

Supporting Information

Z-Selective Access to α -Trifluoromethyl Arylenes Through Pd-Catalysed Fluoroarylation of 1,1-Difluoroallenes

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Content

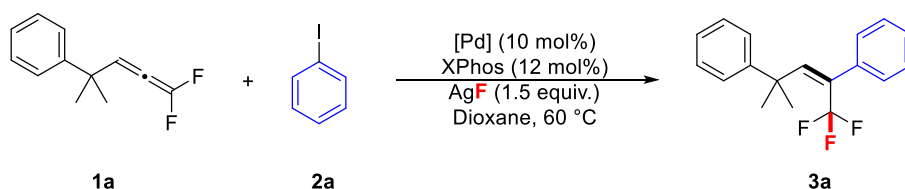
I. General.....	S1
II. Optimization of reaction conditions.....	S1
III. Preparation of the starting materials	S3
IV. General procedure for the synthesis of Z- α -trifluoromethylated alkenes 3.....	S5
V. Gram scale-up experiment of 1d	S5
VI. Synthesis of Monofluoroalkenes 4d from 3d	S5
VII. Radical trapping experiments.....	S6
VIII. NMR spectrum comparison between E- 3g and Z- 3g	S7
IX. References.....	S8
X. Characterization of all products	S9
XI. NMR spectra	S18

I. General

Unless otherwise stated, all experiments were carried out under nitrogen atmosphere. The reagents and solvents were purchased from commercial suppliers and used without further purification unless noted. ^1H NMR and ^{13}C NMR spectra were obtained on Bruker AVANCE III 400 instrument in CDCl_3 using TMS as an internal standard, operating at 400 MHz and 101 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. For CDCl_3 , the chemical shifts are reported as parts per million (ppm) to residual proton or carbon of the solvents; CHCl_3 δ H (7.28 ppm) and CDCl_3 δ C (77.03 ppm). ^{19}F NMR were recorded on a Bruker AVANCE III 400. NOESY was recorded on a Bruker AVANCE III 600. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartlet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet. GC experiments were carried out using Agilent 7890B GC. GC-MS experiments that used dodecane as an internal standard were performed with a Thermo DSQ II, Trace GC Ultra. High resolution mass spectra [HRMS (ESI+TOF)] were obtained on an Agilent 6545 Q-TOF LC-MS spectrometer equipped with an ESI source.

II. Optimization of reaction conditions

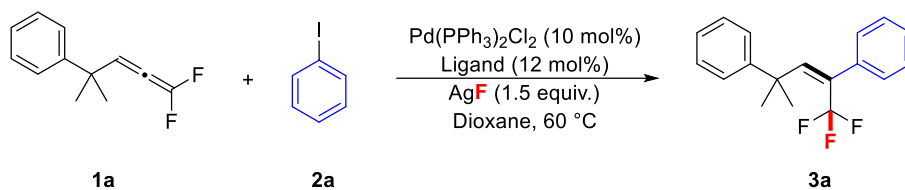
Table S1. Screening of the catalysts^a



Entry	[Pd] (10 mol%)	Yield (%)	E/Z
1	$\text{Pd}(\text{OAc})_2$	38	17/83
2	PdCl_2	48	8/92
3	$\text{Pd}(\text{TFA})_2$	55	15/85
4	$\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$	84	10/90
5	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	93(87^b)	2/98
6	$\text{Pd}_2(\text{dba})_3$	47	28/72
7	$[\text{Pd}(\text{allyl})\text{Cl}_2]_2$	45	9/91

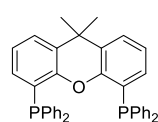
^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv.), [Pd] (0.01 mmol, 10 mol%), XPhos (0.012 mmol, 12 mol%), AgF (1.5 equiv.), Dioxane (1.0 mL), 60 °C, 12 h, under N_2 atmosphere. Yields and E/Z selectivity were determined by GC analysis (based on **1a**) using dodecane as an internal standard. ^bIsolated yield.

Table S2. Screening of the ligand^a

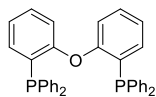


Entry	Ligands	Yield (%)	E/Z
1	Xantphos	62	65/35
2	DPEPhos	57	68/32
3	Berttphos	84	11/89
4	XPhos	93(87^b)	2/98
5	PPh ₃	22	10/90
6	BINAP	trace	/
7	DPPB	51	28/72

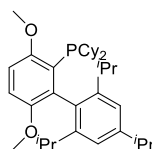
^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv.), Pd(PPh₃)₂Cl₂ (0.01 mmol, 10 mol%), Ligand (0.012 mmol, 12 mol%), AgF (1.5 equiv.), Dioxane (1.0 mL), 60 °C, 12 h, under N₂ atmosphere. Yields and E/Z selectivity were determined by GC analysis (based on **1a**) using dodecane as an internal standard. ^bIsolated yield.



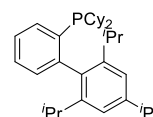
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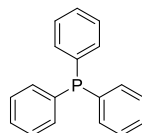
DPEPhos



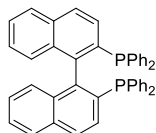
Berttphos



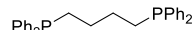
XPhos



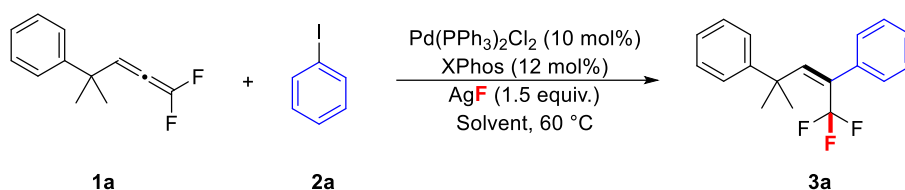
PPh₃



BINAP

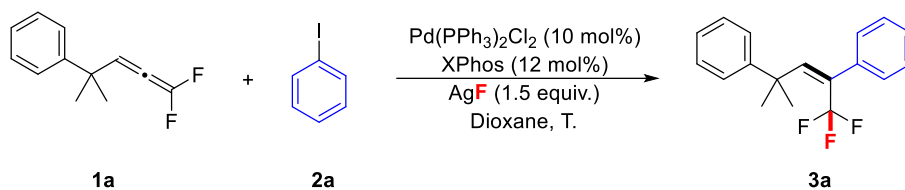


DPPB

Table S3. Screening of the solvents^a

Entry	Solvents	Yield (%)	E/Z
1	THF	84	4/96
2	Cyclohexane	60	18/82
3	Dioxane	93(87^b)	2/98
4	DCE	78	12/88
5	DMF	54	10/90
6	CH ₃ CN	45	22/78

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv.), Pd(PPh₃)₂Cl₂ (0.01 mmol, 10 mol%), XPhos (0.012 mmol, 12 mol%), AgF (1.5 equiv.), Solvent (1.0 mL), 60 °C, 12 h, under N₂ atmosphere. Yields and E/Z selectivity were determined by GC analysis (based on **1a**) using dodecane as an internal standard. ^bIsolated yield.

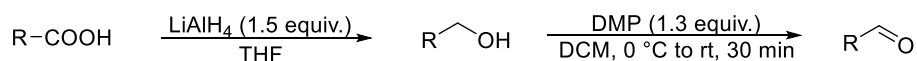
Table S4. Screening of the temperatures^a

Entry	Temperatures (°C)	Yield (%)	E/Z
1	40	79	2/98
2	60	93	2/98
3	80	93	2/98

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv.), Pd(PPh₃)₂Cl₂ (0.01 mmol, 10 mol%), XPhos (0.012 mmol, 12 mol%), AgF (1.5 equiv.), Dioxane (1.0 mL), T, 12 h, under N₂ atmosphere. Yields and E/Z selectivity were determined by GC analysis (based on **1a**) using dodecane as an internal standard. ^bIsolated yield.

III. Preparation of the starting materials

1. General procedure for the synthesis of aldehydes



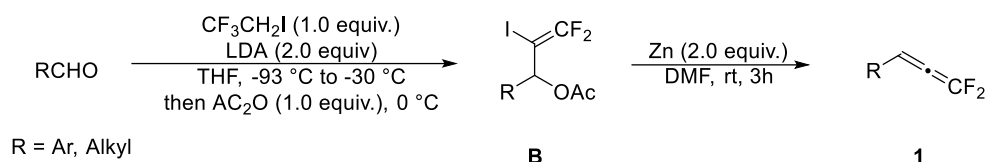
R = alkyl, aryl

A solution of carboxylic acid (10.00 mmol, 1.0 equiv.) in THF (20 mL) was added dropwise to

a solution of LiAlH₄ (2.4 M in THF, 15 mmol, 1.5 equiv.) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 hours. After diluting with Et₂O (30 mL), water (7.0 mL) was added slowly at 0 °C, followed by the dropwise addition of 15% aq. NaOH (20 mL). The reaction mixture was allowed to warm to room temperature and stirred for 30 min before salts were filtered off, and the filtrate was washed with water (10 mL), and the aqueous layer extracted with Et₂O (2 × 20 mL). The combined organic layers were washed with 1 M HCl (25 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The colorless crude product was used in the next step without further purification.^[1]

To a solution of alcohol (6.0 mmol, 1.0 equiv.) in DCM (45 mL), Dess-Martin periodinane (7.8 mmol, 1.3 equiv.) was added portionwise at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and then allowed to warm to room temperature. After 30 min, the reaction mixture was quenched by adding a solution of NaHCO₃ (20 mL) dropwise at 0 °C and the mixture was stirred for 20 min before washing it with water (2 × 10 mL) and extraction of the aqueous phase with DCM (2 × 20 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired aldehyde.

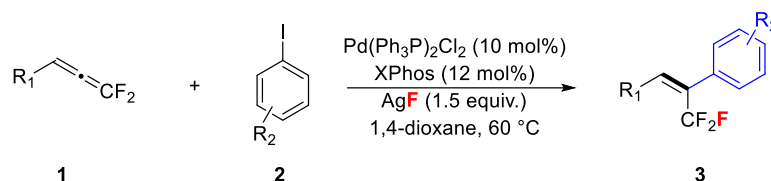
2、 General procedure for the synthesis of *gem*-difluoroallenes



According to reported method, to a solution of (i-Pr)₂NH (20 mmol) in THF (10 mL) was added *n*-BuLi (20.0 mmol) over 10 min at 0 °C under argon. The resulting solution was allowed to stir for an additional 15 min, and then cooled to -93 °C in a cold hexane bath. To the cold LDA solution was added a solution of CF₃CH₂I (10.0 mmol) in THF (5 mL) over 10 min, keeping the temperature between -93 °C and -85 °C. After the mixture was stirred for 20 min at that same temperature, a solution of aldehyde (10.0 mmol) in THF (5 mL) was added over 5 min, while keeping the temperature between -93 °C and -85 °C. The mixture was stirred for an additional 30 min, then warmed to -30 °C over 90 min. After Ac₂O (12.0 mmol) was added, the mixture was allowed to warm to 0 °C over 2 h. The reaction was quenched with sat. aq NH₄Cl (20 mL), and the products were extracted with Et₂O (3 × 20 mL). The combined organic layer was washed with brine (20 mL) and dried (Na₂SO₄). After the solvent was removed under reduced pressure, the residue was purified by column chromatography, the acetate B was obtained.

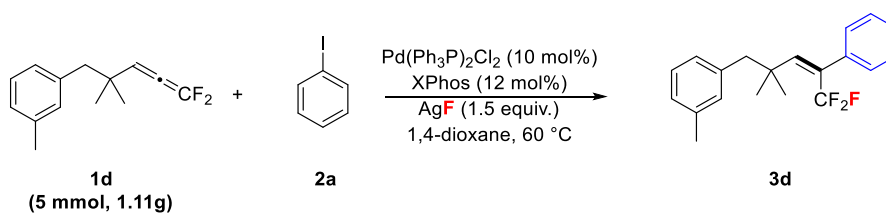
To a suspension of zinc powder (17.0 mmol) in DMF (26 mL) was added a solution of B (8.50 mmol) in DMF (17 mL) at r.t. under argon, and the mixture was stirred for 3 h. The resulting mixture was filtered to remove the excess zinc and then diluted with Et₂O (20 mL) and brine (15 mL). The products were extracted with Et₂O (3 × 15 mL). The combined organic layer was washed with brine (15 mL) and dried (Na₂SO₄). After the solvent was removed under reduced pressure, the residue was purified by column chromatography (pentane) to give **1**.^[2]

IV. General procedure for the synthesis of *Z*- α -trifluoromethylated alkenes **3**



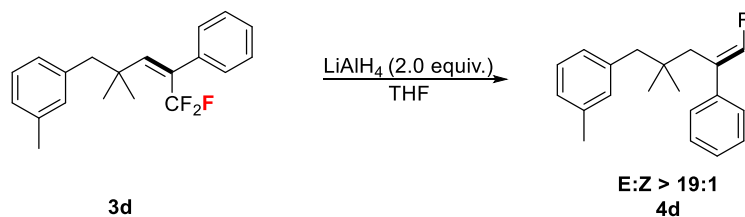
The 25 mL Schlenk tube was purged with argon for three times. Then the tube was added Pd(PPh₃)₂Cl₂ (14.0 mg, 0.02 mmol, 10 mol%), XPhos (11.3 mg, 0.024 mmol, 12 mol%), AgF (38.1 mg, 0.3 mmol, 1.5 equiv.), aromatic iodide (0.3 mmol, 1.5 equiv.), 1,1-difluoroallene **1** (0.2 mmol), and Dioxane (1 mL) under argon atmosphere. The formed mixture was stirred at 60 °C for 12 h. The resulted mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel to afford the corresponding *Z*- α -trifluoromethylated alkenes **3**.

V. Gram scale-up experiment of **1d**



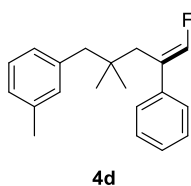
The 50 mL Schlenk tube was purged with argon for three times. Then the tube was added Pd(PPh₃)₂Cl₂ (0.35 g, 10 mol%), XPhos (0.238 g, 12 mol%), AgF (0.95 g, 7.5 mmol, 1.5 equiv.), iodobenzene (7.5 mmol, 1.5 equiv., 1.52 g), 1,1-difluoroallene **1d** (5.0 mmol, 1.11g), and Dioxane (15 mL) under argon atmosphere. The formed mixture was stirred at 60 °C for 12 h. The resulted mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel to afford the corresponding trifluoromethylated alkenes **3d**.

VI. Synthesis of Monofluoroalkenes **4d** from **3d**



The procedure was followed on the basis of literature.^[3] A dry tube under inert atmosphere was

loaded with **3d** (0.3 mmol) and freshly distilled tetrahydrofuran (1 mL). In a second tube LiAlH₄ (0.3 mmol, 95%) was mixed with tetrahydrofuran (2 mL) and this suspension was slowly added to the reaction mixture at room temperature. It was then allowed to stir at room temperature for 24 hours. The reaction was carefully quenched with a 30% potassium sodium tartrate solution (5 mL) at room temperature and the resulting mixture was stirred for 30 minutes. The mixture was diluted with diethyl ether (10 mL) and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over Na₂SO₄, filtered off and concentrated under reduced pressure. The residue was finally purified by column chromatography on silica gel to afford the product **4d**.



(E)-1-(5-fluoro-2,2-dimethyl-4-phenylpent-4-en-1-yl)-3-methylbenzene (4d): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **4d** (77.8 mg, 92% yield) as colorless oil (E:Z > 19:1). ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.31 (m, 5H), 7.23 (tt, *J* = 7.8, 2.2 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.00 (m, 2H), 6.79 (dd, *J*₁ = 80.4 Hz, *J*₂ = 1.8 Hz, 1H), 2.69 (t, *J* = 2.8 Hz, 2H), 2.57 (d, *J* = 1.6 Hz, 2H), 2.41 (s, 3H), 0.84 (d, *J* = 2.8 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 147.2 (d, *J* = 261.8 Hz), 139.0, 138.7 (d, *J* = 9.3 Hz), 137.1, 131.6, 128.6, 127.8, 127.6, 127.3, 127.1 (d, *J* = 2.9 Hz), 126.6, 123.6 (d, *J* = 8.6 Hz), 49.5, 39.7 (d, *J* = 2.1 Hz), 36.3 (d, *J* = 2.6 Hz), 26.9, 21.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -125.08 (d, *J* = 85.7 Hz) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₂₀H₂₃F₁Na: 305.1676; found: 305.1682.

VII. Radical trapping experiments

Table S5. Radical trapping experiments with radical scavengers

Entry	additives	Yield of 3d	E/Z
1	TEMPO	92	2/98
2	BHT	92	2/98

The 25 mL Schlenk tube was purged with argon for three times. Then the tube was added Pd(PPh₃)₂Cl₂ (7.0 mg, 0.01 mmol, 10 mol%), XPhos (5.5 mg, 0.012 mmol, 12 mol%), AgF (18.4 mg, 0.15 mmol, 1.5 equiv.), iodobenzene (0.3 mmol, 1.5 equiv.), additive (1.2 equiv.), **1d** (0.1 mmol), and dioxane (1 mL) under argon atmosphere. The formed mixture was stirred at 60 °C for 12 h. Radical trapping experiments demonstrated that the radical process may not be involved in the reaction mechanism.

VIII. NMR spectrum comparison between *E*-3g and *Z*-3g

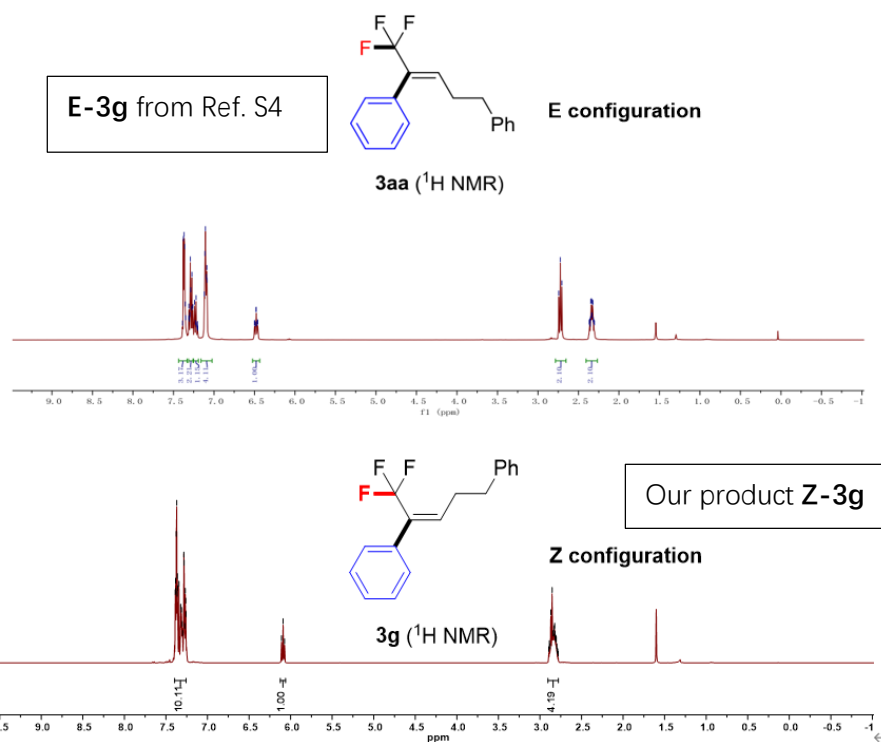


Fig. S1. ¹H NMR spectrum of *Z*-3g and *E*-3g

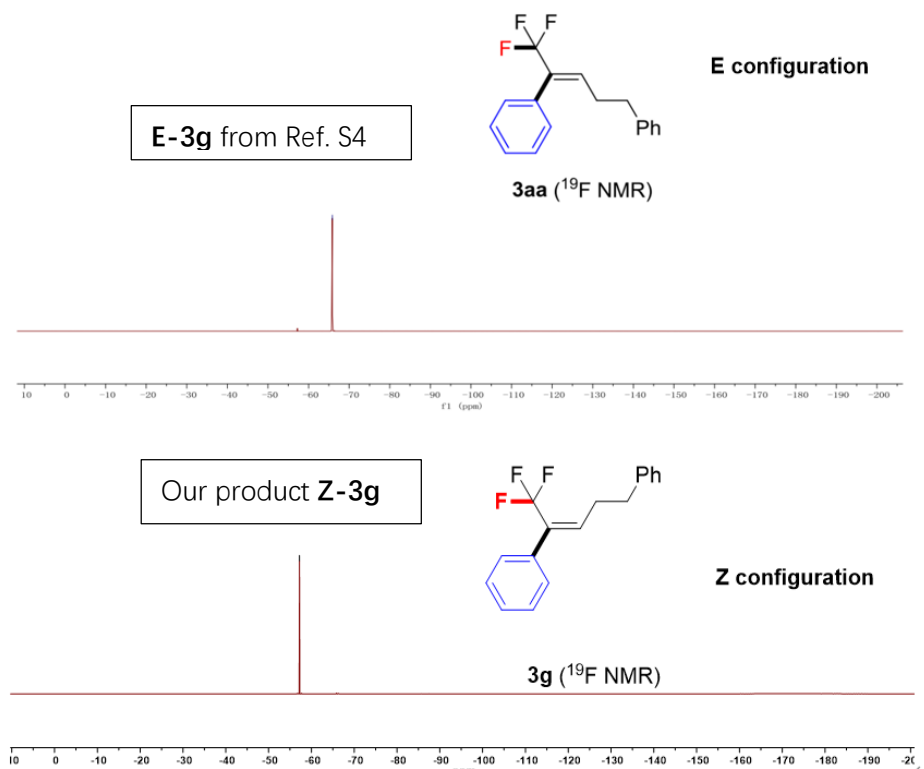


Fig. S2. ¹⁹F NMR spectrum of *Z*-3g and *E*-3g

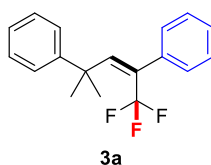
To determine the absolute configuration of our products, we compared the NMR spectrum of our product **Z-3g** with that of its known stereoisomer **E-3g**. The compound **E-3g** was reported by the group of Shi in the analogous *E*-selective fluoroarylation of 1,1-difluoroallenes (*Green Synth. Catal.*, 2020, 1, 134-142).^[4] The ¹H NMR spectra of **Z-3g** is of significant difference from its known stereoisomer **E-3g** (Fig. S1), it is found that the chemical shift (δ) of the alkenyl hydrogen in **E-3g** is from 6.52 to 6.43 ppm, while that of **Z-3g** is significantly smaller (around 6.09 ppm). Moreover, the chemical shift (δ) of aromatic hydrogens and methylene hydrogens of these two stereoisomers are different as well, given their distinguished configurations. In addition, we also compared the ¹⁹F NMR spectrum of these two isomers (Fig. S2), it is found that CF₃ chemical shift δ of **E-3g** is -65.9 ppm, while that of **Z-3g** is -57.23 ppm. Furthermore, the *Z*-configuration of the major products in our method was unambiguously determined by the NOESY analysis of **Z-3g** (see page S27 for details).

In conclusion, we have developed a facile synthesis of the otherwise challenging *Z*-configured α -trifluoromethyl arylenes, which constitutes an interesting complementary to the previous reports. Moreover, this work also provided the spectral information for the unusual *Z*-configured α -trifluoromethyl arylenes. It was found that the typical chemical shift of alkenyl hydrogen in ¹H NMR spectrum of our *Z*-configured products were around 6.0 ppm, which were significantly smaller than that of the *E*-configured products (around 6.5 ppm from Shi's work). The chemical shift of CF₃ group in ¹⁹F NMR spectrum of our *Z*-configured products were around -57.0 ppm, while that of the stereoisomeric *E*-configured products were around -65.0 ppm. The significant difference between *E* and *Z* isomers might be helpful for the researches in this research area.

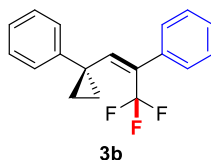
IX. References

- [1] Y. You, J. Wu, L. Yang, and T. Wu, *Chem. Commun.*, 2022, **58**, 1970-1973.
- [2] X. Han, M. Wang, Y. Liang, Y. Zhao, and Z. Shi, *Nat. Synth.*, 2022, **1**, 227-234.
- [3] P. Poutrel, X. Pannecoucke, P. Jubault, and T. Poisson, *Org. Lett.*, 2020, **22**, 4858-4863.
- [4] H. Luo, Y. Zhao, D. Wang, M. Wang, and Z. Shi, *Green Synth. Catal.*, 2020, **1**, 134-142.

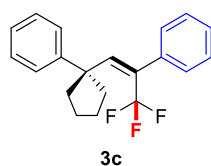
X. Characterization of all products



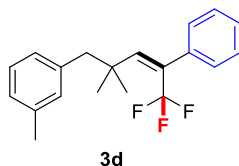
(Z)-(1,1,1-trifluoro-4-methylpent-2-ene-2,4-diyl)dibenzene (3a): The reaction between 1,1-difluoroallene **1a** (38.8 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3a** (50.4 mg, 87%, E/Z = 2/98) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45-7.35 (m, 9H), 7.31-7.24 (m, 1H), 6.46 (s, 1H), 1.66 (s, 6H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.4 (q, $J = 3.1$ Hz), 149.1 (q, $J = 2.1$ Hz), 137.9 (q, $J = 1.9$ Hz), 130.9 (q, $J = 32.1$ Hz), 128.3, 128.3, 128.1, 128.1, 125.9, 125.7, 122.9 (q, $J = 275.0$ Hz), 41.1, 31.6 (q, $J = 1.9$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -56.24 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{18}\text{F}_3$: 291.1355; found: 291.1358.



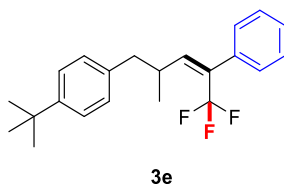
(Z)-(3,3,3-trifluoro-1-(1-phenylcyclopropyl)prop-1-en-2-yl)benzene (3b): The reaction between 1,1-difluoroallene **1b** (38.4 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3b** (51.8 mg, 90%, E/Z = 3/97) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54-7.22 (m, 10H), 6.59 (s, 1H), 1.32 (s, 4H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.7, 143.0 (q, $J = 3.0$ Hz), 136.3, 134.1 (q, $J = 30.6$ Hz), 128.4, 128.4, 128.0, 126.3, 126.0, 123.4 (q, $J = 275.8$ Hz), 24.0, 18.0 (q, $J = 2.7$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.42 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{Na}$: 311.1018; found: 311.1021.



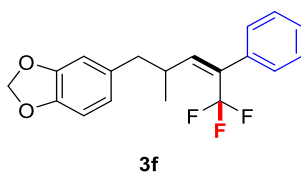
(Z)-(3,3,3-trifluoro-1-(1-phenylcyclopentyl)prop-1-en-2-yl)benzene (3c): The reaction between 1,1-difluoroallene **1c** (44.0 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3c** (54.3 mg, 86%, E/Z = 2/98) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43-7.34 (m, 9H), 7.30-7.24 (m, 1H), 6.63 (s, 1H), 2.43-2.36 (m, 2H), 2.26 (m, 2H), 1.83 (q, $J = 5.0$ Hz, 4H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.2 (q, $J = 3.3$ Hz), 147.5 (q, $J = 2.1$ Hz), 137.7 (q, $J = 2.1$ Hz), 131.2 (q, $J = 31.8$ Hz), 128.3, 128.3, 128.1, 128.0, 126.4, 125.8, 123.0 (q, $J = 275.1$ Hz), 52.9, 42.0 (q, $J = 1.9$ Hz), 23.9. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.95 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{Na}$: 339.1331; found: 339.1335.



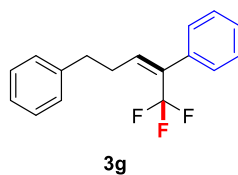
(Z)-1-methyl-3-(5,5,5-trifluoro-2,2-dimethyl-4-phenylpent-3-en-1-yl)benzene (3d): The reaction between 1,1-difluoroallene **1d** (44.4 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3d** (58.5 mg, 92%, E/Z = 2/98) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42-7.38 (m, 3H), 7.34-7.27 (m, 3H), 7.17-7.05 (m, 3H), 5.99 (s, 1H), 2.89 (s, 2H), 2.43 (s, 3H), 1.36 (s, 6H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.6 (q, $J = 3.3$ Hz), 138.7 (q, $J = 2.2$ Hz), 138.2, 137.4, 131.6, 130.5 (q, $J = 32.3$ Hz), 128.3, 128.2, 127.8, 127.8, 127.8, 127.1, 123.5 (q, $J = 275.3$ Hz), 49.22 (q, $J = 2.2$ Hz), 37.9, 28.5 (q, $J = 3.1$ Hz), 21.5 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -53.4 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{21}\text{F}_3\text{Na}$: 341.1488; found: 341.1491.



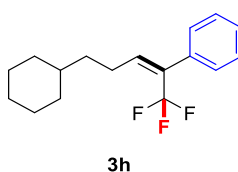
(Z)-1-(tert-butyl)-4-(5,5,5-trifluoro-2-methyl-4-phenylpent-3-en-1-yl)benzene (3e): The reaction between 1,1-difluoroallene **1e** (50.0 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3e** (60.2 mg, 87%, E/Z = 7/93) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44-7.35 (m, 5H), 7.32-7.27 (m, 2H), 7.20-7.15 (m, 2H), 5.91 (d, $J = 10.8$ Hz, 1H), 3.35-3.16 (m, 1H), 2.80 (dd, $J = 13.5, 6.2$ Hz, 1H), 2.66 (dd, $J = 13.4, 7.9$ Hz, 1H), 1.38 (s, 9H), 1.14 (d, $J = 6.5$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.1, 147.3 (q, $J = 3.0$ Hz), 136.7, 136.3, 130.3 (q, $J = 30.0$ Hz), 129.0, 128.4, 128.2, 128.0, 125.2, 124.0 (q, $J = 275.6$ Hz), 42.8, 35.2 (q, $J = 2.1$ Hz), 34.4, 31.5, 20.0 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -56.96 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{22}\text{H}_{25}\text{F}_3\text{Na}$: 369.1801; found: 369.1805.



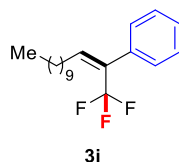
(Z)-5-(5,5,5-trifluoro-2-methyl-4-phenylpent-3-en-1-yl)benzo[d][1,3]dioxole (3f): The reaction between 1,1-difluoroallene **1f** (47.6 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3f** (59.4 mg, 89%, E/Z = 5/95) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42-7.35 (m, 3H), 7.32-7.24 (m, 2H), 6.83-6.61 (m, 5H), 5.97 (s, 2H), 5.85 (d, $J = 10.9$ Hz, 1H), 3.25-3.07 (m, 1H), 2.70 (dd, $J = 13.4, 6.5$ Hz, 1H), 2.59 (dd, $J = 13.4, 7.6$ Hz, 1H), 1.11 (d, $J = 6.6$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.6, 146.9 (q, $J = 2.9$ Hz), 146.0, 136.6, 133.2, 130.5 (q, $J = 29.7$ Hz), 128.3, 128.2, 128.0, 122.5 (q, $J = 276.4$ Hz), 122.1, 109.5, 108.1, 100.8, 43.1, 35.5, 20.0 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -56.93 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{NaO}_2$: 357.1073; found: 357.1078.



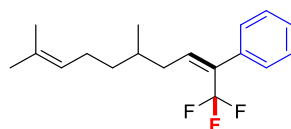
(Z)-(5,5,5-trifluoropent-3-ene-1,4-diyl)dibenzene (3g): The reaction between 1,1-difluoroallene **1g** (50.0 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3g** (43.1 mg, 78%, E/Z = 14/86) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.26 (m, 10H), 6.09 (t, *J* = 7.2 Hz, 1H), 2.91-2.77 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 140.8, 136.5 (q, *J* = 1.6 Hz), 132.2 (q, *J* = 29.7 Hz), 128.6, 128.5, 128.3, 128.2, 128.1, 126.3, 122.6 (q, *J* = 276.8 Hz), 35.4, 30.5 (q, *J* = 2.0 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -57.23 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₁₇H₁₅F₃Na: 299.1018; found: 299.1021.



(Z)-(5-cyclohexyl-1,1,1-trifluoropent-2-en-2-yl)benzene (3h): The reaction between 1,1-difluoroallene **1h** (37.2 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3h** (41.7 mg, 74%, E/Z = 11/89) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.30 (m, 5H), 6.05 (t, *J* = 7.8 Hz, 1H), 2.47 (d, *J* = 8.2 Hz, 2H), 2.03-1.64 (m, 5H), 1.41 (q, *J* = 7.1 Hz, 2H), 1.35-1.15 (m, 4H), 1.03-0.87 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 142.7 (q, *J* = 3.1 Hz), 136.8, 131.3 (q, *J* = 29.6 Hz), 128.2, 127.9, 124.1 (q, *J* = 276.8 Hz), 37.3, 37.0, 33.2, 26.6, 26.3 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -57.1 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₁₇H₂₁F₃Na: 305.1488; found: 305.1492.

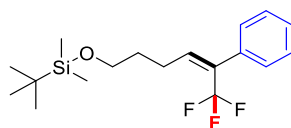


(Z)-(1,1,1-trifluorotridec-2-en-2-yl)benzene (3i): The reaction between 1,1-difluoroallene **1i** (43.2 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3i** (44.9 mg, 72%, E/Z = 10/90) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.30 (m, 5H), 6.05 (t, *J* = 7.6 Hz, 1H), 2.50-2.43 (m, 2H), 1.63-1.46 (m, 2H), 1.31 (s, 14H), 0.92 (t, *J* = 6.7 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 142.5 (q, *J* = 3.0 Hz), 136.8, 131.4 (q, *J* = 29.5 Hz), 128.2, 127.9, 125.4 (q, *J* = 276.5 Hz), 31.9, 29.6, 29.6, 29.4, 29.4, 29.3, 29.3, 28.8, 22.7, 14.1 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -57.1 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₁₉H₂₇F₃Na: 335.1957; found: 335.1954.



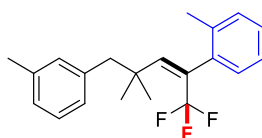
3j

(Z)-(1,1,1-trifluoro-5,9-dimethyldeca-2,8-dien-2-yl)benzene (3j): The reaction between 1,1-difluoroallene **1j** (40.0 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3j** (44.4 mg, 75%, E/Z = 12/88) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.30 (m, 5H), 6.07 (t, *J* = 7.7 Hz, 1H), 5.14 (t, *J* = 6.2 Hz, 1H), 2.58-2.43 (m, 1H), 2.39-2.25 (m, 1H), 2.19-1.95 (m, 2H), 1.72 (s, 3H), 1.70-1.67 (m, 1H), 1.65 (s, 3H), 1.51-1.38 (m, 1H), 1.34-1.23 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 141.4 (q, *J* = 2.9 Hz), 136.9, 132.1 (q, *J* = 29.5 Hz), 131.5, 128.2, 128.0, 124.0 (q, *J* = 276.8 Hz), 124.5, 36.8, 35.9, 33.0, 25.7, 25.5, 19.5, 17.7 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -56.8 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₁₈H₂₃F₃Na: 319.1644; found: 319.1648.



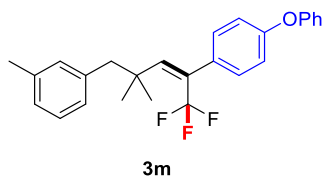
3k

(Z)-tert-butyl dimethyl((6,6,6-trifluoro-5-phenylhex-4-en-1-yl)oxy)silane (3k): The reaction between 1,1-difluoroallene **1k** (49.6 mg, 0.2 mmol, 1.0 equiv.) and iodobenzene (30.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3k** (43.1 mg, 78%, E/Z = 16/84) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.30 (m, 5H), 6.08 (t, *J* = 7.7 Hz, 1H), 3.70 (t, *J* = 6.1 Hz, 2H), 2.65-2.47 (m, 2H), 1.74 (p, *J* = 6.7 Hz, 2H), 0.92 (s, 9H), 0.08 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 141.8 (q, *J* = 3.3 Hz), 136.7, 131.7 (q, *J* = 29.9 Hz), 128.2, 128.2, 128.0, 124.0 (q, *J* = 277.0), 62.4, 32.4, 25.9, 25.5, 18.3, -5.3 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -57.16 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₁₈H₂₇F₃NaOSi: 367.1675; found: 367.1672.



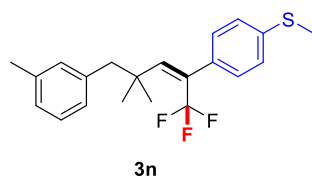
3l

(Z)-1-methyl-2-(1,1,1-trifluoro-4,4-dimethyl-5-(m-tolyl)pent-2-en-2-yl)benzene (3l): The reaction between 1,1-difluoroallene **1d** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 1-iodo-2-methylbenzene (65.1 mg, 0.3 mmol, 1.5 equiv.) afforded **3l** (56.4 mg, 85%, E/Z = 2/98) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.24 (m, 4H), 7.24-7.06 (m, 4H), 5.94 (s, 1H), 2.87 (s, 2H), 2.44 (s, 3H), 2.35 (s, 3H), 1.38 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 151.2 (q, *J* = 3.4 Hz), 138.3 (q, *J* = 2.5 Hz), 138.1, 137.4, 136.8, 131.4, 130.1, 130.1, 129.4 (q, *J* = 33.0 Hz), 128.2, 127.8, 127.7, 127.2, 125.6, 123.3 (q, *J* = 274.3 Hz), 49.7, 38.3, 27.9, 21.5, 19.9 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -53.65 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₂₁H₂₄F₃: 333.1825; found: 333.1827.



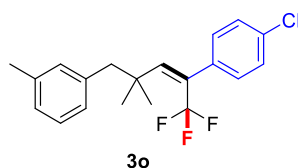
(Z)-1-methyl-3-(5,5,5-trifluoro-2,2-dimethyl-4-(4-phenoxyphenyl)pent-3-en-1-yl)benzene

(3m): The reaction between 1,1-difluoroallene **1d** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 1-iodo-4-phenoxybenzene (88.5 mg, 0.3 mmol, 1.5 equiv.) afforded **3m** (73.8 mg, 90%, E/Z = 2/98) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 7.1 Hz, 2H), 7.19-6.87 (m, 11H), 5.86 (s, 1H), 2.78 (s, 2H), 2.31 (s, 3H), 1.24 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 157.2, 156.9, 151.3 (q, *J* = 3.3 Hz), 138.2, 137.4, 133.5, 131.6, 129.9, 129.8, 129.8 (q, *J* = 32.4 Hz), 127.8, 127.8, 127.1, 123.4 (q, *J* = 275.8 Hz), 119.3, 118.2, 49.2, 37.9, 28.5 (q, *J* = 3.4 Hz), 21.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -53.62 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₂₆H₂₅F₃NaO: 433.1750; found: 433.1756.



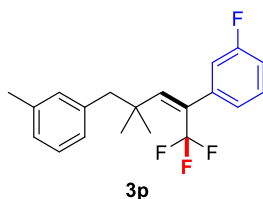
(Z)-methyl(4-(1,1,1-trifluoro-4,4-dimethyl-5-(m-tolyl)pent-2-en-2-yl)phenyl)sulfane (3n):

The reaction between 1,1-difluoroallene **1d** (44.0 mg, 0.2 mmol, 1.0 equiv.) and (4-iodophenyl)(methyl)sulfane (75.0 mg, 0.3 mmol, 1.5 equiv.) afforded **3n** (64.8 mg, 89%, E/Z = 3/97) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.18 (m, 5H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 9.1 Hz, 2H), 5.95 (s, 1H), 2.86 (s, 2H), 2.54 (s, 3H), 2.41 (s, 3H), 1.33 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 151.4 (q, *J* = 3.3 Hz), 138.5, 138.2, 137.3, 135.4 (q, *J* = 2.4 Hz), 131.5, 130.0 (q, *J* = 32.3 Hz), 128.7, 127.8, 127.8, 127.1, 126.1, 123.4 (q, *J* = 274.5 Hz), 49.2 (q, *J* = 2.3 Hz), 37.9, 28.4 (q, *J* = 3.2 Hz), 21.5, 15.7 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -53.5 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₂₁H₂₃F₃NaS: 387.1365; found: 387.1366.

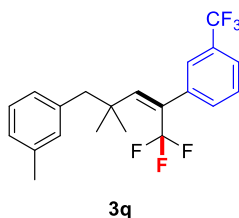


(Z)-1-(4-(4-chlorophenyl)-5,5,5-trifluoro-2,2-dimethylpent-3-en-1-yl)-3-methylbenzene (3o):

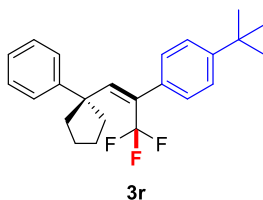
The reaction between 1,1-difluoroallene **1d** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 1-chloro-4-iodobenzene (71.1 mg, 0.3 mmol, 1.5 equiv.) afforded **3o** (61.2 mg, 87%, E/Z = 3/97) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.32 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 5.94 (s, 1H), 2.85 (s, 2H), 2.40 (s, 3H), 1.33 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 152.0 (q, *J* = 3.3 Hz), 138.0, 137.4, 137.1 (q, *J* = 2.4 Hz), 133.9, 131.5, 129.7, 129.4, 128.4, 127.8, 127.7, 127.2, 123.2 (q, *J* = 274.4 Hz), 49.2 (q, *J* = 2.2 Hz), 38.0, 28.4 (q, *J* = 3.2 Hz), 21.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -53.57 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₂₀H₂₀ClF₃Na: 375.1098; found: 375.1095.



(Z)-1-fluoro-3-(1,1,1-trifluoro-4,4-dimethyl-5-(m-tolyl)pent-2-en-2-yl)benzene (3p): The reaction between 1,1-difluoroallene **1d** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 1-fluoro-3-iodobenzene (66.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3p** (62.5 mg, 93%, E/Z = 3/97) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.21 (m, 2H), 7.17-6.96 (m, 6H), 5.97 (s, 1H), 2.86 (s, 2H), 2.41 (s, 3H), 1.33 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 162.4 (d, *J* = 246.3 Hz), 152.3 (q, *J* = 3.3 Hz), 140.7, 138.0, 137.4, 131.5, 129.7, 129.7 (d, *J* = 8.4 Hz), 129.6, 127.8 (d, *J* = 13.4 Hz), 127.20, 124.06 (d, *J* = 2.9 Hz), 123.1 (q, *J* = 275.4 Hz), 115.5 (d, *J* = 22.3 Hz), 114.79 (d, *J* = 21.0 Hz), 49.21 (q, *J* = 2.4 Hz), 38.0, 28.3 (q, *J* = 3.2 Hz), 21.4 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -53.58 (s, 3F), -113.09 (s, 1F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₂₀H₂₀F₄Na: 359.1393; found: 359.1397.

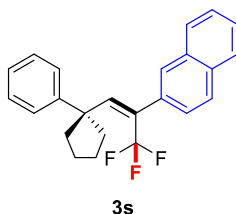


(Z)-1-methyl-3-(5,5,5-trifluoro-2,2-dimethyl-4-(3-(trifluoromethyl)phenyl)pent-3-en-1-yl)benzene (3q): The reaction between 1,1-difluoroallene **1d** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 1-iodo-3-(trifluoromethyl)benzene (81.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3q** (65.6 mg, 85%, E/Z = 2/98) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 6.7 Hz, 1H), 7.60-7.41 (m, 3H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.00 (s, 1H), 2.90 (s, 2H), 2.43 (s, 3H), 1.38 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 152.9 (q, *J* = 3.4 Hz), 139.4 (q, *J* = 2.4 Hz), 137.9, 137.5, 131.7, 131.4, 130.8 (q, *J* = 32.4 Hz), 129.5 (q, *J* = 32.9 Hz), 128.7, 127.9, 127.7, 127.3, 125.2 (q, *J* = 3.9 Hz), 124.7 (q, *J* = 3.8 Hz), 123.1 (q, *J* = 275.4 Hz), 49.3 (q, *J* = 2.2 Hz), 38.2, 28.3 (q, *J* = 3.3 Hz), 21.4 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -53.40 (s, 3F), -62.60 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd. for C₂₁H₂₀F₆Na: 409.1361; found: 409.1365.

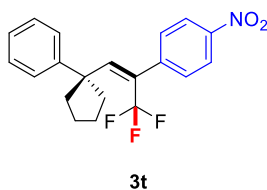


(Z)-1-(tert-butyl)-4-(3,3,3-trifluoro-1-(1-phenylcyclopentyl)prop-1-en-2-yl)benzene (3r): The reaction between 1,1-difluoroallene **1c** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 1-(tert-butyl)-4-iodobenzene (78.0 mg, 0.3 mmol, 1.5 equiv.) afforded **3r** (68.4 mg, 92%, E/Z = 3/97) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.32 (m, 8H), 7.28-7.22 (m, 1H), 6.63 (s, 1H), 2.38-2.26 (m, 2H), 2.22-2.09 (m, 2H), 1.82 (q, *J* = 5.3 Hz, 4H), 1.40 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 151.2, 150.7 (q, *J* = 3.1 Hz), 147.7 (q, *J* = 1.8 Hz), 134.7 (q, *J* = 1.8 Hz), 131.1 (q, *J* = 31.6 Hz), 128.0, 127.9, 126.4, 125.8, 125.3, 123.1 (q, *J* = 275.2 Hz), 52.9, 42.1 (q, *J* = 2.0 Hz), 34.6, 31.3, 23.9 ppm; ¹⁹F NMR (376 MHz, CDCl₃)

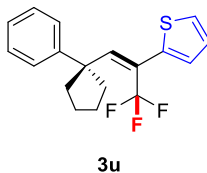
δ -57.01 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[M + Na]^+$ Calcd. for $C_{24}H_{27}F_3Na$: 395.1957; found: 395.1961.



(Z)-2-(3,3,3-trifluoro-1-(1-phenylcyclopentyl)prop-1-en-2-yl)naphthalene (3s): The reaction between 1,1-difluoroallene **1c** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 2-iodonaphthalene (75.9 mg, 0.3 mmol, 1.5 equiv.) afforded **3s** (64.4 mg, 88%, $E/Z = 2/98$) as a colorless oil. **1H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.82 (m, 4H), 7.66-7.53 (m, 3H), 7.50-7.39 (m, 4H), 7.35-7.27 (m, 1H), 6.77 (s, 1H), 2.46-2.33 (m, 2H), 2.28-2.16 (m, 2H), 1.87 (q, $J = 7.2$ Hz, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7 (q, $J = 3.2$ Hz), 147.5 (q, $J = 2.1$ Hz), 135.2 (q, $J = 2.1$ Hz), 133.2, 132.9, 131.3 (q, $J = 31.8$ Hz), 128.2, 128.1, 128.0, 127.7, 127.4, 126.5, 126.5, 126.1, 125.9, 123.1 (q, $J = 275.2$ Hz), 53.0, 42.0 (q, $J = 1.9$ Hz), 23.9 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.59 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[M + Na]^+$ Calcd. for $C_{24}H_{21}F_3Na$: 389.1488; found: 389.1452.

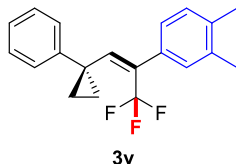


(Z)-1-nitro-4-(3,3,3-trifluoro-1-(1-phenylcyclopentyl)prop-1-en-2-yl)benzene (3t): The reaction between 1,1-difluoroallene **1c** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 1-iodo-4-nitrobenzene (74.4 mg, 0.3 mmol, 1.5 equiv.) afforded **3t** (62.8 mg, 87%, $E/Z = 2/98$) as a colorless oil. **1H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, $J = 8.8$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.39-7.33 (m, 4H), 7.28-7.23 (m, 1H), 6.70 (s, 1H), 2.43-2.28 (m, 2H), 2.17-2.03 (m, 2H), 1.80 (q, $J = 6.2$ Hz, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.7 (q, $J = 3.1$ Hz), 147.6, 146.6 (q, $J = 2.1$ Hz), 144.0 (q, $J = 2.1$ Hz), 129.7 (q, $J = 32.7$ Hz), 129.1, 128.1, 126.4, 126.1, 123.6, 122.4 (q, $J = 276.3$ Hz), 53.1, 41.7 (q, $J = 1.9$ Hz), 23.7 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.60 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[M + Na]^+$ Calcd. for $C_{20}H_{18}F_3NNaO_2$: 384.1182; found: 384.1187.

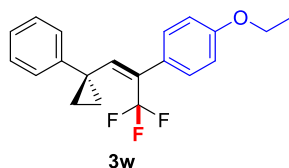


(E)-2-(3,3,3-trifluoro-1-(1-phenylcyclopentyl)prop-1-en-2-yl)thiophene (3u): The reaction between 1,1-difluoroallene **1c** (44.0 mg, 0.2 mmol, 1.0 equiv.) and 2-iodothiophene (60.0 mg, 0.3 mmol, 1.5 equiv.) afforded **3u** (55.4 mg, 86%, $E/Z = 98/2$) as a colorless oil. **1H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 4H), 7.32-7.28 (m, 1H), 7.27-7.21 (m, 1H), 7.16-7.13 (m, 1H), 7.10-7.04 (m, 1H), 6.90 (s, 1H), 2.45-2.24 (m, 2H), 2.18-2.04 (m, 2H), 1.82 (q, $J = 4.2$ Hz, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$)

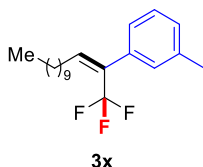
δ 150.5 (q, $J = 2.9$ Hz), 147.7 (q, $J = 2.2$ Hz), 138.8 (q, $J = 1.9$ Hz), 128.0, 127.6, 126.6 (q, $J = 1.7$ Hz), 126.2, 125.8, 125.1 (q, $J = 33.0$ Hz), 122.3 (q, $J = 275.4$ Hz), 53.1, 42.6 (q, $J = 1.9$ Hz), 24.2 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -58.67 (s, 3F) ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{NaS}$: 345.0895; found: 345.0899.



(Z)-1,2-dimethyl-4-(3,3,3-trifluoro-1-(1-phenylcyclopropyl)prop-1-en-2-yl)benzene (3v): The reaction between 1,1-difluoroallene **1b** (38.4 mg, 0.2 mmol, 1.0 equiv.) and 4-iodo-1,2-dimethylbenzene (69.3 mg, 0.3 mmol, 1.5 equiv.) afforded **3v** (52.4 mg, 83%, E/Z = 3/97) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.32 (m, 2H), 7.31-7.27 (m, 2H), 7.26-7.21 (m, 1H), 7.20-7.10 (m, 3H), 6.54 (s, 1H), 2.32 (d, $J = 2.9$ Hz, 6H), 1.31 (d, $J = 3.8$ Hz, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 143.9, 142.3 (q, $J = 3.1$ Hz), 137.0, 136.6, 134.1 (q, $J = 30.4$ Hz), 129.6, 129.1, 128.4, 126.3, 125.9, 125.4, 123.4 (q, $J = 275.8$ Hz), 23.9, 19.8, 19.5, 18.0 (q, $J = 2.6$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -57.51 (s, 3F) ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{Na}$: 339.1331; found: 339.1337.

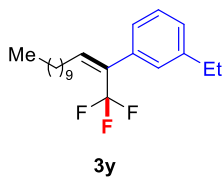


(Z)-1-ethoxy-4-(3,3,3-trifluoro-1-(1-phenylcyclopropyl)prop-1-en-2-yl)benzene (3w): The reaction between 1,1-difluoroallene **1b** (38.4 mg, 0.2 mmol, 1.0 equiv.) and 1-ethoxy-4-iodobenzene (74.4 mg, 0.3 mmol, 1.5 equiv.) afforded **3w** (59.7 mg, 90%, E/Z = 3/97) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.27 (m, 6H), 7.24-7.17 (m, 1H), 6.94-6.87 (m, 2H), 6.51 (s, 1H), 4.07 (q, $J = 7.0$ Hz, 2H), 1.45 (t, $J = 7.0$ Hz, 3H), 1.33-1.27 (m, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 159.1, 143.9, 141.9, 133.7 (q, $J = 30.7$ Hz), 129.2, 128.4, 126.2, 125.9, 123.4 (q, $J = 276.5$ Hz), 114.3, 63.5, 23.9, 18.0 (d, $J = 2.9$ Hz), 14.8 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -57.69 (s, 3F) ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NaO}$: 355.1280; found: 355.1286.



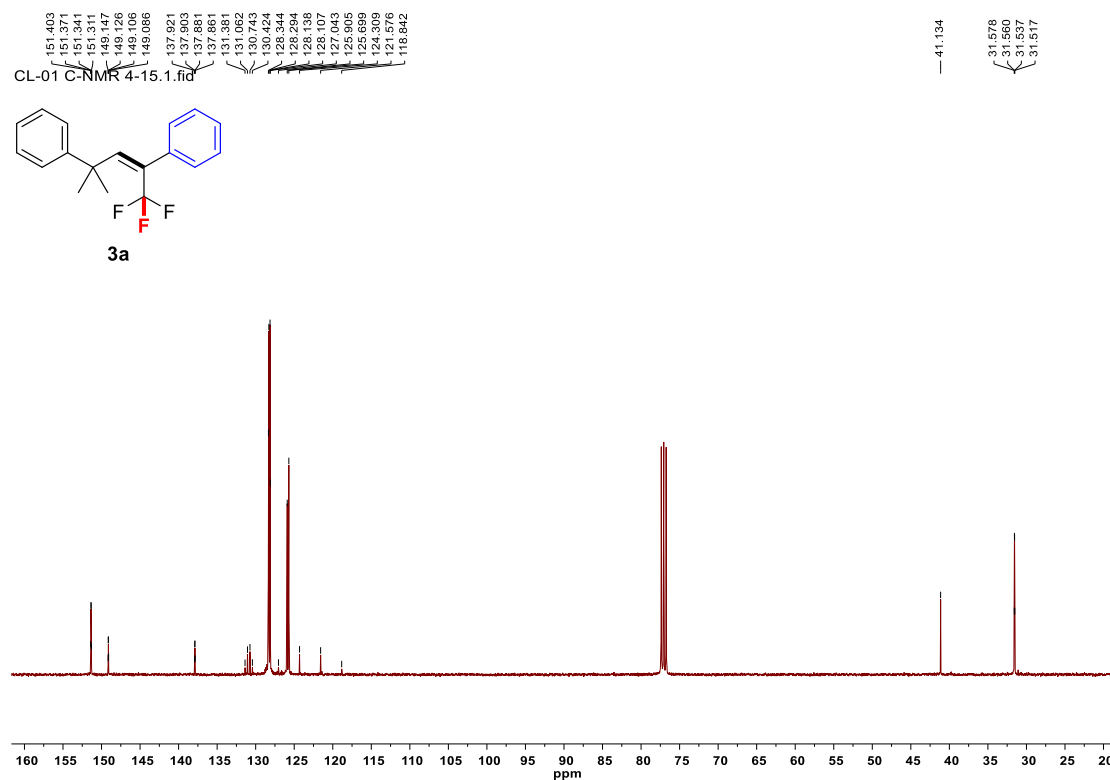
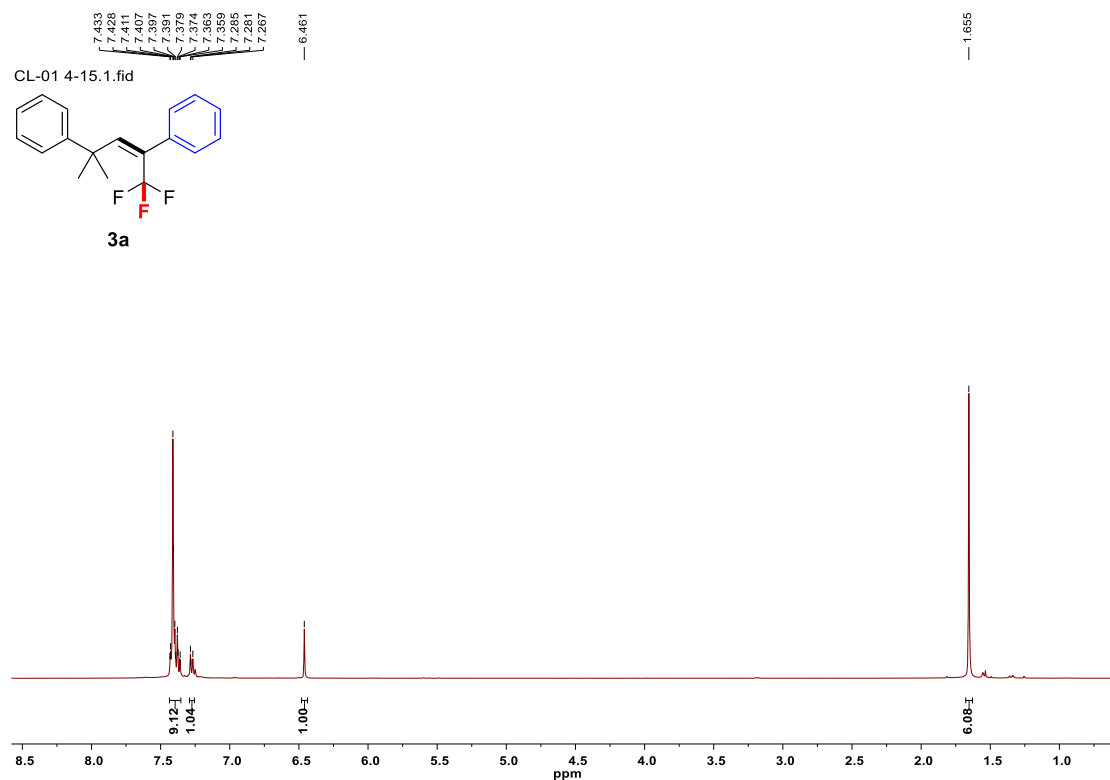
(Z)-1-methyl-3-(1,1,1-trifluorotridec-2-en-2-yl)benzene (3x): The reaction between 1,1-difluoroallene **1i** (43.2 mg, 0.2 mmol, 1.0 equiv.) and 1-iodo-3-methylbenzene (65.4 mg, 0.3 mmol, 1.5 equiv.) afforded **3x** (45.6 mg, 70%, E/Z = 15/85) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.22 (m, 1H), 7.19-7.09 (m, 3H), 6.03 (t, $J = 7.7$ Hz, 1H), 2.49-2.41 (m, 2H), 2.39 (s, 3H), 1.52 (t, $J = 7.3$ Hz, 2H), 1.36-1.25 (m, 14H), 1.02-0.82 (m, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 142.2 (q, $J = 3.1$ Hz), 137.9, 136.7 (q, $J = 1.5$ Hz), 131.5 (q, $J = 29.6$ Hz), 128.9, 128.7, 128.1, 125.4, 121.3 (q, $J =$

275.7 Hz), 31.9, 29.6, 29.6, 29.4, 29.4, 29.3, 29.3, 28.8, 22.7, 21.4, 14.1 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -57.02 (s, 3F) ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{29}\text{F}_3\text{Na}$: 349.2114; found: 349.2118.

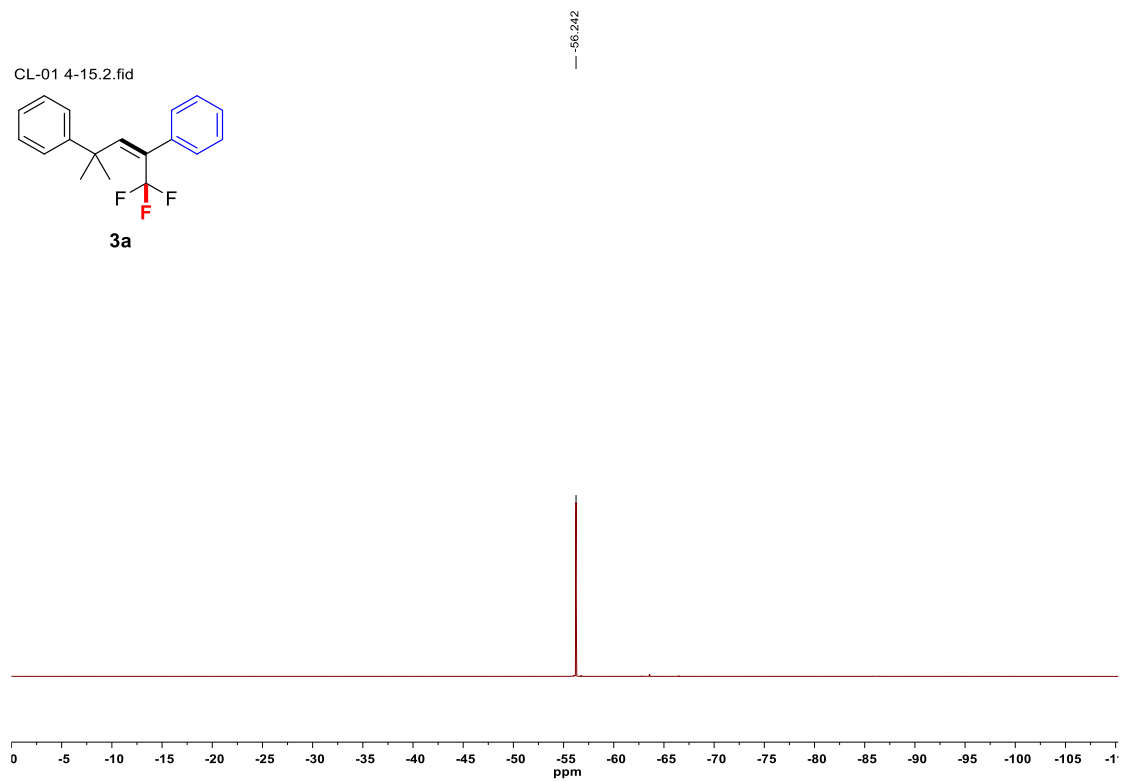


(Z)-1-ethyl-3-(1,1,1-trifluorotridec-2-en-2-yl)benzene (3y): The reaction between 1,1-difluoroallene **1i** (43.2 mg, 0.2 mmol, 1.0 equiv.) and 1-ethyl-3-iodobenzene (69.6 mg, 0.3 mmol, 1.5 equiv.) afforded **3y** (52.3 mg, 77%, E/Z = 17/83) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 8.4$ Hz, 1H), 7.19 (d, $J = 7.7$ Hz, 1H), 7.16-7.11 (m, 2H), 6.04 (t, $J = 7.7$ Hz, 1H), 2.69 (q, $J = 7.6$ Hz, 2H), 2.54-2.37 (m, 2H), 1.52 (p, $J = 7.3$ Hz, 2H) 1.35-1.19 (m, 17H), 0.91 (t, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 144.2, 142.2 (q, $J = 3.1$ Hz), 136.8, 131.6 (q, $J = 29.4$ Hz), 128.1, 127.8, 127.5, 125.5, 124.1 (q, $J = 276.8$ Hz), 31.9, 29.6, 29.6, 29.4, 29.3, 29.3, 28.8, 22.7, 15.6, 14.1 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -56.99 (s, 3F) ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{21}\text{H}_{31}\text{F}_3\text{Na}$: 363.2270; found: 363.2278.

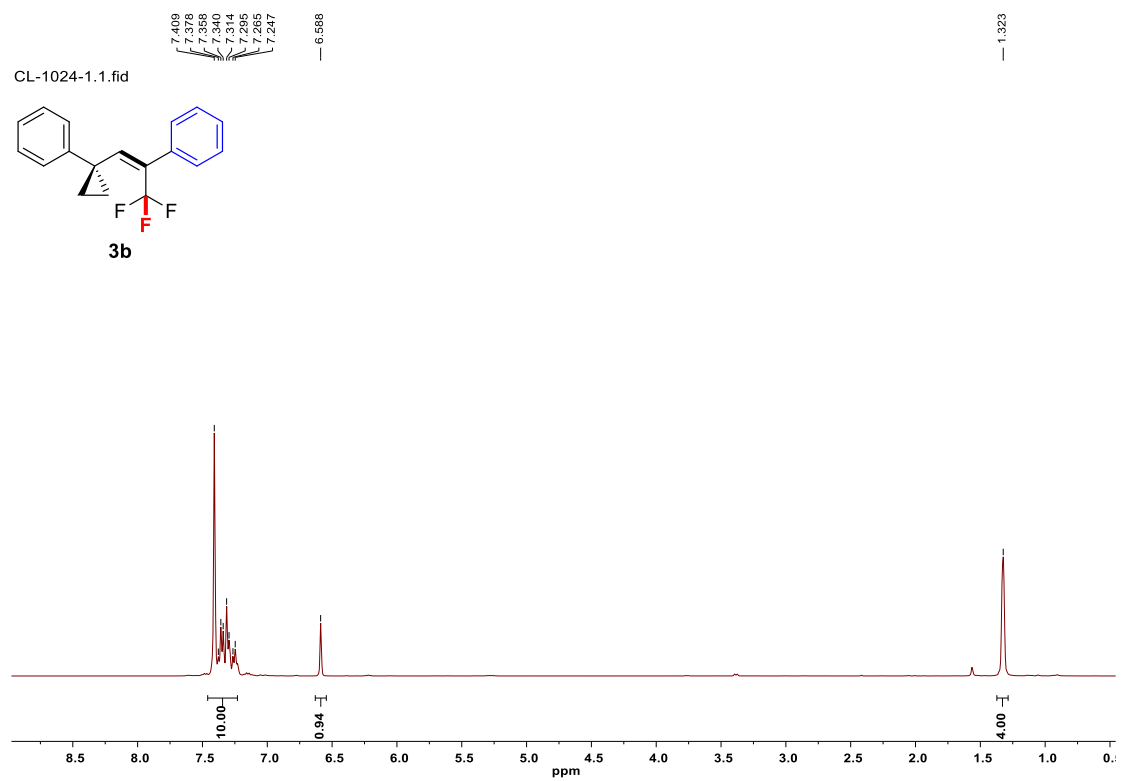
XI. NMR spectra



^{13}C NMR spectrum of **3a** (101 MHz, CDCl_3)

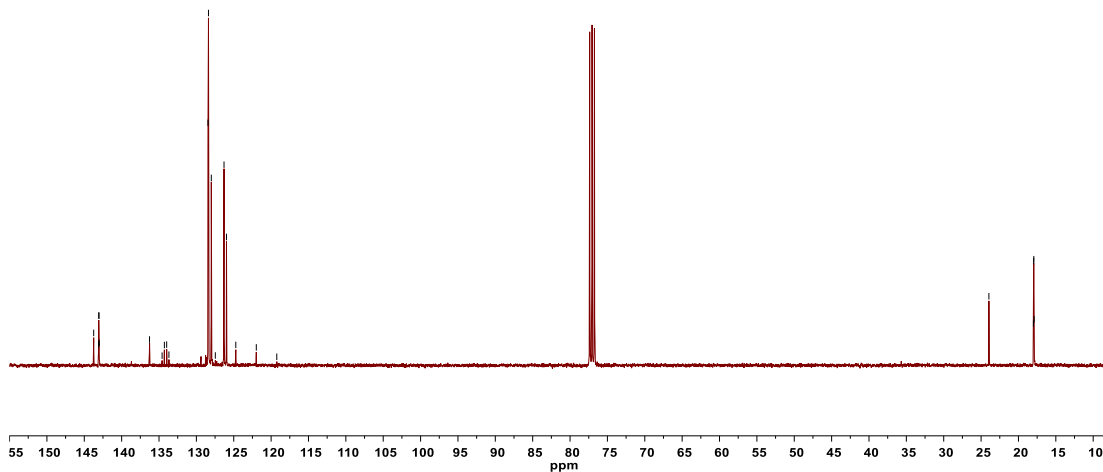
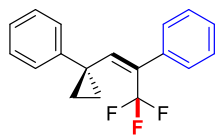


^{19}F NMR spectrum of **3a** (376 MHz, CDCl_3)



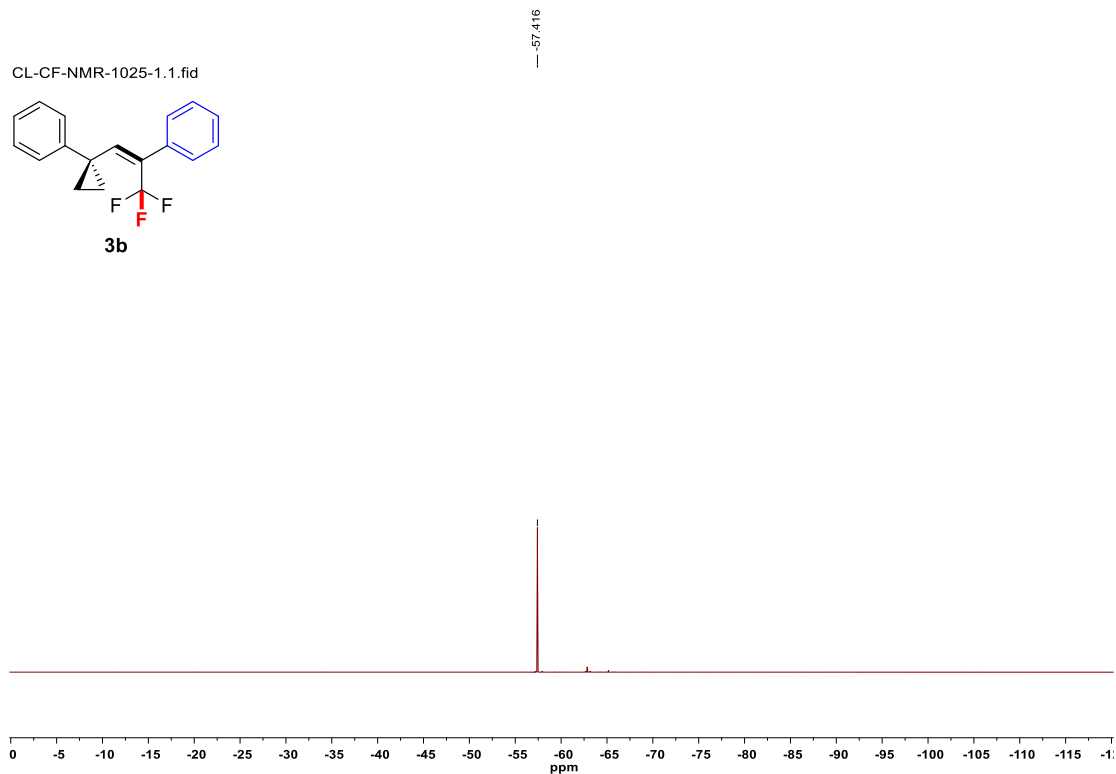
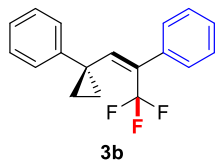
^1H NMR spectrum of **3b** (400 MHz, CDCl_3)

CL-CF-NMR-1025-1.2.fid

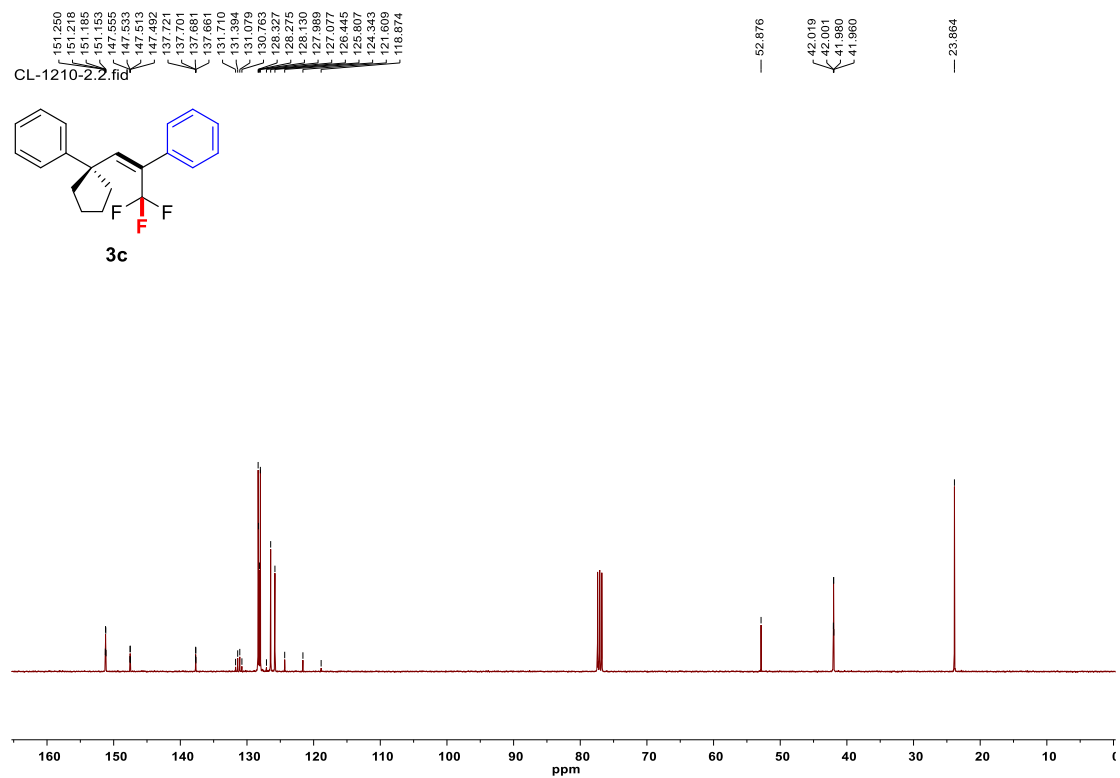
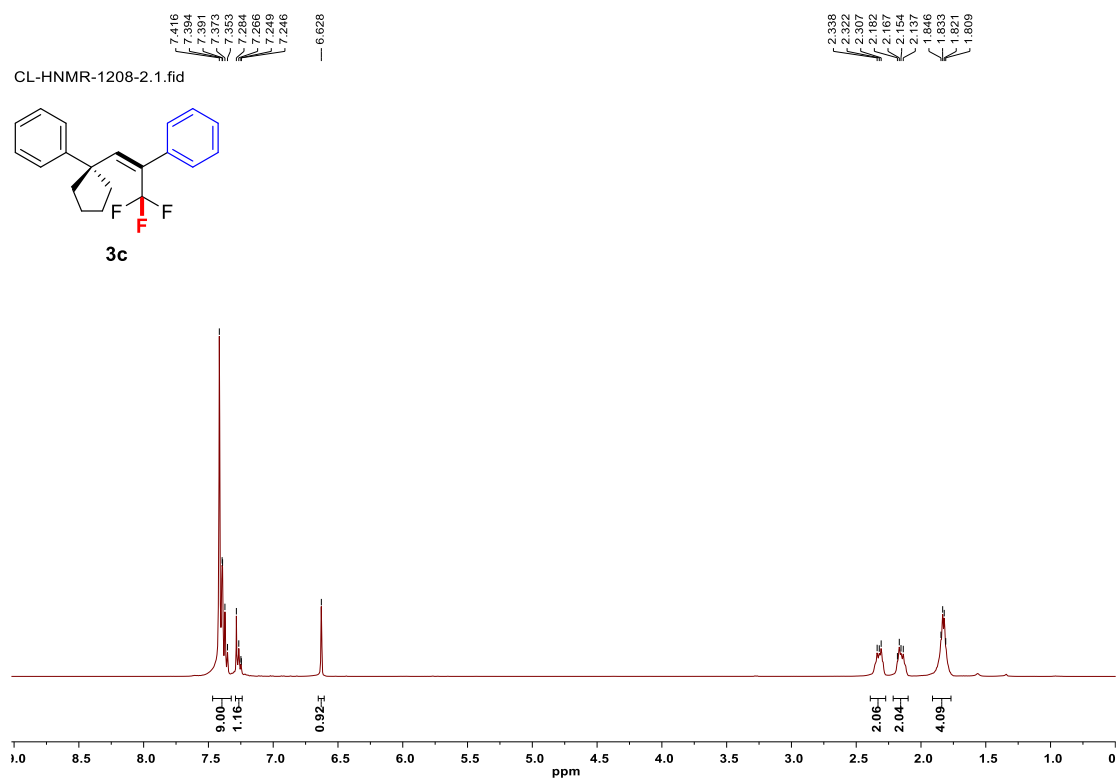


^{13}C NMR spectrum of **3b** (101 MHz, CDCl_3)

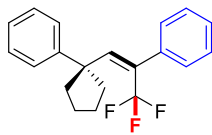
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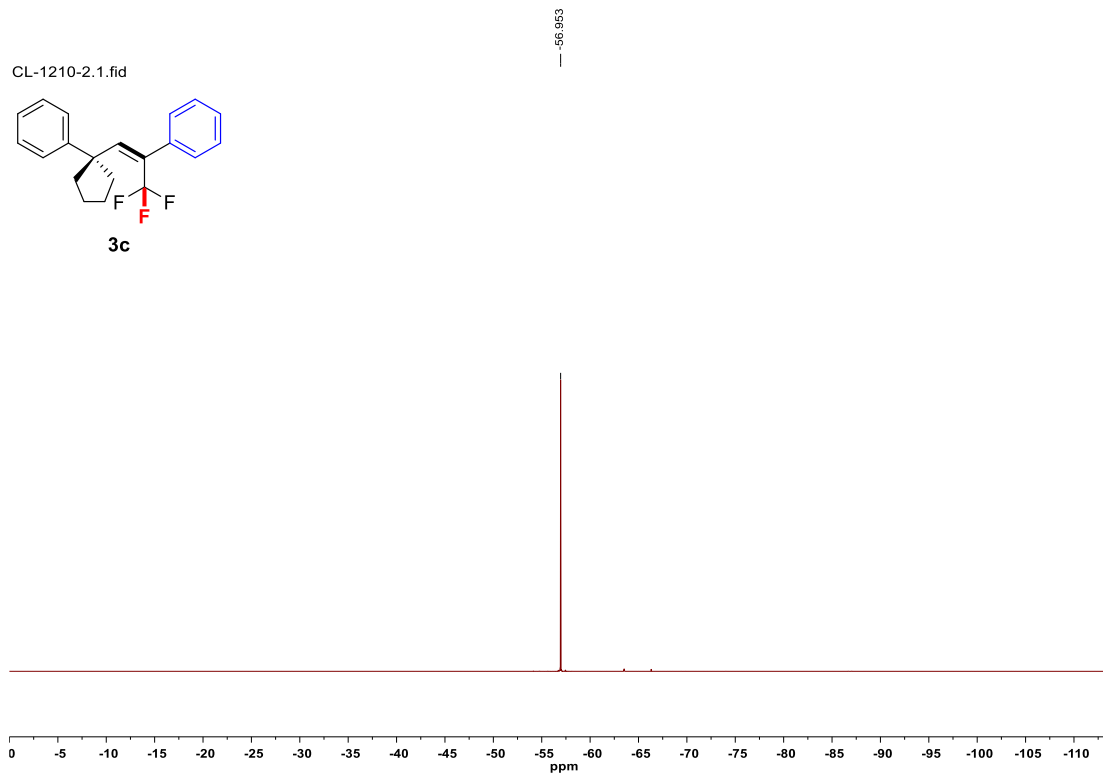
^{19}F NMR spectrum of **3b** (376 MHz, CDCl_3)



CL-1210-2.1.fid

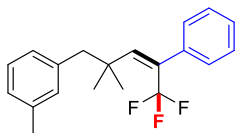


3c

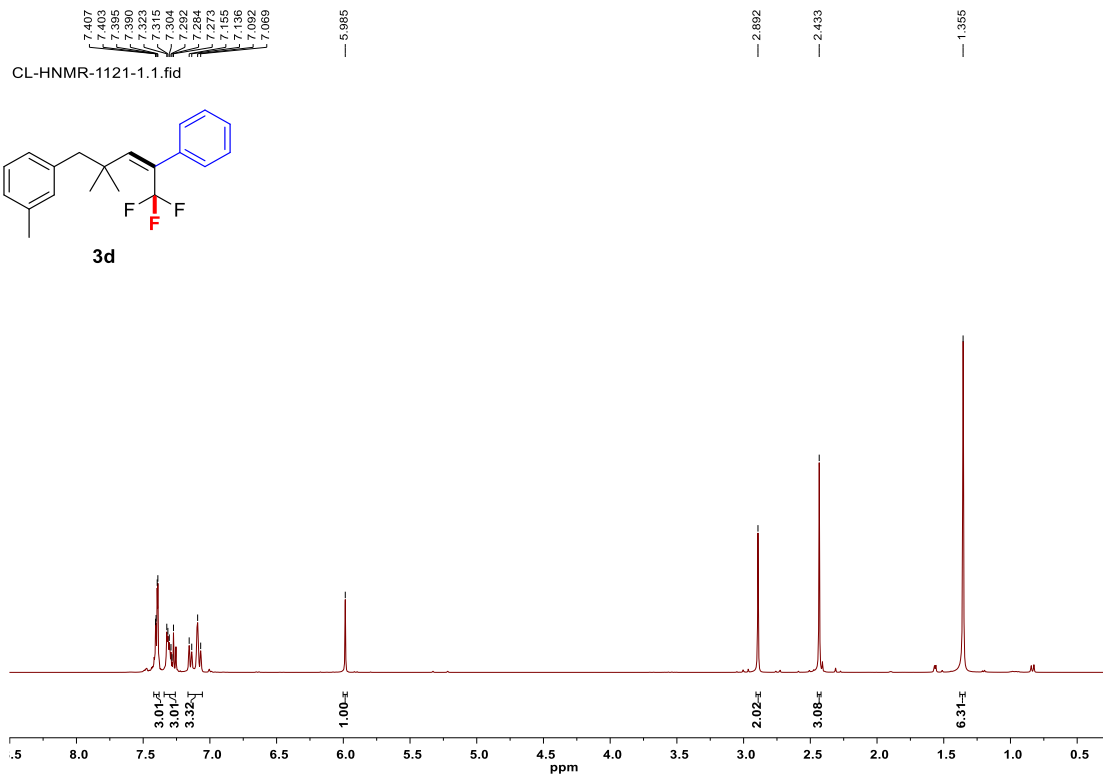


^{19}F NMR spectrum of **3c** (376 MHz, CDCl_3)

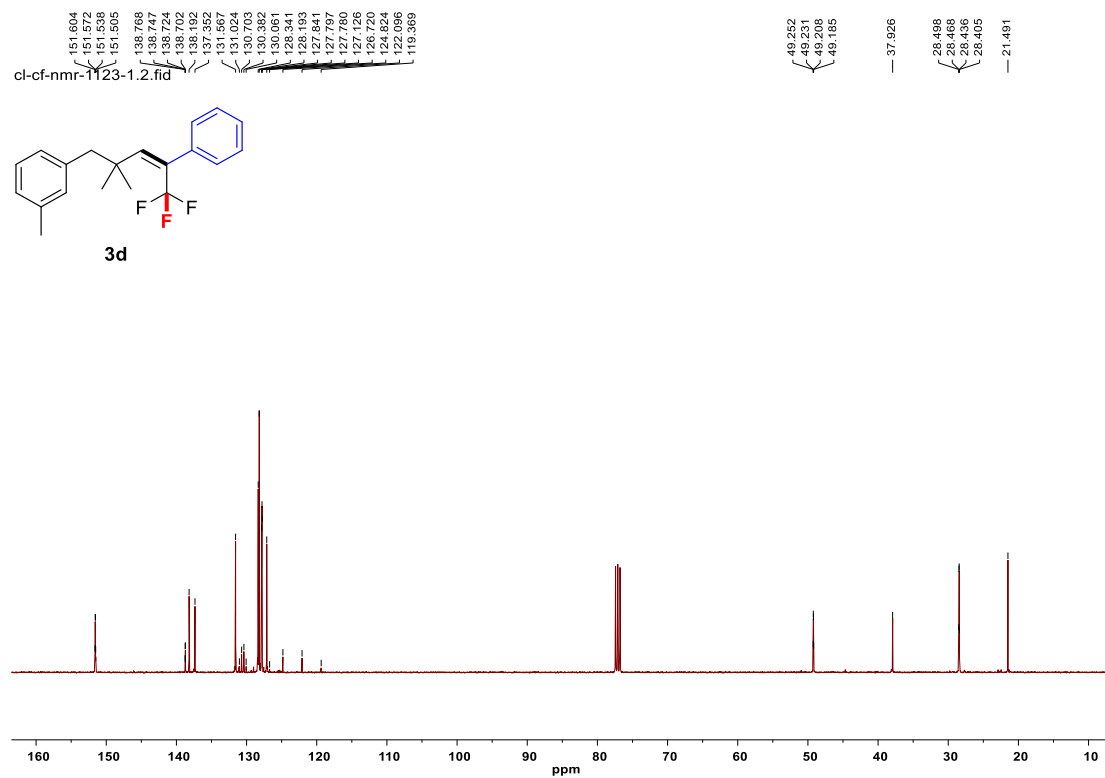
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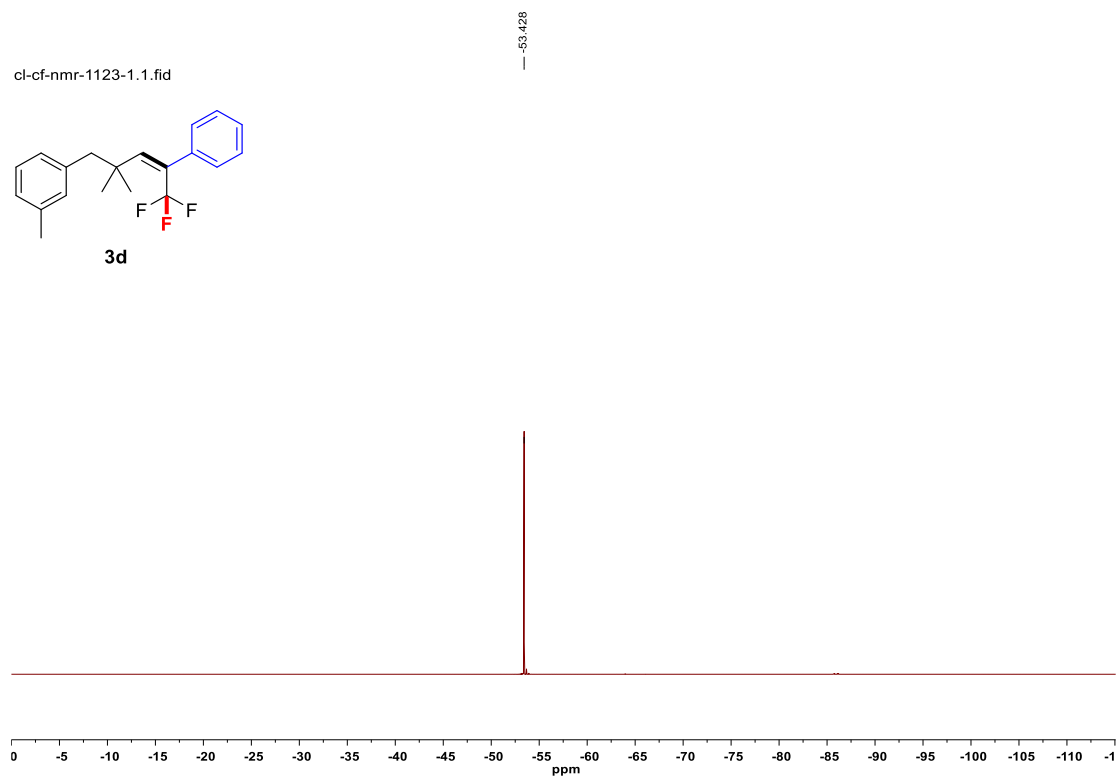
3d



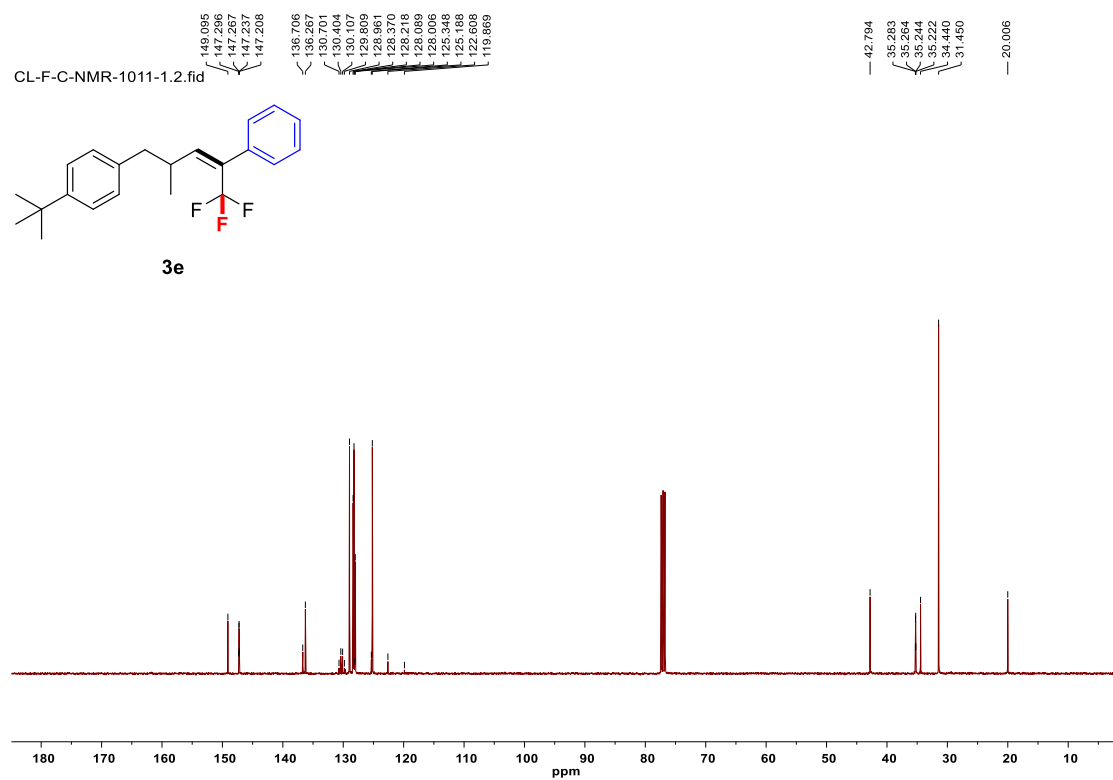
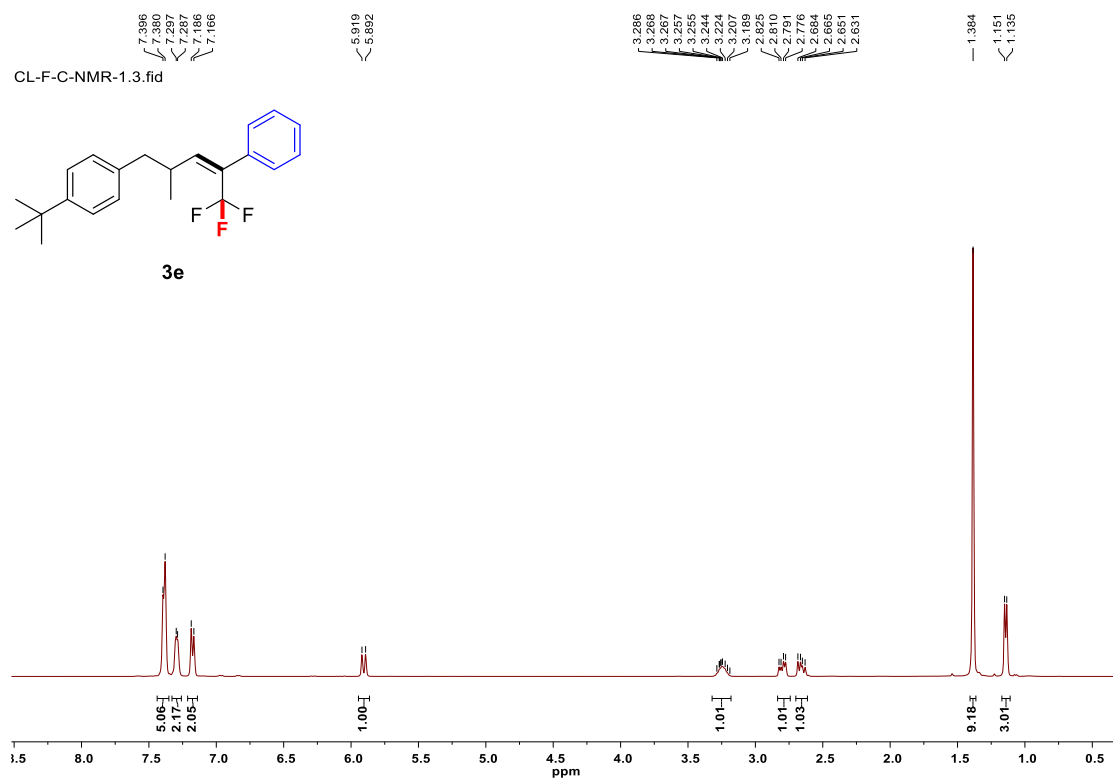
^1H NMR spectrum of **3d** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3d** (101 MHz, CDCl_3)

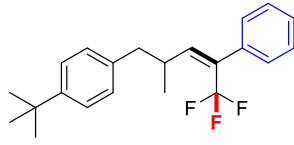


^{19}F NMR spectrum of **3d** (376 MHz, CDCl_3)

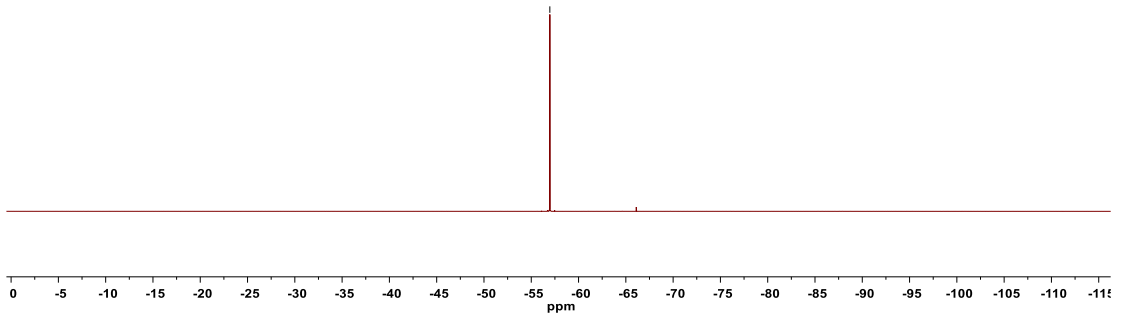


CL-F-C-NMR-1011-1.1.fid

-56.964

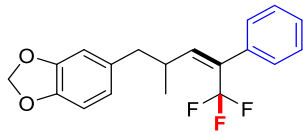


3e

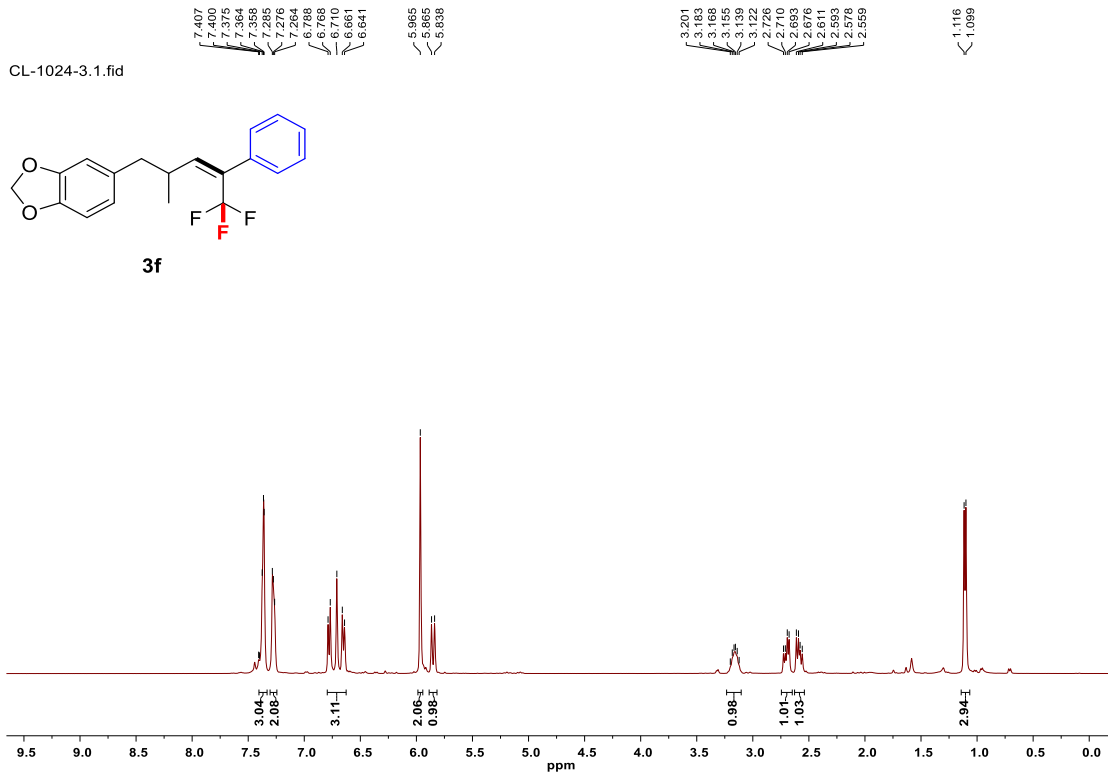


^{19}F NMR spectrum of **3e** (376 MHz, CDCl_3)

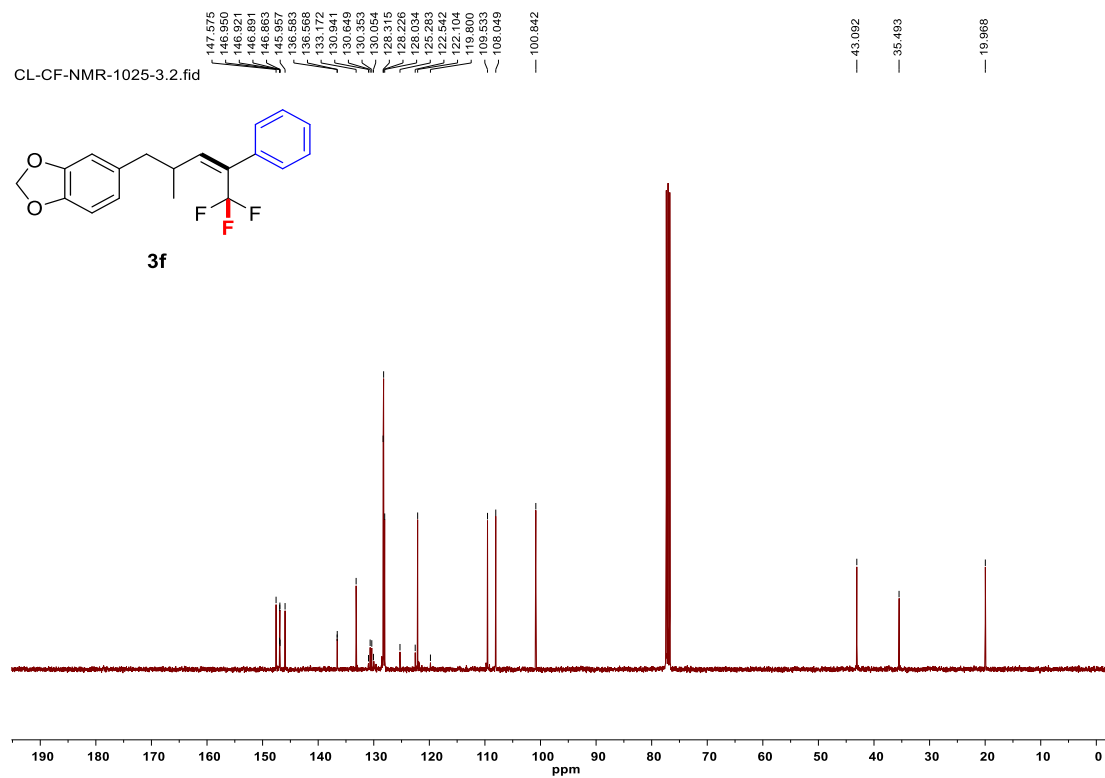
CL-1024-3.1.fid



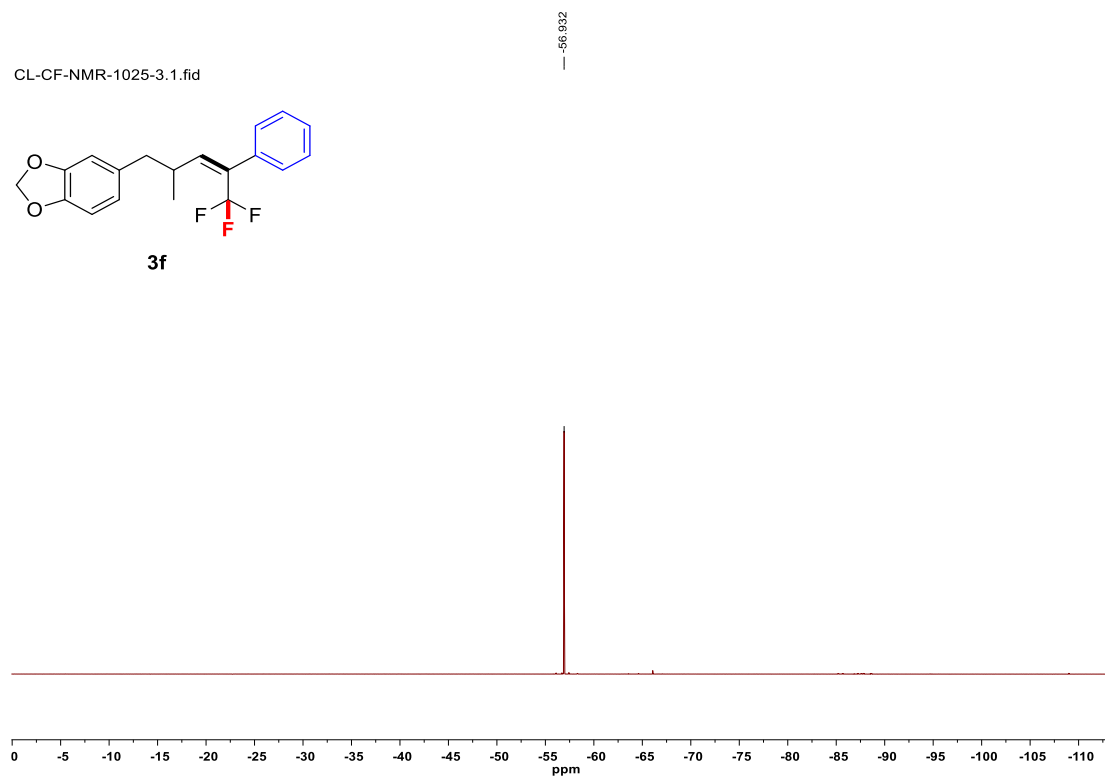
3f



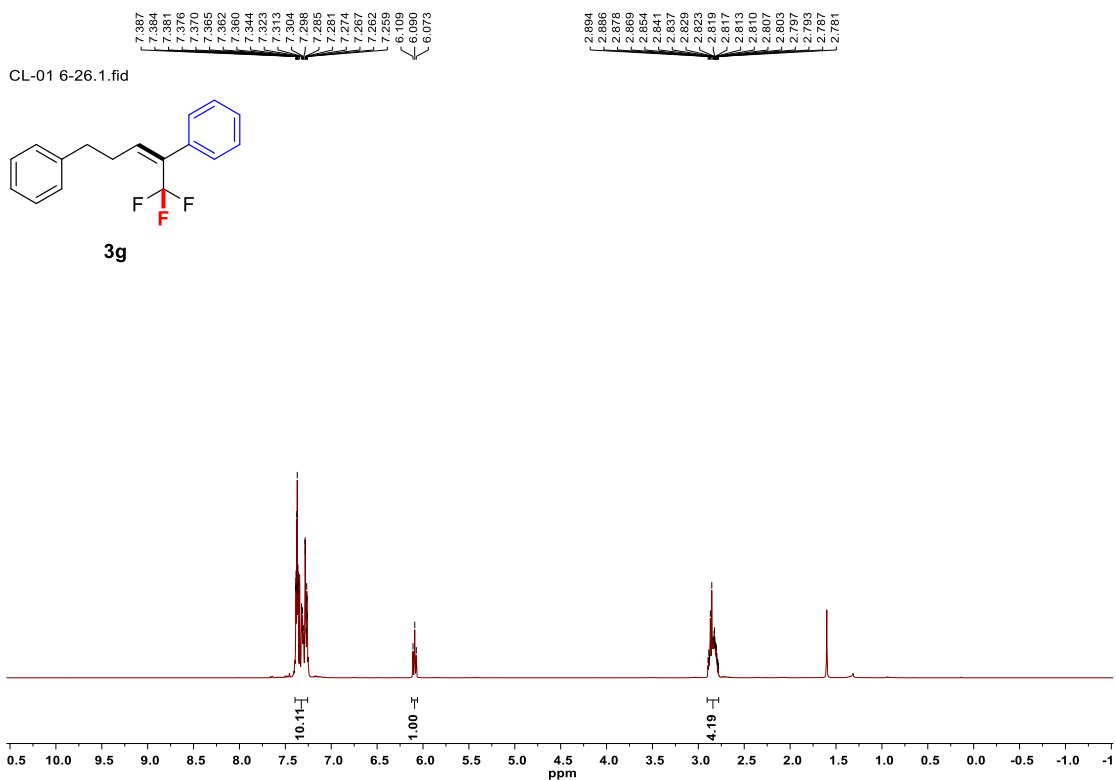
^1H NMR spectrum of **3f** (400 MHz, CDCl_3)



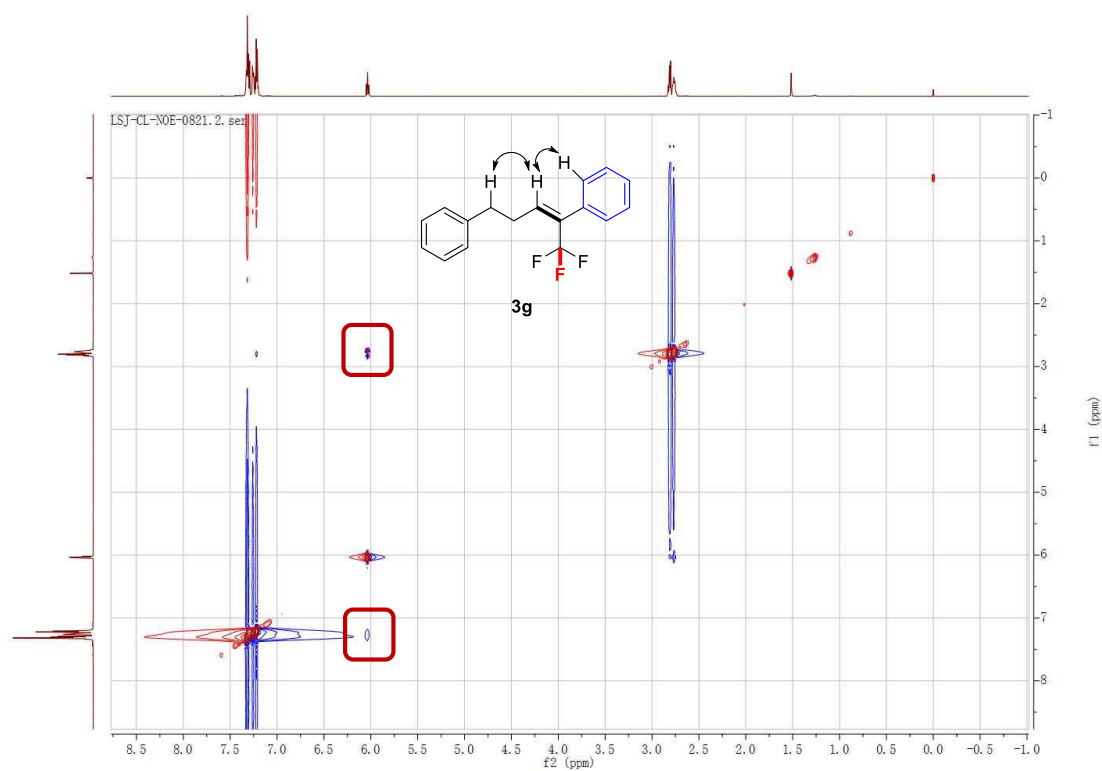
^{13}C NMR spectrum of **3f** (101 MHz, CDCl_3)



^{19}F NMR spectrum of **3f** (376 MHz, CDCl_3)



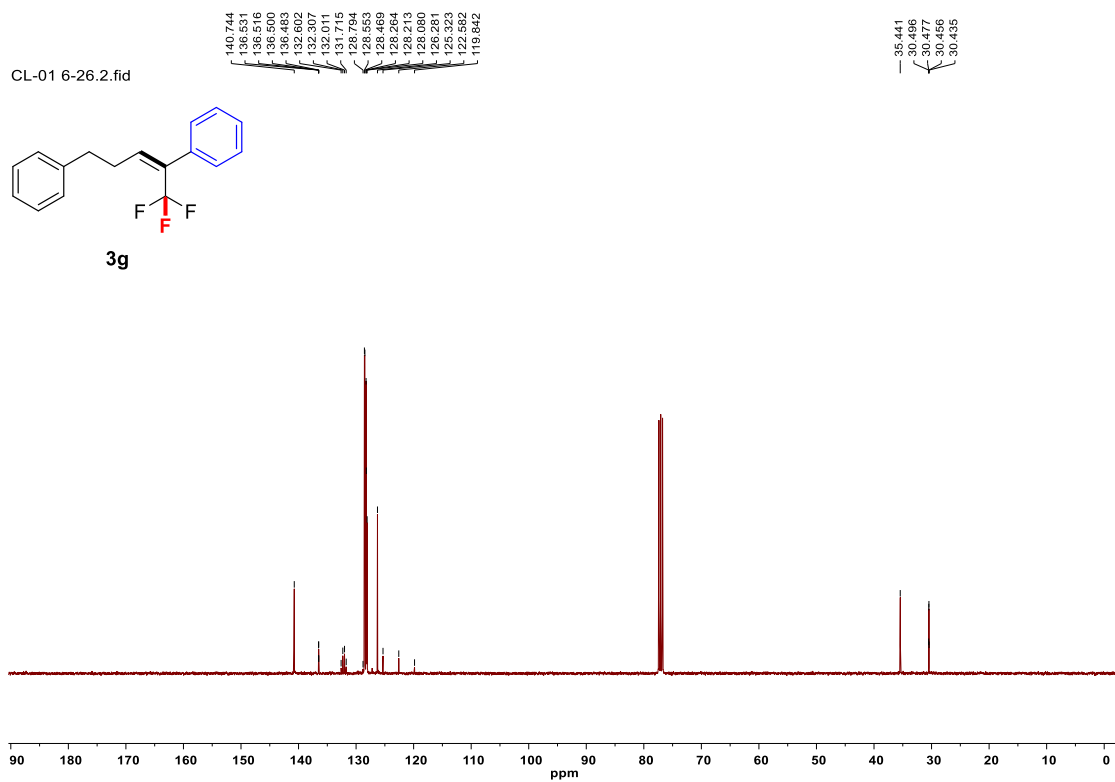
^1H NMR spectrum of **3g** (400 MHz, CDCl_3)



nOe Spectrum of **3g** (CDCl_3 , 600 M)



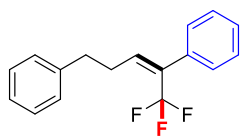
^1H - ^{19}F COSY Spectrum of **3g** (CDCl_3 , 600 M)



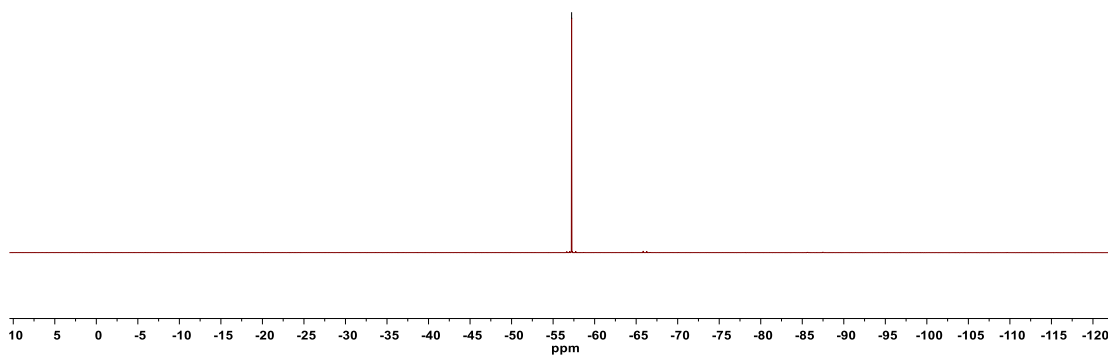
^{13}C NMR spectrum of **3g** (101 MHz, CDCl_3)

CL-01 6-26.3.fid

---57.228

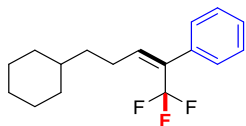


3g

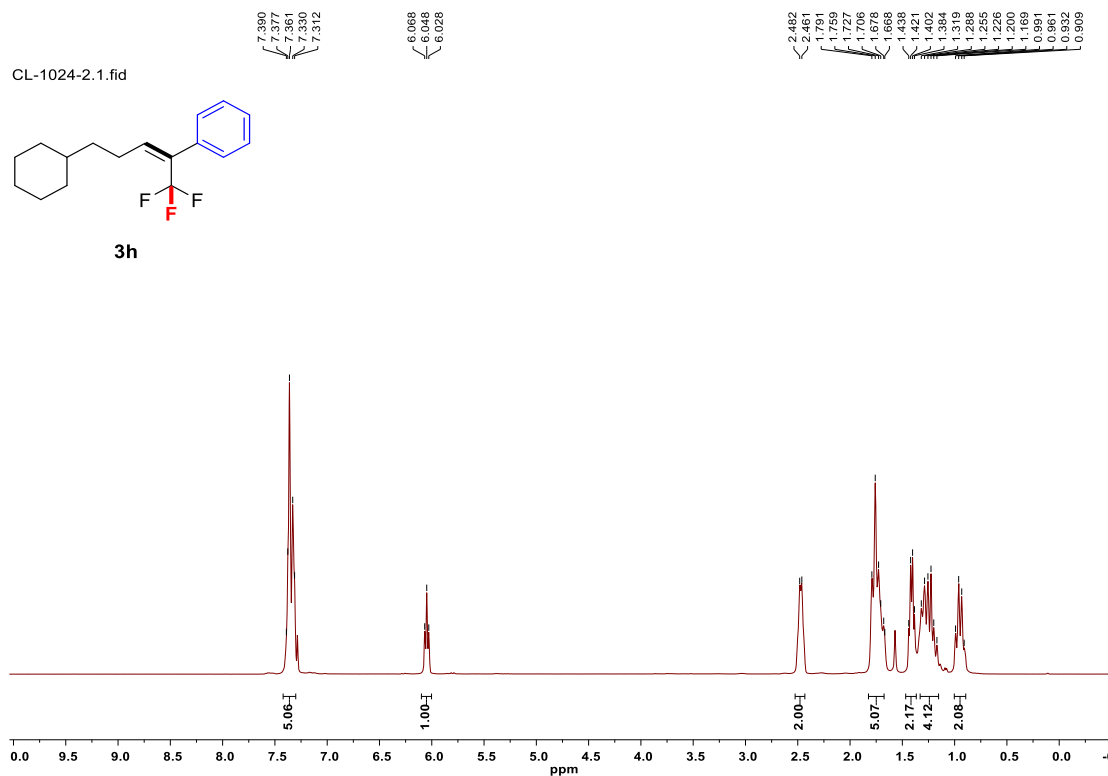


^{19}F NMR spectrum of **3g** (376 MHz, CDCl_3)

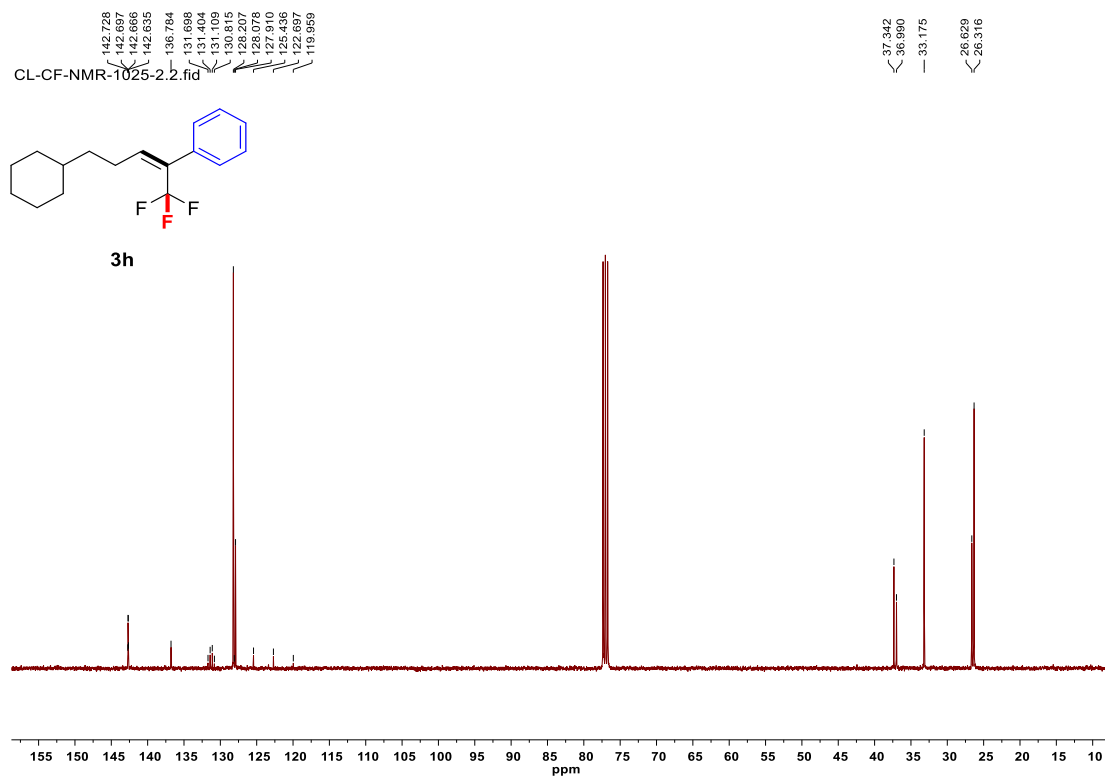
CL-1024-2.1.fid



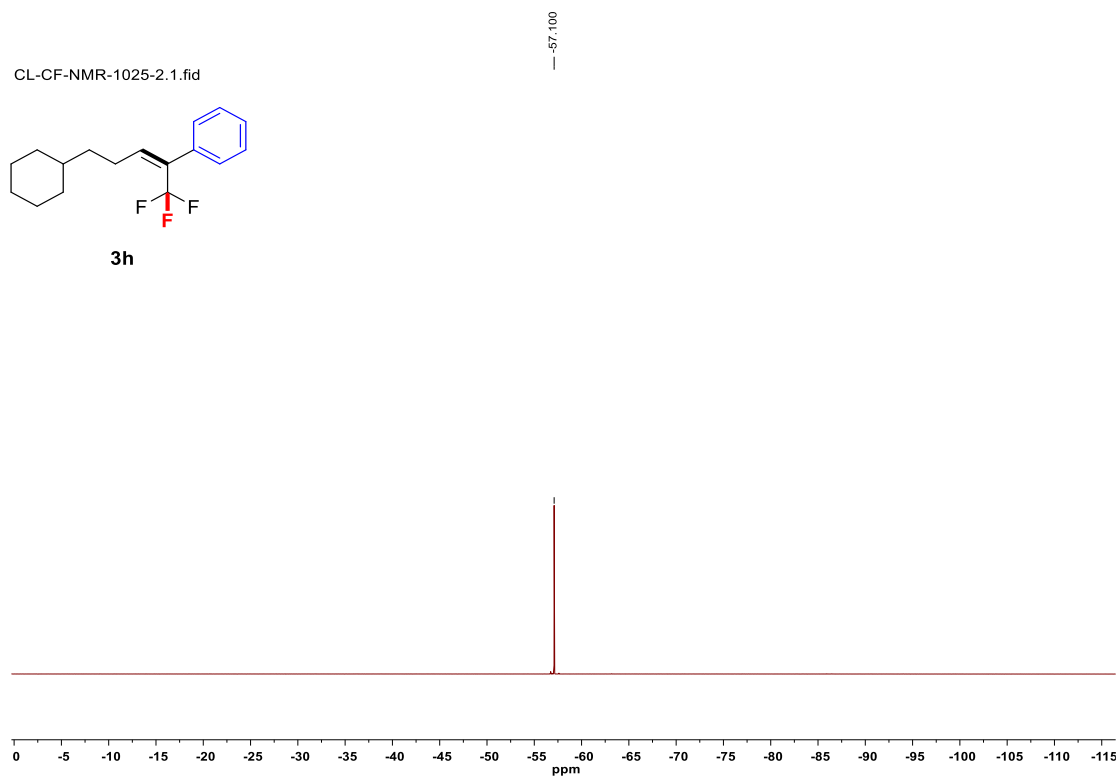
3h



^1H NMR spectrum of **3h** (400 MHz, CDCl_3)

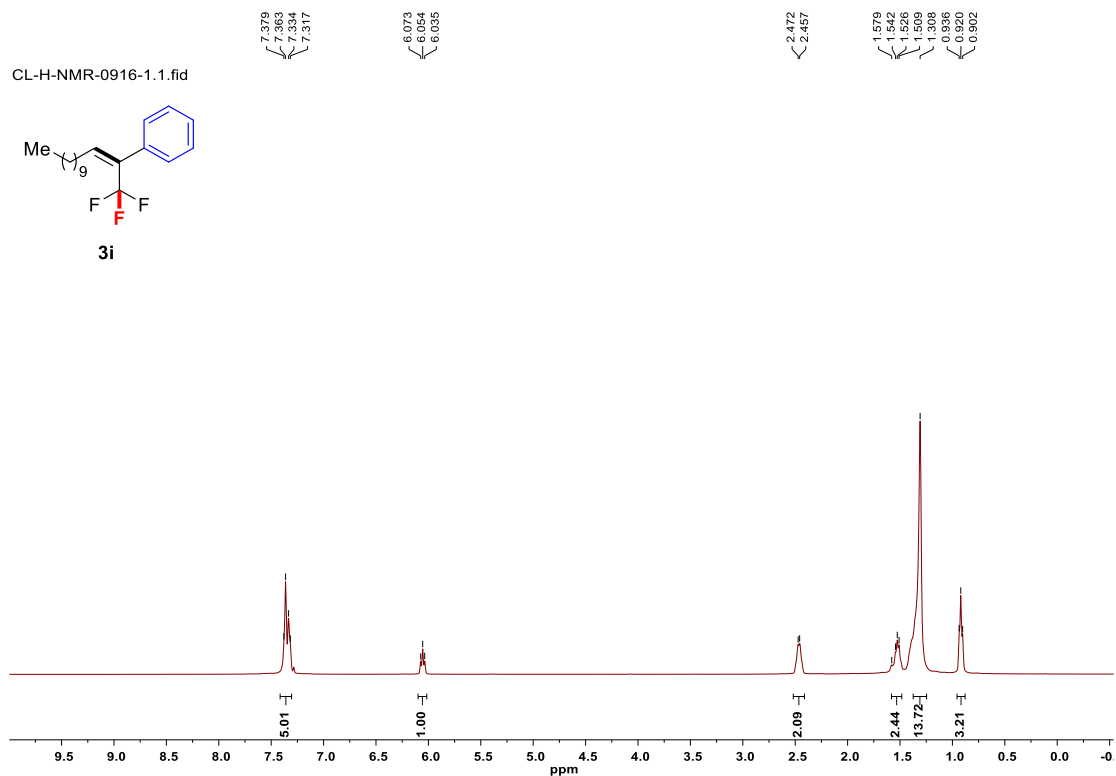
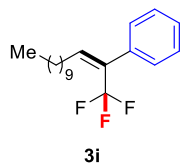


^{13}C NMR spectrum of **3h** (101 MHz, CDCl_3)



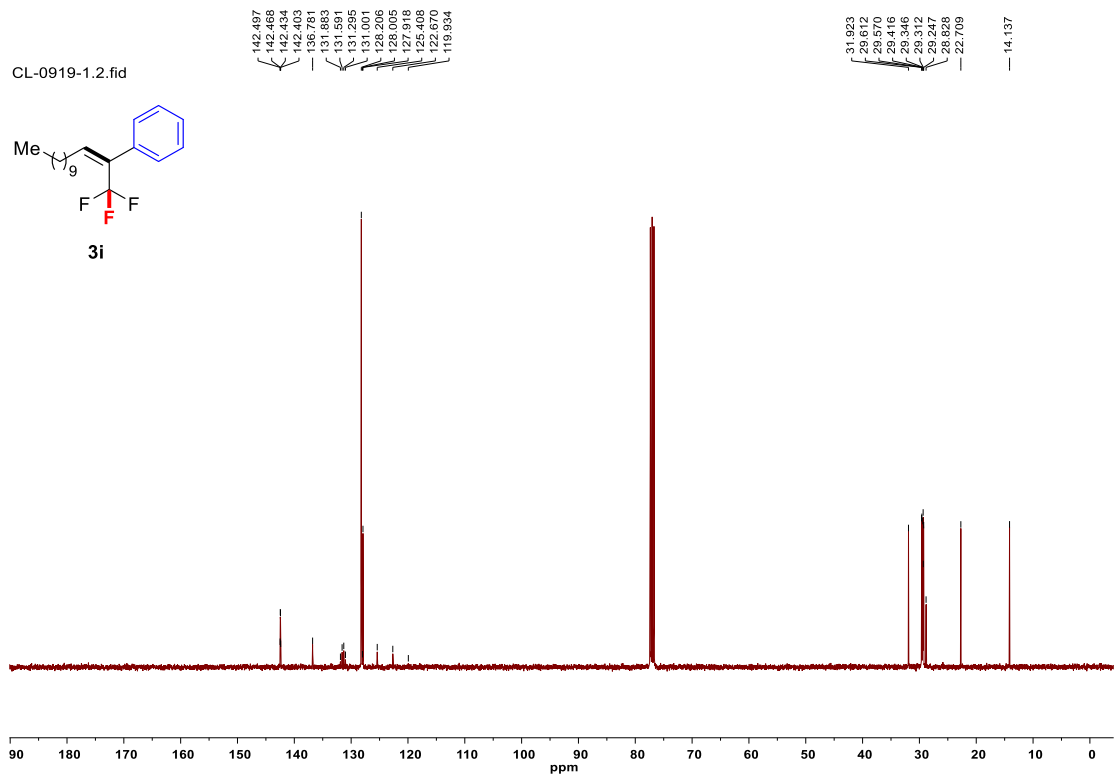
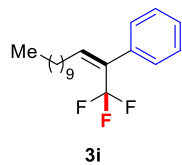
^{19}F NMR spectrum of **3h** (376 MHz, CDCl_3)

CL-H-NMR-0916-1.1.fid

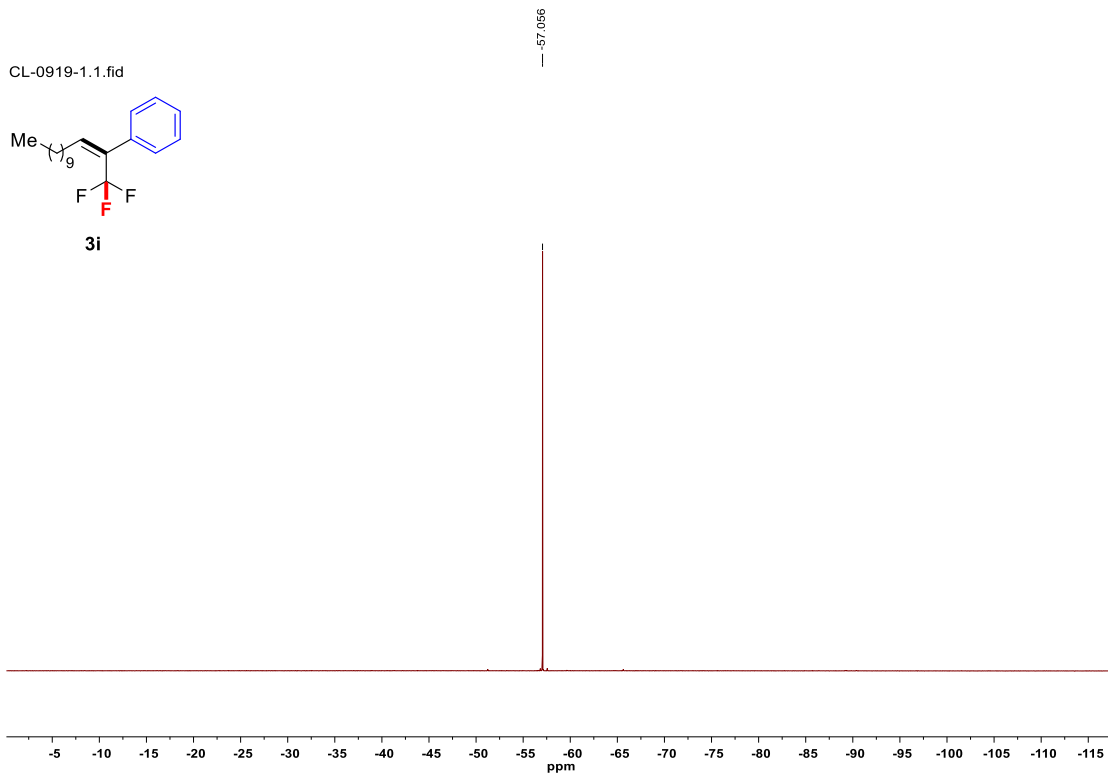


¹H NMR spectrum of **3i** (400 MHz, CDCl₃)

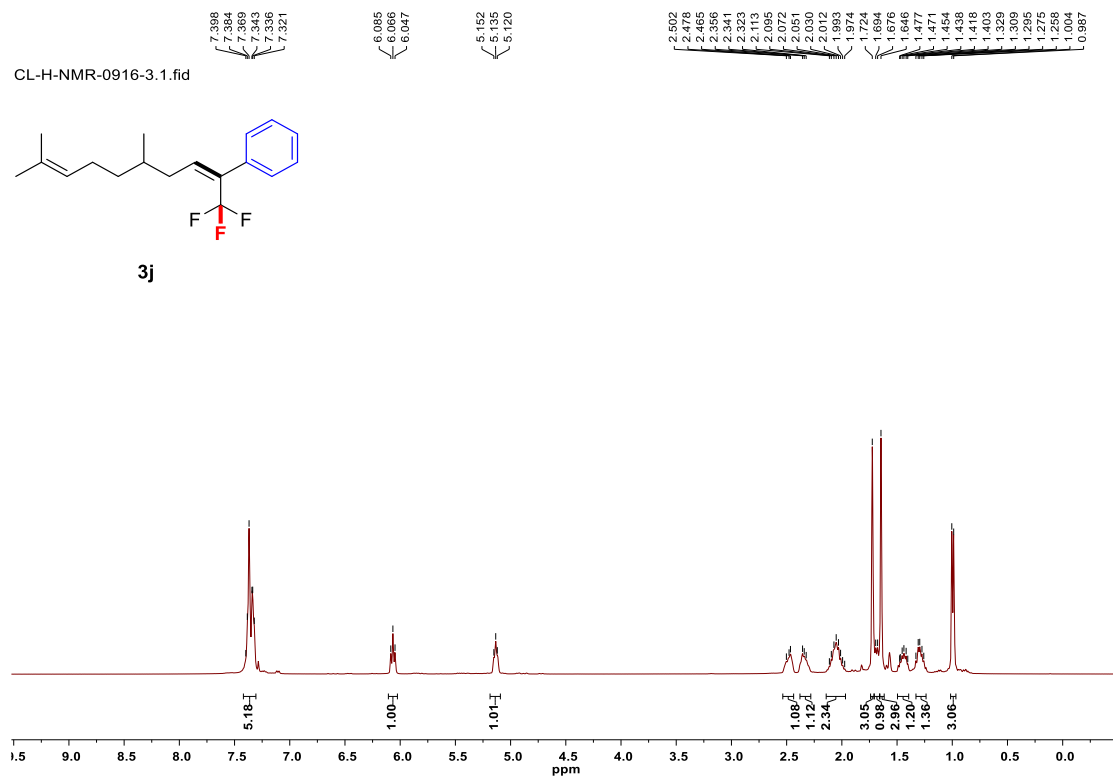
CL-0919-1.2.fid



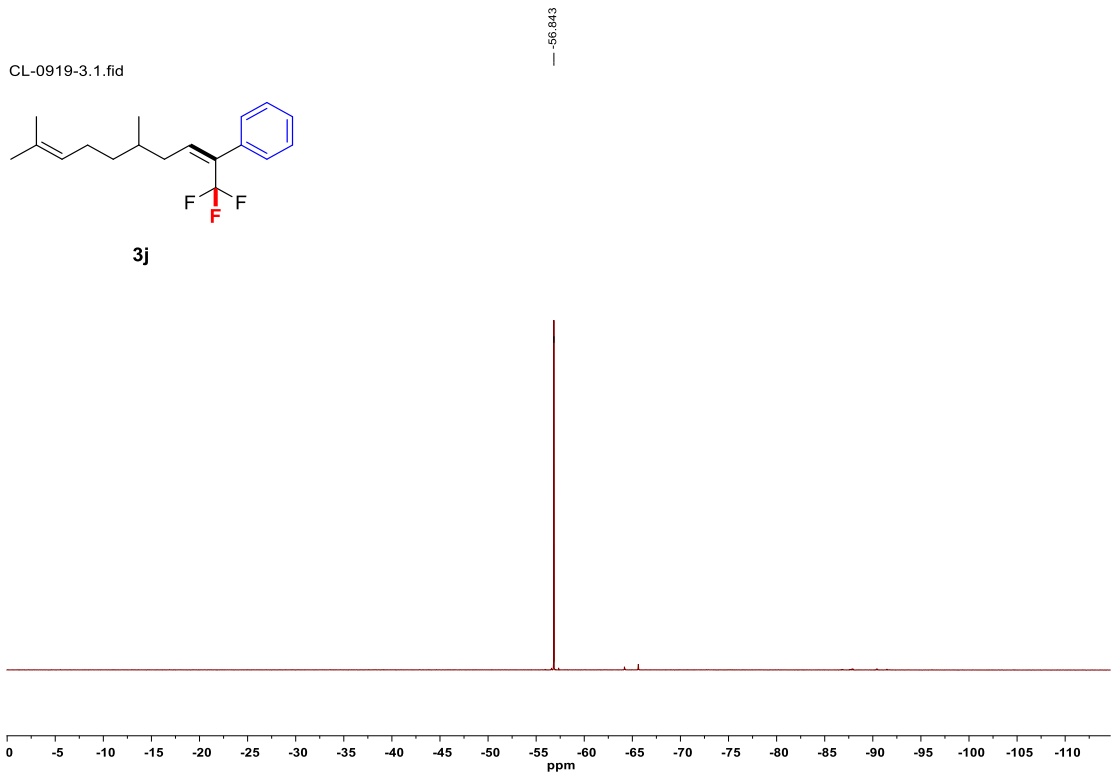
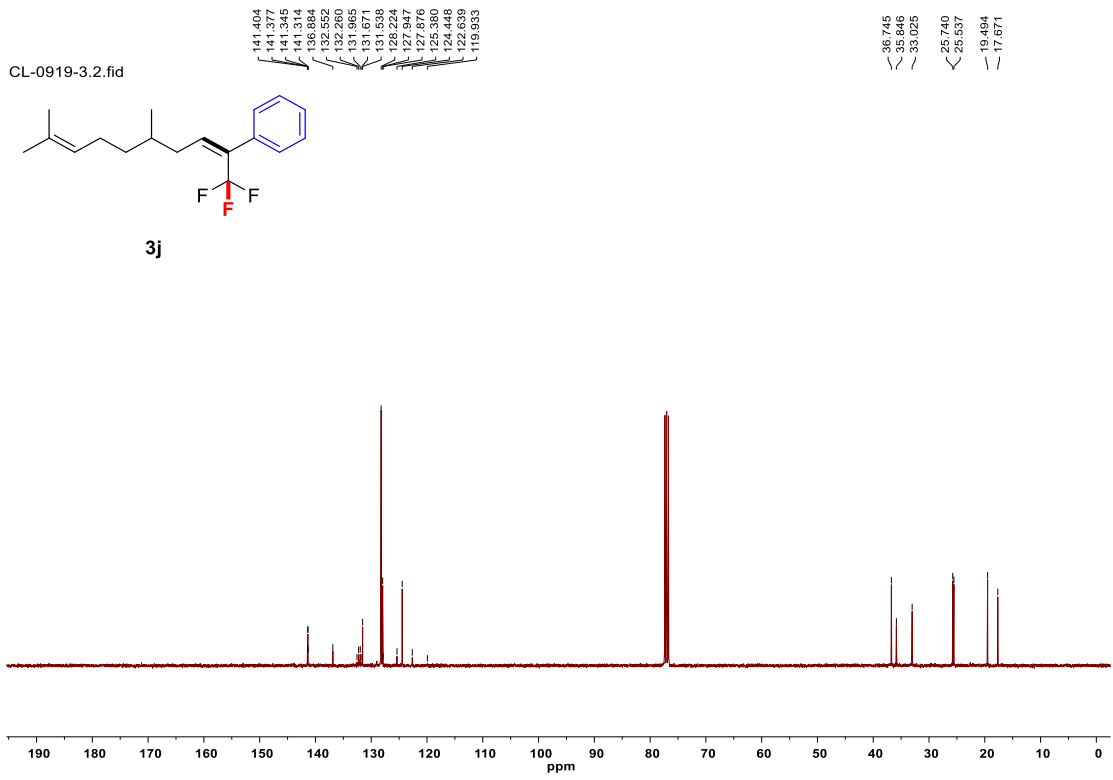
¹³C NMR spectrum of **3i** (101 MHz, CDCl₃)

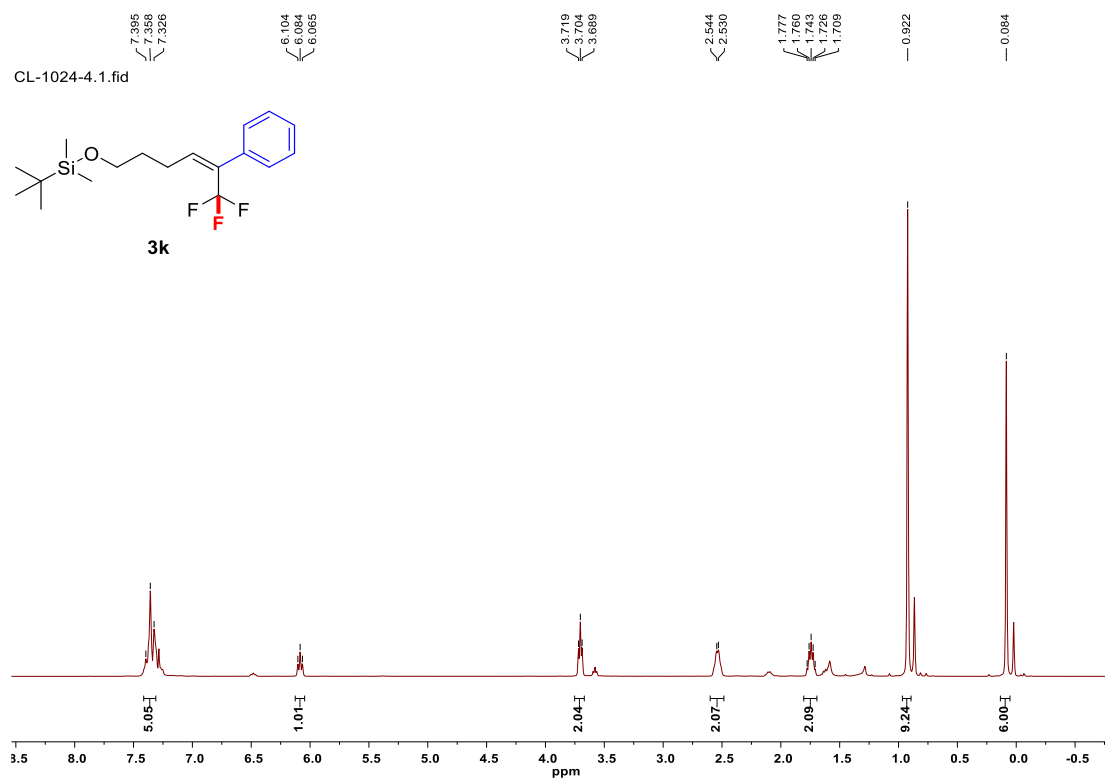


^{19}F NMR spectrum of **3i** (376 MHz, CDCl_3)

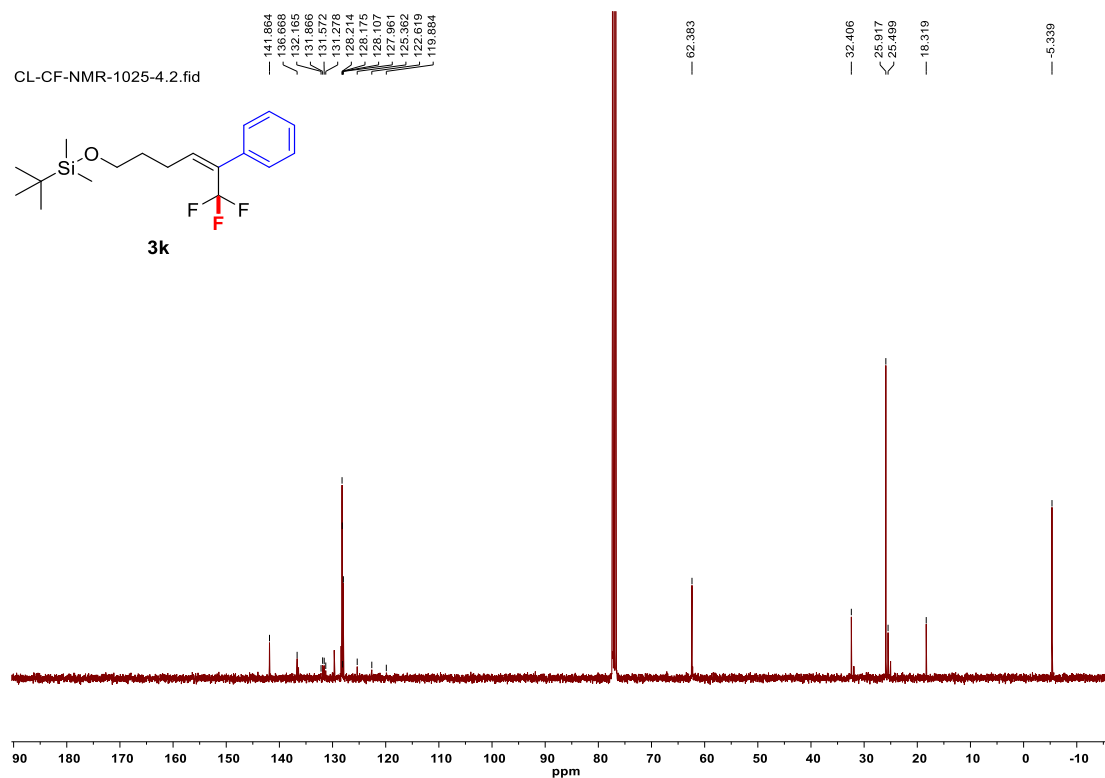


^1H NMR spectrum of **3j** (400 MHz, CDCl_3)





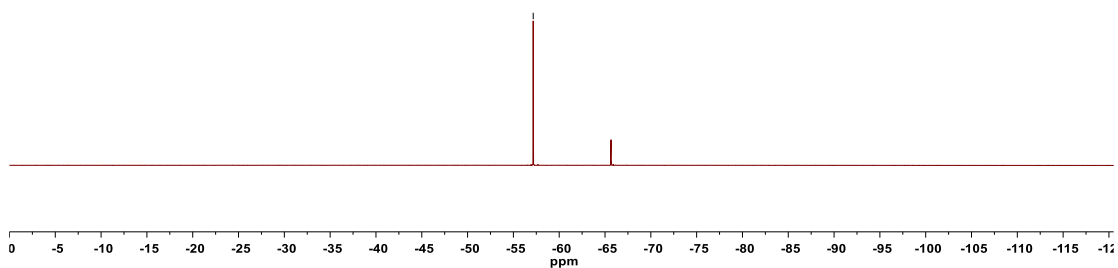
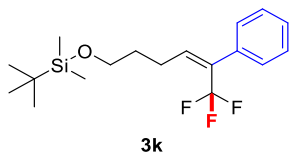
^1H NMR spectrum of **3k** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **3k** (101 MHz, CDCl_3)

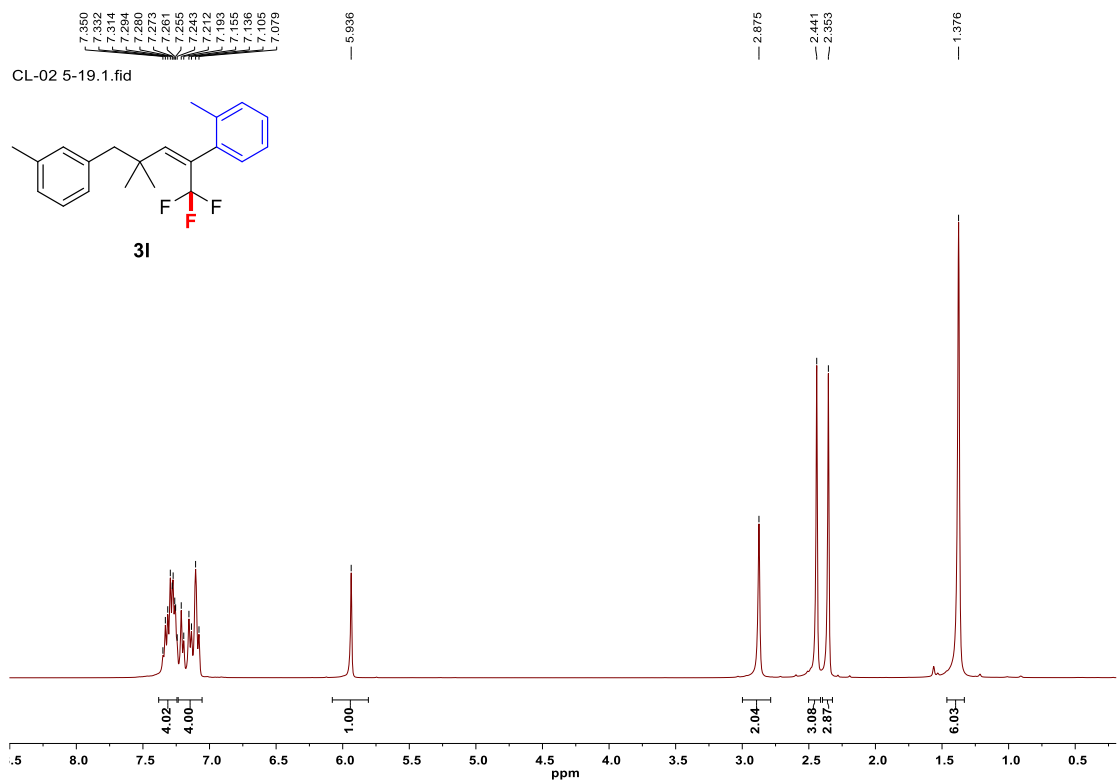
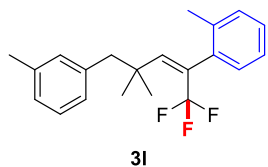
CL-CF-NMR-1025-4.1.fid

— 57.163

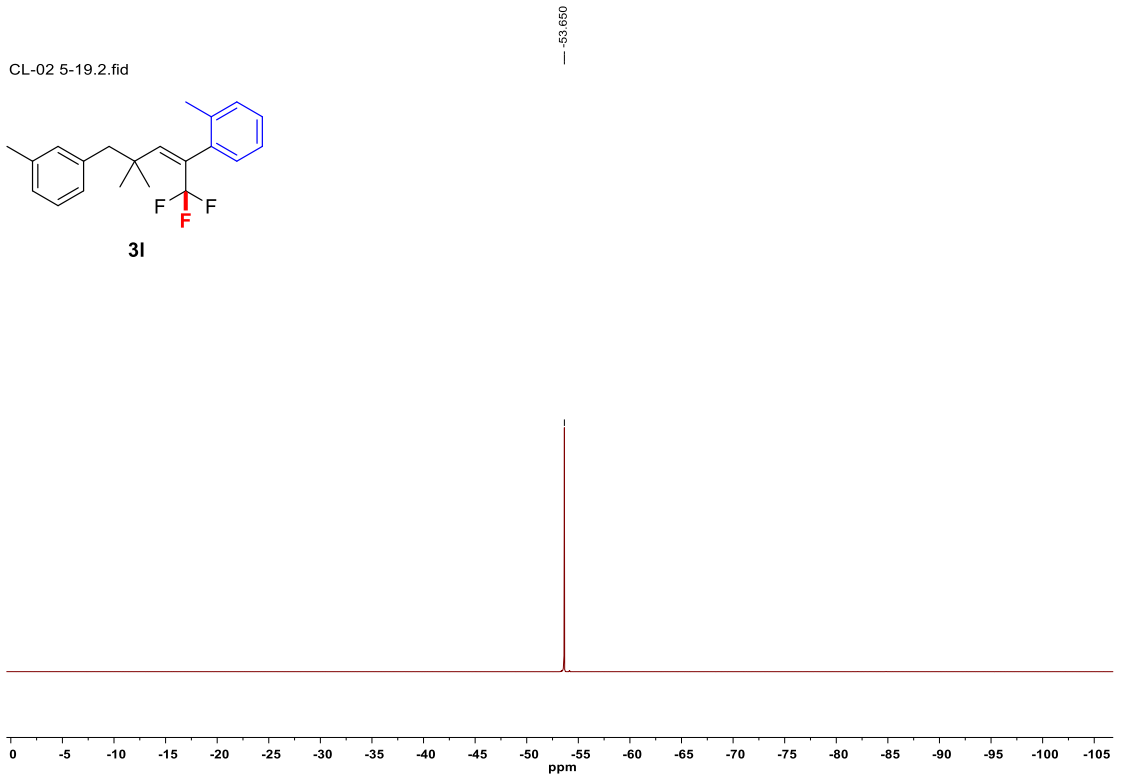
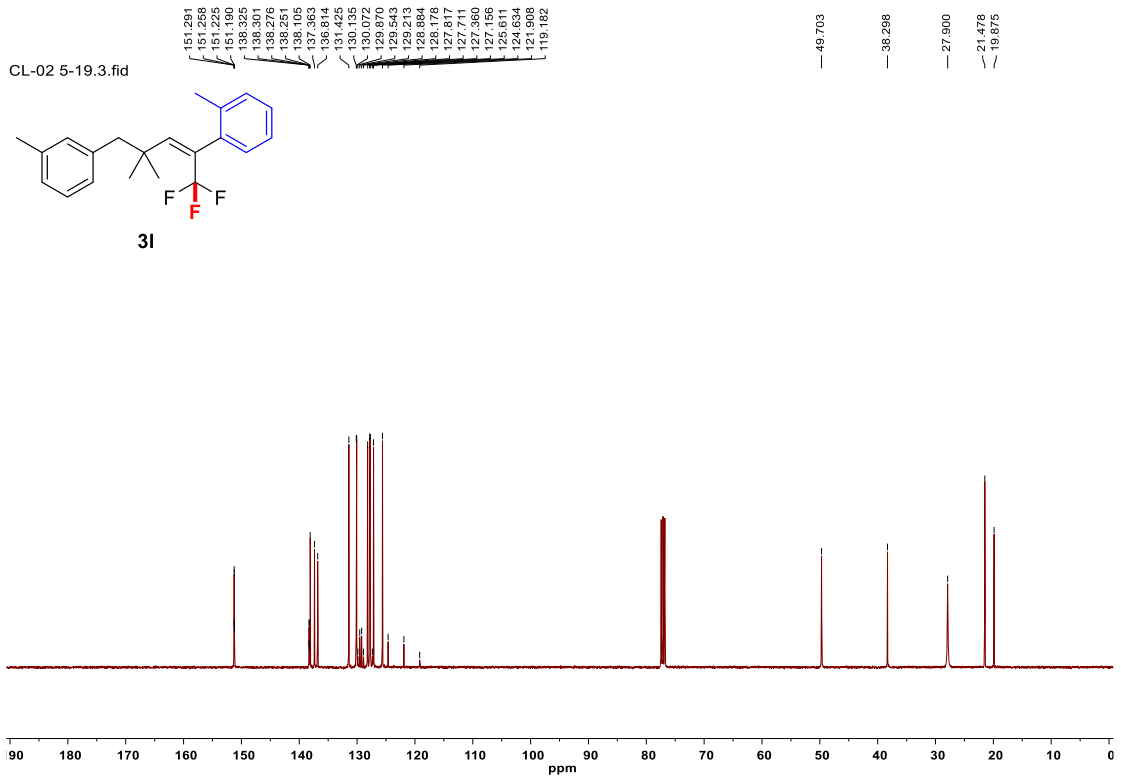


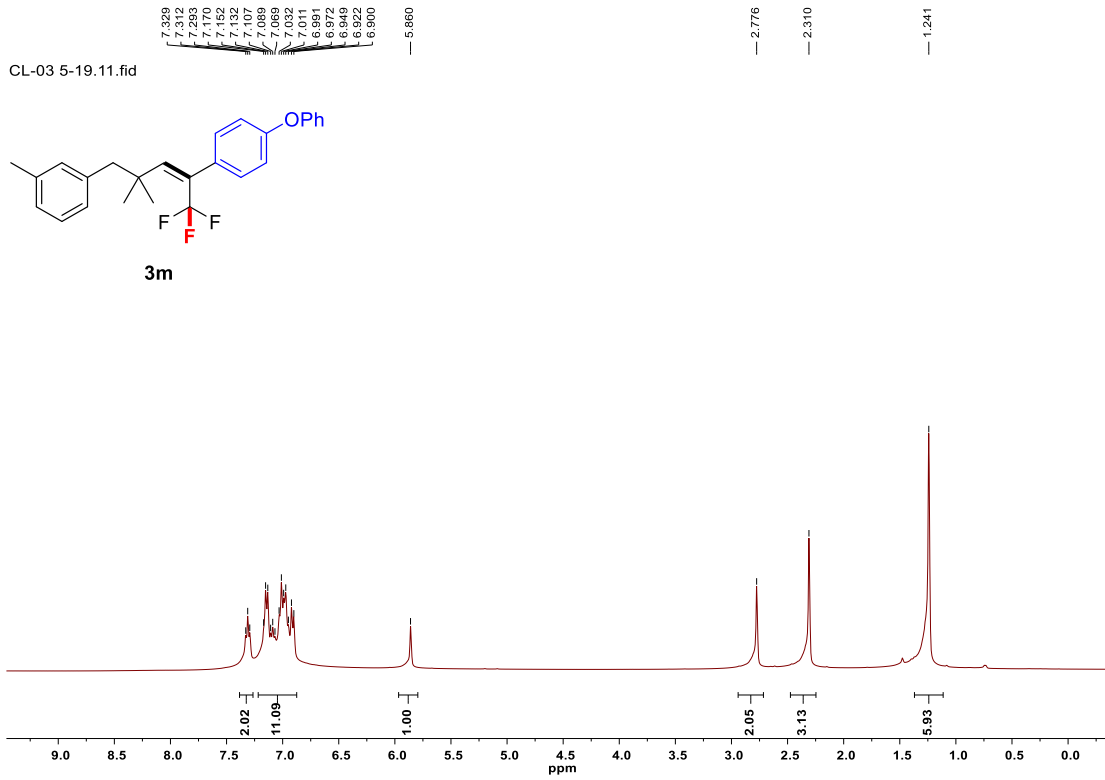
¹⁹F NMR spectrum of **3k** (376 MHz, CDCl₃)

CL-02 5-19.1.fid

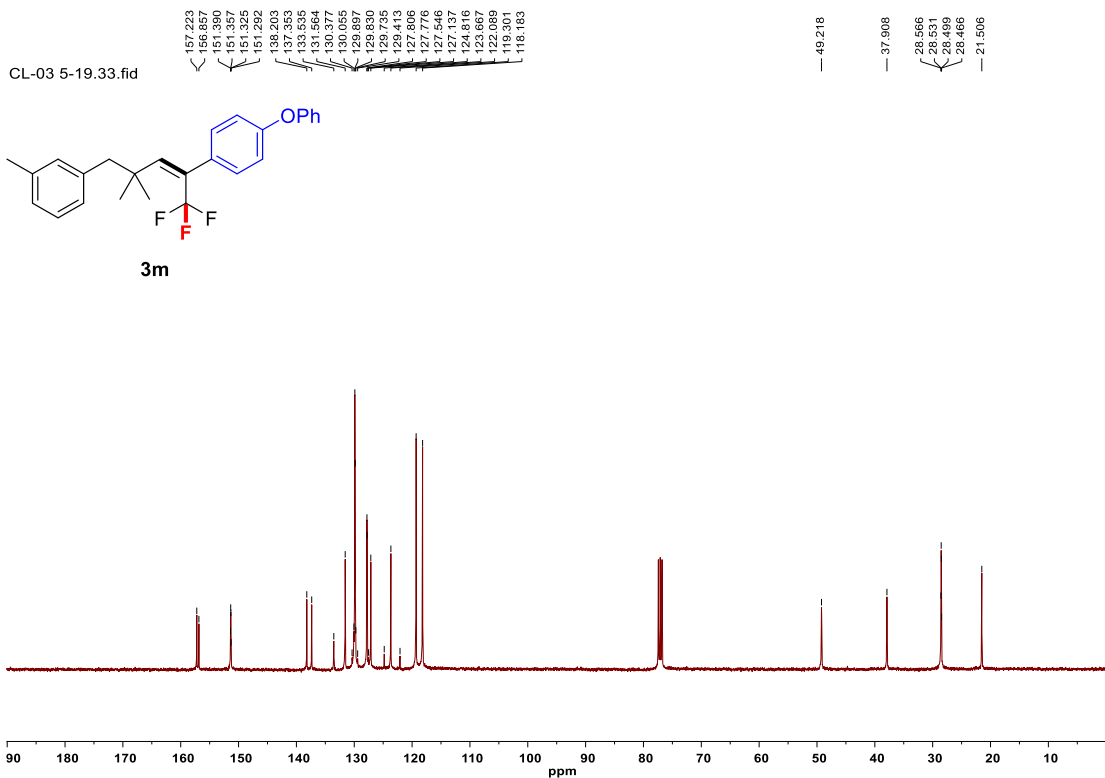


¹H NMR spectrum of **3l** (400 MHz, CDCl₃)





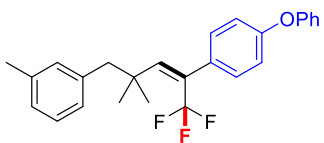
^1H NMR spectrum of **3m** (400 MHz, CDCl_3)



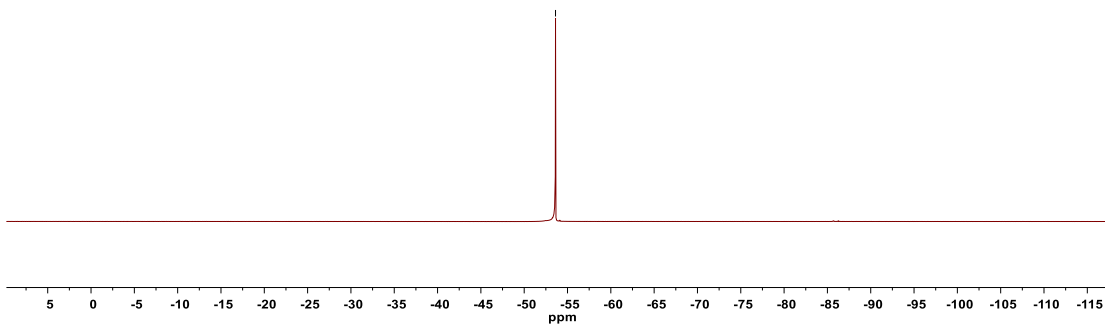
^{13}C NMR spectrum of **3m** (101 MHz, CDCl_3)

CL-03 5-19.22.fid

-53.617



3m



^{19}F NMR spectrum of **3m** (376 MHz, CDCl_3)

CL-HNMR-1121-2.1.fid

7.276
7.271
7.255
7.254
7.234
7.194
7.137
7.118
7.063
7.041

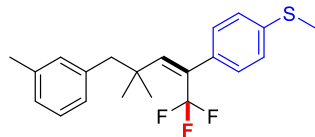
-6.953

-2.865

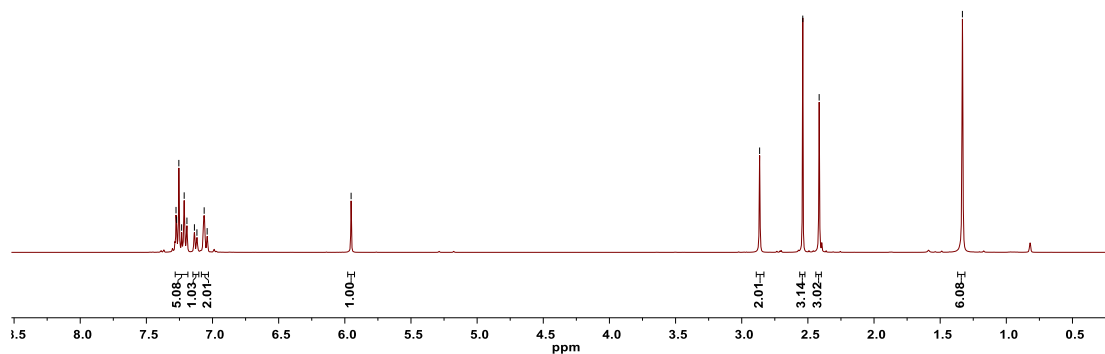
-2.539

-2.415

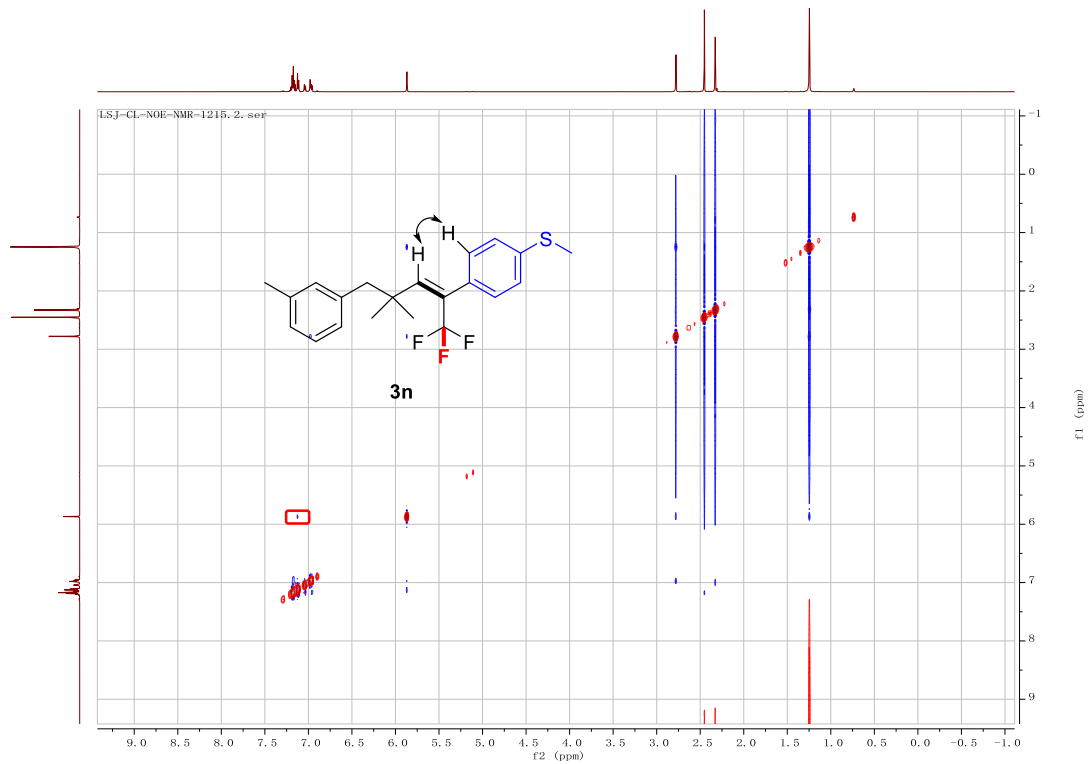
-1.332



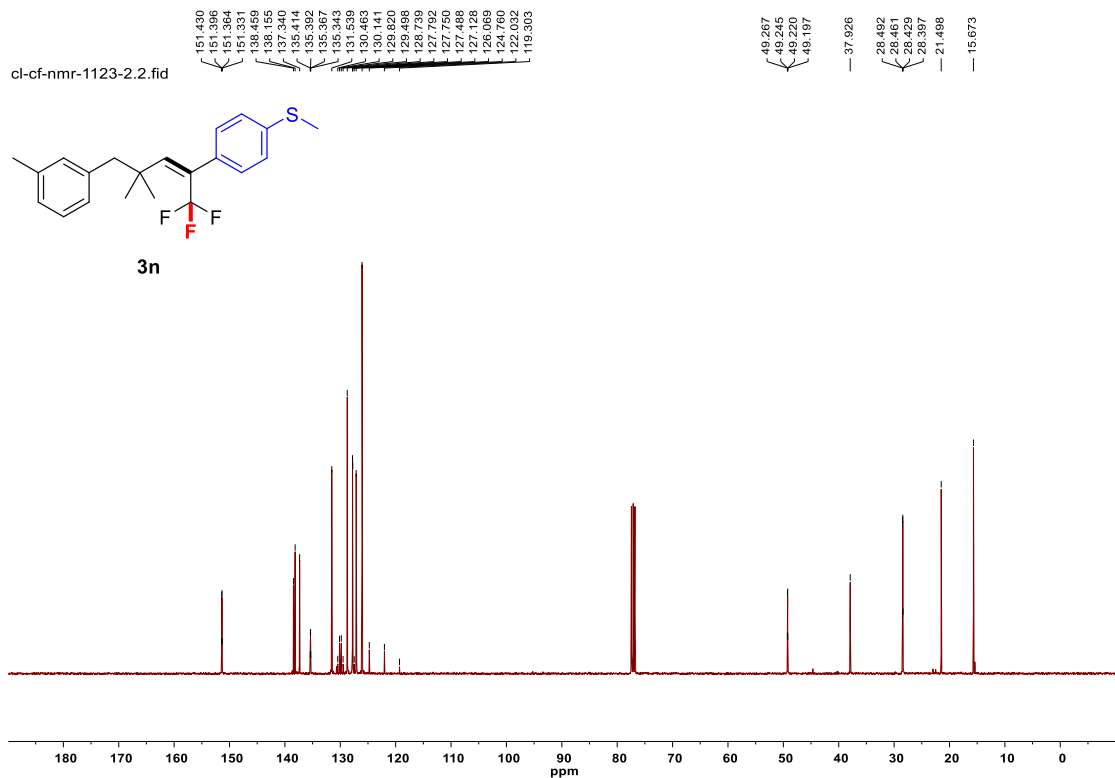
3n



^1H NMR spectrum of **3n** (400 MHz, CDCl_3)



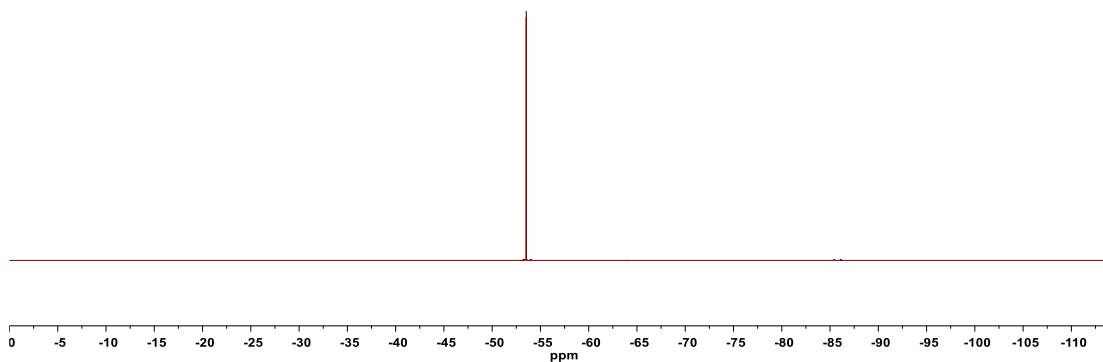
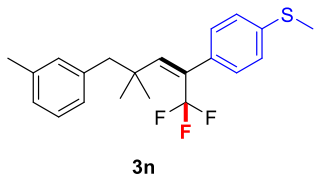
nOe Spectrum of **3n** (CDCl₃, 600 M)



¹³C NMR spectrum of **3n** (101 MHz, CDCl₃)

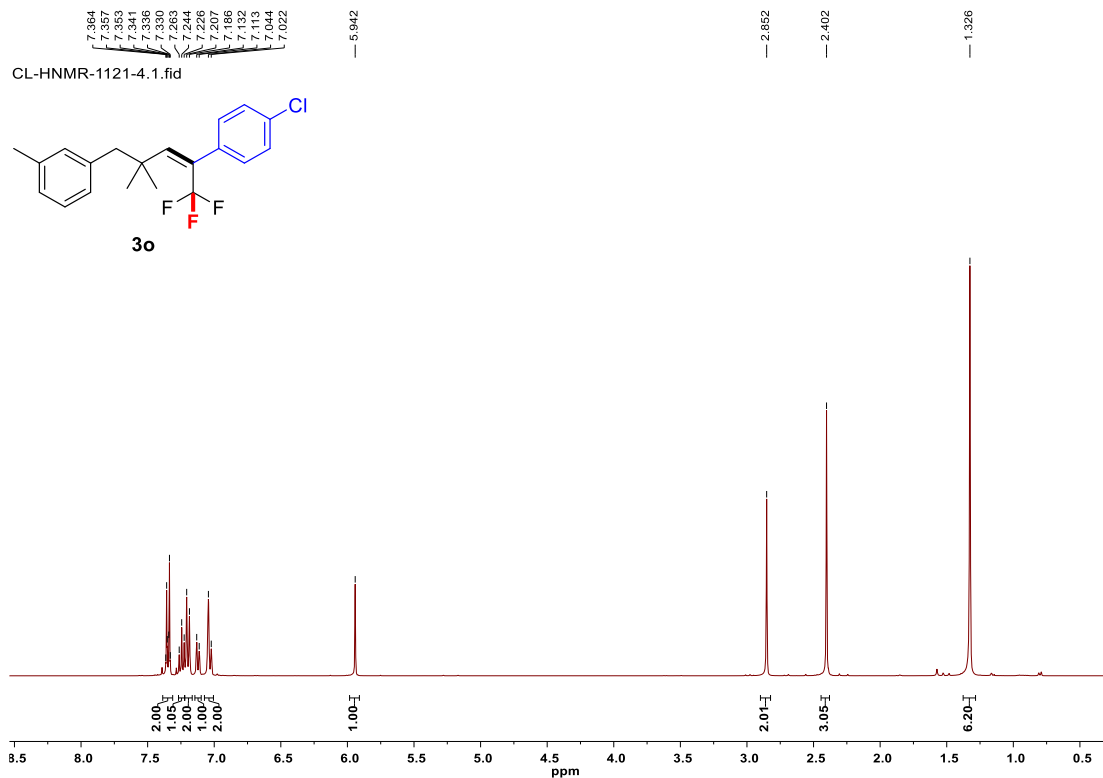
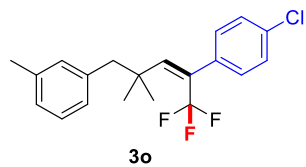
cl-cf-nmr-1123-2.1.fid

— 53.628

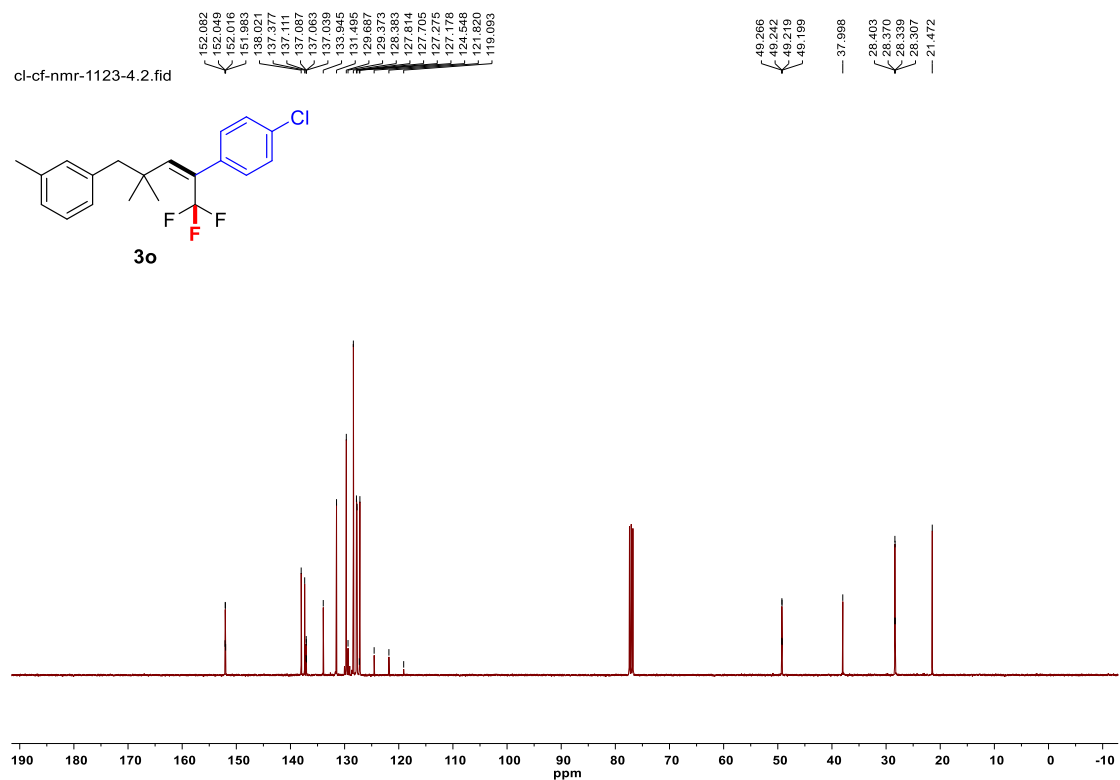


¹⁹F NMR spectrum of **3n** (376 MHz, CDCl₃)

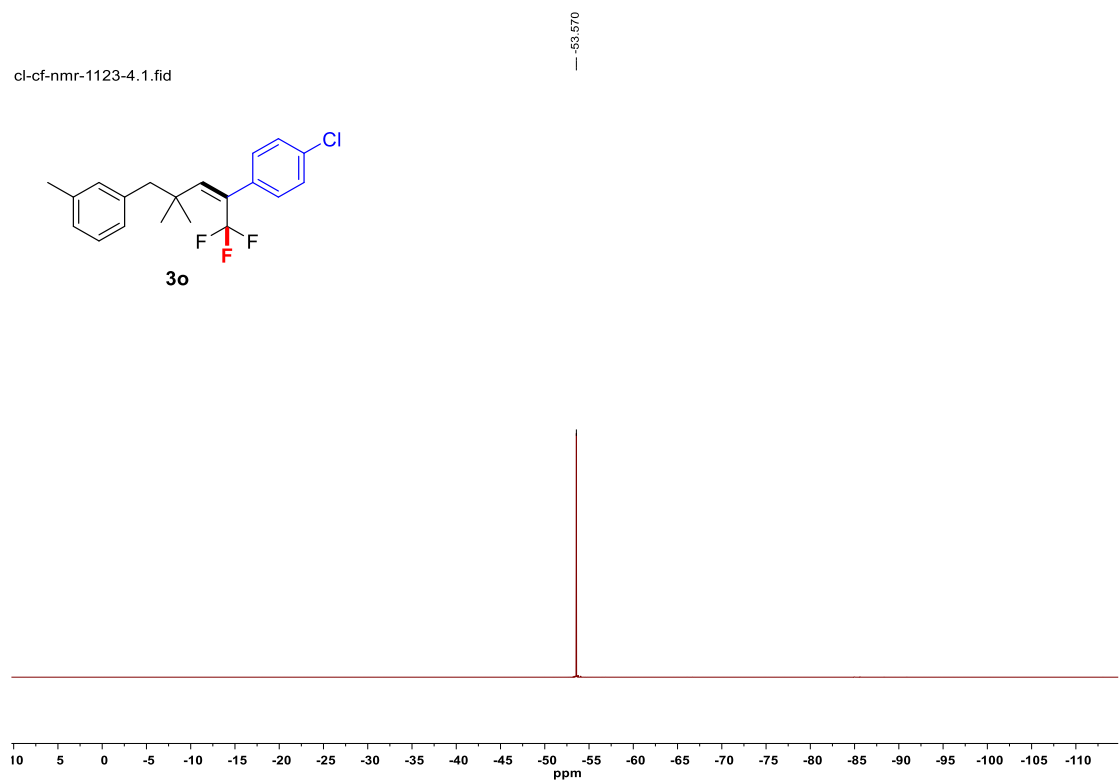
CL-HNMR-1121-4.1.fid



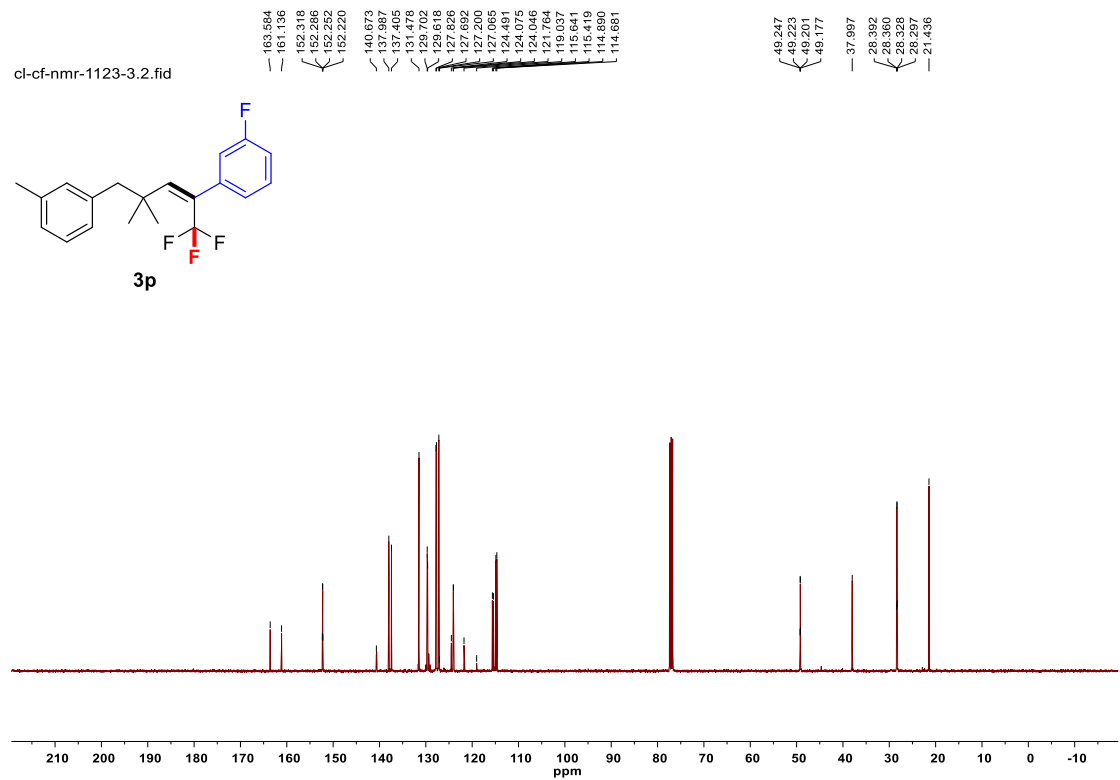
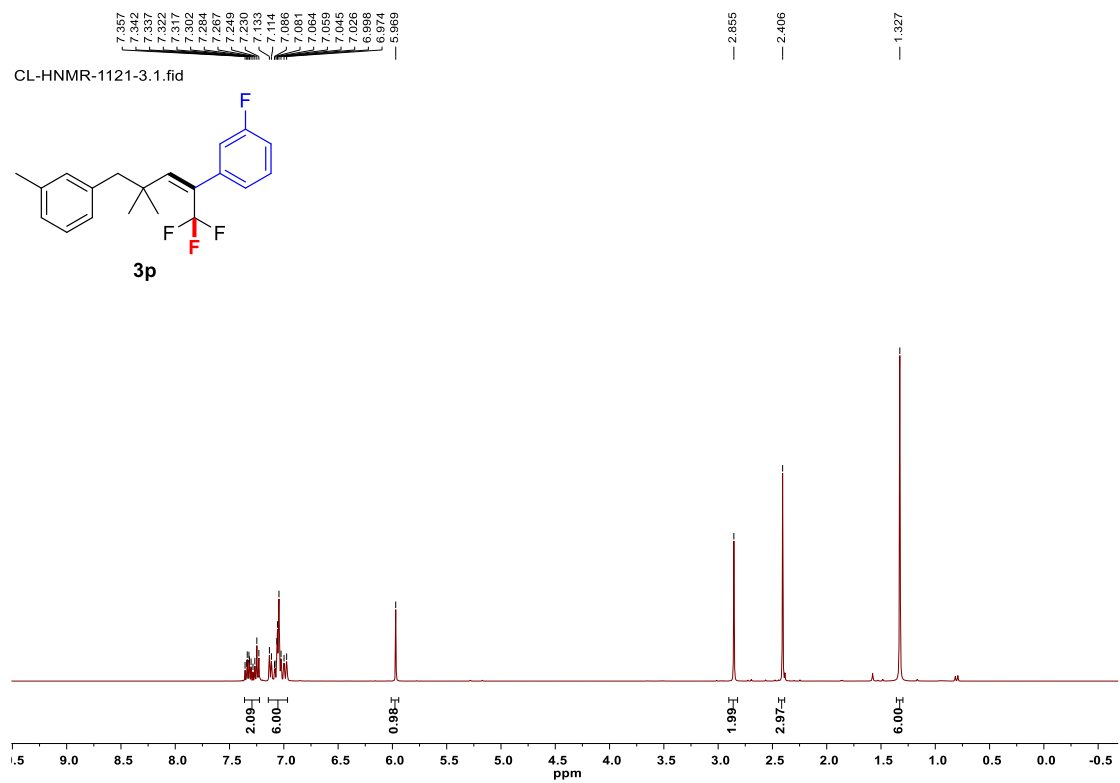
¹H NMR spectrum of **3o** (400 MHz, CDCl₃)



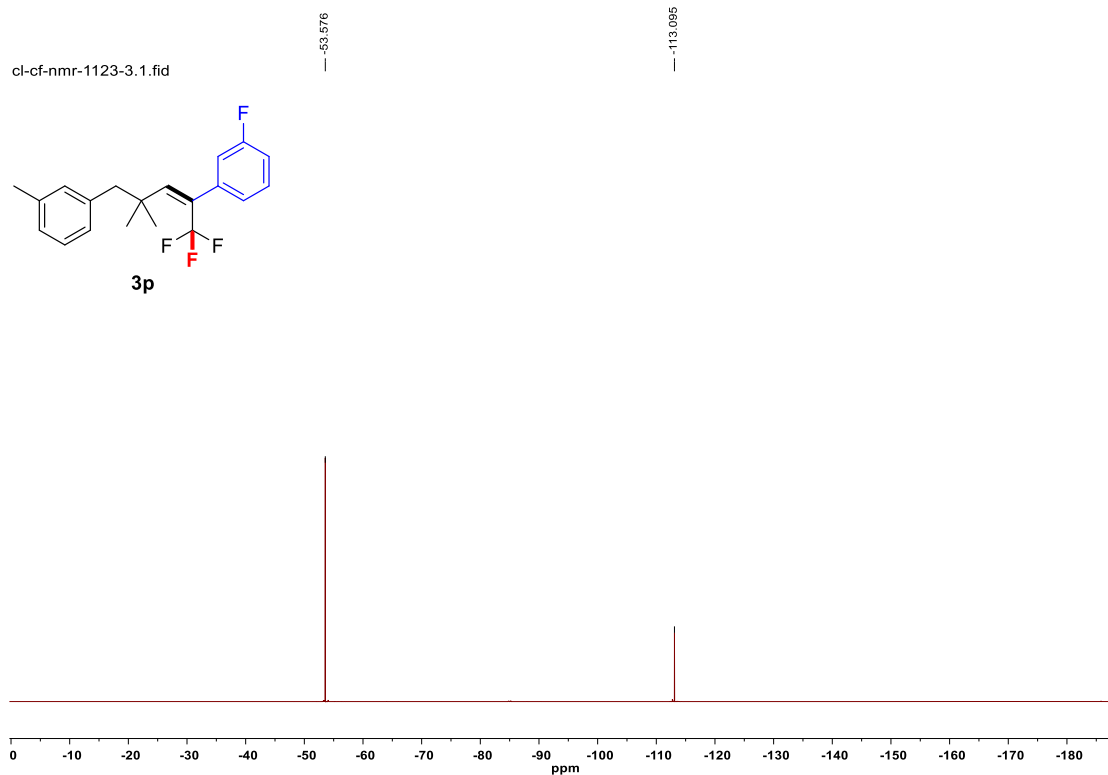
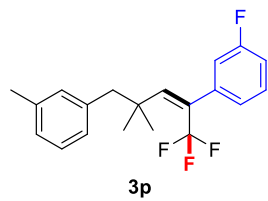
^{13}C NMR spectrum of **3o** (101 MHz, CDCl_3)



^{19}F NMR spectrum of **3o** (376 MHz, CDCl_3)

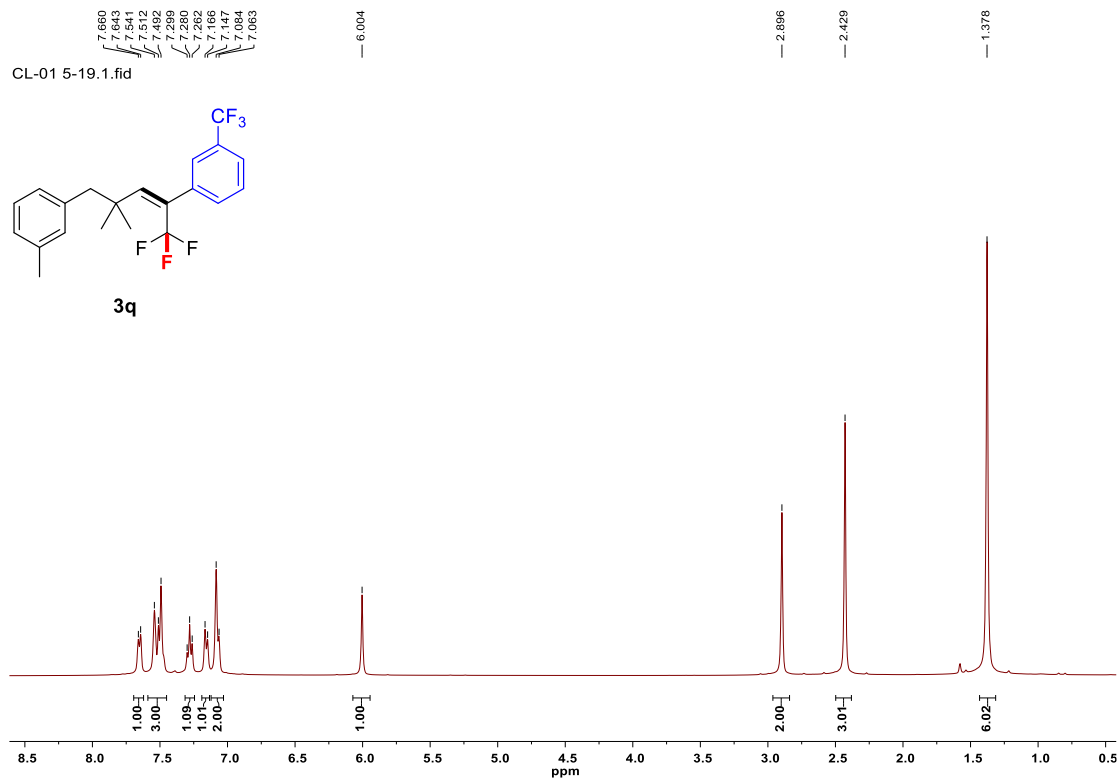
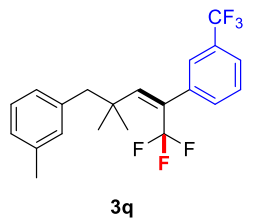


cl-cf-nmr-1123-3.1.fid

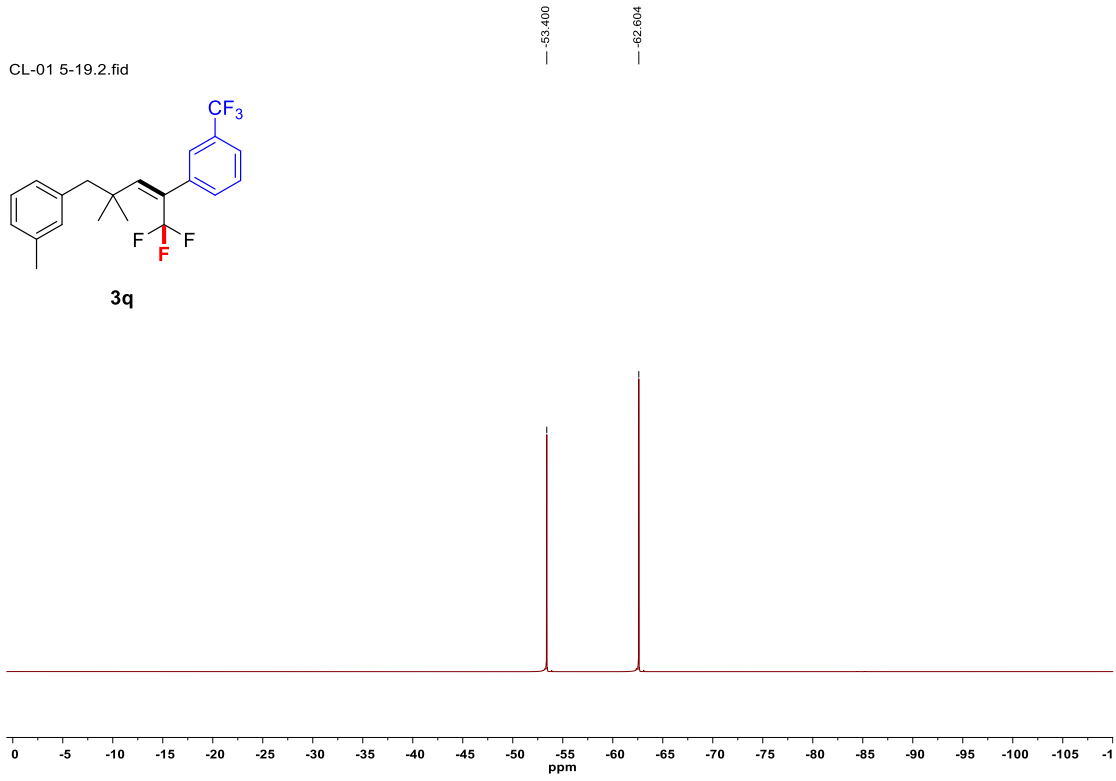
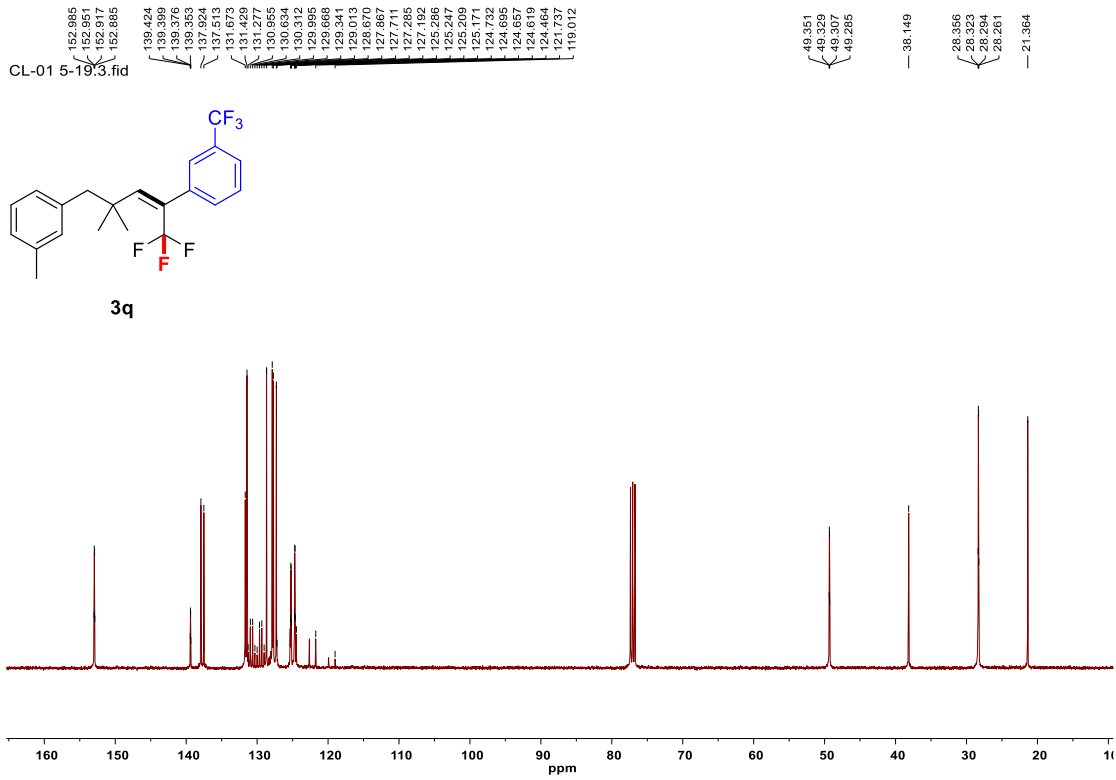


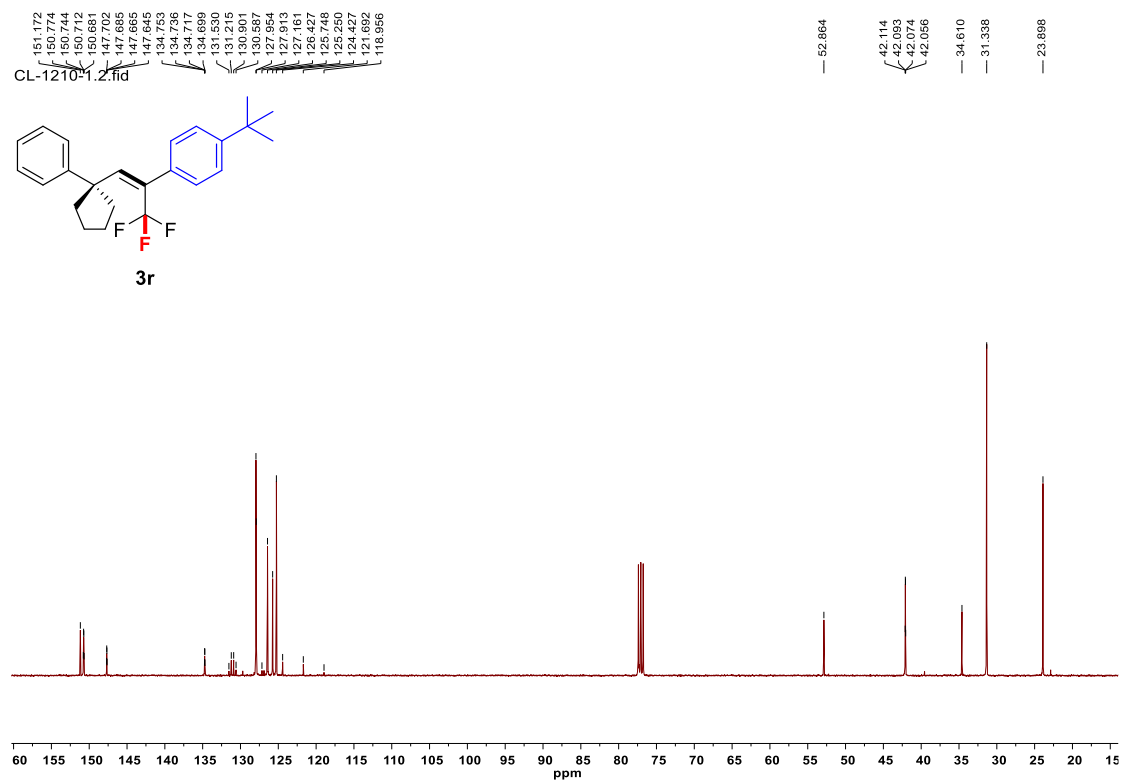
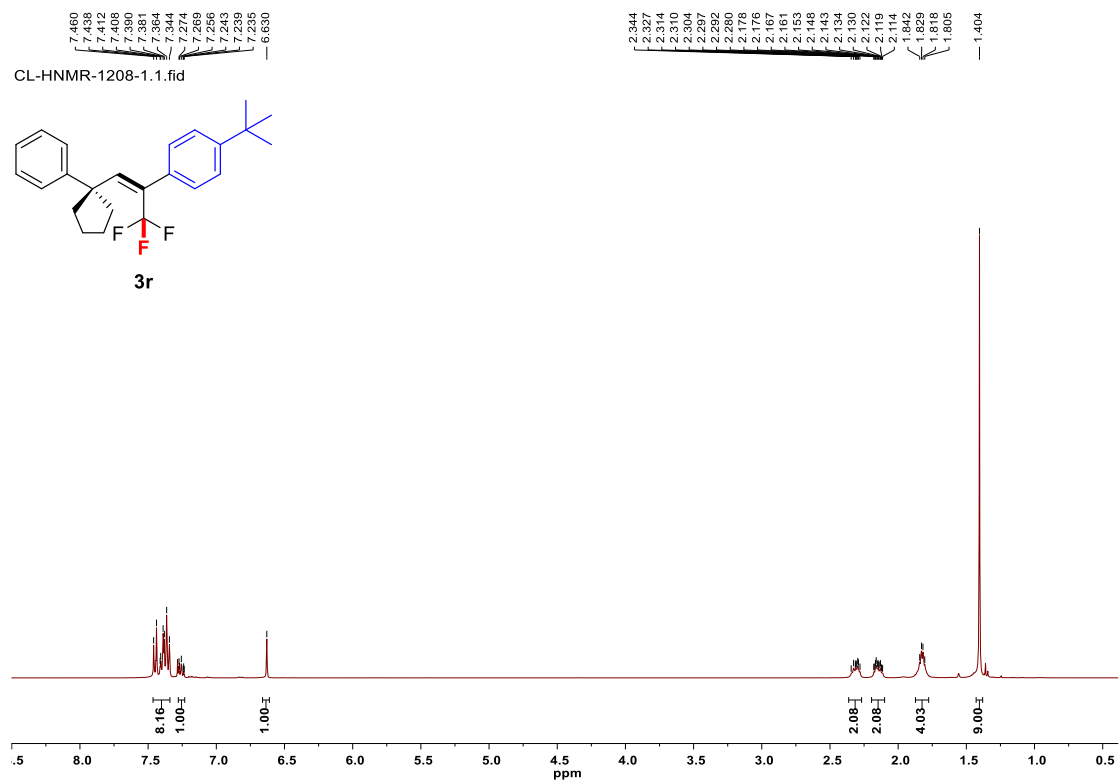
^{19}F NMR spectrum of **3p** (376 MHz, CDCl_3)

CL-01 5-19.1.fid



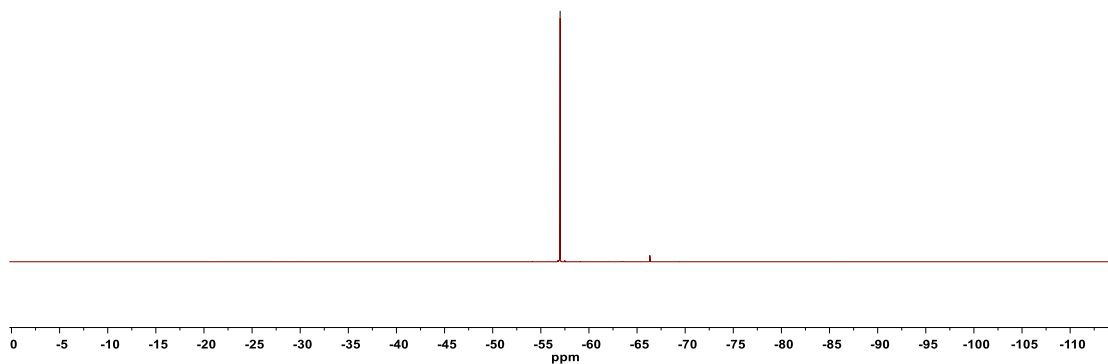
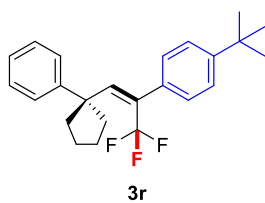
^1H NMR spectrum of **3q** (400 MHz, CDCl_3)





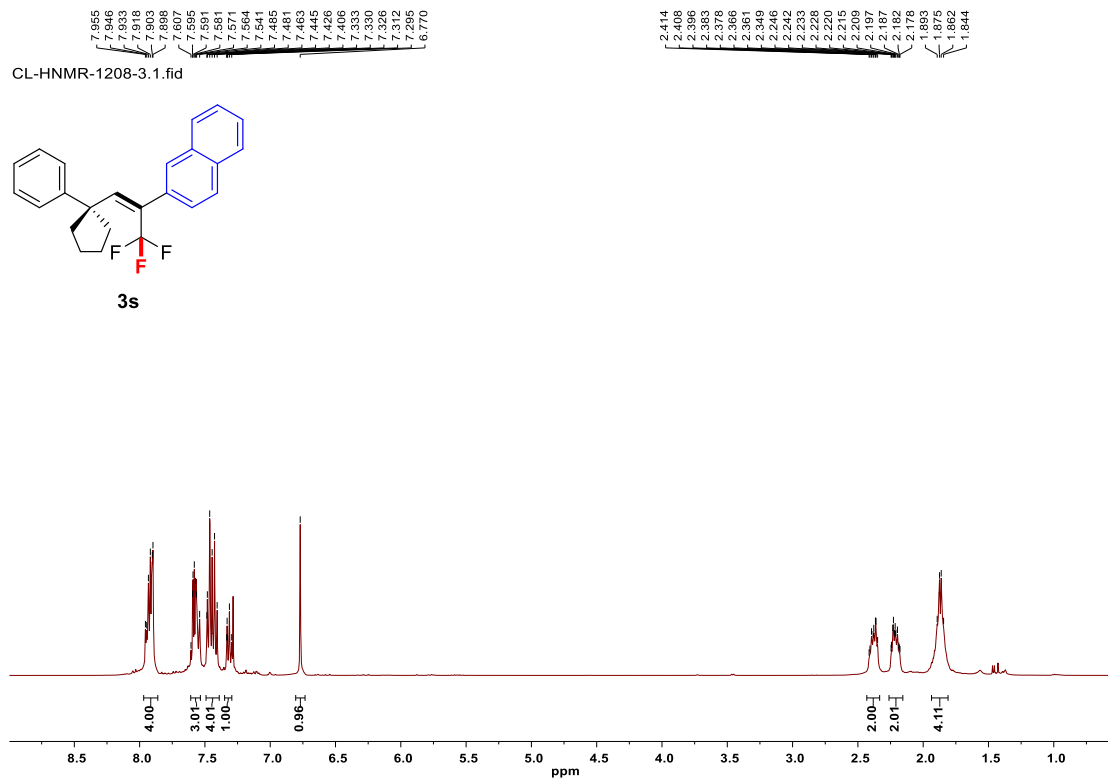
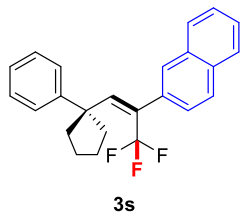
CL-1210-1.1.fid

— 57.006

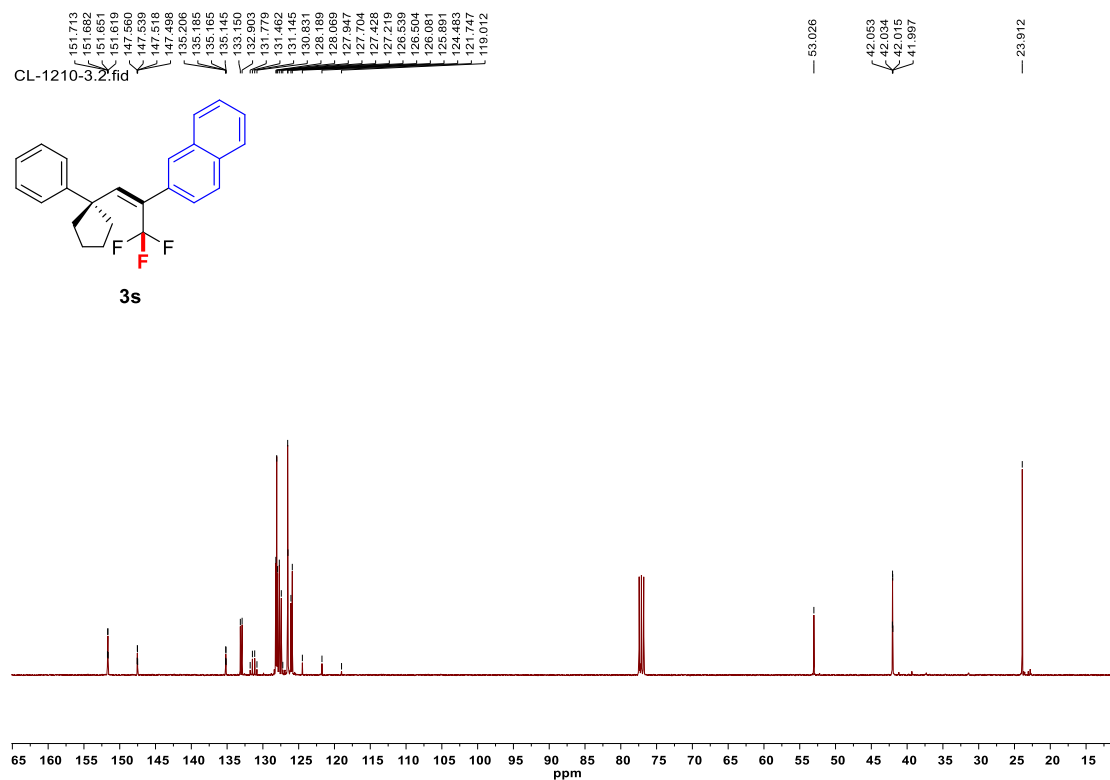


^{19}F NMR spectrum of **3r** (376 MHz, CDCl_3)

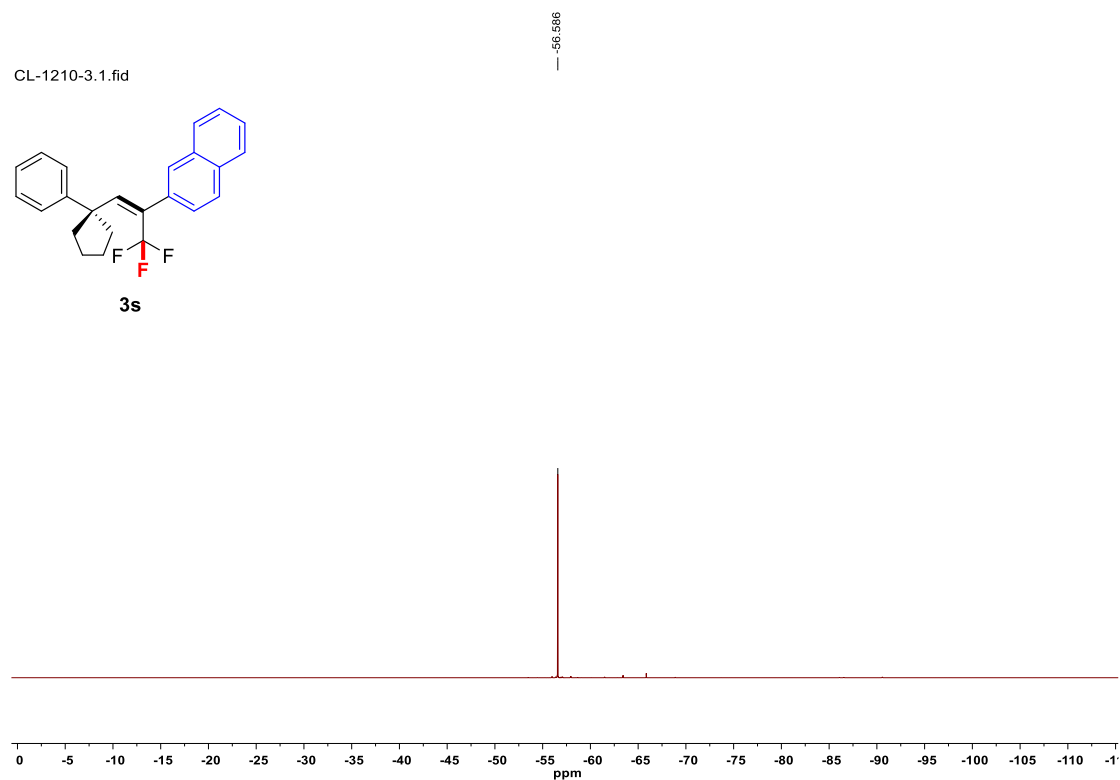
CL-HNMR-1208-3.1.fid



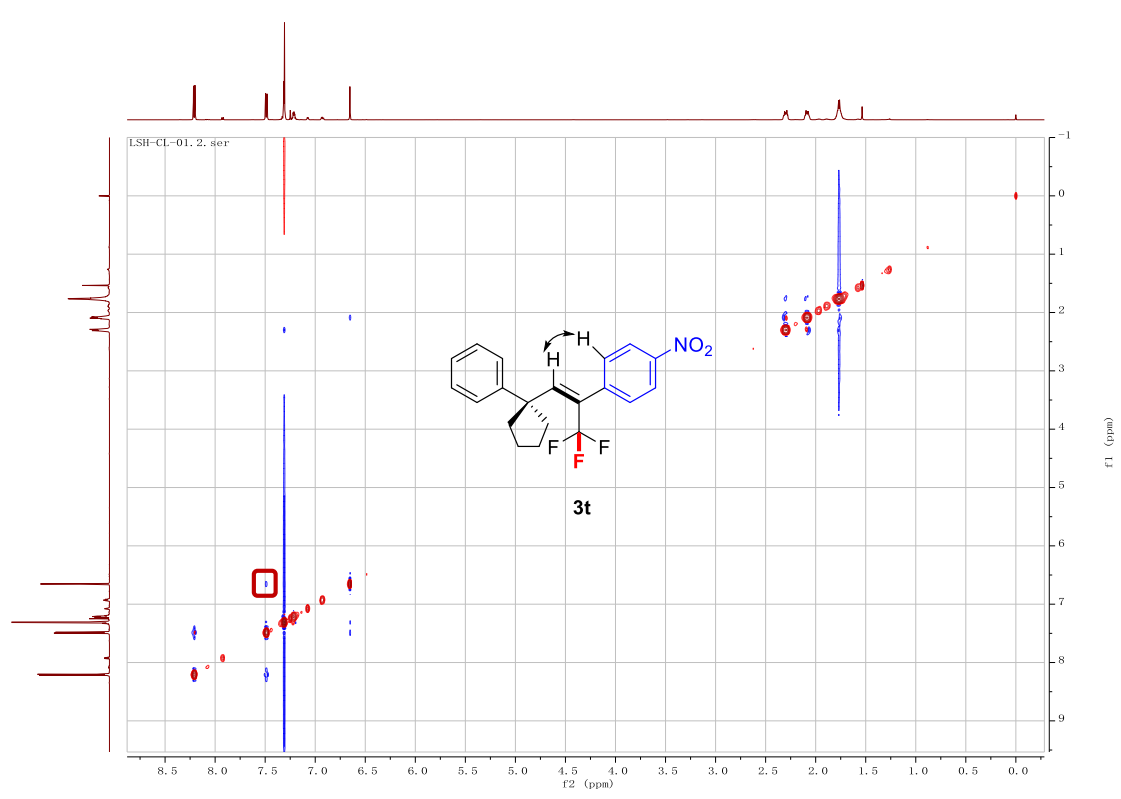
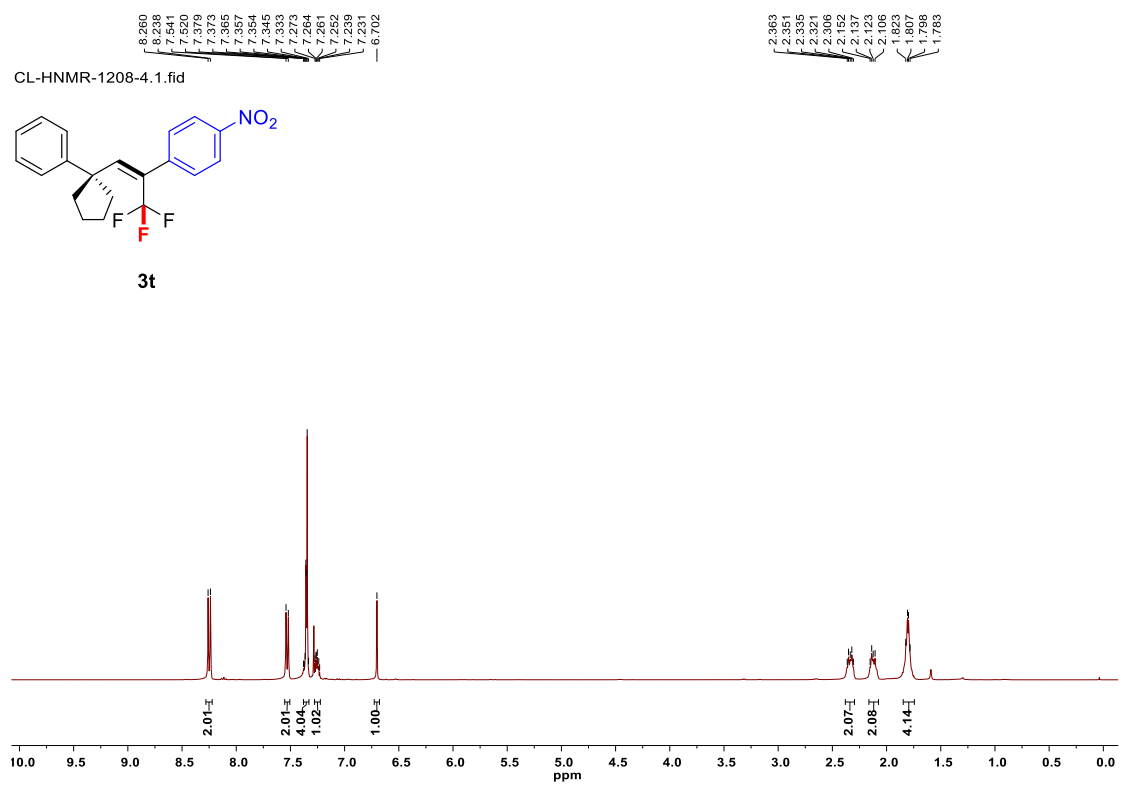
^1H NMR spectrum of **3s** (400 MHz, CDCl_3)

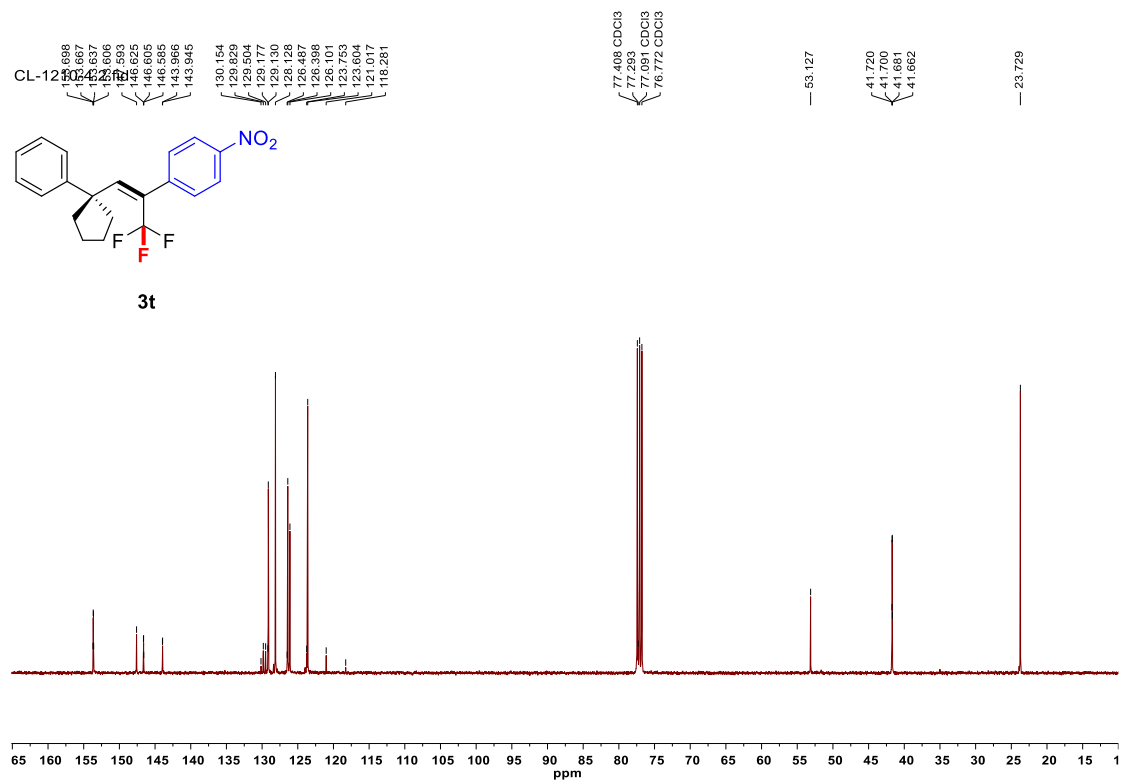


^{13}C NMR spectrum of **3s** (101 MHz, CDCl_3)

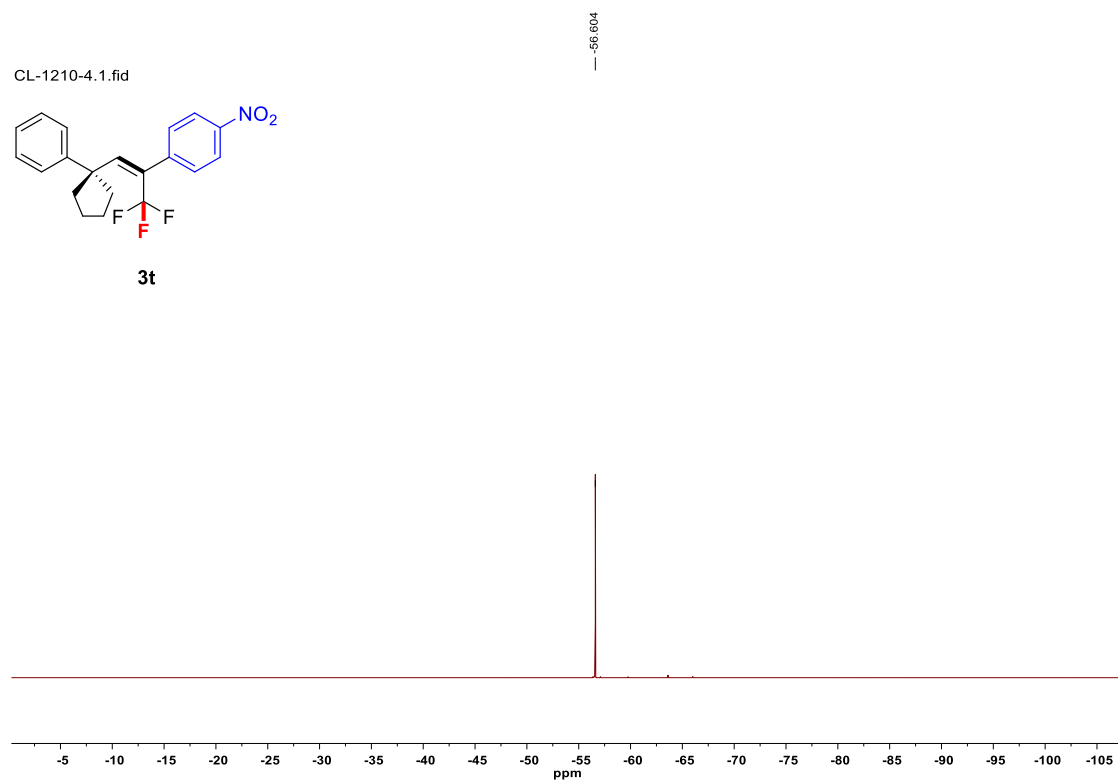


^{19}F NMR spectrum of **3s** (376 MHz, CDCl_3)

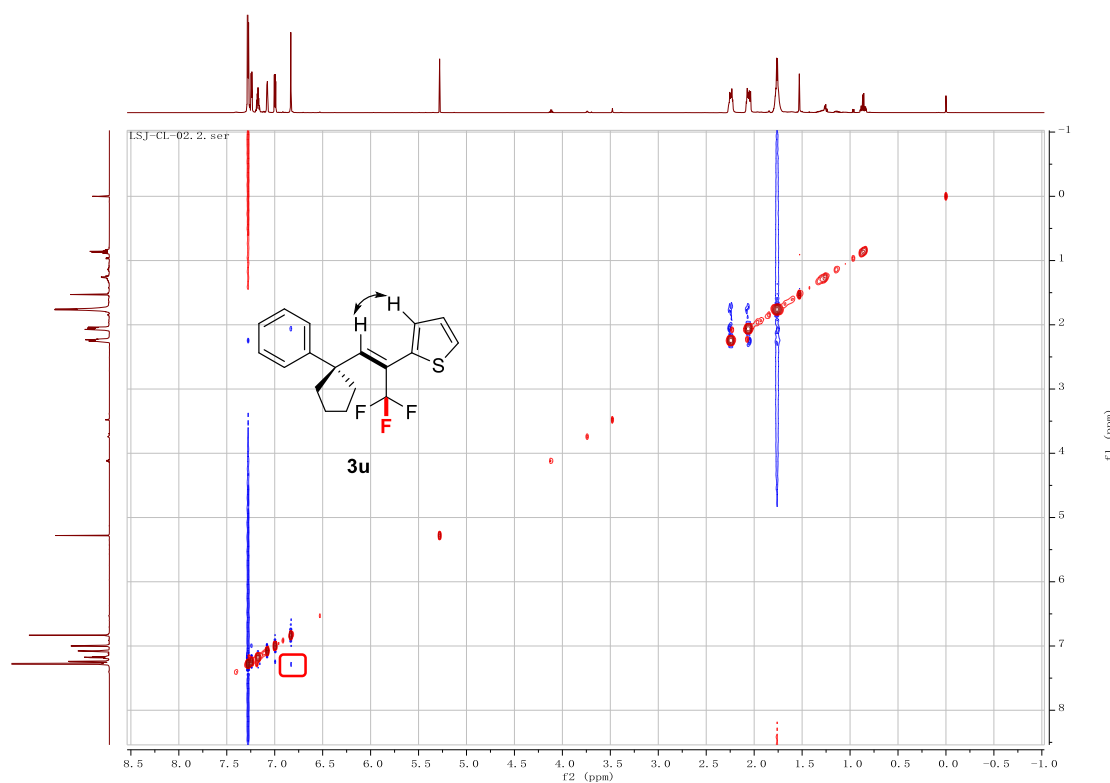
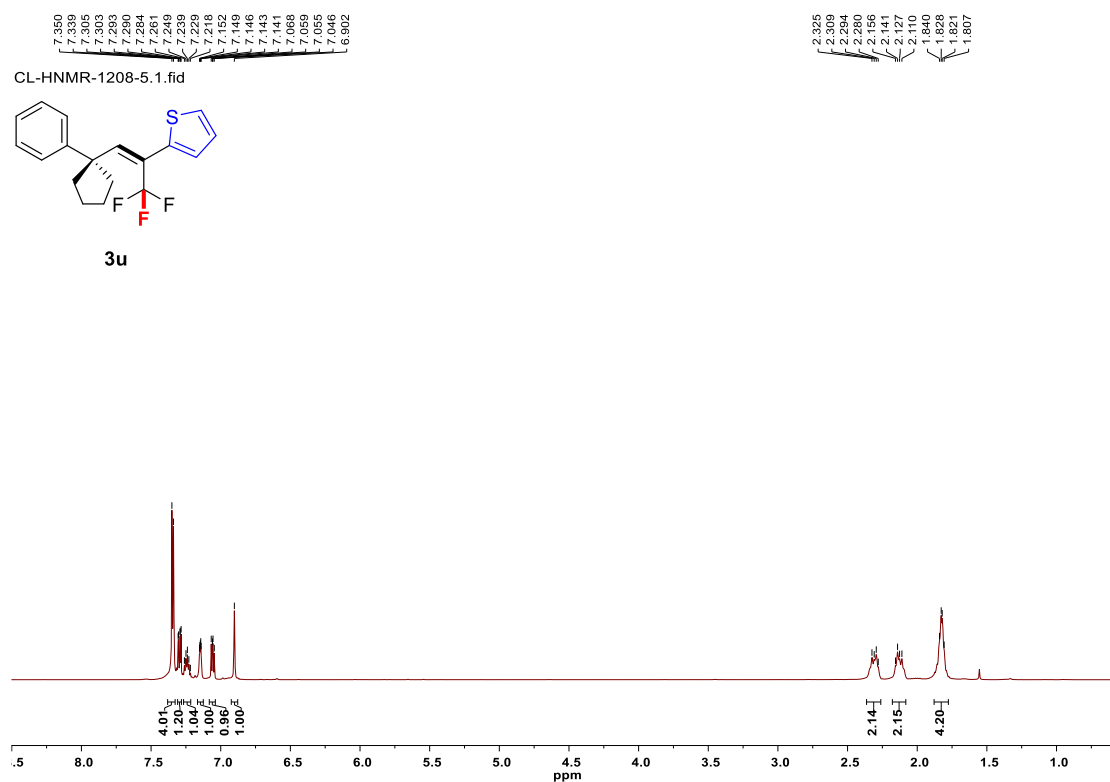


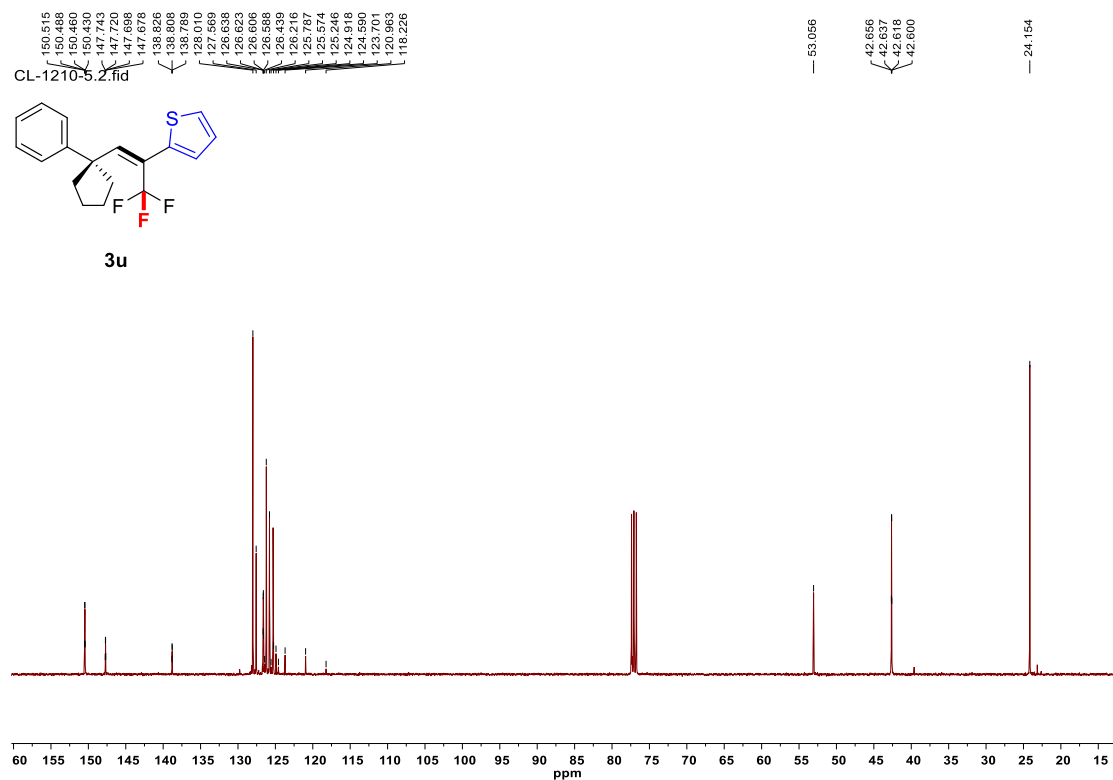


¹³C NMR spectrum of **3t** (101 MHz, CDCl₃)

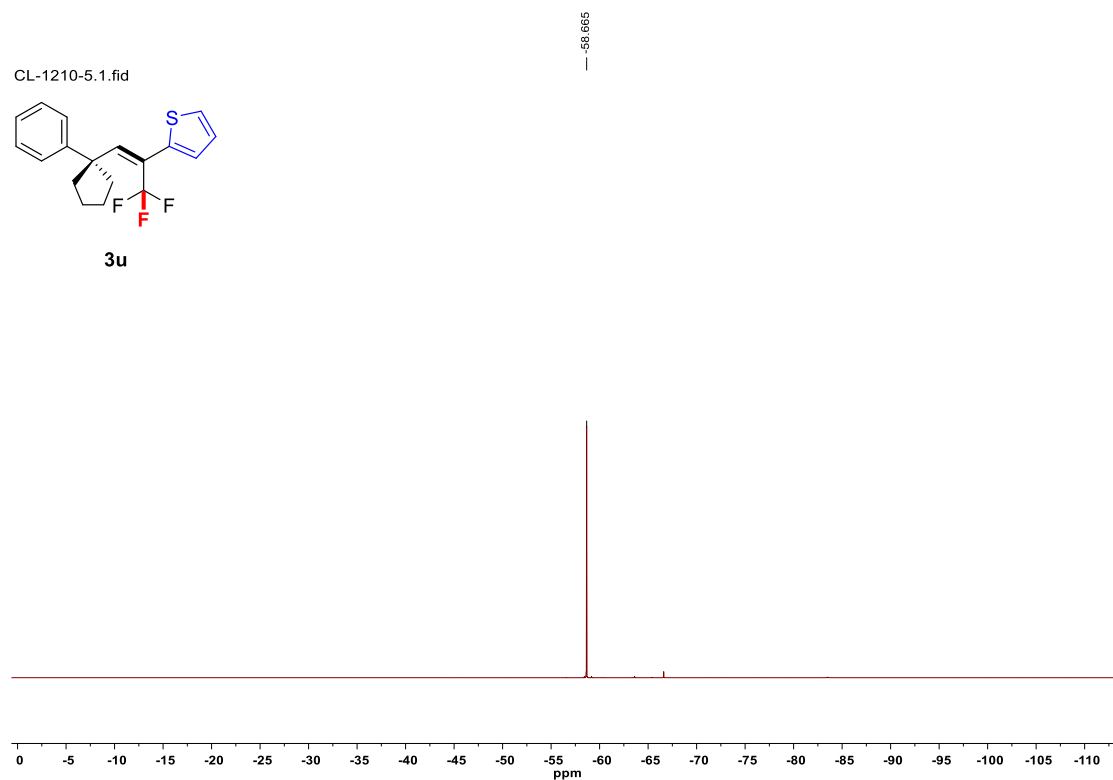


¹⁹F NMR spectrum of **3t** (376 MHz, CDCl₃)

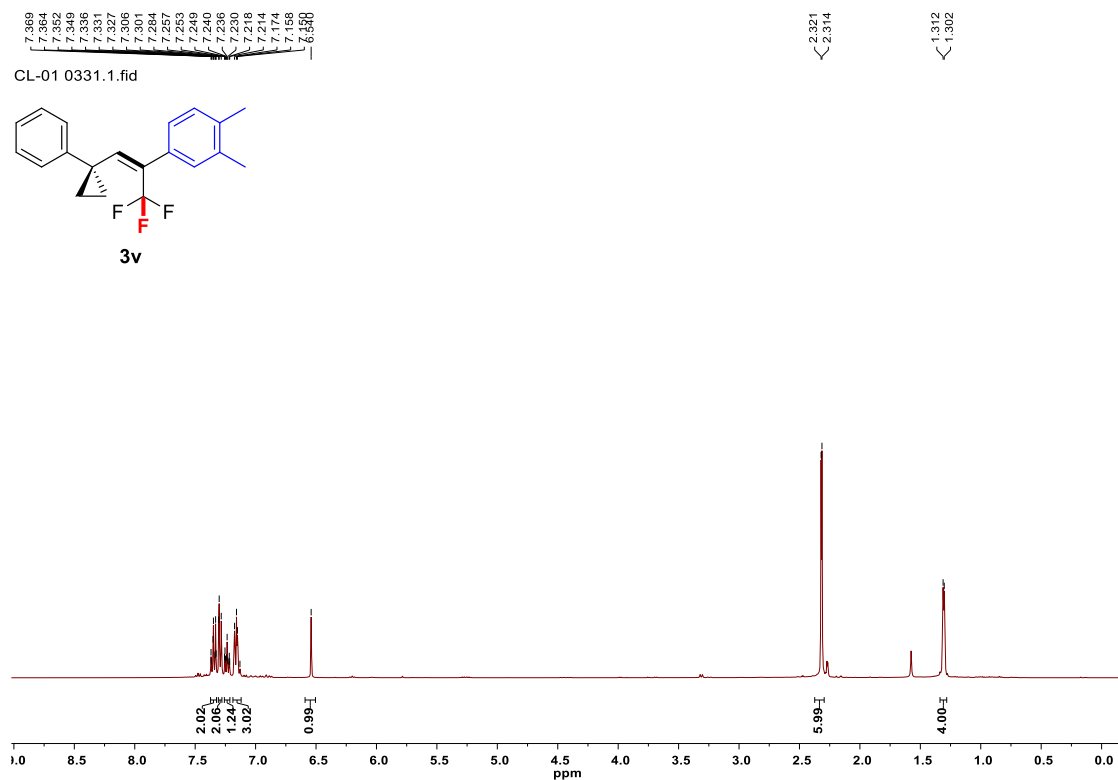




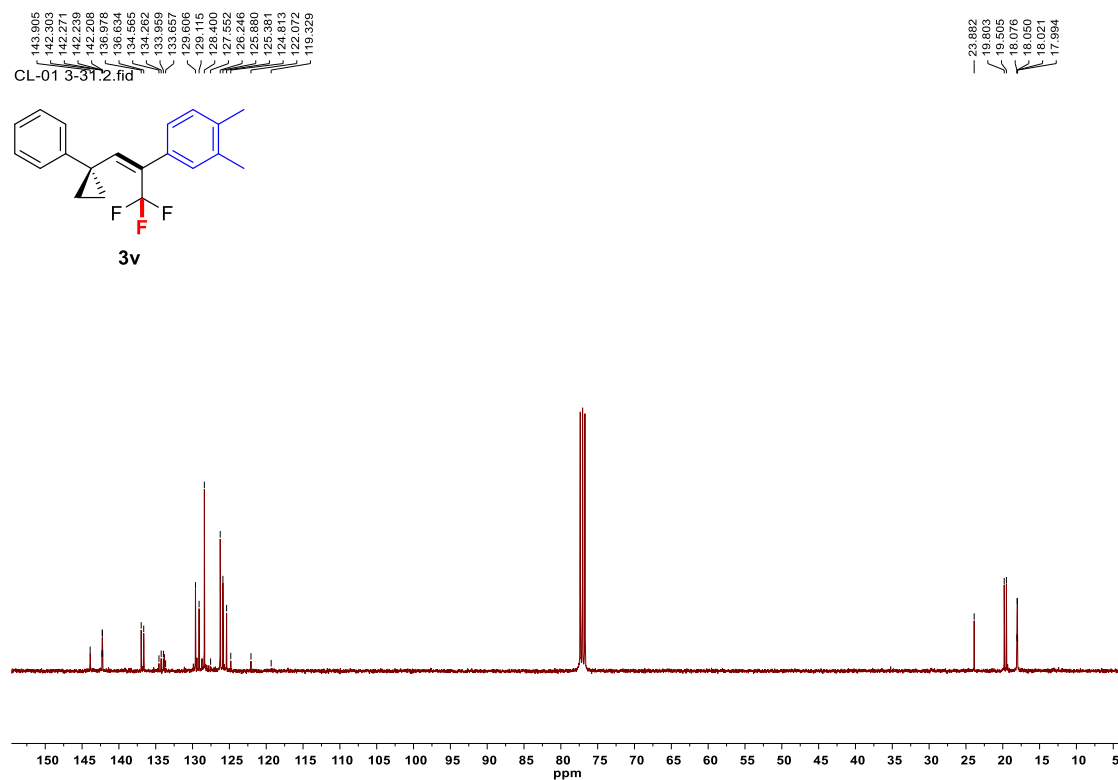
^{13}C NMR spectrum of **3u** (101 MHz, CDCl_3)



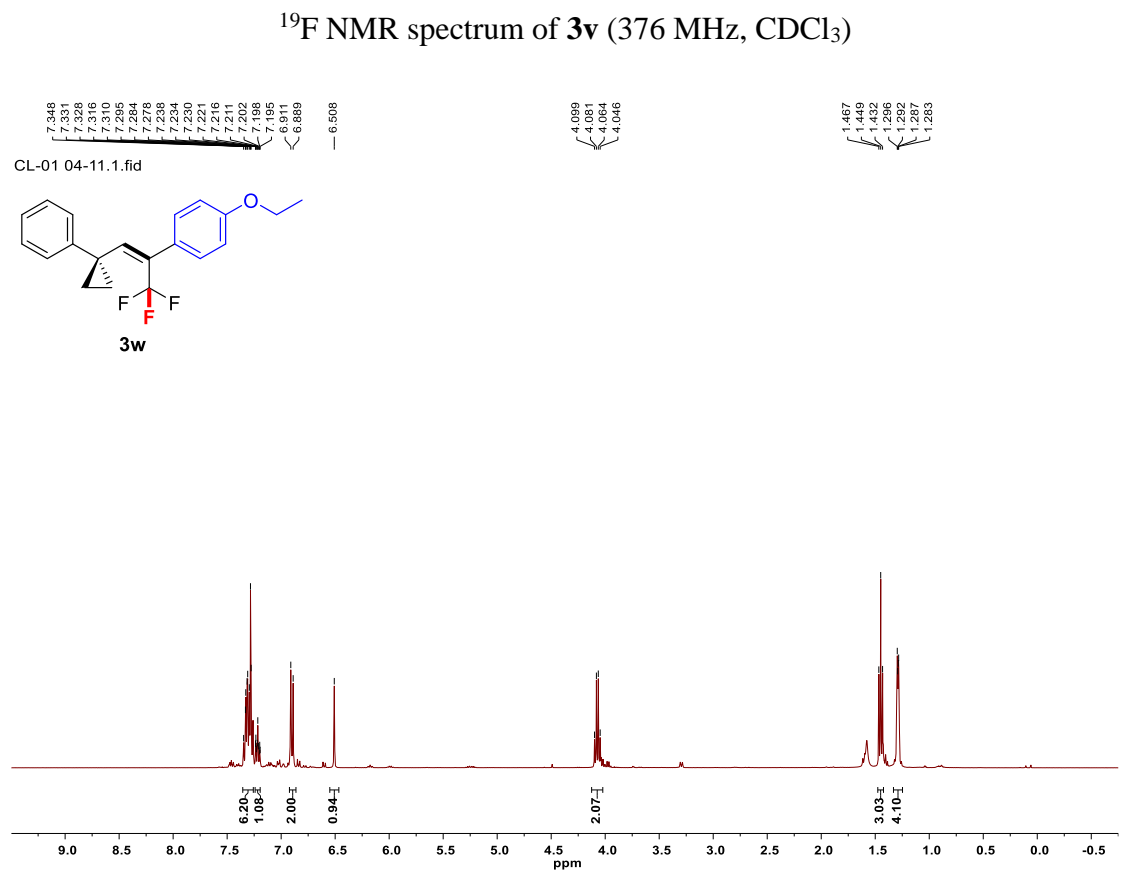
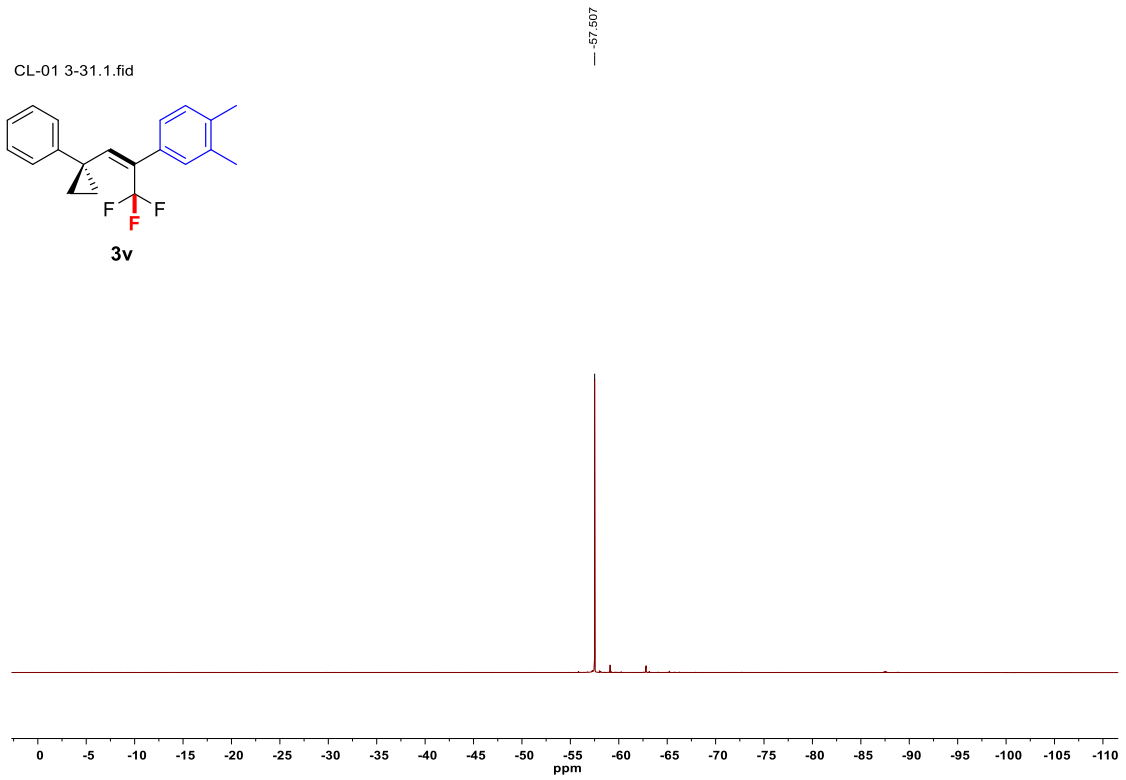
^{19}F NMR spectrum of **3u** (376 MHz, CDCl_3)

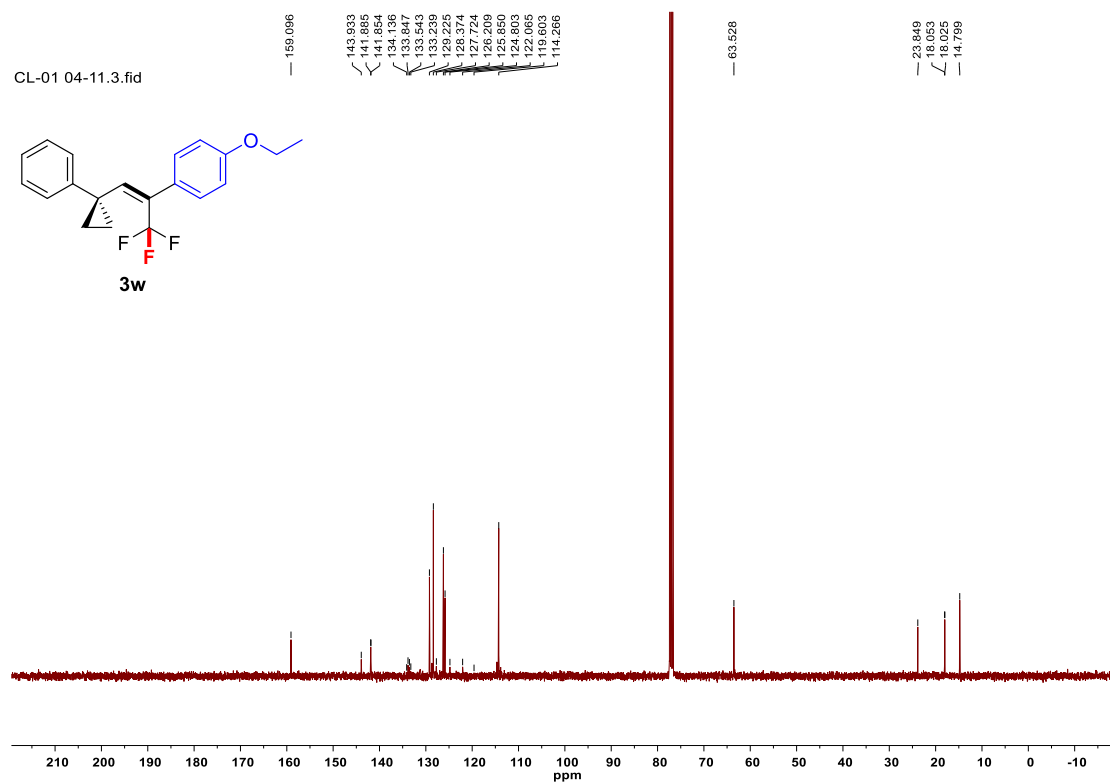


^1H NMR spectrum of **3v** (400 MHz, CDCl_3)

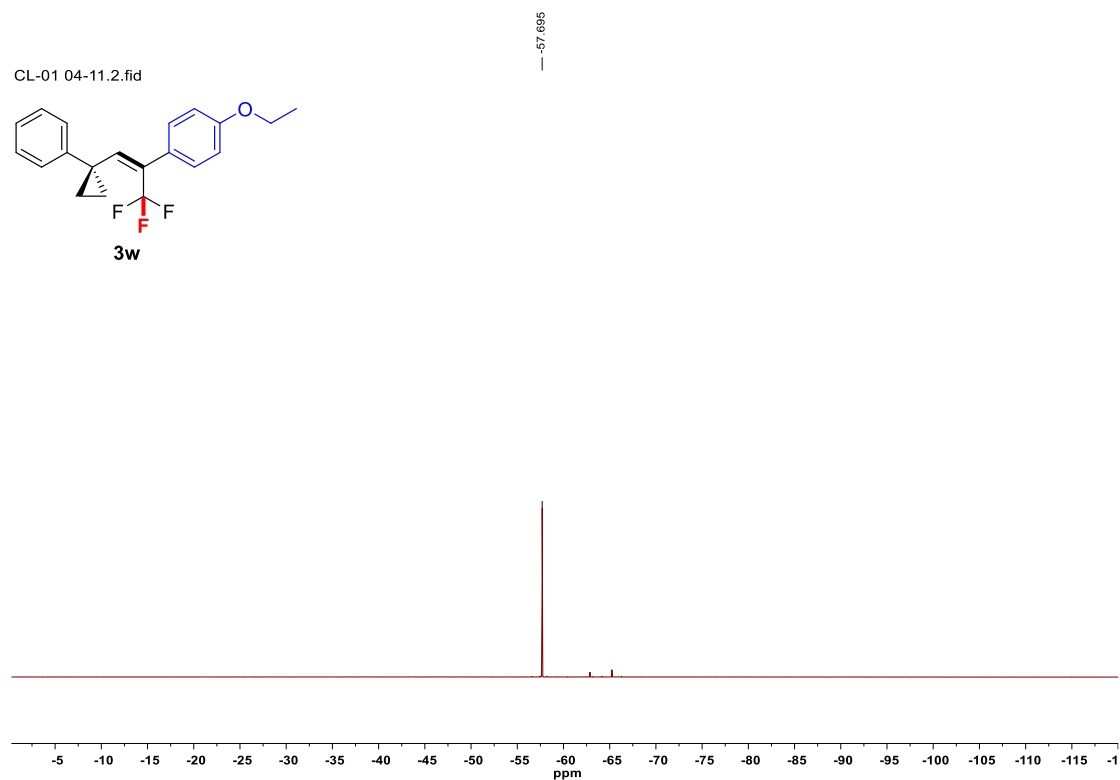


^{13}C NMR spectrum of **3v** (101 MHz, CDCl_3)

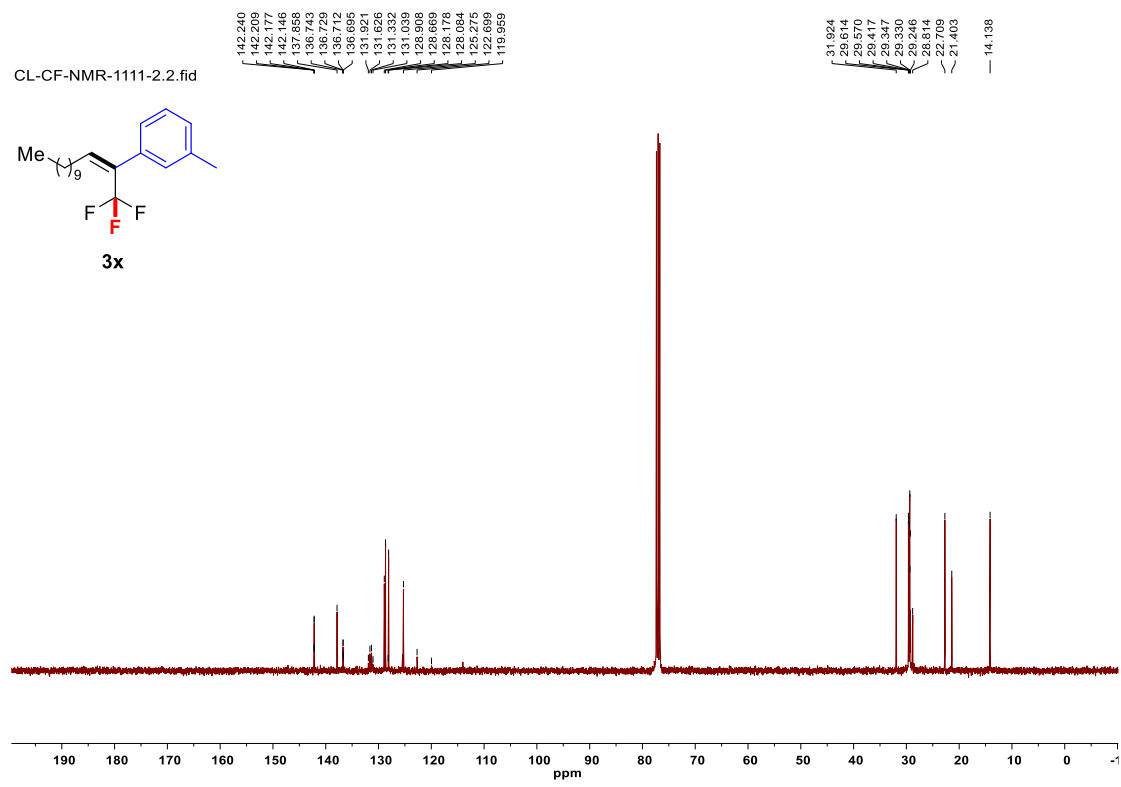
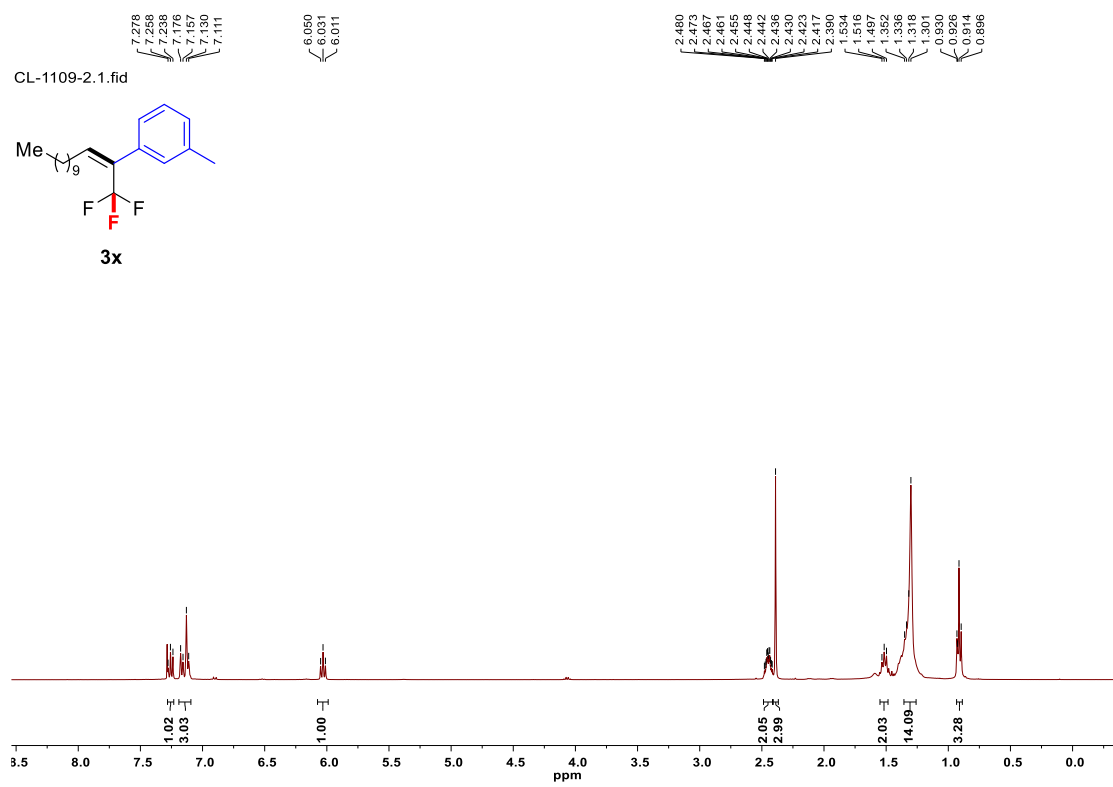




^{13}C NMR spectrum of **3w** (101 MHz, CDCl_3)

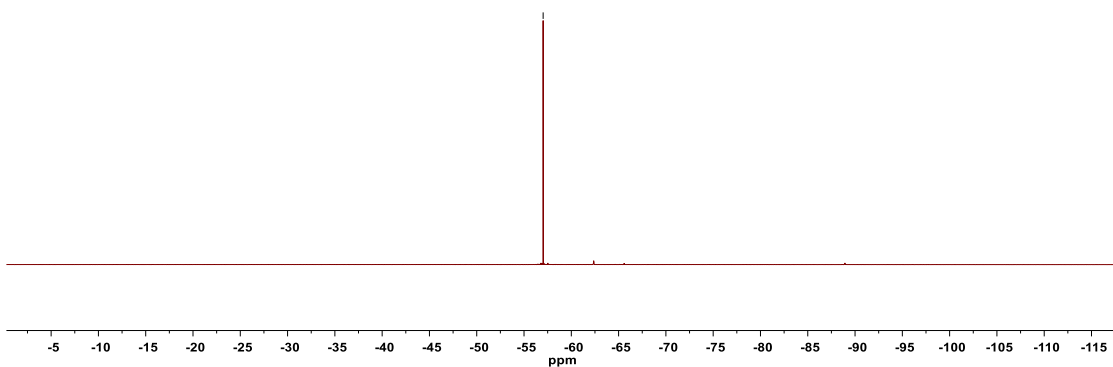
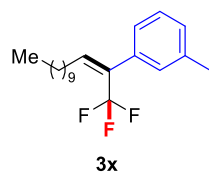


^{19}F NMR spectrum of **3w** (376 MHz, CDCl_3)



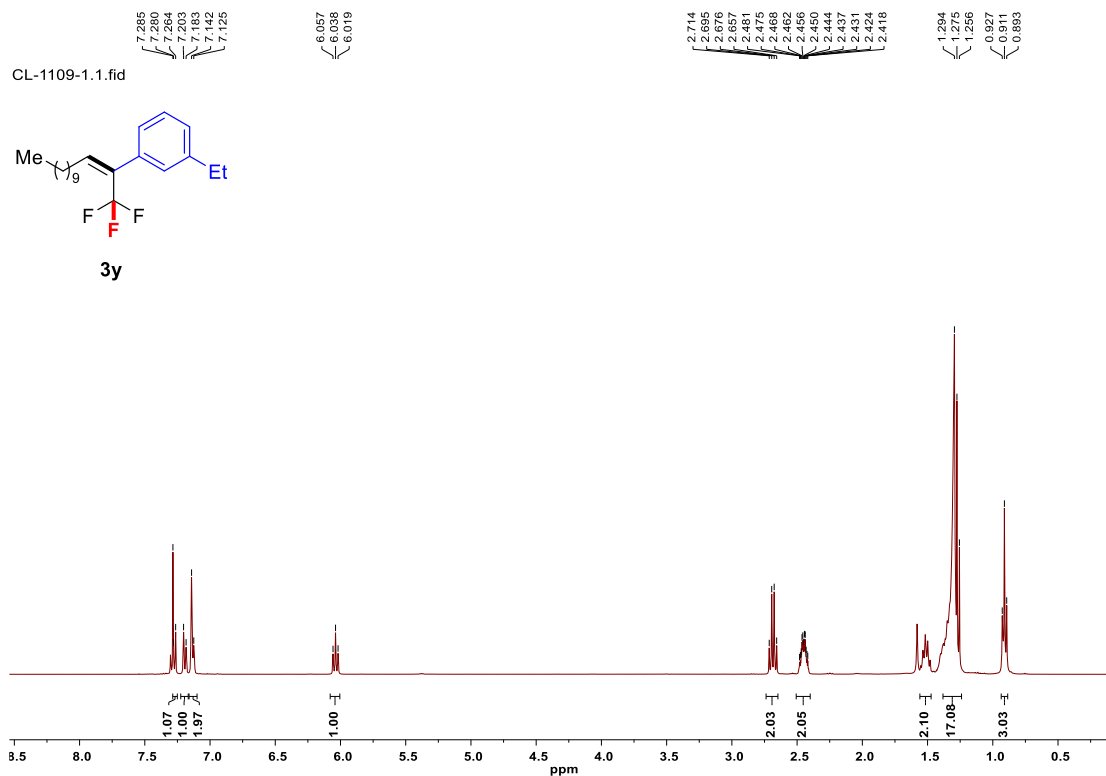
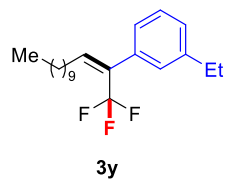
CL-CF-NMR-1111-2.1.fid

—57.022

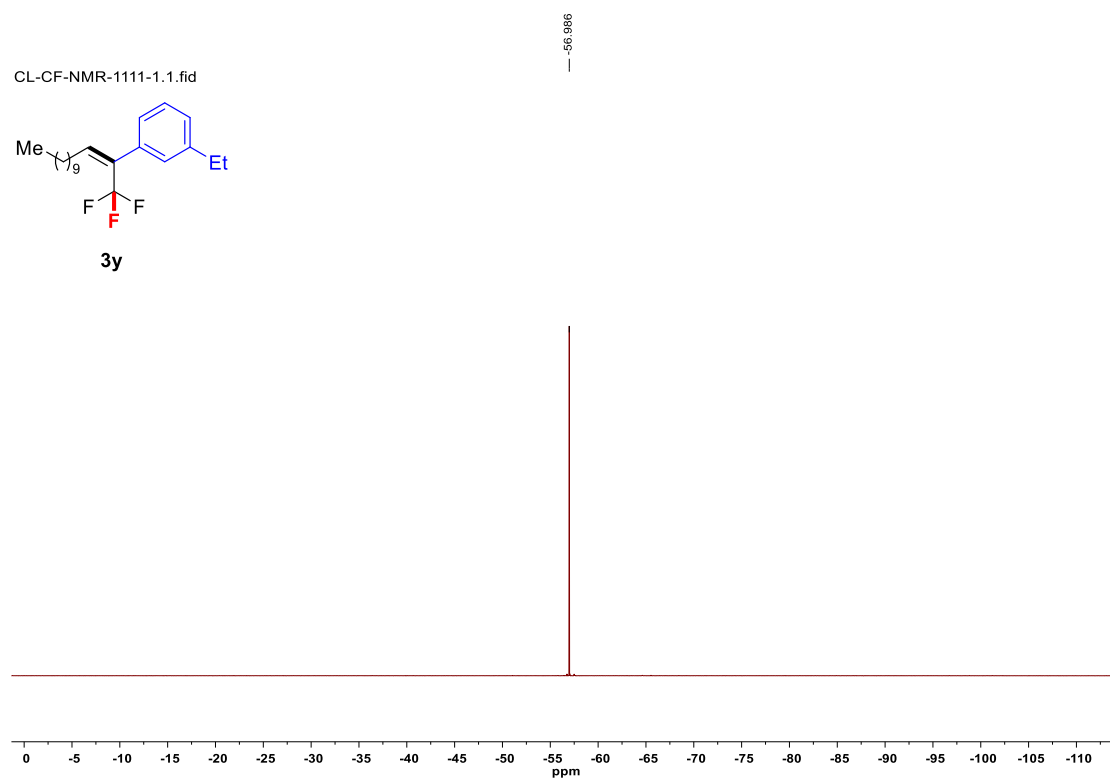
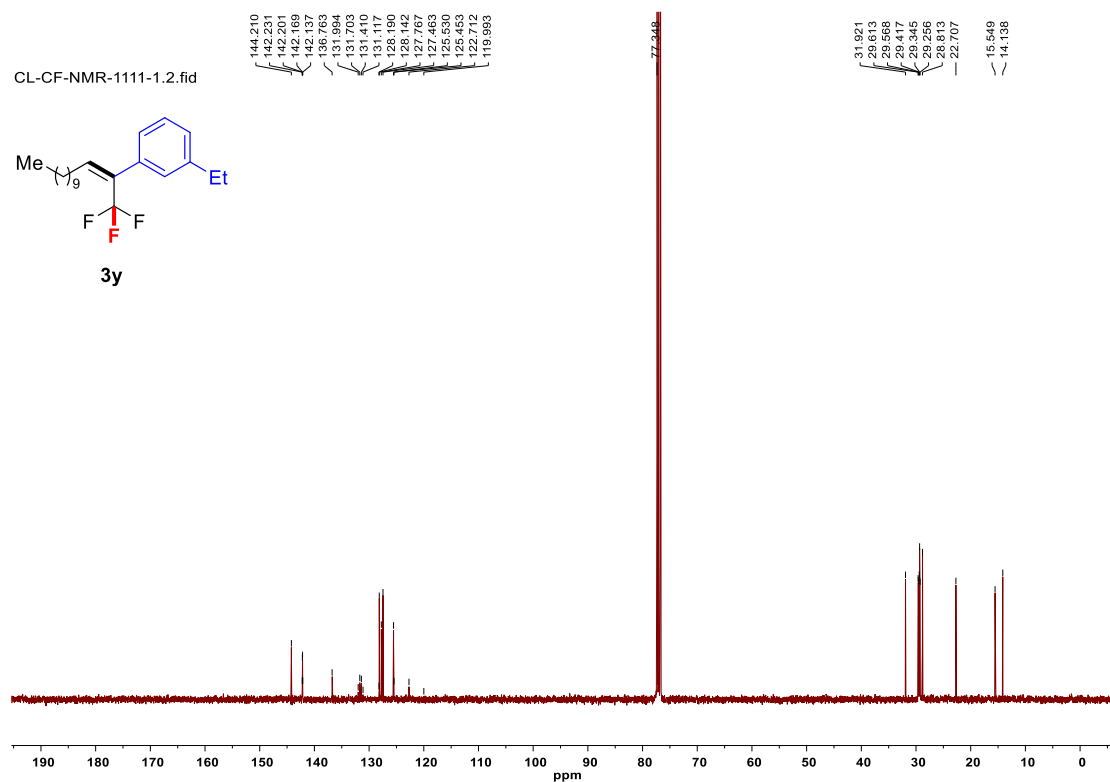


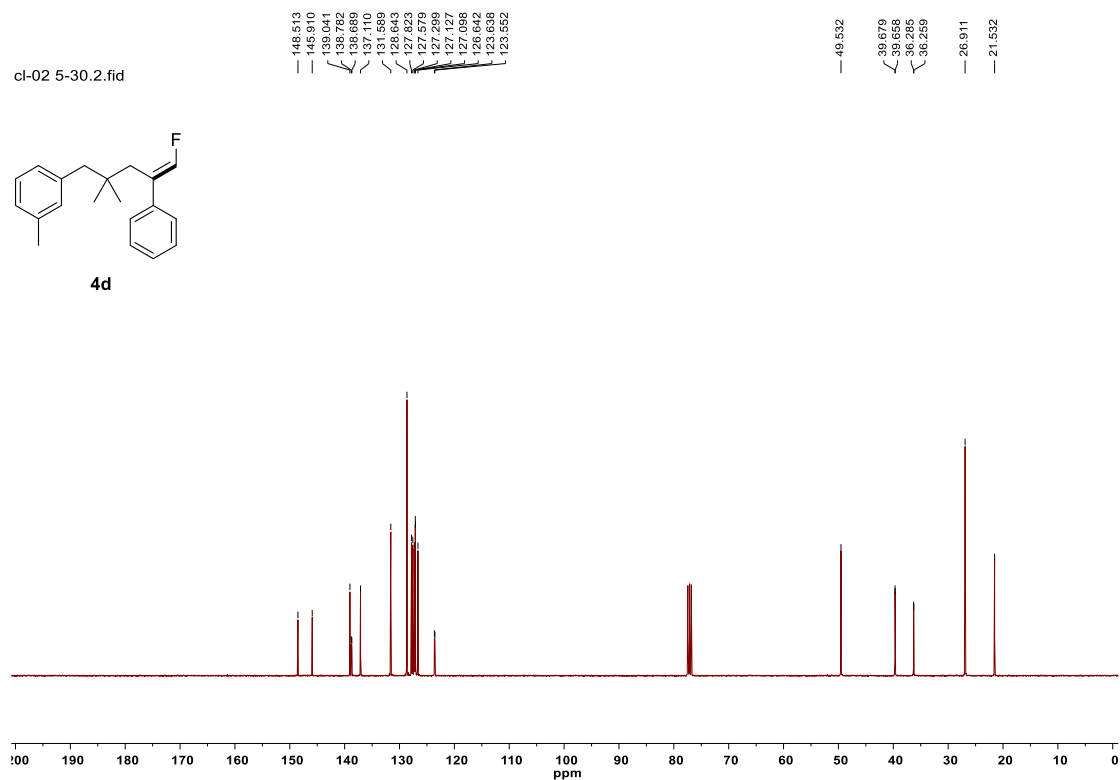
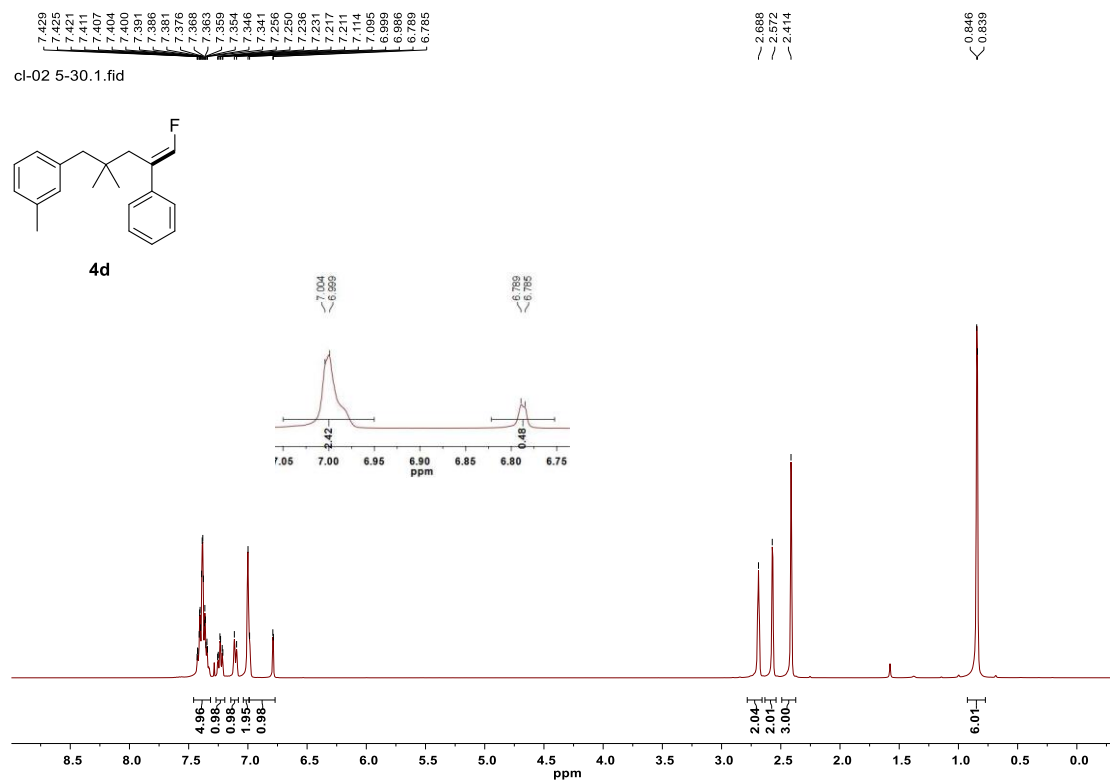
^{19}F NMR spectrum of **3x** (376 MHz, CDCl_3)

CL-1109-1.1.fid

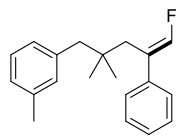


^1H NMR spectrum of **3y** (400 MHz, CDCl_3)



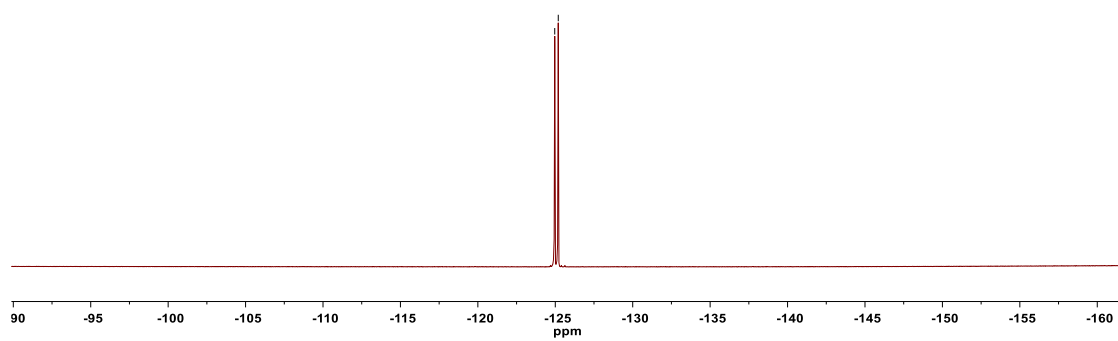


cl-02 5-30.3.fid



4d

-124.965
-125.193



^{19}F NMR spectrum of **4d** (376 MHz, CDCl_3)