Photocatalyst size controls electron and energy transfer: Selectable E/Z isomer synthesis via C-F alkenylation.

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Supporting Information
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General Experimental

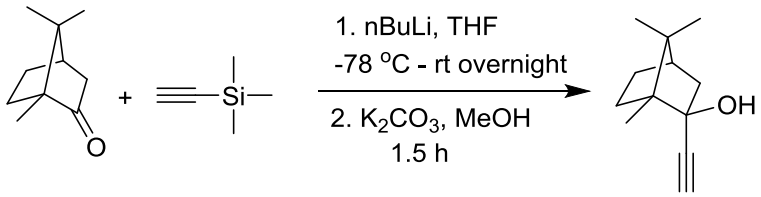
All reagents were obtained from commercial suppliers (Sigma-Aldrich, Oakwood chemicals, Alfa Aesar, Matrix Scientific, VWR) and used without further purification unless otherwise noted. Acetonitrile (CH_3CN) was dried over molecular sieves. *N,N*-diisopropylethylamine was purchased from Sigma-Aldrich and was distilled and stored over anhydrous potassium hydroxide. Photocatalysts $Ir(ppy)_3$ *fac*-tris(2-phenyl pyridinato-C^2, *N*)iridium(III), $Ir(tbppy)_3$ *fac*-tris[2-(4-*tert*-butylphenyl)pyridinato-C^2, *N*)]iridium(III), $Ir(CF_3ppy)_3$ *fac*-tris[2-(4-trifluoromethylphenyl)pyridinato-C^2, *N*)]iridium(III), $Ir(Fppy)_3$, *fac*-tris[2-(4-fluorophenyl)pyridinato-C^2, *N*)]]iridium(III), $Ir(dFppy)_3$ *fac*-tris(2-(4,6-difluorophenyl)pyridinato- C^2, *N*)iridium(III), $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ [4,4'-Bis(tert-butyl)-2,2'-bipyridine]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl]phenyl]iridium(III) hexafluorophosphate, $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ [2,2'-bipyridine]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl]phenyl]iridium(III) hexafluorophosphate, $[Ir(dF(CF_3)ppy)_2(phen)](PF_6)$ [phenothroline]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl]phenyl]iridium(III) hexafluorophosphate, $[Ir(dFppy)_2(dtbbpy)](PF_6)$ [4,4'-Bis(tert-butyl)-2,2'-bipyridine]bis[3,5-difluoro-[2-pyridinyl]phenyl]iridium(III) hexafluorophosphate, $[Ir(dFppy)_2(bpy)](PF_6)$ [2,2'-bipyridine]bis[3,5-difluoro-2-pyridinyl]phenyl]iridium(III) hexafluorophosphate, $[Ir(Fppy)_2(dtbbpy)](PF_6)$ [4,4'-Bis(tert-butyl)-2,2'-bipyridine]bis[3-fluoro-2-pyridinyl]phenyl]iridium(III) hexafluorophosphate, and $[Ir(Fppy)_2(bpy)](PF_6)$ [2,2'-bipyridine]bis[3 fluoro-2-pyridinyl]phenyl]iridium(III) hexafluorophosphate were synthesized according to literature procedure.[1] *N*-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide and ethyl (2-(perfluoropyridin-4-yl)acetyl) glycinate were synthesized according to literature procedures.[2,3] 1-hexyne and 4-octyne were distilled before use. NMR spectra were obtained on a 400 MHz Bruker Avance III spectrometer or a 400 MHz Unity Inova spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak while ^{19}F is set relative to an external standard. IR spectra were recorded on a Nicolet iS50 FT-IR. Melting points were determined on a Mel-Temp apparatus. High resolution mass spectra were obtained on LTQ-OrbitrapXL by Thermo Scientific ltd. Purifications were carried out using Teledyne Isco Combiflash Rf 200i flash chromatograph with normal phase silica (4 g, 12 g, 24 g, 40 g, or 80 g) as well as reverse phase Redisep Rf C18 (26 g) column with product detection at 254, 280 nm and by ELSD (evaporative light scattering detector). 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 synthesis reactions 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.

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 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 bath. Isopropanol was added to the bath such that the tubes were submerged in the isopropanol which was maintained at 0 ^{o}C by placing a copper coil in the bath that was connected to a recirculating chiller.

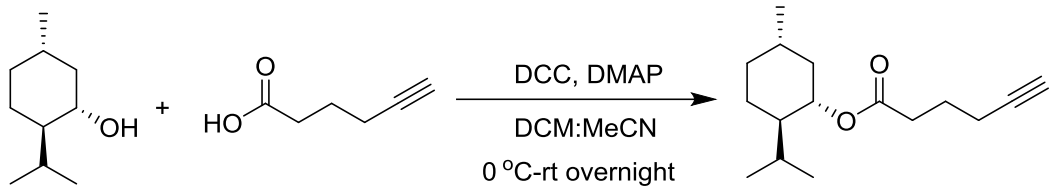
Synthesis of (1S,2S,4R)-2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol



(1S,2S,4R)-2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol was synthesized according to the literature procedure.[4] To a 100 mL round bottom flask, trimethylsilyl acetylene (2.2 mL, 15.7 mmol) and anhydrous THF (20 mL) were added and cooled to -78 ^{o}C under argon atmosphere. Then nBuLi (9.8 mL, 15.7 mmol) was added slowly and stirred for 50 min. Next, a solution of camphor (2 g, 13.1 mmol) in THF (8 mL) was added. The reaction was allowed to warm to room temperature and stirred for overnight. Reaction was quenched with the addition of water (10 mL) and then the THF was removed by rotary evaporation. The residue was partitioned between water and ether. Ether portion was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The resultant crude residue was purified by automated flash chromatography using 1% triethyl amine buffered hexane :DCM (0 % DCM for 5 cv and ramped to 100 % DCM for 15-20 cv and then held at 100% MeOH 20-25 cv) on a 24 g silica column to afford **(1S,2R,4R)-1,7,7-trimethyl-2-((trimethylsilyl)ethynyl)bicyclo[2.2.1]heptan-2-ol** in 57% yield (1.86 g, 7.4 mmol) as a white solid. To a solution of (1S,2R,4R)-1,7,7-trimethyl-2-((trimethylsilyl)ethynyl)bicyclo[2.2.1]heptan-2-ol (1.86 g, 7.4 mmol) in methanol (15 mL),

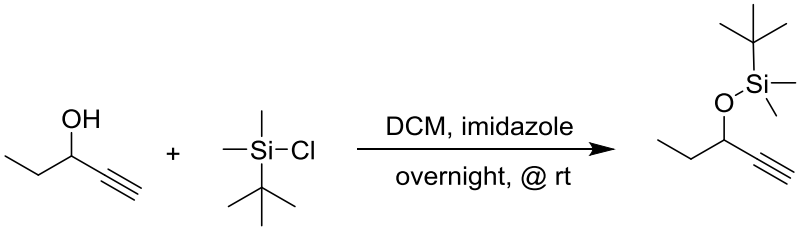
potassium carbonate (2 g, 14.86 mmol) was added and stirred for 1.5 h at room temperature. The methanol was removed (*in vacuo*) and the residue was dissolved in DCM. The DCM portion was washed with water, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to obtain (1S,2S,4R)-2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol in quant yield. NMR matched with the literature value.[5] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.45 (s, 1H), 2.22 (dt, *J* = 13.6, 3.9 Hz, 1H), 1.99 (s, 1H), 1.94 – 1.81 (m, 1H), 1.79 (t, *J* = 4.4 Hz, 1H), 1.70-1.65 (m, 1H), 1.50-1.44 (m, 1H), 1.2-1.08 (m, 1H), 1.06 (s, 3H), 0.95 (s, 3H), 0.87 (s, 3H).

Synthesis of (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl hex-5-ynoate



(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl hex-5-ynoate was synthesized according to the literature[6] procedure. In a 100 mL round bottom flask, L-menthol (1 g, 6.4 mmol), 5-hexynoic acid (0.68 mL, 6.6 mmol), 4-dimethylaminopyridine (195 mg, 1.6 mmol) in DCM:MeCN (1:1, 13 mL), *N*,*N*′-dicyclohexylcarbodiimide (1.5 g, 7.1 mmol) was added dropwise for 10 min at 0 °C. and then allowed to warm to room temperature and stirred overnight. Reaction mixture was filtered and concentrated *in vacuo*. The residue was dissolved in DCM (20 mL) and sequentially washed with 1M HCl (15 mL), 10% aq. $NaHCO_3$ (15 mL) and water (15 mL). The organic portion dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography using hexane:DCM (0 % DCM for 5 cv and ramped slowly to 100 % EtOAc for 5-20 cv and then held at 100% EtOAc 20-25 cv) on a 24 g silica column to afford **(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl hex-5-ynoate** in 38% yield (0.6 g, 2.4 mmol) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.70 (td, *J* = 10.9, 4.5 Hz, 1H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.27 (t, *J* = 7.1 Hz, 2H), 1.99 (d, *J* = 10.9 Hz, 2H), 1.87 (q, *J* = 7.0 Hz, 2H), 1.74 – 1.64 (m, 2H), 1.43 – 1.24 (m, 2H), 1.32 (m, 3H), 1.02 (m, 1H), 0.91 (d, *J* = 9.4 Hz, 6H), 0.77 (d, *J* = 7.0 Hz, 3H).

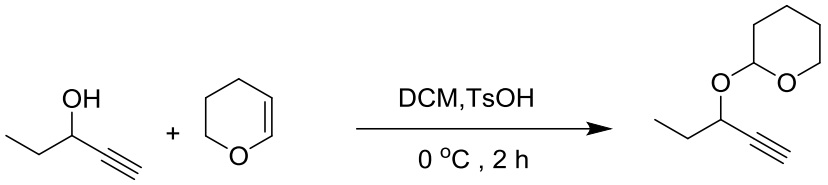
Synthesis of tert-butyldimethyl(pent-1-yn-3-yloxy)silane



tert-Butyldimethyl(pent-1-yn-3-yloxy)silane was synthesized according to the literature[7] procedure. To a 100 mL round bottom flask, pent-1-yn-3-ol (2.2 mL, 23.8 mmol), tert-butylchlorodimethylsilane (3.6 g, 23.8 mmol), imidazole (3.24 g, 47.6 mmol), and

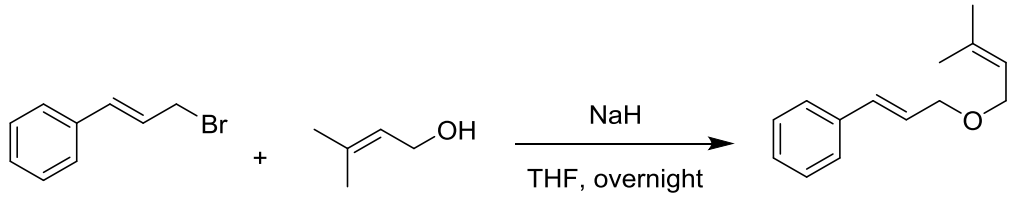
dichloromethane (10 mL) were added and the mixture was stirred at rt overnight. Dichloromethane was removed via rotary evaporation and residue was dissolved in ether (50 mL). The ether portion was washed with aq. NH_4Cl (20 mL), sat. aq. $NaHCO_3$ (20 mL), brine (20 mL), dried over anhydrous $MgSO_4$, concentrated to afford tert-butyldimethyl(pent-1-yn-3-yloxy)silane in 100% yield (4.7 g, 23.8 mmol) as a colorless liquid. NMR matched with the literature value.[7]

Synthesis of 2-(pent-1-yn-3-yloxy)tetrahydro-2H-pyran



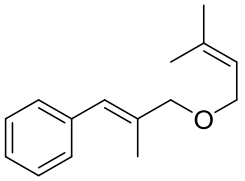
2-(pent-1-yn-3-yloxy)tetrahydro-2H-pyran was synthesized according to the literature[8] procedure. To a 100 mL round bottom flask, pent-1-yn-3-ol (2.2 mL, 23.8 mmol), 3,4-dihydropyran (3.2 mL, 35.7 mmol), *p*-tolunesulfonic acid (6 mg, 0.03 mmol), and dichloromethane (10 mL) were added and the mixture was stirred at 0 °C for 2 h.[8] The dichloromethane was removed via rotary evaporation and residue was dissolved in ether (50 mL) and washed with sat. aq. $NaHCO_3$ (20 mL), brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated to afford 2-(pent-1-yn-3-yloxy)tetrahydro-2H-pyran in 95% yield (3.8 g, 22.6 mmol) as a colorless liquid. NMR matched with the literature value.[9]

Synthesis of (E)-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-1-yl)benzene



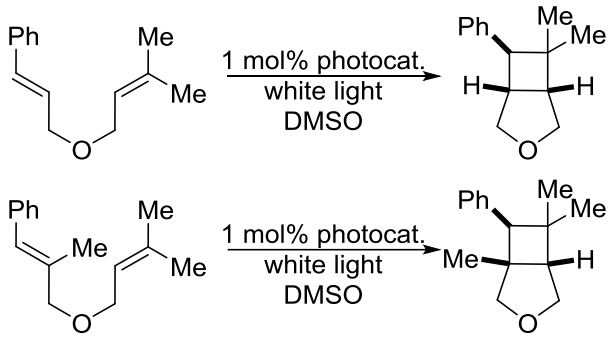
To a flame dried 50 mL two necked round bottom flask, cinnamyl bromide (1 g, 5.08 mmol), 3-methyl-2-butenol (0.6 mL, 6.09 mmol), and THF (10 mL) were added and the mixture was stirred at 0 °C for 15 min under argon atmosphere. Sodium hydride (146 mg, 6.09 mmol) was added to the reaction portionwise. The suspension was stirred for 1 h at 0 °C and then warmed to room temperature and stirring was continued for overnight. The reaction was quenched with sat. aq. NH_4Cl and extracted with ether (3 x 10 mL), organic phase was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by flash chromatography using hexane:ethyl acetate (0 % ethyl acetate for 5 cv and ramped slowly to 100 % EtOAc for 5-20 cv and then held at 100% EtOAc 20-25 cv) on a 24 g silica column to afford **(E)-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-1-yl)benzene** in 70% yield (0.7 g, 3.47 mmol) as a colorless liquid. NMR matched with the literature value[14].

Synthesis of (E)-(2-methyl-3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-1-yl)benzene



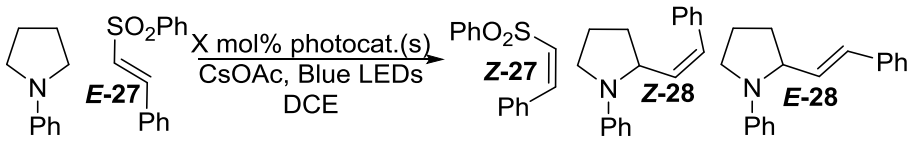
(E)-(2-methyl-3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-1-yl)benzene was synthesized according to the literature procedure[14].

General Procedure for photocatalytic [2+2] cycloaddition reaction



The procedure was adapted from the literature. [14] To a test tube (18 x 150 mm), 1 mol% photocatalyst, 1 equiv of styrene substrate, and DMSO (0.01 M) were added. After degassing with argon for 15 min, the reaction tube was placed in front of two compact fluorescent lamps (each 13 W) and stirred for 7 h. The reaction mixture was diluted with water, and then extracted three times with ether. The combined organic layers were washed with water, brine, dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The mixture was analyzed by ^1H NMR.

General Procedure for C–H Styrenylation of Amines

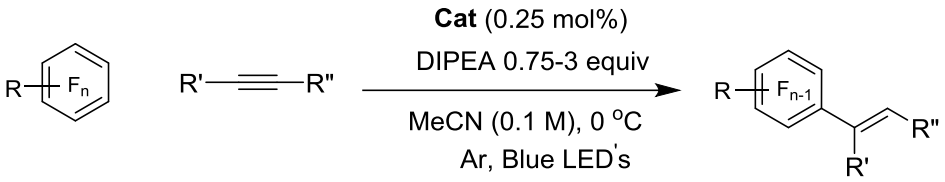


The reaction procedure for C–H styrenylation of amines was followed from literature[15] . To a dry test tube (13 x 100 mm), 1 mol% photocatalyst, and (*E*)-(2- (phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.) were added. The tube was sealed with septum and evacuated and then refilled with argon. This evacuation and refilling process was repeated for three times. The reaction tube was taken to the glove box to add CsOAc (288 mg, 1.50 mmol, 3.0 equiv.). After that the tube was taken out from glove box and then added DCE (5.0 mL) and *N*-phenylpyrrolidine (181 μL, 2.50 equiv) under argon. The reaction was degassed for 15 min. The tube was kept infront of two compact fluorescent light (CFL) bulbs (13 w) and stirred at room temperature. The conversion was determined by ^1H NMR and *E*:Z ratio was determined by GCMS.

The case in which two photocatalysts were used (**Cat 7** and **Cat 2**, 0.5 mol%, and 0.125% respectively) in one reaction tube, reaction was performed in blue LED light bath, as described in the general procedures.

Synthesis of (*Z*)-1-phenyl-2-styrylpyrrolidine The crude material (91:9 *Z*:*E* by GCMS) obtained from the reaction that contains two photocatalysts was purified by reverse phase flash chromatography using water:acetonitrile (0 % water for 10 cv and ramped slowly to 100 % acetontile for 10-40 cv and then held at 100% acetonitrile 40-50 cv) on a 28 g C18 column to afford **(*Z*)-1-phenyl-2-styrylpyrrolidine** in 94% yield (117 mg, 0.47 mmol) as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.27 (m, 5H), 7.12 (td, *J* = 7.2, 1.9 Hz, 2H), 6.72 – 6.65 (m, 1H), 6.55 (d, *J* = 11.7 Hz, 1H), 6.45 – 6.36 (m, 2H), 5.68 (dd, *J* = 11.8, 9.2 Hz, 1H), 4.74 – 4.53 (m, 1H), 3.64 – 3.50 (m, 1H), 3.34-3.26 (m, 1H), 2.47 – 2.31 (m, 1H), 2.24 – 1.85 (m, 3H).

Photocatalytic C-F Alkenylation



General procedure A for the photocatalytic C-F Alkenylation reaction

An NMR tube was charged with fluoroarenes (0.1 mmol, 1.0 equiv), alkyne (0.6 mmol, 6.0 equiv), *N*,*N*-diisopropylethylamine (0.5-3 equiv, amine added portionwise and starting with 0.25 equiv), *fac*-tris(2- phenyl pyridinato-C^2, *N*) Iridium(III) ($Ir(ppy)_3$) (0.25 mM, 1 mL in MeCN), and a sealed glass capillary containing C_6D_6. It was then capped with NMR septum (Ace glass, part no. 9096-25). When reaction was run in greater than 0.1 mmol of fluoroarenes, more than one NMR tube was used to set up reaction and each NMR tube had 1 mL of reaction mixture. The reaction mixture was degassed via Ar bubbling for 15 min at 0 °C (to avoid evaporation of *N*,*N*-diisopropylethylamine) and then placed in a light bath (*vide supra*) such that the lower portion of the tube was submerged under the water bath which was maintained at 0 °C. The reaction was monitored periodically by ^{19}F NMR. At the start of the reaction only 0.25 equiv of amine was added to the reaction which was monitored by ^{19}F NMR. After 7-8 h, more amine (0.25 equiv) was added and the reaction was again degassed, and resubmerged in the light bath. This process was repeated until the complete consumption of starting material was observed by ^{19}F NMR. The CH_3CN was removed via rotavap. The residue was treated with deionized water (2 mL) and extracted with DCM (3 x 1 mL). The organic portions were combined and dried with anhydrous $MgSO_4$. The crude product was concentrated *in vacuo* and purified by normal phase or reverse phase chromatography.

General procedure B for the photocatalytic C-F Alkenylation reaction followed by isomerization

An NMR tube was charged with purified alkenylated product (0.1 mmol, 1.0 equiv, *fac*-tris[2-(4-fluorophenyl)pyridinato-C^2, *N*)]]iridium(III) ($Ir(Fppy)_3$) (0.25 mol%, 0.0002 mmol), DMF (0.5 mL),), sealed glass capillary containing C_6D_6 and was capped with NMR septum (Ace glass, part no. 9096-25). and placed in a light bath (*vide supra*) such that the lower portion of the tube was submerged under the water bath which was maintained at 65 °C. Isomerization reaction was monitored by ^{19}F NMR. After completion of reaction, reaction mixture was diluted with ether (3 mL) and washed with water (4x2 mL), dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by normal phase or reverse phase chromatography.

General procedure C for the photocatalytic C-F alkenylation reaction to obtain Z-isomer

The reaction procedure is the same as **General procedure A**, except the photocatalyst *fac*-tris[2-(4-fluorophenyl)pyridinato-C^2, *N*)]]iridium(III) ($Ir(Fppy)_3$) instead of Ir(ppy)3 used. In some cases to get better Z:E ratio, isomerization reaction was carried out after the removal of acetonitrile, excess volatile alkyne and amine, in DMF at 65 °C.

General procedure D for the photocatalytic C-F alkenylation reaction to obtain E-isomer

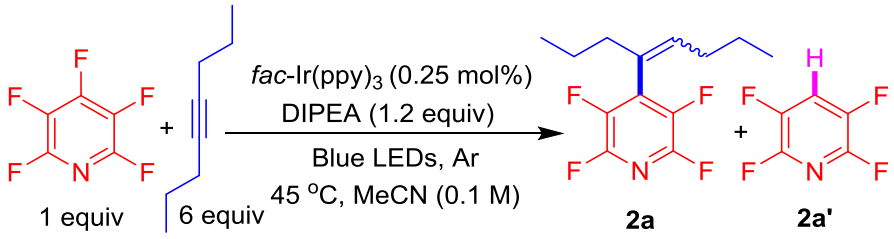
The reaction procedure is the same as **General procedure A**, except the photocatalyst *fac*-tris[2-(4-*tert*-butylphenyl)pyridinato-C^2, *N*)]iridium(III) ($Ir(tbppy)_3$) instead of Ir(ppy)3 used.

General procedure E for the photocatalytic C-F alkenylation reaction

The reaction procedure is the same as **General procedure A**, except the alkyne (1 equiv), perfluoroarenes (3 equiv) used.

Optimization of phtocatalytic reaction with different photocatalysts

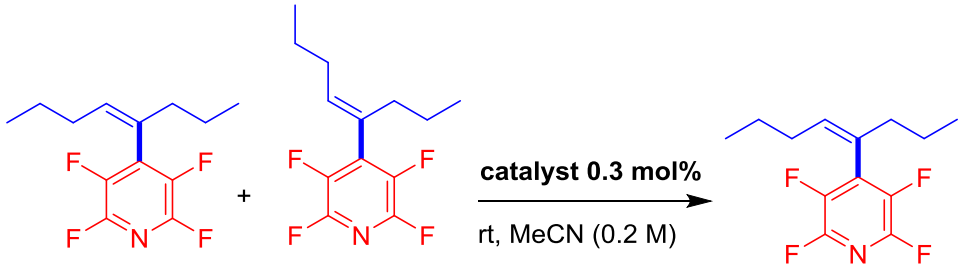
[a]Determined by ^{19}F NMR. [b]Full conversion.



Catalysts Screening Entry	Catalysts	2a/2a'	Conversion to the product[a]	Time, h
1.	$Ir(ppy)_3$	5	67/70	17/47[b]
2.	$Ir(CF_3ppy)_3$	5.4	38/57	17/47
3.	$Ir(Fppy)_3$	5.4	37/65	17/47
4.	$Ir(dFppy)_3$	5.8	9/18	17/47
5.	$Ir(t\text{Buppy})_3$	4.9	54/74	17/47
6.	$Ir(dF(CF_3)ppy)_2(phen)PF_6$	1.7	5	47
7.	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	4.7	27/45	17/47
8.	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	5	24/39	17/47
9.	$Ir(dFppy)_2(bpy)PF_6$	4.3	20/36	17/47
10.	$Ir(dFppy)_2(dtbbpy)PF_6$	5	34/44	17/47
11.	$Ir(Fppy)_2(bpy)PF_6$	5.7	14/22	17/47
12.	$Ir(Fppy)_2(dtbbpy)PF_6$	3.8	17/33	17/47

Optimization of Isomerization reaction

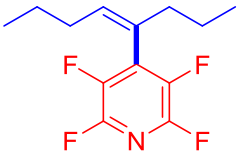
a. analysis was done using ^{19}F NMR



Entry	Catalysts (triplet state energy)	time	ratio Z:E[a]
1.	$Ir(ppy)_3$ (55.2 Kcal/mol)	begin	1:0.85
		40 min	1:0.89
		18 h	1:0.84
2.	$Ir(Fppy)_3$ (58.6 Kcal/mol)	begin	1:0.88
		40 min	1:0.84
		18 h	1:0.68
3.	$Ir(dFppy)_3$ (60.1 Kcal/mol)	begin	1:0.87
		40 min	1:0.91
		18 h	1:0.82
4.	$Ir(CF_3dFppy)_2bpy$ (60.4 Kcal/mol)	begin	1:0.86
		40 min	1:0.86
		18 h	1:0.87
5.	$Ir(Fppy)_2bpy$ (51.4 Kcal/mol)	begin	1:0.88
		40 min	1:0.88
		18 h	1:0.87
6.	$Ir(tBuppy)_3$ (54.5 Kcal/mol)	begin	1:0.89
		40 min	1:0.88
		18 h	1:0.86
7.	$Ir(CF_3ppy)_3$ (56.4 Kcal/mol)	begin	1:0.87
		40 min	1:0.87
		18 h	1:0.86
8.	$Ir(ppy)_3$ @60 ^oC and in DMF instead of rt and MeCN	begin	1:0.89
		45 min	1:0.89
		15 h	1:0.59
		35 h	1:0.44
		60 h	1:0.35
9.	$Ir(Fppy)_3$ @60 ^oC instead of rt and in DMF instead of rt and MeCN	begin	1:0.87
		45 min	1:0.53
		15 h	1:0.06
10.	$Ir(dFppy)_3$ @60 ^oC instead of rt and in DMF instead of rt and MeCN	begin	1:0.89
		45 min	1:0.85
		15 h	1:0.55
		35 h	1:0.34
		60 h	1:0.23
11.	no catalyst @60 ^oC instead of rt and in DMF instead of rt and MeCN	na	na

Started with E or Z isomer for isomerization reaction:

Two isomers were separated by running prep tlc using hexane as a solvent and then performed isomerization reaction on each isomers. a. ^{19}F NMR was used for analysis.

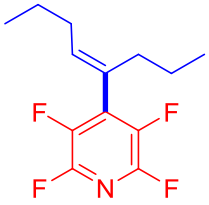


Z-isomer

Ir(Fppy)$_3$ 0.3 mol%

@ 60 °C, DMF 0.2 M

time	Z:E ratio[a]
begin	1:0.04
50 min	1:0.05
16 h	1:0.04
40 h	1:0.03



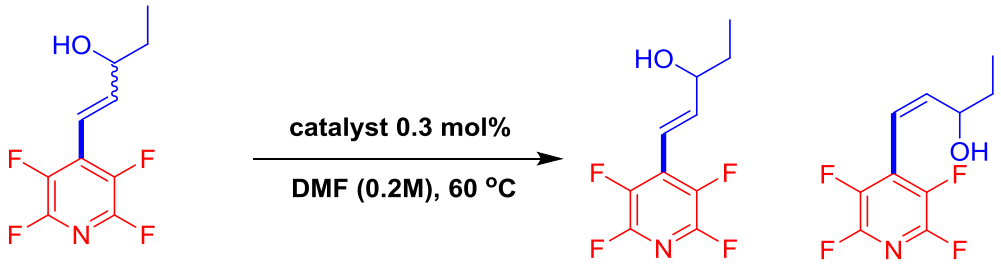
E-isomer

Ir (Fppy)$_3$ 0.3 mol%

@ 60 °C, DMF 0.2 M

time	Z:E ratio[a]
begin	0.03:1
50 min	1:0.71
16 h	1:0.02

Optimization of isomerization reaction with various catalyst on disubstituted alkene



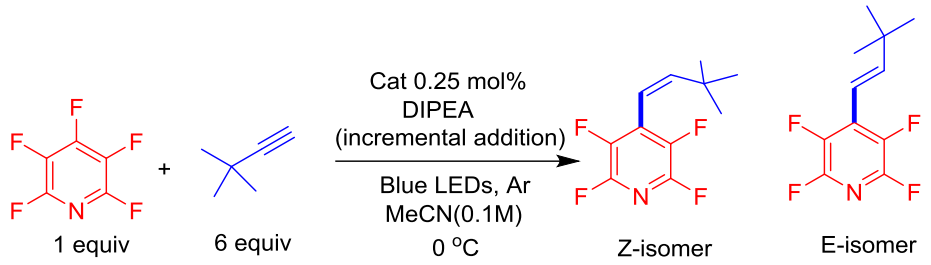
catalyst 0.3 mol%

DMF (0.2M), 60 °C

E-isomer Z-isomer

Entry	Catalysts (triplet state energy)	Time, h	Z:E ratio[a]
1.	Ir(ppy)$_3$ 55.2 kcal/mol	begin	1:1.19
		18 h	1:0.41
		35 h	1:0.33
2.	Ir(Fppy)$_3$ 58.6 kcal/mol	begin	1:1.19
		18 h	1:0.10
3.	Ir(CF$_3$ppy)$_3$ 56.4 kcal/mol	begin	1:1.19
		18 h	1:0.23
		35 h	1:0.19
4.	Ir(dFppy)$_3$ 60.1 kcal/mol	begin	1:1.19
		18 h	1:0.07
5.	Ir(*t*Buppy)$_3$ 54.5 kcal/mol	begin	1:1.19
		18 h	1:0.65
		35 h	1:0.52
		60 h	1:0.40
6.	Ir(CF$_3$dFppy)$_2$dtbbpy 60 kcal/mol	begin	1:1.16
		18 h	1:0.11
		35 h	1:0.08
7.	Ir(Fppy)$_2$bpy 51.4 kcal/mol	begin	1:1.19
		18 h	1:0.68
		35 h	1:0.52
		60 h	1:0.40

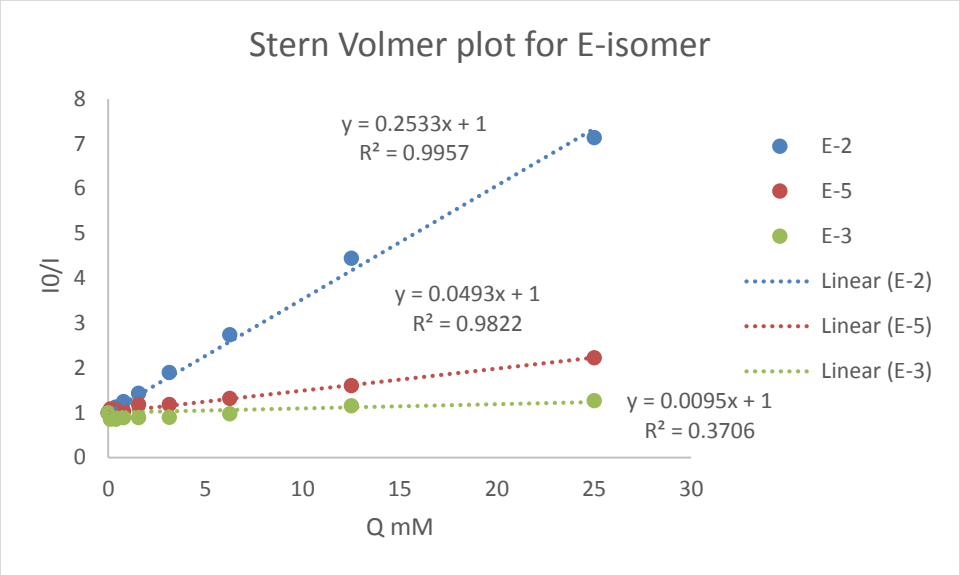
.**Electron and energy transfer study with several catalysts**. a. ^{19}F NMR was used for analysis of conversion to product as well as Z:E ratio. ^{19}F NMR spectrum containing both isomers is on page S110

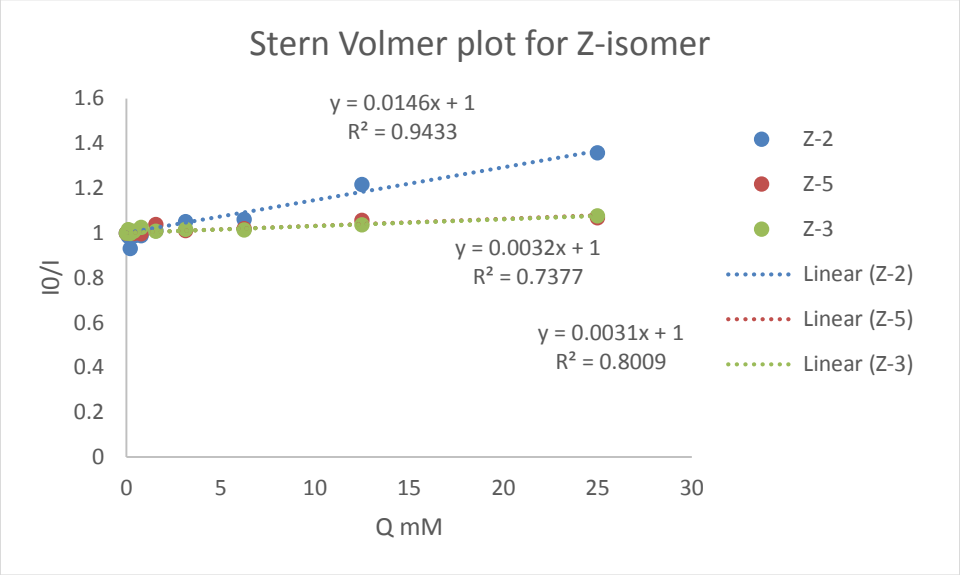


Entry	Catalysts	DIPEA equiv	time	conversion to product%[a]	Z:E ratio[a]
1.	$Ir(ppy)_3$ cat 3	0.5 equiv	22 h	72	1:8
		1.0 equiv	39 h	87	1:2.7
2.	$Ir(CF_3ppy)_3$ cat 4	0.5 equiv	20 h	13%	0:1
		1.0 equiv	39 h	19%	1:26
		1.5 equiv	59 h	33%	1:17.3
3.	$Ir(Fppy)_3$ cat 5	0.5 equiv	20 h	8%	2:1
		1.0 equiv	39 h	15%	2:1
		1.5 equiv	59 h	22%	2.1:1
4.	$Ir(t\text{Buppy})_3$ cat 2	0.5 equiv	20 h	17%	0:1
		1.0 equiv	39 h	23%	0:1
		1.5 equiv	59 h	32%	1:50
5.	$Ir(CF_3dFppy)_2dtbbpy$ cat 6	0.5 equiv	20 h	16%	0:1
		1.0 equiv	39 h	29%	1:22.5
		1.5 equiv	59 h	40%	1:30
6.	$Ir(Fppy)_2bpy$ cat 1	0.5 equiv	20 h	16%	1:9
		1.0 equiv	39 h	28%	1:6
		1.5 equiv	59 h	35%	1:4.9
7.	$Ir(dFppy)_3$ cat 7	1.0 equiv	40 h	11%	2.3:1
		1.5 equiv	66 h	21%	2.1:1

Quenching study on E- and Z- of 4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine with catalysts 2, 3 and 5

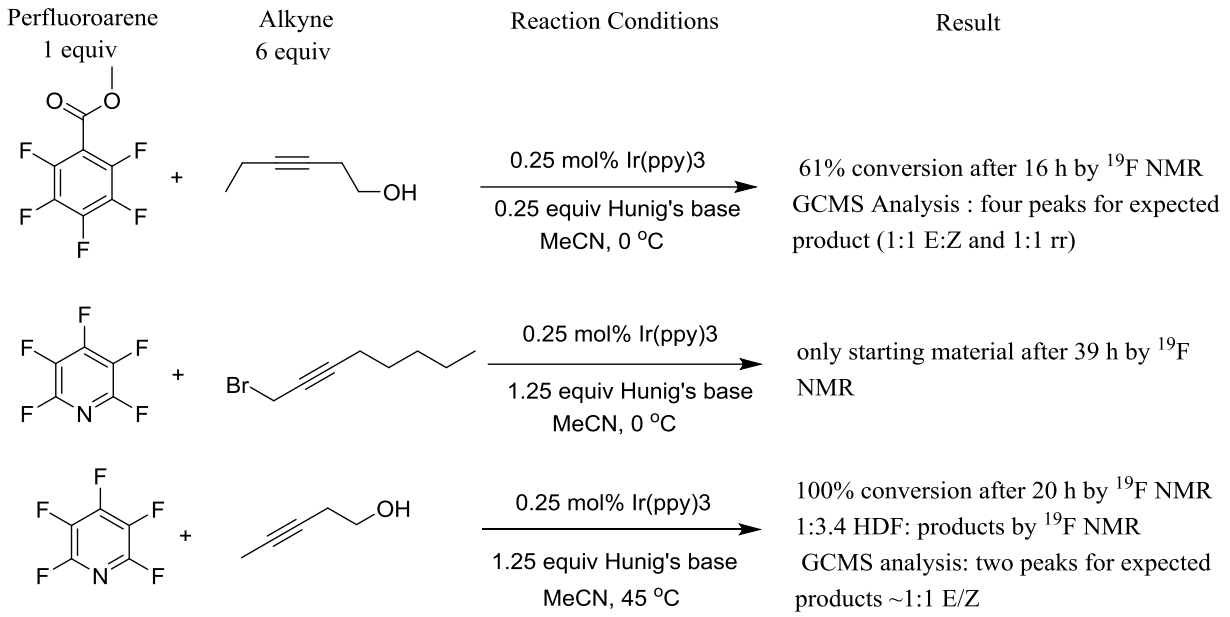
2.5 μM solutions of 2, 3 and 5 catalysts were prepared in acetonitrile. 50 mM stock solutions of E and Z- isomers of 4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine were prepared in acetonitrile. 50 mM of E or Z- isomer of 4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine (2 mL) was taken in a vial. 1 mL of this solution was transferred to the second vial and diluted with 1 mL of acetonitrile. 1 mL of this diluted solution was transferred to the third vial and this way a series of dilution was performed. After that 2.5 μM of catalyst (1 mL) solution was added to all the vials. The solution was mixed properly and fluorescence was measured. Catalyst 2,3, and 5 were excited at 390 nm, 385 nm and 380 nm respectively. The emission was observed at 520 nm, 516 nm, and 485 nm for catalysts 2,3, and 5 respectively.



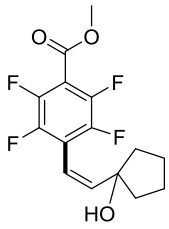


Io = emission in the absence of quencher
I = emission in the presence of quencher

Alkenylation study with internal alkynes

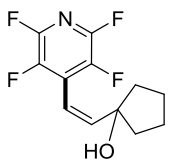


Synthesis of S-3a (methyl (Z)-2,3,5,6-tetrafluoro-4-(2-(1-hydroxycyclopentyl)vinyl)benzoate)



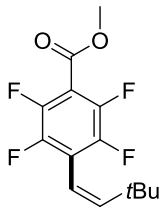
The **General procedure A** was followed using methyl 2,3,4,5,6-pentafluorobenzoate (89 µL, 0.6 mmol, 1 equiv), 1-ethynylcyclopentan-1-ol (412 µL, 3.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (78 µL, 0.45 mmol, 0.75 equiv) and 6.0 mL of stock solution of Ir(ppy)3 (0.9 mg, 0.0015 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : ethyl acetate (0-5% EtOAc for 30 cv and ramped to 100% EtOAc for 30-45 cv and then held at 100% EtOAc 45-50 cv), on a 24 g silica column to afford **S-3a** in 68% yield (129 mg, 0.41 mmol) as a white solid. ^{19}F NMR (376 MHz, Chloroform-d) δ -138.38 – -138.70 (m, 2F), -141.01 – -141.33 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.11 (d, J = 12.2 Hz, 1H), 6.01 (dt, J = 12.2, 1.4 Hz, 1H), 3.96 (s, 3H), 1.77 (m, 8H), 1.02 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.5, 145.2, 145.1 (ddt, J = 84.5, 13.2, 5.1 Hz), 142.6 (ddt, J = 74.1, 14.0, 4.9 Hz), 121.9 (t, J = 19.1 Hz), 110.9, 110.4 (t, J = 15.6 Hz), 83.0, 53.1, 40.8, 23.6. FT-IR cm^{-1} 3501, 3024, 2979, 1640, 1481. GC/MS (m/z, relative intensity) 318 (M^+, 10), 289 (20), 97 (100), 41 (70). HRMS (ESI^+) *m/z* calcd. $C_{15}H_{14}F_4O_3Na$: 341.0777; found $[M+Na]^+$ 341.0763. Melting point 46-48 °C.

Synthesis of S-4a ((Z)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol)



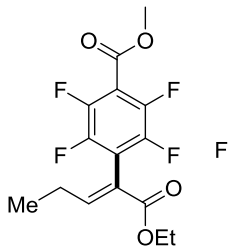
The **General procedure** C was followed using pentafluoropyridine (44 µL, 0.4 mmol, 1 equiv), 1-ethynylcyclopentan-1-ol (274 µL, 2.4 mmol, 6 equiv), N,N-diisopropylethylamine (140 µL, 0.8 mmol, 2 equiv) and 4 mL of stock solution of Ir(Fppy)3 (0.7 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using 1% triethylamine buffered hexane : ethyl acetate (0-15% EtOAc for 35 cv, ramped to 100% EtOAc for 35-45 cv and then held at 100% EtOAc for 40-50 cv), on a 12 g silica column to afford **S-4a** in 63% yield (66 mg, 0.25 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-d) δ -92.7 – -93.0 (m, 2F), -140.8 – -141.2 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.15 (d, J = 12.3 Hz, 1H), 6.00 (d, J = 12.3 Hz, 1H), 1.78 (m, 8H), 1.04 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.3, 144.6 – 141.5 (m), 140.9 – 137.5 (m), 133.0 – 132.4 (m), 110.5 (t, J = 2.5 Hz), 83.3, 41.1, 23.8. FT-IR cm^{-1} 3480, 3024, 2963, 2877, 1644, 1256. GC/MS (m/z, relative intensity) 261 (M^+, 15), 232 (50), 204 (25), 97 (100). HRMS (ESI^+) *m/z* calcd. $C_{12}H_{11}F_4NONH_4$: 279.1121; found $[M+NH_4]^+$ 279.1194.

Synthesis of S-5a (methyl (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluorobenzoate)



The **General procedure A** was followed using methyl 2,3,4,5,6-pentafluorobenzoate (74 µL, 0.5 mmol, 1 equiv), 3,3-dimethylbut-1-yne (367 µL, 3.0 mmol, 6 equiv), N,N-diisopropylethylamine (65 µL, 0.38 mmol, 0.75 equiv) and 5.0 mL of stock solution of Ir(ppy)3 (0.8 mg, 0.00125 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using water : MeCN (0-65% MeCN for 45 cv and ramped to 100 % for 45-50 then held at 100% MeCN 50-60 cv), on a 26 g C18 reverse column to afford **S-5a** in 86% yield (124 mg, 0.43 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-d) δ -138.0 – -138.5 (m, 2F), -140.2 – -140.8 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.00 (d, *J* = 12.6 Hz, 1H), 5.81 (d, *J* = 12.5 Hz, 1H), 3.98 (s, 3H), 0.98 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.5, 150.1, 145.4 (ddt, *J* = 80.8, 13.0, 4.9 Hz), 143.6 – 142.1 (m), 122.1 (t, *J* = 20.0 Hz), 111.0 (t, *J* = 15.7 Hz), 108.7, 53.4, 35.0, 29.6. FT-IR cm^{-1} 3014, 2957, 2909, 1741, 1473, 1227. GC/MS (m/z, relative intensity) 290 (M^+, 20), 275 (60), 259 (10), 59 (75), 41 (100). HRMS (ESI^+) *m/z* calcd. $C_{14}H_{14}F_4O_2NH_4$: 308.1274; found $[M+NH_4]^+$ 308.1260.

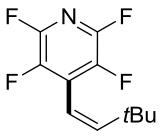
Synthesis of S-6a (methyl (E)-4-(1-ethoxy-1-oxopent-2-en-2-yl)-2,3,5,6-tetrafluorobenzoate)



The **General procedure A** was followed using methyl 2,3,4,5,6-pentafluorobenzoate (89 µL, 0.6 mmol, 1 equiv), ethyl pent-2-ynoate (395 µL, 3.0 mmol, 6 equiv), N,N-diisopropylethylamine (130 µL, 0.75 mmol, 1.25 equiv) and 6.0 mL of stock solution of $Ir(ppy)_3$ (0.9 mg, 0.0015 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane :ethyl acetate (0-45% EtOAc for 41 cv and

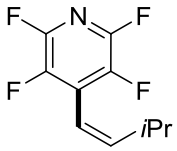
ramped to 100% EtOAc for 41-50 and held at 100% EtOAc for 50-60 cv), on a 24 g silica column to afford **S-6a** in 53% yield (105 mg, 0.3 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-d) δ -138.2 – -138.3 (m, 2F), -139.9 – -140.0 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 7.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 2.06 (p, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 164.3, 160.3, 153.0, 145.6 (ddt, *J* = 45.3, 13.3, 4.9 Hz), 143.1 (ddt, *J* = 37.2, 14.1, 4.7 Hz), 119.4 (t, *J* = 2.0 Hz), 118.3 (t, *J* = 19.4 Hz), 112.3 (t, J = 16.0 Hz), 61.7, 53.5, 23.9, 14.2, 12.5. FT-IR cm^{-1} 2981, 1714, 1473, 1302. GC/MS (m/z, relative intensity) 334 (M^{+}, 30), 306 (30), 261 (60), 59 (100), 43 (80). HRMS (ESI^{+}) *m/z* calcd. $C_{15}H_{14}F_5O_4Na$: 357.0726; found [M+Na]$^{+}$ 357.0708.

Synthesis of S-7a (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine



The **General procedure C** was followed using pentafluoropyridine (44 µL, 0.40 mmol, 1 equiv), 3,3-dimethylbut-1-yne (293 µL, 2.4 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (60 µL, 0.34 mmol, 0.86 equiv) and 4 mL of stock solution of Ir(Fppy)$_3$ (0.6 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. After removal of excess amine, and alkyne, the crude material was resubjected to isomerization reaction with DMF (2 mL) at 65 ^{o}C. The crude product was purified by flash chromatography using hexane : DCM (0% DCM for 6 cv, ramped to 100% DCM for 6-16 cv and then held at 100% DCM for 16-20 cv), on a 4 g silica column to afford **S-7a** in 85% yield (79 mg, 0.34 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.4 – -91.9 (m, 2F), -140.4 – -140.6 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.06 (d, *J* = 12.8 Hz, 1H), 5.81 (d, *J* = 12.7 Hz, 1H), 1.00 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.7, 144.8 – 141.5 (m), 140.9 – 137.4 (m), 133.0 – 132.0 (m), 108.1 (t, *J* = 2.4 Hz), 35.0, 29.3. FT-IR cm^{-1} 3022, 2965, 2877, 1639, 1409, 1256. GC/MS (m/z, relative intensity) 233 (M^{+}, 20), 218 (60), 198 (30), 41 (100). HRMS (ESI^{+}) *m/z* calcd. $C_{11}H_{11}F_4NNH_4$: 251.1171; found [M+NH$_4$]$^{+}$ 251.1246.

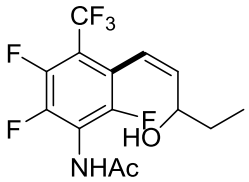
Synthesis of S-8a ((Z)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine)



The **General procedure C** was followed using pentafluoropyridine (44 µL, 0.40 mmol, 1 equiv), 3-methylbut-1-yne (245 µL, 2.4 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (139 µL, 0.8 mmol, 2.0 equiv) and 4.0 mL of stock solution of Ir(Fppy)$_3$ (0.6 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : ethyl acetate (0%EtOAc for 7 cv, ramped to 100% EtOAc for 7-10 cv and then held at 100% EtOAc for 10-14 cv) on a 4 g silica column to afford **S-8a** in 74% yield (65 mg, 0.3 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.4 – -91.9 (m, 2F), -141.3 – -142.0 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.03 – 5.88 (m, 2H), 2.32 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 144.9 – 141.7 (m), 140.9 – 137.2 (m), 130.4 (td, *J* = 17.5, 16.9, 3.0 Hz), 109.5 (t, *J* = 2.5 Hz), 29.9, 22.0. FT-IR cm^{-1} 2971, 2874, 1647, 1478. GC/MS (m/z, relative intensity) 219

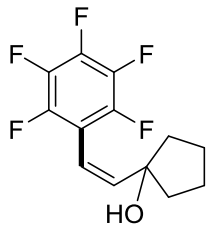
(M^+, 25), 204(35), 184 (35), 164 (30), 56 (100), 39 (70). HRMS (ESI^+) *m/z* calcd. $C_{10}H_9F_4NNH_4$: 237.1015; found $[M+NH_4]^+$ 237.1091.

Synthesis of S-9a ((Z)-*N*-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)-4-(trifluoromethyl)phenyl)acetamide)



The **General procedure C** was followed using *N*-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl) acetamide (110 mg, 0.4 mmol, 1 equiv), pent-1-yn-3-ol (227 µL, 2.4 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (60 µL, 0.35 mmol, 1.15 equiv) and 4.0 mL of stock solution of $Ir(Fppy)_3$ (0.7 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : ethyl acetate (0-18 % EtOAc for 28 cv, ramped to 100 % EtOAc for 28-40 cv and then held at 100% EtOAc for 40-45 cv), on a 12 g silica column to afford **S-9a** in 51% yield (70 mg, 0.21 mmol) as a yellow highly viscous liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -55.08 (dd, *J* = 25.7, 3.1 Hz, 3F), -119.54 (d, *J* = 13.3 Hz, 1F), -137.29 (d, *J* = 21.5 Hz, 1F), -139.64 – -140.01 (m, 1F). ^1H NMR (400 MHz, Chloroform-*d*) δ 6.22 (d, *J* = 10.6 Hz, 1H), 5.92 (dd, *J* = 11.5, 8.9 Hz, 1H), 3.89 (q, *J* = 7.4 Hz, 1H), 2.22 (s, 3H), 1.51 (dtt, *J* = 38.0, 13.8, 6.9 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 149.2 (d, *J* = 244.1 Hz), 146.8 (ddd, *J* = 86.1, 15.2, 4.1 Hz), 144.3 (ddd, *J* = 82.0, 15.6, 4.6 Hz), 139.8, 123.8 – 120.6 (m), 119.1 (dd, *J* = 19.9, 13.2 Hz), 118.4 – 117.6 (m), 118.0, 116.5 – 115.0 (m), 70.5, 29.5, 23.1, 9.3. FT-IR cm^{-1} 3437, 3249, 3193, 3027, 2968, 2877, 1682, 1500, 1454, 1371, 1315. GC/MS (m/z, relative intensity) 341 (M^+-29, 5), 292 (60), 250 (20), 202 (15), 46 (100). HRMS (ESI^+) *m/z* calcd. $C_{14}H_{13}F_6NO_2Na$: 364.0748; found $[M+Na]^+$ 364.0748.

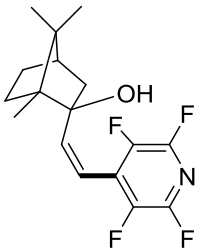
Synthesis of S-10a (((Z)-1-(2-(perfluorophenyl)vinyl)cyclopentan-1-ol)



The **General procedure C** was followed using hexafluorobenzene (58 µL, 0.5 mmol, 1 equiv), 1-ethynylcyclopentan-1-ol (343 µL, 3.0 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (261 µL, 1.5 mmol, 3.0 equiv) and 5.0 mL of stock solution of $Ir(Fppy)_3$ (0.9 mg, 0.00125 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : ether(0-10% ether for 25 cv, ramped to 100% ether for 25-32 cv and then held at 100% ether for 32-40 cv), on a 12 g silica column followed by prep tlc in hexane to afford **S-10a** in 61% yield (85 mg, 0.31 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -139.4 (dt, *J* = 23.2, 6.4 Hz, 2F), -157.3 (td, *J* = 20.9, 4.6 Hz, 1F), -163.7 (tt, *J* = 22.1, 6.4 Hz, 2F). ^1H NMR (400 MHz, Chloroform-*d*) δ 6.09 (dd, *J* = 12.1, 6.4 Hz, 1H), 5.98 (dd, *J* = 12.4, 5.0 Hz, 1H), 1.90 – 1.65 (m, 8H), 1.01 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.0, 143.0 – 141.0 (m), 139.3 – 138.1 (m), 136.5 – 135.7 (m), 113.6 – 112.9 (m), 110.7, 83.1, 41.0, 23.7. FT-IR cm^{-1}3480, 2959, 2876, 1518, 1492. GC/MS (m/z, relative intensity) 278 (M^+, 20), 249 (40),

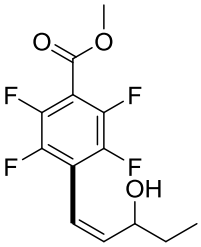
221 (30), 181 (30), 97 (100), 41 (80).). HRMS (ESI$^+$) *m/z* calcd. $C_{13}H_{12}F_5O$: 279.0808; found $[M+H]^+$ 279.0535.

Synthesis of S-11a ((1S,2S,4R)-1,7,7-trimethyl-2-((Z)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol)



The **General procedure B** was followed using pentafluoropyridine (55 µL, 0.50 mmol, 1 equiv), (1S,2S,4R)-2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (534 mg, 3.0 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (43 µL, 0.25 mmol, 0.5 equiv) and 5.0 mL of stock solution of $Ir(Fppy)_3$ (0.2 mg, 0.0002 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by reverse phase chromatography using water:acetonitrile (0-75% MeCN for 30 cv, ramped to 100% MeCN and then held at 100% MeCN for 35-50 cv), on a 26 g of C18 column to afford **S-11a** in 68% yield (112 mg, 0.34 mmol) as a colorless liquid. After isolation the compound (112 mg, 0.34 mmol) was resubjected to isomerization reaction in DMF (1.7, mL) with $Ir(Fppy)_3$ (1.1 mg, 0.0015 mmol, 0.004 equiv) to obtain Z-isomer in quantitative yield as a yellow solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.7 – -91.2 (m, 2F), -140.9 – -141.5 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.14 (d, *J* = 11.4 Hz, 1H), 5.76 (t, *J* = 11.2 Hz, 1H), 2.57 (t, *J* = 9.4 Hz, 1H), 2.49 – 2.36 (m, 2H), 2.16 (t, *J* = 4.6 Hz, 1H), 1.85 (d, *J* = 18.4 Hz, 1H), 1.24 (dd, *J* = 13.0, 4.3 Hz, 2H), 0.96 (s, 3H), 0.84 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.6 – 141.7 (m), 142.8, 139.2 (dd, *J* = 258.0, 33.8 Hz), 129.8 (t, *J* = 16.9 Hz), 114.4 (t, *J* = 2.4 Hz), 62.8, 48.3, 44.3, 42.5, 42.4, 34.7, 20.3, 19.4, 8.1. FT-IR cm^{-1} 2949, 2872, 1650, 1462, 1414. GC/MS (m/z, relative intensity) 327 (M^+-2, 10), 244 (20), 124 (60), 98 (100), 41 (60). HRMS (ESI$^+$) *m/z* calcd. $C_{17}H_{20}F_4NO$: 330.1481; found $[M+H]^+$ 330.1403. Melting point 100-103 °C

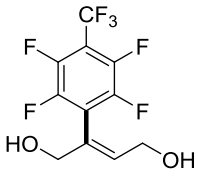
Synthesis of S-12a (methyl (Z)-2,3,5,6-tetrafluoro-4-(3-hydroxypent-1-en-1-yl)benzoate)



The **General procedure A** was followed using methyl 2,3,4,5,6-pentafluorobenzoate (74 µL, 0.50 mmol, 1 equiv), pent-1-yn-3-ol (258 µL, 3.0 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (100 µL, 0.58 mmol, 1.2 equiv) and 5.0 mL of stock solution of $Ir(ppy)_3$ (0.7 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : ether (0-30% ether for 40 cv, ramped to 100% ether and then held at 100% ether for 40-50 cv) on a 24 g silica column to afford **S-12a** in 72% yield (105 mg, 0.36 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -139.3 – -139.5 (m, 2F), -139.5 – -139.7 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.19 (d, *J* = 11.6 Hz, 1H), 6.07 (ddd, *J* = 11.2, 9.2, 1.3 Hz, 1H), 4.04 (q, *J* = 7.7 Hz, 1H), 3.99 (s, 3H), 1.60 (m, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.3, 146.3 – 144.7 (m), 143.7 – 142.4 (m), 142.4, 119.5 (t, *J* = 17.8 Hz), 114.0, 111.6 (t, *J* = 15.5 Hz), 71.0, 53.5, 29.5, 9.6. FT-IR cm^{-1} 3399, 3030,

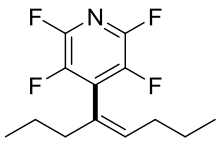
2973, 1741, 1476, 1315. GC/MS (m/z, relative intensity) 292 (M+, 5), 263 (20), 243 (35), 57 (100). HRMS (ESI$^+$) *m/z* calcd. $C_{13}H_{13}F_4O_3$: 293.0801; found $[M+H]^+$ 293.0990.

Synthesis of S-13a ((E)-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)but-2-ene-1,4-diol)



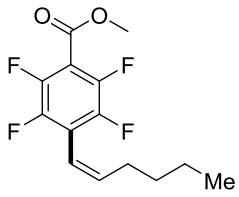
The **General procedure C** was followed using 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (65 µL, 0.5 mmol, 1 equiv), but-2-yne-1,4-diol (258 mg, 3.0 mmol, 6.0 equiv), *N*,*N*-diisopropylethylamine (75 µL, 0.43 mmol, 0.86 equiv) and 5.0 mL of stock solution of $Ir(Fppy)_3$ (0.9 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using DCM:MeOH (0% MeOH for 45 cv, ramped to 20% MeOH and then held at 20% MeOH for 45-60 cv) on a 24 g silica column to afford **S-13a** in 63% yield (76 mg, 0.25 mmol) as a white solid. ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -57.2 (t, *J* = 21.8 Hz, 3F), -140.2 (td, *J* = 15.8, 6.4 Hz, 2F), -143.3 – -143.9 (m, 2F). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 6.20 (t, *J* = 6.2 Hz, 1H), 4.20 (d, *J* = 5.1 Hz, 2H), 4.00 – 3.81 (m, 2H), 3.20 (t, *J* = 6.1 Hz, 1H), 2.87 (t, *J* = 5.5 Hz, 1H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 146.7 – 146.0 (m), 144.2 – 143.5 (m), 134.6, 126.2 – 118.0 (m, supposed to be q one peak could not observe it might be under CD_3CN peak), 128.3, 123.2 (t, *J* = 20.4 Hz), 109.6 – 108.2 (m), 65.0, 59.9. FT-IR cm^{-1} 3271, 2963, 2872, 1347. GC/MS (m/z, relative intensity) 286 (M^+ -18, 30), 273 (20), 258 (100), 169 (40). HRMS (ESI$^+$) *m/z* calcd. $C_{11}H_7F_7O_2Na$: 327.0232; found $[M+Na]^+$ 327.0069. Melting point 90-92 °C.

Synthesis of S-14a ((Z)-2,3,5,6-tetrafluoro-4-(oct-4-en-4-yl)pyridine)



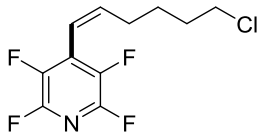
The **General procedure C** was followed using pentafluoropyridine (11 µL, 0.10 mmol, 1 equiv), oct-4-yne (88 µL, 0.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (13 µL, 0.075 mmol, 0.75 equiv) and 1.0 mL of stock solution of $Ir(Fppy)_3$ (0.18 mg, 0.00025 mmol, 0.0025 equiv) in CH_3CN was used. After removal of excess amine, and alkyne, the crude material was resubjected to isomerization reaction with DMF (0.5 mL) at 65 °C. After completion of reaction, extraction was done in hexane (2 mL) and washed with water (5x1 mL). Hexane portion was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude material was passed through a silica plug and the compound was eluted with hexane to afford **S-14a** in 81% yield (21 mg, 0.08 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -88.1 – -96.3 (m, 2F), -139.0 – -144.9 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.82 (t, *J* = 7.1 Hz, 1H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.80 (q, *J* = 6.6 Hz, 2H), 1.41.1.31 (m, 4H), 0.90 (td, *J* = 7.3, 2.4 Hz, 3H), 0.84 (td, *J* = 7.4, 2.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.2 – 141.9 (m), 141.1 – 137.5 (m), 134.8, 134.7 – 134.0 (m), 126.3, 38.8, 31.9, 22.3, 21.3, 13.7, 13.5. FT-IR cm^{-1} 2965, 2874, 1642, 1462. GC/MS (m/z, relative intensity) 261 (M+, 15), 219 (20), 191 (60), 170 (35), 41 (100). HRMS (ESI$^+$) *m/z* calcd. $C_{13}H_{15}F_4N$: 261.1141; found $[M]^+$ 261.1089.

Synthesis of S-15a (methyl (Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)benzoate)



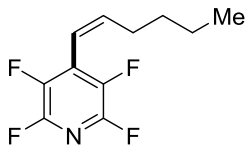
The **General procedure A** was followed using 2 methyl 2,3,4,5,6-pentafluorobenzoate (60 µL, 0.4 mmol, 1 equiv), cyclohexene (276 µL, 2.4 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (52 µL, 0.3 mmol, 0.75 equiv) and 4.0 mL of stock solution of $Ir(ppy)_3$ (0.6 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using water:acetonitrile (0-75% MeCN for 45 cv and ramped to 100% MeCN and then held at 100% MeCN for 45-50 cv) on a 26 g C18 column to afford **S-15a** in 82% yield (95 mg, 0.3 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -139.0 – -139.2 (m, 2F), -140.3 – -140.5 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.08 (m, 2H), 3.98 (s, 3H), 2.03 (q, *J* = 7.2, 2H), 1.40 (p, *J* = 7.0 Hz, 2H), 1.30 (h, *J* = 7.0 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.5, 146.3 – 144.8 (m), 143.7 – 142.2 (m), 141.8, 120.4 (t, *J* = 18.7 Hz), 112.8 (t, *J* = 2.3 Hz), 110.9 (t, *J* = 15.7 Hz), 53.3 (d, *J* = 1.4 Hz), 31.0, 30.0 (t, *J* = 2.1 Hz), 22.4, 14.0. FT-IR cm^{-1} 3027, 2955, 2864, 1736, 1468, 1433. GC/MS (m/z, relative intensity) 290 (M^+, 5), 234 (85), 203 (70), 41 (100). HRMS (ESI^+) *m/z* calcd. $C_{14}H_{14}F_4O2NH_4$: 308.1274; found $[M+NH_4]^+$ 308.1261.

Synthesis of S-16a ((Z)-4-(6-chlorohex-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)



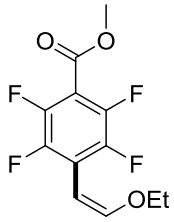
The **General procedure C** was followed using pentafluoropyridine (55 µL, 0.50 mmol, 1 equiv), 6-chlorohex-1-yne (364 µL, 3.0 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (152 µL, 0.88 mmol, 1.75 equiv) and 5.0 mL of stock solution of $Ir(Fppy)_3$ (0.9 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. After removal of excess amine, and alkyne, the crude material was resubjected to isomerization reaction with DMF (2.5 mL) at 65 °C. The crude material was purified by flash chromatography using hexane : ethyl acetate (0% EtOAc for 25 cv, ramped to 100% EtOAc and then held at 100% EtOAc for 30-35 cv) on a 12 g silica column to afford **S-16a** in 64% yield (86 mg, 0.32 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.4 m, 2F), -141.1 – -141.5 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.20 – 6.15 (m, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.18 – 2.04 (m, 2H), 1.77 (dt, *J* = 12.6, 6.3 Hz, 2H), 1.62 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.0 – 142.1 (m), 142.1, 139.0 (dd, *J* = 257.8, 33.5 Hz), 130.3 – 129.7 (m), 113.0 (t, *J* = 2.5 Hz), 44.6, 32.0, 29.5 (d, *J* = 2.4 Hz), 25.9. FT-IR cm^{-1} 3032, 2941, 2869, 1644, 1468. GC/MS (m/z, relative intensity) 267 (M^+, 5), 232 (5), 177 (85), 41 (100). HRMS (ESI^+) *m/z* calcd. $C_{11}H_{10}ClF_4NNH_4$: 285.0782; found $[M+NH_4]^+$ 285.0915.

Synthesis of S-17a (Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)pyridine



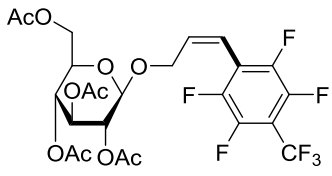
The **General procedure C** was followed using pentafluoropyridine (55 µL, 0.5 mmol, 1 equiv), hex-1-yne (346 µL, 3.0 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (21 µL, 0.12 mmol, 1.2 equiv) and 4.0 mL of stock solution of $Ir(Fppy)_3$ (0.9 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. After removal of excess amine, and alkyne, the crude material was resubjected to isomerization reaction with DMF (2.5 mL) at 65 °C. The crude material was purified by flash chromatography using hexane : EtOAc (0% EtOAc for 6 cv, ramped to 100% EtOAc and then held at 100% EtOAc for 10-14 cv), on a 4 g silica column to afford **S-17a** in 66% yield (77 mg, 0.33 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.7 (m, 2F), -141.1 – -141.8 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.21 – 5.97 (m, 2H), 1.98 (q, *J* = 7.3 Hz, 2H), 1.35 (p, *J* = 7.1 Hz), 1.24 (h, *J* = 7.2 Hz, 2H), 0.80 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.1 – 142.1 (m), 143.3, 139.2 (dd, *J* = 258.0, 33.5 Hz), 130.5 (tt, *J* = 17.2, 3.3 Hz), 112.4 (t, *J* = 2.5 Hz), 30.9, 30.2 (t, *J* = 2.3 Hz), 22.4, 14.0. FT-IR cm^{-1} 2965, 2866, 1639, 1253. GC/MS (m/z, relative intensity) 233 (M^+, 15), 191 (5), 177 (80), 58 (100), 41 (100). HRMS (ESI^+) *m/z* calcd. $C_{11}H_{12}F_4N$: 234.0906; found $[M+H]^+$ 234.0216.

Synthesis of S-18a (methyl (Z)-4-(2-ethoxyvinyl)-2,3,5,6-tetrafluorobenzoate)



The **General procedure A** was followed using methyl 2,3,4,5,6-pentafluorobenzoate (66 µL, 0.45 mmol, 1 equiv), ethoxyethyne (526 µL, 2.7 mmol, 6 equiv), N,N-diisopropylethylamine (117 µL, 0.68 mmol, 1.5 equiv) and 4.5 mL of stock solution of Ir(ppy)3 (0.7 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : EtOAc (0-3% EtOAc for 40 cv and ramped to 100% EtOAc 40-50 cv and then held at 100% EtOAc 50-60 cv), on a 24 g silica column to afford **S-18a** in 55% yield (69 mg, 0.25 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-d) δ -136.9 – -137.5 (m, 2F), -141.1 – -141.5 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.48 (d, J = 6.7 Hz, 1H), 5.15 (dt, J = 6.8, 1.3 Hz, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.96 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.8, 151.5, 146.4 – 144.9 (m), 143.8 – 142.5 (m), 118.9 (t, J = 18.5 Hz), 109.5 (t, J = 15.7 Hz), 89.7 (t, J = 2.6 Hz), 69.7, 53.2, 15.4. FT-IR cm^{-1} 2990, 2896, 1738, 1644, 1484, 1312. GC/MS (m/z, relative intensity) 278 (M^+, 30), 250 (45), 220 (100), 143 (40). HRMS (ESI^+) *m/z* calcd. $C_{12}H_{10}F_4O_3Na$: 301.0464; found $[M+Na]^+$ 301.0449.

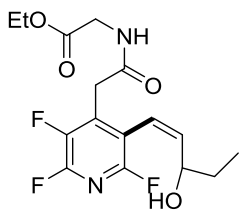
Synthesis of S-19a ((2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((Z)-3-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)allyl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate)



The **General procedure E** was followed using 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (77 µL, 0.6 mmol, 3 equiv), 2-propynyl-tetra-*O*-acetyl-β-D-glucopyranoside (77 mg, 0.2 mmol, 1 equiv), *N*,*N*-diisopropylethylamine (52 µL, 0.3 mmol, 1.5 equiv) and 2.0 mL of

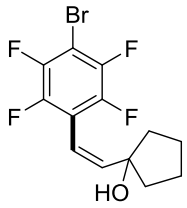
stock solution of $Ir(Fppy)_3$ (0.36 mg, 0.0005 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : EtOAc (0-15% EtOAc for 60 cv, ramped to 100% EtOAc and then held at 100% EtOAc for 65-70 cv) on a 12 g silica column to afford **S-19a** in 56% yield (67 mg, 0.11 mmol) as a colorless highly viscous liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.3 (t, *J* = 21.7 Hz, 3F), -138.4 (td, *J* = 15.9, 6.0 Hz, 2F), -140.5 – -141.0 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.34 – 6.20 (m, 2H), 5.19 (t, *J* = 9.5 Hz, 1H), 5.08 (t, *J* = 9.3 Hz, 1H), 5.00 – 4.93 (m, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 4.36 (dd, *J* = 13.6, 5.2 Hz, 1H), 4.25 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.11 (dt, *J* = 12.2, 5.0 Hz, 2H), 3.67 (ddd, *J* = 10.1, 5.0, 2.6 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 170.4, 169.5, 169.4, 145.7 – 144.8 (m), 143.1 – 142.3 (m), 136.9, 122.3 – 119.4 (m), 120.0 (t, *J* = 18.1 Hz), 114.6, 100.4, 100.2 – 99.7 (m), 72.8, 72.0, 71.2, 68.4, 67.0 (t, *J* = 4.4 Hz), 61.9, 20.8, 20.75, 20.72, 20.71. FT-IR cm^{-1} 3030, 2973, 1757, 1494, 1334. GC/MS (m/z, relative intensity) 604 (M^+- sugar unit (-347), 10), 43 (100). HRMS (ESI^+) *m/z* calcd. $C_{24}H_{23}F_7O_{10}Na$: 627.1077; found $[M+Na]^+$ 627.1052.

Synthesis of S-20a (ethyl (Z)-(2-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)pyridin-4-yl)acetyl)glycinate)



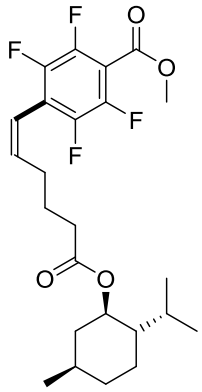
The **General procedure C** was followed using ethyl (2-(perfluoropyridin-4-yl)acetyl)glycinate (155 mg, 0.5 mmol, 1 equiv), pent-1-yn-3-ol (283 µL, 3.0 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (150 µL, 0.86 mmol, 1.7 equiv) and 5.0 mL of stock solution of $Ir(Fppy)_3$ (0.9 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : ethyl acetate (0-30% EtOAc for 45 cv, ramped to 100% EtOAc and then held at 100% EtOAc for 50-60 cv) on a 12 g silica column to afford **S-20a** in 53% yield (95 mg, 0.27 mmol) as a yellow viscous liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.3 (dd, *J* = 27.6, 12.8 Hz, 1F), -89.4 (dd, *J* = 22.9, 12.7 Hz, 1F), -148.2 (dd, *J* = 26.3, 24.1 Hz, 1F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.38 (s, 1H), 6.11 (d, *J* = 11.3 Hz, 1H), 6.01 (dd, *J* = 11.3, 8.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.01 (t, *J* = 5.2 Hz, 2H), 3.94 (q, *J* = 7.2 Hz, 1H), 3.80 (dd, *J* = 15.3, 1.6 Hz, 1H), 3.68 (dd, *J* = 15.2, 2.3 Hz, 1H), 3.20 (s, 1H), 1.57 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.7, 167.9, 152.0 (dd, *J* = 241.8, 11.9 Hz), 147.8 (ddd, *J* = 245.4, 17.5, 15.2 Hz), 142.4, 141.6 (ddd, *J* = 253.6, 25.6, 6.0 Hz), 138.2 (d, *J* = 12.7 Hz), 118.0 (dd, *J* = 33.6, 6.5 Hz), 117.6 (d, *J* = 3.3 Hz), 69.9, 62.0, 41.8, 35.4 – 32.0 (m), 29.2, 14.1, 9.6. FT-IR cm^{-1}3314, 2976, 2960, 1752, 1714, 1540, 1210. GC/MS (m/z, relative intensity) 360 (M+, 5), 303 (40), 257 (60), 229 (40), 200 (50), 104 (100), 57 (85). HRMS (ESI^+) *m/z* calcd. $C_{16}H_{19}F_3N_2O_4Na$: 383.1195; found $[M+Na]^+$ 383.1107.

Synthesis of S-21a ((Z)-1-(4-bromo-2,3,5,6-tetrafluorostyryl)cyclopentan-1-ol)



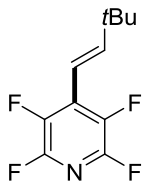
The **General procedure C** was followed using 1,4-dibromo-2,3,5,6-tetrafluorobenzene (62 mg, 0.20 mmol, 1 equiv), 1-ethynylcyclopentan-1-ol (137 µL, 1.2 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (104 µL, 0.6 mmol, 3 equiv) and 2.0 mL of stock solution of $Ir(Fppy)_3$ (0.36 mg, 0.0005 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : DCM (0-45% DCM for 30 cv, ramped to 100% DCM and then held at 100% DCM for 40-50 cv), on a 12 g silica column to afford **S-21a** in 78% yield (53 mg, 0.16 mmol) as a yellow liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -135.0 – -135.2 (m, 2F), -137.9 – -138.2 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.10 (d, *J* = 12.2 Hz, 1H), 5.97 (dt, *J* = 12.2, 1.4 Hz, 1H), 1.92 – 1.65 (m, 8H), 1.03 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.0 – 144.7 (m), 145.0, 143.70 – 142.28 (m), 118.1 (t, *J* = 19.4 Hz), 111.3, 97.9 (t, *J* = 22.4 Hz), 83.1, 41.0, 23.7. FT-IR cm^{-1} 3472, 3030, 2960, 1462. GC/MS (m/z, relative intensity) 338 (M^+-1, 25), 309 (30), 281 (30), 174 (25), 97 (100).). HRMS (ESI^+) *m/z* calcd. $C_{13}H_{12}BrF_4O$: 339.0008; found $[M+H]^+$ 339.1771.

Synthesis of S-22a (methyl 2,3,5,6-tetrafluoro-4-((Z)-6-(((1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-6-oxohex-1-en-1-yl)benzoate)



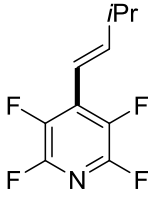
The **General procedure E** was followed using methyl 2,3,4,5,6-pentafluorobenzoate (45 µL, 0.3 mmol, 3 equiv), (1R,2R,5R)-2-isopropyl-5-methylcyclohexyl hex-5-ynoate (25 mg, 0.1 mmol, 1 equiv), *N*,*N*-diisopropylethylamine (83 µL, 0.48 mmol, 1.2 equiv) and 1.0 mL of stock solution of $Ir(Fppy)_3$ (0.18 mg, 0.00025 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : DCM (0-15% DCM for 30 cv, ramped to 100 % DCM and then held at 100% DCM for 45-50 cv) on a 12 g silica column to afford **S-22a** in 72% yield (33 mg, 0.07 mmol) as a colorless viscous liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -138.9 (td, *J* = 15.7, 4.7 Hz, 2F), -139.9 – -140.2 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.25 – 6.01 (m, 2H), 4.66 (td, *J* = 10.9, 4.5 Hz, 1H), 3.98 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.94 (dq, *J* = 12.5, 3.8, 3.3 Hz, 1H), 1.87 – 1.72 (m, 3H), 1.66 (ddd, *J* = 13.4, 6.5, 3.1 Hz, 2H), 1.47 (td, *J* = 6.2, 3.2 Hz, 1H), 1.34 (ddt, *J* = 14.1, 10.9, 3.1 Hz, 1H), 1.04 (qd, *J* = 13.5, 12.8, 3.8 Hz, 2H), 0.88 (dd, *J* = 6.7, 4.3 Hz, 7H), 0.73 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 160.5, 146.4 – 144.7 (m), 143.8 – 142.3 (m), 140.5 (d, *J* = 7.7 Hz), 120.4 – 119.7 (m), 113.8, 111.5 – 110.7 (m), 74.3, 53.4 (d, *J* = 8.6 Hz), 47.1 , 41.1 (d, *J* = 6.9 Hz), 34.6 – 34.3 (m), 34.1 (d, *J* = 8.5 Hz), 31.5, 29.6 (d, *J* = 6.1 Hz), 26.4, 24.3, 23.6, 22.1, 20.8, 16.4 FT-IR cm^{-1}3024, 2955, 2869, 1725, 1650, 1473, 1229. GC/MS (m/z, relative intensity) 458 (M^+- 138 loss of menthol unit, 40), 288 (25), 260 (20), 138 (30), 80 (100). HRMS (ESI^+) *m/z* calcd. $C_{24}H_{30}F_4O_4Na$: 481.1978; found $[M+Na]^+$ 481.1947.

Synthesis of S-23a ((E)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)



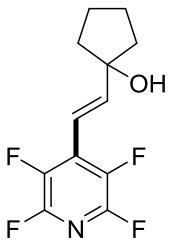
The **General procedure D** was followed using pentafluoropyridine (55 µL, 0.50 mmol, 1 equiv), 3,3-dimethylbut-1-yne (367 µL, 3.0 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (174 µL, 1.0 mmol, 2 equiv) and 5.0 mL of stock solution of Ir(*t*Buppy)$_3$ (1.0 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : EtOAc (0% EtOAc for 15 cv, ramped to 100% EtOAc and then held at 100% EtOAc for 20-25 cv) on a 4 g silica column to afford **S-23a** in 77% yield (90 mg, 0.39 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -92.4 – -92.8 (m, 2F), -143.9 – -148.0 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.90 (d, *J* = 16.6 Hz, 1H), 6.32 (d, *J* = 16.6 Hz, 1H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.6, 143.9 (dt, *J* = 245.9, 15.7 Hz), 141.4 – 137.7 (m), 130.6 – 129.6 (m), 110.3, 35.1, 28.9. FT-IR cm^{-1} 2963, 2880, 1636, 1476, 1315. GC/MS (m/z, relative intensity) 233 (M^+, 20), 218 (45), 198 (30), 170 (20), 69 (40), 42 (100). HRMS (ESI$^+$) *m/z* calcd. $C_{11}H_{11}F_4NNH_4$: 251.1171; found $[M+NH_4]^+$ 251.1246.

Synthesis of S-24a (E)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine



The **General procedure D** was followed using pentafluoropyridine (22 µL, 0.20 mmol, 1 equiv), 3-dimethylbut-1-yne (123 µL, 1.2 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (52 µL, 0.3 mmol, 1.5 equiv) and 2.0 mL of stock solution of Ir(*t*Buppy)$_3$ (0.4 mg, 0.0005 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was passed through silica pipette using hexane to afford **S-24a** in 66% yield (29 mg, 0.13 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -92.4 – -92.8 (m, 2F), -145.4 – -146.3 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.85 (dd, *J* = 16.4, 7.1 Hz, 1H), 6.38 (dd, *J* = 16.5, 1.3 Hz, 1H), 2.70 – 2.45 (m, 1H), 1.14 (d, *J* = 6.8 Hz, 6H). GC/MS (m/z, relative intensity) 219 (M^+, 25), 204(50), 184 (40), 164 (35), 56 (100), 39 (70). FT-IR cm^{-1} 2965, 1647, 1478. HRMS (ESI$^+$) *m/z* calcd. $C_{10}H_9F_4NNH_4$: 237.1015; found $[M+NH_4]^+$ 237.1090.

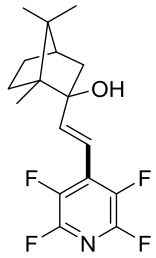
Synthesis of S-25a (E)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol



The **General procedure D** was followed pentafluoropyridine (44 µL, 0.40 mmol, 1 equiv), 1-ethynylcyclopentan-1-ol (275 µL, 2.4 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (52 µL, 0.3 mmol, 0.75 equiv) and 4.0 mL of stock solution of Ir(*t*Buppy)$_3$ (0.8 mg, 0.0015 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using DCM : MeOH (0-10% MeOH for 30 cv, ramped to 20% MeOH and then held at 20% MeOH for 30-35 cv) on a 12 g basic alumina column to afford **S-25a** in 71% yield (74 mg, 0.28 mmol) as a white solid. ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -93.3 – -93.7 (m, 2F), -145.2 – -146.3 (m, 2F). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.00 (d, *J* = 16.3 Hz, 1H), 6.78 (d, *J* = 16.3 Hz, 1H), 2.09 – 1.67 (m, 8H), 1.26 (s, 1H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 151.1

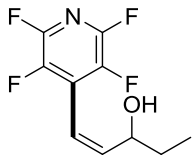
(t, *J* = 7.3 Hz), 145.2 – 142.2 (m), 141.2 – 137.9 (m), 129.6 – 129.1 (m), 111.2 (t, *J* = 3.0 Hz), 82.2, 40.9, 24.0. FT-IR cm^{-1} 3397, 2952, 2874, 1744, 1481. GC/MS (m/z, relative intensity) 261 (M+, 10), 232 (15), 199 (20) 97 (45), 41 (100). HRMS (ESI^+) *m/z* calcd. $C_{12}H_{11}F_4NOK$: 300.0414; found $[M+K]^+$ 300.0473. Melting point 77-79 °C.

Synthesis of S-26a (1S,2S,4R)-1,7,7-trimethyl-2-((E)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol



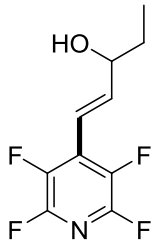
The **General procedure D** was followed using pentafluoropyridine (49 µL, 0.45 mmol, 1 equiv), (1S,2S,4R)-2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (480 mg, 2.7 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (52 µL, 0.3 mmol, 0.75 equiv) and 4.5 mL of stock solution of Ir(*t*Buppy)$_3$ (0.9 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : ethyl acetate (0-3% EtOAc for 25 cv, ramped to 100% EtOAc and then held at 100% EtOAc for 35-40 cv) on a 12 g silica column to afford **S-26a** in 68% yield (101 mg, 0.31 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -92.1 (m, 2F), -144.9 – -145.2 (m, 2F). ^1H NMR (400 MHz, Chloroform-*d*) δ 6.48 – 6.31 (m, 2H), 2.79 – 2.68 (m, 1H), 2.44 (dddd, *J* = 15.7, 10.6, 8.0, 3.6 Hz, 2H), 2.21 (t, *J* = 4.6 Hz, 1H), 1.87 (d, *J* = 18.2 Hz, 1H), 1.38 (dd, *J* = 13.0, 4.3 Hz, 1H), 1.25 (s, 1H), 1.07 (s, 3H), 0.90 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.9 (t, *J* = 7.8 Hz), 145.2 – 142.1 (m), 141.0 – 137.7 (m), 128.8 – 128.4 (m), 116.0 (t, *J* = 2.9 Hz), 63.0, 48.3, 47.0, 43.9, 42.4, 34.4, 20.2, 19.2, 8.1. FT-IR cm^{-1} 3472, 2963, 1636, 1482. GC/MS (m/z, relative intensity) 329 (M^+-2, 10), 284 (20), 244 (20), 124 (30), 98 (100), 41 (80).). HRMS (ESI^+) *m/z* calcd. $C_{17}H_{20}F_4NO$: 329.1403; found $[M]^+$ 329.1370.

Synthesis of S-27 ((Z)-1-(perfluoropyridin-4-yl)pent-1-en-3-ol)



The **General procedure A** was followed using pentafluoropyridine (55 µL, 0.5 mmol, 1 equiv), pent-1-yn-3-ol (258 µL, 3.0 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (101 µL, 0.58 mmol, 1.16 equiv) and 5.0 mL of stock solution of Ir(ppy)$_3$ (0.8 mg, 0.00125 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : ether(0-20% Ether for 30 cv, ramped to 100% ether and then held at 100% ether for 30-40 cv), on a 24 g silica column to afford **S-27** in 64% yield (76 mg, 0.32 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.8 – -91.1 (m, 2F), -141.6 – -141.8 (m, 2F). ^1H NMR (400 MHz, Chloroform-*d*) δ 6.27 – 6.13 (m, 2H), 4.10 (q, *J* = 7.2, 3.8 Hz, 1H), 1.81 (b, 1H), 1.76 – 1.47 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 143.4 (dddd, *J* = 245.2, 16.9, 13.2, 2.9 Hz), 141.0 – 137.3 (m), 129.7 (tt, *J* = 17.0, 3.0 Hz), 113.2 (t, *J* = 2.4 Hz), 70.9 (t, *J* = 1.8 Hz), 29.4, 9.4. FT-IR cm^{-1} 3390, 2961, 1630, 1460. GC/MS (m/z, relative intensity) 235 (M^+-1, 5), 216 (5), 206 (70), 138 (20), 57 (100).

Synthesis of S-27a (E)-1-(perfluoropyridin-4-yl)pent-1-en-3-ol



The **General procedure E** was followed using pentafluoropyridine (165 µL, 1.5 mmol, 3 equiv), pent-1-yn-3-ol (45 µL, 0.50 mmol, 1 equiv), *N*,*N*-diisopropylethylamine (101 µL, 0.58 mmol, 1.16 equiv) and 5.0 mL of stock solution of Ir(*t*Buppy)$_3$ (1 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. The crude material was purified by flash chromatography using hexane : DCM (0-5% EtOAc for 18 cv, ramped to 100% EtOAc then held at 100% EtOAc for 18-40 cv), on a 24 g silica column to afford **S-27a** in 84% yield (99 mg, 0.42 mmol) as a colorless liquid.

The **General procedure D** was followed using pentafluoropyridine (44 µL, 0.40 mmol, 1 equiv), tert-butyldimethyl(pent-1-yn-3-yloxy)silane (476 µL, 2.4 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (70 µL, 0.4 mmol, 1.0 equiv) and 4.0 mL of stock solution of Ir(*t*Buppy)$_3$ (1 mg, 0.001 mmol, 0.0025 equiv) in CH_3CN was used. After the completion of reaction, solvent was removed. The crude material, **S-27b**, was dissolved in THF (2 mL) and treated with TBAF (2 mL) and stirred for 1 h at room temperature. THF was removed and the desilylated crude material was purified by prep tlc using hexane ether (70:30) to afford **S-27a** in 41% yield (39 mg, 0.17 mmol) as a colorless liquid.

The **General procedure D** was followed using pentafluoropyridine (66 µL, 0.60 mmol, 1 equiv), 2-(pent-1-yn-3-yloxy)tetrahydro-2H-pyran (600 mg, 3.6 mmol, 6 equiv), *N*,*N*-diisopropylethylamine (130 µL, 0.75 mmol, 1.25 equiv) and 6.0 mL of stock solution of Ir(*t*Buppy)$_3$ (1.2 mg, 0.0015 mmol, 0.0025 equiv) in CH_3CN was used. After the completion of reaction solvent was removed. The crude material, **S-27c**, was dissoled in MeOH (2 mL) and 2M HCl (1 mL) added and then stirred overnight at room temperature. After removal of methanol, the crude material was purified by prep tlc using hexane:ether (70:30) to afford **S-27a** in 85% yield (120 mg, 0.51 mmol) as a colorless liquid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.7 – -92.2 (m, 2F), -144.7 – -145.2 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.81 (dd, *J* = 16.4, 5.0 Hz, 1H), 6.64 (dd, *J* = 16.4, 1.6 Hz, 1H), 4.29 (b, 1H), 1.68 – 1.59 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). FT-IR cm^{-1} 3394, 2971, 2877, 1634, 1468. GC/MS (m/z, relative intensity) 235 (M^+, 5), 218 (5), 206 (50), 57 (100), 43 (25). HRMS (ESI^+) *m/z* calcd. $C_{10}H_{10}F_4NO$: 236.0699; found $[M+H]^+$ 236.0399.

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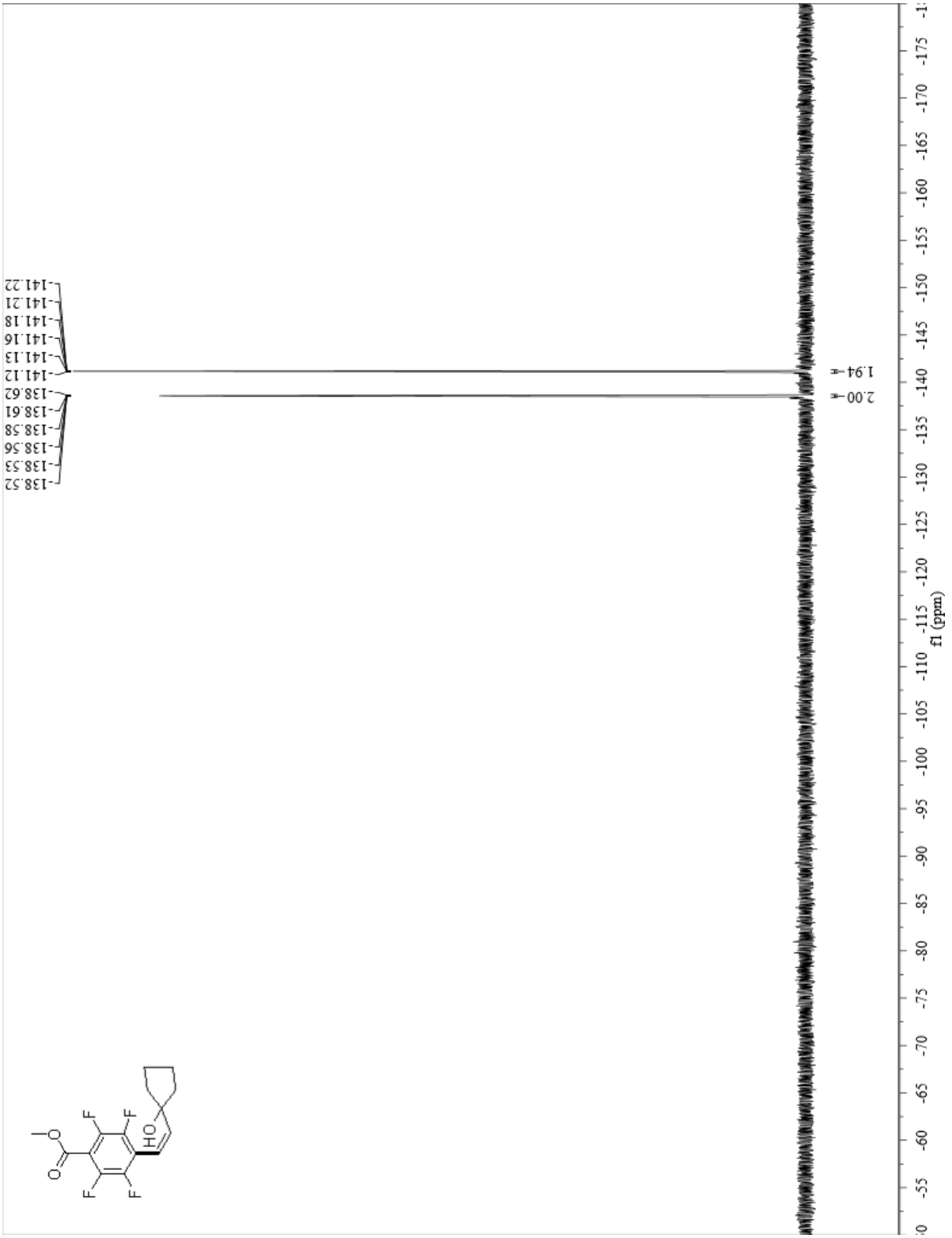
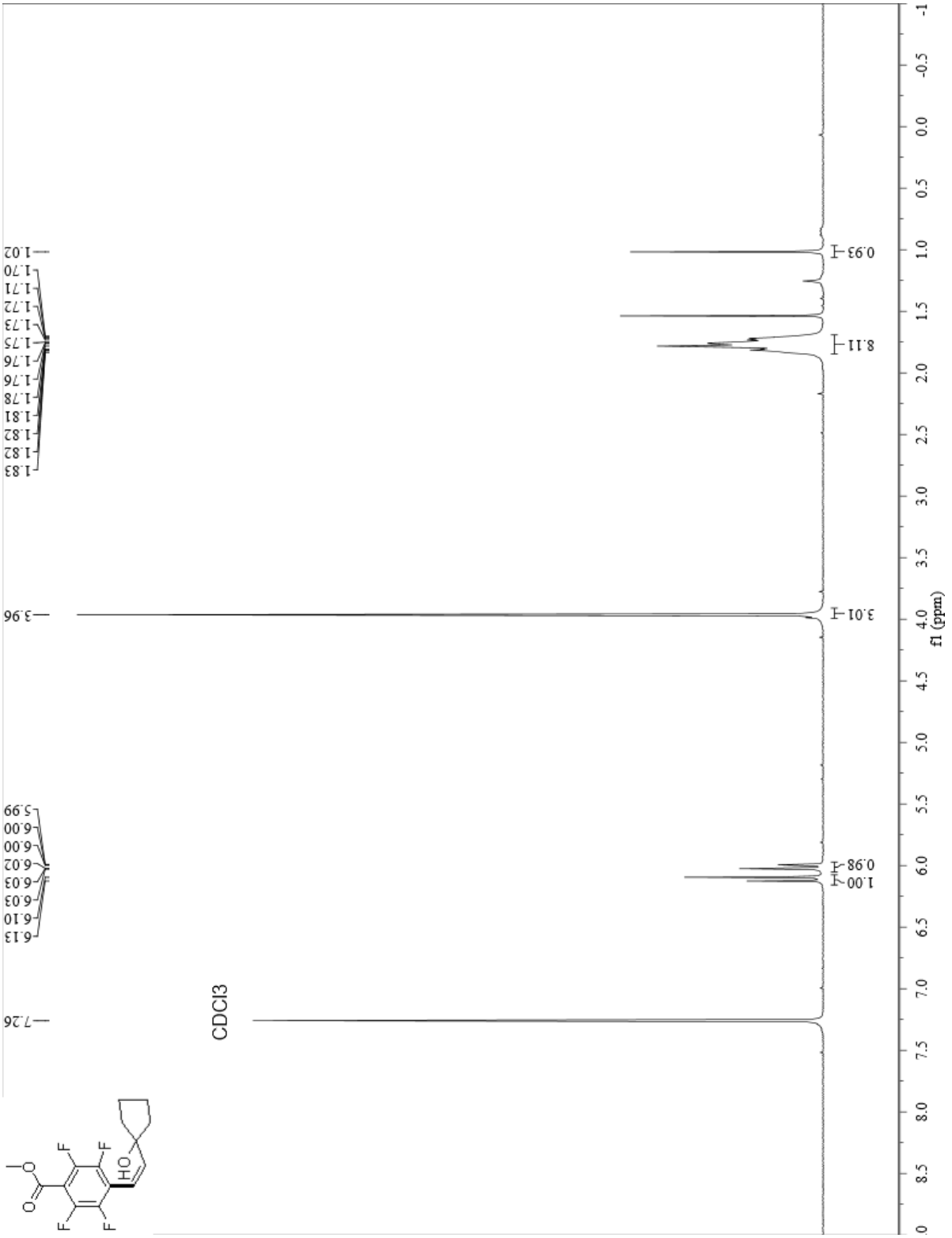
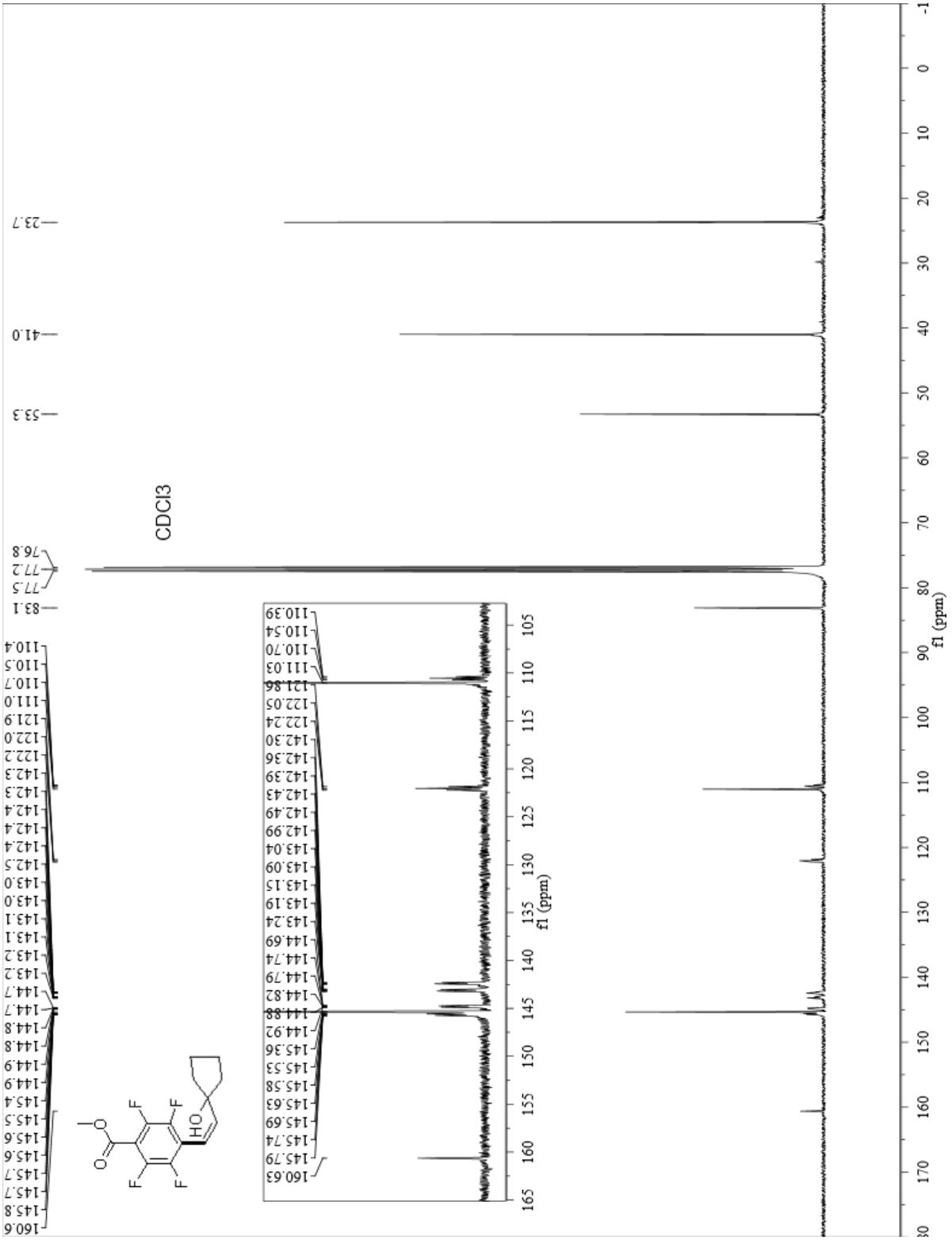
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-3a (methyl (Z)-2,3,5,6-tetrafluoro-4-(2-(1-hydroxycyclopentyl)vinyl)benzoate)



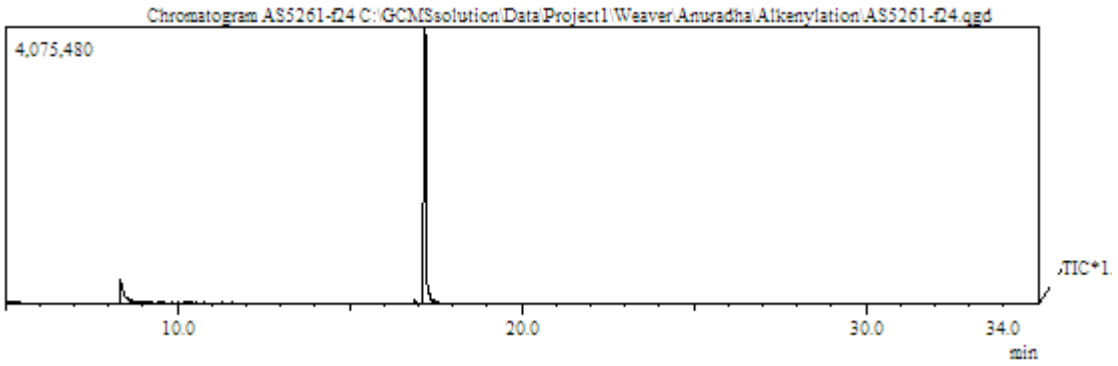
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-3a (methyl (Z)-2,3,5,6-tetrafluoro-4-(2-(1-hydroxycyclopentyl)vinyl)benzoate)

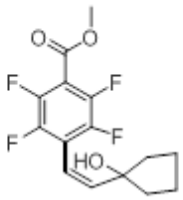


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of 3a (methyl (Z)-2,3,5,6-tetrafluoro-4-(2-(1-hydroxycyclopentyl)vinyl)benzoate)

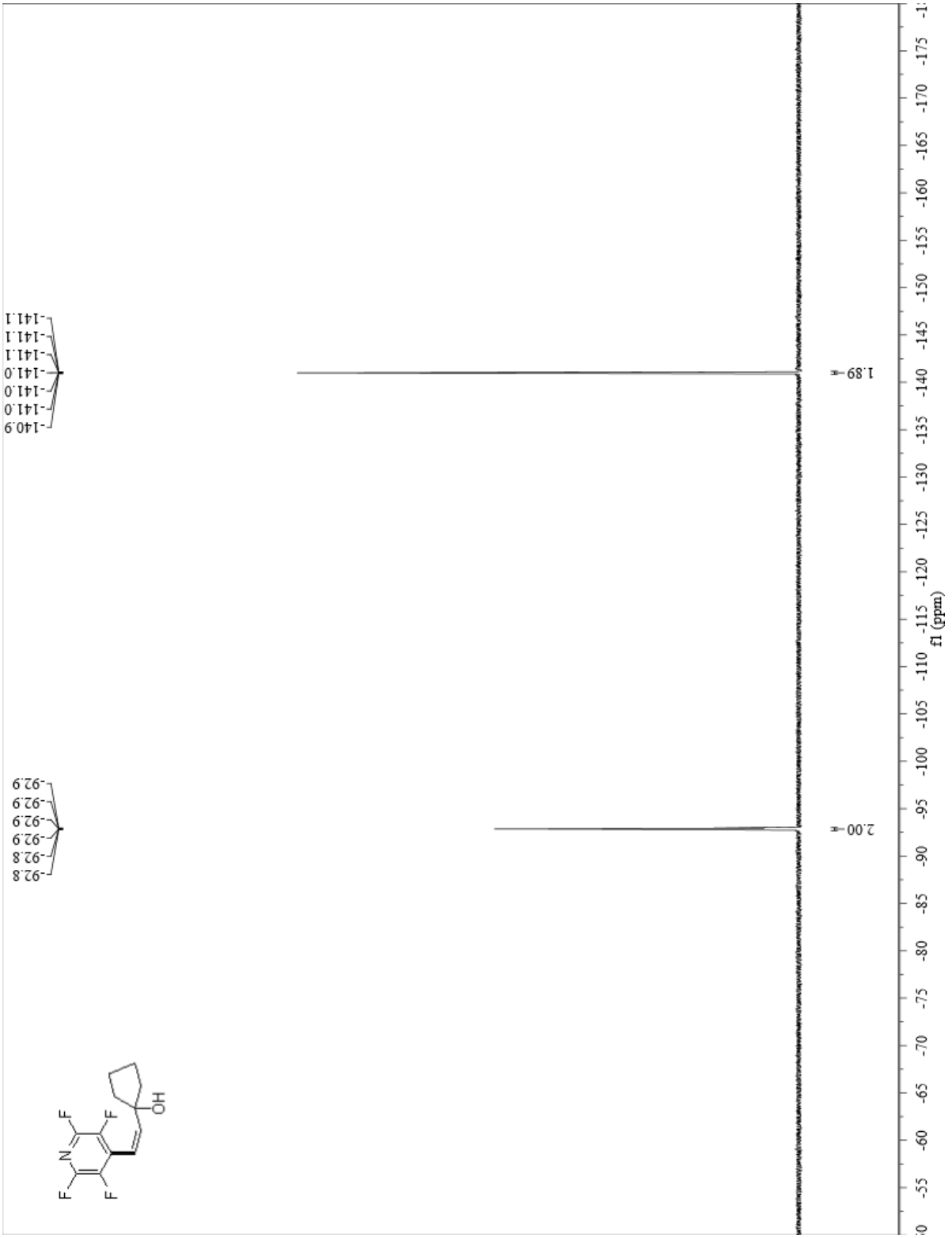


GC and MS of 3a (methyl (Z)-2,3,5,6-tetrafluoro-4-(2-(1-hydroxycyclopentyl)vinyl)benzoate)

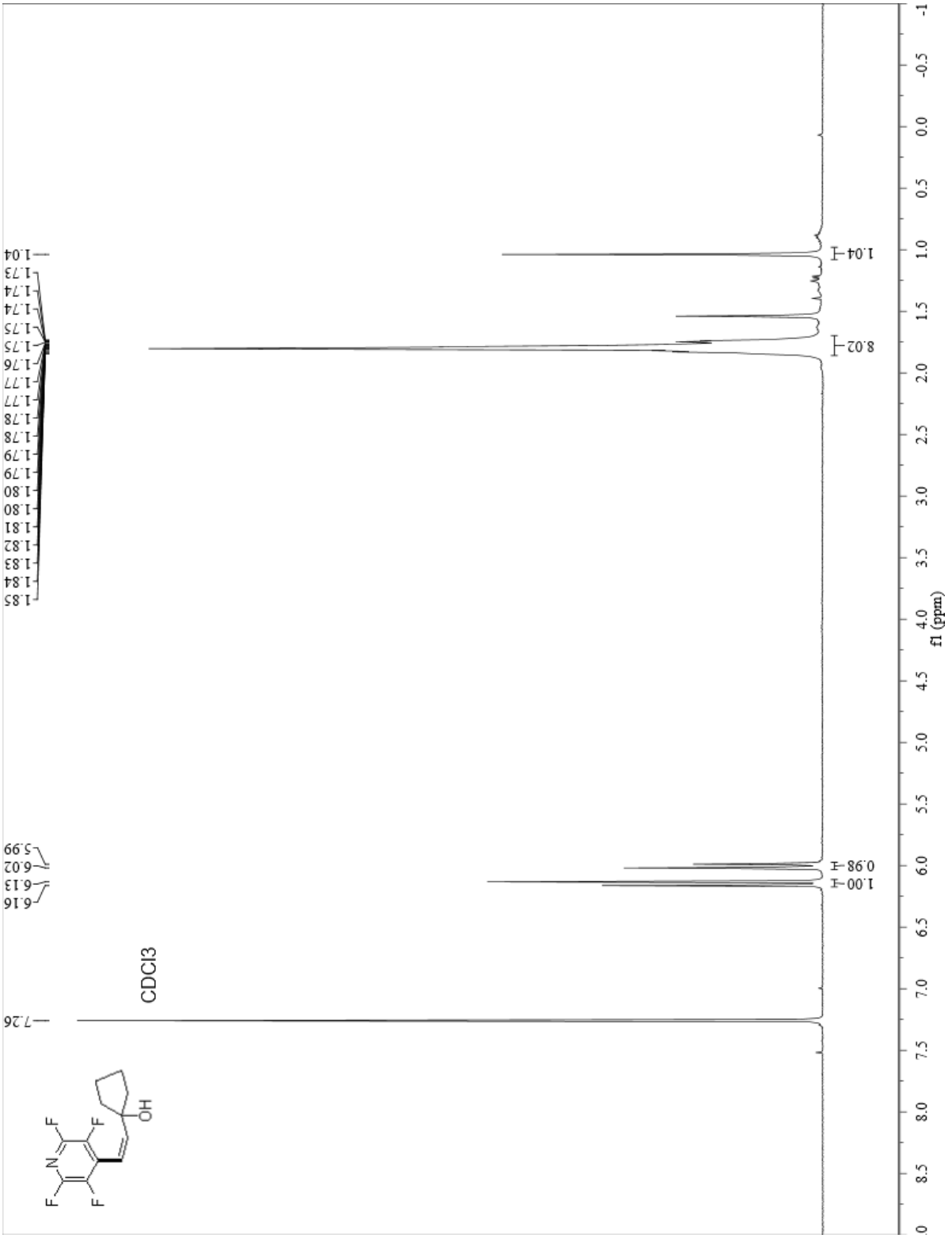




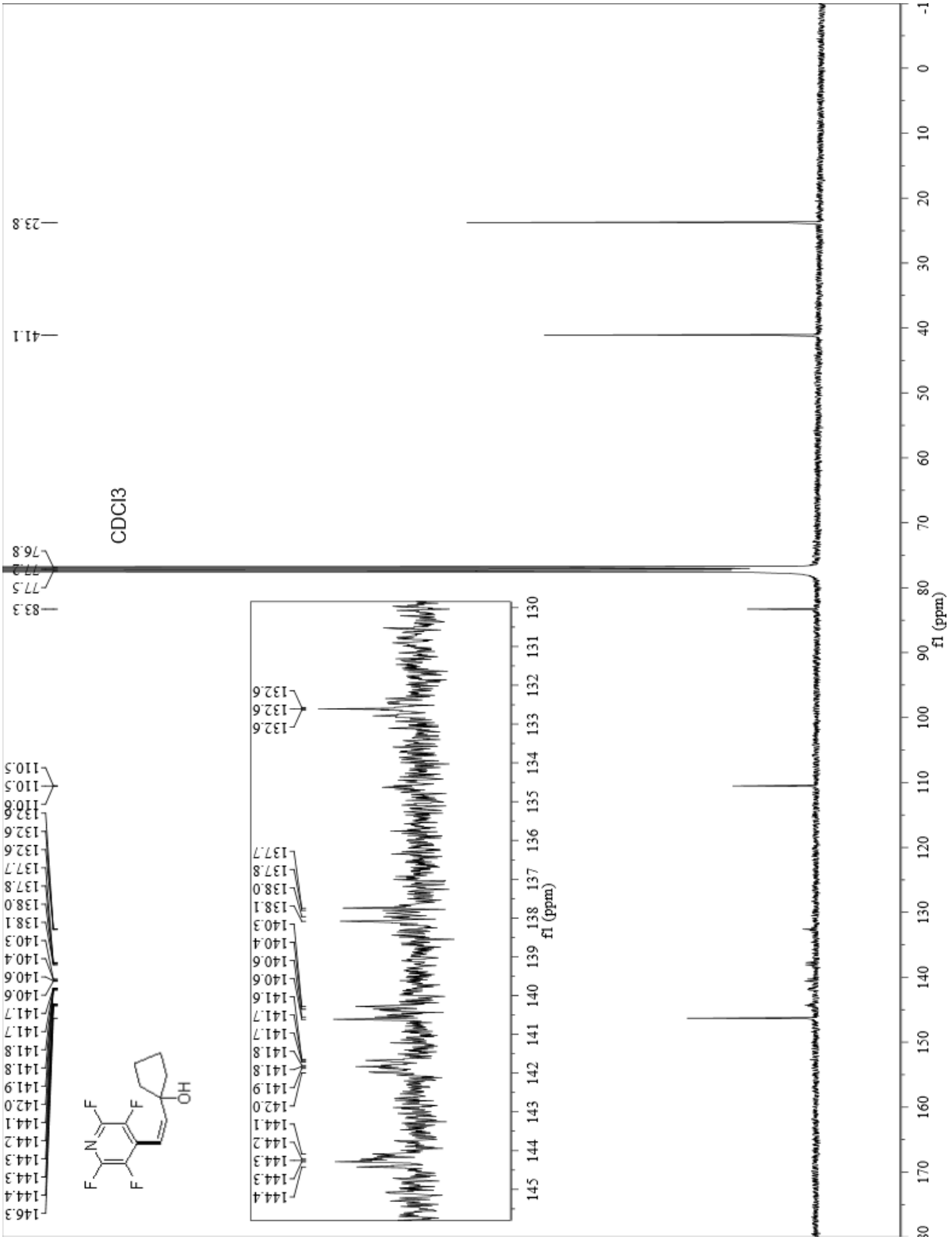
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-4a (Z)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol)



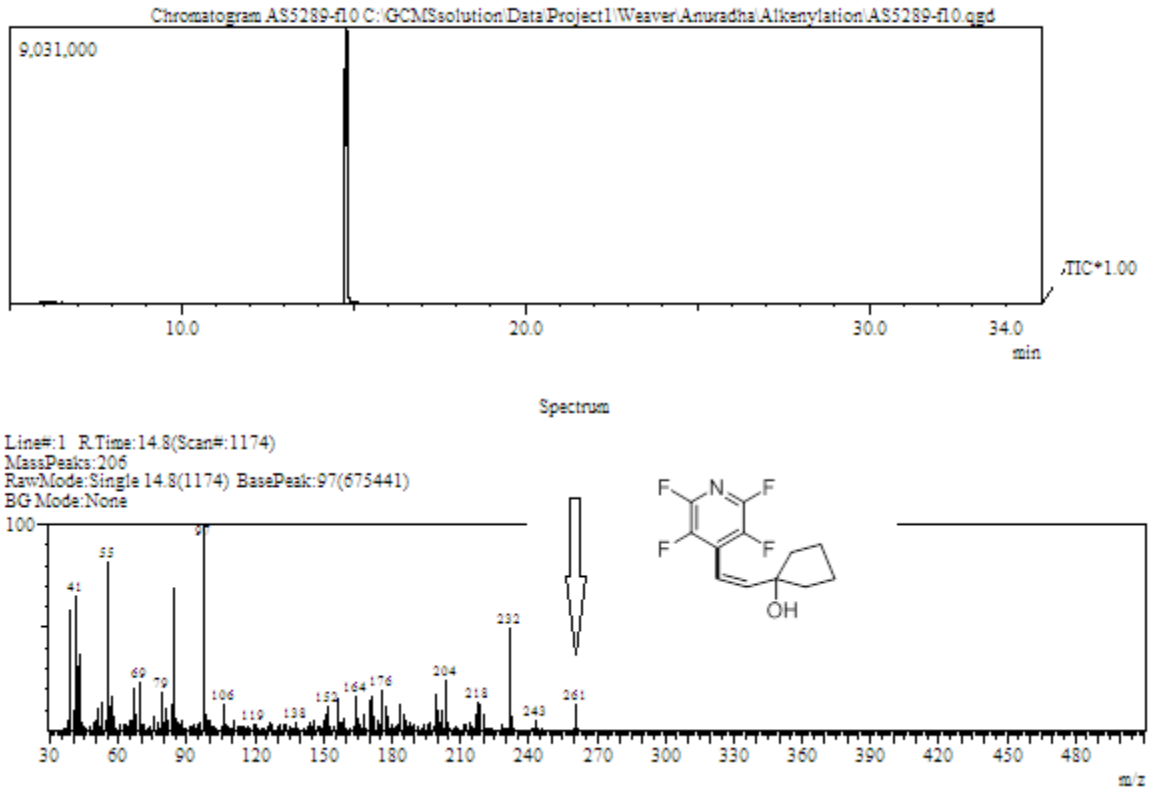
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-4a (Z)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol)



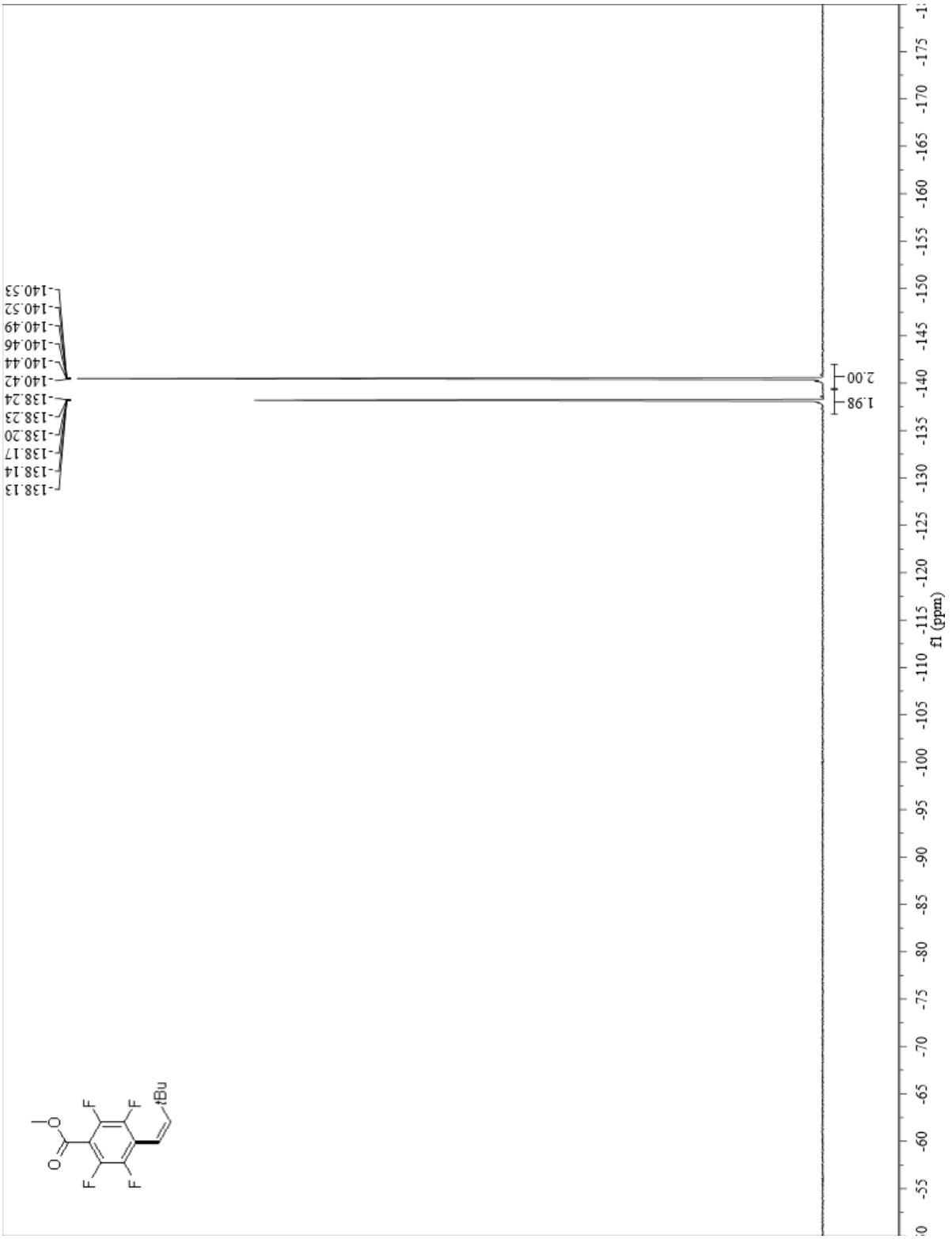
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-4a (Z)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol)



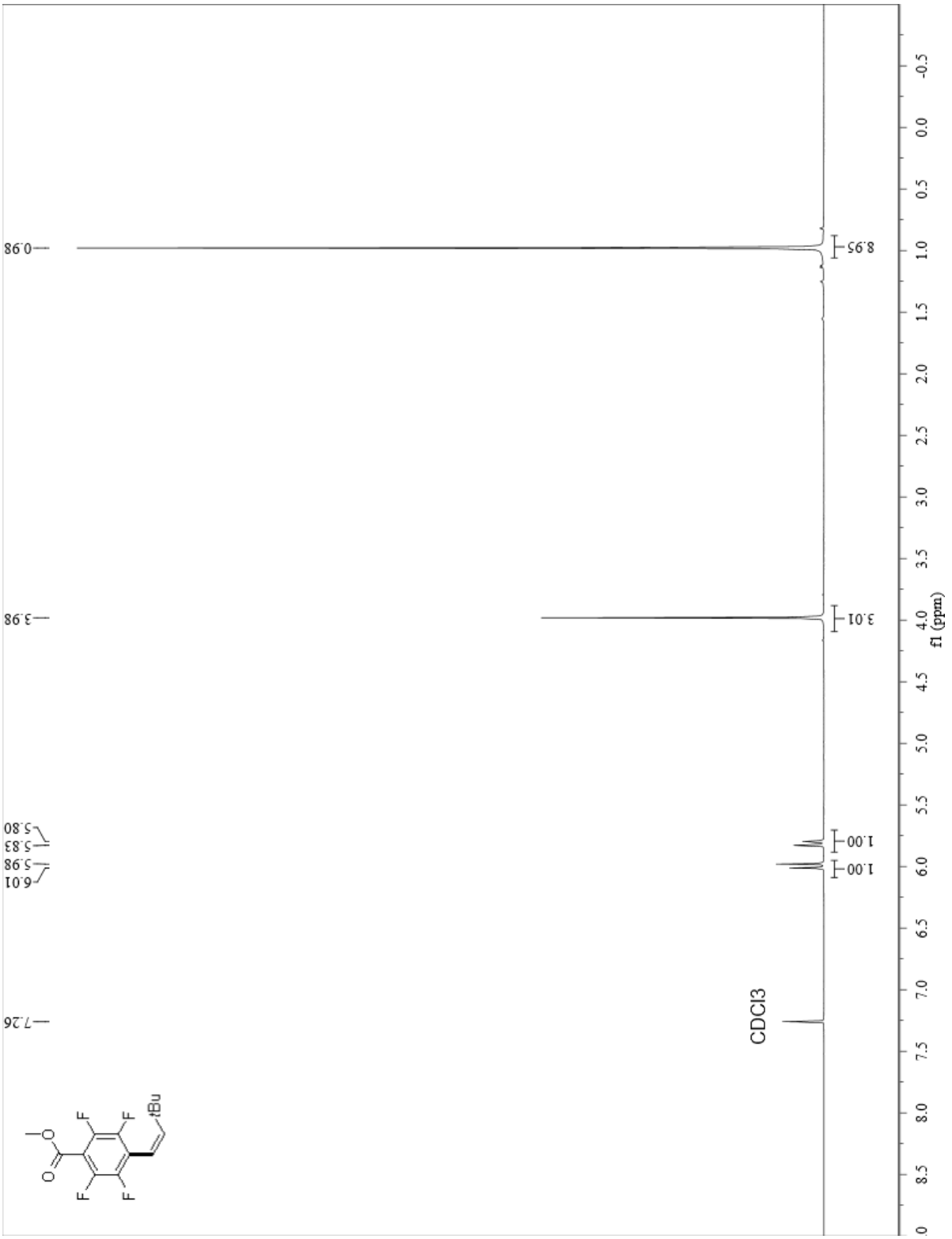
GC and MS of S-4a (Z)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol)



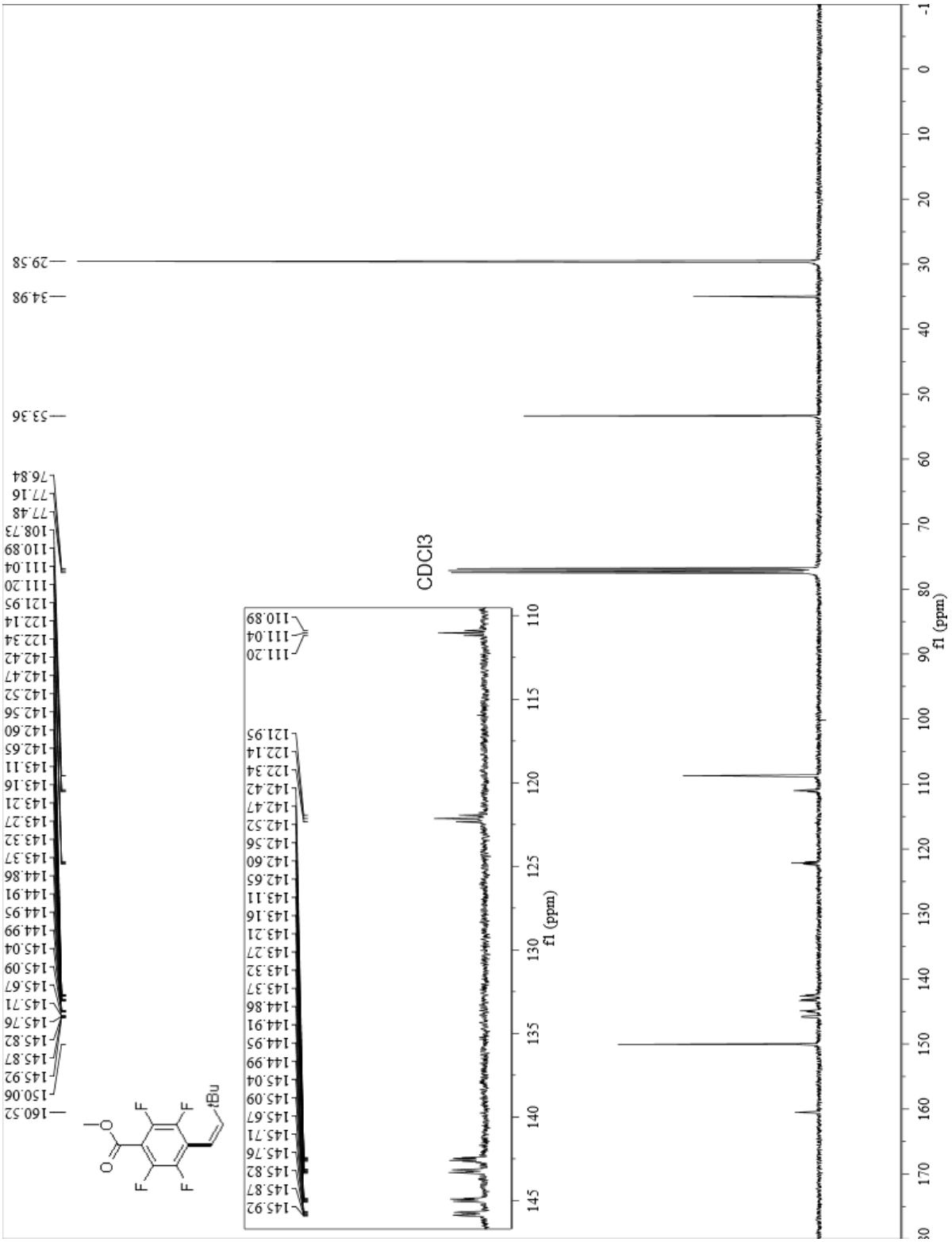
^{19}F NMR (400 MHz, Chloroform-*d*, at rt) of S-5a (methyl (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluorobenzoate)



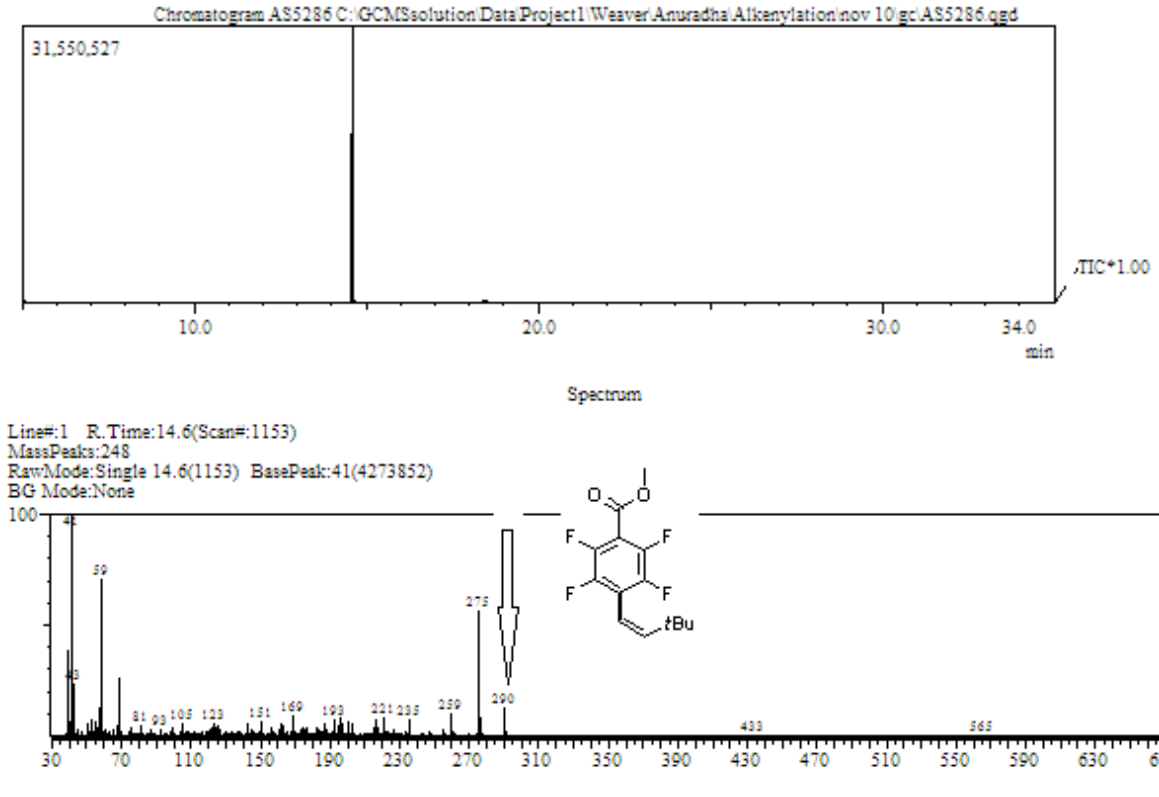
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-5a (methyl (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluorobenzoate)



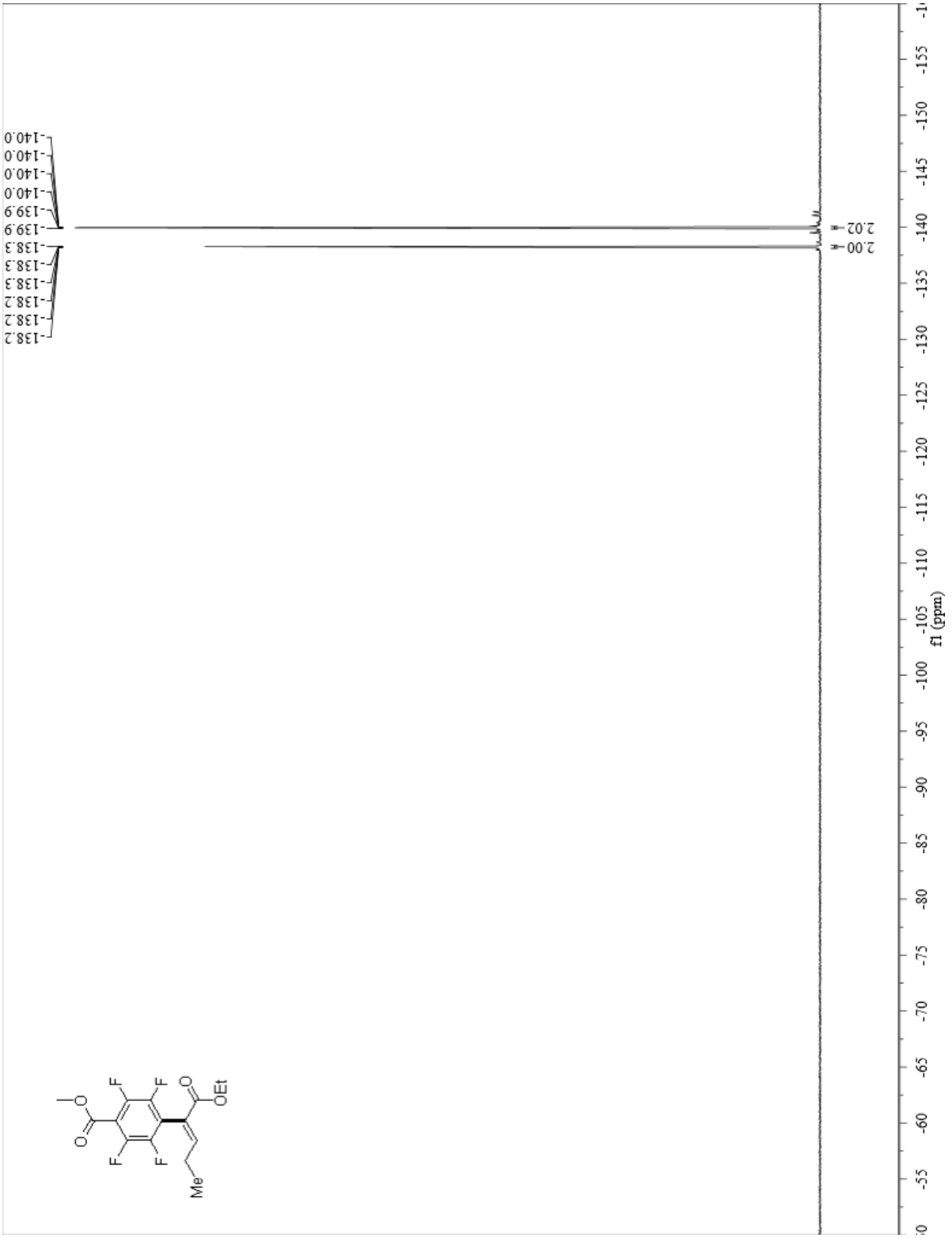
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-5a (methyl (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluorobenzoate)



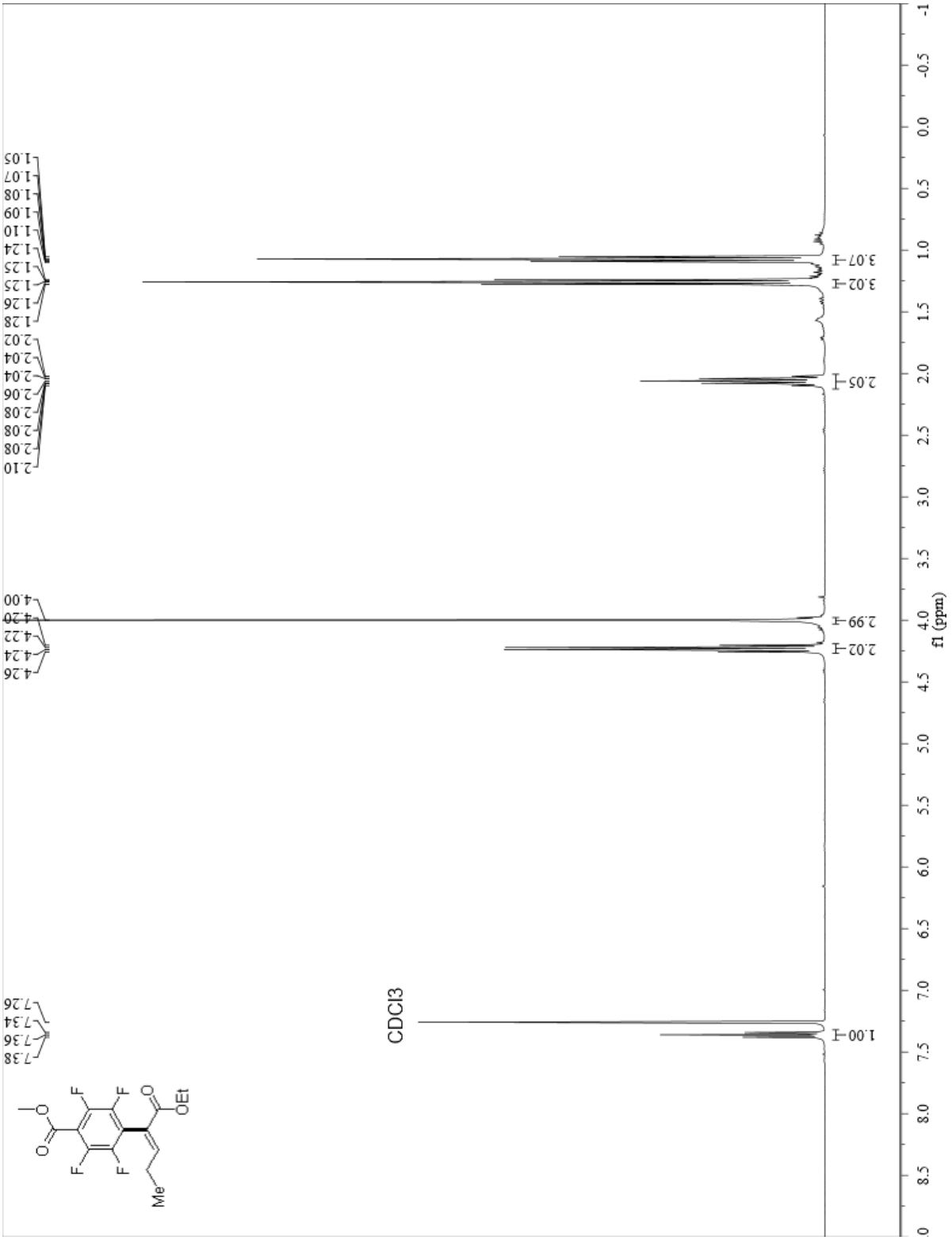
GC and MS of S-5a of S-5a (methyl (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluorobenzoate)



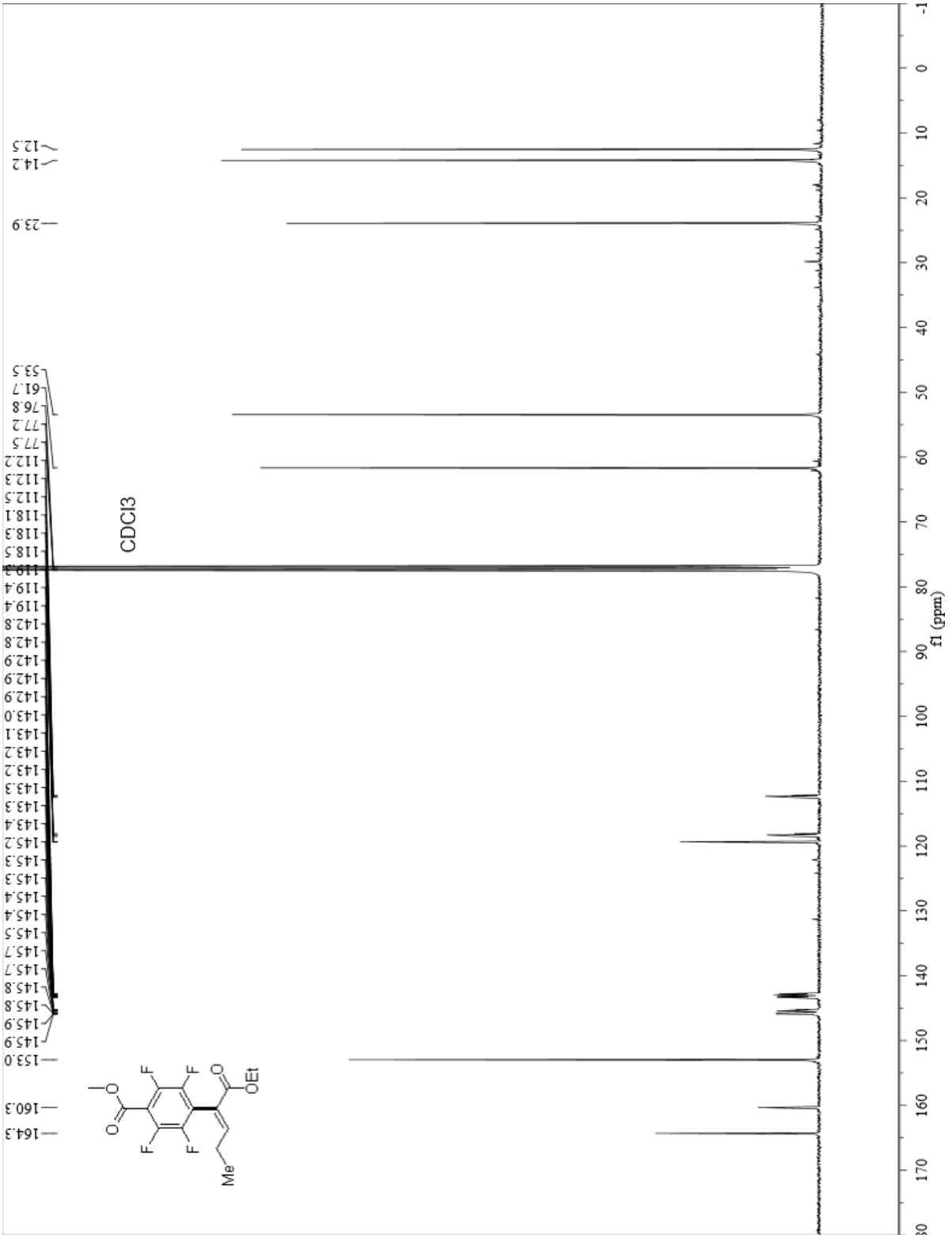
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-6a (methyl (E)-6-(1-ethoxy-1-oxopent-2-en-2-yl)-2,3,5,6-tetrafluorobenzoate)



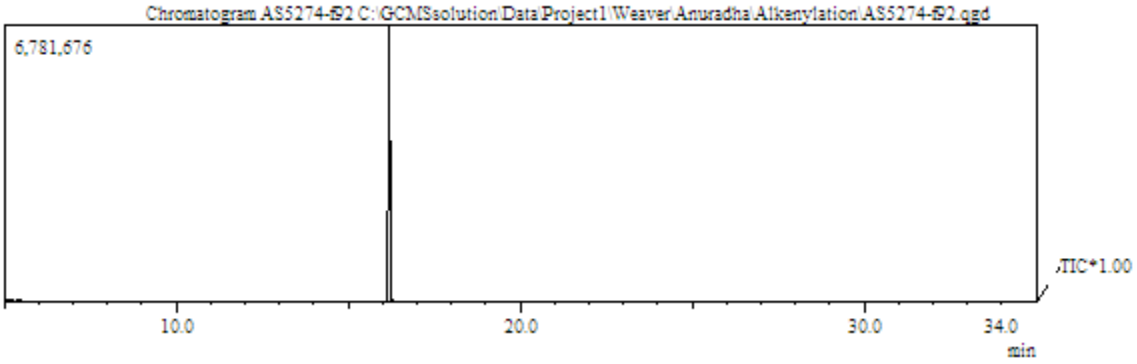
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-6a (methyl (E)-4-(1-ethoxy-1-oxopent-2-en-2-yl)-2,3,5,6-tetrafluorobenzoate)

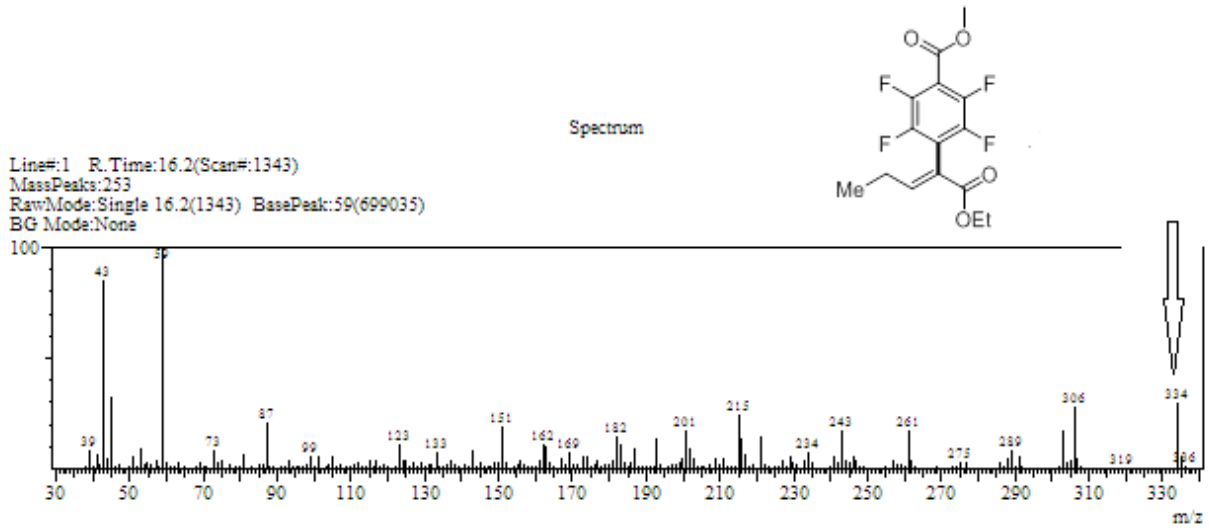


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-6a (methyl (E)-4-(1-ethoxy-1-oxopent-2-en-2-yl)-2,3,5,6-tetrafluorobenzoate)

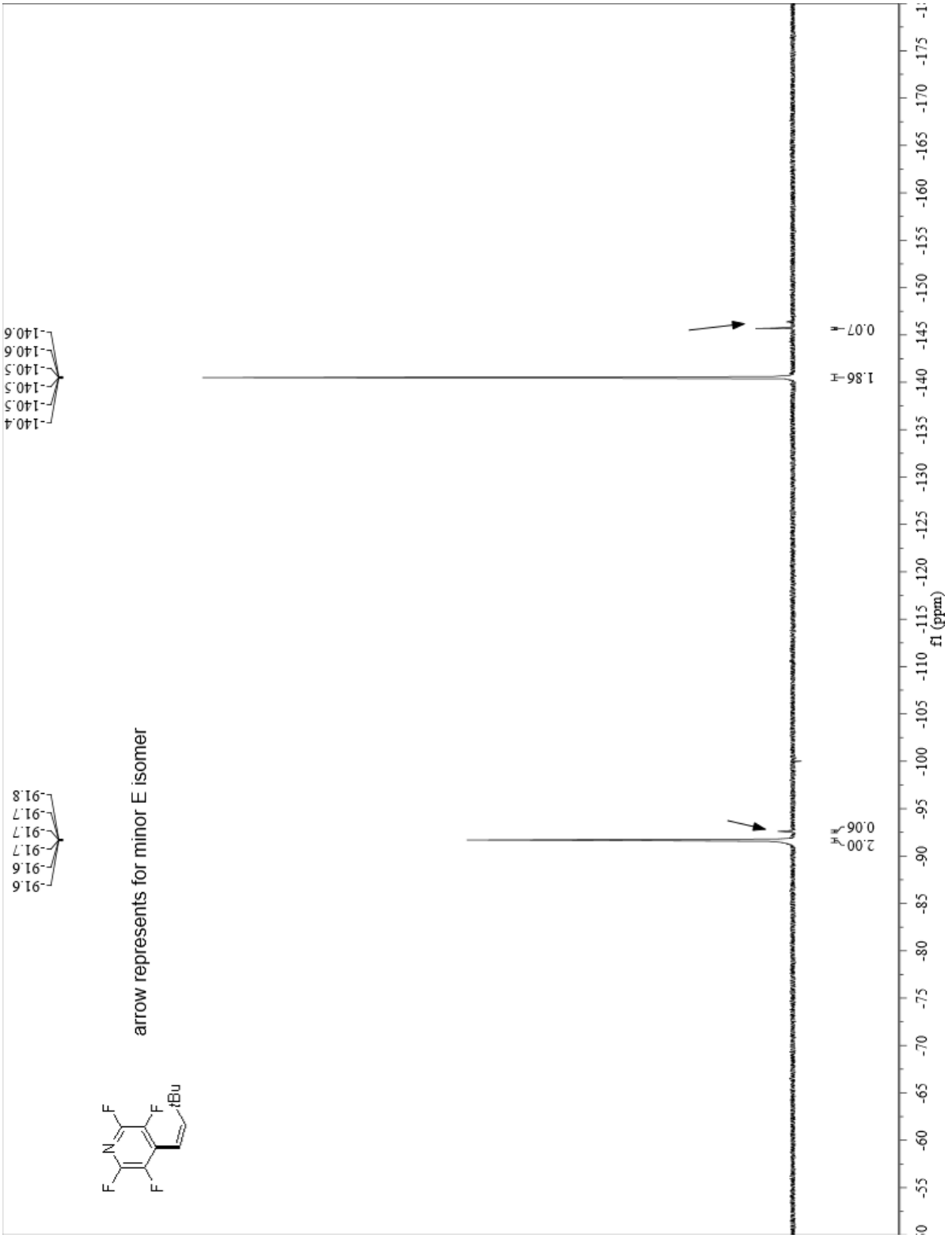


GC and MS of S-6a (methyl (E)-4-(1-ethoxy-1-oxopent-2-en-2-yl)-2,3,5,6-tetrafluorobenzoate)

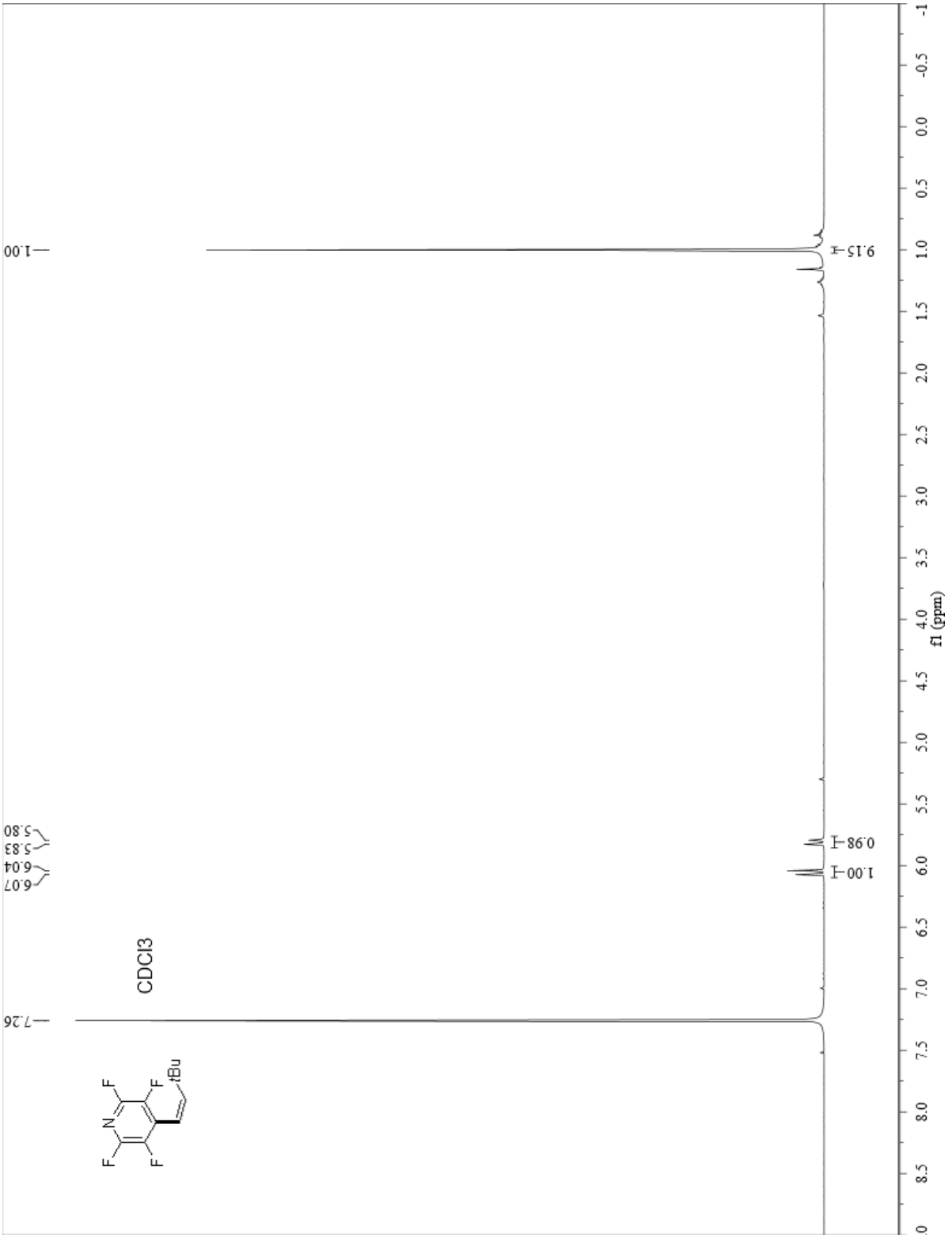




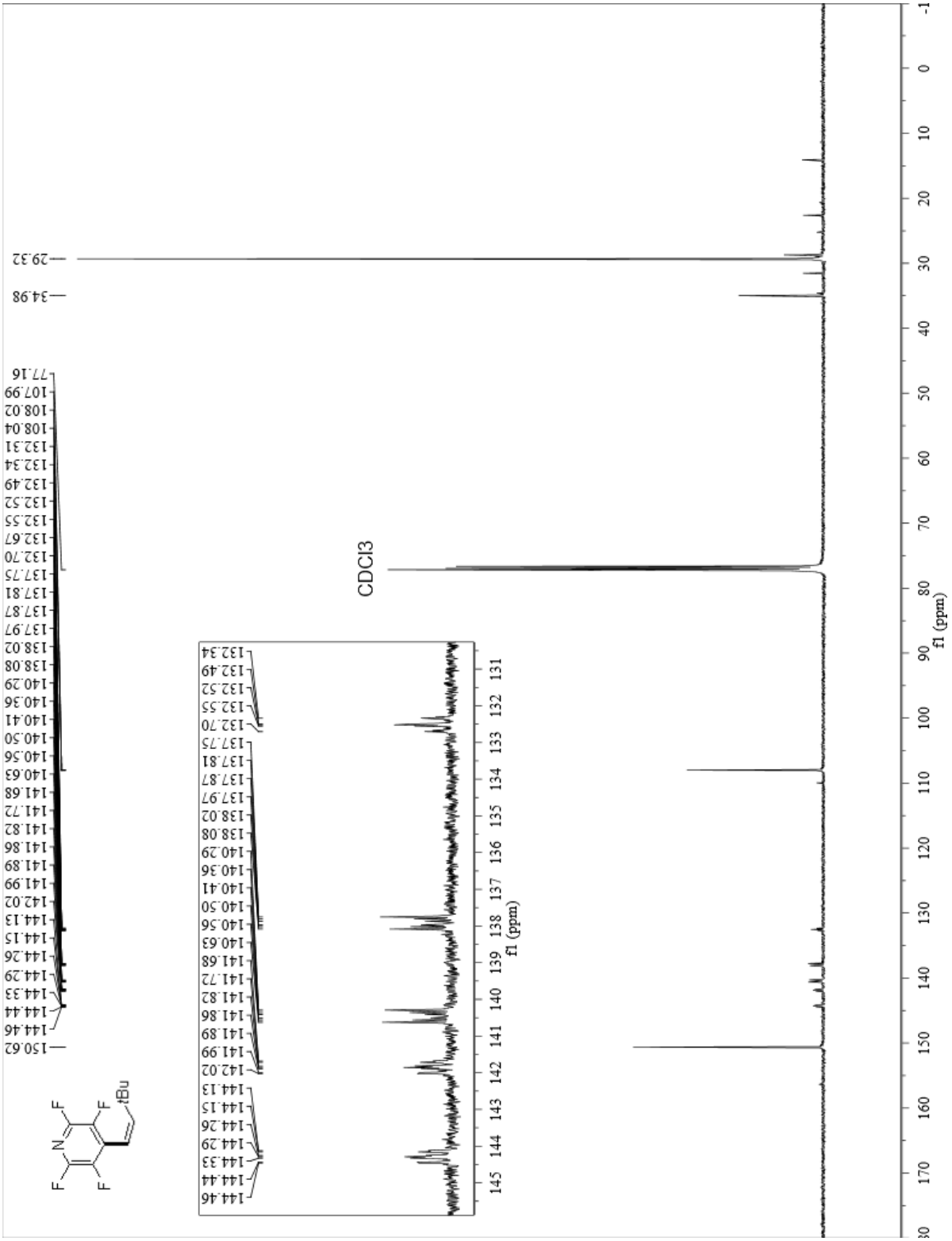
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-7a (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine



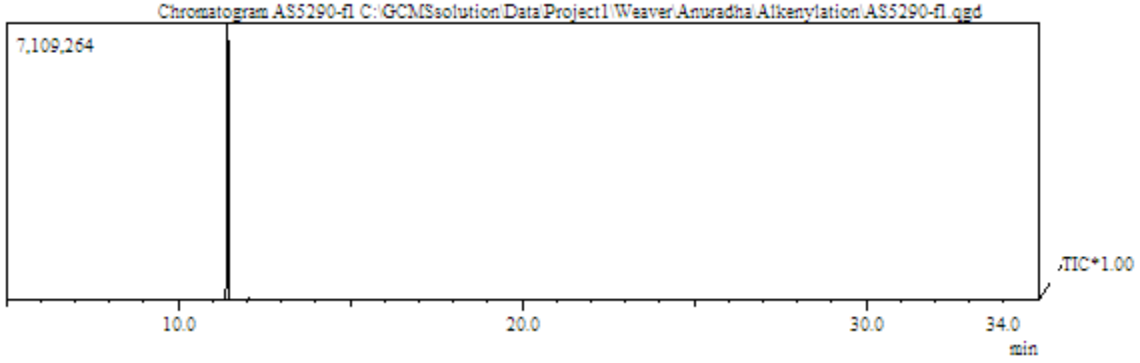
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-7a (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine

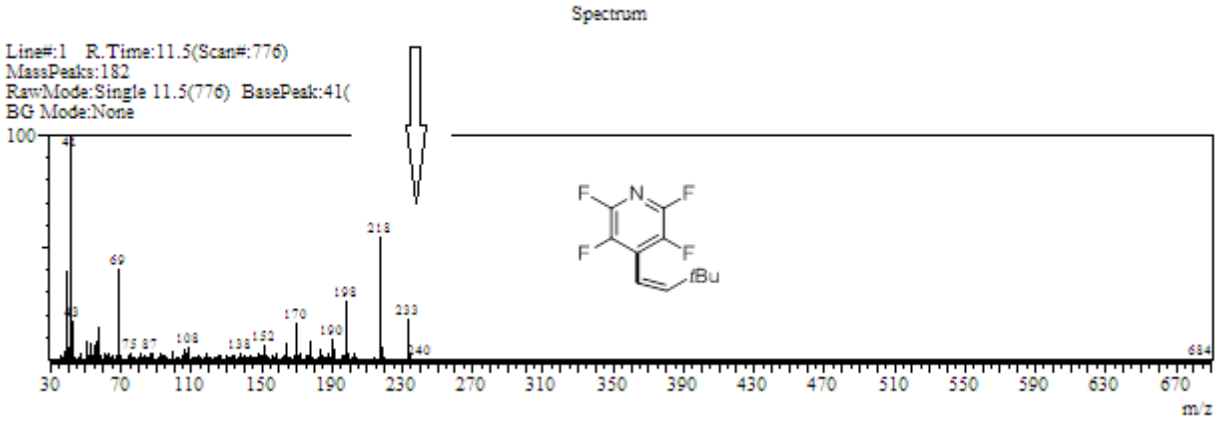


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-7a (Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine

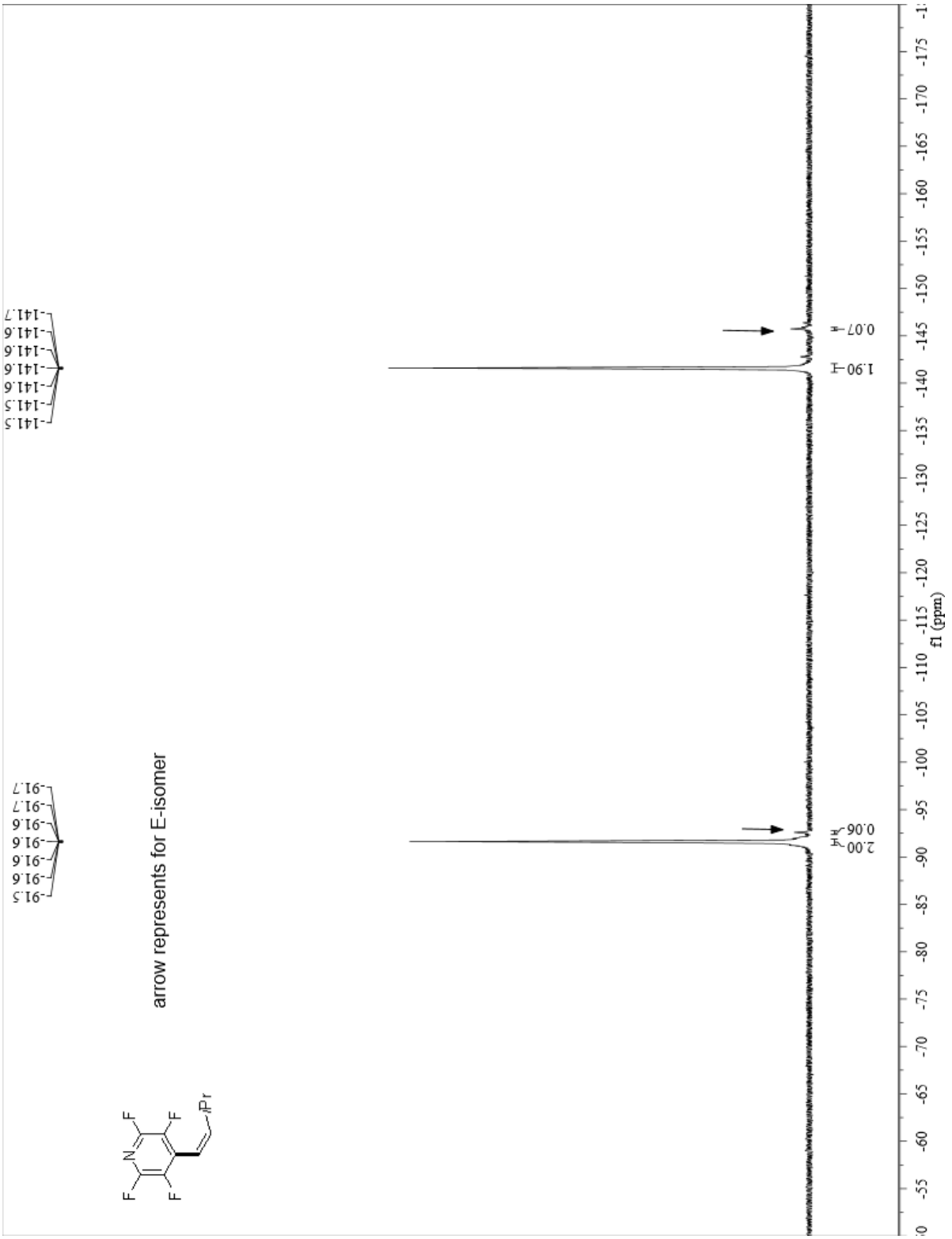


GC and MS of S-7a 3(Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine

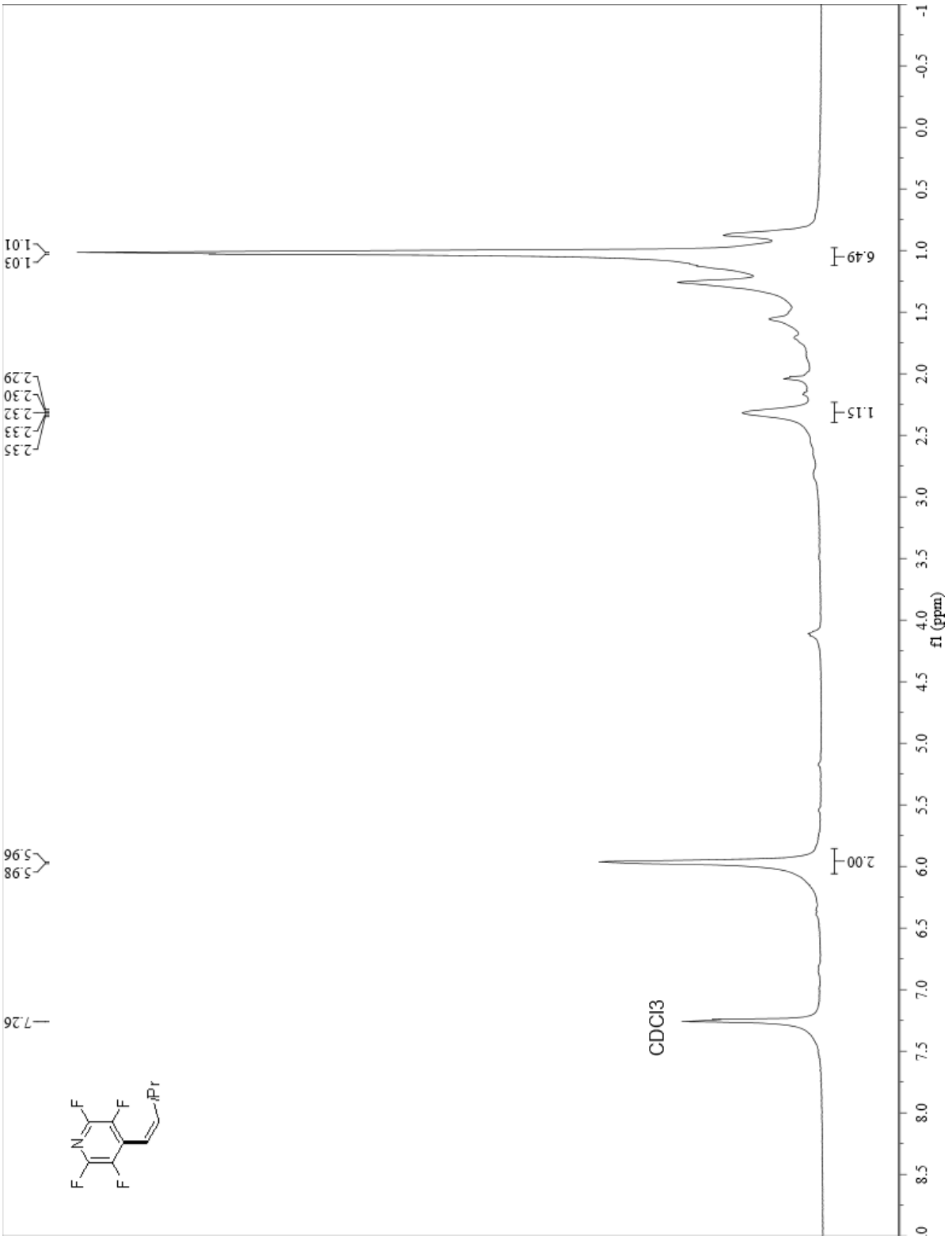




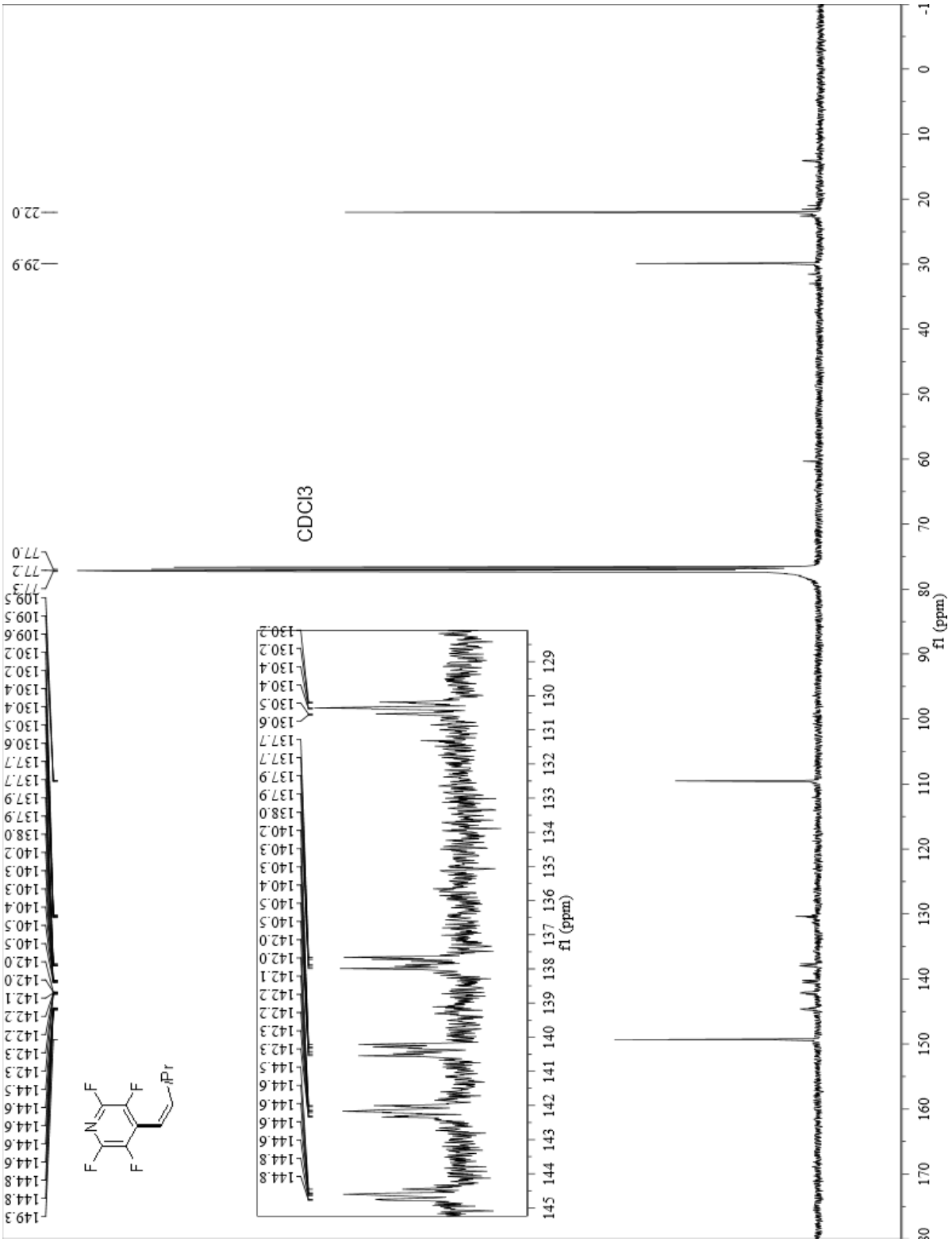
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-8a ((Z)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine)



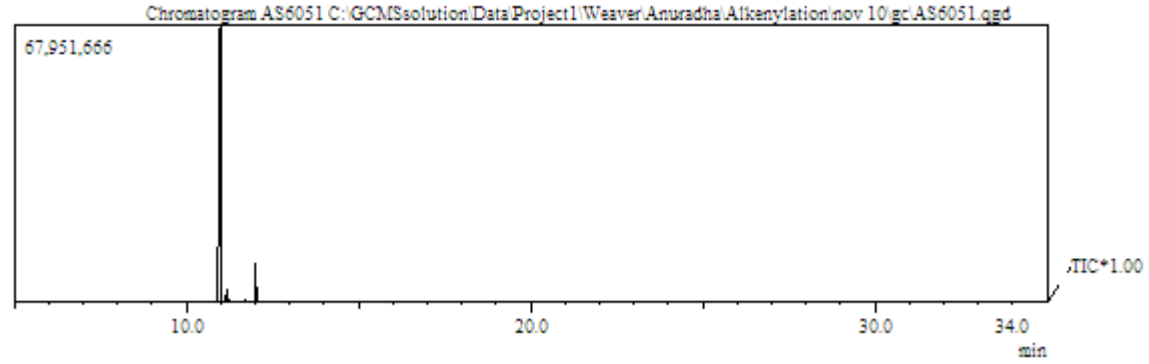
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-8a ((Z)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine

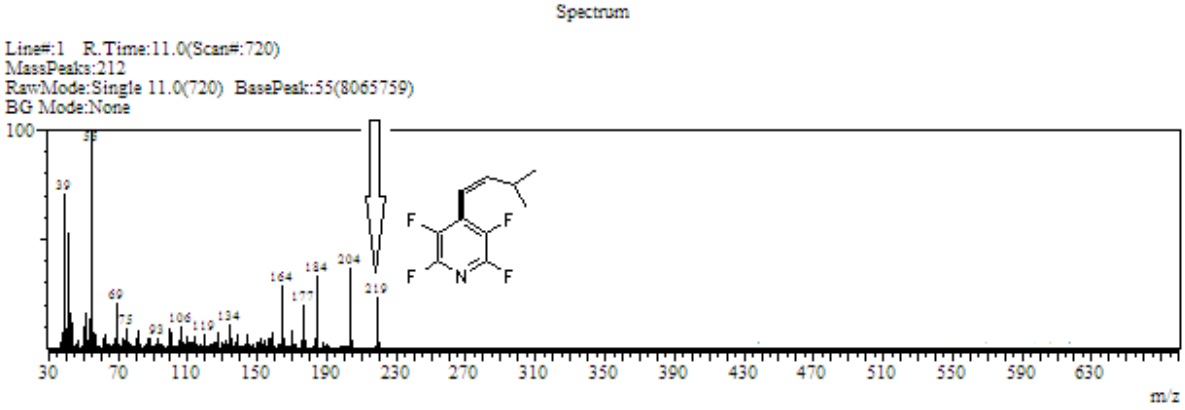


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-8a ((Z)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine)

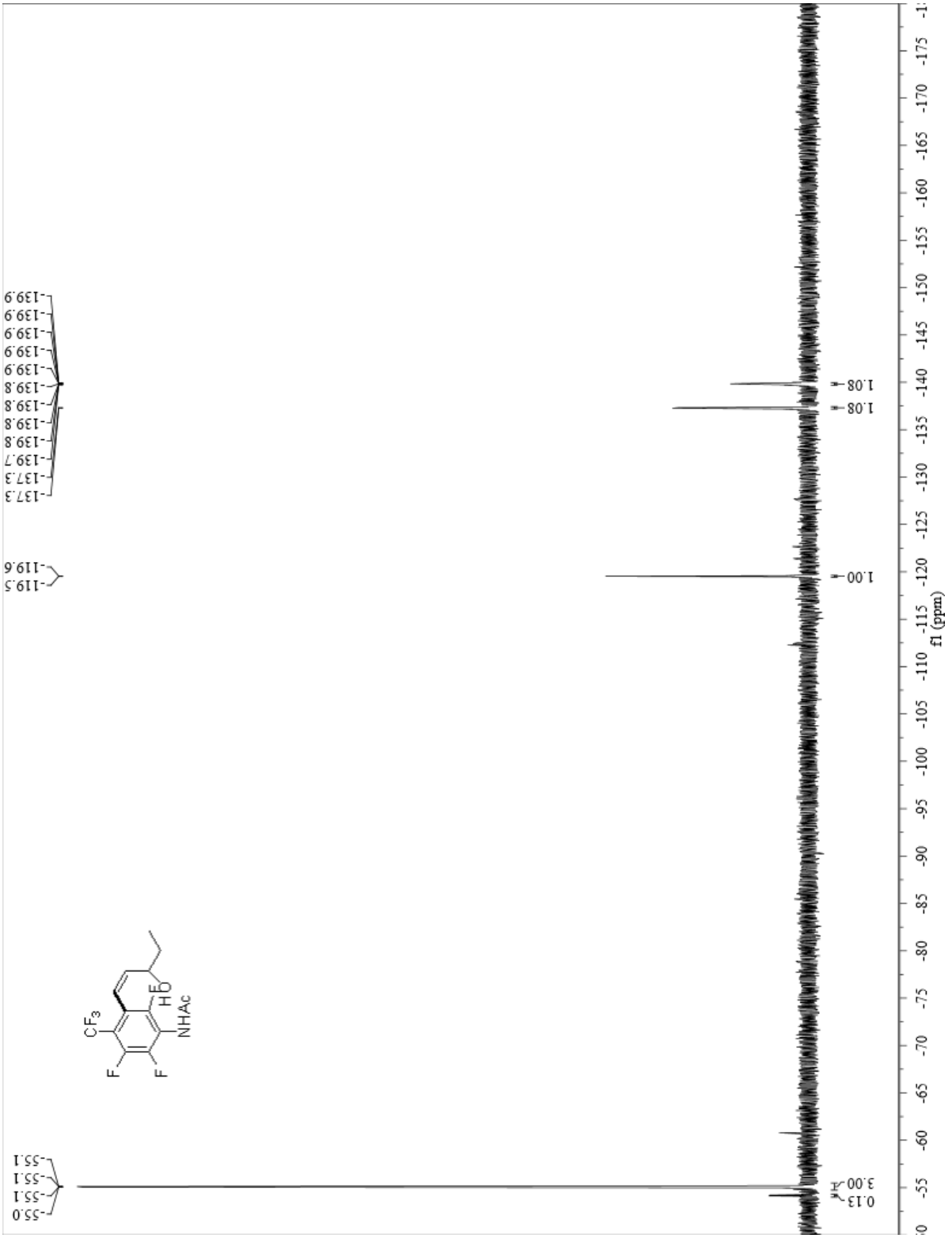


GC and MS of S-8a ((Z)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine)

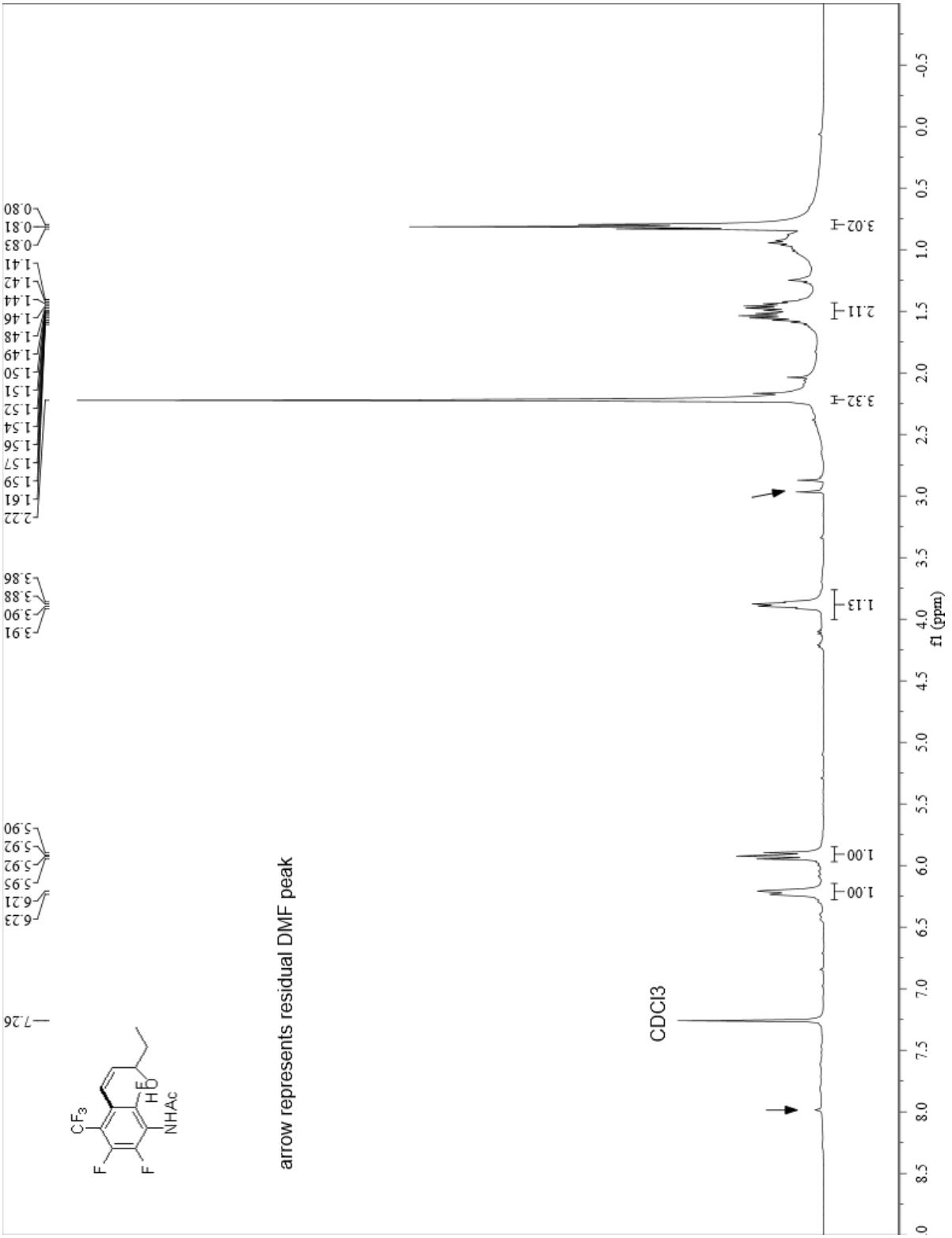




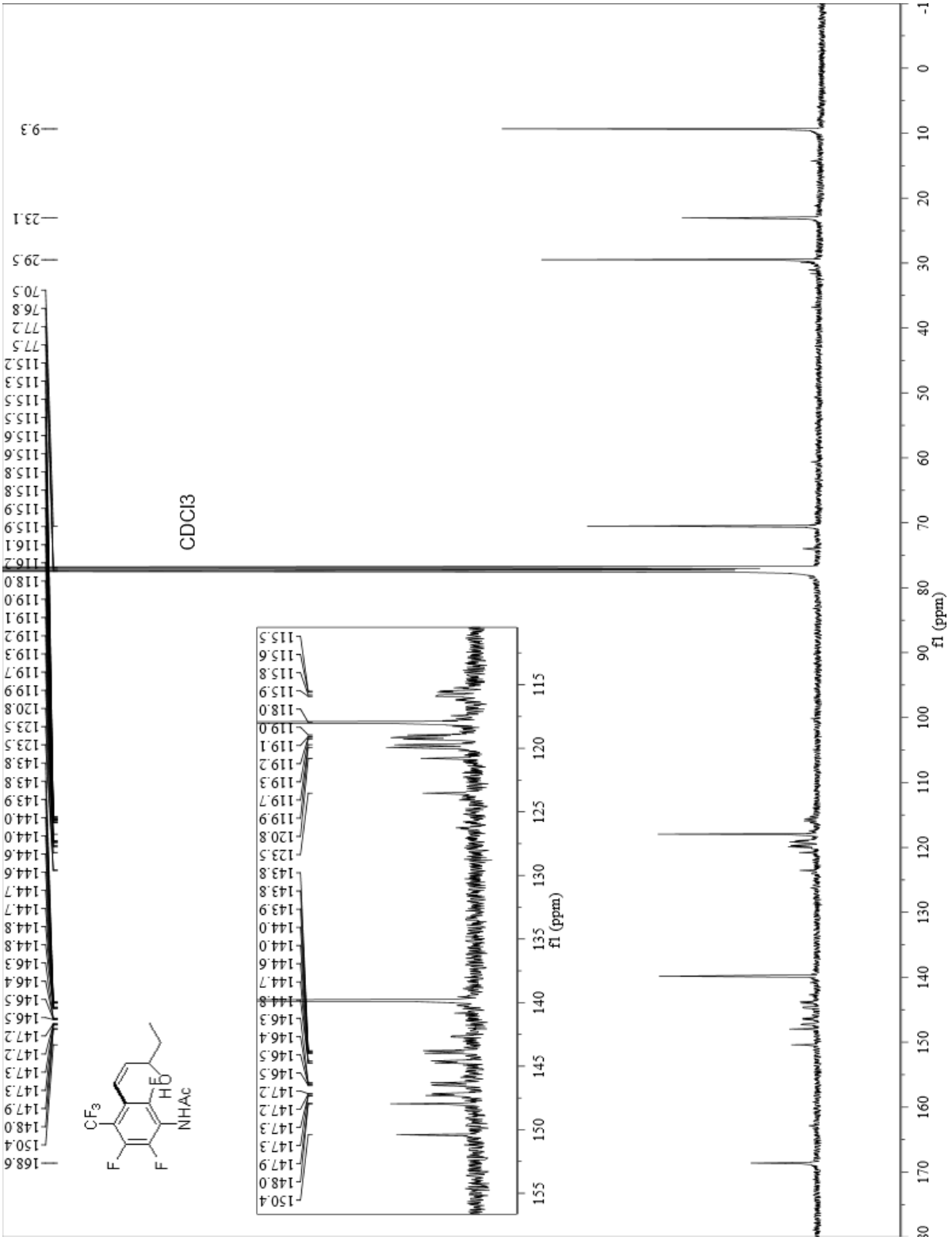
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-9a (Z)-N-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)-4-(trifluoromethyl)phenyl)acetamide)



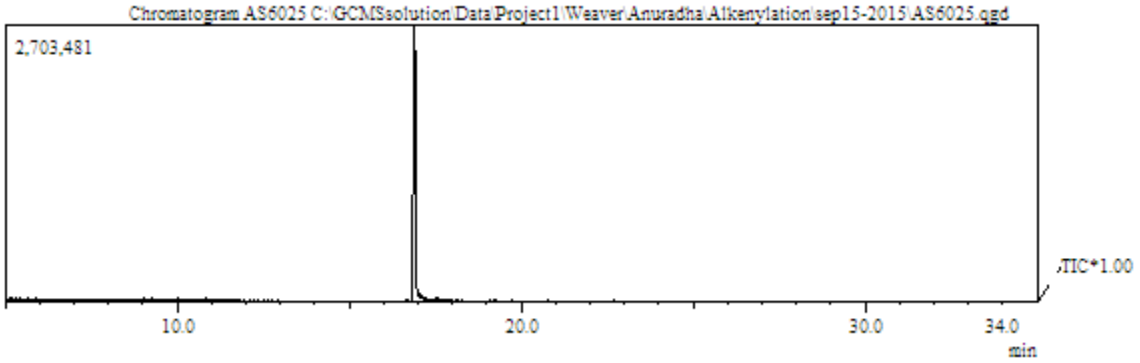
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-9a (Z)-N-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)-4-(trifluoromethyl)phenyl)acetamide)

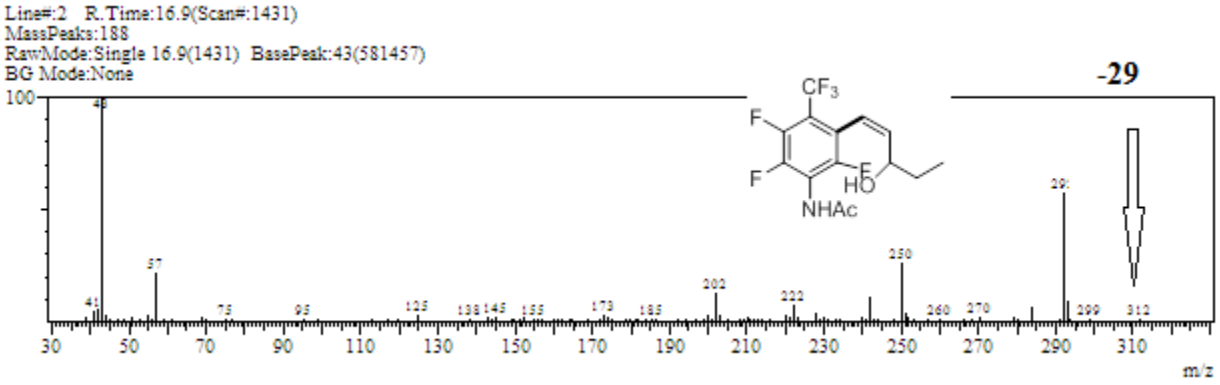


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-9a ((Z)-N-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)-4-(trifluoromethyl)phenyl)acetamide)

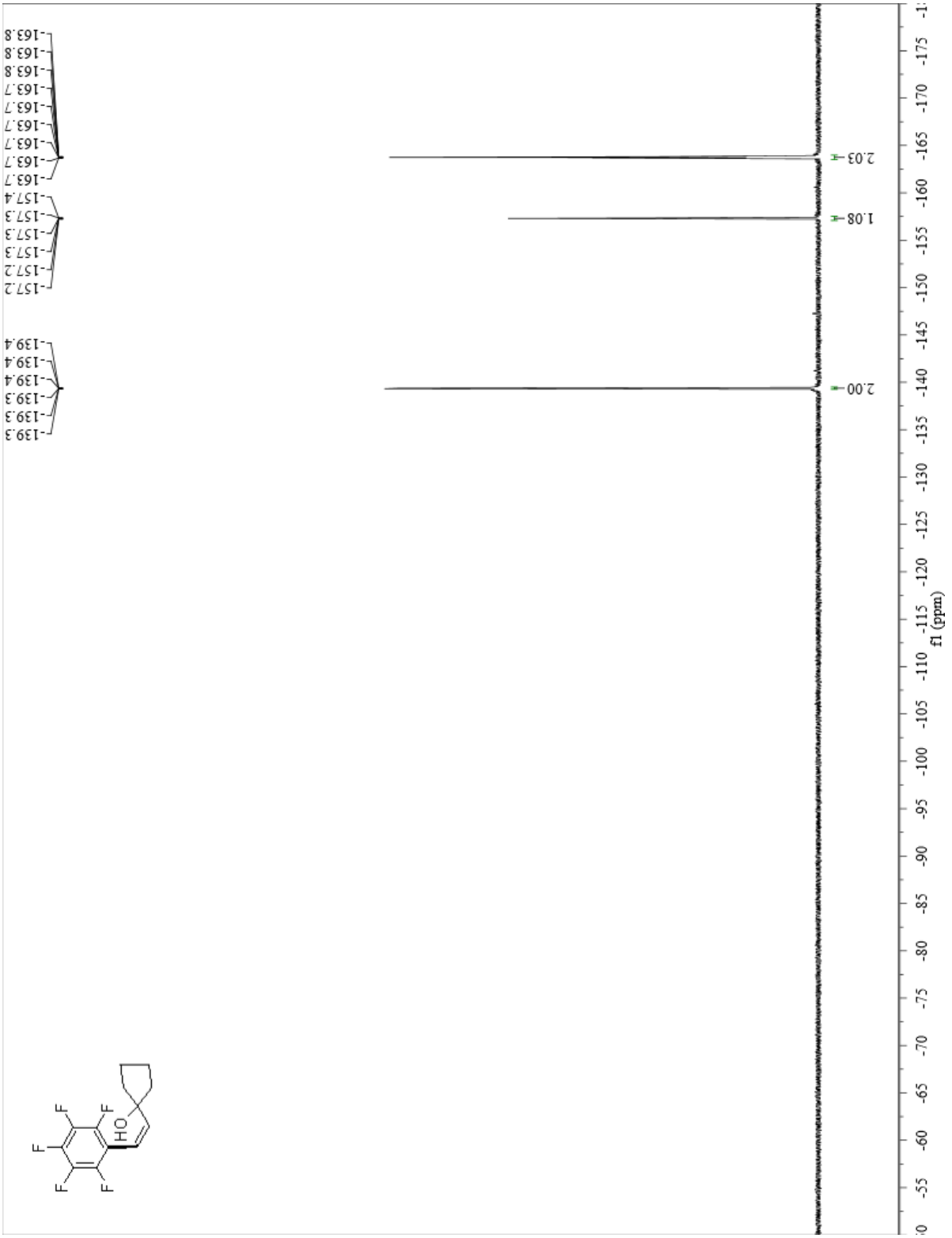


GC and MS of S-9a (Z)-N-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)-4-(trifluoromethyl)phenyl)acetamide)

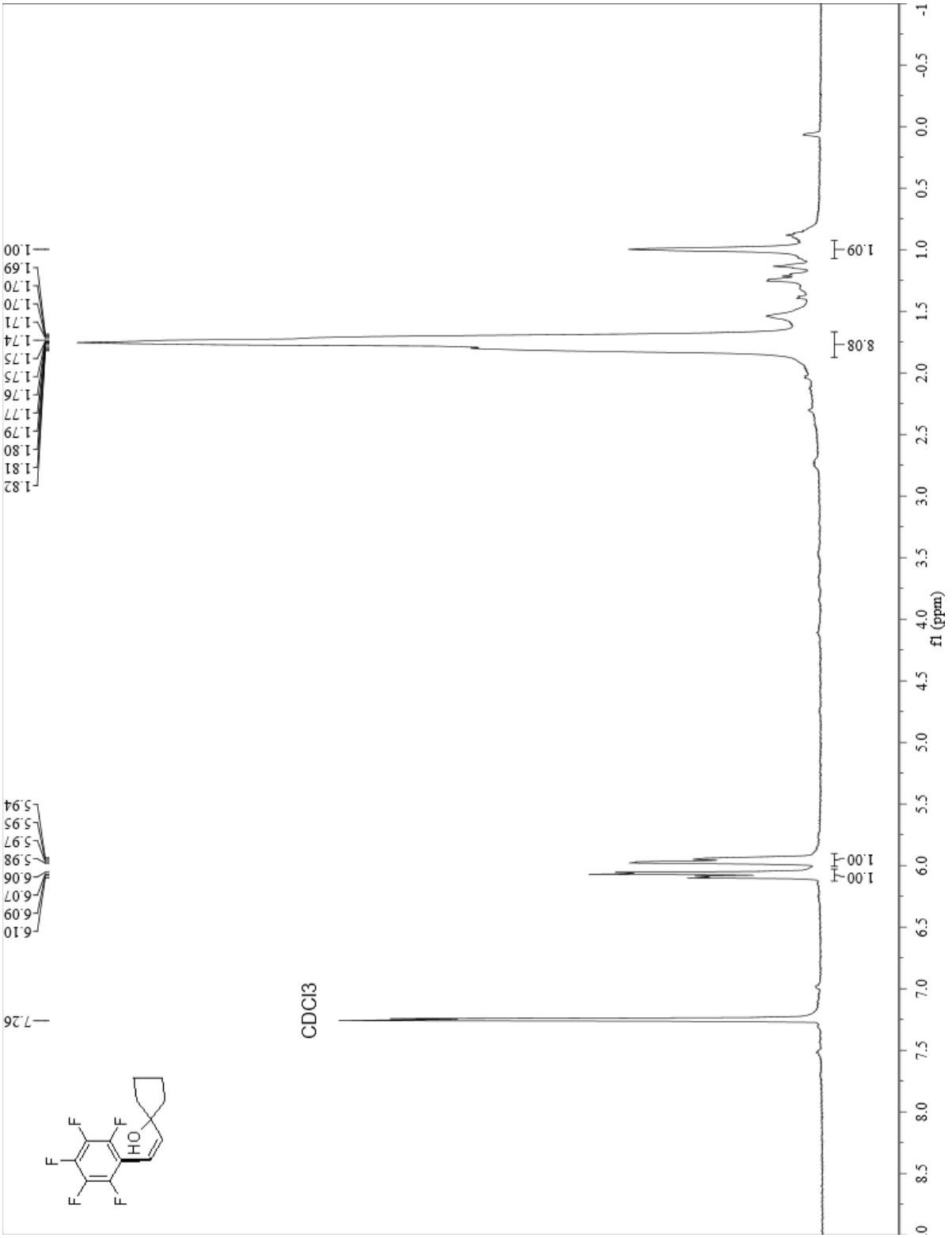




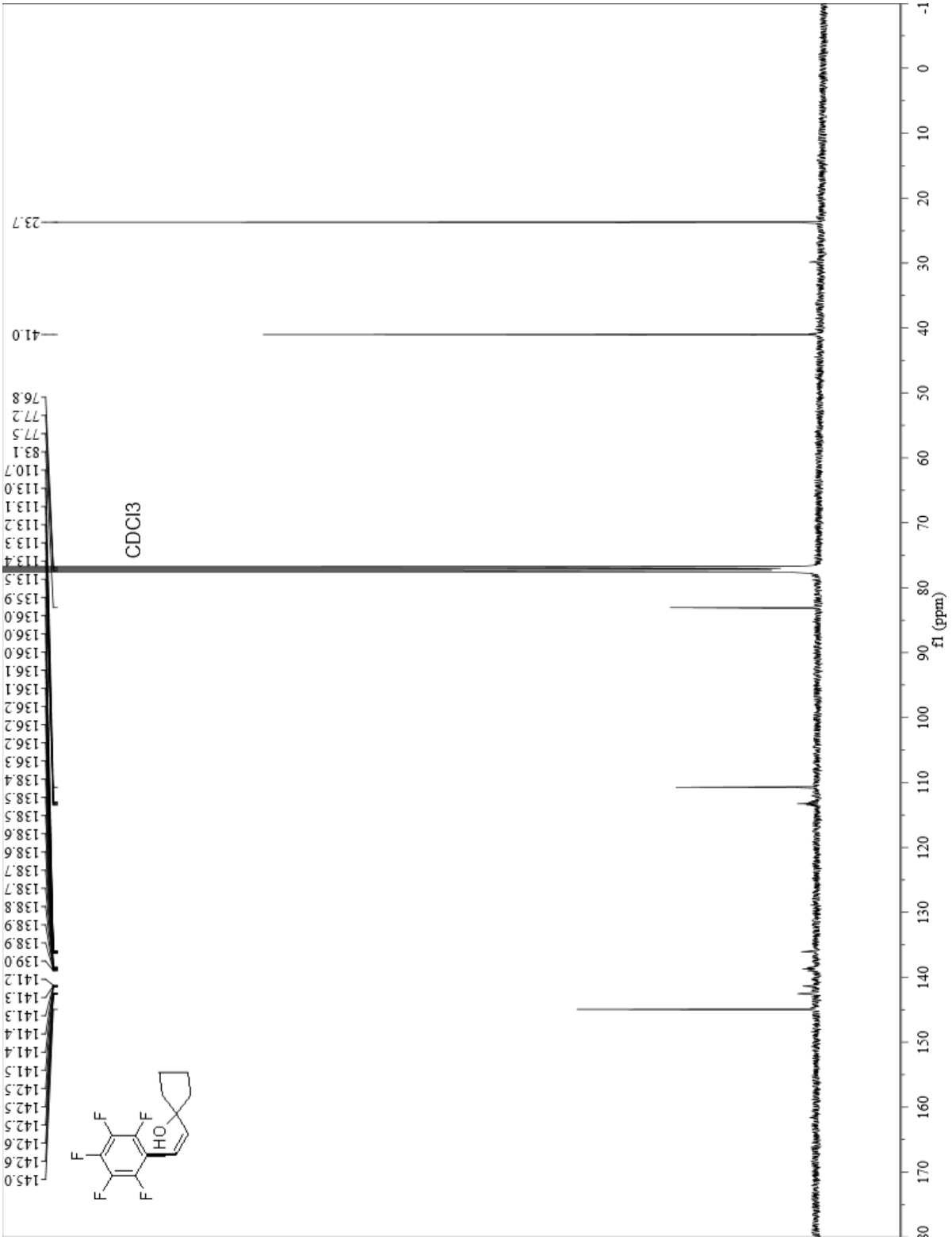
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-10a (Z)-1-(2-(perfluorophenyl)vinyl)cyclopentan-1-ol



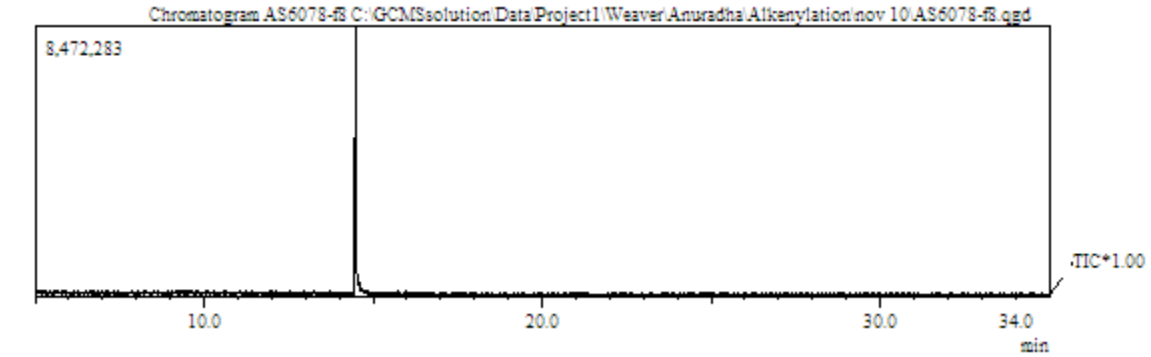
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-10a (Z)-1-(2-(perfluorophenyl)vinyl)cyclopentan-1-ol

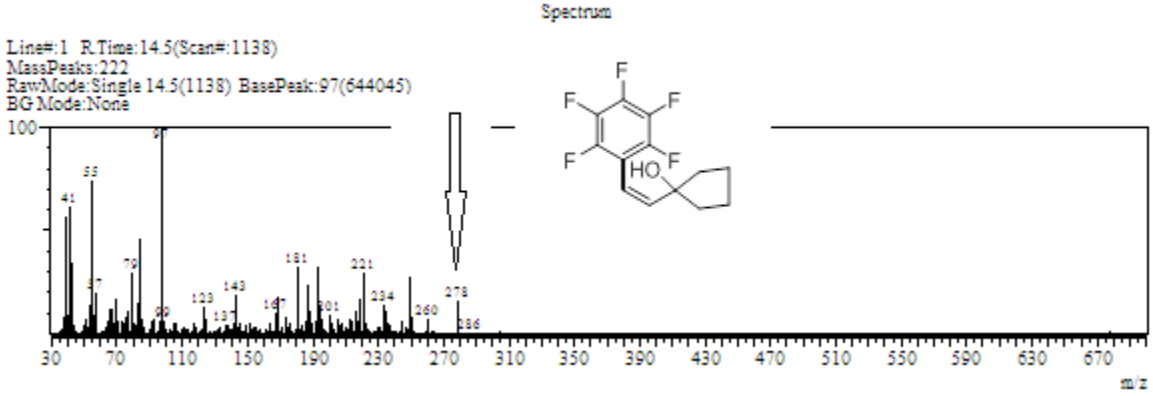


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-10a (Z)-1-(2-(perfluorophenyl)vinyl)cyclopentan-1-ol

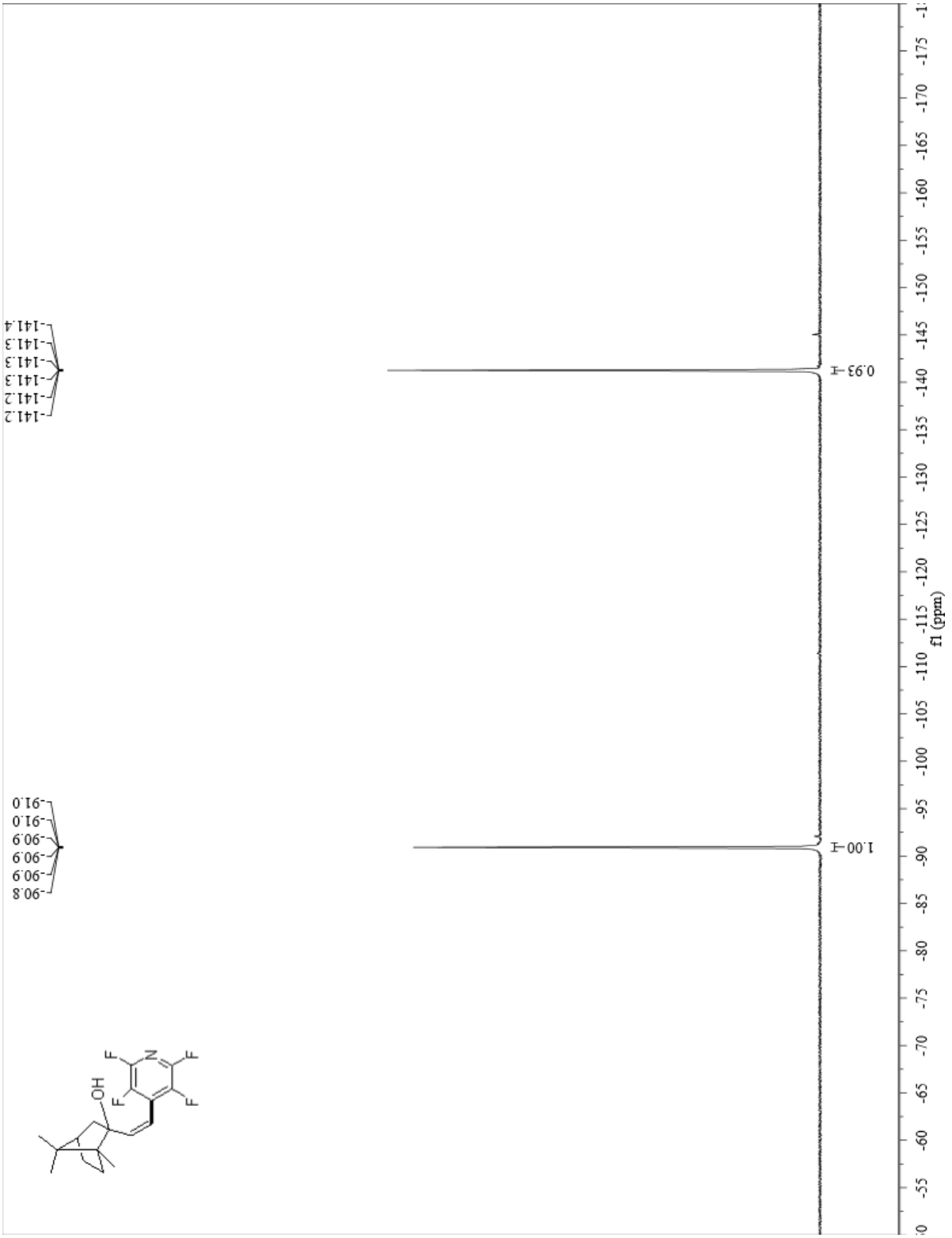


GC and MS of S-10a (Z)-1-(2-(perfluorophenyl)vinyl)cyclopentan-1-ol

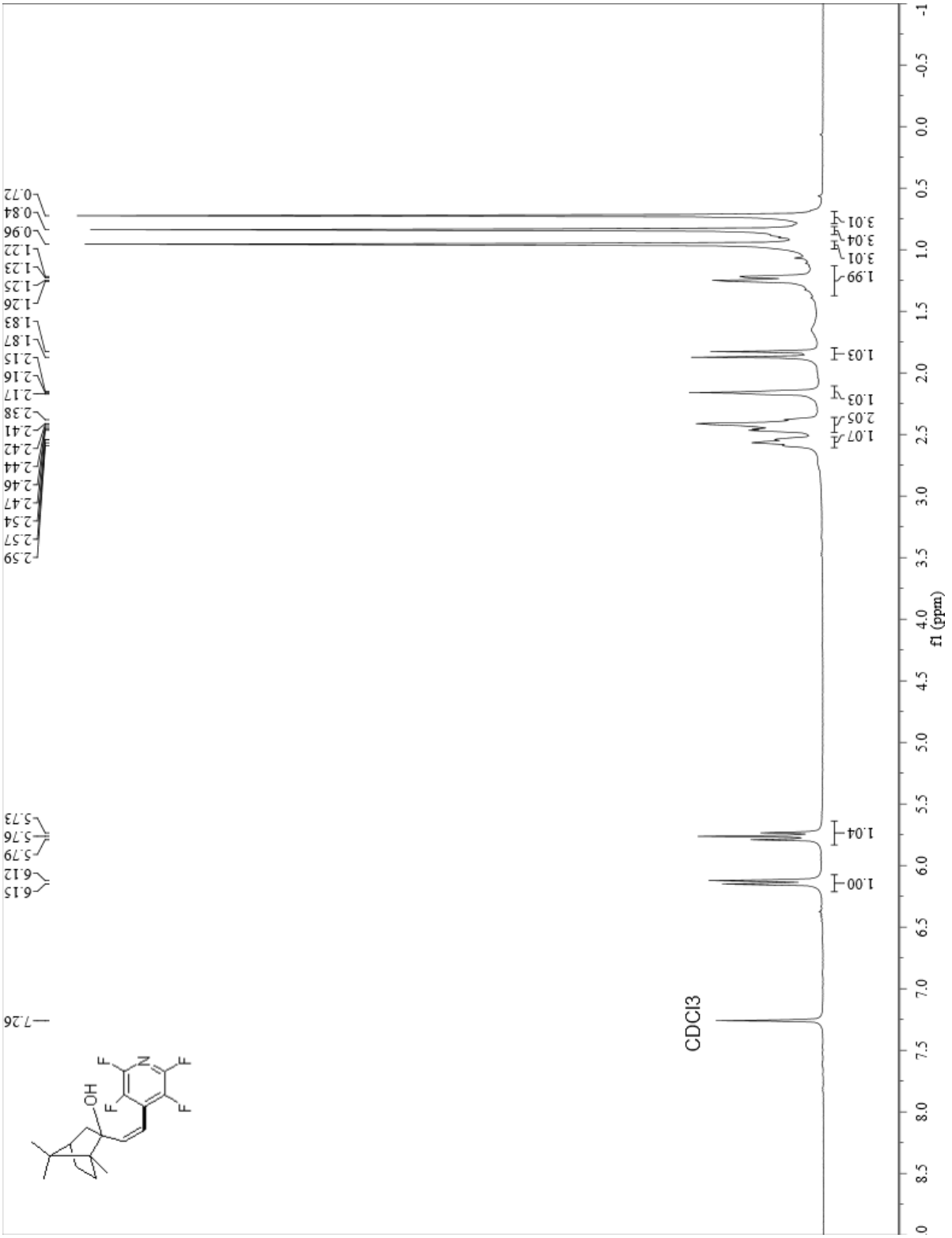




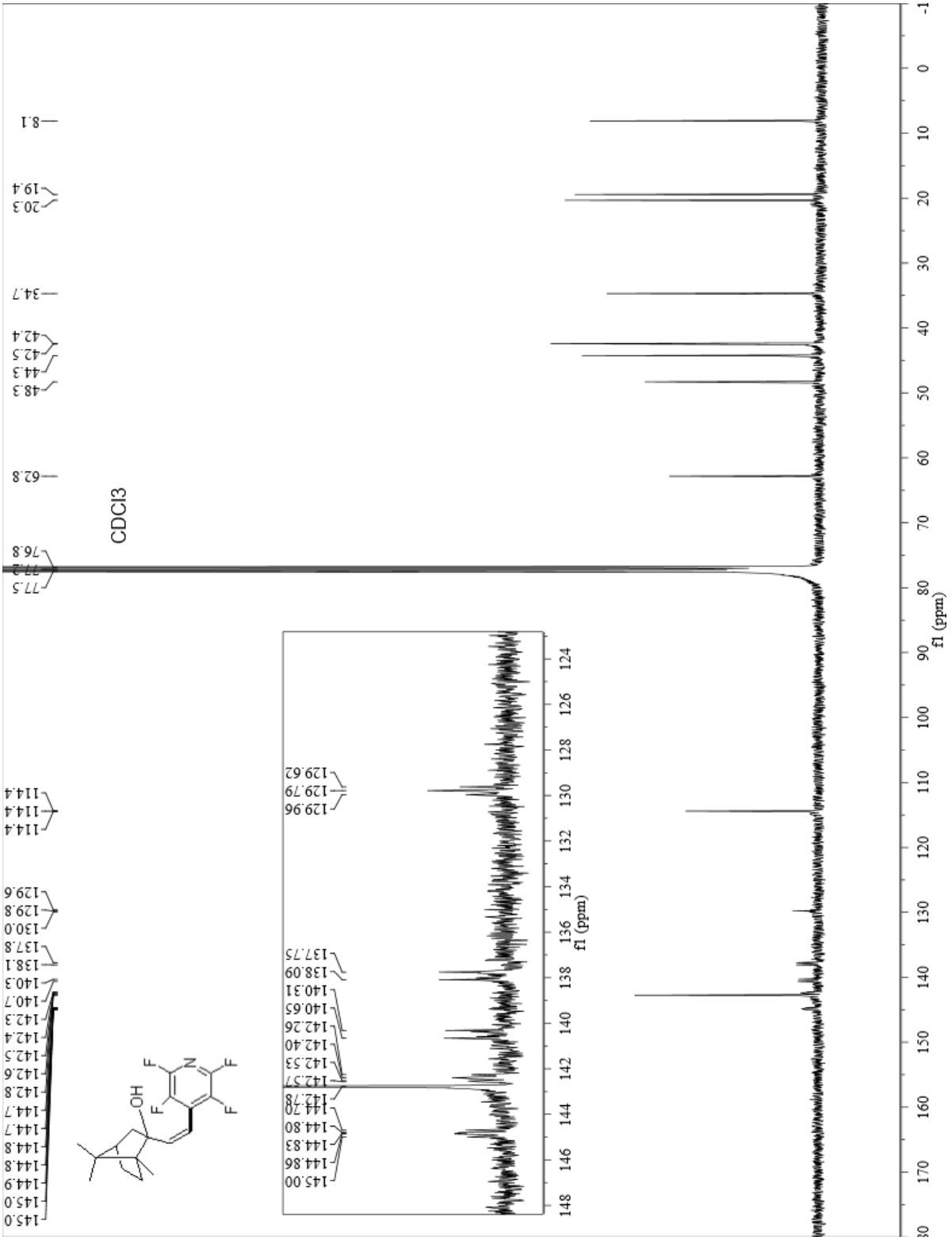
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-11a ((1S,2S,4R)-1,7,7-trimethyl-2-((Z)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol)



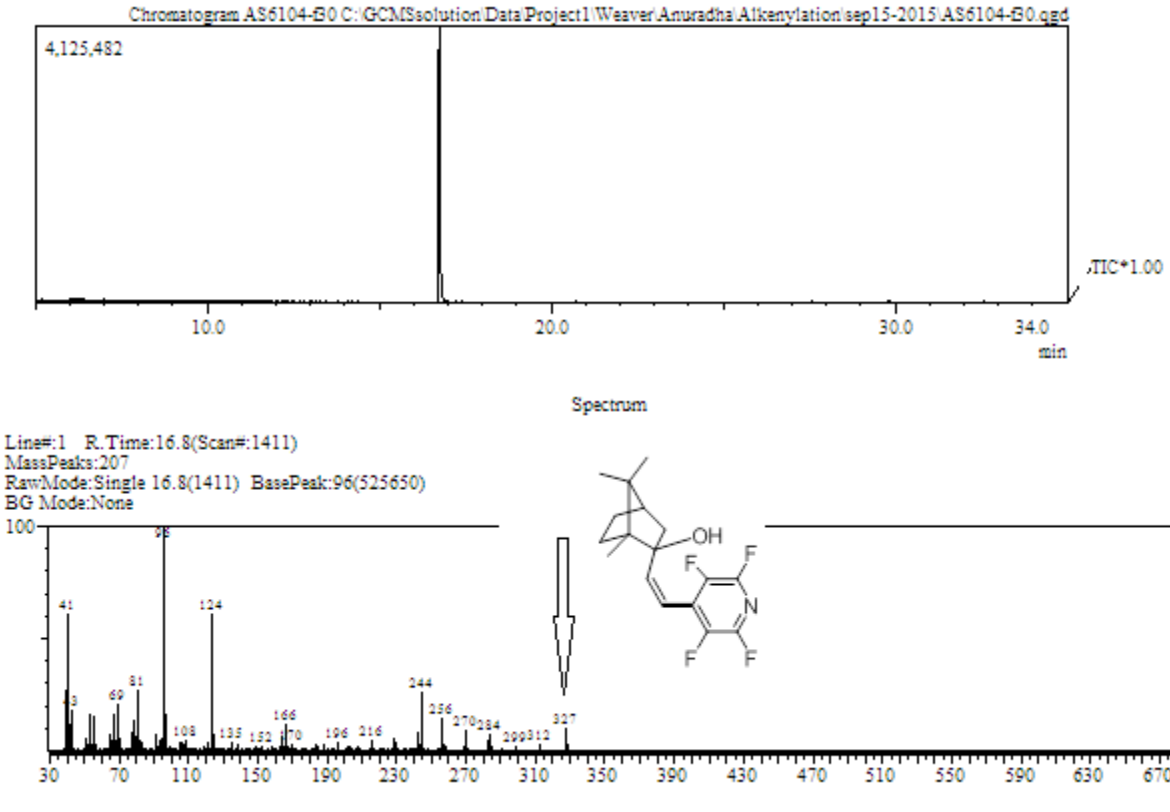
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-11a ((1S,2S,4R)-1,7,7-trimethyl-2-((Z)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol)



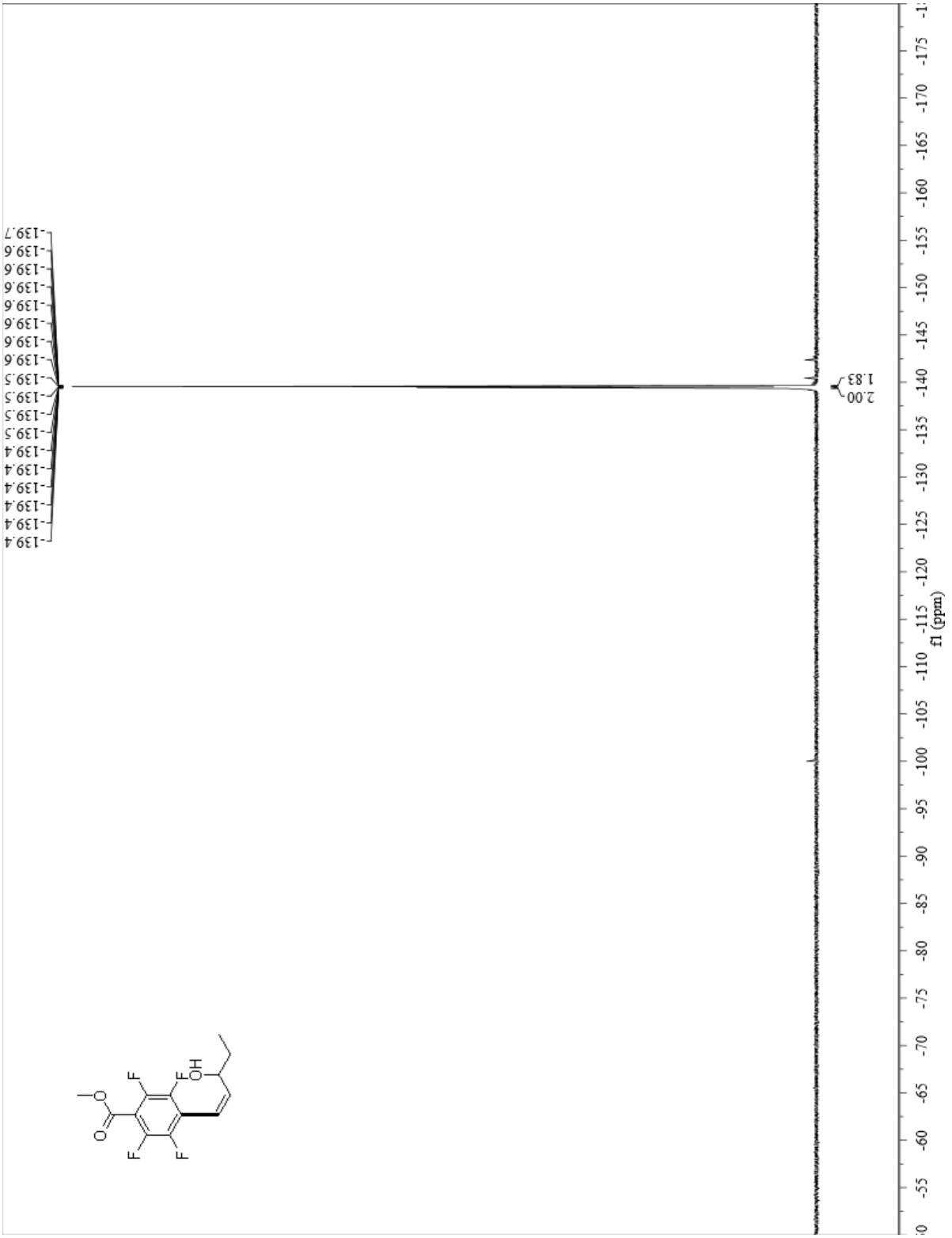
^{13}C NMR of (101 MHz, Chloroform-*d*, at rt) S-11a ((1S,2S,4R)-1,7,7-trimethyl-2-((Z)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol)



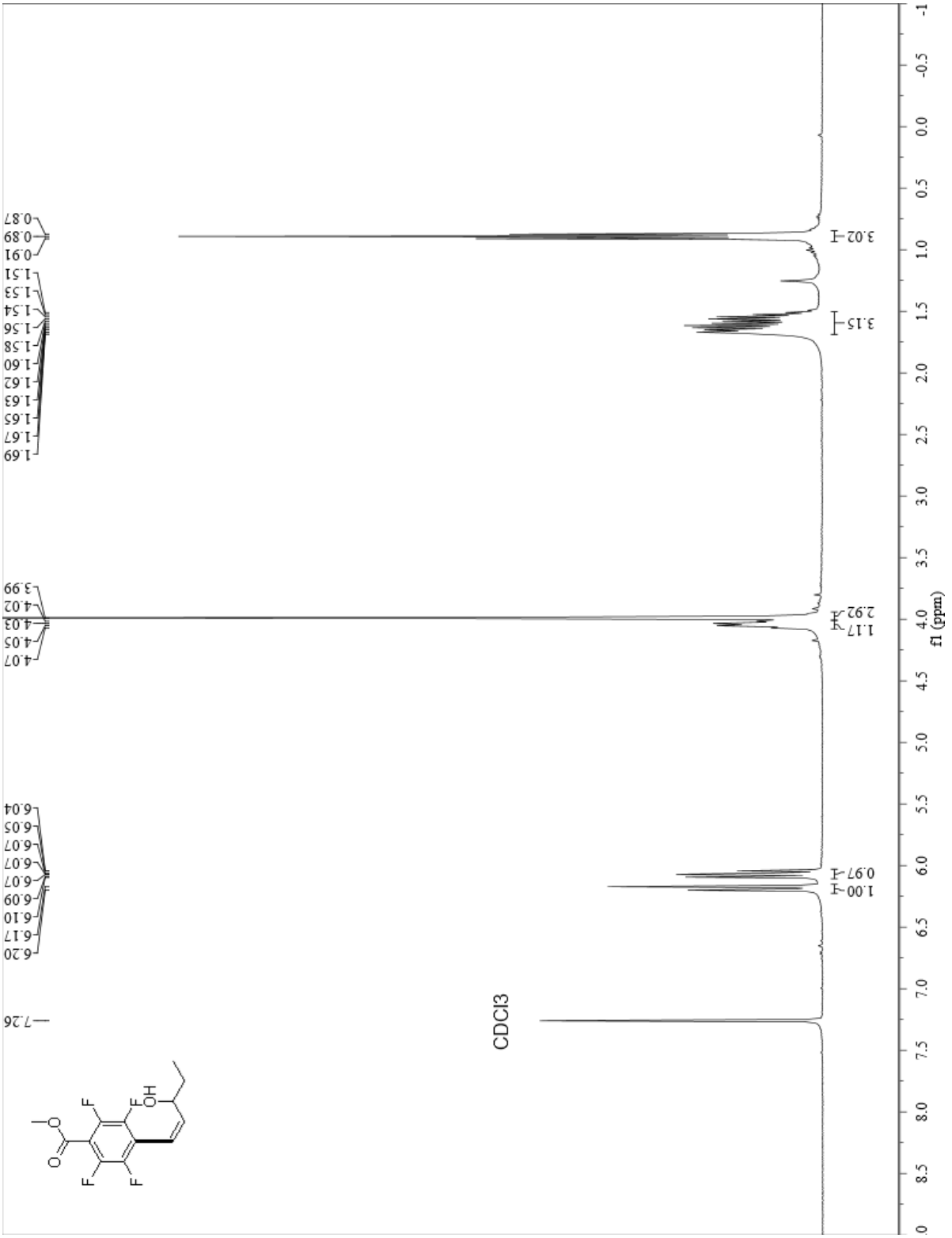
GC and MS of S-11a ((1S,2S,4R)-1,7,7-trimethyl-2-((Z)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol)



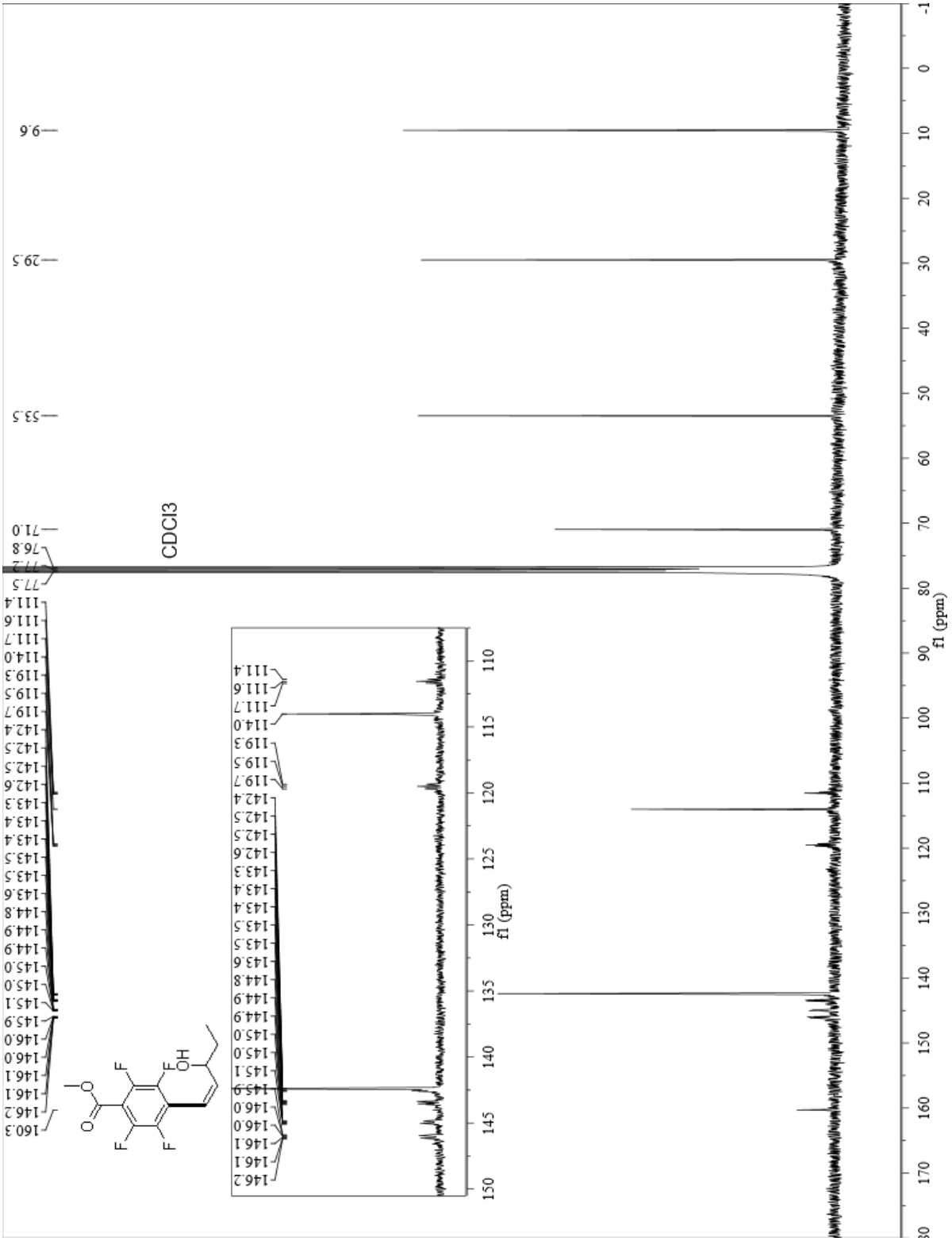
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-12a (methyl (Z)-2,3,5,6-tetrafluoro-4-(3-hydroxypent-1-en-1-yl)benzoate)



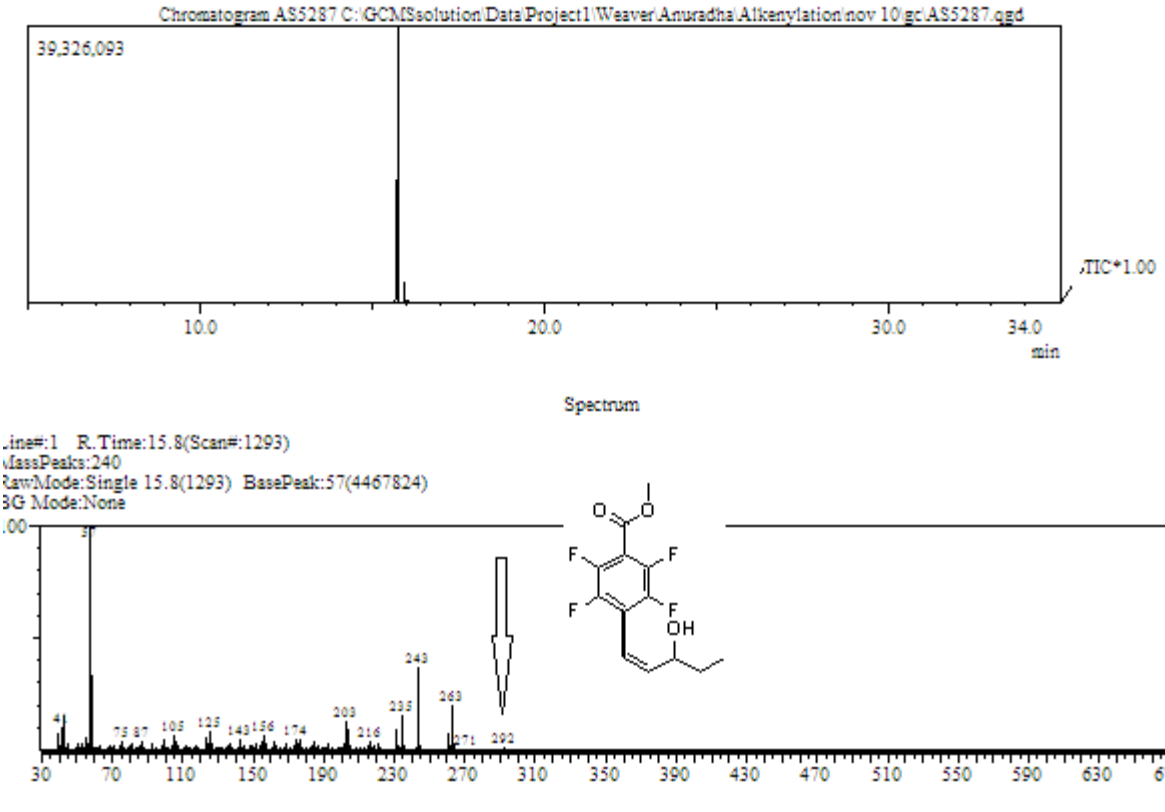
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-12a (methyl (Z)-2,3,5,6-tetrafluoro-4-(3-hydroxypent-1-en-1-yl)benzoate)



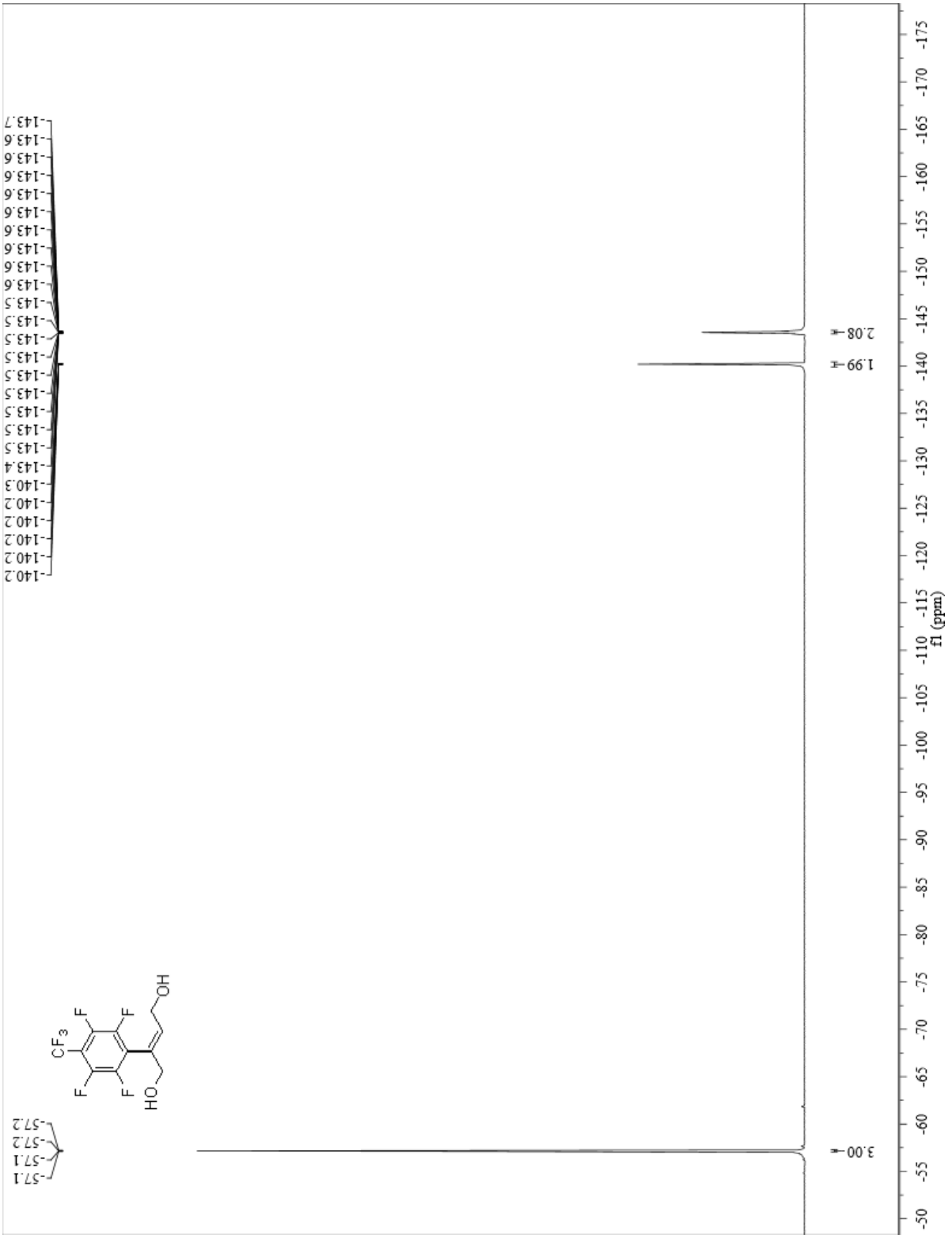
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-12a (methyl (Z)-2,3,5,6-tetrafluoro-4-(3-hydroxypent-1-en-1-yl)benzoate)



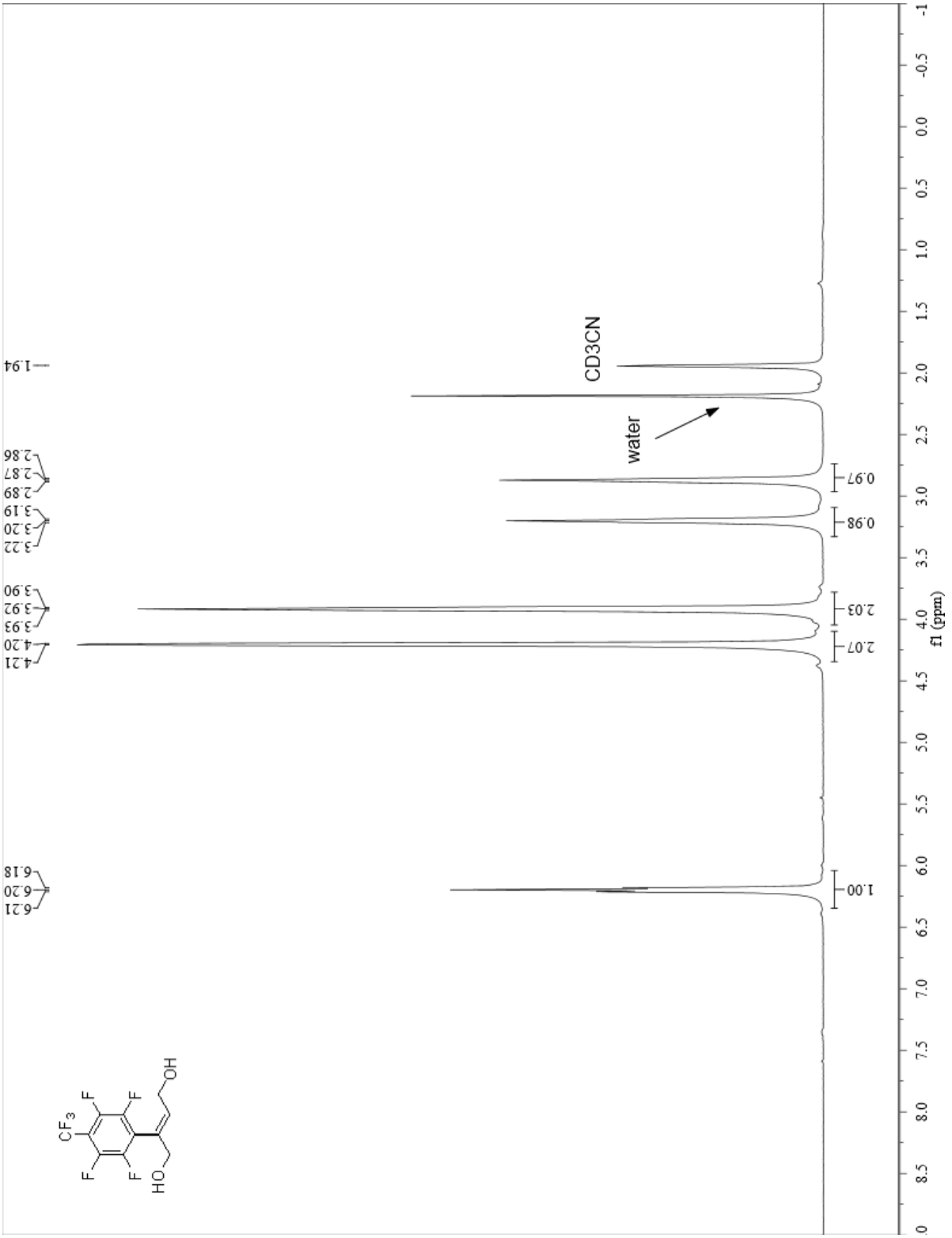
GC and MS of S-12a (methyl (Z)-2,3,5,6-tetrafluoro-4-(3-hydroxypent-1-en-1-yl)benzoate)



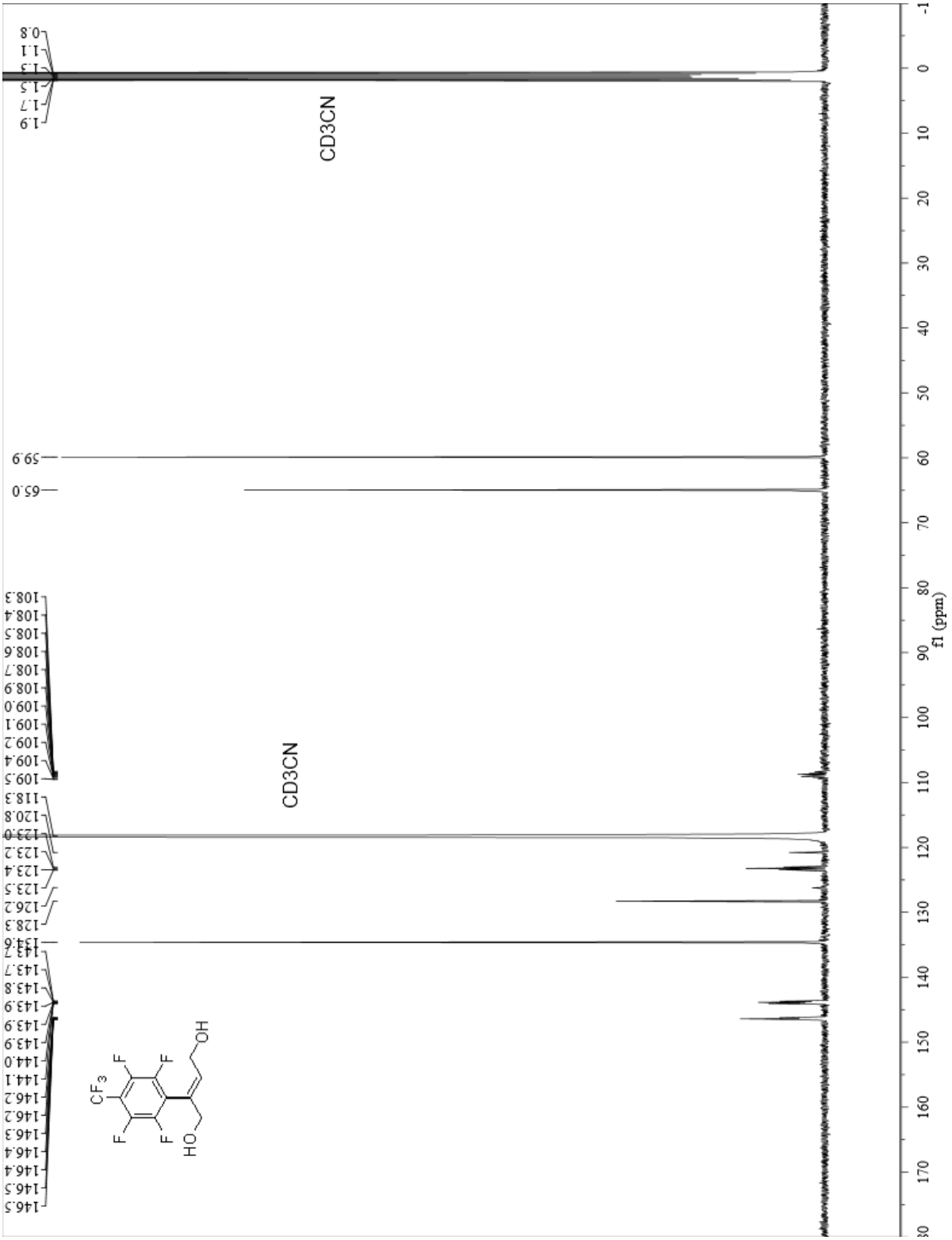
^{19}F NMR (376 MHz, Acetonitrile-*d*$_3$, at rt) of S-13a ((E)-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)but-2-ene-1,4-diol)



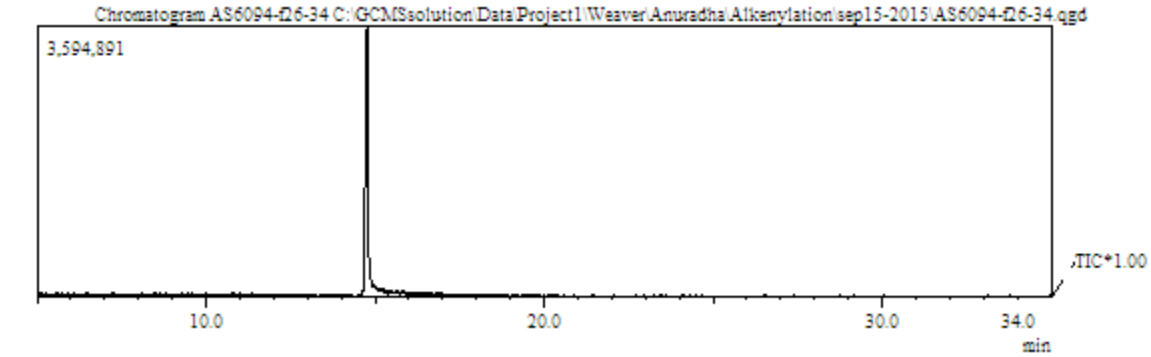
^{1}H NMR (400 MHz, Acetonitrile-d_3, at rt) of S-13a ((E)-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)but-2-ene-1,4-diol)

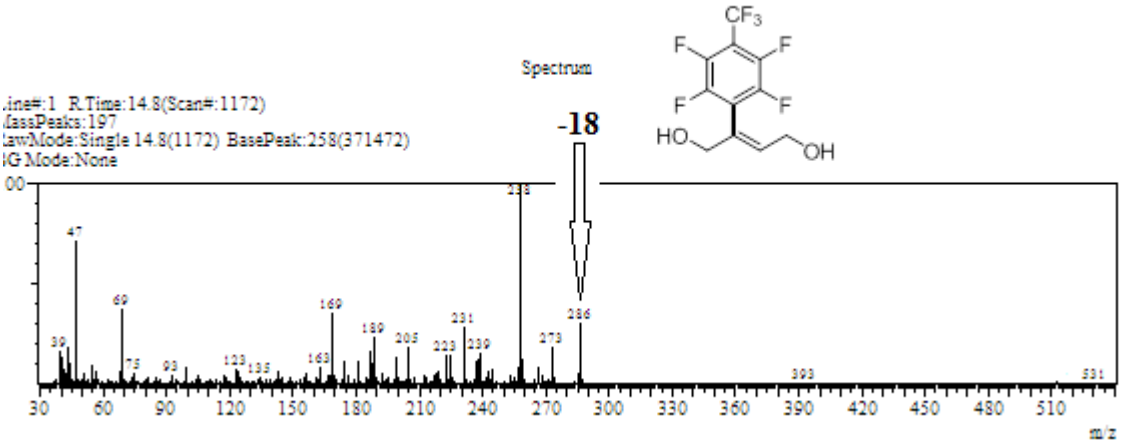


^{13}C NMR (101 MHz, Acetonitrile-d_3, at rt) of S-13a ((E)-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)but-2-ene-1,4-diol)

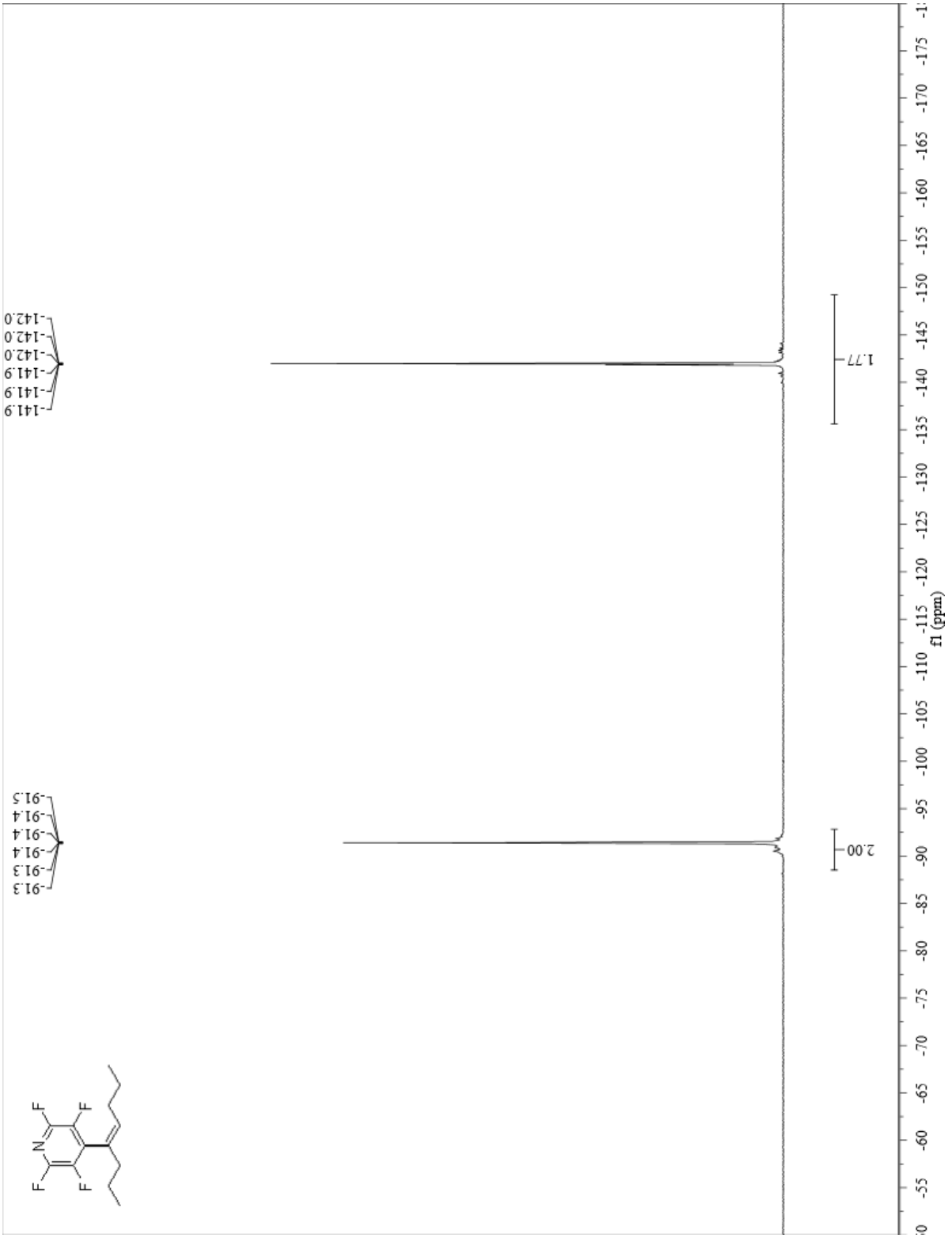


GC and MS of S-13a ((E)-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)but-2-ene-1,4-diol)

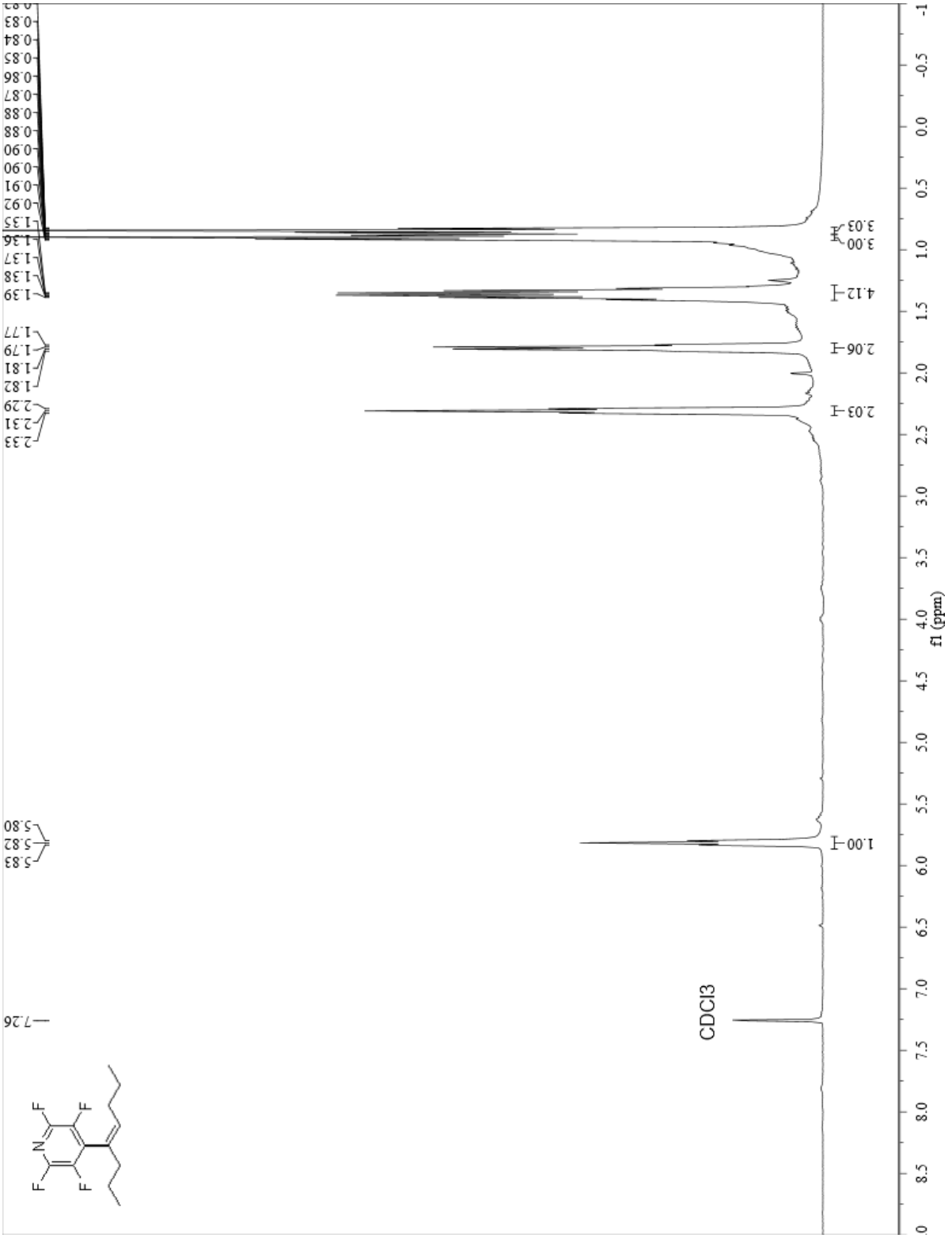




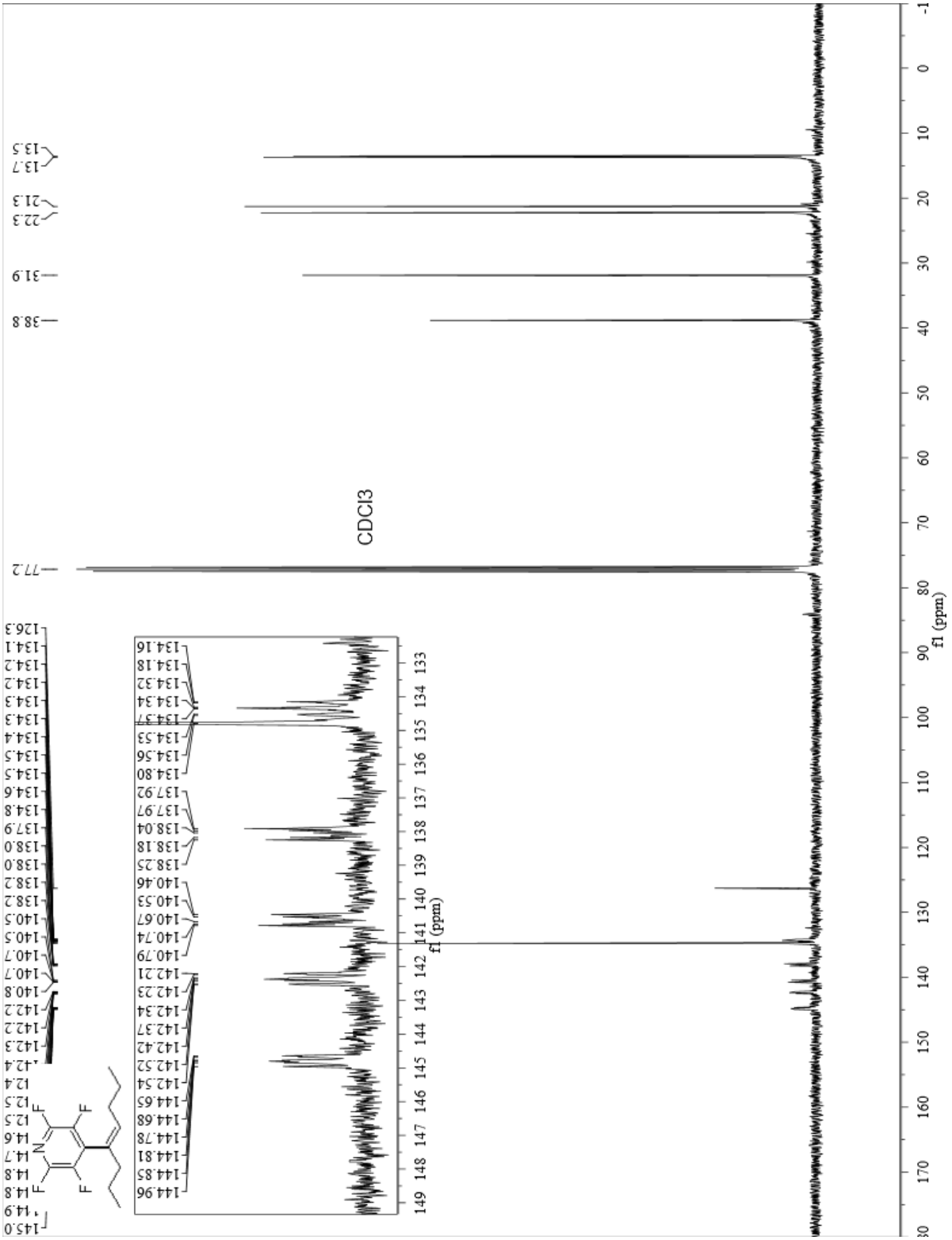
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-14a ((Z)-2,3,5,6-tetrafluoro-4-(oct-4-en-4-yl)pyridine)



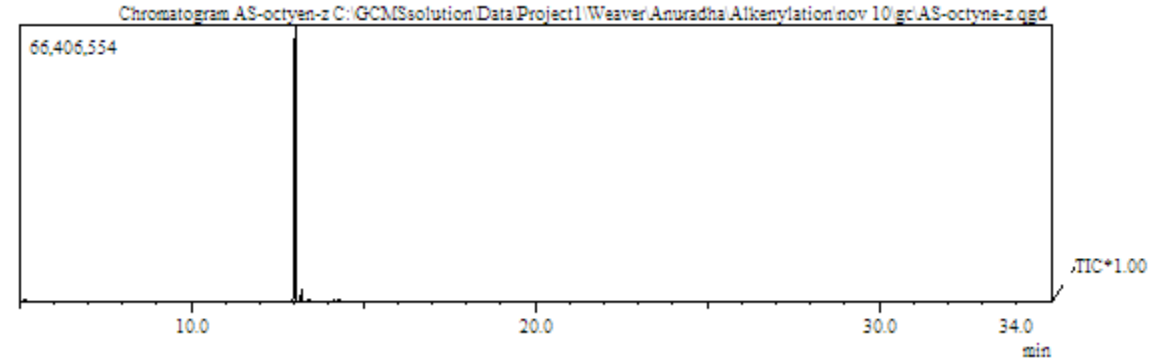
^{1}H NMR (376 MHz, Chloroform-*d*, at rt) of S-14a ((Z)-2,3,5,6-tetrafluoro-4-(oct-4-en-4-yl)pyridine)



^{13}C NMR (376 MHz, Chloroform-*d*, at rt) of S-14a ((Z)-2,3,5,6-tetrafluoro-4-(oct-4-en-4-yl)pyridine)



GC and MS of of S-14a ((Z)-2,3,5,6-tetrafluoro-4-(oct-4-en-4-yl)pyridine)



Spectrum

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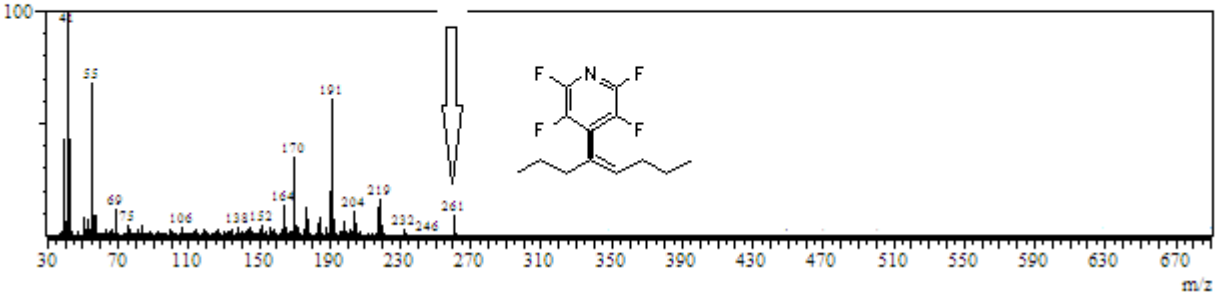
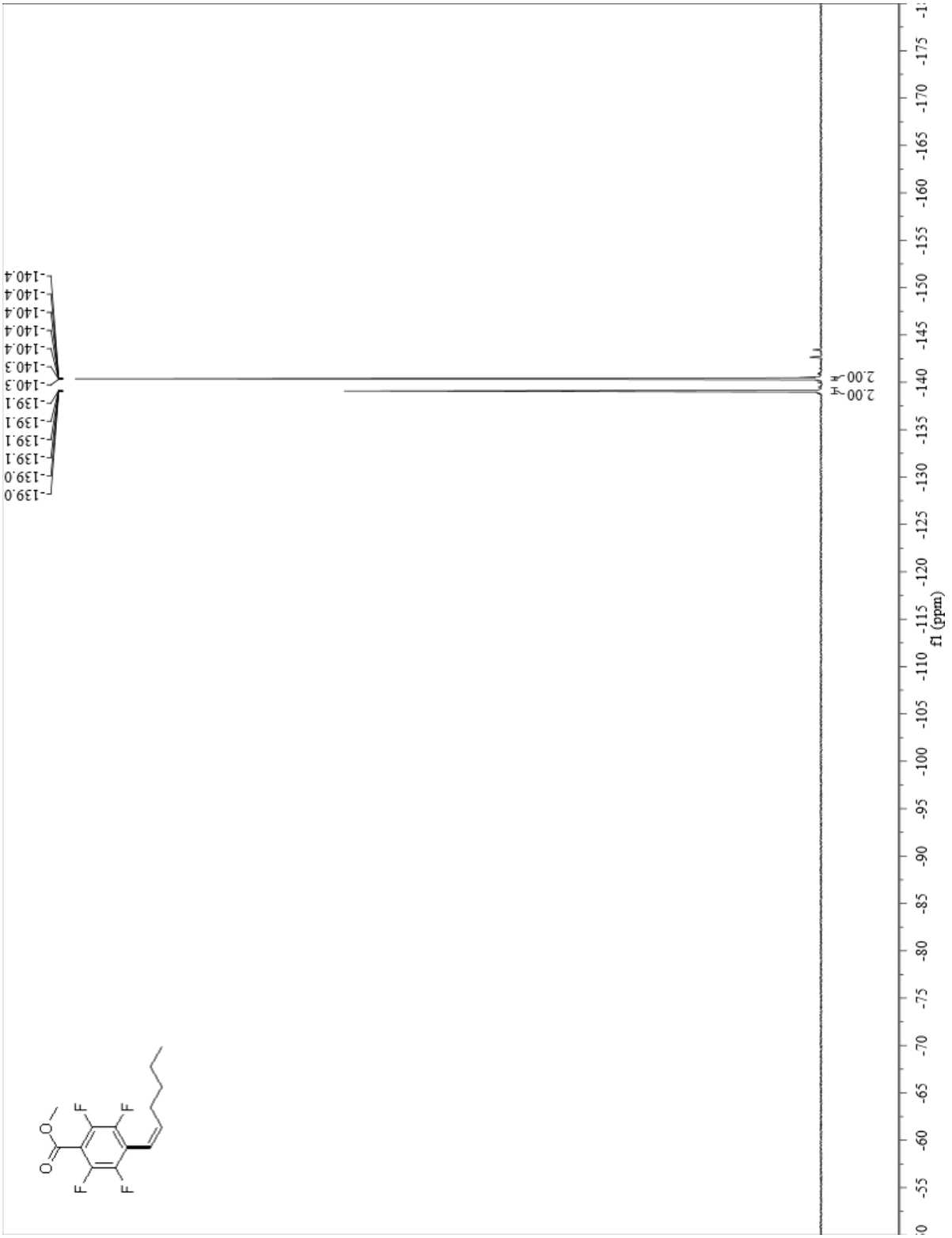
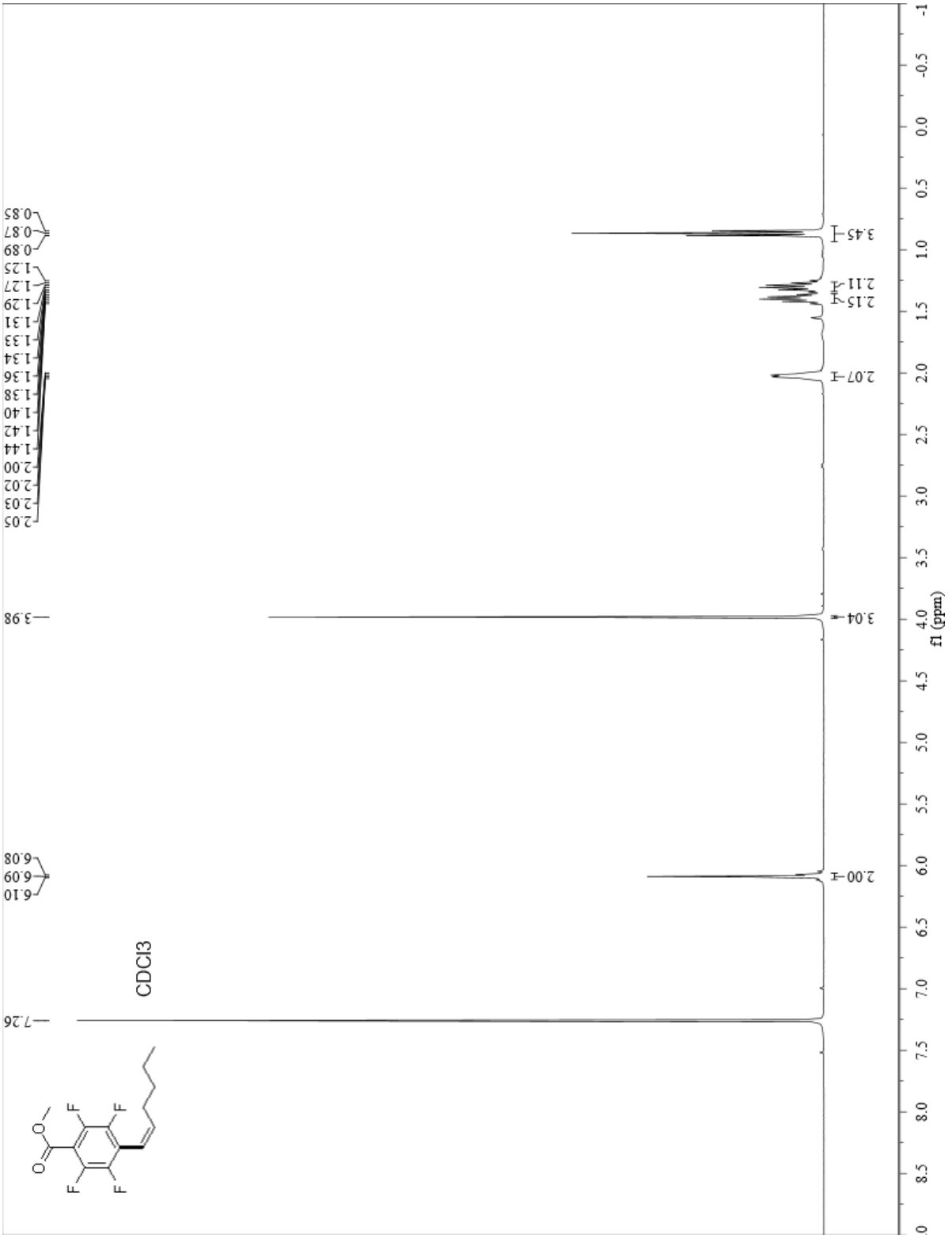


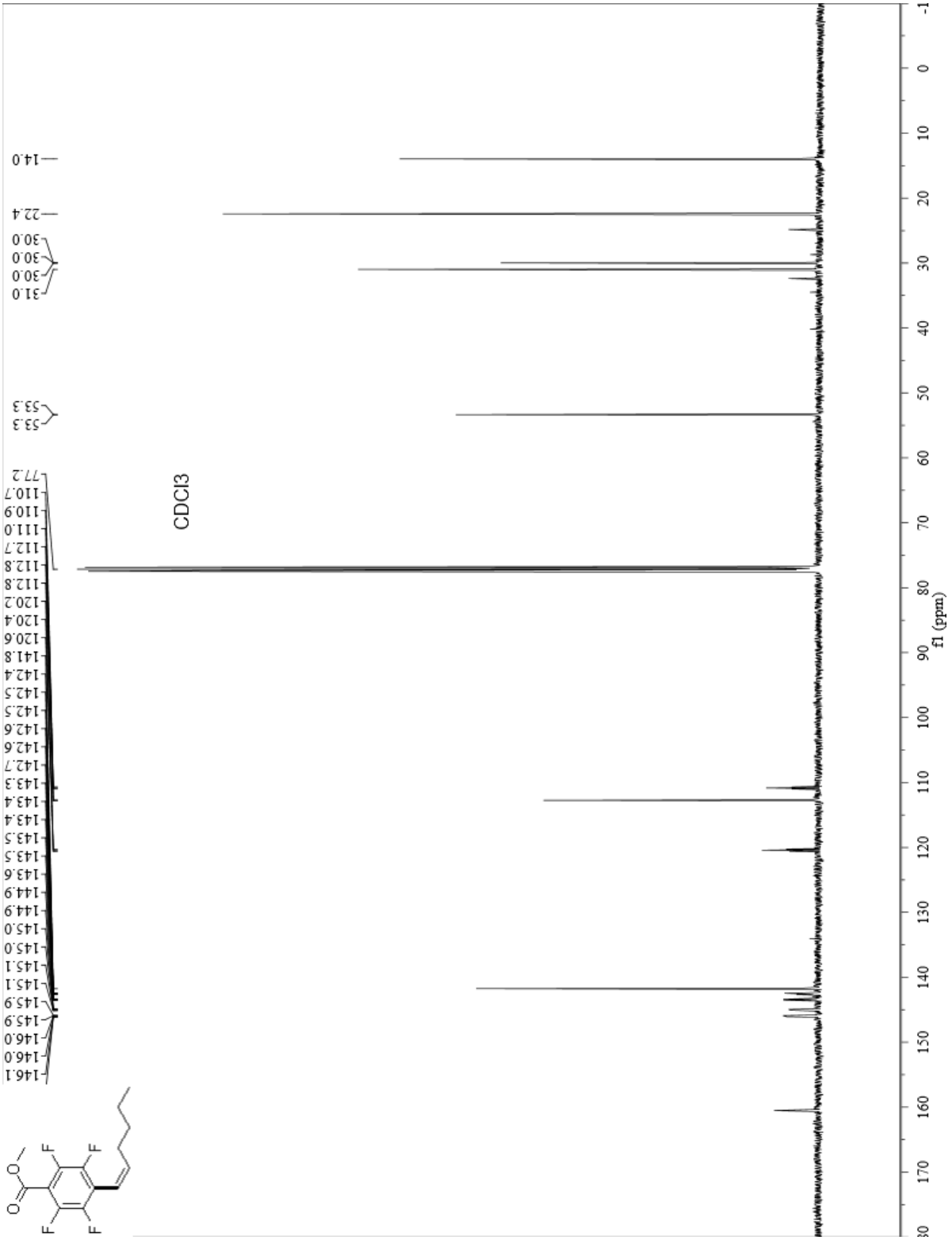
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-15a (methyl (Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)benzoate)



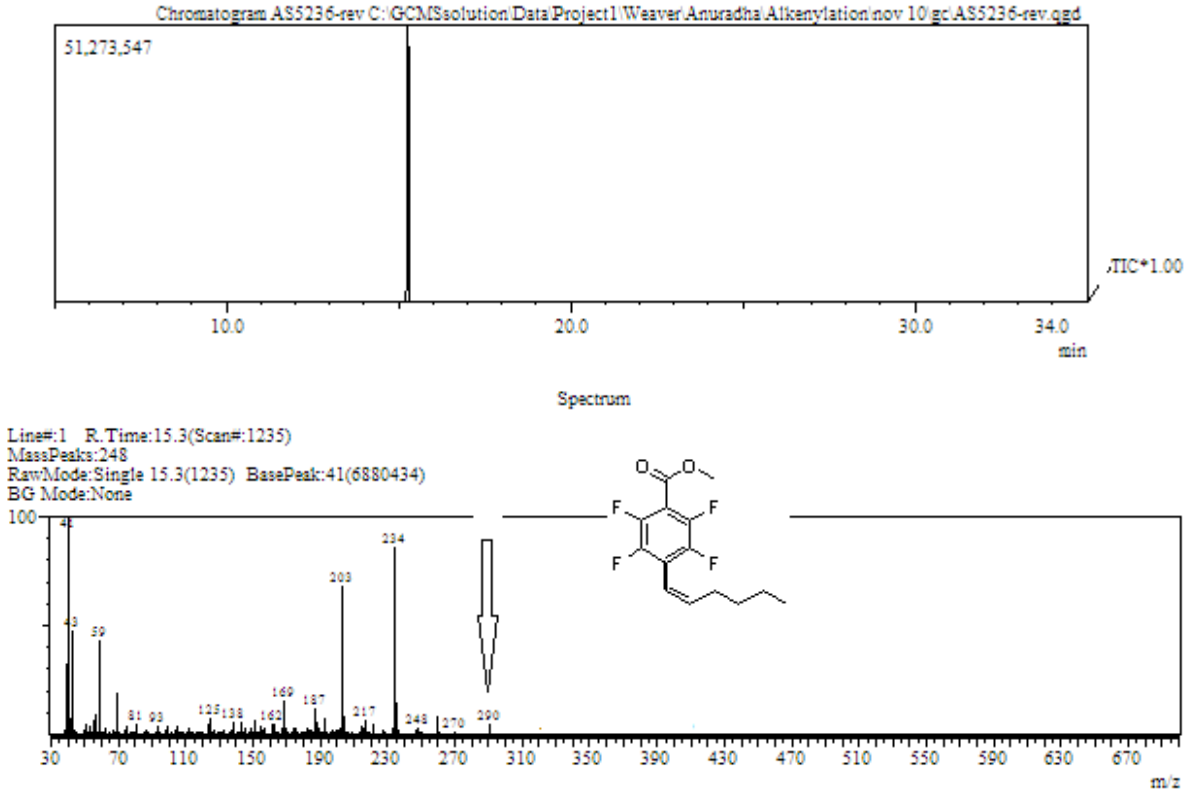
^{19}H NMR (400 MHz, Chloroform-*d*, at rt) of S-15a (methyl (Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)benzoate)



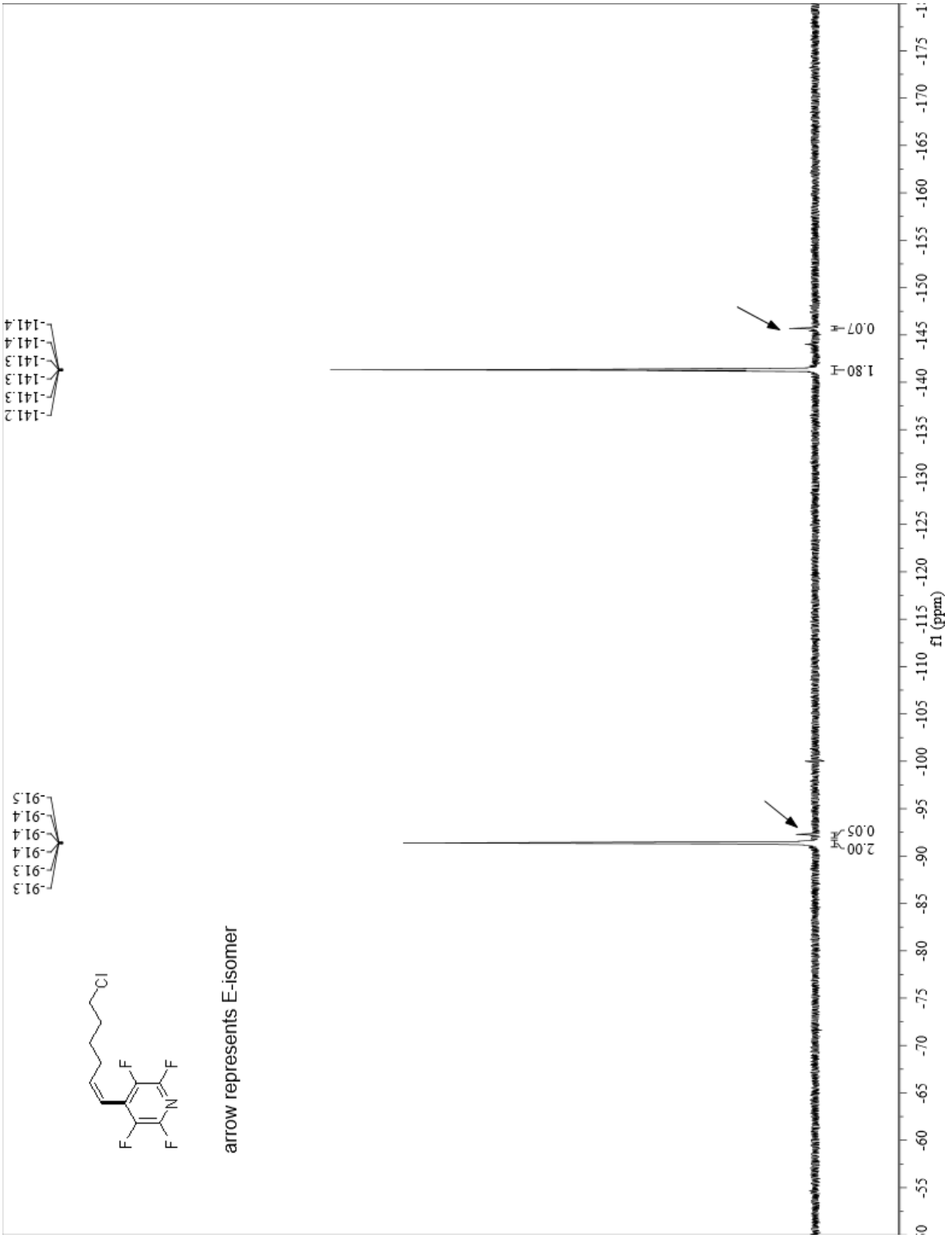
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-15a (methyl (Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)benzoate)



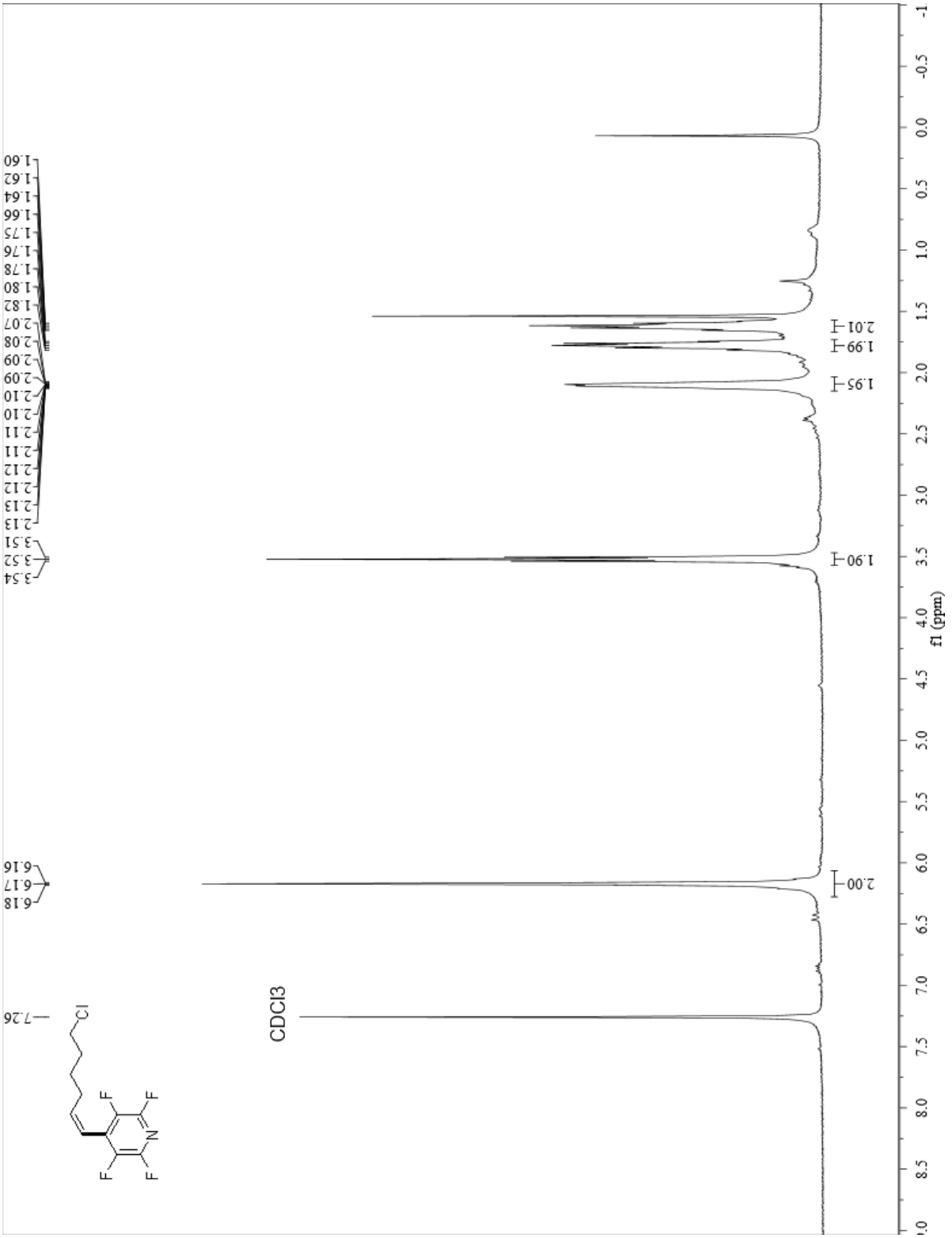
GC and MS of S-15a (methyl (Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)benzoate)



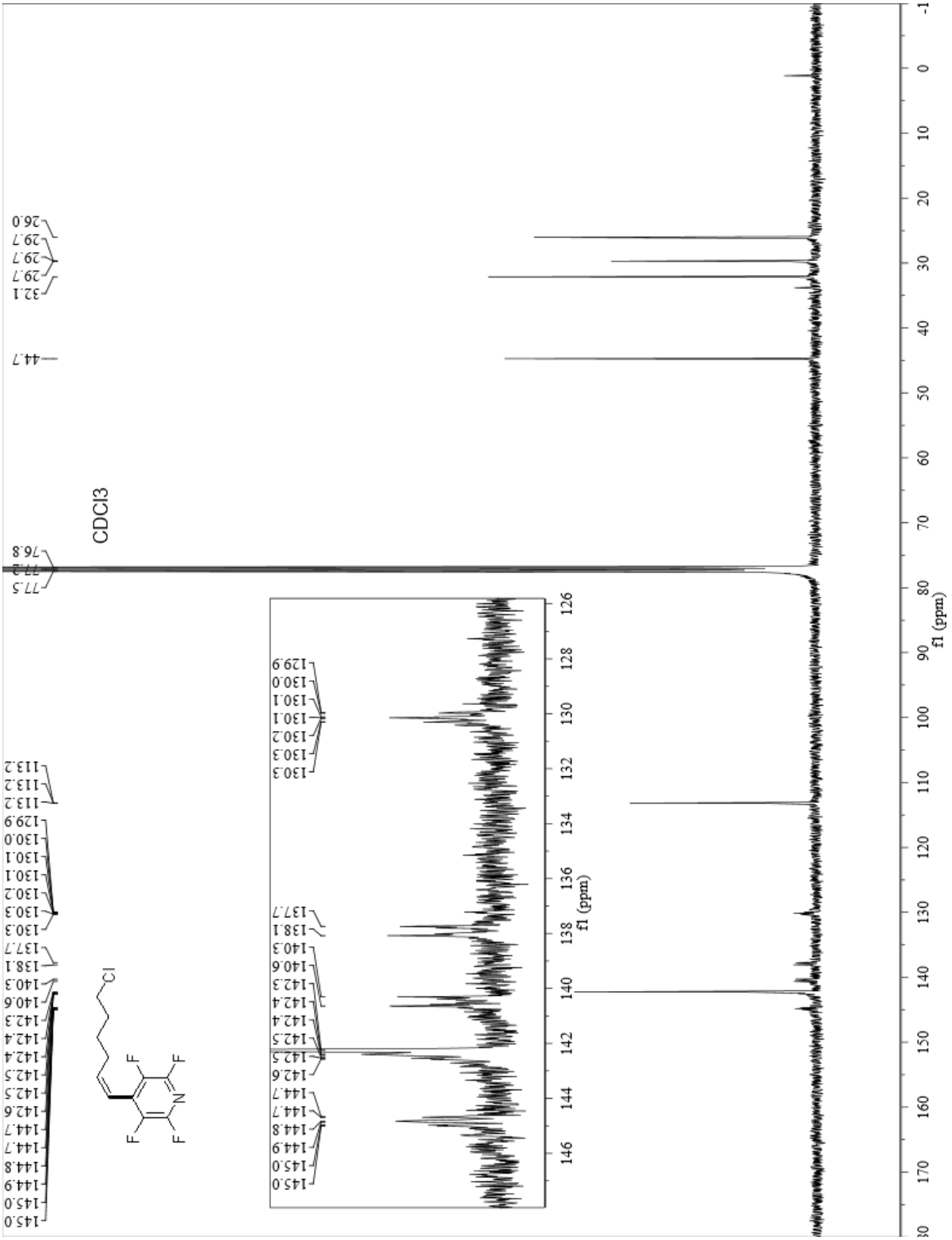
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-16a ((Z)-4-(6-chlorohex-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)



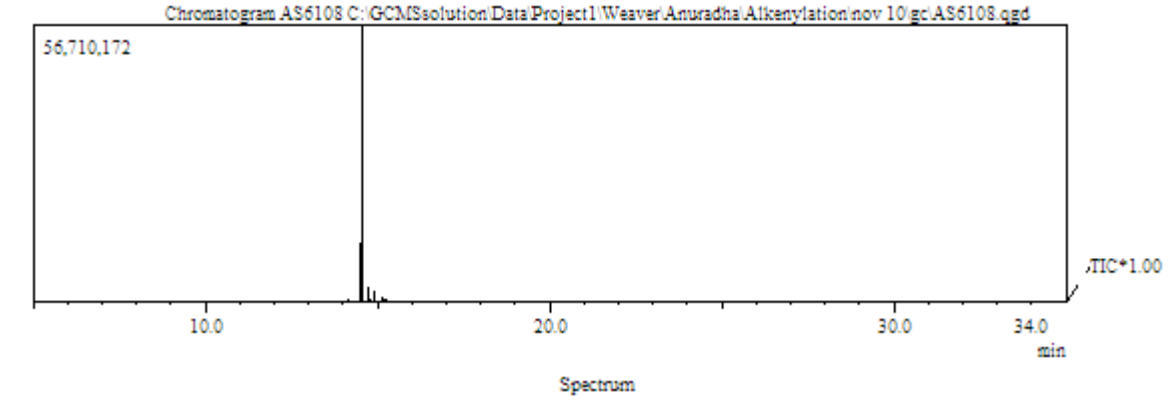
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-16a ((Z)-4-(6-chlorohex-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)



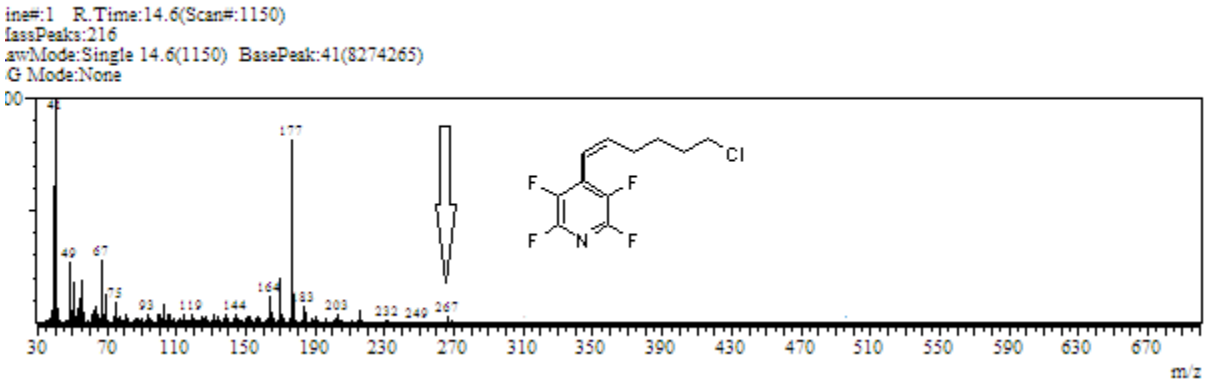
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-16a ((Z)-4-(6-chlorohex-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)



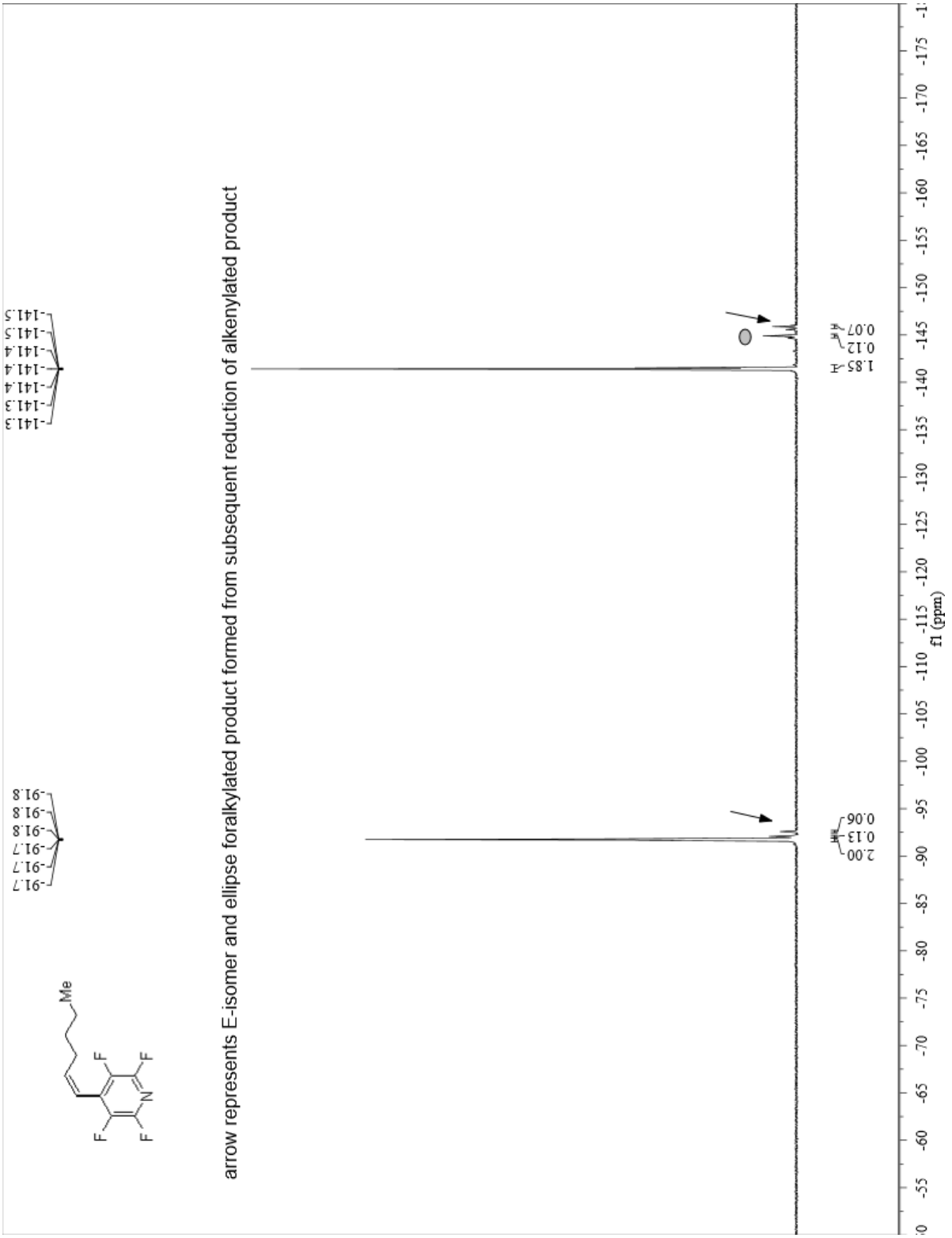
GC and MS of S-16a ((Z)-4-(6-chlorohex-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)



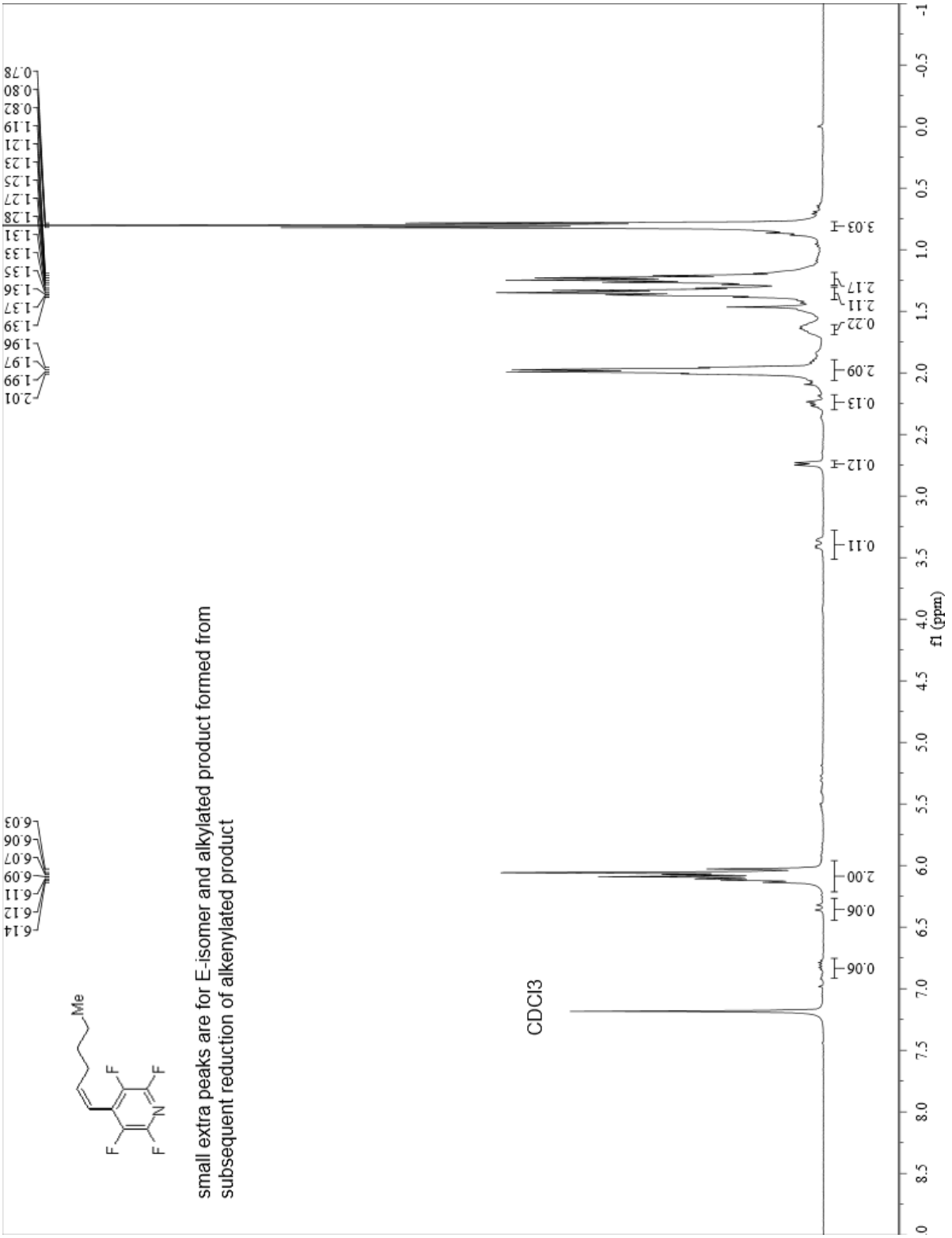
Spectrum



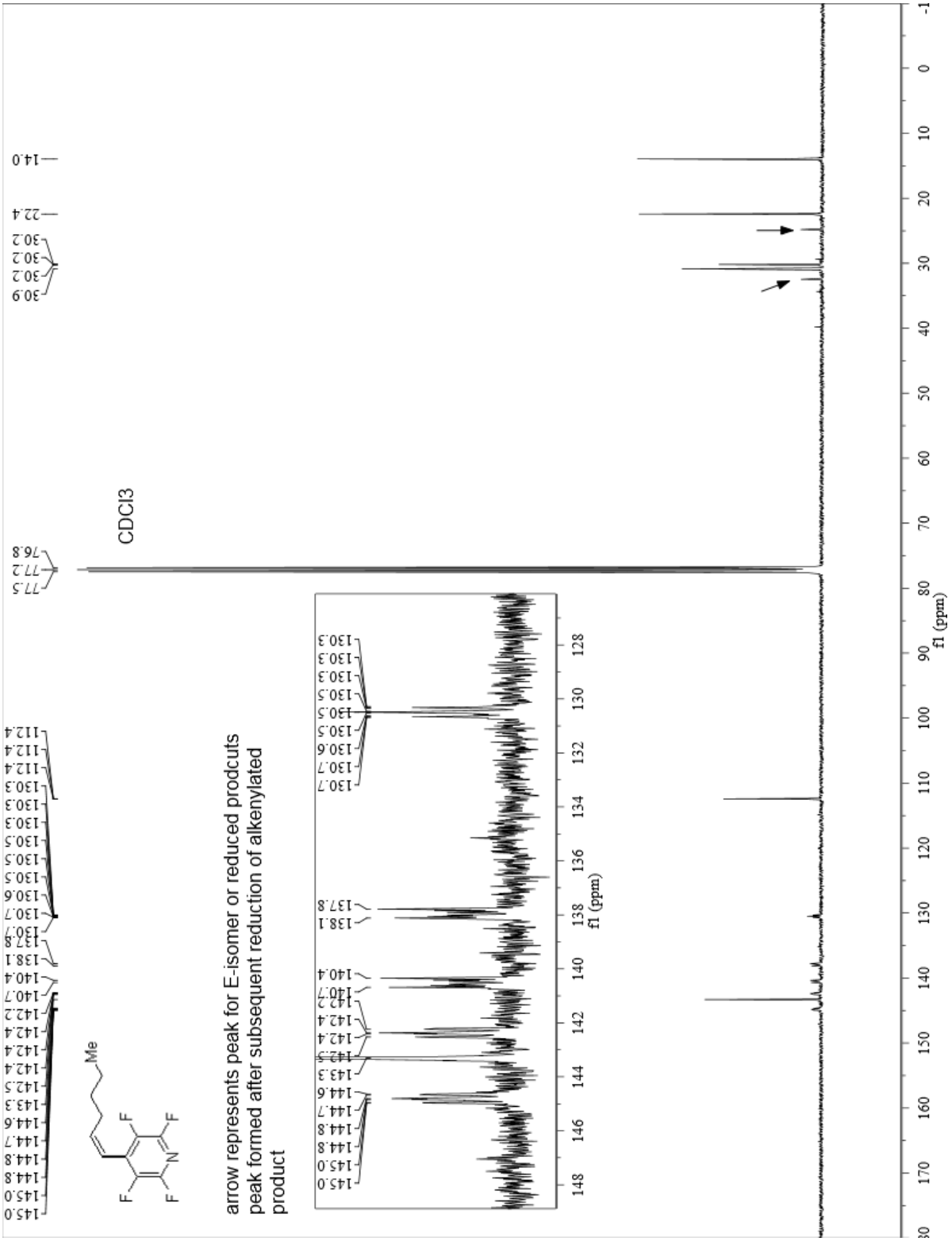
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-17a (Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)pyridine



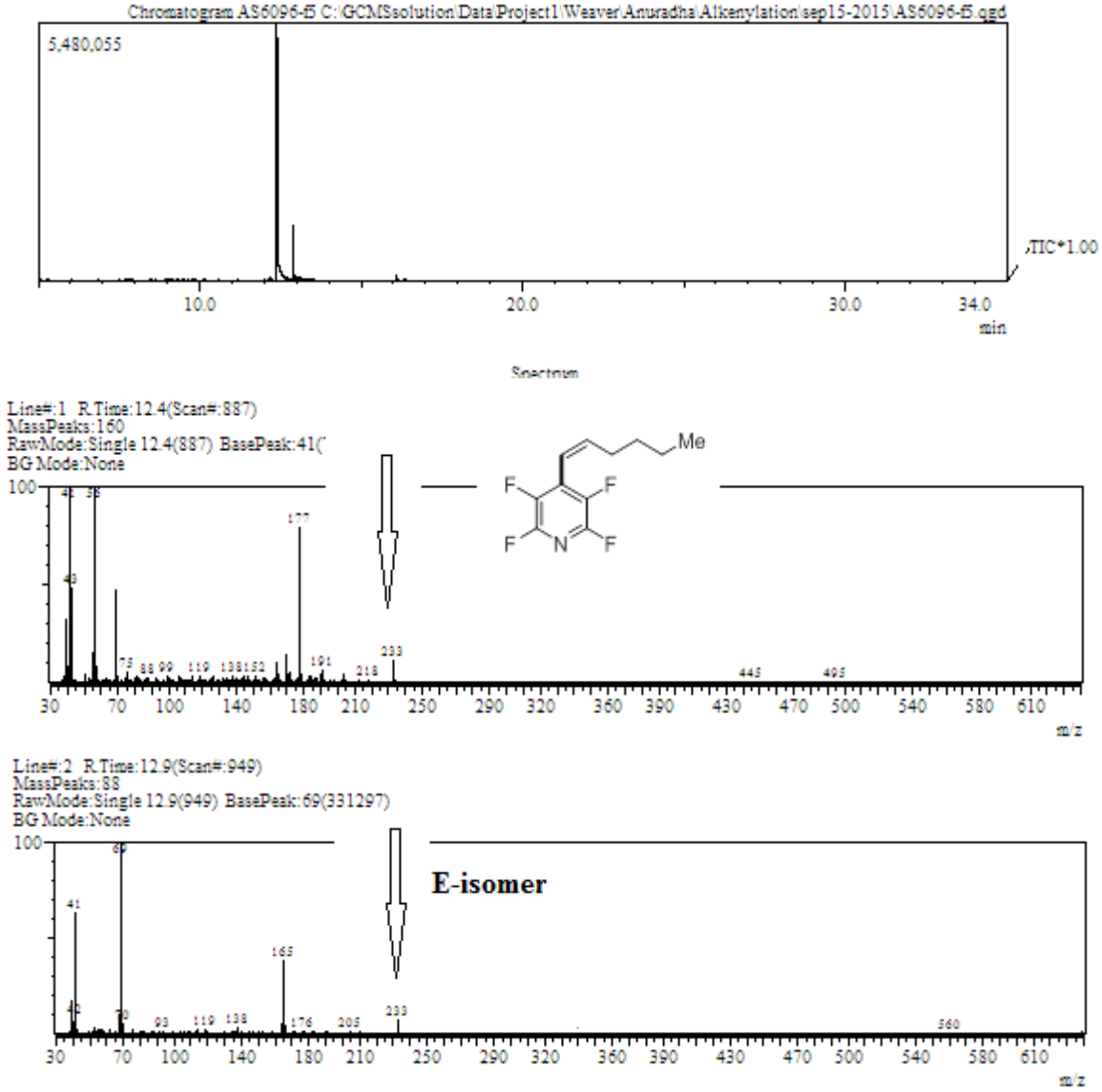
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-17a (Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)pyridine



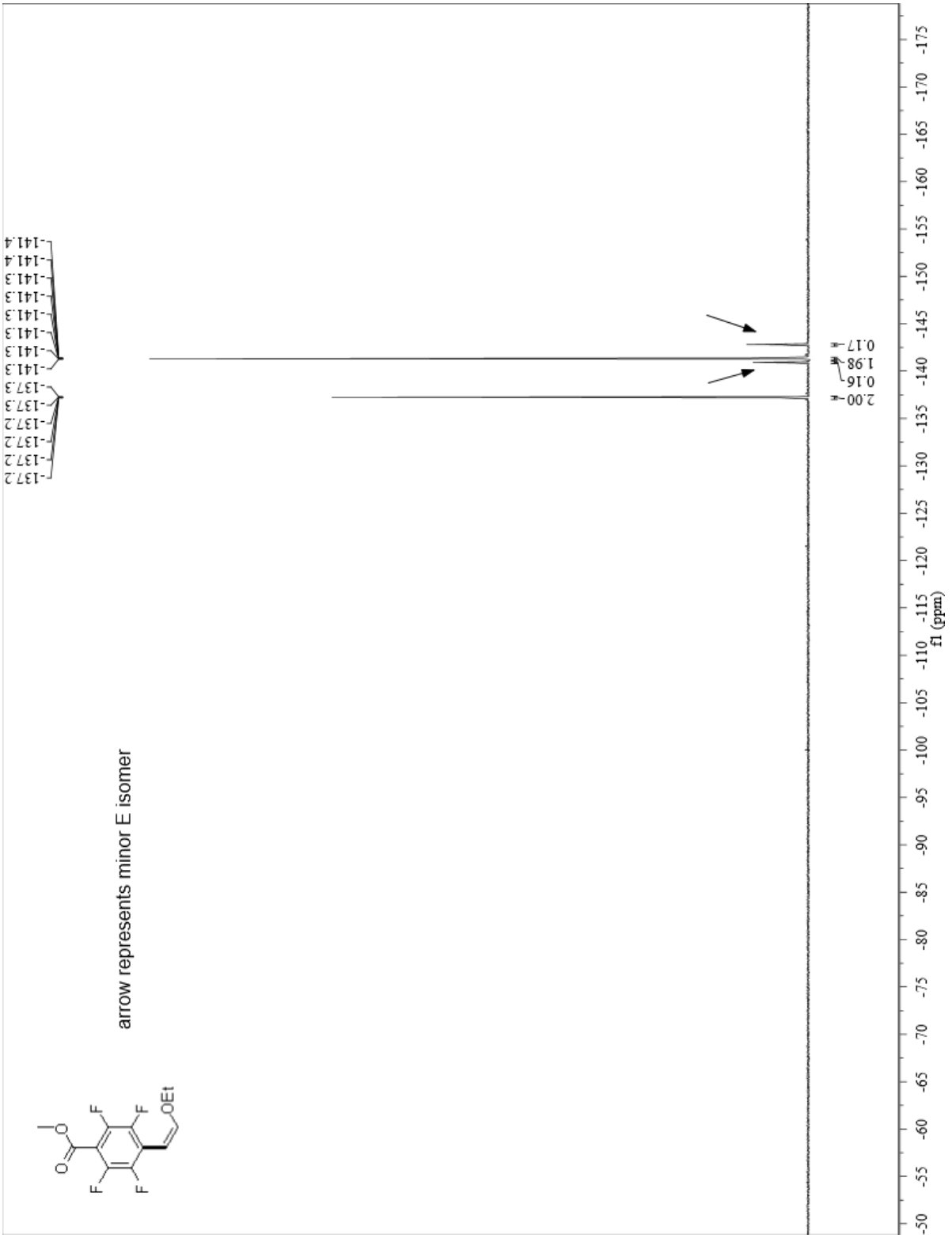
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-17a S-(Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)pyridine



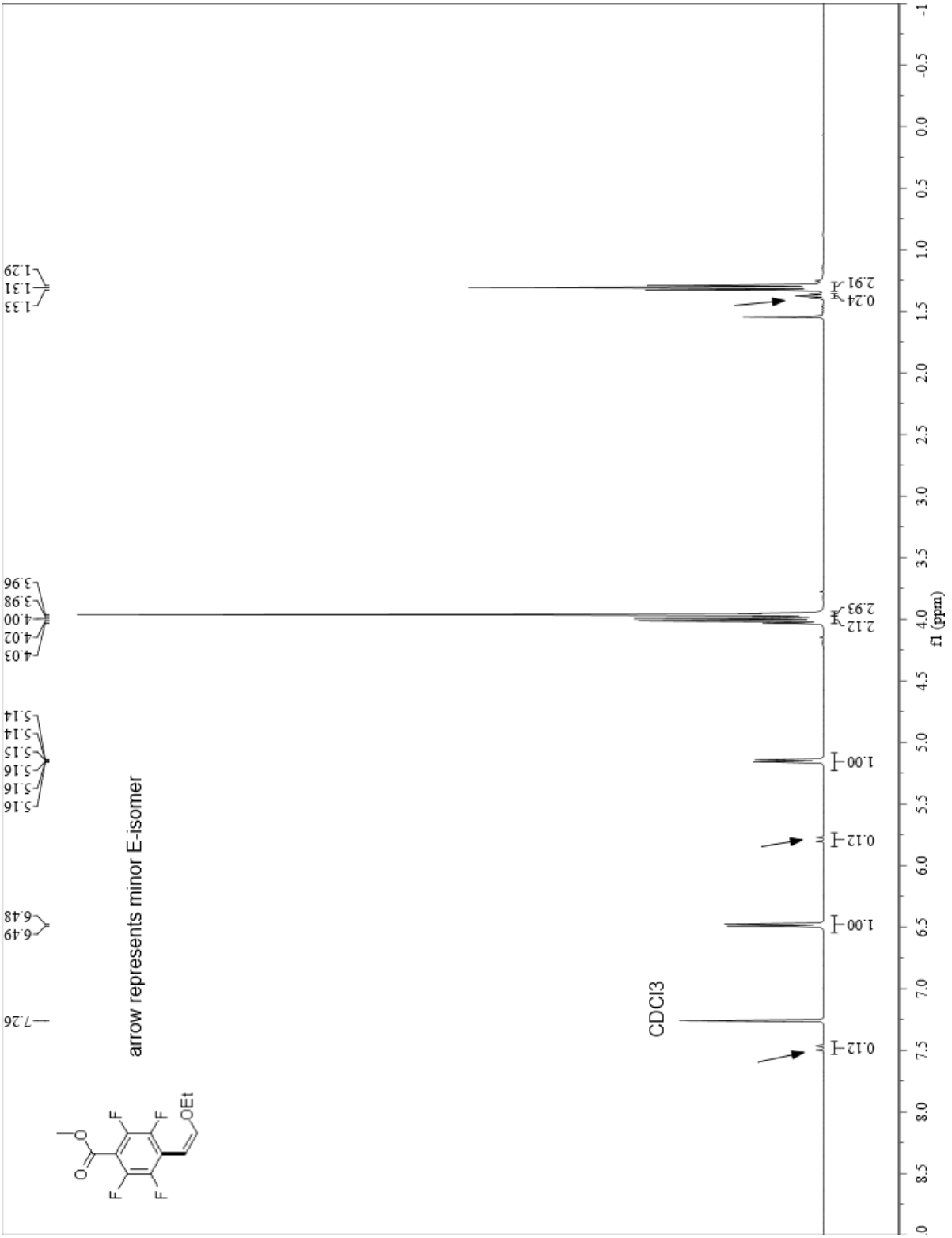
GC and MS of S-16a S-17a S-(Z)-2,3,5,6-tetrafluoro-4-(hex-1-en-1-yl)pyridine



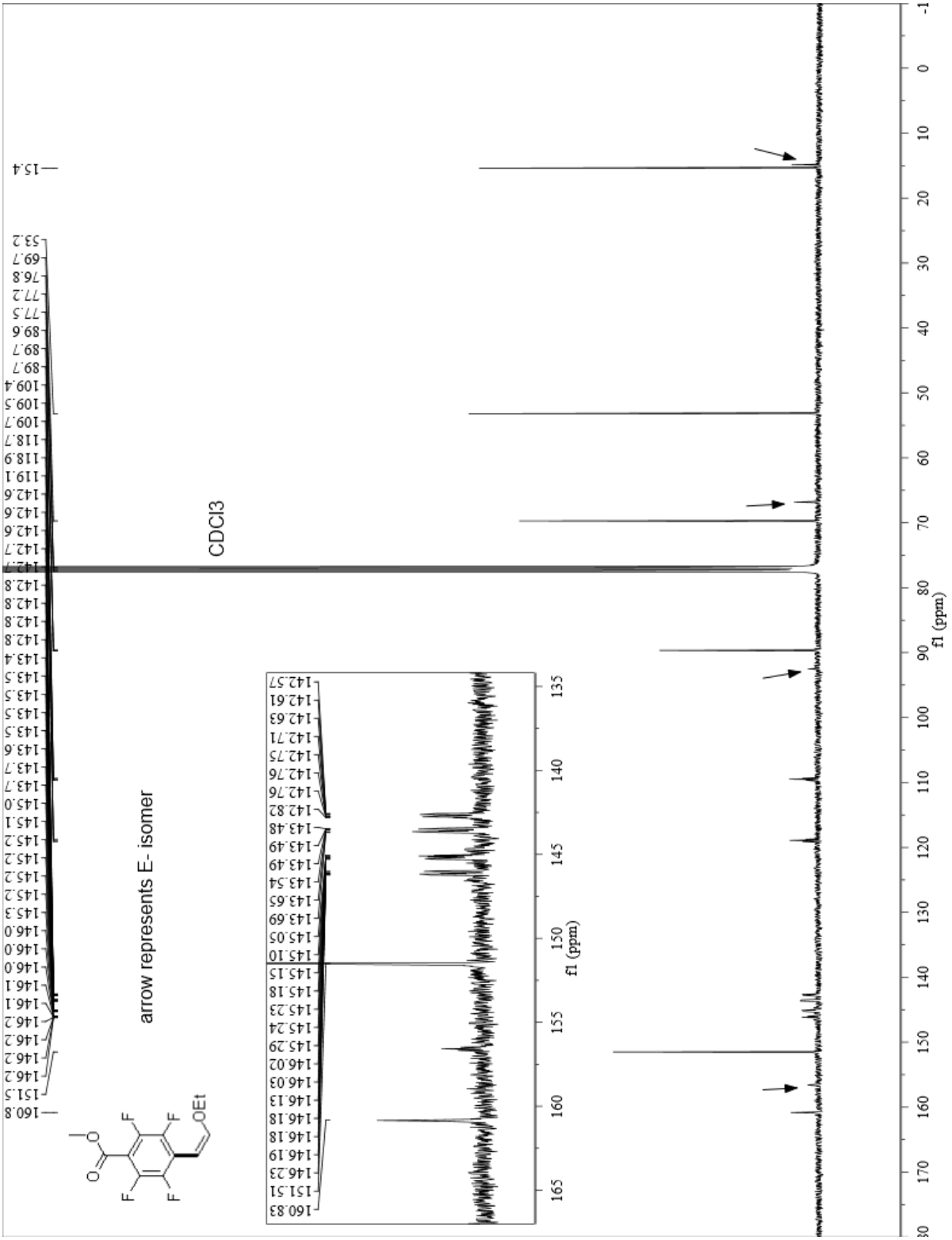
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-18a (methyl (Z)-4-(2-ethoxyvinyl)-2,3,5,6-tetrafluorobenzoate)



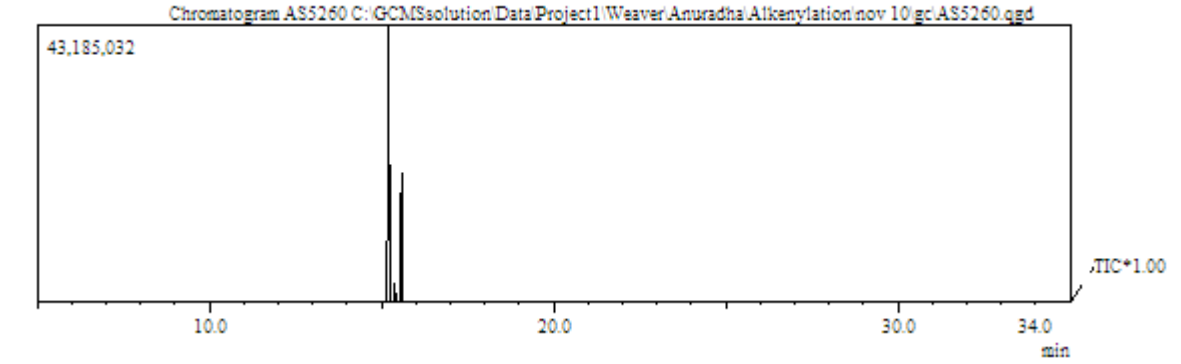
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-18a (methyl (Z)-4-(2-ethoxyvinyl)-2,3,5,6-tetrafluorobenzoate)

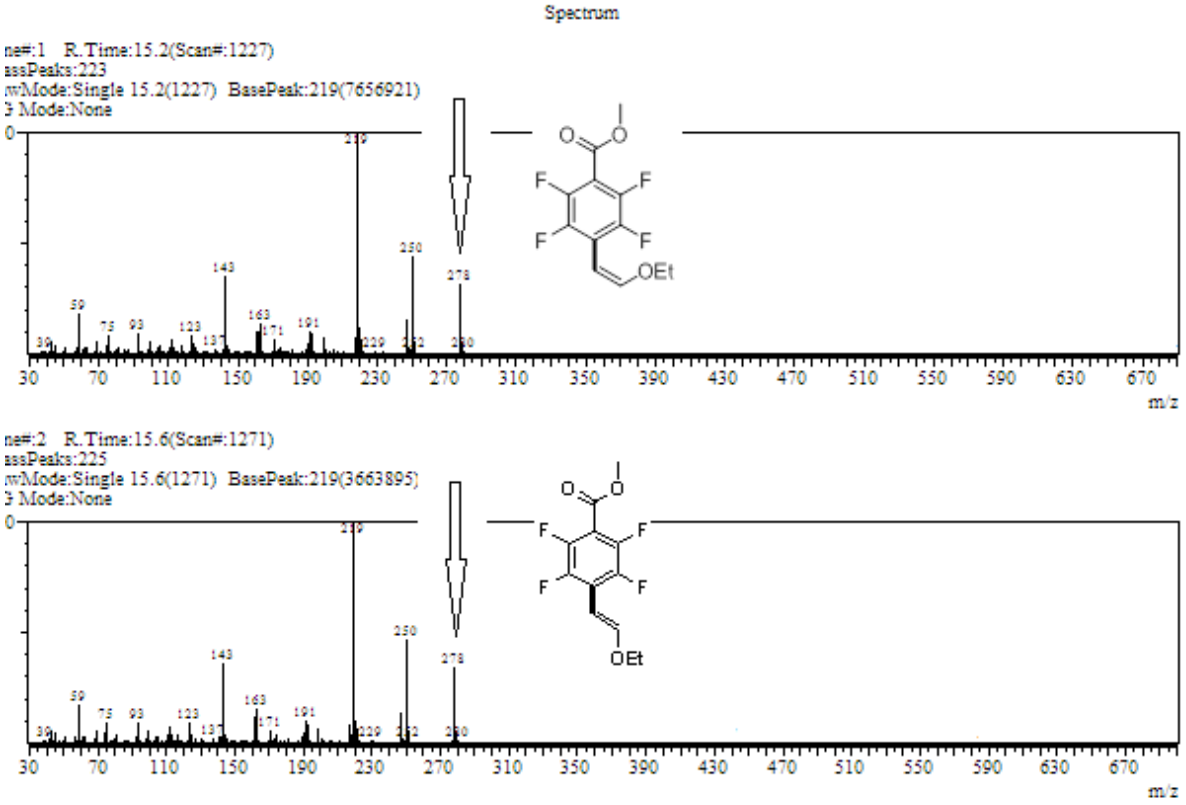


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-18a (methyl (Z)-4-(2-ethoxyvinyl)-2,3,5,6-tetrafluorobenzoate

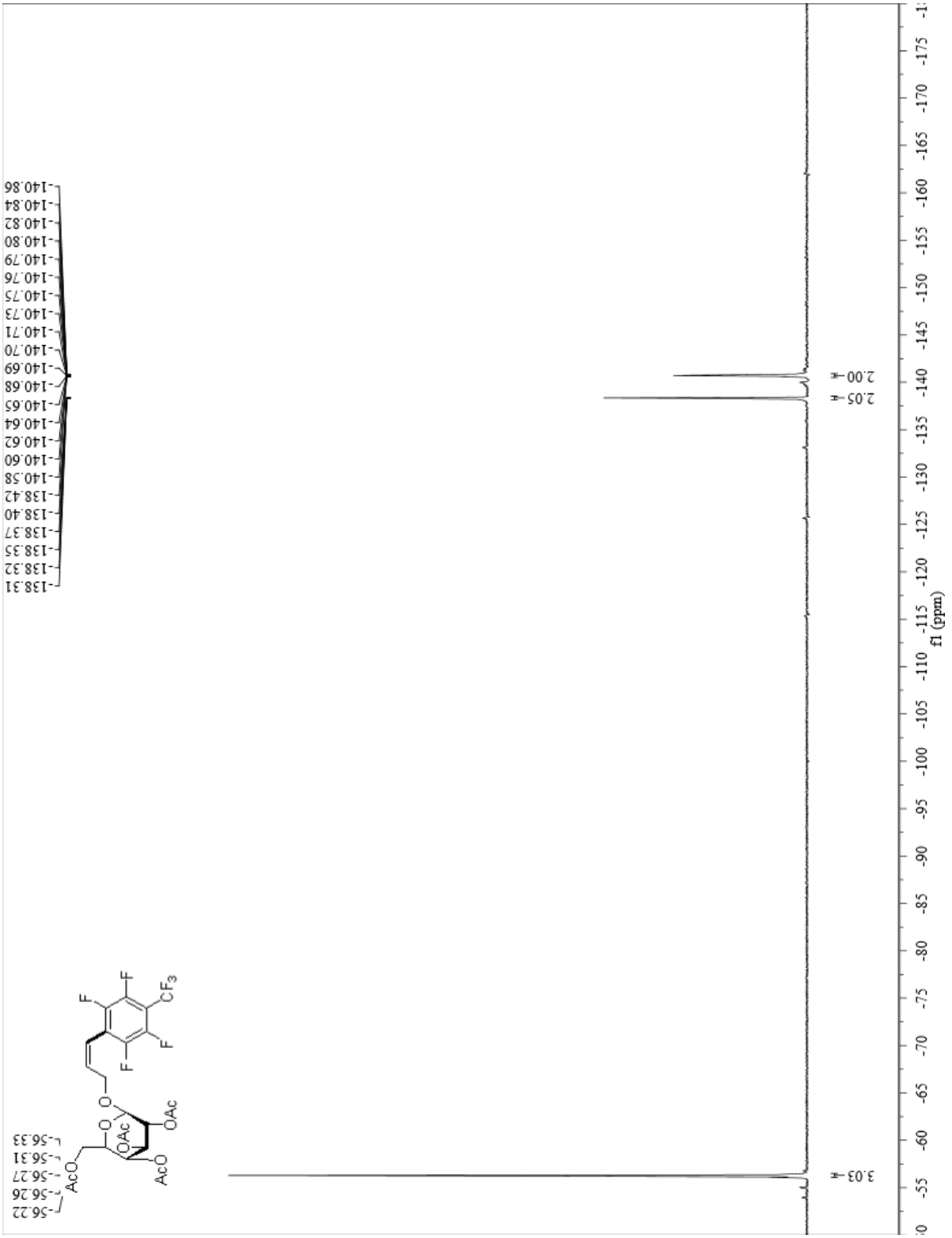


GC and MS of S-18a (methyl (Z)-4-(2-ethoxyvinyl)-2,3,5,6-tetrafluorobenzoate)

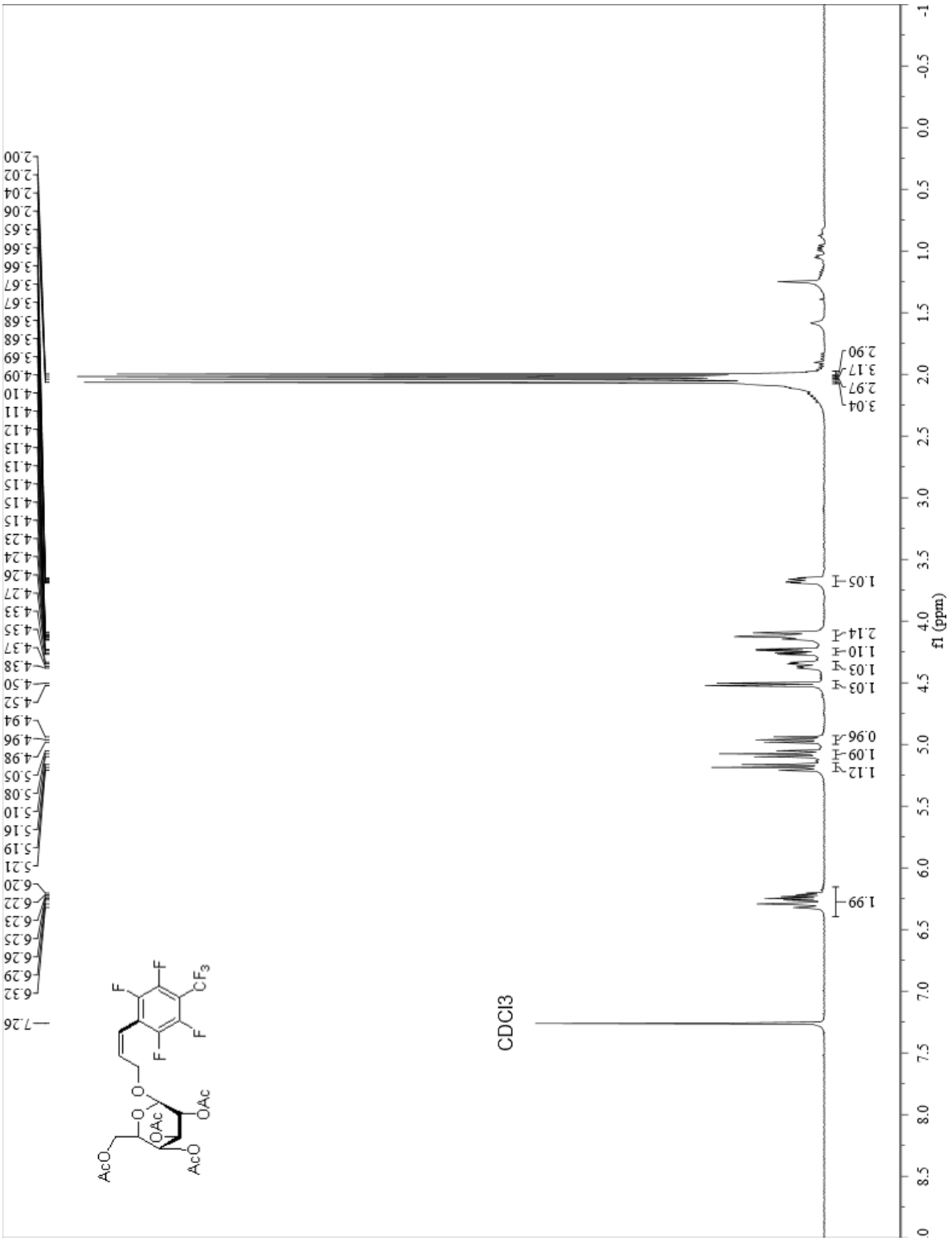




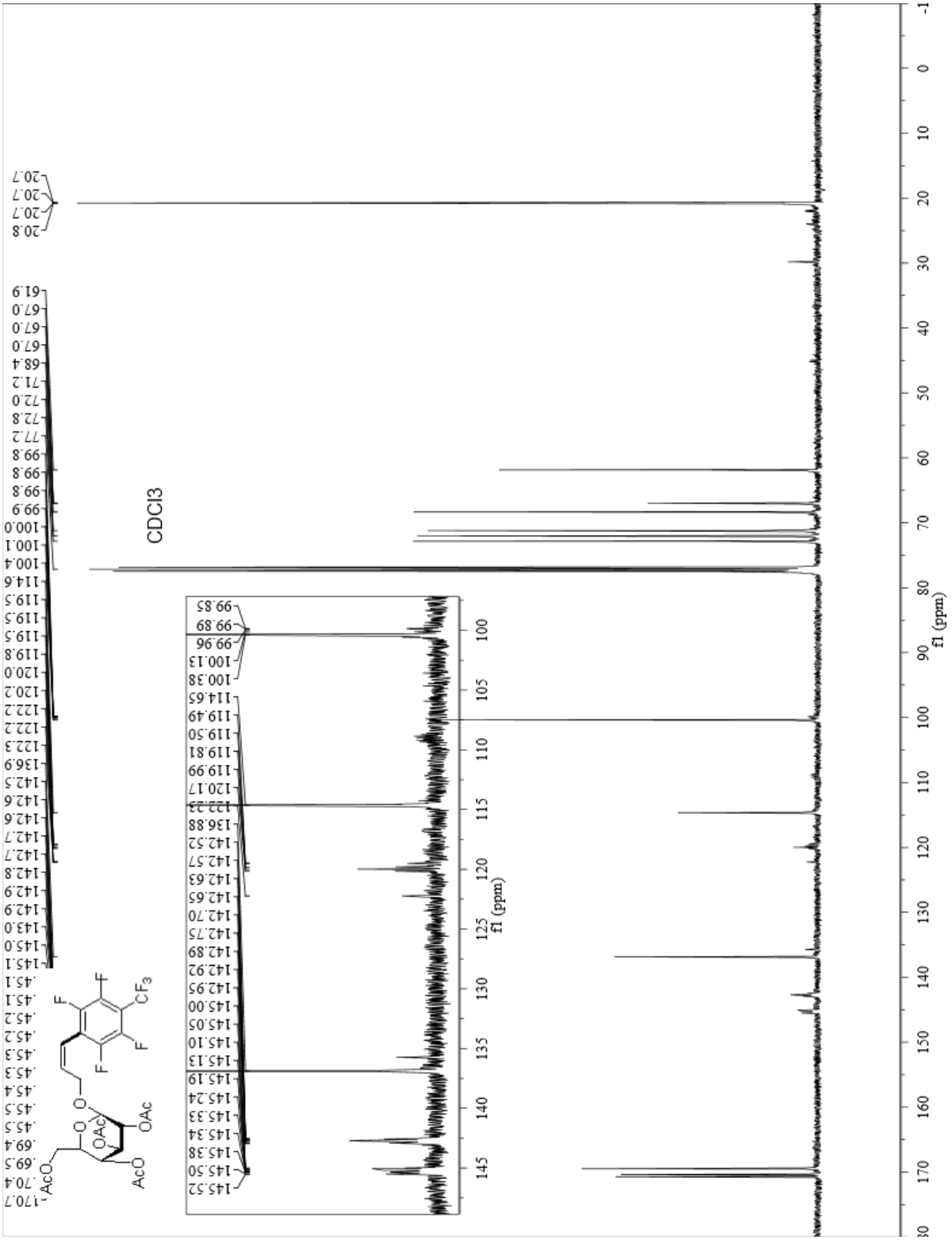
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-19a ((2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((Z)-3-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)allyl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate)



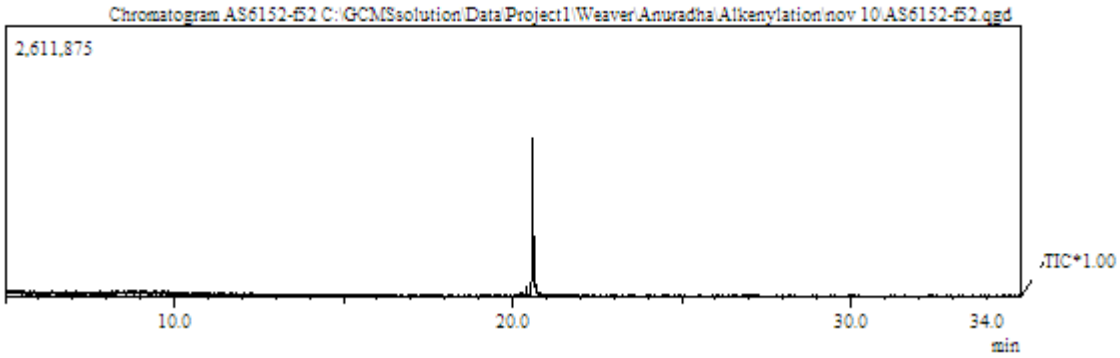
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-19a ((2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((Z)-3-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)allyl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate)

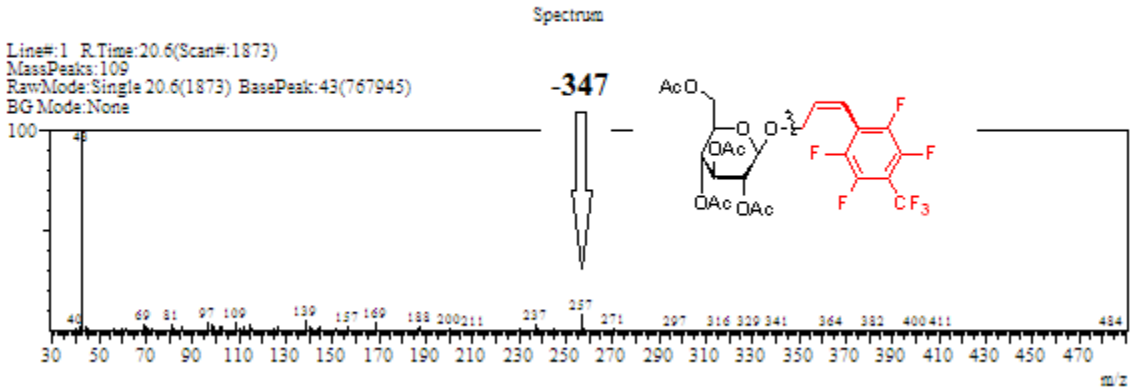


^{13}C NMR (151 MHz, Chloroform-*d*, at rt) of S-19a ((2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((Z)-3-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)allyl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate)

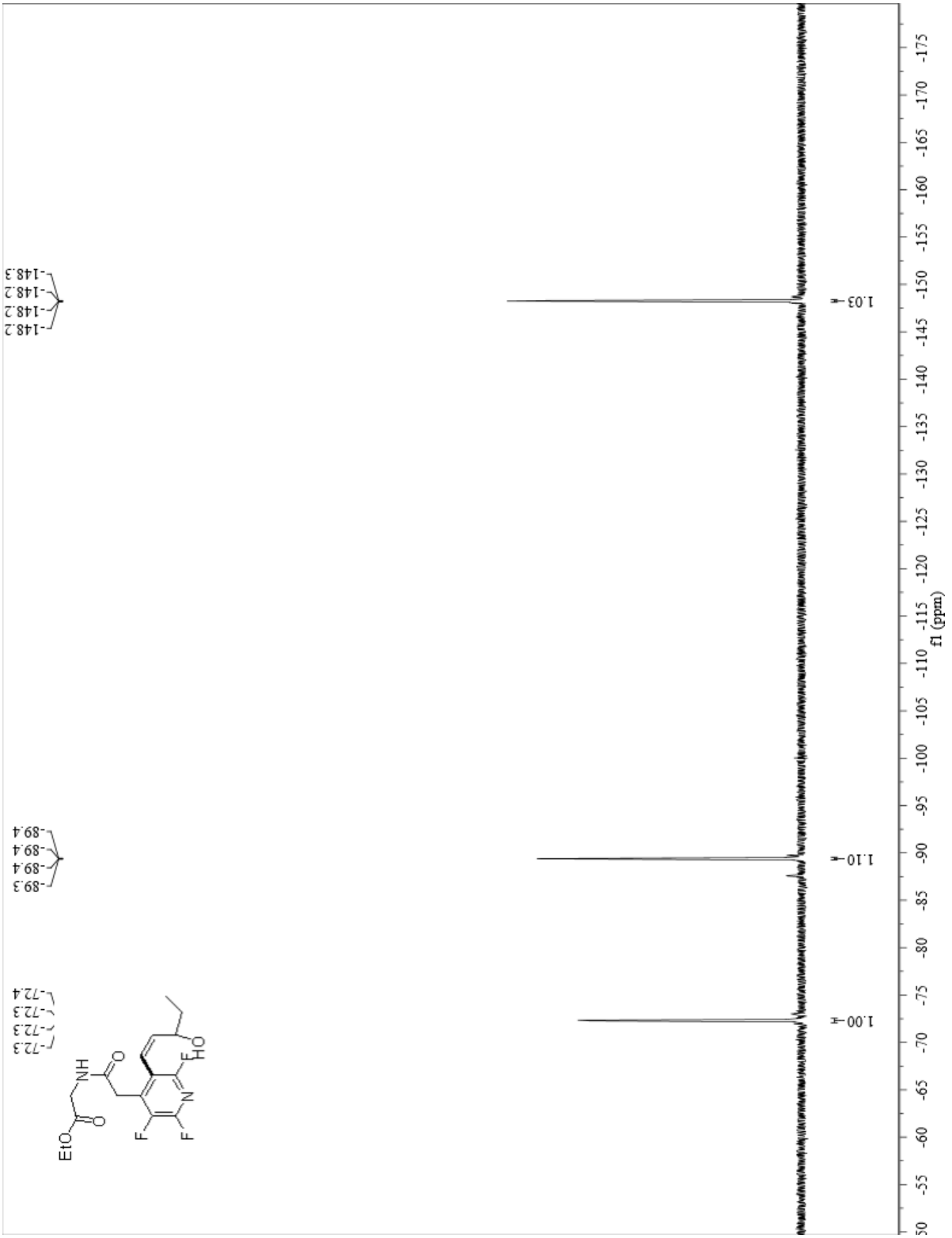


GC and MS of S-19a ((2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((Z)-3-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)allyl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate)

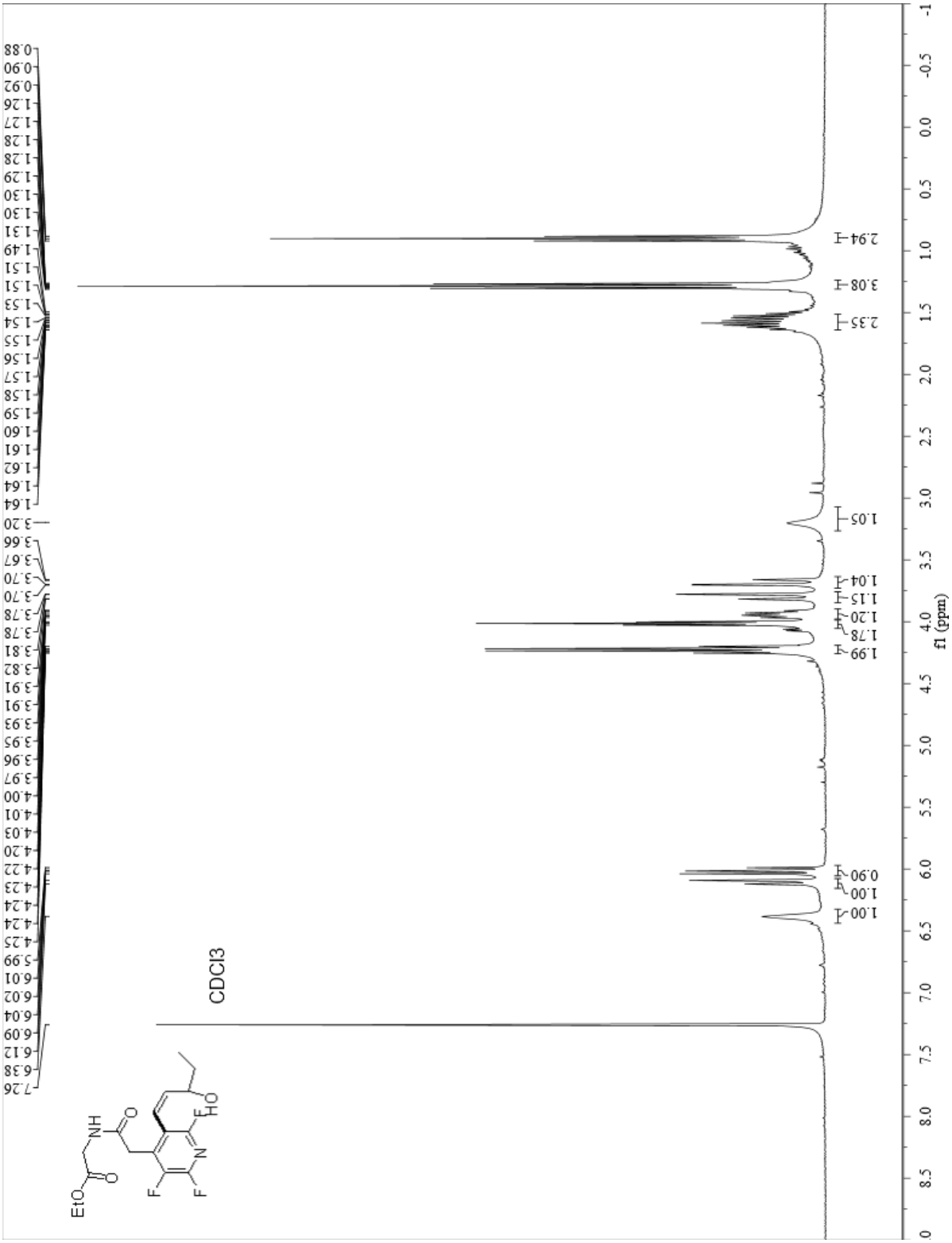




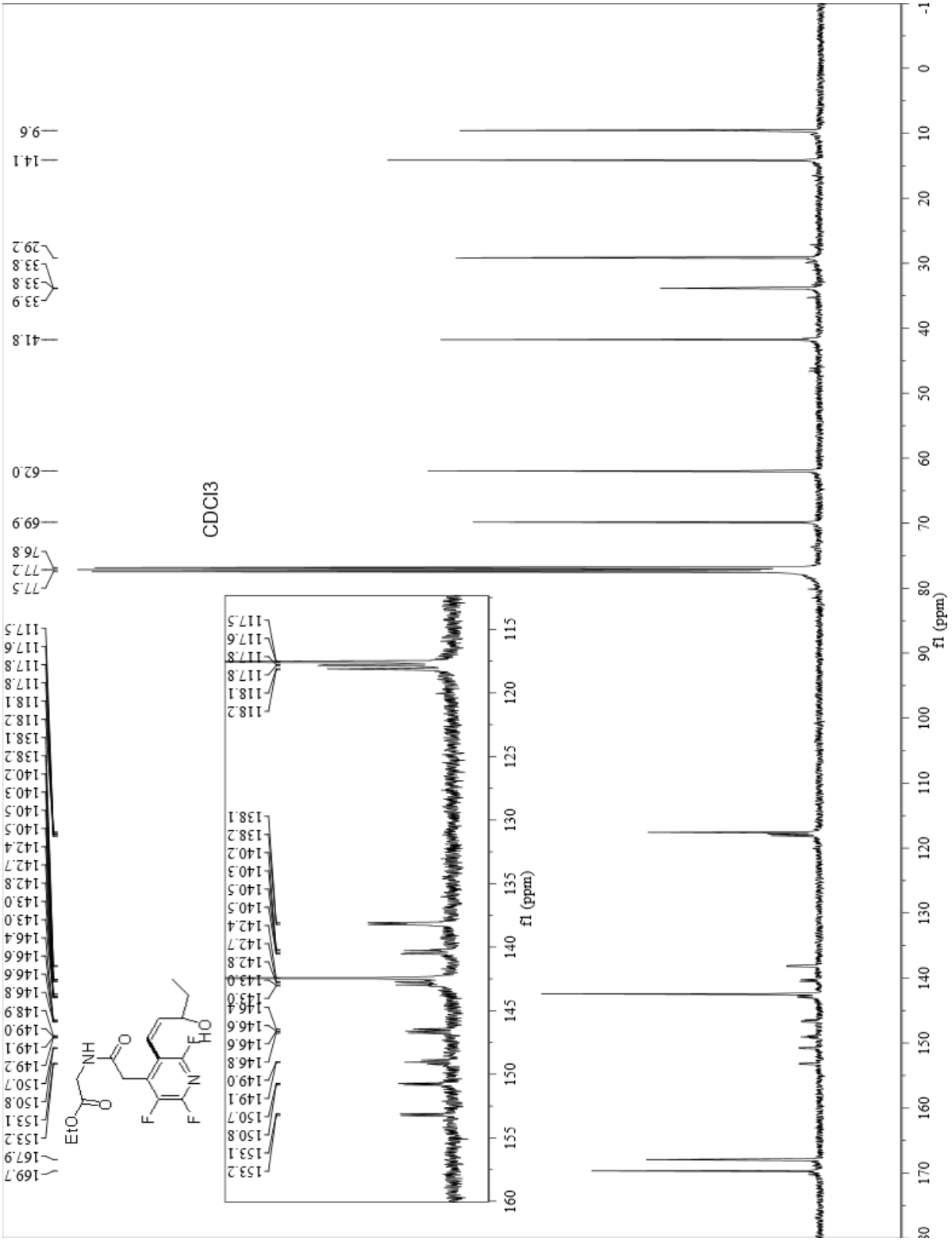
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-20a (ethyl (Z)-(2-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)pyridin-4-yl)acetyl)glycinate



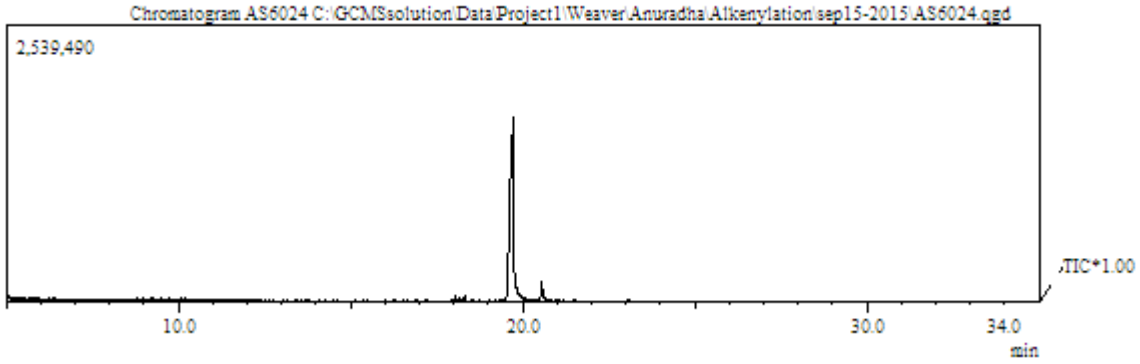
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-20a (ethyl (Z)-(2-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)pyridin-4-yl)acetyl)glycinate

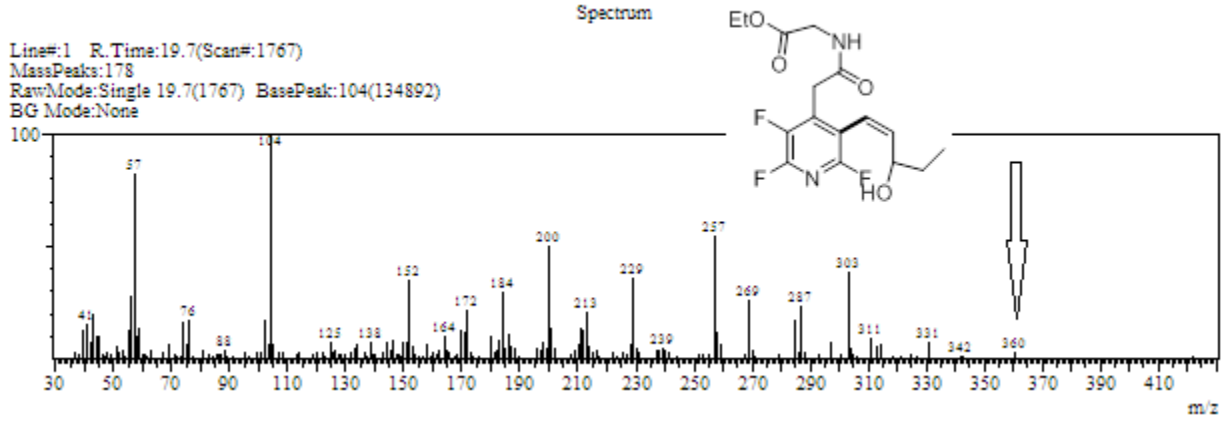


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-20a (ethyl (Z)-(2-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)pyridin-4-yl)acetyl)glycinate

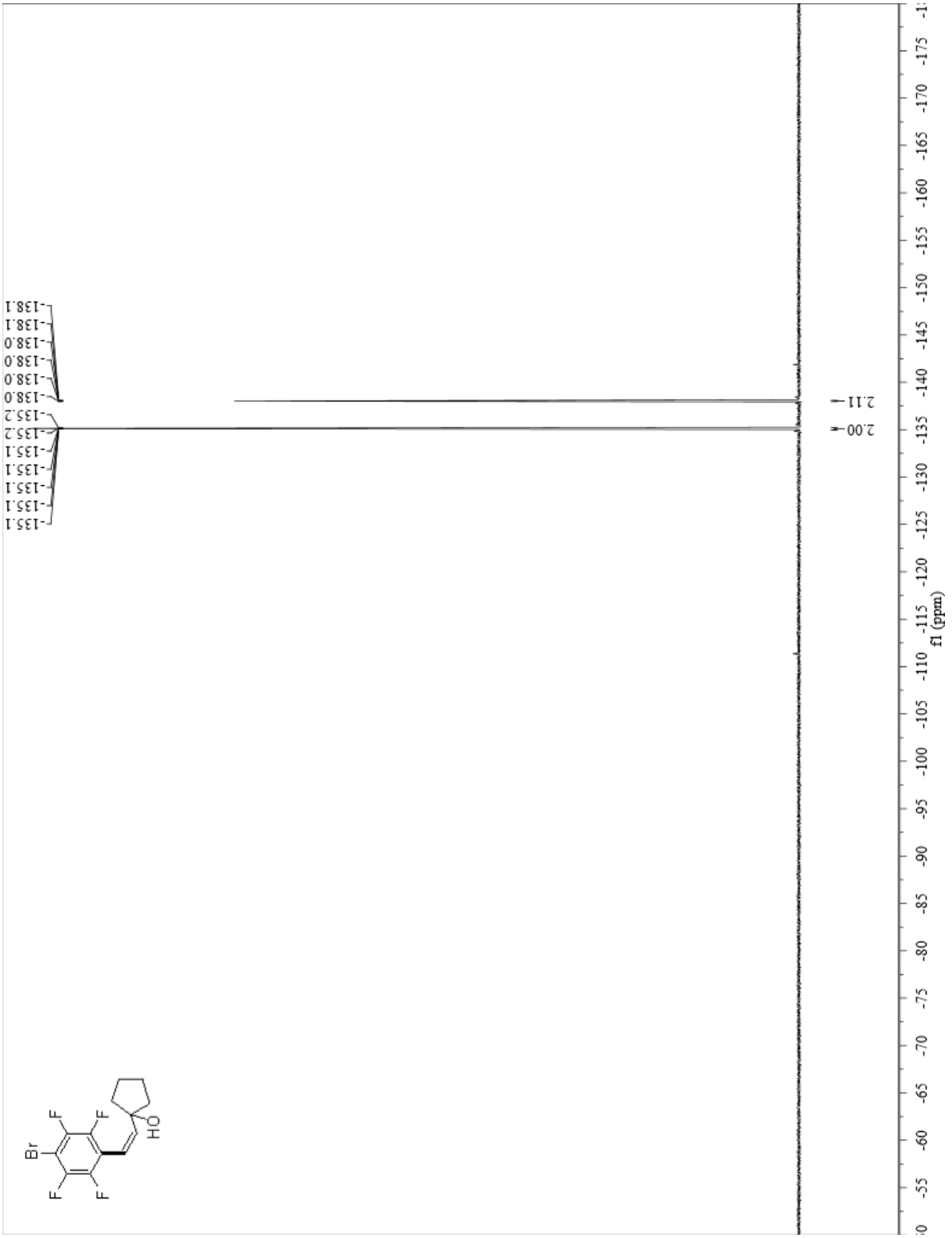


GC and MS of S-20a (ethyl (Z)-(2-(2,3,6-trifluoro-5-(3-hydroxypent-1-en-1-yl)pyridin-4-yl)acetyl)glycinate

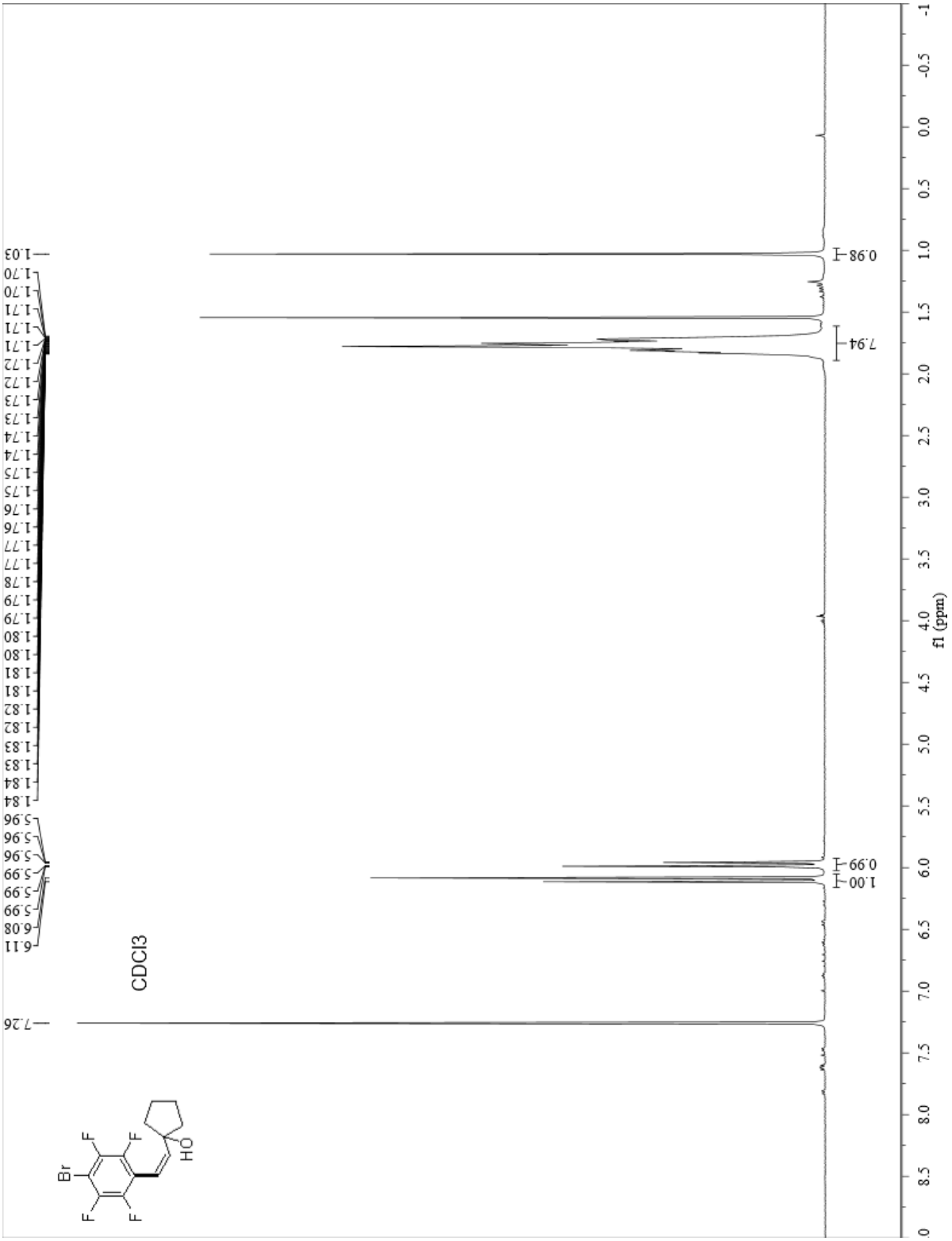




^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-21a (Z)-1-(4-bromo-2,3,5,6-tetrafluorostyryl)cyclopentan-1-ol

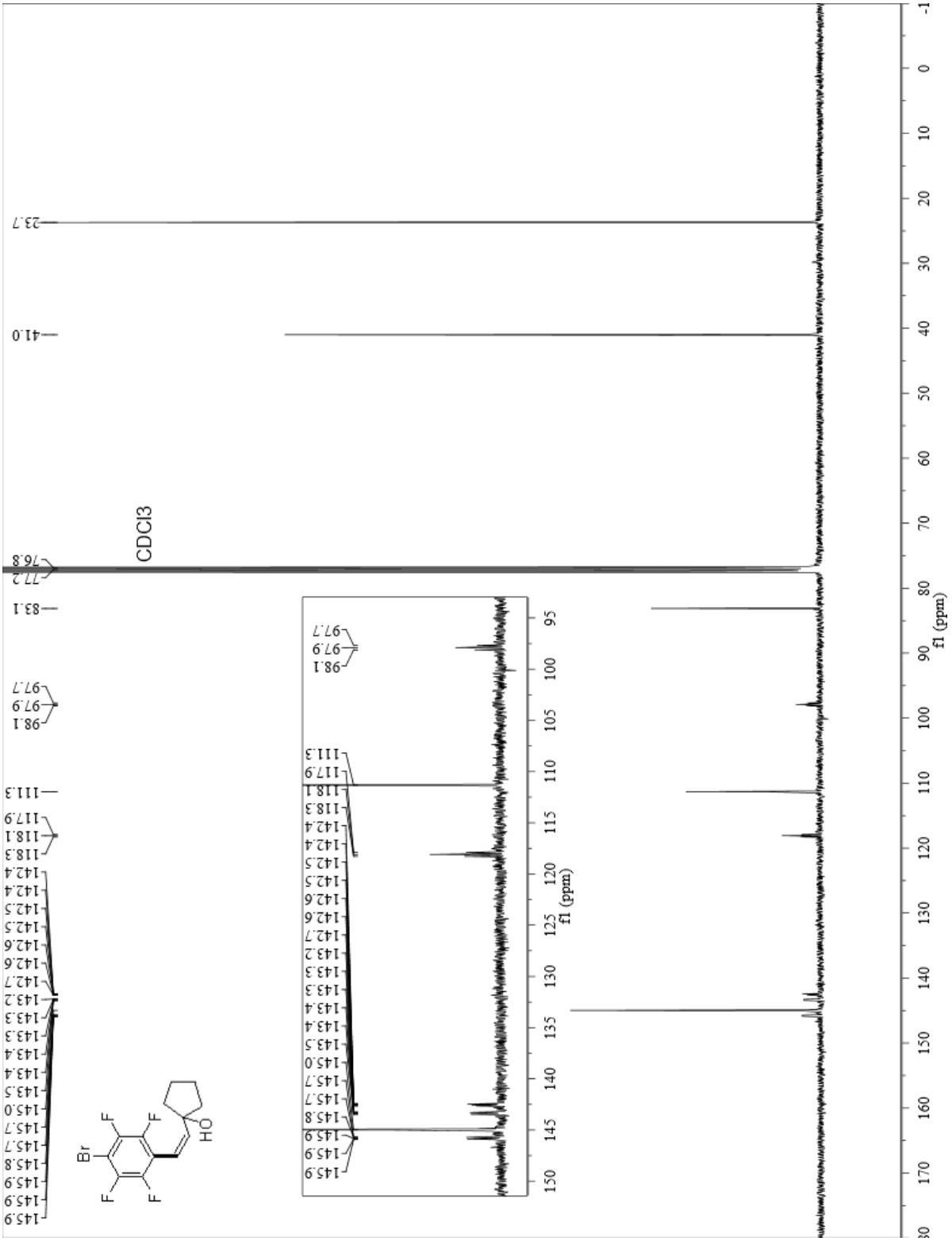


^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-21a (Z)-1-(4-bromo-2,3,5,6-tetrafluorostyryl)cyclopentan-1

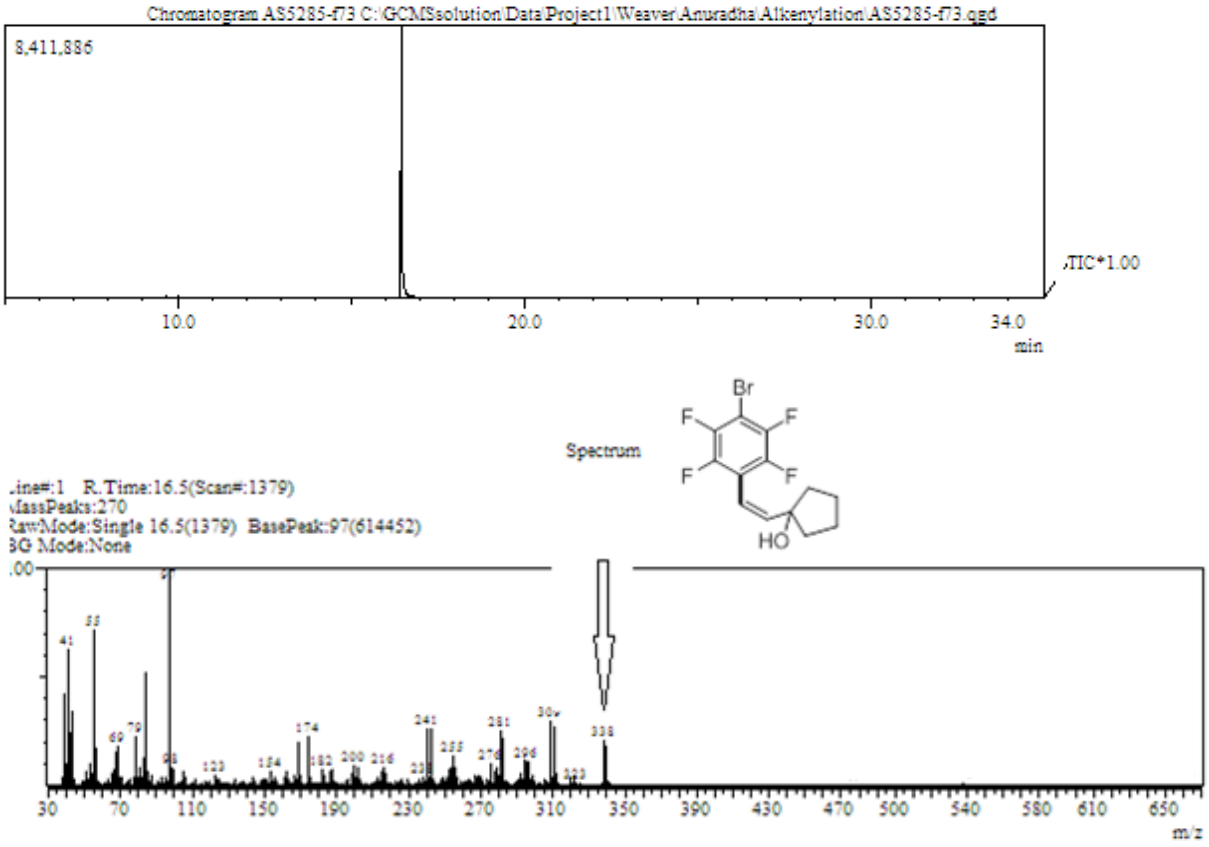


-ol

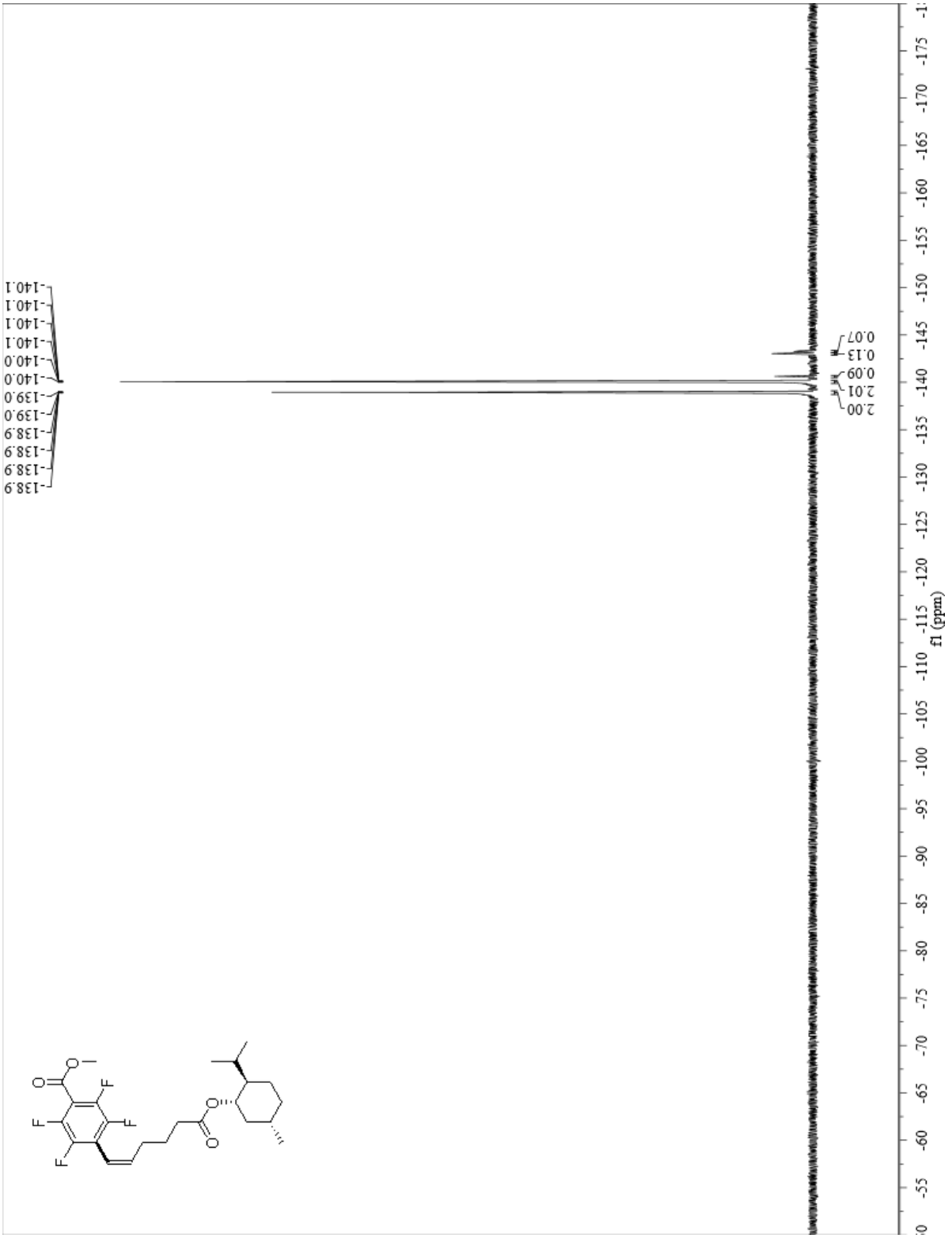
^{13}C NMR of (101 MHz, Chloroform-*d*, at rt) S-21a (Z)-1-(4-bromo-2,3,5,6-tetrafluorostyryl)cyclopentan-1-ol



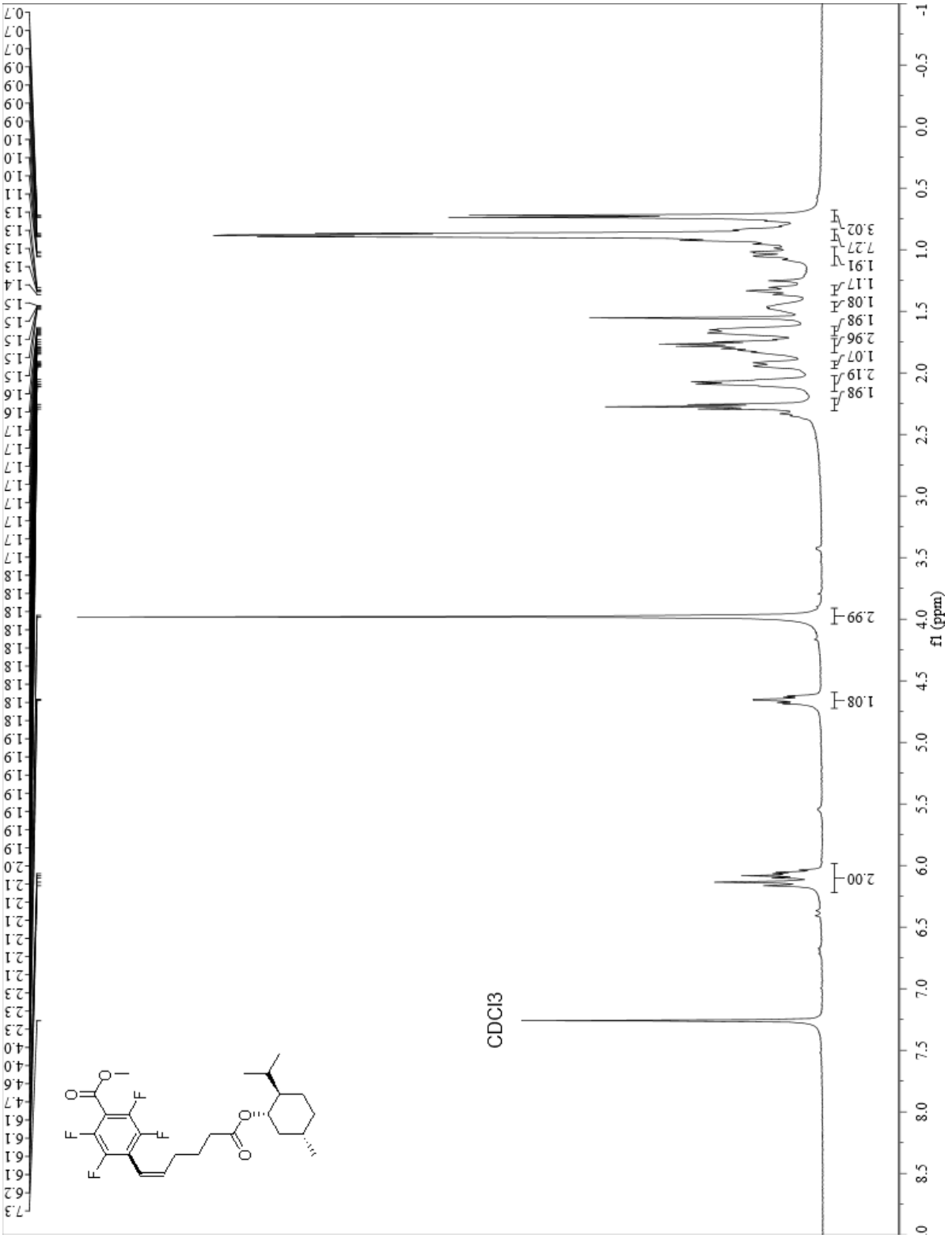
GC and MS of S-21a ((Z)-1-(4-bromo-2,3,5,6-tetrafluorostyryl)cyclopentan-1-ol



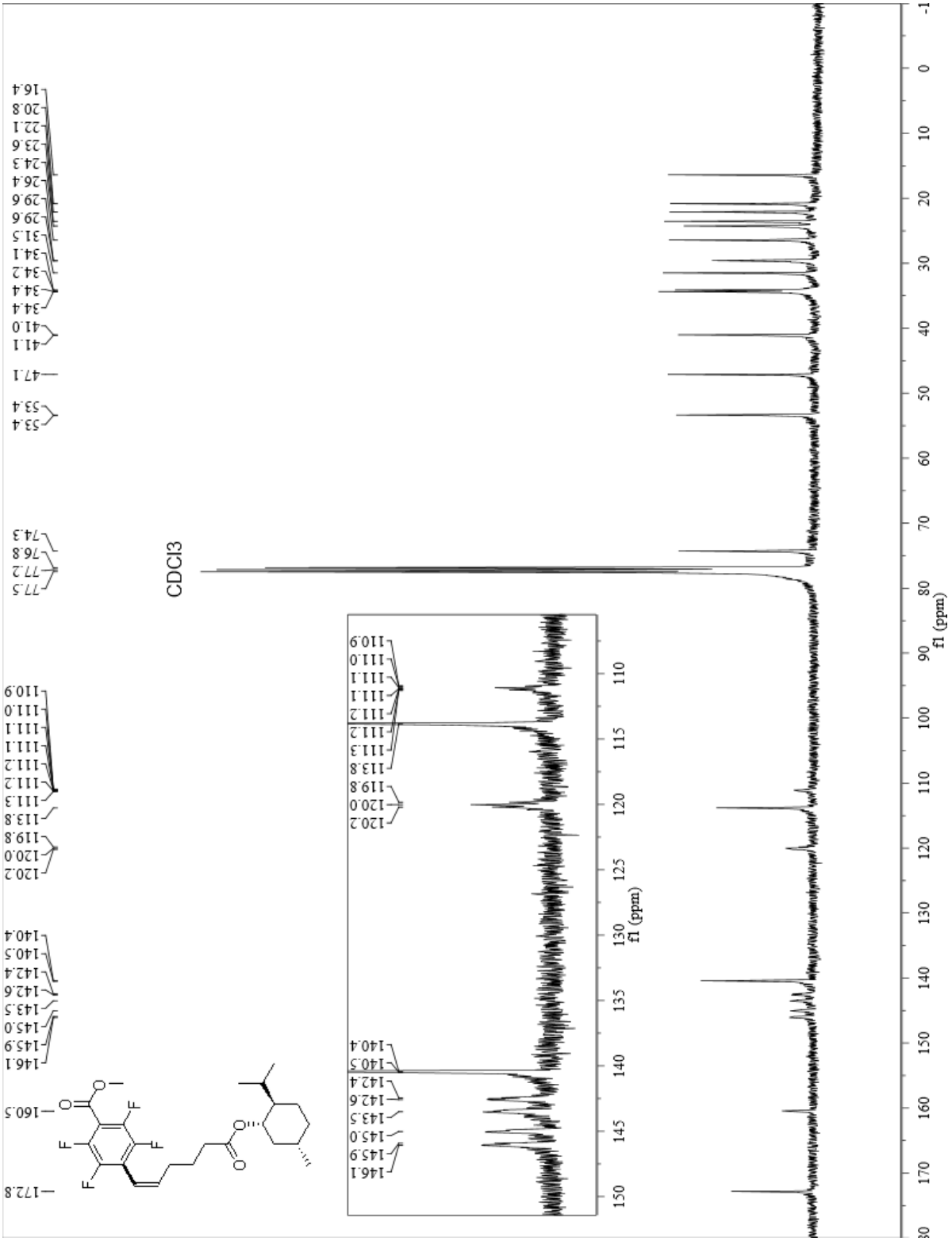
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-22a (methyl 2,3,5,6-tetrafluoro-4-((Z)-6-(((1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-6-oxohex-1-en-1-yl)benzoate)



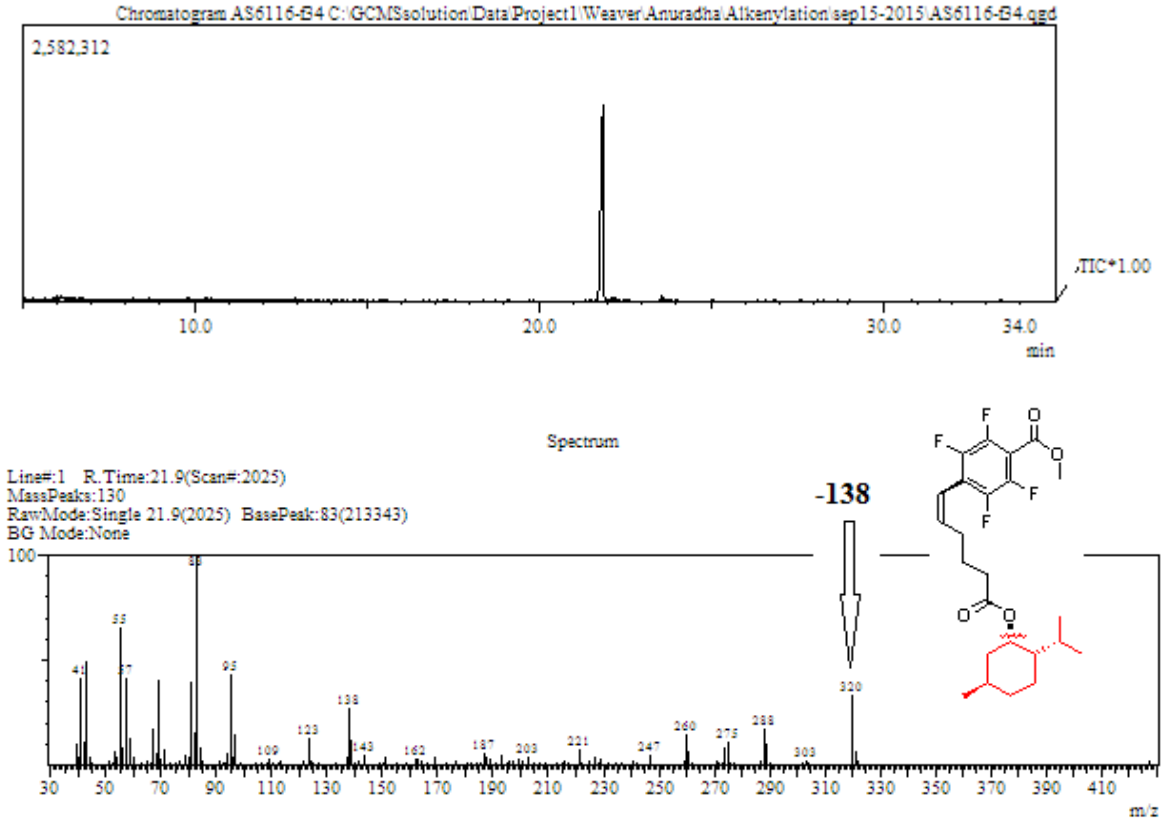
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-22a (methyl 2,3,5,6-tetrafluoro-4-((Z)-6-(((1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-6-oxohex-1-en-1-yl)benzoate)



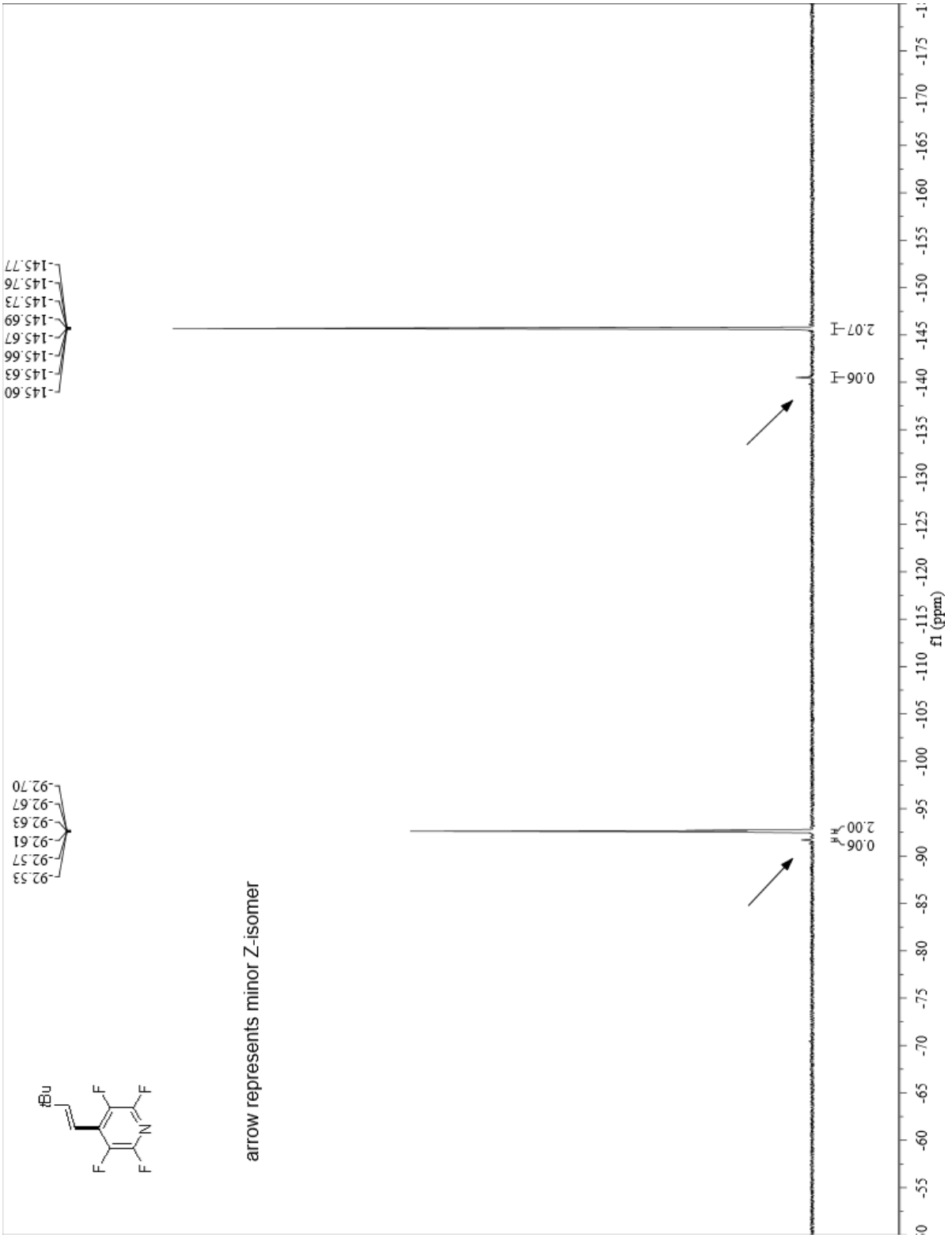
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-22a (methyl 2,3,5,6-tetrafluoro-4-((Z)-6-(((1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-6-oxohex-1-en-1-yl)benzoate)



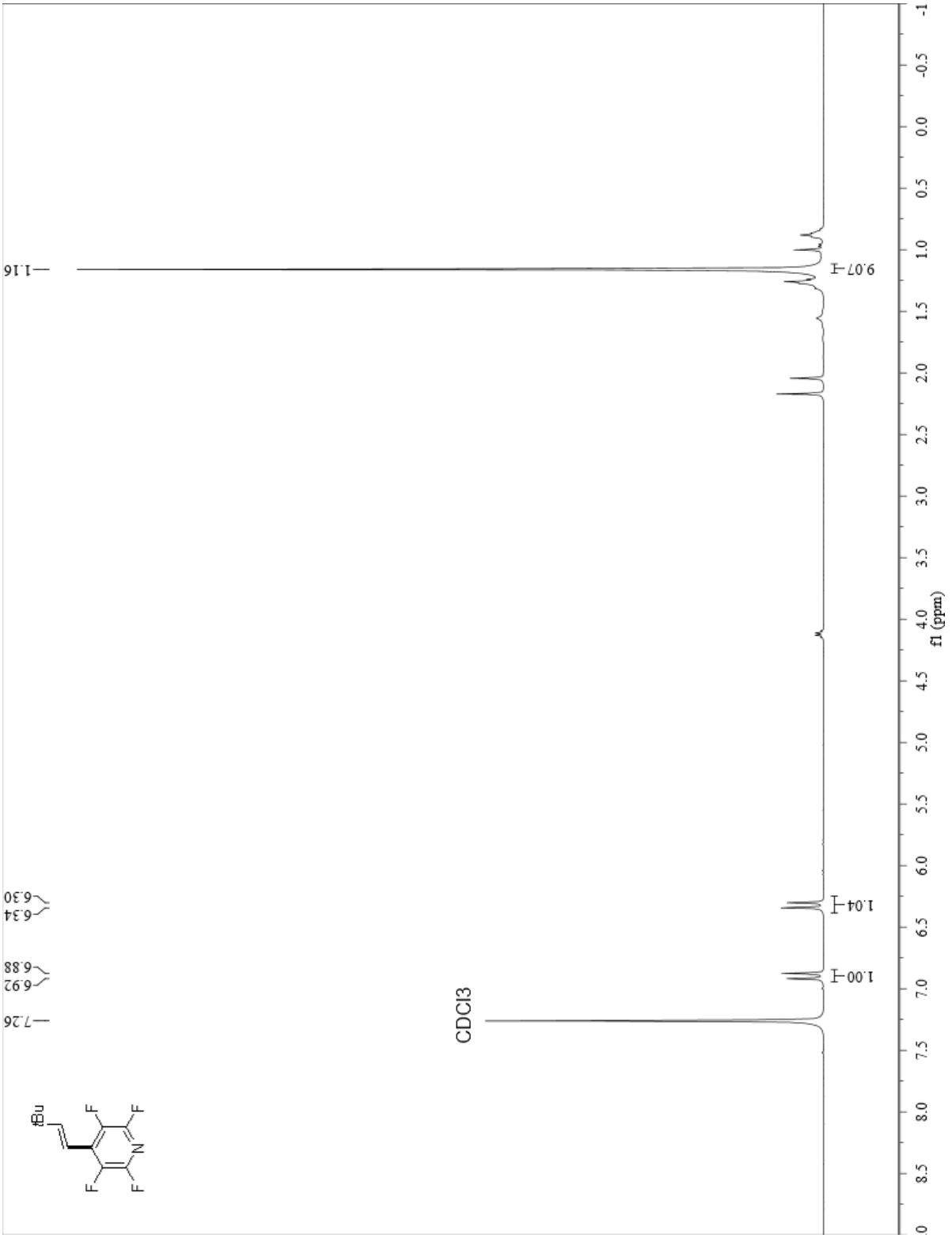
GC and MS of S-22a (methyl 2,3,5,6-tetrafluoro-4-((Z)-6-(((1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-6-oxohex-1-en-1-yl)benzoate)



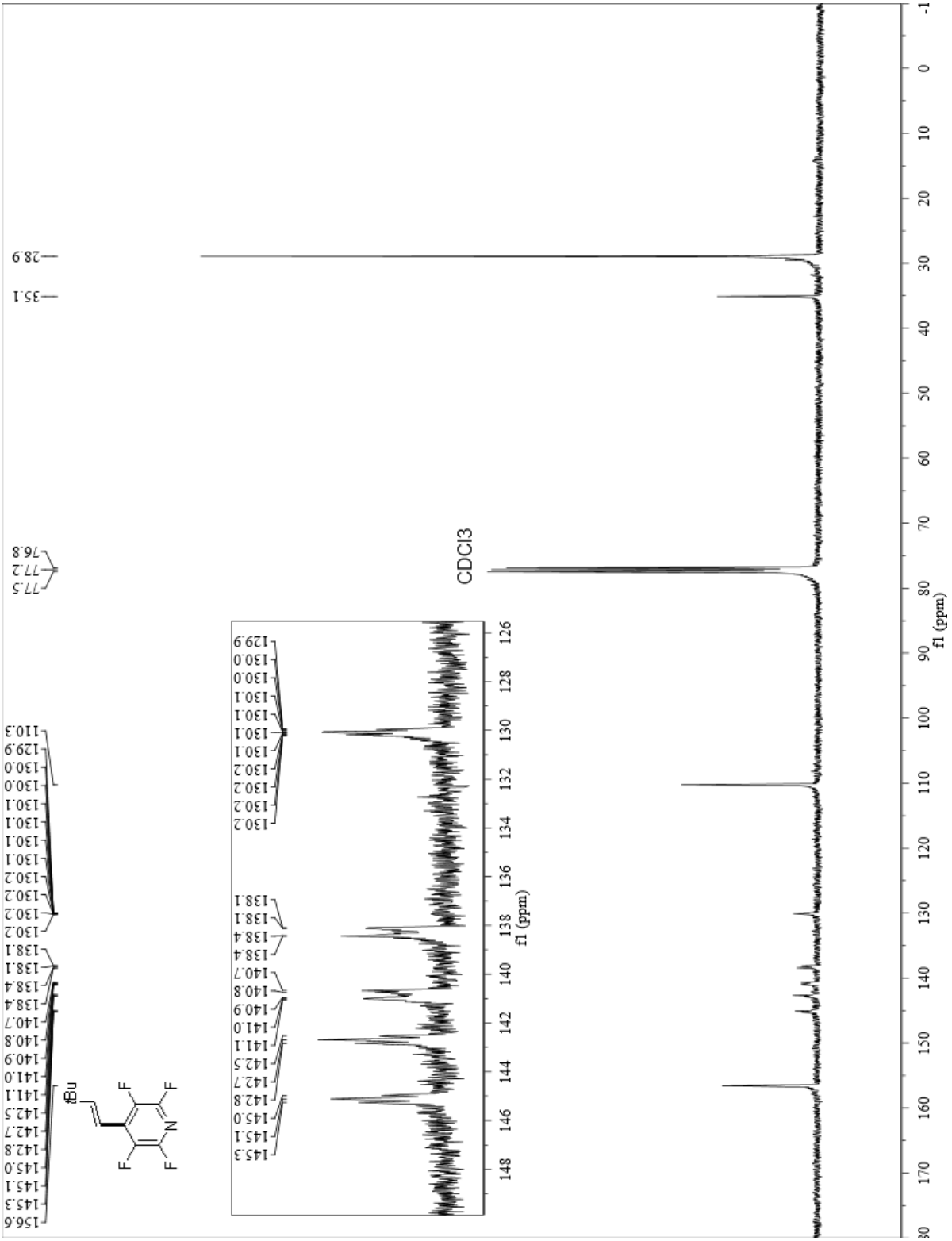
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-23a ((E)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)



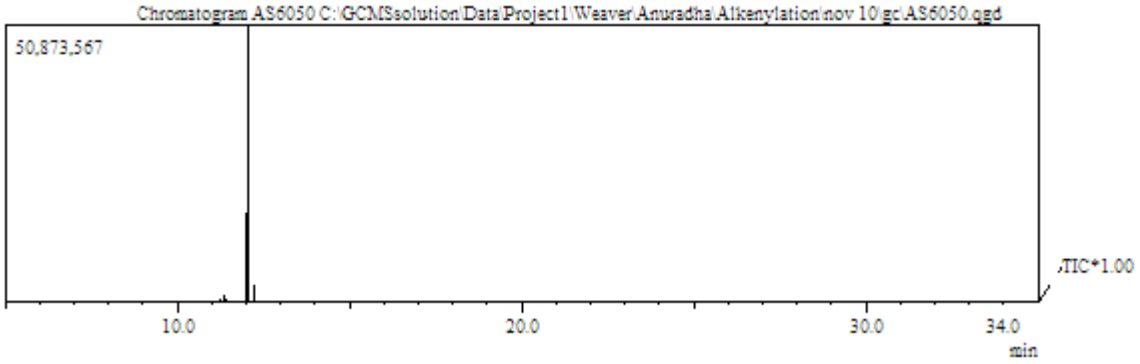
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-23a ((E)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)

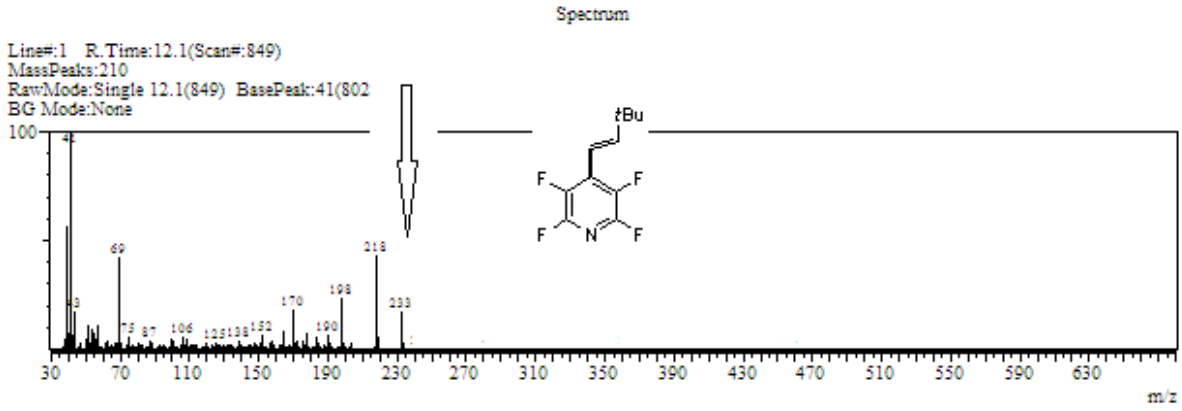


^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-23a ((E)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)

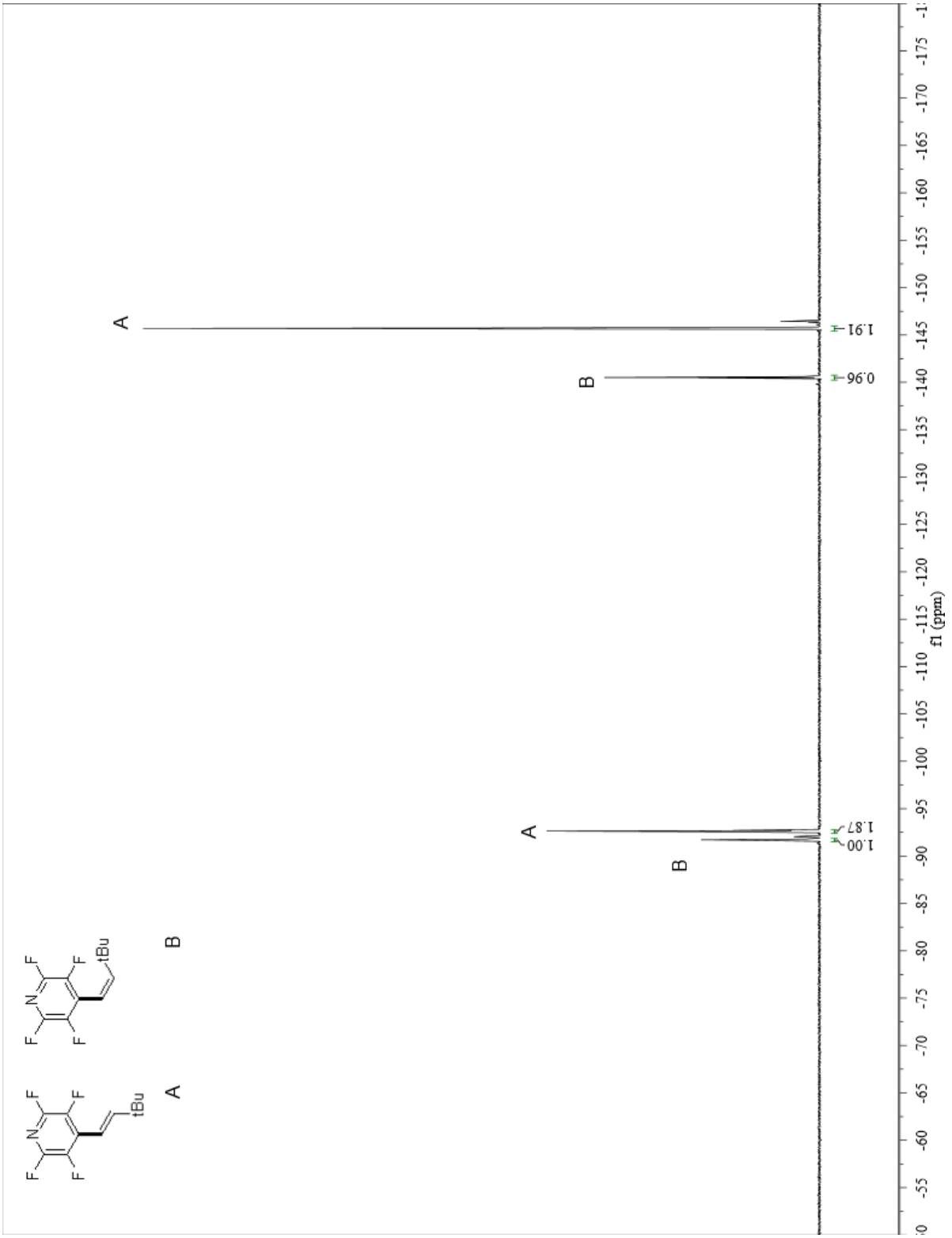


GC and MS of S-23a ((E)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)

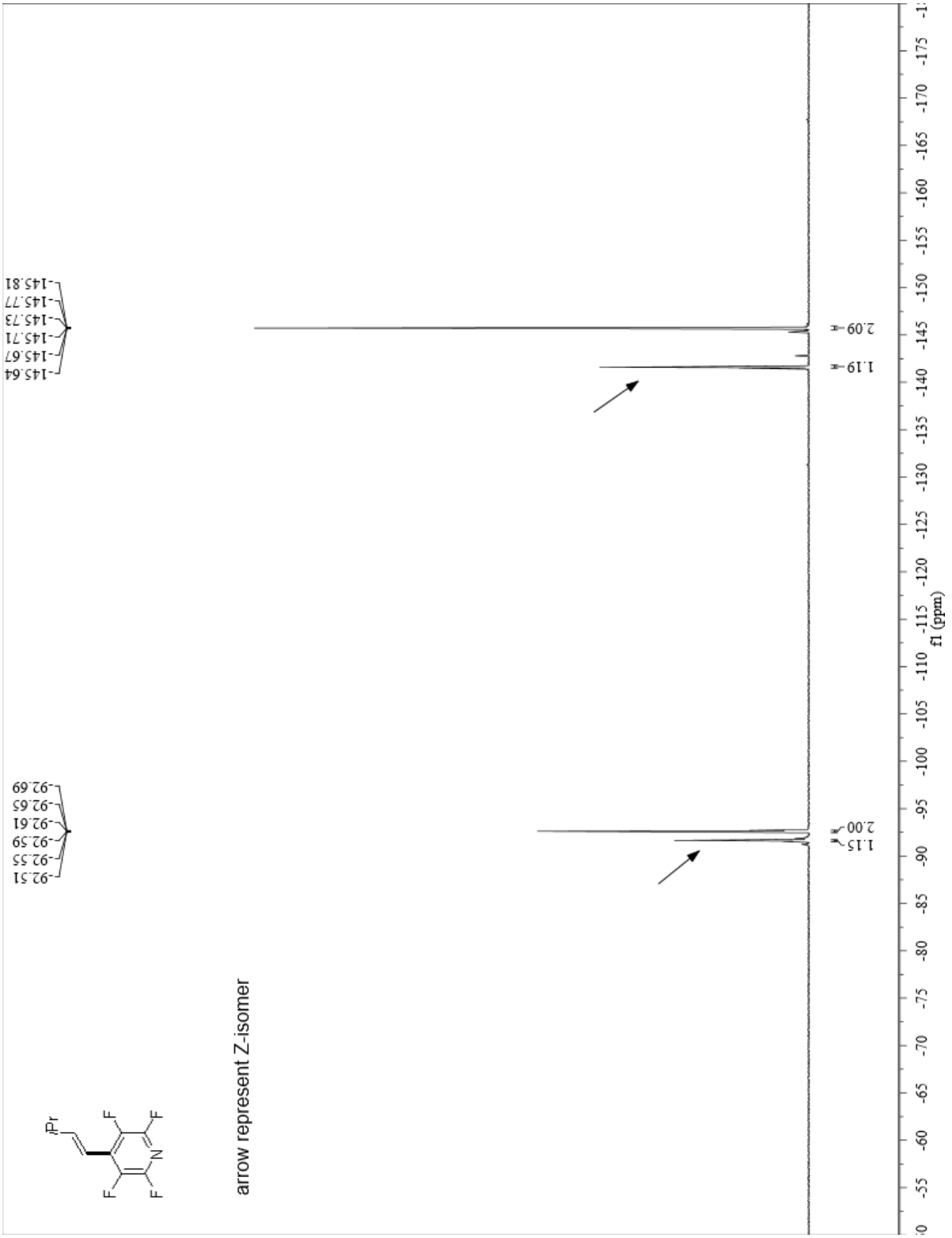




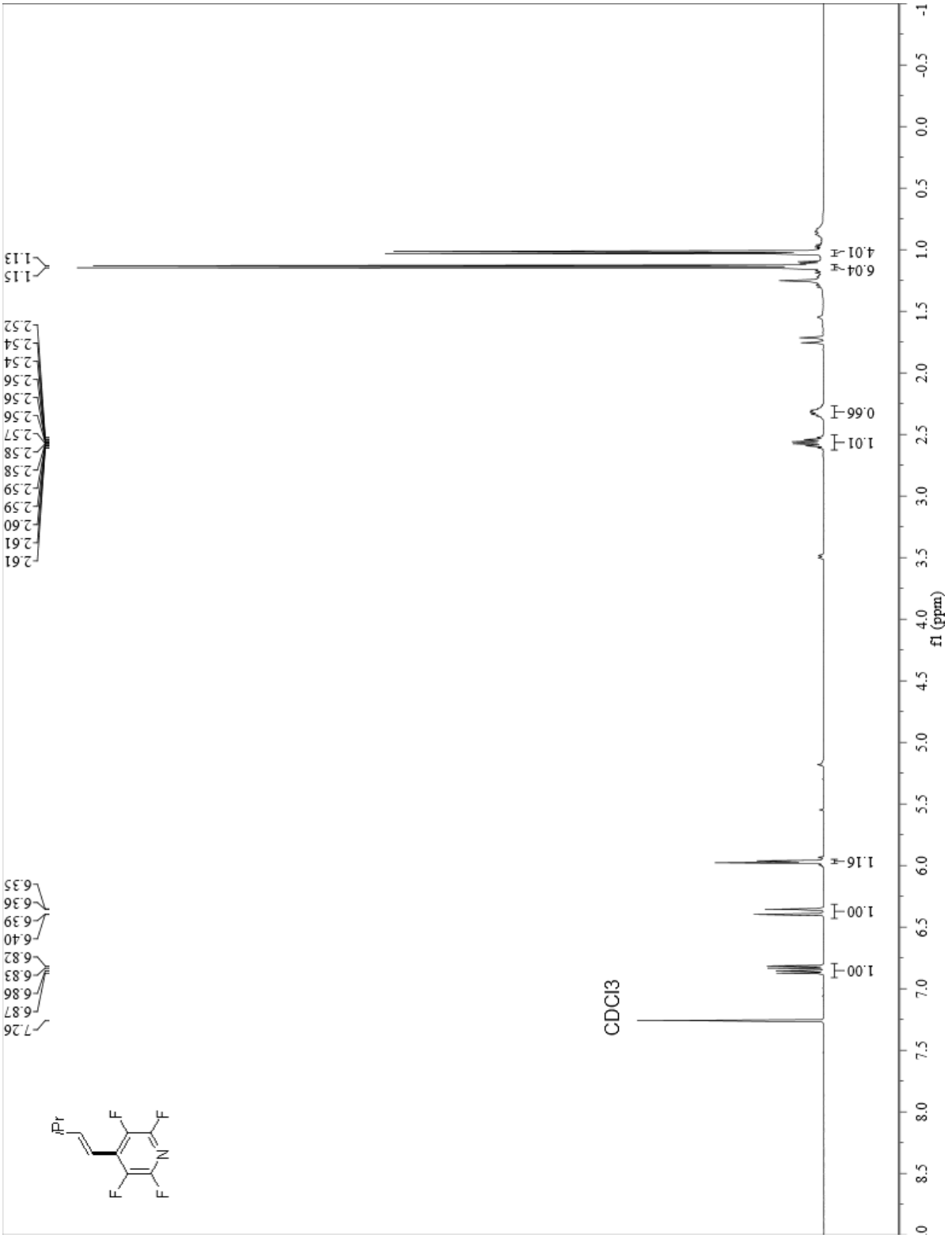
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-23a and S-7a((E/Z)-4-(3,3-dimethylbut-1-en-1-yl)-2,3,5,6-tetrafluoropyridine)



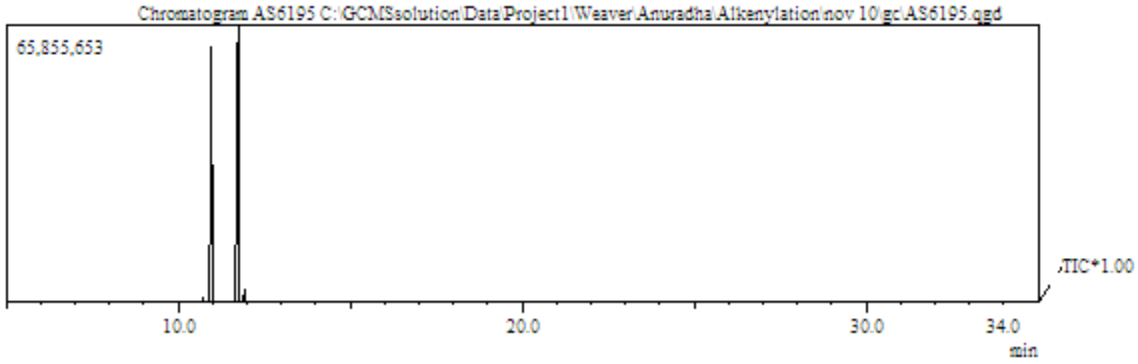
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-24a (E)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine



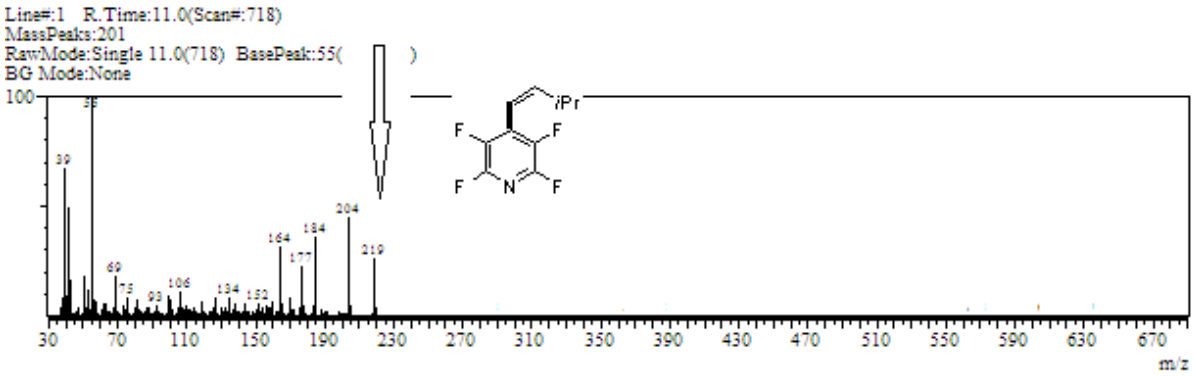
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-24a (E)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine

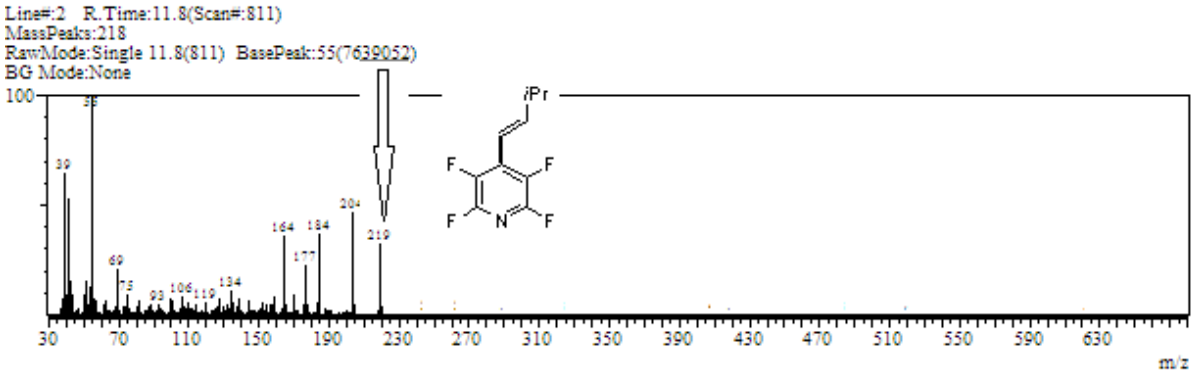


GC and MS of of S-24a (E)-2,3,5,6-tetrafluoro-4-(3-methylbut-1-en-1-yl)pyridine

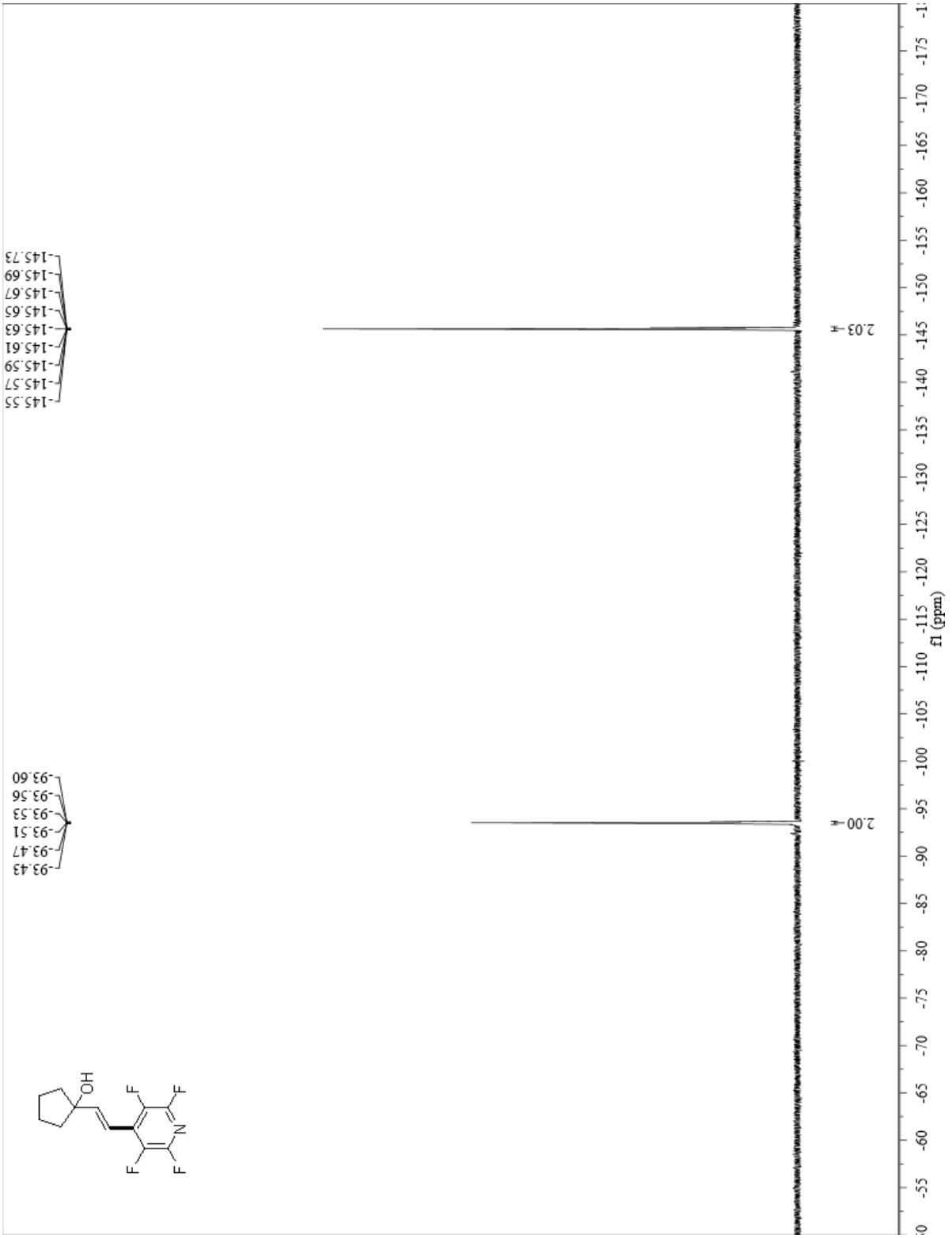


Spectrum

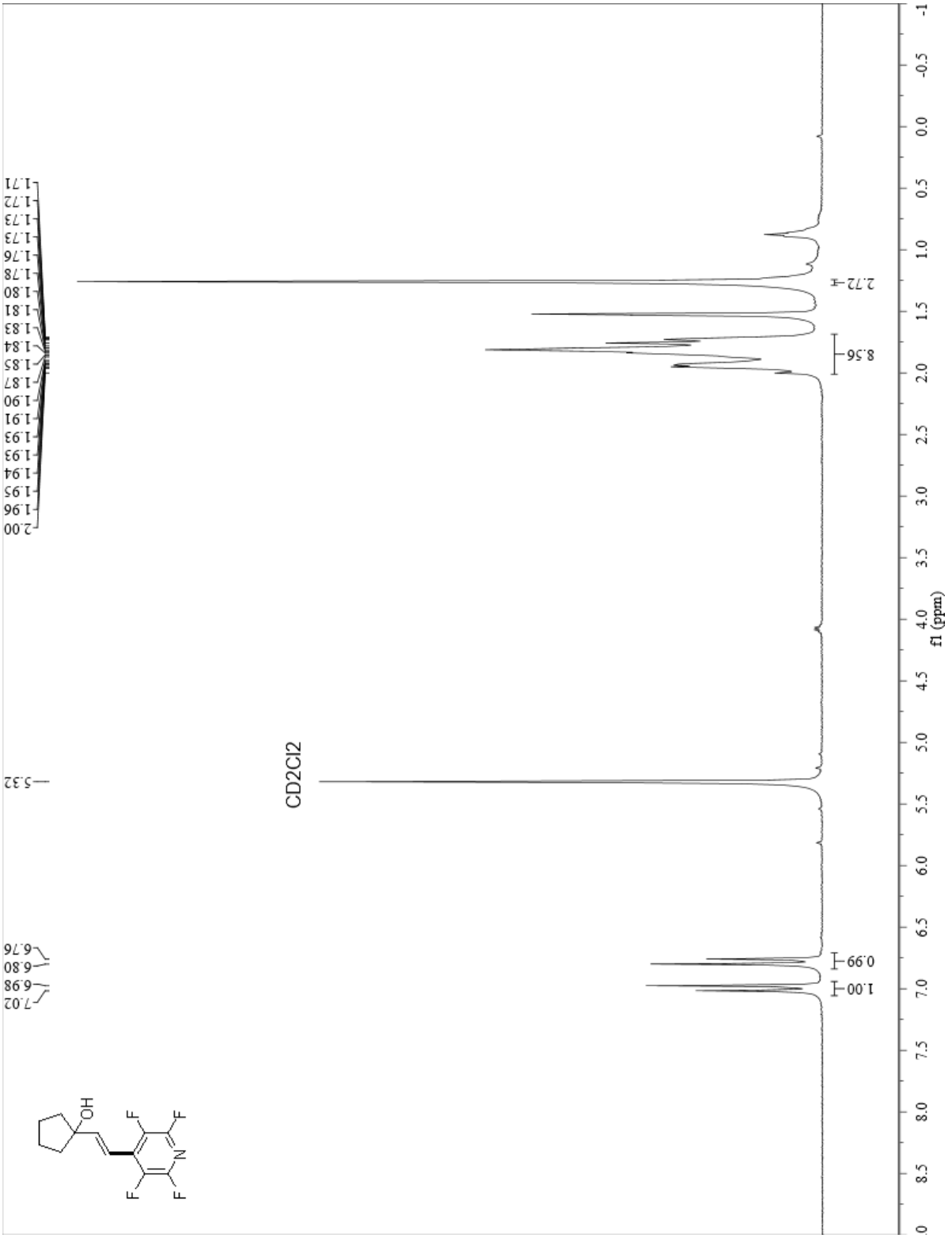




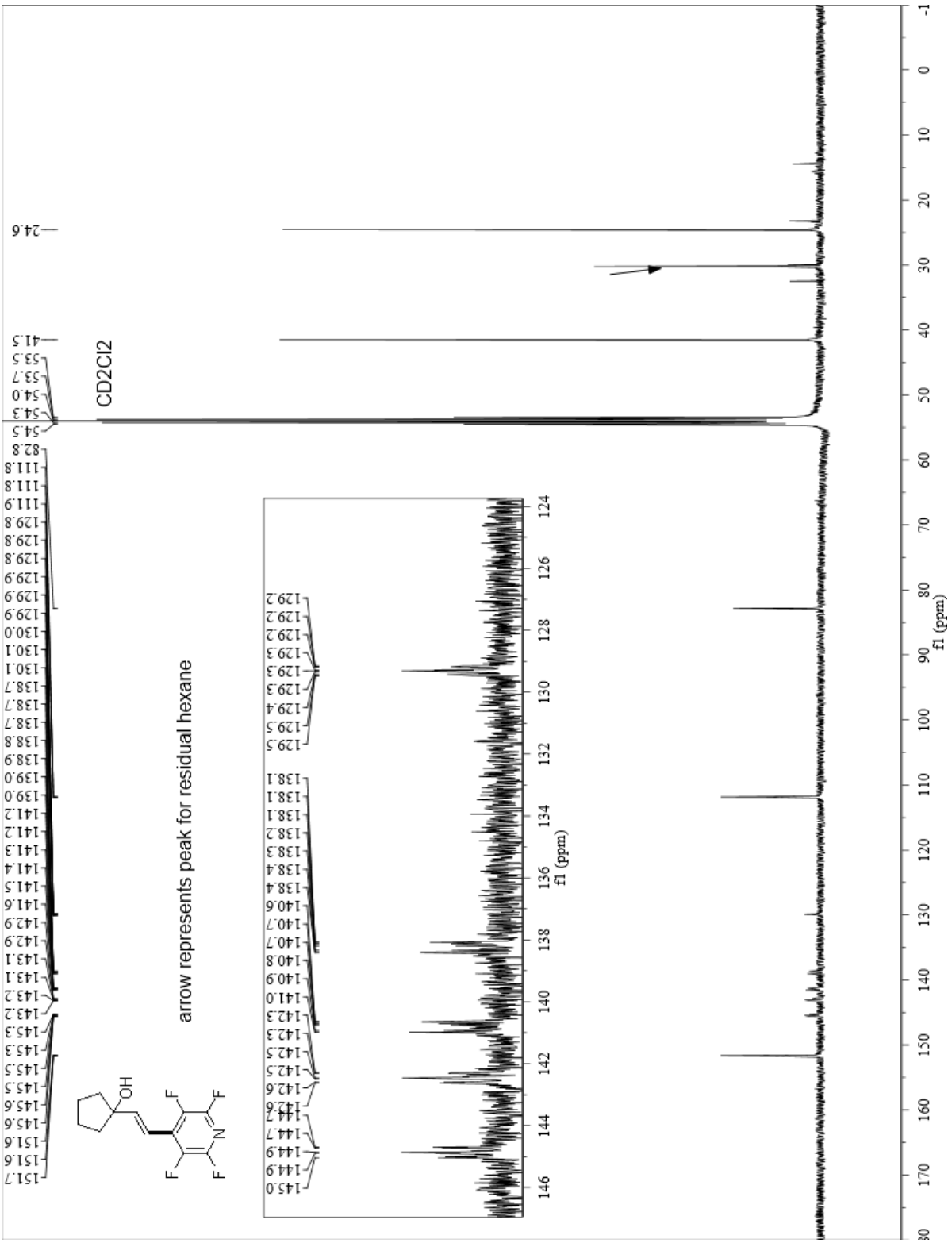
^{19}F NMR (376 MHz, Methylene Chloride-d_2, at rt) of S-25a (E)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol



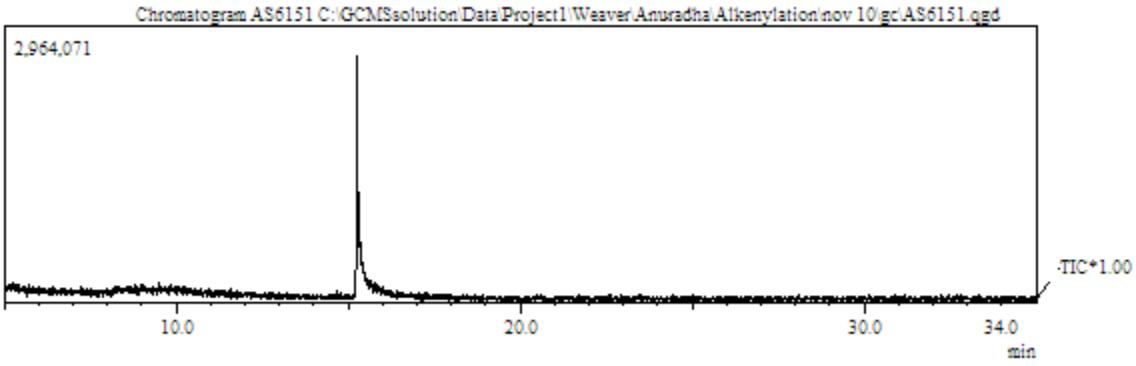
[1]H NMR (400 MHz, Methylene Chloride-*d*2, at rt) of S-25a (E)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol

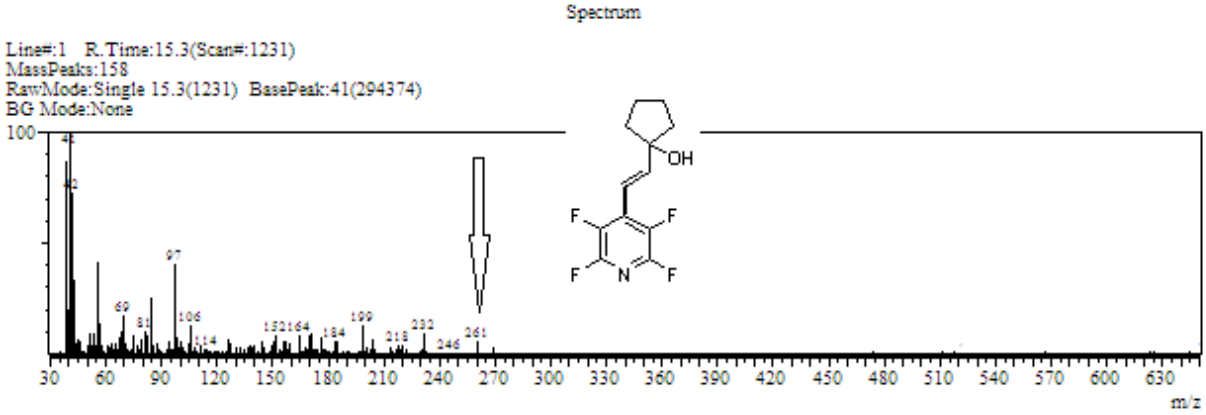


^{13}C NMR (101 MHz, Methylene Chloride-d_2, at rt) of S-25a (E)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol

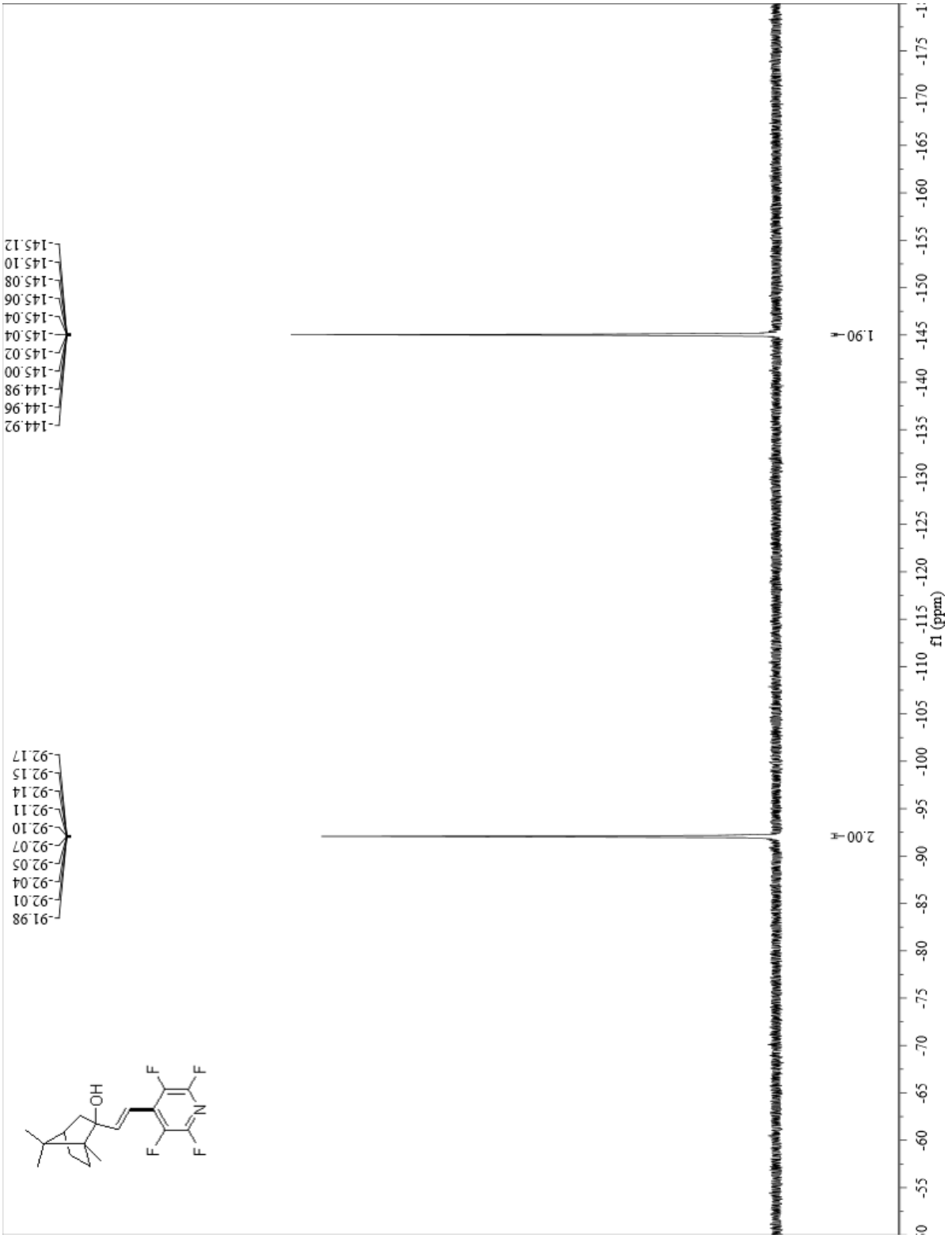

CD2Cl2
arrow represents peak for residual hexane
OH
F
F
F
N
f1 (ppm)

GC and MS of S-25a (E)-1-(2-(perfluoropyridin-4-yl)vinyl)cyclopentan-1-ol

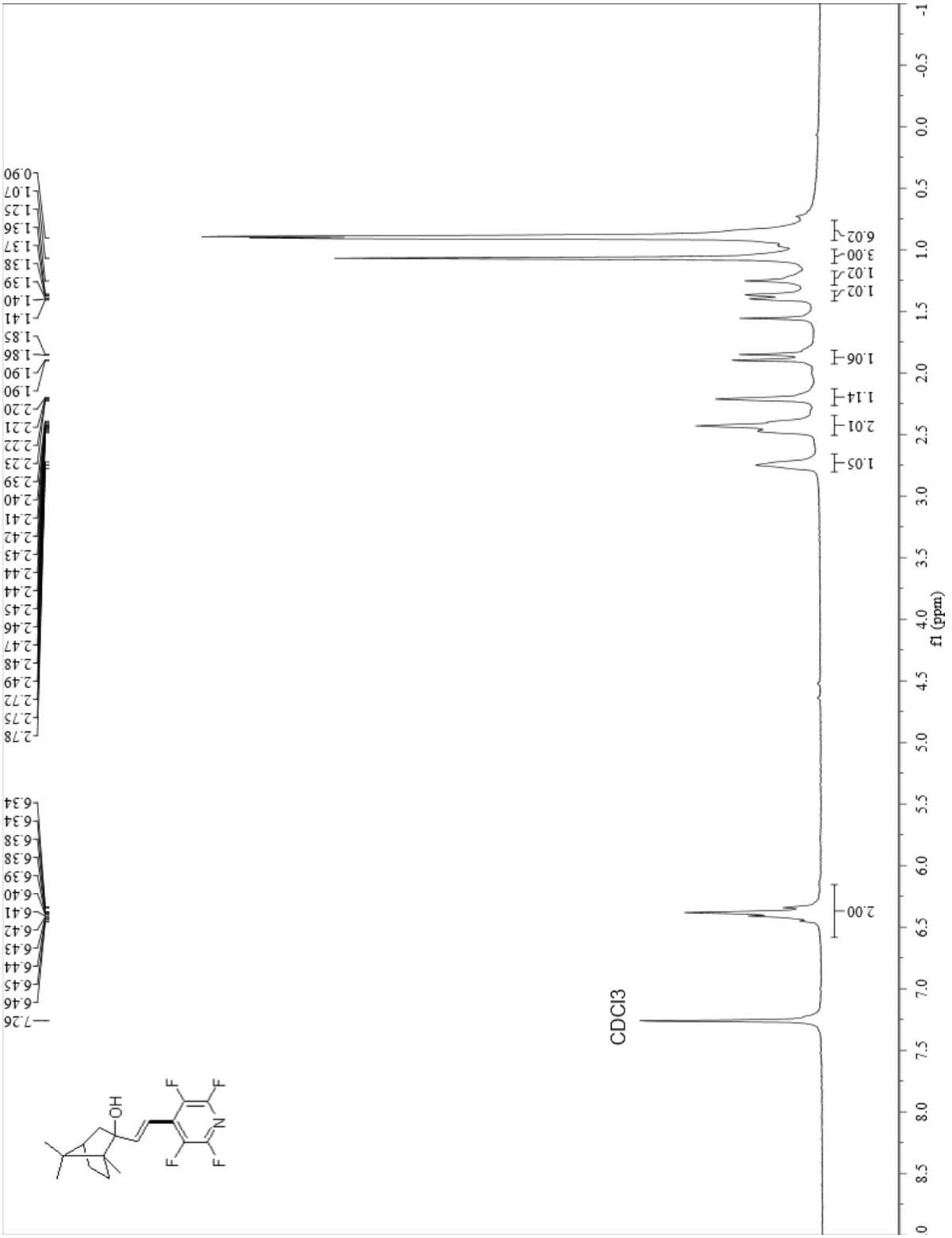




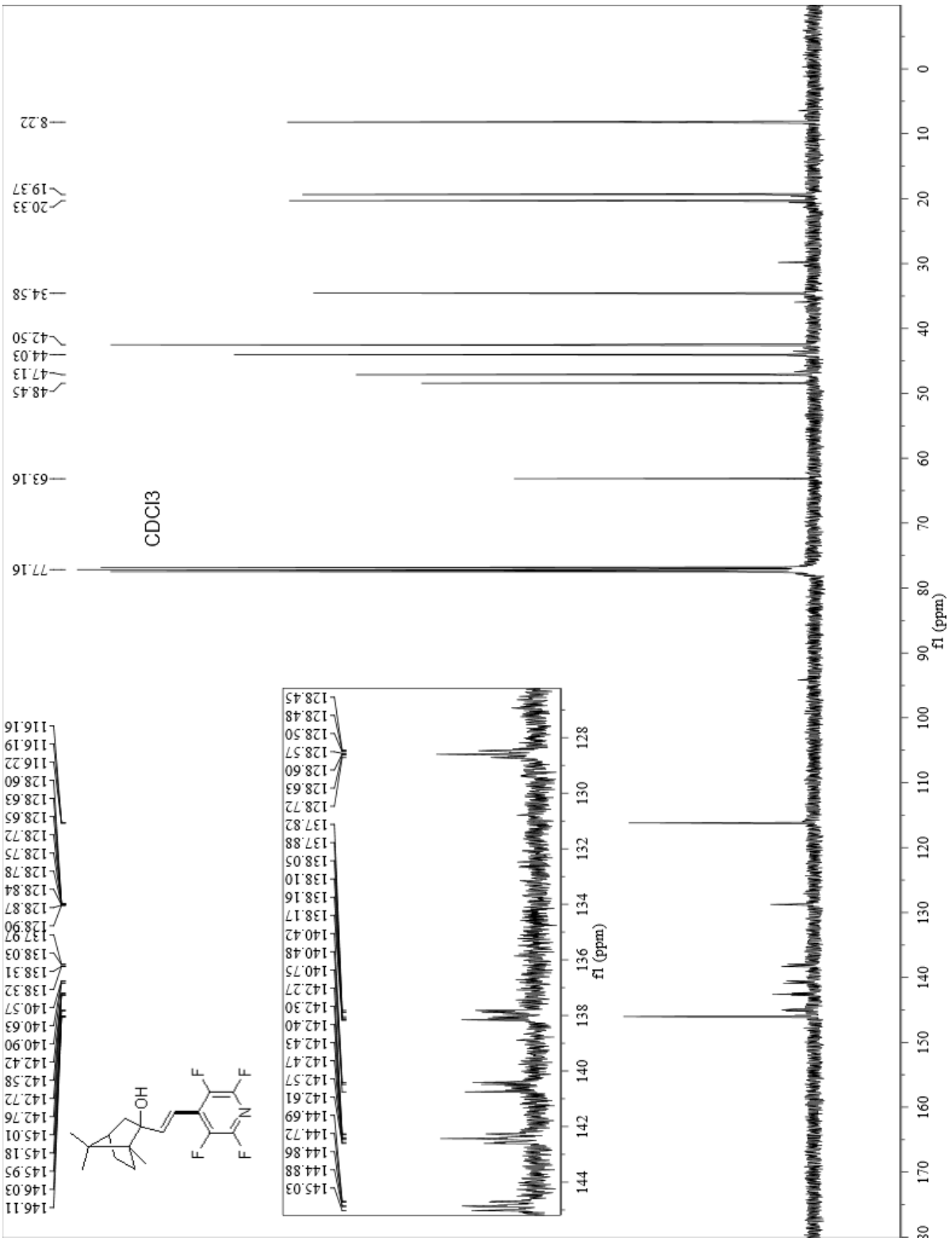
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-26a (1S,2S,4R)-1,7,7-trimethyl-2-((E)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol



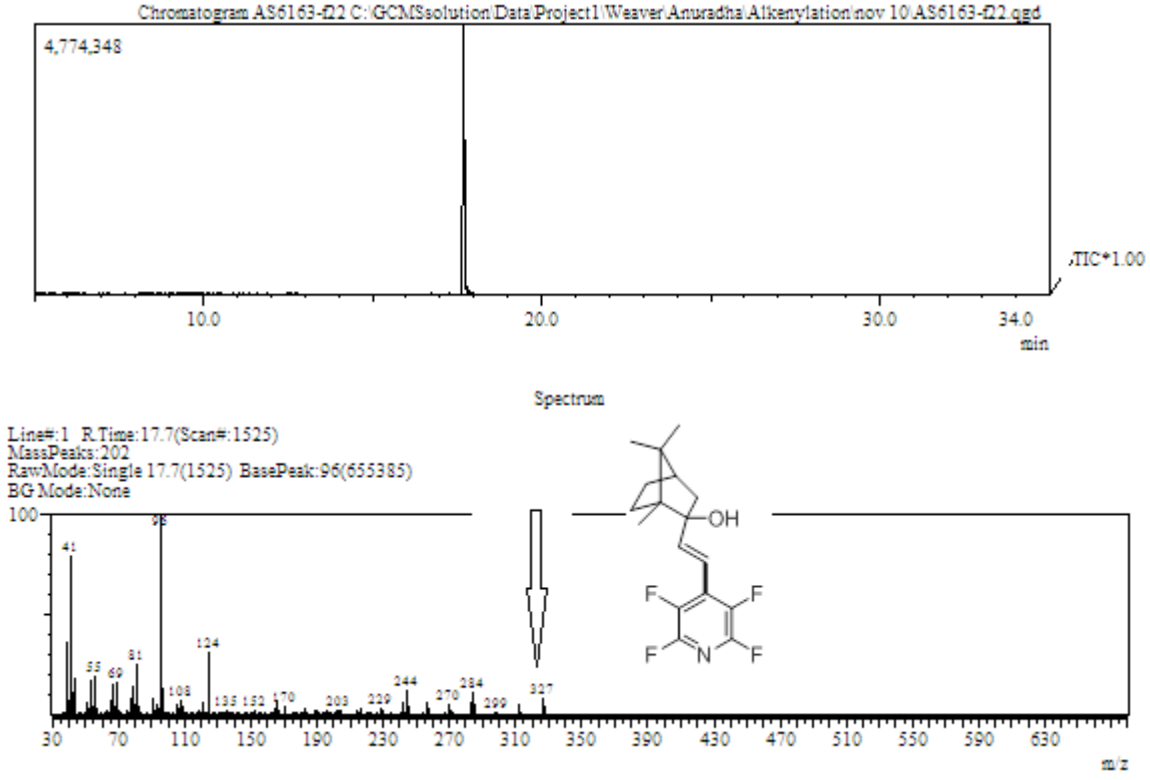
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-26a (1S,2S,4R)-1,7,7-trimethyl-2-((E)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol



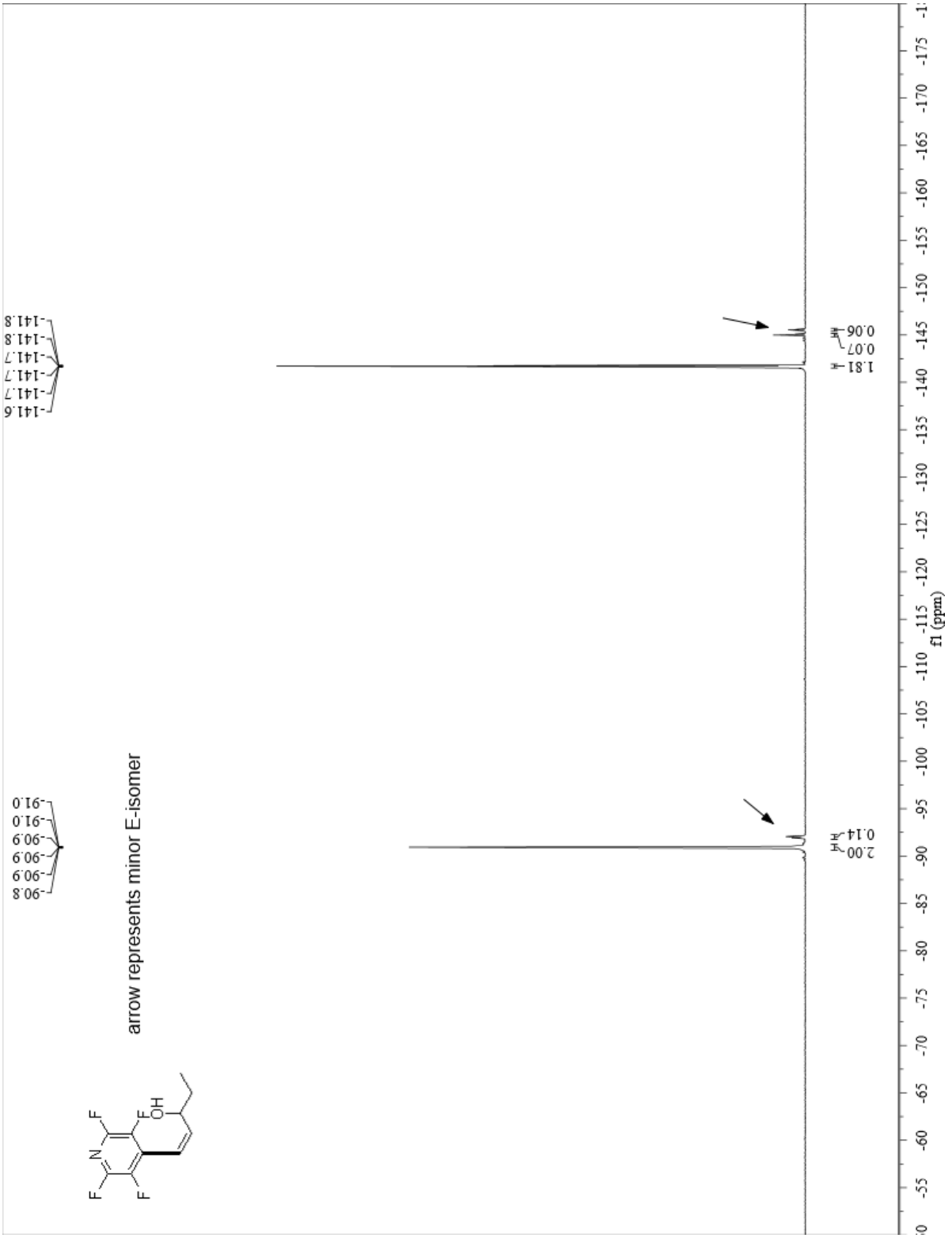
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-26a (1S,2S,4R)-1,7,7-trimethyl-2-((E)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol


CDCl3
f1 (ppm)

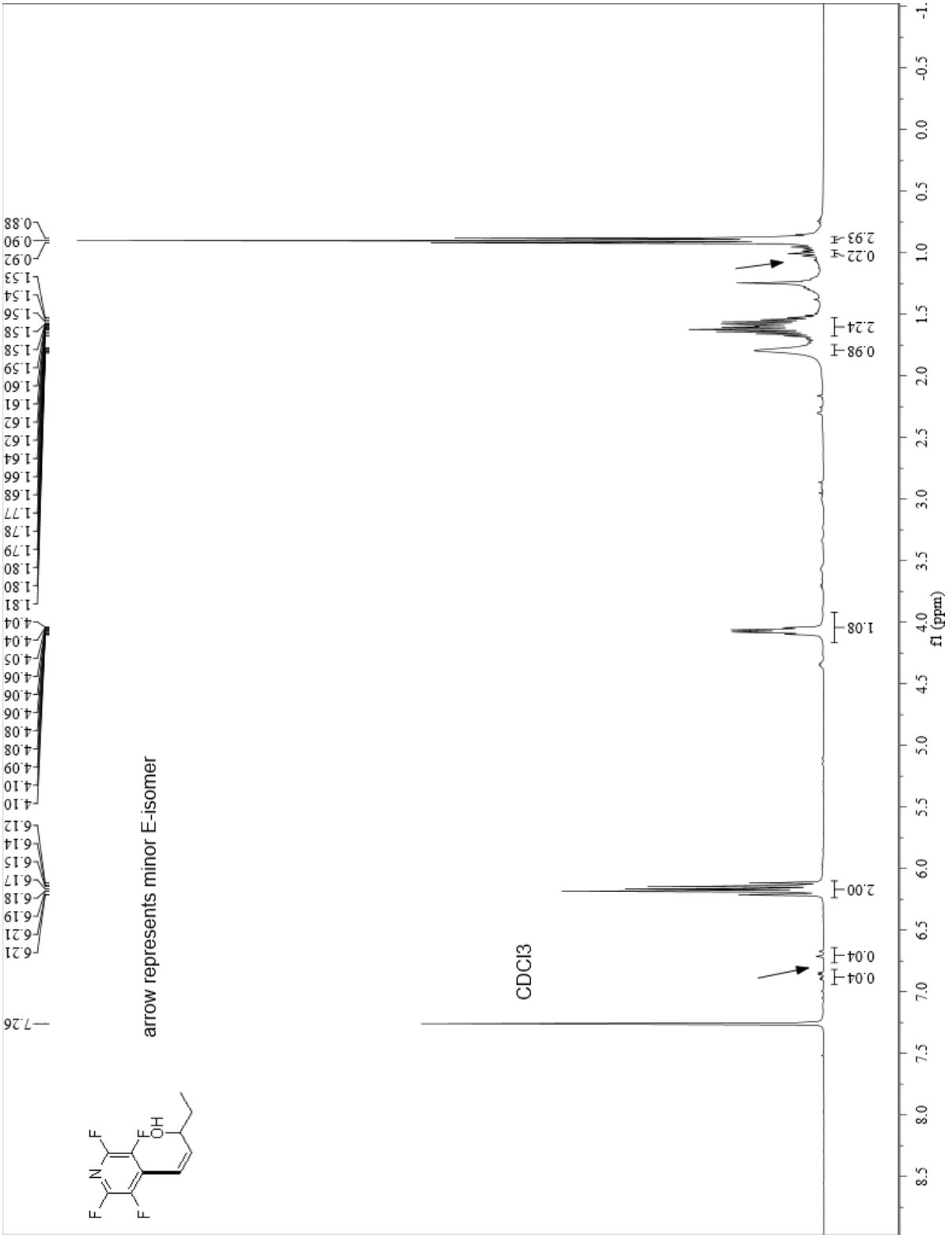
GC and MS of S-26a (1S,2S,4R)-1,7,7-trimethyl-2-((E)-2-(perfluoropyridin-4-yl)vinyl)bicyclo[2.2.1]heptan-2-ol



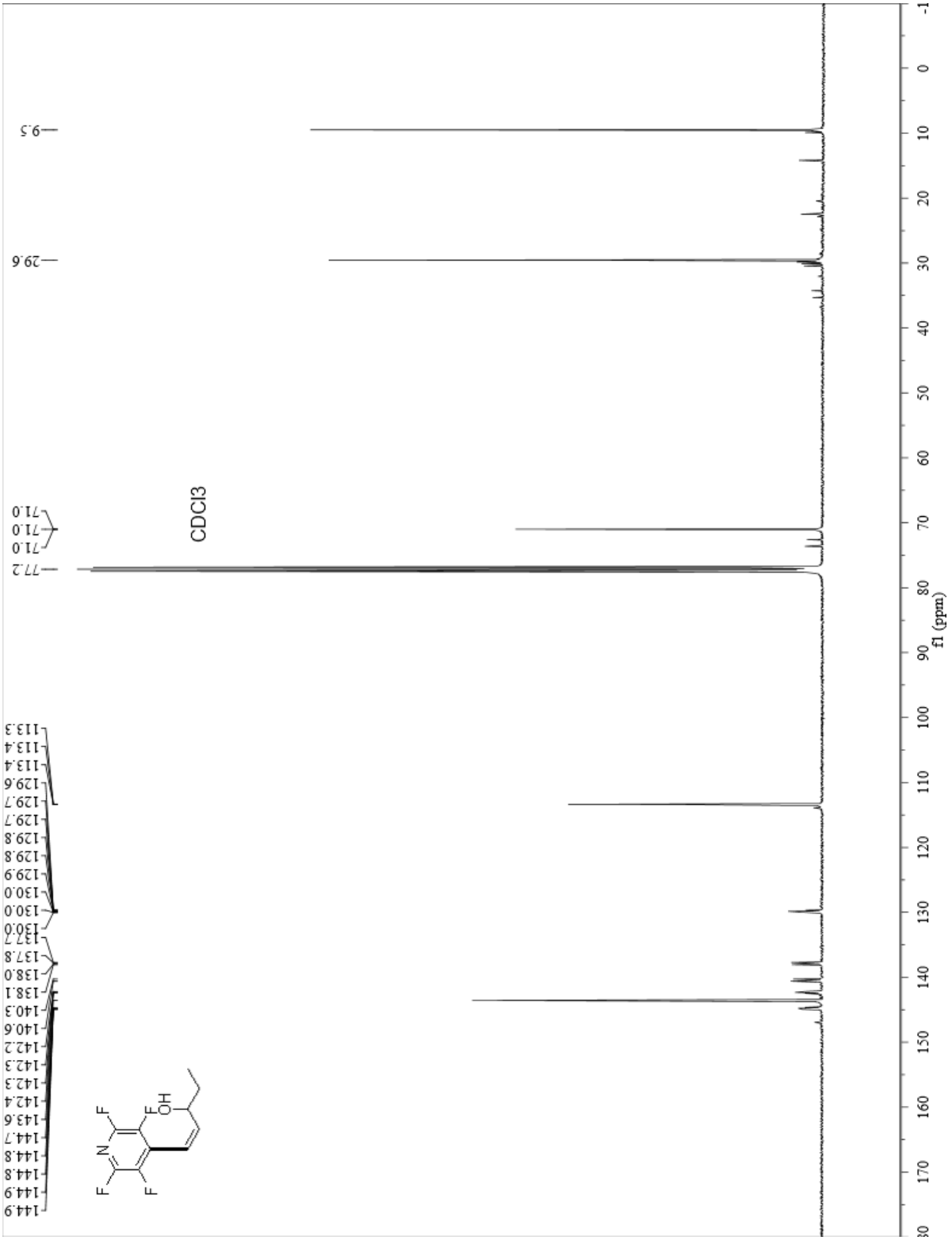
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-27 (Z)-1-(perfluoropyridin-4-yl)pent-1-en-3-ol



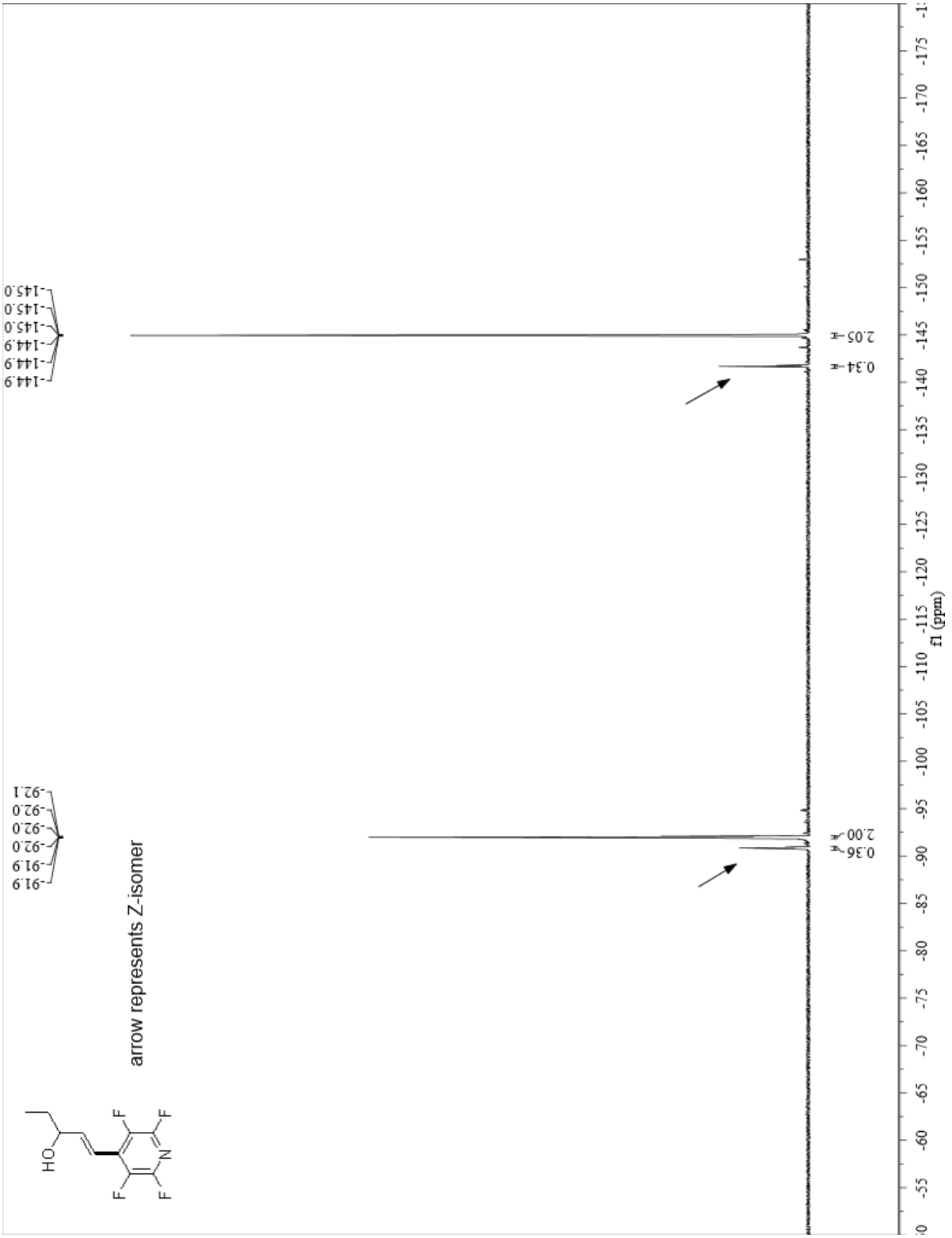
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-27 (Z)-1-(perfluoropyridin-4-yl)pent-1-en-3-o



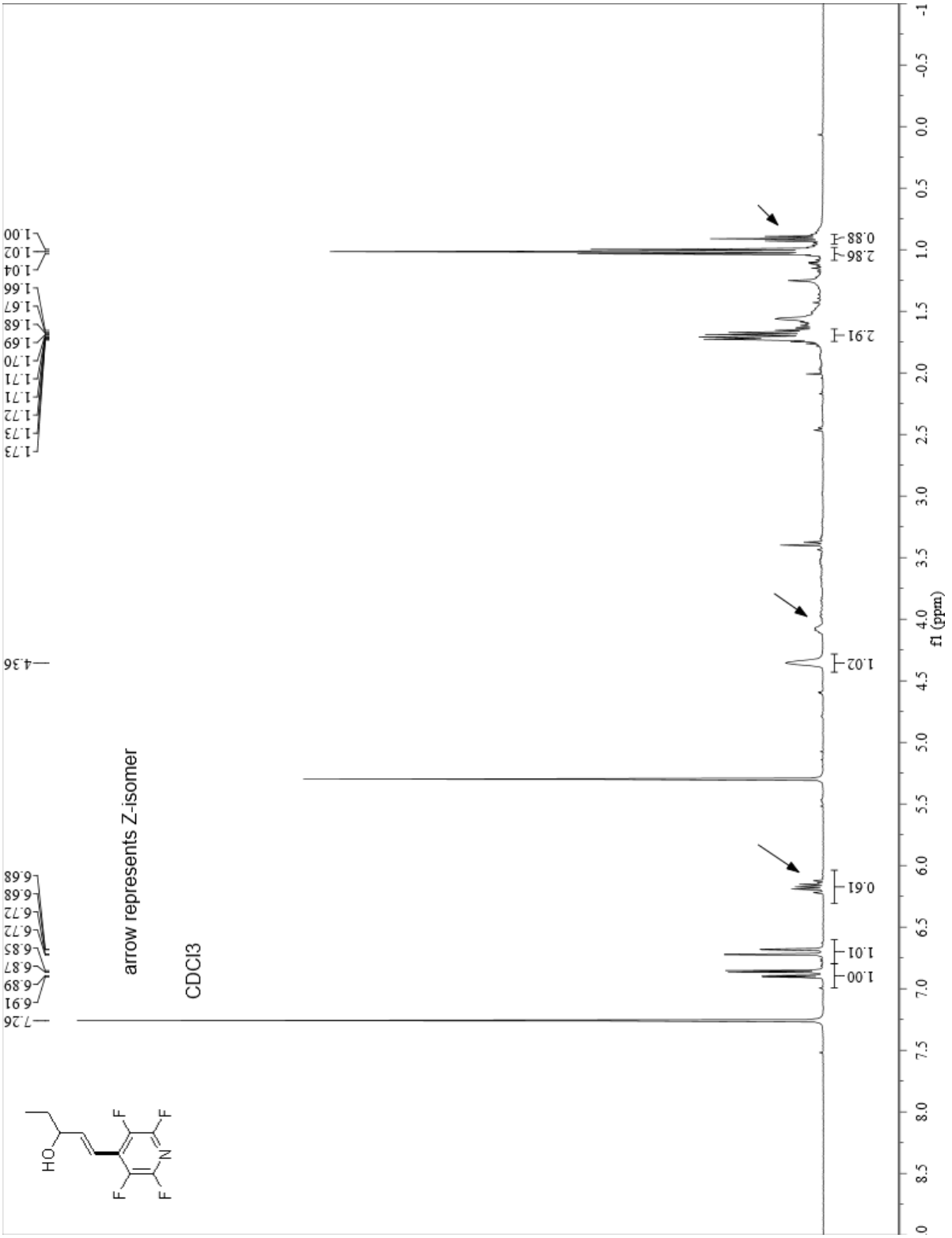
^{13}C NMR (101 MHz, Chloroform-*d*, at rt) of S-27 (Z)-1-(perfluoropyridin-4-yl)pent-1-en-3-ol



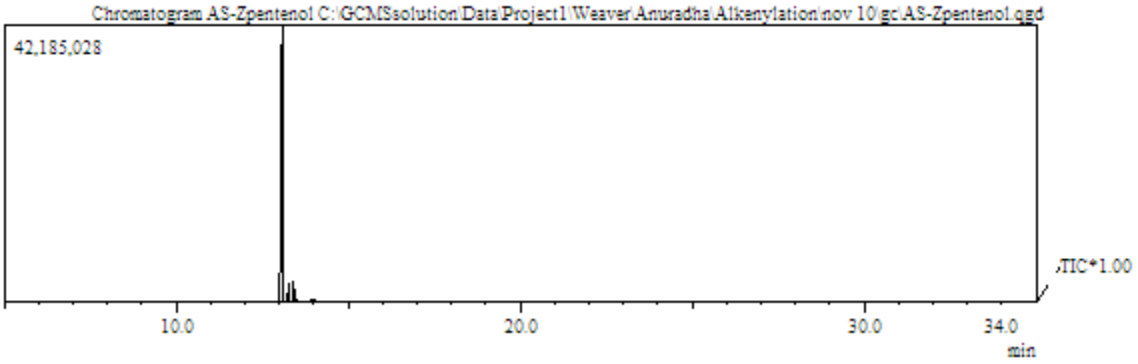
^{19}F NMR (376 MHz, Chloroform-*d*, at rt) of S-27 (E)-1-(perfluoropyridin-4-yl)pent-1-en-3-ol

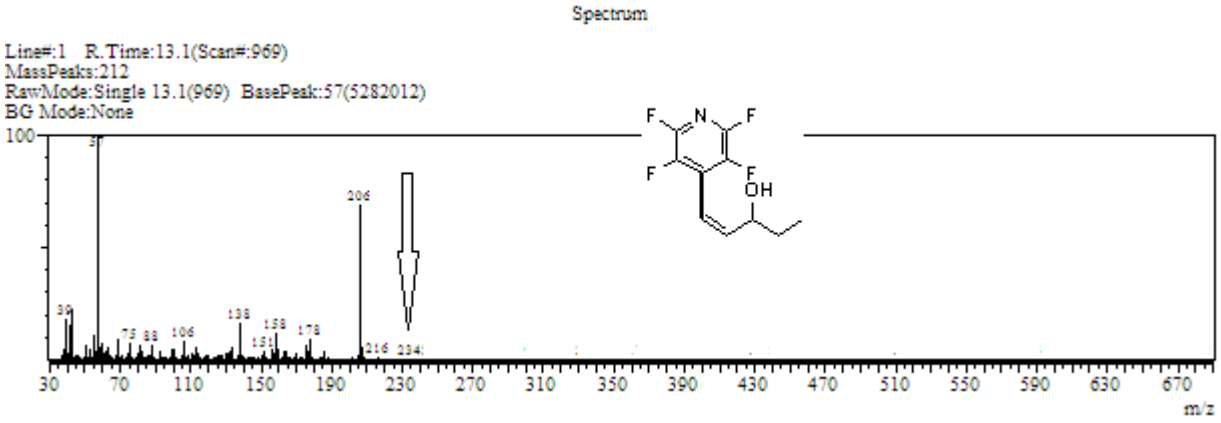


^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of S-27 (E)-1-(perfluoropyridin-4-yl)pent-1-en-3-ol

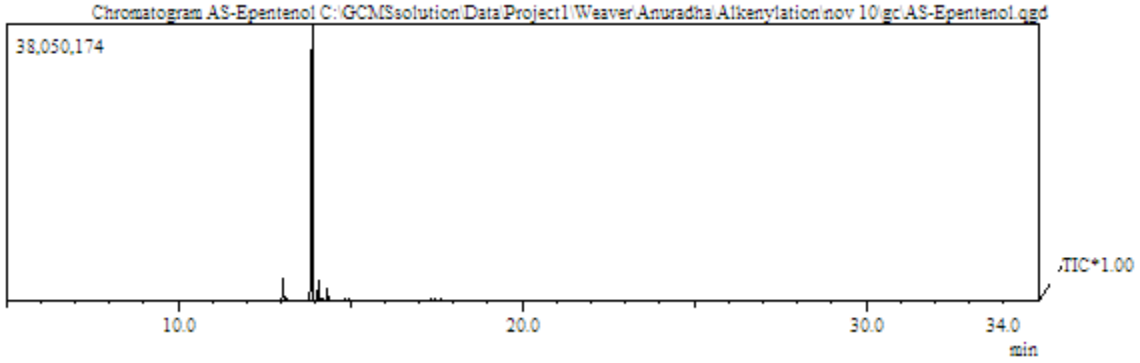


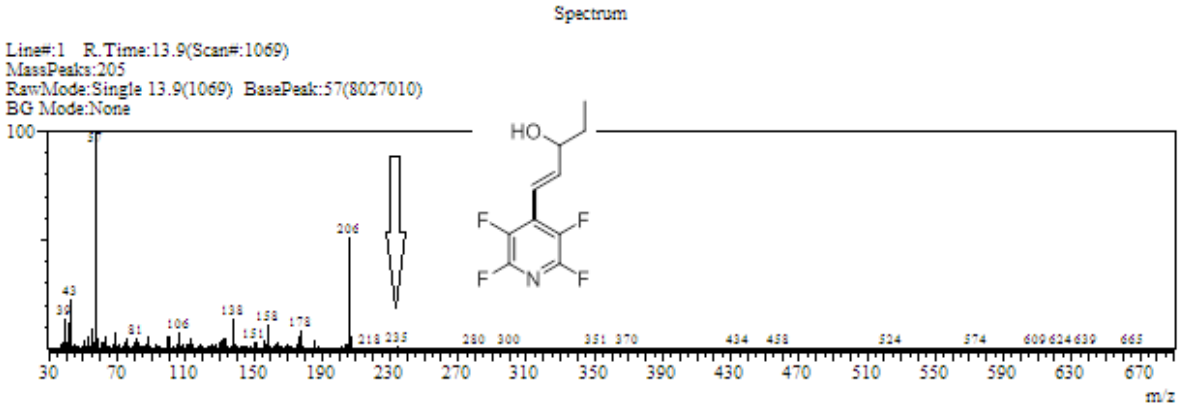
GC and MS of S-27a (Z)-1-(perfluoropyridin-4-yl)pent-1-en-3-ol





GC and MS of S-27a (E)-1-(perfluoropyridin-4-yl)pent-1-en-3-ol

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F
F
F
N
F
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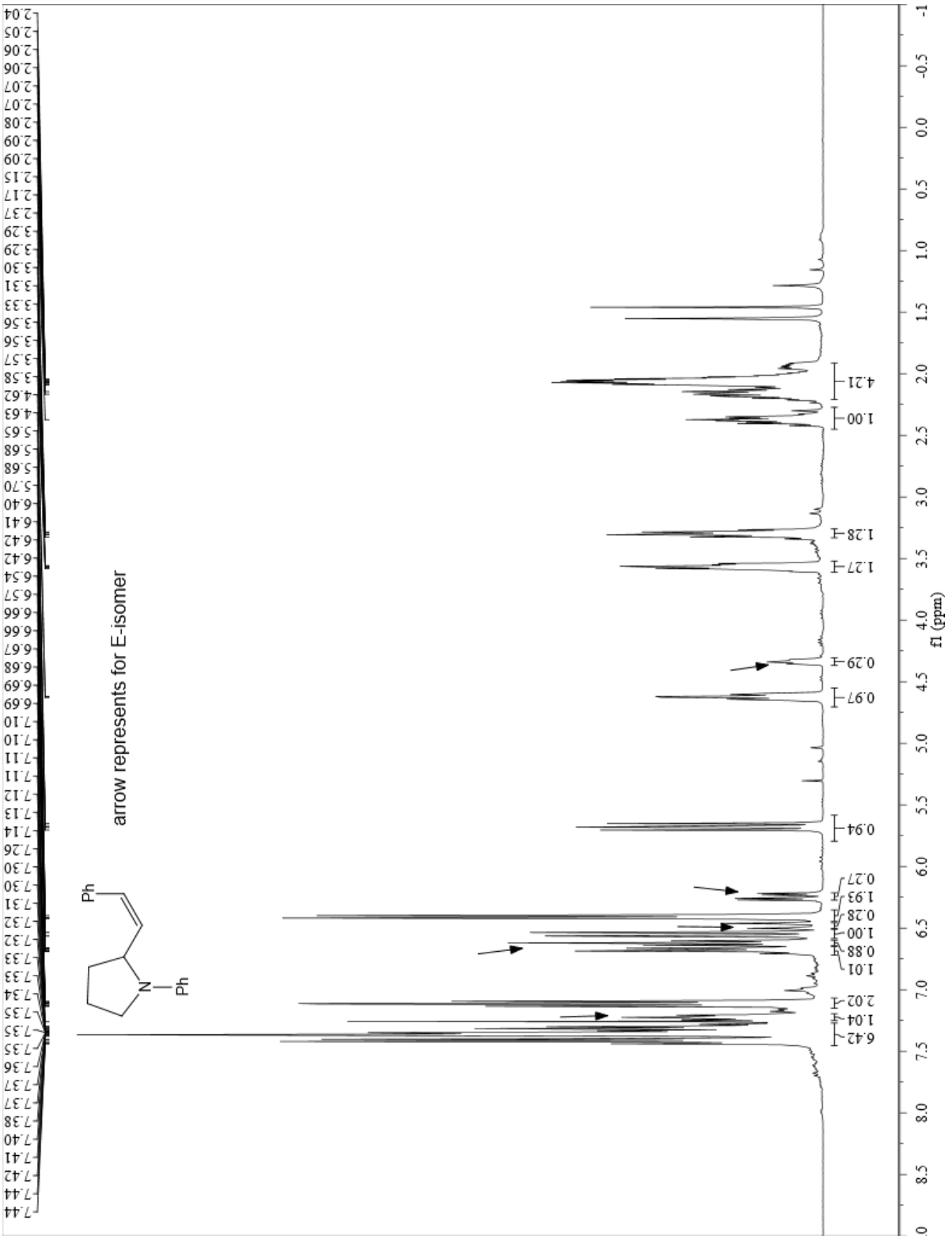
351
370
434
458
524
574
609
624
639
665
30
70
110
150
190
230
270
310
350
390
430
470
510
550
590
630
670
m/z

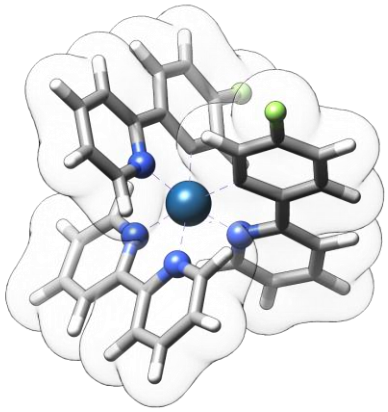
^{1}H NMR (400 MHz, Chloroform-*d*, at rt) of (Z)-1-phenyl-2-styrylpyrrolidine



Calculated photocatalyst structures

Geometry optimized structures were produced using standard ground-state optimization calculations of the tested photocatalysts using Gaussian09.[12] The TPSS functional and QZVP basis set were selected due to their expected quality for describing noble metal complex geometry and energetics.[10-12] These gas-phase geometry optimizations were performed until variation in structure energies between optimization cycles fell below 0.059 kcal/mol (0.1 k_BT at standard temperature). Images in the 0.001 e-/Å^3 electron density isosurfaces and PDB coordinates for the final molecular structures are provided below.

Cat-1, $Ir(Fppy)_2bpy^+$



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HETATM    3  C   LIG     1      -1.311   1.181   0.786  1.00  0.00           C
HETATM    4  C   LIG     1      -1.641   2.321   0.001  1.00  0.00           C
HETATM    5  C   LIG     1      -2.605   3.247   0.437  1.00  0.00           C
HETATM    6  C   LIG     1      -3.257   3.071   1.649  1.00  0.00           C
HETATM    7  C   LIG     1      -2.923   1.952   2.406  1.00  0.00           C
HETATM    8  N   LIG     1      -0.001   1.444  -1.479  1.00  0.00           N
HETATM    9  C   LIG     1       0.723   1.449  -2.620  1.00  0.00           C
HETATM   10  C   LIG     1       0.586   2.427  -3.589  1.00  0.00           C
HETATM   11  C   LIG     1      -0.340   3.452  -3.377  1.00  0.00           C
HETATM   12  C   LIG     1      -1.087   3.454  -2.210  1.00  0.00           C
HETATM   13  C   LIG     1      -0.918   2.442  -1.254  1.00  0.00           C
HETATM   14  C   LIG     1      -1.978  -1.014  -2.006  1.00  0.00           C
HETATM   15  C   LIG     1      -1.311  -1.181  -0.786  1.00  0.00           C
HETATM   16  C   LIG     1      -1.641  -2.321  -0.001  1.00  0.00           C
HETATM   17  C   LIG     1      -2.605  -3.247  -0.437  1.00  0.00           C
HETATM   18  C   LIG     1      -3.257  -3.071  -1.649  1.00  0.00           C
HETATM   19  C   LIG     1      -2.923  -1.952  -2.406  1.00  0.00           C
HETATM   20  N   LIG     1      -0.001  -1.444   1.479  1.00  0.00           N
HETATM   21  C   LIG     1       0.723  -1.449   2.620  1.00  0.00           C
HETATM   22  C   LIG     1       0.586  -2.427   3.589  1.00  0.00           C
HETATM   23  C   LIG     1      -0.340  -3.452   3.377  1.00  0.00           C
HETATM   24  C   LIG     1      -1.087  -3.454   2.210  1.00  0.00           C
```

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HETATM   25  C   LIG     1      -0.918  -2.442   1.254  1.00  0.00           C
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HETATM   27  N   LIG     1       1.848  -1.058  -0.804  1.00  0.00           N
HETATM   28  C   LIG     1       3.077  -0.598  -0.431  1.00  0.00           C
HETATM   29  C   LIG     1       4.243  -1.245  -0.852  1.00  0.00           C
HETATM   30  C   LIG     1       4.155  -2.370  -1.663  1.00  0.00           C
HETATM   31  C   LIG     1       2.895  -2.833  -2.037  1.00  0.00           C
HETATM   32  N   LIG     1       1.848   1.058   0.804  1.00  0.00           N
HETATM   33  C   LIG     1       1.771   2.154   1.587  1.00  0.00           C
HETATM   34  C   LIG     1       2.895   2.833   2.037  1.00  0.00           C
HETATM   35  C   LIG     1       4.155   2.370   1.663  1.00  0.00           C
HETATM   36  C   LIG     1       4.243   1.245   0.852  1.00  0.00           C
HETATM   37  C   LIG     1       3.077   0.598   0.431  1.00  0.00           C
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HETATM   39  F   LIG     1      -3.553  -1.765  -3.591  1.00  0.00           F
HETATM   40  H   LIG     1      -1.791   0.167   2.656  1.00  0.00           H
HETATM   41  H   LIG     1      -2.852   4.114  -0.168  1.00  0.00           H
HETATM   42  H   LIG     1      -4.005   3.769   2.006  1.00  0.00           H
HETATM   43  H   LIG     1      -1.814   4.236  -2.028  1.00  0.00           H
HETATM   44  H   LIG     1      -1.791  -0.167  -2.656  1.00  0.00           H
HETATM   45  H   LIG     1      -2.852  -4.114   0.168  1.00  0.00           H
HETATM   46  H   LIG     1      -4.005  -3.769  -2.006  1.00  0.00           H
HETATM   47  H   LIG     1      -1.814  -4.236   2.028  1.00  0.00           H
HETATM   48  H   LIG     1       0.768  -2.473  -1.844  1.00  0.00           H
HETATM   49  H   LIG     1       5.213  -0.875  -0.545  1.00  0.00           H
HETATM   50  H   LIG     1       5.055  -2.877  -1.993  1.00  0.00           H
HETATM   51  H   LIG     1       2.777  -3.707  -2.666  1.00  0.00           H
HETATM   52  H   LIG     1       0.768   2.473   1.844  1.00  0.00           H
HETATM   53  H   LIG     1       5.055   2.877   1.993  1.00  0.00           H
HETATM   54  H   LIG     1       5.213   0.875   0.545  1.00  0.00           H
HETATM   55  F   LIG     1      -3.553   1.765   3.591  1.00  0.00           F
HETATM   56  H   LIG     1      -0.477  -4.234   4.116  1.00  0.00           H
HETATM   57  H   LIG     1       1.188  -2.381   4.488  1.00  0.00           H
HETATM   58  H   LIG     1       1.419  -0.629   2.741  1.00  0.00           H
HETATM   59  H   LIG     1      -0.477   4.234  -4.116  1.00  0.00           H
HETATM   60  H   LIG     1       1.188   2.381  -4.488  1.00  0.00           H
HETATM   61  H   LIG     1       1.419   0.629  -2.741  1.00  0.00           H
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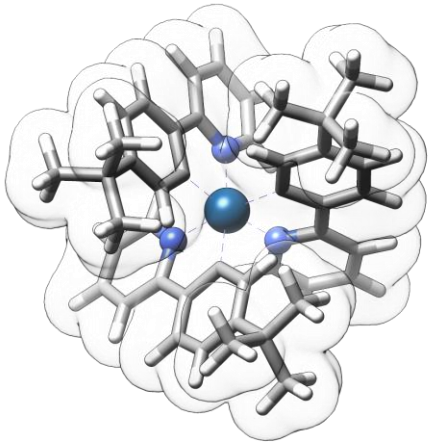
Cat-2, *fac*-Ir(*t*Buppy)$_3$



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HETATM    1 IR   LIG     1      -1.005  -0.030   0.051  1.00  0.00          Ir
HETATM    2  C   LIG     1      -3.034  -1.602   1.874  1.00  0.00           C
HETATM    3  N   LIG     1      -2.012  -1.689   1.000  1.00  0.00           N
HETATM    4  C   LIG     1      -1.508  -2.920   0.672  1.00  0.00           C
HETATM    5  C   LIG     1      -2.069  -4.077   1.240  1.00  0.00           C
HETATM    6  C   LIG     1      -3.129  -3.979   2.129  1.00  0.00           C
HETATM    7  C   LIG     1      -3.622  -2.713   2.460  1.00  0.00           C
HETATM    8  C   LIG     1       0.035  -1.602  -0.702  1.00  0.00           C
HETATM    9  C   LIG     1       1.114  -1.563  -1.608  1.00  0.00           C
HETATM   10  C   LIG     1       1.759  -2.711  -2.078  1.00  0.00           C
HETATM   11  C   LIG     1       1.304  -3.965  -1.621  1.00  0.00           C
HETATM   12  C   LIG     1       0.247  -4.051  -0.732  1.00  0.00           C
HETATM   13  C   LIG     1      -0.395  -2.888  -0.268  1.00  0.00           C
HETATM   14  C   LIG     1       1.294  -0.520   2.071  1.00  0.00           C
HETATM   15  C   LIG     1       0.126   0.191   1.724  1.00  0.00           C
HETATM   16  C   LIG     1      -0.334   1.165   2.654  1.00  0.00           C
HETATM   17  C   LIG     1       0.360   1.391   3.856  1.00  0.00           C
HETATM   18  C   LIG     1       1.502   0.670   4.156  1.00  0.00           C
HETATM   19  C   LIG     1       1.995  -0.302   3.261  1.00  0.00           C
HETATM   20  N   LIG     1      -2.084   1.532   1.086  1.00  0.00           N
HETATM   21  C   LIG     1      -3.188   2.162   0.640  1.00  0.00           C
HETATM   22  C   LIG     1      -3.816   3.175   1.348  1.00  0.00           C
HETATM   23  C   LIG     1      -3.274   3.564   2.576  1.00  0.00           C
HETATM   24  C   LIG     1      -2.132   2.925   3.039  1.00  0.00           C
HETATM   25  C   LIG     1      -1.533   1.902   2.284  1.00  0.00           C
HETATM   26  C   LIG     1       1.062   2.164  -0.661  1.00  0.00           C
HETATM   27  C   LIG     1      -0.063   1.402  -1.038  1.00  0.00           C
HETATM   28  C   LIG     1      -0.630   1.678  -2.314  1.00  0.00           C
HETATM   29  C   LIG     1      -0.078   2.670  -3.143  1.00  0.00           C
HETATM   30  C   LIG     1       1.026   3.397  -2.732  1.00  0.00           C
HETATM   31  C   LIG     1       1.621   3.154  -1.477  1.00  0.00           C
HETATM   32  N   LIG     1      -2.206  -0.011  -1.745  1.00  0.00           N
HETATM   33  C   LIG     1      -3.264  -0.805  -2.001  1.00  0.00           C
HETATM   34  C   LIG     1      -3.973  -0.756  -3.191  1.00  0.00           C
HETATM   35  C   LIG     1      -3.568   0.155  -4.171  1.00  0.00           C
HETATM   36  C   LIG     1      -2.474   0.971  -3.919  1.00  0.00           C
HETATM   37  C   LIG     1      -1.789   0.884  -2.695  1.00  0.00           C
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HETATM   38  H   LIG     1      -4.818  -1.417  -3.348  1.00  0.00           H
HETATM   39  C   LIG     1       3.264  -1.084   3.631  1.00  0.00           C
HETATM   40  C   LIG     1       2.934  -2.654  -3.065  1.00  0.00           C
HETATM   41  H   LIG     1      -3.375  -0.599   2.100  1.00  0.00           H
HETATM   42  H   LIG     1      -1.667  -5.049   0.982  1.00  0.00           H
HETATM   43  H   LIG     1      -3.561  -4.873   2.568  1.00  0.00           H
HETATM   44  H   LIG     1       1.451  -0.591  -1.946  1.00  0.00           H
HETATM   45  H   LIG     1       1.782  -4.878  -1.962  1.00  0.00           H
HETATM   46  H   LIG     1      -0.080  -5.032  -0.397  1.00  0.00           H
HETATM   47  H   LIG     1       1.658  -1.264   1.372  1.00  0.00           H
HETATM   48  H   LIG     1       0.005   2.134   4.566  1.00  0.00           H
HETATM   49  H   LIG     1       2.016   0.863   5.093  1.00  0.00           H
HETATM   50  H   LIG     1      -3.562   1.830  -0.321  1.00  0.00           H
HETATM   51  H   LIG     1      -4.703   3.650   0.945  1.00  0.00           H
HETATM   52  H   LIG     1      -3.736   4.352   3.161  1.00  0.00           H
HETATM   53  H   LIG     1      -1.694   3.218   3.986  1.00  0.00           H
HETATM   54  H   LIG     1       1.504   1.967   0.308  1.00  0.00           H
HETATM   55  H   LIG     1      -0.515   2.881  -4.116  1.00  0.00           H
HETATM   56  H   LIG     1       1.431   4.159  -3.391  1.00  0.00           H
HETATM   57  C   LIG     1       2.839   3.987  -1.050  1.00  0.00           C
HETATM   58  H   LIG     1      -3.533  -1.498  -1.212  1.00  0.00           H
HETATM   59  H   LIG     1      -4.097   0.223  -5.116  1.00  0.00           H
HETATM   60  H   LIG     1      -2.141   1.676  -4.671  1.00  0.00           H
HETATM   61  H   LIG     1      -4.442  -2.589   3.157  1.00  0.00           H
HETATM   62  C   LIG     1       3.324  -1.213  -3.441  1.00  0.00           C
HETATM   63  C   LIG     1       2.553  -3.404  -4.364  1.00  0.00           C
HETATM   64  C   LIG     1       4.169  -3.338  -2.431  1.00  0.00           C
HETATM   65  C   LIG     1       3.377   3.584   0.334  1.00  0.00           C
HETATM   66  C   LIG     1       2.443   5.483  -0.997  1.00  0.00           C
HETATM   67  C   LIG     1       3.978   3.802  -2.081  1.00  0.00           C
HETATM   68  C   LIG     1       3.663  -2.112   2.557  1.00  0.00           C
HETATM   69  C   LIG     1       3.028  -1.842   4.960  1.00  0.00           C
HETATM   70  C   LIG     1       4.442  -0.098   3.815  1.00  0.00           C
HETATM   71  H   LIG     1       2.202  -2.553   4.858  1.00  0.00           H
HETATM   72  H   LIG     1       2.786  -1.156   5.776  1.00  0.00           H
HETATM   73  H   LIG     1       3.929  -2.399   5.242  1.00  0.00           H
HETATM   74  H   LIG     1       2.876  -2.853   2.390  1.00  0.00           H
HETATM   75  H   LIG     1       4.563  -2.645   2.882  1.00  0.00           H
HETATM   76  H   LIG     1       3.887  -1.630   1.601  1.00  0.00           H
HETATM   77  H   LIG     1       4.642   0.446   2.887  1.00  0.00           H
HETATM   78  H   LIG     1       5.350  -0.644   4.096  1.00  0.00           H
HETATM   79  H   LIG     1       4.235   0.637   4.599  1.00  0.00           H
HETATM   80  H   LIG     1       2.496  -0.679  -3.916  1.00  0.00           H
HETATM   81  H   LIG     1       4.160  -1.235  -4.148  1.00  0.00           H
HETATM   82  H   LIG     1       3.643  -0.638  -2.566  1.00  0.00           H
HETATM   83  H   LIG     1       4.467  -2.824  -1.512  1.00  0.00           H
HETATM   84  H   LIG     1       5.014  -3.314  -3.128  1.00  0.00           H
HETATM   85  H   LIG     1       3.966  -4.384  -2.182  1.00  0.00           H
HETATM   86  H   LIG     1       1.682  -2.940  -4.838  1.00  0.00           H
HETATM   87  H   LIG     1       2.313  -4.453  -4.168  1.00  0.00           H
HETATM   88  H   LIG     1       3.387  -3.375  -5.074  1.00  0.00           H
HETATM   89  H   LIG     1       2.622   3.713   1.116  1.00  0.00           H
HETATM   90  H   LIG     1       4.234   4.216   0.588  1.00  0.00           H
HETATM   91  H   LIG     1       3.711   2.542   0.350  1.00  0.00           H
HETATM   92  H   LIG     1       4.281   2.752  -2.140  1.00  0.00           H
HETATM   93  H   LIG     1       4.852   4.394  -1.787  1.00  0.00           H
HETATM   94  H   LIG     1       3.675   4.123  -3.081  1.00  0.00           H
HETATM   95  H   LIG     1       1.638   5.644  -0.273  1.00  0.00           H
HETATM   96  H   LIG     1       2.100   5.844  -1.971  1.00  0.00           H
HETATM   97  H   LIG     1       3.304   6.090  -0.695  1.00  0.00           H
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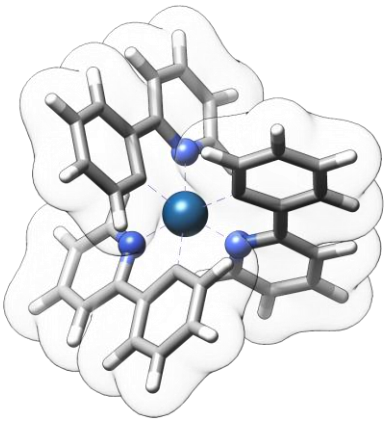
Cat-3, *fac*-Ir(ppy)$_3$



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HETATM    1 IR   LIG     1       0.001   0.000   0.018  1.00  0.00          Ir
HETATM    2  C   LIG     1      -2.240  -0.405  -2.145  1.00  0.00           C
HETATM    3  N   LIG     1      -1.603  -0.932  -1.079  1.00  0.00           N
HETATM    4  C   LIG     1      -1.998  -2.150  -0.593  1.00  0.00           C
HETATM    5  C   LIG     1      -3.050  -2.840  -1.215  1.00  0.00           C
HETATM    6  C   LIG     1      -3.694  -2.295  -2.316  1.00  0.00           C
HETATM    7  C   LIG     1      -3.282  -1.049  -2.795  1.00  0.00           C
HETATM    8  C   LIG     1      -0.243  -1.724   1.061  1.00  0.00           C
HETATM    9  C   LIG     1       0.472  -2.154   2.196  1.00  0.00           C
HETATM   10  C   LIG     1       0.212  -3.377   2.810  1.00  0.00           C
HETATM   11  C   LIG     1      -0.779  -4.231   2.312  1.00  0.00           C
HETATM   12  C   LIG     1      -1.507  -3.843   1.196  1.00  0.00           C
HETATM   13  C   LIG     1      -1.250  -2.608   0.573  1.00  0.00           C
HETATM   14  C   LIG     1      -2.109   0.657   2.193  1.00  0.00           C
HETATM   15  C   LIG     1      -1.375   1.067   1.063  1.00  0.00           C
HETATM   16  C   LIG     1      -1.638   2.383   0.578  1.00  0.00           C
HETATM   17  C   LIG     1      -2.582   3.219   1.203  1.00  0.00           C
HETATM   18  C   LIG     1      -3.284   2.777   2.315  1.00  0.00           C
HETATM   19  C   LIG     1      -3.041   1.490   2.808  1.00  0.00           C
HETATM   20  N   LIG     1      -0.003   1.861  -1.071  1.00  0.00           N
HETATM   21  C   LIG     1       0.775   2.158  -2.130  1.00  0.00           C
HETATM   22  C   LIG     1       0.741   3.386  -2.773  1.00  0.00           C
HETATM   23  C   LIG     1      -0.138   4.361  -2.294  1.00  0.00           C
HETATM   24  C   LIG     1      -0.936   4.068  -1.198  1.00  0.00           C
HETATM   25  C   LIG     1      -0.864   2.808  -0.583  1.00  0.00           C
HETATM   26  C   LIG     1       1.625   1.481   2.204  1.00  0.00           C
HETATM   27  C   LIG     1       1.613   0.650   1.066  1.00  0.00           C
HETATM   28  C   LIG     1       2.883   0.219   0.581  1.00  0.00           C
HETATM   29  C   LIG     1       4.080   0.606   1.212  1.00  0.00           C
HETATM   30  C   LIG     1       4.049   1.426   2.331  1.00  0.00           C
HETATM   31  C   LIG     1       2.813   1.861   2.825  1.00  0.00           C
HETATM   32  N   LIG     1       1.612  -0.920  -1.078  1.00  0.00           N
HETATM   33  C   LIG     1       1.478  -1.731  -2.146  1.00  0.00           C
HETATM   34  C   LIG     1       2.558  -2.308  -2.797  1.00  0.00           C
HETATM   35  C   LIG     1       3.842  -2.041  -2.315  1.00  0.00           C
HETATM   36  C   LIG     1       3.989  -1.216  -1.211  1.00  0.00           C
HETATM   37  C   LIG     1       2.863  -0.653  -0.588  1.00  0.00           C
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```
HETATM   38  H   LIG     1       2.392  -2.953  -3.651  1.00  0.00           H
HETATM   39  H   LIG     1      -3.585   1.136   3.680  1.00  0.00           H
HETATM   40  H   LIG     1       0.786  -3.672   3.685  1.00  0.00           H
HETATM   41  H   LIG     1      -1.888   0.567  -2.468  1.00  0.00           H
HETATM   42  H   LIG     1      -3.361  -3.801  -0.824  1.00  0.00           H
HETATM   43  H   LIG     1      -4.508  -2.830  -2.794  1.00  0.00           H
HETATM   44  H   LIG     1       1.246  -1.514   2.607  1.00  0.00           H
HETATM   45  H   LIG     1      -0.980  -5.184   2.792  1.00  0.00           H
HETATM   46  H   LIG     1      -2.278  -4.505   0.810  1.00  0.00           H
HETATM   47  H   LIG     1      -1.941  -0.334   2.602  1.00  0.00           H
HETATM   48  H   LIG     1      -2.770   4.219   0.820  1.00  0.00           H
HETATM   49  H   LIG     1      -4.011   3.424   2.796  1.00  0.00           H
HETATM   50  H   LIG     1       1.445   1.370  -2.456  1.00  0.00           H
HETATM   51  H   LIG     1       1.390   3.570  -3.621  1.00  0.00           H
HETATM   52  H   LIG     1      -0.193   5.336  -2.765  1.00  0.00           H
HETATM   53  H   LIG     1      -1.616   4.814  -0.804  1.00  0.00           H
HETATM   54  H   LIG     1       0.684   1.832   2.613  1.00  0.00           H
HETATM   55  H   LIG     1       5.039   0.268   0.829  1.00  0.00           H
HETATM   56  H   LIG     1       4.973   1.723   2.817  1.00  0.00           H
HETATM   57  H   LIG     1       2.780   2.501   3.702  1.00  0.00           H
HETATM   58  H   LIG     1       0.461  -1.912  -2.472  1.00  0.00           H
HETATM   59  H   LIG     1       4.714  -2.475  -2.794  1.00  0.00           H
HETATM   60  H   LIG     1       4.976  -1.003  -0.817  1.00  0.00           H
HETATM   61  H   LIG     1      -3.760  -0.579  -3.646  1.00  0.00           H
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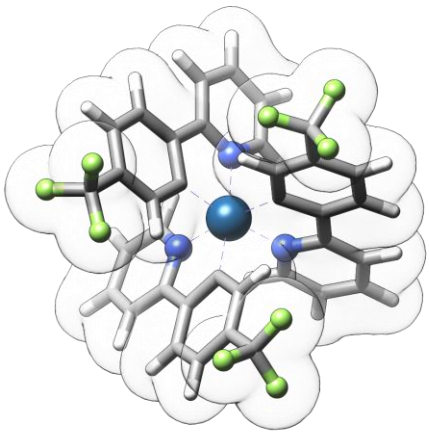
Cat-4, *fac*-Ir(CF$_3$ppy)$_3$



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HETATM    1 IR   LIG     1       0.986  -0.015   0.008  1.00  0.00          Ir
HETATM    2  C   LIG     1       3.136   0.604   2.214  1.00  0.00           C
HETATM    3  N   LIG     1       2.083   1.071   1.515  1.00  0.00           N
HETATM    4  C   LIG     1       1.594   2.320   1.789  1.00  0.00           C
HETATM    5  C   LIG     1       2.197   3.103   2.783  1.00  0.00           C
HETATM    6  C   LIG     1       3.287   2.618   3.493  1.00  0.00           C
HETATM    7  C   LIG     1       3.769   1.340   3.203  1.00  0.00           C
HETATM    8  C   LIG     1      -0.031   1.740   0.051  1.00  0.00           C
HETATM    9  C   LIG     1      -1.136   2.109  -0.742  1.00  0.00           C
HETATM   10  C   LIG     1      -1.730   3.363  -0.622  1.00  0.00           C
HETATM   11  C   LIG     1      -1.250   4.305   0.300  1.00  0.00           C
HETATM   12  C   LIG     1      -0.166   3.972   1.093  1.00  0.00           C
HETATM   13  C   LIG     1       0.446   2.711   0.976  1.00  0.00           C
HETATM   14  C   LIG     1      -1.214  -0.389   2.153  1.00  0.00           C
HETATM   15  C   LIG     1      -0.086  -0.904   1.483  1.00  0.00           C
HETATM   16  C   LIG     1       0.371  -2.188   1.894  1.00  0.00           C
HETATM   17  C   LIG     1      -0.275  -2.903   2.918  1.00  0.00           C
HETATM   18  C   LIG     1      -1.380  -2.369   3.559  1.00  0.00           C
HETATM   19  C   LIG     1      -1.846  -1.106   3.167  1.00  0.00           C
HETATM   20  N   LIG     1       2.047  -1.882   0.231  1.00  0.00           N
HETATM   21  C   LIG     1       3.110  -2.283  -0.494  1.00  0.00           C
HETATM   22  C   LIG     1       3.722  -3.514  -0.316  1.00  0.00           C
HETATM   23  C   LIG     1       3.210  -4.379   0.654  1.00  0.00           C
HETATM   24  C   LIG     1       2.113  -3.976   1.401  1.00  0.00           C
HETATM   25  C   LIG     1       1.530  -2.719   1.183  1.00  0.00           C
HETATM   26  C   LIG     1      -1.180  -1.671  -1.459  1.00  0.00           C
HETATM   27  C   LIG     1      -0.051  -0.831  -1.534  1.00  0.00           C
HETATM   28  C   LIG     1       0.441  -0.538  -2.838  1.00  0.00           C
HETATM   29  C   LIG     1      -0.175  -1.064  -3.989  1.00  0.00           C
HETATM   30  C   LIG     1      -1.280  -1.891  -3.880  1.00  0.00           C
HETATM   31  C   LIG     1      -1.779  -2.191  -2.604  1.00  0.00           C
HETATM   32  N   LIG     1       2.096   0.726  -1.686  1.00  0.00           N
HETATM   33  C   LIG     1       3.162   1.549  -1.633  1.00  0.00           C
HETATM   34  C   LIG     1       3.805   2.024  -2.766  1.00  0.00           C
HETATM   35  C   LIG     1       3.320   1.637  -4.018  1.00  0.00           C
HETATM   36  C   LIG     1       2.219   0.796  -4.082  1.00  0.00           C
HETATM   37  C   LIG     1       1.606   0.339  -2.904  1.00  0.00           C
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HETATM   38  H   LIG     1       4.658   2.686  -2.668  1.00  0.00           H
HETATM   39  C   LIG     1      -3.045  -0.538   3.880  1.00  0.00           C
HETATM   40  C   LIG     1      -2.901   3.752  -1.487  1.00  0.00           C
HETATM   41  H   LIG     1       3.462  -0.397   1.958  1.00  0.00           H
HETATM   42  H   LIG     1       1.802   4.088   3.001  1.00  0.00           H
HETATM   43  H   LIG     1       3.750   3.223   4.266  1.00  0.00           H
HETATM   44  H   LIG     1      -1.536   1.405  -1.461  1.00  0.00           H
HETATM   45  H   LIG     1      -1.721   5.277   0.386  1.00  0.00           H
HETATM   46  H   LIG     1       0.207   4.703   1.804  1.00  0.00           H
HETATM   47  H   LIG     1      -1.606   0.581   1.875  1.00  0.00           H
HETATM   48  H   LIG     1       0.084  -3.882   3.219  1.00  0.00           H
HETATM   49  H   LIG     1      -1.881  -2.919   4.348  1.00  0.00           H
HETATM   50  H   LIG     1       3.461  -1.579  -1.239  1.00  0.00           H
HETATM   51  H   LIG     1       4.573  -3.788  -0.929  1.00  0.00           H
HETATM   52  H   LIG     1       3.656  -5.353   0.818  1.00  0.00           H
HETATM   53  H   LIG     1       1.695  -4.638   2.151  1.00  0.00           H
HETATM   54  H   LIG     1      -1.598  -1.919  -0.491  1.00  0.00           H
HETATM   55  H   LIG     1       0.209  -0.829  -4.977  1.00  0.00           H
HETATM   56  H   LIG     1      -1.756  -2.296  -4.766  1.00  0.00           H
HETATM   57  C   LIG     1      -2.978  -3.096  -2.502  1.00  0.00           C
HETATM   58  H   LIG     1       3.491   1.827  -0.640  1.00  0.00           H
HETATM   59  H   LIG     1       3.790   1.993  -4.928  1.00  0.00           H
HETATM   60  H   LIG     1       1.822   0.493  -5.042  1.00  0.00           H
HETATM   61  H   LIG     1       4.611   0.916   3.738  1.00  0.00           H
HETATM   62  F   LIG     1      -3.292   2.770  -2.333  1.00  0.00           F
HETATM   63  F   LIG     1      -2.615   4.846  -2.259  1.00  0.00           F
HETATM   64  F   LIG     1      -3.993   4.095  -0.743  1.00  0.00           F
HETATM   65  F   LIG     1      -3.391  -3.296  -1.227  1.00  0.00           F
HETATM   66  F   LIG     1      -2.726  -4.332  -3.033  1.00  0.00           F
HETATM   67  F   LIG     1      -4.049  -2.604  -3.192  1.00  0.00           F
HETATM   68  F   LIG     1      -3.441   0.661   3.390  1.00  0.00           F
HETATM   69  F   LIG     1      -2.801  -0.356   5.214  1.00  0.00           F
HETATM   70  F   LIG     1      -4.124  -1.371   3.808  1.00  0.00           F
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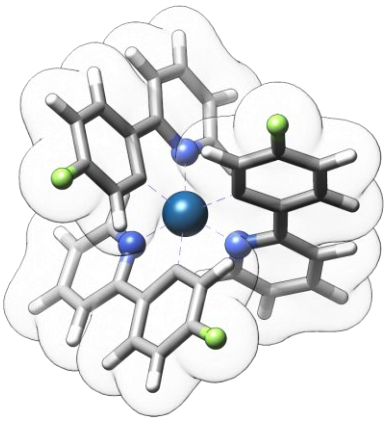
Cat-5, *fac*-Ir(Fppy)$_3$



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HETATM    1 IR   LIG     1       0.001   0.001  -0.254  1.00  0.00          Ir
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HETATM    3  N   LIG     1      -0.004   1.858  -1.346  1.00  0.00           N
HETATM    4  C   LIG     1      -0.859   2.808  -0.852  1.00  0.00           C
HETATM    5  C   LIG     1      -0.928   4.069  -1.468  1.00  0.00           C
HETATM    6  C   LIG     1      -0.137   4.357  -2.569  1.00  0.00           C
HETATM    7  C   LIG     1       0.734   3.377  -3.055  1.00  0.00           C
HETATM    8  C   LIG     1      -1.371   1.067   0.792  1.00  0.00           C
HETATM    9  C   LIG     1      -2.100   0.646   1.919  1.00  0.00           C
HETATM   10  C   LIG     1      -3.017   1.501   2.512  1.00  0.00           C
HETATM   11  C   LIG     1      -3.274   2.790   2.052  1.00  0.00           C
HETATM   12  C   LIG     1      -2.567   3.225   0.941  1.00  0.00           C
HETATM   13  C   LIG     1      -1.628   2.387   0.311  1.00  0.00           C
HETATM   14  C   LIG     1       1.615   1.491   1.921  1.00  0.00           C
HETATM   15  C   LIG     1       1.612   0.652   0.792  1.00  0.00           C
HETATM   16  C   LIG     1       2.884   0.213   0.309  1.00  0.00           C
HETATM   17  C   LIG     1       4.078   0.603   0.938  1.00  0.00           C
HETATM   18  C   LIG     1       4.059   1.432   2.051  1.00  0.00           C
HETATM   19  C   LIG     1       2.814   1.855   2.513  1.00  0.00           C
HETATM   20  N   LIG     1       1.611  -0.923  -1.349  1.00  0.00           N
HETATM   21  C   LIG     1       1.475  -1.736  -2.416  1.00  0.00           C
HETATM   22  C   LIG     1       2.552  -2.323  -3.060  1.00  0.00           C
HETATM   23  C   LIG     1       3.837  -2.064  -2.573  1.00  0.00           C
HETATM   24  C   LIG     1       3.986  -1.237  -1.472  1.00  0.00           C
HETATM   25  C   LIG     1       2.862  -0.663  -0.855  1.00  0.00           C
HETATM   26  C   LIG     1       0.484  -2.145   1.918  1.00  0.00           C
HETATM   27  C   LIG     1      -0.241  -1.722   0.790  1.00  0.00           C
HETATM   28  C   LIG     1      -1.258  -2.601   0.306  1.00  0.00           C
HETATM   29  C   LIG     1      -1.519  -3.831   0.937  1.00  0.00           C
HETATM   30  C   LIG     1      -0.792  -4.228   2.050  1.00  0.00           C
HETATM   31  C   LIG     1       0.198  -3.364   2.511  1.00  0.00           C
HETATM   32  N   LIG     1      -1.602  -0.930  -1.351  1.00  0.00           N
HETATM   33  C   LIG     1      -2.236  -0.405  -2.419  1.00  0.00           C
HETATM   34  C   LIG     1      -3.280  -1.046  -3.067  1.00  0.00           C
HETATM   35  C   LIG     1      -3.699  -2.289  -2.583  1.00  0.00           C
HETATM   36  C   LIG     1      -3.060  -2.831  -1.478  1.00  0.00           C
HETATM   37  C   LIG     1      -2.004  -2.144  -0.858  1.00  0.00           C
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HETATM   38  H   LIG     1      -3.754  -0.578  -3.922  1.00  0.00           H
HETATM   39  F   LIG     1       2.783   2.671   3.605  1.00  0.00           F
HETATM   40  F   LIG     1      -3.708   1.063   3.603  1.00  0.00           F
HETATM   41  H   LIG     1       1.431   1.359  -2.741  1.00  0.00           H
HETATM   42  H   LIG     1      -1.602   4.819  -1.072  1.00  0.00           H
HETATM   43  H   LIG     1      -0.192   5.332  -3.041  1.00  0.00           H
HETATM   44  H   LIG     1      -1.957  -0.340   2.344  1.00  0.00           H
HETATM   45  H   LIG     1      -4.001   3.417   2.555  1.00  0.00           H
HETATM   46  H   LIG     1      -2.751   4.226   0.566  1.00  0.00           H
HETATM   47  H   LIG     1       0.690   1.861   2.348  1.00  0.00           H
HETATM   48  H   LIG     1       5.038   0.261   0.562  1.00  0.00           H
HETATM   49  H   LIG     1       4.966   1.746   2.553  1.00  0.00           H
HETATM   50  H   LIG     1       0.457  -1.909  -2.746  1.00  0.00           H
HETATM   51  H   LIG     1       2.385  -2.968  -3.914  1.00  0.00           H
HETATM   52  H   LIG     1       4.707  -2.508  -3.046  1.00  0.00           H
HETATM   53  H   LIG     1       4.972  -1.032  -1.075  1.00  0.00           H
HETATM   54  H   LIG     1       1.269  -1.529   2.343  1.00  0.00           H
HETATM   55  H   LIG     1      -2.296  -4.490   0.561  1.00  0.00           H
HETATM   56  H   LIG     1      -0.976  -5.170   2.553  1.00  0.00           H
HETATM   57  F   LIG     1       0.919  -3.745   3.603  1.00  0.00           F
HETATM   58  H   LIG     1      -1.878   0.563  -2.747  1.00  0.00           H
HETATM   59  H   LIG     1      -4.516  -2.820  -3.058  1.00  0.00           H
HETATM   60  H   LIG     1      -3.377  -3.788  -1.083  1.00  0.00           H
HETATM   61  H   LIG     1       1.377   3.559  -3.908  1.00  0.00           H
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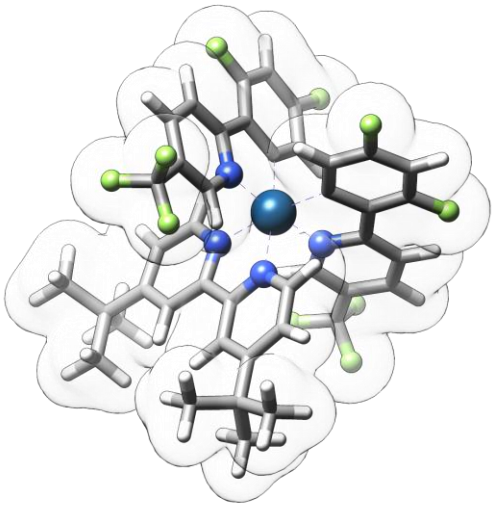
Cat-6, $Ir(diFPhCF_3Pyr)_2dtbbpy^+$



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HETATM    1 IR   LIG     1      -0.794  -0.079  -0.005  1.00  0.00          Ir
HETATM    2  C   LIG     1      -3.072   0.999  -1.766  1.00  0.00           C
HETATM    3  C   LIG     1      -2.255  -0.078  -1.409  1.00  0.00           C
HETATM    4  C   LIG     1      -2.412  -1.321  -2.098  1.00  0.00           C
HETATM    5  C   LIG     1      -3.385  -1.407  -3.110  1.00  0.00           C
HETATM    6  C   LIG     1      -4.197  -0.349  -3.471  1.00  0.00           C
HETATM    7  C   LIG     1      -4.014   0.842  -2.777  1.00  0.00           C
HETATM    8  N   LIG     1      -0.663  -2.029  -0.670  1.00  0.00           N
HETATM    9  C   LIG     1       0.208  -2.933  -0.177  1.00  0.00           C
HETATM   10  C   LIG     1       0.278  -4.234  -0.644  1.00  0.00           C
HETATM   11  C   LIG     1      -0.594  -4.628  -1.665  1.00  0.00           C
HETATM   12  C   LIG     1      -1.493  -3.708  -2.174  1.00  0.00           C
HETATM   13  C   LIG     1      -1.532  -2.393  -1.675  1.00  0.00           C
HETATM   14  C   LIG     1      -2.730  -1.686   1.762  1.00  0.00           C
HETATM   15  C   LIG     1      -2.210  -0.440   1.397  1.00  0.00           C
HETATM   16  C   LIG     1      -2.678   0.727   2.079  1.00  0.00           C
HETATM   17  C   LIG     1      -3.643   0.571   3.090  1.00  0.00           C
HETATM   18  C   LIG     1      -4.162  -0.656   3.458  1.00  0.00           C
HETATM   19  C   LIG     1      -3.683  -1.766   2.771  1.00  0.00           C
HETATM   20  N   LIG     1      -1.153   1.844   0.655  1.00  0.00           N
HETATM   21  C   LIG     1      -0.528   2.933   0.165  1.00  0.00           C
HETATM   22  C   LIG     1      -0.790   4.213   0.622  1.00  0.00           C
HETATM   23  C   LIG     1      -1.746   4.382   1.630  1.00  0.00           C
HETATM   24  C   LIG     1      -2.391   3.270   2.139  1.00  0.00           C
HETATM   25  C   LIG     1      -2.094   1.983   1.652  1.00  0.00           C
HETATM   26  C   LIG     1       0.899  -0.393   2.621  1.00  0.00           C
HETATM   27  N   LIG     1       0.936  -0.143   1.295  1.00  0.00           N
HETATM   28  C   LIG     1       2.144   0.109   0.721  1.00  0.00           C
HETATM   29  C   LIG     1       3.319   0.092   1.478  1.00  0.00           C
HETATM   30  C   LIG     1       3.299  -0.177   2.848  1.00  0.00           C
HETATM   31  C   LIG     1       2.035  -0.419   3.411  1.00  0.00           C
HETATM   32  N   LIG     1       0.876   0.398  -1.301  1.00  0.00           N
HETATM   33  C   LIG     1       0.786   0.656  -2.619  1.00  0.00           C
HETATM   34  C   LIG     1       1.893   0.918  -3.415  1.00  0.00           C
HETATM   35  C   LIG     1       3.178   0.918  -2.859  1.00  0.00           C
HETATM   36  C   LIG     1       3.256   0.646  -1.487  1.00  0.00           C
HETATM   37  C   LIG     1       2.114   0.392  -0.728  1.00  0.00           C
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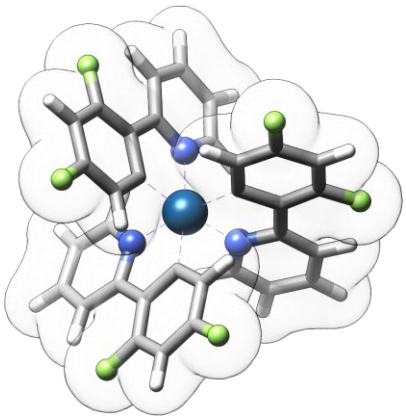
HETATM   38  H   LIG     1       1.735   1.119  -4.467  1.00  0.00           H
HETATM   39  F   LIG     1      -4.172  -2.978   3.107  1.00  0.00           F
HETATM   40  H   LIG     1      -3.007   1.960  -1.271  1.00  0.00           H
HETATM   41  F   LIG     1      -3.560  -2.571  -3.789  1.00  0.00           F
HETATM   42  H   LIG     1      -4.939  -0.448  -4.253  1.00  0.00           H
HETATM   43  H   LIG     1      -2.176  -3.994  -2.959  1.00  0.00           H
HETATM   44  H   LIG     1      -2.422  -2.603   1.274  1.00  0.00           H
HETATM   45  F   LIG     1      -4.107   1.656   3.762  1.00  0.00           F
HETATM   46  H   LIG     1      -4.906  -0.742   4.239  1.00  0.00           H
HETATM   47  H   LIG     1      -3.134   3.381   2.914  1.00  0.00           H
HETATM   48  H   LIG     1      -0.084  -0.584   3.034  1.00  0.00           H
HETATM   49  H   LIG     1       4.261   0.293   0.987  1.00  0.00           H
HETATM   50  C   LIG     1       4.559  -0.219   3.711  1.00  0.00           C
HETATM   51  H   LIG     1       1.923  -0.632   4.468  1.00  0.00           H
HETATM   52  H   LIG     1      -0.216   0.651  -3.030  1.00  0.00           H
HETATM   53  C   LIG     1       4.445   1.189  -3.672  1.00  0.00           C
HETATM   54  H   LIG     1       4.224   0.631  -1.002  1.00  0.00           H
HETATM   55  F   LIG     1      -4.795   1.893  -3.105  1.00  0.00           F
HETATM   56  H   LIG     1      -1.980   5.371   2.009  1.00  0.00           H
HETATM   57  C   LIG     1      -0.059   5.398   0.048  1.00  0.00           C
HETATM   58  H   LIG     1       0.194   2.758  -0.620  1.00  0.00           H
HETATM   59  H   LIG     1      -0.570  -5.641  -2.051  1.00  0.00           H
HETATM   60  H   LIG     1       0.856  -2.590   0.617  1.00  0.00           H
HETATM   61  F   LIG     1       0.824   5.032  -0.918  1.00  0.00           F
HETATM   62  F   LIG     1       0.643   6.058   1.006  1.00  0.00           F
HETATM   63  F   LIG     1      -0.914   6.294  -0.502  1.00  0.00           F
HETATM   64  C   LIG     1       1.272  -5.206  -0.065  1.00  0.00           C
HETATM   65  F   LIG     1       2.030  -4.639   0.910  1.00  0.00           F
HETATM   66  F   LIG     1       2.123  -5.670  -1.017  1.00  0.00           F
HETATM   67  F   LIG     1       0.658  -6.286   0.476  1.00  0.00           F
HETATM   68  C   LIG     1       4.130   1.480  -5.149  1.00  0.00           C
HETATM   69  C   LIG     1       5.365  -0.055  -3.593  1.00  0.00           C
HETATM   70  C   LIG     1       5.180   2.412  -3.069  1.00  0.00           C
HETATM   71  H   LIG     1       3.638   0.632  -5.636  1.00  0.00           H
HETATM   72  H   LIG     1       5.063   1.671  -5.686  1.00  0.00           H
HETATM   73  H   LIG     1       3.497   2.365  -5.264  1.00  0.00           H
HETATM   74  H   LIG     1       4.557   3.309  -3.116  1.00  0.00           H
HETATM   75  H   LIG     1       6.096   2.602  -3.635  1.00  0.00           H
HETATM   76  H   LIG     1       5.461   2.244  -2.025  1.00  0.00           H
HETATM   77  H   LIG     1       4.874  -0.936  -4.016  1.00  0.00           H
HETATM   78  H   LIG     1       5.653  -0.284  -2.563  1.00  0.00           H
HETATM   79  H   LIG     1       6.280   0.133  -4.162  1.00  0.00           H
HETATM   80  C   LIG     1       5.833   0.063   2.896  1.00  0.00           C
HETATM   81  C   LIG     1       4.679  -1.626   4.351  1.00  0.00           C
HETATM   82  C   LIG     1       4.436   0.844   4.831  1.00  0.00           C
HETATM   83  H   LIG     1       5.984  -0.678   2.105  1.00  0.00           H
HETATM   84  H   LIG     1       6.701   0.016   3.558  1.00  0.00           H
HETATM   85  H   LIG     1       5.818   1.061   2.447  1.00  0.00           H
HETATM   86  H   LIG     1       4.355   1.851   4.412  1.00  0.00           H
HETATM   87  H   LIG     1       5.324   0.808   5.468  1.00  0.00           H
HETATM   88  H   LIG     1       3.563   0.664   5.465  1.00  0.00           H
HETATM   89  H   LIG     1       4.764  -2.402   3.585  1.00  0.00           H
HETATM   90  H   LIG     1       3.816  -1.859   4.981  1.00  0.00           H
HETATM   91  H   LIG     1       5.573  -1.665   4.979  1.00  0.00           H
```

Cat-7, *fac*-Ir(diFppy)$_3$



HETATM	1	IR	LIG	1	-0.001	-0.001	-0.282	1.00	0.00	Ir
HETATM	2	C	LIG	1	1.872	1.268	-2.425	1.00	0.00	C
HETATM	3	N	LIG	1	1.070	1.508	-1.369	1.00	0.00	N
HETATM	4	C	LIG	1	0.927	2.790	-0.900	1.00	0.00	C
HETATM	5	C	LIG	1	1.616	3.838	-1.537	1.00	0.00	C
HETATM	6	C	LIG	1	2.433	3.578	-2.628	1.00	0.00	C
HETATM	7	C	LIG	1	2.567	2.267	-3.087	1.00	0.00	C
HETATM	8	C	LIG	1	-0.506	1.668	0.757	1.00	0.00	C
HETATM	9	C	LIG	1	-1.342	1.723	1.883	1.00	0.00	C
HETATM	10	C	LIG	1	-1.620	2.940	2.483	1.00	0.00	C
HETATM	11	C	LIG	1	-1.110	4.151	2.025	1.00	0.00	C
HETATM	12	C	LIG	1	-0.286	4.090	0.917	1.00	0.00	C
HETATM	13	C	LIG	1	0.046	2.895	0.258	1.00	0.00	C
HETATM	14	C	LIG	1	2.157	0.302	1.888	1.00	0.00	C
HETATM	15	C	LIG	1	1.695	-0.395	0.760	1.00	0.00	C
HETATM	16	C	LIG	1	2.486	-1.483	0.261	1.00	0.00	C
HETATM	17	C	LIG	1	3.683	-1.795	0.925	1.00	0.00	C
HETATM	18	C	LIG	1	4.143	-1.113	2.036	1.00	0.00	C
HETATM	19	C	LIG	1	3.348	-0.066	2.492	1.00	0.00	C
HETATM	20	N	LIG	1	0.775	-1.680	-1.370	1.00	0.00	N
HETATM	21	C	LIG	1	0.171	-2.257	-2.427	1.00	0.00	C
HETATM	22	C	LIG	1	0.695	-3.355	-3.091	1.00	0.00	C
HETATM	23	C	LIG	1	1.902	-3.885	-2.634	1.00	0.00	C
HETATM	24	C	LIG	1	2.531	-3.307	-1.540	1.00	0.00	C
HETATM	25	C	LIG	1	1.958	-2.192	-0.900	1.00	0.00	C
HETATM	26	C	LIG	1	-0.822	-2.025	1.882	1.00	0.00	C
HETATM	27	C	LIG	1	-1.193	-1.274	0.756	1.00	0.00	C
HETATM	28	C	LIG	1	-2.531	-1.409	0.258	1.00	0.00	C
HETATM	29	C	LIG	1	-3.400	-2.293	0.917	1.00	0.00	C
HETATM	30	C	LIG	1	-3.041	-3.038	2.025	1.00	0.00	C
HETATM	31	C	LIG	1	-1.737	-2.875	2.482	1.00	0.00	C
HETATM	32	N	LIG	1	-1.843	0.172	-1.370	1.00	0.00	N
HETATM	33	C	LIG	1	-2.038	0.985	-2.427	1.00	0.00	C
HETATM	34	C	LIG	1	-3.251	1.085	-3.089	1.00	0.00	C
HETATM	35	C	LIG	1	-4.317	0.310	-2.631	1.00	0.00	C
HETATM	36	C	LIG	1	-4.132	-0.527	-1.539	1.00	0.00	C
HETATM	37	C	LIG	1	-2.880	-0.594	-0.901	1.00	0.00	C

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HETATM   38  H   LIG     1      -3.353   1.757  -3.934  1.00  0.00           H
HETATM   39  F   LIG     1       3.778   0.622   3.583  1.00  0.00           F
HETATM   40  F   LIG     1      -2.434   2.970   3.572  1.00  0.00           F
HETATM   41  H   LIG     1       1.944   0.232  -2.732  1.00  0.00           H
HETATM   42  H   LIG     1       1.509   4.846  -1.165  1.00  0.00           H
HETATM   43  H   LIG     1       2.963   4.391  -3.112  1.00  0.00           H
HETATM   44  H   LIG     1      -1.777   0.822   2.300  1.00  0.00           H
HETATM   45  H   LIG     1      -1.340   5.092   2.506  1.00  0.00           H
HETATM   46  F   LIG     1       0.208   5.285   0.472  1.00  0.00           F
HETATM   47  H   LIG     1       1.592   1.127   2.305  1.00  0.00           H
HETATM   48  F   LIG     1       4.473  -2.819   0.481  1.00  0.00           F
HETATM   49  H   LIG     1       5.072  -1.385   2.520  1.00  0.00           H
HETATM   50  H   LIG     1      -0.767  -1.808  -2.732  1.00  0.00           H
HETATM   51  H   LIG     1       0.167  -3.778  -3.936  1.00  0.00           H
HETATM   52  H   LIG     1       2.349  -4.745  -3.121  1.00  0.00           H
HETATM   53  H   LIG     1       3.460  -3.712  -1.170  1.00  0.00           H
HETATM   54  H   LIG     1       0.175  -1.951   2.300  1.00  0.00           H
HETATM   55  F   LIG     1      -4.683  -2.462   0.473  1.00  0.00           F
HETATM   56  H   LIG     1      -3.741  -3.707   2.506  1.00  0.00           H
HETATM   57  F   LIG     1      -1.357  -3.595   3.571  1.00  0.00           F
HETATM   58  H   LIG     1      -1.178   1.569  -2.732  1.00  0.00           H
HETATM   59  H   LIG     1      -5.286   0.359  -3.116  1.00  0.00           H
HETATM   60  H   LIG     1      -4.949  -1.127  -1.169  1.00  0.00           H
HETATM   61  H   LIG     1       3.200   2.018  -3.931  1.00  0.00           H
```

***fac*-Ir(ppy)$_3$ structure comparison**

To validate the use of the TPSS density functional theory DFT calculations for quantitative depiction of photocatalyst geometries, we performed structural comparisons between the calculated geometry of *fac*-Ir(ppy)$_3$ and the available gas-phase electron diffraction (GED) structure.[13] A structural alignment of the heavy atoms for both systems was performed resulting in a root-mean-square deviation of atomic positions of 0.094 Å (0.122 Å with hydrogen atoms present). Comparisons of the atom-metal coordination distances and angles, comparisons of the torsion angle between the aromatic rings of the 2-phenylpyridine molecules, and image of the superimposed structural alignment (GED = orange; TPSS = blue) are included below.

Structural parameters of fac-Ir(ppy)$_3$ measured from a gas-phase electron diffraction structure[13] and TPSS DFT calculations.

	GED	TPSS
Ir-N (Å)	2.158(7)	2.155
Ir-C (Å)	2.033(6)	2.030
N-Ir-N_b (deg)	98(1)	97
C-Ir-C_b (deg)	93(1)	96
τ(C–C–C–N) (deg)	-5(3)	-1