Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

NHCs and Photoredox Catalysis Dual-Catalyzed 1,4-Mono/di-fluoromethylative Acylation of 1,3-Enynes

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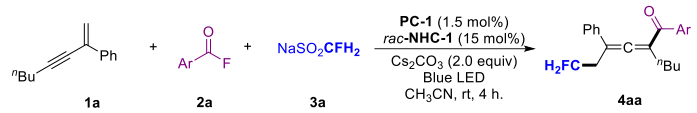
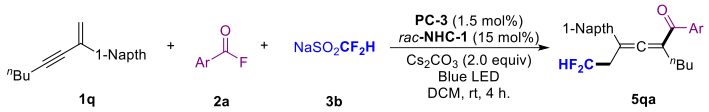
I. General Information

All reactions were carried out under nitrogen atmosphere. Reagents were purchased from commercial sources and used without further purification, unless otherwise noted. All of the solvents were anhydrous according to distillation. The reactions were monitored with the aid of thin-layer chromatography (TLC) on 0.25 mm precoated silica gel plates. Melting points were measured on Büchi B-540 apparatus. ^{1}H NMR spectra were recorded at 25 ^{o}C on a Bruker 600 or 500, Varian 500 MHz, ^{13}C NMR spectra were recorded at 25 ^{o}C on a Bruker 151, Varian 126 MHz, respectively in $CDCl_3$ by using TMS as internal standard. ^{19}F NMR spectra were recorded at 25 ^{o}C on a Bruker 565 MHz. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm for ^{1}H NMR) and $CDCl_3$ (77.0 ppm for ^{13}C NMR), respectively. Letters m, s, d, t, and q stand for multiplet, singlet, doublet, triplet, and quartet, respectively. High-resolution mass spectra (HRMS) were recorded on Bruck microtof. We use RLH-18 8-position Photo Reaction System, which is manufactured by Beijing Rogertech Co.ltd base in Beijing PRC. This Photo reactor we used has equipped with 8 blue light 10 W LED. This blue light 10 W LED's energy peak wavelength is 453.6 nm, and peak width at half-height is 20.4 The irradiationtion vessel is a borosilicate glass test tube, LED irradiates through a high-reflection channel to the test tube, the path length is 2 cm and no filter between LED and test tube.

II. General Procedure for the Synthesis of Tetrasubstituted Allenyl Ketones



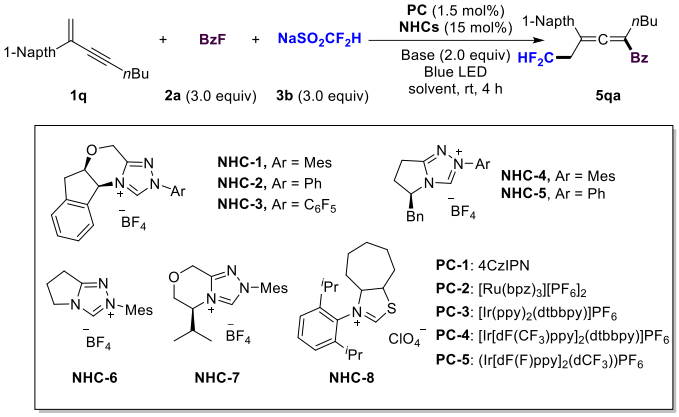
Taking 4aa as an example: Into a nitrogen-filled glove box, a vial equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-1** (2.4 mg, 0.003 mmol), sulfinate **3a** (72.0 mg, 0.6 mmol) and CH_3CN (5.0 mL). Then **1a** (0.2 mmol) and **2a** (0.6 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100 : 1) to give the corresponding product **4aa.**



Taking 5qa as an example: Into a nitrogen-filled glove box, a vial equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), sulfinate **3b** (82.8 mg, 0.6 mmol) and DCM (10.0 mL). Then **1q** (0.2 mmol) and **2a** (0.6 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100 : 1) to give the corresponding product **5qa.**

III. Reaction Optimization

Table **S1** Condition optimizations of difluoromethylsulfinate.



Entry	NHCs	PC	Solvent (mL)	Yields (%)[a]
1	NHC-1	PC-1	DCM (2)	52
2	NHC-1	PC-2	DCM (2)	n.d.
3	NHC-1	PC-3	DCM (2)	57
4	NHC-1	PC-4	DCM (2)	54
5	NHC-1	PC-5	DCM (2)	50
6	NHC-1	PC-3	CH_3CN (2)	45
7	NHC-1	PC-3	1,4-dioxane (2)	trace
8	NHC-1	PC-3	THF (2)	30
9	NHC-1	PC-3	Et_2O (2)	40
10	NHC-1	PC-3	$CHCl_3$ (2)	54
11	NHC-2	PC-3	DCM (2)	18
12	NHC-3	PC-3	DCM (2)	16
13	NHC-4	PC-3	DCM (2)	32
14	NHC-5	PC-3	DCM (2)	14
15	NHC-6	PC-3	DCM (2)	24
16	NHC-7	PC-3	DCM (2)	42
17	NHC-8	PC-3	DCM (2)	23
18	NHC-1	PC-3	DCM (3)	60
19	NHC-1	PC-3	DCM (5)	78
20	***rac*-NHC-1**	**PC-3**	**DCM (5)**	76 (77[b])

a) Unless otherwise noted, all the reactions were carried out with **1q** (0.1 mmol), **2a** (0.3 mmol), **3b** (0.3 mmol), **NHCs** (0.015 mmol), Cs_2CO_3 (0.2 mmol), and **PC** (0.0015 mmol) in the anhydrous solvent, irradiation with Blue LED (453.5 nm, 10 W) at room temperature for 4 h. isolated yields. b) reaction was carried out at 0.2 mmol scales.

IV. Preparation of the Starting Materials

List of 1,3-Enyne

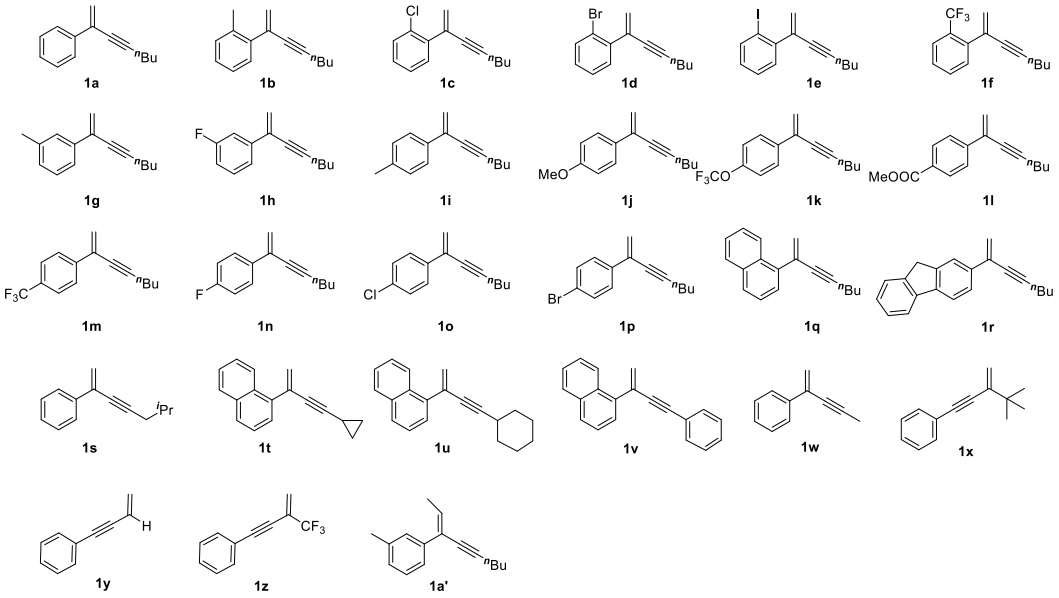
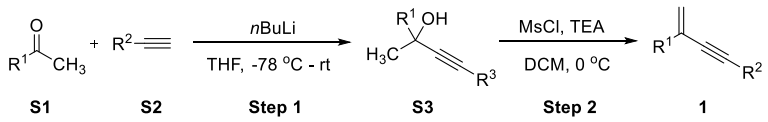


Table **S2**. The Substrates for 1,3-Enynes

Synthesis of 1,3-Enyne



Following a reported procedure, [1] **Step 1**: A 100.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with compound **S2** (20.0 mmol, 1.0 equiv) and 40.0 mL of THF. The solution was cooled to -78 °C and ^{n}BuLi (2.5 M in THF, 8.0 mL, 20.0 mmol, 1.0 equiv) was added. The resulting solution was stirred for 20 minutes at room temperature and then cooled to -78 °C again. Ketone **S1** (20.0 mmol, 1.0 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and monitored by TLC for completion. On completion, the reaction was quenched with saturated aqueous NH_4Cl (40.0 mL). The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine (30.0 mL), dried over Na_2SO_4 and filtered, then concentrated under reduced pressure to afford the crude material **S3**.

Step 2: The resulting crude material **S3** was dissolved in dry DCM (40 mL) and poured into 100.0 mL round-bottomed flask equipped with a magnetic stir bar, then the mixture was cooled to 0 °C with a cooling bath. To this solution was added TEA (100.0 mmol, 5.0 equiv) and methylsulfonyl chloride (50.0 mmol, 2.5 equiv) sequentially. After 30 min, the reaction was monitored by TLC for completion. On completion, the reaction was quenched with saturated aqueous NH_4Cl (40.0 mL). The aqueous layer was extracted with DCM, and the combined organic layers were washed with brine (30.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield the 1,3-enynes.[2]

List of Acyl Fluoride

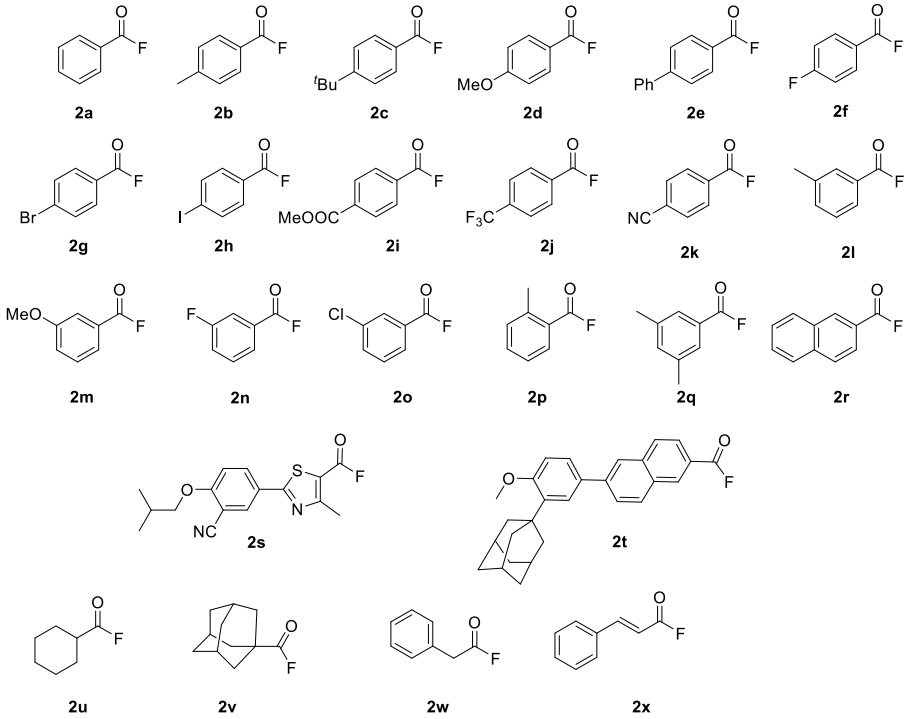
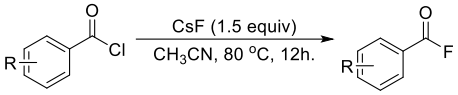


Table **S3**. The Substrates for Acyl Fluorides

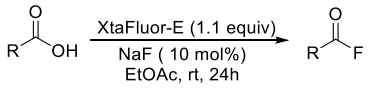
Synthesis of Acyl Fluoride

General procedure A



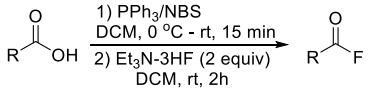
A 25.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with benzoyl chloride (5.0 mmol) and anhydrous acetonitrile (5.0 mL). Cesium fluoride (1.1 g, 7.5 mmol, 1.5 equiv) was added and the mixture was stirred for 2-4 h (monitored by TLC) at 80 °C under a nitrogen atmosphere. After that, the resulting crude product was purified by column chromatography to yield the acyl fluorides **2a-2t**. [3]

General procedure B



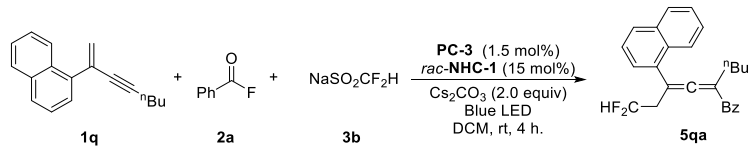
A 25.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with carboxylic acid (1.0 equiv, 1.0 mmol) in dry EtOAc (0.5M) was added NaF (10 mol %, 0.10 mmol, 4.2 mg), followed byXtalFluor-E (1.1 equiv, 1.1 mmol, 252 mg). After 24 h of stirring atroom temperature under argon, the reaction mixture was purified by filtration over a pad of silica gel to yield the aliphatic acyl fluorides **2u-2v**. [4]

General procedure C



A 25.0 mL round-bottomed flask equipped with a magnetic stir bar was charged withcarboxylic acid derivative **1** (1 equiv, 0.5 mmol) and triphenylphosphine, PPh_3 (2 equiv, 1 mmol, 262.3 mg) and anhydrous DCM (5 mL) were charged into an oven-dried screw-cap vial equipped with a magnetic stir bar. The vial was capped, and this mixture was then cooled to 0 ^oC using an ice-bath. Subsequently, N-bromosuccinimide, NBS (2.1 equiv, 1.05 mmol, 187 mg) was added as a solid in one portion, the vial was re-capped, and the mixture was kept in the ice-bath for two minutes. After this time, the ice-bath was removed, and this solution was further stirred for 15 min. After this time, the vial was opened and 3HF-Et_3N (2 equiv, 1 mmol, 163 uL) was added via micropipette. This mixture was stirred further for 2 h at room temperature. After this time, the vial was opened, and the reaction mixture was diluted with hexanes (20 mL), and the mixture was stirred for 10 min. During this time, large amounts of succinimide and triphenylphosphine oxide precipitate, which are then removed by passing the mixture through a short pad of silica. Subsequently, the silica pad was further washed with hexanes The filtrate was then concentrated under reduced pressure to afford pure product without the need of further purification (**2w-2x**). [5]

V. Procedure for Large-Scale Synthesis



Into a nitrogen-filled glove box, a round-bottom flask (250.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (126.0 mg, 0.3 mmol), Cs_2CO_3 (1303.0 mg, 4.0 mmol), **PC-3** (27.0 mg, 0.03 mmol) sulfinate **3b** (828.0 mg, 6.0 mmol) and DCM (100.0 mL). Then **1q** (2.0 mmol) and **2a** (6.0 mmol) were added. The round-bottom flask was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100 : 1) to give the corresponding product **5qa** (62%).

VI. Preliminary Attempt for Enantioselective Transformations

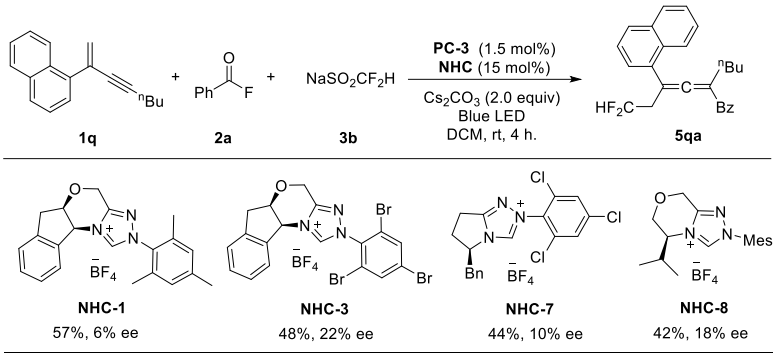
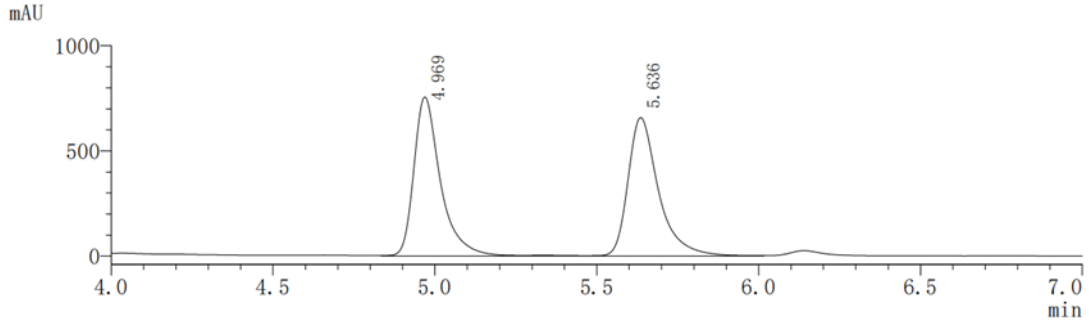


Table **S4**. Preliminary Attempt for Enantioselective Transformations

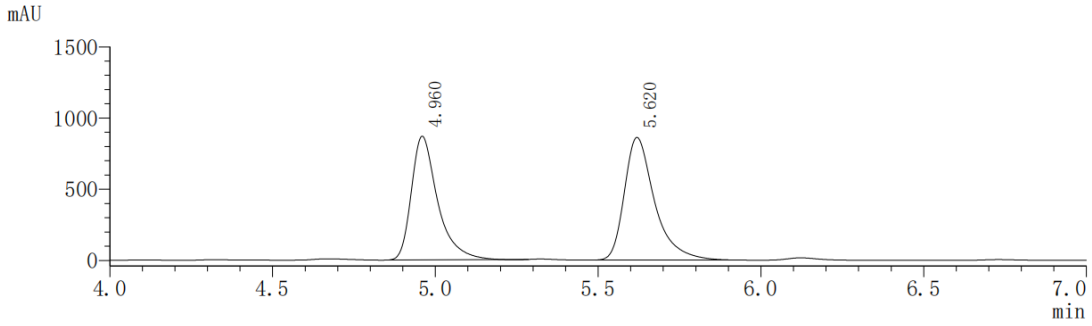
Screening of chiral NHC catalysts. Reaction conditions: **1q** (0.1 mmol), **2a** (0.3 mmol), **3b** (0.3 mmol), **NHC** (15 mol%), **PC-3** (1.5 mol%), and Cs_2CO_3 (0.4 mmol) in DCM (2.0 mL), Blue LEDs, nitrogen atmosphere, room temperature, 4 h.

When *rac*-**NHC-1** was used as a catalyst, 50:49 er was determined by HPLC (IA-3, Hexane/IPA = 95/5, 0.8 mL/min, 254 nm). tR (major) = 4.969 min, tR (minor) = 5.636 min.



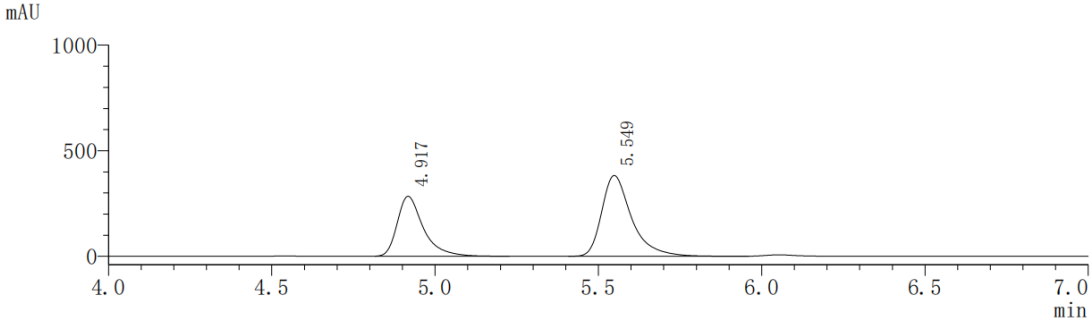
Peak	PetTime	Type	Area(mAU*S)	Hight(mAU)	Area%
1	4.969	M	4373941	752198	50.205
2	5.636	M	4338177	656008	49.795

When **NHC-1** was used as catalyst, 47:53 er was determined by HPLC (IA-3, Hexane/IPA = 95/5, 0.8 mL/min, 254 nm). tR (major) = 4.960 min, tR (minor) = 5.620 min.



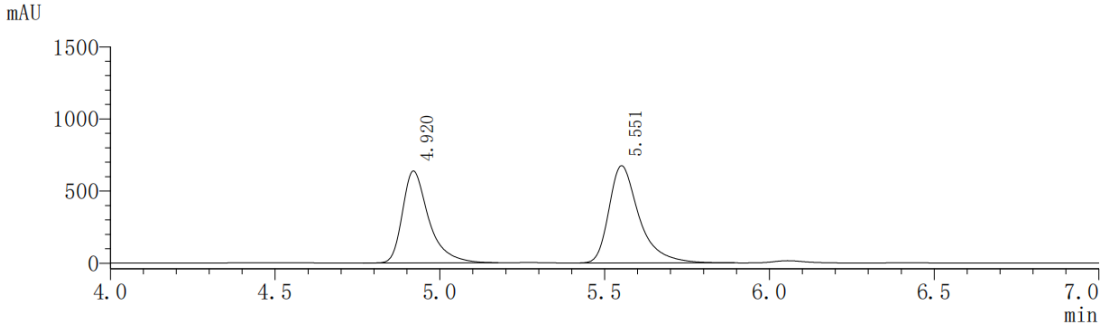
Peak	PetTime	Type	Area(mAU*S)	Hight(mAU)	Area%
1	4.960	M	4875680	861687	46.672
2	5.620	M	5571054	858680	53.328

When **NHC-3** was used as catalyst, 39:61 er was determined by HPLC (IA-3, Hexane/IPA = 95/5, 0.8 mL/min, 254 nm). tR (major) = 4.917 min, tR (minor) = 5.549 min.



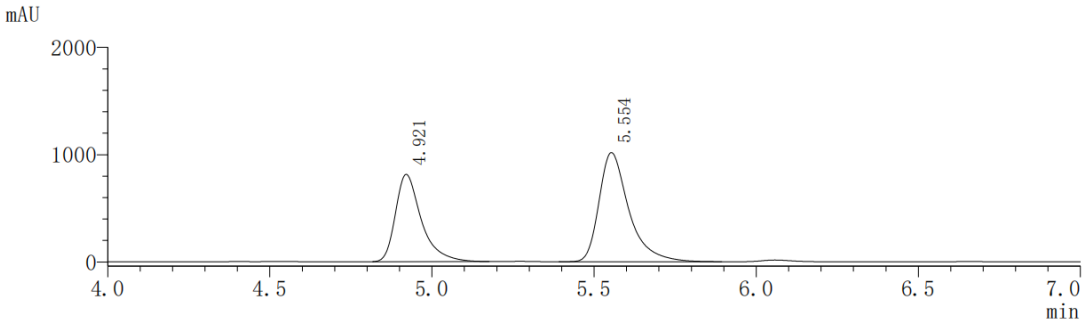
Peak	PetTime	Type	Area(mAU*S)	Hight(mAU)	Area%
1	4.917	M	1572322	281073	39.231
2	5.549	M	2435501	381458	60.769

When **NHC-7** was used as catalyst, 45:55 er was determined by HPLC (IA-3, Hexane/IPA = 95/5, 0.8 mL/min, 254 nm). tR (major) = 4.920 min, tR (minor) = 5.551 min.



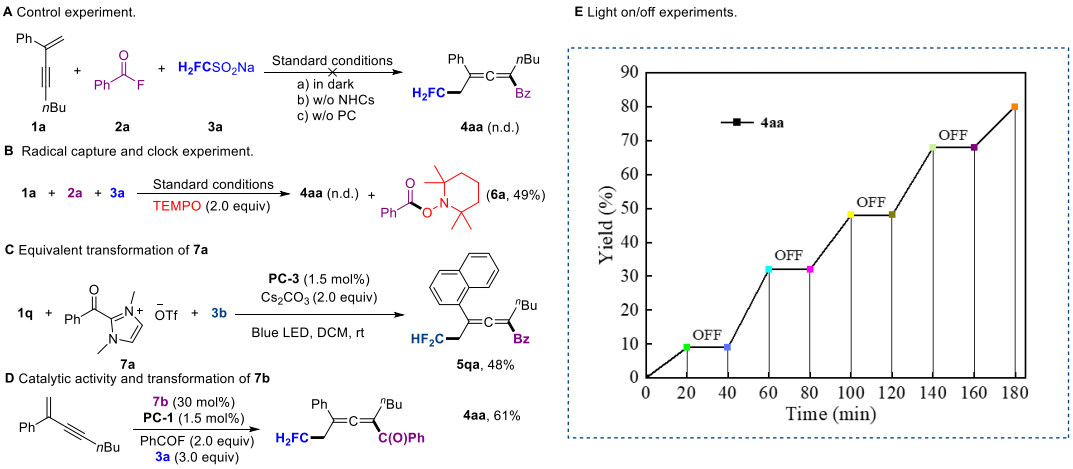
Peak	PetTime	Type	Area(mAU*S)	Hight(mAU)	Area%
1	4.920	M	3544587	635239	45.202
2	5.551	M	4297120	670240	54.798

When **NHC-8** was used as catalyst, 41:59 er was determined by HPLC (IA-3, Hexane/IPA = 95/5, 0.8 mL/min, 254 nm). tR (major) = 4.921 min, tR (minor) = 5.554 min.



Peak	PetTime	Type	Area(mAU*S)	Hight(mAU)	Area%
1	4.921	M	4524396	811580	40.951
2	5.554	M	6523910	1015585	59.049

VII. Mechanistic Studies



Scheme **S1** 1,4-monofluoromethylative acylation of 1,3-enynes mechanistic investigations

Control Experiment

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-1** (2.4 mg, 0.003 mmol) **3a** (72.0 mg, 0.6 mmol) and CH_3CN (5.0 mL). Then **1a** (0.2 mmol) and **2a** (0.6 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was stirred in the dark for 4 hours at rt. After that, the residue was analyzed by ^{1}H NMR, the product **4aa** was not detected.

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-1** (2.4 mg, 0.003 mmol) **3a** (72.0 mg, 0.6 mmol) and CH_3CN (5.0 mL). Then **1a** (0.2 mmol) and **2a** (0.6 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was analyzed by ^{1}H NMR, the product **4aa** was not detected.

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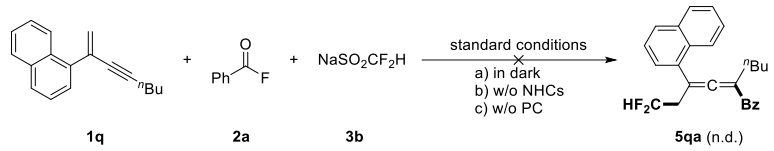


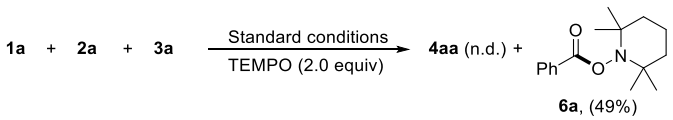
1q **2a** **3b** **5qa** (n.d.)

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3b** (82.8 mg, 0.6 mmol) and DCM (10.0 mL). Then **1q** (0.2 mmol) and **2a** (0.6 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was stirred in the dark for 4 hours at rt. After that, the residue was analyzed by ^{1}H NMR, the product **5qa** was not detected.

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3b** (82.8 mg, 0.6 mmol) and DCM (10.0 mL). Then **1q** (0.2 mmol) and **2a** (0.6 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was analyzed by ^{1}H NMR, and product **5qa** was not detected.

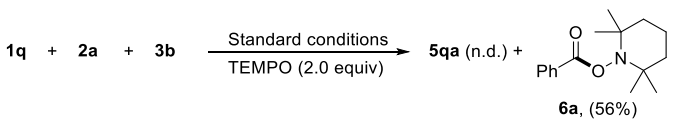
Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **3b** (82.8 mg, 0.6 mmol) and DCM (10.0 mL). Then **1q** (0.2 mmol) and **2a** (0.6 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that the residue was analyzed by ^{1}H NMR, the product **5qa** was not detected.

The Radical Scavenger Experiment



6a, (49%)

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-1** (2.4 mg, 0.003 mmol) **3a** (72.0 mg, 0.6 mmol) and CH_3CN (5.0 mL). Then **1a** (0.2 mmol) and **2a** (0.6 mmol) were added. Finally, TEMPO (0.4 mmol, 2.0 equiv) was added to the mixture. The vial was removed from the glovebox and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was analyzed by ^{1}H NMR, the product **4aa** was not detected, then the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20 : 1) to give the corresponding product **6a** with 49% yield (25.6 mg).

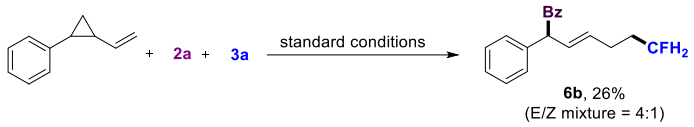


6a, (56%)

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with

rac-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3b** (82.8 mg, 0.6 mmol) and DCM (10.0 mL). Then **1q** (0.2 mmol) and **2a** (0.6 mmol) were added. Finally, TEMPO (0.6 mmol, 3.0 equiv) was added to the mixture. The vial was removed from the glovebox and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that，the residue was analyzed by ^{1}H NMR, the product **5qa** was not detected, then the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20 : 1) to give the corresponding product **6a** with 56% yield (29.2 mg).

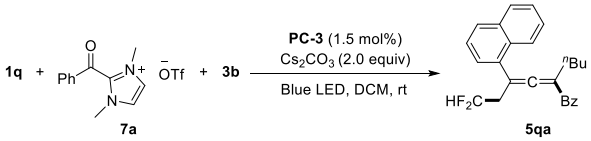
The Radical Clock Experiment



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-1** (2.4 mg, 0.003 mmol) **3a** (72.0 mg, 0.6 mmol) and CH_3CN (5.0 mL). Then alkene (0.2 mmol) and **2a** (0.6 mmol) were added. The vial was removed from the glovebox and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100 : 1) to give the corresponding product **6c.** with 26% yield.

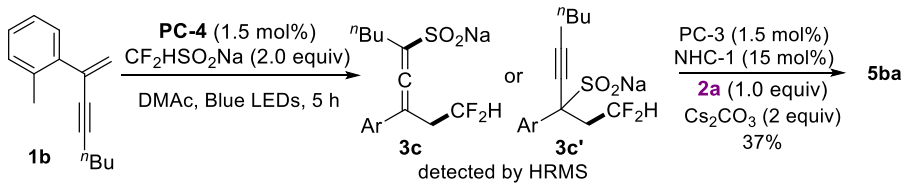
Possible Intermediate

Equivalent transformation of 7a



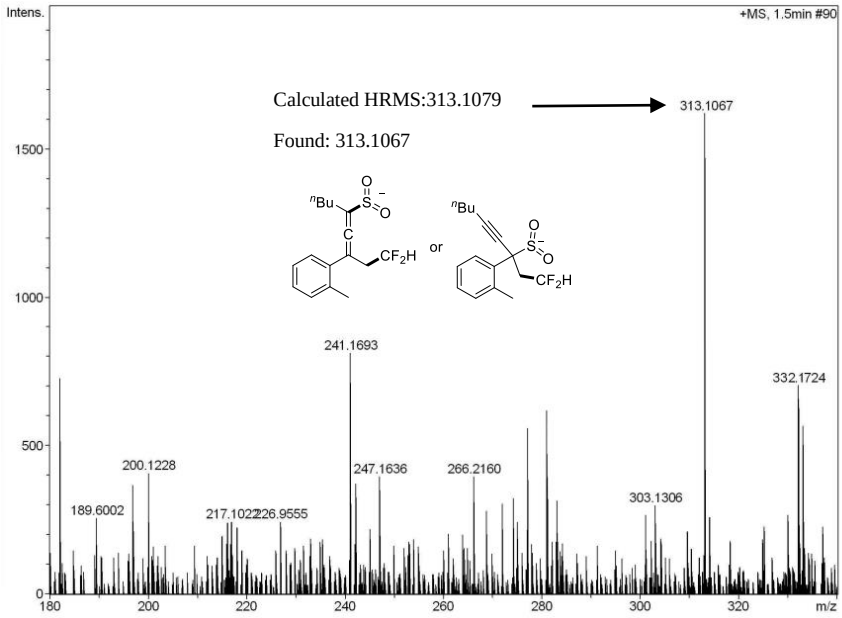
Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3b** (82.8 mg, 0.6 mmol) and DCM (10.0 mL). Then **1q** (0.2 mmol) and **7a** (0.6 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that，the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100 : 1) to give the corresponding product **5qa** (48%).

Possible role of SO_2 in radical fluoromethylation of 1,3-enynes



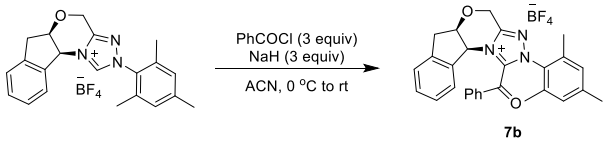
Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with PC-4 (2.4 mg, 0.003 mmol), **3b** (55.2 mg, 0.2 mmol) and DMA (2.0 mL). Then **1b** (0.2 mmol) was added. Remove the vial from the glove box and stir the reaction mixture at room temperature

for 5 hours under light conditions. Then, the mixture was concentrated under reduced pressure to afford the crude material. After that, the resulting solid was washed with Et_2O/petroleum ether (1:4) 3 ×10 mL to remove soluble organics, delivering a white solid. Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with crude material, dry DCM (10 mL), PC-3 (1.5 mol%), *rac*-NHC-1 (15 mol%), Cs_2CO_3 (2.0 equiv) and **2a** (0.2 mmol). The vial was removed from the glovebox and then the reaction mixture was irradiated with Blue LED at room temperature for 8 hours. After 8h, the reaction was monitored by TLC for completion. After that, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100 : 1) to give the corresponding product **5ba** with 37% yield.



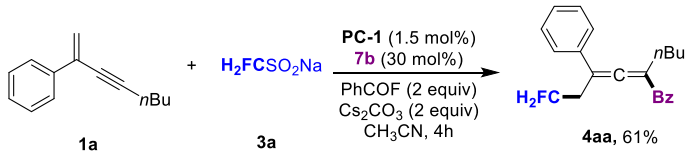
HRMS test of reaction system

Synthesis of Acyl Azolium 7b

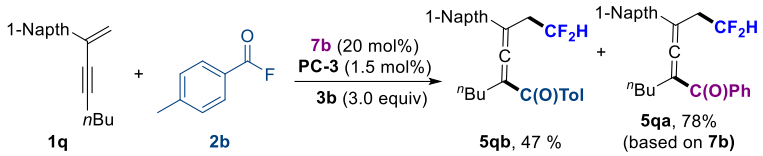


A dry Schlenk tube under an atmosphere of Argon, containing carbene precursor (2 mmol) and benzoyl chloride (3 equiv) in dry acetonitrile, is cooled to 0 °C. NaH (60% wt. in oil; 3 equiv) is added portion-wise to the stirred solution over 1.5 hours. The reaction mixture was allowed to warm to room temperature and monitored by TLC for completion. After that, the precipitate was collected by filtration, washed with Et_2O several times and dried under vacuum to give the corresponding product **7b** as a white solid (679.5 mg, 65%).

Catalytic activity and transformation of 7b

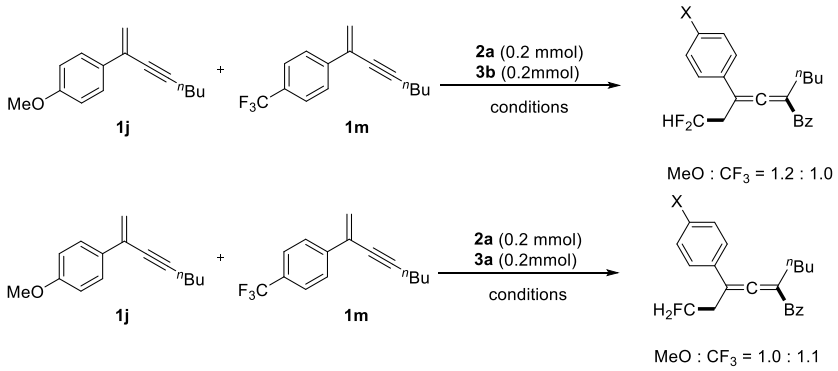


Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-1** (2.4 mg, 0.003 mmol) **3a** (72.0 mg, 0.6 mmol) and CH_3CN (5.0 mL). Then **1a** (0.2 mmol), PhCOF (2.0 equiv) and **7b** (30 mol%) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that， the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100 : 1) to give the corresponding product **4aa** (32.5 mg, 61%).



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3b** (82.8 mg, 0.6 mmol) and DCM (10.0 mL). Then **1q** (0.2 mmol), **2b** (0.6 mmol), and **7b** (0.04 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that，the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100 : 1) to give the corresponding product **5qb** (37.7 mg, 47%) and **5qa** (12.2 mg, 78% based on **7b**).

Competing experiment



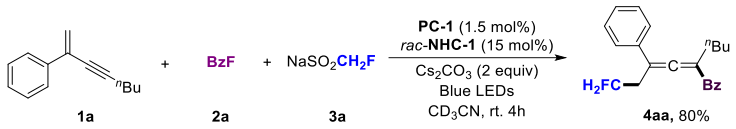
Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3b** (27.6 mg, 0.2 mmol) and DCM (10.0 mL). Then **1j** (0.2 mmol) **1m** (0.2 mmol) and **2a** (0.2 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was analyzed by ^1H NMR, the ratio of product **5ja** to **5ma** was 1.2 : 1.0.

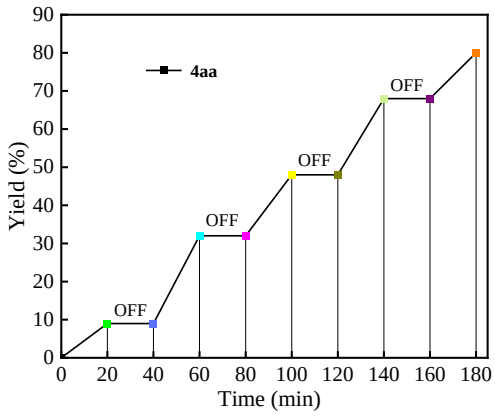
Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-1** (2.4 mg, 0.003 mmol) **3a** (24.1 mg, 0.2 mmol) and CH_3CN (5.0 mL). Then **1j** (0.2 mmol) **1m** (0.2 mmol) and **2a** (0.2 mmol)

were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After that, the residue was analyzed by ^{1}H NMR, the ratio of product **4ja** to **4ma** was 1.0 : 1.1.

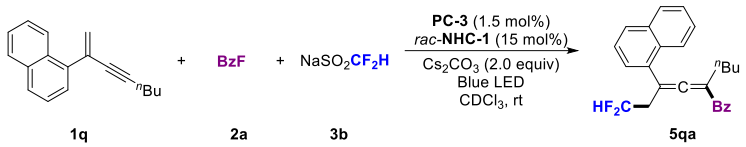
Light on-off Experiment

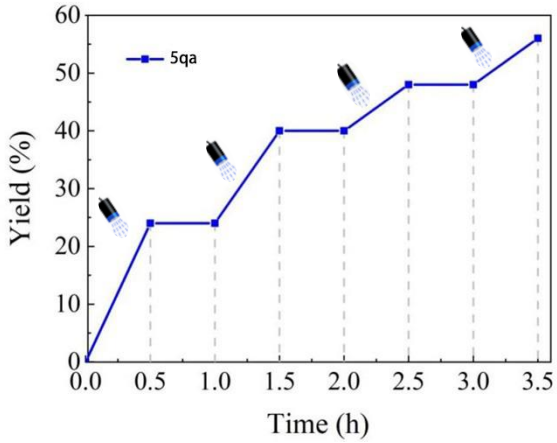
Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-1** (2.4 mg, 0.003 mmol) sodium monofluoromethanesulfinate **3a** (72.0 mg, 0.6 mmol) and CD_3CN (5.0 mL). Then **1a** (0.2 mmol), **2a** (0.6 mmol) and dibromomethane (14 µl, 0.2 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED and kept in the dark in 20 minutes intervals at room temperature. Yields of the **4aa** were determined by ^{1}H NMR monitors with dibromomethane as the internal standard. The reaction proceeded well under the irradiation of visible light, but no further transformation was observed without the light irradiation, indicating that the continuous irradiation of visible light is essential for this catalytic reaction.





Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) sodium difluoromethanesulfinate **3b** (82.8 mg, 0.6 mmol) and $CDCl_3$ (10.0 mL). Then **1q** (0.2 mmol), **2a** (0.6 mmol) and dibromomethane (14 µl, 0.2 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED and kept in the dark in 30 minutes intervals at room temperature. Yields of the **5qa** were determined by ^{1}H NMR monitors with dibromomethane as the internal standard. The reaction proceeded well under the irradiation of visible light, but no further transformation was observed without the light irradiation, indicating that the continuous irradiation of visible light is essential for this catalytic reaction.





UV-vis Absorption

The UV-Vis absorption spectrum of 1,3-enynes **1q** (10^{-4} M in DCM), benzoyl fluoride **2a** (10^{-4} M in DCM), CF_2HSO_2Na **3b** (10^{-4} M in DCM), **NHC-1** (10^{-4} M in DCM), **PC-3** (10^{-4} M in DCM) or acyl azolium **7b** (10^{-4} M in DCM) were respectively measured by Scary60 UV-Visible Spectrophotometer. And the absorption spectrum of different combination of the reagents were also measured in DCM using the same method. As shown in the following figure, the absorption spectrum of **PC-3** revealed a significant absorption of visible light. By contrast, other compounds have little absorptions at the visible light region.

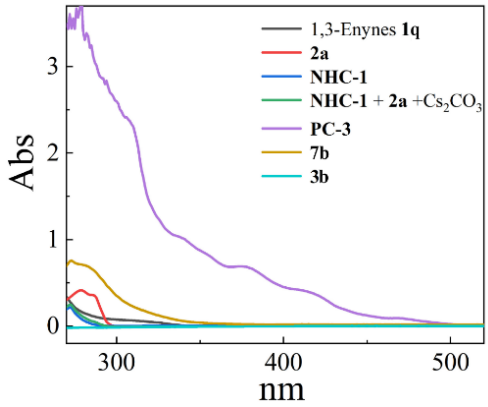


Figure **S2**. UV-Vis absorption spectra.

Emission Quenching Experiment

To support the proposed reductive quenching of photocatalyst (**PC-3**) by acyl azolium ion **7a**, we conducted emission quenching experiments by using acyl azolium ion **7a** (Figure **S3**)，1,3-enynes **1q** (Figure **S4**) and sodium difluoromethanesulfinate **3b** (Figure **S5**) as quenching agent. It was found that the acyl azolium ion **7a** are easier than sodium difluoromethanesulfinate **3b** and 1,3-enynes **1q** to quench the excited photosensitizer.

Emission quenching experiments by acyl azolium ion 7a

Experimental protocol: Emission intensities were recorded using a spectrofluorometer at ambient temperature. The emission spectra of a solution of **PC-3** (5 x 10^{-5} M in CH_3CN) upon excitation at 400 nm were recorded (Figure **S3**, black line). Then, acyl azolium ion **7a** (1 x 10^{-2} M) was added to the solution, and another emission spectra were recorded. The addition of **7a** and the recordation was repeated 5 consecutive times.

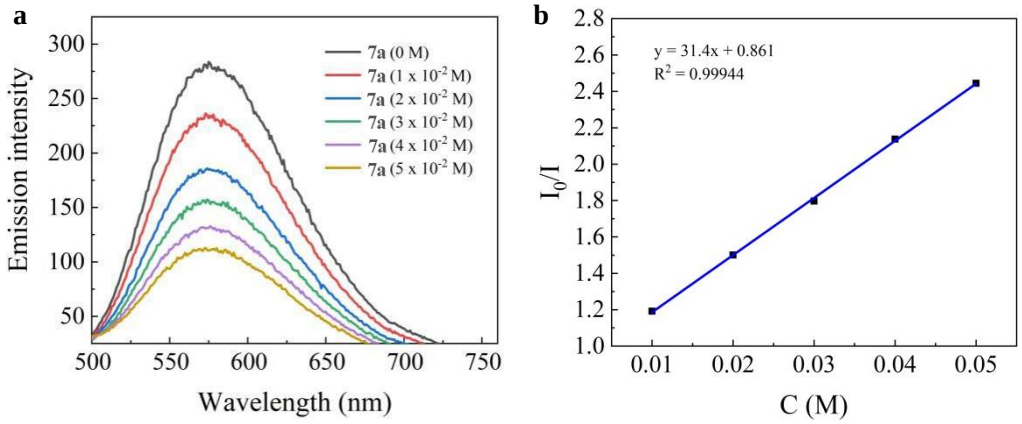


Figure **S3**. $[Ir(dtbbpy)(ppy)_2]PF_6$ emission quenching by acyl azolium ion **7a**

Emission quenching experiments by 1,3-enynes 1q

Experimental protocol: Emission intensities were recorded using a spectrofluorometer at ambient temperature. The emission spectra of a solution of **PC-3** (5 x 10^{-5} M in CH_3CN) upon excitation at 400 nm was recorded (Figure **S4**, black line). Then, 1,3-enynes **1q** (1 x 10^{-2} M) was added to the solution, and another emission spectra was recorded. The addition of **1q** and the recordation were repeated 5 consecutive times.

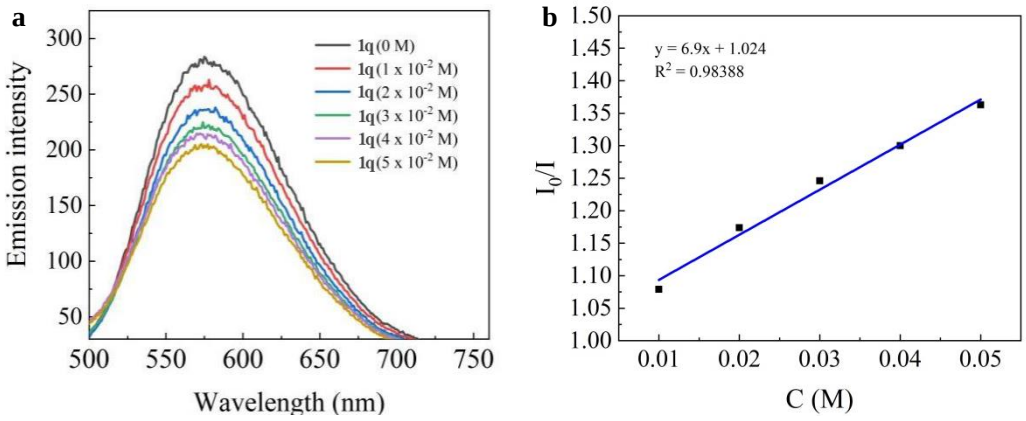


Figure **S4**. $[Ir(dtbbpy)(ppy)_2]PF_6$ emission quenching by 1,3-enynes **1q**

Emission quenching experiments by sodium difluoromethanesulfinate 3b

Experimental protocol: Emission intensities were recorded using a spectrofluorometer at ambient temperature. The emission spectra of a solution of **PC-3** (5 x 10^{-5} M in CH_3CN and H_2O (10 : 1)) upon excitation at 400 nm was recorded (Figure **S5**, black line). Then, sodium difluoromethanesulfinate **3b** (1 x 10^{-2} M) was added to the solution, and another emission spectra was recorded. The addition of **3b** and the recordation were repeated 5 consecutive times.

a **b**

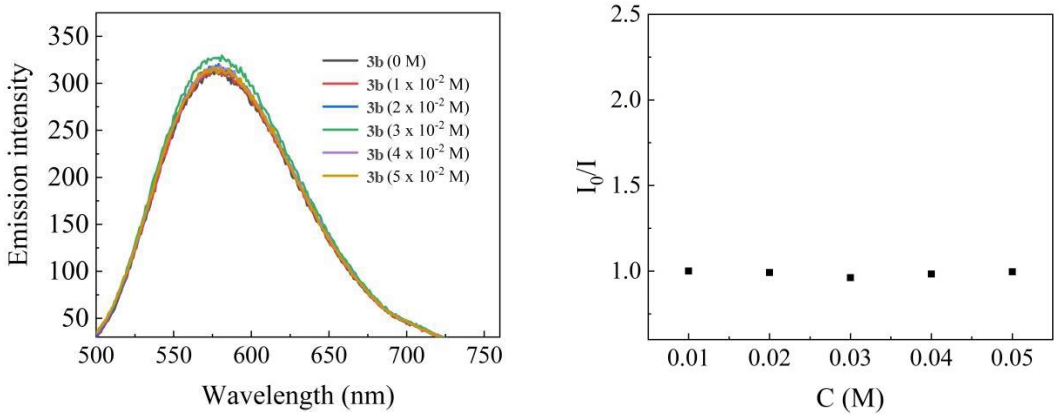


Figure **S5**. [Ir(dtbbpy)(ppy)$_2$]PF$_6$ emission quenching by sodium difluoromethanesulfinate **3b**

Emission quenching experiments

Experimental protocol: Emission intensities were recorded using a spectrofluorometer at ambient temperature. The emission spectra of a solution of **PC-1** (5 x 10^{-5} M in CH_3CN) upon excitation at 425 nm were recorded (Figure **S6**, black line). Then, sodium monofluoromethanesulfinate **3a**, 1,3-enynes **1a,** benzoyl fluoride **2a** and acyl azolium ion **7b** (5 x 10^{-2} M) were separately added to the solution, and the emission spectra were recorded separately.

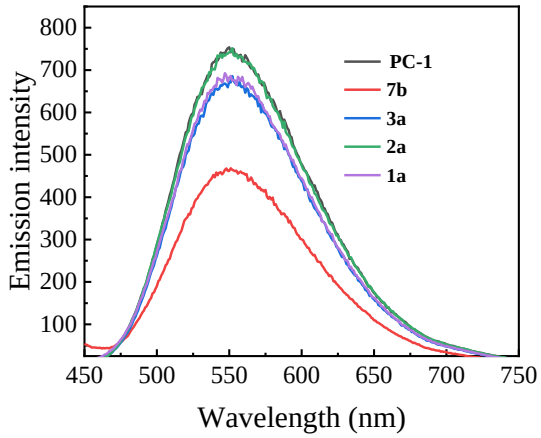


Figure **S6**. 4CzIPN emission quenching by sodium monofluoromethanesulfinate **3a**, 1,3-enynes **1a**, azolium ion **7b** and benzoyl fluoride **2a**

Experimental protocol: Emission intensities were recorded using a spectrofluorometer at ambient temperature. The emission spectra of a solution of **PC-3** (5 x 10^{-5} M in CH_3CN) upon excitation at 400 nm were recorded (Figure **S7**, black line). Then, sodium difluoromethanesulfinate **3b**, 1,3-enynes **1q** acyl azolium ion **7a** and acyl azolium **7b** (5 x 10^{-2} M) were separately added to the solution, and the emission spectra were recorded separately.

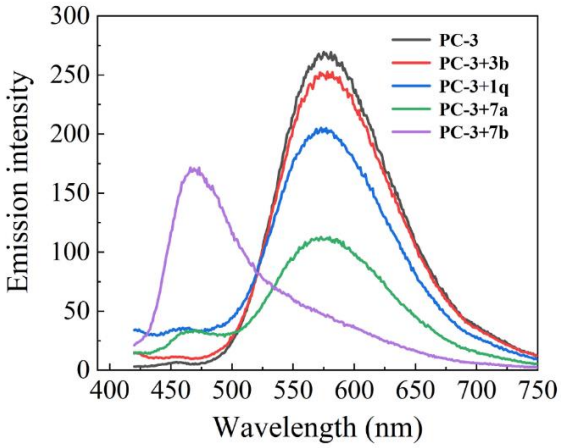


Figure **S7**. $[Ir(dtbbpy)(ppy)_2]PF_6$ emission quenching by sodium difluoromethanesulfinate **3b**, 1,3-enynes **1q**, azolium ion **7a** and **7b**

VIII. References

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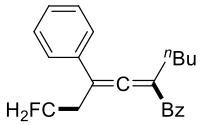
IX. Characterization Data of New Compounds



2-Butyl-6-fluoro-1,4-diphenylhexa-2,3-dien-1-one (4aa)

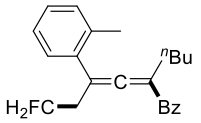
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 25.7 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.7 Hz, 2H), 7.44 – 7.33 (m, 3H), 7.32 –7.22 (m, 5H), 4.45 (dt, J = 46.8, 6.6 Hz, 2H), 2.92 – 2.78 (m, 2H), 2.59 – 2.47 (m, 2H), 1.61 – 1.50 (m, 2H), 1.49 – 1.38 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.60, 194.80, 138.61, 134.45, 131.95, 128.86, 128.41, 127.85, 127.81, 126.15, 110.90, 105.14 (d, J = 6.0 Hz), 81.52 (d, J = 169.2 Hz), 31.36 (d, J = 21.8 Hz), 30.28, 28.44, 22.66, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.72 – -215.96 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{23}FNaO$ ([M + Na] $^+$), 345.1625; found, 345.1615.



2-Butyl-6-fluoro-1-phenyl-4-(o-tolyl)hexa-2,3-dien-1-one (4ba)

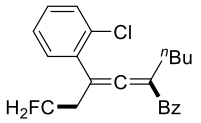
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 29.6 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.7 Hz, 2H), 7.22 – 7.10 (m, 3H), 6.94 (d, J = 7.5 Hz, 1H), 4.56 – 4.31 (m, 2H), 2.87 – 2.71 (m, 1H), 2.71 – 2.58 (m, 1H), 2.56 – 2.39 (m, 2H), 2.01 (s, 3H), 1.64 – 1.49 (m, 2H), 1.50 – 1.35 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.19, 195.55, 143.20, 139.16, 135.84, 135.12, 131.78, 130.62, 128.69, 128.47, 127.88 (d, J = 1.8 Hz), 125.98, 107.83, 104.24 (d, J = 6.0 Hz), 80.97 (d, J = 169.4 Hz), 35.14 (d, J = 21.3 Hz), 30.48, 28.12, 22.54, 19.69, 13.94.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.60 – -216.85 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{25}FNaO$ ([M + Na] $^+$), 359.1782; found, 359.1784.



2-Butyl-4-(2-chlorophenyl)-6-fluoro-1-phenylhexa-2,3-dien-1-one (4ca)

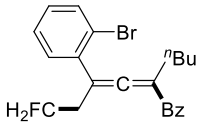
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 28.1 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.55 (dd, J = 8.1, 1.3 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.23 (dd, J = 7.6, 1.3 Hz, 1H), 7.14 (td, J = 7.7, 1.7 Hz, 1H), 6.93 (dd, J = 7.6, 1.7 Hz, 1H), 4.52 – 4.38 (m, 2H), 2.90 – 2.71 (m, 2H), 2.54 – 2.46 (m, 2H), 1.62 – 1.56 (m, 2H), 1.41 (q, J = 7.4 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.44, 195.15, 138.98, 136.72, 133.25, 131.91, 130.60, 129.39, 128.76, 128.00, 127.49, 122.66, 108.68, 104.97 (d, J = 6.0 Hz), 81.07 (d, J = 169.3 Hz), 34.48 (d, J = 21.0 Hz), 30.41, 28.10, 22.53, 13.97.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.60 – -217.05 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{22}ClFNaO$ ([M + Na] $^+$), 379.1235; found, 379.1248.



4-(2-bromophenyl)-2-butyl-6-fluoro-1-phenylhexa-2,3-dien-1-one (4da)

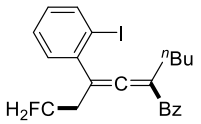
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 29.2 mg, 73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 10.0 Hz, 1H), 7.67 (d, J = 10.0 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 5.0 Hz, 2H), 7.27 (d, J = 10.0 Hz, 1H), 6.97 (td, J = 7.7, 1.6 Hz, 1H), 6.86 (dd, J = 7.7, 1.6 Hz, 1H), 4.66 – 4.36 (m, 2H), 3.03 – 2.63 (m, 2H), 2.60 – 2.43 (m, 2H), 1.65 – 1.57 (m, 2H), 1.47 – 1.36 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.85, 195.15, 138.88, 134.62, 132.88, 131.89, 130.42, 130.07, 129.21, 128.70, 127.94, 126.94, 108.60, 103.51 (d, J = 6.0 Hz), 81.13 (d, J = 169.5 Hz), 34.23 (d, J = 21.0 Hz), 30.27, 28.09, 22.53, 13.95.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.73 – -217.04 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{22}BrFNaO$ ([M + Na] $^+$), 423.0730; found, 423.0744.



2-Butyl-6-fluoro-4-(2-iodophenyl)-1-phenylhexa-2,3-dien-1-one (4ea)

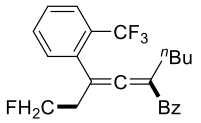
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 35.8 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 10.0 Hz, 2H), 7.49 (t, J = 10.0 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.25 – 7.17 (m, 2H), 6.98 (dd, J = 7.3, 2.0 Hz, 1H), 4.68 – 4.22 (m, 2H), 3.00 – 2.70 (m, 2H), 2.48 (td, J = 7.3, 1.9 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.47 – 1.35 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.69, 194.98, 138.72, 134.45, 132.72, 131.73, 130.26, 129.91, 129.04, 128.54, 127.77, 126.78, 108.44, 103.35 (d, J = 6.3 Hz), 80.96 (d, J = 169.4 Hz), 34.06 (d, J = 21.0 Hz), 30.10, 27.93, 22.36, 13.79.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.12 – -217.05 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{22}FINaO$ ([M + Na] $^+$), 471.0592; found, 471.0601.



2-Butyl-6-fluoro-1-phenyl-4-(2-(trifluoromethyl)phenyl)hexa-2,3-dien-1-one (4fa)

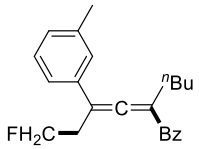
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 32.4 mg, 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 7.7 Hz, 2H), 7.56 – 7.46 (m, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 7.7 Hz, 2H), 7.00 – 6.96 (m, 1H), 6.87 (dd, J = 7.7, 1.6 Hz, 1H), 4.56 – 4.38 (m, 2H), 2.92 – 2.66 (m, 2H), 2.65 – 2.40 (m, 2H), 1.65 – 1.57 (m, 2H), 1.49 – 1.38 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.13, 195.27, 139.01, 134.71, 131.97, 131.83, 130.89, 128.70,128.39 (q, J = 271.5 Hz), 128.06, 127.91, 126.59 (q, J = 5.5 Hz), 108.81, 102.64 (d, J = 6.0 Hz), 80.94 (d, J = 169.2 Hz), 35.74 (d, J = 21.0 Hz), 30.41, 28.41, 22.57, 13.86.

^{19}F NMR (565 MHz, $CDCl_3$) δ -59.12, -214.83 – -218.62 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{22}F_4NaO$ ([M + Na] $^+$), 413.1499; found, 413.1499.



2-butyl-6-fluoro-1-phenyl-4-(m-tolyl)hexa-2,3-dien-1-one (4ga)

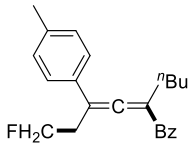
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 18.2 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 6.6 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.21 – 7.12 (m, 3H), 6.94 (d, J = 7.5 Hz, 1H), 4.58 – 4.31 (m, 2H), 2.85 – 2.71 (m, 1H), 2.70 – 2.57 (m, 1H), 2.52 – 2.42 (m, 2H), 2.00 (s, 3H), 1.61 – 1.51 (m, 2H), 1.47 – 1.36 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.21, 195.57, 139.14, 135.84, 135.10, 131.79, 130.63, 128.70, 128.47, 127.89, 125.98, 107.81, 104.23 (d, J = 5.9 Hz), 80.98 (d, J = 169.3 Hz), 35.14 (d, J = 21.3 Hz), 30.47, 28.11, 22.55, 19.70, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.58 – -216.93 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{25}FNaO$ ([M + Na] $^+$), 359.1782; found, 359.1785.



2-butyl-6-fluoro-1-phenyl-4-(p-tolyl)hexa-2,3-dien-1-one (4ia)

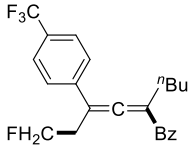
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 20.9 mg, 62%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.0, 1.4 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.29 – 7.22 (m, 4H), 7.10 (d, J = 1.7 Hz, 3H), 4.44 (dt, J = 46.8, 6.6 Hz, 2H), 2.89 – 2.76 (m, 2H), 2.59 – 2.49 (m, 2H), 2.35 (s, 3H), 1.58 – 1.51 (m, 2H), 1.49 – 1.39 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.68, 194.84, 138.64, 138.49, 134.33, 131.90, 128.71, 128.60, 128.42, 127.83, 126.80, 123.30, 110.71, 105.09 (d, J = 7.5 Hz), 81.55 (d, J = 169.2 Hz), 31.41 (d, J = 21.8 Hz), 30.26, 28.42, 22.64, 21.55, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.66– -215.90 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{25}FNaO$ ([M + Na] $^+$), 359.1782; found, 359.1789.



2-Butyl-6-fluoro-1-phenyl-4-(4-(trifluoromethyl)phenyl)hexa-2,3-dien-1-one (4ma)

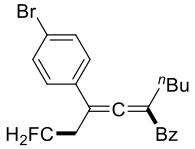
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 33.1 mg, 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (ddd, J = 13.6, 8.0, 1.4 Hz, 3H), 7.54 – 7.50 (m, 1H), 7.49 – 7.43 (m, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 6.91 (d, J = 7.6 Hz, 1H), 4.45 (dt, J = 46.8, 6.6 Hz, 2H), 2.80 – 2.65 (m, 2H), 2.49 – 2.42 (m, 2H), 1.55 – 1.47 (m, 2H), 1.45 – 1.35 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.14, 195.28, 139.00, 134.72, 131.98, 131.84, 130.89, 128.71, 128.07, 127.91, 126.59 (q, J = 5.1 Hz), 124.76, 122.95, 108.81, 102.63 (d, J = 6.0 Hz), 80.95 (d, J = 169.3 Hz), 35.75 (d, J = 20.3 Hz), 30.41, 28.41, 22.58, 13.87.

^{19}F NMR (565 MHz, $CDCl_3$) δ -59.12, -216.94 – -217.23 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{22}F_4NaO$ ([M + Na] $^+$), 413.1499; found, 413.1493.



4-(4-bromophenyl)-2-butyl-6-fluoro-1-phenylhexa-2,3-dien-1-one (4pa)

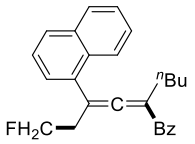
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 29.6 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 6.8 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.27 – 7.17 (m, 2H), 6.98 (dd, J = 7.4, 2.0 Hz, 1H), 4.60 – 4.33 (m, 2H), 2.91 – 2.68 (m, 2H), 2.54 – 2.41 (m, 2H), 1.61 – 1.53 (m, 2H), 1.46 – 1.37 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.85, 195.15, 138.88, 134.61, 132.88, 131.89, 130.42, 130.07, 129.21, 128.70, 127.94, 126.94, 108.60, 103.51 (d, J = 6.3 Hz), 81.13 (d, J = 169.3 Hz), 34.23 (d, J = 21.0 Hz), 30.27, 28.09, 22.53, 13.95.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.73 – -217.05 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{23}BrFO$ ([M + H] $^+$), 401.0911; found, 401.0904.



2-Butyl-6-fluoro-4-(naphthalen-1-yl)-1-phenylhexa-2,3-dien-1-one (4qa)

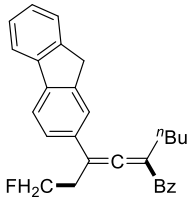
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 30.1 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 2H), 7.56 (d, J = 7.7 Hz, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.25 (t, J = 7.6 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.10 (d, J = 7.0 Hz, 1H), 4.48 – 4.26 (m, 2H), 2.91 – 2.78 (m, 1H), 2.78 - 2.63 (m, 1H), 2.51 – 2.33 (m, 2H), 1.62 – 1.49 (m, 2H), 1.42 – 1.27 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.78, 195.55, 139.33, 133.91, 133.49, 131.70, 130.97, 128.73, 128.38, 128.38, 128.00, 126.22, 126.10, 126.02, 125.34, 125.17, 108.10, 103.63 (d, J = 5.6 Hz), 80.98 (d, J = 169.6 Hz), 35.85 (d, J = 21.3 Hz), 30.42, 28.11, 22.54, 13.97.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.89 – -218.36 (m).

HRMS (ESI) (m/z): calcd for $C_{26}H_{25}FNaO$ ([M + Na] $^+$), 395.1782; found, 395.1776.



2-Butyl-4-(9H-fluoren-3-yl)-6-fluoro-1-phenylhexa-2,3-dien-1-one (4ra)

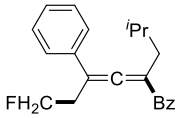
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 26.6 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (t, J = 7.7 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.55 (d, J = 7.4 Hz, 1H), 7.46 (s, 1H), 7.39 (q, J = 7.2 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.22 (d, J = 8.0 Hz, 3H), 4.48 (dt, J = 46.8, 6.6 Hz, 2H), 3.91 (s, 2H), 3.10 – 2.80 (m, 2H), 2.57 (dd, J = 8.8, 6.8 Hz, 2H), 1.62 – 1.54 (m, 2H), 1.52 – 1.41 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.97, 194.81, 143.92, 143.40, 141.58, 141.08, 138.66, 132.79, 131.94, 128.44, 127.85, 127.04, 126.92, 125.10, 125.02, 122.69, 120.15, 120.01, 110.85, 105.52 (d, J = 7.0 Hz), 81.62 (d, J = 169.4 Hz), 36.97, 31.58 (d, J = 21.0 Hz), 30.33, 28.52, 22.67, 13.97.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.53 – -215.83 (m).

HRMS (ESI) (m/z): calcd for $C_{29}H_{27}FNaO$ ([M + Na] $^+$), 433.1938; found, 433.1932.



6-Fluoro-2-isobutyl-1,4-diphenylhexa-2,3-dien-1-one (4sa)

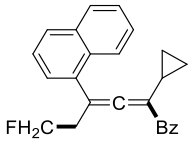
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 22.5 mg, 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.1, 1.5 Hz, 2H), 7.42 (td, J = 7.3, 1.4 Hz, 1H), 7.35 (dd, J = 8.4, 7.0 Hz, 2H), 7.28 (d, J = 7.7 Hz, 3H), 7.25 – 7.23 (m, 1H), 4.44 (dt, J = 46.8, 6.6 Hz, 2H), 2.93 – 2.62 (m, 2H), 2.45 (d, J = 7.1 Hz, 2H), 1.90 (dt, J = 13.5, 6.7 Hz, 1H), 1.00 (dd, J = 8.6, 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.98, 194.78, 138.60, 134.39, 131.99, 128.83, 128.47, 127.88, 127.77, 126.25, 109.51, 104.36 (d, J = 7.6 Hz), 81.50 (d, J = 169.4 Hz), 38.01, 31.58 (d, J = 21.0 Hz), 27.67, 22.79, 22.70.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.55 – -215.84 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{23}FNaO$ ([M + Na] $^+$), 345.1625; found, 345.1617.



2-Cyclopropyl-6-fluoro-4-(naphthalen-1-yl)-1-phenylhexa-2,3-dien-1-one (4ta)

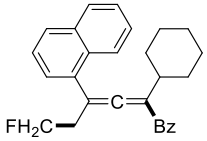
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 30.6 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 16.3, 8.2 Hz, 2H), 7.69 – 7.62 (m, 2H), 7.57 – 7.50 (m, 1H), 7.45 – 7.38 (m, 2H), 7.36 – 7.28 (m, 3H), 7.27 – 7.20 (m, 1H), 7.15 (dd, J = 7.1, 1.1 Hz, 1H), 4.67 – 4.25 (m, 2H), 2.97 – 2.83 (m, 1H), 2.82 – 2.67 (m, 1H), 1.93 – 1.83 (m, 1H), 1.04 – 0.96 (m, 1H), 0.94 – 0.86 (m, 1H), 0.77 – 0.67 (m, 1H), 0.63 – 0.53 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.78, 195.58, 139.32, 133.86, 133.26, 131.74, 130.78, 128.72, 128.49, 128.40, 128.05, 126.29, 126.19, 126.04, 125.37, 125.08, 112.21, 106.31 (d, J = 5.0 Hz), 80.83 (d, J = 169.2 Hz), 35.97 (d, J = 21.0 Hz), 8.39, 7.93, 7.88.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.77 – -217.21 (m).

HRMS (ESI) (m/z): calcd for $C_{25}H_{21}FNaO$ ([M + Na] $^+$), 379.1474; found, 379.1476.



2-Cyclohexyl-6-fluoro-4-(naphthalen-1-yl)-1-phenylhexa-2,3-dien-1-one (4ua)

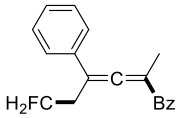
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 31.4 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 15.5, 8.2 Hz, 2H), 7.70 – 7.62 (m, 2H), 7.54 (dd, J = 8.2, 6.6 Hz, 1H), 7.42 (td, J = 7.6, 4.7 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.28 – 7.19 (m, 3H), 4.79 – 4.17 (m, 2H), 3.00 – 2.88 (m, 1H), 2.84 – 2.68 (m, 2H), 2.09 – 2.01 (m, 1H), 1.91 – 1.83 (m, 1H), 1.83 – 1.72 (m, 3H), 1.51 – 1.34 (m, 3H), 1.33 – 1.21 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.74, 195.50, 139.72, 133.84, 133.66, 131.69, 130.83, 128.74, 128.32, 128.03, 126.33, 126.13, 125.95, 125.36, 125.26, 113.84, 105.06 (d, J = 5.5 Hz), 81.06 (d, J = 169.4 Hz), 36.60, 35.93 (d, J = 21.0 Hz), 32.76, 32.51, 26.57, 26.45, 26.28.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.41 – -216.79 (m).

HRMS (ESI) (m/z): calcd for $C_{28}H_{27}FNaO$ ([M + Na] $^+$), 421.1938; found, 421.1943.



6-fluoro-2-methyl-1,4-diphenylhexa-2,3-dien-1-one (4wa)

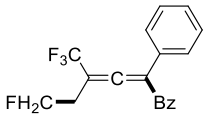
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 12.6 mg, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.2 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.35 (t, J = 7.7 Hz, 2H), 7.30 – 7.26 (m, 1H), 4.54 – 4.38 (m, 2H), 2.47 (dt, J = 24.0, 6.1 Hz, 2H), 1.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 208.33, 194.23, 138.76, 133.79, 132.59, 129.18, 128.51, 128.12, 128.02, 127.59, 108.78, 101.82 (d, J = 5.0 Hz), 81.43 (d, J = 168.8 Hz), 34.68 (d, J = 21.0 Hz), 18.52.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.56 – -216.85 (m).

HRMS (ESI) (m/z): calcd for $C_{19}H_{18}FO$ ([M + H] $^+$), 281.1312; found, 281.1313.



6-Fluoro-1,2-diphenyl-4-(trifluoromethyl)hexa-2,3-dien-1-one (4za)

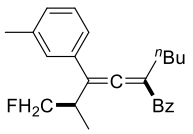
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 9.4 mg, 28 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.93 (m, 2H), 7.60 (td, J = 7.2, 1.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.43 – 7.33 (m, 5H), 4.62 – 4.45 (m, 2H), 2.77 – 2.57 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 205.68 (d, J = 4.0 Hz), 191.07, 136.85, 133.92, 130.89, 129.63, 129.04, 129.00, 128.61, 127.83, 122.80 (q, J = 274.7 Hz), 115.26, 100.37 (dd, J = 35.2, 5.3 Hz), 80.36 (d, J = 170.5 Hz), 28.37 (d, J = 21.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.44, -217.84 (tt, J = 46.4, 23.1 Hz).

HRMS (ESI) (m/z): calcd for $C_{19}H_{14}F_4NaO$ ([M + Na] $^+$), 357.0878; found, 357.0870.



2-Butyl-6-fluoro-5-methyl-1-phenyl-4-(m-tolyl)hexa-2,3-dien-1-one (4a'a)

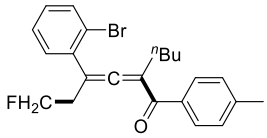
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 14.0 mg, 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 11.3, 8.1, 1.4 Hz, 4H), 7.43 – 7.37 (m, 2H), 7.29 (dd, *J* = 7.8, 3.1 Hz, 2H), 7.21 (dt, *J* = 11.3, 7.7 Hz, 4H), 7.12 (dt, *J* = 11.3, 5.0 Hz, 6H), 4.52 – 3.75 (m, 4H), 3.14 – 2.84 (m, 2H), 2.58 – 2.50 (m, 4H), 2.38 (d, *J* = 3.1 Hz, 6H), 1.57 – 1.52 (m, 4H),1.51 – 1.40 (m, 4H), 1.22 – 1.15 (m, 3H), 0.99 – 0.91 (m, 6H), 0.91 – 0.86 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.61 (d, *J* = 16.3 Hz), 195.20 (d, *J* = 3.4 Hz), 138.70 , 138.53 , 134.73 , 134.49 , 131.73 , 131.67 , 128.76 , 128.65 (d, *J* = 3.4 Hz), 128.37 , 128.32 , 127.72 , 127.68 , 127.33 , 127.24 , 112.10 (d, *J* = 20.8 Hz), 111.23 (d, *J* = 6.2 Hz), 86.68 (d, *J* = 17.9 Hz), 85.54 (d, *J* = 17.8 Hz), 36.02 – 35.15 (m), 30.42 (d, *J* = 5.2 Hz), 28.22 (d, *J* = 3.5 Hz), 22.72 , 21.57 , 16.47 (d, *J* = 4.0 Hz), 15.57 (d, *J* = 4.5 Hz), 13.97 .

^{19}F NMR (565 MHz, $CDCl_3$) δ -217.87 (td, J = 47.4, 14.9 Hz), -219.06 (td, J = 47.2, 17.5 Hz).

HRMS (ESI) (m/z): calcd for $C_{24}H_{27}FNaO$ ([M + Na] $^+$), 373.1944; found, 373.1940.



4-(2-Bromophenyl)-2-butyl-6-fluoro-1-(p-tolyl)hexa-2,3-dien-1-one (4db)

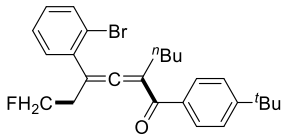
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 28.1 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.16 (d, *J* = 7.8 Hz, 3H), 6.99 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.63 – 4.27 (m, 2H), 2.92 – 2.71 (m, 2H), 2.48 (dd, *J* = 8.8, 6.7 Hz, 2H), 2.39 (s, 3H), 1.60 – 1.52 (m, 2H), 1.46 – 1.34 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.80, 194.59, 142.68, 136.85, 136.12, 133.26, 130.65, 129.36, 129.05, 128.69, 127.51, 122.72, 108.45, 104.66 (d, *J* = 6.4 Hz), 81.17 (d, *J* = 169.3 Hz), 34.47 (d, *J* = 21.3 Hz), 30.43, 28.32, 22.55, 21.65, 13.99.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.63 – -217.11 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{24}BrFNaO$ ([M + Na] $^+$), 437.0892; found, 437.0890.



4-(2-Bromophenyl)-2-butyl-1-(4-(tert-butyl)phenyl)-6-fluorohexa-2,3-dien-1-one (4dc)

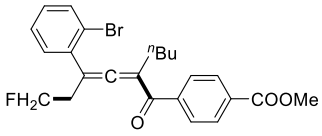
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 23.0 mg, 51%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.15 (td, *J* = 7.7, 1.6 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 4.58 – 4.35 (m, 2H), 2.95 – 2.71 (m, 2H), 2.48 (dd, *J* = 8.7, 6.6 Hz, 2H), 1.62 – 1.54 (m, 2H), 1.47 – 1.36 (m, 2H), 1.32 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.00, 194.85, 155.54, 136.91, 136.16, 133.23, 130.77, 129.35, 128.77, 127.45, 124.95, 122.64, 108.60, 104.78 (d, *J* = 6.3 Hz), 81.15 (d, *J* = 169.3 Hz), 35.00, 34.46 (d, *J* = 21.3 Hz), 31.17, 30.38, 28.23, 22.54, 13.99.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.67 – -217.22 (m).

HRMS (ESI) (m/z): calcd for $C_{26}H_{30}BrFNaO$ ([M + Na] $^+$), 479.1362; found, 479.1369.



Methyl-4-(4-(2-bromophenyl)-2-butyl-6-fluorohexa-2,3-dienoyl)benzoate (4di)

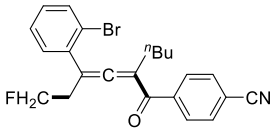
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 29.5 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.27 – 7.23 (m, 1H), 7.16 (td, J = 7.7, 1.7 Hz, 1H), 6.91 (dd, J = 7.6, 1.7 Hz, 1H), 4.55 – 4.35 (m, 2H), 3.94 (s, 3H), 2.95 – 2.67 (m, 2H), 2.55 – 2.43 (m, 2H), 1.61 – 1.54 (m, 2H), 1.41 (h, J = 7.4 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.07, 194.59, 166.45, 142.83, 136.33, 133.34, 132.69, 130.47, 129.56, 129.26, 128.55, 127.62, 122.57, 108.91, 105.69 (d, J = 5.4 Hz), 80.89 (d, J = 169.8 Hz), 52.38, 34.50 (d, J = 21.1 Hz), 30.38, 27.87, 22.53, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.62 – -216.94 (m).

HRMS (ESI) (m/z): calcd for $C_{24}H_{24}BrFNaO_3$ ([M + Na] $^+$), 481.0791; found, 481.0794.



4-(4-(2-Bromophenyl)-2-butyl-6-fluorohexa-2,3-dienoyl)benzonitrile (4dk)

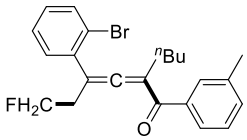
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 29.5 mg, 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 3.8, 1.2 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.30 (td, J = 7.5, 1.3 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.21 – 7.14 (m, 1H), 7.05 (dd, J = 4.9, 3.8 Hz, 1H), 4.66 – 4.47 (m, 2H), 3.08 – 2.84 (m, 2H), 2.60 – 2.43 (m, 2H), 1.69 – 1.46 (m, 2H), 1.39 (h, J = 7.3 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.44, 184.82, 143.10, 136.72, 133.46, 133.13, 133.04, 130.68, 129.51, 127.69, 127.60, 122.58, 108.69, 105.79 (d, J = 6.2 Hz), 81.12 (d, J = 169.1 Hz), 34.67 (d, J = 21.0 Hz), 30.42, 28.70, 22.51, 13.95.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.30 – -217.58 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{21}BrFNNaO$ ([M + Na] $^+$), 448.0688; found, 448.0680.



4-(2-Bromophenyl)-2-butyl-6-fluoro-1-(m-tolyl)hexa-2,3-dien-1-one (4dl)

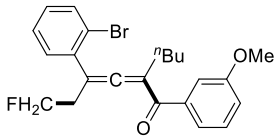
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 28.9 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.47 – 7.37 (m, 1H), 7.27 – 7.22 (m, 3H), 7.15 – 7.06 (m, 3H), 4.44 (dt, J = 46.8, 6.6 Hz, 2H), 2.86 – 2.79 (m, 2H), 2.62 – 2.47 (m, 2H), 2.35 (s, 3H), 1.55 – 1.50 (m, 2H), 1.43 (q, J = 7.3 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.69, 194.85, 138.65, 138.50, 134.34, 131.91, 128.72, 128.61, 128.43, 127.84, 126.81, 123.31, 110.72, 105.10 (d, *J* = 7.6 Hz), 81.56 (d, *J* = 169.3 Hz), 31.43 (d, *J* = 21.5 Hz), 30.28, 28.43, 22.65, 21.56, 13.97.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.64 – -215.92 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{24}BrFNaO$ ([M + Na] $^+$), 437.0892; found, 437.0900.



4-(2-Bromophenyl)-2-butyl-6-fluoro-1-(3-methoxyphenyl)hexa-2,3-dien-1-one (4dm)

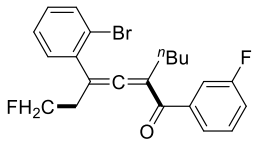
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 26.6 mg, 62%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.19 – 7.13 (m, 2H), 7.04 (dt, *J* = 7.6, 2.2 Hz, 1H), 6.99 – 6.95 (m, 1H), 4.56 – 4.31 (m, 2H), 3.75 (s, 3H), 2.95 – 2.70 (m, 2H), 2.55 – 2.34 (m, 2H), 1.69 – 1.51 (m, 2H), 1.44 – 1.22 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.20, 195.02, 159.28, 140.30, 136.72, 133.26, 130.64, 129.38, 128.98, 127.53, 122.68, 121.41, 118.36, 113.25, 108.74, 104.97 (d, *J* = 6.3 Hz), 81.11 (d, *J* = 169.3 Hz), 55.31, 34.48 (d, *J* = 21.2 Hz), 30.39, 28.15, 22.54, 13.98.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.76 – -217.13 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{24}BrFNaO_2$ ([M + Na] $^+$), 453.0841; found, 453.0852.



4-(2-Bromophenyl)-2-butyl-6-fluoro-1-(3-fluorophenyl)hexa-2,3-dien-1-one (4dn)

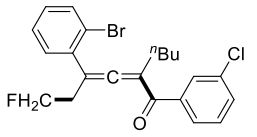
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 21.7 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.44 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.27 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.22 – 7.14 (m, 2H), 6.98 (dd, *J* = 7.6, 1.8 Hz, 1H), 4.60 – 4.32 (m, 2H), 2.95 – 2.70 (m, 2H), 2.54 – 2.35 (m, 2H), 1.62 – 1.53 (m, 2H), 1.47 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.57, 193.72, 163.02, 161.38, 140.90 (d, *J* = 6.3 Hz), 136.42, 133.33, 130.57, 129.68 (d, *J* = 7.6 Hz), 129.54, 127.62, 124.47 (d, *J* = 3.0 Hz), 122.56, 118.82 (d, *J* = 21.2 Hz), 115.70 (d, *J* = 22.6 Hz), 108.59, 105.57 (d, *J* = 5.6 Hz), 80.93 (d, *J* = 169.5 Hz), 34.51 (d, *J* = 20.9 Hz), 30.38, 28.02, 22.52, 13.95.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.78 (q, *J* = 5.6, 3.7 Hz), -214.86 – -218.69 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}BrF_2NaO$ ([M + Na] $^+$), 441.0642; found, 441.0645.



4-(2-Bromophenyl)-2-butyl-1-(3-chlorophenyl)-6-fluorohexa-2,3-dien-1-one (4do)

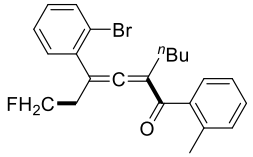
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 26.0 mg, 53%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 1H), 7.55 (t, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.24 (m, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.00 (dd, *J* = 7.5, 1.9 Hz, 1H), 4.66 – 4.32 (m, 2H), 2.93 – 2.69 (m, 2H), 2.51 – 2.43 (m, 2H), 1.65 – 1.53 (m, 2H), 1.48 – 1.30 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.64, 193.73, 140.54, 136.37, 133.98, 133.34, 131.82, 130.56, 129.52, 129.48, 128.83, 127.69, 126.82, 122.56, 108.64, 105.66 (d, *J* = 5.3 Hz), 80.93 (d, *J* = 169.5 Hz), 34.53 (d, *J* = 20.9 Hz), 30.38, 27.96, 22.53, 13.95.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.63 – -217.52 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}BrF_2NaO$ ([M + Na] $^+$), 459.0371; found, 459.0371.



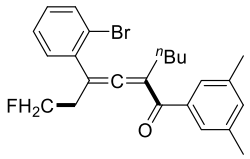
4-(2-Bromophenyl)-2-butyl-6-fluoro-1-(o-tolyl)hexa-2,3-dien-1-one (4dp)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.30 (td, *J* = 7.4, 1.6 Hz, 1H), 7.21 – 7.10 (m, 5H), 6.61 (dd, *J* = 7.5, 1.8 Hz, 1H), 4.43 – 4.25 (m, 2H), 2.66 (dtd, *J* = 22.9, 6.4, 1.9 Hz, 2H), 2.45 (h, *J* = 7.3 Hz, 2H), 2.22 (s, 3H), 1.62 – 1.56 (m, 2H), 1.46 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.87, 198.35, 140.57, 136.46, 135.45, 133.07, 130.54, 130.50, 129.61, 129.35, 127.31, 127.18, 124.85, 122.52, 111.20, 105.37 (d, *J* = 6.9 Hz), 80.97 (d, *J* = 169.3 Hz), 34.17 (d, *J* = 21.3 Hz), 30.30, 26.88, 22.53, 19.31, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -216.61 – -217.10 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{24}BrFNaO$ ([M + Na] $^+$), 437.0892; found, 437.0896.



4-(2-Bromophenyl)-2-butyl-1-(3,5-dimethylphenyl)-6-fluorohexa-2,3-dien-1-one (4dq)

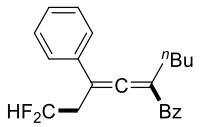
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 26.9 mg, 63%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H), 7.12 (s, 1H), 7.00 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.56 – 4.32 (m, 2H), 2.88 – 2.70 (m, 2H), 2.56 – 2.44 (m, 2H), 2.25 (s, 6H), 1.64 – 1.51 (m, 2H), 1.50 – 1.33 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.89, 195.57, 138.96, 137.47, 136.89, 133.71, 133.31, 130.60, 129.29, 127.55, 126.62, 122.70, 108.70, 104.65 (d, *J* = 6.7 Hz), 81.18 (d, *J* = 169.4 Hz), 34.40 (d, *J* = 21.0 Hz), 30.44, 28.19, 22.57, 21.14, 13.98.

^{19}F NMR (565 MHz, $CDCl_3$) δ -215.53 – -218.20 (m).

HRMS (ESI) (m/z): calcd for $C_{24}H_{26}BrFNaO$ ([M + Na] $^+$), 451.1049; found, 451.1049.



2-Butyl-6,6-difluoro-1,4-diphenylhexa-2,3-dien-1-one (5aa)

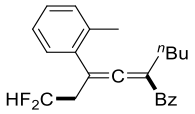
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 40.8 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.45 – 7.35 (m, 3H), 7.34 – 7.27 (m, 3H), 7.28 – 7.22 (m, 2H), 5.75 (tt, *J* = 56.1, 4.7 Hz, 1H), 3.08 – 2.87 (m, 2H), 2.55 (t, *J* = 8.0 Hz 2H), 1.57 – 1.52 (m, 2H), 1.48 – 1.49 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.78, 194.45, 138.41, 134.02, 132.13, 128.95, 128.38, 128.04, 127.91, 126.09, 115.46 (t, *J* = 239.8 Hz) 110.92, 102.06, 35.63 (t, *J* = 23.4 Hz) 30.15, 28.47, 22.63, 13.90.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.26 – -114.87 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{22}F_2NaO$ ([M + Na] $^+$), 363.1531; found, 363.1521.



2-Butyl-6,6-difluoro-1-phenyl-4-(o-tolyl)hexa-2,3-dien-1-one (5ba)

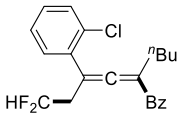
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 56.7 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.52 – 7.47 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.13 (m, 3H), 6.98 – 6.94 (m, 1H), 5.73 (tt, *J* = 56.1, 4.7 Hz, 1H), 2.97 – 2.72 (m, 2H), 2.55 – 2.42 (m, 2H), 2.01 (s, 3H), 1.60– 1.52 (m, 2H), 1.48 – 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.68, 195.17, 138.94, 135.69, 134.70, 132.01, 130.79, 128.67, 128.40, 128.16, 127.99, 126.17, 115.24 (t, *J* = 239.7 Hz), 107.95, 100.94 (t, *J* = 7.4 Hz), 38.99 (t, *J* = 22.8 Hz), 30.38, 28.12, 22.55, 19.69, 13.92

^{19}F NMR (565 MHz, CDCl3) δ -114.85 – -115.19 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{24}F_2NaO$ ([M + Na] $^+$), 377.1687; found, 377.1694.



2-Butyl-4-(2-chlorophenyl)-6,6-difluoro-1-phenylhexa-2,3-dien-1-one (5ca)

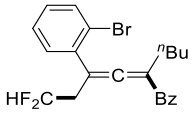
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 59.9 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.51 – 7.45 (m, 1H), 7.38-7.31 (m, 3H), 7.25-7.17 (m, 2H), 6.99 (dd, *J* = 7.4, 1.9 Hz, 1H), 5.74 (tt, *J* = 56.1, 4.7 Hz, 1H),3.01-2.82 (m, 2H), 2.52-2.44 (m, 2H), 1.61 – 1.51 (m, 2H), 1.46 – 1.34 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.37, 194.75, 138.69, 134.29, 132.75, 132.09, 130.41, 130.14, 129.47, 128.63, 128.01, 127.08, 115.27 (t, *J* = 241.5 Hz), 108.72, 100.20 (t, *J* =6.0 Hz), 38.07 (t, *J* = 23.1 Hz), 30.16, 28.11, 22.50, 13.90.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.07 – -115.44 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}ClF_2NaO$ ([M + Na] $^+$), 397.1141; found, 397.1136.



4-(2-Bromophenyl)-2-butyl-6,6-difluoro-1-phenylhexa-2,3-dien-1-one (5da)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 58.7 mg, 70%).

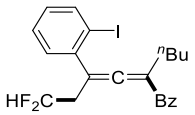
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28-7.24 (m, 1H), 7.19-7.15 (m, 1H), 6.99 – 6.94 (m, 1H), 5.78 (tt, *J* =

56.1, 4.8 Hz, 1H), 3.06 – 2.81 (m, 2H), 2.51 (t, *J* = 7.7 Hz, 2H), 1.62-1.55 (m，2H), 1.46-1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.96, 194.77, 138.79, 136.38, 133.33, 132.11, 130.59, 129.65, 128.70, 128.08, 127.63, 122.51, 115.25 (t, *J* = 241.6 Hz),108.81, 101.60 (t, *J* = 7.1 Hz), 38.31 (t, *J* = 23.0 Hz), 30.28, 28.13, 22.51, 13.92.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.75 – -115.86 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}BrF_2NaO$ ([M + Na] $^+$), 441.0636; found, 441.0602.



2-Butyl-6,6-difluoro-4-(2-iodophenyl)-1-phenylhexa-2,3-dien-1-one (5ea)

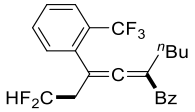
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 78.3 mg, 84%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.42 (td, *J* = 7.3, 1.4 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.19 (td, *J* = 7.5, 1.3 Hz, 1H), 6.89 (td, *J* = 7.6, 1.6 Hz, 1H), 6.81 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.70 (tt, *J* = 56.5, 4.7 Hz, 1H), 2.89 – 2.73 (m, 2H), 2.49 – 2.38 (m, 2H), 1.55 – 1.47 (m, 2H), 1.36 – 1.29 (m, 2H), 0.86 (td, *J* = 7.4, 1.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.47, 194.77, 140.50, 139.80, 138.92, 132.18, 129.93, 129.63, 128.83, 128.39, 128.20, 115.21 (t, *J* = 240.5Hz), 108.91, 97.63, 38.73 (t, *J* = 22.8 Hz), 30.59, 28.15, 22.55, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.27 – -116.35 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}F_2INaO$ ([M + Na] $^+$), 489.0497; found, 489.0497.



2-Butyl-6,6-difluoro-1-phenyl-4-(2-(trifluoromethyl)phenyl)hexa-2,3-dien-1-one (5fa)

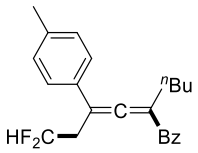
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 69.4 mg, 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.57-7.51 (m, 1H), 7.51 – 7.46 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.78 (tt, *J* = 56.0, 4.7 Hz, 1H), 2.99 – 2.73 (m, 2H), 2.53 – 2.41 (m, 2H), 1.57 – 1.50 (m, 2H), 1.40 (h, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H)..

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.60, 194.87, 138.83, 134.30, 132.20, 131.98, 130.84, 128.66, 128.39, 128.34 , 128.00, 126.70 (q, *J* = 10.3 Hz), 125.53 (q, *J* = 272.3 Hz), 115.11 (t, *J* = 241.3 Hz), 108.91, 99.14 (t, *J* = 7.1 Hz), 39.48 (t, *J* = 23.1 Hz), 30.27, 28.45, 22.54, 13.82.

^{19}F NMR (565 MHz, $CDCl_3$) δ -59.12 , -113.68 – -115.94 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{21}F_5NaO$ ([M + Na] $^+$), 431.1405; found, 431.1401.



2-Butyl-6,6-difluoro-1-phenyl-4-(p-tolyl)hexa-2,3-dien-1-one (5ia)

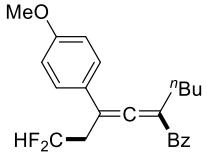
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 43.2 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.45 – 7.39 (m, 1H), 7.29 – 7.22 (m, 2H)，7.19 (d, *J* = 1.5 Hz, 4H), 5.74 (tt, *J* = 56.2, 4.8 Hz, 1H), 3.04 – 2.84 (m, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.36 (s, 3H), 1.56 – 1.52 (m, 2H), 1.47 – 1.39 (m, 2H), 0.94 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.81, 194.53, 138.48, 138.02, 132.05, 130.92, 129.68, 128.38, 127.90, 125.98, 115.53 (t, *J* = 240.0 Hz), 110.88, 104.99, 35.65 (t, *J* = 23.4 Hz), 30.16, 28.47, 22.64, 21.13, 13.92.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.20 – -114.80 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{24}F_2NaO$ ([M + Na] $^+$), 377.1687; found, 377.1681.



2-Butyl-6,6-difluoro-4-(4-methoxyphenyl)-1-phenylhexa-2,3-dien-1-one (5ja)

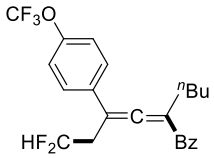
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 61.5 mg, 83%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.44 – 7.40 (m, 1H), 7.28 – 7.21 (m, 4H), 6.93 – 6.90 (m, 2H), 5.72 (tt, *J* = 47.0, 3.5 Hz, 1H), 3.83 (s, 3H), 3.02 – 2.86 (m, 2H), 2.54 (t, *J* = 7.8 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.49 – 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.64, 194.58, 159.48, 138.50, 132.04, 128.39, 127.89, 127.33, 126.05, 115.57 (t, *J* = 240.0 Hz), 114.42, 110.87, 101.69, 55.36, 35.76 (t, *J* = 23.3 Hz), 30.19, 28.50, 22.64, 13.92.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.25 – -114.63 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{24}F_2NaO_2$ ([M + Na] $^+$), 393.1637; found, 393.1637.



2-Butyl-6,6-difluoro-1-phenyl-4-(4-(trifluoromethoxy)phenyl)hexa-2,3-dien-1-one (5ka)

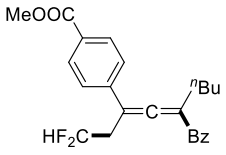
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 55.1 mg, 65%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.47 – 7.42 (m, 1H), 7.34 – 7.26 (m, 4H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.76 (tt, *J* = 56.1, 4.7 Hz, 1H), 3.02 – 2.85 (m, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.56 – 1.51 (m, 2H), 1.47 – 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.46, 194.12, 148.81, 138.30, 132.89, 132.33, 128.33, 128.01, 127.49, 121.69 (q, *J* = 180.3 Hz), 121.34, 115.31 (t, *J* = 241.5 Hz), 111.21, 101.09, 35.70 (t, *J* = 24.0 Hz), 30.15, 28.52, 22.61, 13.87.

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.87 , -112.93 – -115.84 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{21}F_5NaO_2$ ([M + Na] $^+$), 447.1354; found, 447.1362.



Methyl-4-(5-benzoyl-1,1-difluorononona-3,4-dien-3-yl)benzoate (5la)

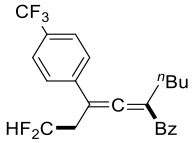
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 63.7 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.64 – 7.60 (m, 2H), 7.43 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.24 (m, 2H), 5.76 (tt, *J* = 56.0, 4.6 Hz, 1H), 3.93 (s, 3H), 3.07 – 2.89 (m, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.49 – 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.19, 194.00, 166.51, 138.83, 138.27, 132.35, 130.18, 129.60, 128.30, 128.02, 125.98, 115.28(t, *J* = 240.3 Hz), 111.29, 101.62, 52.23, 35.43(t, *J* = 23.6 Hz), 30.15, 28.52, 22.62, 13.88.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.19 – -115.07 (m).

HRMS (ESI) (m/z): calcd for $C_{24}H_{24}F_2NaO_3$ ([M + Na] $^+$), 421.1586; found, 421.1586.



2-Butyl-6,6-difluoro-1-phenyl-4-(4-(trifluoromethyl)phenyl)hexa-2,3-dien-1-one (5ma)

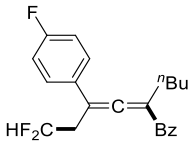
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 50.6 mg, 62%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 4H), 7.48 – 7.43 (m, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 5.76 (tt, *J* = 56.0, 4.6 Hz, 1H), 3.08 – 2.89 (m, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 1.57 – 1.51 (m, 2H), 1.49 – 1.39 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.85, 193.91, 138.24, 138.00, 132.42, 129.99 (q, *J* = 32.7 Hz), , 128.29, 128.06, 126.35, 125.89 (q, *J* = 3.5 Hz), 123.93 (q, *J* = 111.8 Hz), 115.23 (t, *J* = 240.6 Hz), 111.41, 101.24, 35.50(t, *J* = 23.6 Hz), 30.14, 28.53, 22.61, 13.87.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.68 , -113.32 – -114.83 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{21}F_5NaO$ ([M + Na] $^+$), 431.1405; found, 431.1400.



2-Butyl-6,6-difluoro-4-(4-fluorophenyl)-1-phenylhexa-2,3-dien-1-one (5na)

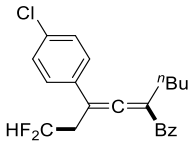
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 40.1 mg, 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.47 – 7.41 (m, 1H), 7.30 – 7.23 (m, 4H), 7.08 (t, *J* = 8.6 Hz, 2H), 5.74 (tt, *J* = 56.1, 4.7 Hz, 1H), 3.04 – 2.83 (m, 2H), 2.55 (t, *J* = 7.8 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.49 – 1.37 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.38, 194.33, 162.46 (d, *J* = 246.9 Hz), 138.37, 132.23, 130.13 (d, *J* = 3.5 Hz), 128.36, 127.97, 127.80 (d, *J* = 7.9 Hz), 115.99 (d, *J* = 21.8 Hz), 115.39 (t, *J* = 240.1 Hz), 111.02, 101.30 (t, *J* = 6.8 Hz), 35.85(t, *J* = 23.25 Hz), 30.18, 28.49, 22.63, 13.90.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.46 – -113.60 (m), -113.38 – -114.60 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}F_3NaO$ ([M + Na] $^+$), 381.1437; found, 381.1436.



2-Butyl-4-(4-chlorophenyl)-6,6-difluoro-1-phenylhexa-2,3-dien-1-one (5oa)

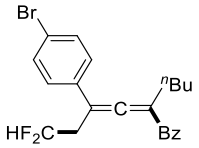
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 39.7 mg, 53%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.47 – 7.41 (m, 1H), 7.37 – 7.33 (m, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.20 (m, 2H), 5.73 (tt, *J* = 56.1, 4.6 Hz, 1H), 3.01 – 2.85 (m, 2H), 2.55 (t, *J* = 7.7 Hz, 2H), 1.56 – 1.51 (m, 2H), 1.49 – 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.53, 194.16, 138.31, 133.97, 132.62, 132.28, 129.15, 128.31, 128.00, 127.33, 115.33 (t, *J* = 240.2 Hz), 111.21, 101.28, 35.59(t, *J* = 23.4 Hz), 30.15, 28.49, 22.62, 13.89.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.62 – -115.44 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}ClF_2NaO$ ([M + Na] $^+$), 397.1141; found, 397.1148.



4-(4-Bromophenyl)-2-butyl-6,6-difluoro-1-phenylhexa-2,3-dien-1-one (5pa)

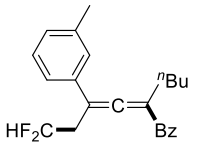
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 43.6 mg, 52%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.60 (m, 2H), 7.52 – 7.48(m, 2H), 7.47 – 7.41 (m, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.18 – 7.15 (m, 2H), 5.73 (tt, *J* = 56.1, 4.7 Hz, 1H), 3.02 – 2.82 (m, 2H), 2.55 (t, *J* = 7.7 Hz, 2H), 1.56 – 1.49 (m, 2H), 1.48 – 1.39 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.50, 194.10, 138.31, 133.13, 132.29, 132.10, 128.31, 128.01, 127.63, 122.09, 115.32 (t, *J* = 240.3 Hz), 111.26, 101.34, 35.53 (t, *J* = 23.4 Hz), 30.15, 28.46, 22.61, 13.89.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.80 – -115.56 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}BrF_2NaO$ ([M + Na] $^+$), 441.0636; found, 441.0642.



2-Butyl-6,6-difluoro-1-phenyl-4-(m-tolyl)hexa-2,3-dien-1-one (5ga)

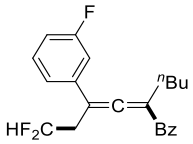
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 43.2 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.45 – 7.40 (m, 1H), 7.29 – 7.23 (m, 3H), 7.14 – 7.06 (m, 3H), 5.75 (tt, *J* = 56.2, 4.7 Hz, 1H), 3.06 – 2.86 (m, 2H), 2.58– 2.52 (m, 2H), 2.36 (s, 3H), 1.59 – 1.52(m, 2H), 1.49 – 1.40 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.86, 194.49, 138.64, 138.46, 133.93, 132.09, 128.86, 128.82, 128.41, 127.91, 126.76, 123.26, 115.50 (t, *J* = 249.8 Hz), 110.76, 102.03 (t, *J* = 7.1 Hz), 35.71(t, *J* = 23.4 Hz), 30.16, 28.48, 22.63, 21.54, 13.92.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.04 – -116.02 (m).

HRMS (ESI) (m/z): calcd for $C_{23}H_{24}F_2NaO$ ([M + Na] $^+$), 377.1687; found, 377.1677.



2-Butyl-6,6-difluoro-4-(3-fluorophenyl)-1-phenylhexa-2,3-dien-1-one (5ha)

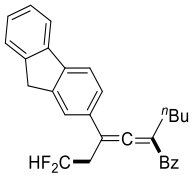
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 48.0 mg, 67%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 6.8 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.37 – 7.32 (m, 1H), 7.28 – 7.26 (m, 2H), 7.09 (dt, J = 7.9, 1.3 Hz, 1H), 7.03 – 6.96 (m, 2H), 5.75 (tt, J = 56.1, 4.7 Hz, 1H),3.03–2.85 (m, 2H), 2.56 (t, J = 8.0 Hz, 2H), 1.57 – 1.51 (m, 2H), 1.49 – 1.39 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.61, 194.09, 163.10 (d, J = 244.9 Hz), 138.29, 136.59 (d, J = 7.4Hz), 132.30, 130.43 (d, J = 8.1 Hz), 128.33, 128.00, 121.77 (d, J = 2.9 Hz), 115.27 (t, J = 240.0 Hz), 114.94 (d, J = 21.2 Hz), 113.09 (d, J = 22.9 Hz), 111.26, 101.36, 35.59(t, J = 23.6 Hz), 30.13, 28.49, 22.62, 13.88.

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.77 – -112.10 (m), -113.30 – -114.95 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{21}F_3NaO$ ([M + Na] $^+$), 381.1437; found, 381.1435.



2-Butyl-4-(9H-fluoren-2-yl)-6,6-difluoro-1-phenylhexa-2,3-dien-1-one (5ra)

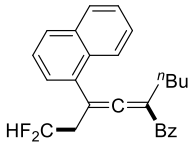
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 55.7 mg, 65%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.67 (d, J = 7.7 Hz, 2H), 7.56 (d, J = 7.5 Hz, 1H), 7.46 (s, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.22 (m, 2H), 5.78 (tt, J =4.8, 56.4 Hz, 1H), 3.92 (s, 2H), 3.10 – 2.94 (m, 2H), 2.59 (t, J = 7.9 Hz, 2H), 1.62 – 1.56 (m, 2H), 1.50 – 1.43 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.15, 194.50, 144.02, 143.42, 141.83, 140.96, 138.46, 132.29, 132.14, 128.43, 127.94, 127.16, 126.96, 125.12, 124.98, 122.64, 120.24, 120.08, 115.57 (t, J = 241.6 Hz), 110.88, 102.47 (t, J = 6.7 Hz), 36.98, 35.84 (t, J = 23.5 Hz), 30.20, 28.56, 22.67, 13.95.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.18 – -114.81 (m).

HRMS (ESI) (m/z): calcd for $C_{29}H_{26}F_2NaO$ ([M + Na] $^+$), 451.1844; found, 451.1818.



2-Butyl-6,6-difluoro-4-(naphthalen-1-yl)-1-phenylhexa-2,3-dien-1-one (5qa)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 60.1 mg, 77%).

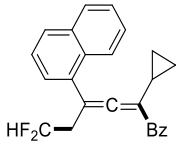
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 2H), 7.64 – 7.60 (m, 2H), 7.55 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 7.38 – 7.31 (m, 3H), 7.30 – 7.27 (m, 1H), 7.22 – 7.19 (m, 1H), 5.76 (tt, J = 56.1,

4.7 Hz, 1H), 3.12 – 2.86 (m, 2H), 2.56 – 2.46 (m, 2H), 1.63 – 1.59 (m, 2H), 1.48 – 1.39 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.32, 195.17, 139.09, 133.94, 133.02, 131.92, 130.67, 128.70, 128.52, 128.10, 126.45, 126.16, 125.39, 124.87, 115.22 (t, *J* = 241.3 Hz), 108.24, 100.26, 39.56 (t, *J* = 23.3 Hz), 30.32, 28.11, 22.55, 13.97.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.72 – -115.93 (m).

HRMS (ESI) (m/z): calcd for $C_{26}H_{24}F_2NaO$ ([M + Na] $^+$), 413.1687; found, 413.1677.



2-Cyclopropyl-6,6-difluoro-4-(naphthalen-1-yl)-1-phenylhexa-2,3-dien-1-one (5ta)

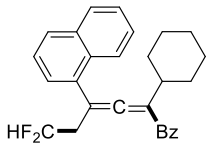
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 56.9 mg, 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.62 (d, *J* = 6.5 Hz, 2H), 7.54 (t, *J* = 6.0 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 2.3 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 1H), 5.75 (tt, *J* = 55.9, 4.7 Hz, 1H), 3.08 – 2.84 (m, 2H), 1.90 – 1.82 (m, 1H), 1.06 – 0.87 (m, 2H), 0.78 – 0.55 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.41, 195.16, 139.09, 133.90, 132.88, 131.92, 130.48, 128.80, 128.66, 128.52, 128.11, 126.48, 126.17(d, *J* = 3.6 Hz), 125.39, 124.76, 115.07(t, *J* = 240.0 Hz), 112.35, 102.81, 39.61(t, *J* = 23.0 Hz), 8.45, 7.87(d, *J* = 8.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.25 – -115.67 (m).

HRMS (ESI) (m/z): calcd for $C_{25}H_{20}F_2NaO$ ([M + Na] $^+$), 397.1374; found, 397.1364.



2-Cyclohexyl-6,6-difluoro-4-(naphthalen-1-yl)-1-phenylhexa-2,3-dien-1-one (5ua)

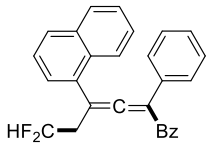
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 65.8 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 12.9, 8.2 Hz, 2H), 7.65 – 7.60 (m, 2H), 7.56 – 7.51 (m, 1H), 7.43 (dt, *J* = 8.0, 6.3 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.15 (m, 3H), 5.79 (tt, *J* = 56.1, 4.8 Hz, 1H), 3.10 – 2.83 (m, 2H), 2.76 – 2.68 (m, 1H), 2.04 (d, *J* = 12.4 Hz, 1H), 1.89 – 1.82 (m, 1H), 1.82 – 1.70 (m, 3H), 1.50 – 1.32 (m, 3H), 1.32 – 1.19 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.24, 195.13, 139.53, 133.89, 133.25, 131.90, 130.56, 128.70, 128.64, 128.46, 128.12, 126.37, 126.34, 126.08, 125.40, 124.94, 115.29 (t, *J* = 241.5 Hz), 113.97, 101.73, 101.69, 39.66 (t, *J* = 23.1 Hz), 36.77, 32.62, 32.39, 26.53, 26.43, 26.23.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.87 – -116.12 (m).

HRMS (ESI) (m/z): calcd for $C_{28}H_{26}F_2NaO$ ([M + Na] $^+$), 439.1844; found, 439.1835.



6,6-Difluoro-4-(naphthalen-1-yl)-1,2-diphenylhexa-2,3-dien-1-one (5va)

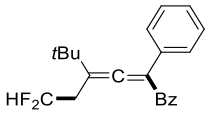
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 62.4 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.76 – 7.72 (m, 2H), 7.55 – 7.50 (m, 3H), 7.48 – 7.38 (m, 5H), 7.37 – 7.26 (m, 4H), 7.25 – 7.21 (m, 1H), 5.84 (tt, *J* = 56.0, 4.7 Hz, 1H), 3.21 – 3.00 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.20, 193.43, 138.47, 133.97, 132.83, 132.67 (d, *J* = 2.2 Hz), 130.66, 129.36, 128.93, 128.71, 128.56, 128.34, 128.28, 128.15, 126.60, 126.22, 126.04, 125.39, 124.84, 115.18 (t, *J* = 241.6 Hz), 109.58, 102.50, 39.47 (t, *J* = 23.3 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.98 – -115.39 (m).

HRMS (ESI) (m/z): calcd for $C_{28}H_{20}F_2NaO$ ([M + Na] $^+$), 433.1374; found, 433.1365.



4-(Tert-butyl)-6,6-difluoro-1,2-diphenylhexa-2,3-dien-1-one (5xa)

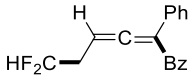
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 23.8 mg, 35%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.54- 7.50 (m, 1H), 7.45 – 7.39 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 1H), 5.88 (tt, *J* = 56.3, 4.8 Hz, 1H), 2.71 – 2.53 (m, 2H), 1.05 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 205.54, 194.09, 138.71, 133.37, 132.51, 128.99, 128.63, 128.20, 127.69, 127.38, 116.19 (t, *J* = 240.6 Hz), 112.64, 112.08 (t, *J* = 5.9 Hz), 35.53, 33.21 (t, *J* = 23.3 Hz), 28.68.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.84 – -114.46 (m).

HRMS (ESI) (m/z): calcd for $C_{22}H_{22}F_2NaO$ ([M + Na] $^+$), 363.1531; found, 363.1534.



6,6-Difluoro-1,2-diphenylhexa-2,3-dien-1-one (5ya)

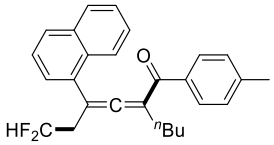
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 26.1 mg, 46%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.39 – 7.34 (m, 2H), 7.31 – 7.26 (m, 5H), 6.57 (t, *J* = 2.1 Hz, 1H), 6.10 (tt, *J* = 56.7, 4.7 Hz, 1H), 3.26– 2.95 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 216.34, 193.01, 137.41, 132.58, 131.27, 129.06, 128.78, 128.32, 128.05, 127.56, 115.39 (t, *J* = 238.8 Hz), 102.73 (t, *J* = 6.3 Hz), 98.96, 34.38 (t, *J* = 23.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.43 – -116.08 (m).

HRMS (ESI) (m/z): calcd for $C_{18}H_{14}F_2NaO$ ([M + Na] $^+$), 307.0905; found, 307.0901.



2-Butyl-6,6-difluoro-4-(naphthalen-1-yl)-1-(p-tolyl)hexa-2,3-dien-1-one (5qb)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 50.1 mg, 62%).

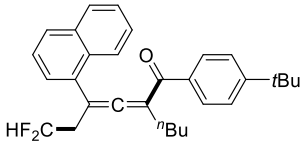
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 18.5, 8.2 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.50 – 7.43 (m, 2H), 7.43 – 7.39 (m, 1H), 7.30 – 7.23 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.77 (tt, *J* = 55.2, 4.2 Hz, 1H),

3.12 – 2.87 (m, 2H), 2.56 – 2.47 (m, 2H), 2.42 (s, 3H), 1.66 – 1.52 (m, 2H), 1.47 – 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.78, 194.72, 142.65, 136.31, 133.97, 133.22, 130.72, 128.94, 128.76, 128.66, 128.51, 126.29, 126.18, 126.12, 125.41, 125.04, 115.31 (t, *J* = 241.5 Hz), 108.11, 100.01 (t, J = 7.1 Hz), 39.59 (t, *J* = 23.2 Hz), 30.35, 28.28, 22.55, 21.62, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.09 – -115.40 (m).

HRMS (ESI) (m/z): calcd for $C_{27}H_{26}F_2NaO$ ([M + Na] $^+$), 427.1844; found, 427.1834.



2-Butyl-1-(4-(tert-butyl)phenyl)-6,6-difluoro-4-(naphthalen-1-yl)hexa-2,3-dien-1-one (5qc)

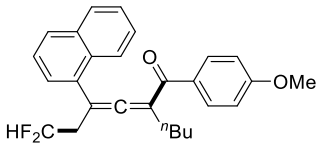
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 62.5 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 14.6, 8.3 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.49 – 7.41 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.27 – 7.22 (m, 2H), 5.77 (tt, *J* = 56.0, 4.8 Hz, 1H), 3.15 – 2.84 (m, 2H), 2.52 (t, *J* = 7.7 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 1.34 (s, 9H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.79, 194.64, 155.74, 136.11, 133.98, 133.25, 130.64, 128.81, 128.68, 128.55, 126.33, 126.09, 125.41, 125.03, 125.01, 115.32 (t, *J* = 241.5 Hz), 108.00, 100.11 (t, *J* = 7.1 Hz), 39.58 (t, *J* = 23.2 Hz), 35.04, 31.19, 30.31, 28.30, 22.53, 13.96.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.07 – -115.57 (m).

HRMS (ESI) (m/z): calcd for $C_{30}H_{32}F_2NaO$ ([M + Na] $^+$), 469.2314; found, 469.2313.



2-Butyl-6,6-difluoro-1-(4-methoxyphenyl)-4-(naphthalen-1-yl)hexa-2,3-dien-1-one (5qd)

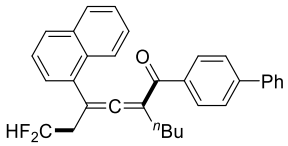
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 53.8 mg, 64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.34 – 7.31 (m, 1H), 7.31 – 7.28 (m, 1H), 6.78 – 6.70 (m, 2H), 5.78 (tt, *J* = 56.1, 4.8 Hz, 1H), 3.83 (s, 3H), 3.12 – 2.90 (m, 2H), 2.52 (t, *J* = 7.7 Hz, 2H), 1.65 – 1.50 (m, 2H), 1.45 – 1.38 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.98, 193.39, 162.95, 134.00, 133.35, 131.39, 131.19, 130.71, 128.67, 128.57, 126.33, 126.25, 126.14, 125.43, 125.11, 115.34 (t, *J* = 241.4 Hz), 113.32, 107.79, 99.80, 55.42, 39.59 (t, *J* = 23.1 Hz), 30.39, 28.57, 22.55, 13.95.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.22 – -115.37 (m).

HRMS (ESI) (m/z): calcd for $C_{27}H_{26}F_2NaO_2$ ([M + Na] $^+$), 443.1793; found, 443.1785.



1-([1,1'-Biphenyl]-4-yl)-2-butyl-6,6-difluoro-4-(naphthalen-1-yl)hexa-2,3-dien-1-one (5qe)

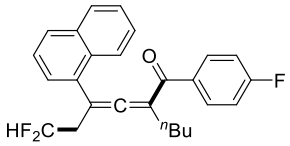
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 63.5 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 11.2, 8.3 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 7.9 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.39 (m, 4H), 7.27 (d, J = 7.0 Hz, 1H), 7.25 – 7.19 (m, 1H), 5.78 (tt, J = 56.1, 4.8 Hz, 1H), 3.16 – 2.86 (m, 2H), 2.55 (t, J = 7.7 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.51 -1.38 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.06, 194.65, 144.73, 140.06, 137.72, 133.98, 133.11, 130.68, 129.39, 128.98, 128.76, 128.57, 128.11, 127.23, 126.71, 126.42, 126.24, 126.18, 125.44, 124.94, 115.27 (t, J = 241.5 Hz), 108.24, 100.38 (t, J = 7.0 Hz), 39.61 (t, J = 23.2 Hz), 30.36, 28.22, 22.58, 13.99.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.08 – -115.42 (m).

HRMS (ESI) (m/z): calcd for $C_{32}H_{28}F_2NaO$ ([M + Na] $^+$), 489.2000; found, 489.2008.



2-Butyl-6,6-difluoro-1-(4-fluorophenyl)-4-(naphthalen-1-yl)hexa-2,3-dien-1-one (5qf)

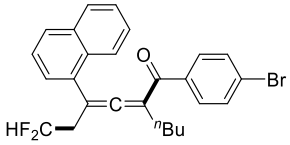
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 45.7 mg, 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.67 – 7.59 (m, 2H), 7.52 – 7.42 (m, 3H), 7.35 (t, J = 7.6 Hz, 1H), 7.28 – 7.22 (m, 1H), 6.99 – 6.92 (m, 2H), 5.76 (tt, J = 56.0, 4.8 Hz, 1H), 3.12 – 2.88 (m, 2H), 2.57 – 2.47 (m, 2H), 1.66 – 1.54 (m, 2H), 1.47 – 1.35 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.85, 193.43, 165.11 (d, J = 253.2 Hz), 135.05 (d, J = 3.1 Hz), 134.01, 132.93, 131.29 (d, J = 9.0 Hz), 130.60, 128.85, 128.64, 126.48, 126.29, 126.17, 125.43, 124.79, 115.16 (d, J = 21.8 Hz), 115.15 (t, J = 241.5 Hz), 108.03, 100.42 (t, J = 7.0 Hz), 39.51 (t, J = 23.2 Hz), 30.37, 28.29, 22.55, 13.94.

^{19}F NMR (565 MHz, $CDCl_3$) δ -106.72 – -106.84 (m), -115.16 – -115.68 (m).

HRMS (ESI) (m/z): calcd for $C_{26}H_{23}F_3NaO$ ([M + Na] $^+$), 431.1593; found, 431.1590.



1-(4-Bromophenyl)-2-butyl-6,6-difluoro-4-(naphthalen-1-yl)hexa-2,3-dien-1-one (5qg)

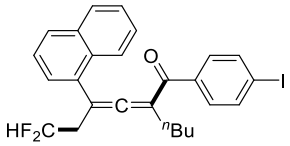
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 56.3 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 2H), 7.52 – 7.47 (m, 1H), 7.45 (d, J = 8.4 Hz, 3H), 7.43 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.26 – 7.23 (m, 1H), 5.76 (tt, J = 56.0, 4.8 Hz, 1H), 3.10 – 2.84 (m, 2H), 2.55 – 2.45 (m, 2H), 1.67 – 1.57 (m, 2 H), 1.47 – 1.39 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.20, 194.02, 137.72, 133.98, 132.79, 131.36, 130.52, 130.23, 128.89, 128.62, 126.72, 126.54, 126.32, 126.20, 125.44, 124.77, 115.10 (t, J = 241.6 Hz), 108.15, 100.75 (t, J = 6.9 Hz), 39.48 (t, J = 23.2 Hz), 30.32, 28.07, 22.54, 13.94. 115.10.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.25 – -115.57 (m).

HRMS (ESI) (m/z): calcd for $C_{26}H_{23}BrF_2NaO$ ([M + Na] $^+$), 491.0793; found, 491.0786.



2-Butyl-6,6-difluoro-1-(4-iodophenyl)-4-(naphthalen-1-yl)hexa-2,3-dien-1-one (5qh)

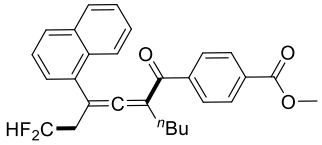
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 62.0 mg, 63%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.64 – 7.59 (m, 2H), 7.53 – 7.49 (m, 1H), 7.48 – 7.44 (m, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 7.27 – 7.23 (m, 1H), 5.76 (tt, *J* = 56.0, 4.7 Hz, 1H), 3.12 – 2.82 (m, 2H), 2.60 – 2.42 (m, 2H), 1.69 – 1.51 (m, 2H), 1.51 – 1.36 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.25, 194.31, 138.30, 137.35, 133.98, 132.79, 130.50, 130.14, 128.89, 128.61, 126.58, 126.33, 126.23, 125.44, 124.79, 115.10 (t, *J* = 240.0 Hz), 108.13, 100.80, 99.13, 39.46 (t, *J* = 23.2 Hz), 30.30, 28.01, 22.54, 13.93.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.05 – -115.73 (m).

HRMS (ESI) (m/z): calcd for $C_{26}H_{23}F_2INaO$ ([M + Na] $^+$), 539.0654; found, 539.0660.



Methyl-4-(2-butyl-6,6-difluoro-4-(naphthalen-1-yl)hexa-2,3-dienoyl)benzoate (5qi)

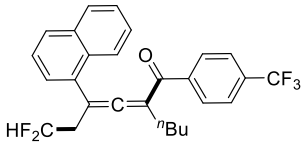
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 53.8 mg, 64%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.84 (dd, *J* = 13.3, 8.2 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 5.75 (tt, *J* = 56.1, 4.8 Hz, 1H), 3.98 (s, 3H), 3.10 – 2.84 (m, 2H), 2.57 – 2.45 (m, 2H), 1.65 – 1.59 (m, 2H), 1.49 – 1.39 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.84, 194.65, 166.39, 142.96, 133.96, 132.74, 132.66, 130.54, 129.33, 128.88, 128.62, 128.44, 126.52, 126.26, 126.11, 125.42, 124.63, 115.04 (t, *J* = 241.5 Hz), 108.52, 100.91 (t, *J* = 7.0 Hz), 52.42, 39.46 (t, *J* = 23.3 Hz), 30.31, 27.87, 22.54, 13.93.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.77 – -116.46 (m).

HRMS (ESI) (m/z): calcd for $C_{28}H_{26}F_2NaO_3$ ([M + Na] $^+$), 471.1742; found, 471.1739.



2-Butyl-6,6-difluoro-4-(naphthalen-1-yl)-1-(4-(trifluoromethyl)phenyl)hexa-2,3-dien-1-one (5qj)

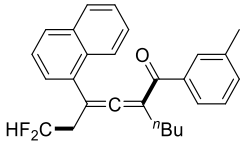
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 40.3 mg, 44%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 11.6, 8.3 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.42 (m, 2H), 7.26 (q, *J* = 4.5, 2.7 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 1H), 5.75 (tt, *J* = 56.0, 4.7 Hz, 1H), 3.10 – 2.85 (m, 2H), 2.57 – 2.48 (m, 2H), 1.68 – 1.58 (m, 2H), 1.50 – 1.40 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.82, 194.17, 142.18, 133.99, 133.09(t, J = 32.4 Hz),132.56, 130.40, 129.00, 128.82, 128.68, 126.52, 126.35, 126.24, 125.42, 125.11 (q, J = 3.7 Hz), 124.52, 114.99 (t, J = 241.6 Hz), 108.42, 101.26, 39.39 (t, J = 23.2 Hz), 30.29, 27.87, 22.54, 13.92.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.90 , -115.24 – -115.92 (m).

HRMS (ESI) (m/z): calcd for $C_{27}H_{23}F_5NaO$ ([M + Na] $^+$), 481.1561; found, 481.1564.



2-Butyl-6,6-difluoro-4-(naphthalen-1-yl)-1-(m-tolyl)hexa-2,3-dien-1-one (5ql)

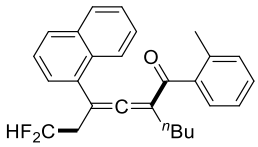
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 55.0 mg, 68%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, J = 17.2, 8.2 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.39 (dd, J = 8.5, 1.1 Hz, 1H), 7.34 (d, J = 1.8 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 5.76 (tt, J = 56.1, 5.2 Hz, 1H), 3.11 – 2.81 (m, 2H), 2.56 – 2.48 (m, 2H), 2.14 (s, 3H), 1.69 – 1.50 (m, 2H), 1.51 – 1.37 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.03, 195.43, 139.13, 137.82, 133.98, 133.15, 132.71, 130.67, 129.28, 128.66, 128.52, 127.98, 126.40, 126.17, 126.14, 125.84, 125.42, 124.86, 115.27 (t, J = 241.4 Hz), 108.25, 100.19 (t, J = 7.0 Hz), 39.52 (t, J = 23.2 Hz), 30.35, 28.17, 22.56, 21.04, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.14 – -115.49 (m).

HRMS (ESI) (m/z): calcd for $C_{27}H_{26}F_2NaO$ ([M + Na] $^+$), 427.1844; found, 427.1833.



2-Butyl-6,6-difluoro-4-(naphthalen-1-yl)-1-(o-tolyl)hexa-2,3-dien-1-one (5qp)

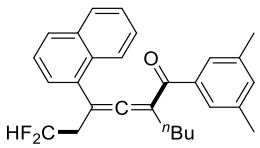
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 32.3 mg, 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.18 – 7.11 (m, 2H), 7.00 (d, J = 7.0 Hz, 1H), 5.68 (tt, J = 56.2, 4.8 Hz, 1H), 3.00 – 2.72 (m, 2H), 2.56 – 2.41 (m, 2H), 2.14 (s, 3H), 1.69 – 1.53 (m, 2H), 1.49 – 1.37 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.44, 198.09, 140.54, 135.68, 133.82, 132.72, 130.77, 130.63, 129.69, 128.63, 128.39, 127.21, 126.52, 126.16, 126.10, 125.27, 124.99, 124.77, 115.11 (t, J = 241.5 Hz), 110.58, 100.77, 39.31 (t, J = 23.3 Hz), 30.22, 26.99, 22.53, 19.26, 13.94.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.73 – -116.20 (m).

HRMS (ESI) (m/z): calcd for $C_{27}H_{26}F_2NaO$ ([M + Na] $^+$), 427.1844; found, 427.1837.



2-Butyl-1-(3,5-dimethylphenyl)-6,6-difluoro-4-(naphthalen-1-yl)hexa-2,3-dien-1-one (5qq)

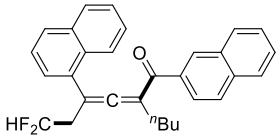
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 51.9 mg, 62%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 2H), 7.51 – 7.37 (m, 3H), 7.32 – 7.23 (m, 2H), 7.17 (s, 2H), 7.12 (s, 1H), 5.76 (tt, *J* = 56.1, 4.8 Hz, 1H), 3.14 – 2.79 (m, 2H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.12 (s, 6H), 1.68 – 1.57 (m, 2H), 1.50 – 1.39 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.75, 195.62, 139.14, 137.67, 134.01, 133.67, 133.25, 130.68, 128.62, 128.53, 126.50, 126.38, 126.17, 126.14, 125.44, 124.86, 115.31 (t, *J* = 241.5 Hz), 108.23, 100.08 (t, *J* = 7.1 Hz), 39.50 (t, *J* = 23.1 Hz), 30.37, 28.25, 22.58, 20.94, 13.96.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.98 – -116.10 (m).

HRMS (ESI) (m/z): calcd for $C_{28}H_{28}F_2NaO$ ([M + Na] $^+$), 441.2000; found, 441.1998.



2-Butyl-6,6-difluoro-4-(naphthalen-1-yl)-1-(naphthalen-2-yl)hexa-2,3-dien-1-one (5qr)

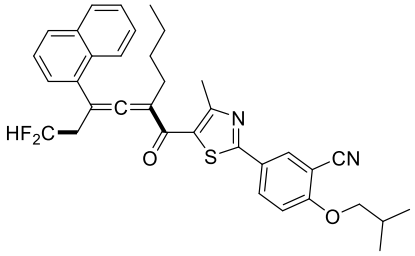
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 40.5 mg, 62 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.6 Hz, 1H), 7.88 – 7.81 (m, 3H), 7.81 (s, 1H), 7.79 – 7.75 (m, 1H), 7.58 – 7.54 (m, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.35 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.21 (d, 1H), 7.02 – 6.84 (m, 1H), 5.77 (tt, *J* = 56.1, 5.3 Hz, 1H), 3.11 – 2.83 (m, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 1.77 – 1.58 (m, 2H), 1.53 – 1.39 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.09, 194.97, 136.00, 135.13, 133.94, 133.09, 132.13, 130.65, 130.15, 129.27, 128.71, 128.47, 128.03, 127.93, 127.64, 126.51, 126.37, 126.30, 126.17, 125.39, 124.95, 124.77, 115.24 (t, *J* = 241.4 Hz), 108.23, 100.31, 39.46 (t, *J* = 23.2 Hz), 30.46, 28.37, 22.63, 13.99.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.11 – -115.55 (m).

HRMS (ESI) (m/z): calcd for $C_{30}H_{26}F_2NaO$ ([M + Na] $^+$), 463.1844; found, 463.1846.



5-(5-(2-Butyl-6,6-difluoro-4-(naphthalen-1-yl)hexa-2,3-dienoyl)-4-methylthiazol-2-yl)-2-isobutoxybenzonitrile (5qs)

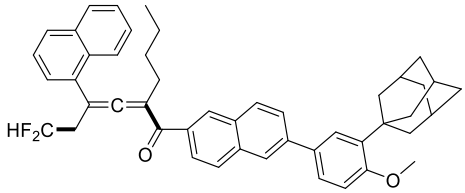
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 77.2 mg, 66%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.79 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.55 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.44 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.38 – 7.33 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 5.85 (tt, *J* = 56.0, 5.3, 4.0 Hz, 1H), 3.89 (d, *J* = 6.5 Hz, 2H), 3.27 – 3.06 (m, 2H), 2.69 (s, 3H), 2.64 – 2.52 (m, 2H), 2.26 – 2.17 (m, 1H), 1.65 – 1.59 (m, 2H), 1.50 – 1.41 (m, 2H), 1.10 (d, *J* = 6.7 Hz, 6H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.38, 184.71, 166.04, 162.40, 161.09, 134.17, 133.11, 132.30, 131.79, 130.45, 129.26, 129.10, 128.11, 126.61, 126.36, 126.31, 125.75, 125.60, 124.75, 115.28, 115.22 (t, J = 241.6 Hz), 112.46, 111.13, 102.82, 75.72, 39.47 (t, J = 23.1 Hz), 30.54, 29.69, 28.96, 28.18, 22.61, 19.05, 18.20, 13.91.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.98 – -116.36 (m).

HRMS (ESI) (m/z): calcd for $C_{35}H_{34}F_2N_2NaO_2S$ ([M + Na] $^+$), 607.2201; found, 607.2211.



1-(6-(3-((3r,5r,7r)-Adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-2-butyl-6,6-difluoro-4-(naphthalen-1-yl)hexa-2,3-dien-1-one (5qt)

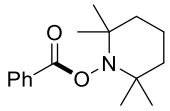
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 93.9 mg, 69%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (dd, J = 15.1, 1.6 Hz, 2H), 7.85 (dd, J = 8.5, 1.8 Hz, 3H), 7.79 (dd, J = 8.5, 1.6 Hz, 1H), 7.66 (dd, J = 8.5, 1.8 Hz, 1H), 7.61 (d, J = 2.3 Hz, 1H), 7.55 (dd, J = 8.3, 2.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.29 – 7.21 (m, 1H), 7.04 – 6.95 (m, 2H), 5.78 (tt, J = 56.1, 4.7 Hz, 1H), 3.92 (s, 3H), 3.11 – 2.84 (m, 2H), 2.61 (t, J = 7.8 Hz, 2H), 2.20 (d, J = 2.9 Hz, 6H), 2.15 – 2.10 (m, 3H), 1.82 (d, J = 3.0 Hz, 6H), 1.71 – 1.61 (m, 2H), 1.52 – 1.45 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.90, 194.82, 158.95, 141.10, 139.06, 135.60, 135.51, 133.96, 133.18, 132.64, 130.84, 130.70, 130.09, 129.63, 128.69, 128.47, 128.12, 126.43, 126.31, 126.29, 126.17, 125.95, 125.69, 125.41, 125.29, 124.83, 124.60, 115.28 (t, J = 238.8 Hz), 112.18, 108.19, 100.26, 90.62, 55.20, 40.67, 39.49 (t, J = 23.1 Hz), 37.26, 37.16, 30.48, 29.69, 29.16, 28.44, 22.63, 13.98.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.15 – -115.52 (m).

HRMS (ESI) (m/z): calcd for $C_{47}H_{46}F_2NaO_2$ ([M + Na] $^+$), 703.3358; found, 703.3362.



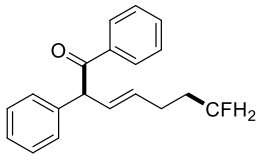
2,2,6,6-tetramethylpiperidin-1-yl benzoate (6a)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) affords the title compound as a red solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 7.0 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 1.83 – 1.74 (m, 2H), 1.75 – 1.66 (m, 1H), 1.61 – 1.57 (m, 2H), 1.50 – 1.43 (m, 1H), 1.28 (s, 6H), 1.12 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.42, 132.88, 129.79, 129.60, 128.49, 60.44, 39.11, 32.01, 20.89, 17.05.

HRMS (ESI) (m/z): Calcd for $C_{16}H_{23}NNaO_2$ ([M + Na] $^+$), 284.1621, found 284.1614.



(E)-1,2-diphenyl-7l1-hept-3-en-1-one compound with l2-fluorane (6b)

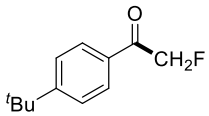
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) affords the title compound as a yellow oil (yield 11.3 mg, 20%, E/Z = 4 : 1).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.97 – 7.88 (m, 2H), 7.51 – 7.46 (m, 1H), 7.38 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 4.5 Hz, 4H), 7.20 (q, J = 4.4 Hz, 1H), 5.80 – 5.35 (m, 2H), 4.57 (t, J = 6.8 Hz, 1H), 4.38 – 4.26 (m, 2H), 2.90 (dq, J = 14.5, 7.8, 7.1 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.38 – 2.25 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-d) δ 199.33, 139.08, 136.78, 132.87, 130.80, 128.90, 128.70 (d, J = 4.0 Hz), 128.51, 128.24, 127.09, 126.86 (d, J = 7.2 Hz), 83.82 (d, J = 173.2 Hz), 53.97, 37.05, 34.45 – 29.55 (m).

^{19}F NMR (565 MHz, Chloroform-d) δ -217.03 – -217.45 (m).

HRMS (ESI) (m/z): calcd for $C_{19}H_{20}FO$ ([M + H] $^{+}$), 282.1420; found, 282.1426.



1-(4-(tert-butyl)phenyl)-2-fluoroethan-1-one (6c)

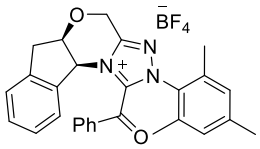
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 130:1, v/v) affords the title compound as a colorless oil (yield 7.2 mg, 26%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 5.51 (d, *J* = 47.0 Hz, 1H), 1.34 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.09, 131.14, 127.83 (d, *J* = 2.7 Hz), 125.90, 83.54 (d, *J* = 182.4 Hz), 35.29, 31.02.

^{19}F NMR (565 MHz, $CDCl_3$) δ 29.61 (t, *J* = 47.1 Hz).

HRMS (ESI) (m/z): calcd for $C_{12}H_{15}FNaO$ ([M + Na] $^{+}$), 217.0999; found, 217.0993.



(5aR,10bS)-1-benzoyl-2-mesityl-2,5a,6,10b-tetrahydro-4H-indeno[2,1-b][1,2,4]triazolo[4,3-d][1,4]oxazin-11-ium tetrafluoroborate (7b)

The white precipitate was filtered off and washed with diethyl ether. Drying under vacuum afforded the corresponding product as a white solid.

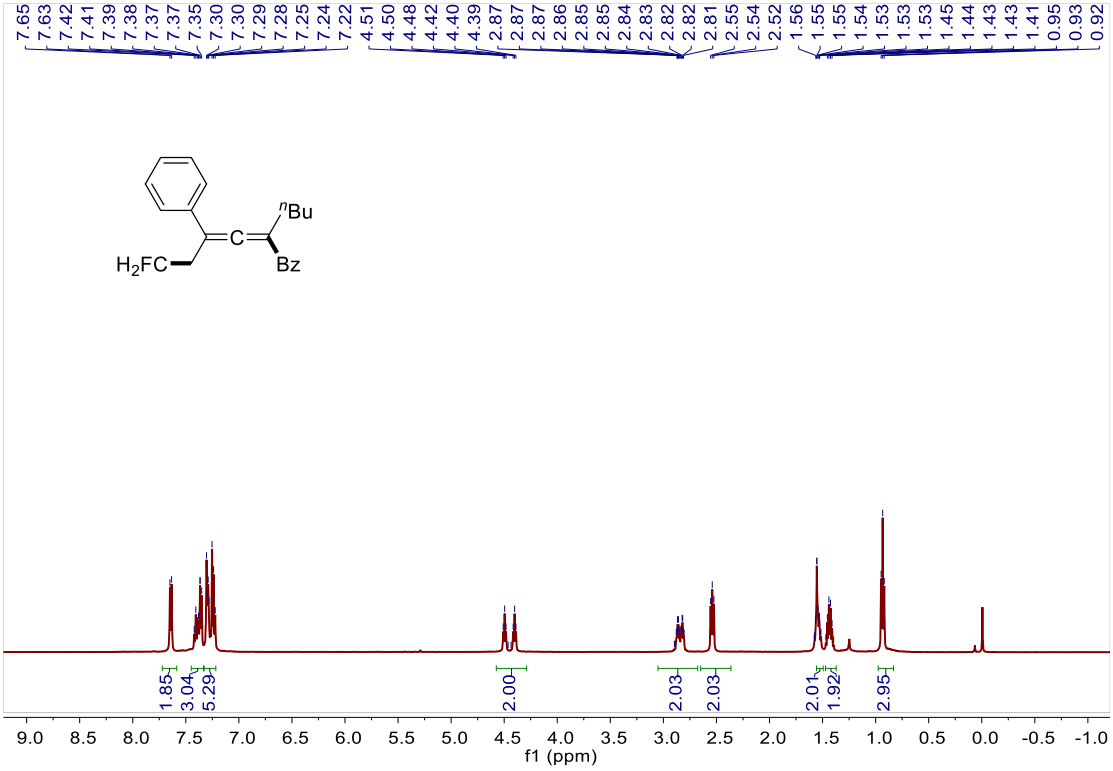
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.24 (d, *J* = 7.8 Hz, 2H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 4.4 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.01 (s, 1H), 6.93 (s, 1H), 5.72 (d, *J* = 3.3 Hz, 1H), 5.51 (d, *J* = 16.3 Hz, 1H), 5.49 – 5.46 (m, 1H), 5.12 (d, *J* = 16.3 Hz, 1H), 3.30 (dd, *J* = 17.1, 4.0 Hz, 1H), 3.20 (d, *J* = 17.1 Hz, 1H), 2.32 (s, 3H), 2.17 (d, *J* = 13.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) *δ* 179.11, 150.88, 147.75, 142.66, 140.83, 138.21, 135.66, 135.31, 132.10, 131.04, 130.72, 130.25, 130.13, 129.86, 129.40, 127.82, 126.34, 123.02, 63.80, 60.82, 37.25, 21.20, 17.58, 17.47. **^{19}F NMR** (565 MHz, $CDCl_3$) *δ* -151.49.

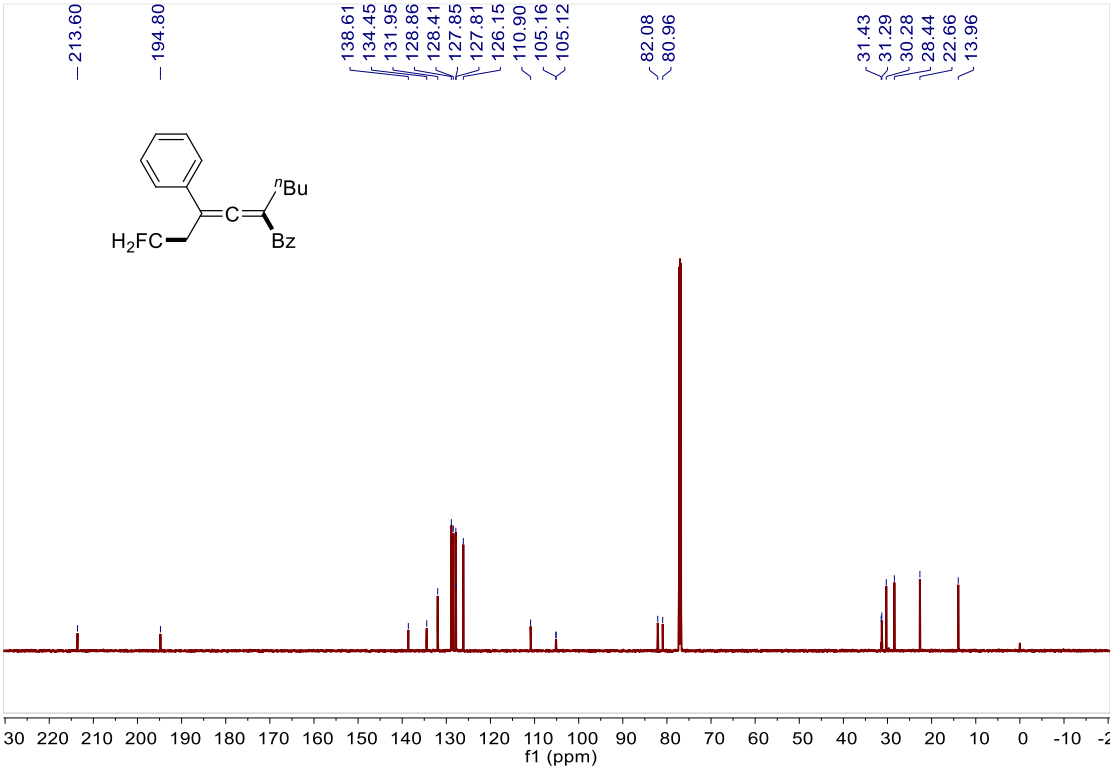
HRMS (ESI) (m/z): calcd for $C_{28}H_{26}N_3O_2^{+}$, 437.2098; found, 437.2090.

X. NMR Spectra of New Compounds.

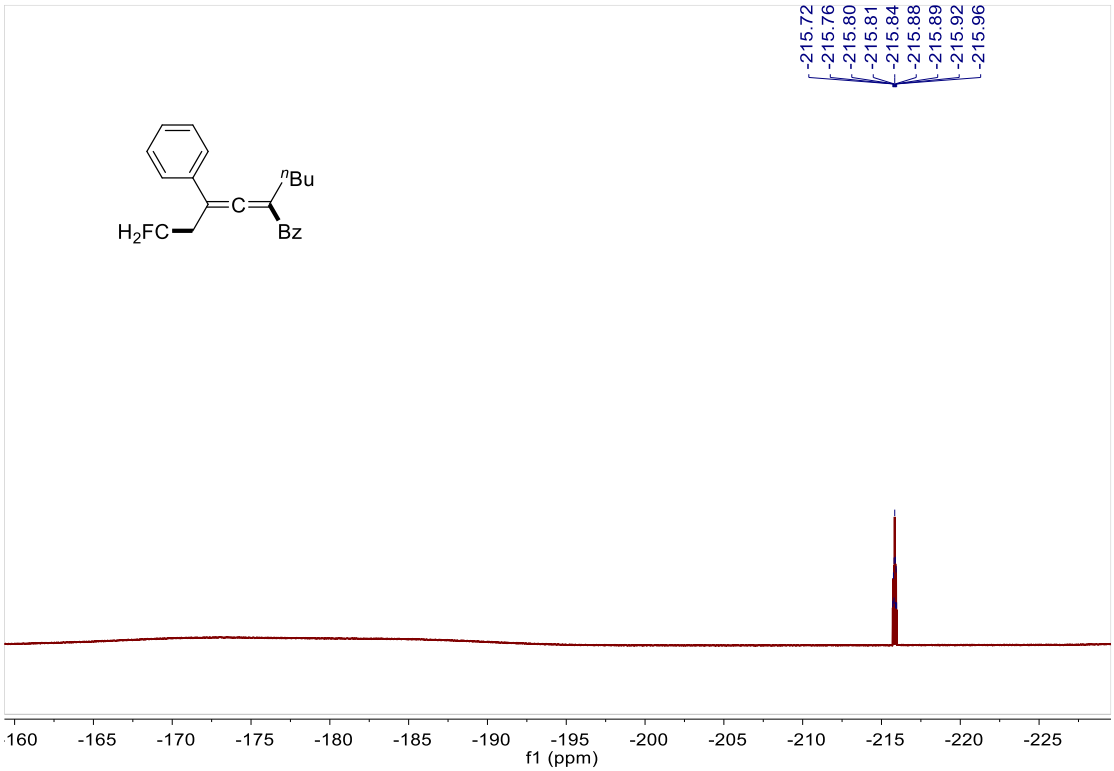
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4aa**.



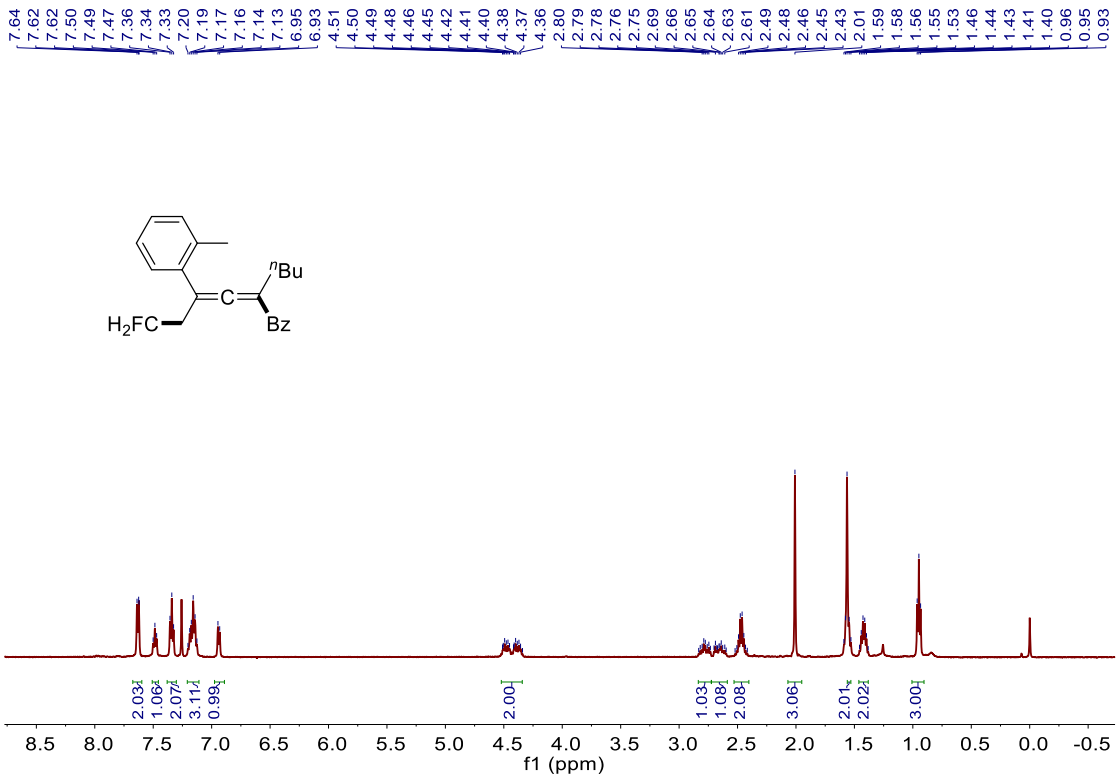
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4aa**.



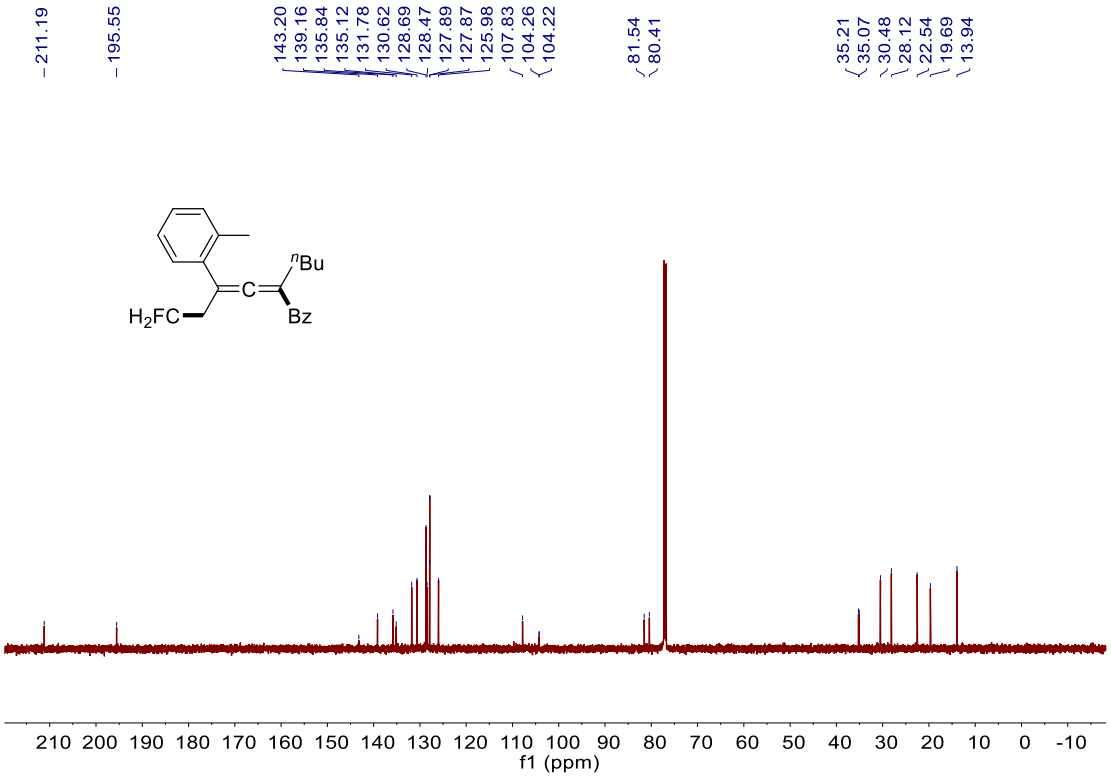
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4aa**.



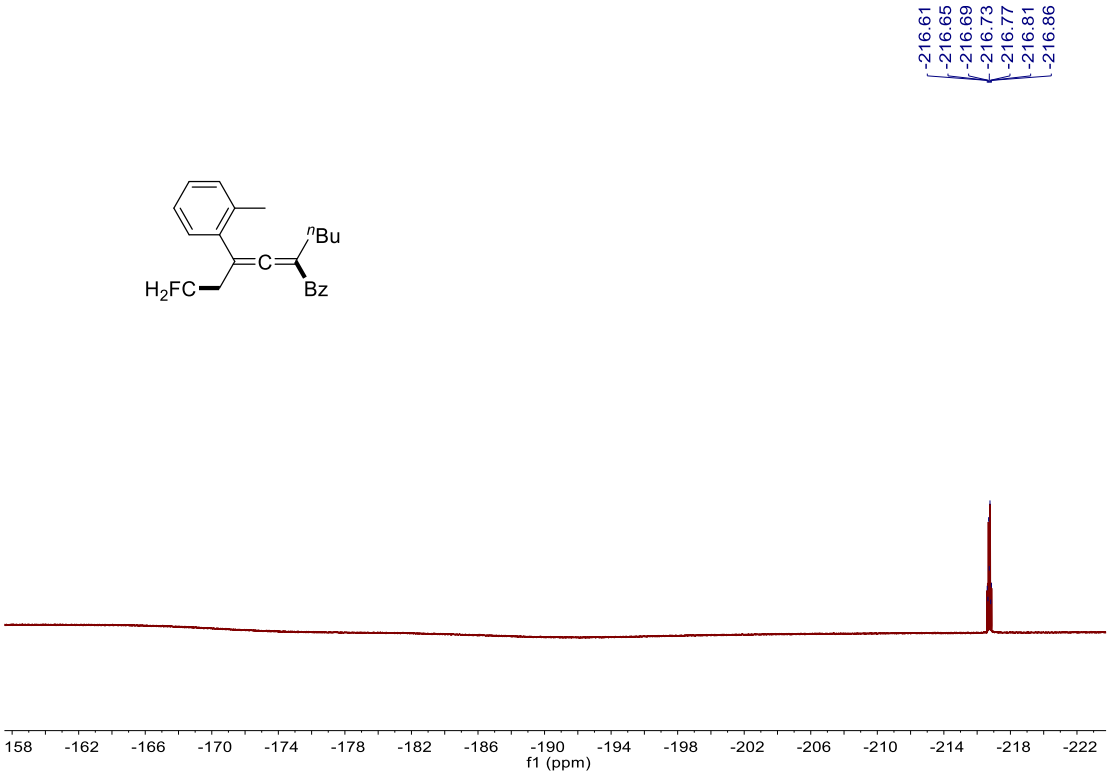
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ba**.



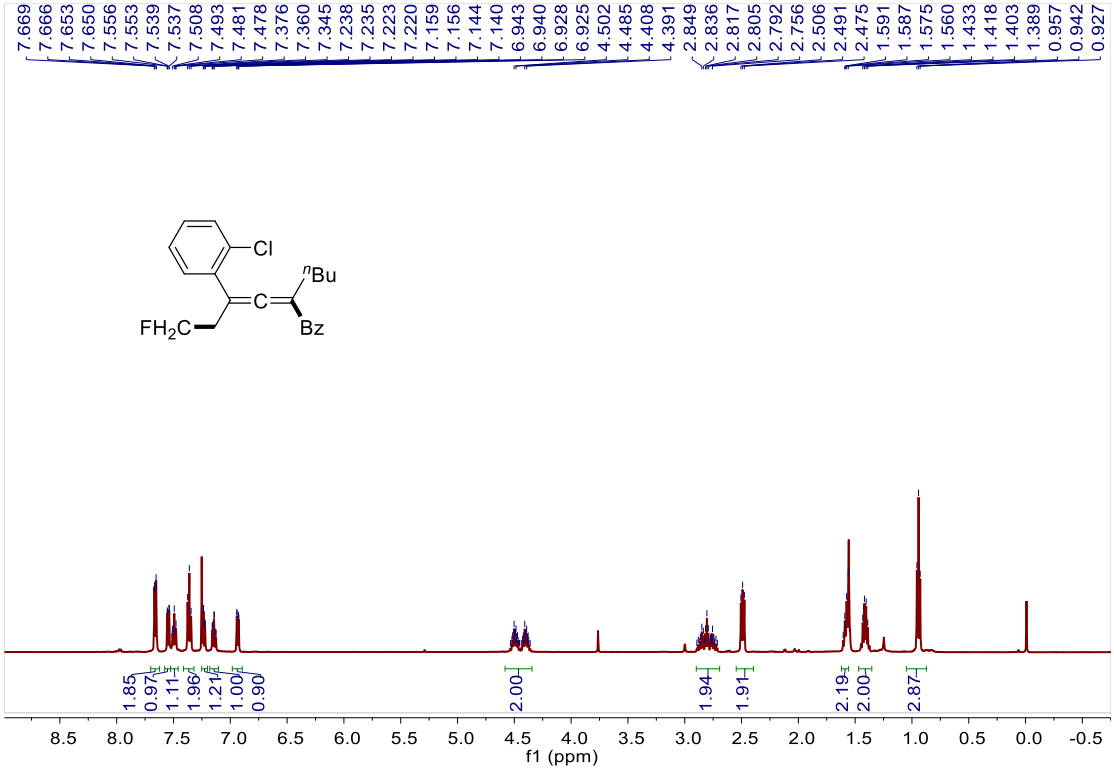
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ba**.



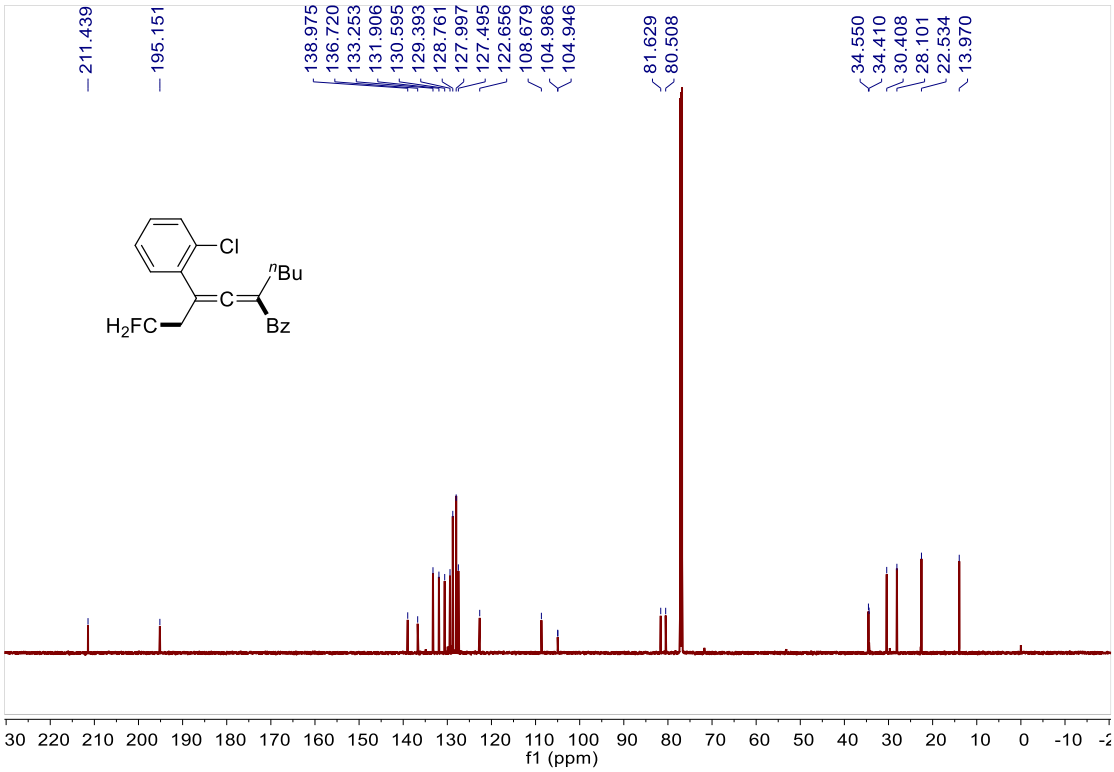
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ba**.



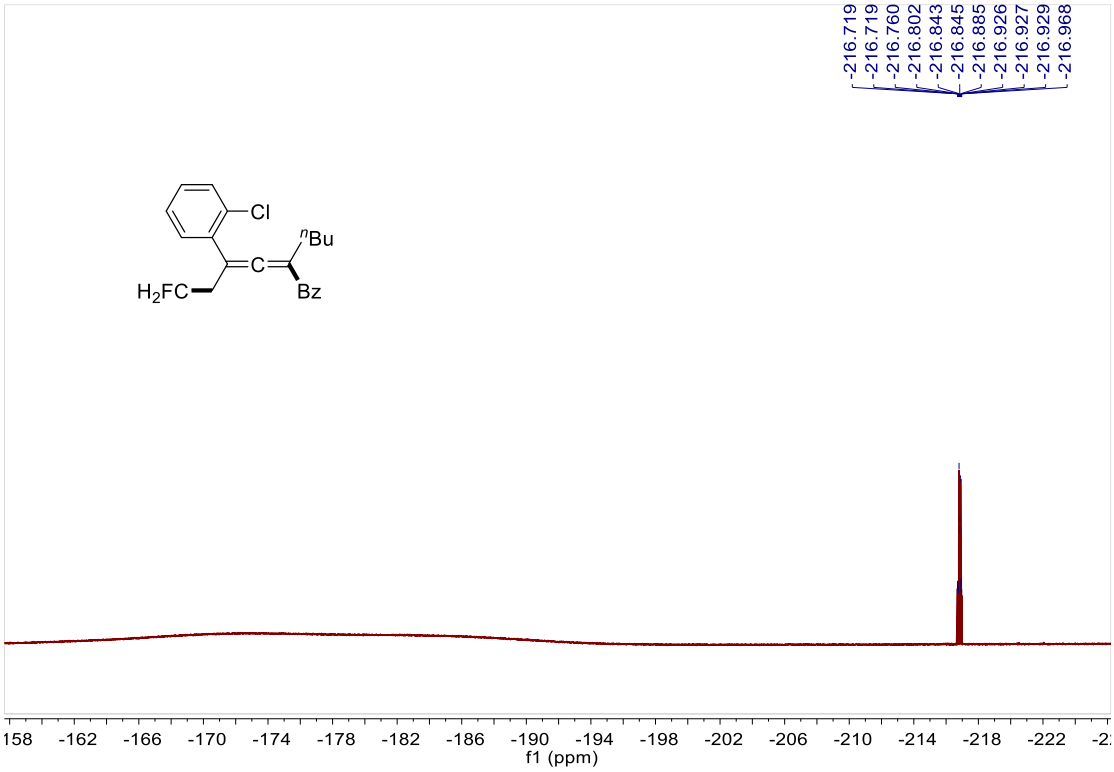
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ca**.



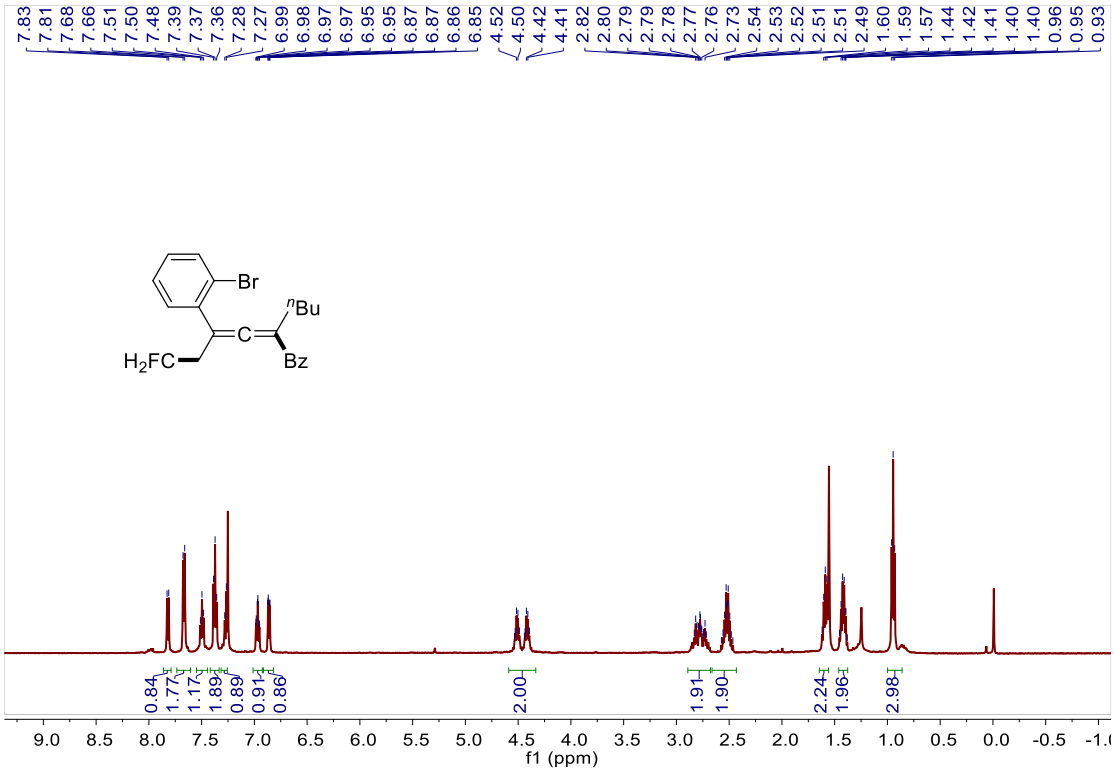
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ca**.



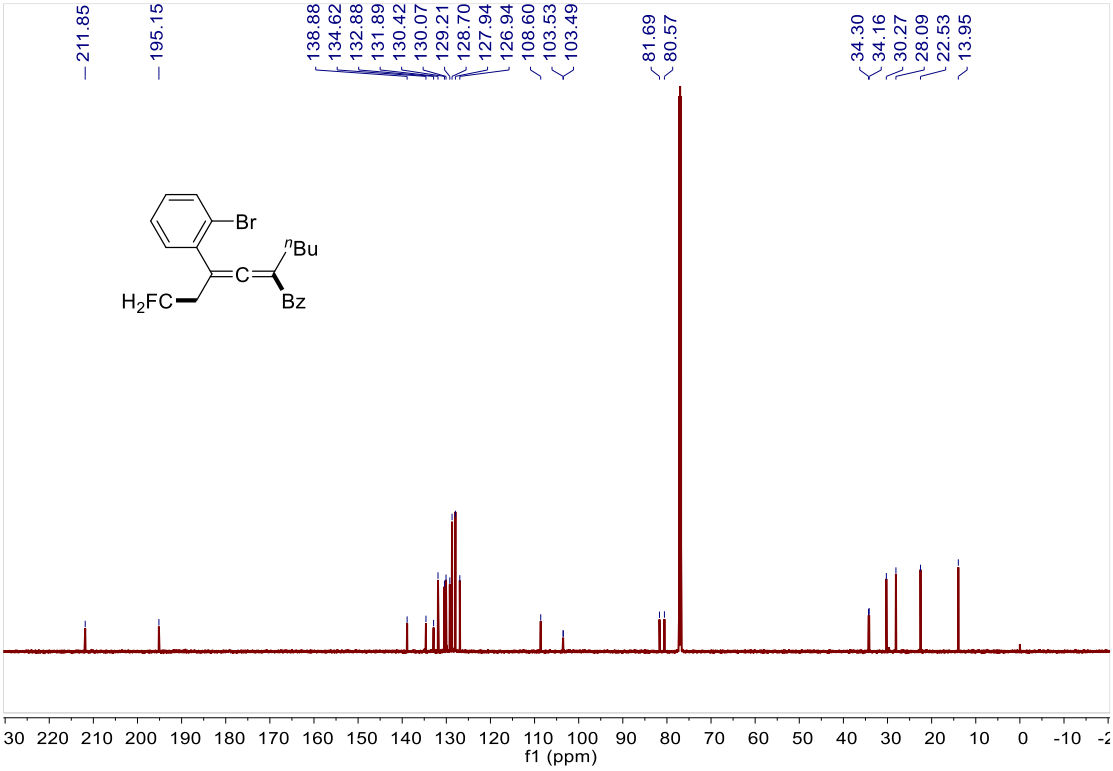
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ca**.



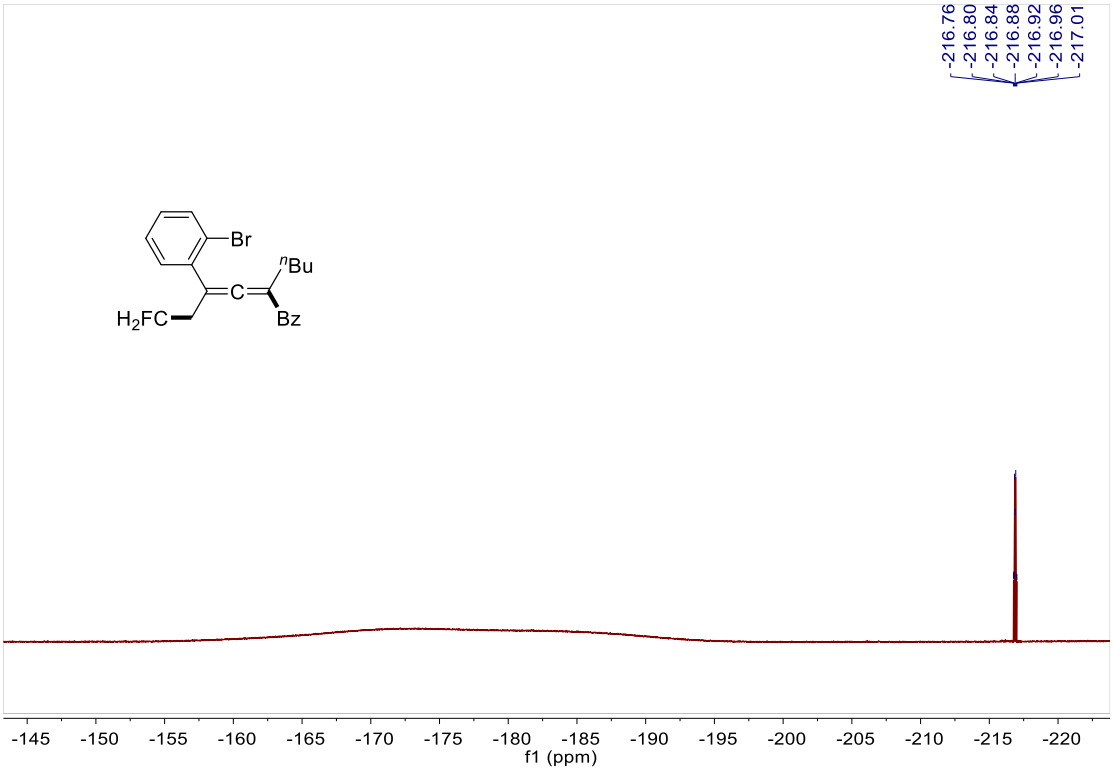
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4da**.



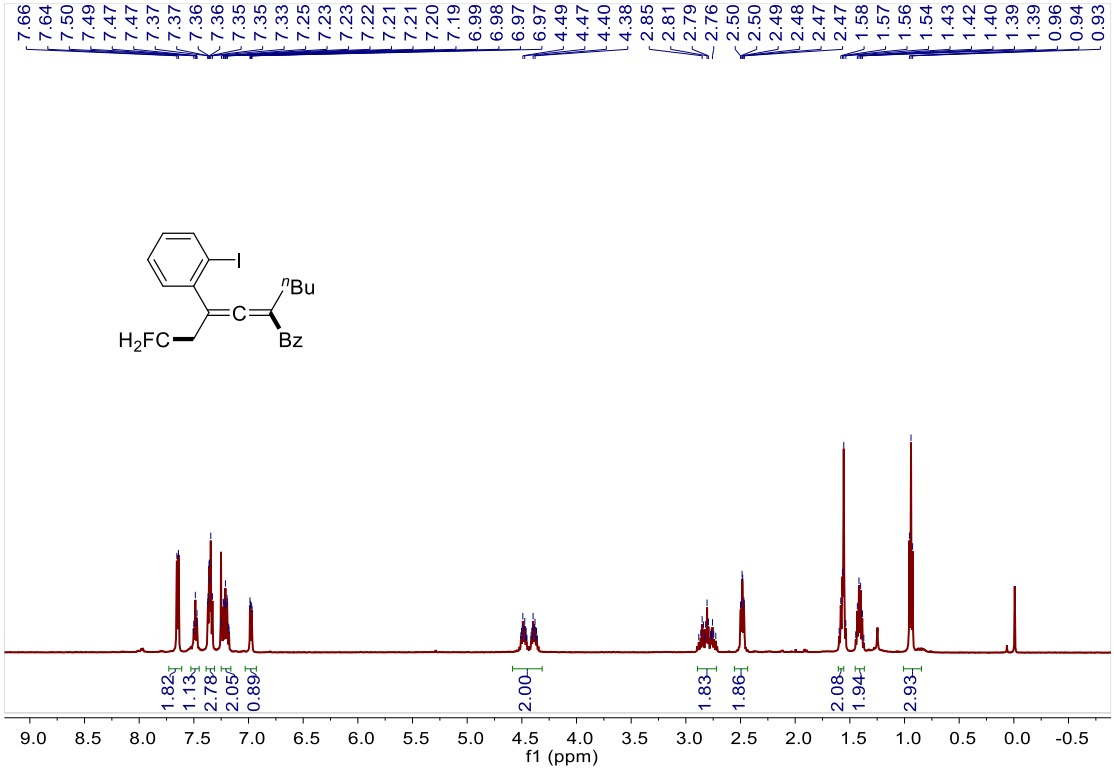
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4da**.



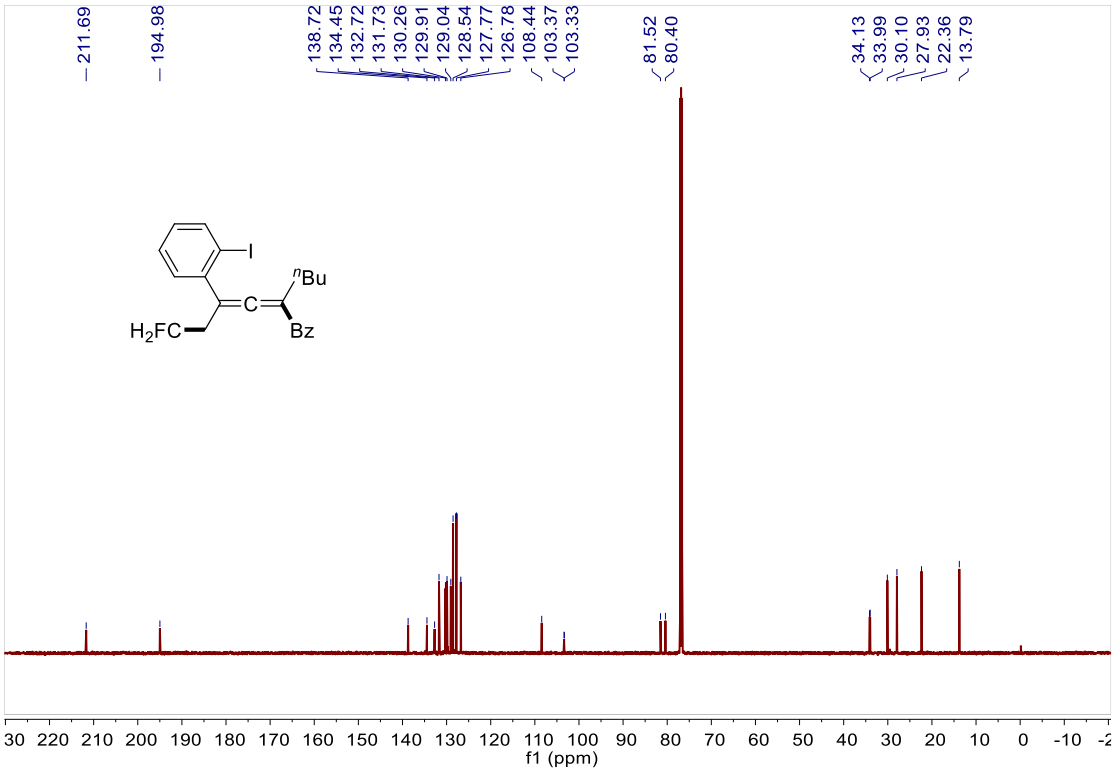
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4da**.



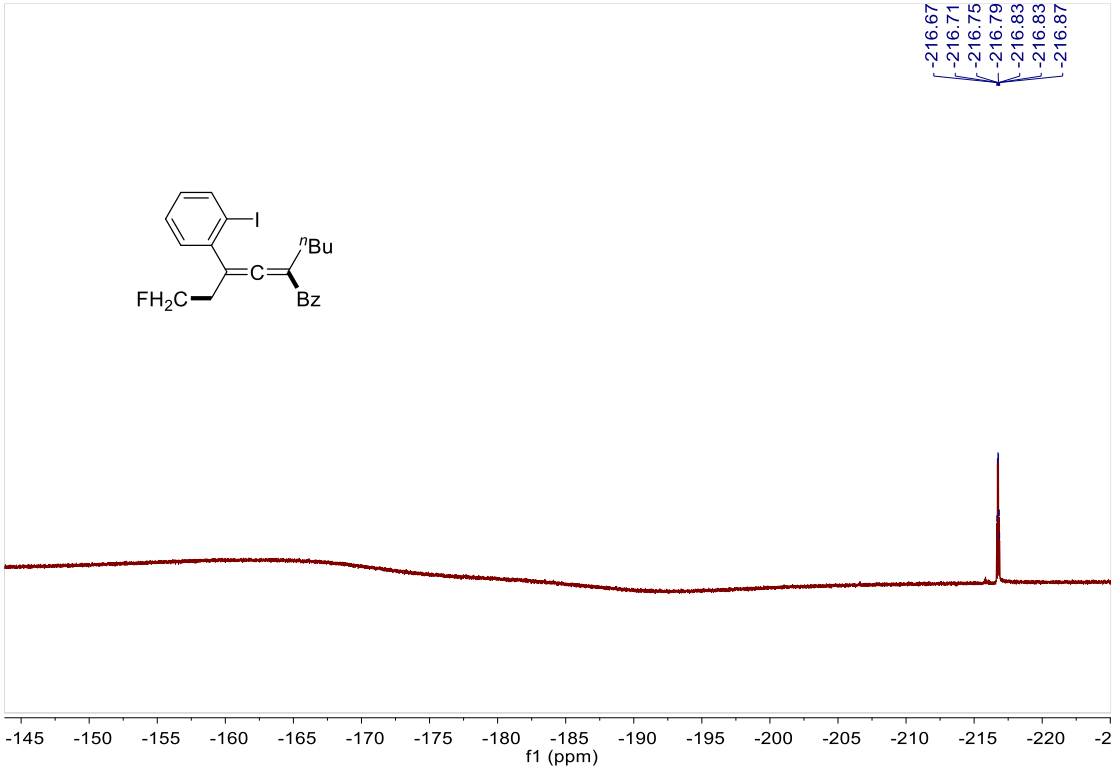
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ea**.



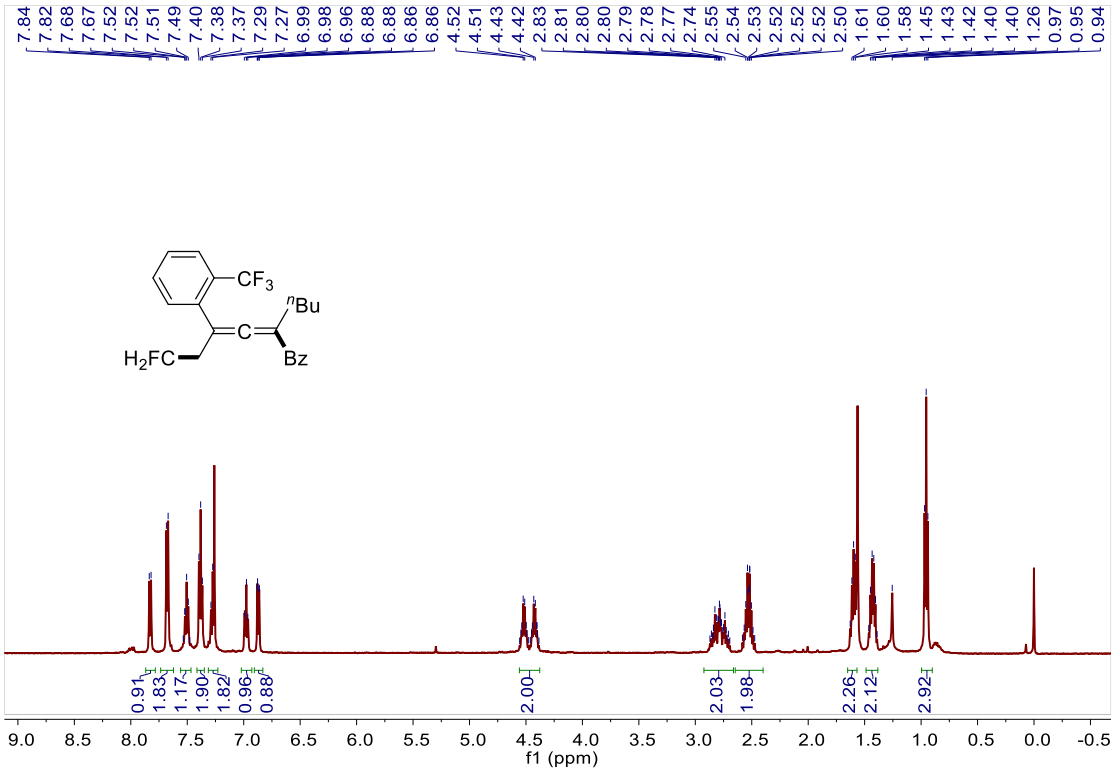
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ea**.



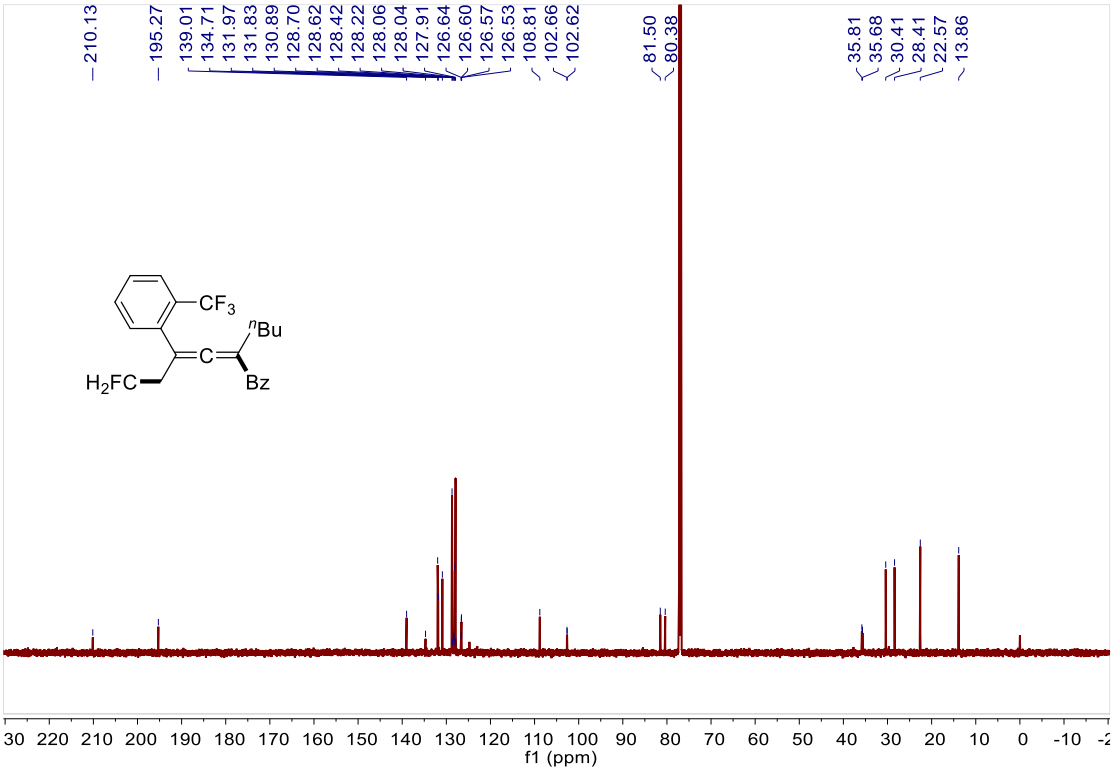
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ea**.



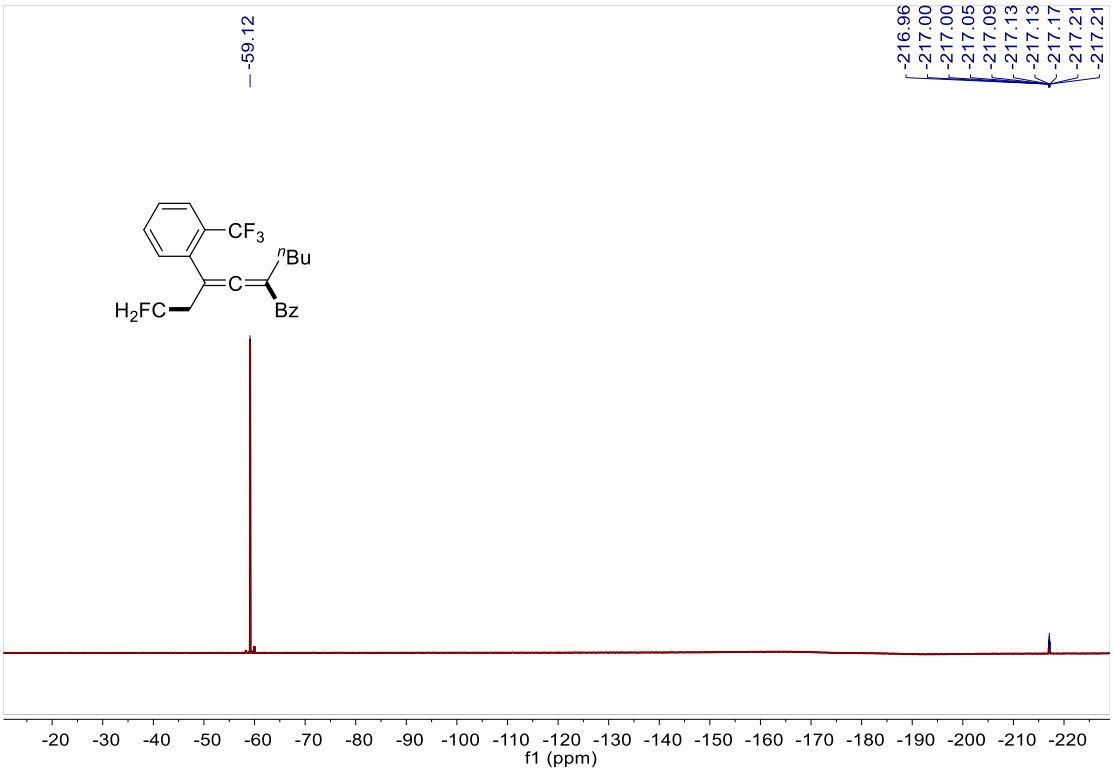
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4fa**.



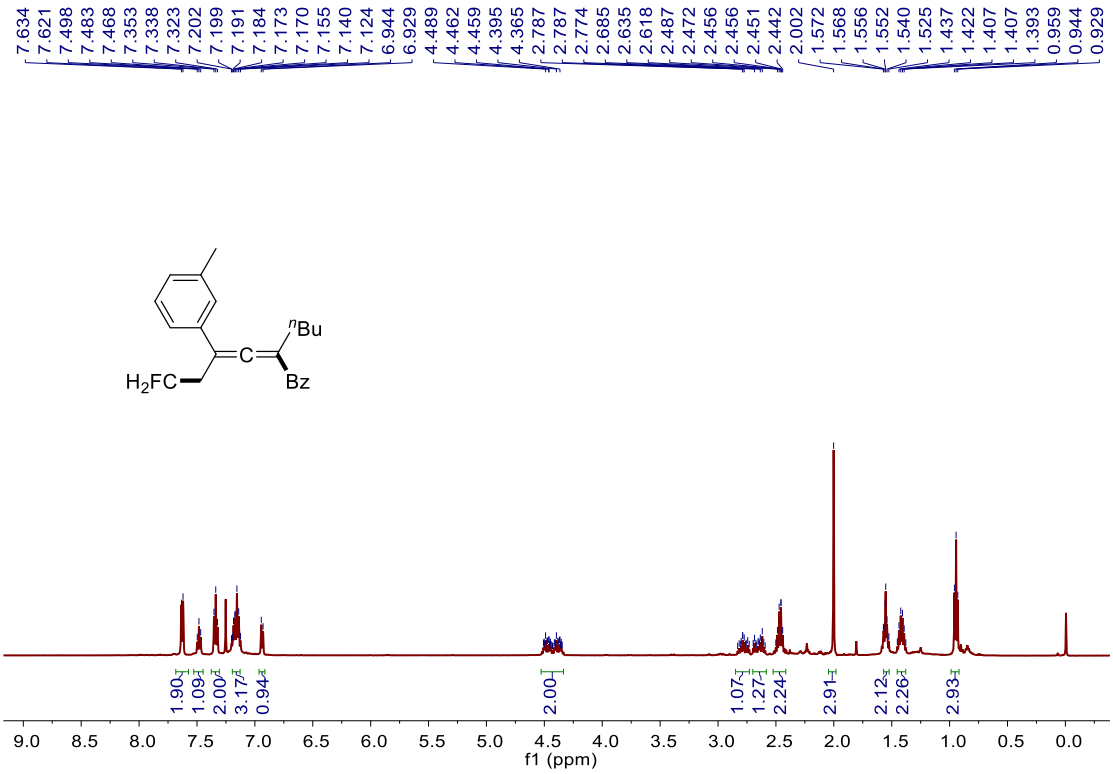
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4fa**.



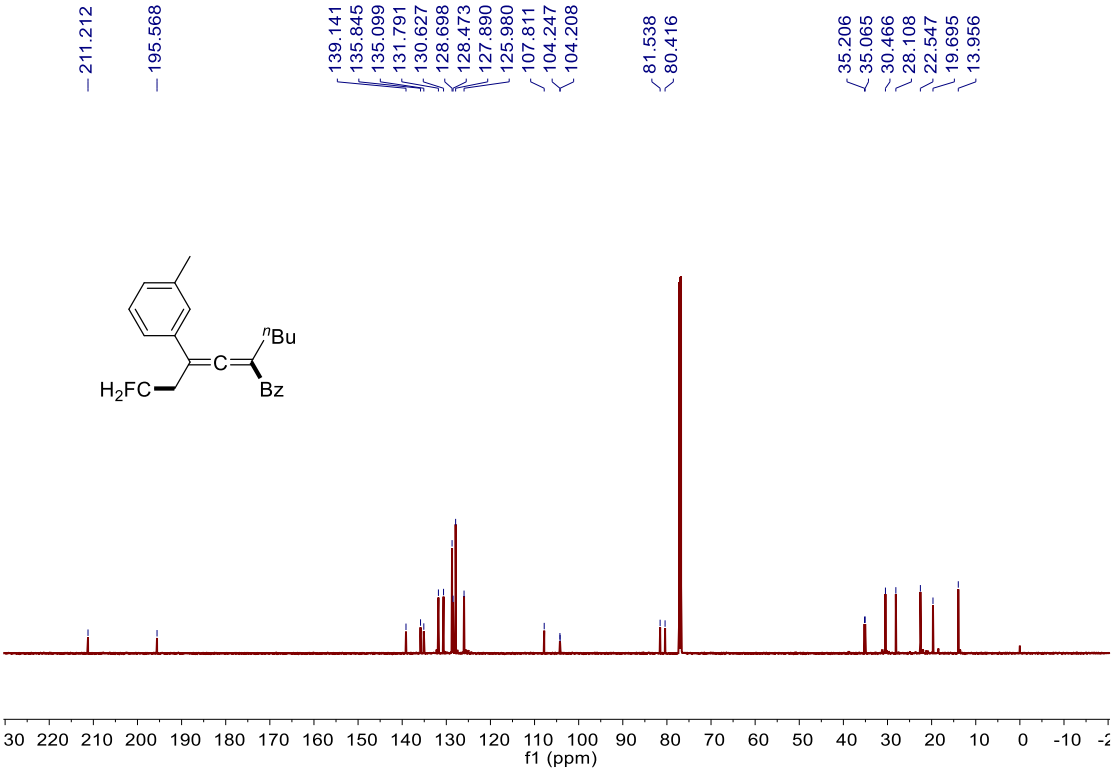
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4fa**.



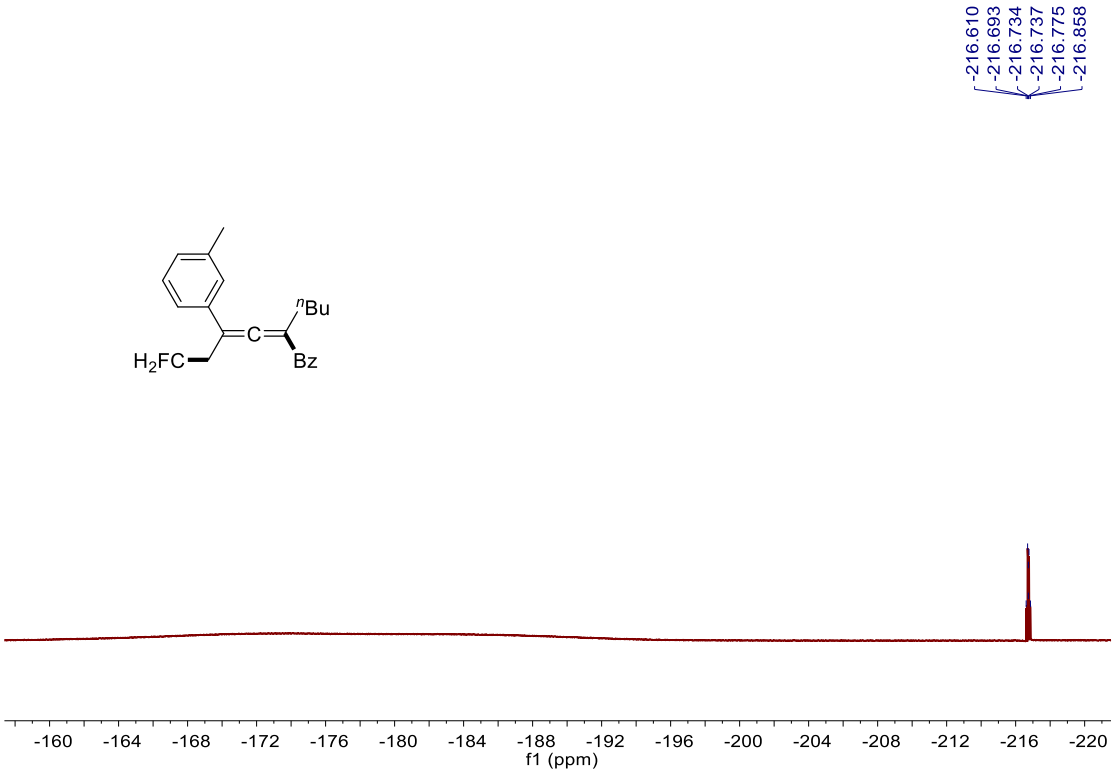
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ga**.



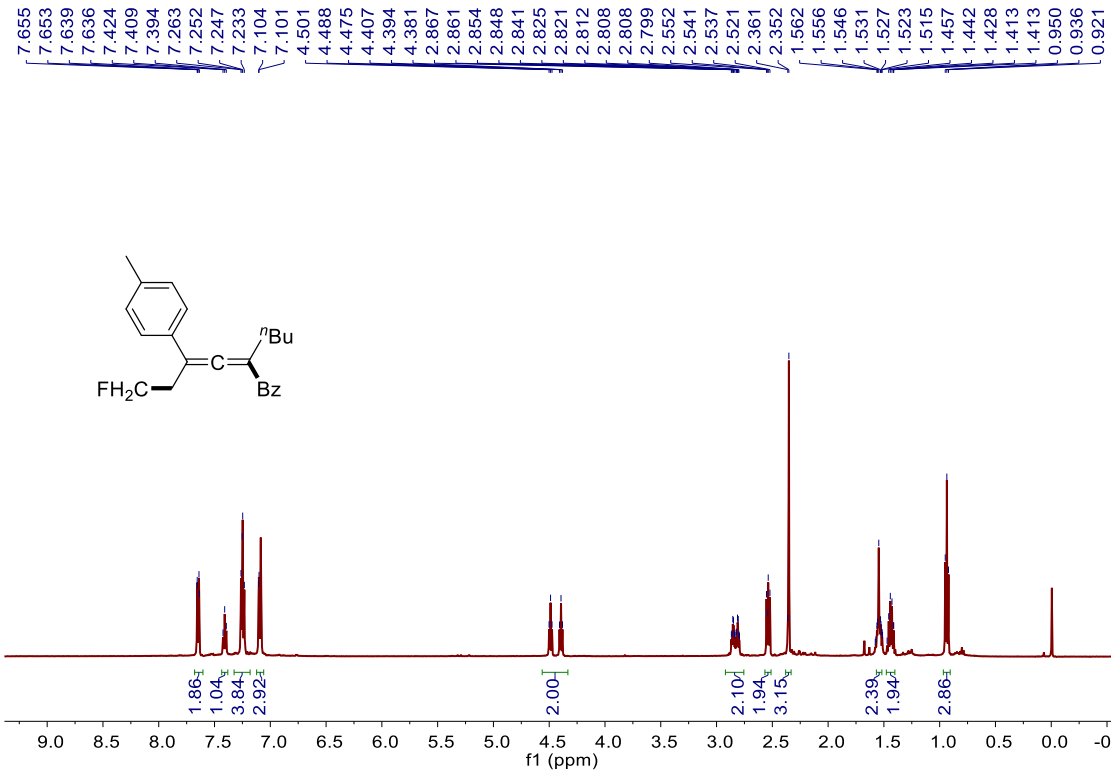
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ga**.



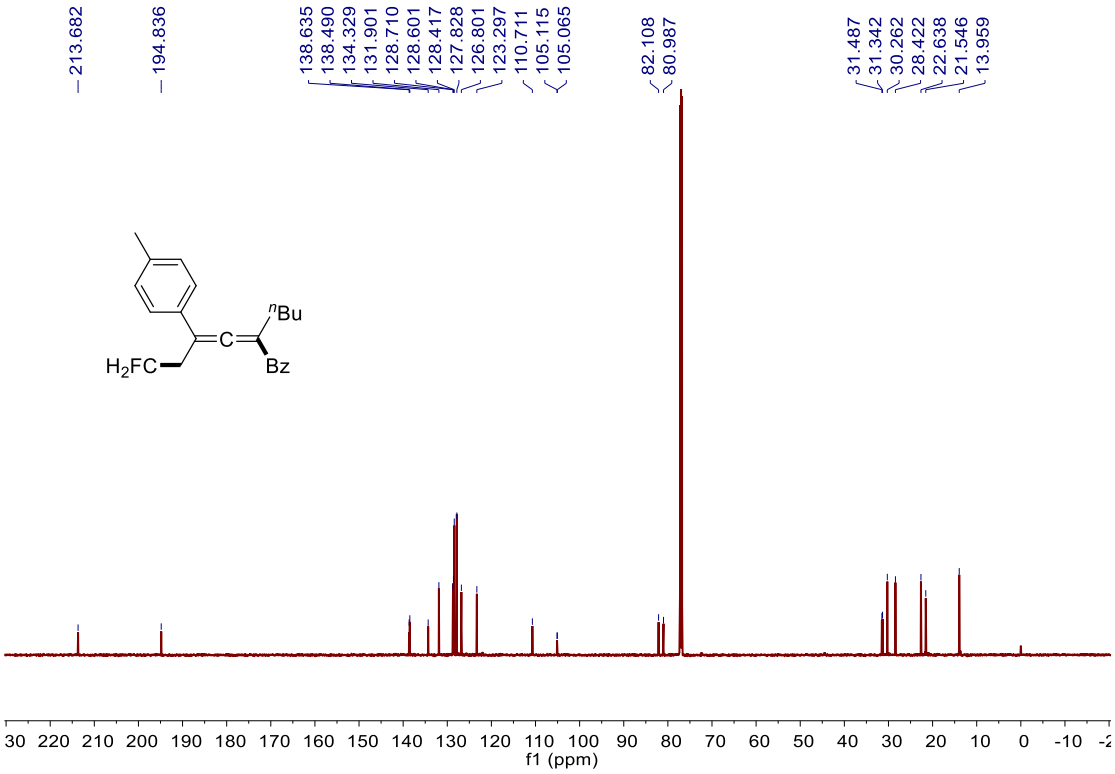
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ga**.



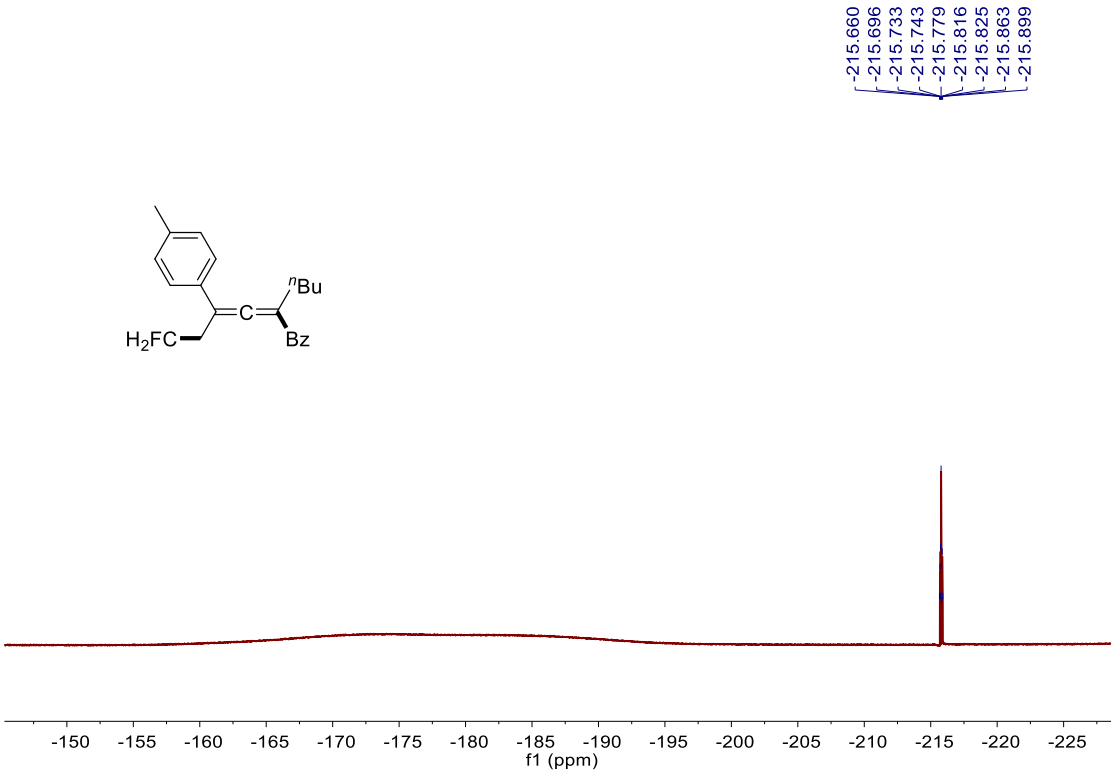
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ia**.



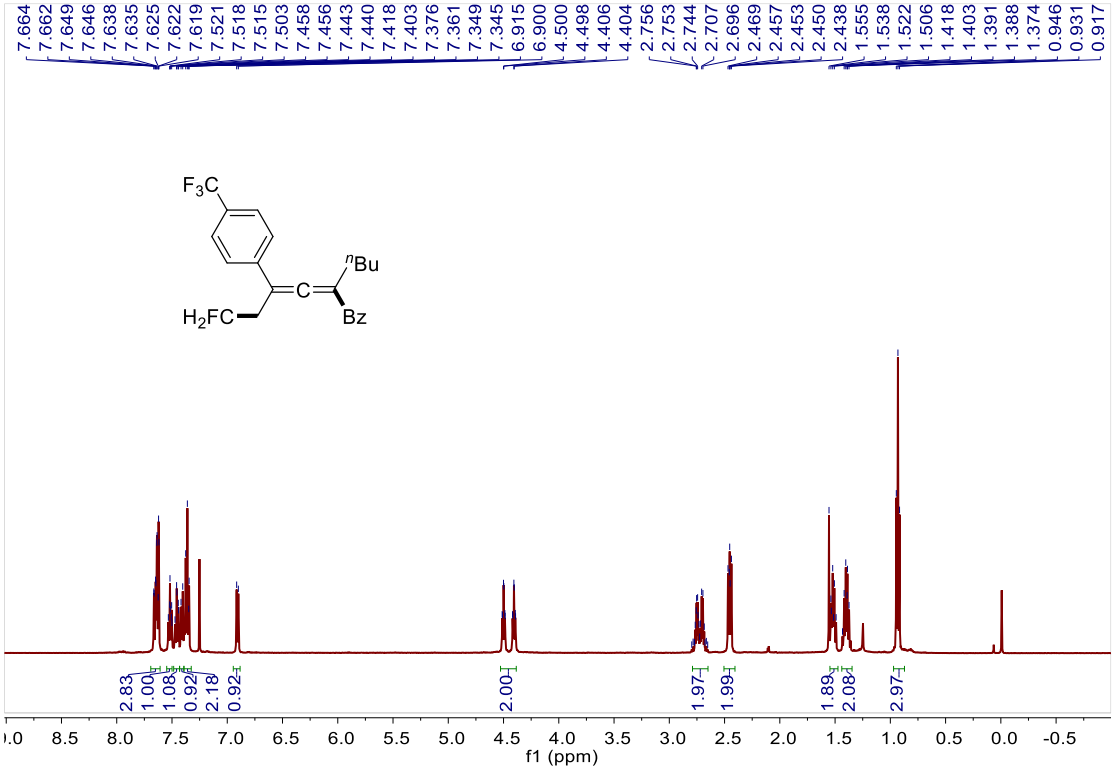
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ia**.



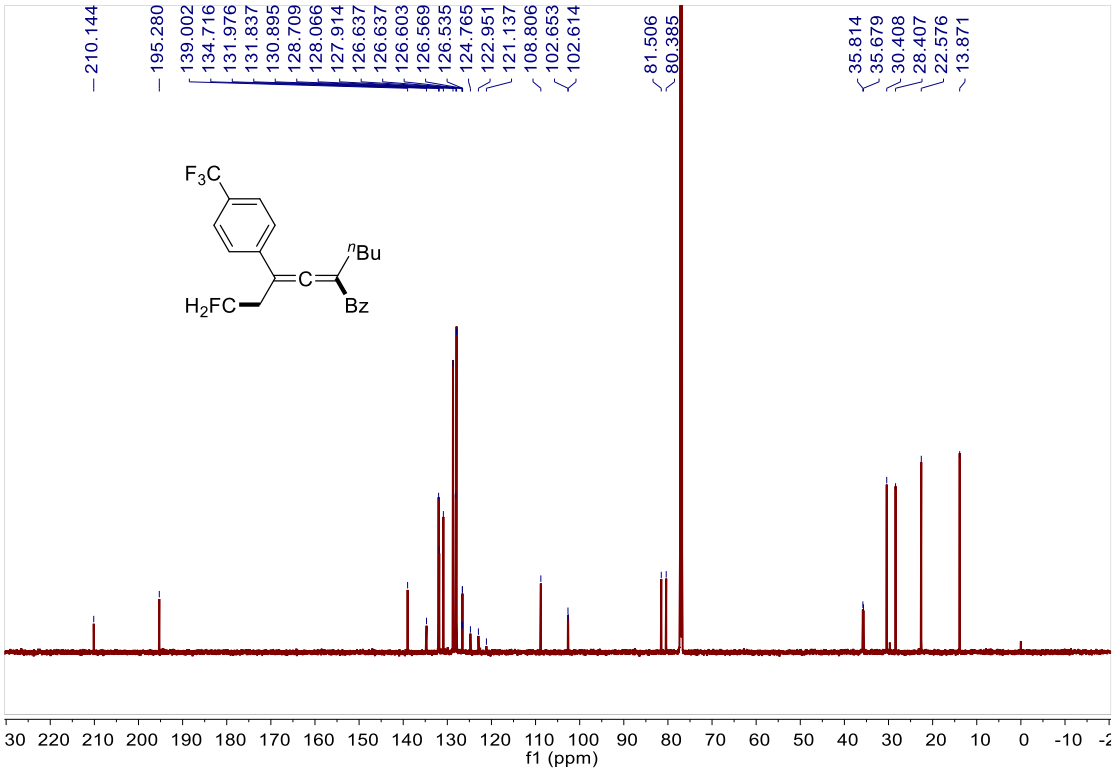
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ia**.



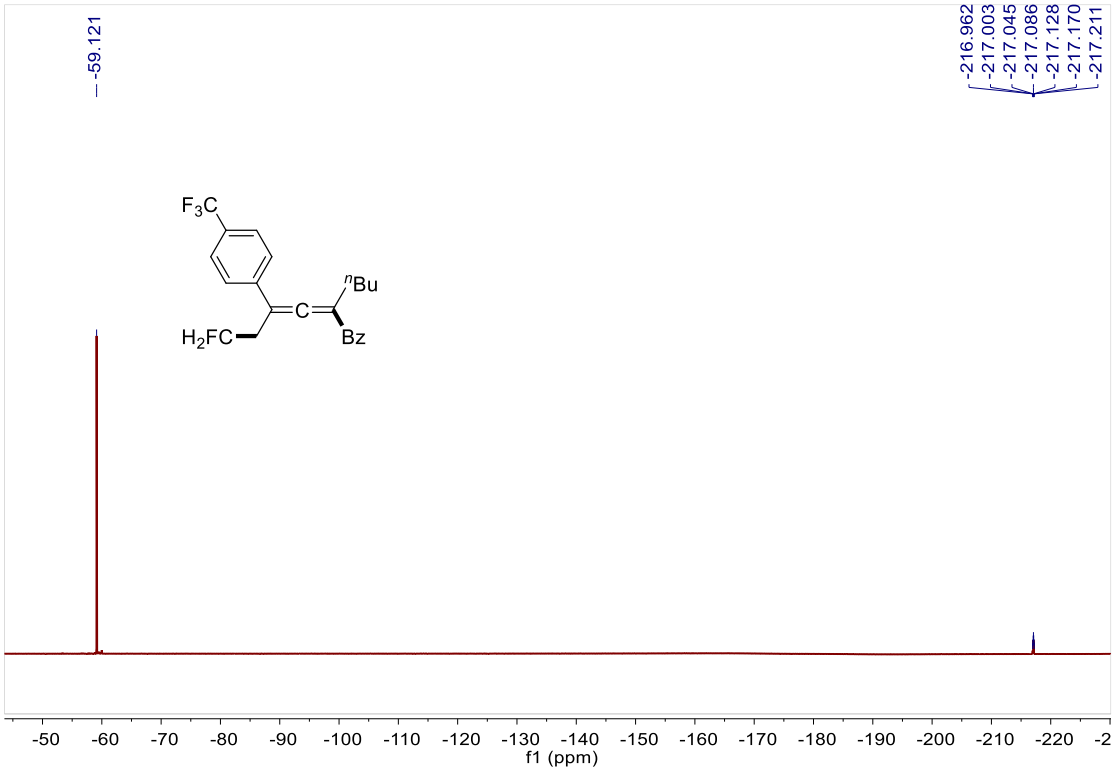
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ma**.



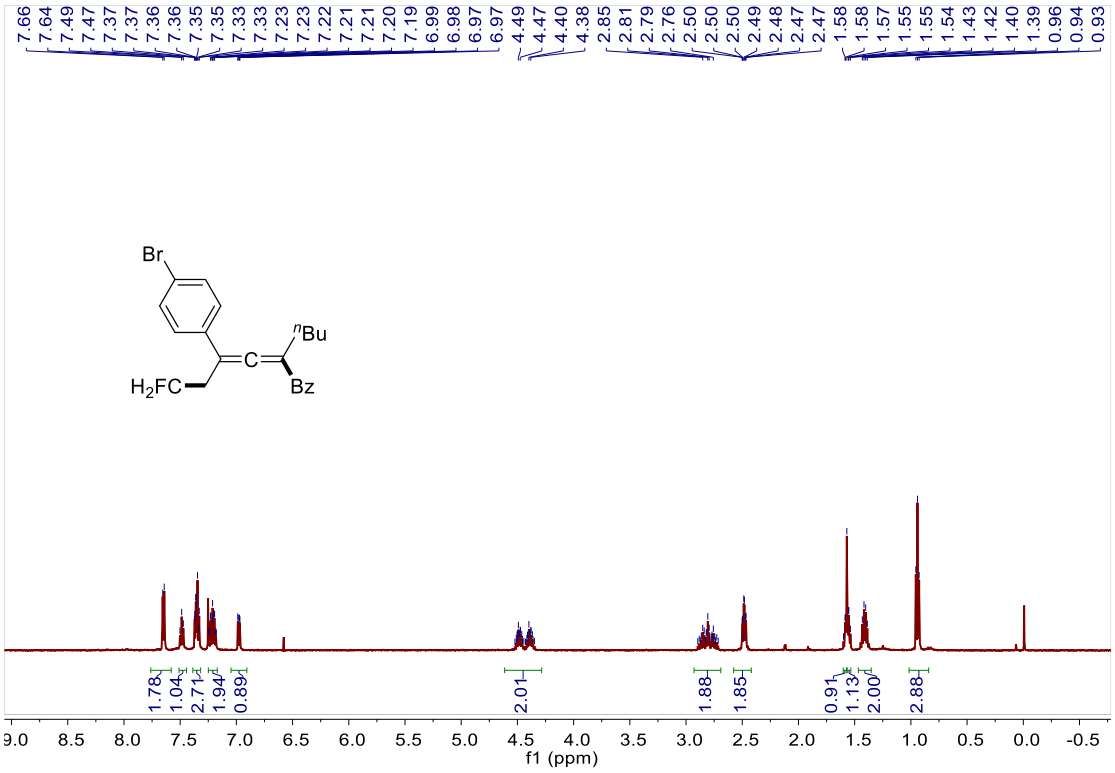
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ma**.



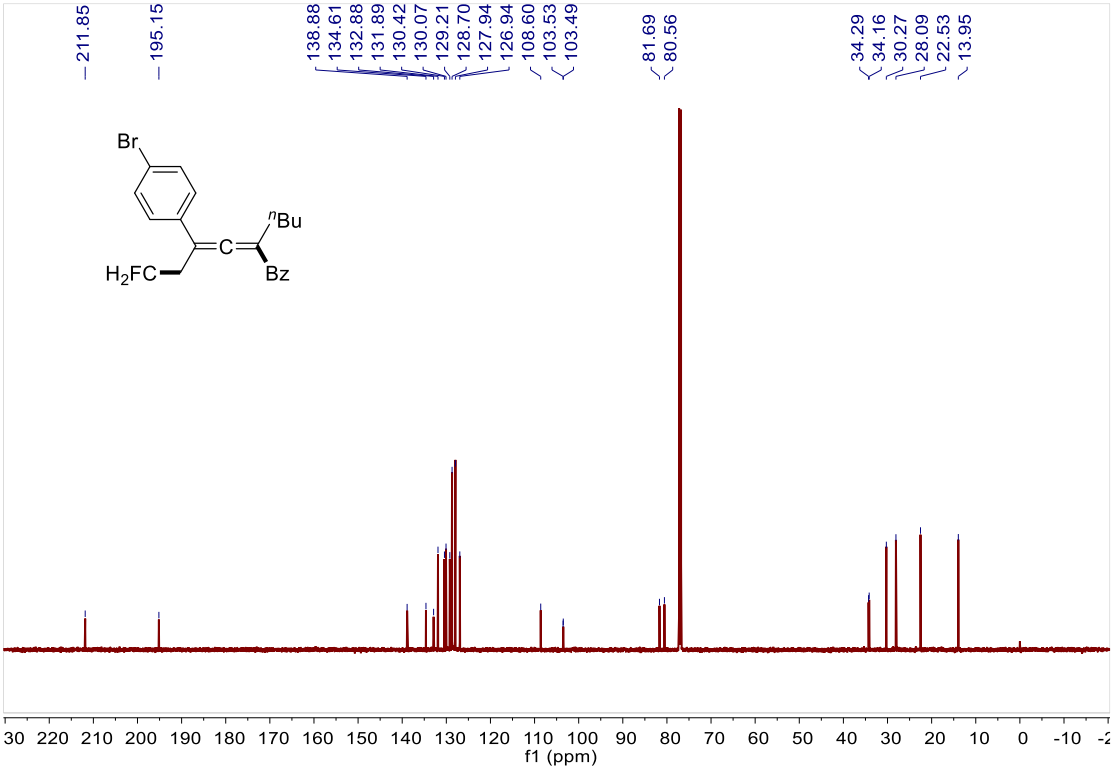
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ma**.



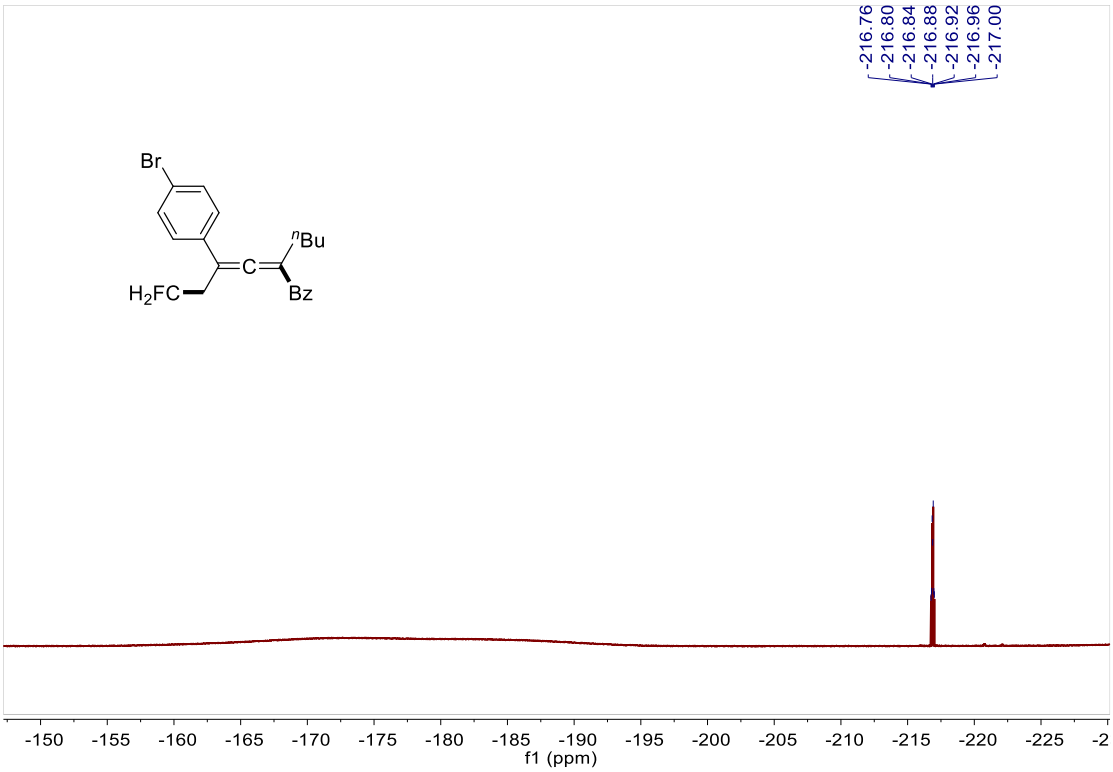
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4pa**.



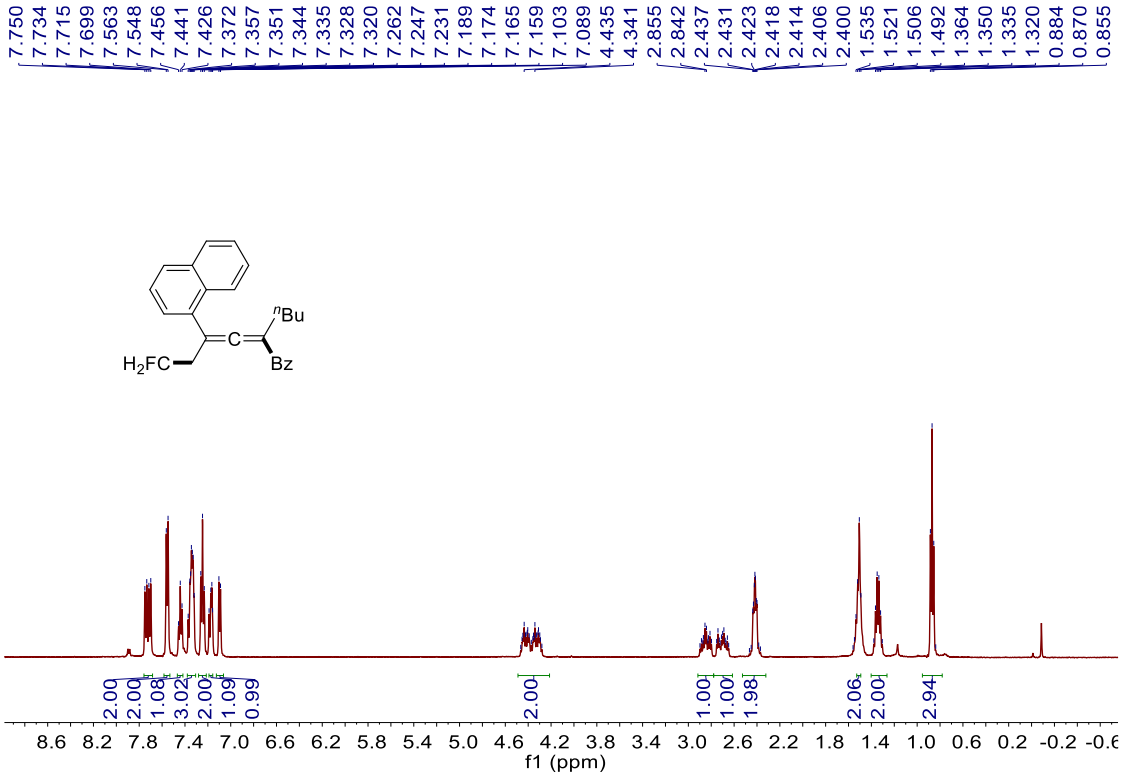
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4pa**.



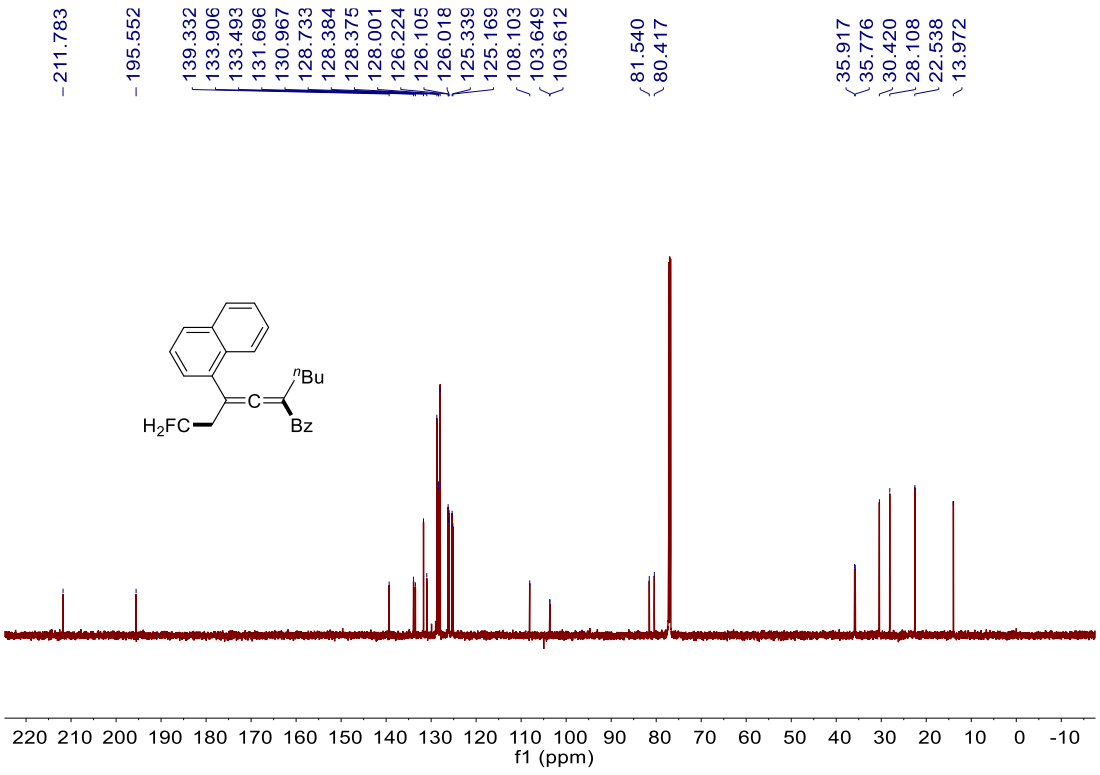
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4pa**.



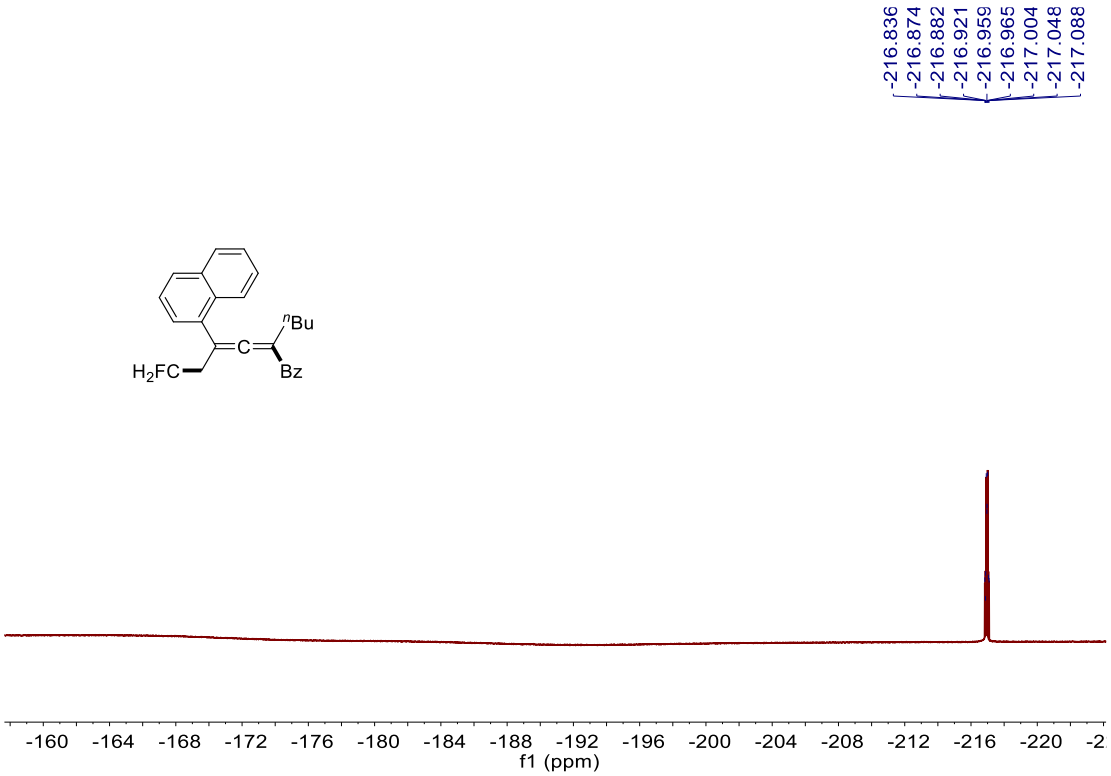
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4qa**.



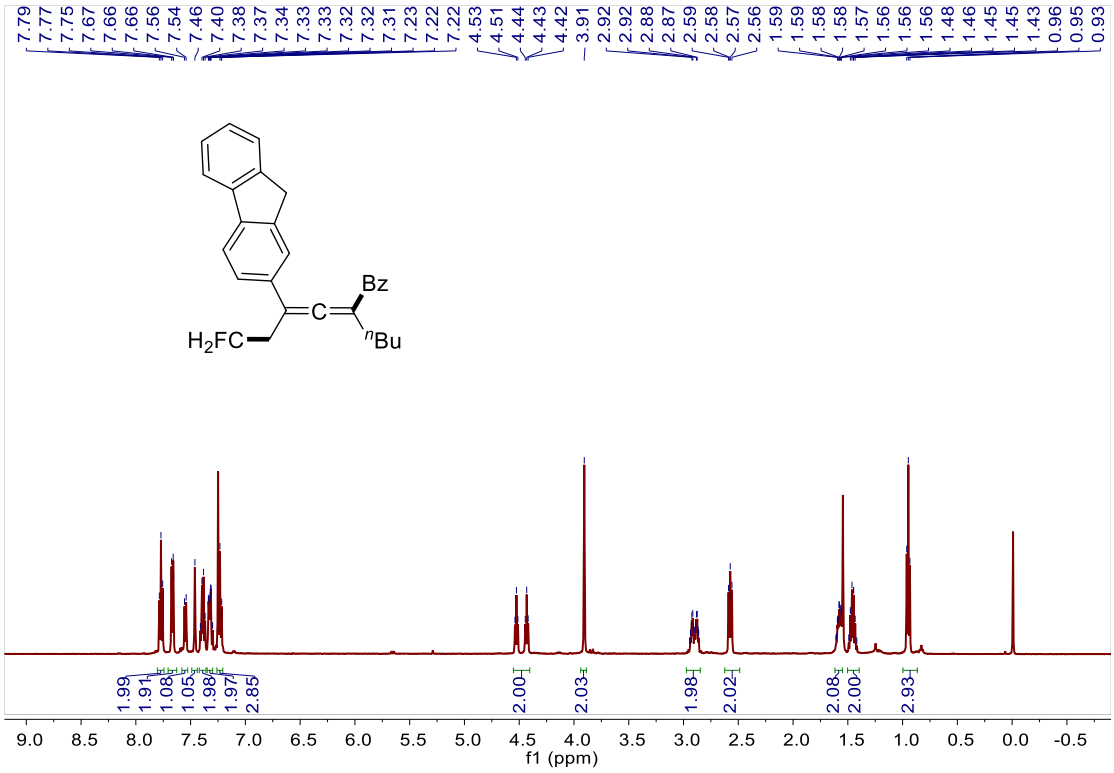
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4qa**.



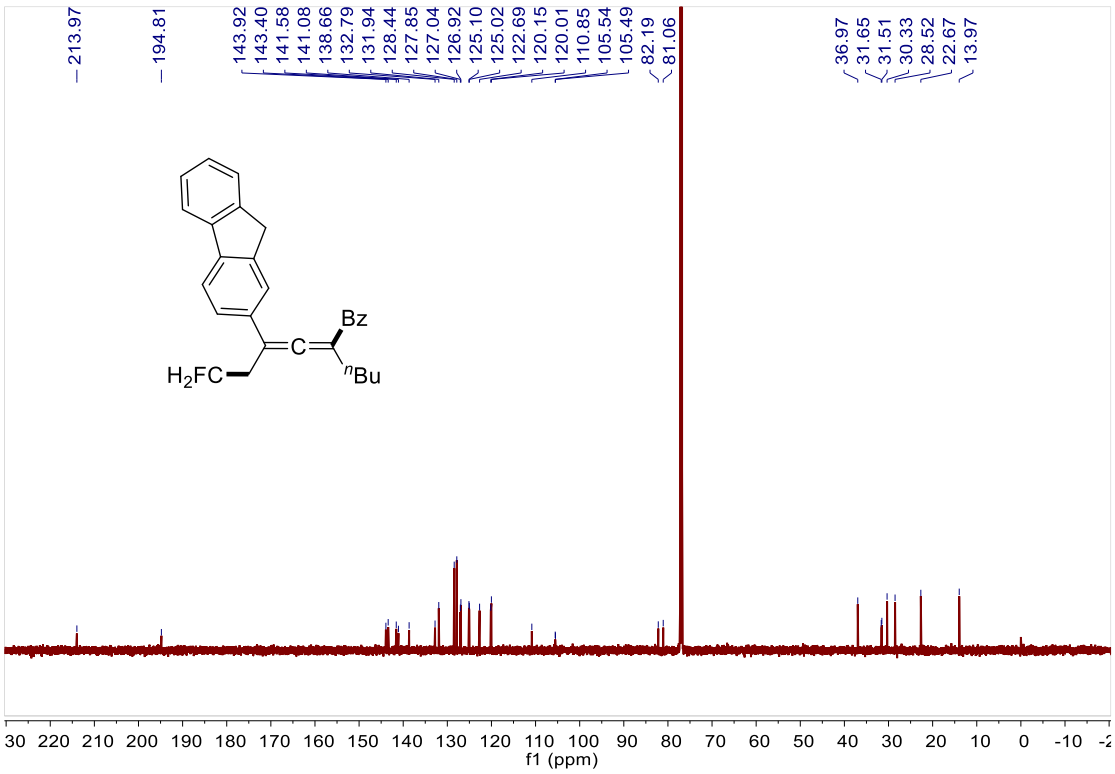
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4qa**.



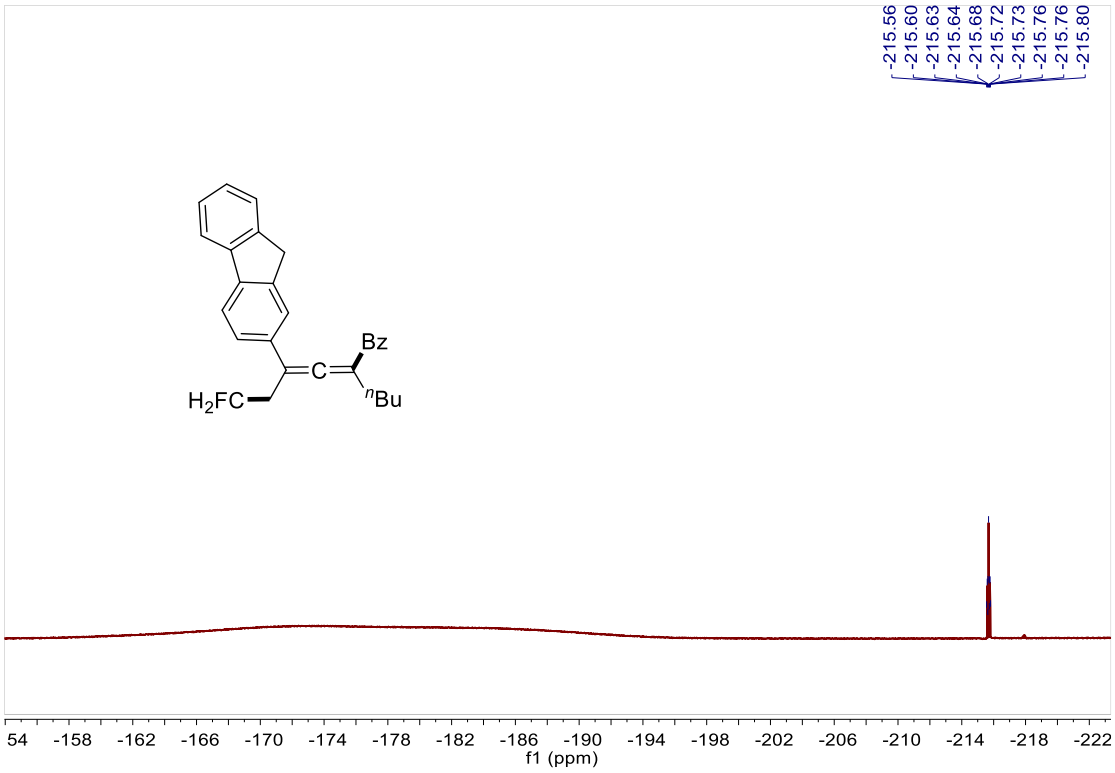
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ra**.



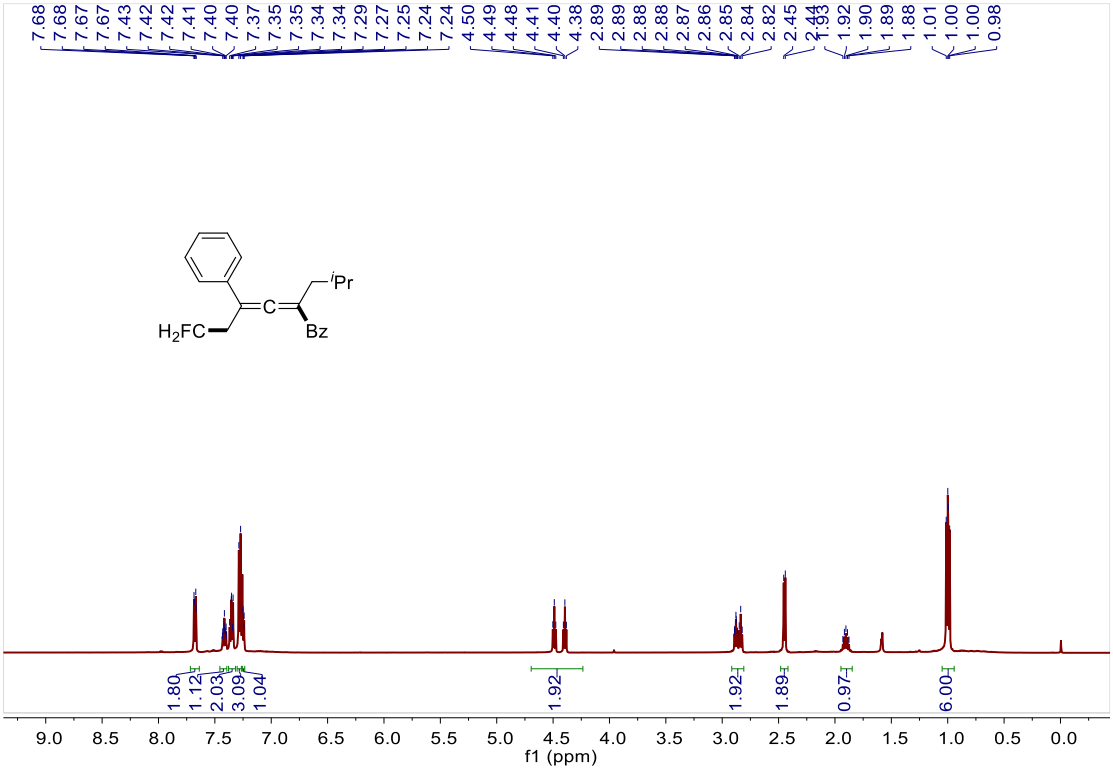
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ra**.



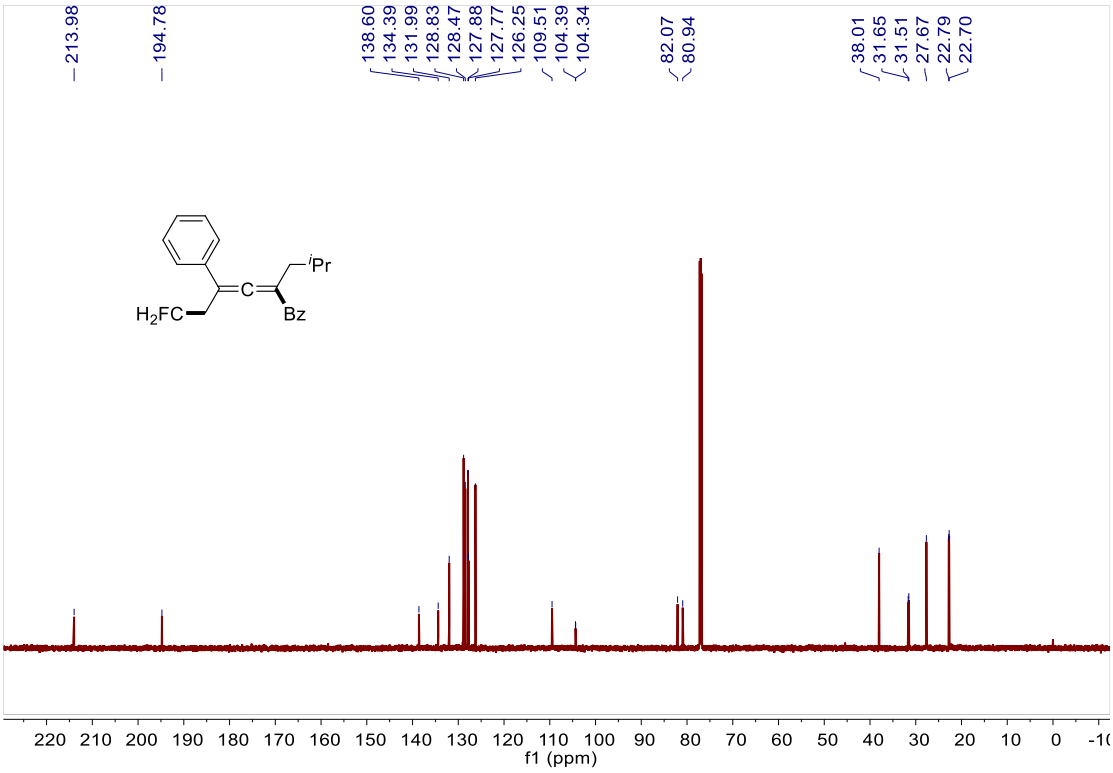
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ra**.



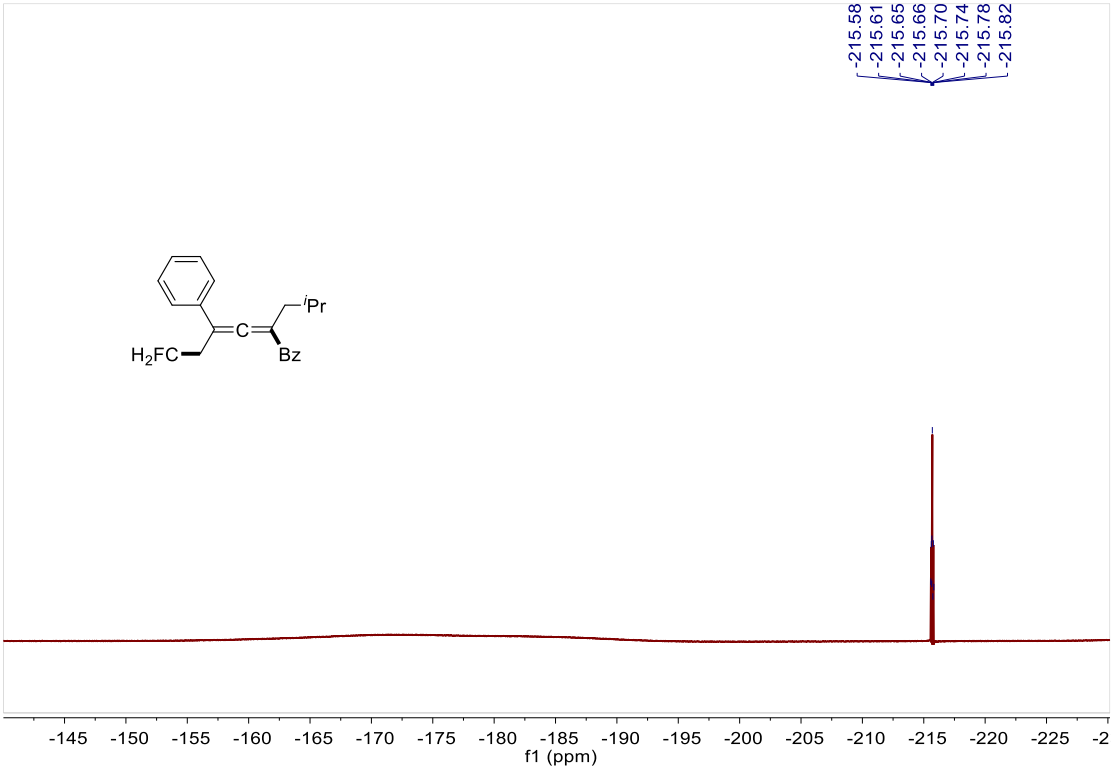
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4sa**.



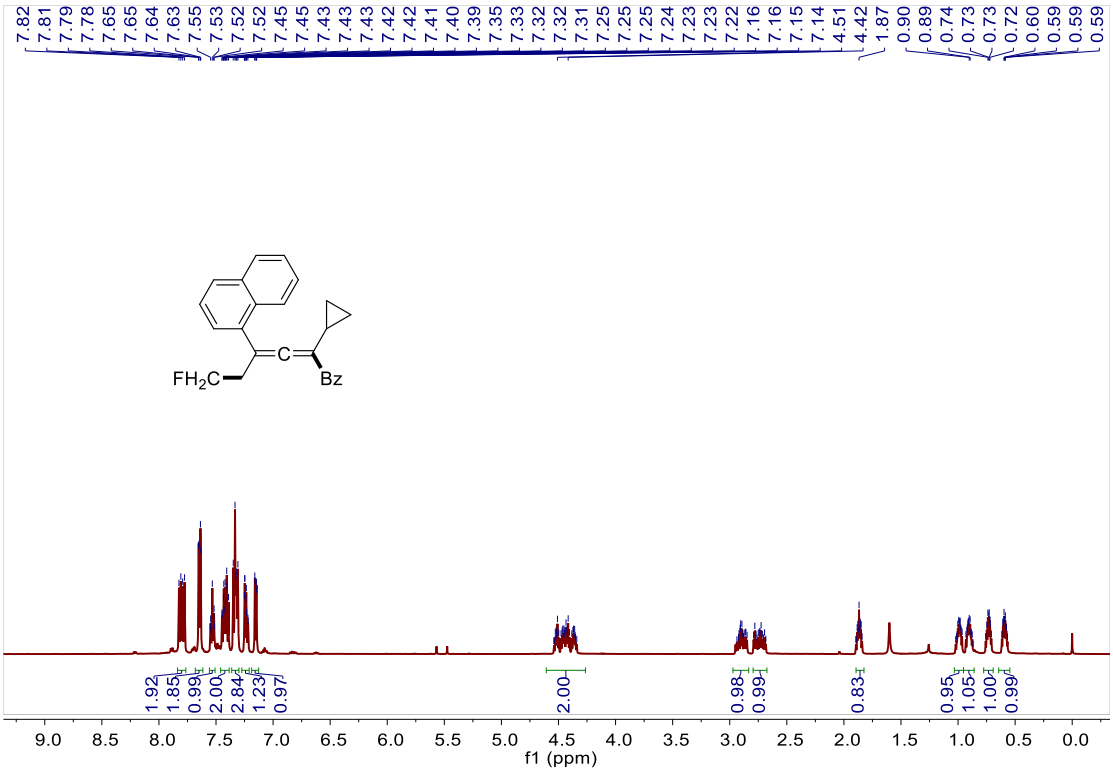
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4sa**.



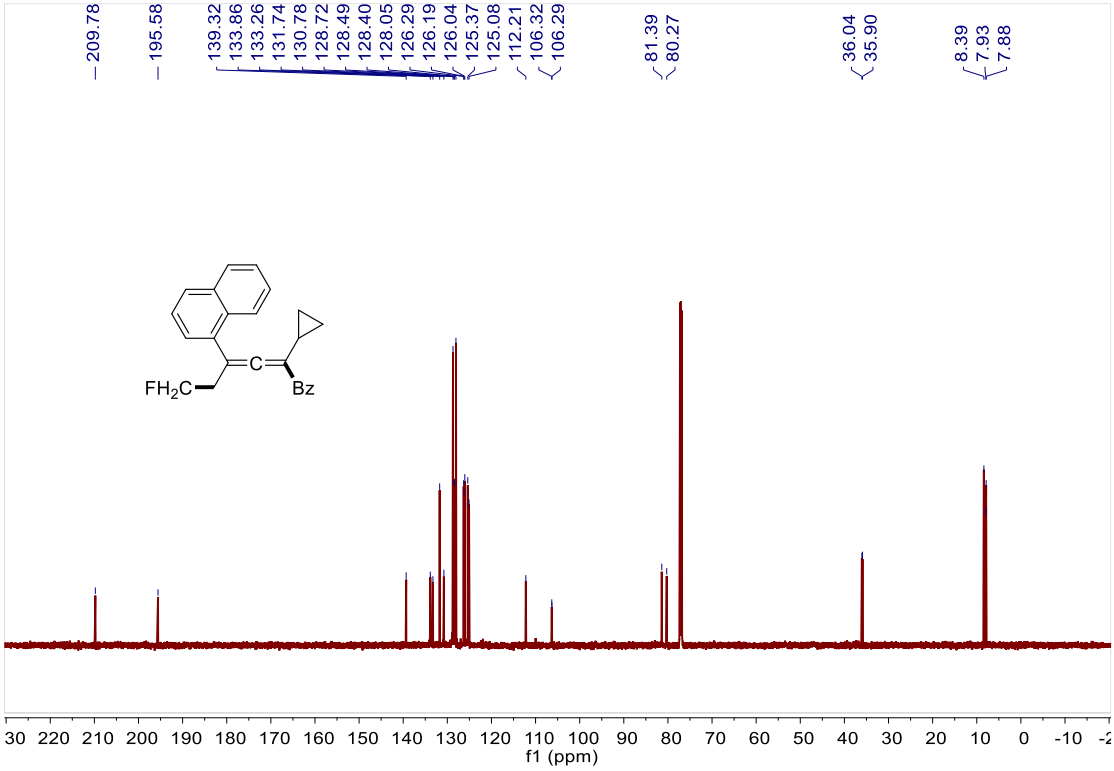
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4sa**.



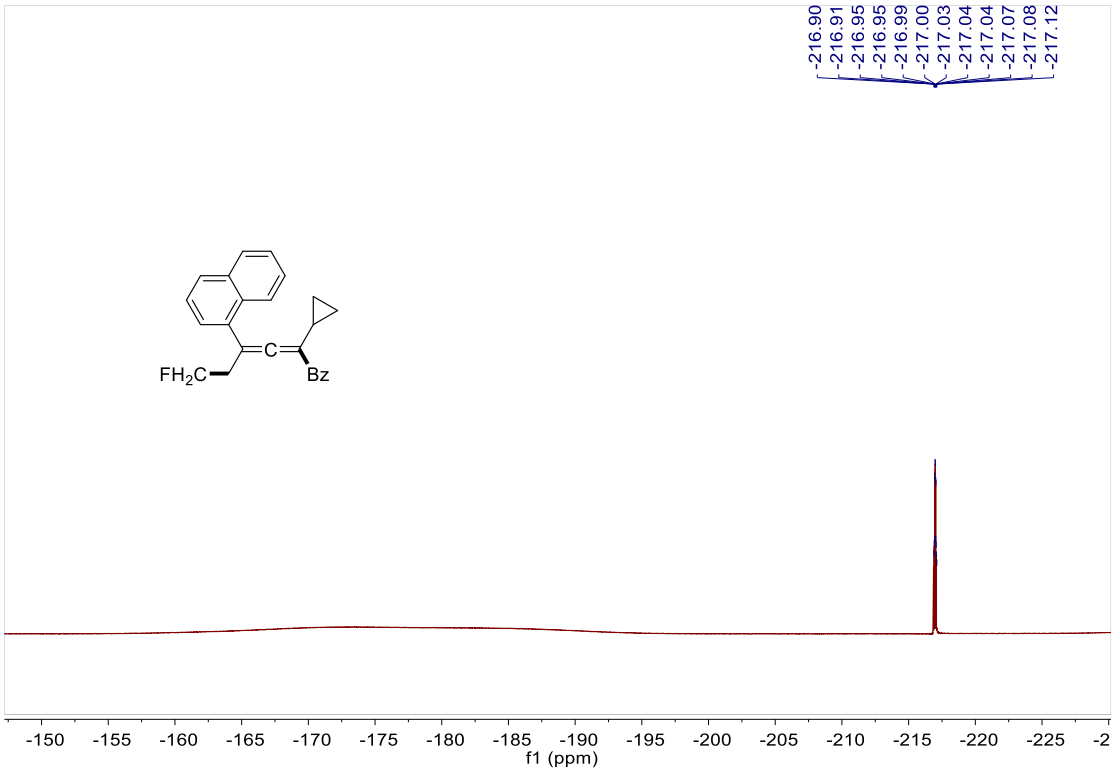
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ta**.



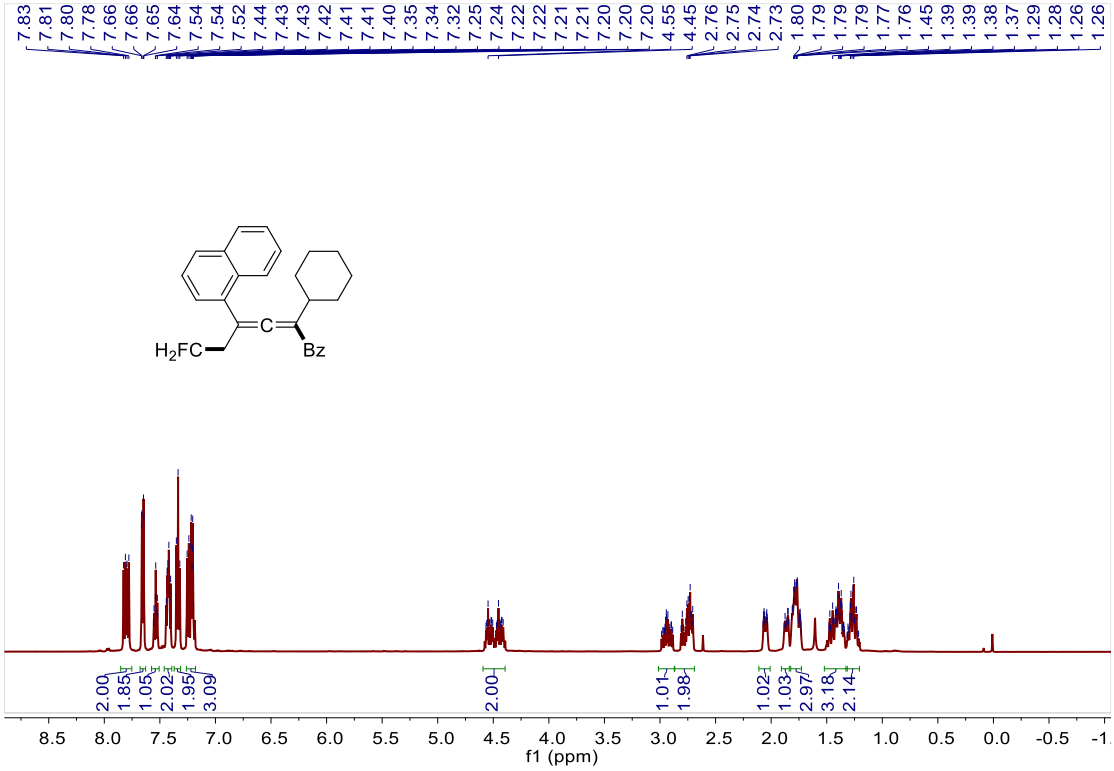
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ta**.



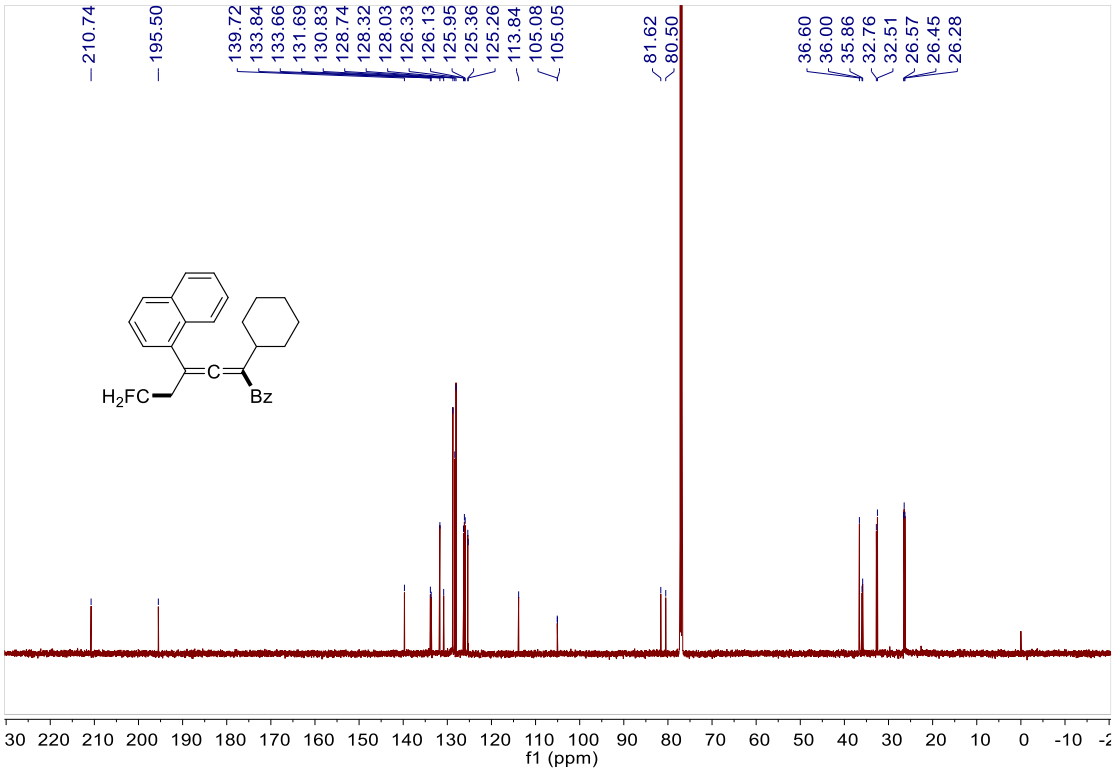
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ta**.



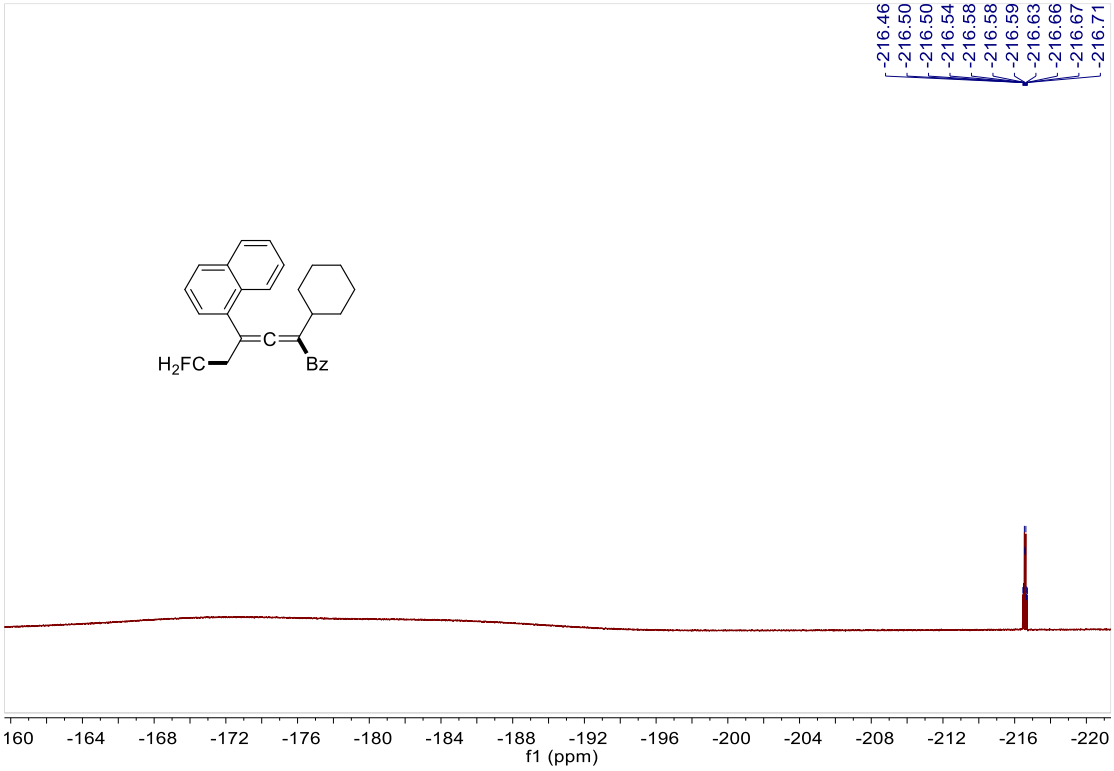
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4ua**.



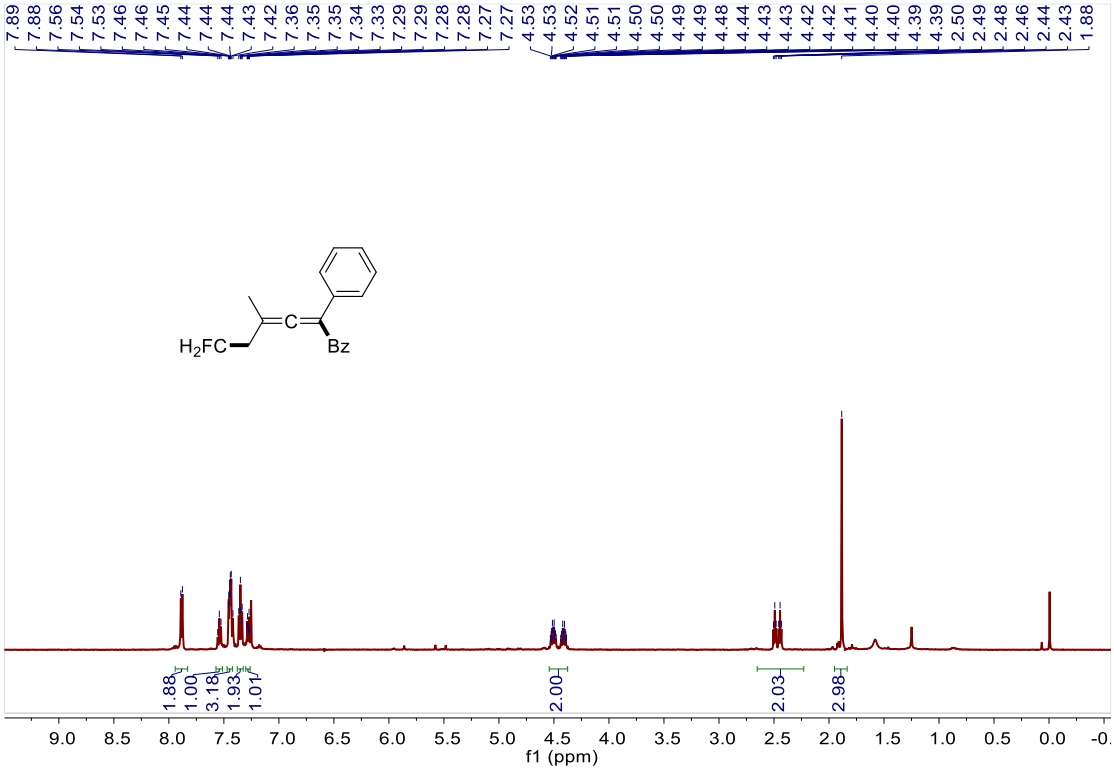
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4ua**.



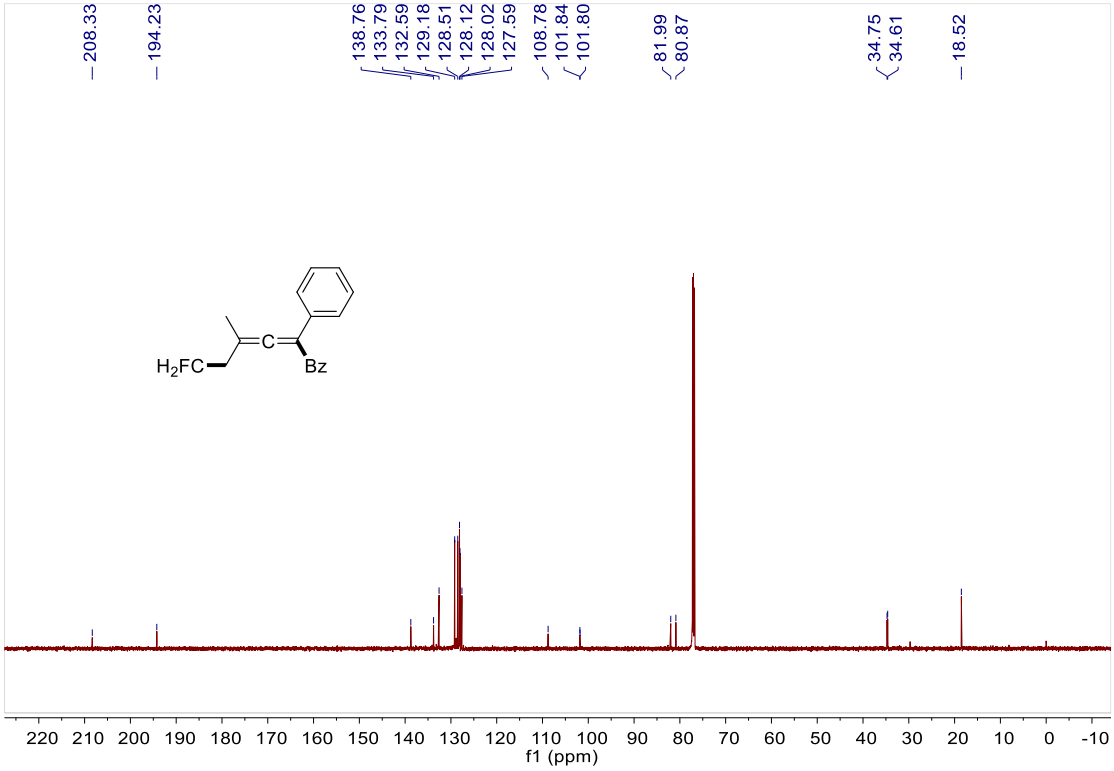
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4ua**.



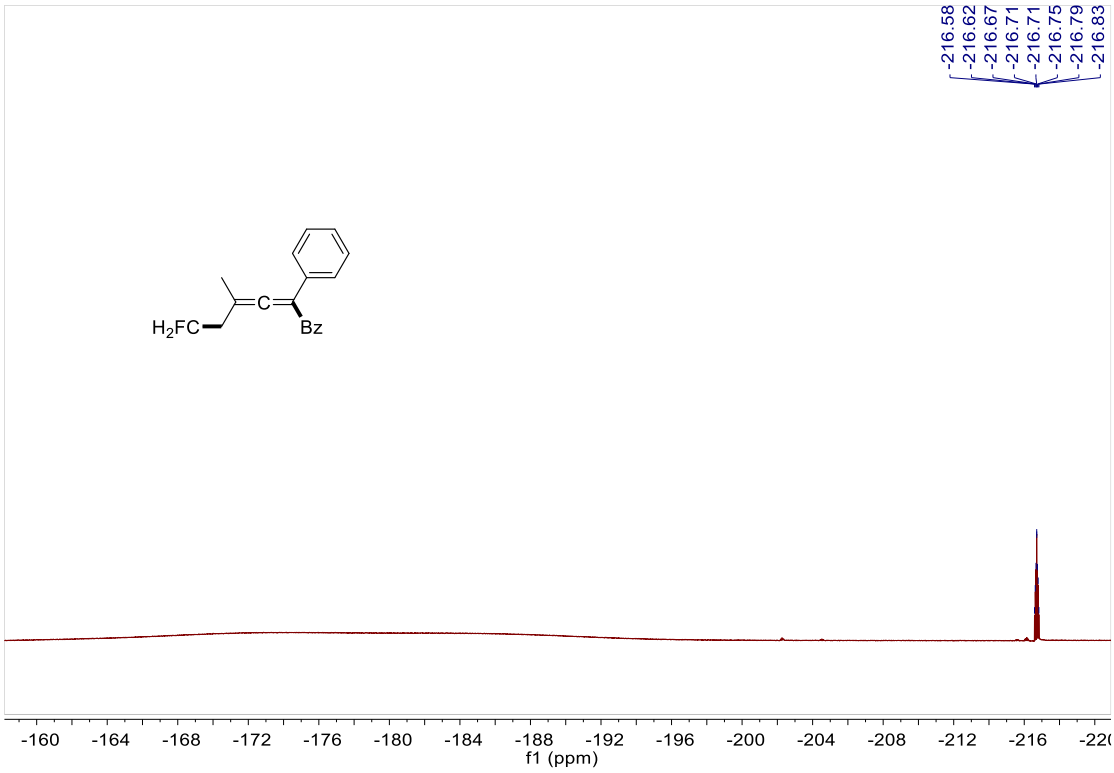
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4wa**.



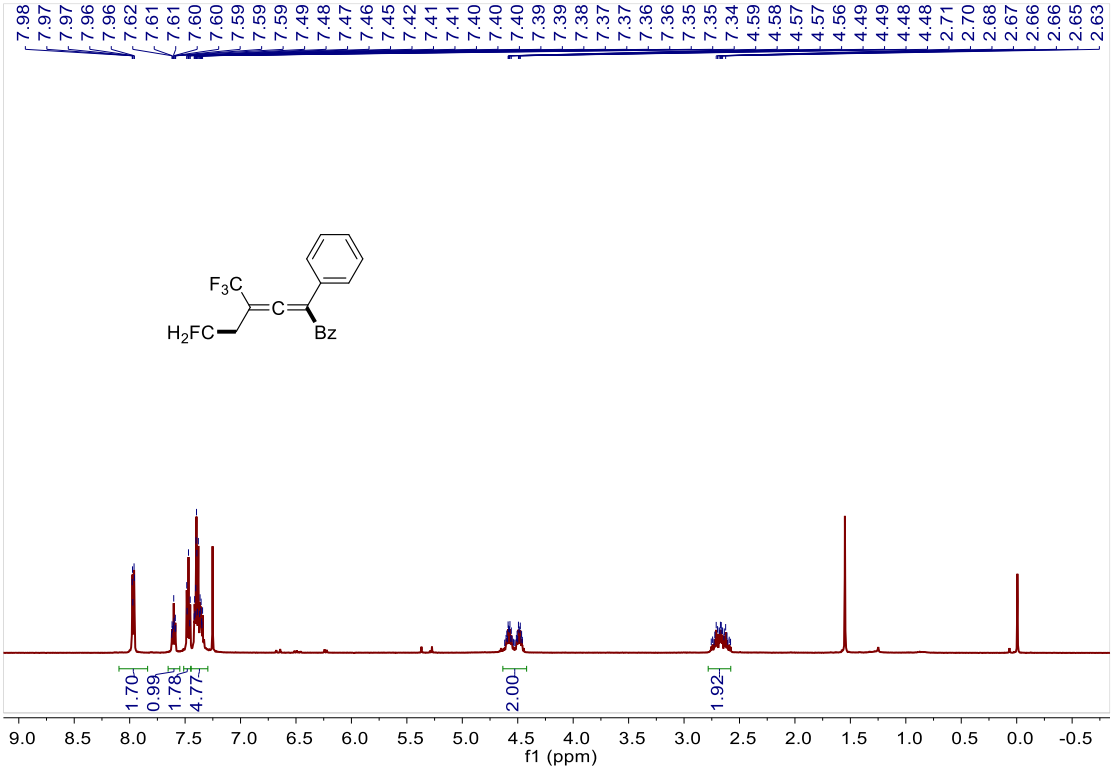
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4wa**.



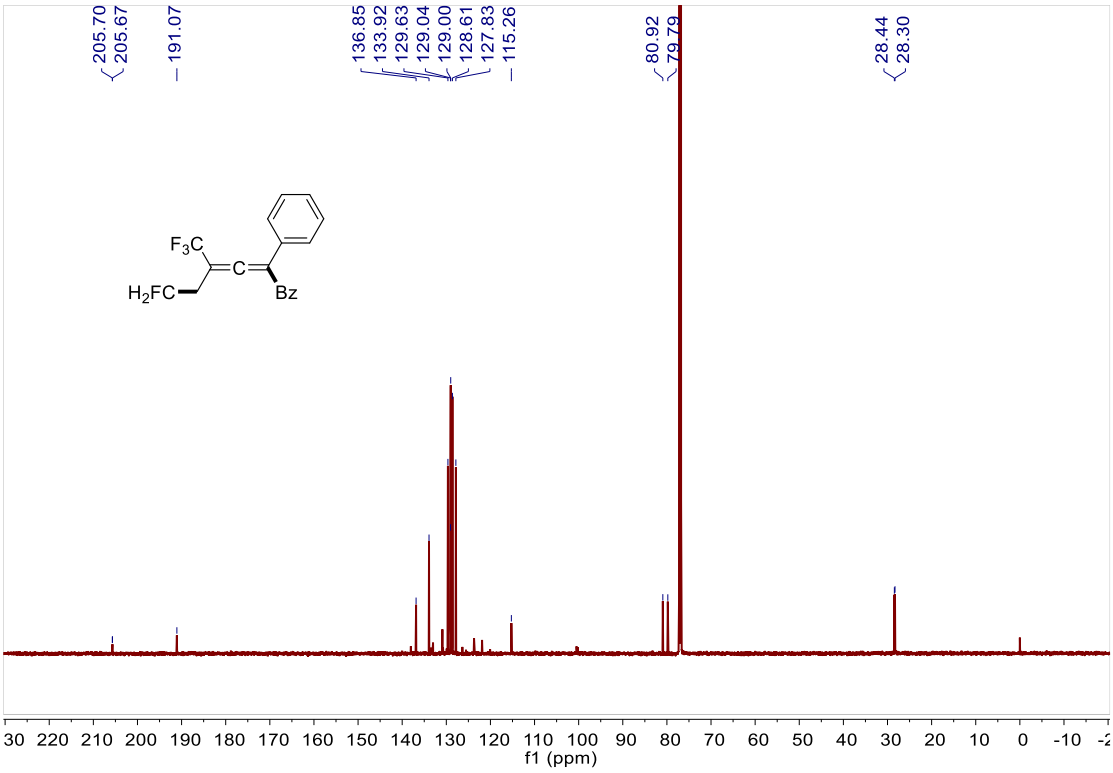
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4wa**.



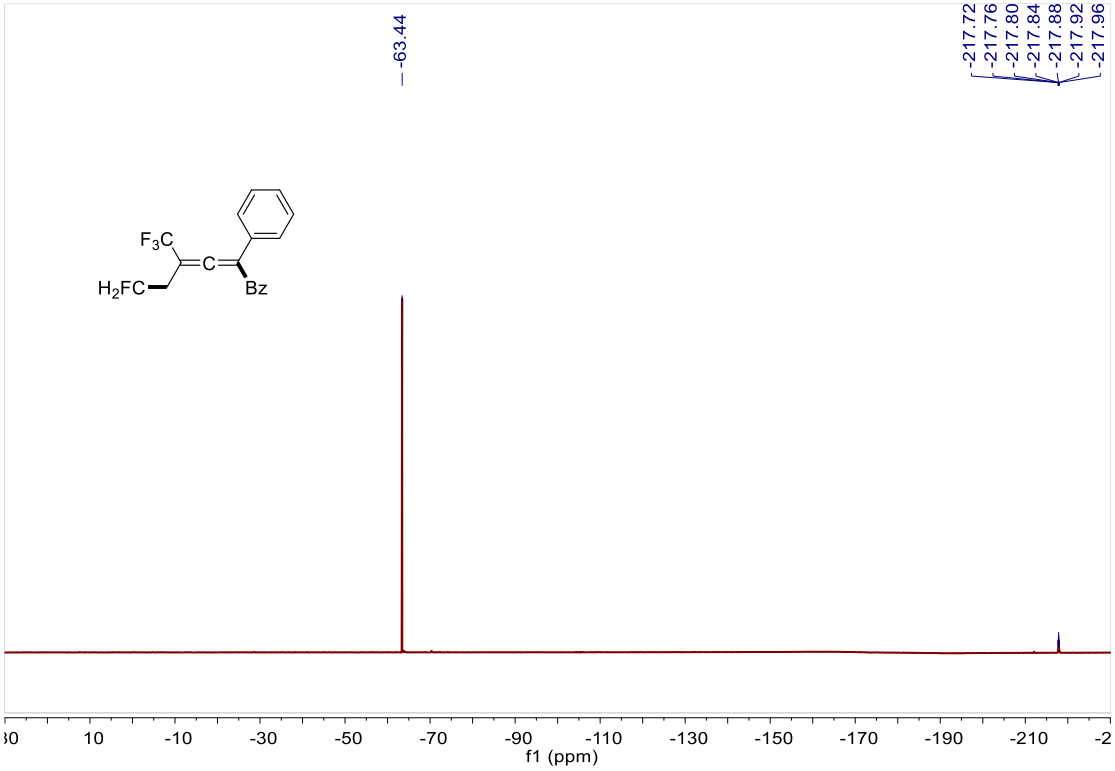
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4za**.



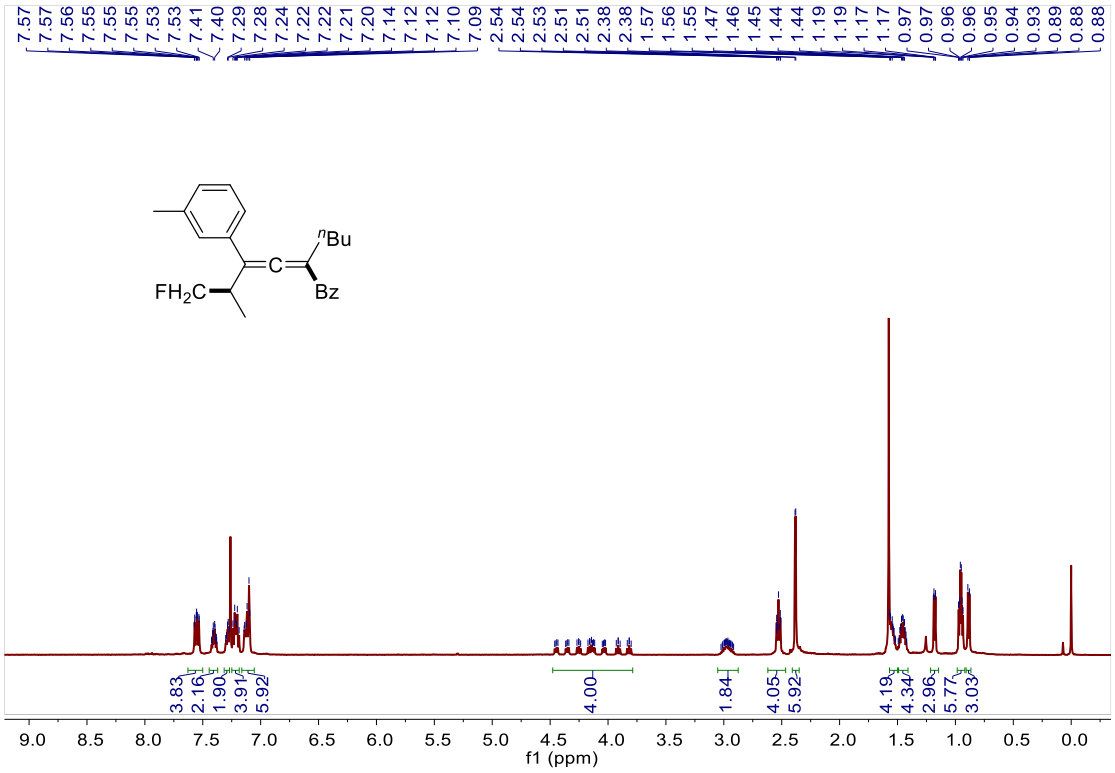
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4za**.



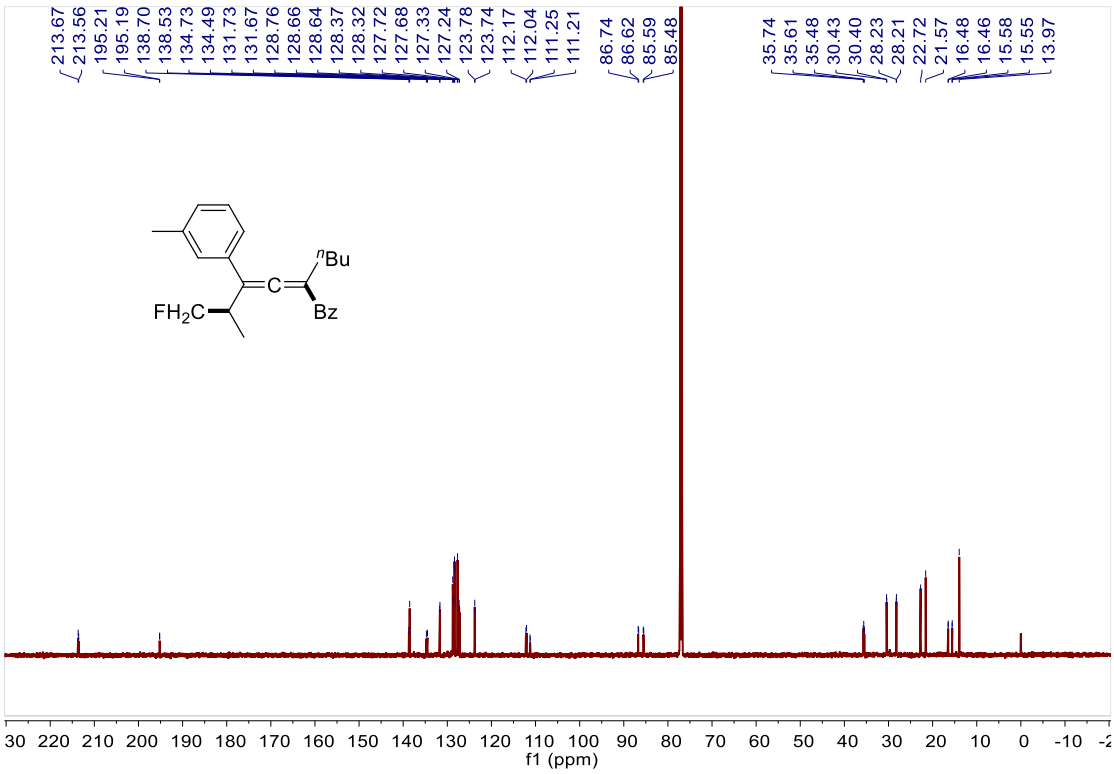
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4za**.



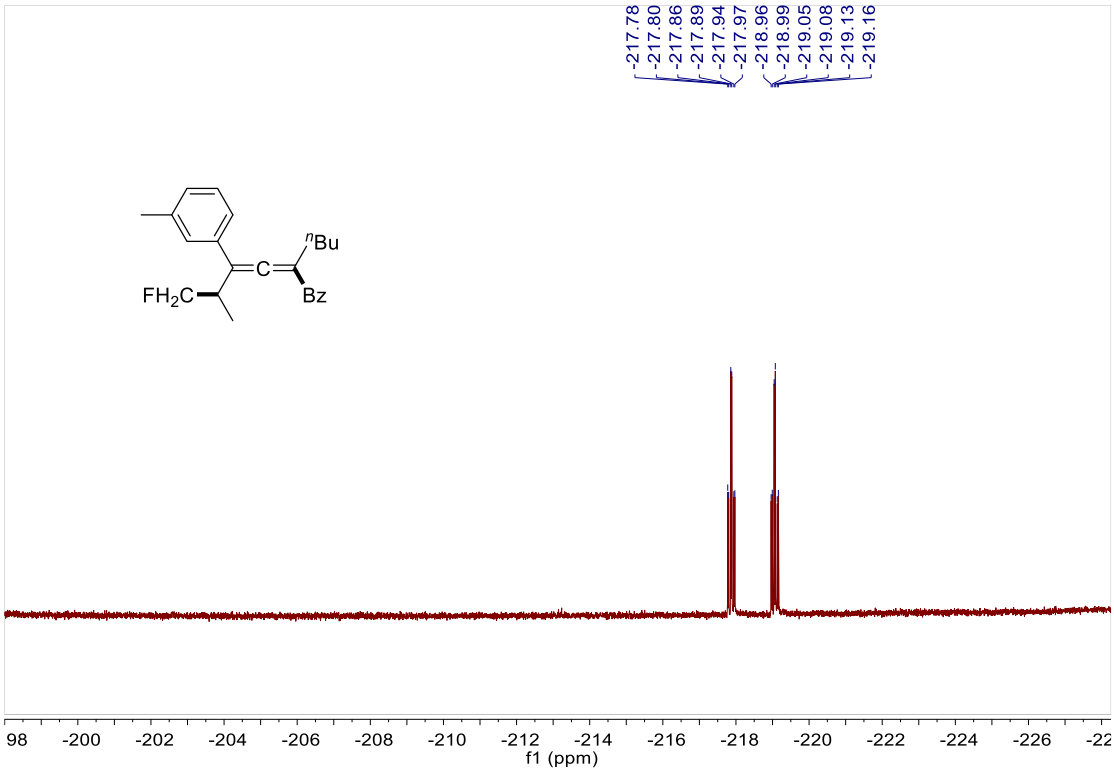
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4a'a**.



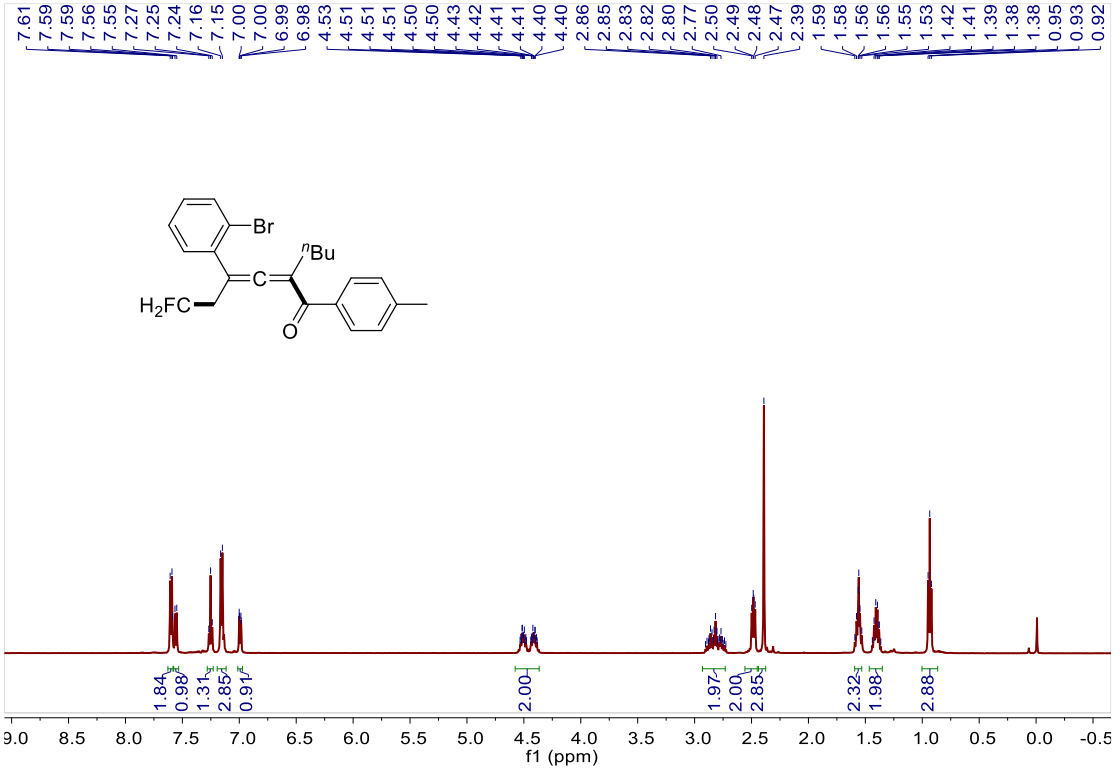
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4a'a**.



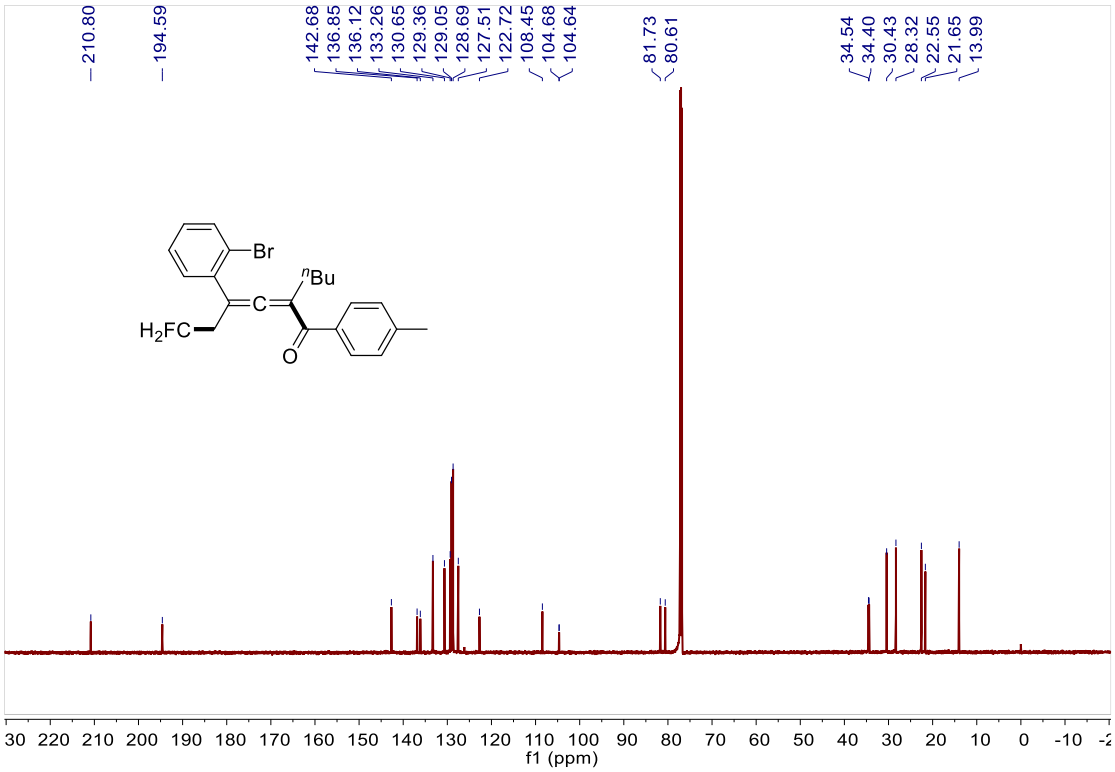
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4a'a**.



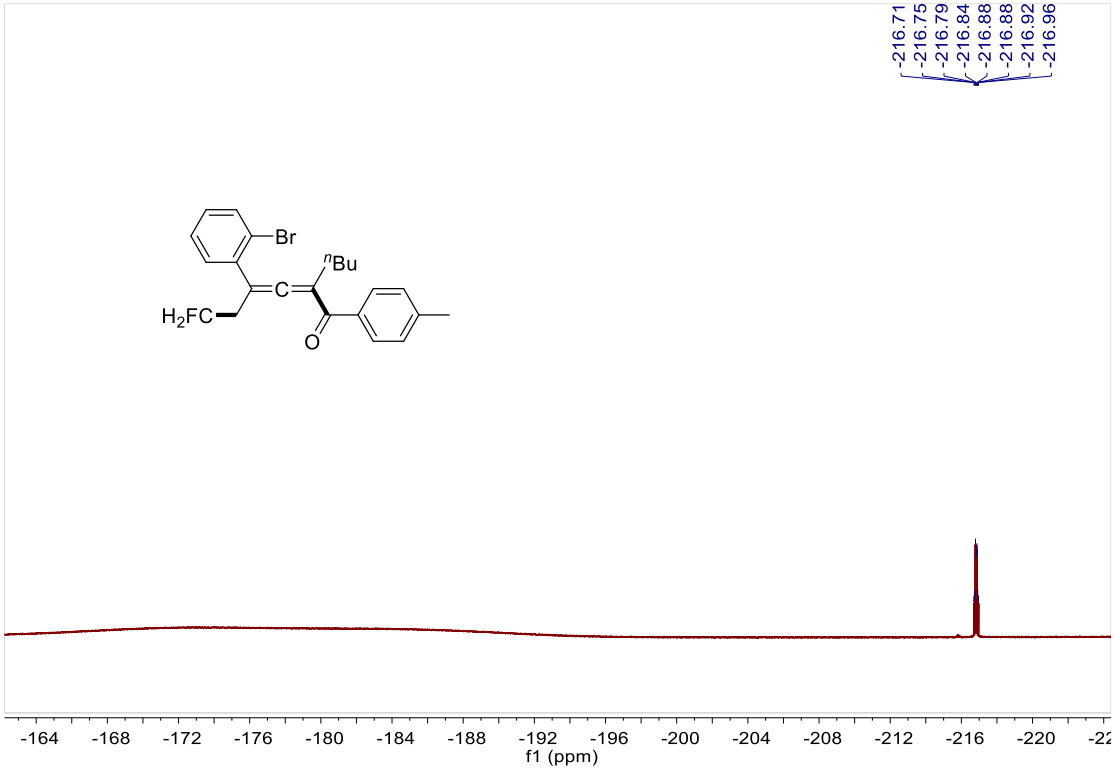
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4db**.



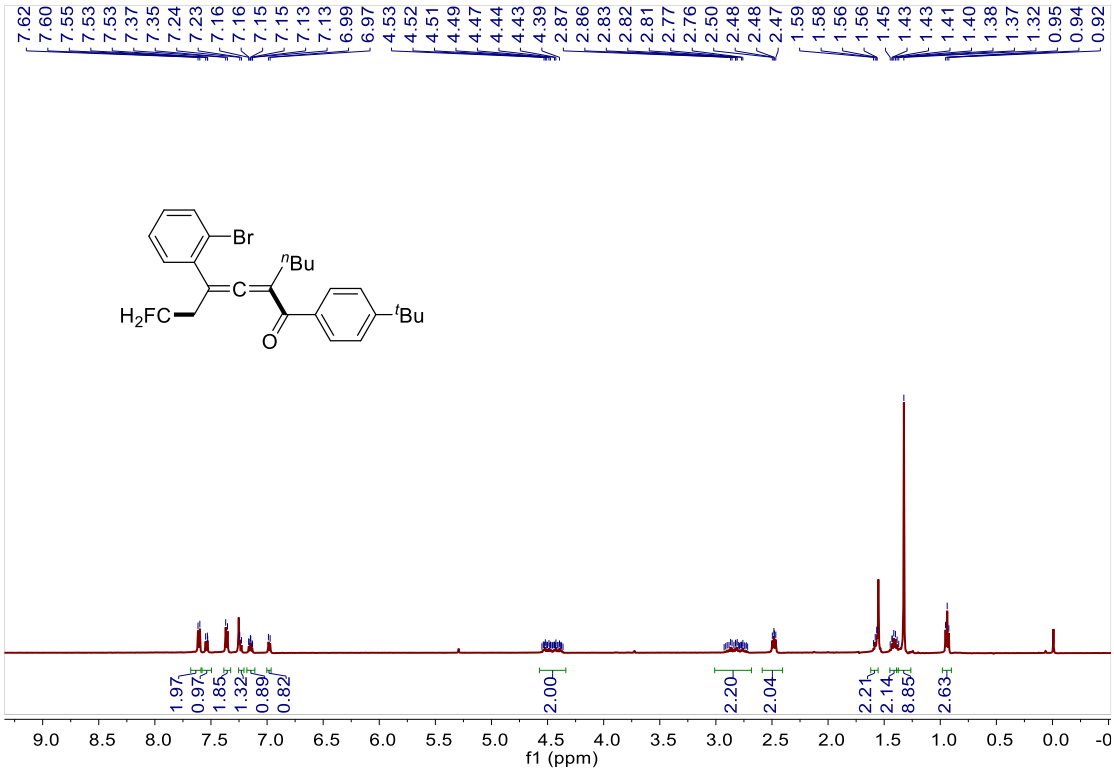
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4db**.



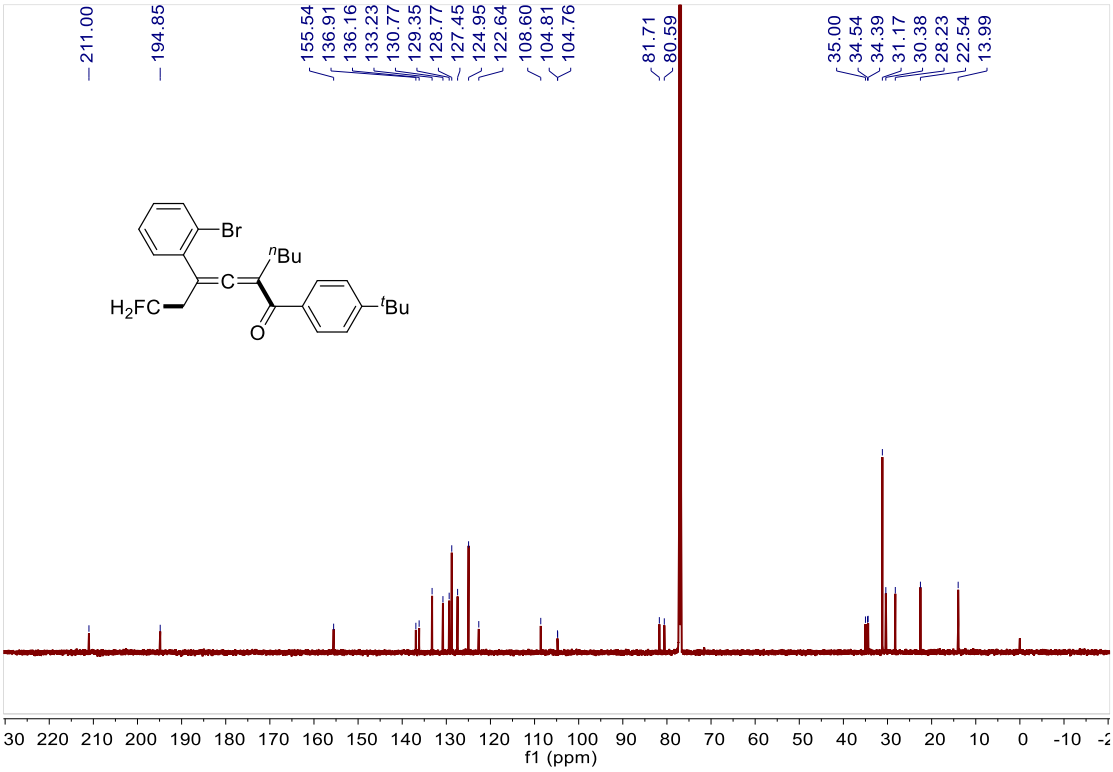
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4db**.



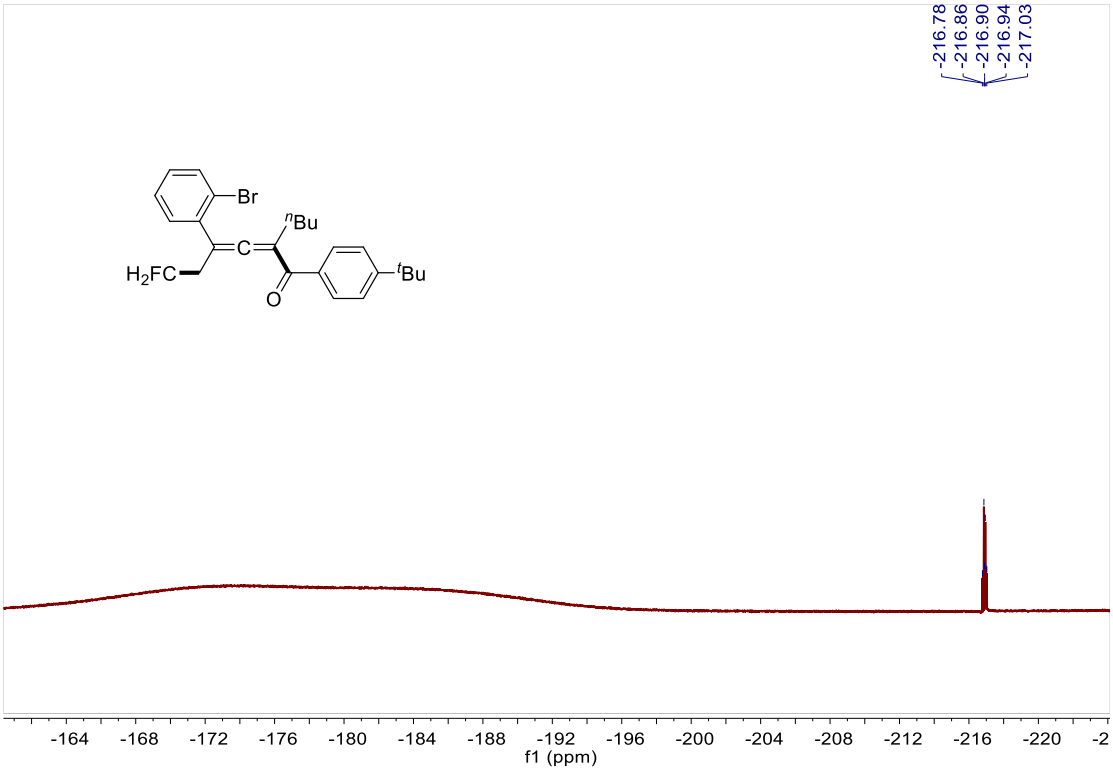
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4dc**.



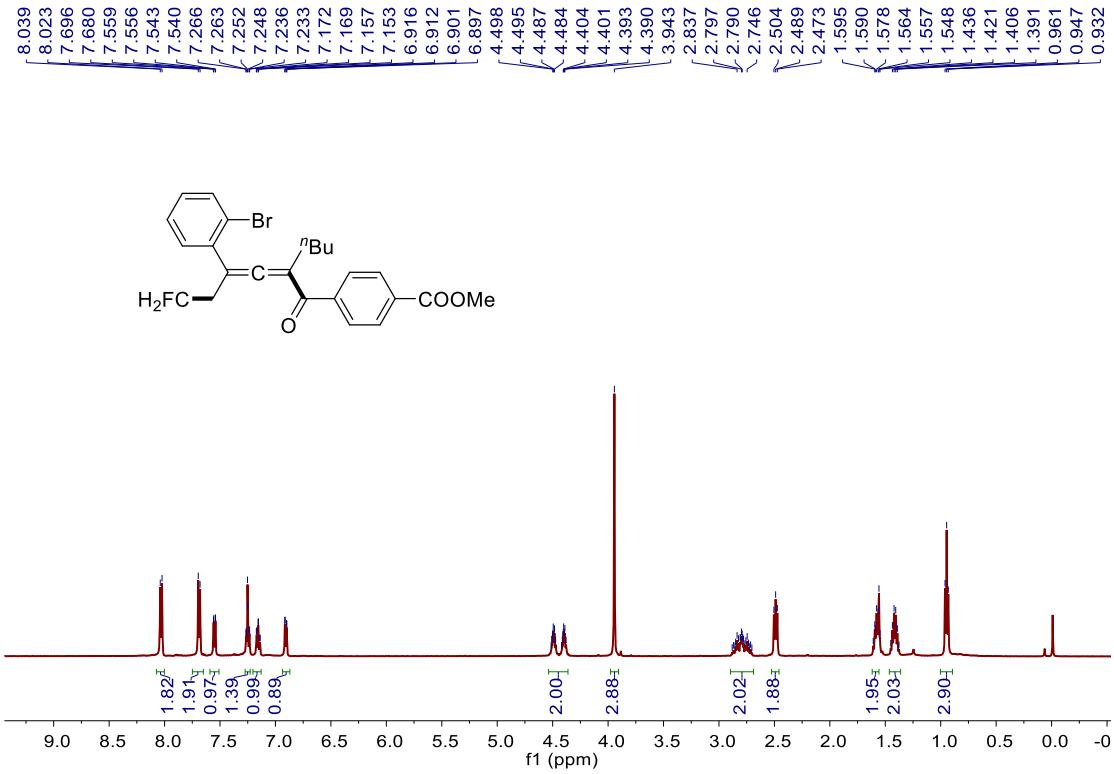
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4dc**.



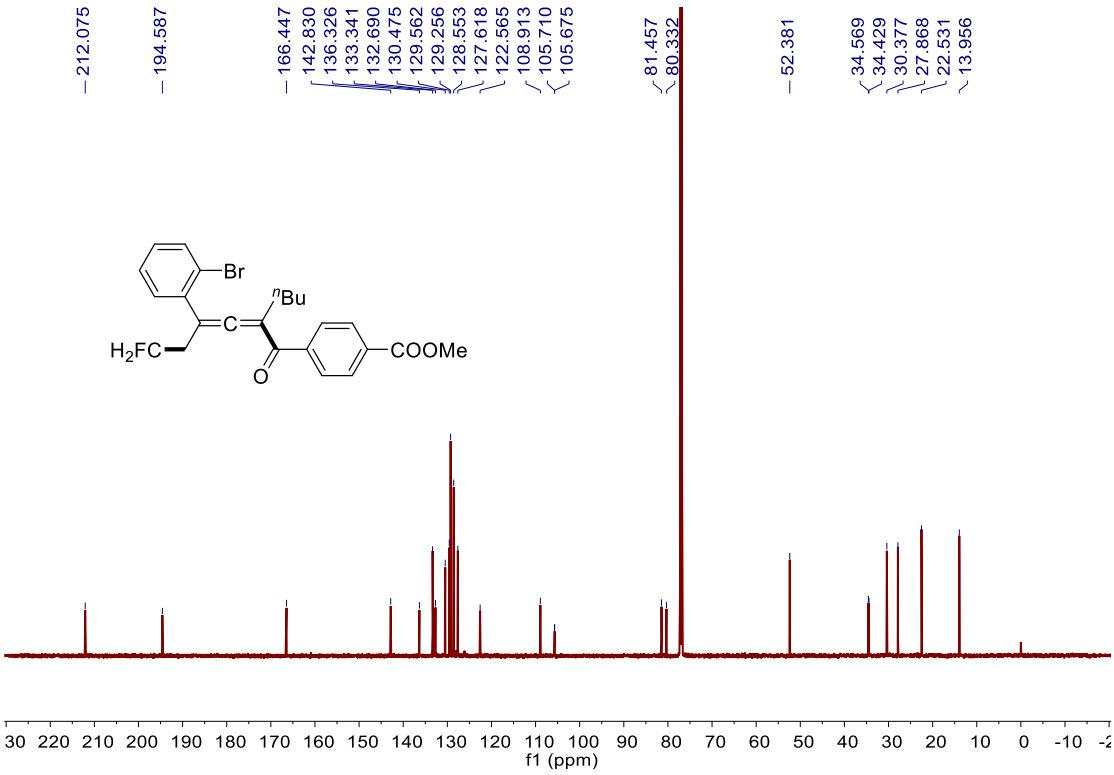
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4dc**.



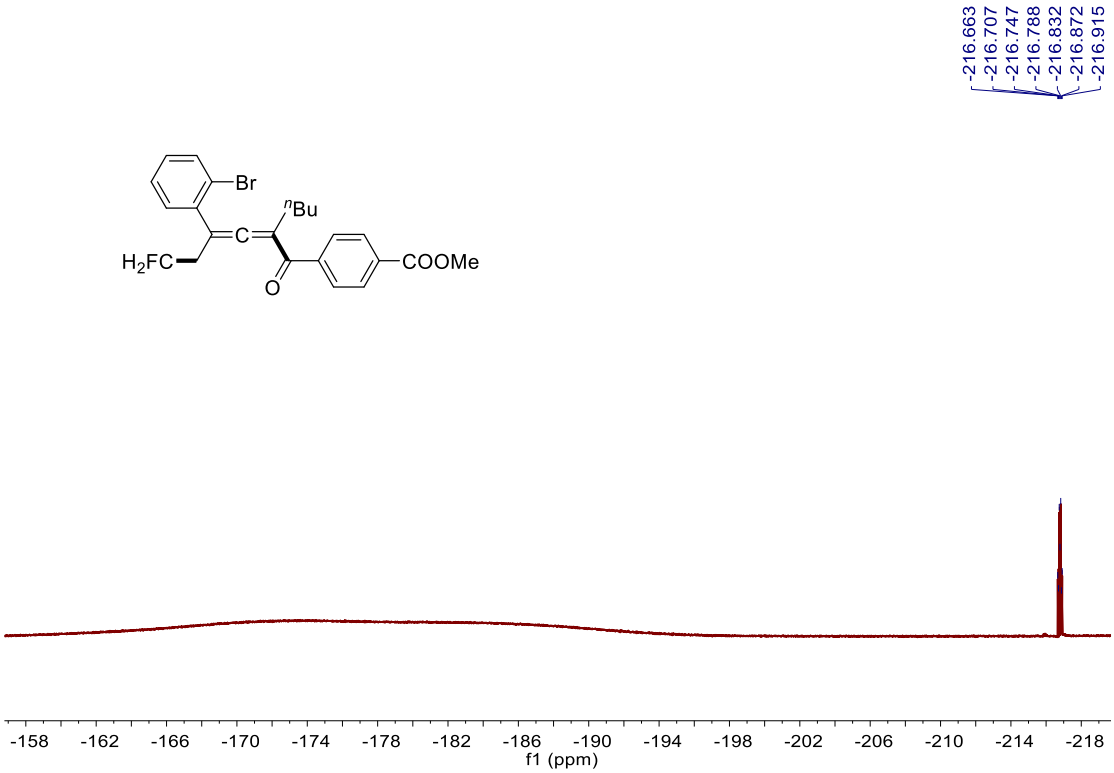
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4di**.



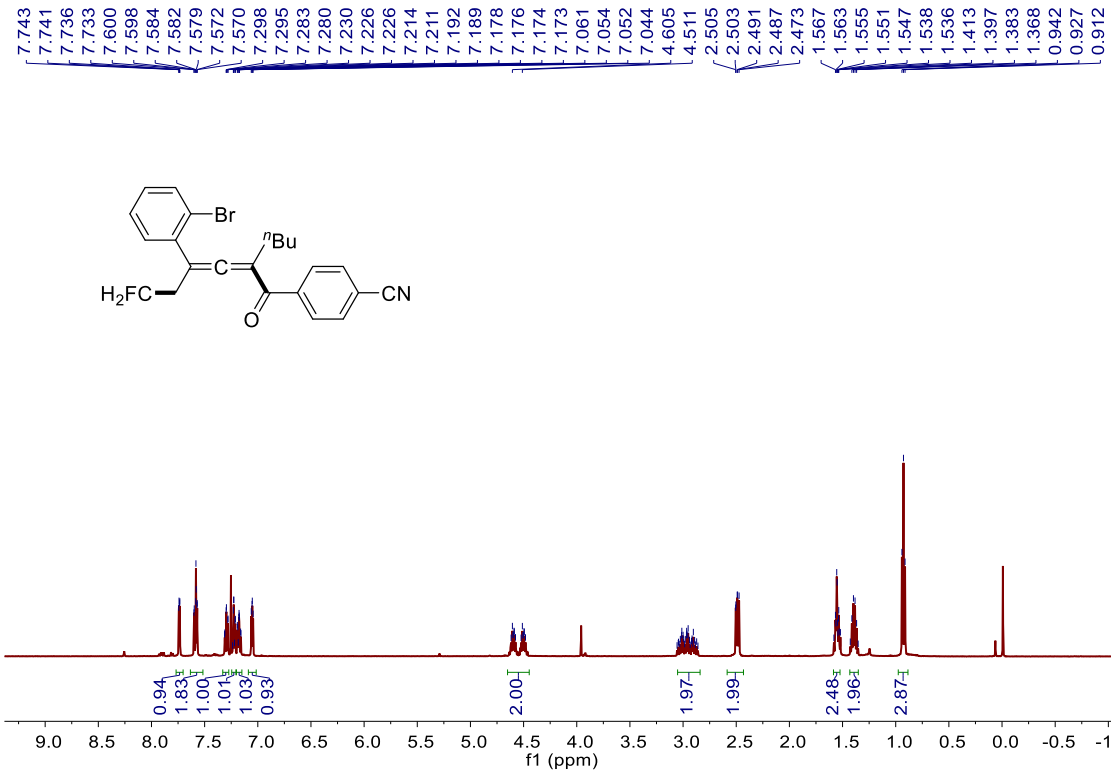
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4di**.



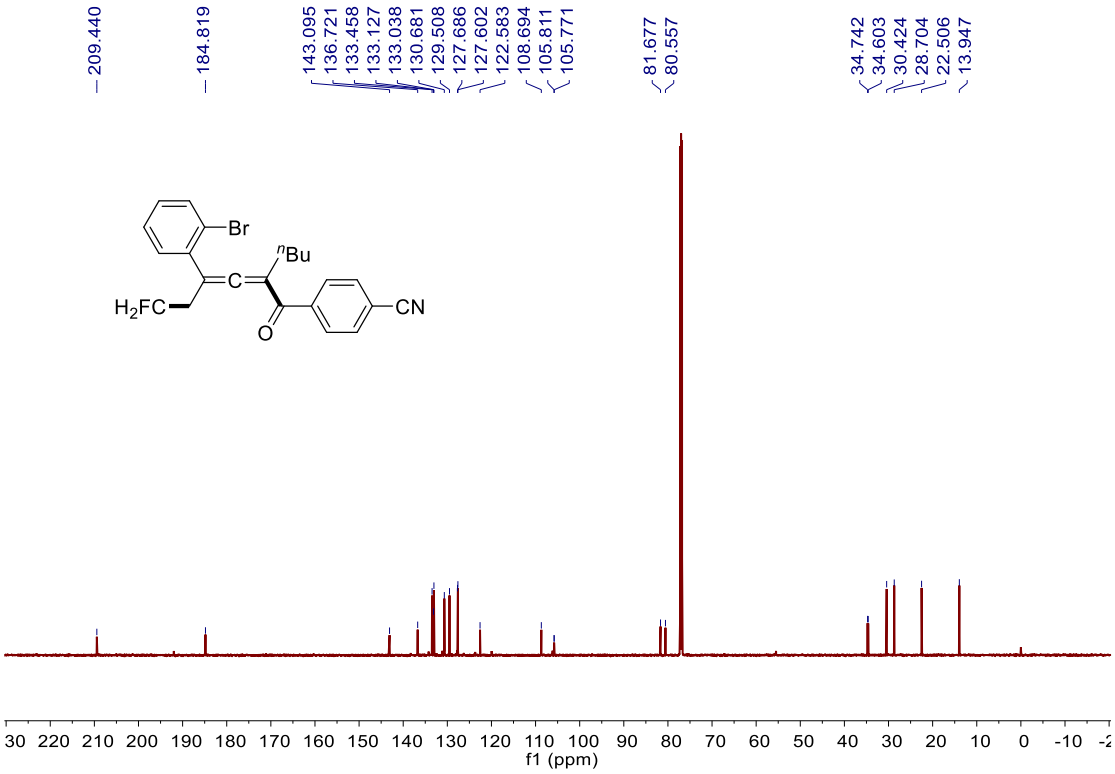
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4di**.



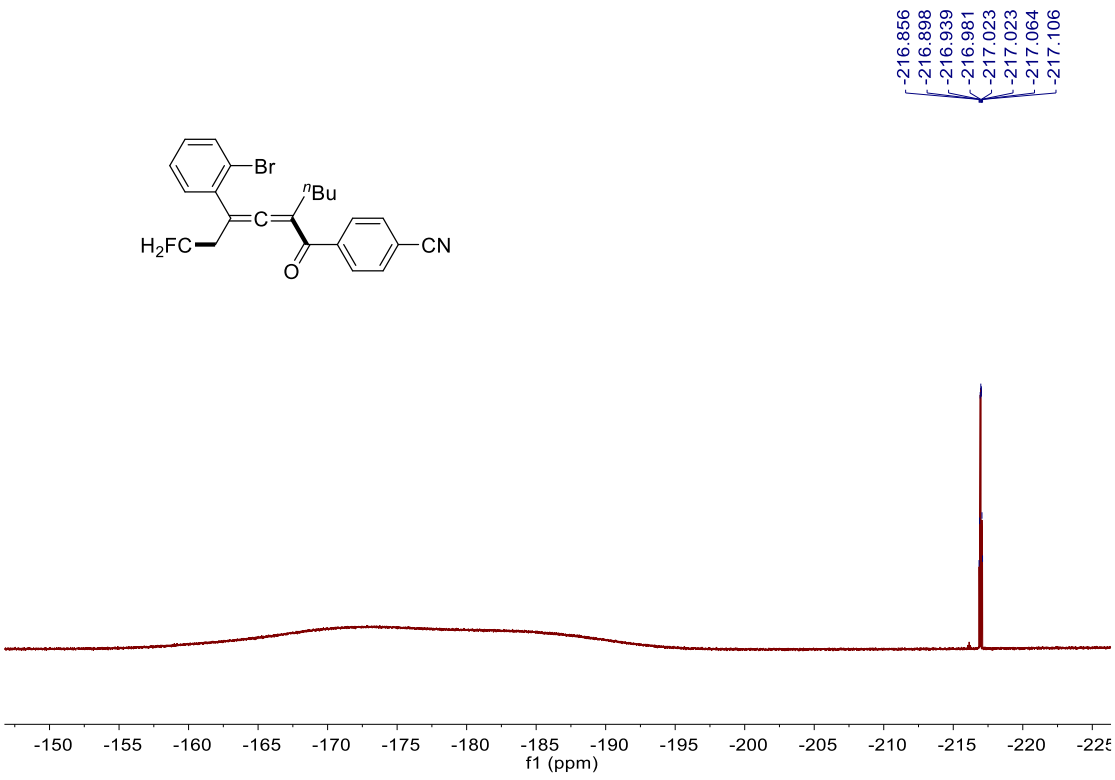
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4dk**.



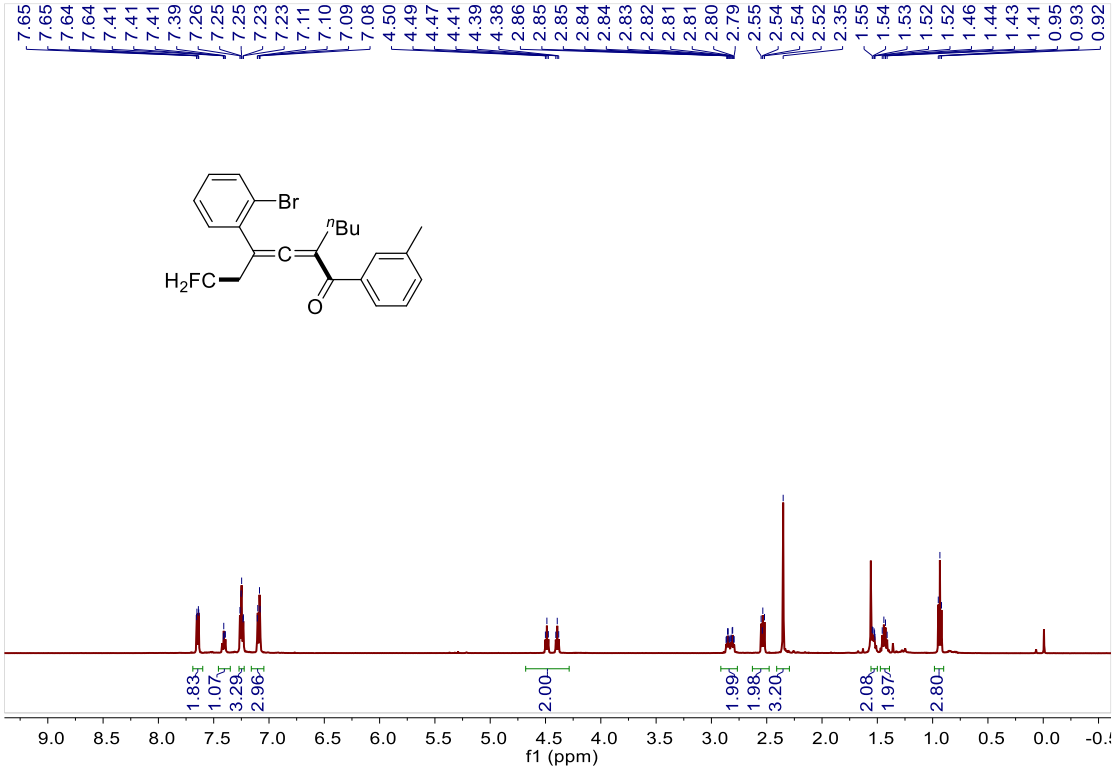
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4dk**.



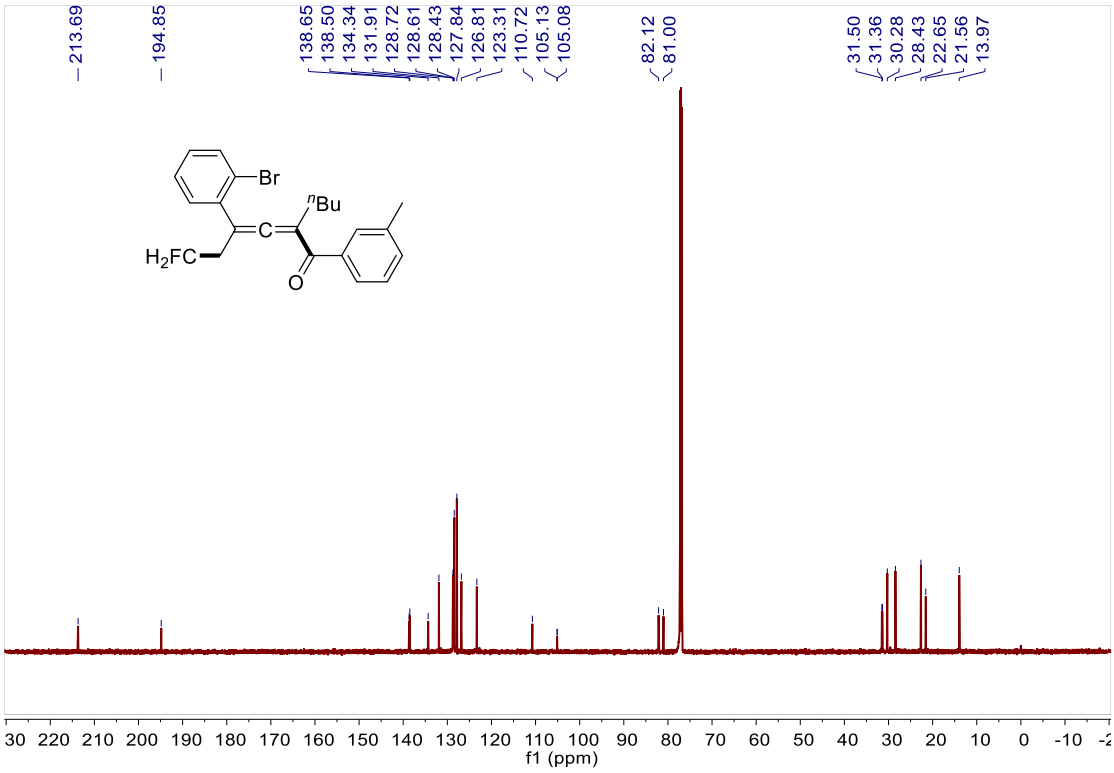
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4dk**.



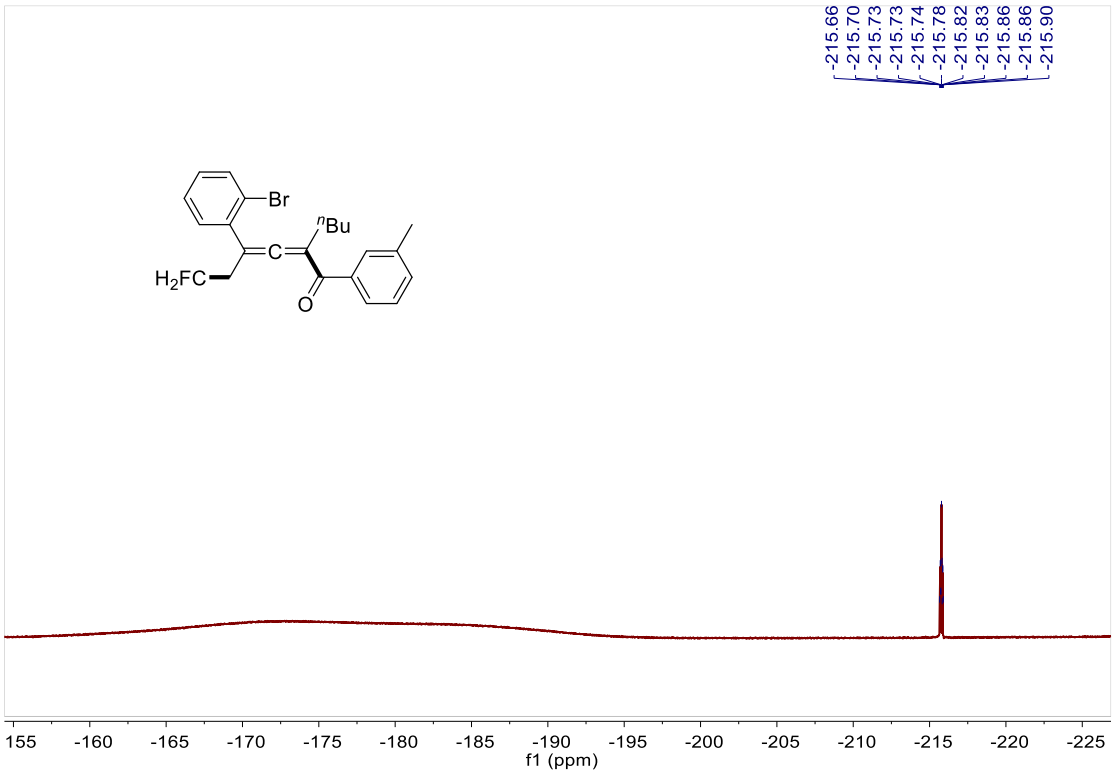
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4dl**.



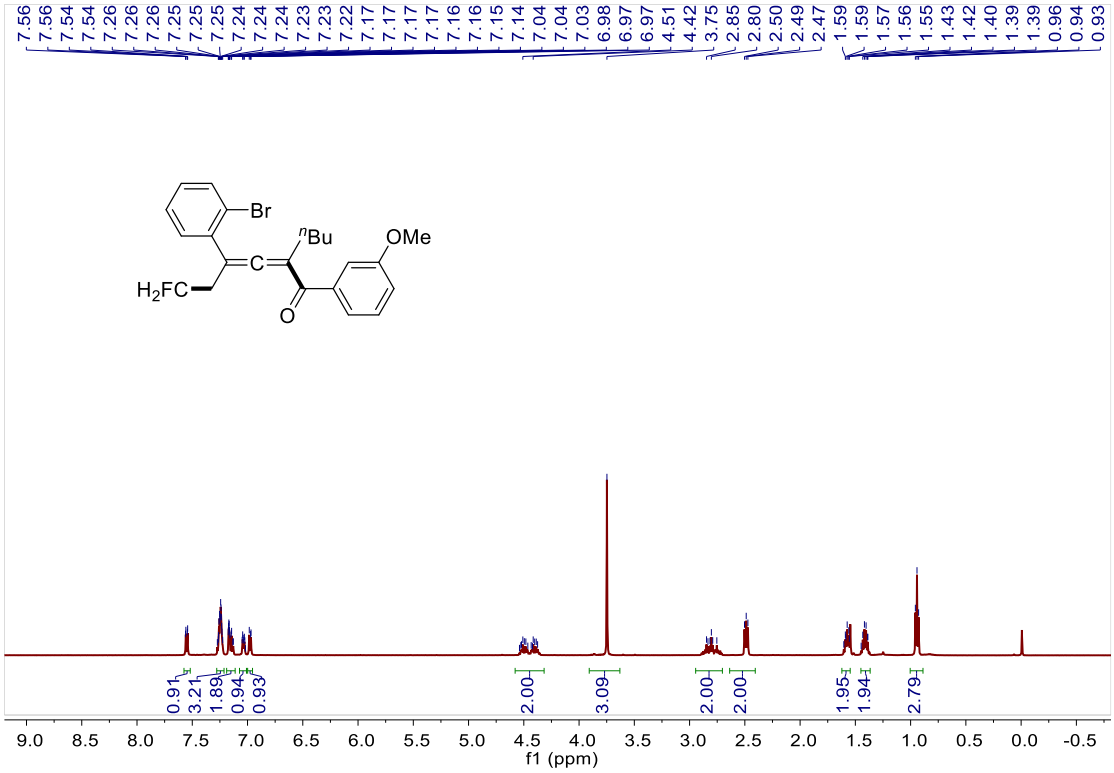
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4dl**.



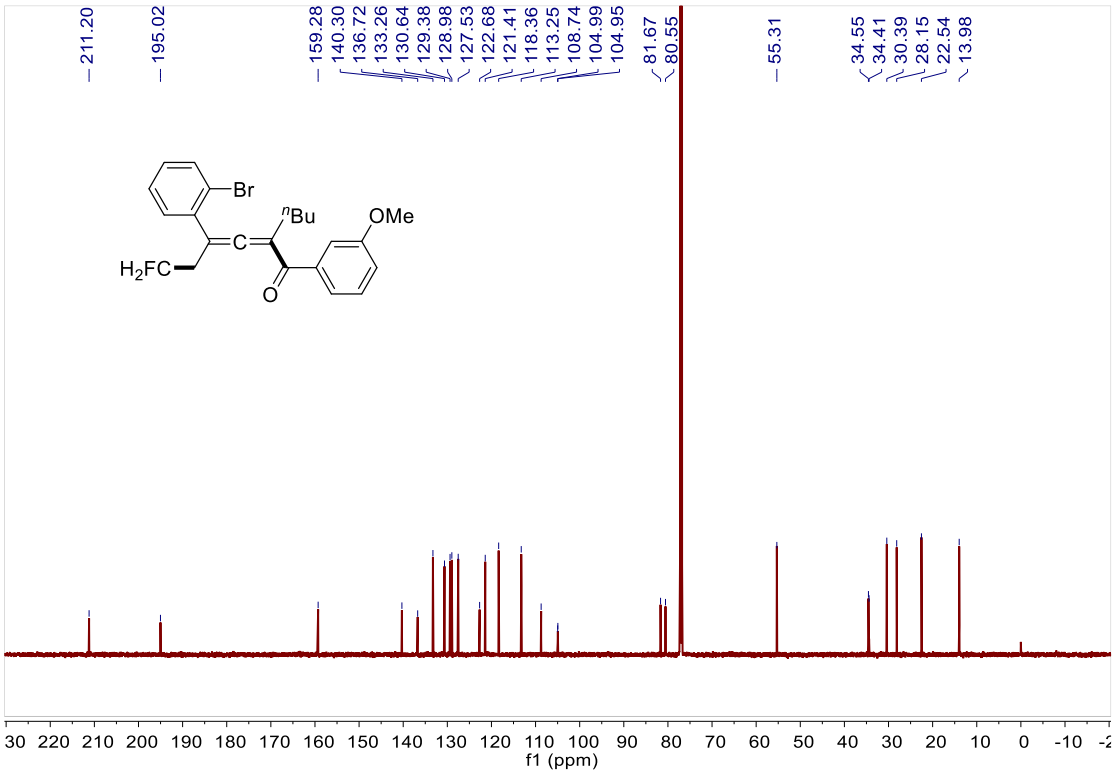
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4dl**.



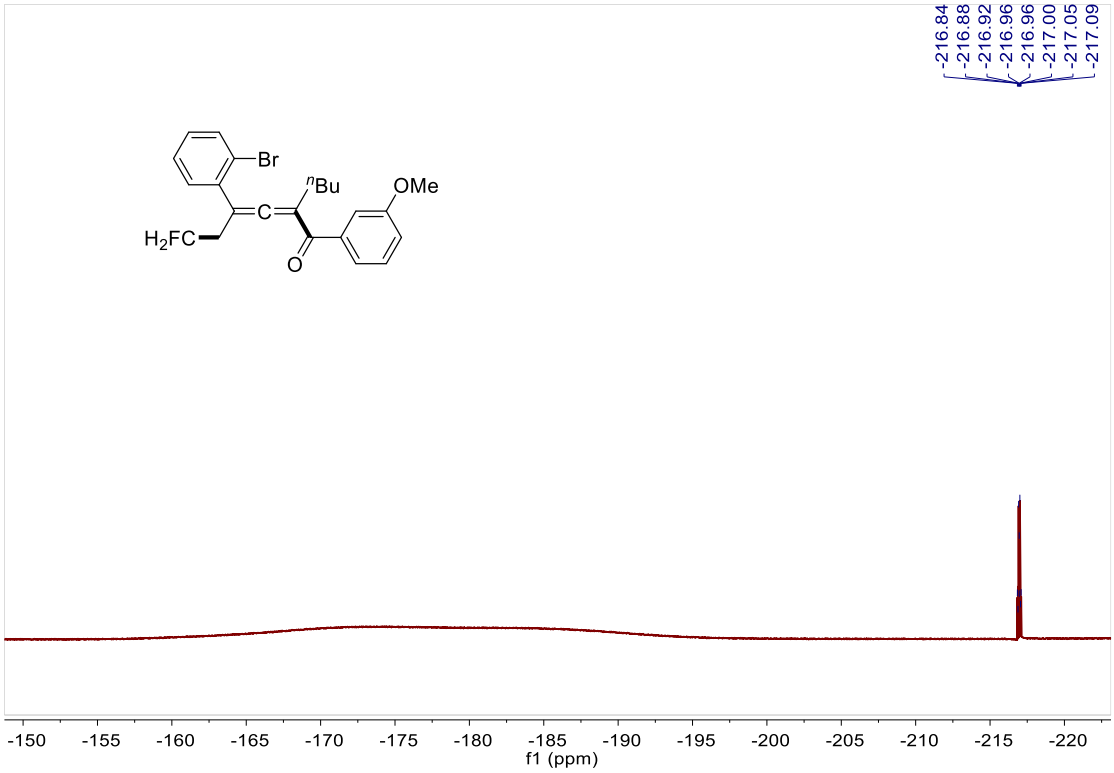
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4dm**.



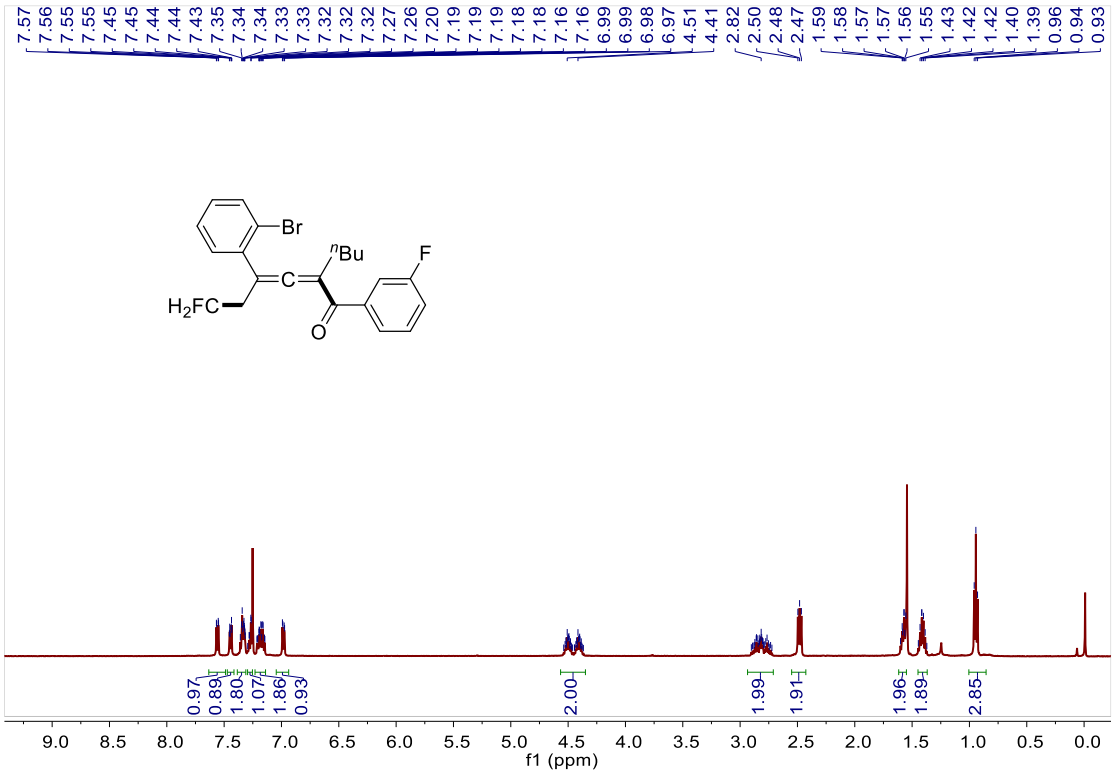
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4dm**.



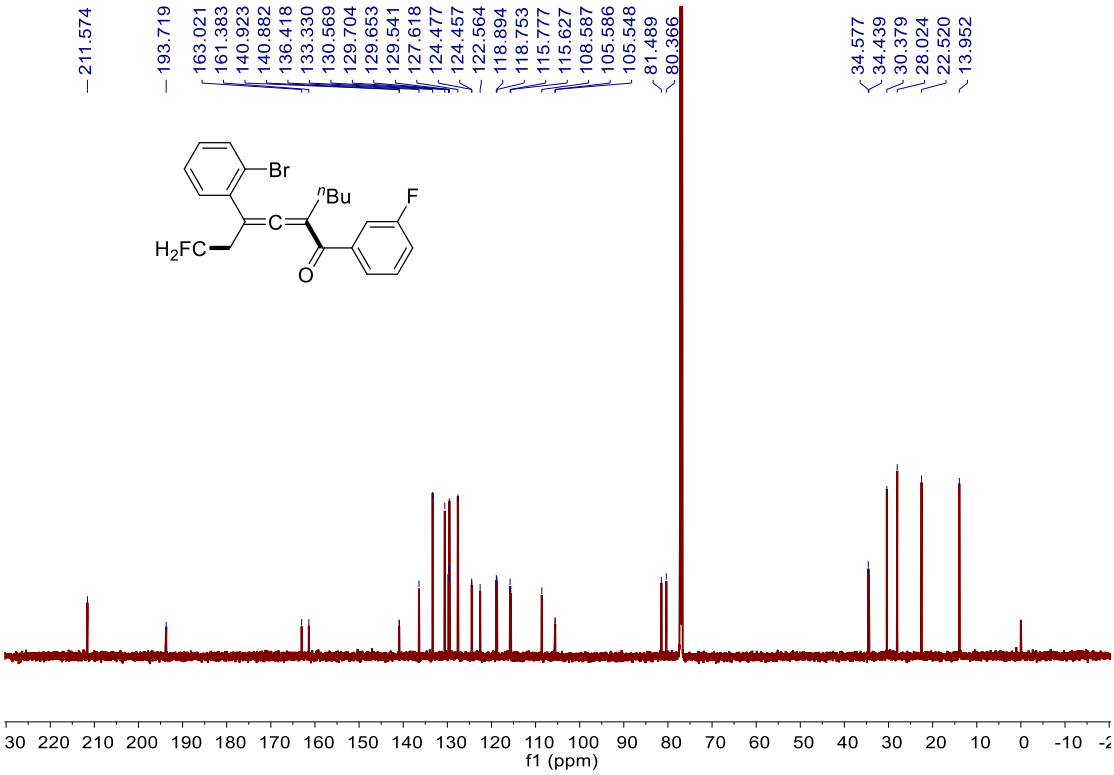
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4dm**.



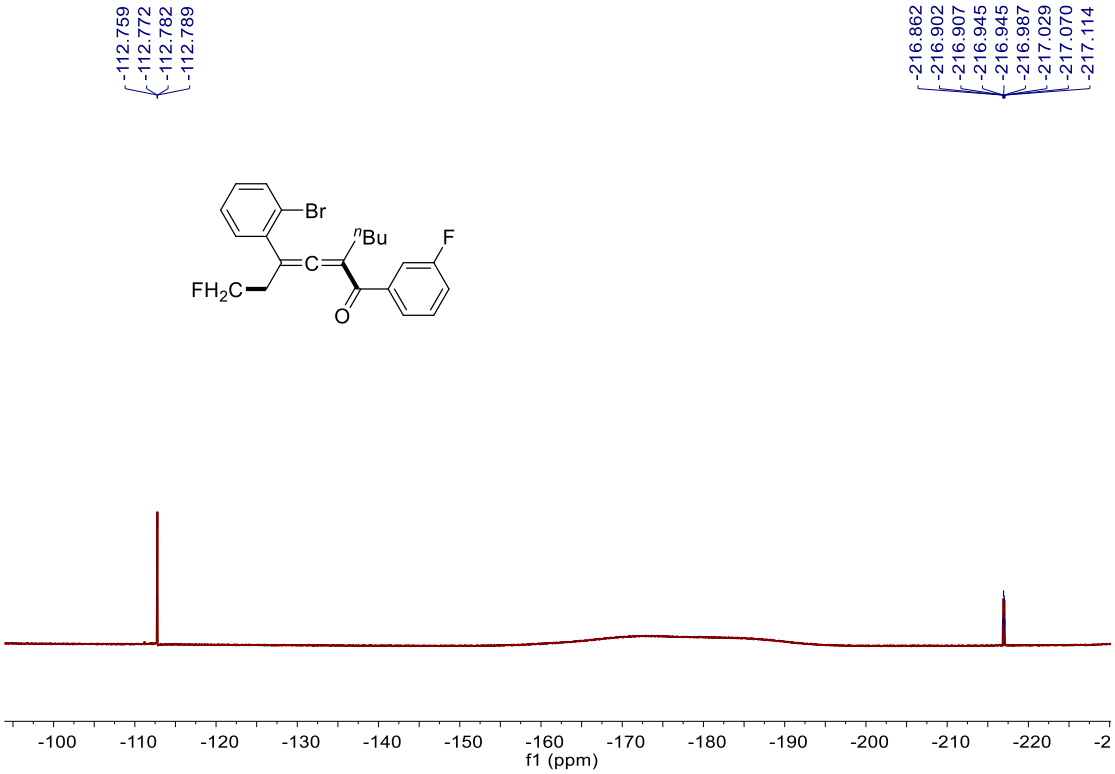
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4dn**.



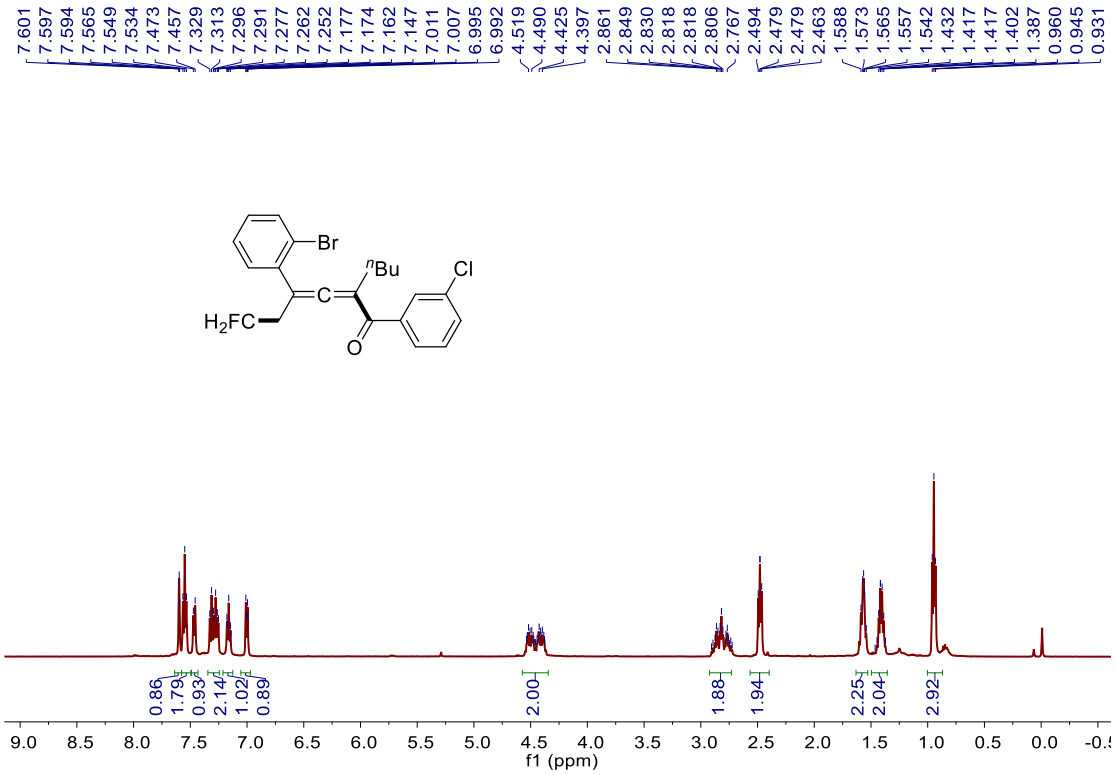
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4dn**.



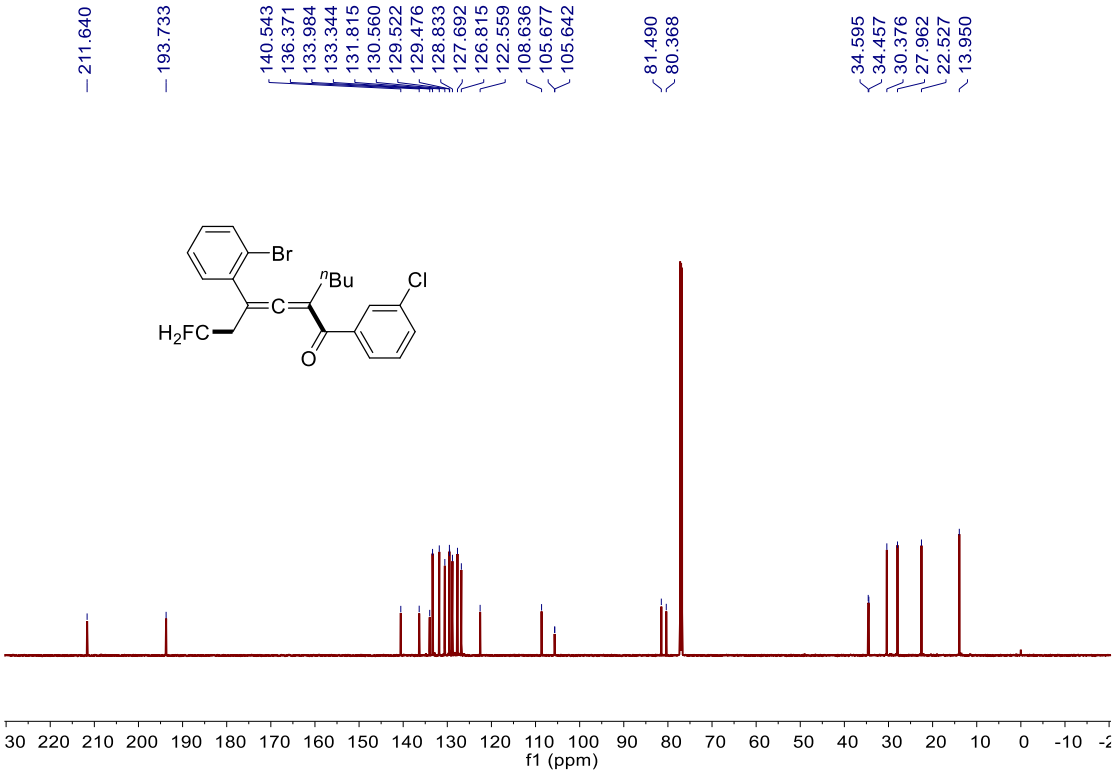
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4dn**.



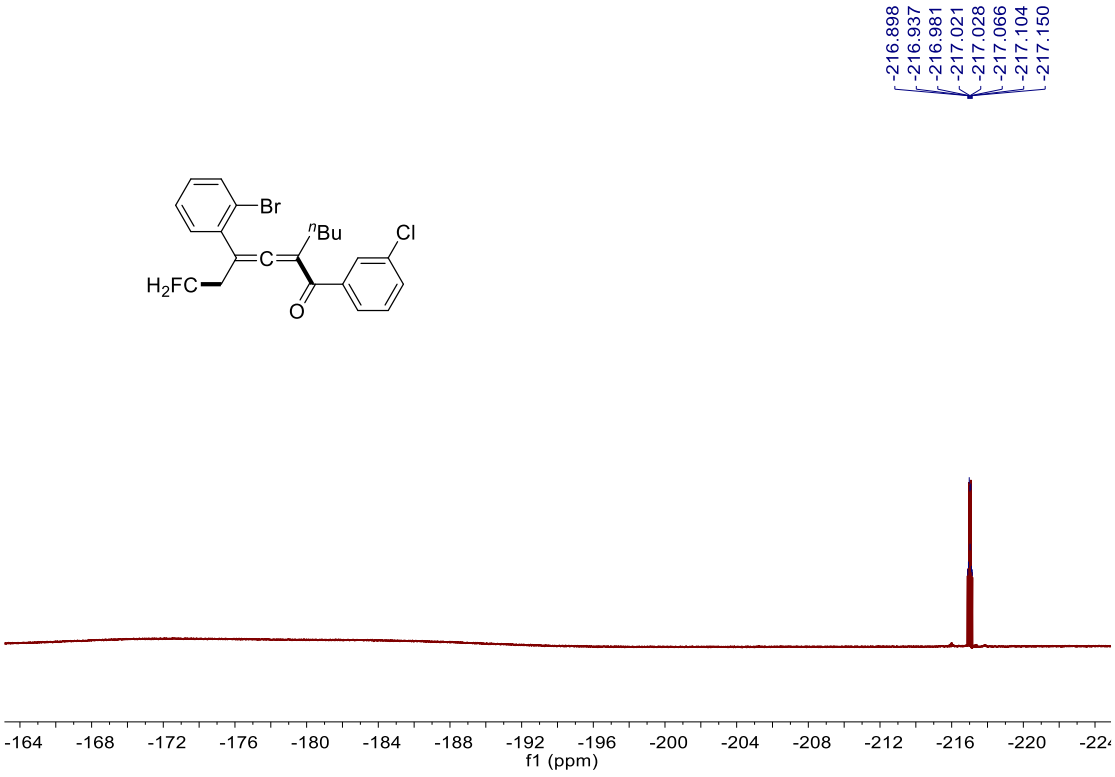
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4do**.



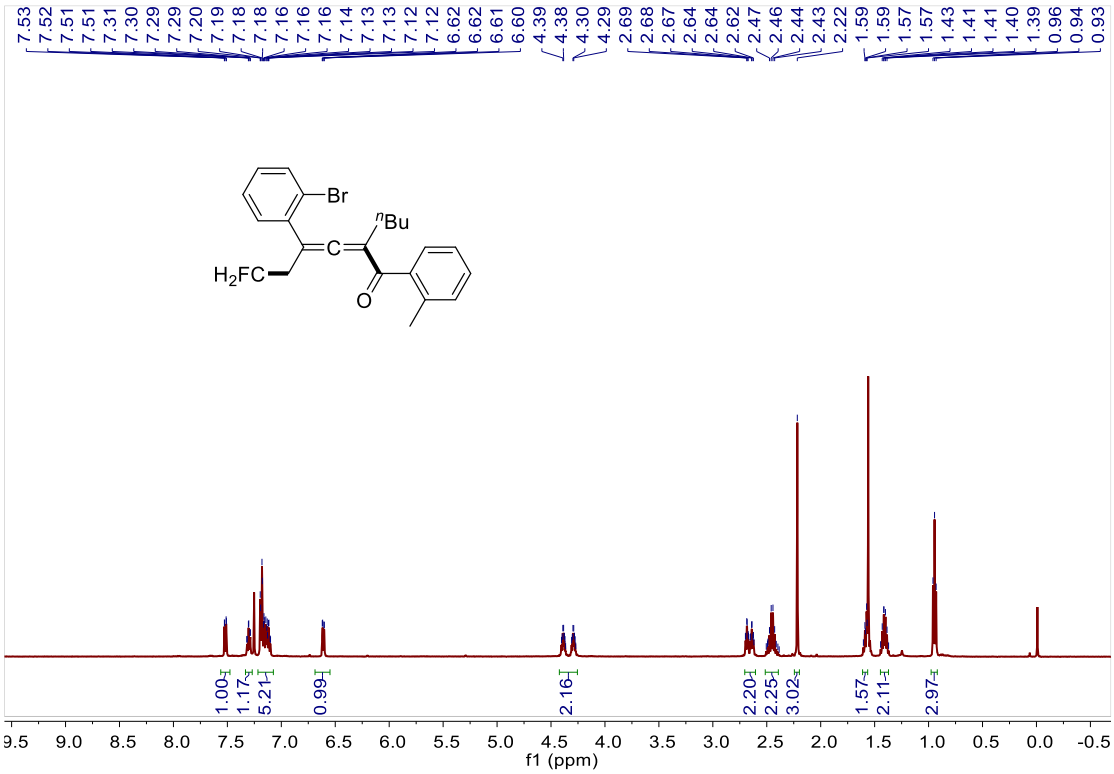
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4do**.



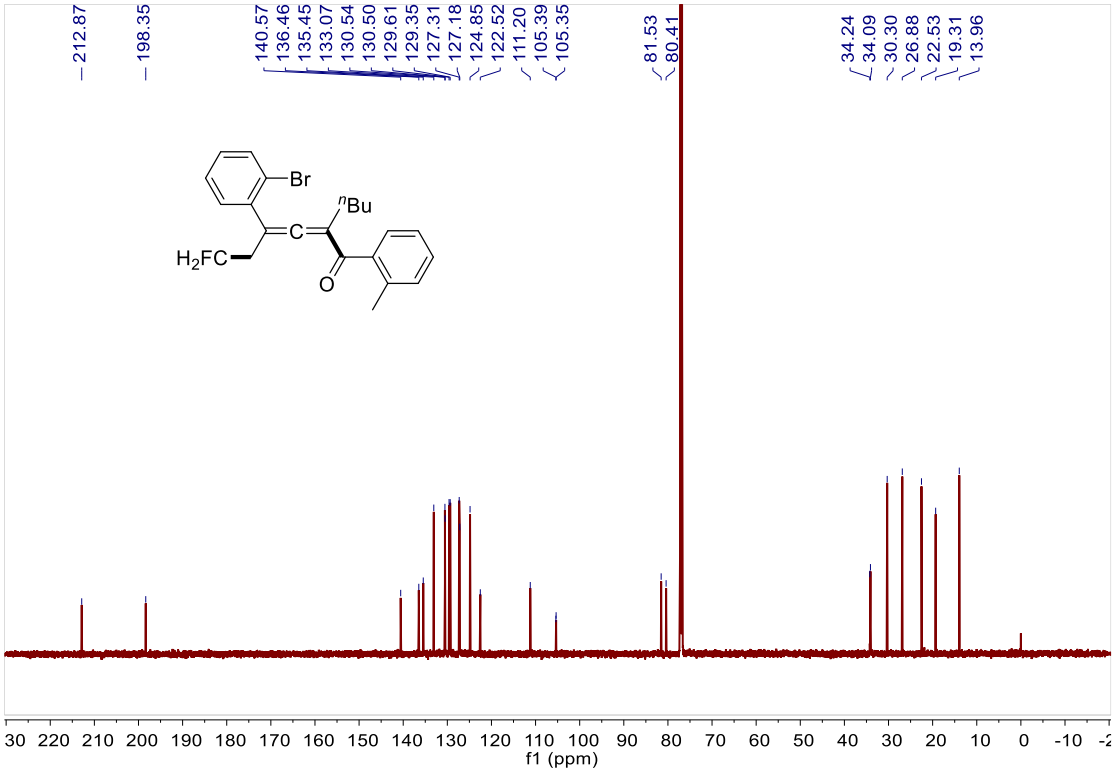
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4do**.



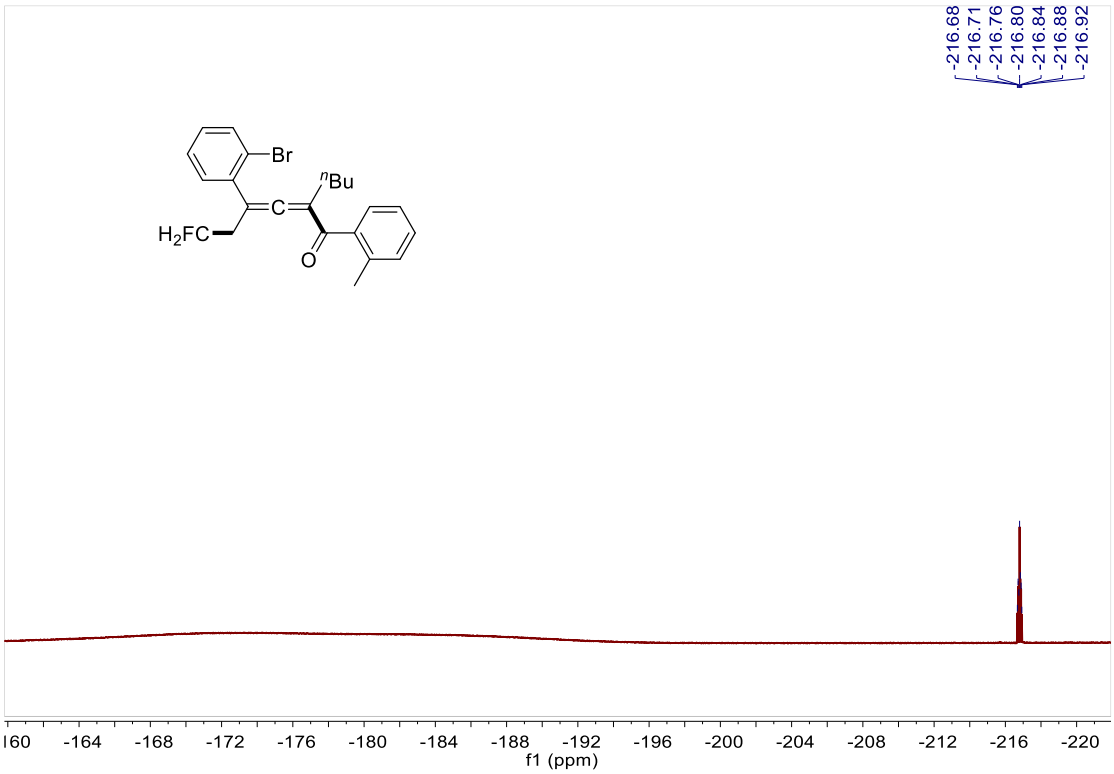
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4dp**.



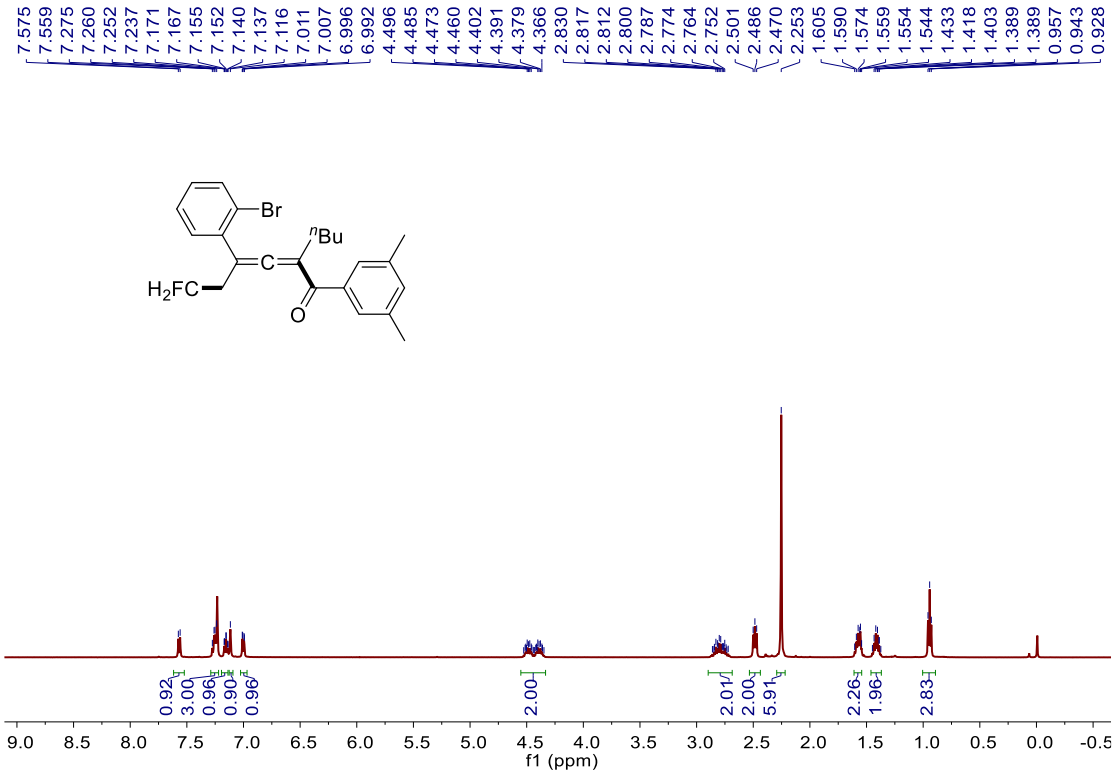
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4dp**.



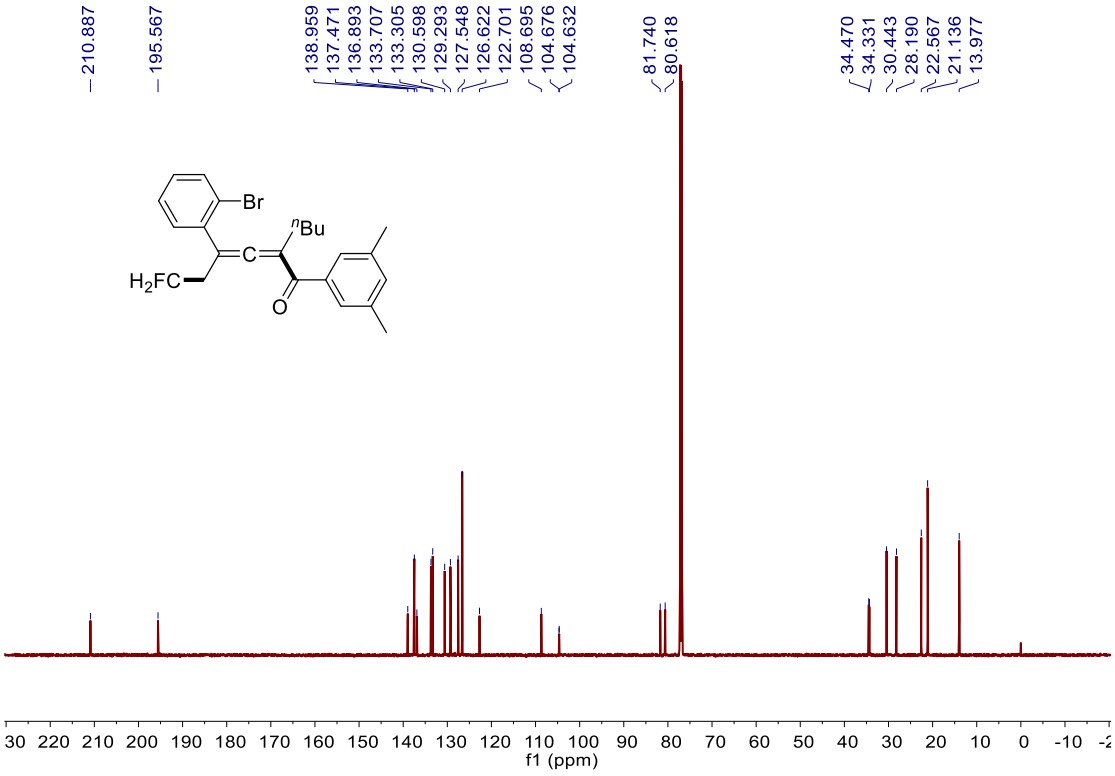
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4dp**.



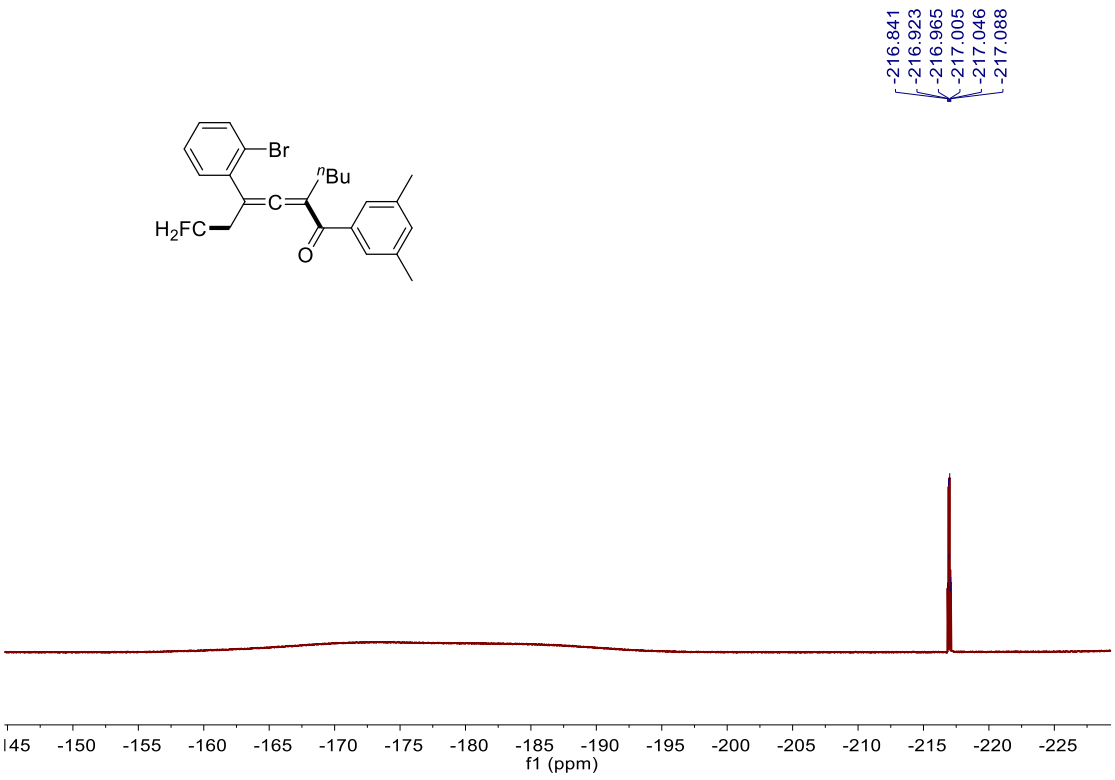
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **4dq**.



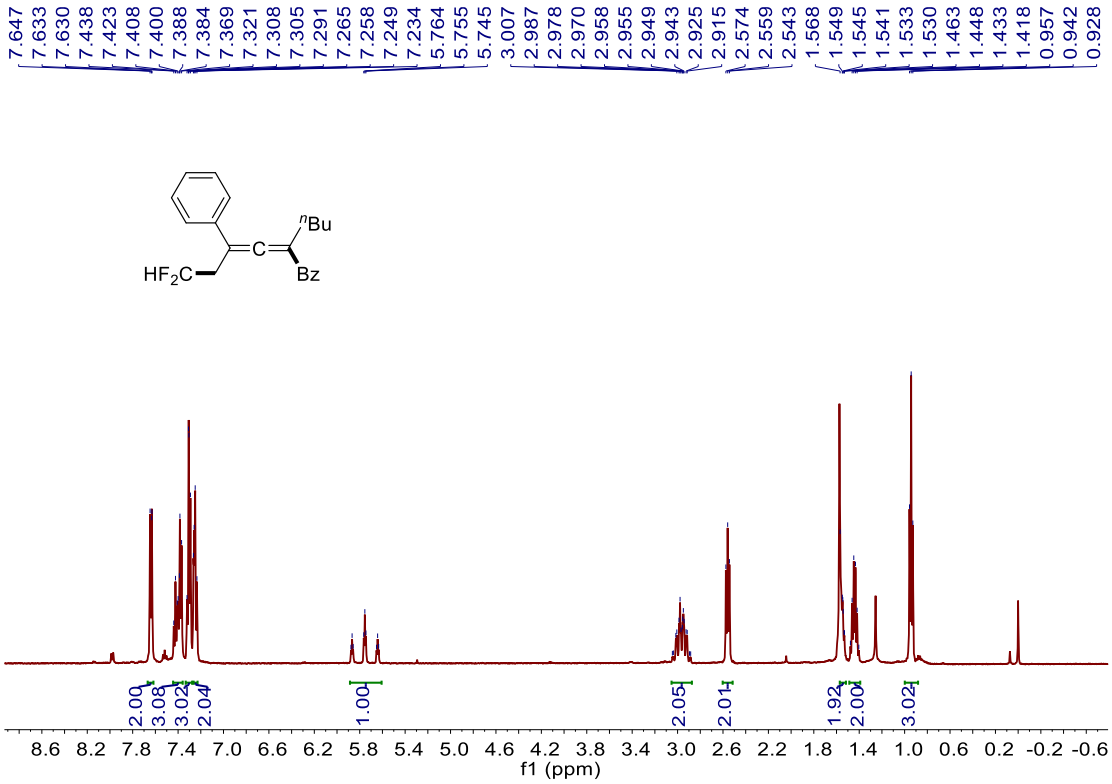
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4dq**.



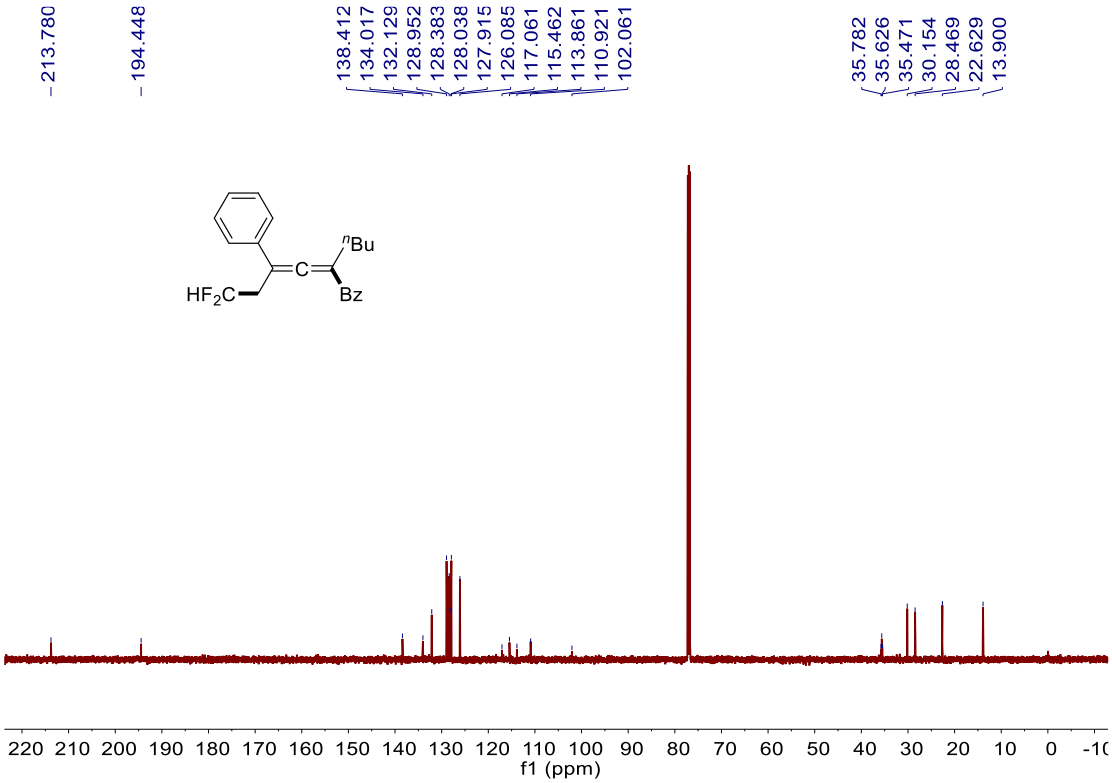
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **4dq**.



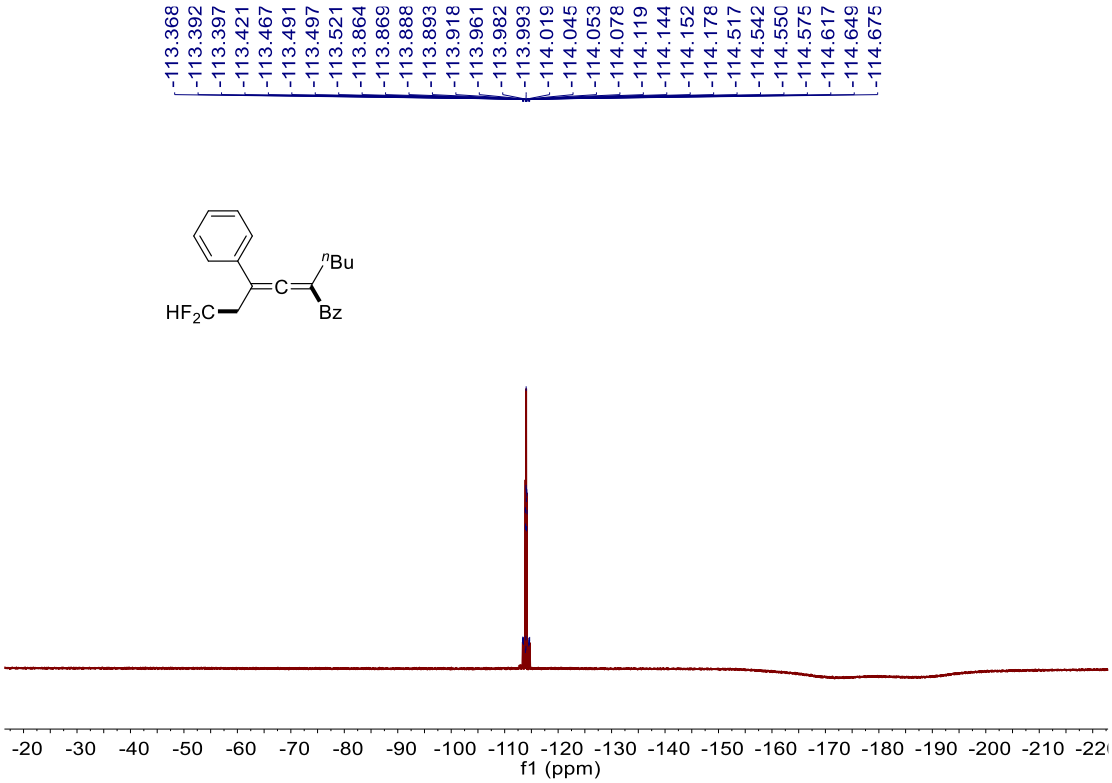
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5aa**.



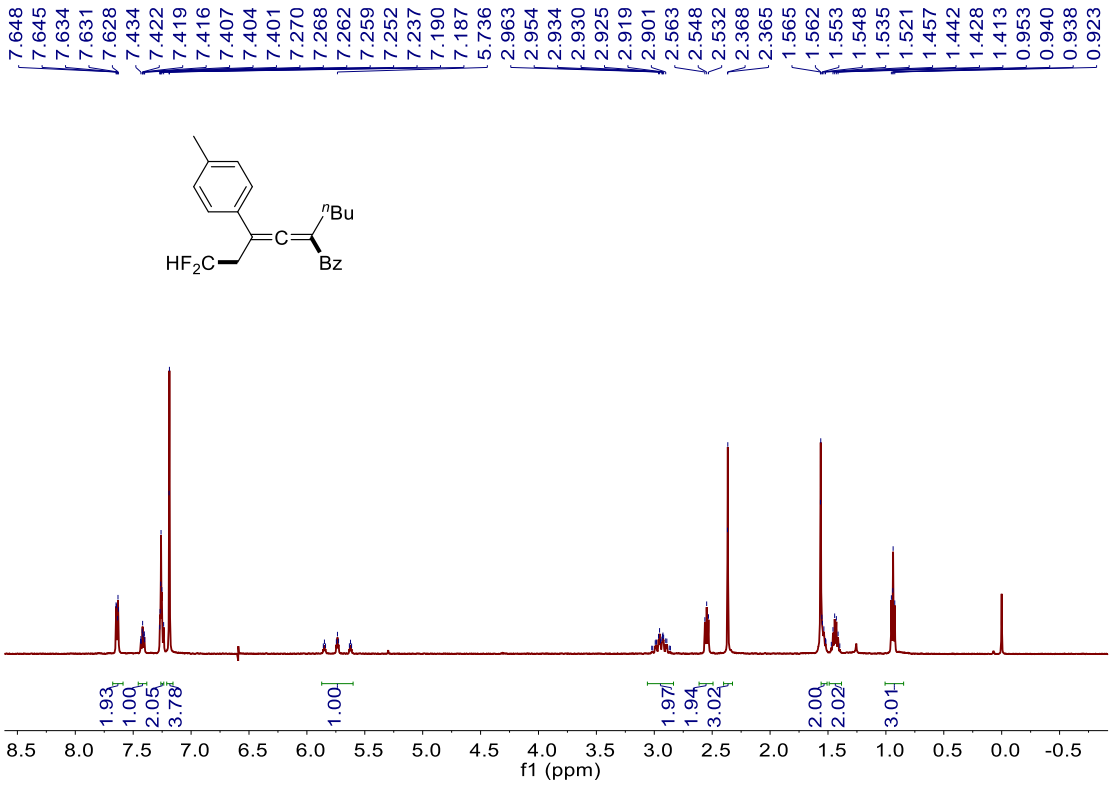
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5aa**.



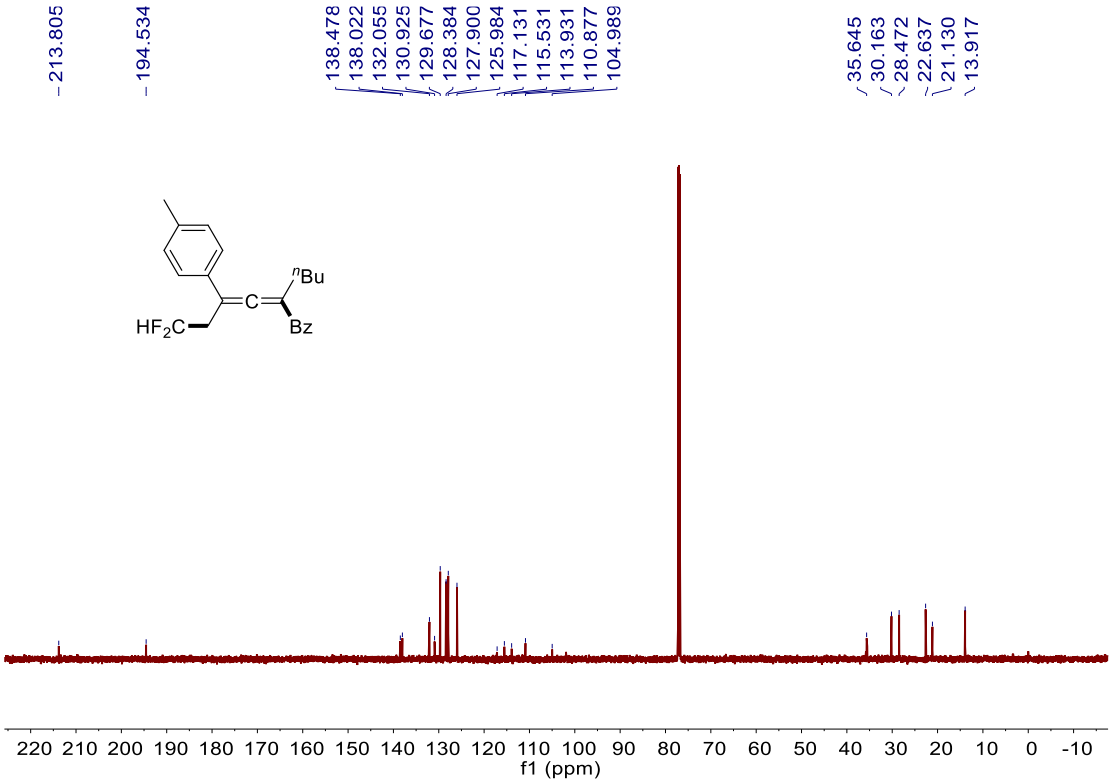
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5aa**.



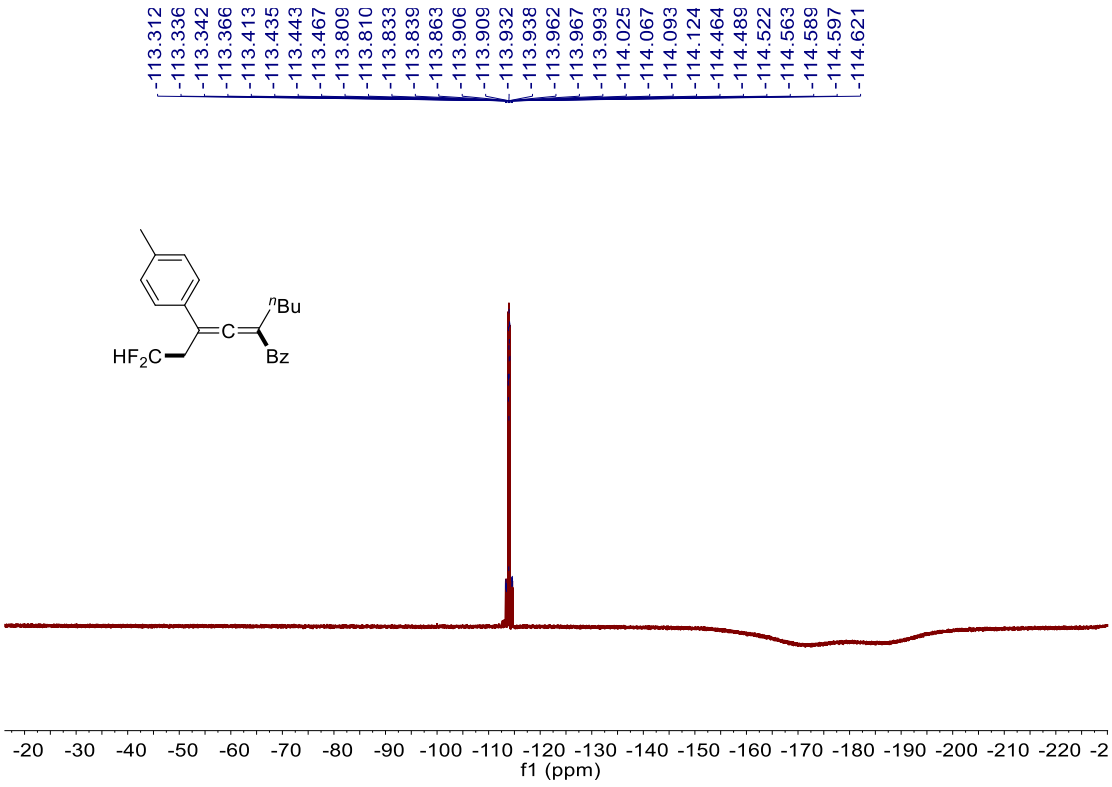
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ia**.



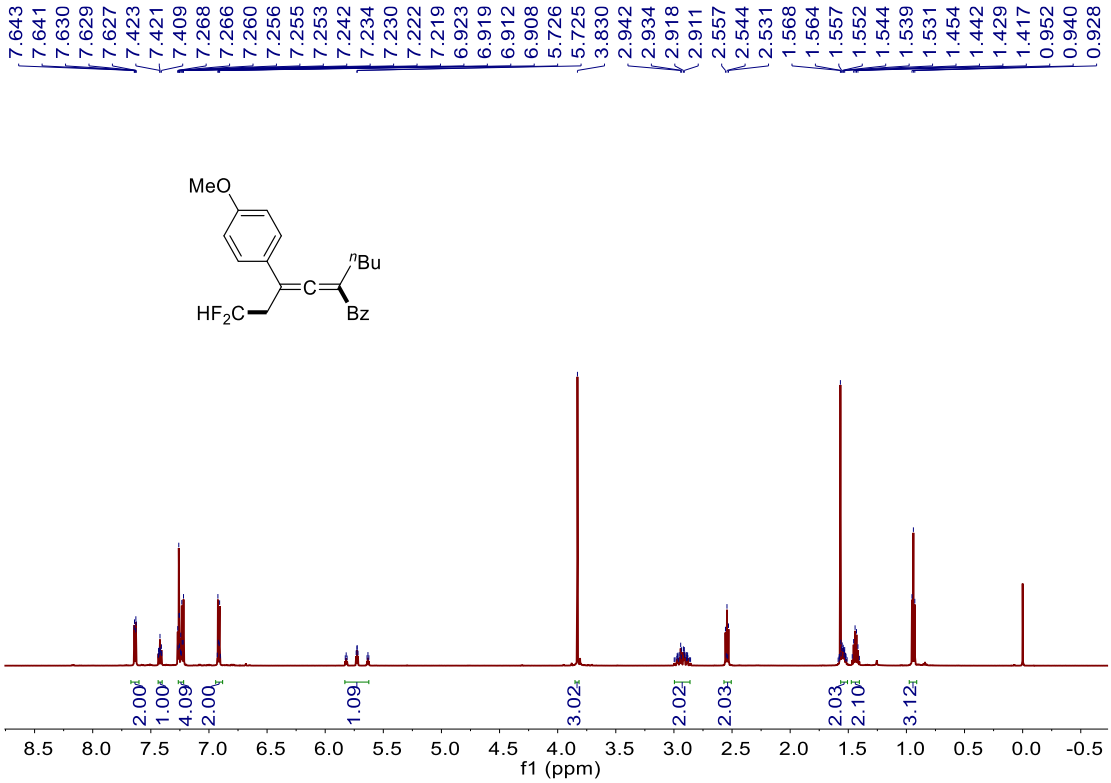
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ia**.



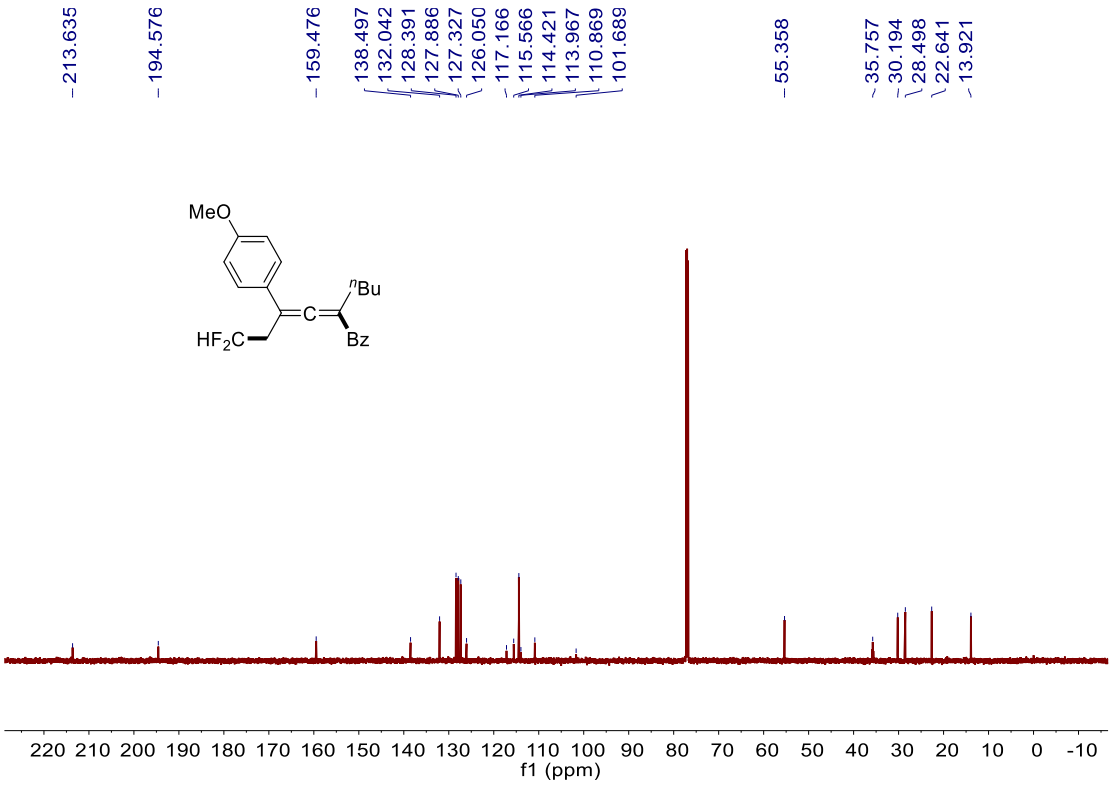
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ia**.



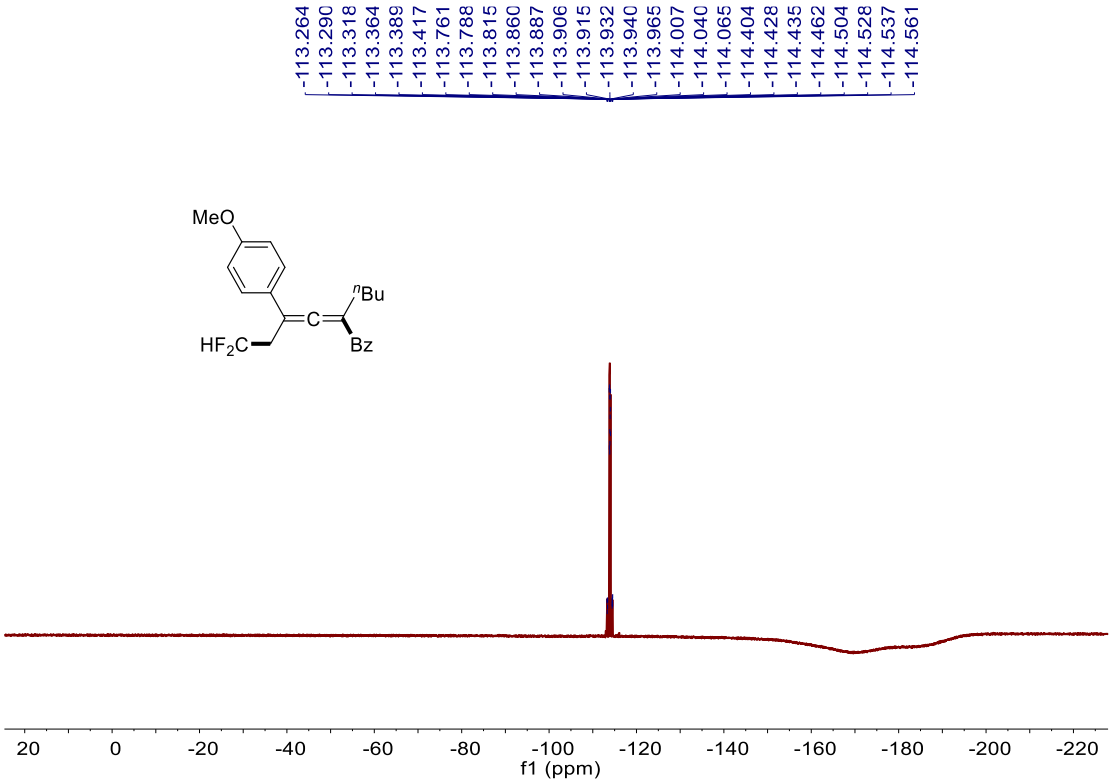
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ja**.



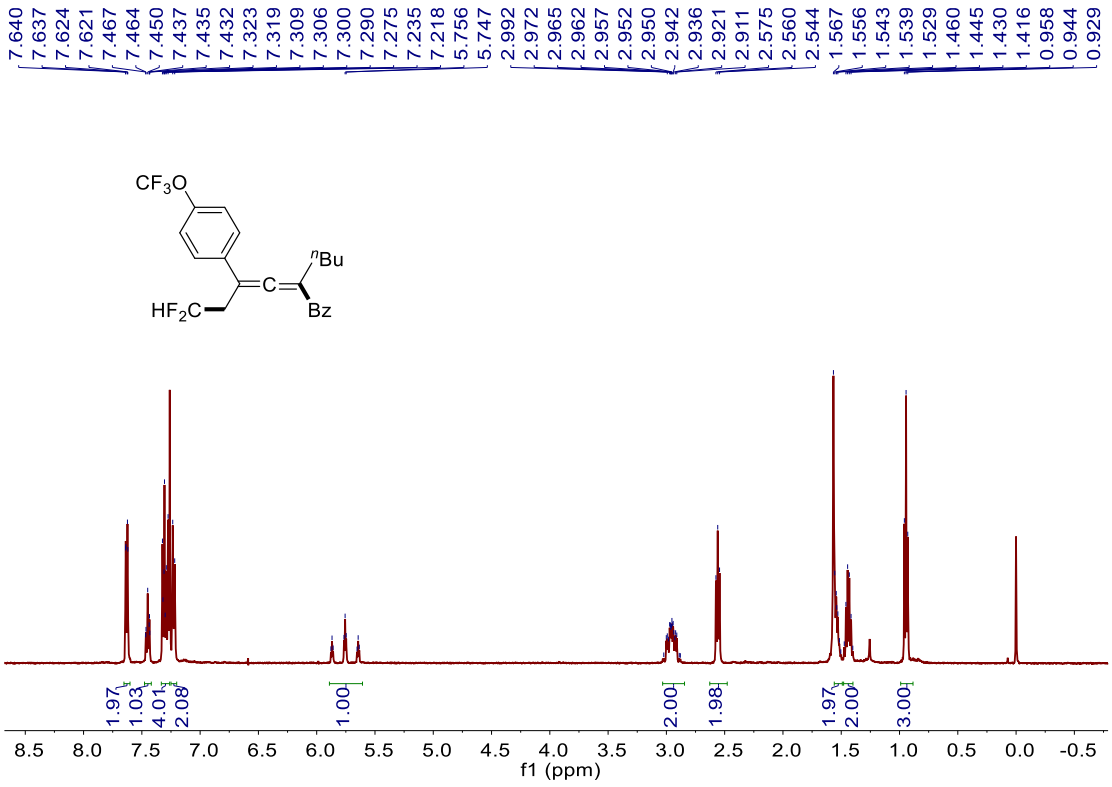
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ja**.



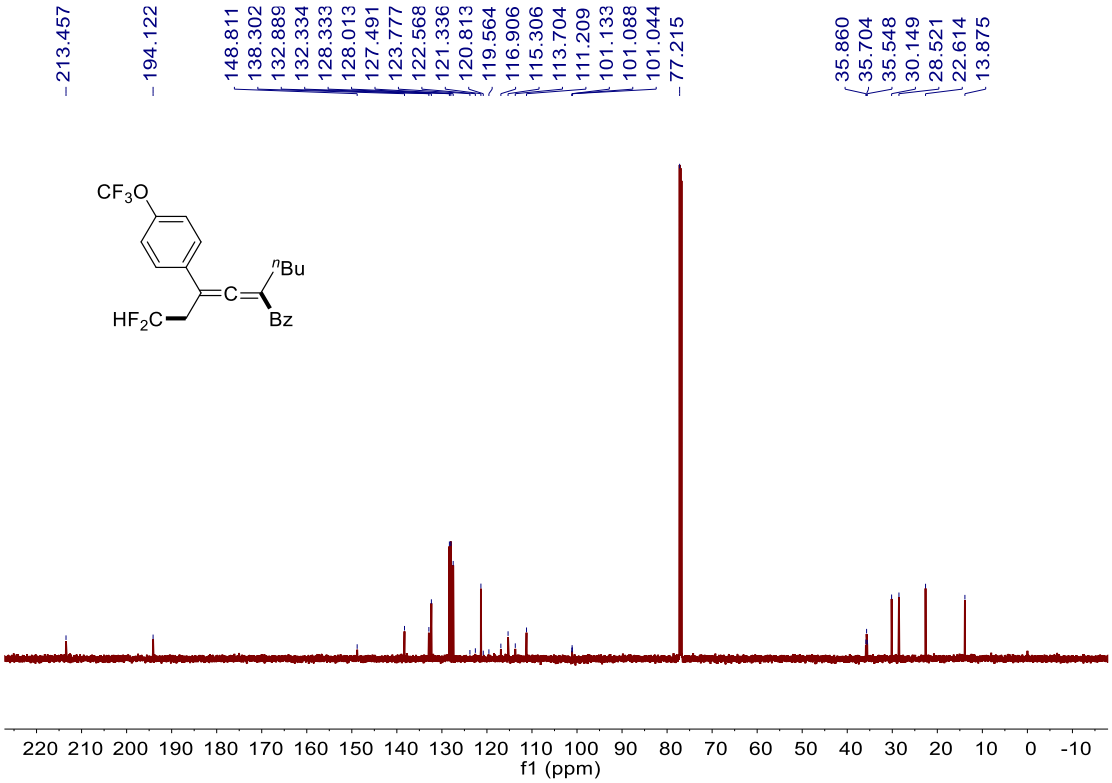
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ja**.



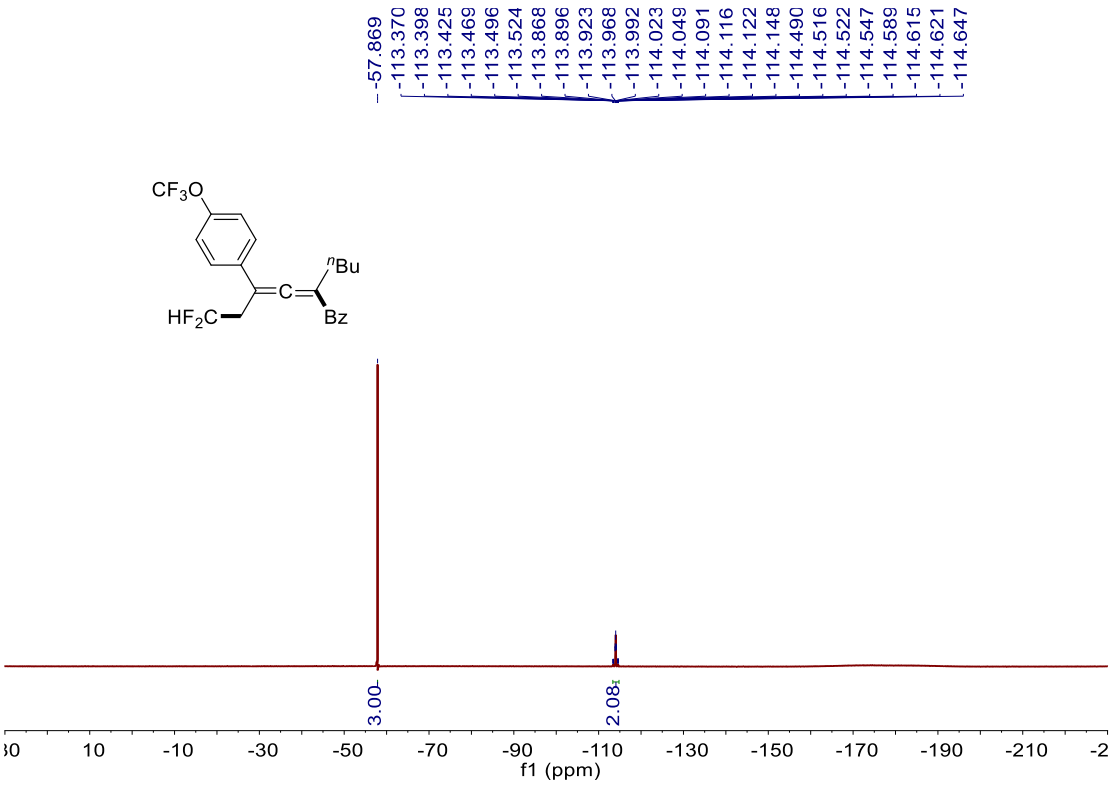
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ka**.



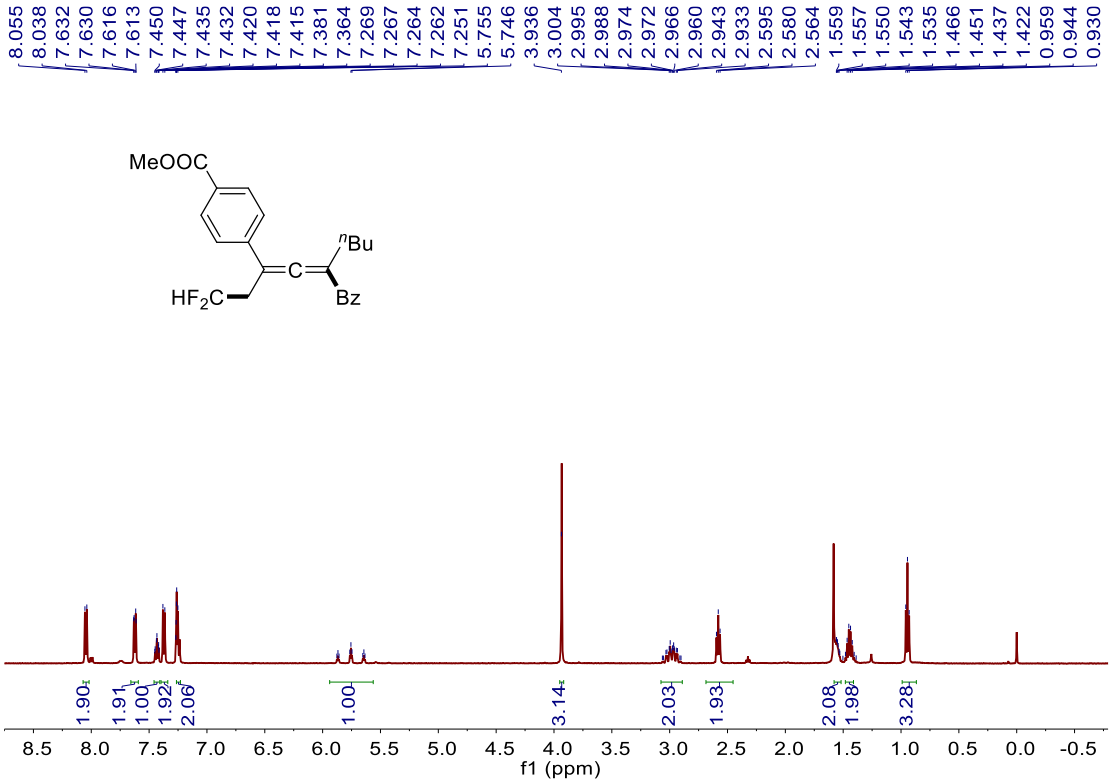
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ka**.



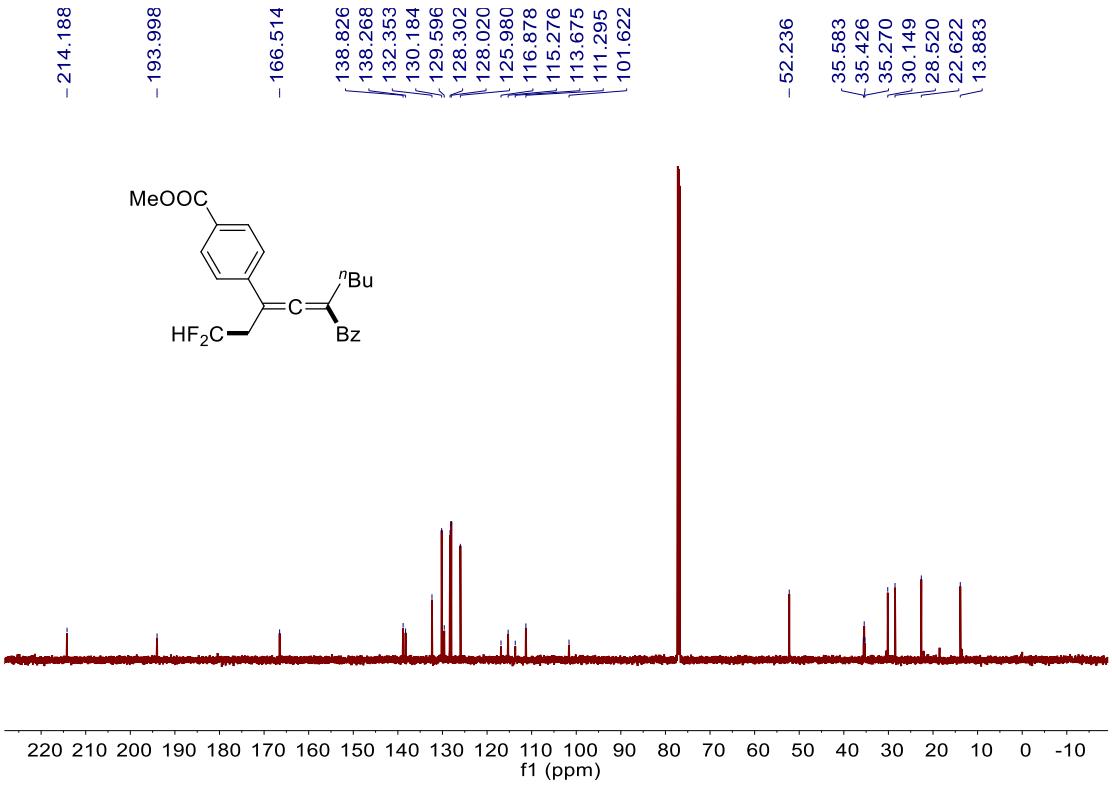
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ka**.



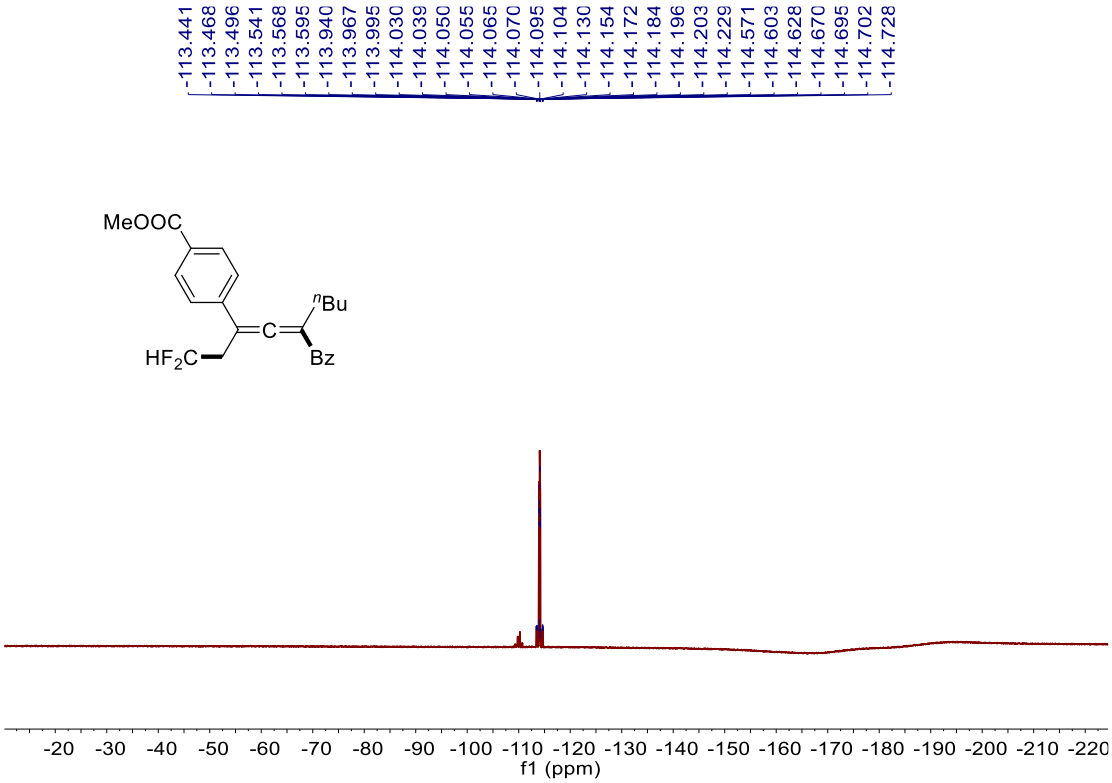
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5la**.



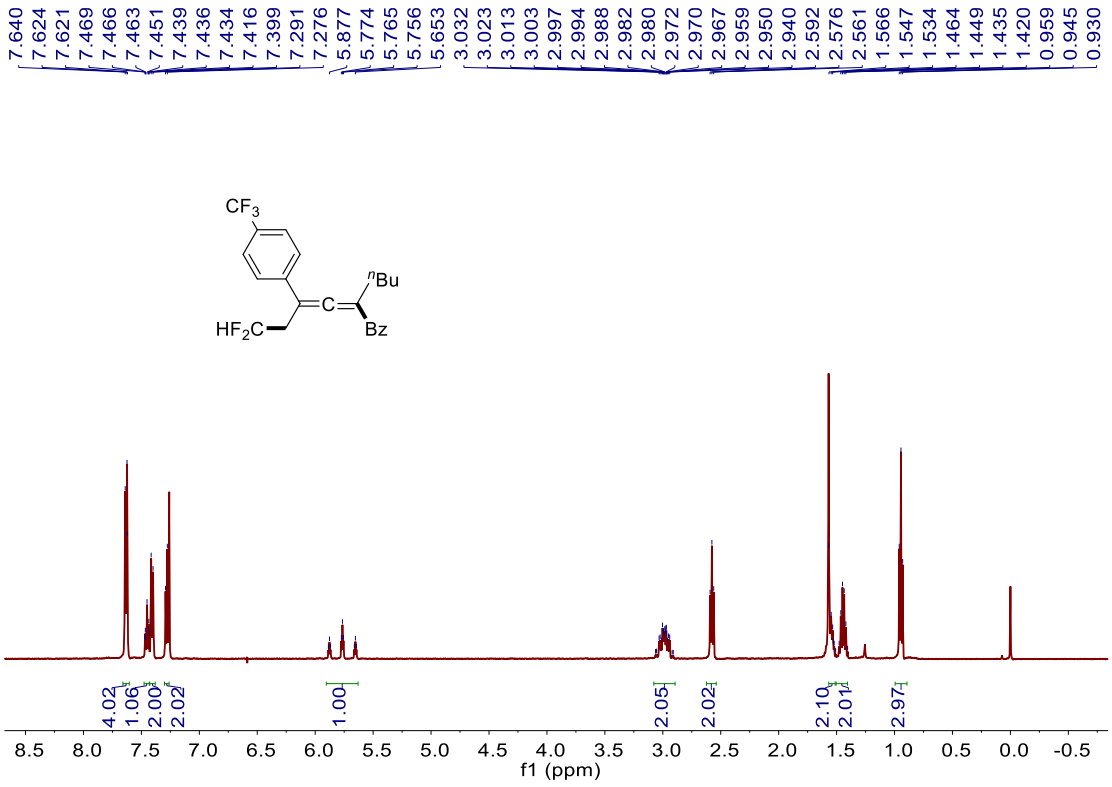
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5la**.



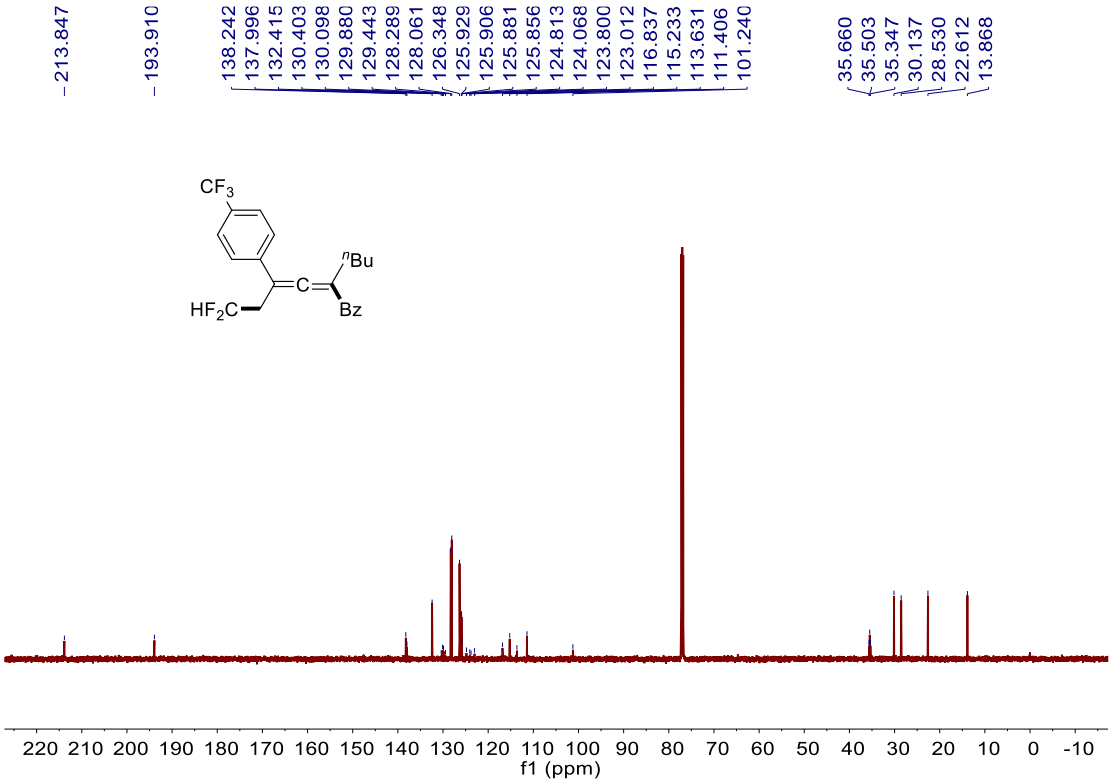
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5la**.



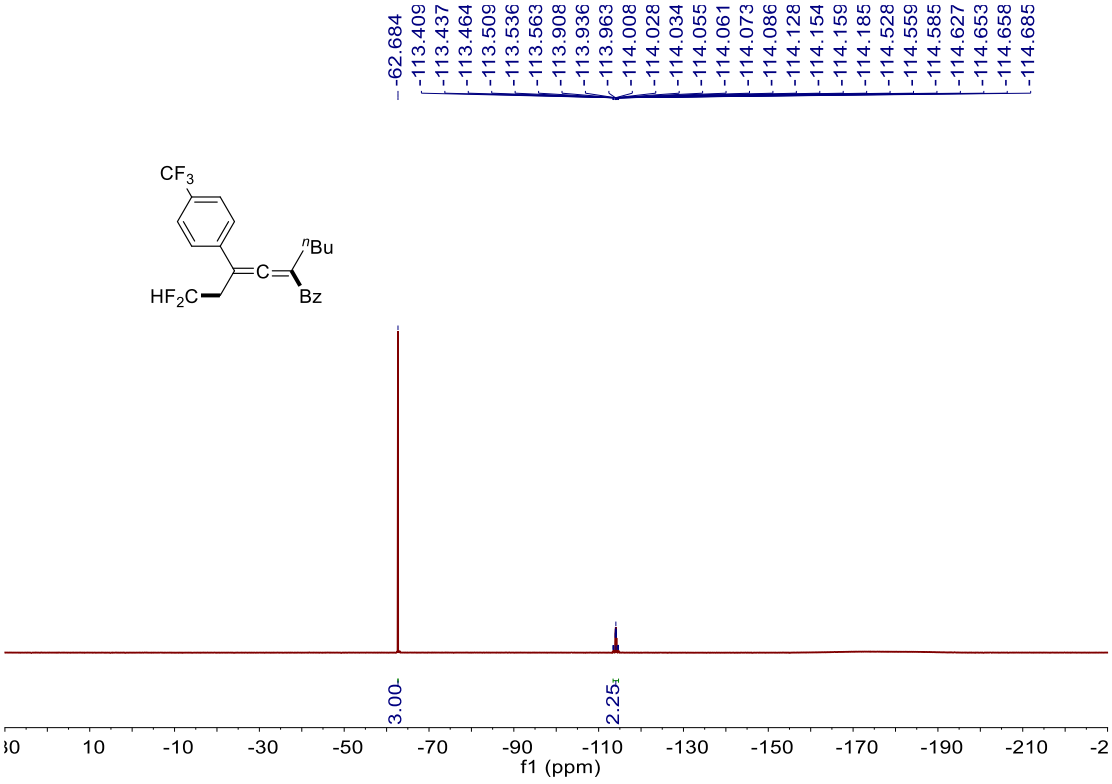
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ma**.



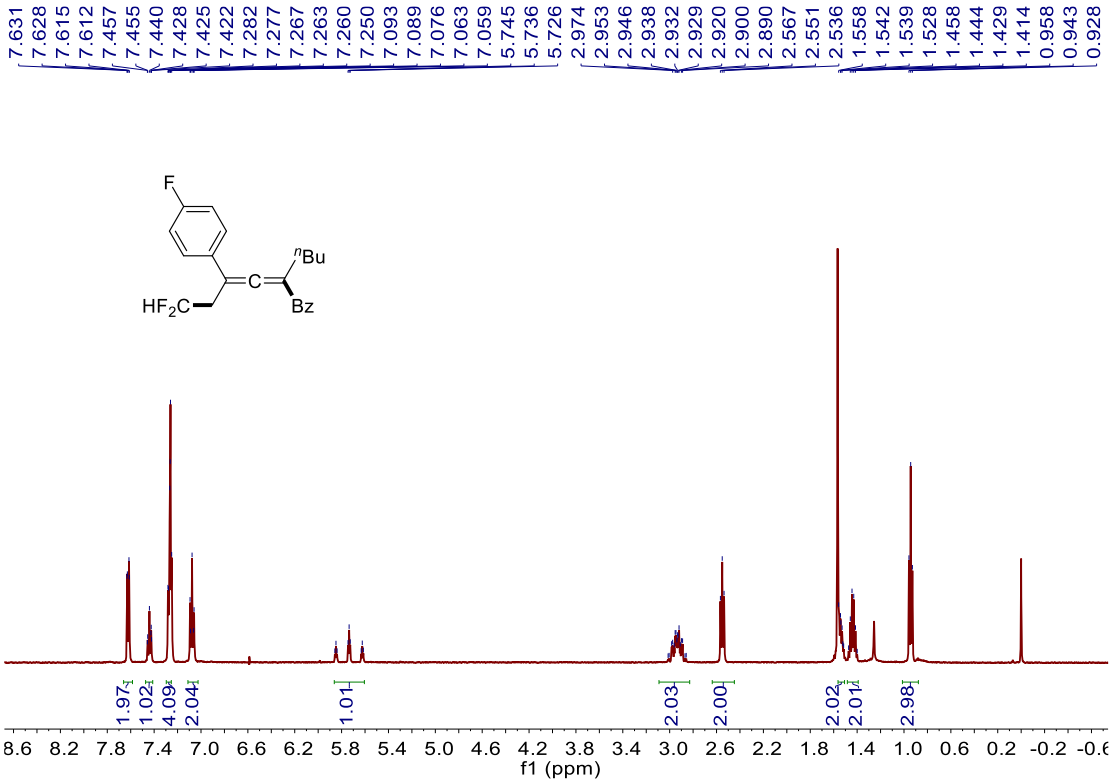
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ma**.



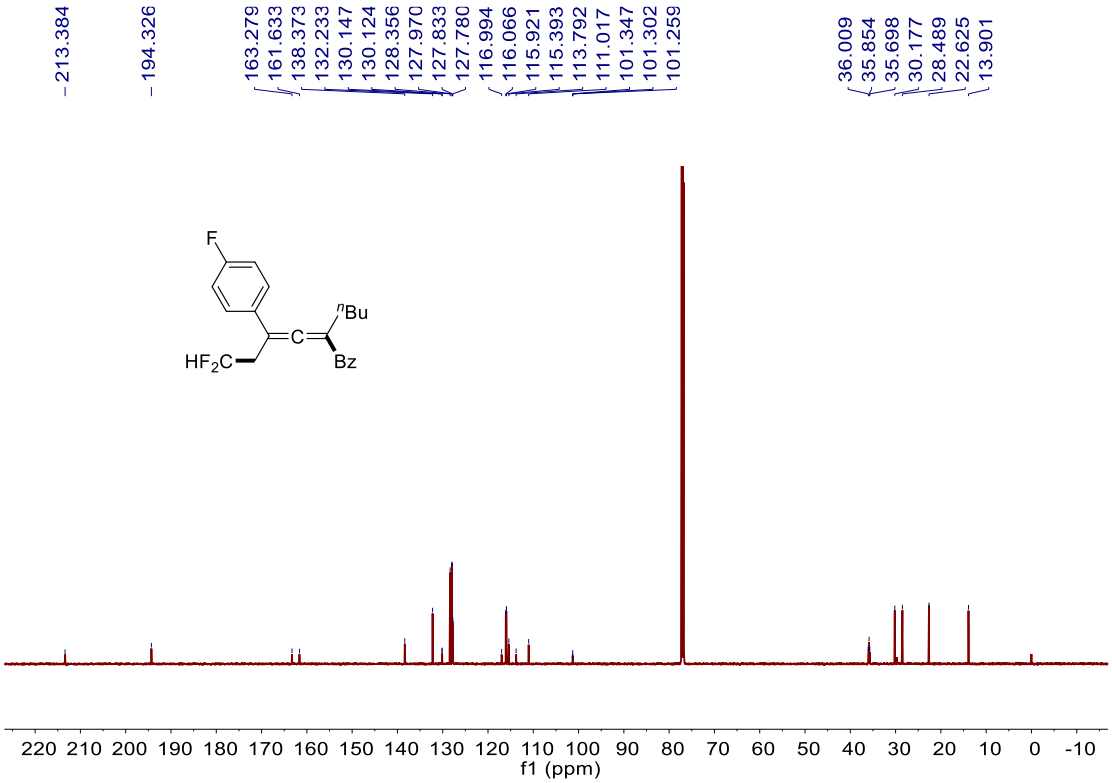
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ma**.



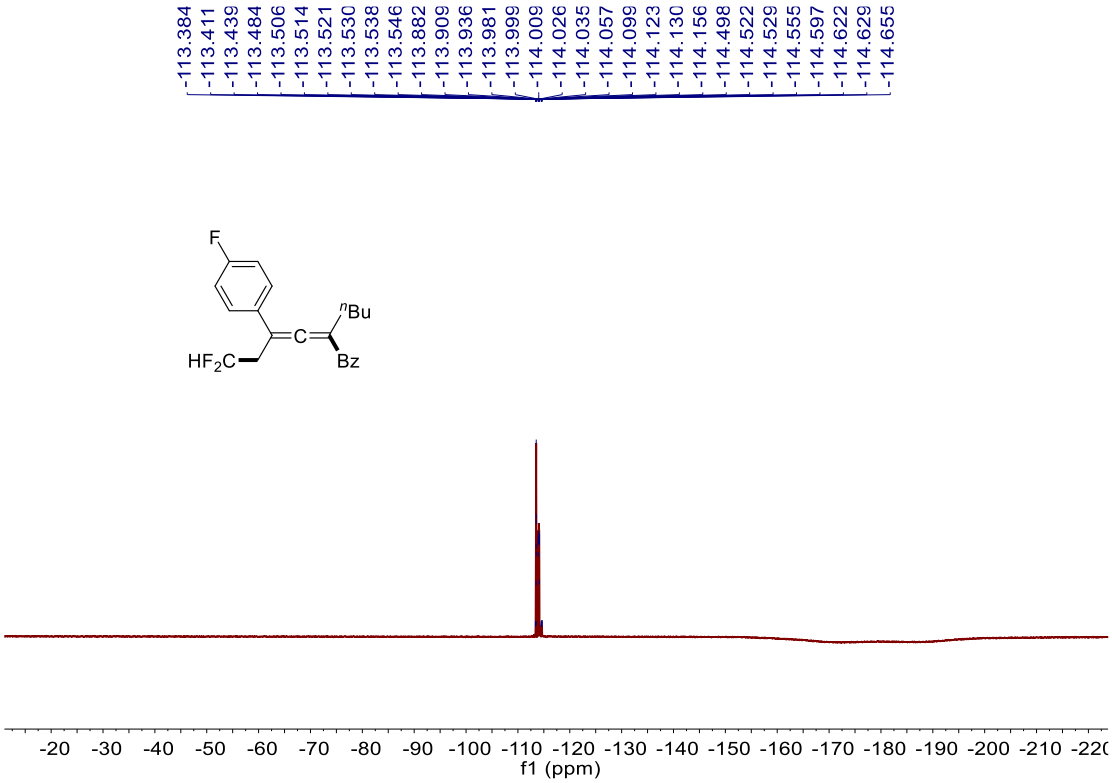
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5na**.



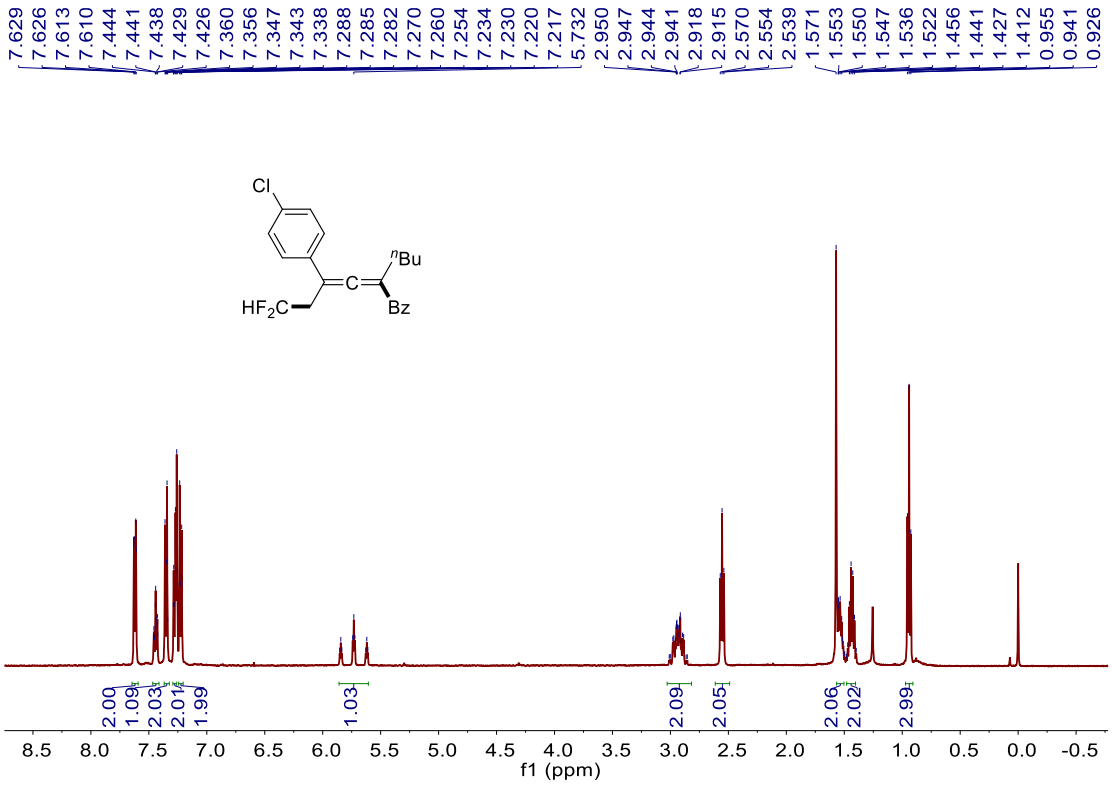
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5na**.



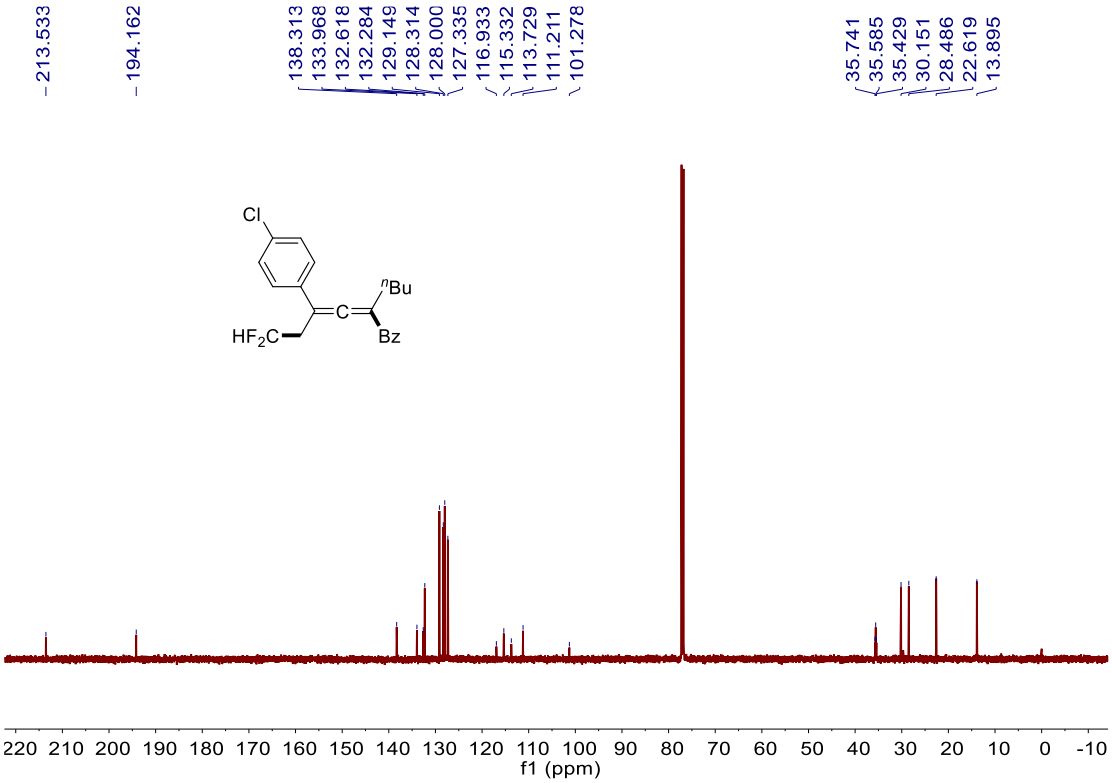
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5na.**



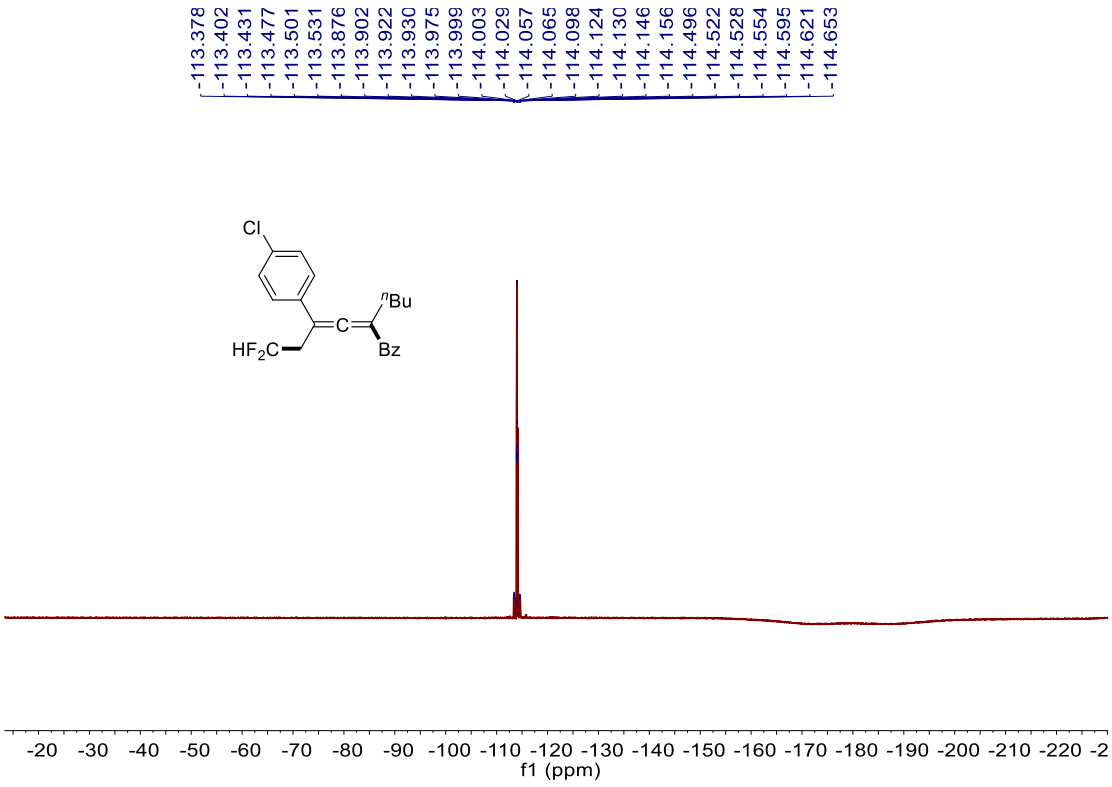
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5oa**.



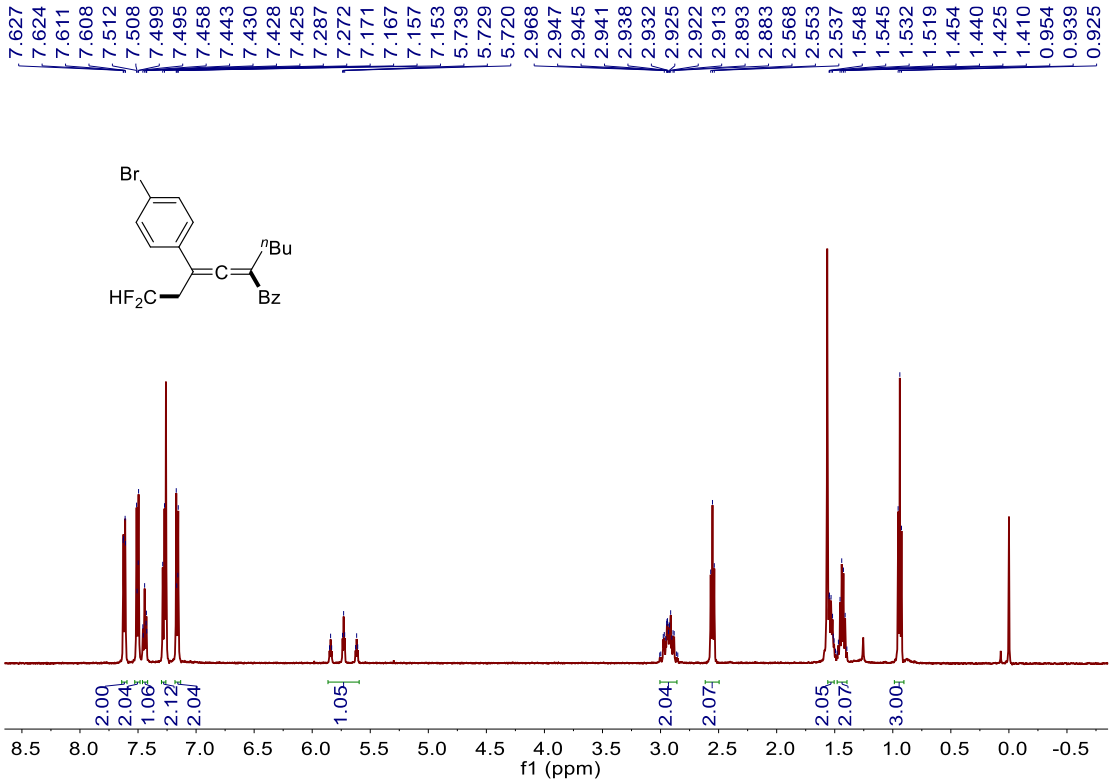
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5oa**.



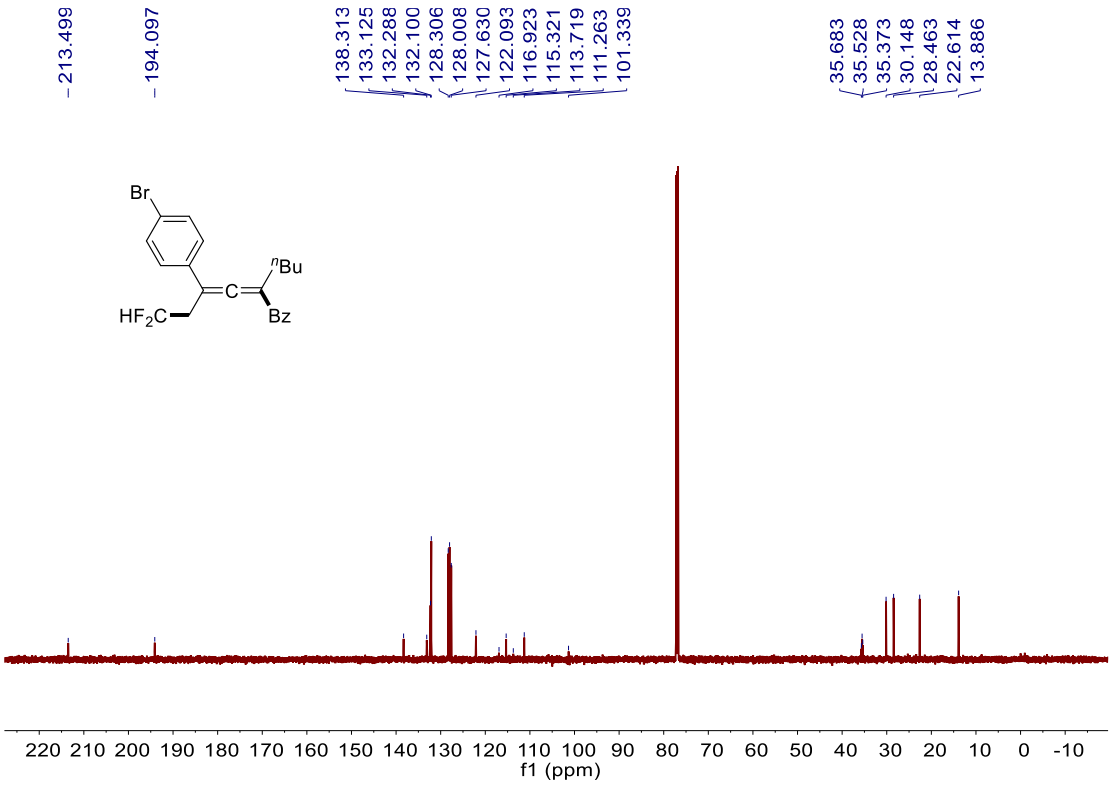
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5oa**.



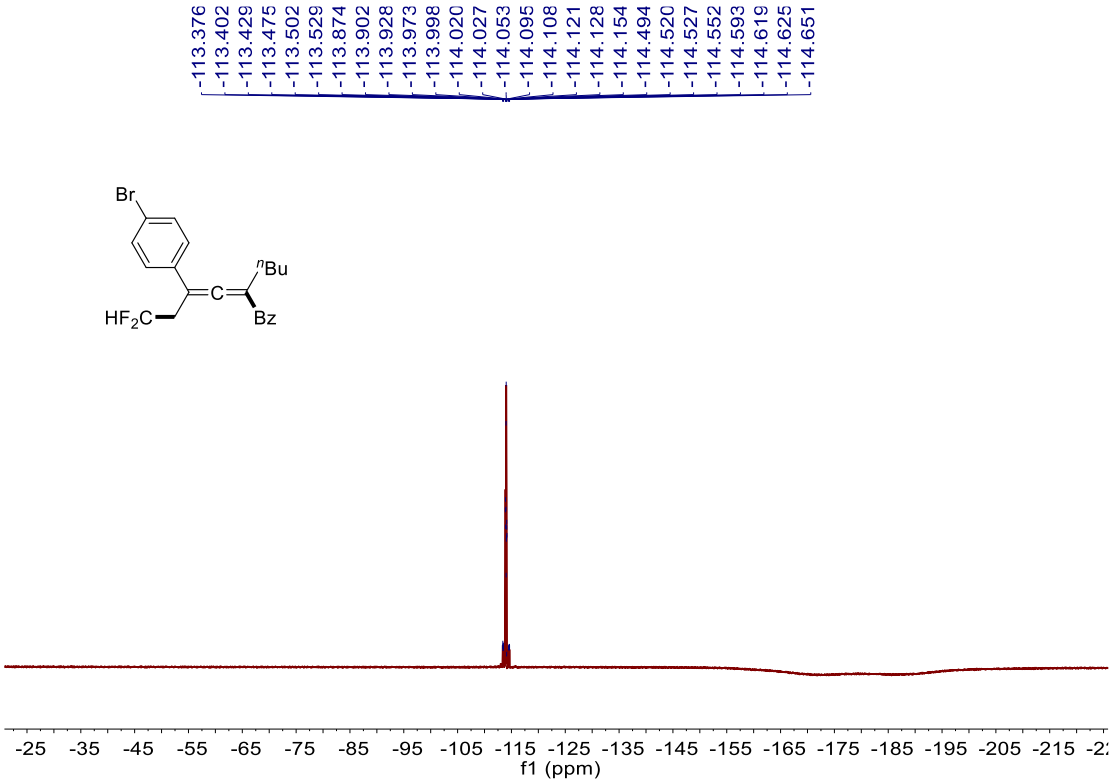
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5pa**.



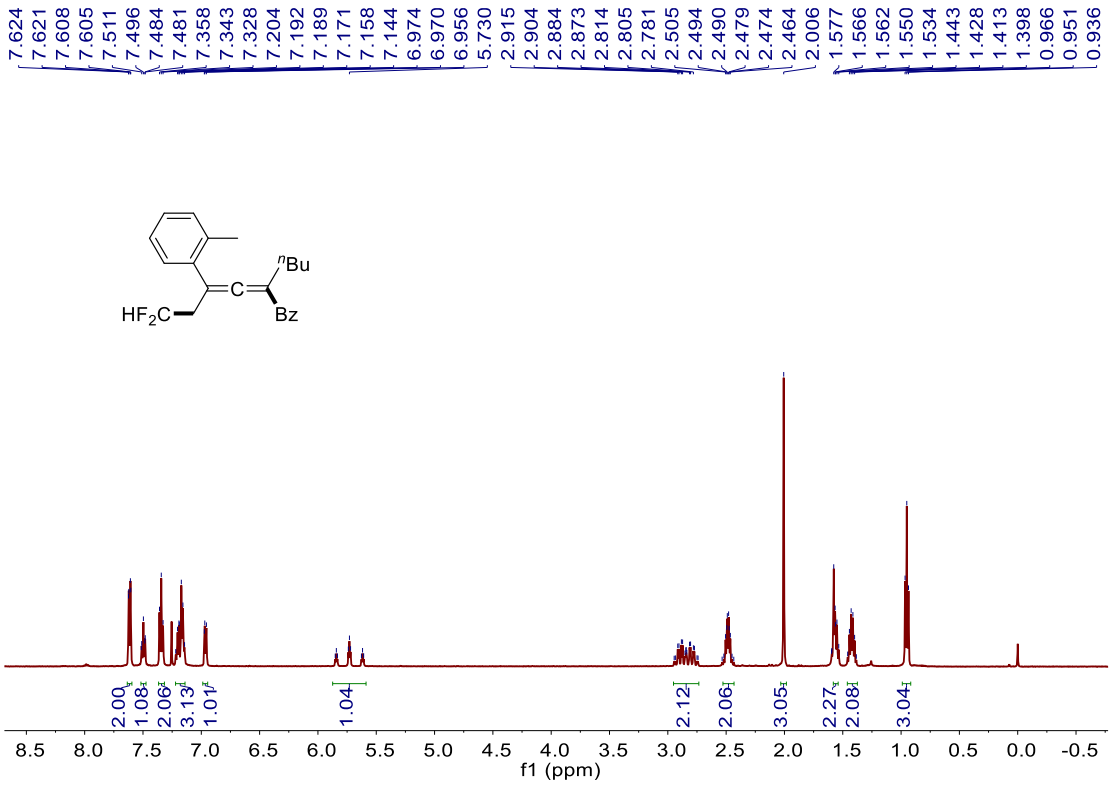
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5pa**.



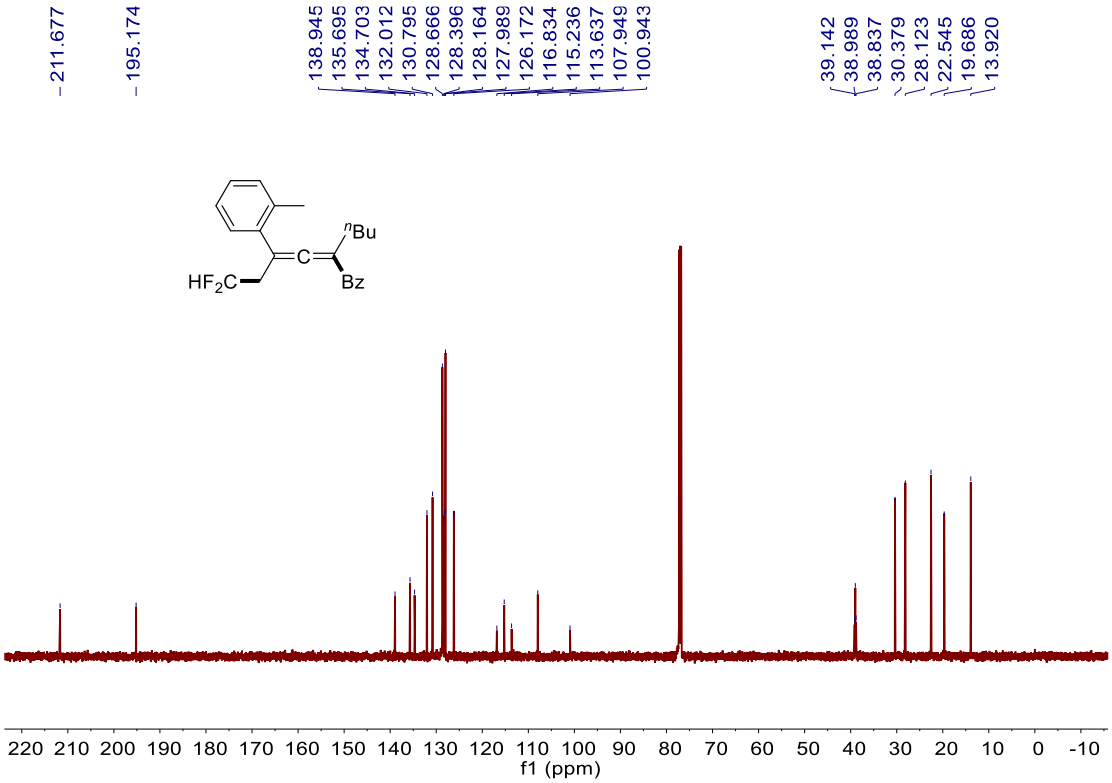
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5pa**.



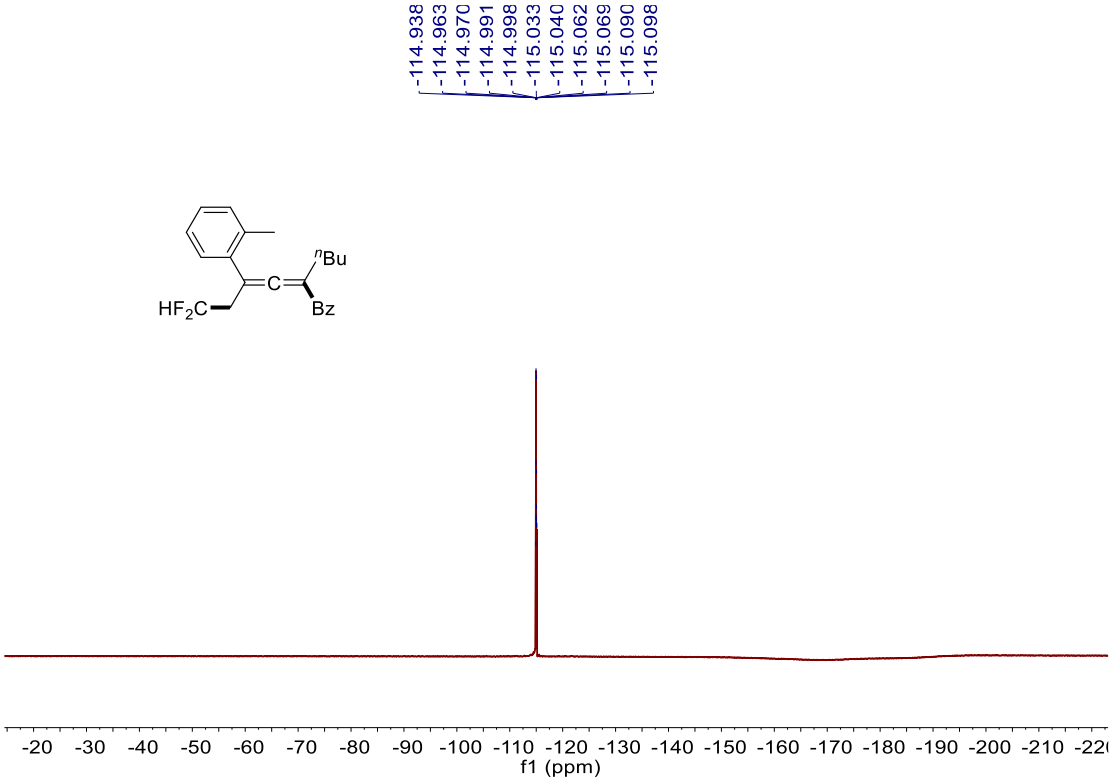
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ba**.



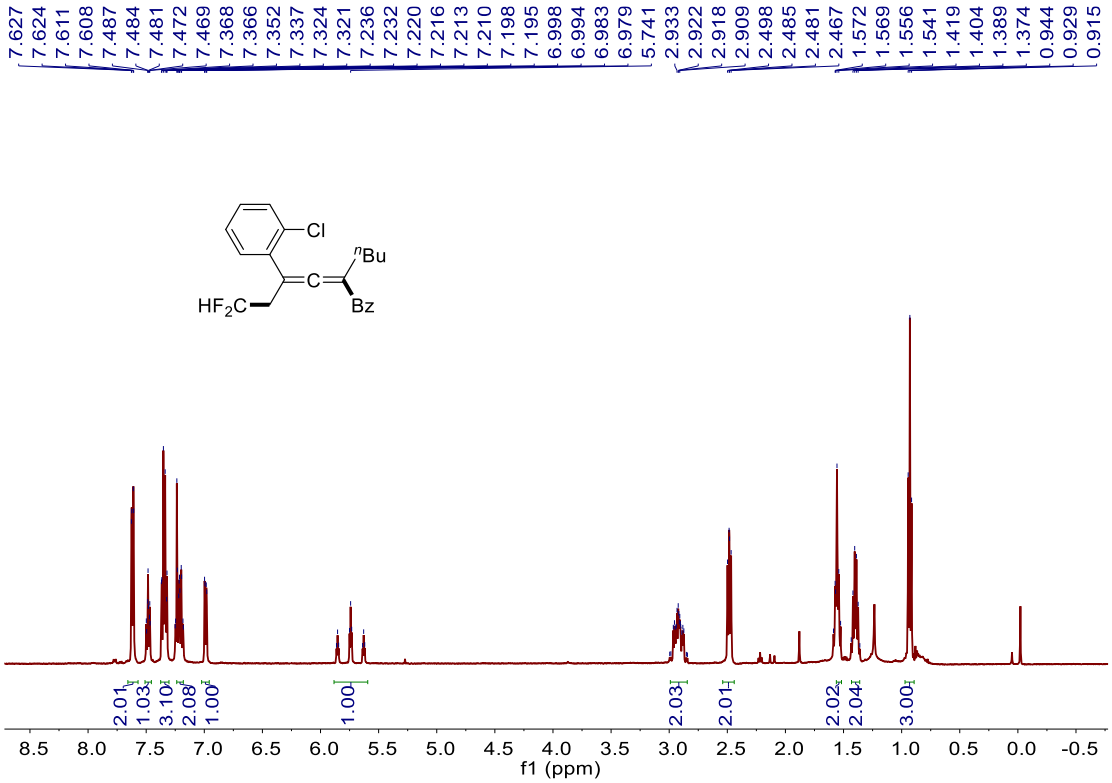
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ba**.



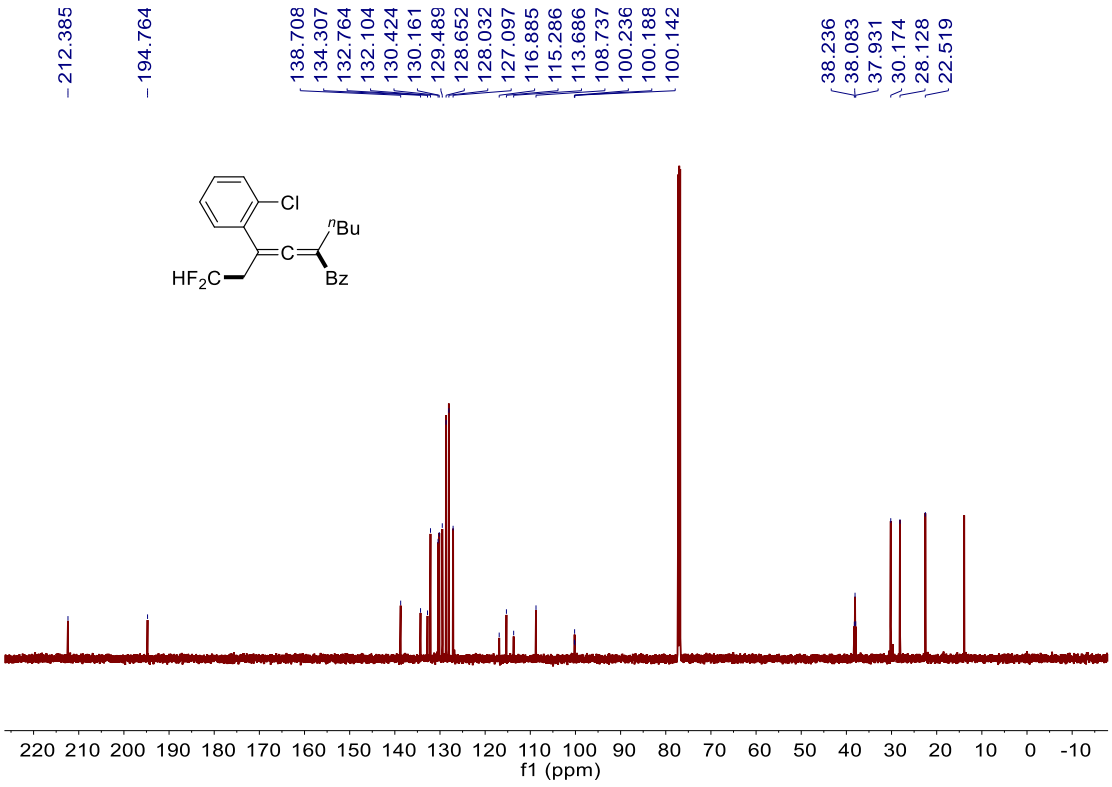
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ba**.



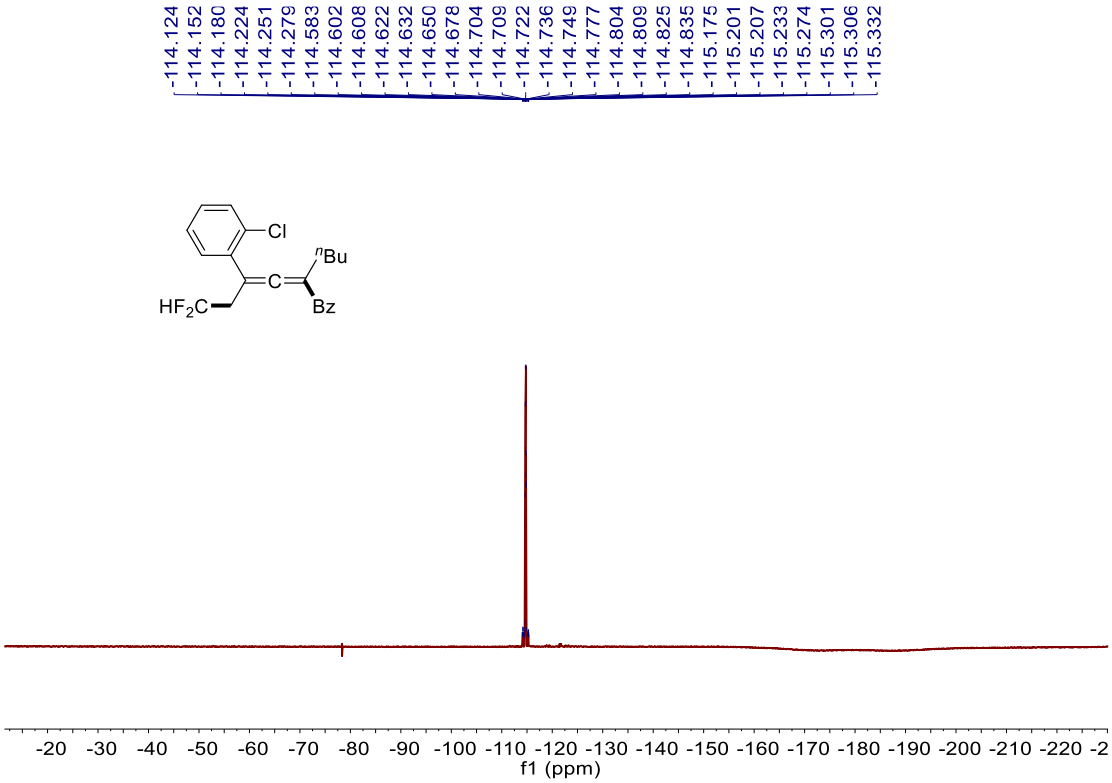
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ca**.



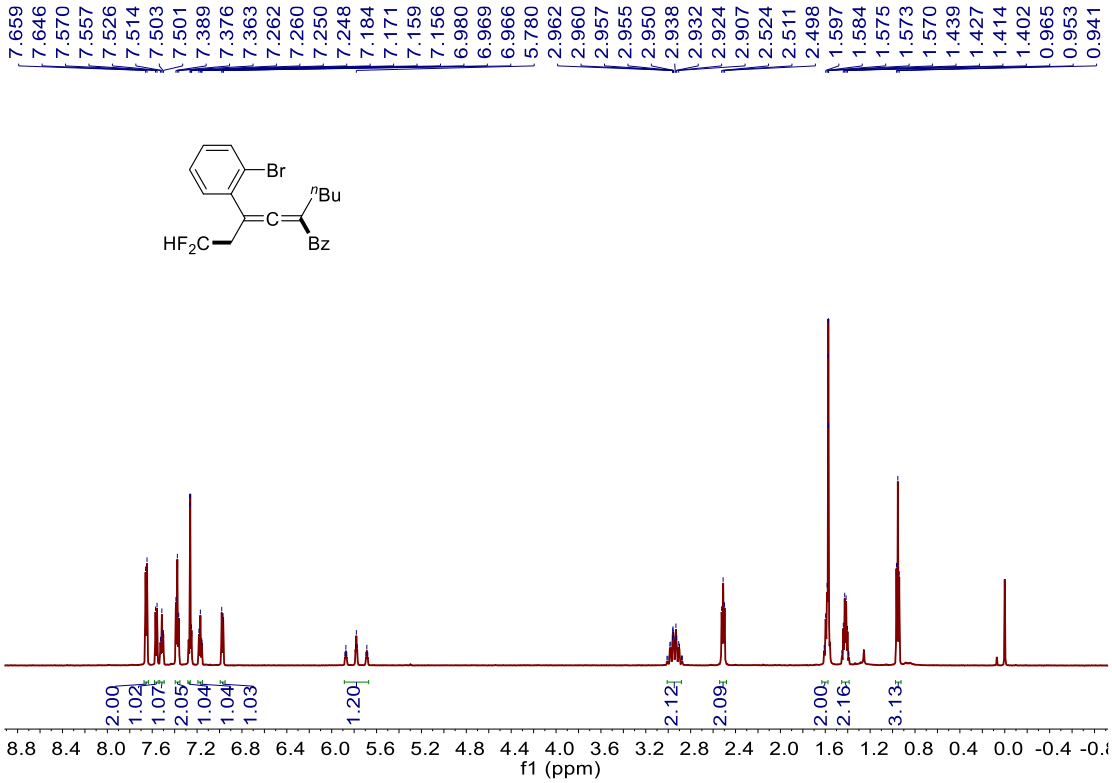
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ca**.



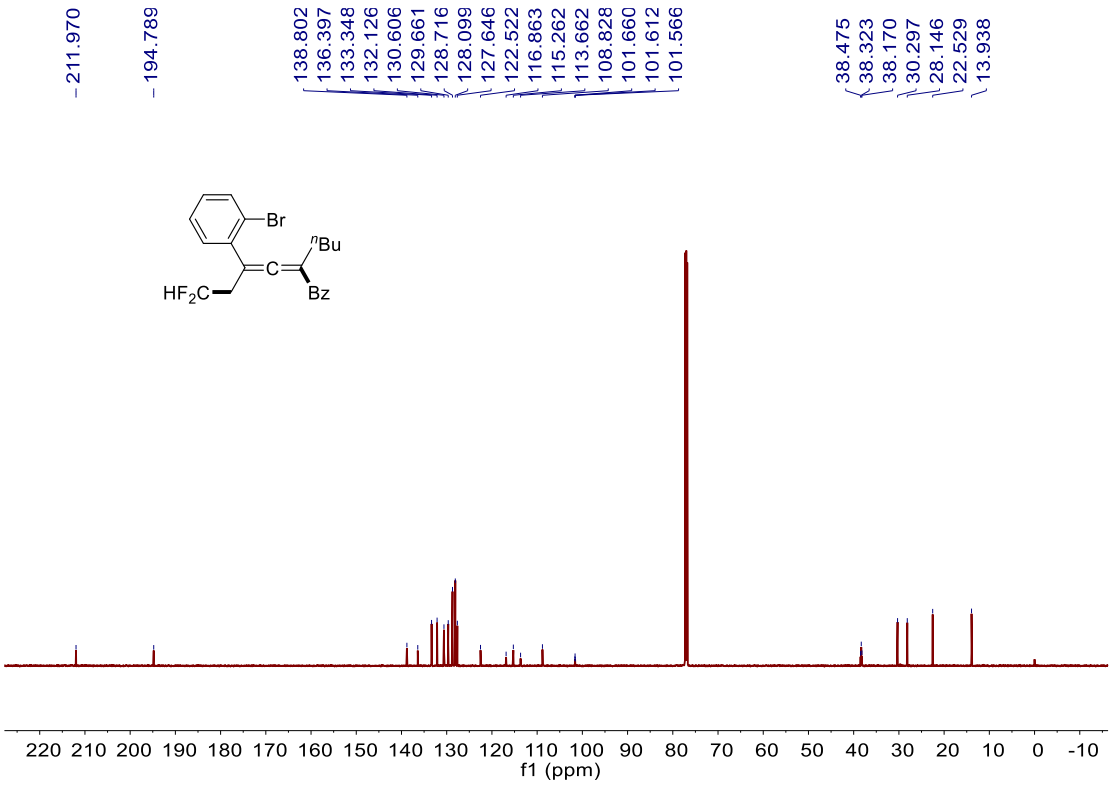
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ca**.



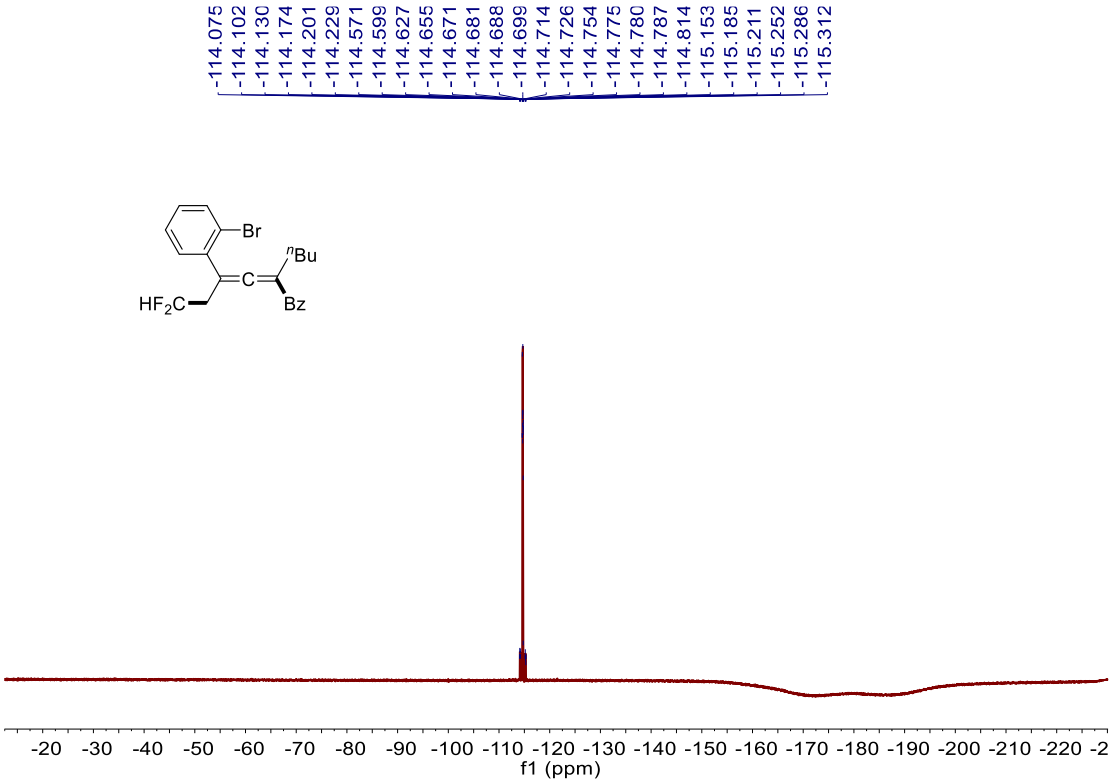
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5da**.



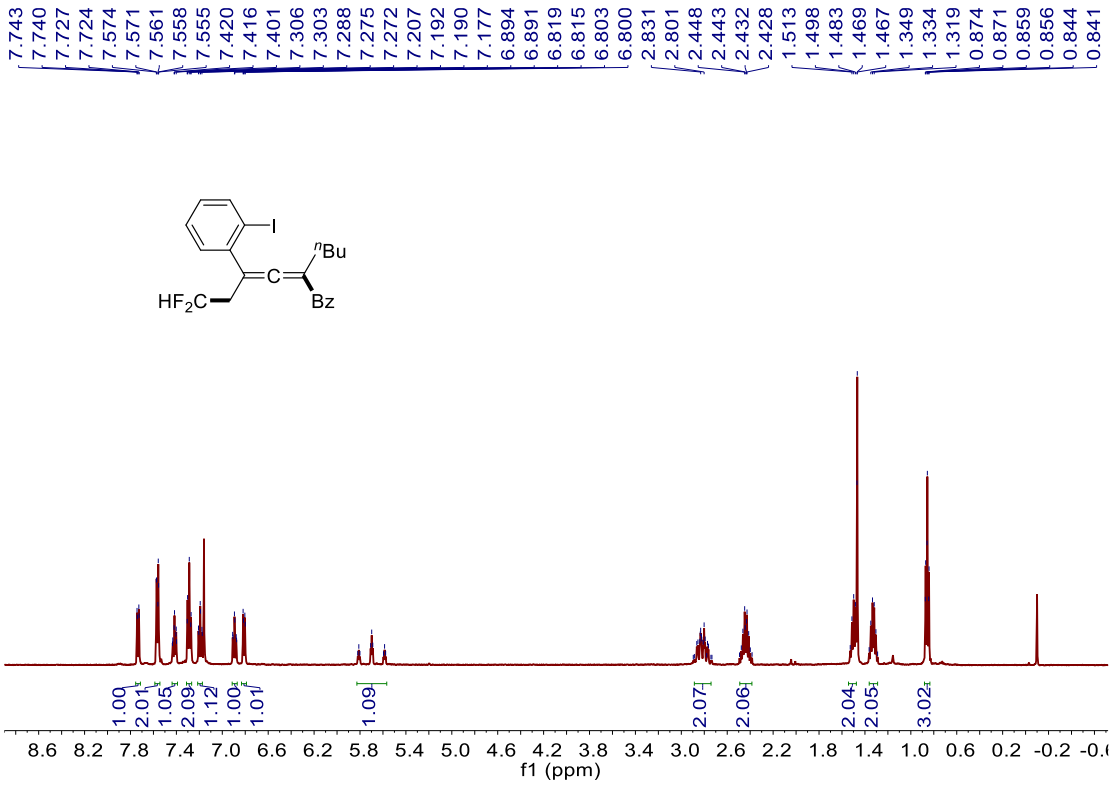
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5da**.



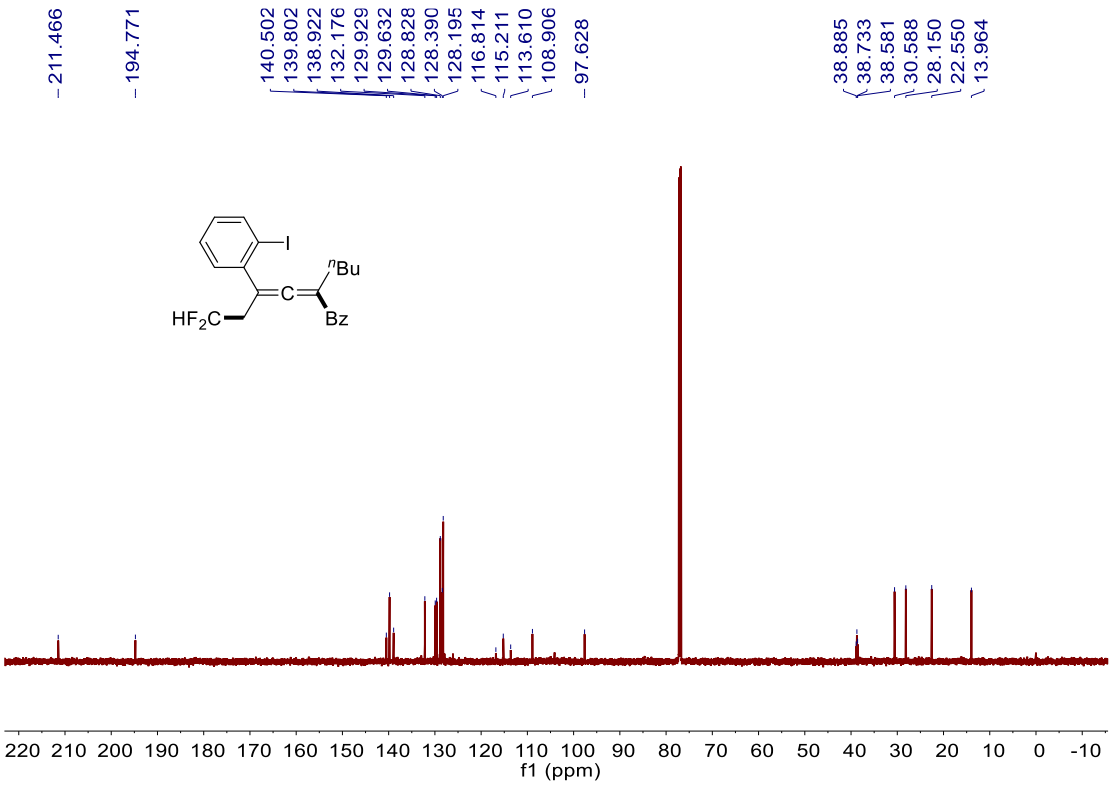
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5da**.



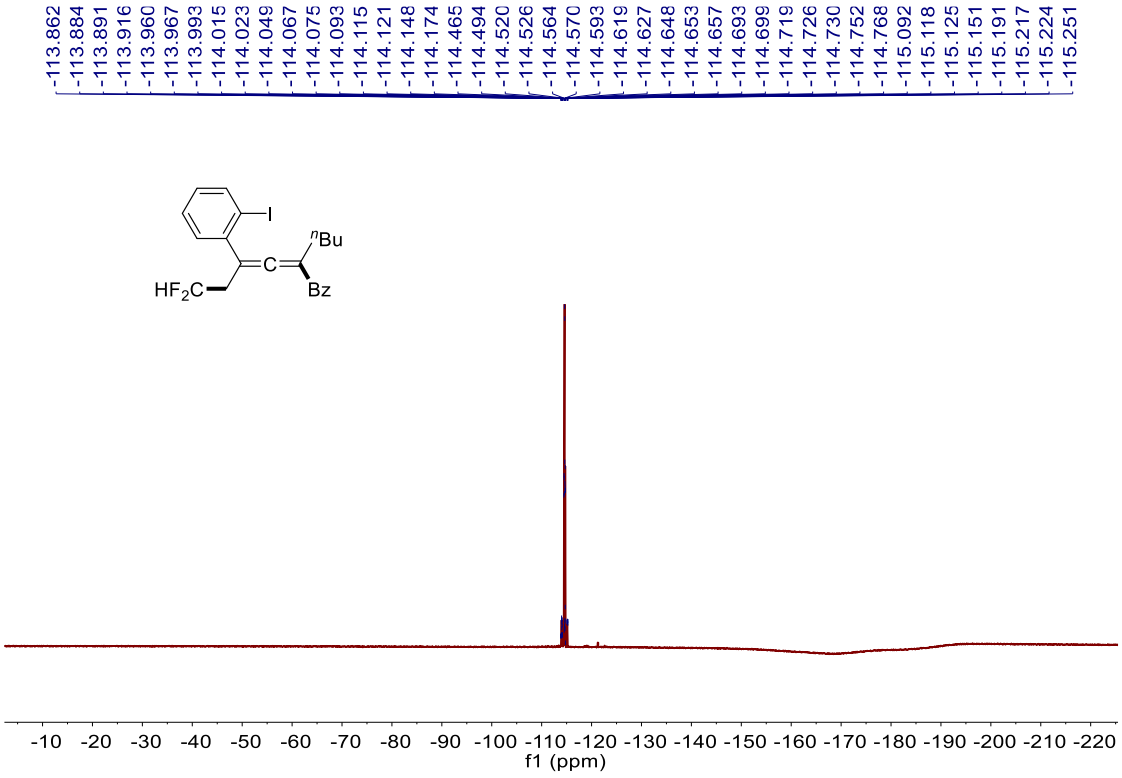
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ea**.



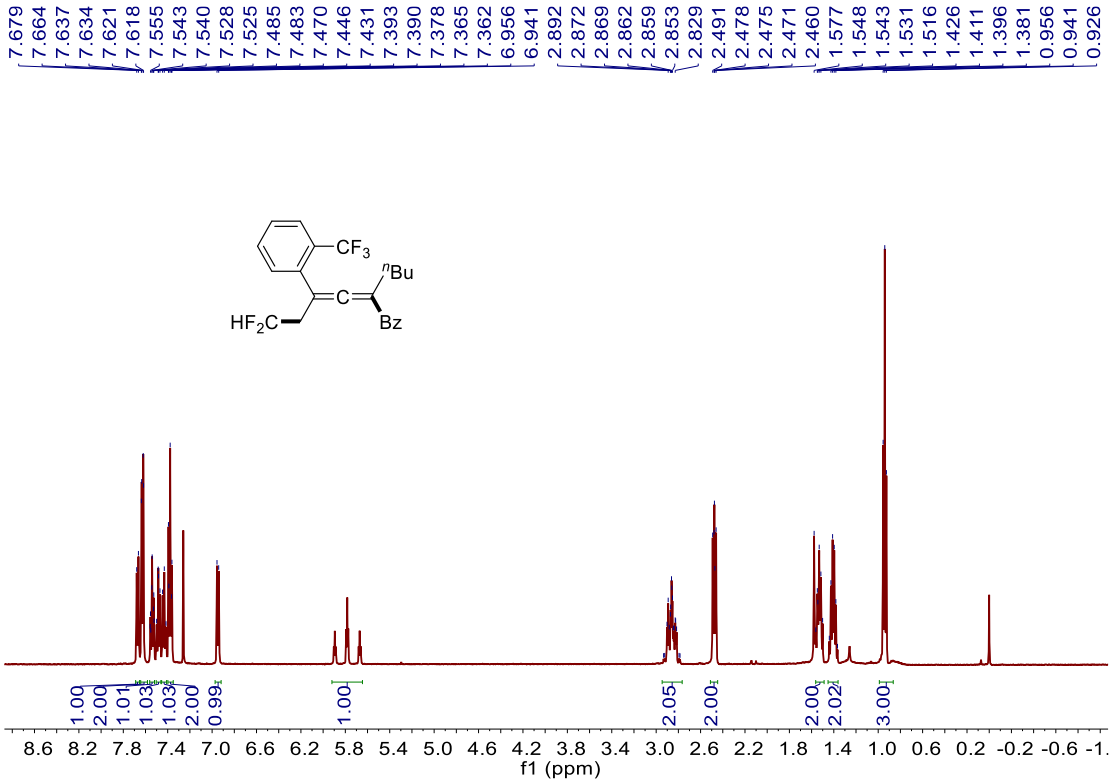
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ea**.



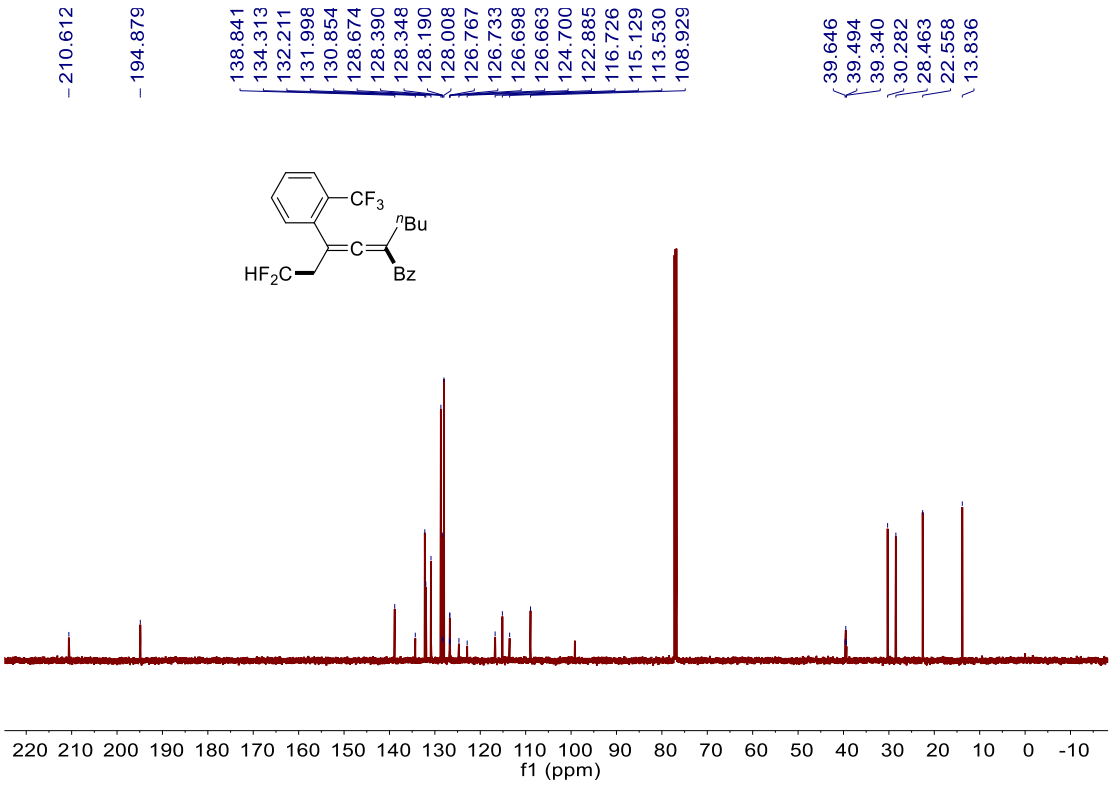
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ea**.



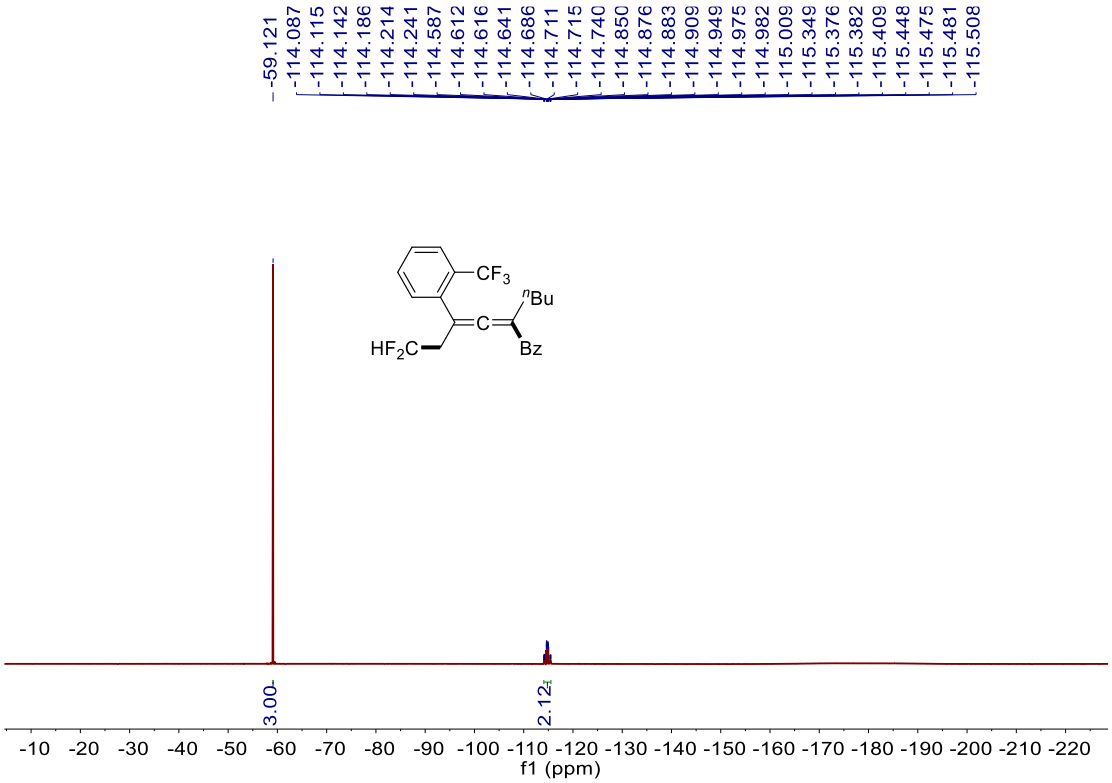
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5fa**.



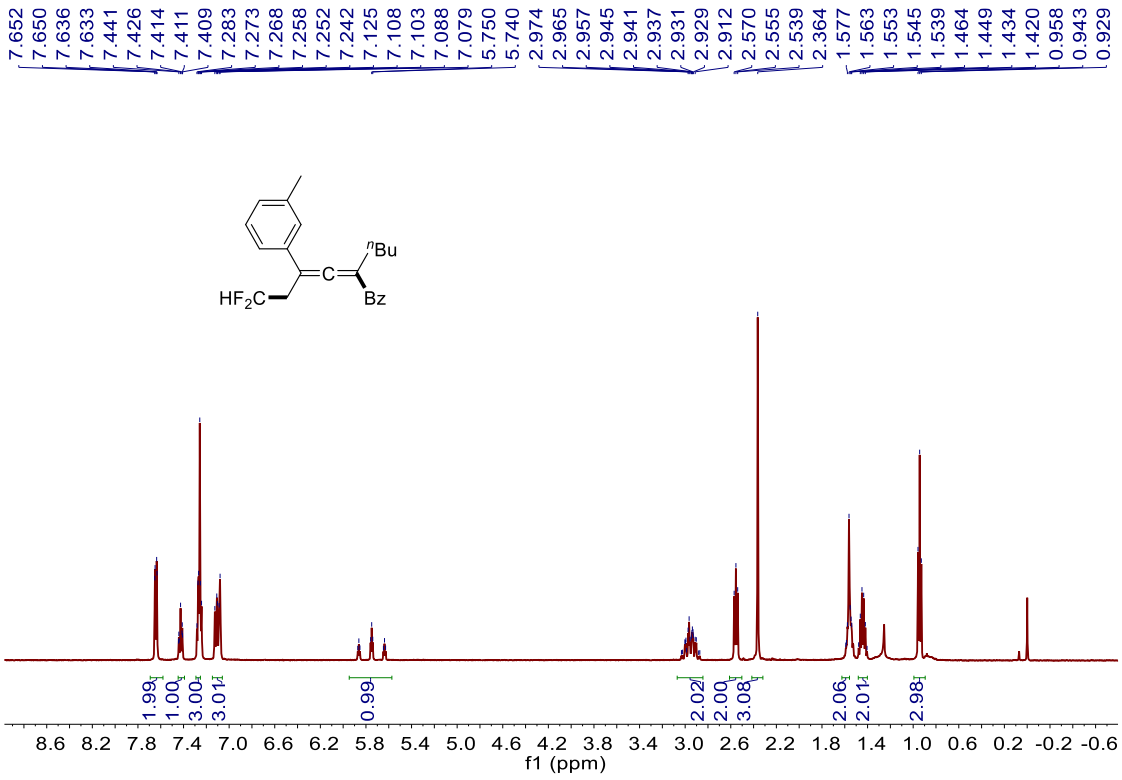
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5fa**.



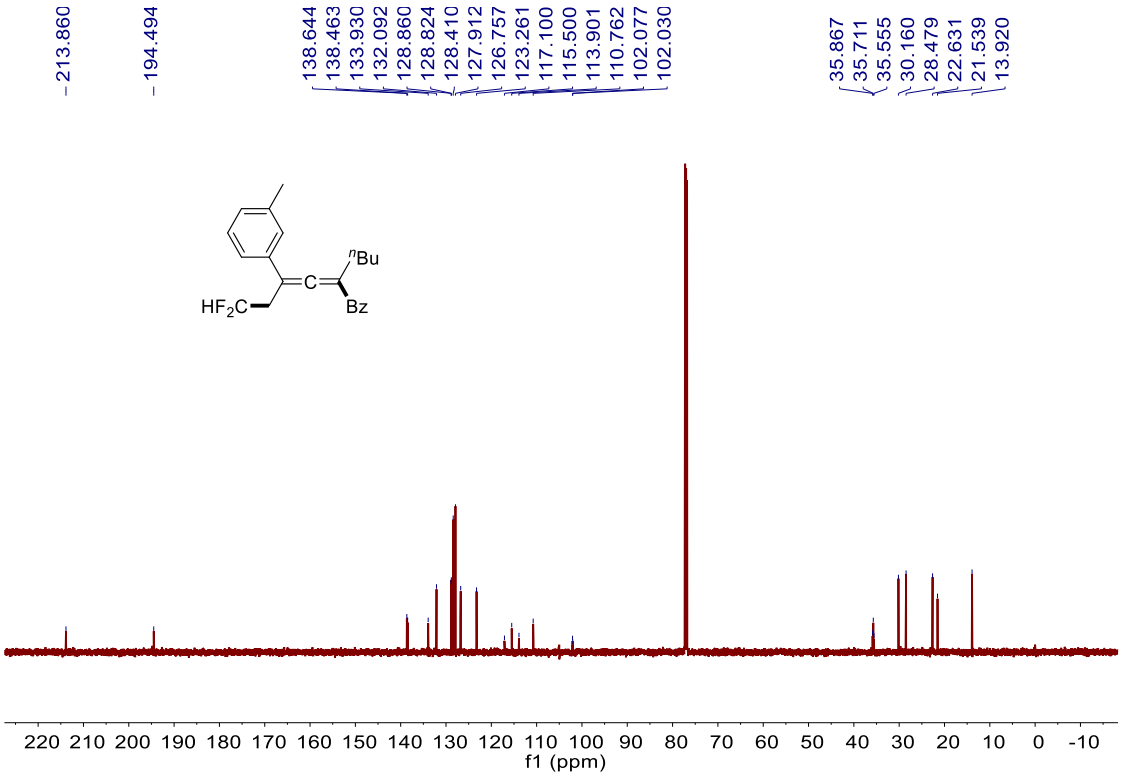
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5fa**.



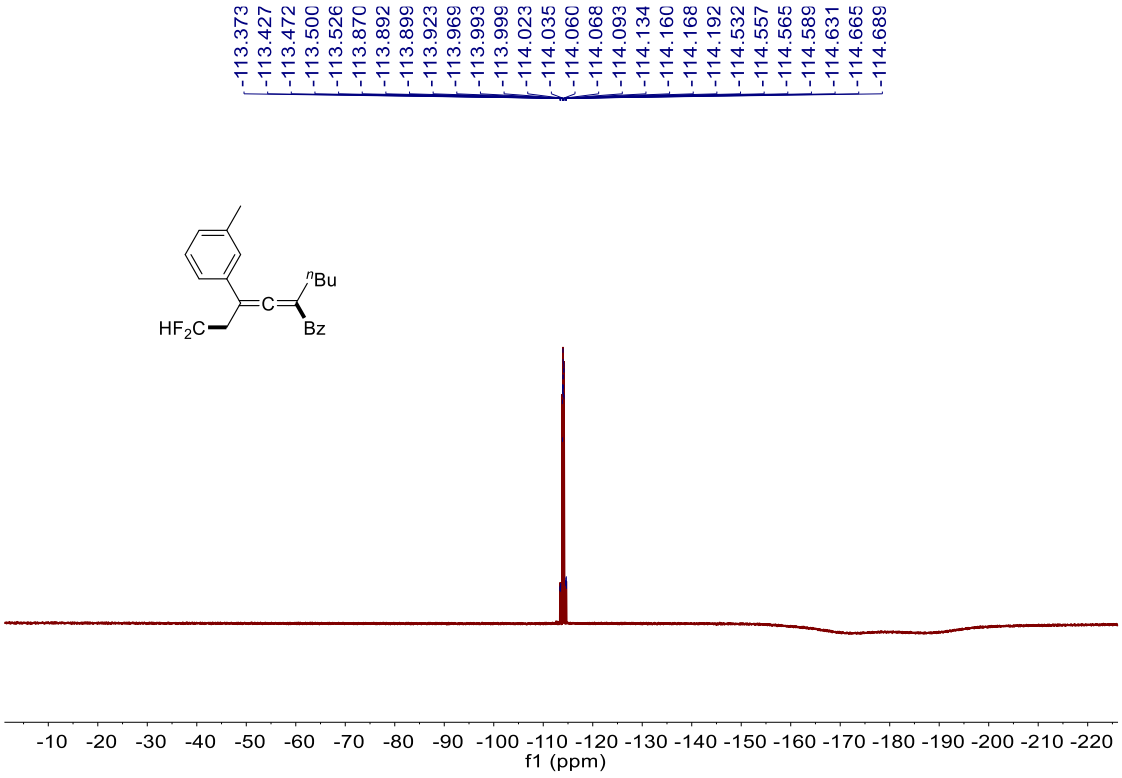
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ga**.



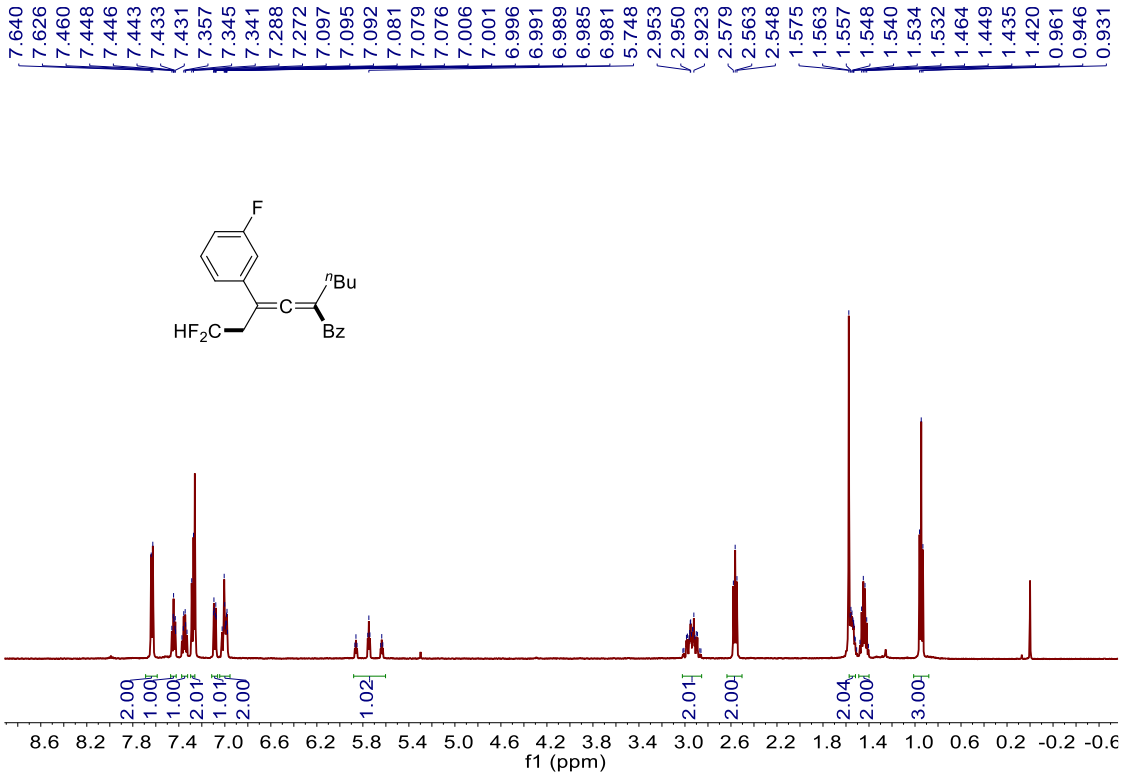
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ga**.



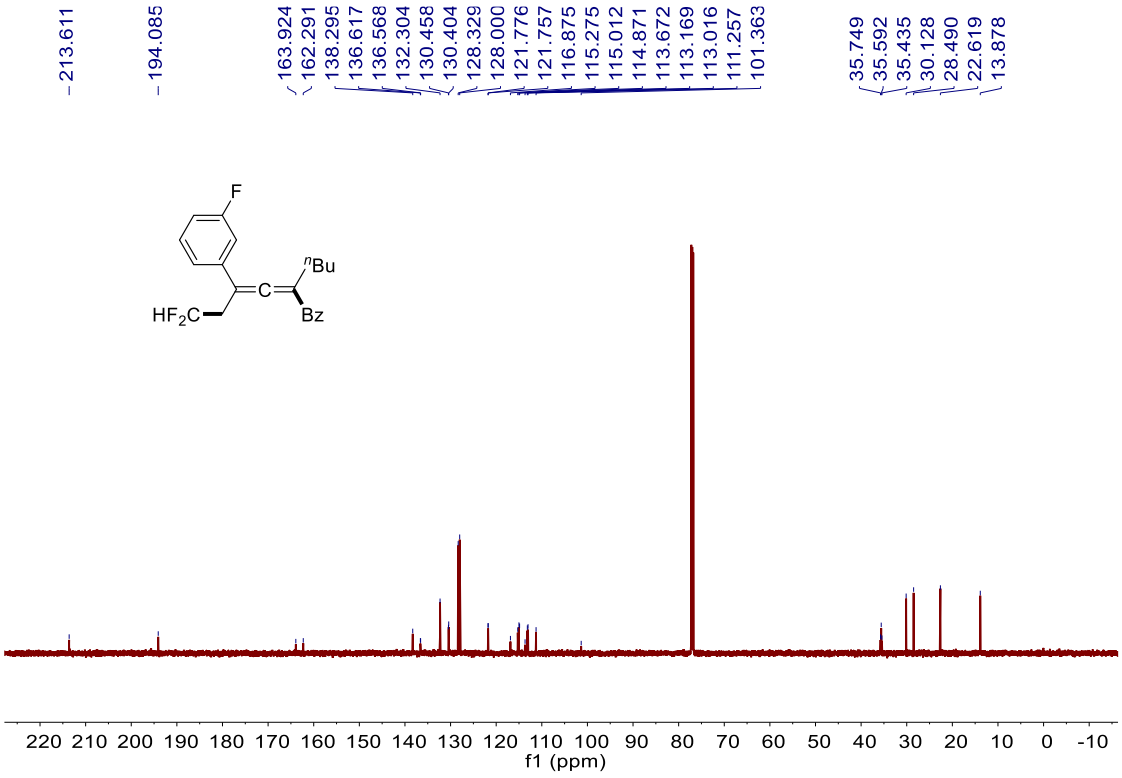
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ga**.



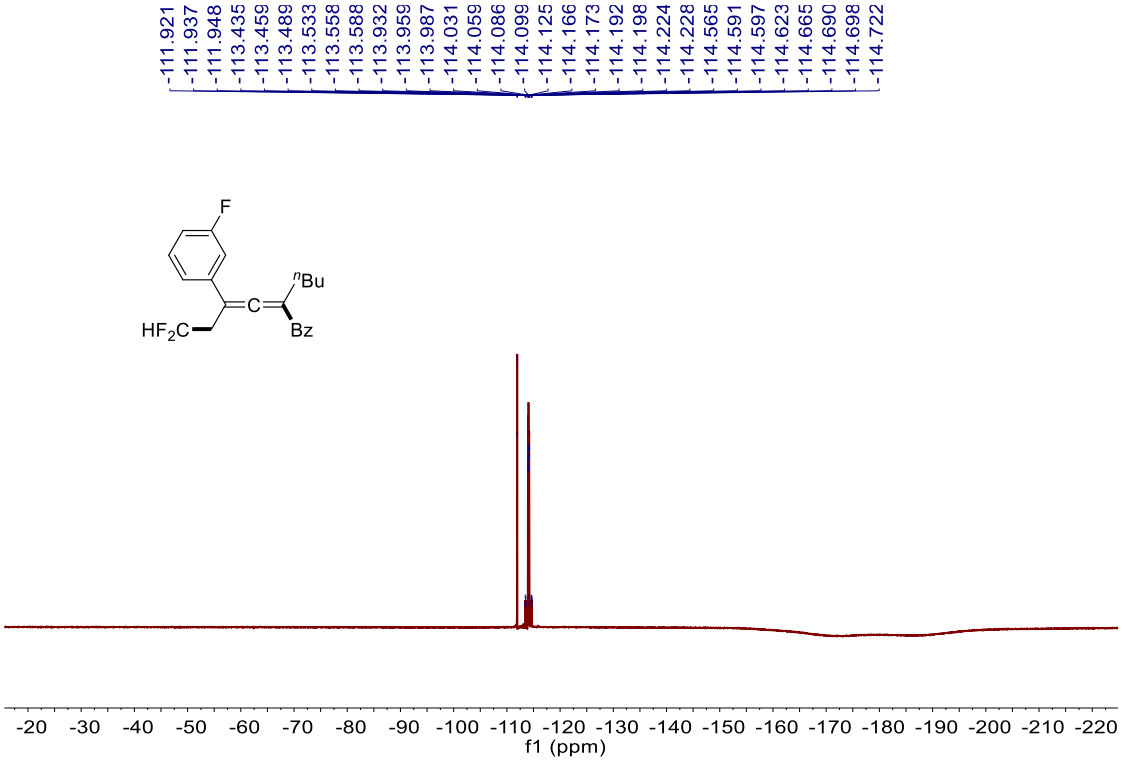
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ha**.



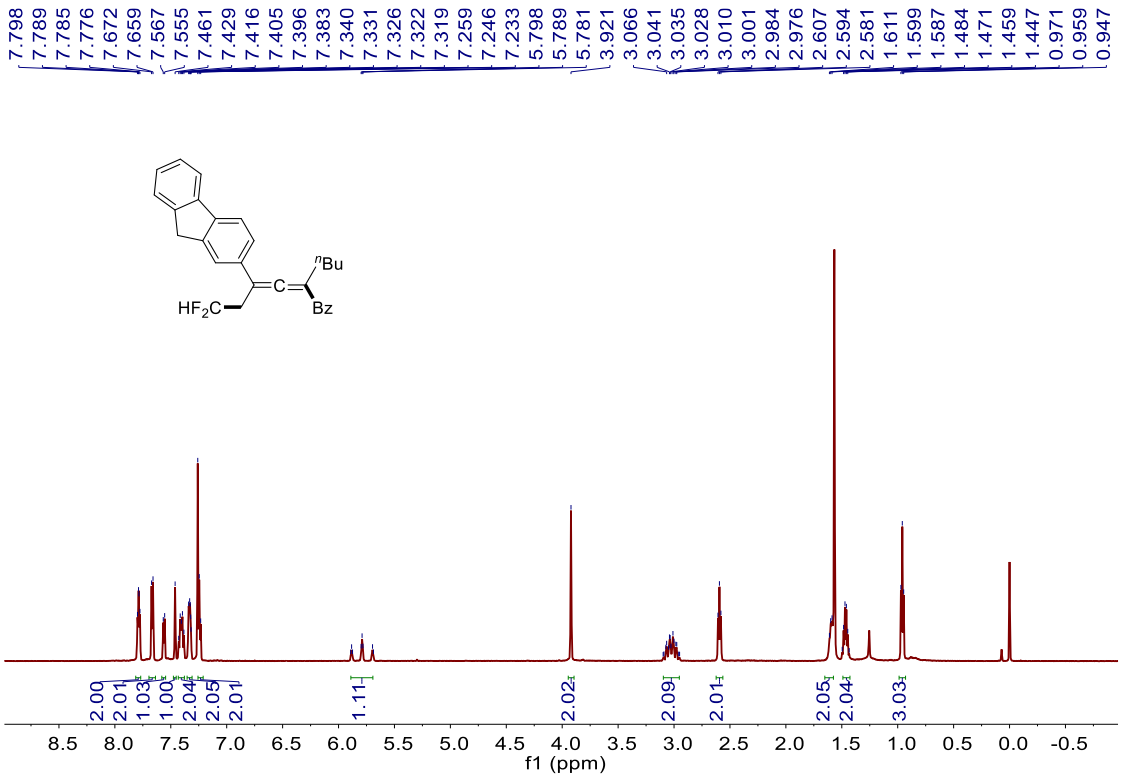
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ha**.



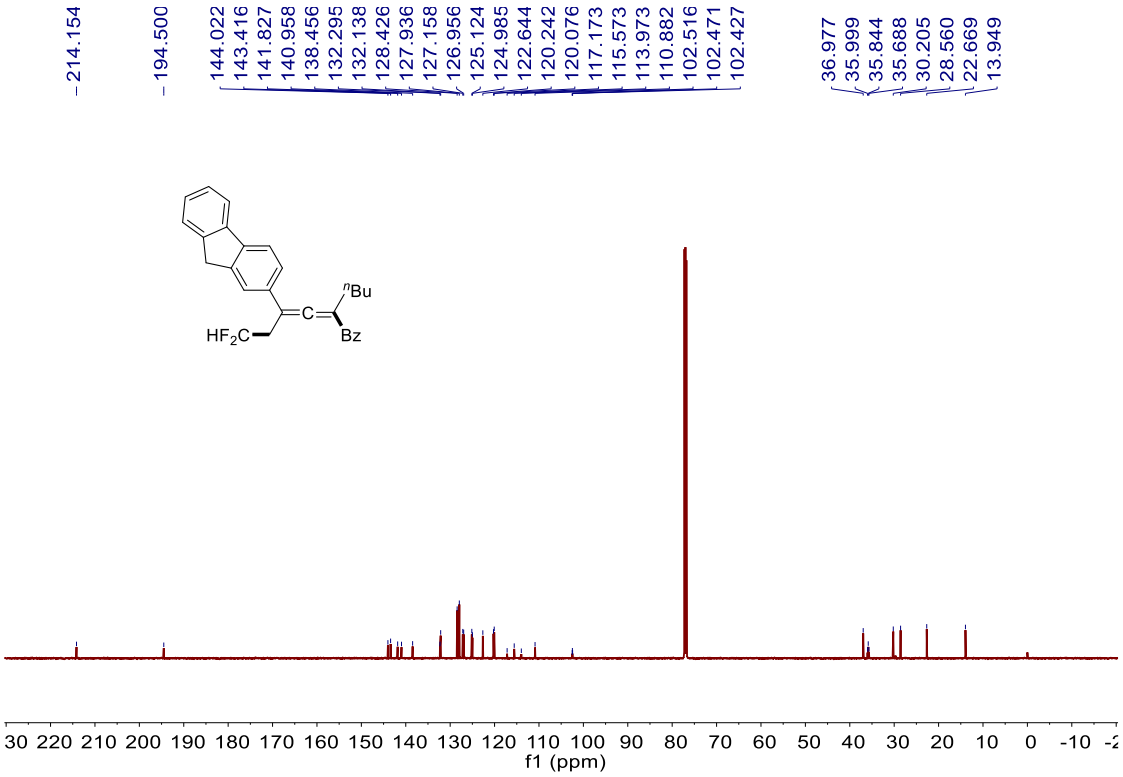
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ha**.



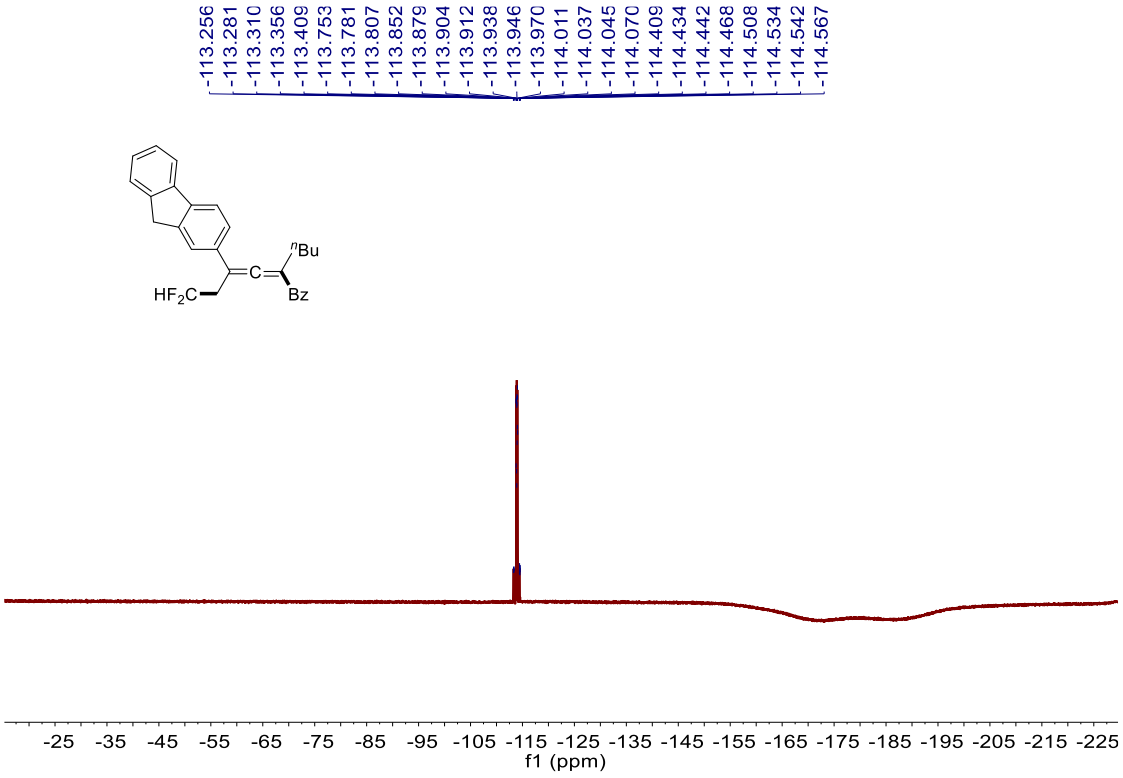
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ra**.



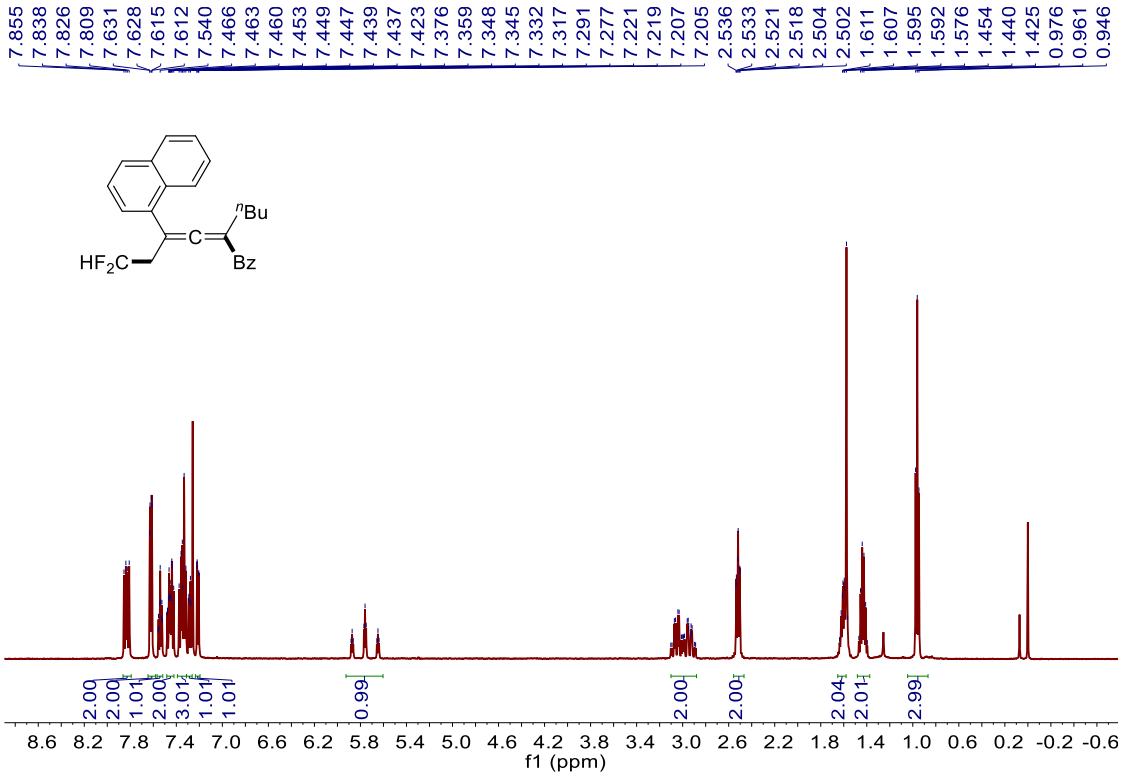
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ra**.



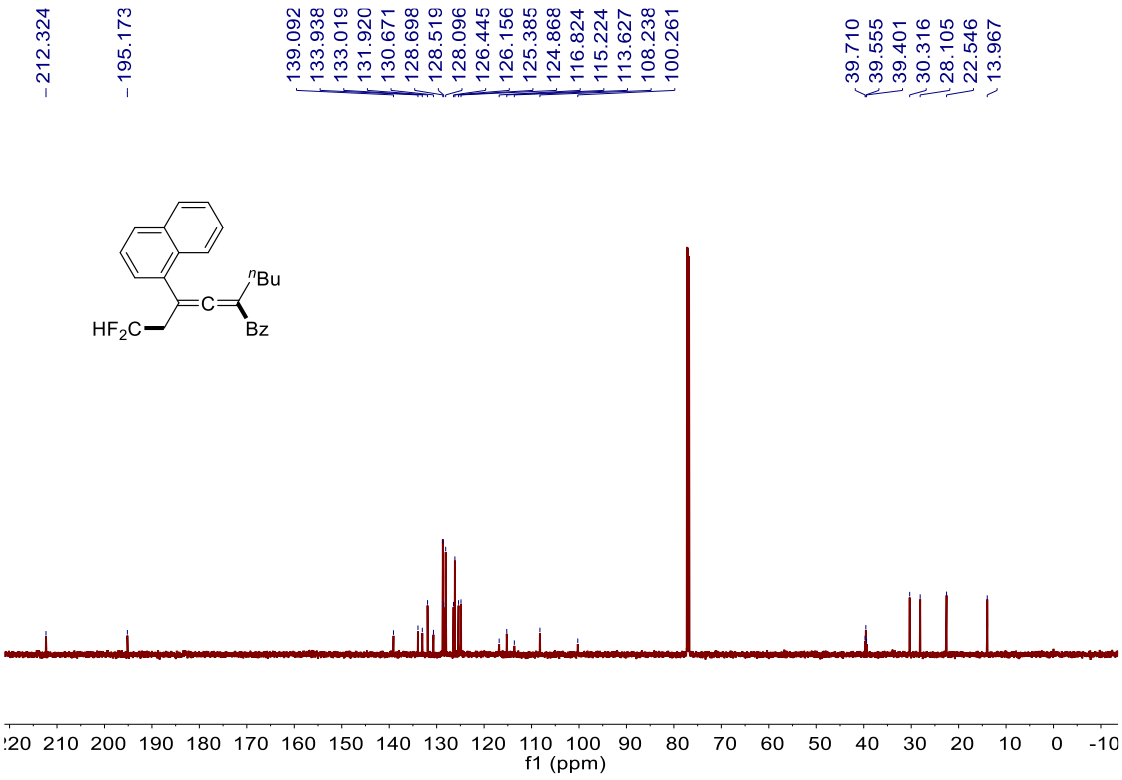
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ra**.



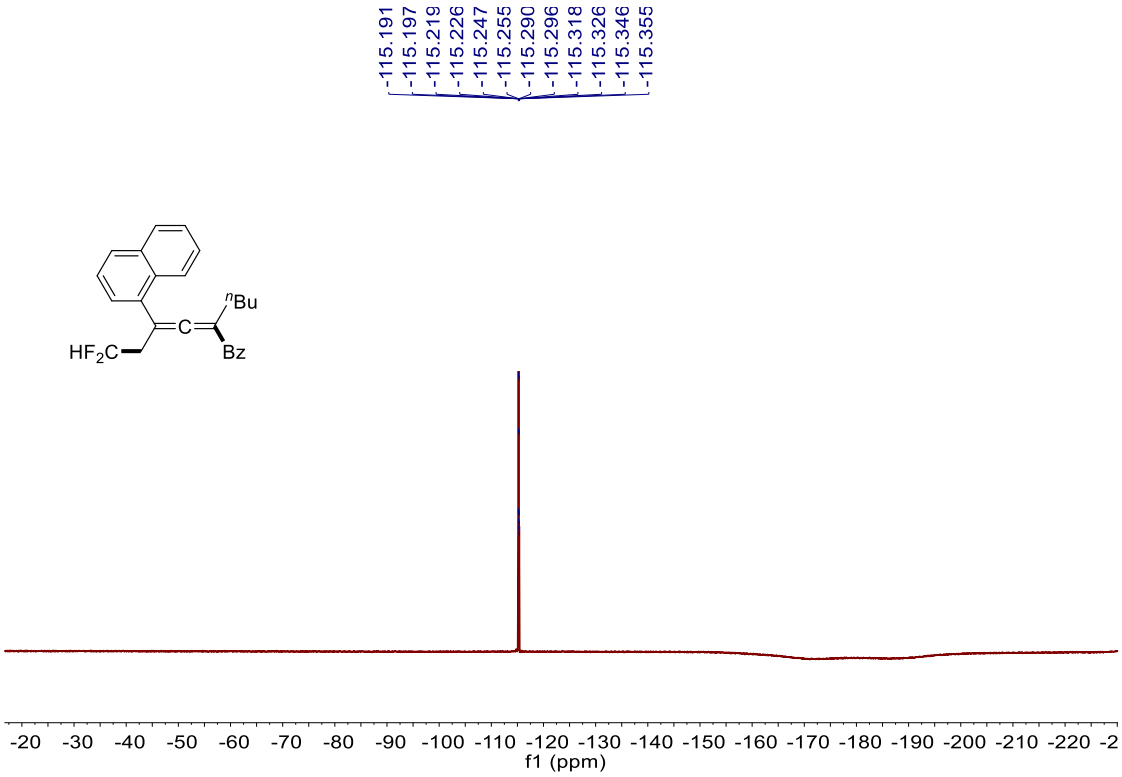
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qa**.



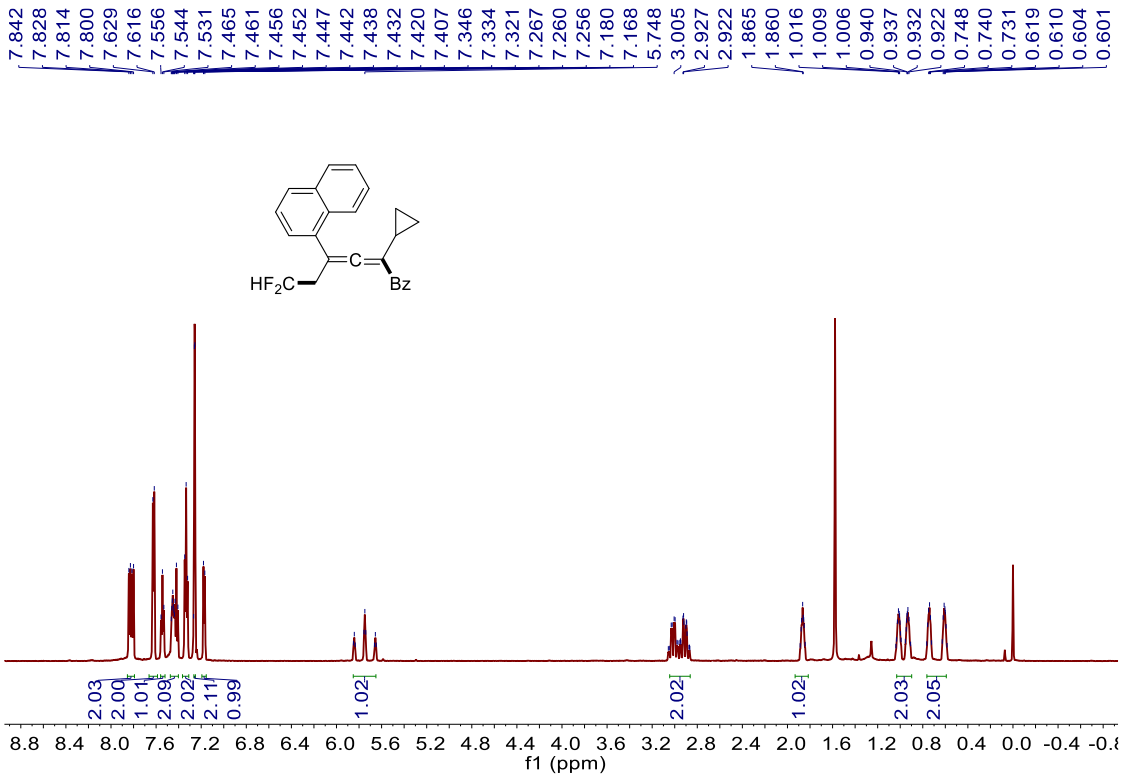
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qa**.



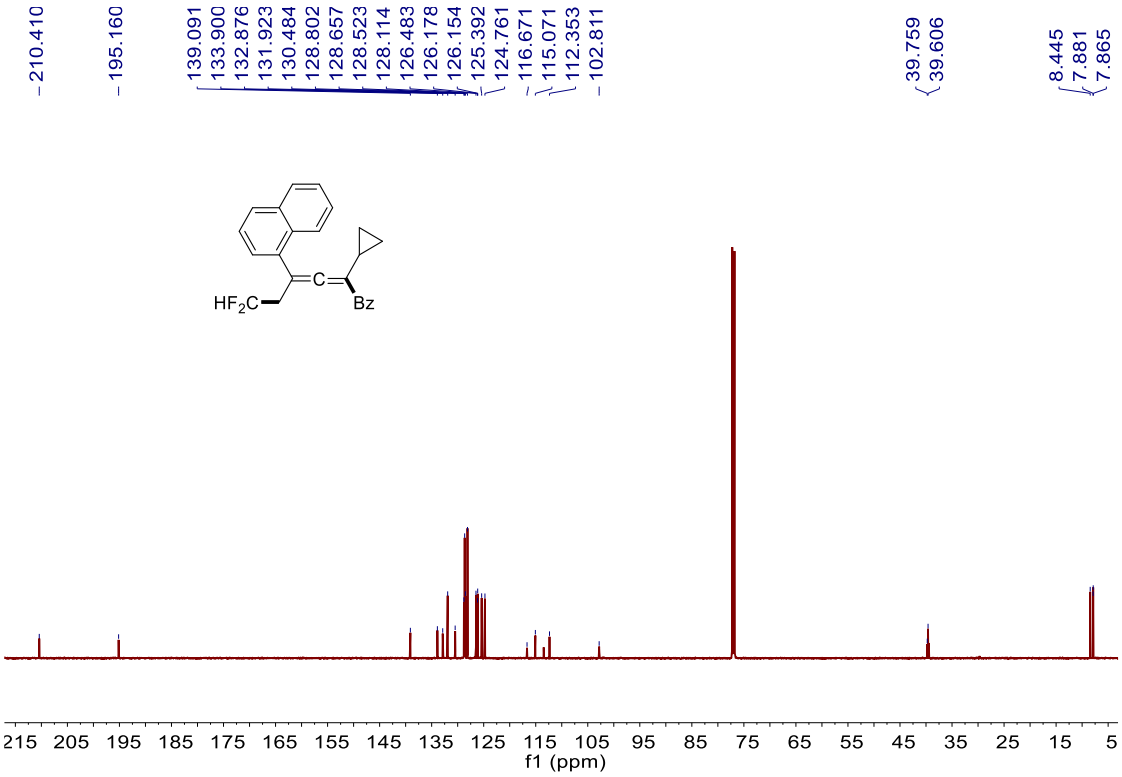
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qa**.



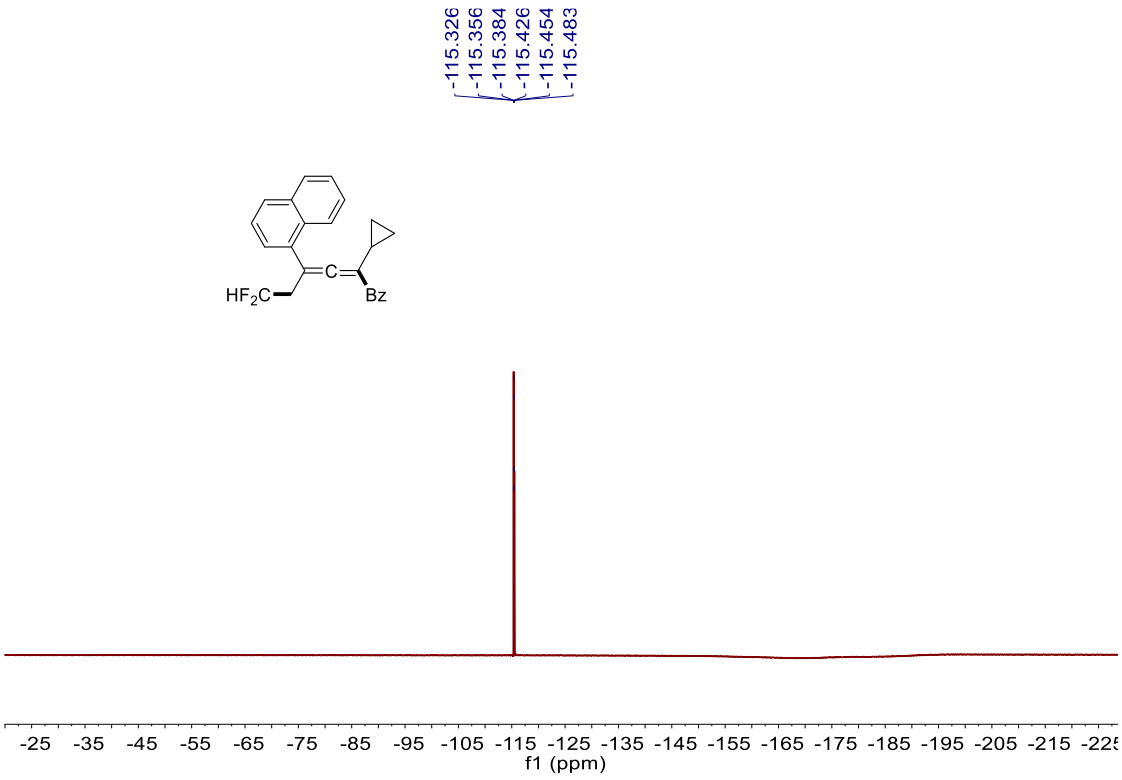
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ta**.



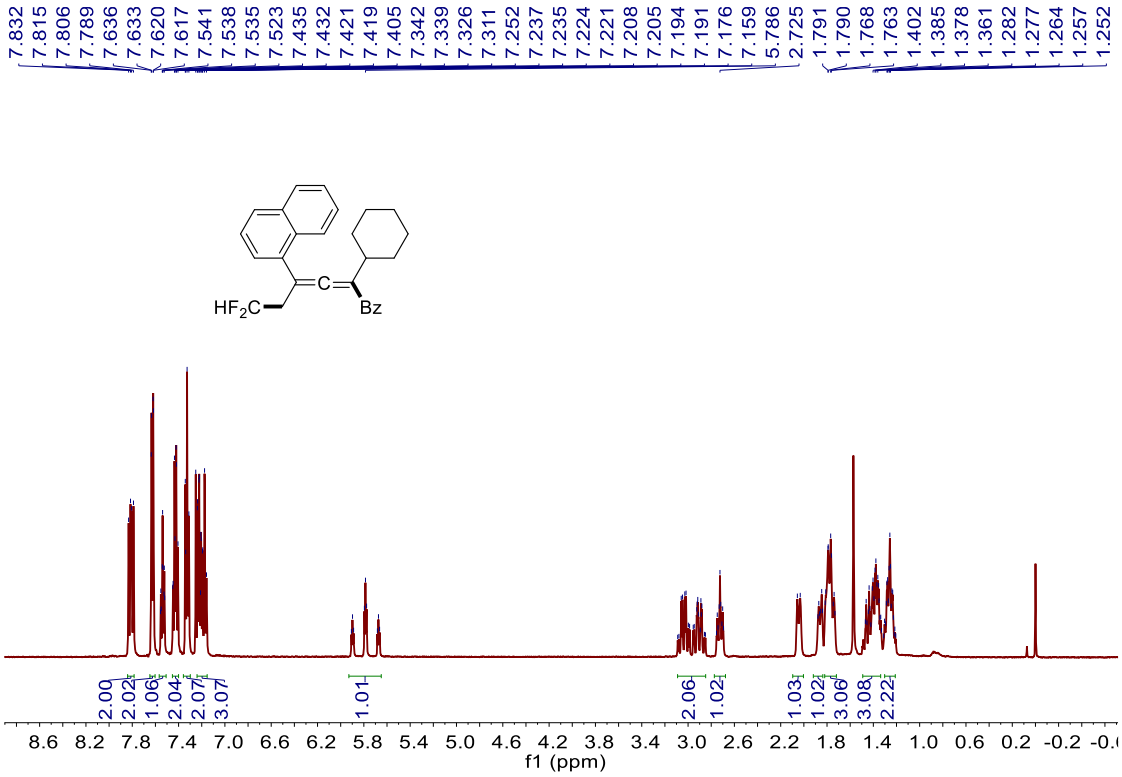
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ta**.



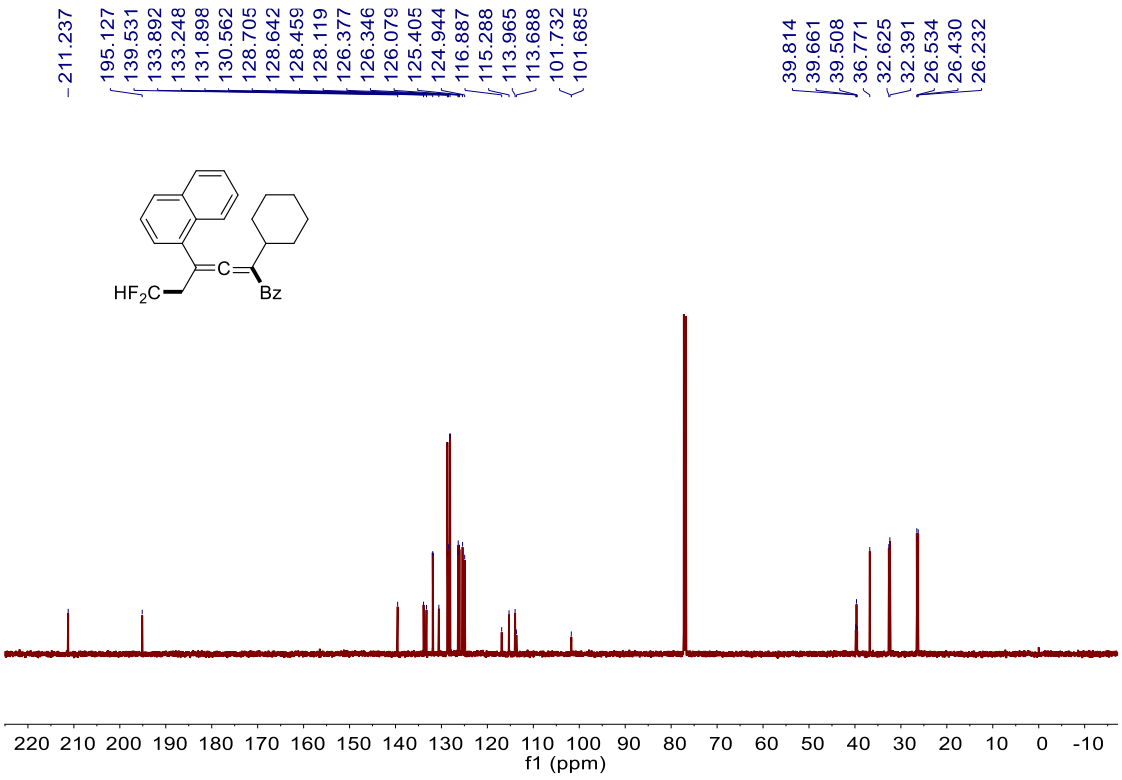
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ta**.



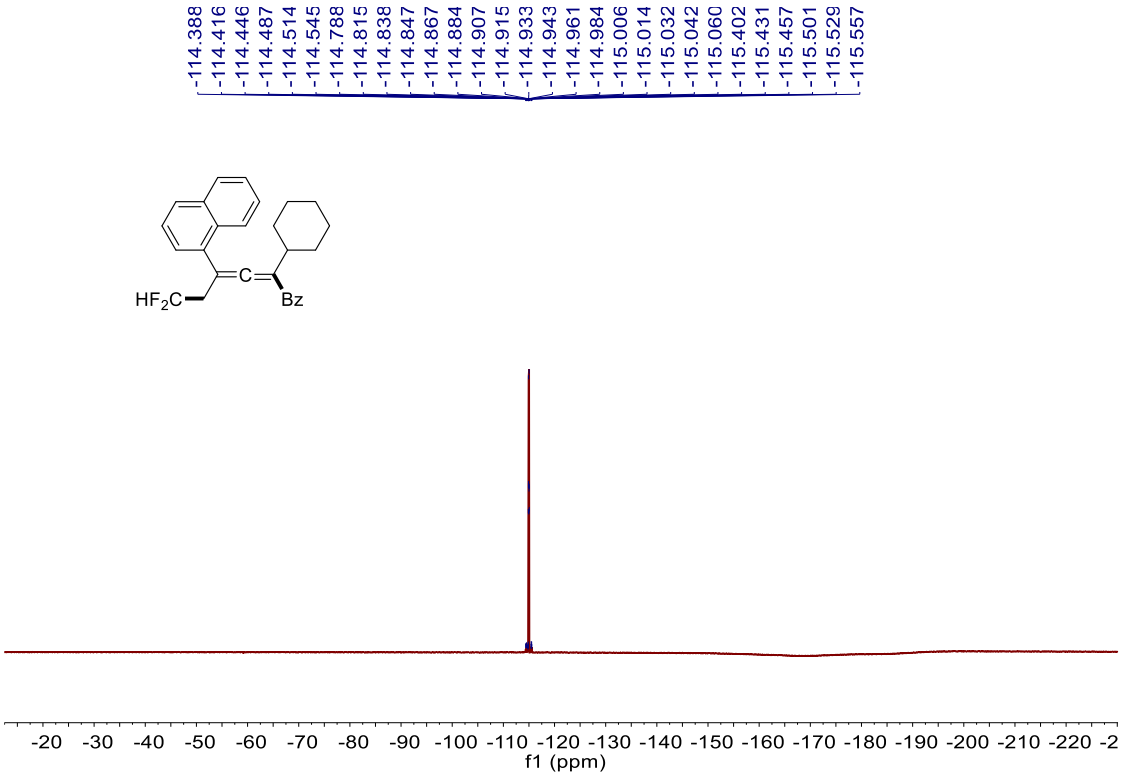
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ua**.



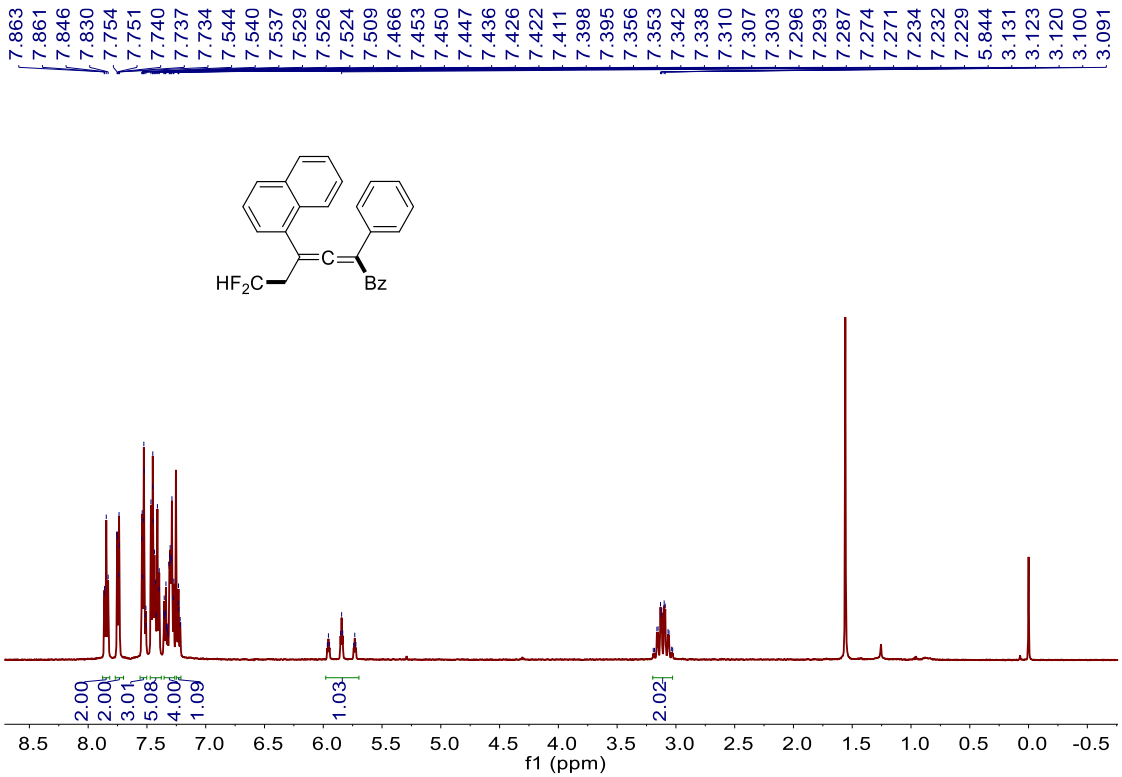
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ua**.



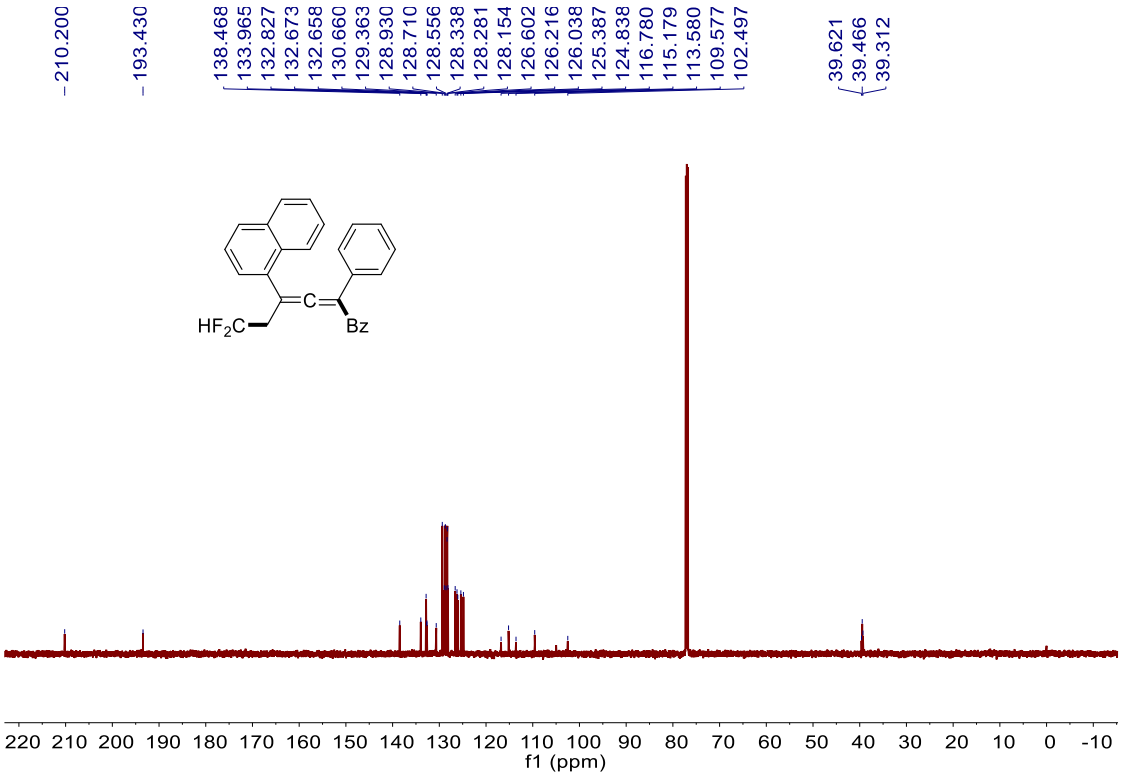
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ua**.



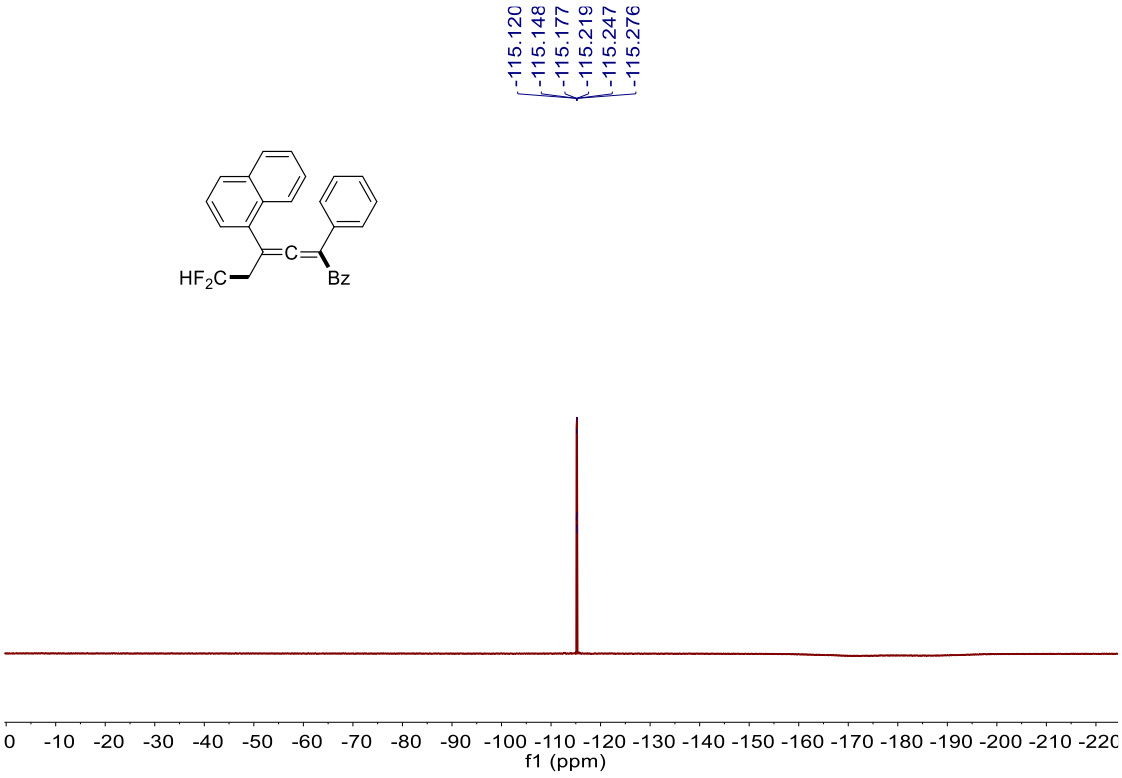
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5va**.



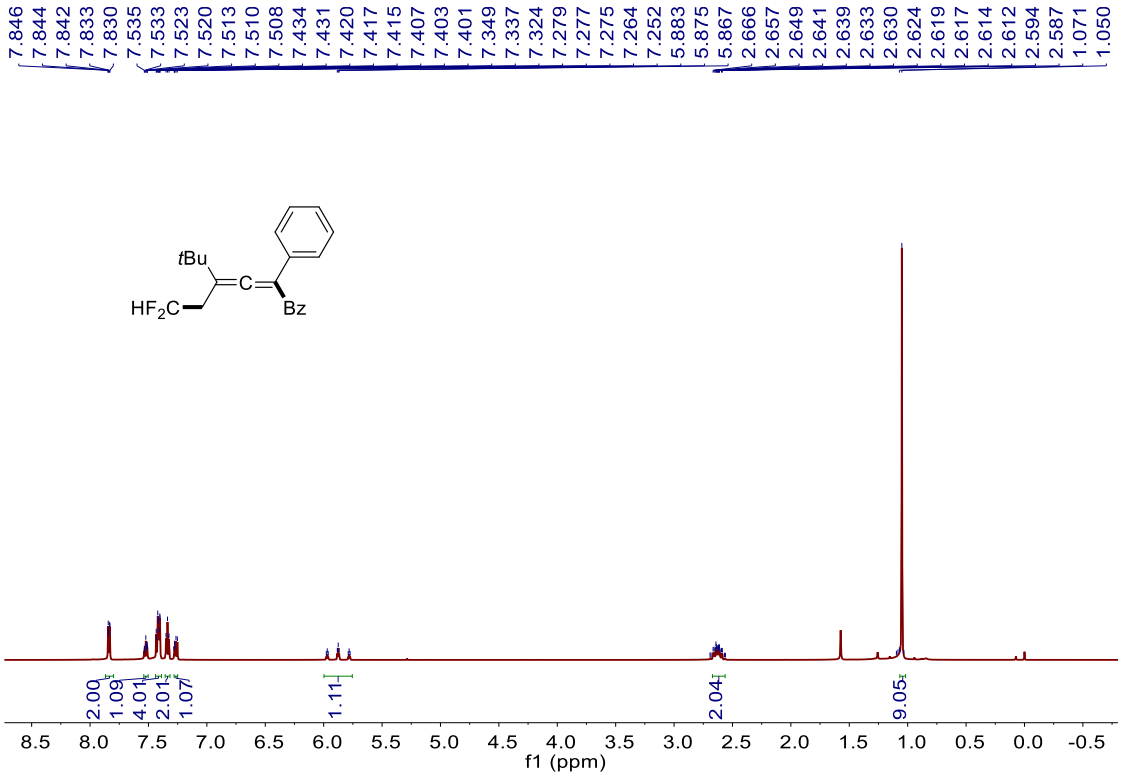
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5va**.



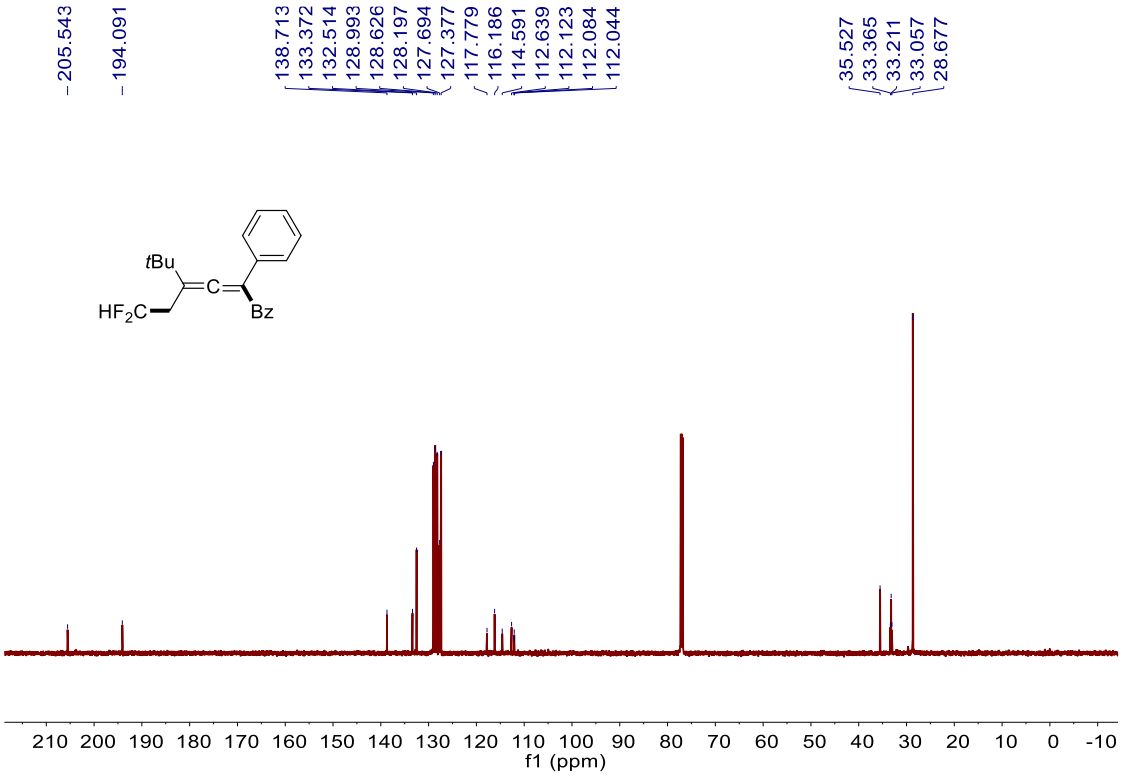
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5va**.



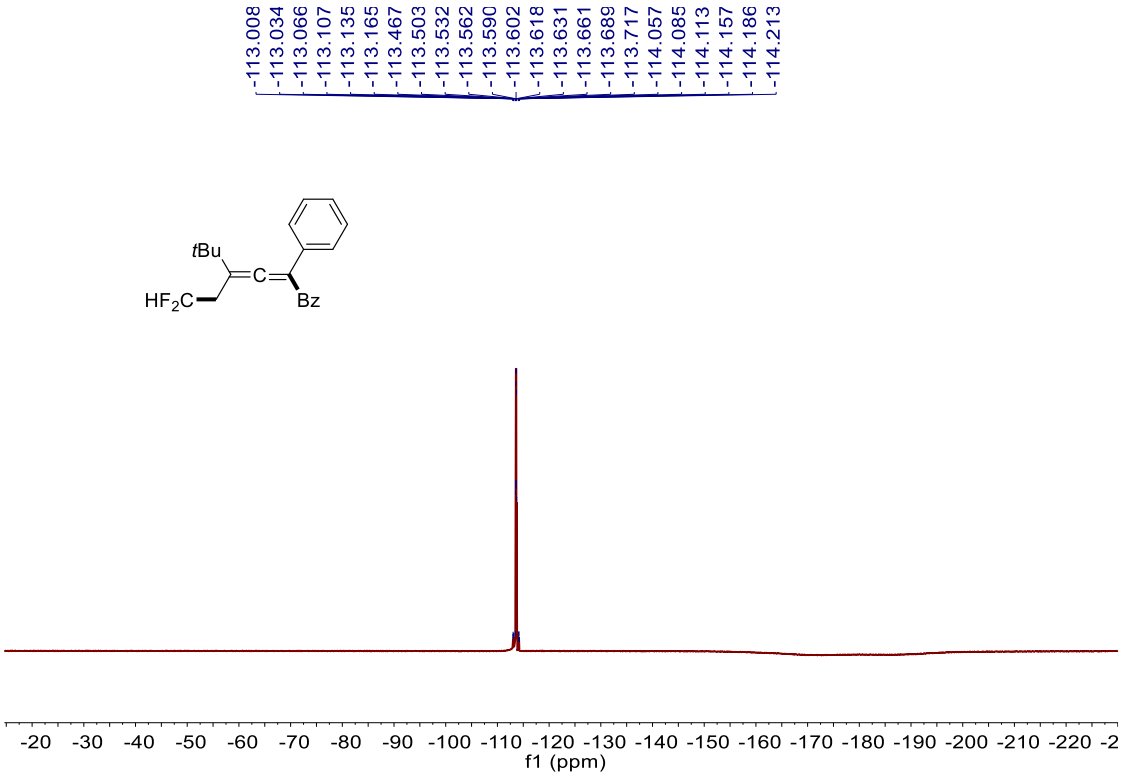
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5xa**.



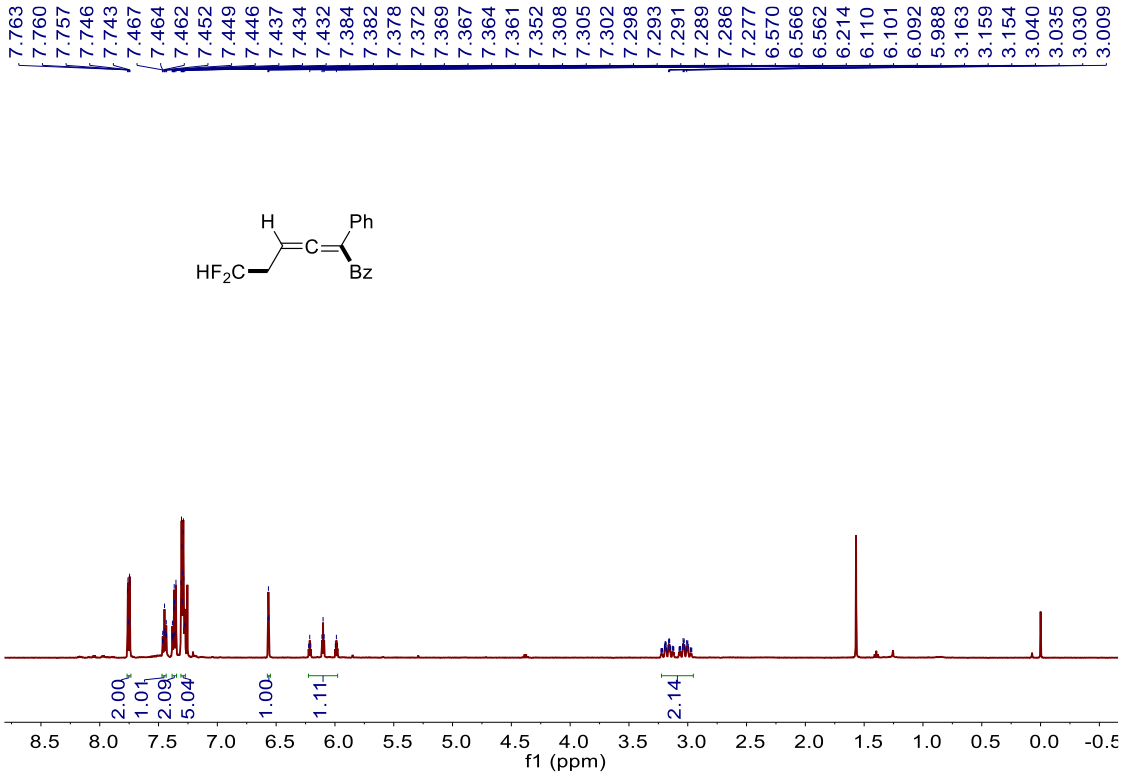
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5xa**.



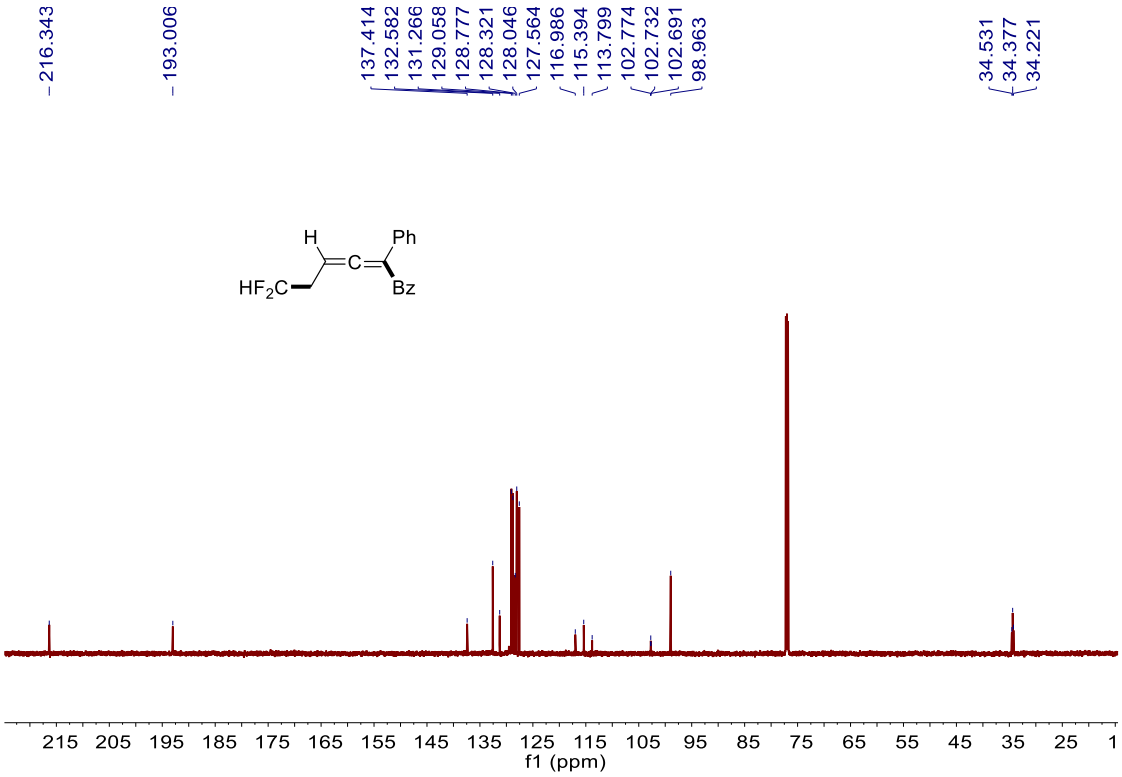
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5xa**.



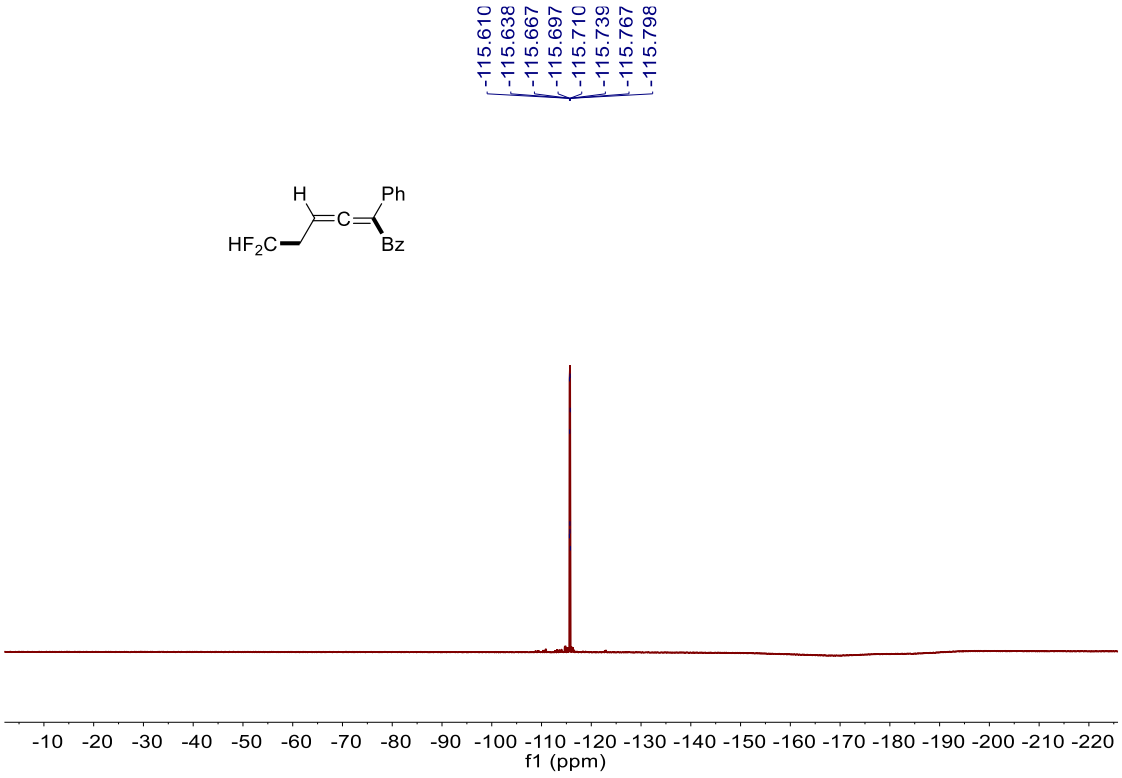
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ya**.



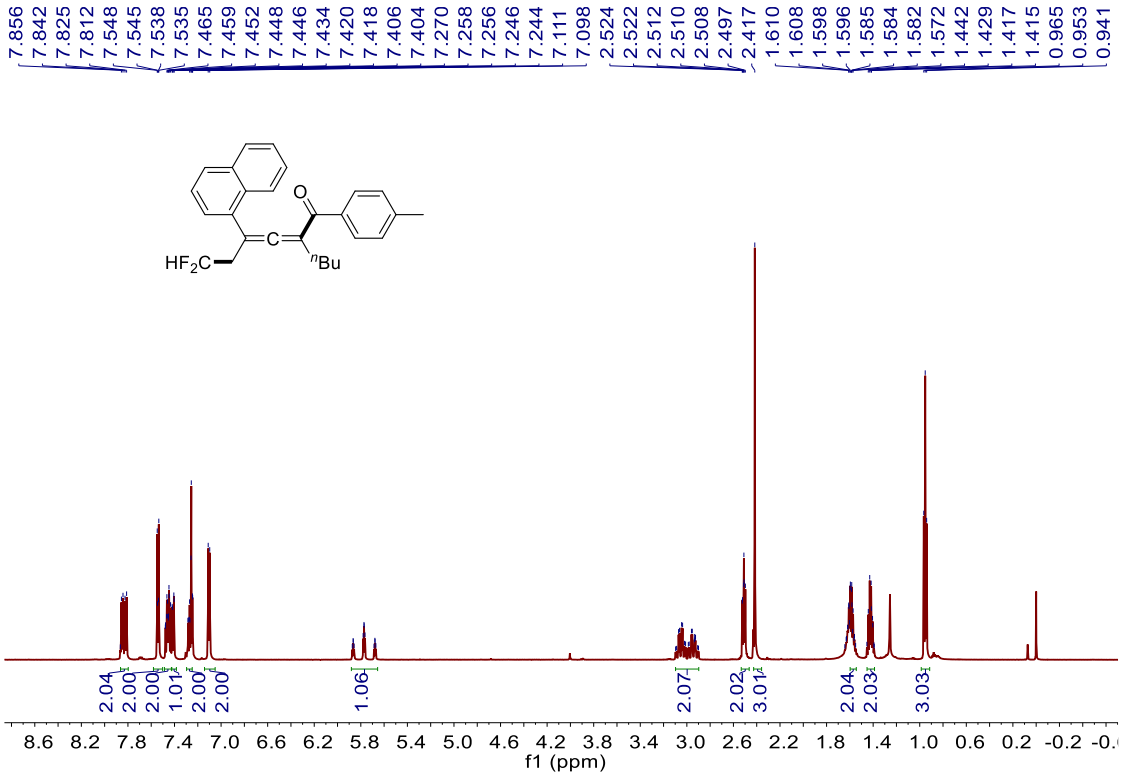
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ya**.



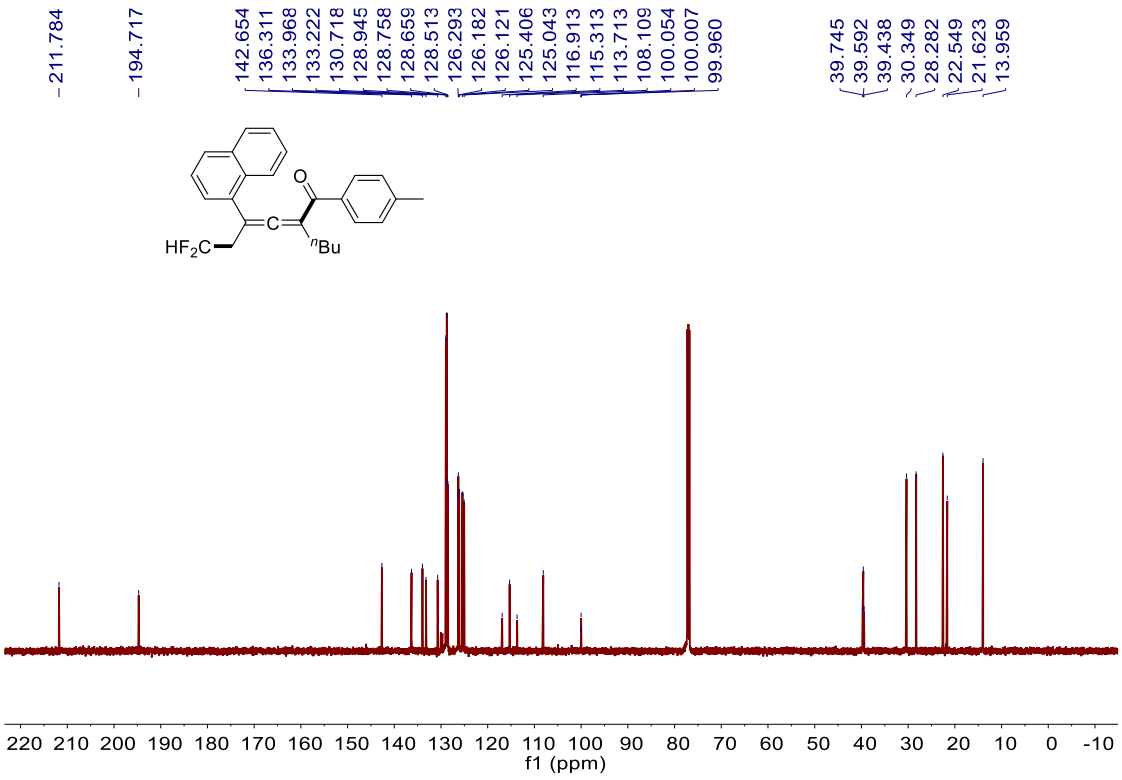
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ya**.



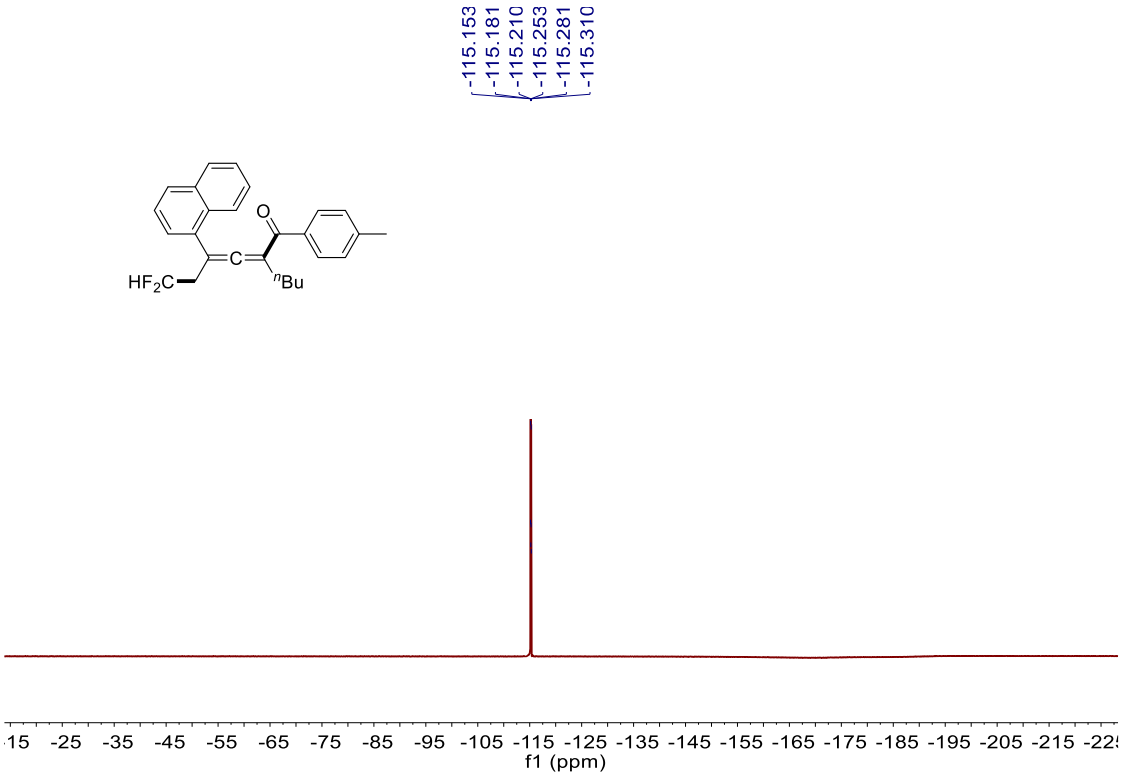
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qb**.



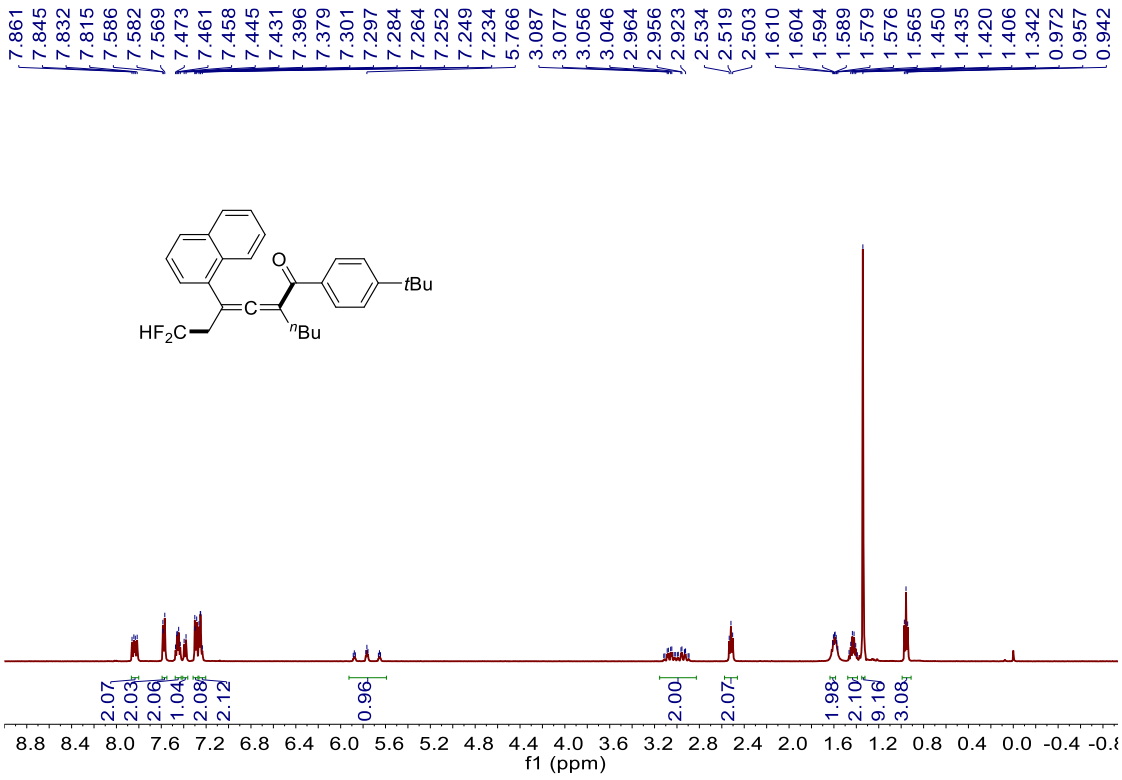
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qb**.



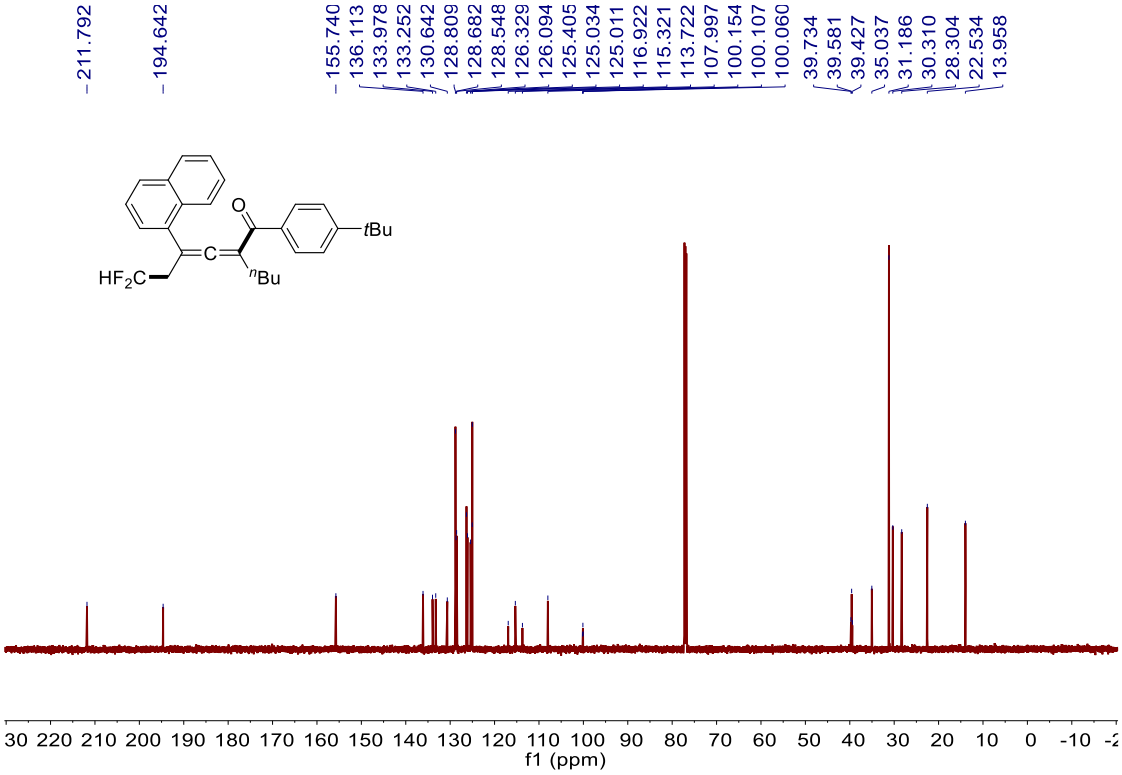
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qb**.



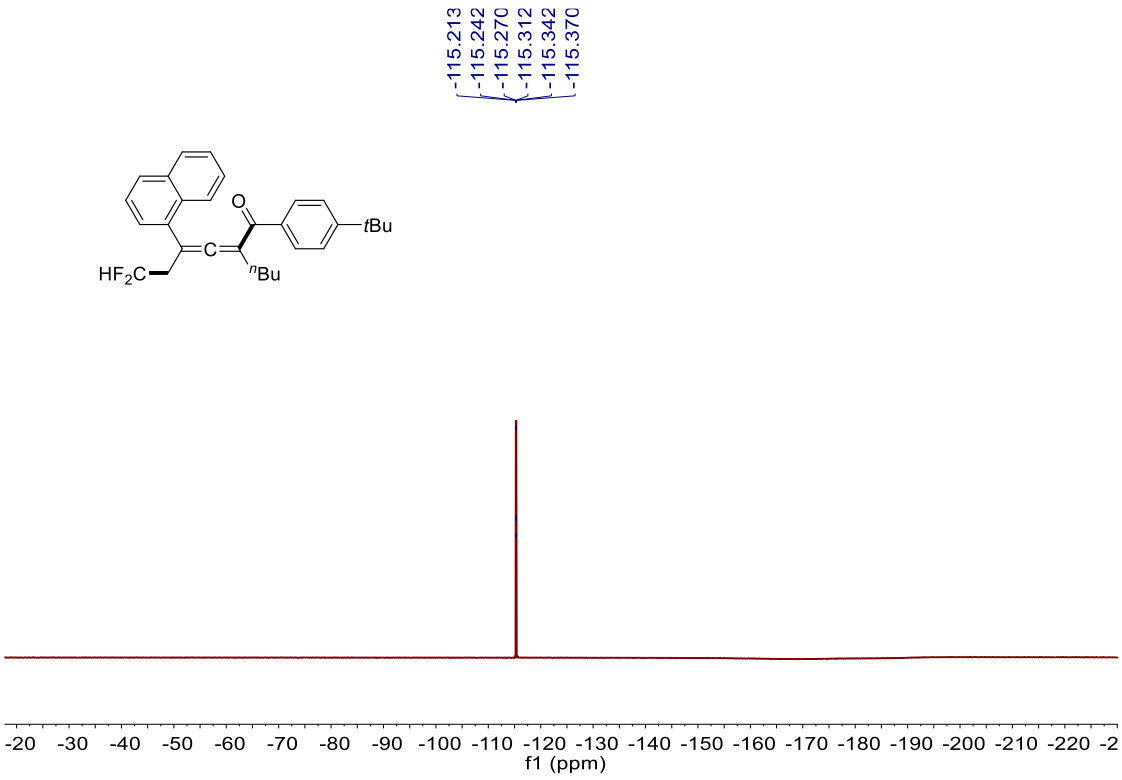
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qc**.



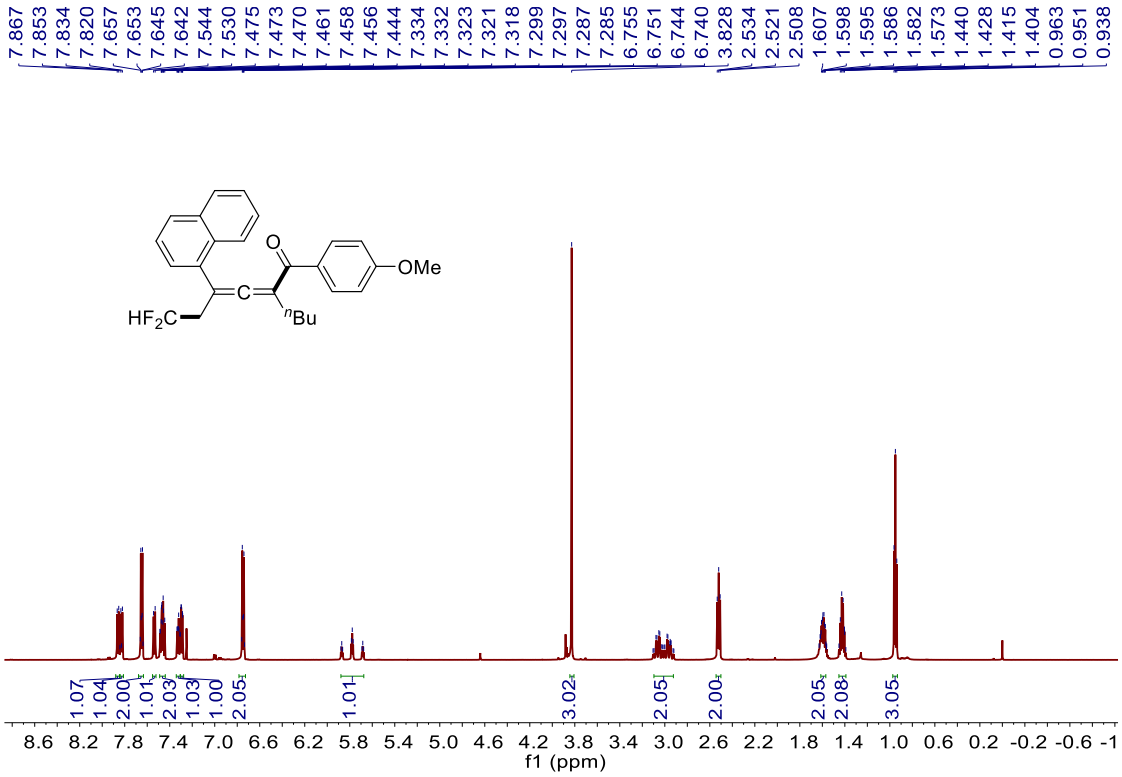
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qc**.



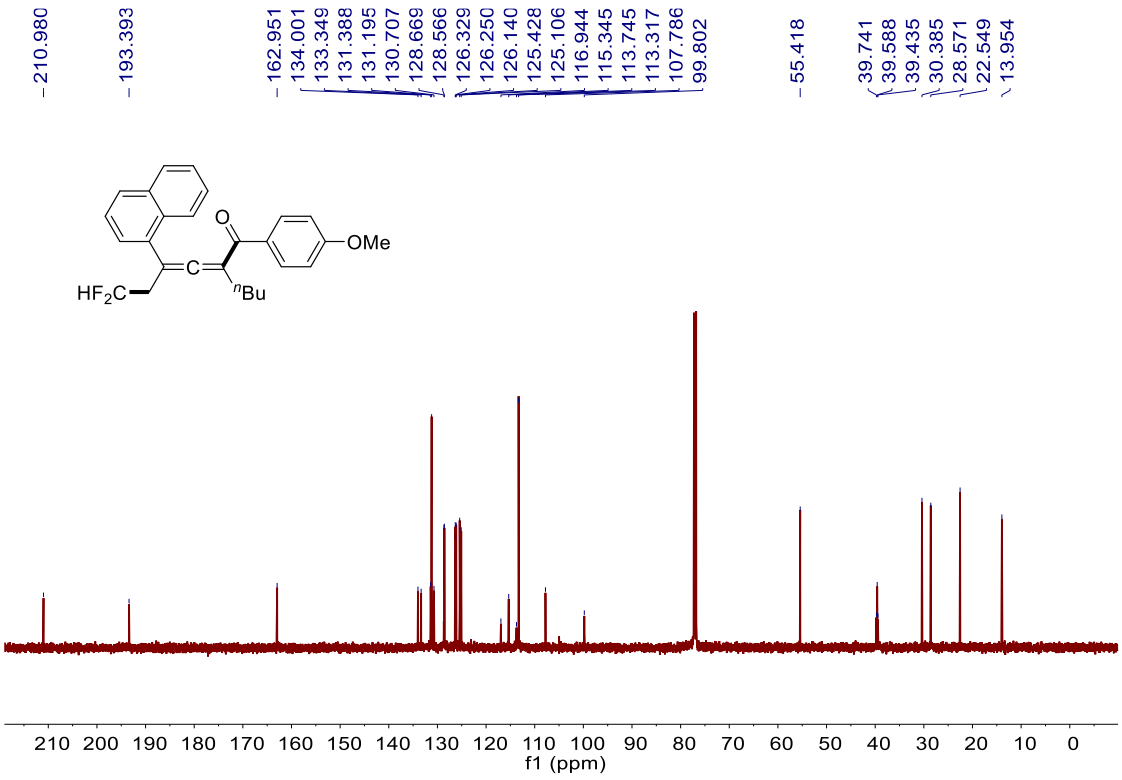
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qc**.



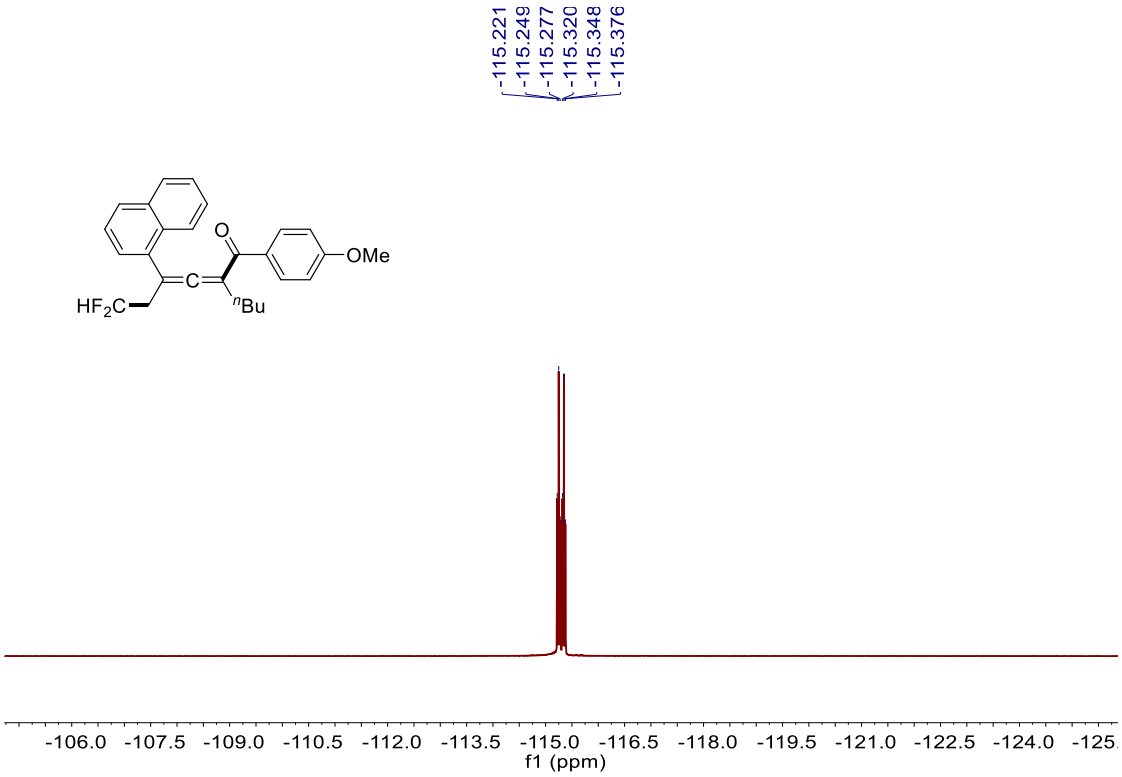
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qd**.



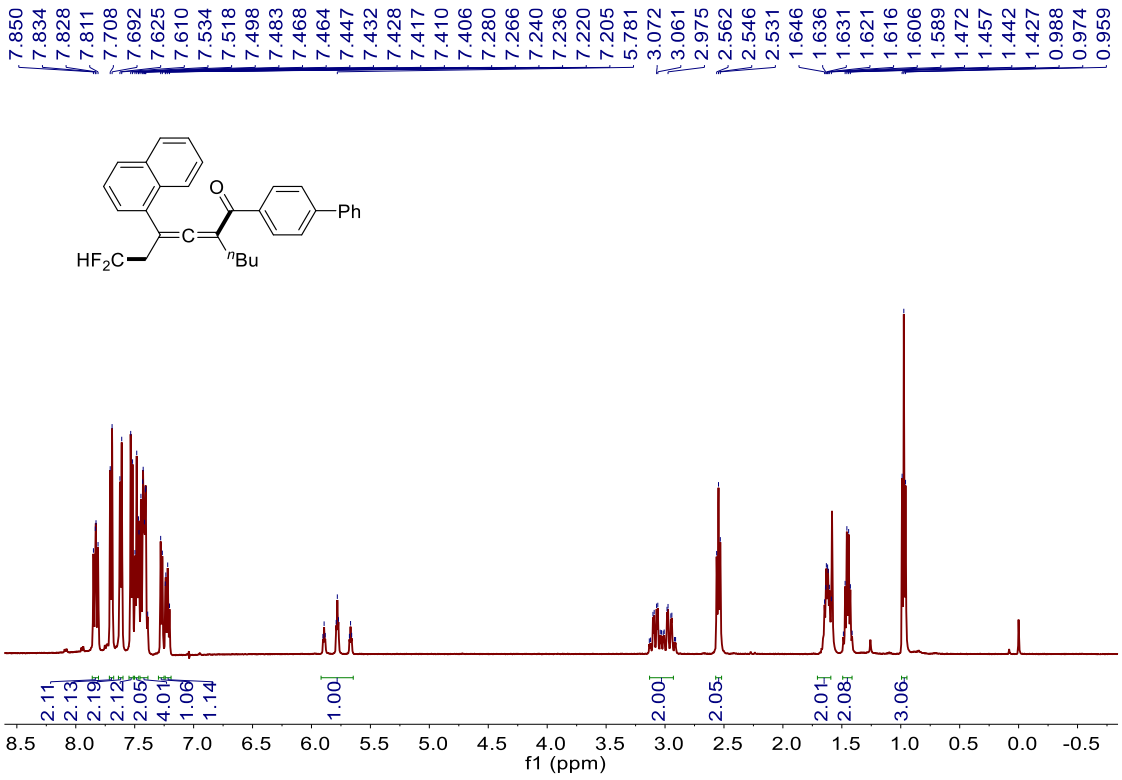
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qd**.



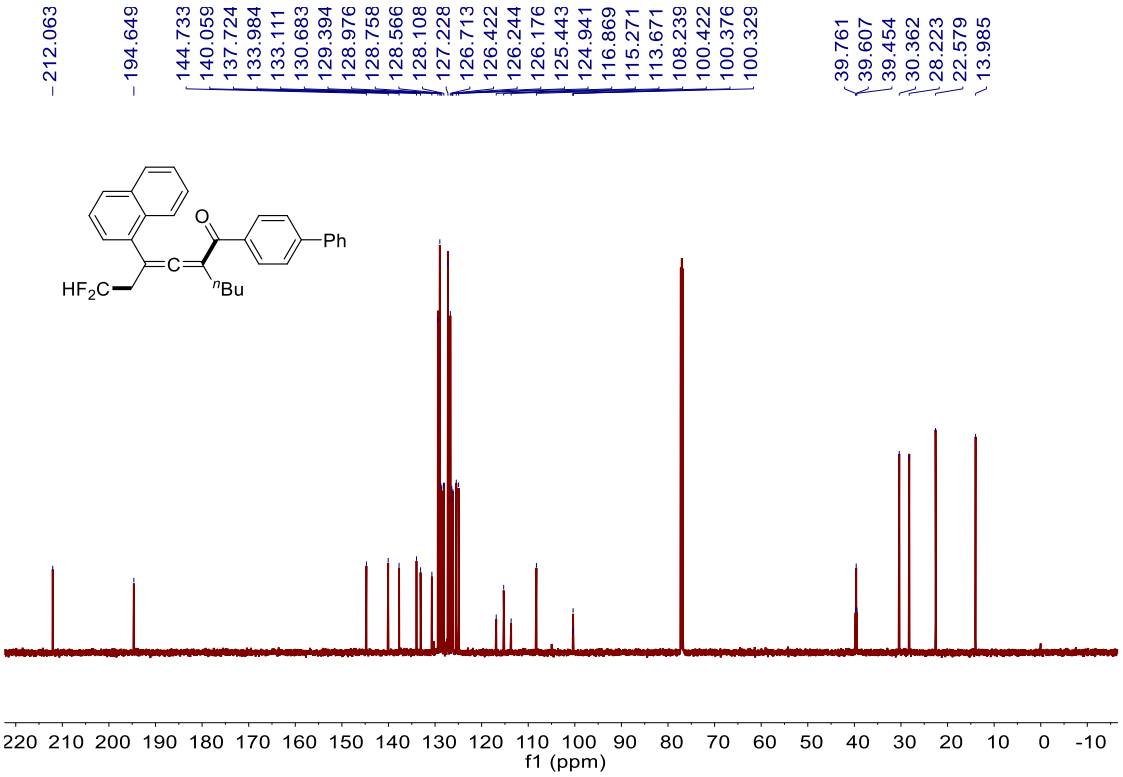
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qd**.



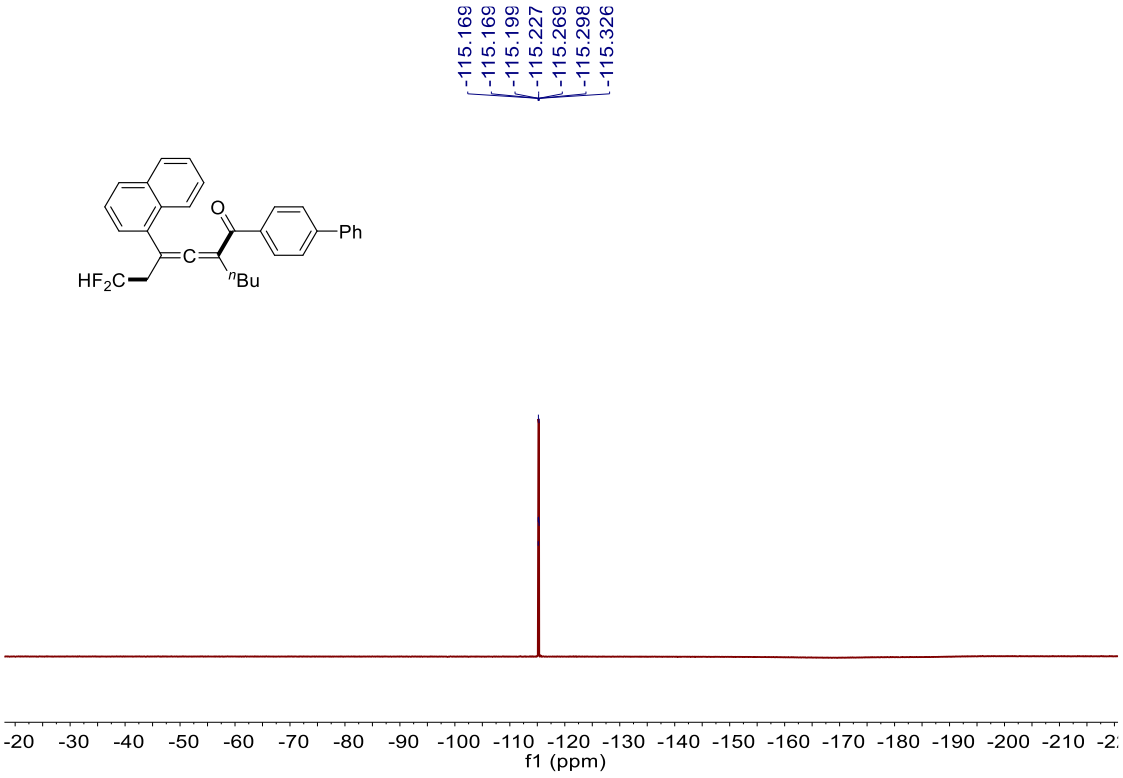
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qe**.



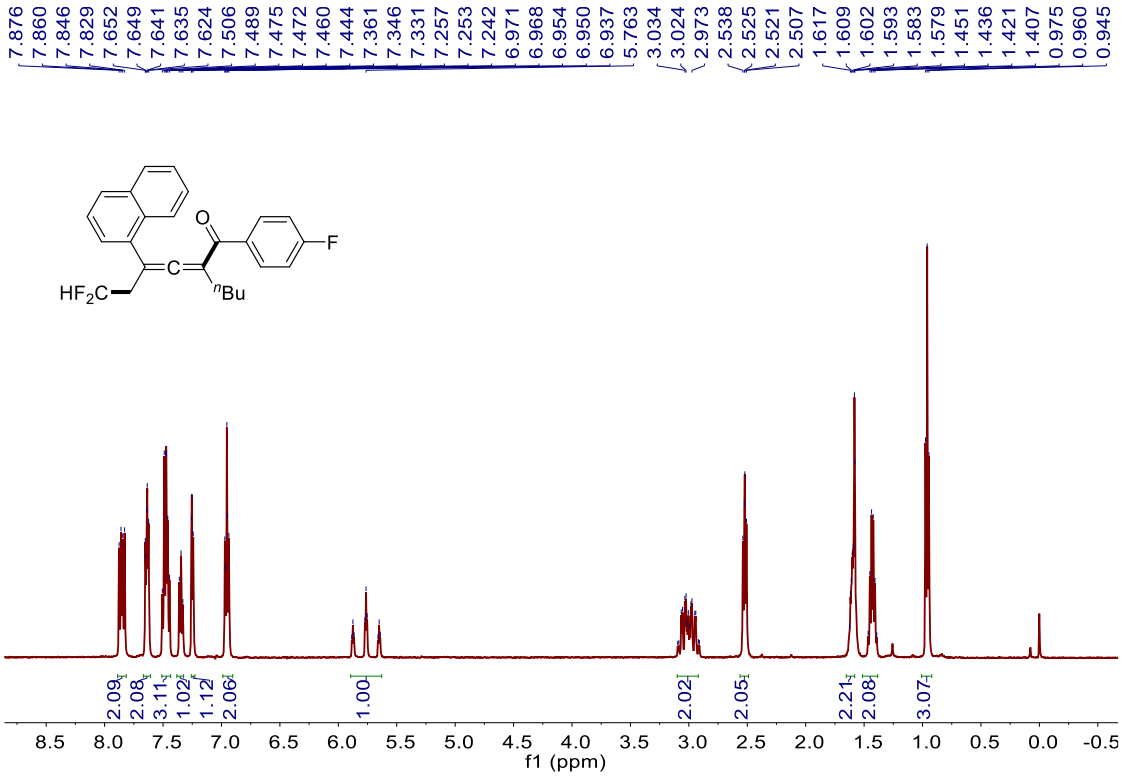
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qe**.



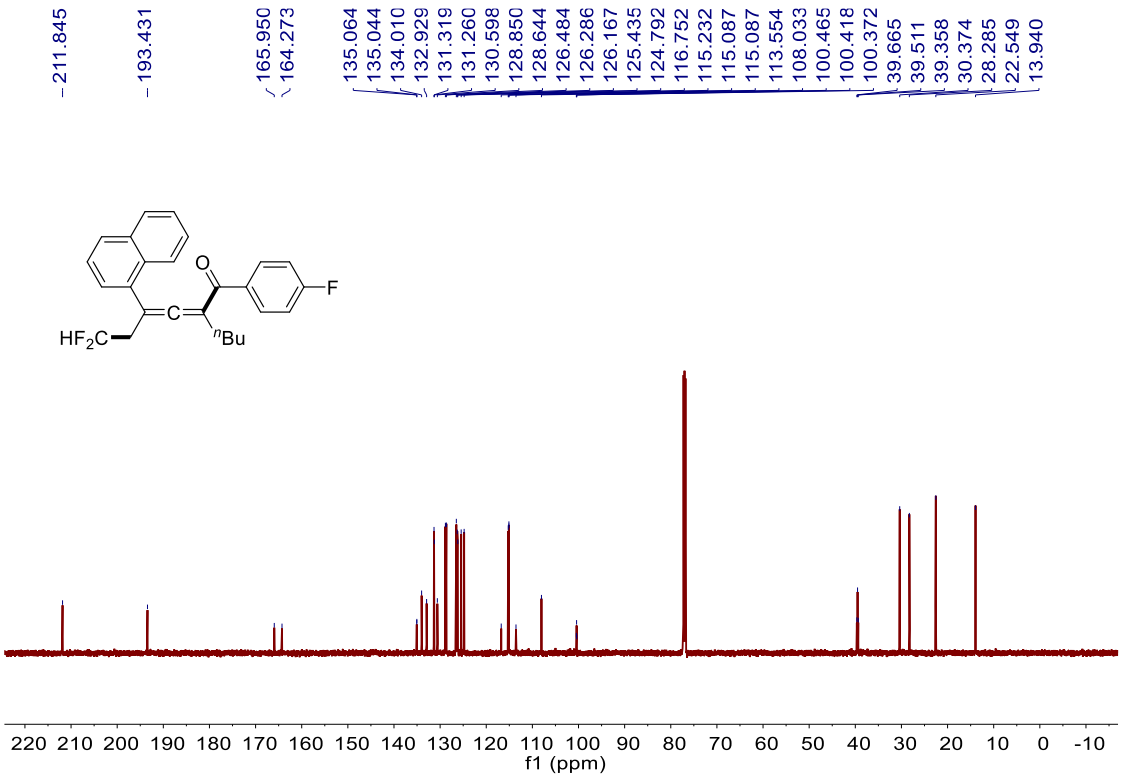
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qe**.



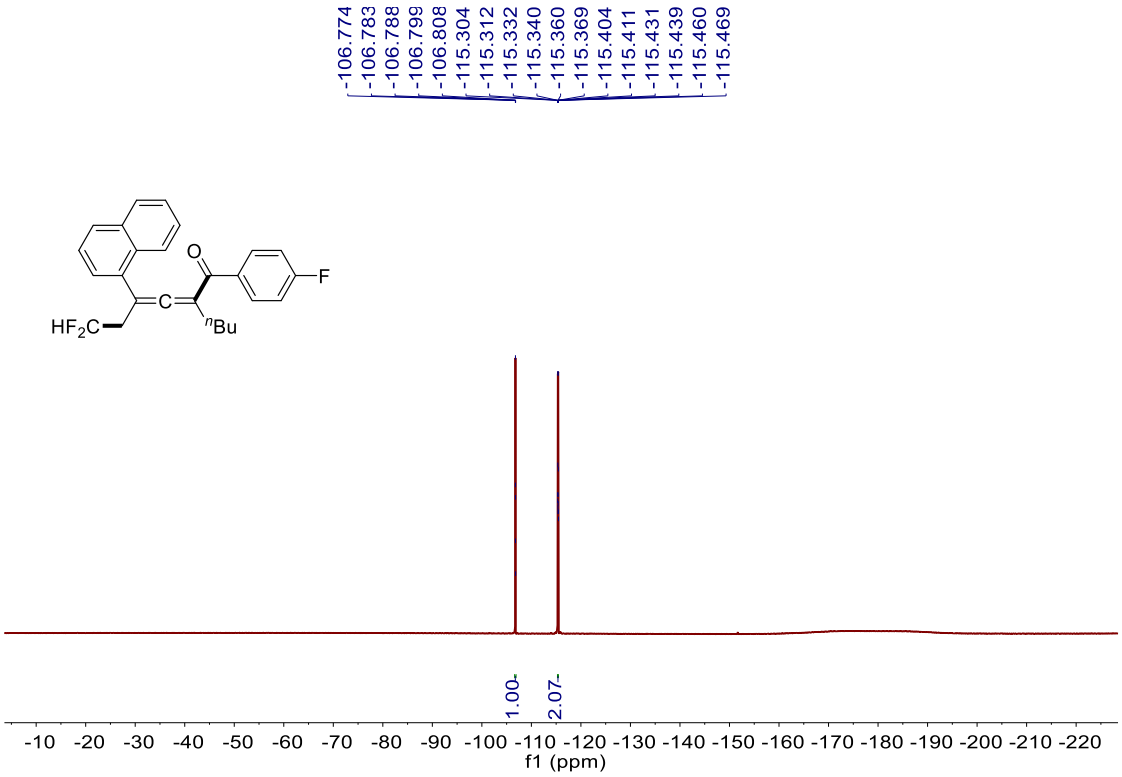
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qf**.



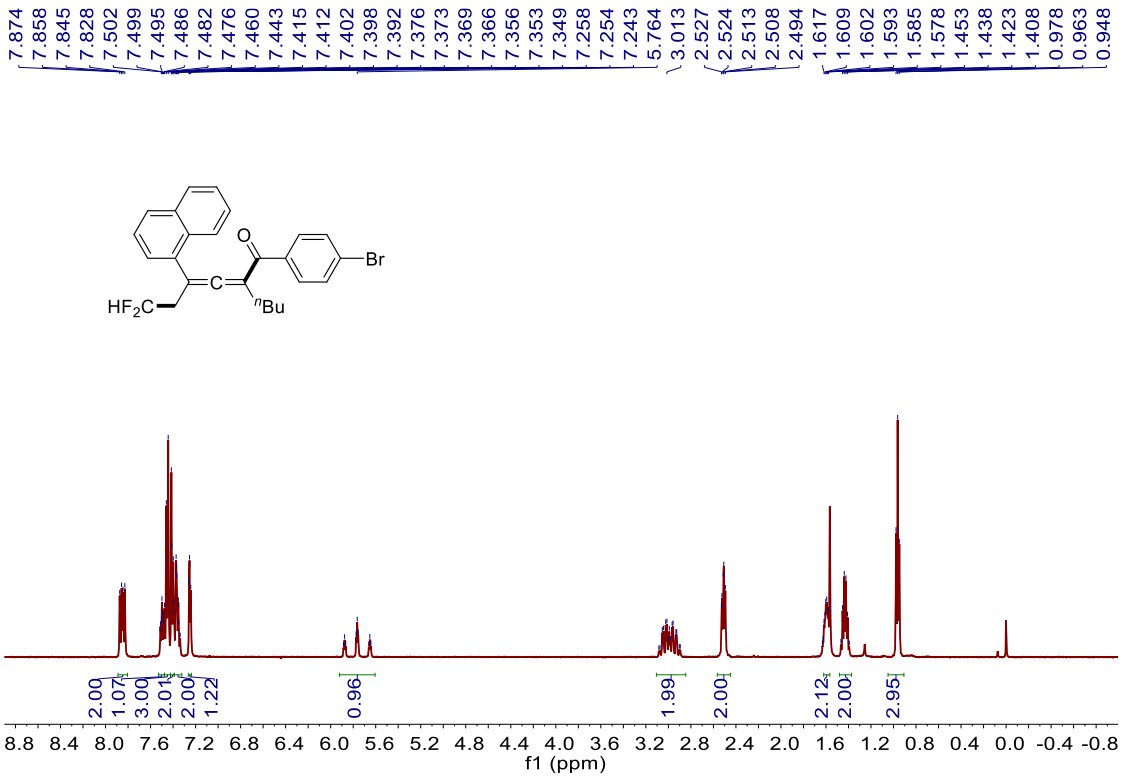
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qf**.



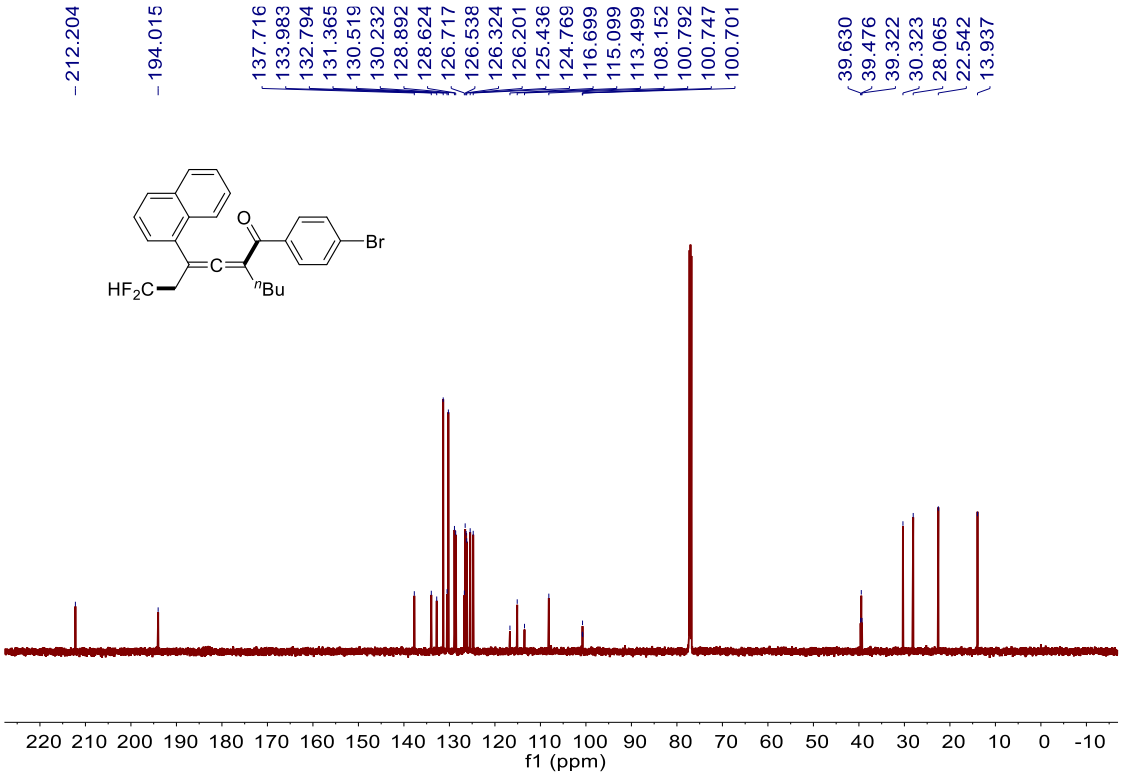
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qf**.



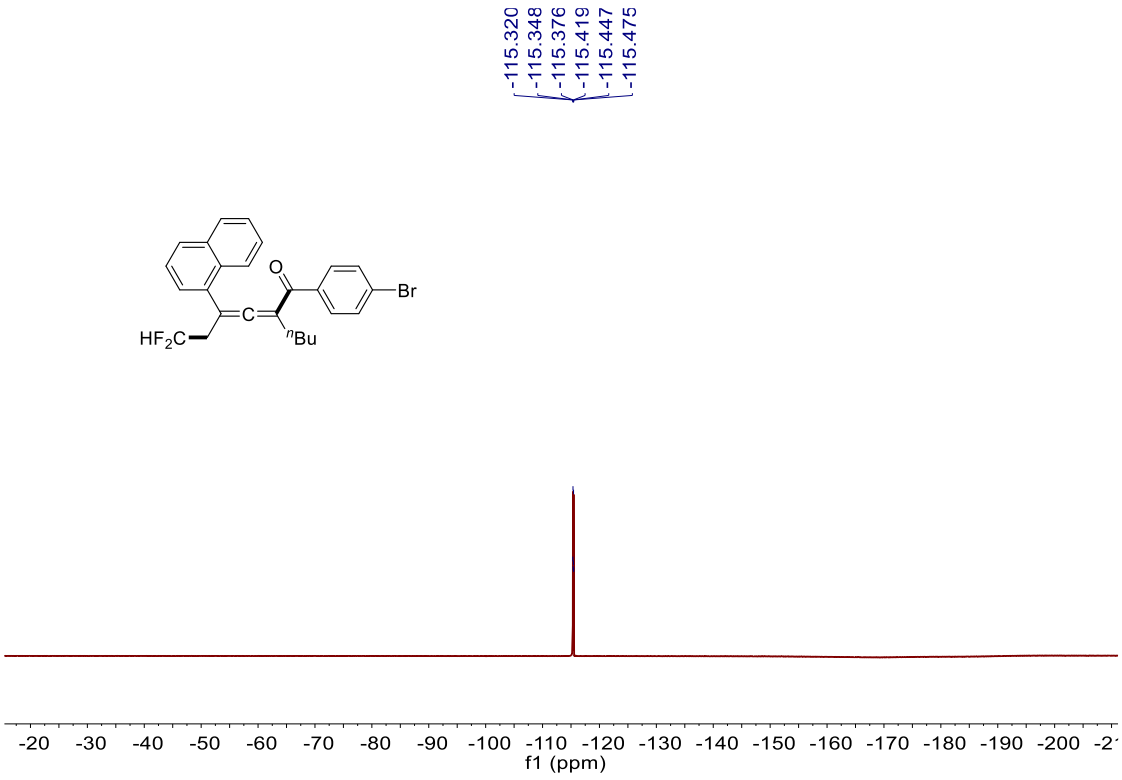
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qg**.



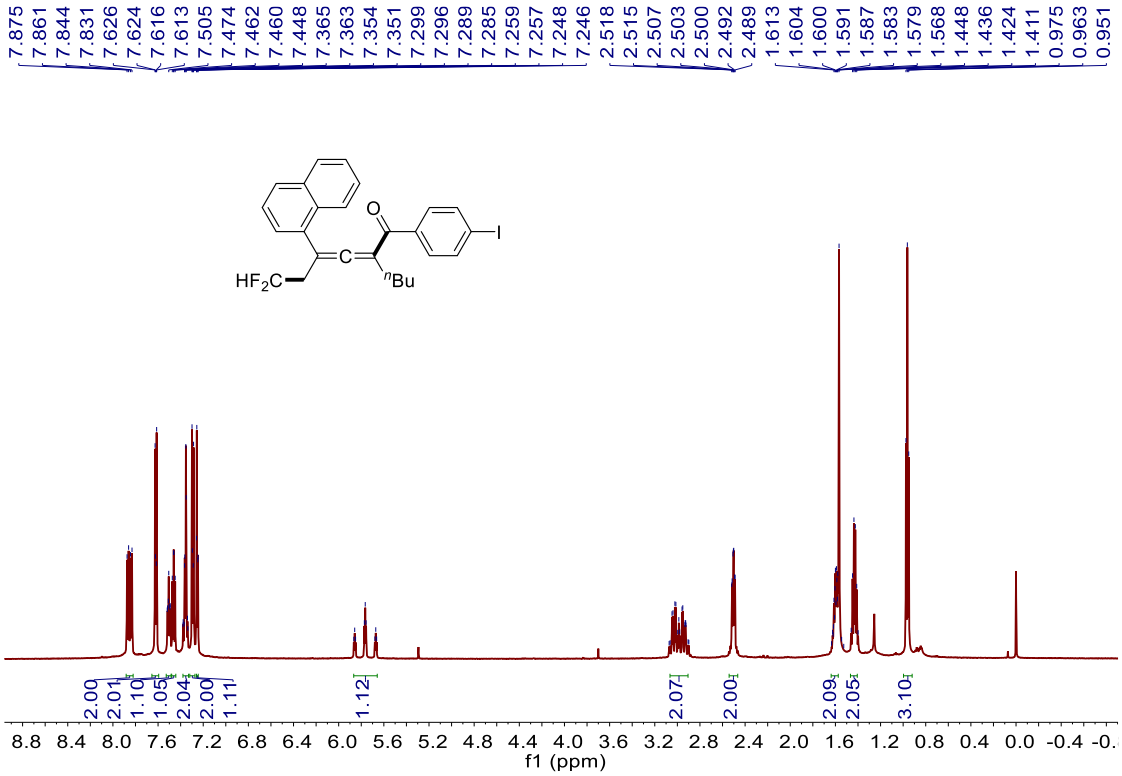
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qg**.



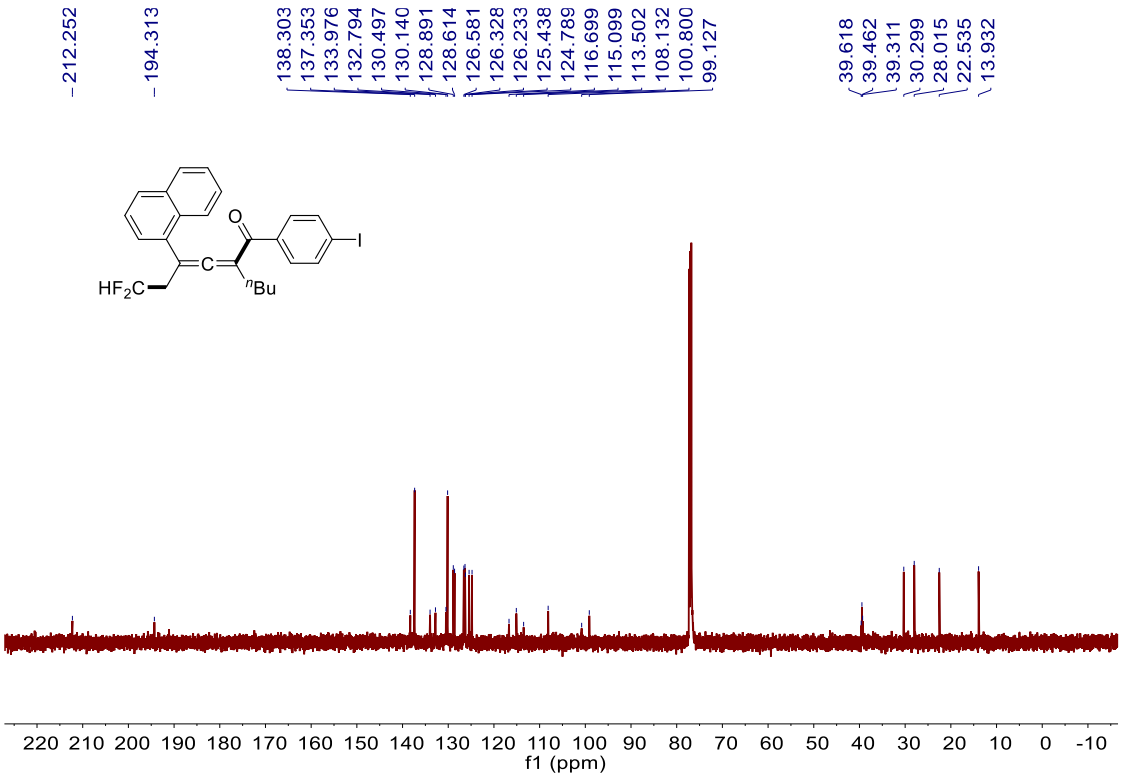
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qg**.



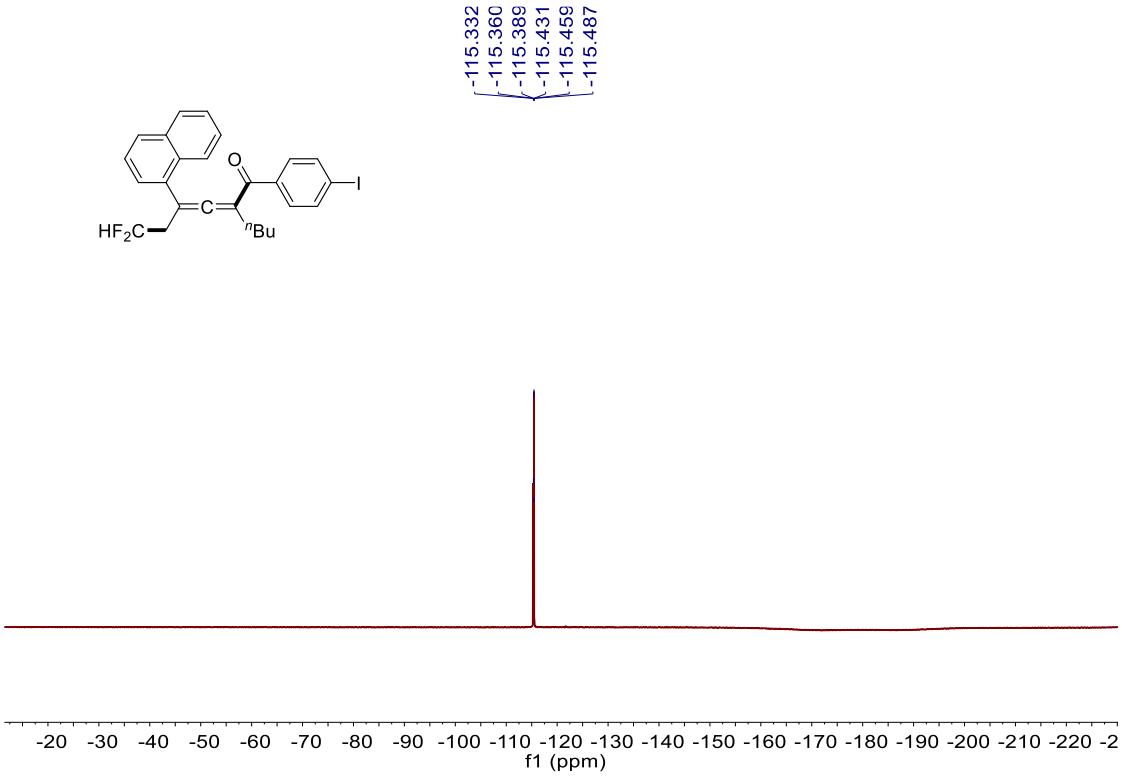
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qh**.



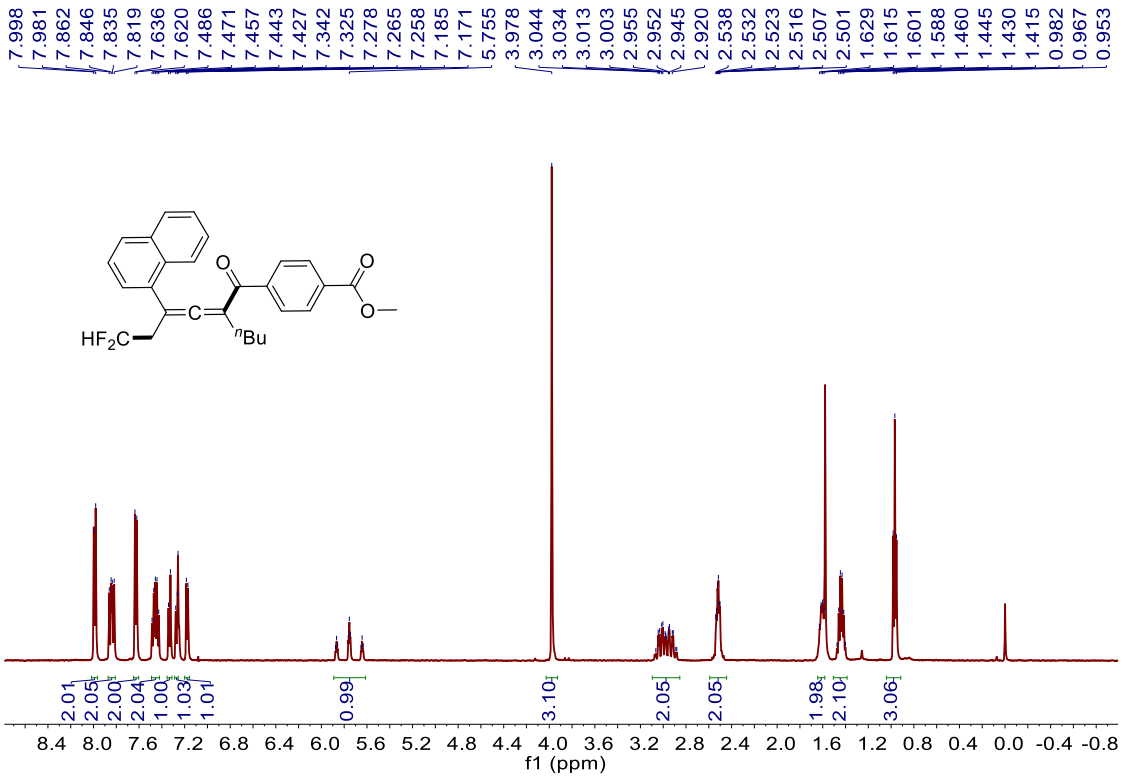
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qh**.



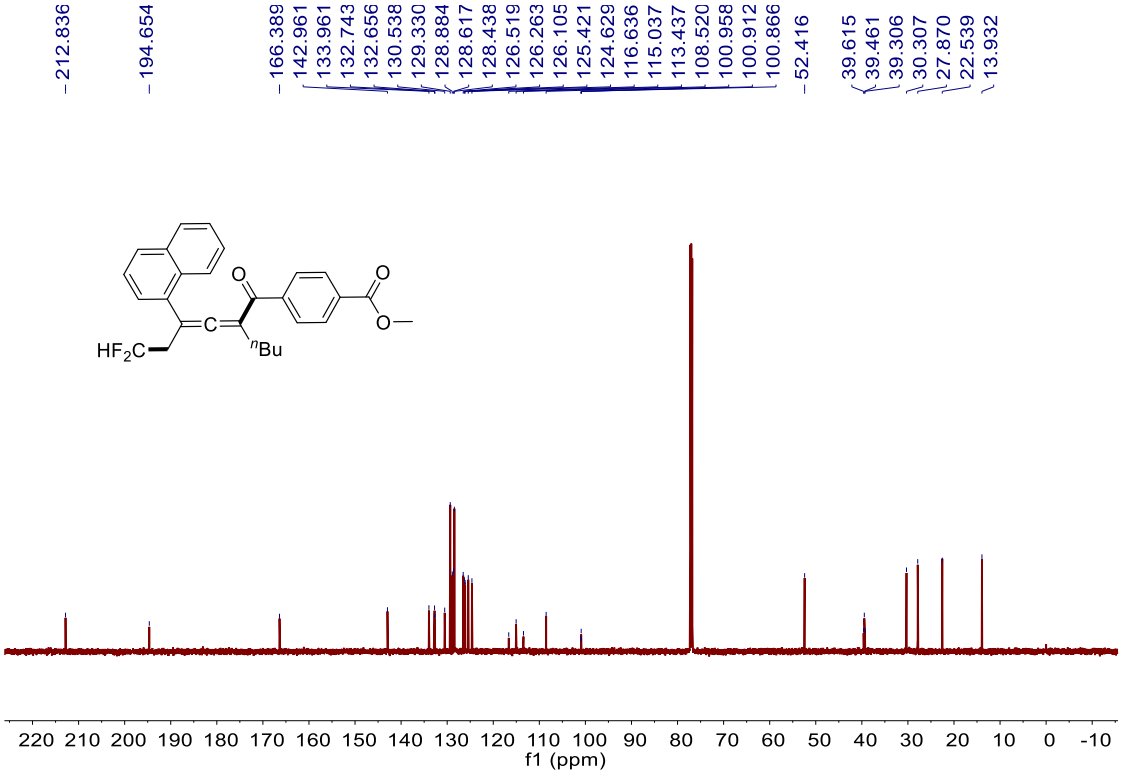
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qh**.



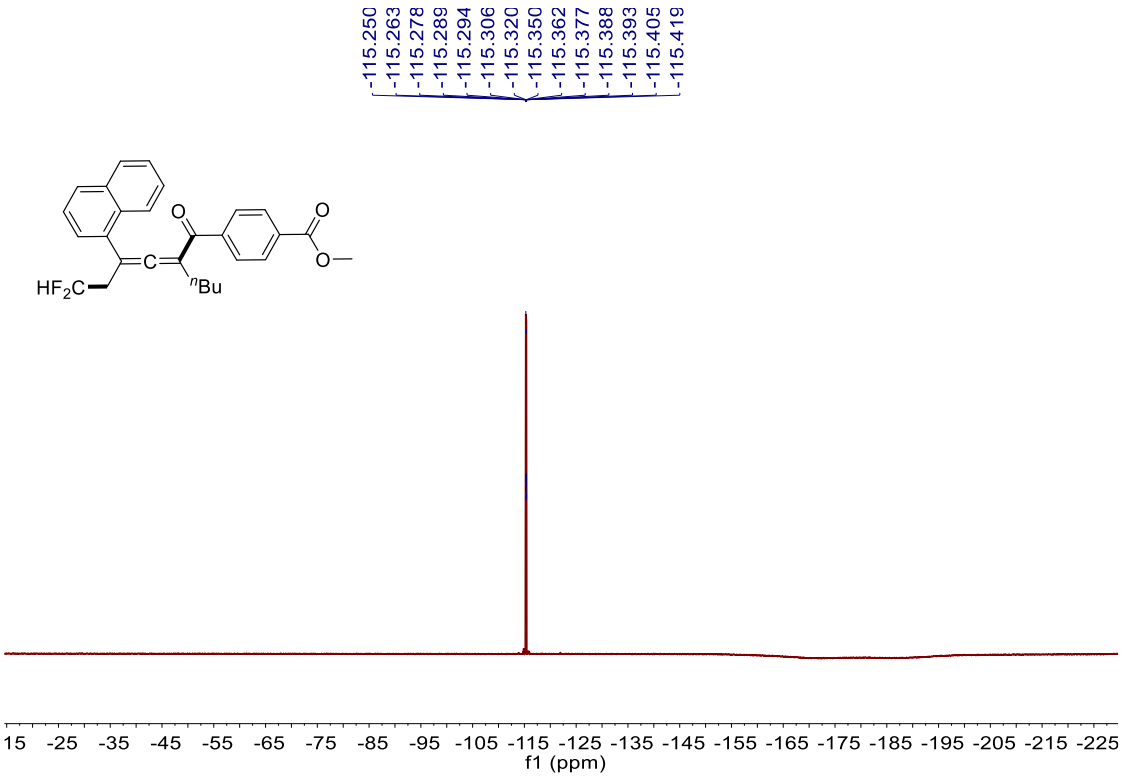
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qi**.



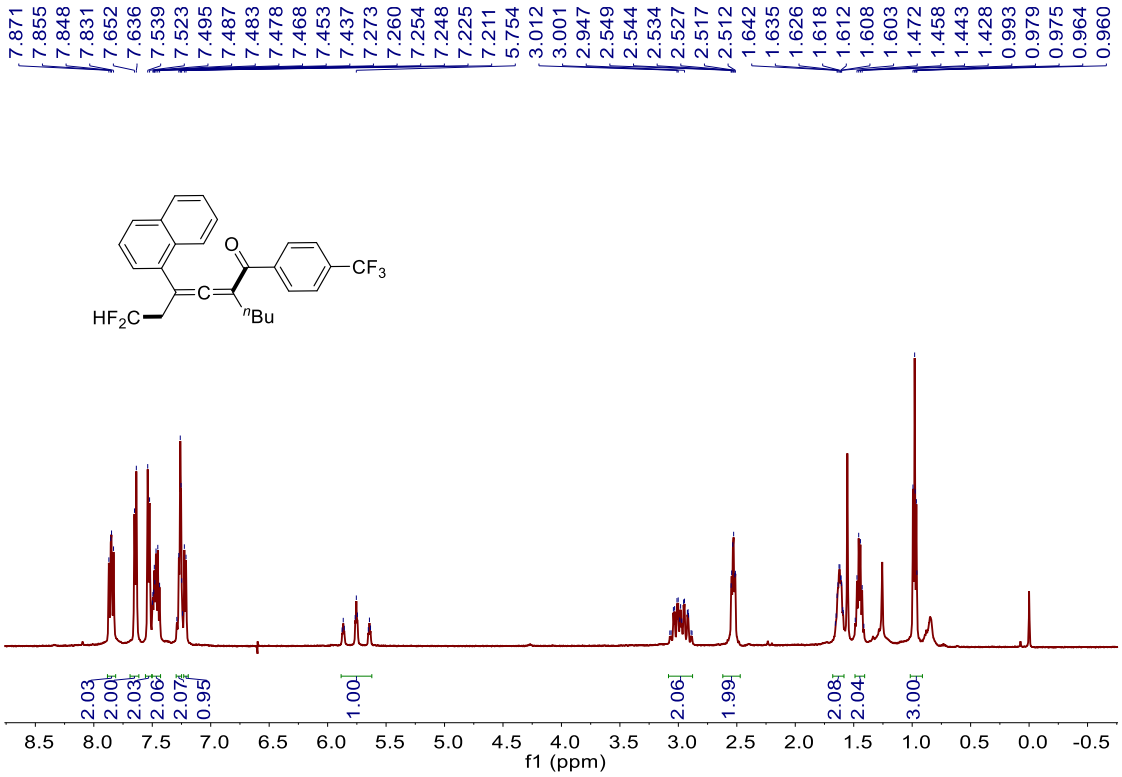
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qi**.



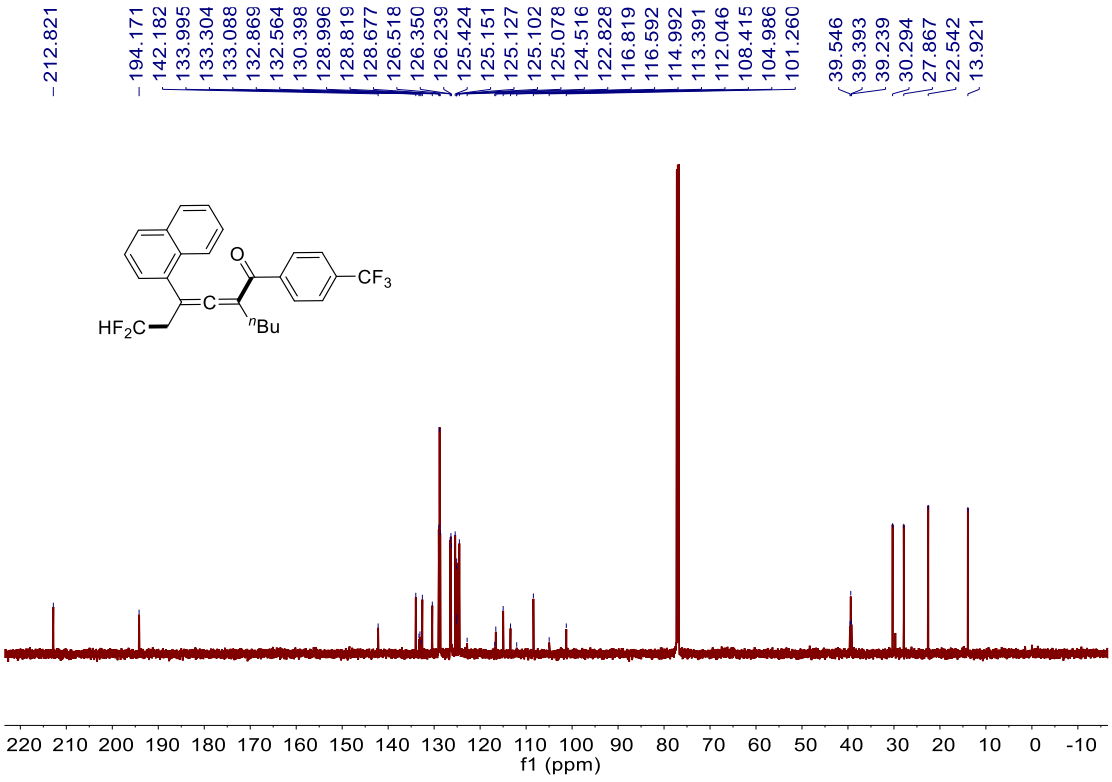
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qi**.



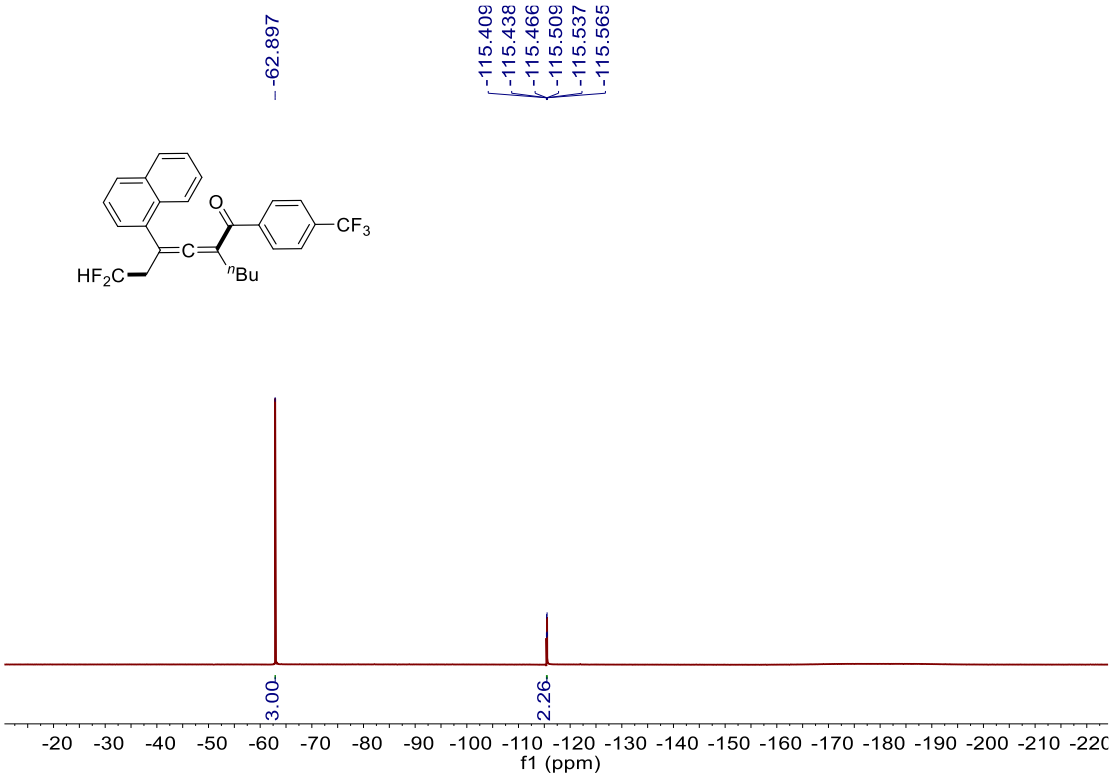
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qj**.



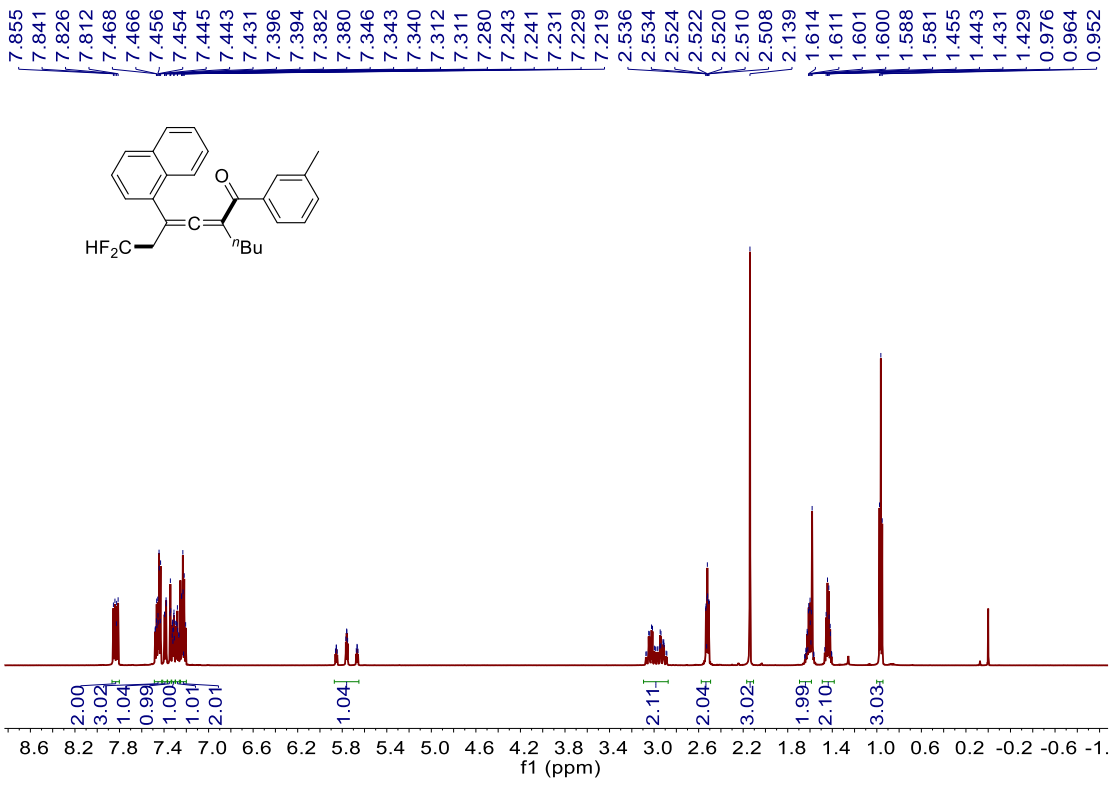
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qj**.



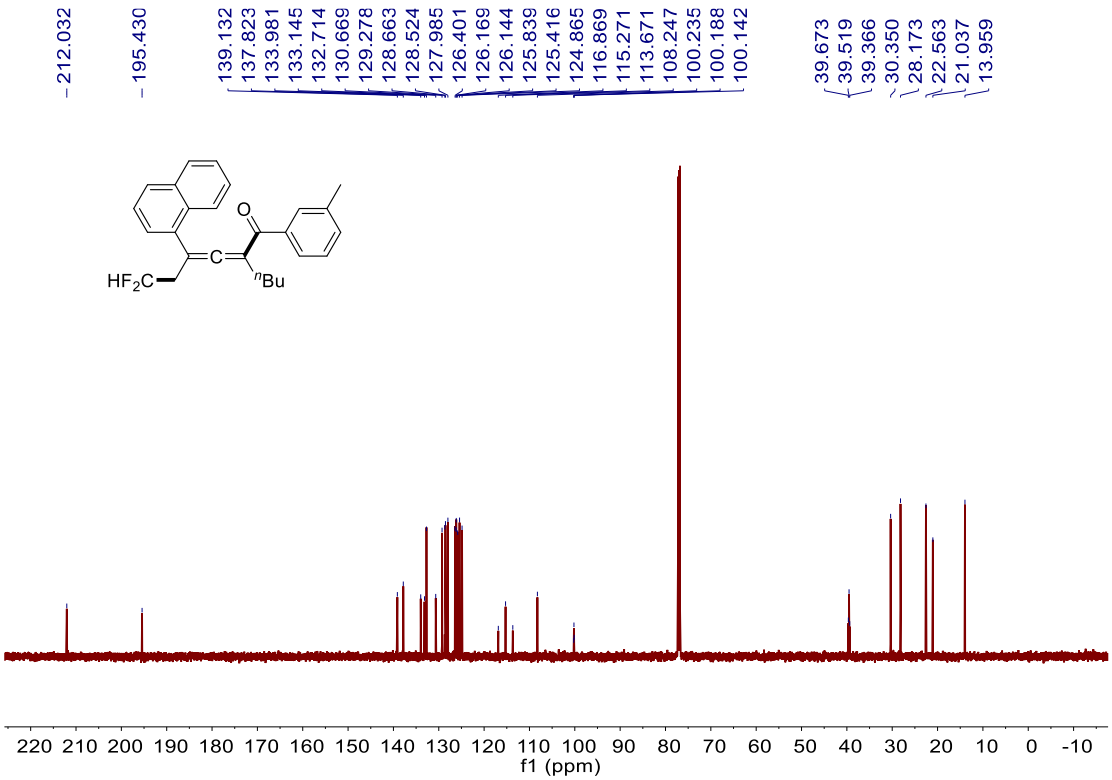
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qj**.



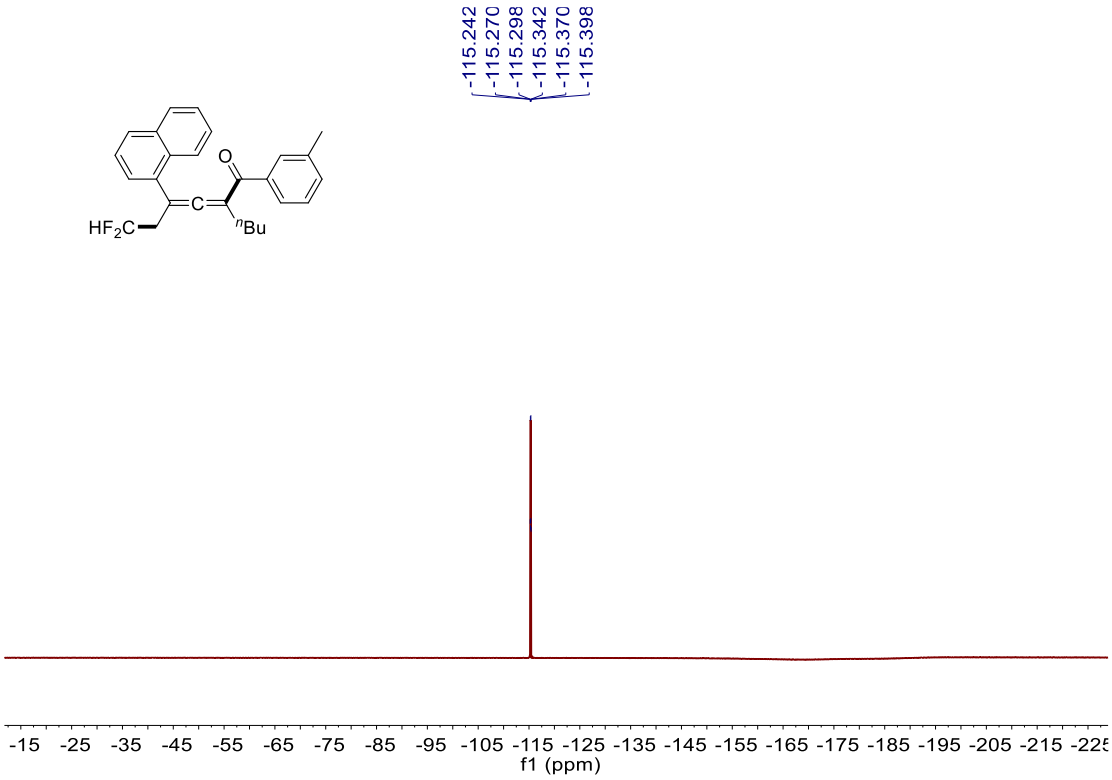
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5ql**.



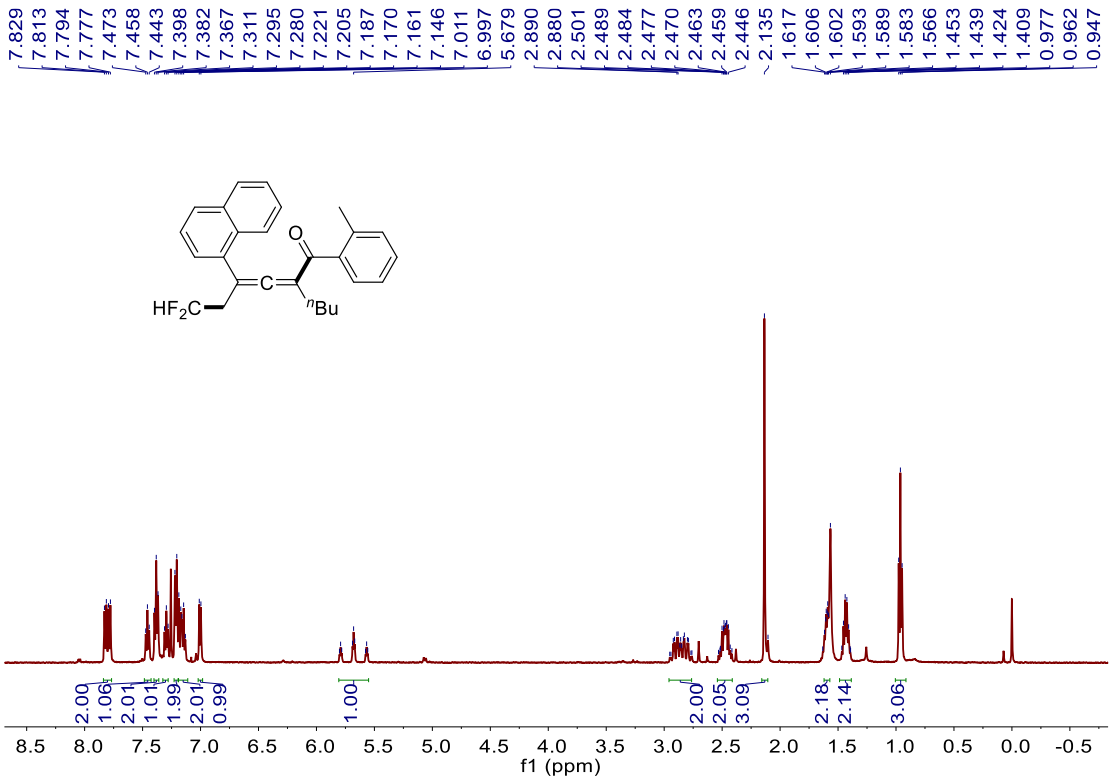
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5ql**.



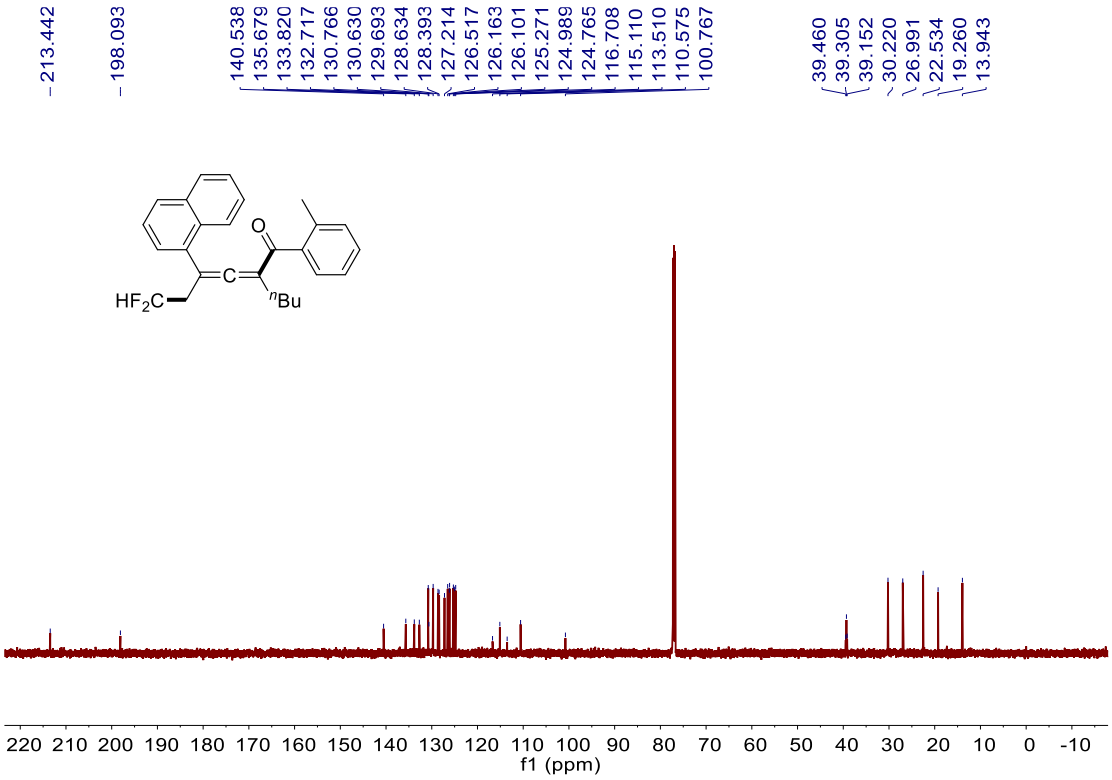
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5ql**.



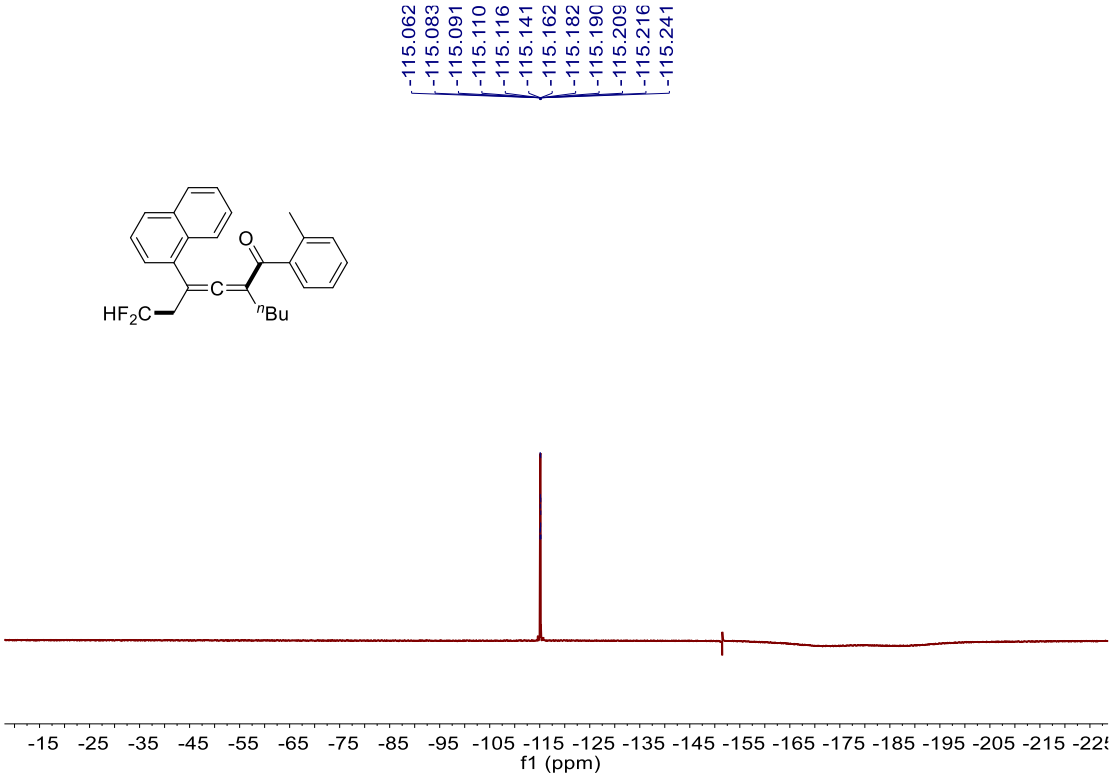
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qp**.



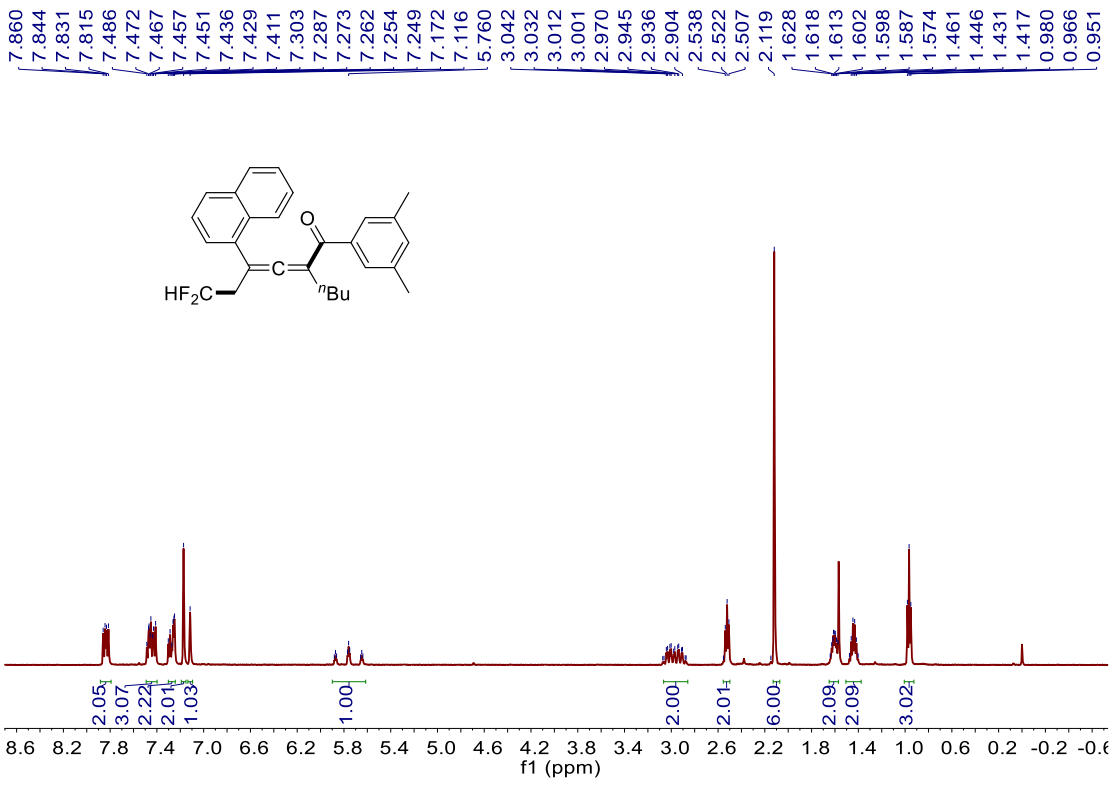
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qp**.



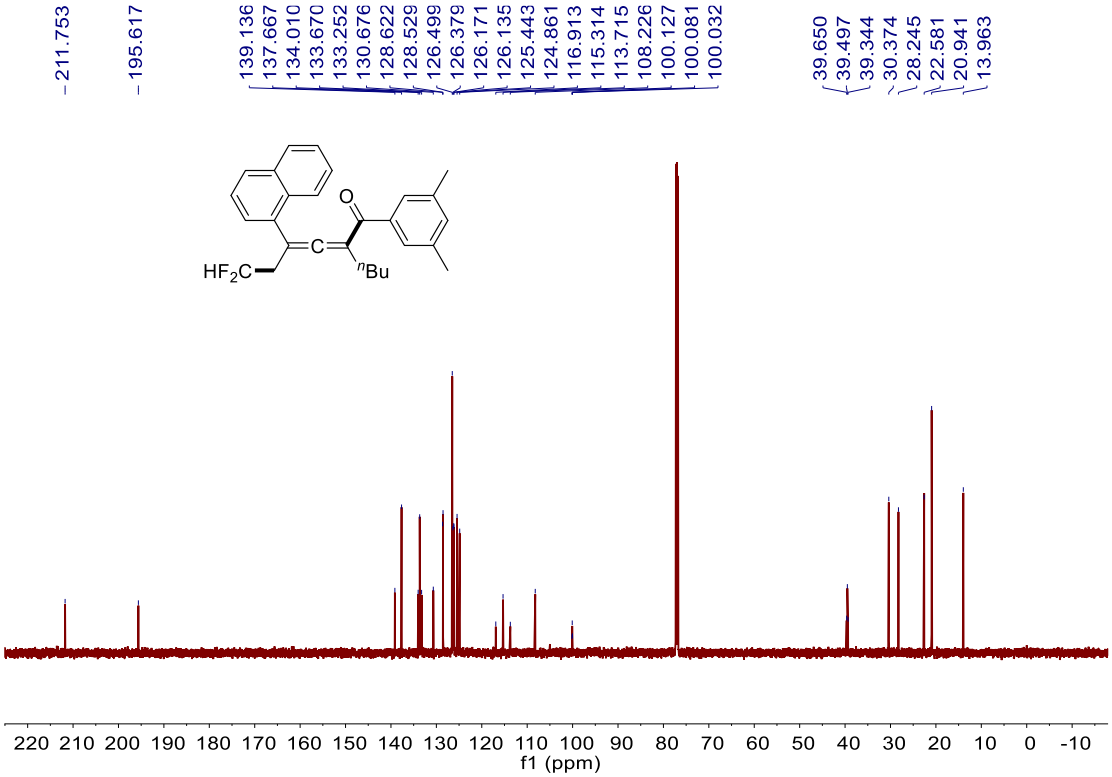
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qp**.



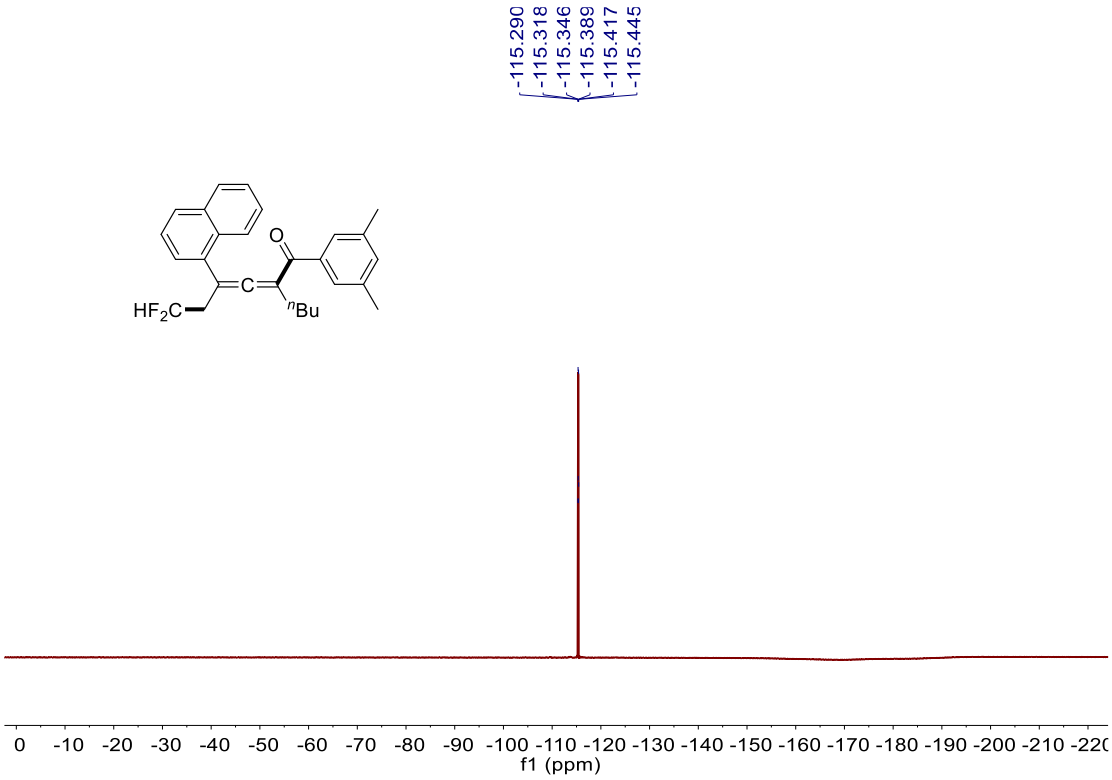
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qq**.



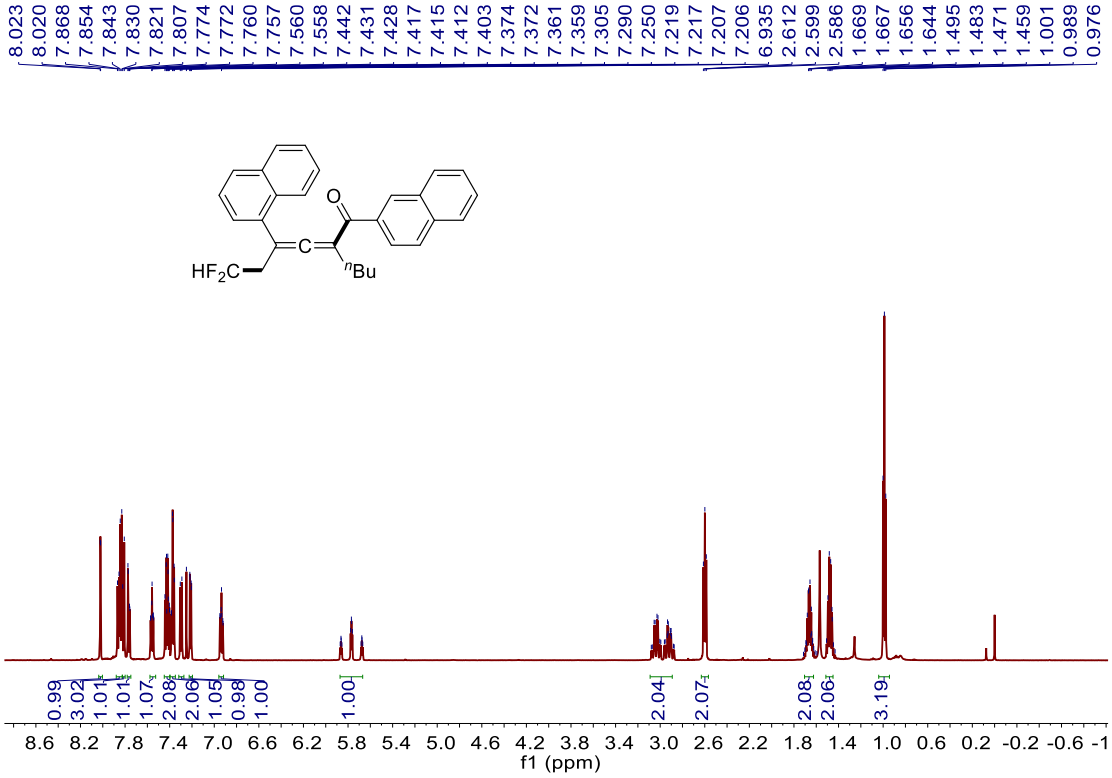
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qq**.



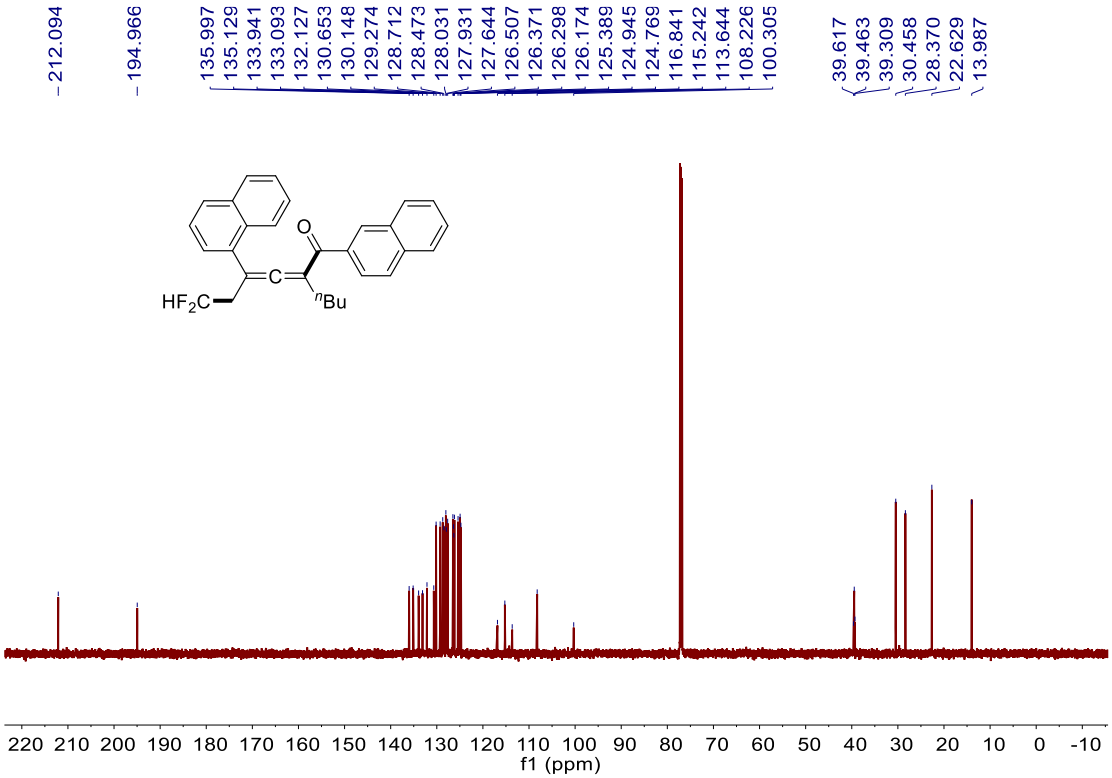
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qq**.



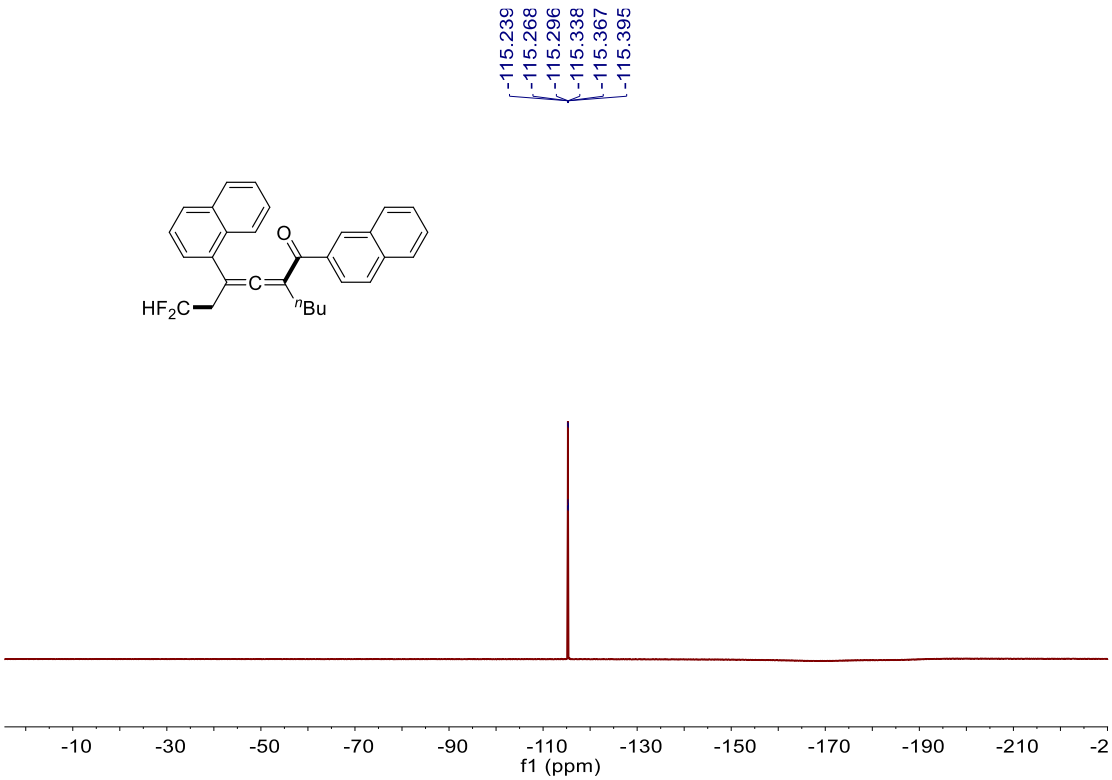
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qr**.



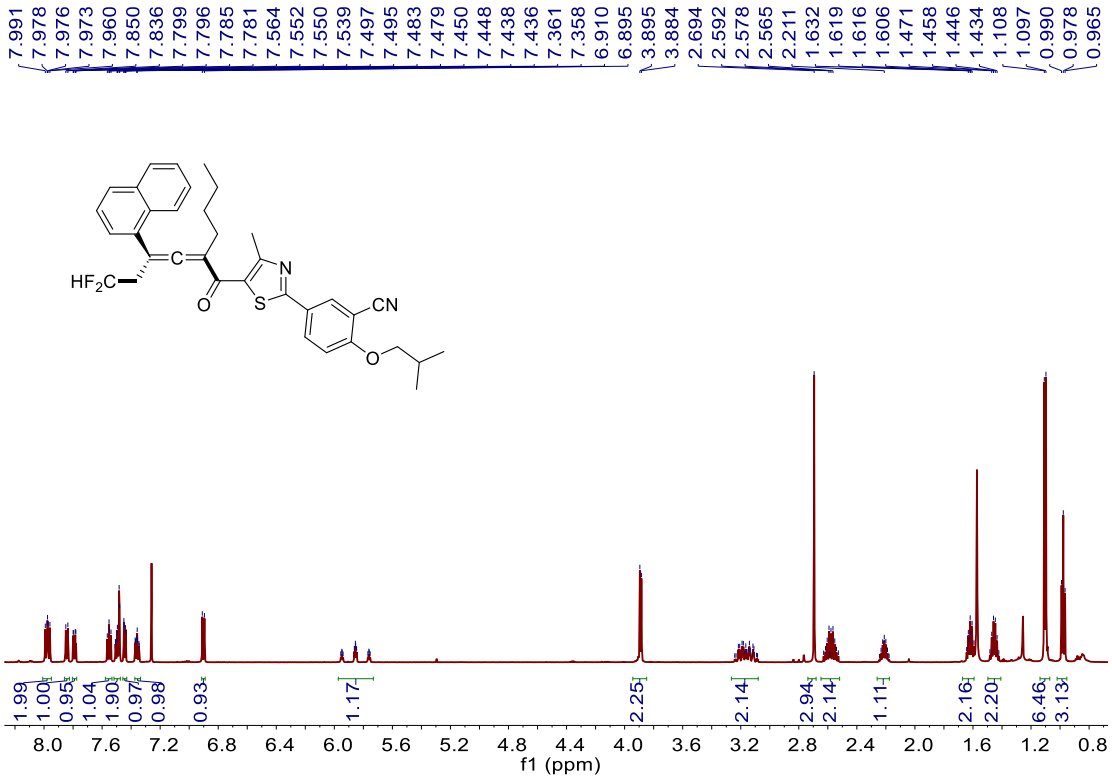
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qr**.



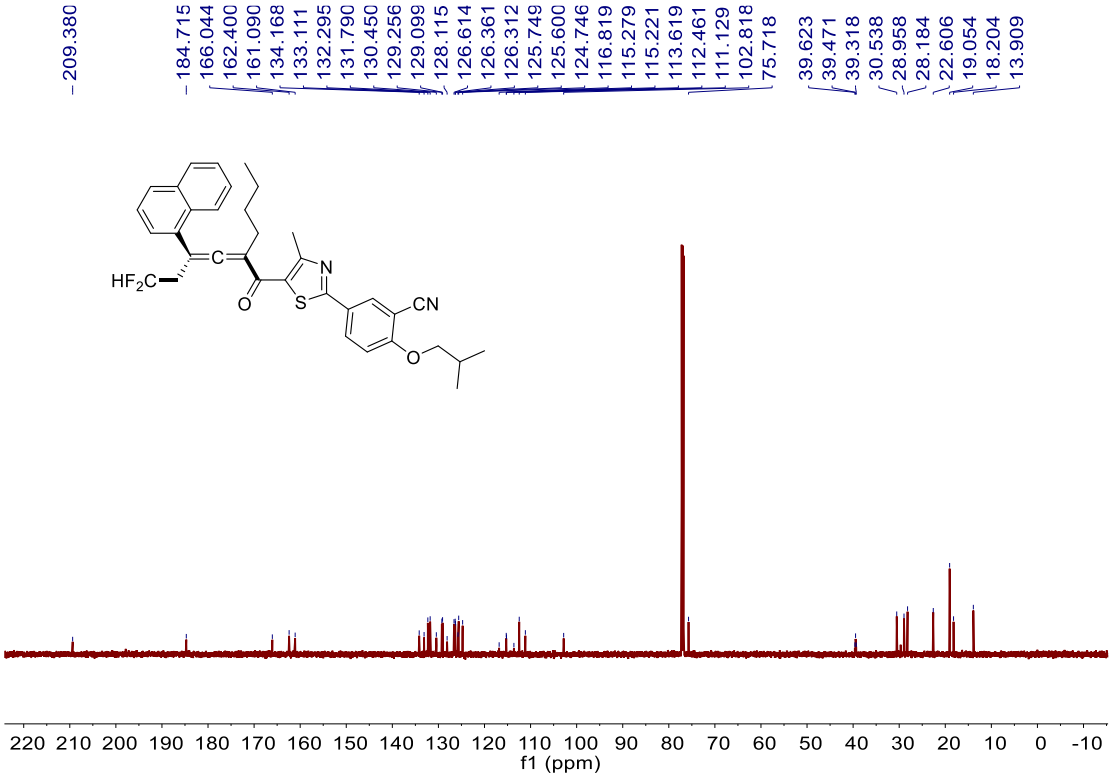
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qr**.



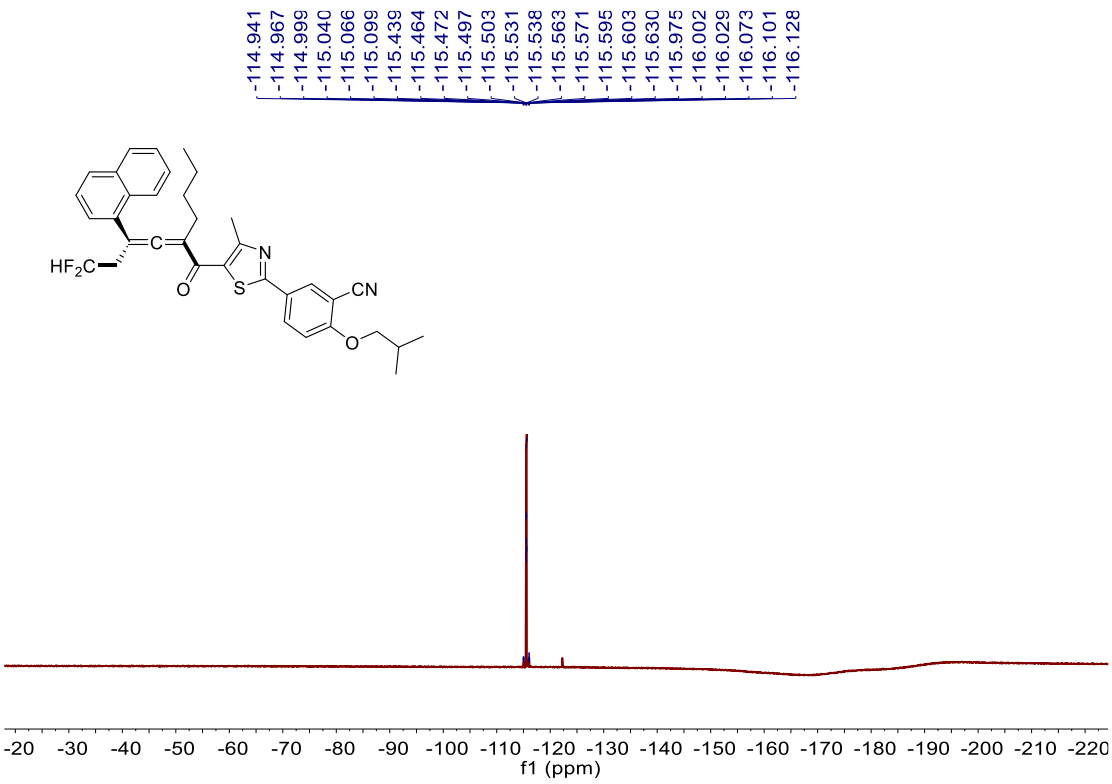
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qs**.



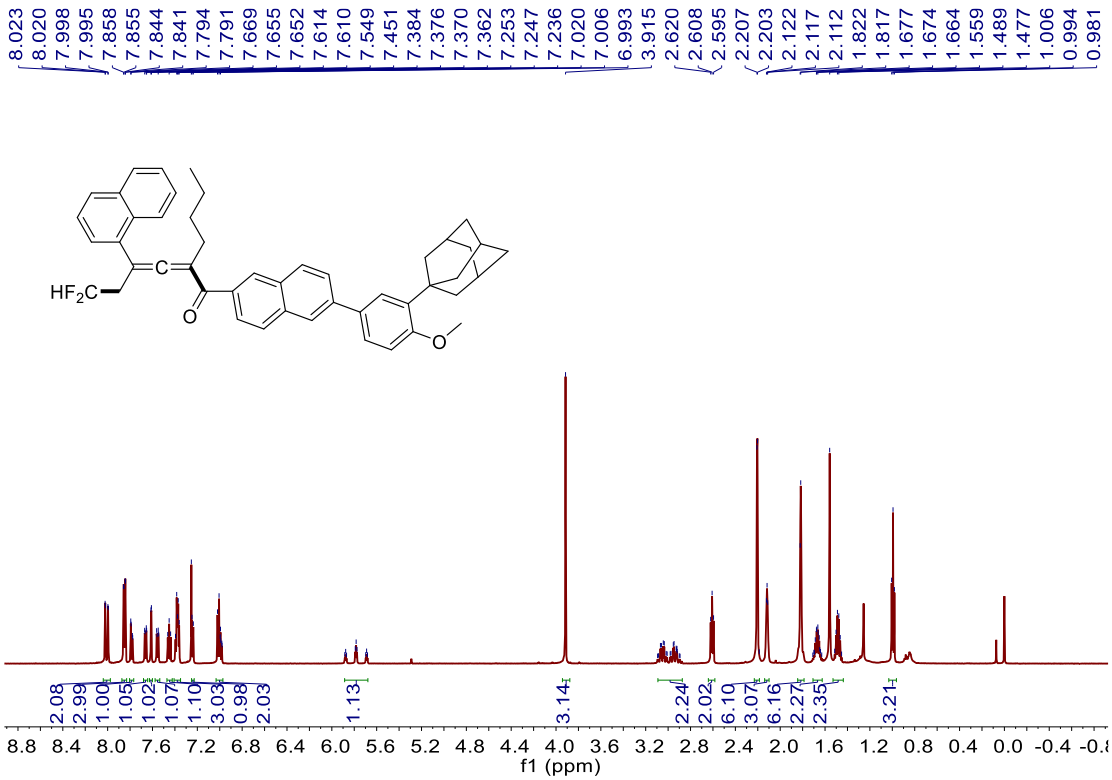
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qs**.



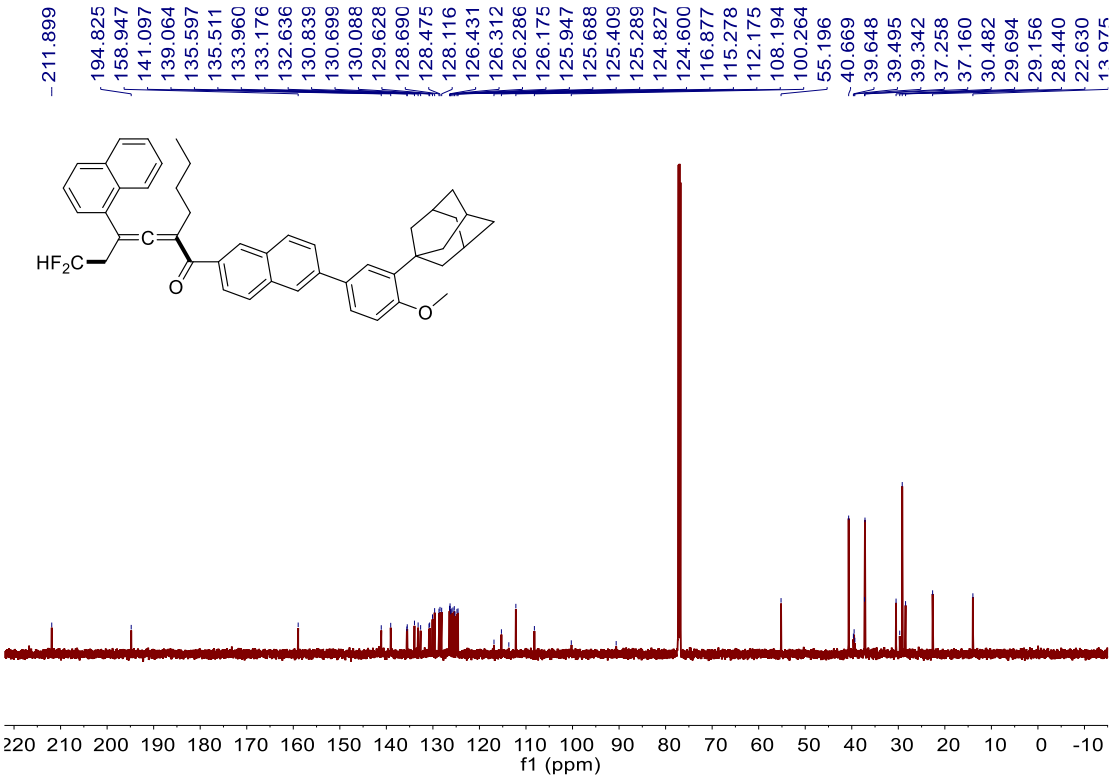
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qs**.



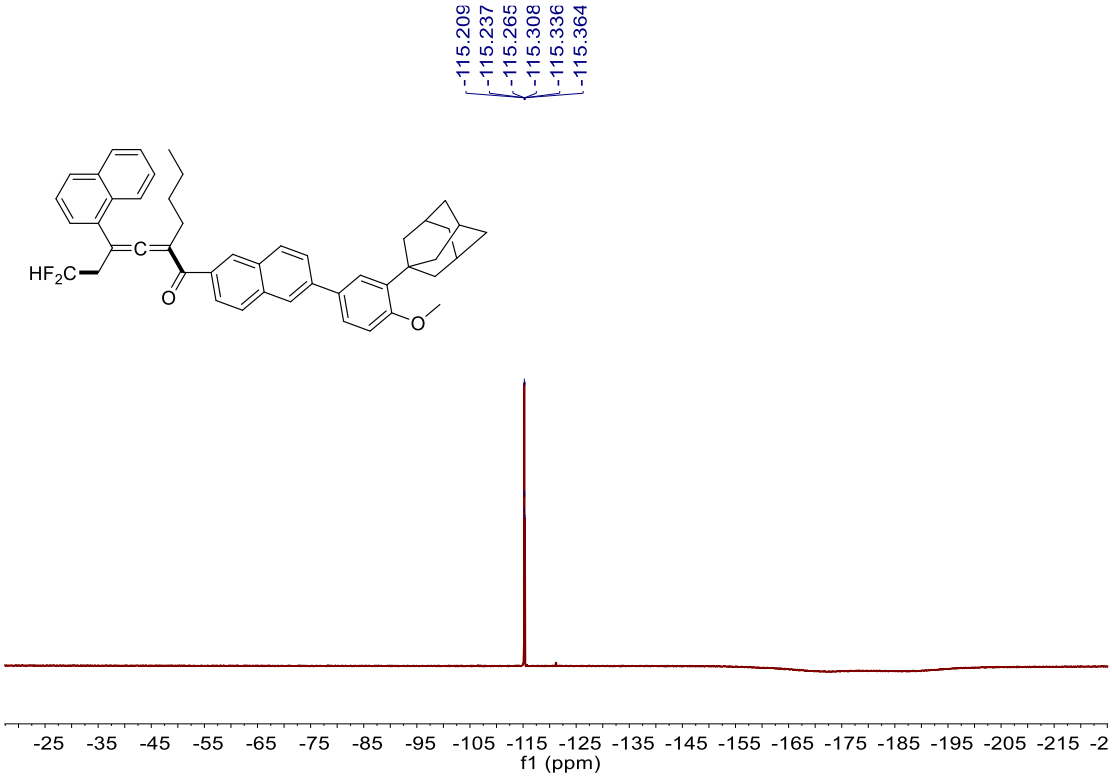
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5qt**.



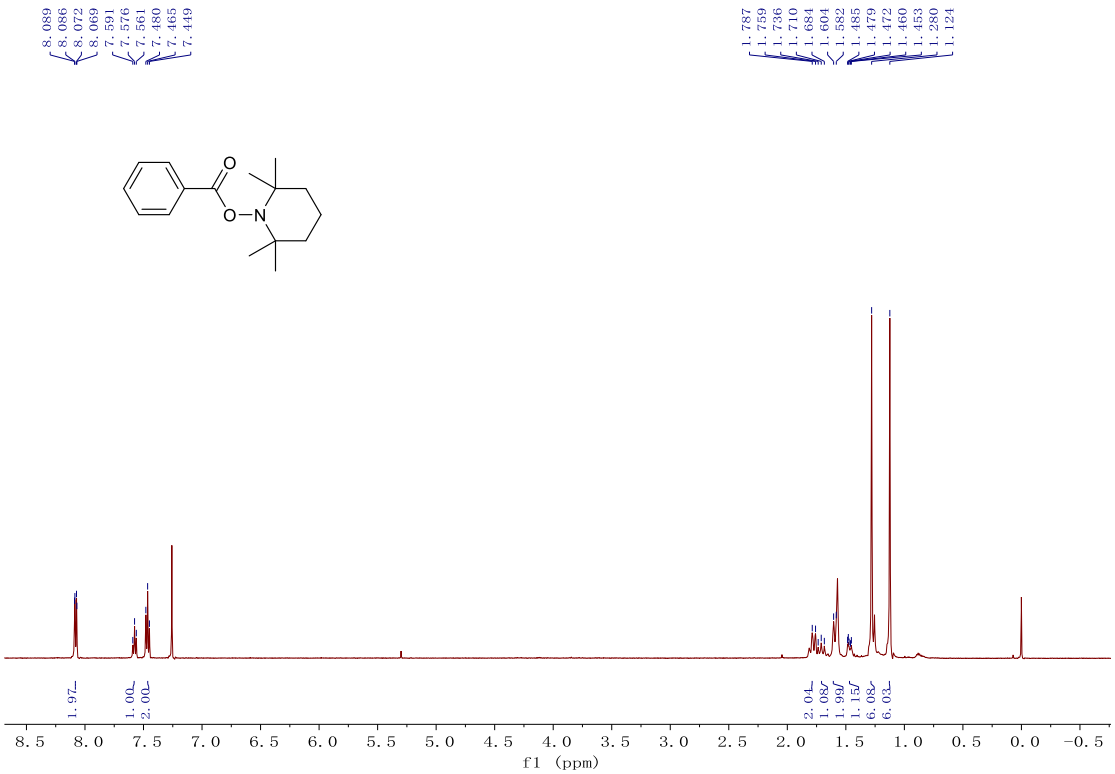
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5qt**.



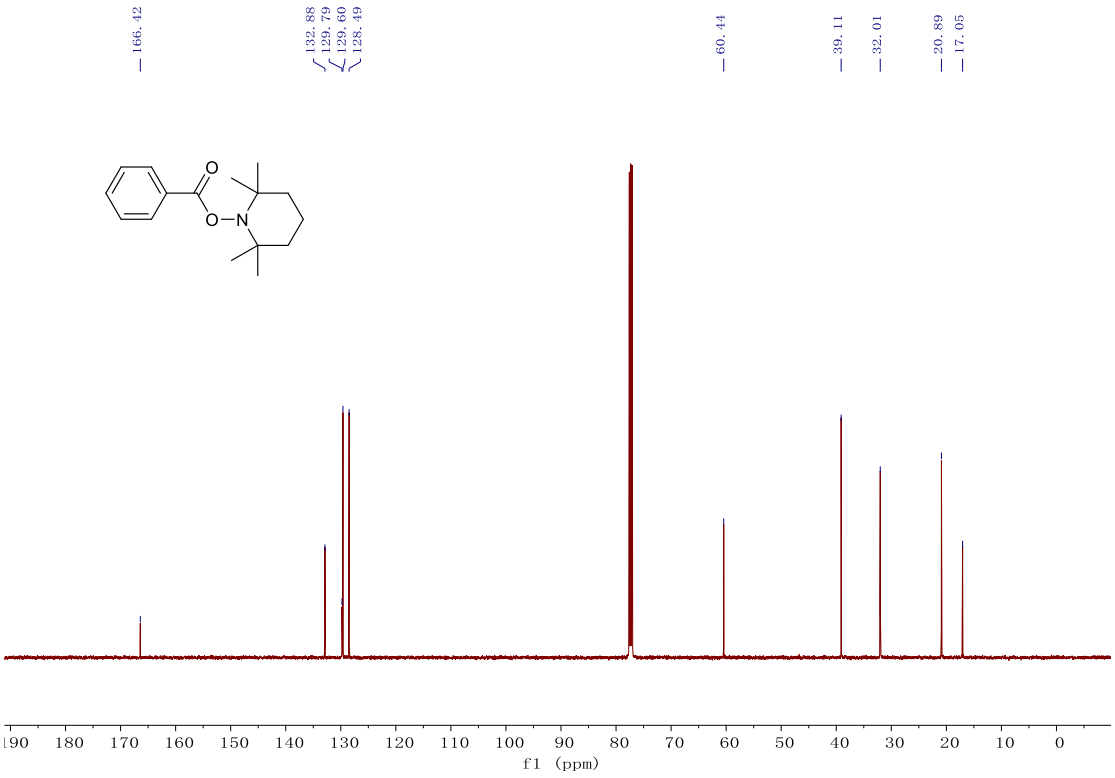
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **5qt**.



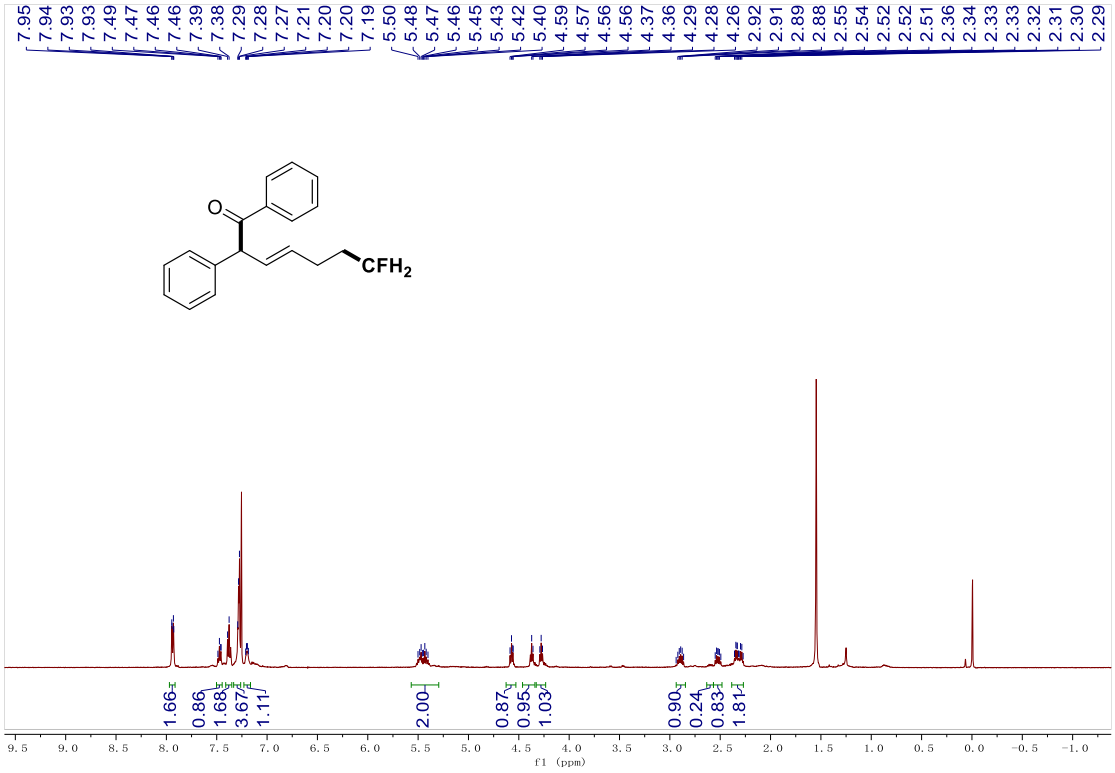
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **6a**.



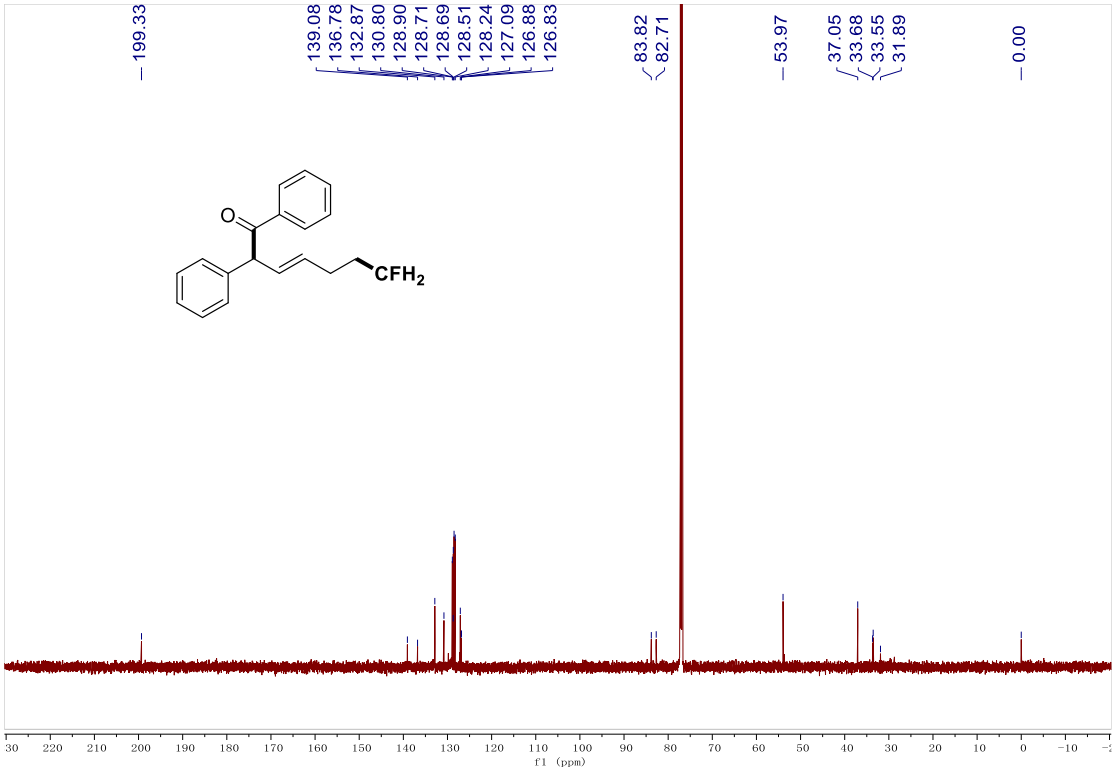
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **6a**.



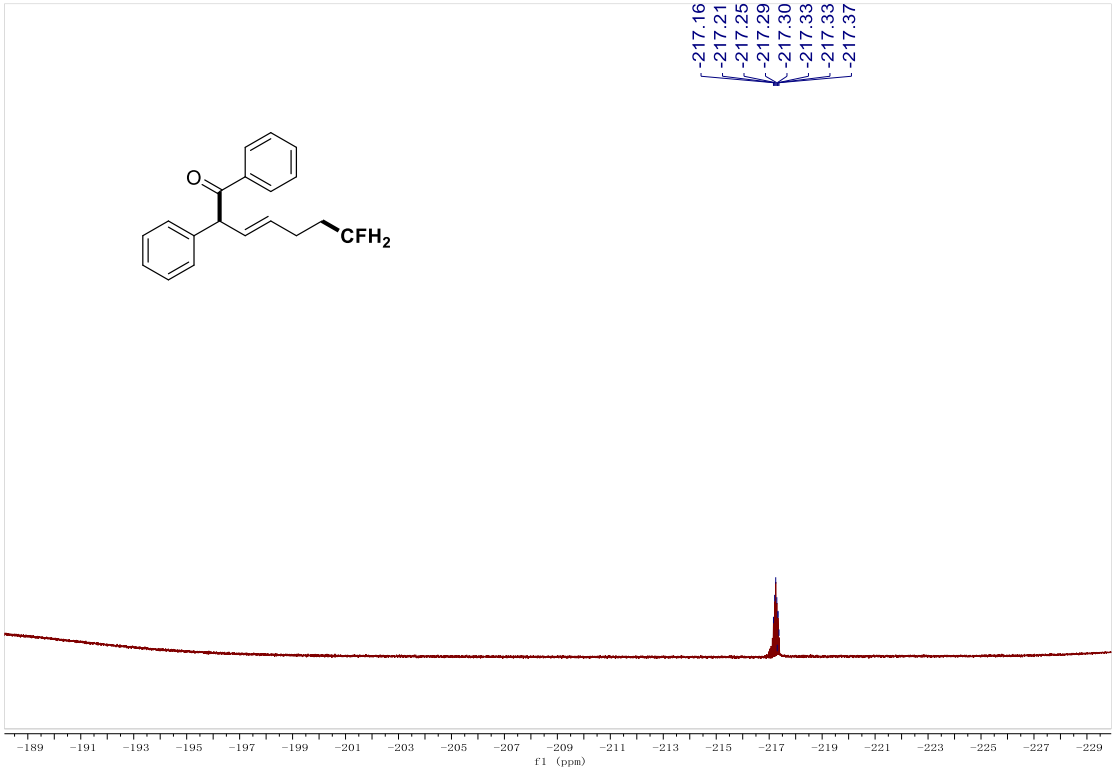
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **6b**.



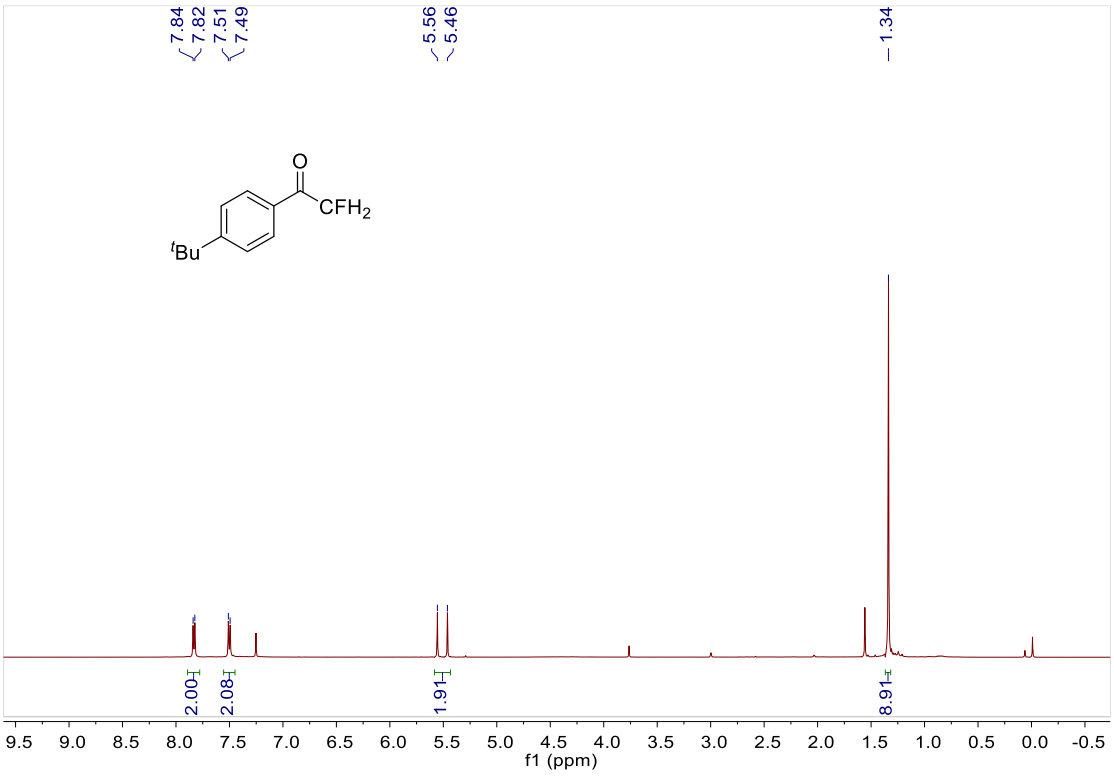
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **6b**.



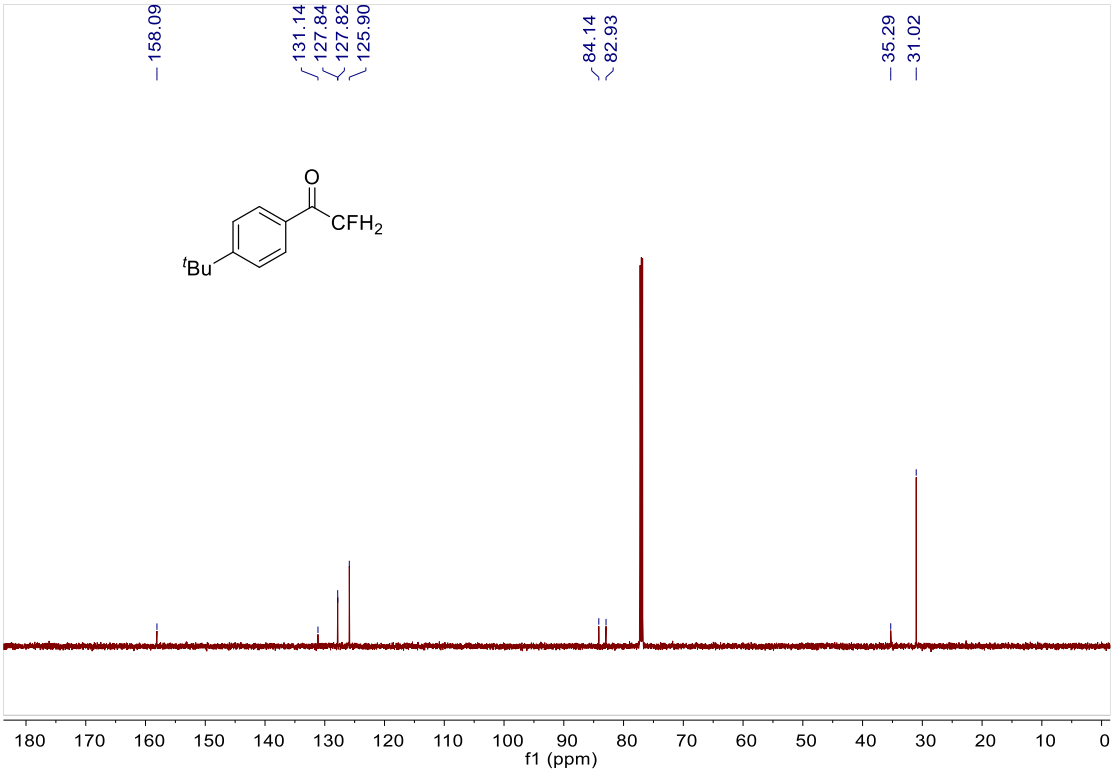
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **6b**.



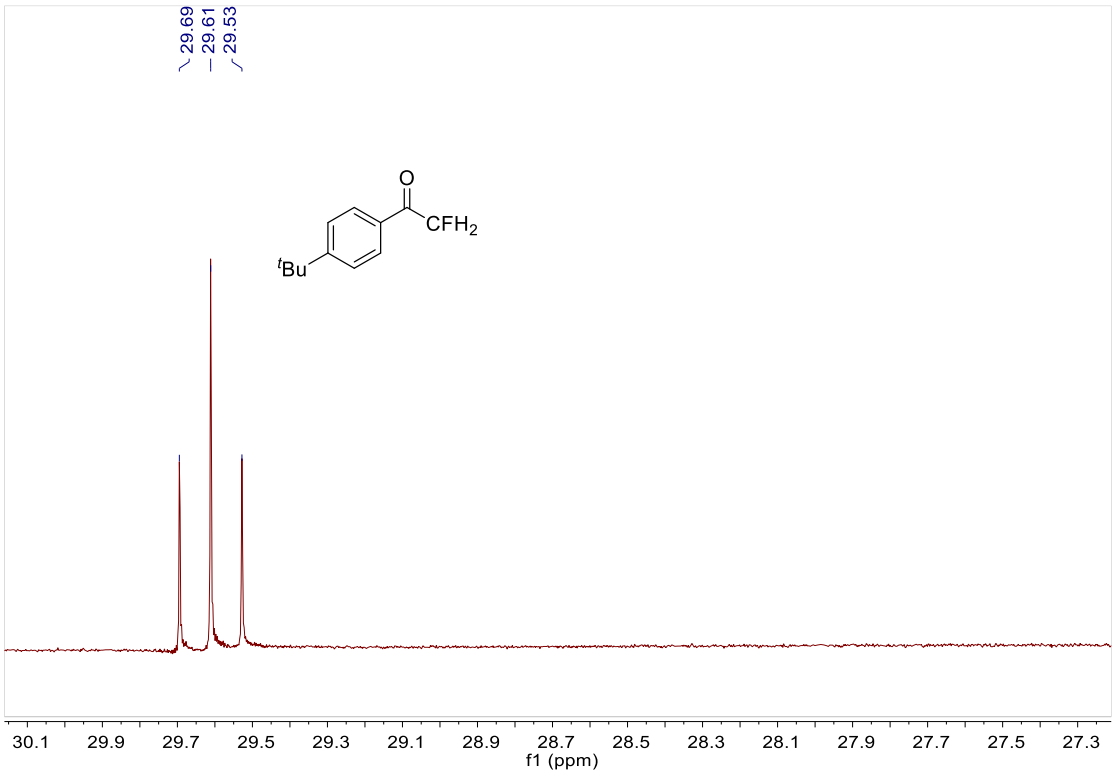
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **6c**.



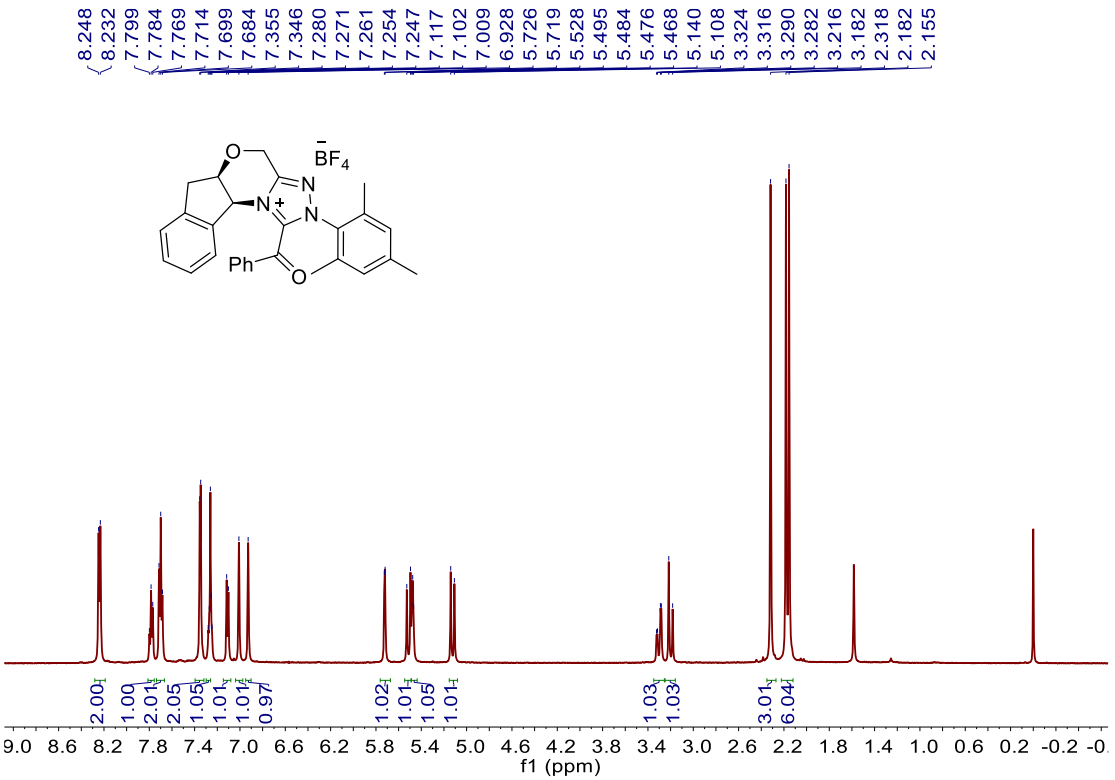
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **6c**.



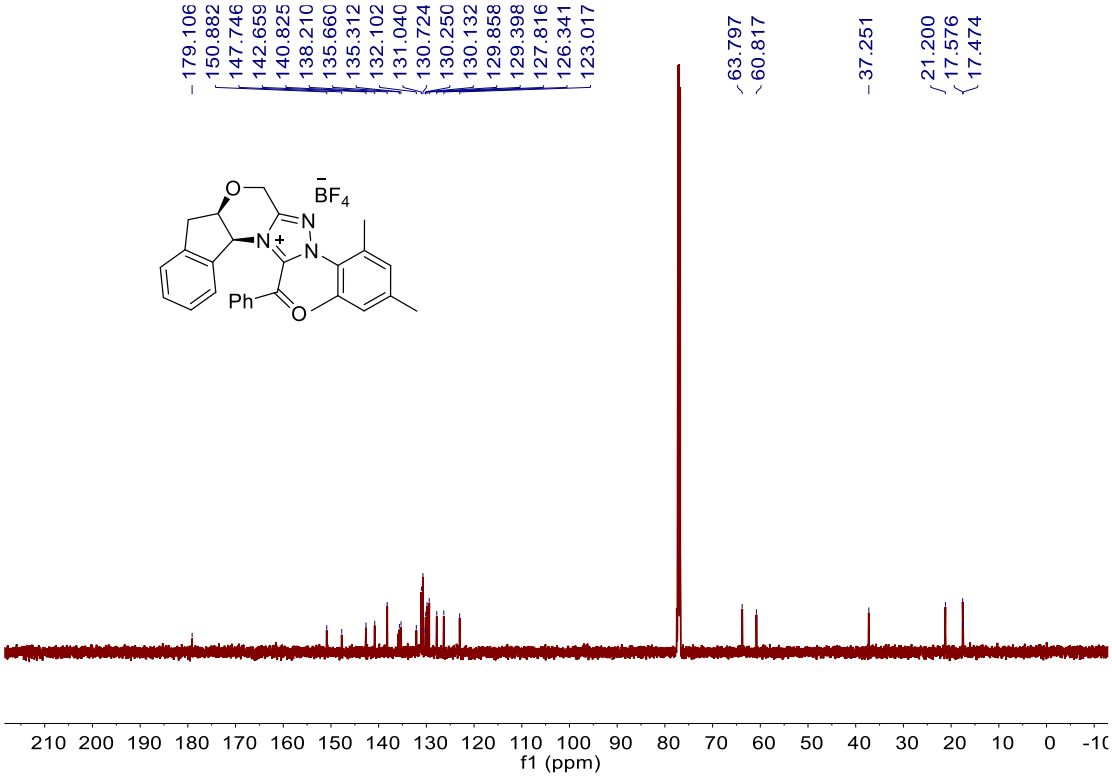
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **6c**.



^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **7b**.



^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **7b**.



^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **7b**.