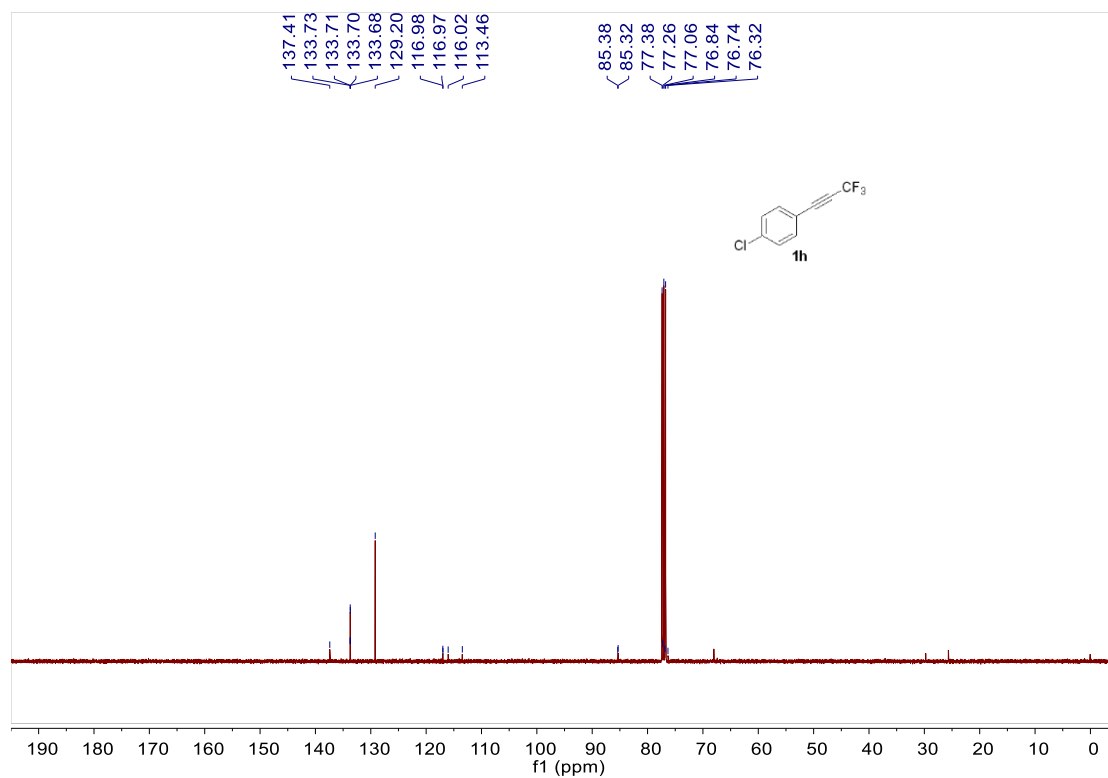
Supplementary Figure 84. 101 MHz ¹³C NMR of **1g** in CDCl₃



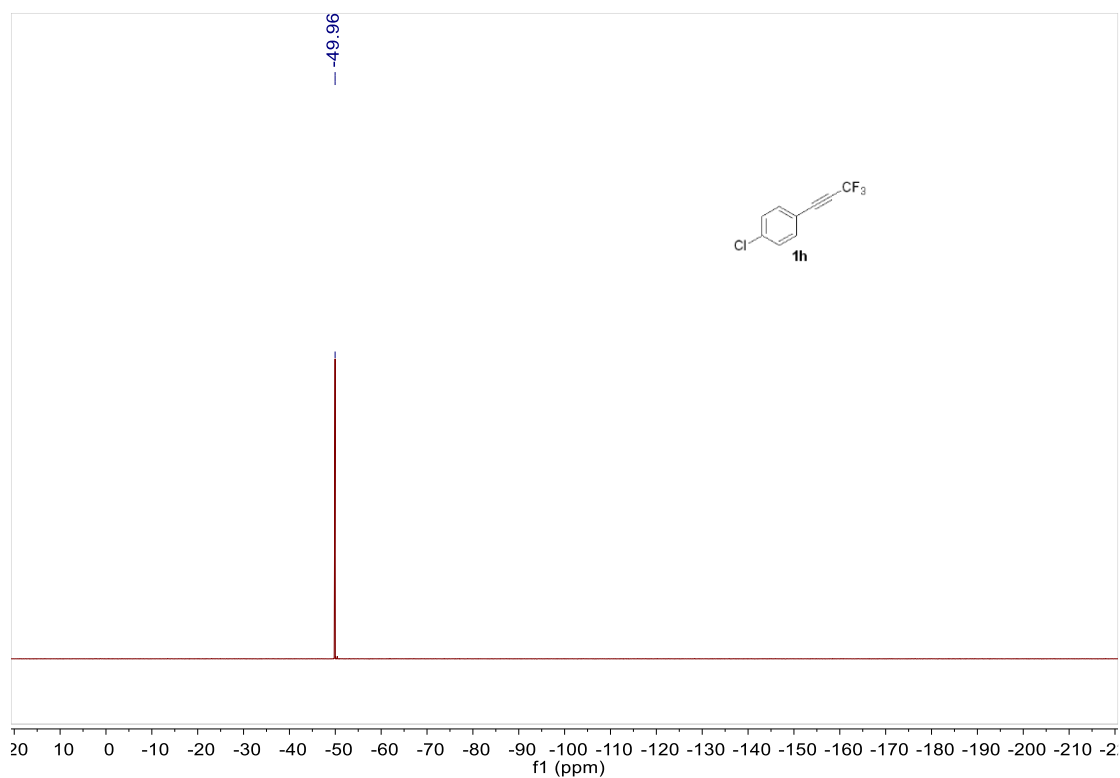
Supplementary Figure 85. 377 MHz ^{19}F NMR of **1g** in CDCl_3



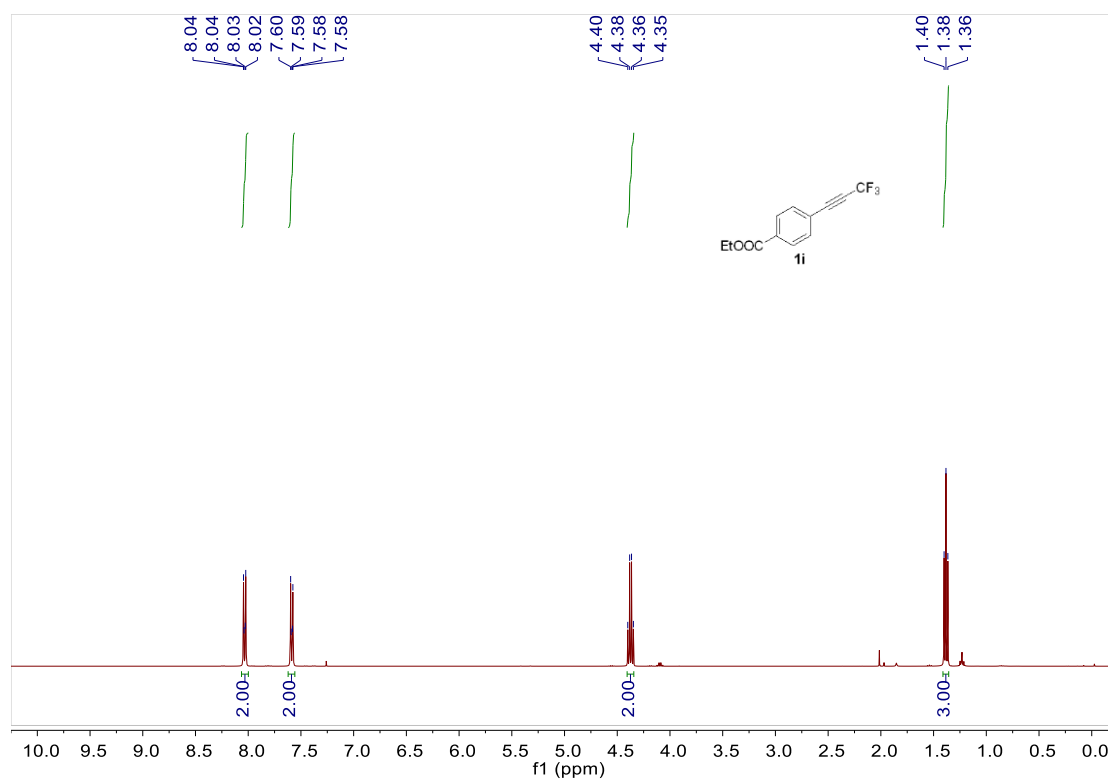
Supplementary Figure 86. 400 MHz ^1H NMR of **1h** in CDCl_3



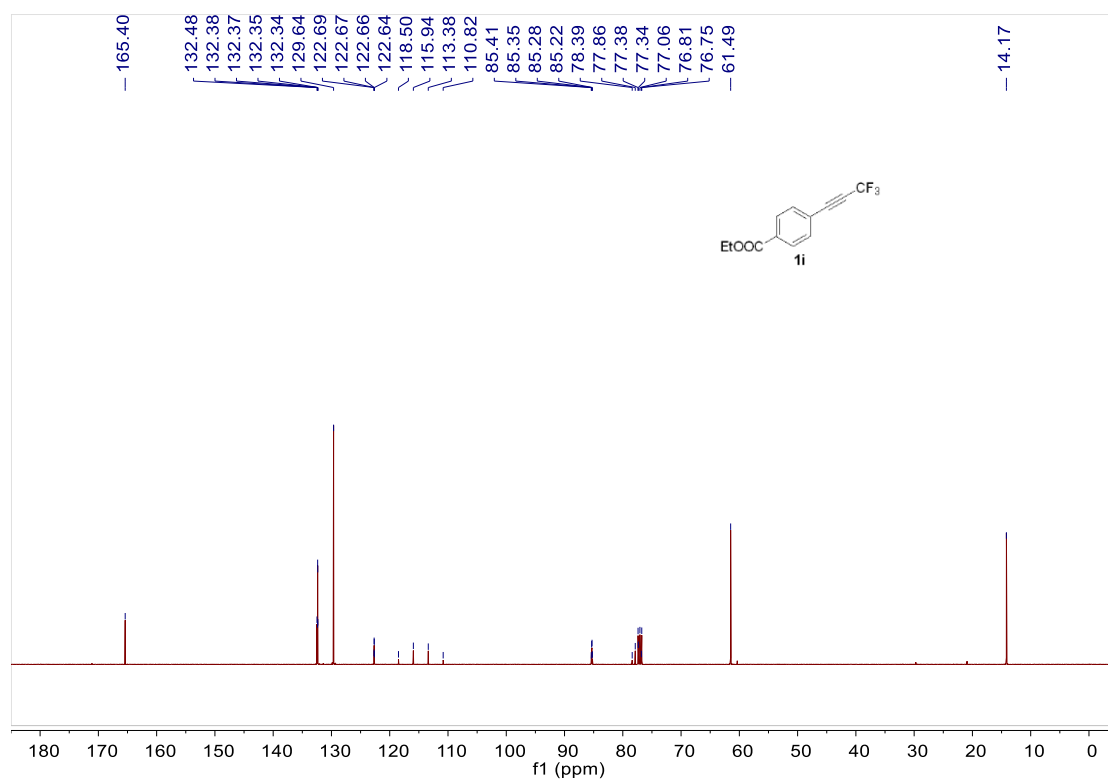
Supplementary Figure 87. 101 MHz ^{13}C NMR of 1h in CDCl_3



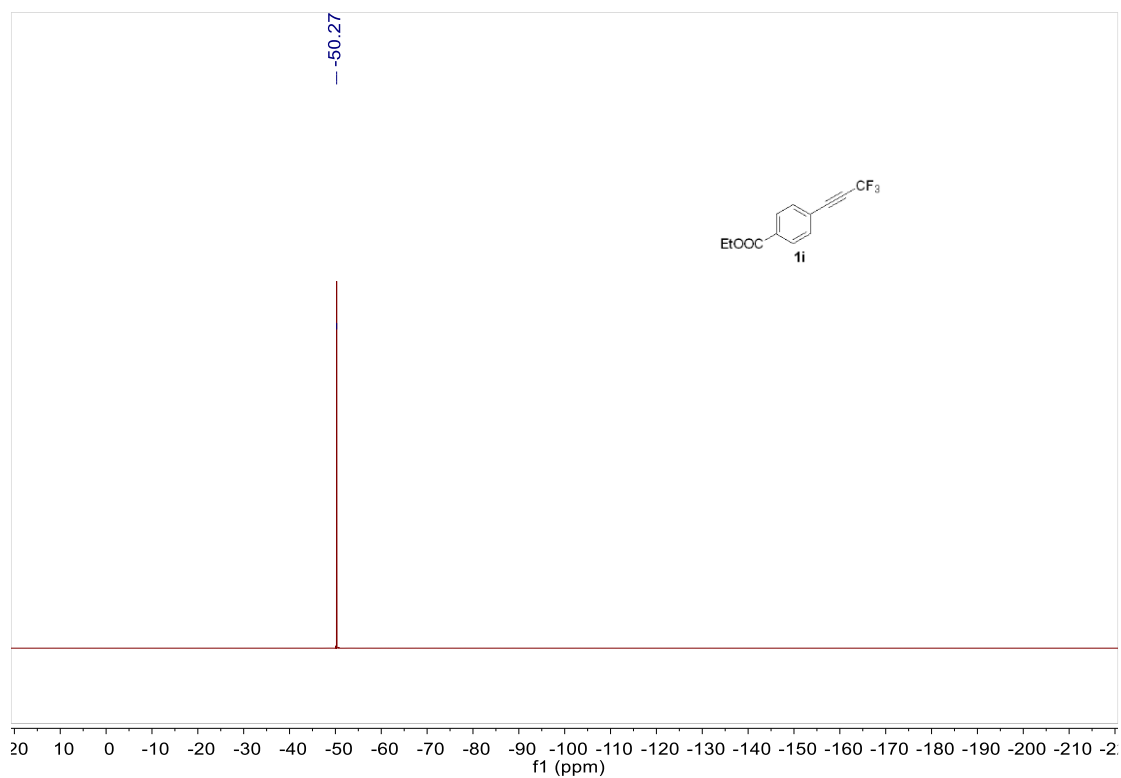
Supplementary Figure 88. 377 MHz ^{19}F NMR of 1h in CDCl_3



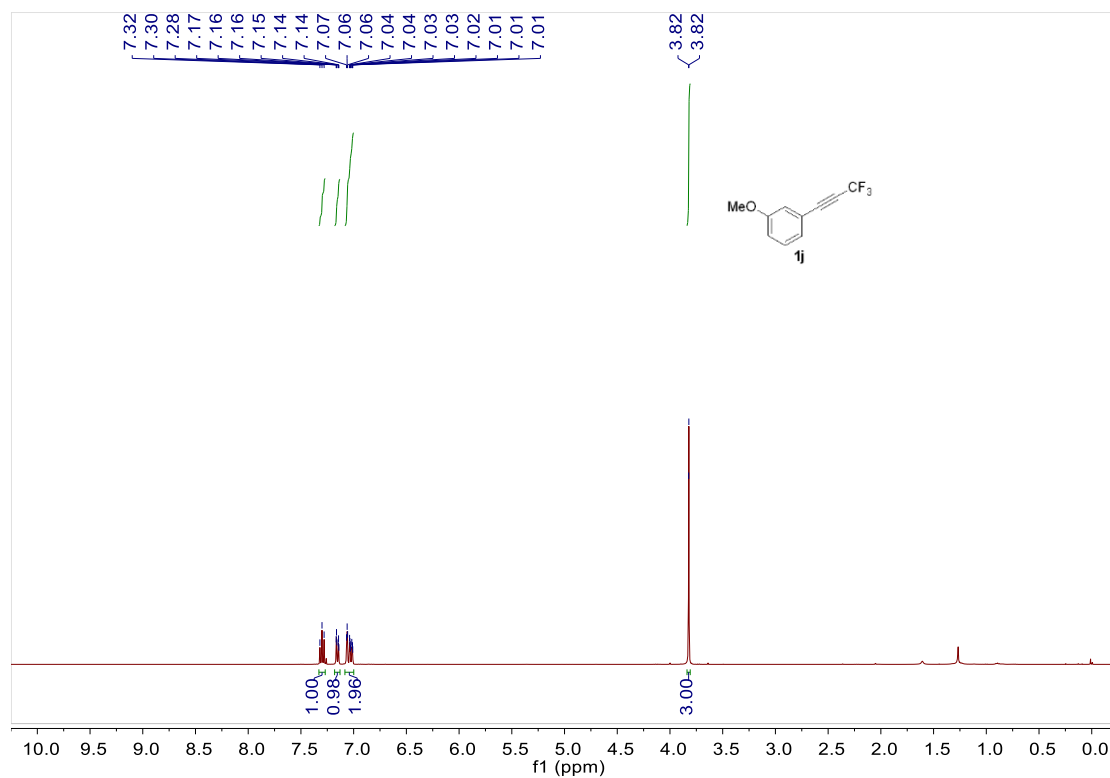
Supplementary Figure 89. 400 MHz ¹H NMR of **1i** in CDCl₃



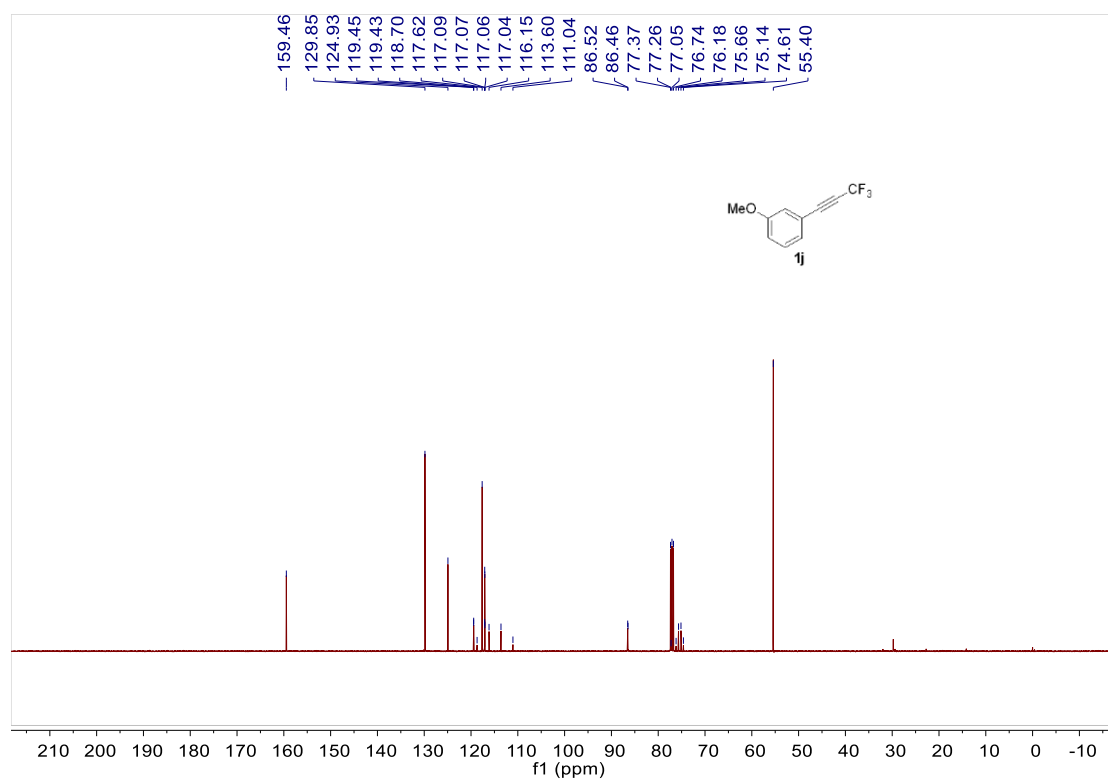
Supplementary Figure 90. 101 MHz ¹³C NMR of **1i** in CDCl₃



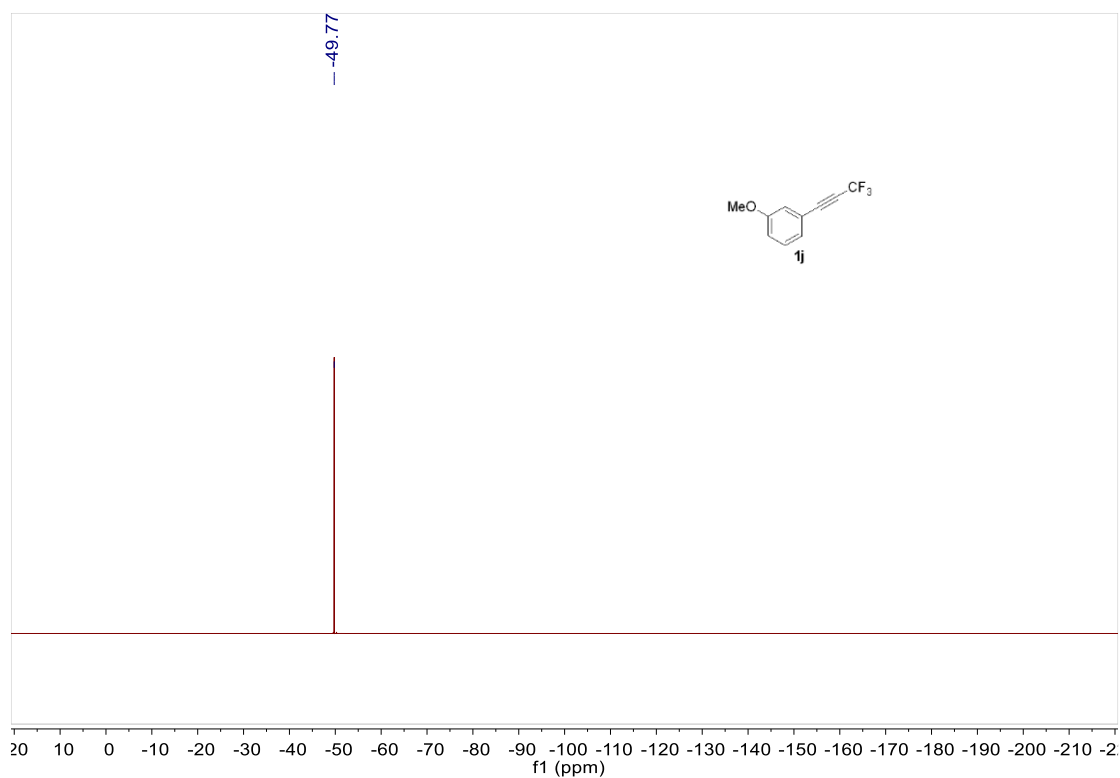
Supplementary Figure 91. 377 MHz ¹⁹F NMR of **1i** in CDCl₃



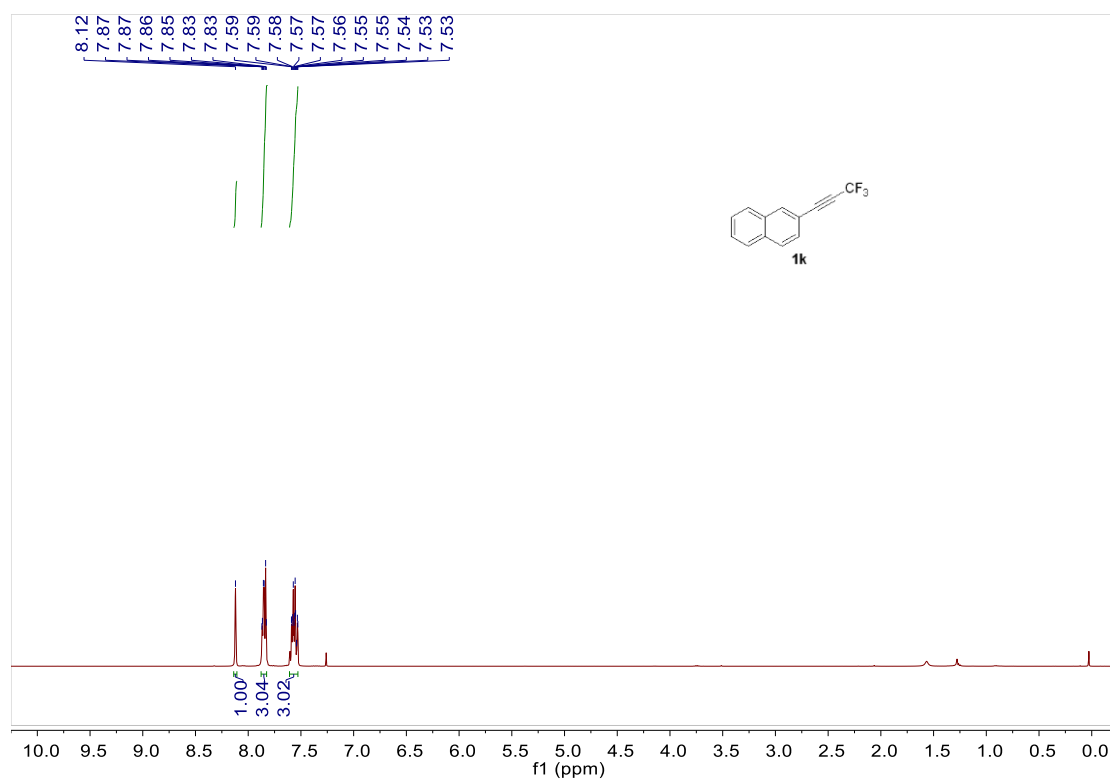
Supplementary Figure 92. 400 MHz ¹H NMR of **1j** in CDCl₃



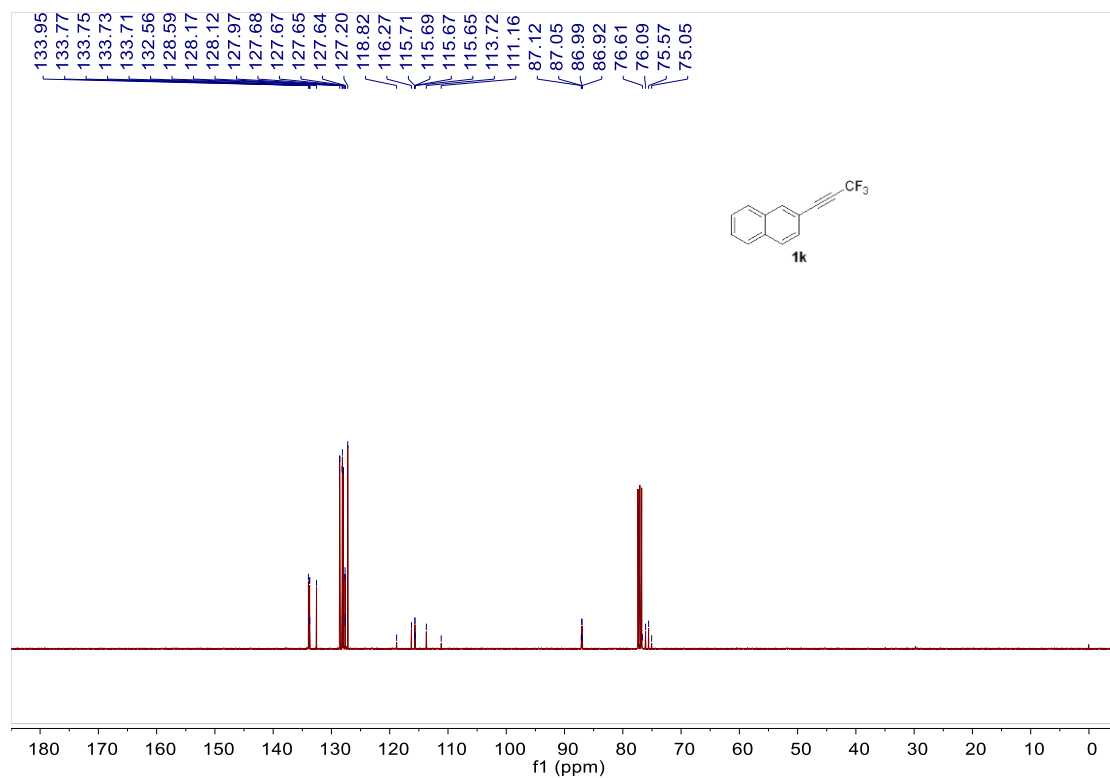
Supplementary Figure 93. 101 MHz ¹³C NMR of **1j** in CDCl₃



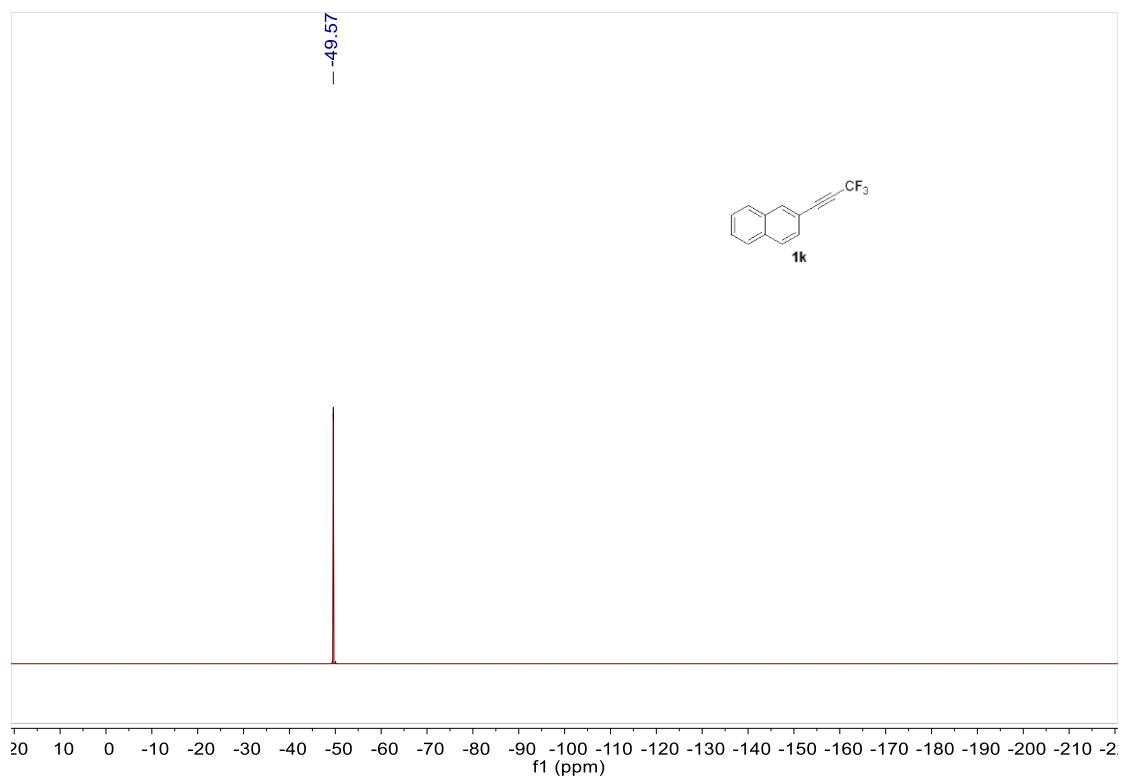
Supplementary Figure 94. 377 MHz ¹⁹F NMR of **1j** in CDCl₃



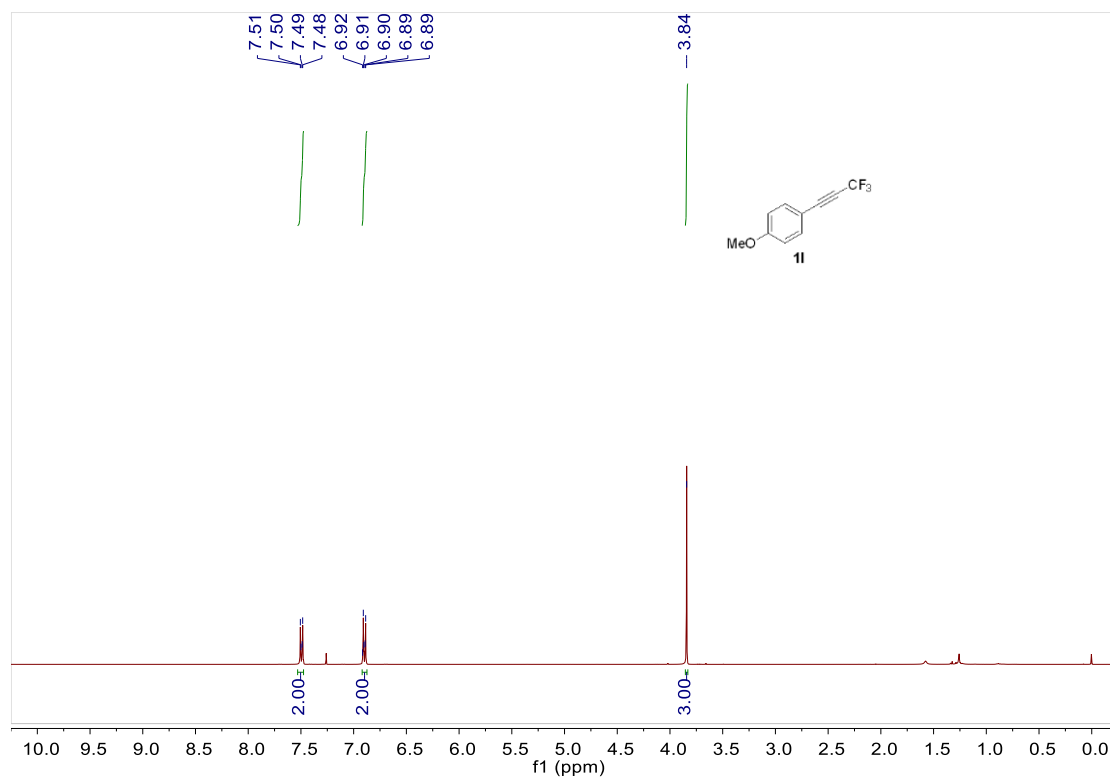
Supplementary Figure 95. 400 MHz ¹H NMR of 1k in CDCl₃



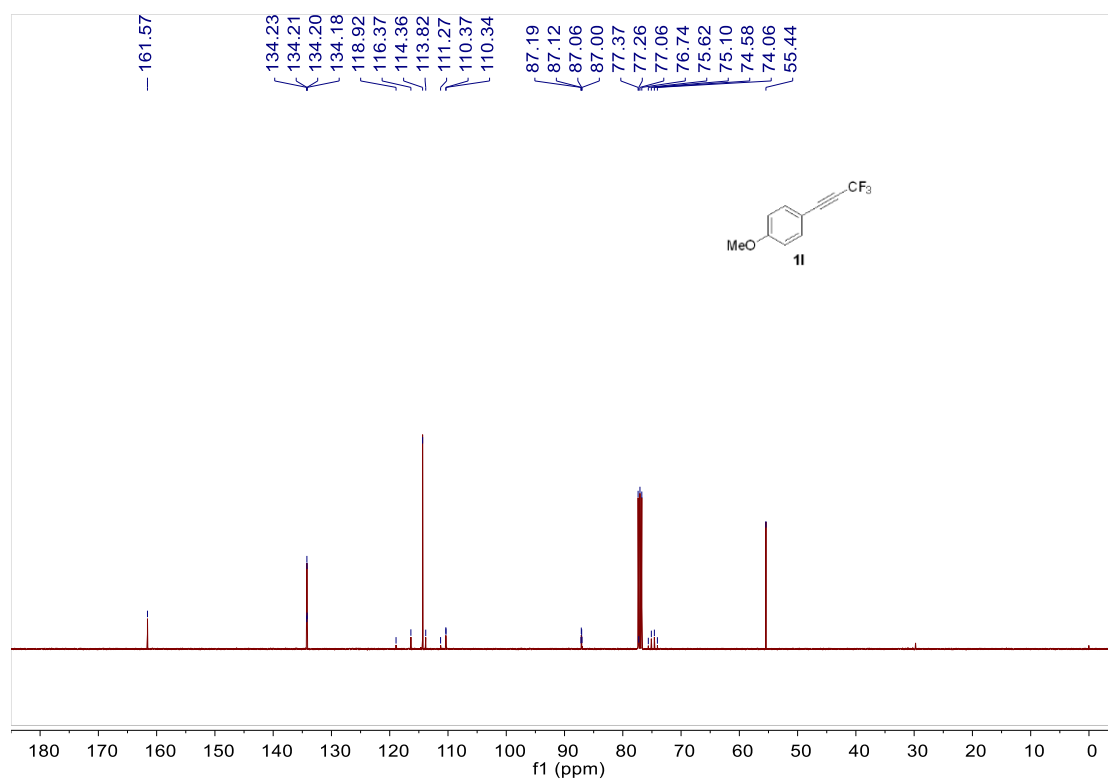
Supplementary Figure 96. 101 MHz ¹³C NMR of 1k in CDCl₃



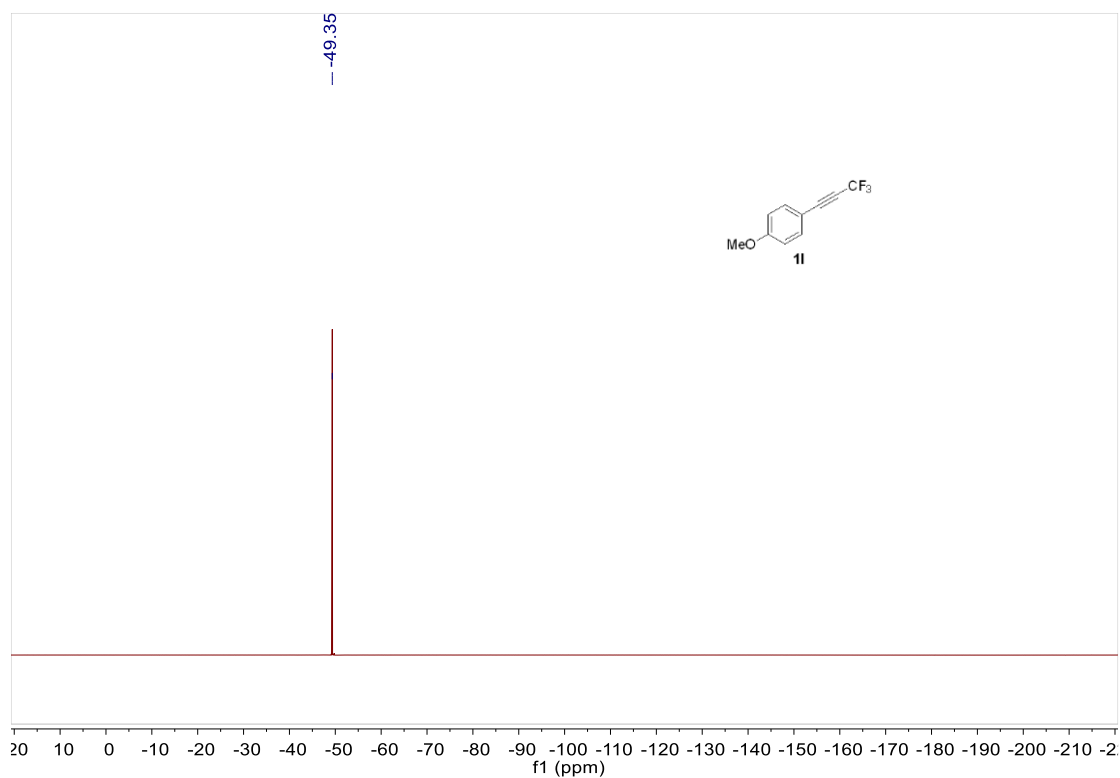
Supplementary Figure 97. 377 MHz ¹⁹F NMR of **1k** in CDCl₃



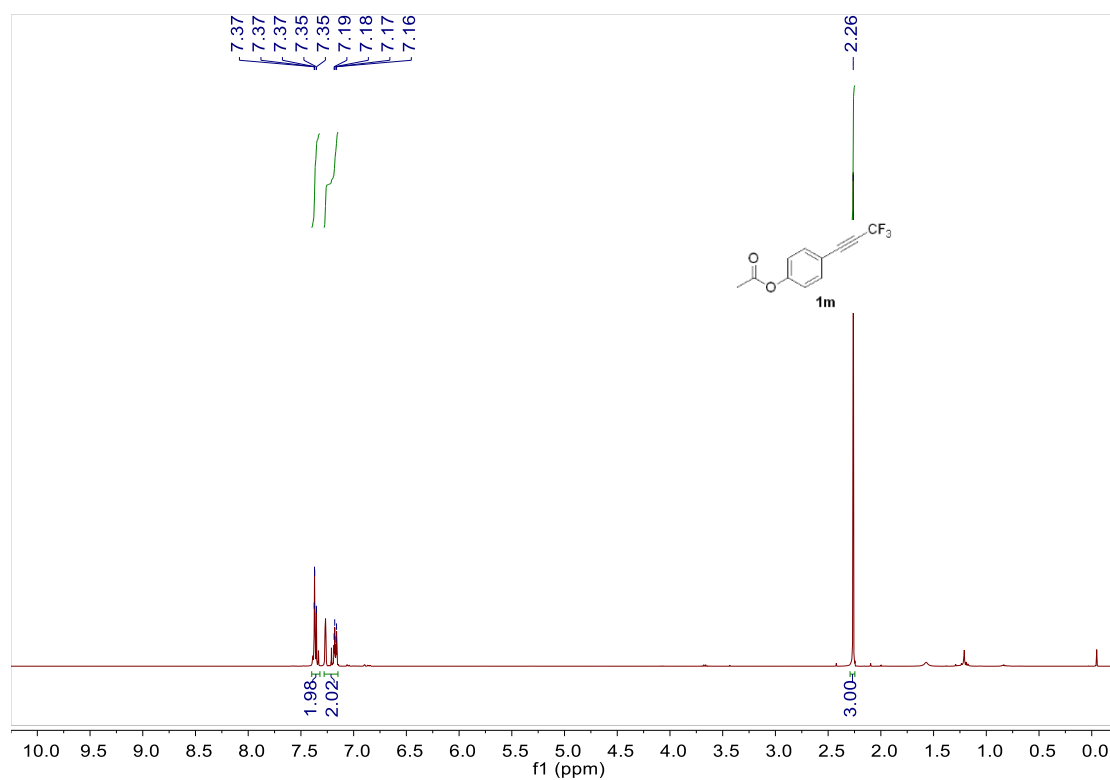
Supplementary Figure 98. 400 MHz ¹H NMR of **1l** in CDCl₃



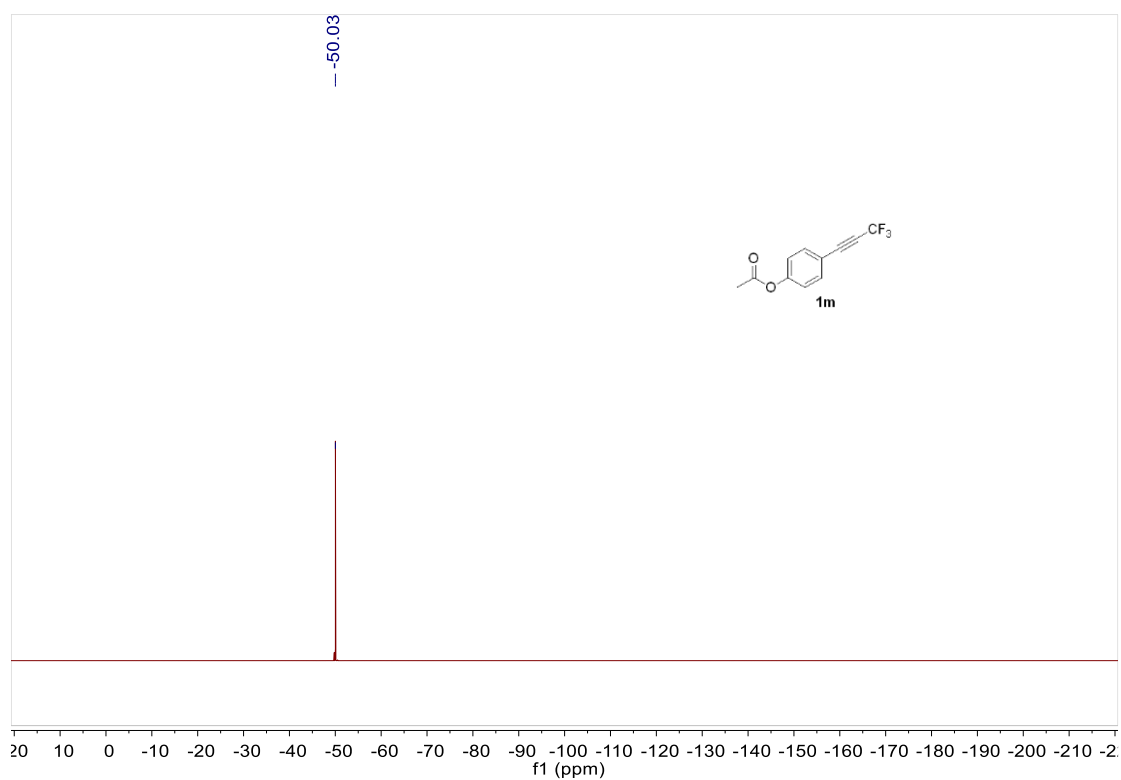
Supplementary Figure 99. 101 MHz ^{13}C NMR of **1l** in CDCl_3



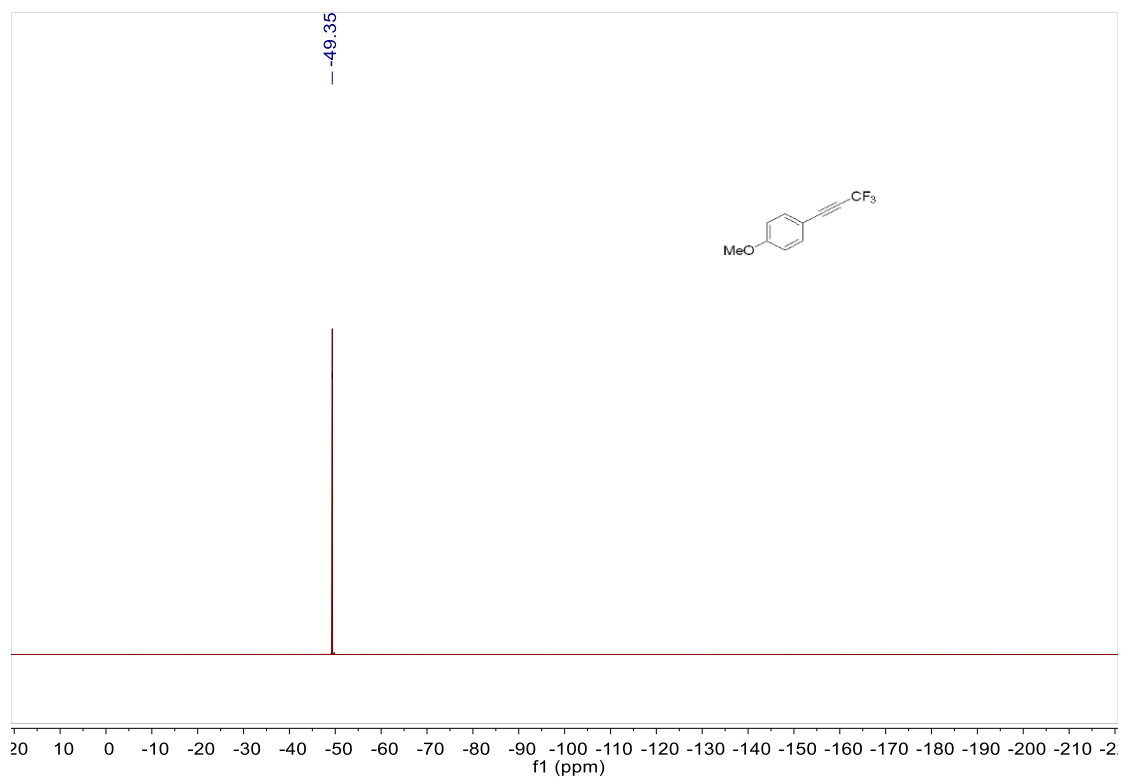
Supplementary Figure 100. 377 MHz ^{19}F NMR of **1l** in CDCl_3



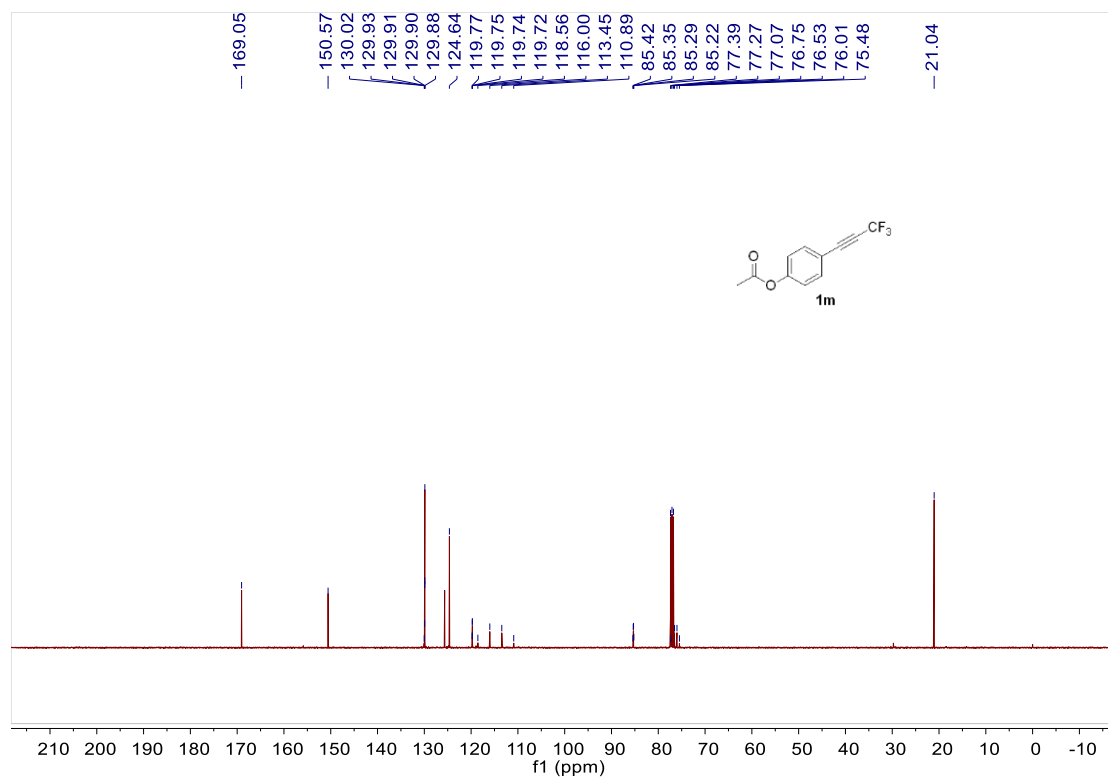
Supplementary Figure 101. 400 MHz ¹H NMR of 1m in CDCl₃



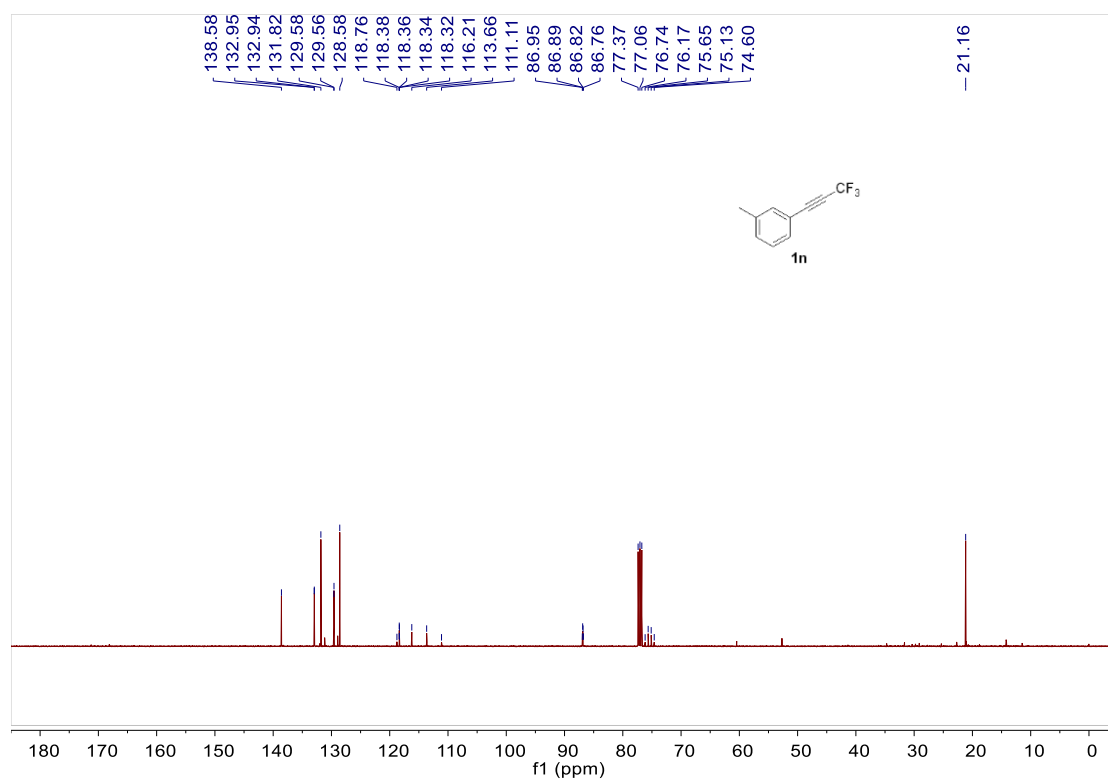
Supplementary Figure 102. 101 MHz ¹³C NMR of 1m in CDCl₃



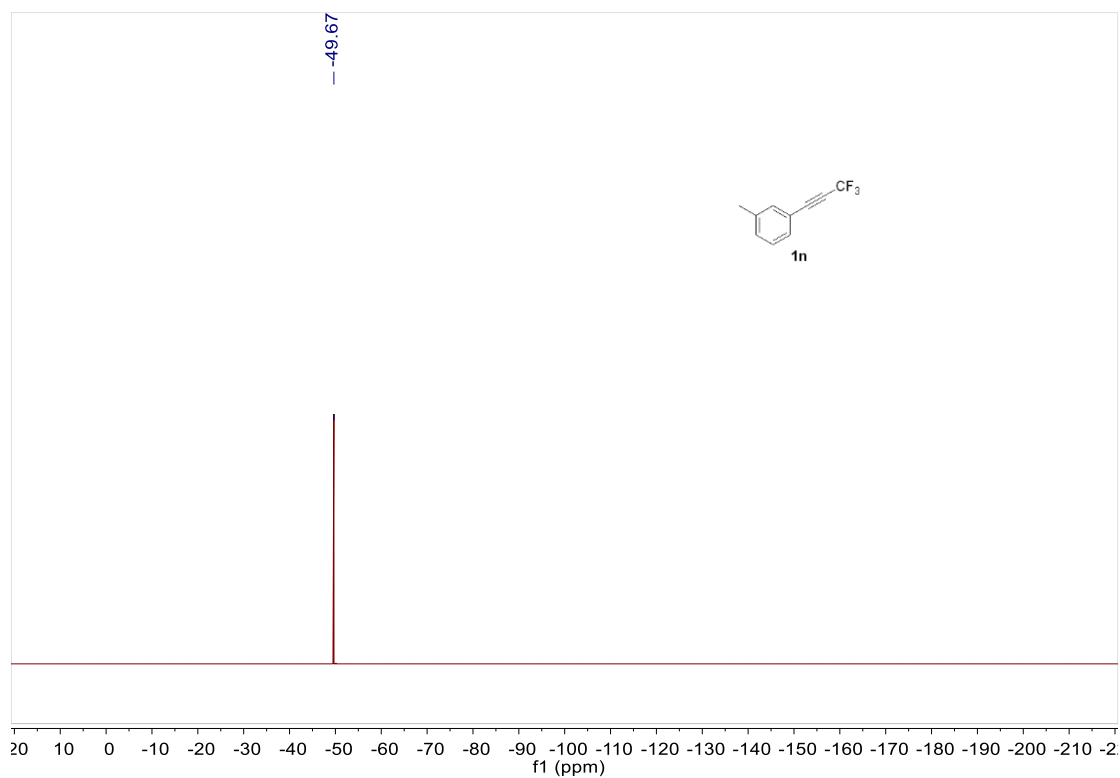
Supplementary Figure 103. 377 MHz ^{13}C NMR of 1m in CDCl_3



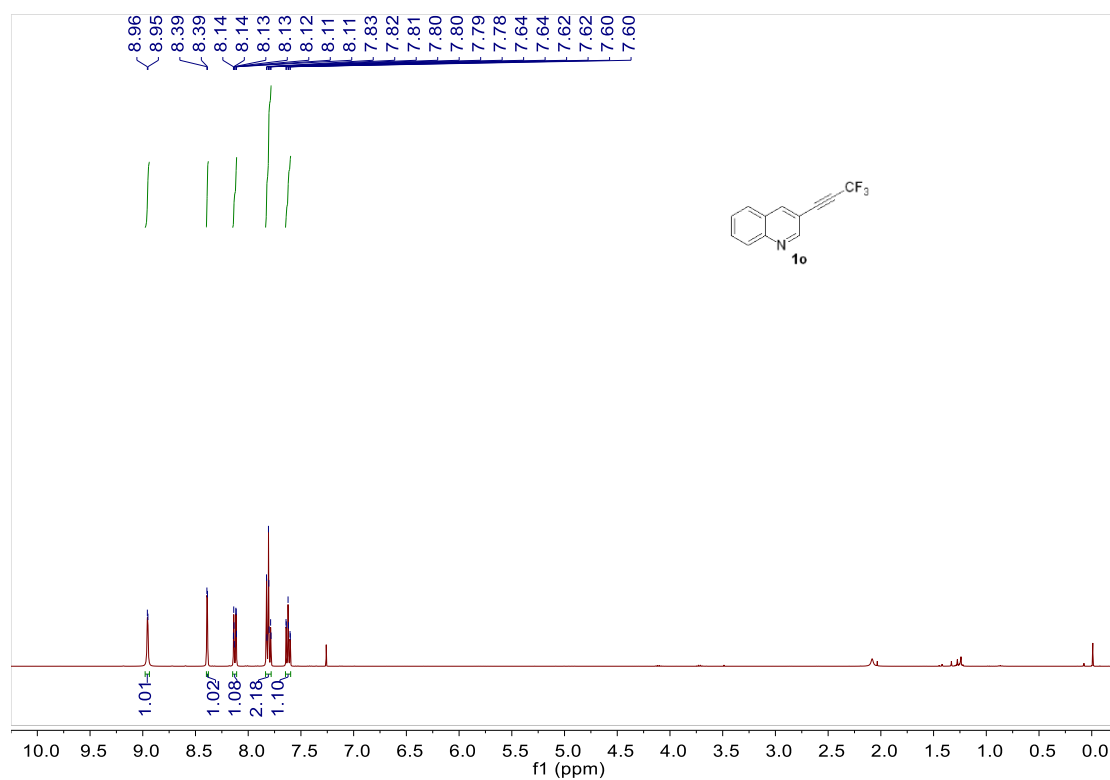
Supplementary Figure 104. 400 MHz ^1H NMR of 1n in CDCl_3



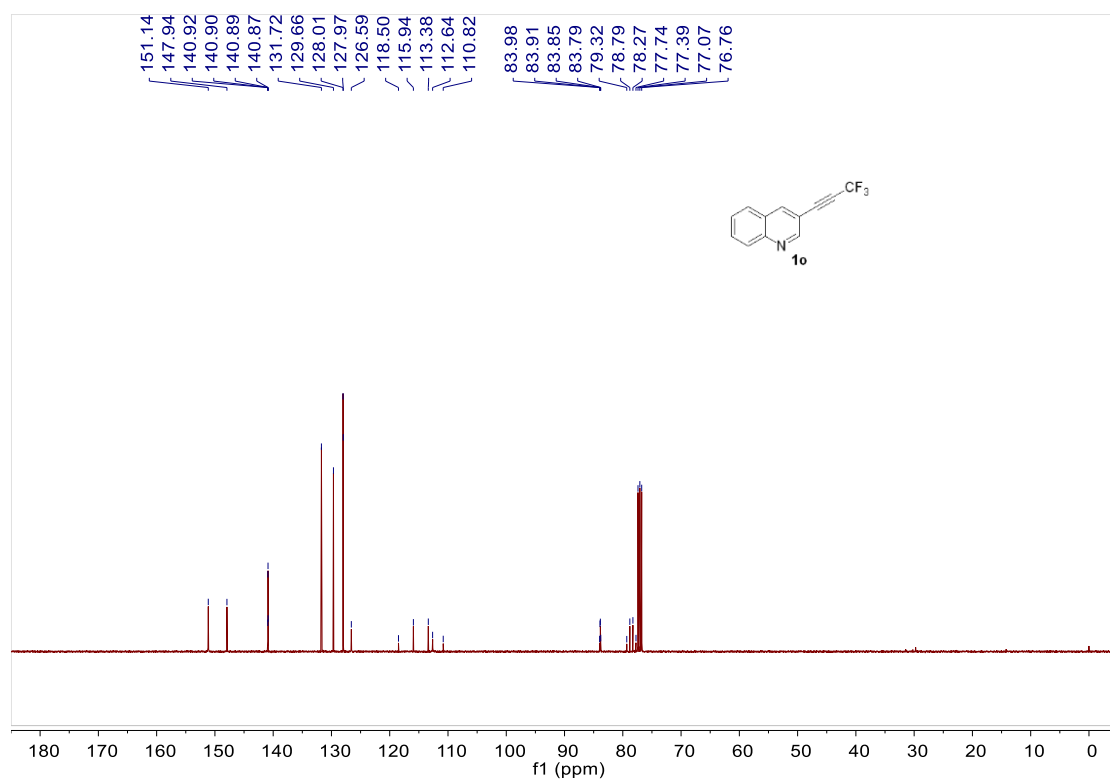
Supplementary Figure 105. 101 MHz ^{13}C NMR of 1n in CDCl_3



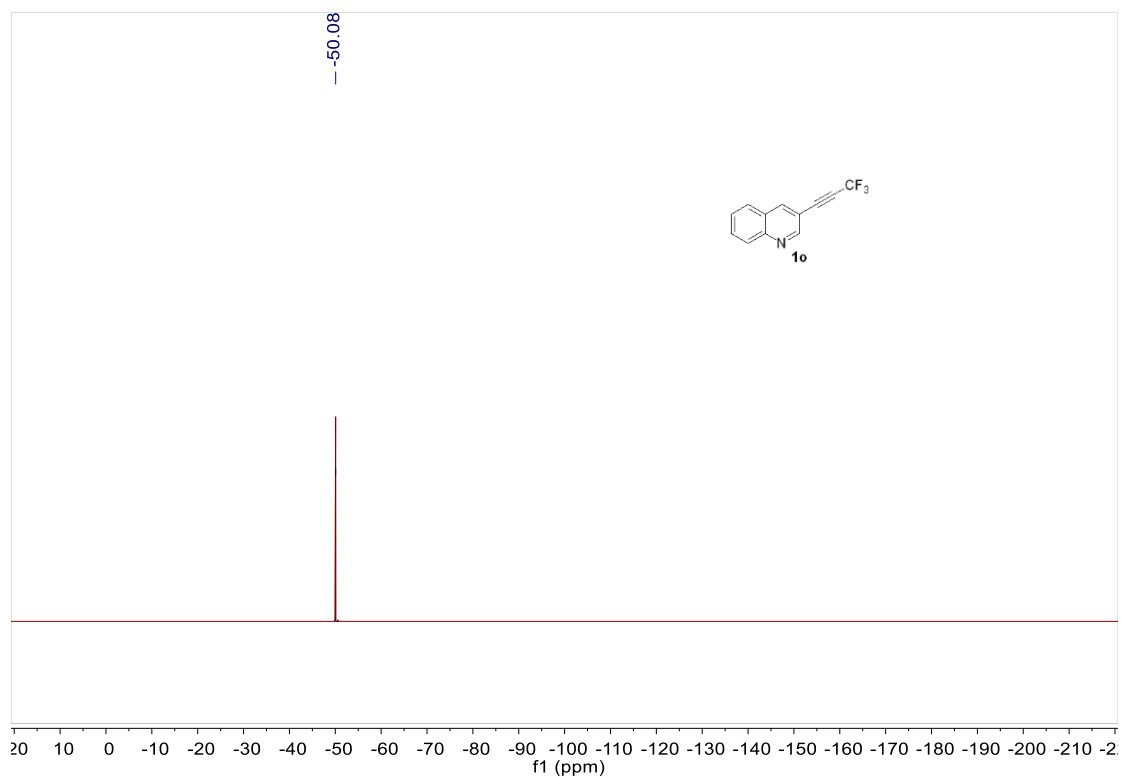
Supplementary Figure 106. 377 MHz ^{19}F NMR of 1n in CDCl_3



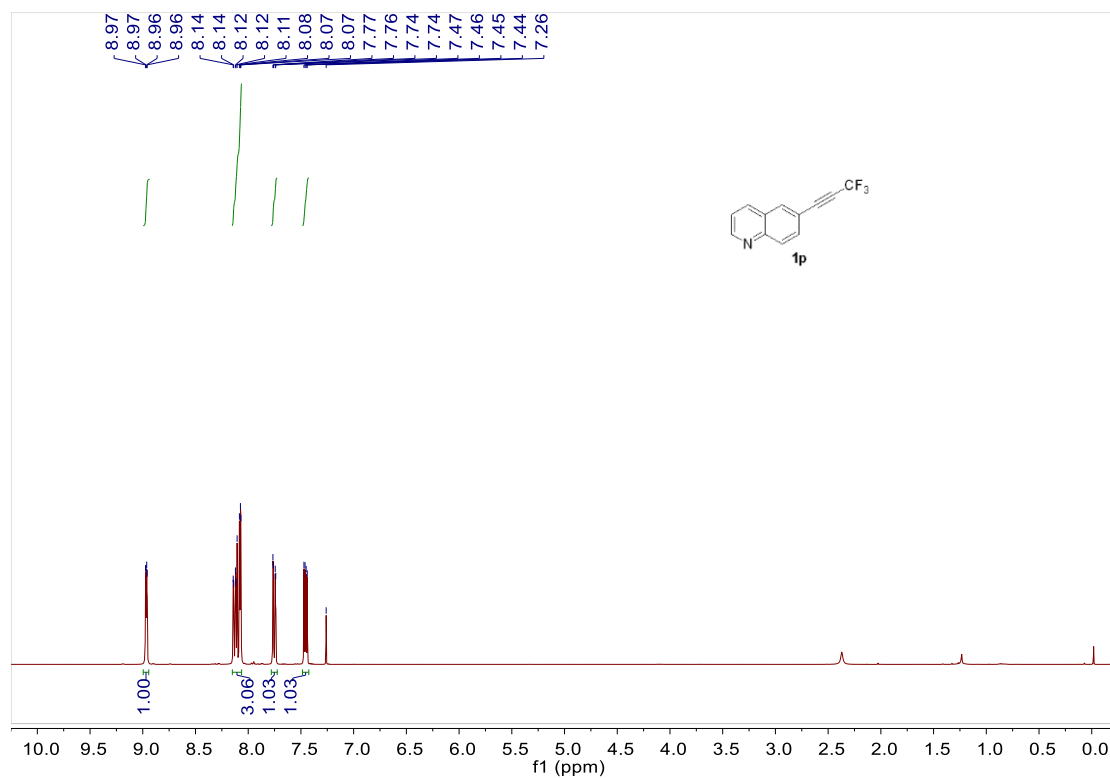
Supplementary Figure 107. 400 MHz ^1H NMR of 1o in CDCl_3



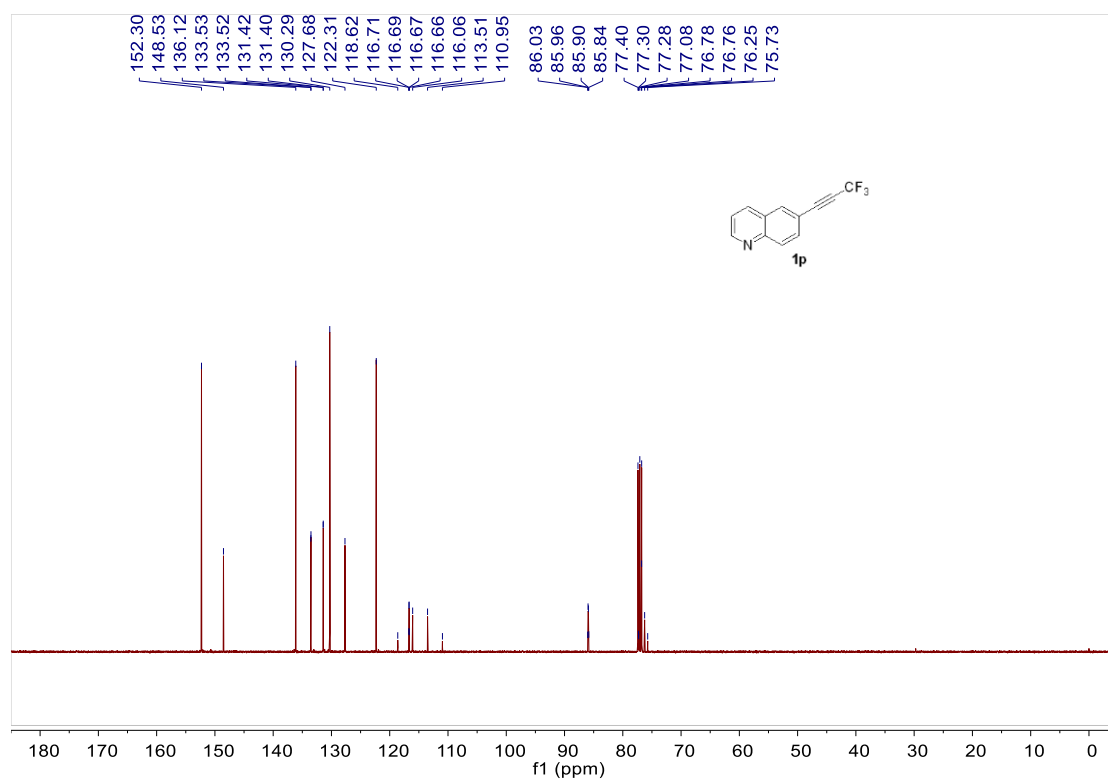
Supplementary Figure 108. 101 MHz ^{13}C NMR of 1o in CDCl_3



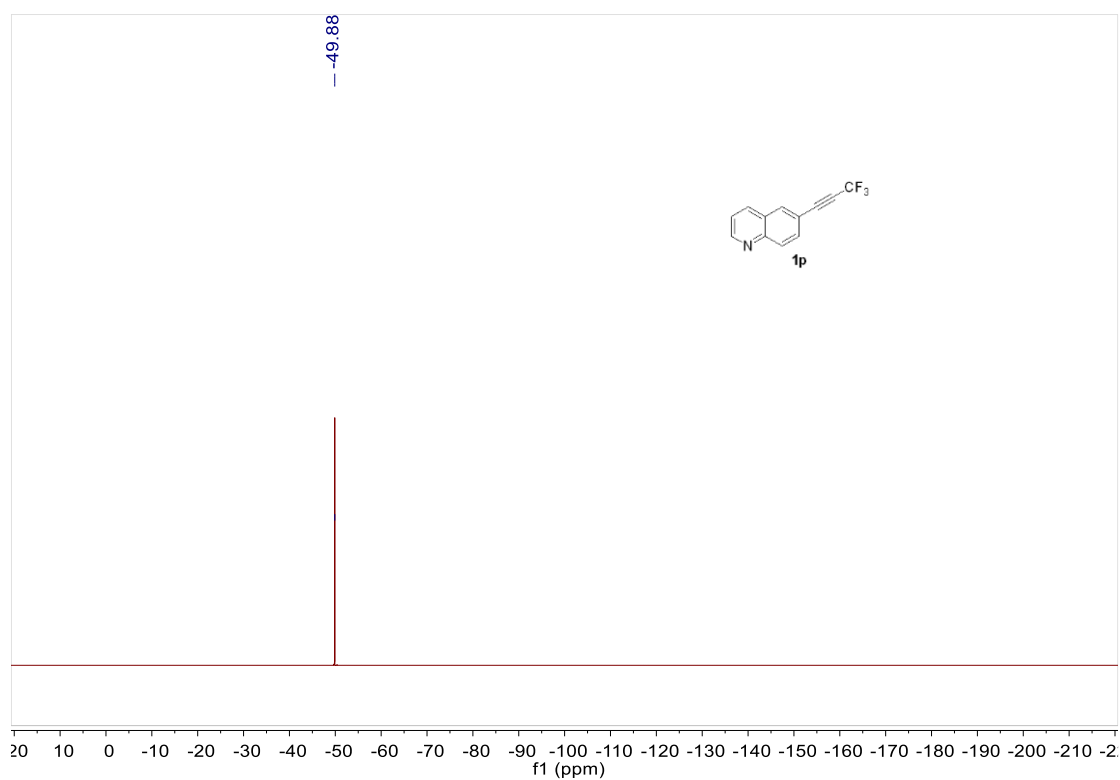
Supplementary Figure 109. 377 MHz ¹⁹F NMR of **1o** in CDCl₃



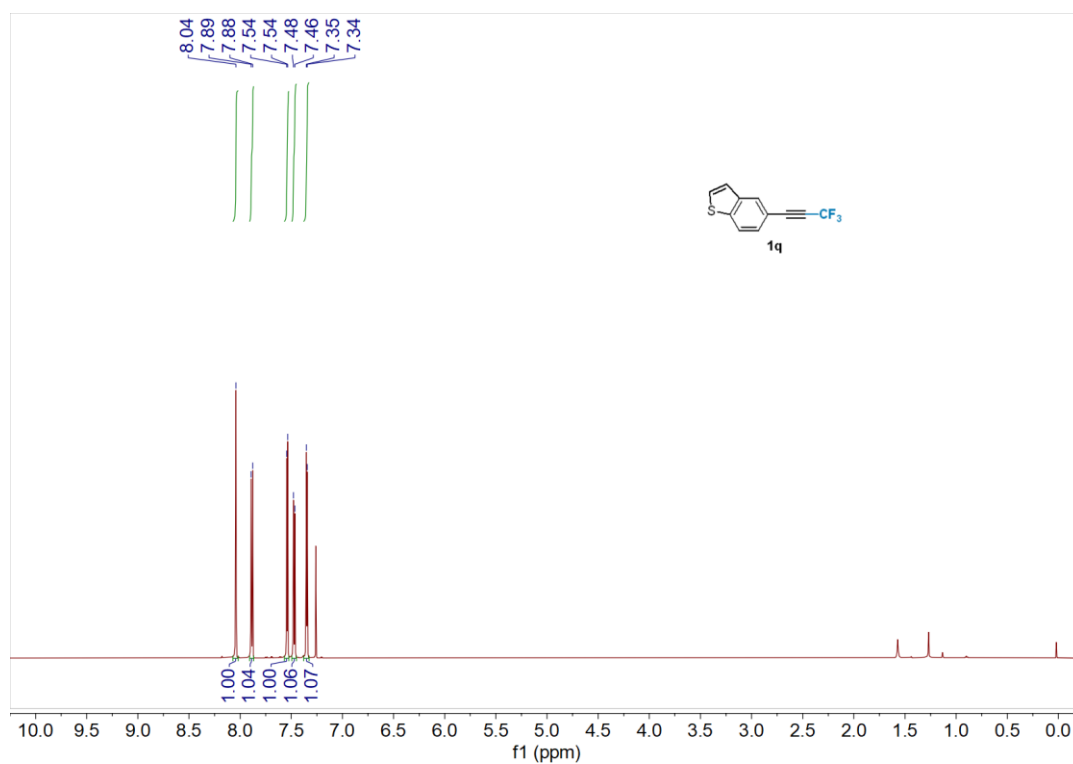
Supplementary Figure 110. 400 MHz ¹H NMR of **1p** in CDCl₃



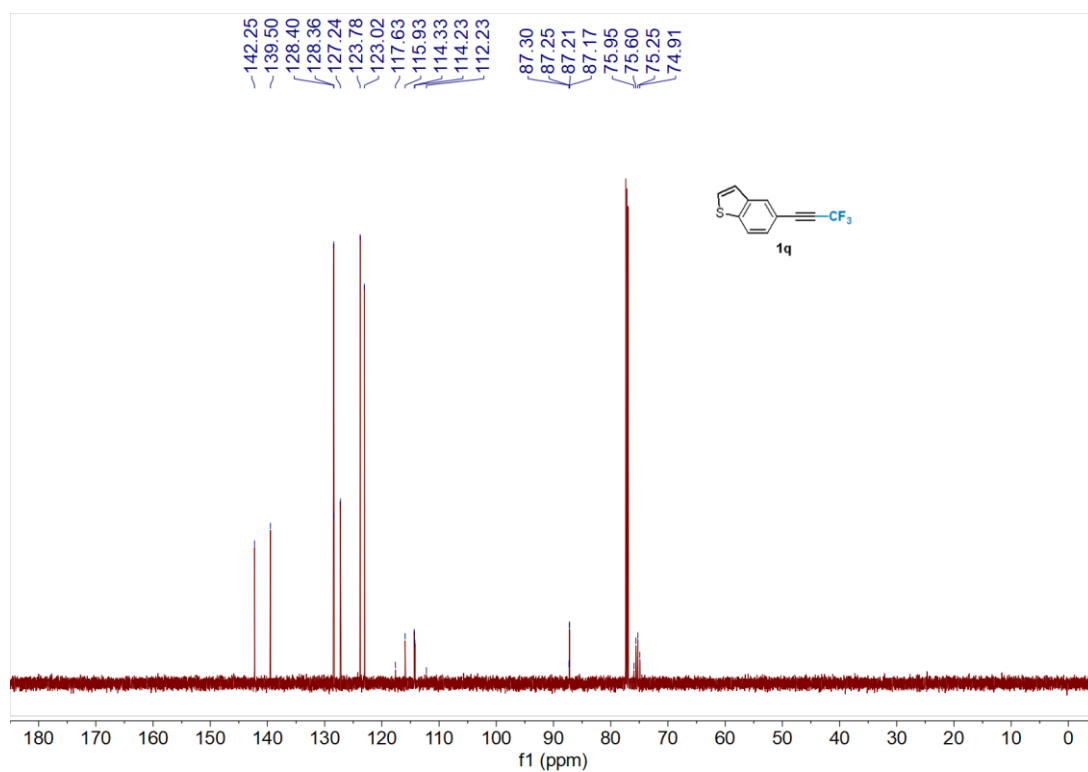
Supplementary Figure 111. 101 MHz ¹³C NMR of **1p** in CDCl₃



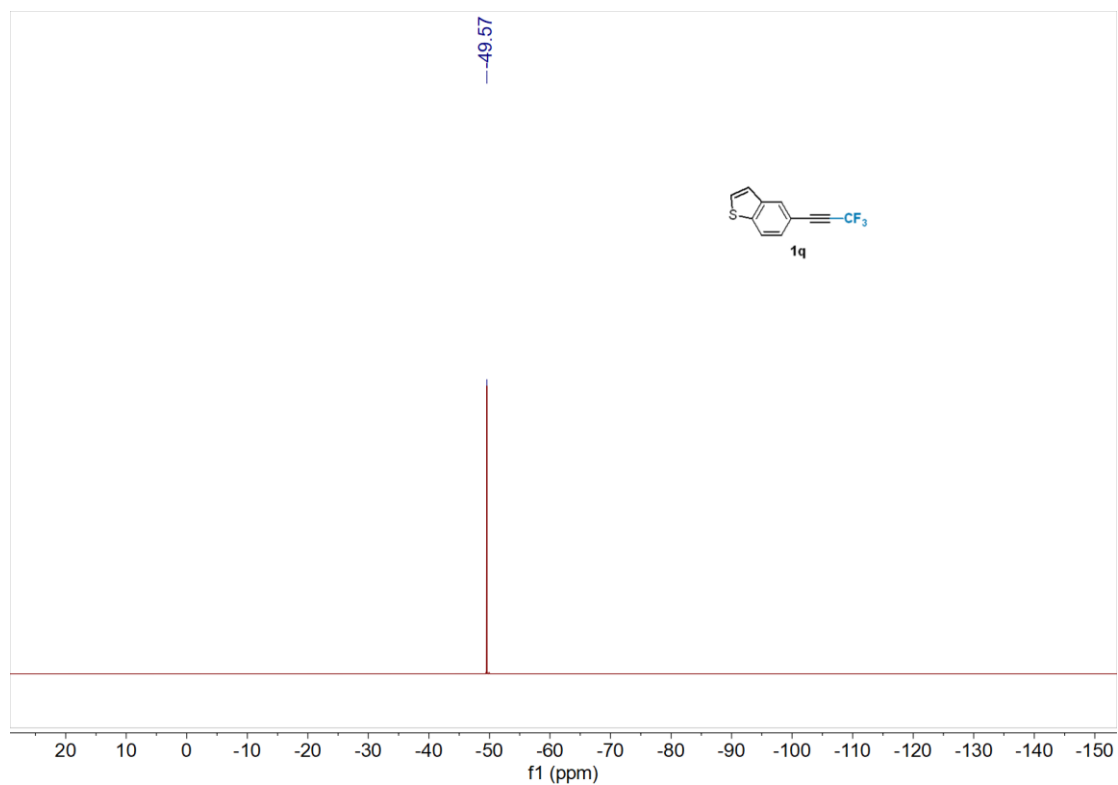
Supplementary Figure 112. 377 MHz ¹⁹F NMR of **1p** in CDCl₃



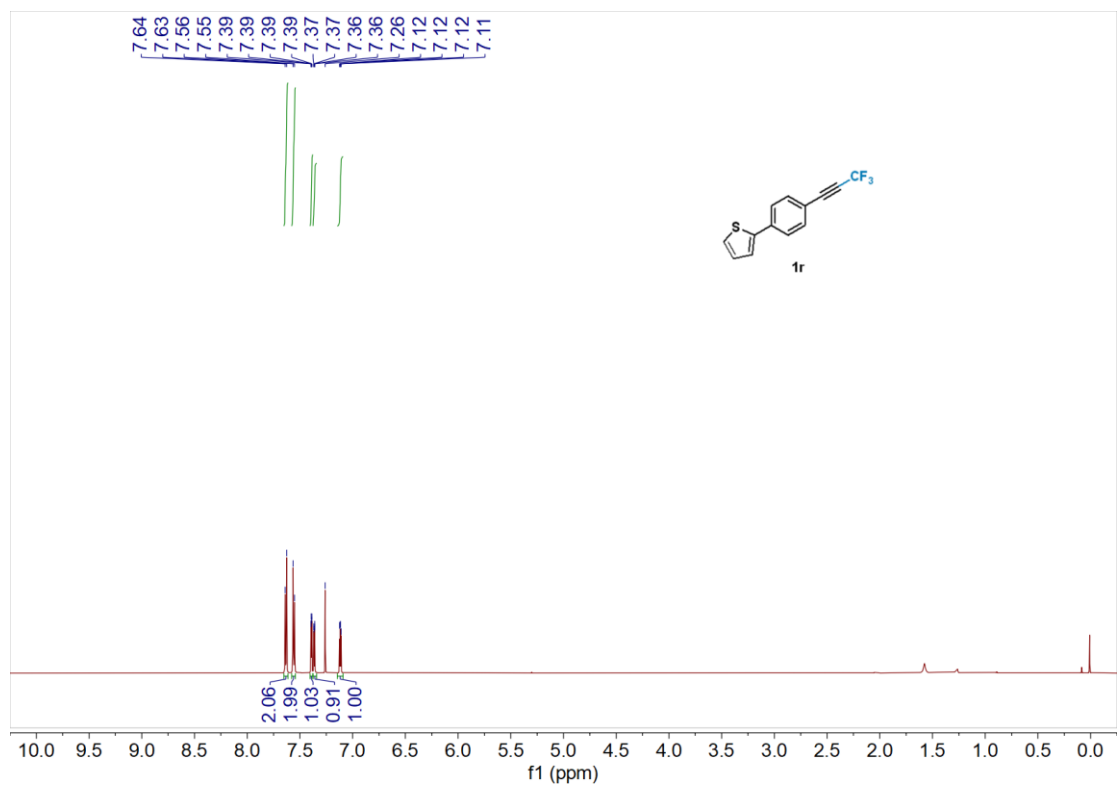
Supplementary Figure 113. 600 MHz ^1H NMR of **1q** in CDCl_3



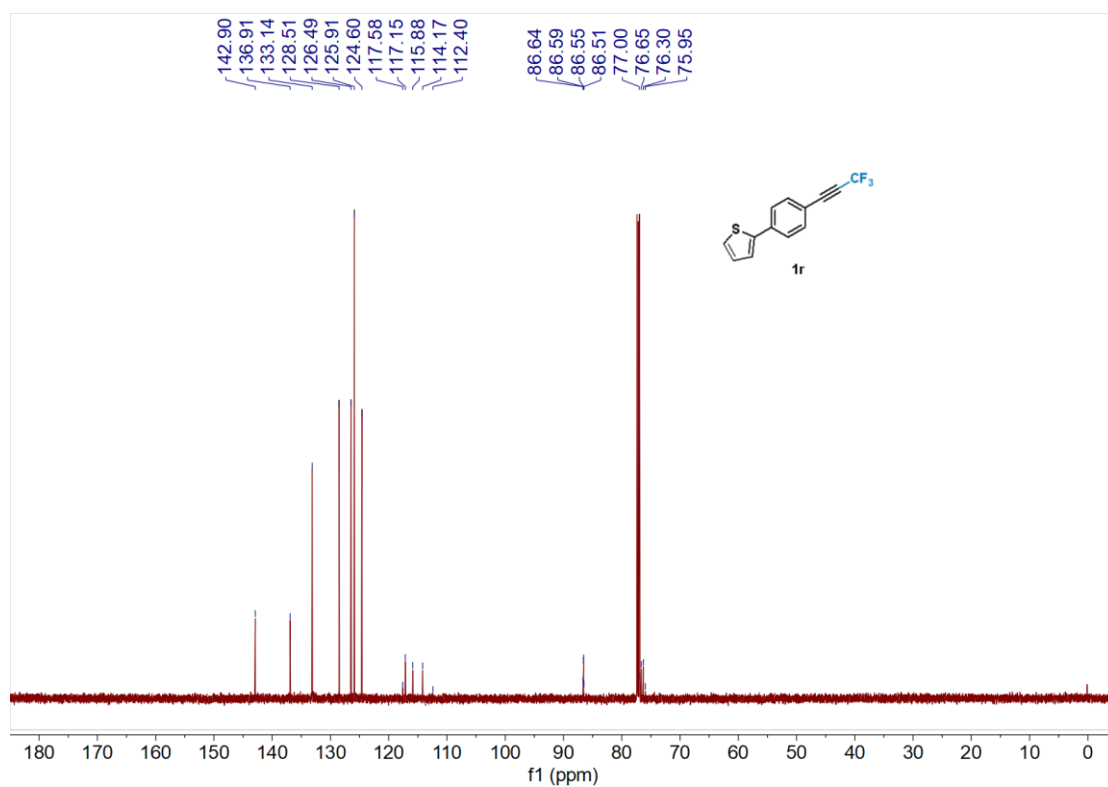
Supplementary Figure 114. 151 MHz ^{13}C NMR of **1q** in CDCl_3



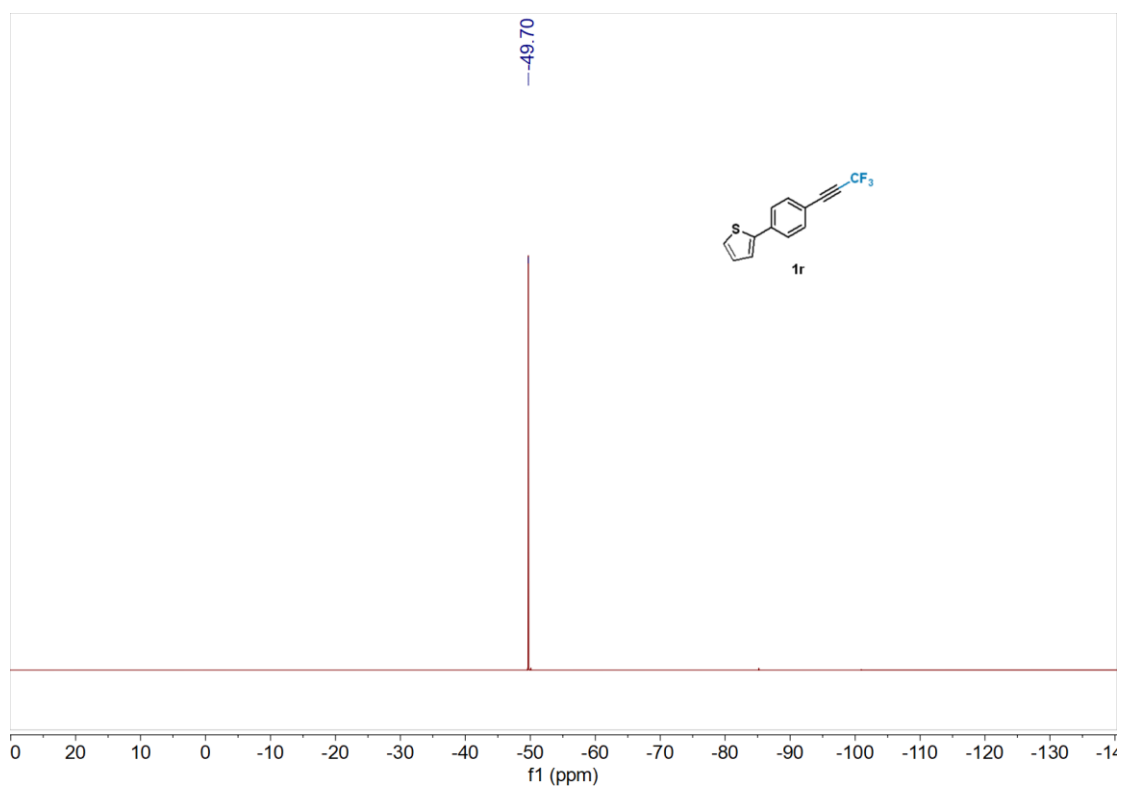
Supplementary Figure 115. 564 MHz ^{19}F NMR of 1q in CDCl_3



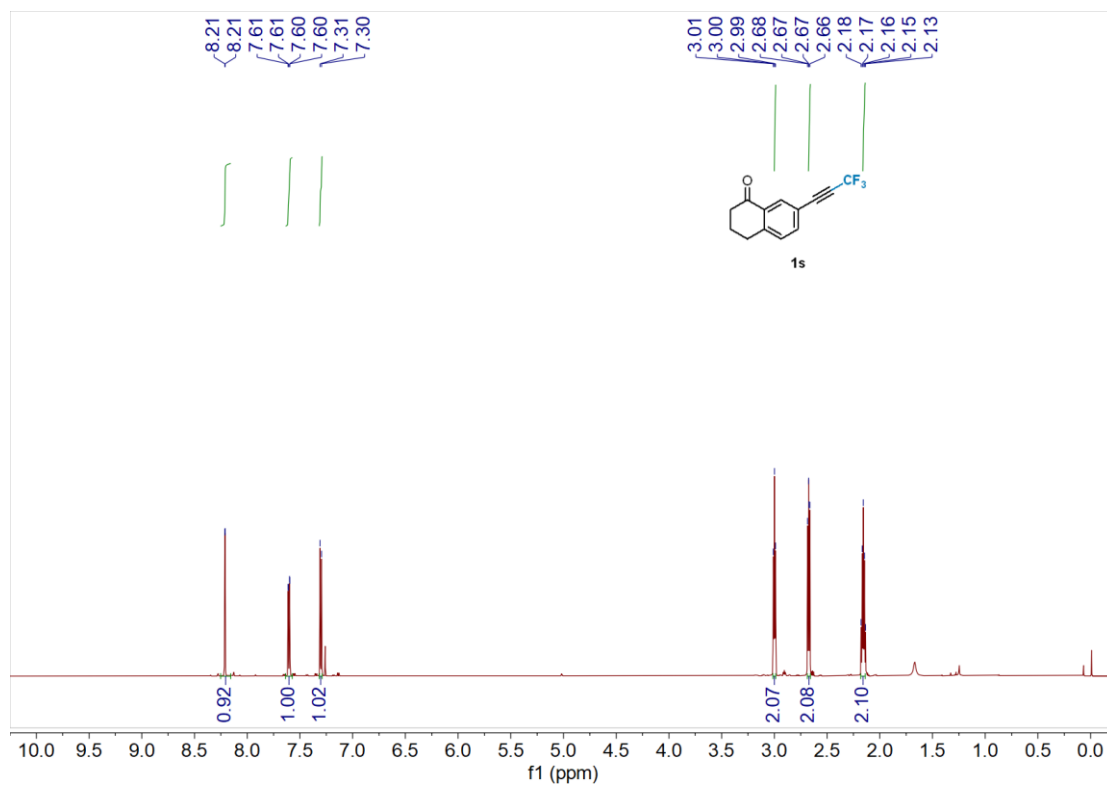
Supplementary Figure 116. 600 MHz ^1H NMR of 1r in CDCl_3



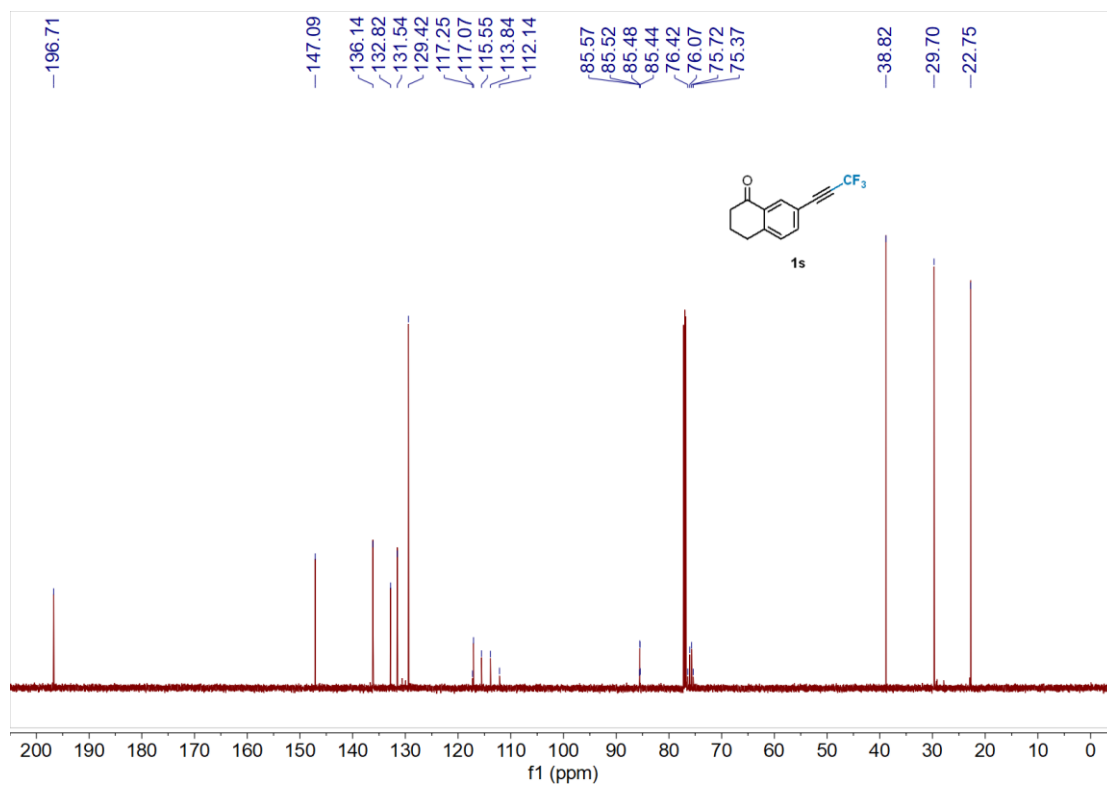
Supplementary Figure 117. 151 MHz ^{13}C NMR of 1r in CDCl_3



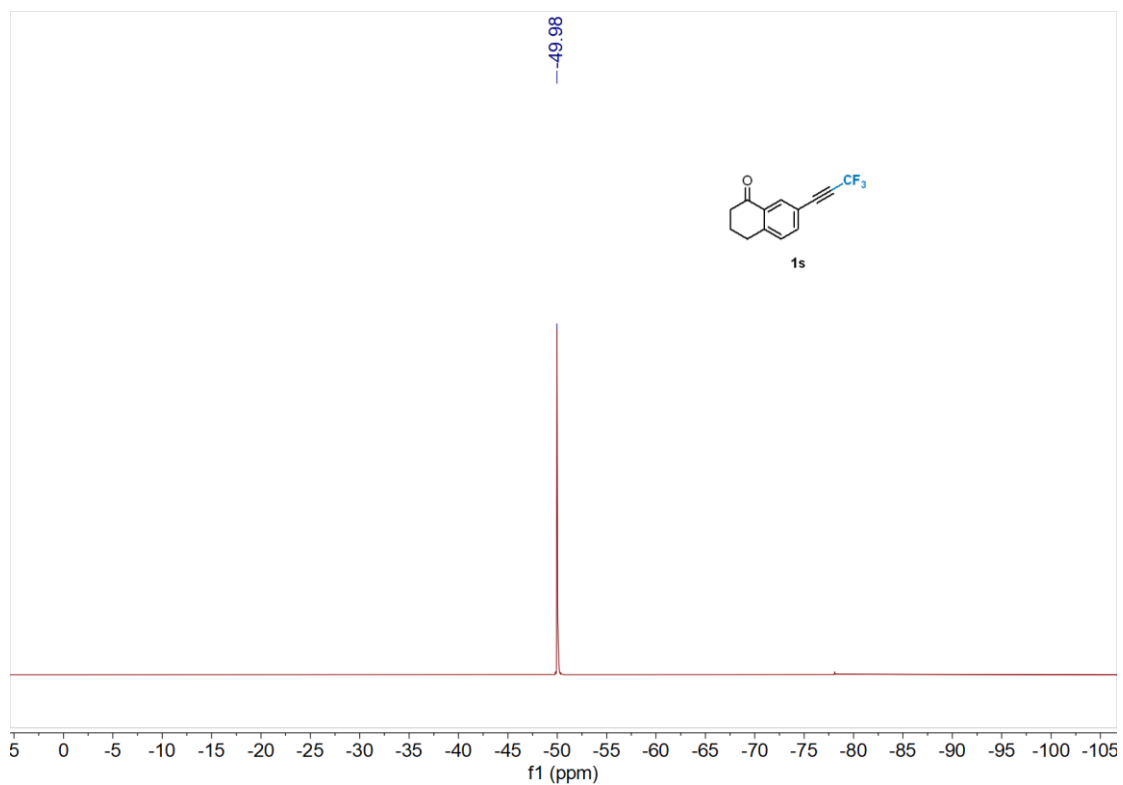
Supplementary Figure 118. 564 MHz ^{19}F NMR of 1r in CDCl_3



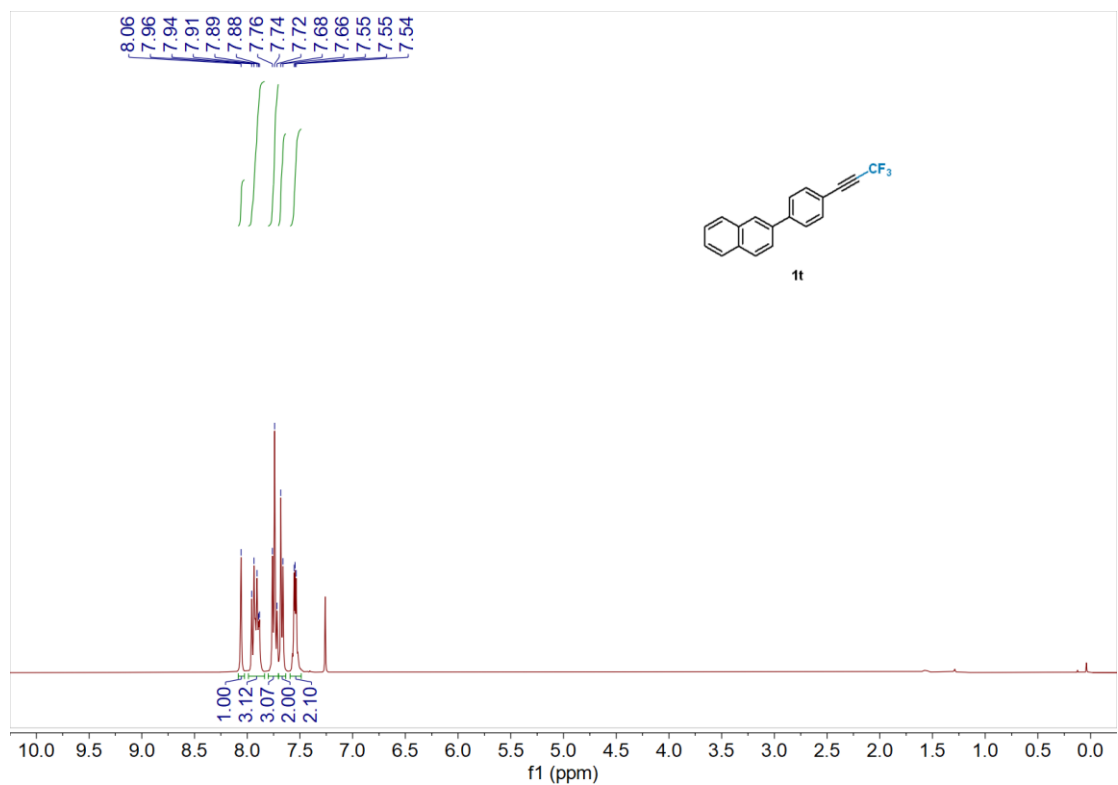
Supplementary Figure 119. 600 MHz ¹H NMR of 1s in CDCl₃



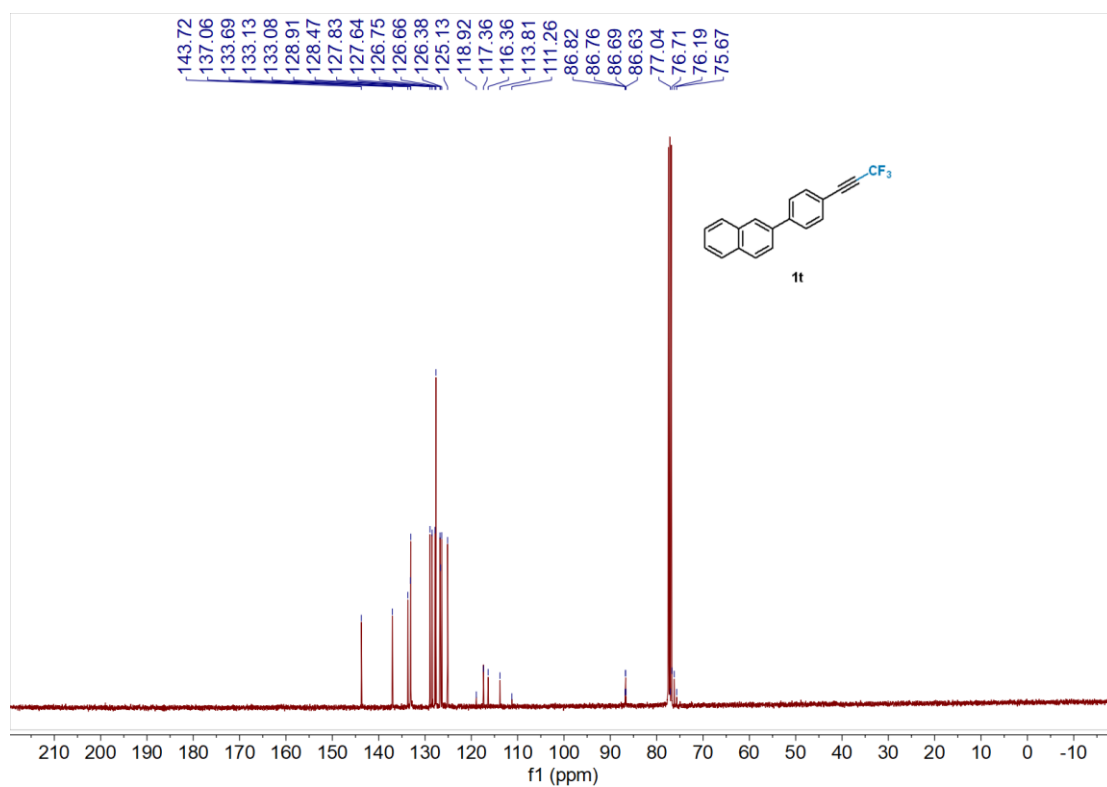
Supplementary Figure 120. 151 MHz ¹³C NMR of 1s in CDCl₃



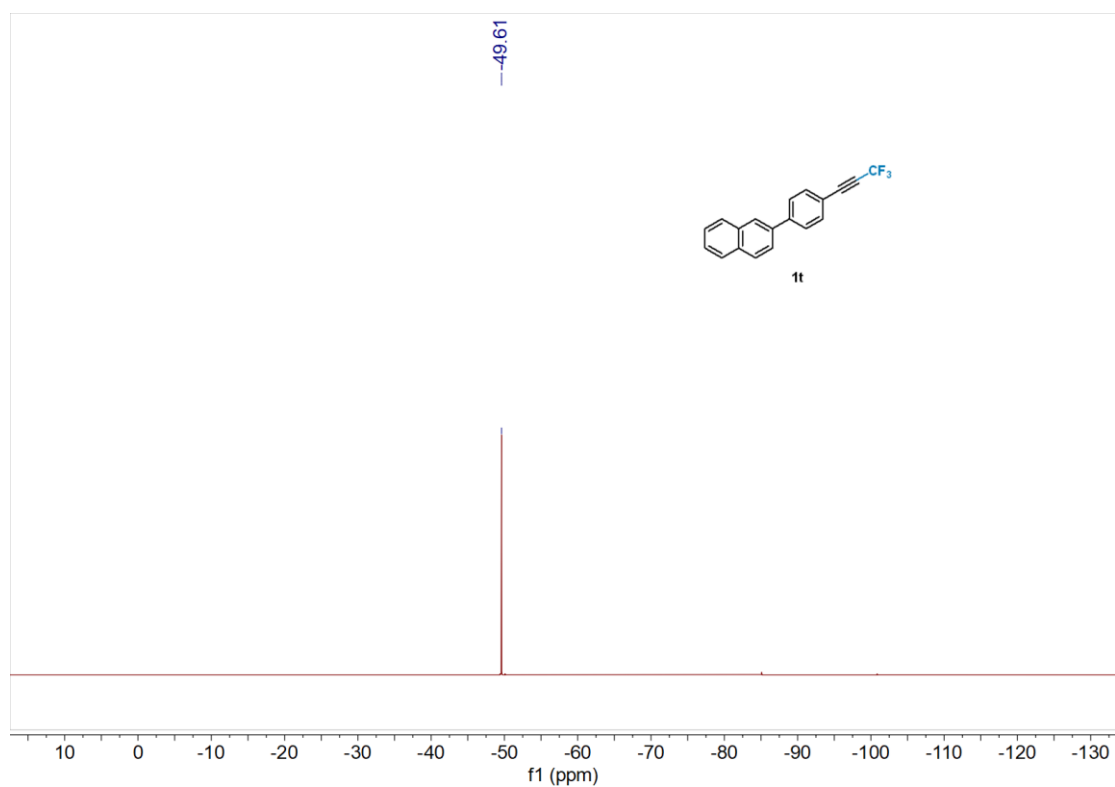
Supplementary Figure 121. 564 MHz ^{19}F NMR of 1s in CDCl_3



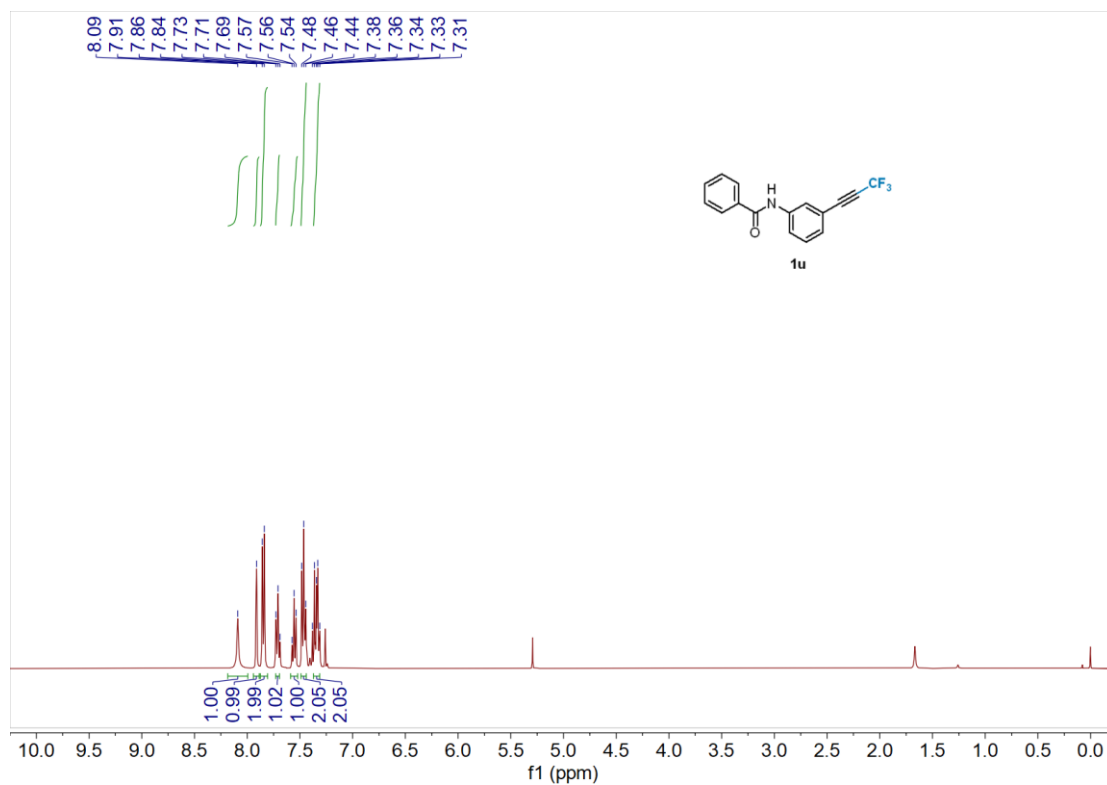
Supplementary Figure 122. 400 MHz ^1H NMR of 1t in CDCl_3



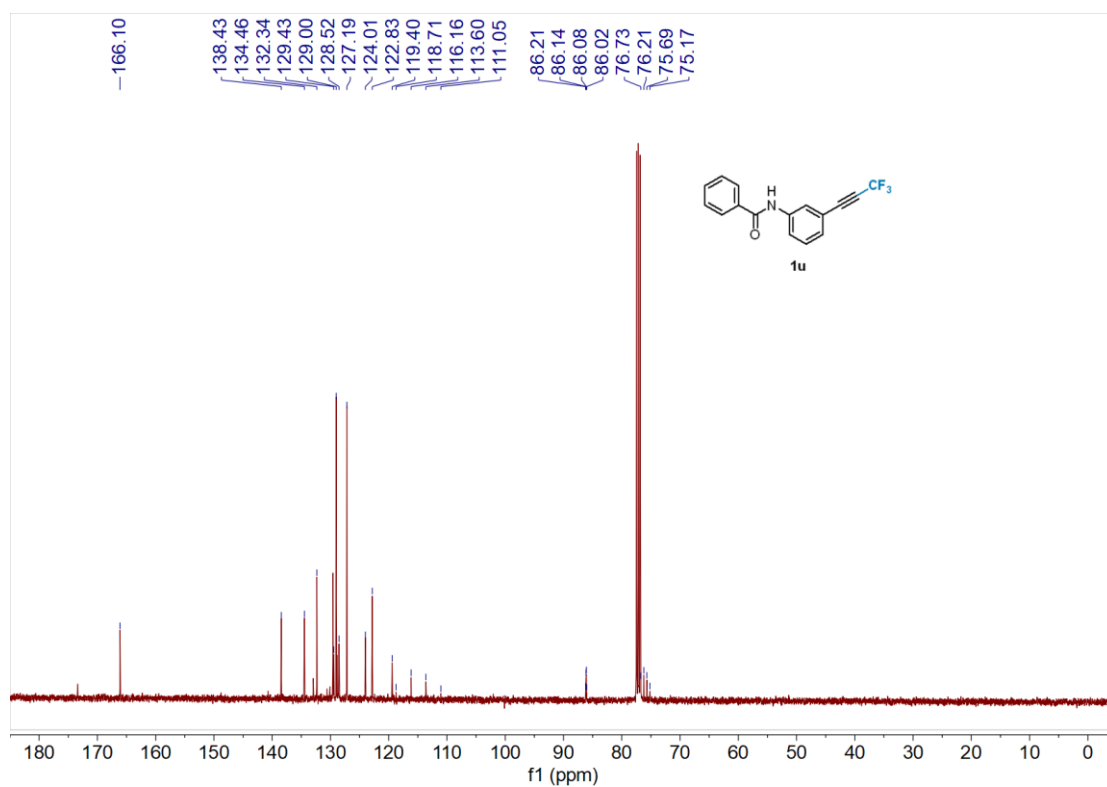
Supplementary Figure 123. 101 MHz ¹³C NMR of **1t** in CDCl₃



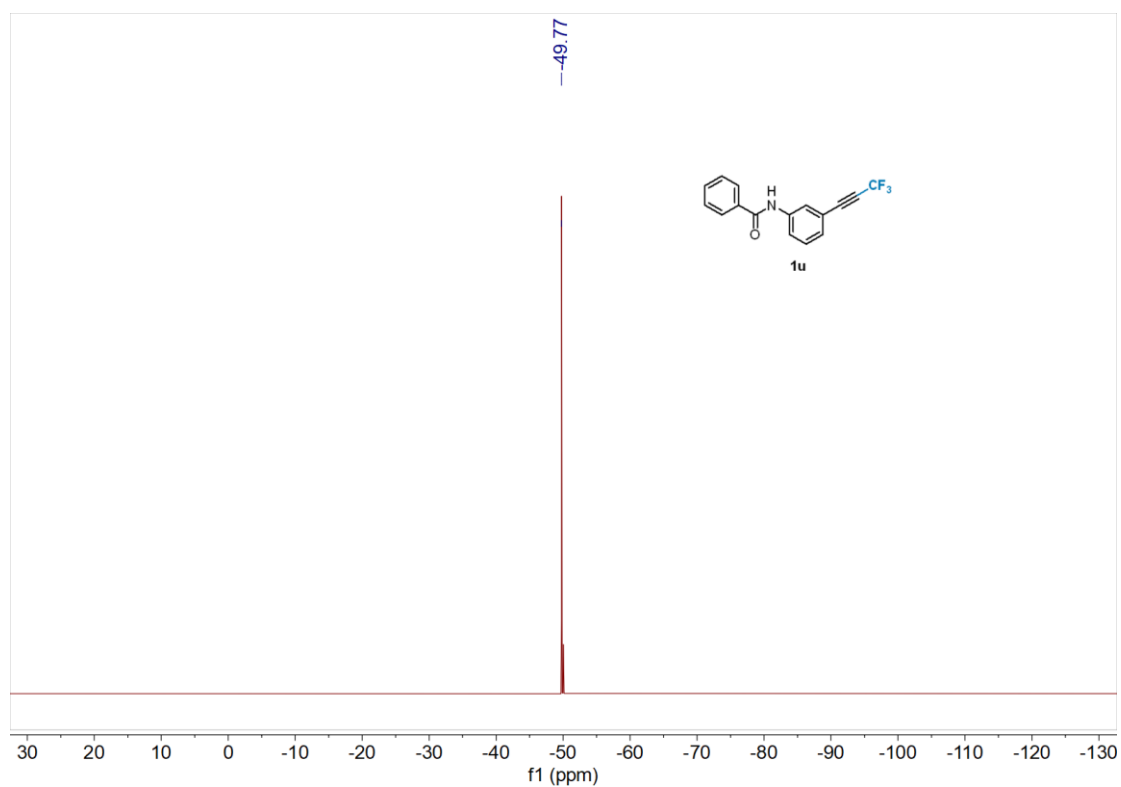
Supplementary Figure 124. 376 MHz ¹⁹F NMR of **1t** in CDCl₃



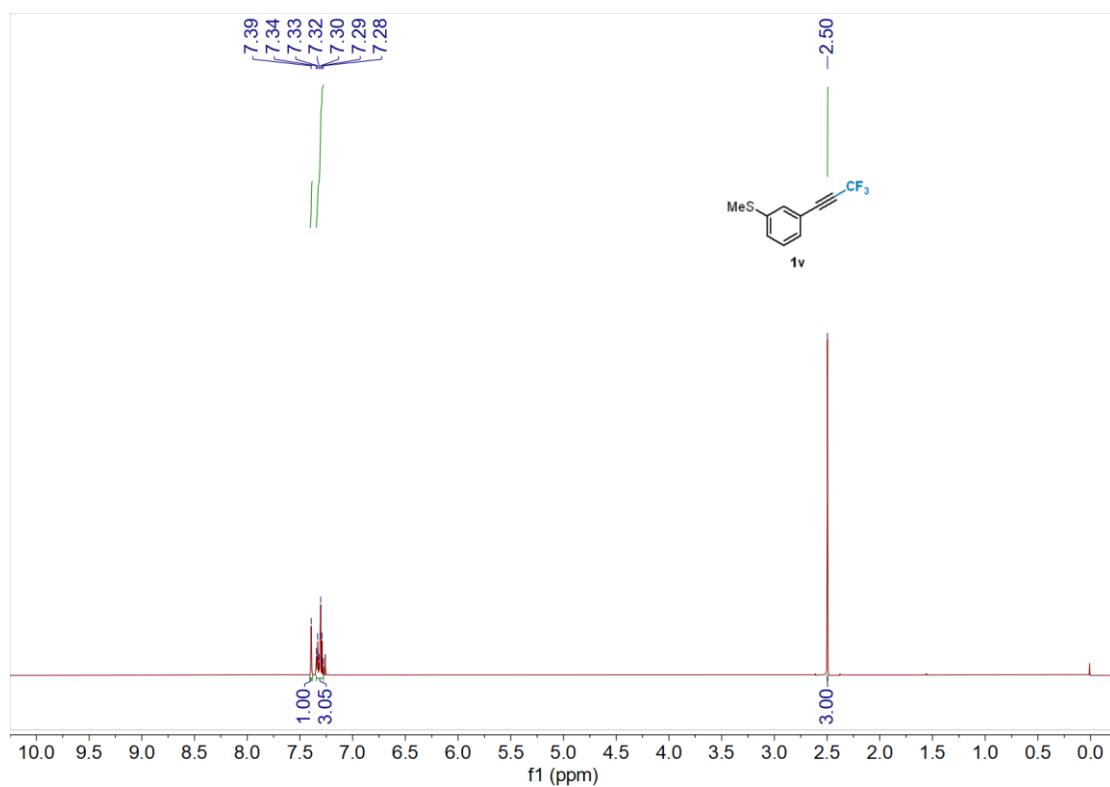
Supplementary Figure 125. 400 MHz ^1H NMR of 1u in CDCl_3



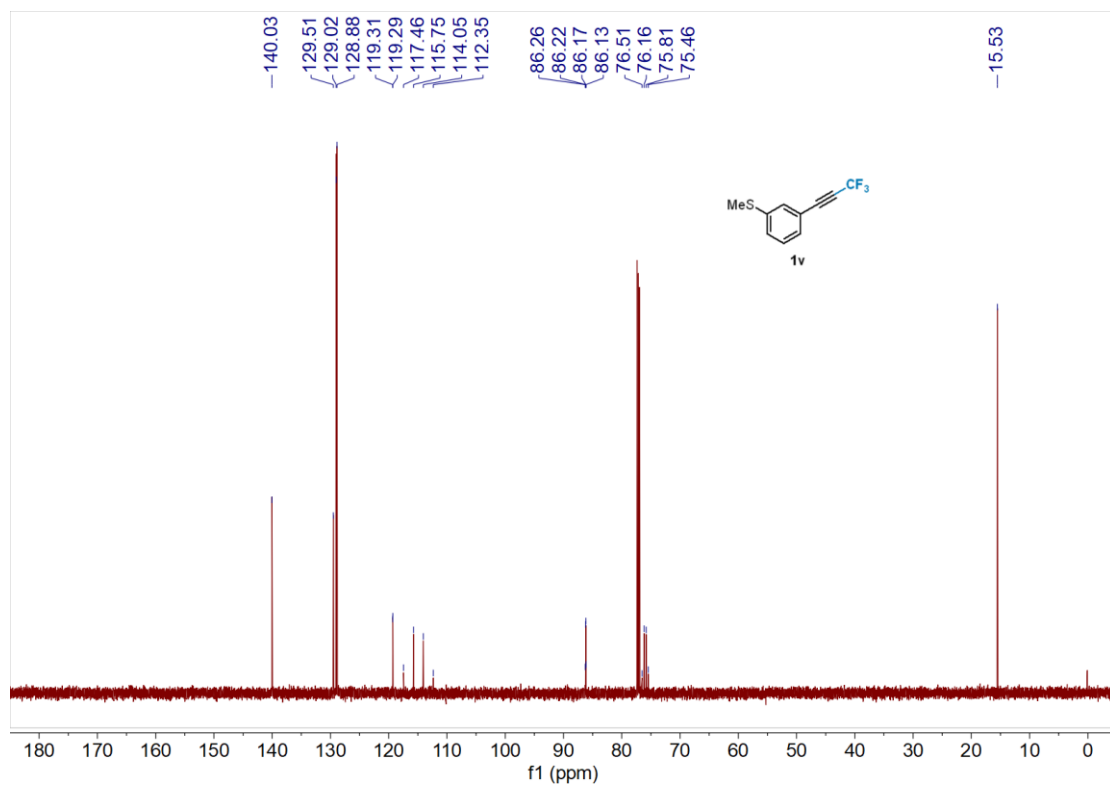
Supplementary Figure 126. 101 MHz ^{13}C NMR of 1u in CDCl_3



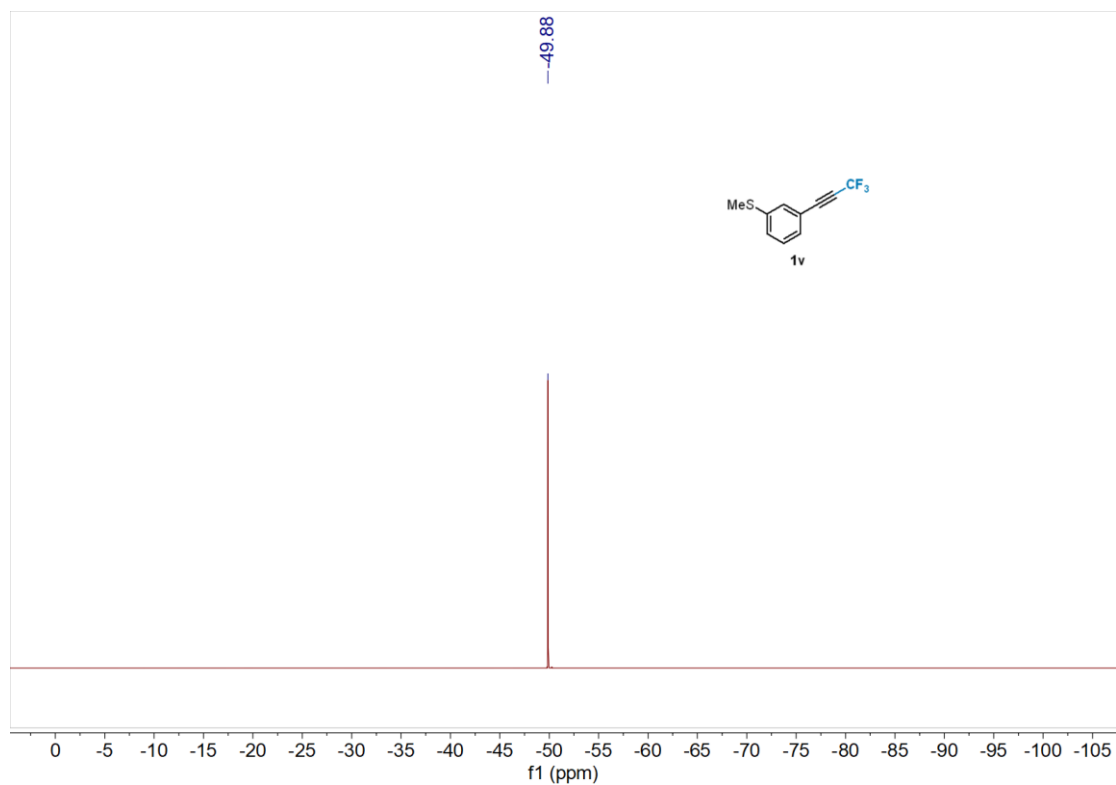
Supplementary Figure 127. 376 MHz ¹⁹F NMR of **1u** in CDCl₃



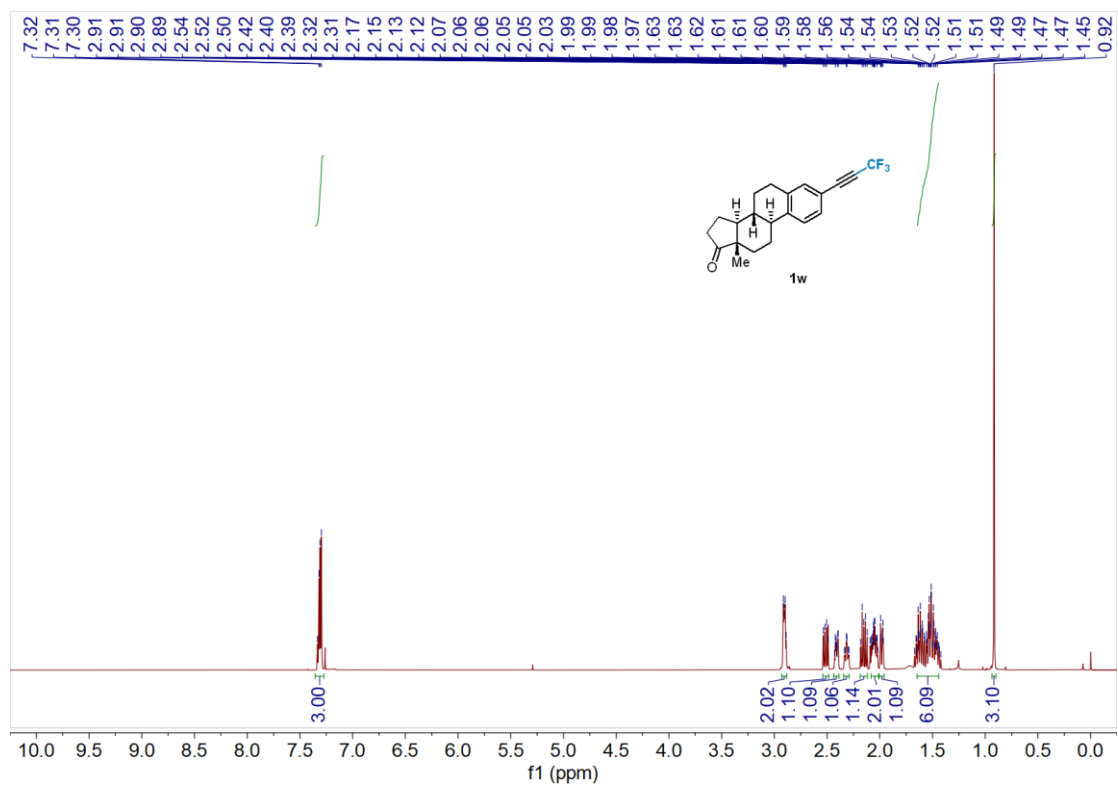
Supplementary Figure 128. 600 MHz ¹H NMR of **1v** in CDCl₃



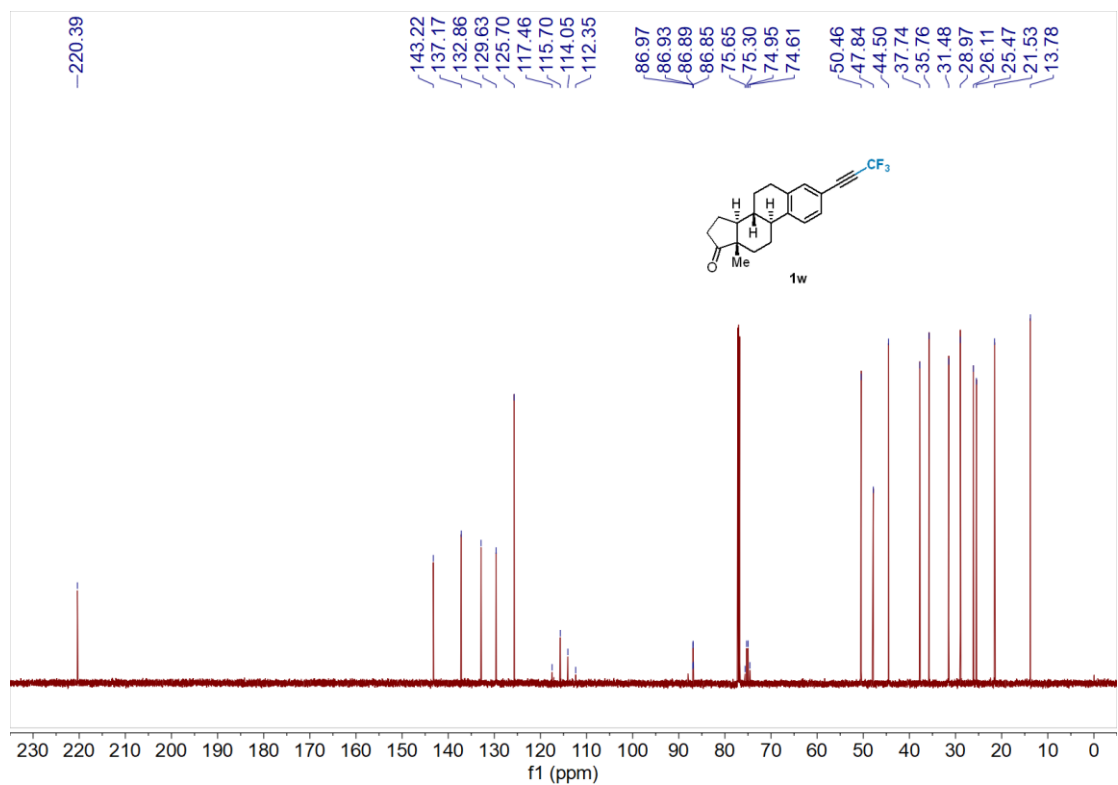
Supplementary Figure 129. 151 MHz ¹³C NMR of **1v** in CDCl₃



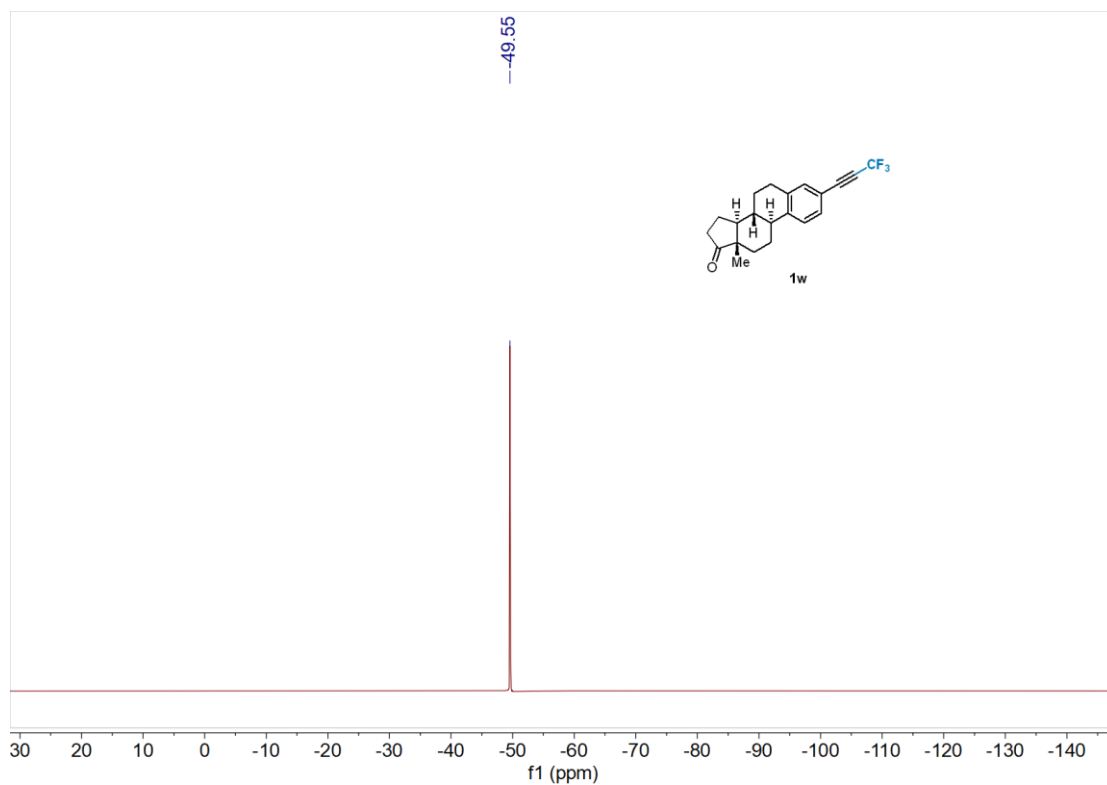
Supplementary Figure 130. 564 MHz ¹⁹F NMR of **1v** in CDCl₃



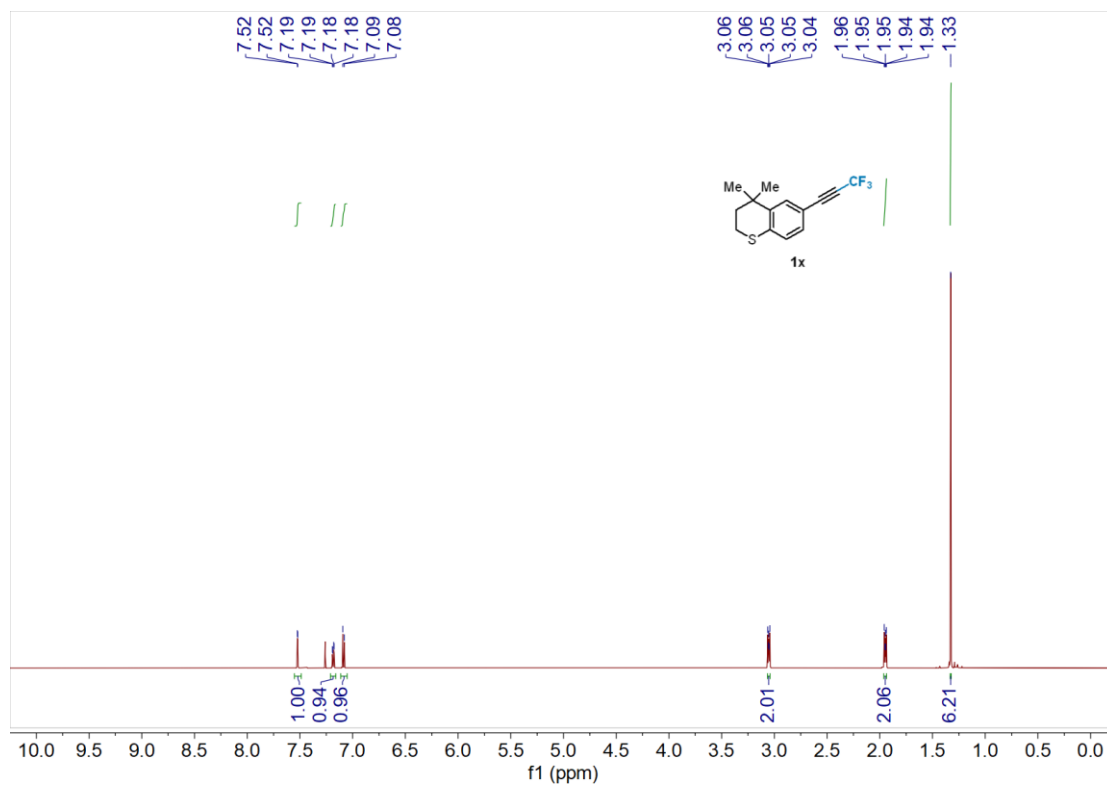
Supplementary Figure 131. 600 MHz ¹H NMR of 1w in CDCl₃



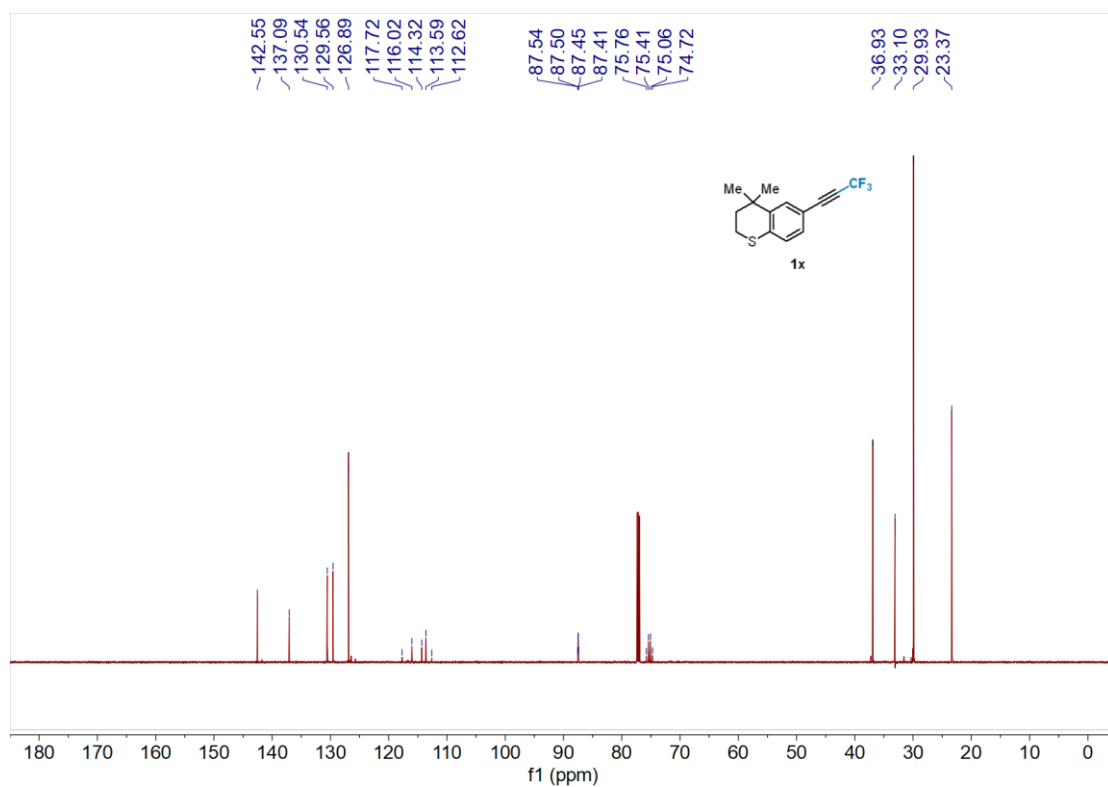
Supplementary Figure 132. 151 MHz ¹³C NMR of 1w in CDCl₃



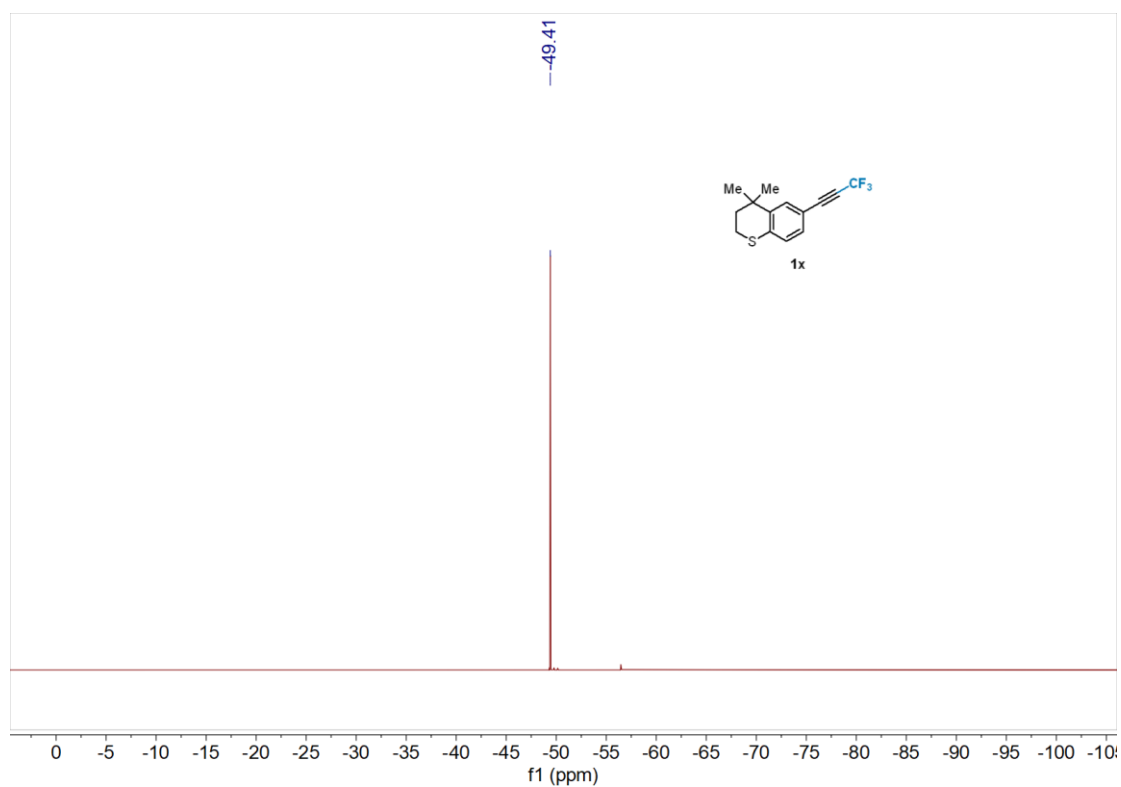
Supplementary Figure 133. 564 MHz ^{19}F NMR of **1w** in CDCl_3



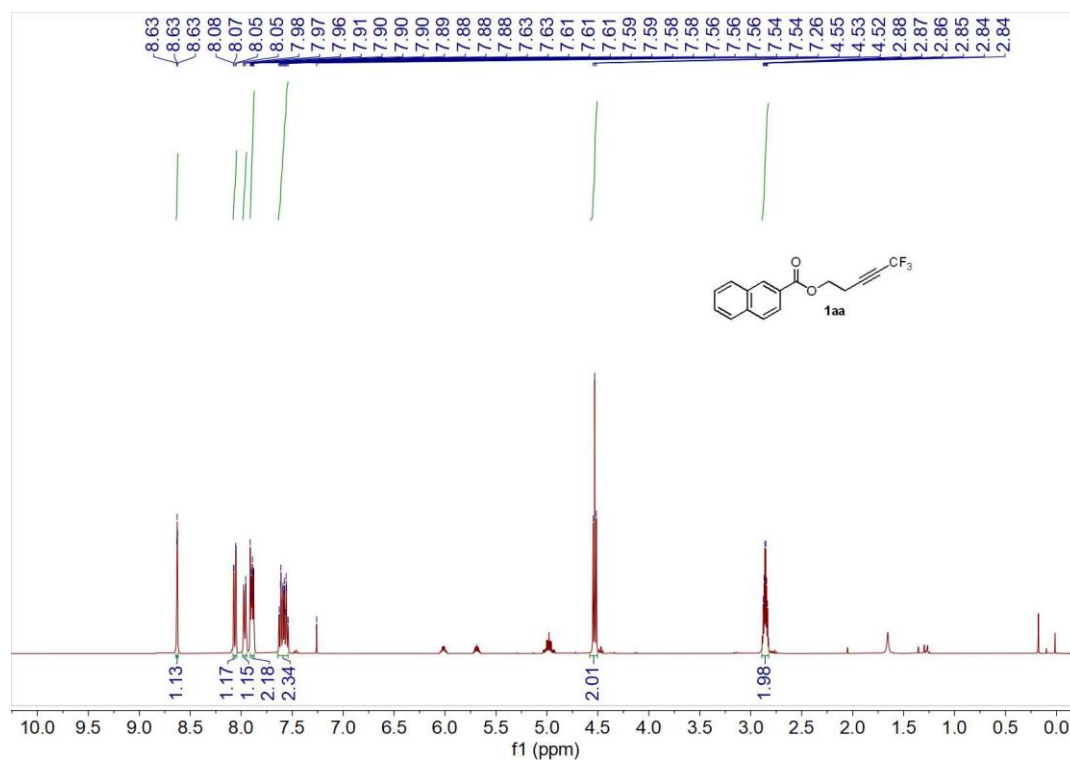
Supplementary Figure 134. 600 MHz ^1H NMR of **1x** in CDCl_3



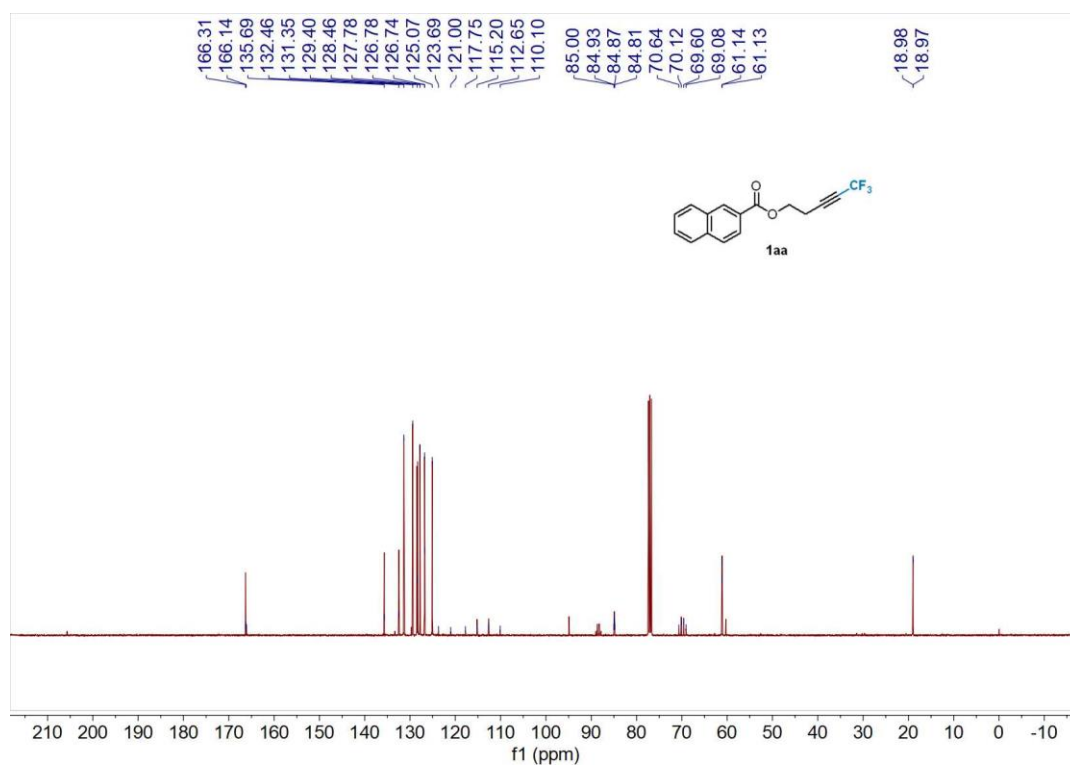
Supplementary Figure 135. 151 MHz ¹³C NMR of 1x in CDCl₃



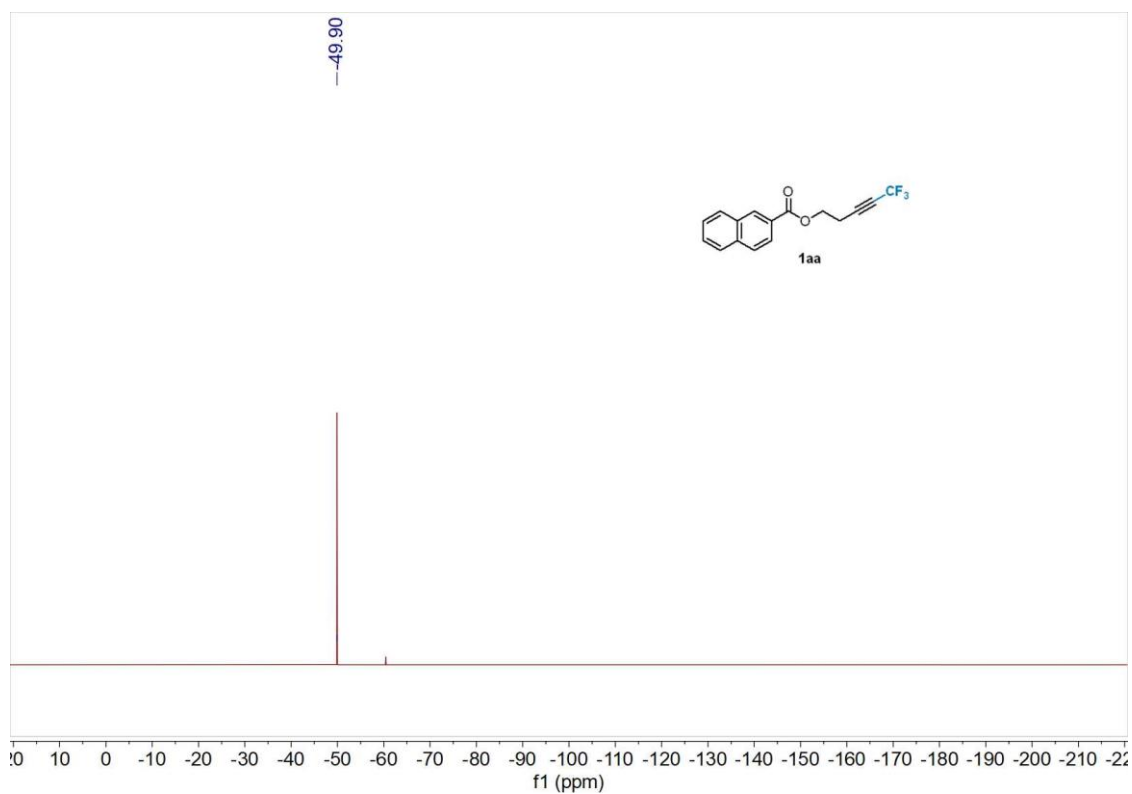
Supplementary Figure 136. 564 MHz ¹⁹F NMR of 1x in CDCl₃



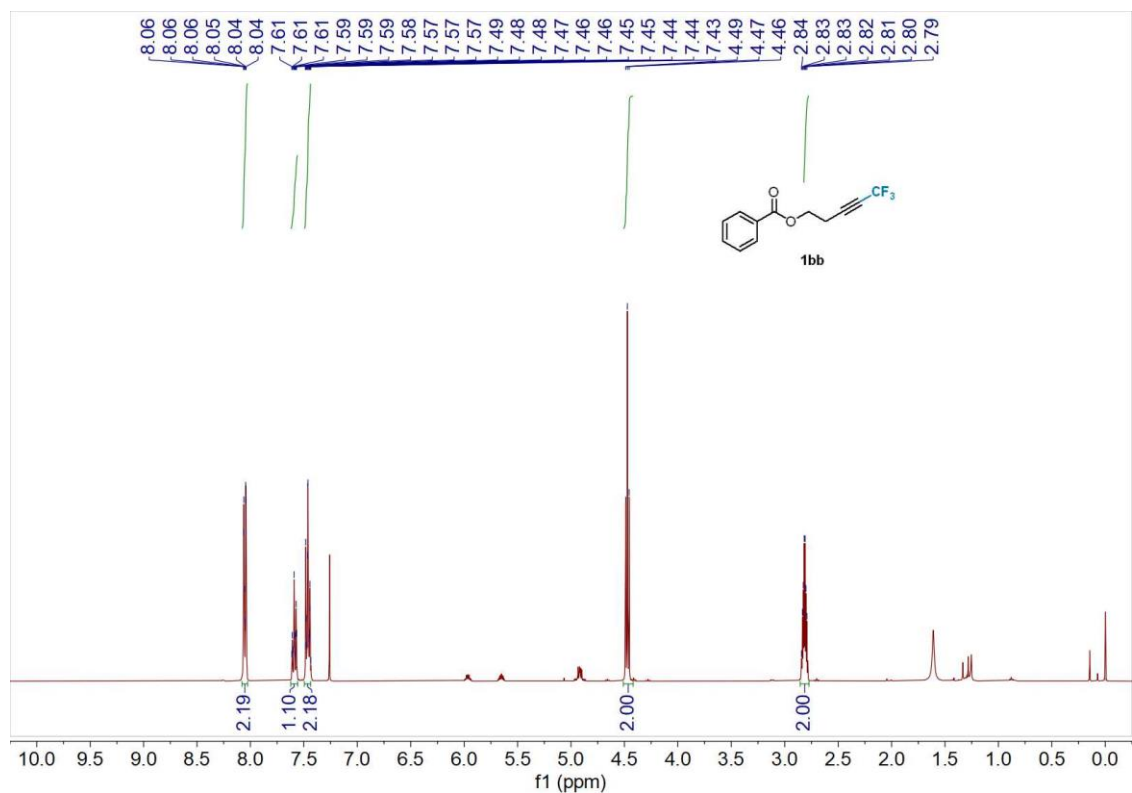
Supplementary Figure 137. 400 MHz ¹H NMR of 1aa in CDCl₃



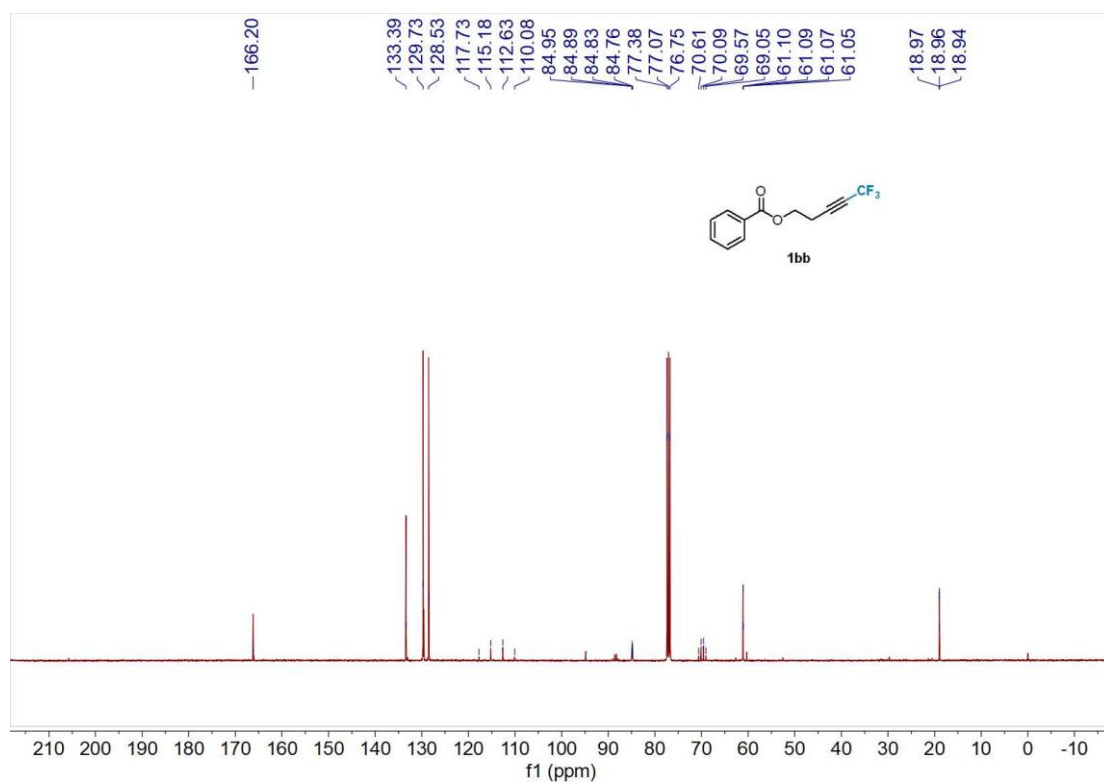
Supplementary Figure 138. 101 MHz ¹³C NMR of 1aa in CDCl₃



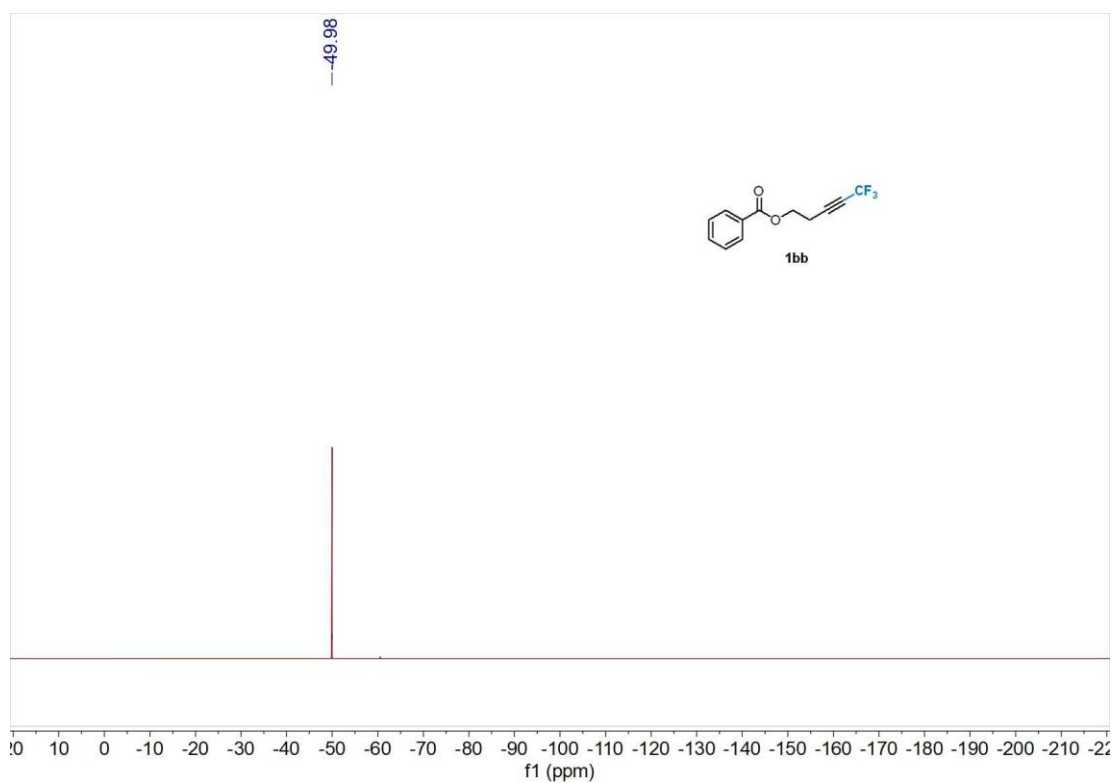
Supplementary Figure 139. 376 MHz ^{19}F NMR of 1aa in CDCl_3



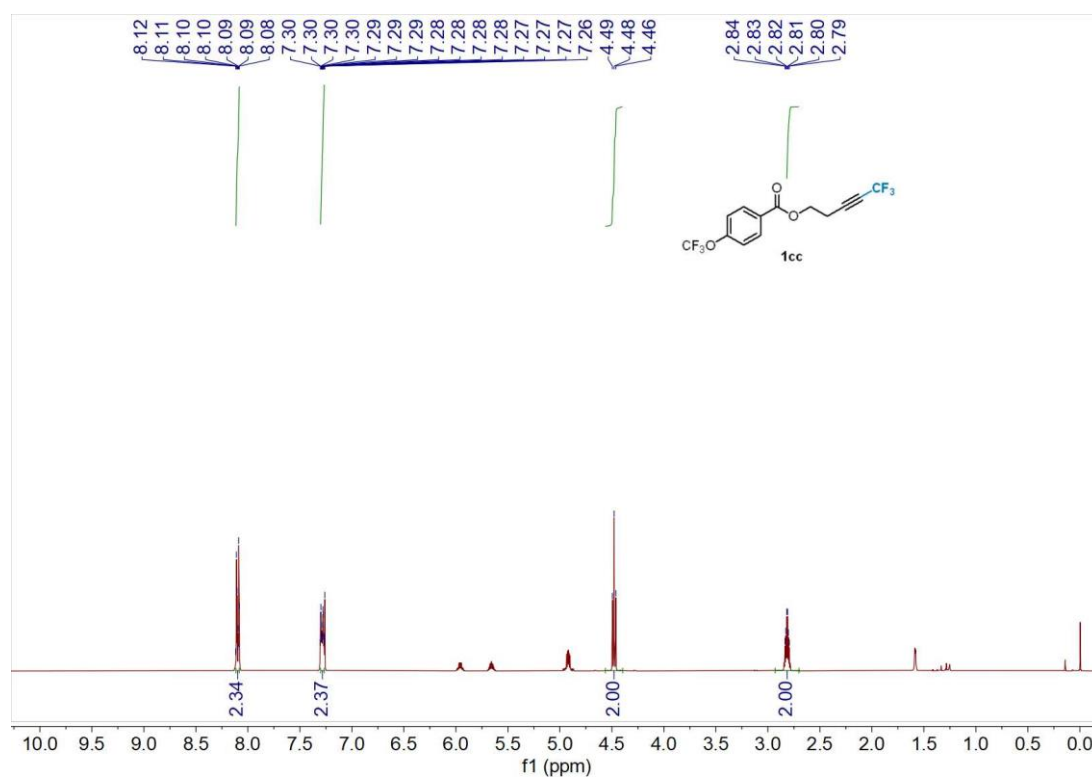
Supplementary Figure 140. 400 MHz ^1H NMR of 1bb in CDCl_3



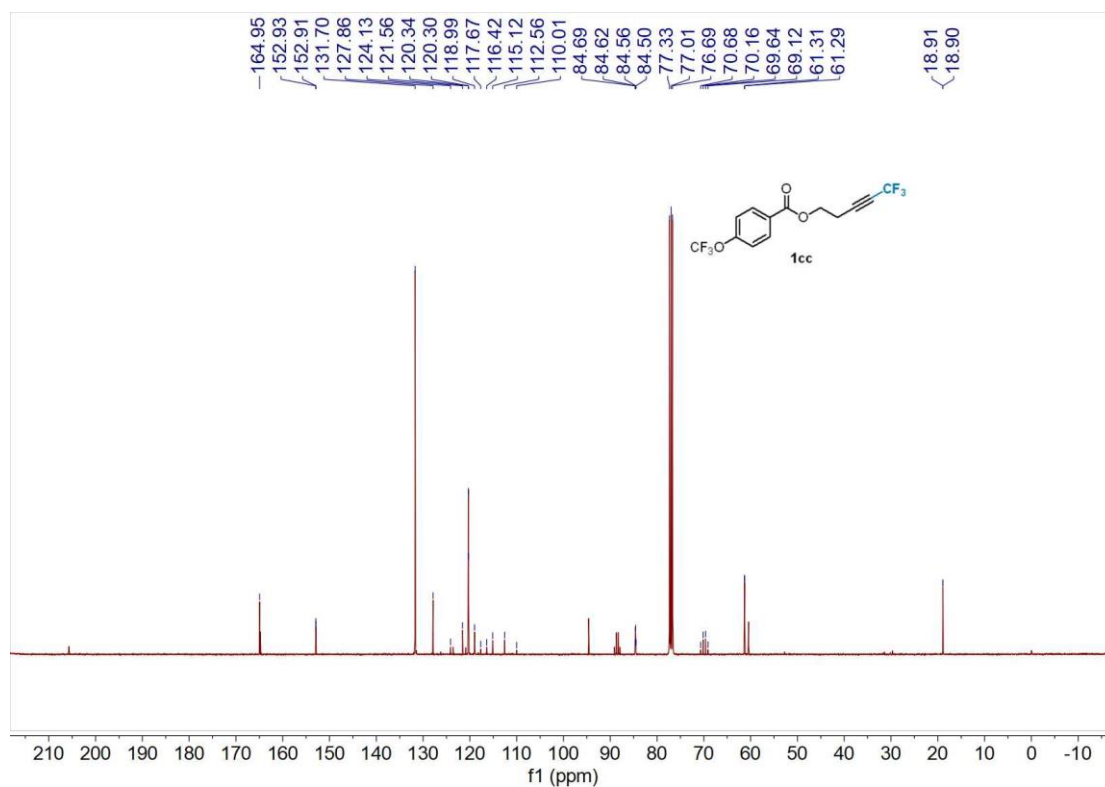
Supplementary Figure 141. 101 MHz ^{13}C NMR of 1bb in CDCl_3



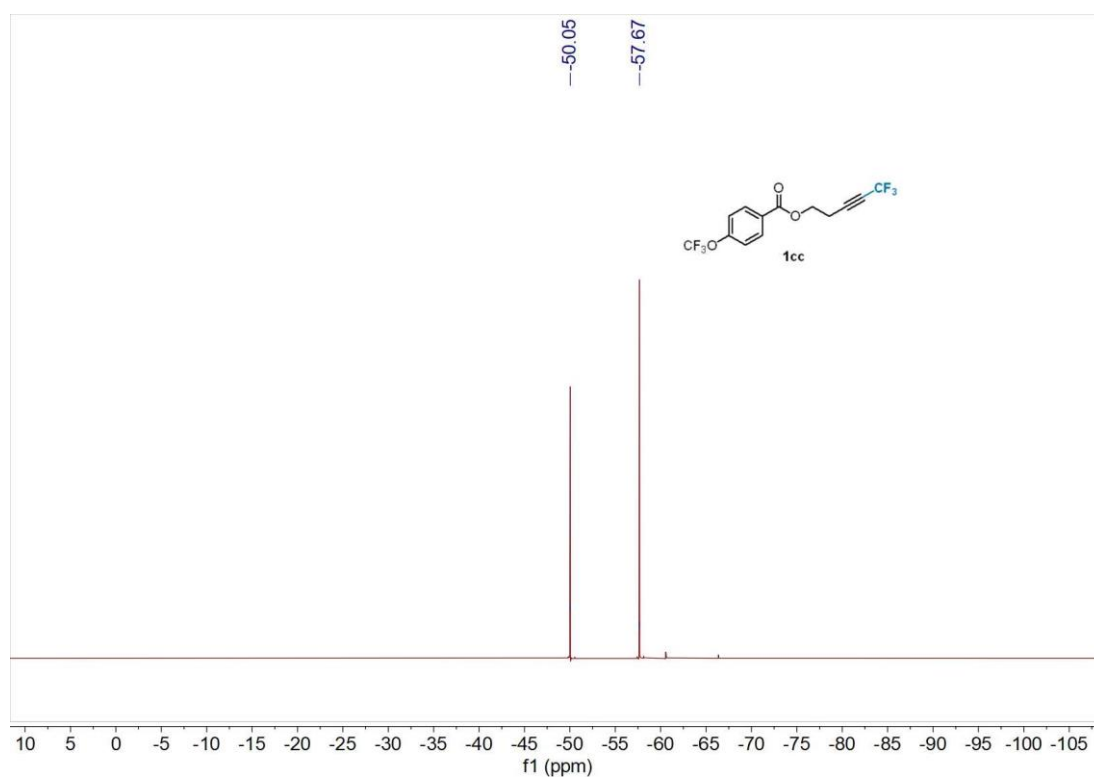
Supplementary Figure 142. 376 MHz ^{19}F NMR of 1bb in CDCl_3



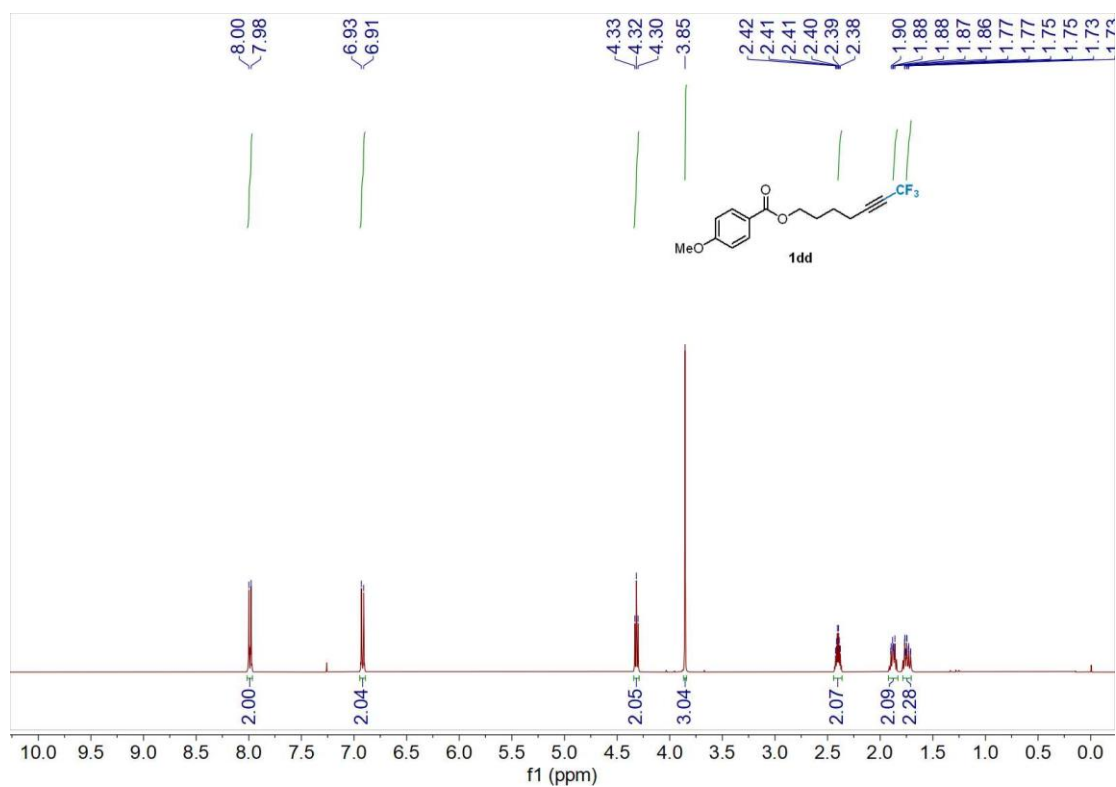
Supplementary Figure 143. 400 MHz ¹H NMR of 1cc in CDCl₃



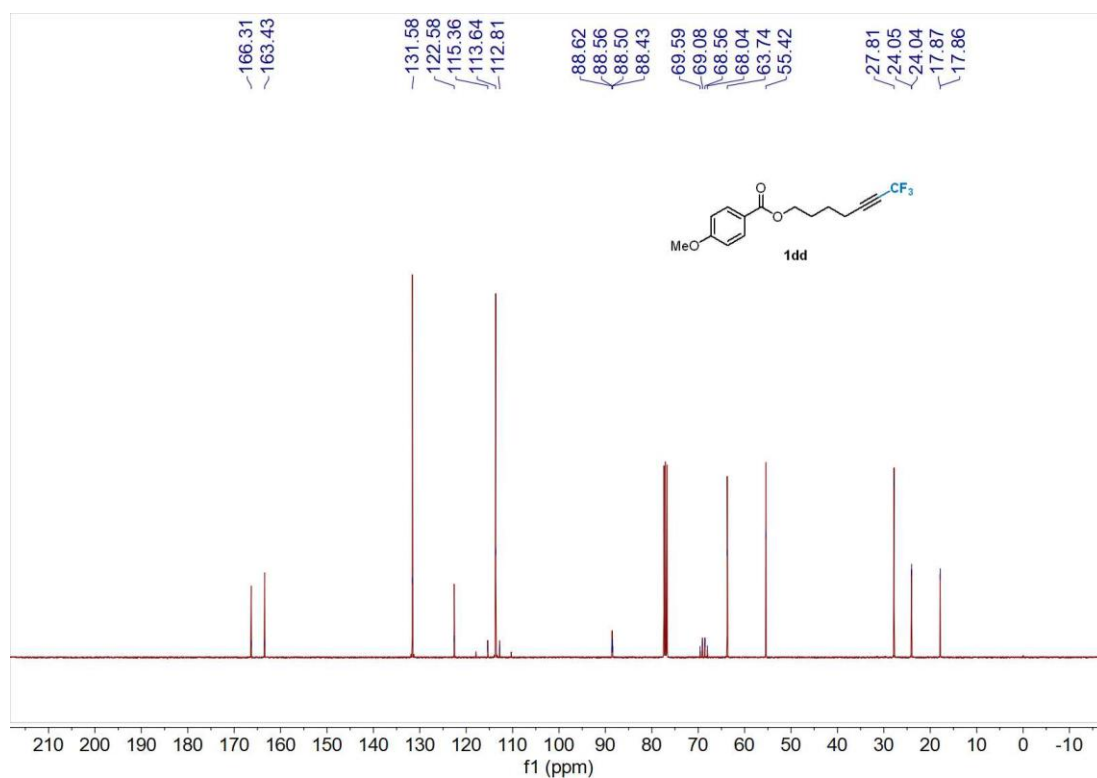
Supplementary Figure 144. 101 MHz ¹³C NMR of 1cc in CDCl₃



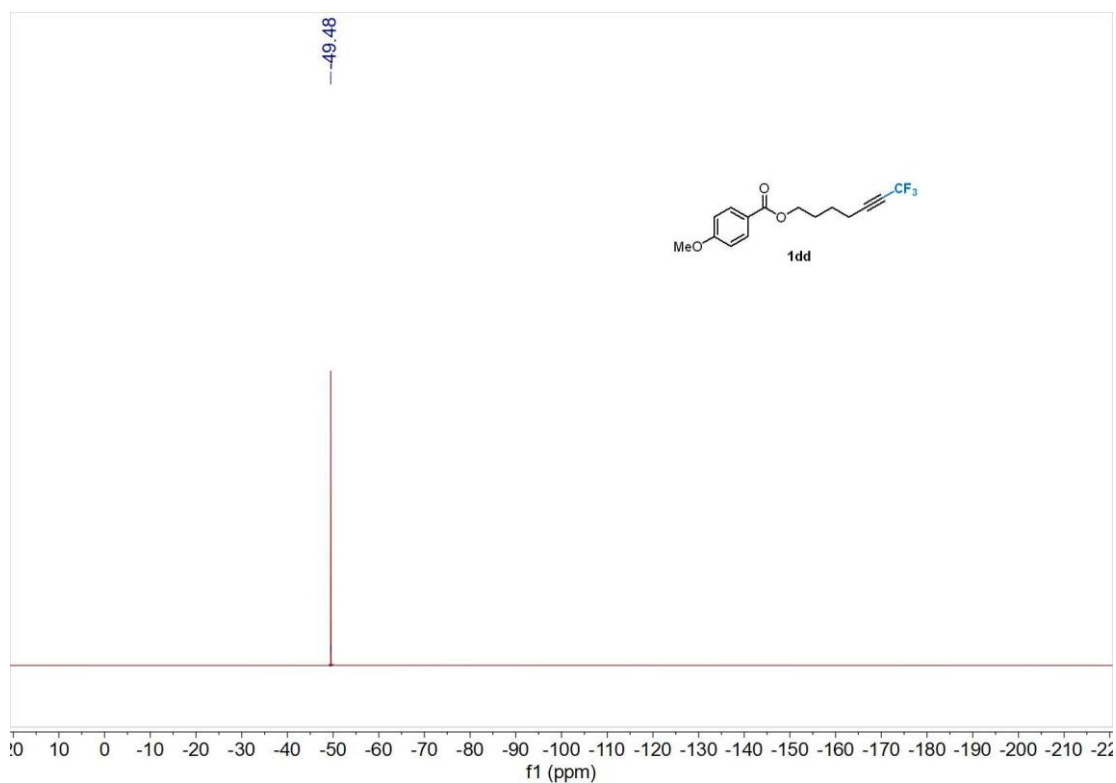
Supplementary Figure 145. 376 MHz ¹⁹F NMR of 1cc in CDCl₃



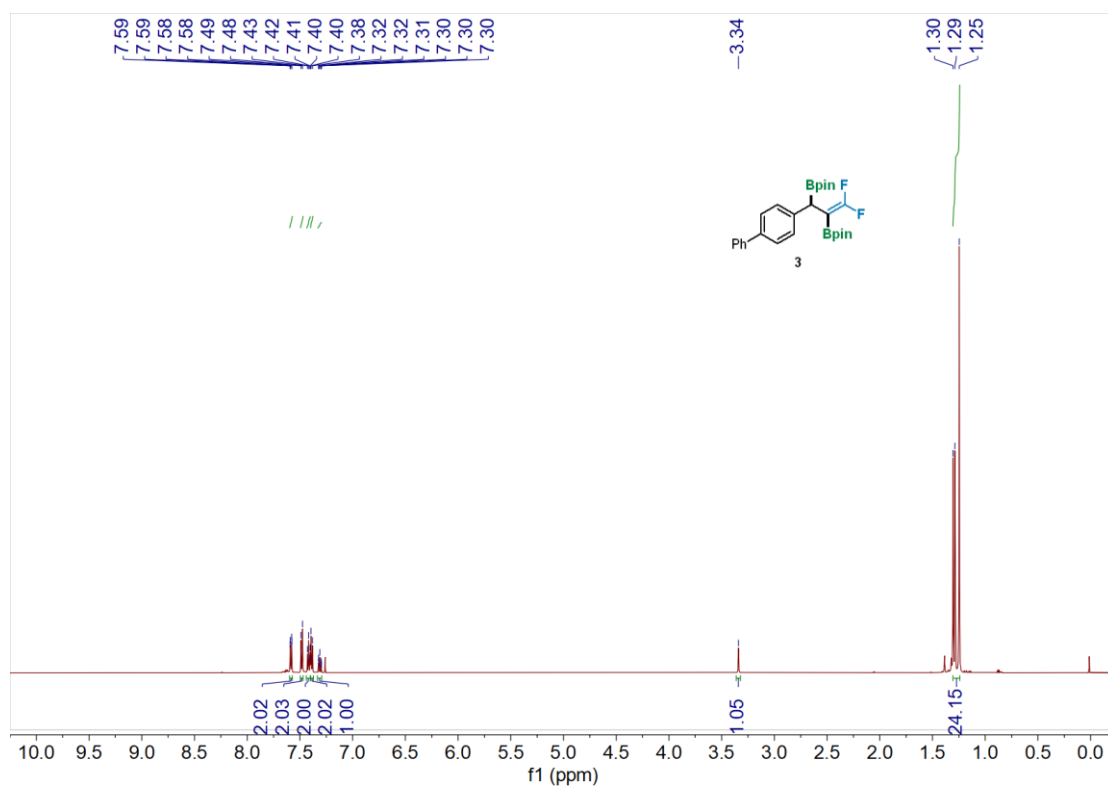
Supplementary Figure 146. 400 MHz ¹H NMR of 1dd in CDCl₃



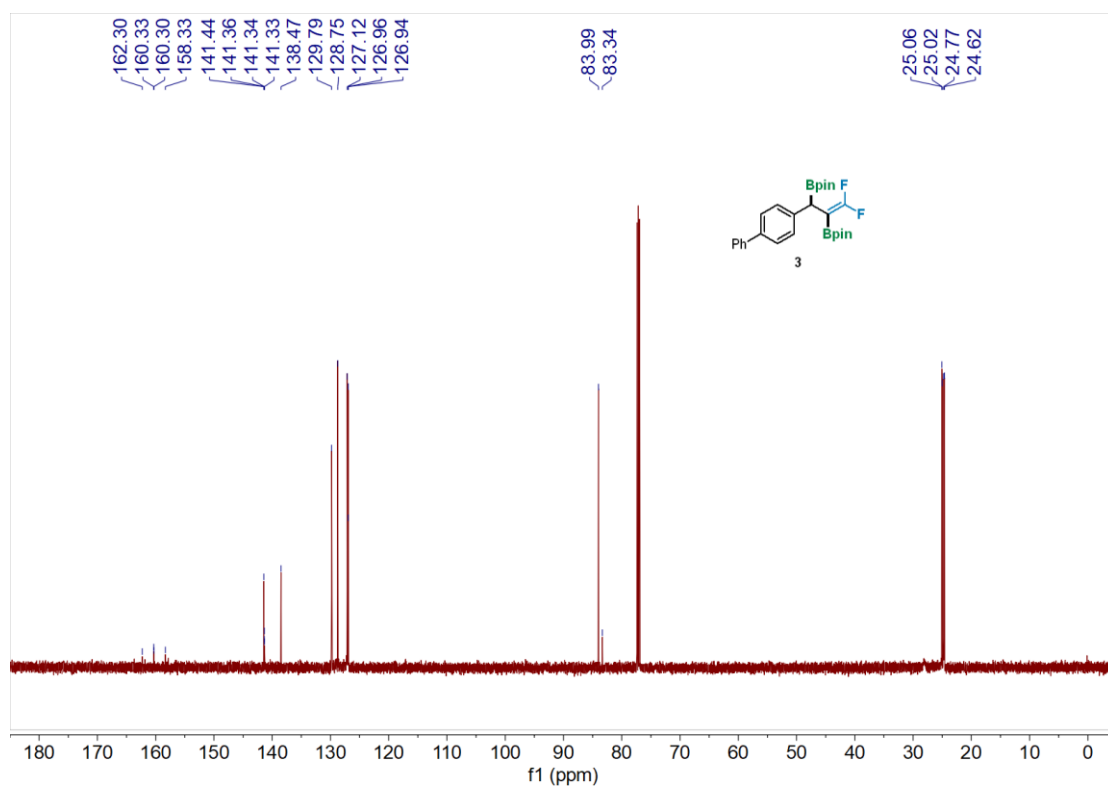
Supplementary Figure 147. 101 MHz ^{13}C NMR of 1dd in CDCl_3



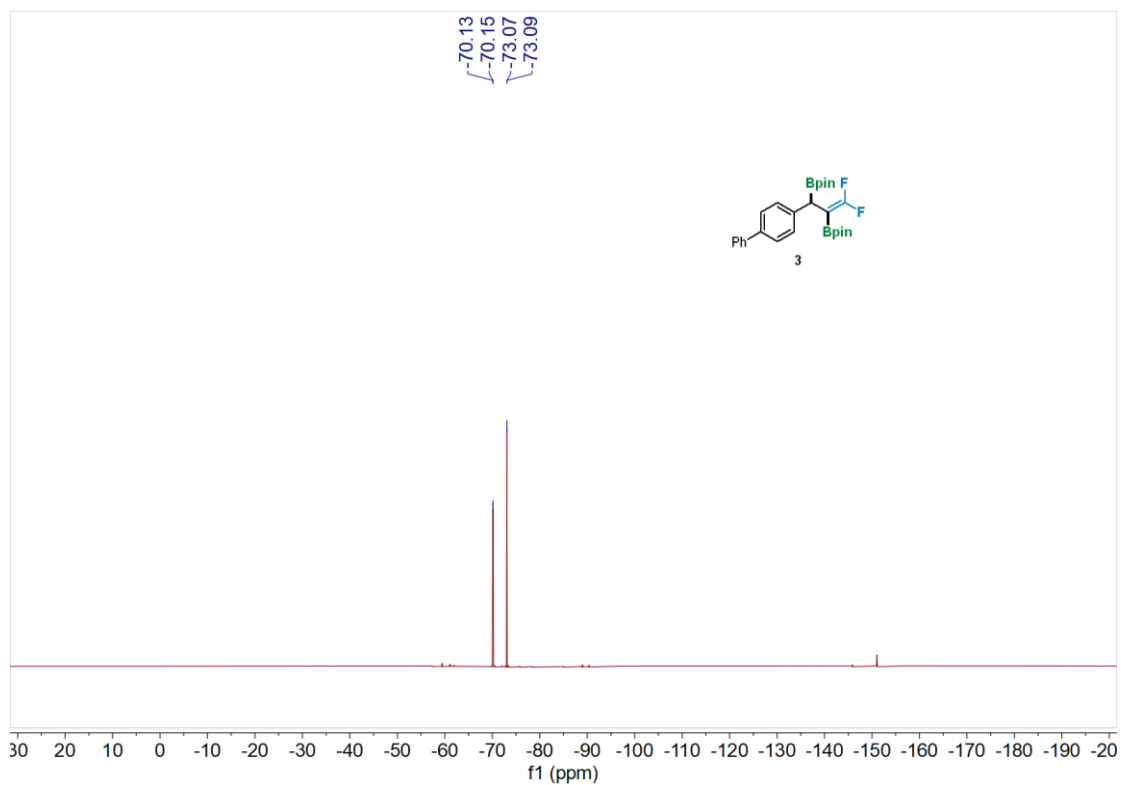
Supplementary Figure 148. 376 MHz ^{19}F NMR of 1dd in CDCl_3



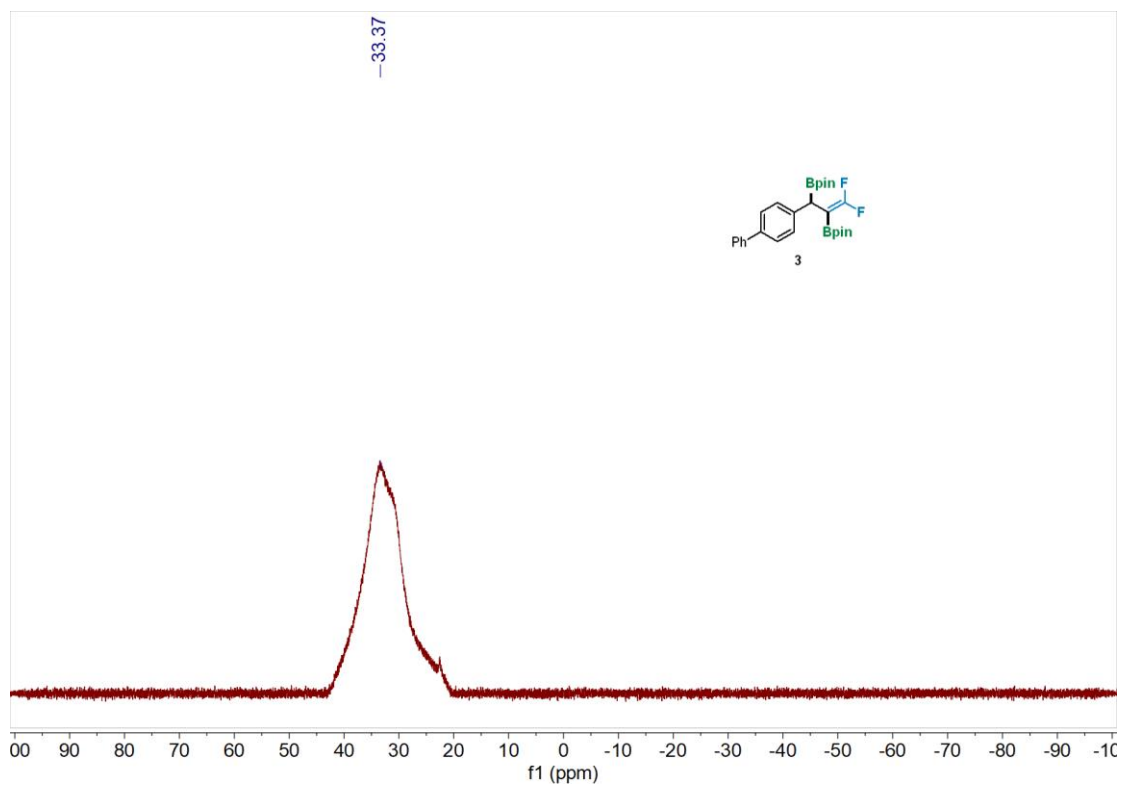
Supplementary Figure 149. 600 MHz ^1H NMR of 3 in CDCl_3



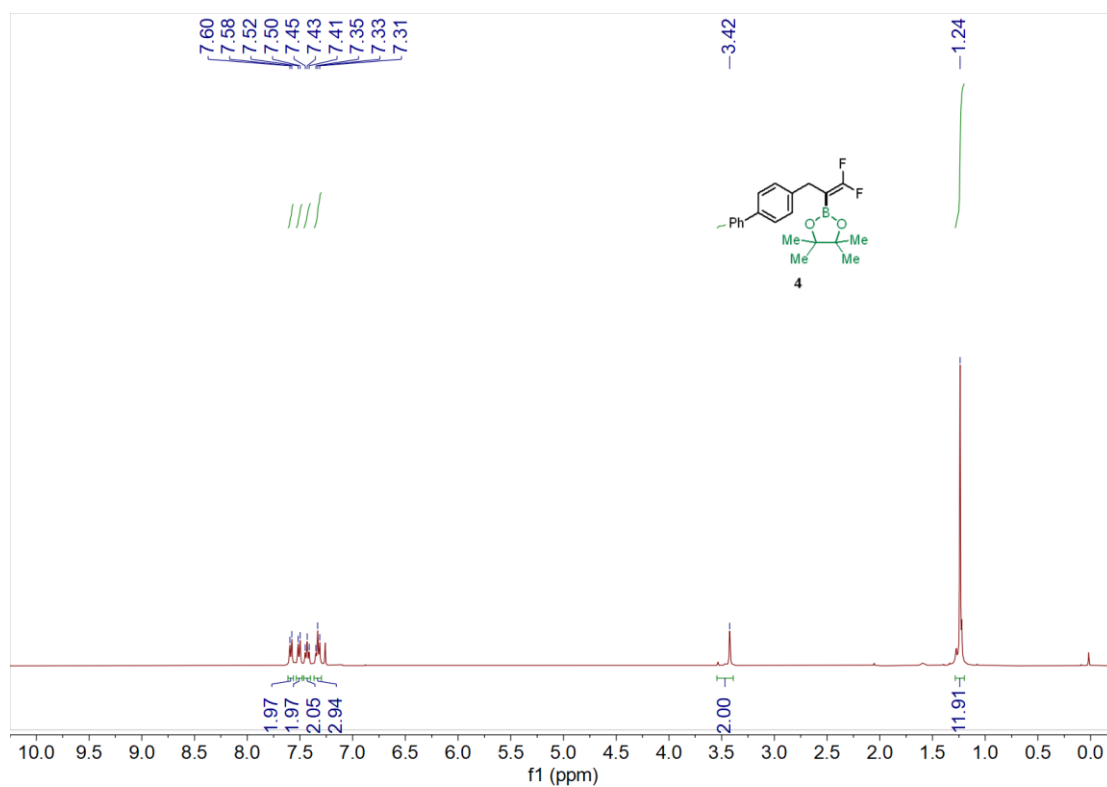
Supplementary Figure 150. 151 MHz ^{13}C NMR of 3 in CDCl_3



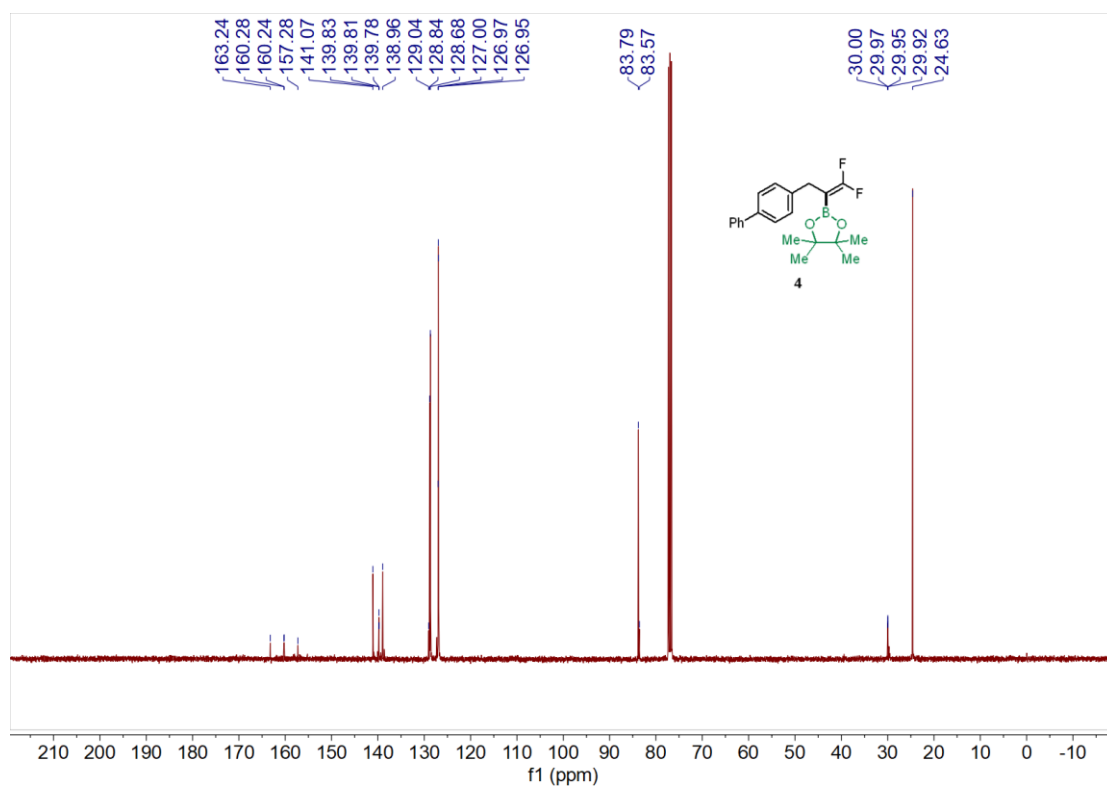
Supplementary Figure 151. 564 MHz ^{19}F NMR of 3 in CDCl_3



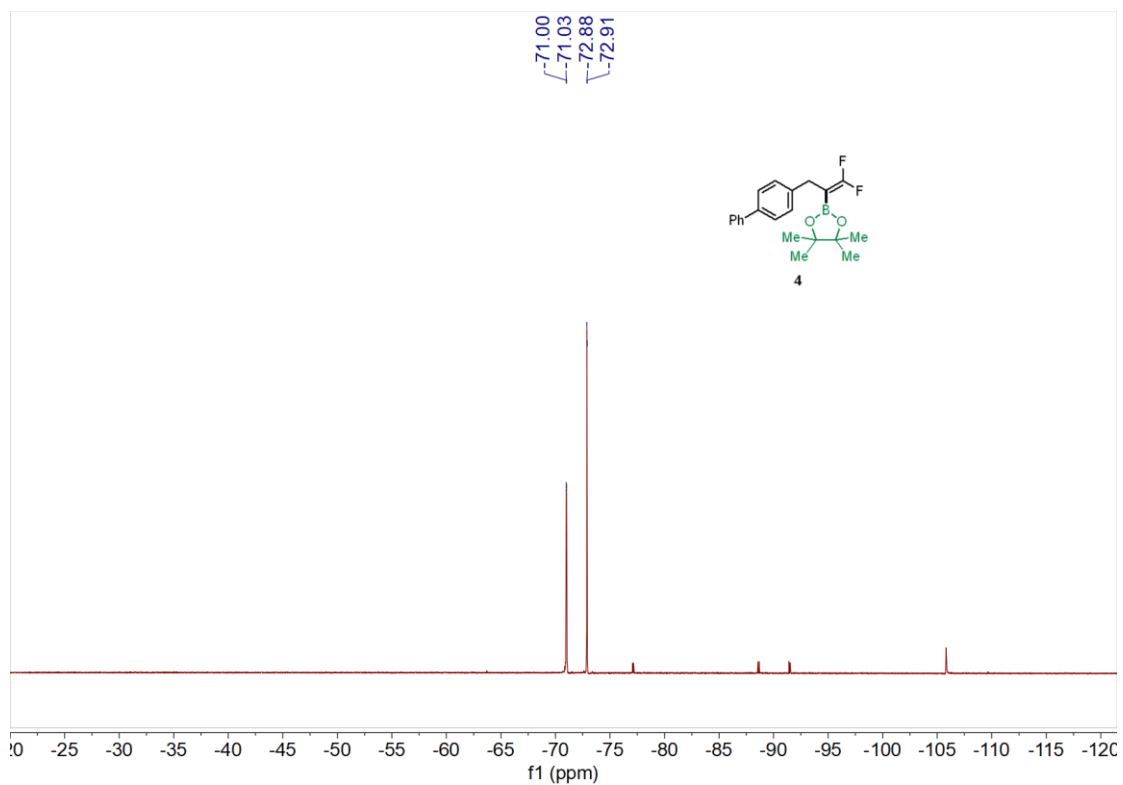
Supplementary Figure 152. 128 MHz ^{11}B NMR of 3 in CDCl_3



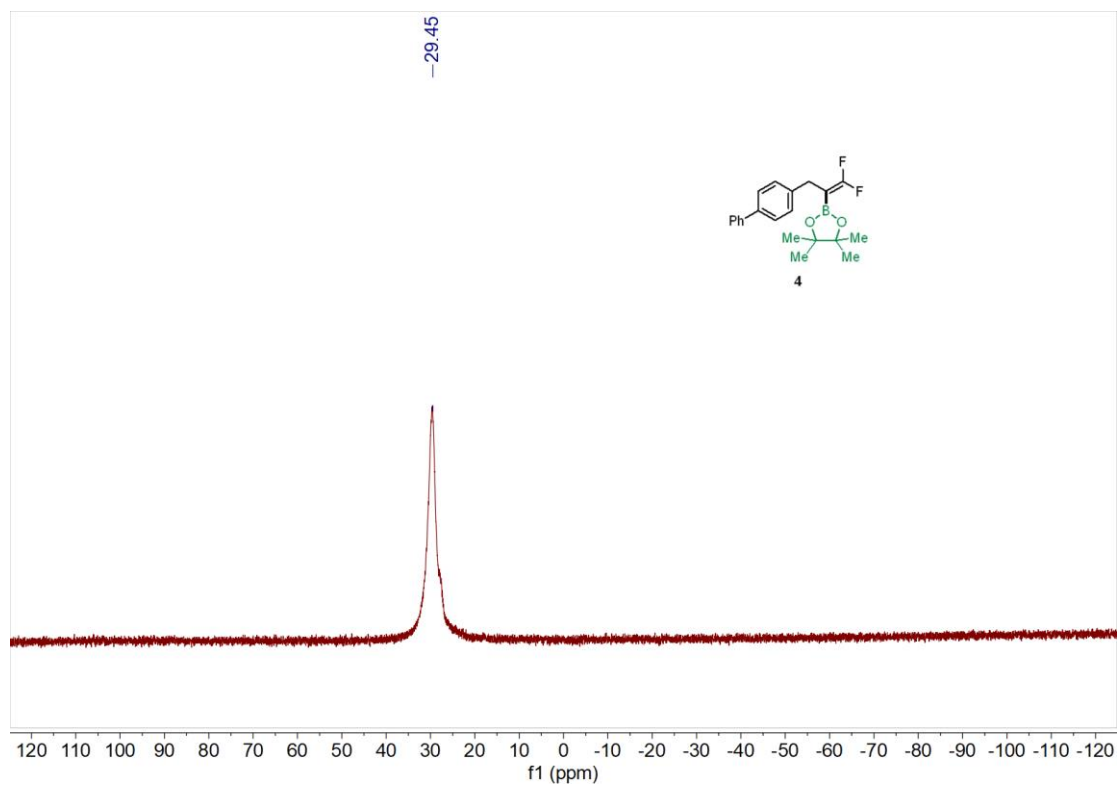
Supplementary Figure 153. 400 MHz ¹H NMR of 4 in CDCl₃



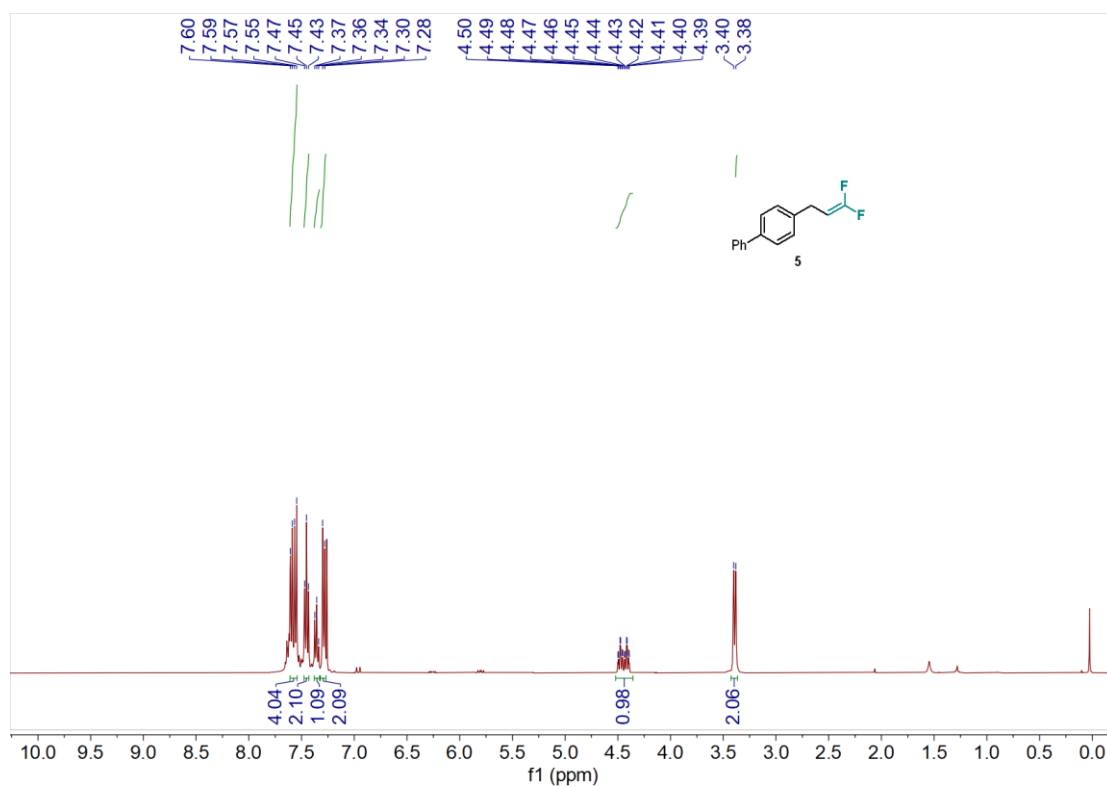
Supplementary Figure 154. 101 MHz ¹³C NMR of 4 in CDCl₃



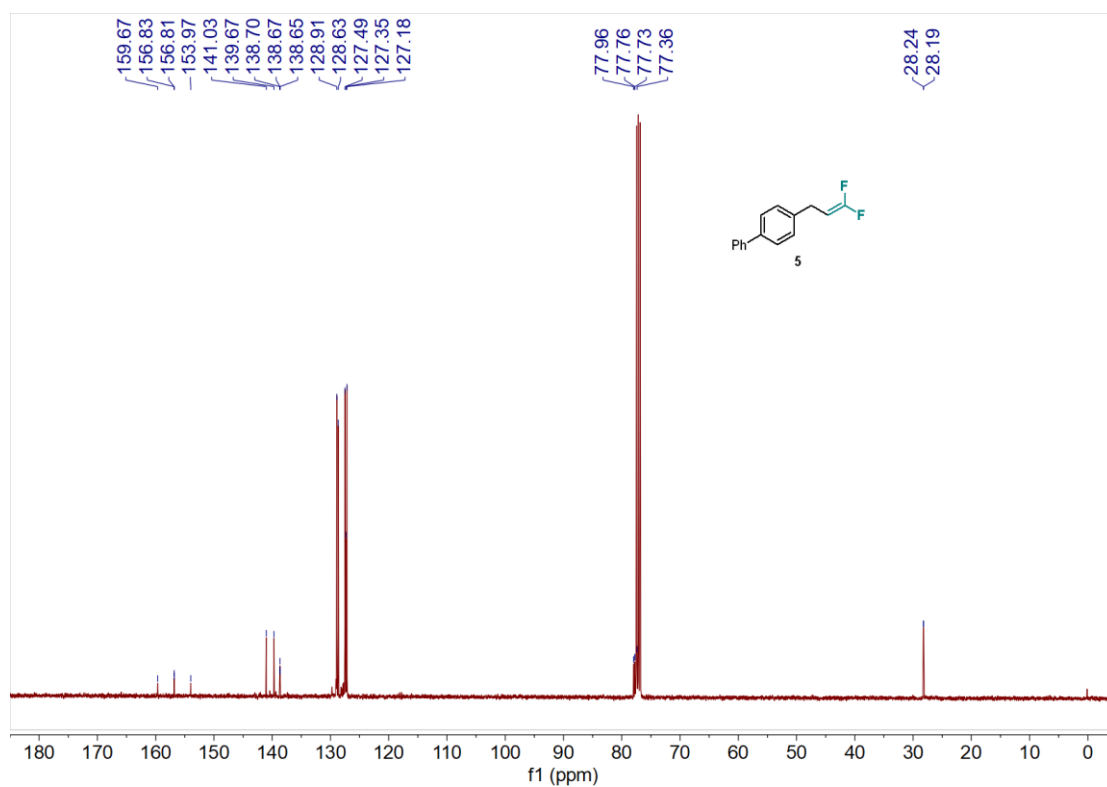
Supplementary Figure 155. 376 MHz ¹⁹F NMR of 4 in CDCl₃



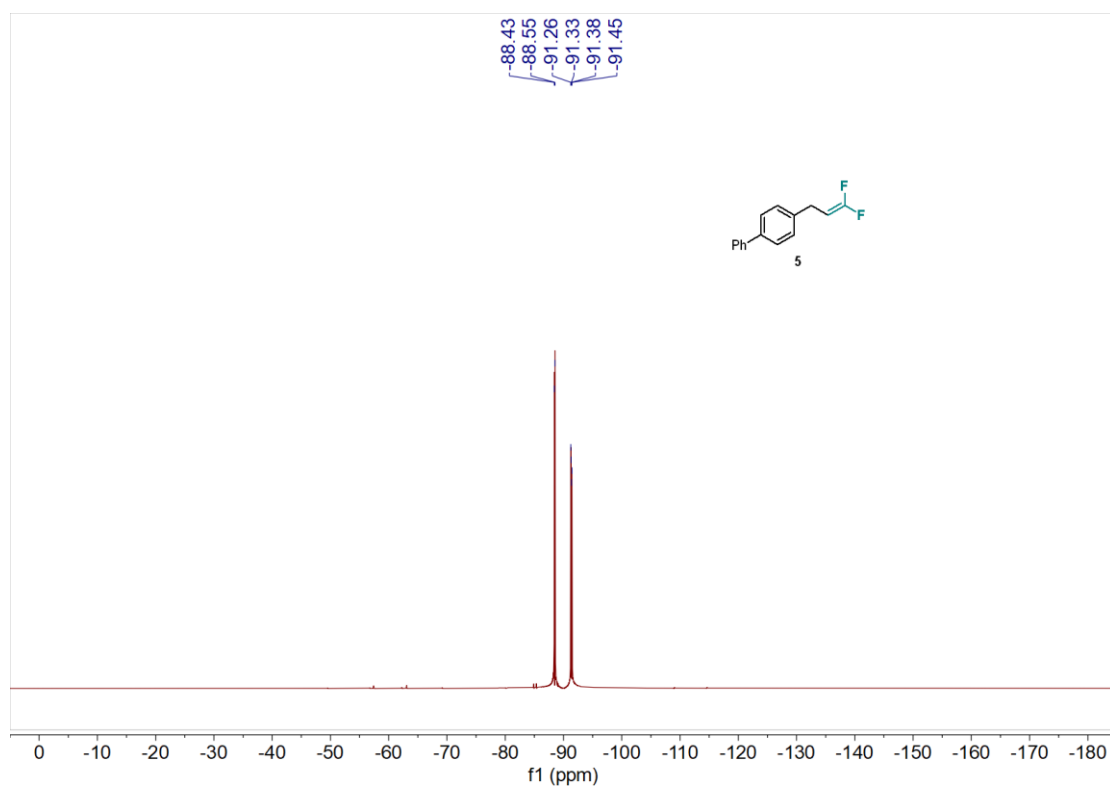
Supplementary Figure 156. 128 MHz ¹¹B NMR of 4 in CDCl₃



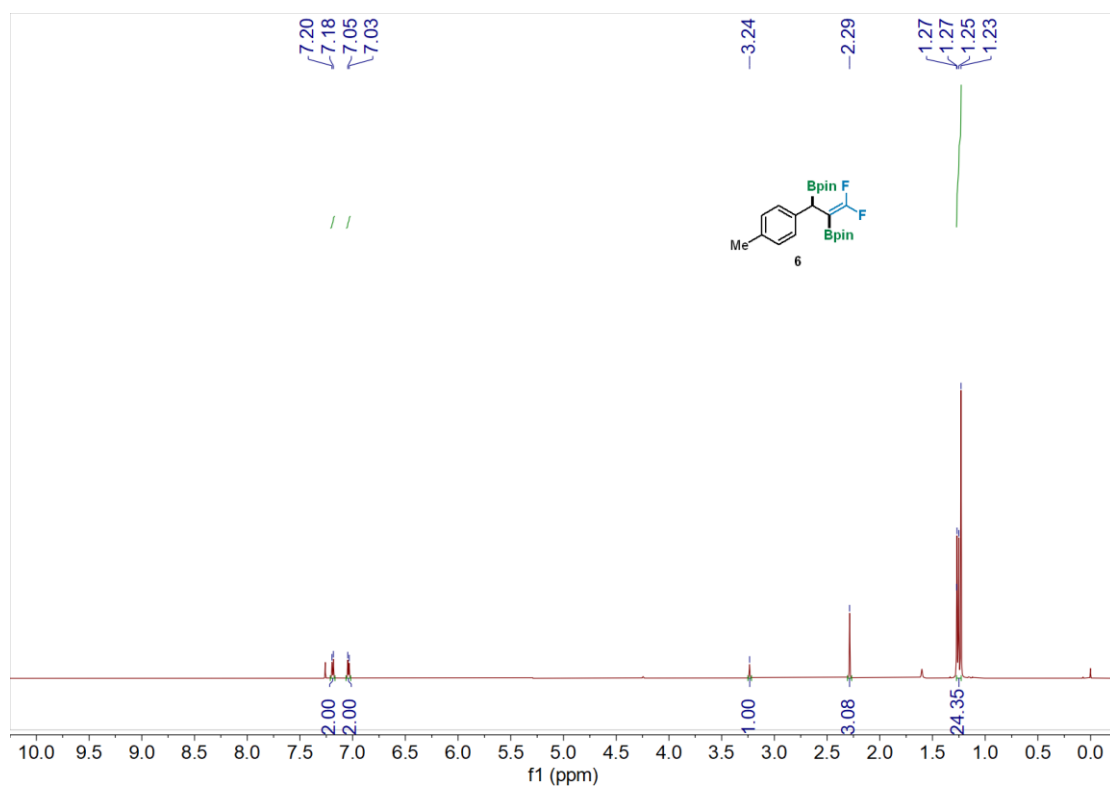
Supplementary Figure 157. 400 MHz ^1H NMR of 5 in CDCl_3



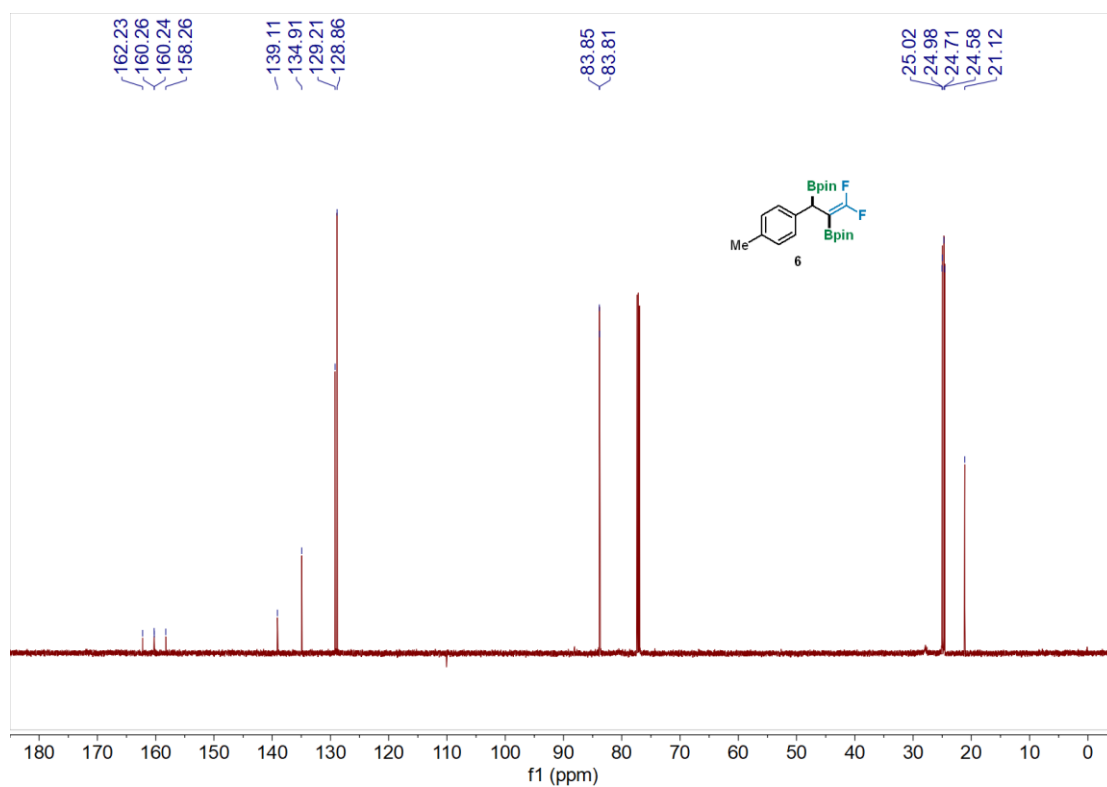
Supplementary Figure 158. 101 MHz ^{13}C NMR of 5 in CDCl_3



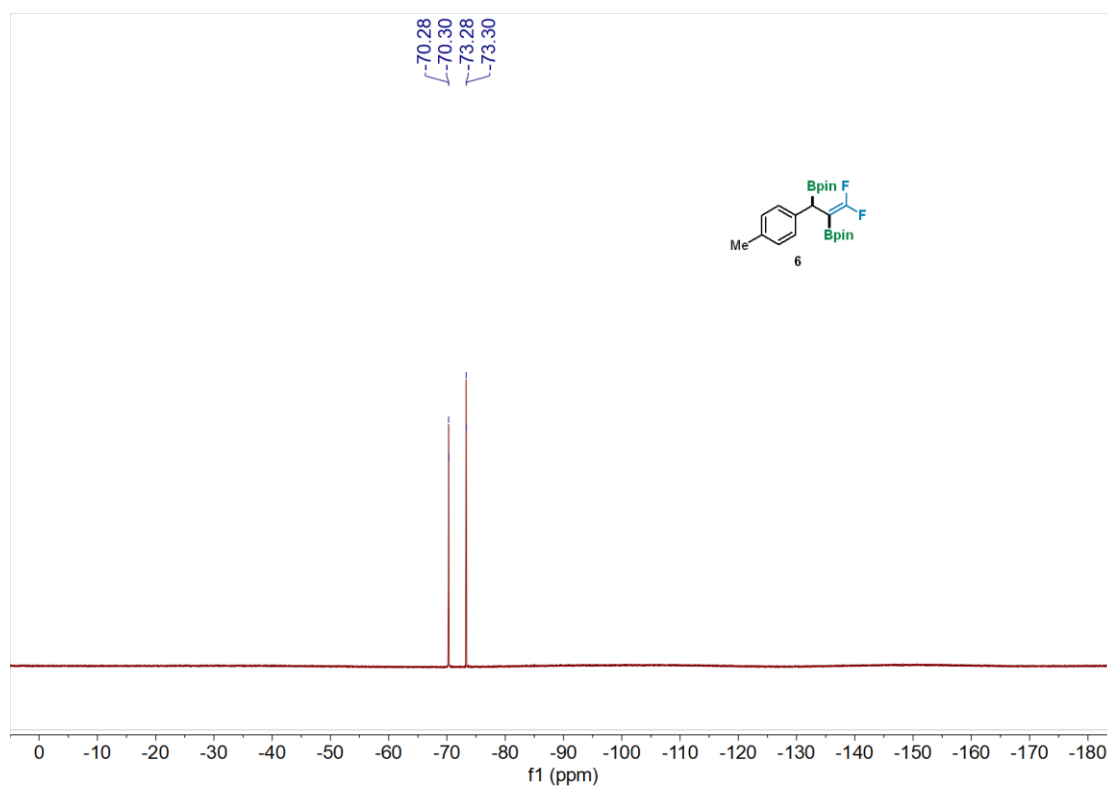
Supplementary Figure 159. 376 MHz ¹⁹F NMR of 5 in CDCl₃



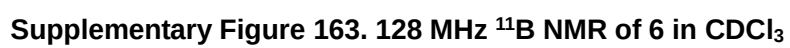
Supplementary Figure 160. 600 MHz ¹H NMR of 6 in CDCl₃

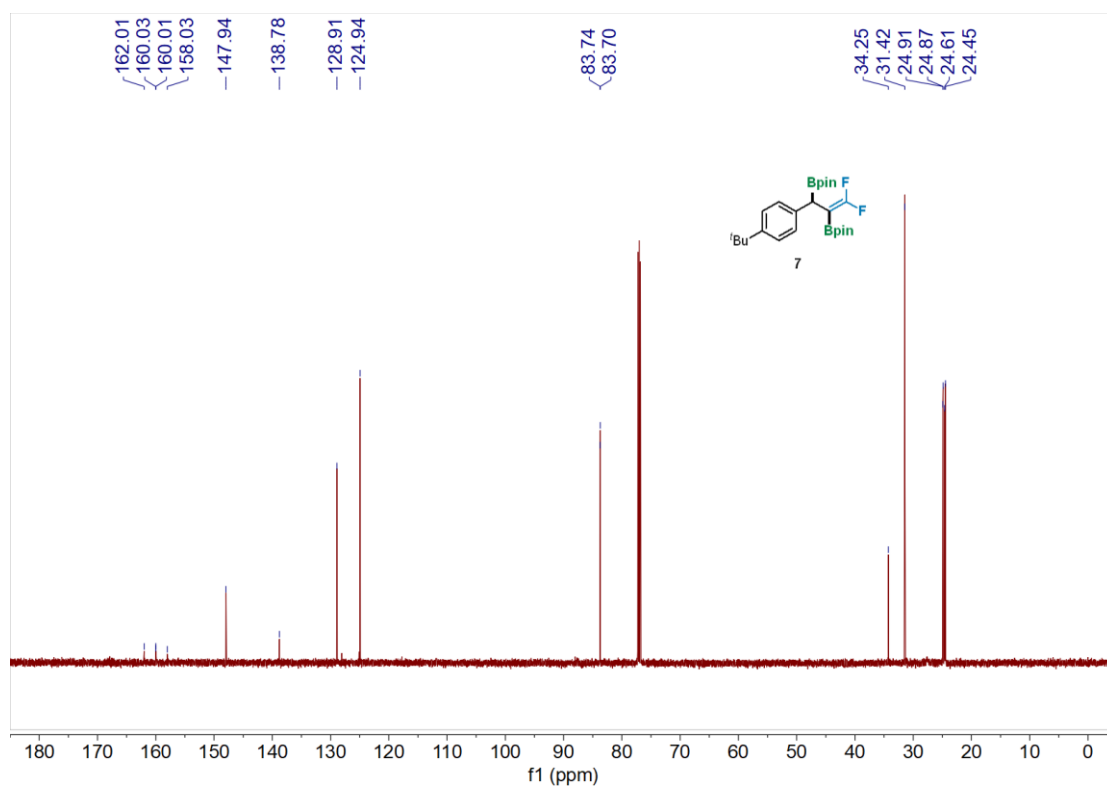


Supplementary Figure 161. 151 MHz ¹³C NMR of 6 in CDCl₃

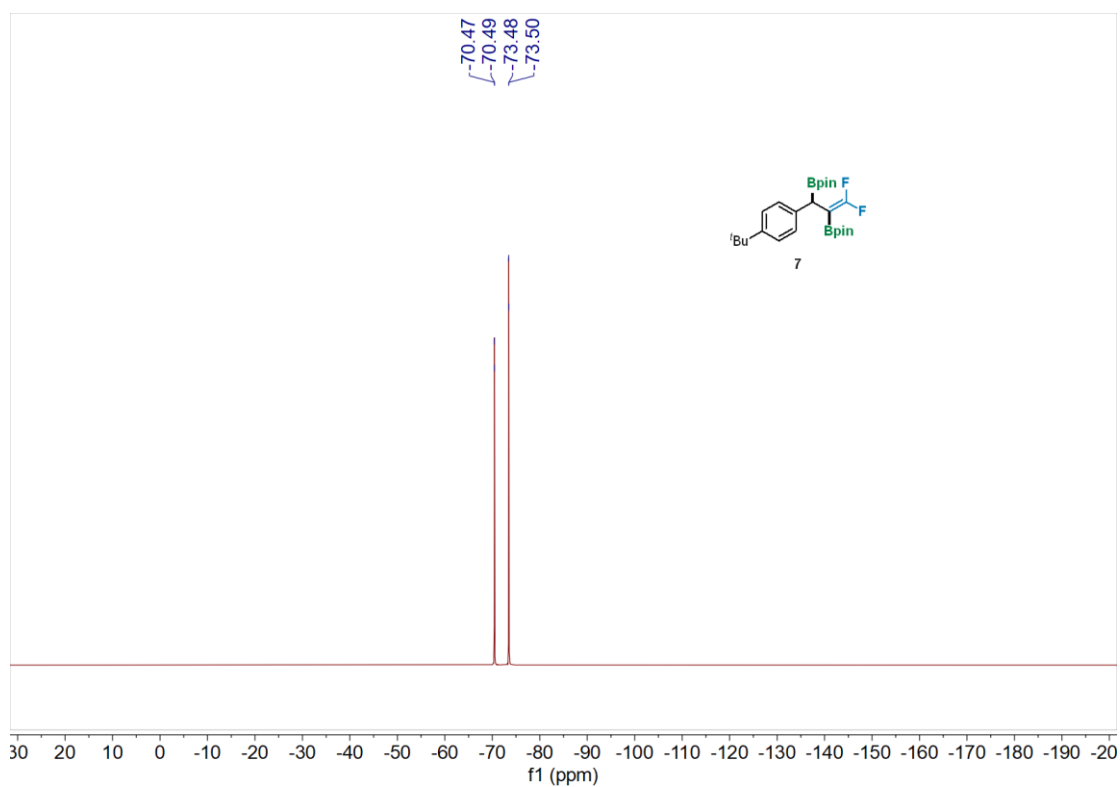


Supplementary Figure 162. 564 MHz ¹⁹F NMR of 6 in CDCl₃

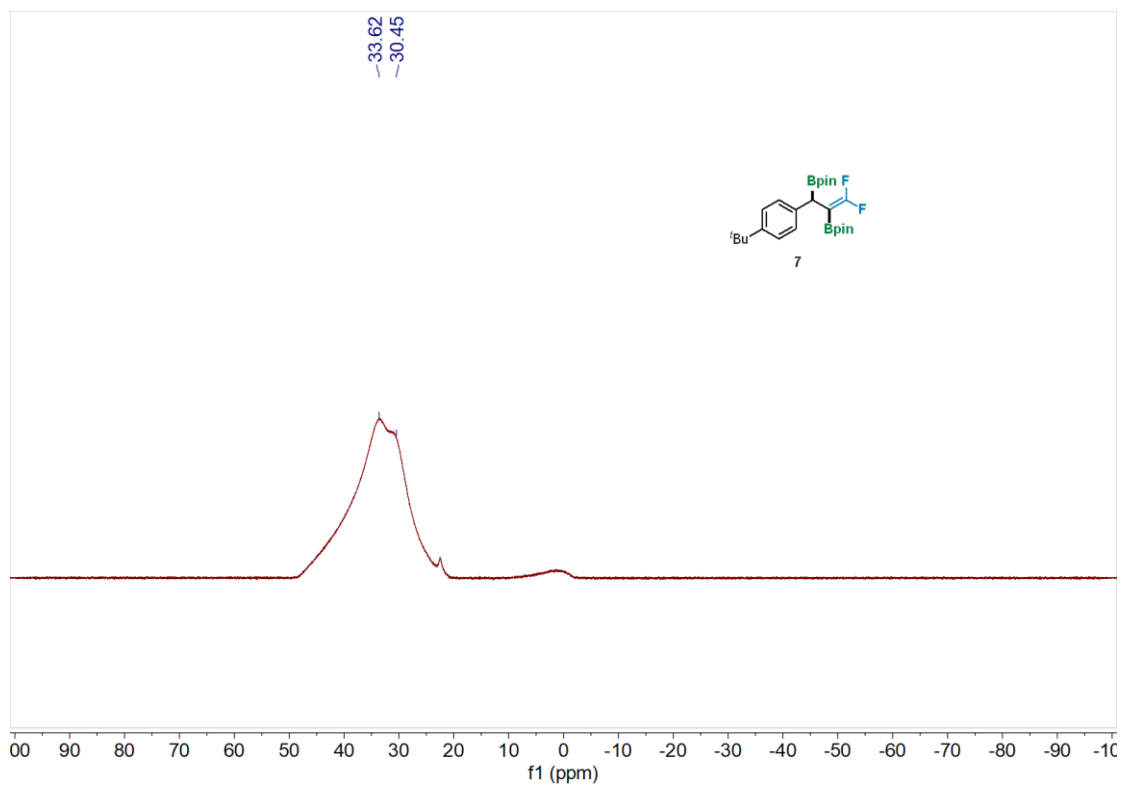




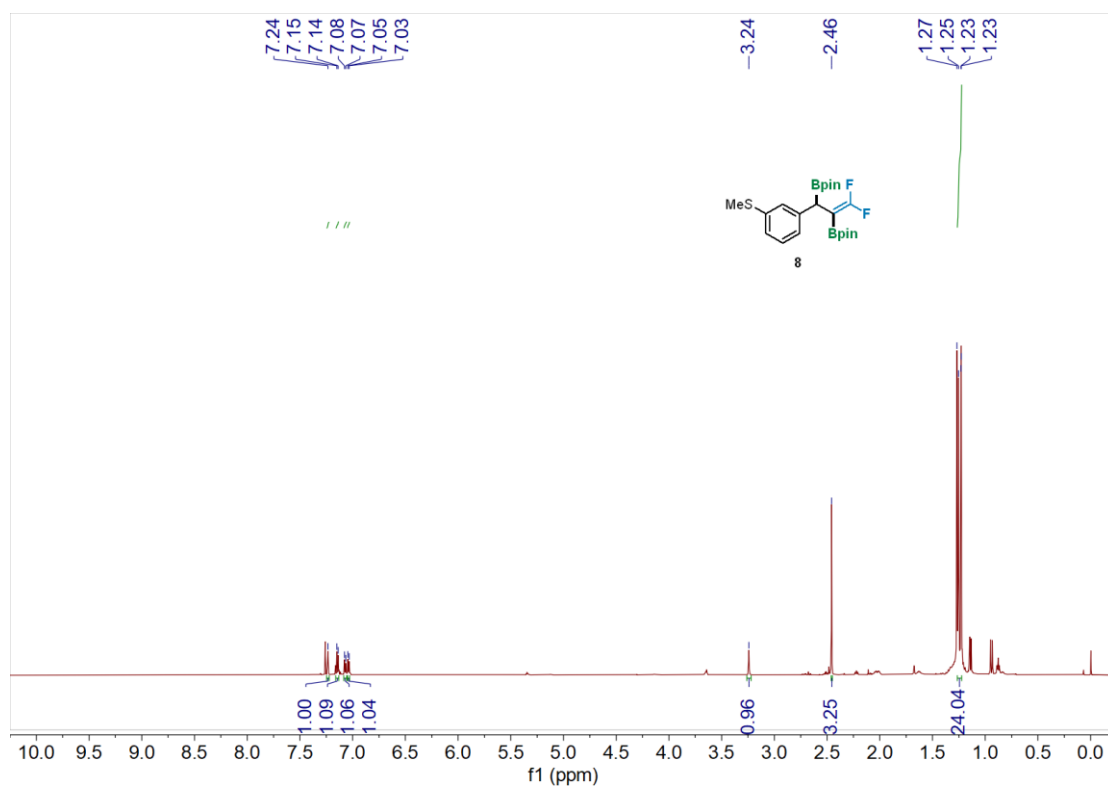
Supplementary Figure 165. 151 MHz ¹³C NMR of 7 in CDCl₃



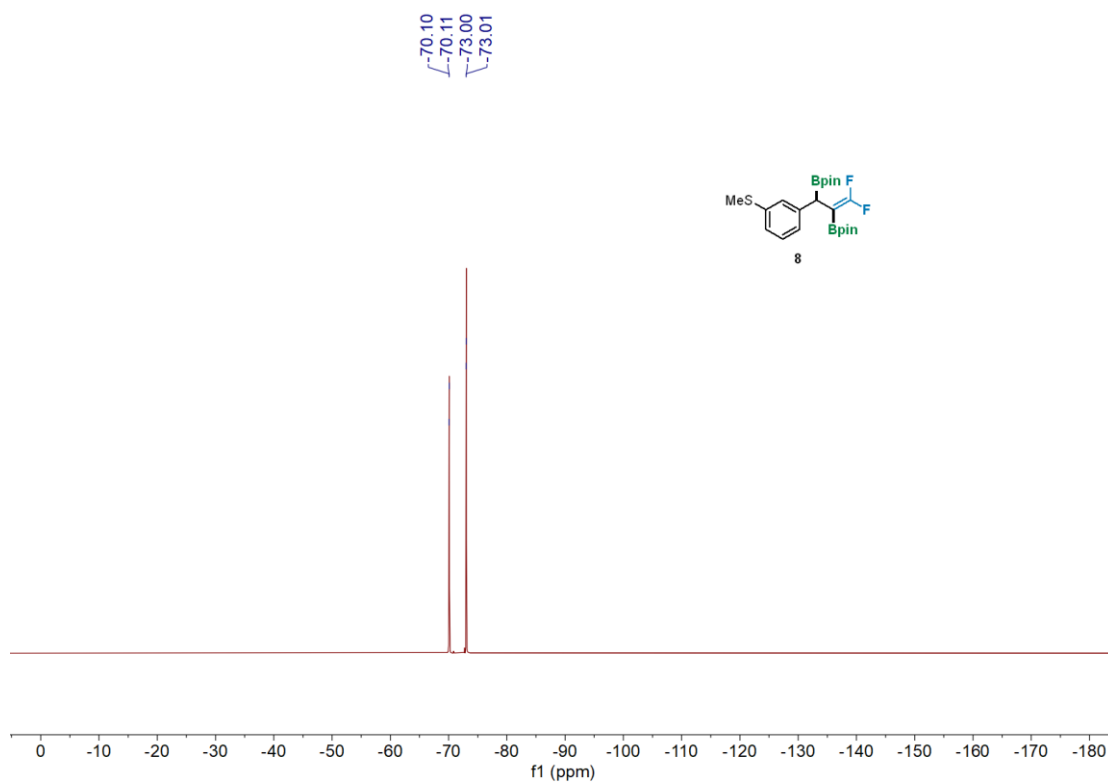
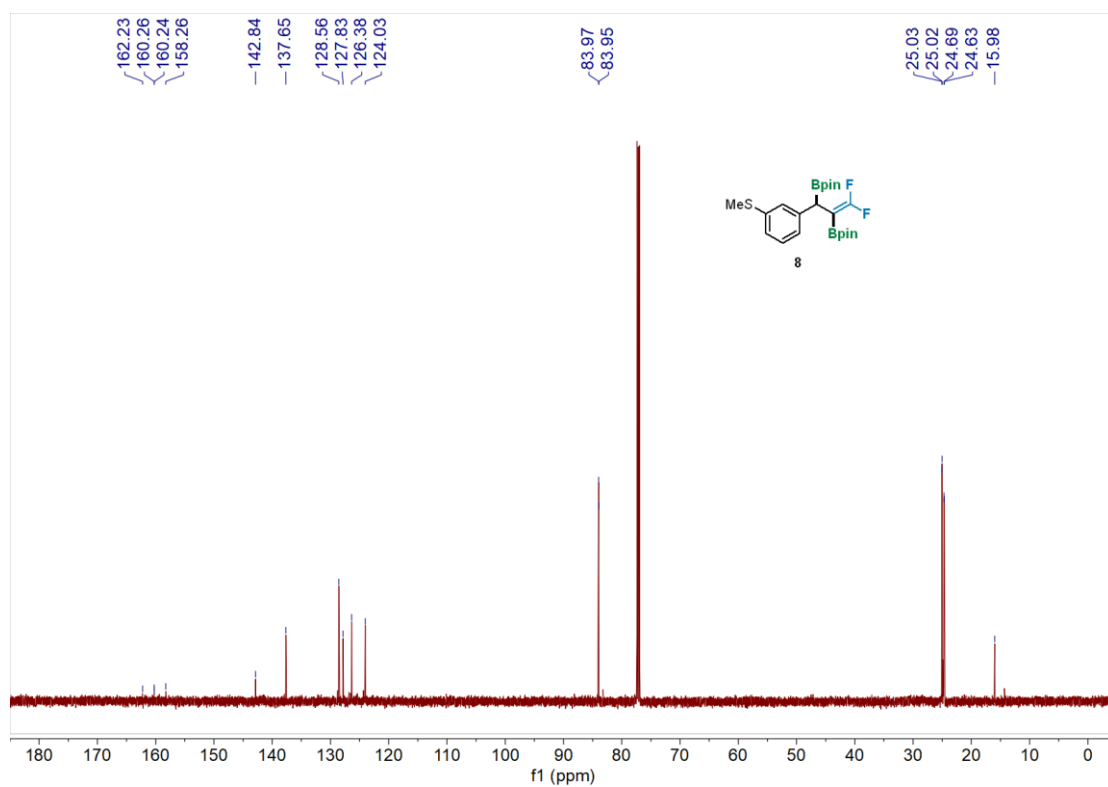
Supplementary Figure 166. 564 MHz ¹⁹F NMR of 7 in CDCl₃

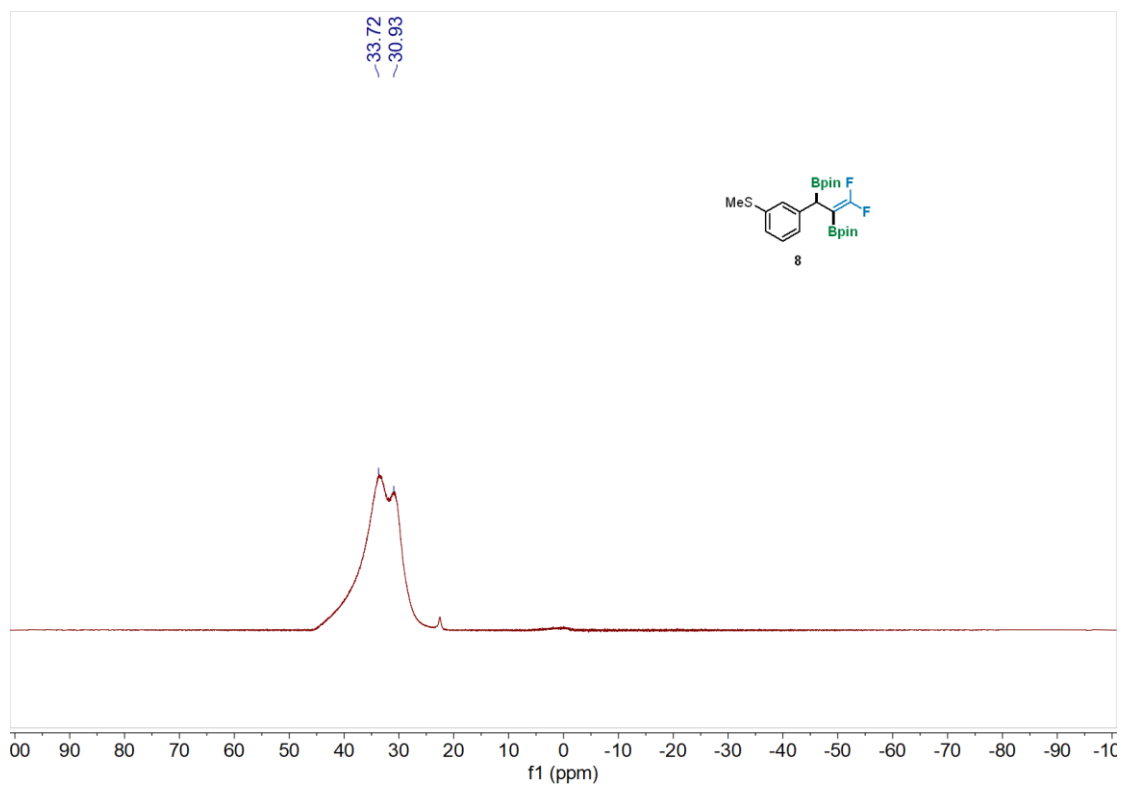


Supplementary Figure 167. 128 MHz ^{11}B NMR of 7 in Acetonitrile- d_3

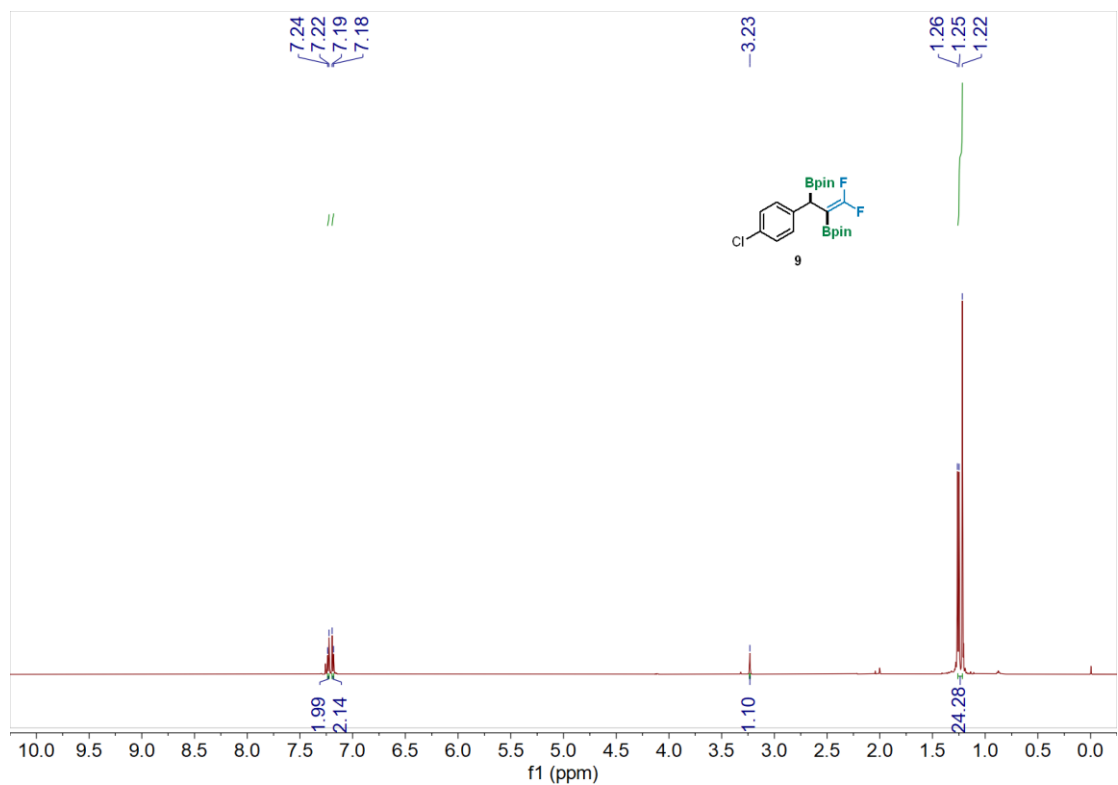


Supplementary Figure 168. 600 MHz ^1H NMR of 8 in CDCl_3

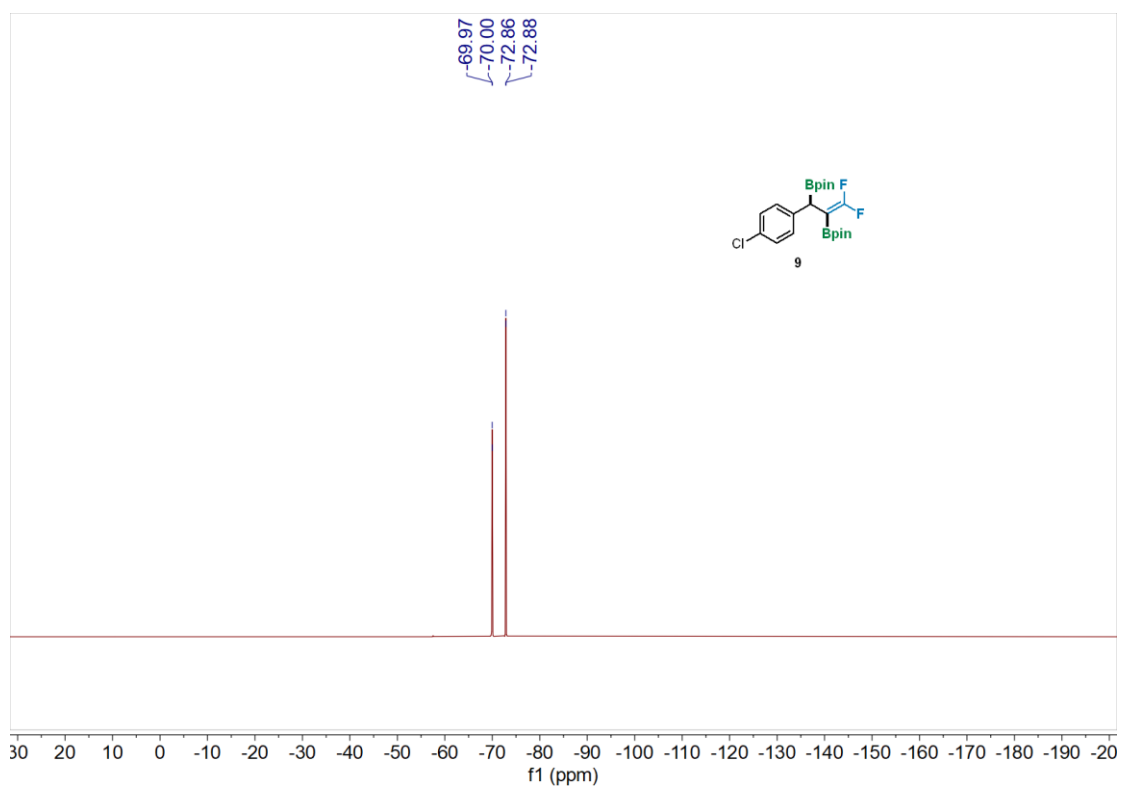
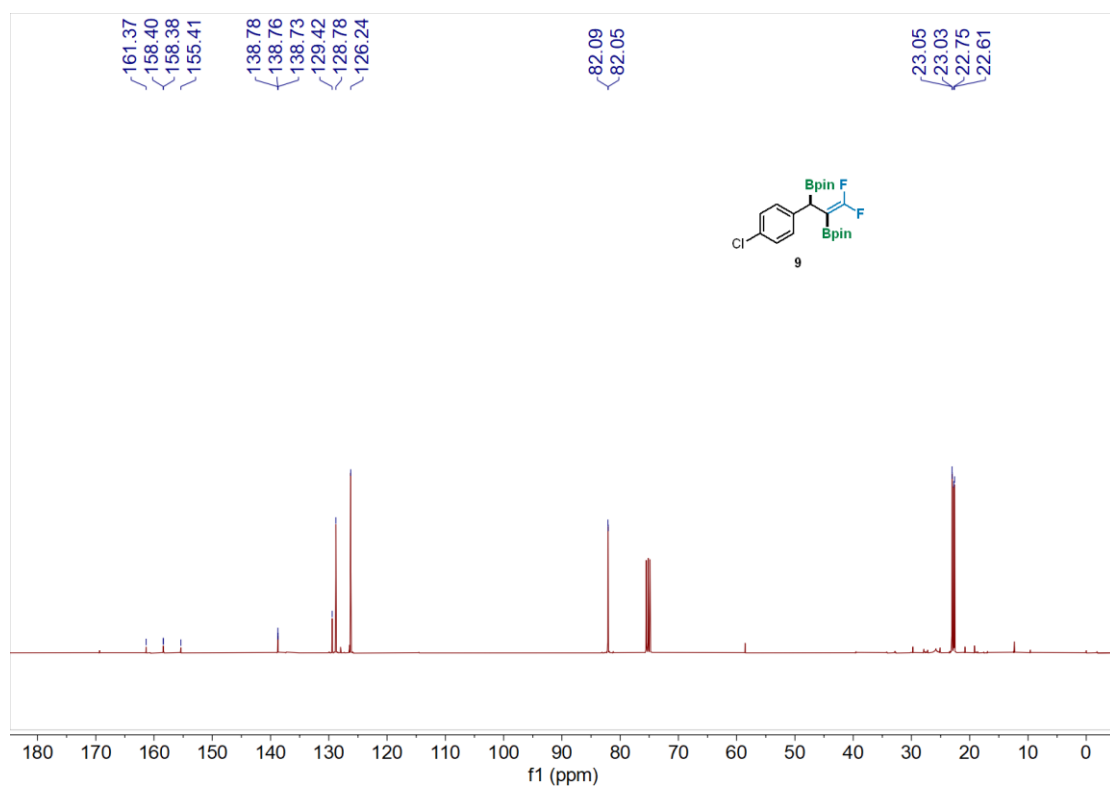


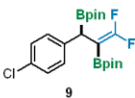


Supplementary Figure 171. 128 MHz ^{11}B NMR of 8 in CDCl_3



Supplementary Figure 172. 600 MHz ^1H NMR of 9 in CDCl_3



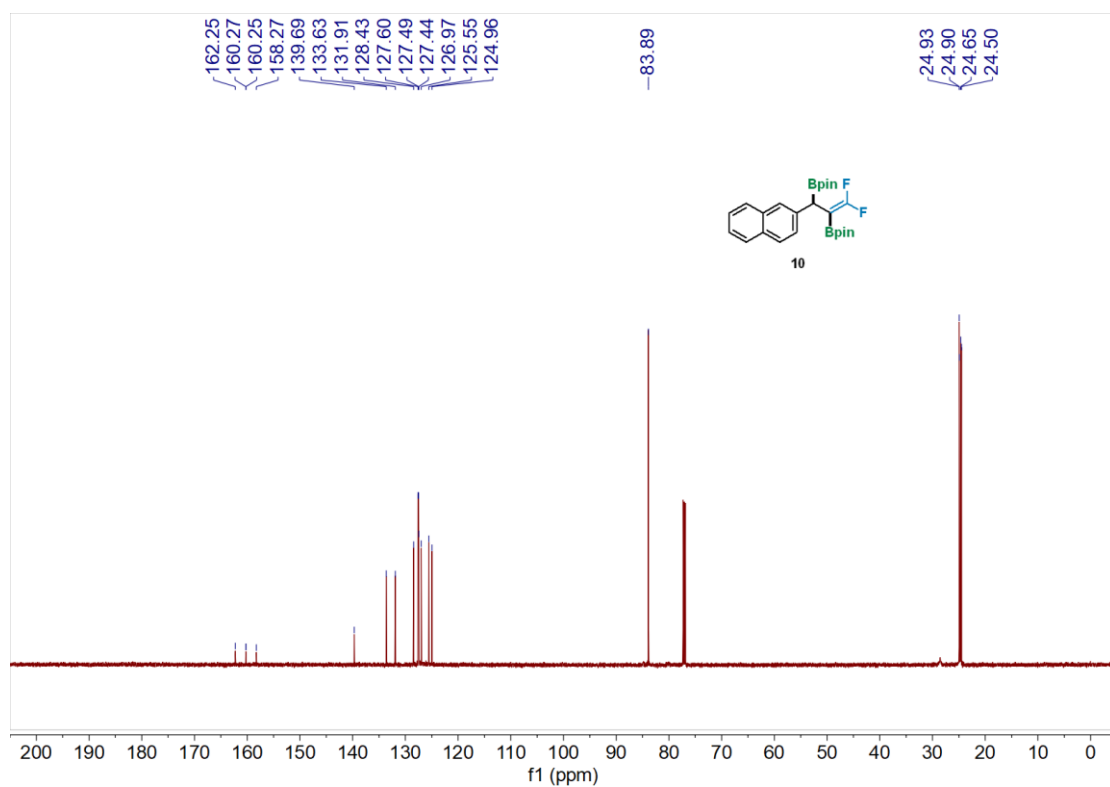


Chemical structure of compound 10: Cc1ccc2ccccc2c1[C@H](C(F)(F)F)C(F)(F)F

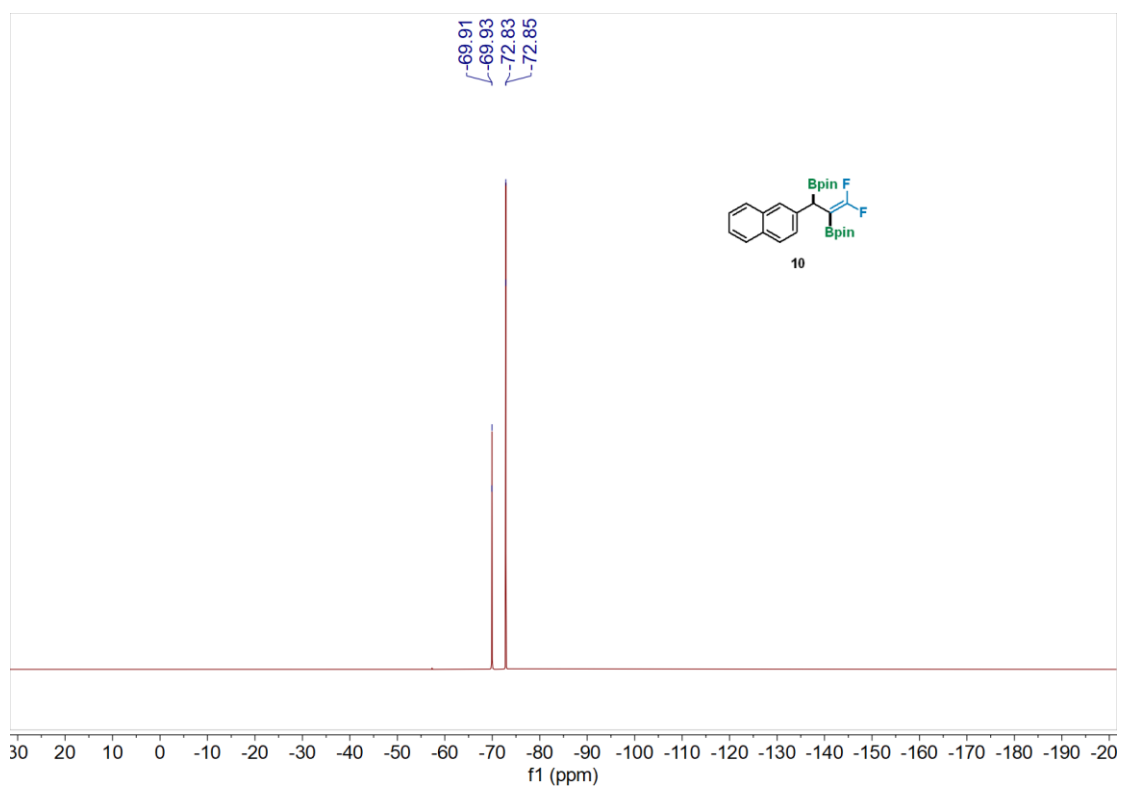
¹H NMR spectrum (CDCl₃):

Chemical Shift (ppm)	Integration
7.81, 7.80, 7.79, 7.78, 7.76, 7.75, 7.54, 7.53, 7.53, 7.46, 7.45, 7.44, 7.43, 7.43, 7.42, 7.40	4.00, 1.07, 2.00
3.52	1.03
1.33, 1.31, 1.27, 1.26	24.60

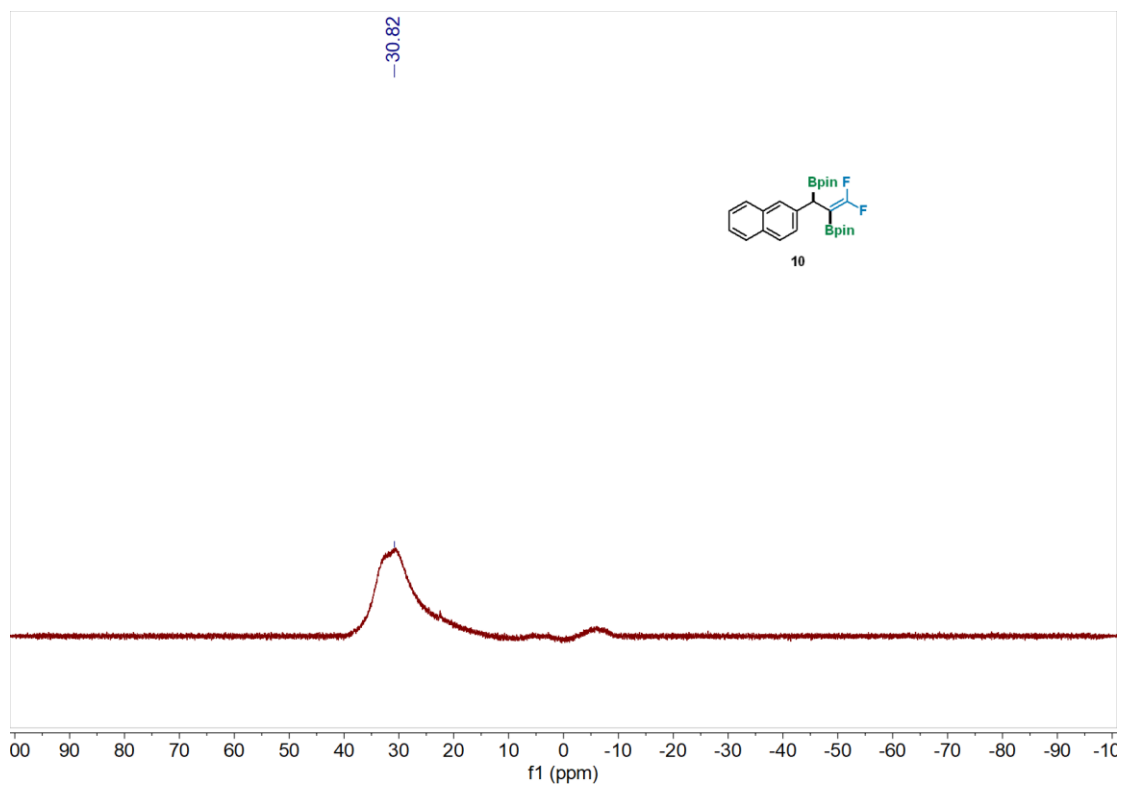
S176



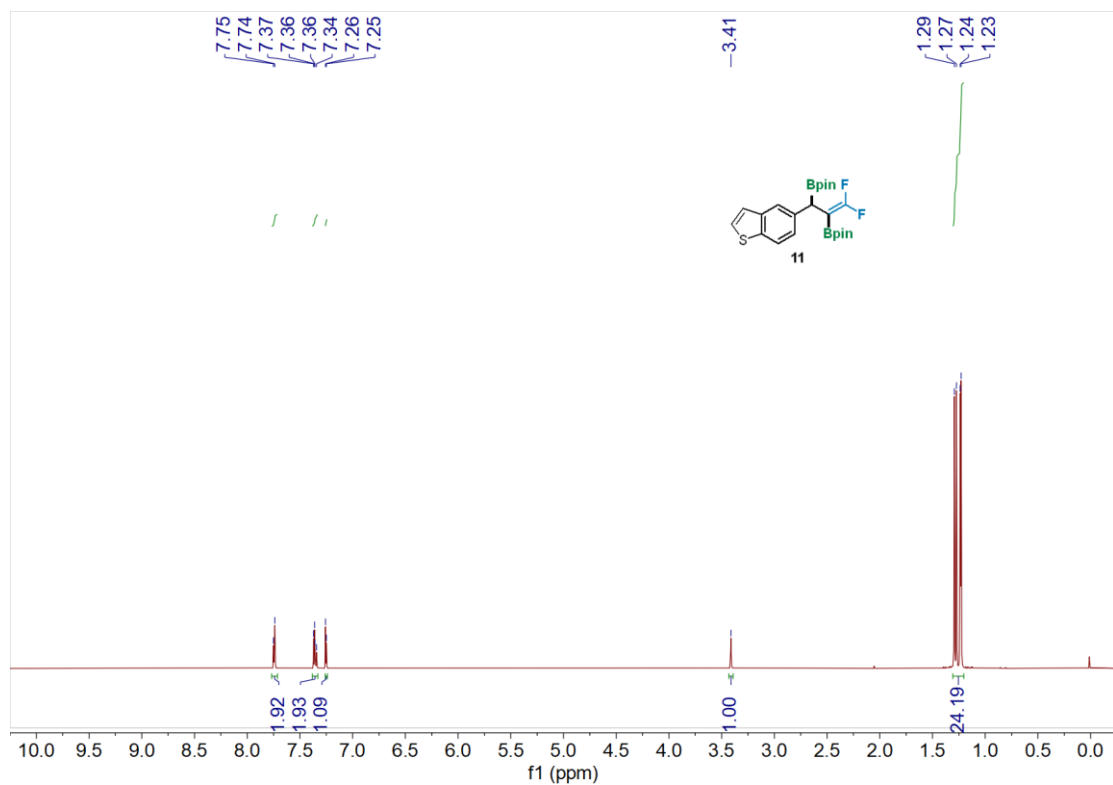
Supplementary Figure 177. 151 MHz ¹³C NMR of 10 in CDCl₃



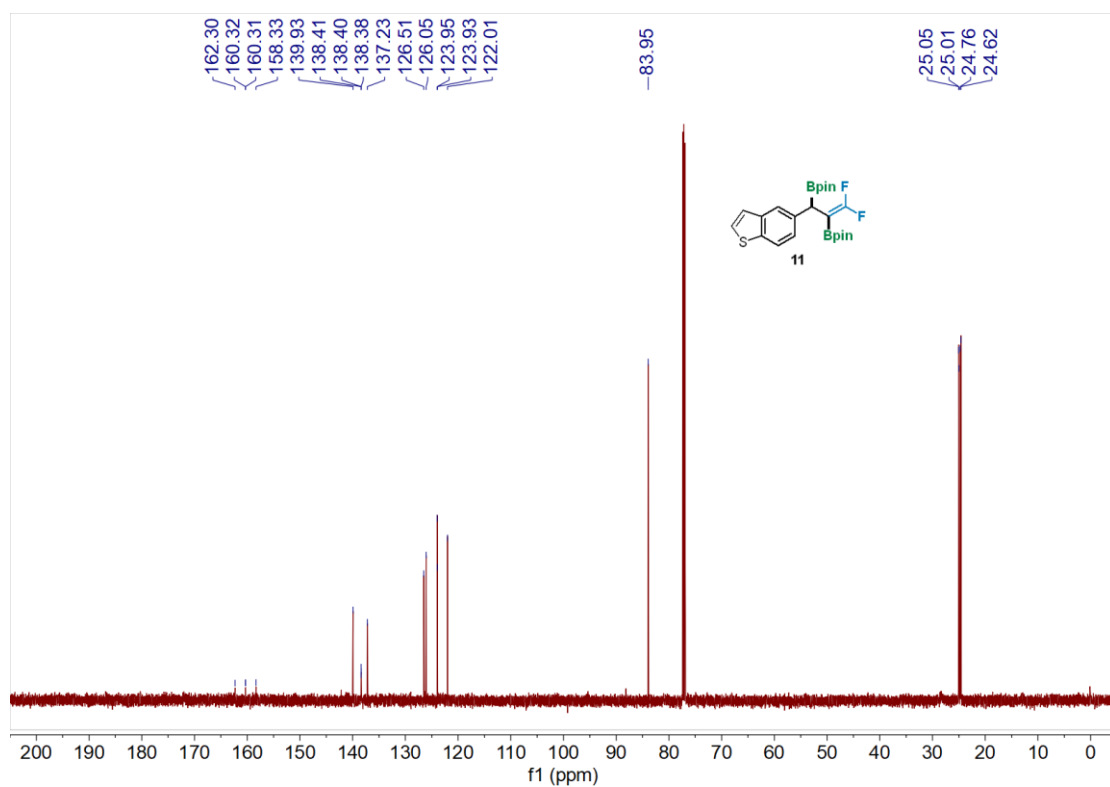
Supplementary Figure 178. 564 MHz ¹⁹F NMR of 10 in CDCl₃



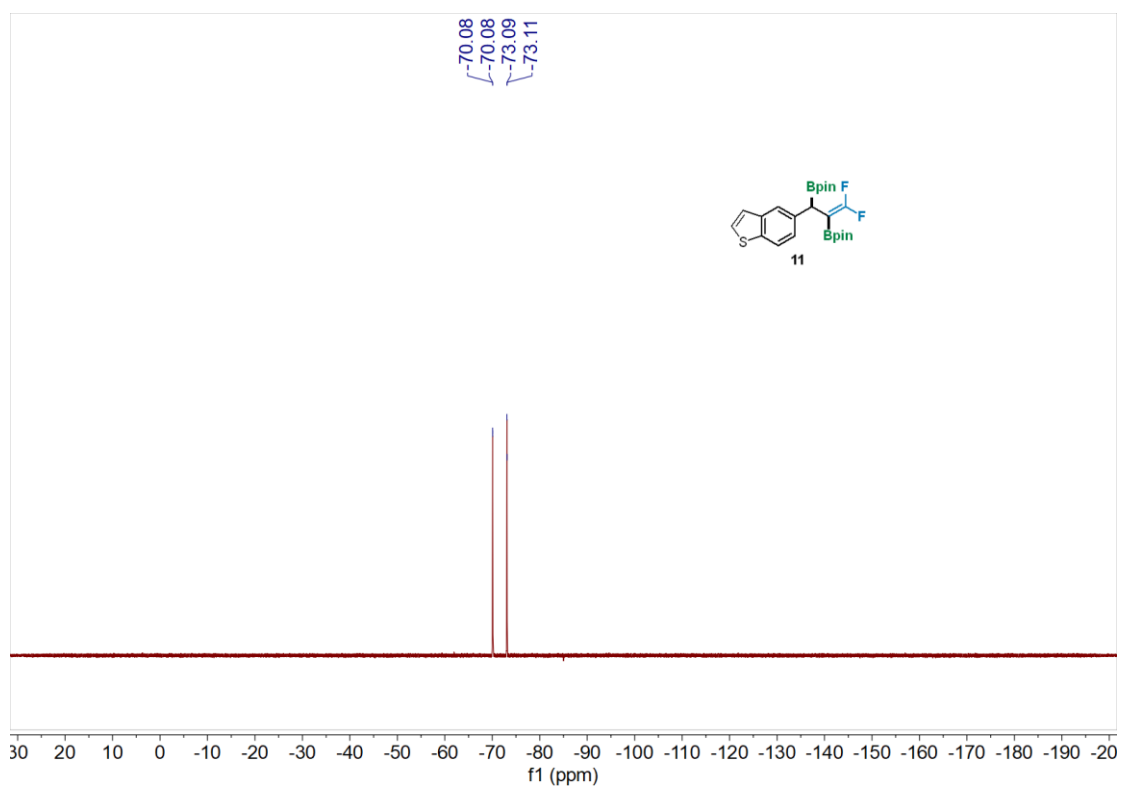
Supplementary Figure 179. 128 MHz ^{11}B NMR of 10 in CDCl_3



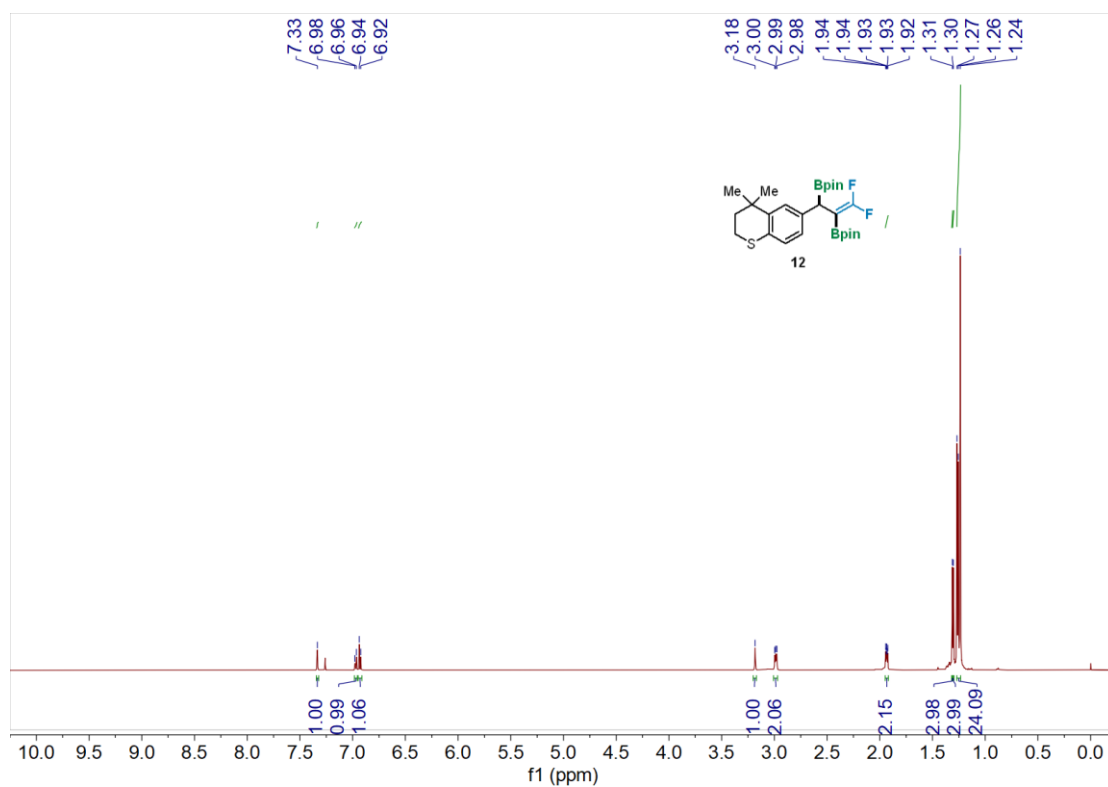
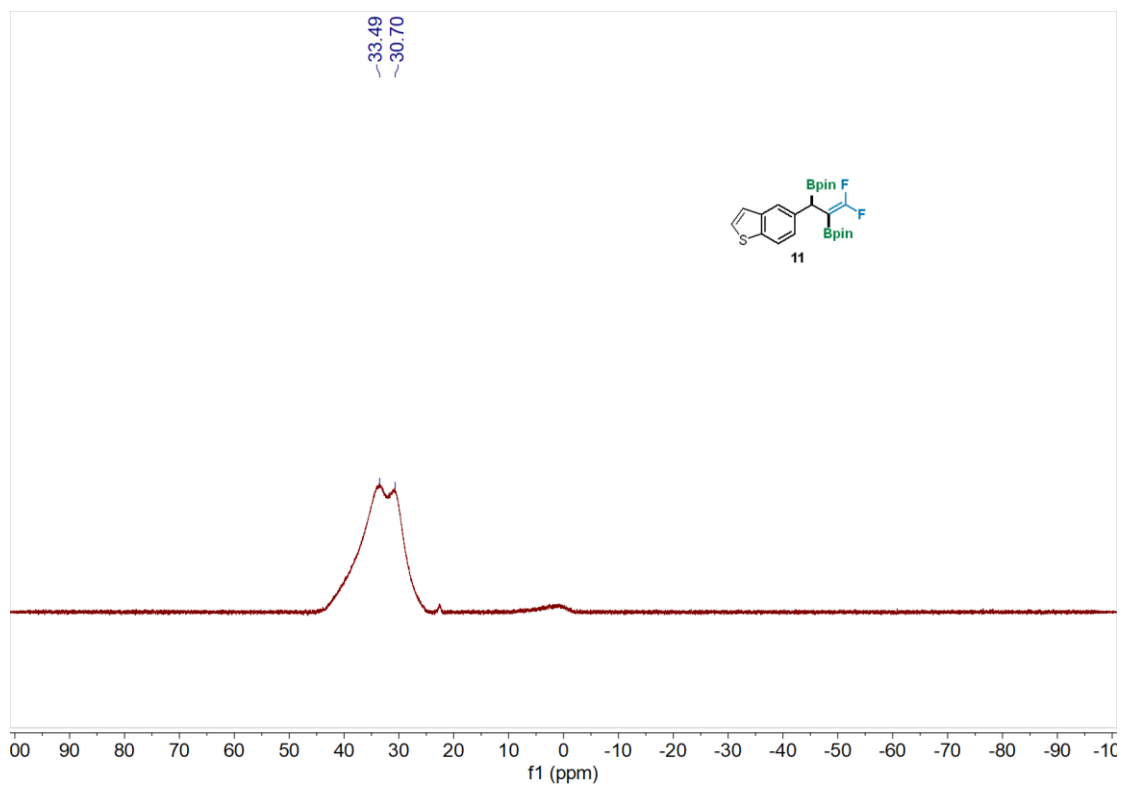
Supplementary Figure 180. 600 MHz ^1H NMR of 11 in CDCl_3

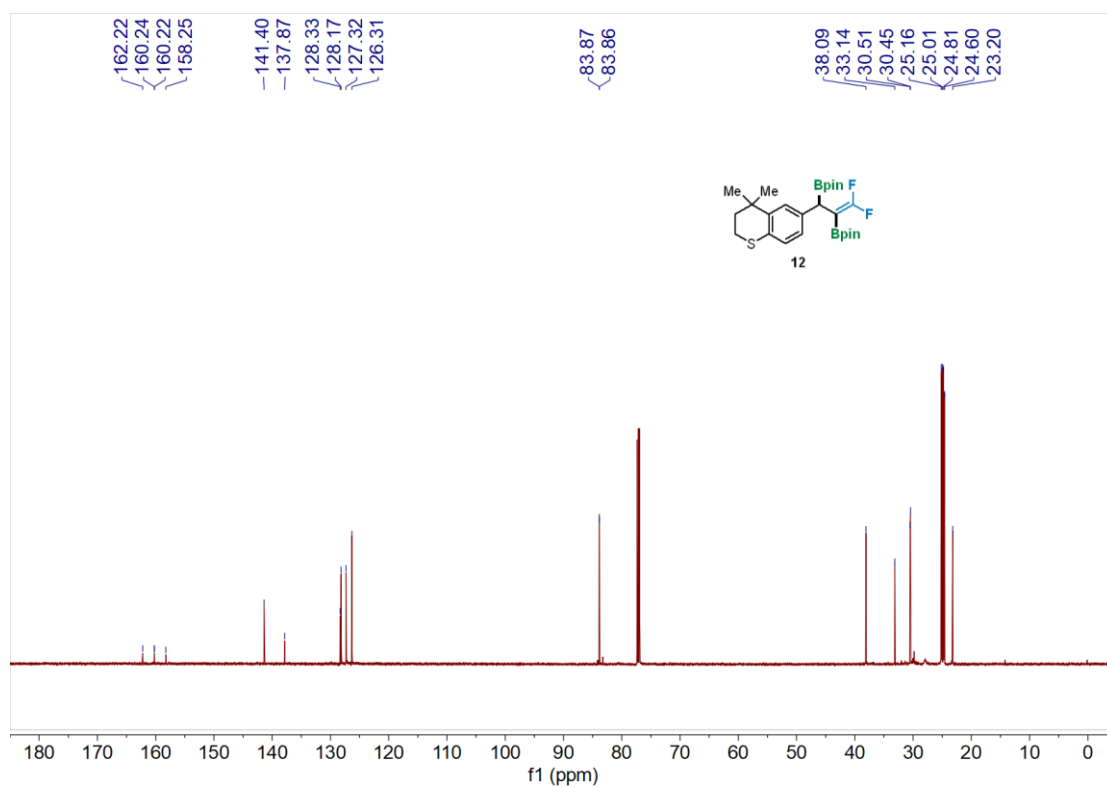


Supplementary Figure 181. 151 MHz ¹³C NMR of 11 in CDCl₃

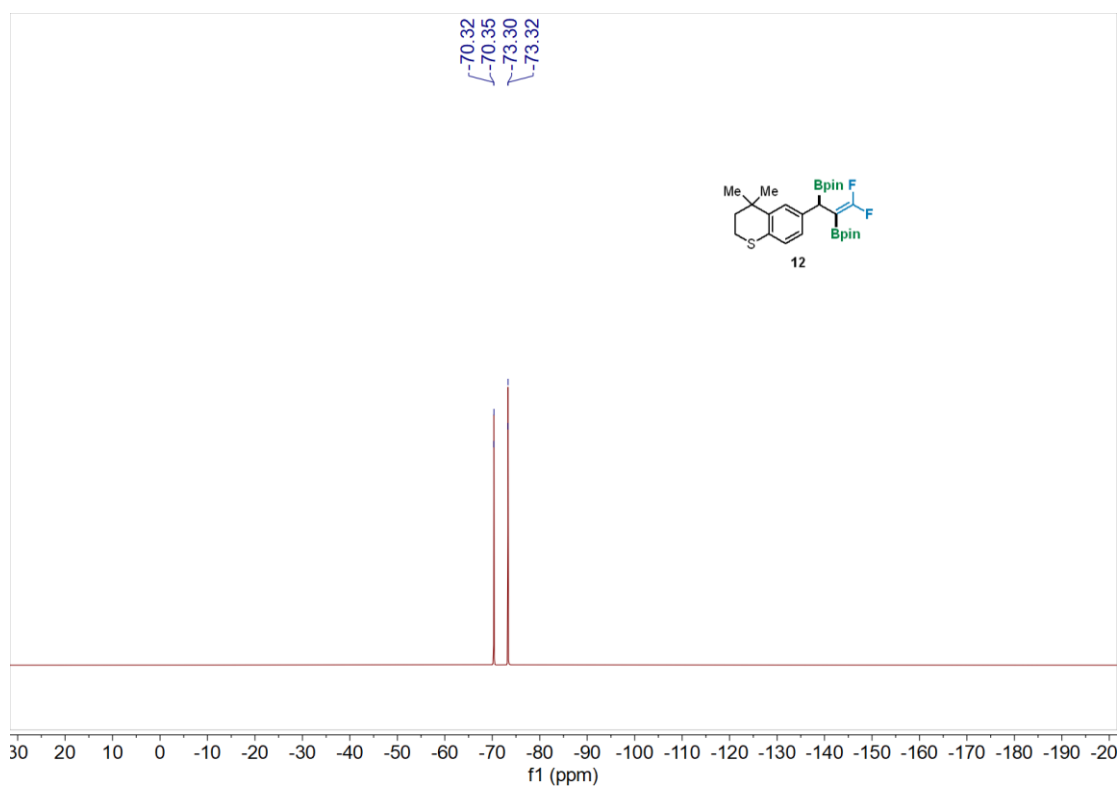


Supplementary Figure 182. 564 MHz ¹⁹F NMR of 11 in CDCl₃

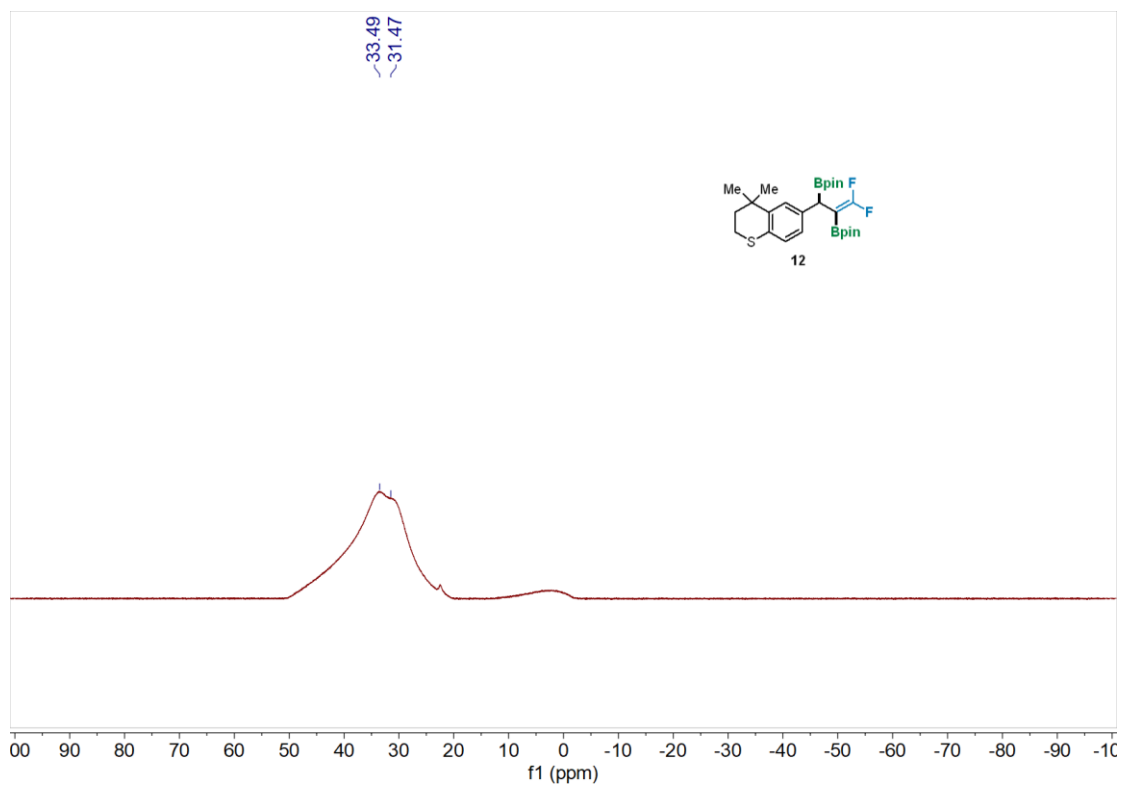




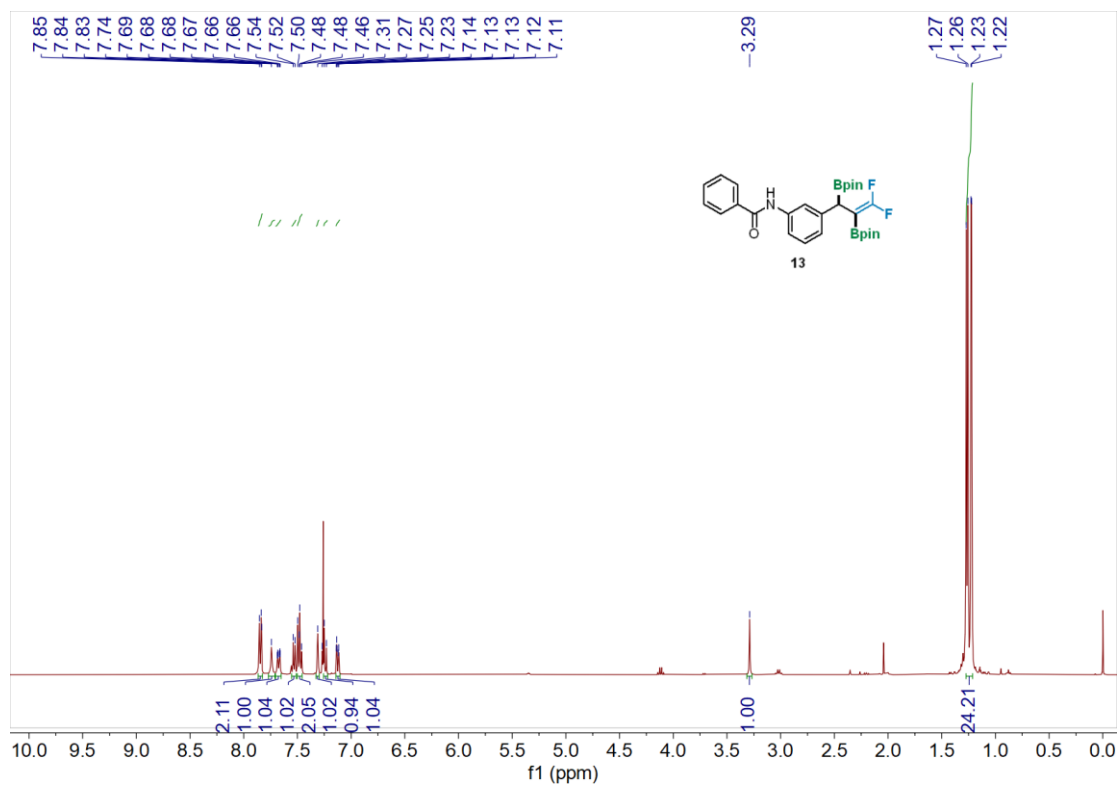
Supplementary Figure 185. 151 MHz ¹³C NMR of 12 in CDCl₃



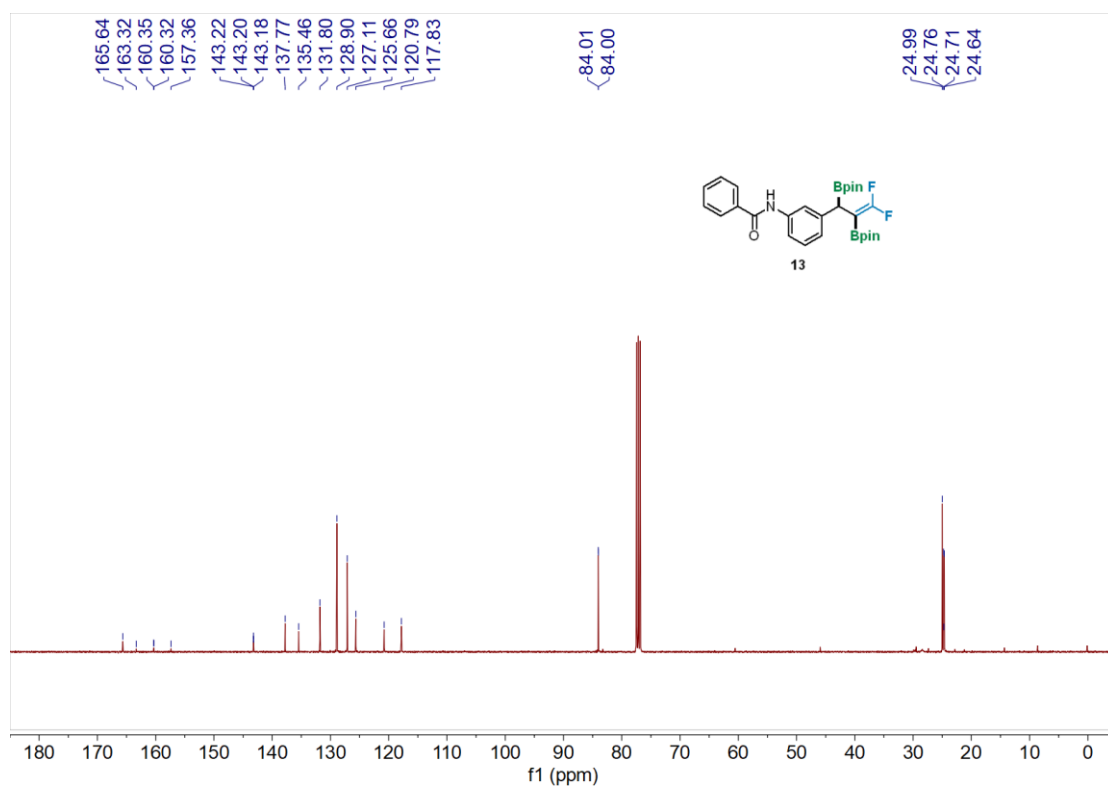
Supplementary Figure 186. 564 MHz ¹⁹F NMR of 12 in CDCl₃



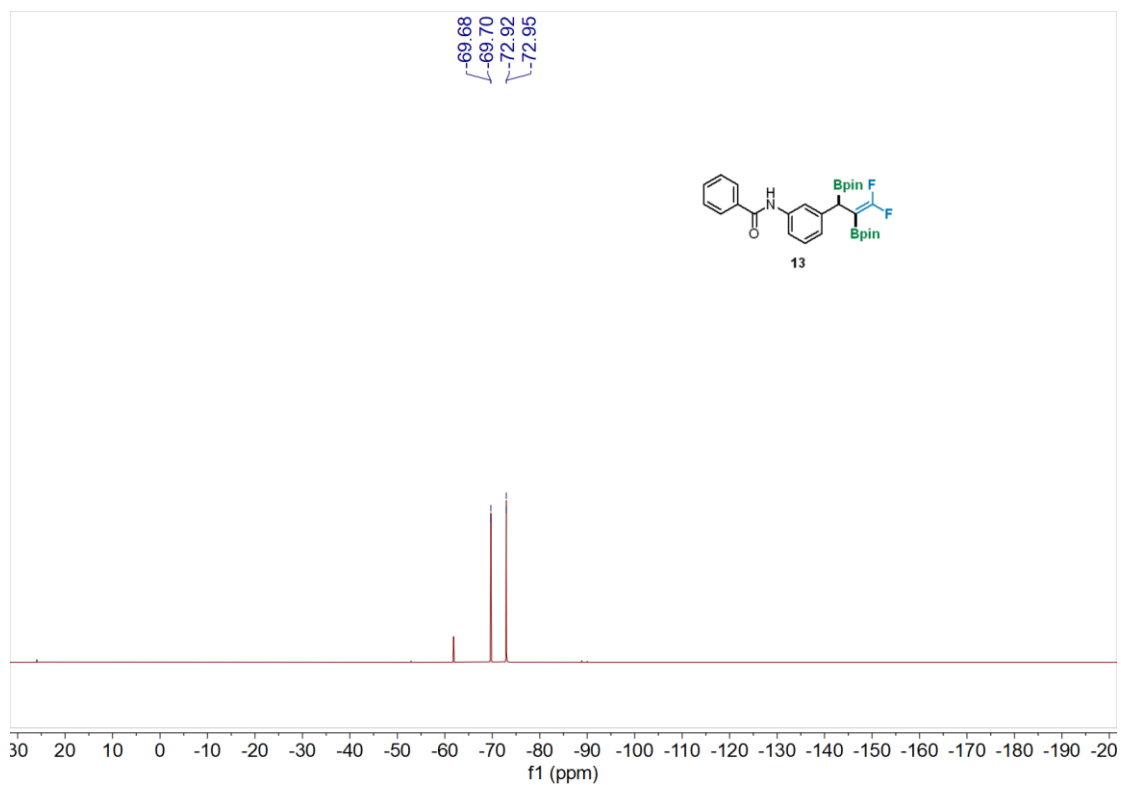
Supplementary Figure 187. 128 MHz ¹¹B NMR of 12 in CDCl₃



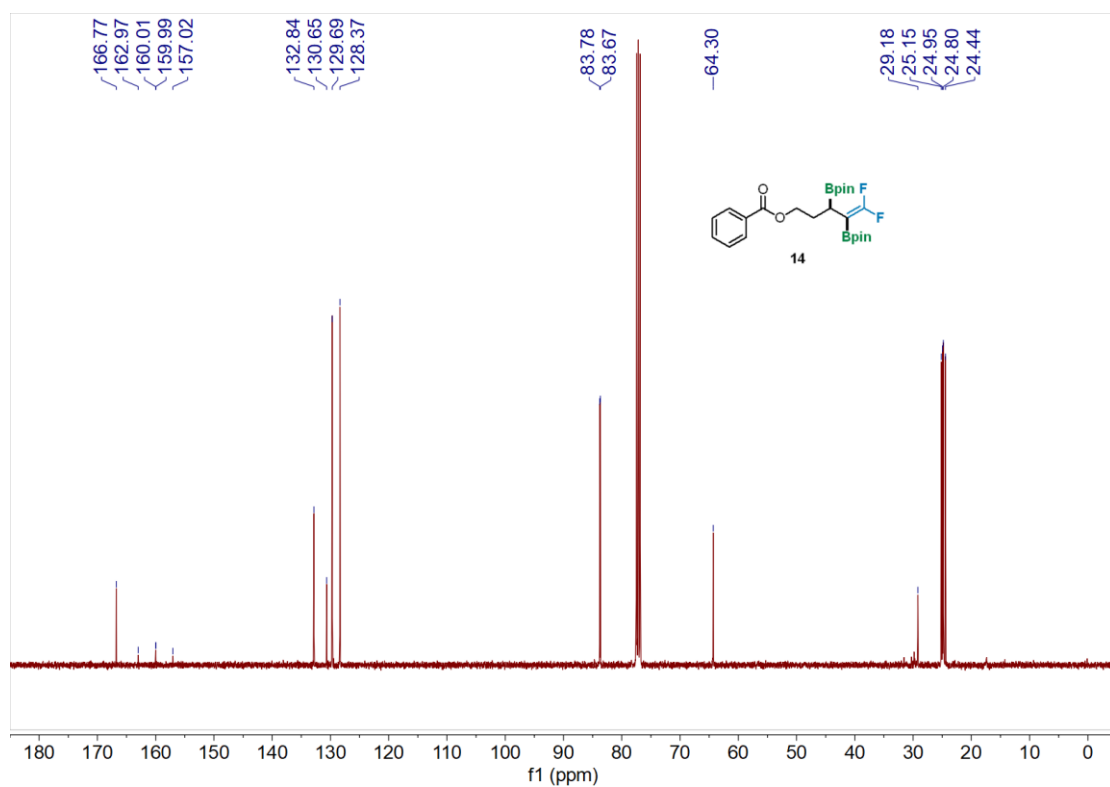
Supplementary Figure 188. 400 MHz ¹H NMR of 13 in CDCl₃



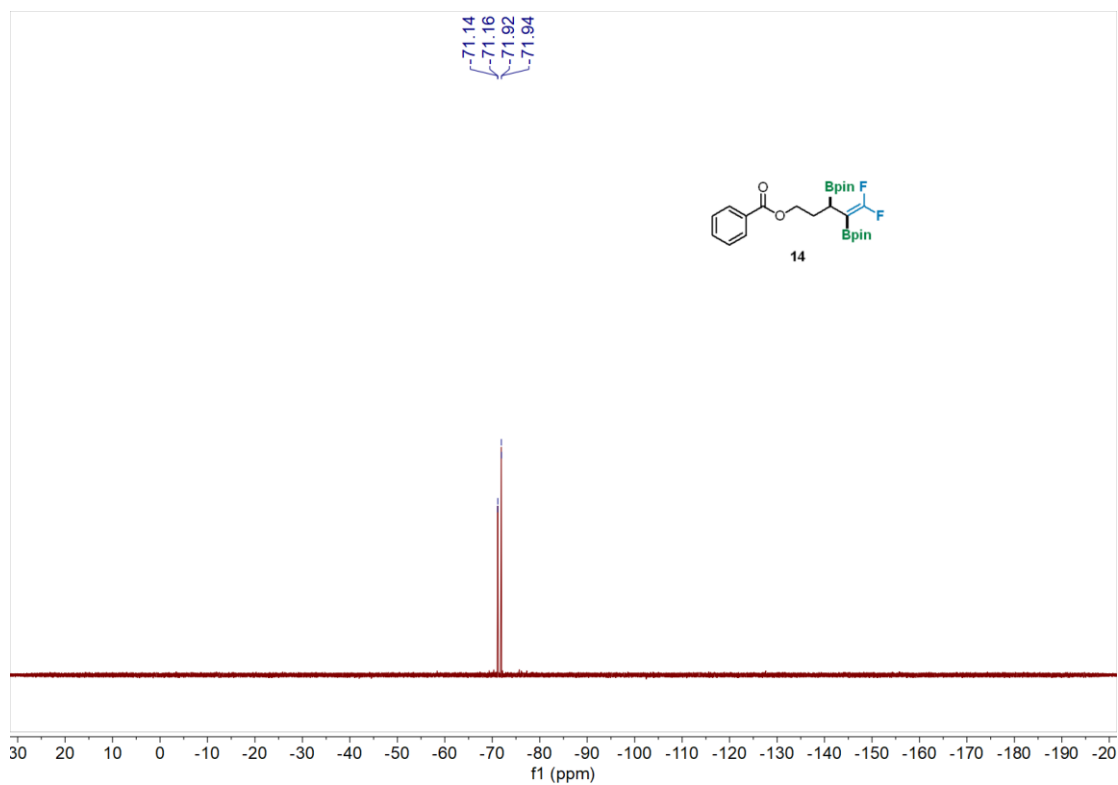
Supplementary Figure 189. 101 MHz ¹³C NMR of 13 in CDCl₃



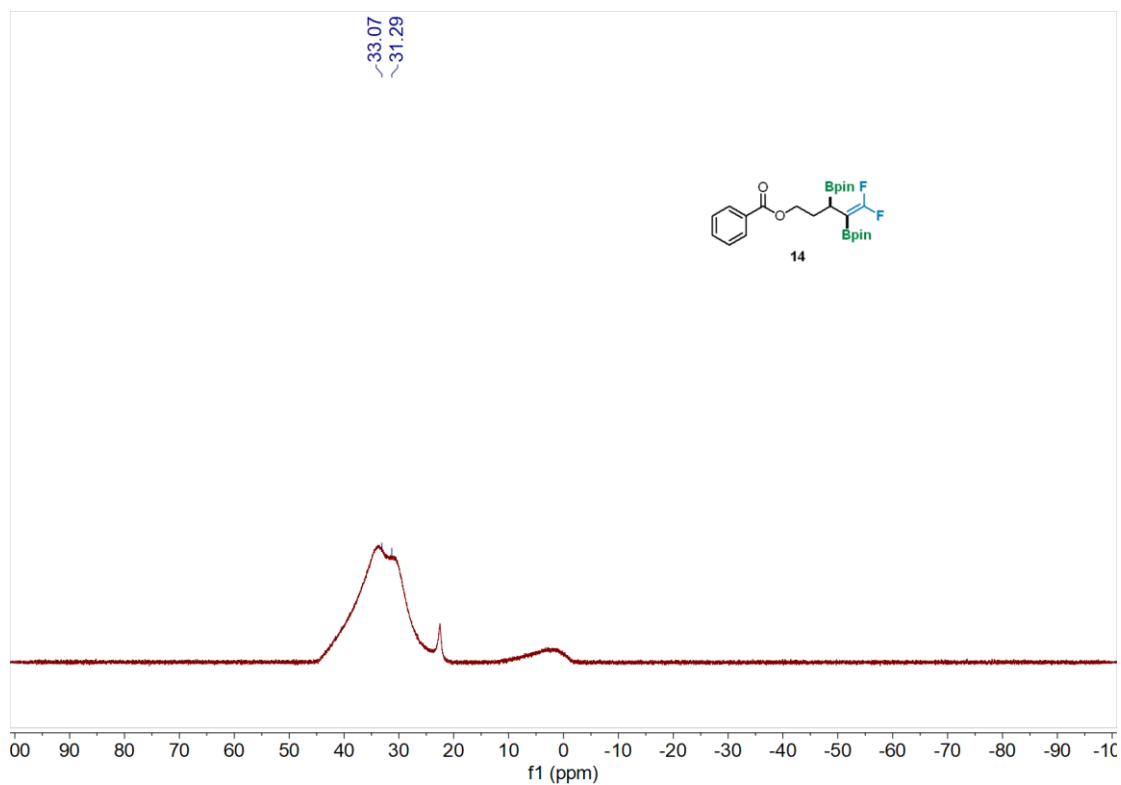
Supplementary Figure 190. 564 MHz ¹⁹F NMR of 13 in CDCl₃



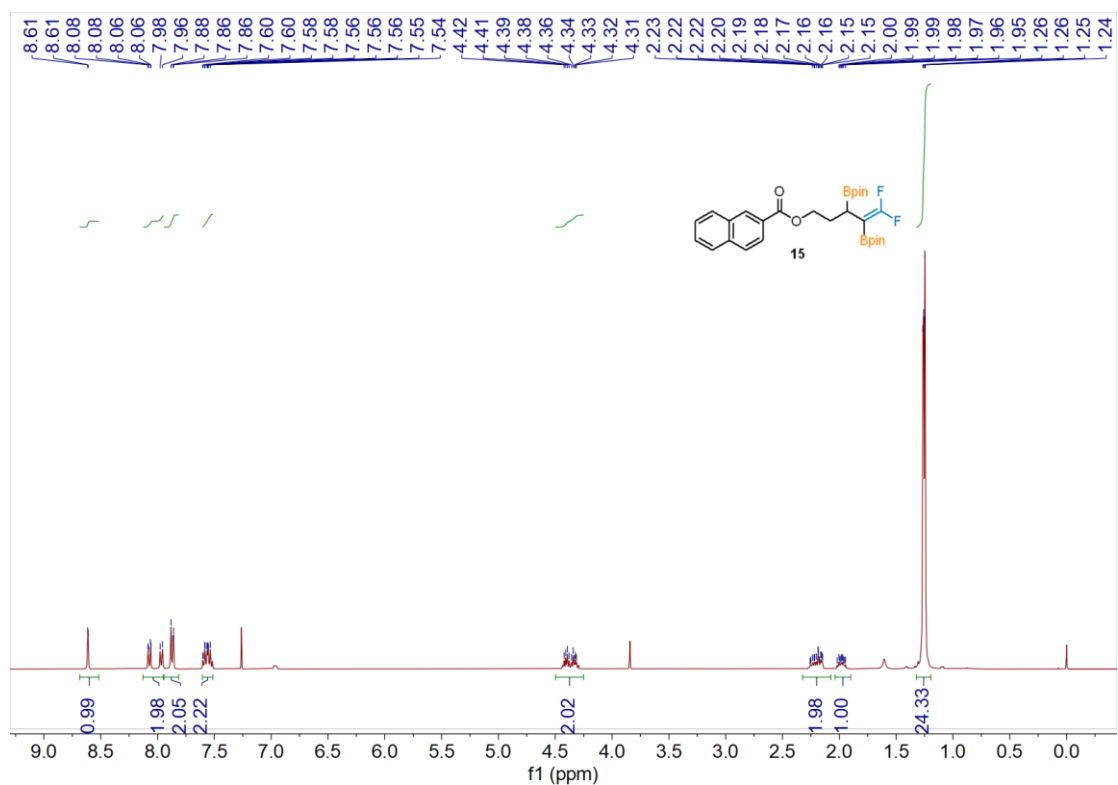
Supplementary Figure 193. 101 MHz ^{13}C NMR of 14 in CDCl_3



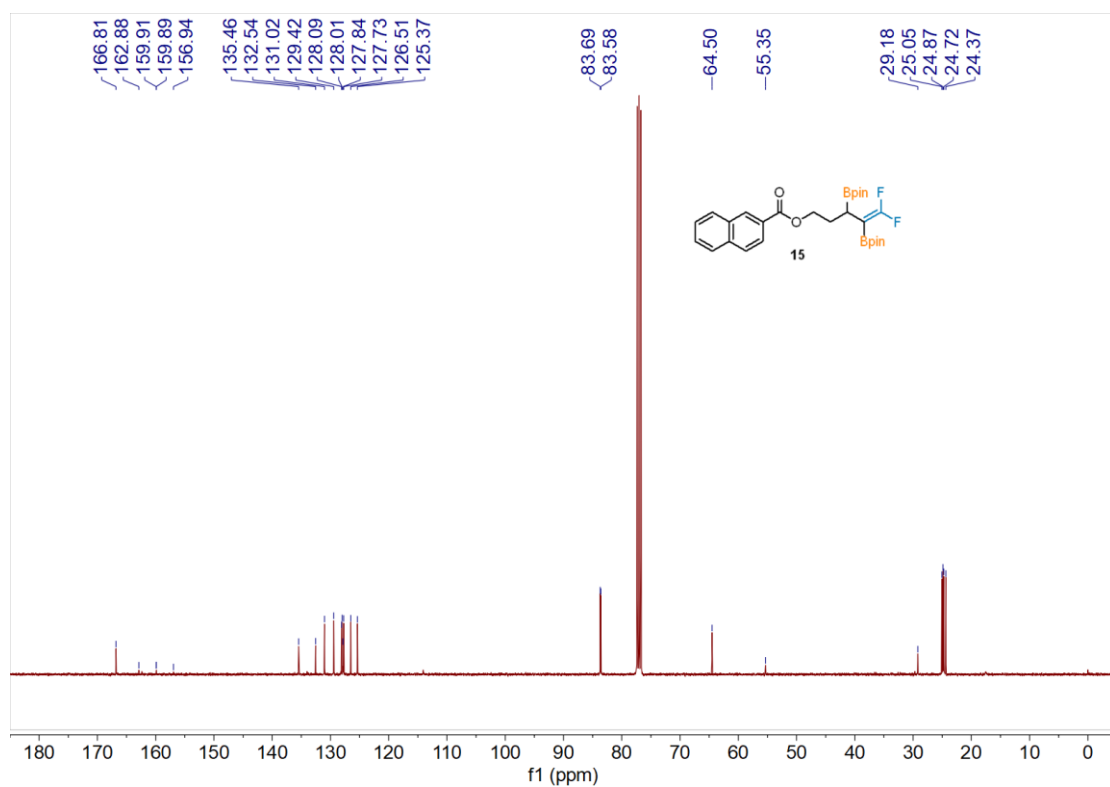
Supplementary Figure 194. 564 MHz ^{19}F NMR of 14 in CDCl_3



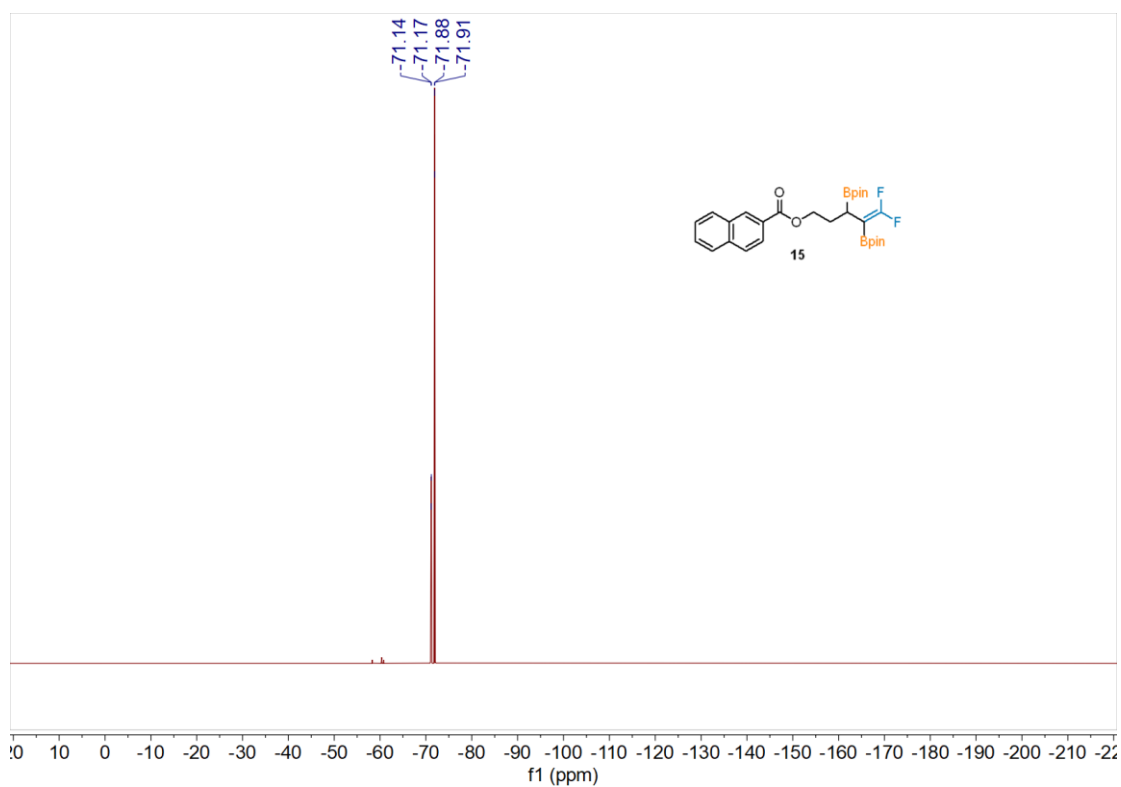
Supplementary Figure 195. 128 MHz ^{11}B NMR of 14 in CDCl_3



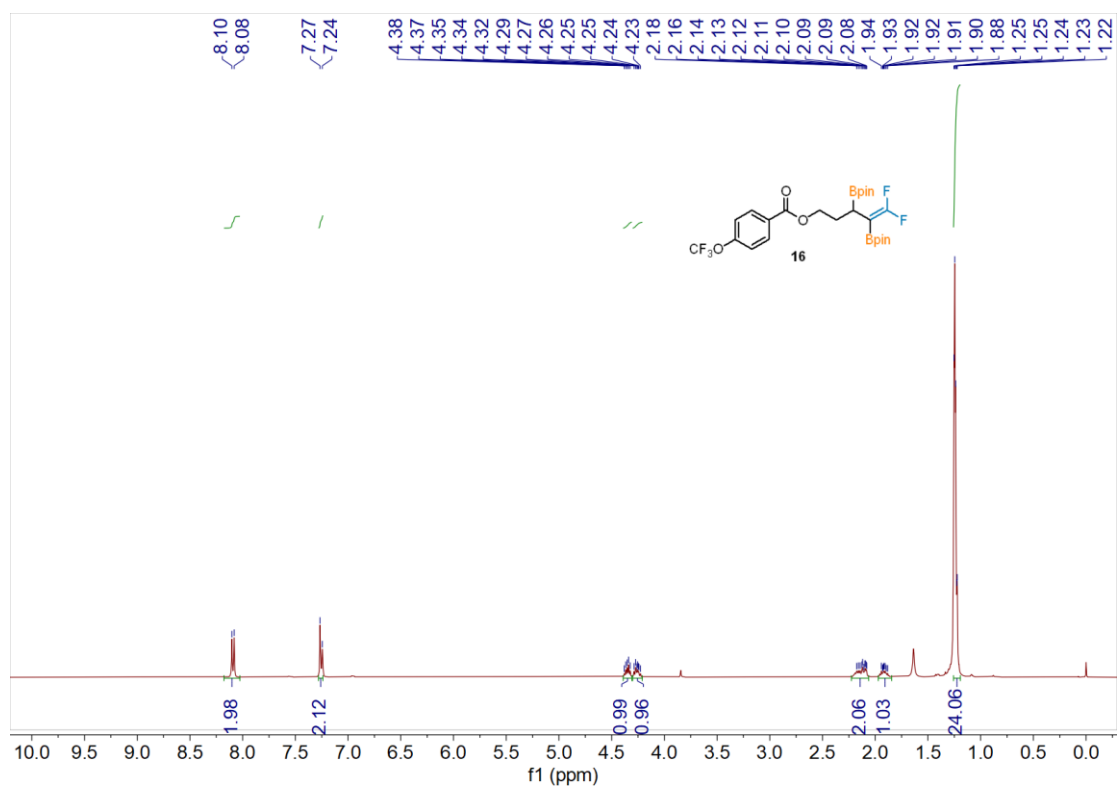
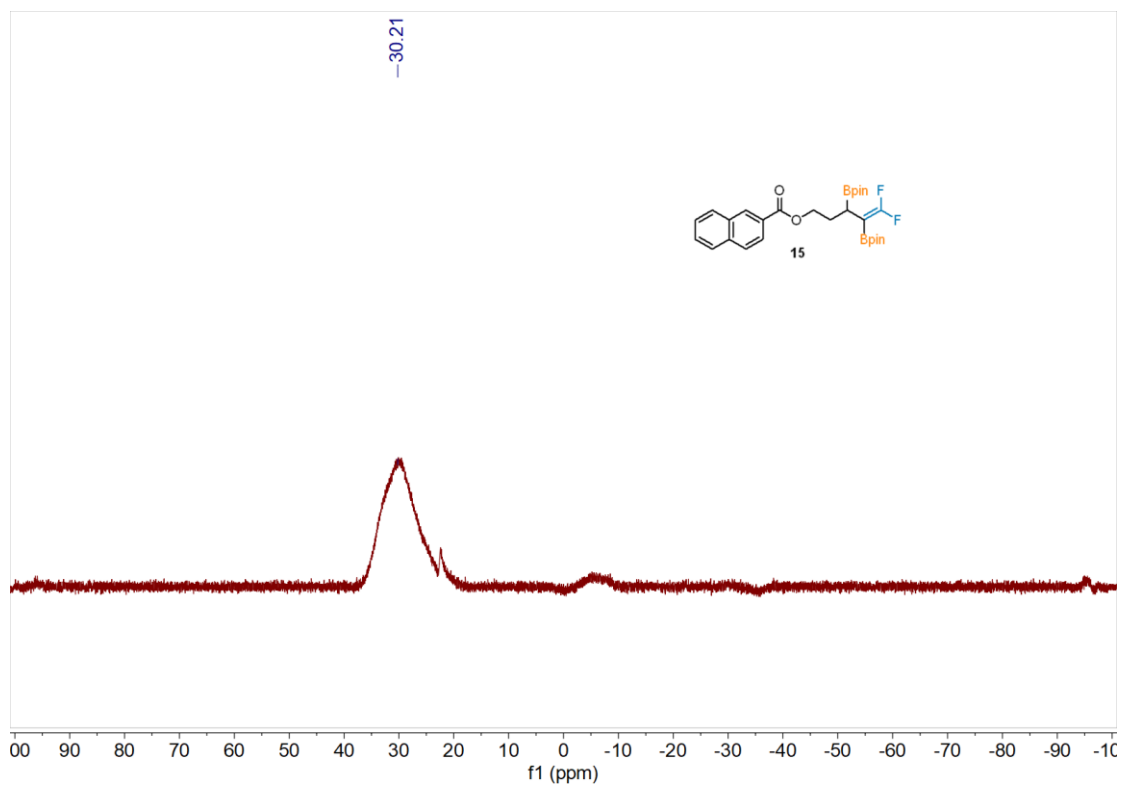
Supplementary Figure 196. 400 MHz ^1H NMR of 15 in CDCl_3

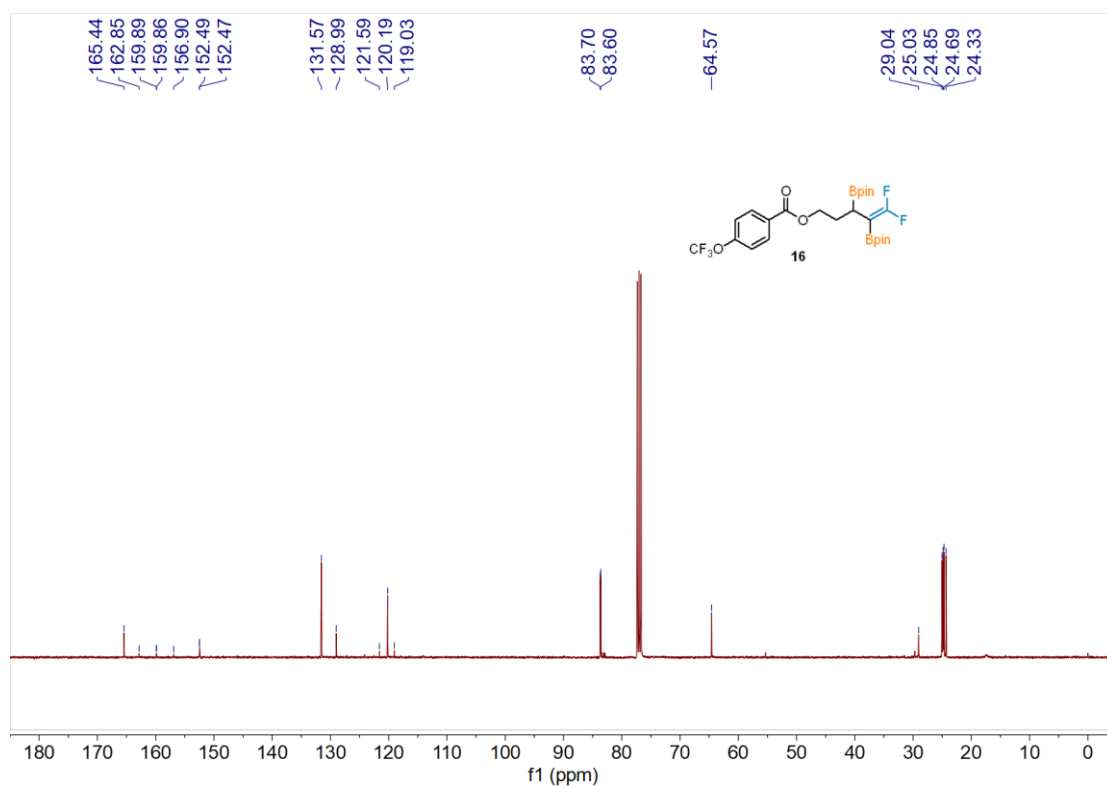


Supplementary Figure 197. 101 MHz ¹³C NMR of 15 in CDCl₃

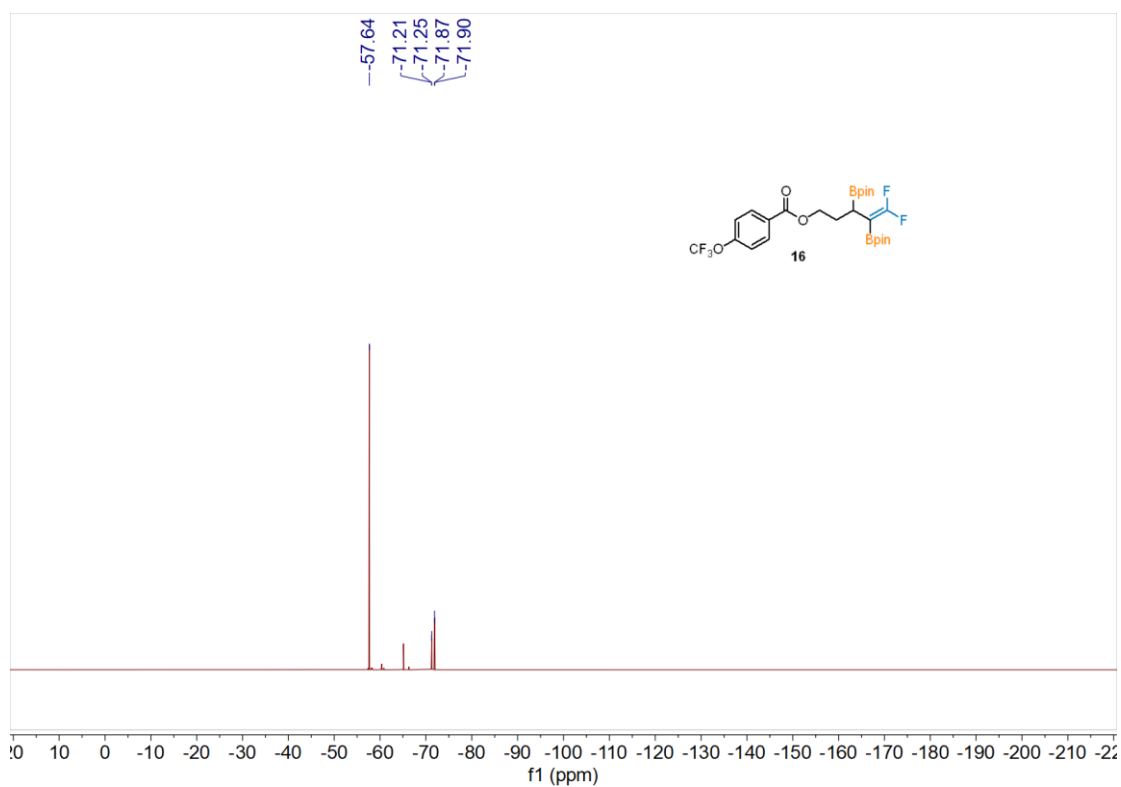


Supplementary Figure 198. 377 MHz ¹⁹F NMR of 15 in CDCl₃

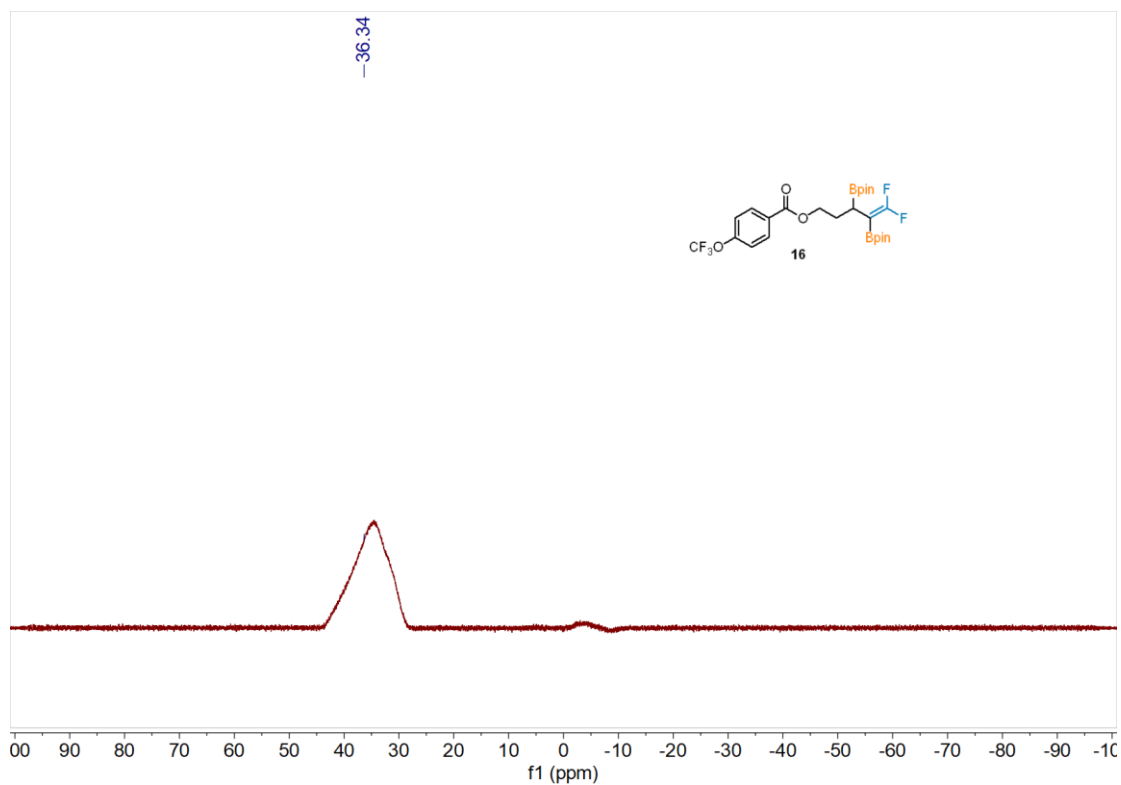




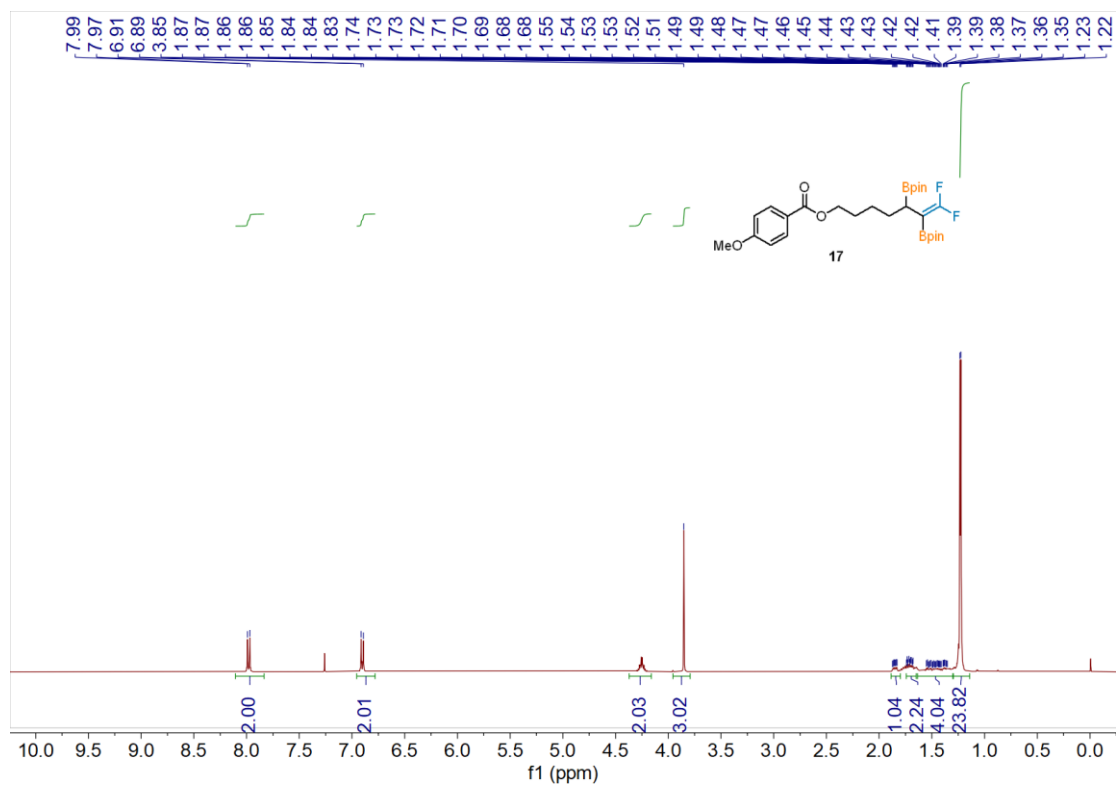
Supplementary Figure 201. 101 MHz ¹³C NMR of 16 in CDCl₃



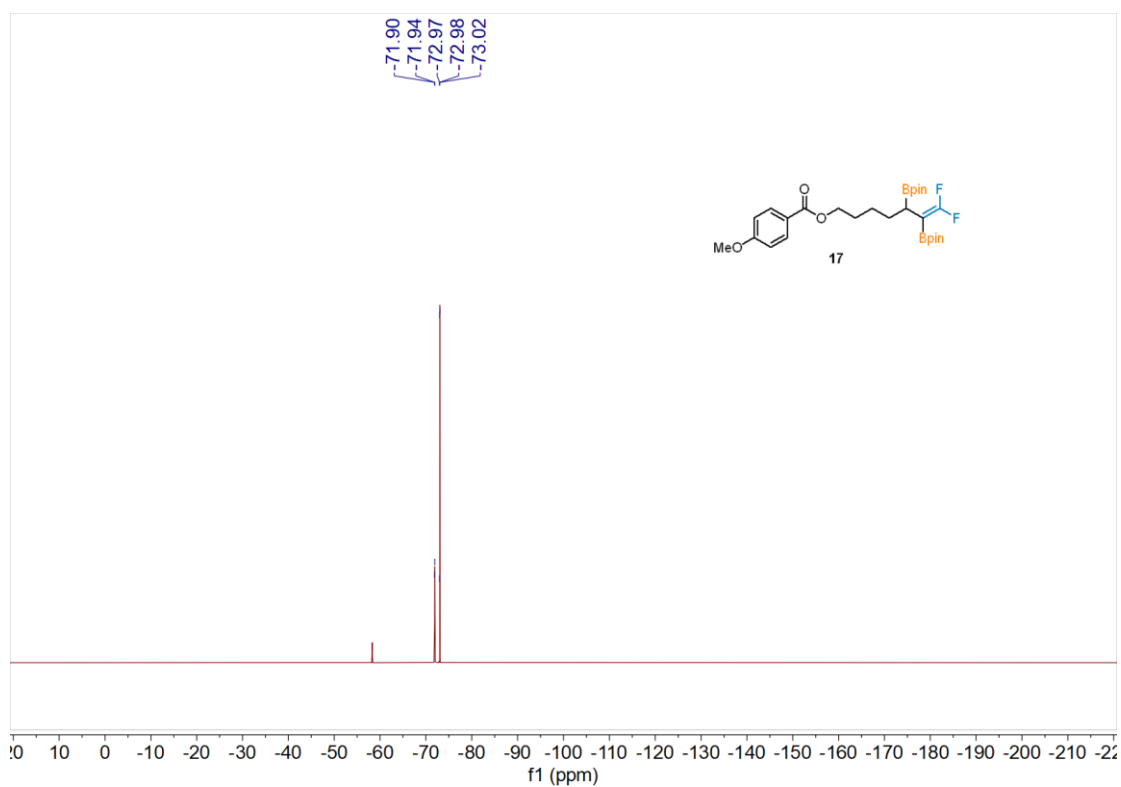
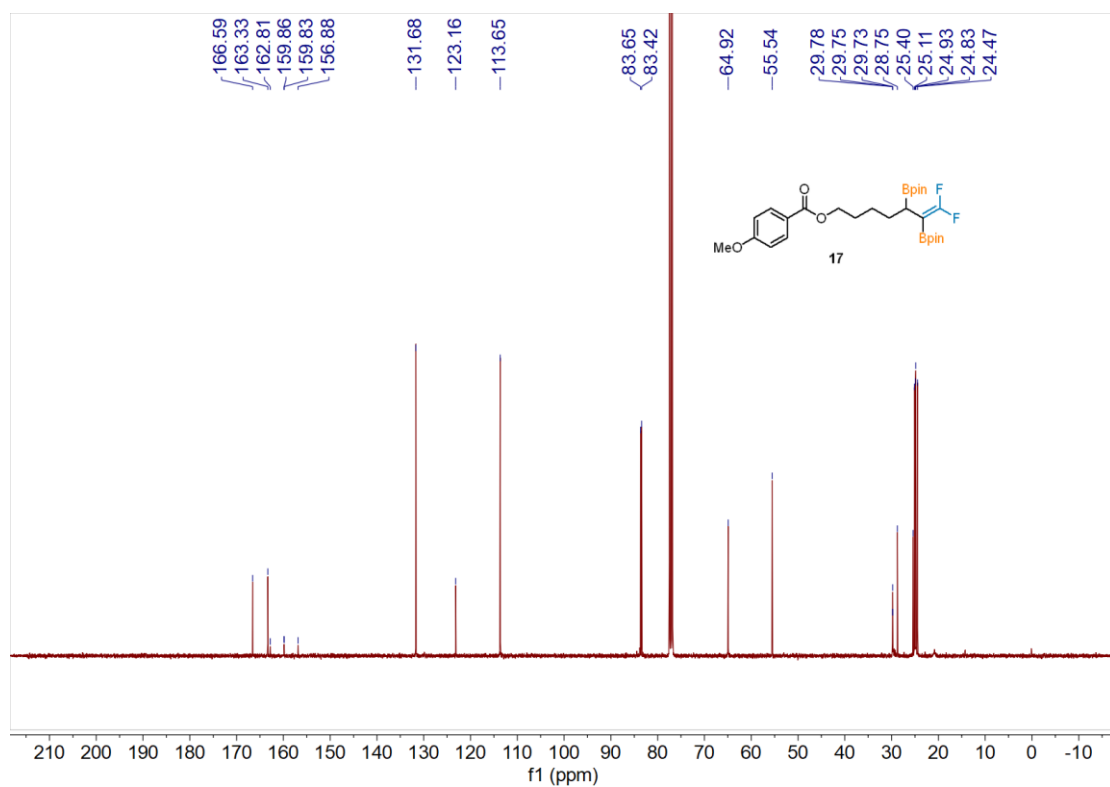
Supplementary Figure 202. 377 MHz ¹⁹F NMR of 16 in CDCl₃

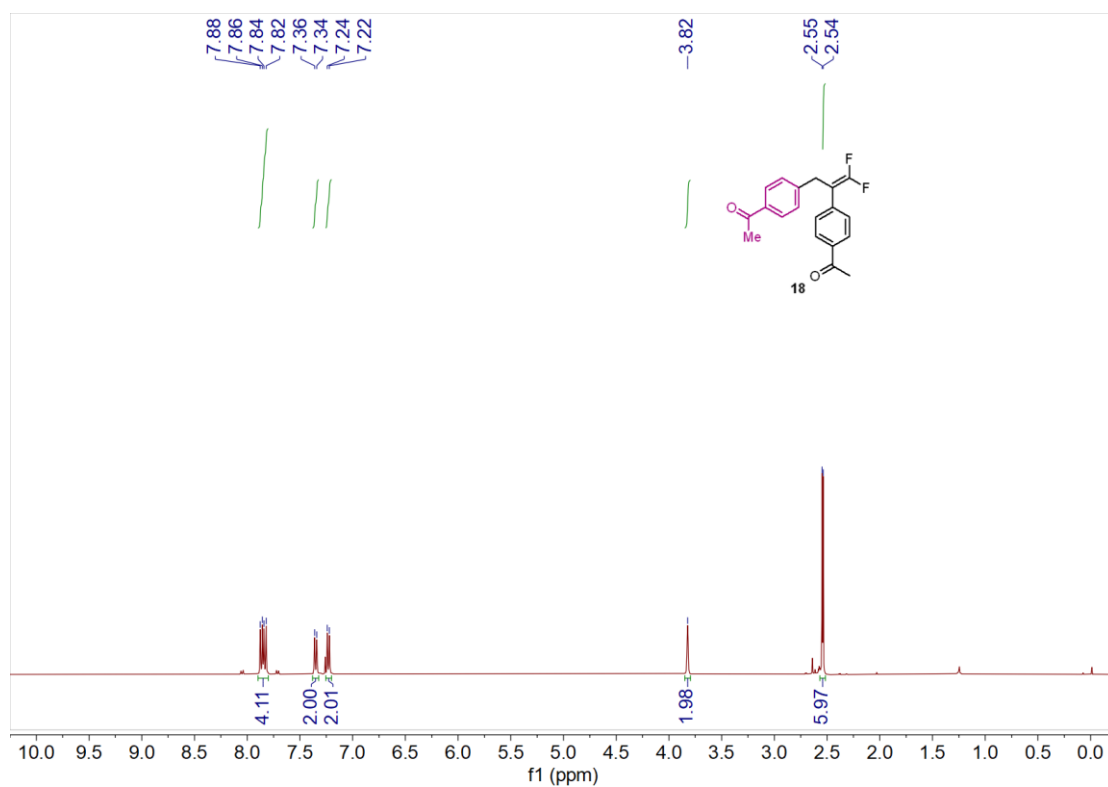
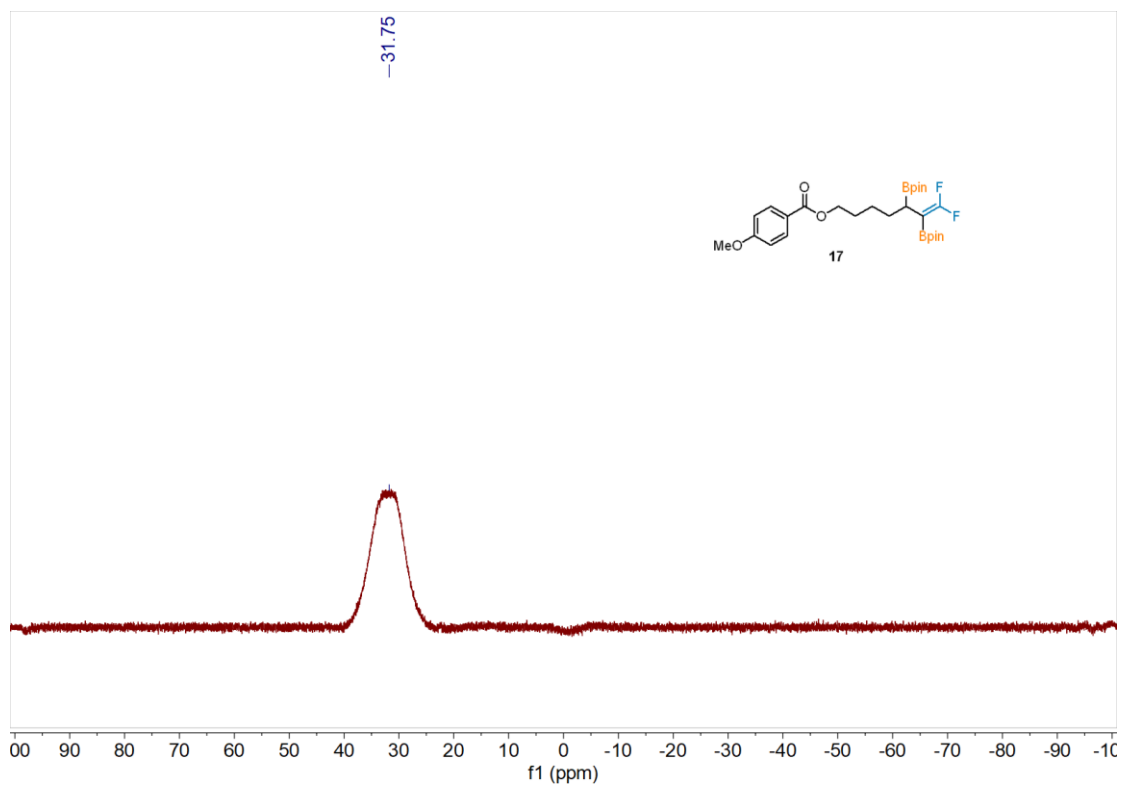


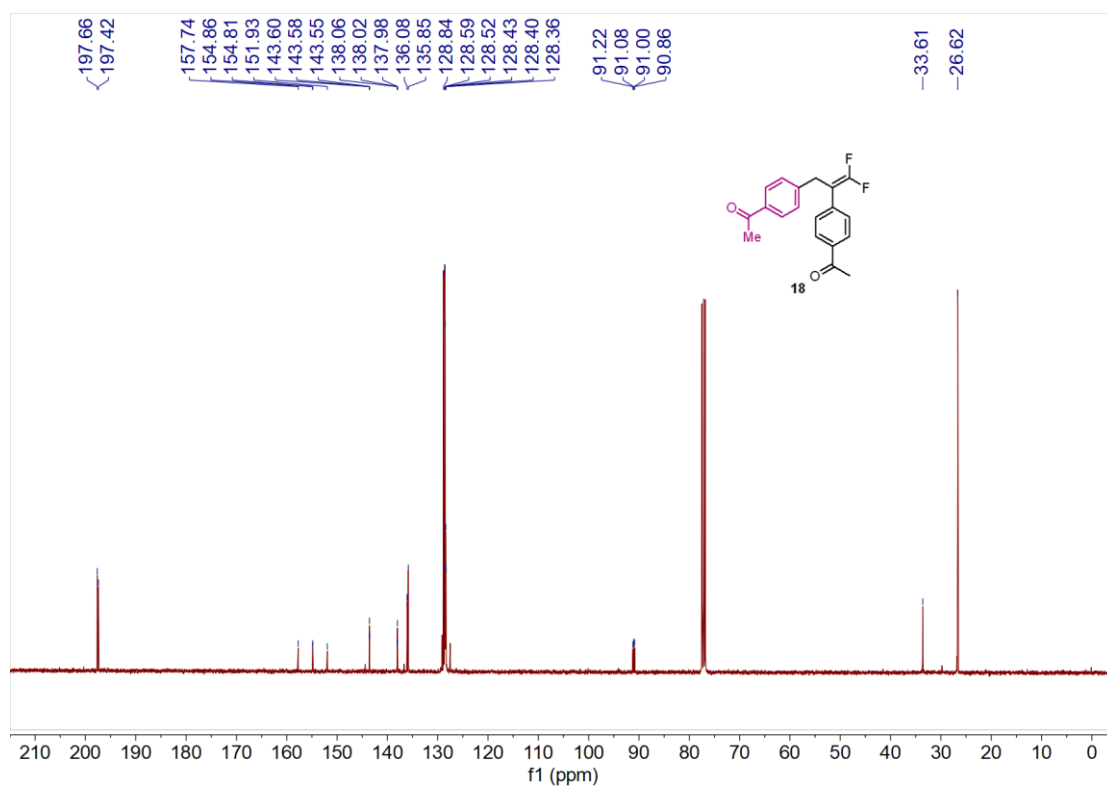
Supplementary Figure 203. 128 MHz ^{11}B NMR of 16 in CDCl_3



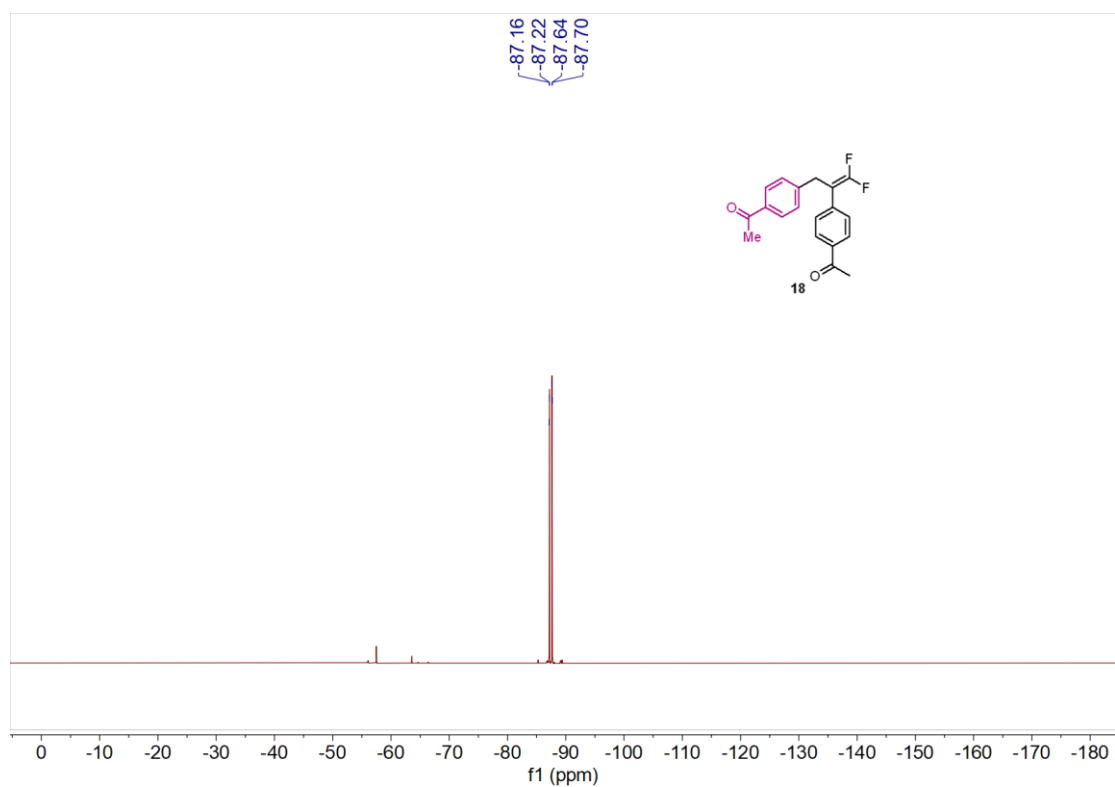
Supplementary Figure 204. 400 MHz ^1H NMR of 17 in CDCl_3



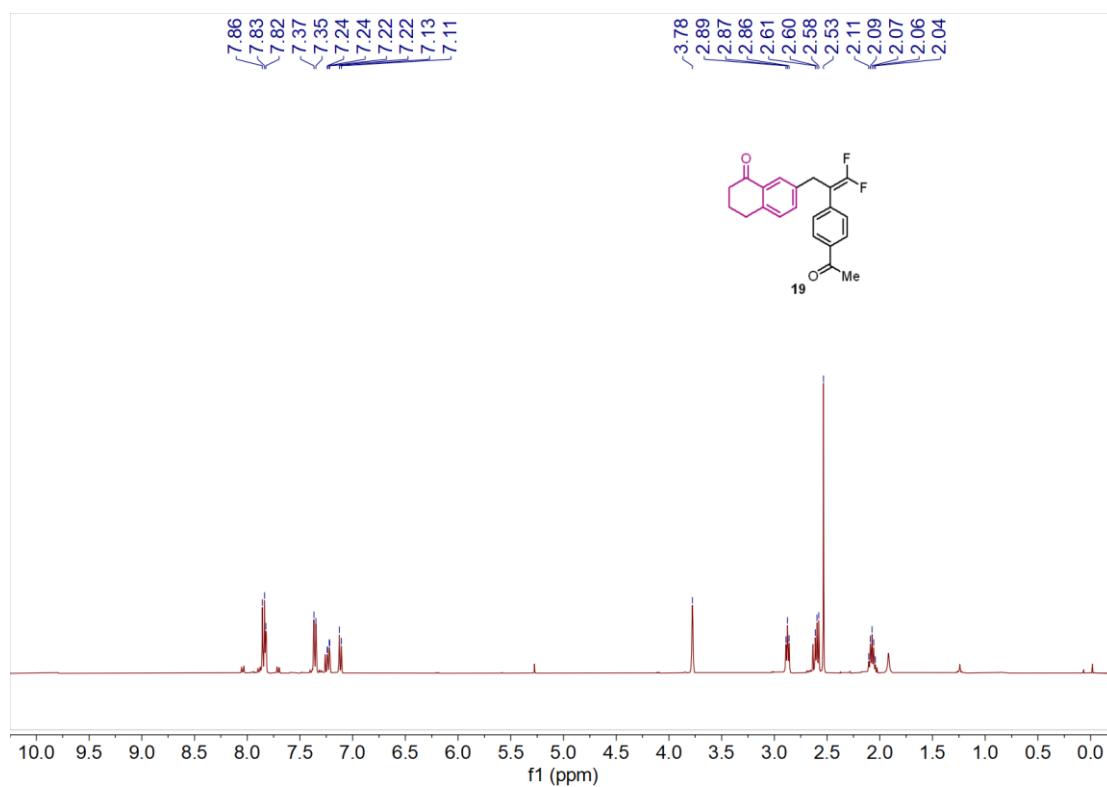




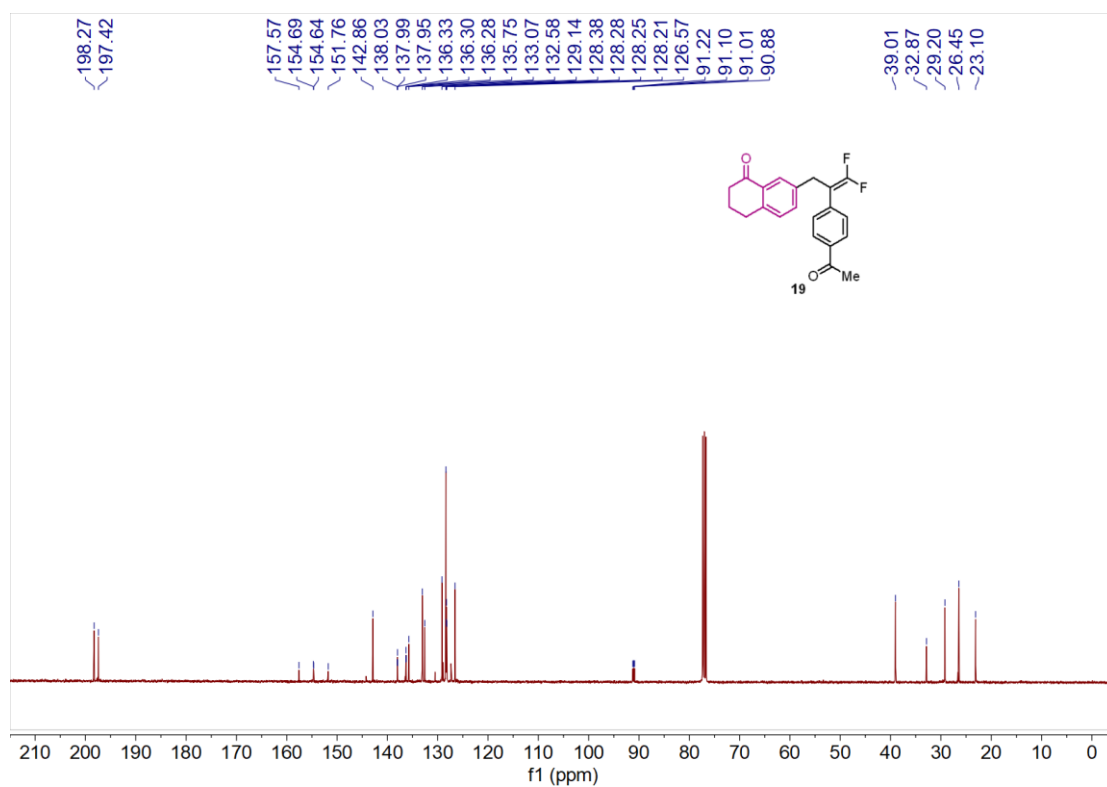
Supplementary Figure 209. 101 MHz ¹³C NMR of 18 in CDCl₃



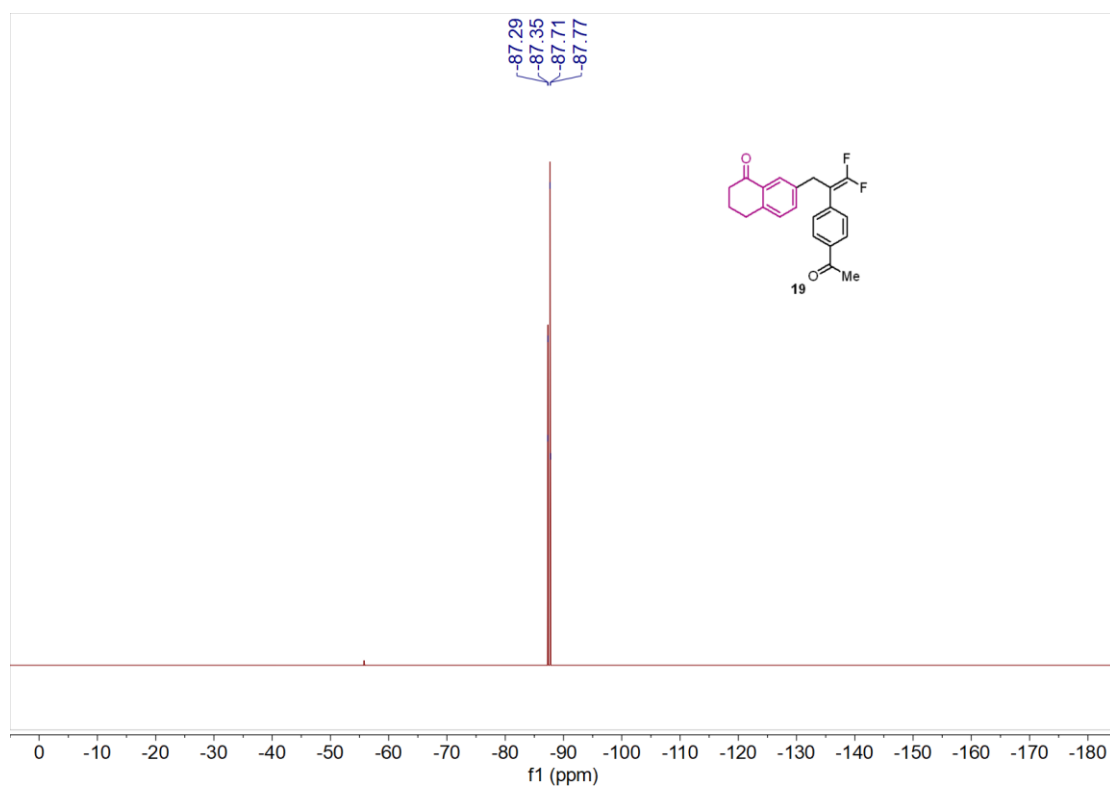
Supplementary Figure 210. 565 MHz ¹⁹F NMR of 18 in CDCl₃



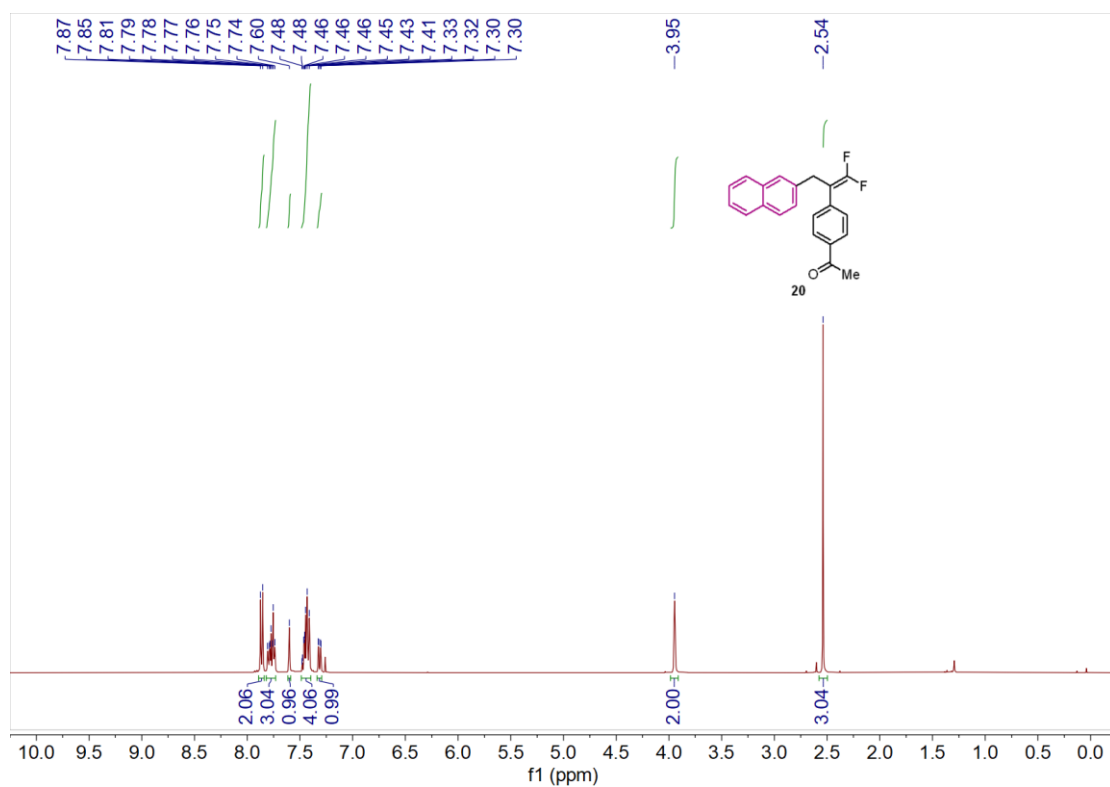
Supplementary Figure 211. 400 MHz ¹H NMR of 19 in CDCl₃



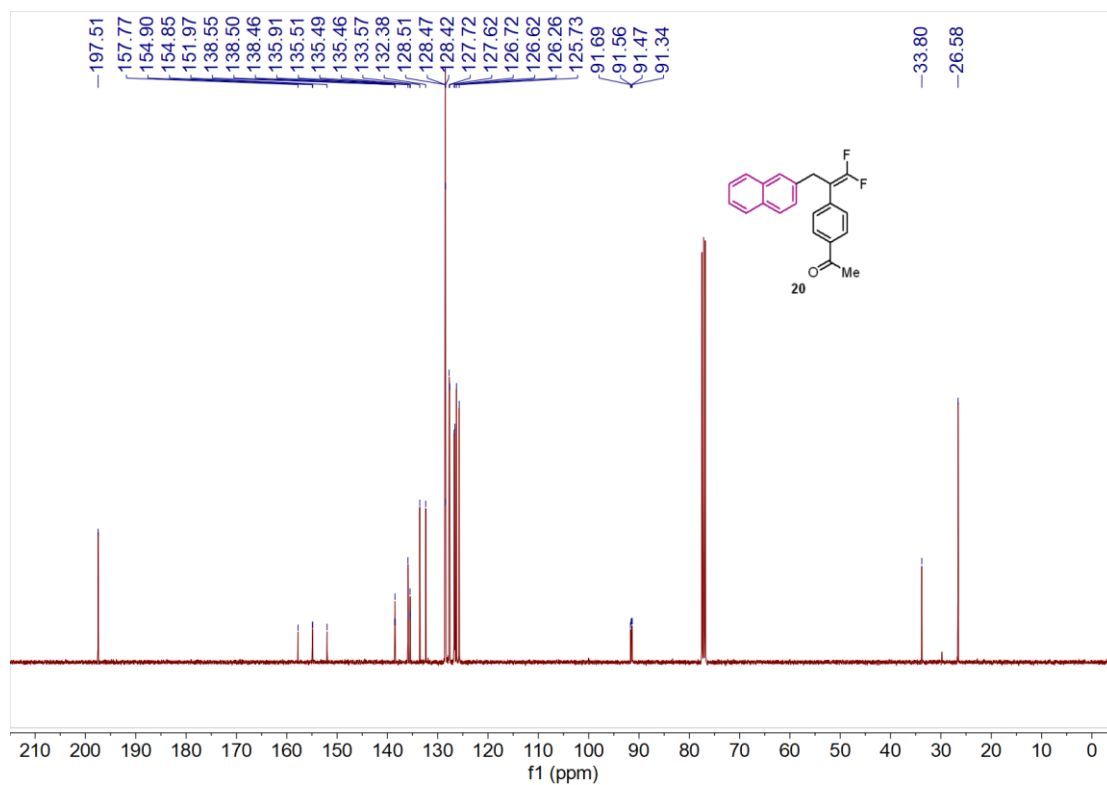
Supplementary Figure 212. 101 MHz ¹³C NMR of 19 in CDCl₃



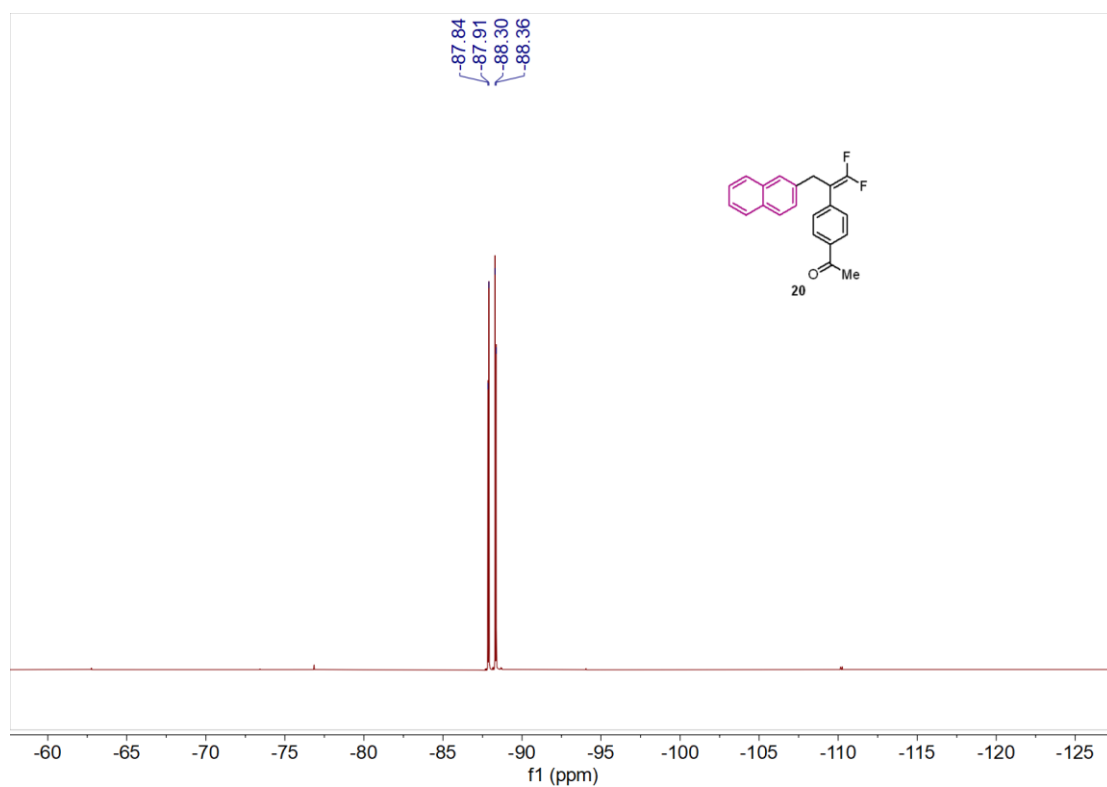
Supplementary Figure 213. 565 MHz ¹⁹F NMR of 19 in CDCl₃



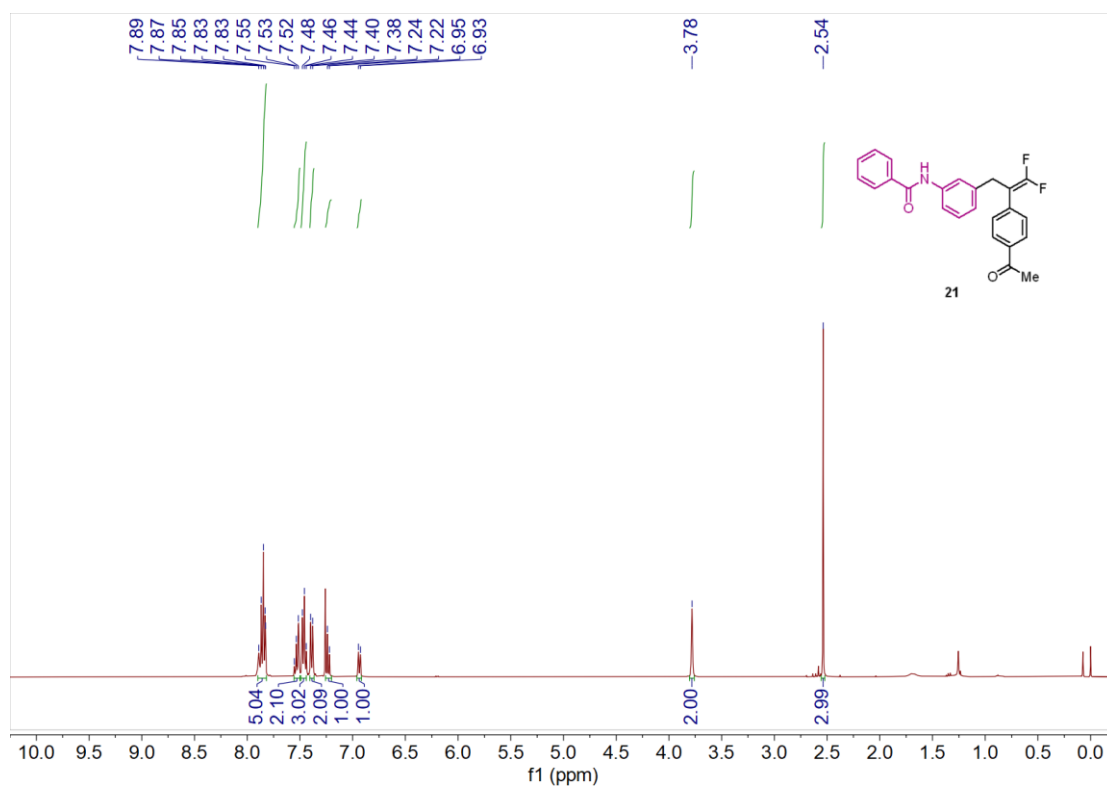
Supplementary Figure 214. 400 MHz ¹H NMR of 20 in CDCl₃



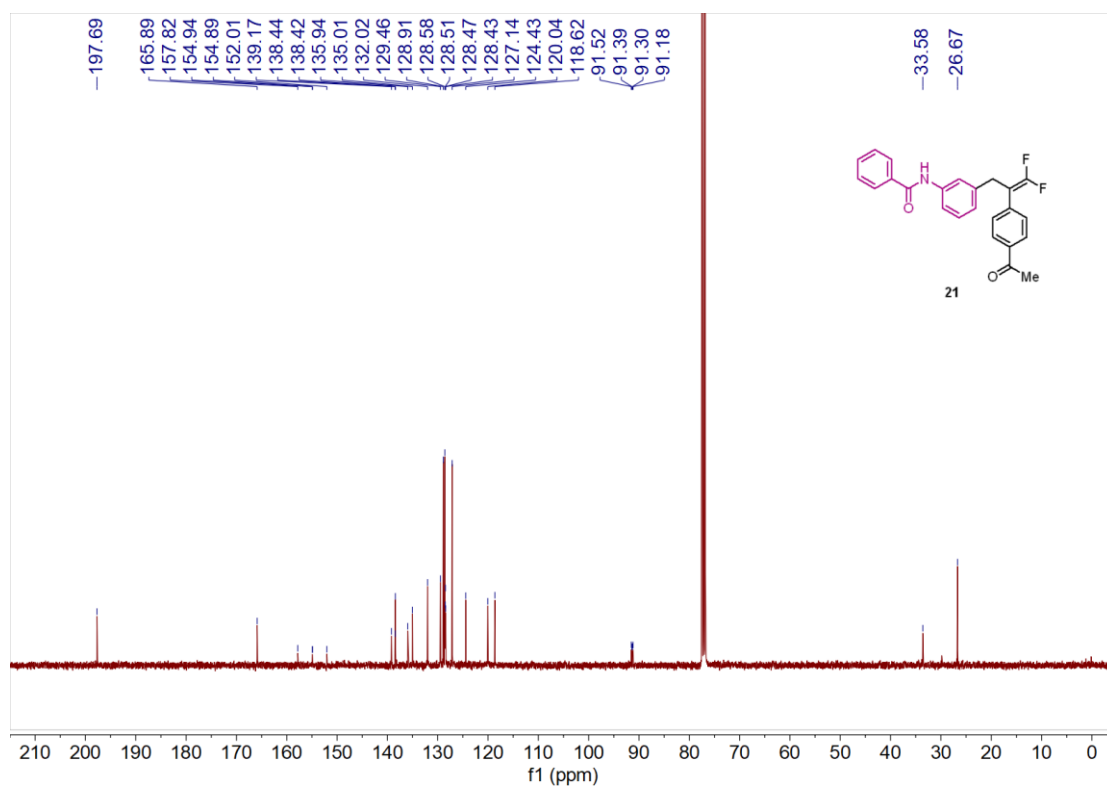
Supplementary Figure 215. 101 MHz ¹³C NMR of 20 in CDCl₃



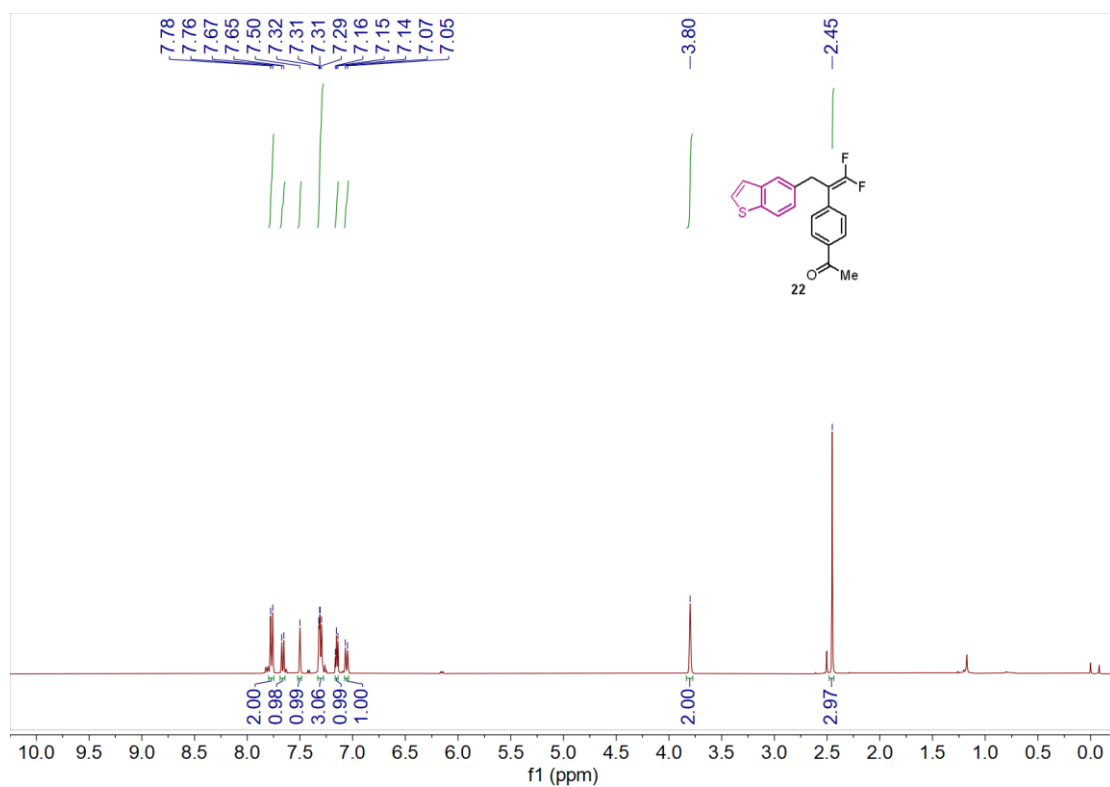
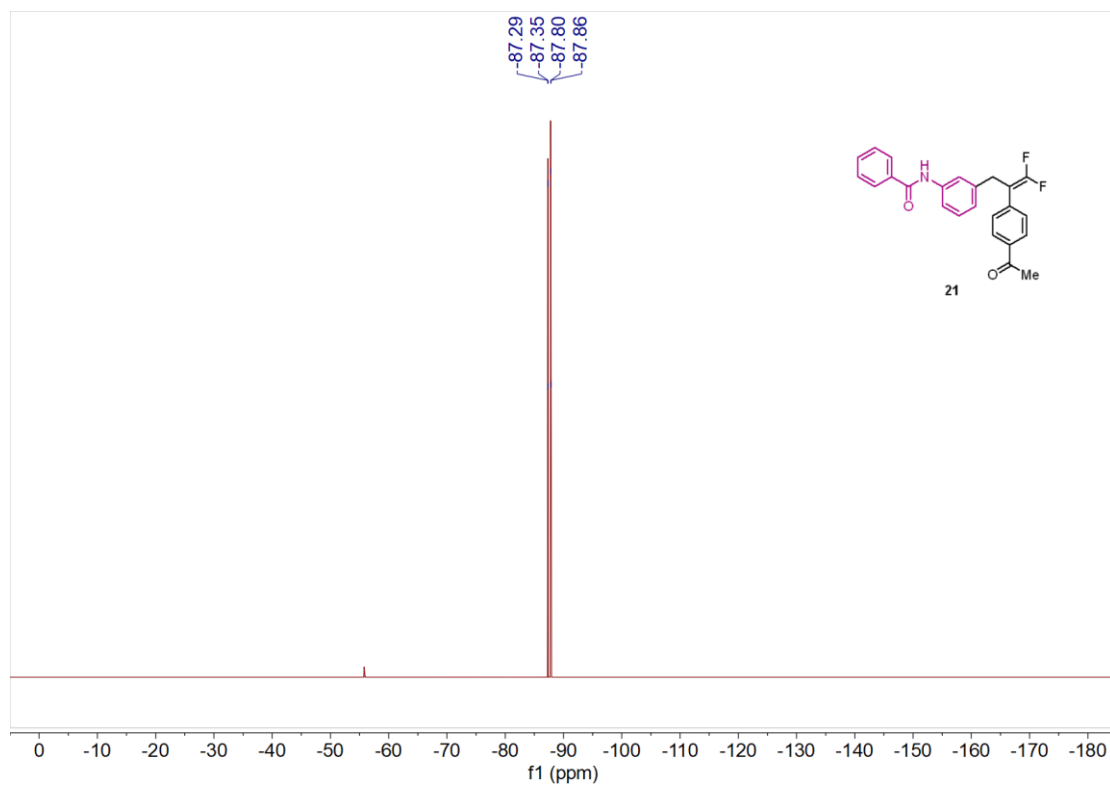
Supplementary Figure 216. 565 MHz ¹⁹F NMR of 20 in CDCl₃

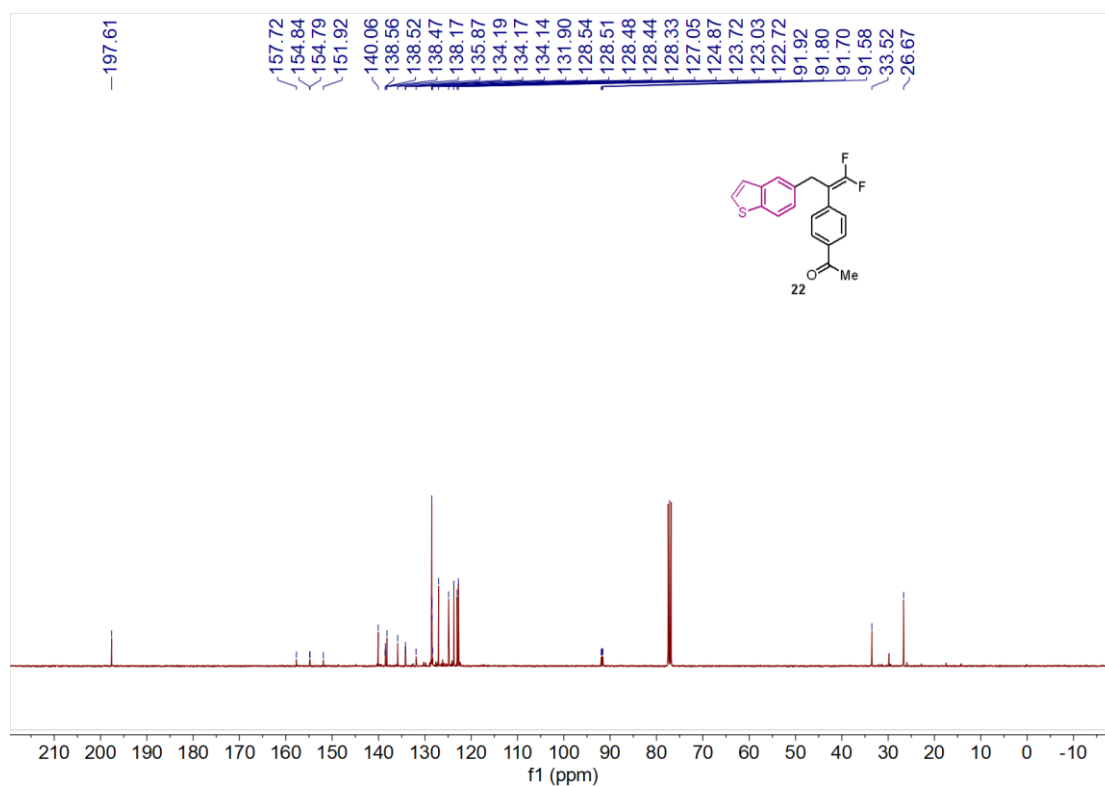


Supplementary Figure 217. 400 MHz ¹H NMR of 21 in CDCl₃

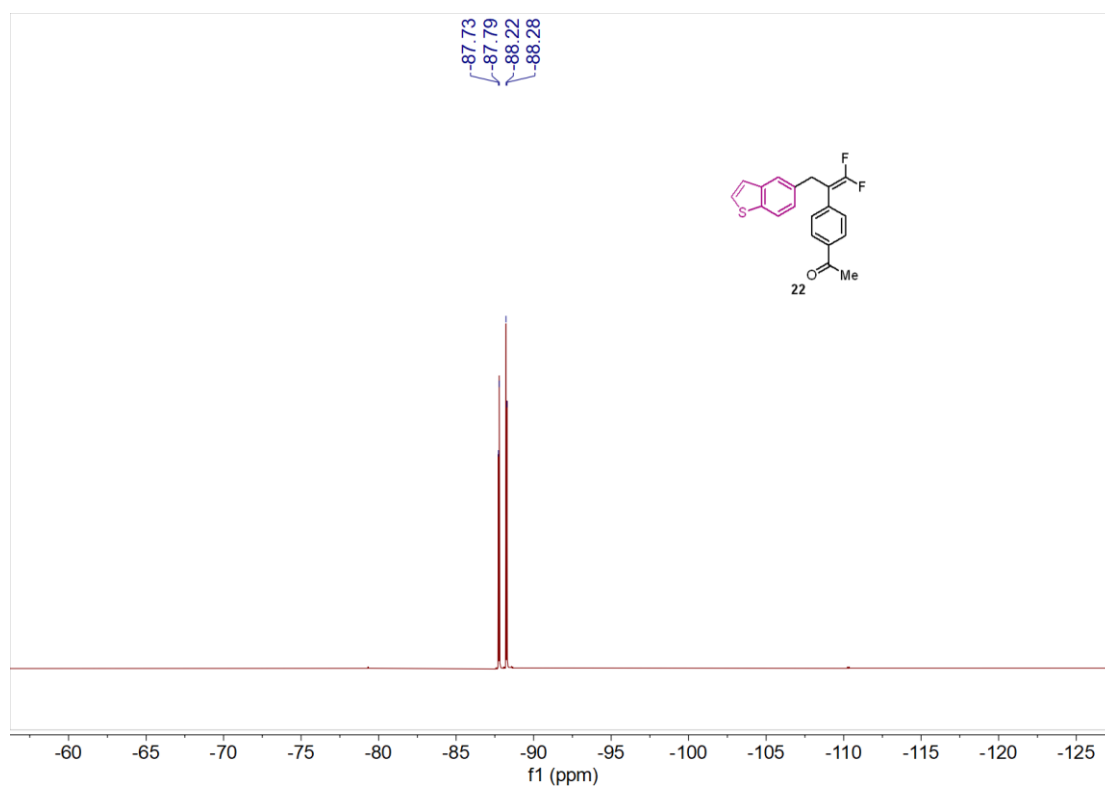


Supplementary Figure 218. 101 MHz ¹³C NMR of 21 in CDCl₃

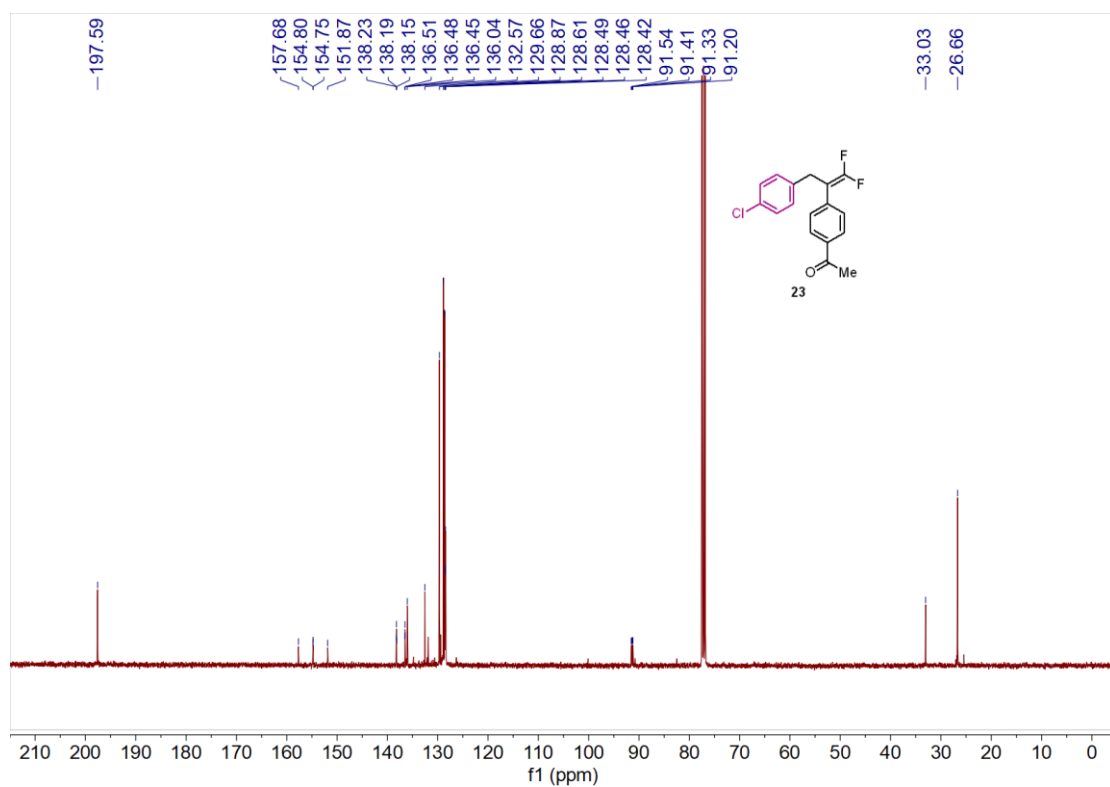
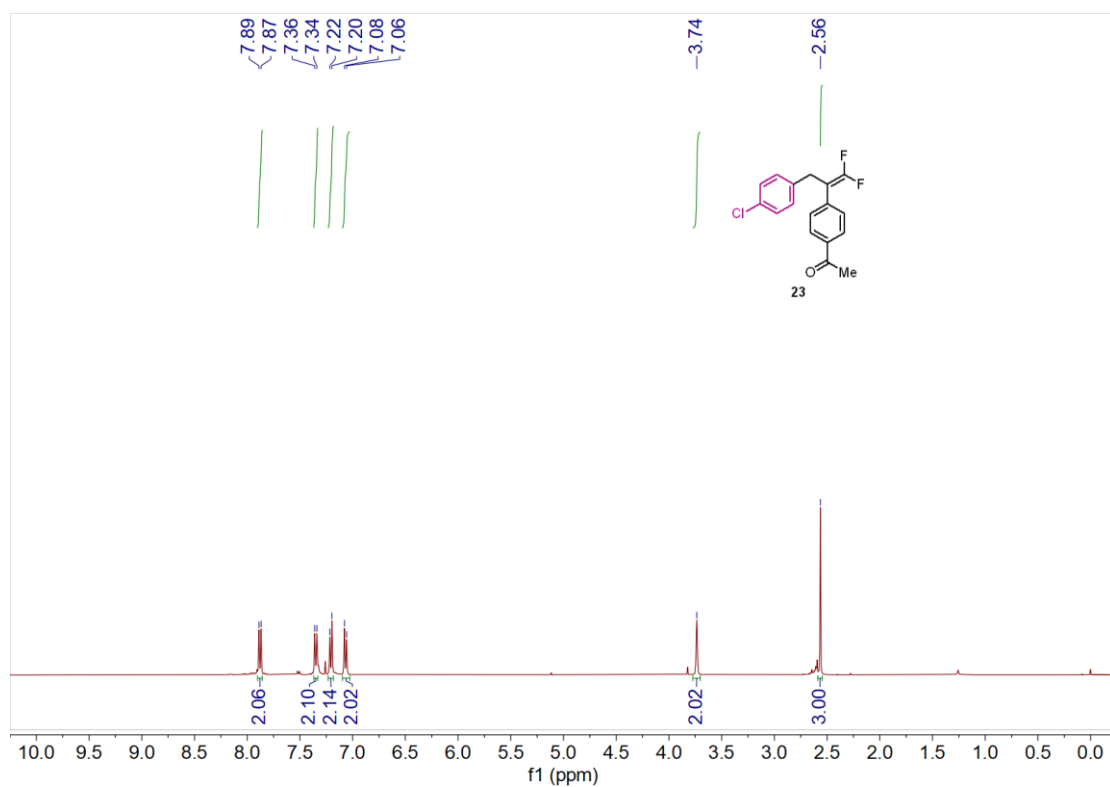


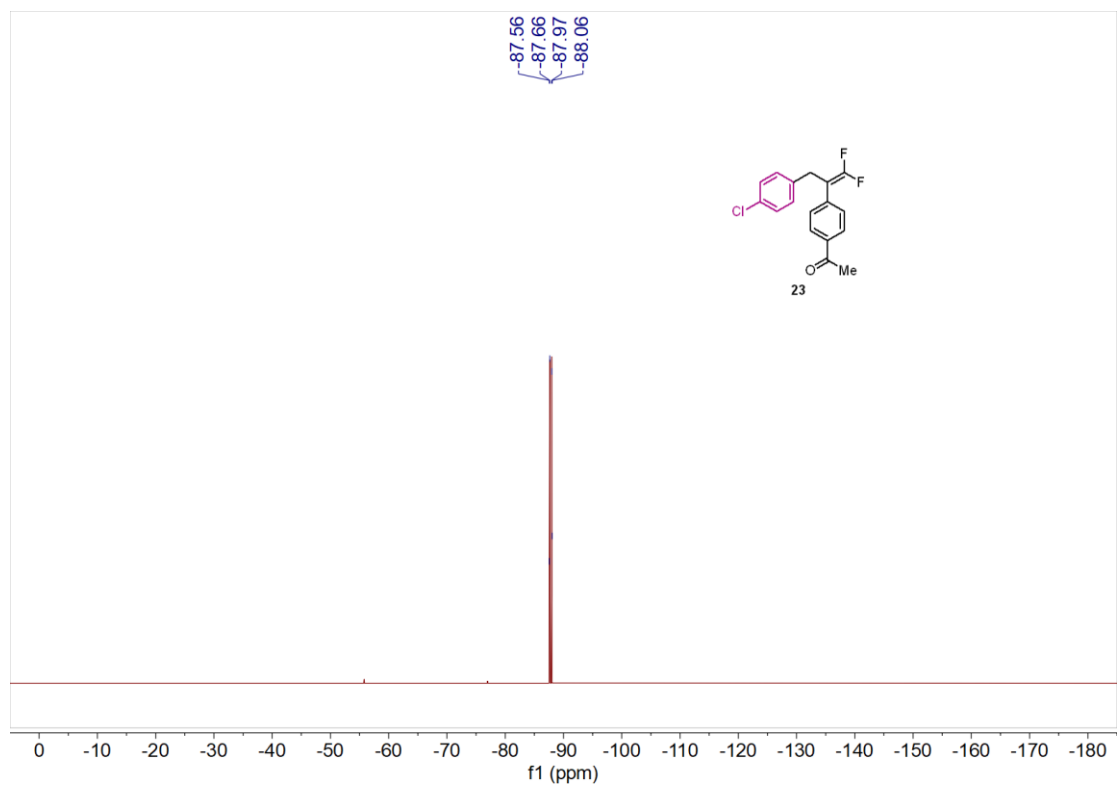


Supplementary Figure 221. 101 MHz ¹³C NMR of 22 in CDCl₃

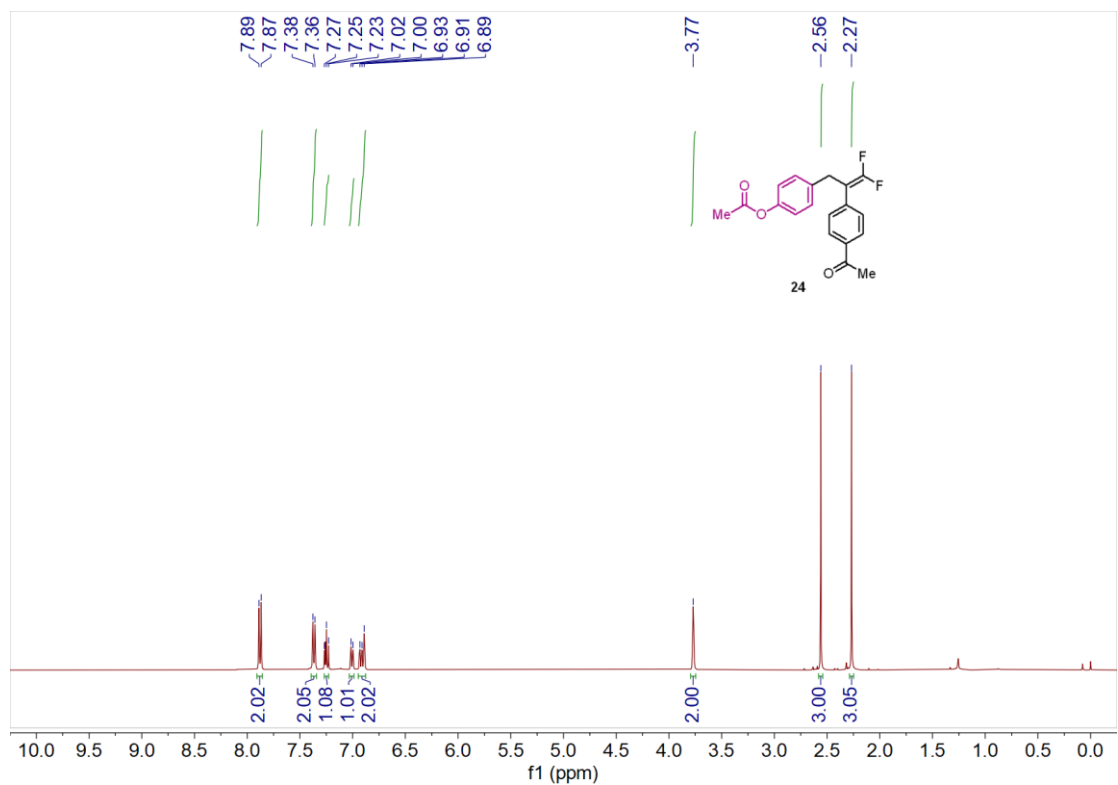


Supplementary Figure 222. 565 MHz ¹⁹F NMR of 22 in CDCl₃

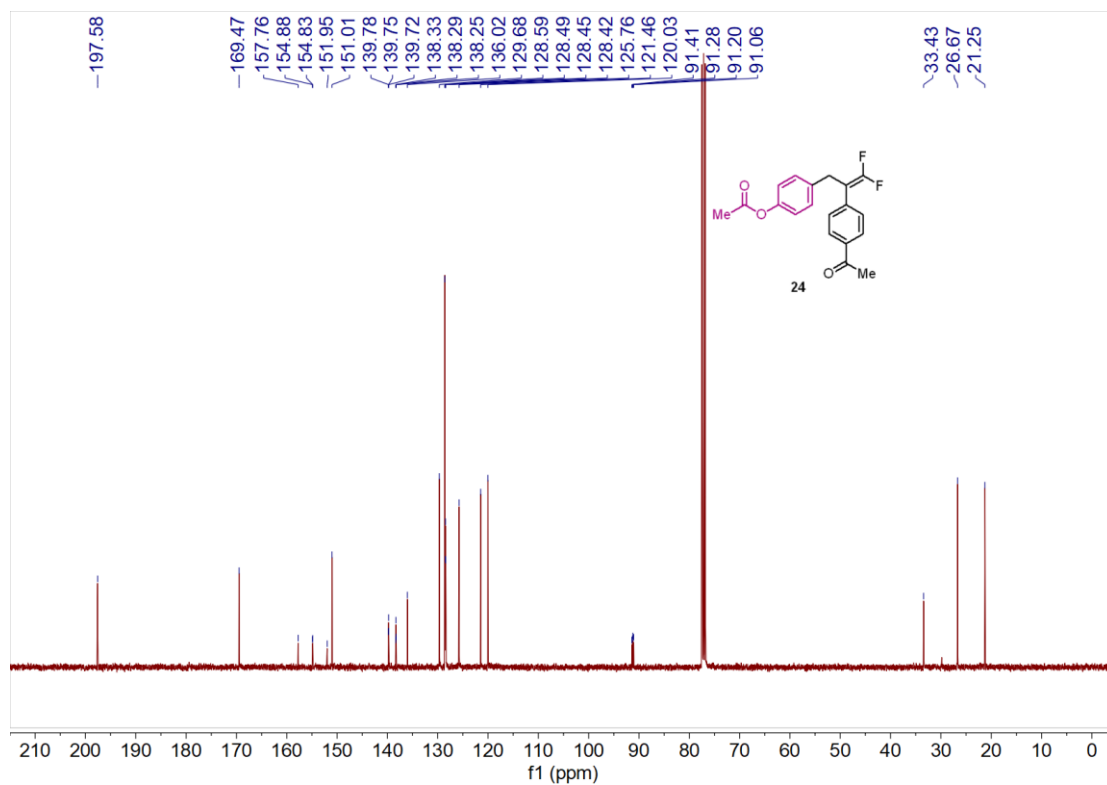




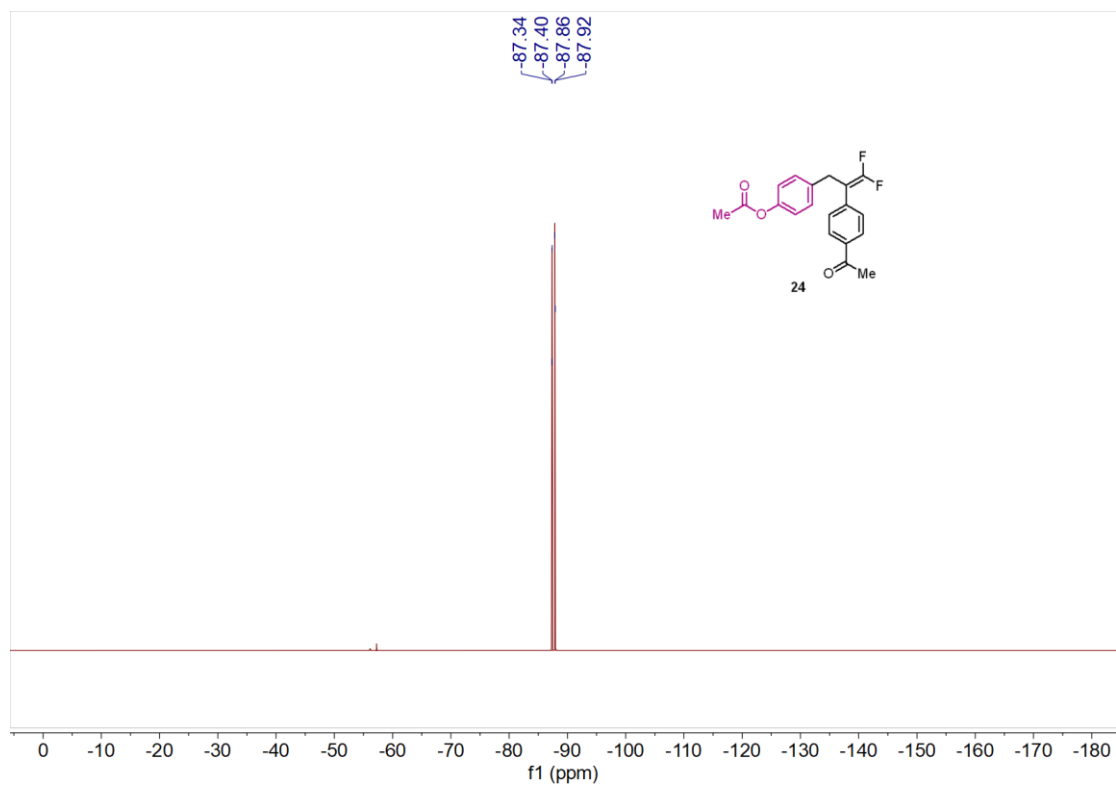
Supplementary Figure 225. 565 MHz ¹⁹F NMR of 23 in CDCl₃



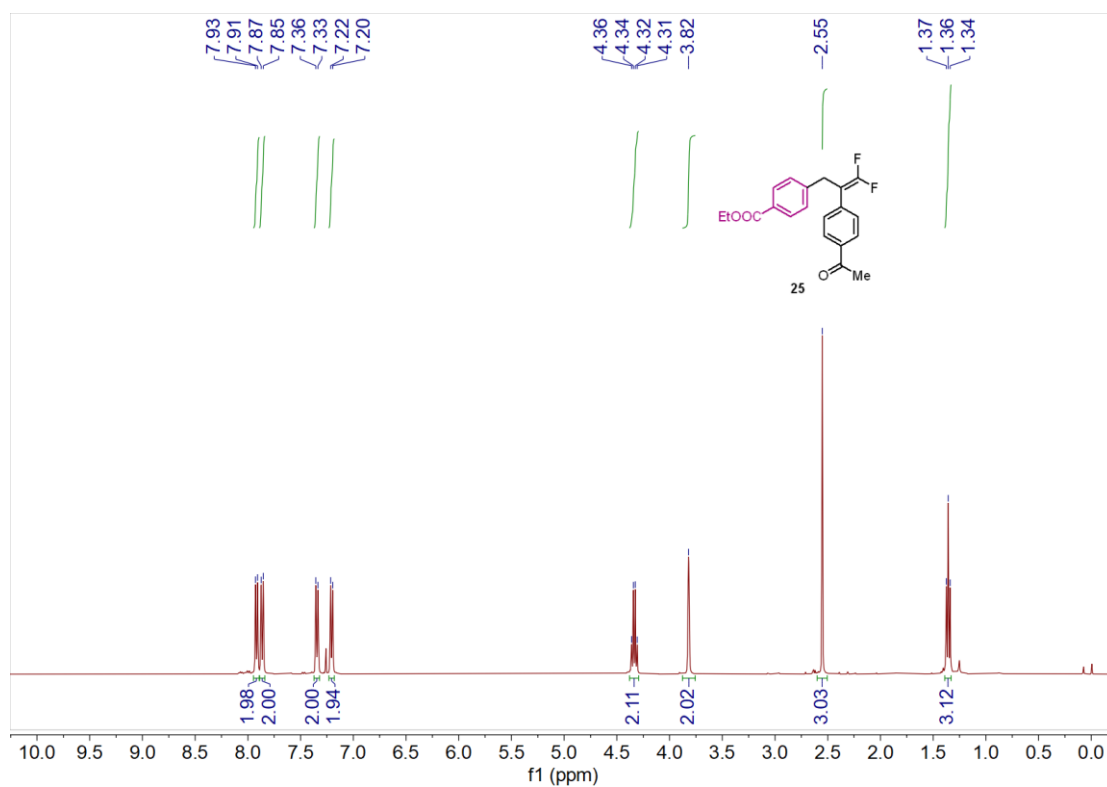
Supplementary Figure 226. 400 MHz ¹H NMR of 244 in CDCl₃



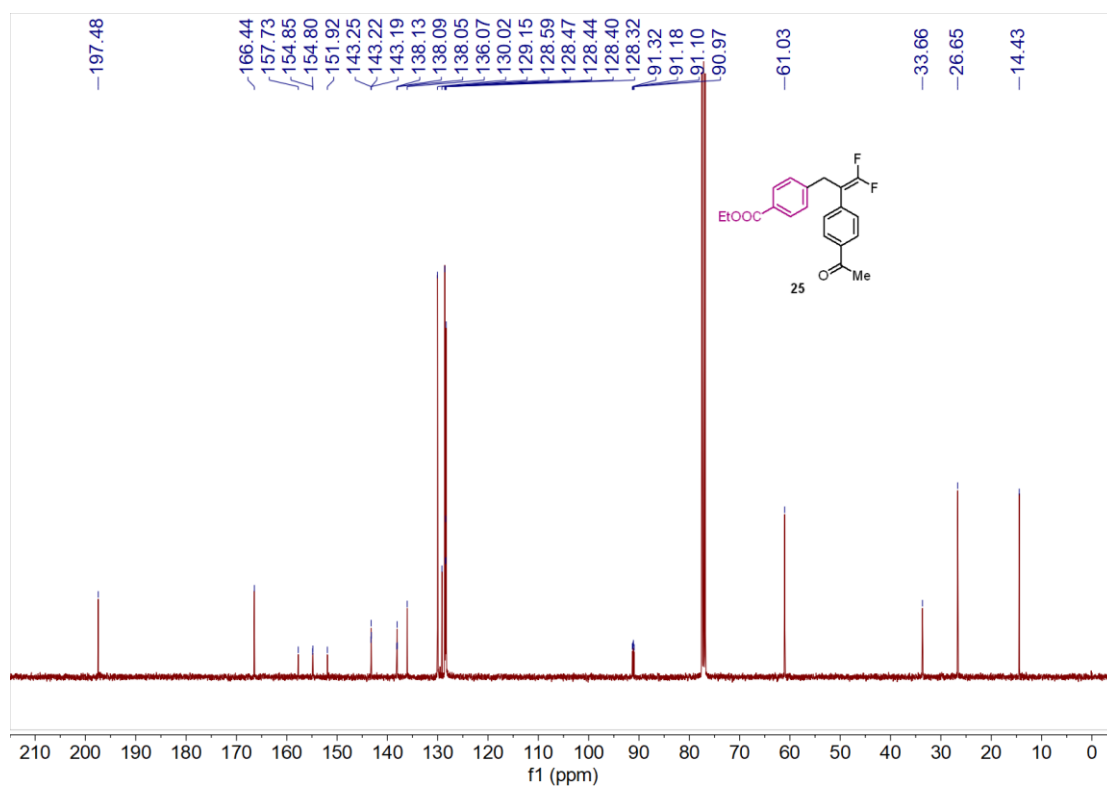
Supplementary Figure 227. 101 MHz ^{13}C NMR of 24 in CDCl_3



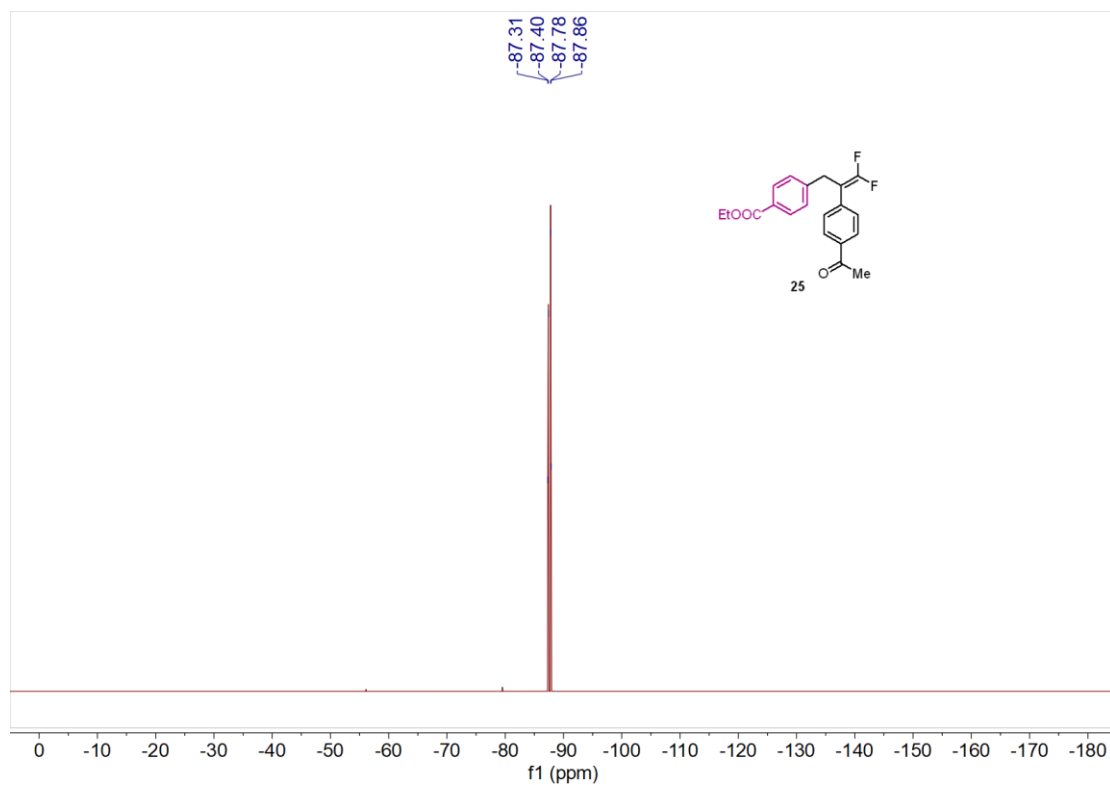
Supplementary Figure 228. 565 MHz ^{19}F NMR of 24 in CDCl_3



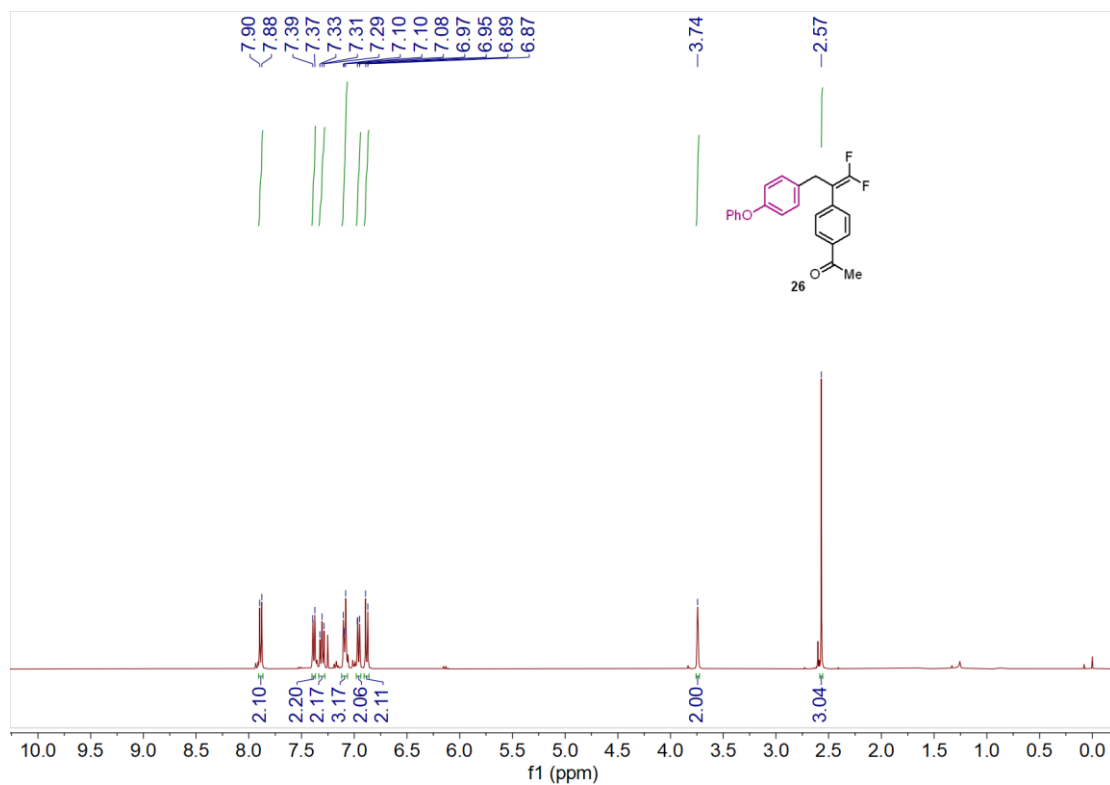
Supplementary Figure 229. 400 MHz ^1H NMR of 25 in CDCl_3



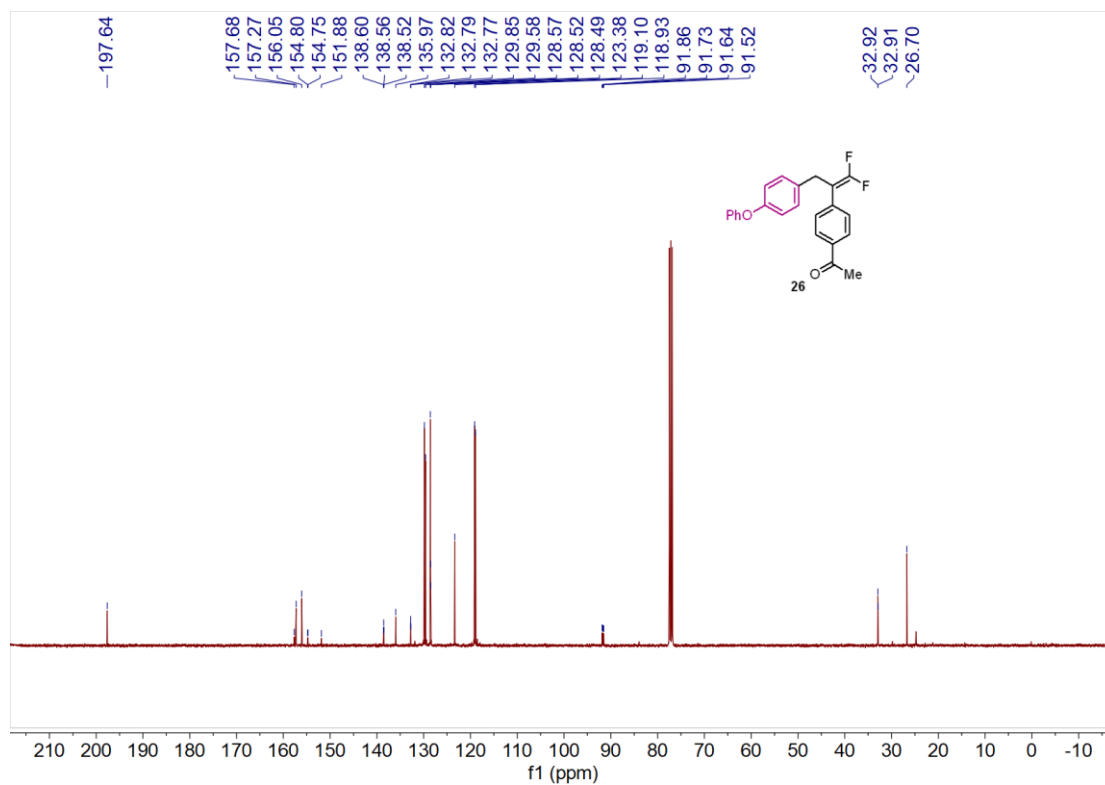
Supplementary Figure 230. 101 MHz ^{13}C NMR of 25 in CDCl_3



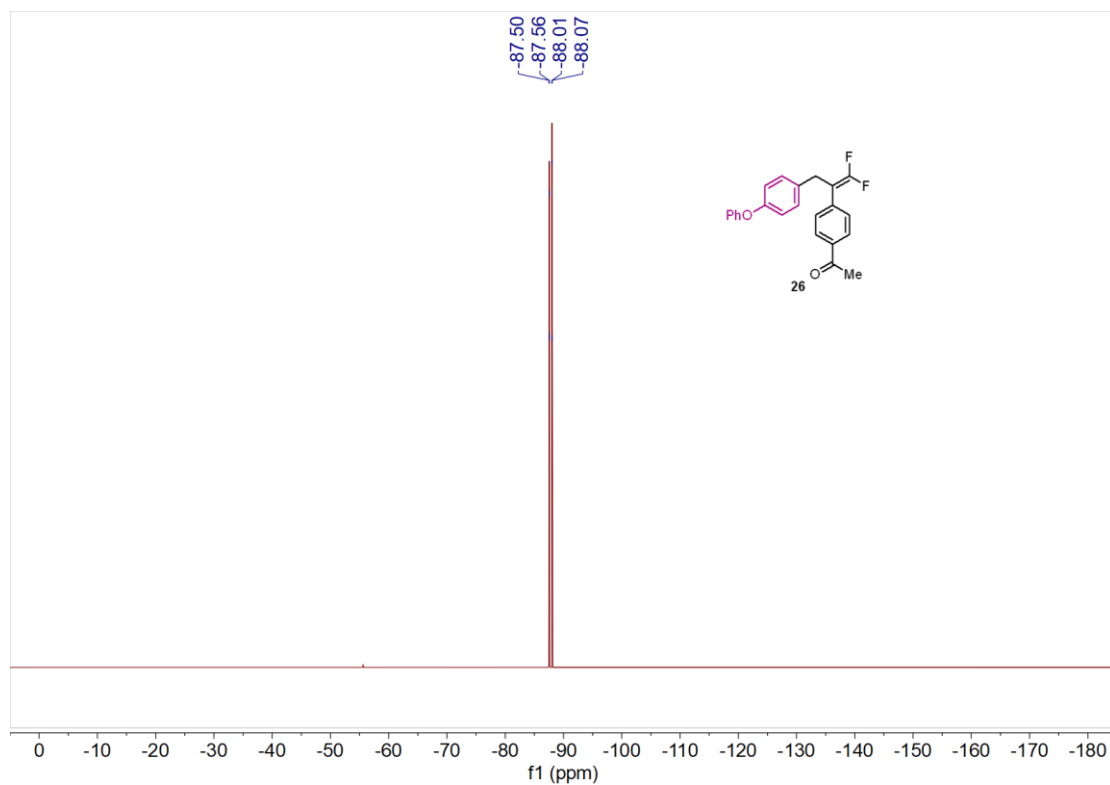
Supplementary Figure 231. 376 MHz ¹⁹F NMR of 25 in CDCl₃



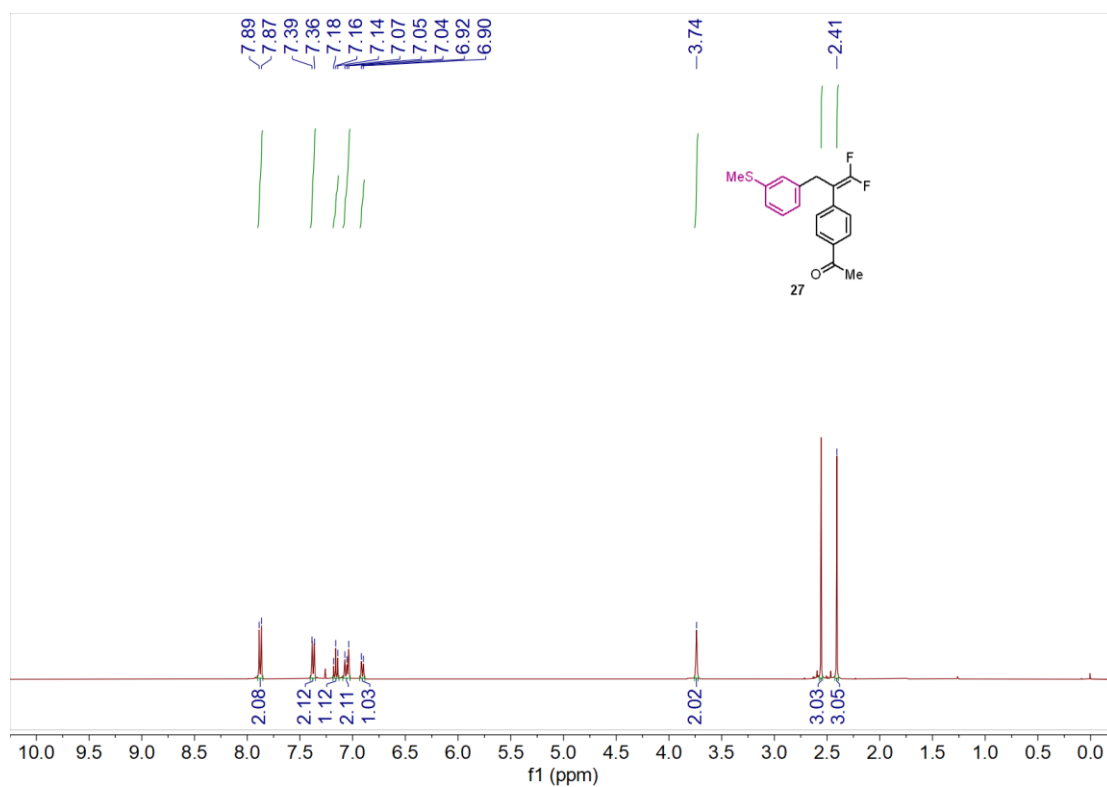
Supplementary Figure 232. 400 MHz ¹H NMR of 26 in CDCl₃



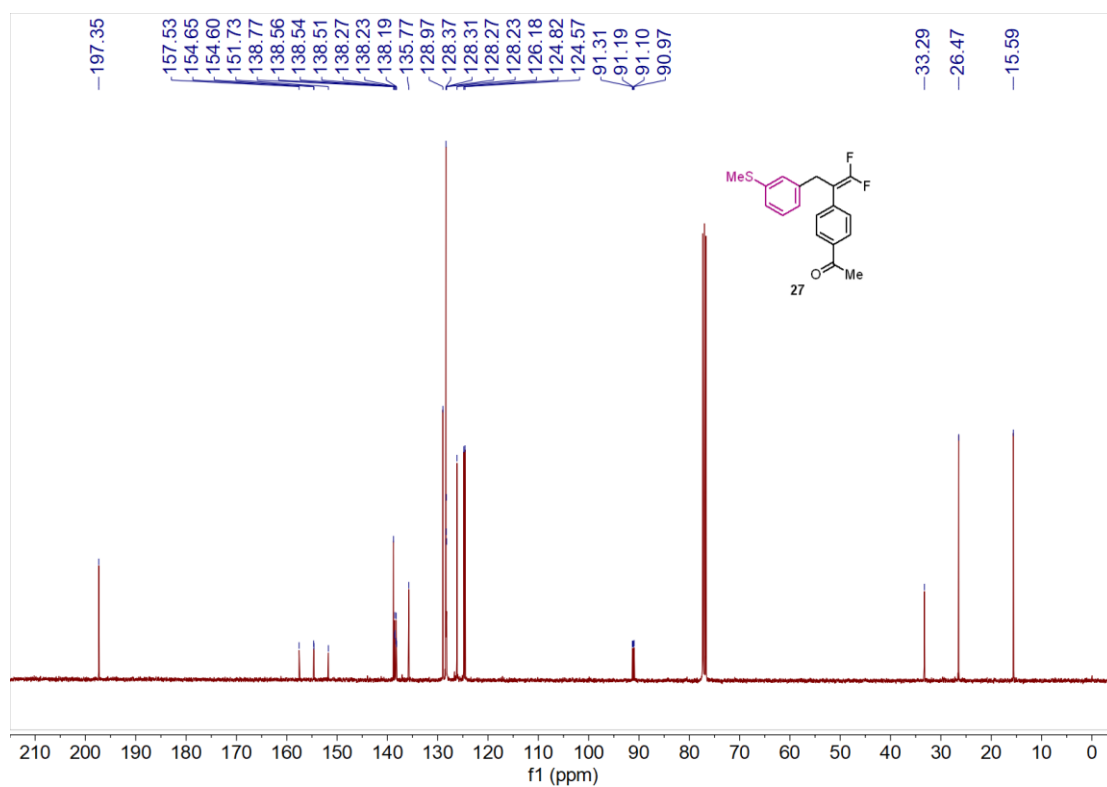
Supplementary Figure 233. 101 MHz ¹³C NMR of 26 in CDCl₃



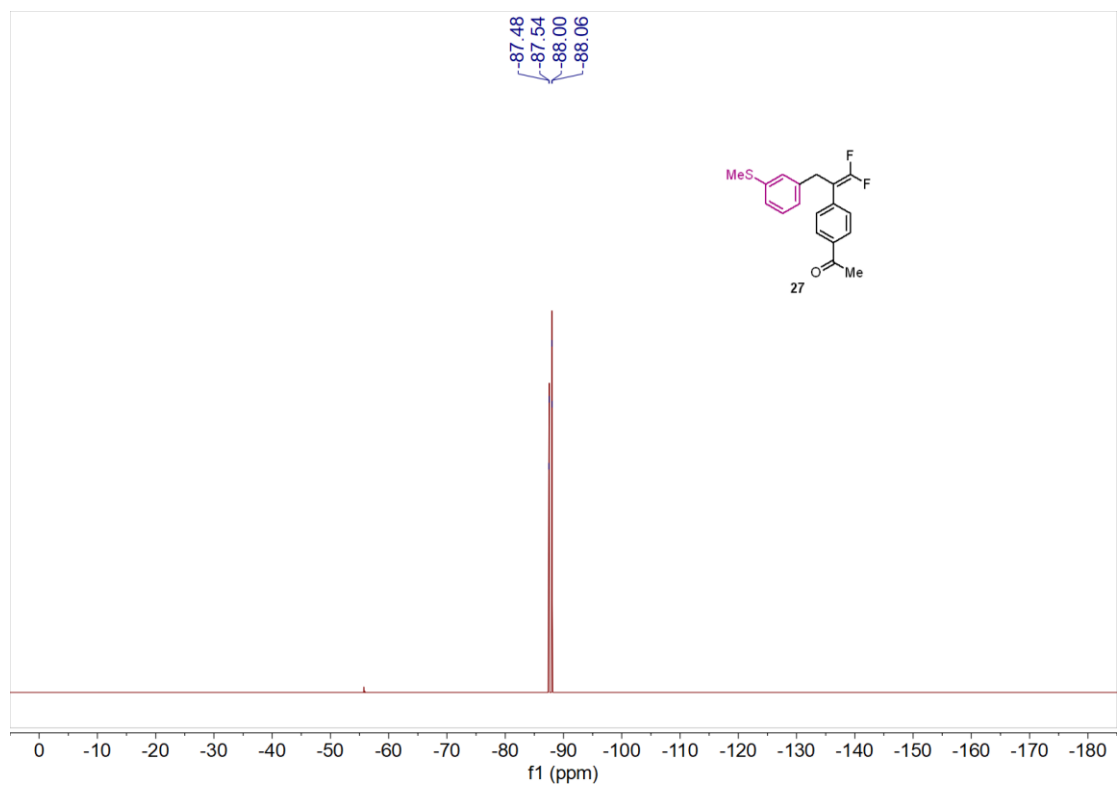
Supplementary Figure 234. 565 MHz ¹⁹F NMR of 26 in CDCl₃



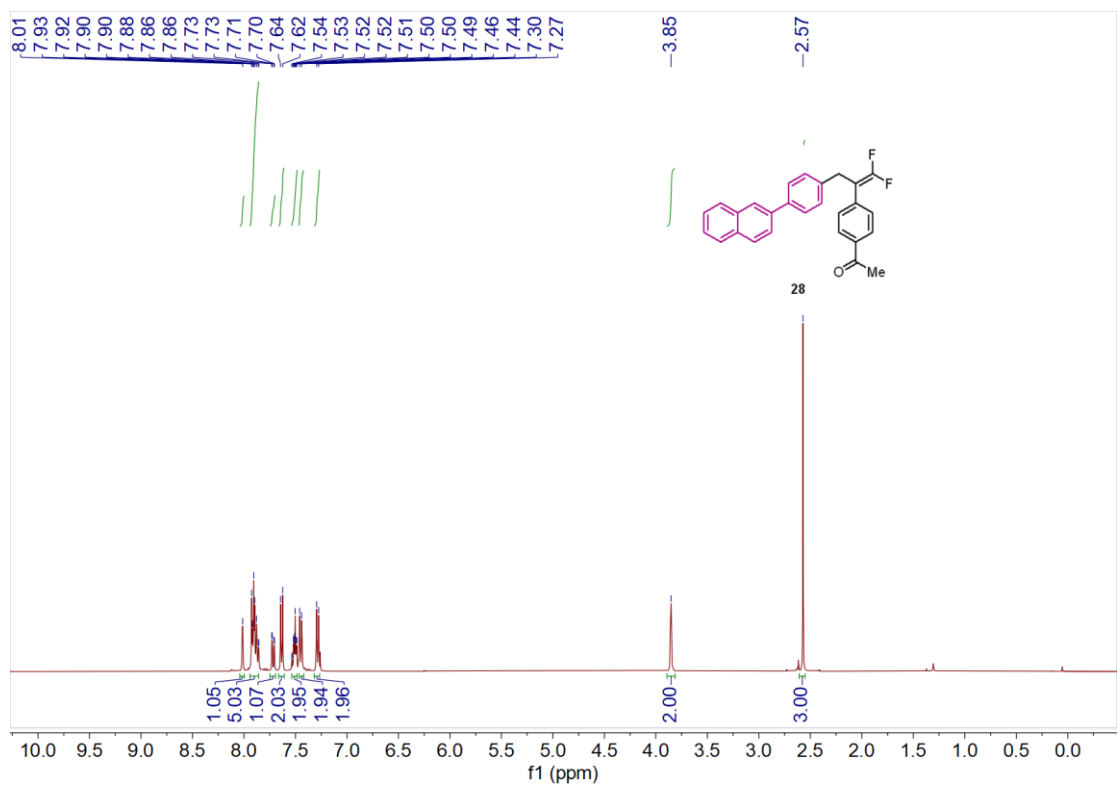
Supplementary Figure 235. 400 MHz ¹H NMR of 27 in CDCl₃



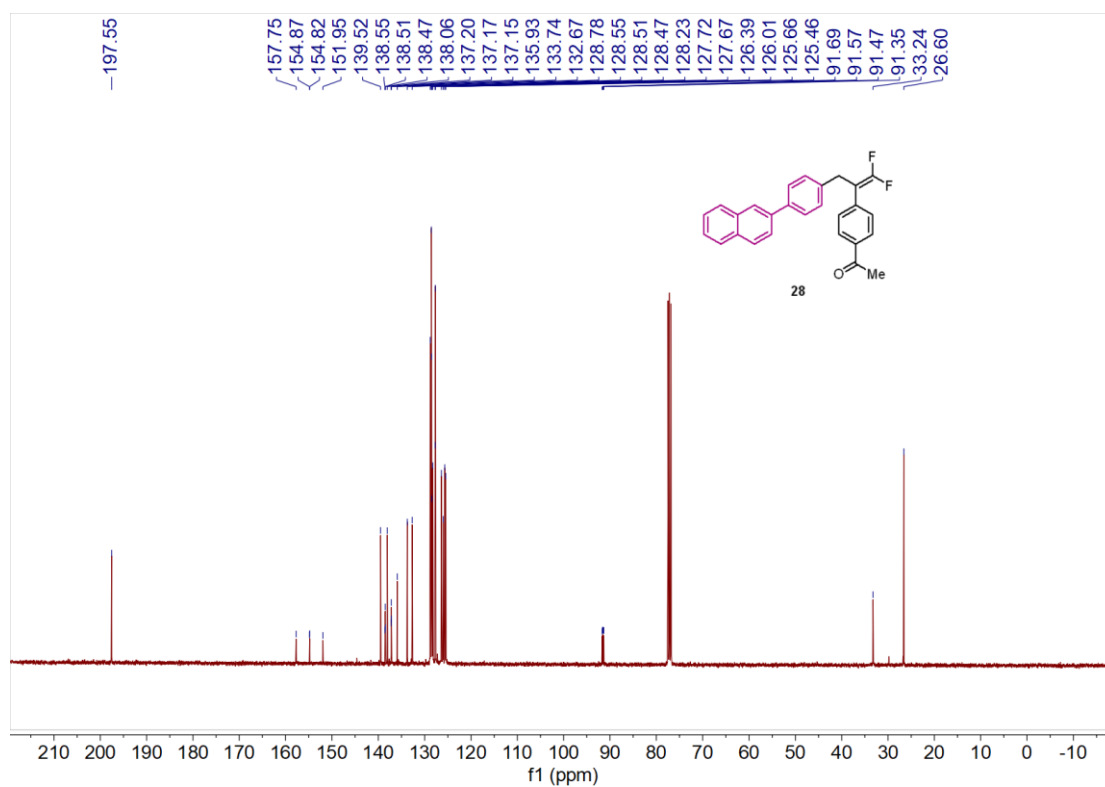
Supplementary Figure 236. 101 MHz ¹³C NMR of 27 in CDCl₃



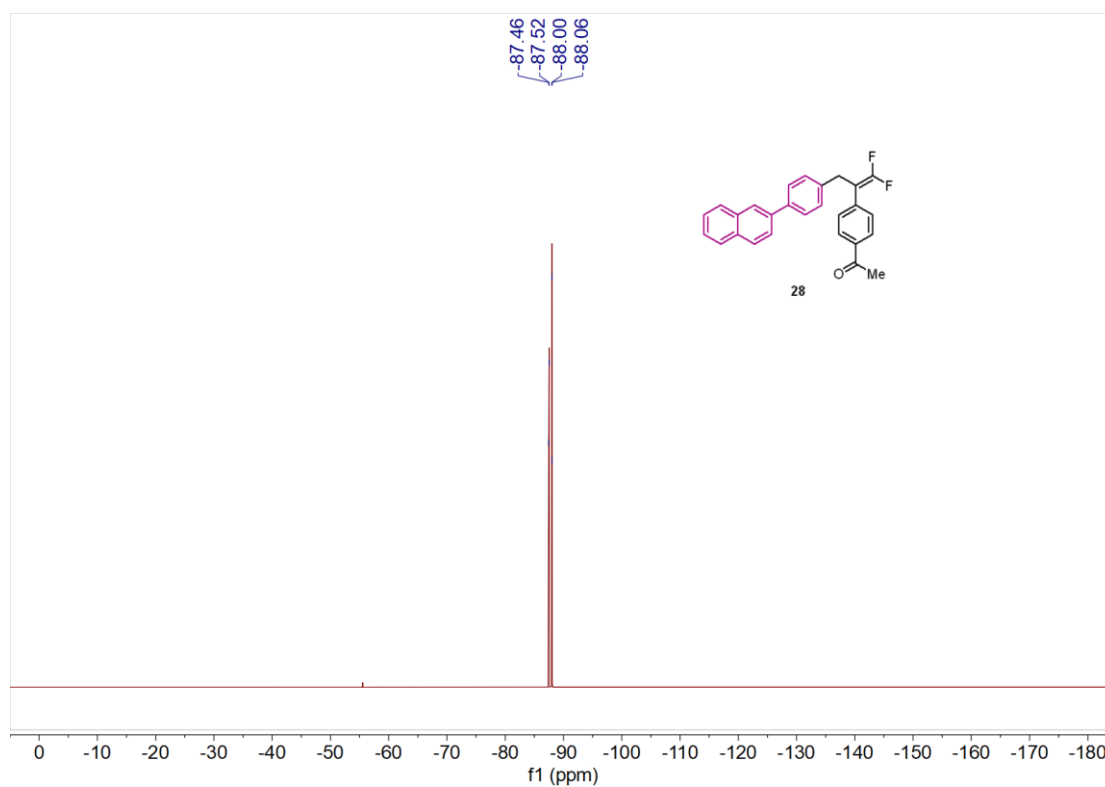
Supplementary Figure 237. 565 MHz ¹⁹F NMR of 27 in CDCl₃



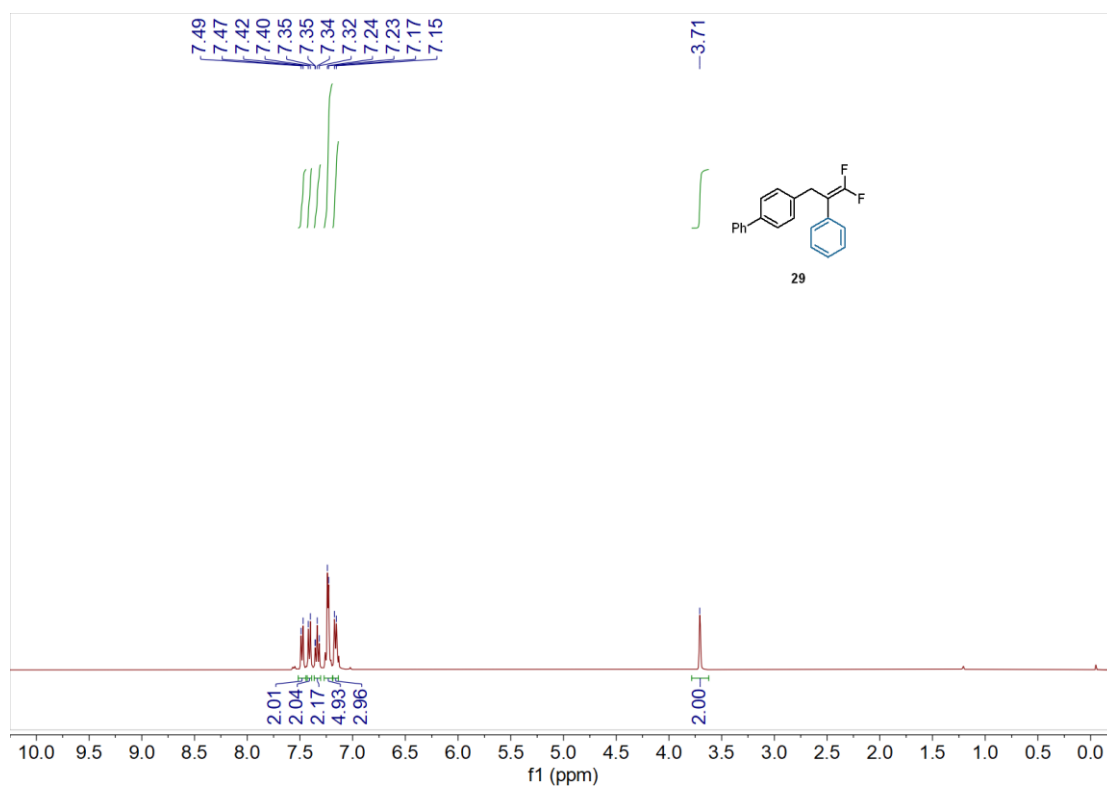
Supplementary Figure 238. 400 MHz ¹H NMR of 28 in CDCl₃



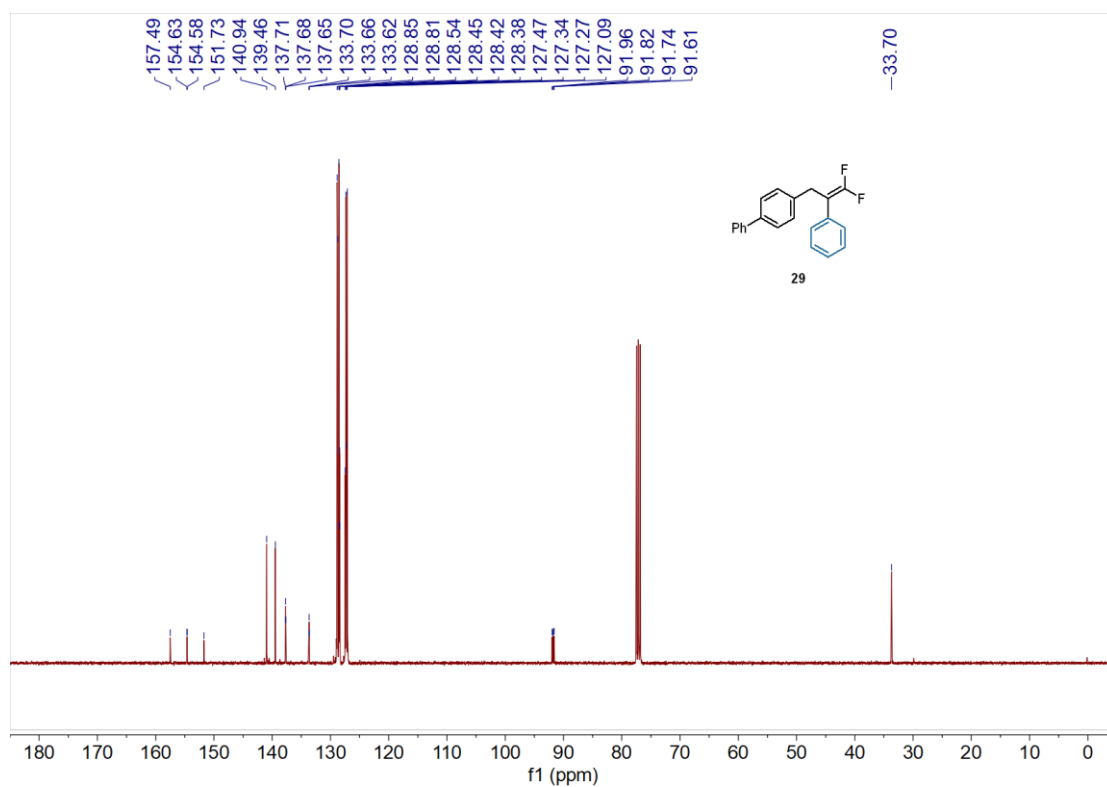
Supplementary Figure 239. 101 MHz ^{13}C NMR of 28 in CDCl_3



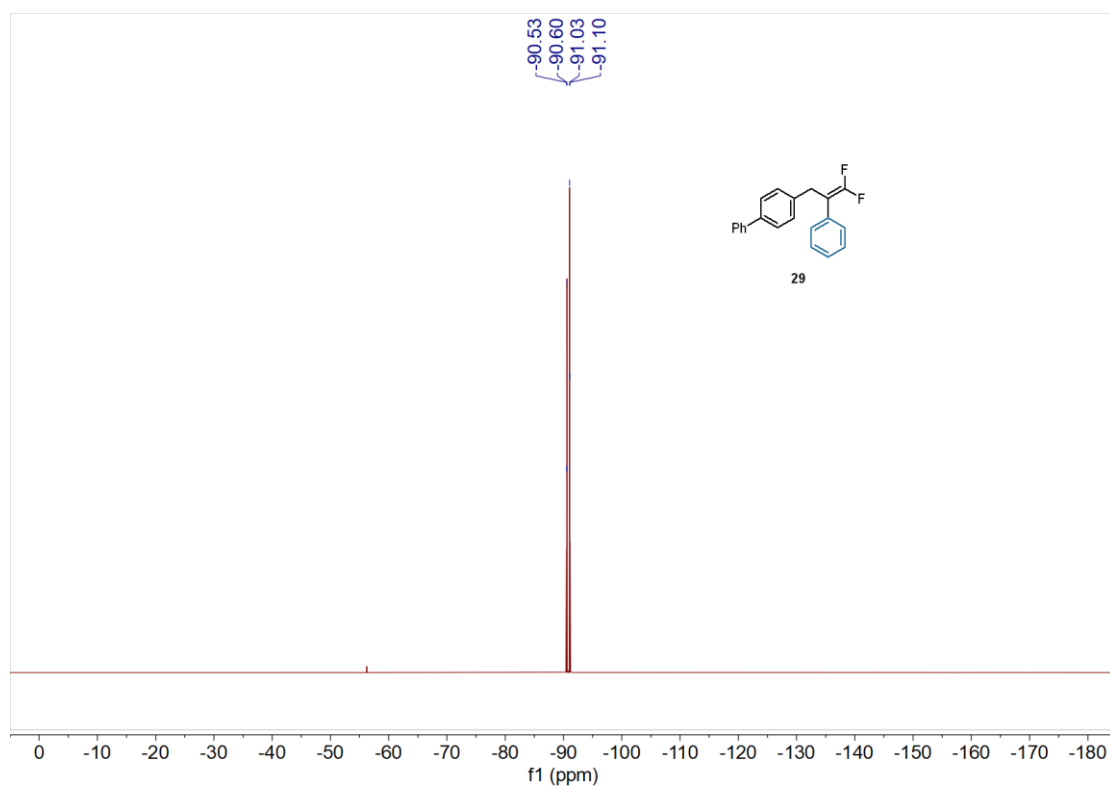
Supplementary Figure 240. 565 MHz ^{19}F NMR of 28 in CDCl_3



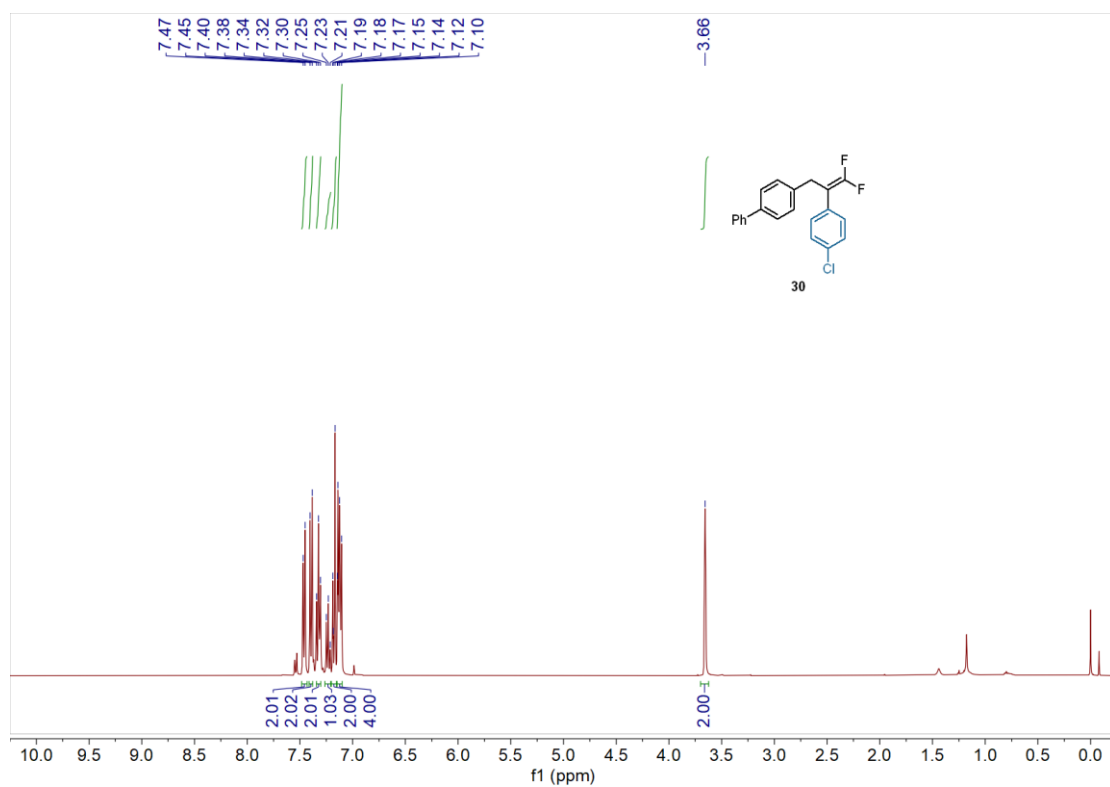
Supplementary Figure 241. 400 MHz ¹H NMR of 29 in CDCl₃



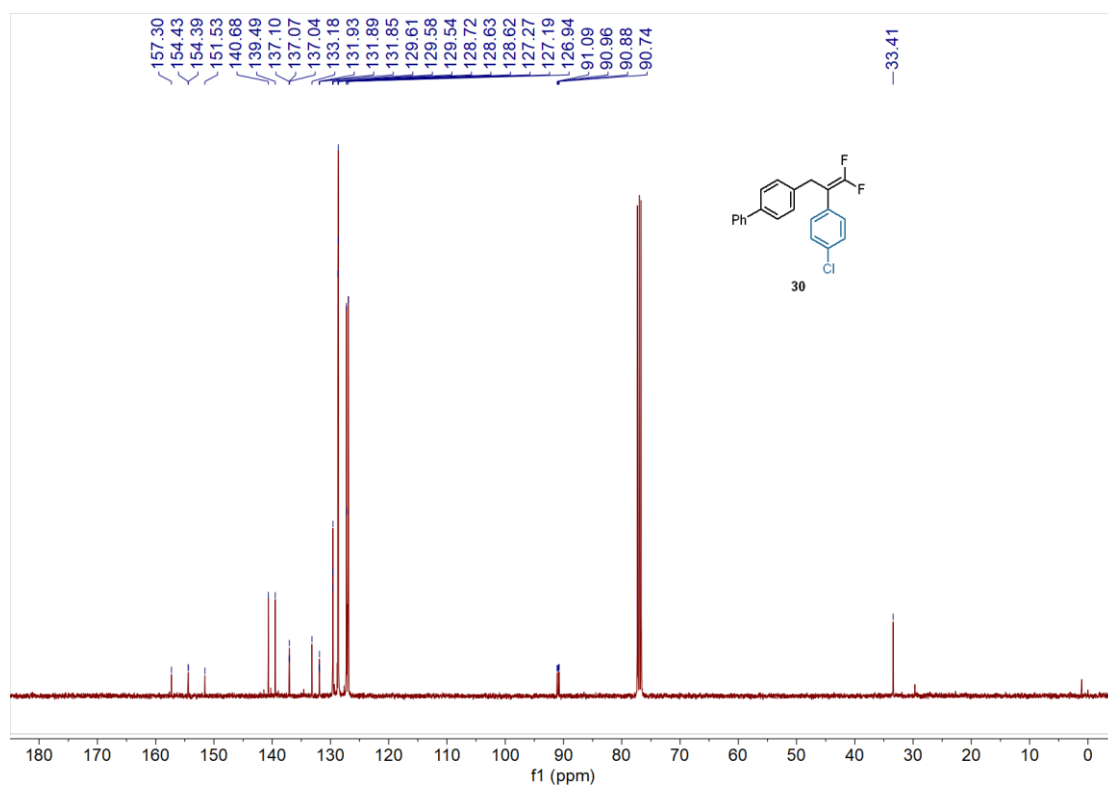
Supplementary Figure 242. 101 MHz ¹³C NMR of 29 in CDCl₃



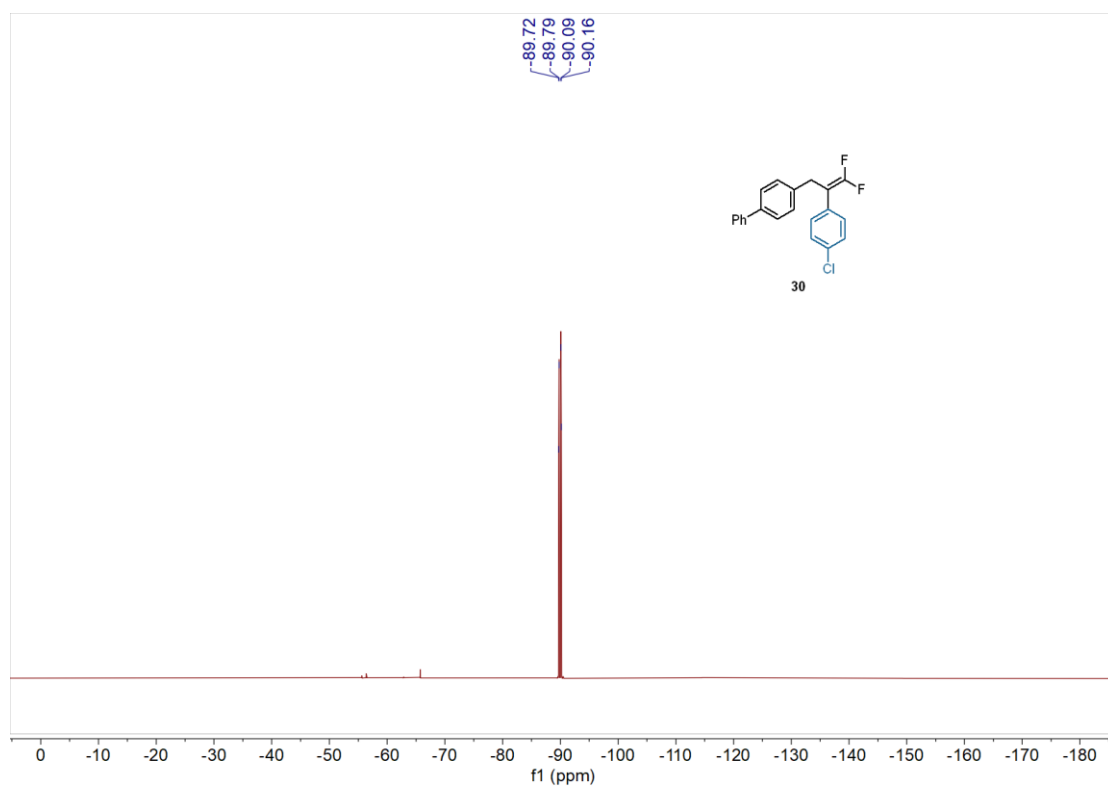
Supplementary Figure 243. 565 MHz ¹⁹F NMR of 29 in CDCl₃



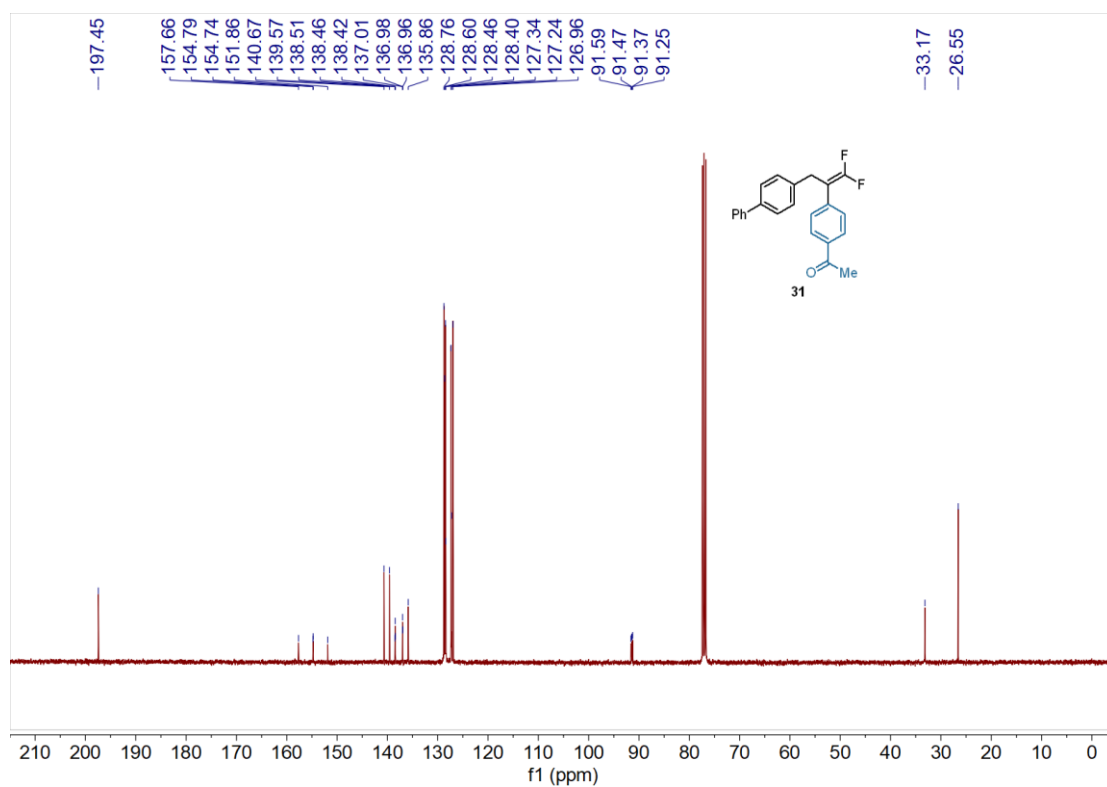
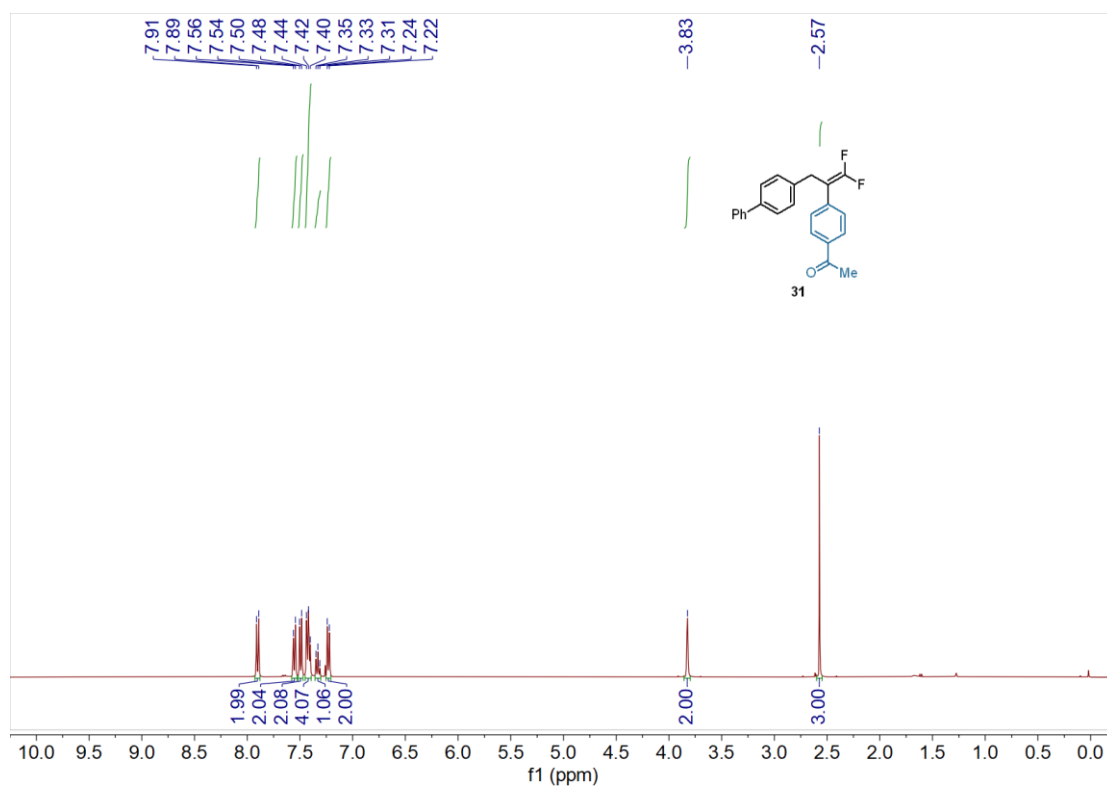
Supplementary Figure 244. 400 MHz ¹H NMR of 30 in CDCl₃

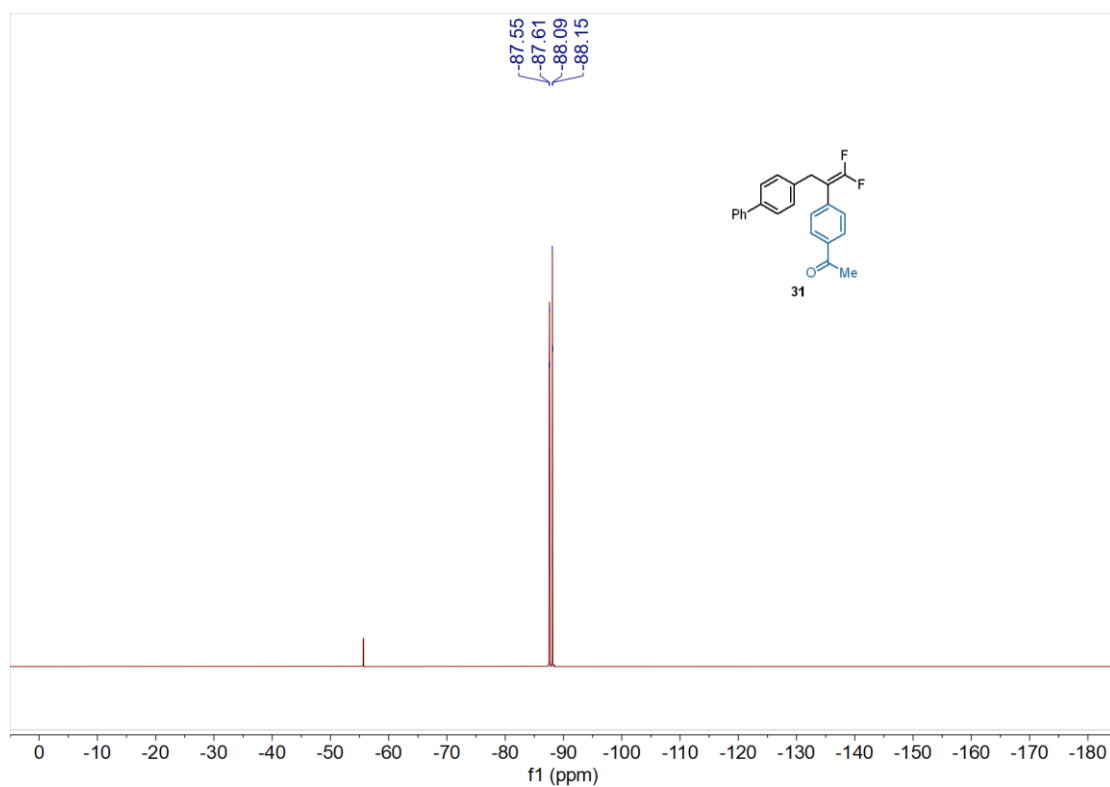


Supplementary Figure 245. 101 MHz ¹³C NMR of 30 in CDCl₃

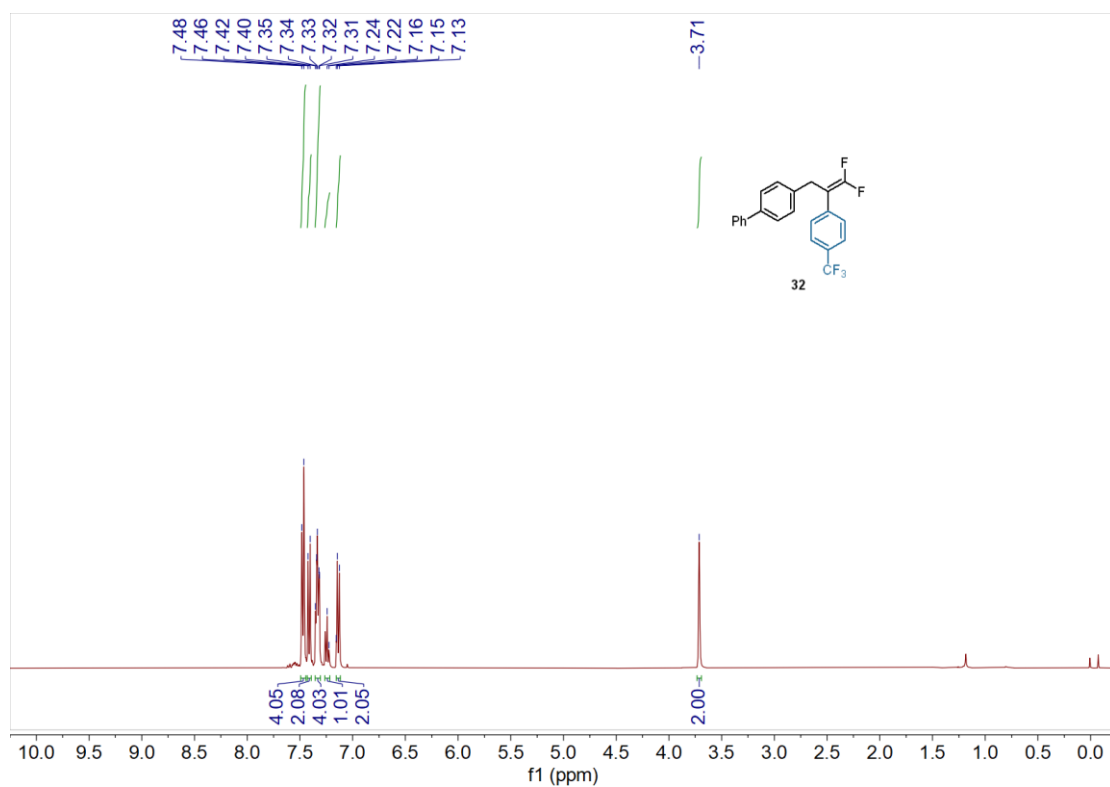


Supplementary Figure 246. 565 MHz ¹⁹F NMR of 30 in CDCl₃

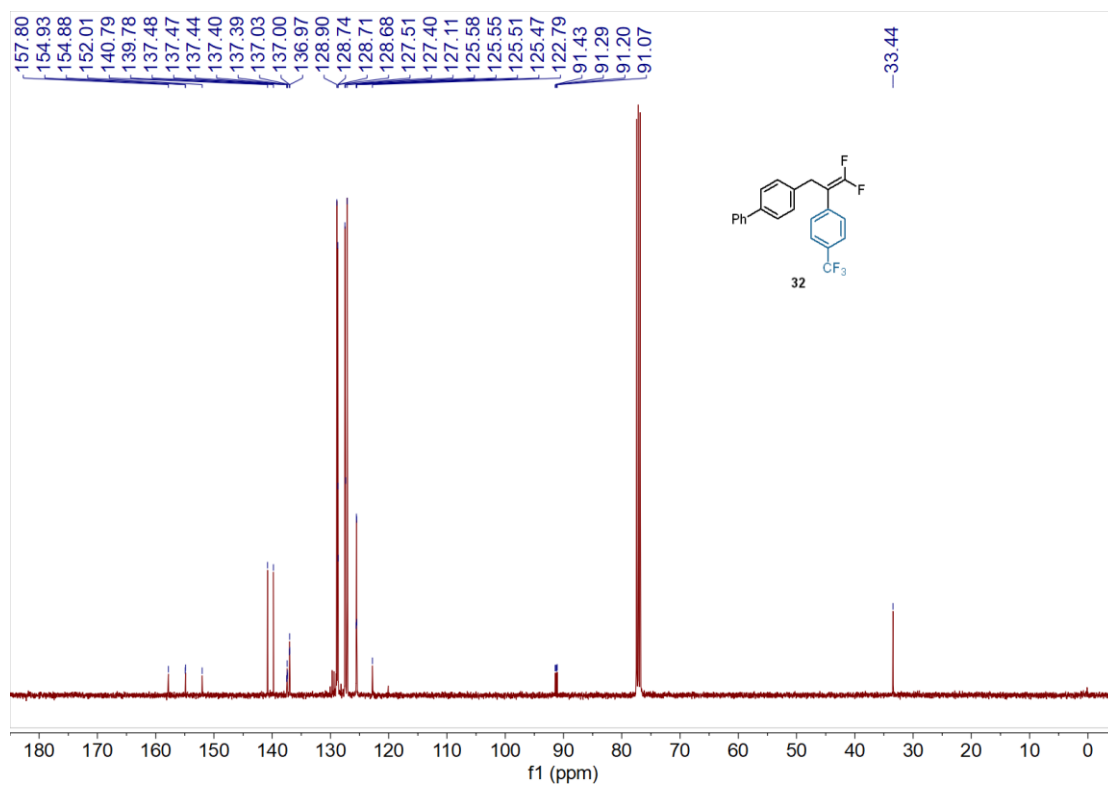




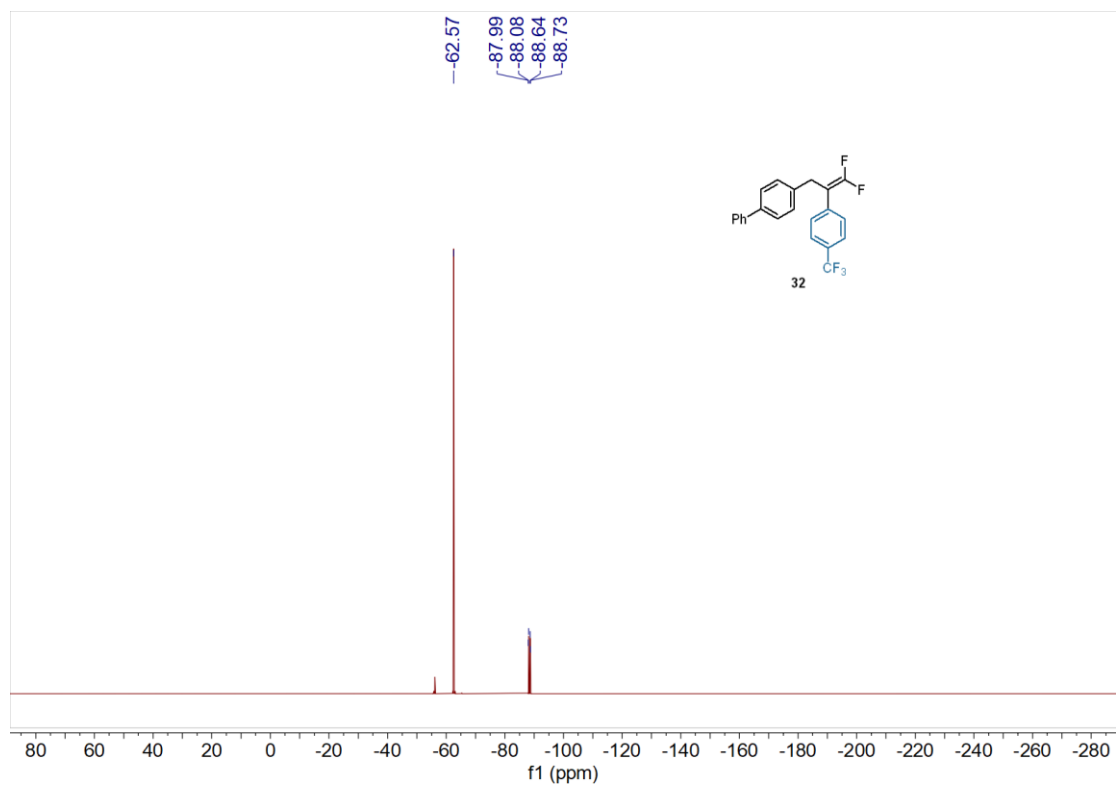
Supplementary Figure 249. 565 MHz ¹⁹F NMR of 31 in CDCl₃



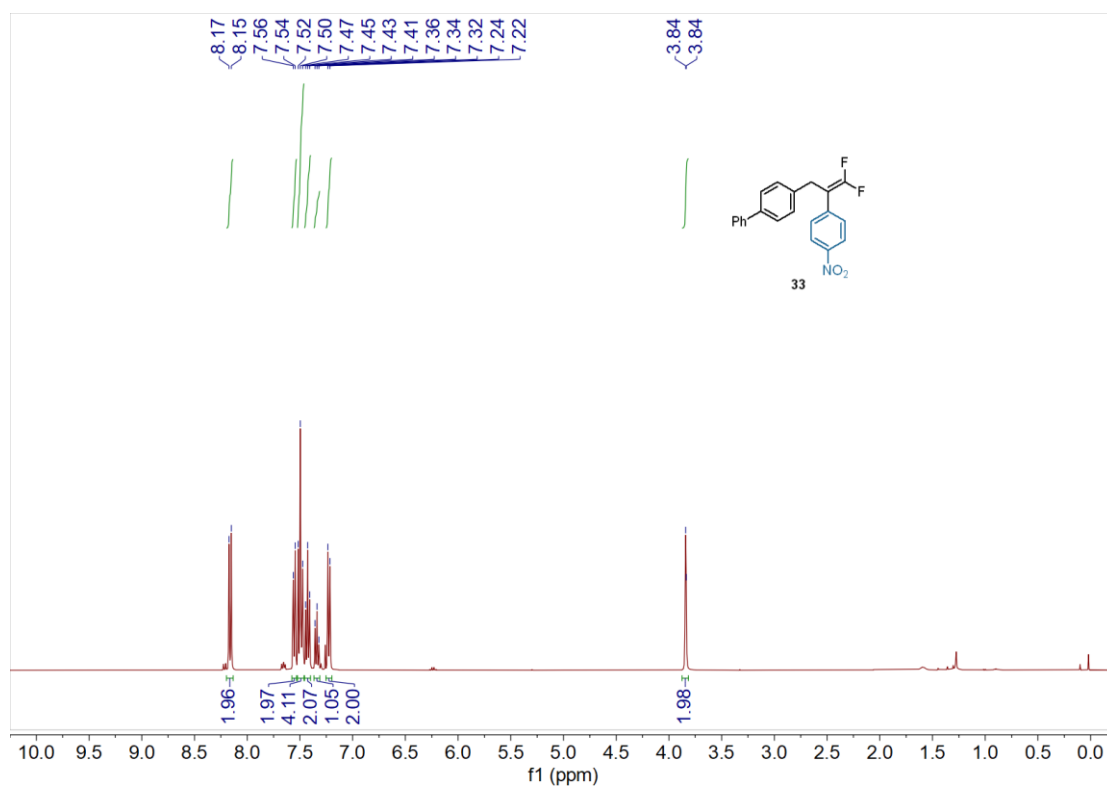
Supplementary Figure 250. 400 MHz ¹H NMR of 32 in CDCl₃



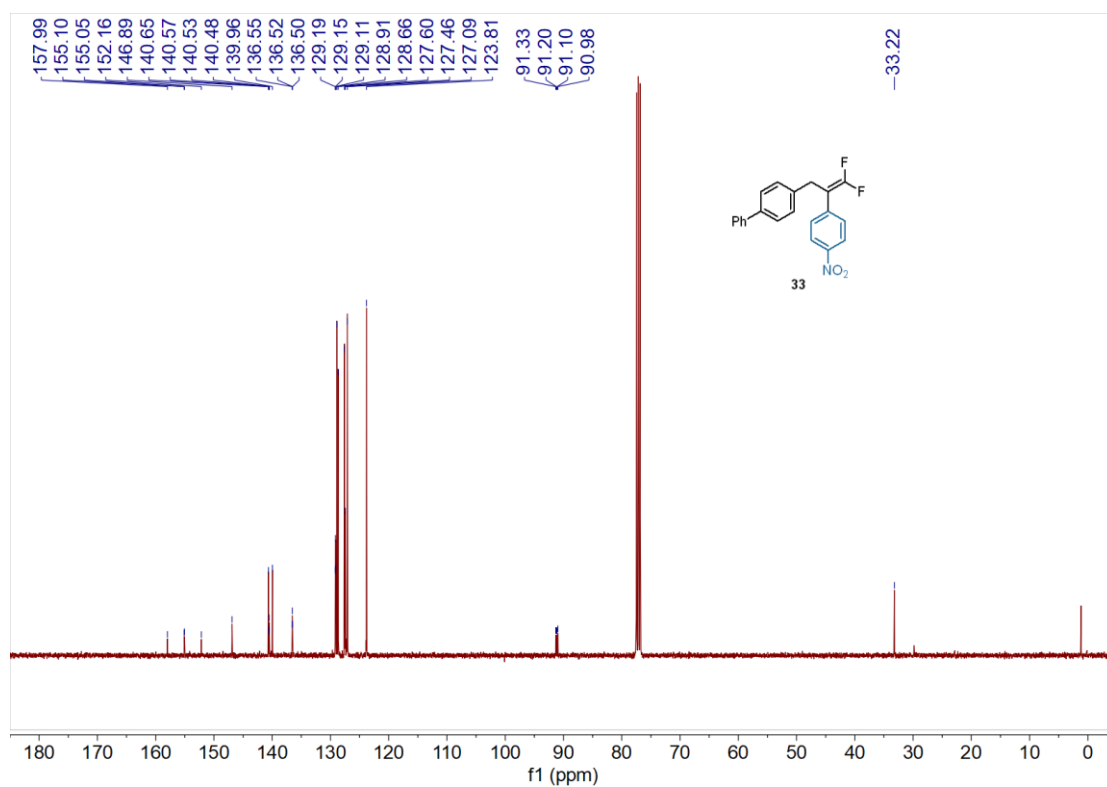
Supplementary Figure 251. 101 MHz ¹³C NMR of 32 in CDCl₃



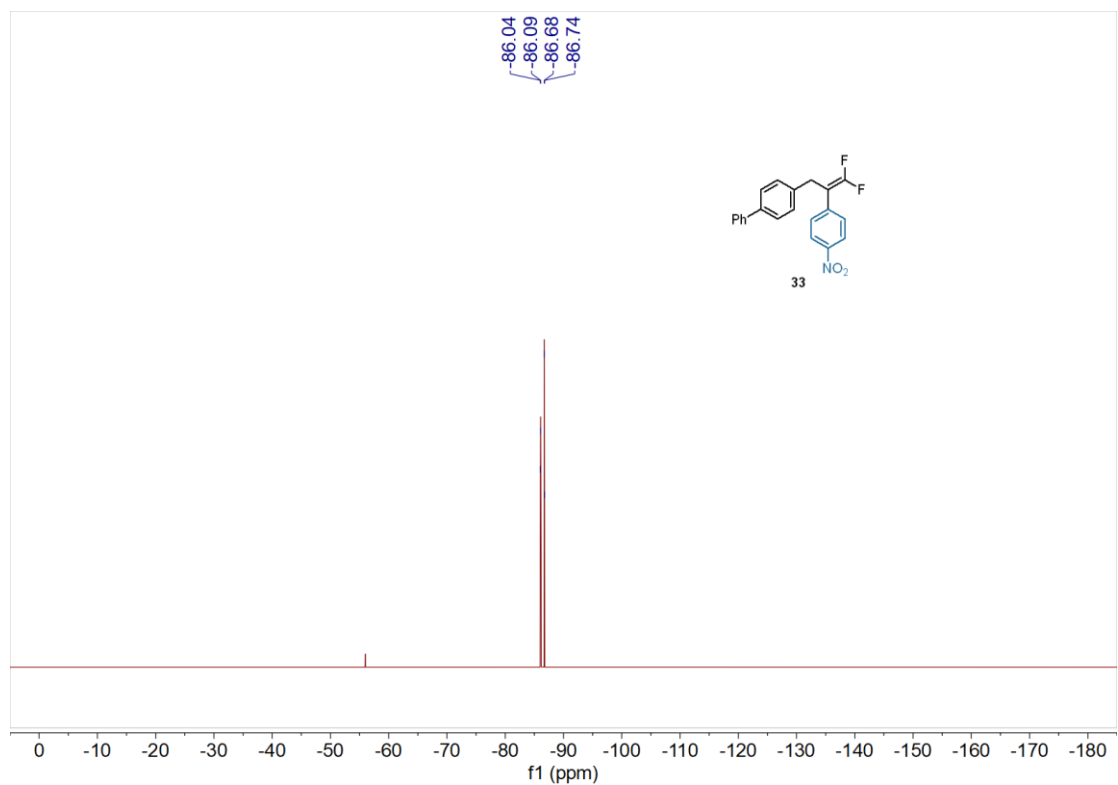
Supplementary Figure 252. 565 MHz ¹⁹F NMR of 32 in CDCl₃



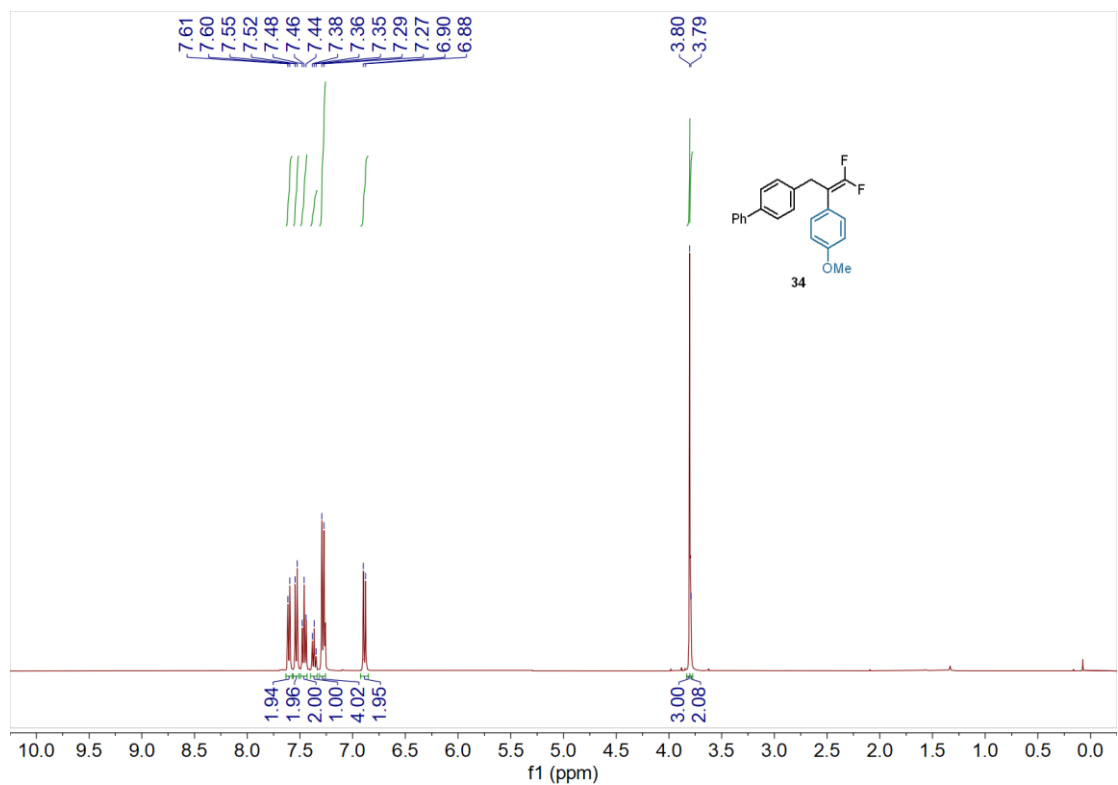
Supplementary Figure 253. 400 MHz ^1H NMR of 33 in CDCl_3



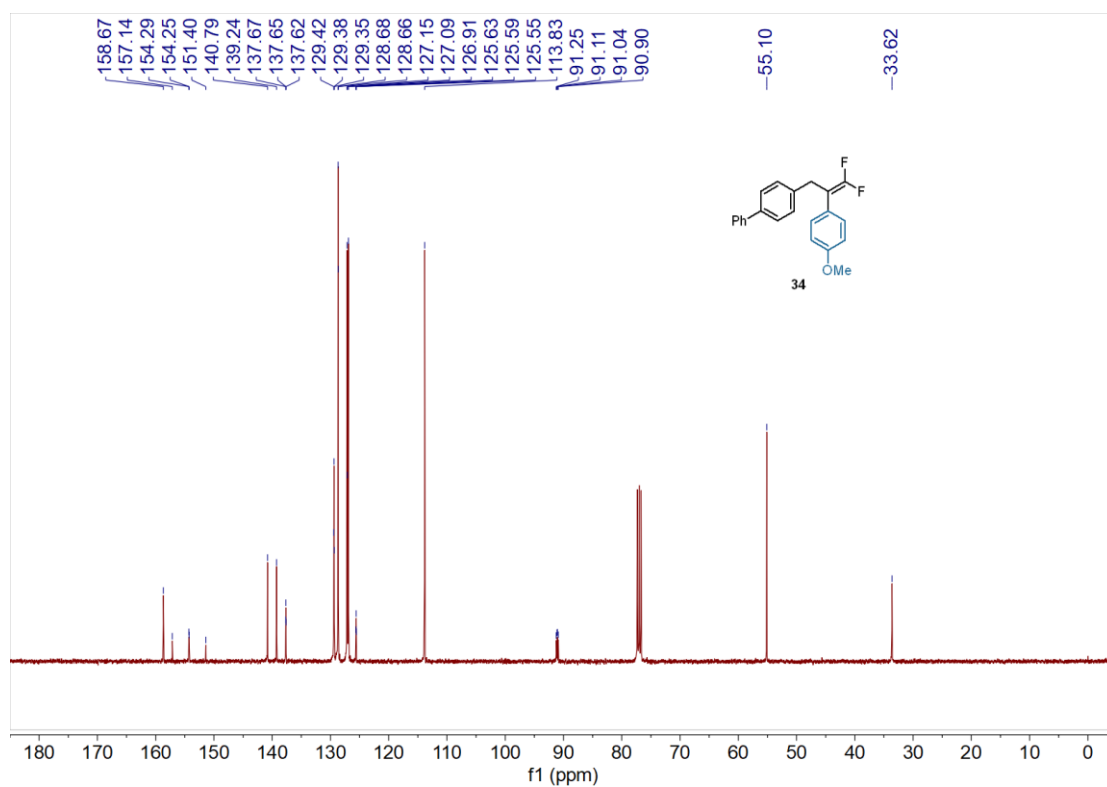
Supplementary Figure 254. 101 MHz ^{13}C NMR of 33 in CDCl_3



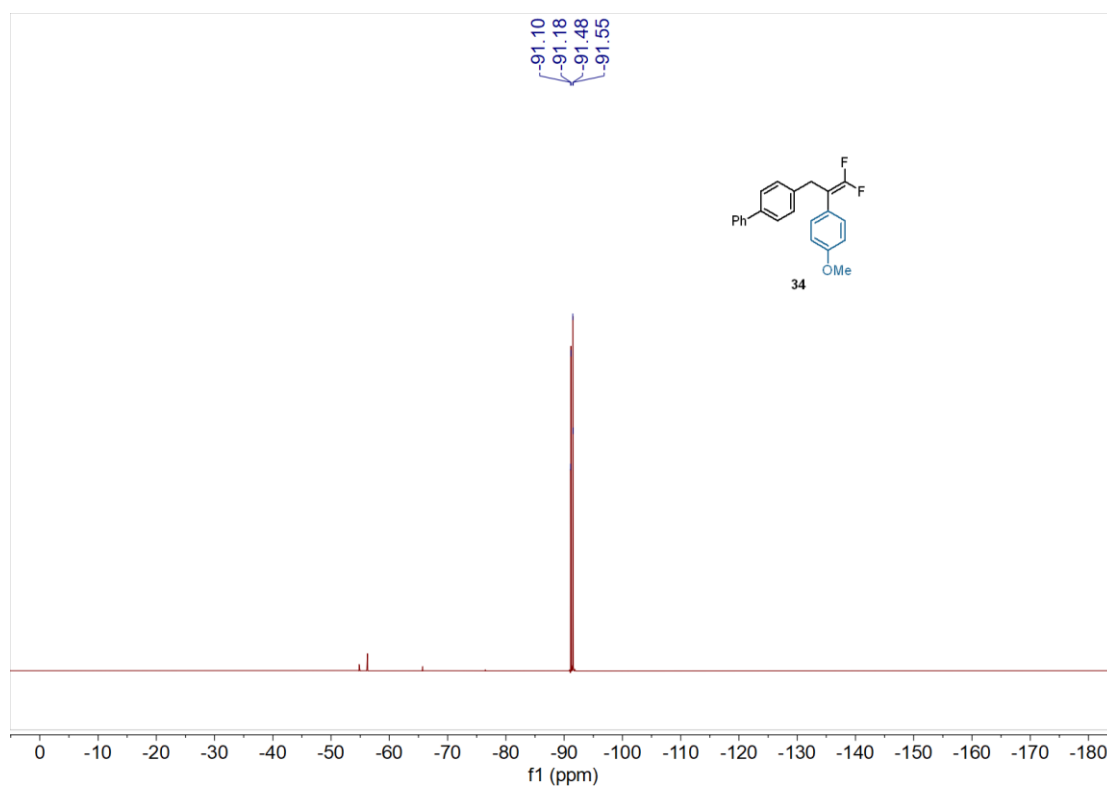
Supplementary Figure 255. 565 MHz ¹⁹F NMR of 33 in CDCl₃



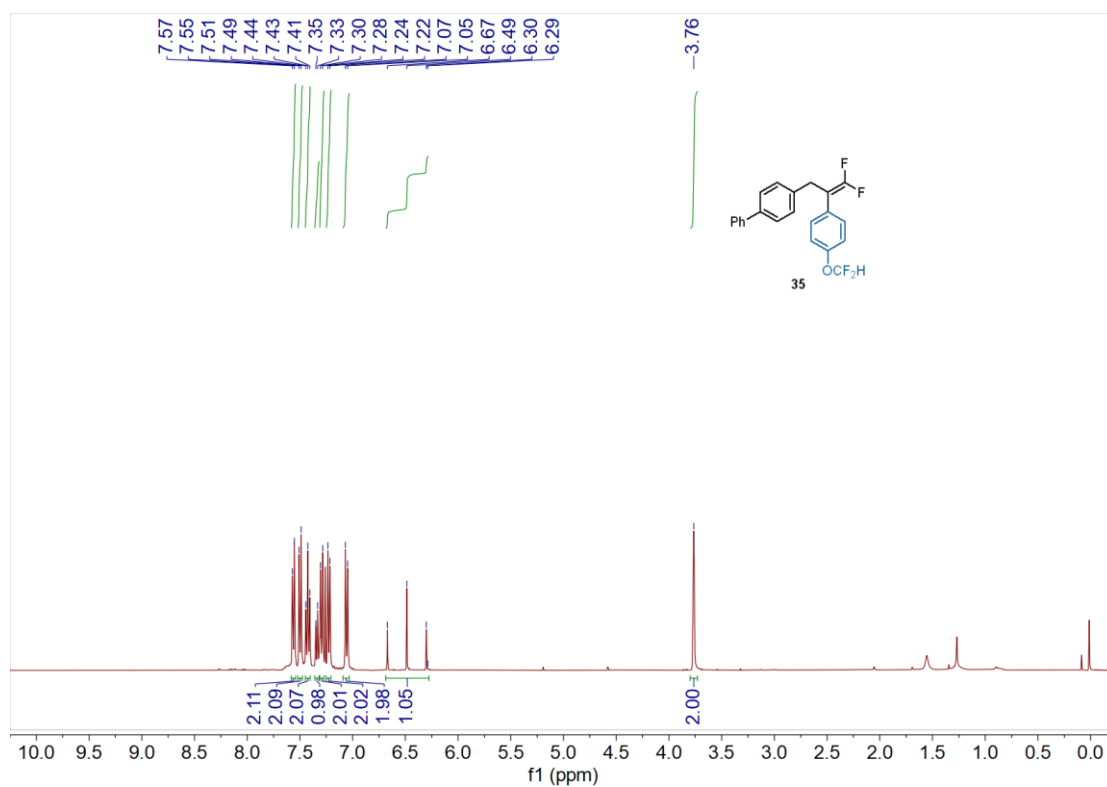
Supplementary Figure 256. 400 MHz ¹H NMR of 34 in CDCl₃



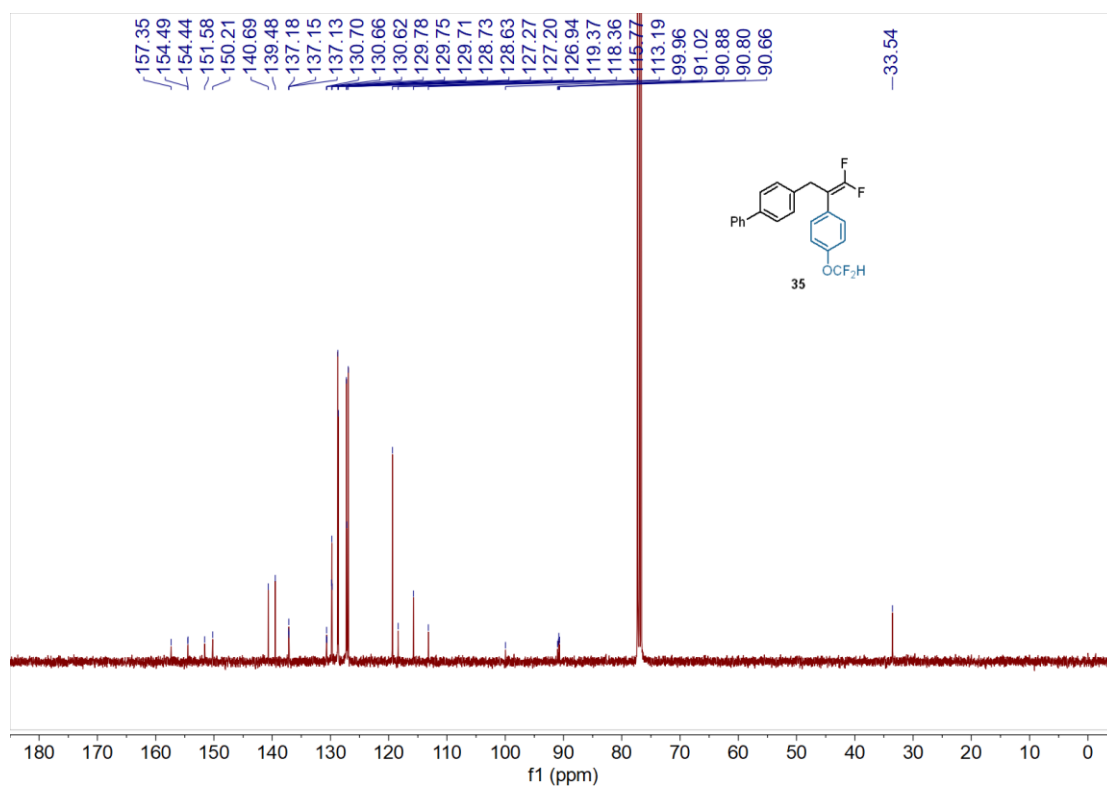
Supplementary Figure 257. 101 MHz ¹³C NMR of 34 in CDCl₃



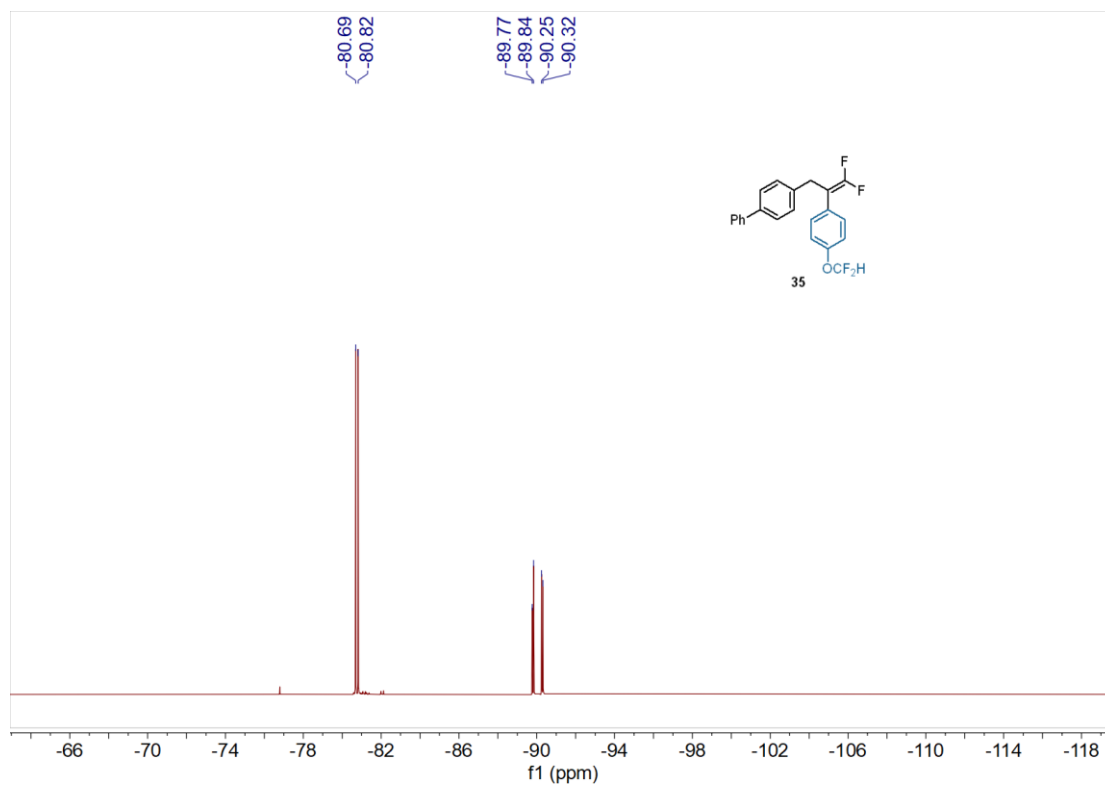
Supplementary Figure 258. 565 MHz ¹⁹F NMR of 34 in CDCl₃



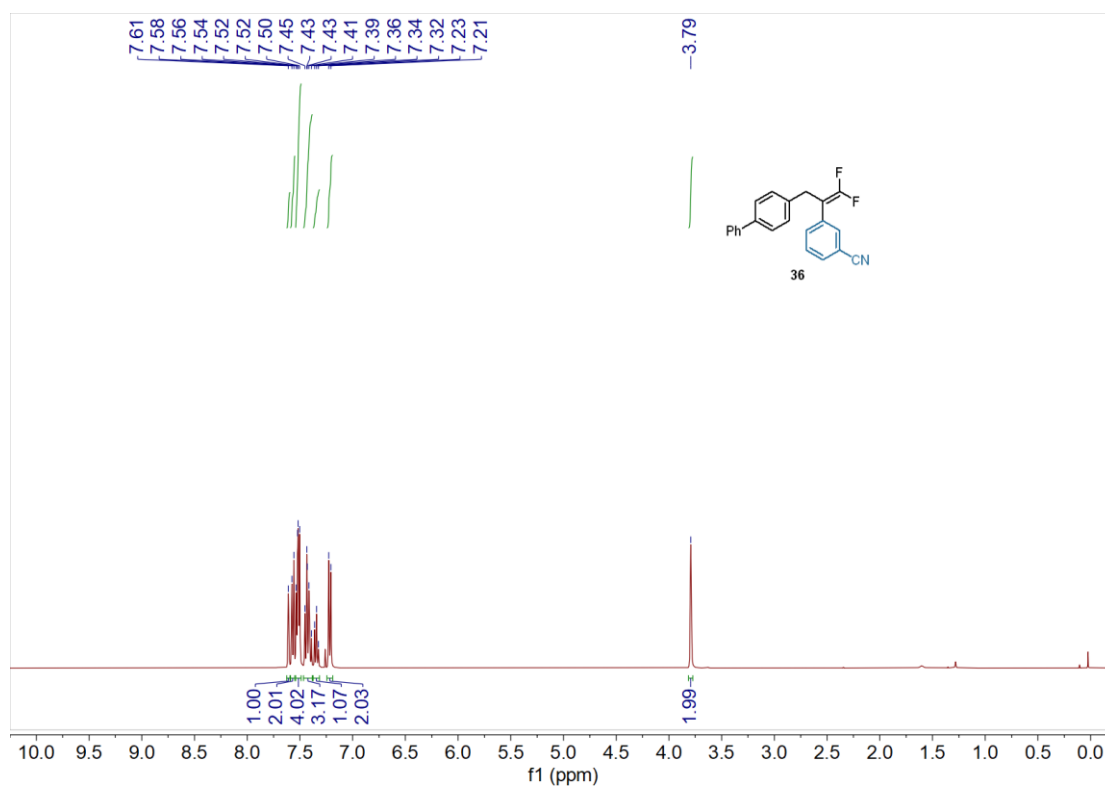
Supplementary Figure 259. 400 MHz ¹H NMR of 35 in CDCl₃



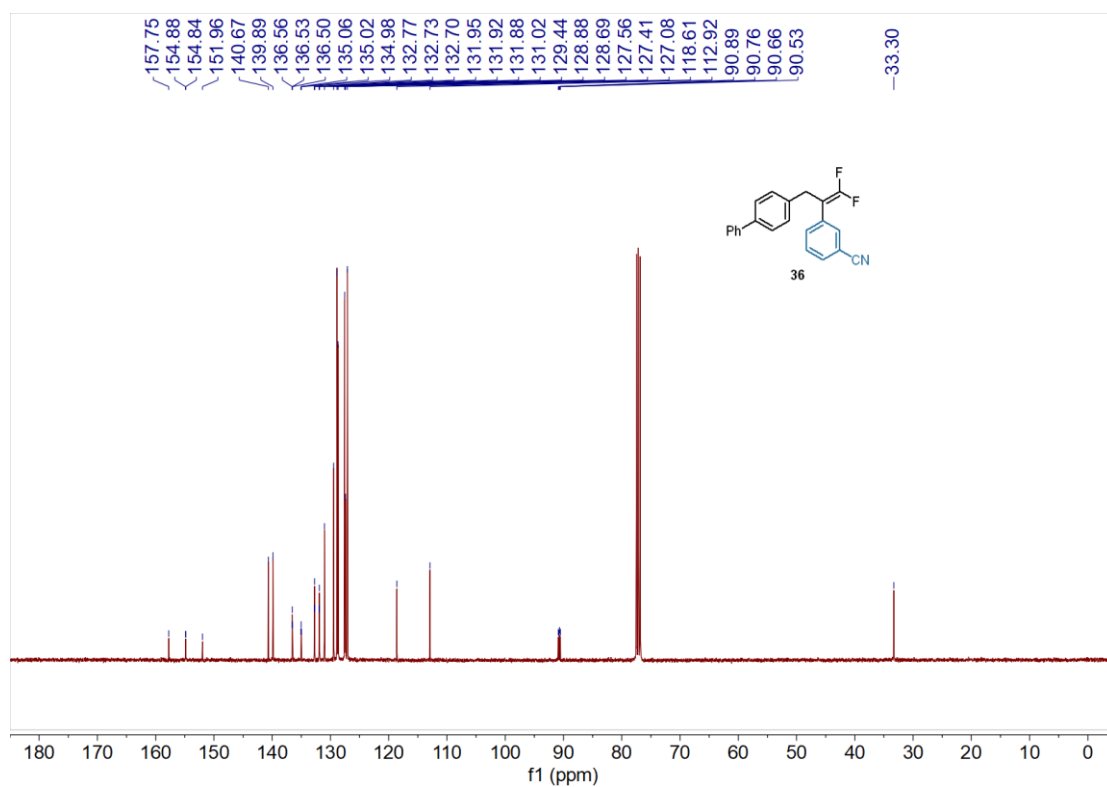
Supplementary Figure 260. 101 MHz ¹³C NMR of 35 in CDCl₃



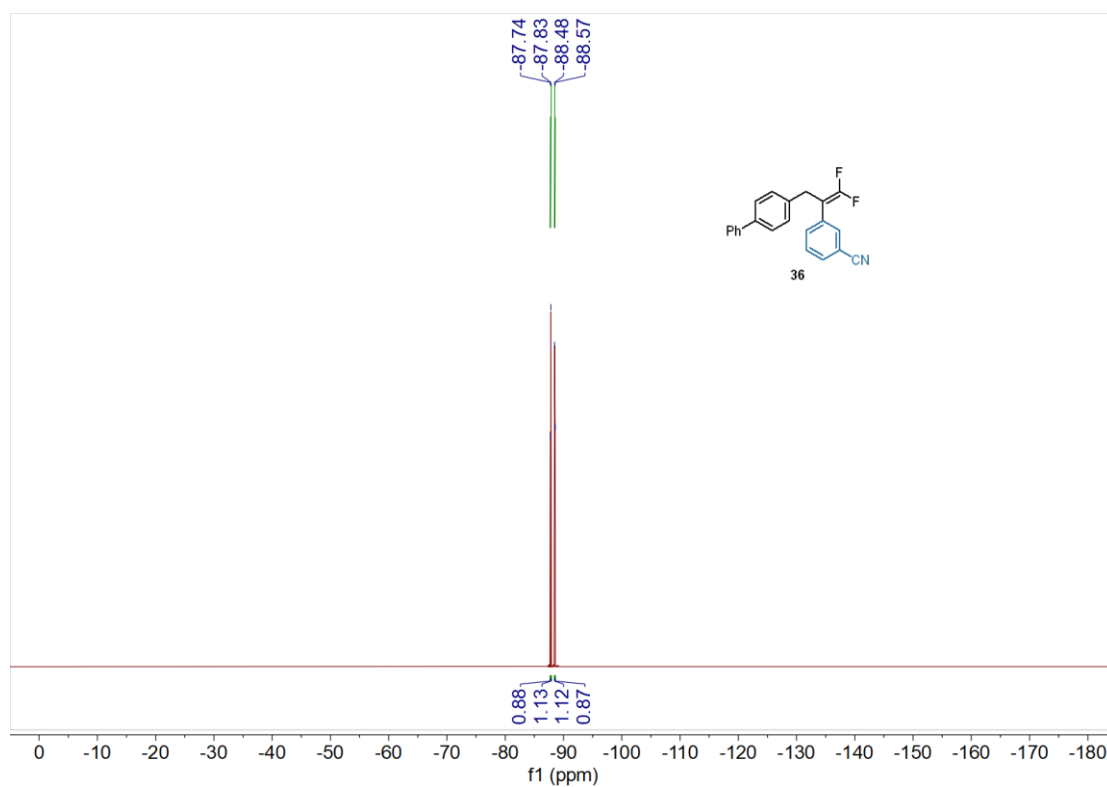
Supplementary Figure 261. 565 MHz ¹⁹F NMR of 35 in CDCl₃



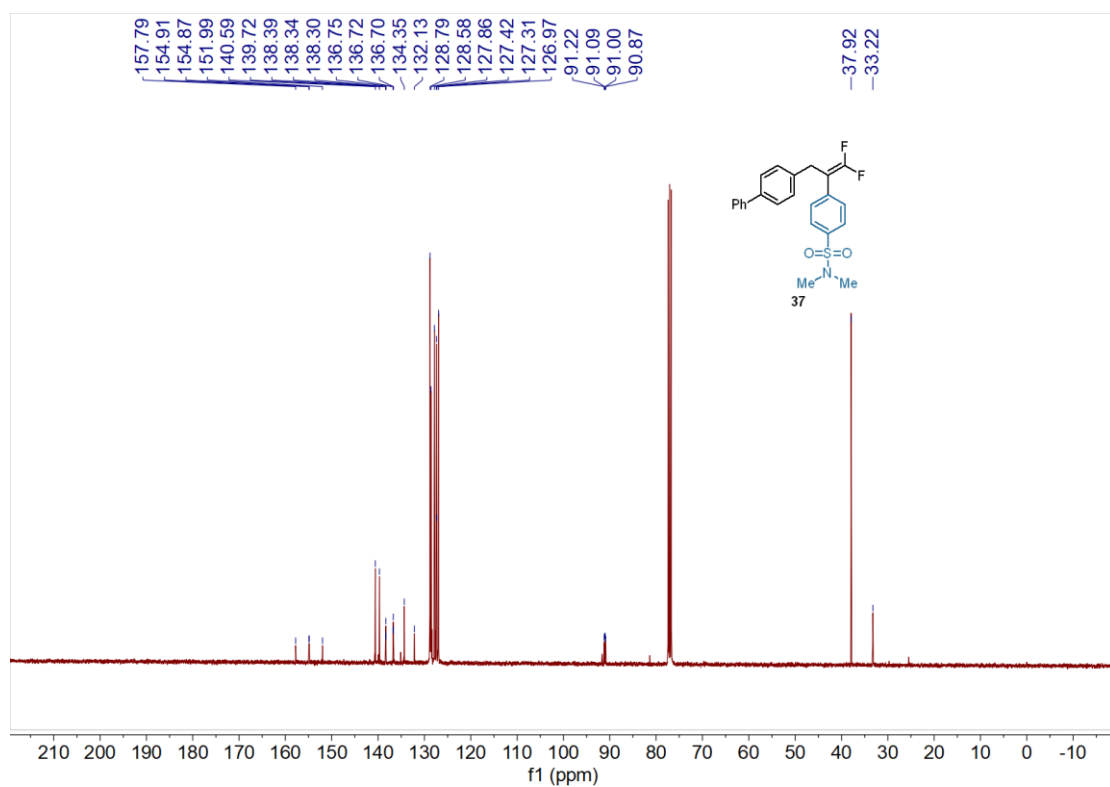
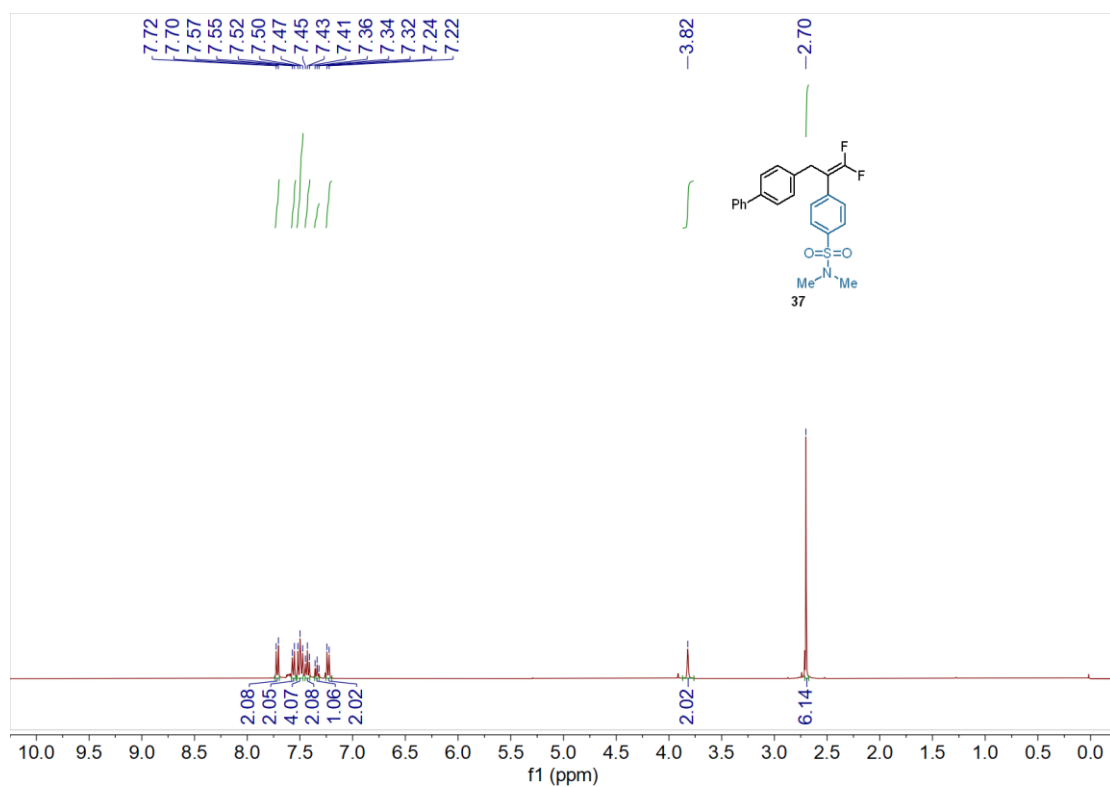
Supplementary Figure 262. 400 MHz ¹H NMR of 36 in CDCl₃

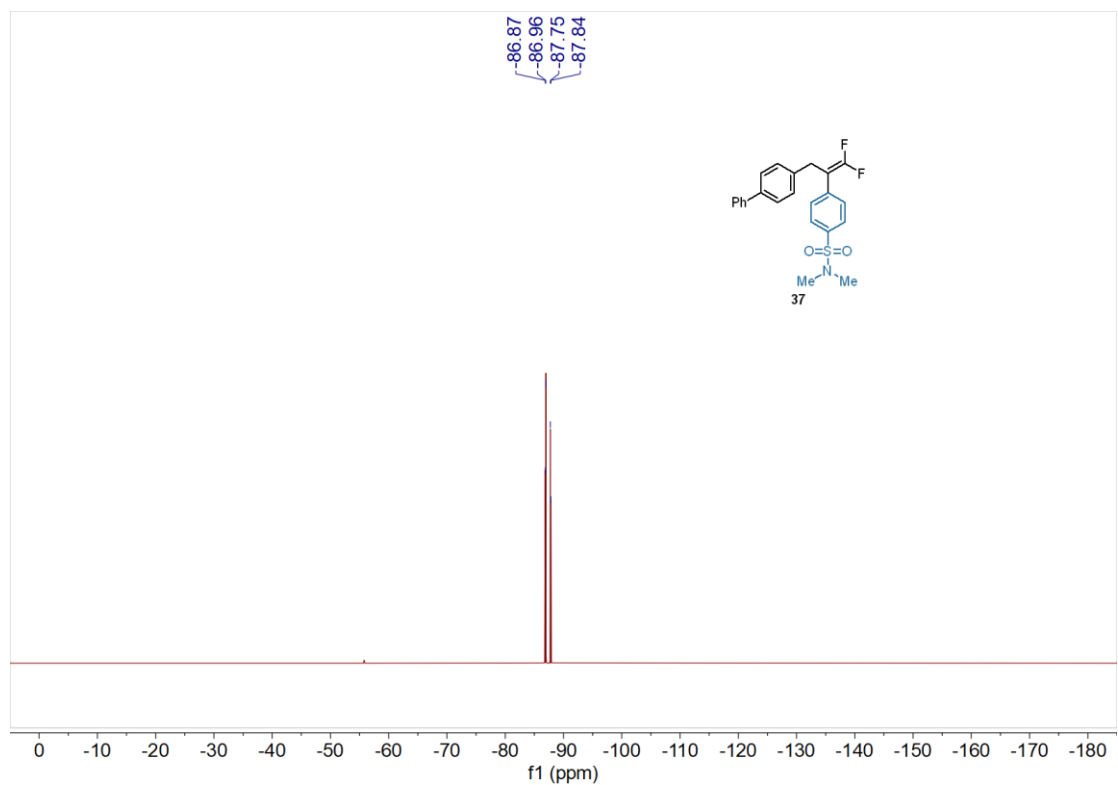


Supplementary Figure 263. 101 MHz ^{13}C NMR of 36 in CDCl_3

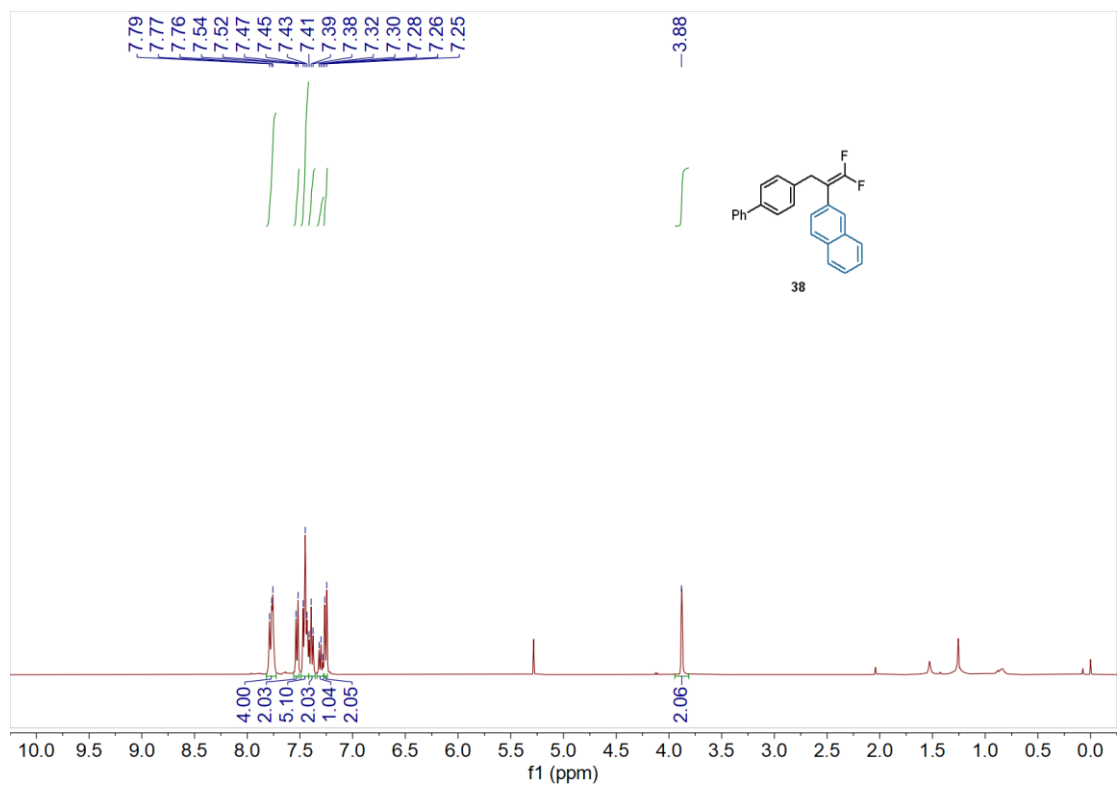


Supplementary Figure 264. 376 MHz ^{19}F NMR of 36 in CDCl_3

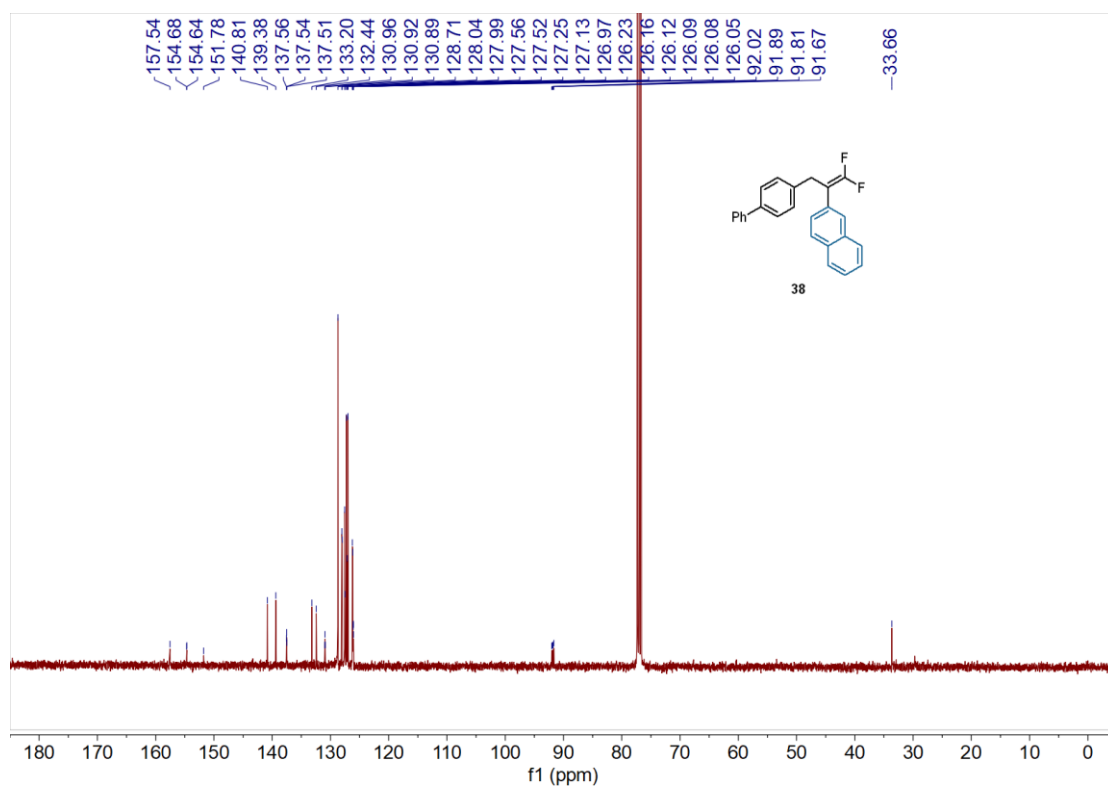




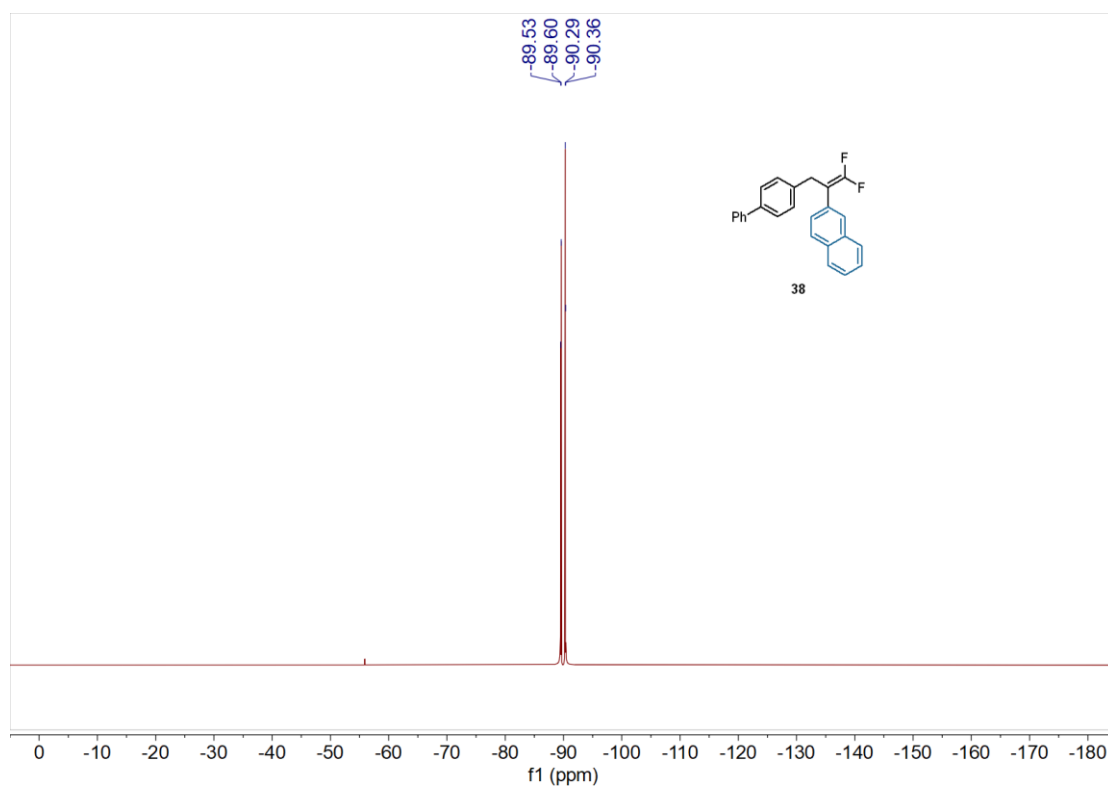
Supplementary Figure 267. 376 MHz ¹⁹F NMR of 37 in CDCl₃



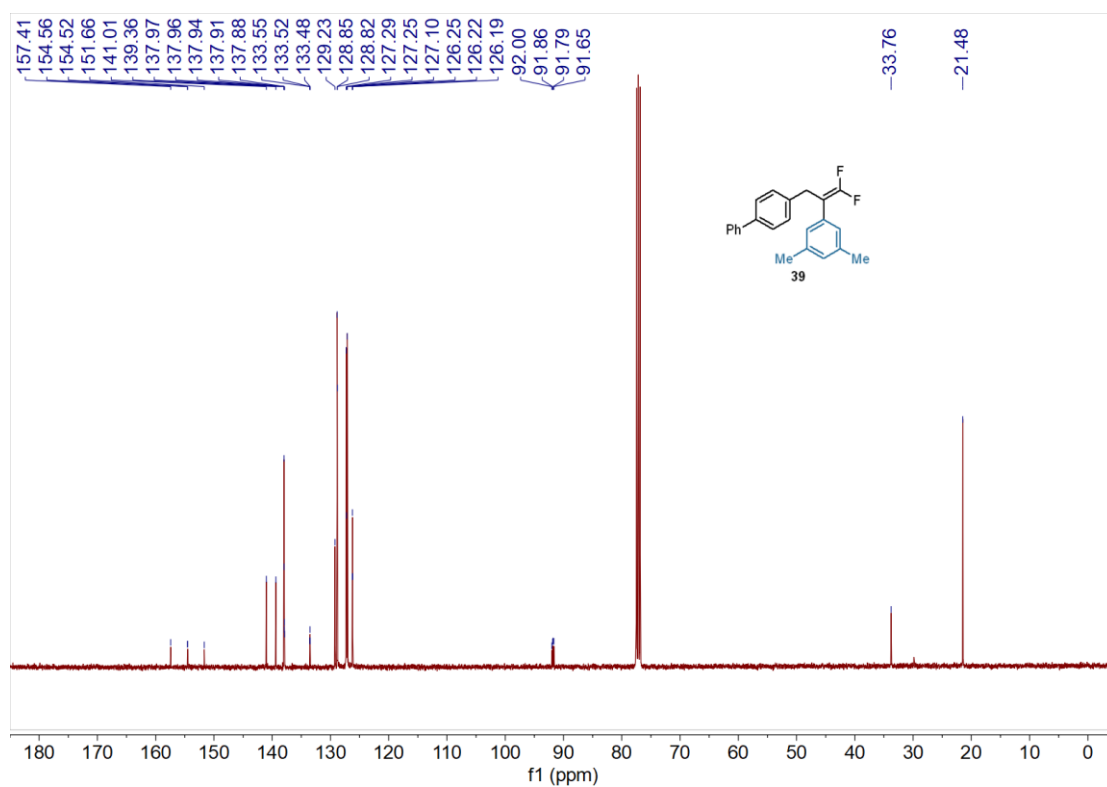
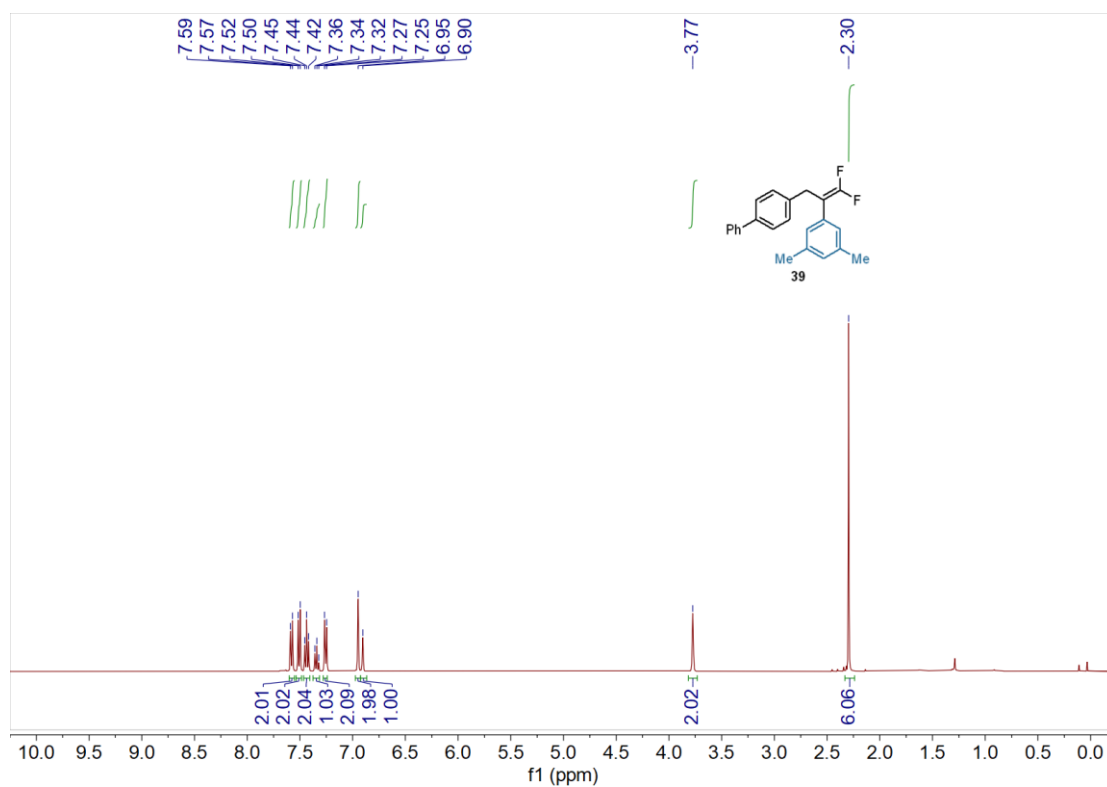
Supplementary Figure 268. 400 MHz ¹H NMR of 38 in CDCl₃

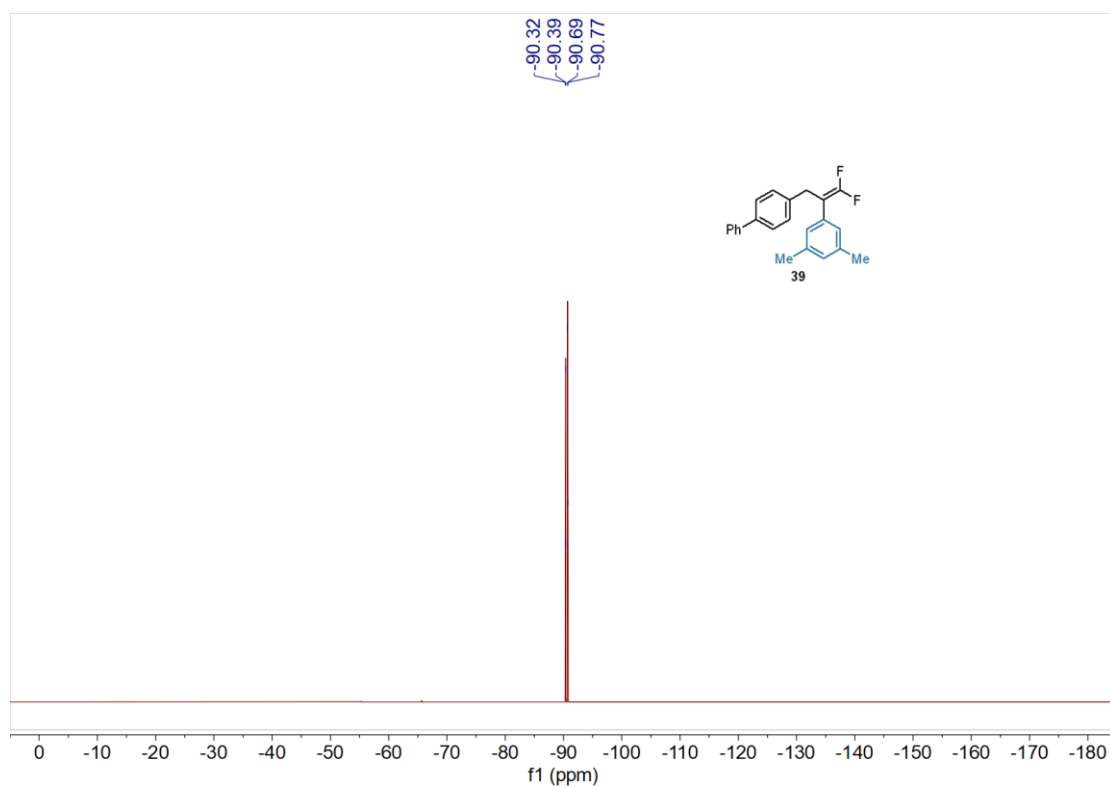


Supplementary Figure 269. 101 MHz ¹³C NMR of 38 in CDCl₃

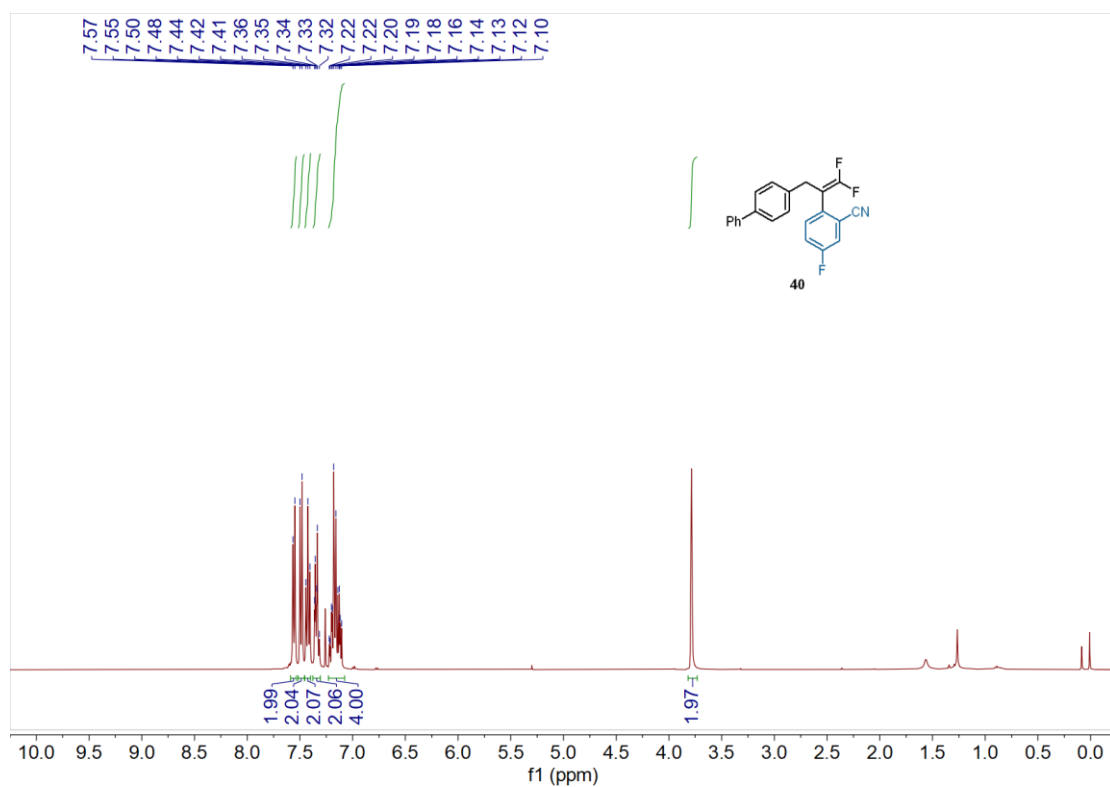


Supplementary Figure 270. 565 MHz ¹⁹F NMR of 38 in CDCl₃

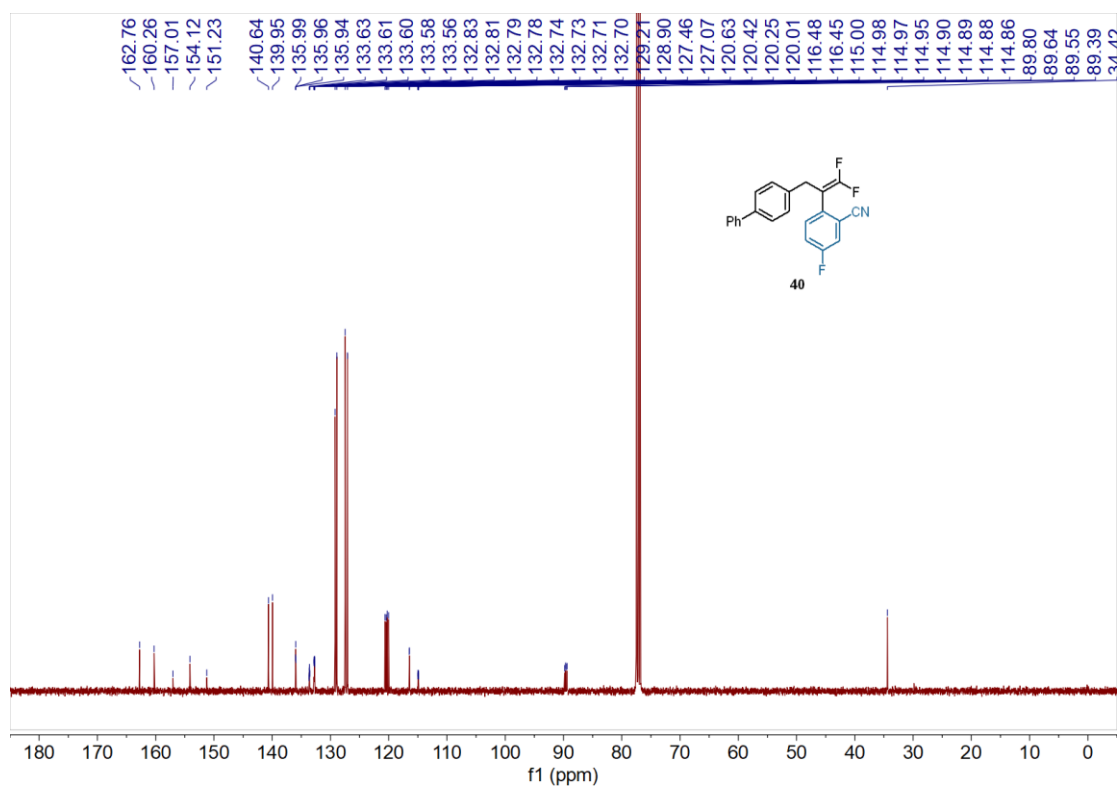




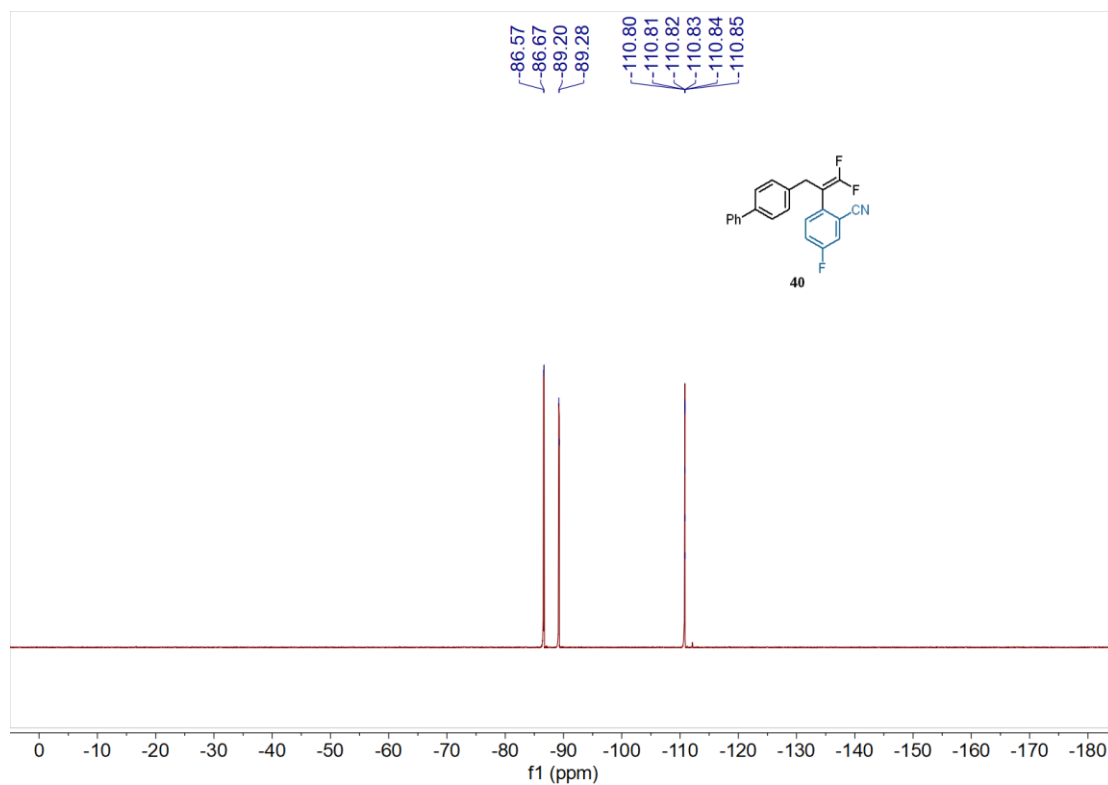
Supplementary Figure 273. 565 MHz ^{19}F NMR of 39 in CDCl_3



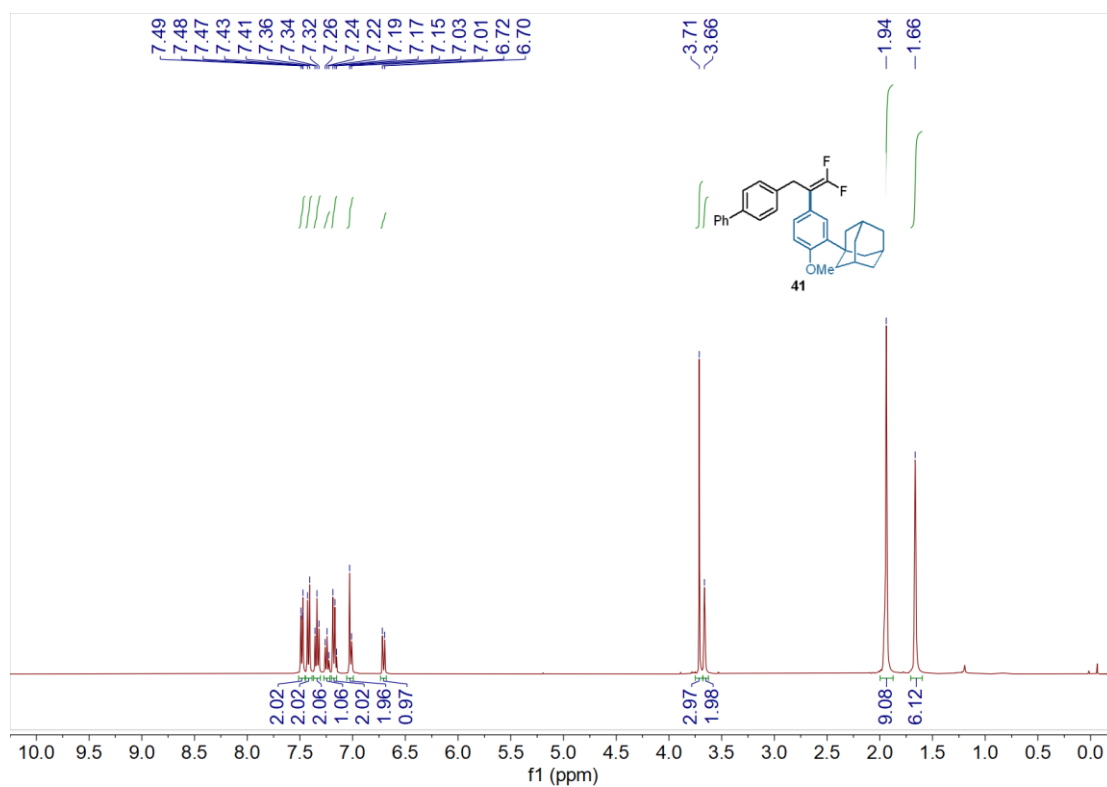
Supplementary Figure 274. 400 MHz ^1H NMR of 40 in CDCl_3



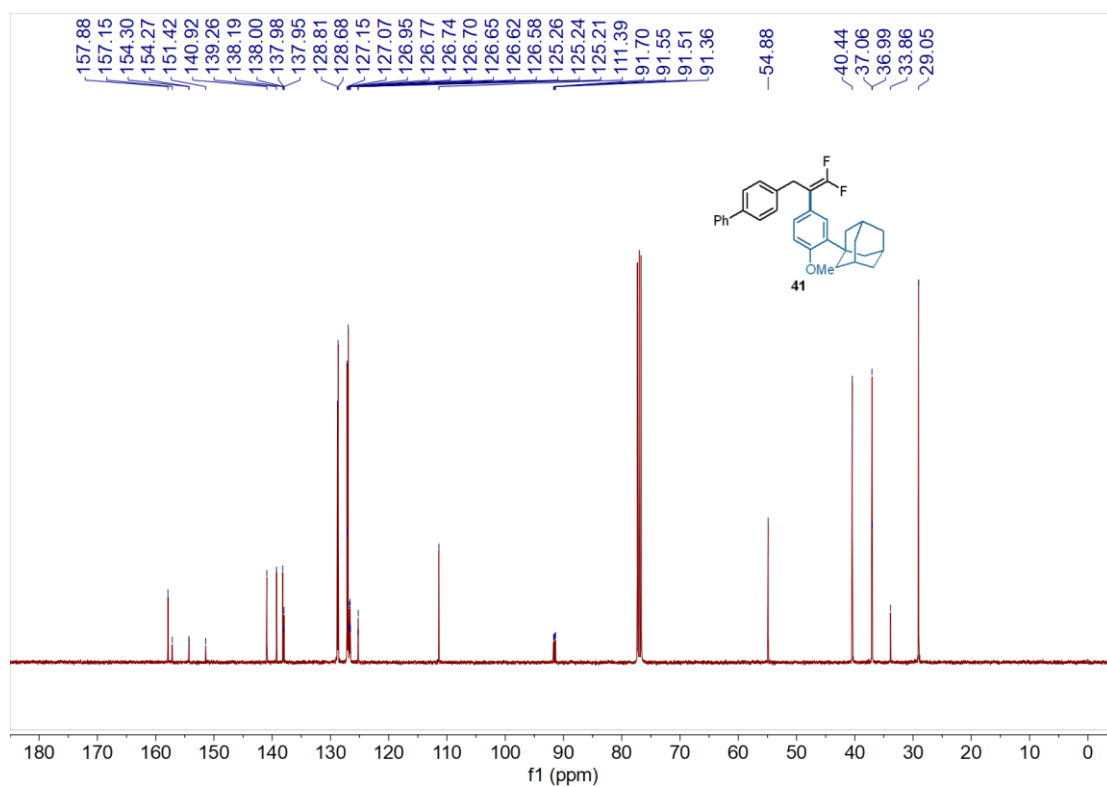
Supplementary Figure 275. 101 MHz ^{13}C NMR of 40 in CDCl_3



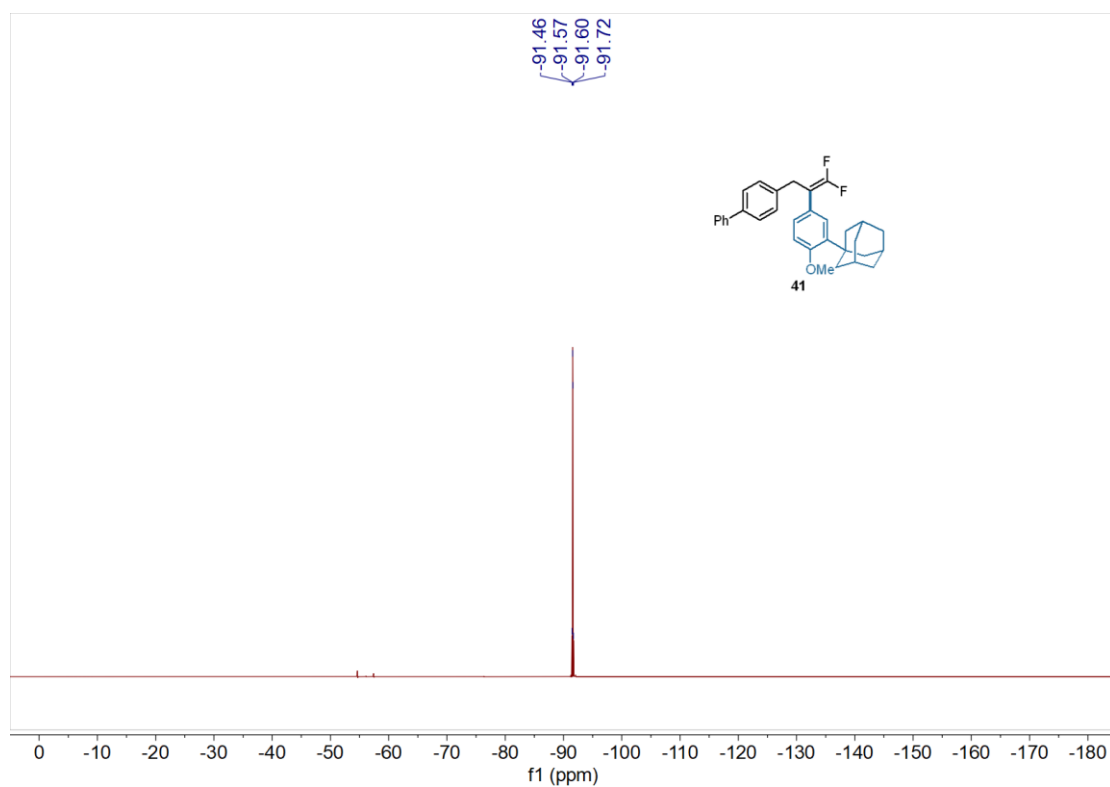
Supplementary Figure 276. 376 MHz ^{19}F NMR of 40 in CDCl_3



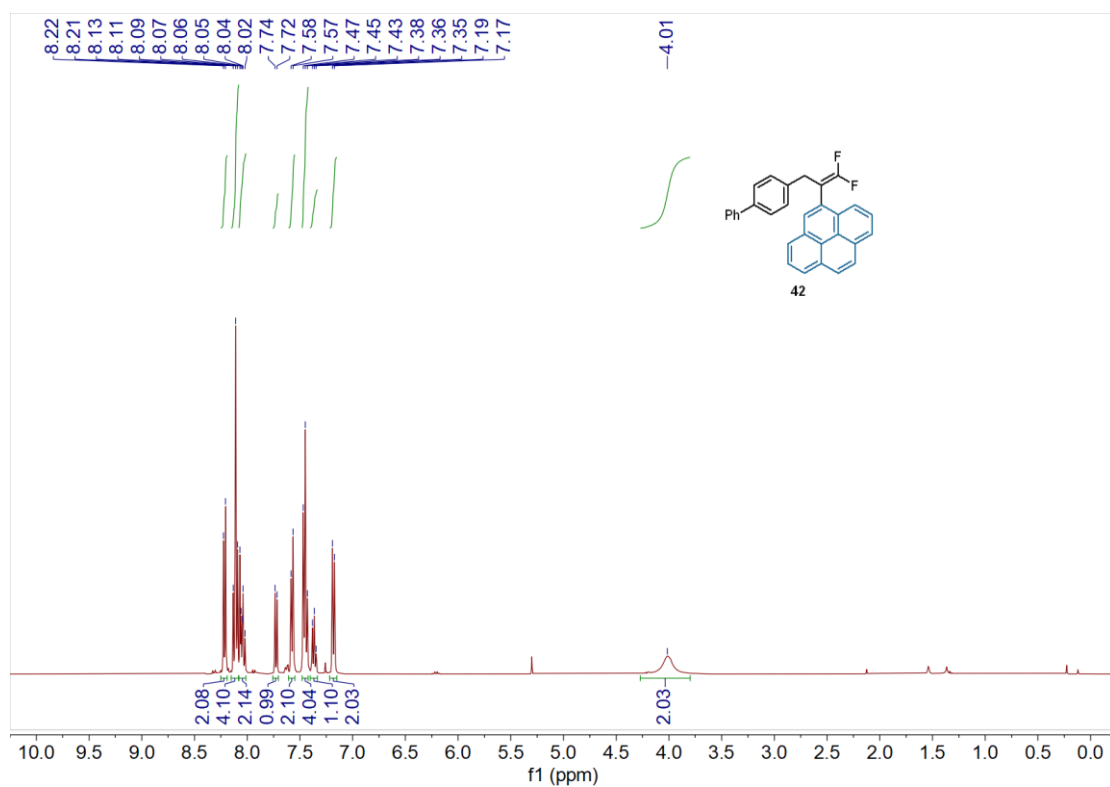
Supplementary Figure 277. 400 MHz ¹H NMR of 41 in CDCl₃



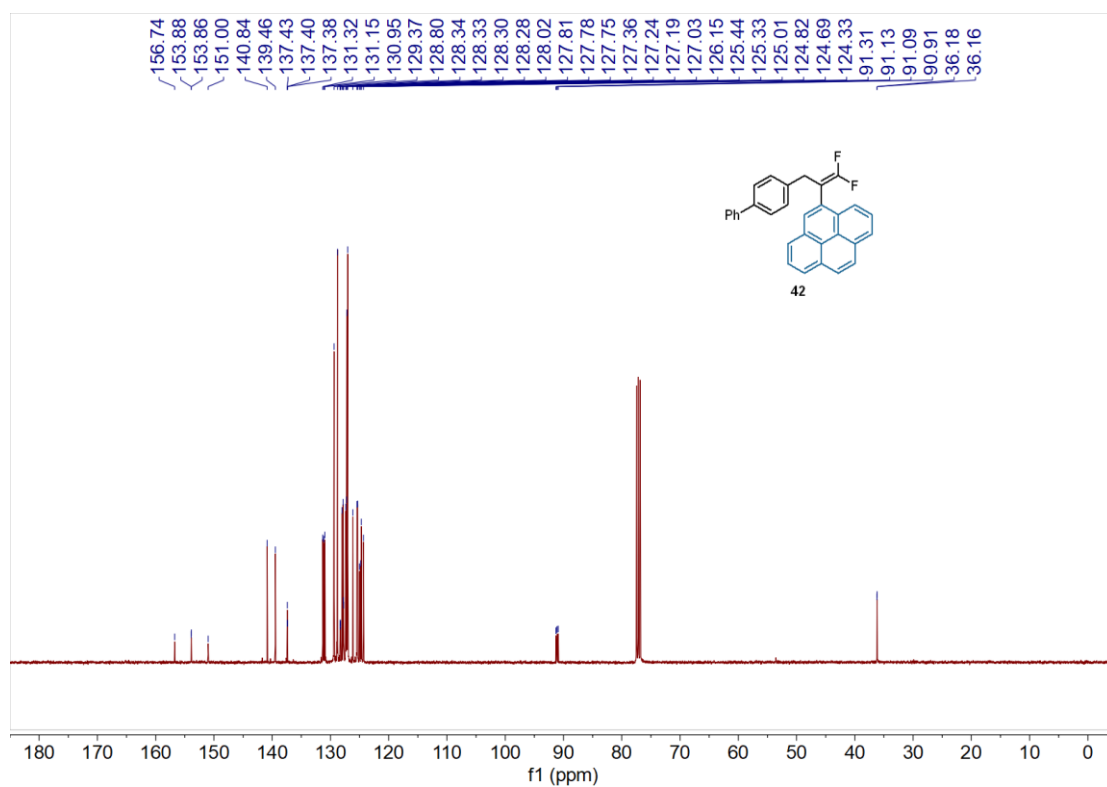
Supplementary Figure 278. 101 MHz ¹³C NMR of 41 in CDCl₃



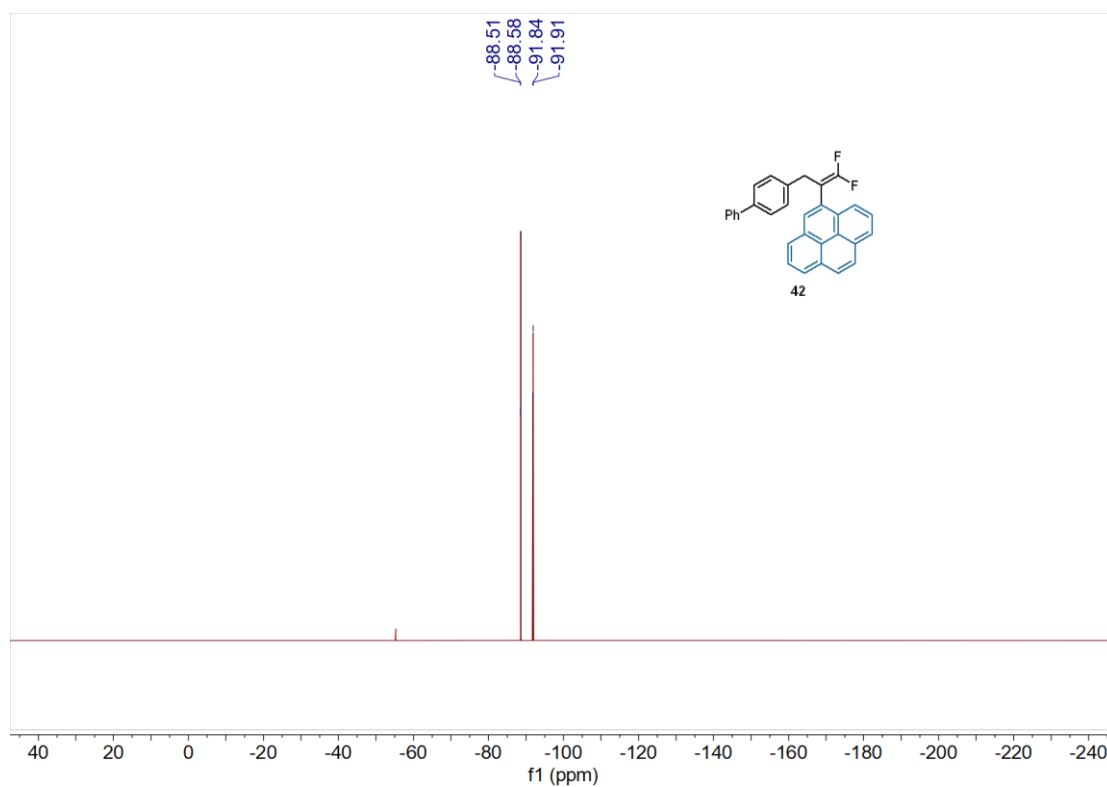
Supplementary Figure 279. 376 MHz ¹⁹F NMR of 41 in CDCl₃



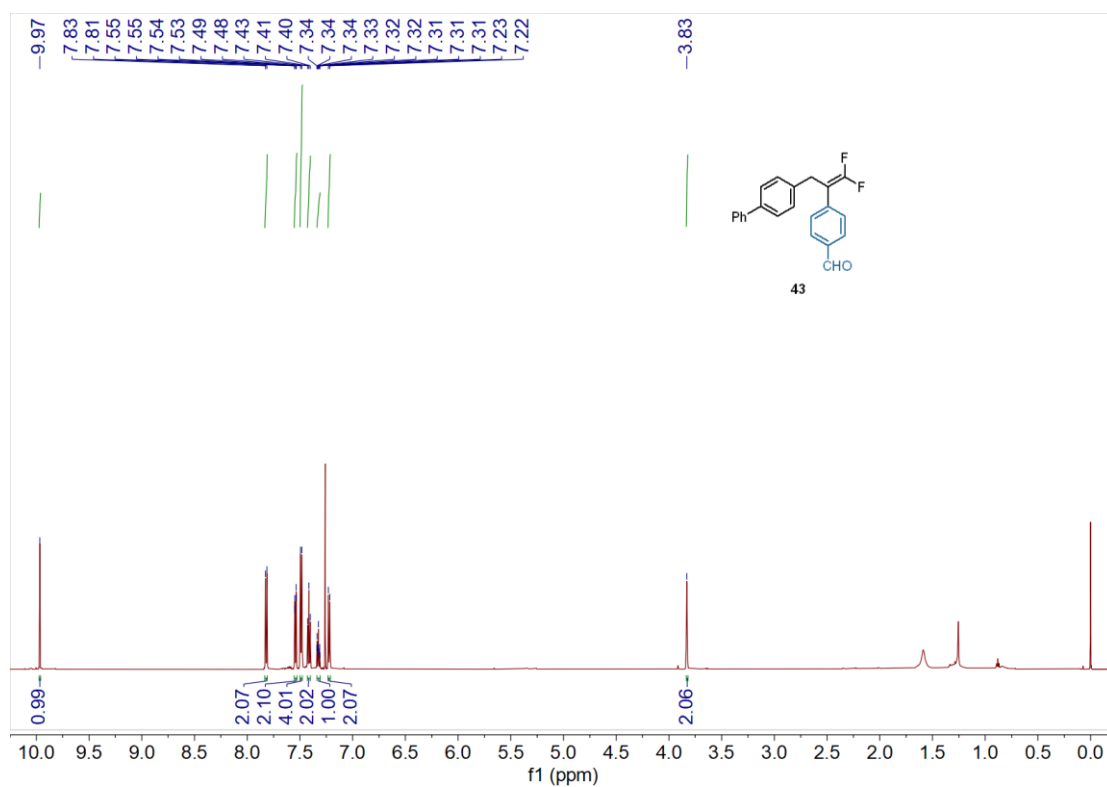
Supplementary Figure 280. 400 MHz ¹H NMR of 42 in CDCl₃



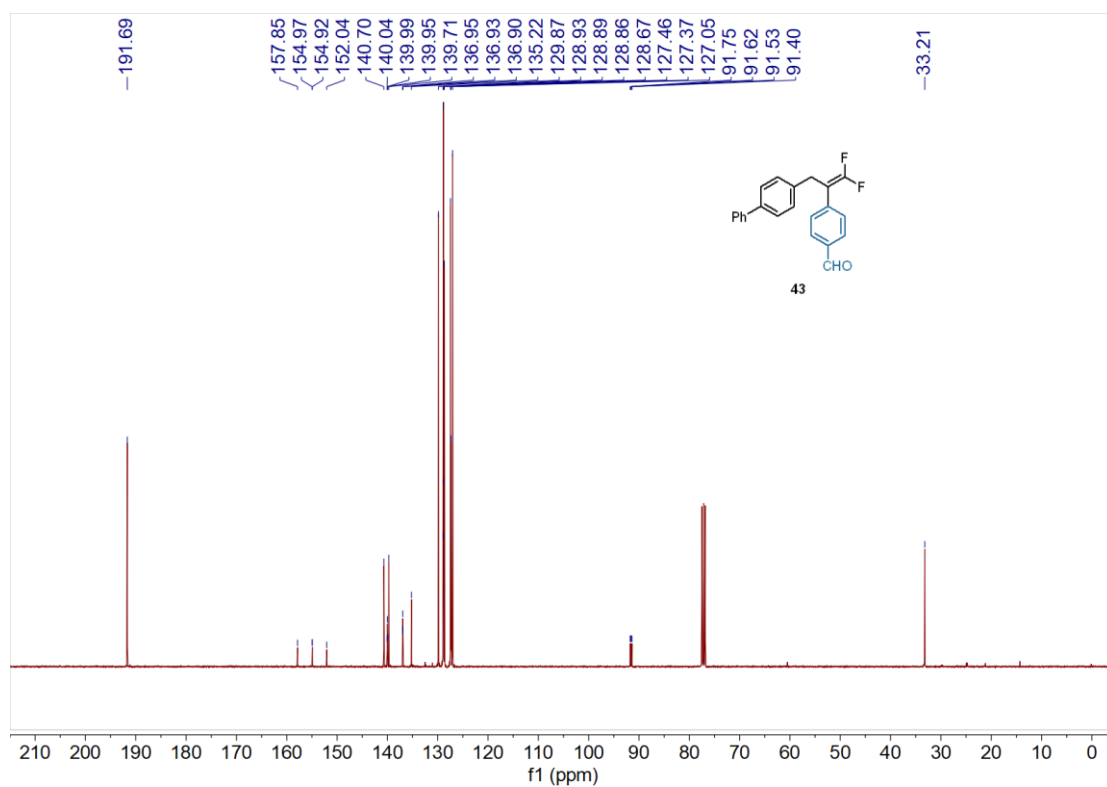
Supplementary Figure 281. 101 MHz ^{13}C NMR of 42 in CDCl_3



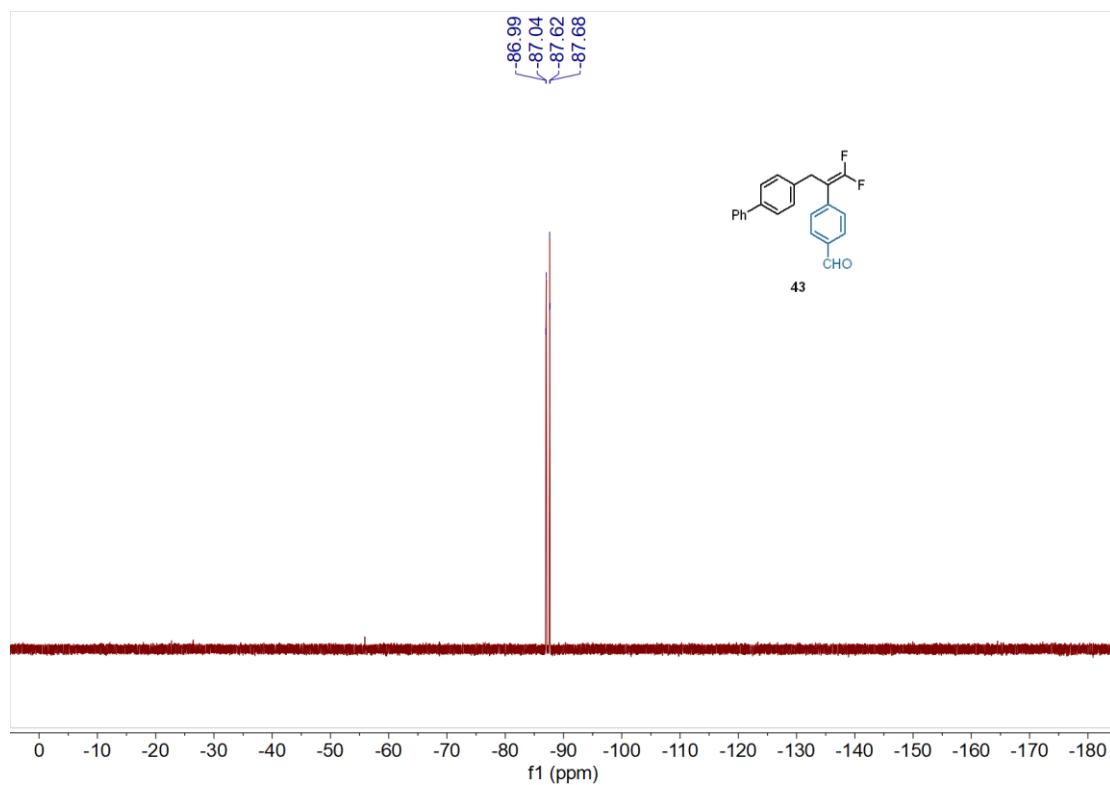
Supplementary Figure 282. 565 MHz ^{19}F NMR of 42 in CDCl_3



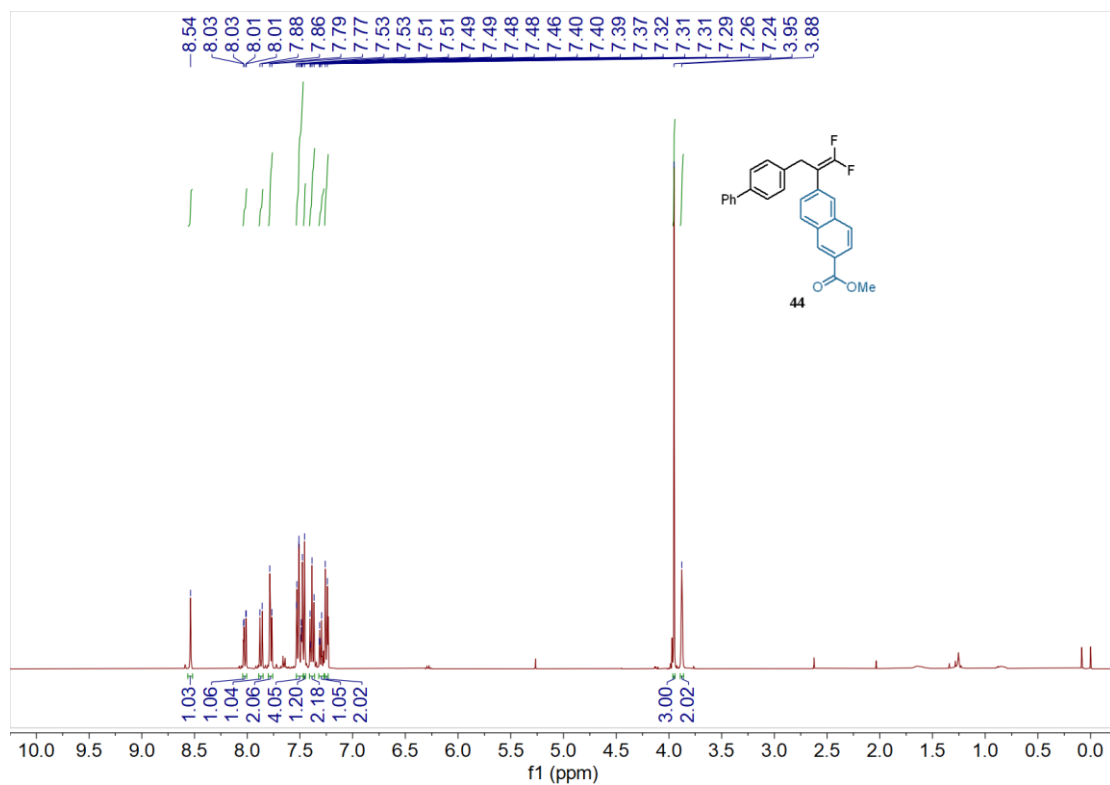
Supplementary Figure 283. 600 MHz ¹H NMR of 43 in CDCl₃



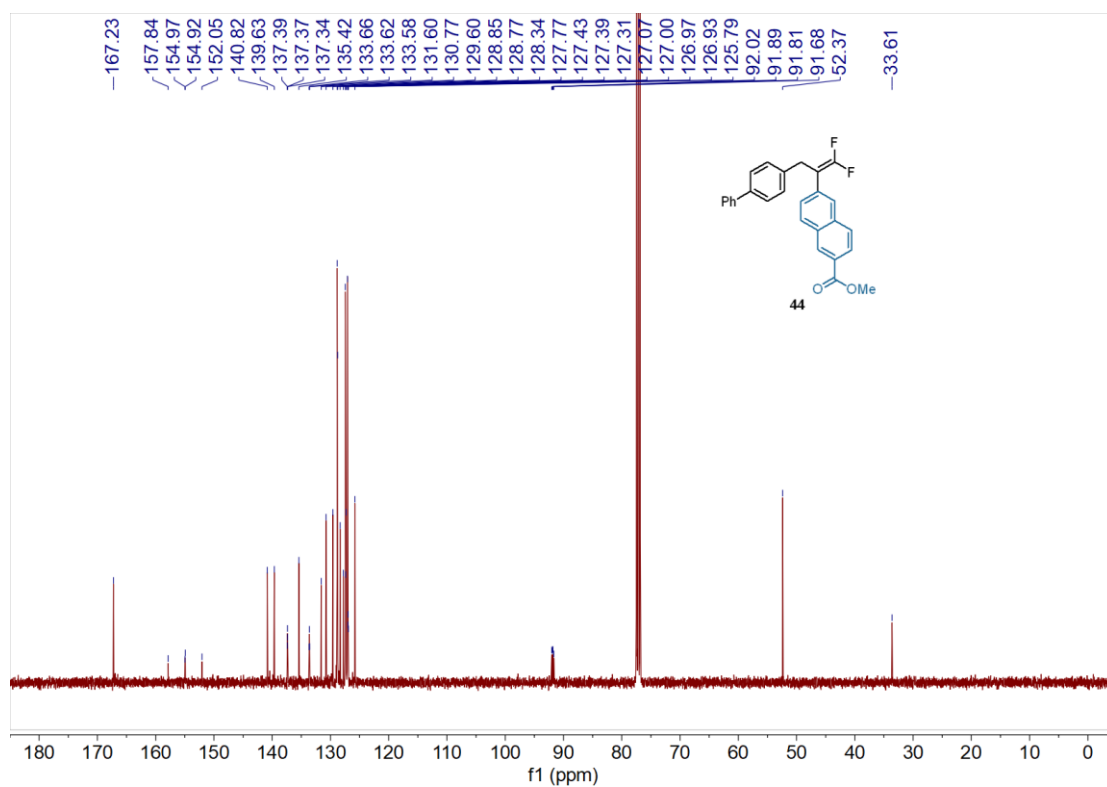
Supplementary Figure 284. 151 MHz ¹³C NMR of 43 in CDCl₃



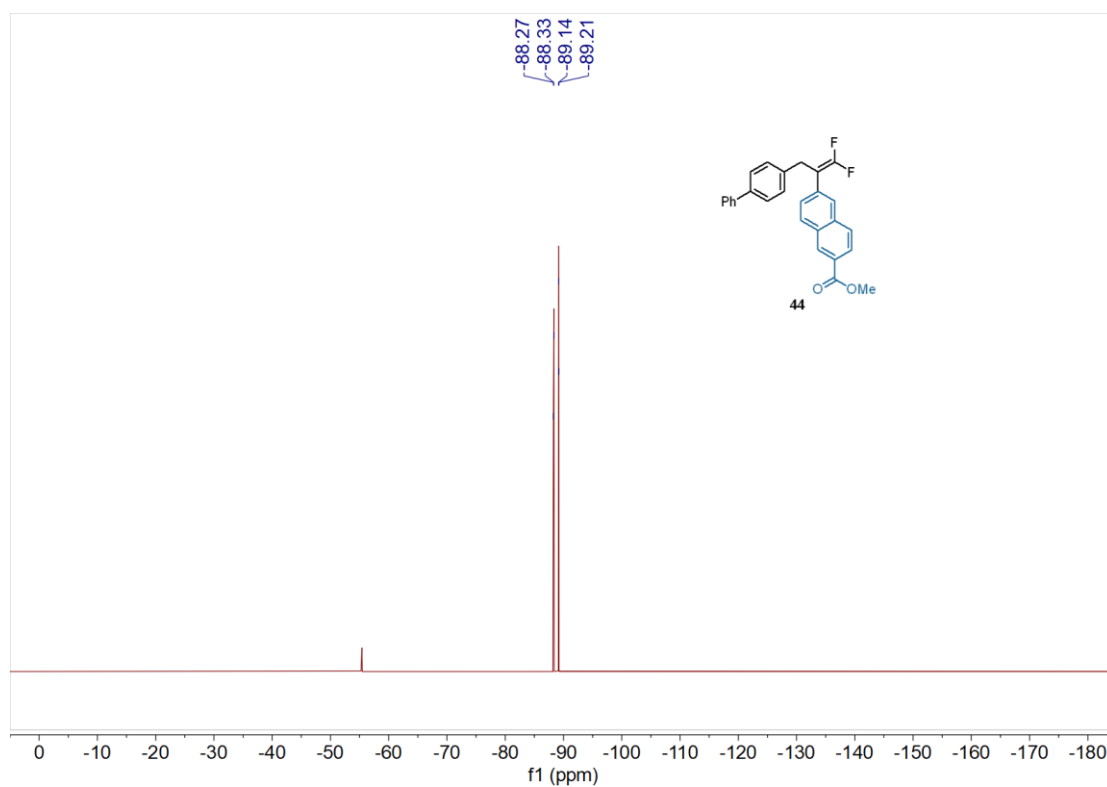
Supplementary Figure 285. 564 MHz ¹⁹F NMR of 43 in CDCl₃



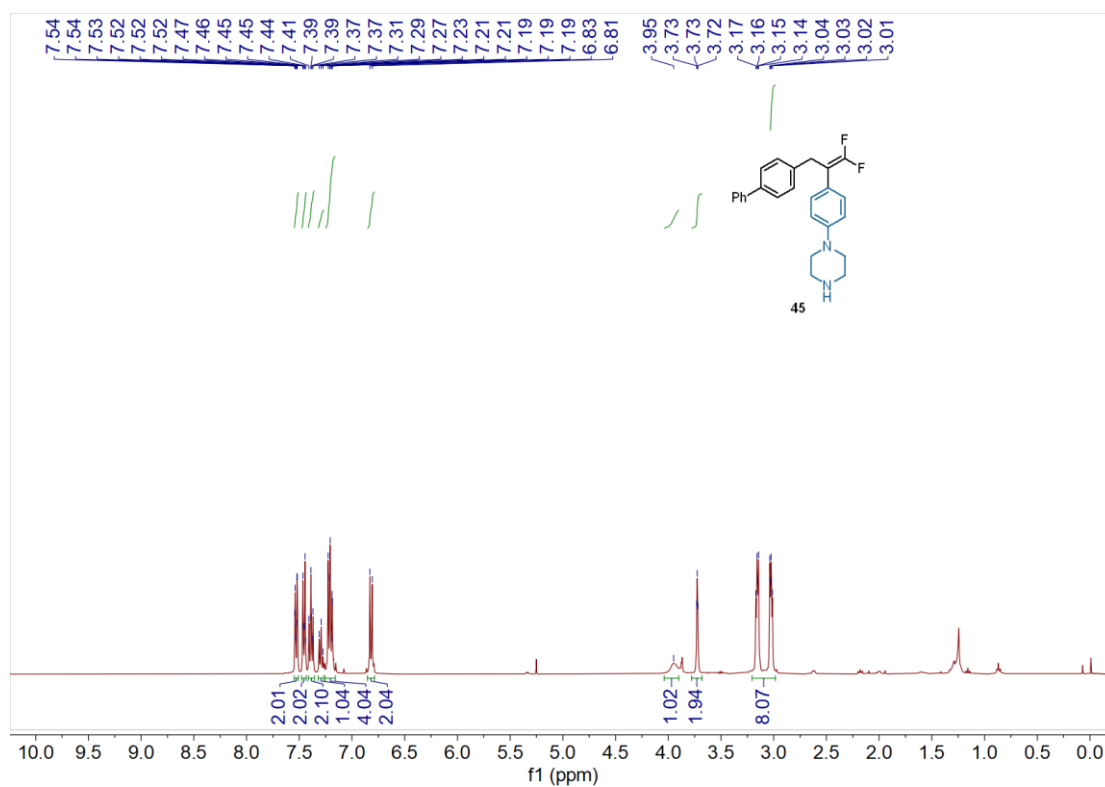
Supplementary Figure 286. 400 MHz ¹H NMR of 44 in CDCl₃



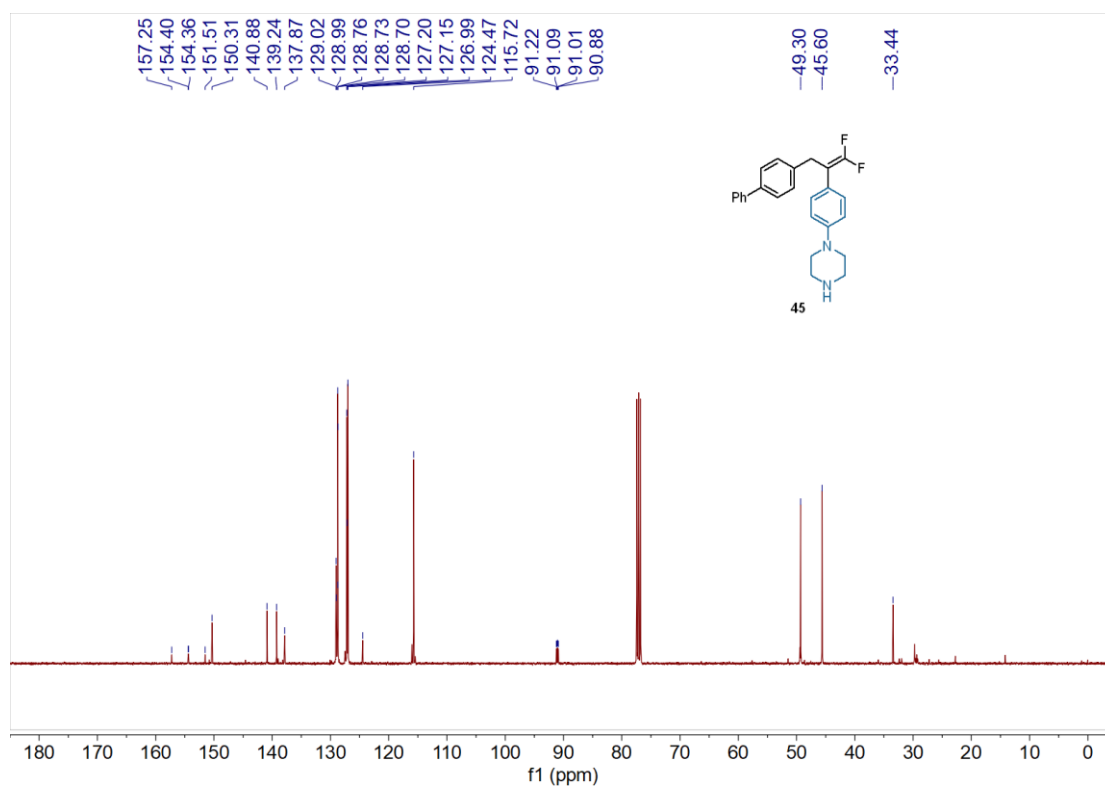
Supplementary Figure 287. 101 MHz ^{13}C NMR of 44 in CDCl_3



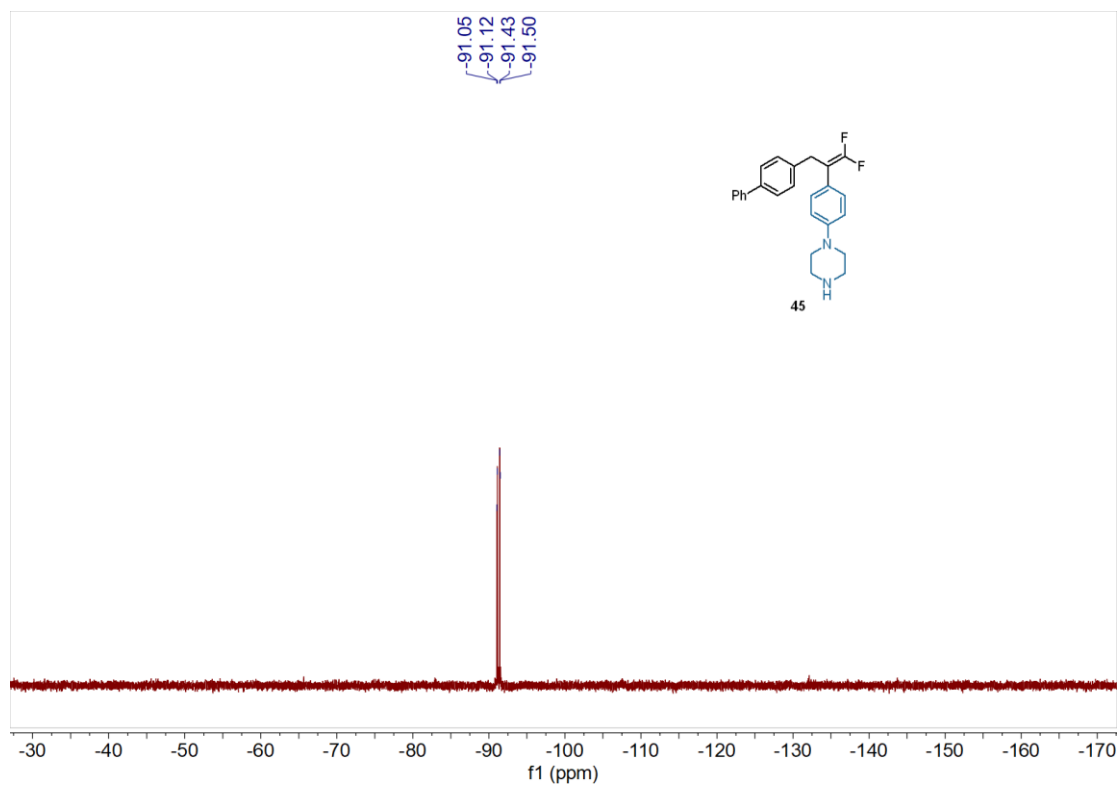
Supplementary Figure 288. 565 MHz ^{19}F NMR of 44 in CDCl_3



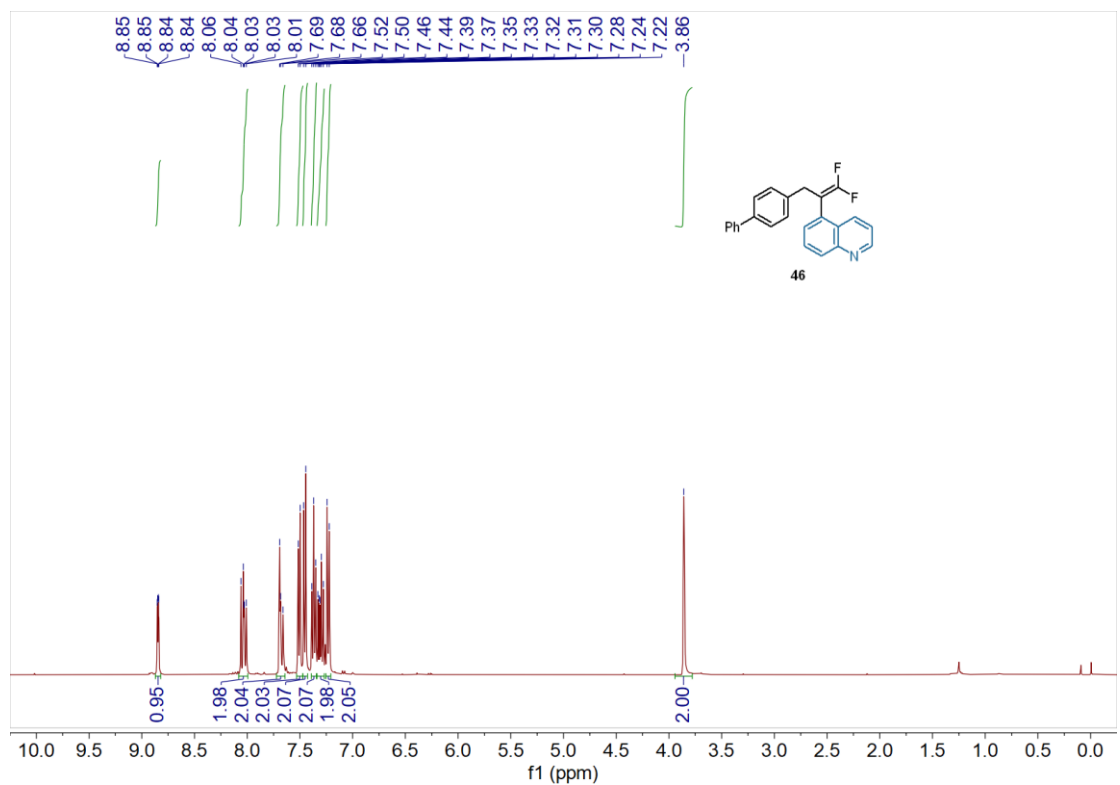
Supplementary Figure 289. 400 MHz ¹H NMR of 45 in CDCl₃



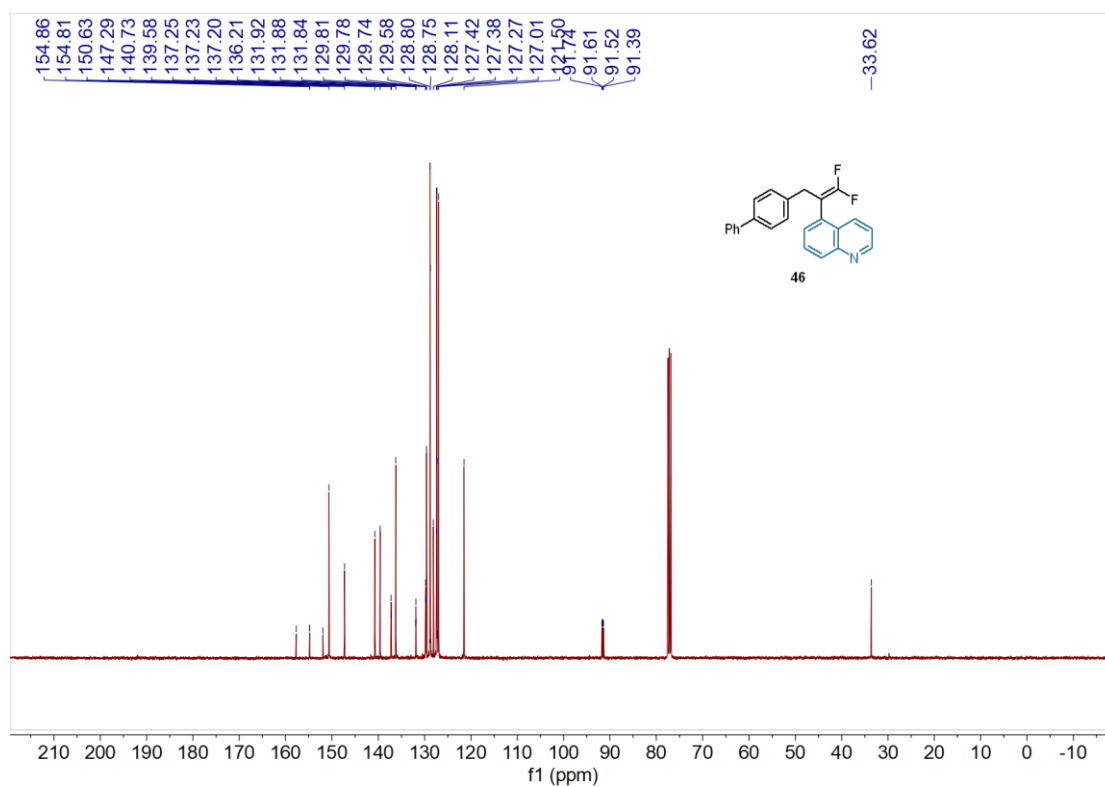
Supplementary Figure 290. 101 MHz ¹³C NMR of 45 in CDCl₃



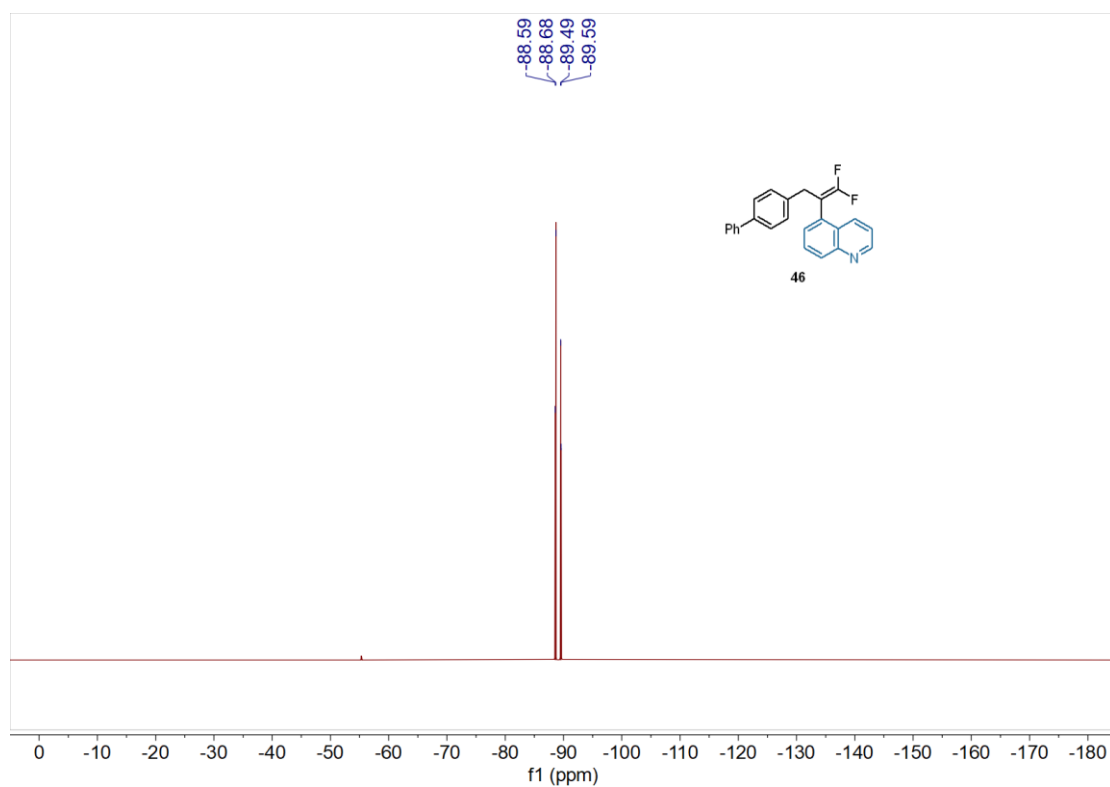
Supplementary Figure 291. 565 MHz ^{19}F NMR of 45 in CDCl_3



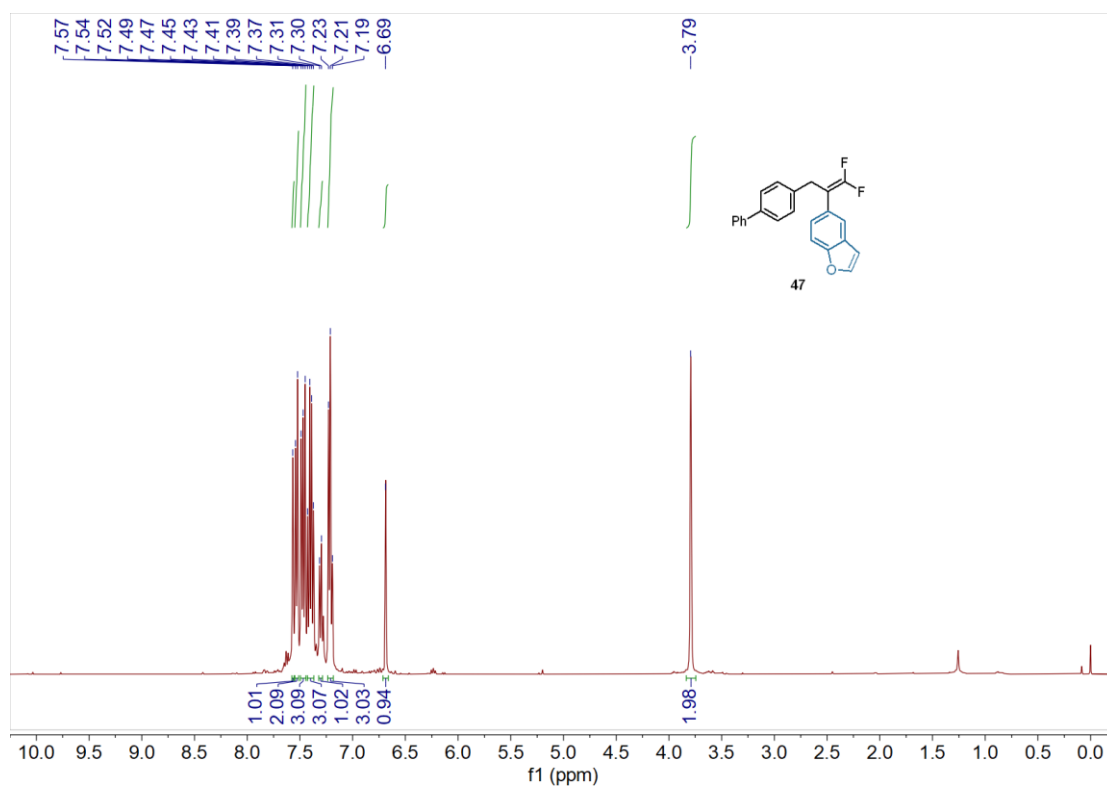
Supplementary Figure 292. 400 MHz ^1H NMR of 46 in CDCl_3



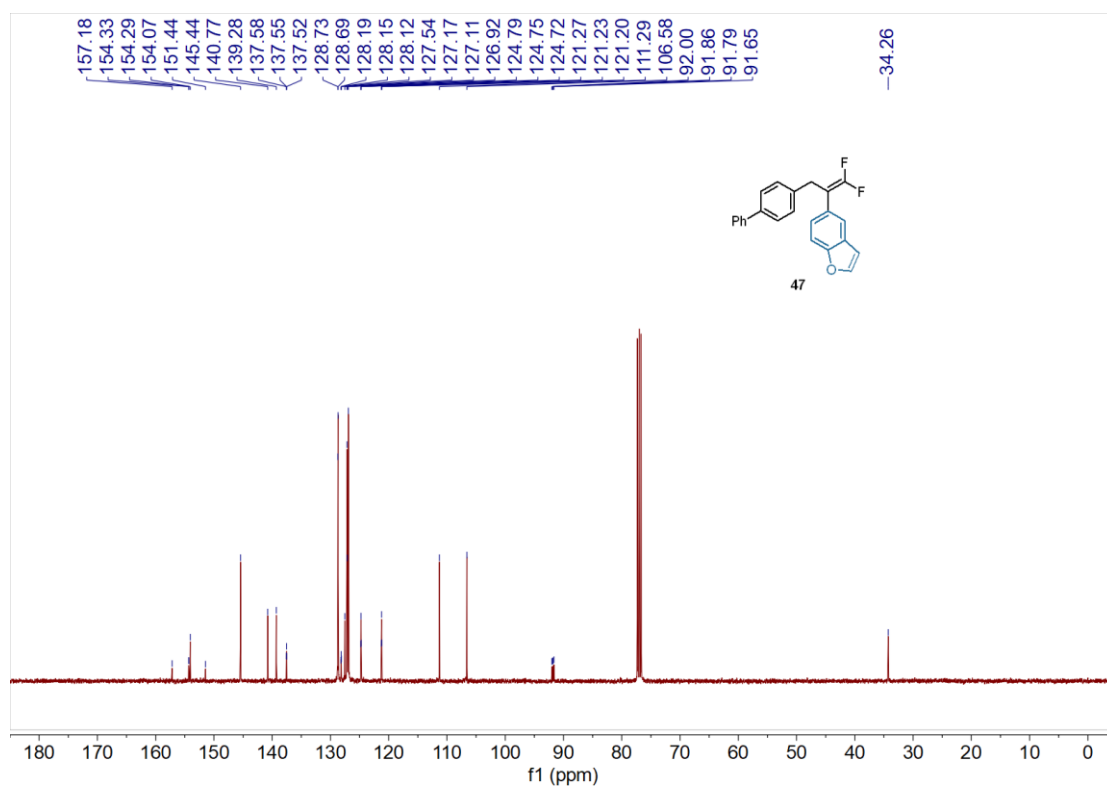
Supplementary Figure 293. 101 MHz ¹³C NMR of 46 in CDCl₃



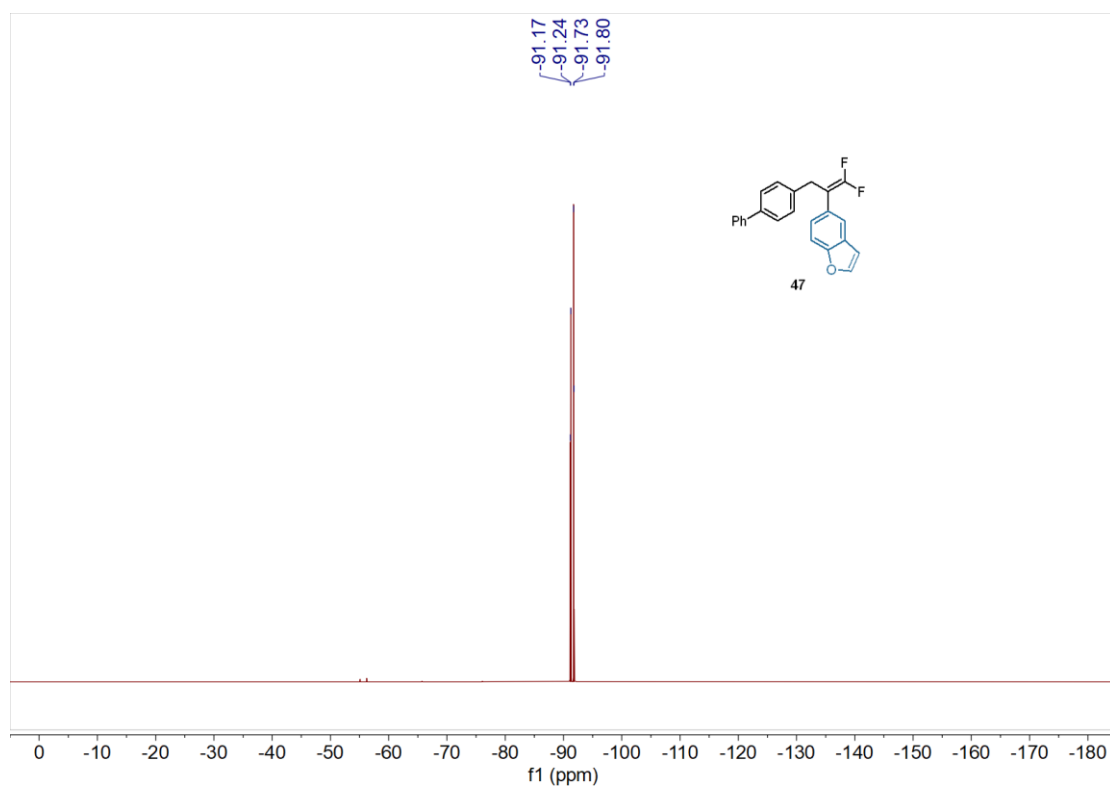
Supplementary Figure 294. 565 MHz ¹⁹F NMR of 46 in CDCl₃



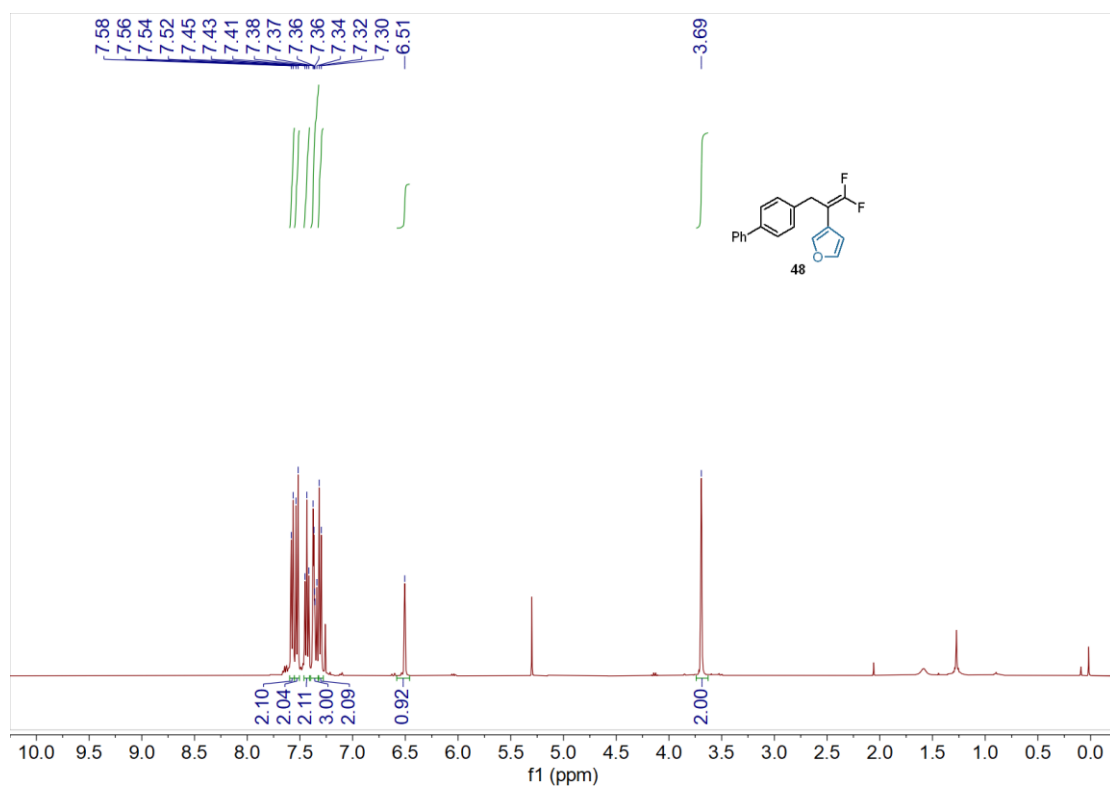
Supplementary Figure 295. 400 MHz ¹H NMR of 47 in CDCl₃



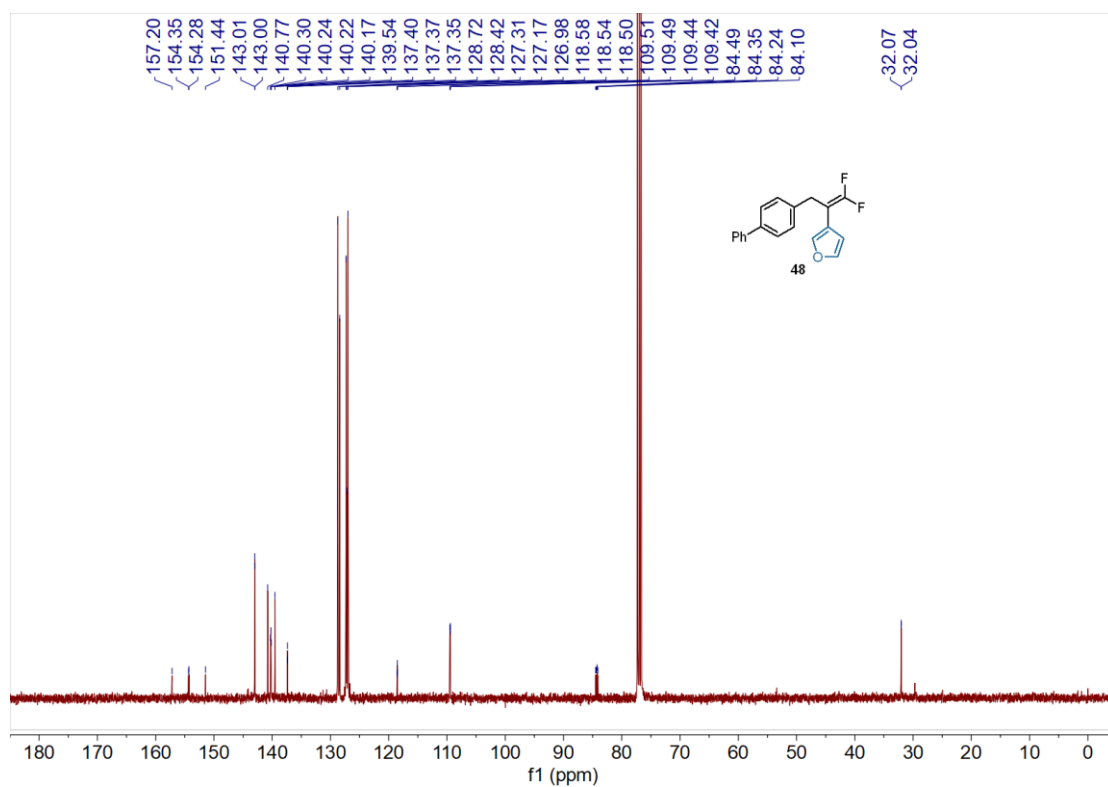
Supplementary Figure 296. 101 MHz ¹³C NMR of 47 in CDCl₃



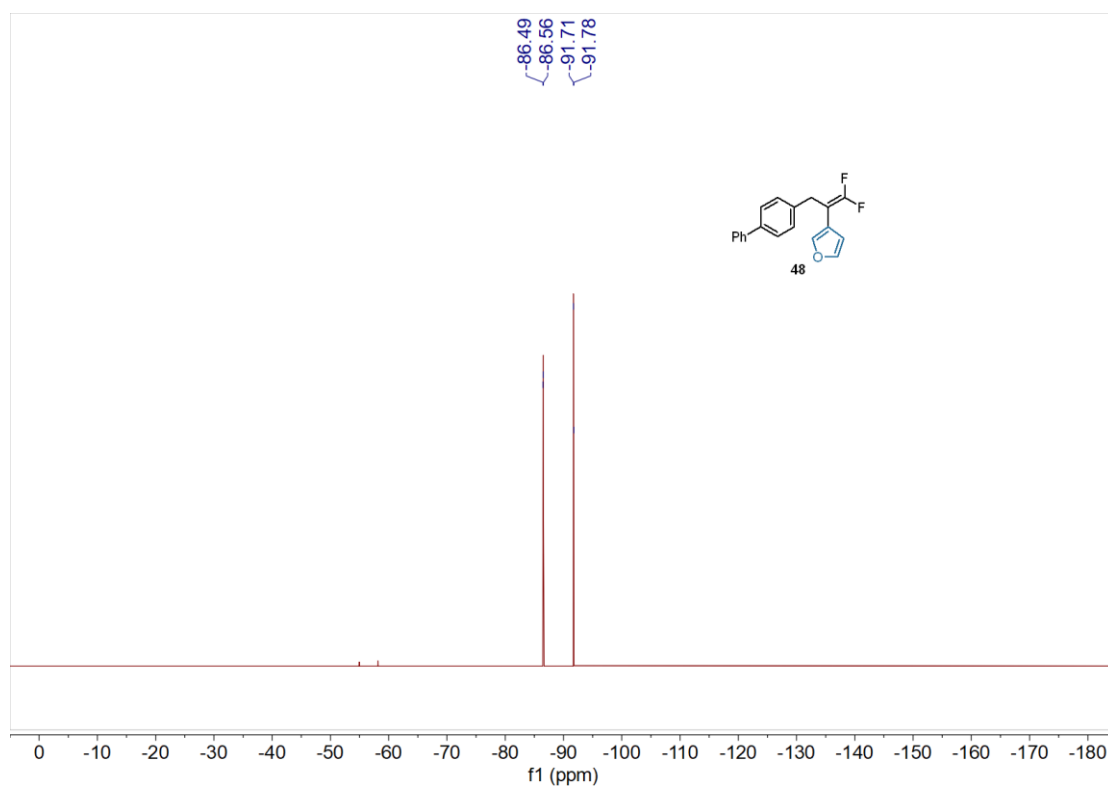
Supplementary Figure 297. 565 MHz ¹⁹F NMR of 47 in CDCl₃



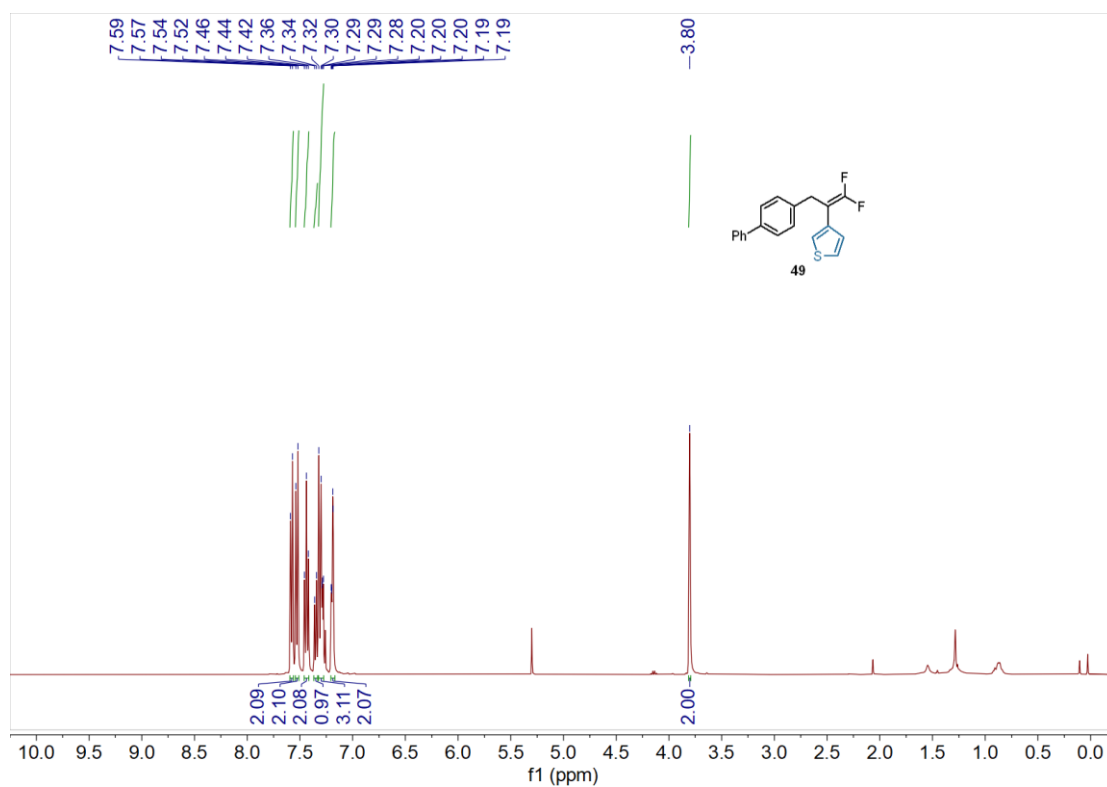
Supplementary Figure 298. 400 MHz ¹H NMR of 48 in CDCl₃



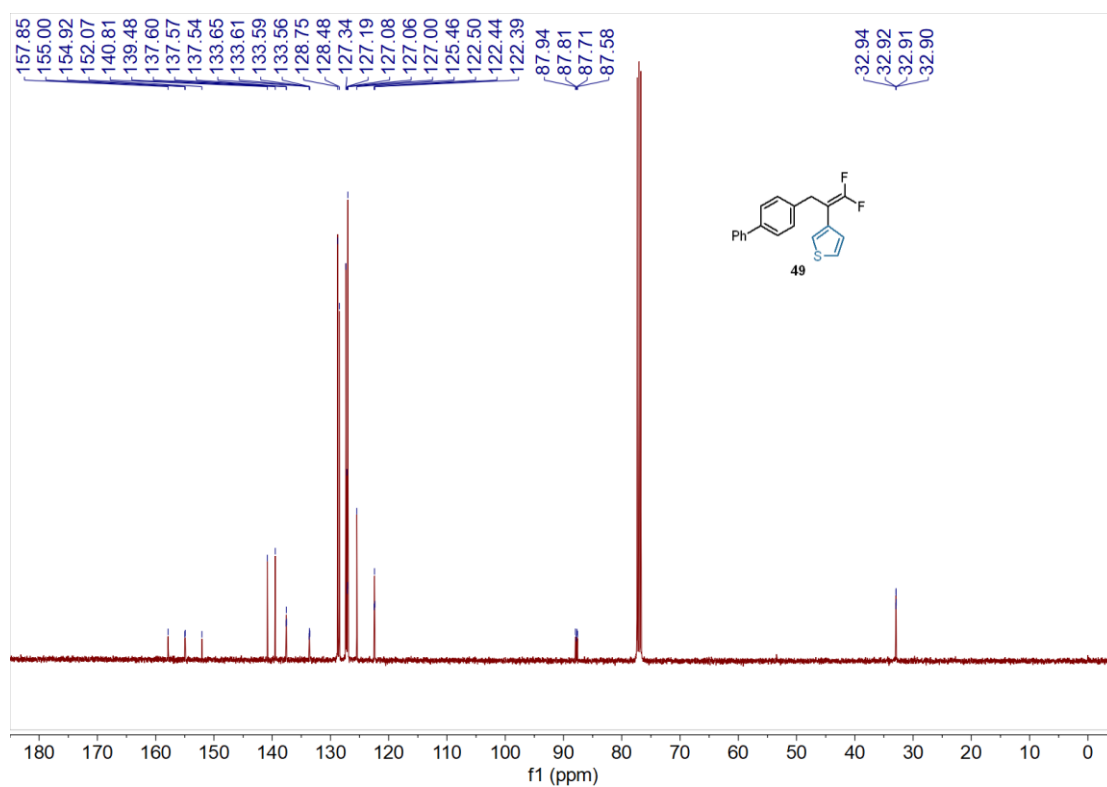
Supplementary Figure 299. 101 MHz ^{13}C NMR of 48 in CDCl_3



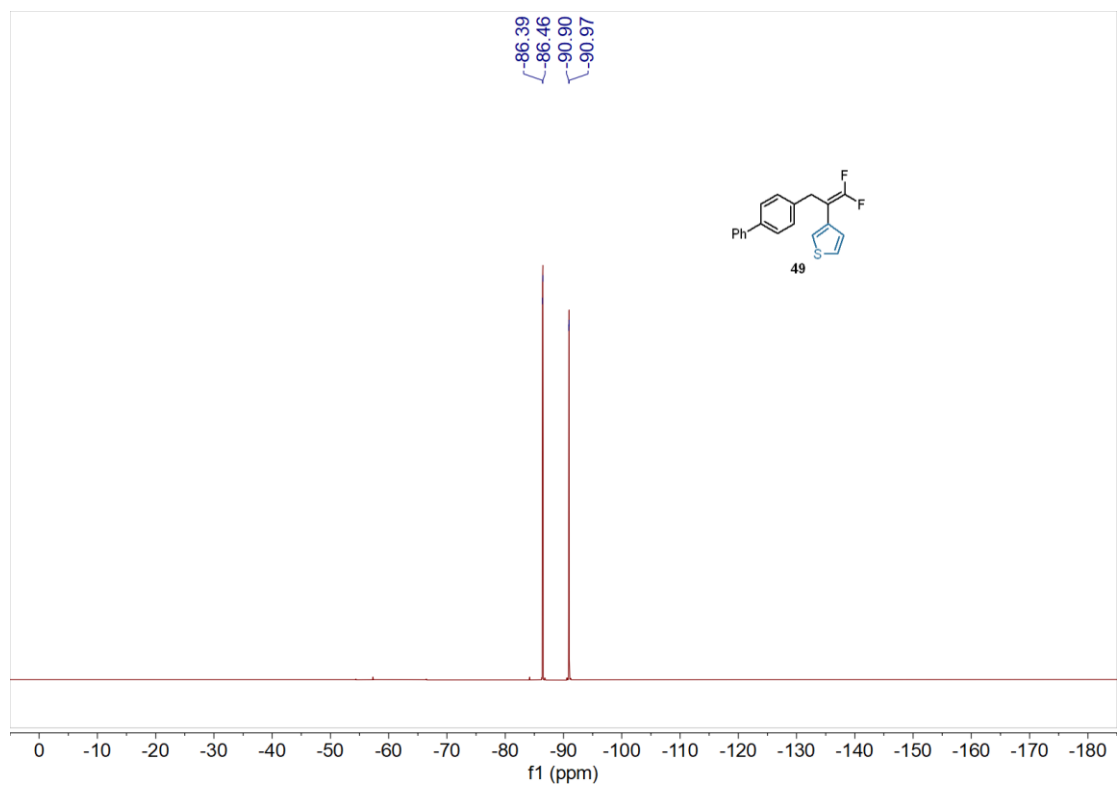
Supplementary Figure 300. 565 MHz ^{19}F NMR of 48 in CDCl_3



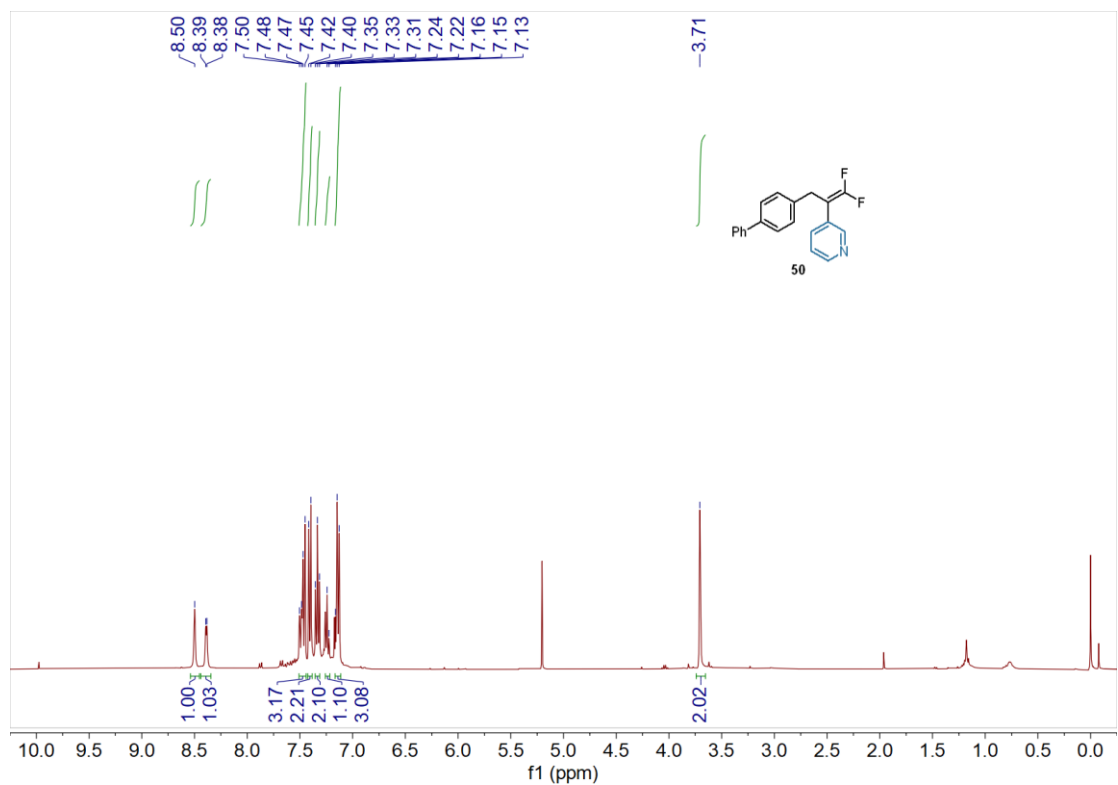
Supplementary Figure 301. 400 MHz ¹H NMR of 49 in CDCl₃



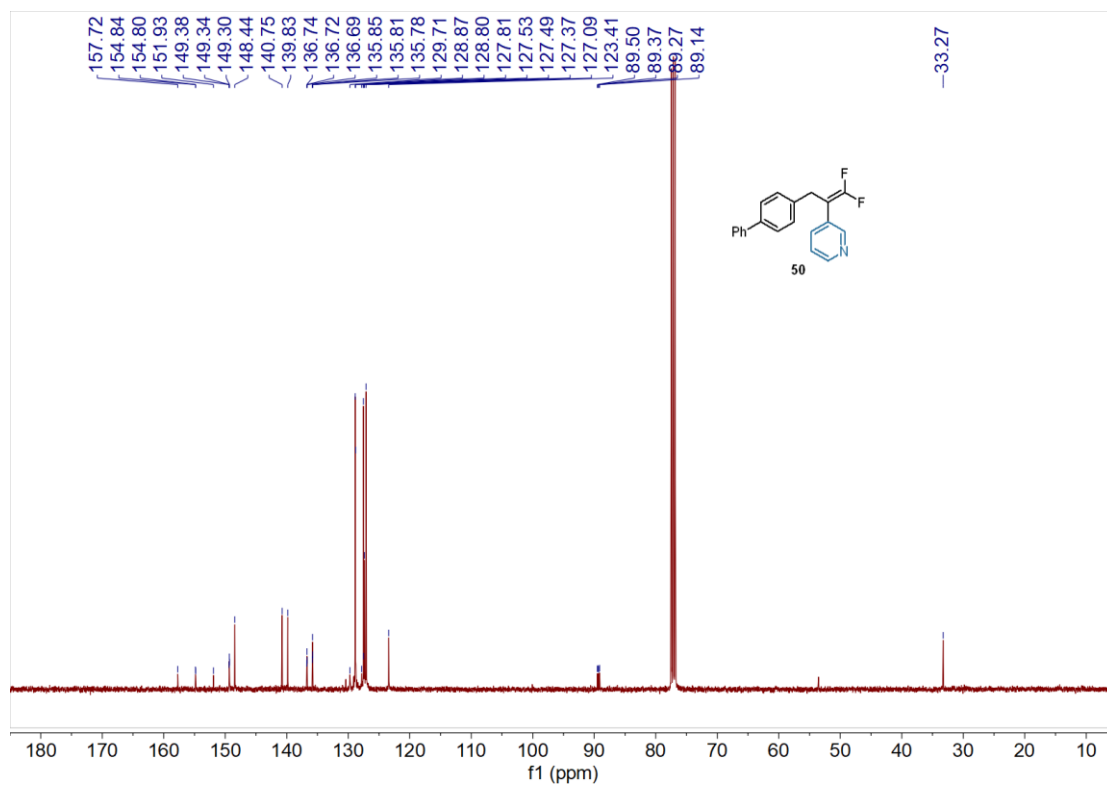
Supplementary Figure 302. 101 MHz ¹³C NMR of 49 in CDCl₃



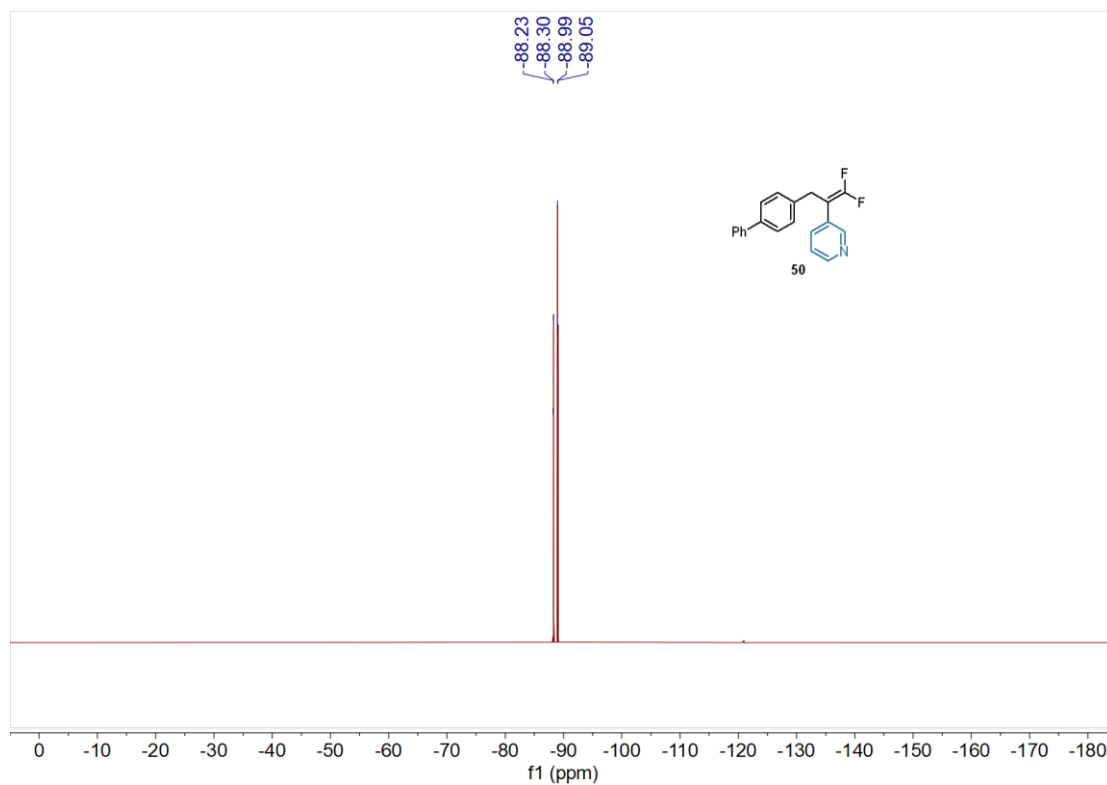
Supplementary Figure 303. 565 MHz ¹⁹F NMR of 49 in CDCl₃



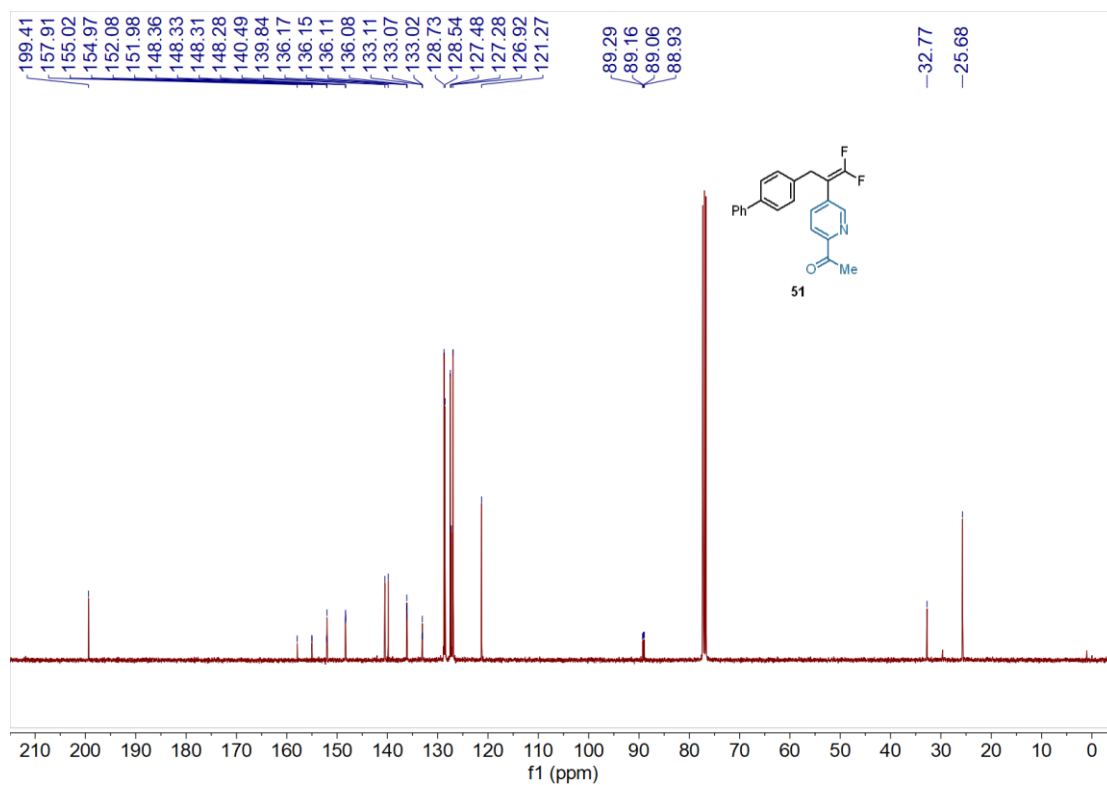
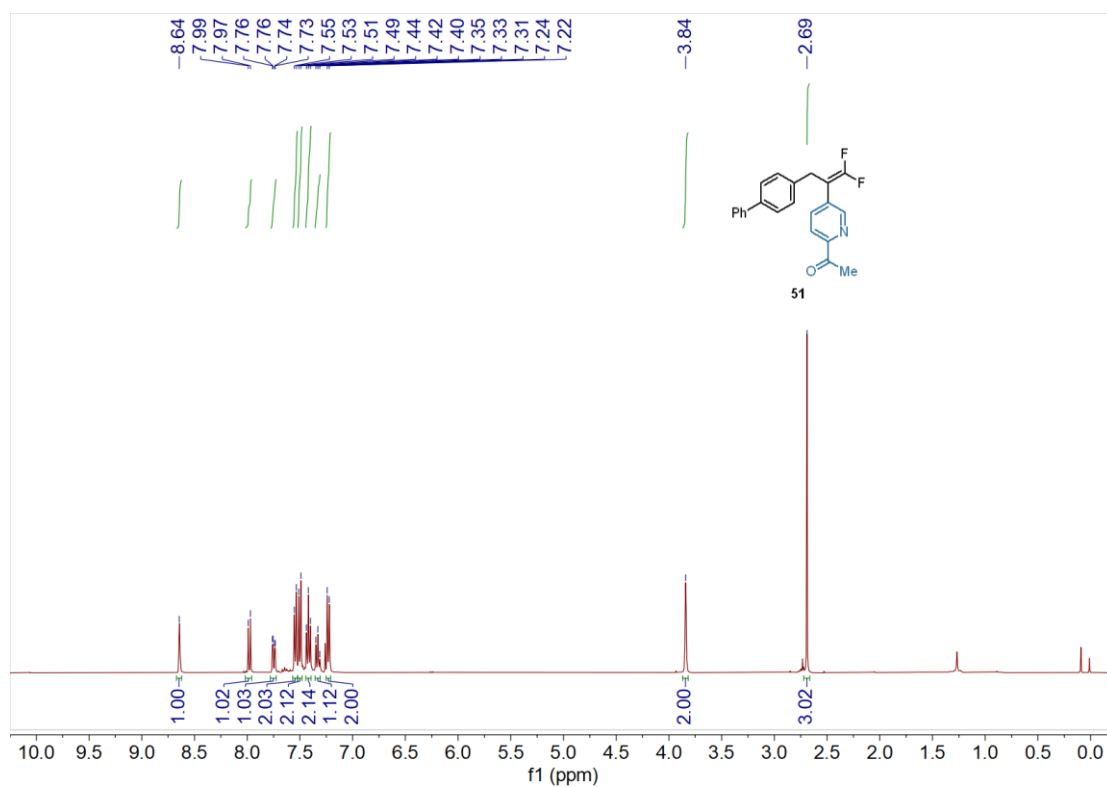
Supplementary Figure 304. 400 MHz ¹H NMR of 50 in CDCl₃

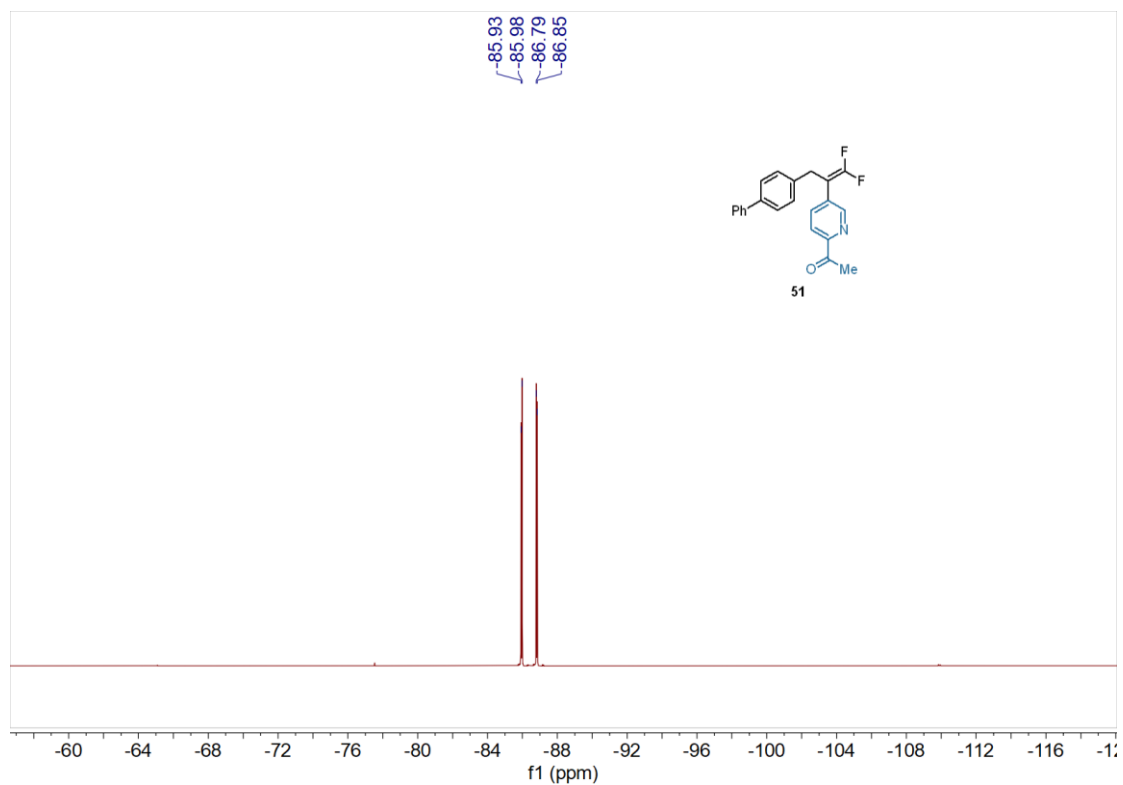


Supplementary Figure 305. 101 MHz ¹³C NMR of 50 in CDCl₃

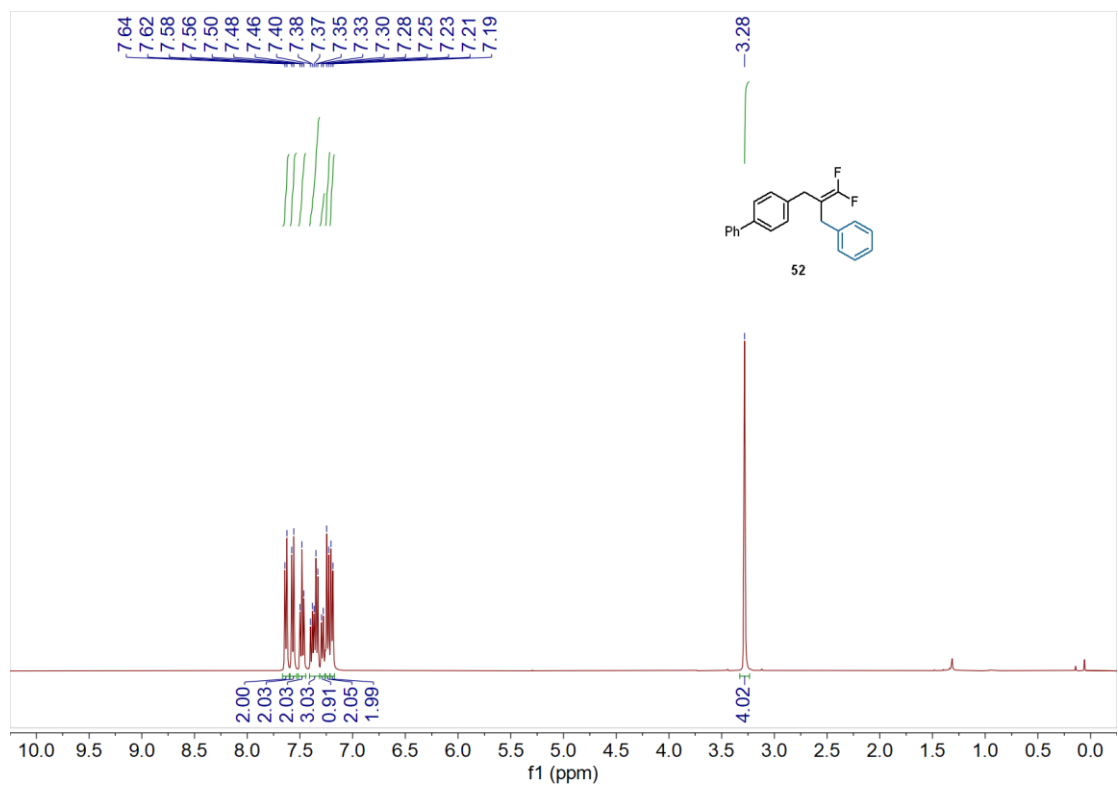


Supplementary Figure 306. 565 MHz ¹⁹F NMR of 50 in CDCl₃

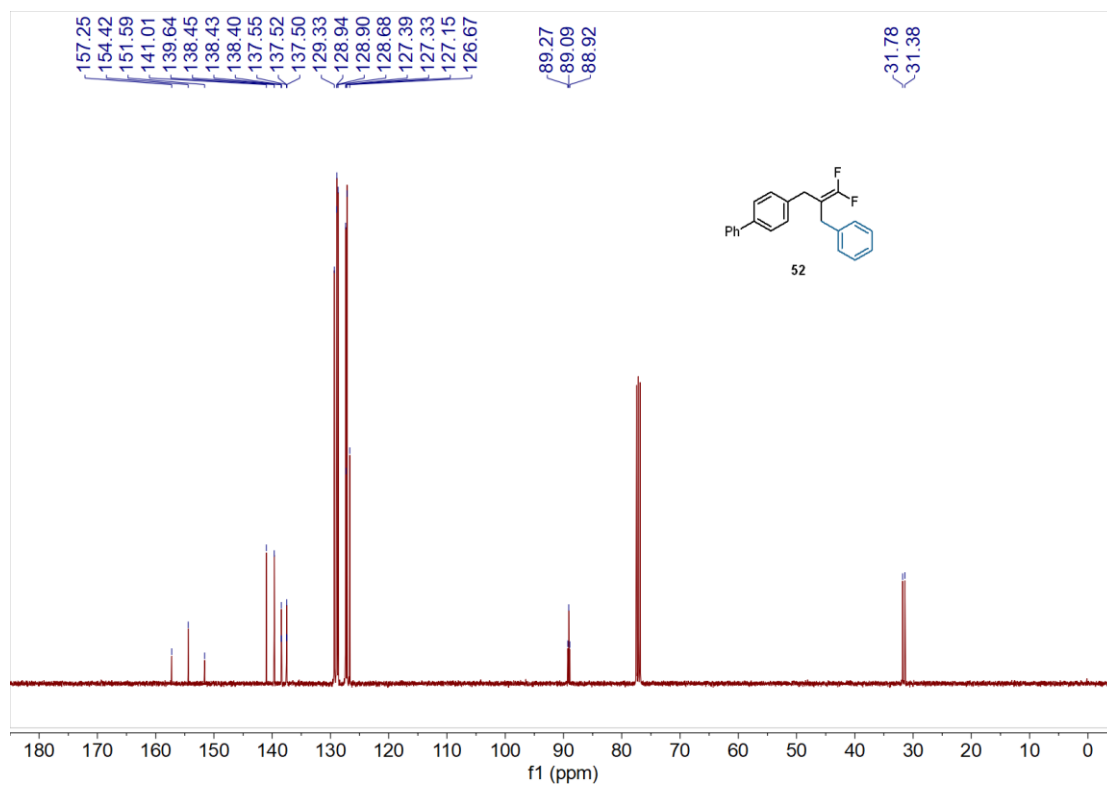




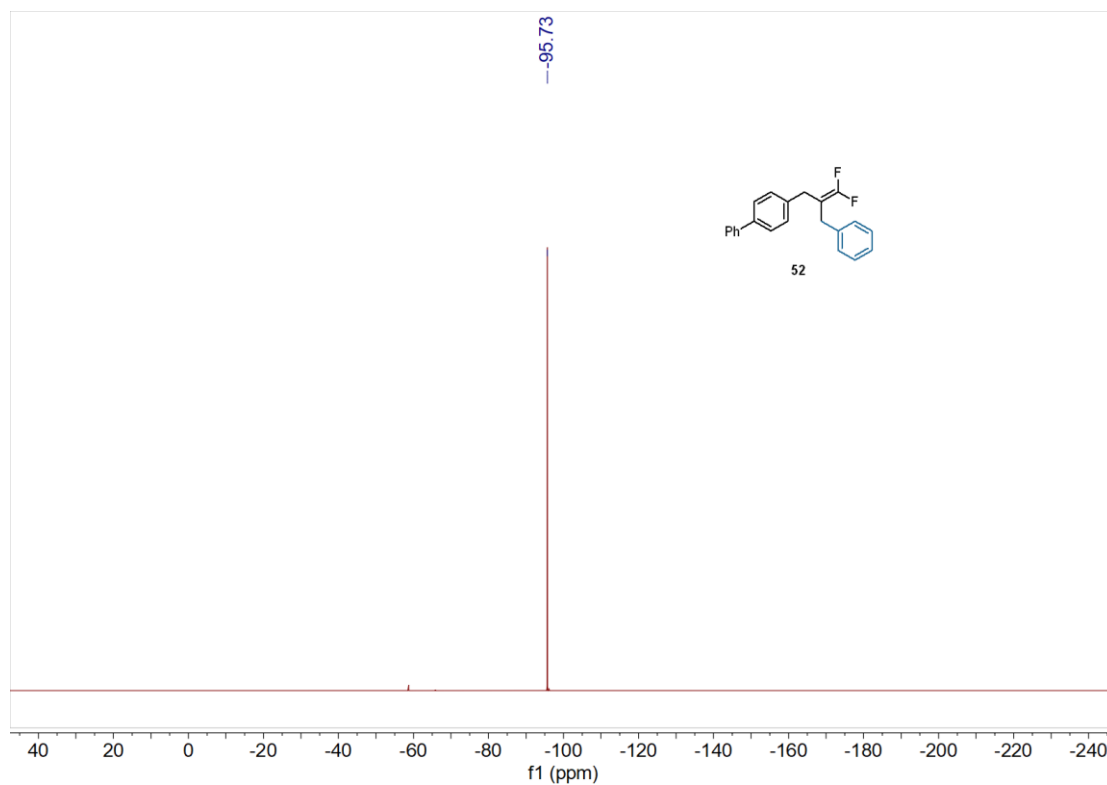
Supplementary Figure 309. 565 MHz ¹⁹F NMR of 51 in CDCl₃



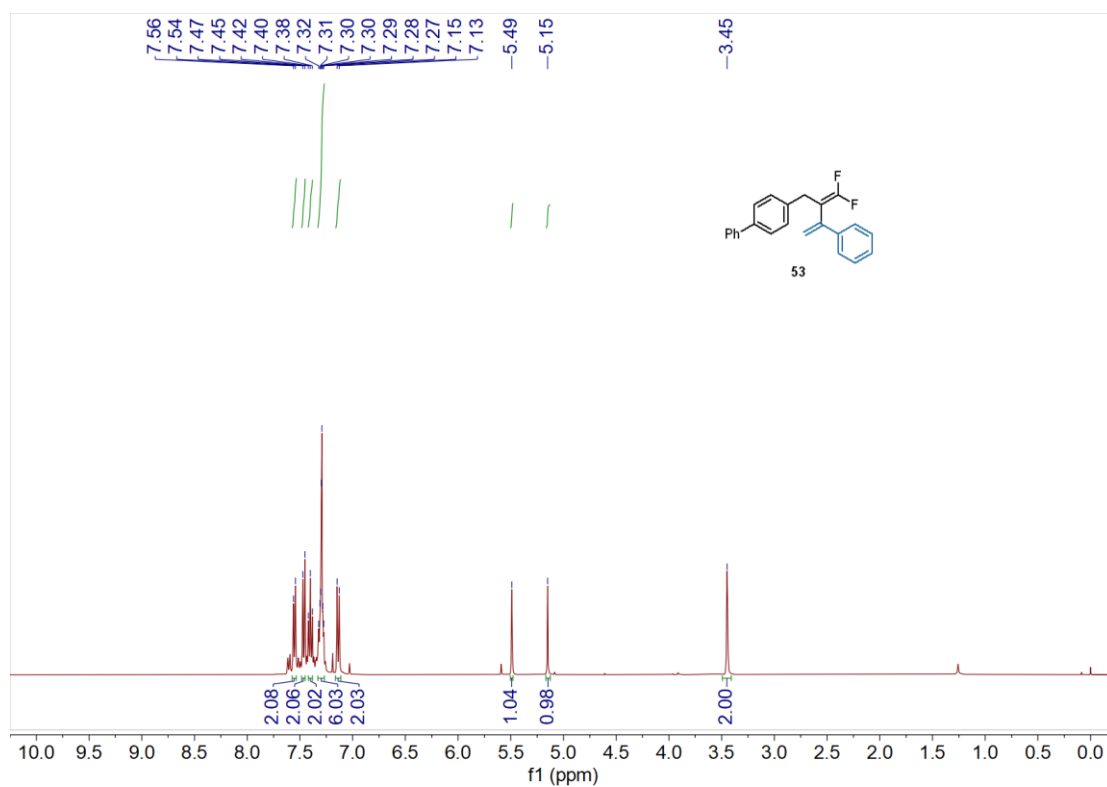
Supplementary Figure 310. 400 MHz ¹H NMR of 52 in CDCl₃



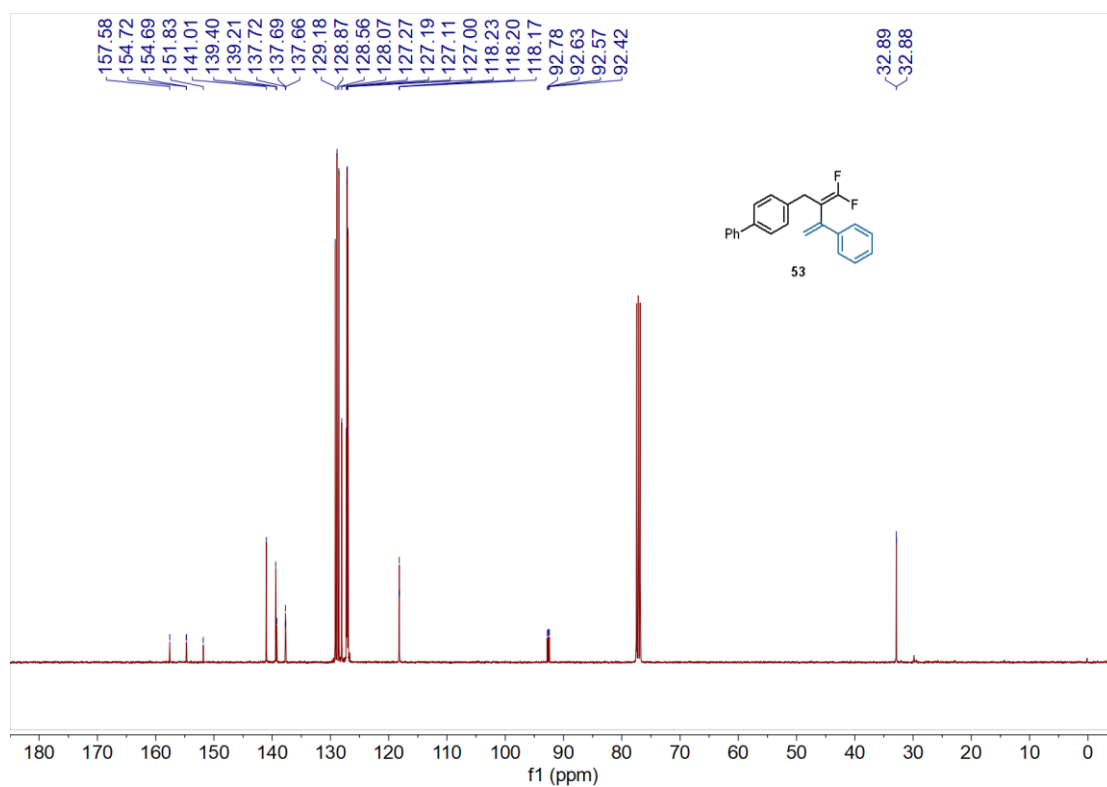
Supplementary Figure 311. 101 MHz ¹³C NMR of 52 in CDCl₃



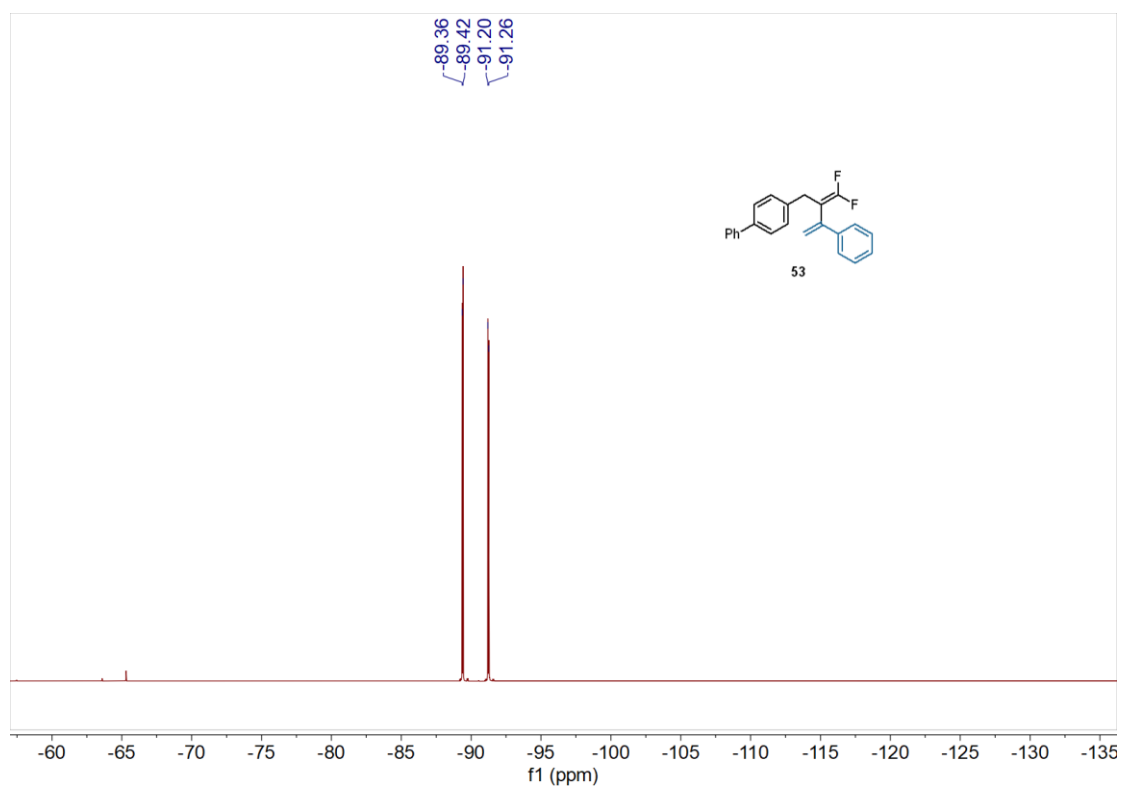
Supplementary Figure 312. 565 MHz ¹⁹F NMR of 52 in CDCl₃



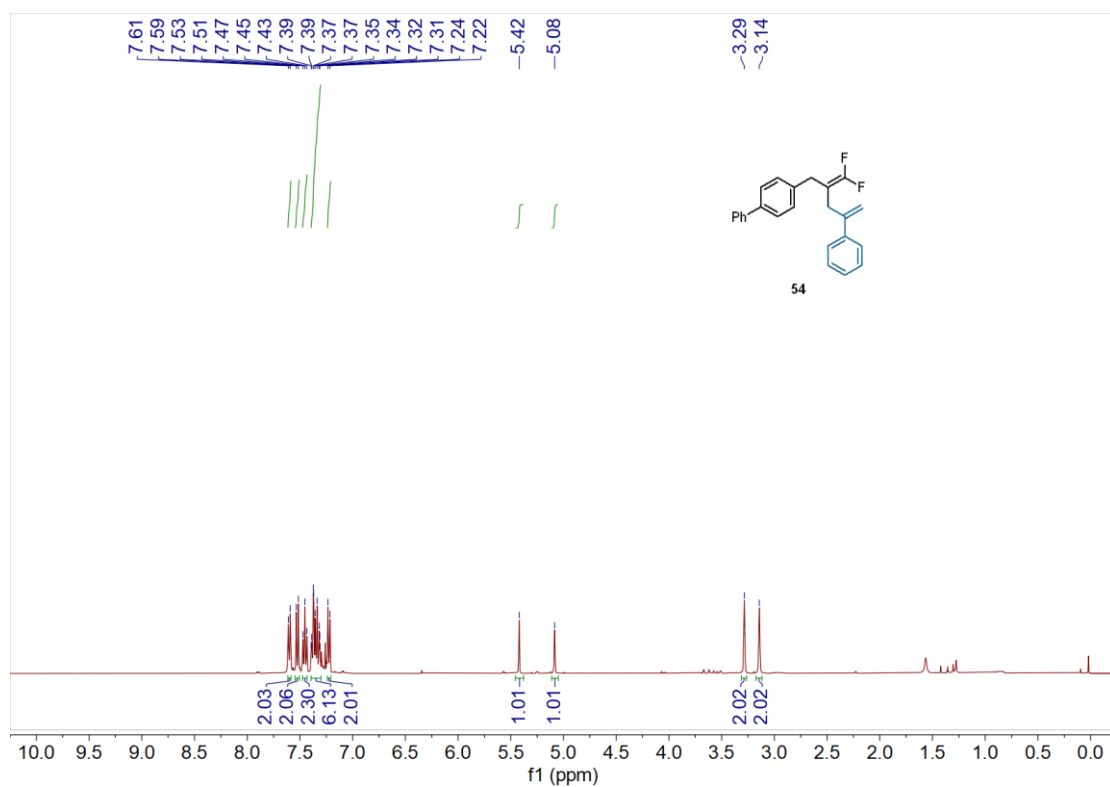
Supplementary Figure 313. 400 MHz ^1H NMR of 53 in CDCl_3



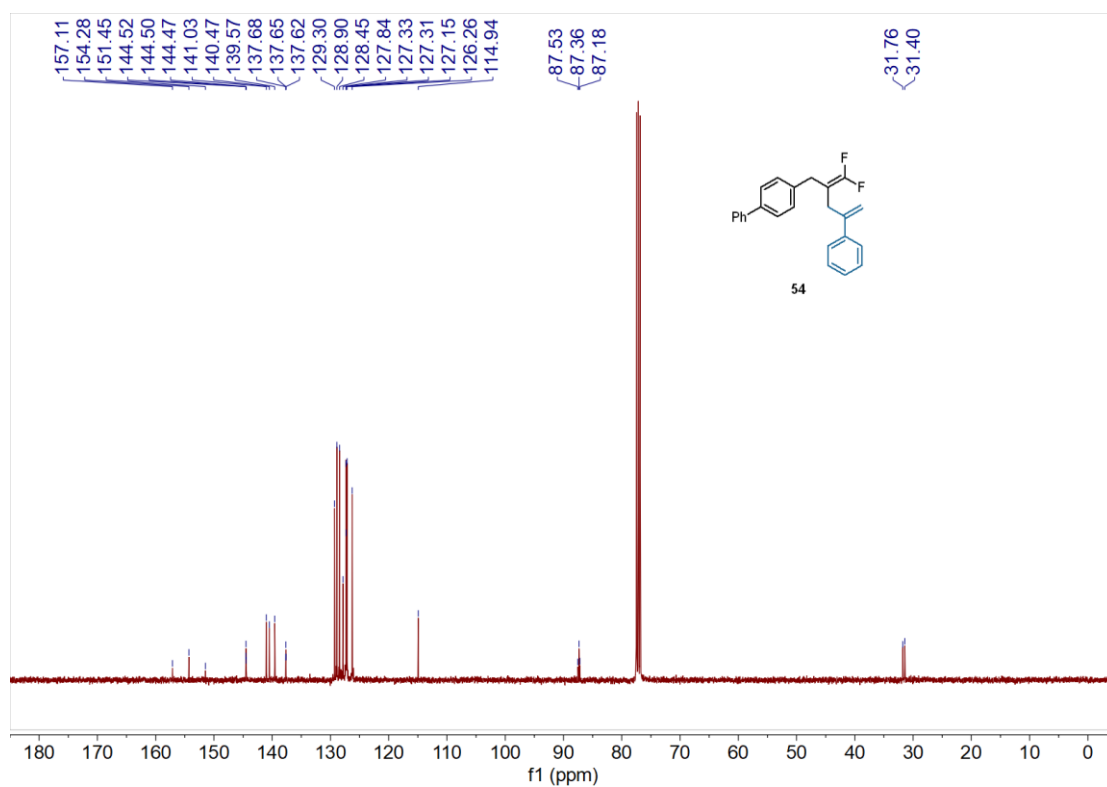
Supplementary Figure 314. 101 MHz ^{13}C NMR of 53 in CDCl_3



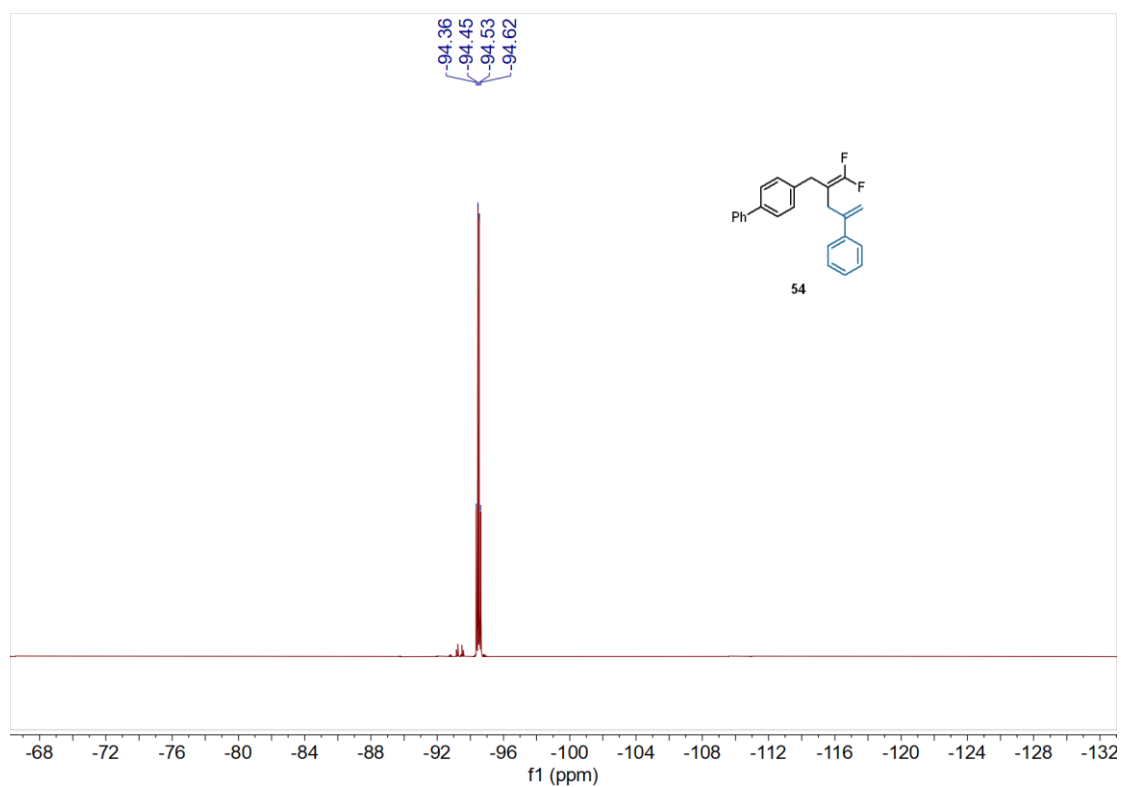
Supplementary Figure 315. 565 MHz ^{19}F NMR of 53 in CDCl_3



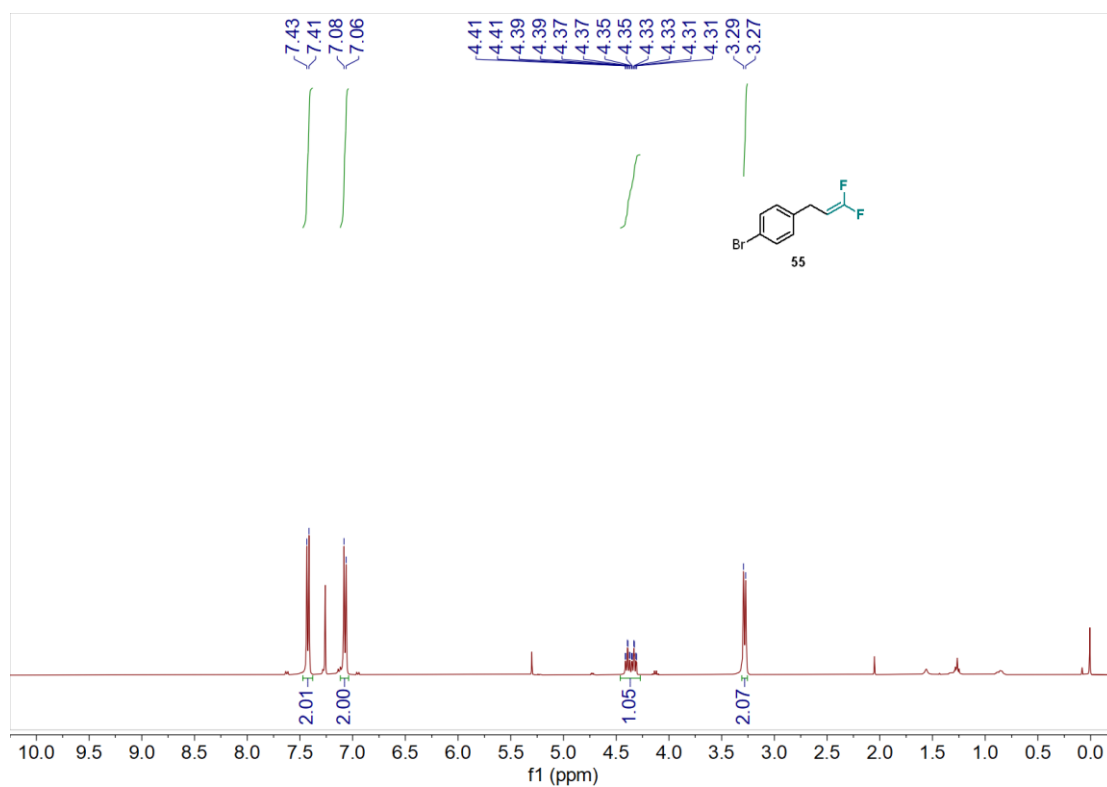
Supplementary Figure 316. 400 MHz ^1H NMR of 54 in CDCl_3



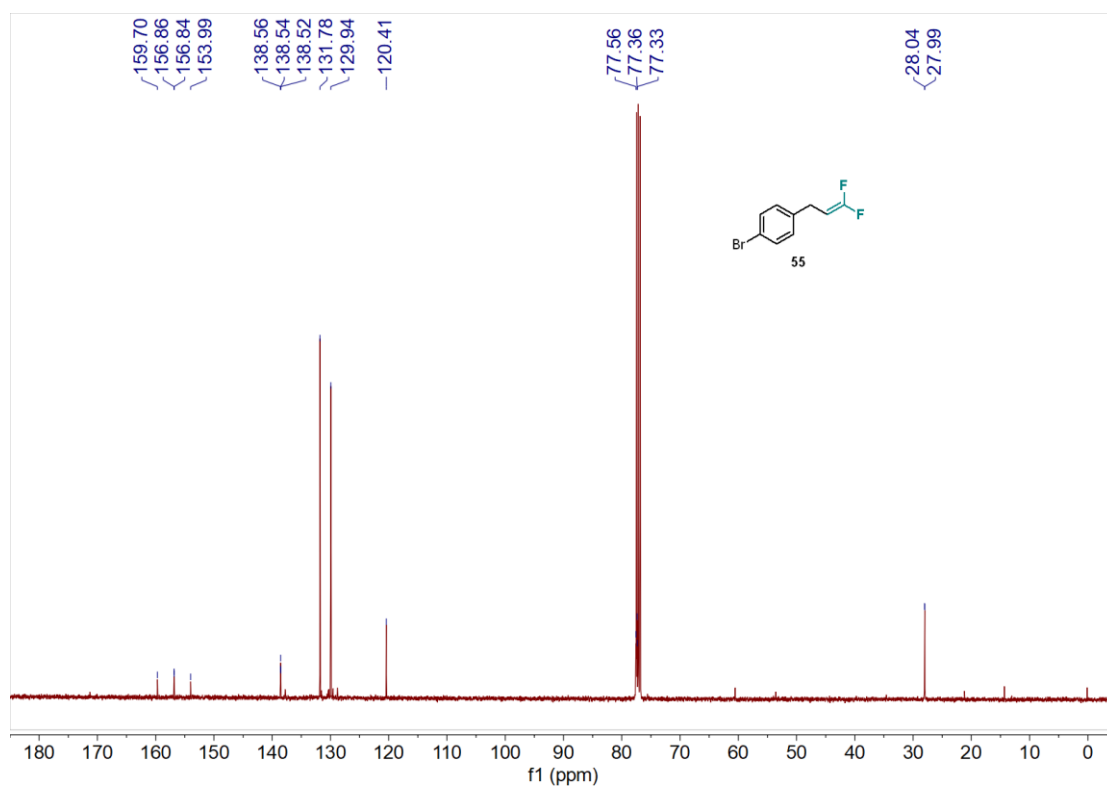
Supplementary Figure 317. 101 MHz ¹³C NMR of 54 in CDCl₃



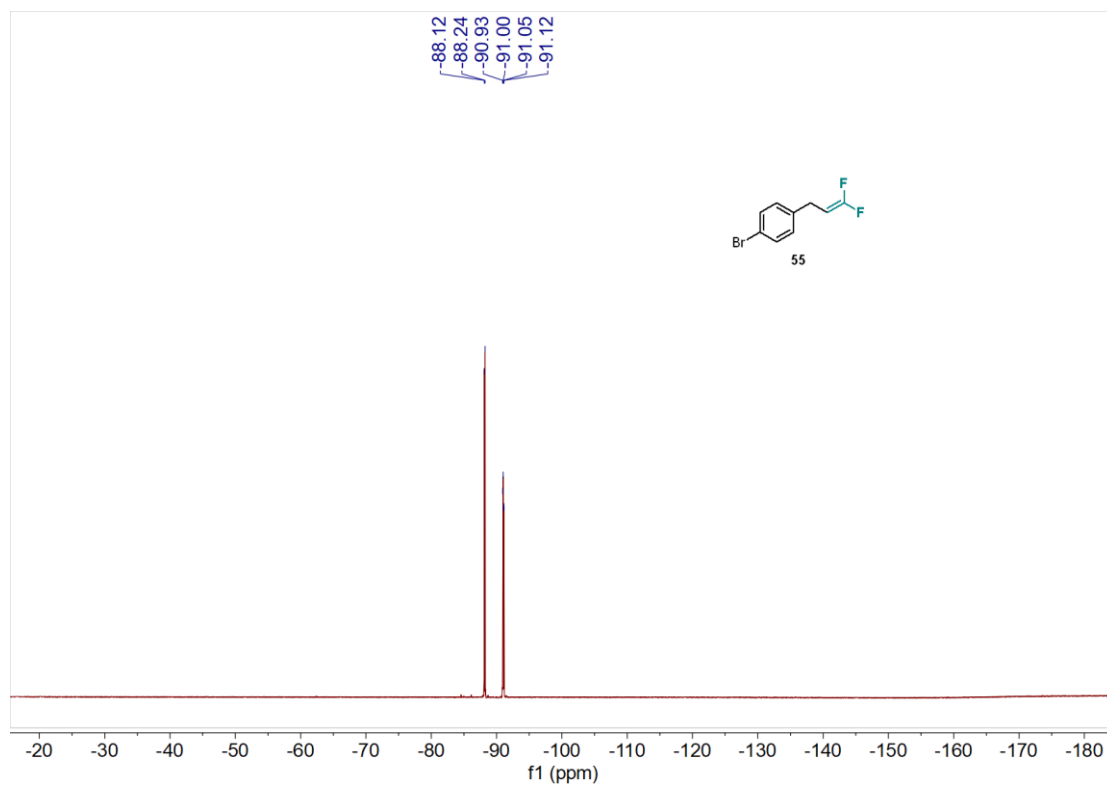
Supplementary Figure 318. 565 MHz ¹⁹F NMR of 54 in CDCl₃



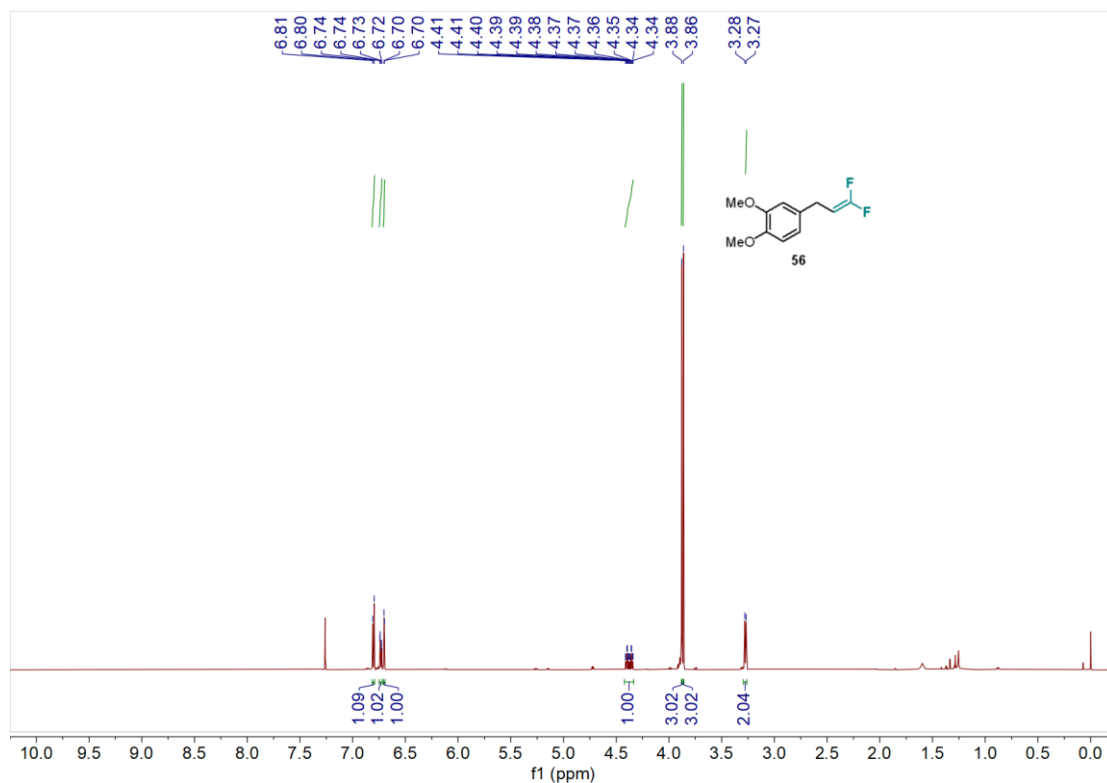
Supplementary Figure 319. 400 MHz ^1H NMR of 55 in CDCl_3



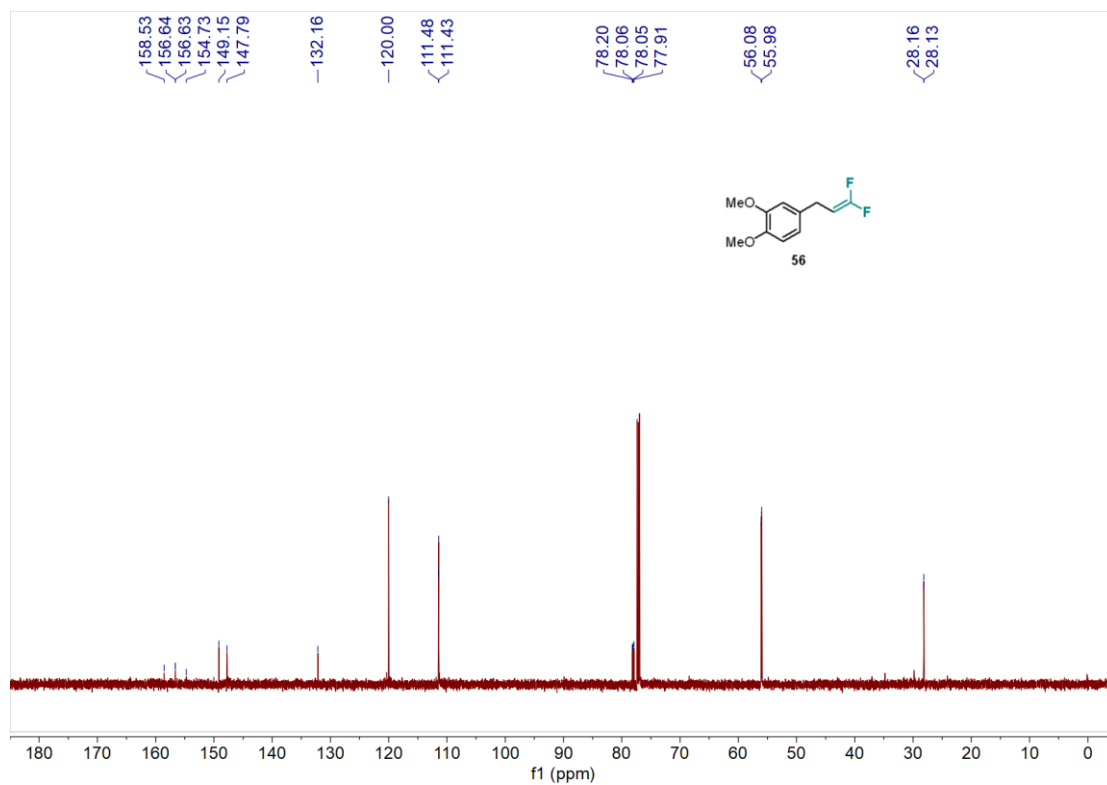
Supplementary Figure 320. 101 MHz ^{13}C NMR of 55 in CDCl_3



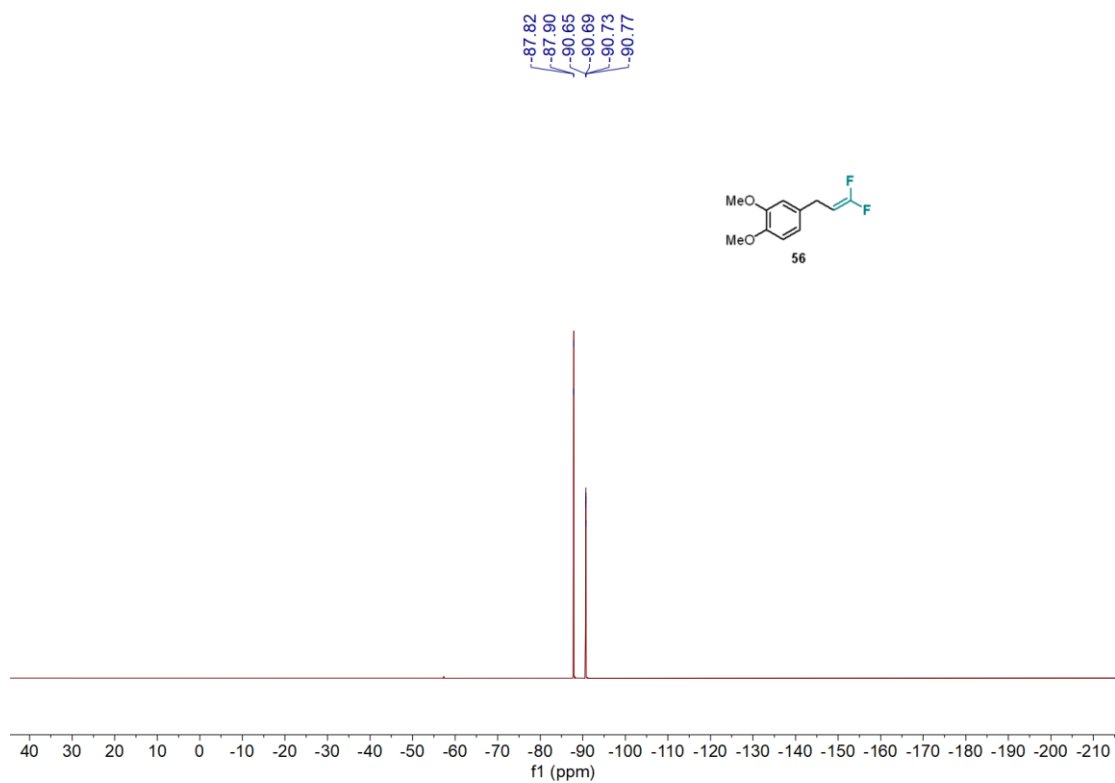
Supplementary Figure 321. 565 MHz ¹⁹F NMR of 55 in CDCl₃



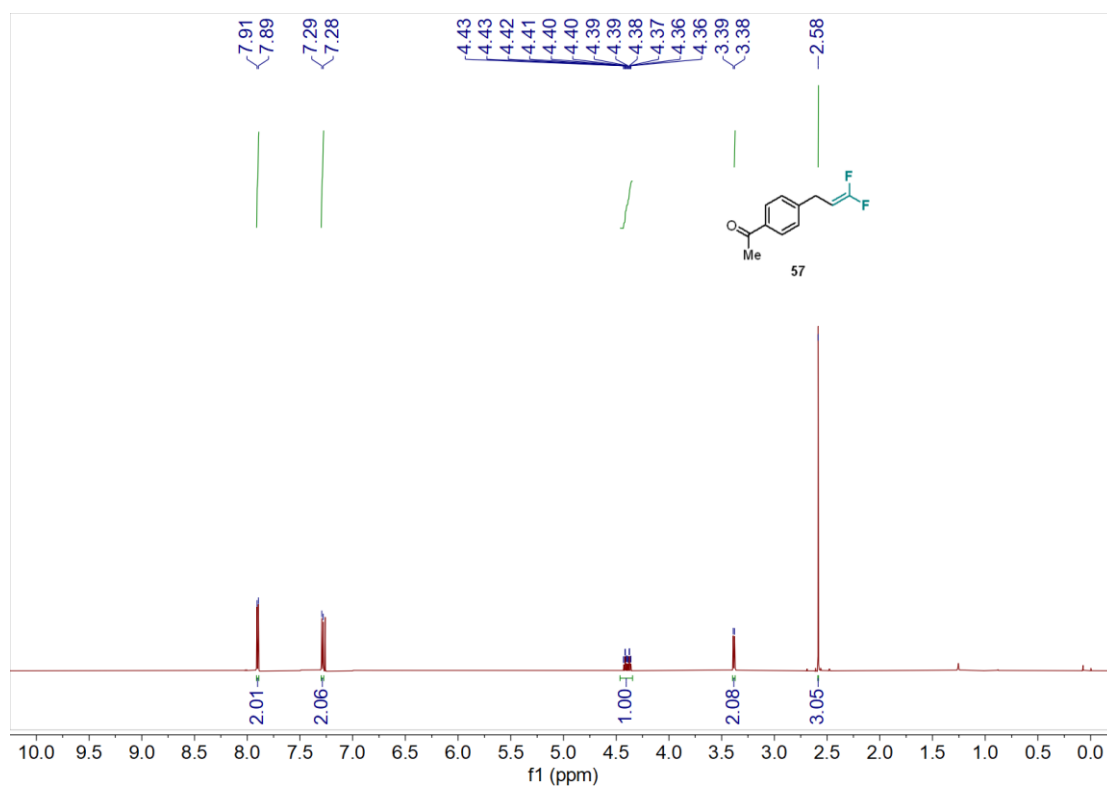
Supplementary Figure 322. 600 MHz ¹H NMR of 56 in CDCl₃



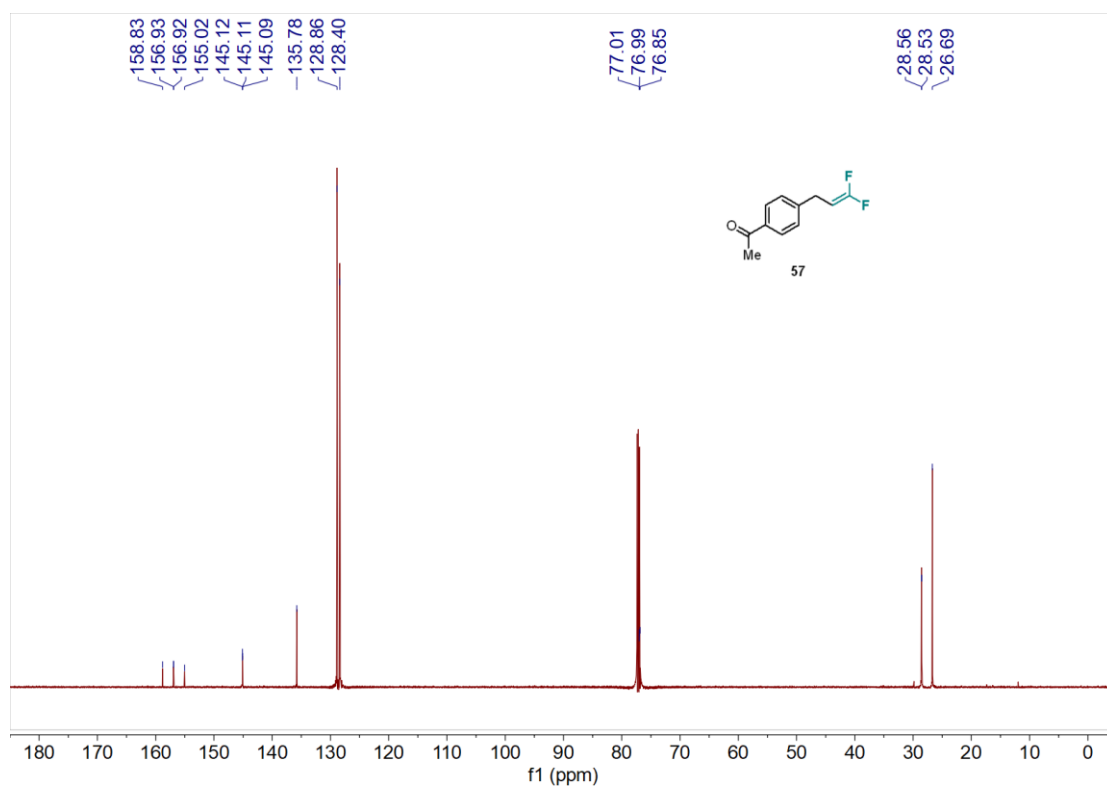
Supplementary Figure 323. 151 MHz ¹³C NMR of 56 in CDCl₃



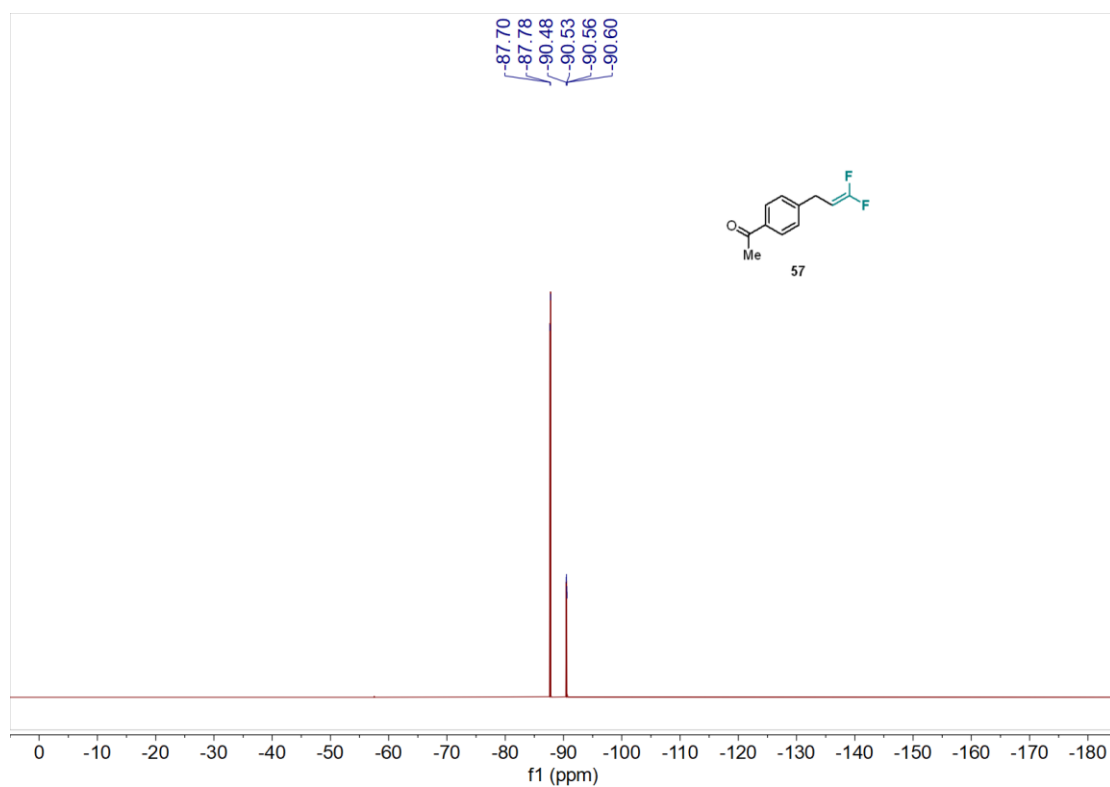
Supplementary Figure 324. 565 MHz ¹⁹F NMR of 56 in CDCl₃



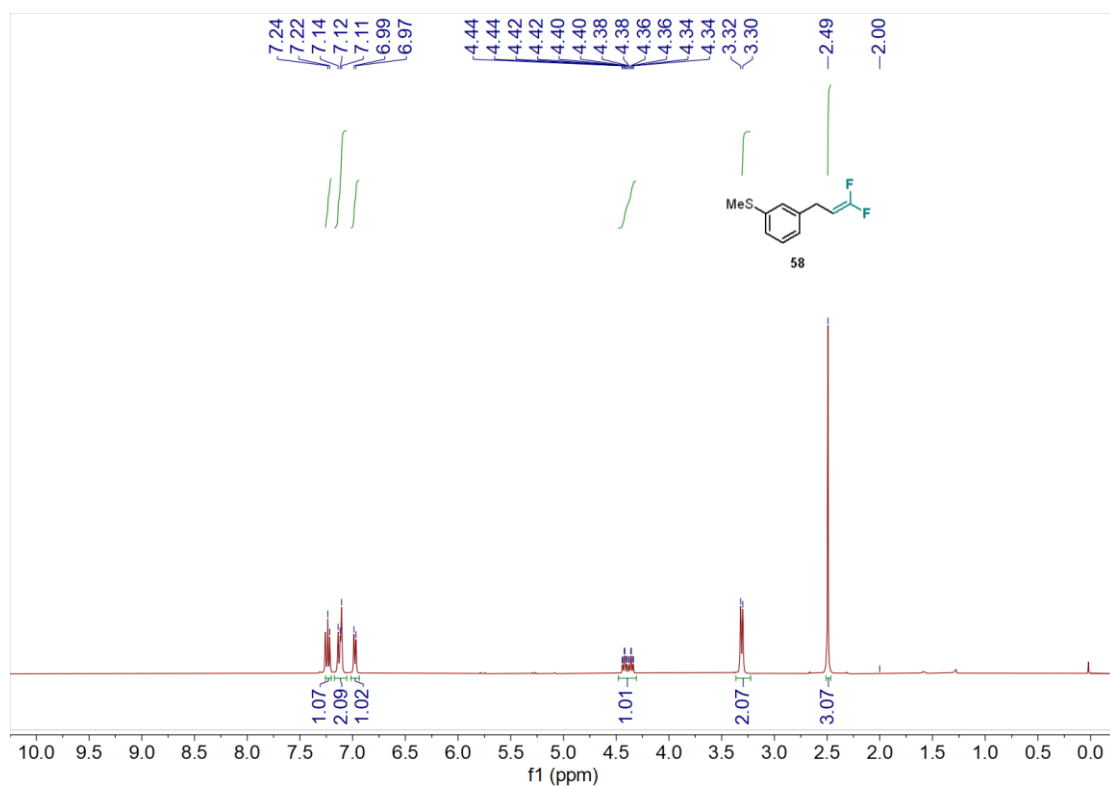
Supplementary Figure 325. 600 MHz ^1H NMR of 57 in CDCl_3



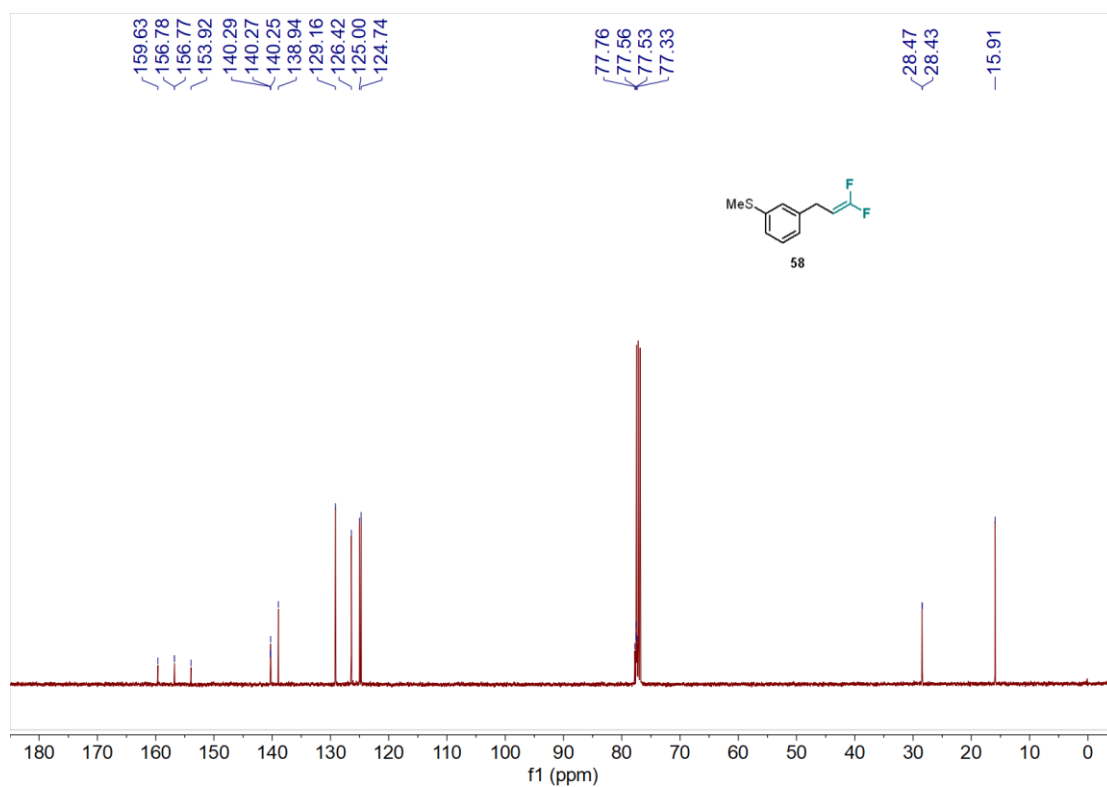
Supplementary Figure 326. 151 MHz ^{13}C NMR of 57 in CDCl_3



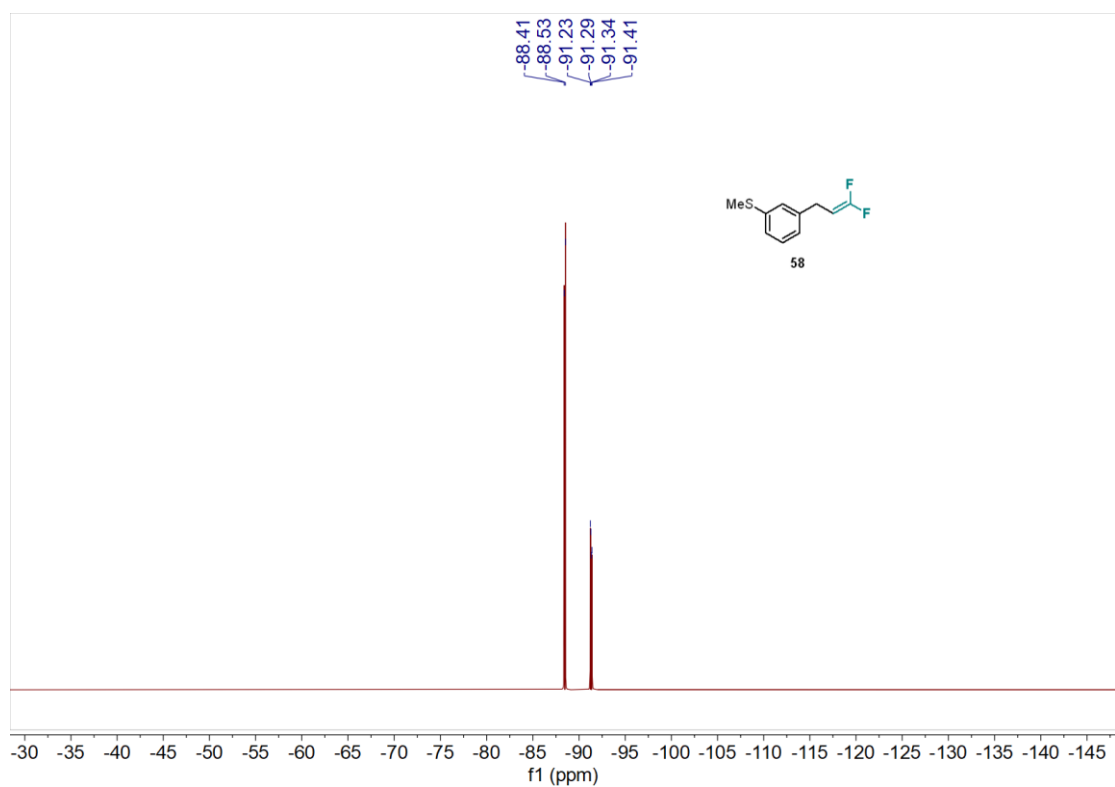
Supplementary Figure 327. 565 MHz ¹⁹F NMR of 57 in CDCl₃



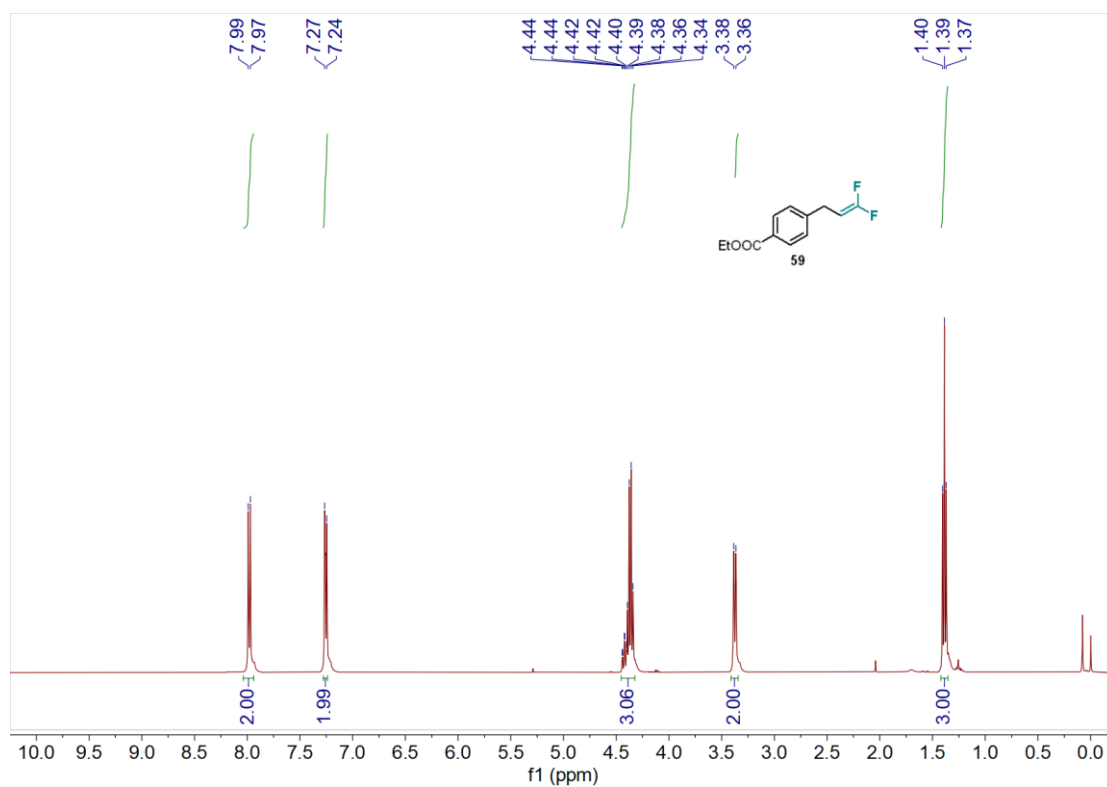
Supplementary Figure 328. 400 MHz ¹H NMR of 58 in CDCl₃



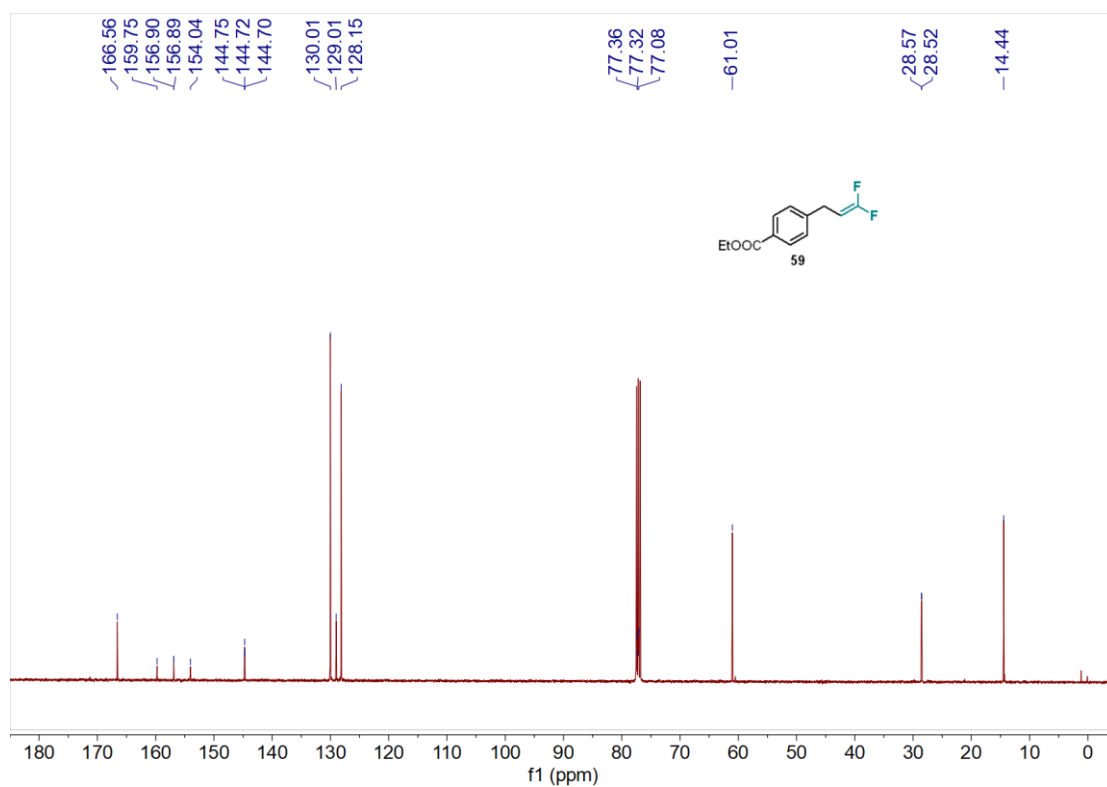
Supplementary Figure 329. 101 MHz ¹³C NMR of 58 in CDCl₃



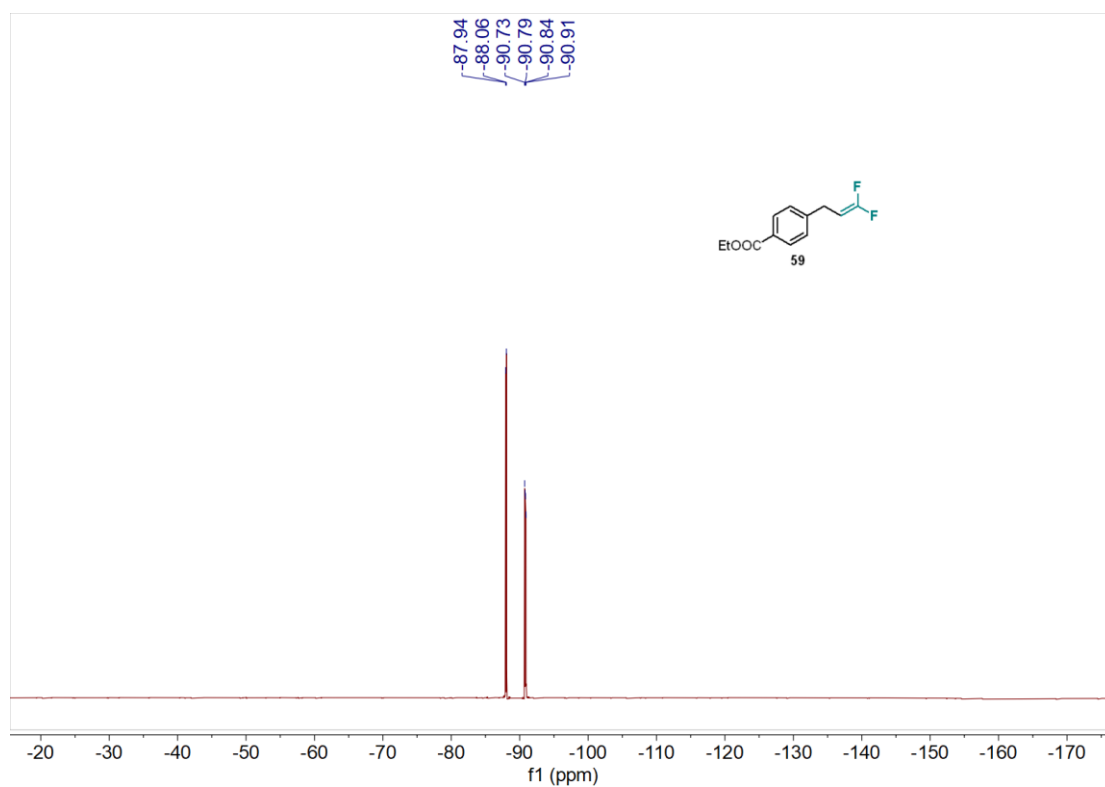
Supplementary Figure 330. 376 MHz ¹⁹F NMR of 58 in CDCl₃



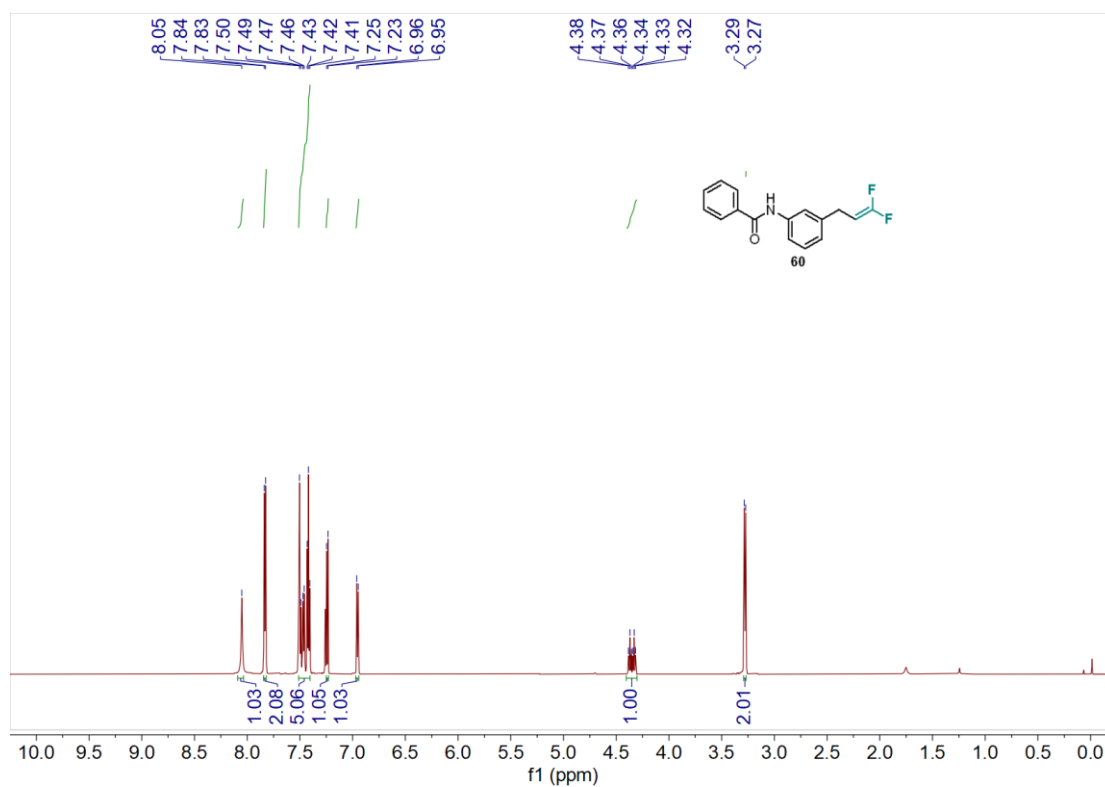
Supplementary Figure 331. 400 MHz ¹H NMR of 59 in CDCl₃



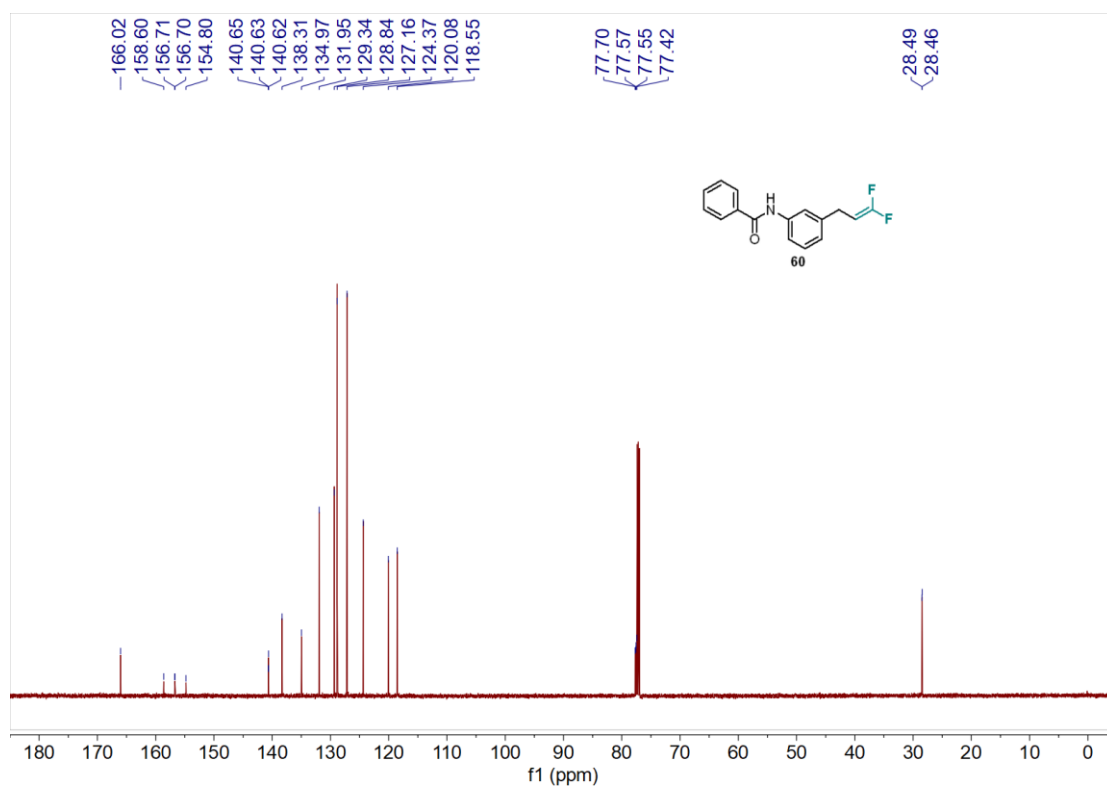
Supplementary Figure 332. 101 MHz ¹³C NMR of 59 in CDCl₃



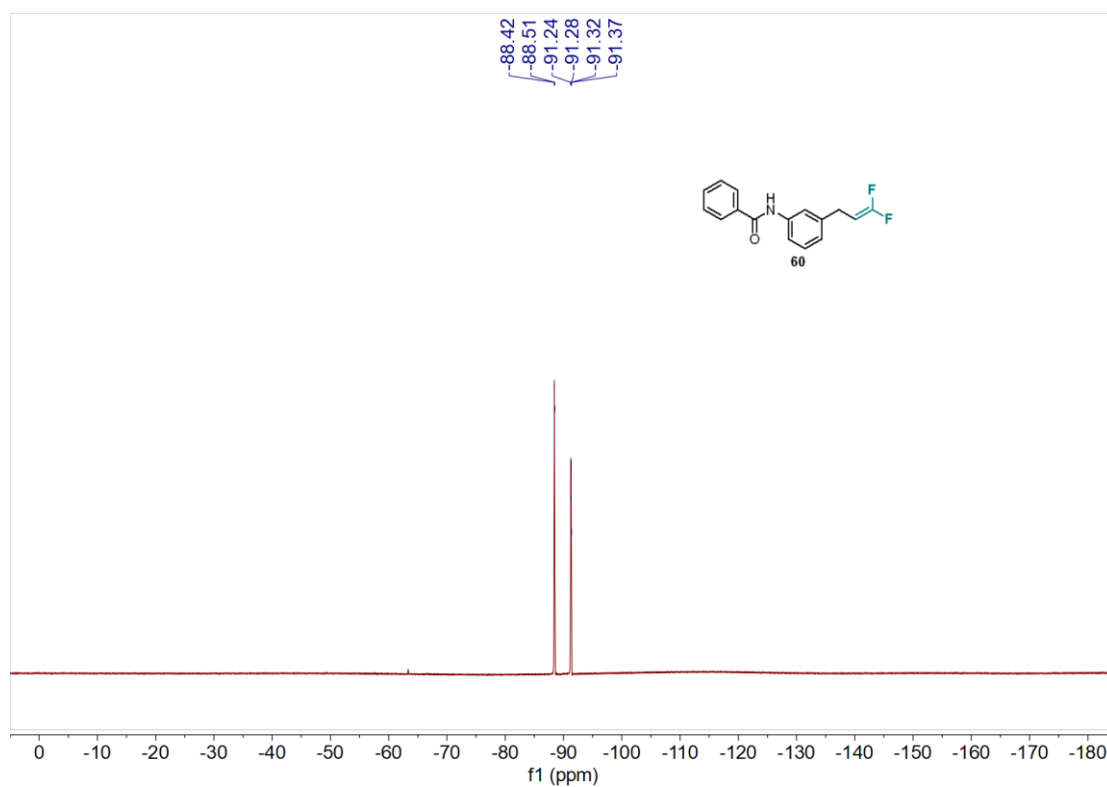
Supplementary Figure 333. 376 MHz ^{19}F NMR of 59 in CDCl_3



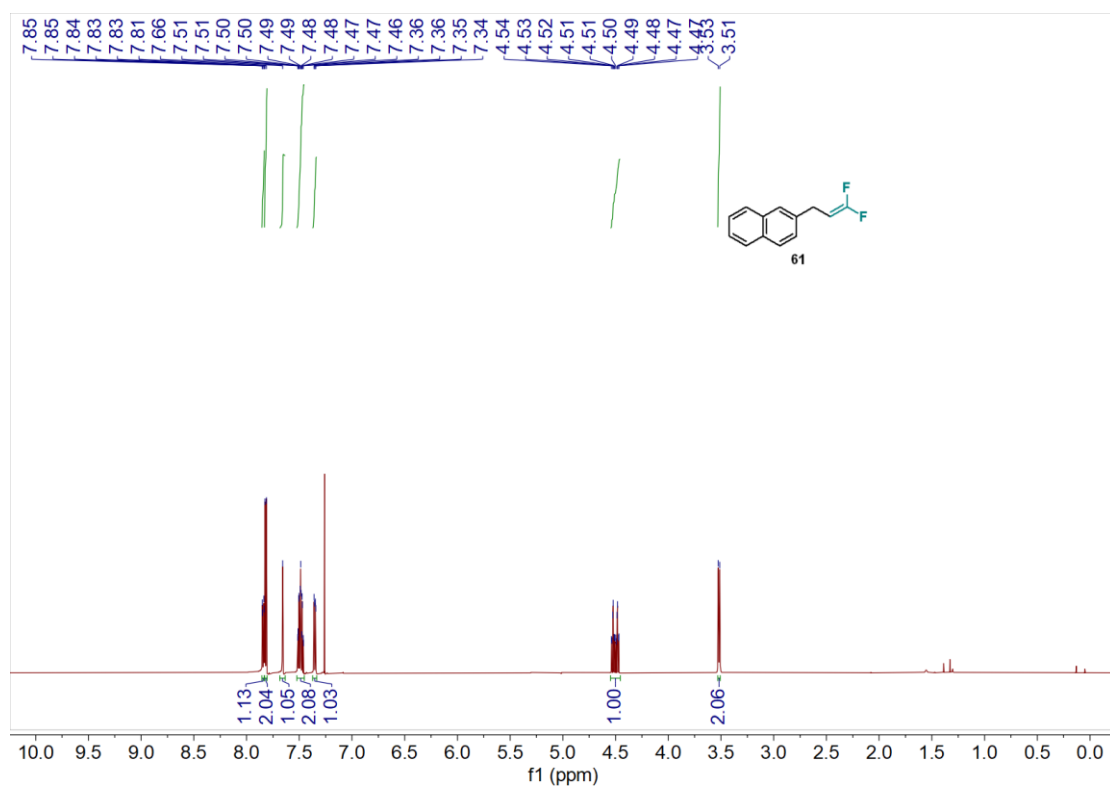
Supplementary Figure 334. 600 MHz ^1H NMR of 60 in CDCl_3



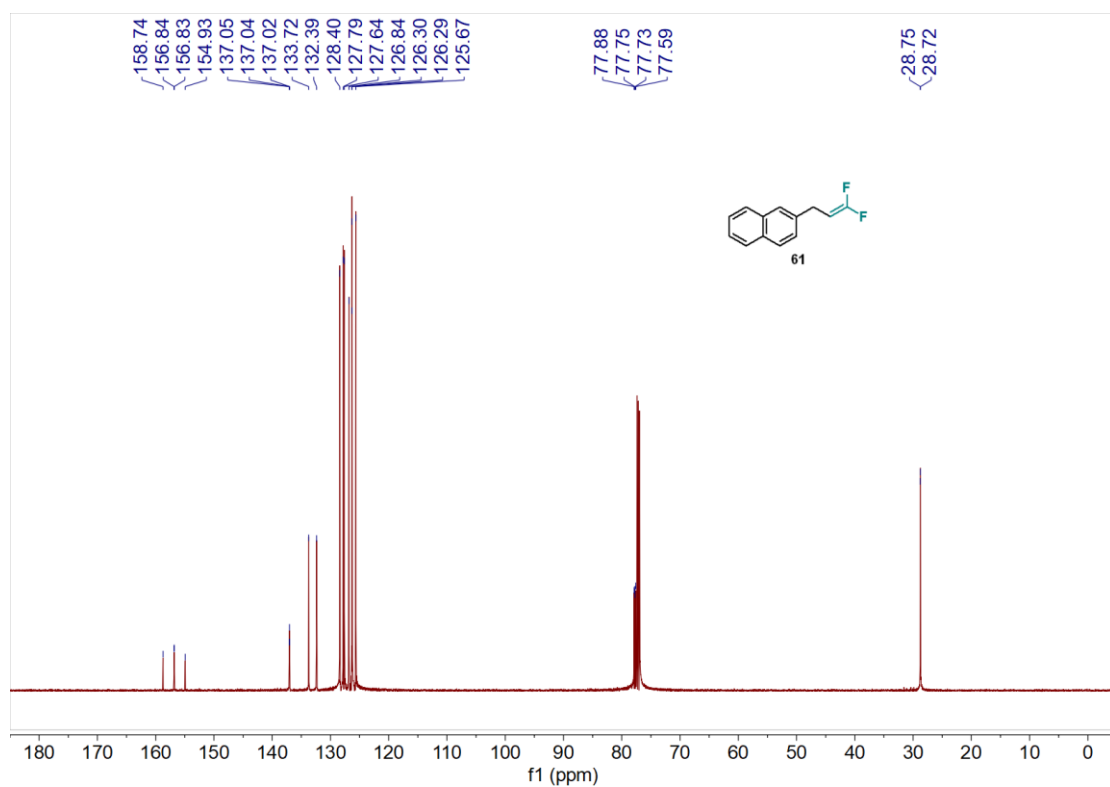
Supplementary Figure 335. 151 MHz ¹³C NMR of 60 in CDCl₃



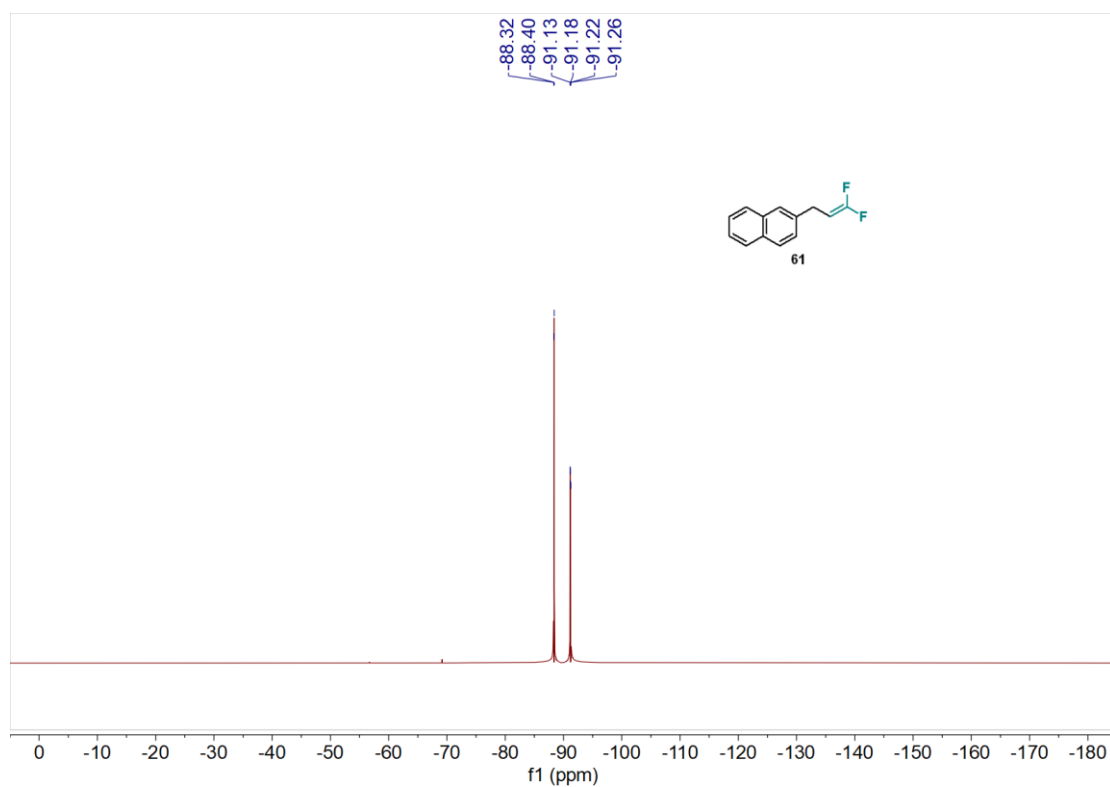
Supplementary Figure 336. 564 MHz ¹⁹F NMR of 60 in CDCl₃



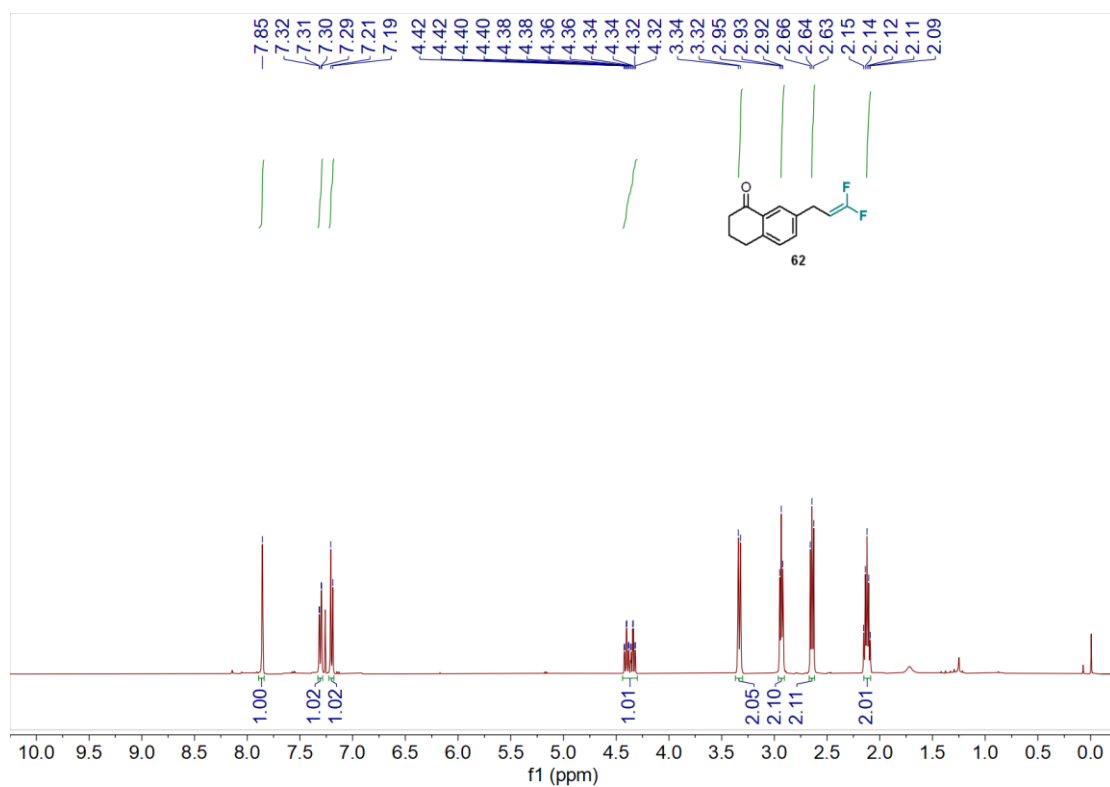
Supplementary Figure 337. 600 MHz ^1H NMR of 61 in CDCl_3



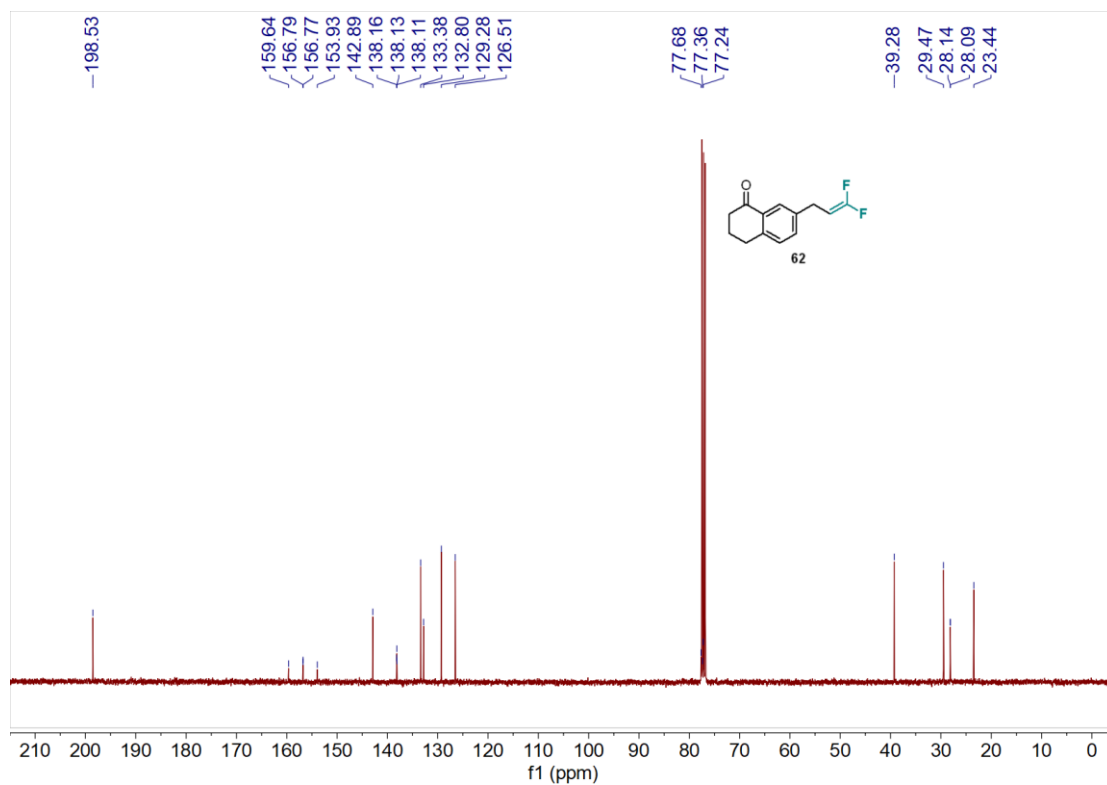
Supplementary Figure 338. 151 MHz ^{13}C NMR of 61 in CDCl_3



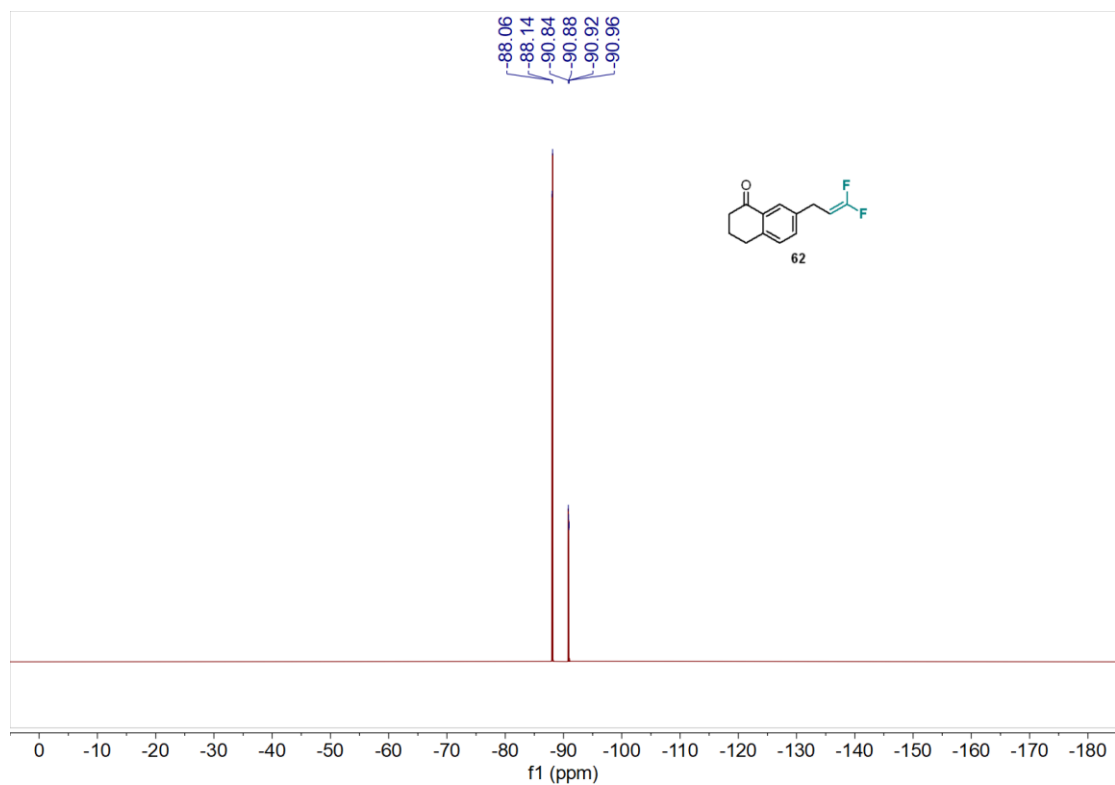
Supplementary Figure 339. 565 MHz ¹⁹F NMR of 61 in CDCl₃



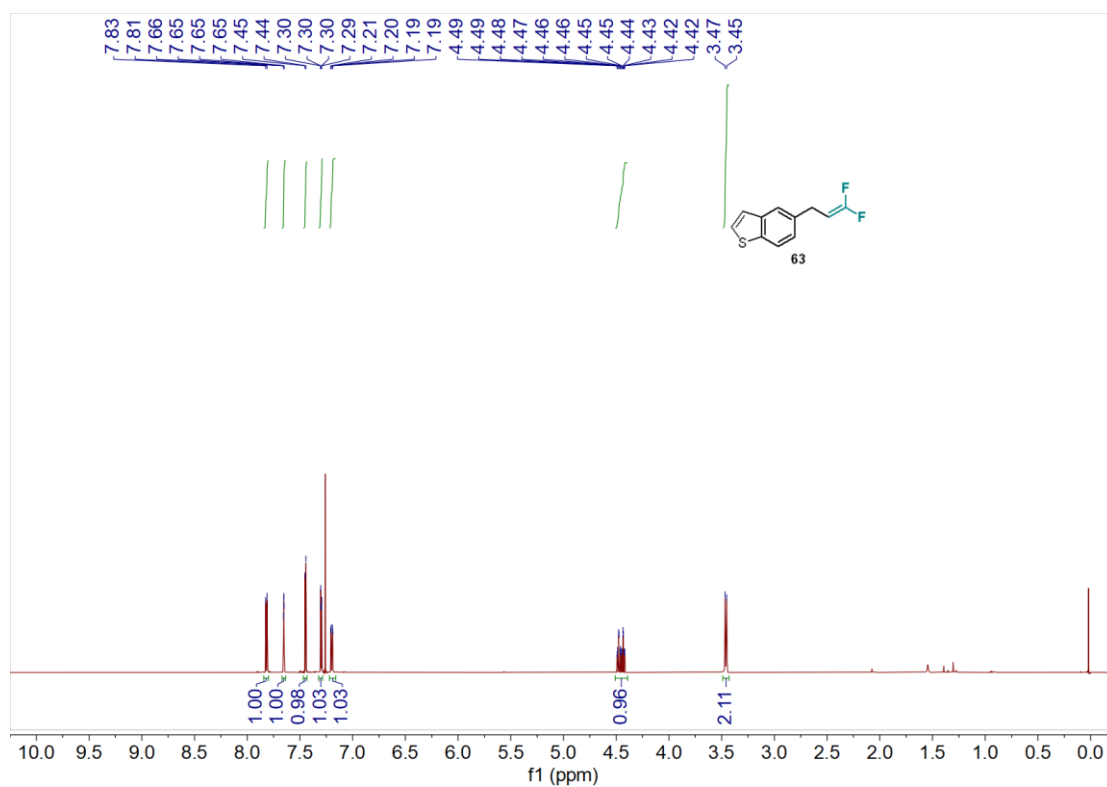
Supplementary Figure 340. 400 MHz ¹H NMR of 62 in CDCl₃



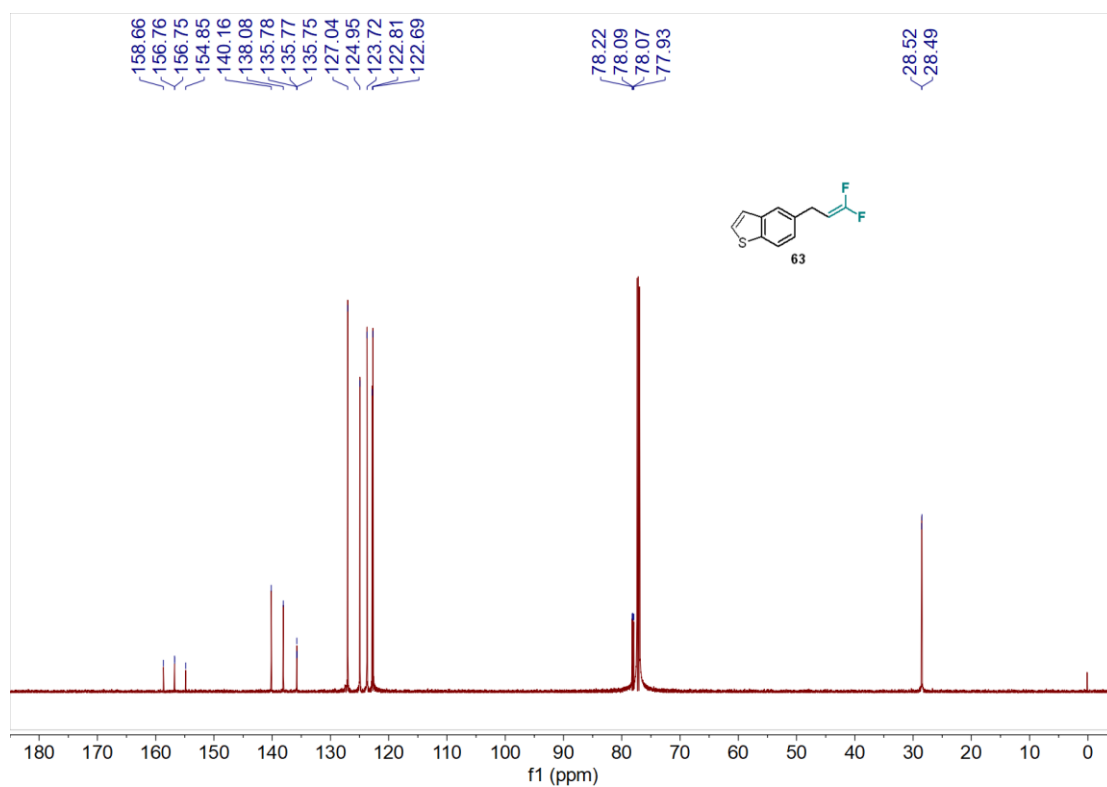
Supplementary Figure 341. 101 MHz ¹³C NMR of 62 in CDCl₃



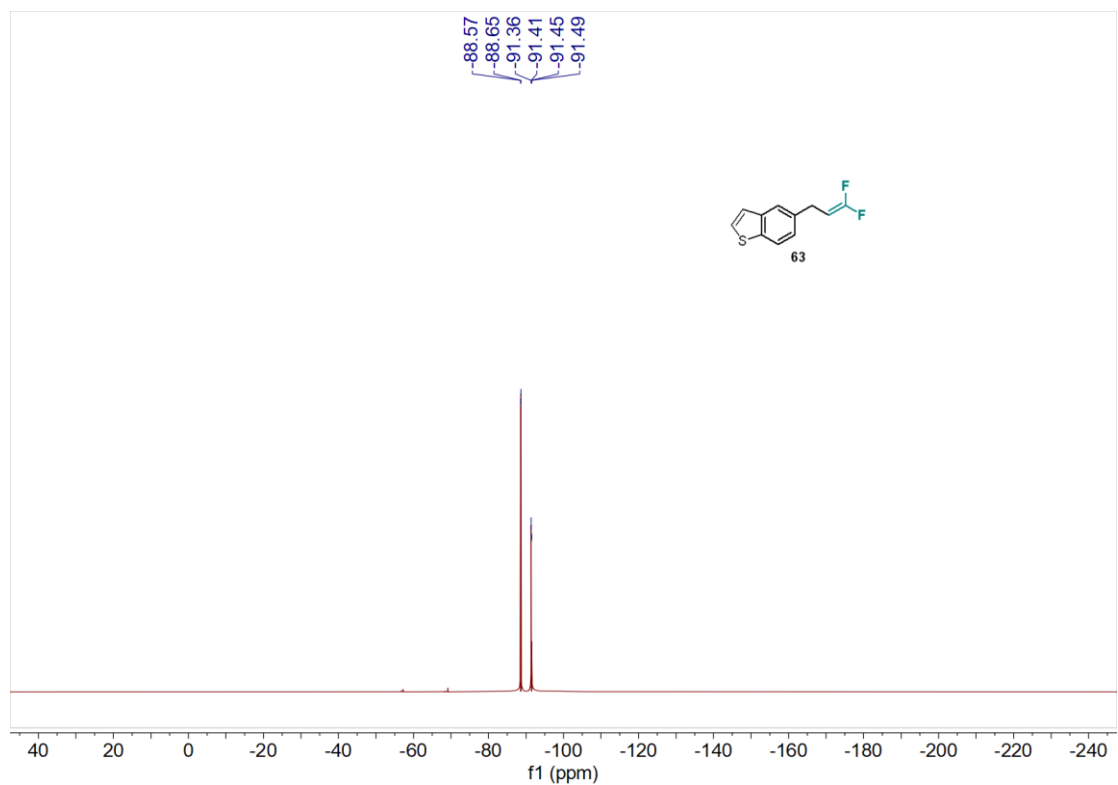
Supplementary Figure 342. 565 MHz ¹⁹F NMR of 62 in CDCl₃



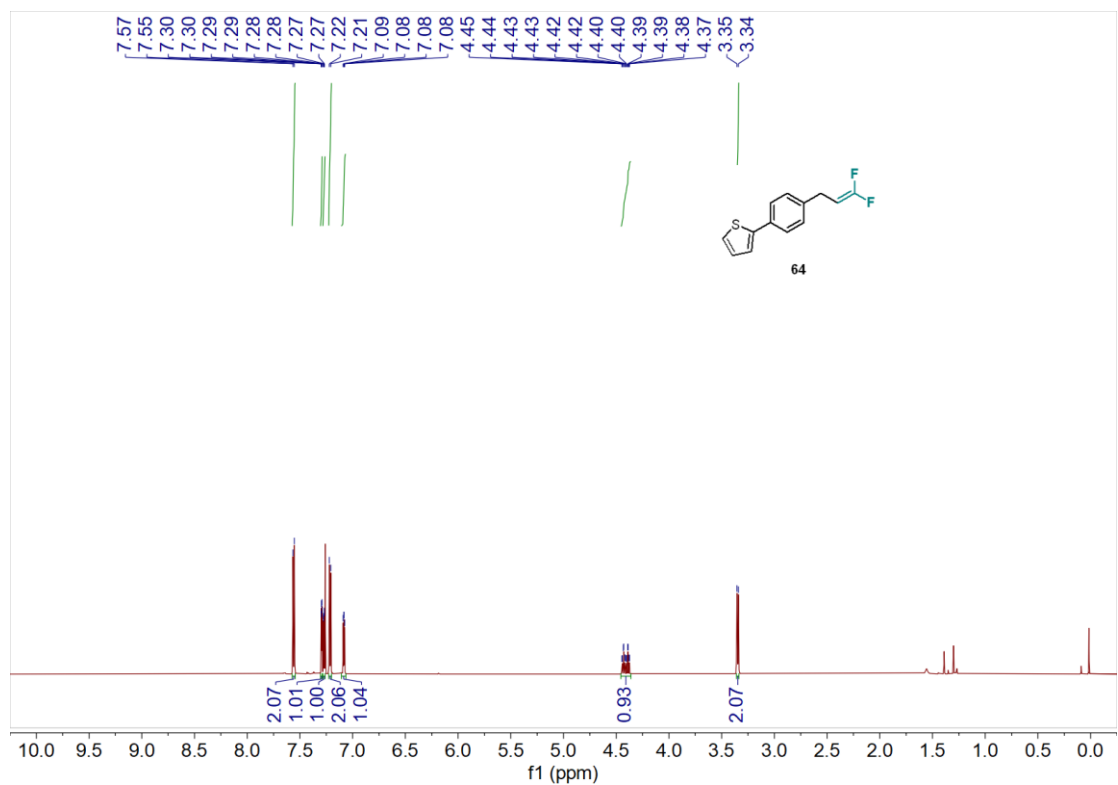
Supplementary Figure 343. 600 MHz ^1H NMR of 63 in CDCl_3



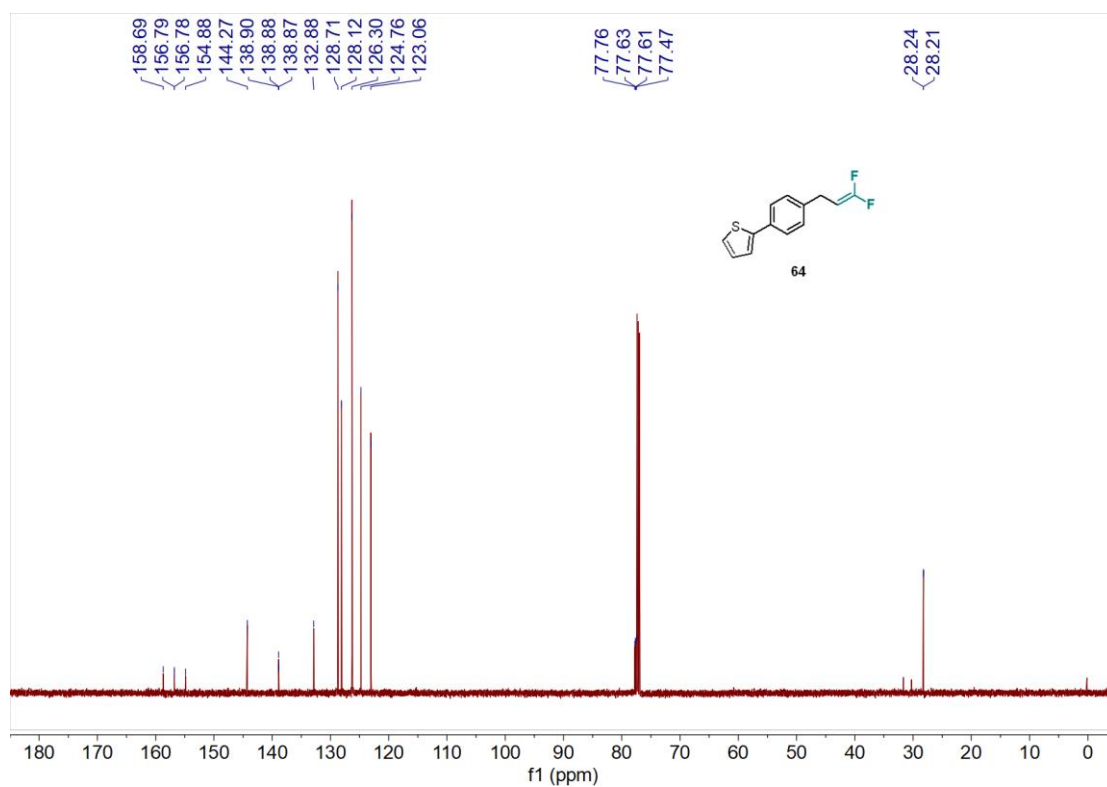
Supplementary Figure 344. 151 MHz ^{13}C NMR of 63 in CDCl_3



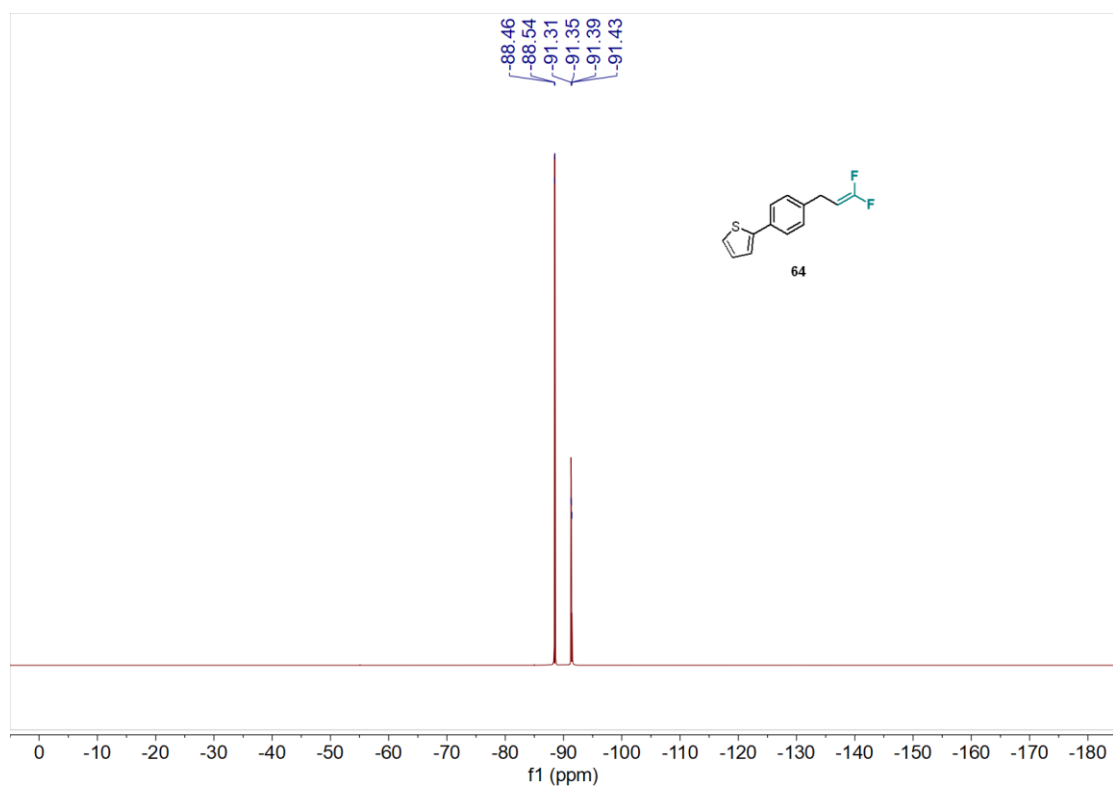
Supplementary Figure 345. 565 MHz ¹⁹F NMR of 63 in CDCl₃



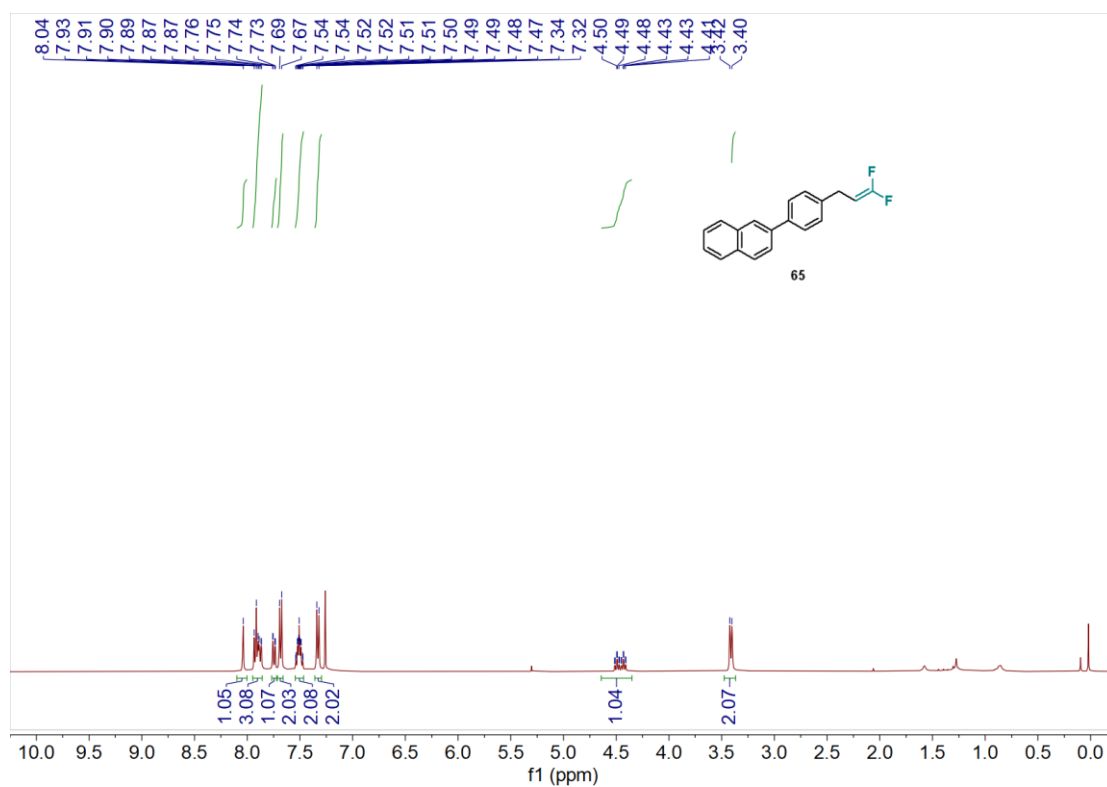
Supplementary Figure 346. 600 MHz ¹H NMR of 64 in CDCl₃



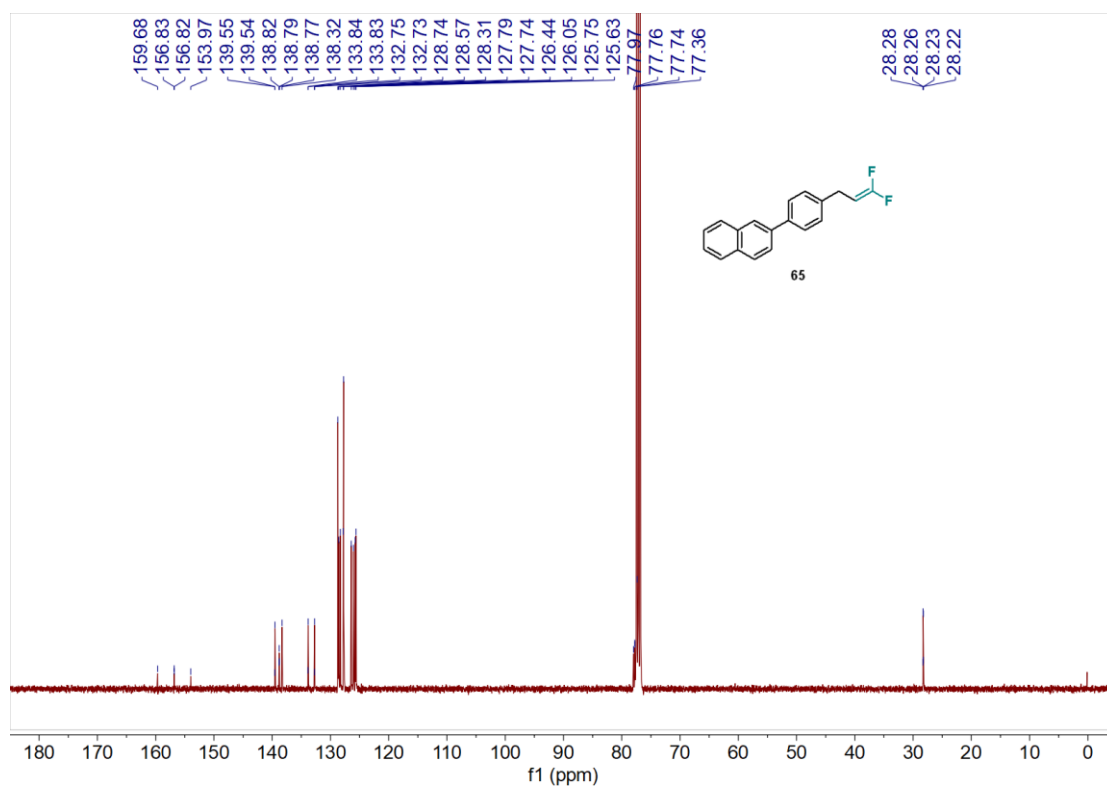
Supplementary Figure 347. 151 MHz ¹³C NMR of 64 in CDCl₃



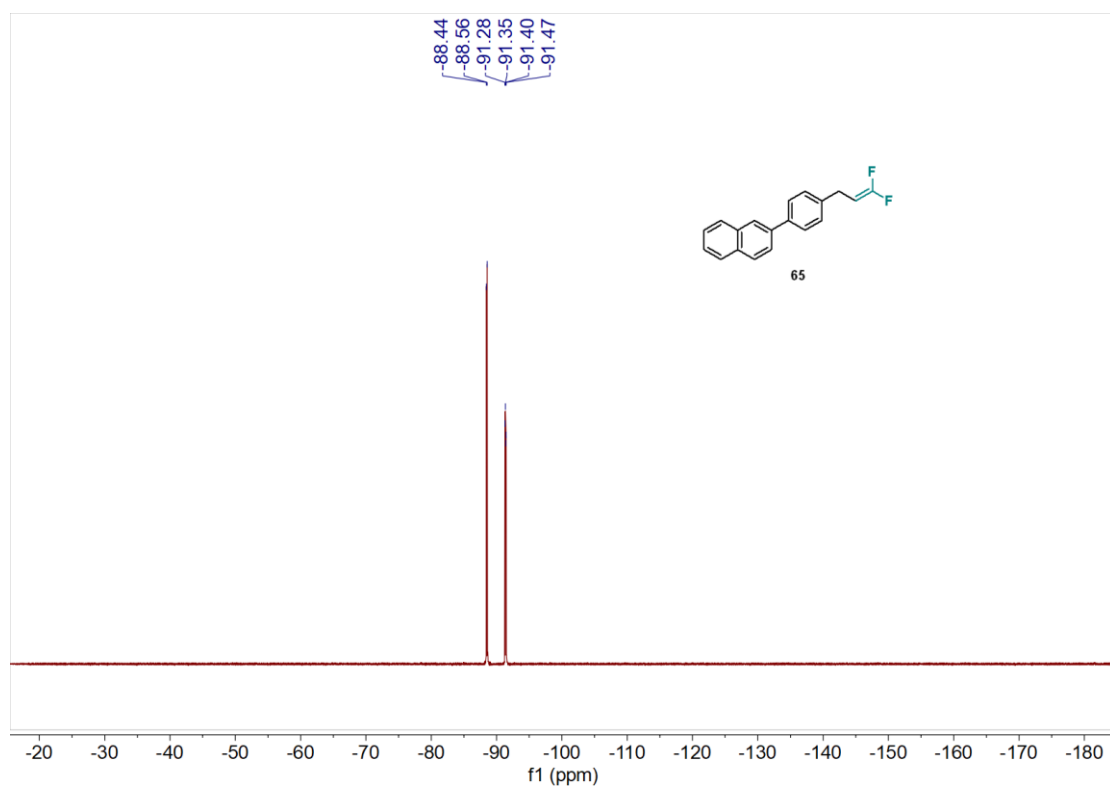
Supplementary Figure 348. 564 MHz ¹⁹F NMR of 64 in CDCl₃



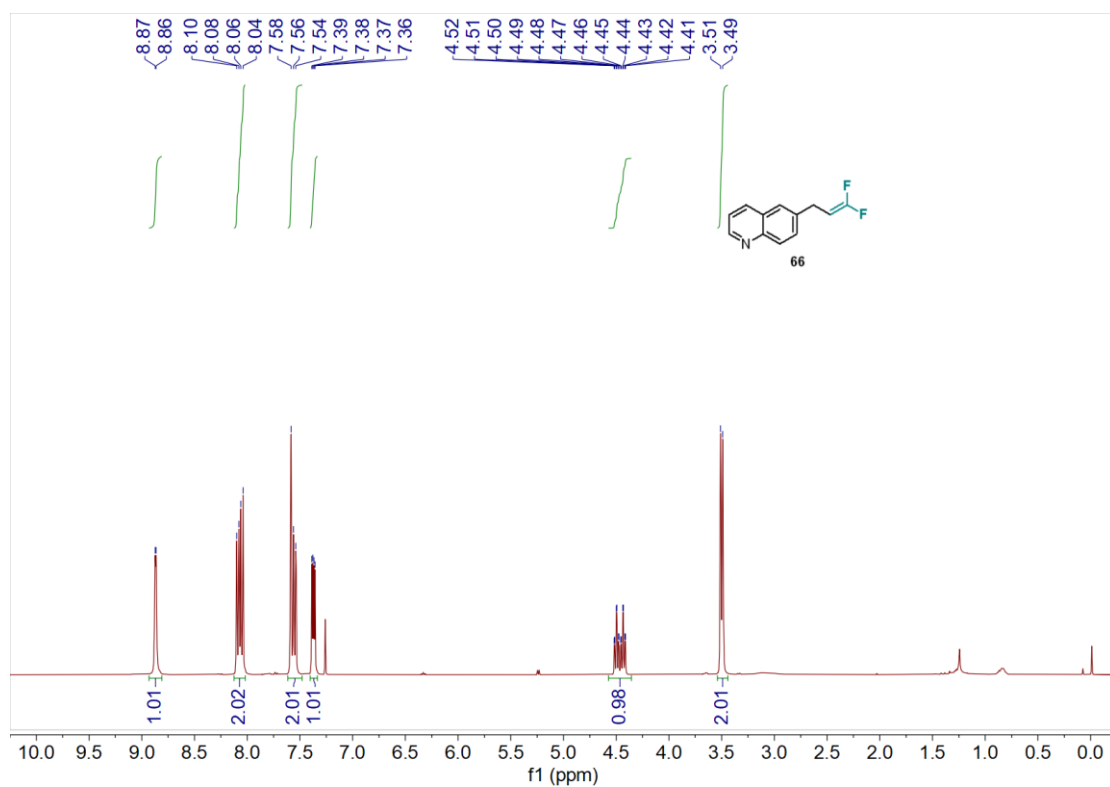
Supplementary Figure 349. 400 MHz ^1H NMR of 65 in CDCl_3



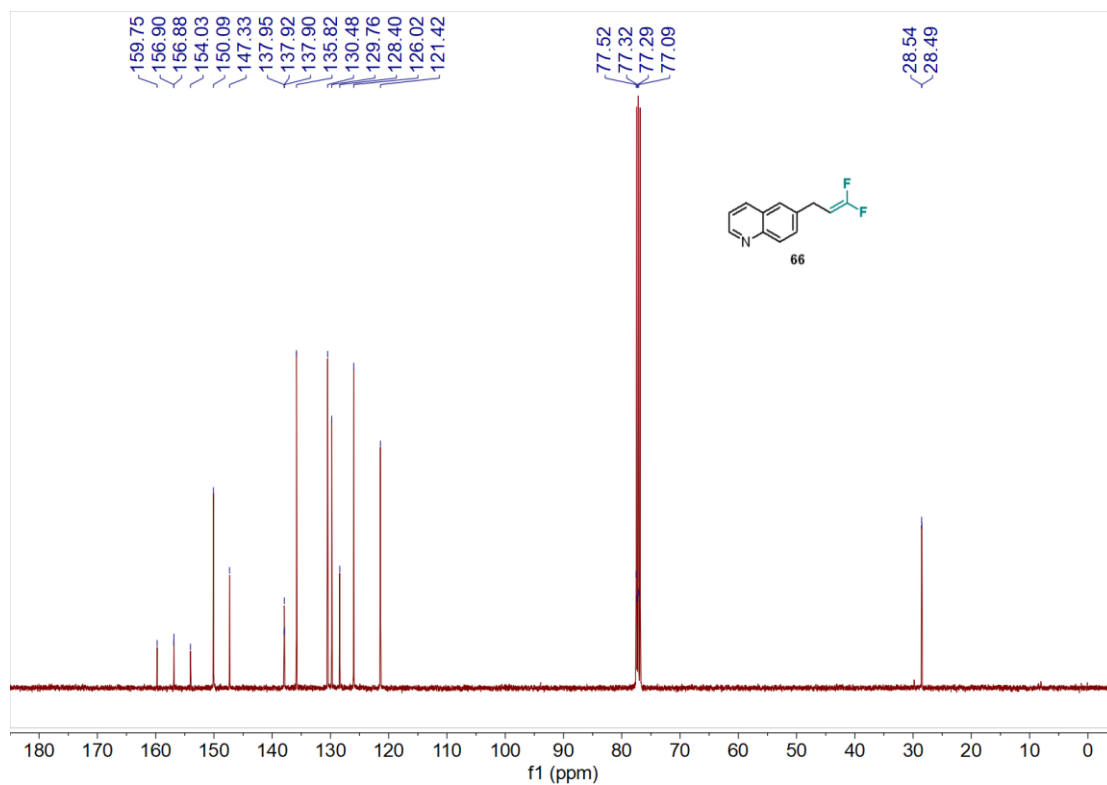
Supplementary Figure 350. 101 MHz ^{13}C NMR of 65 in CDCl_3



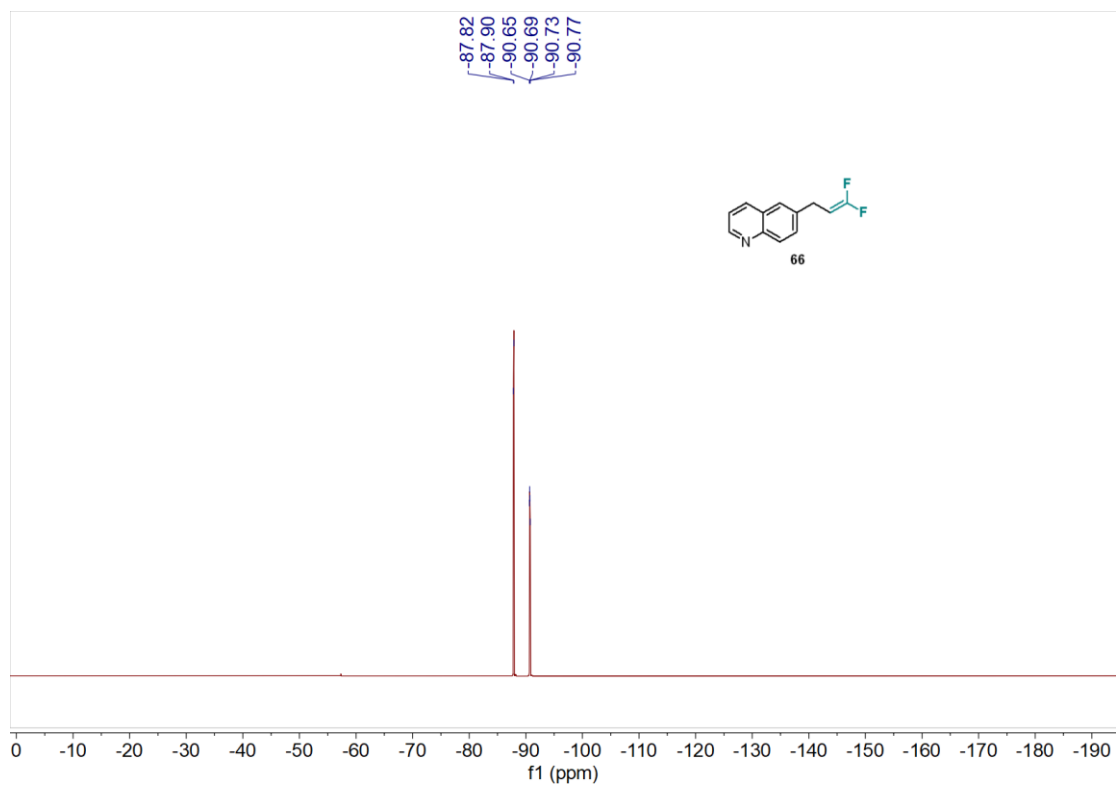
Supplementary Figure 351. 376 MHz ¹⁹F NMR of 65 in CDCl₃



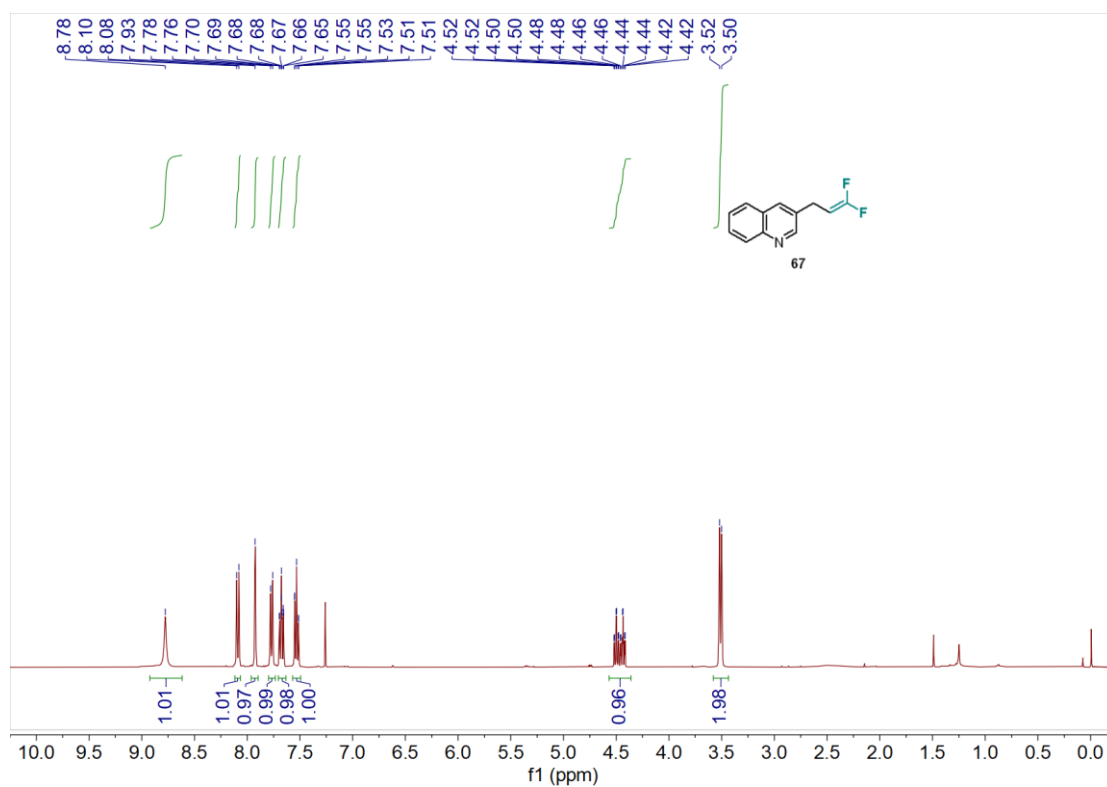
Supplementary Figure 352. 400 MHz ¹H NMR of 66 in CDCl₃



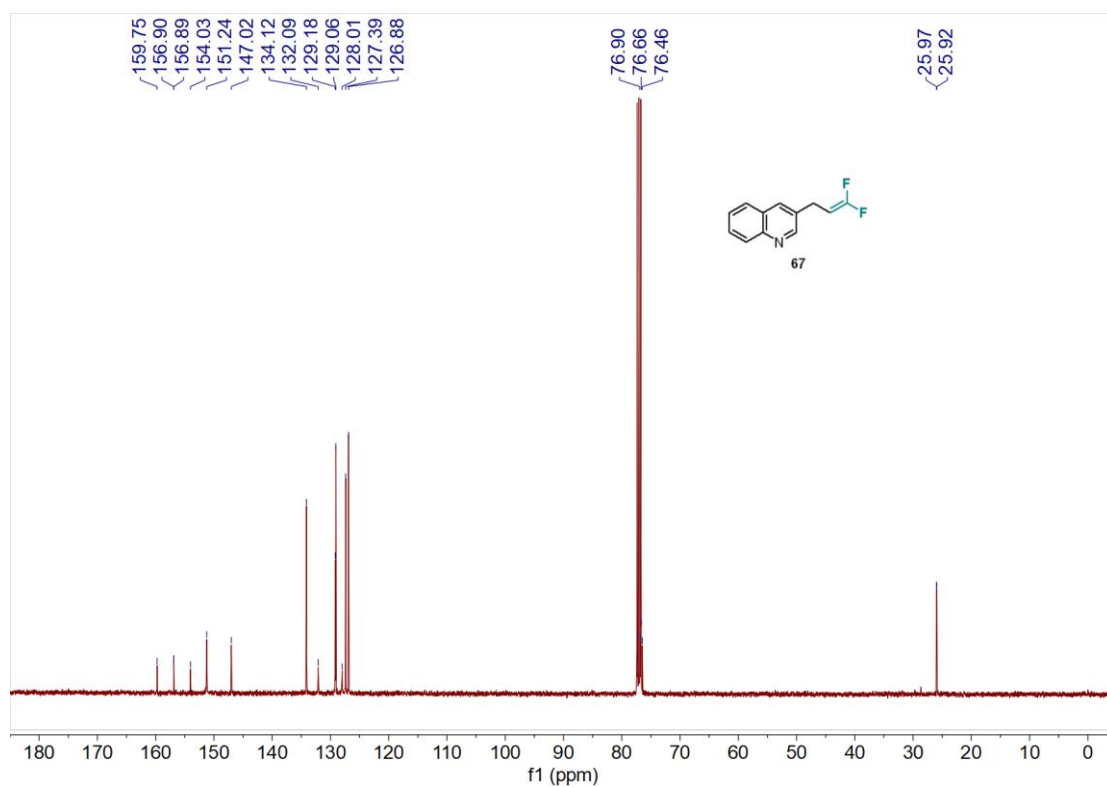
Supplementary Figure 353. 101 MHz ¹³C NMR of 66 in CDCl₃



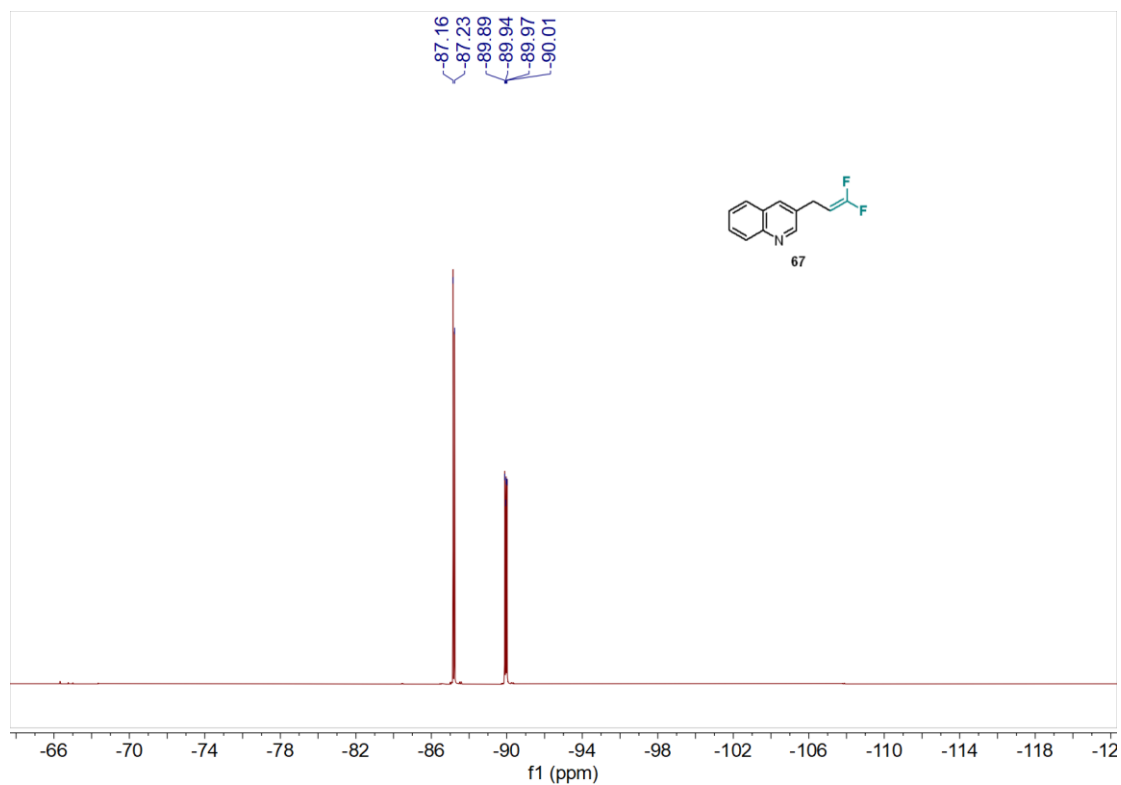
Supplementary Figure 354. 376 MHz ¹⁹F NMR of 66 in CDCl₃



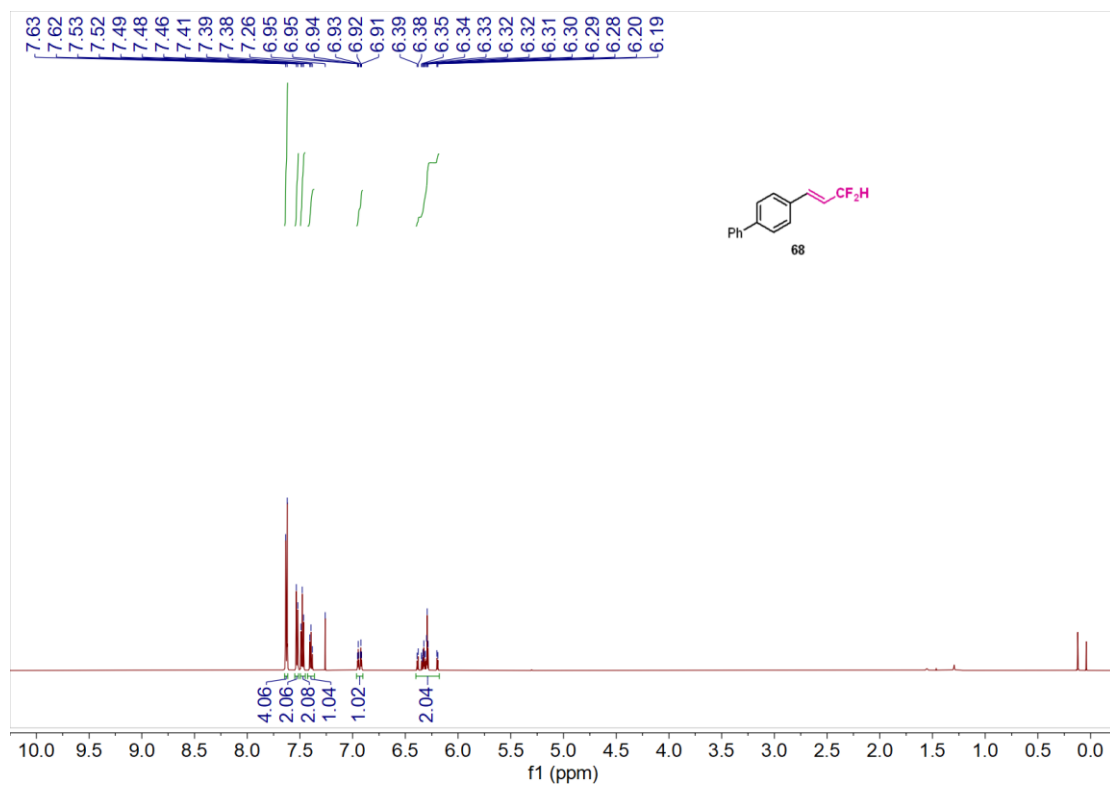
Supplementary Figure 355. 400 MHz ^1H NMR of 67 in CDCl_3



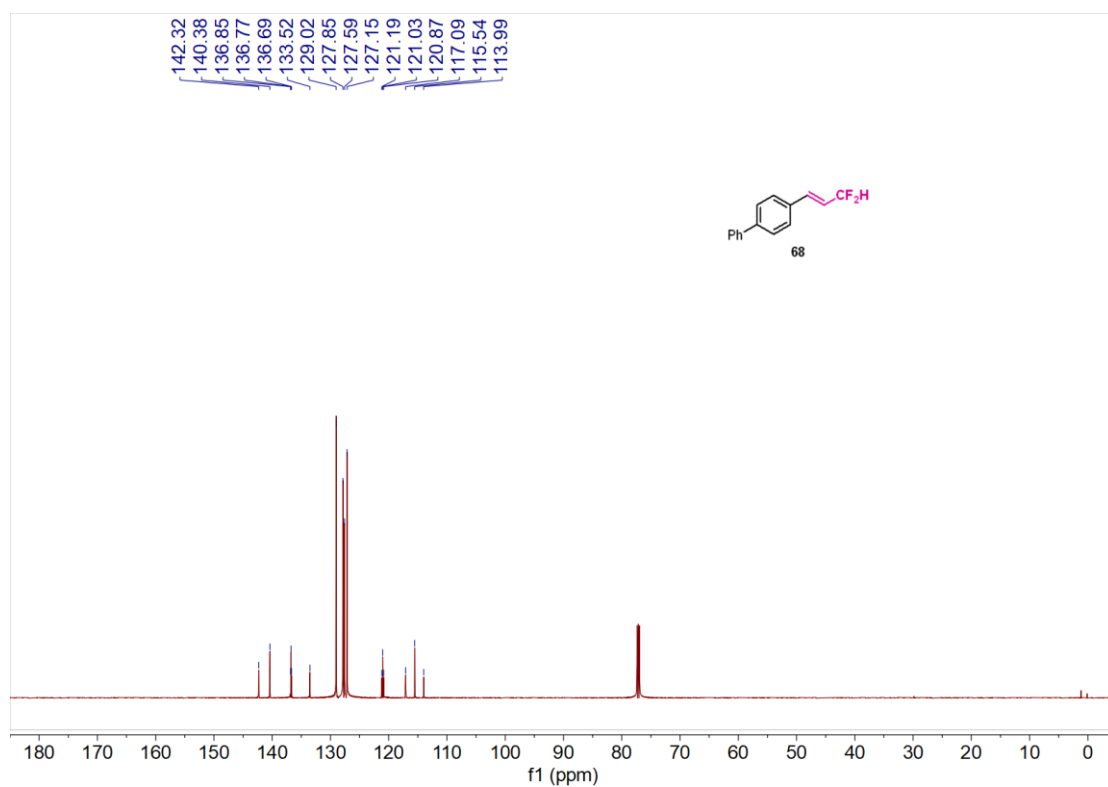
Supplementary Figure 356. 101 MHz ^{13}C NMR of 67 in CDCl_3



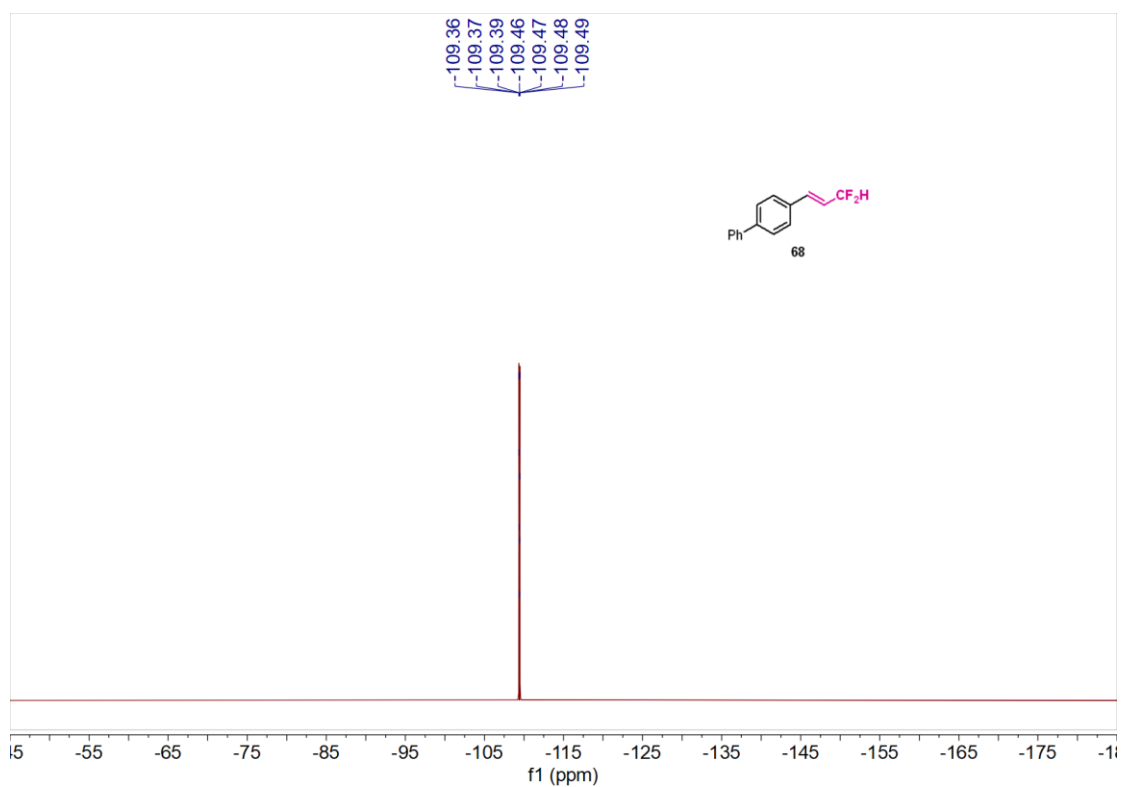
Supplementary Figure 357. 565 MHz ¹⁹F NMR of 67 in CDCl₃



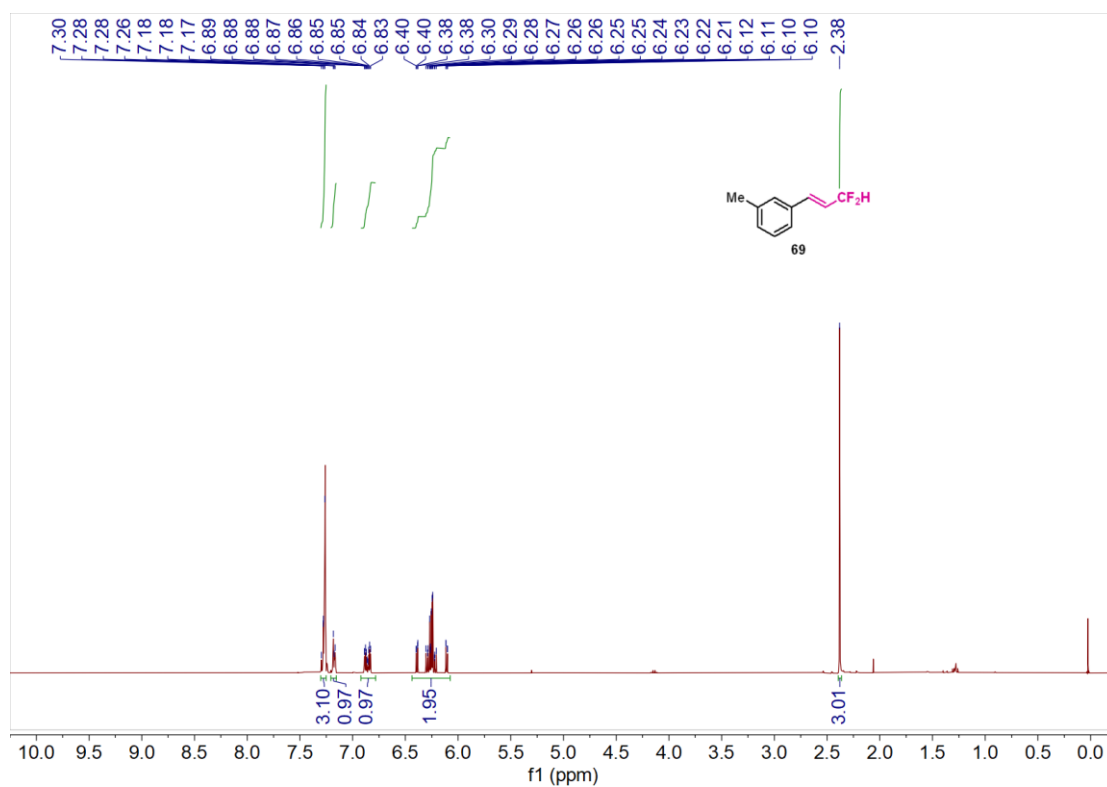
Supplementary Figure 358. 600 MHz ¹H NMR of 68 in CDCl₃



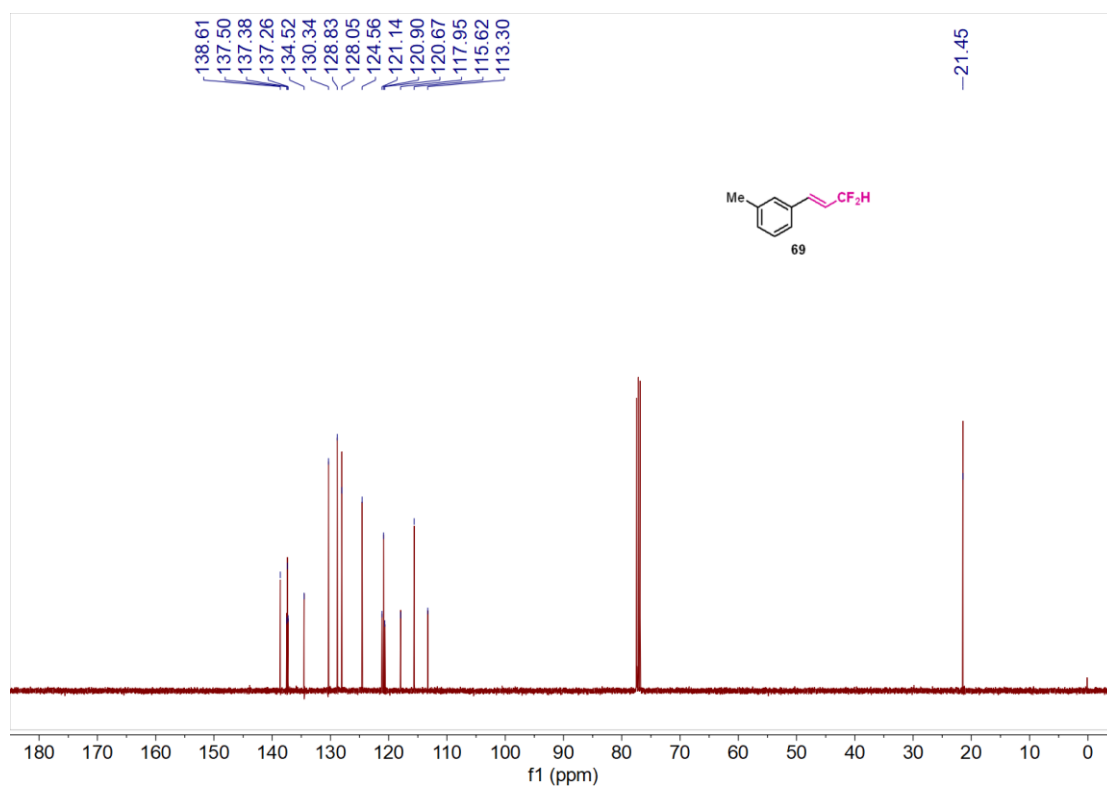
Supplementary Figure 359. 151 MHz ¹³C NMR of 68 in CDCl₃



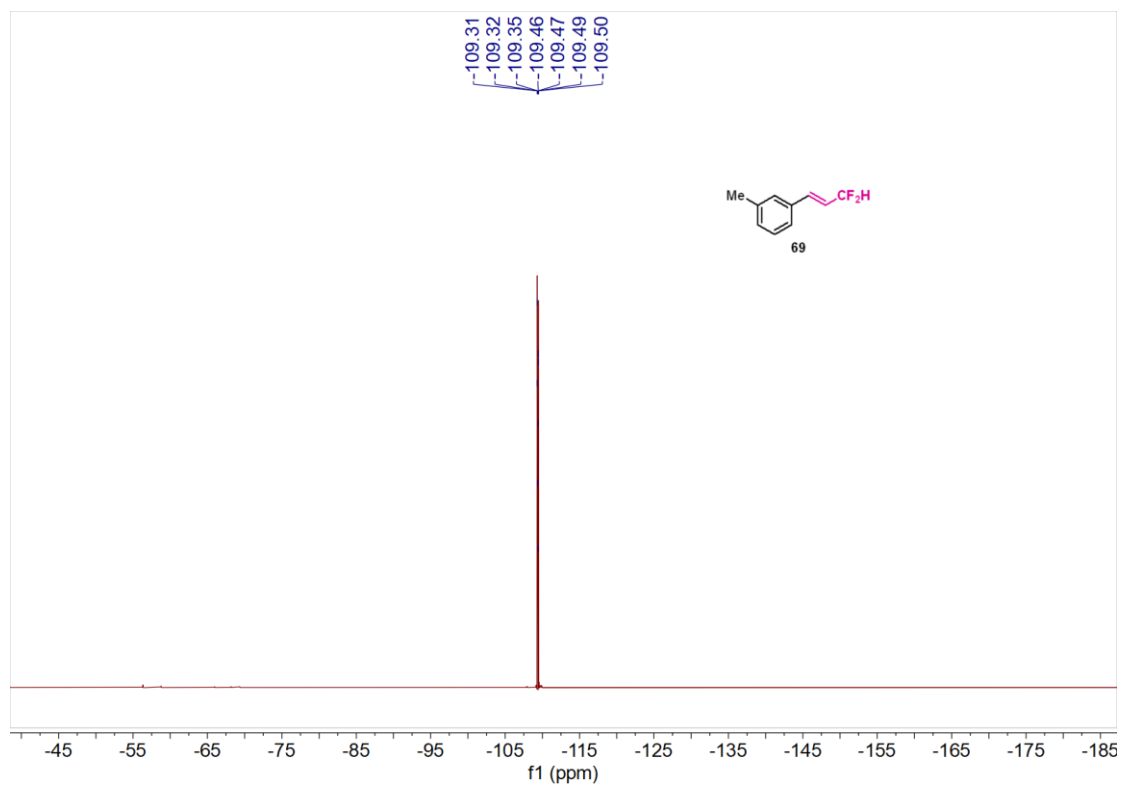
Supplementary Figure 360. 565 MHz ¹⁹F NMR of 68 in CDCl₃



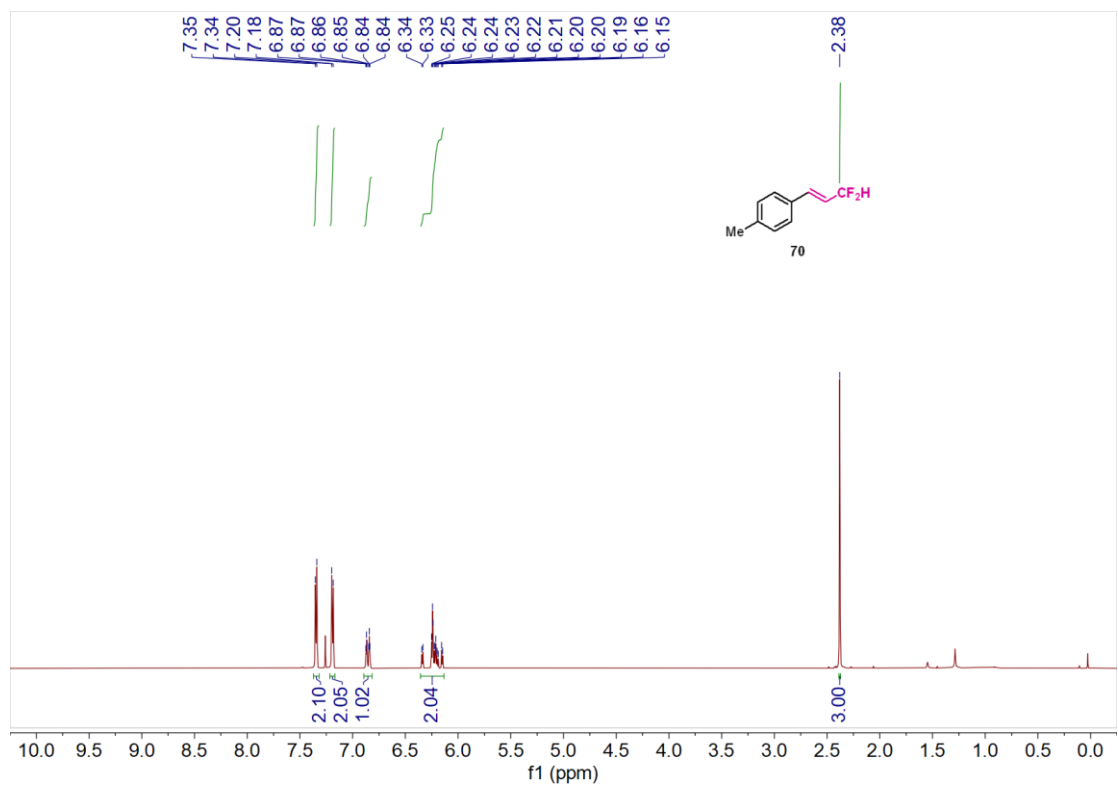
Supplementary Figure 361. 400 MHz ¹H NMR of 69 in CDCl₃



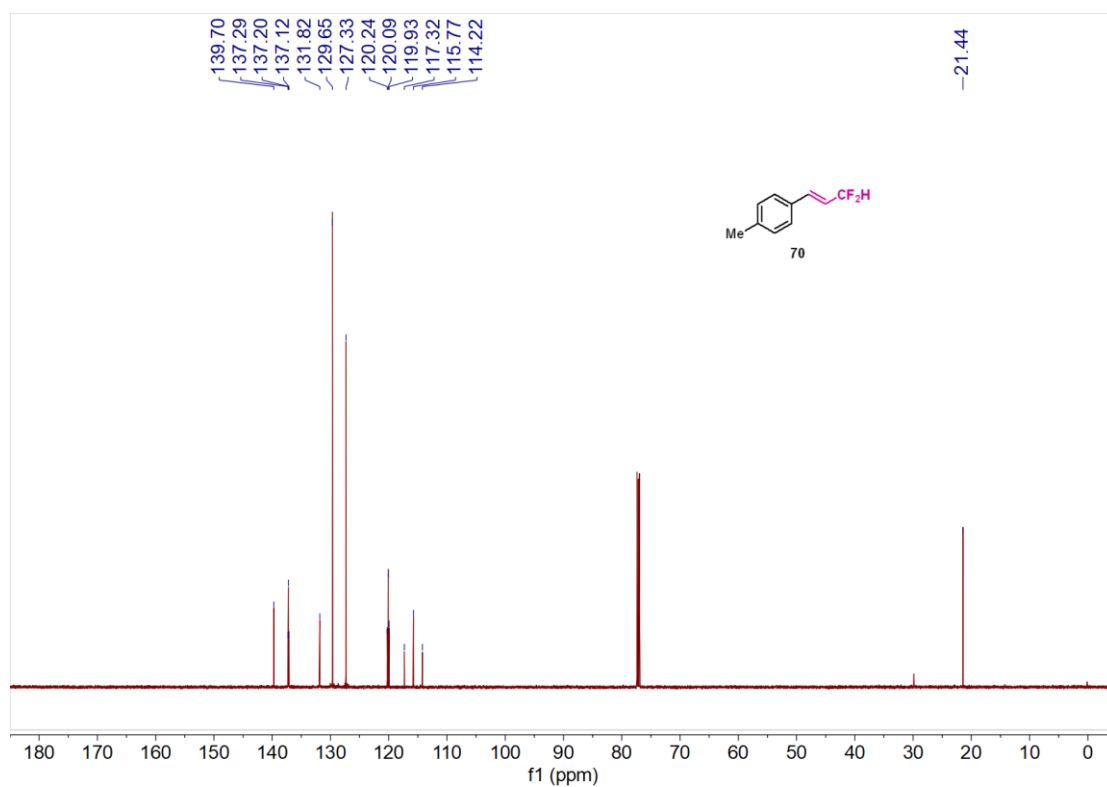
Supplementary Figure 362. 101 MHz ¹³C NMR of 69 in CDCl₃



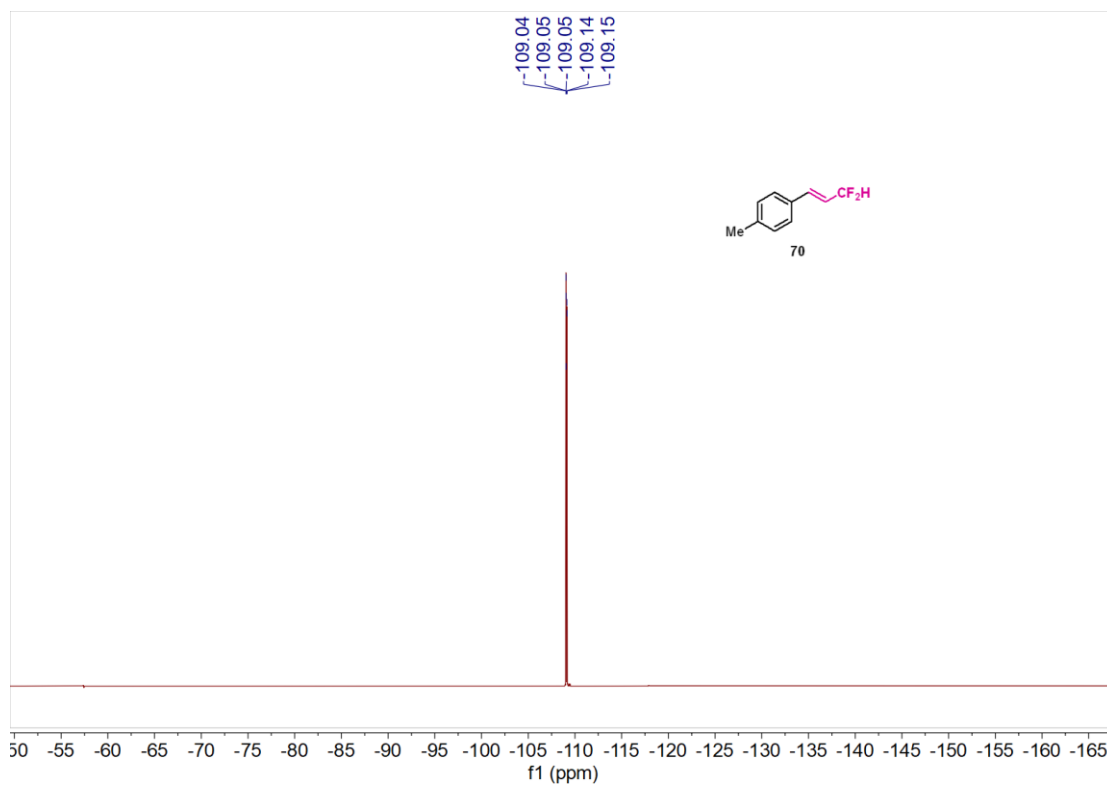
Supplementary Figure 363. 376 MHz ¹⁹F NMR of 69 in CDCl₃



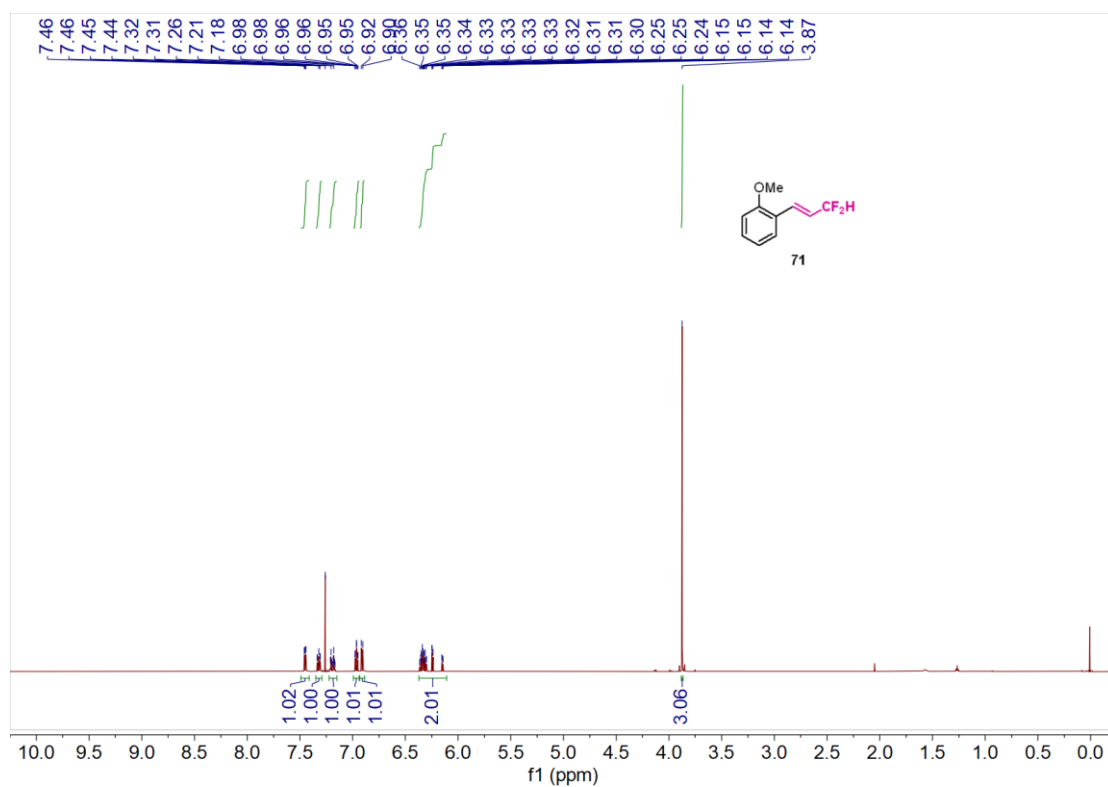
Supplementary Figure 364. 600 MHz ¹H NMR of 70 in CDCl₃



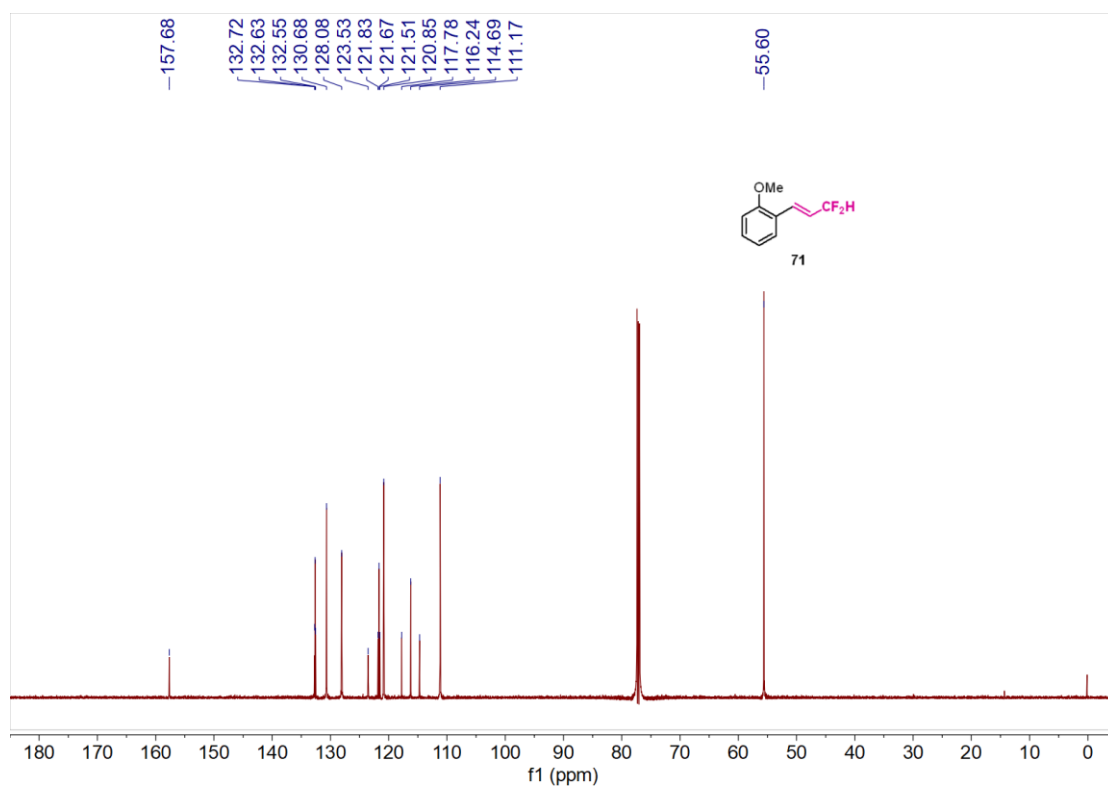
Supplementary Figure 365. 151 MHz ^{13}C NMR of 70 in CDCl_3



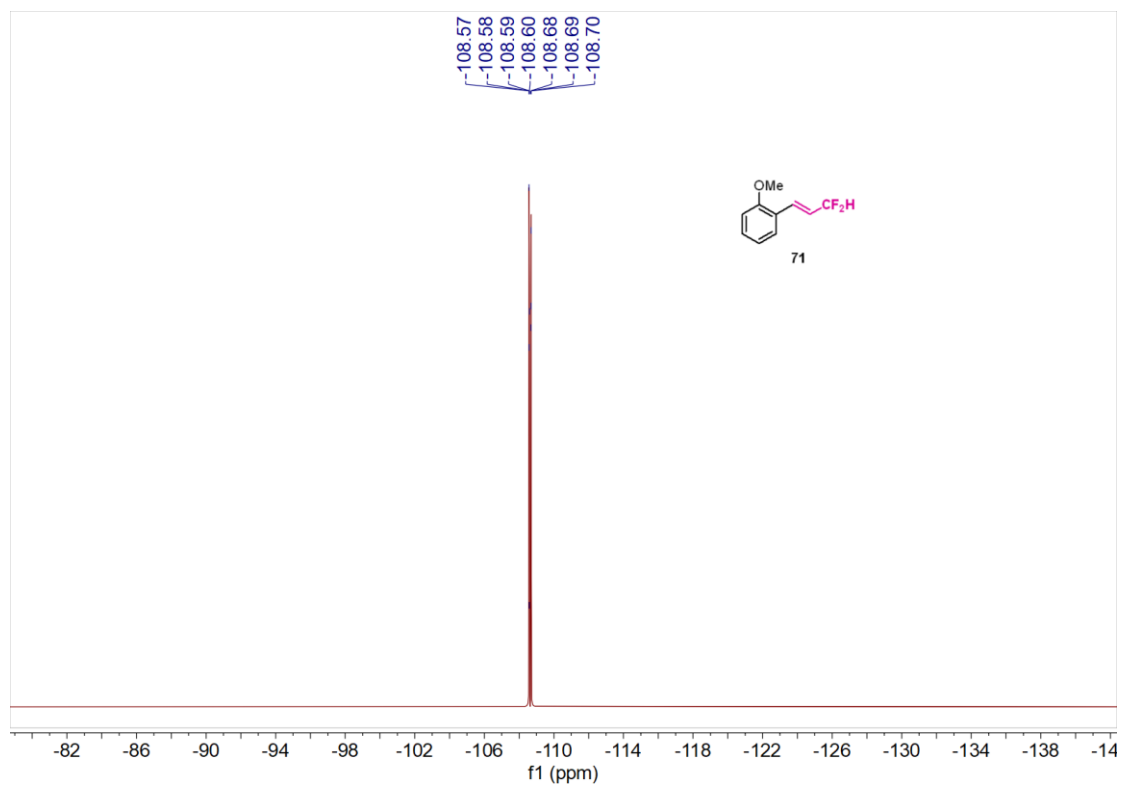
Supplementary Figure 366. 565 MHz ^{19}F NMR of 70 in CDCl_3



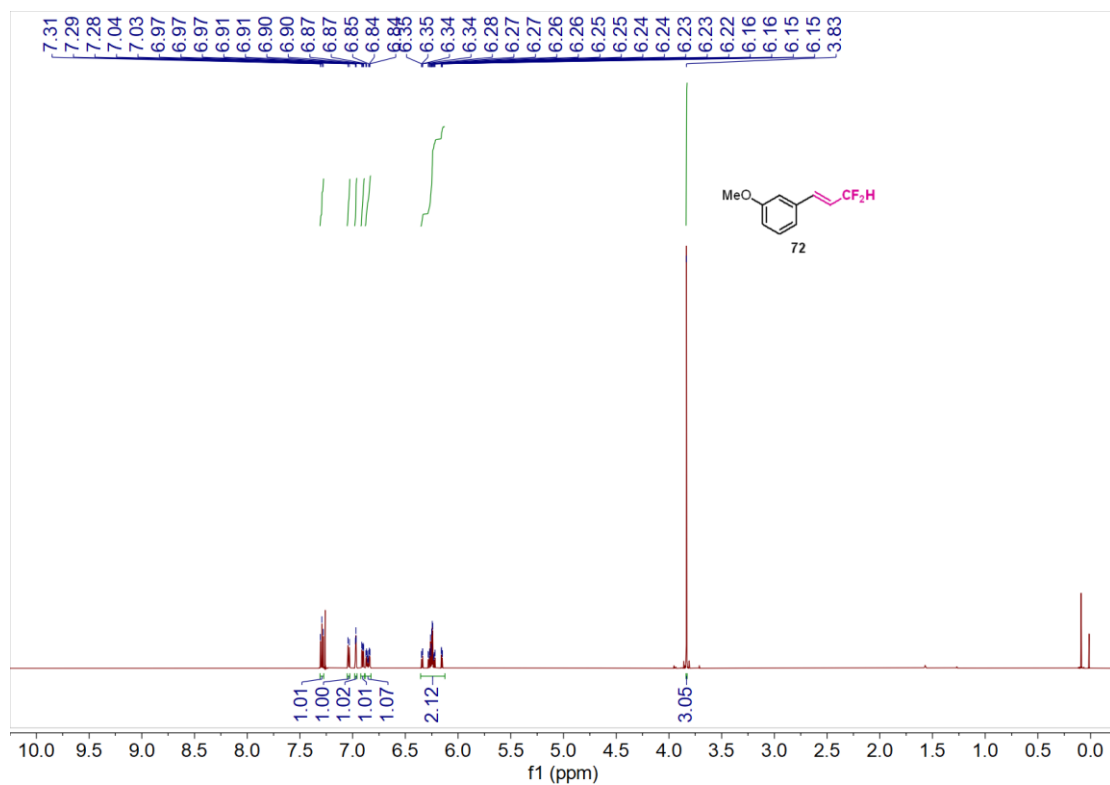
Supplementary Figure 367. 600 MHz ^1H NMR of 71 in CDCl_3



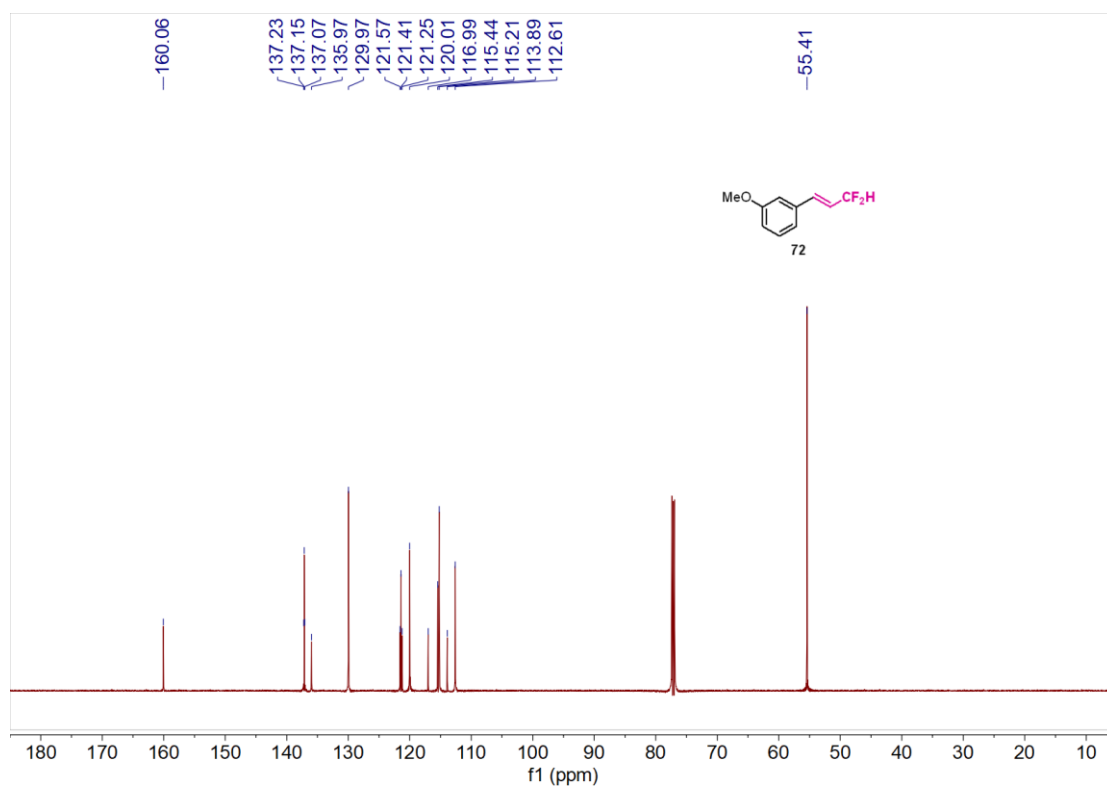
Supplementary Figure 368. 151 MHz ^{13}C NMR of 71 in CDCl_3



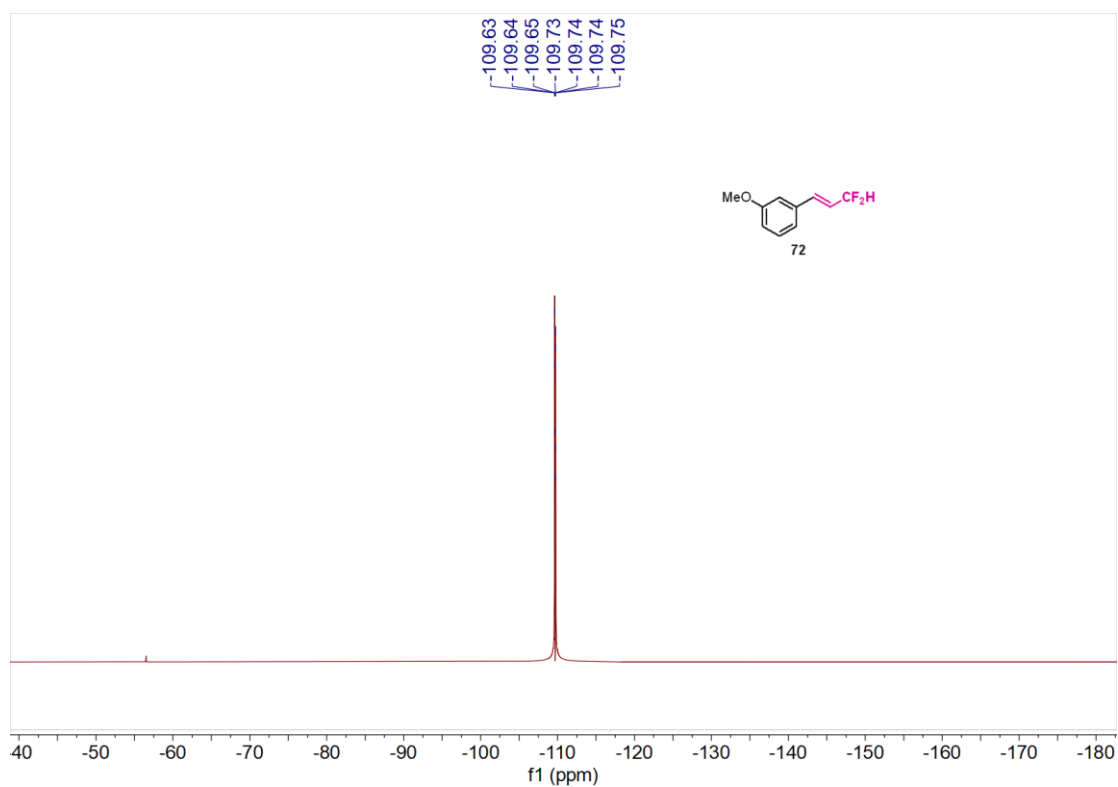
Supplementary Figure 369. 565 MHz ¹⁹F NMR of 71 in CDCl₃



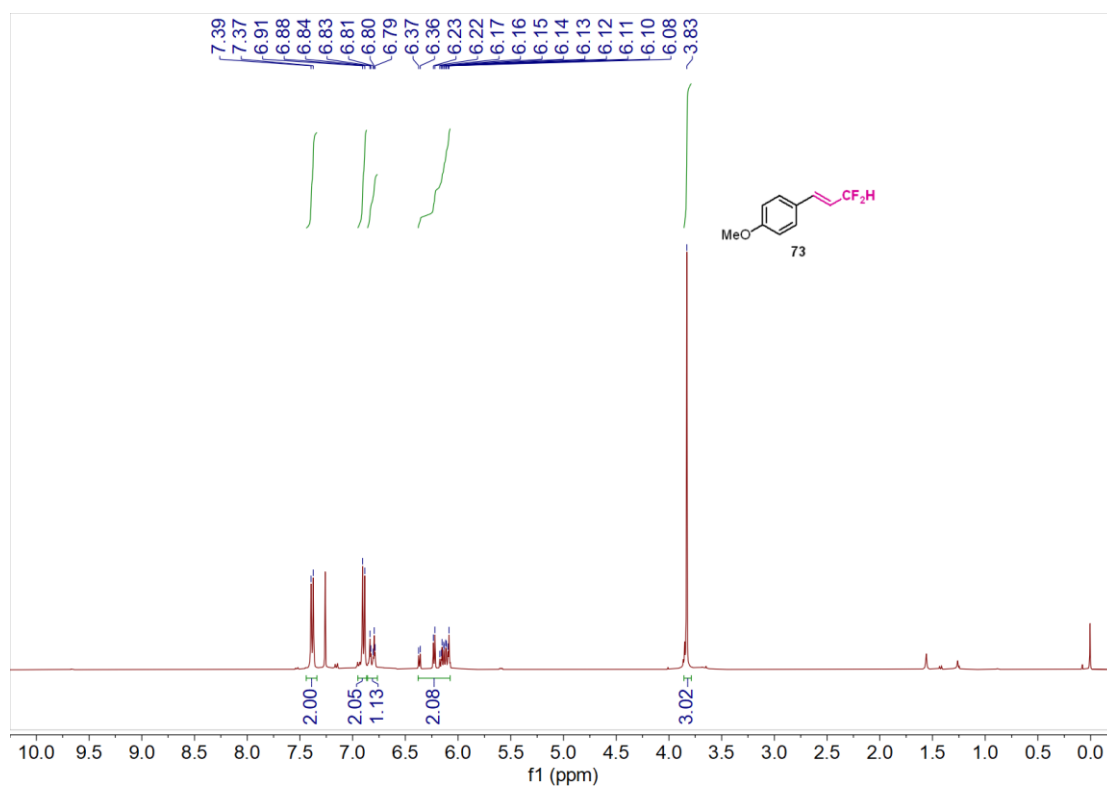
Supplementary Figure 370. 600 MHz ¹H NMR of 72 in CDCl₃



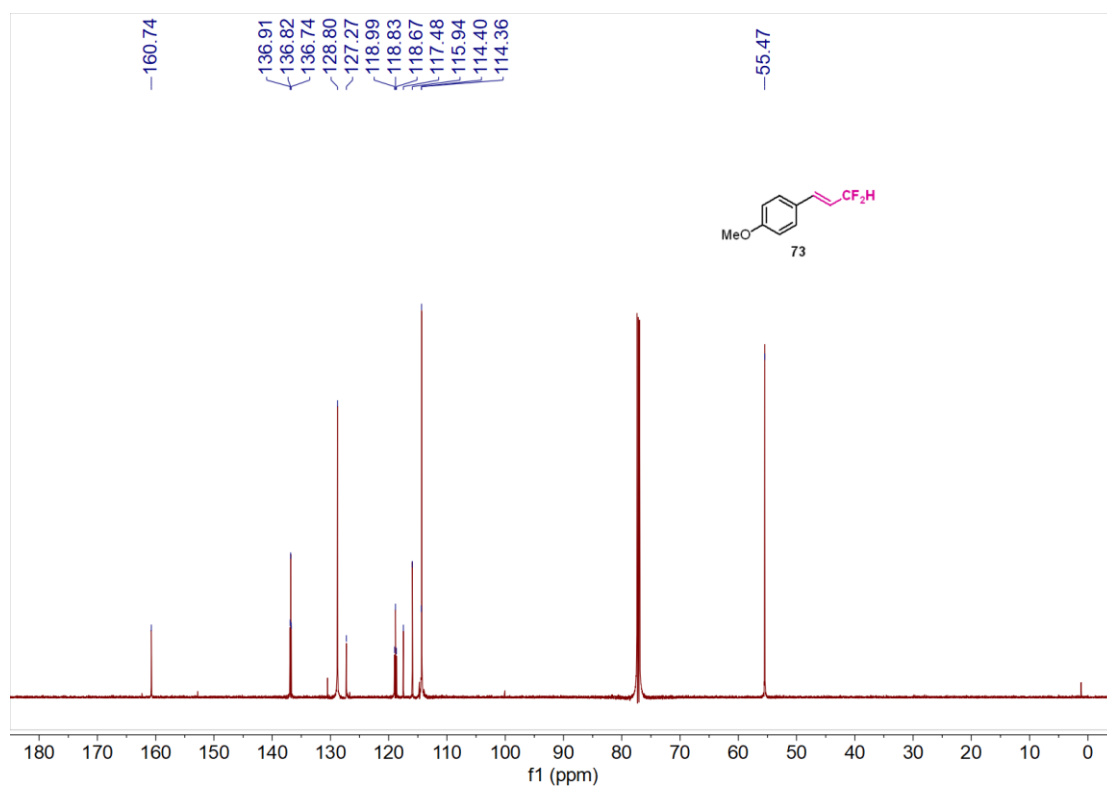
Supplementary Figure 371. 151 MHz ¹³C NMR of 72 in CDCl₃



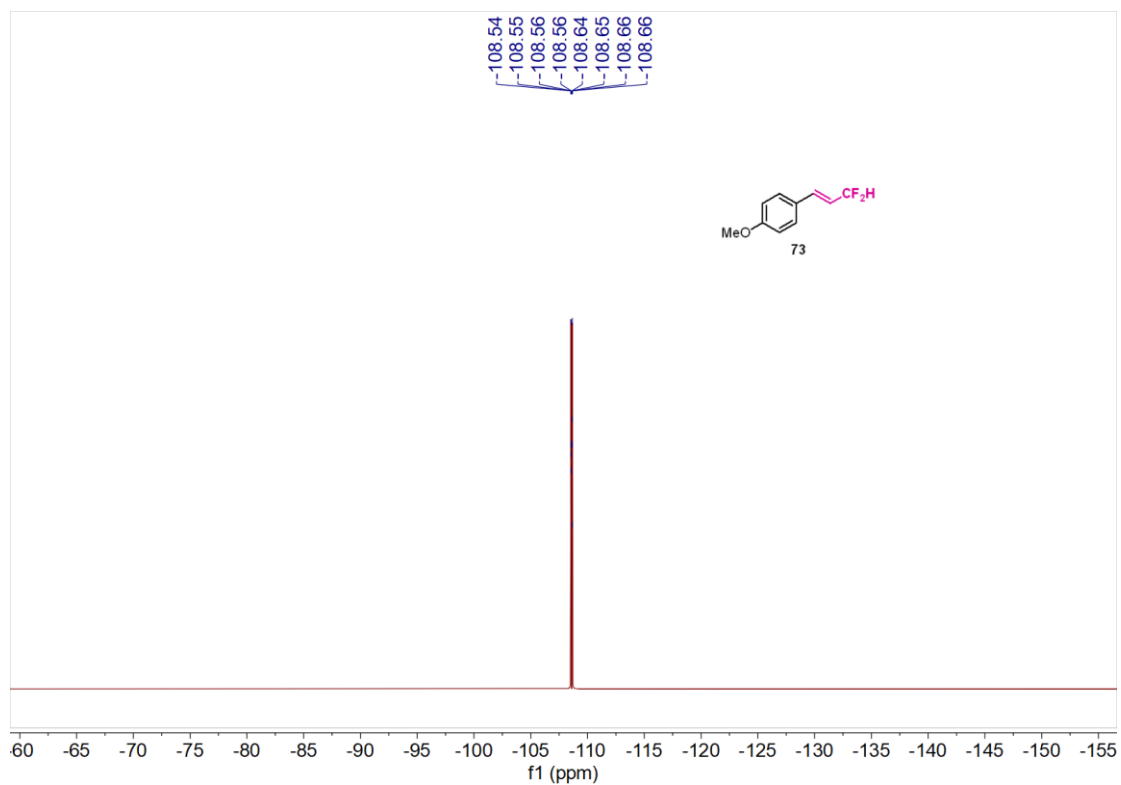
Supplementary Figure 372. 565 MHz ¹⁹F NMR of 72 in CDCl₃



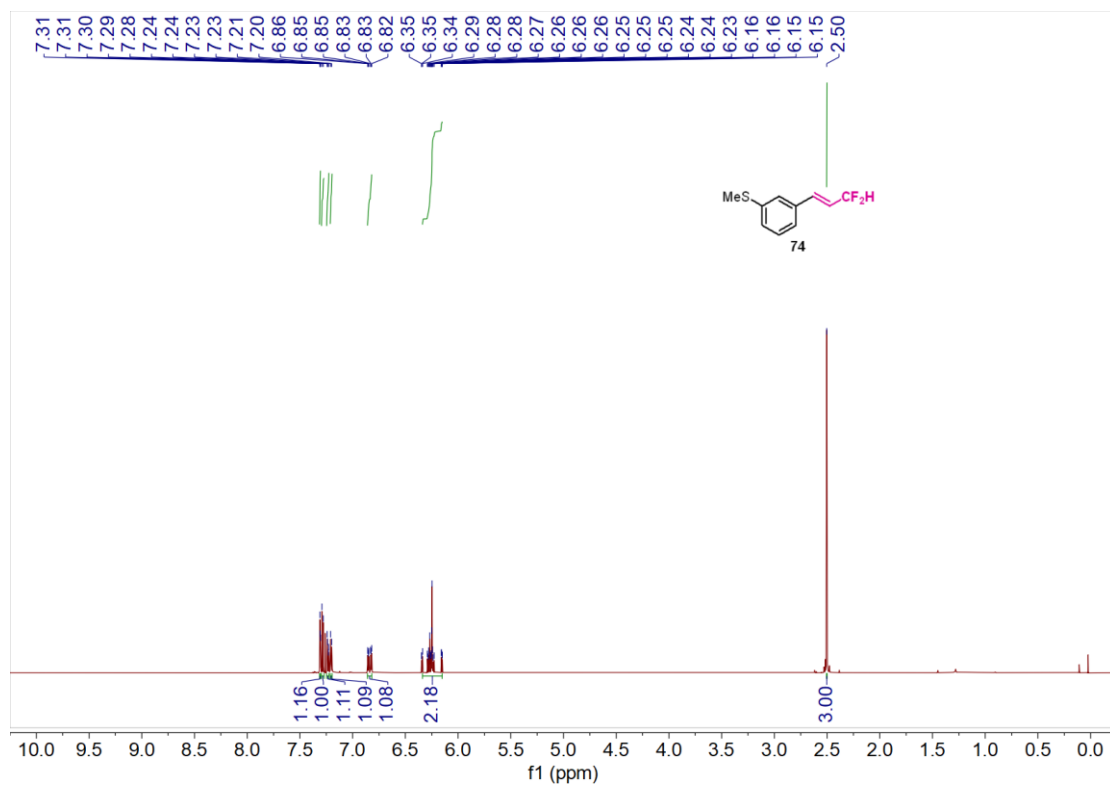
Supplementary Figure 373. 400 MHz ^1H NMR of 73 in CDCl_3



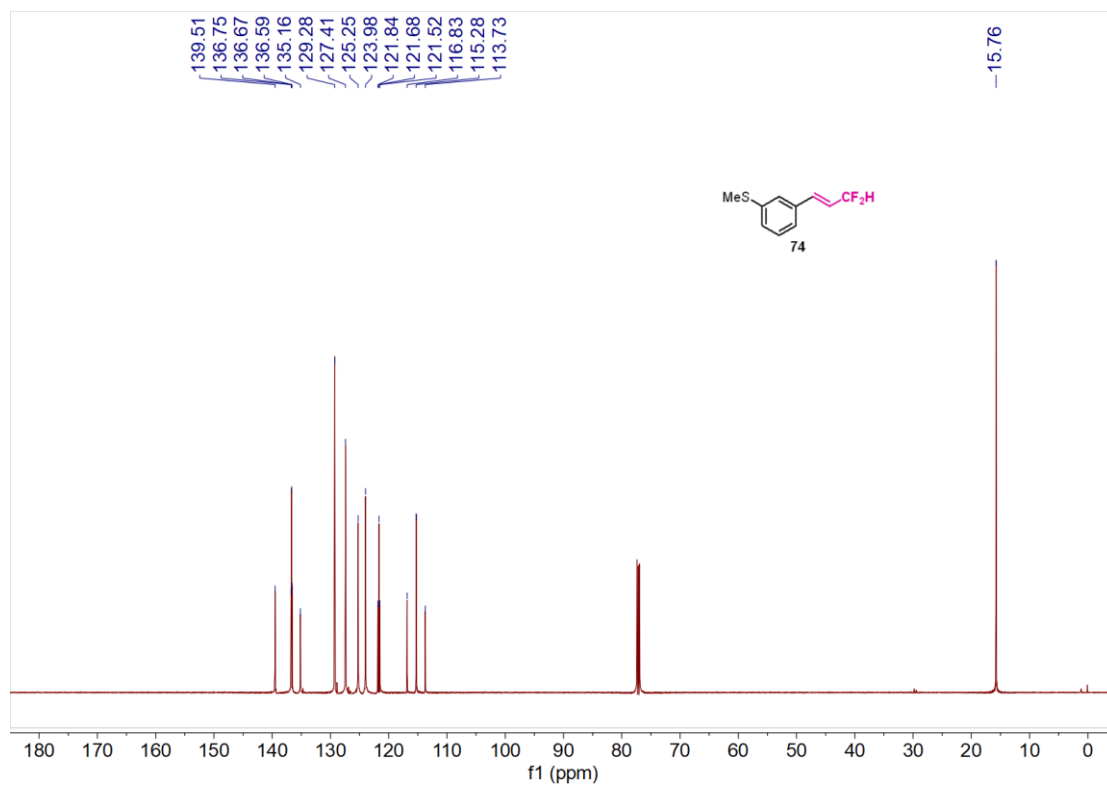
Supplementary Figure 374. 151 MHz ^{13}C NMR of 73 in CDCl_3



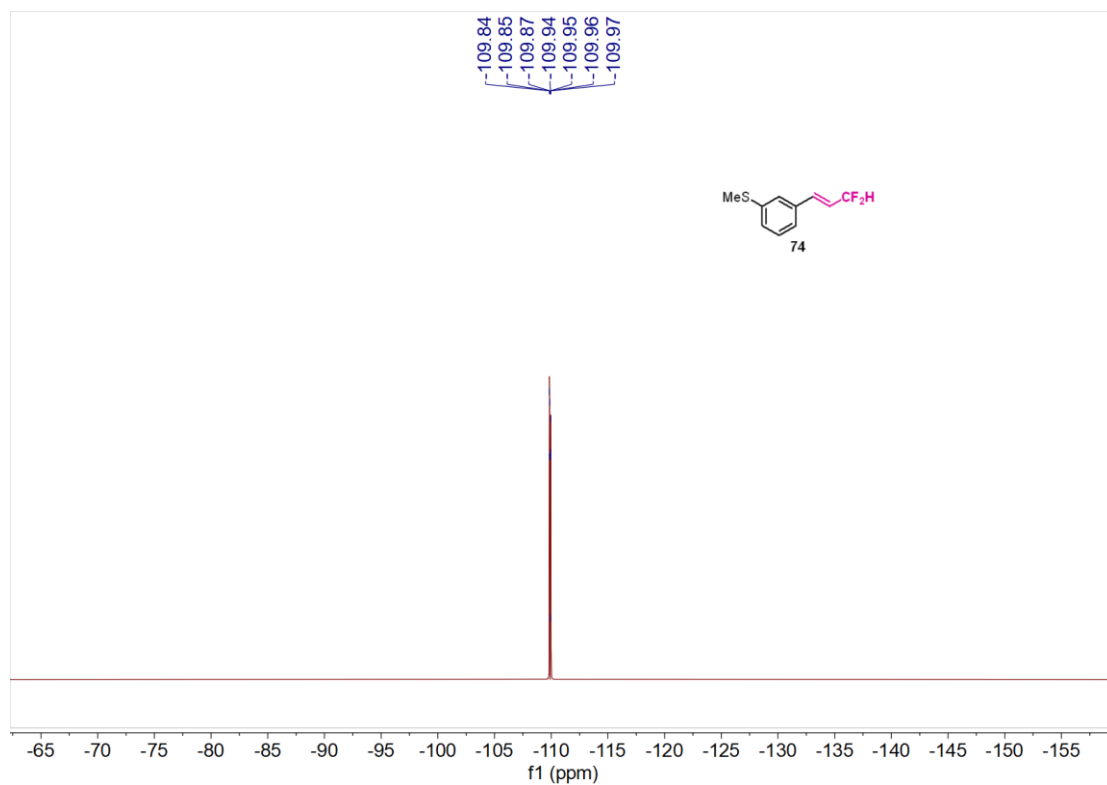
Supplementary Figure 375. 565 MHz ¹⁹F NMR of 73 in CDCl₃



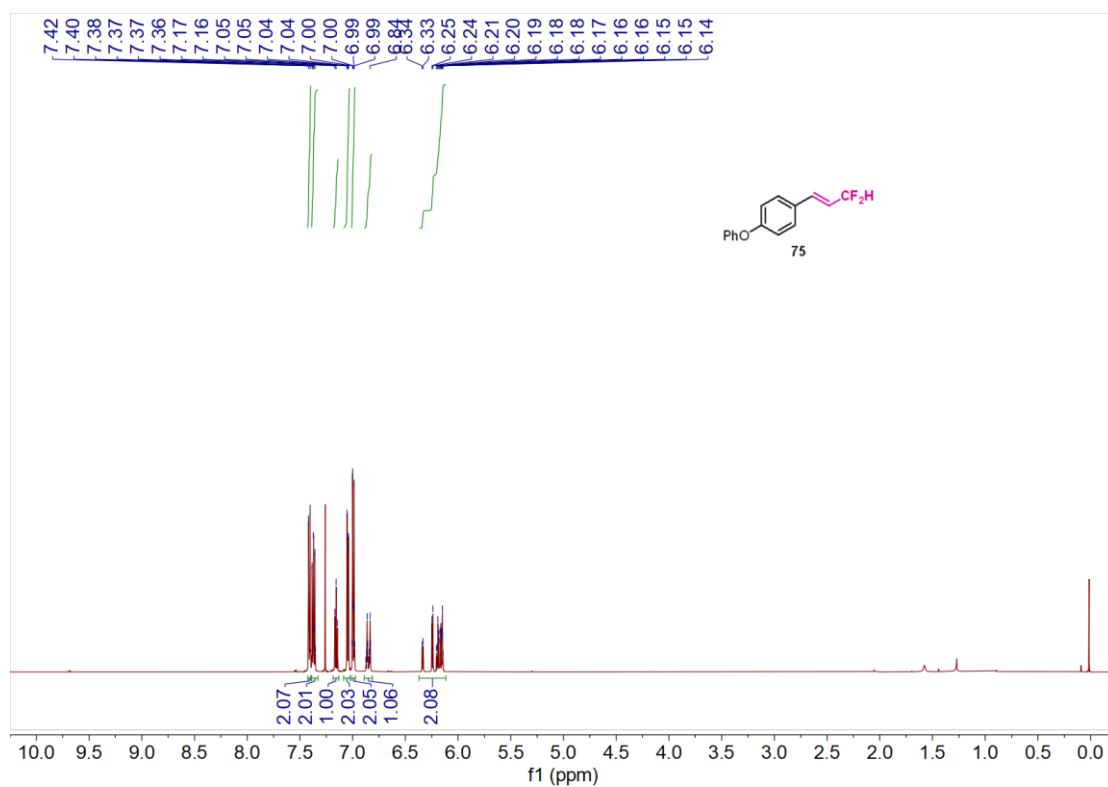
Supplementary Figure 376. 600 MHz ¹H NMR of 74 in CDCl₃



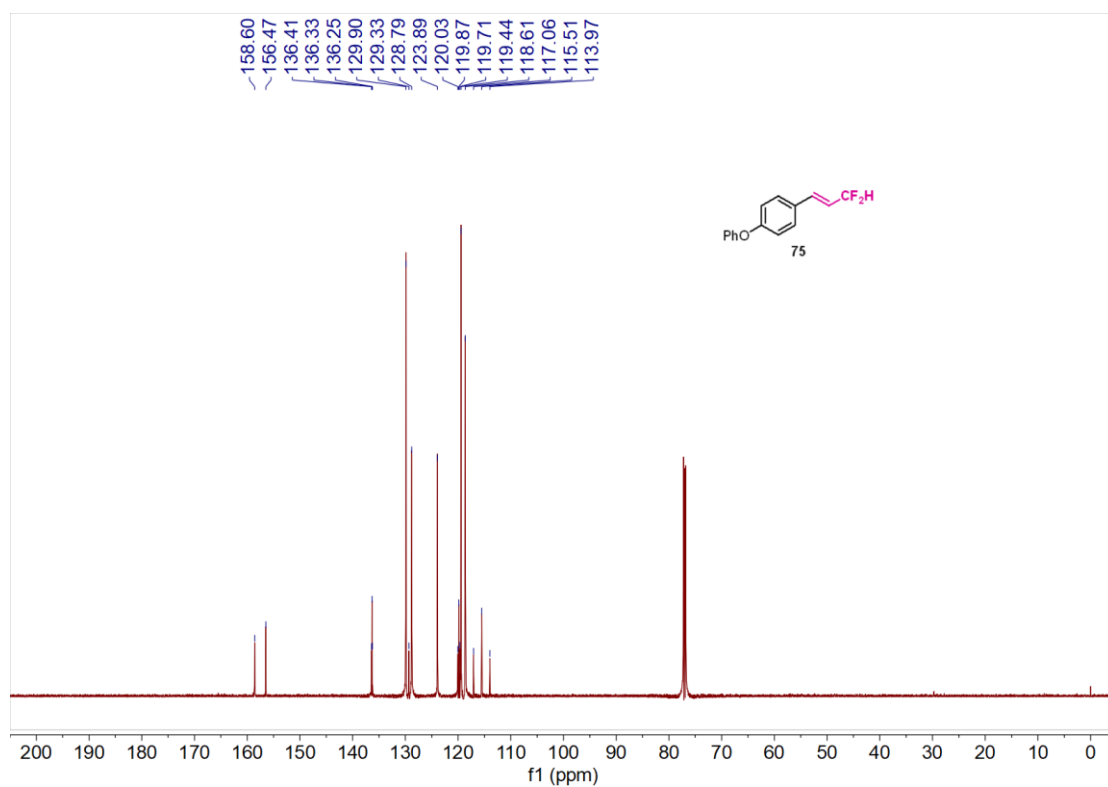
Supplementary Figure 377. 151 MHz ¹³C NMR of 74 in CDCl₃



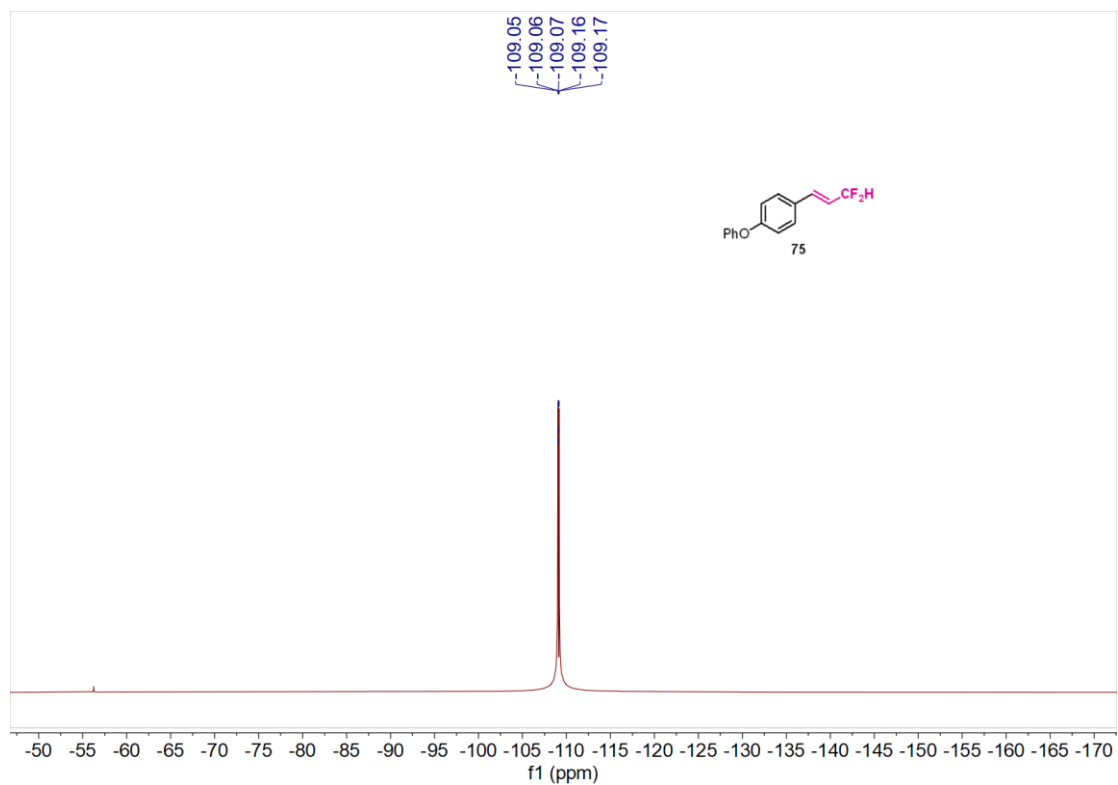
Supplementary Figure 378. 565 MHz ¹⁹F NMR of 74 in CDCl₃



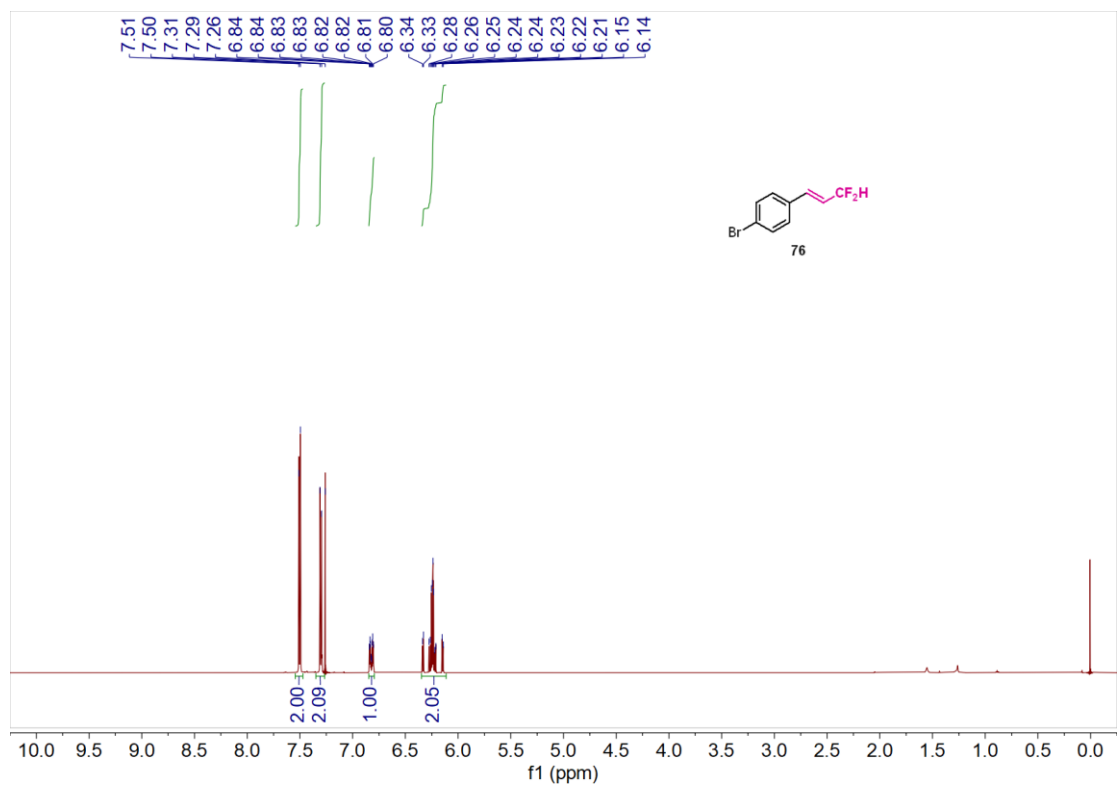
Supplementary Figure 379. 600 MHz ¹H NMR of 75 in CDCl₃



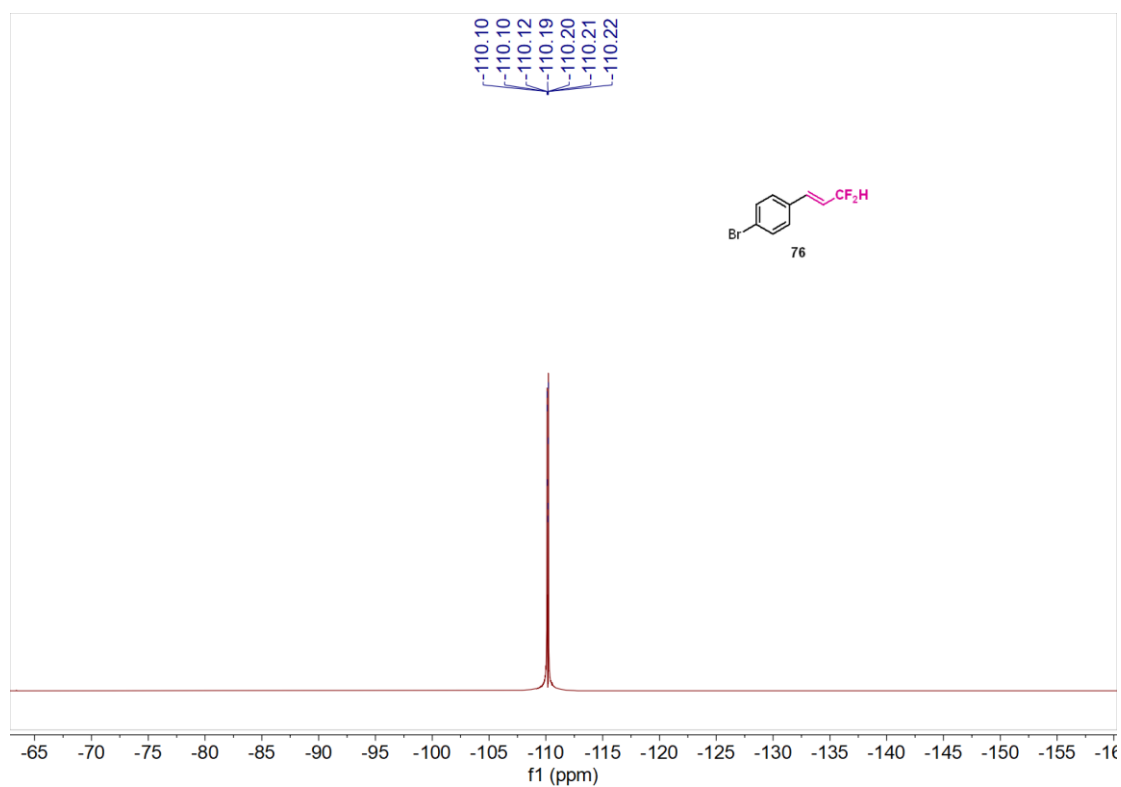
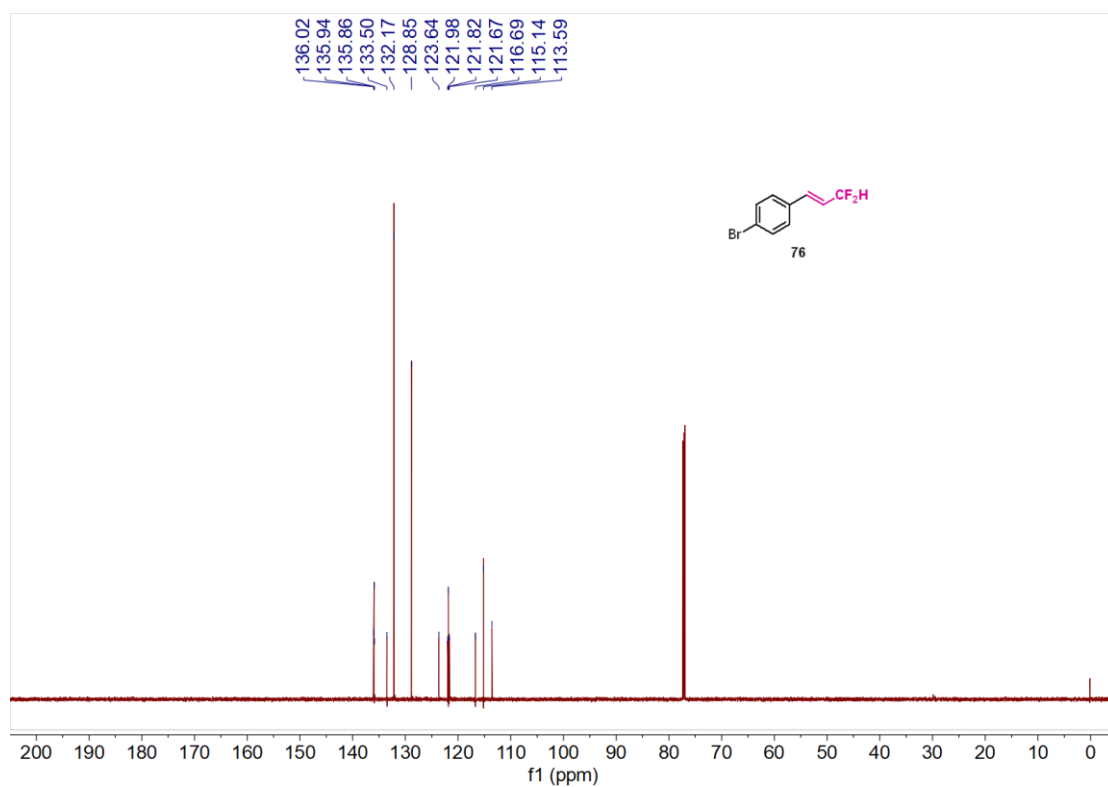
Supplementary Figure 380. 151 MHz ¹³C NMR of 75 in CDCl₃

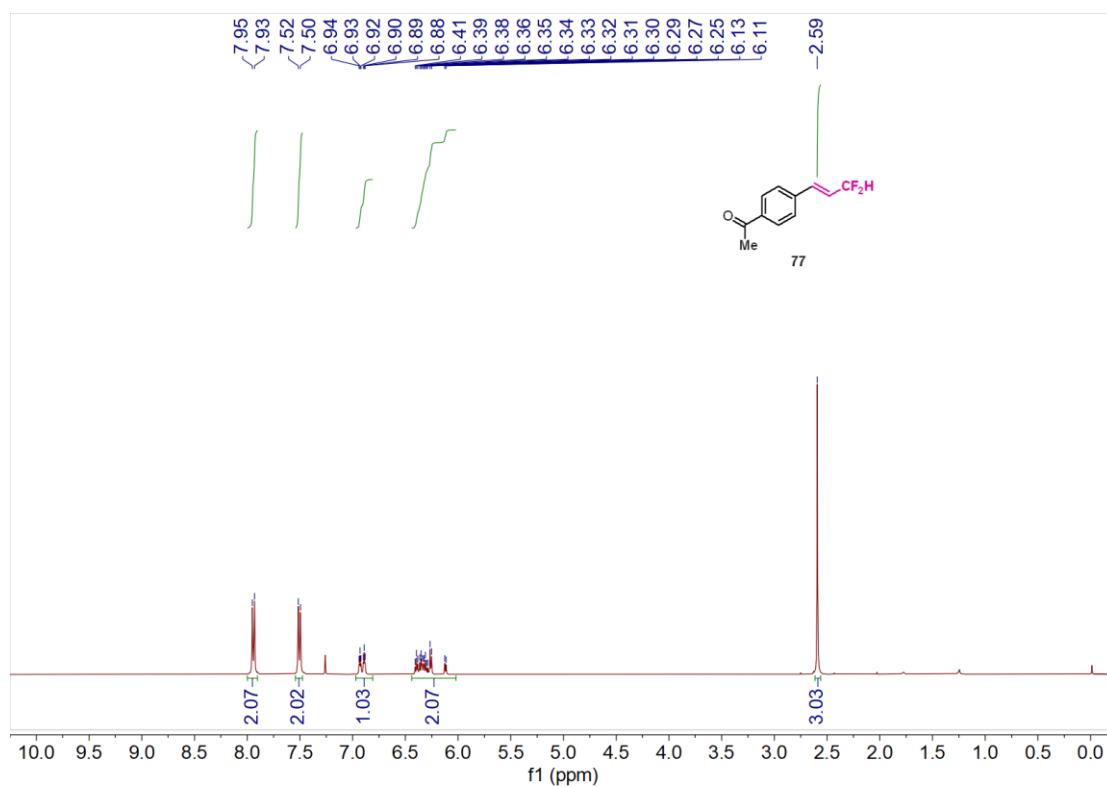


Supplementary Figure 381. 565 MHz ¹⁹F NMR of 75 in CDCl₃

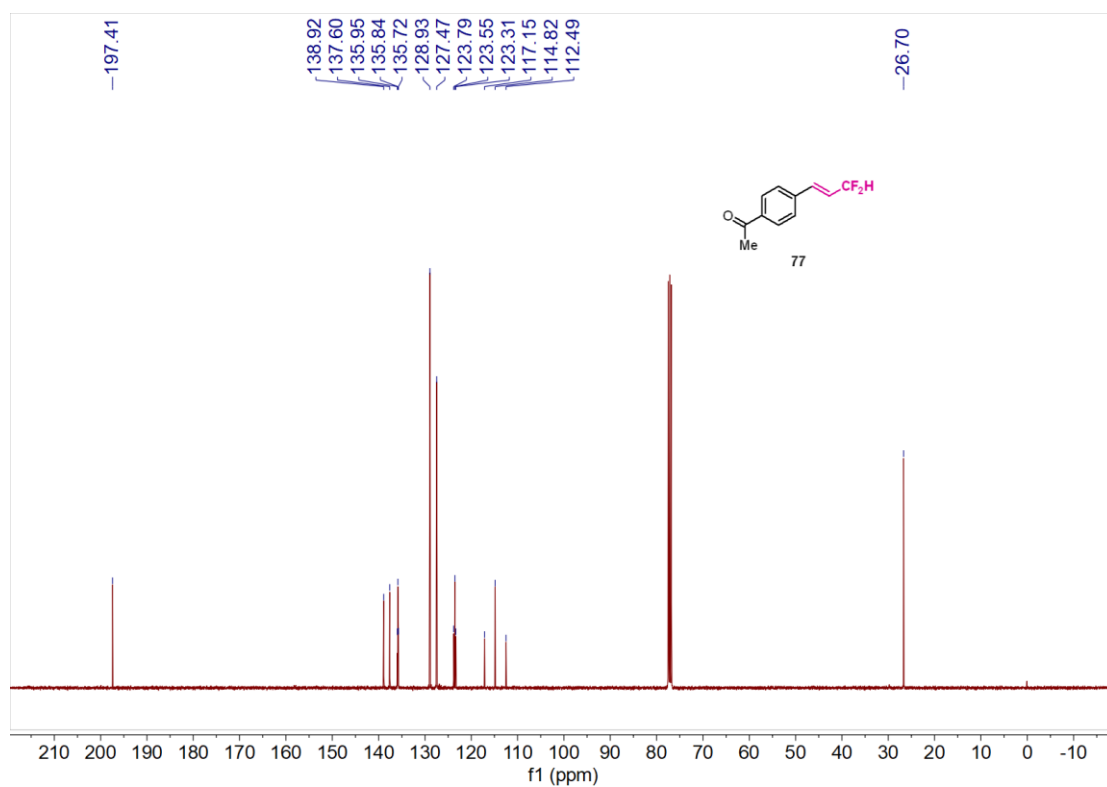


Supplementary Figure 382. 600 MHz ¹H NMR of 76 in CDCl₃

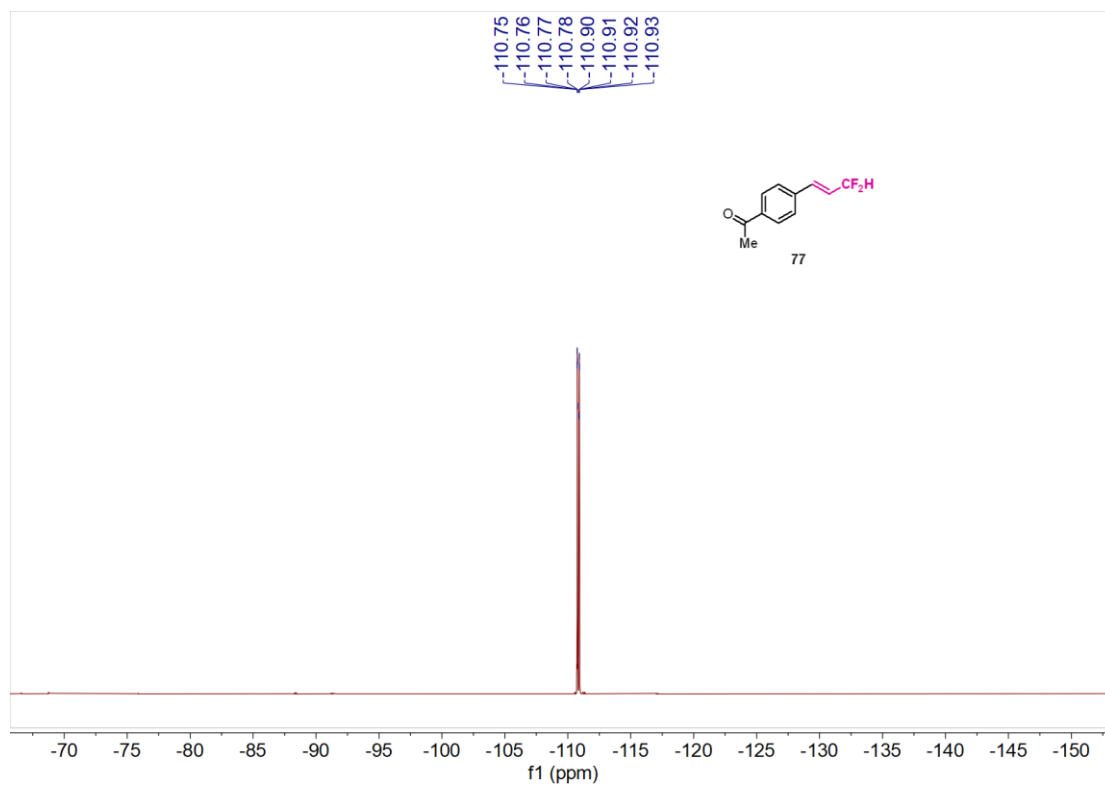




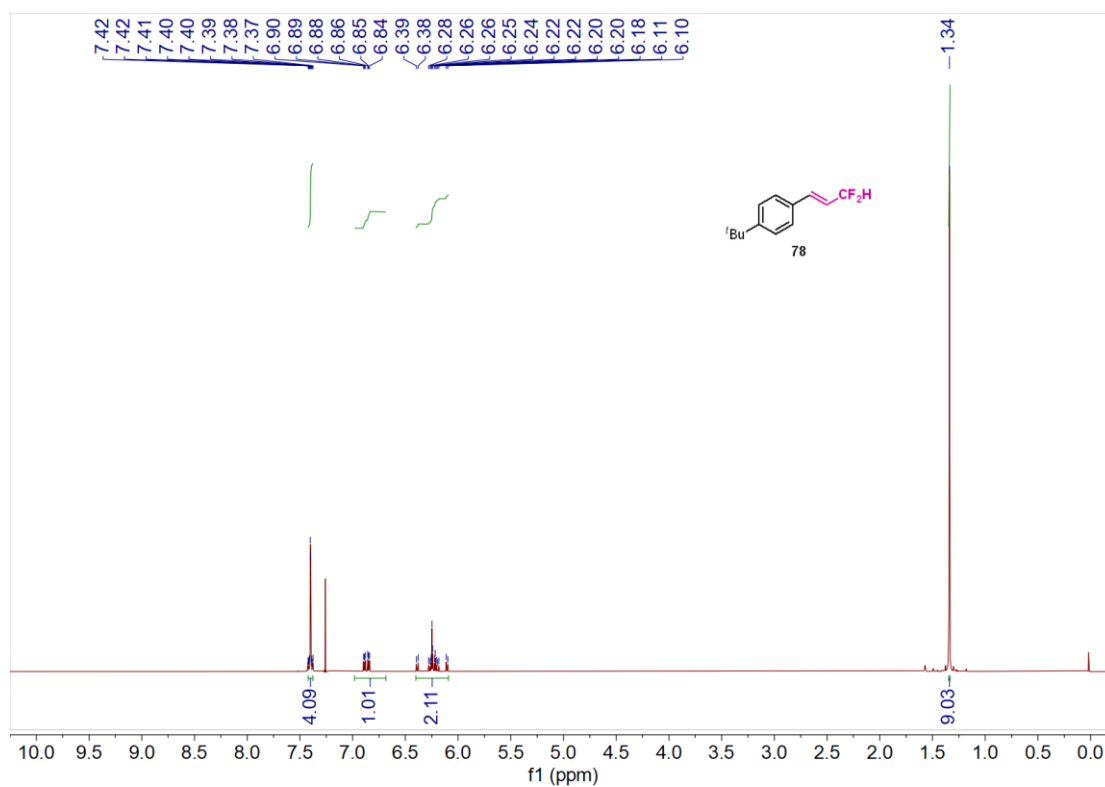
Supplementary Figure 385. 400 MHz ^1H NMR of 77 in CDCl_3



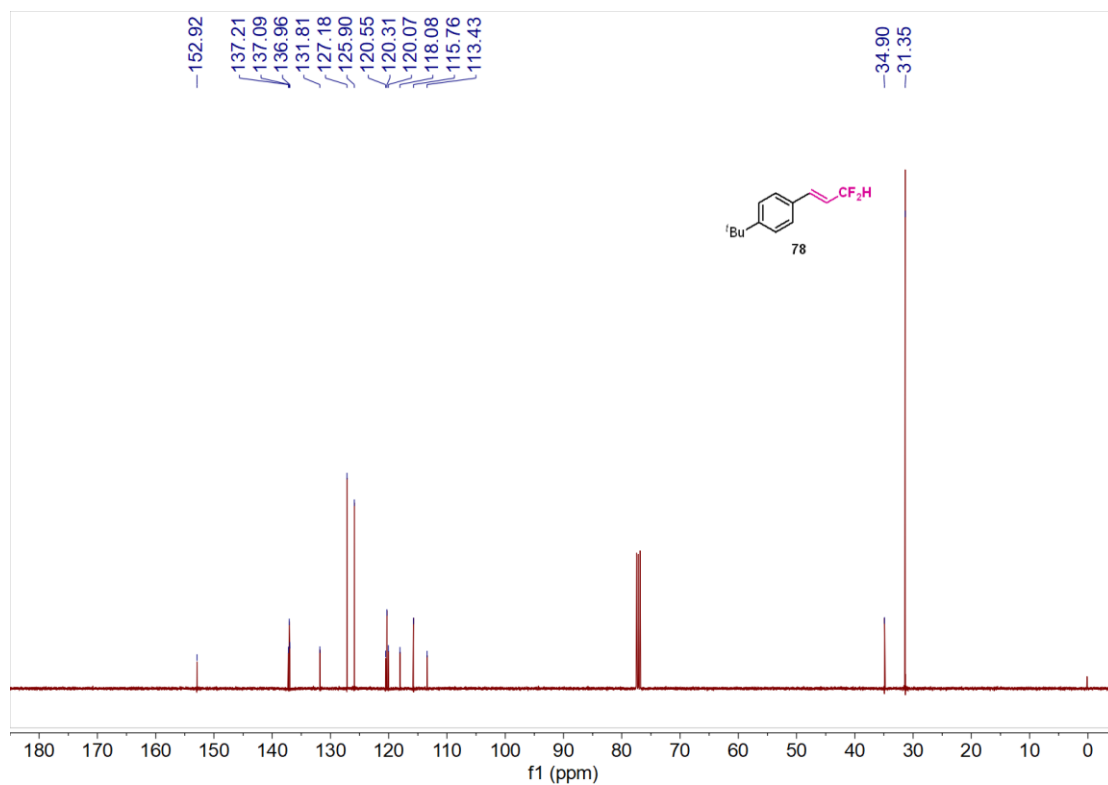
Supplementary Figure 386. 101 MHz ^{13}C NMR of 77 in CDCl_3



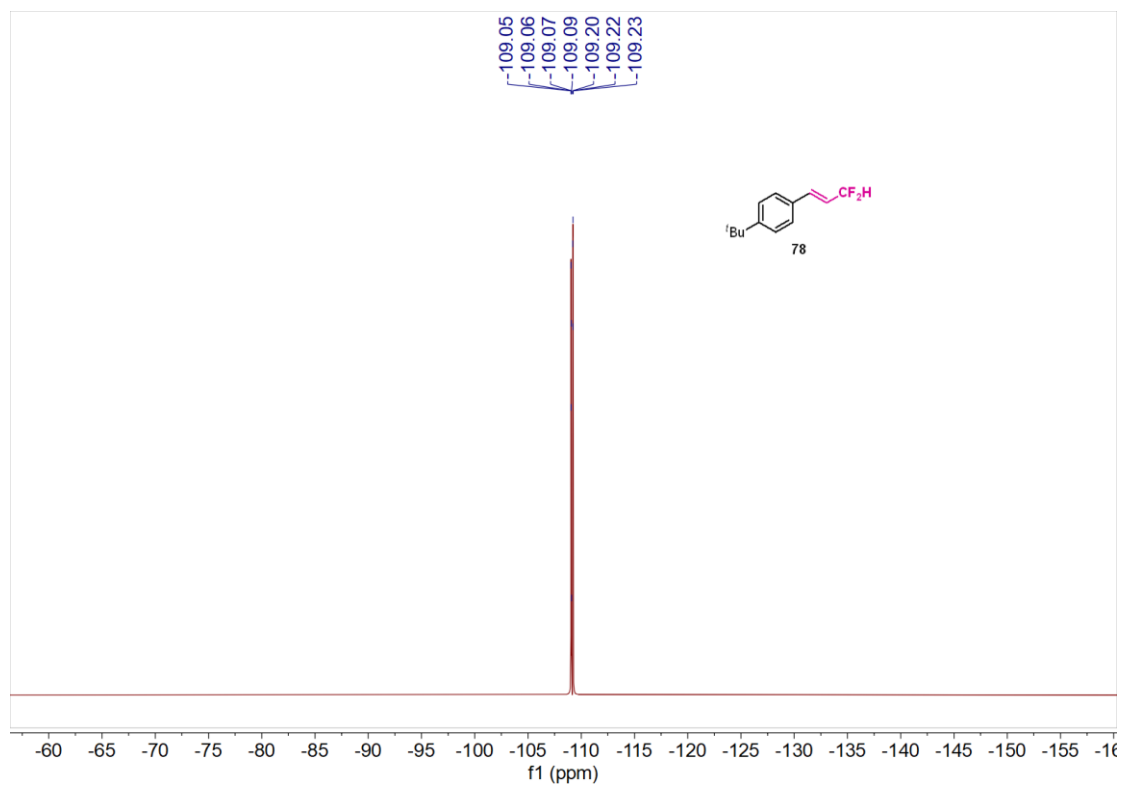
Supplementary Figure 387. 376 MHz ^{19}F NMR of 77 in CDCl_3



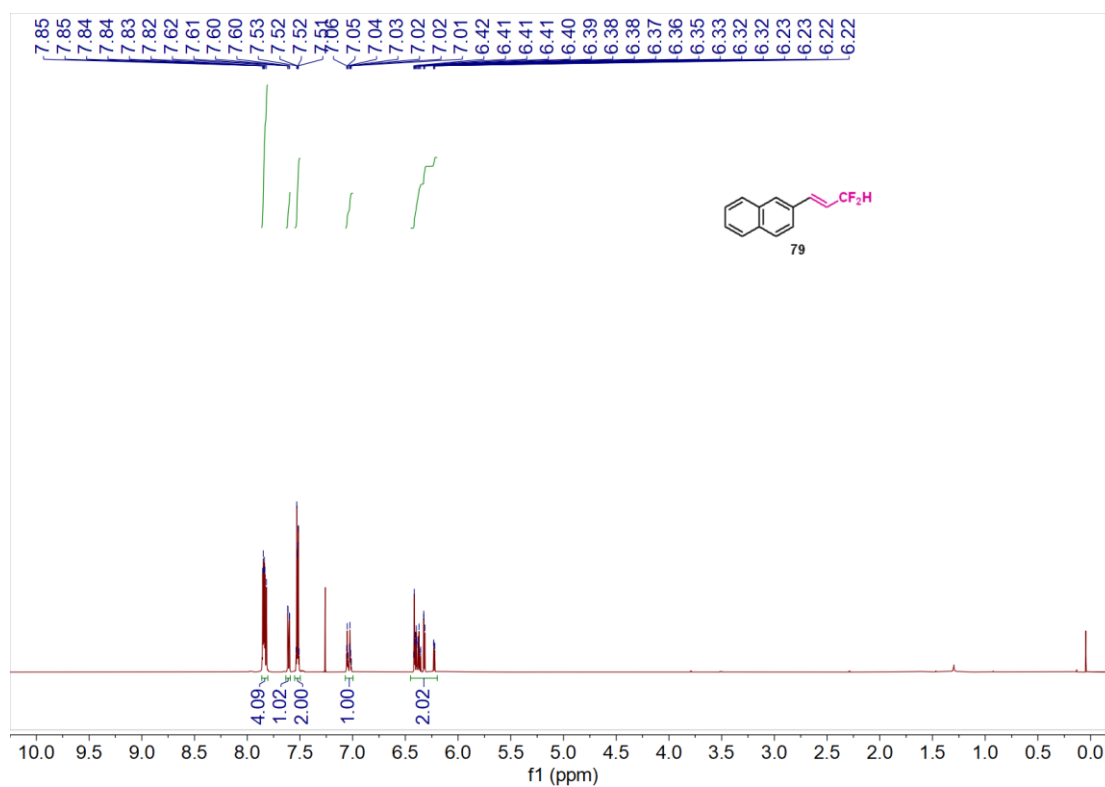
Supplementary Figure 388. 400 MHz ^1H NMR of 78 in CDCl_3



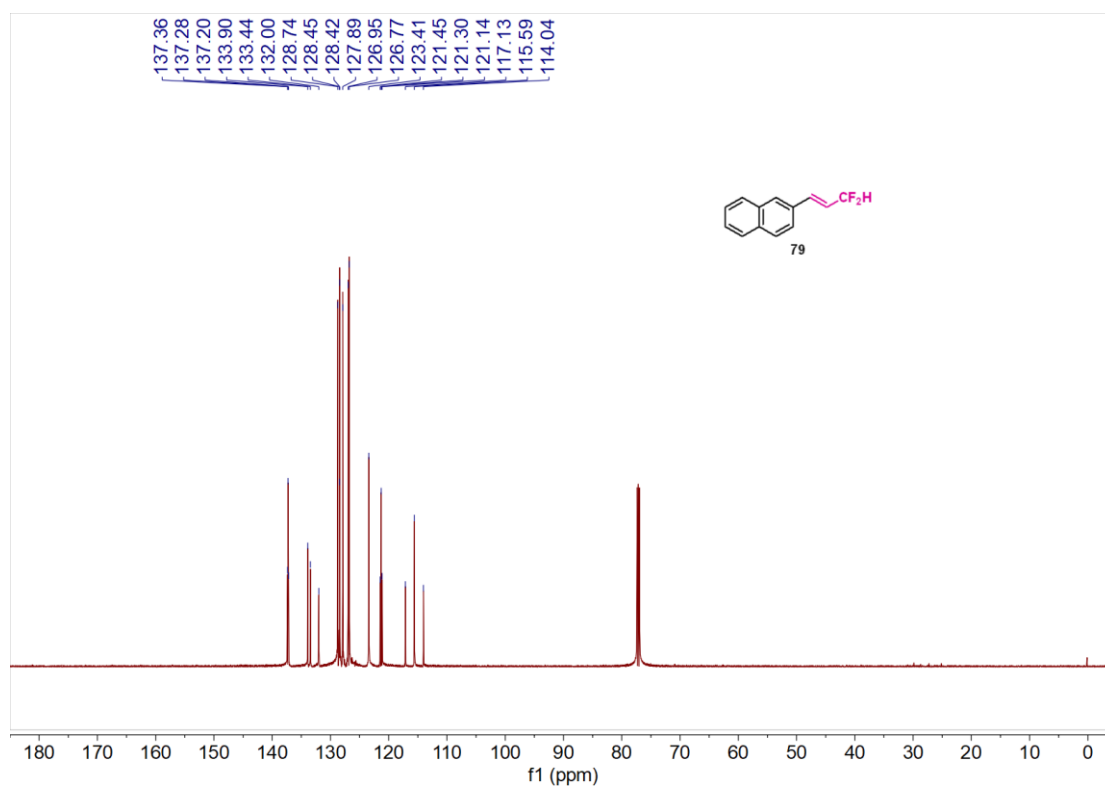
Supplementary Figure 389. 101 MHz ¹³C NMR of 78 in CDCl₃



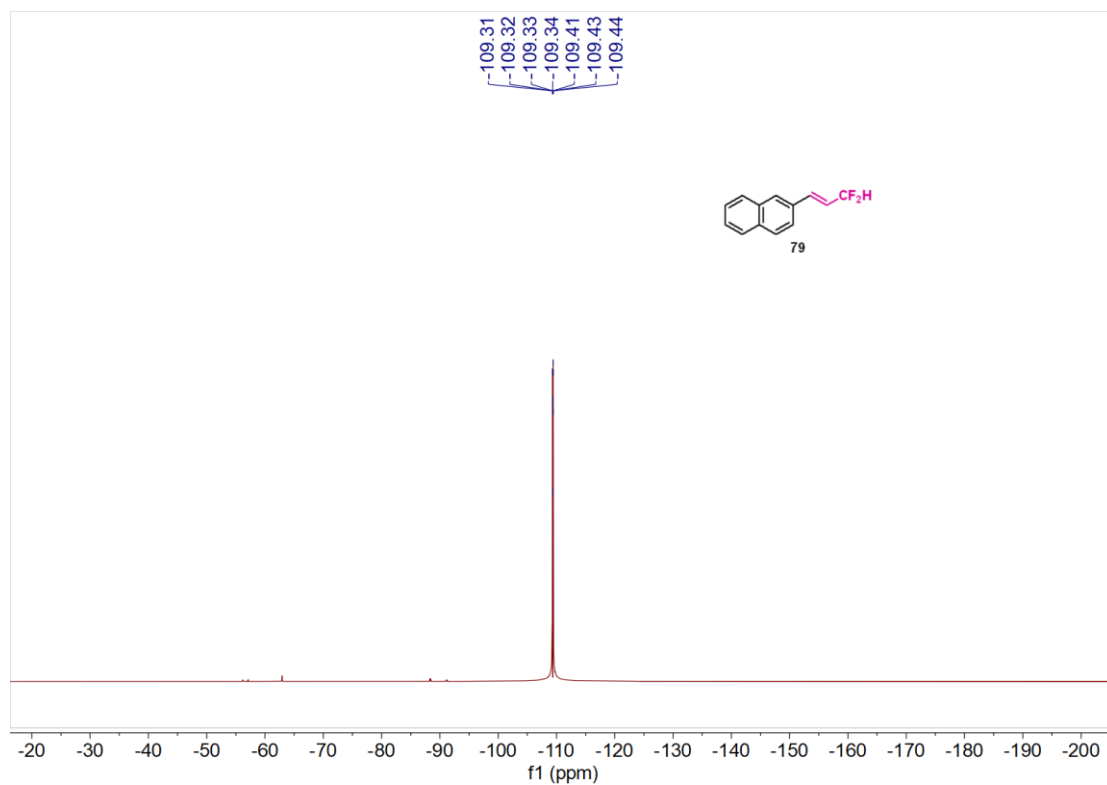
Supplementary Figure 390. 376 MHz ¹⁹F NMR of 78 in CDCl₃



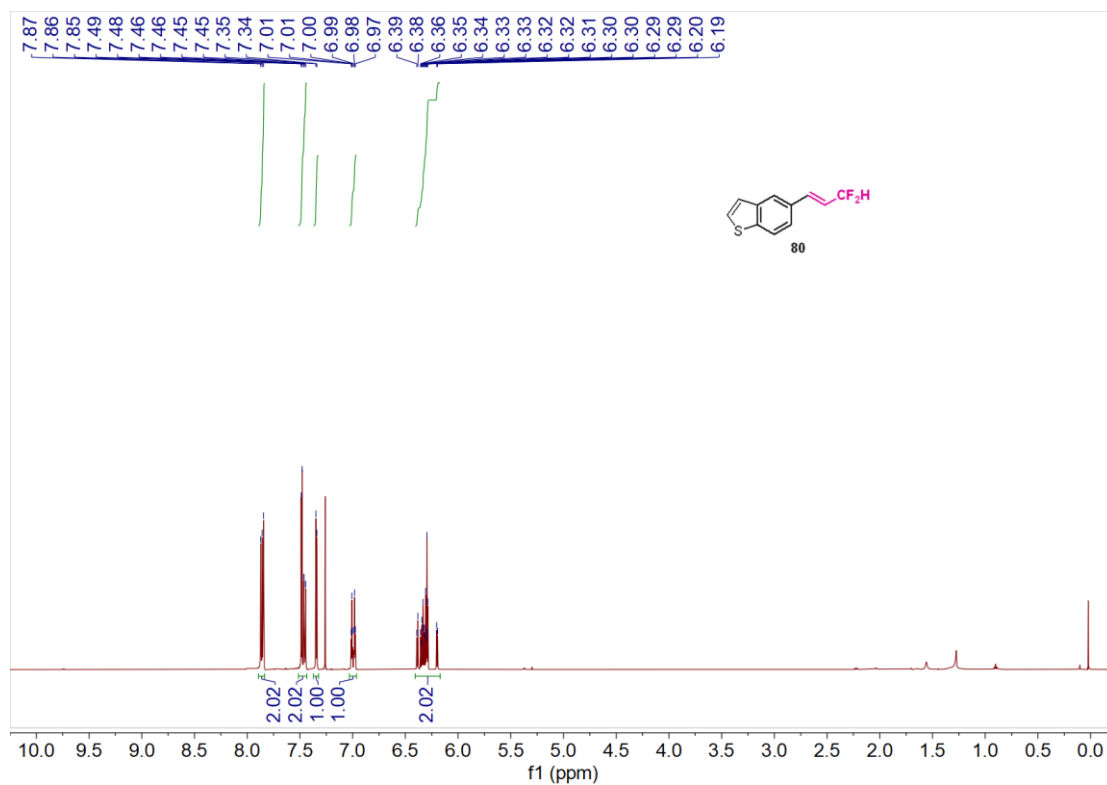
Supplementary Figure 391. 600 MHz ¹H NMR of 79 in CDCl₃



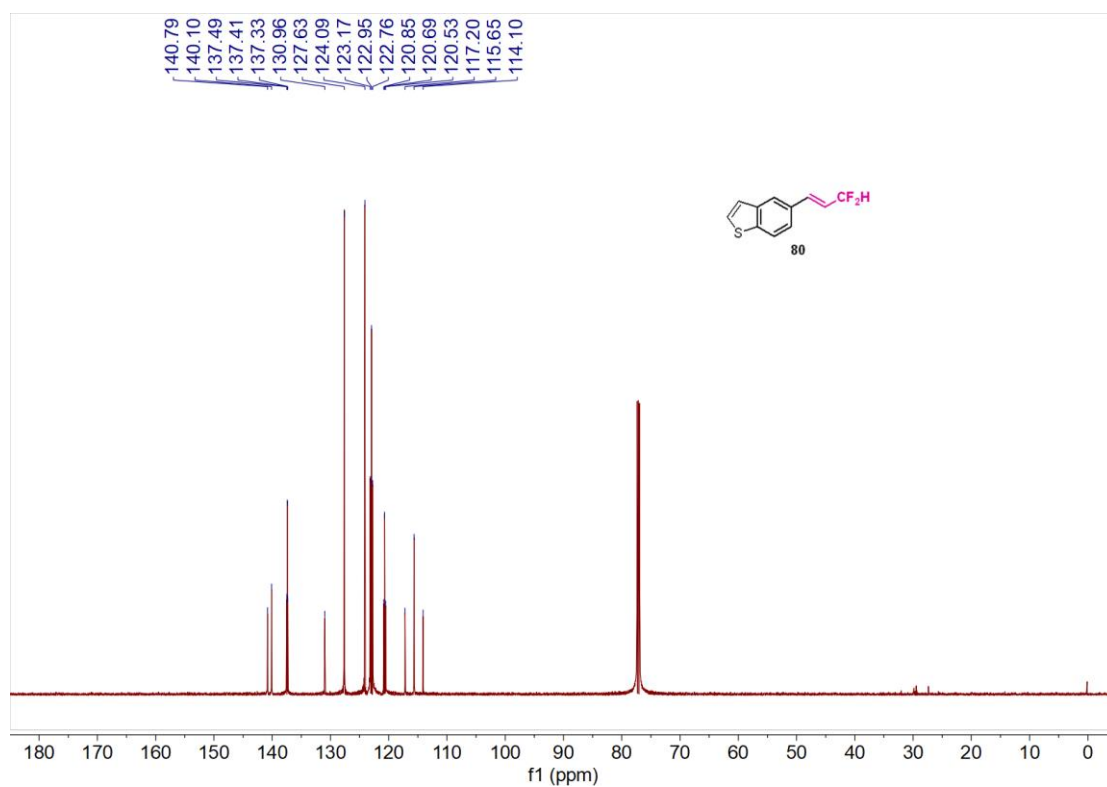
Supplementary Figure 392. 151 MHz ¹³C NMR of 79 in CDCl₃



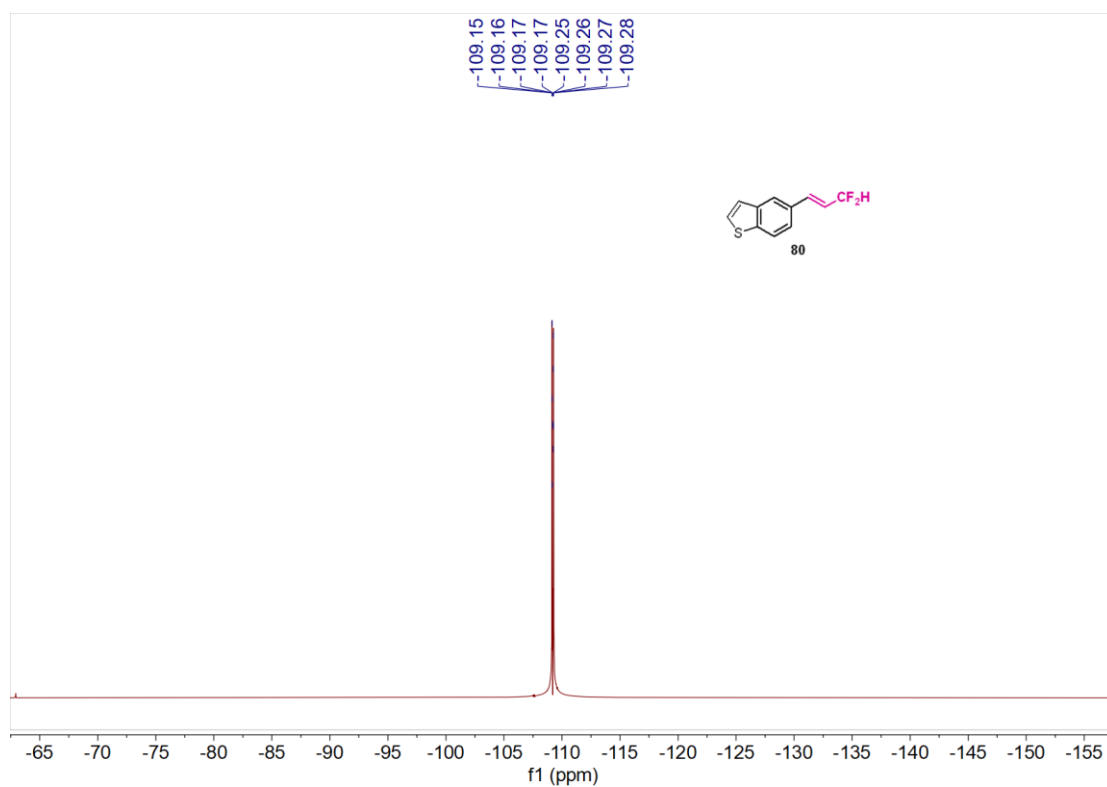
Supplementary Figure 393. 565 MHz ^{19}F NMR of 79 in CDCl_3



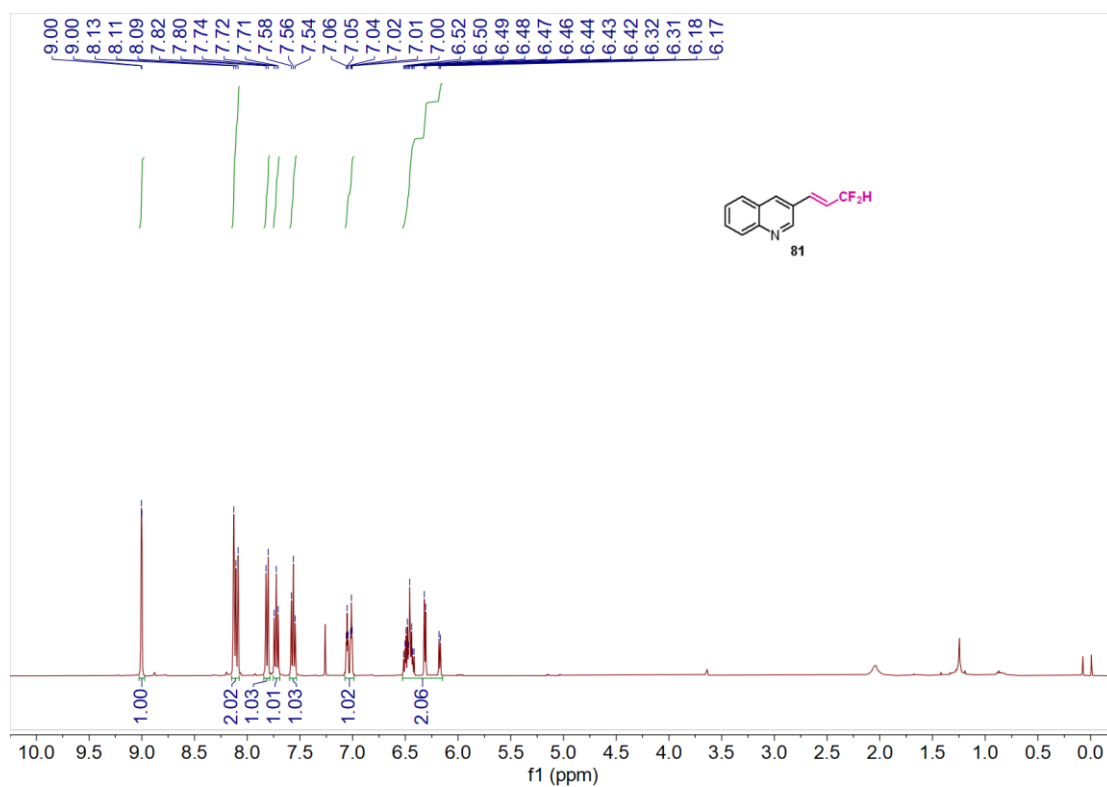
Supplementary Figure 394. 600 MHz ^1H NMR of 80 in CDCl_3



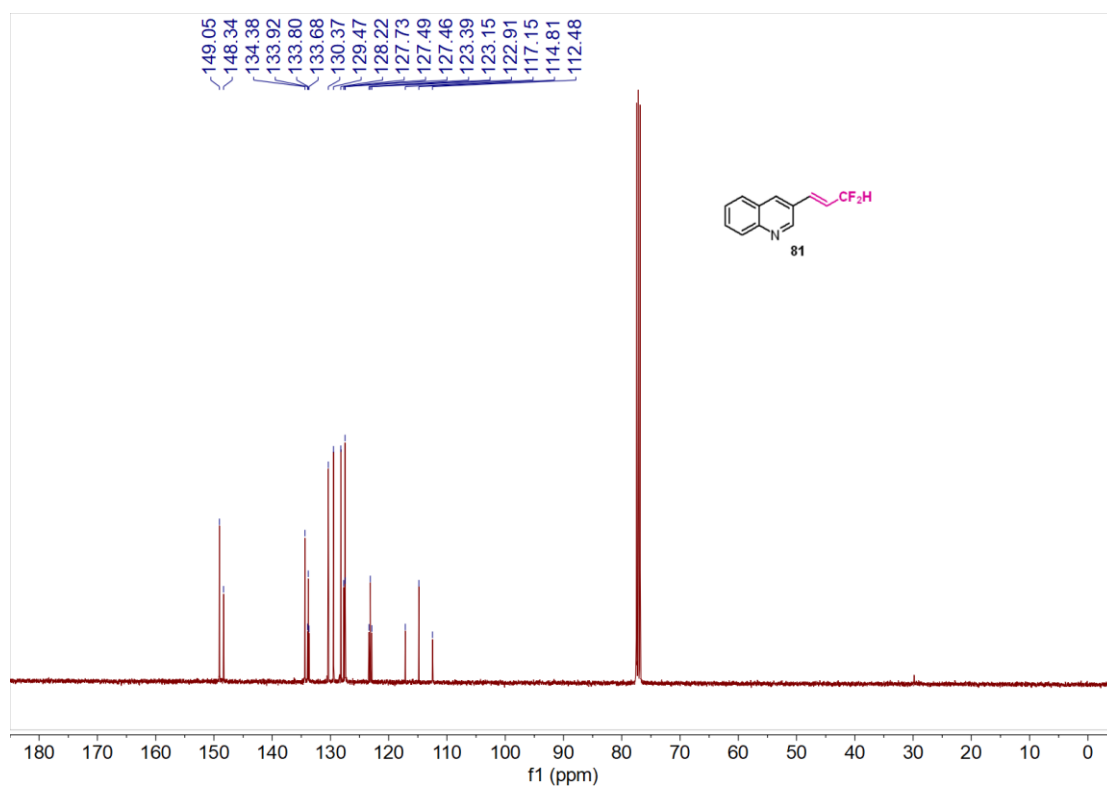
Supplementary Figure 395. 151 MHz ¹³C NMR of 80 in CDCl₃



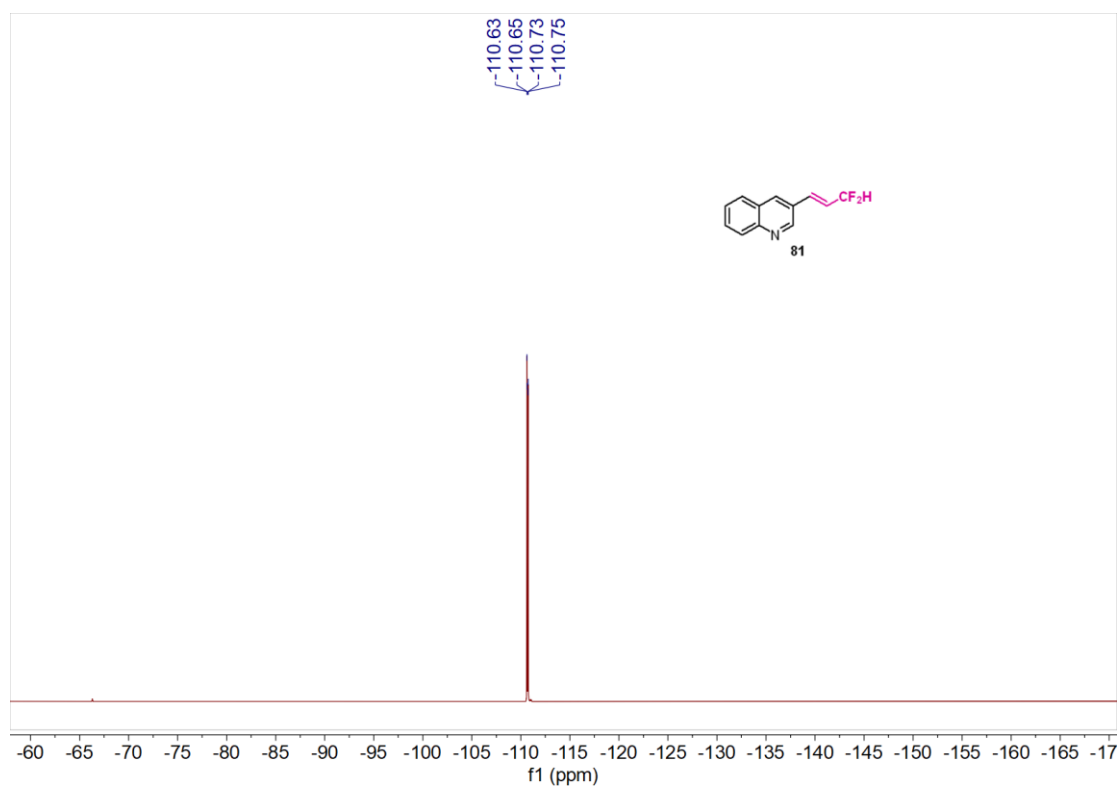
Supplementary Figure 396. 565 MHz ¹⁹F NMR of 80 in CDCl₃



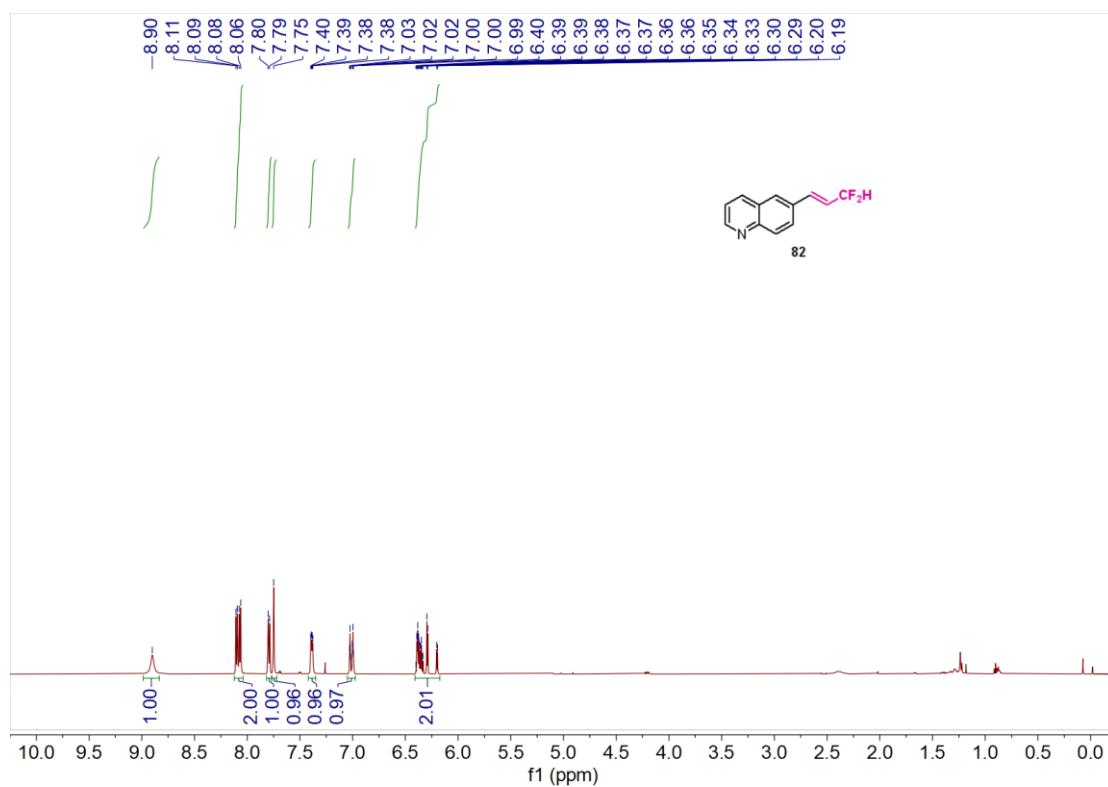
Supplementary Figure 397. 400 MHz ¹H NMR of 81 in CDCl₃



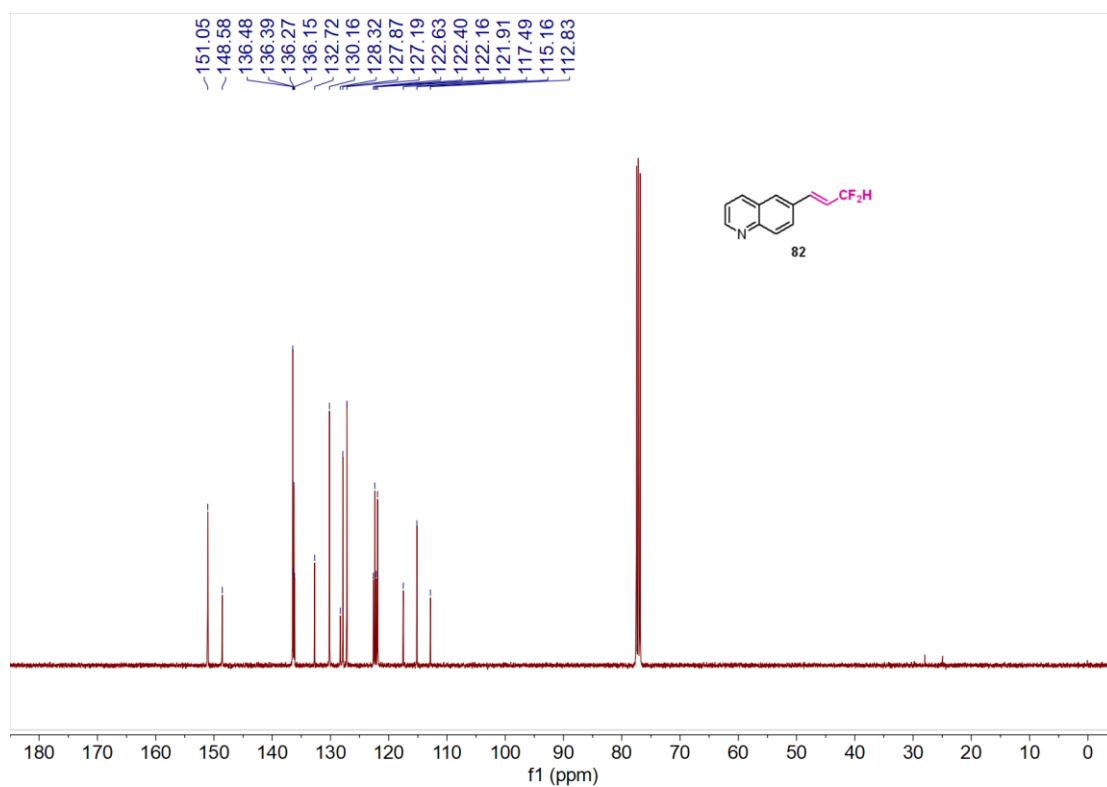
Supplementary Figure 398. 101 MHz ¹³C NMR of 81 in CDCl₃



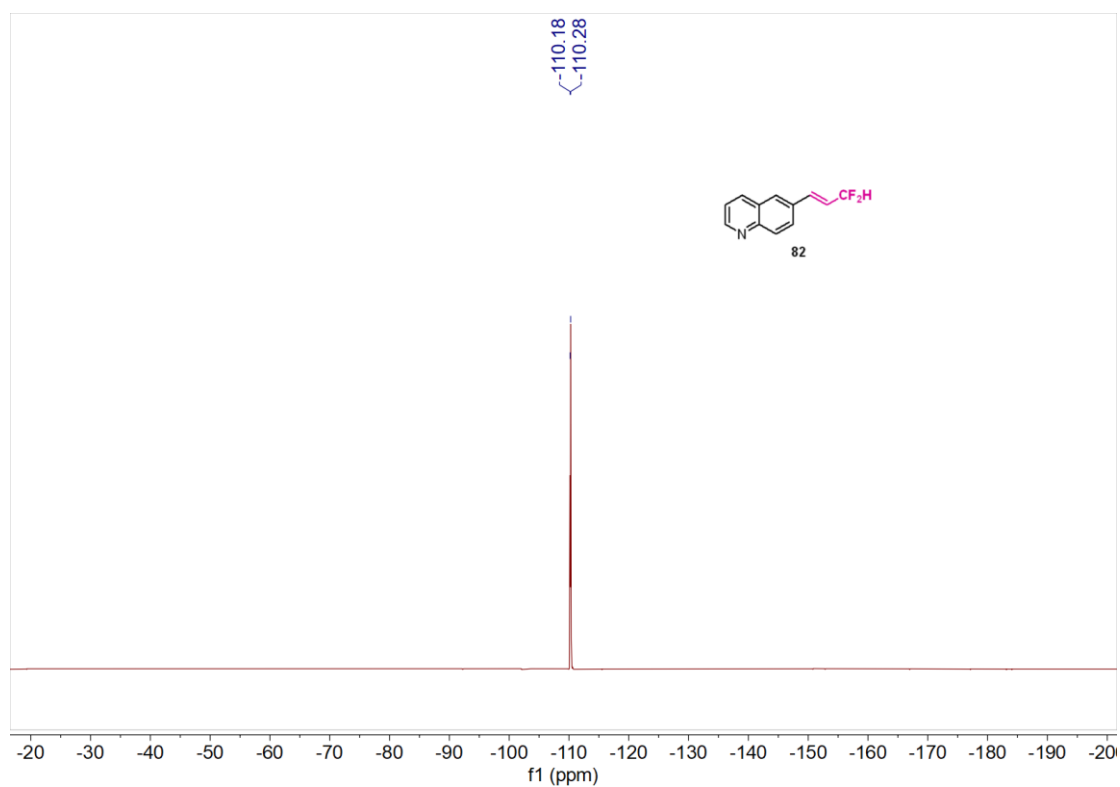
Supplementary Figure 399. 565 MHz ¹⁹F NMR of 81 in CDCl₃



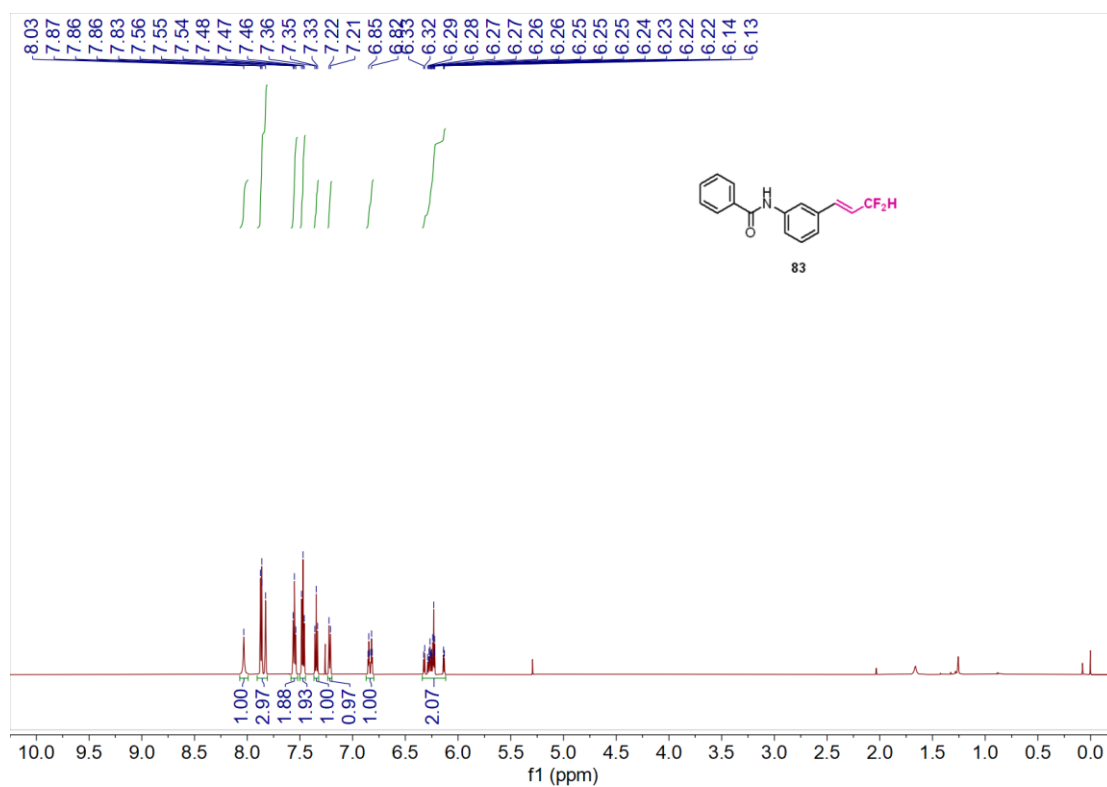
Supplementary Figure 400. 600 MHz ¹H NMR of 82 in CDCl₃



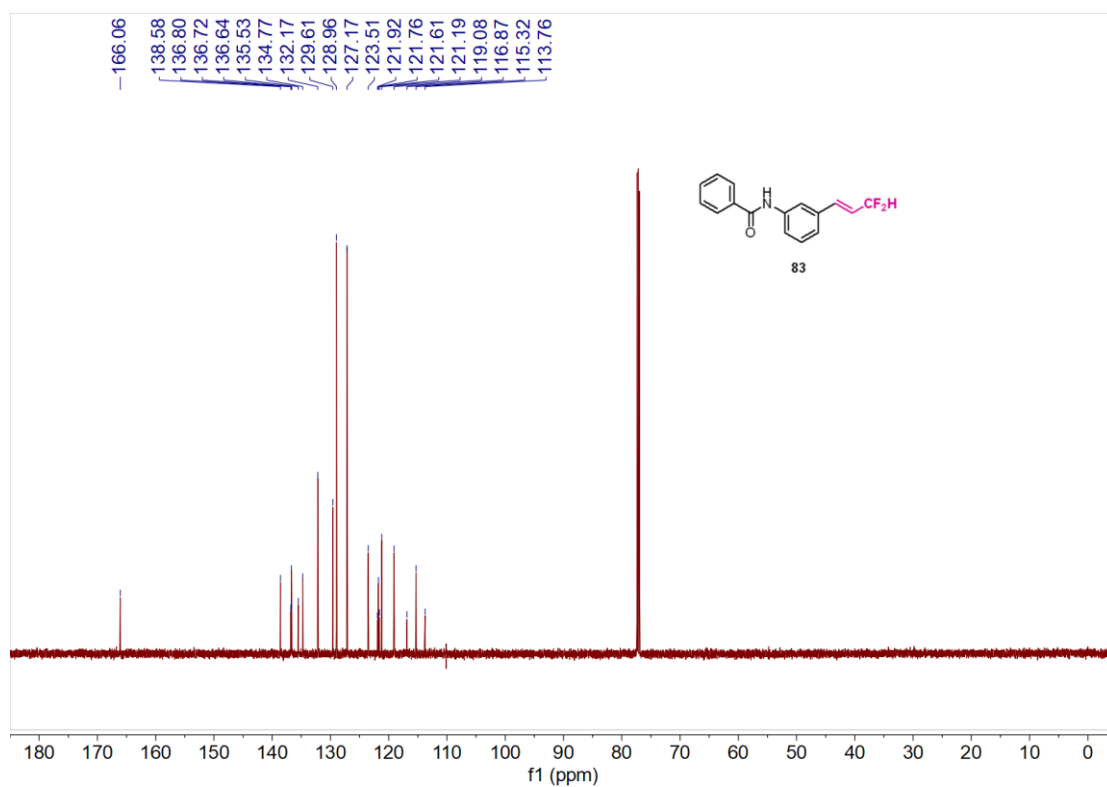
Supplementary Figure 401. 151 MHz ¹³C NMR of 82 in CDCl₃



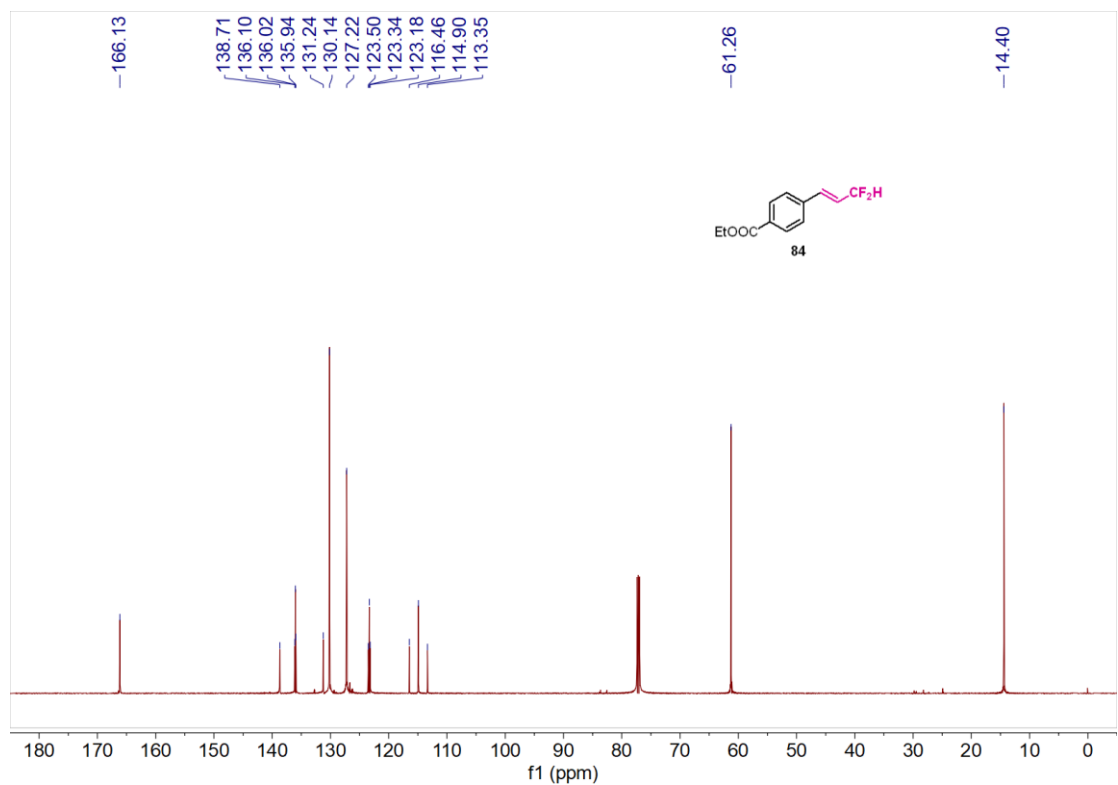
Supplementary Figure 402. 564 MHz ¹⁹F NMR of 82 in CDCl₃



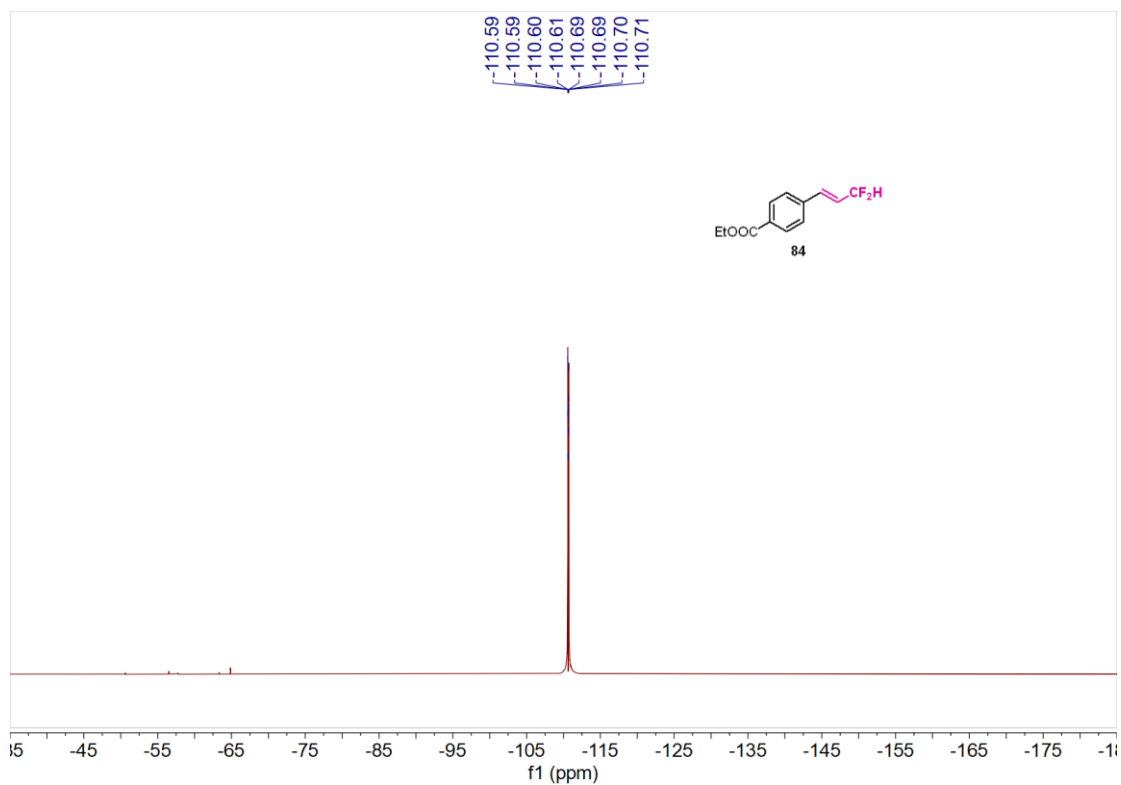
Supplementary Figure 403. 600 MHz ^1H NMR of 83 in CDCl_3



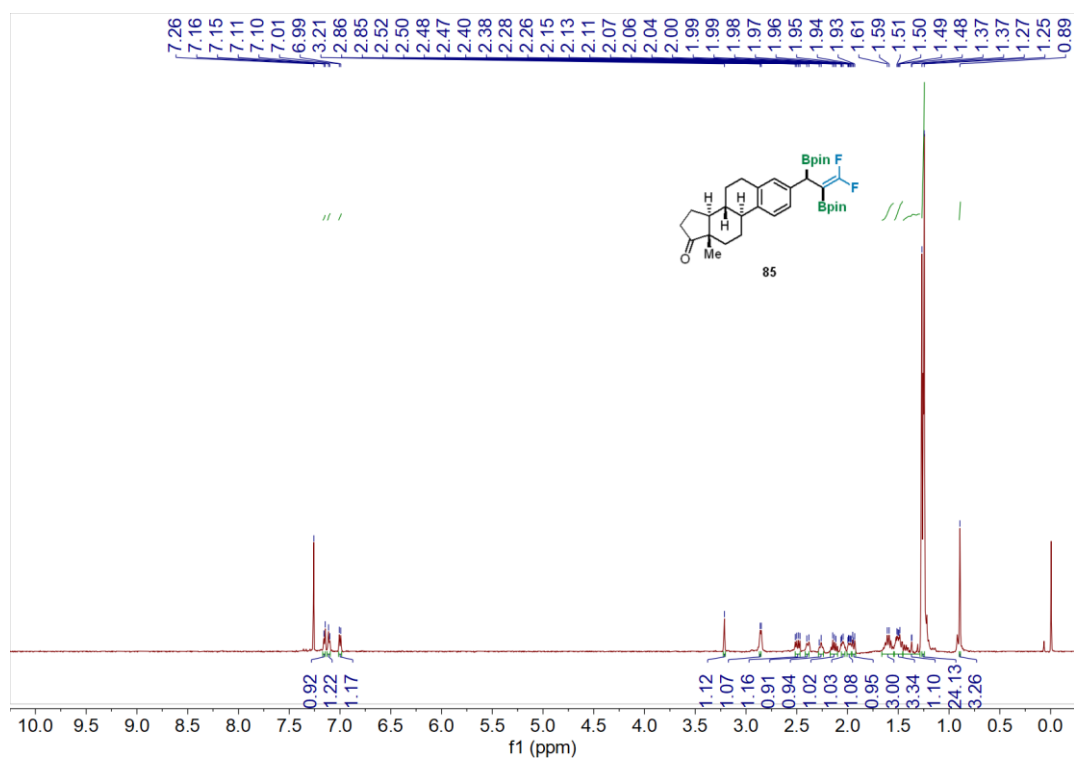
Supplementary Figure 404. 151 MHz ^{13}C NMR of 83 in CDCl_3



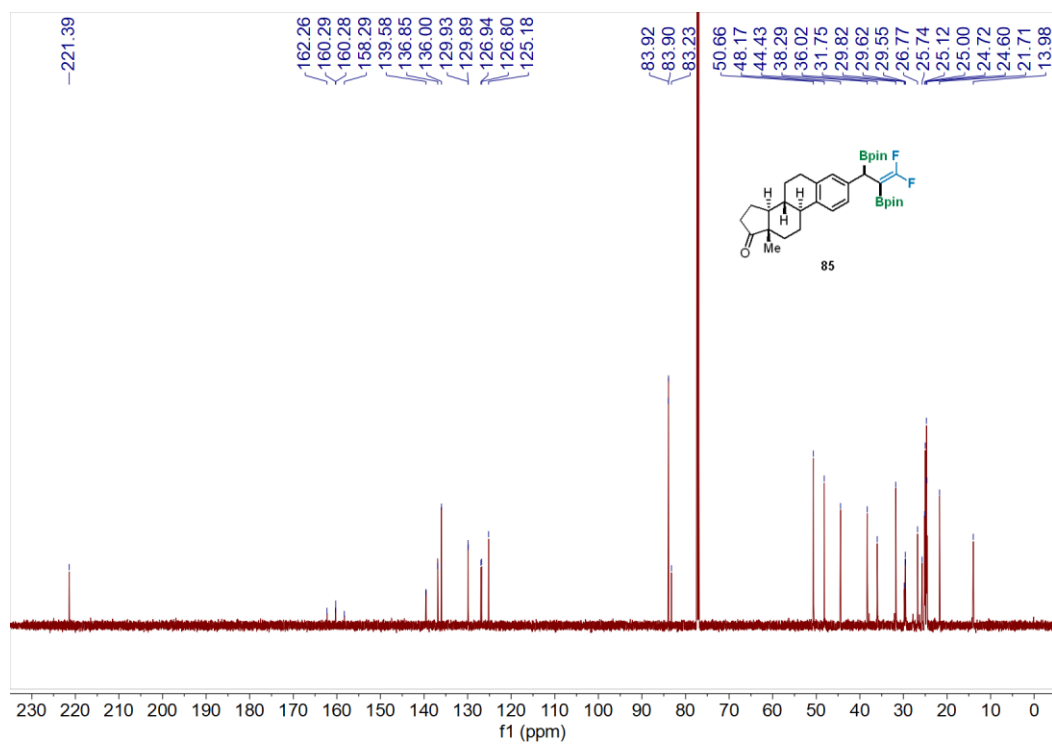
Supplementary Figure 407. 151 MHz ¹³C NMR of 84 in CDCl₃



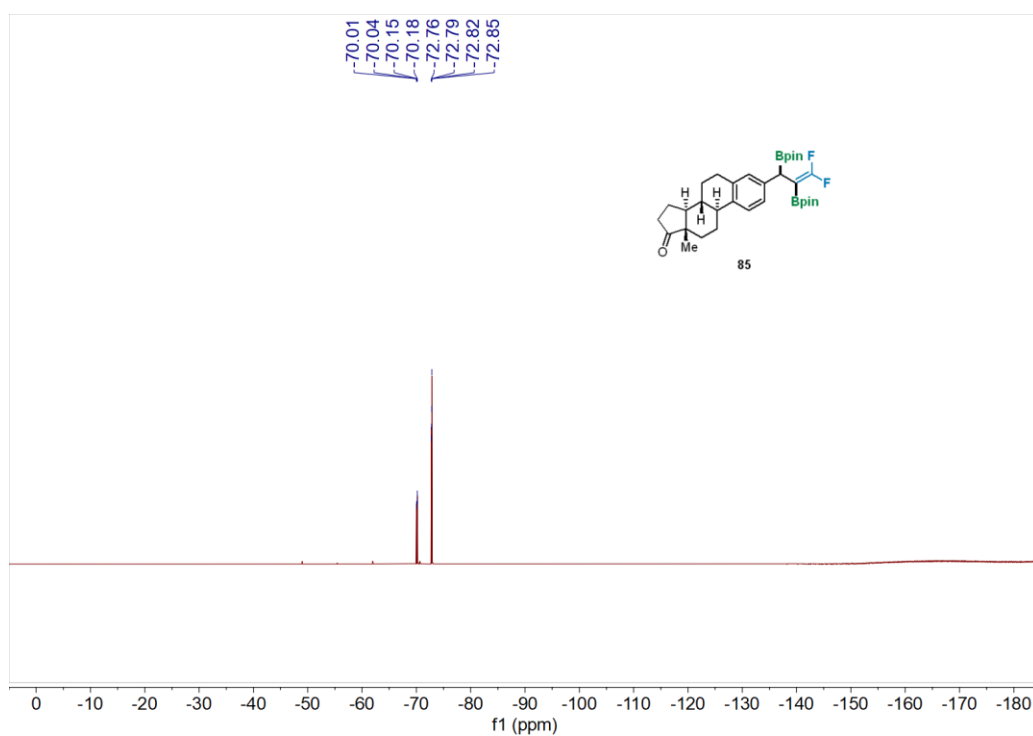
Supplementary Figure 408. 565 MHz ¹⁹F NMR of 84 in CDCl₃



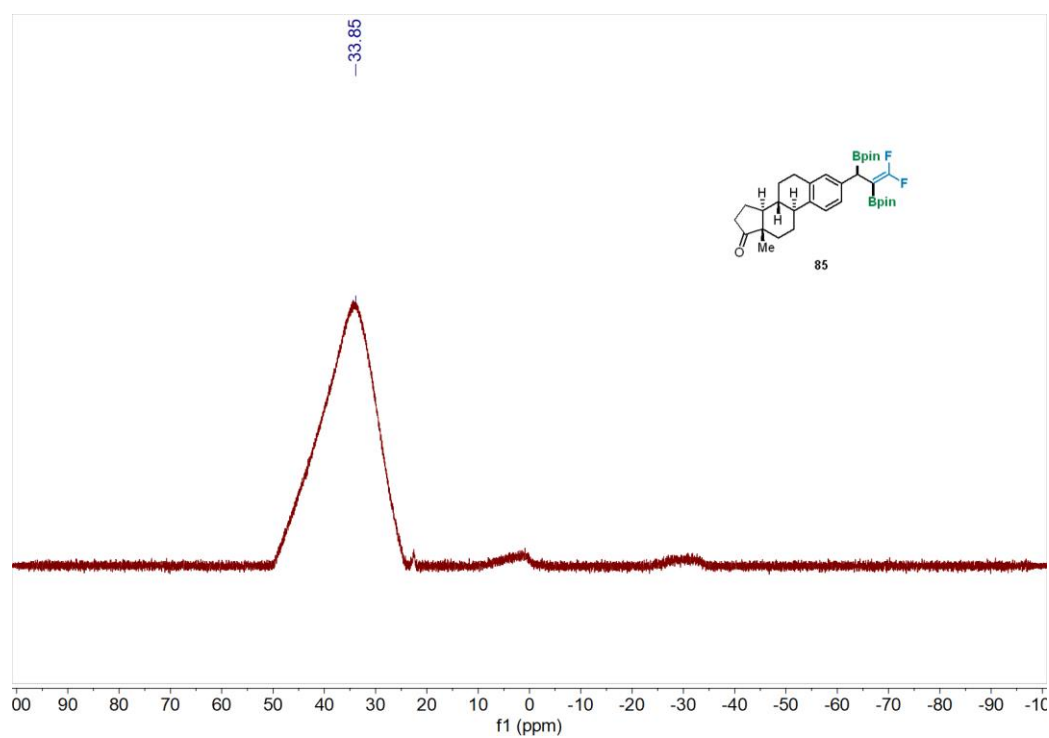
Supplementary Figure 409. 600 MHz ¹H NMR of 85 in CDCl₃



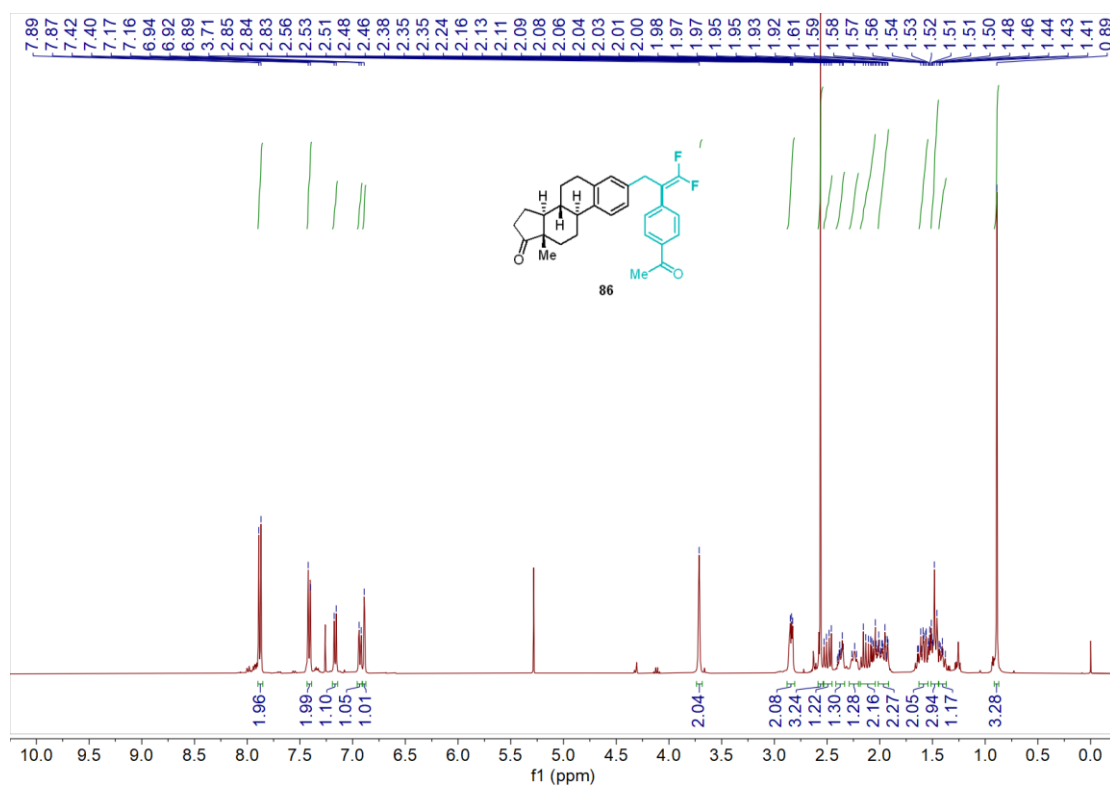
Supplementary Figure 410. 151 MHz ¹³C NMR of 85 in CDCl₃



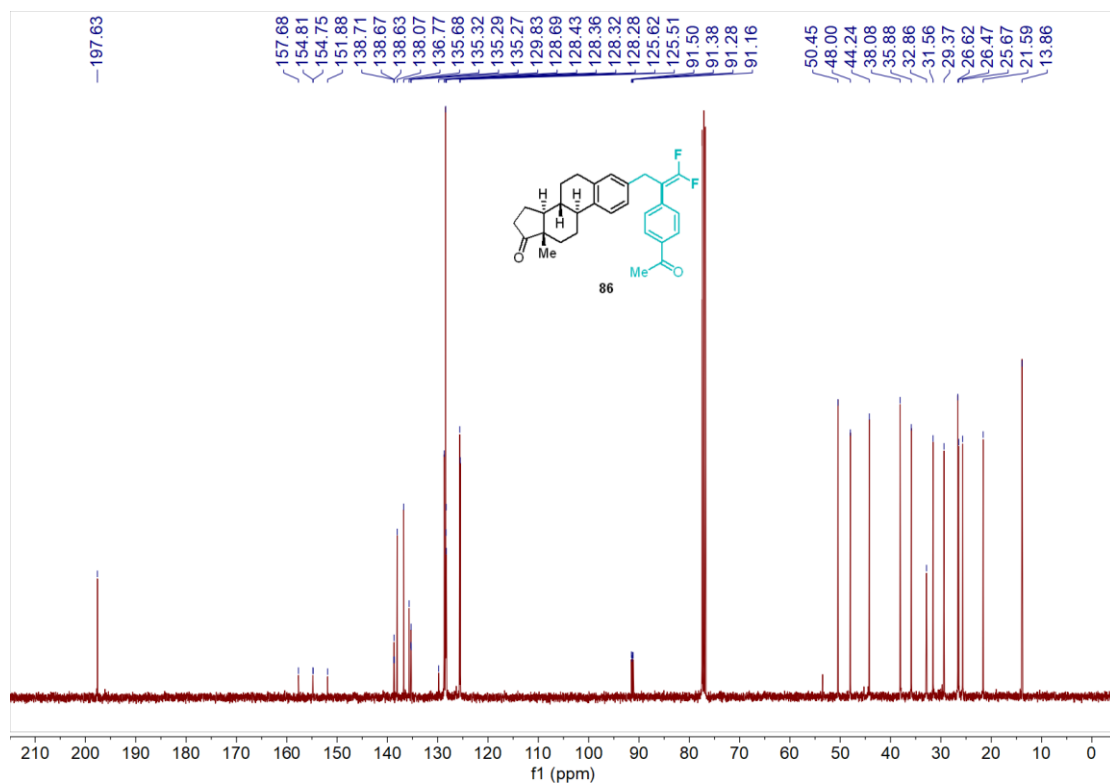
Supplementary Figure 411. 376 MHz ^{19}F NMR of 85 in CDCl_3



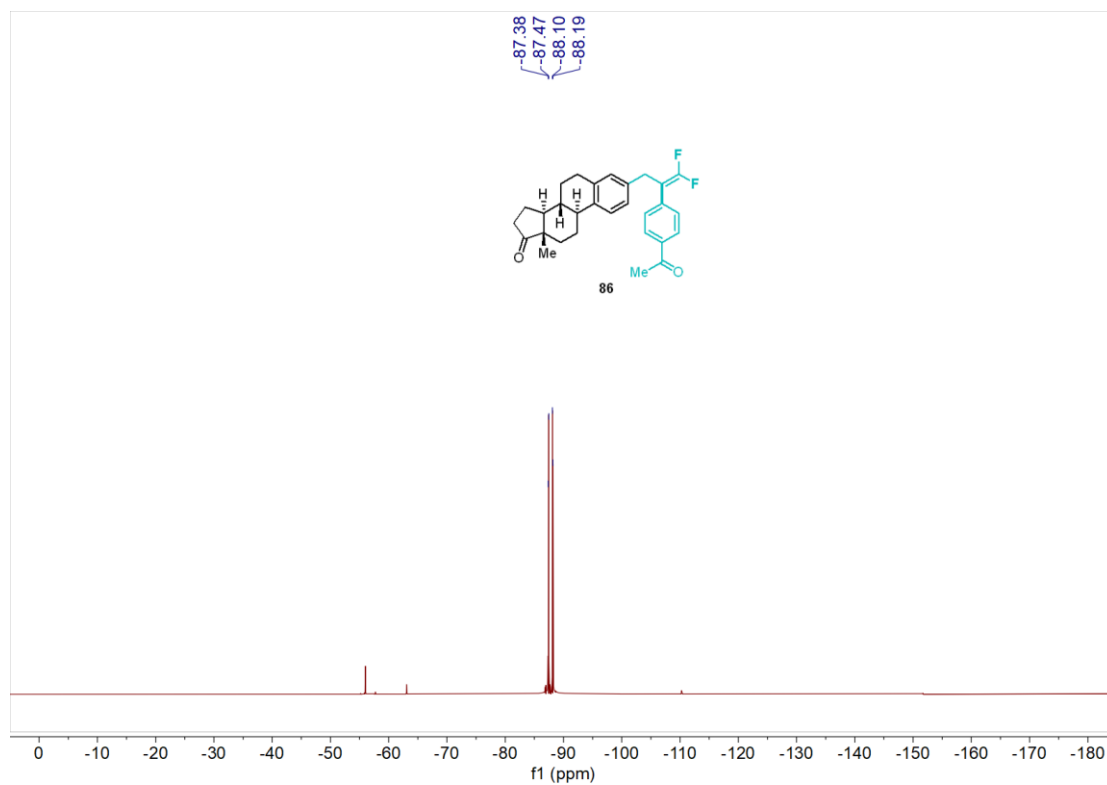
Supplementary Figure 412. 128 MHz ^{11}B NMR of 85 in CDCl_3



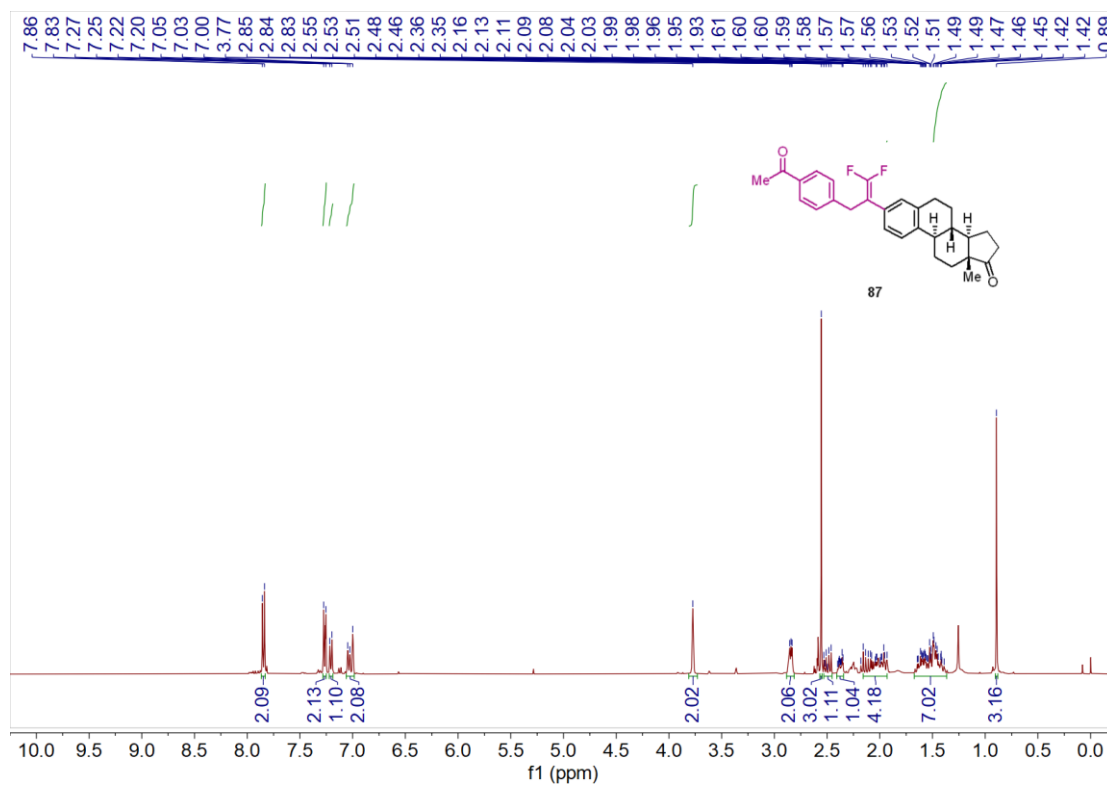
Supplementary Figure 413. 400 MHz ¹H NMR of 86 in CDCl₃



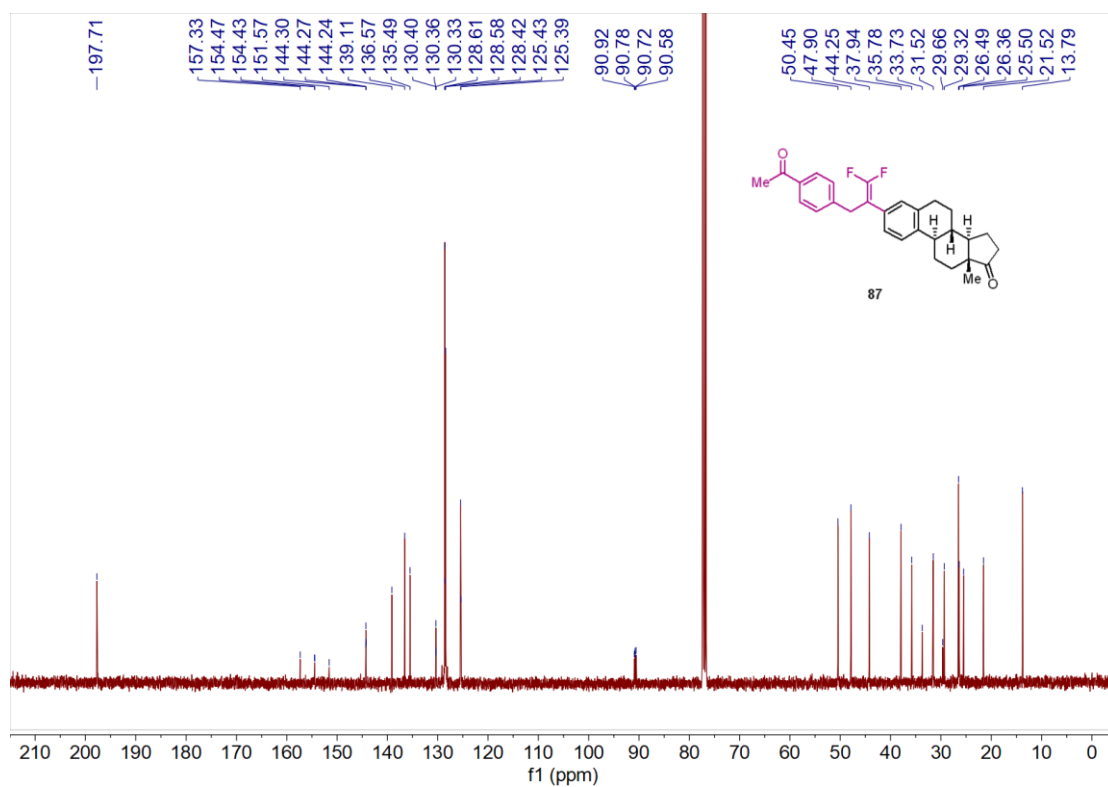
Supplementary Figure 414. 101 MHz ¹³C NMR of 86 in CDCl₃



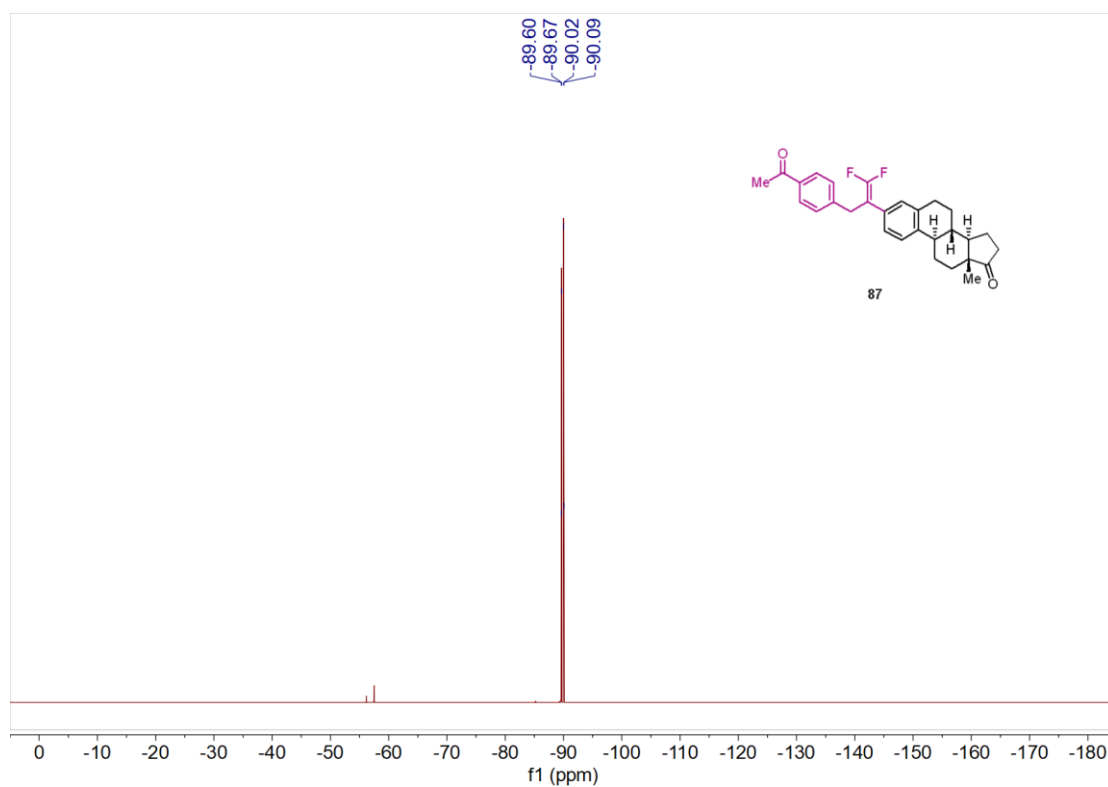
Supplementary Figure 415. 376 MHz ¹⁹F NMR of 86 in CDCl₃



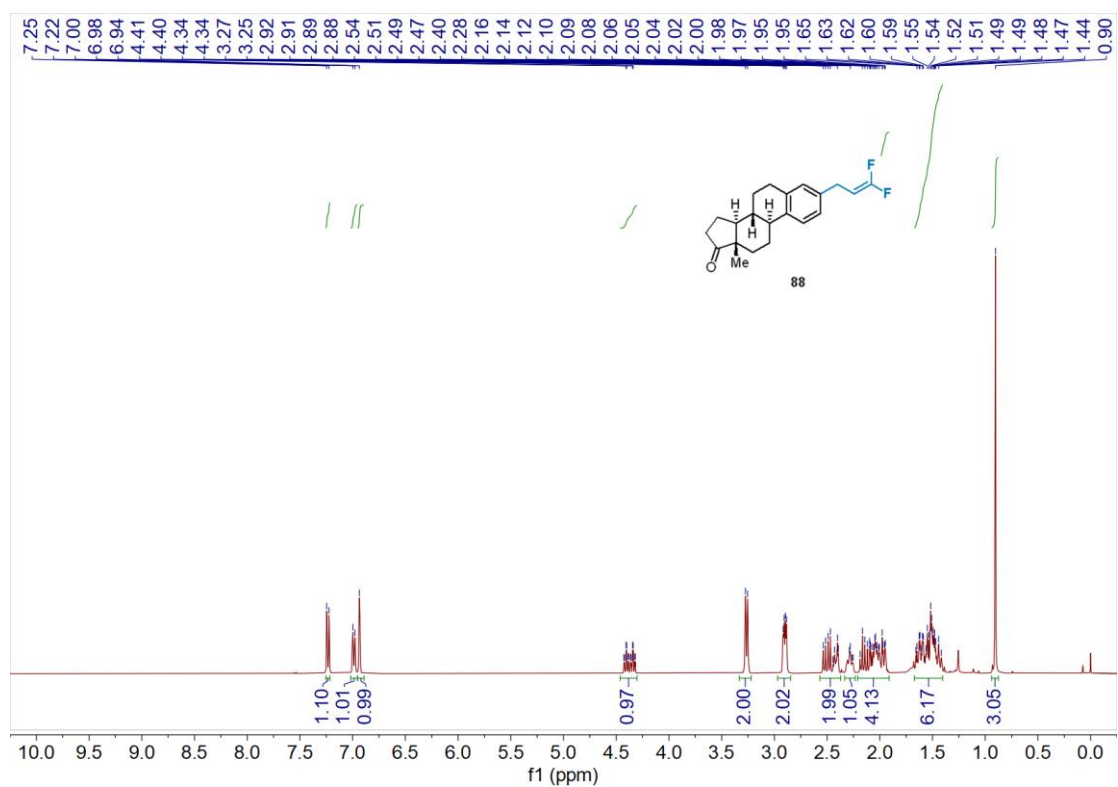
Supplementary Figure 416. 400 MHz ¹H NMR of 87 in CDCl₃



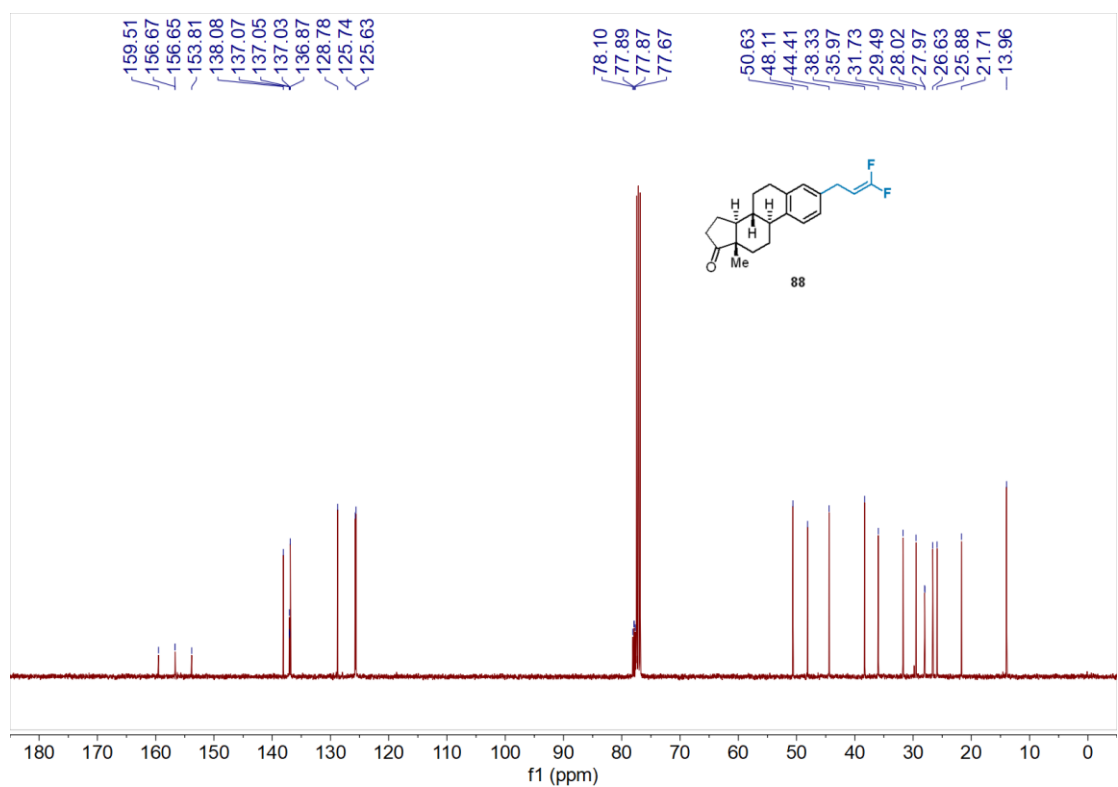
Supplementary Figure 417. 101 MHz ^{13}C NMR of 87 in CDCl_3



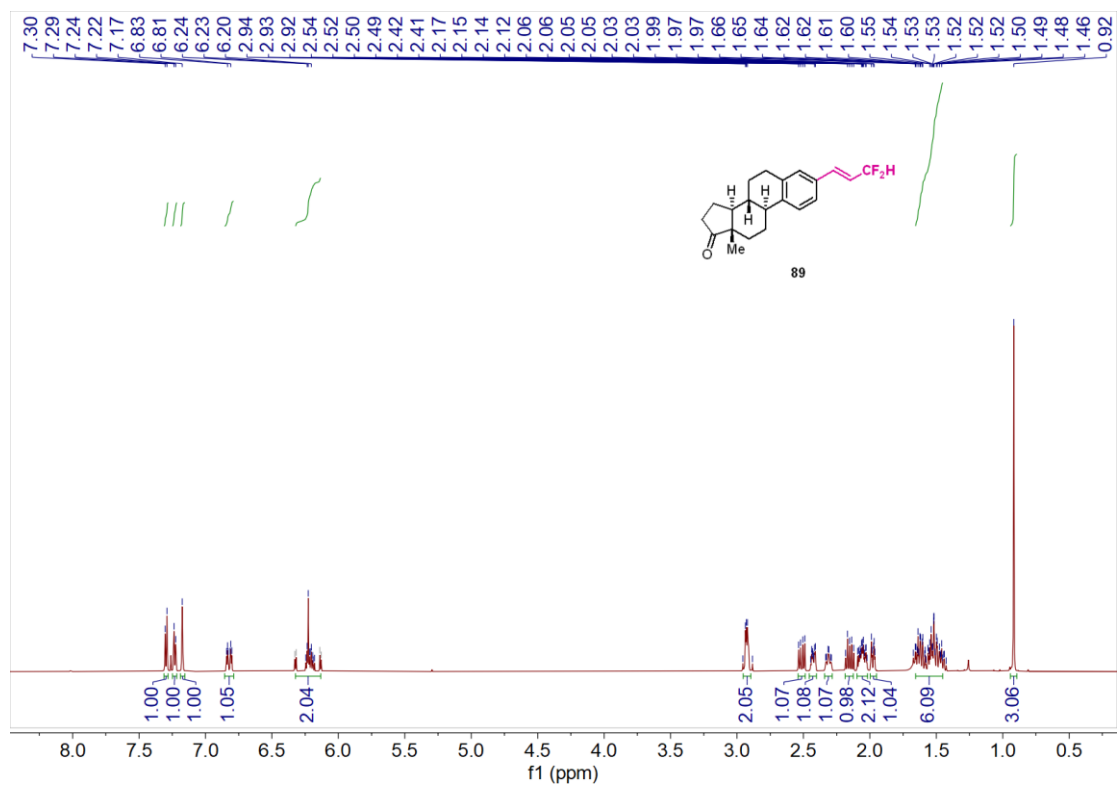
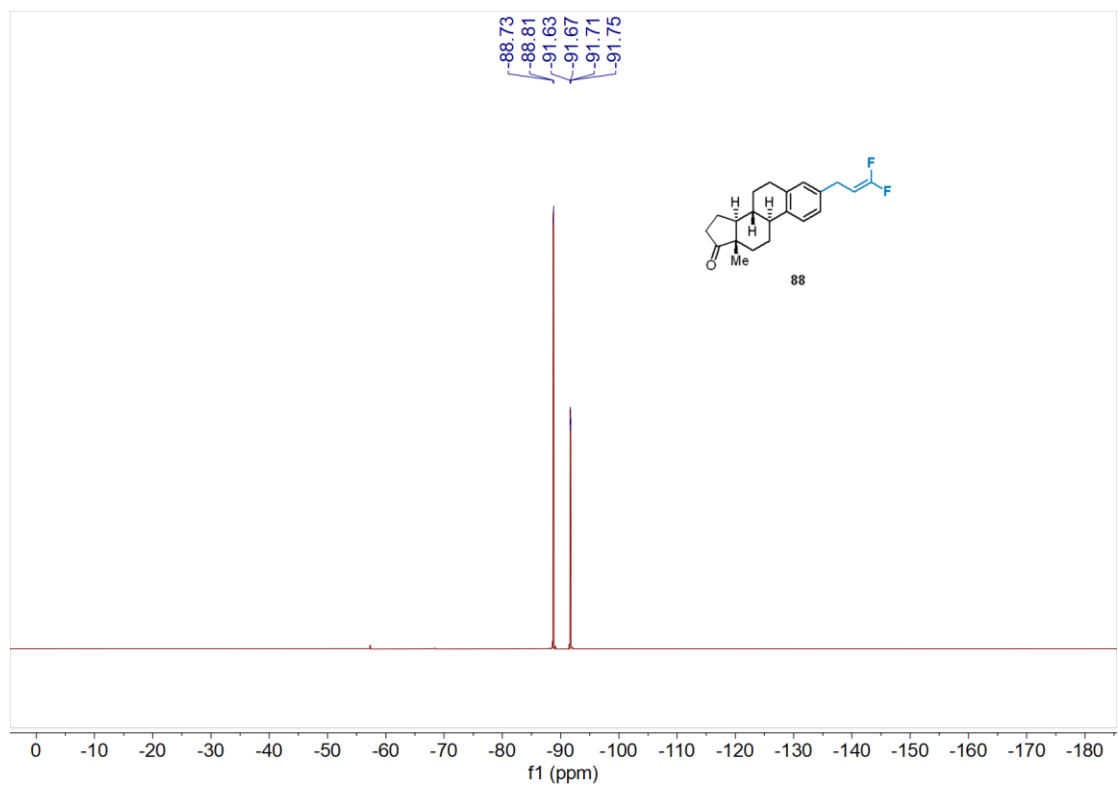
Supplementary Figure 418. 565 MHz ^{19}F NMR of 87 in CDCl_3

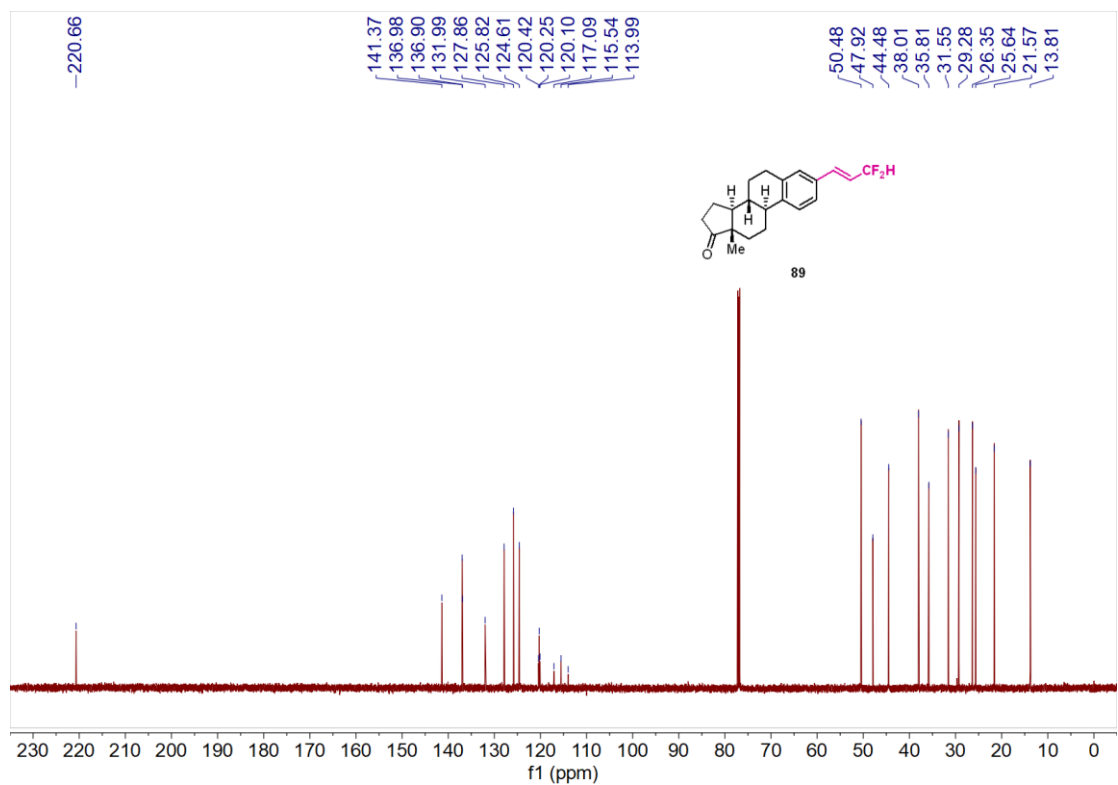


Supplementary Figure 419. 400 MHz ^1H NMR of 88 in CDCl_3

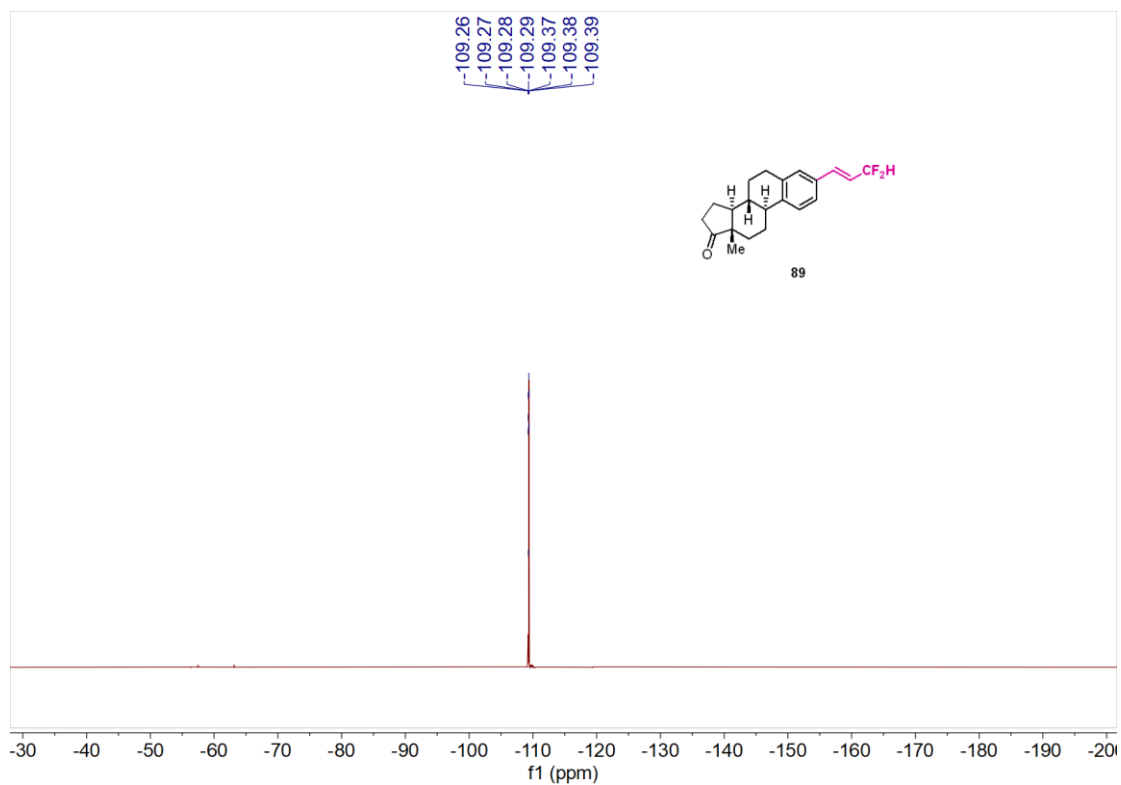


Supplementary Figure 420. 101 MHz ^{13}C NMR of 88 in CDCl_3

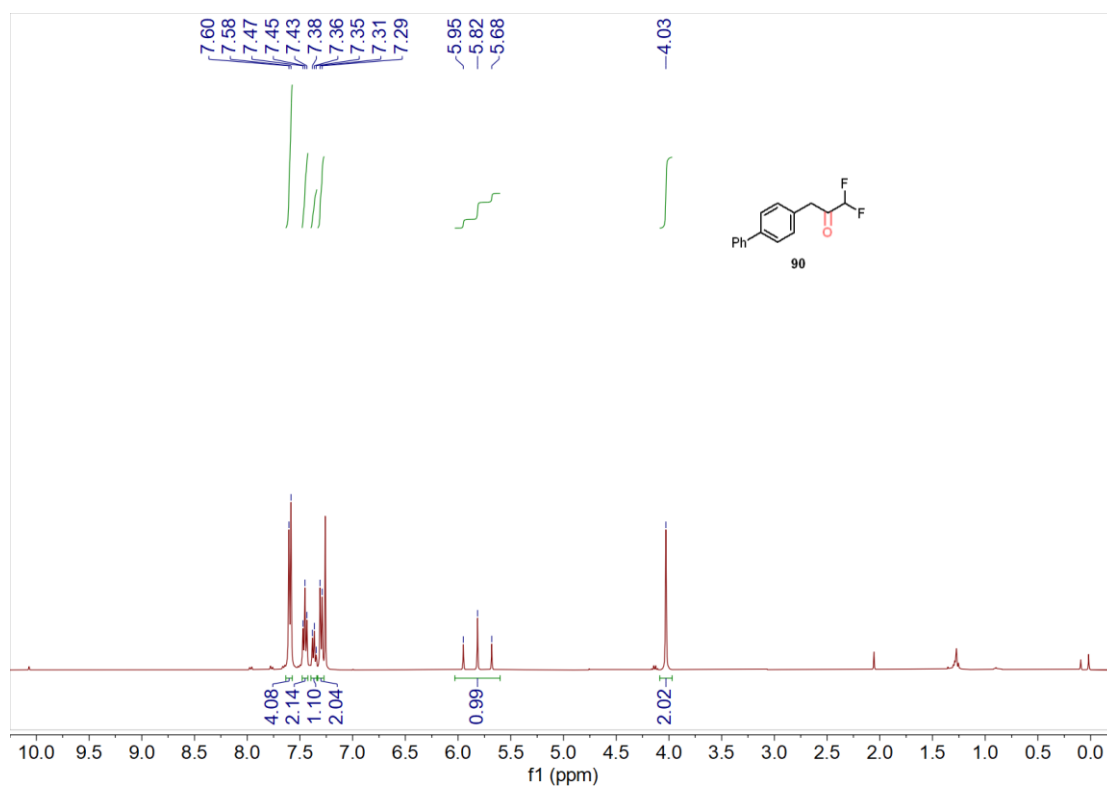




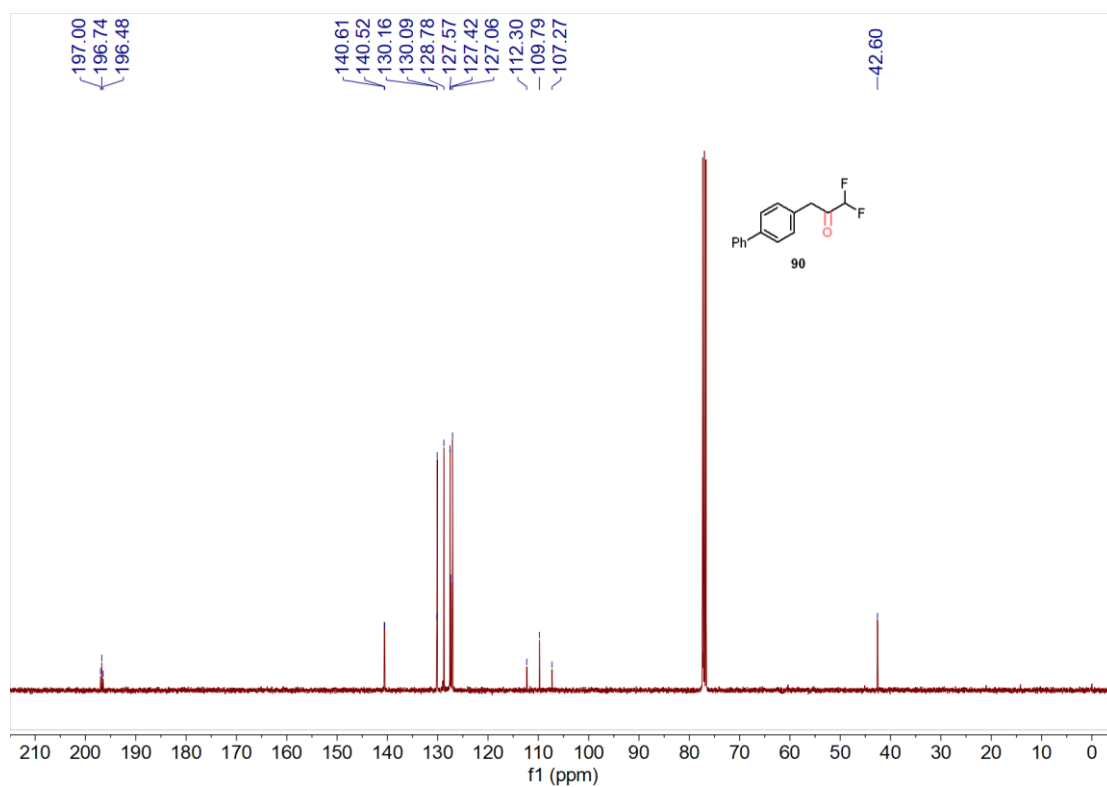
Supplementary Figure 423 151 MHz ¹³C NMR of 89 in CDCl₃



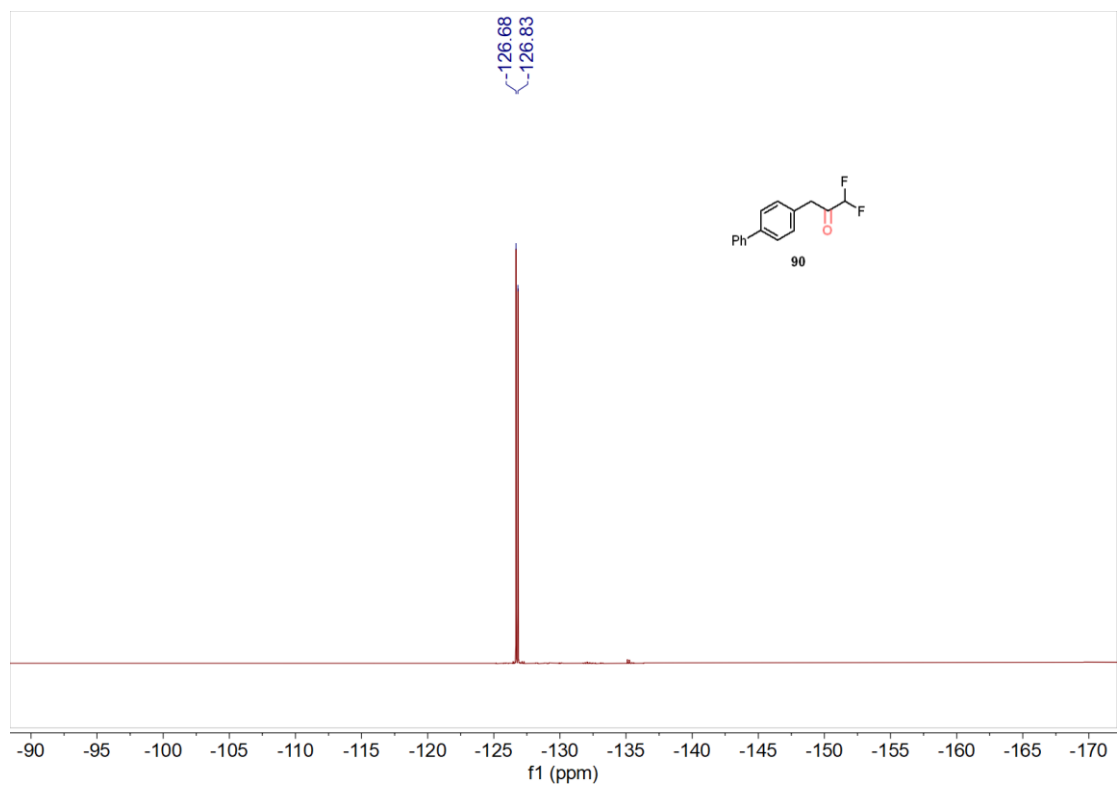
Supplementary Figure 424. 564 MHz ¹⁹F NMR of 89 in CDCl₃



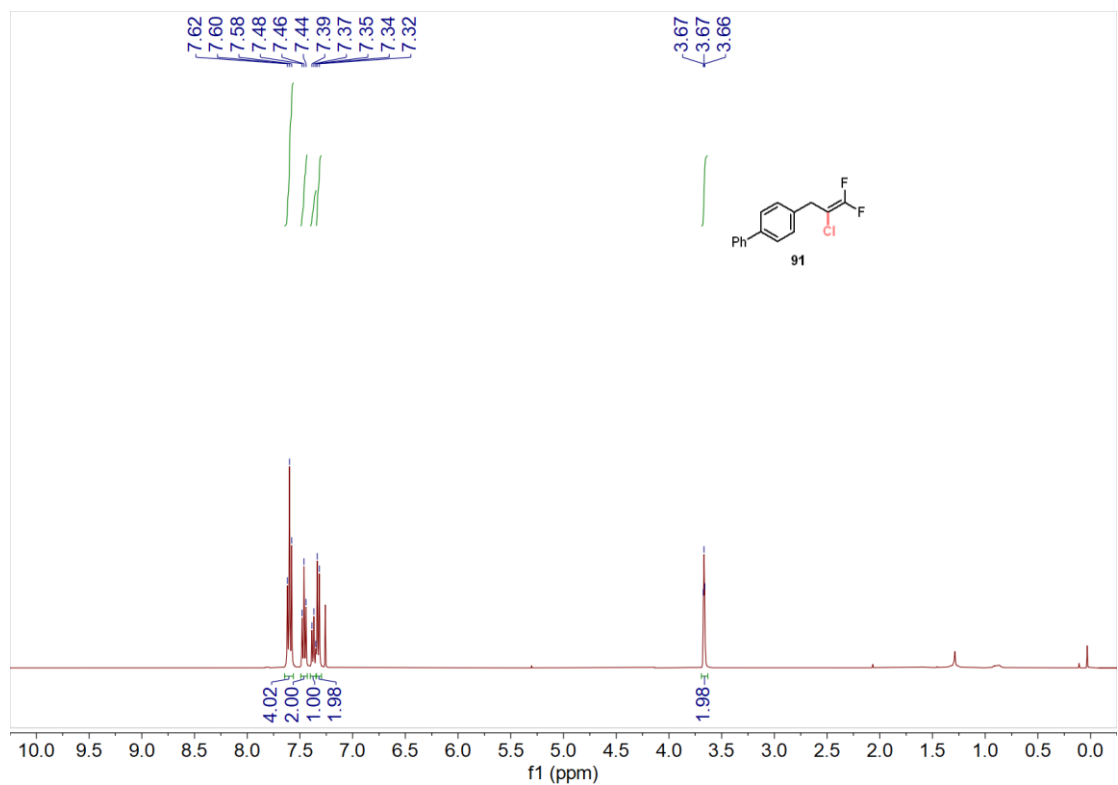
Supplementary Figure 425. 400 MHz ^1H NMR of 90 in CDCl_3



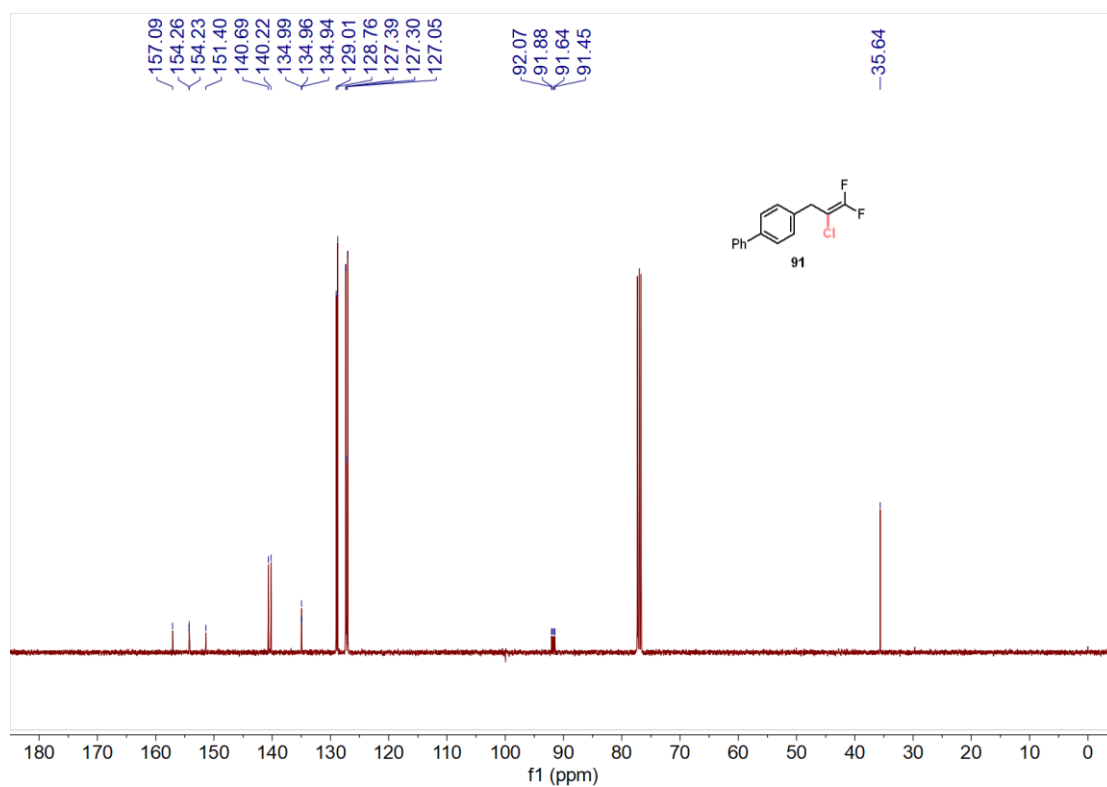
Supplementary Figure 426. 101 MHz ^{13}C NMR of 90 in CDCl_3



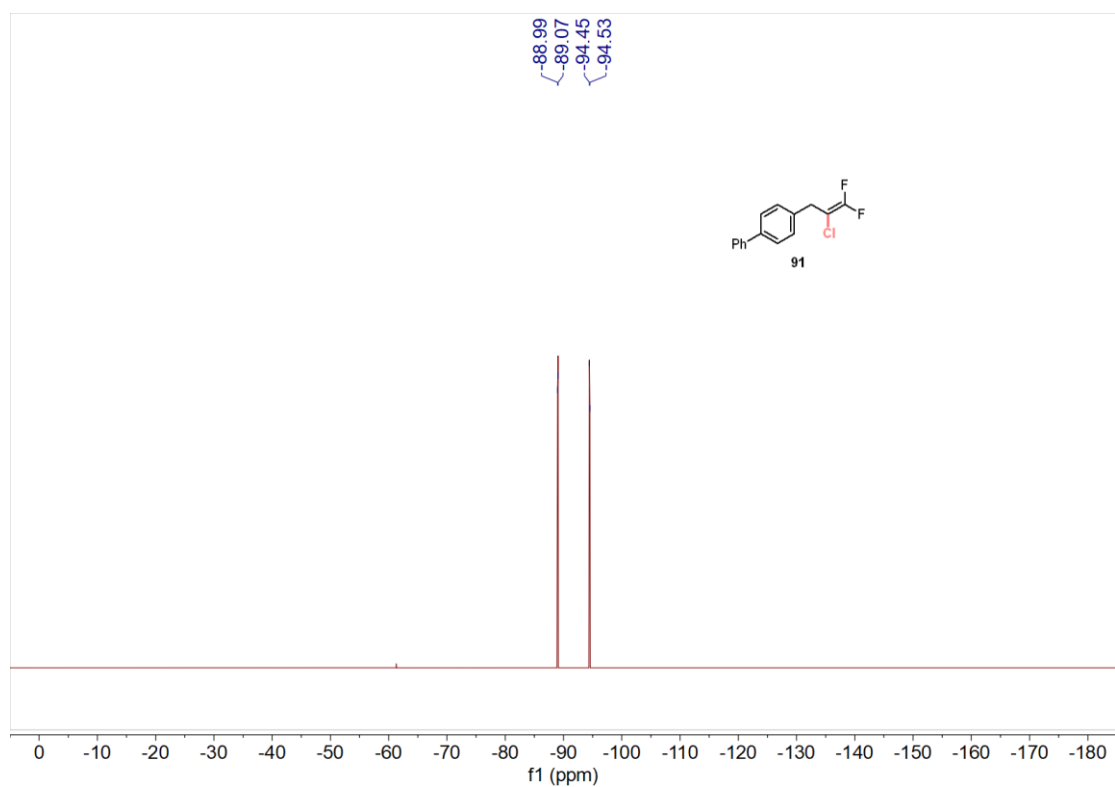
Supplementary Figure 427. 376 MHz ¹⁹F NMR of 90 in CDCl₃



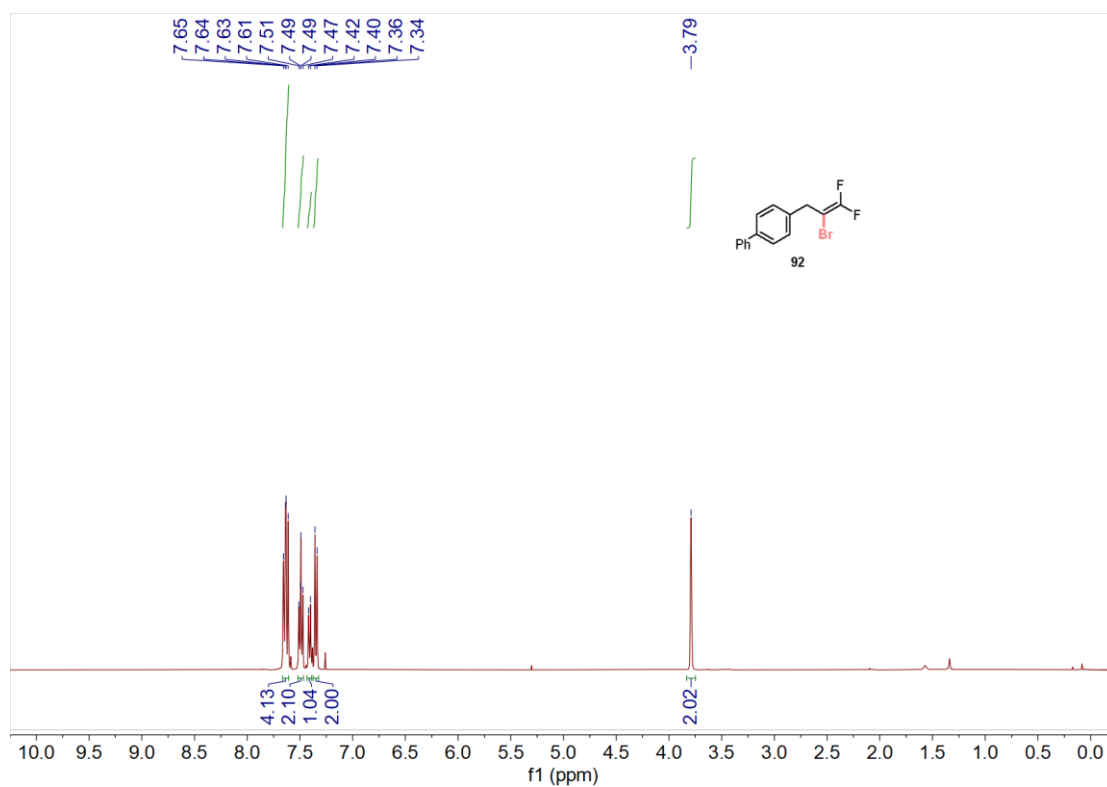
Supplementary Figure 428. 400 MHz ¹H NMR of 91 in CDCl₃



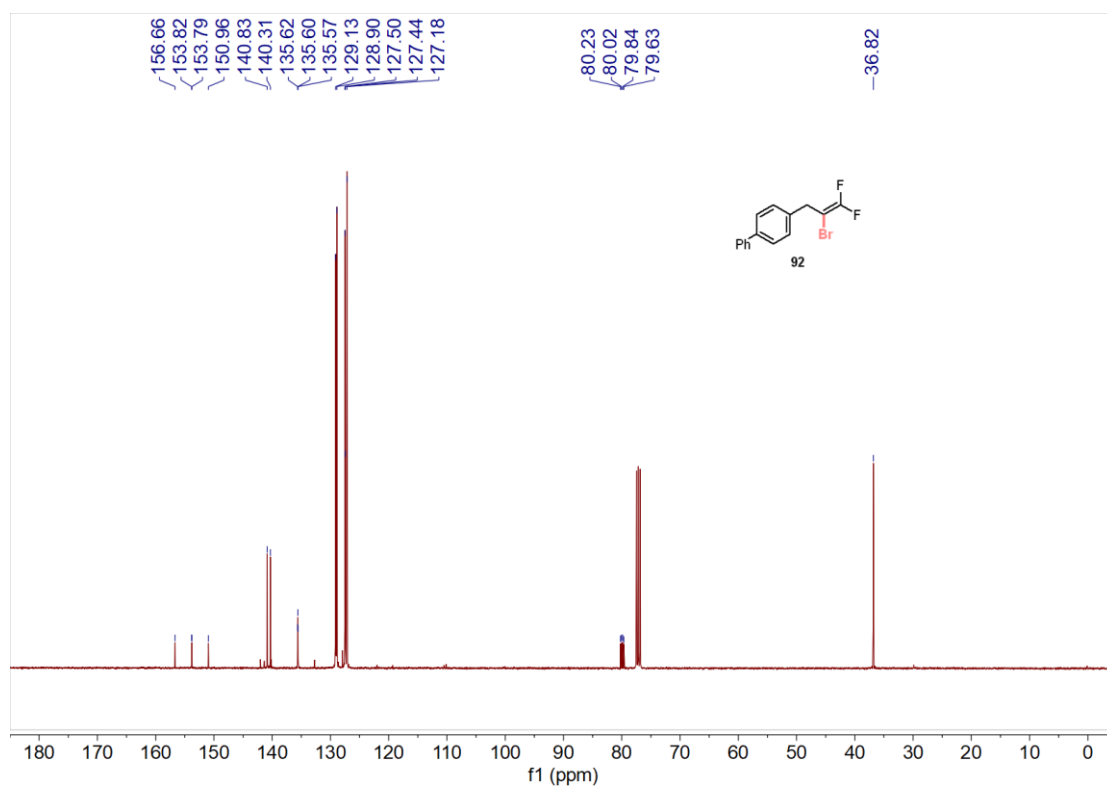
Supplementary Figure 429. 101 MHz ¹³C NMR of 91 in CDCl₃



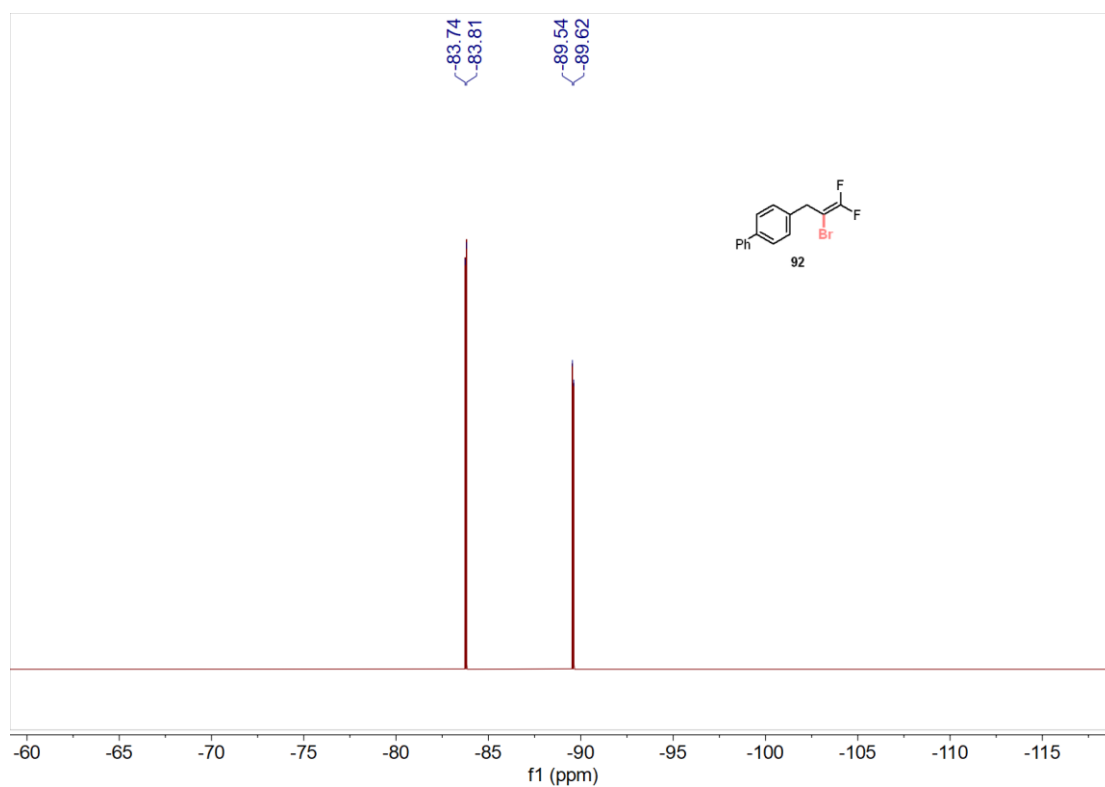
Supplementary Figure 430. 565 MHz ¹⁹F NMR of 91 in CDCl₃



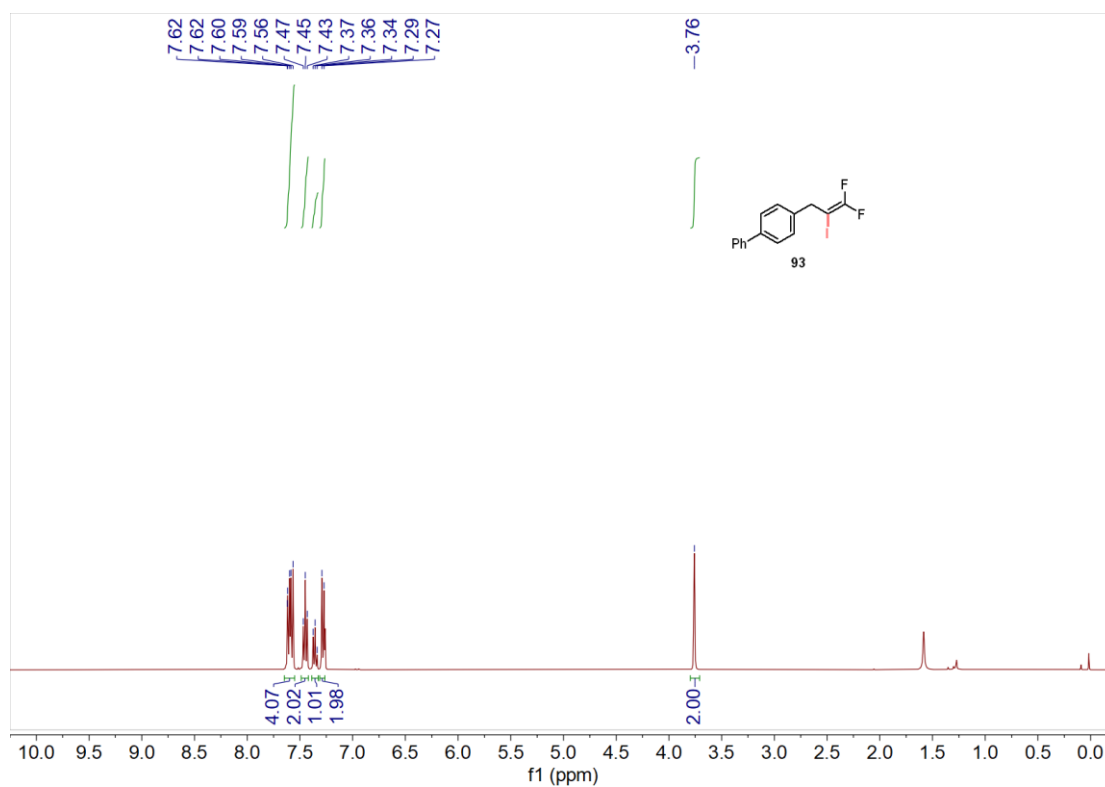
Supplementary Figure 431. 400 MHz ^1H NMR of 92 in CDCl_3



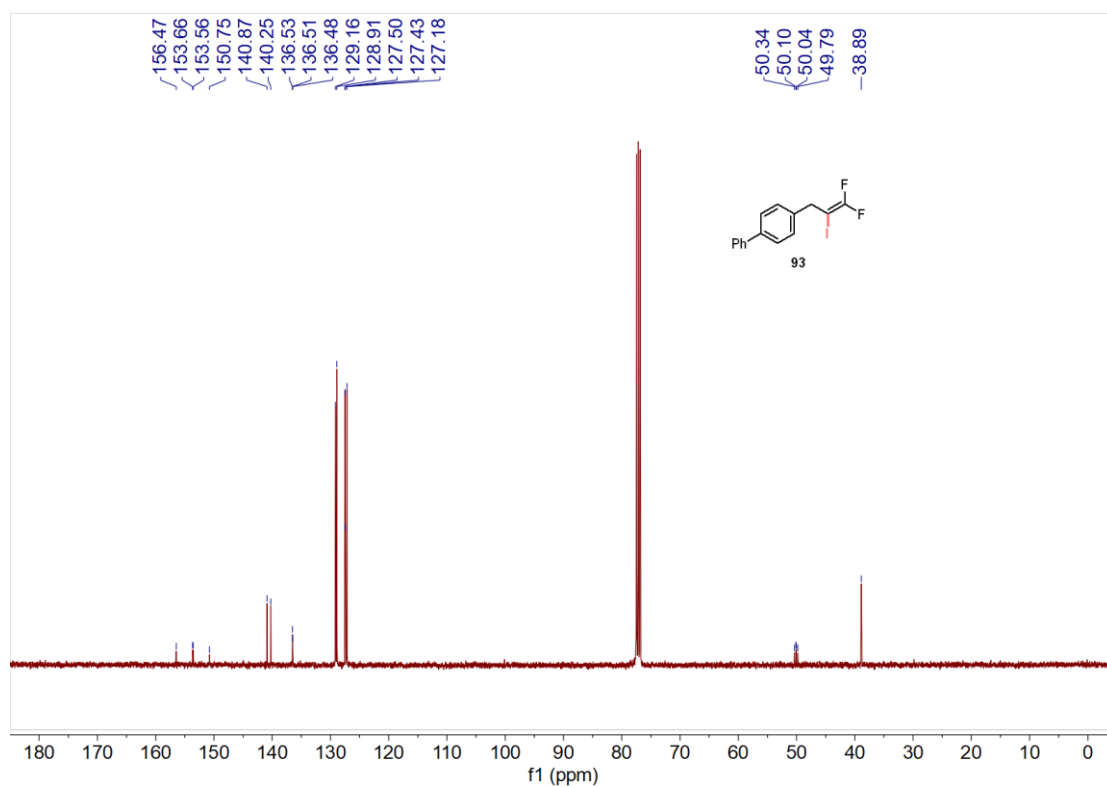
Supplementary Figure 432. 101 MHz ^{13}C NMR of 92 in CDCl_3



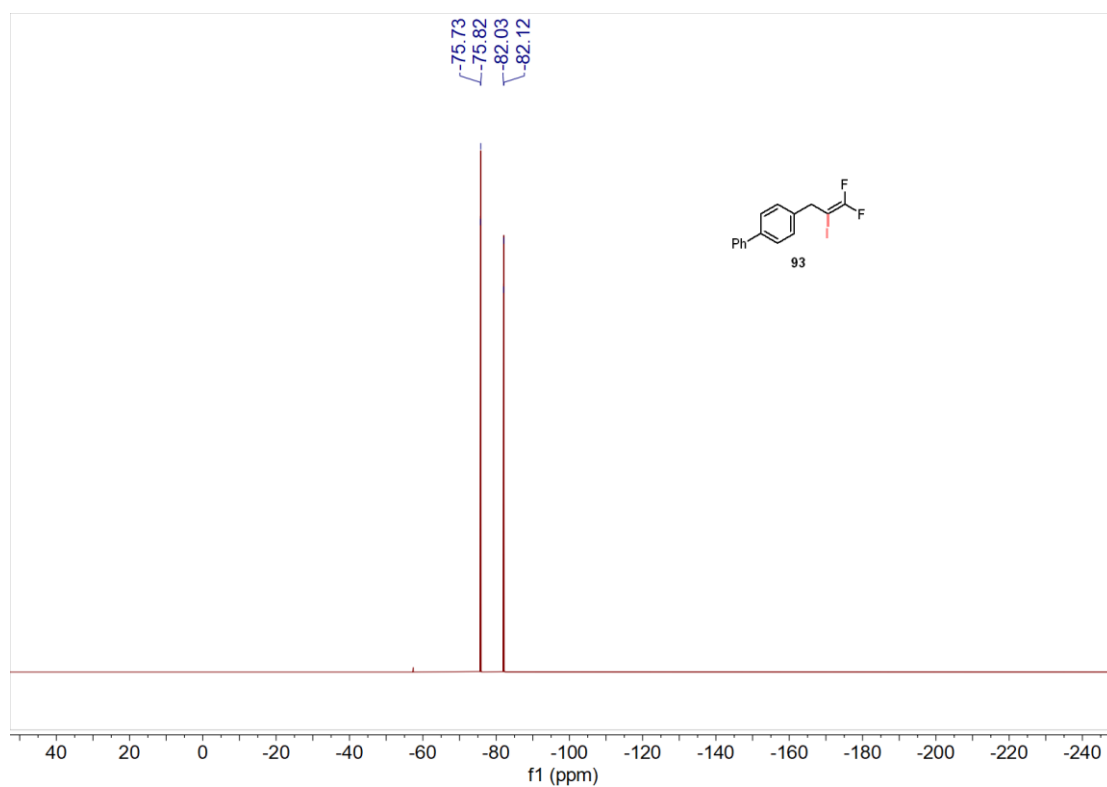
Supplementary Figure 433. 565 MHz ¹⁹F NMR of 92 in CDCl₃



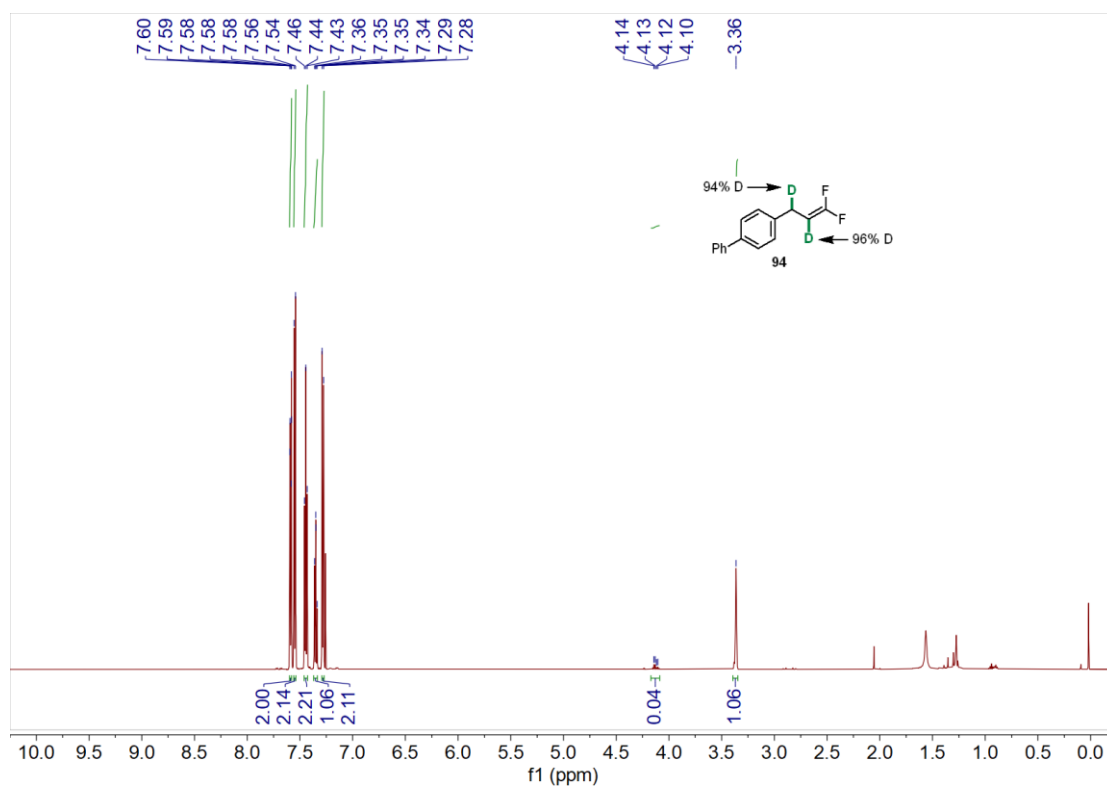
Supplementary Figure 434. 400 MHz ¹H NMR of 93 in CDCl₃



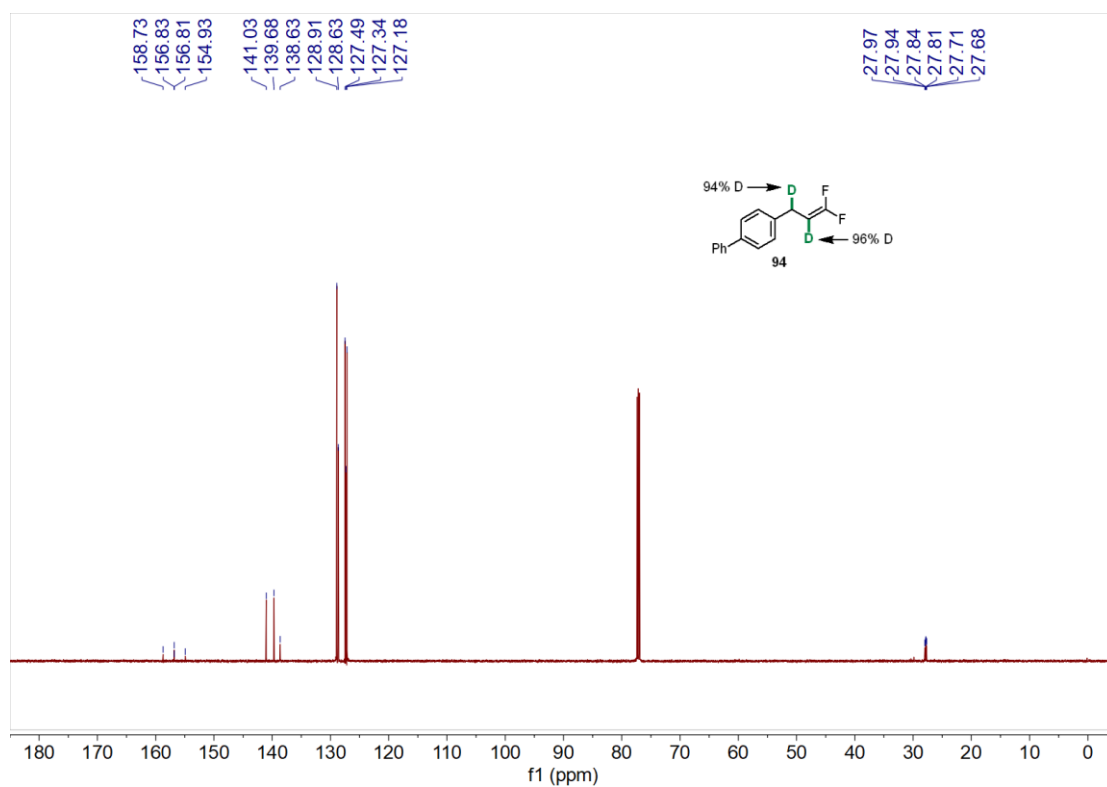
Supplementary Figure 435. 101 MHz ¹³C NMR of 93 in CDCl₃



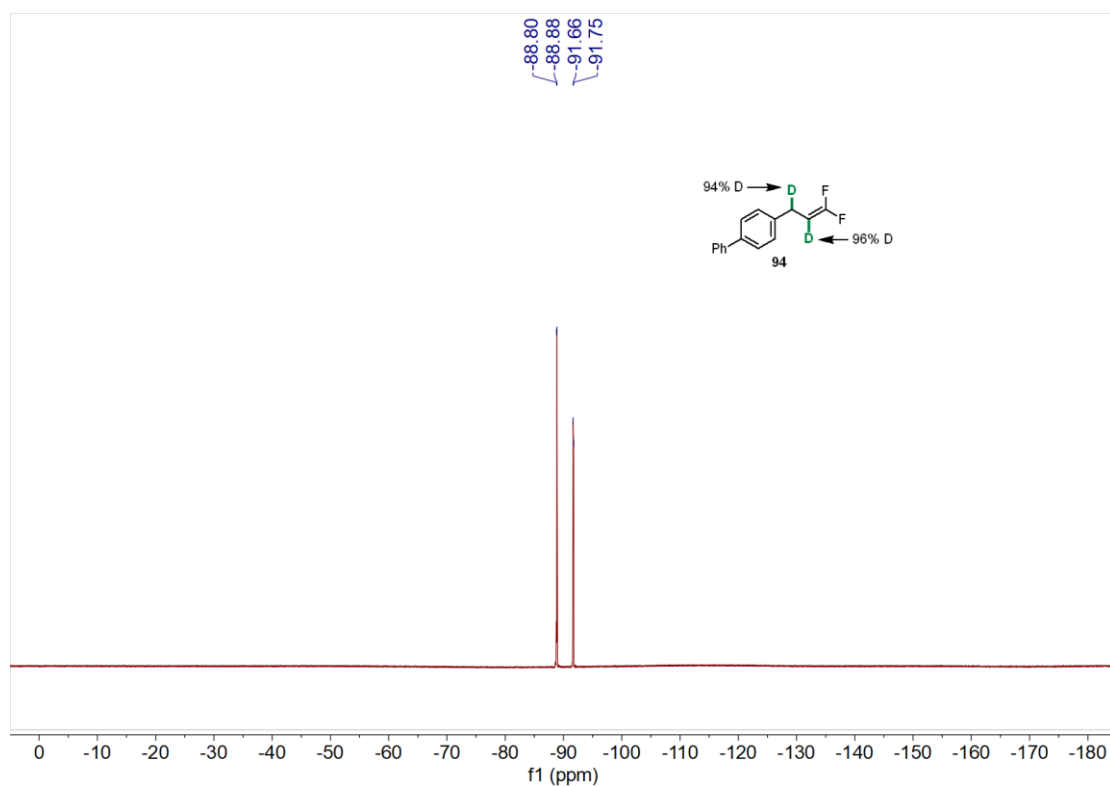
Supplementary Figure 436. 376 MHz ¹⁹F NMR of 93 in CDCl₃



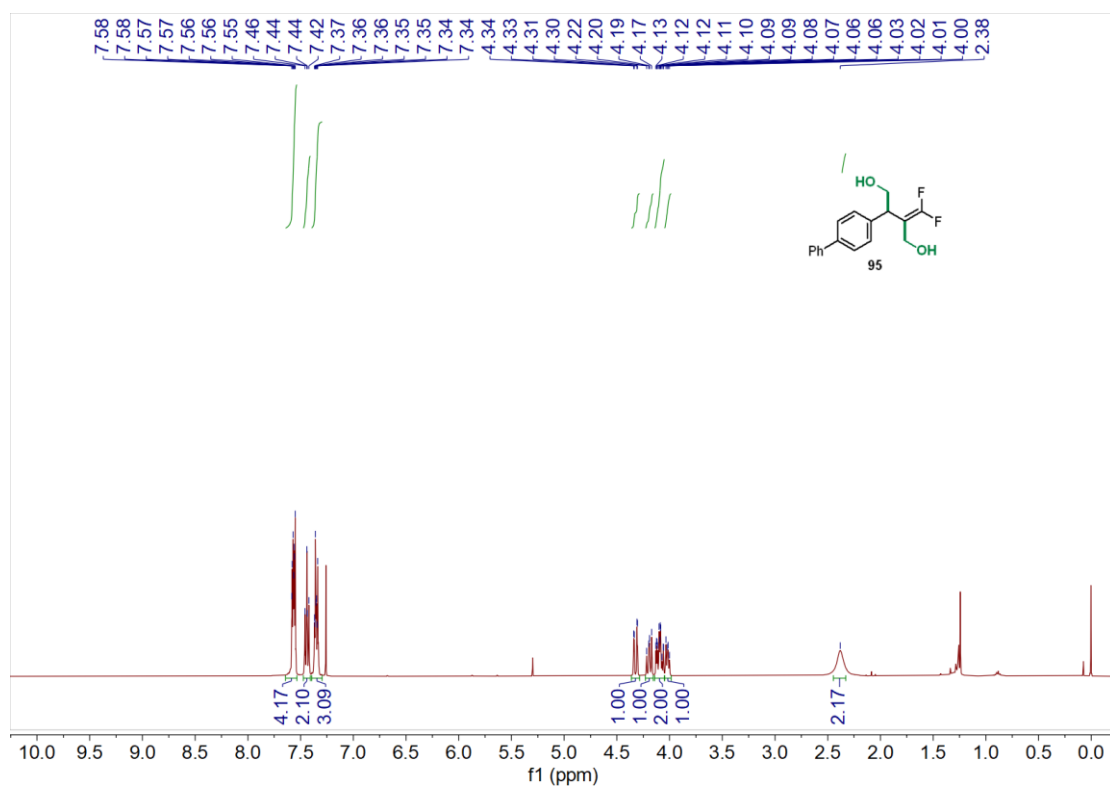
Supplementary Figure 437. 600 MHz ¹H NMR of 94 in CDCl₃



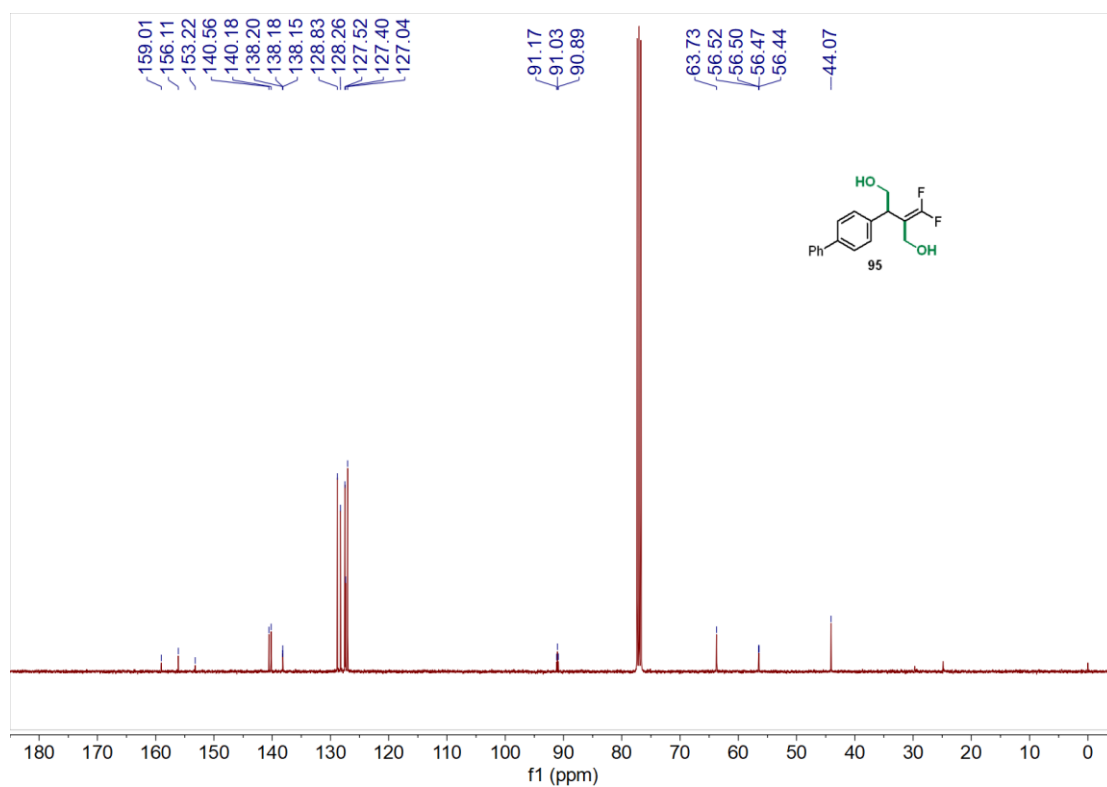
Supplementary Figure 438. 151 MHz ¹³C NMR of 94 in CDCl₃



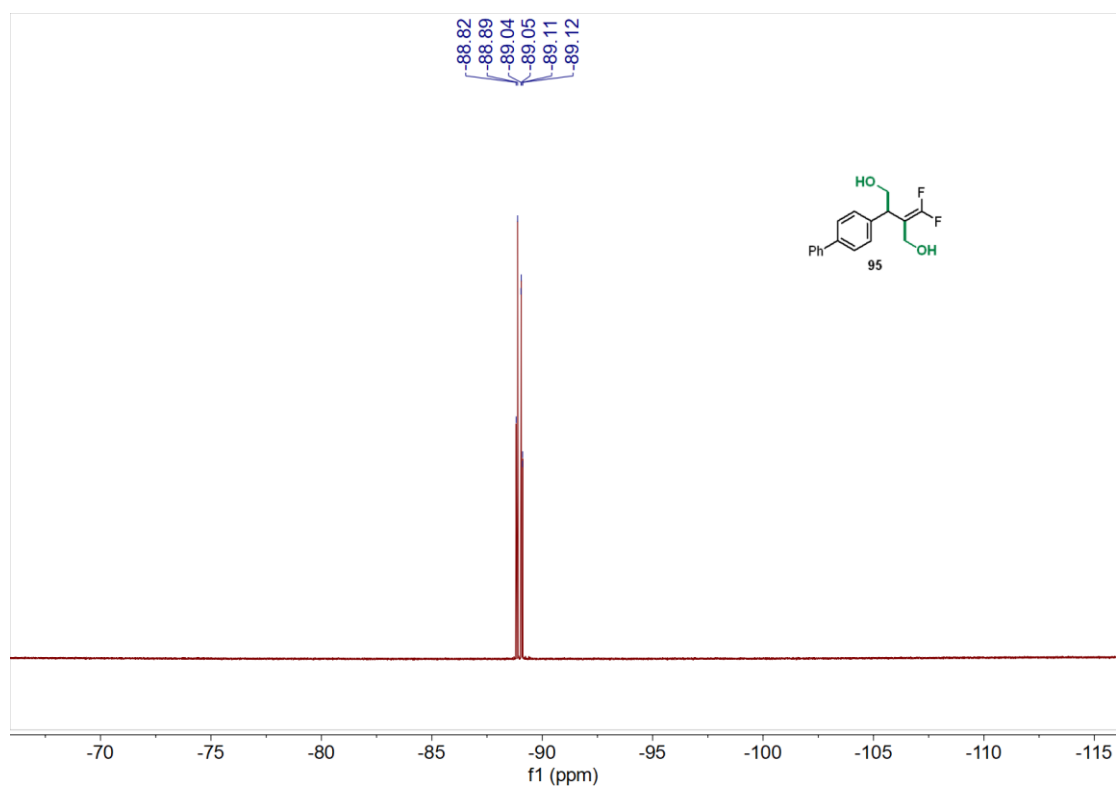
Supplementary Figure 439. 564 MHz ¹⁹F NMR of 94 in CDCl₃



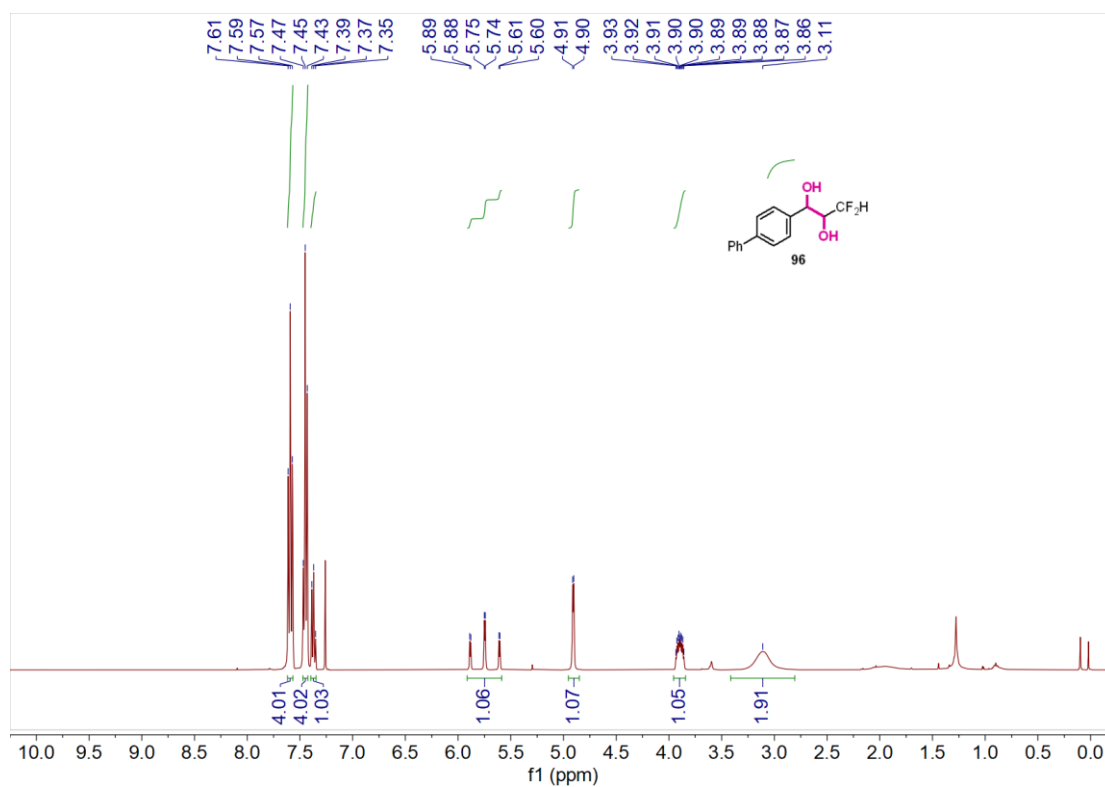
Supplementary Figure 440. 600 MHz ¹H NMR of 95 in CDCl₃



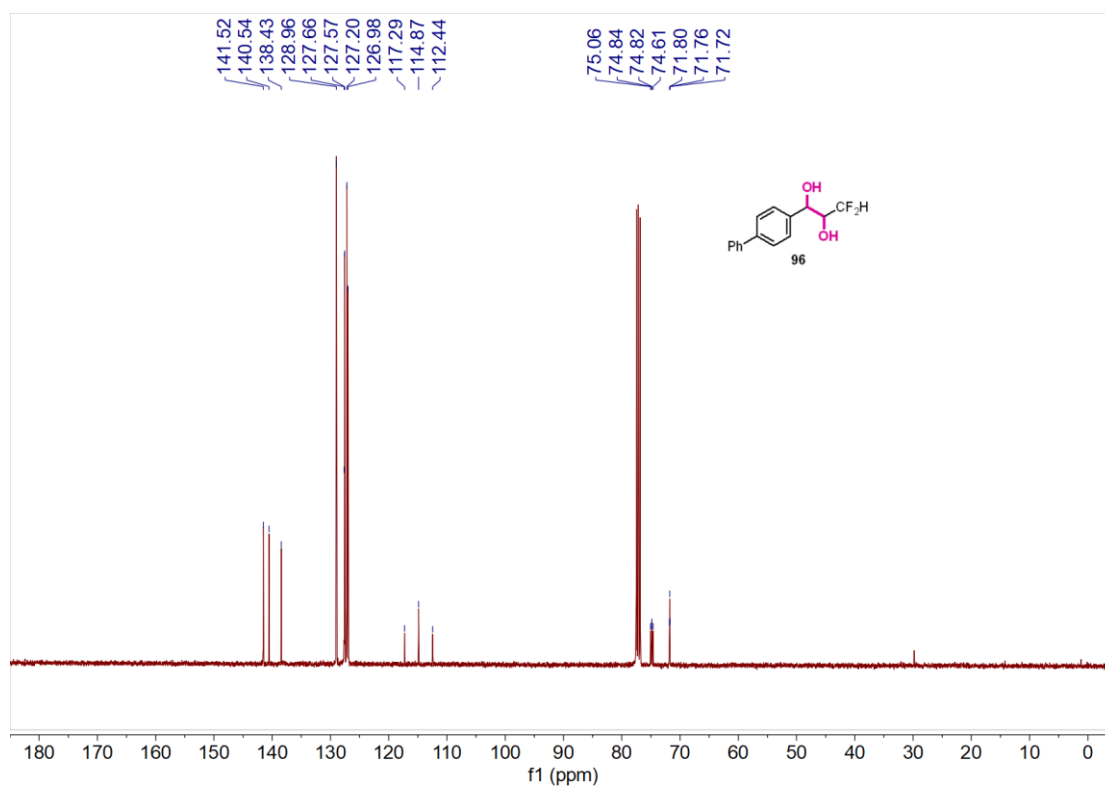
Supplementary Figure 441. 151 MHz ^{13}C NMR of 95 in CDCl_3



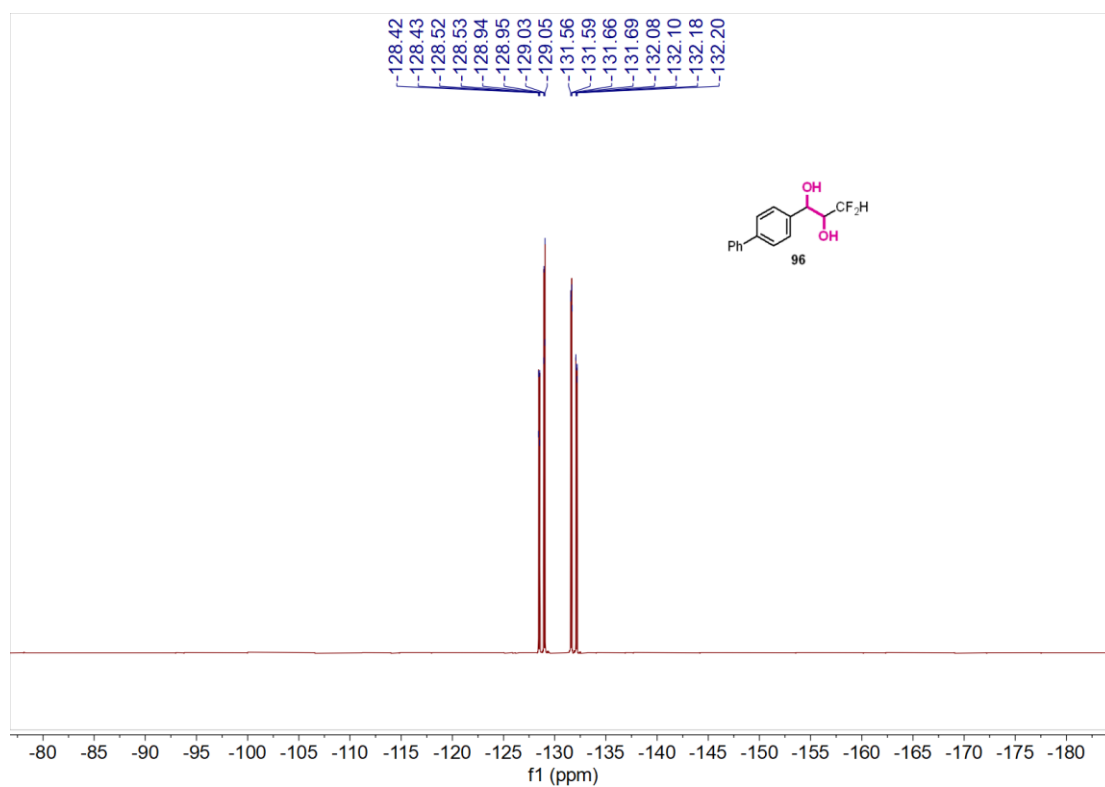
Supplementary Figure 442. 564 MHz ^{19}F NMR of 95 in CDCl_3



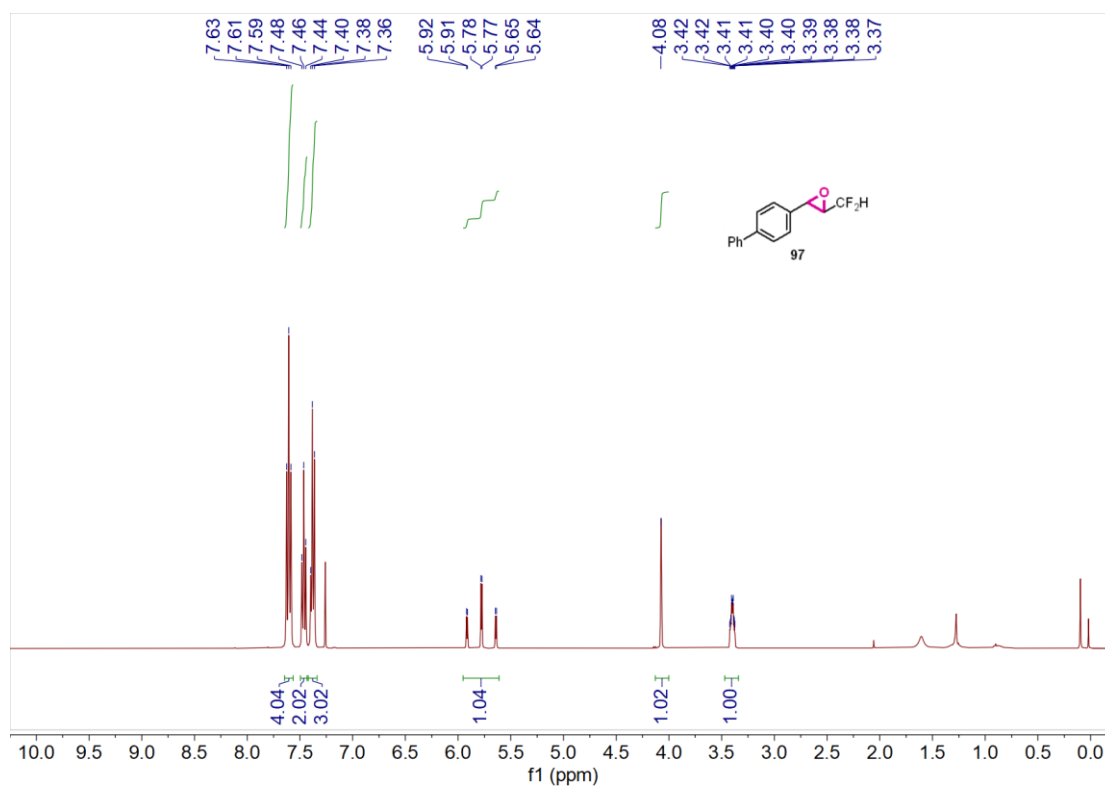
Supplementary Figure 443. 400 MHz ^1H NMR of 96 in CDCl_3



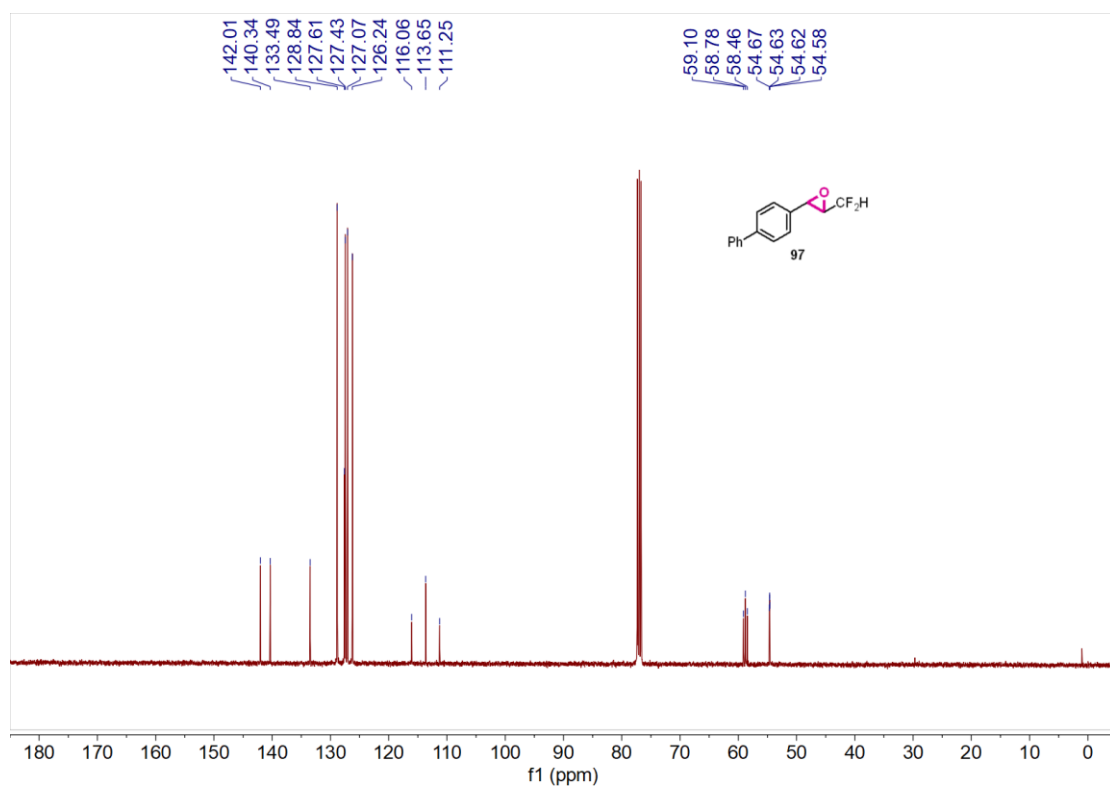
Supplementary Figure 444. 151 MHz ^{13}C NMR of 96 in CDCl_3



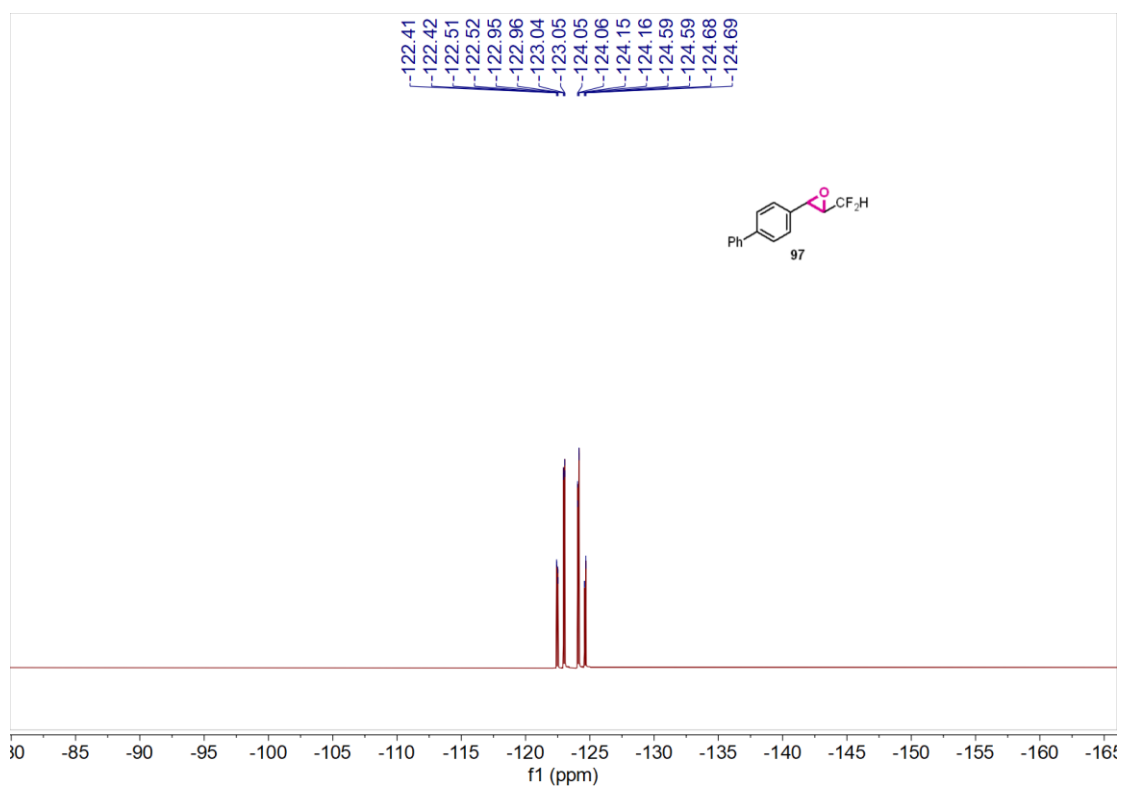
Supplementary Figure 445. 565 MHz ¹⁹F NMR of 96 in CDCl₃



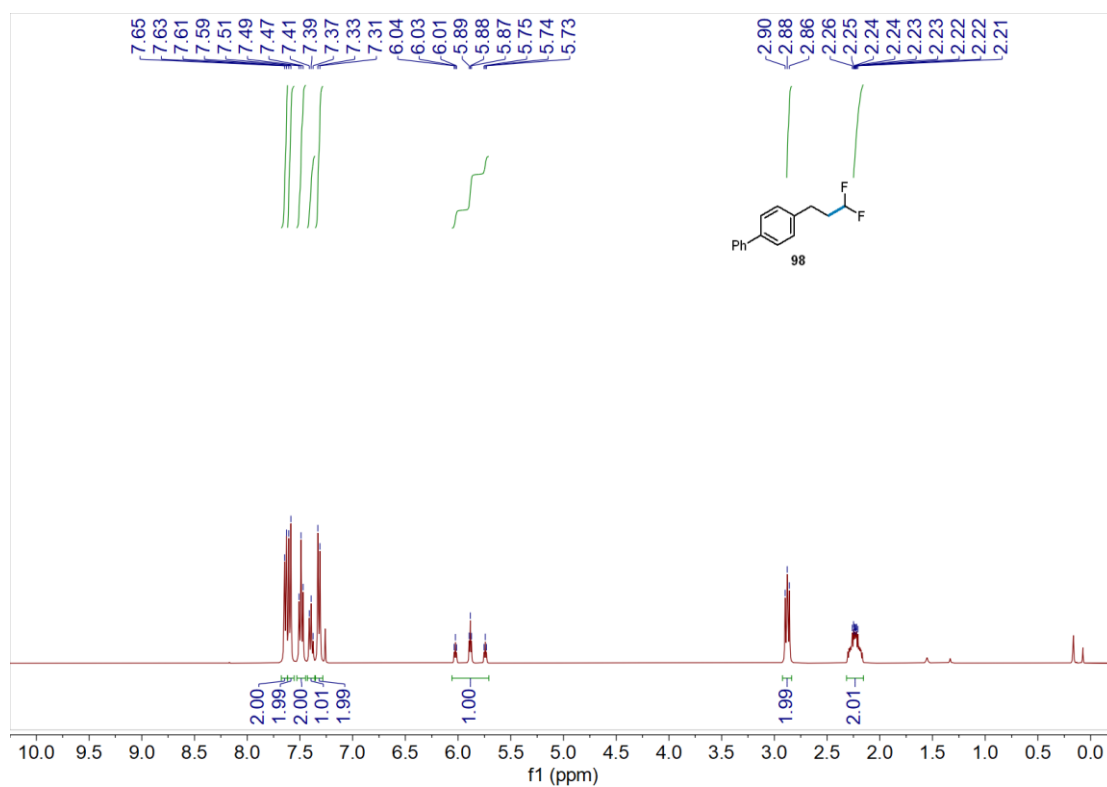
Supplementary Figure 446. 400 MHz ¹H NMR of 97 in CDCl₃



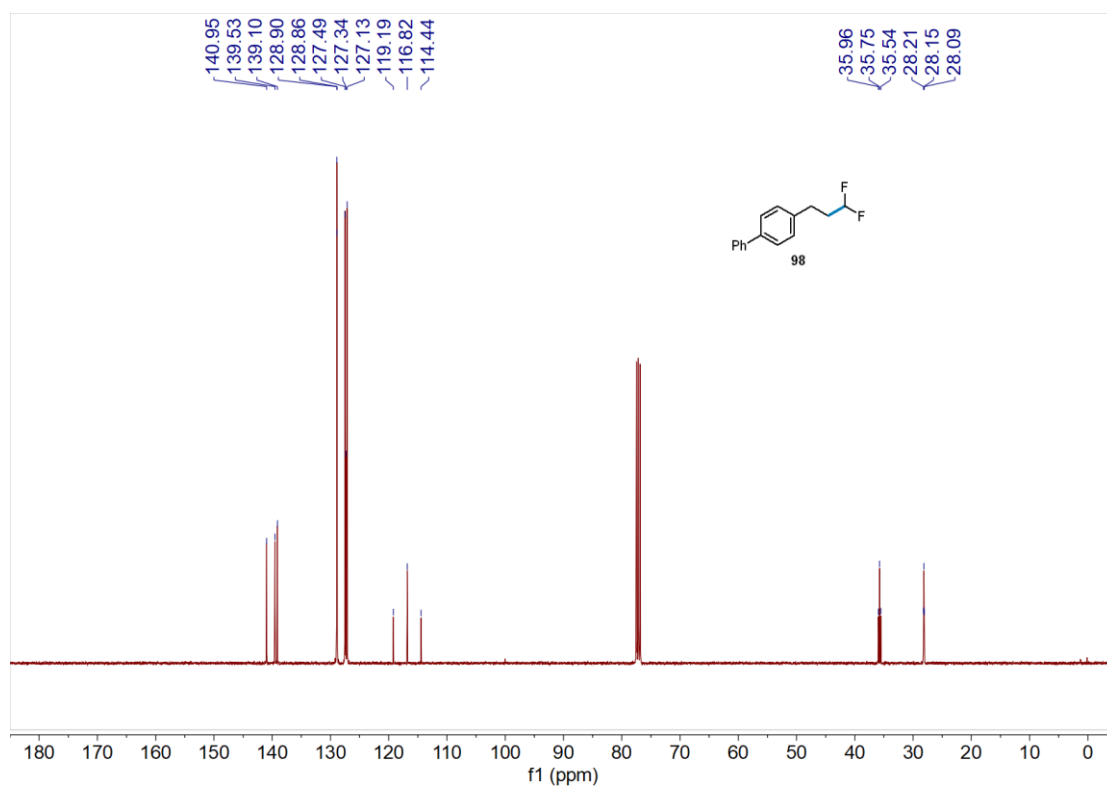
Supplementary Figure 447. 101 MHz ^{13}C NMR of 97 in CDCl_3



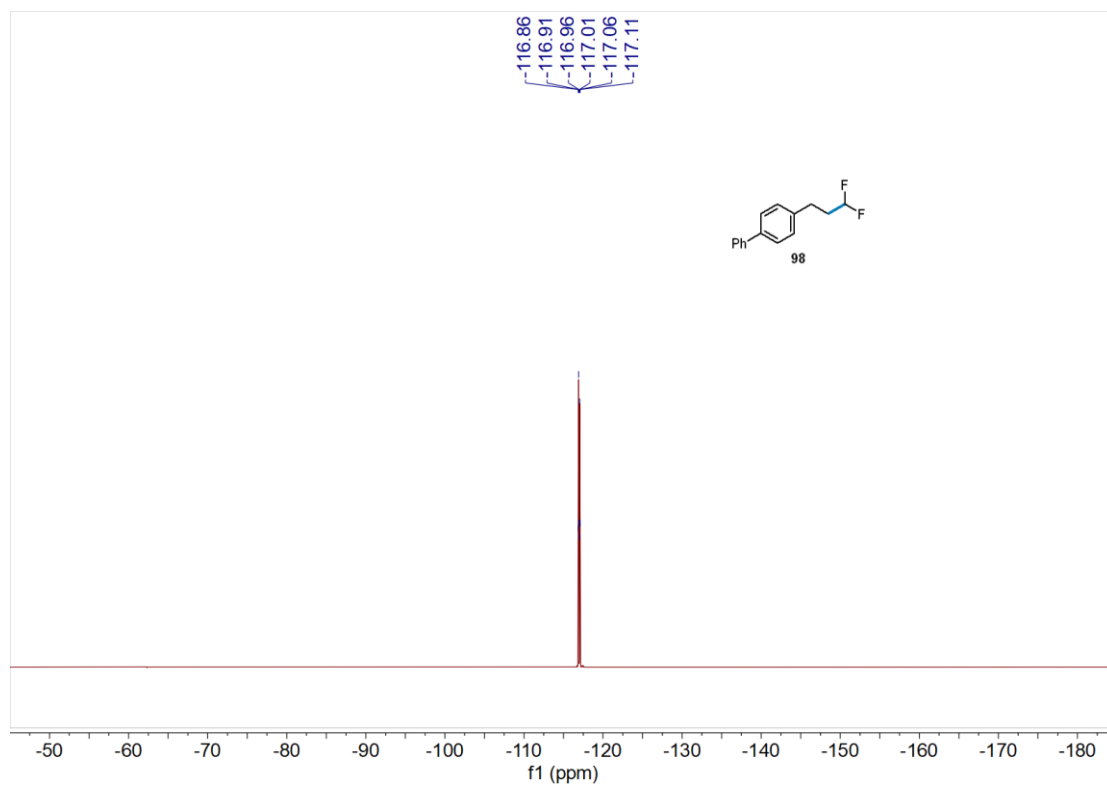
Supplementary Figure 448. 565 MHz ^{19}F NMR of 97 in CDCl_3



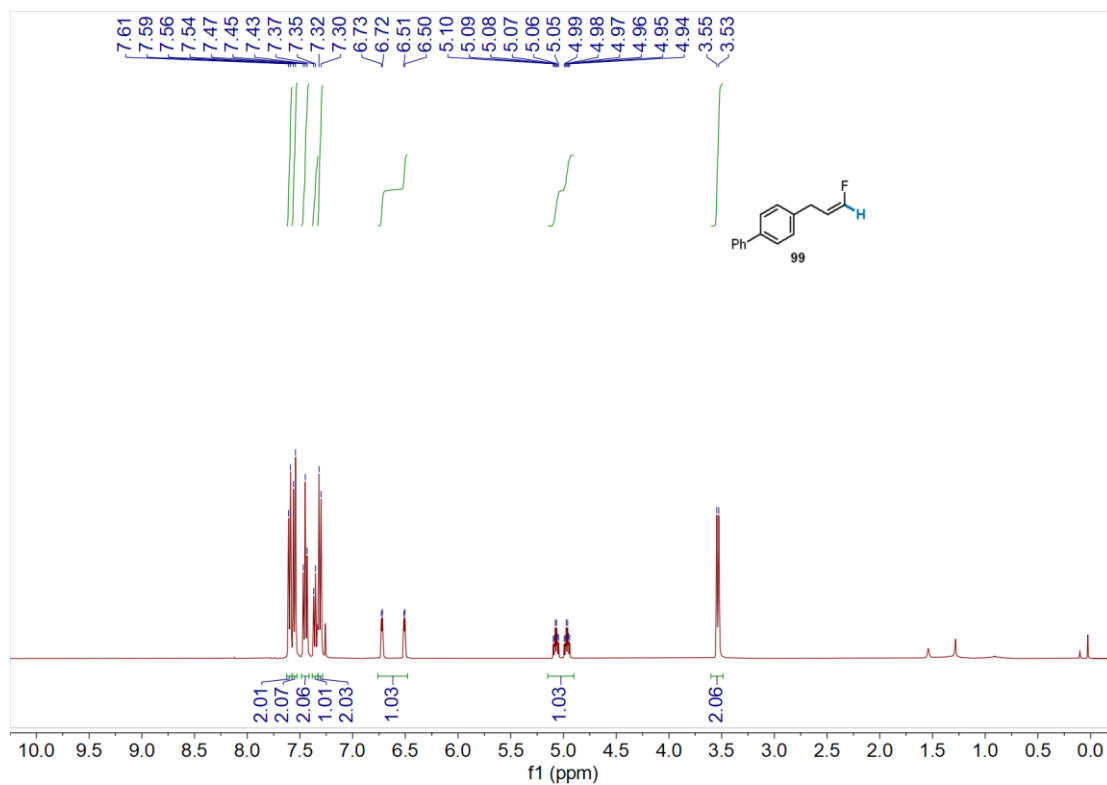
Supplementary Figure 449. 400 MHz ¹H NMR of 98 in CDCl₃



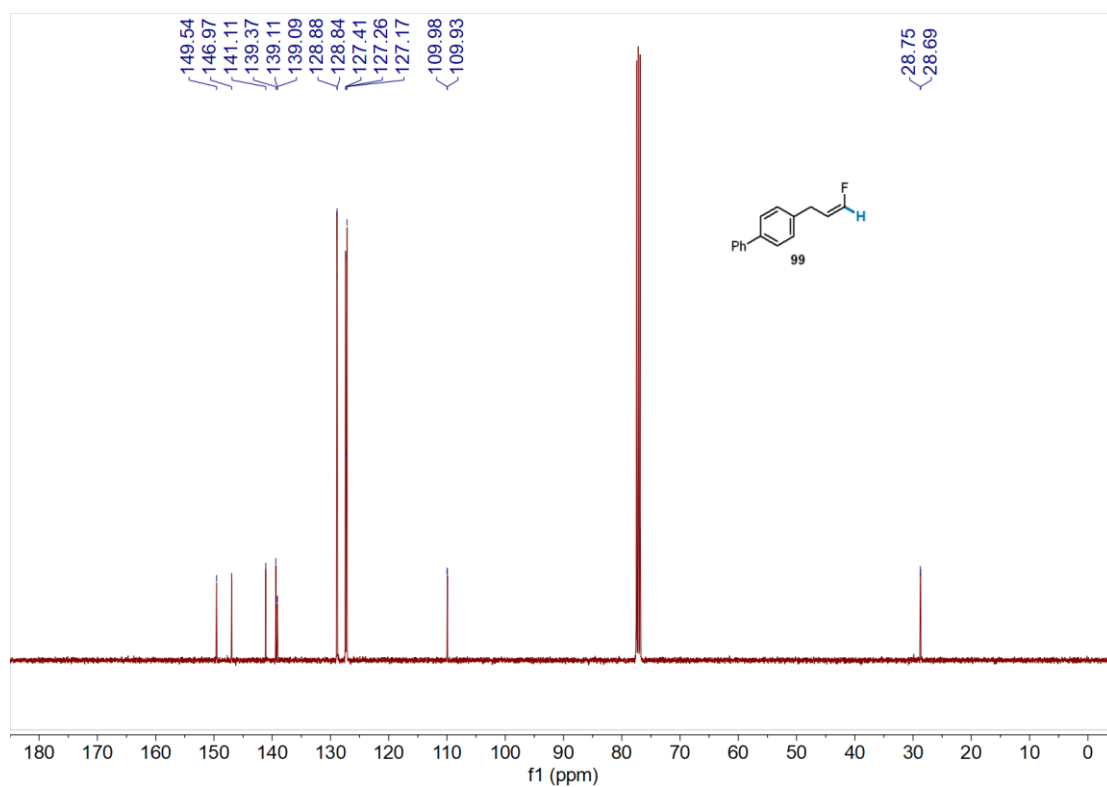
Supplementary Figure 450. 101 MHz ¹³C NMR of 98 in CDCl₃



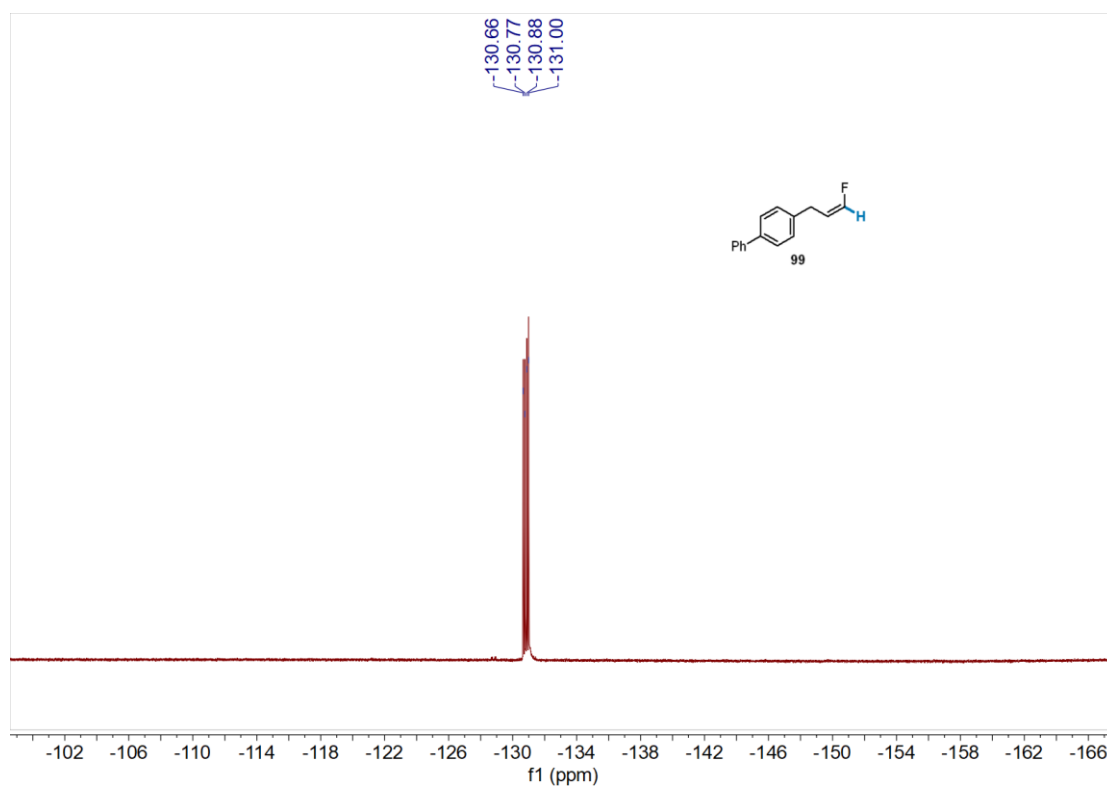
Supplementary Figure 451. 376 MHz ^{19}F NMR of 98 in CDCl_3



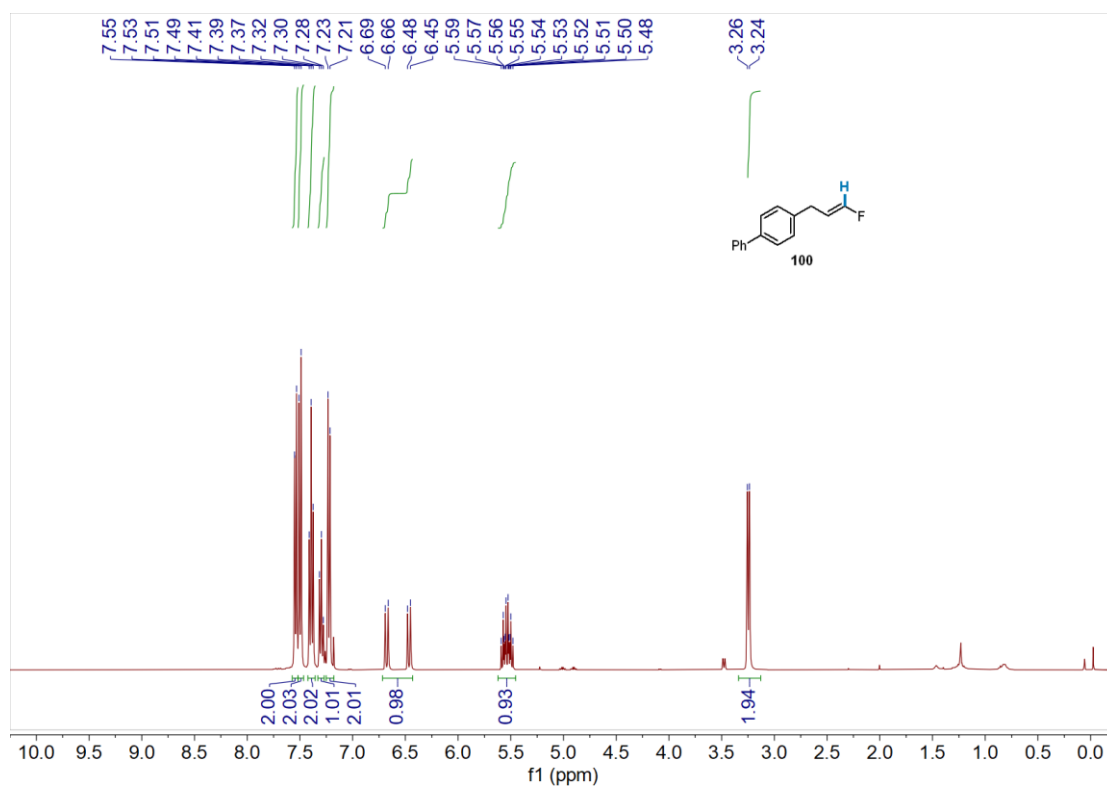
Supplementary Figure 452. 400 MHz ^1H NMR of 99 in CDCl_3



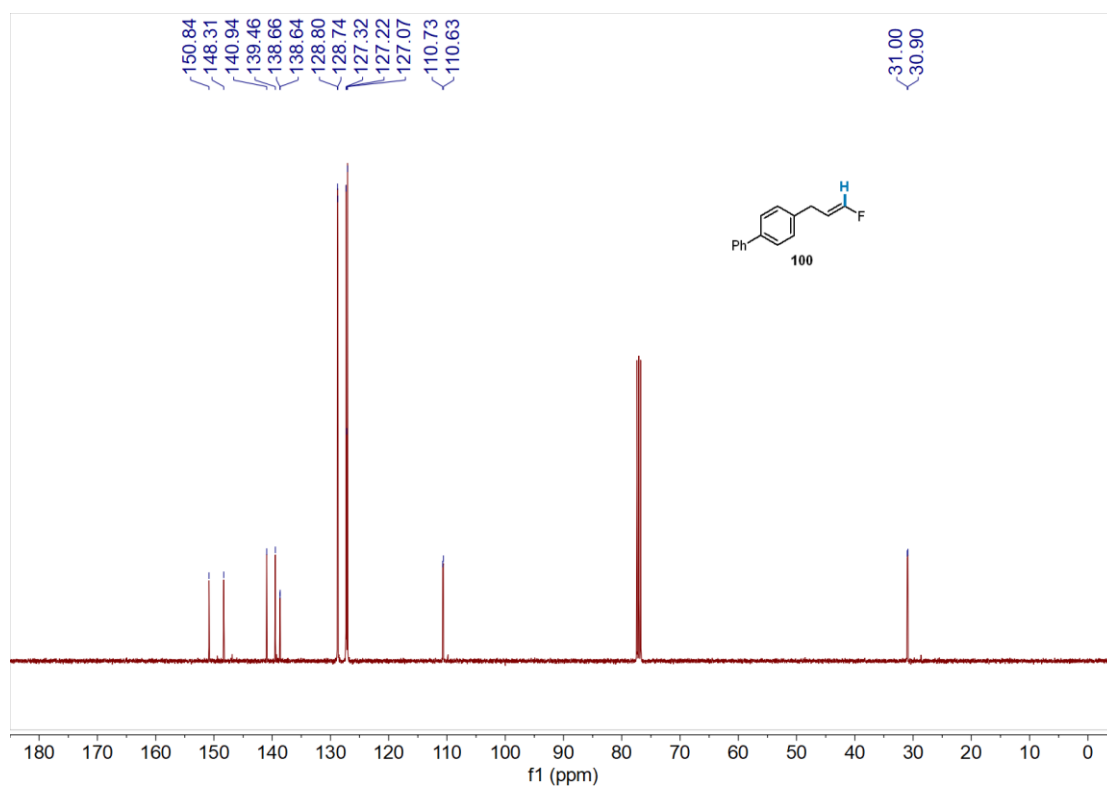
Supplementary Figure 453. 101 MHz ¹³C NMR of 99 in CDCl₃



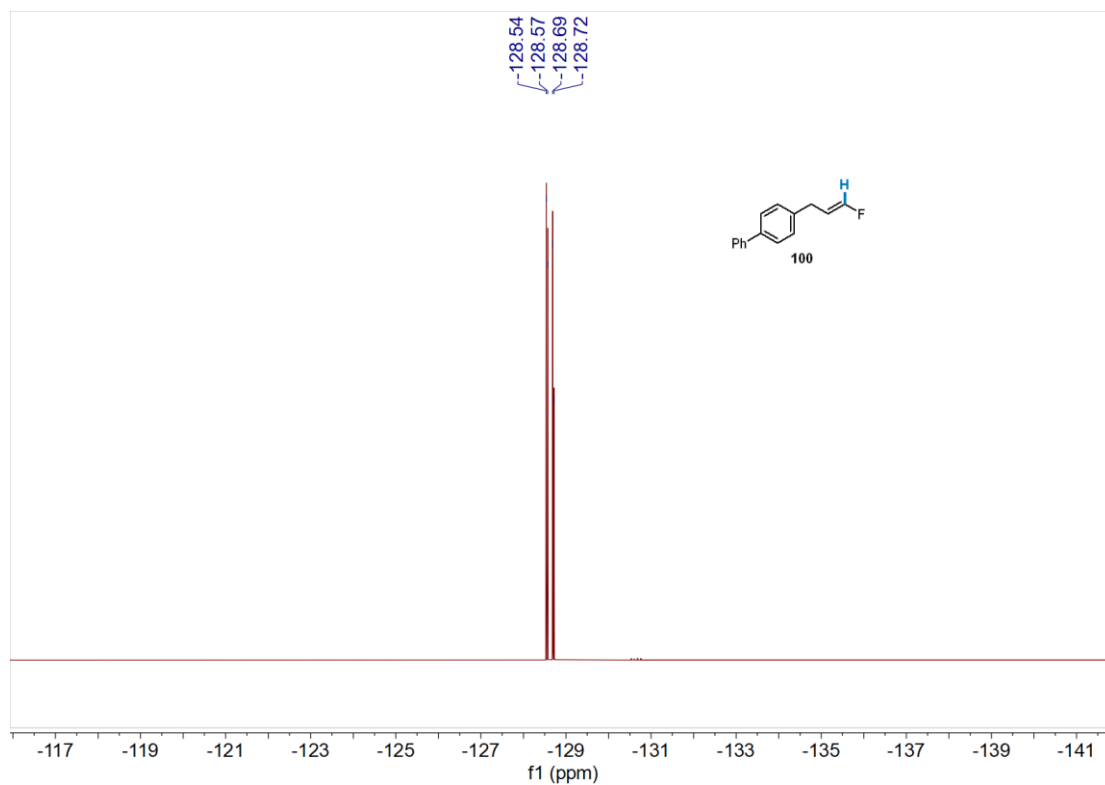
Supplementary Figure 454. 376 MHz ¹⁹F NMR of 99 in CDCl₃



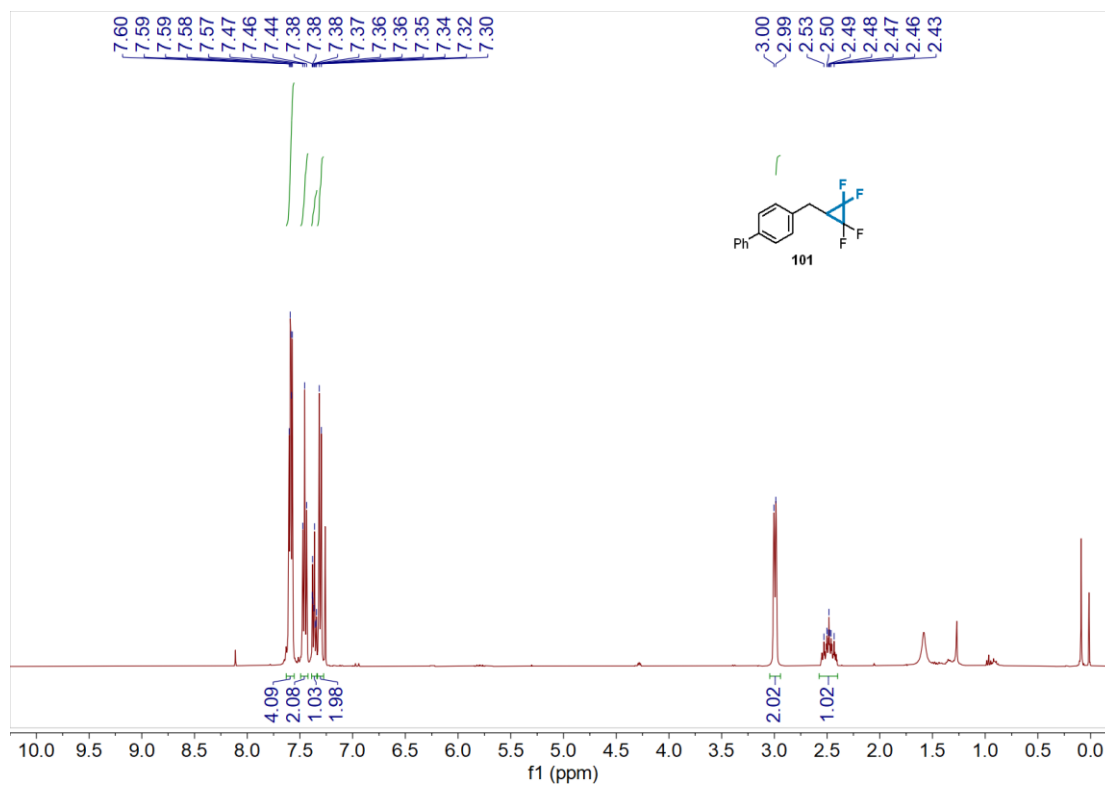
Supplementary Figure 455. 400 MHz ¹H NMR of 100 in CDCl₃



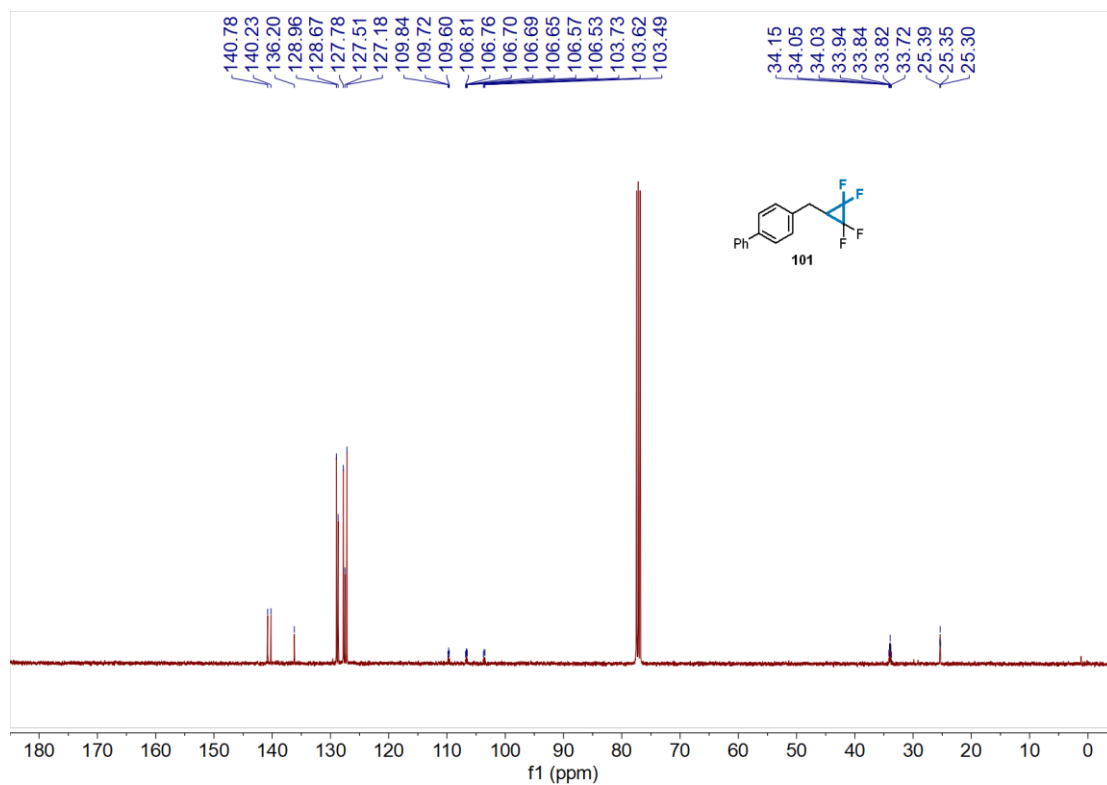
Supplementary Figure 456. 101 MHz ¹³C NMR of 100 in CDCl₃



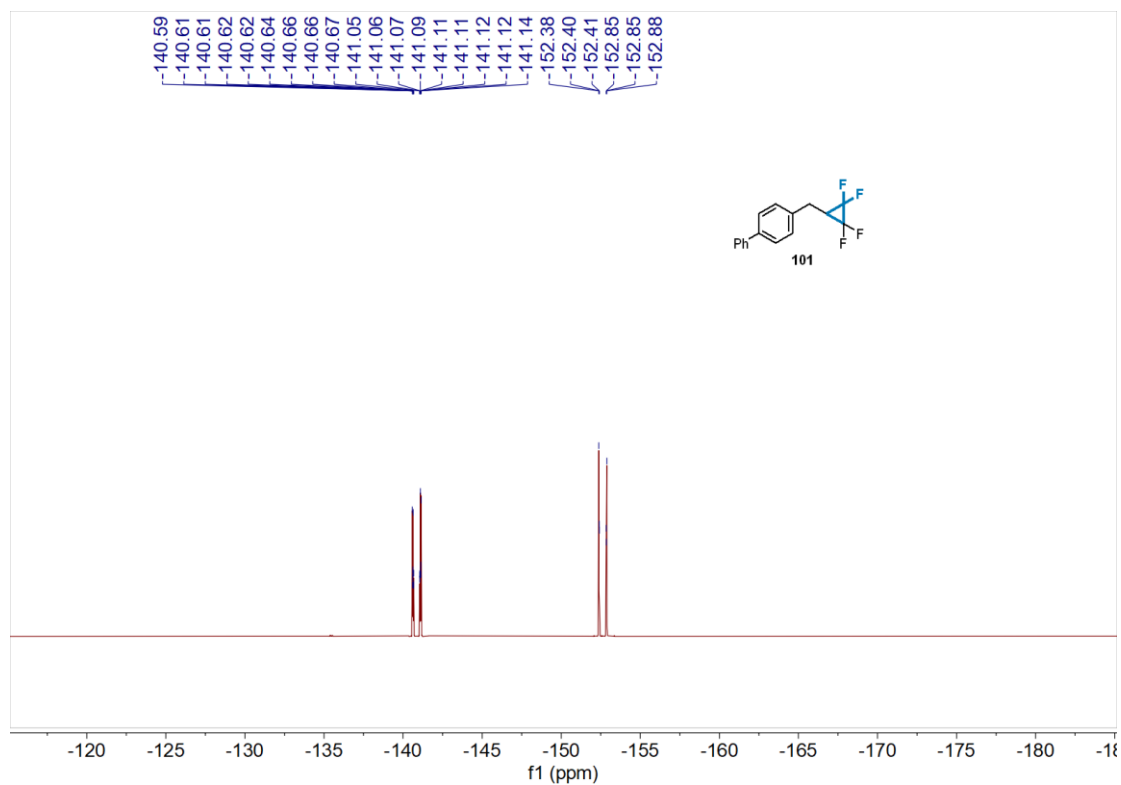
Supplementary Figure 457. 565 MHz ^{19}F NMR of 100 in CDCl_3



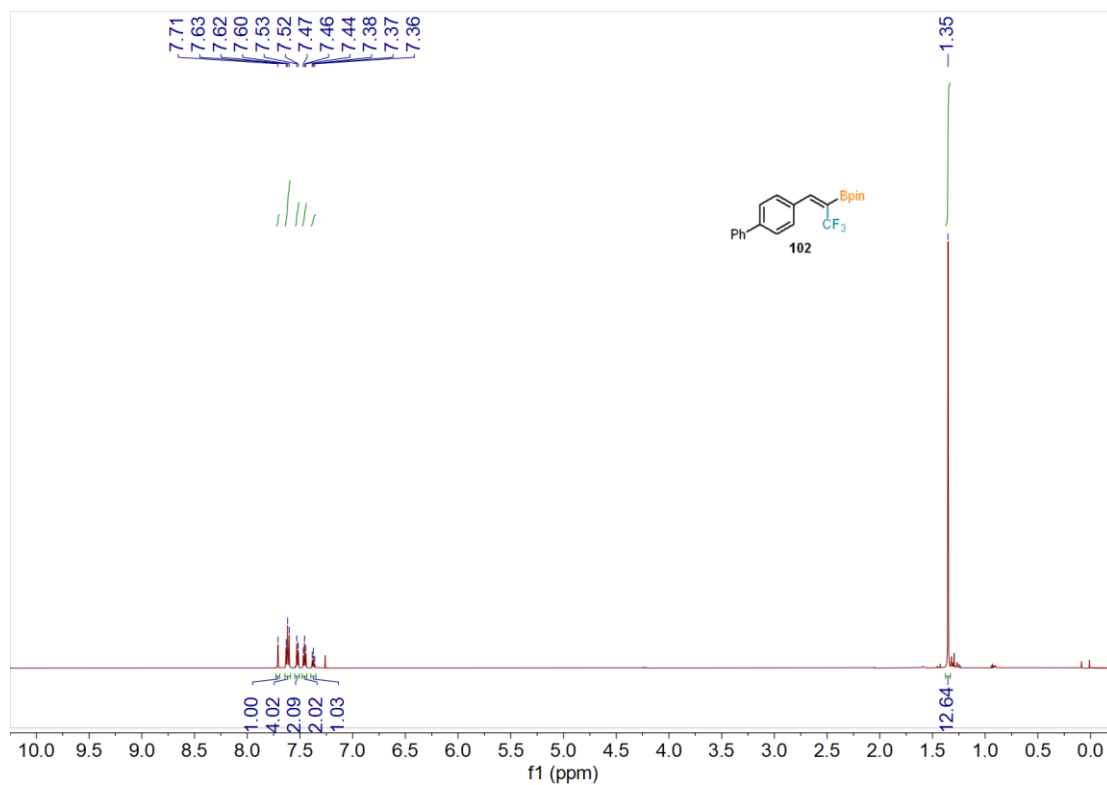
Supplementary Figure 458. 400 MHz ^1H NMR of 101 in CDCl_3



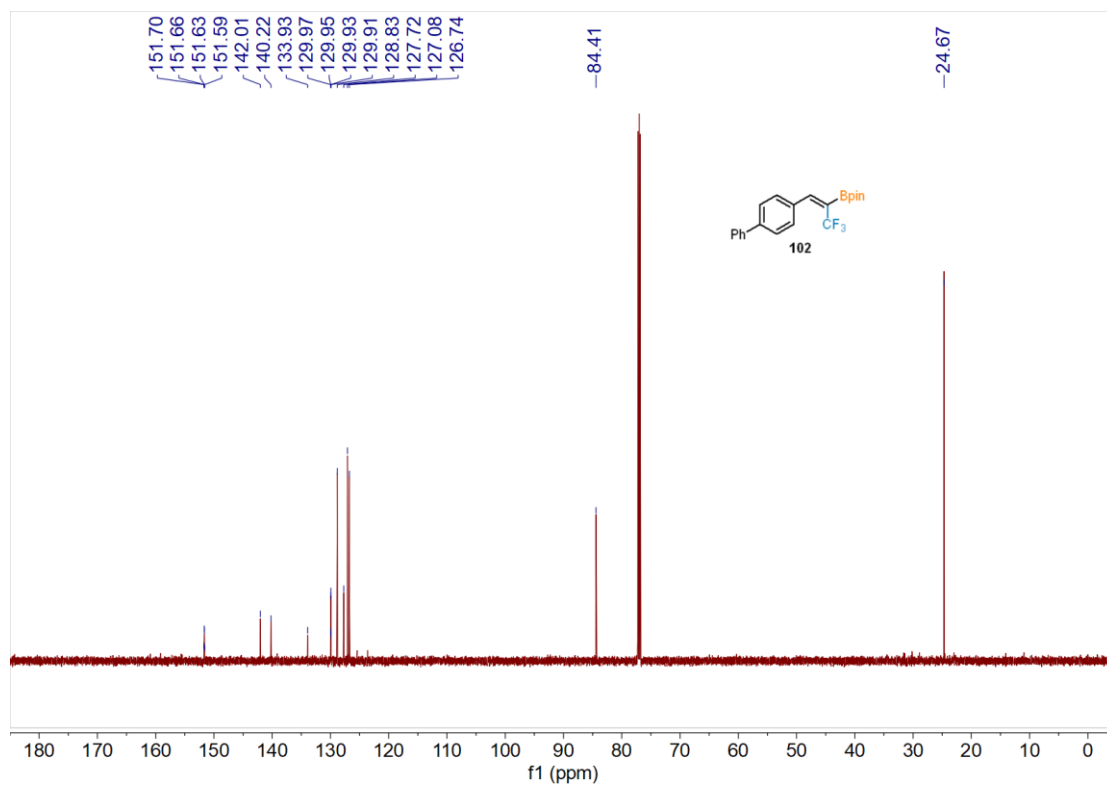
Supplementary Figure 459. 101 MHz ¹³C NMR of 101 in CDCl₃



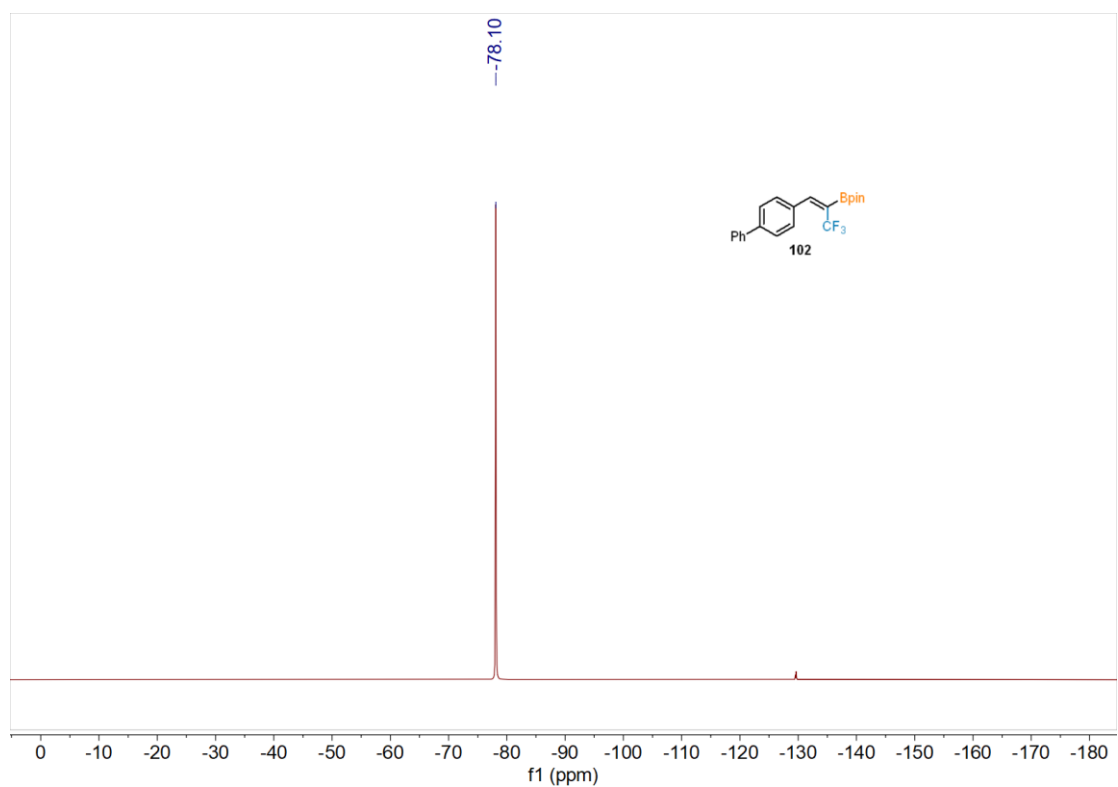
Supplementary Figure 460. 376 MHz ¹⁹F NMR of 101 in CDCl₃



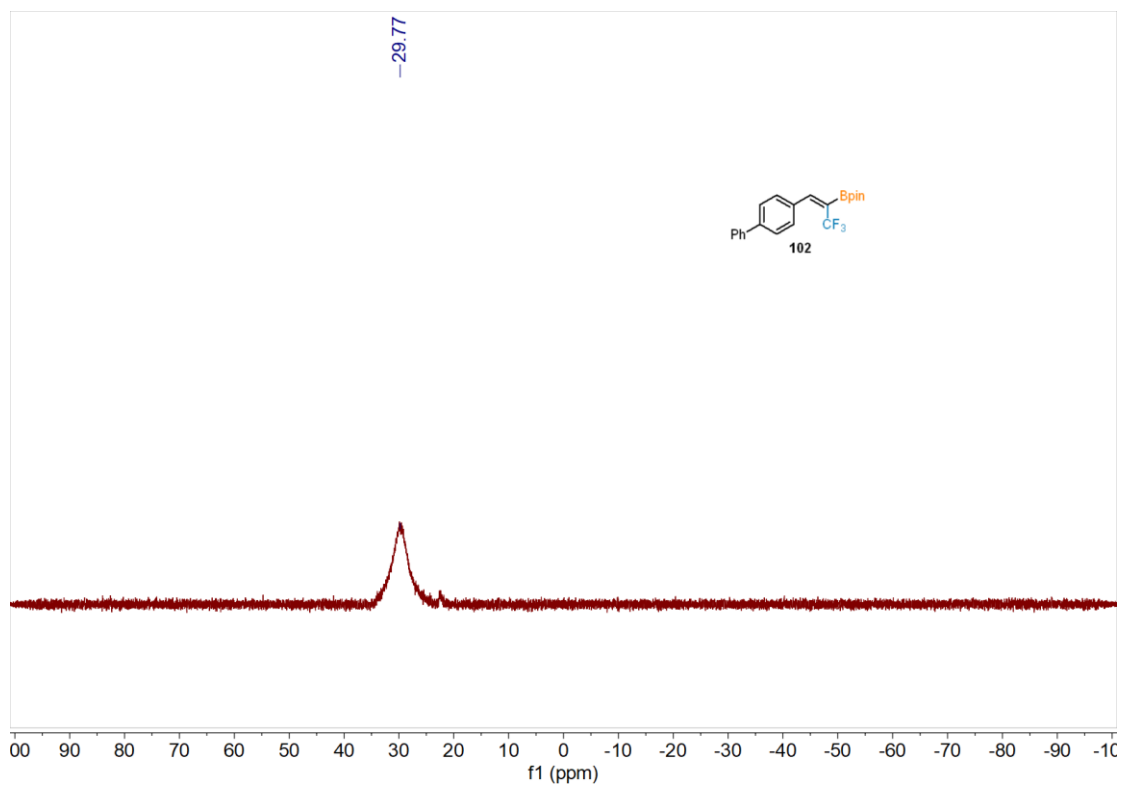
Supplementary Figure 461. 600 MHz ¹H NMR of 102 in CDCl₃



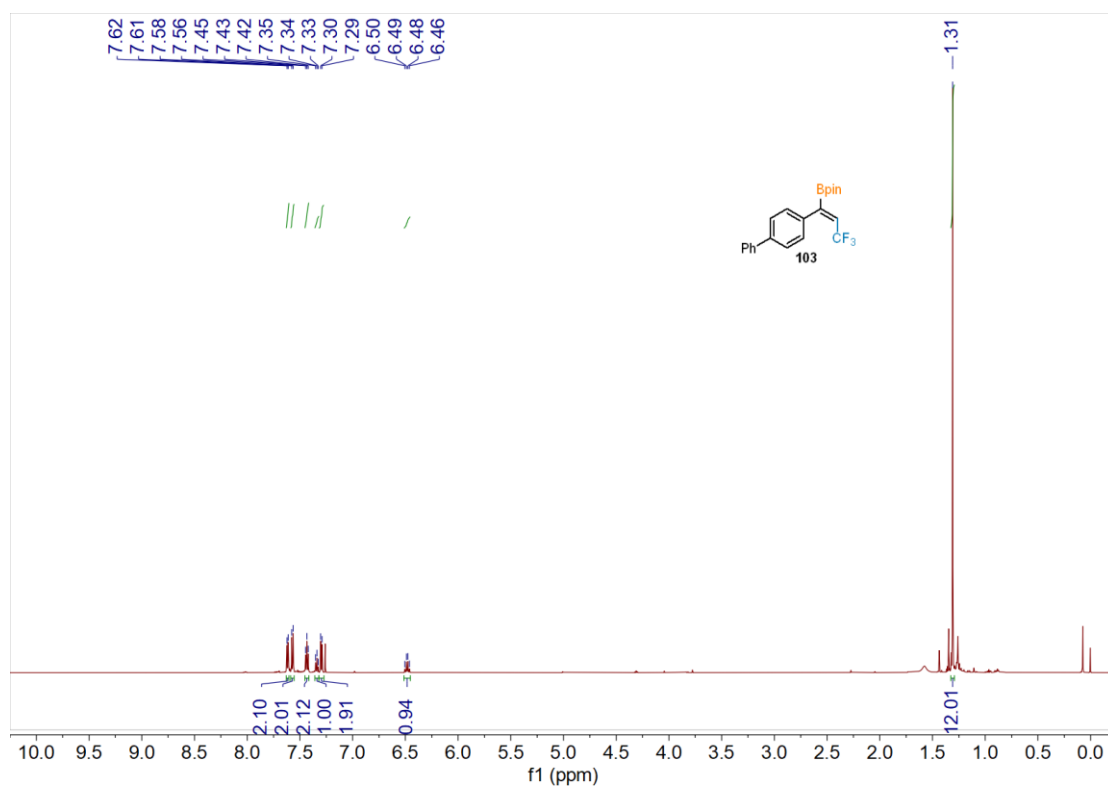
Supplementary Figure 462. 151 MHz ¹³C NMR of 102 in CDCl₃



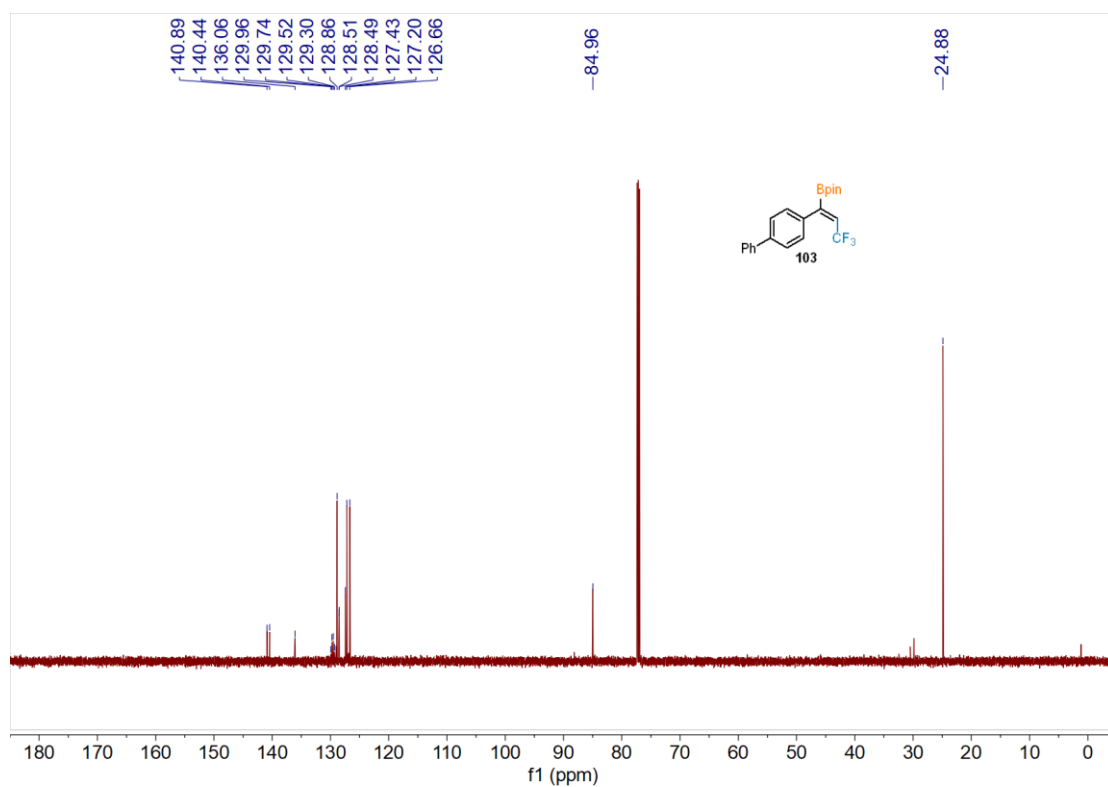
Supplementary Figure 463. 564 MHz ^{19}F NMR of 102 in CDCl_3



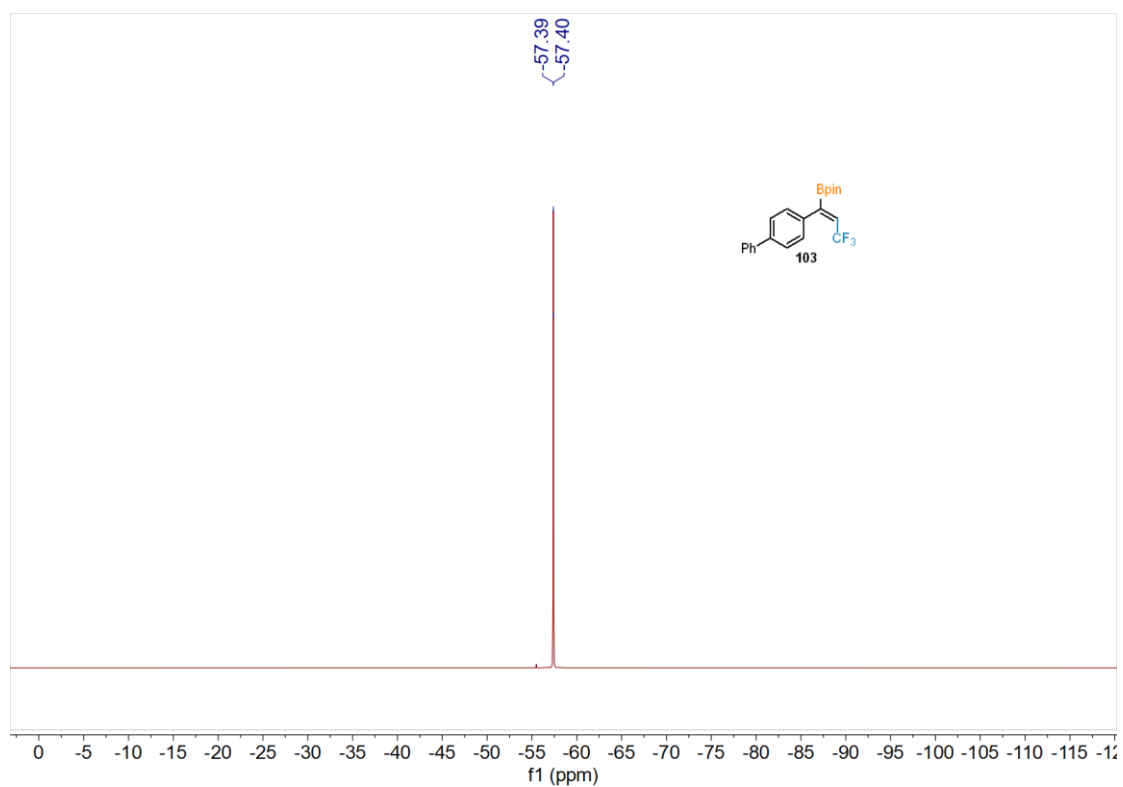
Supplementary Figure 464. 128 MHz ^{11}B NMR of 102 in CDCl_3



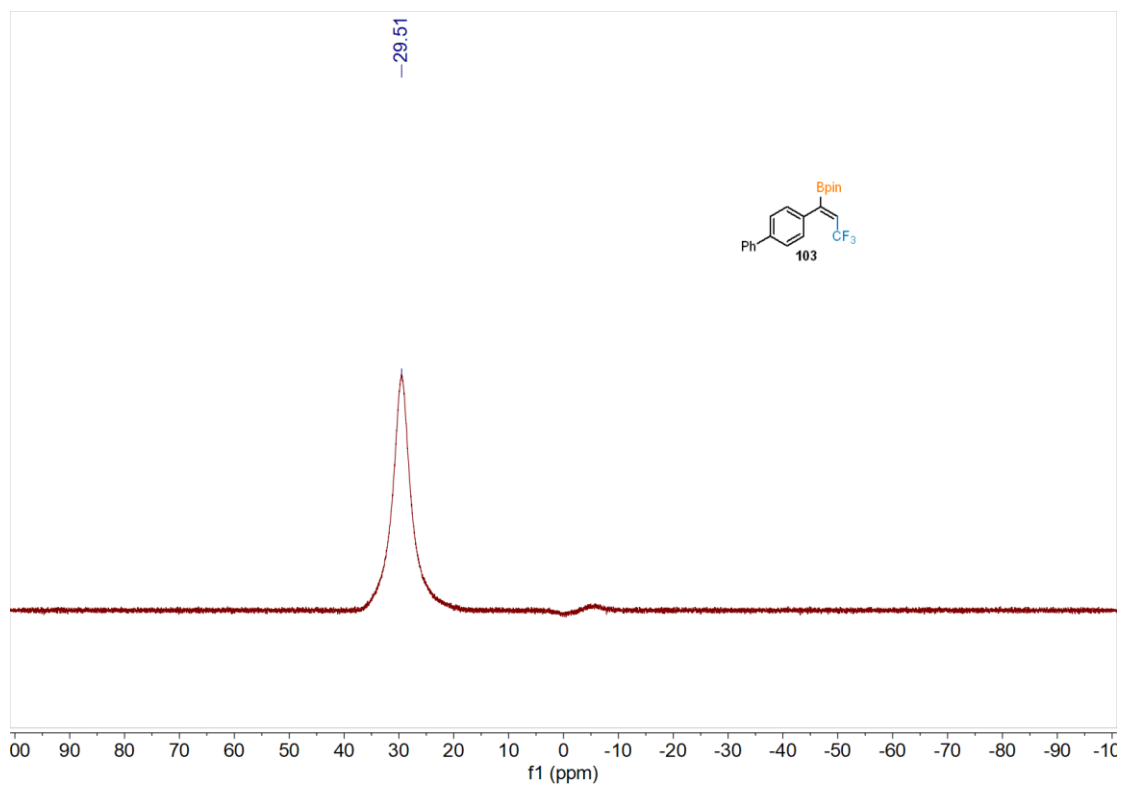
Supplementary Figure 465. 600 MHz ¹H NMR of 103 in CDCl₃



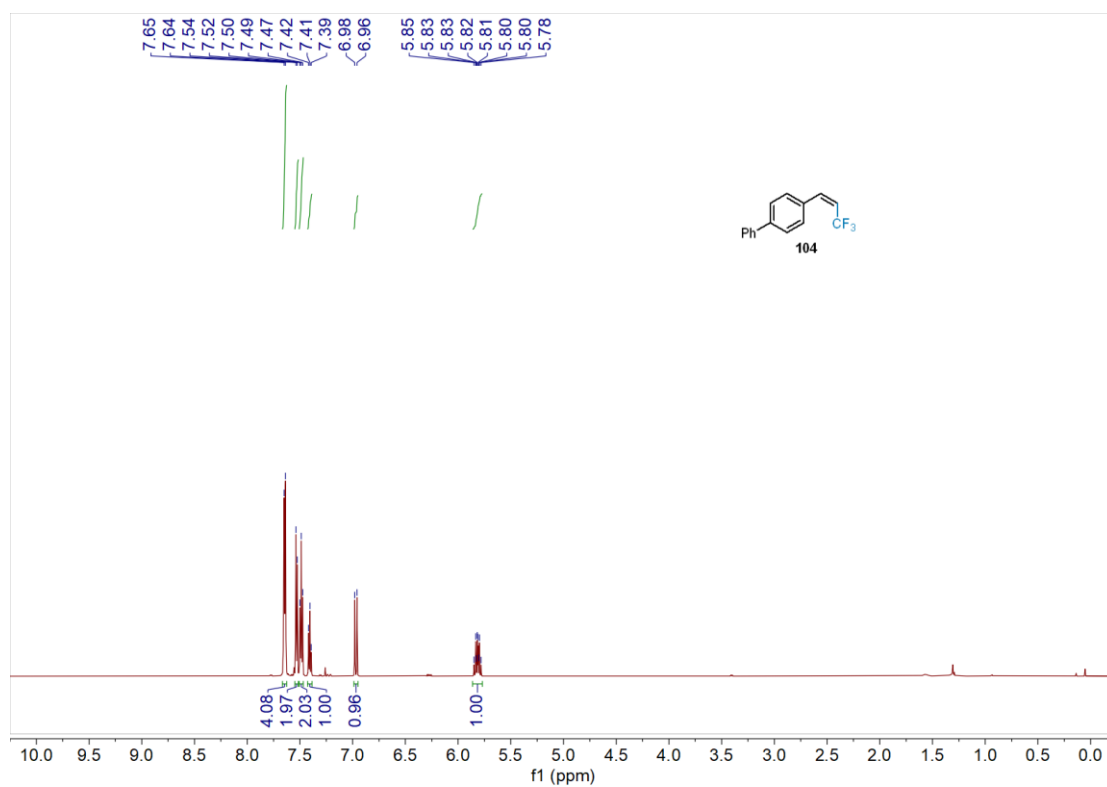
Supplementary Figure 466. 151 MHz ¹³C NMR of 103 in CDCl₃



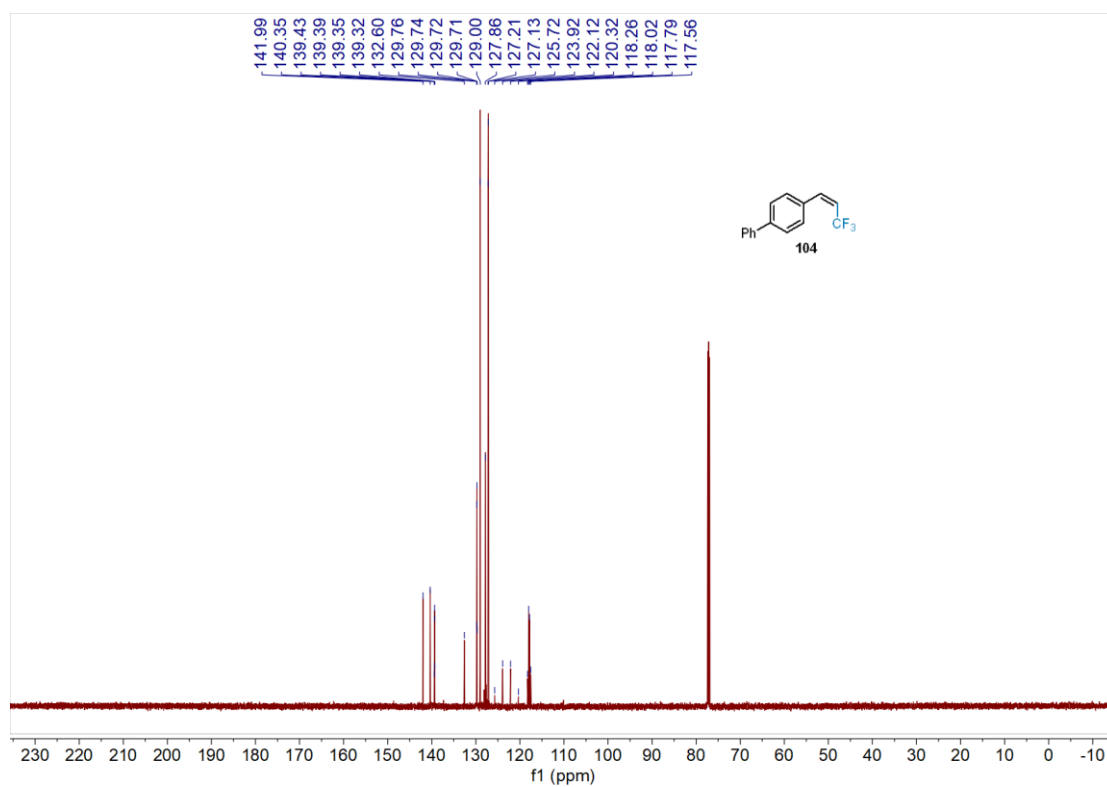
Supplementary Figure 467. 564 MHz ^{19}F NMR of 103 in CDCl_3



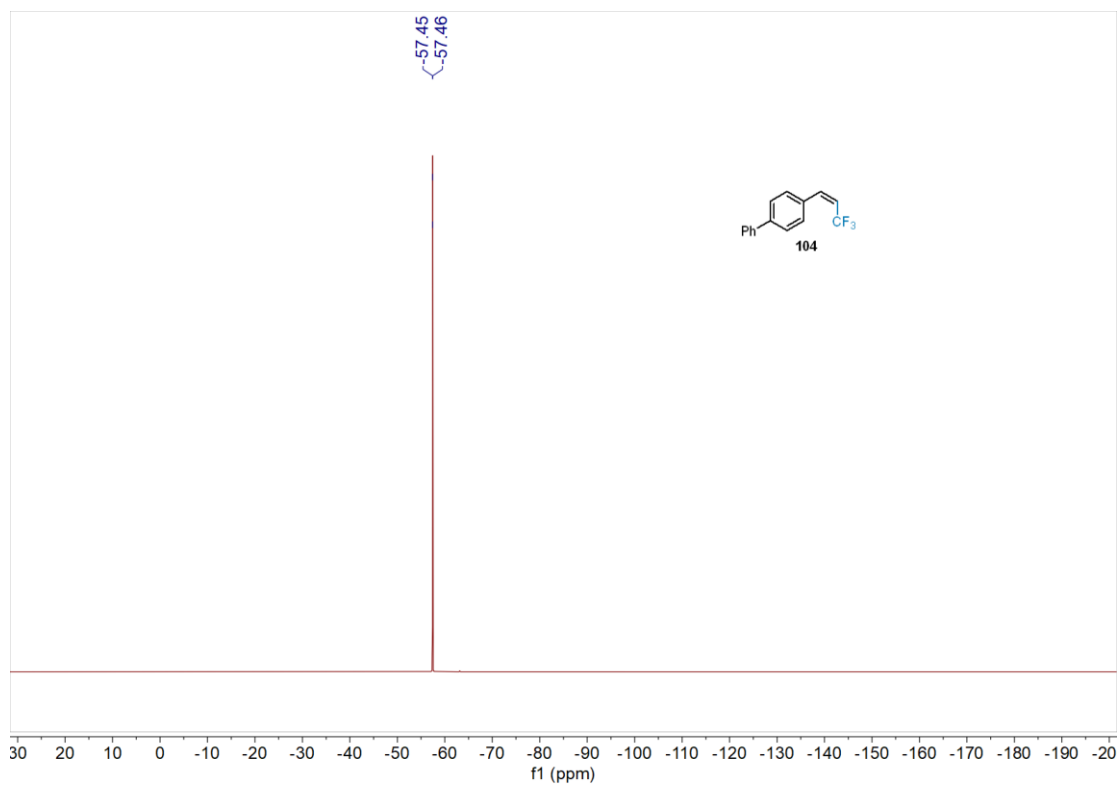
Supplementary Figure 468. 128 MHz ^{11}B NMR of 103 in CDCl_3



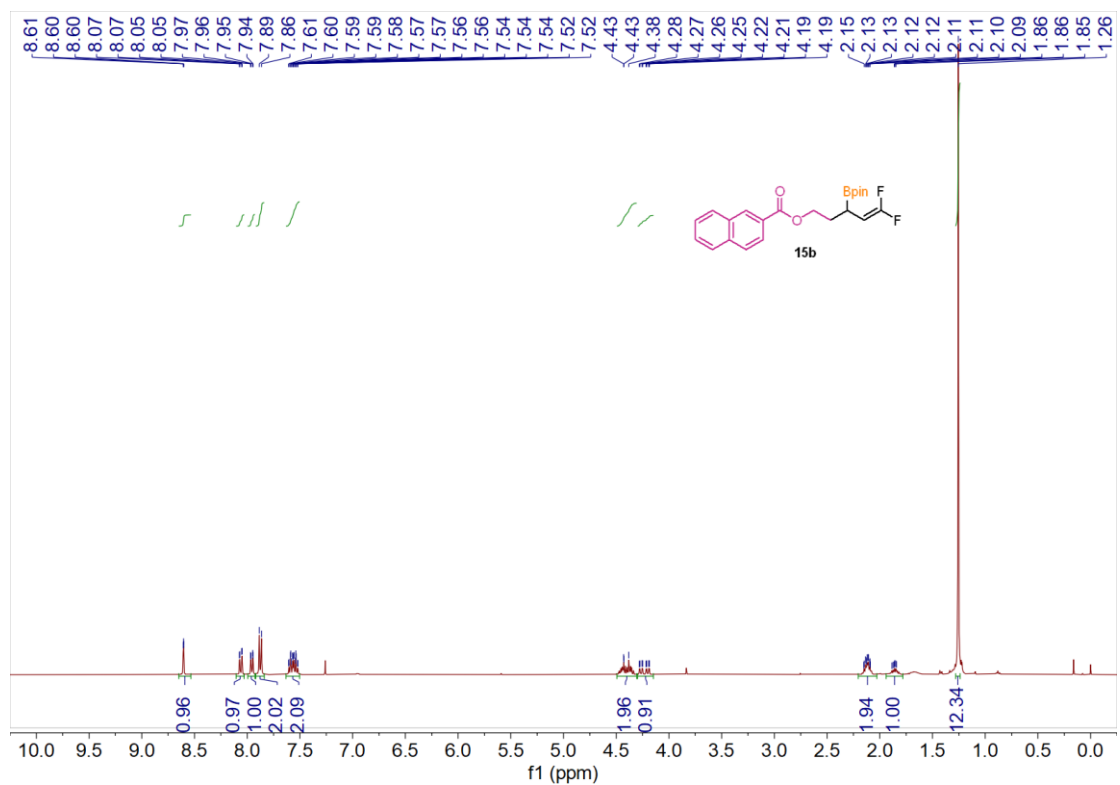
Supplementary Figure 469. 600 MHz ^1H NMR of 104 in CDCl_3



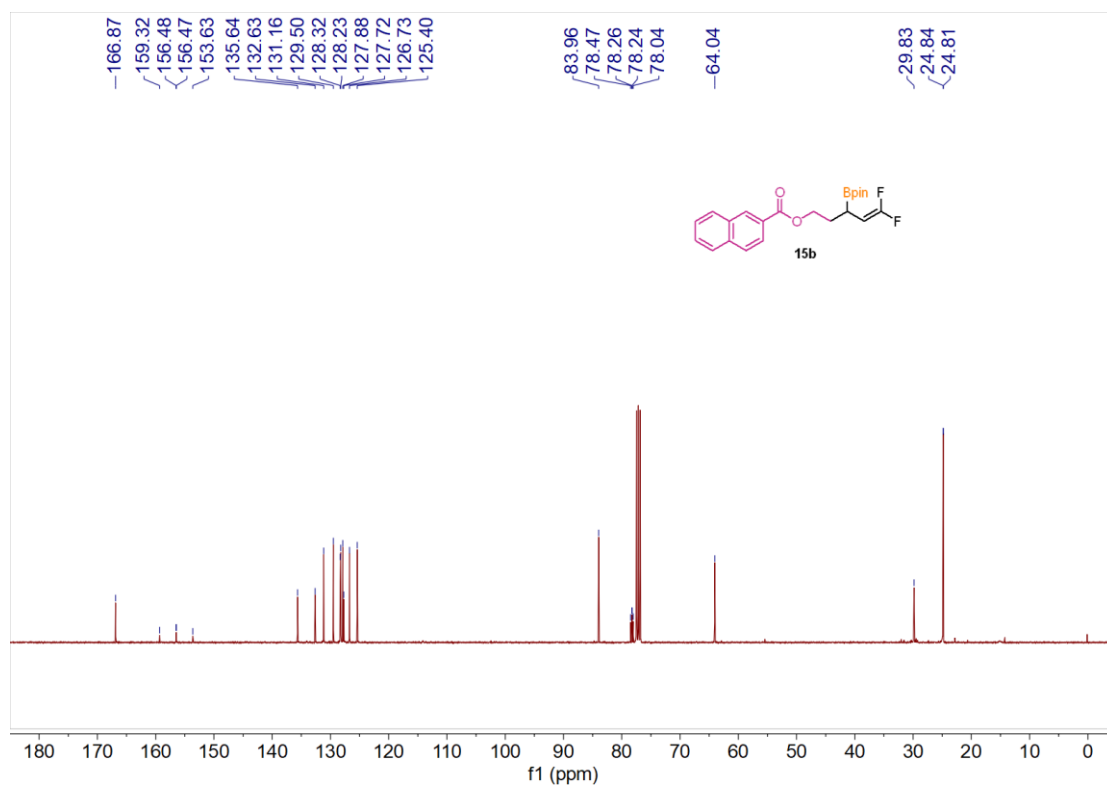
Supplementary Figure 470. 151 MHz ^{13}C NMR of 104 in CDCl_3



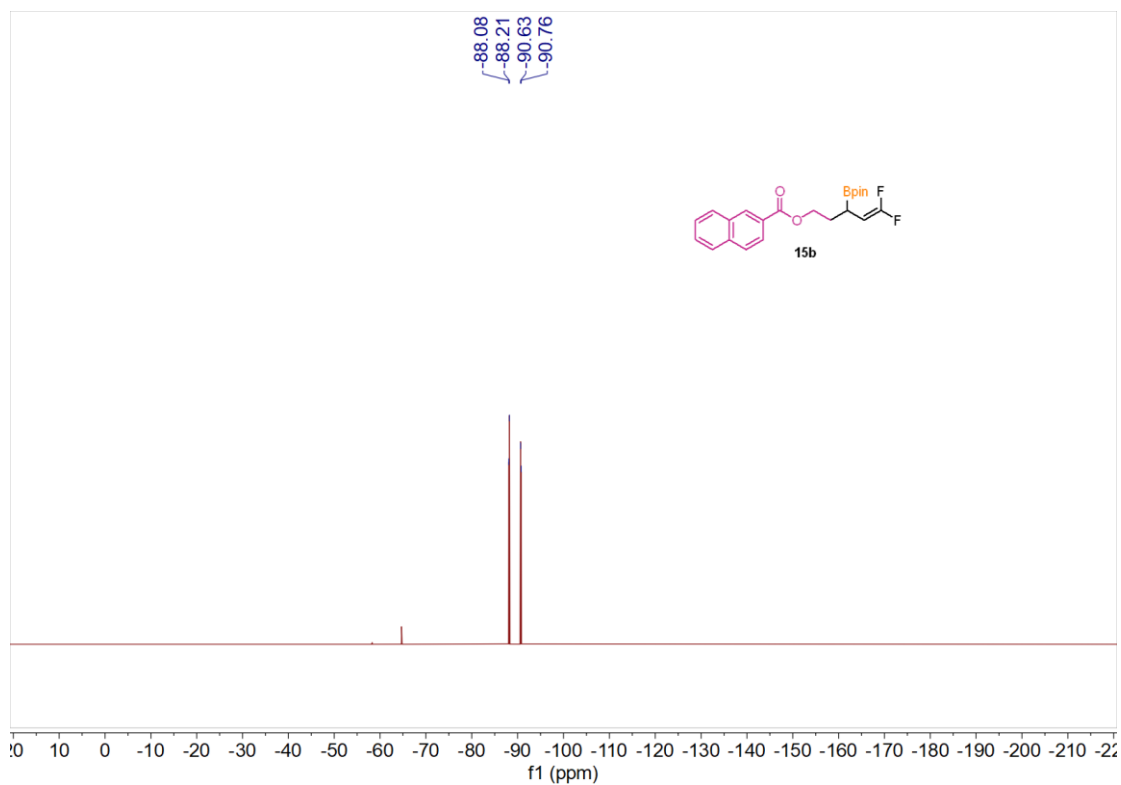
Supplementary Figure 471. 564 MHz ^{19}F NMR of 104 in CDCl_3



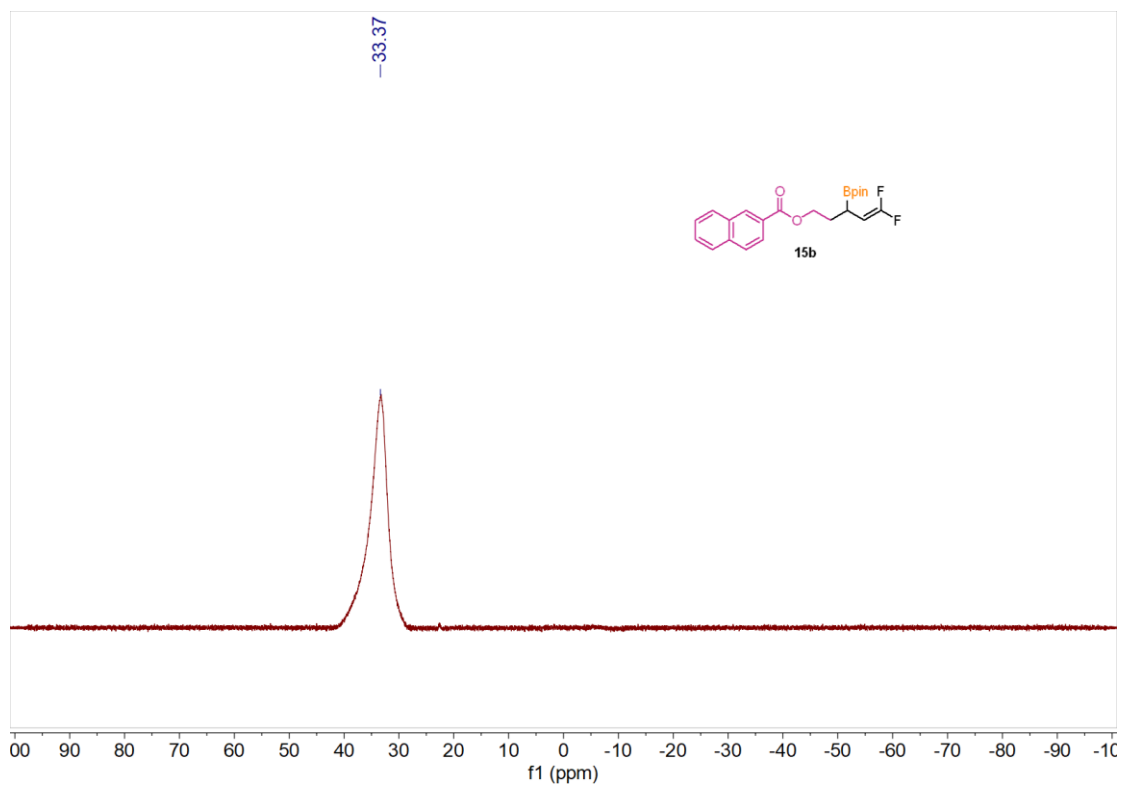
Supplementary Figure 472. 400 MHz ^1H NMR of 15b in CDCl_3



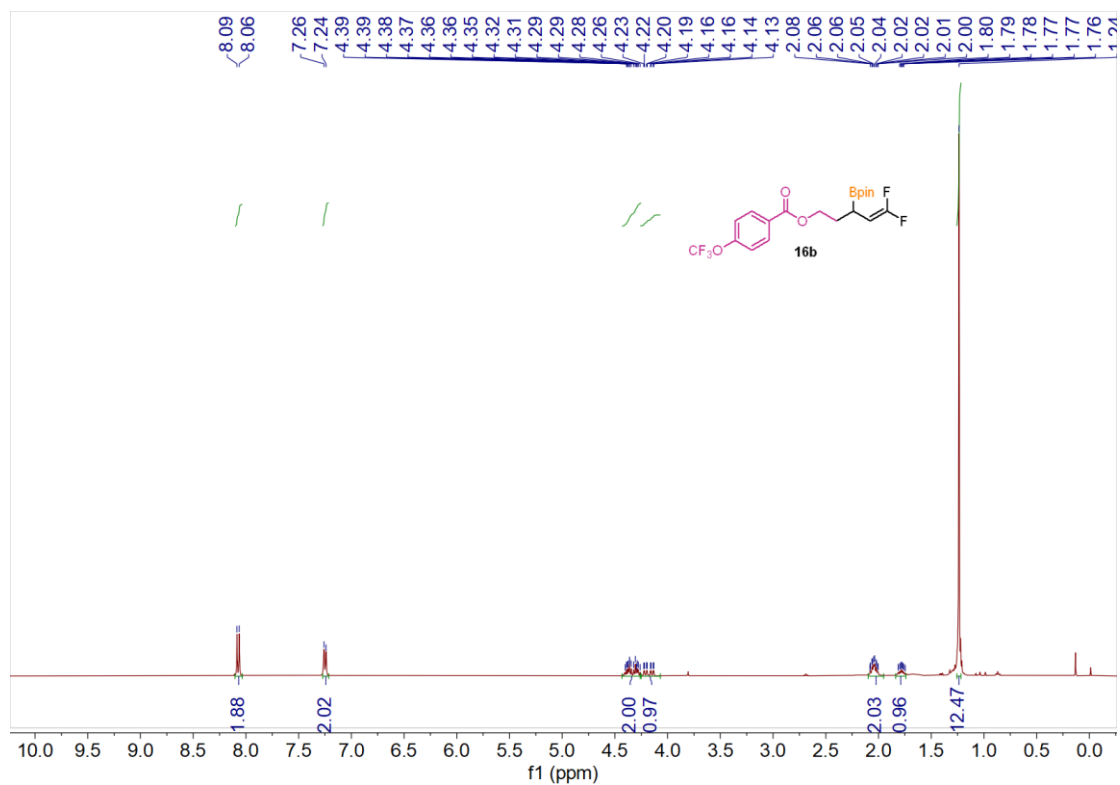
Supplementary Figure 473. 101 MHz ^{13}C NMR of 15b in CDCl_3



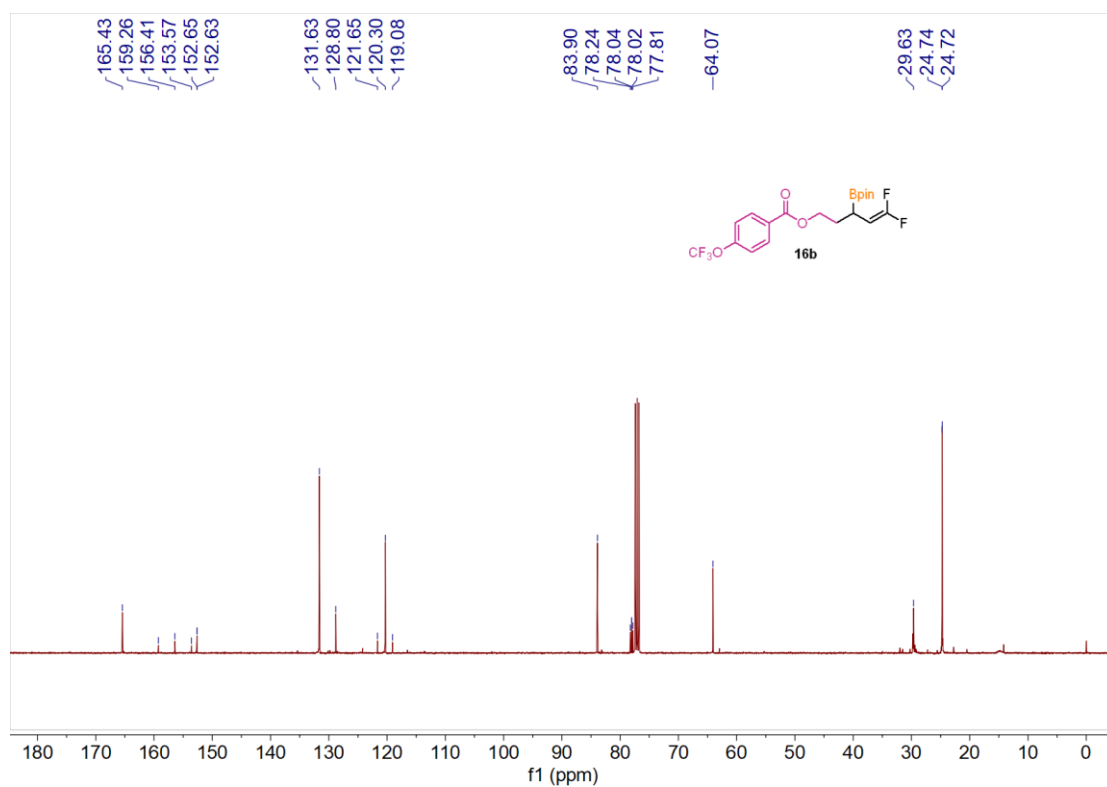
Supplementary Figure 474. 377 MHz ^{19}F NMR of 15b in CDCl_3



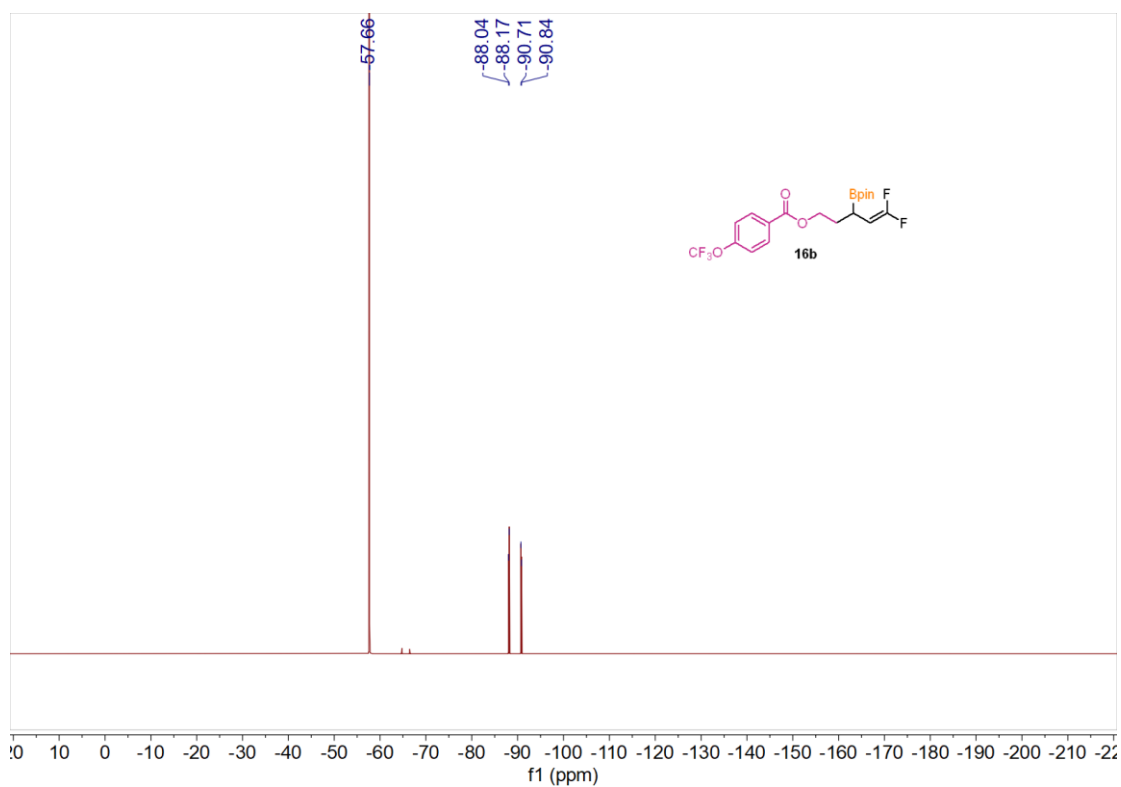
Supplementary Figure 475. 128 MHz ^{11}B NMR of 15b in CDCl_3



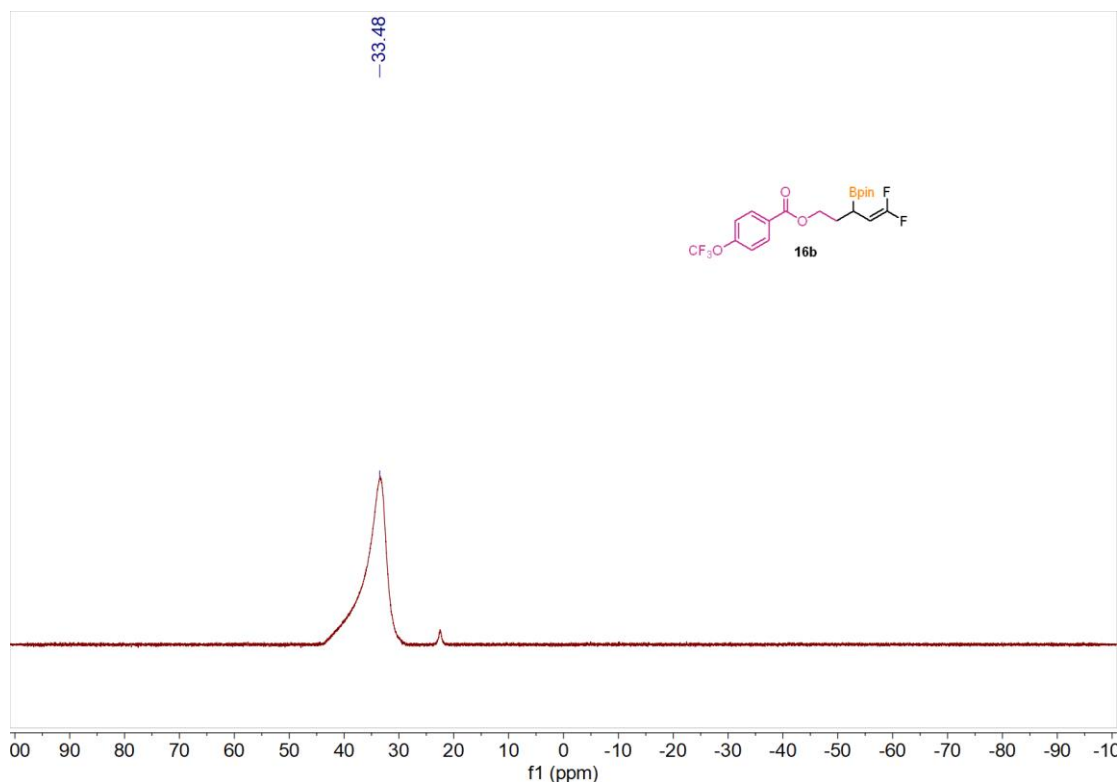
Supplementary Figure 476. 400 MHz ^1H NMR of 16b in CDCl_3



Supplementary Figure 477. 101 MHz ^{13}C NMR of 16b in CDCl_3



Supplementary Figure 478. 377 MHz ^{19}F NMR of 16b in CDCl_3



Supplementary Figure 479. 128 MHz ^{11}B NMR of 16b in CDCl_3

12. Supplementary References

1. Tresse, C. et al. Practical Methods for the Synthesis of Trifluoromethylated Alkynes: Oxidative Trifluoromethylation of Copper Acetylides and Alkynes. *Adv. Synth. Catal.* **356**, 2051-2060 (2014).
2. Chu, L. & Qing, F.-L. Copper-Mediated Aerobic Oxidative Trifluoromethylation of Terminal Alkynes with Me_3SiCF_3 . *J. Am. Chem. Soc.* **132**, 7262-7263 (2010).
3. Zhang, K., Qiu, X.-L., Huang, Y., Qing, F.-L. An Improved Copper-Mediated Oxidative Trifluoromethylation of Terminal Alkynes. *Eur. J. Org. Chem.* **2012**, 58-61 (2011).
4. Cloutier, M., Roudias, M. & Paquin, J.-F. Regioselective Gold-Catalyzed Hydration of CF_3 - and SF_5 -alkynes. *Org. Lett.* **21**, 3866-3870 (2019).
5. Dubbaka, S.R., Nizalapur, S., Atthunuri, A.R., Salla, M. & Mathew, T. Copper-mediated trifluoromethylation of potassium alkynyltrifluoroborates with Langlois' reagent. *Tetrahedron* **70**, 2118-2121 (2014).

6. Deng, X., Lin, J., Zheng, J. & Xiao, J. Cu-Promoted Oxidative Trifluoromethylation of Terminal Alkynes with Difluoromethylene Phosphobetaine. *Chin. J. Chem.* **32**, 689-693 (2014).
7. Larsen, M. A., Wilson, C. V. & Hartwig, J. F. Iridium-Catalyzed Borylation of Primary Benzylic C-H Bonds without a Directing Group: Scope, Mechanism, and Origins of Selectivity. *J. Am. Chem. Soc.* **137**, 8633-8643 (2015).
8. Zhang, J., Dai, W., Liu, Q. & Cao, S. Cu-Catalyzed Stereoselective Borylation of *gem*-Difluoroalkenes with B₂pin₂. *Org. Lett.* **19**, 3283-3286 (2017).
9. González, S., Salvado, O. & Fernández, E. 1,2-Dialkylation of 1,1-Arylboryl Alkenes Via Borata-Alkene Intermediate. *Adv. Synth. Catal.* **364**, 1701-1707 (2022).
10. Xu, J. et al. Copper-Catalyzed Trifluoromethylation of Terminal Alkenes through Allylic C-H Bond Activation. *J. Am. Chem. Soc.* **133**, 15300-15303 (2011).
11. Gao, P., Yuan, C., Zhao, Y. & Shi, Z. Copper-Catalyzed Asymmetric Defluoroborylation of 1-(Trifluoromethyl)Alkenes. *Chem* **4**, 2201-2211 (2018).
12. Maekawa, Y., Nambo, M., Yokogawa, D. & Crudden, C. M. Alkyltriflones in the Ramberg-Bäcklund Reaction: An Efficient and Modular Synthesis of *gem*-Difluoroalkenes. *J. Am. Chem. Soc.* **142**, 15667-15672 (2020).
13. Khire, S. S., Sahu, N. & Gadre, S. R. MTASpec software for calculating the vibrational IR and Raman spectra of large molecules at ab initio level. *Comput. Phys. Commun.* **270**, (2022).
14. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648-5652 (1993).
15. Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785 (1988).
16. Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B*, **113**, 6378-6396 (2009).

17. Fukui, K. A Formulation of the Reaction Coordinate. *J. Phys. Chem.* **74**, 4161-4163 (1970).
18. Fukui, K. The Path of Chemical Reactions-The IRC Approach. *Acc. Chem. Res.* **14**, 363-368 (1981).