Supporting Information

Prenyl Praxis: A Method for Direct Photocatalytic Defluoroprenylation

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Table of Contents:-

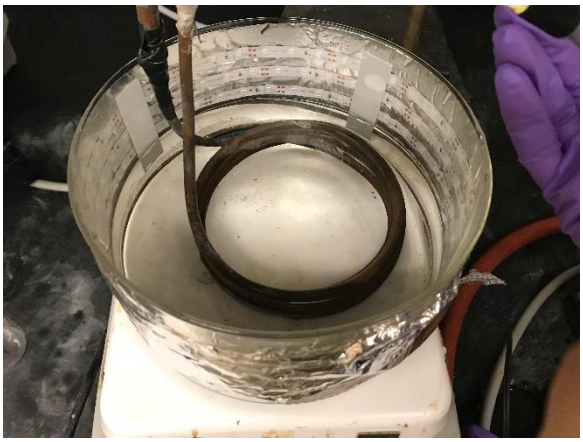
General Experimental	S-2
Photocatalytic Reaction Set up	S-3
Synthesis of substrates	S-3
Optimization conditions	S-13
Photocatalytic reactions on perfluoroarenes	S-22
Working mechanism	S-41
Evidence for ortho-geranylation	S-43
UV-Vis experiments and NMR Titrations	S-46
References	S-60
NMR and MS Spectra	S-61

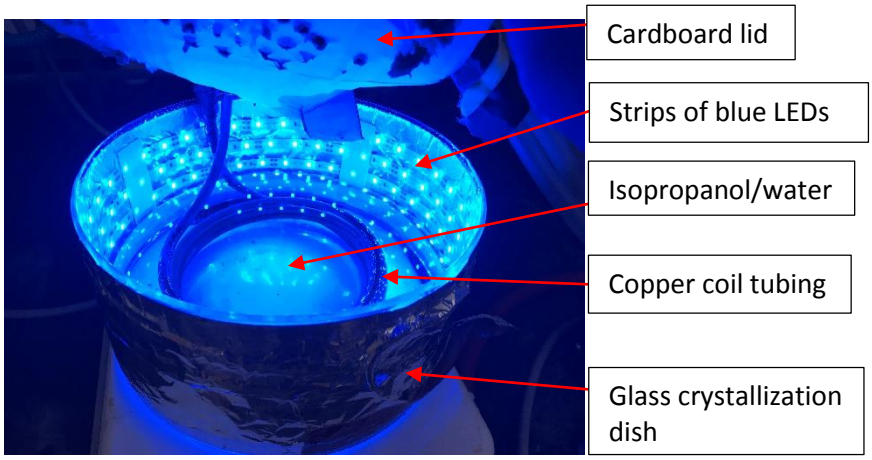
General Experimental

All reagents were obtained from commercial suppliers (Sigma-Aldrich, Oakwood chemicals, Alfa Aesar, Matrix Scientific) and used without further purification unless otherwise noted. Acetonitrile (CH_3CN) was dried over molecular sieves. *N*,*N*-diisopropylethylamine was purchased from Sigma-Aldrich and stored over KOH pellets. Photocatalyst *tris*(2-phenyl pyridinato-C2, *N*)iridium(III)($Ir(ppy)_3$), 99%(purity), $Ir(ppy)_3$ was synthesized according to literature procedure.[1] Photocatalyst *tris*[4,4'-bis(tert-butyl)-2,2'-bipyridine]ruthenium(II) hexafluorophosphate and *tris*(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II) hexafluorophosphate were purchased from Aspira Chemical. Isopropyl 2,3,4,5,6-pentafluorobenzoate, tert-butyl 2,3,4,5,6-pentafluorobenzoate, 4-chloro-2,3,5,6-tetrafluoropyridine, 3,4-dichloro-2,5,6-trifluoropyridine, 3,4,5-trichloro-2,6-difluoropyridine, 2-(perfluorophenyl)benzo[d]oxazole, 2-(perfluorophenyl)-1H-benzo[d]imidazole and 2-(perfluorophenyl)benzo[d]thiazole were synthesized according to literature procedures.[2] Reactions were monitored by ^{19}F and GC-MS (QP 2010S, Shimadzu equipped with auto sampler). NMR spectra were obtained on 400 MHz Bruker Avance III spectrometer and 400 MHz Unity Inova spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual protio solvent peak (^{1}H, ^{13}C) and ^{19}F NMR shifts are reported using fluorobenzene as a standard. Melting points were determined on Mel-Temp apparatus and reported uncorrected. GC analyses were carried out using QP 2010S Shimadzu, equipped with auto sampler. Isolations were carried out using Teledyne Isco Combiflash Rf 200i flash chromatograph with Sorbtech Rf normal phase silica (4 g, or 12 g columns). Some isolations were performed using Sorbent Technology Silica Prep TLC Plates, w/UV254, glass backed, 1000 μm, 20 x 20 cm, and were visualized with ultraviolet light. Substrate syntheses were monitored by thin layer chromatography (TLC) obtained from Sorbent Technology; Silica XHL TLC Plates, w/UV254, glass backed, 250 μm, and were visualized with ultraviolet light or potassium permanganate. No attempts were made to report ^{13}C spectra of volatile compounds.

Photocatalytic Reaction Set up

Photocatalytic reactions were set up in a light bath as described below. Strips of blue LEDs (18 LEDs/ft.) were purchased from Solid Apollo. The strips (4.9 ft) were wrapped around on the walls of glass crystallization dish and secured with masking tape and then wrapped with aluminum foil. A lid which rest on the top was fashioned from cardboard and holes were made such that NMR tubes were held firmly in the cardboard lid which was placed on the top of the bath. Isopropanol/water bath was prepared such that the tubes were submerged in it, and was maintained at 0 ^{o}C with the aid of a chiller that circulated coolant through a coil of copper tubing placed in the bath. In some cases the same light bath set up was used with water in it which was maintained at 45 ^{o}C with the aid of a sand bath connected to a thermostat.[2b]



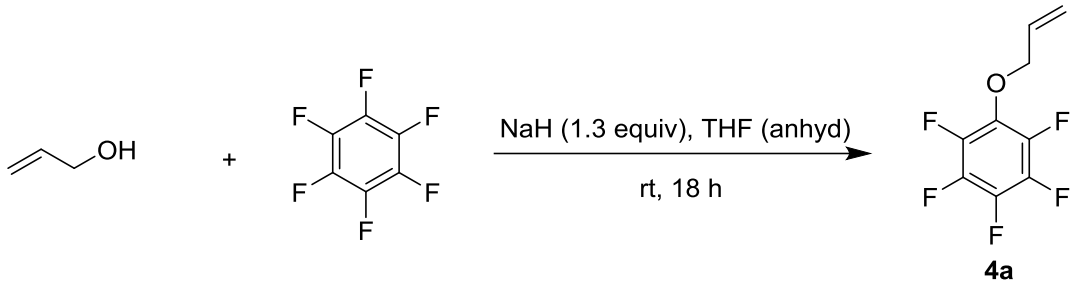


Synthesis of Substrates

General Procedure A for synthesis of aryl ethers:

To a stirred solution of alcohol (1.0 equiv) in THF (anhyd) in a flame-dried 250 mL round bottom flask, was added NaH (1.3 equiv) portion wise under Ar. The resulting mixture was stirred for 20 minutes at room temperature. Hexafluorobenzene (1.3-4.0 equiv) was then added all at once and the reaction was monitored by TLC until the spot for alcohol disappeared. After completion, the reaction mixture was slowly quenched with water. Aqueous phase was extracted with diethyl ether and the combined organic extracts were washed with brine (3 x 30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude material was purified by normal phase chromatography using hexane:ethyl acetate.[3]

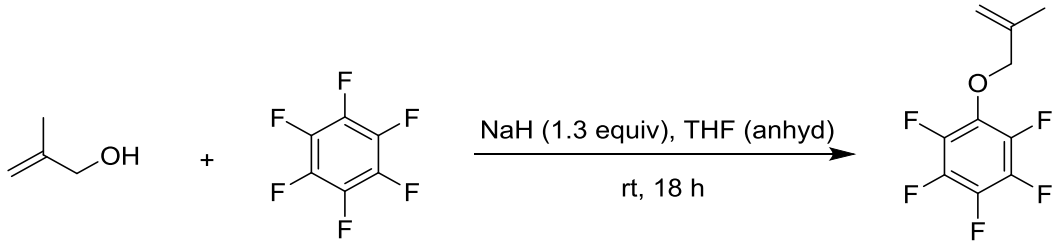
Synthesis of 1-(allyloxy)-2,3,4,5,6-pentafluorobenzene (4a)



4a

1-(allyloxy)-2,3,4,5,6-pentafluorobenzene (4a) was synthesized using **general procedure A**. 2-propen-1-ol (3.51 mL, 51.6 mmol), NaH (1.61 g, 66.6 mmol) was stirred in anhyd. THF (30 mL) at room temperature for 20 minutes. Then hexafluorobenzene (7 mL, 66.6 mmol) was added and stirred for 18 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0 % EtOAc for 0-15 cv and ramped to 50 % EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 85% yield (9.8 g, 43.8 mmol) as a colorless liquid.

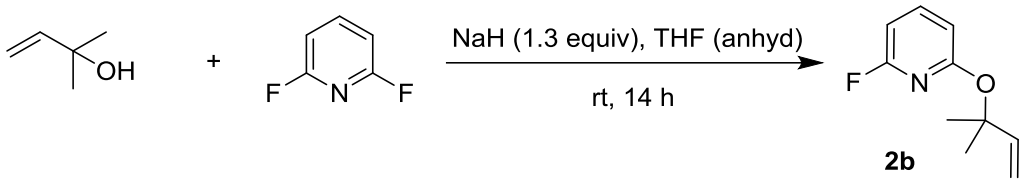
Synthesis of 1,2,3,4,5-pentafluoro-6-((2-methylallyl)oxy)benzene (4b)



4b

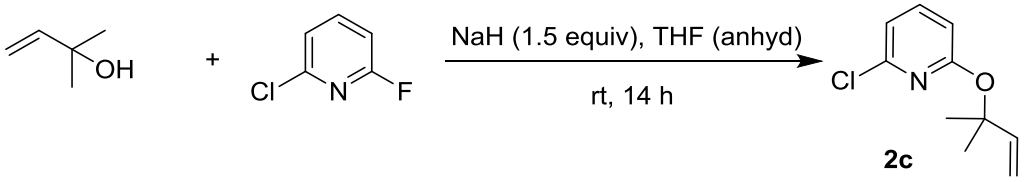
1,2,3,4,5-pentafluoro-6-((2-methylallyl)oxy)benzene (4b) was synthesized using **general procedure A**. 2-methylprop-2-en-1-ol (3.51 mL, 41.6 mmol), NaH (1.29 g, 54.1 mmol) was stirred in anhyd. THF (30 mL) at room temperature for 20 minutes. Then hexafluorobenzene (6.24 mL, 54.1 mmol) was added and stirred for 18 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 86% yield (8.52 g, 35.77 mmol) as a colorless liquid.

Synthesis of 2-fluoro-6-((2-methylbut-3-en-2-yl)oxy)pyridine (2b)



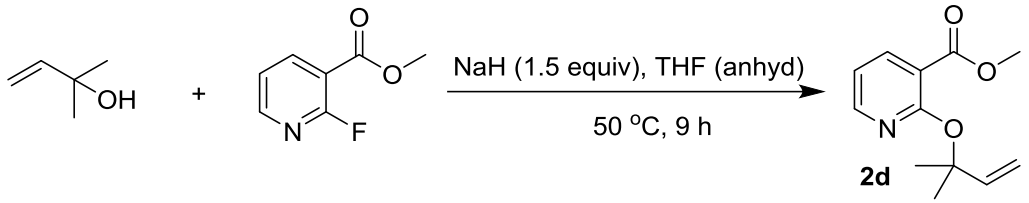
2-fluoro-6-((2-methylbut-3-en-2-yl)oxy)pyridine (2b) was synthesized using a modified version of **general procedure A**. 2-methylbut-3-en-2-ol (3 mL, 28.7 mmol), NaH (0.908 g, 37.7 mmol) was stirred in anhyd. THF (35 mL) at room temperature for 20 minutes. Then, 2,6-difluoropyridine (3.12 mL, 34.4 mmol) (rather than C_6F_6) was added and stirred for 14 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 88% yield (4.57 g, 25.26 mmol) as a colorless liquid.

Synthesis of 2-chloro-6-((2-methylbut-3-en-2-yl)oxy)pyridine (2c)



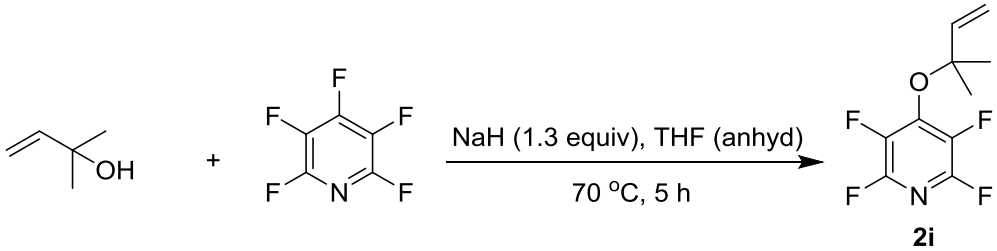
2-chloro-6-((2-methylbut-3-en-2-yl)oxy)pyridine (2c) was synthesized using a modified version of **general procedure A**. 2-methylbut-3-en-2-ol (2 mL, 19 mmol), NaH (0.684 g, 28.5 mmol) was stirred in anhyd THF (35 mL) at room temperature for 20 minutes. Then 2-chloro-6-fluoropyridine (3 g, 22.8 mmol) (rather than C_6F_6) was added and stirred for 14 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 87% yield (3.25 g, 16.53 mmol) as a colorless liquid.

Synthesis of methyl 2-((2-methylbut-3-en-2-yl)oxy)nicotinate (2d)



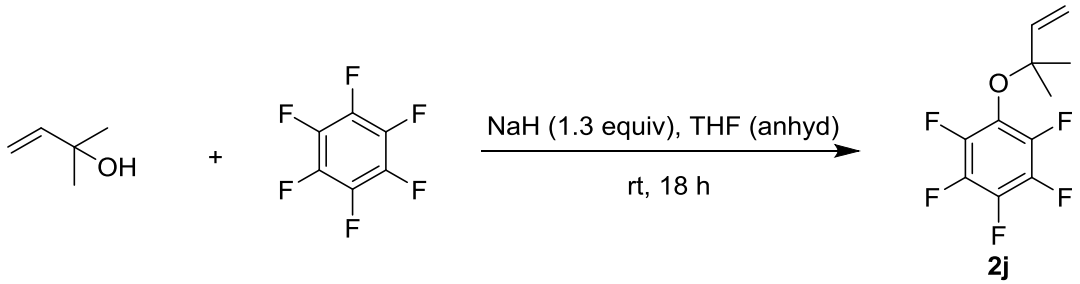
Methyl 2-((2-methylbut-3-en-2-yl)oxy)nicotinate (2d) was synthesized using a modified version of **general procedure A**. 2-methylbut-3-en-2-ol (1.7 mL, 16.11 mmol), NaH (0.58 g, 24.16 mmol) was stirred in anhyd THF (35 mL) at room temperature for 20 minutes. Then methyl 2-fluoronicotinate (3 g, 19.33 mmol) (rather than C_6F_6) was added, heated at 50 °C and stirred for 9 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 44% yield (1.568 g, 7.088 mmol) as a colorless liquid.

Synthesis of 2,3,5,6-tetrafluoro-4-((2-methylbut-3-en-2-yl)oxy)pyridine (2i)



2,3,5,6-tetrafluoro-4-((2-methylbut-3-en-2-yl)oxy)pyridine (2i) was synthesized using a modified version of **general procedure A**. 2-methylbut-3-en-2-ol (3 mL, 28.7 mmol), NaH (0.91 g, 37.31 mmol) was stirred in anhyd THF (40 mL) at room temperature for 20 minutes. Then pentafluoropyridine (3.8 mL, 34.44 mmol) (rather than C_6F_6) was added, heated at 70 °C and stirred for 5 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 35% yield (2.362 g, 10.04 mmol) as a colorless liquid.

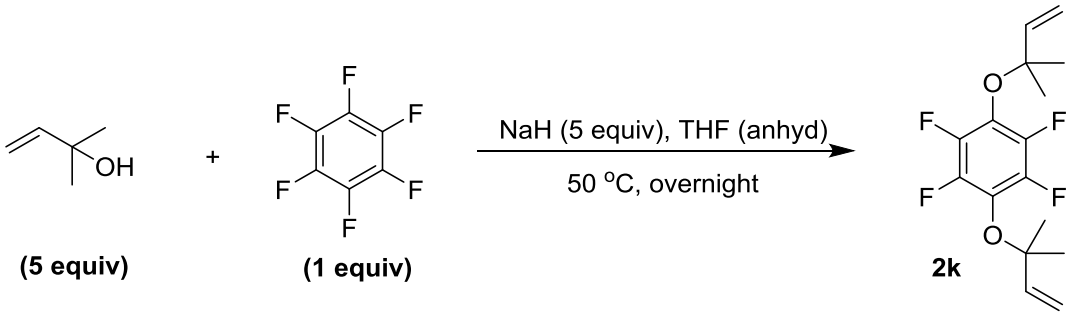
Synthesis of 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (2j)



2j

1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (2j) was synthesized using **general procedure A**. 2-methylbut-3-en-2-ol (5.2 mL, 49.44 mmol), NaH (1.54 g, 64.2 mmol) was stirred in anhyd. THF (40 mL) at room temperature for 20 minutes. Then hexafluorobenzene (8 mL, 69.2 mmol) was added and stirred for 18 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 83% yield (10.3 g, 41.03 mmol) as a colorless liquid.

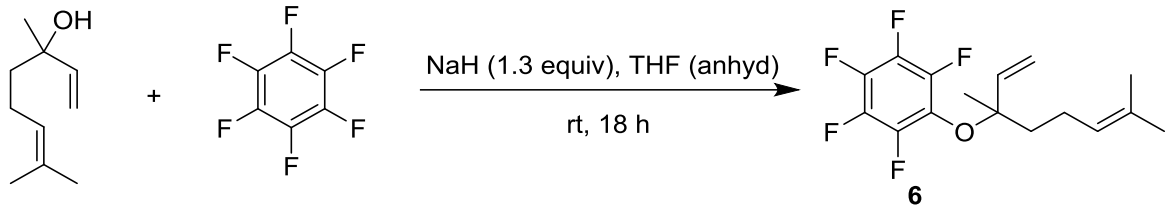
Synthesis of 1,2,4,5-tetrafluoro-3,6-bis((2-methylbut-3-en-2-yl)oxy)benzene (2k)



(5 equiv) **(1 equiv)** **2k**

1,2,4,5-tetrafluoro-3,6-bis((2-methylbut-3-en-2-yl)oxy)benzene (2k) was synthesized using a modified version of **general procedure A**. 2-methylbut-3-en-2-ol (5.6 mL, **53.7 mmol**), NaH (1.28 g, 53.7 mmol) was stirred in anhyd. THF (40 mL) at room temperature for 20 minutes. Then hexafluorobenzene (1.24 mL, **10.7 mmol**) was added and stirred at 50 °C overnight. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 51% yield (1.74 g, 5.45 mmol) as a colorless liquid.

Synthesis of 1-((3,7-dimethylocta-1,6-dien-3-yl)oxy)-2,3,4,5,6-pentafluorobenzene (6)



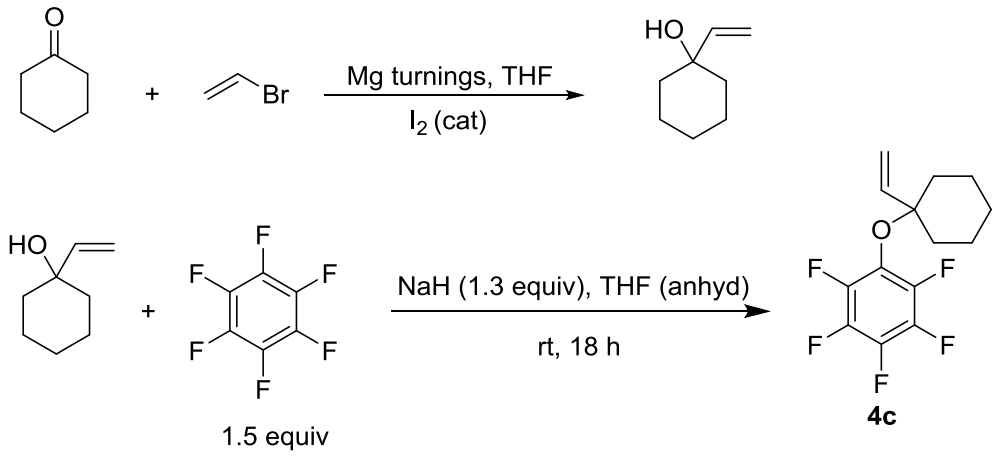
6

1-((3,7-dimethylocta-1,6-dien-3-yl)oxy)-2,3,4,5,6-pentafluorobenzene (6) was synthesized using **general procedure A**. Linalool (1.8 mL, 9.9 mmol), NaH (0.31 g, 12.9 mmol) was stirred in anhyd. THF (40 mL) at room temperature for 20 minutes. Then hexafluorobenzene (1.5 mL, 12.9 mmol) was added and stirred for 18 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford the product in 81% yield (2.56 g, 8.02 mmol) as a colorless liquid.

General Procedure B for synthesis of aryl ethers via Grignard reagent:

To a suspension of fresh Mg turnings in anhydrous THF was added catalytic amount of I_2. A solution of vinyl bromide (1 M in THF) was then added, and the mixture was heated to initiate the Grignard reaction. The remainder of vinyl bromide solution was added at a rate to maintain gentle reflux. After complete addition, a solution of corresponding ketone in THF was added over 15 minutes and the reaction was left to stir at room temperature overnight. The reaction was carefully quenched with saturated NH_4Cl solution, and then extracted with ether (4x40 mL). The ether extract was washed with brine (40 mL), dried over $MgSO_4$ and then concentrated using rotatory evaporator. The product was isolated using column chromatography.

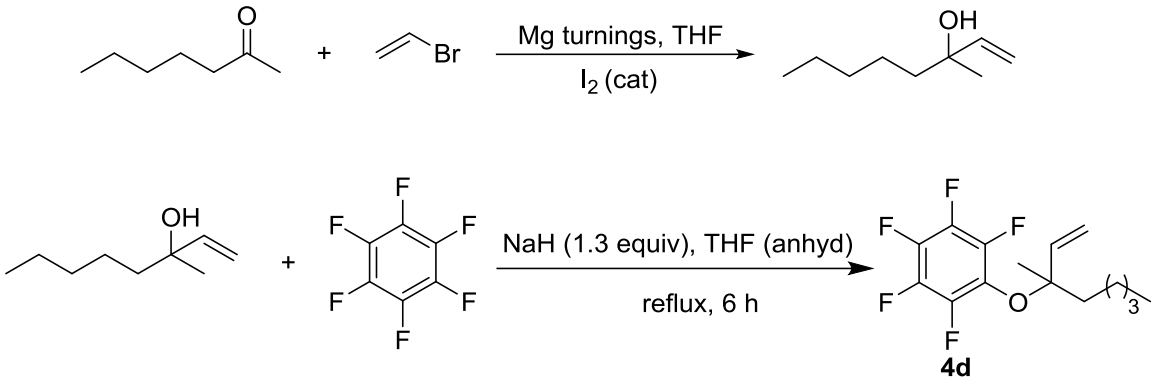
Synthesis of 1,2,3,4,5-pentafluoro-6-((1-vinylcyclohexyl)oxy)benzene (4c)



1,2,3,4,5-pentafluoro-6-((1-vinylcyclohexyl)oxy)benzene (4c) was synthesized using **general procedure B** followed by **general procedure A**. A solution of 1 M vinyl bromide in THF (32 mL, 32 mmol) was added to Mg turnings (0.77 g) in THF (45 mL) and heated to initiate Grignard reaction. It was followed by addition of cyclohexanone (2.54 mL, 24.6 mmol) over 15 minutes and left to stir overnight at room temperature. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-10 cv, ramped to 10% EtOAc for 10-25 cv, ramped again to 50% for 25-30 cv and then held at 100% EtOAc for 30-40 cv) on a 24 g silica column to afford **1-vinylcyclohexan-1-ol** in 29.7% yield (0.92 g, 7.3 mmol) as a pale yellow liquid.

1-vinylcyclohexan-1-ol was then used to carry out general procedure **A** for synthesis of aryl ether. 1-vinylcyclohexan-1-ol (0.96 mL, 7.3 mmol), NaH (0.262 g, 10.94 mmol) was stirred in anhyd. THF (40 mL) at room temperature for 20 minutes. Then hexafluorobenzene (1.26 mL, 10.94 mmol) was added and stirred at the same temperature for 18 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford **1,2,3,4,5-pentafluoro-6-((1-vinylcyclohexyl)oxy)benzene (4c)** in 63% yield (1.34 g, 4.58 mmol) as a colorless liquid.

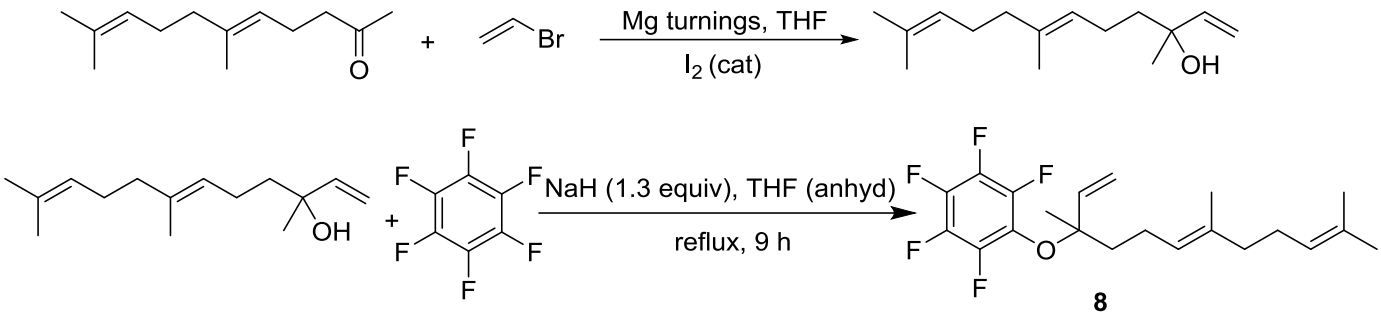
Synthesis of 1,2,3,4,5-pentafluoro-6-((3-methyloct-1-en-3-yl)oxy)benzene (4d)



1,2,3,4,5-pentafluoro-6-((3-methyloct-1-en-3-yl)oxy)benzene (4d) was synthesized using **general procedure B** followed by **general procedure A**. A solution of 1 M vinyl bromide in THF (36 mL, 36 mmol) was added to Mg turnings (0.864 g) in THF (45 mL) and heated to initiate Grignard reaction. It was followed by addition of heptan-2-one (2.8 mL, 20.0 mmol) over 15 minutes and left to stir overnight at room temperature. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-10 cv, ramped to 10% EtOAc for 10-25 cv, ramped again to 50% for 25-30 cv and then held at 100% EtOAc for 30-40 cv) on a 24 g silica column to afford **3-methyloct-1-en-3-ol** in 44% yield (1.25 g, 8.8 mmol) as a colorless liquid.

3-methyloct-1-en-3-ol was then used to carry out general procedure **A** for synthesis of aryl ether. 3-methyloct-1-en-3-ol (1.49 mL, 8.8 mmol), NaH (0.316 g, 13.2 mmol) was stirred in anhyd. THF (40 mL) at room temperature for 20 minutes. Then hexafluorobenzene (4.07 mL, 35.2 mmol) was added and refluxed for 6 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford **1,2,3,4,5-pentafluoro-6-((3-methyloct-1-en-3-yl)oxy)benzene** (**4d**) in 66% yield (1.78 g, 5.81 mmol) as a colorless liquid.

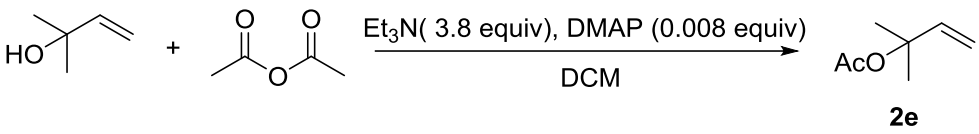
Synthesis of (E)-1,2,3,4,5-pentafluoro-6-((3,7,11-trimethyldodeca-1,6,10-trien-3-yl)oxy)benzene (7)



(E)-1,2,3,4,5-pentafluoro-6-((3,7,11-trimethyldodeca-1,6,10-trien-3-yl)oxy)benzene (8) was synthesized using **general procedure B** followed by **general procedure A**. A solution of 1 M vinyl bromide in THF (25 mL, 25 mmol) was added to Mg turnings (0.519 g) in THF (45 mL) and heated to initiate Grignard reaction. It was followed by addition of (E)-6,10-dimethylundeca-5,9-dien-2-one (3.71 mL, 16.67 mmol) over 15 minutes and left to stir overnight at room temperature. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0 % EtOAc for 0-10 cv, ramped to 10 % EtOAc for 10-25 cv, ramped again to 50% for 25-30 cv and then held at 100% EtOAc for 30-40 cv) on a 24 g silica column to afford **(E)-3,7,11-trimethyldodeca-1,6,10-trien-3-ol** in 32.7% yield (1.21 g, 5.45 mmol) as a pale yellow liquid.

(E)-3,7,11-trimethyldodeca-1,6,10-trien-3-ol was then used to carry out general procedure **A** for synthesis of aryl ether. (E)-3,7,11-trimethyldodeca-1,6,10-trien-3-ol (1.38 mL, 5.45 mmol), NaH (0.261 g, 10.9 mmol) was stirred in anhyd. THF (45 mL) at room temperature for 20 minutes. Then hexafluorobenzene (0.95 mL, 8.17 mmol) was added and refluxed for 9 h. The crude residue was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford **(E)-1,2,3,4,5-pentafluoro-6-((3,7,11-trimethyldodeca-1,6,10-trien-3-yl)oxy)benzene (8)** in 61% yield (1.29 g, 3.32 mmol) as a colorless liquid.

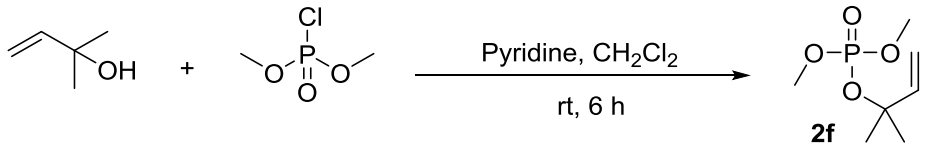
General procedure C for synthesis of aryl ether via acetylation:



2e

To a flame dried 250 mL round bottom flask was added 2-methylbut-3-en-2-ol (2.5 mL, 23 mmol), Et_3N (10.4 mL, 87.4 mmol), DMAP (0.04 mL, 0.184 mmol) and DCM (20 mL) via syringe. Flask was cooled in ice-bath and acetic anhydride (7.2 mL, 87.4 mmol) was added dropwise with constant stirring. The resulting solution was stirred under an Ar atmosphere at room temperature and was monitored by TLC (hexane : ethyl acetate 95:5) until no alcohol was observed. The mixture was washed with $NaHCO_3$ (2 x 150 mL), 10% NaOH (2 x 50 mL), brine (50 mL) and dried over $MgSO_4$. Solvent was removed in vacuo and crude product was obtained as a yellow oil which was distilled (130-150 ^oC at 760 mm Hg) to yield **2-methylbut-3-en-2-yl acetate** in 91% yield (2.9 mL, 20.93 mmol) as a colorless liquid.

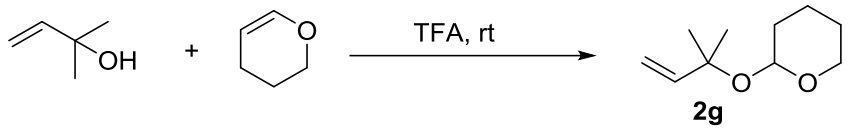
General Procedure D for synthesis of aryl ether using dimethyl phosphorochloridate :



2f

Dimethyl phosphorochloridate (3.61g, 25 mmol) was added to a solution of 2-methylbut-3-en-2-ol (1.94 g, 22.5 mmol) and pyridine (2.0 mL) in CH_2Cl_2 (30 mL) at 0 ^oC over 5 minutes. The resulting white slurry was stirred for 6 h at room temperature. The reaction mixture was diluted with diethyl ether and was washed successfully with a 10% HCl solution, saturated $NaHCO_3$ (2 x 50 mL) and brine (3 x 50 mL). The organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the crude product was purified by automated flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-15 cv and ramped to 50% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford **dimethyl (2-methylbut-3-en-2-yl) phosphate** in 76% yield (3.32 g, 17.1 mmol) as a colorless liquid.

General Procedure E for synthesis of aryl ether from pyran :

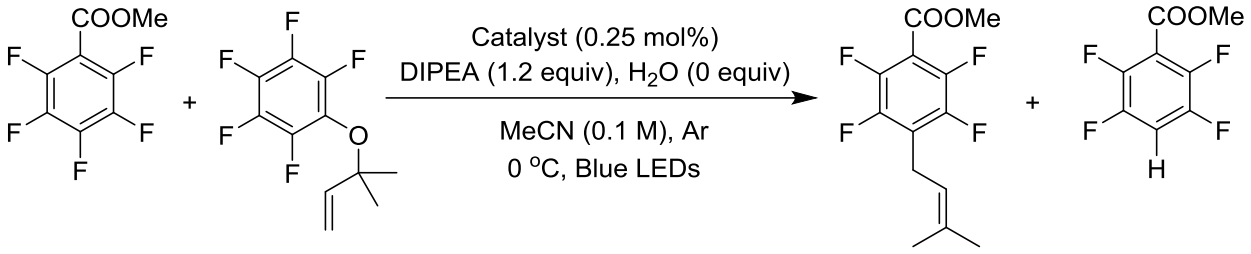


2g

To a solution of 2-methylbut-3-en-2-ol (0.9 ml, 9 mmol) in DCM (30 mL) 2,3-dihydro-4H-pyran (0.8 mL, 9 mmol) and trifluoroacetic acid (0.1 mL, 1.8 mmol) were added. The reaction was stirred at room temperature and monitored by TLC. After completion of the reaction, it was quenched with $NaHCO_3$ and extracted with DCM. The organic phase was then washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by automated flash chromatography using hexane : ethyl acetate (0% EtOAc for 0-15 cv and ramped to 30% EtOAc for 15-25 cv and then held at 100% EtOAc 25-35 cv) on a 24 g silica column to afford **2-((2-methylbut-3-en-2-yl)oxy)tetrahydro-2H-pyran** in 70% yield (1.07 g, 6.3 mmol) as a colorless oil.

Optimization conditions:-

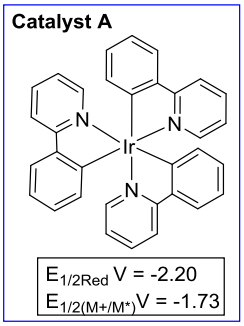
Optimization of Catalyst:

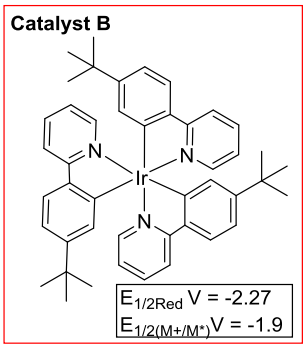


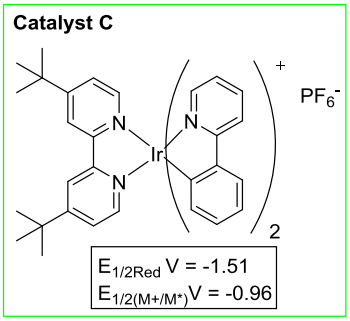
1 **2j** **3a** **3a'**

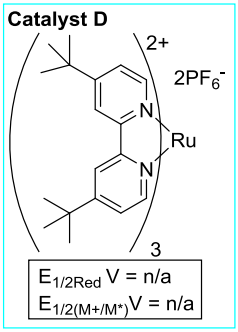
Entry	modification	Time (h)	1	3a	3a' (% compound)
1.	no catalyst	24	100	-	-
2.	Catalyst A	21	12	58	30
3.	Catalyst B	21	15	53	32
4.	Catalyst C	24	48	29	23
5.	Catalyst D	24	72	17	11
6.	Catalyst E	24	67	20	12

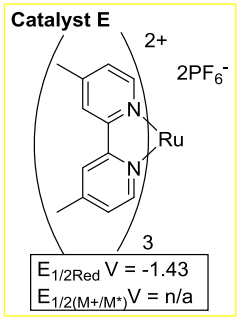
(Determined by 19F NMR)







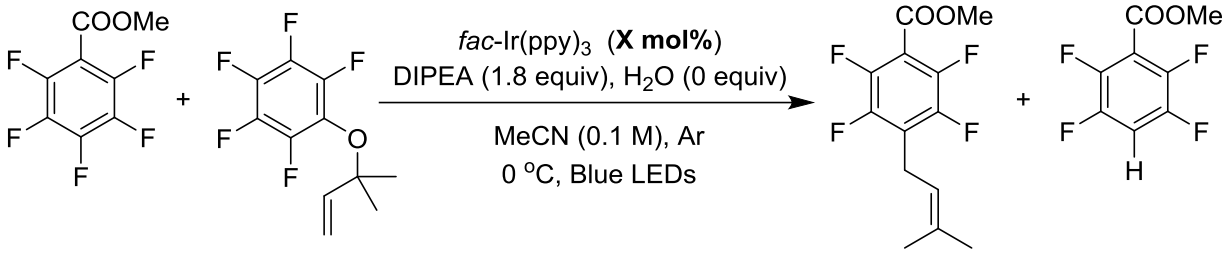




The presence of the photocatalyst was required, as indicated by the control reaction without the photocatalyst was run (Entry 1), in which no conversion was observed. Catalyst A (*fac*-Ir(ppy)$_3$) produced considerable amount of prenylated product (58%) within 21 h. Catalyst B worked well producing 53% of desired prenylated product within 21 h, however the Pdt:HDF ratio was observed to be better in case of Catalyst A, albeit modest. Less reducing Catalyst C also facilitated

the reaction, resulting in the desired C–C coupled product, albeit at significantly diminished rates and with diminished product selectivity. Remarkably, both Catalyst D and E also facilitated prenylation despite an anticipated substantial underpotential. The reaction in these cases were slow with no considerable progress after 24 h.

Catalyst loading:



1 **2j** **3a** **3a'**

Entry	X mol%	Time	1	3a	3a'
1.	0.3	18 h	8	61	31
2.	0.25	5 h	46	35	19
		20 h	12	58	30
3.	0.20	20 h	26	41	33
4.	0.10	20 h	38	32	30
5.	0.05	20 h	46	25	39
6.	0.025	5 h	90	4.2	5.5
		20 h	54	17	28
7.	0.0125	20 h	68	12	19
8.	0.25, 10 equiv H_2O	8 h	Trace	64	35
9.	0.025, 10 equiv H_2O	2.5 d	51	30.7	18

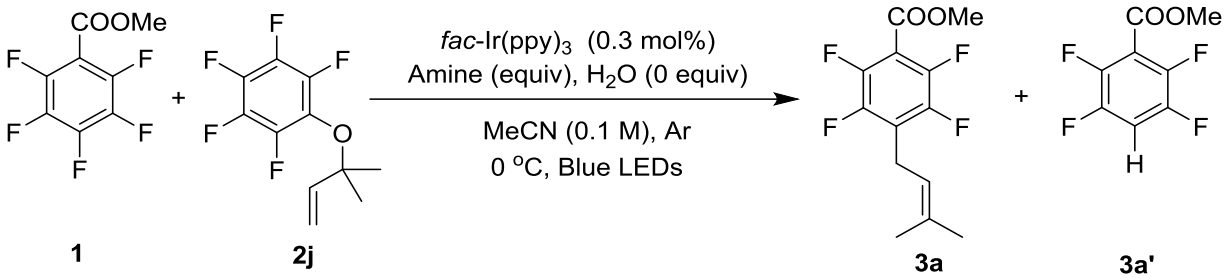
(% compound)

(Determined by ^{19}F NMR)

The catalyst loading experiments clearly demonstrated the rate dependency on the concentration of the catalyst. Higher concentrations of the catalyst (Entry 1, 2) produced the fastest reactions with good conversions within 20 h. The rate of reaction significantly dropped with subsequent decrease in concentration of the catalyst. Interestingly, while water seems to accelerate the

reaction at 0.25 mol%, this acceleration is reduced at much lower catalyst loadings (compare entries 2 & 8 to 6 & 9).

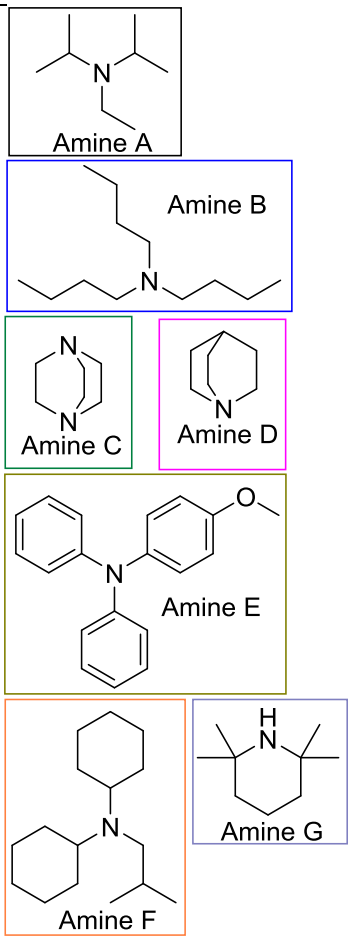
Optimization of Amine:



(Determined by ^{19}F NMR)

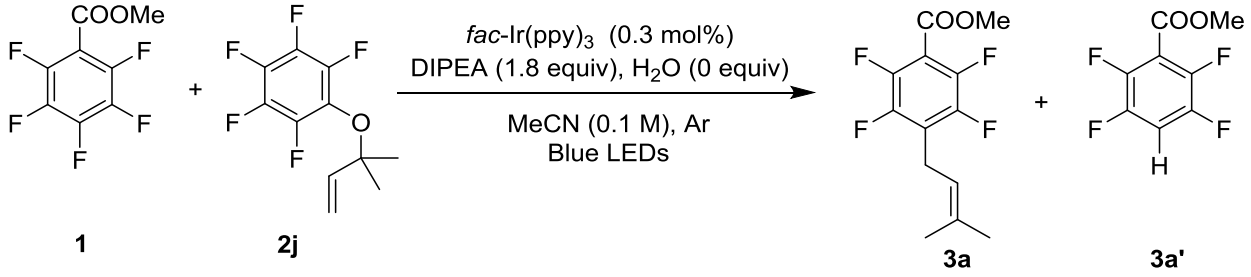
Entry	Amine	Time	1	3a	3a'
1.	Amine A, 1.2 equiv	18 h	8	61	30
2.	Amine A, 1.8 equiv	18 h	2	64	33
3.	Amine A, 2.5 equiv	18 h	-	57	44
4.	Amine B, 1.8 equiv	18 h	17	44	37
5.	Amine C, 1.8 equiv	18 h	100	-	-
6.	Amine C, 1.8 equiv, rt instead of 0 °C	18 h	100	-	-
7.	Amine D, 2.5 equiv, rt instead of 0 °C	18 h	100	-	-
8.	Amine E, 2.5 equiv, rt instead of 0 °C	18 h	100	-	-
9.	Amine F, 2.5 equiv	18 h	95	2	3
10.	Amine F, 2.5 equiv, rt instead of 0 °C	18 h	81	8	11
11.	Amine G, 2.5 equiv, rt instead of 0 °C	18 h	100	-	-

(% compound)



Amine A (DIPEA) produced prenylated products in moderate to high yields in 18 h (entry 1-3). Increasing amine concentration to 1.8 equiv produced better conversion as compared to 1.2 equiv. When amine concentration was further increased to 2.5 equiv, it resulted in complete consumption of starting material within 18 h but it also produced more of HDF side-product. Therefore, 1.8 equiv DIPEA was chosen to be the best condition. Amine B (entry 4) was also able to form desired prenylated product but in slightly lower yield. Switching the amine to Amines C-E (entry 5-8) did not result in any product formation even when the reaction was warmed to room temperature (27 ^{o}C) instead of running at 0 ^{o}C. Compared to Amine A, Amine F gave lower conversion of the starting material at 0 ^{o}C, as well as at room temperature (entry 9, 10) probably because of its lower solubility. Amine G did not result in any conversion.

Temperature Screening:



Entry	Temperature (^{0}C)	Time	1	3a	3a'	Other
1.[a]	-10	24 h	19	55	26	
2.	0	18 h	3	63	34	
3.	25	16 h	-	55	36	8
4.	45	12 h	-	32	47	21

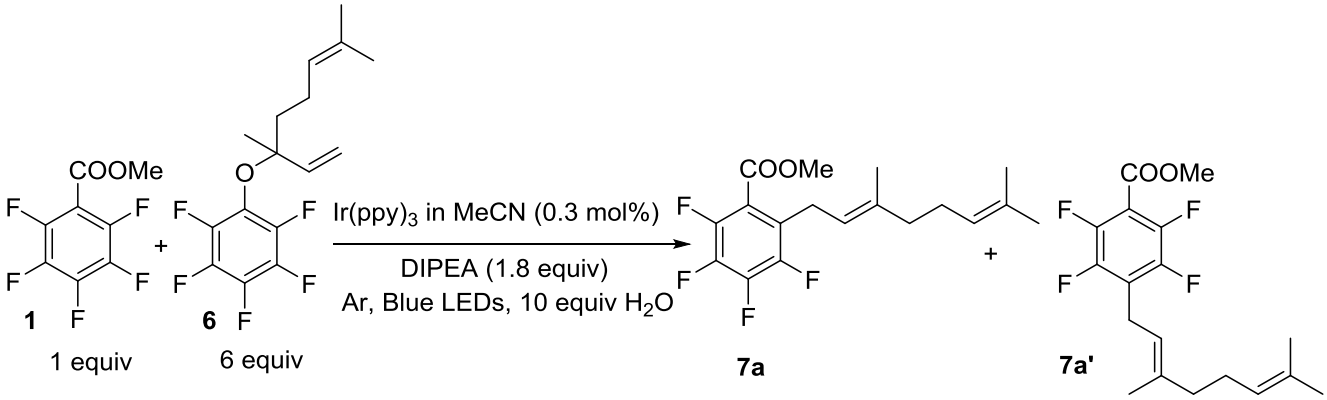
[a]Reaction produced more HDF over extended time.

(Determined by ^{19}F NMR)

Temperature screening was yet another important set of experiments that greatly affected the rate of reactions. Reaction at -10 ^{o}C was slow, resulting in 55% prenylated product in 24 h. Carrying out the reaction at 0 ^{o}C produced 63% of product with reasonable Pdt:HDF ratio. As expected, at

higher temperature the rate increased (entries 3-4). Though the starting material was fully consumed within 16 h (and 12 h), warmer temperatures always produced more HDF, in addition to another minor side product that was observed. Entry 2 was chosen to be the optimal condition which produced the cleanest reaction within a reasonable time frame.

Effect of temperature on selectivity of major (o-Ger) product

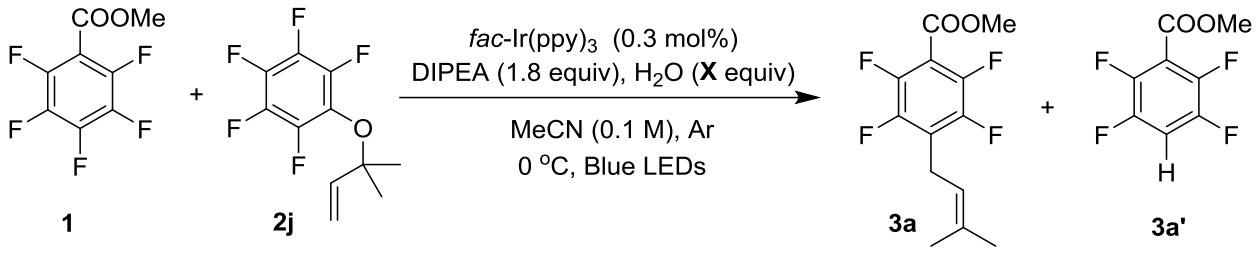


Entry	Temperature (°C)	Time	1	HDF	7a	7a'
1.	-15	25 h	-	30	41	29
2.	0	4 h	-	31	42	27
3.	26	4 h	-	36	39	25

(Determined by ^{19}F NMR)

In an attempt to improve the regioselectivity by varying the reaction temperature (-15 °C to 26 °C), no significant change in the relative amounts of **7a** and **7a'** was observed. However, a substantially increased reaction time was required at -15 °C. Also, a subtle decrease in the amount of HDF product was observed upon cooling, but appeared to reach a limit somewhere near 0°C.

Effect of Water:

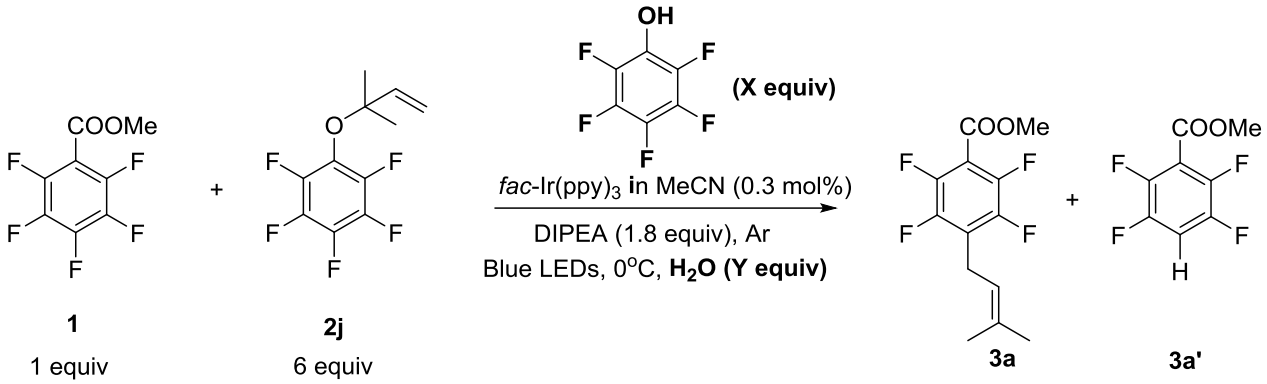


Entry	Equiv of H_2O	Time	1	3a	3a'
1.	0	4 h	79	13	8
		18 h	-	63	36
2.	5	4 h	18	54	28
		8 h	-	63	35
3.	10	4 h	-	65	34
4.	20	4 h	-	65	35

Inclusion of water played a very important role in improving the reaction rate significantly. The presence of 5 equiv H_2O in the reaction mixture caused the reaction to complete in 8 h, as compared to 18 h when the reaction was carried out in the absence of water. As the amount of water was increased to 10 equiv (entry 3), the reaction completed within 4 h. One plausible explanation could be that pentafluorophenol (by-product that develops during the course of reaction) produces an inhibitory effect under anhydrous reaction conditions. Several more experiments support this suggestion as shown below.

Control experiments to demonstrate inhibitory effect of pentafluorophenol:

Photocatalytic reaction in the presence of Pentafluorophenol :

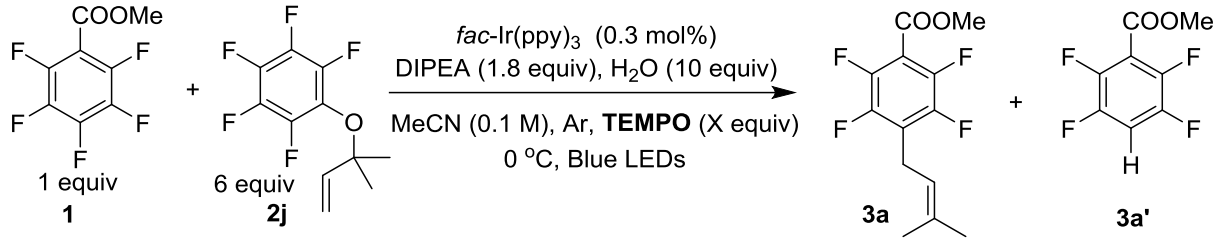


Entry	X equiv	Y equiv	Time	1	3a	3a'	3a:3a'	Other
1.	0.0	10	4 h	-	65	35	1.9:1	
2.	0.5	0	4 h	71	17	11	1.54:1	
			10 h	66	20	14	1.42:1	
3.	1.0	0	4 h	17	40	29	1.4:1	at least 2 more pdts
			10 h	3	55	38	**1.44:1**	+2 more pdts
4.	1.0	10	4 h	-	47	26	**1.8:1**	+ 2 side pdts

By running an experiment in which pentafluorophenol was intentionally added at the beginning of the reaction, the reaction was retarded. Upon addition of 10 equiv H_2O the rate was restored. This can be seen from the improvement in ratio from 1.44:1 in the absence of H_2O to 1.8:1 when H_2O was present. The Pdt:HDF ratio in the standard conditions is 1.9:1.

One potential explanation is that the water acidifies pentafluorophenol facilitating deprotonation and ionization by DIPEA in the reaction, effectively removing phenol-OH by converting it to phenoxide. We suspect phenol may serve as an HAT shuttle which can facilitate HDF and can generate a problematic persistent radical, which may inhibit catalytic turnover.

Effect of TEMPO on the rate and selectivity of the reaction:



1) 0 equiv TEMPO

Time	1	3a'	3a	3a:3a'
2 h	27%	24%	49%	2.04:1
4 h	-	34%	66%	1.9:1

(Standard)

2) 0.4 equiv TEMPO

Time	1	3a'	3a	3a:3a'
2 h	86%	4.2%	9.6%	2.25:1
4 h	43%	17%	39%	2.21:1
7 h	23%	24%	52%	2.16:1
10 h	-	32%	68%	2.1:1

3) 1.0 equiv TEMPO

Time	1	3a'	3a	3a:3a'
2 h	94%	1.6%	4.4%	2.75:1
4 h	68%	9%	23%	2.55:1
7 h	41%	16%	42%	2.6:1
10 h	13%	27%	59%	2.2:1
15 h	11%	29%	60%	2.06:1

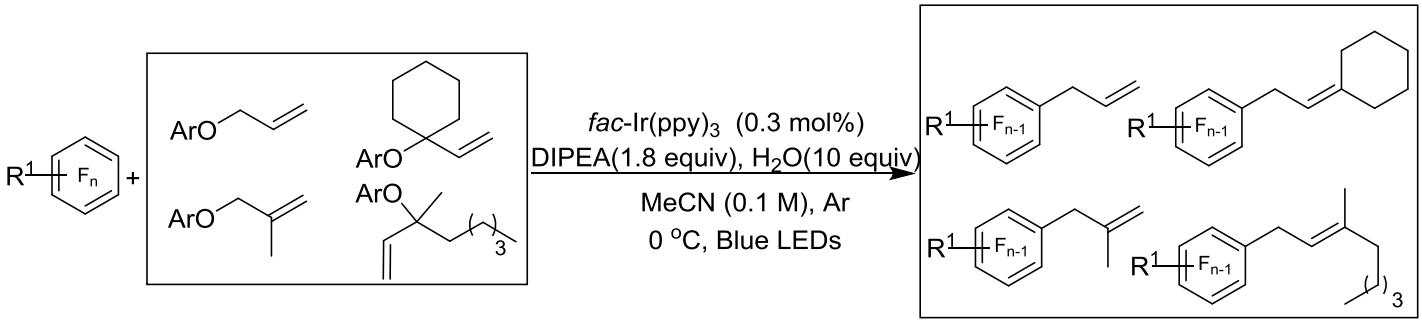
4) 1.5 equiv TEMPO

Time	1	3a'	3a	3a:3a'
2 h	97%	0.8%	2.2%	2.75:1
4 h	91%	2.4%	6.6%	2.71:1
7 h	83%	4.6%	12.4%	2.69:1
10 h	79%	6%	15%	2.5:1
15 h	77%	7.5%	15.6%	2.1:1

TEMPO had a significant effect on the progress of the reaction. TEMPO could extract H-atom from amine radical cation formed during the reaction forcing the aryl radical to react with prenyl source. The Pdt:HDF ratio (3a:3a') was seen to improve during the initial time points. But as the reaction progressed, the Pdt:HDF ratio eventually returned to almost the same as observed in standard reaction conditions. Also, the presence of TEMPO slowed the progress of reaction (from 4 h to 10 h when 0.4 equiv was used) and increasing the amount of TEMPO decreased the rate of reaction, thus causing incomplete conversion of **1a** over extended time possibly due to quenching of necessary aryl radical intermediate.

Photocatalytic Reactions on Perfluoroarenes

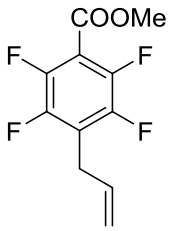
General procedure F for photocatalytic allylation reaction



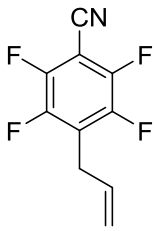
1 **4a-d** **5a-f**

An NMR tube was charged with fluoroarene (0.1 mmol, 1.0 equiv), allyl-OAr (0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (0.18 mmol, 1.8 equiv), distilled water (1 mmol, 10 equiv), *fac*-tris(2-phenyl pyridinato-*C*2, *N*) Iridium(III) ($Ir(ppy)_3$) (0.3 mM, 1 mL in MeCN), sealed glass capillary containing C_6D_6 and was capped with an NMR septum (Ace glass, part no. 9096-25). When reaction was run in greater than 0.1 mmol of fluoroarene, more than one NMR tube was used to set up the reaction and each NMR tube had 1 mL of reaction mixture. The reaction was degassed via Ar bubbling for 15 min at 0 °C (to avoid evaporation of *N*,*N* diisopropylethylamine and other volatile starting materials) and then placed in a light bath (*vide supra*) such that the lower portion of the tube was submerged under the isopropanol/water bath.

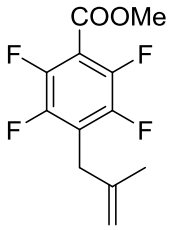
The reaction was monitored periodically by ^{19}F NMR (care was taken to exclude light while in transit). After the complete consumption of starting material, CH_3CN was removed via rotavap. The crude material was purified using prep TLC plate 10:1 hexane:ether. If the reaction did not go to completion with the first addition of *N*,*N* diisopropylethylamine, an additional 0.2 - 1.2 equiv of *N*,*N* -diisopropylethylamine was added to the reaction. Then the reaction was re-degassed and returned to the light bath. This sequence was repeated until the reaction reached completion as judged by ^{19}F NMR.



General procedure F was followed using methyl 2,3,4,5,6-pentafluorobenzoate (14.75 μL, 0.1 mmol, 1 equiv), 1-(allyloxy)-2,3,4,5,6-pentafluorobenzene (97.5 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **methyl 4-allyl-2,3,5,6-tetrafluorobenzoate (5a)** as a colorless liquid in 72% ^{19}F NMR yield and 66% isolated yield (14.89 mg, 0.06 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.04 – -140.19 (m, 2F), -143.12 (td, *J* = 15.8, 4.8 Hz, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 – 5.82 (m, 1H), 5.12 (d, 2H), 3.97 (s, 3H), 3.50 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 146.1 – 143.6 (ddd, *J* = 12.9, 6.4, 4.8 Hz), 145.8 – 143.3 (dt, *J* = 15.9, 4.6 Hz), 132.2, 121.9 (t, *J* 18.4 Hz), 117.6, 110.6 (t, *J* = 15.7 Hz), 53.2, 27.1. GC/MS (m/z, relative intensity) 248 (M+, 48), 229 (2), 217 (100), 169 (28).

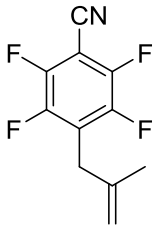


General procedure F was followed using methyl pentafluorobenzonitrile (12.6 μL, 0.1 mmol, 1 equiv), 1-(allyloxy)-2,3,4,5,6-pentafluorobenzene (97.6 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **4-allyl-2,3,5,6-tetrafluorobenzonitrile (5b)** as a colorless liquid in 81% ^{19}F NMR yield and 72% isolated yield (15.48 mg, 0.07 mmol). Not much effort was given to evaporate the solvents due to low volatility of compound. The crude product also contained hydrodefluorinated product. ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.67 – -133.24 (m, 2F), -133.68 – -134.38 (m, 2F, minor), -140.50 (td, *J* = 15.8, 4.8 Hz, 2F), -140.94 – -141.51 (m, 2F, minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.68 (m, 1H), 5.09 (d, 2H), 3.47 (d, 2H).

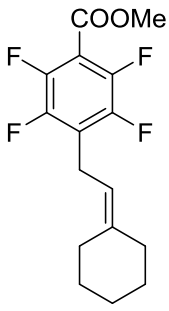


General procedure F was followed using methyl 2,3,4,5,6-pentafluorobenzoate (14.75 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylallyl)oxy)benzene (107.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1

mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **methyl 2,3,5,6-tetrafluoro-4-(2-methylallyl)benzoate (5c)** as a colorless liquid in 74% ^{19}F NMR yield and 68% isolated yield (18.34 mg, 0.07 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.02 – -140.44 (m, 2F), -142.50 (td, *J* = 15.8, 4.8 Hz, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (s, 1H), 4.65 (s, 1H), 3.98 (s, 3H), 3.44 (s, 2H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 146.2 – 143.8 (ddd, *J* = 12.9, 6.4, 4.8 Hz), 145.8 – 143.2 (dt, *J* = 15.9, 4.6 Hz), 140.4, 121.9 (t, *J* = 18.4 Hz), 112.8, 110.6 (t, *J* = 15.7 Hz), 53.2, 31.3 – 30.6 (m), 22.3. GC/MS (m/z, relative intensity) 262 (M+, 64), 247 (15), 231 (100).

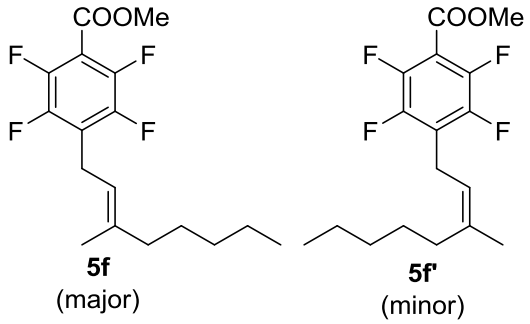


General procedure F was followed using 2,3,4,5,6-pentafluorobenzonitrile (12.6 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylallyl)oxy)benzene (107.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **2,3,5,6-tetrafluoro-4-(2-methylallyl)benzonitrile (5d)** as a colorless liquid in 85% ^{19}F NMR yield and 78% isolated yield (17.86 mg, 0.08 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -133.06 (td, *J* = 17.4, 7.1 Hz, 2F), -139.86 (td, *J* = 16.8, 7.0 Hz, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 (s, 1H), 4.66 (s, 1H), 3.48 (s, 2H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2 – 145.6 (dt, *J* = 16.4, 3.6 Hz), 146.3 – 143.4 (m), 139.7, 125.8 (t, *J* = 18.4 Hz), 113.5, 107.6 (t, *J* = 3.7 Hz), 92.4, 31.2, 22.3. GC/MS (m/z, relative intensity) 229 (M+, 55), 214 (34), 194 (25).



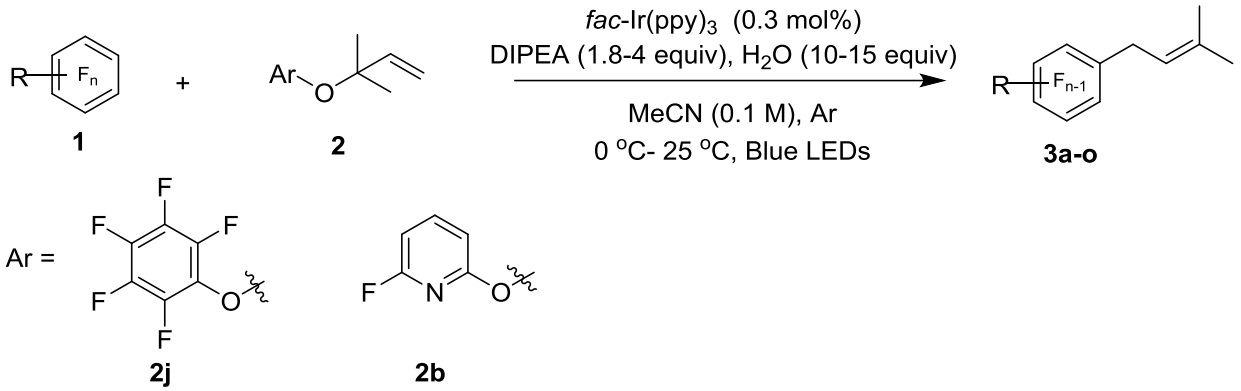
General procedure F was followed using methyl 2,3,4,5,6-pentafluorobenzoate (14.8 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((1-vinylcyclohexyl)oxy)benzene(125 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **methyl 4-(2-cyclohexylideneethyl)-2,3,5,6-tetrafluorobenzoate (5e)** as a colorless liquid in 68% ^{19}F NMR yield and 61% isolated yield

(18.96 mg, 0.06 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.24 – -140.41 (m, 2F, major and minor), -143.41 (td, *J* = 15.7, 4.9 Hz, 2F, major and minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (t, *J* = 7.5 Hz, 1H), 3.96 (s, 3H), 3.45 (d, *J* = 7.5 Hz, 2H), 2.27 (t, *J* = 5.5 Hz, 2H), 2.11 – 2.00 (m, 2H), 1.63 – 1.44 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 146.2 – 143.8 (ddd, *J* = 12.9, 6.4, 4.8 Hz), 145.8 – 143.4 (dt, *J* = 15.9, 4.6 Hz), 143.1, 123.9 (t, *J* = 18.7 Hz), 114.8, 109.7, 53.1, 37.0, 29.7, 28.3, 26.7, 21.3. GC/MS (m/z, relative intensity) 316 (M+, 15), 285 (15), 235 (58).



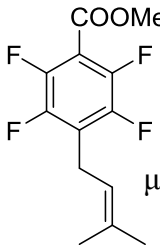
General procedure F was followed using methyl 2,3,4,5,6-pentafluorobenzoate (14.8 μL, 0.1 mmol, 1 equiv1,2,3,4,5-pentafluoro-6-((3-methyloct-1-en-3-yl)oxy)benzene (142 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **methyl (E)-2,3,5,6-tetrafluoro-4-(3-methyloct-2-en-1-yl)benzoate (5f)** with E:Z 1.3:1 as a colorless liquid in 64% ^{19}F NMR yield. Alkene geometry was assigned by NOE correlation of the allylic methylene to the cis substituent. ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.23 – -140.41 (m, 4F, major and minor), -143.13 (tt, *J* = 15.1, 6.7 Hz, 4F, major and minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, *J* = 7.3 Hz, 2H, major and minor), 3.96 (s, 6H, major and minor), 3.45 (d, *J* = 7.3 Hz, 4H, major and minor), 2.22 – 2.09 (m, 2H, minor), 1.95 (d, *J* = 7.8 Hz, 2H), 1.73 (s, 3H), 1.68 (s, 3H, minor), 1.45 – 1.14 (m, 12H, major and minor), 0.95 (t, *J* = 7.2 Hz, 3H, minor) – 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 146.2 – 143.6 (ddd, *J* = 12.9, 6.4, 4.8 Hz), 145.8 – 143.1 (dt, *J* = 15.9, 4.6 Hz), 139.5, 139.3, 123.8 (t, *J* = 18.7 Hz), 118.4, 117.8, 110.3 – 109.3 (m), 53.5 – 52.3 (m), 39.8 – 39.1 (m), 31.8 (d, *J* = 9.9 Hz), 31.4, 27.5, 22.5 (d, *J* = 9.3 Hz), 22.2, 15.9, 14.0. GC/MS (m/z, relative intensity) 332 (M+, 18), 301 (22), 256 (30), 216 (68).

General procedure G for photocatalytic prenylation reaction

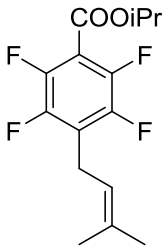


An NMR tube was charged with fluoroarene (0.1 mmol, 1.0 equiv), prenyl-OAr (0.6-0.8 mmol, 6-8 equiv), *N*,*N*-diisopropylethylamine (0.18-0.4 mmol, 1.8-4 equiv), distilled water (1-1.5 mmol, 10-15 equiv), *fac*-tris(2- phenyl pyridinato-*C*2, *N*) Iridium(III) ($Ir(ppy)_3$) (0.3 mM, 1 mL in MeCN), sealed glass capillary containing C_6D_6 and was capped with an NMR septum (Ace glass, part no. 9096-25). When reaction was run in greater than 0.1 mmol of fluoroarene, more than one NMR tube was used to set up the reaction and each NMR tube had 1 mL of reaction mixture. The reaction was degassed via Ar bubbling for 15 min at 0 °C (to avoid evaporation of *N*,*N* diisopropylethylamine and other volatile starting materials) and then placed in a light bath (*vide supra*) such that the lower portion of the tube was submerged under the isopropanol/water bath..

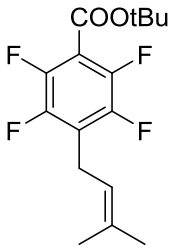
The reaction was monitored periodically by ^{19}F NMR (care was taken to exclude light while in transit). After the complete consumption of starting material, CH_3CN was removed via rotavap. The crude material was purified using prep TLC plate. If the reaction did not go to completion with the first addition of *N*,*N*-diisopropylethylamine, an additional 1 - 3 equiv of *N*,*N* - diisopropylethylamine was added to the reaction. Then the reaction was re-degassed and returned to the light bath. This sequence was repeated until the reaction reached completion as judged by 19F NMR.



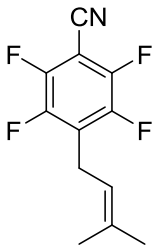
General procedure G was followed using methyl 2,3,4,5,6-pentafluorobenzoate (14.75 µL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 µL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 µL, 0.18 mmol, 1.8 equiv), distilled water (18 µL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **methyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3a)** as a colorless liquid in 68% ^{19}F NMR yield and 61% isolated yield (16.6 mg, 0.06 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.23 – -140.38 (m, 2F), -143.20 (dd, *J* = 21.4, 12.7 Hz, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, *J* = 7.4 Hz, 1H), 3.96 (s, 3H), 3.43 (d, *J* = 7.4 Hz, 2H), 1.74 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 146.1 – 143.6 (ddd, *J* = 12.9, 6.4, 4.8 Hz), 145.8 – 143.3 (dt, *J* = 15.9, 4.6 Hz), 135.3, 123.6 (t, *J* = 18.8 Hz), 118.2, 110.0 (t, *J* = 15.7 Hz), 53.1, 25.6, 22.2, 17.6. GC/MS (m/z, relative intensity) 276 (M+, 20), 261 (35), 245 (15). This product was also obtained when 2-fluoro-6-((2-methylbut-3-en-2-yl)oxy)pyridine was used as the prenyl source. However, in this case the reaction produced a significant side-product which we assume it to be methyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-enoyl)benzoate (oxidized product) based on GC/MS (m/z, relative intensity) 290 (M+, 40) which is the mass of the side product.



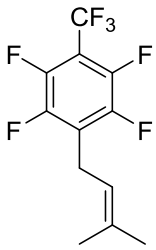
General procedure G was followed using isopropyl 2,3,4,5,6-pentafluorobenzoate (16.6 µL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 µL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 µL, 0.18 mmol, 1.8 equiv), distilled water (18 µL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **isopropyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3b)** as a colorless liquid in 65% ^{19}F NMR yield and 58% isolated yield (18.24 mg, 0.06 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -141.03 – -141.16 (m, 2F), -143.39 – -143.52 (m, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 – 5.25 (m, 1H), 5.15 (t, *J* = 7.3 Hz, 1H), 3.42 (d, *J* = 7.3 Hz, 2H), 1.74 (s, 3H), 1.69 (s, 3H), 1.37 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 145.9 – 143.6 (ddd, *J* = 12.9, 6.4, 4.8 Hz), 145.6 – 143.1 (dt, *J* = 15.9, 4.6 Hz), 135.2, 123.1 (t, *J* = 18.8 Hz), 118.4, 111.0 (t, *J* = 16.3 Hz), 70.6, 25.6, 22.2, 21.7, 17.6. GC/MS (m/z, relative intensity) 304 (M+, 12), 289 (7), 247 (22).



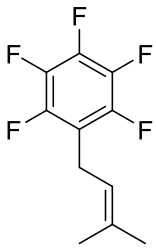
General procedure G was followed using isobutyl 2,3,4,5,6-pentafluorobenzoate (19.8 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **isobutyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3c)** as a colorless liquid in 66% ^{19}F NMR yield and 60% isolated yield (19.08 mg, 0.06 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.84 – -137.99 (m, minor), -141.06 – -141.21 (m, minor), -141.87 – -142.00 (m), -143.61 – -143.73 (m). ^1H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, *J* = 7.4 Hz, 1H), 3.41 (d, *J* = 7.4 Hz, 2H), 1.74 (s, 3H), 1.69 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (t, *J* = 3.0 Hz), 145.8 – 143.4 (ddd, *J* = 13.0, 6.8, 4.5 Hz), 145.4 – 142.9 (dt, *J* = 15.9, 4.6 Hz), 135.0, 122.5 (t, *J* = 18.8 Hz), 118.5, 112.1 (t, *J* = 16.8 Hz), 84.3, 28.1, 25.6, 22.1, 17.6. GC/MS (m/z, relative intensity) 318 (M+, 25), 262 (65), 247 (100).



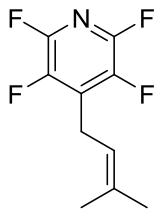
General procedure G was followed using 2,3,4,5,6-pentafluorobenzonitrile (12.9 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzonitrile (3d)** as a colorless liquid in 71% ^{19}F NMR yield and 64% isolated yield (14.58 mg, 0.06 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -133.13 – -133.26 (m, 2F), -140.61 (td, *J* = 16.4, 6.9 Hz, 2F). ^1H NMR (400 MHz, $CDCl_3$) δ 5.13 (t, *J* = 7.2 Hz, 1H), 3.48 (d, *J* = 7.3 Hz, 2H), 1.75 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3 – 145.7 (dt, *J* = 14.3, 3.8 Hz), 145.9 – 143.4 (m), 136.3, 127.5 (t, *J* = 18.6 Hz), 117.3, 107.7 (t, *J* = 3.7 Hz), 29.7, 25.7, 22.7, 17.7. GC/MS (m/z, relative intensity) 243 (M+, 34), 228 (40), 208 (18), 188 (35).



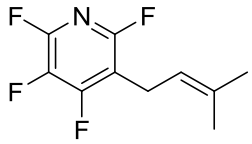
General procedure G was followed using 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (14.16 µL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 µL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 µL, 0.18 mmol, 1.8 equiv), distilled water (18 µL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **1,2,4,5-tetrafluoro-3-(3-methylbut-2-en-1-yl)-6-(trifluoromethyl)benzene (3e)** as a colorless liquid in 61% ^{19}F NMR yield and 57% isolated yield (16.3 mg, 0.057 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.20 (t, *J* = 21.5 Hz, 3F), -141.39 – -141.69 (m, 2F), -142.17 (td, *J* = 16.0, 6.5 Hz, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, *J* = 7.5 Hz, 1H), 3.46 (d, *J* = 7.4 Hz, 2H), 1.75 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2 – 143 (ddd, *J* = 17.1, 6.7, 4.0 Hz), 145.4 – 142.5 (ddd, *J* = 12.6, 7.3, 3.3 Hz), 135.7, 129.0, 128.2, 125.3, 117.8, 25.7, 22.2, 17.7. GC/MS (m/z, relative intensity) 286 (M+, 52), 271 (64), 231 (34).



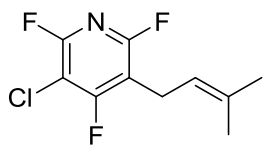
General procedure G was followed using pentafluorobenzene (11.6 µL, 0.1 mmol, 1 equiv), 2-fluoro-6-((2-methylbut-3-en-2-yl)oxy)pyridine (103 µL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 µL, 0.18 mmol, 1.8 equiv), distilled water (18 µL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of Ir(ppy)3 (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 1:1 hexane : DCM to afford **1,2,3,4,5-pentafluoro-6-(3-methylbut-2-en-1-yl)benzene (3f)** as a colorless liquid in 64% ^{19}F NMR yield and 55% isolated yield (13.9 mg, 0.06 mmol). Due to volatile nature of compound, minimal effort was given to remove the solvents. ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.31 (dd, *J* = 22.3, 8.2 Hz, 2F), -158.81 (t, *J* = 20.7 Hz, 1F), -163.29 (td, *J* = 22.3, 8.1 Hz, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, *J* = 7.3 Hz, 1H), 3.37 (d, *J* = 7.4 Hz, 2H), 1.74 (s, 3H), 1.69 (s, 3H). GC/MS (m/z, relative intensity) 236 (M+, 70), 221 (85), 201 (20). The compound produced a thermally generated impurity under GC conditions that was otherwise not observed in ^{1}H or ^{19}F NMR.



General procedure G was followed using pentafluoropyridine (10.9 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC with 100% hexanes to afford **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)pyridine (3g)** as a colorless liquid in 78% ^{19}F NMR yield and 74% isolated yield (15.33 mg, 0.07 mmol). Minimal effort was given to evaporate the solvent due to volatile nature of the product. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.72 – -91.93 (m, 2F), -145.20 – -145.42 (m, 2F). ^1H NMR (400 MHz, $CDCl_3$) δ 5.10 (t, *J* = 7.5 Hz, 1H), 3.42 (d, *J* = 7.5 Hz, 2H), 1.69 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7 – 141.3 (m), 141.5 – 138.7 (m), 136.4, 134.3 (t, *J* = 17.3 Hz), 116.9, 25.7, 22.9, 17.7. GC/MS (m/z, relative intensity) 219 (M+, 100), 204 (84), 184 (62), 177 (40).

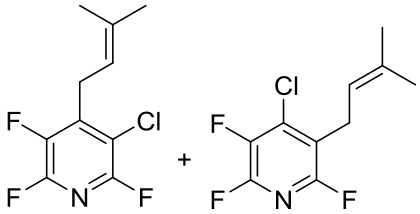


General procedure G was followed using 3-chloro-2,4,5,6-tetrafluoropyridine (12.44 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC with 100% hexanes to **2,3,4,6-tetrafluoro-5-(3-methylbut-2-en-1-yl)pyridine (3i)** as a colorless liquid in 57% ^{19}F NMR yield and 41% isolated yield (8.97 mg, 0.04 mmol). Minimal effort was given to evaporate the solvent due to volatile nature of the product. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.43 – -73.64 (m, 1F), -88.22 – -88.43 (m, 1F), -118.20 (q, *J* = 17.3 Hz, 1F), -167.39 (ddd, *J* = 24.1, 21.7, 19.6 Hz, 1F). ^1H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, *J* = 7.9 Hz, 1H), 3.32 (d, *J* = 7.2 Hz, 2H), 1.74 (s, 3H), 1.70 (s, 3H). GC/MS (m/z, relative intensity) 219 (M+, 95), 204 (80), 184 (60).



General procedure G was followed using 3,5-dichloro-2,4,6-trifluoropyridine (12.44 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv)

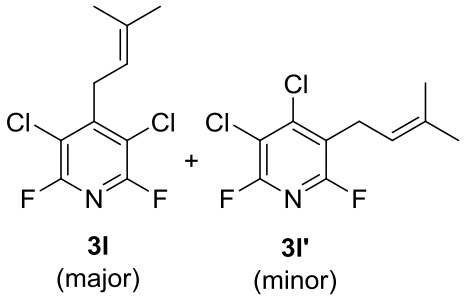
and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC with 100% hexanes to afford **3-chloro-2,4,6-trifluoro-5-(3-methylbut-2-en-1-yl)pyridine (3j)** as a colorless liquid in 55% ^{19}F NMR yield and 48% isolated yield (11.5 mg, 0.05 mmol). Minimal effort was given to evaporate the solvent due to volatile nature of the product. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.52 – -71.67 (m, 1F), -72.44 (t, *J* = 13.6 Hz, 1F), -97.91 (dd, *J* = 19.5, 13.8 Hz, 1F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (t, *J* = 7.4 Hz, 1H), 3.32 (d, *J* = 7.4 Hz, 2H), 1.74 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4 – 164.8 (dd, *J* = 10.5, 4.9 Hz), 158.7 – 156.3 (m), 156.5 – 154.1 (m), 135.2, 118.3, 115.4, 110.4 (ddd, *J* = 35.5, 20.0, 7.2 Hz), 25.6, 21.5, 17.7. GC/MS (m/z, relative intensity) 235 (M+, 50), 220 (100), 180 (70).



3k (major) **3k'** (minor)

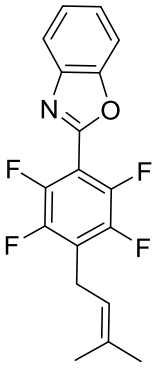
General procedure G was followed using 3,4-dichloro-2,5,6-trifluoropyridine (12.4 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The reaction was run at -15 ^{o}C instead of 0 ^{o}C to control the selectivity, delivering more para substituted product. The crude material was purified by using Prep TLC with 100% hexanes to afford **3-chloro-2,5,6-trifluoro-4-(3-methylbut-2-en-1-yl)pyridine (major, 3k)** as a colorless liquid in 81% ^{19}F NMR yield and 73% isolated yield (16.51 mg, 0.06 mmol). It comprised of a mixture of para substituted product and meta prenylated product in the ratio 14.5:1 (para:meta), as determined by ^{19}F NMR Pdt 1:Pdt 2 peak integrations. Looking at the 19F NMR of both isomers we see that these signals shift very closely to one another. Unfortunately, they shift too close to use recently developed 19F NMR prediction method (*JOC*, 2018, 83, 3220). We unsuccessfully attempted to derivatize the mixture, which might have allowed us to distinguish the molecules so the assignment is unfortunately made based on analogy with 3l/3l'. In the substrate **3k**, which has one fewer meta chlorines, we assume it follows the same pattern. Minimal effort was given to evaporate the solvent due to volatile nature of the product. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.85 (dd, *J* = 26.9, 12.3 Hz, 1F, minor), -74.15 (dd, *J* = 27.8, 12.8 Hz, 1F), -89.54 (dd, *J* = 20.9, 14.1 Hz, 1F, minor), -89.91 (dd, *J* = 21.5, 12.8 Hz), -145.00

(dd, *J* = 25.7, 21.3 Hz, 1F, minor), -145.33 (dd, *J* = 27.8, 21.7 Hz). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (m, 2H, major and minor), 3.58 (d, *J* = 7.2 Hz, 2H), 3.43 (d, *J* = 7.6 Hz, 2H, minor), 1.77 (s, 6H, major and minor), 1.70 (s, 6H, major and minor). GC/MS (m/z, relative intensity) 235 (M+, 52), 220 (100), 180 (90).



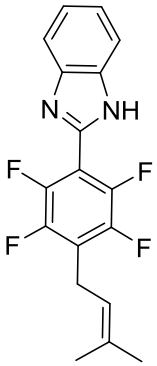
3l (major) **3l'** (minor)

General procedure G was followed using 3,4,5-trichloro-2,6-difluoropyridine (12.44 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC with 100% hexanes to afford **3,5-dichloro-2,6-difluoro-4-(3-methylbut-2-en-1-yl)pyridine (major, 3l)** as a colorless liquid in 77% ^{19}F NMR yield and 69% isolated yield (16.56 mg, 0.06 mmol). It comprised of a mixture of para substituted product (single peak for symmetrical F-atoms at -71.67 ppm) and meta prenylated product in the ratio 6:1 (para:meta), determined by ^{19}F NMR Pdt1:Pdt2 peak integrations. ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.67 (d, *J* = 16.4 Hz, 1F, minor), -71.67(s, 2F), -71.77 (d, *J* = 12.3 Hz, 1F, minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07(m, 1H), 4.99 (m, 1H, minor), 3.73 (d, *J* = 7.0 Hz, 2H), 3.49 (d, *J* = 7.1 Hz, 2H, minor), 1.84 (s, 3H), 1.79 (s, 3H, minor), 1.74 (s, 3H), 1.72 (s, 3H, minor). GC/MS (m/z, relative intensity) 251 (M+, 45), 216 (35), 200 (37).



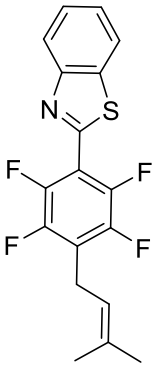
General procedure G was followed using 2-(perfluorophenyl)benzo[d]oxazole (18.6 μL, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC with 1% AcOH in hexanes to afford **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]oxazole (3m)** as a pale yellow solid in 62% ^{19}F NMR yield and 53% isolated yield (17.75 mg, 0.05 mmol),

which includes 20% HDF. ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.11 – -137.33 (m, 2F, minor), -137.68 (tt, *J* = 16.9, 5.2 Hz, 2F, minor), -138.79 – -138.93 (m, 2F), -143.04 (td, *J* = 15.1, 4.8 Hz, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (td, *J* = 7.7, 1.1 Hz, 1H), 7.65 (td, *J* = 7.8, 1.1 Hz 1H), 7.48 – 7.40 (m, 2H), 5.22 (t, *J* = 7.4 Hz, 1H), 3.51 (d, *J* = 7.4 Hz, 2H), 1.78 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 – 153.2 (m), 150.8 – 150.1 (m), 146.6 – 146.0 (m), 143.9 (dd, *J* = 21.2, 11.8 Hz), 141.2, 135.4, 126.6, 126.3, 125.2, 125.0, 123.5, 118.2, 111.0, 25.7, 22.4, 17.7. GC/MS (m/z, relative intensity) 335 (M+, 100), 320 (80), 300 (42), 280 (70).



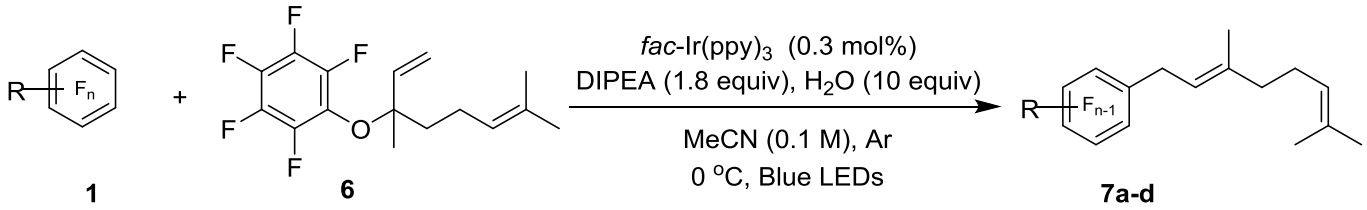
General procedure G was followed using 2-(perfluorophenyl)-1H-benzo[d]imidazole (28.4 mg, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. Due to lower solubility of the perfluoroarene starting material, another 1 mL of dry CH_3CN was added and the reaction mixture (0.05 M) was subjected to sonication after regular intervals. The crude material was purified by using Prep TLC with 100% hexanes followed by re-dipping the plate in 10:1 hexane:ether to afford **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)-1H-benzo[d]imidazole (3n)** as a pale yellow solid in 71% ^{19}F NMR yield and 68% isolated yield (22.7 mg, 0.068 mmol),which includes 12% HDF. ^{19}F NMR (376 MHz, CD_3CN) δ -140.04 – -140.35 (m, 2F, minor), -141.66 – -141.84 (m, 2F, minor), -142.27 – -142.43 (m, 2F), -145.11 – -145.28 (m, 2F). ^{1}H NMR (400 MHz, CD_3CN) δ 7.75 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.38 (dd, *J* = 6.1, 3.2 Hz, 2H), 5.25 (t, *J* = 7.4 Hz, 1H), 3.53 (d, *J* = 7.3 Hz, 2H), 1.79 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9 (m), 146.6 – 144.1 (ddt, *J* = 17.1, 12.7, 6.6 Hz), 145.7 – 143.2 (m), 140.3, 135.3, 124.0, 122.1 (t, *J* = 18.8 Hz), 118.3, 115.5 (dd, *J* = 33.9, 24.7 Hz), 107.0, 25.7, 22.3, 17.7. GC/MS (m/z, relative intensity) 334 (M+, 75), 319 (68), 291 (100), 278 (60).

General procedure G was followed using 2-(perfluorophenyl)benzo[d]thiazole (31.76 mg, 0.1 mmol, 1 equiv), 1,2,3,4,5-pentafluoro-6-((2-methylbut-3-en-2-yl)oxy)benzene (117.3 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003



equiv) in CH_3CN was used. The crude material was purified by using Prep TLC with 100% hexanes followed by re-dipping the plate in 10:1 hexane:ether to afford **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]thiazole (3o)** as a white solid in 68% ^{19}F NMR yield and 62% isolated yield (21.76 mg, 0.06 mmol). ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.17 – -140.29 (m, 2F), -143.38 – -143.51 (m, 2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.57 (td, *J* = 7.6, 1.2 Hz 1H), 7.48 (td, *J* = 7.7, 1.1 Hz, 1H), 5.23 (t, *J* = 7.4 Hz, 1H), 3.50 (d, *J* = 7.4 Hz, 2H), 1.78 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 152.9, 146.6 – 144.1 (ddd, *J* = 13.0, 6.8, 4.5 Hz), 145.4 – 142.9 (dt, *J* = 15.9, 4.6 Hz), 135.6 (t, *J* = 2.5 Hz), 135.2, 126.6, 126.1, 125.2, 124.1, 122.3 (t, *J* = 18.9 Hz), 121.4, 118.5, 25.7, 22.3, 17.7. GC/MS (m/z, relative intensity) 351 (M+, 100), 336 (70), 316 (46), 296 (73).

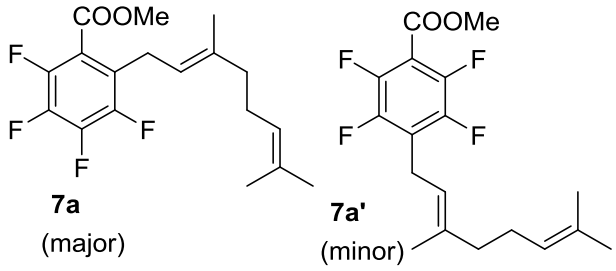
General procedure H for photocatalytic geranylation reaction



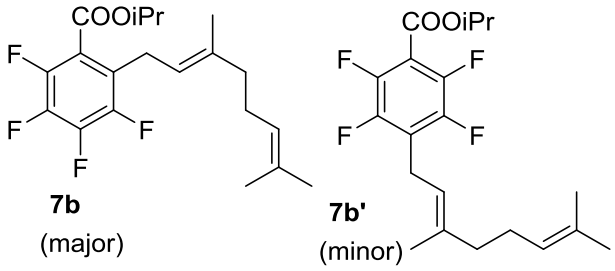
An NMR tube was charged with fluoroarene (0.1 mmol, 1.0 equiv), 1-((3,7-dimethylocta-1,6-dien-3-yl)oxy)-2,3,4,5,6-pentafluorobenzene (0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (0.18 mmol, 1.8 equiv), distilled water (1 mmol, 10 equiv), *fac*-tris(2- phenyl pyridinato-*C*2, *N*) Iridium(III) ($Ir(ppy)_3$) (0.3 mM, 1 mL in MeCN), sealed glass capillary containing C_6D_6 and was capped with an NMR septum (Ace glass, part no. 9096-25). When reaction was run in greater than 0.1 mmol of fluoroarene, more than one NMR tube was used to set up the reaction and each NMR tube had 1 mL of reaction mixture. The reaction was degassed via Ar bubbling for 15 min at 0 °C (to avoid evaporation of *N*,*N*-diisopropylethylamine and other volatile starting materials) and then placed in a light bath (*vide supra*) such that the lower portion of the tube was submerged under the isopropanol/water bath.

The reaction was monitored periodically by ^{19}F NMR (care was taken to exclude light while in transit). After the complete consumption of starting material, CH_3CN was removed via rotavap.

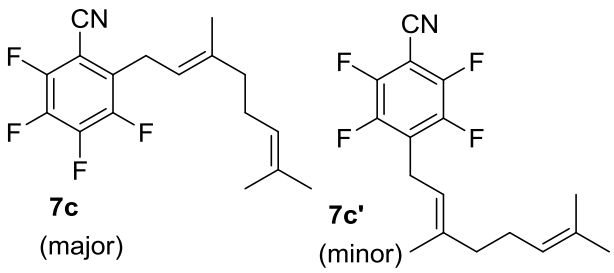
The crude material was purified using prep TLC plate. If the reaction did not go to completion with the first addition of *N*,*N*-diisopropylethylamine, an additional 1-3 equiv of *N*,*N* -diisopropylethylamine was added to the reaction. Then the reaction was re-degassed and returned to the light bath. This sequence was repeated until the reaction reached completion as judged by ^{19}F NMR.



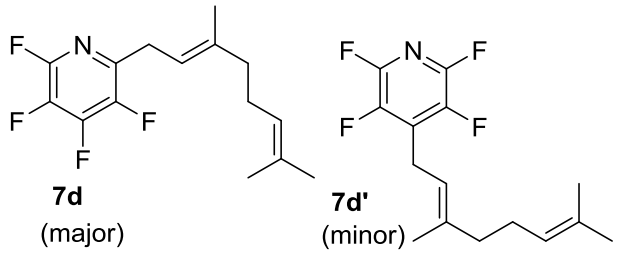
General procedure H was followed using methyl 2,3,4,5,6-pentafluorobenzoate (14.75 μL, 0.1 mmol, 1 equiv), 1-((3,7-dimethylocta-1,6-dien-3-yl)oxy)-2,3,4,5,6-pentafluorobenzene (147 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')** as a colorless liquid in 42% and 27% ^{19}F NMR yield respectively (*o*-Ger : *p*-Ger = 1.55:1). This was determined using ^{19}F NMR peak integrations (four –F peaks as a result of *ortho*-substitution and two peaks arising from *para*-substitution, see the discussion on the assignment on S-43). ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.34 – -134.51 (m, 1F), -138.07 (dd, *J* = 22.8, 12.4 Hz, 1F), -140.14 (ddd, *J* = 21.6, 12.4, 5.2 Hz, 1F), -140.21 – -140.38 (m, 2F, minor), -140.44 (ddd, *J* = 21.8, 12.4, 5.2 Hz, 1F), -142.99 – -143.15 (m, 2F, minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (t, *J* = 7.0 Hz, 1H), 5.16 (t, *J* = 14.6 Hz, 2H, major and minor), 5.03 (t, *J* = 7.5 Hz, 1H, minor), 3.97 (s, 3H), 3.96 (s, 3H, minor), 3.45 (d, *J* = 7.3 Hz, 2H), 3.19 (d, *J* = 10.7 Hz, 2H, minor), 2.34 – 1.96 (m, 8H, major and minor), 1.77 (d, *J* = 1.5 Hz, 3H), 1.74 (s, 3H, minor), 1.70 (s, 3H), 1.69 (s, 3H, minor), 1.64 (s, 3H), 1.63 (s, 3H, minor).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 160.2, 147.1 – 145.4 (m), 146.4 – 143.5 (m), 145.9 – 143.6 (m), 145.5 – 142.8 (m), 140.2, 138.8 (d, *J* = 13.0 Hz), 132.1, 131.7, 127.4 (t, *J* = 17.2 Hz), 123.9, 123.7, 121.8, 118.7, 118.3, 110.1 (t, *J* = 15.7 Hz), 53.1, 49.2, 41.8, 39.5, 37.2, 34.3, 31.8, 30.4, 26.4, 26.3, 26.1, 25.7, 25.6, 25.2, 22.2, 17.6, 16.1. GC/MS (m/z, relative intensity) 344 (M+, 15), 313 (10), 301 (20).



General procedure H was followed using isopropyl 2,3,4,5,6-pentafluorobenzoate (16.7 μL, 0.1 mmol, 1 equiv), 1-((3,7-dimethylocta-1,6-dien-3-yl)oxy)-2,3,4,5,6-pentafluorobenzene (147 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **isopropyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7b) and isopropyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6- tetrafluorobenzoate (7b')** as a colorless liquid in 42% and 26% ^{19}F NMR yield respectively (*o*-Ger : *p*-Ger = 1.6:1). This was determined using ^{19}F NMR peak integrations (assignment was made based on the analogy with **7a**). ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.55 – -134.77 (m, 1F), -138.32 (dd, *J* = 22.8, 12.4 Hz, 1F), -140.82 – -140.97 (m, 1F), -140.99 – -141.17 (m, 2F, minor), -141.17 – -141.27 (m, 1F), -143.22 – -143.44 (m, 2F, minor). ^1H NMR (400 MHz, $CDCl_3$) δ 5.44 (t, *J* = 7.0 Hz, 2H), 5.30 (hept, 2H, major and minor), 5.15 (t, *J* = 9.2 Hz, 2H, major and minor), 5.05 – 5.00 (m, 1H, minor), 3.44 (d, *J* = 7.3 Hz, 3H), 3.18 (d, *J* = 10.7 Hz, 3H, minor), 2.33 – 2.01 (m, 8H, major and minor), 1.76 (s, 3H), 1.73 (s, 3H, minor), 1.70 (d, *J* = 2.3 Hz, 3H, minor), 1.65 (s, 3H), 1.63 (d, 3H, minor), 1.57 (s, 3H), 1.39 (d, 3H), 1.38 (d, 3H, minor), 1.37 (d, 3H), 1.36 (d, 3H, minor). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 159.2, 147.9 – 146.4 (m), 147.2 – 145.8 (m), 147.1 – 143.0 (m), 144.8 – 142.6 (m), 140.2, 138.8, 138.7, 132.1, 131.7, 127.0, 126.6, 123.8, 123.7, 123.1, 121.9, 119.8, 118.9, 118.3, 111.3 – 110.8 (m), 70.7, 70.6, 53.4, 49.2, 41.9, 39.5, 37.2, 34.3, 30.4, 26.3 (d, *J* = 9.9 Hz), 26.1 (d, *J* = 6.7 Hz), 25.7 (d, *J* = 8.6 Hz), 25.3, 22.1 (d, *J* = 5.9 Hz), 21.7, 17.6, 16.0. GC/MS (m/z, relative intensity) 372 (M+, 20), 329 (25), 313 (20).



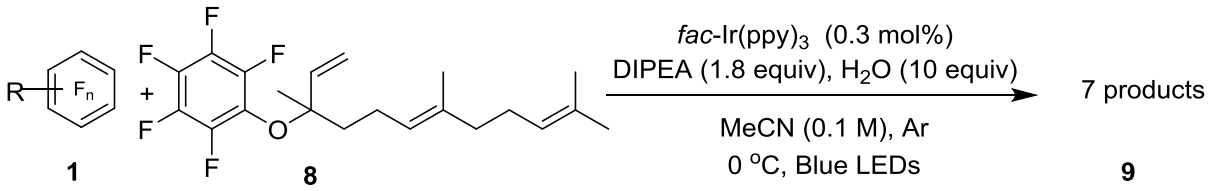
General procedure H was followed using Pentafluorobenzonitrile (12.6 μL, 0.1 mmol, 1 equiv), 1-((3,7-dimethylocta-1,6-dien-3-yl)oxy)-2,3,4,5,6-pentafluorobenzene (147 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzonitrile (7c) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzonitrile (7c')** as a colorless liquid in 45% and 27% ^{19}F NMR yield respectively (*o*-Ger : *p*-Ger = 1.65:1). This was determined using ^{19}F NMR peak integrations (four –F peaks as a result of *ortho*-substitution and two peaks arising from *para*-substitution). Assignment was made based on the analogy with **7a.** ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.13 (ddt, *J* = 16.9, 11.2, 5.6 Hz, 1F), -133.01 (ddd, *J* = 20.6, 12.1, 7.4 Hz, 1F), -133.22 (tt, *J* = 16.6, 8.4 Hz, 2F, minor), -133.47 (ddd, *J* = 22.0, 12.0, 7.3 Hz, 1F), -135.40 (dd, *J* = 22.1, 12.1 Hz, 1F), -140.50 (tt, *J* = 16.5, 8.5 Hz, 2F, minor). ^1H NMR (400 MHz, $CDCl_3$) δ 5.44 (t, *J* = 7.0 Hz, 2H, major and minor), 5.13 (t, *J* = 7.4 Hz, 1H), 5.01 (t, *J* = 7.5 Hz, 1H, minor), 3.49 (d, *J* = 1.8 Hz, 2H), 3.23 (d, 2H, minor), 2.36 – 1.92 (m, 8H, major and minor), 1.77 (s, 3H), 1.74 (s, 3H, minor), 1.69 (s, 3H), 1.64 (s, 3H, minor), 1.62 (s, 3H, minor), 1.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1 (d, *J* = 6.4 Hz), 147.9 (d, *J* = 6.6 Hz), 148.8 – 146.2 (m), 148.1 – 145.8 (m), 144.6 (dt, *J* = 15.9, 4.6 Hz), 143.8 – 142.6 (dt, *J* = 15.9, 4.6 Hz), 140.1, 139.8, 132.2, 131.8, 131.1, 127.7, 127.5, 123.6, 121.7, 117.1, 107.7, 91.8, 49.5, 39.5, 37.4, 34.2, 30.2, 26.2, 25.9 (d, *J* = 6.8 Hz), 25.7, 25.2, 23.2, 22.6, 22.2 (d, *J* = 6.2 Hz), 17.6 (d, *J* = 2.9 Hz), 16.1. GC/MS (m/z, relative intensity) 311 (M+, 15), 296 (5), 268 (35), 255 (10).



General procedure H was followed using Pentafluoropyridine (10.9 μL, 0.1 mmol, 1 equiv), 1-((3,7-dimethylocta-1,6-dien-3-yl)oxy)-2,3,4,5,6-pentafluorobenzene (147 μL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine

(31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of Ir(ppy)3 (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The crude material was purified by using Prep TLC 10:1 hexane:diethyl ether to afford **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluoropyridine (7d) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluoropyridine (7d')** as a colorless liquid in 43% and 26% ^{19}F NMR yield respectively (*o*-Ger : *p*-Ger = 1.67:1). Assignment was made based on the analogy with **7a**. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.62 – -92.13 (m, 3F, major and minor), -92.39 (ddd, *J* = 28.6, 21.8, 14.0 Hz, 1F), -136.75 – -136.99 (m, 1F), -140.61 – -140.98 (m, 1F), -145.00 – -145.32 (m, 2F, minor). ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 – 5.39 (m, 1H), 5.22 – 5.14 (m, 1H), 5.14 – 5.08 (m, 1H, minor), 5.02 (dt, *J* = 6.8, 4.1 Hz, 1H, minor), 3.50 (d, *J* = 7.4 Hz, 2H), 3.23 (d, *J* = 10.9 Hz, 2H, minor), 2.38 – 1.96 (m, 8H, major and minor), 1.77 (s, 3H), 1.75 (s, 3H, minor), 1.69 (s, 3H), 1.64 (s, 3H, minor), 1.62 (s, 3H), 1.57 (s, 3H, minor). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 – 148.9 (m), 148.6 – 147.9 (m), 147.6 – 147.1 (m), 146.9 – 146.2 (m), 145.7 – 142.7 (m), 144.9 – 142.1 (m), 140.2, 139.9, 139.8, 139.1 (d, *J* = 9.0 Hz), 131.8, 123.6, 123.5, 121.7, 117.5, 116.8, 49.7, 41.8, 39.5, 37.1, 34.1, 26.3, 25.7 – 25.4 (m), 25.2, 22.9 – 22.7 (m), 22.6, 22.1 (d, *J* = 6.0 Hz), 17.6, 16.1. GC/MS (m/z, relative intensity) 287 (M+, 30), 272 (10), 258 (8), 244 (35).

General procedure I for the attempted photocatalytic farnesylation reaction

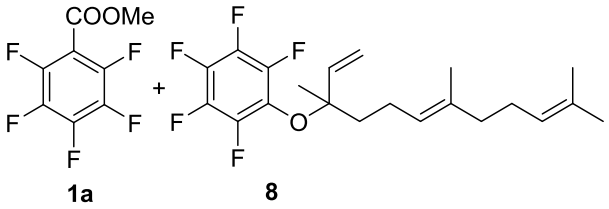


An NMR tube was charged with fluoroarene (0.1 mmol, 1.0 equiv), 1-((3,7-dimethylocta-1,6-dien-3-yl)oxy)-2,3,4,5,6-pentafluorobenzene (0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (0.18 mmol, 1.8 equiv), distilled water (1 mmol, 10 equiv), *fac*-tris(2- phenyl pyridinato-*C*2, *N*) Iridium(III) (Ir(ppy)3) (0.3 mM, 1 mL in MeCN), sealed glass capillary containing C_6D_6 and was capped with an NMR septum (Ace glass, part no. 9096-25). When reaction was run in greater than 0.1 mmol of fluoroarene, more than one NMR tube was used to set up the reaction and each NMR tube had 1 mL of reaction mixture. The reaction was degassed via Ar bubbling for 15 min at 0 °C

(to avoid evaporation of *N,N* diisopropylethylamine and other volatile starting materials) and then placed in a light bath (*vide supra*) such that the lower portion of the tube was submerged under the isopropanol/water bath.

The reaction was monitored periodically by ^{19}F NMR (care was taken to exclude light while in transit). After the complete consumption of starting material, CH_3CN was removed via rotavap. The crude material was purified using prep TLC plate. If the reaction did not go to completion with the first addition of *N,N*-diisopropylethylamine, an additional 1 - 3 equiv of *N,N* - diisopropylethylamine was added to the reaction. Then the reaction was re-degassed and returned to the light bath. This sequence was repeated until the reaction reached completion as judged by ^{19}F NMR.

General procedure I was followed using methyl 2,3,4,5,6-pentafluorobenzoate (14.7 μL, 0.1 mmol, 1 equiv), (E)-1,2,3,4,5-pentafluoro-6-((3,7,11-trimethyldodeca-1,6,10-trien-3-yl)oxy)benzene (154 μL, 0.6 mmol, 6 equiv), *N,N*diisopropylethylamine (31.3 μL, 0.18 mmol, 1.8 equiv), distilled water (18 μL, 1 mmol, 10 equiv) and 1.0 mL of stock solution of $Ir(ppy)_3$ (0.16 mg, 0.0003 mmol, 0.003 equiv) in CH_3CN was used. The reaction produced 7 products (determined by GC/MS). An attempt was made to improve the selectivity by lowering the temperature to -20 ^oC and/or varying the amount of farnesyl ether in the reaction but these multiple products were still observed at those conditions.



1a **8**

$Ir(ppy)_3$ in MeCN (0.3 mol%)
DIPEA (1.8 eq), H_2O (10 equiv)
Blue LEDs, Ar, 0°C
→ 7 C-C coupled products **9a-g**

std: (at 0 °C) 19F NMR :	Time	1a	HDF	9a-g
	3.5 h	-	38%	59%

Optimizations of above reaction at **-20 °C**

Entry	Conditions	Time	1a	HDF	9a-g
1.	6 equiv ether	5 h	56%	17%	26.7%
2.	3 equiv ether	5 h	24%	56%	21%
3.	1 equiv ether	5 h	9%	83%	8%
4.	6 equiv ether, no water	5 h	62%	22%	16%

Multiple C-C coupled product formations observed from the initial stage of reaction.

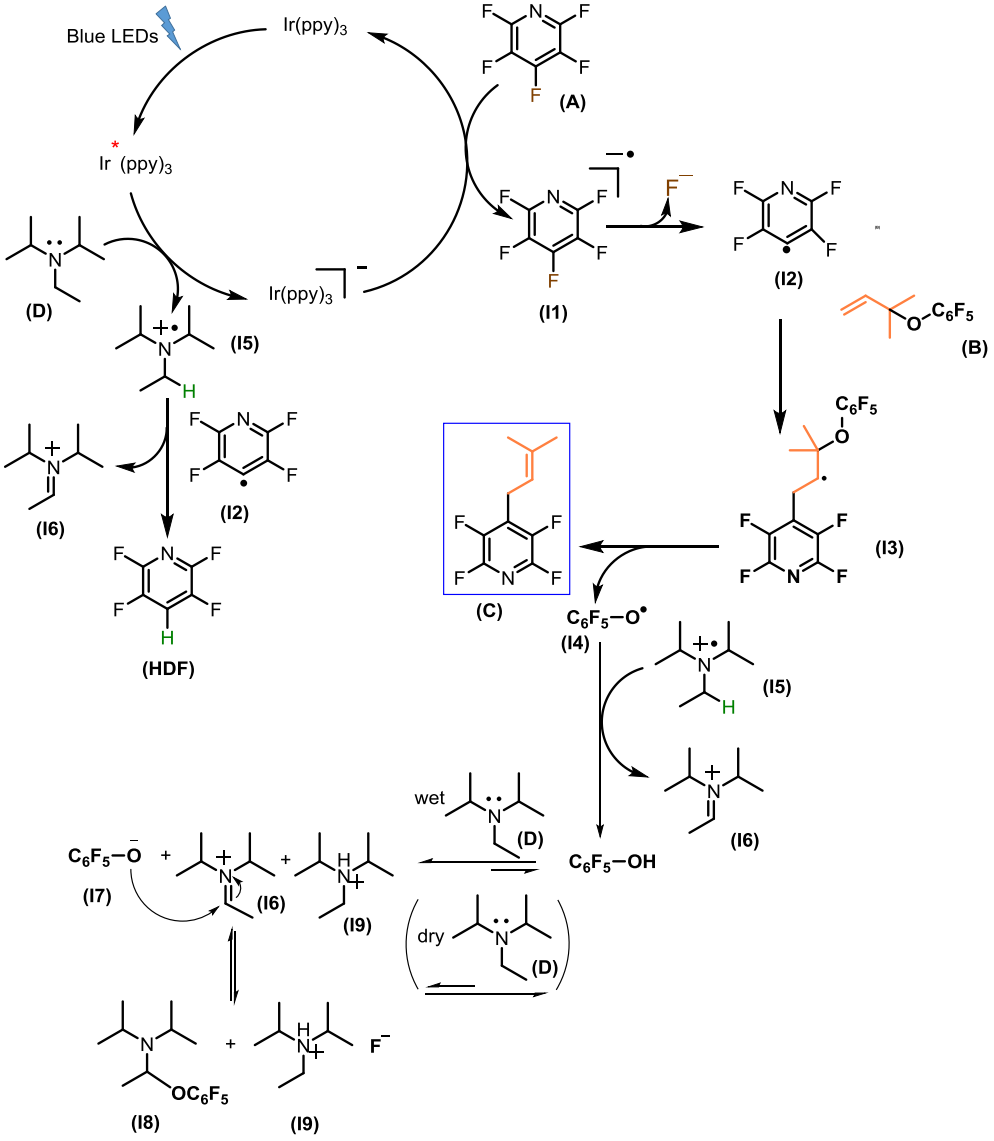
Product ratios appeared to change on varying conditions.

(Determined by calculating peak areas in GC/MS)

Conditions	9a	9b	9c	9d	9e	9f	9g	
6 equiv **8** 10 equiv H_2O	8.13		10.9	1.28	1.15	1	16.74	(std)
3 equiv **8** 10 equiv H_2O	9.19	5.04	12.36	12.64	19.39	1	23.53	
1 equiv **8** 10 equiv H_2O	8.31		7.96	7.76	13.57	1	16.79	
6 equiv **8** no H_2O	3.84		3.11	3.17	5.83	1	6.77	
	Ratio of products →							

In some cases **9a** and **9b** did not resolve completely on GCMS and have been represented by a —— to show a combined peak appearing at a specific retention time.

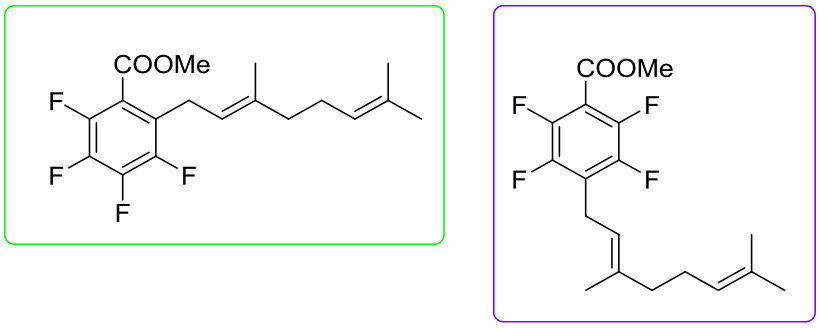
Working mechanism:



We believe that the reaction progresses with excitation of $Ir(ppy)_3$ in the presence of blue LEDs to form a long lived triplet excited state. This further undergoes endothermic single electron transfer from DIPEA forming the radical anion *via* reductive quenching. It can then transfer an electron exothermically to the perfluoroarene (A) resulting in the formation of a perfluoroaryl radical anion (I1) that causes extrusion of fluoride ion to form a perfluoroaryl radical (I2). This perfluoroaryl radical (I2) in turn attacks the prenylating agent (B) selectively at the unsubsituted terminus of the alkene to generate a new radical (I3) followed by the loss of a phenoxy radical (I4) and results in

the desired C–C coupled prenylated product (C). The perfluoroaryl radical (I2) generated upon fluoride fragmentation could also undergo undesired hydrogen atom transfer from the amine radical cation (I5) (and potentially the amine D, α C–H BDE of 91 kcal/mol)[4] to form undesired HDF product. The phenoxy radical (I4) generated (BDE C_6H_5O–H is 87.6 kcal/mol)[5] during the course of reaction is capable of abstracting hydrogen atom from amine radical cation (I5, α C–H BDE ~ 42 kcal/mol)[6] to form pentafluorophenol and generate an iminium ion (I6). We believe that in the presence of water, the equilibrium is shifted towards the ionic forms (the left). Our control studies with C_6F_5OH demonstrate its inhibitory and deleterious effect in the absence of water (see above). This may be because it serves as a good HAT donor. We speculate that the phenolate (I7) could also have a beneficial role by attacking the iminium ion (I6) to form the N-acetal species (I8).

Evidence for ortho C-F Functionalization



One interesting feature of this project was the observed change in regioselectivity of the major product upon moving from prenylation to geranylation. This is the first report of preferential ortho fragmentation based on reagent (we have shown that an intramolecular hydrogen bond can cause the ortho fragmentation to occur preferentially). Thus, we approached this with a healthy skepticism. We based the proposed structure on the basis of several arguments which are outlined below. First, we observed 6 peaks in the ^{19}F NMR which could arise from 3 para-substituted products in which 2 of them were produced in the same ratio, or alternatively the reaction produces two products in total, i.e., expected para-geranylated product that accounts for two 1:1 –F signals and an ortho-geranylated product which accounts for four –F signals in a 1:1:1:1 relationship with one another. We ruled out the possibility of formation of 3 para-substituted products as the four –F signals were found to be present in the same spin system as confirmed by ^{19}F-^{19}F TOCSY. Another major evidence that supported ortho-geranylation was that upon running a $AgNO_3$ impregnated silica column chromatography in an attempt to separate the C–C coupled products from one another, we observed that the compound eluted in such a way that each and every fraction (from very early to late fractions) produced four 1:1:1:1 peaks in ^{19}F NMR, suggesting either perfect co-elution of two compounds or that this was a single compound. Other evidences included appropriate and distinct vinyl protons, methyl ester, methylene and methyl peaks in ^{1}H NMR, two separate peaks of same m/z determined by GCMS, genuine 4-bond F–F couplings observed in ^{19}F-^{19}F COSY[7]. Another very important study to validate ortho C-C coupled product was to calculate predicted ^{19}F NMR shifts for ortho-geranylated product. We observed that the actual ^{19}F NMR

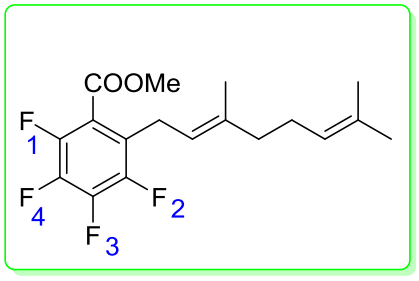
shifts fell in the acceptable range of error.[8] Apart from that, we determined that all the F-atoms were attached to distinct C-atoms by ^{19}F-^{13}C HSQC and ^{1}H-^{13}C HSQC further confirmed our assignment of vinyl, methyl ester, benzylic methylene, methylene from geranyl chain and methyl protons on ^{1}H NMR. Alkene geometry was assigned by NOE correlations.

1. ^{19}F NMR

   Observation:

   - Four distinct 1:1:1:1 peaks with similar splitting pattern supported o-Geranylated pdt (-134.4, -138.2, -140, -140.4)
   - Two 1:1 peaks confirmed p-Geranylated pdt (-140.3 and -143.1)

2. ^{1}H NMR
   - 4 vinyl protons (3.94-4.0 ppm)
   - Methylene (3.2-3.4 ppm and 1.95-2.35 ppm) and methyl peaks (1.55-2.78 ppm) from both compounds
3. GC/MS
   - 2 peaks each of M+ 344 (at 17.4 and 17.6 mins retention time)
4. Isolation using $AgNO_3$ impregnated silica column
   - ^{19}F NMR of various fractions contained either 1:1:1:1 peaks for o-Geranylated product or 1:1 peaks for p-Geranylated product
5. ^{19}F-^{19}F TOCSY
   - 4 –F peaks in the same spin-system
   - 2 –F peaks within another spin-system
6. ^{19}F-^{19}F COSY
   - 4-bond coupling stronger than 3-bond coupling
   - F-1 and F-3 showed strong correlation
   - F-2 showed strong correlation with F-4
   - Weak interaction observed between F-1 and F-4

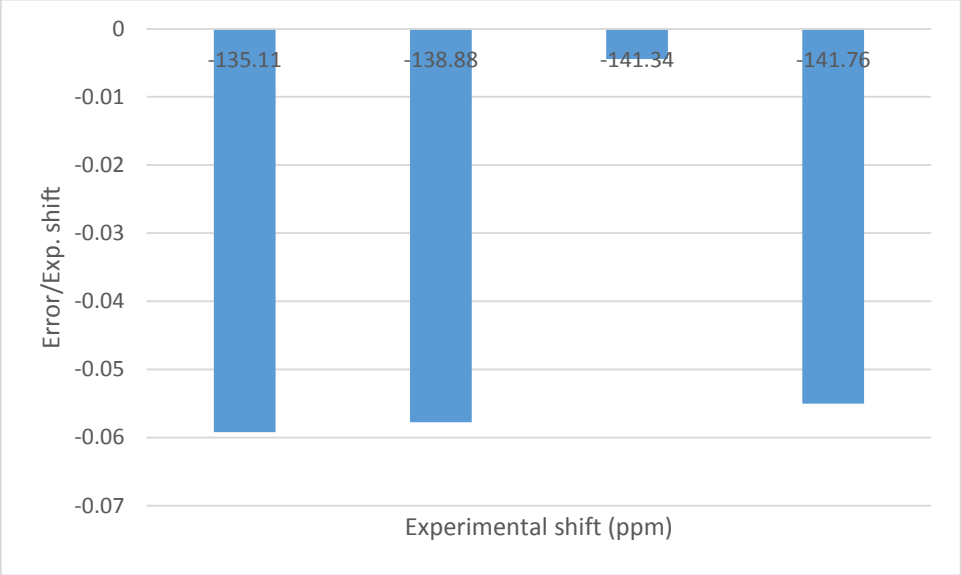


7. Structure prediction using NMR calculations

Experimental Shift	Isotropic	Calculated Shift	Error	
-135.11	312.5896	-127.3452	8	(ppm)
-138.88	315.2231	-129.9849	8.02	
-141.34	327.1844	-141.9751	0.63	
-141.76	334.8345	-149.6436	7.8	

Calculated isotropic values, and shifts of compounds
Geometry optimizations and NMR calculations run using the B3LYP/6-31+G(d,p) method in gas phase using Gaussian09. The shifts were scaled based on the equation y=-0.9968x+184.92.

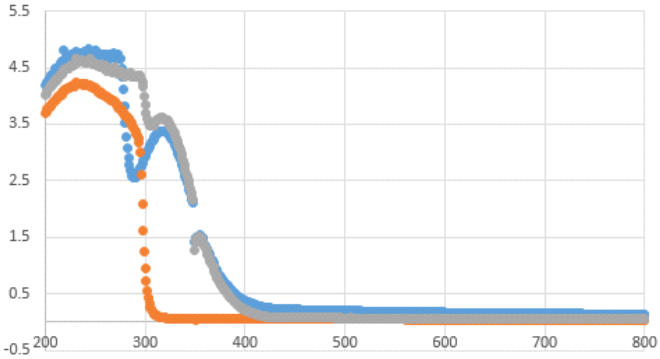
- The actual NMR shifts lie within the acceptable error range.

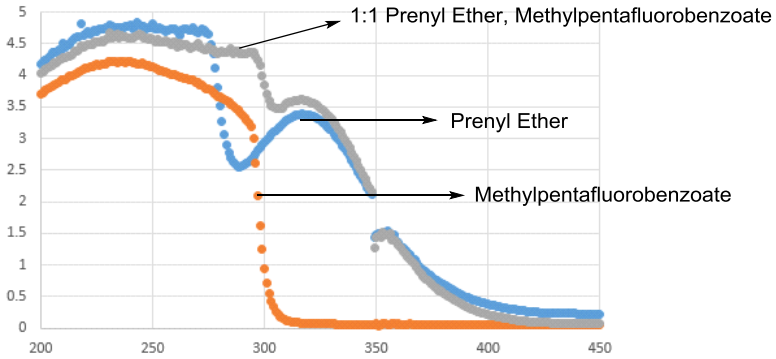


8. $^{19}F - ^{13}C$ HSQC
   - The four –F peaks are attached to four different C-atoms
9. $^{1}H-^{13}C$ HSQC
   - A total of 4 vinyl protons from both molecules 5.0-5.5 ppm
   - 2 separate methyl ester peaks (3.94-4.0 ppm)
   - 2 benzylic methylene signals (3.2 and 3.4 ppm)
   - Presence of 4 types of alkyl methylene signals (1.95-2.35 ppm) [This region includes peaks from minor side-products]
   - Both products produces a total of 6 different methyl signals in the alkyl region (1.55-2.78 ppm) [This region also includes peaks from minor side-products]

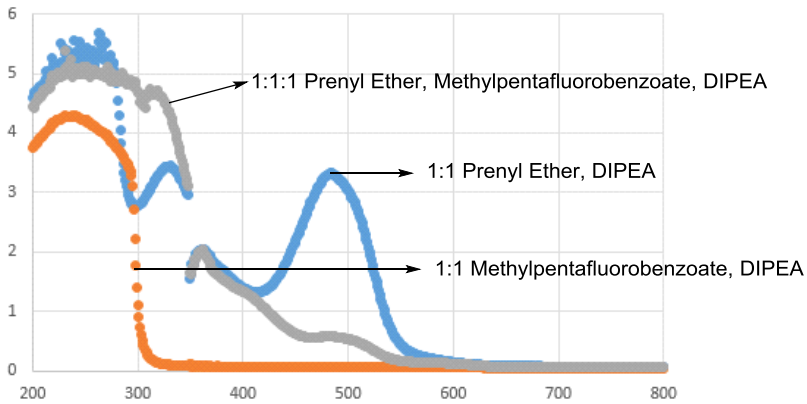
UV-Vis Experiments:

Prenyl ether and Methylpentafluoro benzoate in MeCN (0.1 M)

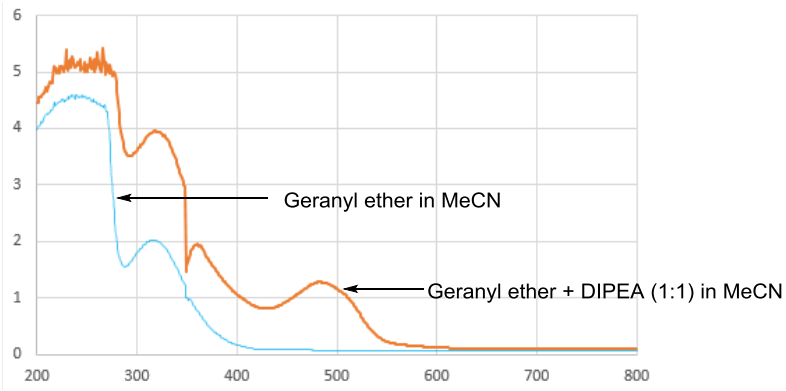


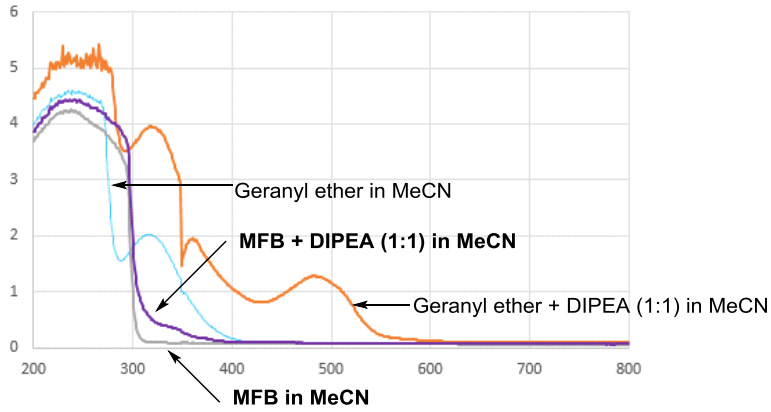


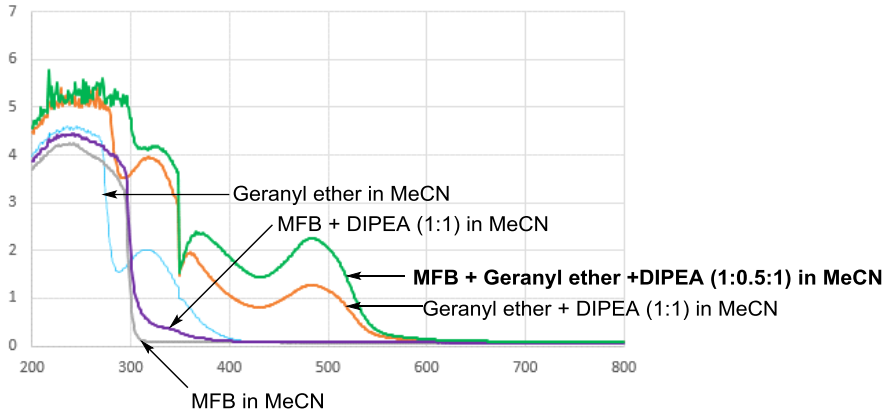
Prenyl Ether Methyl Pentafluorobenzoate DIPEA in MeCN (0.1 M)

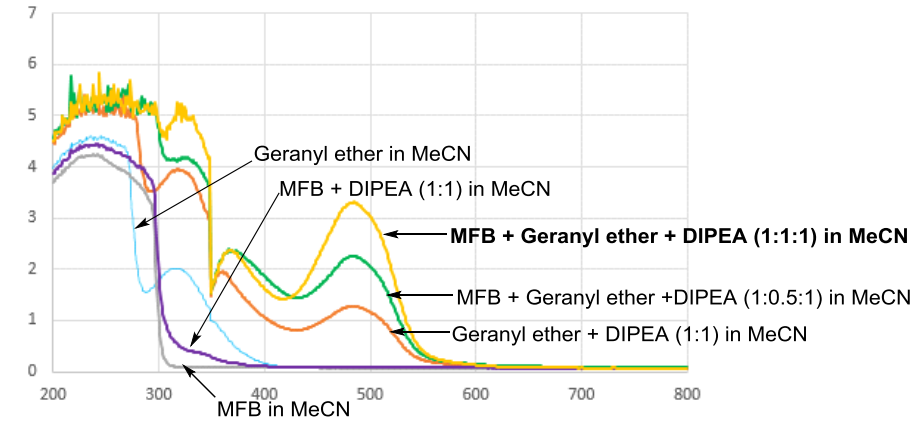


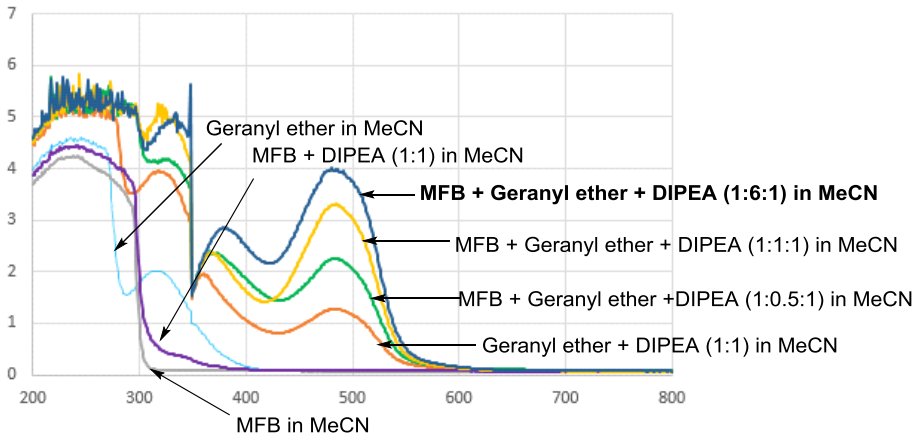
Geranyl ether and methylpentafluoro benzoate (0.1 M) in MeCN

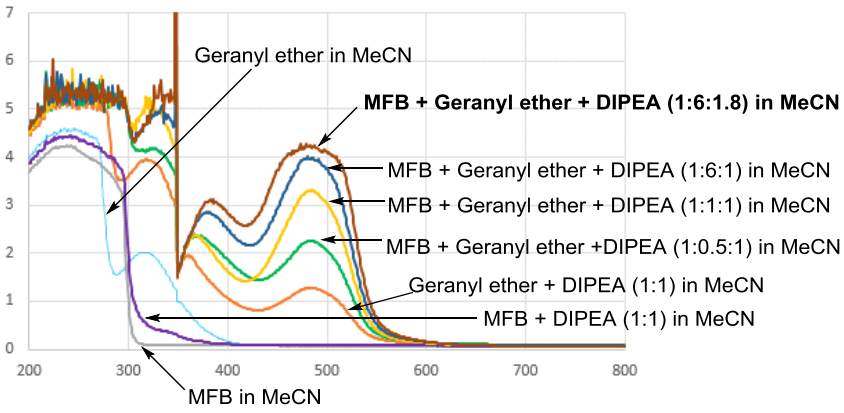


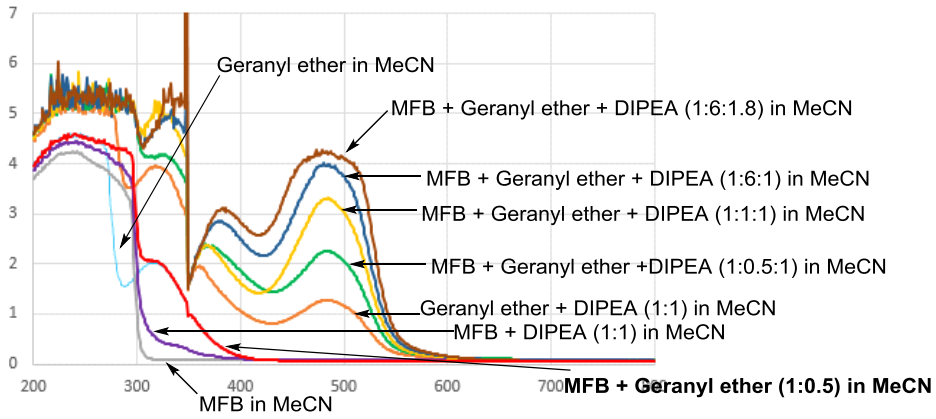


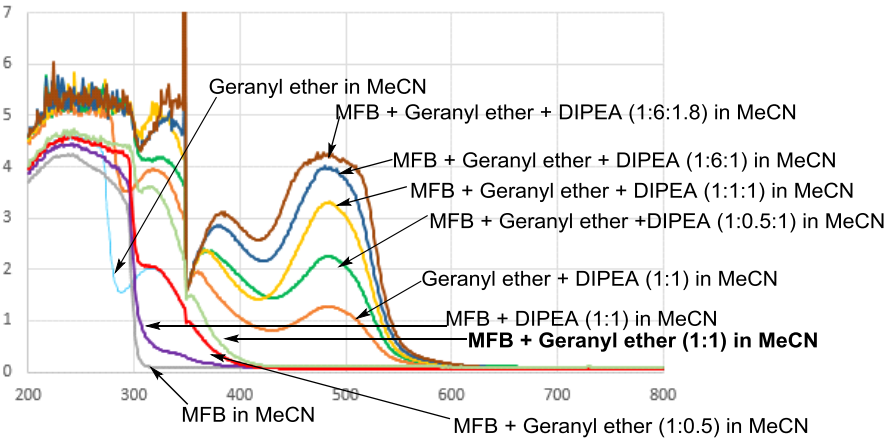


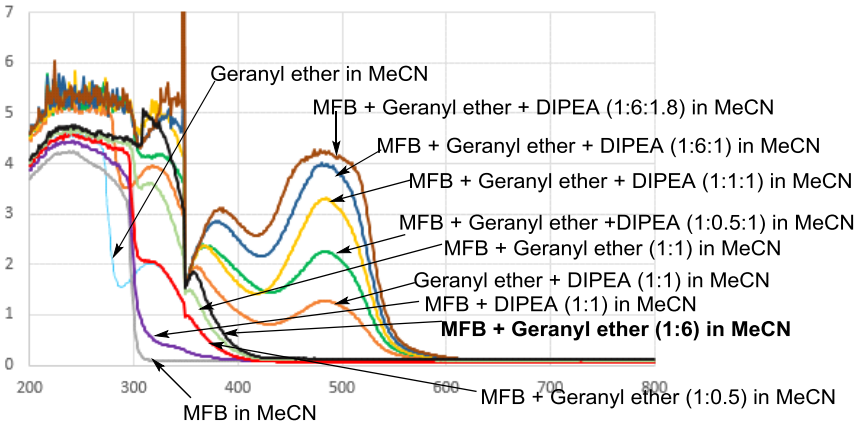

Geranyl ether in MeCN
MFB + DIPEA (1:1) in MeCN
MFB + Geranyl ether + DIPEA (1:1:1) in MeCN
MFB + Geranyl ether +DIPEA (1:0.5:1) in MeCN
Geranyl ether + DIPEA (1:1) in MeCN
MFB in MeCN


Geranyl ether in MeCN
MFB + DIPEA (1:1) in MeCN
MFB + Geranyl ether + DIPEA (1:6:1) in MeCN
MFB + Geranyl ether + DIPEA (1:1:1) in MeCN
MFB + Geranyl ether +DIPEA (1:0.5:1) in MeCN
Geranyl ether + DIPEA (1:1) in MeCN
MFB in MeCN


Geranyl ether in MeCN
MFB + Geranyl ether + DIPEA (1:6:1.8) in MeCN
MFB + Geranyl ether + DIPEA (1:6:1) in MeCN
MFB + Geranyl ether + DIPEA (1:1:1) in MeCN
MFB + Geranyl ether +DIPEA (1:0.5:1) in MeCN
Geranyl ether + DIPEA (1:1) in MeCN
MFB + DIPEA (1:1) in MeCN
MFB in MeCN

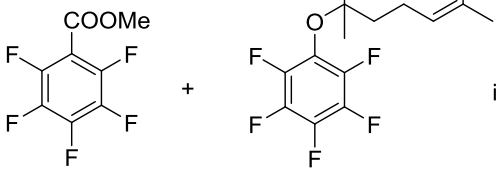

Geranyl ether in MeCN
MFB + Geranyl ether + DIPEA (1:6:1.8) in MeCN
MFB + Geranyl ether + DIPEA (1:6:1) in MeCN
MFB + Geranyl ether + DIPEA (1:1:1) in MeCN
MFB + Geranyl ether +DIPEA (1:0.5:1) in MeCN
Geranyl ether + DIPEA (1:1) in MeCN
MFB + DIPEA (1:1) in MeCN
MFB + Geranyl ether (1:0.5) in MeCN
MFB in MeCN


Geranyl ether in MeCN
MFB + Geranyl ether + DIPEA (1:6:1.8) in MeCN
MFB + Geranyl ether + DIPEA (1:6:1) in MeCN
MFB + Geranyl ether + DIPEA (1:1:1) in MeCN
MFB + Geranyl ether +DIPEA (1:0.5:1) in MeCN
Geranyl ether + DIPEA (1:1) in MeCN
MFB + DIPEA (1:1) in MeCN
MFB + Geranyl ether (1:1) in MeCN
MFB in MeCN
MFB + Geranyl ether (1:0.5) in MeCN


Geranyl ether in MeCN
MFB + Geranyl ether + DIPEA (1:6:1.8) in MeCN
MFB + Geranyl ether + DIPEA (1:6:1) in MeCN
MFB + Geranyl ether + DIPEA (1:1:1) in MeCN
MFB + Geranyl ether +DIPEA (1:0.5:1) in MeCN
MFB + Geranyl ether (1:1) in MeCN
Geranyl ether + DIPEA (1:1) in MeCN
MFB + DIPEA (1:1) in MeCN
MFB + Geranyl ether (1:6) in MeCN
MFB + Geranyl ether (1:0.5) in MeCN
MFB in MeCN

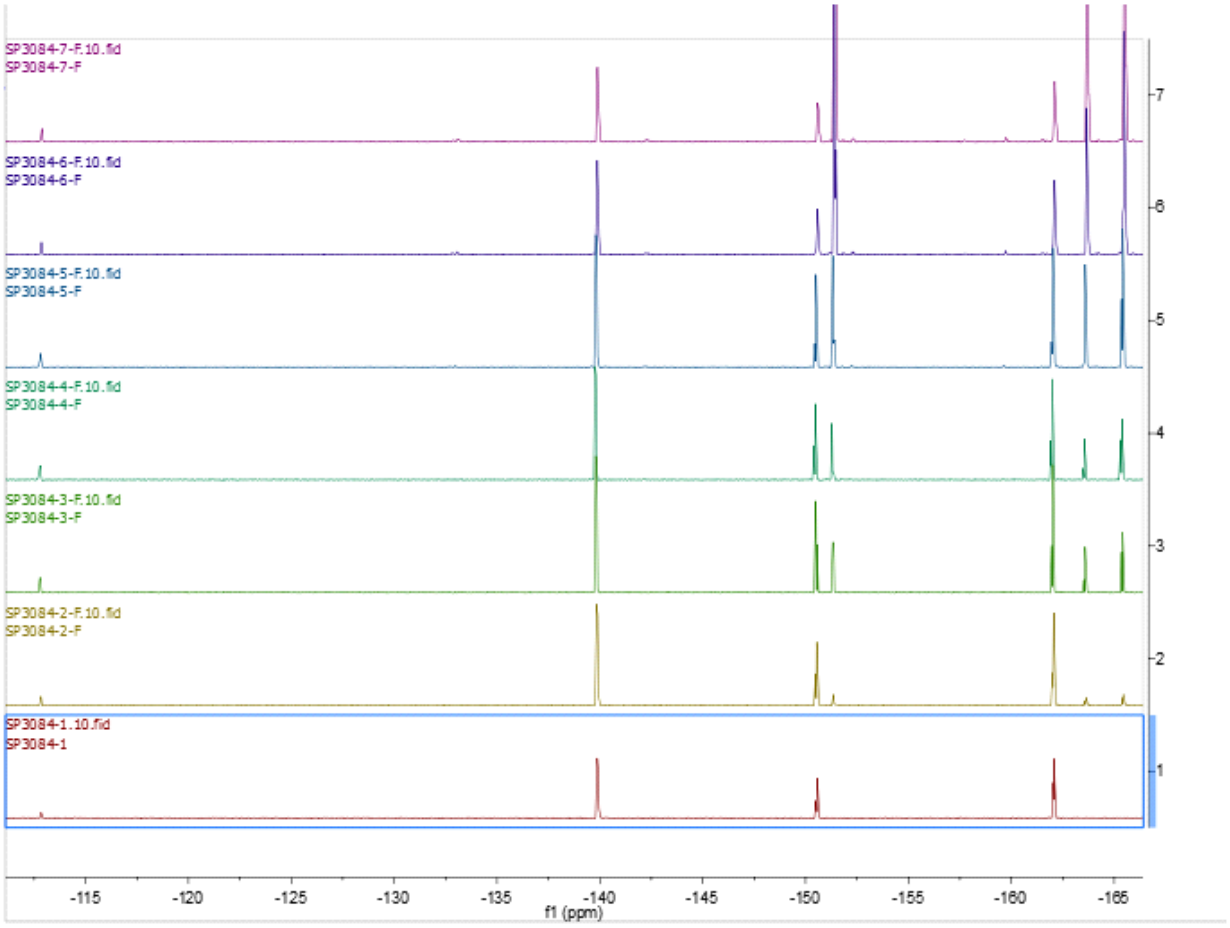
NMR Titration experiments:

Variation in Geranyl ether (without DIPEA)
Internal standard - Fluorobenzene

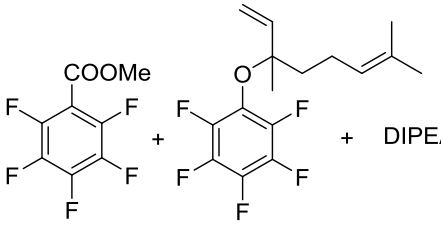


in MeCN (0.1 M)

1) 0 equiv
2) 0.25 equiv
3) 0.5 equiv
4) 1.0 equiv
5) 2.0 equiv
6) 4.0 equiv
7) 6.0 equiv



NMR Titrations - Variation in Geranyl ether (with DIPEA)

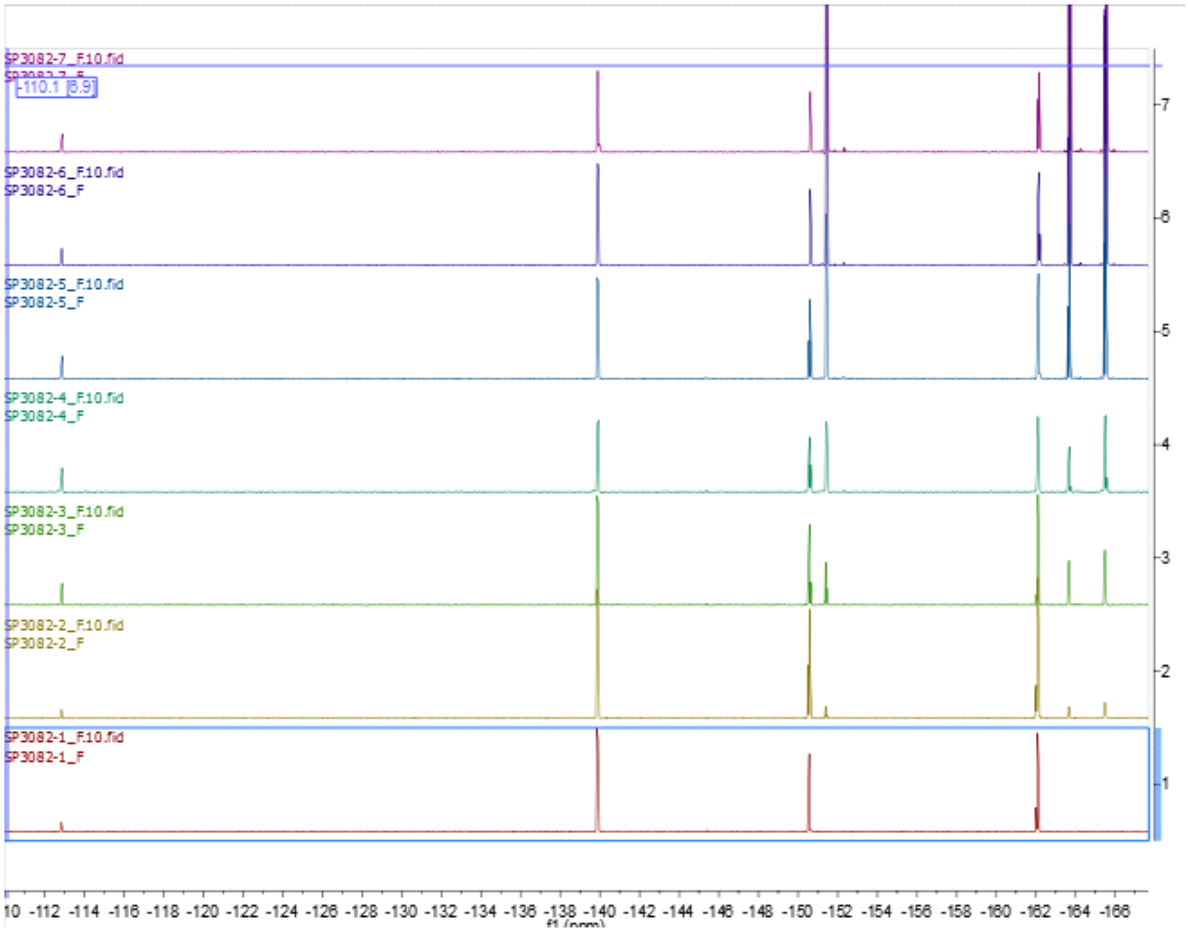


\+ + DIPEA (1.8 equiv) in MeCN (0.1 M)

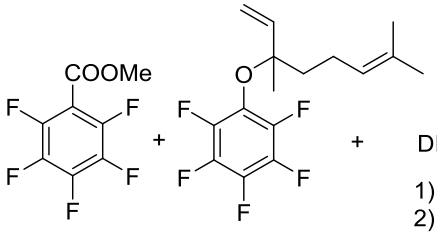
1 equiv

1) 0 equiv
2) 0.25 equiv
3) 0.5 equiv
4) 1.0 equiv
5) 2.0 equiv
6) 4.0 equiv
7) 6.0 equiv

Internal standard - Monofluorobenzene



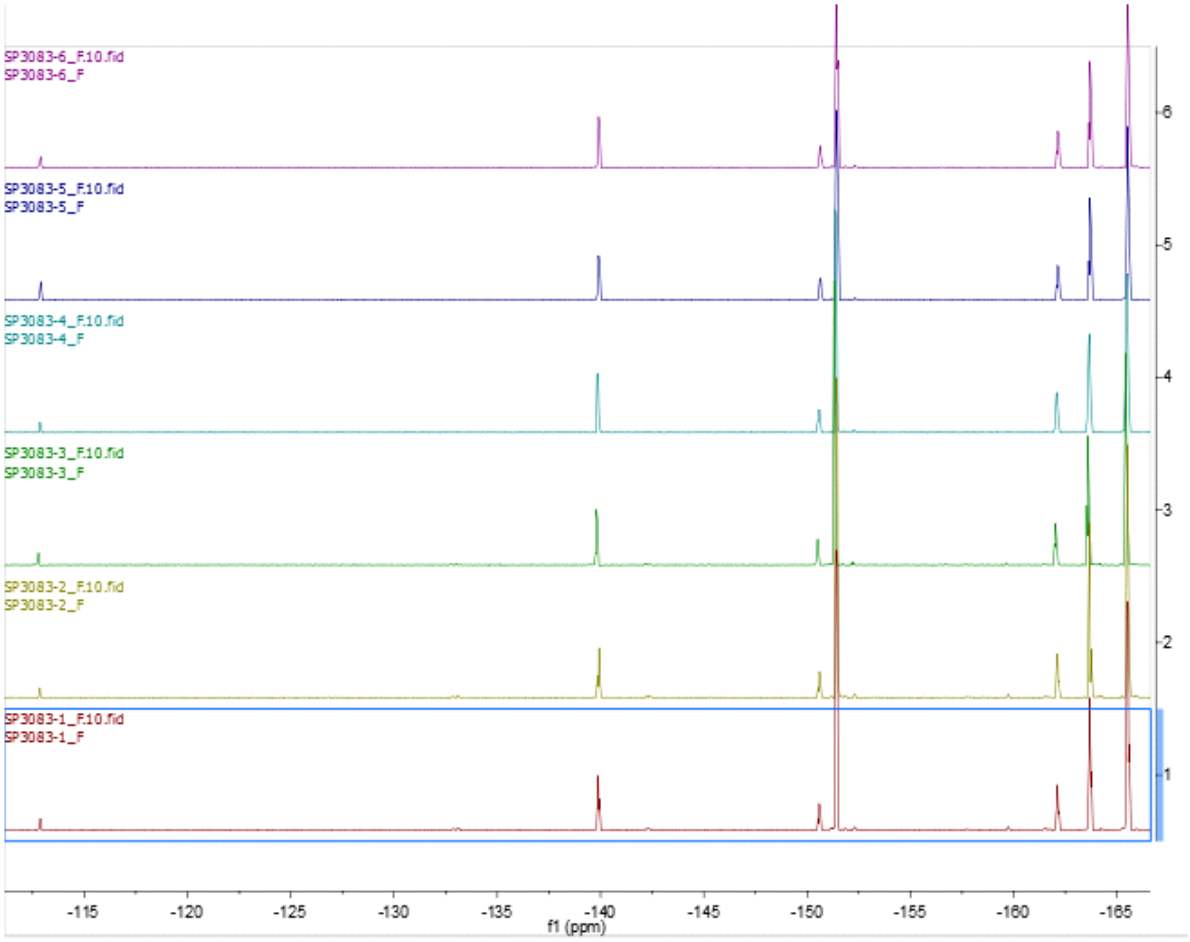
Variation in DIPEA



1 equiv + 6 equiv + DIPEA in MeCN (0.1 M)

1) 0 equiv
2) 0.25 equiv
3) 0.5 equiv
4) 1.0 equiv
5) 1.8 equiv
6) 2.5 equiv

Internal standard - Monofluorobenzene



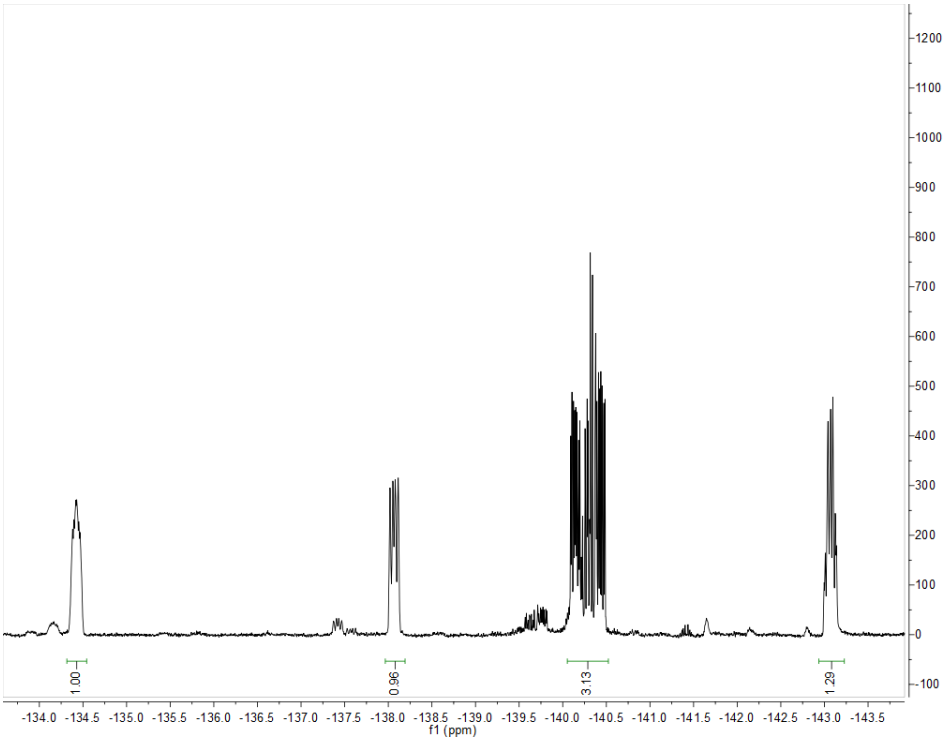
Evidence for no post-reaction isomerization in geranylated products :

Entry	Conditions 0.025 M MeCN	*ortho*-Ger enriched mixture ortho:para ratio[a]	*para*-Ger enriched mixture ortho-para ratio[a]
1	Mixtures at 22 ^{o}C, 3 h	1:0.65	1:0.96
2.	Mixtures heated to 45 ^{o}C, 3 h	1:0.645	1:0.96
3.	Mixtures, 0.3 mol% fac-Ir(ppy)$_3$ blue LEDs, 3 h in 0 ^{o}C	1:0.64	1:0.96
4.	Mixtures, 0.3 mol% fac-Ir(ppy)$_3$ blue LEDs, 3 h in 22 ^{o}C	1:0.65	1:0.955
5.	Mixtures, 0.3 mol% fac-Ir(ppy)$_3$ blue LEDs, 3 h in 45 ^{o}C	1:0.645	1:0.965

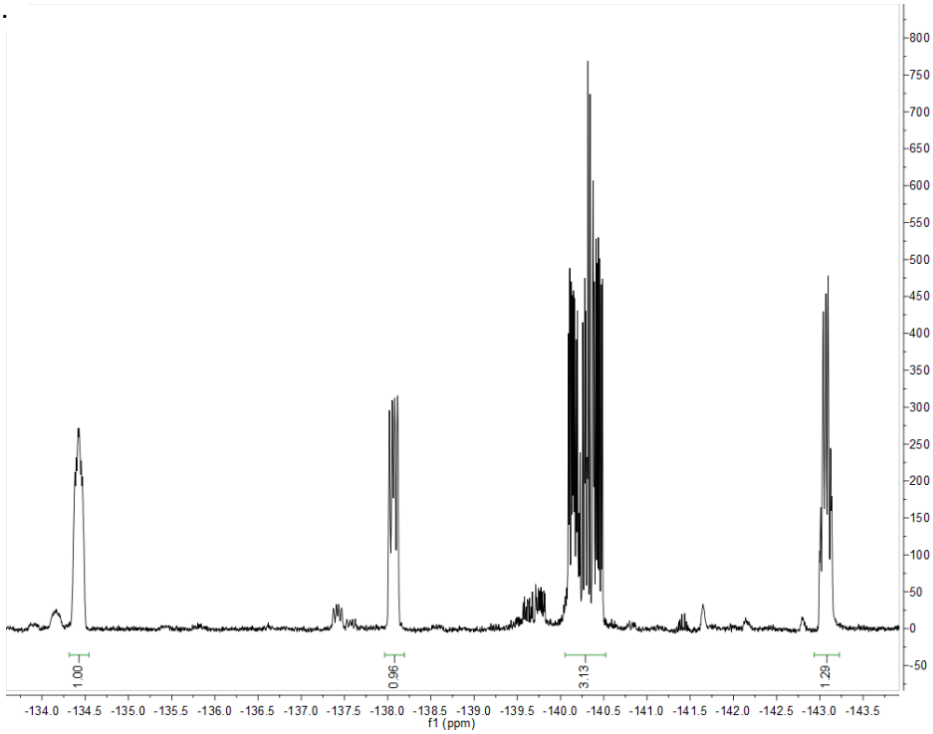
([a]Determined by integration of the ^{19}F NMR signal at -134.4 and -143.1 ppm after normalization)

In order to check for post-reaction isomerization of geranylated products, while we were not able to completely resolve these isomers, we were able to collect samples enriched in one or the other isomers after chromatography by taking early and late fractions. When we re-subjected the enriched mixtures to a number of conditions (see above), we saw that the ratio never changed. This is clear evidence that the selectivity is a kinetic phenomenon and not subject to equilibration.

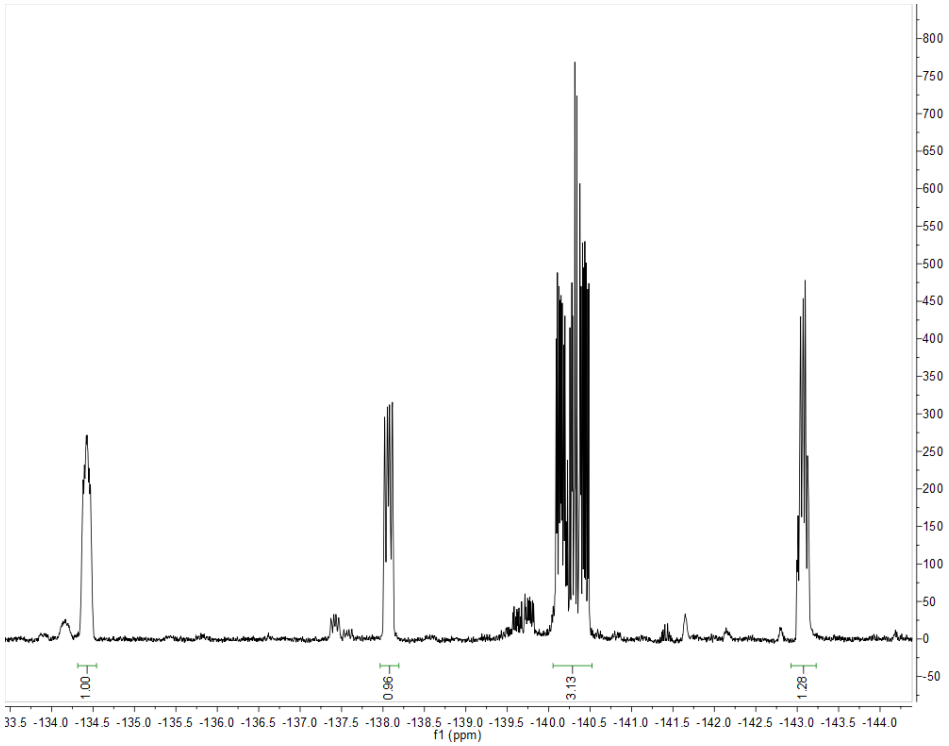
1. *ortho*-Ger enriched mixture



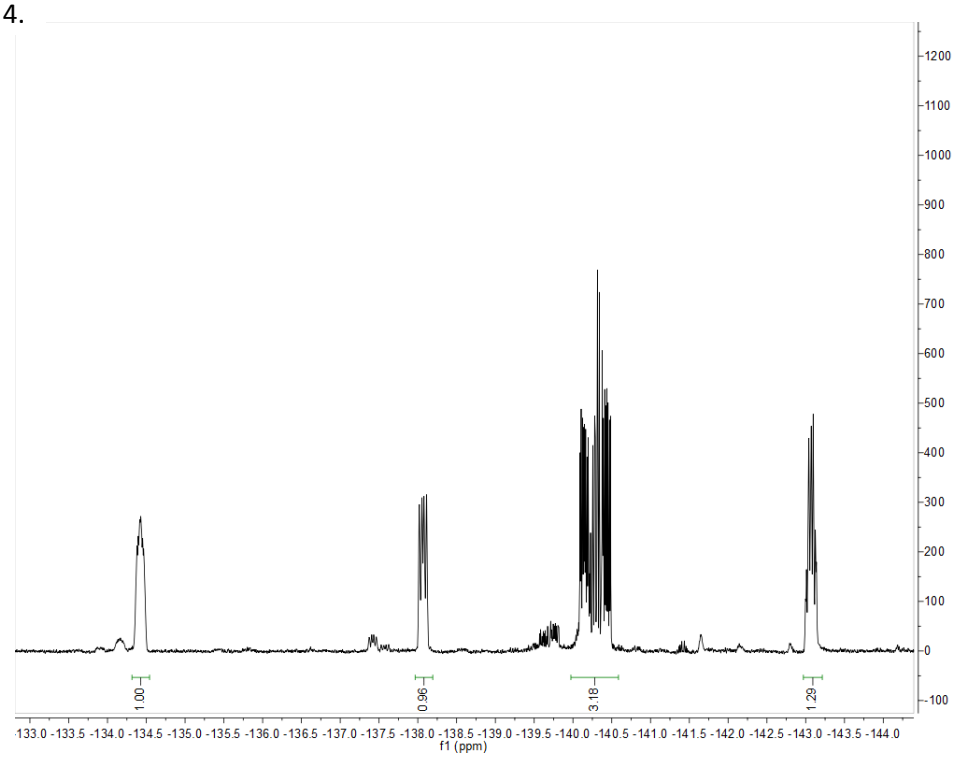
2.



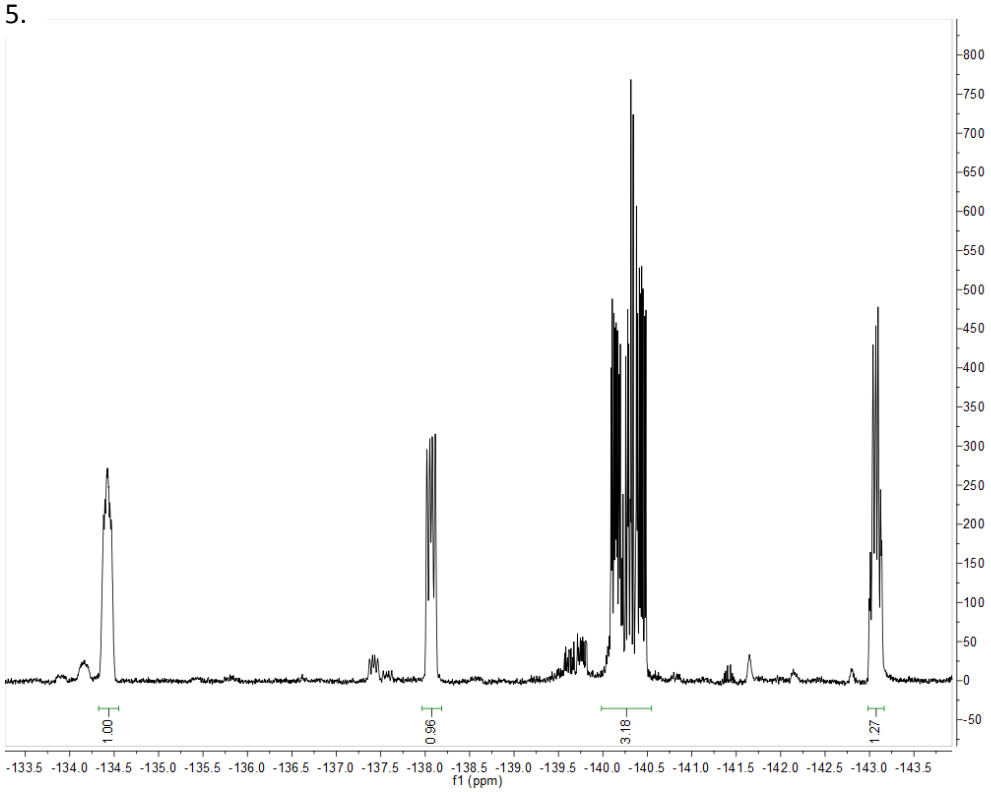
3.



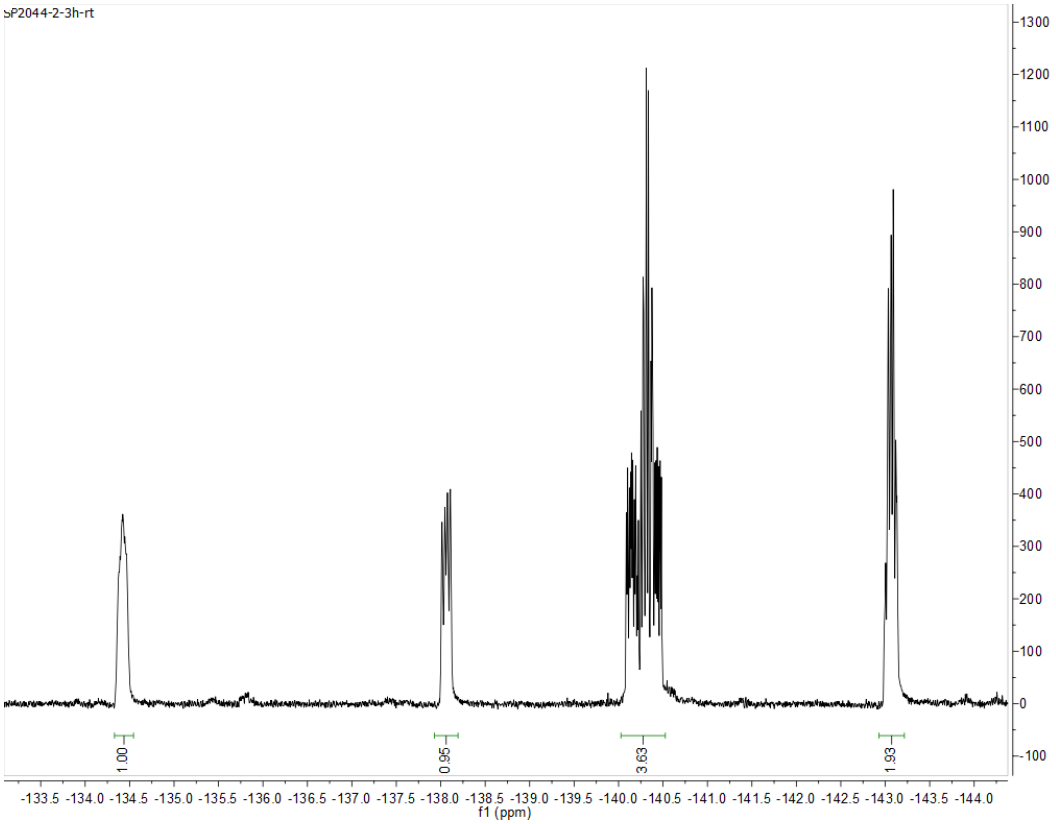
4.



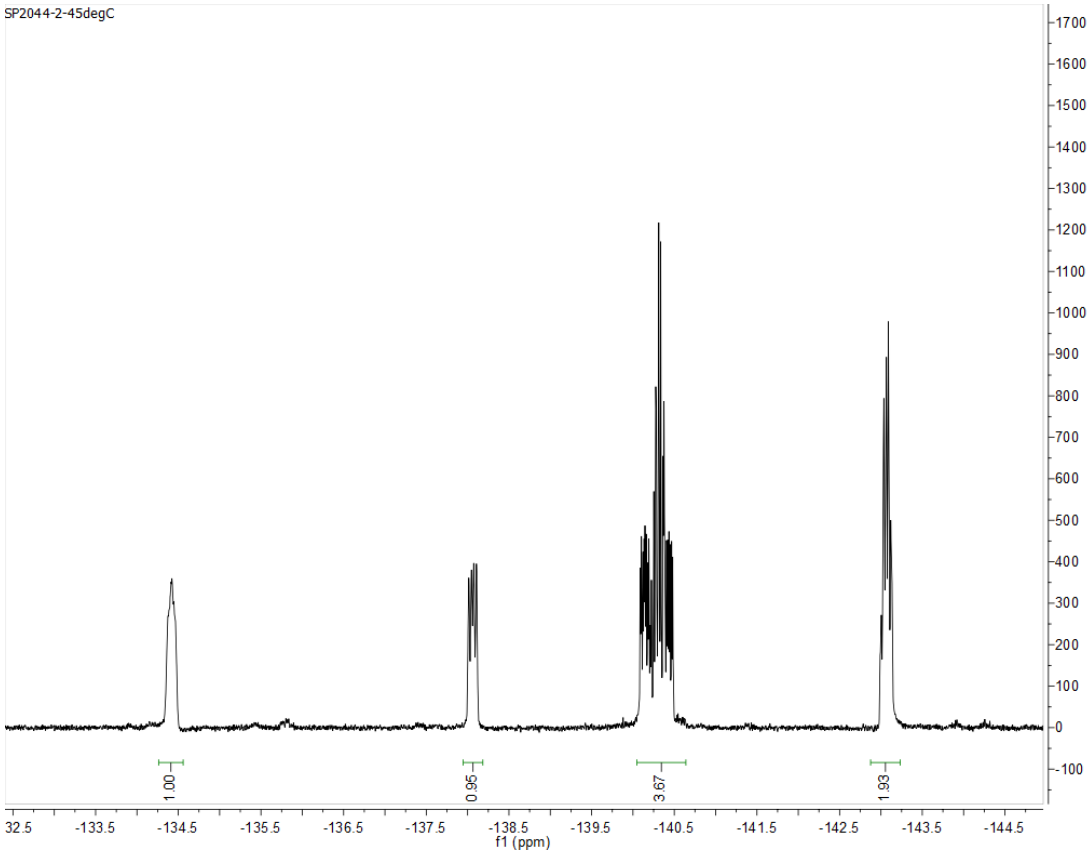
5.


800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
1.00
0.96
3.18
1.27
-133.5 -134.0 -134.5 -135.0 -135.5 -136.0 -136.5 -137.0 -137.5 -138.0 -138.5 -139.0 -139.5 -140.0 -140.5 -141.0 -141.5 -142.0 -142.5 -143.0 -143.5
f1 (ppm)

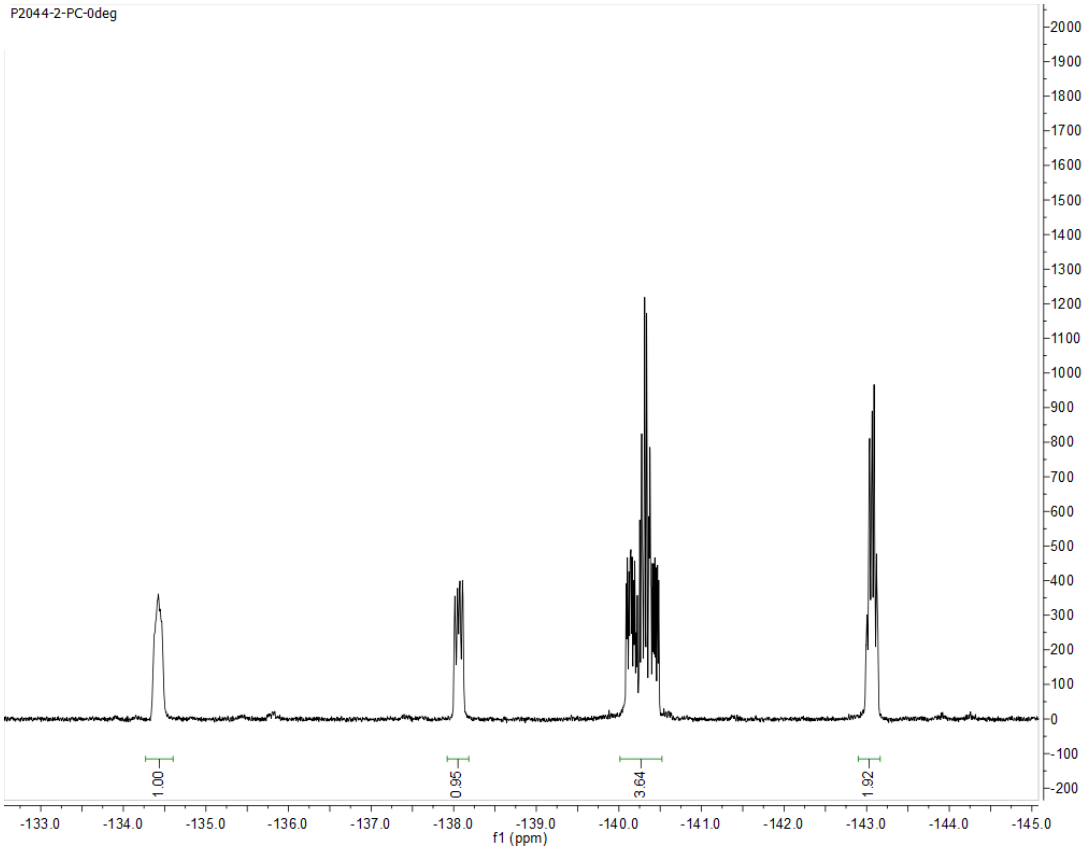
1. *para*-Ger enriched mixture



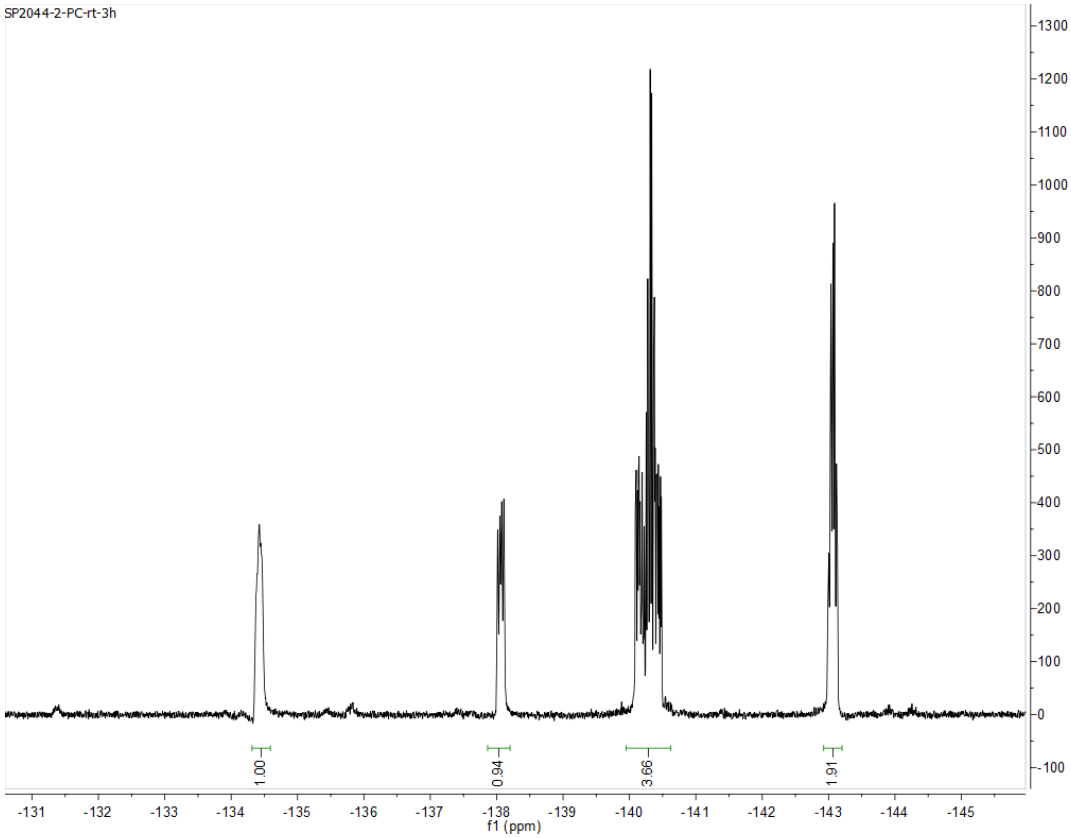
2



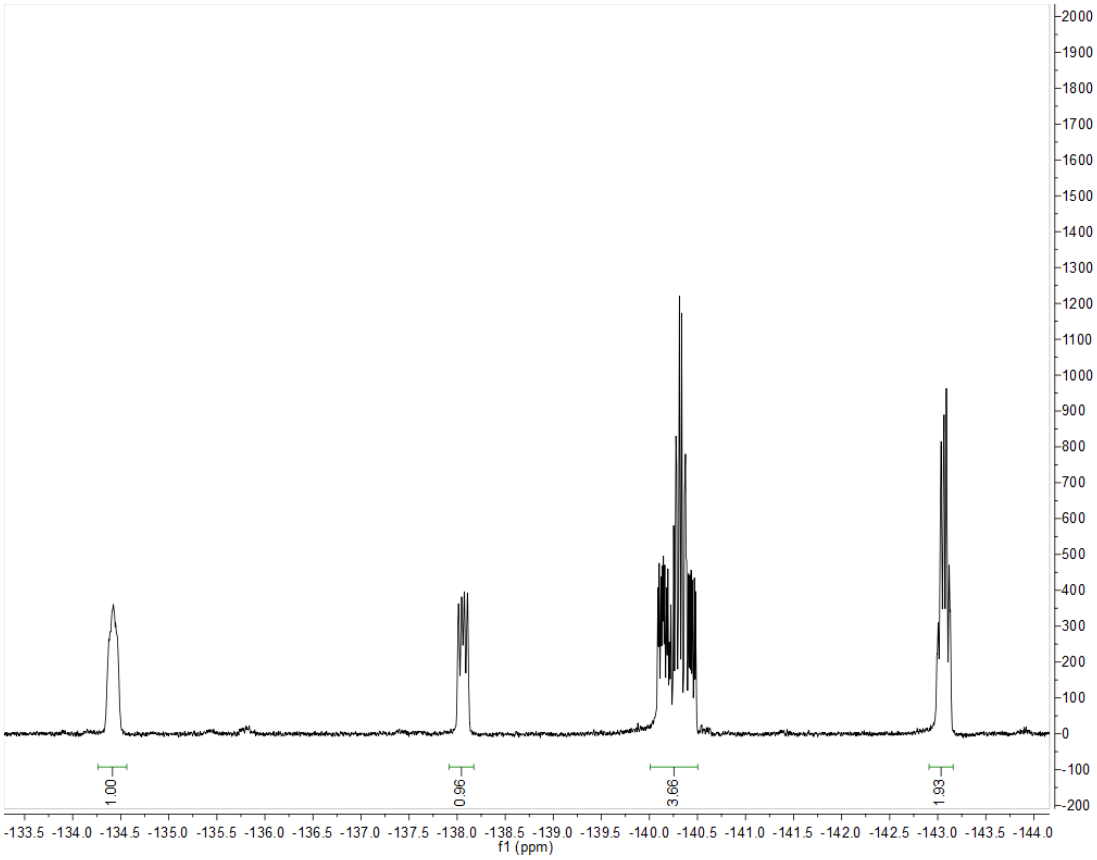
3.


P2044-2-PC-0deg
1.00
0.95
3.64
1.92
f1 (ppm)

4.


SP2044-2-PC-rt-3h
1.00
0.94
3.66
1.91
f1 (ppm)

5.



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2. (a) Eapen, K. C.; Tamborski, C., Synthesis of some benzimidazoles containing 2-perfluoro substituents. *J. Fluorine Chem.* **1981,** *18*, 243; (b) Senaweera, S. M.; Singh, A.; Weaver, J. D., Photocatalytic Hydrodefluorination: Facile Access to Partially Fluorinated Aromatics. *J. Am. Chem. Soc.* **2014,** *136*, 3002; (c) Xie, K.; Yang, Z.; Zhou, X.; Li, X.; Wang, S.; Tan, Z.; An, X.; Guo, C.-C., Pd-Catalyzed Decarboxylative Arylation of Thiazole, Benzoxazole, and Polyfluorobenzene with Substituted Benzoic Acids. *Org. Lett.* **2010,** *12*, 1564; (d) Senaweera, S.; Weaver, J. D., SNAr catalysis enhanced by an aromatic donor-acceptor interaction; facile access to chlorinated polyfluoroarenes. *Chem. Commun.* **2017,** *53*, 7545.
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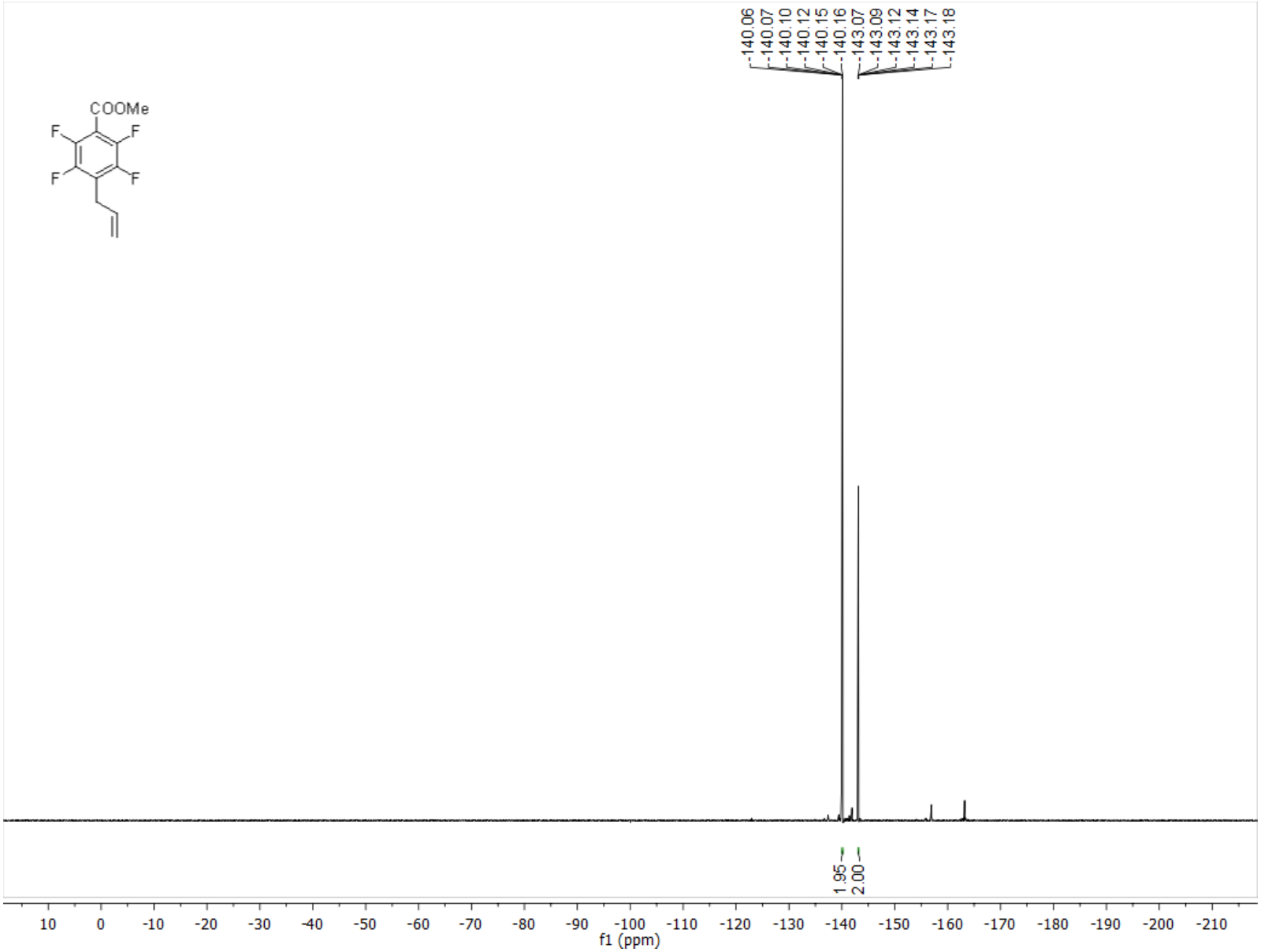
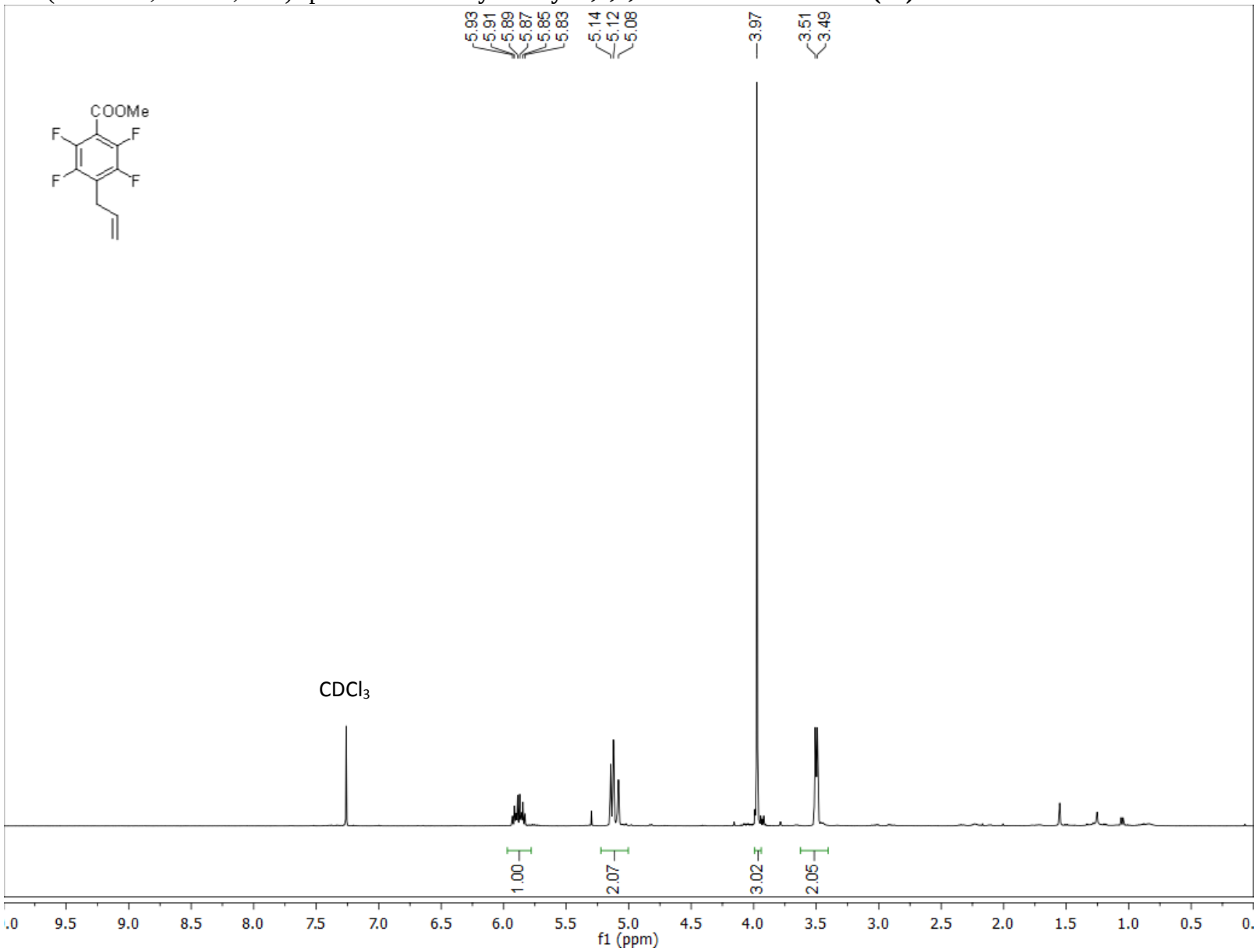
8. Saunders, C.; Khaled, M. B.; Weaver, J. D.; Tantillo, D. J., Prediction of 19F NMR Chemical Shifts for Fluorinated Aromatic Compounds. *J. Org. Chem.* **2018,** *83*, 3220.

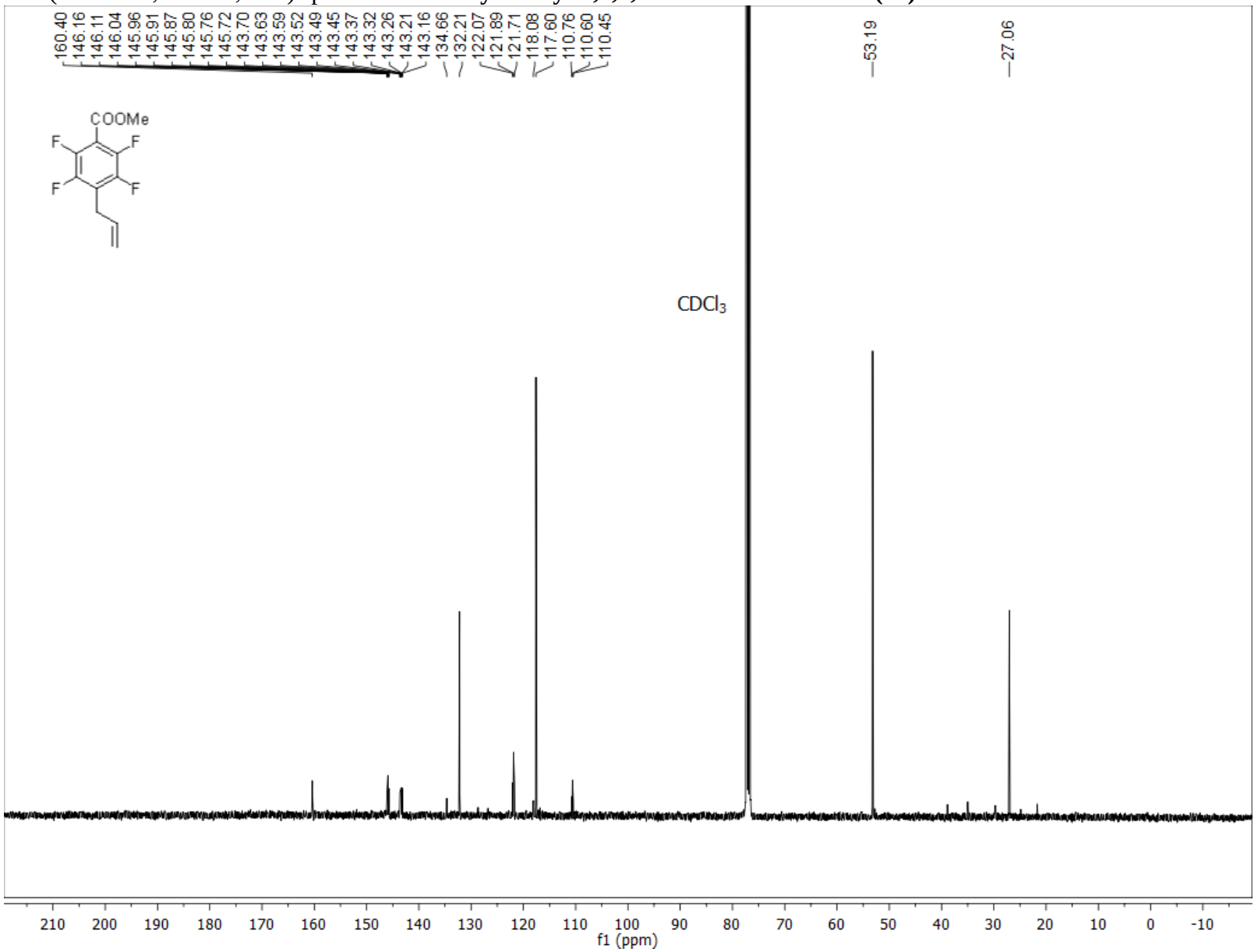
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **methyl 4-allyl-2,3,5,6-tetrafluorobenzoate (5a)**



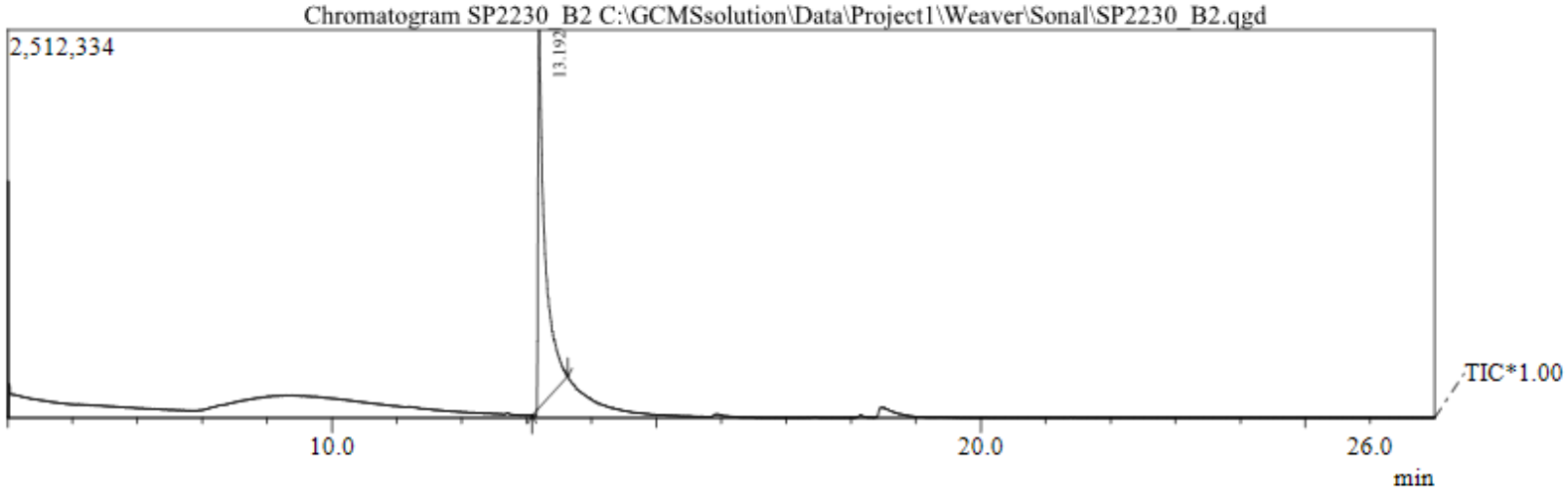
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **methyl 4-allyl-2,3,5,6-tetrafluorobenzoate (5a)**

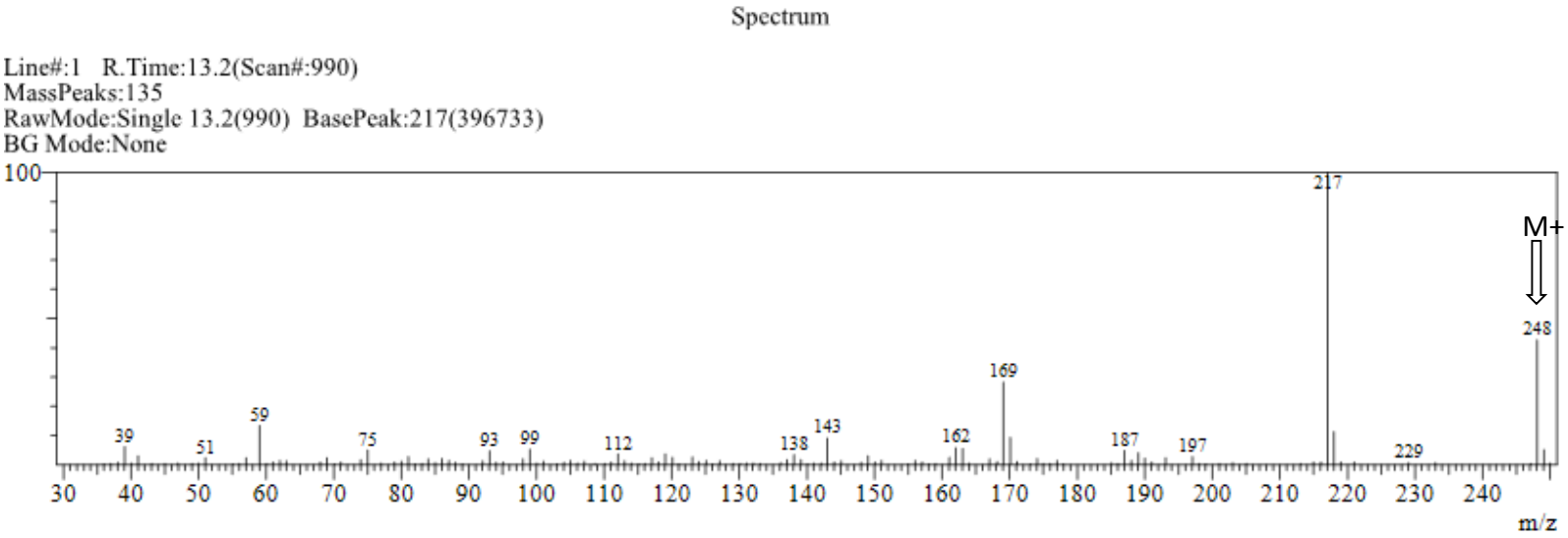


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **methyl 4-allyl-2,3,5,6-tetrafluorobenzoate (5a)**

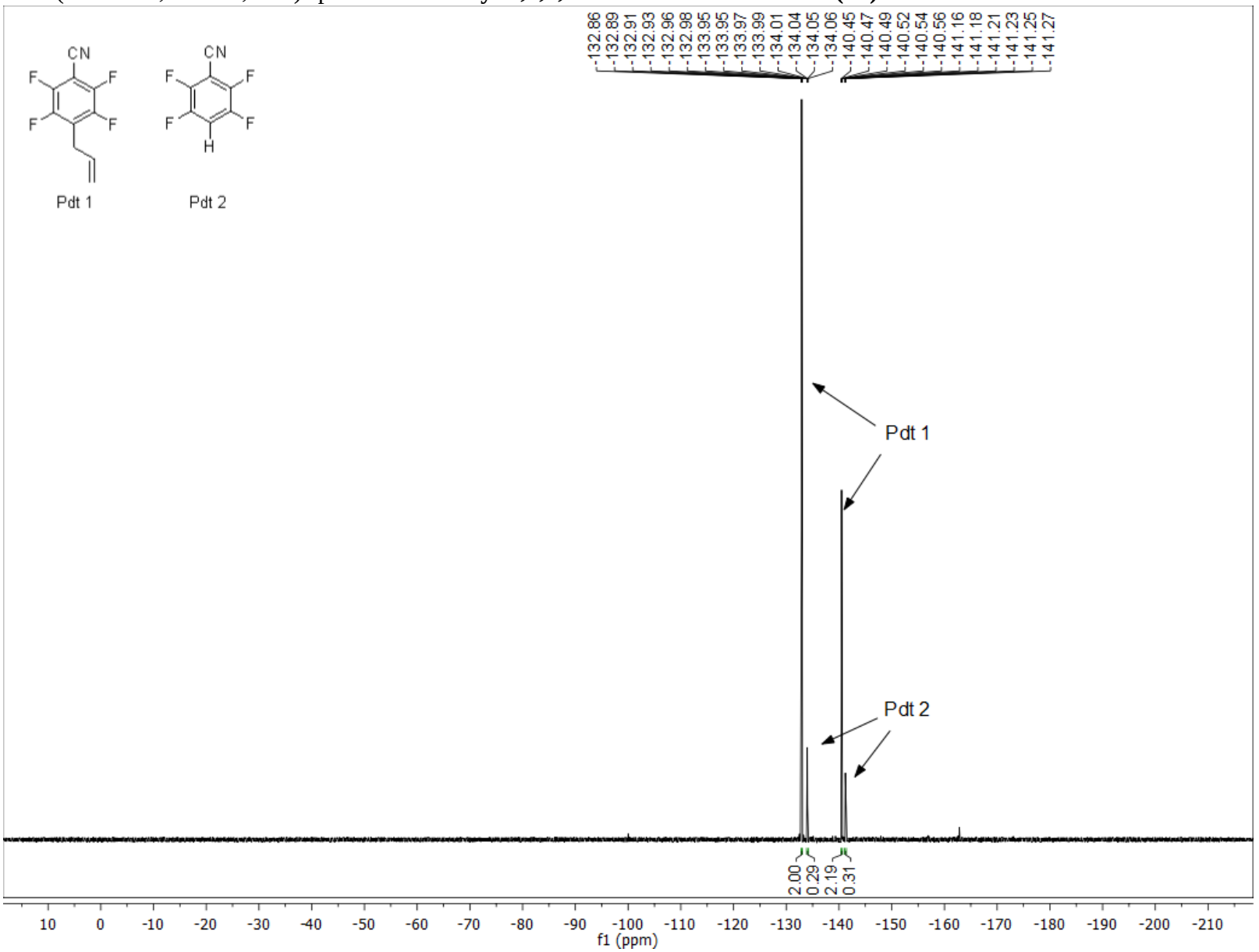


GC and MS of **methyl 4-allyl-2,3,5,6-tetrafluorobenzoate (5a)**

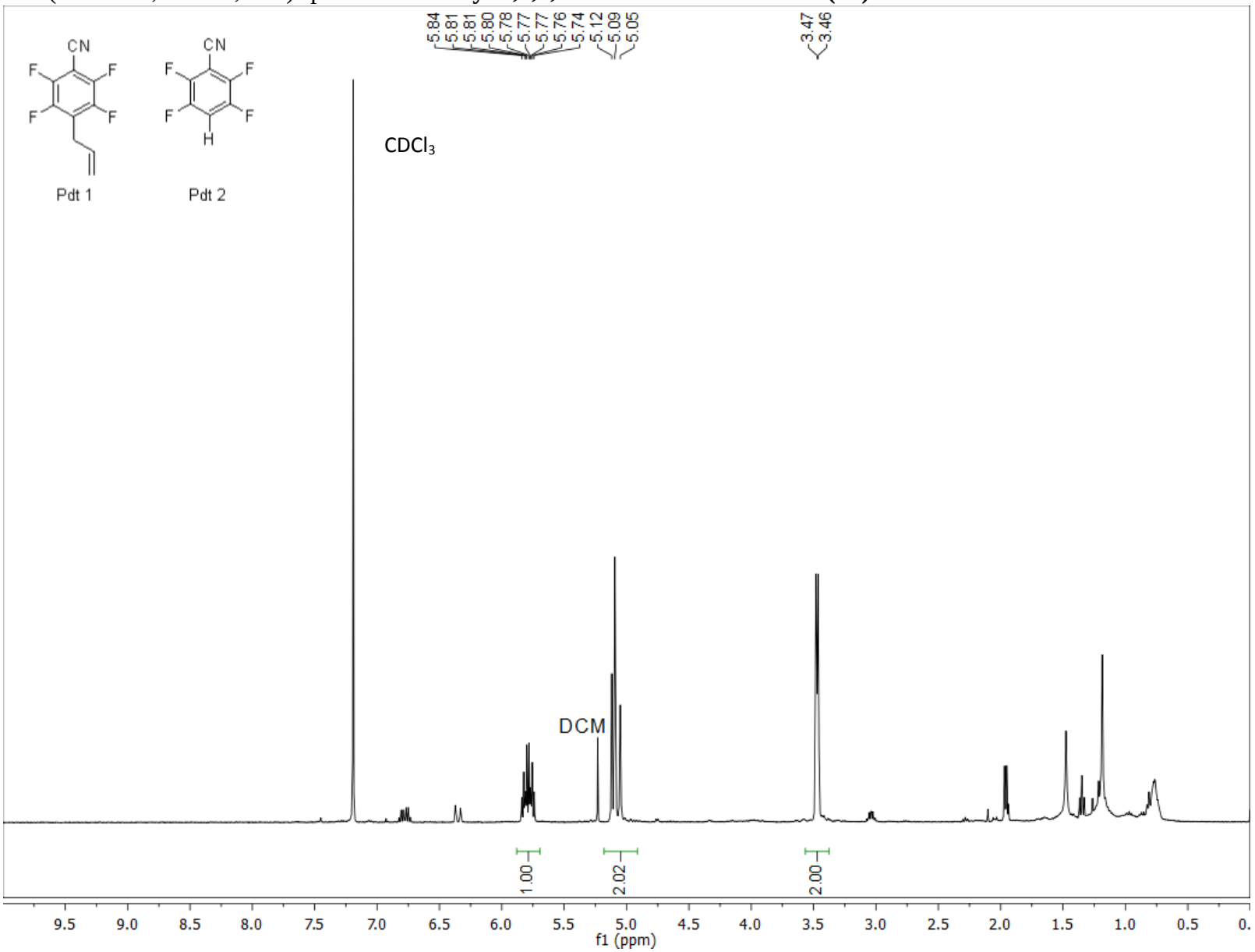




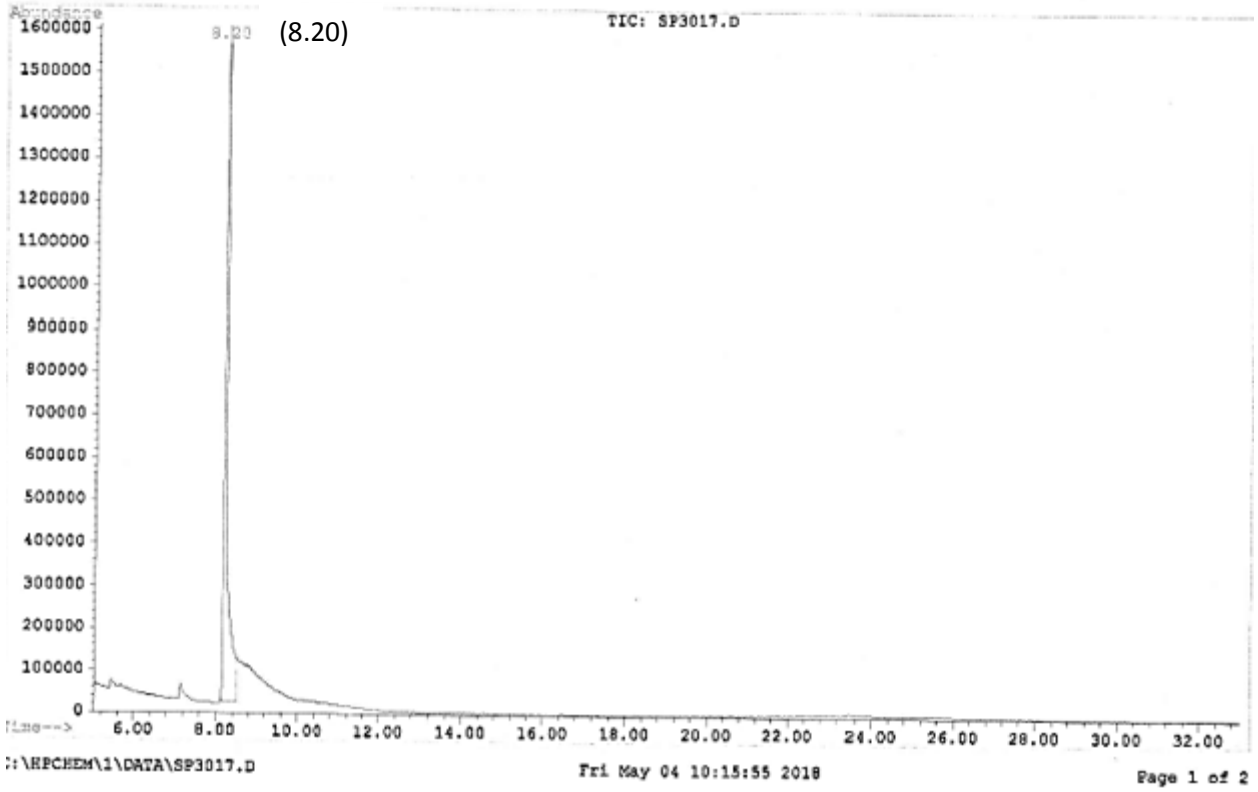
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **4-allyl-2,3,5,6-tetrafluorobenzonitrile (5b)**



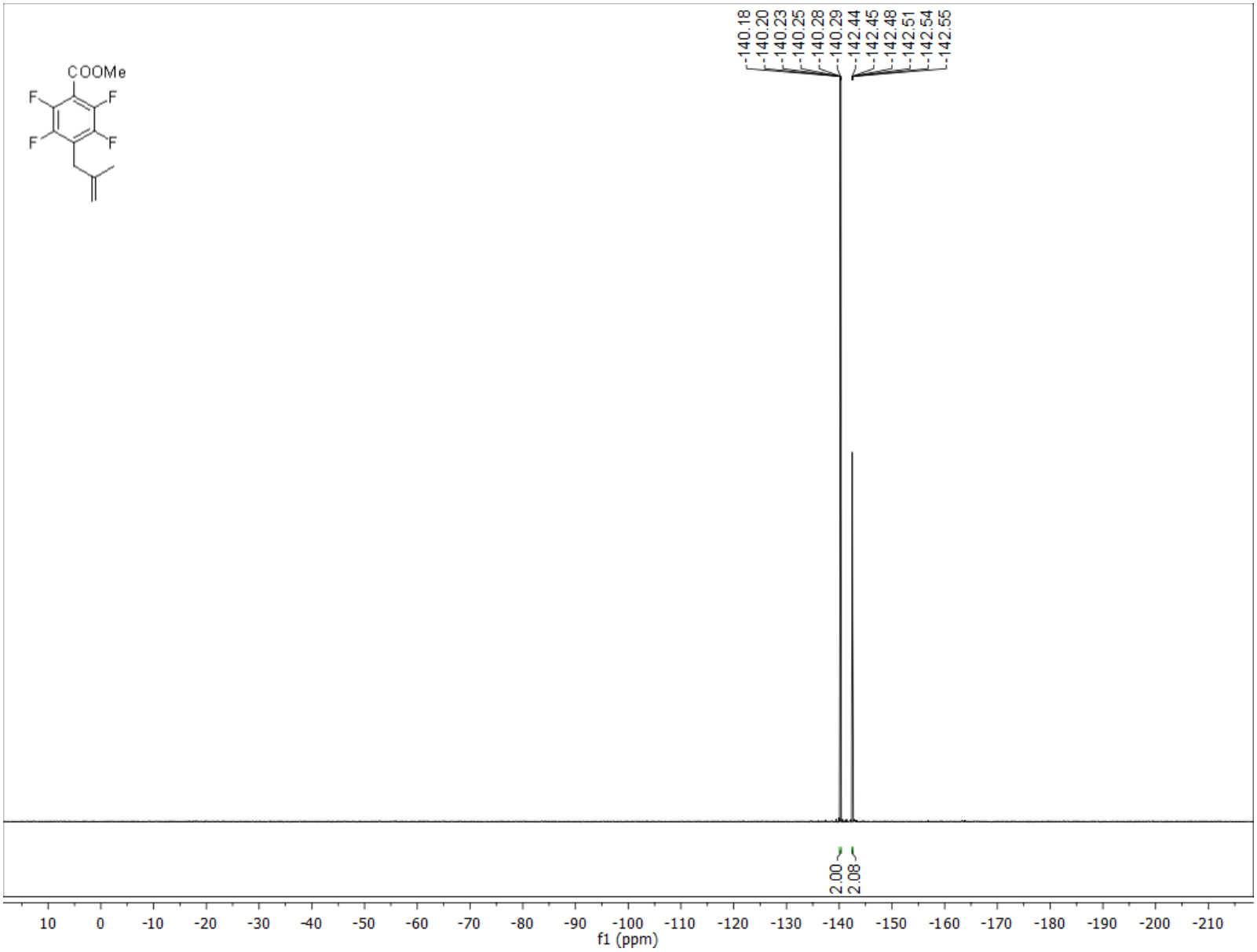
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **4-allyl-2,3,5,6-tetrafluorobenzonitrile (5b)**



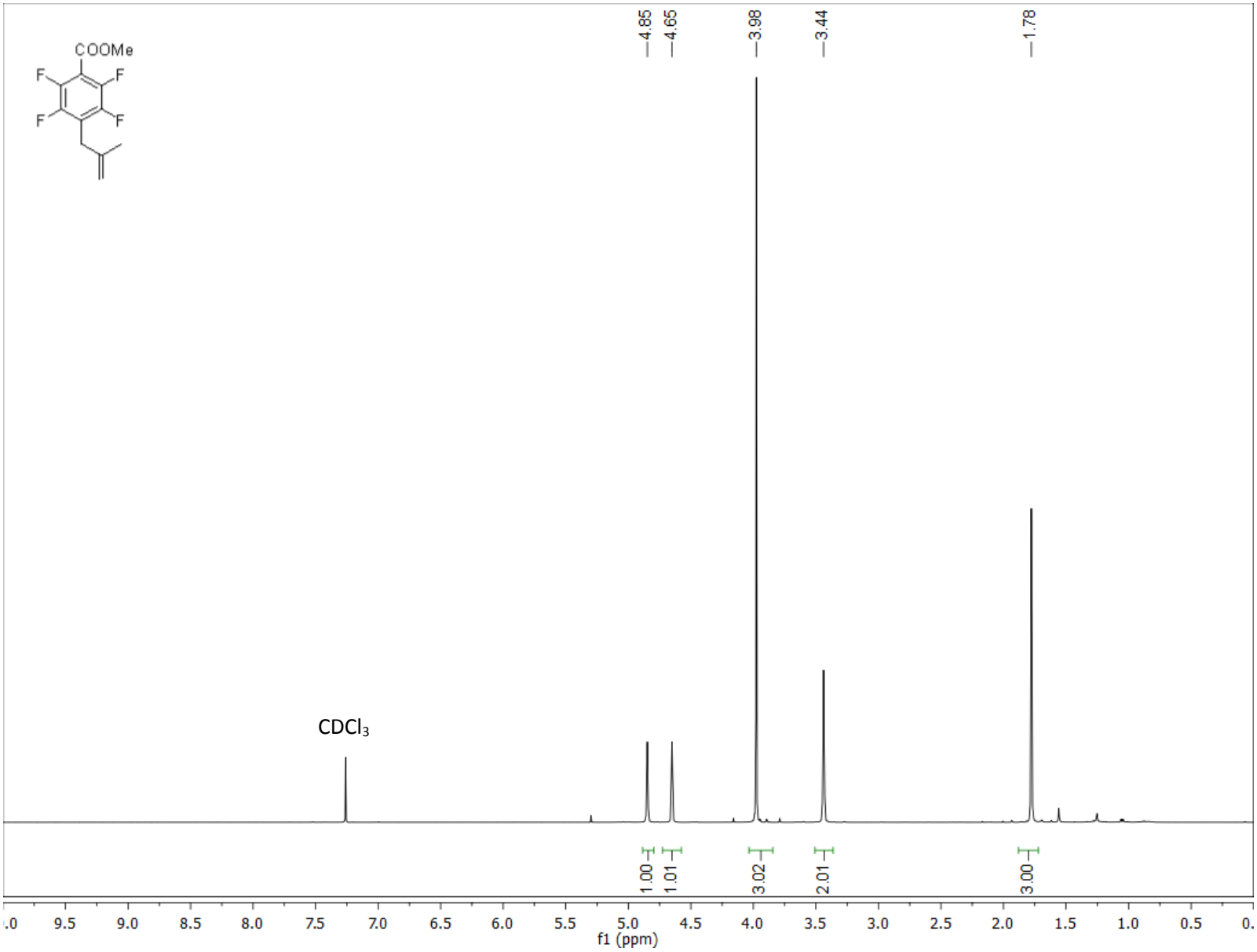
GC and MS of **4-allyl-2,3,5,6-tetrafluorobenzonitrile (5b)**



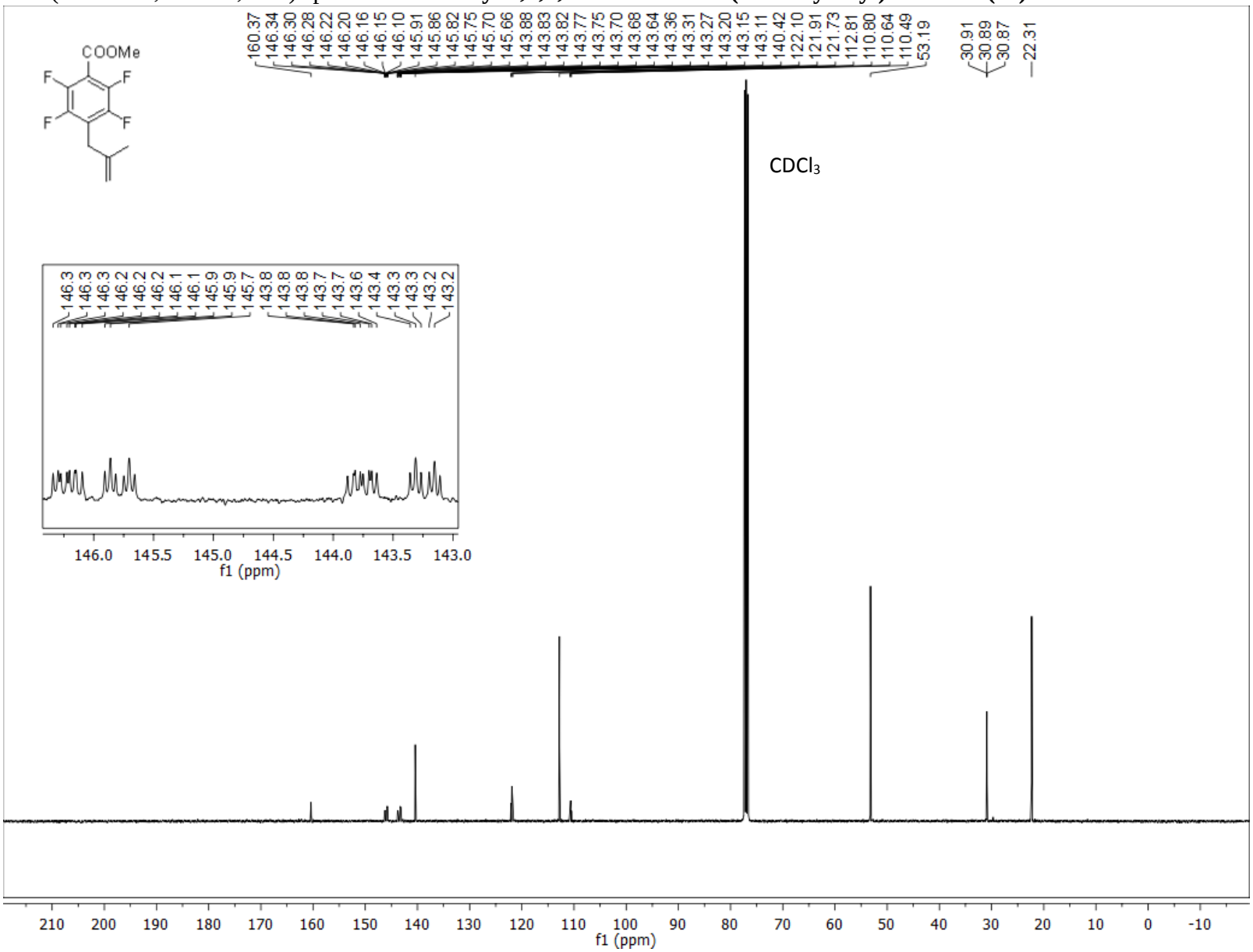
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **methyl 2,3,5,6-tetrafluoro-4-(2-methylallyl)benzoate (5c)**



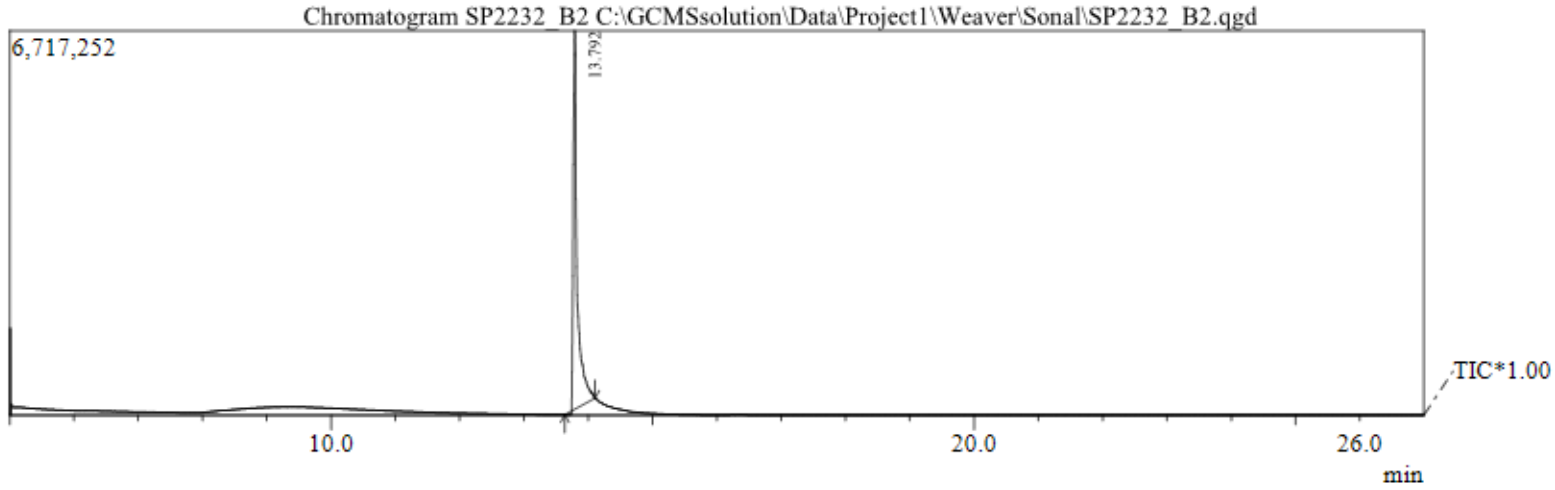
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **methyl 2,3,5,6-tetrafluoro-4-(2-methylallyl)benzoate (5c)**



^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **methyl 2,3,5,6-tetrafluoro-4-(2-methylallyl)benzoate (5c)**



GC and MS of **methyl 2,3,5,6-tetrafluoro-4-(2-methylallyl)benzoate (5c)**



Spectrum

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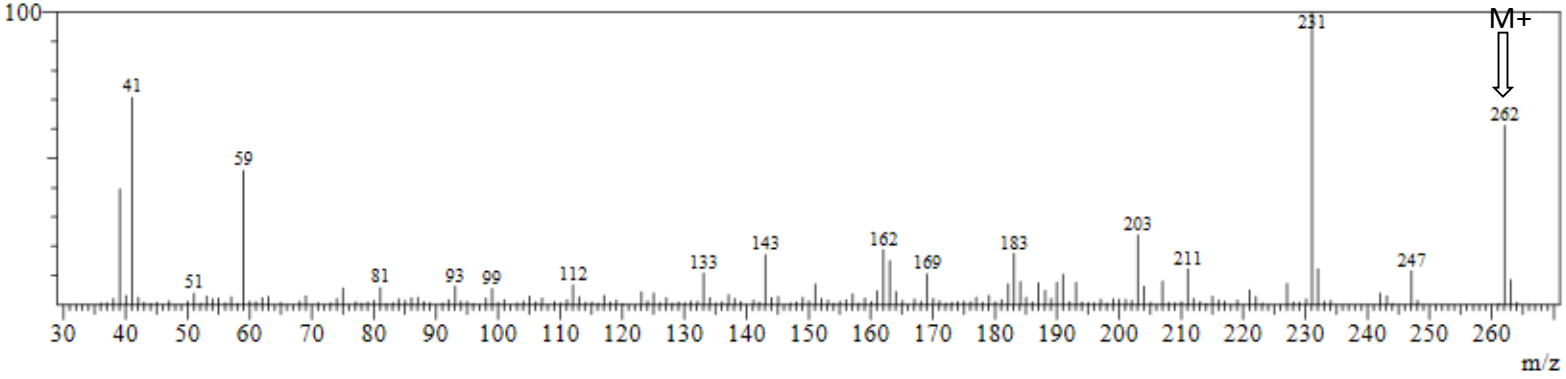
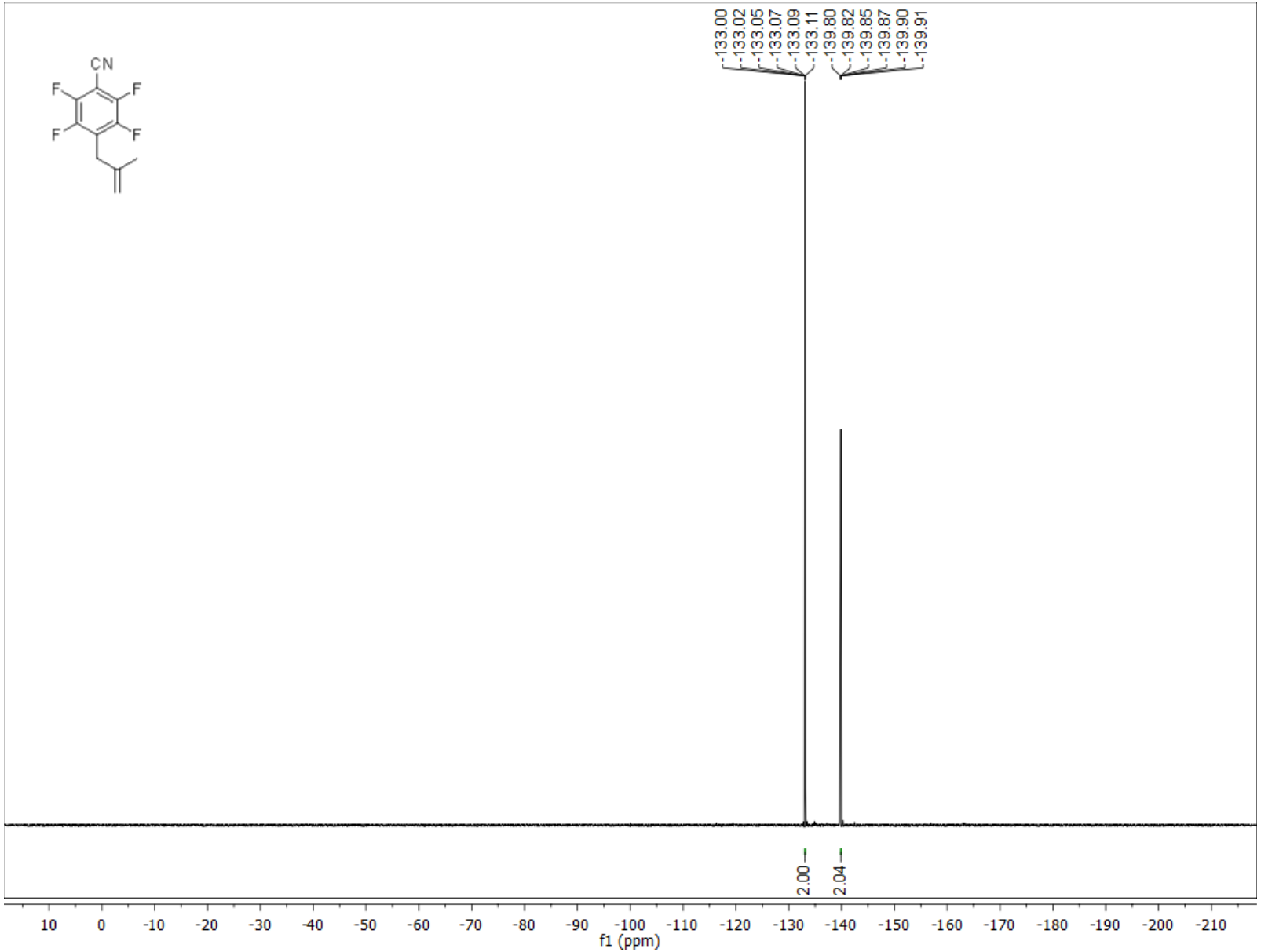
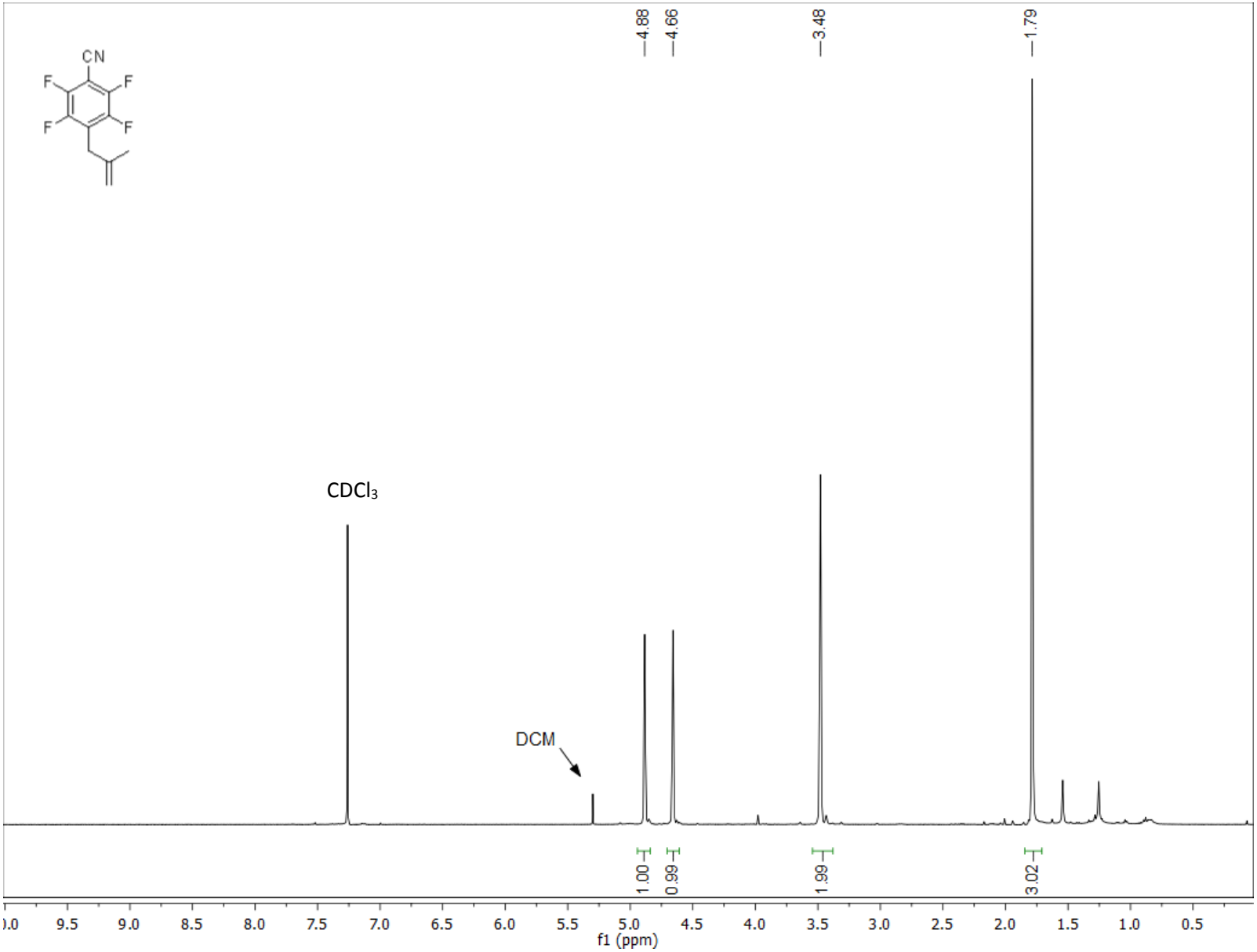
RawMode:Single 13.8(1060) BasePeak:231(255763)
BG Mode:None



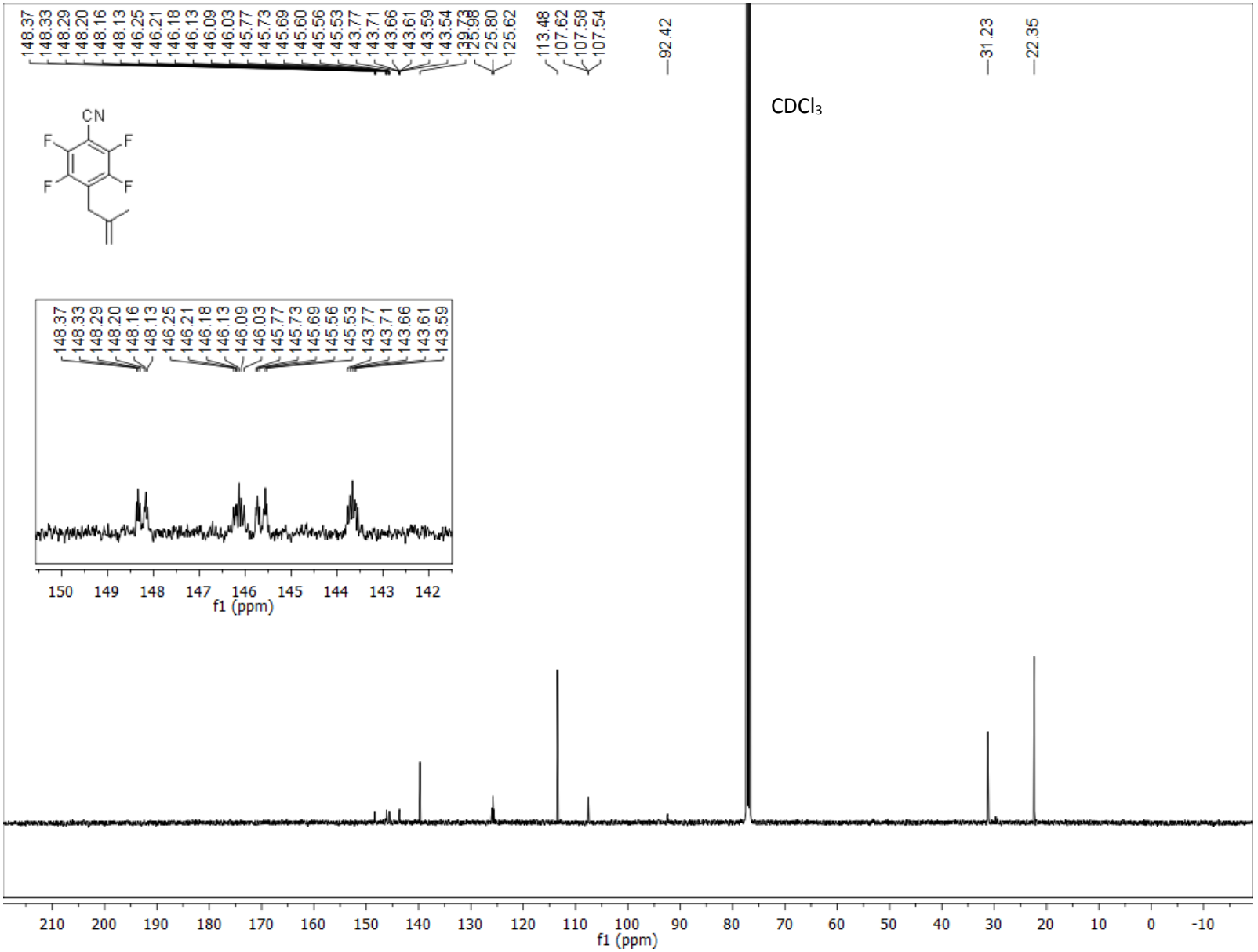
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(2-methylallyl)benzonitrile (5d)**



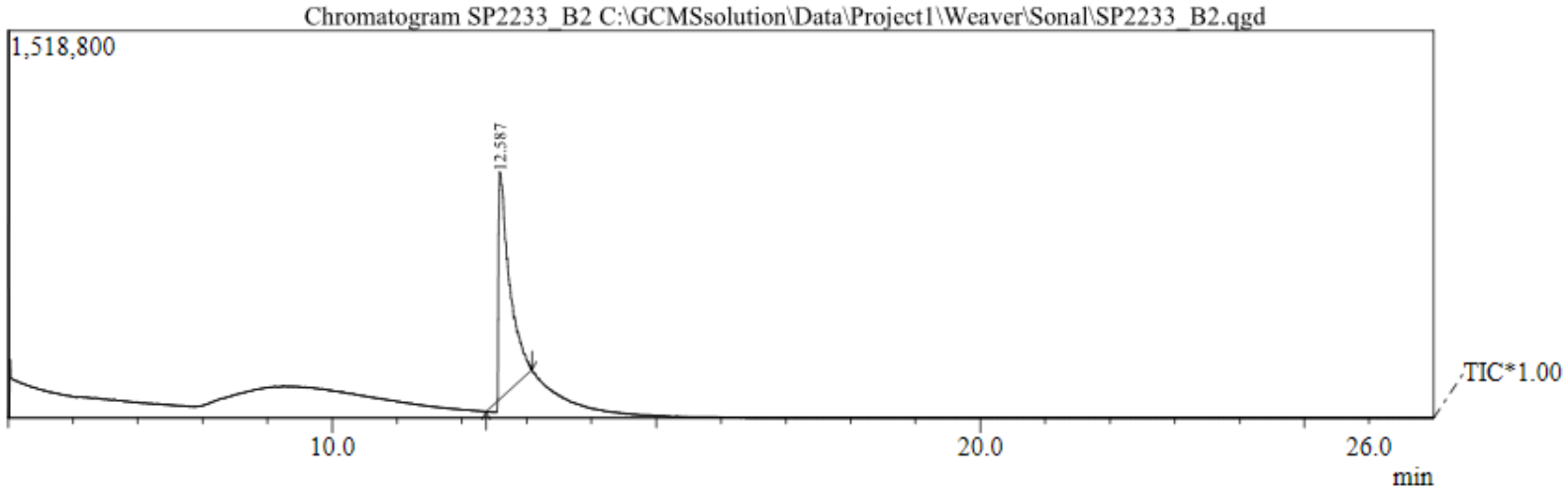
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(2-methylallyl)benzonitrile (5d)**



^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(2-methylallyl)benzonitrile (5d)**



GC and MS of **2,3,5,6-tetrafluoro-4-(2-methylallyl)benzonitrile (5d)**



Spectrum

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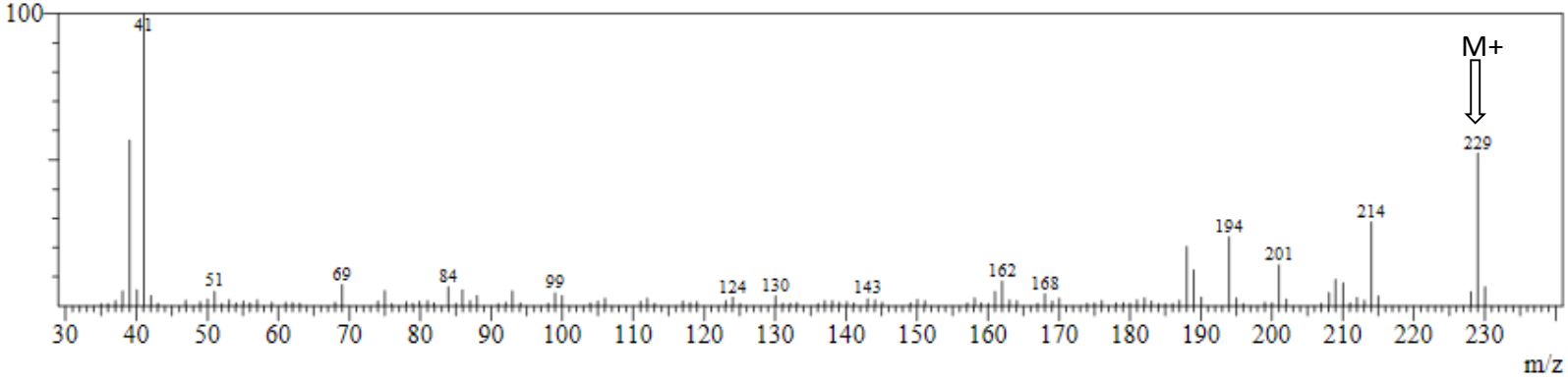
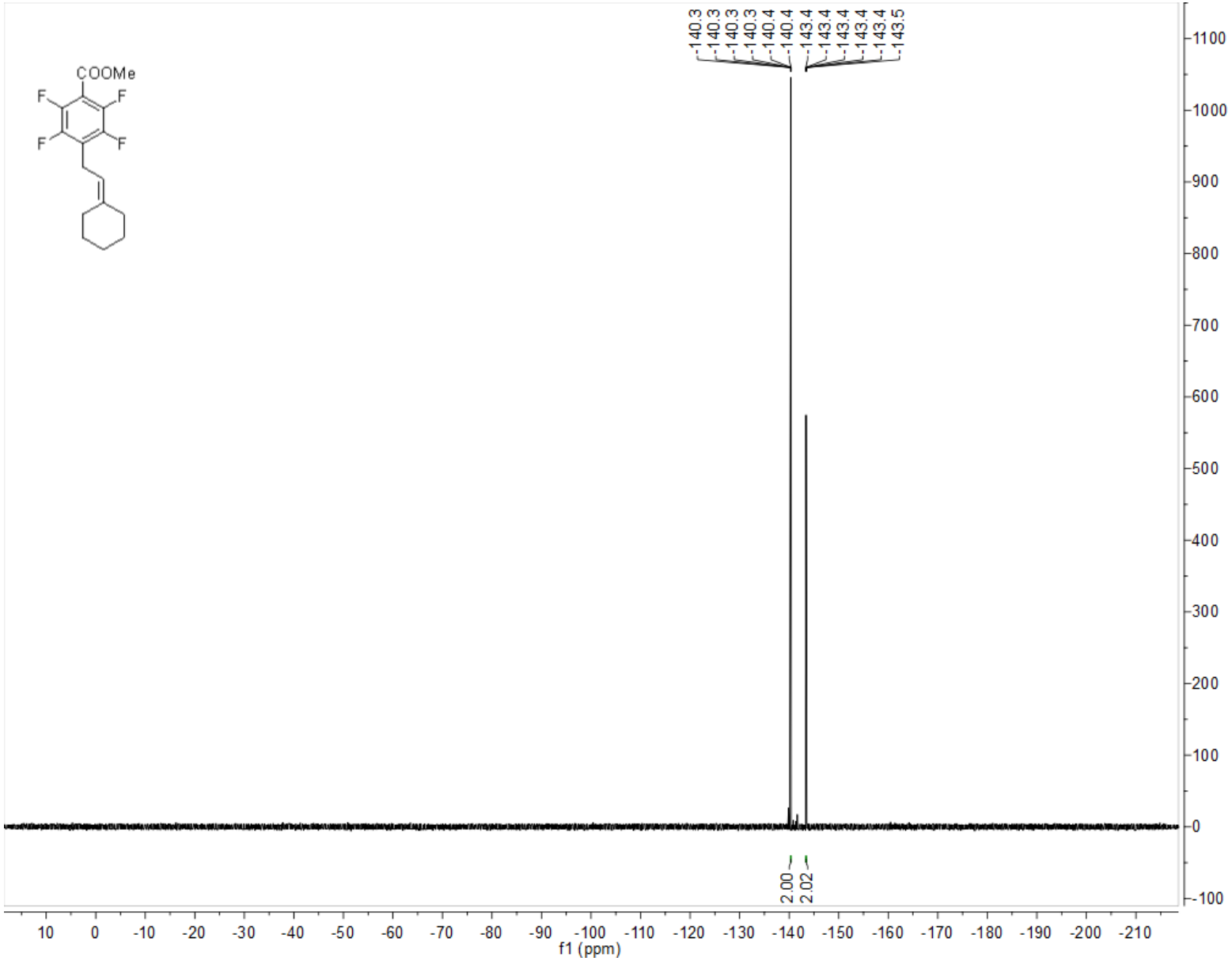
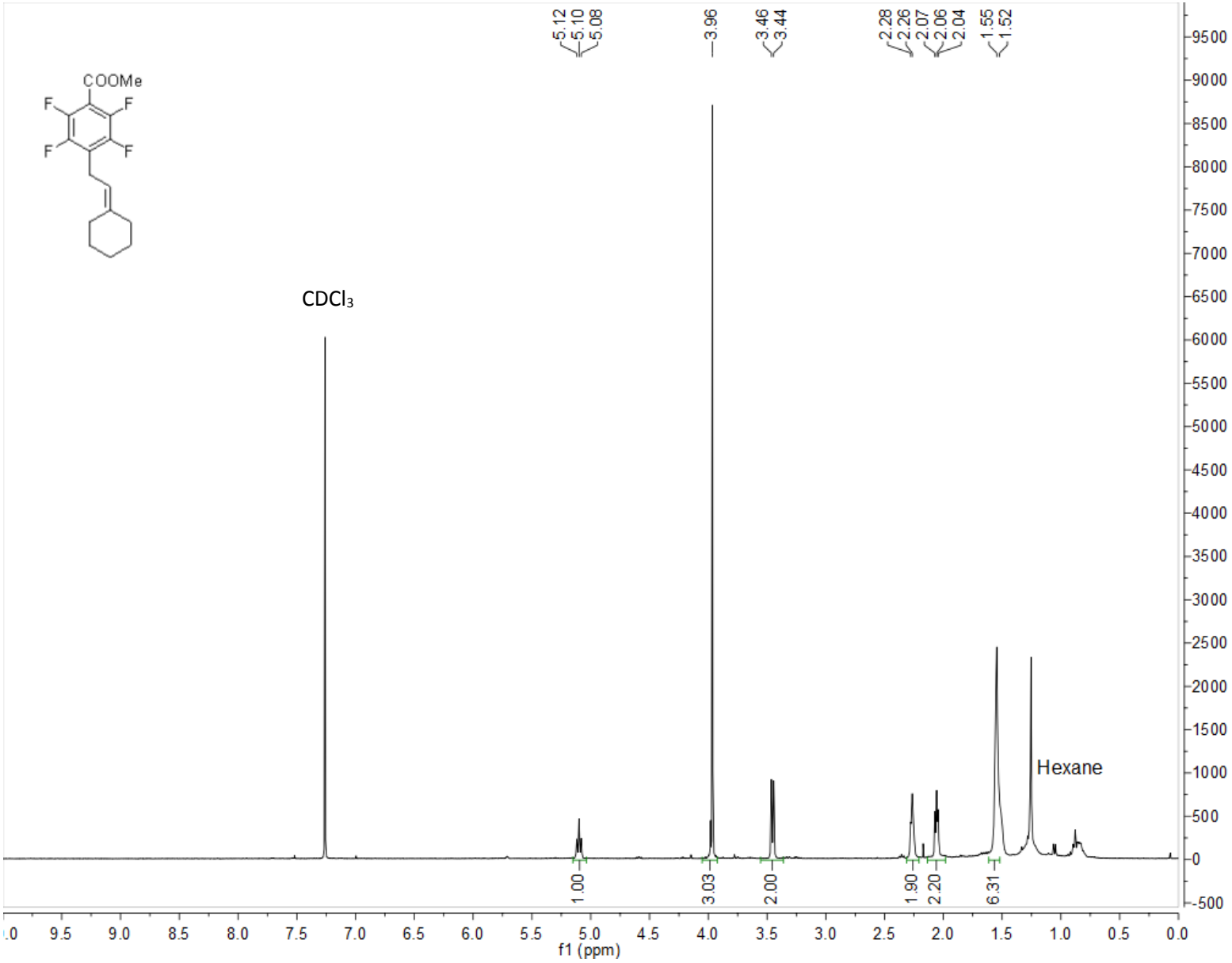


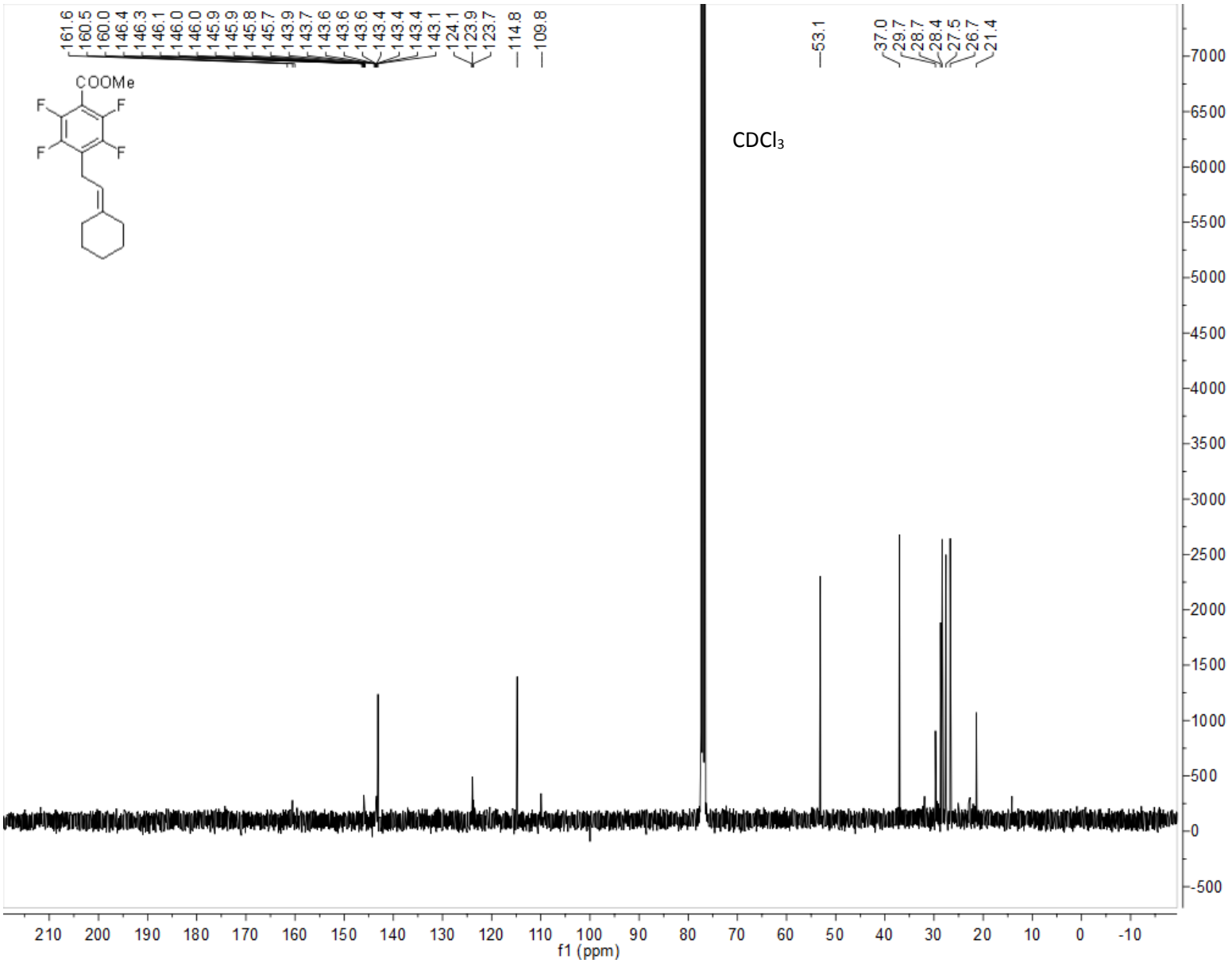
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **methyl 4-(2-cyclohexylideneethyl)-2,3,5,6-tetrafluorobenzoate (5e)**



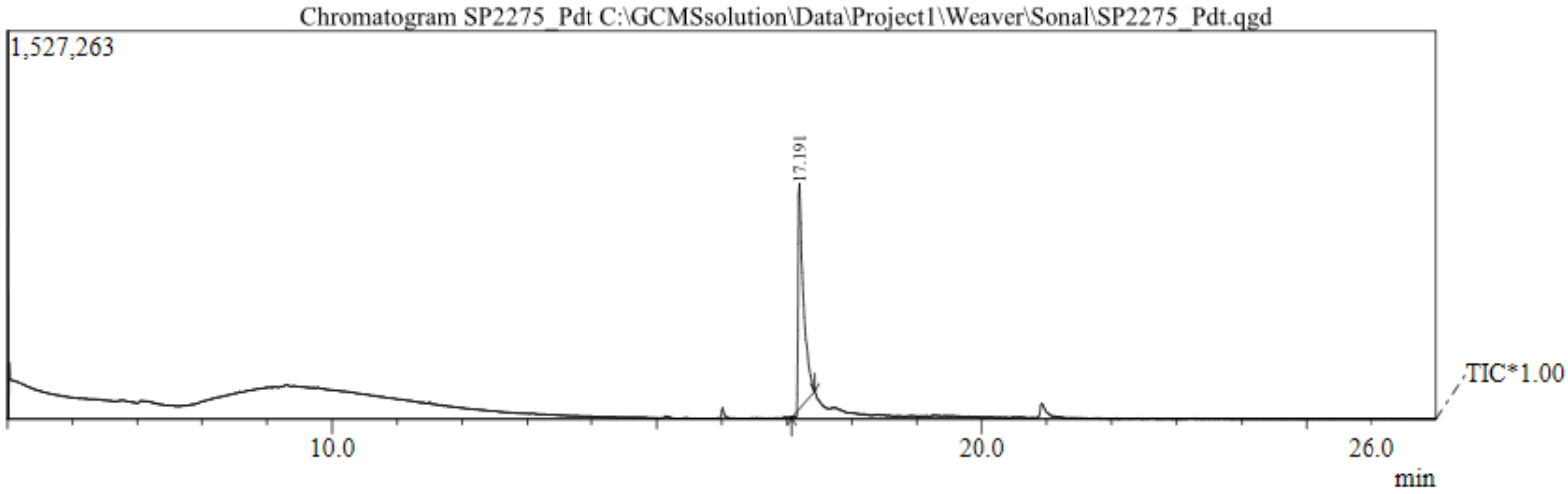
[1]H NMR (400 MHz, CDCl3, at rt) spectrum of **methyl 4-(2-cyclohexylideneethyl)-2,3,5,6-tetrafluorobenzoate (5e)**

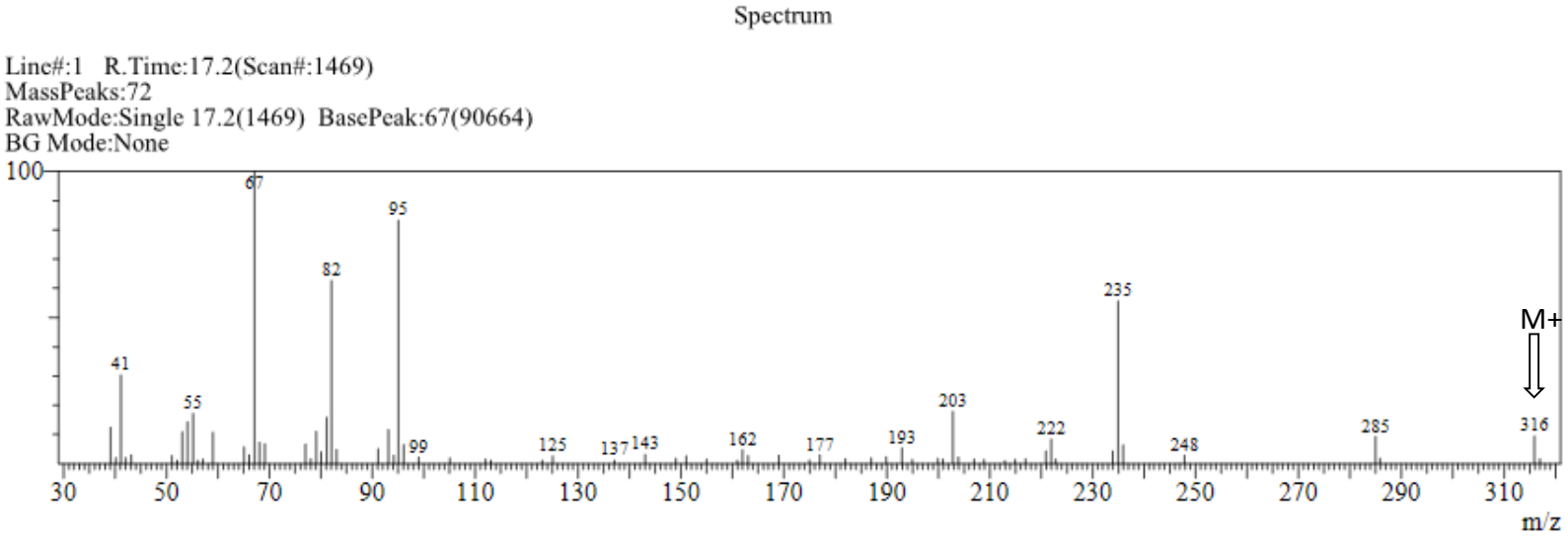


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **methyl 4-(2-cyclohexylideneethyl)-2,3,5,6-tetrafluorobenzoate (5e)**

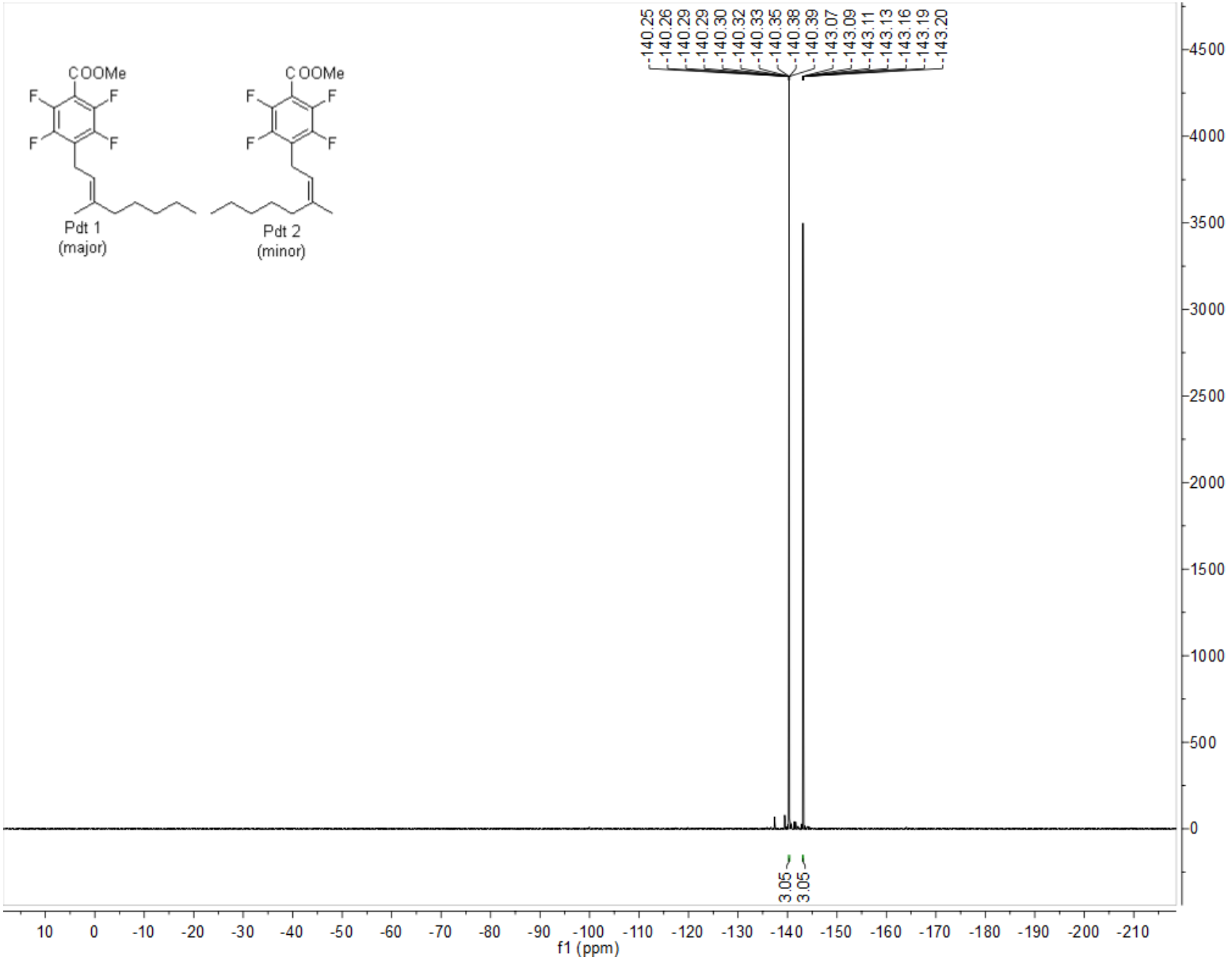


GC and MS of **methyl 4-(2-cyclohexylideneethyl)-2,3,5,6-tetrafluorobenzoate (5e)**

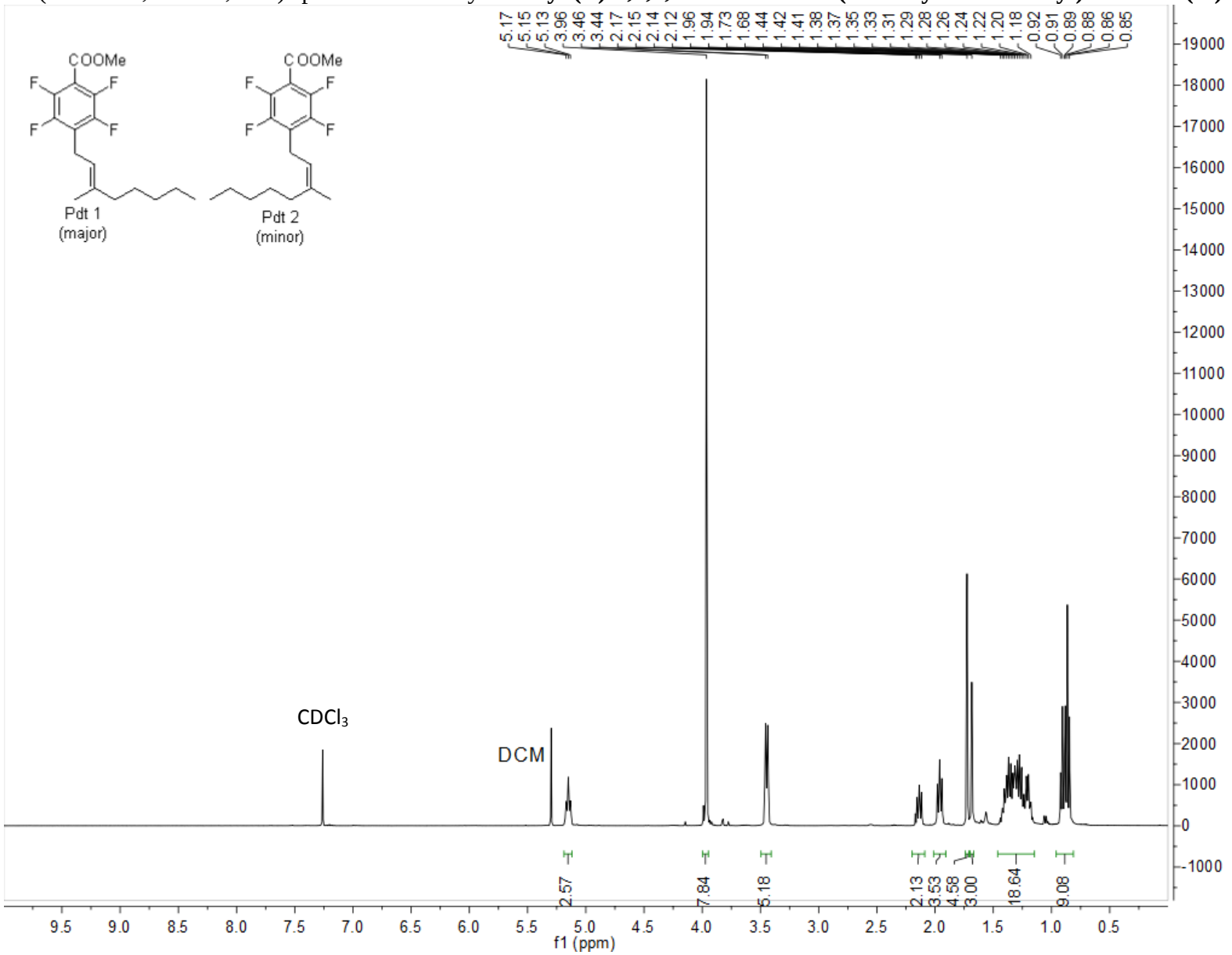




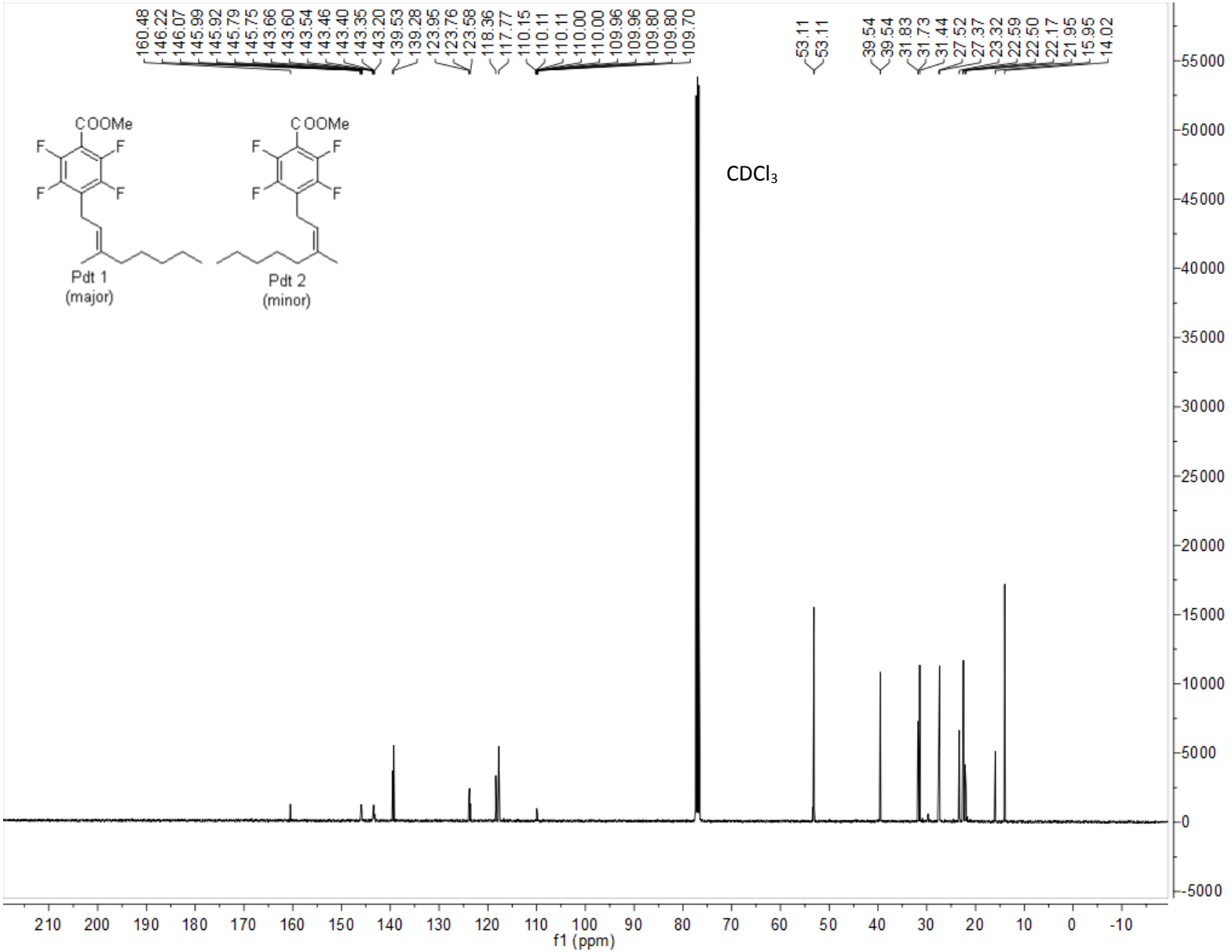
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **methyl (E)-2,3,5,6-tetrafluoro-4-(3-methyloct-2-en-1-yl)benzoate (5f)**



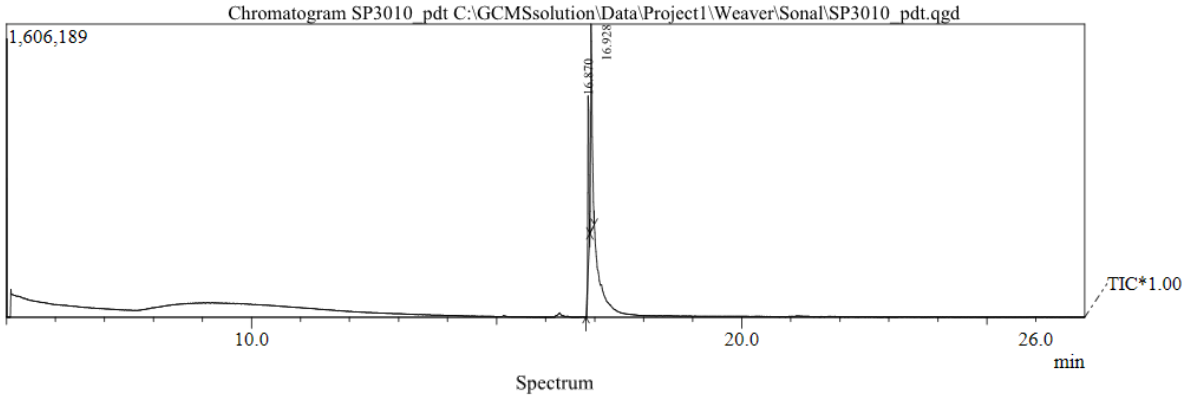
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of methyl **methyl (E)-2,3,5,6-tetrafluoro-4-(3-methyloct-2-en-1-yl)benzoate (5f)**



^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **methyl (E)-2,3,5,6-tetrafluoro-4-(3-methyloct-2-en-1-yl)benzoate (5f)**



GC and MS of **methyl (E)-2,3,5,6-tetrafluoro-4-(3-methyloct-2-en-1-yl)benzoate (5f)**



Spectrum

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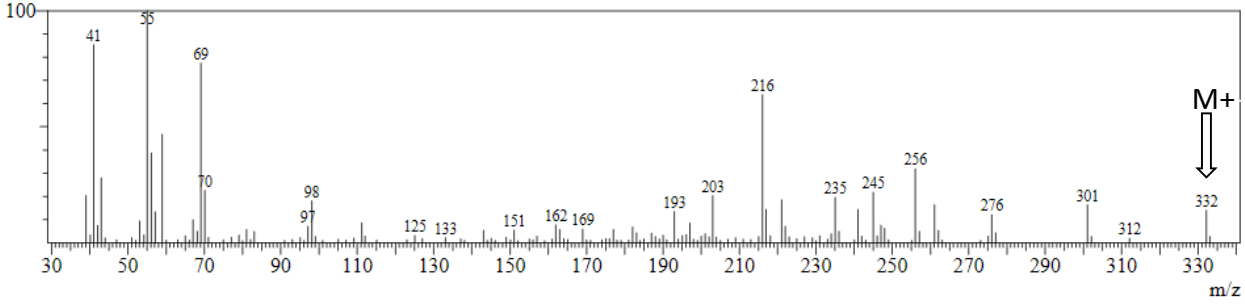

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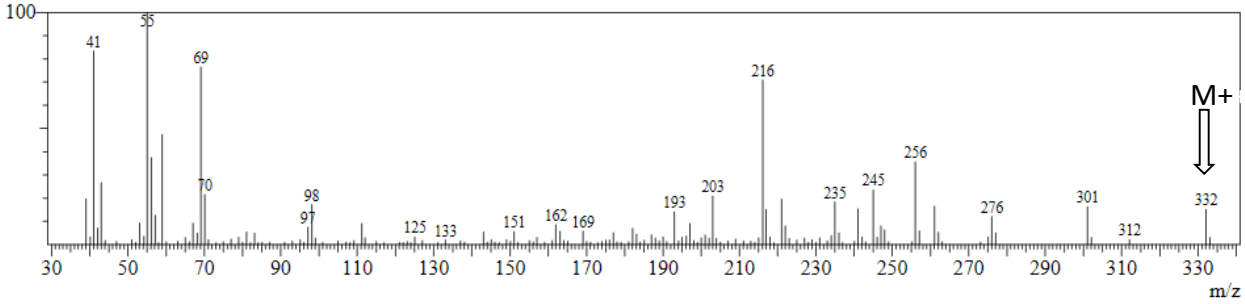
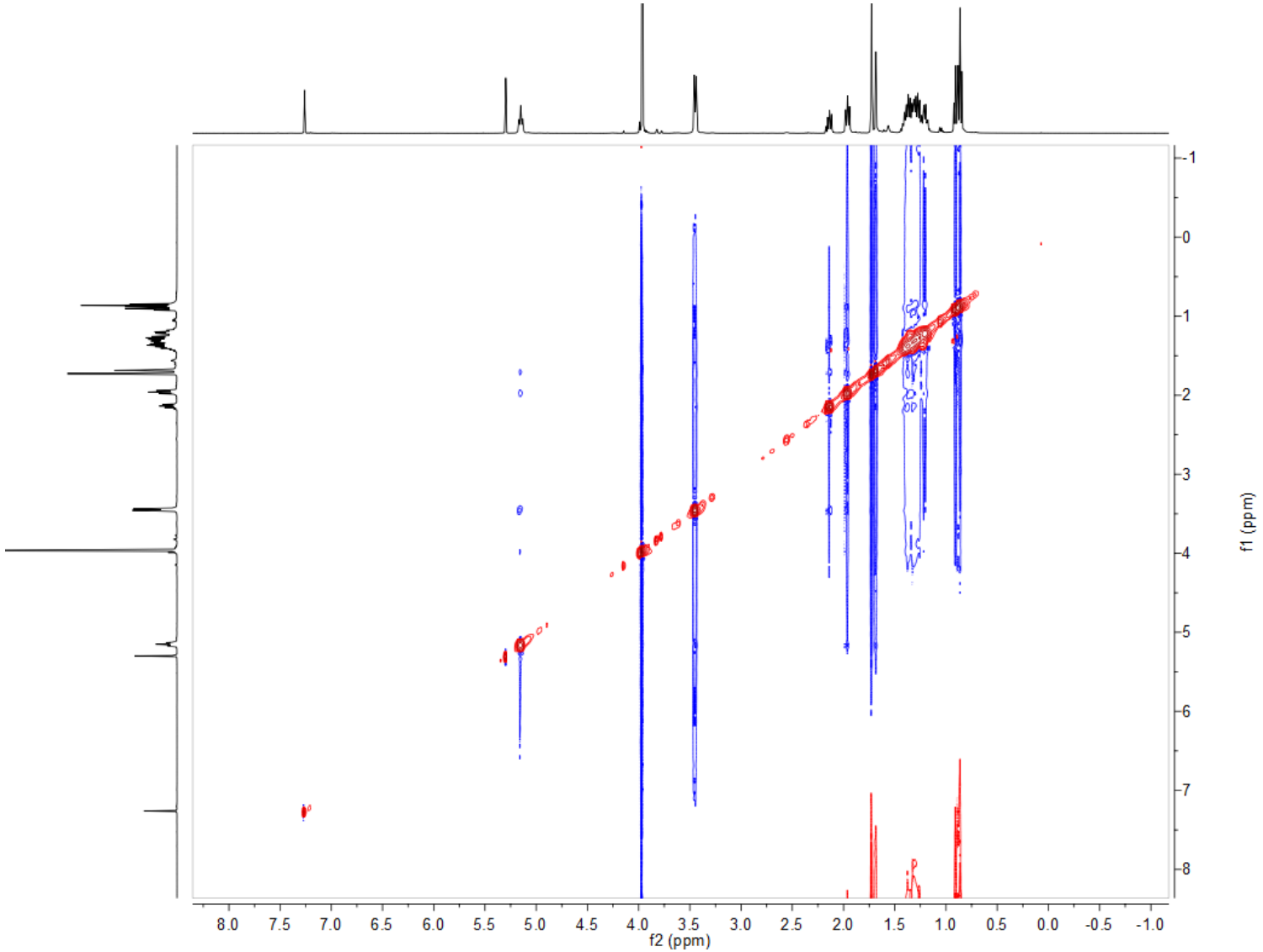
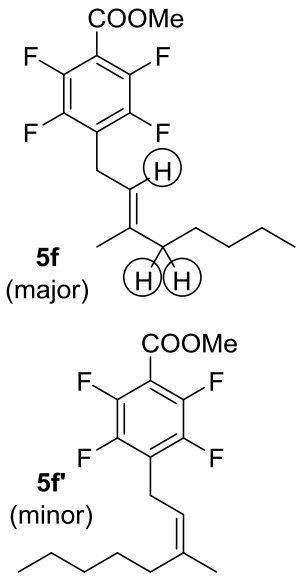
BG Mode:None



NOESY of **methyl (E)-2,3,5,6-tetrafluoro-4-(3-methyloct-2-en-1-yl)benzoate (5f)**

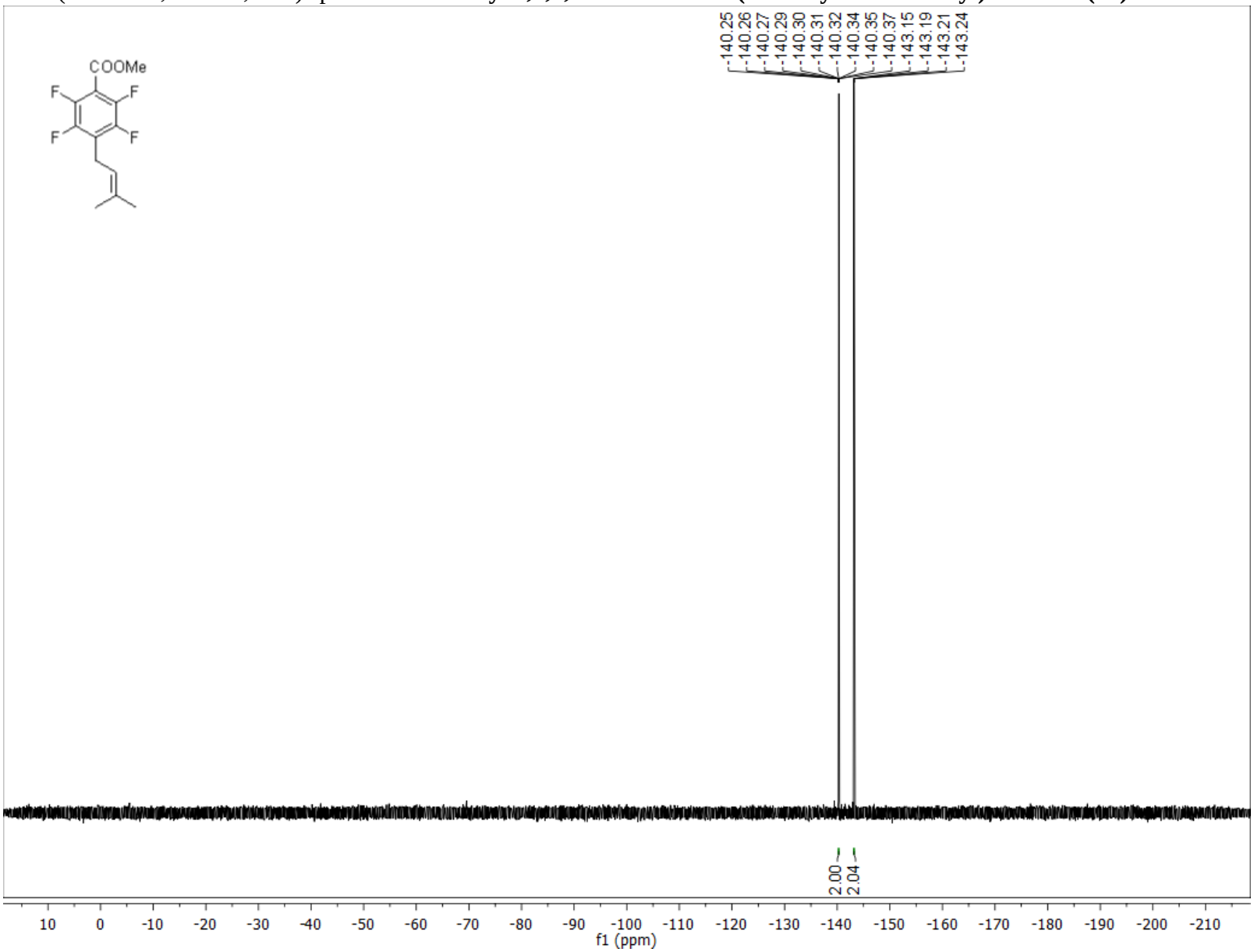




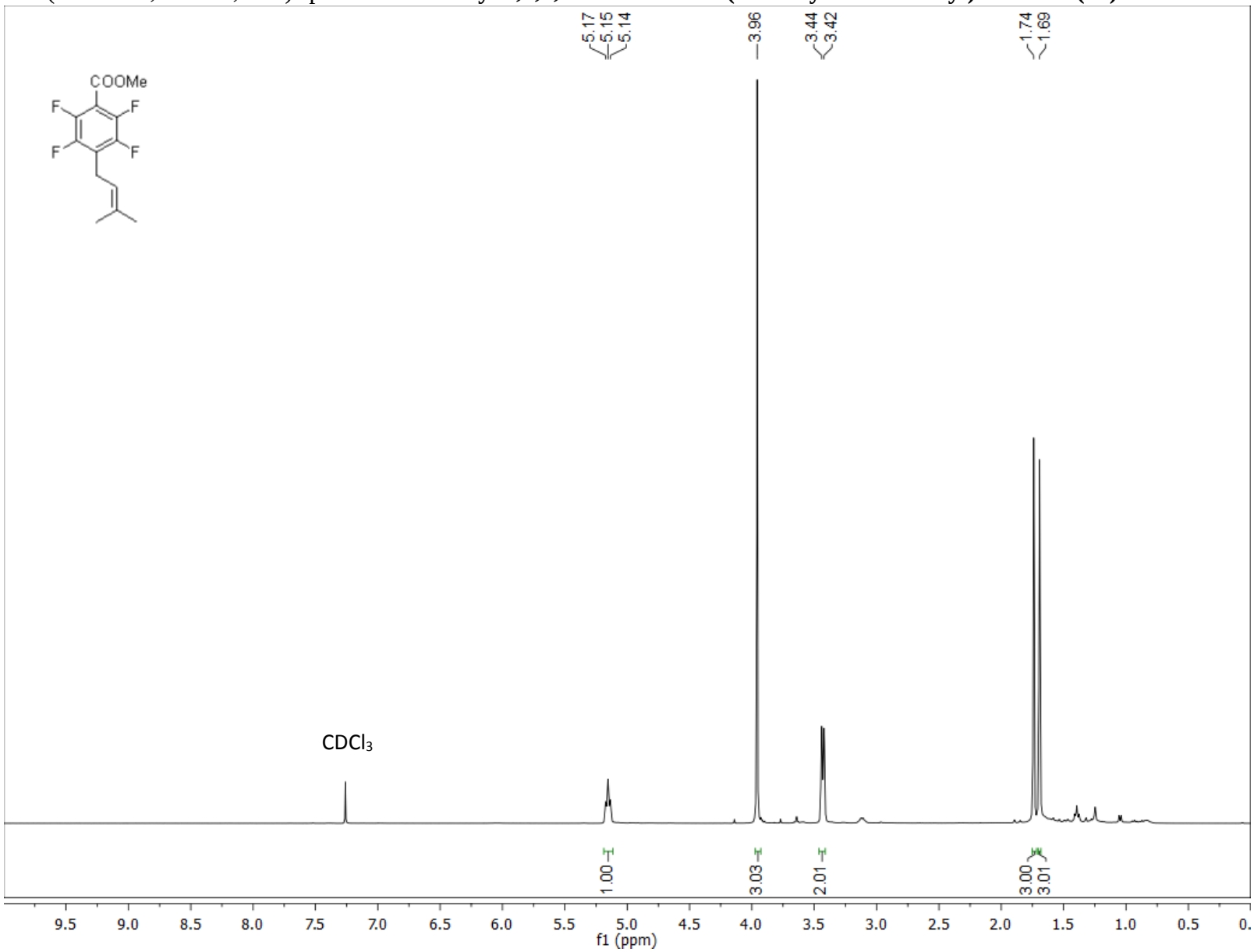
5f
(major)

5f'
(minor)

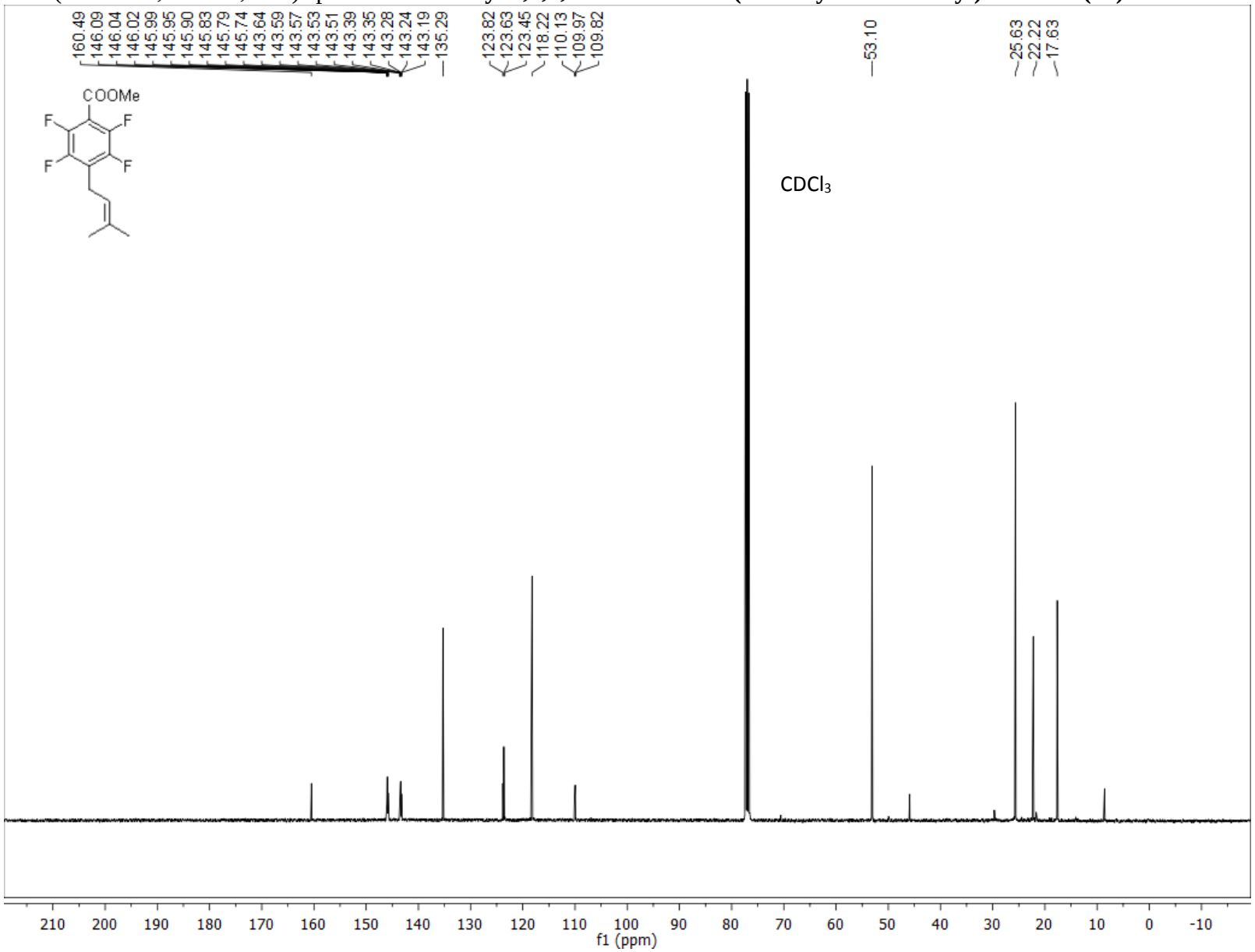
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **methyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3a)**



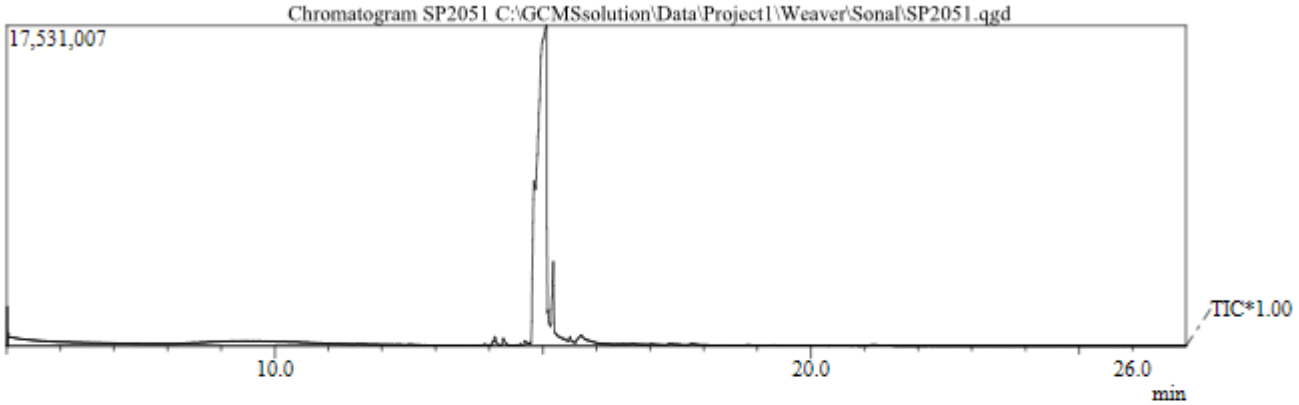
[1]H NMR (400 MHz, CDCl3, at rt) spectrum of **methyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3a)**

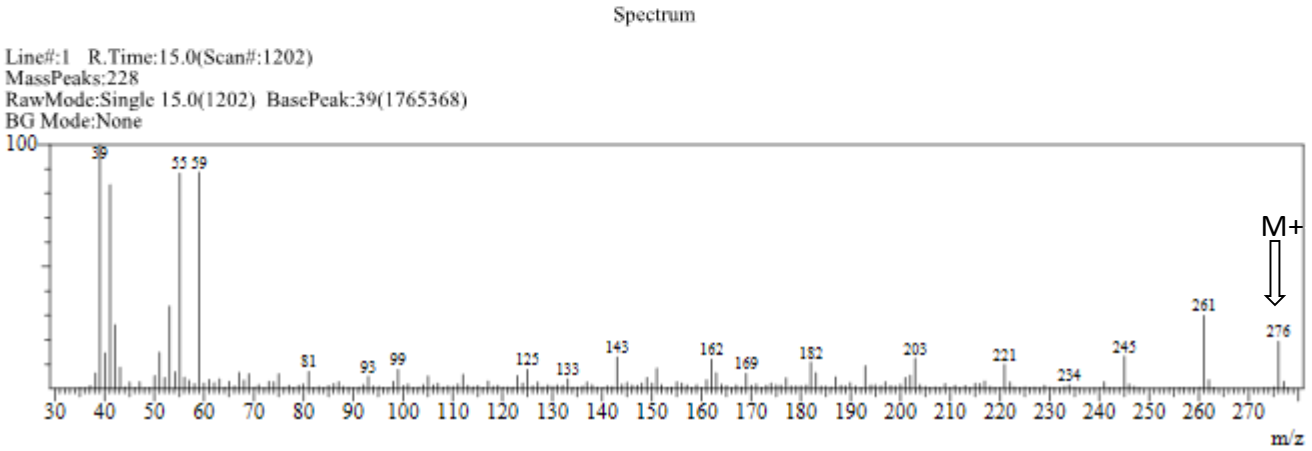


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **methyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3a)**

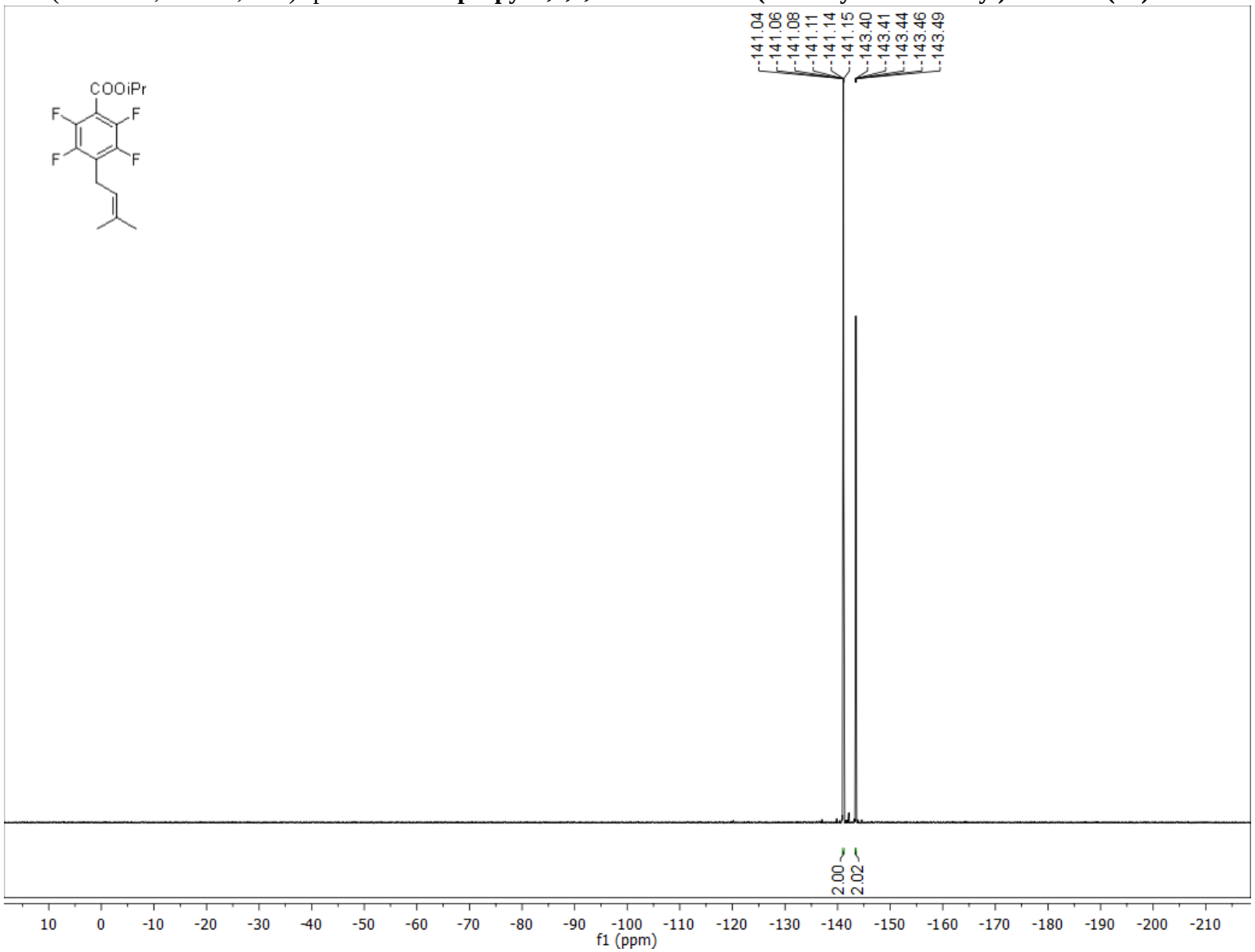


GC and MS of **methyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3a)**

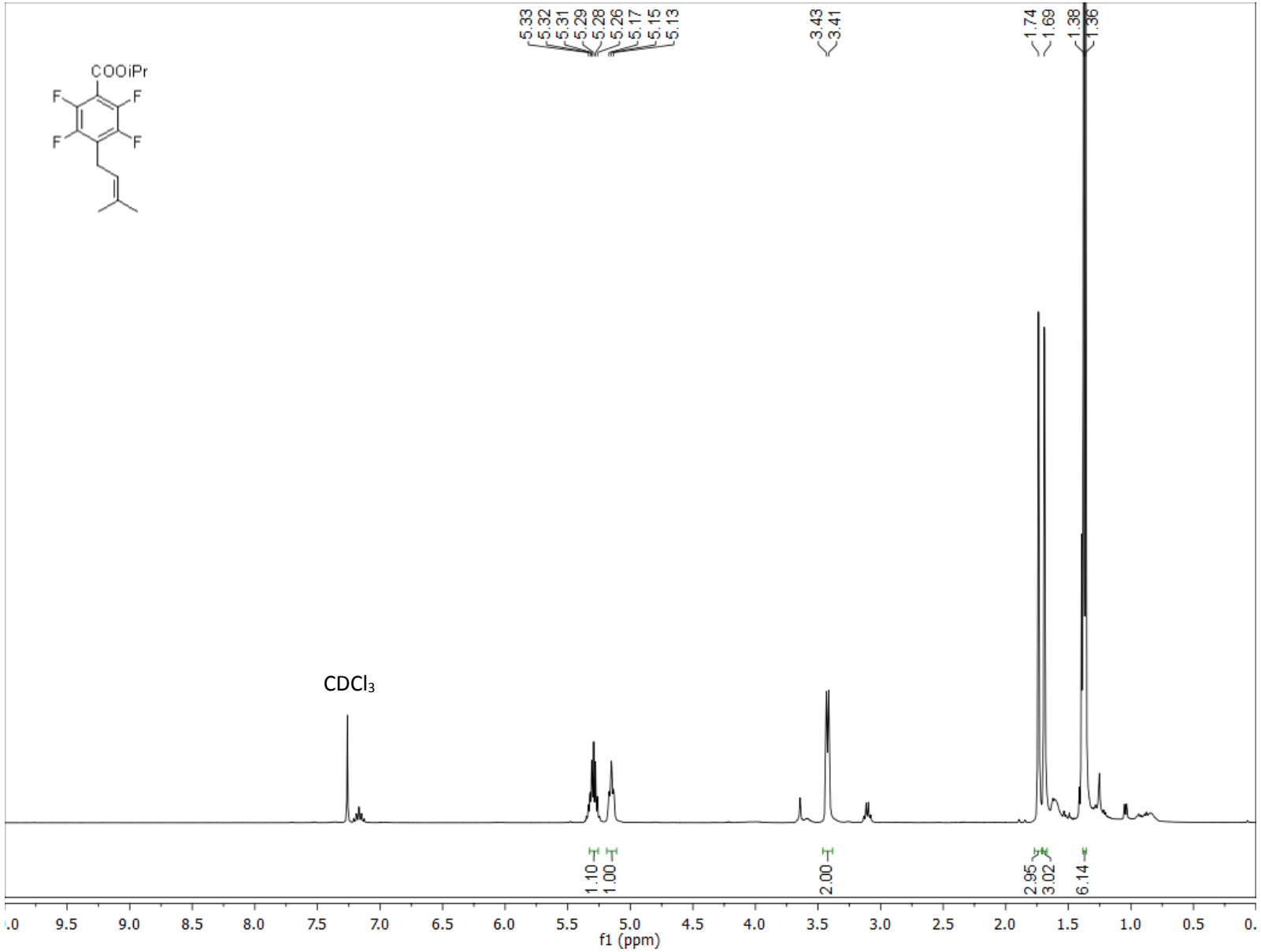




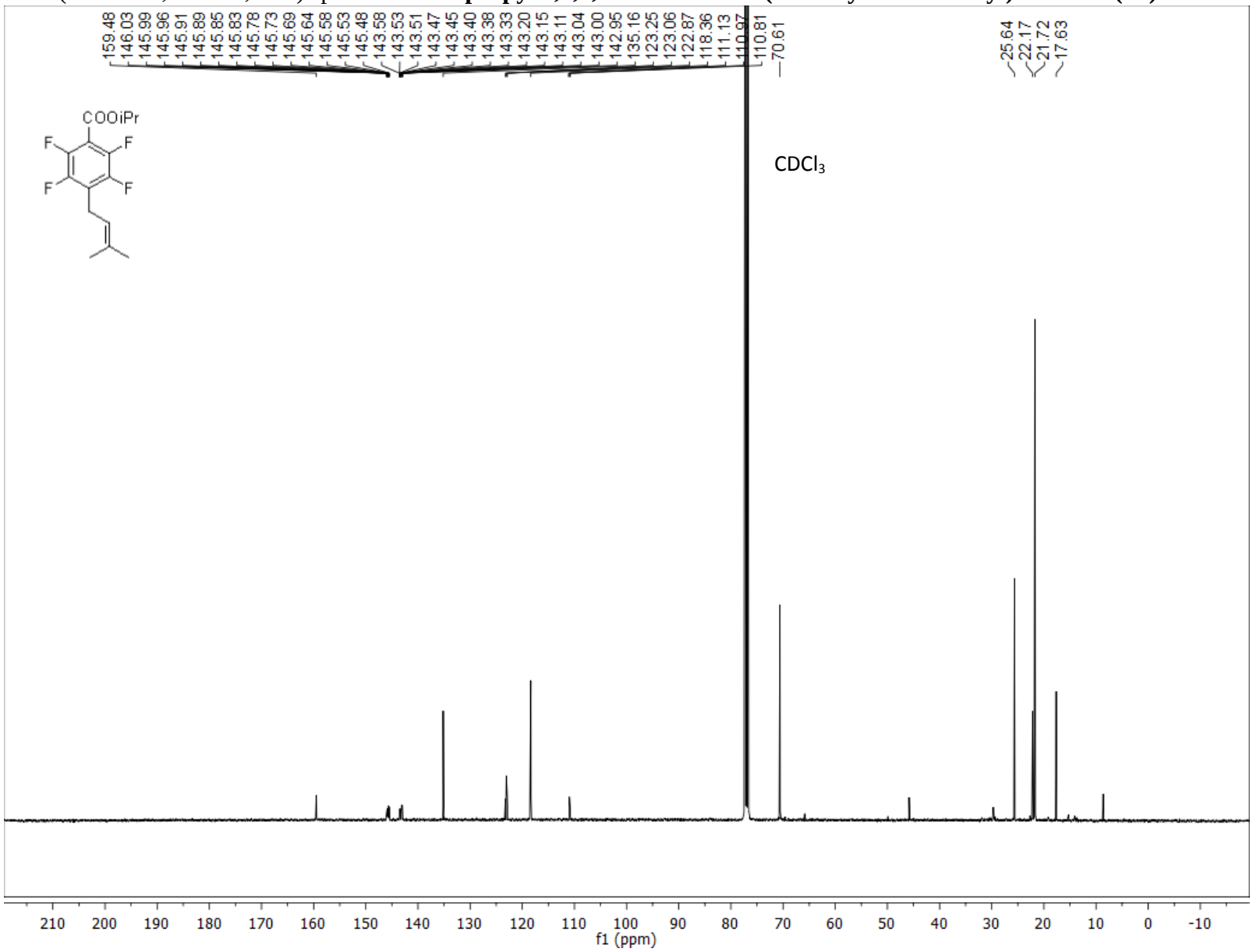
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **isopropyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3b)**



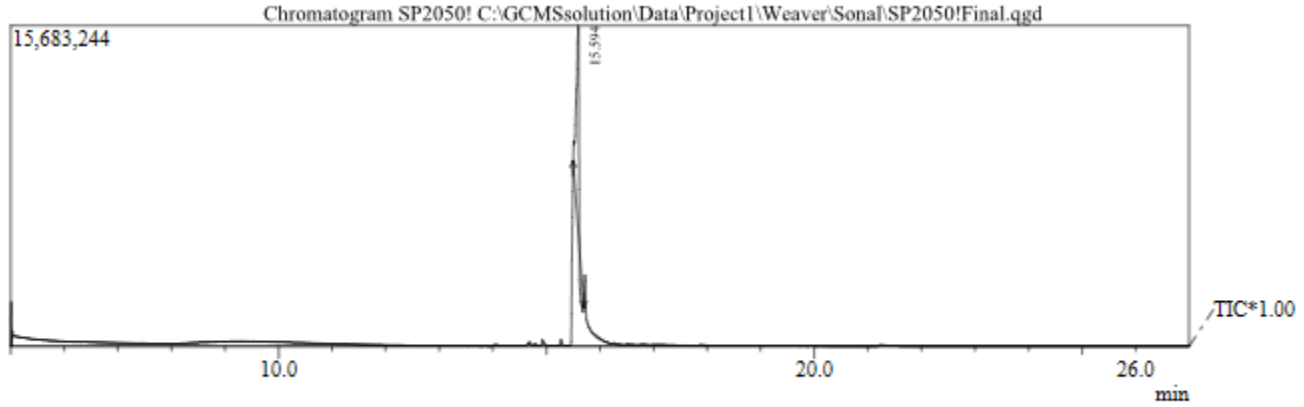
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **isopropyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3b)**

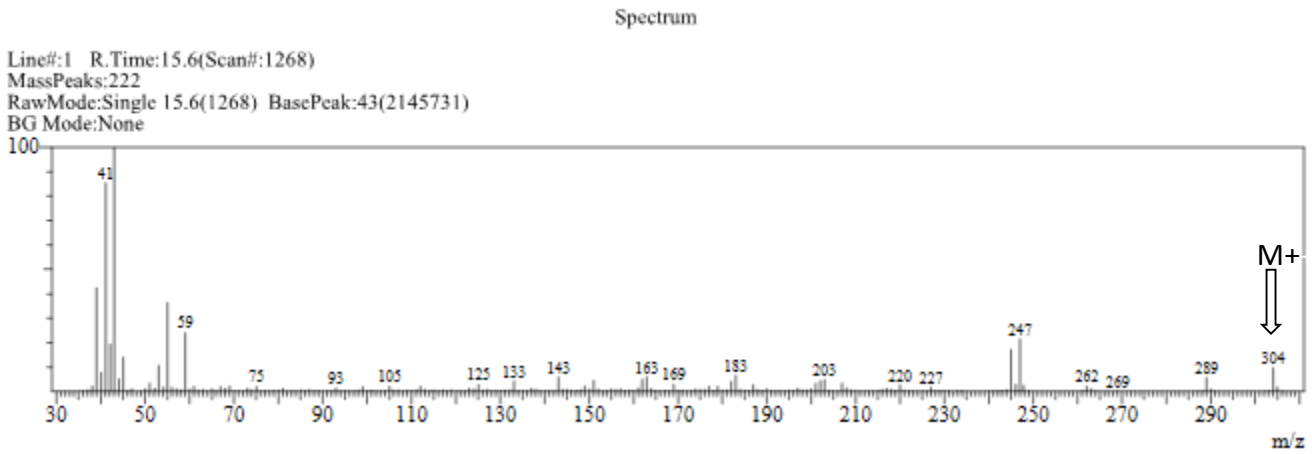


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **isopropyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3b)**

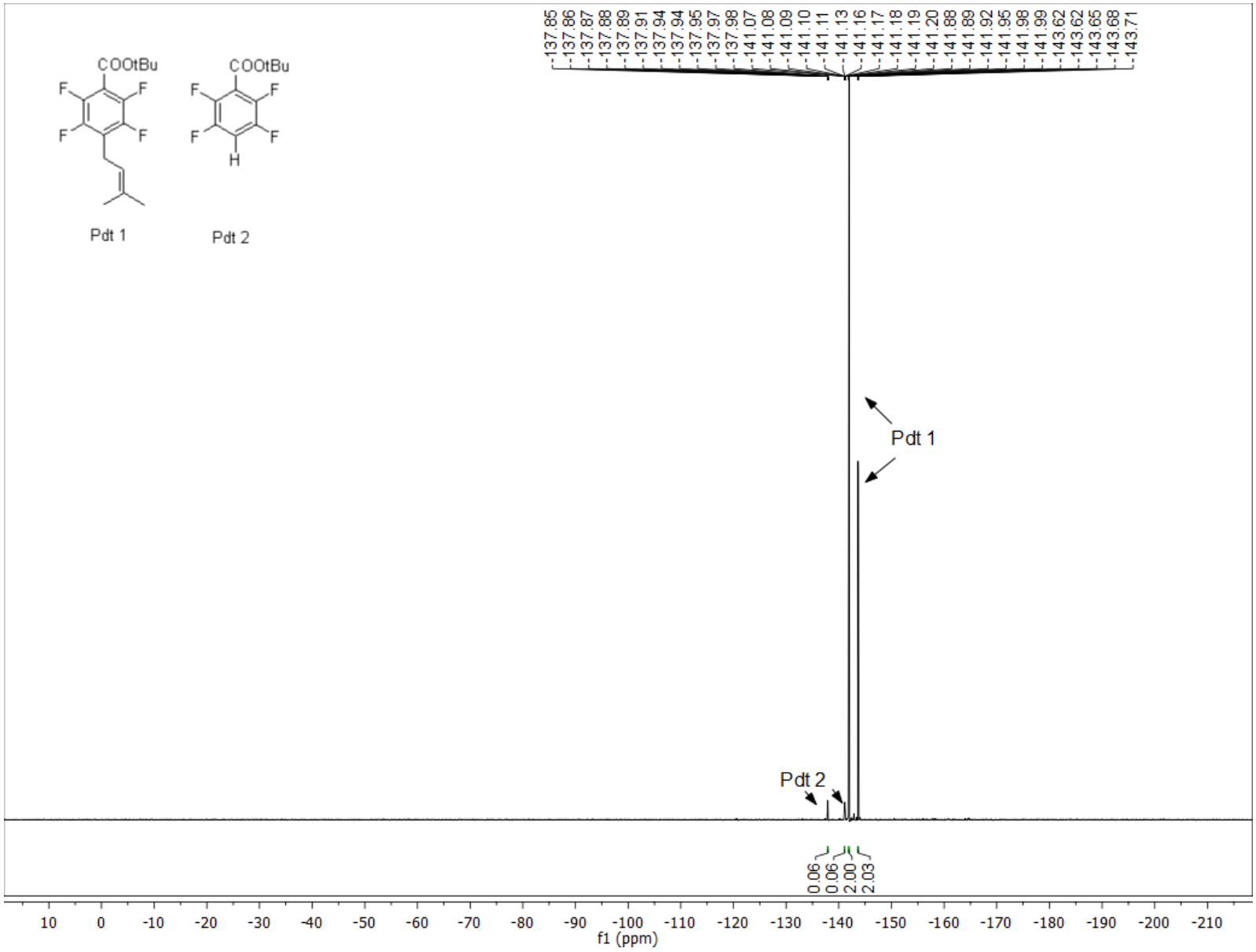


GC and MS of **isopropyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3b)**

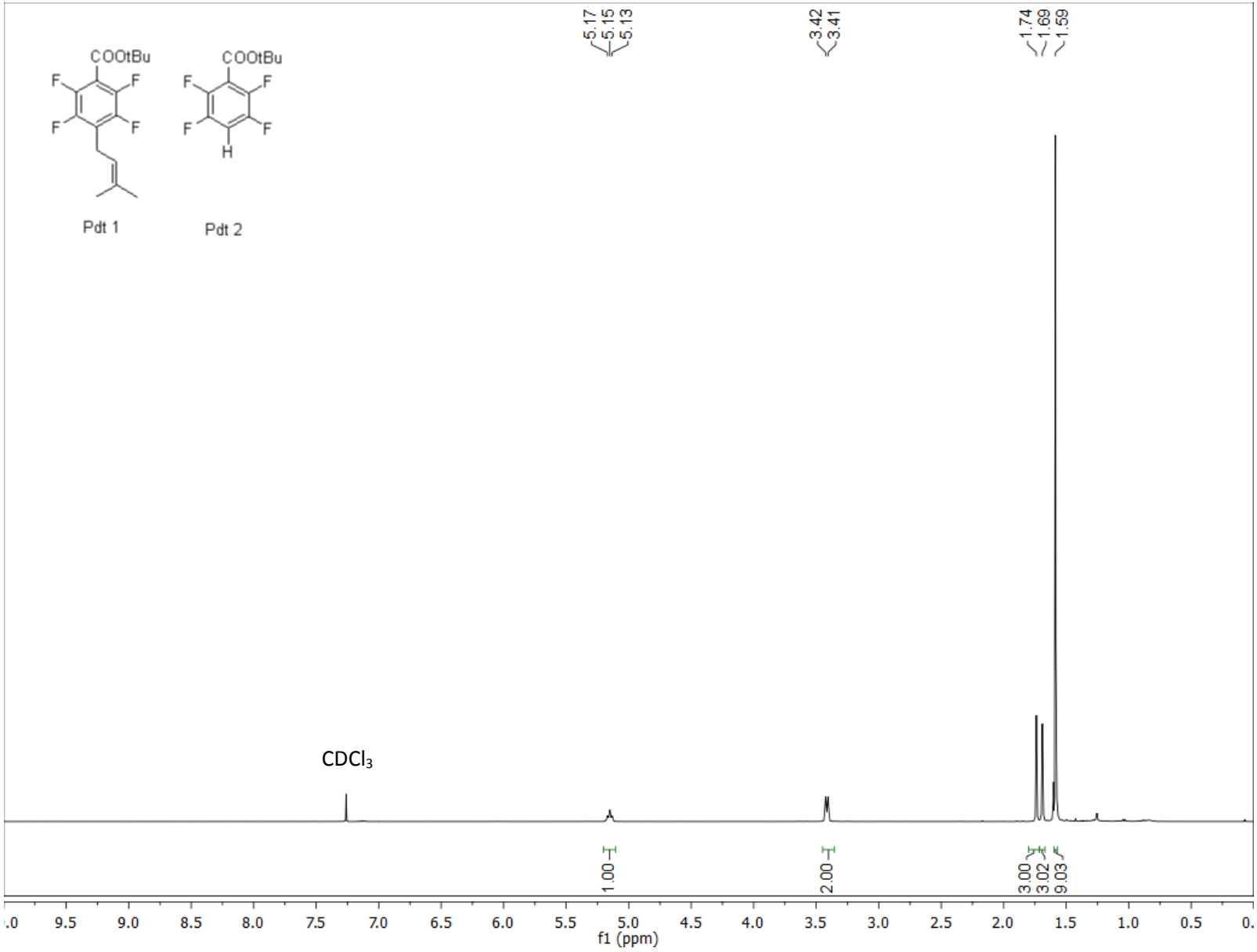




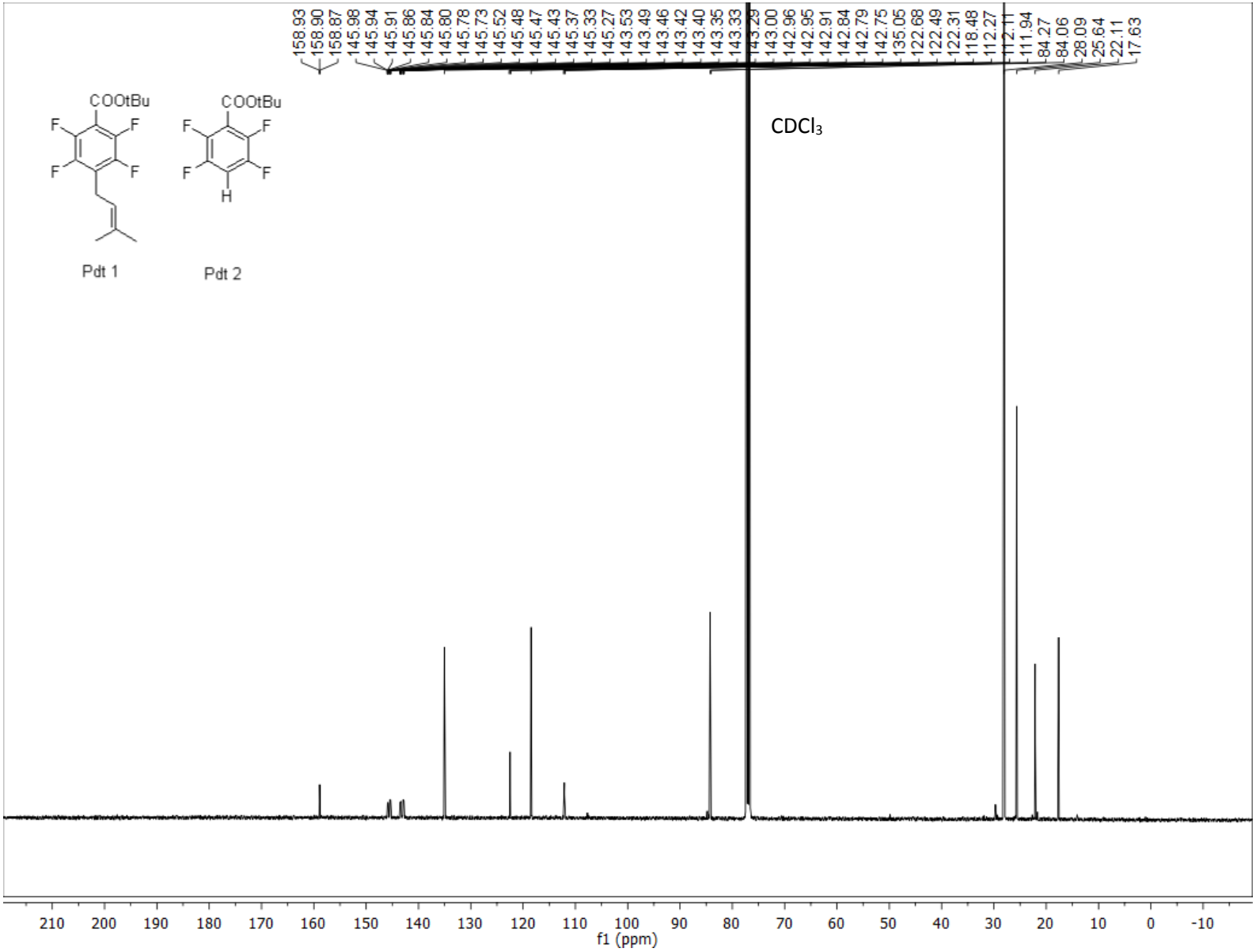
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **isobutyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3c)**



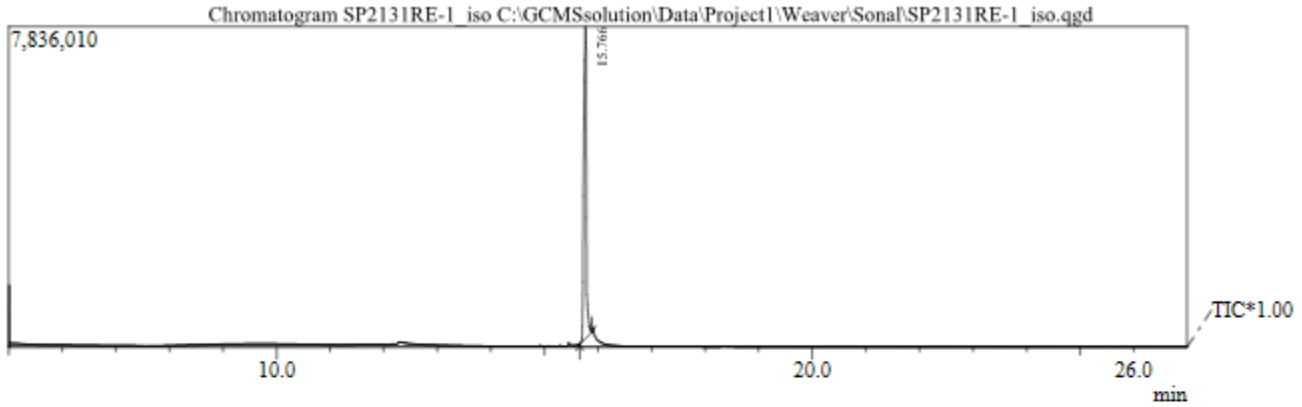
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **isobutyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3c)**

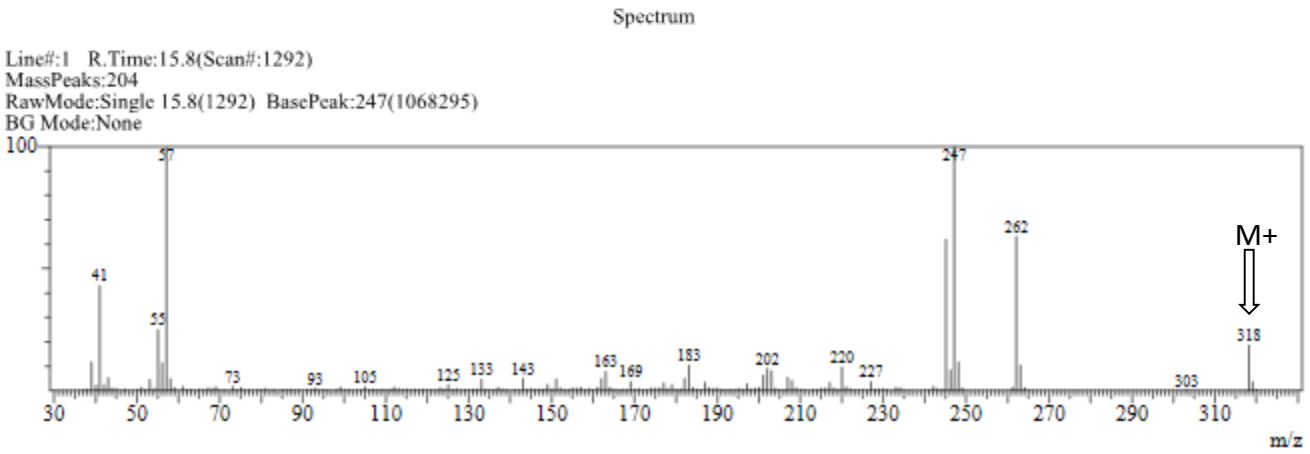


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **isobutyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3c)**

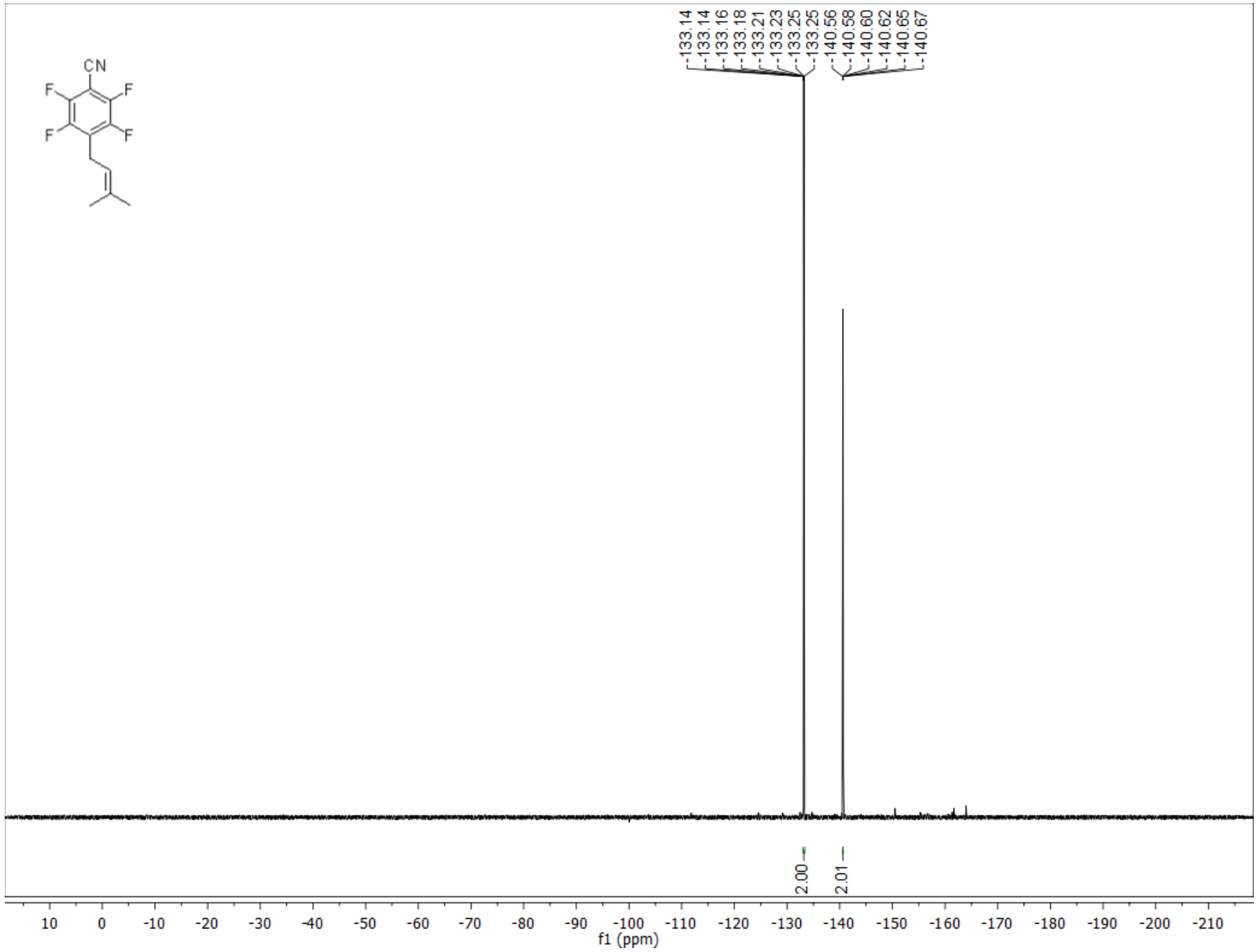


GC and MS of **isobutyl 2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzoate (3c)**

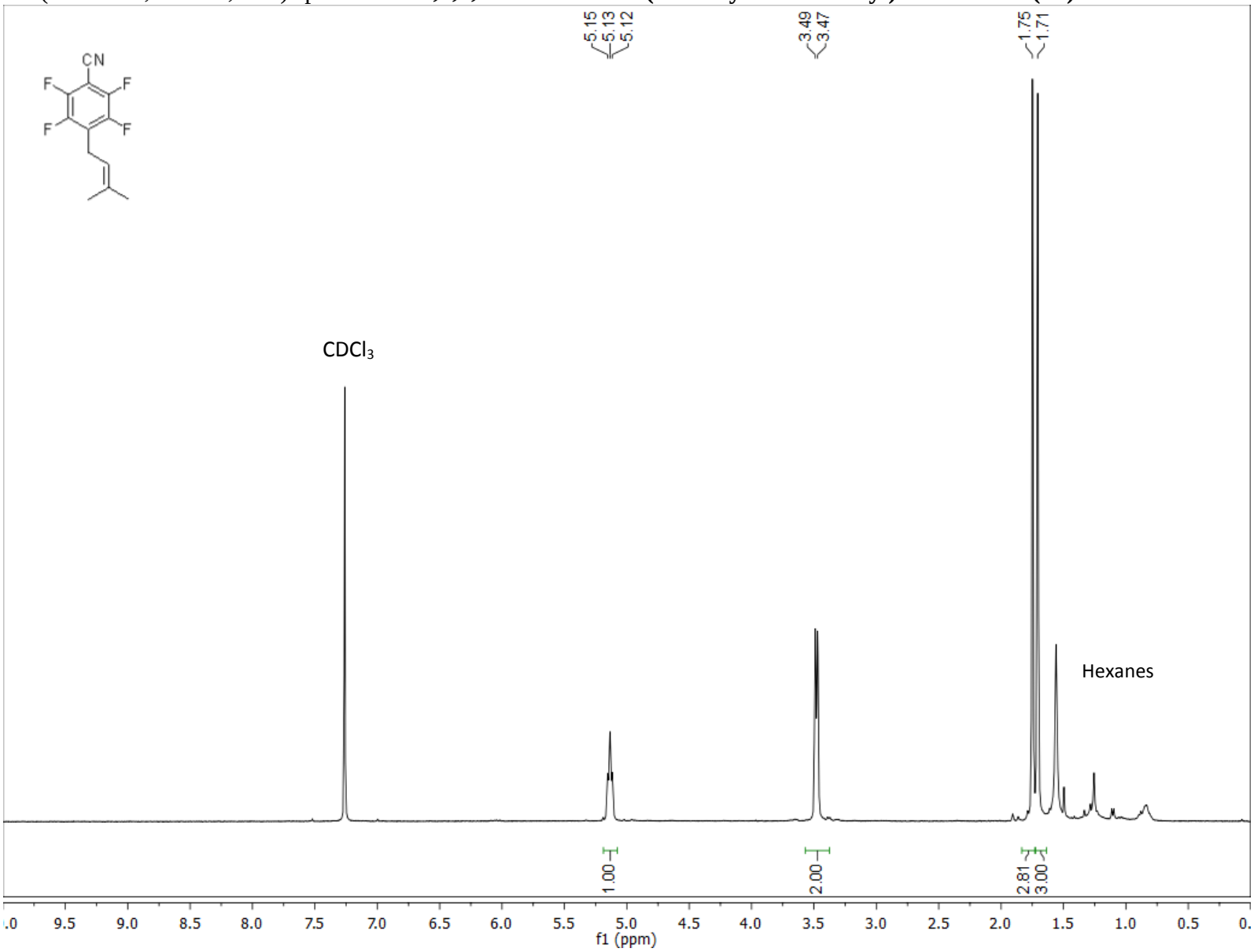




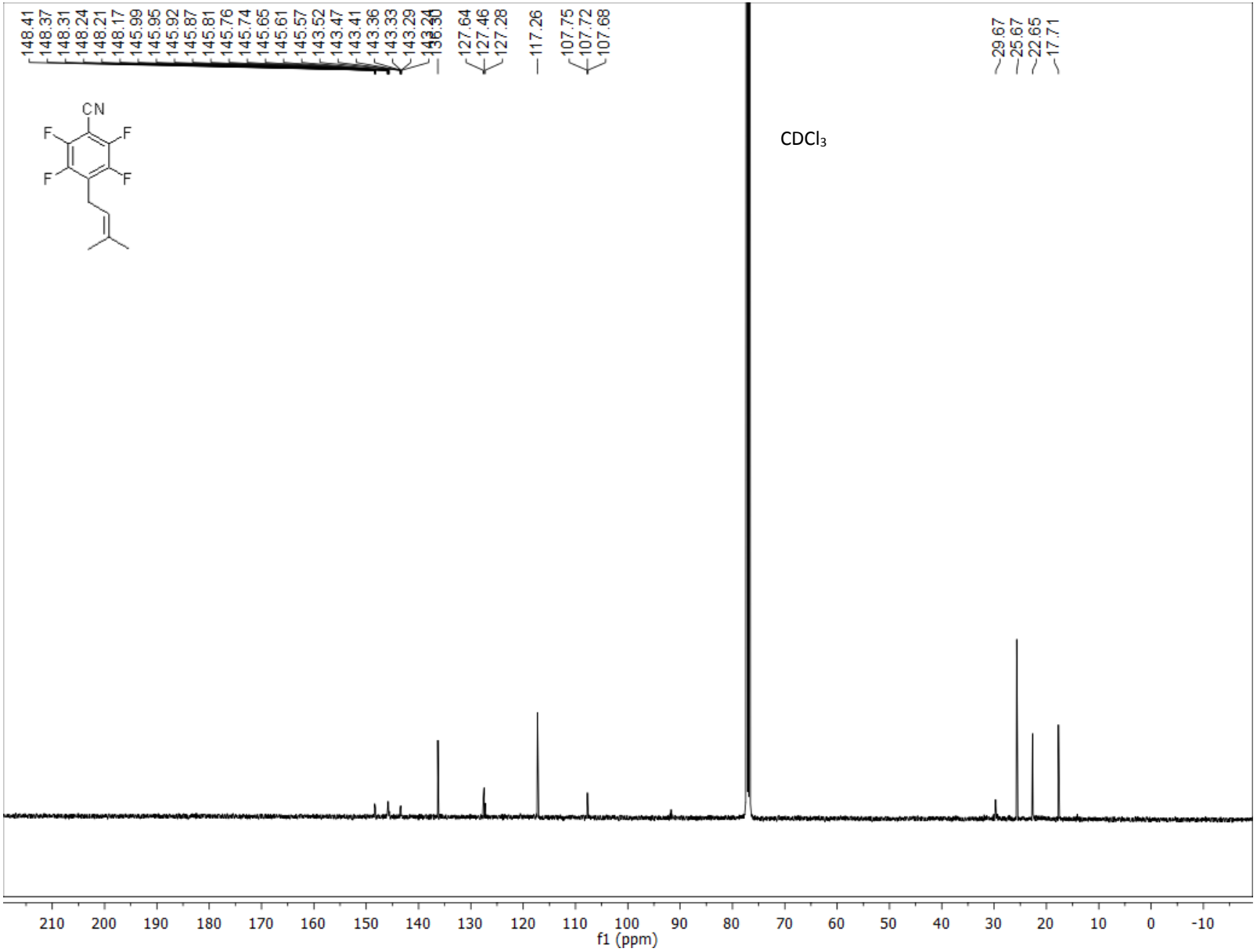
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzonitrile (3d)**



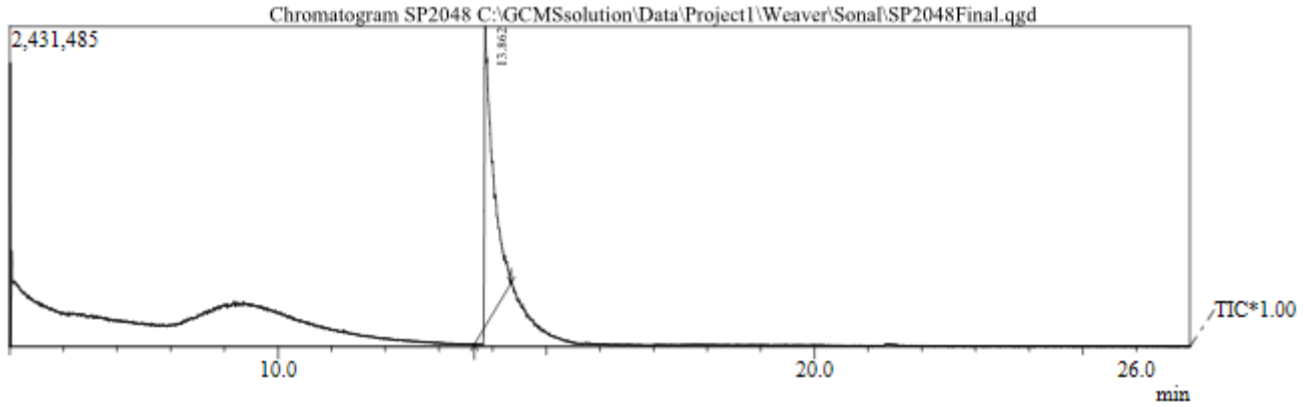
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzonitrile (3d)**

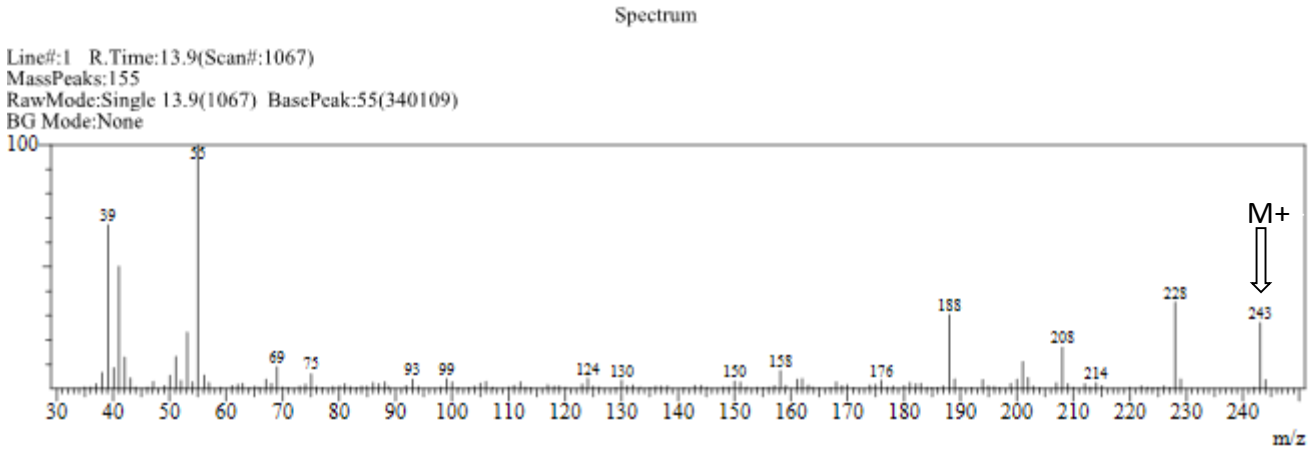


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzonitrile (3d)**

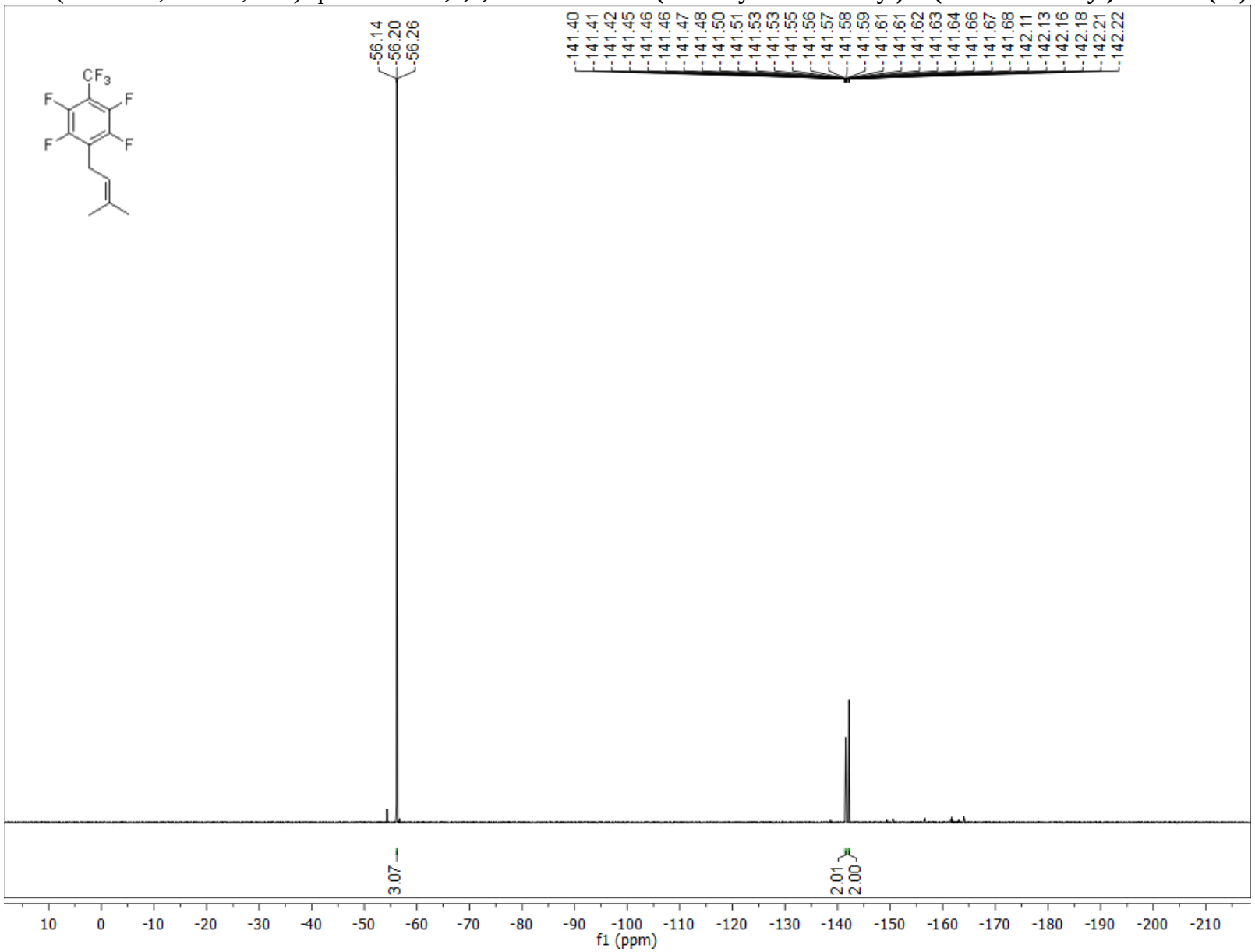


GC and MS of **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)benzonitrile (3d)**

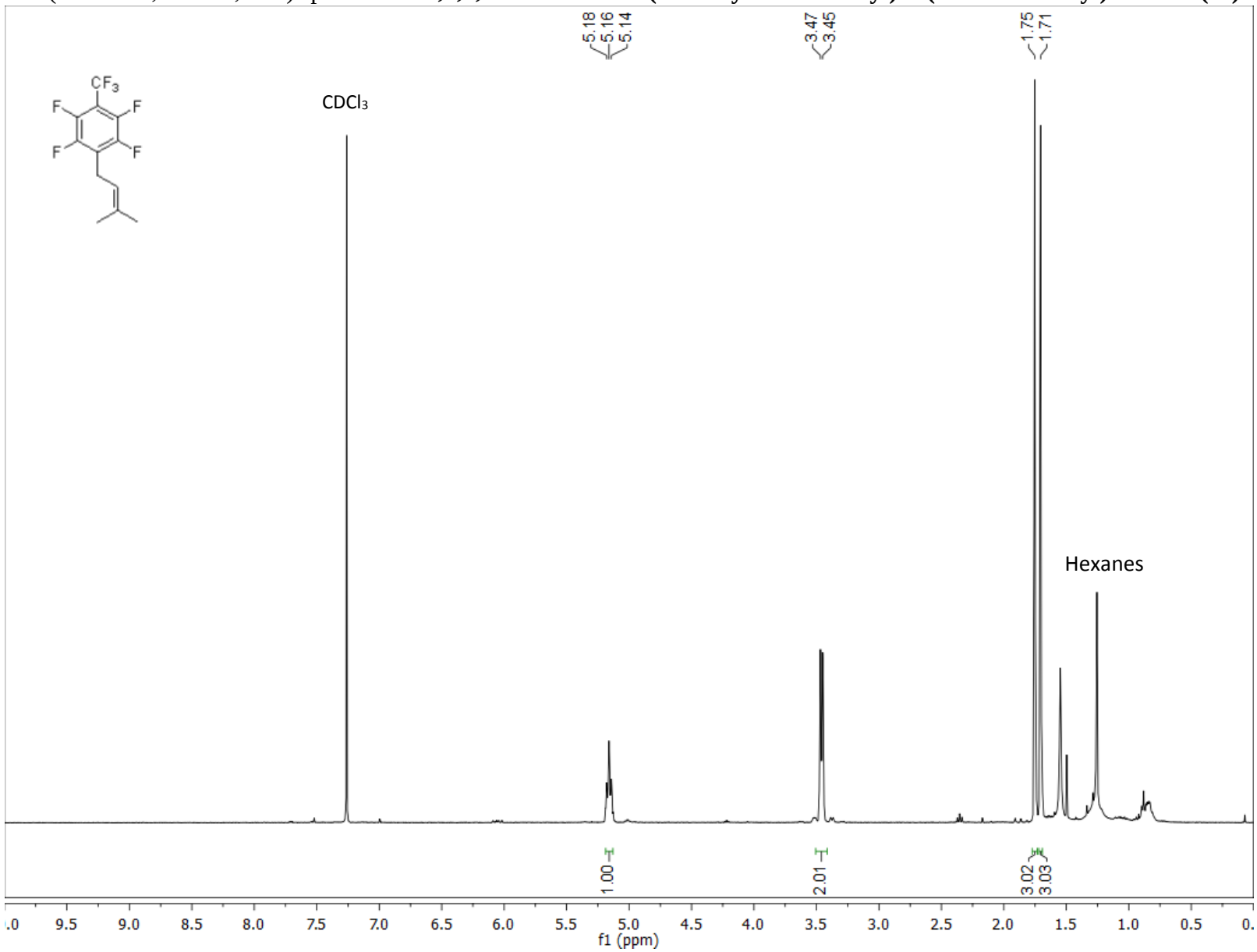




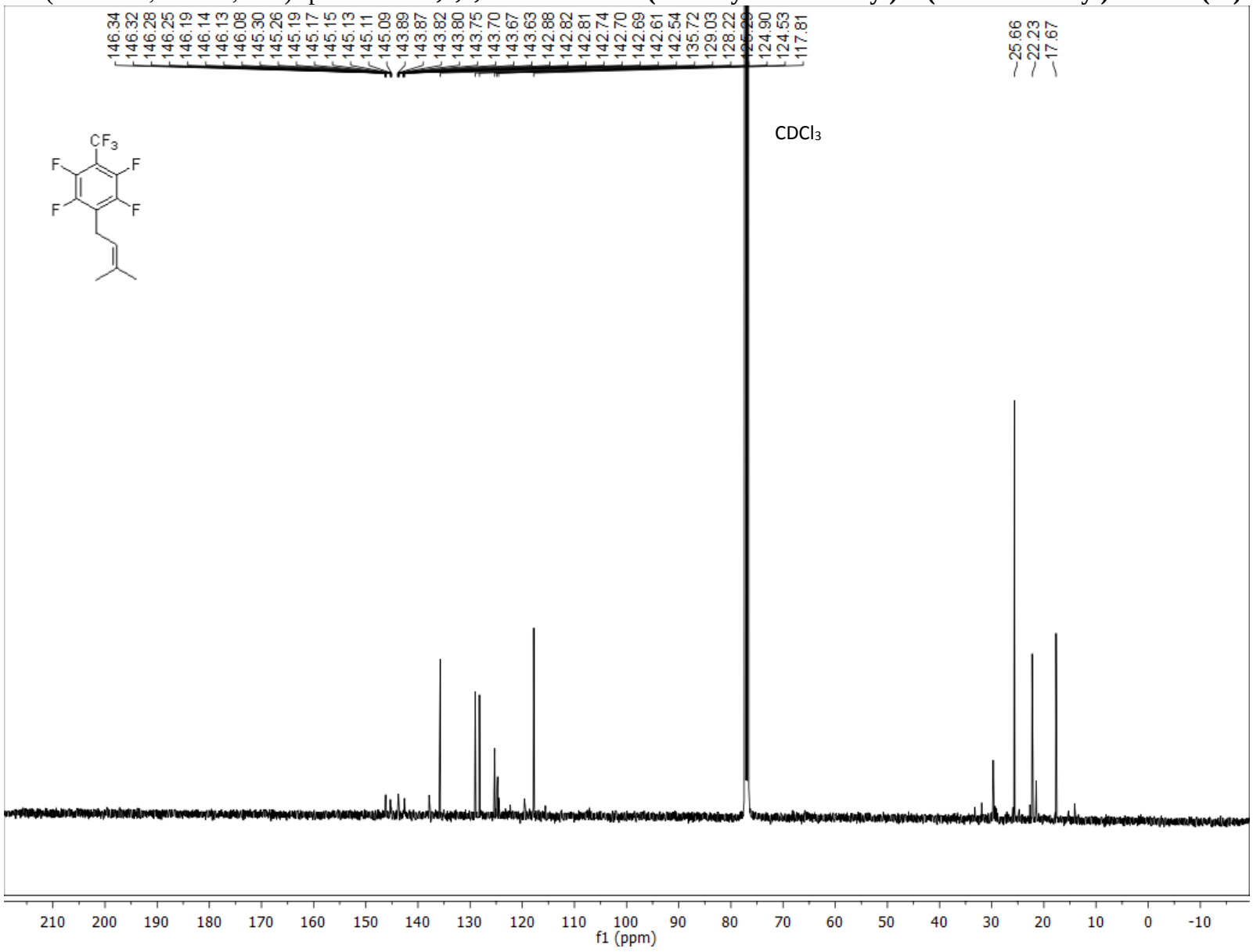
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **1,2,4,5-tetrafluoro-3-(3-methylbut-2-en-1-yl)-6-(trifluoromethyl)benzene (3e)**



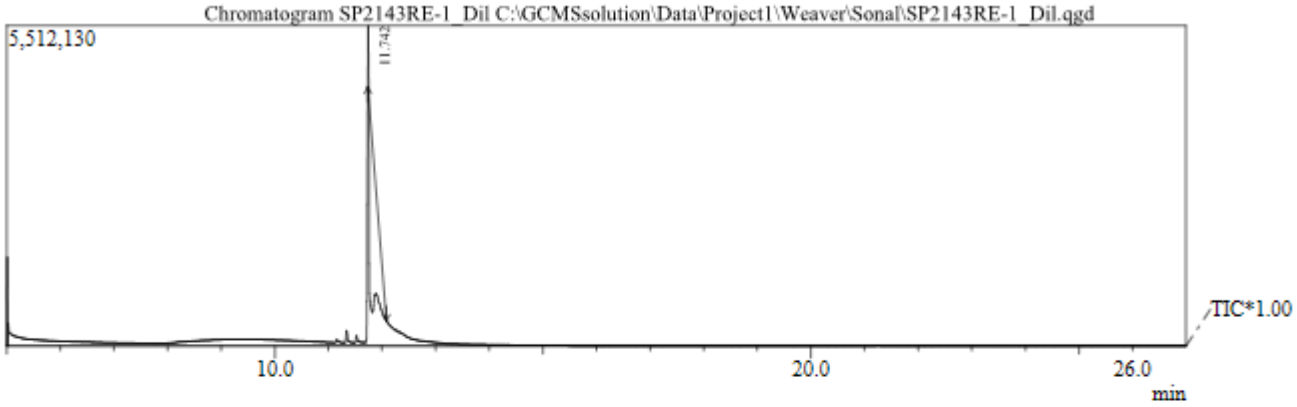
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **1,2,4,5-tetrafluoro-3-(3-methylbut-2-en-1-yl)-6-(trifluoromethyl)benzene (3e)**

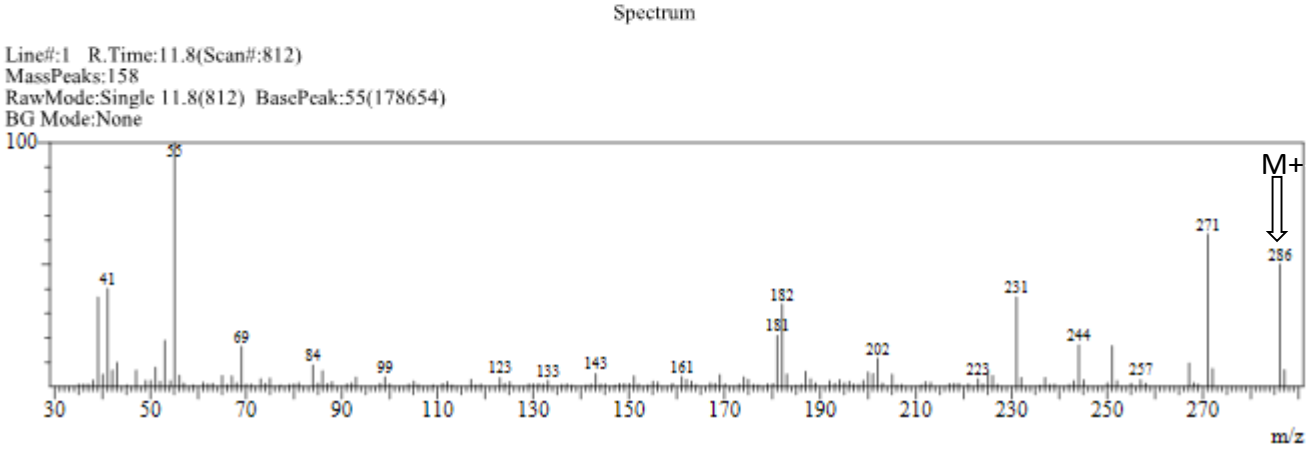


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **1,2,4,5-tetrafluoro-3-(3-methylbut-2-en-1-yl)-6-(trifluoromethyl)benzene (3e)**

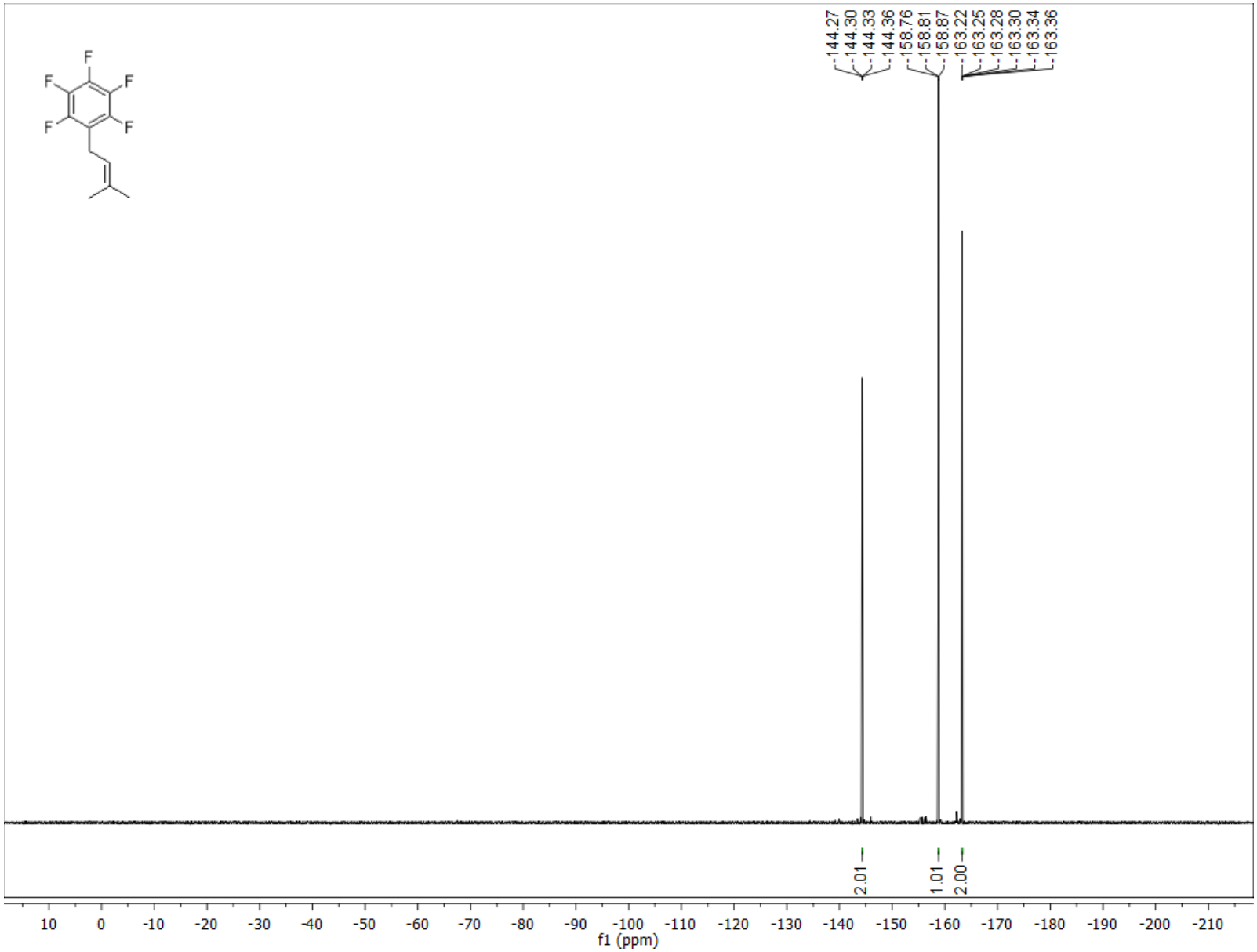


GC and MS of **1,2,4,5-tetrafluoro-3-(3-methylbut-2-en-1-yl)-6-(trifluoromethyl)benzene (3e)**

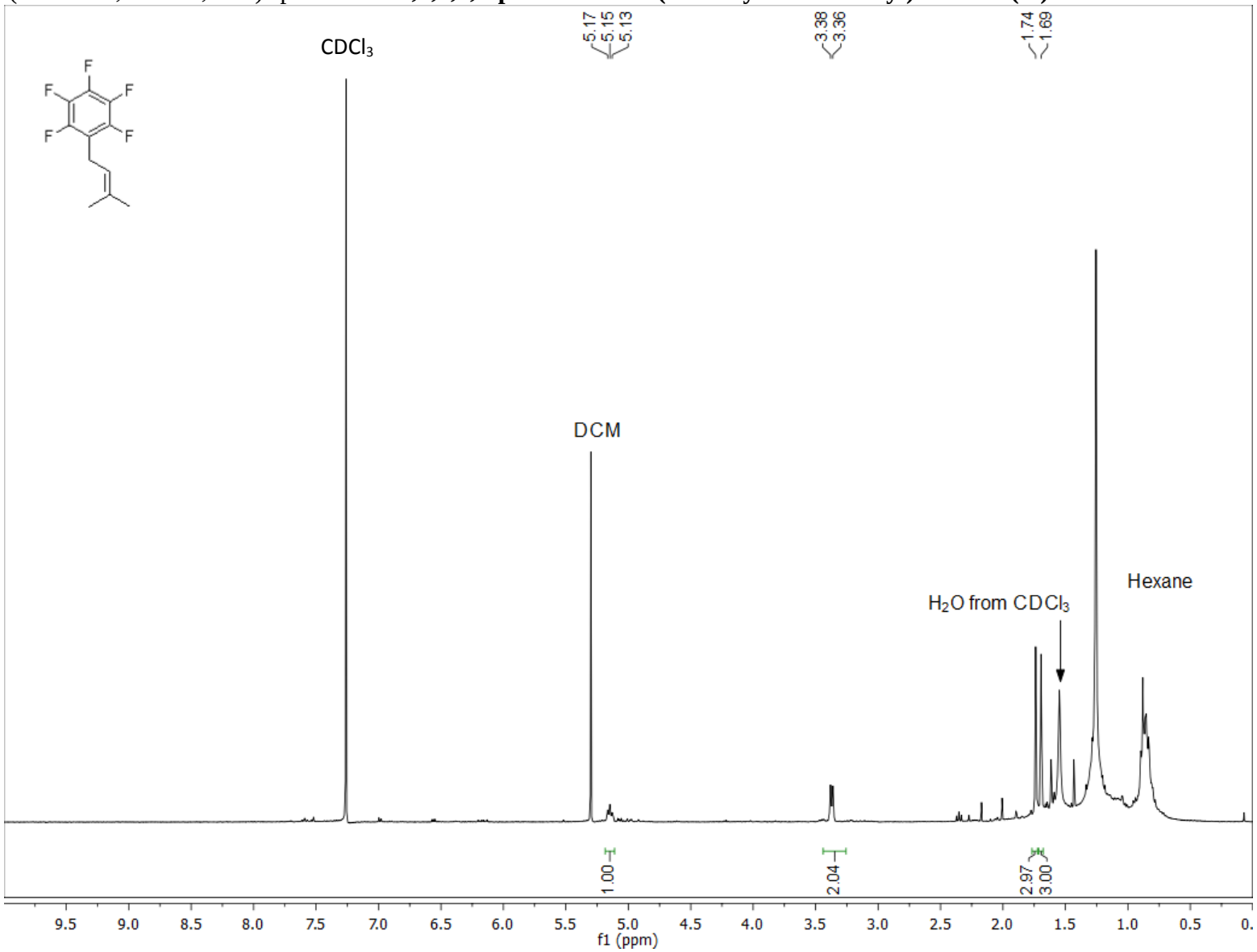




^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **1,2,3,4,5-pentafluoro-6-(3-methylbut-2-en-1-yl)benzene (3f)**

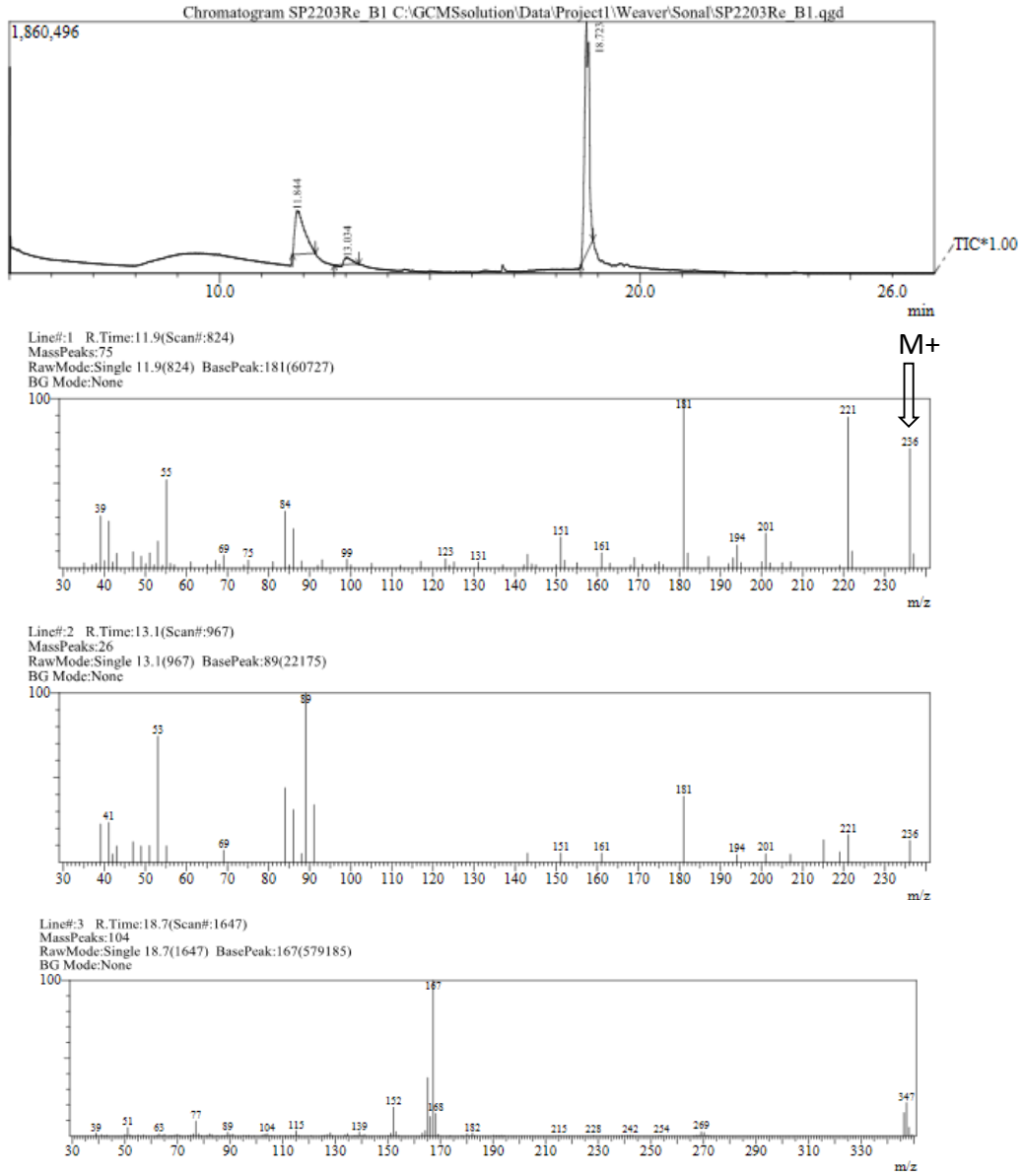


^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **1,2,3,4,5-pentafluoro-6-(3-methylbut-2-en-1-yl)benzene (3f)**

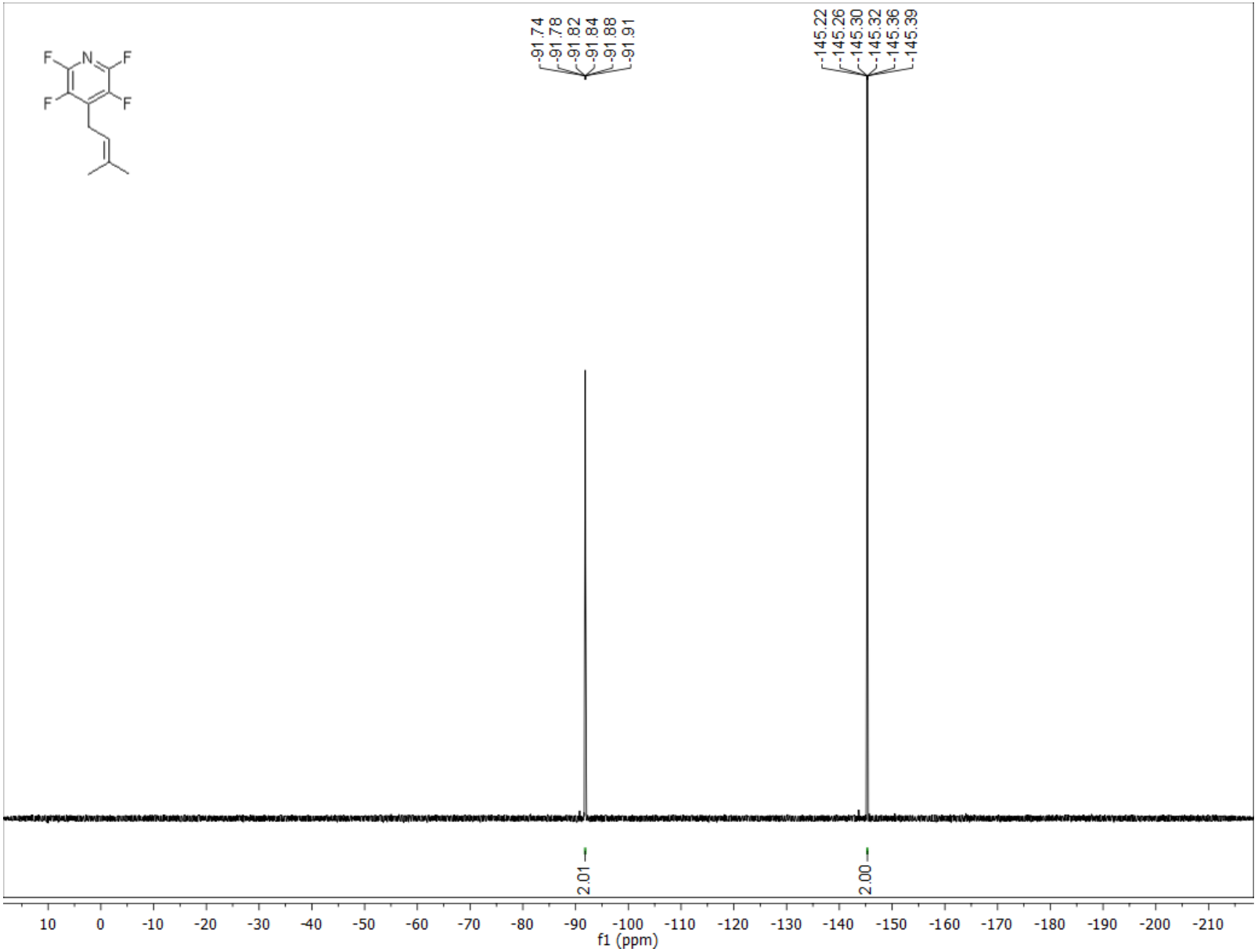


Minimal effort was given to evaporate the solvent due to low volatility of the product.

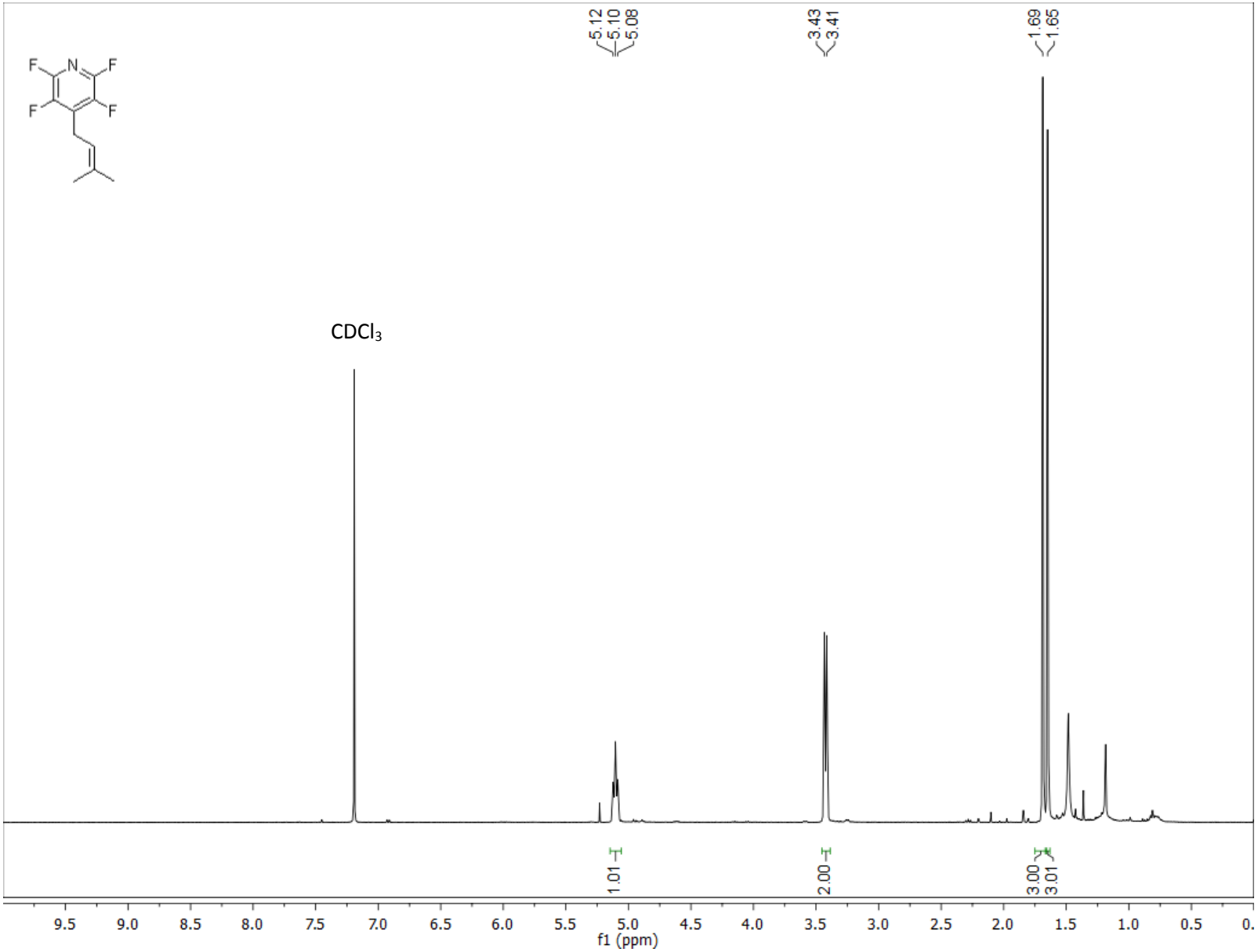
GC and MS of **1,2,3,4,5-pentafluoro-6-(3-methylbut-2-en-1-yl)benzene (3f)**



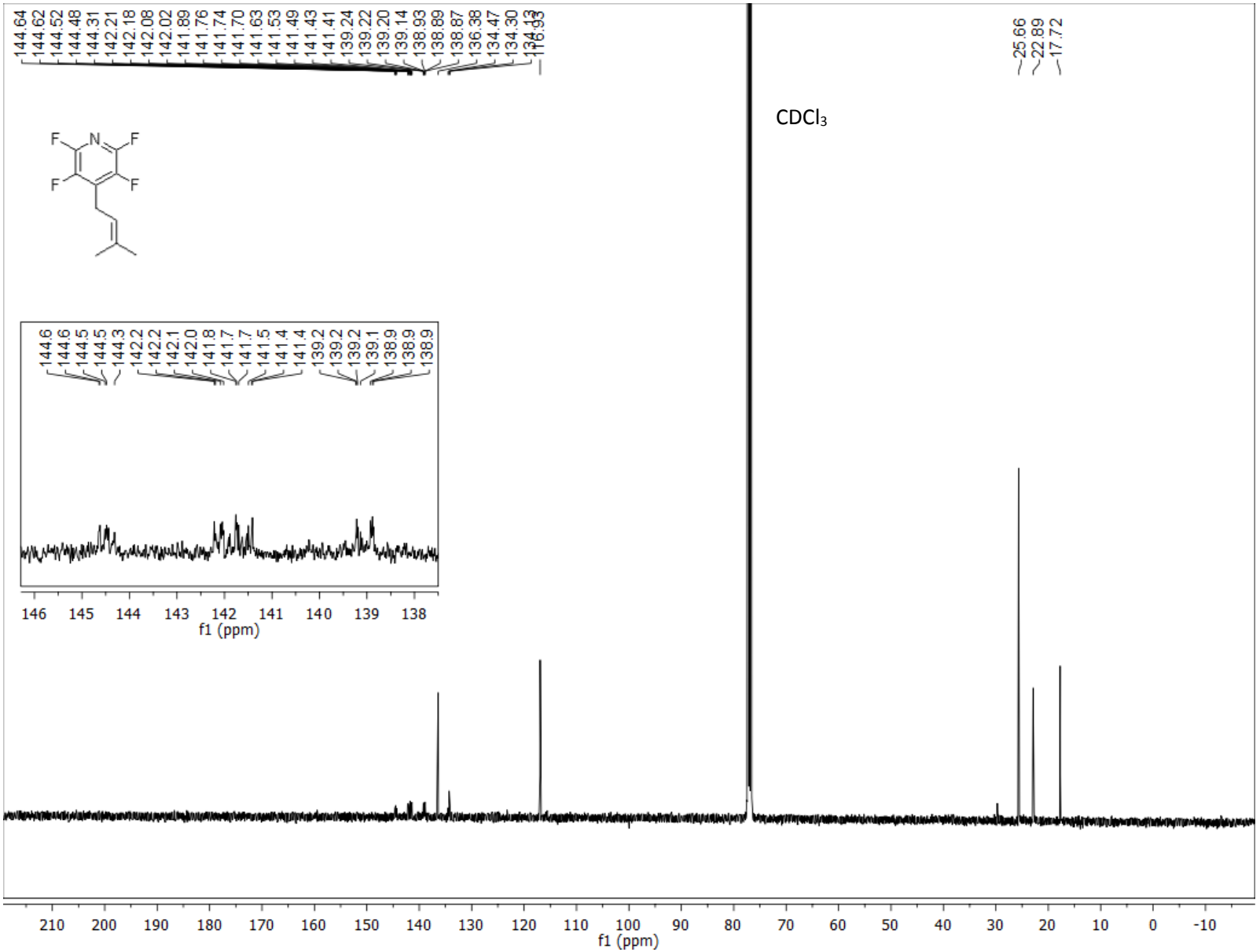
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)pyridine (3g)**



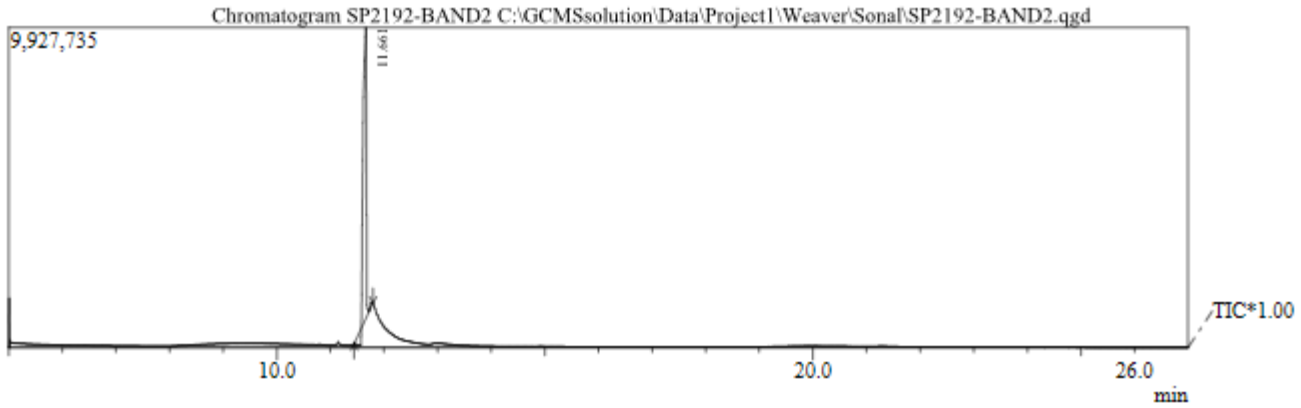
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)pyridine (3g)**

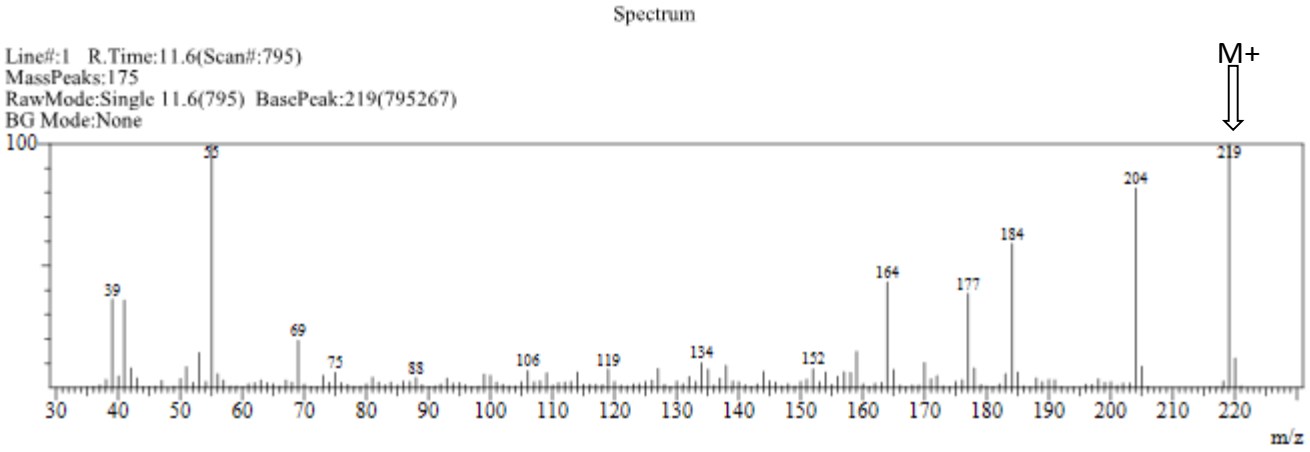


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)pyridine (3g)**

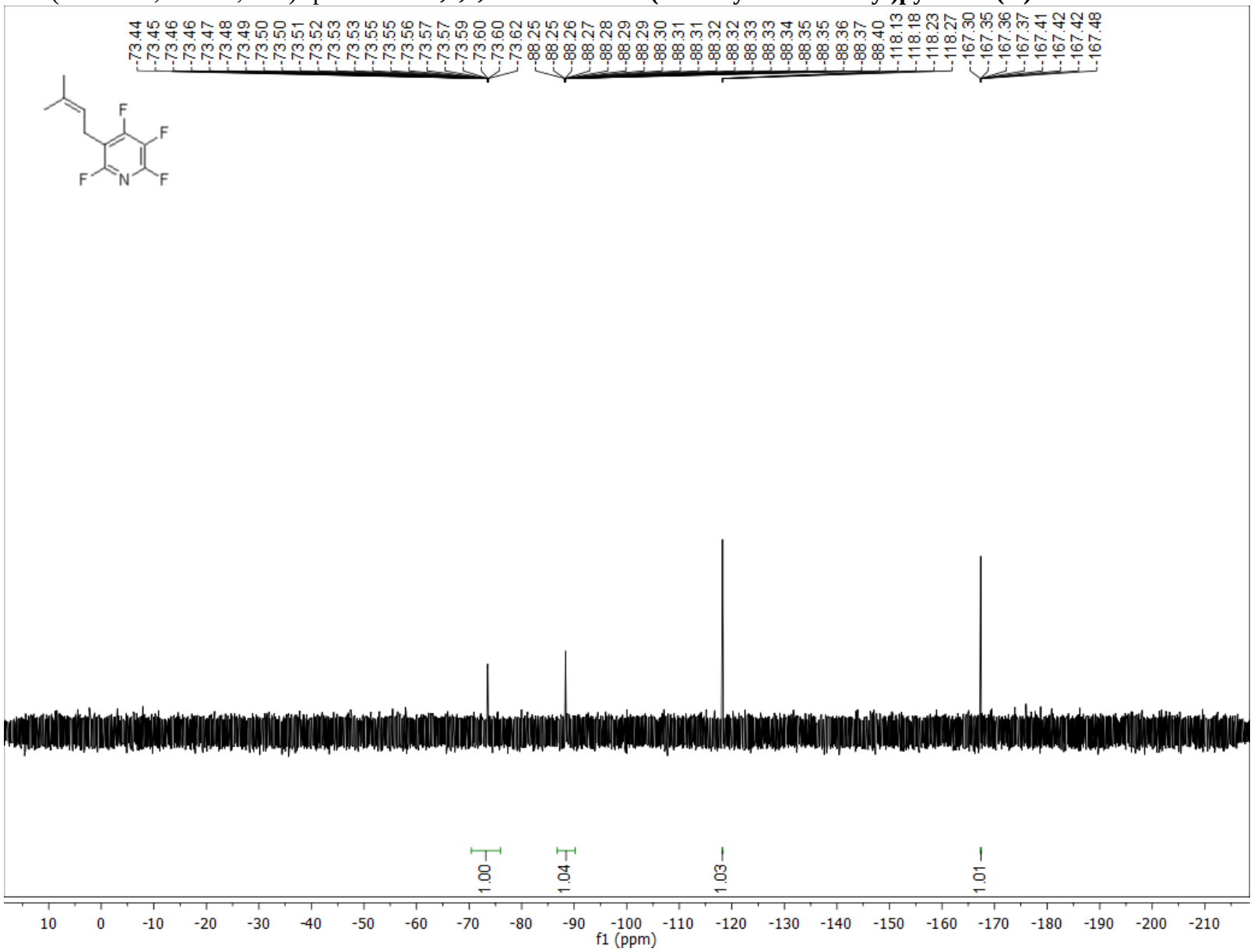


GC and MS of **2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)pyridine (3g)**

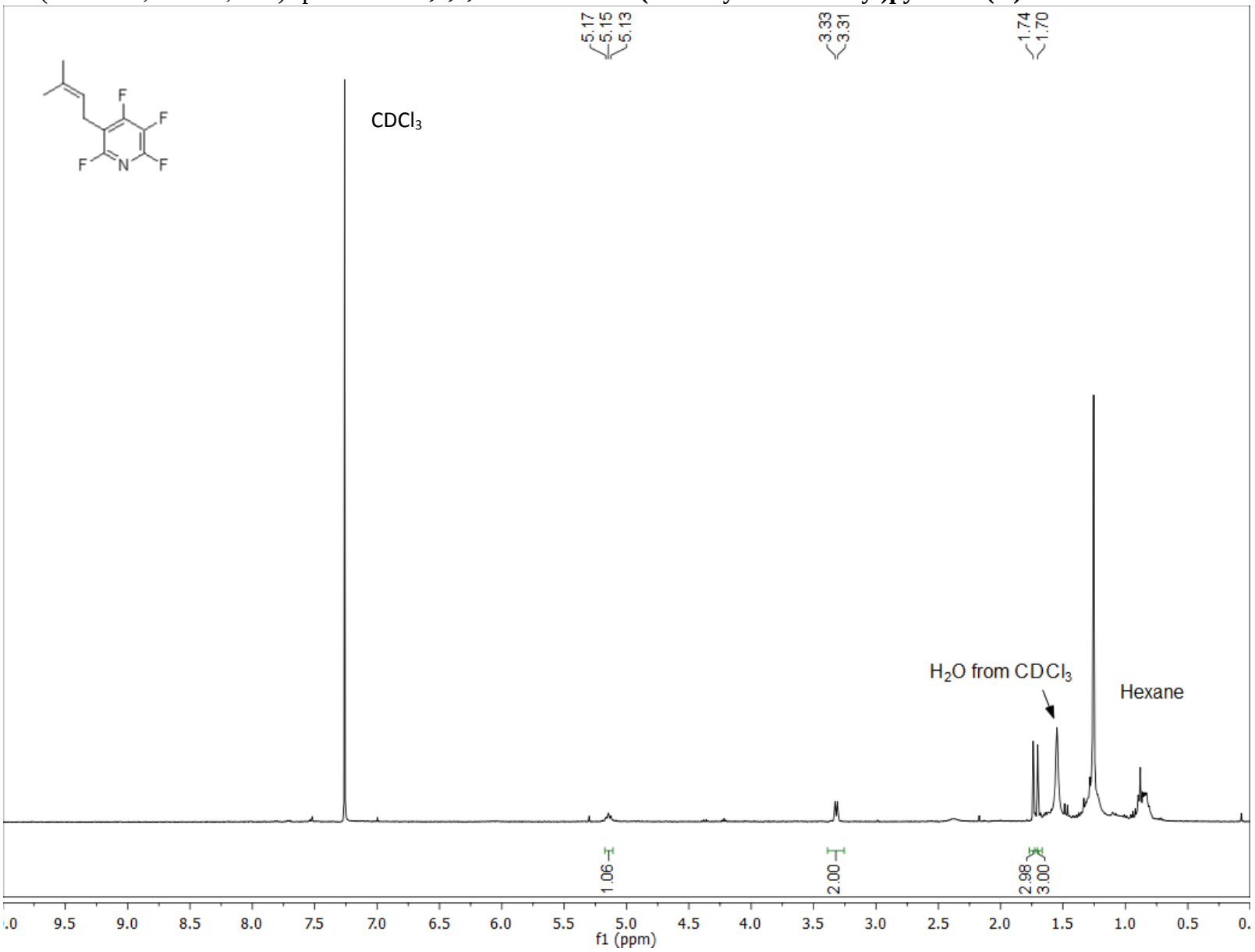




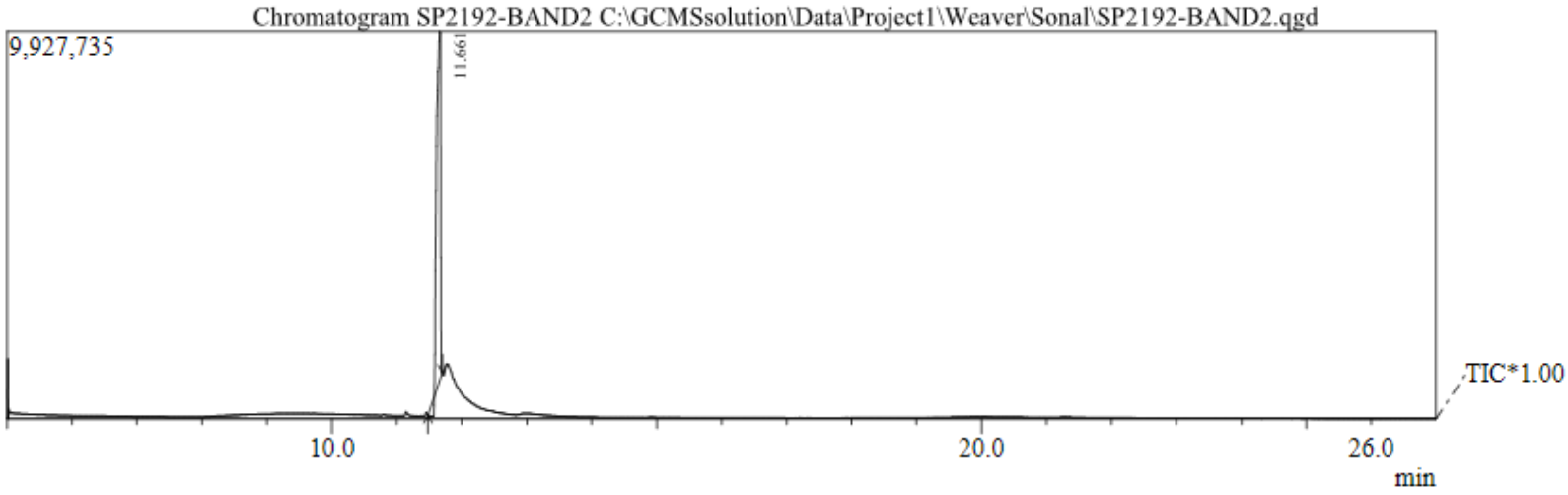
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **2,3,4,6-tetrafluoro-5-(3-methylbut-2-en-1-yl)pyridine (3i)**



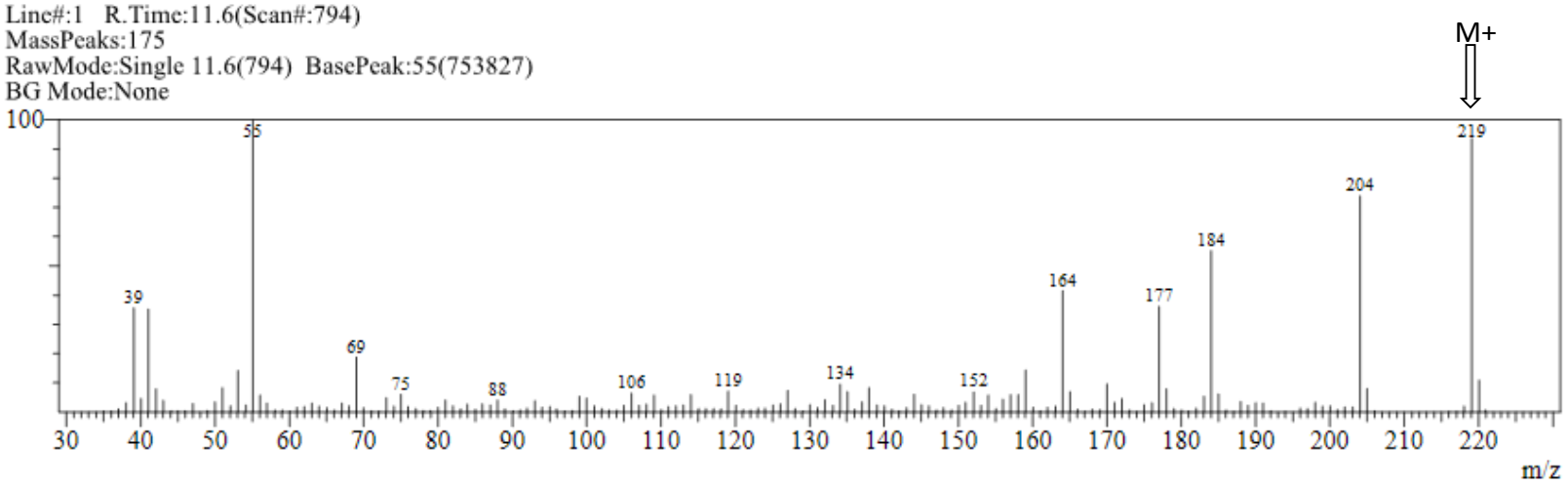
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **2,3,4,6-tetrafluoro-5-(3-methylbut-2-en-1-yl)pyridine (3i)**



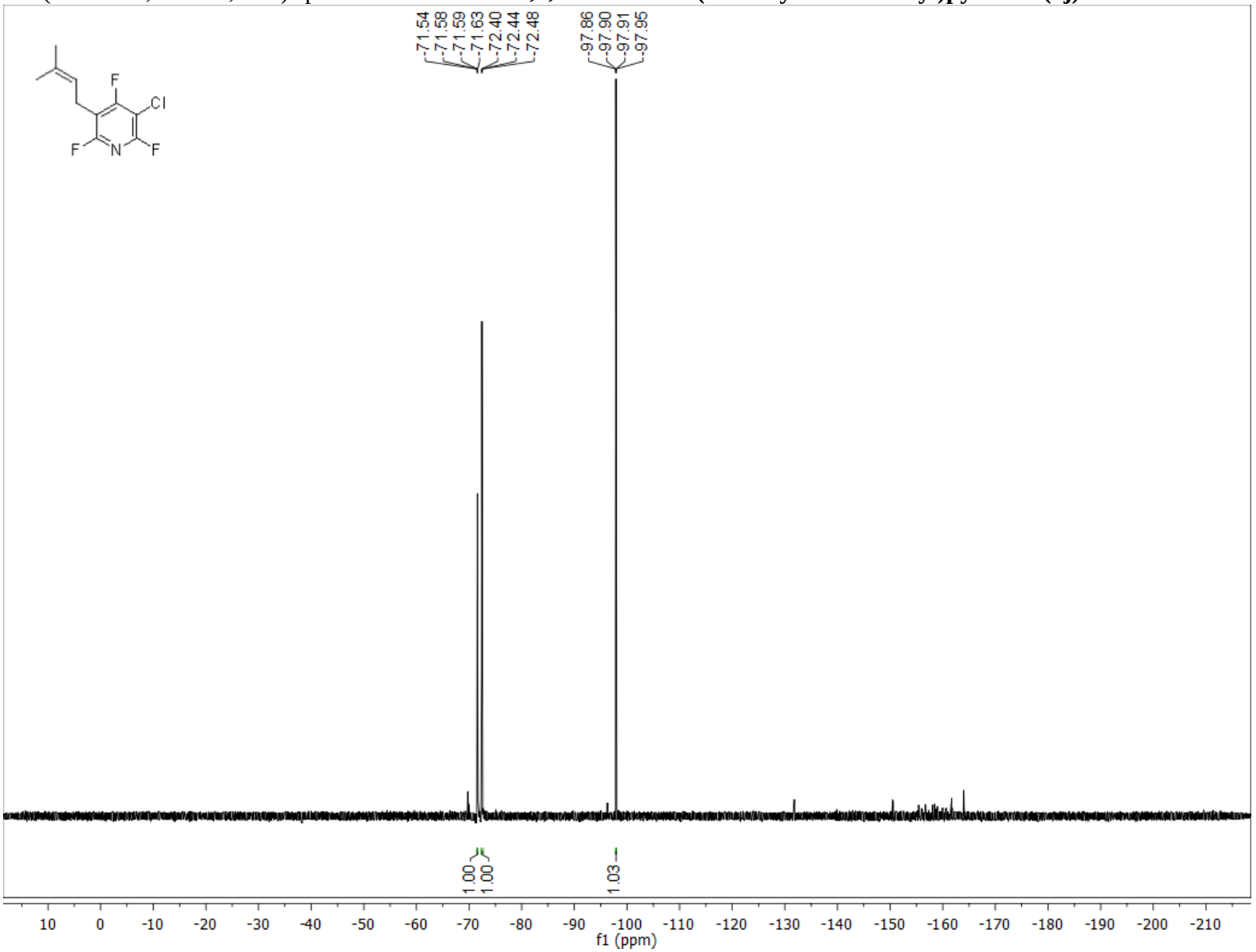
GC and MS of **2,3,4,6-tetrafluoro-5-(3-methylbut-2-en-1-yl)pyridine (3i)**



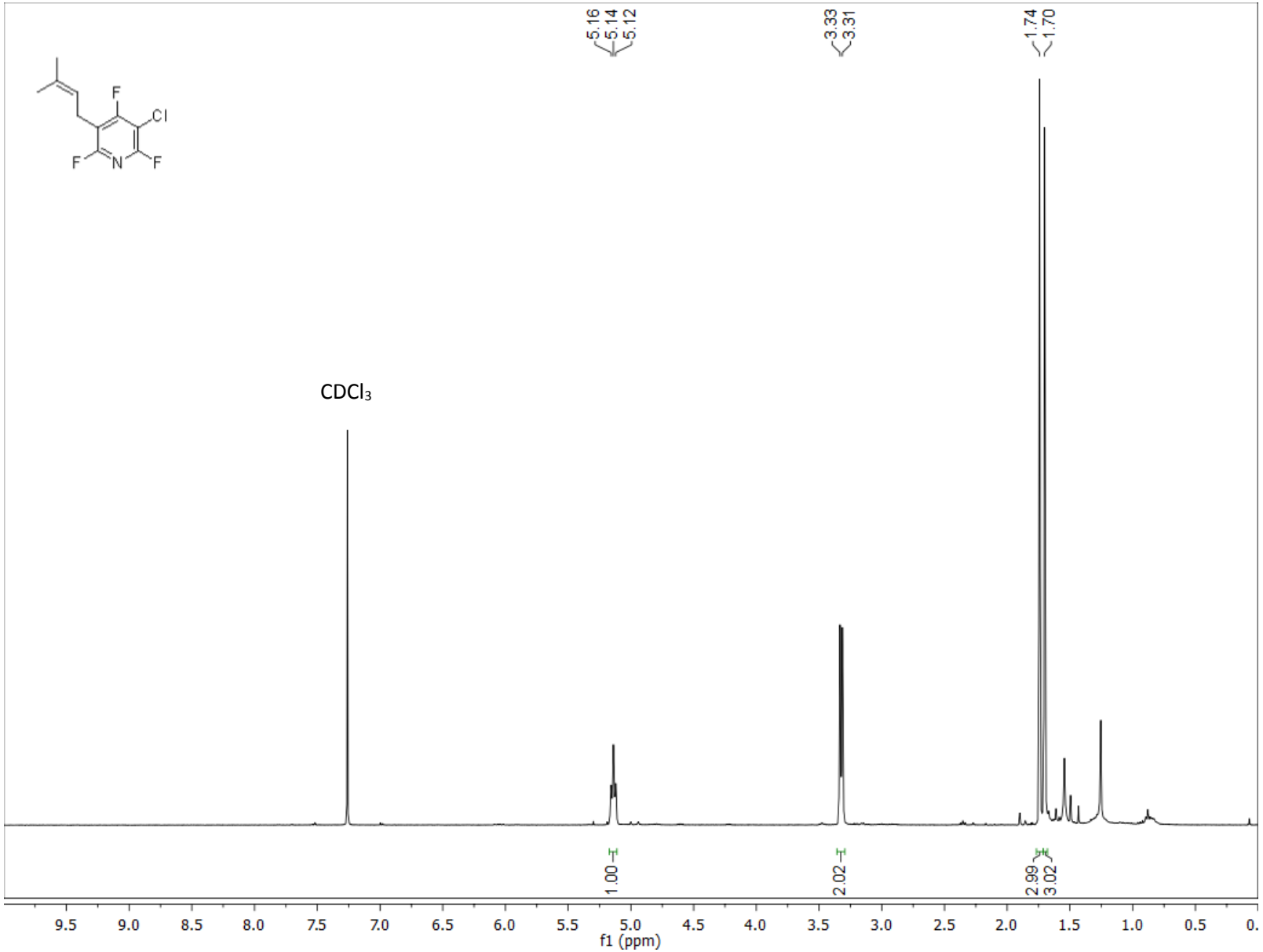
Spectrum



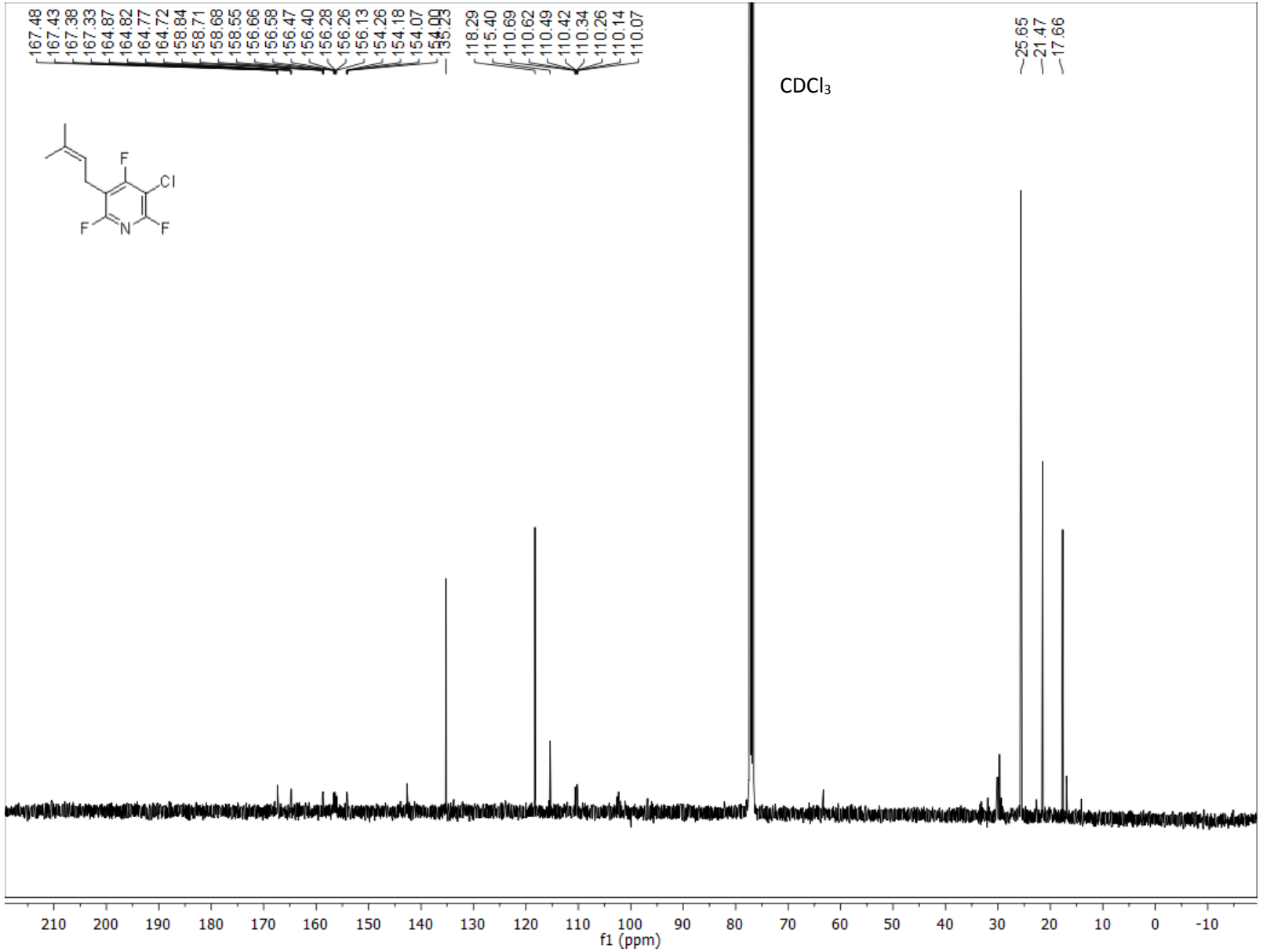
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **3-chloro-2,4,6-trifluoro-5-(3-methylbut-2-en-1-yl)pyridine (3j)**



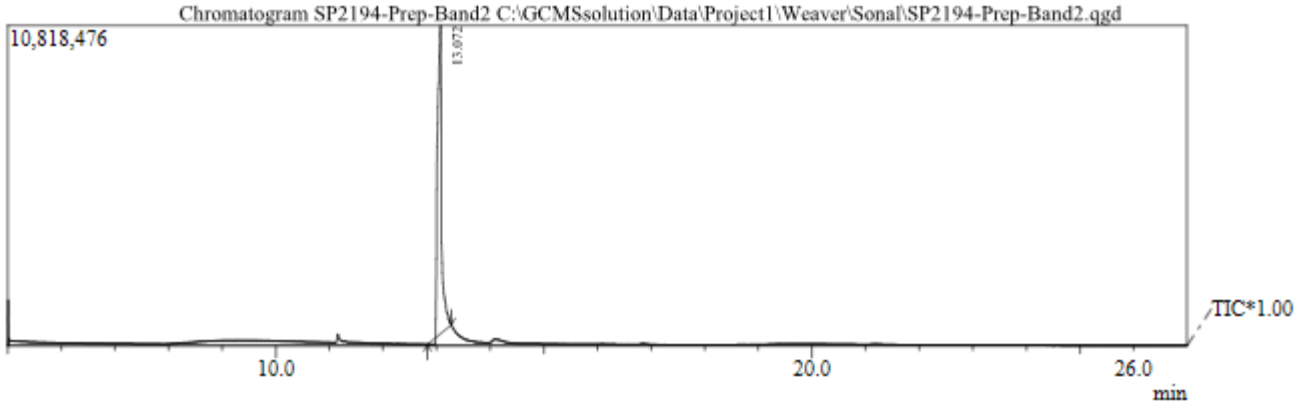
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **3-chloro-2,4,6-trifluoro-5-(3-methylbut-2-en-1-yl)pyridine (3j)**

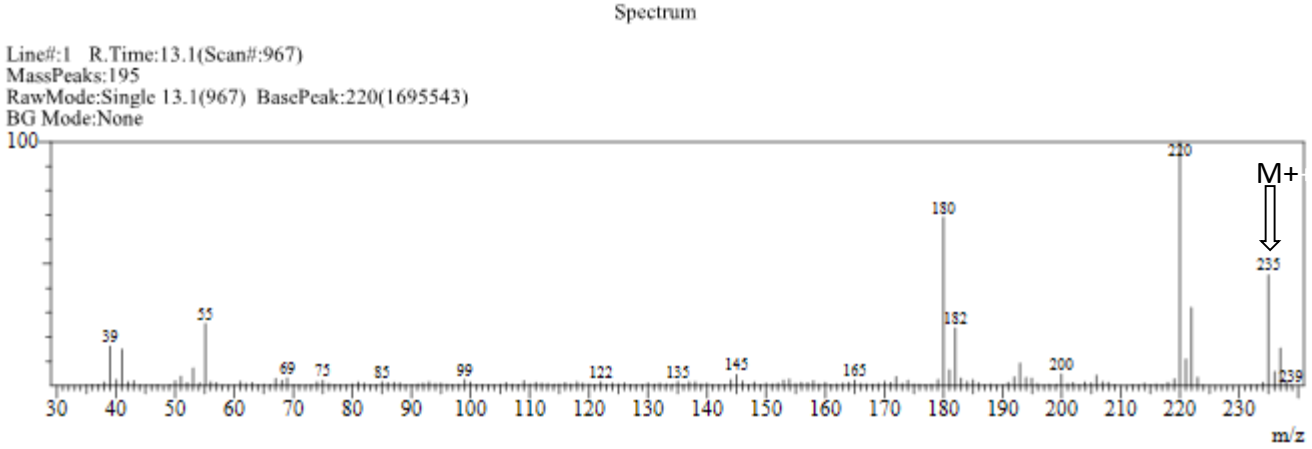


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **3-chloro-2,4,6-trifluoro-5-(3-methylbut-2-en-1-yl)pyridine (3j)**

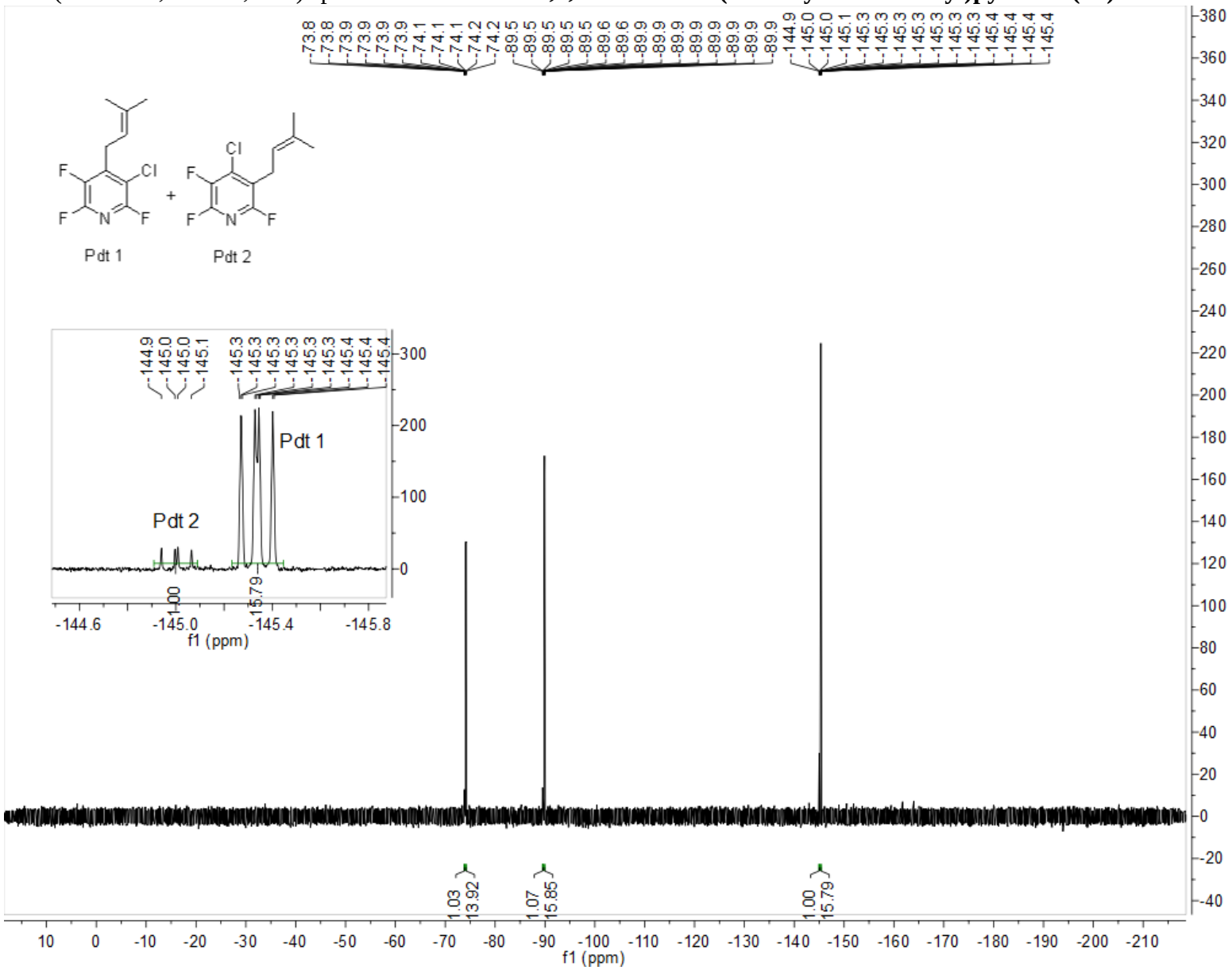


GC and MS of **3-chloro-2,4,6-trifluoro-5-(3-methylbut-2-en-1-yl)pyridine (3j)**

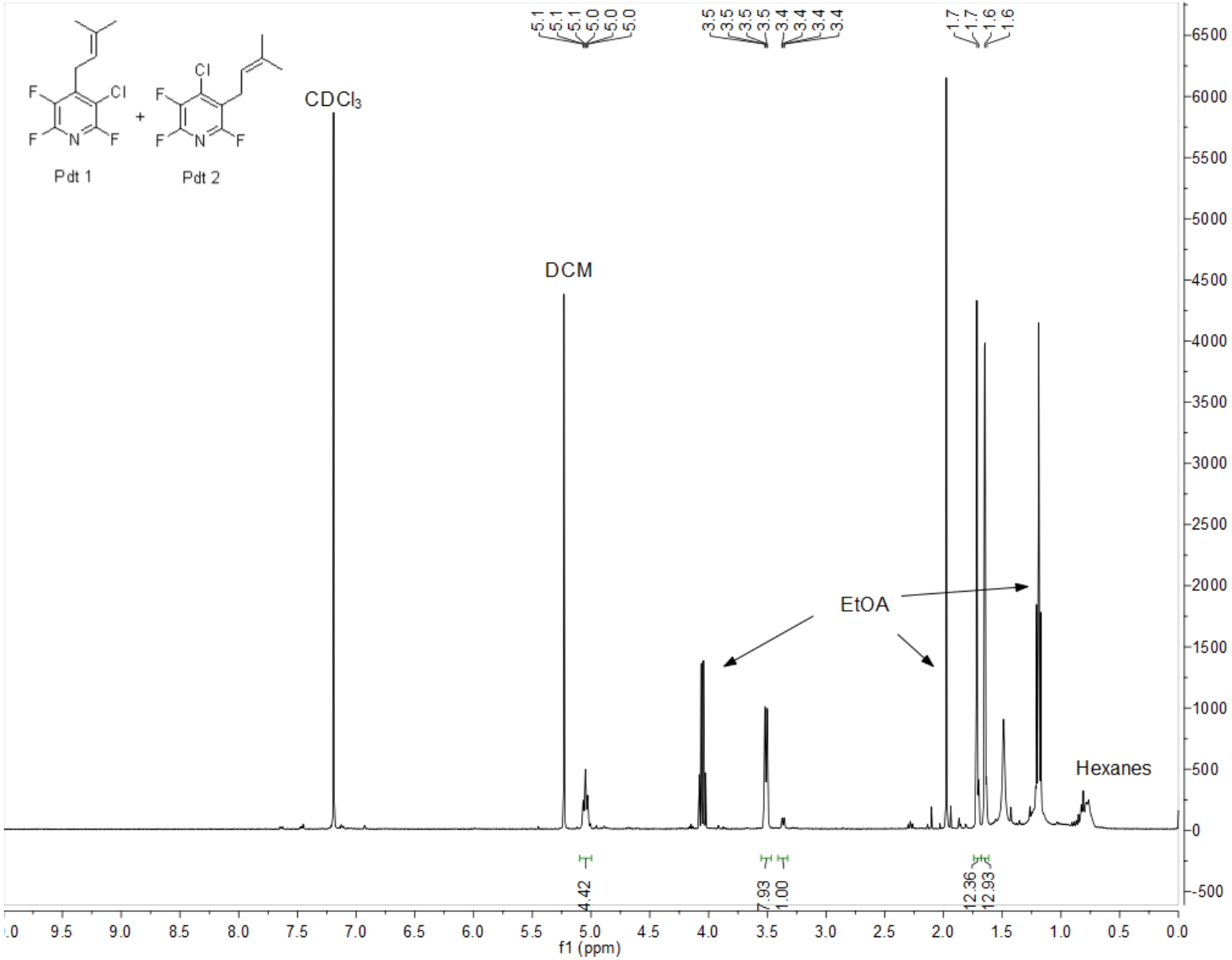




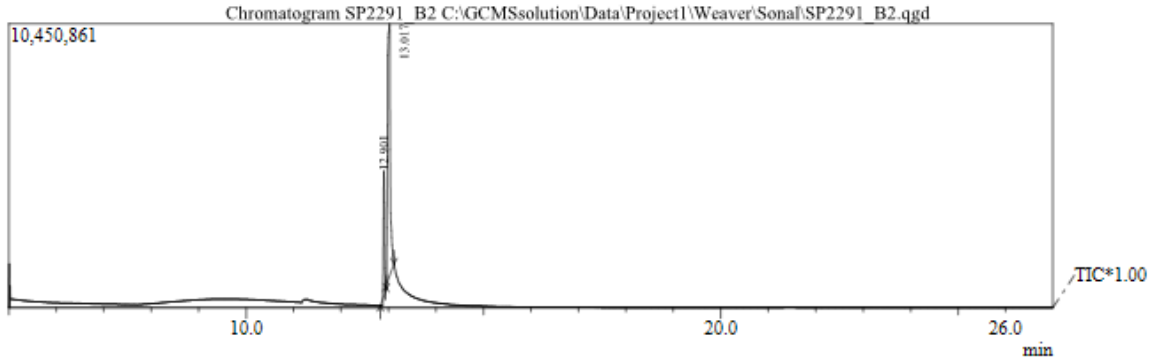
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **3-chloro-2,5,6-trifluoro-4-(3-methylbut-2-en-1-yl)pyridine (3k)**



[1]H NMR (400 MHz, CDCl3, at rt) spectrum of **3-chloro-2,5,6-trifluoro-4-(3-methylbut-2-en-1-yl)pyridine (3k)**



GC and MS of **3-chloro-2,5,6-trifluoro-4-(3-methylbut-2-en-1-yl)pyridine (3k)**



Spectrum

Line#:1 R.Time:12.9(Scan#:950)
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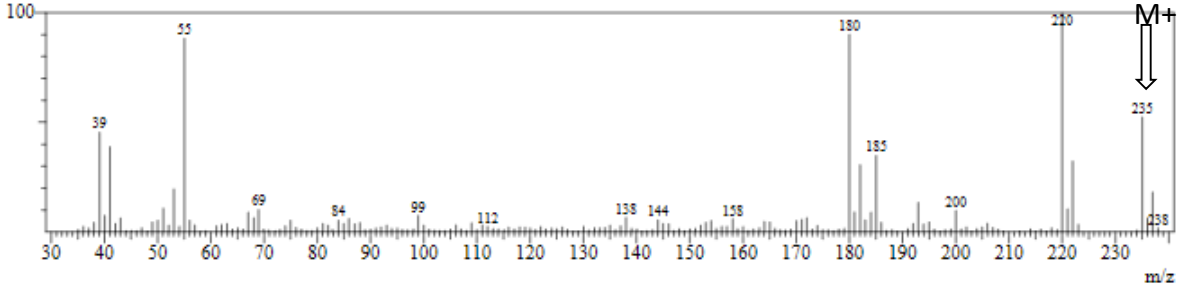
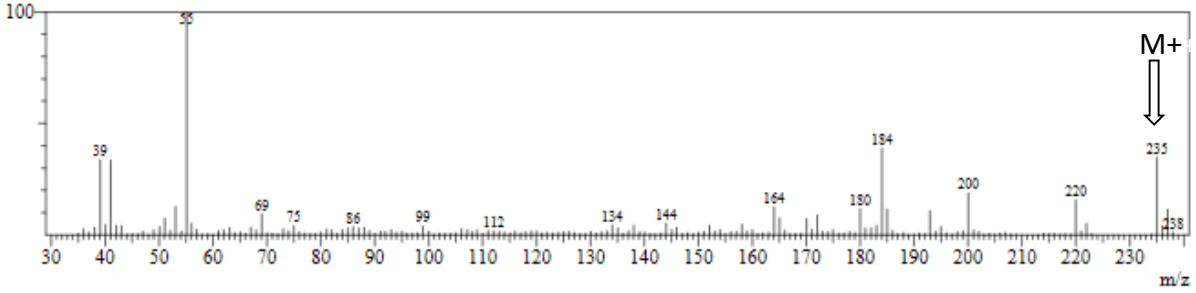
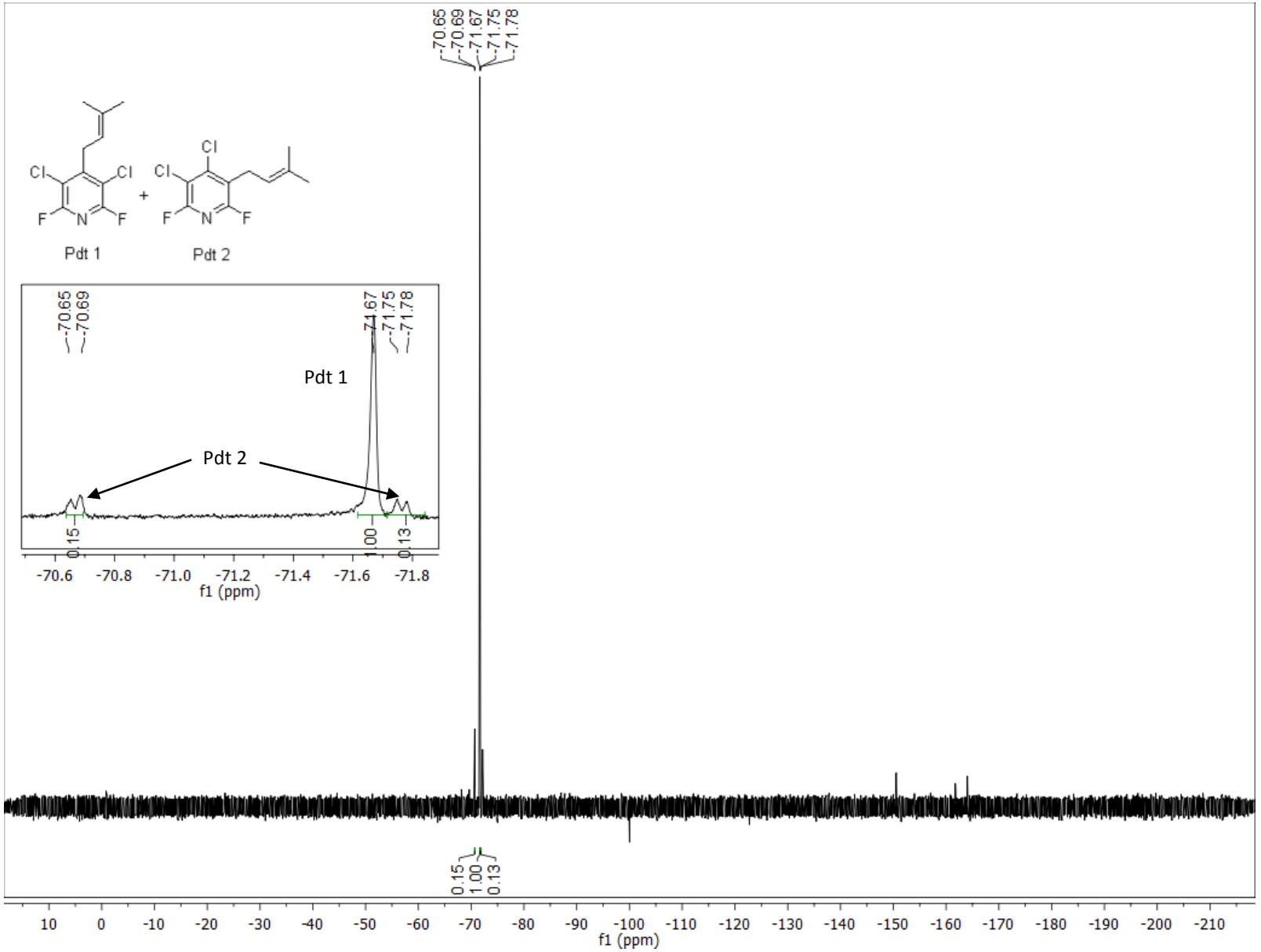
RawMode:Single 12.9(950) BasePeak:220(385938)
BG Mode:None



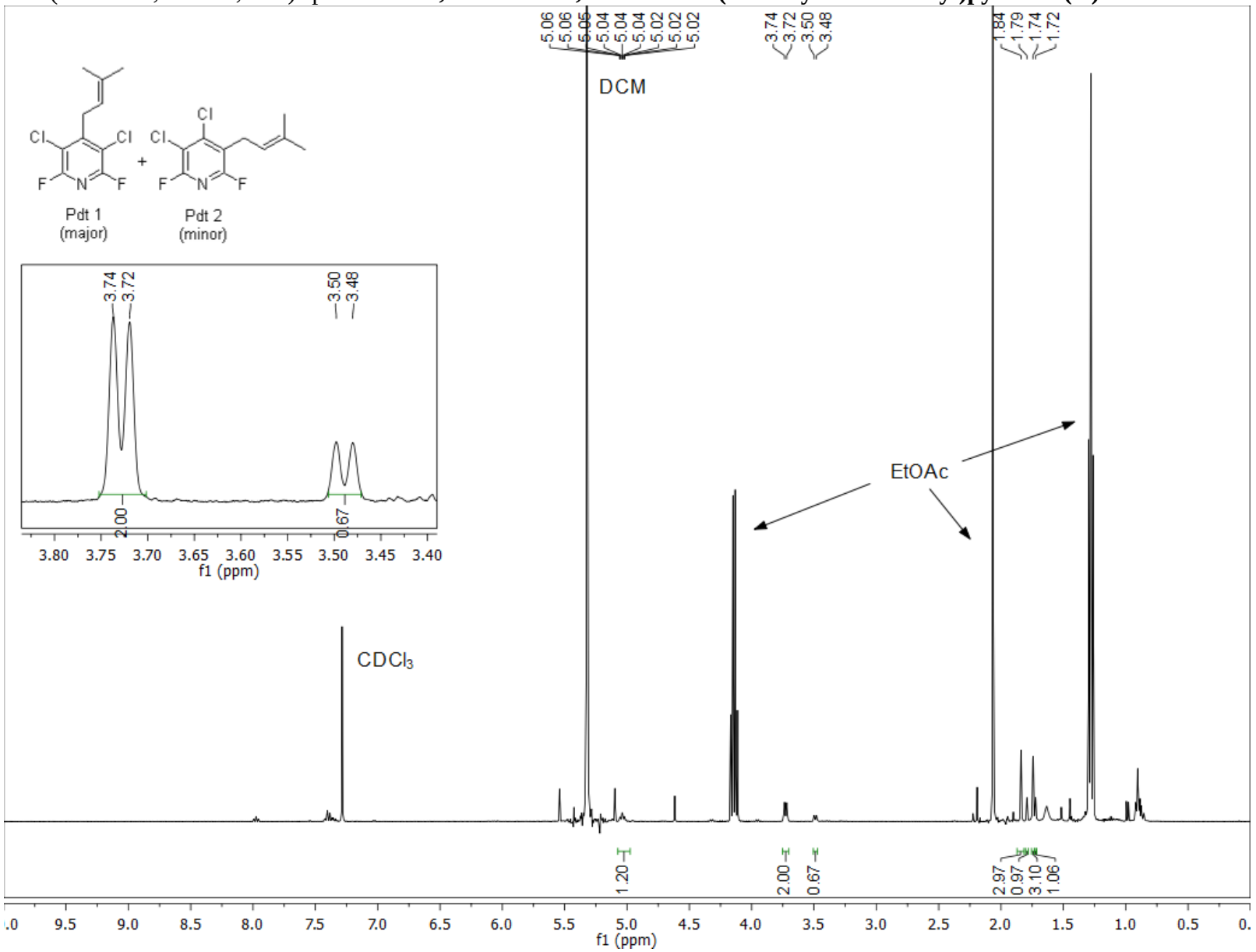
Line#:2 R.Time:13.0(Scan#:965)
MassPeaks:191
RawMode:Single 13.0(965) BasePeak:55(870577)
BG Mode:None



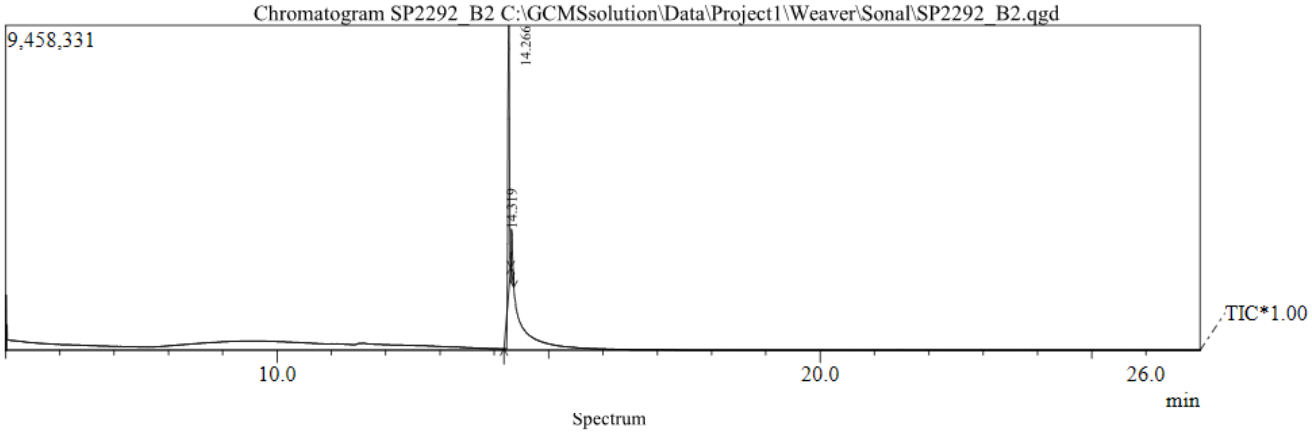
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **3,5-dichloro-2,6-difluoro-4-(3-methylbut-2-en-1-yl)pyridine (3l)**



^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **3,5-dichloro-2,6-difluoro-4-(3-methylbut-2-en-1-yl)pyridine (3l)**



GC and MS of **3,5-dichloro-2,6-difluoro-4-(3-methylbut-2-en-1-yl)pyridine (3l)**



Spectrum

Line#:1 R.Time:14.3(Scan#:1111)
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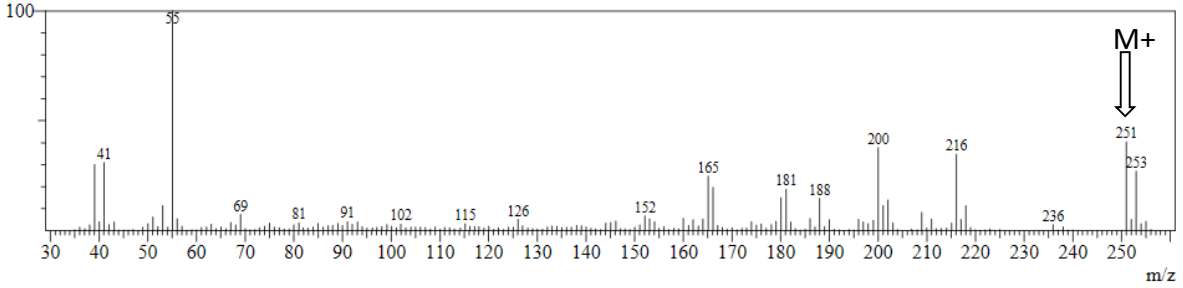
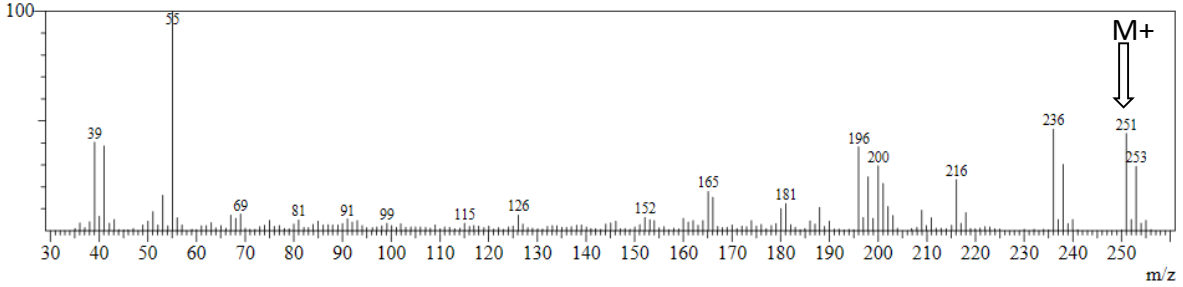
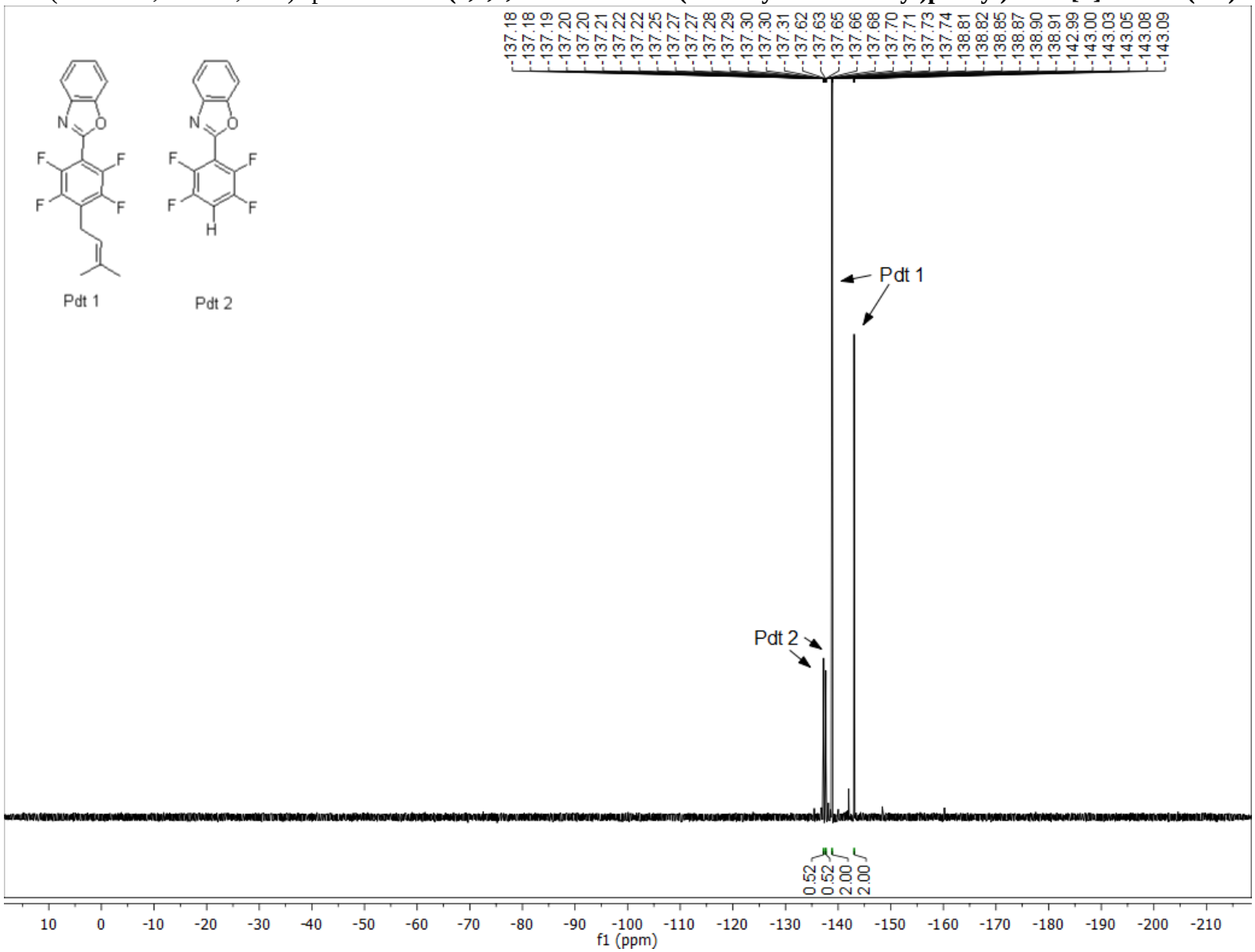
RawMode:Single 14.3(1111) BasePeak:55(830922)
BG Mode:None



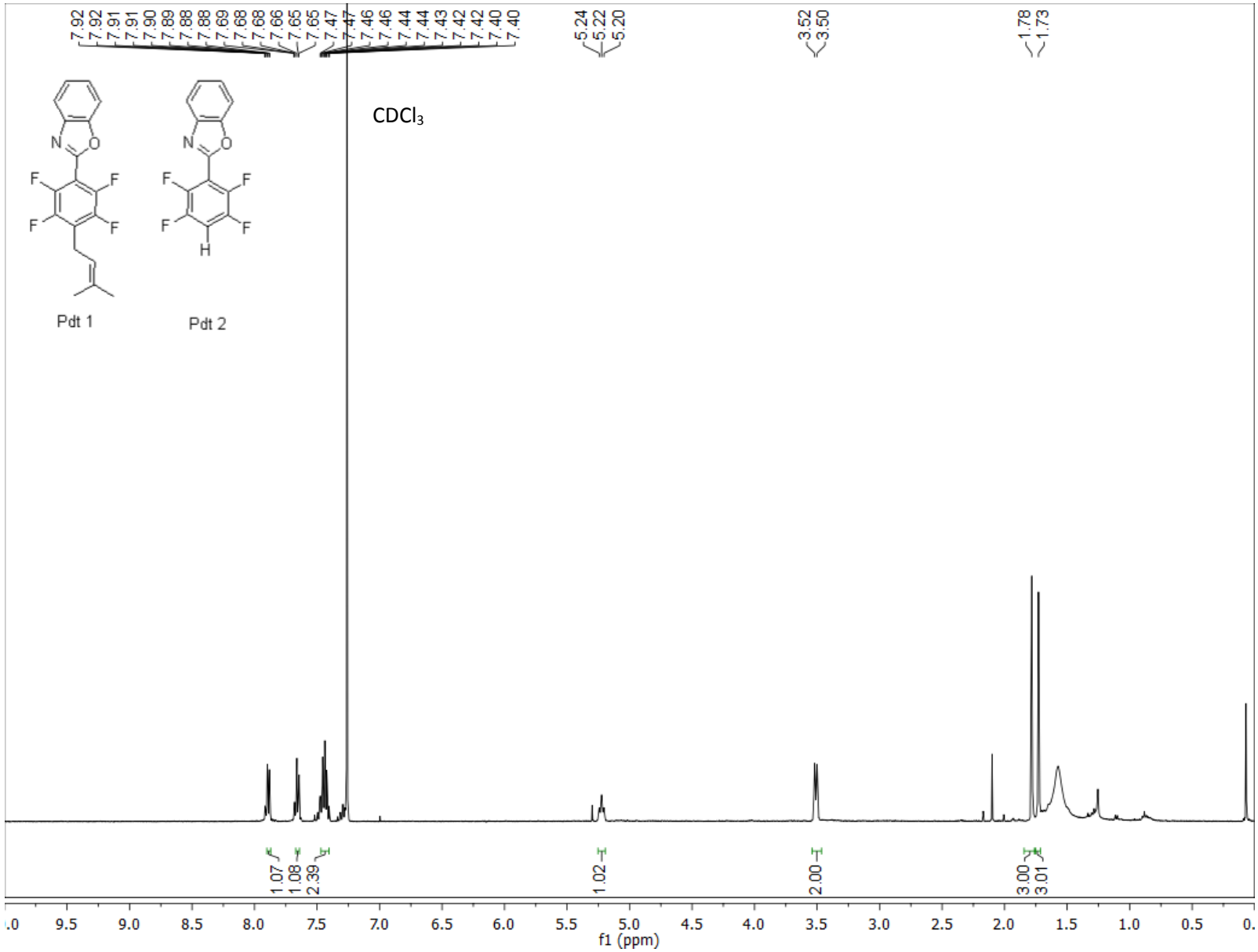
Line#:2 R.Time:14.3(Scan#:1119)
MassPeaks:204
RawMode:Single 14.3(1119) BasePeak:55(346766)
BG Mode:None



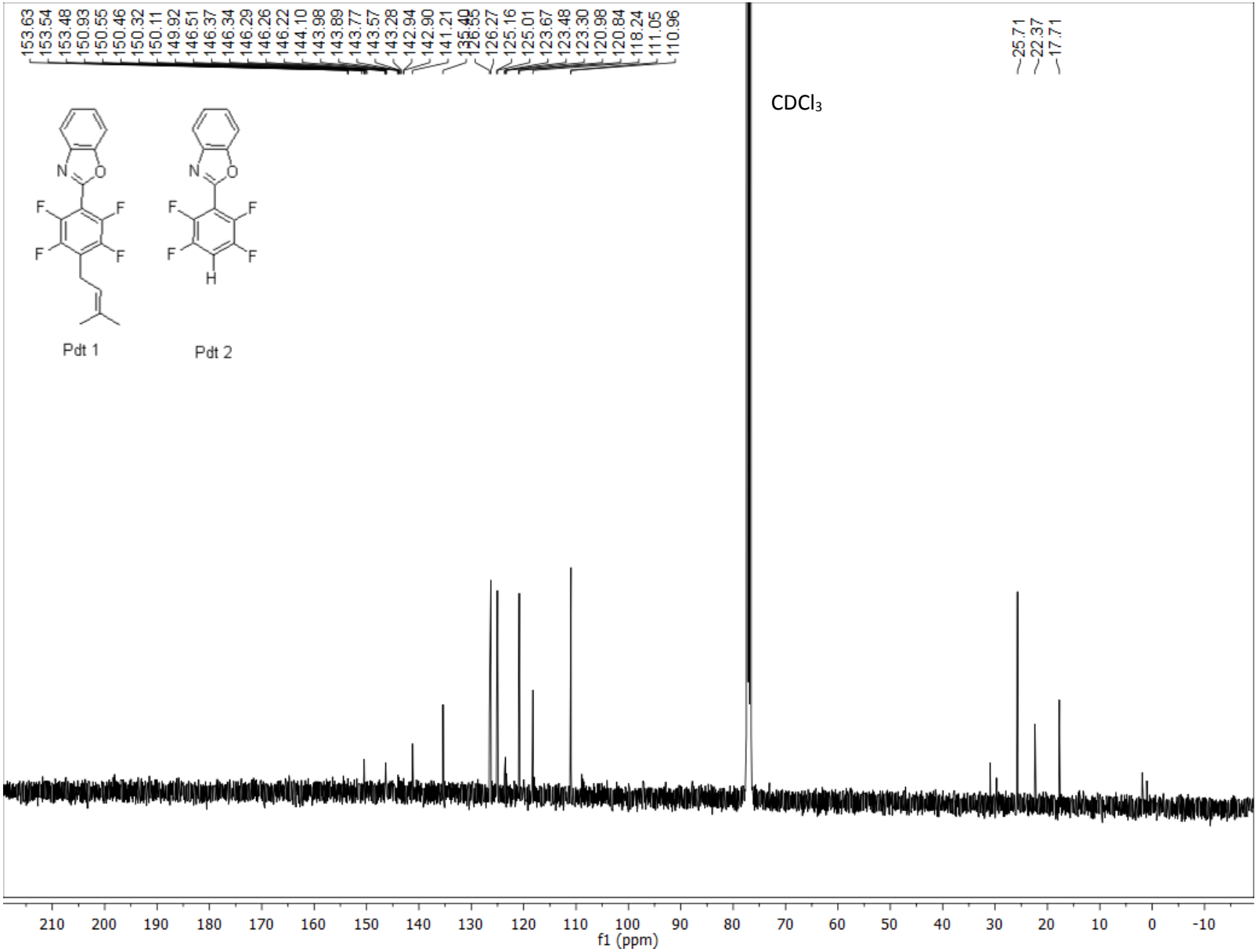
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]oxazole (3m)**



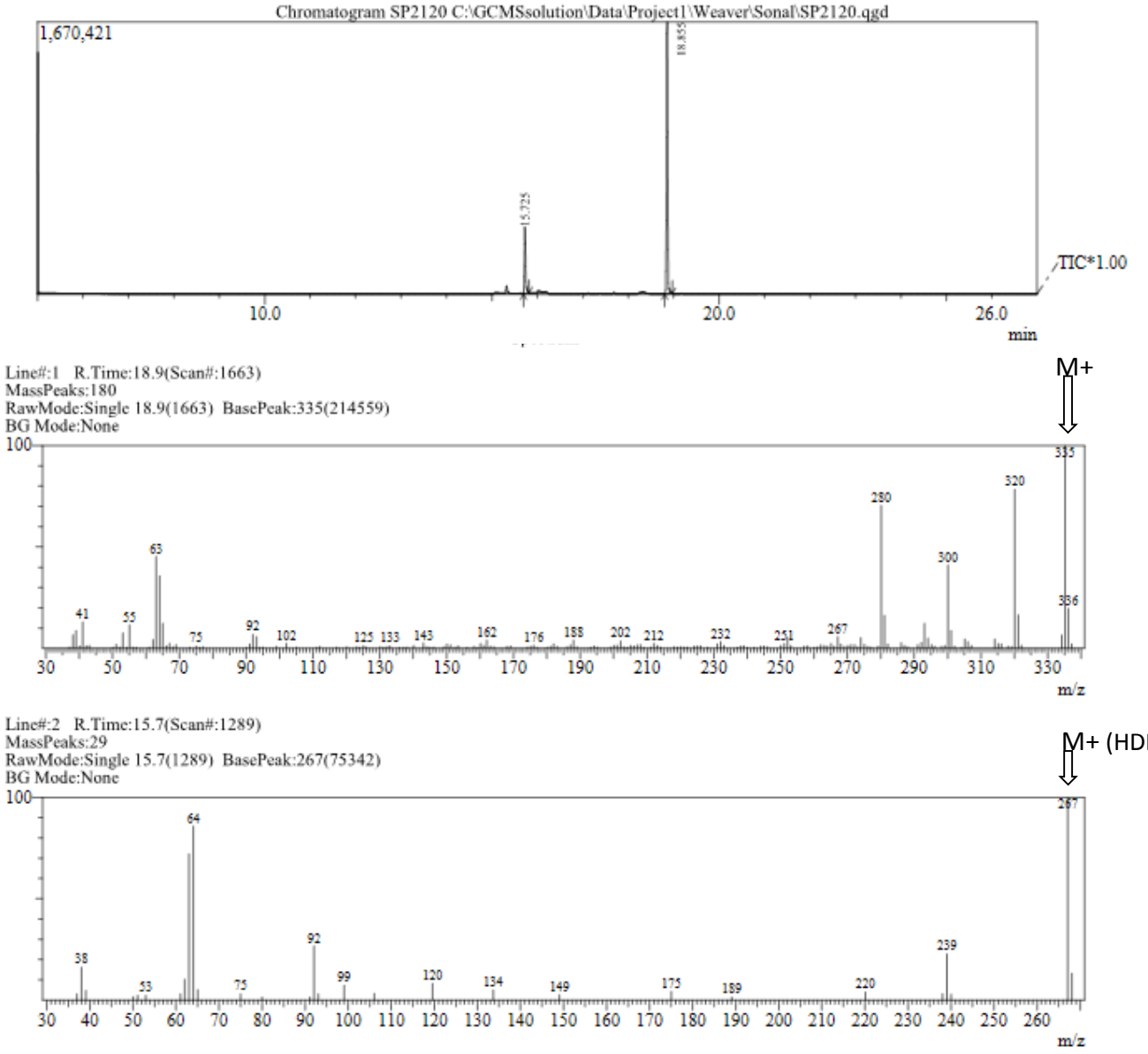
[1]H NMR (400 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]oxazole (3m)**



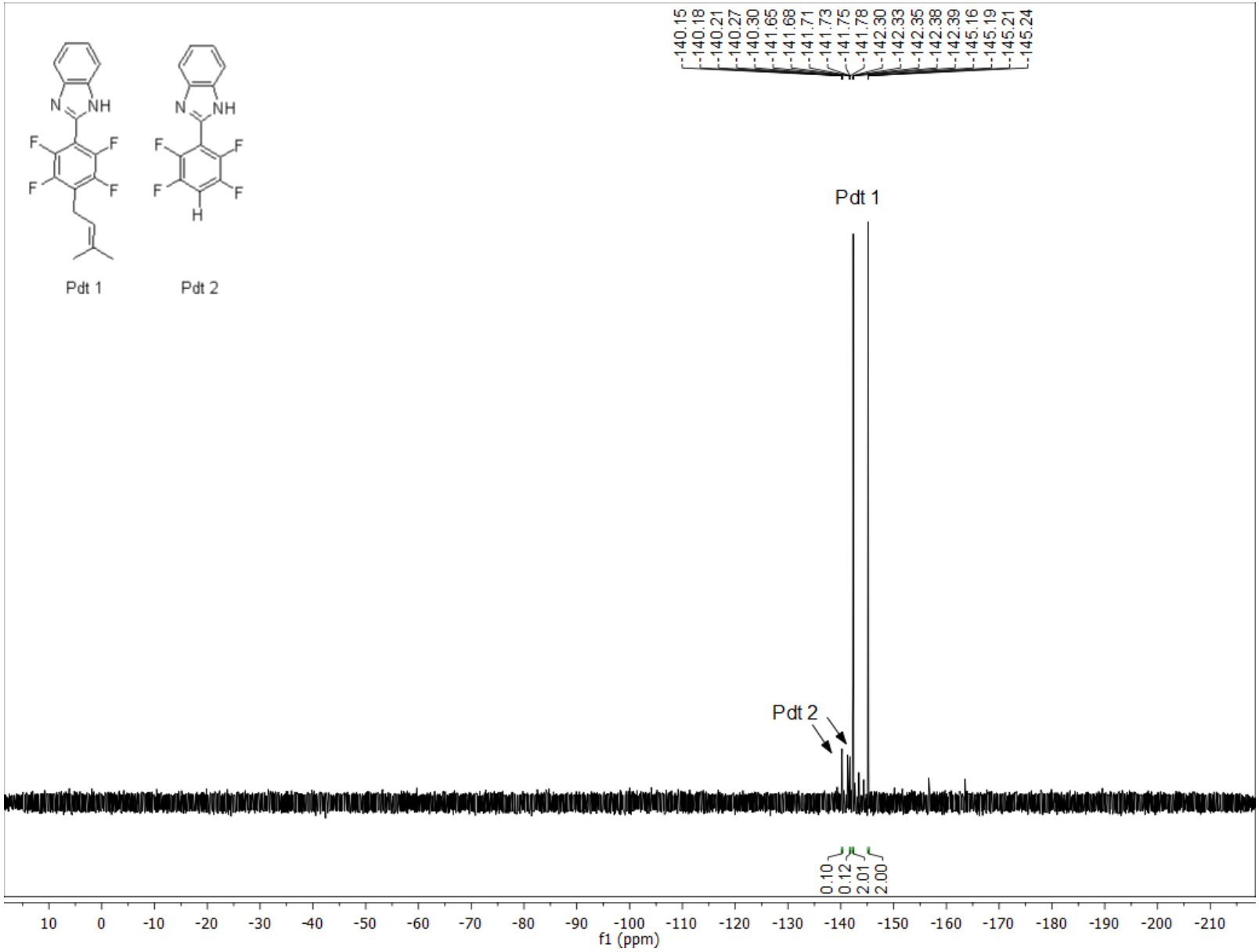
^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]oxazole (3m)**



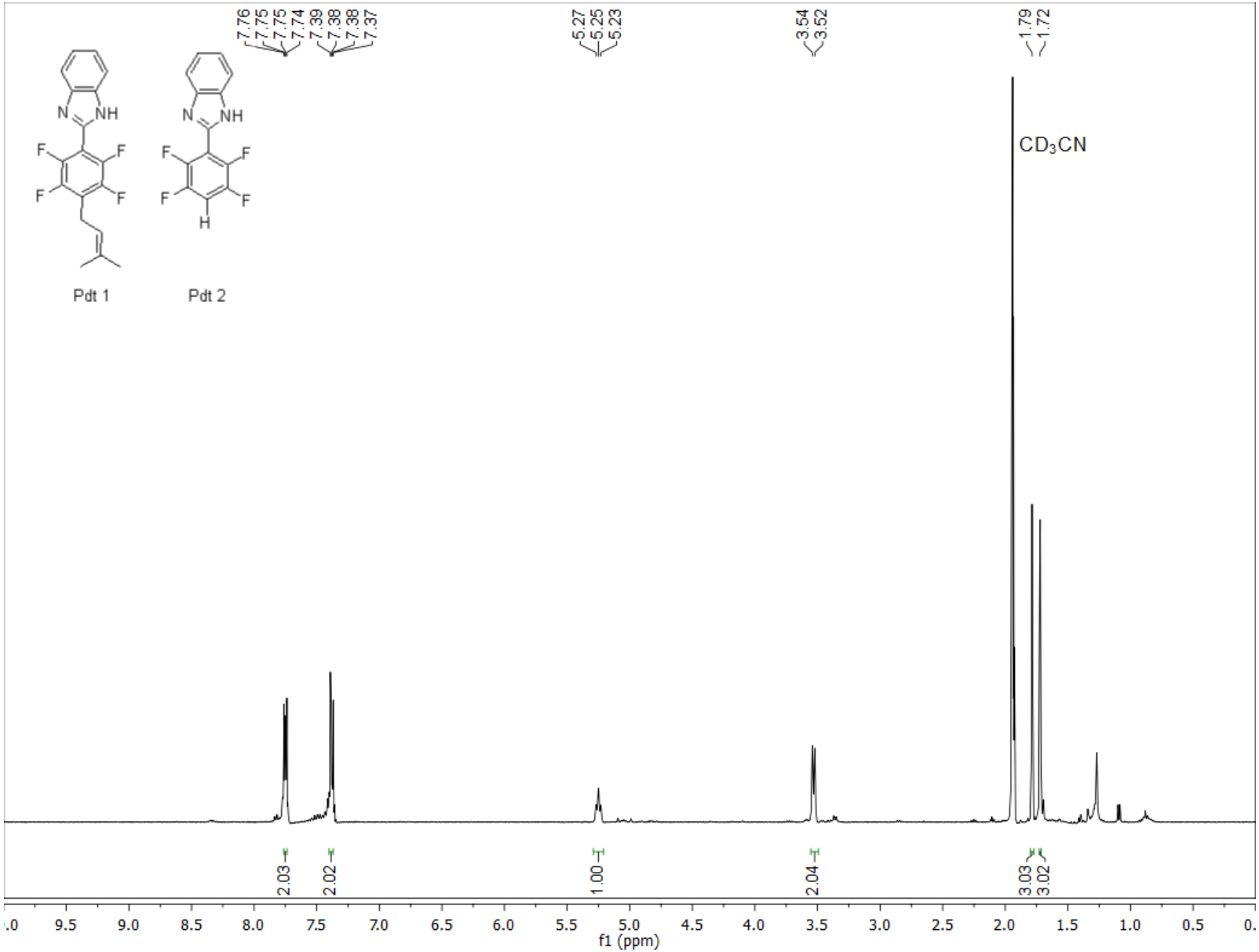
GC and MS of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]oxazole (3m)**



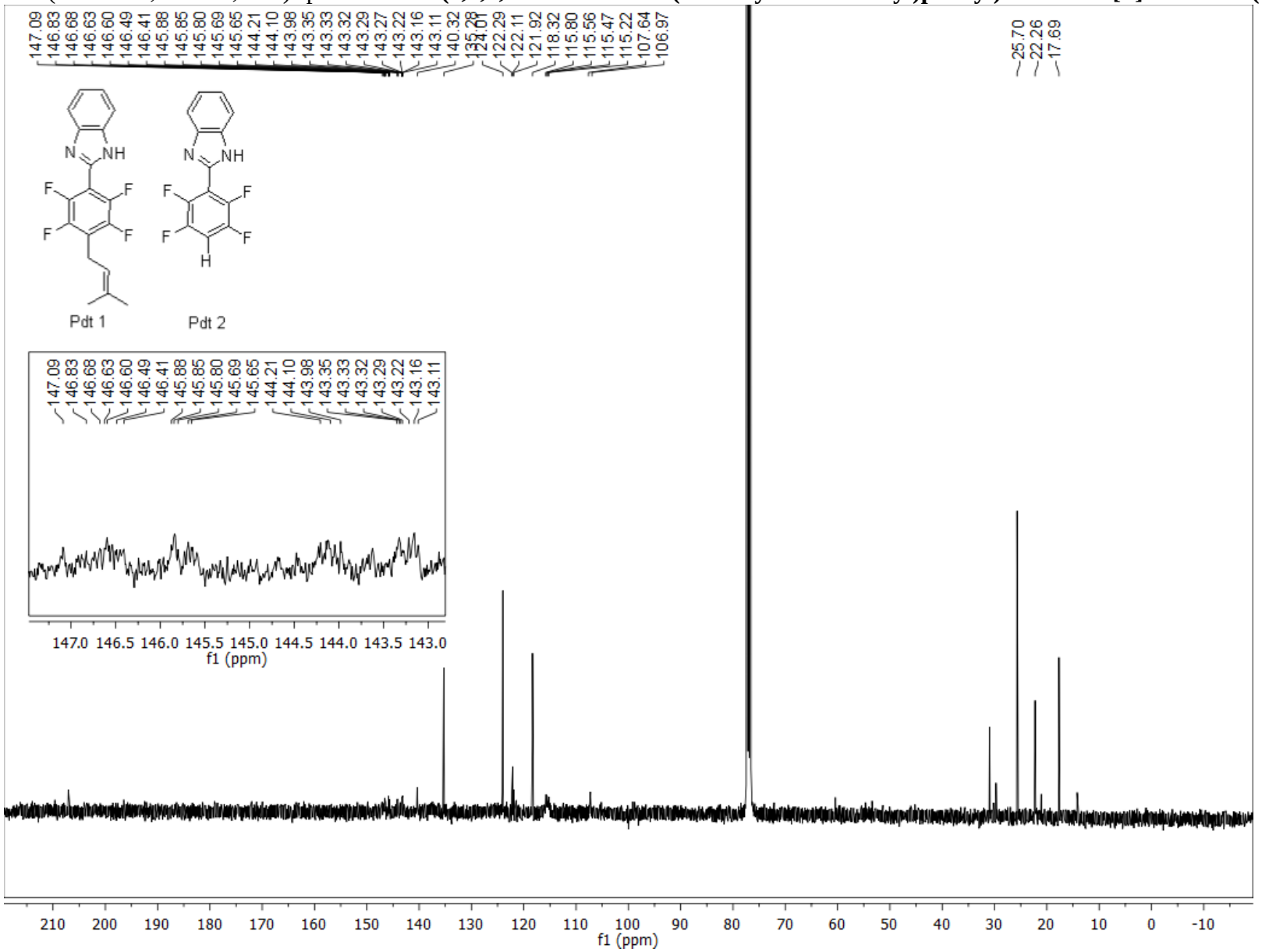
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)-1H-benzo[d]imidazole (3n)**



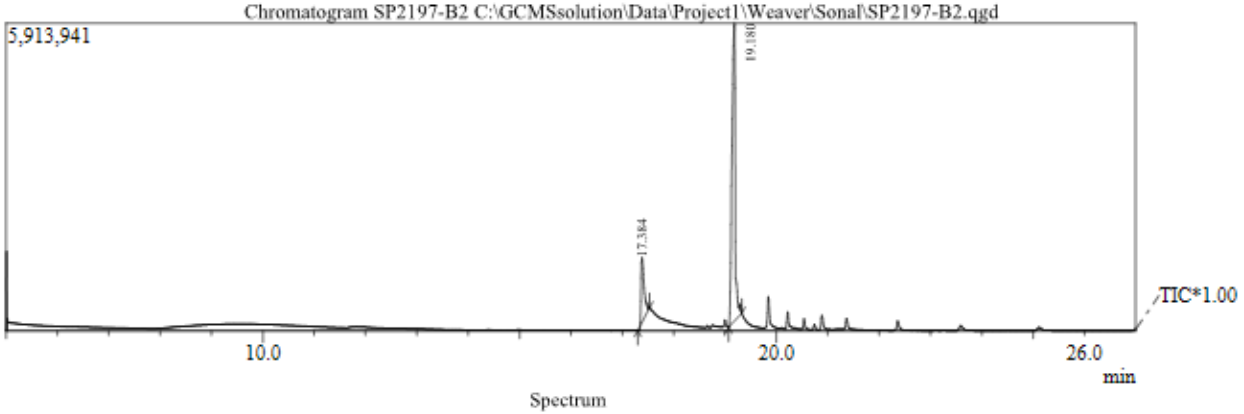
[1]H NMR (400 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)-1H-benzo[d]imidazole (3n)**



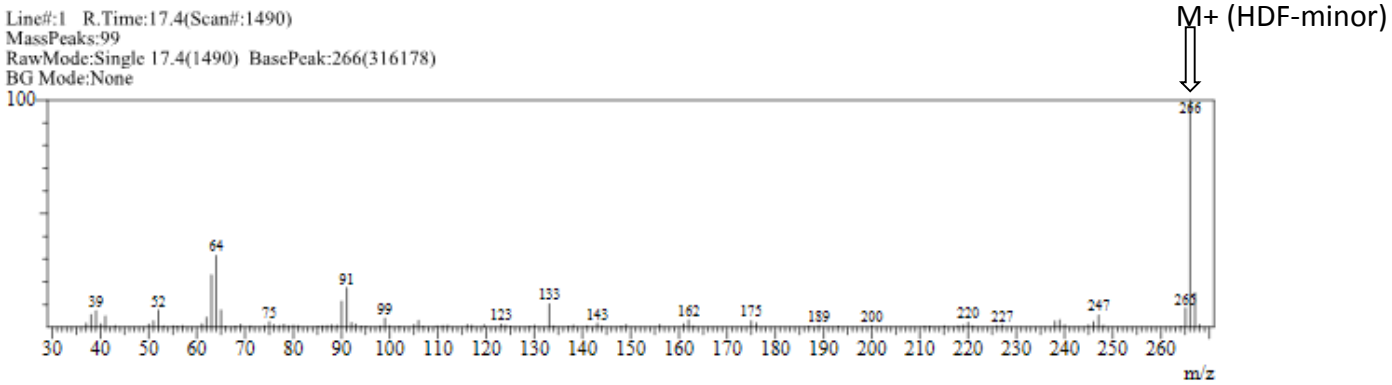
^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)-1H-benzo[d]imidazole (3n)**

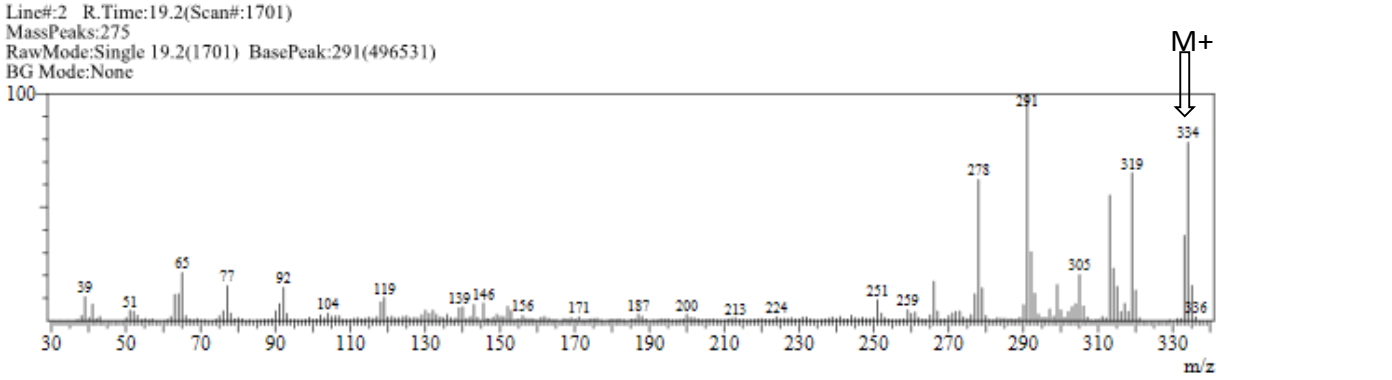


GC and MS of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)-1H-benzo[d]imidazole (3n)**

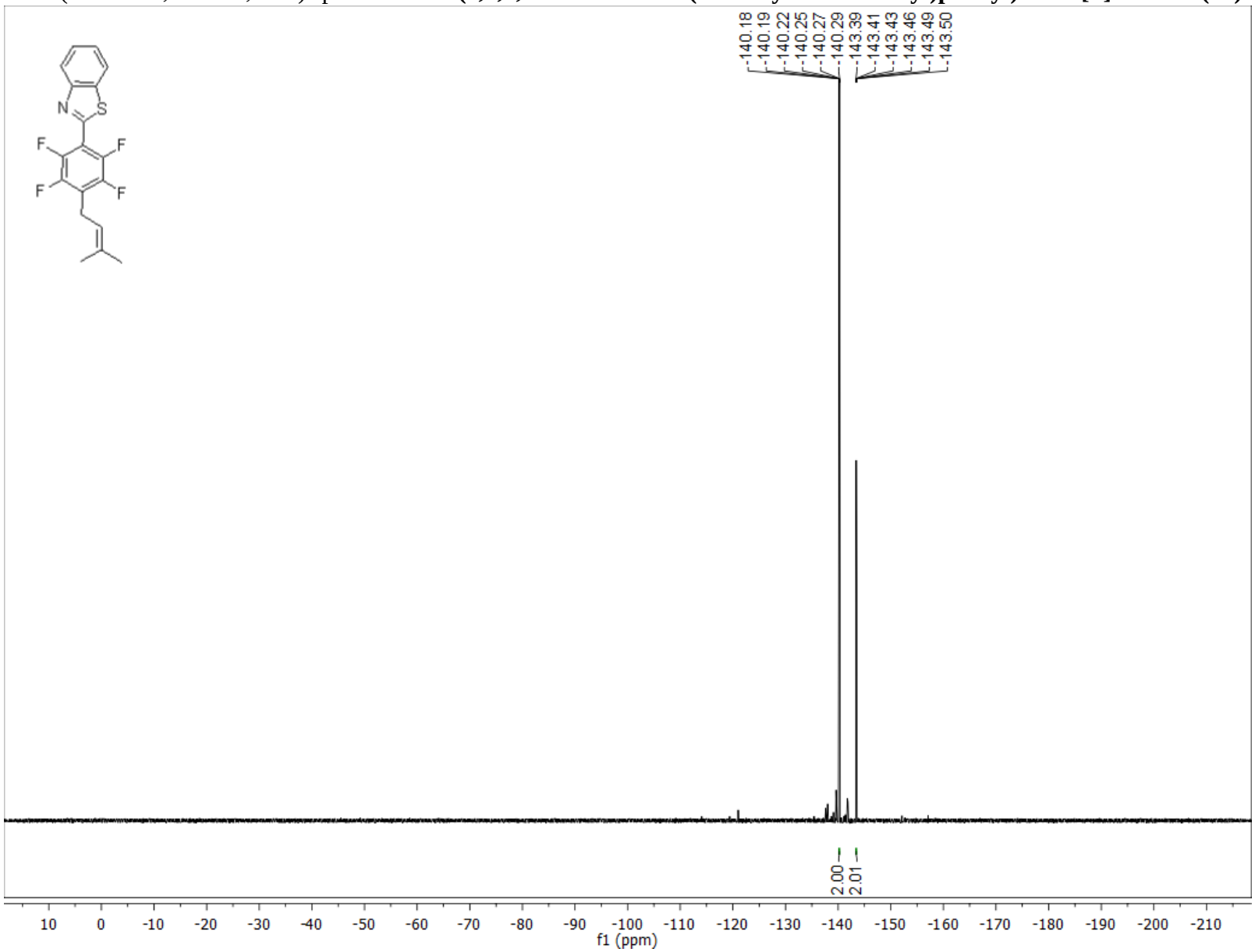


Spectrum

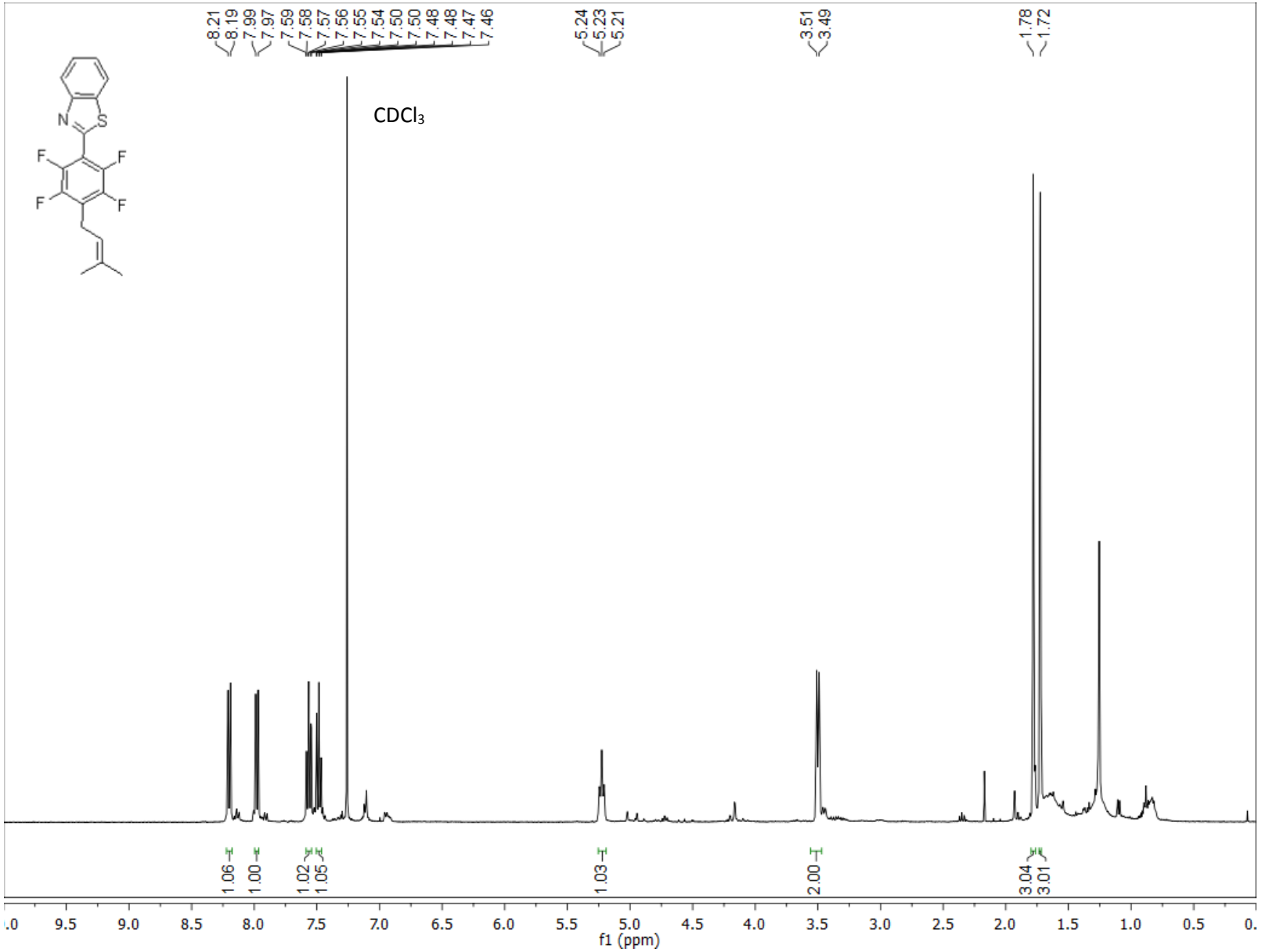




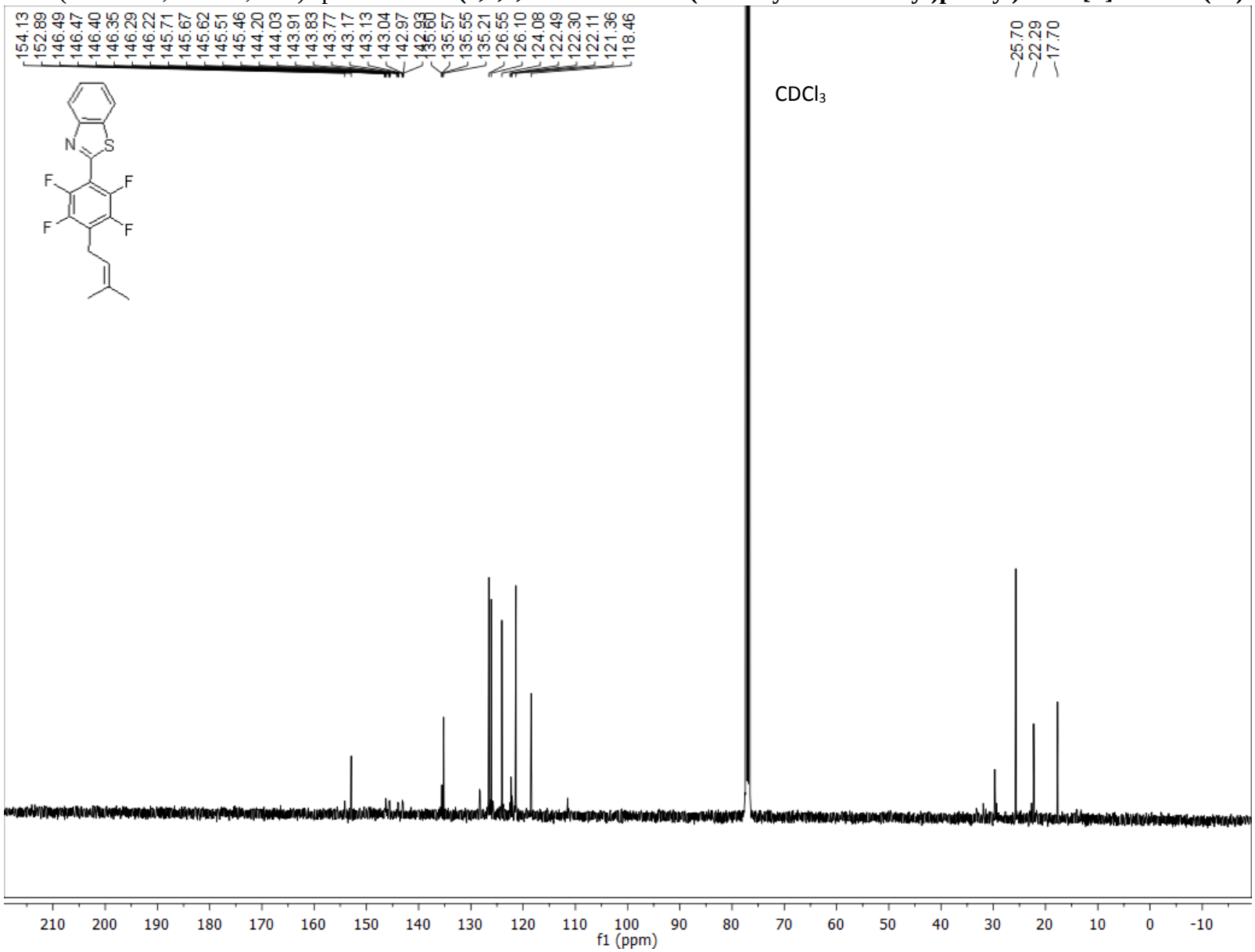
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]thiazole (3o)**



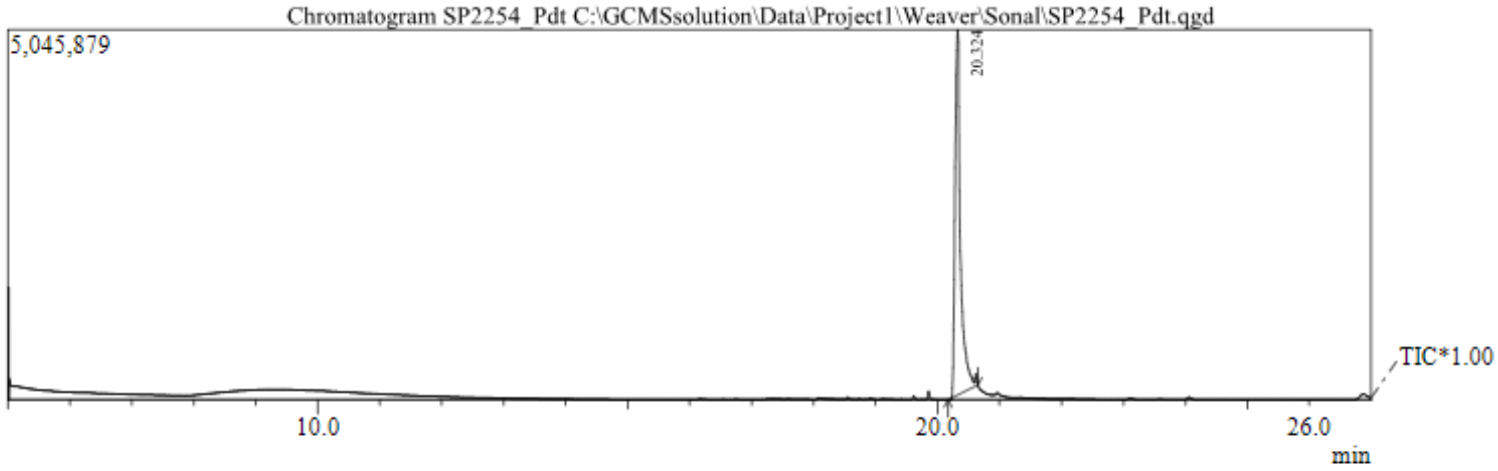
^{1}H NMR (400 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]thiazole (3o)**

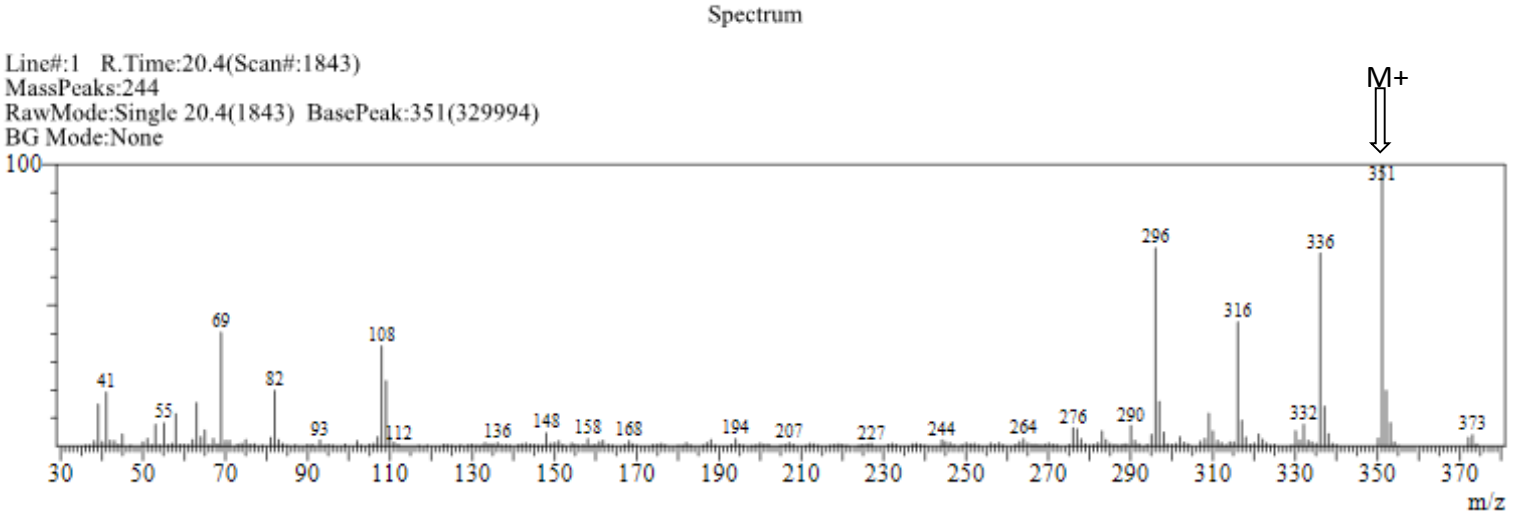


^{13}C NMR (101 MHz, CDCl3, at rt) spectrum of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]thiazole (3o)**

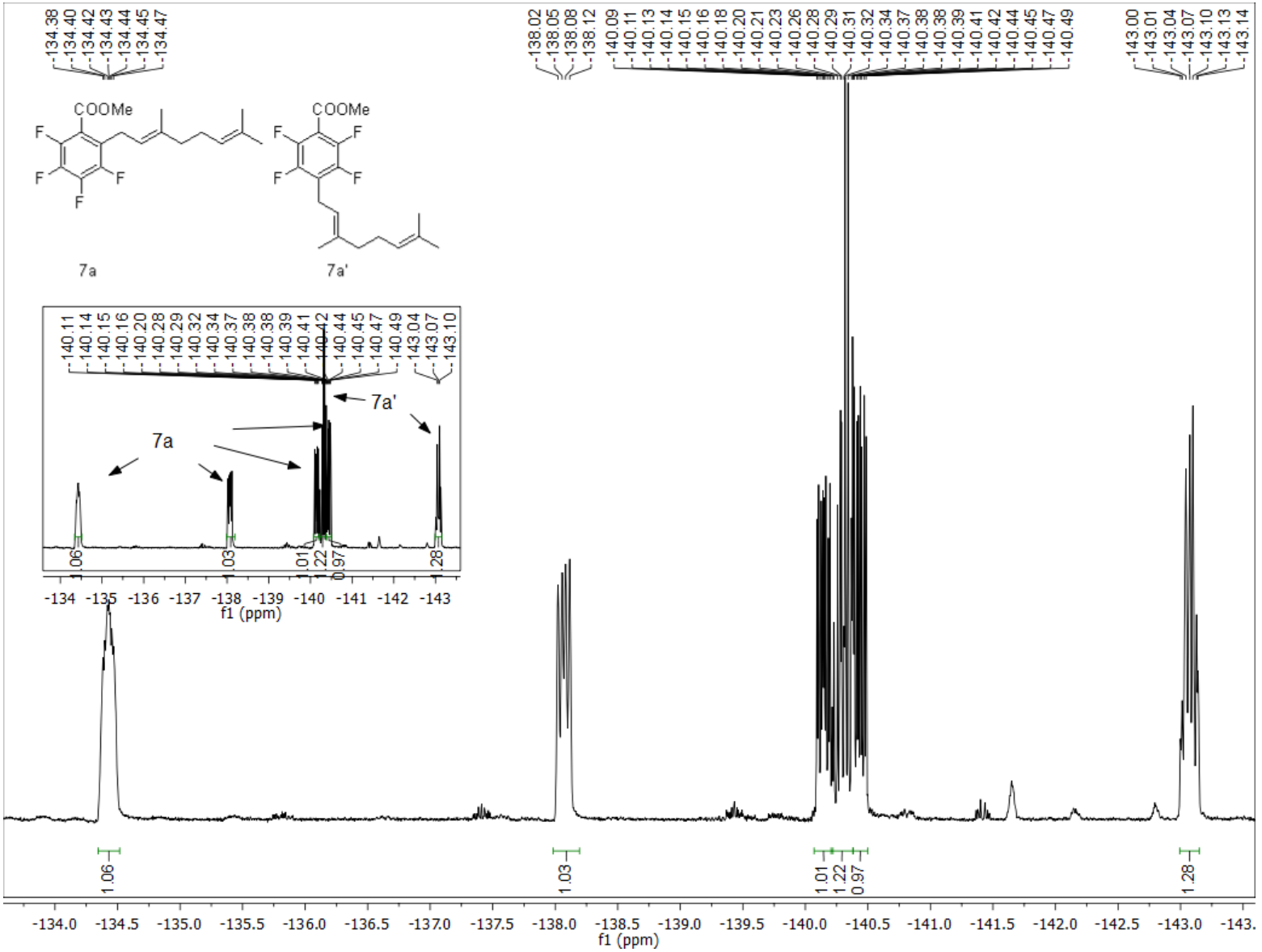


GC and MS of **2-(2,3,5,6-tetrafluoro-4-(3-methylbut-2-en-1-yl)phenyl)benzo[d]thiazole (3o)**

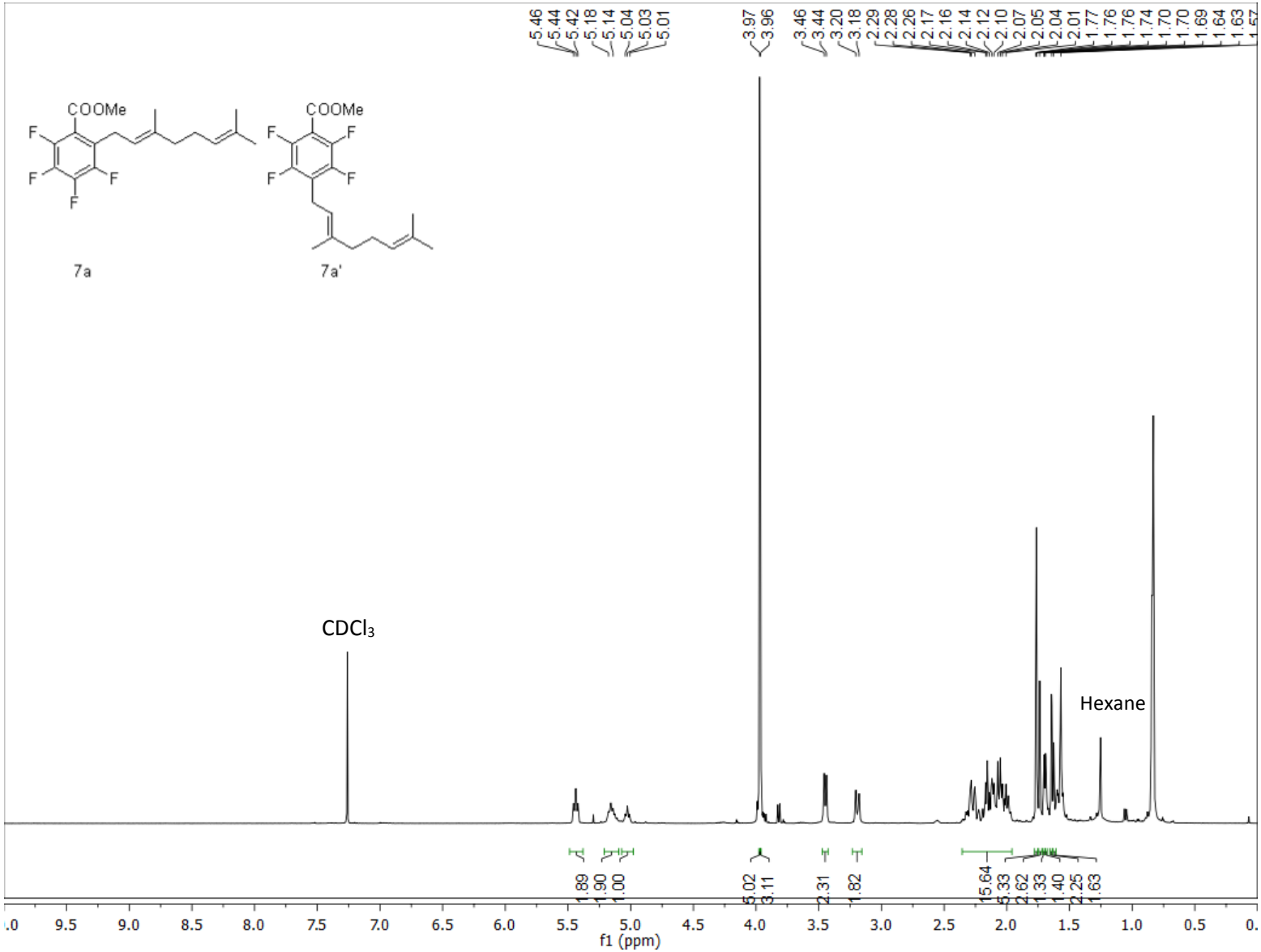




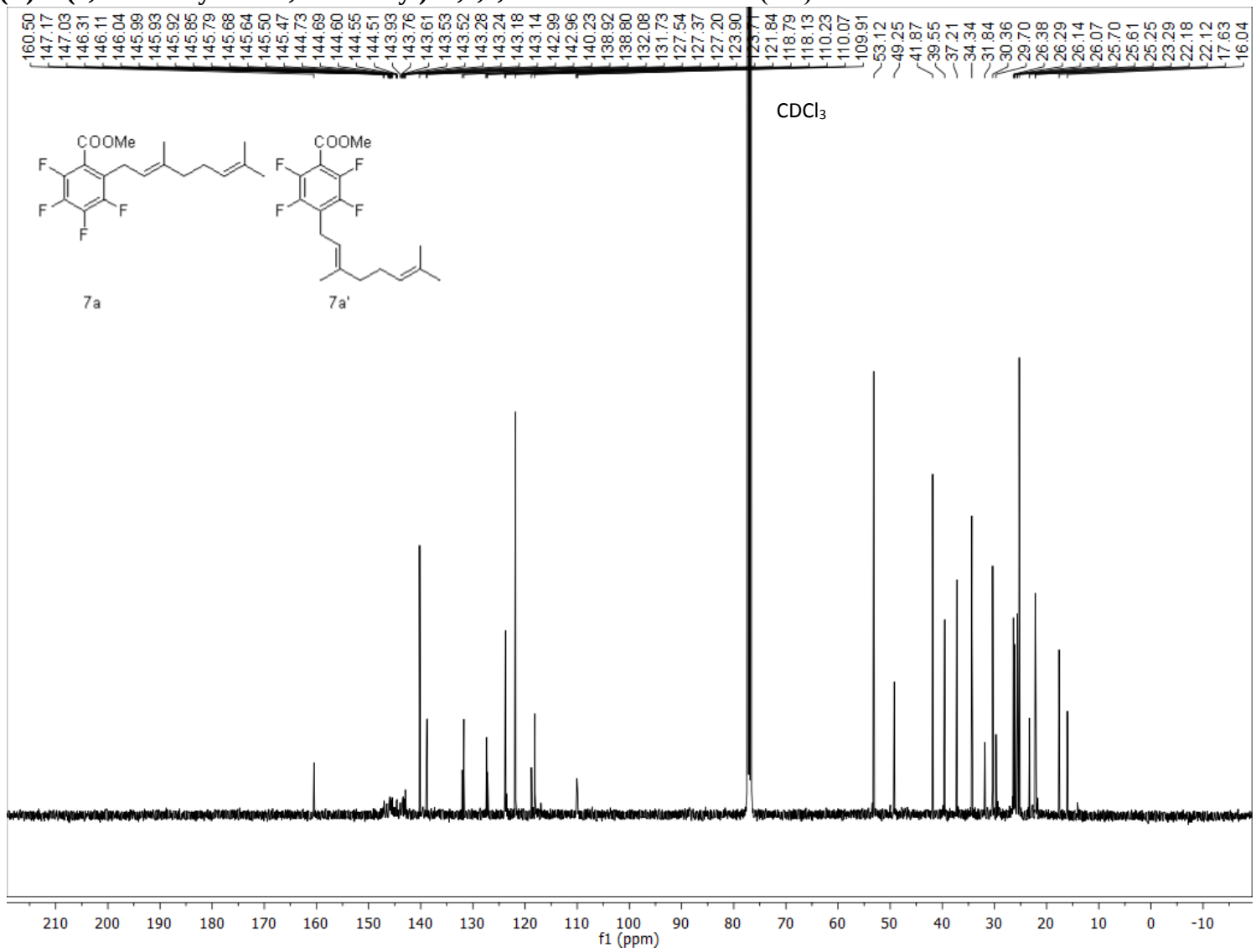
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')**



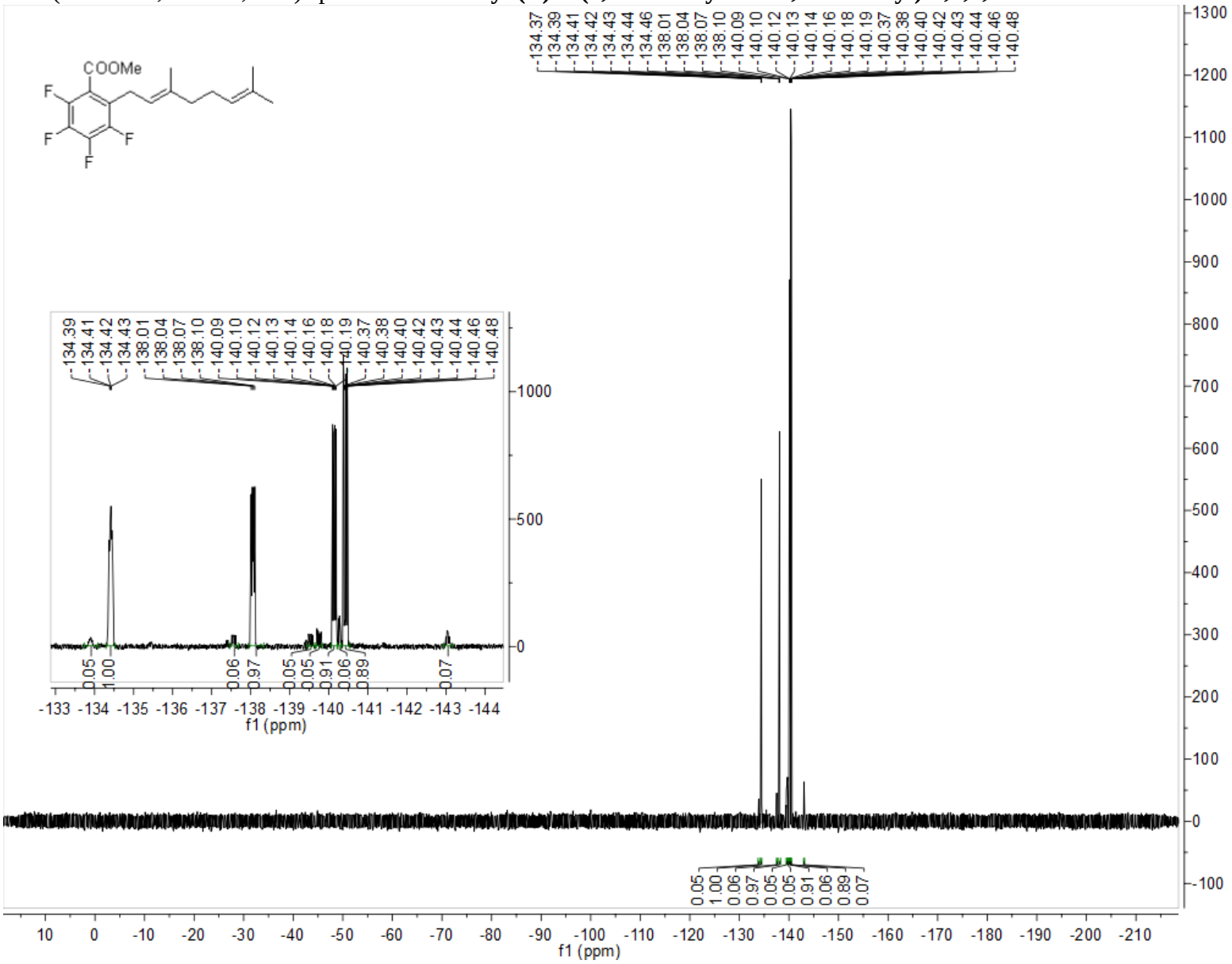
^{1}H NMR (376 MHz, CDCl3, at rt) spectrum of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')**



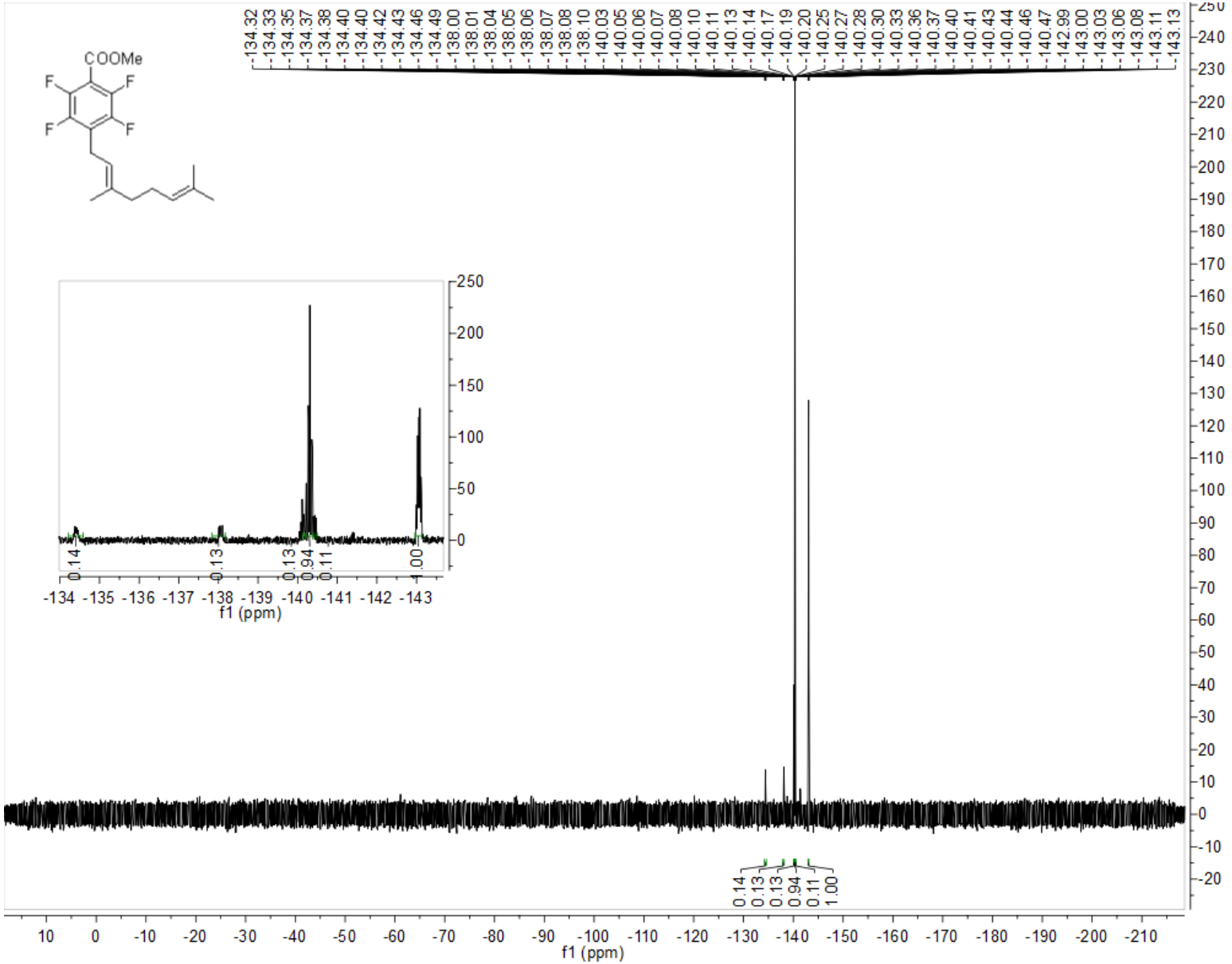
^{13}C NMR (376 MHz, CDCl3, at rt) spectrum of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)- 2,3,5,6-tetrafluorobenzoate (7a')**



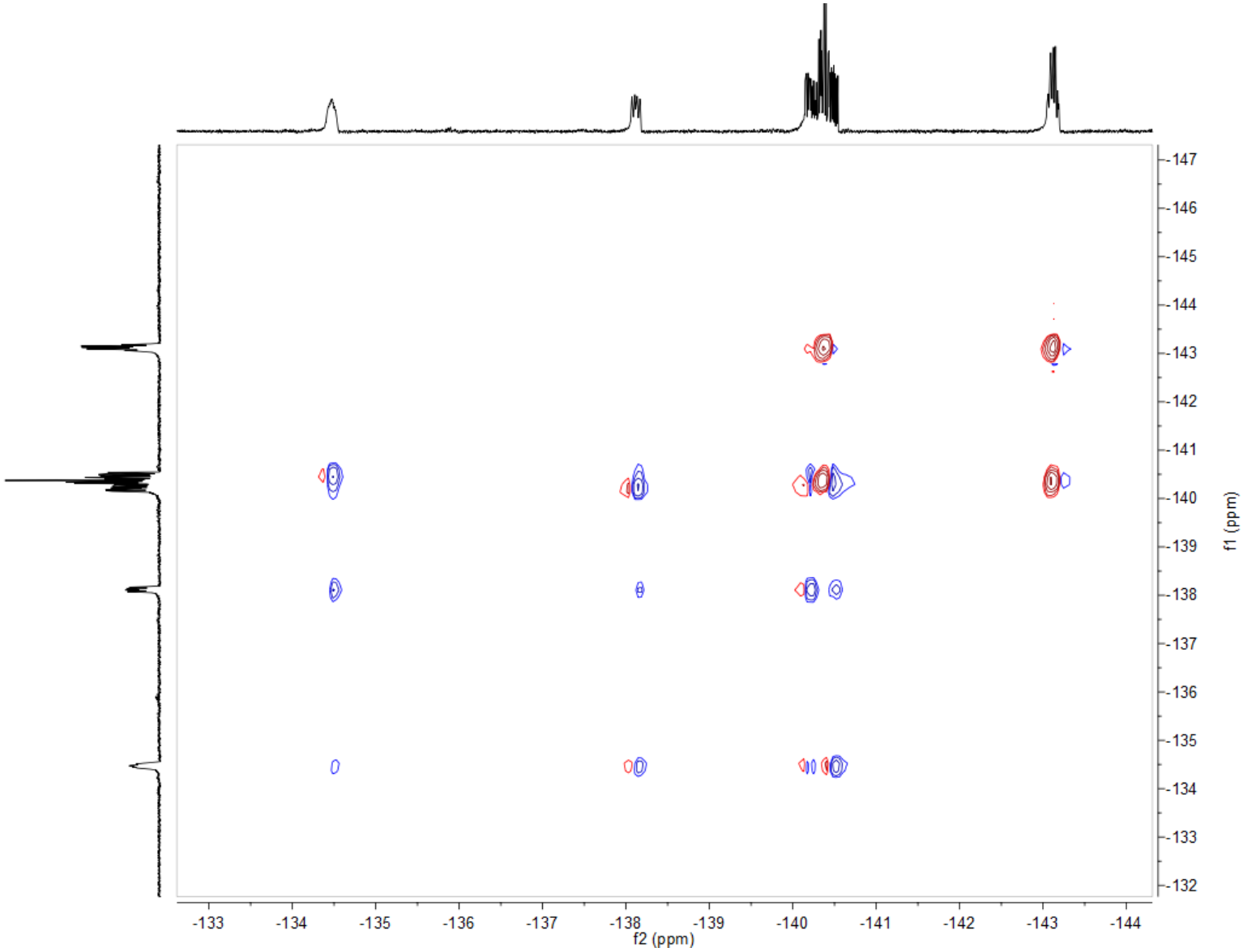
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a)**



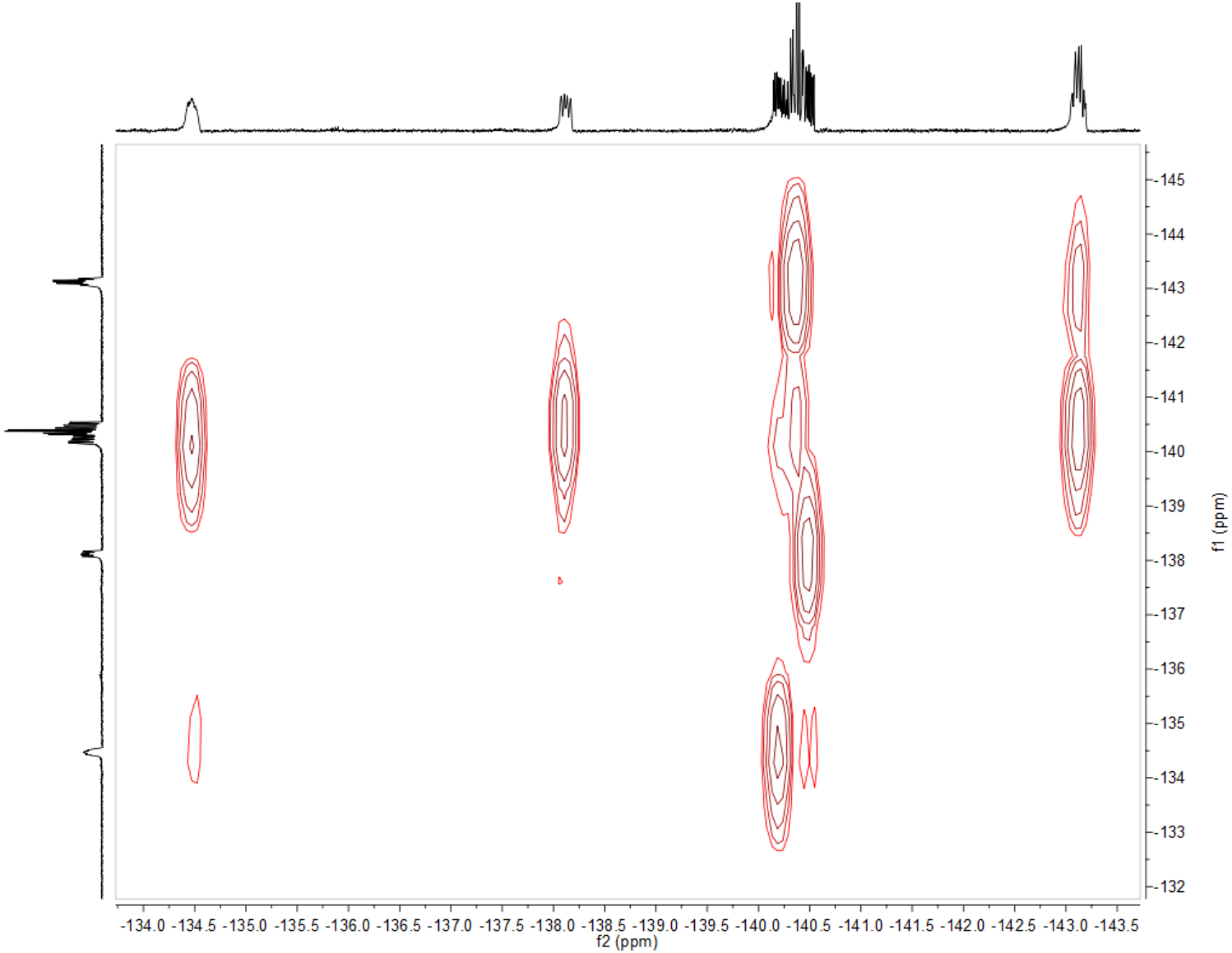
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')**



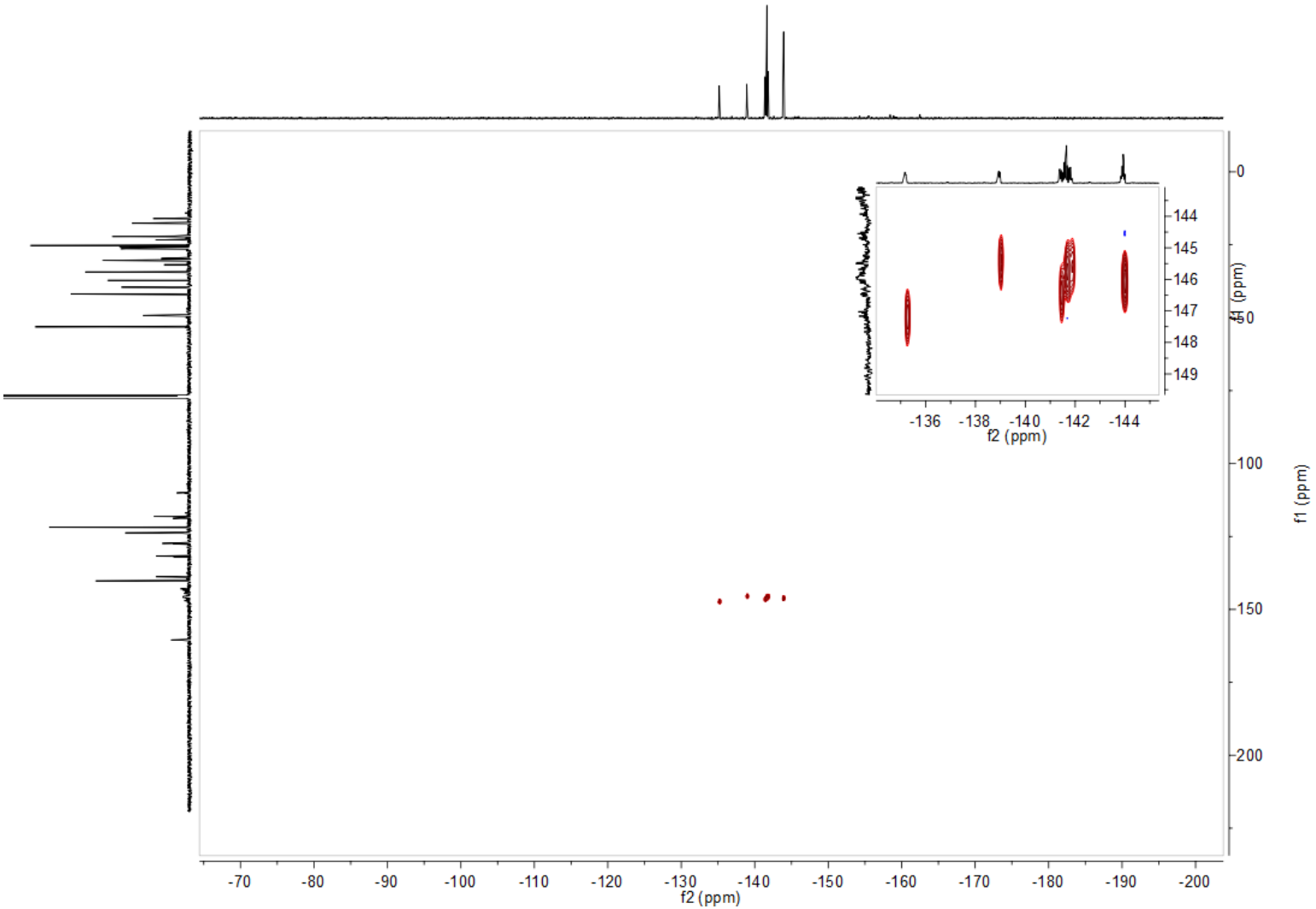
^{19}F -^{19}F TOCSY of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')**



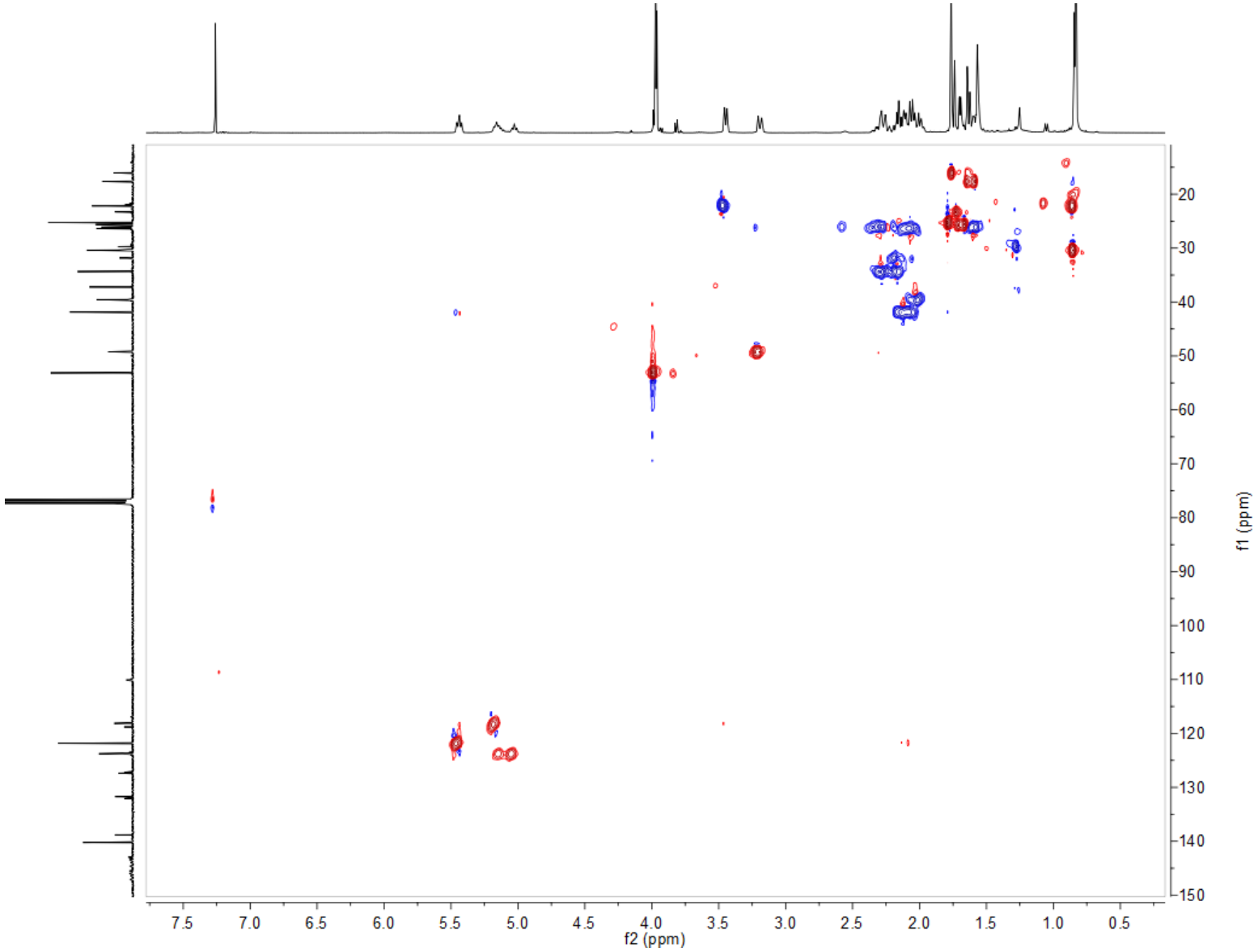
^{19}F -^{19}F COSY of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')**



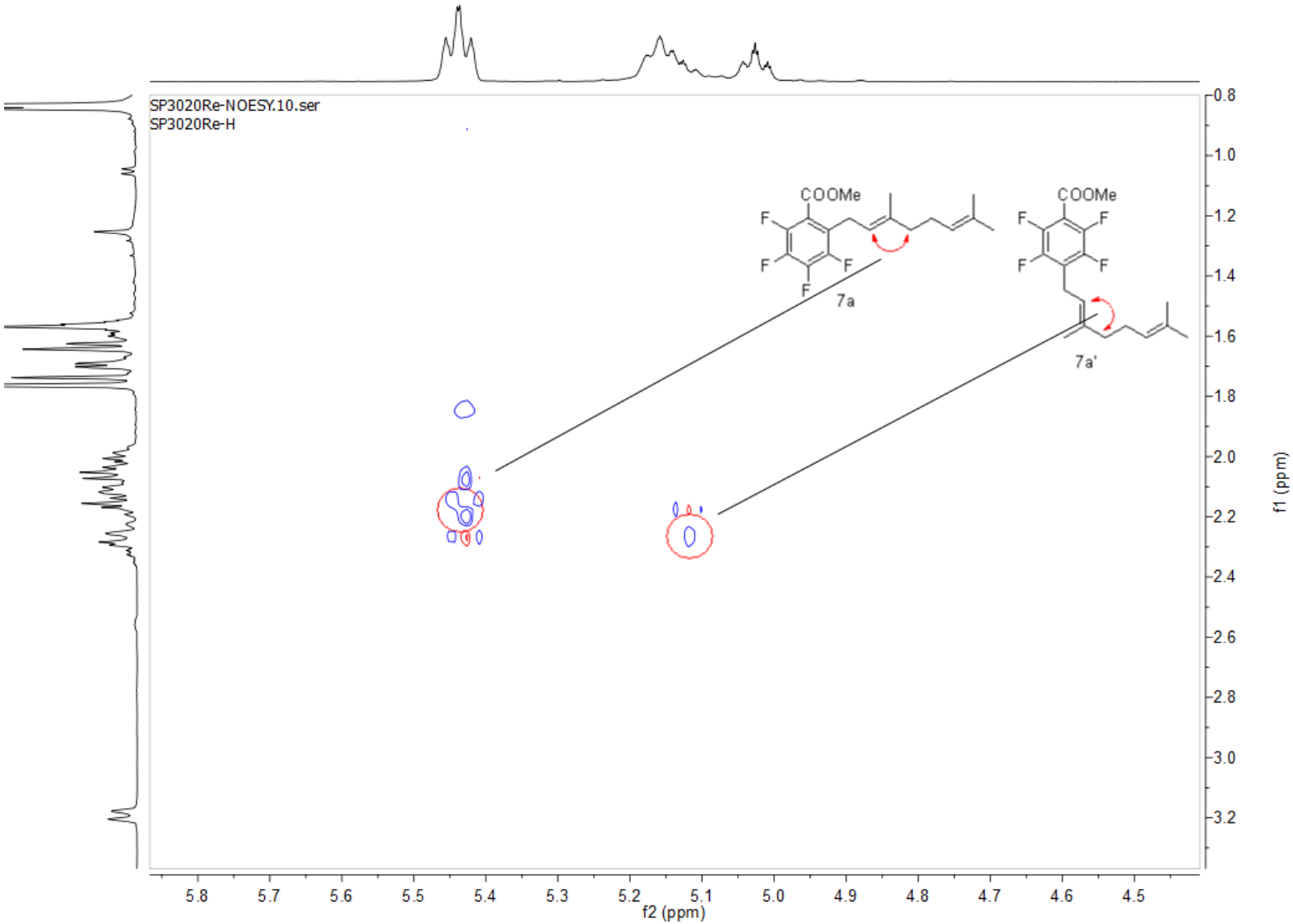
^{19}F-^{13}C HSQC of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')** (in MeCN-d3)



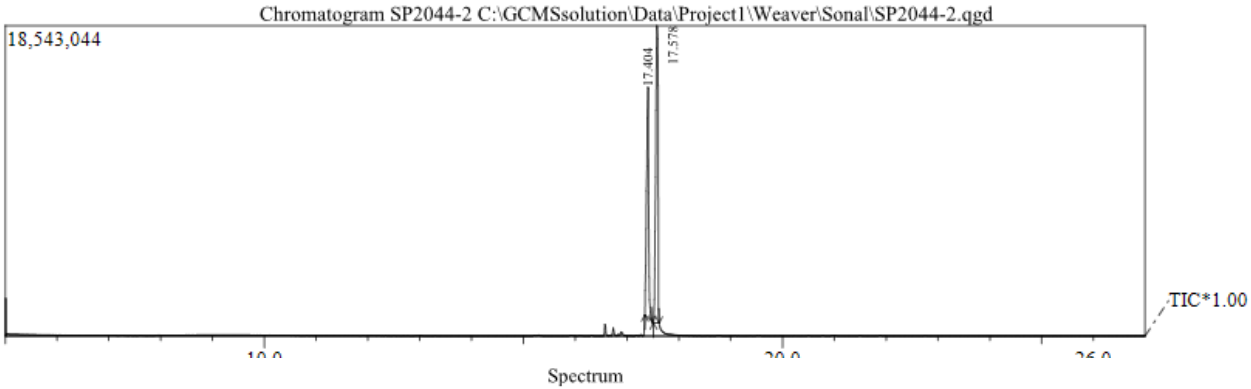
^{1}H-^{13}C HSQC of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')**



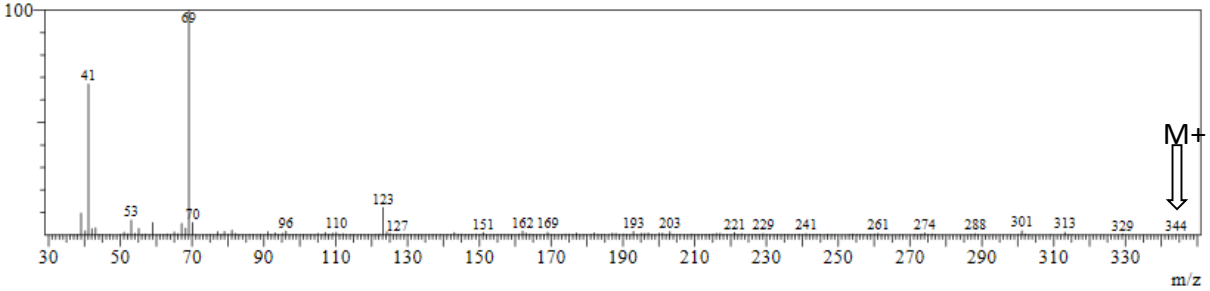
^{1}H-^{1}H NOESY of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')**



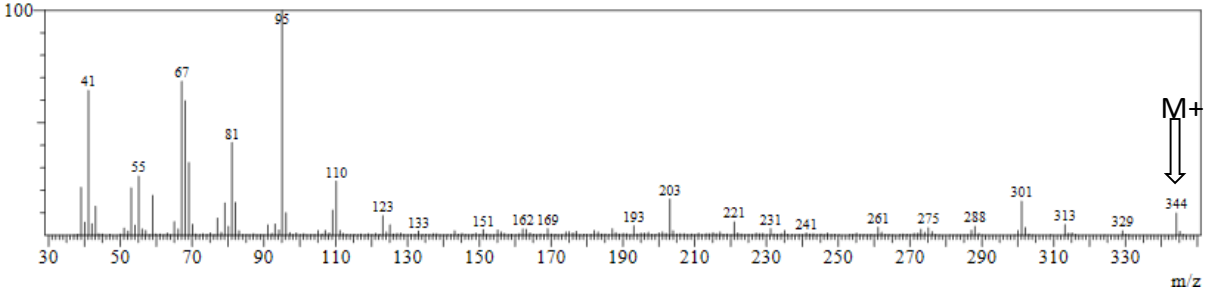
GC and MS of **methyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7a) and methyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7a')**



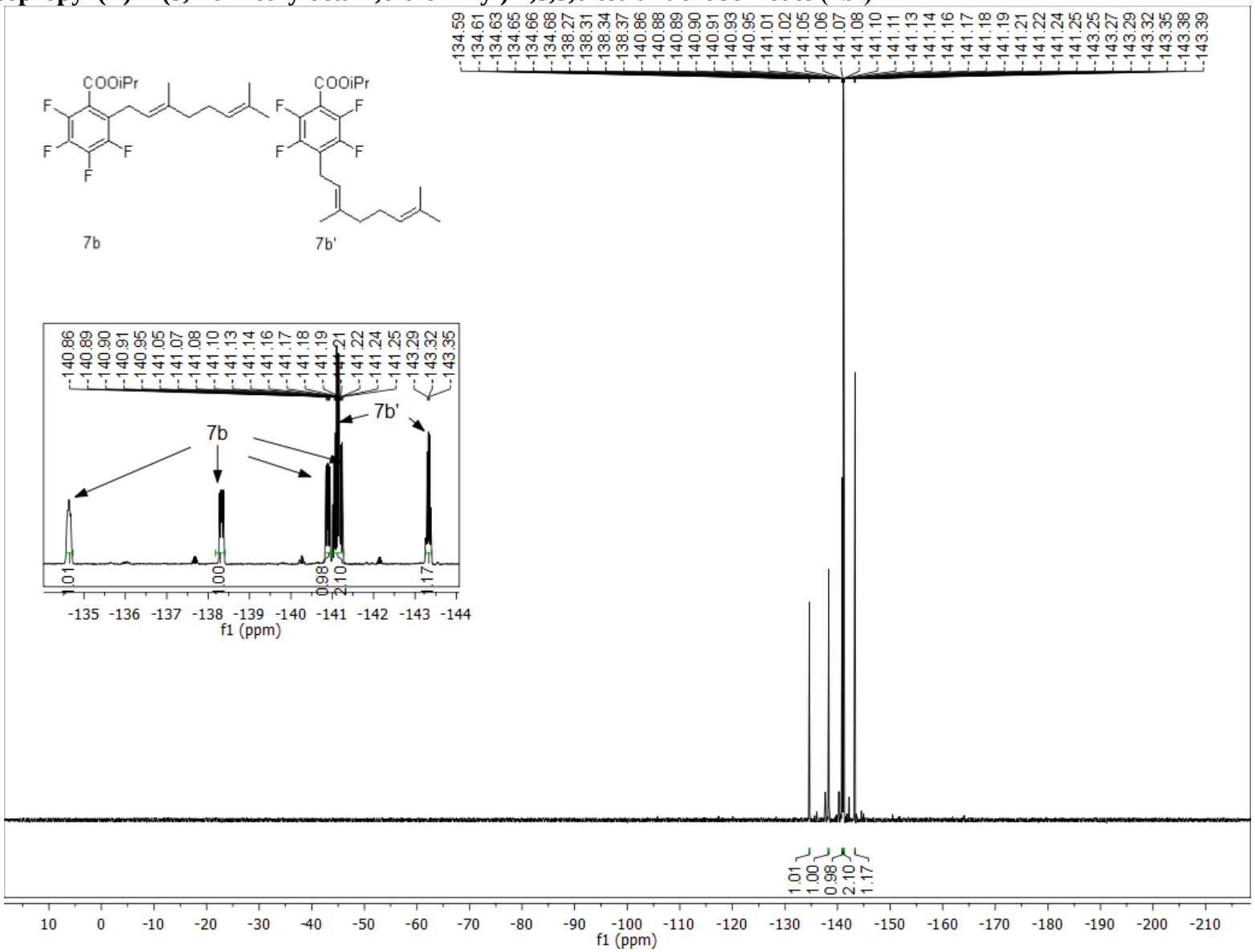
Line#:1 R.Time:17.4(Scan#:1489)
MassPeaks:242
RawMode:Single 17.4(1489) BasePeak:69(4949625)
BG Mode:None



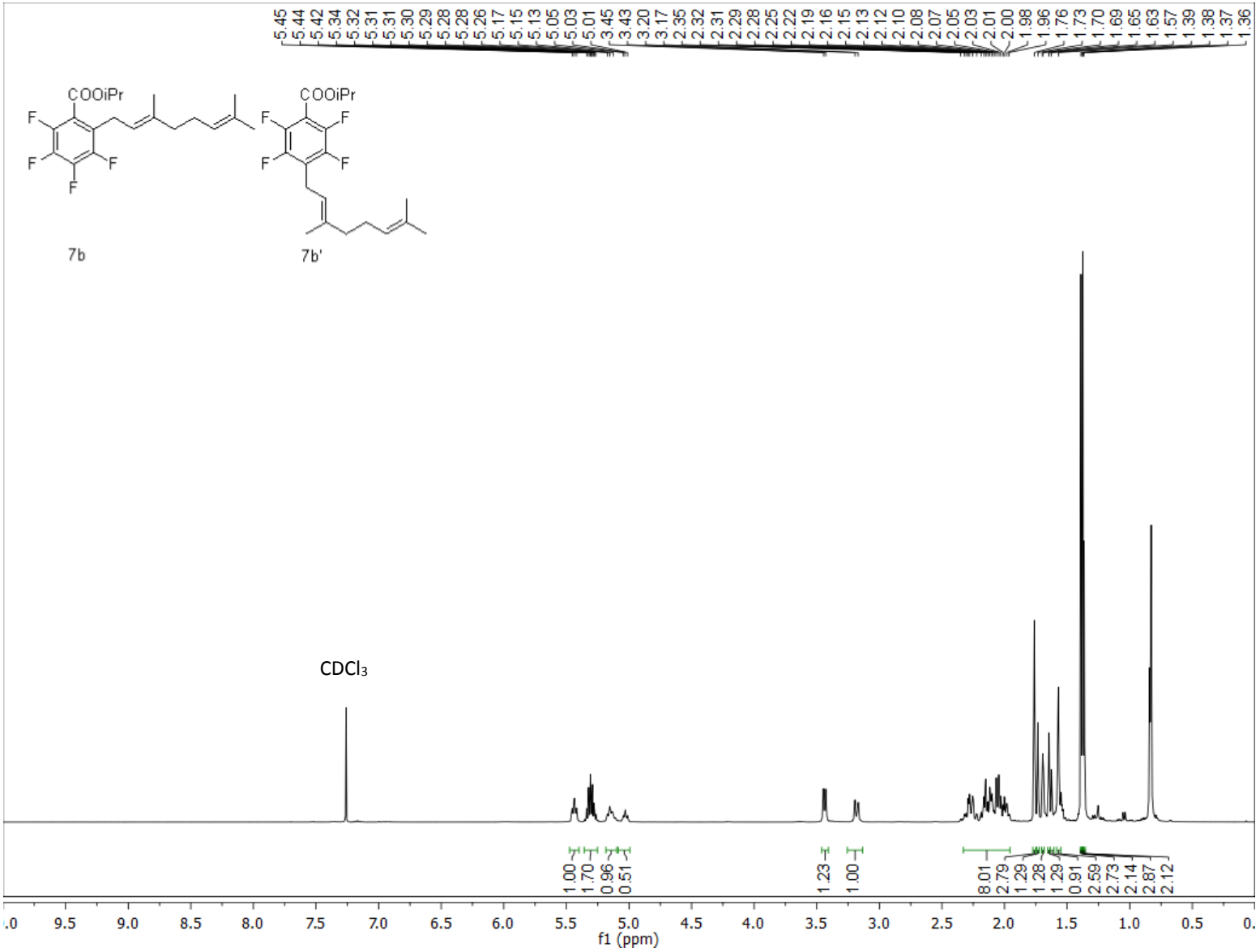
Line#:2 R.Time:17.6(Scan#:1509)
MassPeaks:264
RawMode:Single 17.6(1509) BasePeak:95(2063375)
BG Mode:None



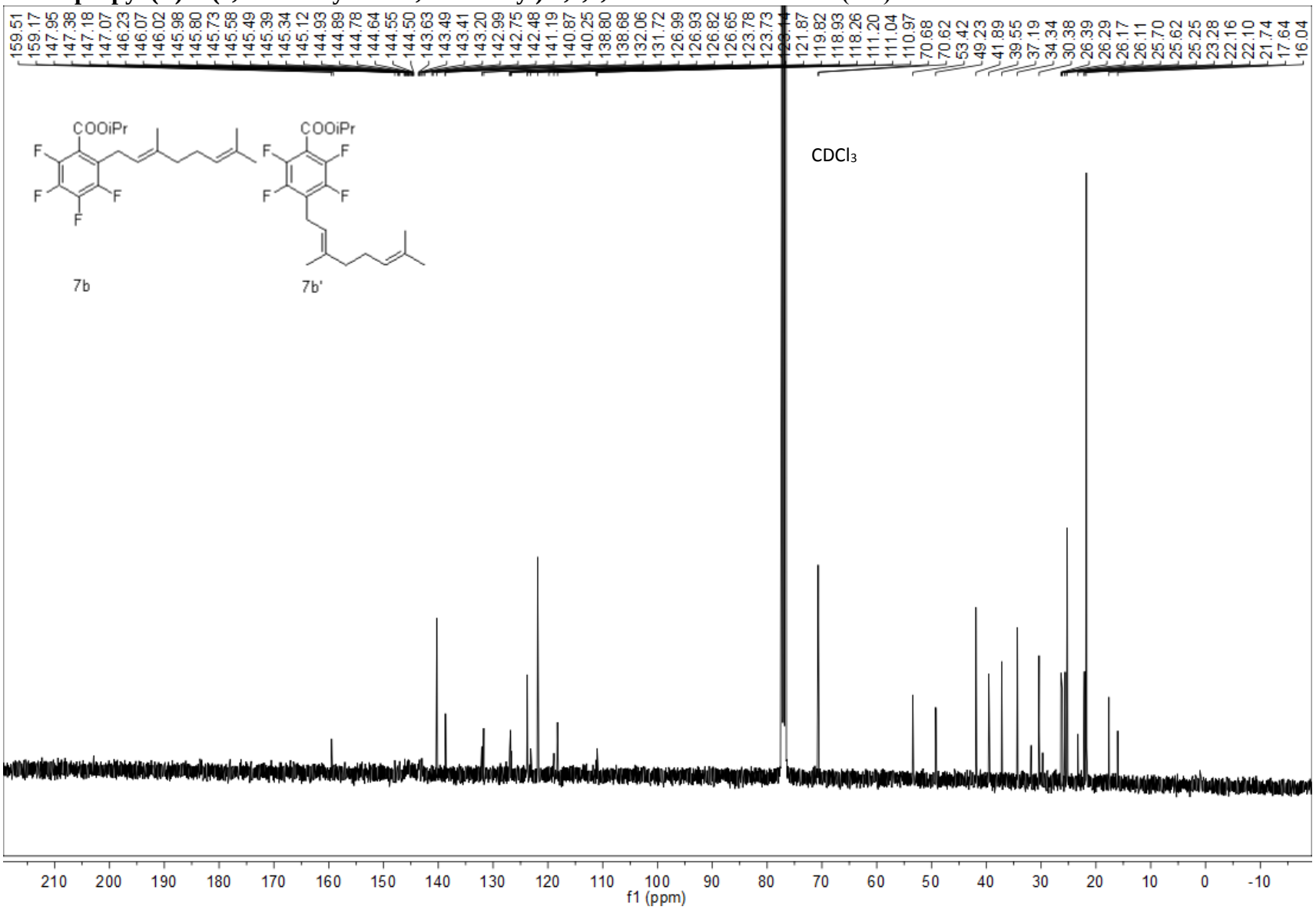
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **isopropyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7b) and isopropyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7b')**



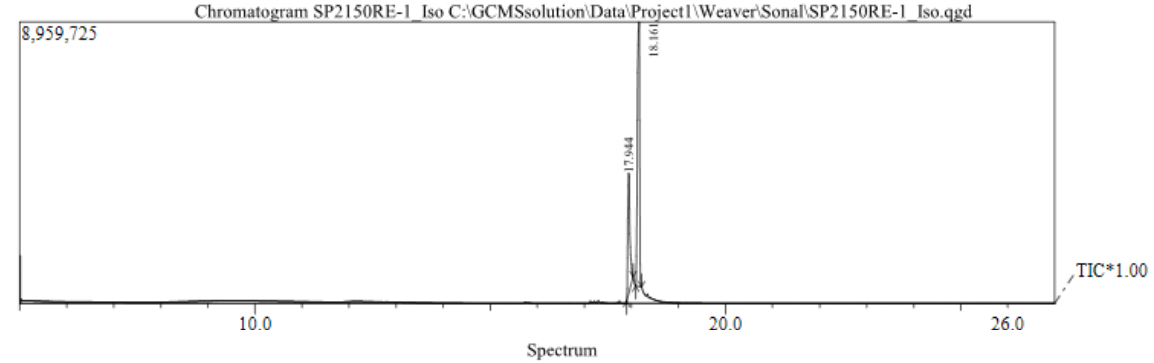
^{1}H NMR (376 MHz, CDCl3, at rt) spectrum of **isopropyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7b) and isopropyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7b')**



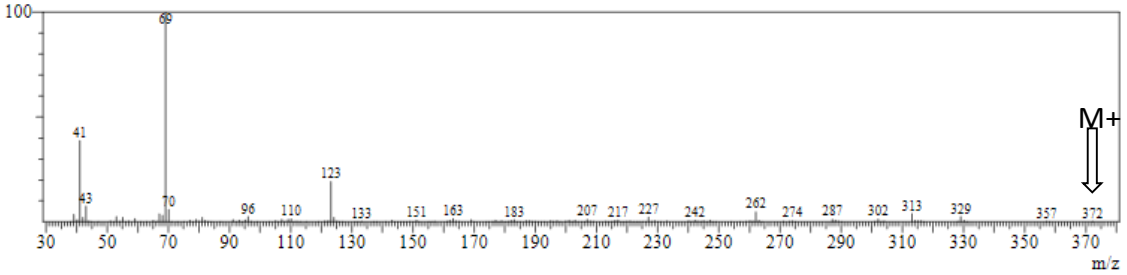
^{13}C NMR (376 MHz, CDCl3, at rt) spectrum of **isopropyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7b) and isopropyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7b')**



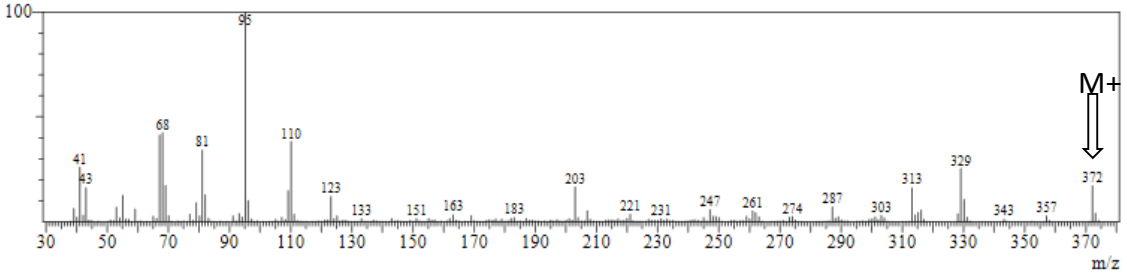
GC and MS of **isopropyl (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzoate (7b) and isopropyl (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzoate (7b')**



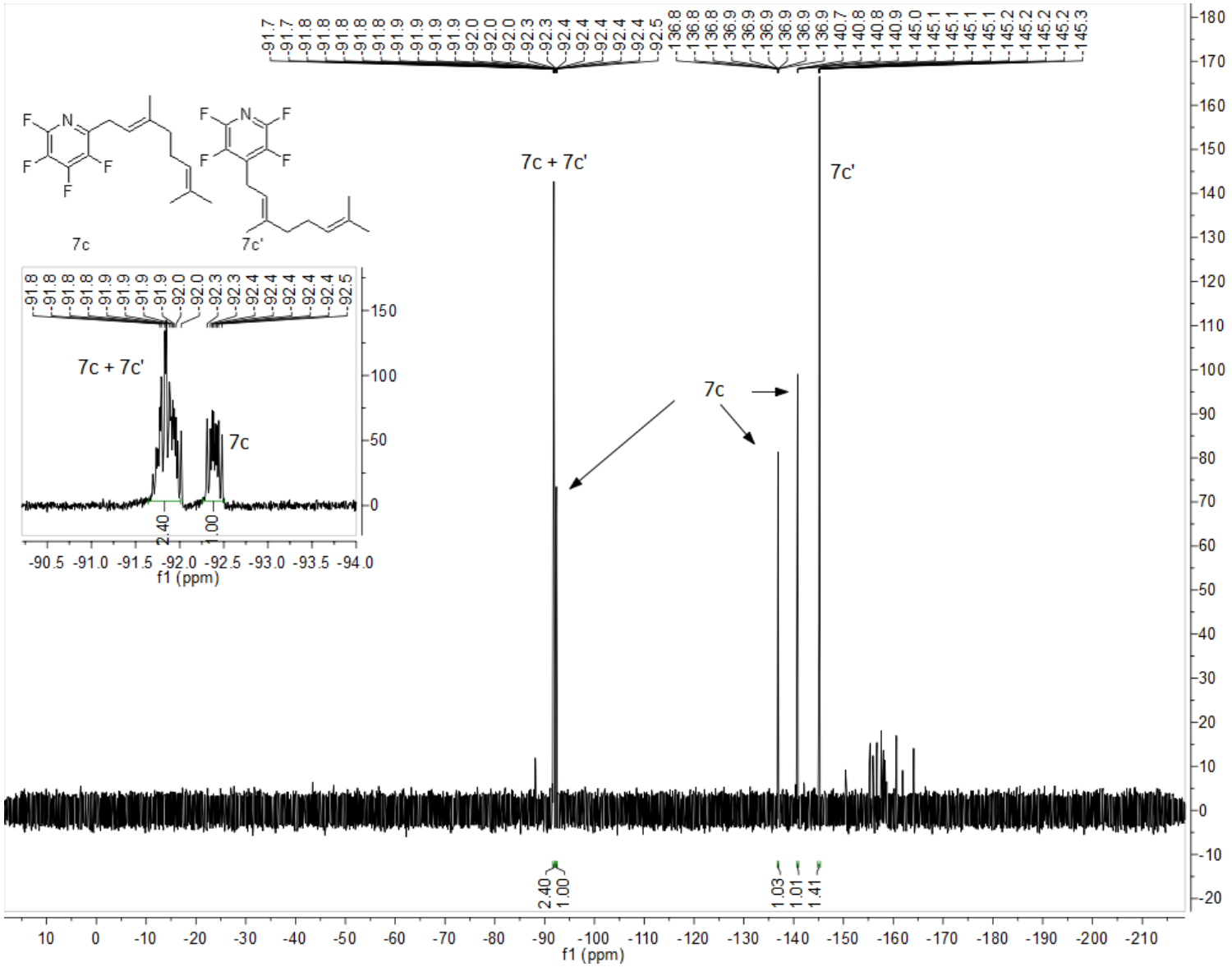
Line#:1 R.Time:17.9(Scan#:1554)
MassPeaks:185
RawMode:Single 17.9(1554) BasePeak:69(1538834)
BG Mode:None



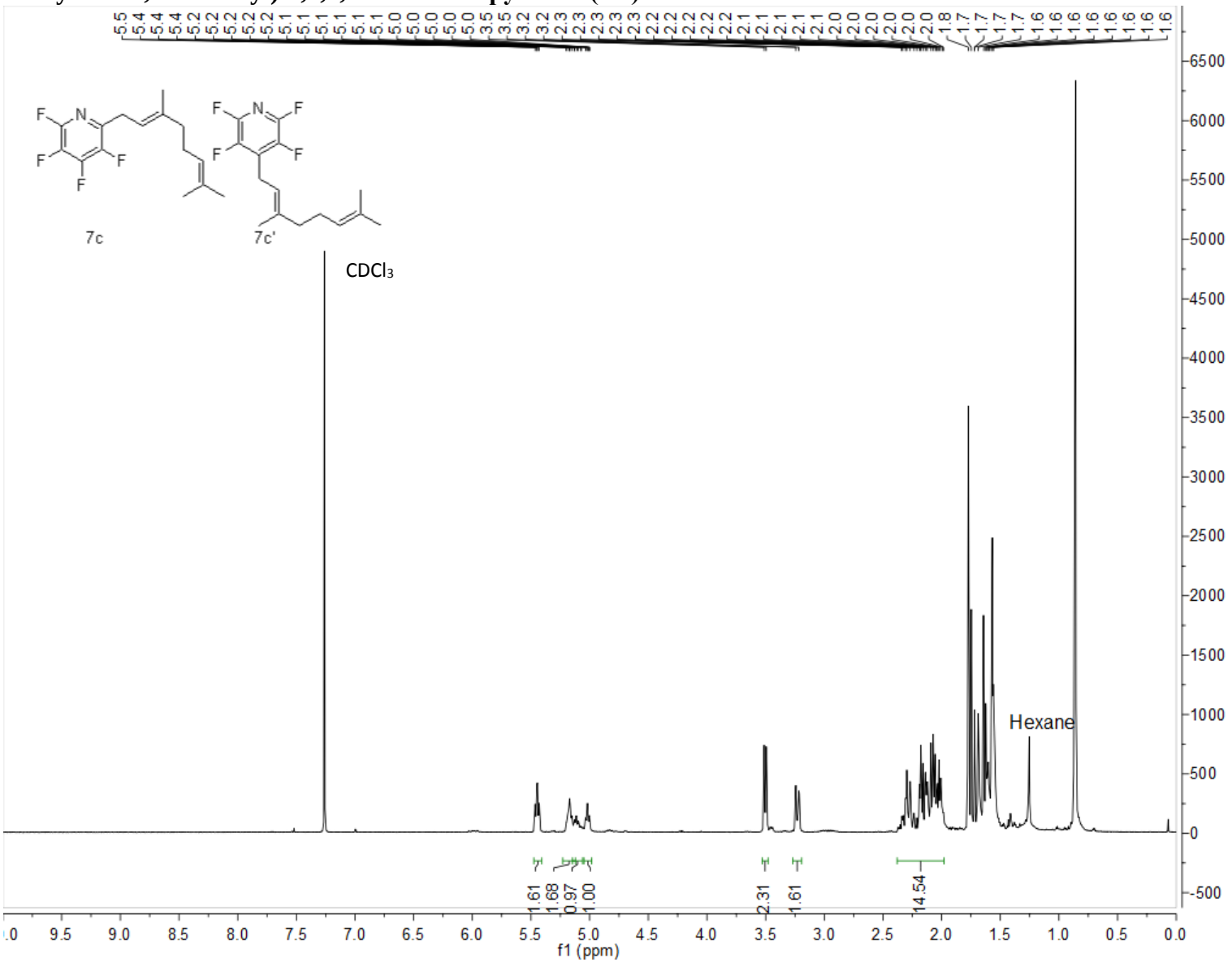
Line#:2 R.Time:18.2(Scan#:1579)
MassPeaks:268
RawMode:Single 18.2(1579) BasePeak:95(1183221)
BG Mode:None



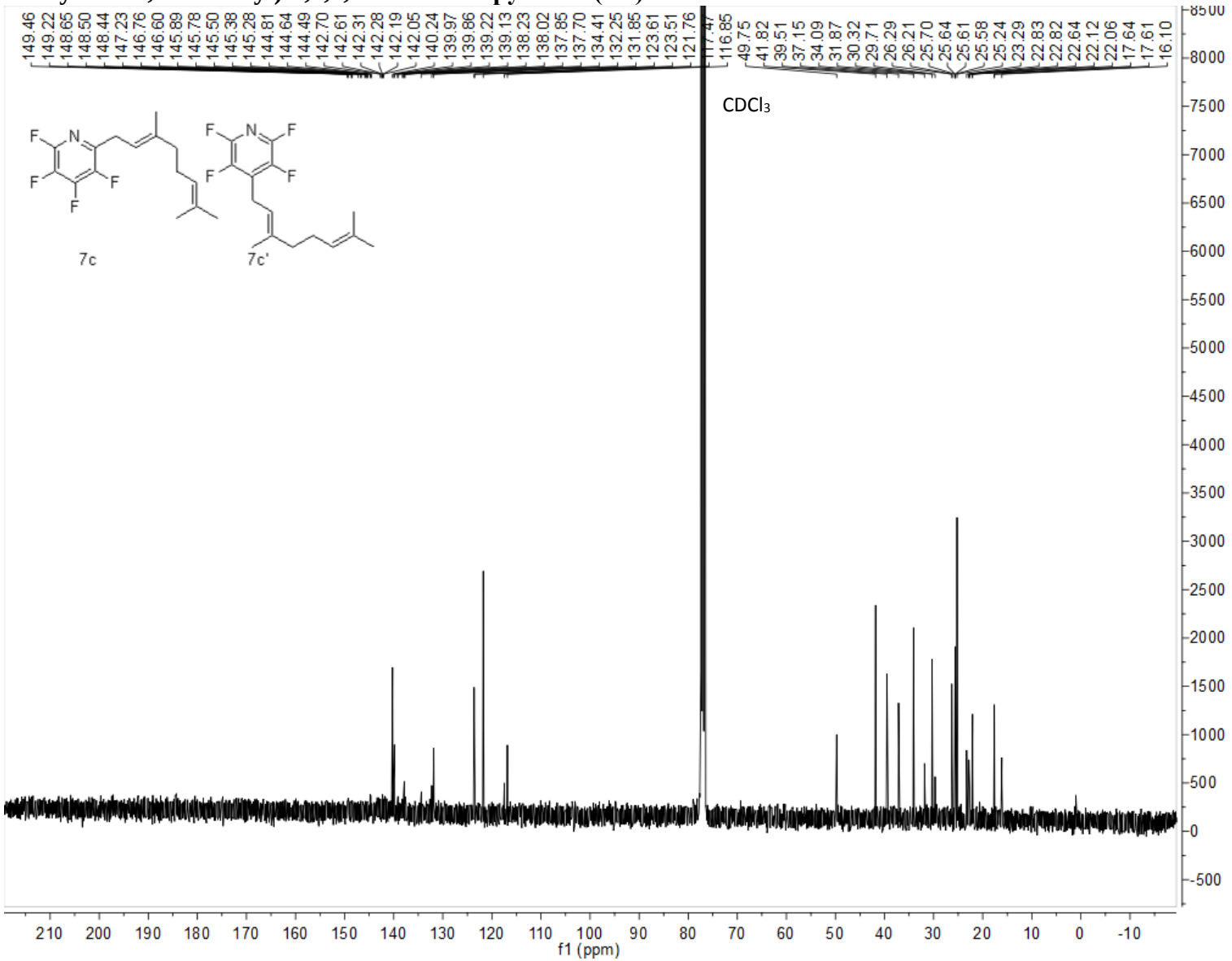
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluoropyridine (7c) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluoropyridine (7c')**



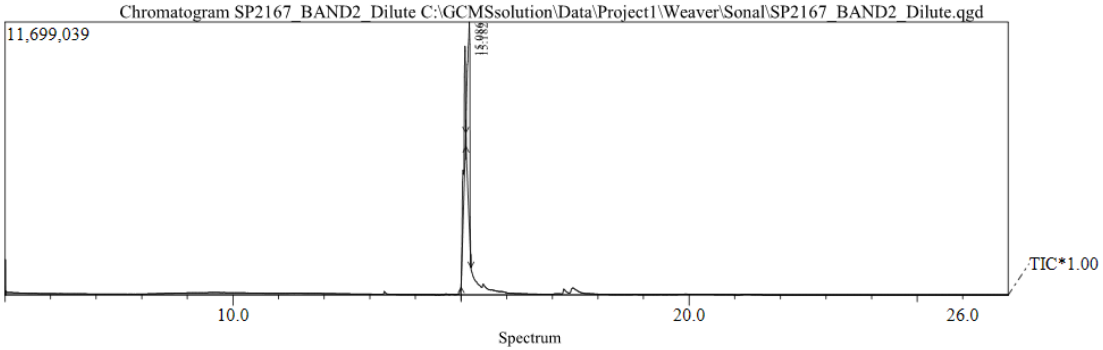
^{1}H NMR (376 MHz, CDCl3, at rt) spectrum of **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluoropyridine (7c) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluoropyridine (7c')**

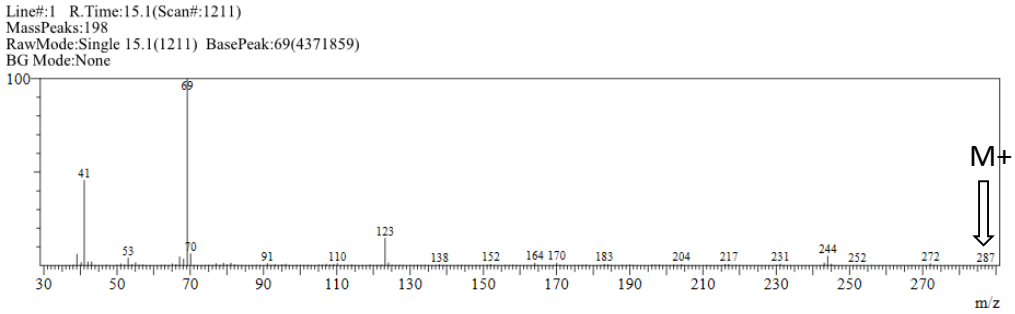


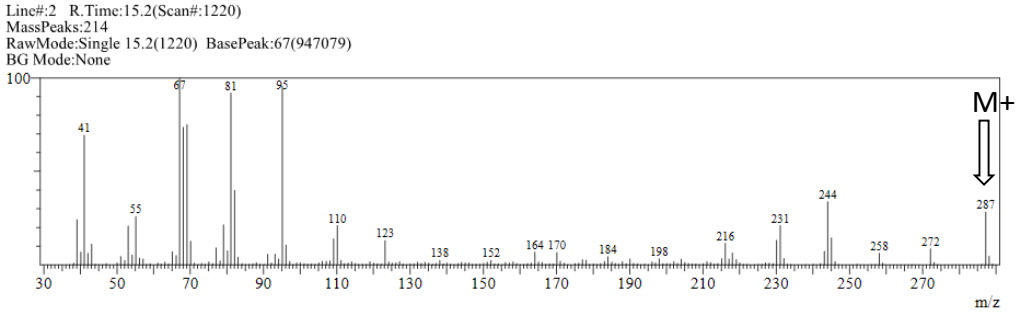
^{13}C NMR (376 MHz, CDCl3, at rt) spectrum of **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluoropyridine (7c) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluoropyridine (7c')**



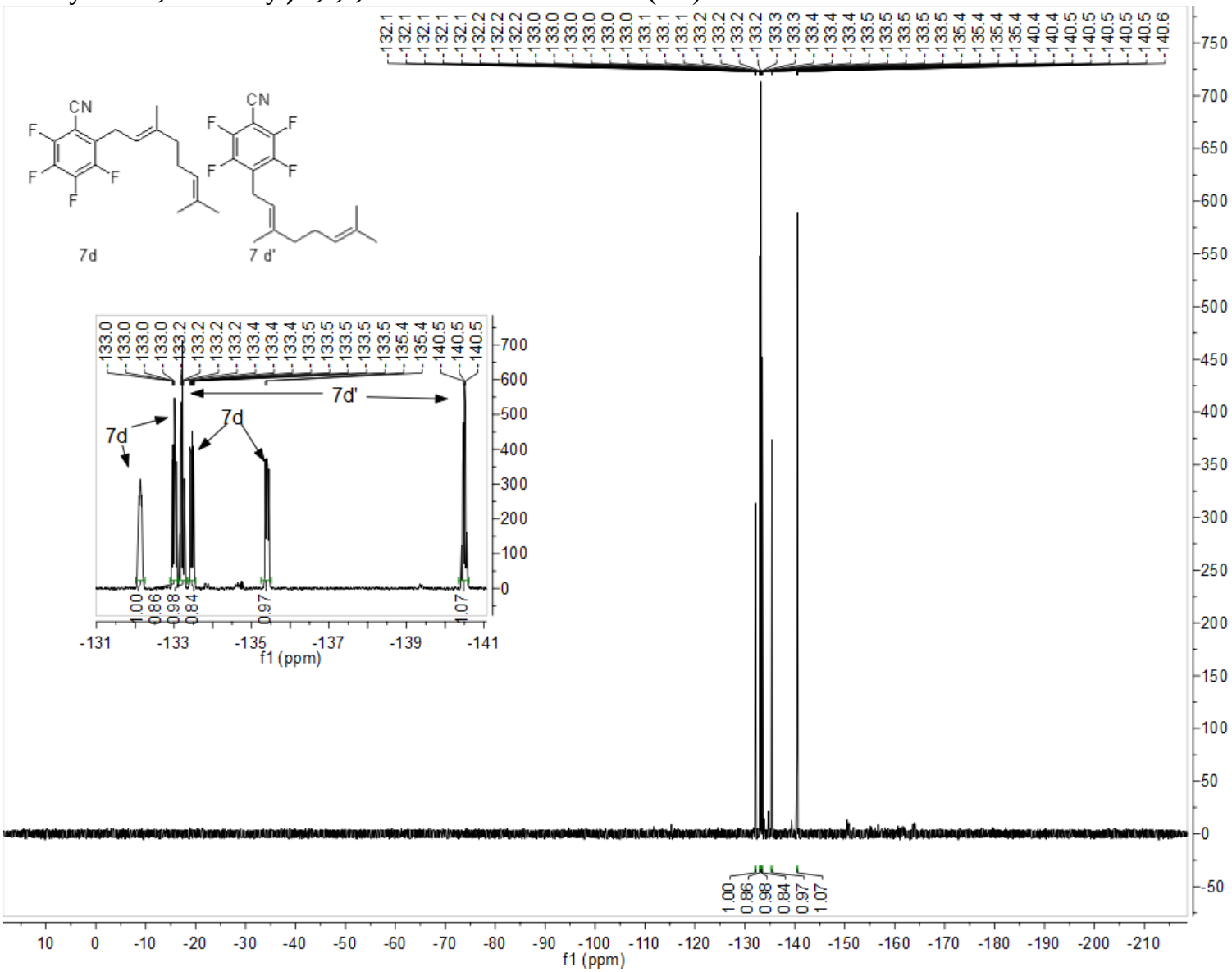
GC and MS of **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluoropyridine (7c) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluoropyridine (7c')**



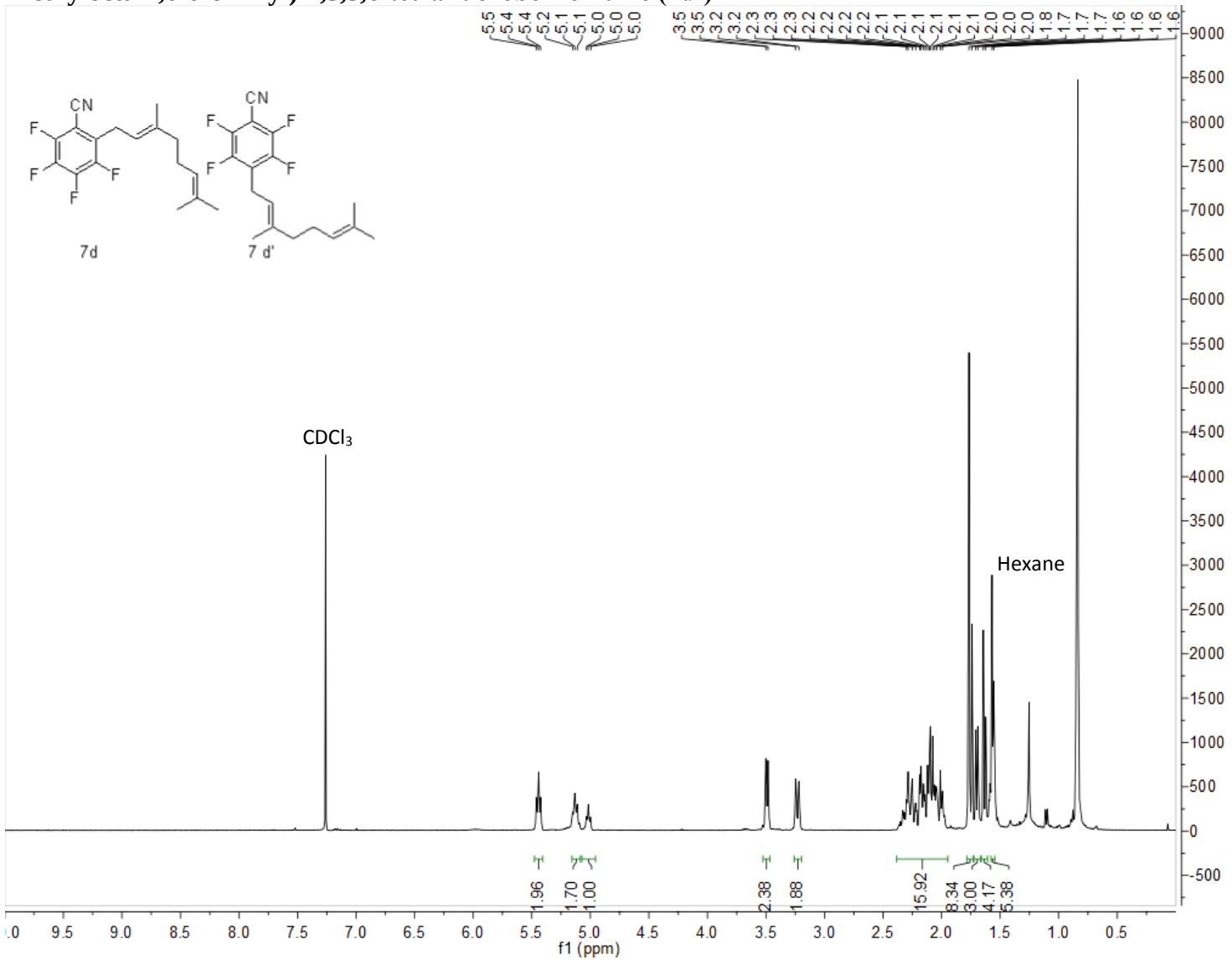




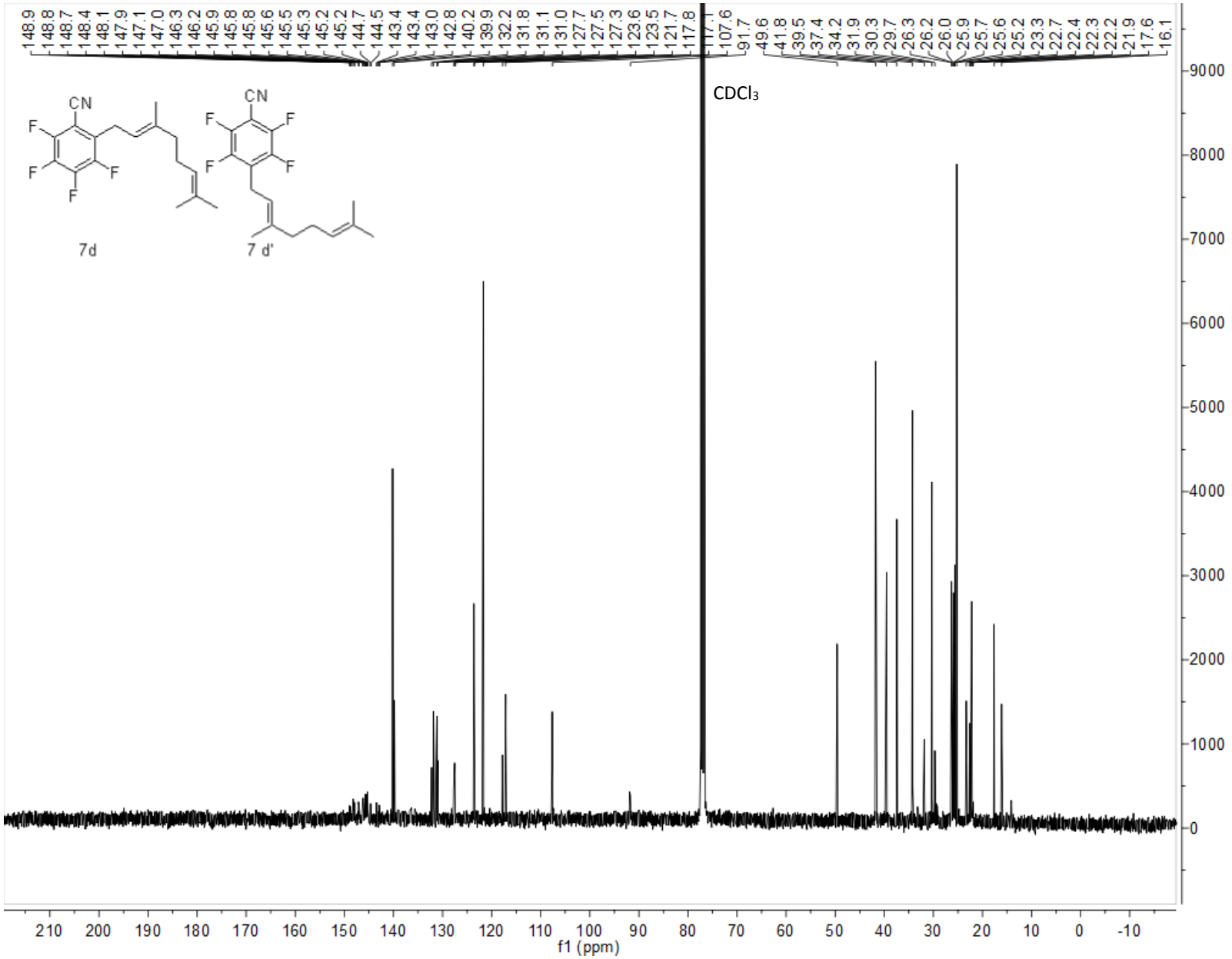
^{19}F NMR (376 MHz, CDCl3, at rt) spectrum of **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzonitrile (7d) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzonitrile (7d')**



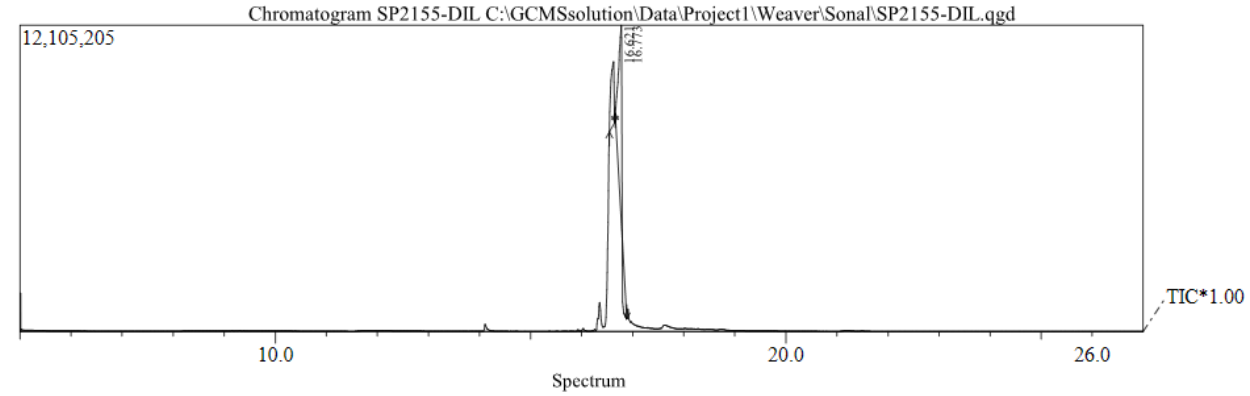
^{1}H NMR (376 MHz, CDCl3, at rt) spectrum of **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzonitrile (7d) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzonitrile (7d')**



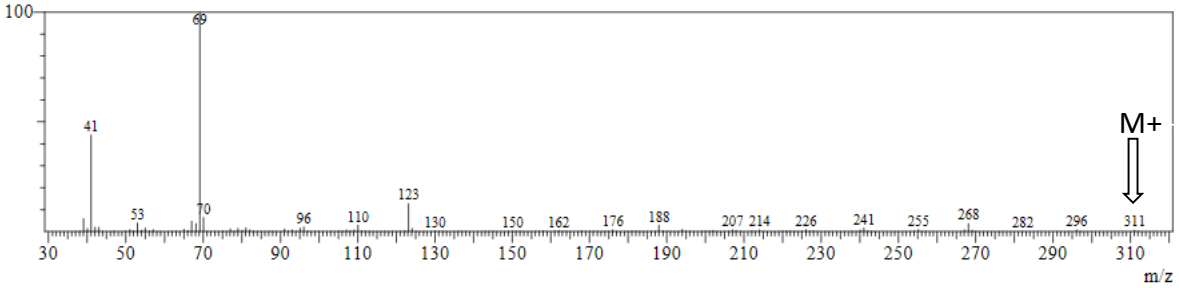
^{13}C NMR (376 MHz, CDCl3, at rt) spectrum of **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzonitrile (7d) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzonitrile (7d')**



GC and MS of **(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4,5,6-tetrafluorobenzonitrile (7d) and (E)-4-(3,7-dimethylocta-2,6-dien-1-yl)-2,3,5,6-tetrafluorobenzonitrile (7d')**



Line#:1 R.Time:16.6(Scan#:1394)
MassPeaks:212
RawMode:Single 16.6(1394) BasePeak:69(4220964)
BG Mode:None



Line#:2 R.Time:16.7(Scan#:1408)
MassPeaks:223
RawMode:Single 16.7(1408) BasePeak:95(1292090)
BG Mode:None