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S_NAr Catalysis Enhanced by an Aromatic Donor-Acceptor Interaction; Facile Access to Chlorinated Polyfluoroarenes

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Supporting Information

Table of contents:-

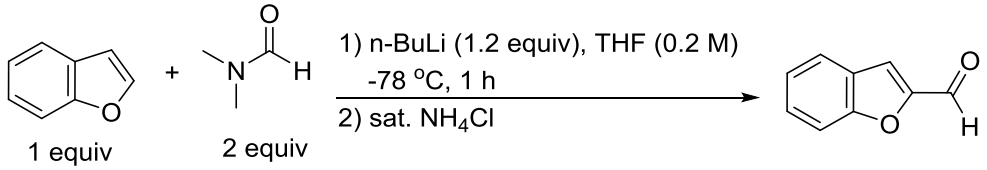
.

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 and THF was obtained from a solvent purification system. 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]oxazole,[1] 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]thiazole[2] were synthesized according to literature procedures. Reactions were monitored by ^{19}F NMR. NMR spectra were obtained on a 400 MHz Bruker Avance III spectrometer or a 400 MHz Unity Inova spectrometer. ^{1}H 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 and reported uncorrected. Purifications were carried out using Teledyne Isco Combiflash Rf 200i flash chromatograph with Redisep Rf normal phase silica (4 g, 12 g, 24 g, 40 g, or 80 g) with product detection at 254, 280 nm and by ELSD (evaporative light scattering detector). 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.

Synthesis of chlorination catalysts

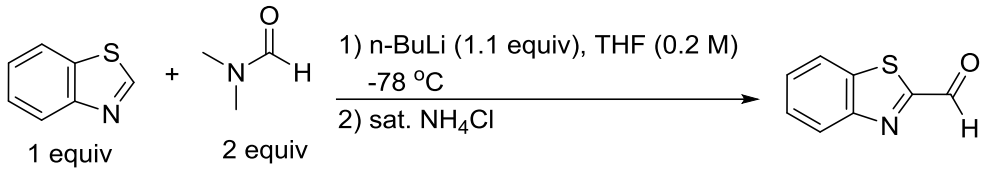
Synthesis of benzofuran-2-carbaldehyde (S1)



S1 was synthesized according to a modified literature procedure.[3] To a solution of benzofuran (2.5 g, 21.16 mmol) in dry THF (0.2 M) cooled at -78 °C under Ar was added *n*-BuLi (15.9 mL, 1.6 M in hexane, 25.39 mmol), dropwise. After stirring the mixture for 1 h at -78 °C, DMF (3.26 mL, 42.32 mmol) was added dropwise and stirred for another 4.5 h at -78 °C. After the complete consumption of benzofuran, judged by TLC (hexane:DCM 1:1), the reaction was quenched with sat. NH_4Cl. The aqueous layer was extracted with EtOAc (3x) and combined organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The resultant crude residue was purified by flash chromatography using hexane:EtOAc (0% EtOAc for 5 cv, 0-10% EtOAc for 5-12 cv, 10% EtOAc for 12-18 cv, 10-100% EtOAc for 18-23 cv and and then held at 100% EtOAc for 23-26

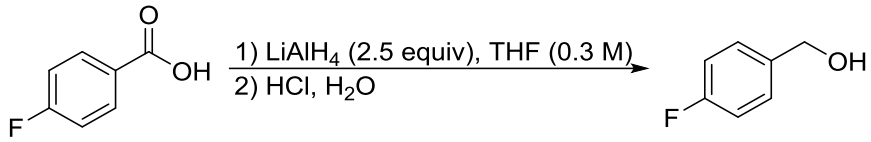
cv) on 40 g silica column to afford **benzofuran-2-carbaldehyde** as a yellow solid in 94% yield (3.1 g, 19.9 mmol). The spectral data of the compound matched with the literature.[3]

Synthesis of benzo[*d*]thiazole-2-carbaldehyde (S2)



S2 was synthesized according to a modified literature procedure.[4] To a solution of benzothiazole (2.5 g, 18.5 mmol) in dry THF (0.4 M) cooled at -78 °C under Ar was added *n*-BuLi (12.7 mL, 1.6 M in hexane, 20.3 mmol), dropwise. After stirring the mixture for 1 h at -78 °C, DMF (2.85 mL, 37.0 mmol) was added dropwise and stirred for another 3.5 h at -78 °C. After the complete consumption of benzothiazole, judged by TLC (hexane:DCM 1:1), the reaction was quenched with sat. NH_4Cl. The aqueous layer was extracted with EtOAc (3x) and combined organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The resultant crude residue was purified by flash chromatography using hexane:EtOAc (0% EtOAc for 5 cv, 0-5% EtOAc for 5-12 cv, 5% EtOAc for 12-35 cv, 5-100% EtOAc for 35-43 cv and then held at 100% EtOAc for 43-47 cv) on 80 g silica column to afford **benzo[*d*]thiazole-2-carbaldehyde** as a yellow solid in 50% yield (1.5 g, 9.2 mmol). The spectral data of the compound matched with the literature.[5]

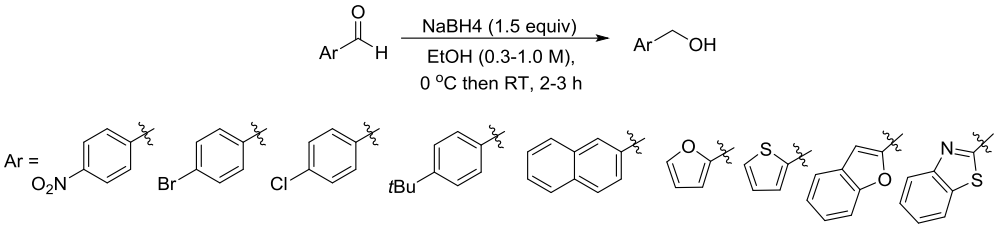
Synthesis of (4-fluorophenyl)methanol (S3)



In a flame dried two-necked round bottom flask charged with a stir bar, an ice cold slurry of $LiAlH_4$ (1.35 g, 35.7 mmol) in THF (35 mL) was added a solution of 4-fluorobenzoic acid (2.0 g, 14.3 mmol) in THF (10 mL) under Ar. The mixture was allowed to warm to room temperature and stirred overnight. After the complete consumption of the 4-fluorobenzoic acid (TLC hexane:EtOAc 70:30, buffered with 1% acetic acid), the reaction was cooled down to 0 °C and quenched carefully with 2 M HCl. The mixture was extracted with EtOAc (2x) and combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield the corresponding alcohol product as a light yellow solid in quantitative yield (1.8 g, 14.3 mmol) which

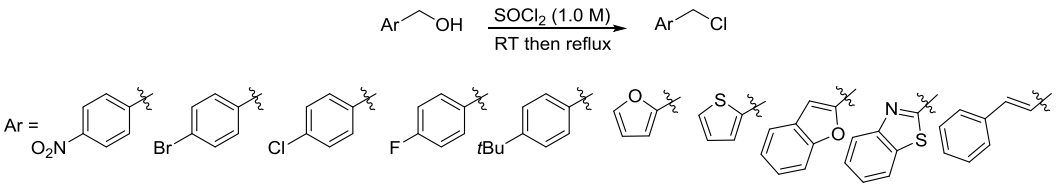
was taken to the next step without further purification. The spectral data of the compound matched with the literature.[6]

General procedure A for the reduction of *para*-substituted benzyl aldehydes



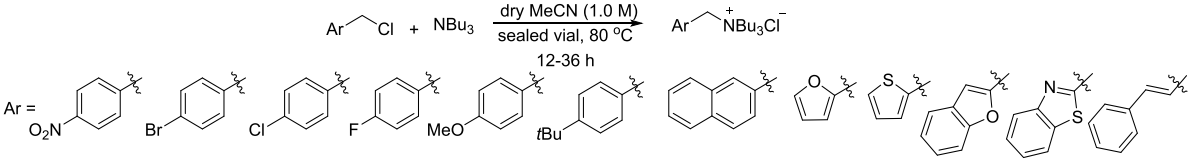
In a flame dried two-necked round bottom flask charged with a stir bar $NaBH_4$ (1.5 equiv) was added in a one portion to a solution of the benzyl aldehyde at 0 °C in EtOH under Ar. The mixture was allowed to warm to room temperature and stirred. After the complete consumption of the aldehyde starting material (TLC, hexane:EtOAc 90:10), the reaction was quenched with 10% NaOH and it was stirred for another ~10 min. The crude mixture was rotavaped to remove EtOH. Then the aqueous mixture was extracted with DCM (3x) and the combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield the corresponding alcohol product which was taken to the next step without further purification.

General procedure B for the chlorination of *para*-substituted benzyl alcohols



In a flame dried two-necked round bottom flask charged with a stir bar, $SOCl_2$ (1.0 M) was added followed by the corresponding benzyl alcohol. The reaction mixture was stirred at reflux until the completion of the reaction (TLC, DCM: MeOH 99:1). The crude mixture was rotavaped, and then placed in a vacuum to remove excess $SOCl_2$ to yield the corresponding chloride product which was taken to the next step without further purification.

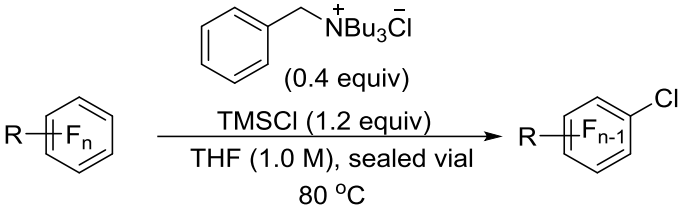
General procedure C for the amine substitution of *para*-substituted benzyl chlorides



A sealed vial was charged with the corresponding benzyl chloride (1.0 equiv), tributylamine (1.2 equiv), MeCN (1.0 M) and the reaction was stirred while heating at 80 °C in an oil bath. Aliquots were taken out and diluted with $CDCl_3$ to monitor the reaction progress (^1H NMR). After the complete consumption of starting material, CH_3CN was removed via rotavap. The compound was purified via trituration. In a 50 mL round bottom flask, the sample was dissolved in a minimal amount of DCM and hexane (10x volume of DCM used) was added all at once with vigorous stirring of the mixture, which resulted in the selective dissolution of the excess tributylamine and DCM into the hexane layer, leaving behind the product as a solid. The product was then separated by simple decantation of the hexane layer and washed twice with fresh hexane. Finally, the product was rotavaped and then, placed in a vacuum to remove any residual hexane to yield the title compound.

If further purification was needed, to the triturated solid was added EtOAc (~50 mg salt per mL of EtOAc) and then heated to boil to selectively extract impurities. The mixture was cooled down to rt and the solid product was separated by simple decantation of the EtOAc layer and washed once with fresh EtOAc. Then the product was rotavaped, placed in a vacuum to remove any residual EtOAc.

General procedure D for the catalytic chlorination of perfluoroarenes



A sealable vial was charged with the fluoroarene (1.0 equiv), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (0.4-1.0 equiv), THF (1.0 M), TMSCl (1.2-2.4 equiv) and sealed. The reaction was stirred while heating at 80 °C in an oil bath. Aliquots were taken out and diluted with $CDCl_3$ to monitor the reaction progress by ^{19}F NMR. After the complete consumption of starting material the reaction was allowed to cool to rt. If the product is volatile, the crude reaction was spiked with a known amount of trifluoroacetic acid (TFA) as an internal standard and an NMR yield was obtained. The appropriate workup depends on the volatility of the substrate, *vide infra*.

General workup method E for the isolation of chlorinated polyfluoroarenes (for volatile products).

After reaction completion as judged by ^{19}F NMR, the reaction was cooled to rt. The crude mixture was extracted with pentane (10 mL) and washed with water (10 mL x 2). The water wash removed most of the remaining catalyst (*N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride) and THF partially, leaving the product primarily in pentane layer. The pentane layer contains the desired product, some THF, small amounts of catalyst, and benzyl chloride which arises from catalyst decomposition was rotavaped with no heat to obtain a concentrated mixture. Then, it was transferred to a microwave vial (Biotage Microwave Reaction Kit, 2-5 mL, part # 351521), and water (2 mL) was added and sealed. The mixture was heated at 175 ^{o}C for 30 minutes (Biotage Initiator) to decompose benzyl chloride formed during the halogenation reaction. Nucleophilic scavengers, which may have helped remove the benzylic chloride, were found to attack the product.

The vial was allowed to cool down to rt and pentane (5 mL) was added. Phases were separated and the organic layer was washed with 1M HCl (2 mL x 3) to remove tributylamine formed during the decomposition of remaining catalyst. The organic layer was dried over $MgSO_4$ and passed through a silica plug. The silica plug was eluted with a minimal amount of additional pentane. Eluted pentane layer was rotavaped with no heat to yield the title compound with moderate yields and moderate purities. To determine purity, the isolated product was spiked with a known amount of 1,2,4,5-tetrafluorobenzene as an internal standard. Both ^{19}F NMR and ^{1}H NMR were recorded. Purity was calculated by integrating and comparing proton signals of 1,2,4,5-tetrafluorobenzene with the extra signals (arise mainly from residual solvents and benzyl chloride) in the isolated material.

General method F for the isolation of chlorinated polyfluoroarenes (for relatively nonvolatile products).

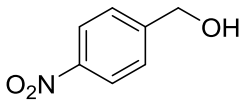
After reaction completion (^{19}F NMR), the reaction was cooled to RT. Then the THF was removed via rotavap. The residue was treated with deionized water (10 mL) and extracted with DCM (2 x 10 mL). The organic portions were combined and washed with 1M HCl to remove residual tributylamine. Then the DCM layer was dried with anhydrous $MgSO_4$, filtered, concentrated *in vacuo,* and purified by normal phase chromatography.

General method G for the isolation of chlorinated polyfluoroarenes (for relatively nonvolatile products).

General method **G** was chosen over General method **F** when the product's water solubility creates problems during the workup. After reaction completion as judged by ^{19}F NMR, the reaction was cooled down to RT. Then the volatiles were removed via rotavap. The residue was purified by normal phase chromatography with no additional workup.

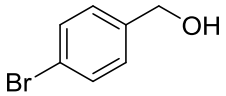
Synthesis of *para*-substituted benzyl alcohols

Synthesis of (4-nitrophenyl)methanol (S-4a)



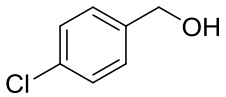
General procedure A was followed using 4-nitrobenzaldehyde (1.5 g, 9.93 mmol), $NaBH_4$ (0.56 g, 14.9 mmol) and EtOH (10 mL) to afford **S-4a** in quantitative yield (1.52 g, 9.93 mmol) as a white solid which was carried to the next step without further purification.

Synthesis of (4-bromophenyl)methanol (S-4b)



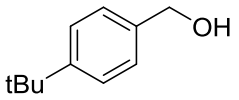
General procedure A was followed using 4-bromobenzaldehyde (1.5 g, 8.10 mmol), $NaBH_4$ (0.46 g, 12.16 mmol) and EtOH (8 mL) to afford **S-4b** in 97% yield (1.47 g, 7.9 mmol) as a white solid which was carried to the next step without further purification.

Synthesis of (4-chlorophenyl)methanol (S-4c)



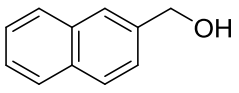
General procedure A was followed using 4-chlorobenzaldehyde (1.5 g, 10.67 mmol), $NaBH_4$ (0.60 g, 16.0 mmol) and EtOH (10 mL) to afford **S-4c** in 94% yield (1.42 g, 10.0 mmol) as a white solid which was carried to the next step without further purification.

Synthesis of (4-(*tert*-butyl)phenyl)methanol (S-4d)



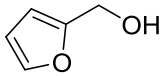
General procedure A was followed using 4-(tert-butyl)benzaldehyde (1.5 g, 9.25 mmol), $NaBH_4$ (0.52 g, 13.88 mmol) and EtOH (9.2 mL) to afford **S-4d** in quantitative yield (1.52 g, 9.25 mmol) as a colorless liquid which was carried to the next step without further purification.

Synthesis of naphthalen-2-ylmethanol (S-4f)



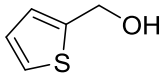
General procedure A was followed using 2-naphthaldehyde (1.0 g, 6.4 mmol), $NaBH_4$ (0.36 g, 9.6 mmol) and EtOH (6.5 mL) to afford **S-4f** in 73% yield (0.74 g, 4.66 mmol) as a white solid which was carried to the next step without further purification.

Synthesis of furan-2-ylmethanol (S-4g)



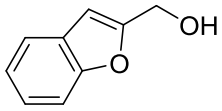
General procedure A was followed using furan-2-carbaldehyde (1.29 mL, 15.61 mmol), $NaBH_4$ (0.88 g, 23.42 mmol) and EtOH (15 mL) to afford **S-4g** in 75% yield (1.15 g, 11.71 mmol) as a colorless oil which was carried to the next step without further purification.

Synthesis of thiophen-2-ylmethanol (S-4h)



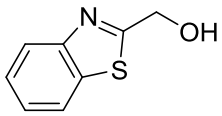
General procedure A was followed using thiophene-2-carbaldehyde (1.67 mL, 17.83 mmol), $NaBH_4$ (1.01 g, 26.74 mmol) and EtOH (17.8 mL) to afford **S-4h** in quantitative yield (2.1 g, 17.83 mmol) as a light yellow liquid which was carried to the next step without further purification.

Synthesis of benzofuran-2-ylmethanol (S-4i)



General procedure A was followed using benzofuran-2-carbaldehyde (1.0 g, 6.84 mmol), $NaBH_4$ (0.39 g, 10.26 mmol) and EtOH (13.7 mL, 0.5 M) to afford **S-4i** in quantitative yield (1.01 g, 6.84 mmol) as a white solid which was carried to the next step without further purification.

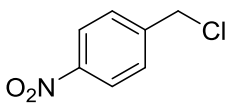
Synthesis of benzo[*d*]thiazol-2-ylmethanol (S-4j)



General procedure A was followed using benzo[*d*]thiazole-2-carbaldehyde (1.0 g, 6.12 mmol), $NaBH_4$ (0.35 g, 9.18 mmol) and EtOH (18 mL, 0.3 M) to afford **S-4j** in 83% yield (0.84 g, 5.08 mmol) as a light yellow solid which was carried to the next step without further purification.

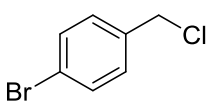
Synthesis of *para*-substituted benzyl chlorides

Synthesis of 1-(chloromethyl)-4-nitrobenzene (S-5a)



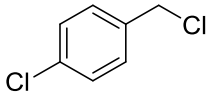
General procedure B was followed using **(4-nitrophenyl)methanol (S-4a)** (0.76 g, 5.0 mmol), $SOCl_2$ (5.0 mL) to afford **S-5a** in 67% yield (0.58 g, 3.4 mmol) as a white solid which was carried to the next step without further purification.

Synthesis of 1-bromo-4-(chloromethyl)benzene (S-5b)



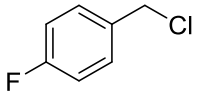
General procedure B was followed using **(4-bromophenyl)methanol (S-4b)** (0.75 g, 4.01 mmol), $SOCl_2$ (4.0 mL) to afford **S-5b** in quantitative yield (0.82 g, 4.0 mmol) as a white solid which was carried to the next step without further purification.

Synthesis of 1-chloro-4-(chloromethyl)benzene (S-5c)



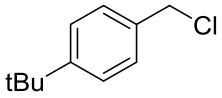
General procedure B was followed using **(4-chlorophenyl)methanol (S-4c)** (0.75 g, 5.26 mmol), $SOCl_2$ (5.3 mL) to afford **S-5c** in quantitative yield (0.84 g, 5.26 mmol) as a white solid which was carried to the next step without further purification.

Synthesis of 1-(chloromethyl)-4-fluorobenzene (S-5d)



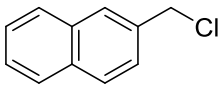
General procedure B was followed using **(4-fluorophenyl)methanol (S2)** (0.70 g, 5.55 mmol), $SOCl_2$ (5.5 mL) to afford **S-5d** in 85% yield (0.68 g, 4.7 mmol) as a brown solid which was carried to the next step without further purification.

Synthesis of 1-(*tert*-butyl)-4-(chloromethyl)benzene (S-5e)



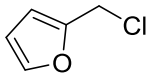
General procedure B was followed using **(4-(*tert*-butyl)phenyl)methanol (S-4d)** (0.75 g, 4.57 mmol), $SOCl_2$ (4.5 mL) to afford **S-5e** in 95% yield (0.79 g, 4.34 mmol) as a colorless oil which was carried to the next step without further purification.

Synthesis of 2-(chloromethyl)naphthalene (S-5g)



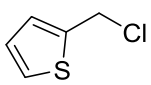
S-5g was synthesized according to a literature procedure.[7] The spectral data of the compound matched with the literature.[7]

Synthesis of 2-(chloromethyl)furan (S-5h)



S-5h was synthesized according to a modified literature procedure.[8] To a solution of **thiophen-2-ylmethanol (S-4g)** (1.0 g, 8.75 mmol) in DCM (17.5 mL, 0.5 M) cooled at 0 ^oC was added $SOCl_2$ dropwise (0.96 mL, 13.14 mmol). The reaction was stirred at 0 ^oC for 1 h. After the completion of the reaction determined by TLC (DCM: MeOH 99:1) the reaction was quenched by adding water (20 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3x) and the combined organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo* to yield **S-5h** as a colorless liquid in 63% yield (600 mg, 5.17 mmol) which was taken to the next step without further purification. The spectral data of the compound matched with the literature.[8]

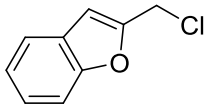
Synthesis of 2-(chloromethyl)thiophene (S-5i)



S-5i was synthesized according to a modified literature procedure.[9] To a solution of **furan-2-ylmethanol (S-4h)** (0.80 g, 8.15 mmol) and trimethylamine (1.13 mL,

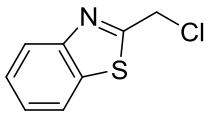
8.15 mmol) in DCM (8.2 mL, 0.1 M) cooled at 0 °C was added $SOCl_2$, dropwise (0.78 mL, 10.6 mmol). After stirring the mixture at 0 °C until the completion of the reaction (determined by TLC, DCM: MeOH 99:1). The reaction was quenched with water (20 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3x) and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield **S-5i** as a colorless oil in 52% yield (600 mg, 4.55 mmol) which was taken to the next step without further purification. The spectral data of the compound matched with the literature.[10]

Synthesis of 2-(chloromethyl)benzofuran (S-5j)



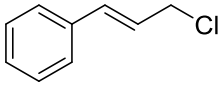
S-5j was synthesized according to a modified literature procedure.[11] To a solution of **benzofuran-2-ylmethanol (S-4i)** (0.50 g, 3.37 mmol) in a mixture of DMF (0.7 mL, 4.8 M) and THF (3.8 mL, 1.0 M) at RT was added $SOCl_2$ dropwise (0.37 mL, 5.06 mmol). After stirring the mixture for at 60 °C until reaction completion (determined by TLC, DCM: MeOH 99:1) the reaction was stirred further at rt for 30 min. Then the volatiles were evaporated *in vacuo* and the crude residue was dissolved in water. The mixture was extracted with EtOAc (3x) and combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield **S-5j** as a white solid in 89% yield (500 mg, 3.01 mmol) which was taken to the next step without further purification. The spectral data of the compound matched with the literature.[11]

Synthesis of 2-(chloromethyl)benzo[*d*]thiazole (S-5k)



S-5k was synthesized according to a modified literature procedure.[12] A solution of **benzo[*d*]thiazol-2-ylmethanol (S-4j)** (0.5 g, 3.02 mmol) in CCl_4 (5.0 mL, 0.6 M) and benzene (6.0 mL, 0.5 M) at rt was added to triphenylphosphine (1.2 g, 4.54 mmol) and the mixture was refluxed with stirring. The reaction progress was monitored by TLC (hexane:EtOAc 9:1). After cooling to rt and filtration through celite, the solvent was evaporated *in vacuo*. The resultant crude residue was purified by flash chromatography using hexane:EtOAc (0% EtOAc for 3 cv, 0-10% EtOAc for 3-10 cv, 10% EtOAc for 10-15 cv and then ramped up to 100% EtOAc for 15-20 cv and then held at 100% EtOAc for 20-30 cv) on 24 g silica column to afford **2-(chloromethyl)benzo[*d*]thiazole** in 91% yield (0.55 g, 2.75 mmol) as a yellow solid. The spectral data of the compound matched with the literature.[12]

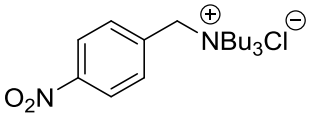
Synthesis of (3-chloroprop-1-en-1-yl)benzene (S-5l)



S-5l was synthesized according to a modified literature procedure.[13] A flame dried round bottom flask equipped with a magnetic stir bar was charged with DCM (45 mL, 0.5 M) and 3-phenylprop-2-en-1-ol (3.0 g, 22.35 mmol) under argon. The solution was cooled to 0 ºC and $SOCl_2$ (16.3 mL, 223.5 mmol) was added dropwise. The reaction was stirred at 0 ºC while the progress was monitored by TLC (hexane:EtOAc 9:1). After 2.5 h, the reaction was stopped and allowed to warm to rt slowly. It was quenched with ice water, extracted with DCM (3x) and washed with sat. $NaHCO_3$. The DCM layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resultant crude residue was purified by flash chromatography using hexane:DCM (0-2% DCM for 0-22 cv, 2-15% DCM for 22-27 cv, 15% DCM for 27-36, 15-100% DCM for 36-46 cv and then held at 100% DCM for 46-52 cv) on 80 g silica column to afford a colorless liquid **(3-chloroprop-1-en-1-yl)benzene** in 25% yield (0.85 g, 5.58 mmol). The spectral data of the compound matched with the literature.[14]

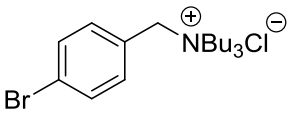
Synthesis of quaternary ammonium chloride salts

Synthesis of *N*,*N*-dibutyl-*N*-(4-nitrobenzyl)butan-1-aminium chloride (1a)



General procedure C was followed using **1-(chloromethyl)-4-nitrobenzene (S-5a)** (0.30 g, 1.74 mmol), tributylamine (0.5 mL, 2.09 mmol) in MeCN (1.8 mL) to afford **1a** in 87% yield (0.54 g, 1.51 mmol) as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.19 (d, J = 8.6 Hz, 2H), 8.00 (d, J = 8.6 Hz, 2H), 5.47 (s, 2H), 3.43 – 3.27 (m, 6H), 1.79 (p, J = 8.1 Hz, 6H), 1.37 (h, J = 7.4 Hz, 6H), 0.97 (t, J = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 148.9, 135.3, 134.6, 123.8, 62.1, 59.5, 24.7, 19.9, 13.7. FT-IR cm^{-1} 3387, 2961, 1523, 1348. HRMS (ESI) calcd, $C_{19}H_{33}N_2O_2^+$ 321.2537; observed, 321.2520. Melting point 192-193 ºC.

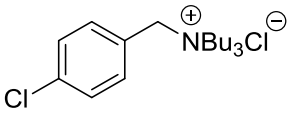
Synthesis of *N*-(4-bromobenzyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1b)



General procedure C was followed using **1-bromo-4-(chloromethyl)benzene (S-5b)** (0.62 g, 3.02 mmol), tributylamine (0.8 mL, 3.31 mmol) in MeCN (3.0 mL) to afford **1b** in 90% yield (1.06 g, 2.72 mmol) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (s, 4H), 5.12 (s, 2H), 3.32 (dd, *J* = 11.8, 5.2 Hz, 6H), 1.75 (dd, *J* = 15.3, 7.4 Hz, 6H), 1.39 (h, *J* = 7.4 Hz, 6H), 0.98 (t, *J* =

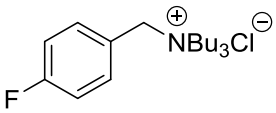
7.3 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.6, 132.4, 126.9, 125.3, 62.6, 58.9, 24.6, 19.9, 13.7. FT-IR cm^{-1} 3390, 2963, 737. HRMS (ESI) calcd, $C_{19}H_{33}BrN^+$ 354.1791; observed, 354.1788. Melting point 165-166 °C.

Synthesis of *N*,*N*-dibutyl-*N*-(4-chlorobenzyl)butan-1-aminium chloride (1c)



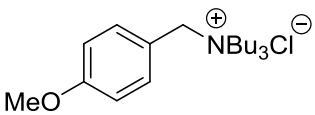
General procedure C was followed using **1-chloro-4-(chloromethyl)benzene (S-5c)** (0.40 g, 2.48 mmol), tributylamine (0.65 mL, 2.73 mmol) in MeCN (2.5 mL) to afford **1c** in 86% yield (0.74 g, 2.13 mmol) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.13 (s, 2H), 3.36 – 3.27 (m, 6H), 1.76 (p, *J* = 8.1 Hz, 6H), 1.38 (h, *J* = 7.4 Hz, 6H), 0.97 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.8, 134.2, 129.3, 126.4, 62.5, 58.8, 24.5, 19.8, 13.6. FT-IR cm^{-1} 3393, 2959. HRMS (ESI) calcd, $C_{19}H_{33}ClN^+$ 310.2296; observed, 310.2280. Melting point 165-166 °C.

Synthesis of *N*,*N*-dibutyl-*N*-(4-fluorobenzyl)butan-1-aminium chloride (1d)



General procedure C was followed using **1-(chloromethyl)-4-fluorobenzene (S-5d)** (0.25 g, 1.73 mmol), tributylamine (0.49 mL, 2.08 mmol) in MeCN (1.73 mL) to afford **1d** in 95% yield (0.54 g, 1.64 mmol) as a white solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.9 (ddd, *J* = 13.4, 8.5, 5.1 Hz). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.4, 5.1 Hz, 2H), 7.11 (t, *J* = 8.3 Hz, 2H), 5.10 (s, 2H), 3.41 – 3.18 (m, 6H), 1.75 (p, *J* = 8.0 Hz, 6H), 1.39 (h, *J* = 7.5 Hz, 6H), 0.98 (t, *J* = 7.2 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7 (d, *J* = 251.9 Hz), 134.8 (d, *J* = 8.5 Hz), 123.7 (d, *J* = 3.4 Hz), 116.2 (d, *J* = 21.6 Hz), 62.4, 58.6, 24.4, 19.7, 13.5. FT-IR cm^{-1} 3388, 2962, 1512, 1227, HRMS (ESI) calcd, $C_{19}H_{33}FN^+$ 294.2592; observed, 294.2570. Melting point 157-159 °C.

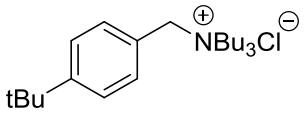
Synthesis of *N*,*N*-dibutyl-*N*-(4-methoxybenzyl)butan-1-aminium chloride (1e)



General procedure C was followed using **1-(chloromethyl)-4-methoxybenzene** (0.34 mL, 2.5 mmol), tributylamine (0.59 mL, 2.5 mmol) in MeCN (2.5 mL) to afford **1e** in 88% yield (0.75 g, 2.2 mmol) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 4.86 (s, 2H), 3.81 (s, 3H), 3.33 – 3.24 (m, 6H), 1.75 (p, *J* = 8.0 Hz, 6H), 1.40 (h, *J* = 7.4 Hz, 6H), 0.98 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 161.1, 133.9, 119.1,

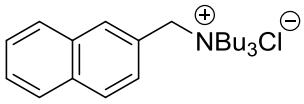
114.5, 62.7, 58.2, 55.3, 24.3, 19.7, 13.6. HRMS (ESI) calcd, $C_{19}H_{33}FN^+$ 294.2592; observed, 294.2570. FT-IR cm^{-1} 3381, 2958, 1514, 1221. HRMS (ESI) calcd, $C_{20}H_{36}NO^+$ 306.2791; observed, 301.2777. Melting point 97-100 ^oC.

Synthesis of *N*,*N*-dibutyl-*N*-(4-(tert-butyl)benzyl)butan-1-aminium chloride (1f)



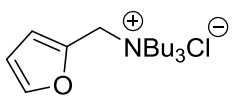
General procedure C was followed using **1-(*tert*-butyl)-4-(chloromethyl)benzene (S-5e)** (0.40 g, 2.18 mmol), tributylamine (0.57 mL, 2.41 mmol) in MeCN (2.2 mL) to afford **1f** in 87% yield (0.70 g, 1.9 mmol) as a white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (s, 4H), 4.85 (s, 2H), 3.39 – 3.28 (m, 6H), 1.77 (p, *J* = 8.0 Hz, 6H), 1.43 (h, *J* = 7.3 Hz, 6H), 1.31 (s, 9H), 1.00 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.2, 132.3, 126.3, 124.3, 62.9, 58.4, 34.9, 31.2, 24.5, 19.8, 13.8. FT-IR cm^{-1} 3390, 2960. HRMS (ESI) calcd, $C_{23}H_{42}N^+$ 332.3312; observed, 332.3295. Melting point 195-197 ^oC.

Synthesis of *N*,*N*-dibutyl-*N*-(naphthalen-2-ylmethyl)butan-1-aminium chloride (1h)



General procedure C was followed using **2-(chloromethyl)naphthalene (S-5g)** (0.30 g, 1.69 mmol), tributylamine (0.49 mL, 2.04 mmol) in MeCN (1.7 mL) to afford **1h** in 92% yield (0.56 g, 1.55 mmol) as a white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.84 (dd, *J* = 10.7, 7.8 Hz, 3H), 7.61 – 7.50 (m, 3H), 5.19 (s, 2H), 3.42 – 3.32 (m, 6H), 1.82 (p, *J* = 8.0 Hz, 6H), 1.42 (h, *J* = 7.3 Hz, 6H), 0.98 (t, *J* = 7.4 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.7, 133.2, 132.8, 129.0, 128.5, 128.3, 127.7, 127.6, 127.0, 124.8, 63.3, 58.6, 24.5, 19.8, 13.6. FT-IR cm^{-1} 3391, 2959, 1484. HRMS (ESI) calcd, $C_{23}H_{36}N^+$ 326.2842; observed, 326.2826. Melting point 145-147 ^oC.

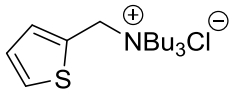
Synthesis of *N*,*N*-dibutyl-*N*-(furan-2-ylmethyl)butan-1-aminium chloride (1i)



General procedure C was followed using **2-(chloromethyl)furan (S-5h)** (0.30 g, 2.57 mmol), tributylamine (0.73 mL, 3.08 mmol) in MeCN (2.6 mL) to afford **1i** in 91% yield (0.70 g, 2.34 mmol) as a white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 1.8 Hz, 1H), 6.93 (d, *J* = 3.3 Hz, 1H), 6.45 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.06 (s, 2H), 3.36 – 3.26 (m, 6H), 1.76 (dq, *J* = 12.0, 7.8 Hz, 6H), 1.41 (h, *J* = 7.3 Hz, 6H), 0.98 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.78, 142.13, 116.66, 111.18, 58.55, 54.85, 23.79,

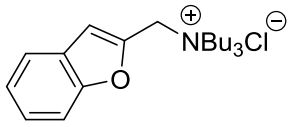
19.38, 13.27. FT-IR cm^{-1} 3392, 2959. HRMS (ESI) calcd, $C_{17}H_{32}NO^+$ 266.2478; observed, 266.2456. Melting point 124-125 °C.

Synthesis of *N*,*N*-dibutyl-*N*-(thiophen-2-ylmethyl)butan-1-aminium chloride (1j)



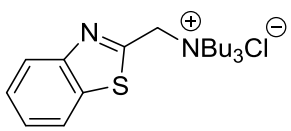
General procedure C was followed using **2-(chloromethyl)thiophene (S-5i)** (0.30 g, 2.26 mmol), tributylamine (0.65 mL, 2.71 mmol) in MeCN (2.3 mL) to afford **1j** in 90% yield (0.65 g, 2.03 mmol) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 3.3 Hz, 1H), 7.49 (d, *J* = 5.1 Hz, 1H), 7.10 (dd, *J* = 5.2, 3.5 Hz, 1H), 5.22 (s, 2H), 3.41 – 3.29 (m, 6H), 1.81 (p, *J* = 8.1 Hz, 6H), 1.44 (h, *J* = 7.4 Hz, 6H), 1.00 (t, *J* = 7.4 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.1, 129.4, 127.5, 127.3, 57.9, 56.4, 23.9, 19.3, 13.3. FT-IR cm^{-1} 3393, 2957. HRMS (ESI) calcd, $C_{17}H_{32}NS^+$ 282.2250; observed, 282.2230. Melting point 152-155 °C.

Synthesis of *N*-(benzofuran-2-ylmethyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1k)



General procedure C was followed using **2-(chloromethyl)benzofuran (S-5j)** (0.25 g, 1.34 mmol), tributylamine (0.30 mL, 1.61 mmol) in MeCN (1.4 mL) to afford **1k** in 89% yield (0.44 g, 1.19 mmol) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.46 – 7.26 (m, 3H), 5.37 (s, 2H), 3.48 – 3.21 (m, 6H), 1.85 (p, *J* = 7.5 Hz, 6H), 1.45 (h, *J* = 7.4 Hz, 6H), 1.01 (t, *J* = 7.5 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.4, 144.8, 127.0, 126.2, 123.7, 122.2, 114.4, 111.3, 59.5, 56.1, 24.3, 19.8, 13.6. FT-IR cm^{-1} 3461, 2960. HRMS (ESI) calcd, $C_{21}H_{34}NO^+$ 316.2635; observed, 316.2619. Melting point 142-145 °C.

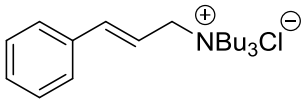
Synthesis of *N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1l)



General procedure C was followed using **2-(chloromethyl)benzo[*d*]thiazole (S-5k)** (0.25 g, 1.50 mmol), tributylamine (0.43 mL, 1.81 mmol) in MeCN (1.5 mL) to afford **1l** in 87% yield (0.46 g, 1.19 mmol) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.57 – 7.45 (m, 2H), 5.57 (s, 2H), 3.59 – 3.49 (m, 6H), 1.87 (p, *J* = 7.8 Hz, 6H), 1.43 (h, *J* = 7.5 Hz, 6H), 0.99 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.6, 152.5, 135.2, 126.6, 126.4, 123.5, 121.6, 59.3, 57.1, 23.9, 19.4, 13.3. FT-

IR cm^{-1} 3458, 2957. HRMS (ESI) calcd, $C_{20}H_{33}N_2S^+$ 333.2359; observed, 333.2342. Melting point 102-104 °C.

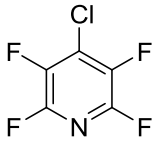
Synthesis of *N*,*N*-dibutyl-*N*-cinnamylbutan-1-aminium chloride (1m)



General procedure C was followed using **(3-chloroprop-1-en-1-yl)benzene (S-5l)** (0.5 g, 3.28 mmol), tributylamine (0.94 mL, 3.93 mmol) in MeCN (3.3 mL) to afford **1m** in 96% yield (1.06 g, 3.15 mmol) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.36 (dtd, *J* = 6.8, 5.2, 4.8, 2.0 Hz, 3H), 7.07 (d, *J* = 15.5 Hz, 1H), 6.17 (dt, *J* = 15.4, 7.6 Hz, 1H), 4.54 (d, *J* = 7.6 Hz, 2H), 3.43 – 3.33 (m, 6H), 1.79 (p, *J* = 15.6, 7.7 Hz, 6H), 1.45 (h, *J* = 7.4 Hz, 6H), 1.01 (t, *J* = 7.4 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.9, 134.7, 129.3, 128.8, 127.1, 114.1, 61.6, 58.7, 24.2, 19.7, 13.6. FT-IR cm^{-1} 3378, 2958, 1649. HRMS (ESI) calcd, $C_{21}H_{36}N^+$ 302.2842; observed, 302.2826. Melting point 145-147 °C.

Catalytic chlorination of perfluoroarenes

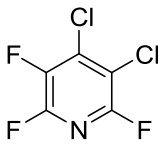
Synthesis of 4-chloro-2,3,5,6-tetrafluoropyridine (2a)



General procedure D was followed using pentafluoropyridine (110 µL, 1.0 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (124.8 mg, 0.4 mmol), TMSCl (152 µL, 1.2 mmol) and THF (1.0 mL) was used to afford **2a** in quantitative yield by ^{19}F NMR after adding trifluoroacetic acid (19.2 µL, 0.25 mmol).

Due to the volatility of the product, **General workup method E** was followed to isolate **2a** in 35% yield (64.9 mg) and >95% purity as a colorless liquid. For the determination of purity the isolated material (10.0 µL, 16.6 mg) was diluted with $CDCl_3$ (0.35 mL) in an NMR tube and it was spiked with 1,2,4,5-tetrafluorobenzene (5.0 µL, 0.045 mmol). The spectral data of the compound matched with the literature.[15] ^{19}F NMR (376 MHz, Chloroform-*d*) δ -88.4 (dq, *J* = 28.1, 14.7 Hz, 2F), -141.3 – -141.7 (m, 2F). FT-IR cm^{-1} 1466, 1238, 952. GC/MS (m/z, relative intensity) 187 (M+2, 10), 185 (M+, 30).

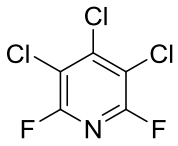
Synthesis of 3,4-dichloro-2,5,6-trifluoropyridine (2b)



General procedure D was followed using 3-chloro-2,4,5,6-tetrafluoropyridine (115.2 µL, 1.0 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (124.8 mg, 0.4 mmol), TMSCl (126.9 µL, 1.0 mmol) and THF (1.0 mL) was used to afford **2b** in 90% yield by ^{19}F NMR after adding trifluoroacetic acid (9.6 µL, 0.125 mmol).

Due to the volatility of the product, **General workup method E** was followed to isolate **2b** in 72% yield (145 mg) and 92% purity. For the determination of purity the isolated material (10.0 µL, 16.1 mg) was diluted with $CDCl_3$ (0.35 mL) in an NMR tube and it was spiked with 1,2,4,5-tetrafluorobenzene (5.0 µL, 0.045 mmol). The spectral data of the compound matched with the literature.[15] ^{19}F NMR (376 MHz, Chloroform-*d*) δ -70.5 (dd, *J* = 26.1, 13.2 Hz, 1F), -86.5 (dd, *J* = 20.3, 13.2 Hz, 1F), -140.2 (dd, *J* = 26.3, 20.5 Hz, 1F). FT-IR cm^{-1} 1449, 1210, 732. GC/MS (m/z, relative intensity) 203 (M+2, 66), 201 (M+, 100).

Synthesis of 3,4,5-trichloro-2,6-difluoropyridine (2c)

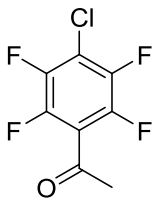


General procedure D was followed using 3,5-dichloro-2,4,6-trifluoropyridine (124.5 µL, 1.0 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (311.93 mg, 1.0 mmol), TMSCl (253 µL, 2.0 mmol) and THF (1.0 mL) was used to afford **2c** in quantitative yield by ^{19}F NMR after adding trifluoroacetic acid (9.6 µL, 0.125 mmol).

General isolation method G was followed to isolate **2c**. The crude material was purified by flash chromatography using hexane:DCM (0% DCM for 0-17 cv, 0-100% DCM for 17-25 cv and then held at 100% DCM for 25-27 cv) on a 40 g silica column to afford **2c** in 63% yield (138 mg) and 72% purity as a colorless liquid. Due to semi-volatile nature of compound **2c** limited effort was made to to remove residual solvents.

For the determination of purity the isolated material (10.0 µL, 15.2 mg) was diluted with $CDCl_3$ (0.35 mL) in an NMR tube and it was spiked with 1,2,4,5-tetrafluorobenzene (5.0 µL, 0.045 mmol). The spectral data of the compound matched with the literature.[15] ^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.4 (2F). FT-IR cm^{-1} 1393, 1225, 729. GC/MS (m/z, relative intensity) 220 (M+2, 100), 218 (M+, 100).

Synthesis of 1-(4-chloro-2,3,5,6-tetrafluorophenyl)ethan-1-one (2d)

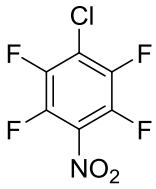


General procedure D was followed using 1-(perfluorophenyl)ethan-1-one (71.2 µL, 0.5 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (77.9 mg, 0.25 mmol), TMSCl (126.9 µL, 1.0 mmol) and THF (0.5 mL) was used to afford **2d** in 76% yield by ^{19}F NMR after adding trifluoroacetic acid (9.6 µL, 0.125 mmol).

General isolation method G was followed to isolate **2d**. The crude material was purified by flash chromatography using hexane:DCM (0% DCM for 0-4 cv, 0-25% DCM for 4-22 cv, 25% DCM for 22-32, 25-100% DCM for 32-35 cv and then held at 100% DCM for 35-37 cv) on a 40 g silica column to afford **2d** in 60% yield (67 mg) as a colorless liquid. Due to volatility of compound **2d** limited effort was made to remove residual solvents. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -139.1 – -139.2 (m, 2F), -140.6 – -140.8 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-d) δ 2.63 (t, J = 1.8

Hz, 3H). FT-IR cm^{-1} 1714, 1477, 1289. GC/MS (m/z, relative intensity) 228 (M+2, 4), 226 (M+, 12).

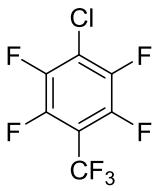
Synthesis of 1-chloro-2,3,5,6-tetrafluoro-4-nitrobenzene (2e)



General procedure D was followed using 1,2,3,4,5-pentafluoro-6-nitrobenzene (128.7 µL, 1.0 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (124.8 mg, 0.4 mmol), TMSCl (152 µL, 1.2 mmol) and THF (1.0 mL) was used.

General isolation method G was followed to isolate **2e**. The crude material was purified by flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-17 cv, 0-100% EtOAc for 17-19 cv and then held at 100% EtOAc for 19-21 cv) on a 40 g silica column to afford **2e** in 80% yield (183 mg, 0.80 mmol) as a white solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -136.2 – -136.3 (m), -136.3 (q, *J* = 12.6 Hz, 2F), -145.4 – -145.6 (m, 2F). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.0 – 143.0 (m), 142.2 – 139.2 (m), 128.9 – 128.4 (m), 117.8 (t, *J* = 18.7 Hz). FT-IR cm^{-1} 1492, 1352, 998, 759. GC/MS (m/z, relative intensity) 231 (M+2, 13), 225 (M+, 40). Melting point 40-42 °C.

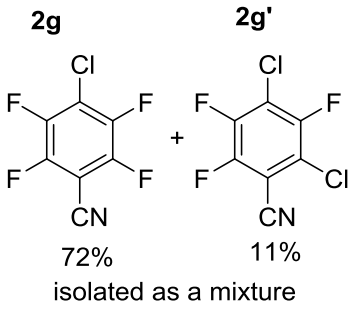
Synthesis of 1-chloro-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (2f)



General procedure D was followed using 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (70.85 µL, 0.5 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (77.9 mg, 0.25 mmol), TMSCl (126.9 µL, 1.0 mmol) and THF (0.5 mL) was used to afford **2f** in 90% yield by ^{19}F NMR after adding trifluoroacetic acid (19.1 µL, 0.25 mmol).

Due to the volatility of the product, **General workup method E** was followed to isolate **2f** in 30% yield (37 mg) as a colorless liquid. Due to volatility of compound **2f** limited effort was made to remove residual solvents. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.2 (t, *J* = 21.9 Hz, 3F), -137.9 – -138.1 (m, 2F), -139.2 – -139.4 (m, 2F). FT-IR cm^{-1} 1483, 1145, 712. GC/MS (m/z, relative intensity) 254 (M+2, 35), 252 (M+, 100).

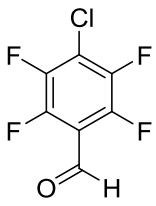
Synthesis of 4-chloro-2,3,5,6-tetrafluorobenzonitrile (2g) and 2,4-dichloro-3,5,6-trifluorobenzonitrile (2g')



General procedure D was followed using 2,3,4,5,6-pentafluorobenzonitrile (126 µL, 1.0 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (124.8 mg, 0.4 mmol), TMSCl (152 µL, 1.2 mmol) and THF (1.0 mL) was used.

General isolation method G was followed to isolate **2g**. The crude material was purified by flash chromatography using hexane:DCM (0% DCM for 0-15 cv, 0-20% DCM for 15-27 cv, 20% DCM for 27-32, 20-100% DCM for 32-35 cv and then held at 100% DCM for 35-37 cv) on a 40 g silica column to afford **2g** in 72% yield and **2g'** in 11% yield as a mixture (175 mg combined) as a white solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.0 (d, *J* = 11.3 Hz, 1F, minor), -129.7 (dd, *J* = 20.7, 11.3 Hz, 1F, minor), -131.5 – -131.6 (m, 2F, major), -131.7 (d, *J* = 20.8 Hz, 1F, minor), -136.7 – -136.9 (m, 2F, major). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4 (dt, *J* = 263.7, 15.6, 4.3 Hz), 145.9 – 142.9 (m), 119.8 (tt, *J* = 18.7, 2.6 Hz), 106.9 (t, *J* = 3.6 Hz), 93.2 (t, *J* = 17.3 Hz). Minor product's (**2g'**) peaks are labelled on the spectrum. FT-IR cm^{-1} 2249, 1470, 860. GC/MS (m/z, relative intensity) **2g** 211 (M+2, 33), 209 (M+, 100) and **2g'** 227 (M+2, 66), 225 (M+, 100). Melting point (mixture) 64-66 ^{o}C.

Synthesis of 4-chloro-2,3,5,6-tetrafluorobenzaldehyde (2h)

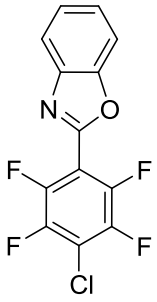


General procedure D was followed using 2,3,4,5,6-pentafluorobenzaldehyde (123.5 µL, 1.0 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (124.8 mg, 0.40 mmol), TMSCl (126.9 µL, 1.0 mmol) and THF (1.0 mL) was used.

General isolation method G was followed to isolate **2h**. The crude material was purified by flash chromatography using hexane:DCM (0% DCM for 1-12 cv, 0-5% DCM for 12-22 cv, 5% DCM for 22-28, 5-100% DCM for 28-35 cv and then held at 100% DCM for 35-37 cv) on a 40 g silica column to afford **2h** in 71% yield (150 mg) as a white solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -138.0 – -138.1 (m, 2F), -140.7 – -140.8 (m, 2F). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5 – 176.3 (m), 144.7 (ddt, *J* = 258.7, 14.5, 5.1 Hz), 145.8 – 143.0 (m), 118.1 – 117.6 (m), 117.1 (t,

J = 14.6 Hz). FT-IR cm^{-1} 1695, 1479, 975. GC/MS (m/z, relative intensity) 213 (M+2, 33), 211 (M+, 100). Melting point 139-141 °C.

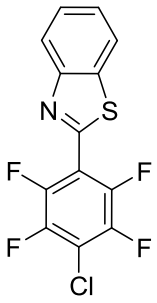
Synthesis of 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]oxazole (2i)



General procedure D was followed using 2-(perfluorophenyl)benzo[*d*]oxazole (142.6 mg, 0.5 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (62.4 mg, 0.2 mmol), TMSCl (76 µL, 0.6 mmol) and THF (0.5 mL) was used.

General isolation method F was followed to isolate **2i**. The crude material was purified by flash chromatography using hexane:ethyl acetate (0% EtOAc for 0-5 cv, 0-5% EtOAc for 5-17 cv, 5% EtOAc for 17-21 cv and ramped to 100% EtOAc for 21-24 cv and then held at 100% EtOAc for 24-25 cv) on a 40 g silica column to afford **2i** in 90% yield (136 mg, 0.45 mmol) as a yellow solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -136.6 – -136.7 (m, 2F), -139.2 – -139.3 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, J = 7.5, 1.8 Hz, 1H), 7.67 (dd, J = 7.4, 1.7 Hz, 1H), 7.51 – 7.42 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.5, 150.4, 145.3 (ddt, J = 261.1, 14.8, 4.7 Hz), 146.1 – 143.1 (m), 141.0, 126.7, 125.2, 120.9, 115.5 (t, J = 18.9 Hz), 111.0, 107.0 (t, J = 13.6 Hz). FT-IR cm^{-1} 3030, 1449. GC/MS (m/z, relative intensity) 303 (M+2, 20), 301 (M+, 60). Melting point 130-131 °C.

Synthesis of 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]thiazole (2j)

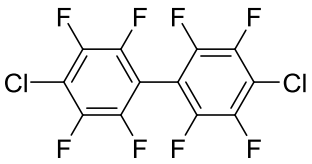


General procedure D was followed using 2-(perfluorophenyl)benzo[*d*]thiazole (75.3 mg, 0.25 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (62.4 mg, 0.2 mmol), TMSCl (63.5 µL, 0.5 mmol) and THF (0.5 mL) was used.

General isolation method F was followed to isolate **2j**. The crude material was purified by flash chromatography using hexane:ethyl acetate (0% EtOAc for 10 cv, 0-10% EtOAc for 10-27 cv, 10% EtOAc for 27-33 cv and ramped to 100% EtOAc for 33-35 cv and then held at 100% EtOAc for 35-37 cv) on a 40 g silica column to afford **2j** in 85% yield (67.4 mg, 0.21 mmol) as a yellow solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -138.0 – -138.1 (m, 2F), -139.6 – -139.8 (m, 2F). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.55 (dt, J = 30.0, 7.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.8, 146.5 – 145.5 (m), 143.8 – 143.1 (m), 135.6 (t, J = 2.7 Hz), 129.0 – 128.2 (m), 126.8, 126.5, 124.2,

121.4, 114.3 (t, *J* = 19.0 Hz), 112.8 (t, *J* = 14.1 Hz). FT-IR cm^{-1} 3061, 2926, 1477. GC/MS (m/z, relative intensity) 319 (M+2, 25), 317 (M+, 75). Melting point 125-126 °C.

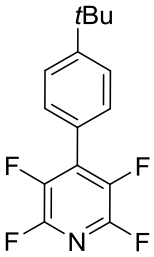
Synthesis of 4,4'-dichloro-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (2k)



General procedure D was followed using perfluoro-1,1'-biphenyl (133.6 mg, 0.40 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (129.8 mg, 0.40 mmol), TMSCl (121.8 µL, 0.96 mmol) and THF (0.4 mL) was used.

General isolation method F was followed to isolate **2k**. The crude material was purified by flash chromatography using hexane:ethyl acetate (0% EtOAc for 20 cv, 0-15% EtOAc for 20-27 cv and ramped to 100% EtOAc for 27-28 cv and then held at 100% EtOAc for 28-34 cv) on a 40 g silica column to afford **2k** in 45% yield (65 mg, 0.18 mmol) as a white solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -136.9 – -137.0 (m, 4F), -139.1 – -139.2 (m, 4F). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.5 (d, *J* = 14.2 Hz), 143.0 (d, *J* = 12.7 Hz), 115.0 (t, *J* = 18.6 Hz), 105.2 (t, *J* = 14.2 Hz). FT-IR cm^{-1} 1457, 1246, 720. GC/MS (m/z, relative intensity) 368 (M+2, 66), 366 (M+, 100). Melting point 96-98 °C.

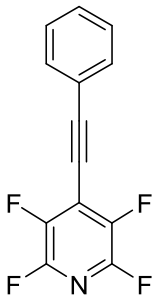
Synthesis of 4-(4-(*tert*-butyl)phenyl)-2,3,5,6-tetrafluoropyridine (5a)



5a was synthesized starting from pentafluoropyridine as the starting material. **General procedure D** was followed using pentafluoropyridine (110 µL, 1.0 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (124.8 mg, 0.4 mmol), TMSCl (152 µL, 1.2 mmol) and THF (1.0 mL) was used to afford a crude reaction containing **4-chloro-2,3,5,6-tetrafluoropyridine (2a).** After reaction completion as judged by ^{19}F NMR, the reaction was cooled down to rt. This material was taken to the next step without further purification. In a flame dried vial under argon, the crude material (0.2 mL, 0.2 mmol) was added followed by (4-(*tert*-butyl)phenyl)boronic acid (42.7 mg, 0.24 mmol) and triphenyl phosphine (4.5 mg, 0.02 mmol), 2 M aqueous K_2CO_3 (0.2 mL, 0.378 mmol) and DME (0.2 mL). The vial was capped and the mixture was degassed via argon bubbling for 5 min at 0 °C (to avoid evaporation of **4-chloro-2,3,5,6-tetrafluoropyridine (2a)**). Then, $Pd(OAc)_2$ was added and the degassing was continued again for 5 min. The reaction was heated at 110 °C overnight. Next day, the reaction was cooled to rt and passed through a celite pad and eluted with

DCM (5 mL). Then, the volatiles were removed via rotavap. The residue was treated with DCM (10 mL) and washed with water (3 x 5 mL). Then the DCM layer was dried with anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography using hexane:DCM (0% DCM for 0-5 cv, 0-3% DCM for 5-15 cv, 3% DCM for 15-27 and ramped to 100% for 27-35 cv and then held at 100% DCM for 35-37 cv) on a 40 g silica column. The isolated fraction which contained an unidentified byproduct was further purified by a reverse phase chromatography using water:MeCN (10% MeCN for 1 cv and ramped to 100% MeCN for 1-22 cv and then held at 100% MeCN for 22-25 cv) on a 26 g C-18 column to afford **5a** in 70% yield (39.6 mg, 0.14 mmol) as a white solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.9 – -91.2 (m), -145.2 – -145.4 (m). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 2H), 7.48 (dt, *J* = 8.6, 1.8 Hz, 2H), 1.38 (s, 9H), 7.59 – 7.54 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.2, 144.2 (dddd, *J* = 244.6, 17.0, 13.4, 2.8 Hz), 141.0 – 137.9 (m), 133.6 (tt, *J* = 14.5, 2.8 Hz), 129.7 (t, *J* = 2.5 Hz), 126.1, 123.1, 35.1, 31.3. FT-IR cm^{-1}2970, 1450. GC/MS (m/z, relative intensity) 283 (M+, 15), 268 (95), 240 (60). Melting point 104-105 °C.

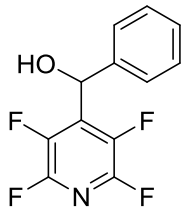
Synthesis of 2,3,5,6-tetrafluoro-4-(phenylethynyl)pyridine (5b)



5b was synthesized by following a modified literature procedure[16] starting from **4-chloro-2,3,5,6-tetrafluoropyridine (2a)**. In a flame dried microwave vial under argon the **2a** (13.7 µL, 0.1 mmol) was added followed by phenylacetylene (13.2 µL, 0.12 mmol) and Cs_2CO_3 (32.5 mg, 0.1 mmol). Then, the capped vial was moved to the glovebox and $PdCl_2(pph_3)_2$ (1.4 mg, 0.002 mmol) and *t*Bu_3P (0.81 mg, 0.004 mmol) were added. The mixture was recapped and it was removed from the glovebox. Degassed DMF (0.4 mL) was added, followed by DBU (1,8-Diazabicyclo(5.4.0)undec-7-ene) (1.5 µL, 0.01 mmol) and the reaction mixture was degassed via argon bubbling for 5 min at 0 °C (to avoid evaporation of **4-chloro-2,3,5,6-tetrafluoropyridine**). Then, the reaction was placed in a microwave reactor (Biotage initiator, 200 °C, 10 min). After cooling to rt, the reaction was diluted with EtOAc and filtered through a pad of celite. The filtrate was rotavaped and hexane (20 mL) was added. The hexane layer was washed with brine (3 x 10 mL). The combined aqueous phase was extracted with hexane (2 x 10 mL) and the combined organic phase was dried with anhydrous $MgSO_4$, filtered, concentrated *in vacuo*. The crude material was purified by flash chromatography using hexane:ethyl acetate (0% EtOAc for 20 cv, 0-12% EtOAc for 20-30 cv, 12% EtOAc for 30-33 cv and ramped to 100% EtOAc for 33-35 cv and then held at 100% EtOAc

for 35-37 cv) on a 40 g silica column to afford **5b** in 80% yield (20.1 mg, 0.08 mmol) as a white solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.4 – -90.6 (m), -138.2 – -138.5 (m). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.45 (dt, *J* = 14.5, 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.1 – 141.9 (m), 143.4 – 140.2 (m), 132.3, 130.6, 128.7, 120.6, 106.7 (t, *J* = 3.5 Hz). FT-IR cm^{-1} 2922, 2215, 735. GC/MS (m/z, relative intensity) 251 (M+, 100), 231 (10). Melting point 136-137 °C.

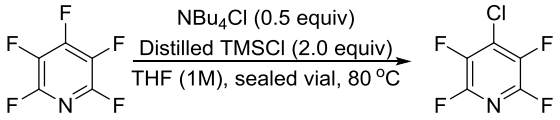
Synthesis of (perfluoropyridin-4-yl)(phenyl)methanol (5c)



5c was synthesized starting from pentafluoropyridine as the starting material. **General procedure D** was followed using pentafluoropyridine (110 µL, 1.0 mmol), *N*-benzyl-*N*,*N*-dibutylbutan-1-aminium chloride (124.8 mg, 0.4 mmol), TMSCl (152 µL, 1.2 mmol) and THF (1.0 mL) was used to afford a crude reaction containing **4-chloro-2,3,5,6-tetrafluoropyridine (5c).** After reaction completion as judged by ^{19}F NMR, the reaction was cooled to rt. An aliquot (0.5 mL, 0.5 mmol) was taken out and diluted with pentane (5.0 mL) and it was washed with 1M HCl (3 x 5 mL). The pentane layer was separated, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. This material was taken to the next step without further purification.

In a flame dried vial under argon the crude material after workup (0.5 mmol) was added followed by THF (1.4 mL) and it was cooled to -78 °C. Then, BuLi (0.53 mL, 0.84 mmol, ~1.6 M solution in hexane) was slowly added over 10 min and stirring was continued for 20 min at -78 °C. To the above mixture, benzaldehyde (86 µL, 0.84 mmol) was added as a one portion and it was allowed to warm to rt slowly while stirring. After 45 min, the reaction was quenched by adding sat. NH_4Cl (3.0 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic phase was dried with anhydrous $MgSO_4$, filtered, concentrated *in vacuo*. The crude material was purified by flash chromatography using hexane:ethyl acetate (0% EtOAc for 5 cv, 0-10% EtOAc for 5-10 cv, 10% EtOAc for 10-15 cv, 10-20% EtOAc for 15-17 cv, 20% EtOAc for 17-22 cv and ramped to 100% EtOAc for 22-24 cv and then held at 100% EtOAc for 24-26 cv) on a 40 g silica column to afford **5c** in 62% yield (80.0 mg, 0.31 mmol) as a white solid. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.0 – -90.2 (m), -143.9 – -144.1 (m). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dt, *J* = 12.5, 6.1 Hz, 5H), 6.27 (s, 1H), 2.99 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.4 – 142.2 (m), 141.3 – 138.1 (m), 139.3, 135.6 (t, *J* = 13.1 Hz), 129.2, 129.0, 125.7, 68.5. FT-IR cm^{-1} 3356, 2914, 1472. GC/MS (m/z, relative intensity) 257 (M+, 20), 178 (15). Melting point 100-101 °C

Table 1. Optimization of the Reaction Conditions



entry	modification	time	conv% to the product
1	Without NBu_4Cl	3/20	NR
2	Without NBu_4Cl at 150 °C, microwave reactor	1	NR
3	NMe_4Cl instead of NBu_4Cl	3/20	NR/NR
4	NEt_4Cl instead of NBu_4Cl	3/20	1/7
5	NPr_4Cl instead of NBu_4Cl	3/20	NR/NR
6	None	3/20	7/69
7	$H_3C(H_2C)_5-\overset{\overset{(CH_2)_5CH_3}{\vert}}{\underset{\underset{(CH_2)_5CH_3}{\vert}}{P^+}}-(CH_2)_{13}CH_3Cl^-$ instead of NBu_4Cl	3/20	3/63
8	Ph_4PCl instead of NBu_4Cl	3/20	NR/<2%
9	DMF instead of THF	3/20	3/20
10	MeCN instead of THF	3/20	NR/<2
11	DCM or toluene instead of THF	3/20	NR/NR
12	at rt	3/20	NR/NR
13	at 45 °C	3/20	NR/5
14	with 20 mol% H_2O	3/20	3/28
15	with 50 mol% H_2O	3/20	2/17
16	with 100 mol% H_2O	3/20	1/10
17	TMSCl (2.0 equiv), NBu_4Cl (2.0 equiv)	3/20	64/100
18	No TMSCl	3/20	22/30
19	KCl instead of TMSCl	3/20	20/25[a]
20	NaCl instead of TMSCl	3/20	45/75[b]
21	$BaCl_2.2H_2O$ instead of TMSCl	3/20	19/55
22	$CaCl_2$ instead of TMSCl	3/20	32/79
23	**Me_2SiHCl instead of TMSCl**	**3/20**	**85/100**
24	**Ph_2SiHCl instead of TMSCl**	**3/20**	**85/100**
25	*t*-$BuMe_2SiCl$ instead of TMSCl	3/20	5/33
26	with $BnNBu_3Cl$ 25 mol%	3/20/40	18/87/>98
27	with $BnNBu_3Cl$ 10 mol%	3/20/40	<1/12/30

[a]another 49% of byproduct observed by ^{19}F NMR, [b]another 20% of byproduct observed by ^{19}F NMR

Notes related to the optimization:

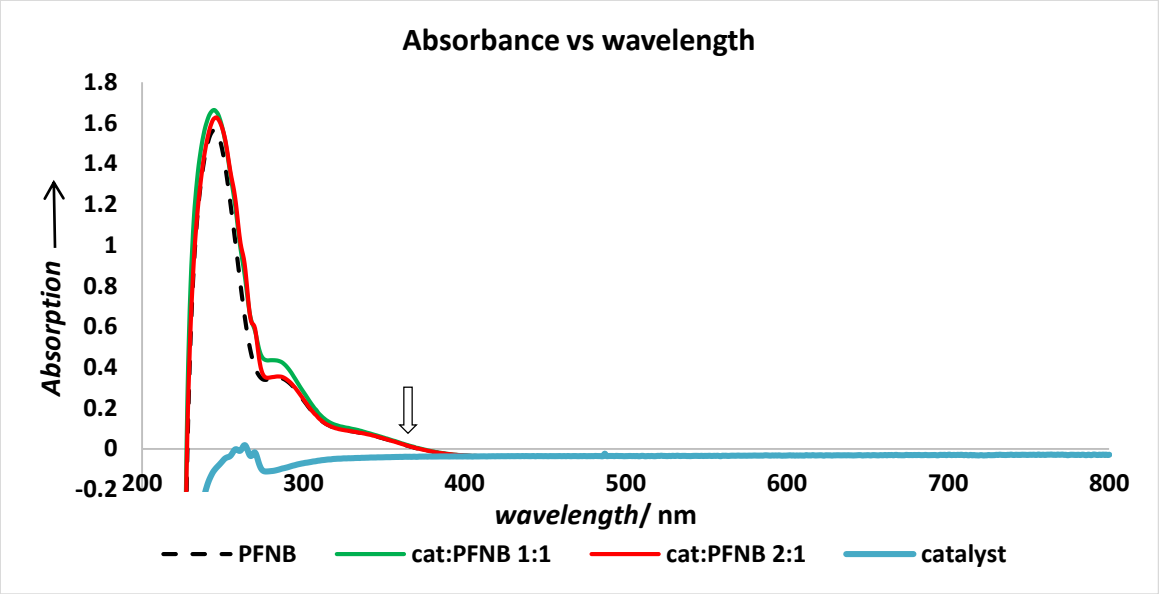
1. Cheap inorganic chloride sources also facilitated the reaction albeit with the formation of unidentified byproducts. When $CaCl_2$ used, a superior reactivity was achieved compared to Bu_4NCl. However, it was excluded from further optimizations due to limitations of substrate scope which had either no or sluggish reactions with some less activated perfluoroarenes ($CaCl_2$ worked with pentafluoronitrobenzene and pentafluoropyridine but not with pentafluoroacetophenone)

2. The reaction was faster with both dimethylchlorosilane and diphenylchlorosilane, however, reduction of carbonyl group was observed when perfluorocarbonyls were used as substrates.

Evidence for pre-complexation between perfluoroarene and $BnBu_3NCl$

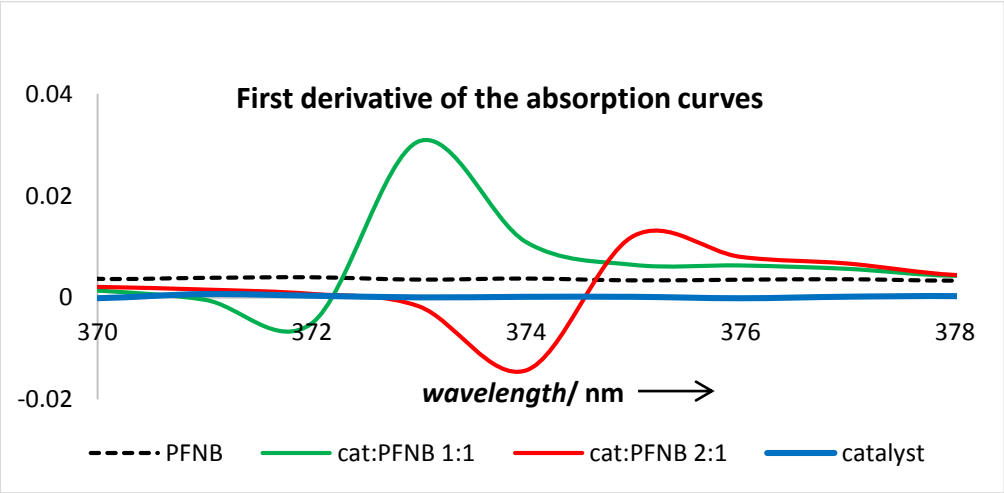
UV-vis experiment

A UV-vis experiment was carried using DCM as the solvent, in which UV-vis spectra were collected for both the individual components and the mixed components, and then compared. The experiment was carried out by mixing pentafluoronitrobenzene (PFNB) and $BnNBu_3Cl$ (1:1 and 1:2 molar ratio) and PFNB:$BnNBu_3Cl$:TMSCl (1:2:2 molar ratio) in DCM. Pentafluoronitrobenzene (PFNB) (0.0064 mmol, 0.8 µL) and $BnBu_3NCl$ (catalyst) (0.0064 mmol, 2.0 mg) were separately dissolved in DCM (20 mL, 3.2×10^{-4} M) to obtain individual solutions. To obtain the two component 1:1 mixture PFNB (0.0064 mmol, 0.8 µL) and catalyst (0.0064 mmol, 2.0 mg) were mixed in DCM (20 mL, 3.2×10^{-4} M) and the 1:2 mixture was obtained by mixing PFNB (0.0064 mmol, 0.8 µL) and catalyst (0.0128 mmol, 4.0 mg) in DCM (20 mL, 3.2×10^{-4} M). Pentafluoronitrobenzene (PFNB) (0.0064 mmol, 0.8 µL), $BnBu_3NCl$ (catalyst) (0.0128 mmol, 4.0 mg) and trimethylsilyl chloride (TMSCl) (0.0128 mmol, 1.6 µL) were mixed in DCM (20 mL, 3.2×10^{-4} M) to obtain the three component mixture. Then the UV-vis spectra were obtained. Following is the overlapped plot showing a new weak absorption band emergence at around 370-380 nm.

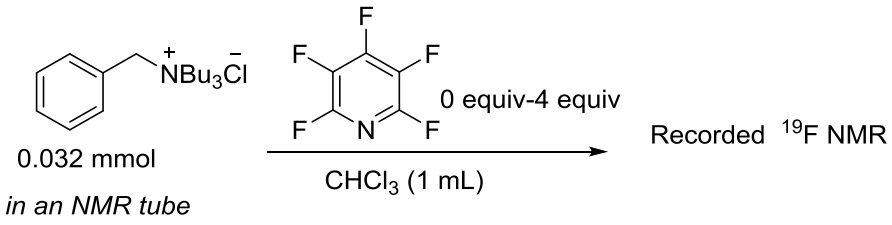


First derivative of the absorption curves

Overlap of PFNB's absorption band with the newly formed band obscures identification of the maximum absorption wavelength (λ_{max}). Therefore, we performed a first derivative analysis which allowed us to identify a new red-shifted λ_{max} of both the 1:1 and 2:1 catalyst:PFNB complexes. The observation of two different λ_{max} values also supports the formation of two distinct types of complexes. The first derivative analysis of above reported absorption curves are shown below.



NMR titration experiment; pentafluoropyridine (PFP) and $BnNBu_3Cl$ in $CHCl_3$

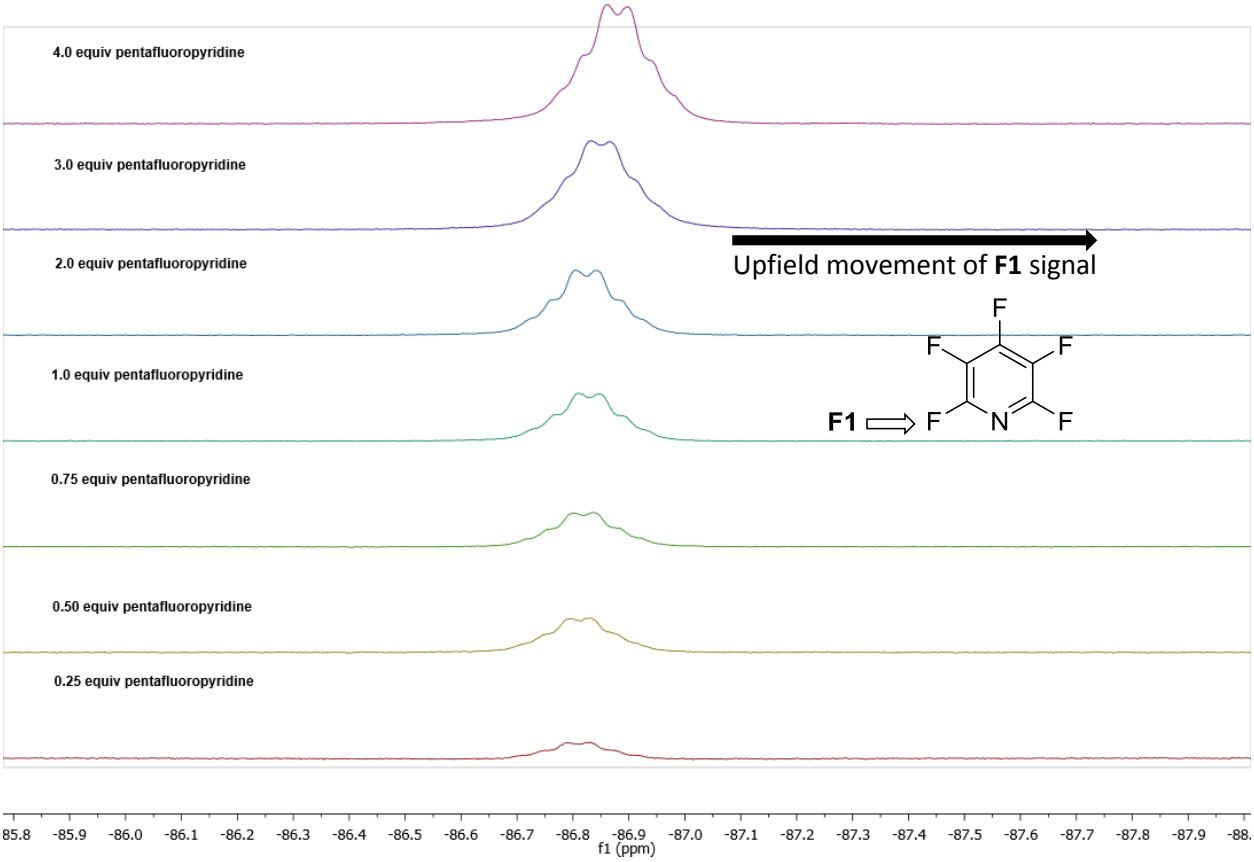


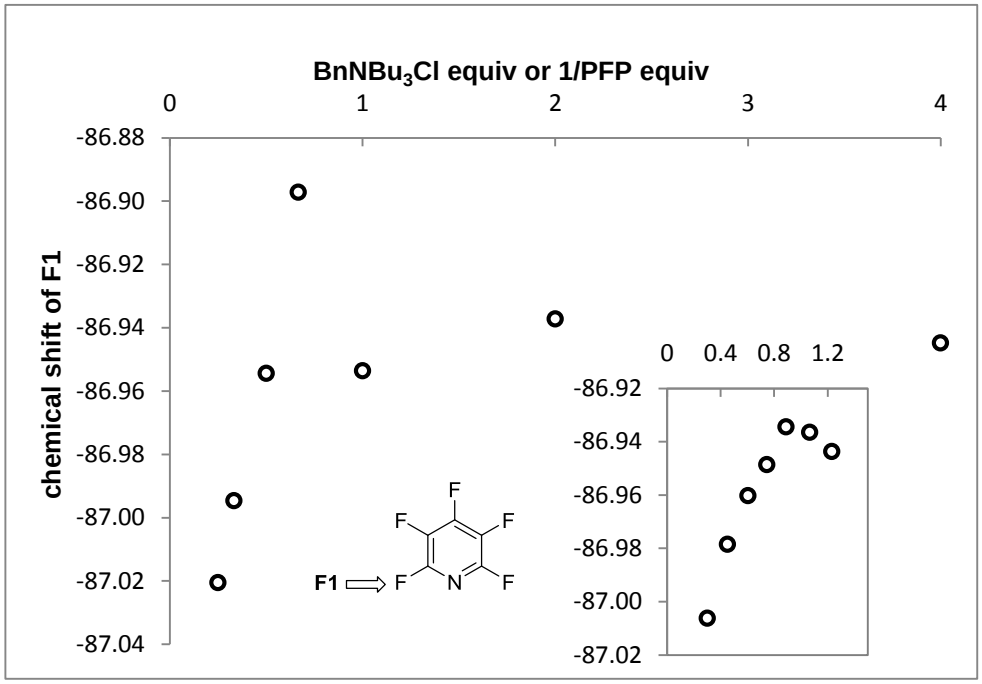
NMR titration was carried out in $CHCl_3$. Two separate stock solutions of $BnBu_3NCl$ and PFP were prepared by dissolving $BnBu_3NCl$ (0.064 M, 99.8 mg in 5.0 mL of $CHCl_3$) and PFP (0.256 M, 140 µL in 5.0 mL of $CHCl_3$). In eight separate NMR tubes above two solutions were added according to the following table to obtain samples with constant amount of $BnBu_3NCl$ and different amounts of PFP. All the samples were topped up to 1 mL by adding $CHCl_3$ according to the table.

equiv of PFP	mmol of PFP	volume PFP solution added (µL)	volume $BnBu_3NCl$ solution added (mL)	volume $CHCl_3$ added (mL)
0.0	0	0.0	0.50	0.50
0.25	8×10^{-3}	31.2	0.50	0.47
0.50	1.6×10^{-2}	62.5	0.50	0.44
1.0	3.2×10^{-2}	125.0	0.50	0.38
1.5	4.8×10^{-2}	187.5	0.50	0.31
2.0	6.4×10^{-2}	250.0	0.50	0.25
3.0	9.6×10^{-2}	375.0	0.50	0.13
4.0	1.3×10^{-1}	500.0	0.50	0.0

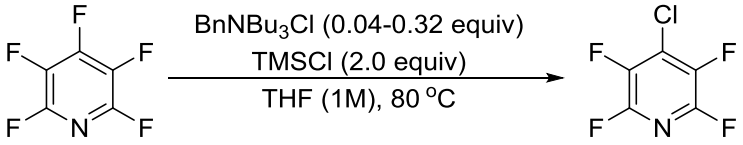
For referencing purposes a sealed glass capillary containing $CDCl_3$:trifluoroacetic acid (100:1 v/v) was placed in each NMR tube and ^{19}F NMR were obtained. Upfield shifts for all three fluorine atoms of pentafluoropyridine were observed. Chemical shift of the fluorine atom at -86 ppm was plotted as a function of the equivalents of $BnBu_3NCl$. The graphs indicate an upfield shift of the fluorine signal with increasing $BnNBu_3Cl$ concentration up to about 0.7 equiv. However, between 0.7-2.0 equivalents, the fluorine signals moved down-field. Finally, after 2.0 equivalents of

$BnNBu_3Cl$, the ^{19}F chemical shifts become constant as displays in the graph below. Initially, we thought the data point at 0.7 is an outlier. However, we performed another titration experiment to collect more data points in the region between 0.3-1.2 equiv of $BnBu_3NCl$ which clearly shows a maximum at around 0.8 equiv. Then the chemical shift started decrease with increasing $BnNBu_3Cl$. These results are consistent with initial formation of a 1:1 and then a 1:2 complex between the fluoroarene and the catalyst.



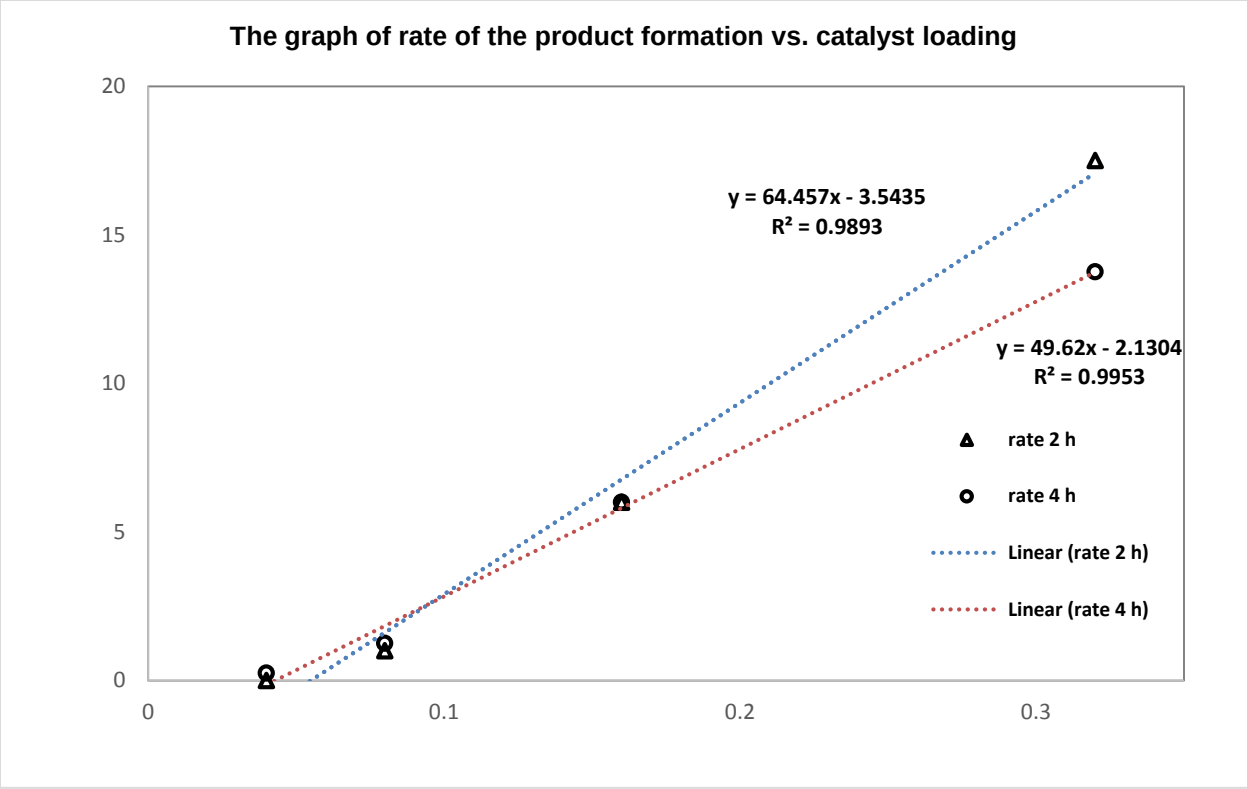


Kinetic study supporting the formation of a 2:1 complex between the catalyst and pentafluoropyridine



A kinetic study was done to determine the rate dependency on the catalyst. A sealable vial was charged with the fluoroarene (1.0 equiv), $BnNBu_3Cl$ (0.04 equiv), THF (1.0 M), TMSCl (2.0 equiv) and sealed. The reaction was stirred while heating at 80 °C in an oil bath. Aliquots were taken out after 2 h and 4 h and diluted with $CDCl_3$ to monitor the conversion by ^{19}F NMR. The reaction was repeated with 0.08, 0.16 and 0.32 equiv of $BnNBu_3Cl$. Then, initial rates were calculated. The rate of product formation was plotted against the catalyst loading and is shown below.

Catalyst loading	Conv % after 2 h	rate (2 h)	Conv % after 4 h	rate (4 h)
0.04	0	0	1	0.25
0.08	2	1	5	1.25
0.16	12	6	24	6
0.32	35	17.5	55	13.75



Initial rate = k [cat]^{a}

After 4 h,

With 0.04 equiv catalyst, rate = 0.25= k [0.04] ^{a}

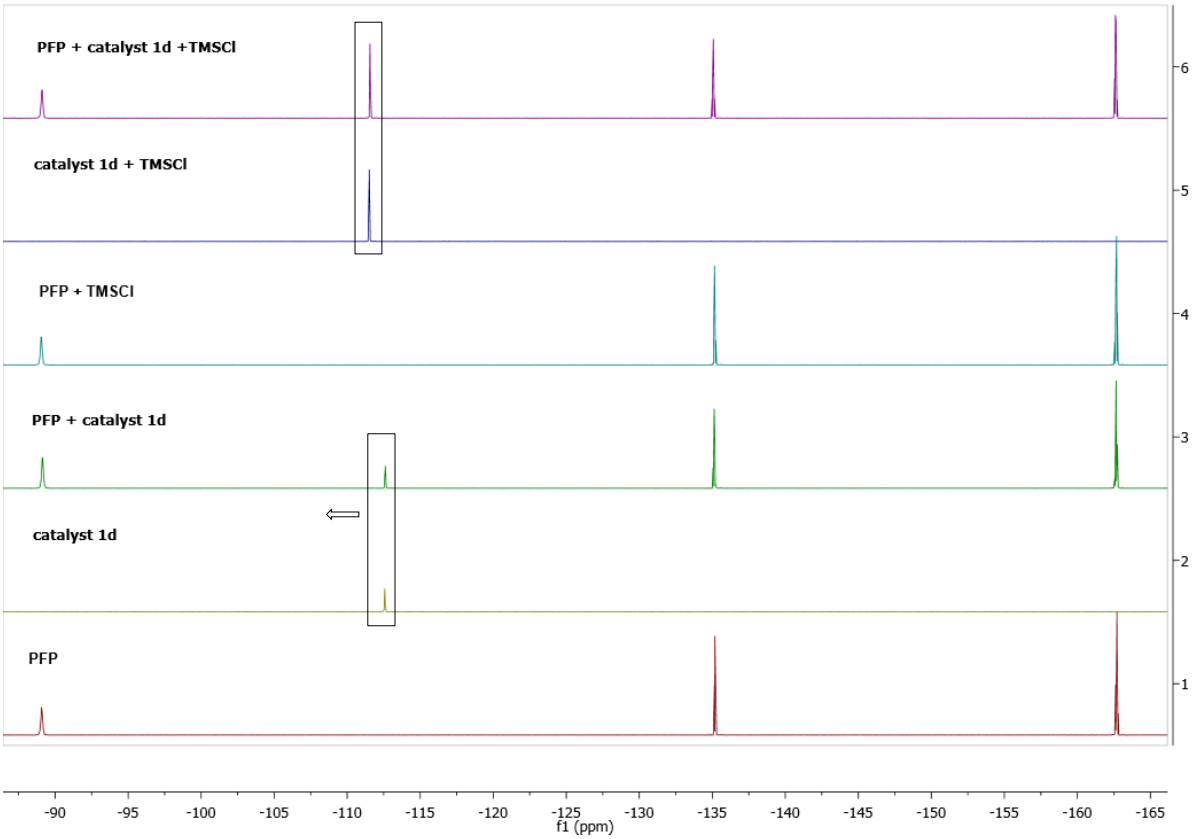
With 0.08 equiv catalyst, rate = 1.25= k [0.08] ^{a}

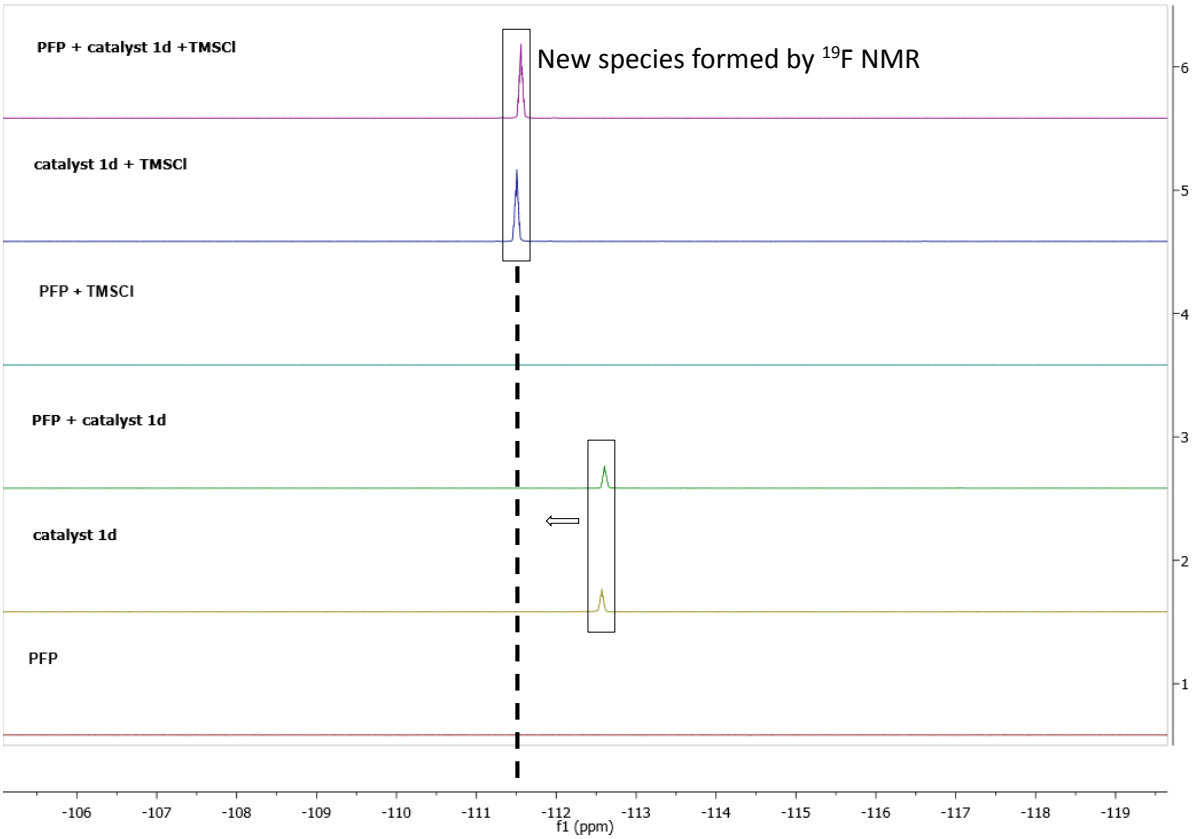
Order of the reaction with respect to the catalyst (a) = 2.3

Evidences for the formation of $Me_3SiCl_2^-$

^{19}F NMR evidence

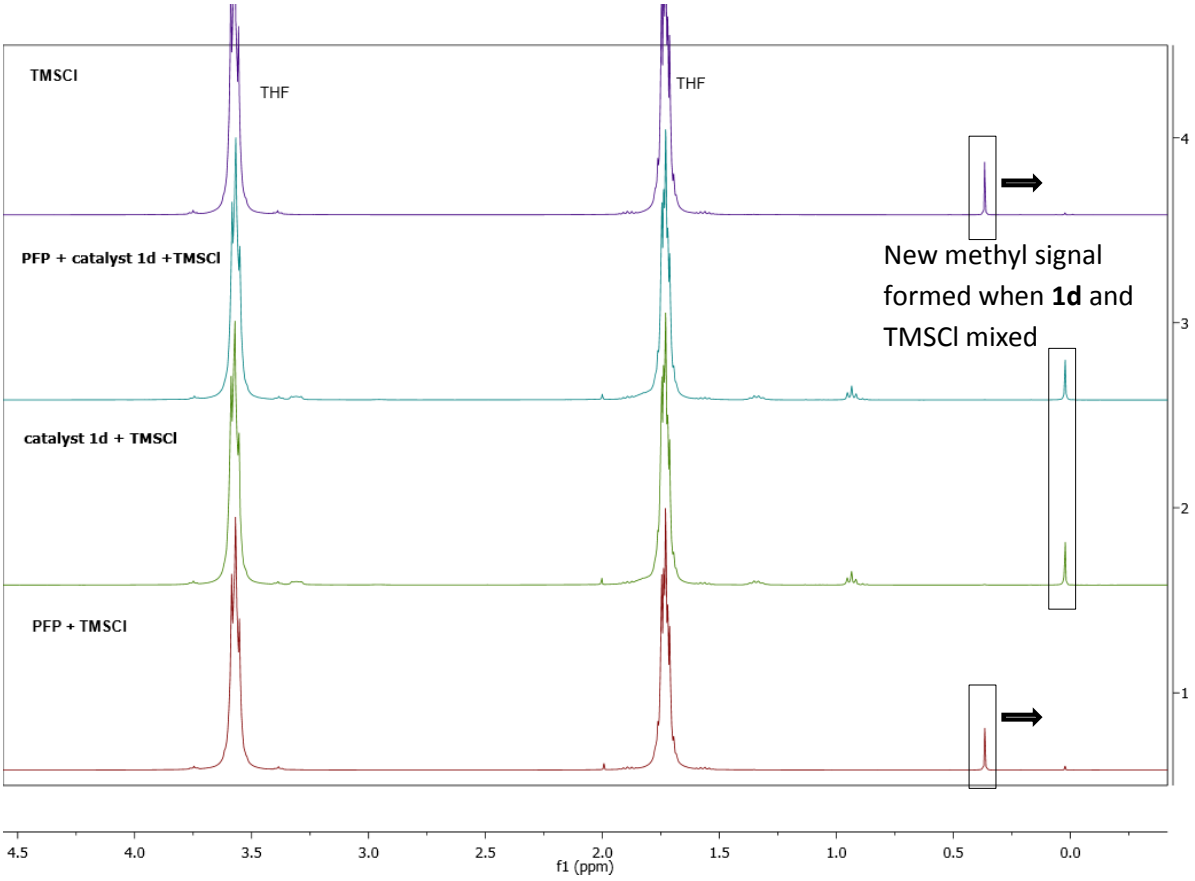
To see individual effects of each reagent in the halogenation reaction the following experiment was carried out. For ease of monitoring catalyst **1d** (4-F-BnNBu$_3$Cl) was chosen such that it could be observed by ^{19}F NMR. NMR spectra were recorded in THF with a sealed C_6D_6 capillary for locking purposes. First, individual ^{19}F NMR spectra of pentafluoropyridine (PFP) and **1d** were recorded (spectra 1 and 2) followed by 1:1 molar mixtures of PFP:**1d** (spectrum 3), PFP:TMSCl (spectrum 4), **1d**:TMSCl (spectrum 5), and a 1:1:1 molar mixture of PFP:**1d**:TMSCl (spectrum 6). The most significant change was observed when catalyst 1d and TMSCl were mixed (compare spectra 2 vs 5 and 6). This suggests a quantitative formation of a new species between catalyst (**1d**) and TMSCl.


PFP + catalyst 1d +TMSCl
catalyst 1d + TMSCl
PFP + TMSCl
PFP + catalyst 1d
catalyst 1d
PFP
6
5
4
3
2
1
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
f1 (ppm)



When comparing ^{1}H NMR of above samples, a similar trend was observed. The samples containing catalyst **1d** and TMSCl lead to quantitative formation of a new species which is in agreement with ^{19}F data obtained.

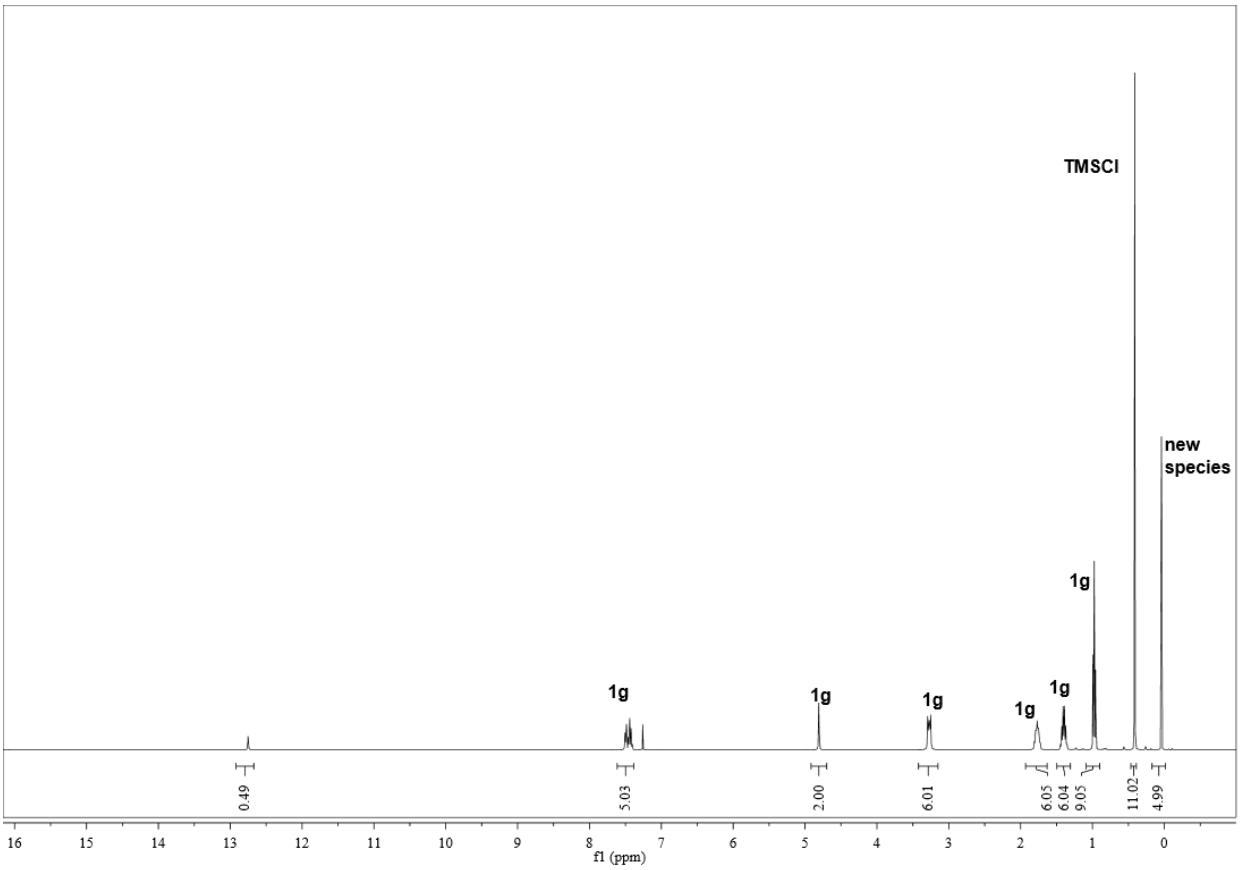
^{1}H NMR evidences



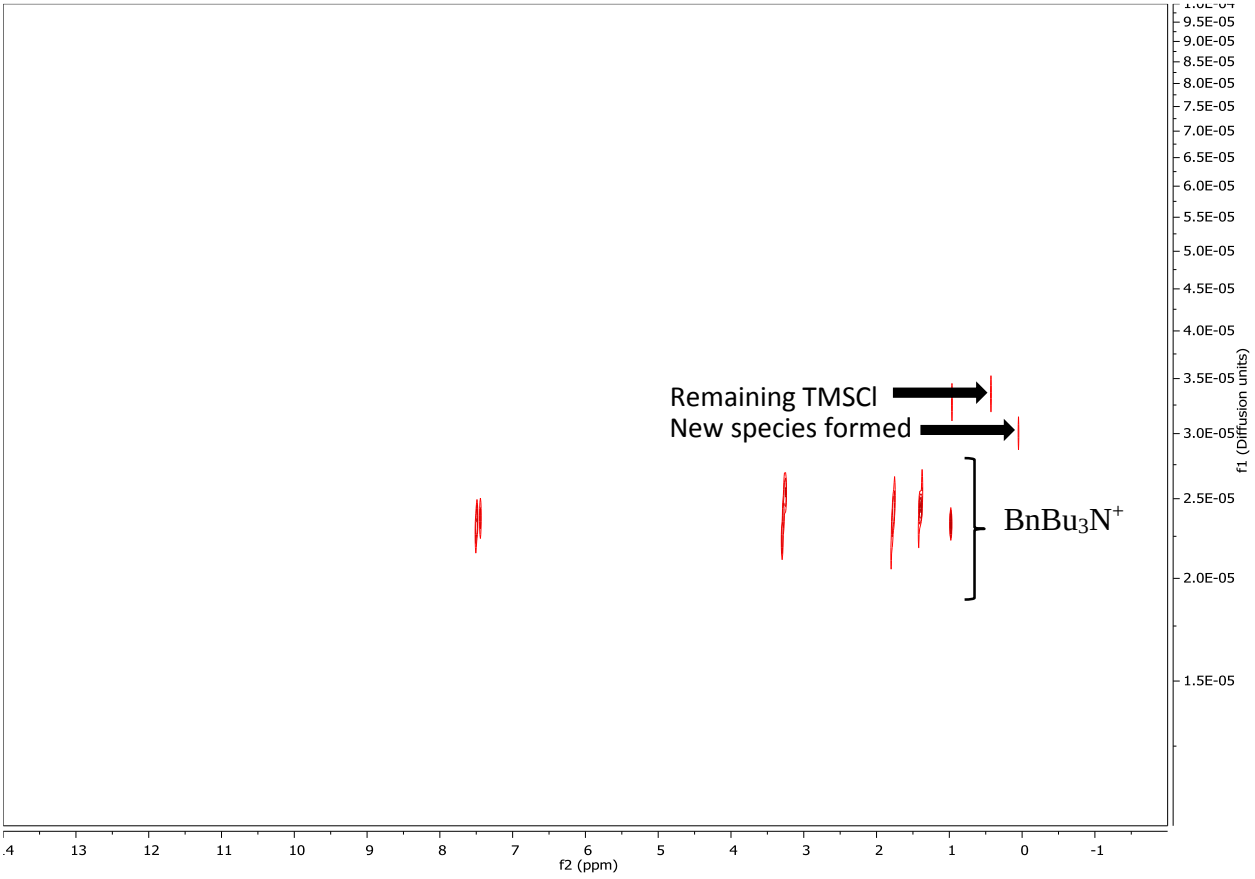
^{1}H DOSY-NMR spectrum

In order to determine the structure of the new species formed we carried out a ^{1}H-DOSY experiment and the molecular mass was obtained by HRMS. For DOSY experiment a NMR sample was prepared by mixing catalyst **1g** (0.025 mmol, 7.79 mg, 1.0 equiv) and TMSCl (0.05 mmol, 6.34 µL, 2.0 equiv) in $CDCl_3$ (0.4 mL). Molecular weight of new species was calculated after plotting ^{1}H-DOSY data.

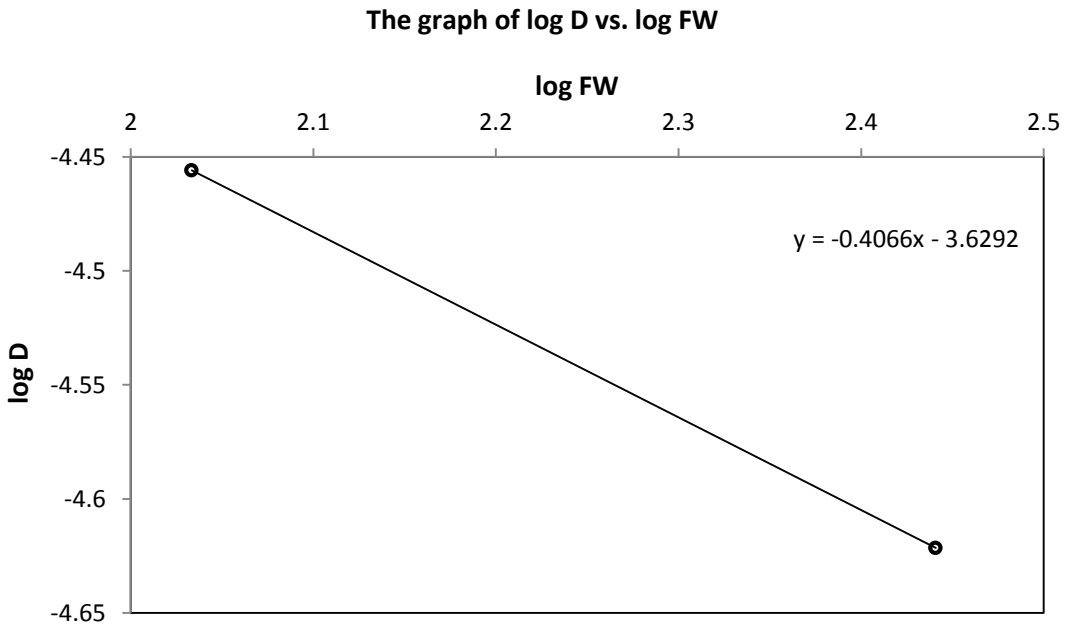
^{1}H NMR after mixing **1g** and TMSCl



^{1}H-DOSY NMR after mixing **1g** and TMSCl



Calculation of unknown formula weight based on diffusion coefficient



y = -0.4066x - 3.6292

D of new species = 3.196 x 10^{-5}, log D = -4.495, substituting this for y value in above equation

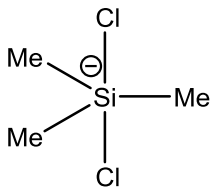
-4.495 = -0.4066x - 3.6292

x = (-4.495+3.6292)/ (-0.4066) = 135

observed molecular weight = 135

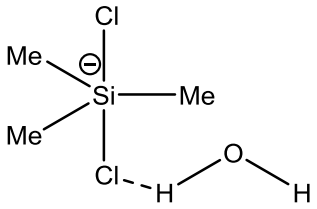
calculated molecular weight for $C_3H_9Cl_2Si^-$ = 144

error% = ((144-135)/144



HRMS evidences

HRMS (ESI) of the above mixture (catalyst **1g** (0.025 mmol, 7.79 mg, 1.0 equiv) and TMSCl (0.05 mmol, 6.34 μL, 2.0 equiv)) after being diluted with a matrix of acetone:MeCN (3:2 v/v) shows signals at 160.8419 and 162.8387 and is consistent with a dichlorosilicate.

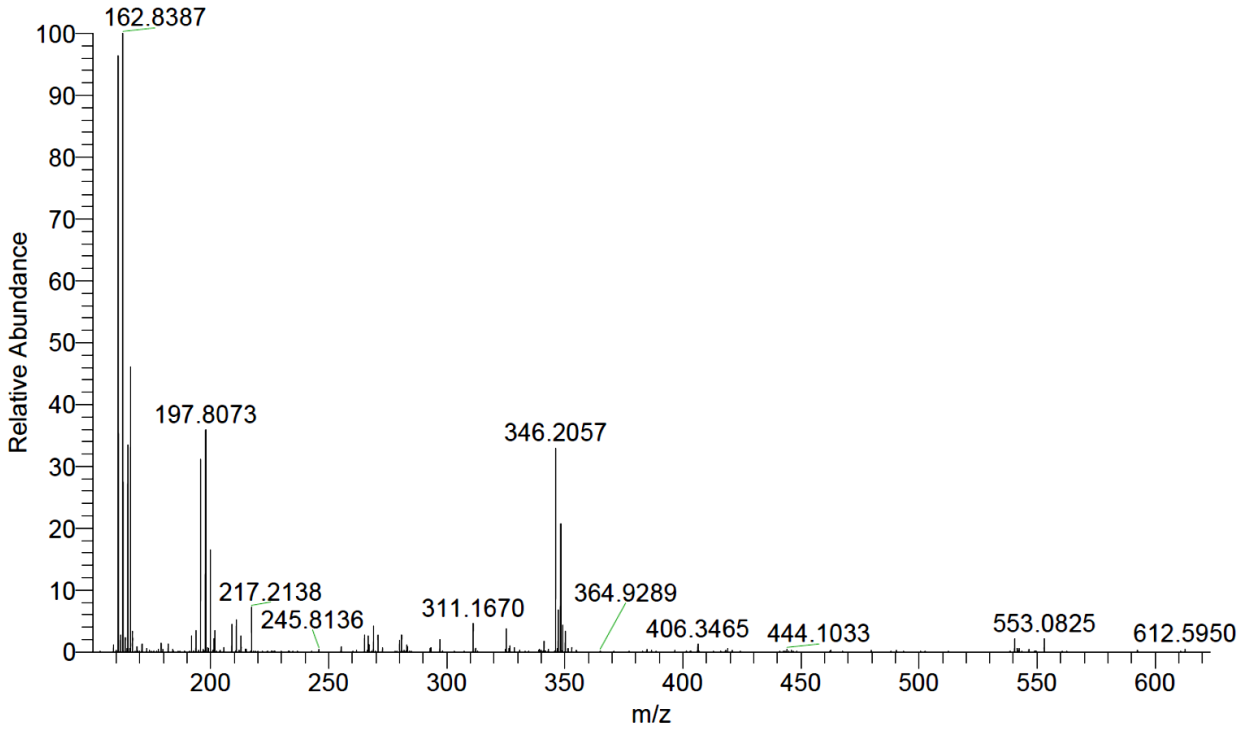


Chemical Formula:

$C_3H_{11}Cl_2OSi^-$

Exact Mass: 161

Molecular Weight: 162



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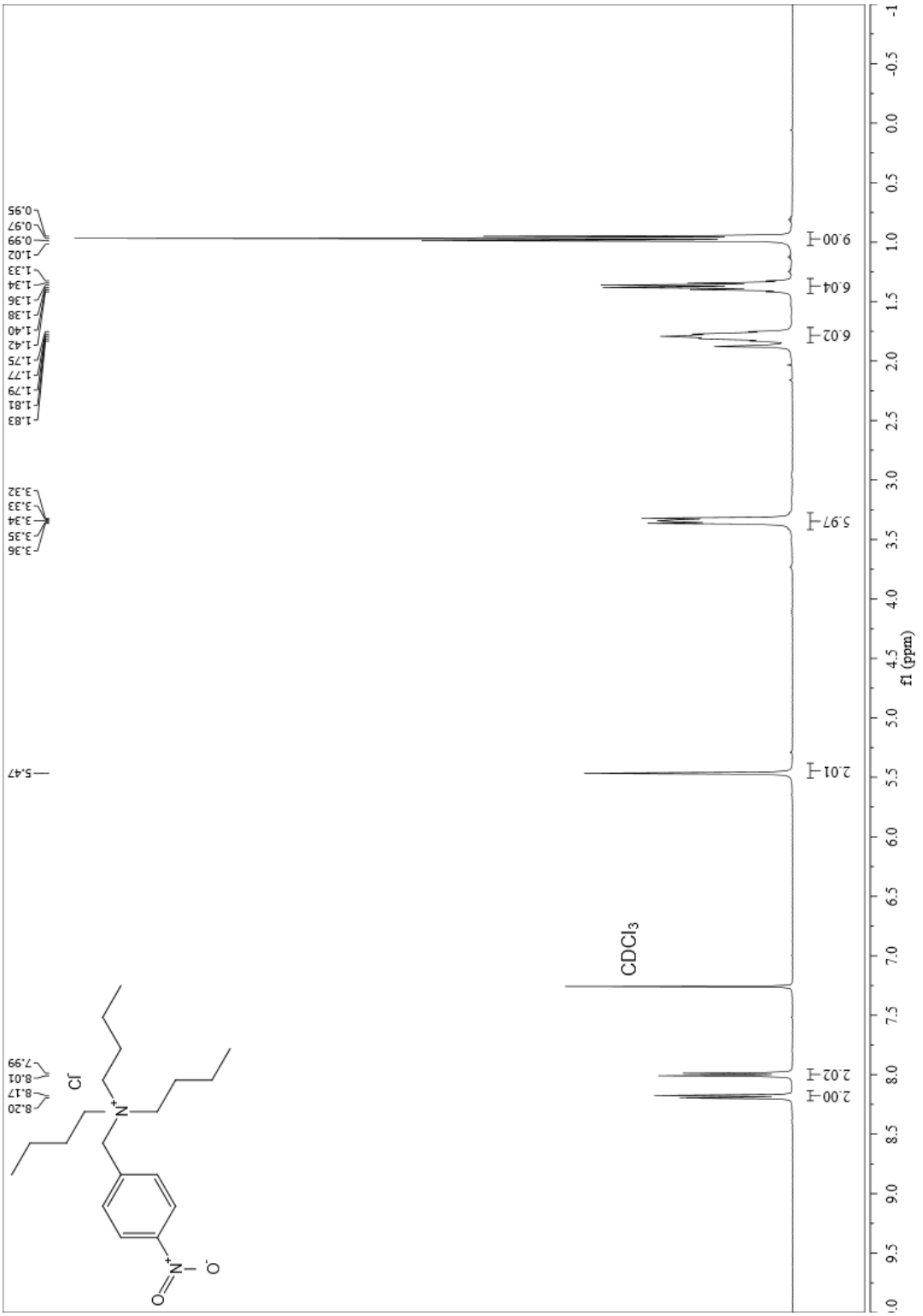
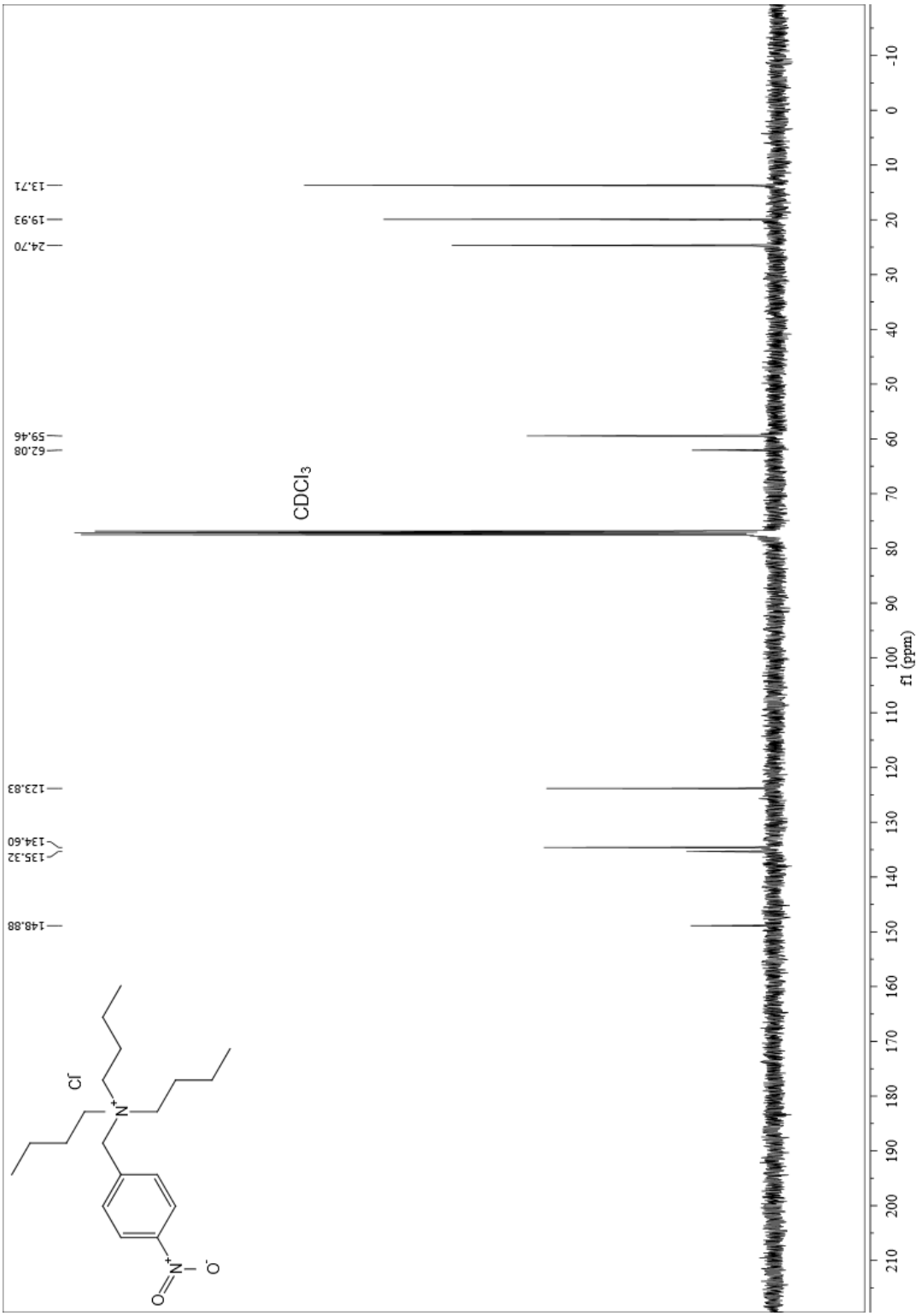
.

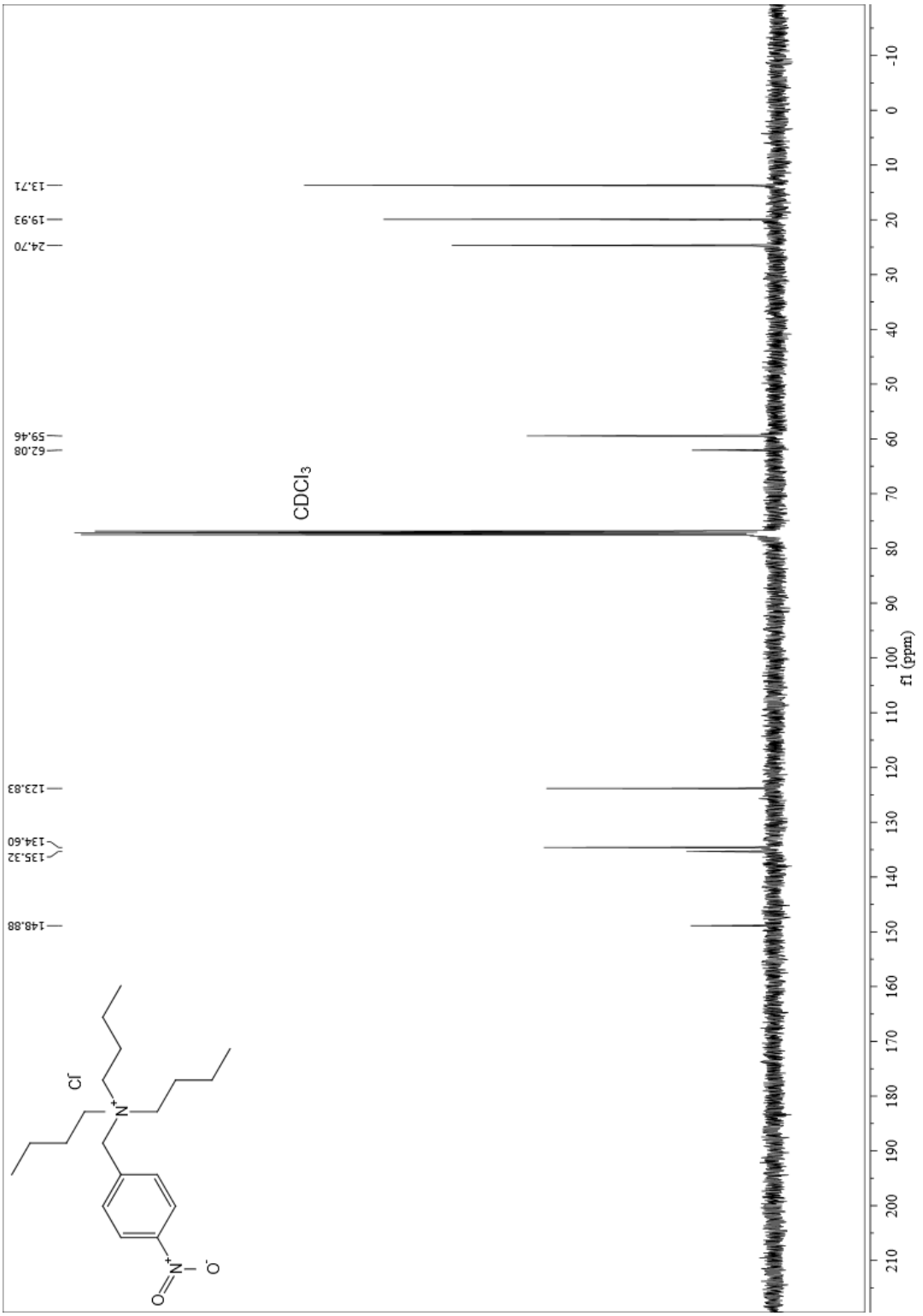
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-nitrobenzyl)butan-1-aminium chloride (1a)



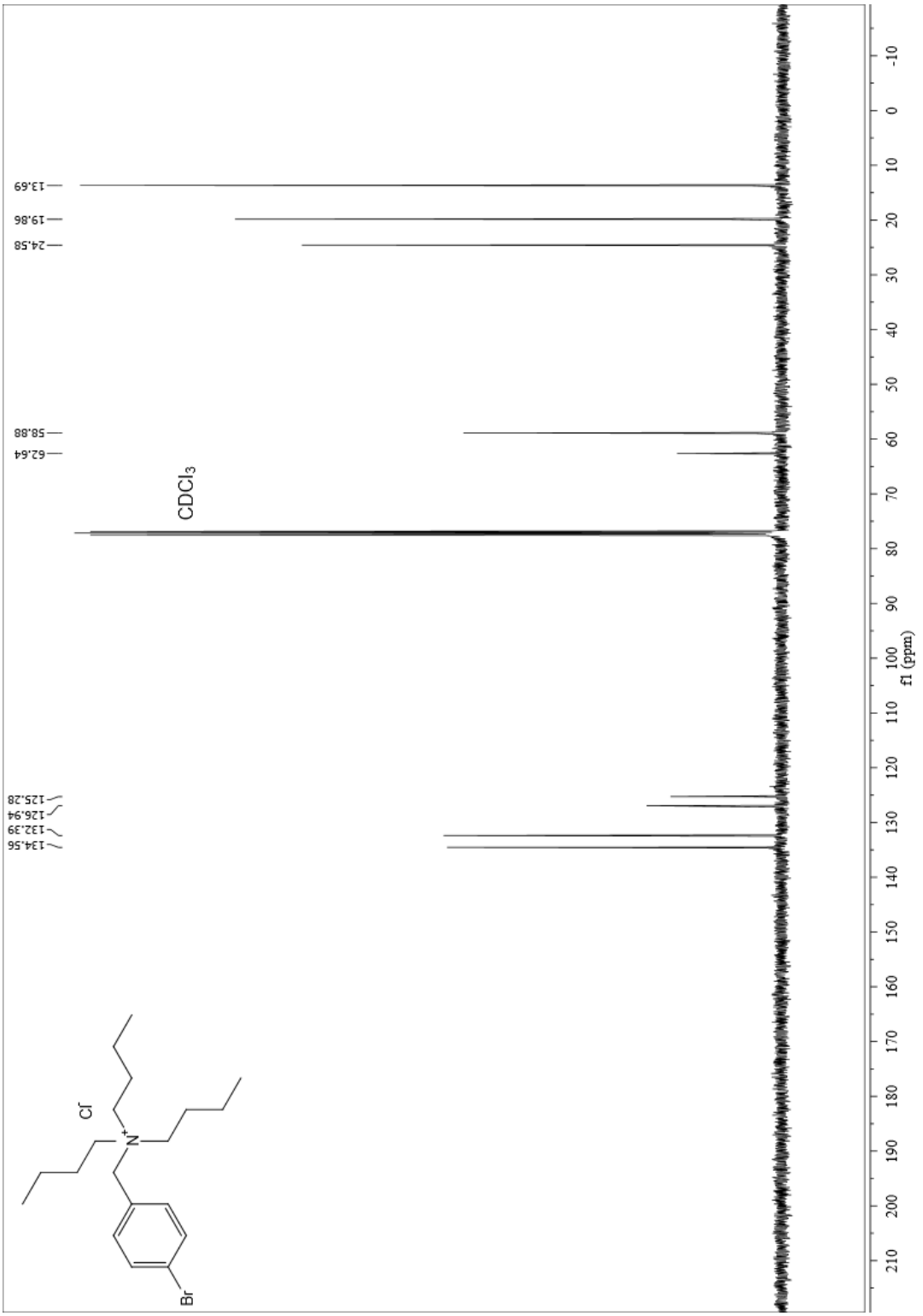
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-nitrobenzyl)butan-1-aminium chloride (1a)



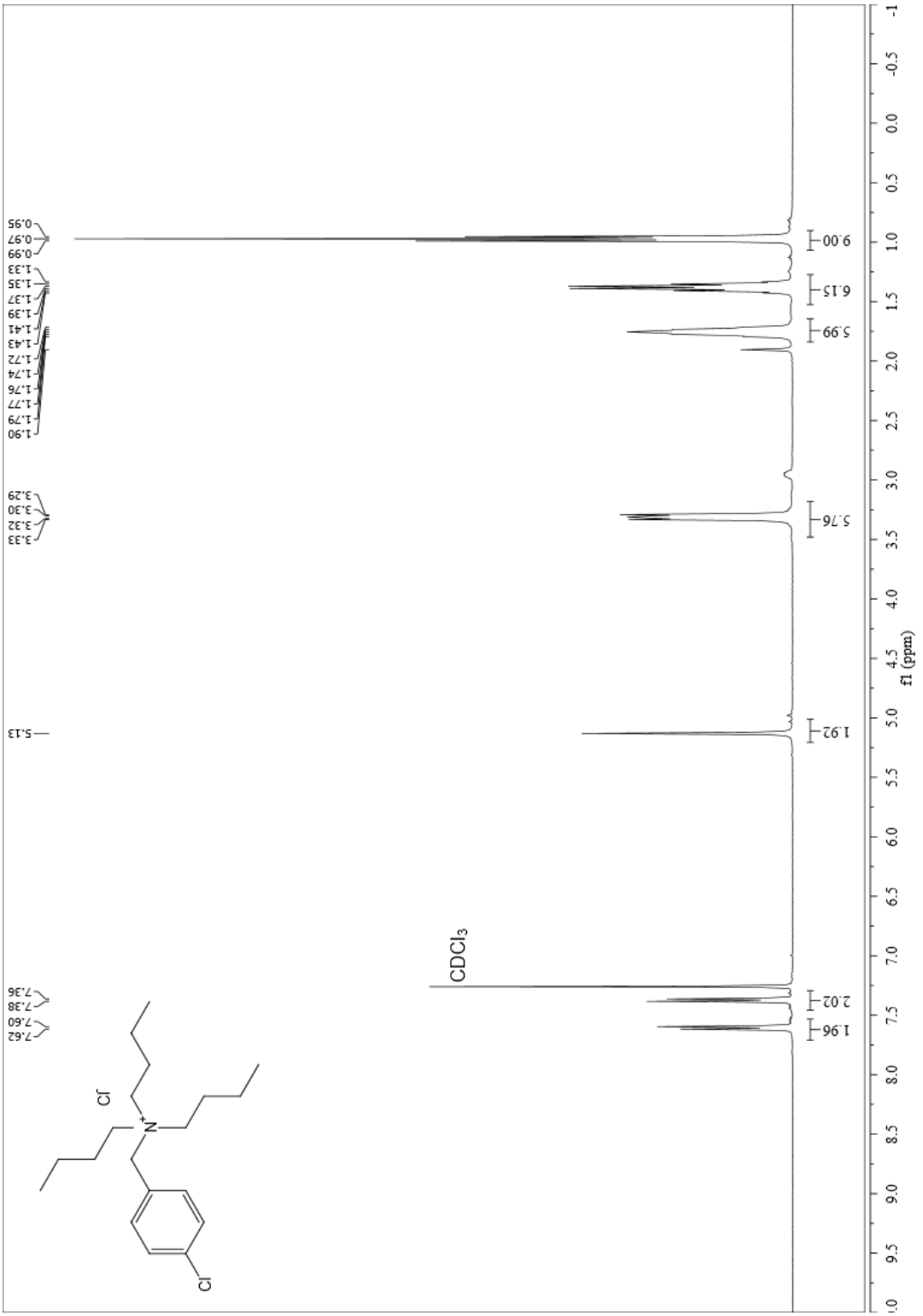
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*-(4-bromobenzyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1b)



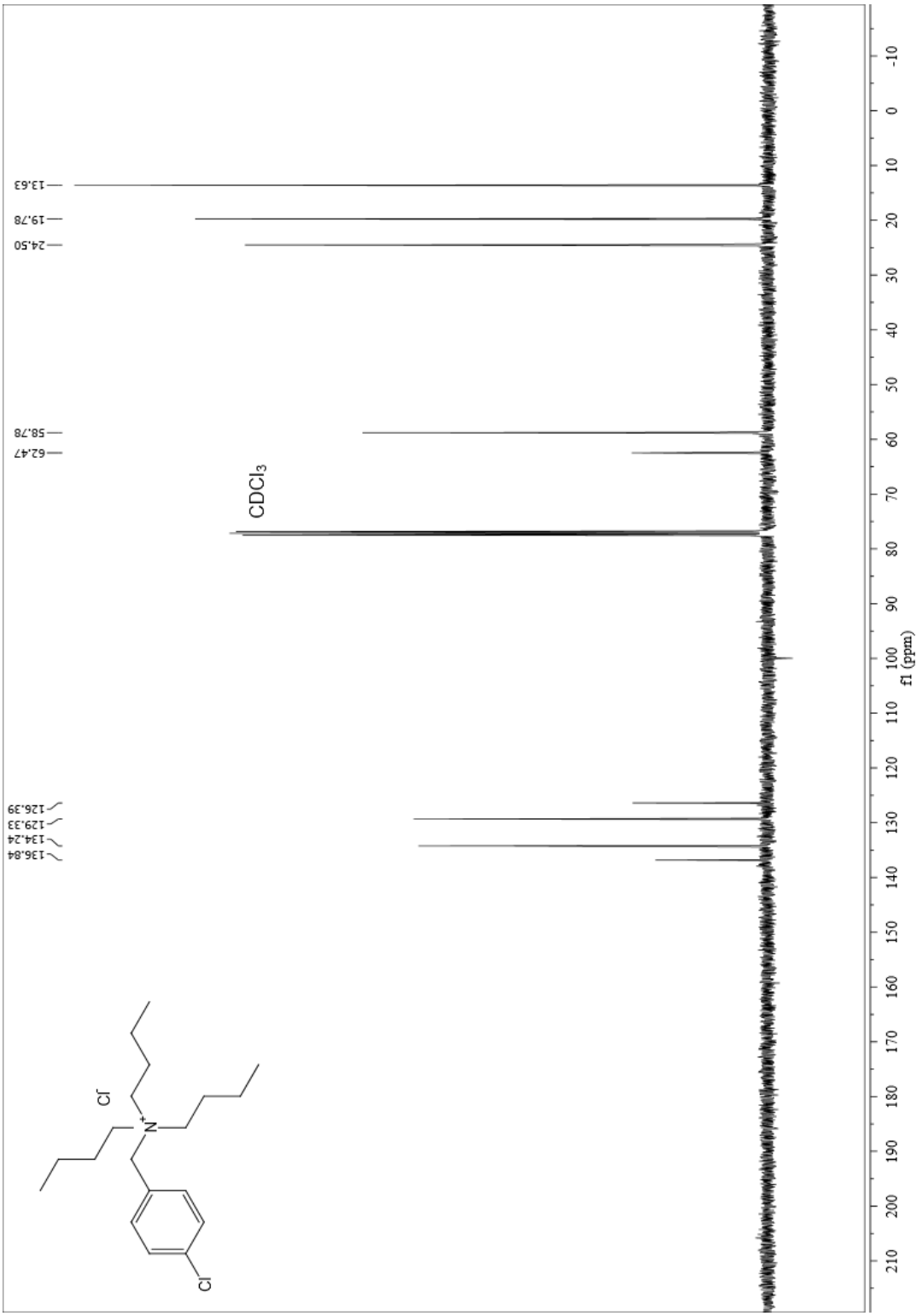
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*-(4-bromobenzyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1b)



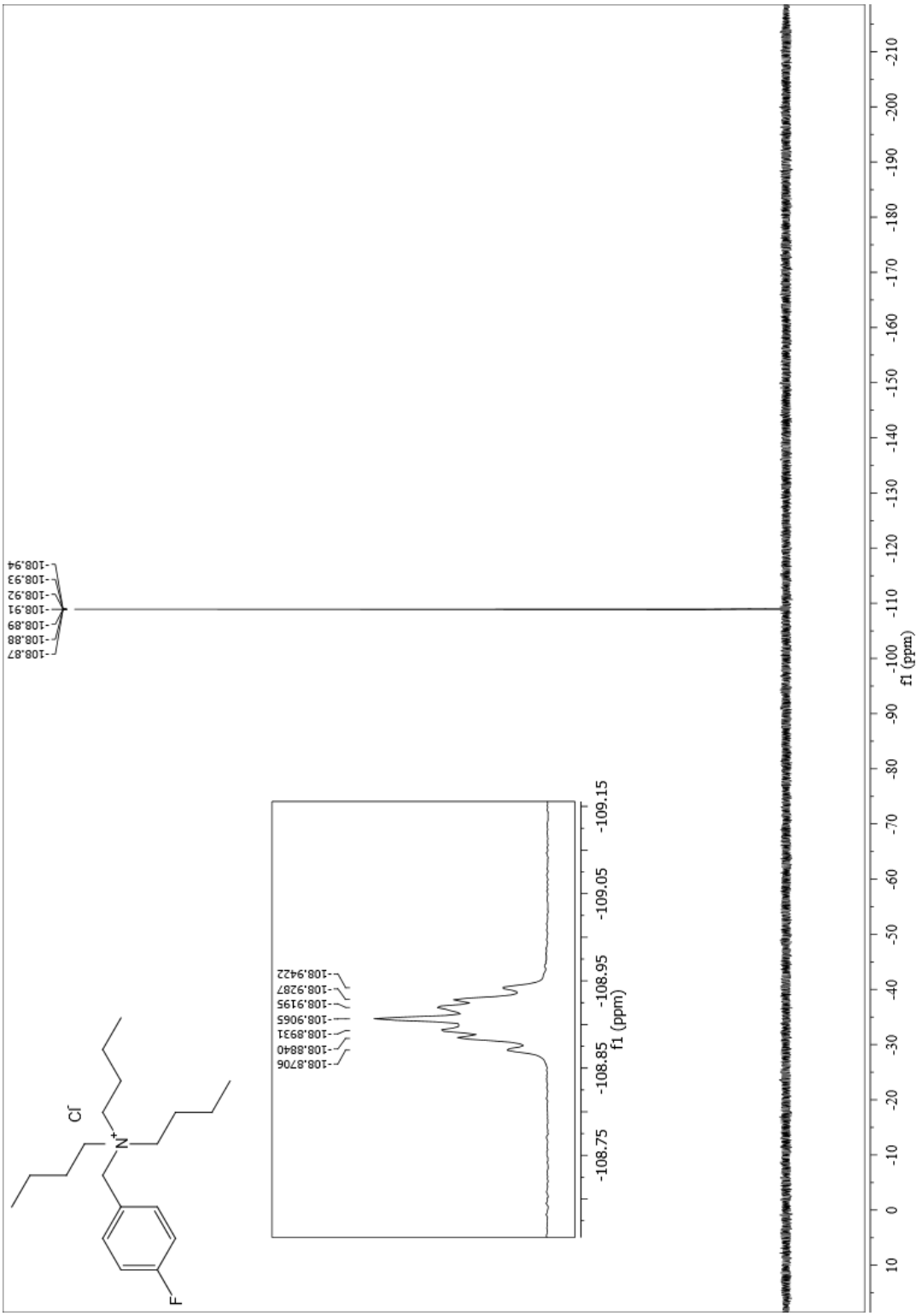
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-chlorobenzyl)butan-1-aminium chloride (1c)



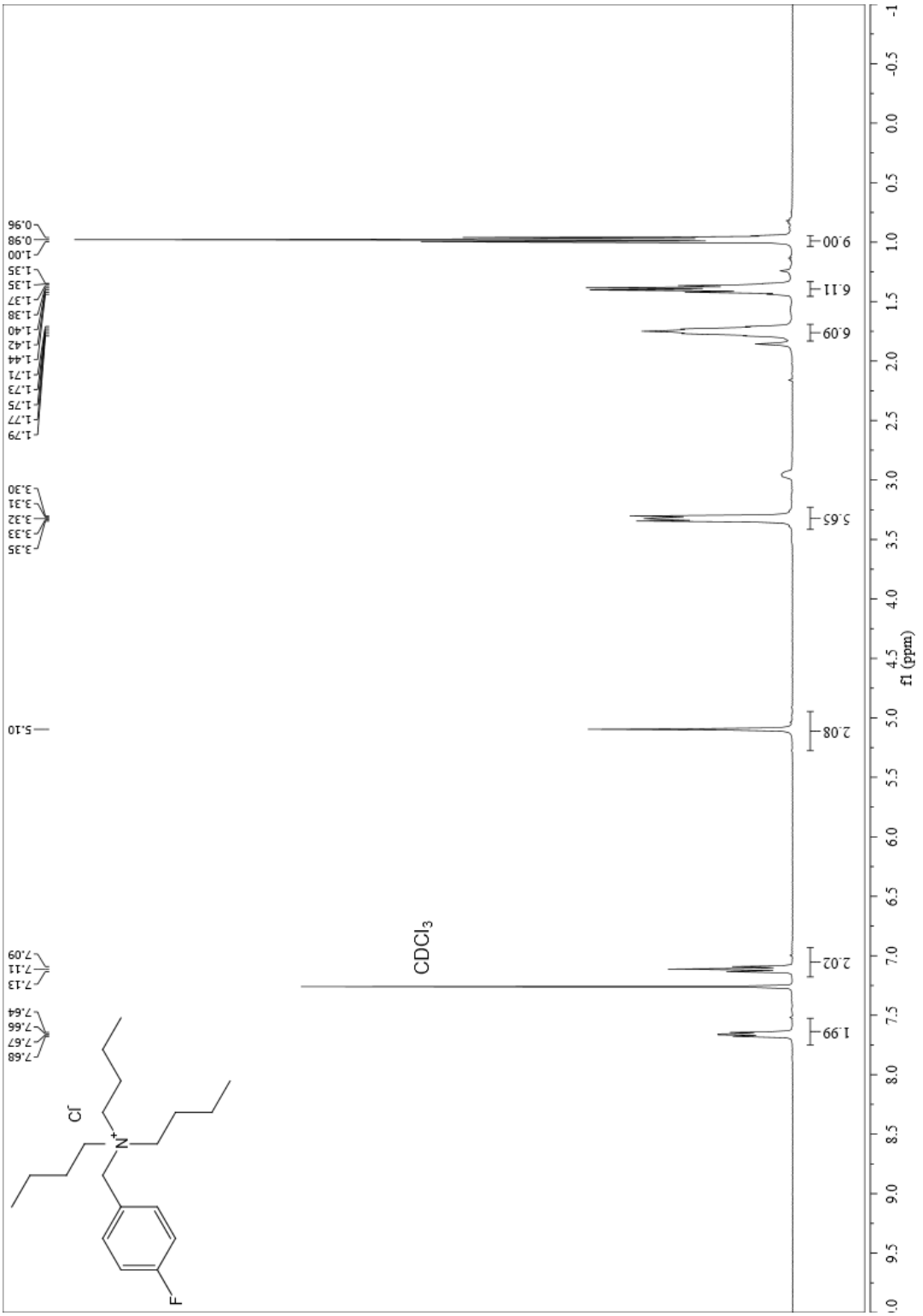
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-chlorobenzyl)butan-1-aminium chloride (1c)



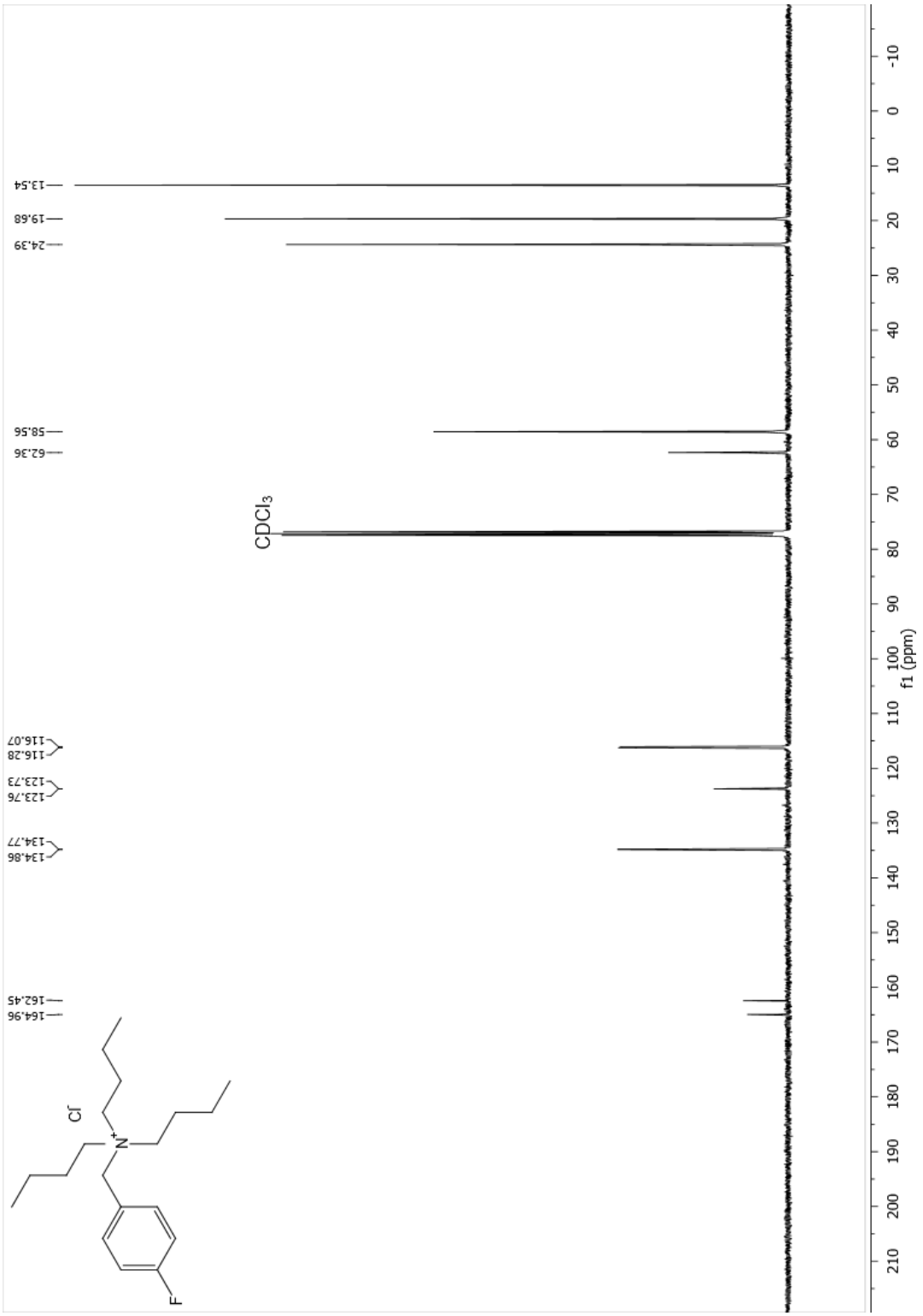
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-fluorobenzyl)butan-1-aminium chloride (1d)



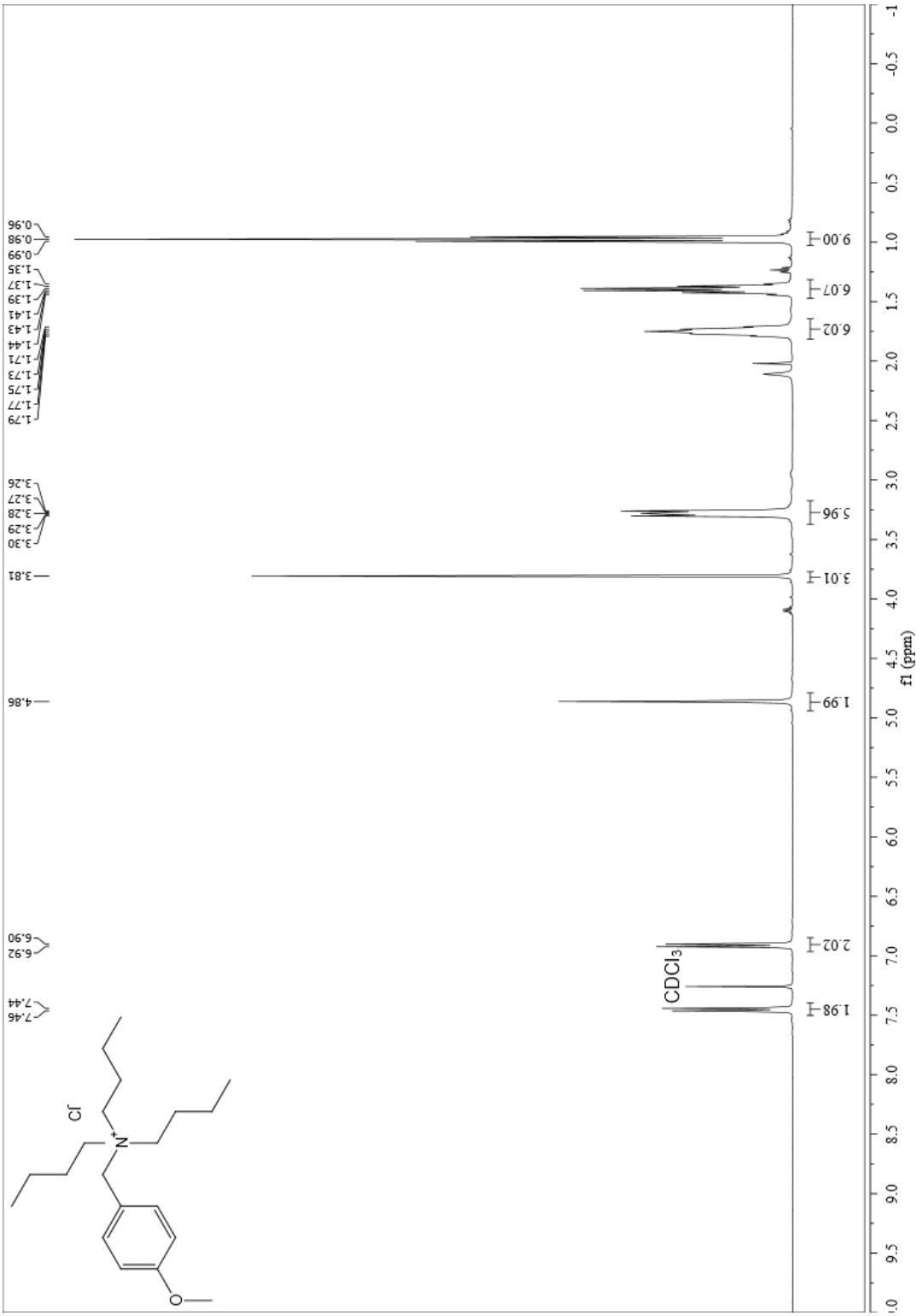
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-fluorobenzyl)butan-1-aminium chloride (1d)



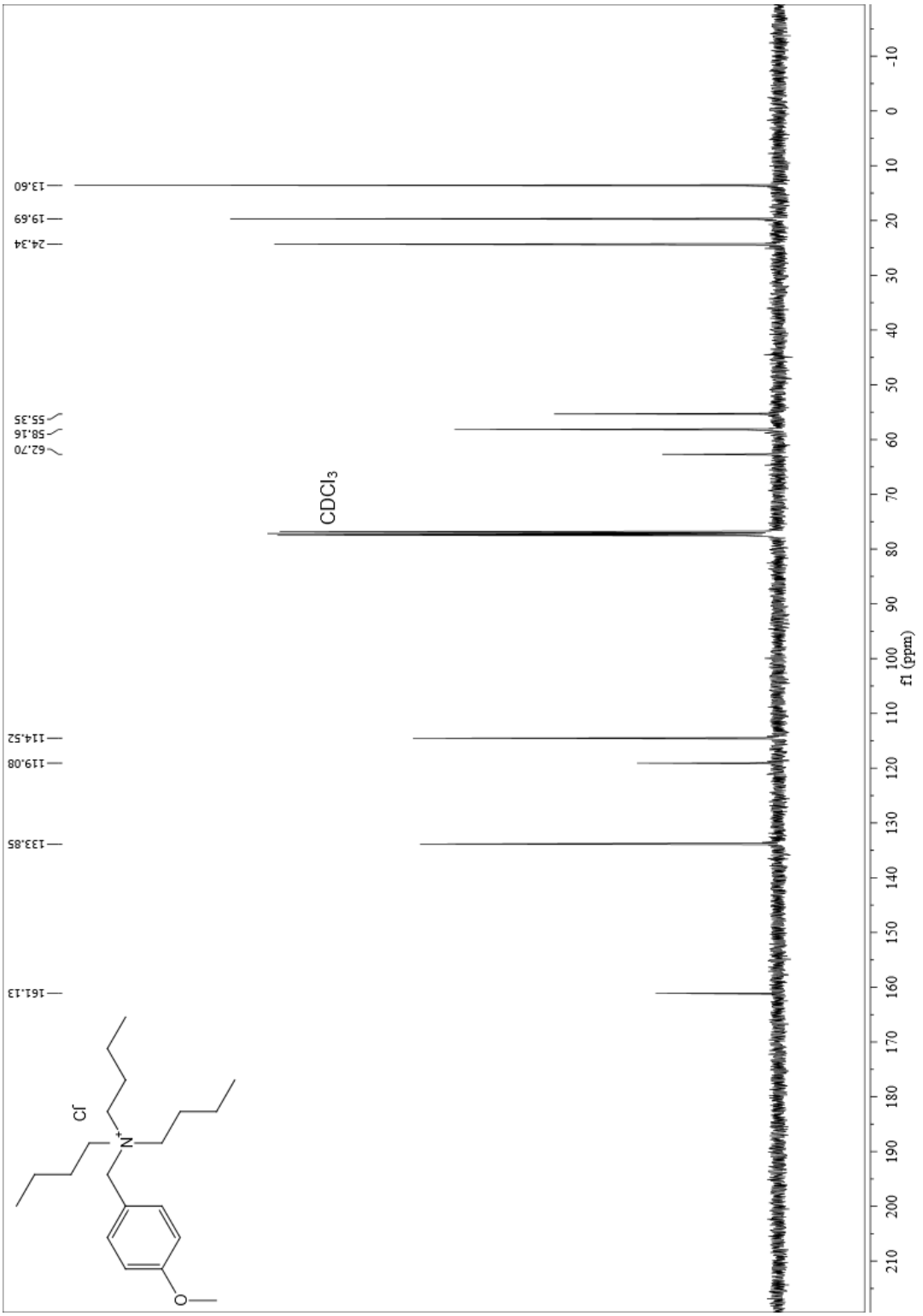
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-fluorobenzyl)butan-1-aminium chloride (1d)



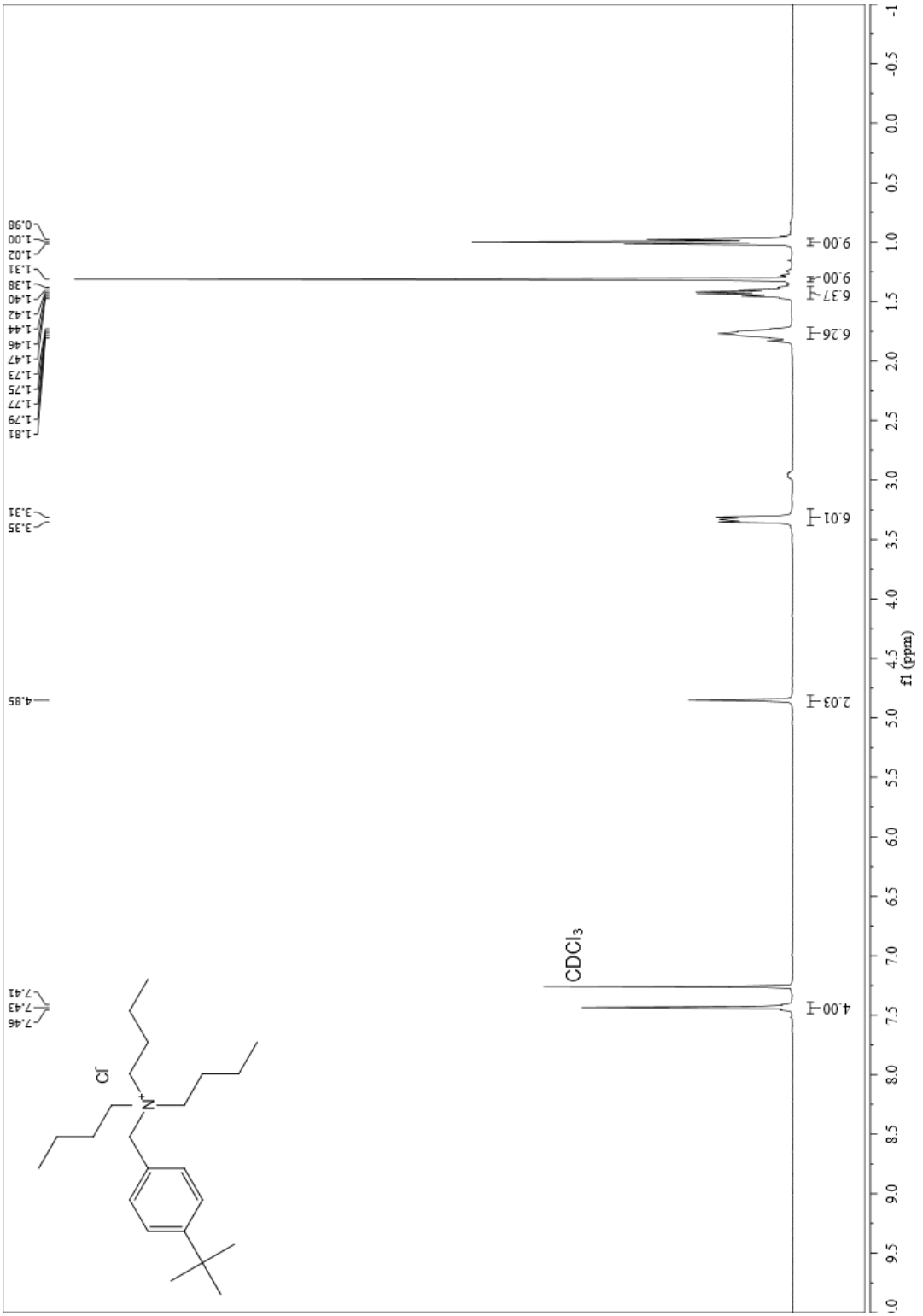
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-methoxybenzyl)butan-1-aminium chloride (1e)



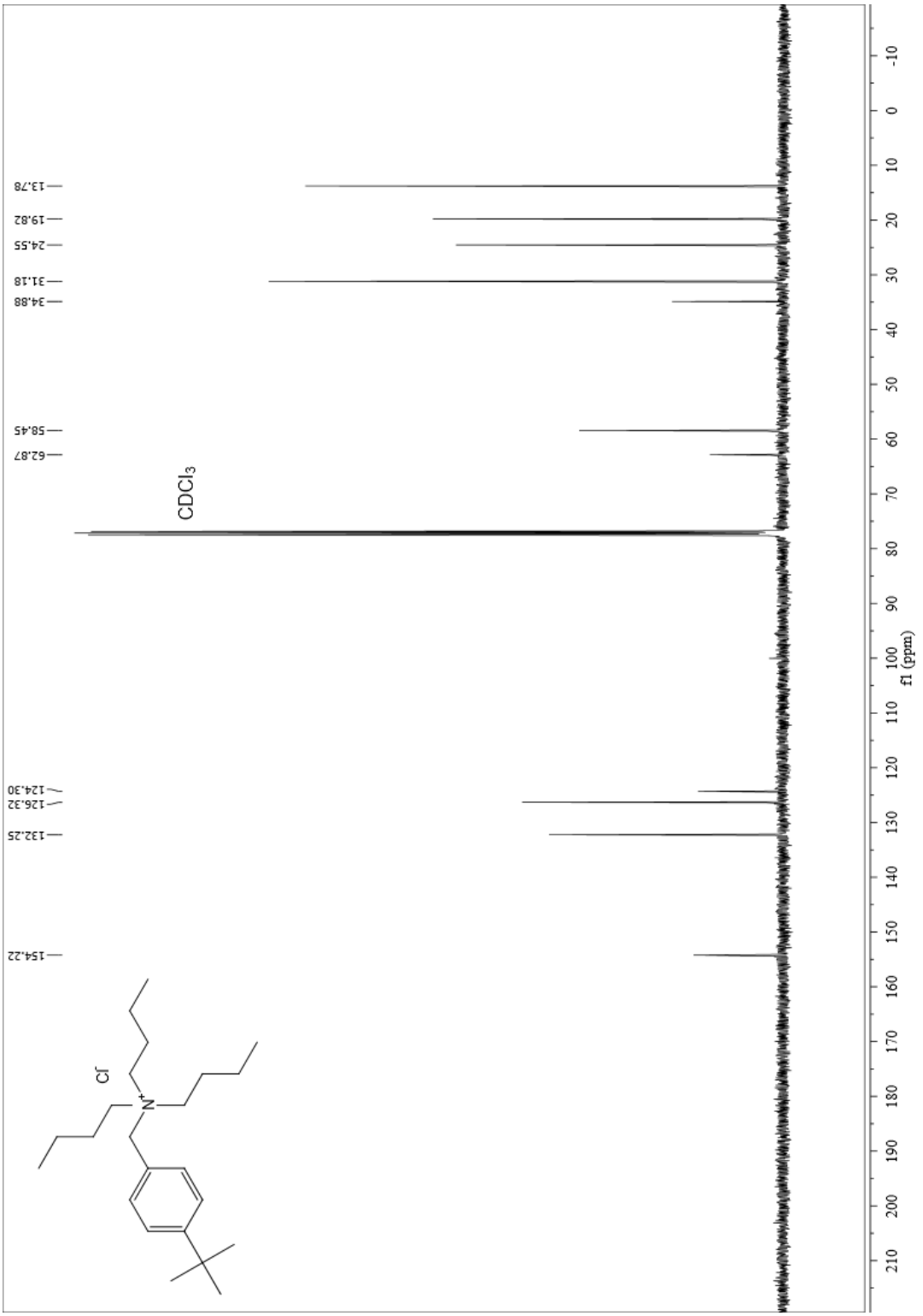
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-methoxybenzyl)butan-1-aminium chloride (1e)



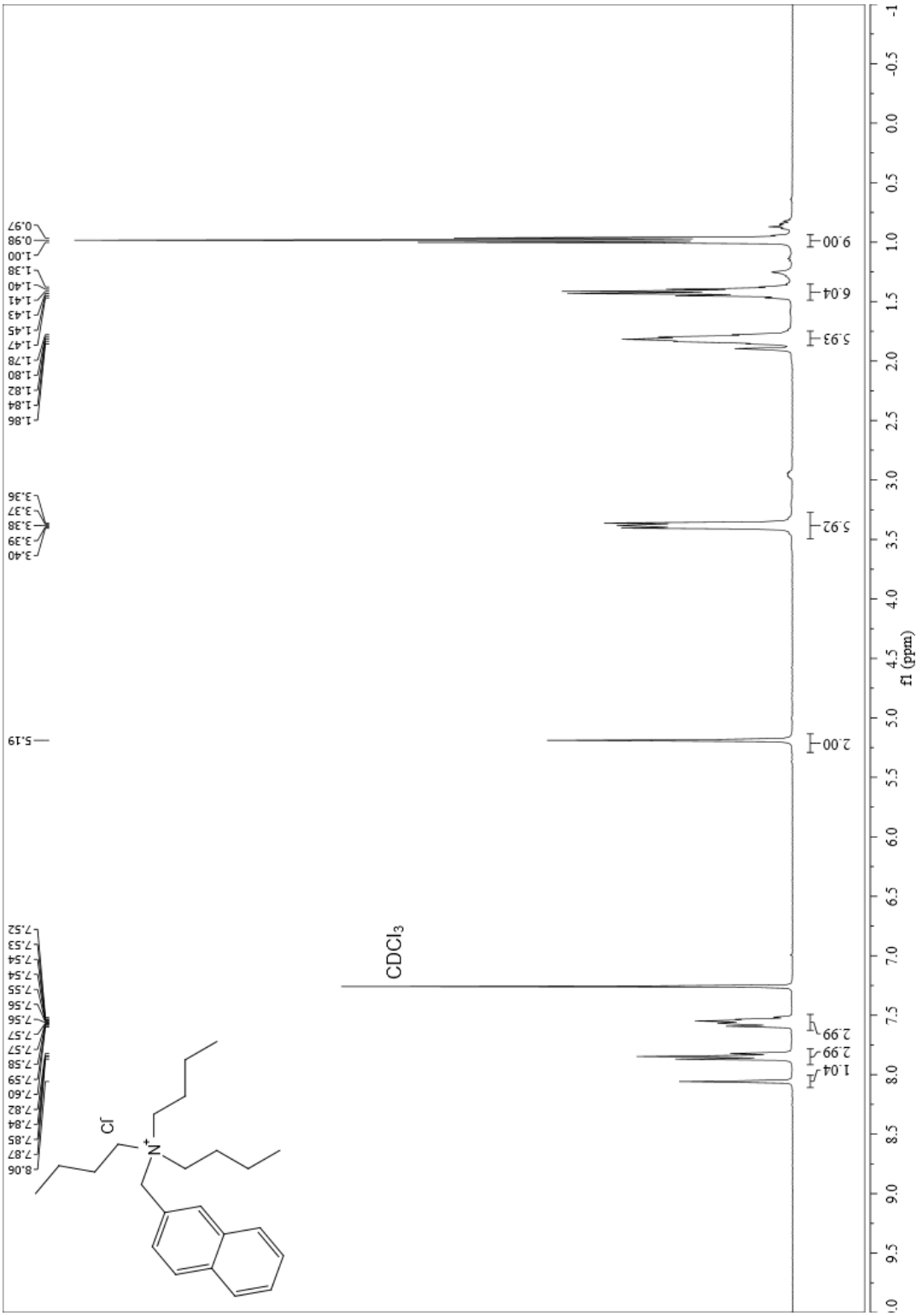
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-(tert-butyl)benzyl)butan-1-aminium chloride (1f)



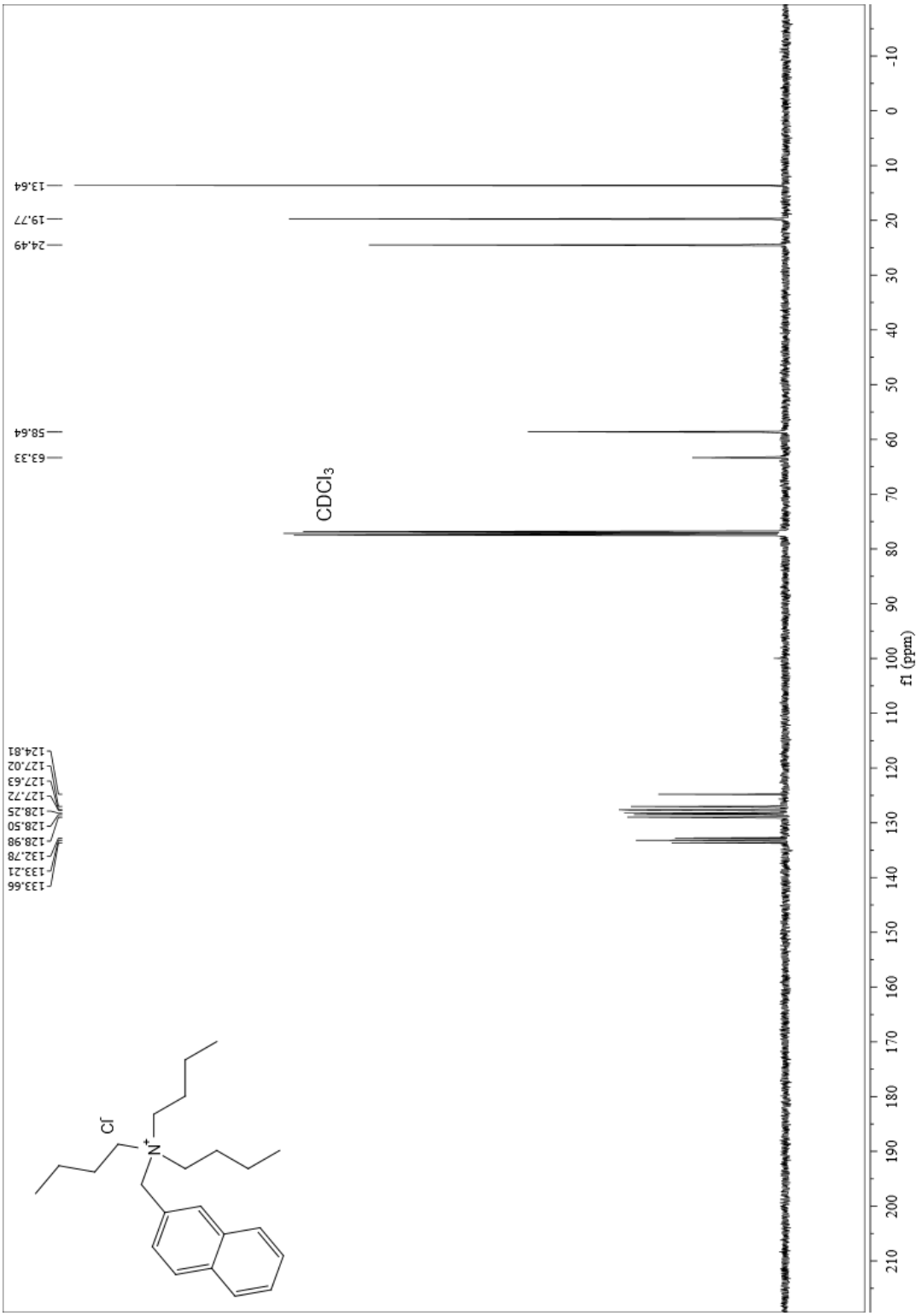
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(4-(tert-butyl)benzyl)butan-1-aminium chloride (1f)



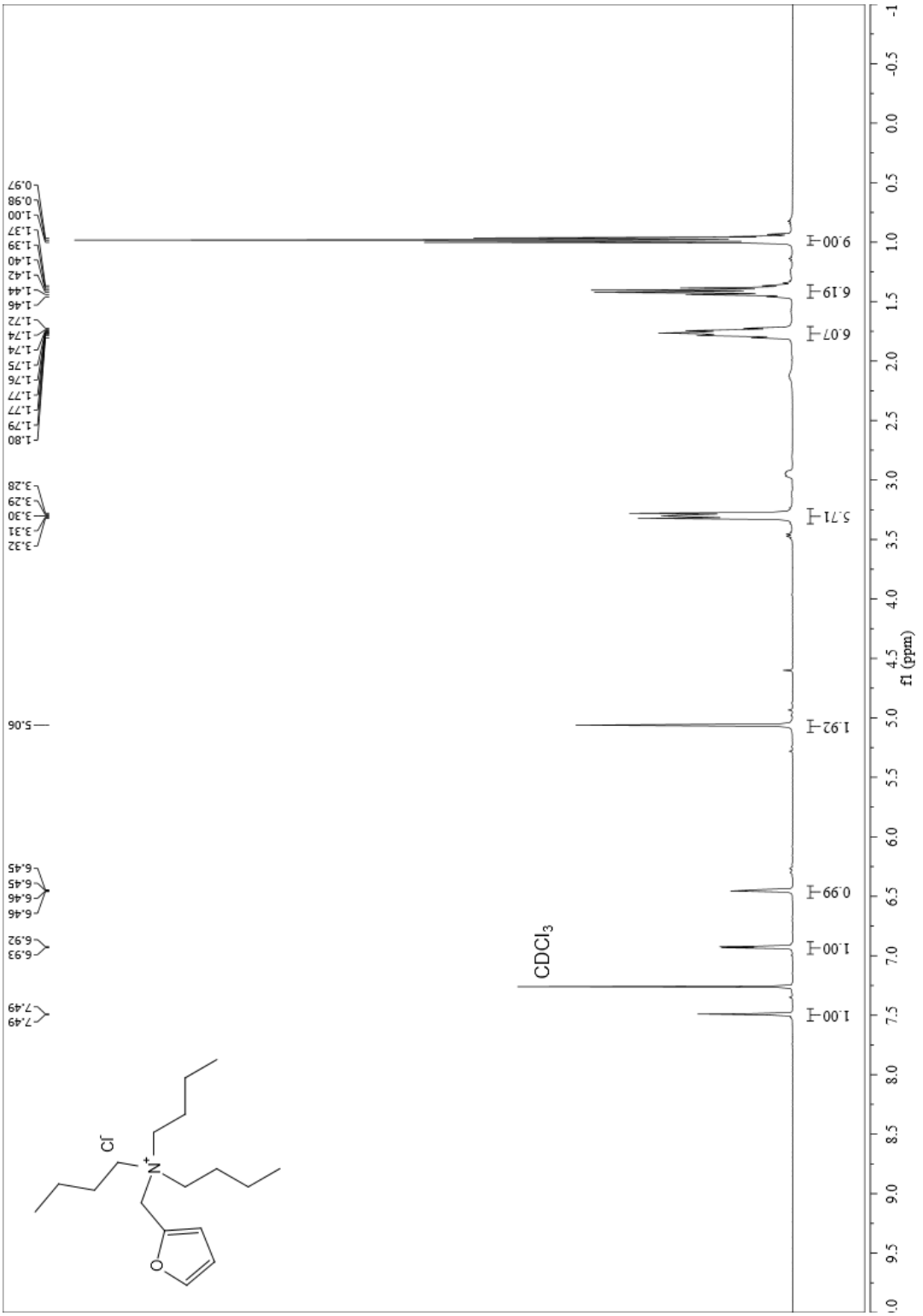
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(naphthalen-2-ylmethyl)butan-1-aminium chloride (1h)



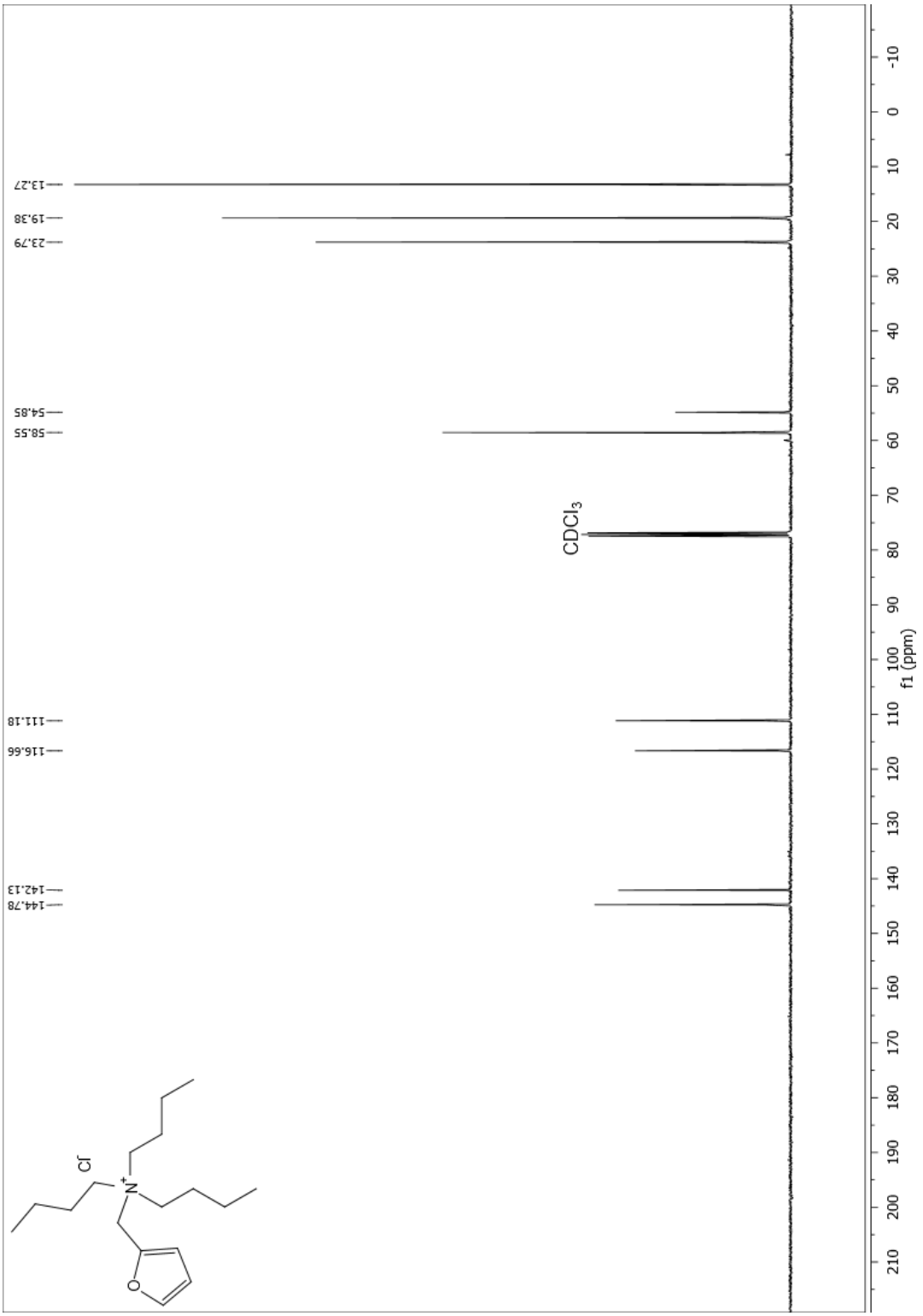
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(naphthalen-2-ylmethyl)butan-1-aminium chloride (1h)



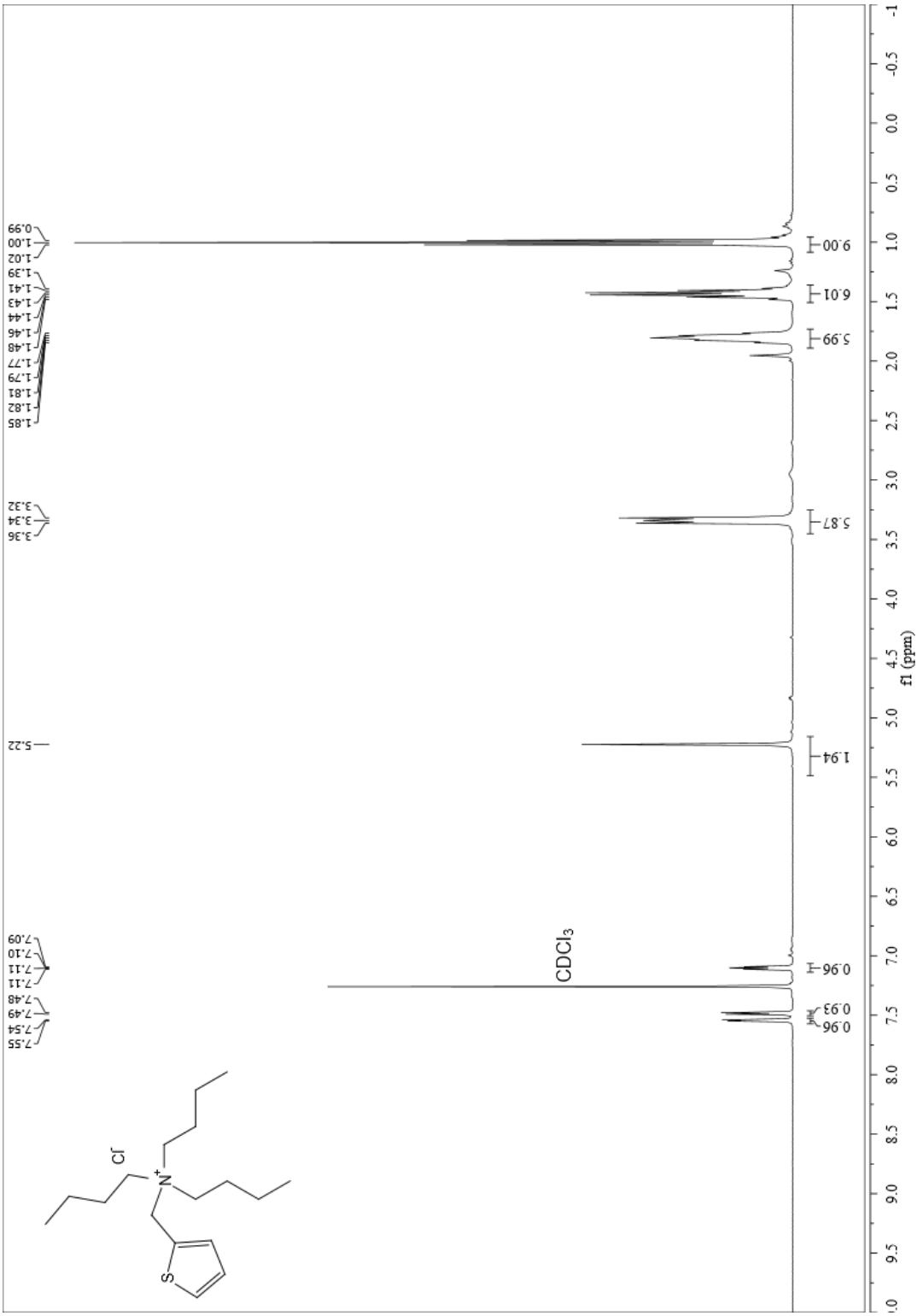
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(furan-2-ylmethyl)butan-1-aminium chloride (1i)



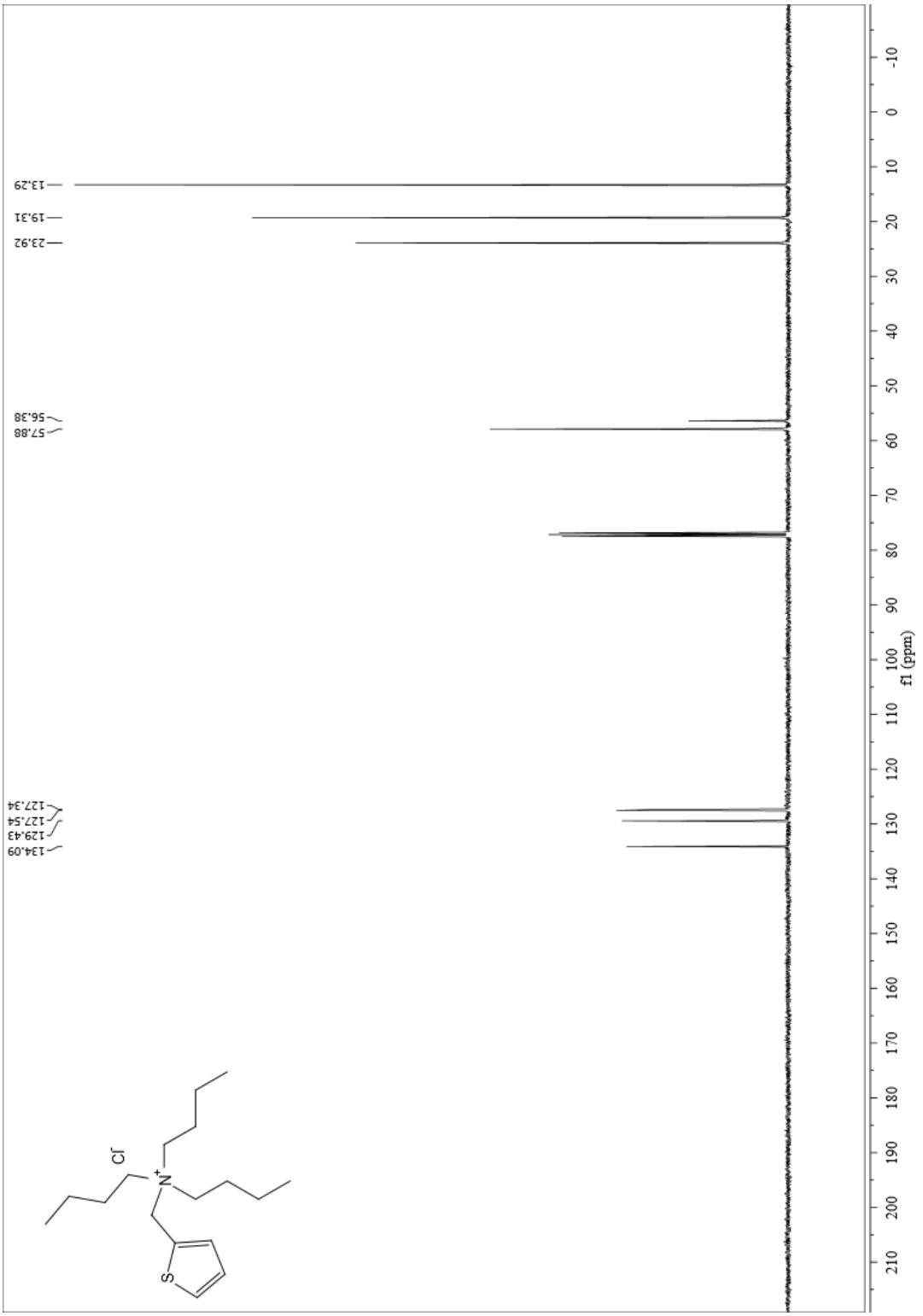
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(furan-2-ylmethyl)butan-1-aminium chloride (1i)



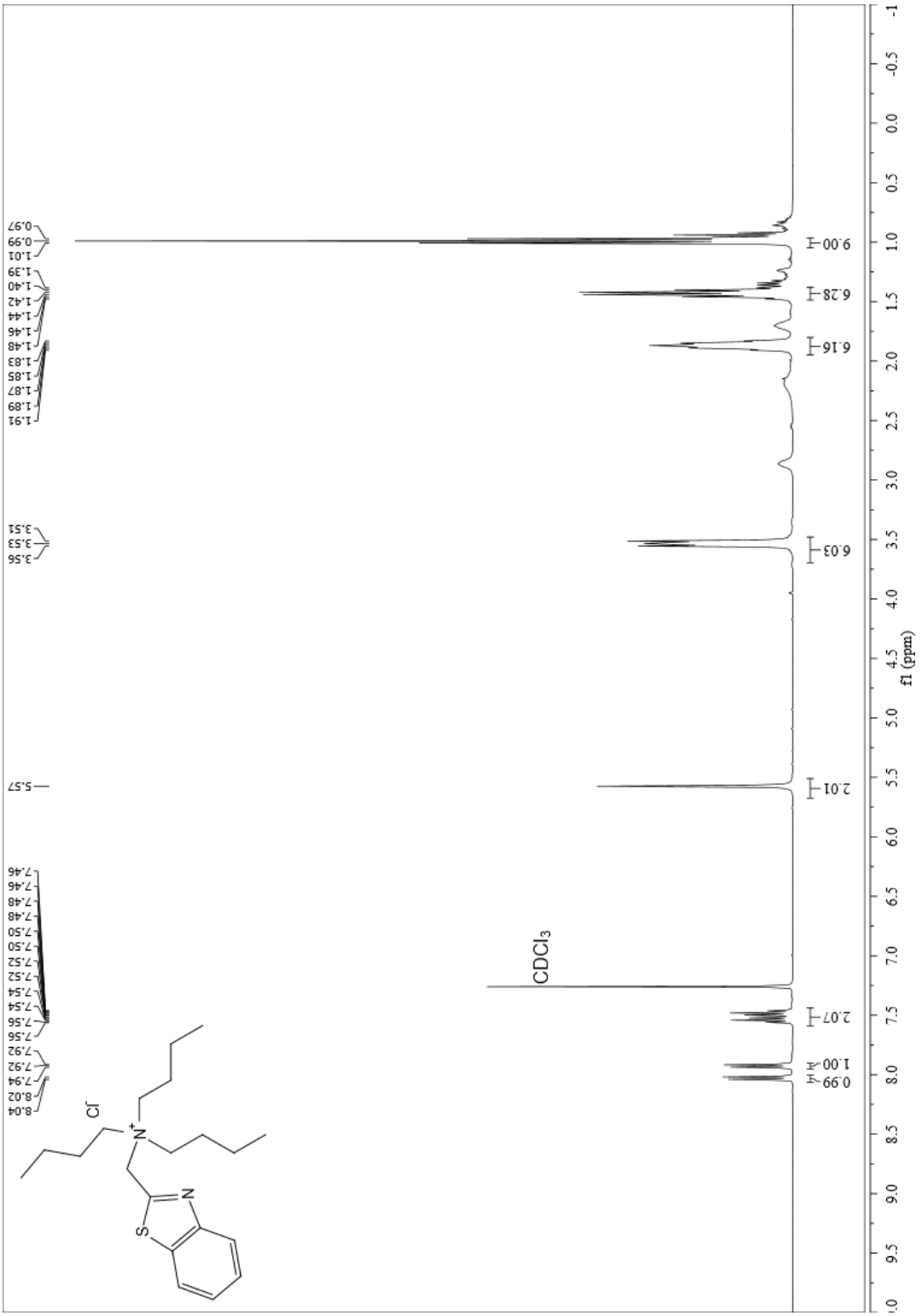
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(thiophen-2-ylmethyl)butan-1-aminium chloride (1j)



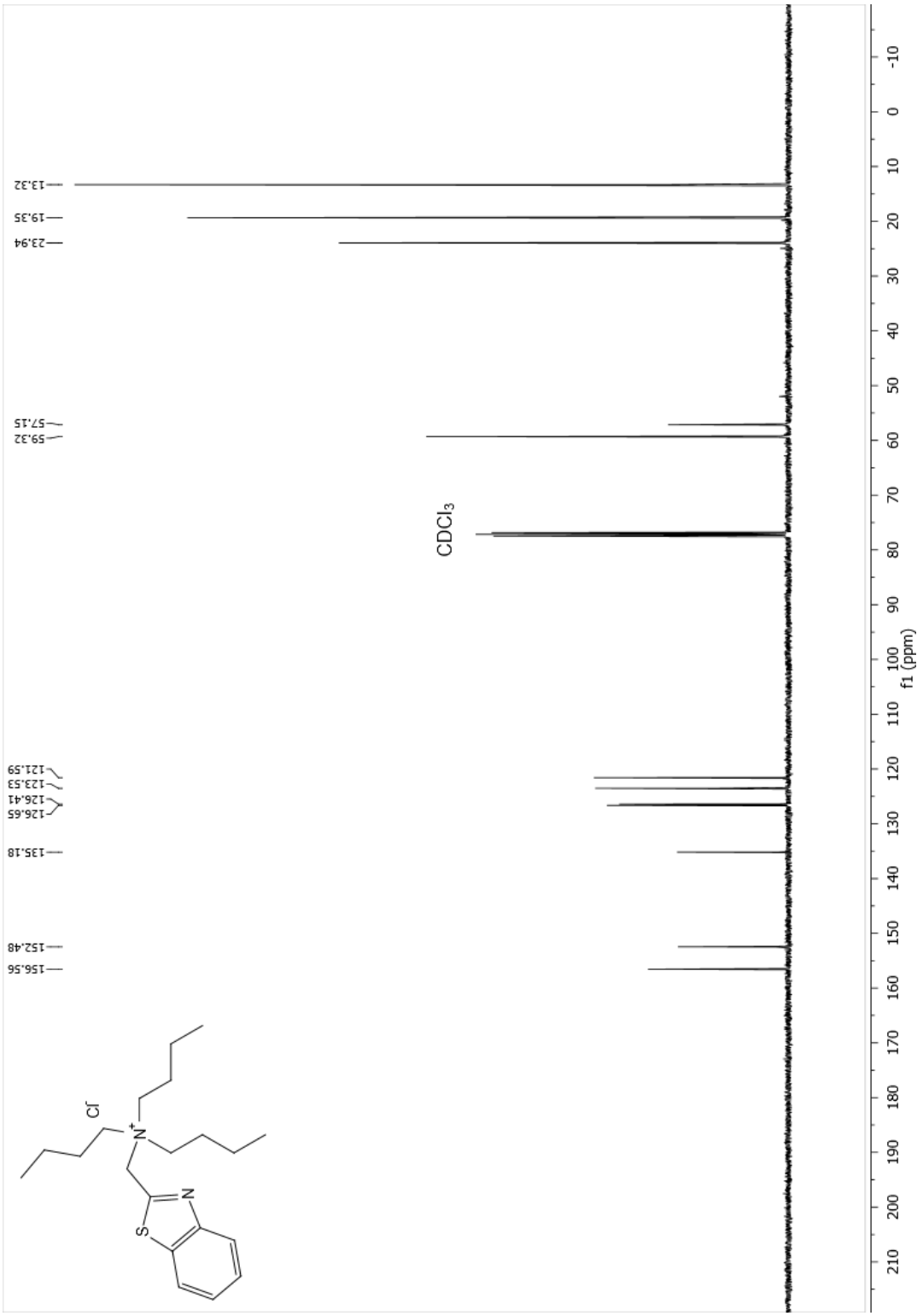
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-(thiophen-2-ylmethyl)butan-1-aminium chloride (1j)



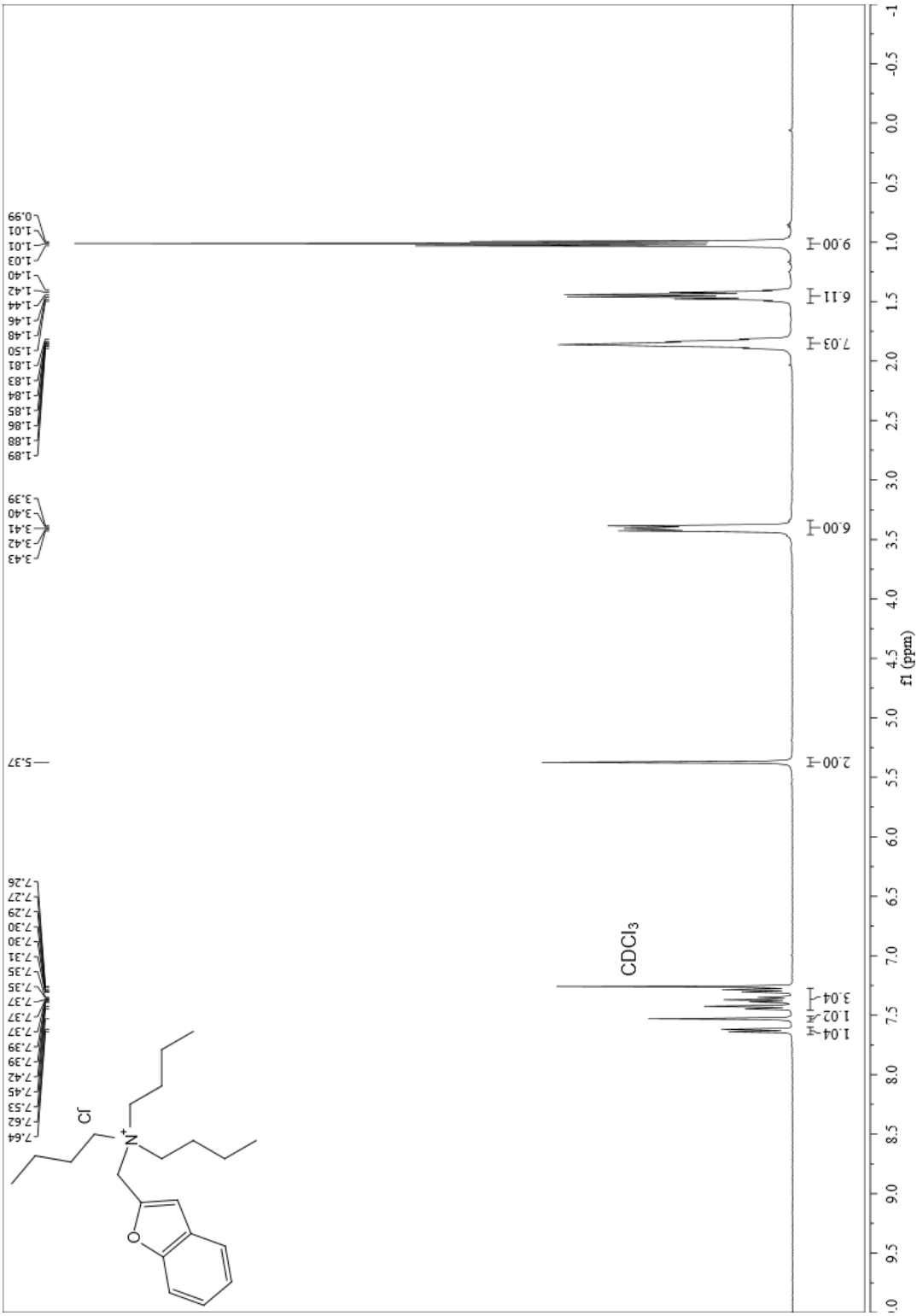
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1k)



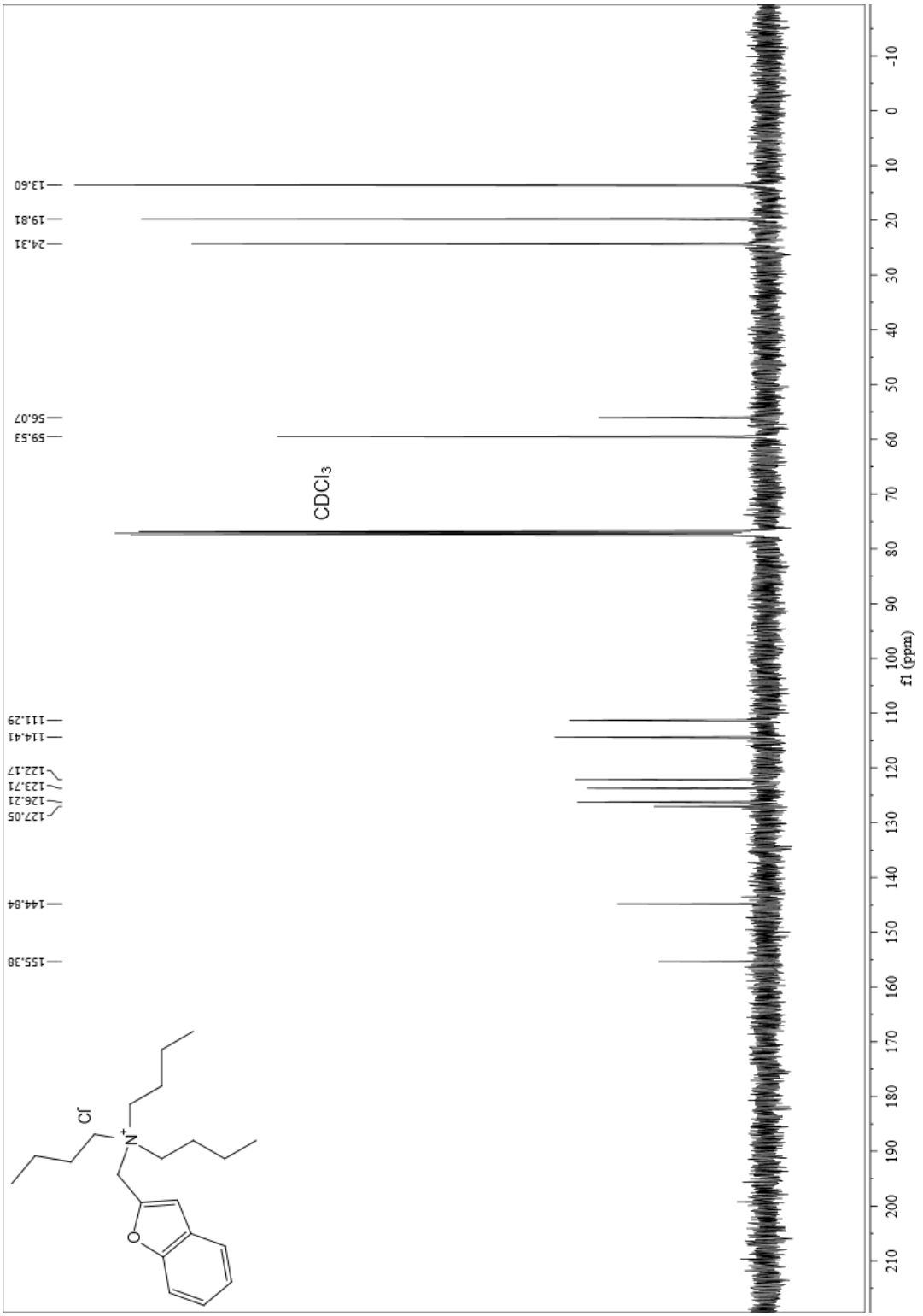
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1k)



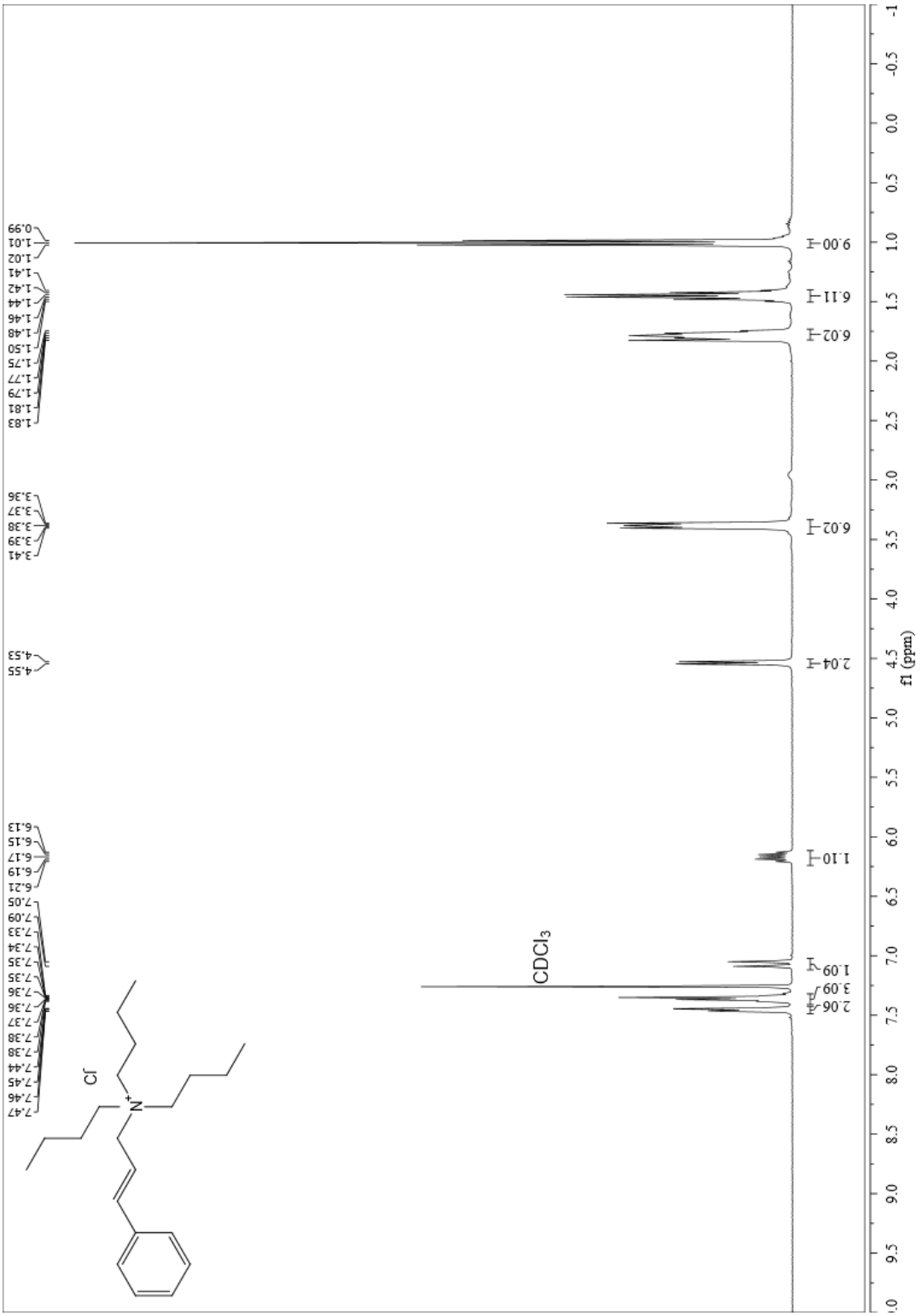
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*-(benzofuran-2-ylmethyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1l)



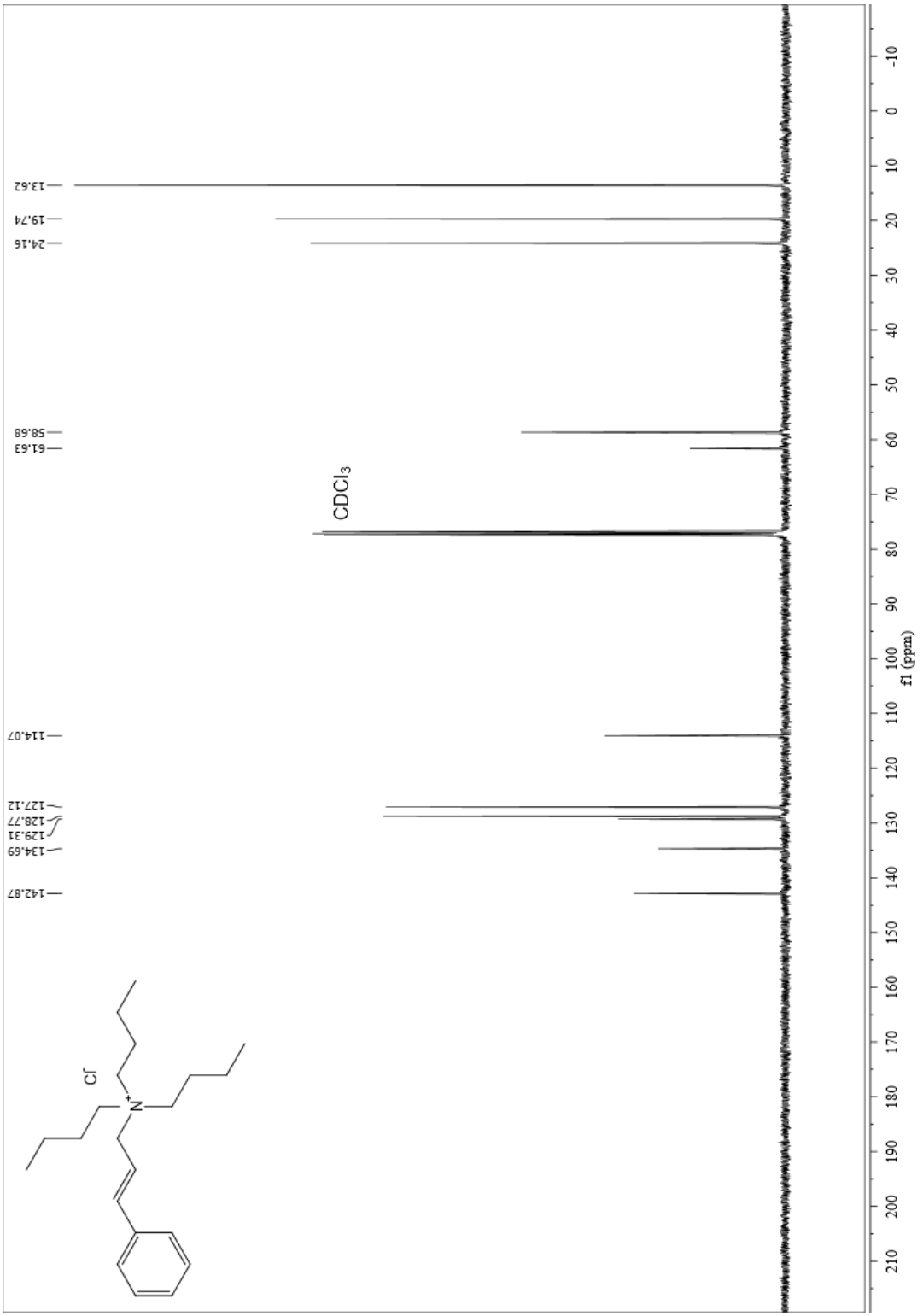
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*-(benzofuran-2-ylmethyl)-*N*,*N*-dibutylbutan-1-aminium chloride (1l)



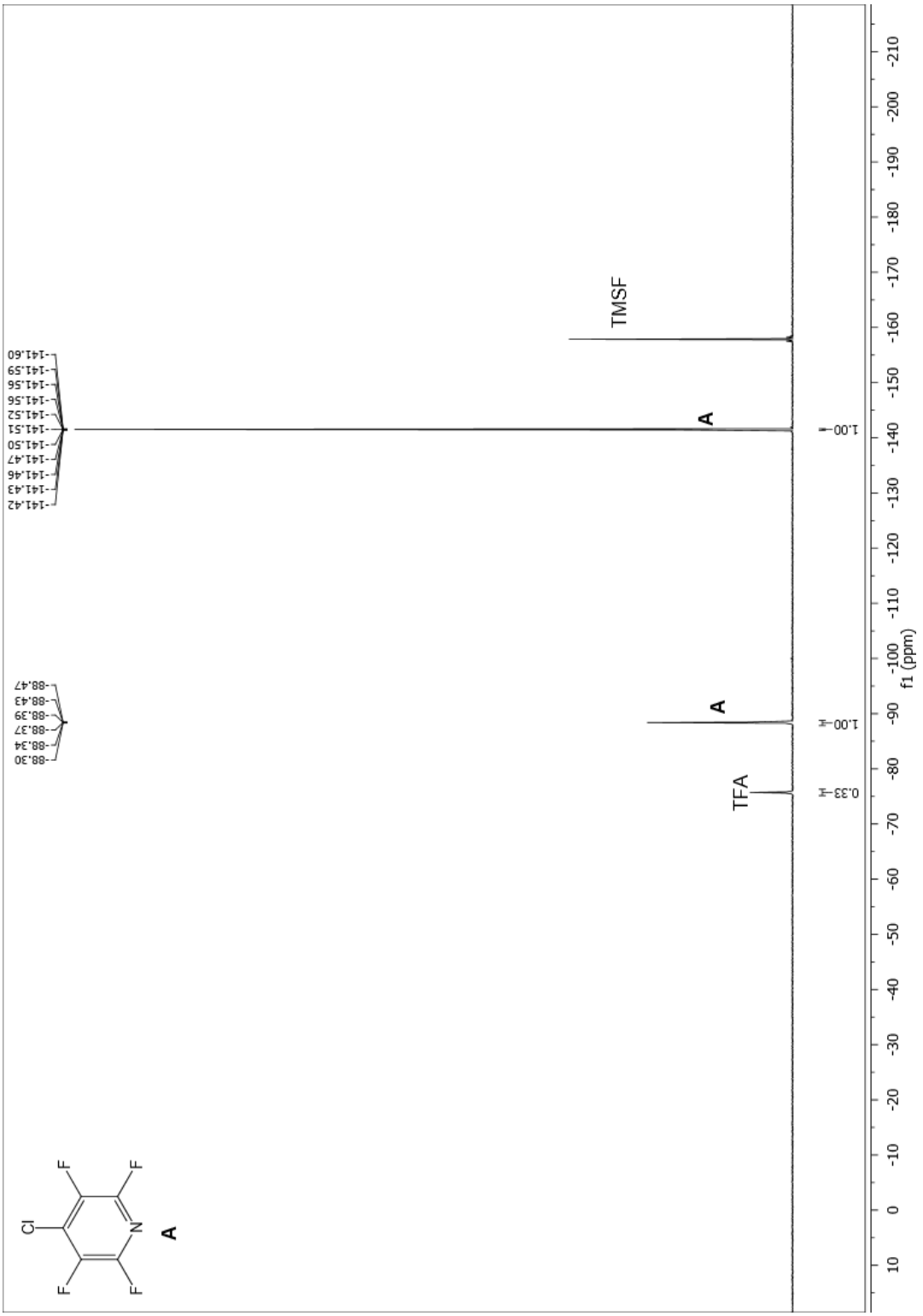
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-cinnamylbutan-1-aminium chloride (1m)



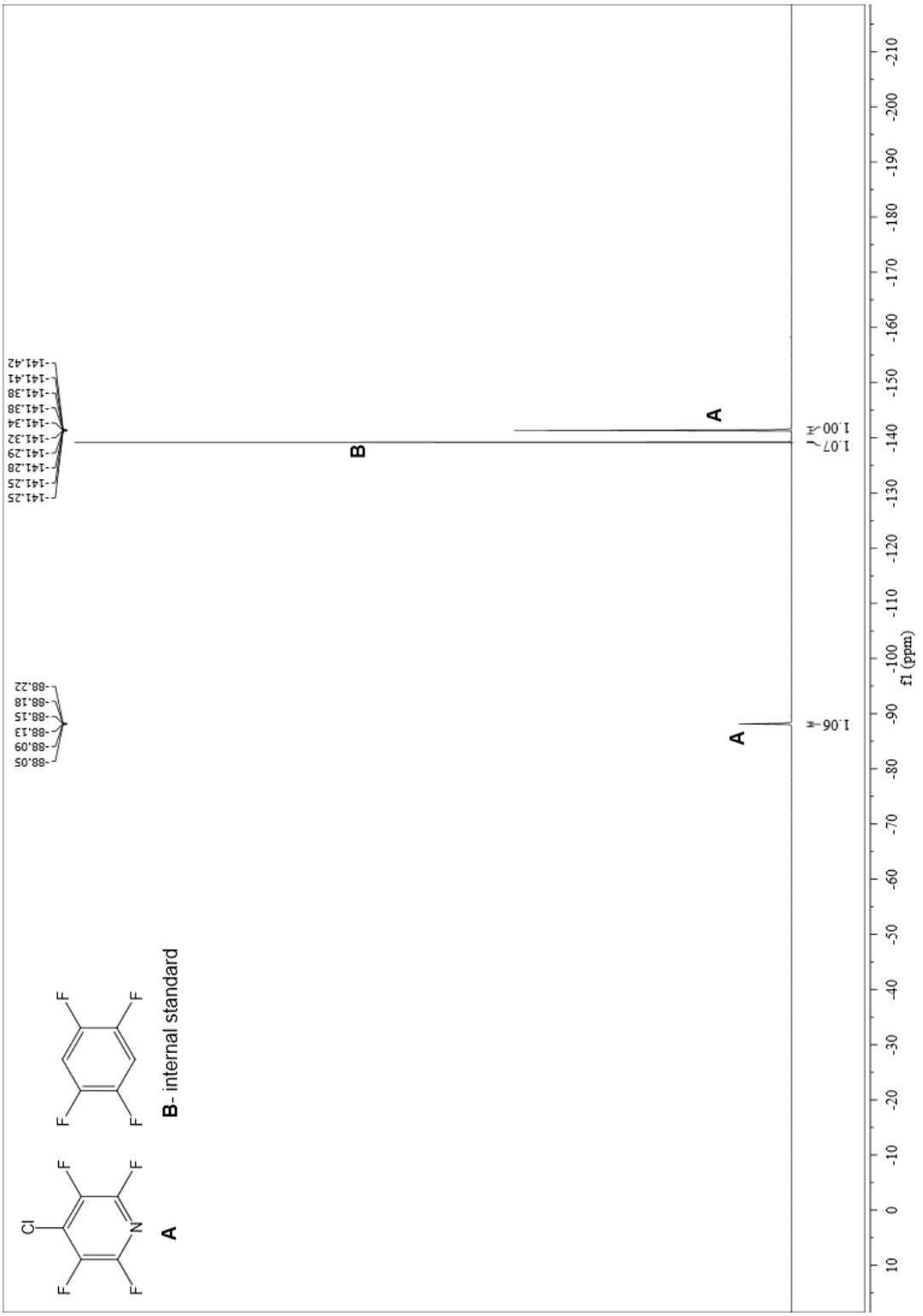
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of *N*,*N*-dibutyl-*N*-cinnamylbutan-1-aminium chloride (1m)



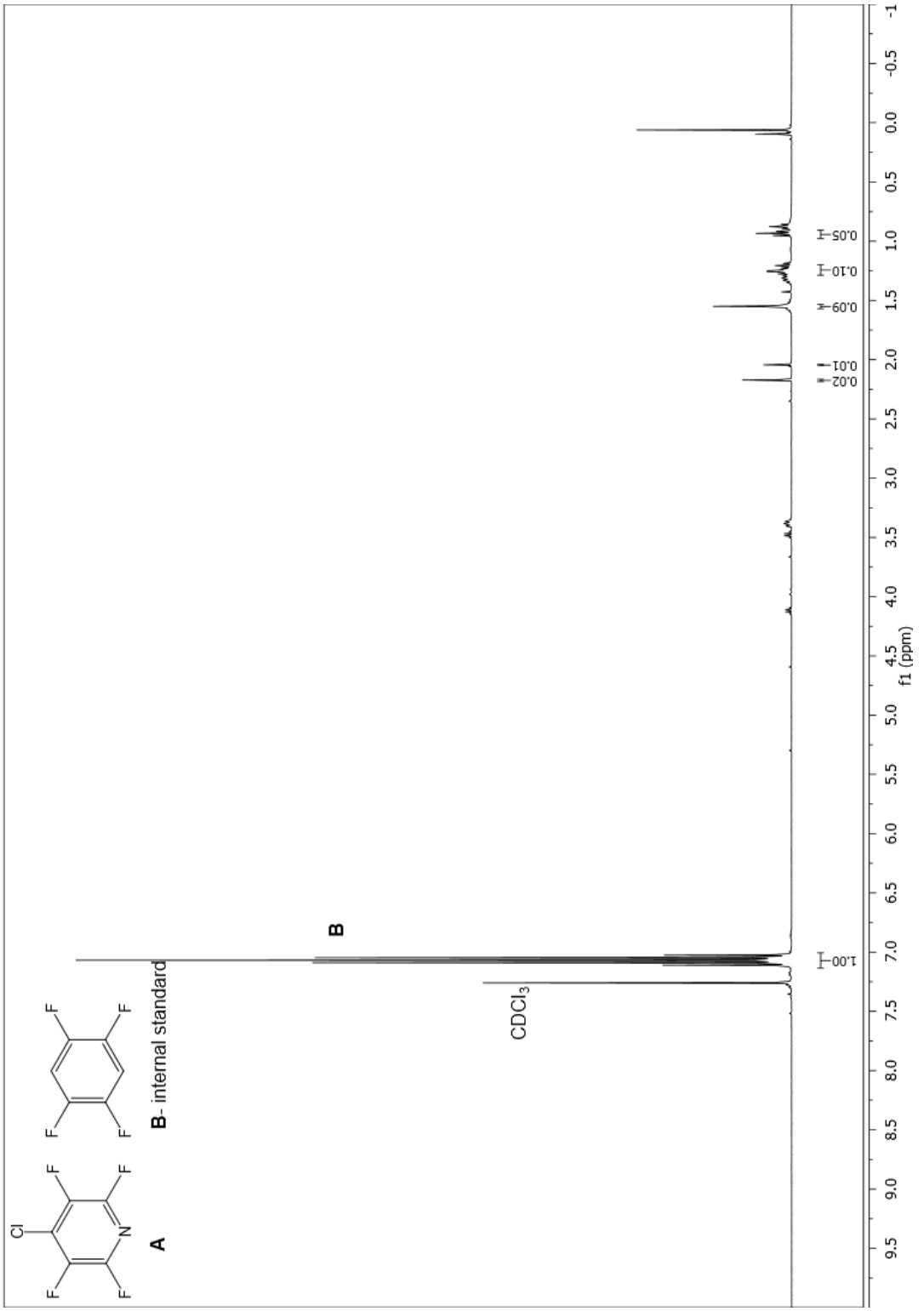
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of crude 4-chloro-2,3,5,6-tetrafluoropyridine (2a) for NMR yield calculation



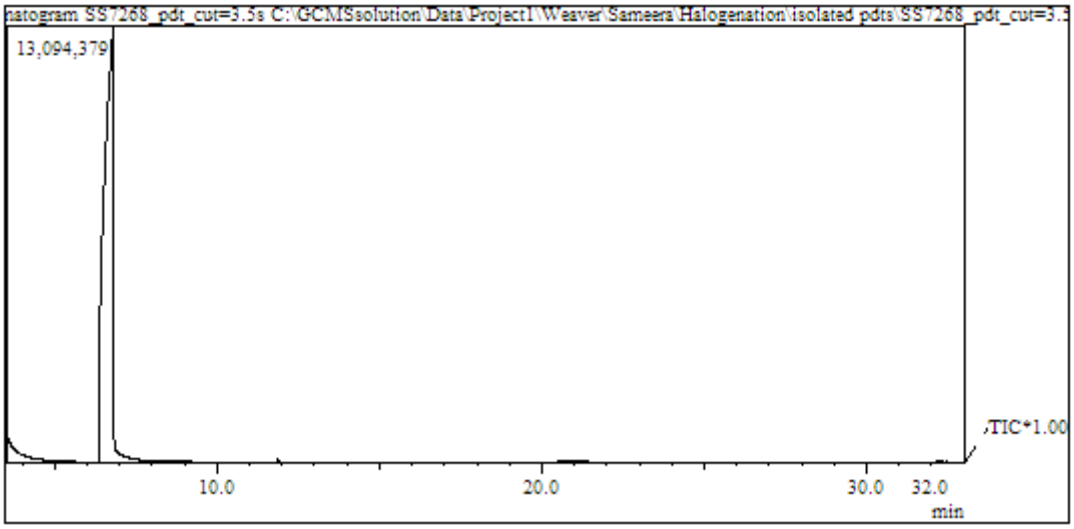
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 4-chloro-2,3,5,6-tetrafluoropyridine (2a) with 1,2,4,5-tetrafluorobenzene as an internal standard

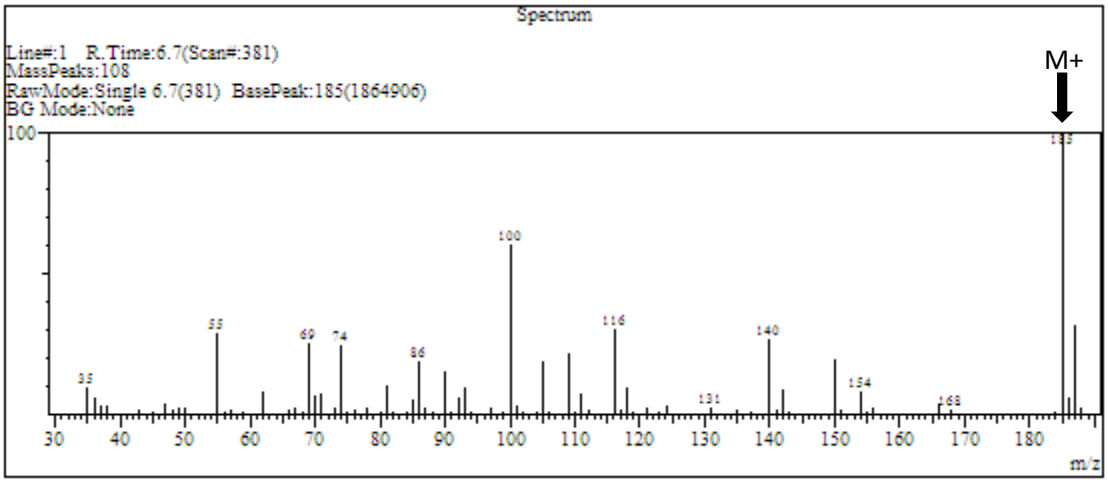


^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of crude 4-chloro-2,3,5,6-tetrafluoropyridine (2a) with 1,2,4,5-tetrafluorobenzene as an internal standard

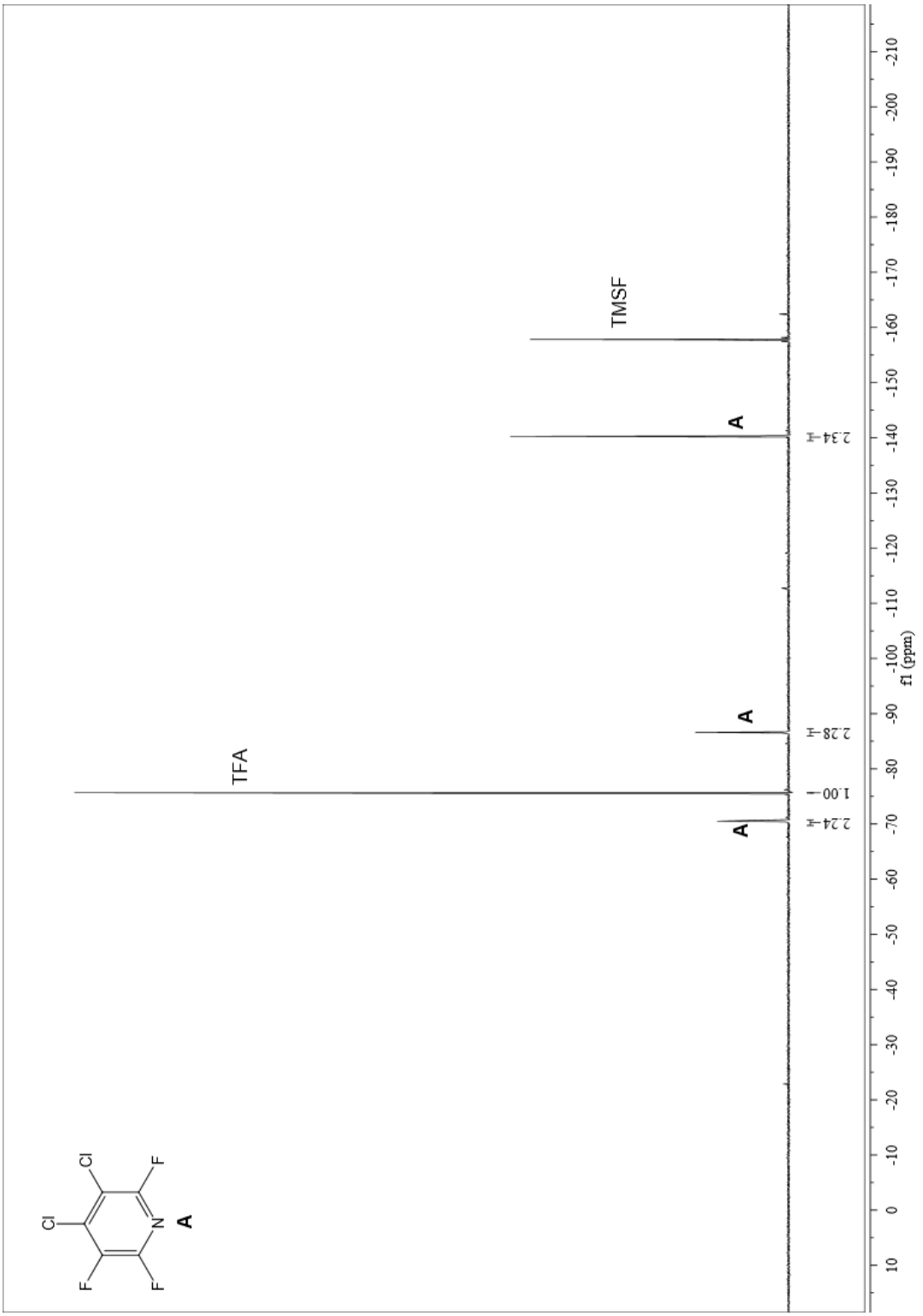


GC and MS of 4-chloro-2,3,5,6-tetrafluoropyridine (2a)

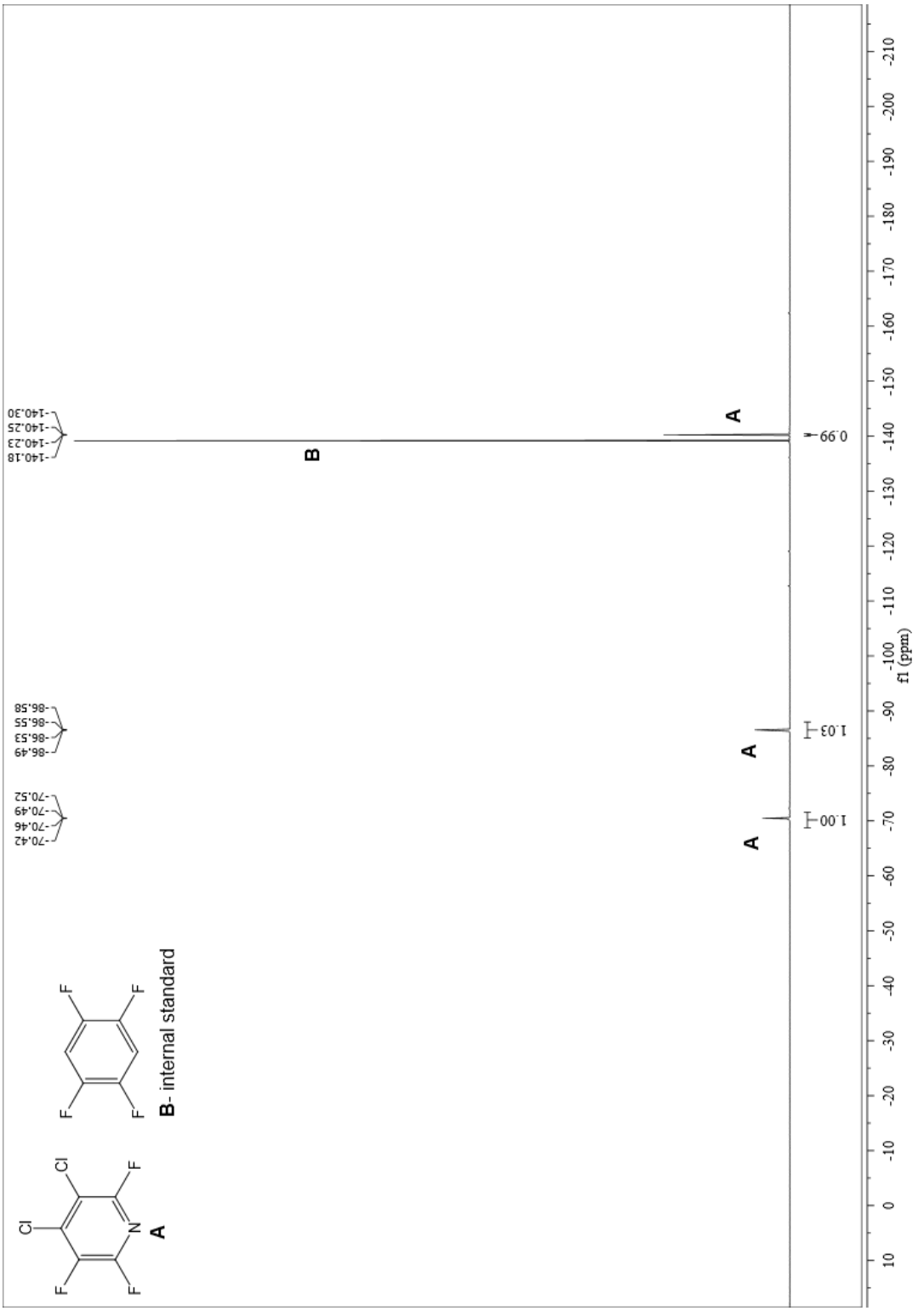




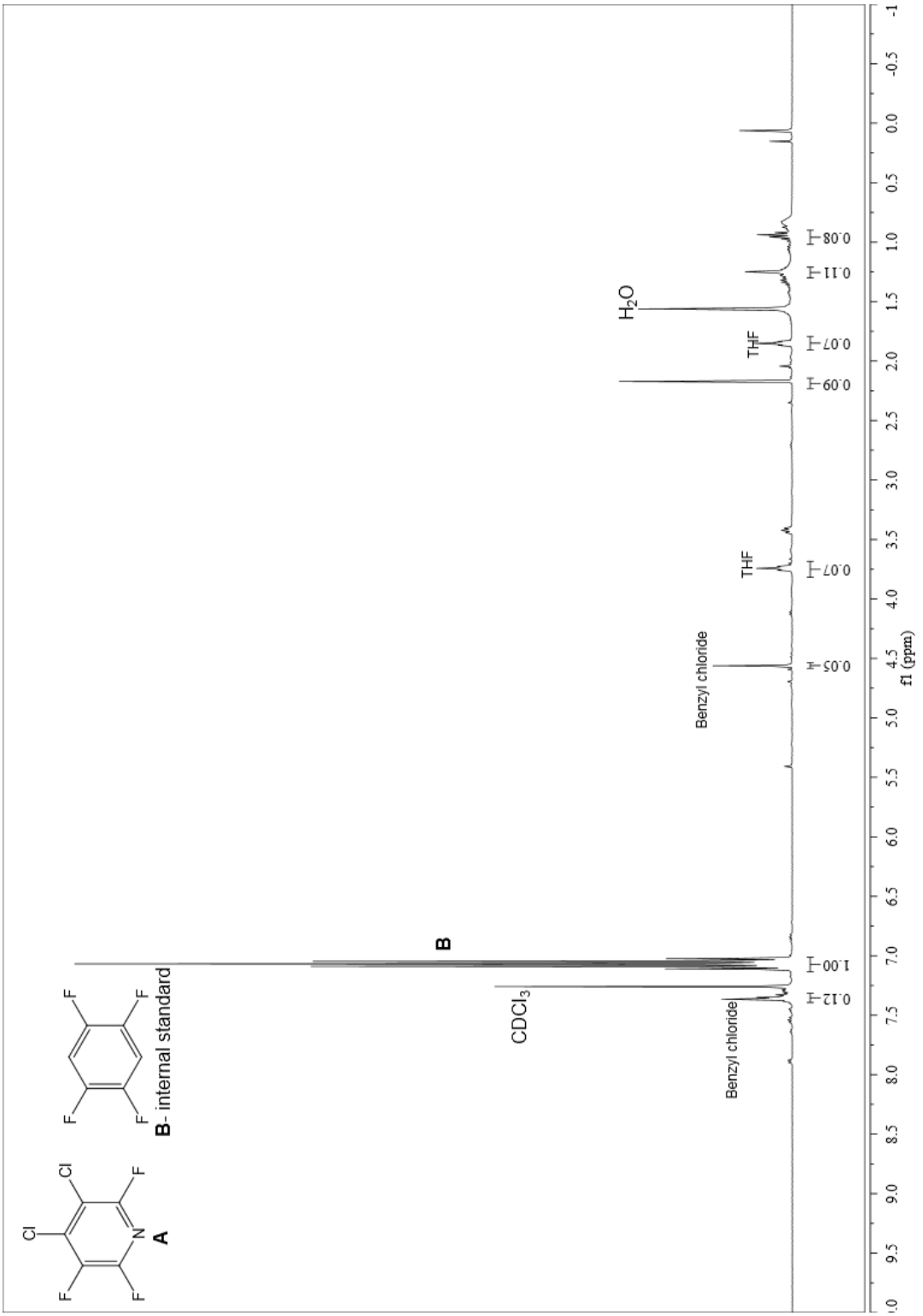
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of crude 3,4-dichloro-2,5,6-trifluoropyridine (2b) for NMR yield calculation



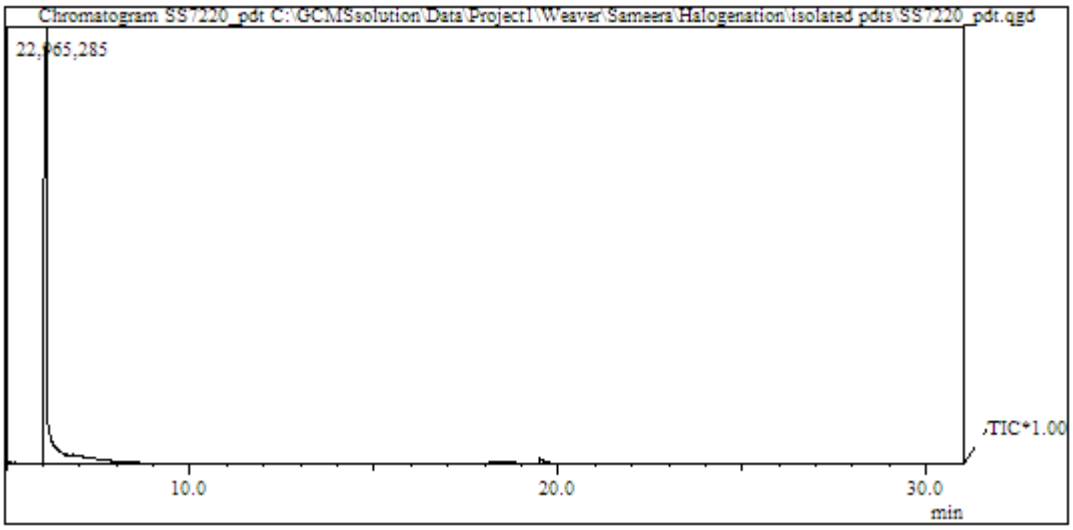
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 3,4-dichloro-2,5,6-trifluoropyridine (2b) with 1,2,4,5-tetrafluorobenzene as an internal standard

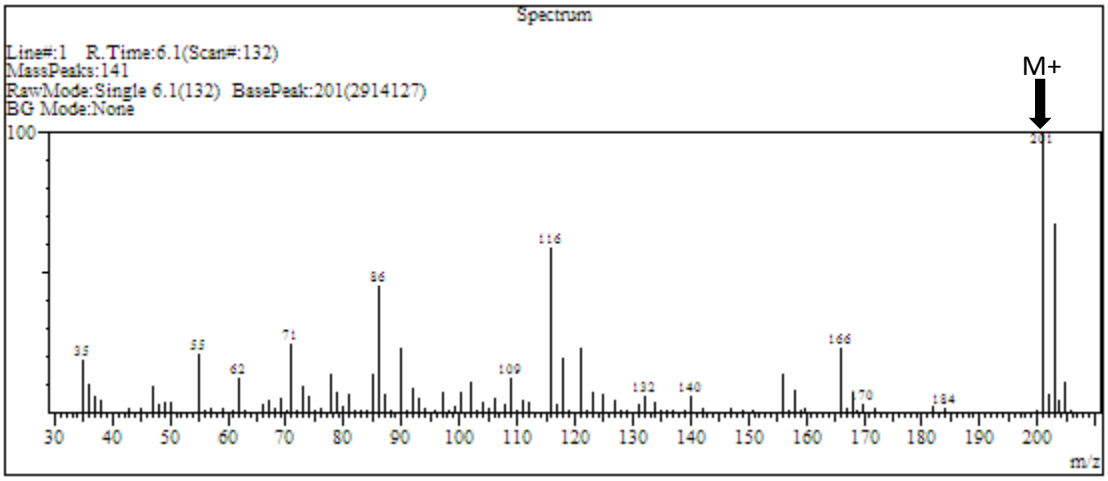


^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of isolated 3,4-dichloro-2,5,6-trifluoropyridine (2b) with 1,2,4,5-tetrafluorobenzene as an internal standard

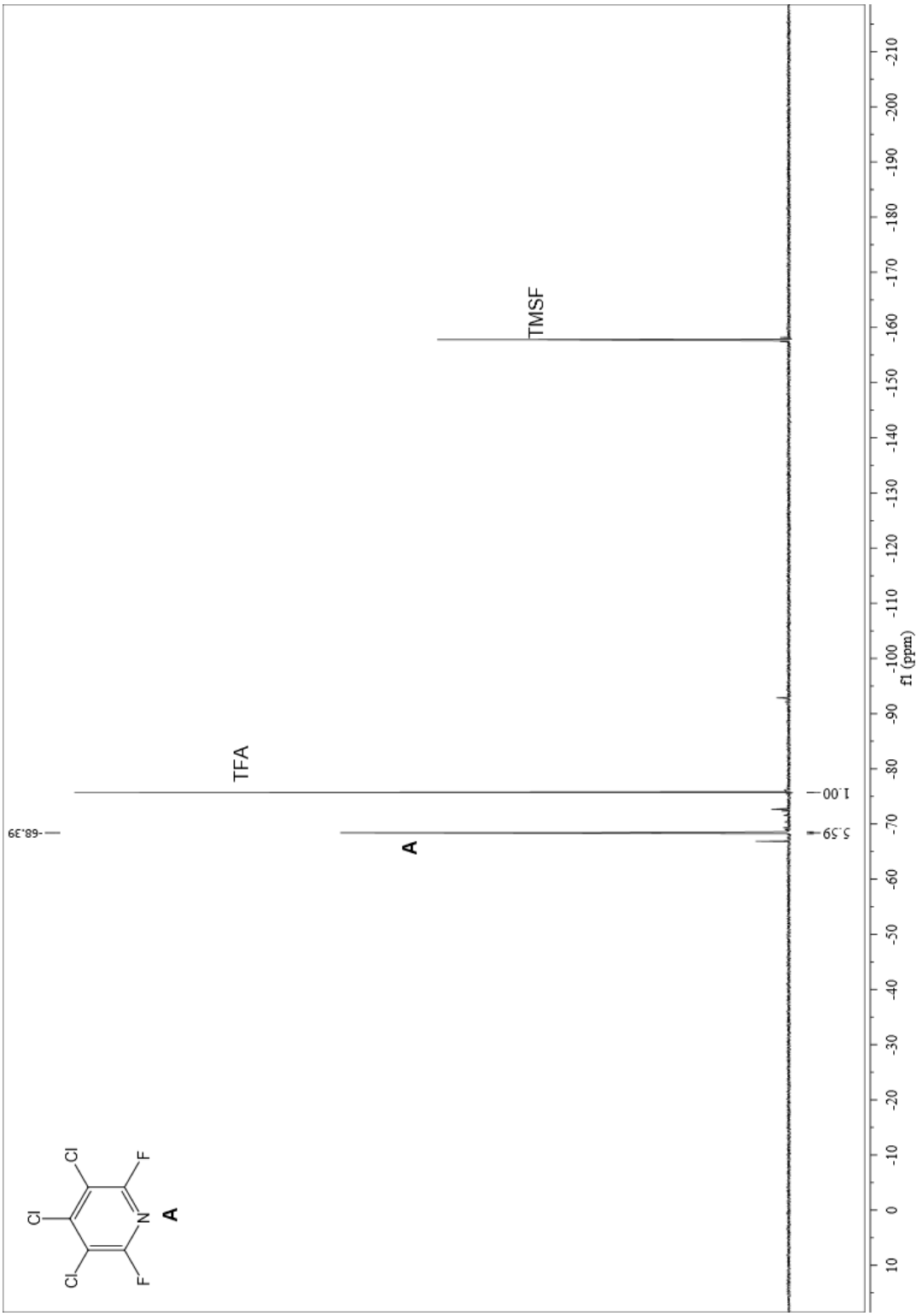


GC and MS of 3,4-dichloro-2,5,6-trifluoropyridine (2b)

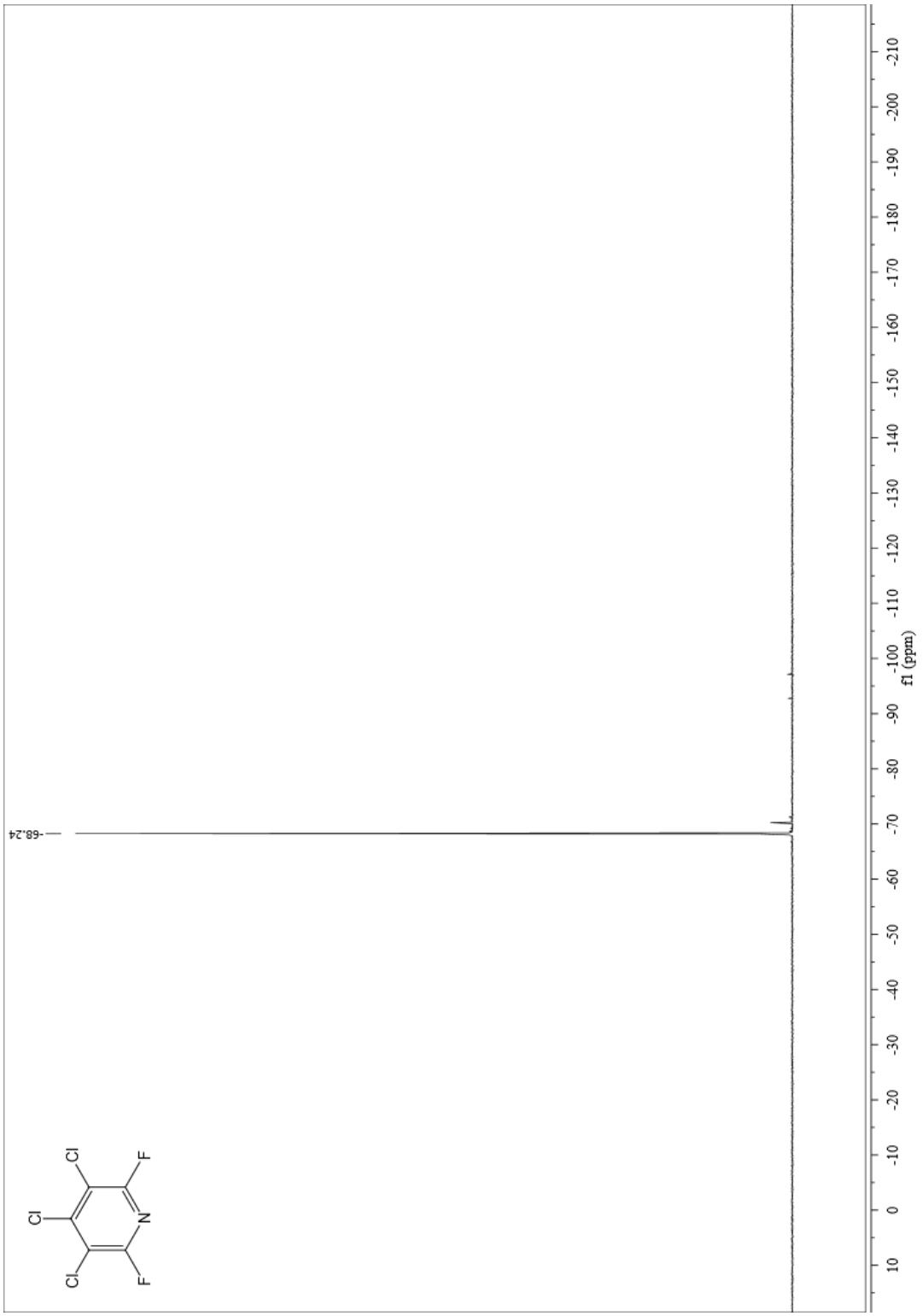




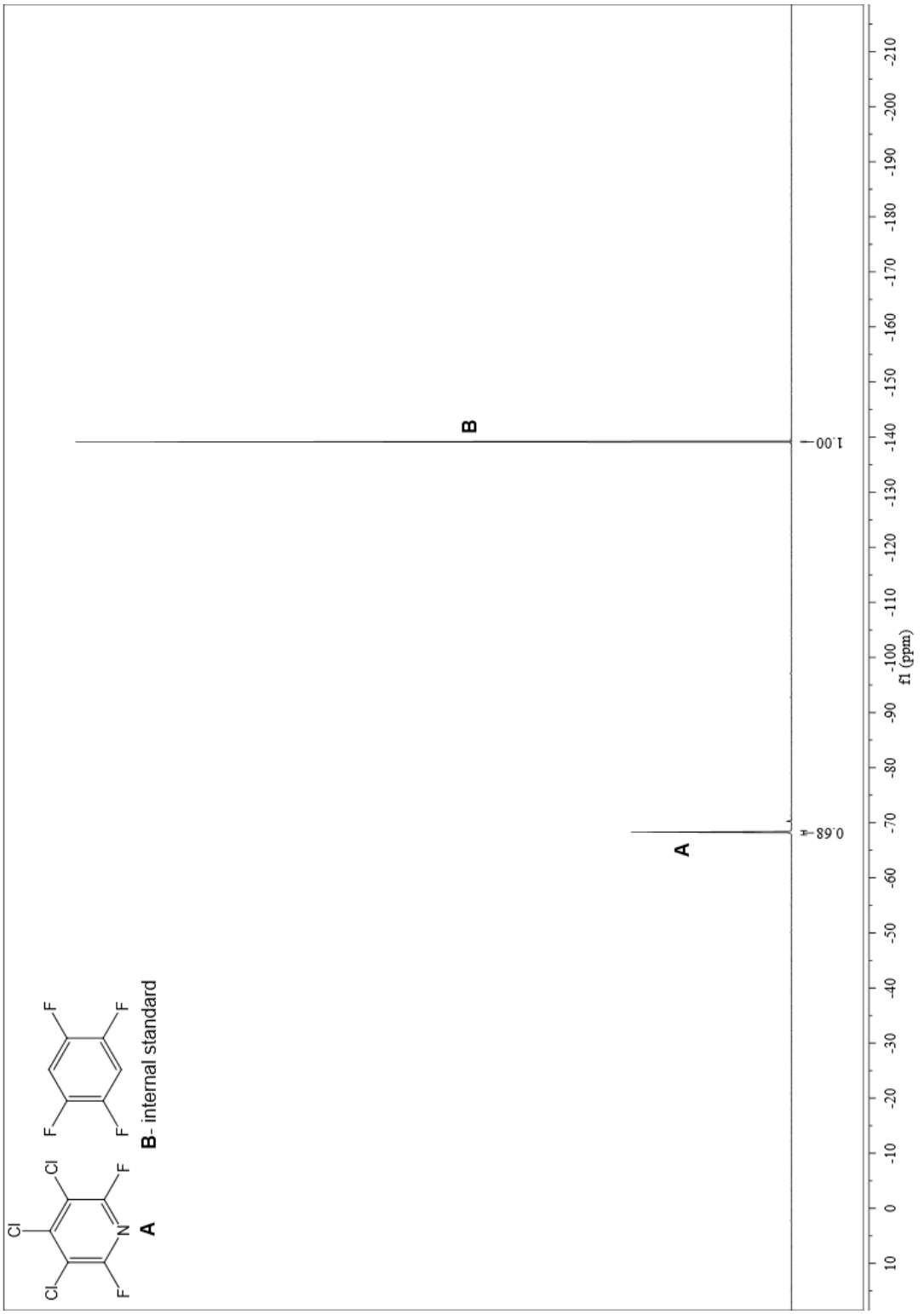
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of crude 3,4,5-trichloro-2,6-difluoropyridine (2c) for NMR yield calculation



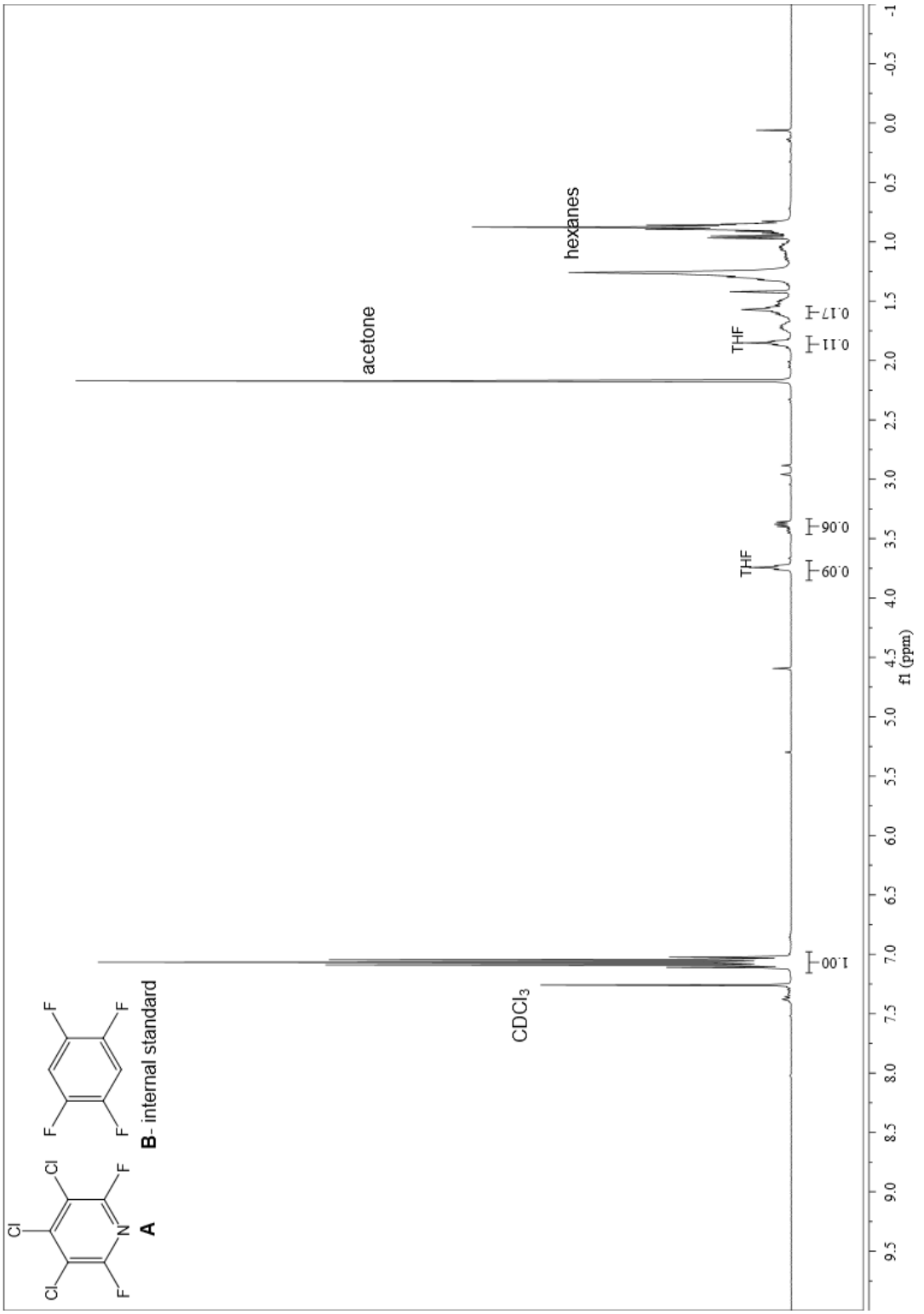
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 3,4,5-trichloro-2,6-difluoropyridine (2c)



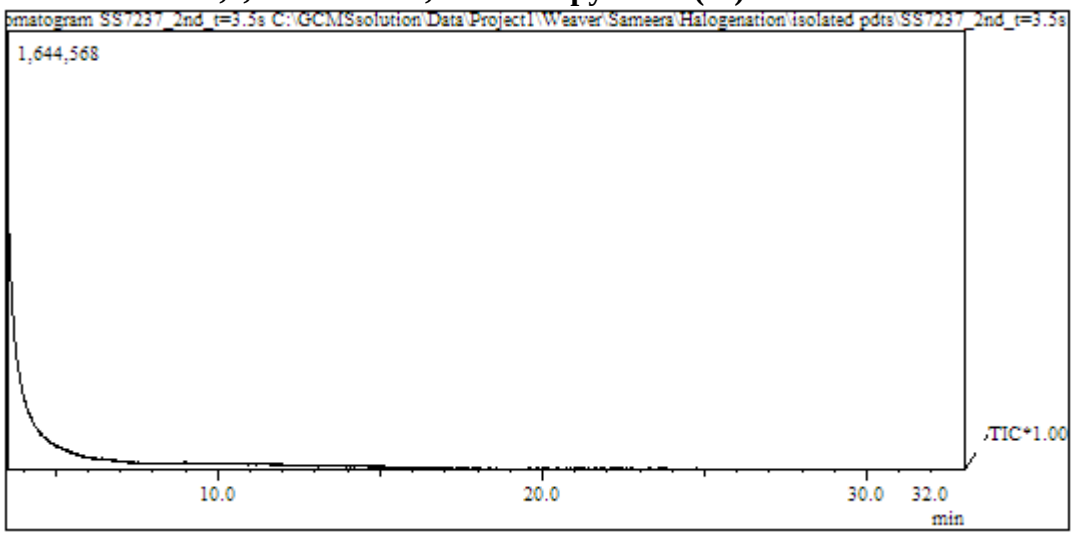
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 3,4,5-trichloro-2,6-difluoropyridine (2c) with 1,2,4,5-tetrafluorobenzene as an internal standard

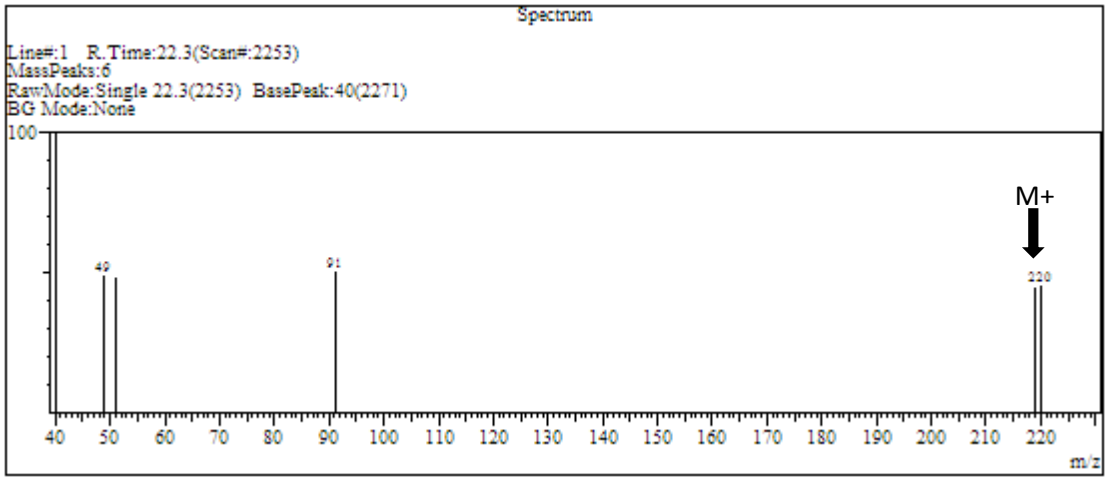


^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of isolated 3,4,5-trichloro-2,6-difluoropyridine (2c) with 1,2,4,5-tetrafluorobenzene as an internal standard

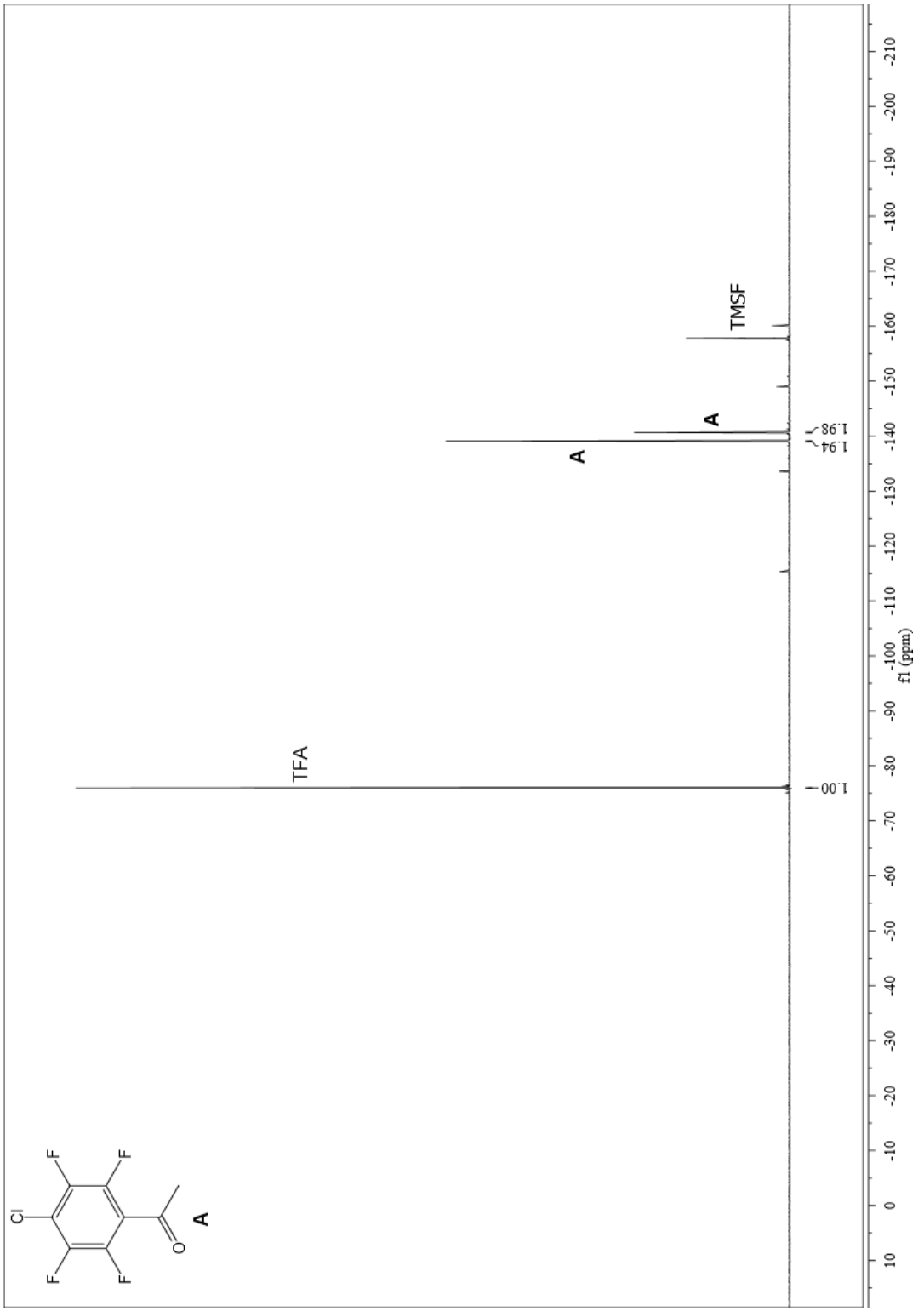


GC and MS of 3,4,5-trichloro-2,6-difluoropyridine (2c)

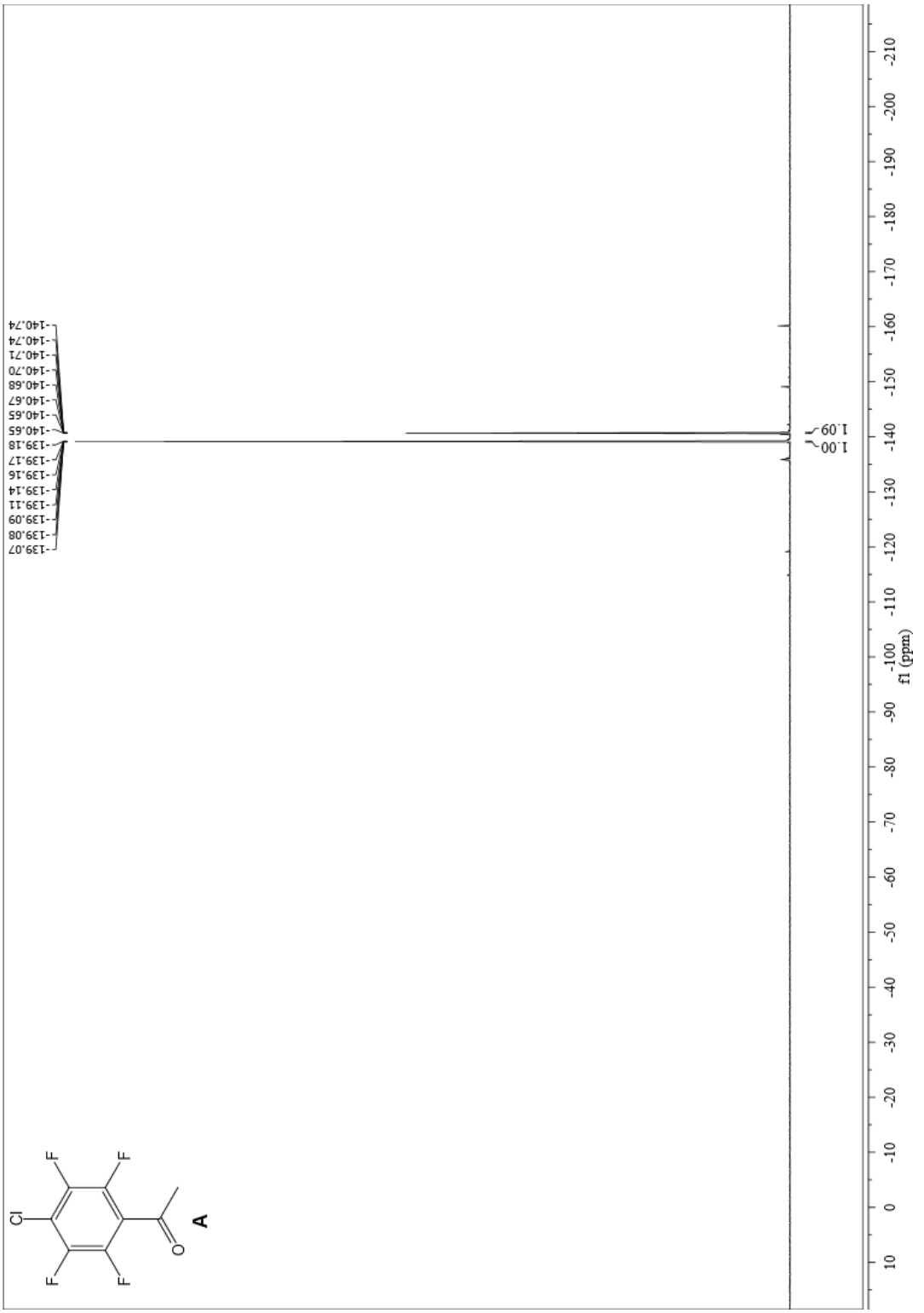




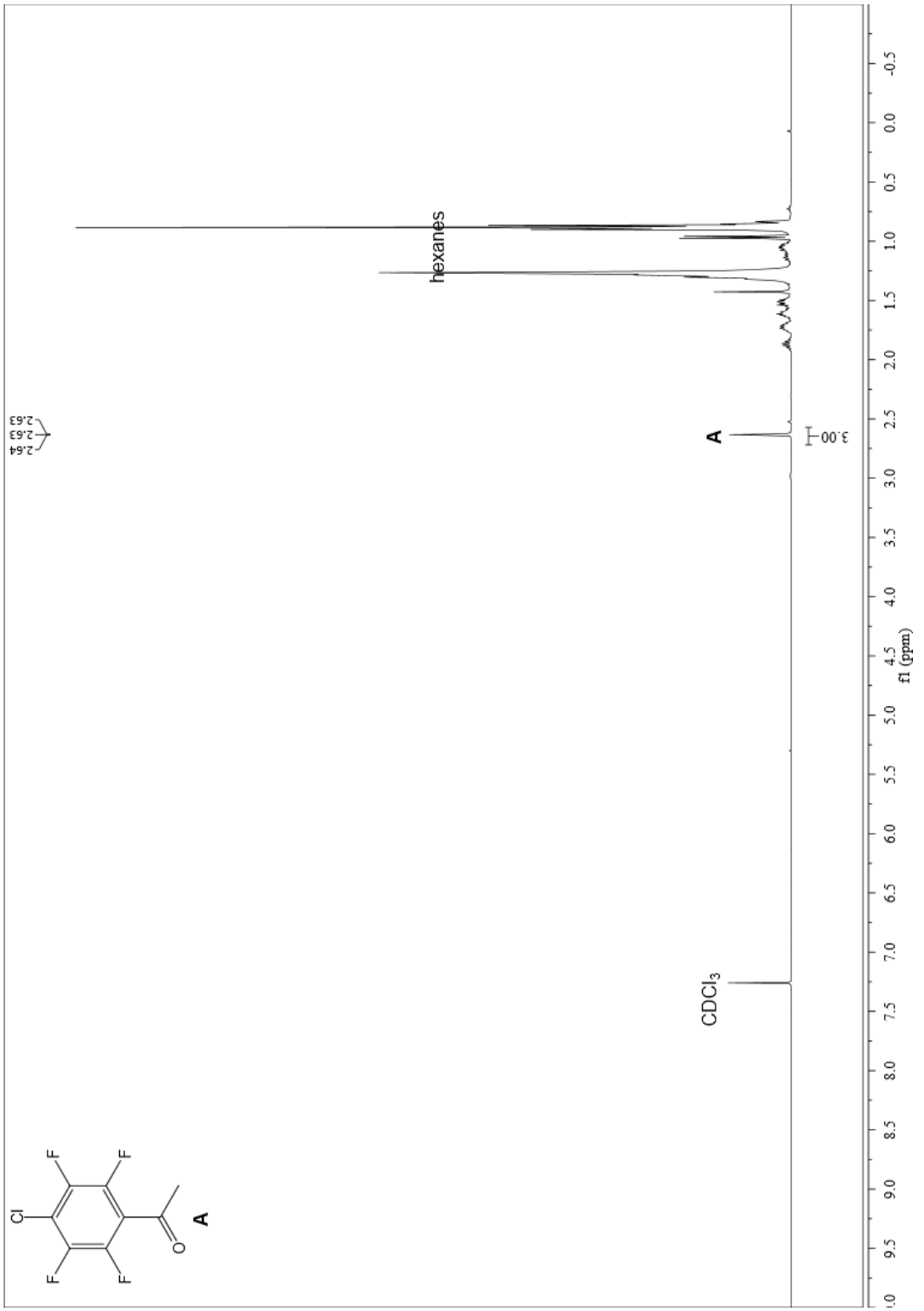
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of crude 1-(4-chloro-2,3,5,6-tetrafluorophenyl)ethan-1-one (2d) for NMR yield calculation



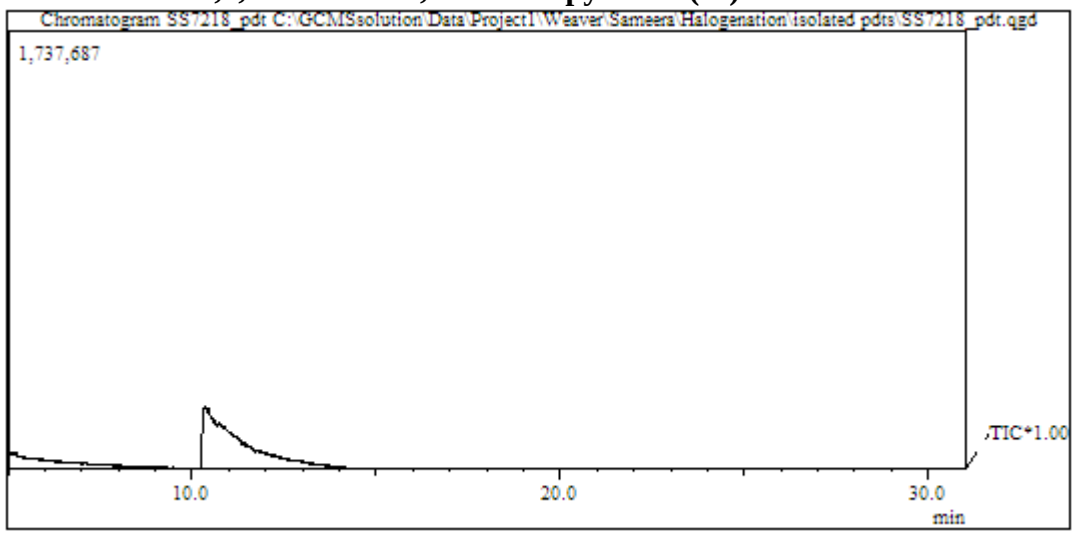
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 1-(4-chloro-2,3,5,6-tetrafluorophenyl)ethan-1-one (2d)

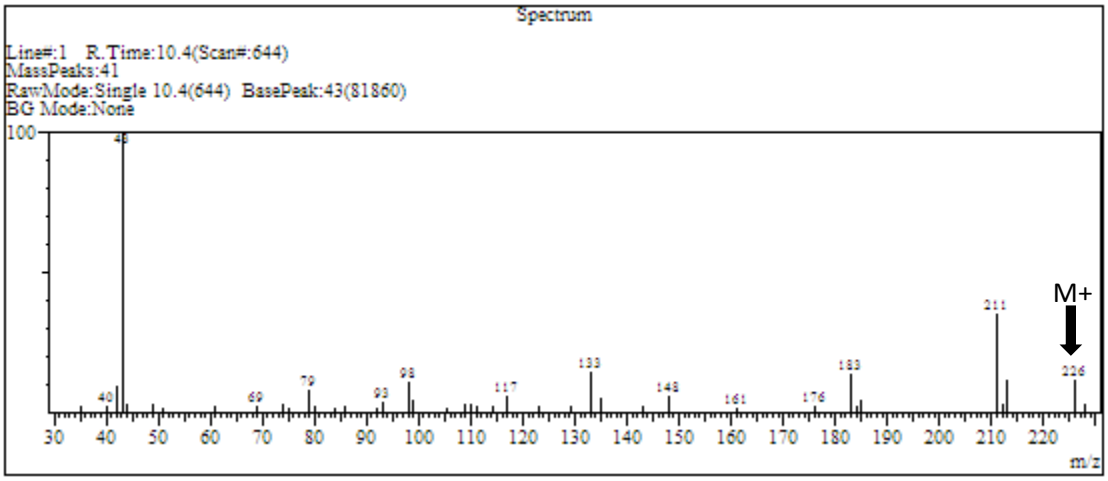


^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of isolated 1-(4-chloro-2,3,5,6-tetrafluorophenyl)ethan-1-one (2d)

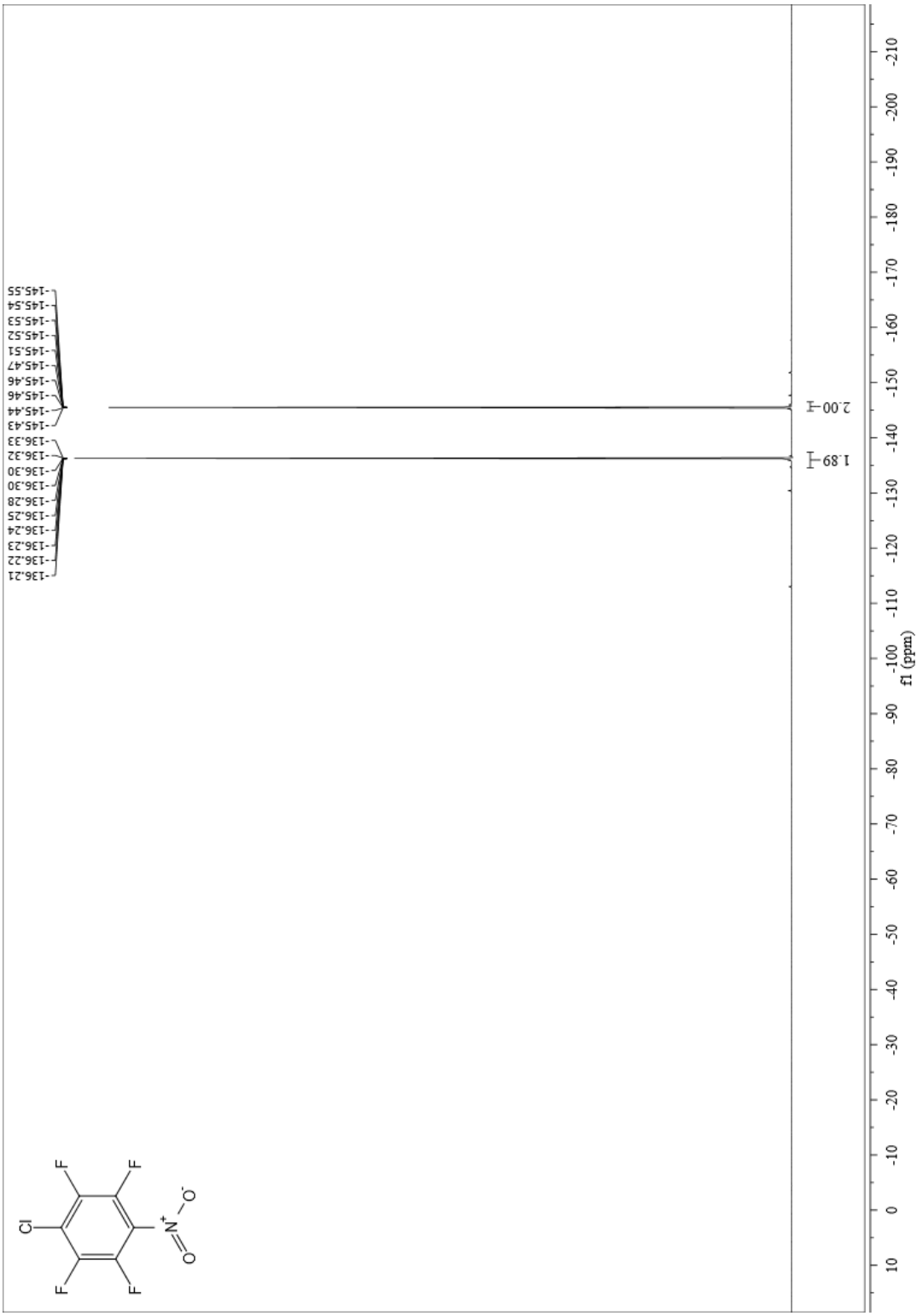


GC and MS of 3,4,5-trichloro-2,6-difluoropyridine (2c)

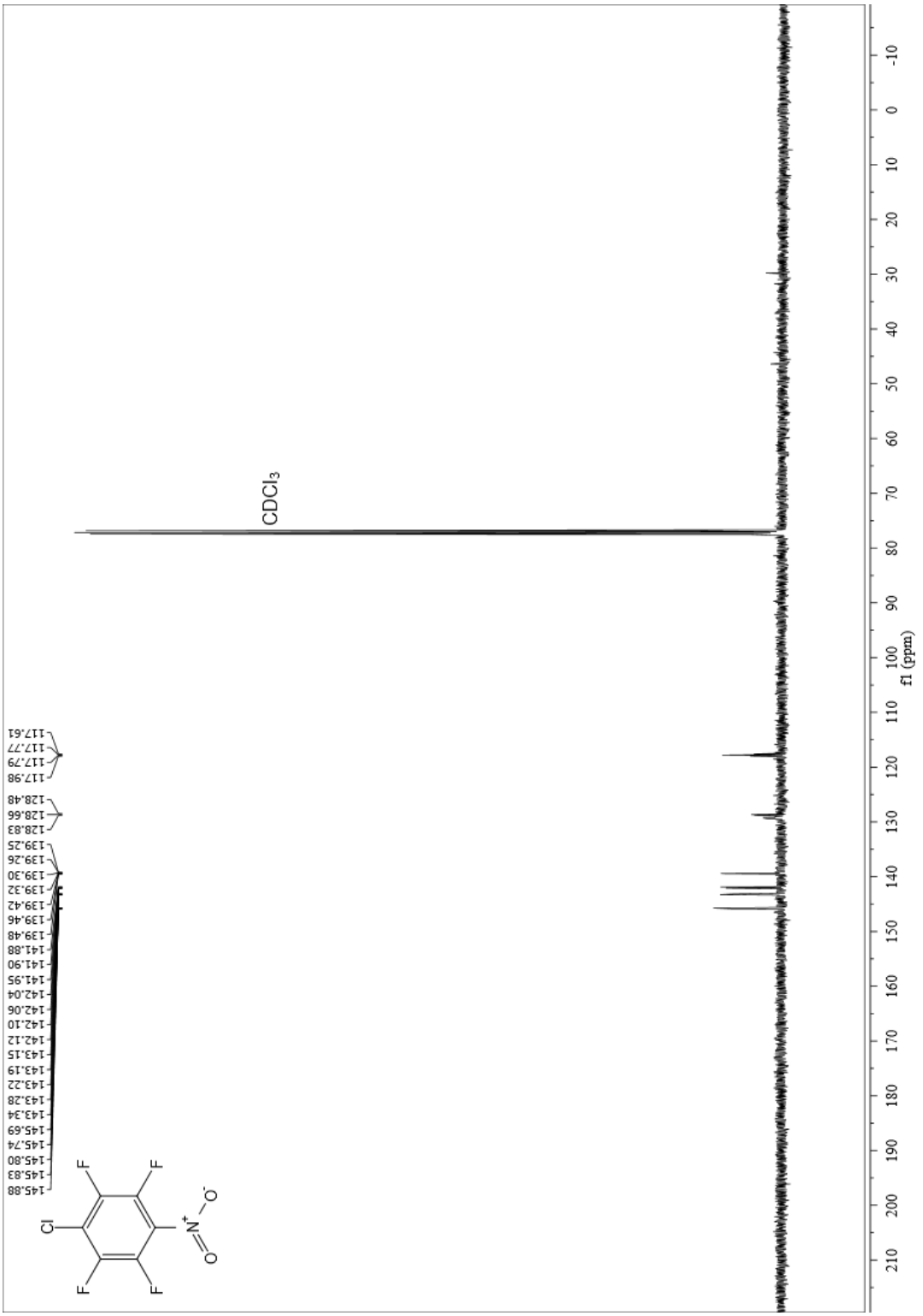




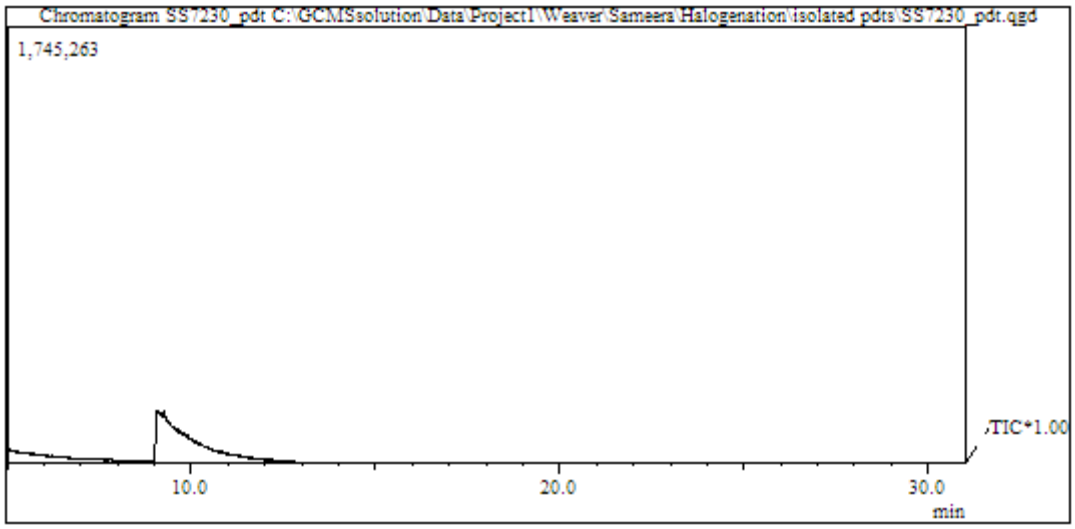
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 1-chloro-2,3,5,6-tetrafluoro-4-nitrobenzene (2e)

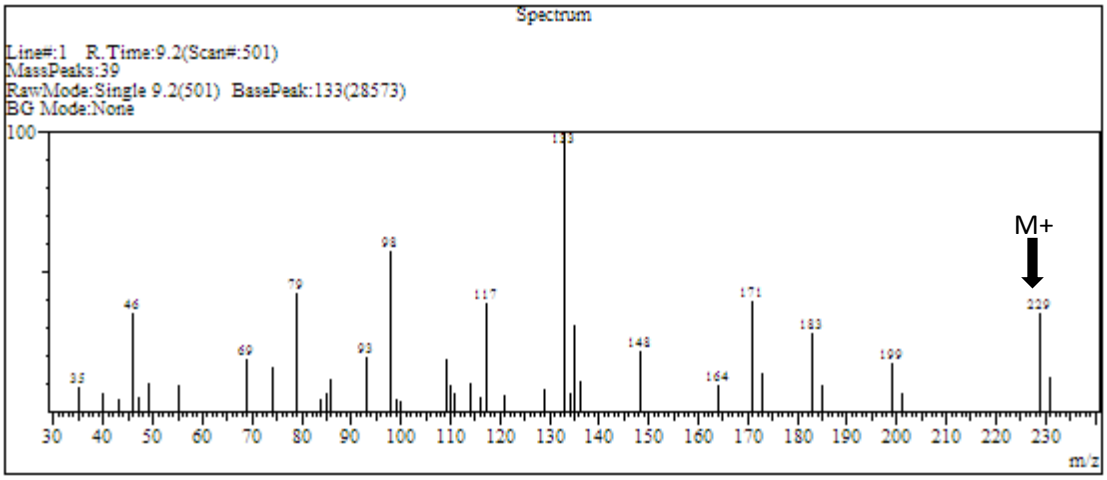


^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of isolated 1-chloro-2,3,5,6-tetrafluoro-4-nitrobenzene (2e)

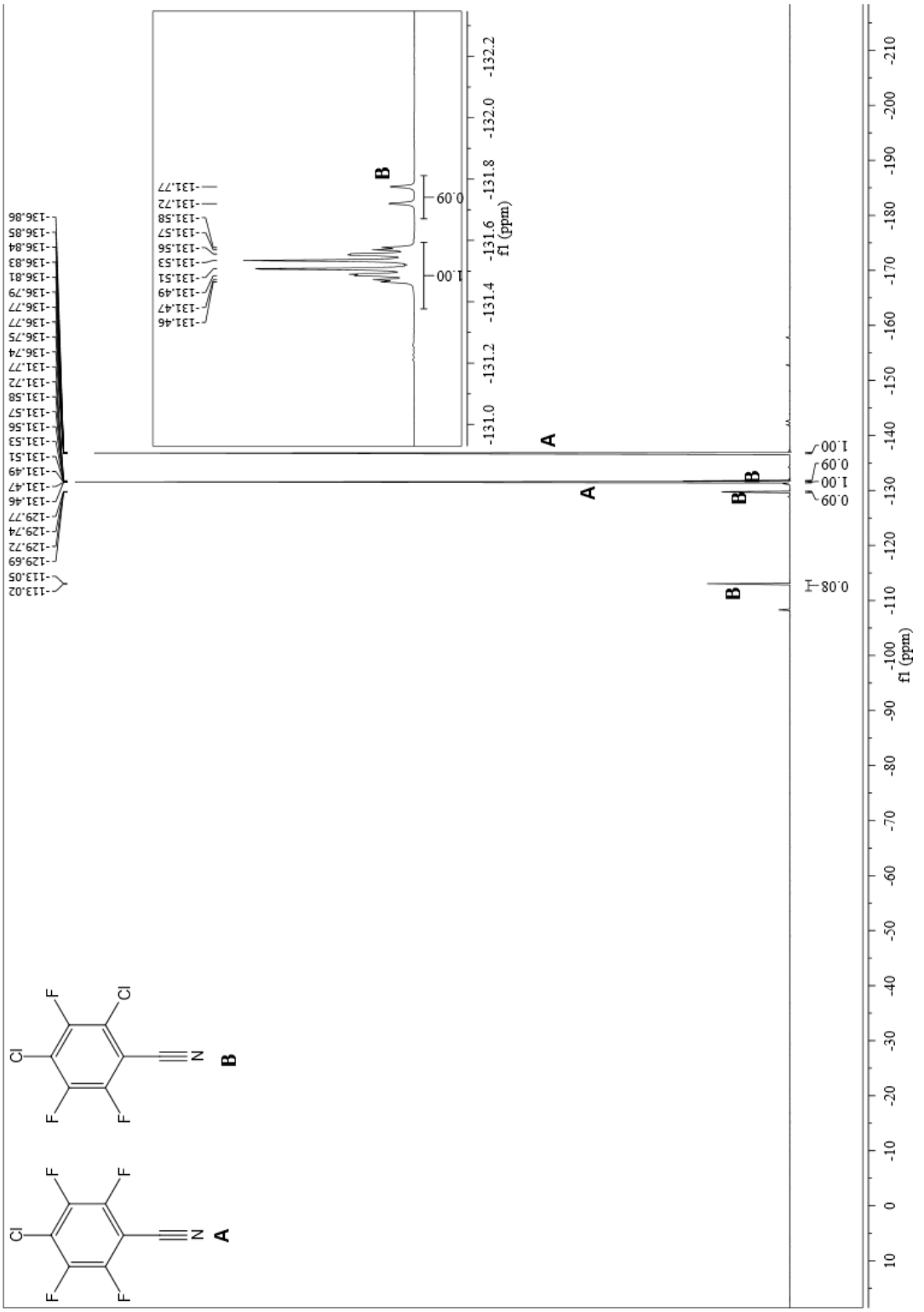


GC and MS of 1-chloro-2,3,5,6-tetrafluoro-4-nitrobenzene (2e)

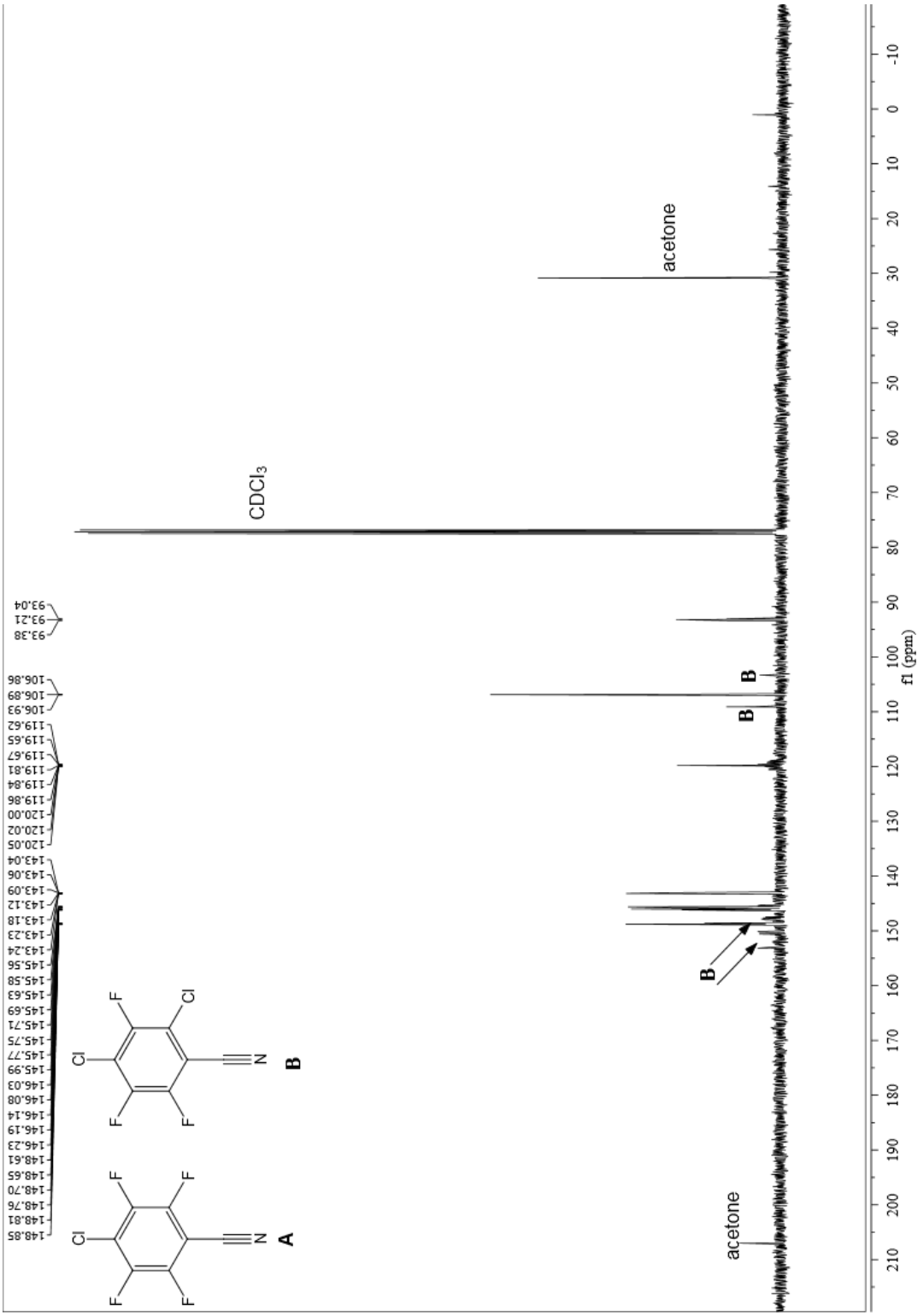




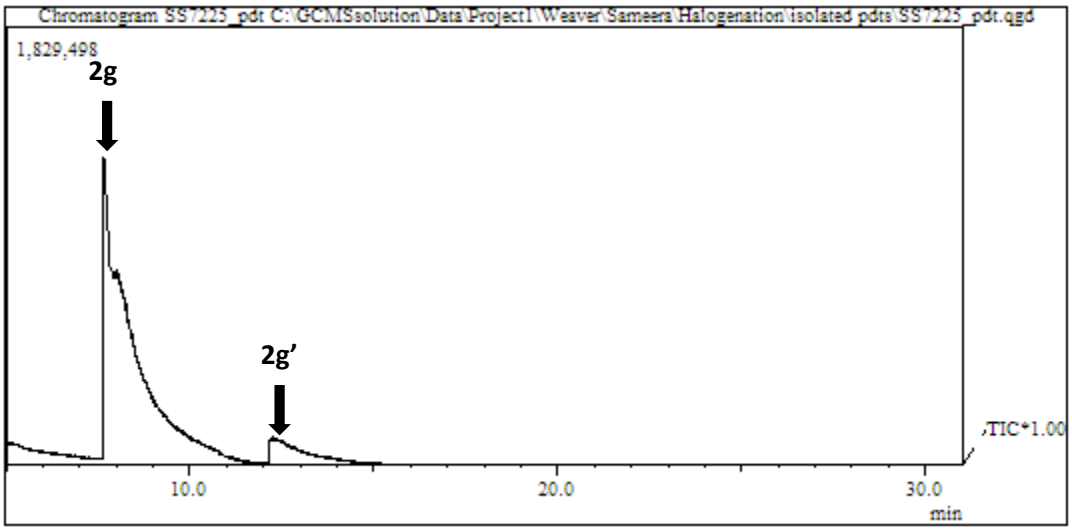
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 4-chloro-2,3,5,6-tetrafluorobenzonitrile (2g) and 2,4-dichloro-3,5,6-trifluorobenzonitrile (2g')



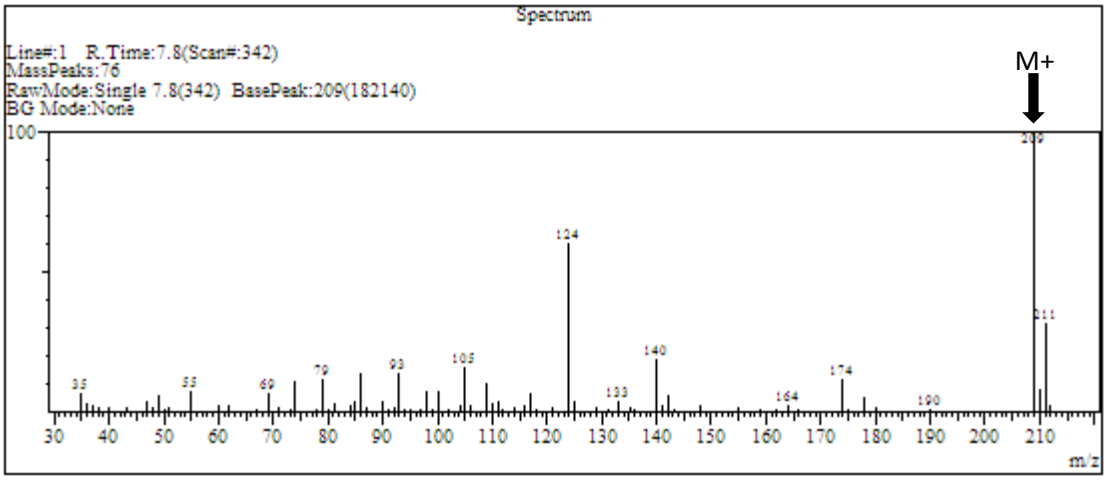
^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of isolated 4-chloro-2,3,5,6-tetrafluorobenzonitrile (2g) and 2,4-dichloro-3,5,6-trifluorobenzonitrile (2g')



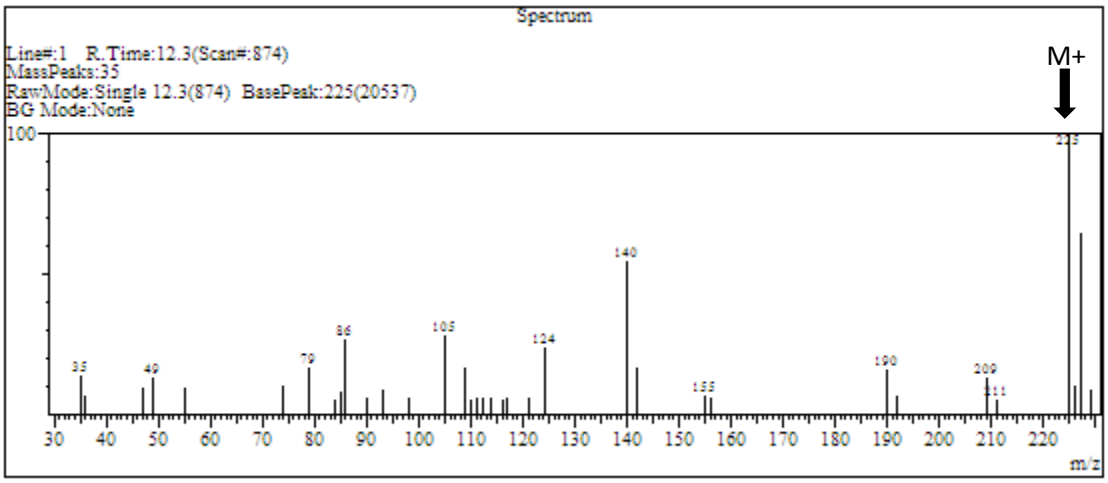
GC of 4-chloro-2,3,5,6-tetrafluorobenzonitrile (2g) and 2,4-dichloro-3,5,6-trifluorobenzonitrile (2g')



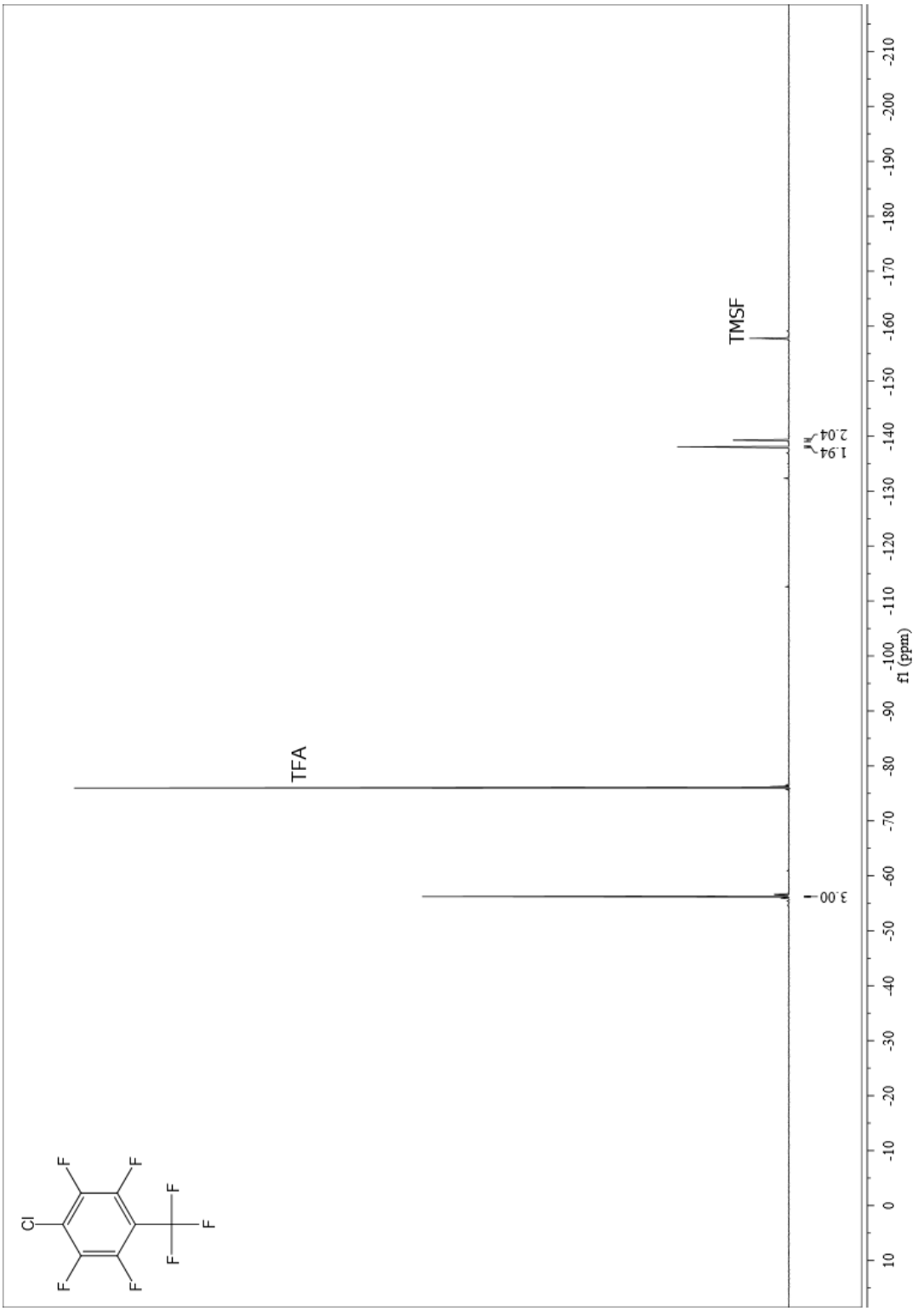
MS of 4-chloro-2,3,5,6-tetrafluorobenzonitrile (2g)



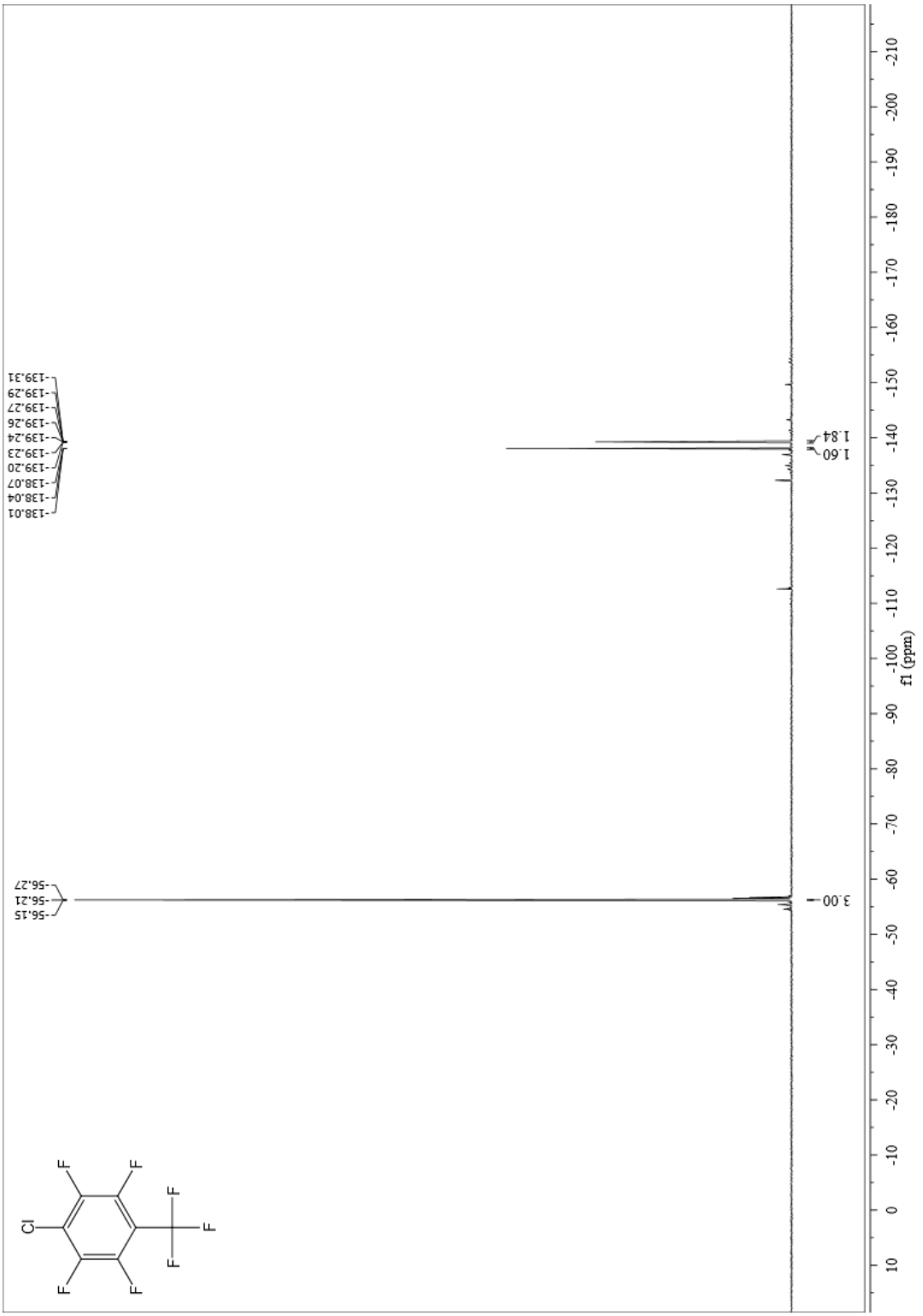
MS of 2,4-dichloro-3,5,6-trifluorobenzonitrile (2g')



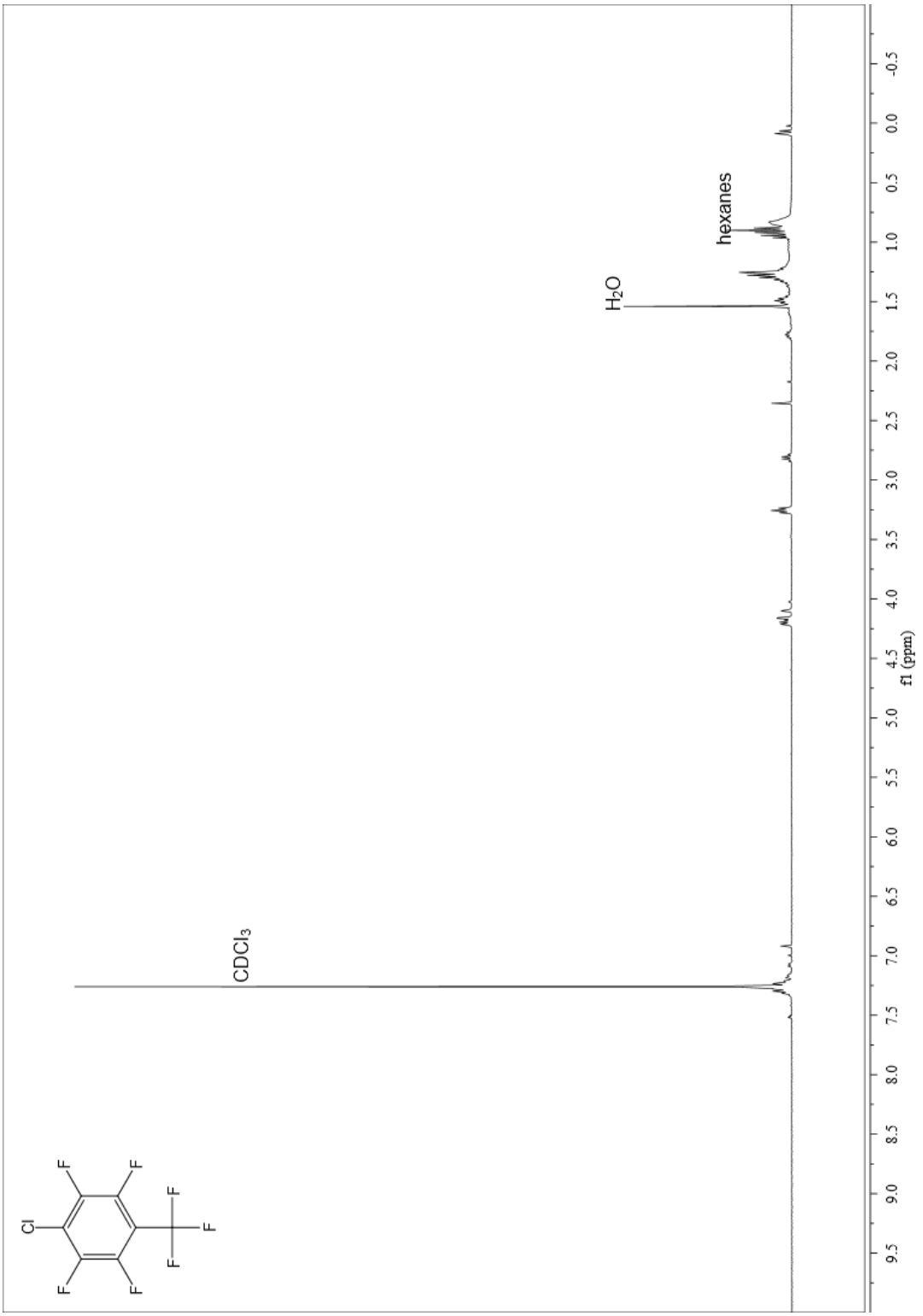
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of crude 1-chloro-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (2f) for NMR yield calculation



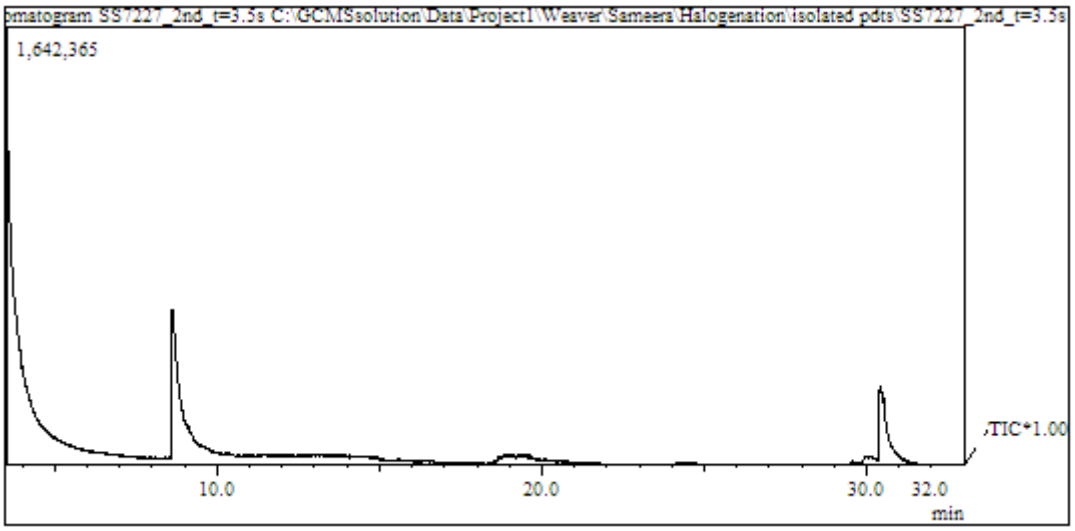
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 1-chloro-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (2f)

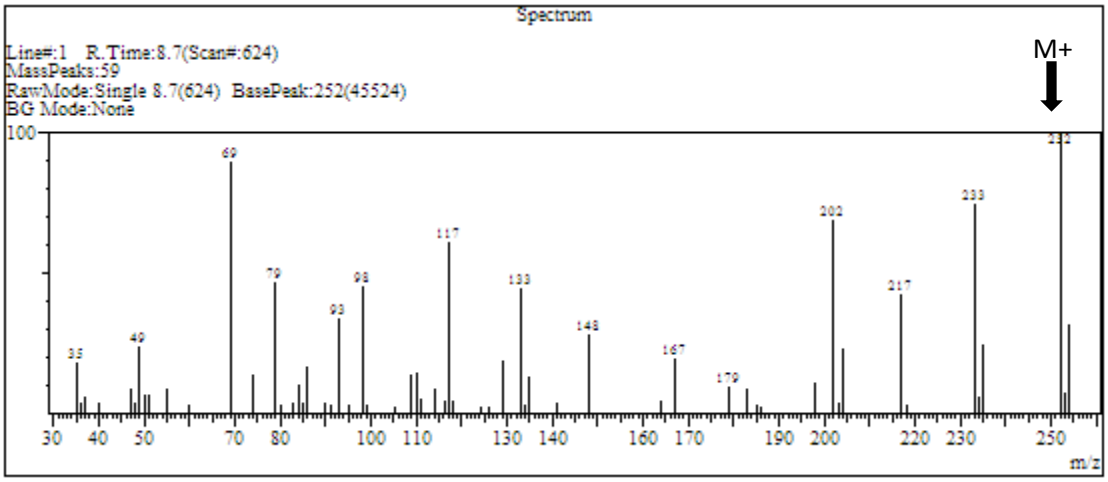


^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of 1-chloro-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (2f)

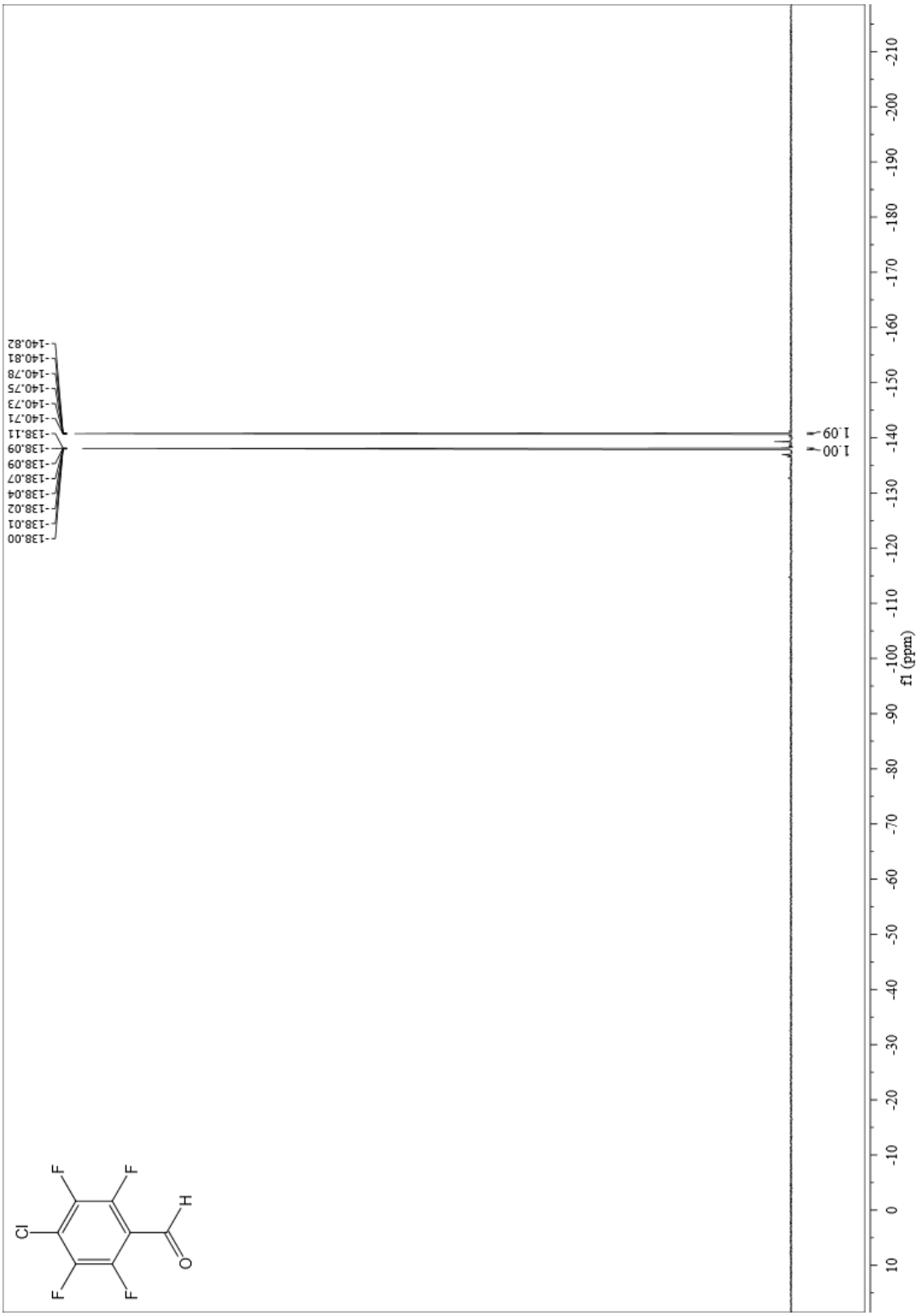


GC and MS of GC and MS of 1-chloro-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (2f)

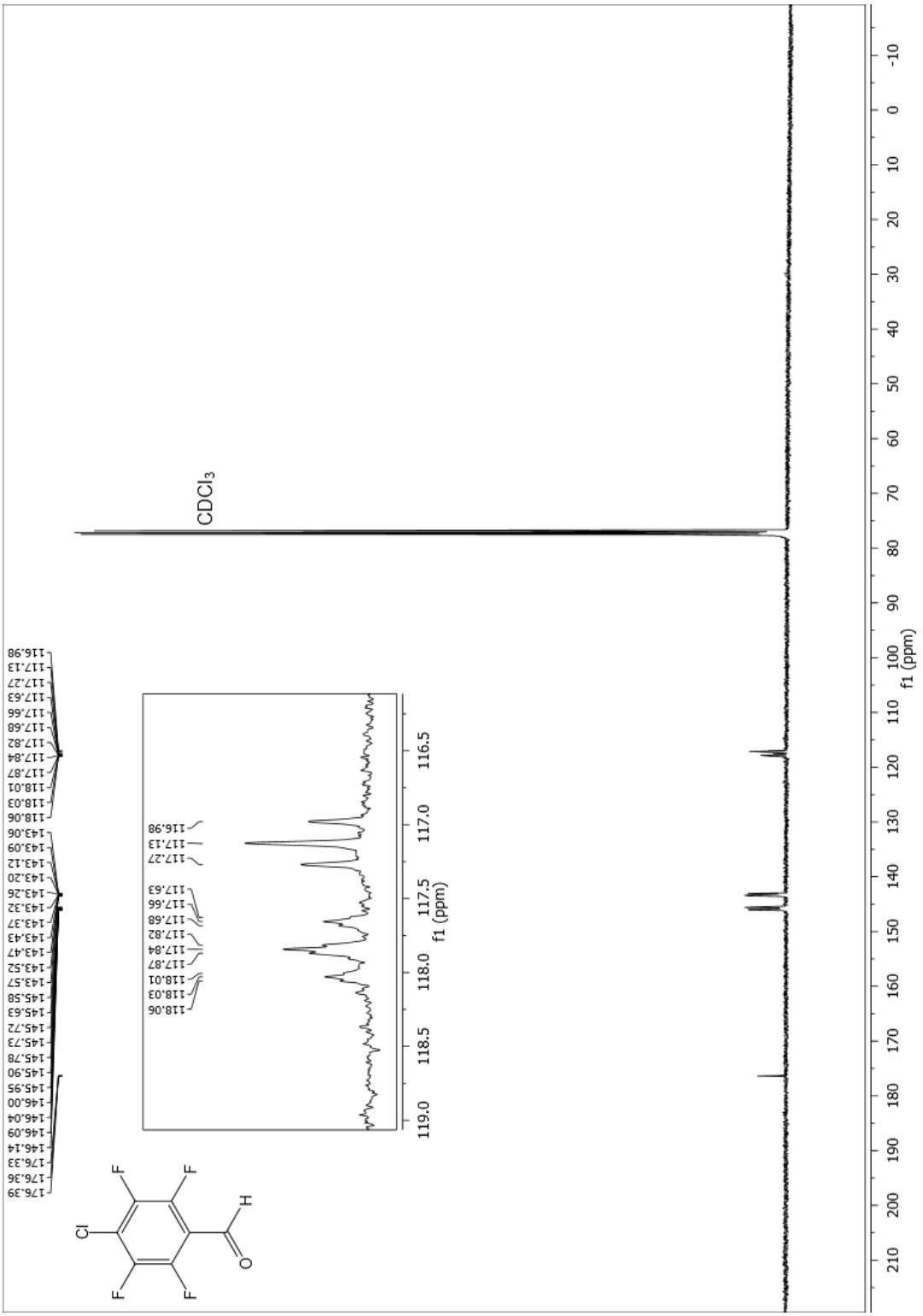




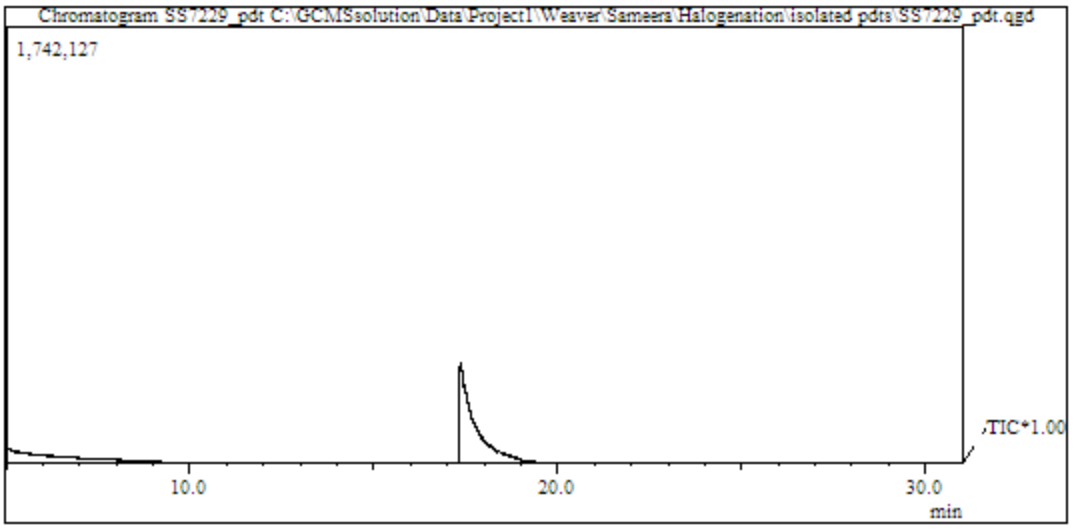
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 4-chloro-2,3,5,6-tetrafluorobenzaldehyde (2h)

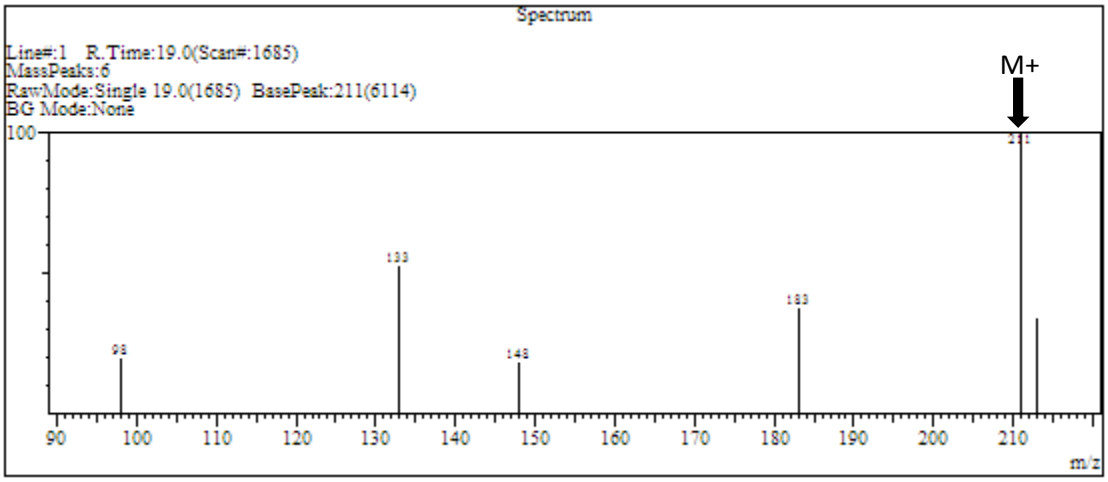


^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of isolated 4-chloro-2,3,5,6-tetrafluorobenzaldehyde (2h)

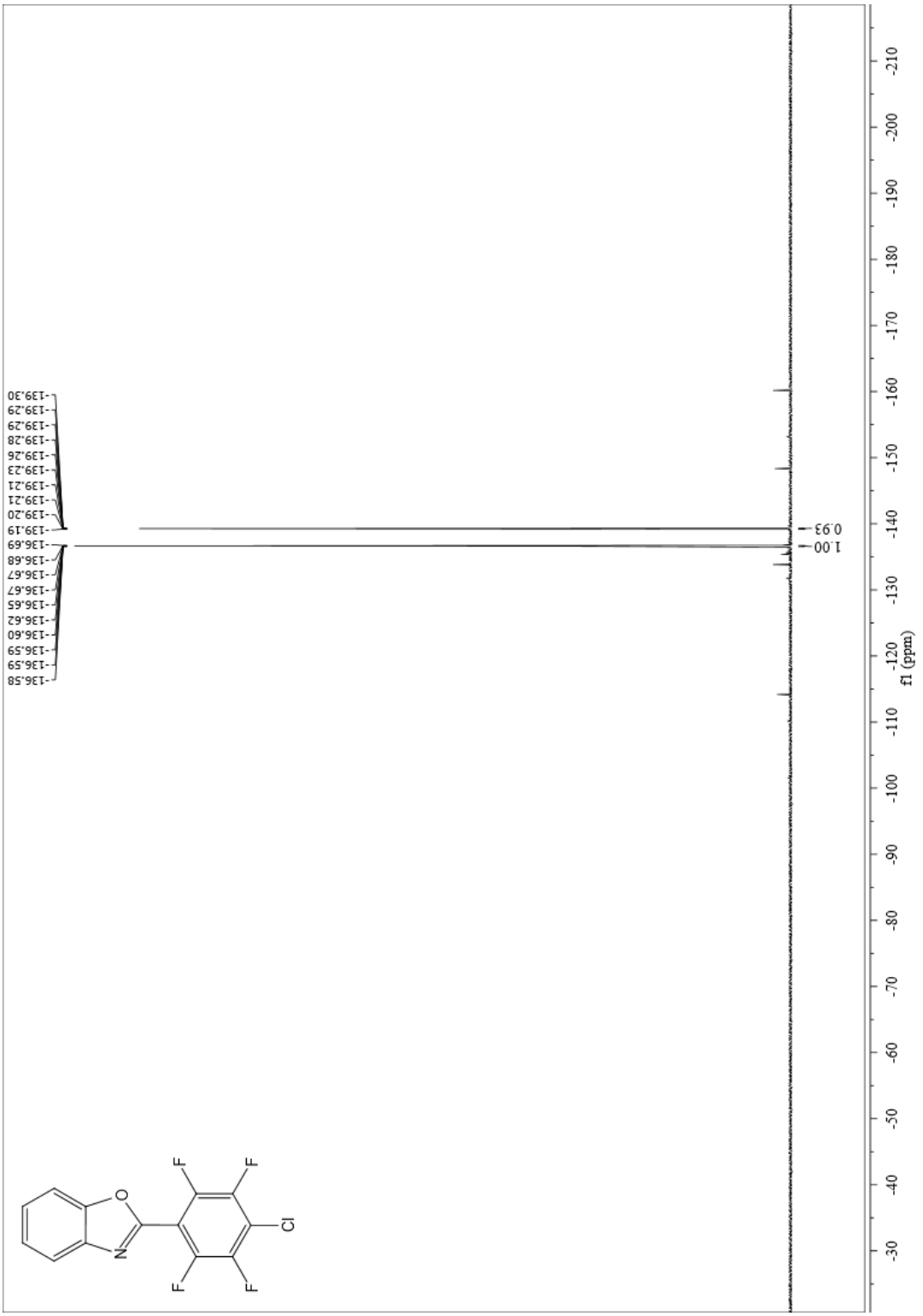


GC and MS of GC and MS of 4-chloro-2,3,5,6-tetrafluorobenzaldehyde (2h)

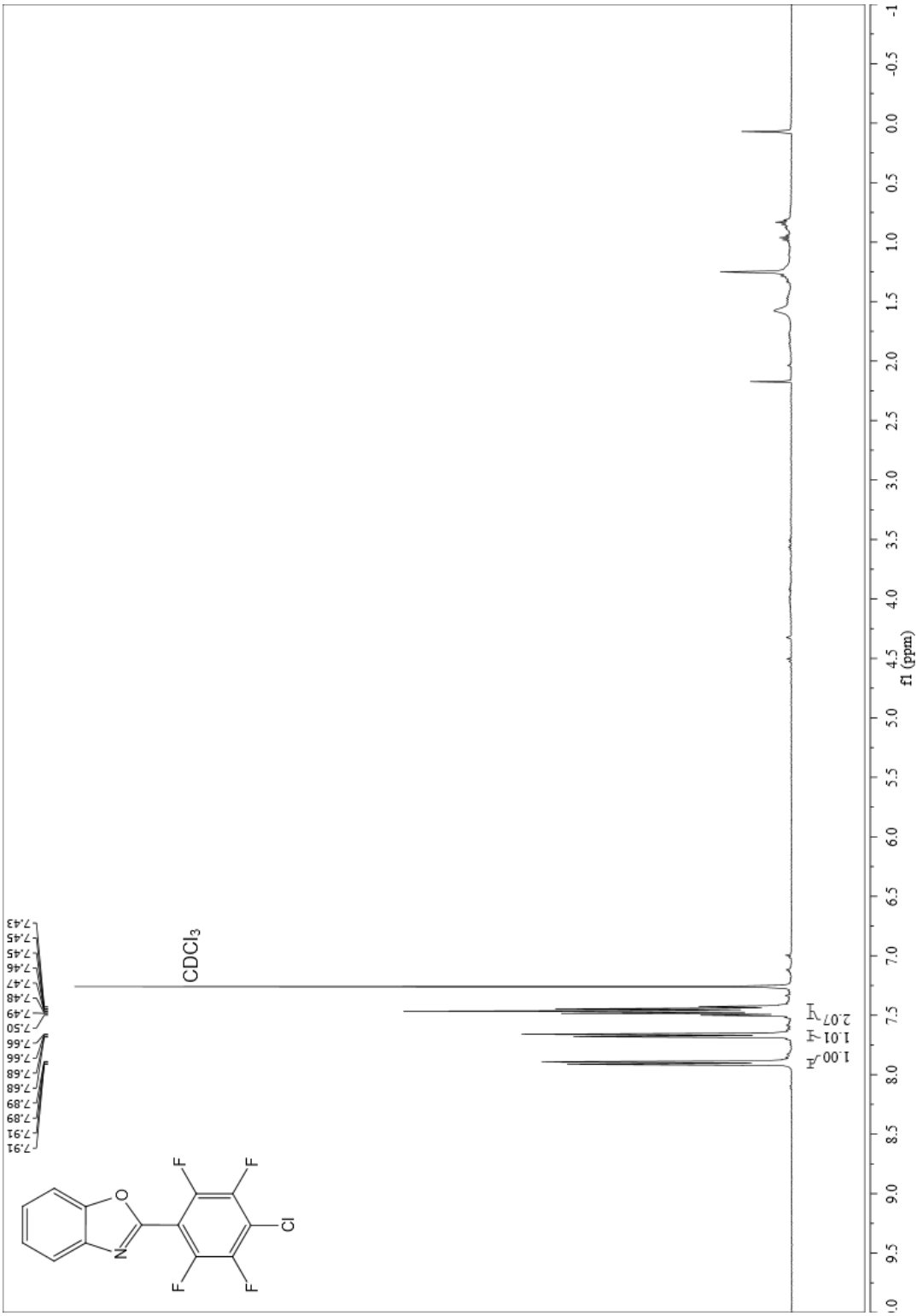




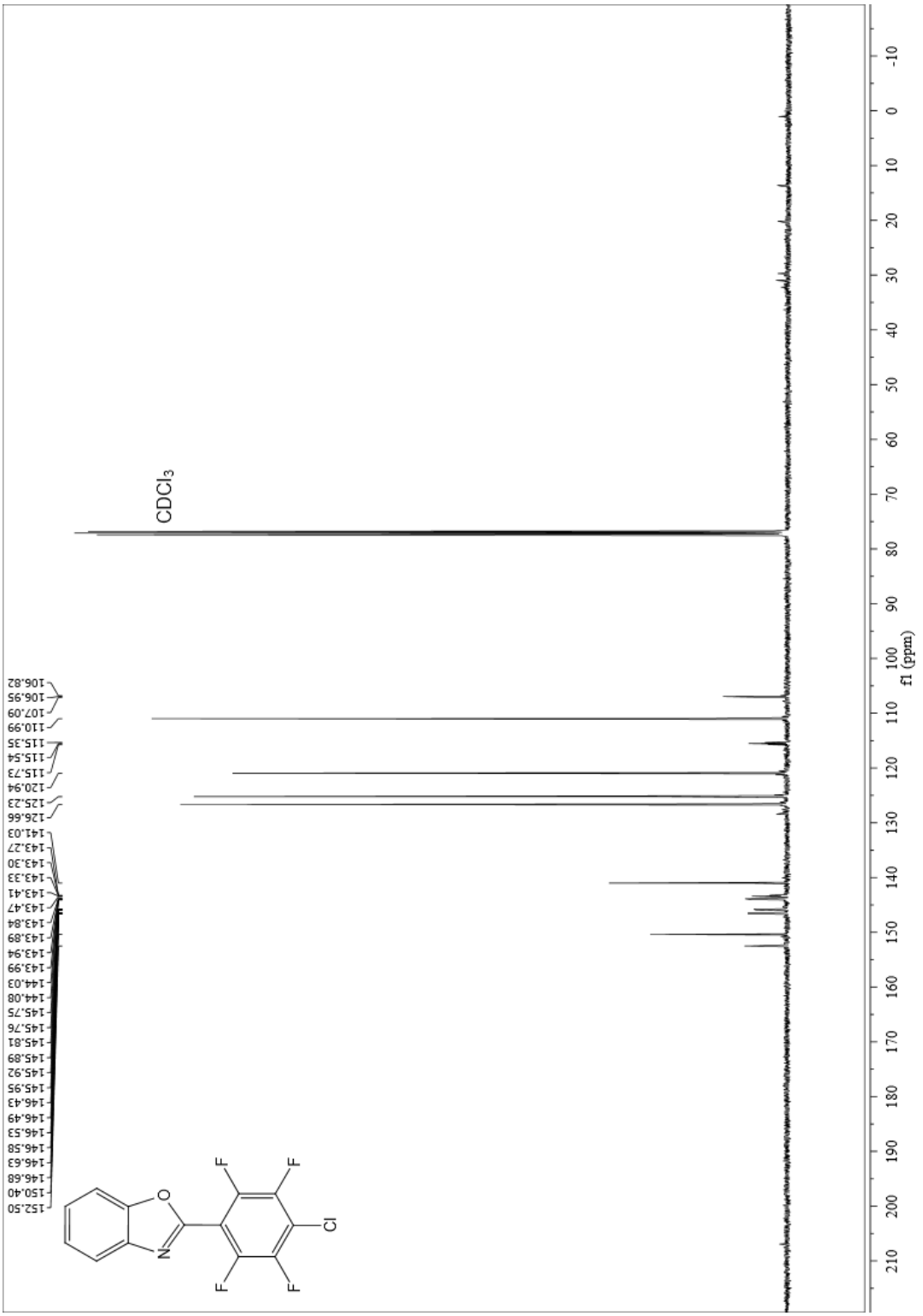
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]oxazole (2i)



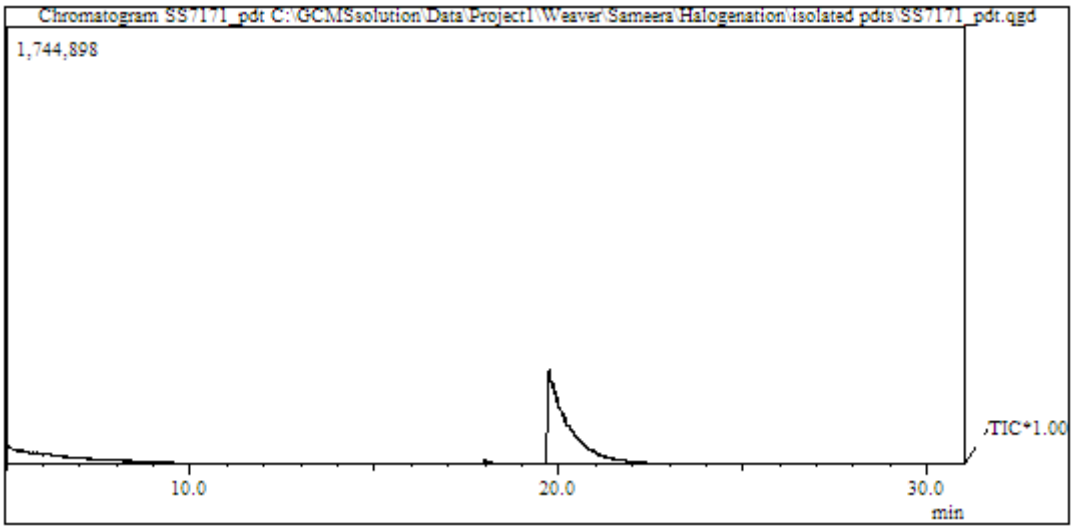
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of isolated 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]oxazole (2i)

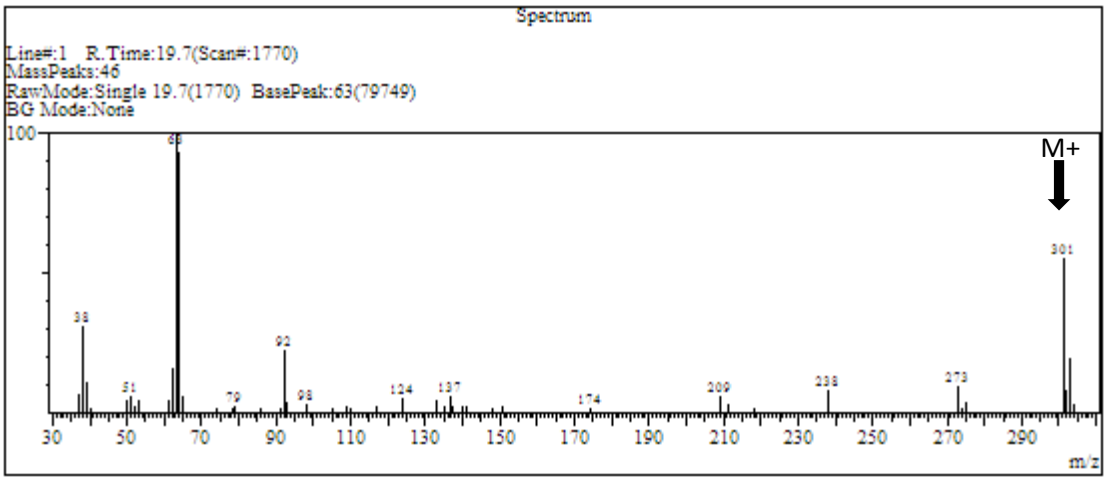


^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of isolated 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]oxazole (2i)

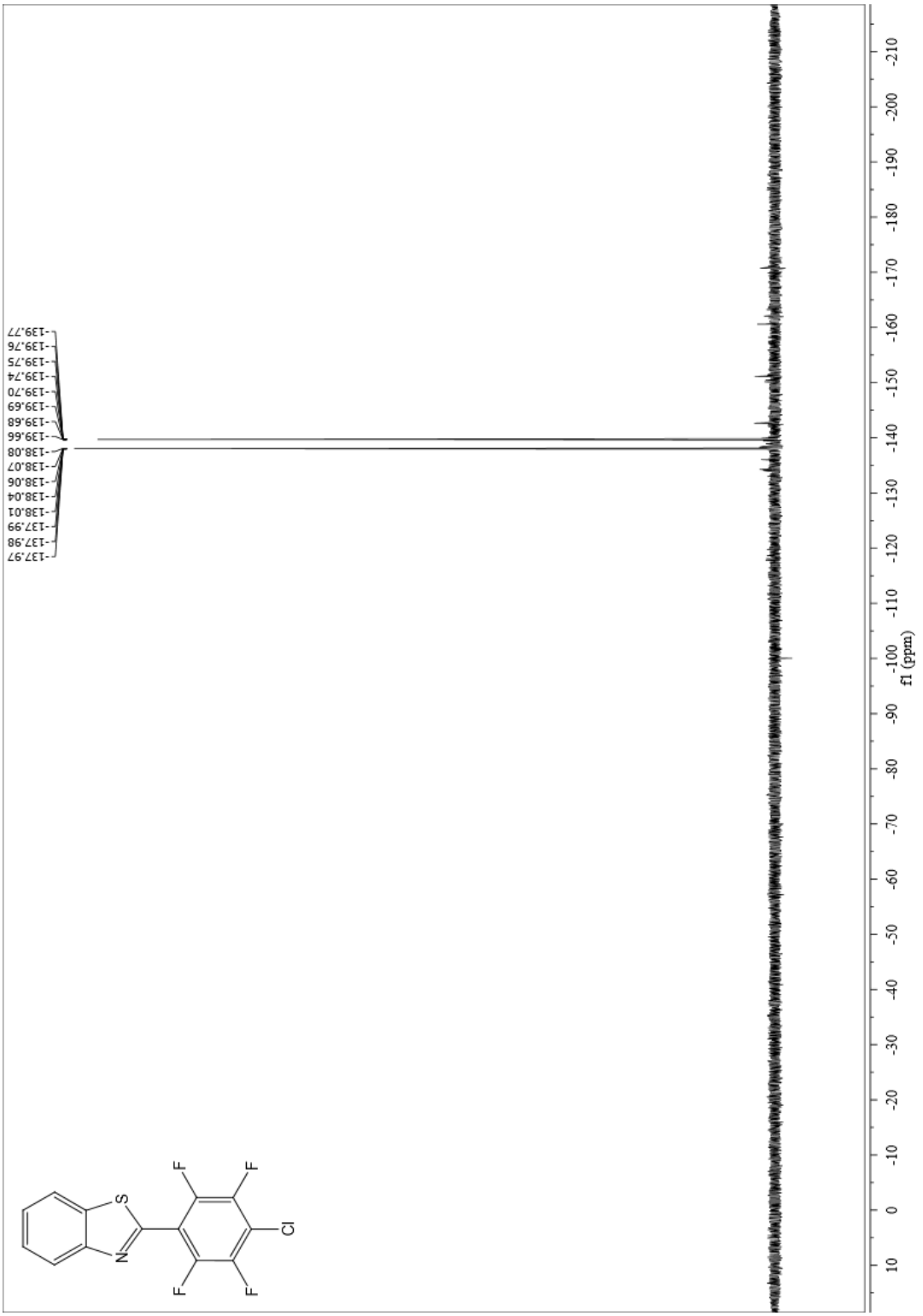


GC and MS of GC and MS of 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]oxazole (2i)

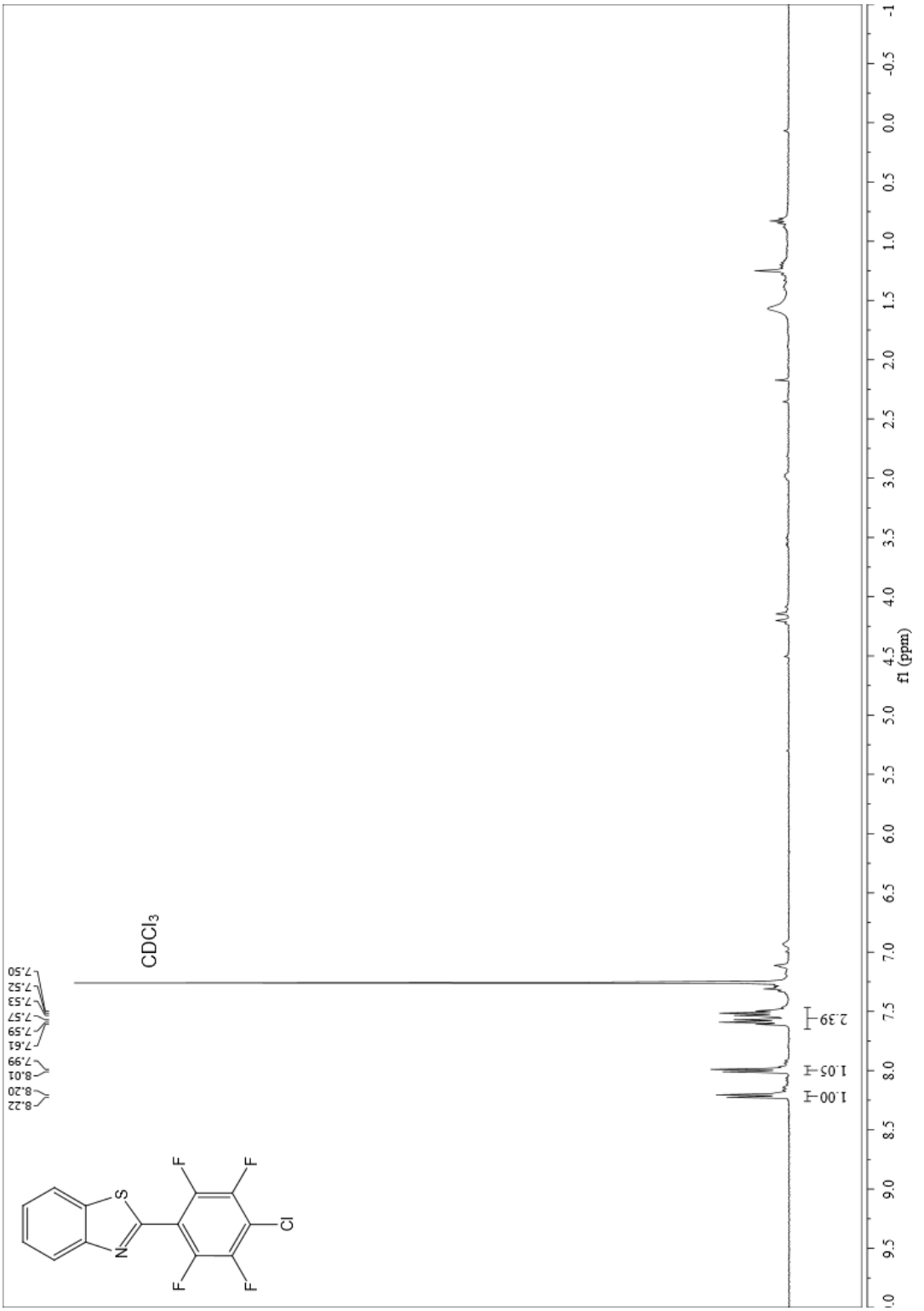




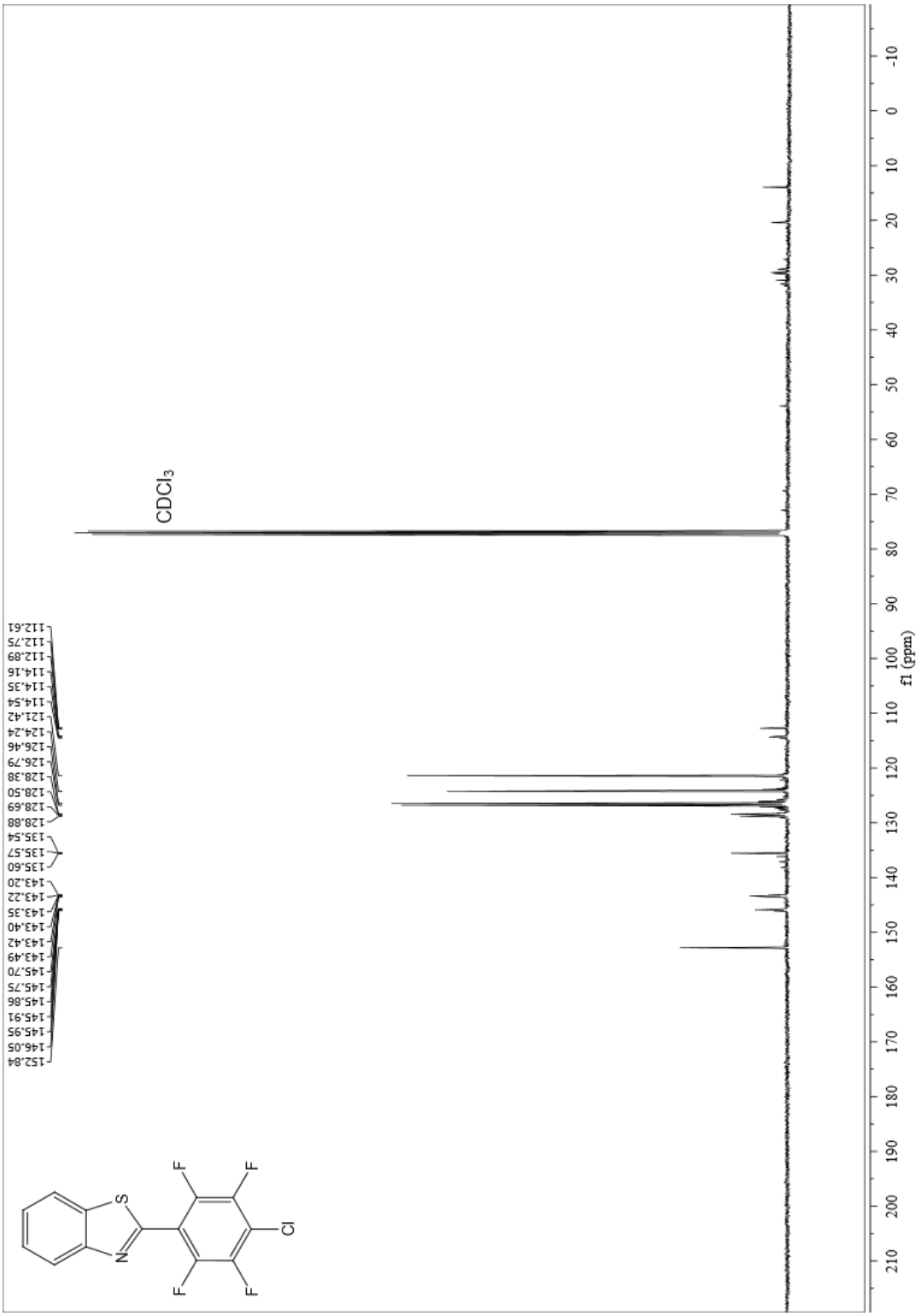
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]thiazole (2j)



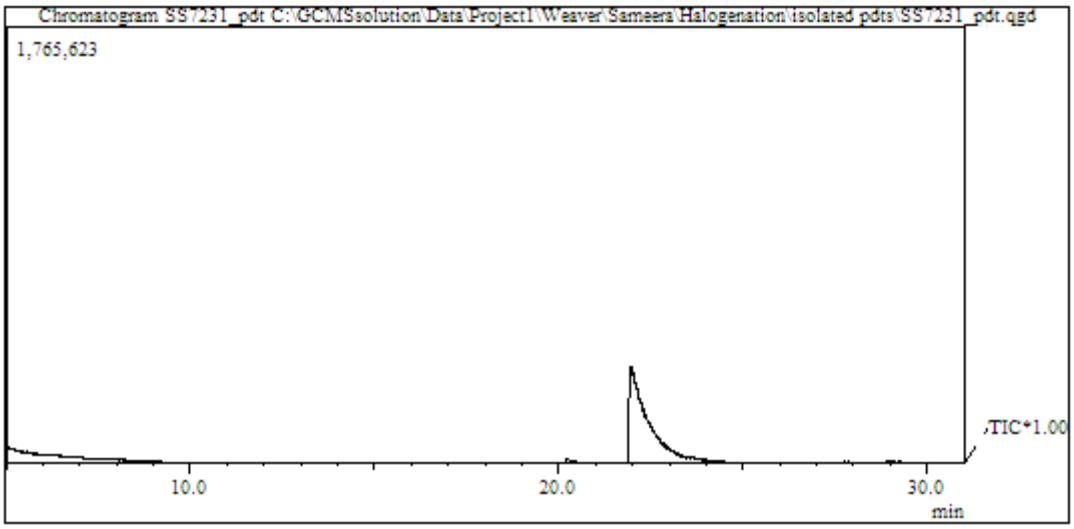
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of isolated 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]thiazole (2j)

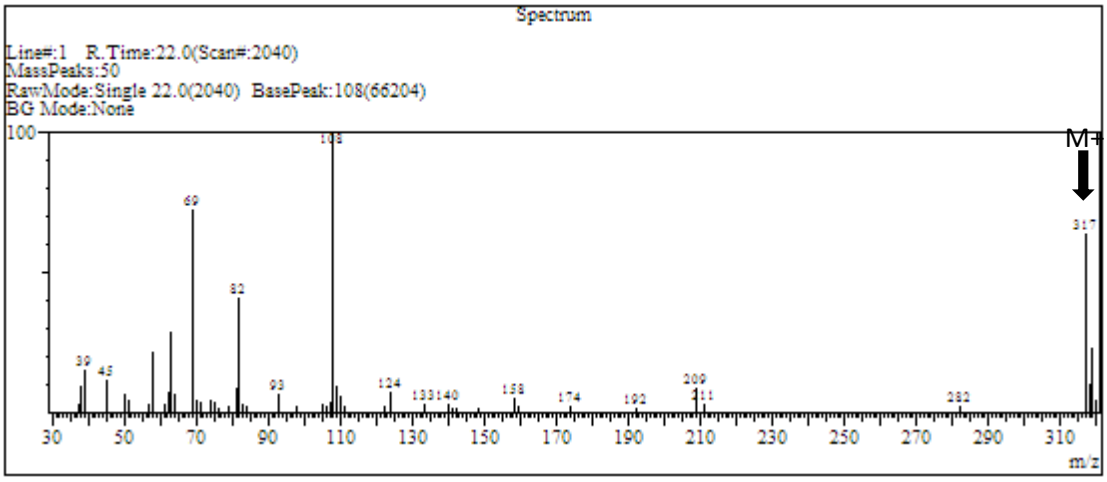


^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]thiazole (2j)

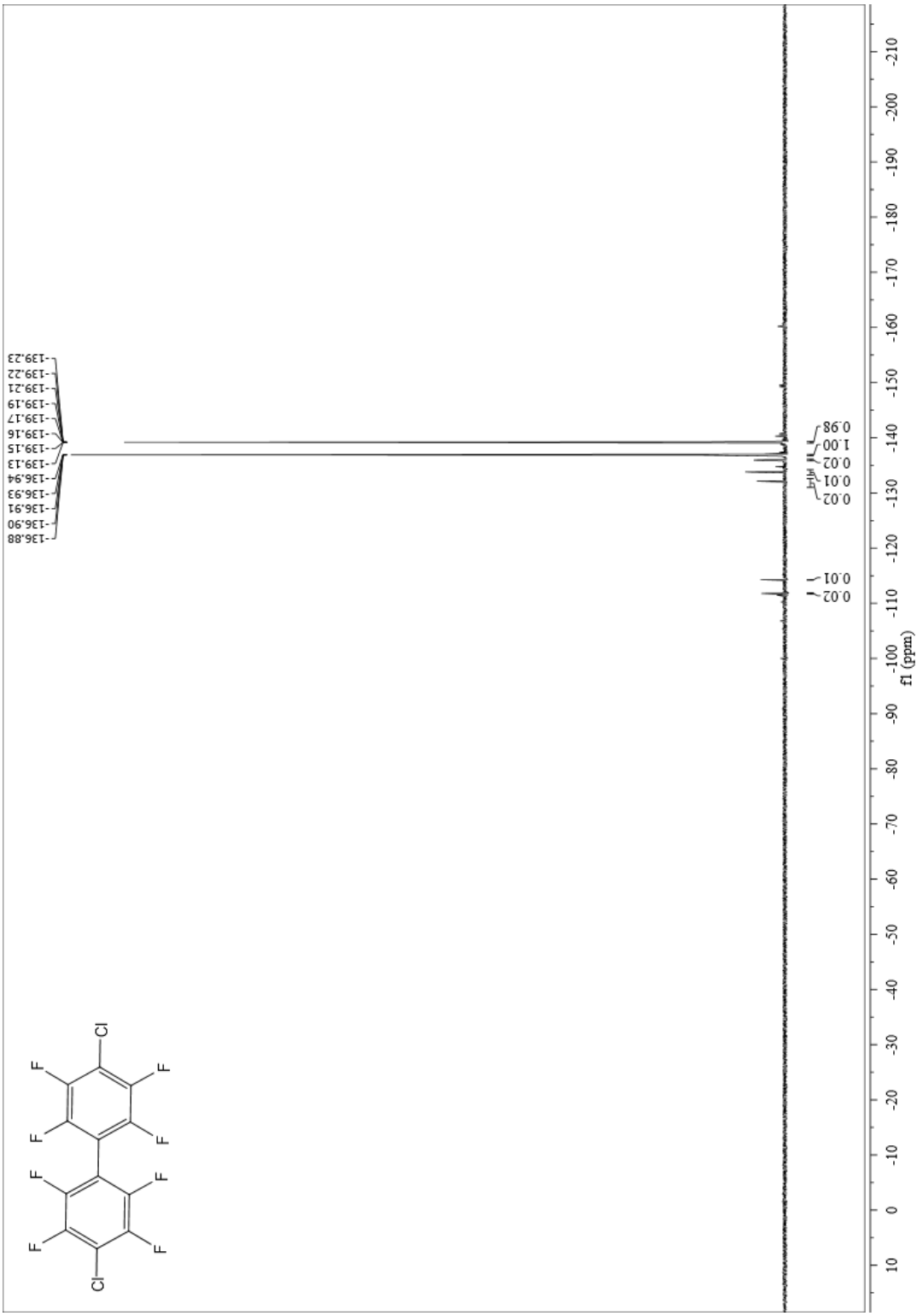


GC and MS of GC and MS of 2-(4-chloro-2,3,5,6-tetrafluorophenyl)benzo[*d*]thiazole (2j)

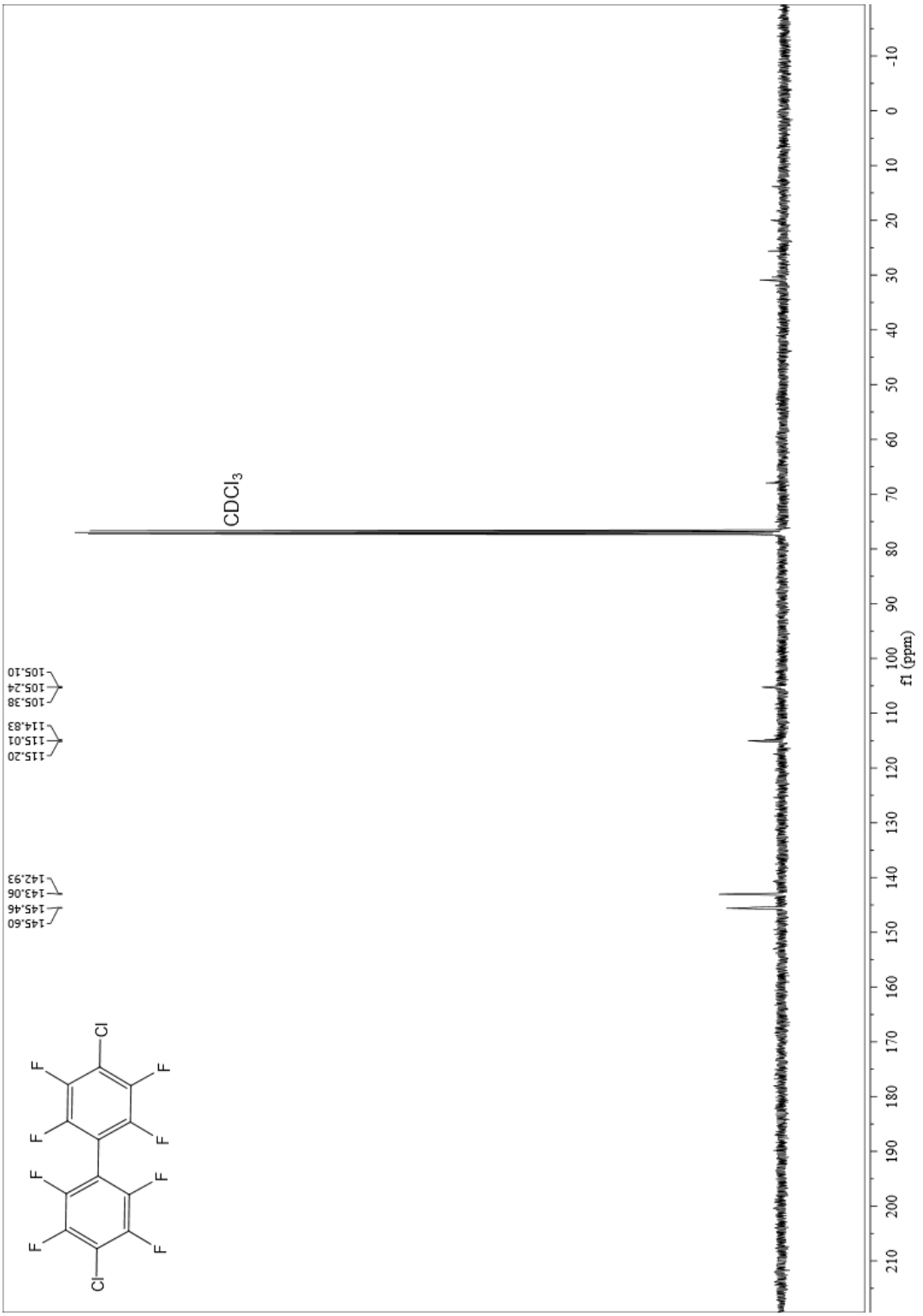




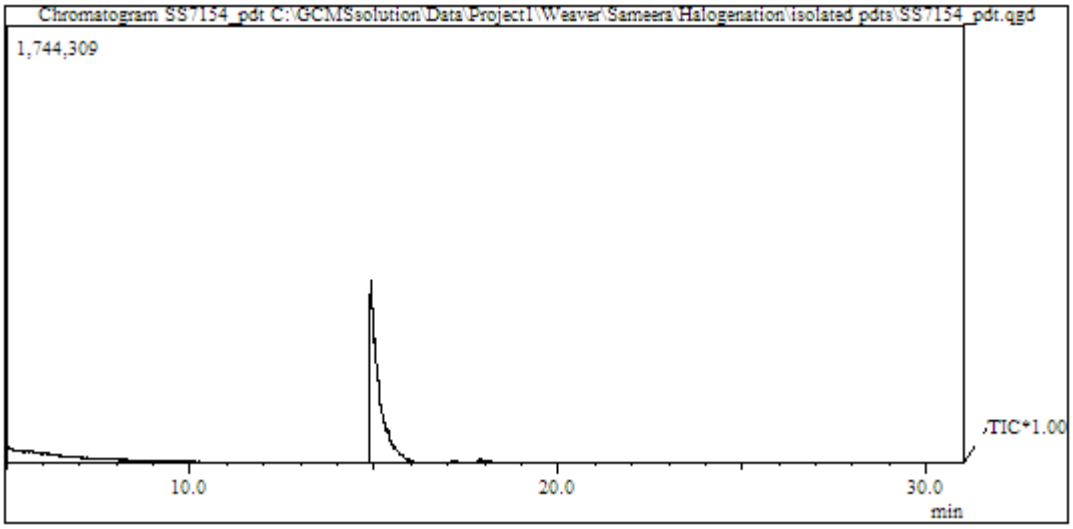
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of isolated 4,4'-dichloro-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (2k)

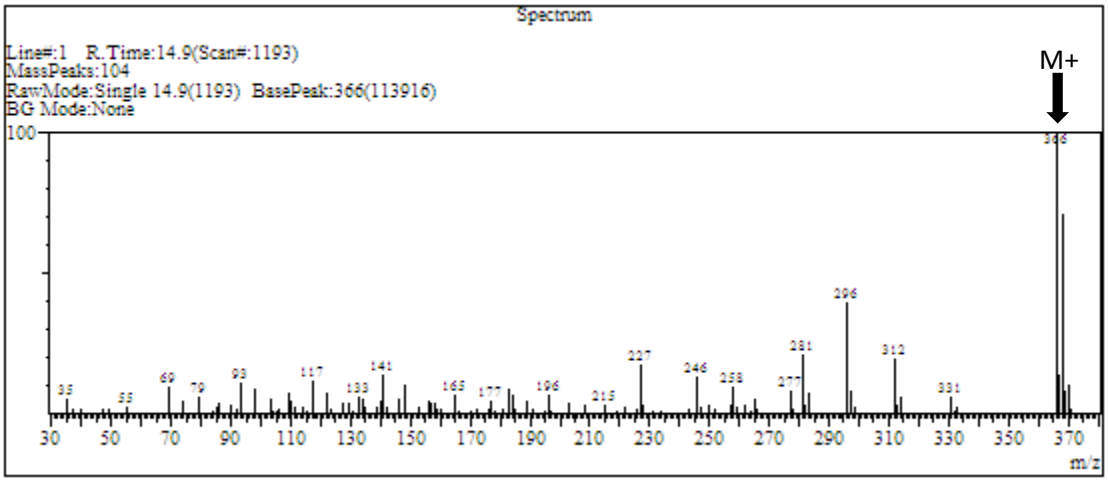


^{1}3C NMR (400 MHz, Chloroform-*d* at rt) spectrum of isolated 4,4'-dichloro-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (2k)

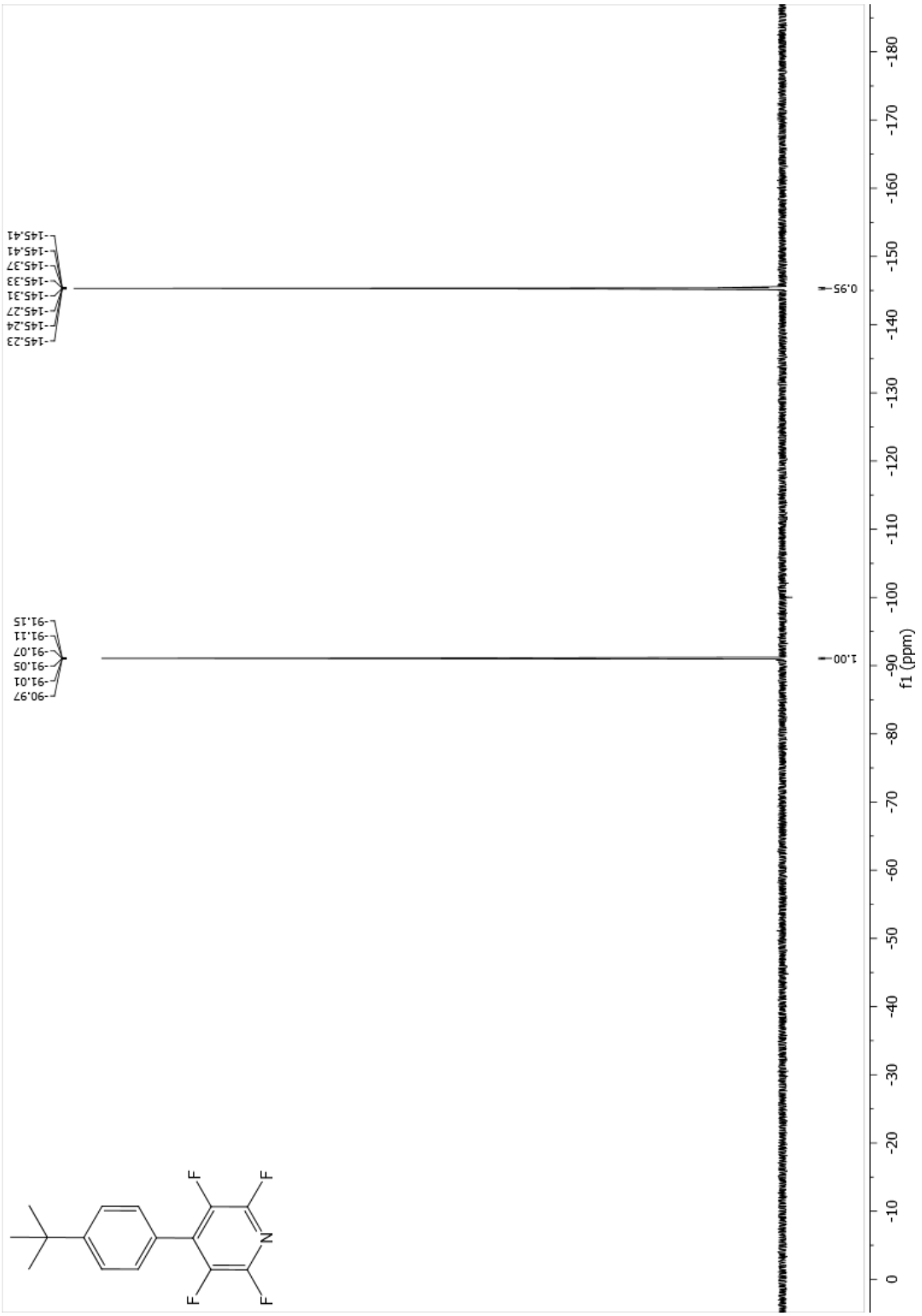


GC and MS of GC and MS of 4,4'-dichloro-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (2k)

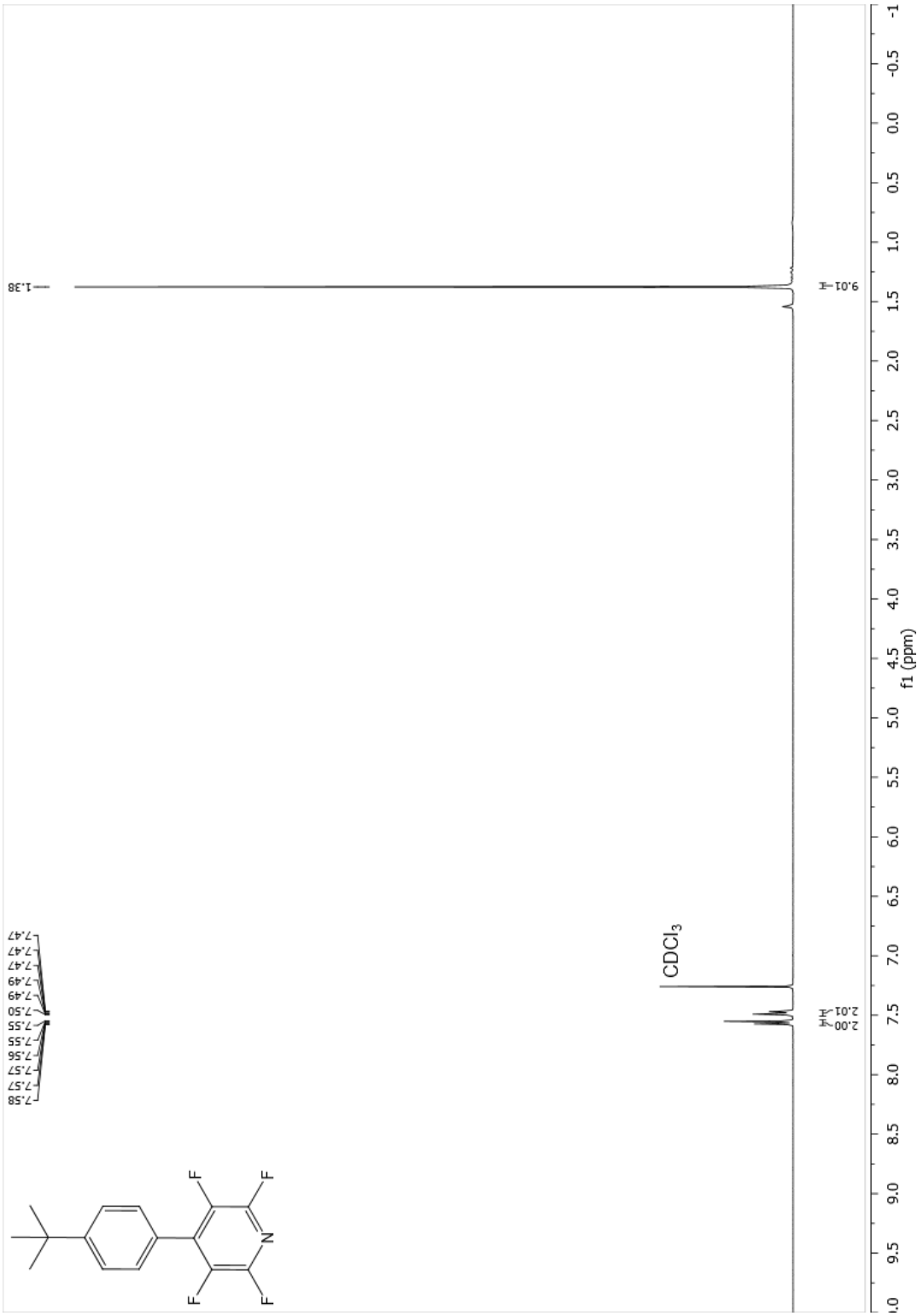




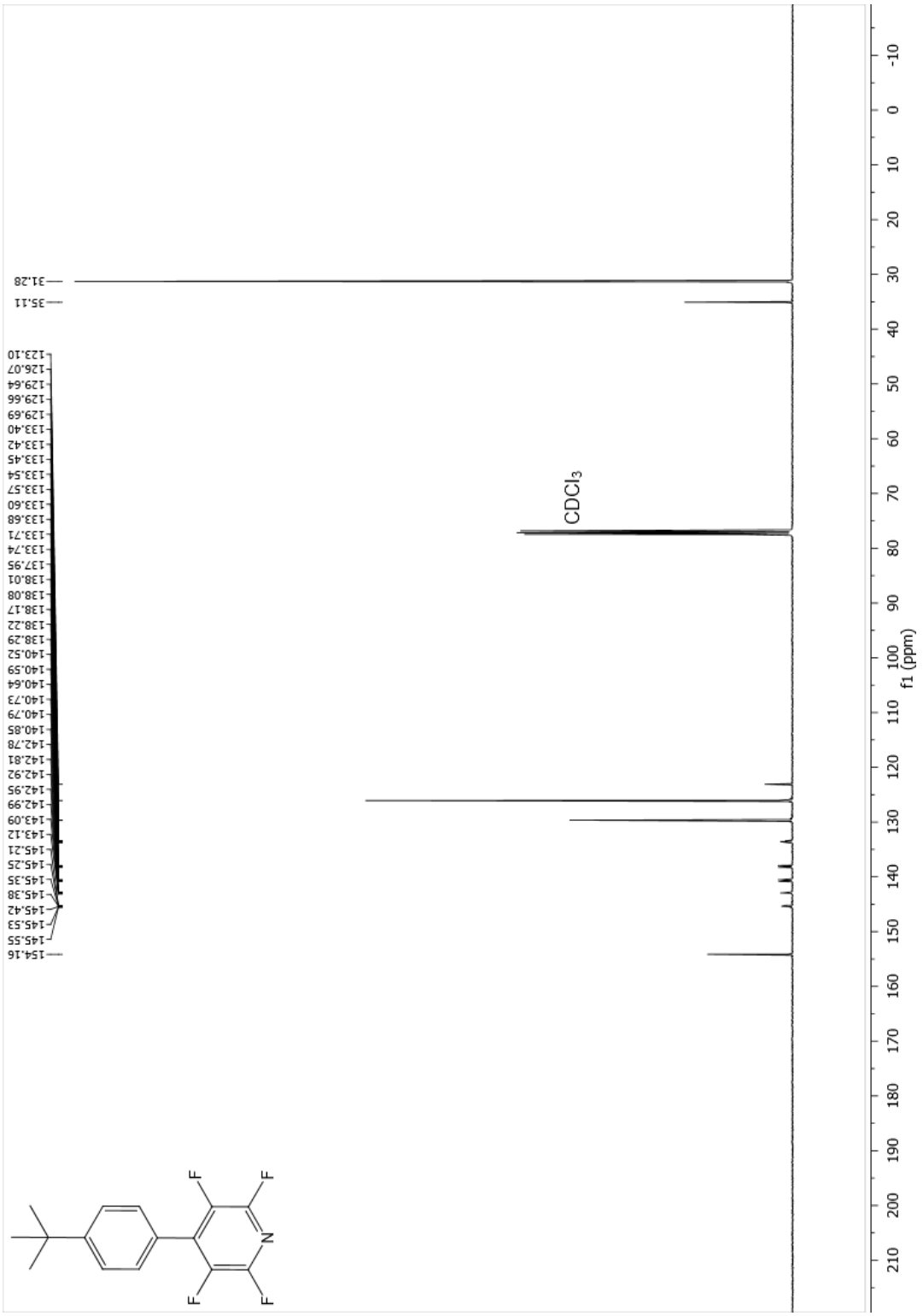
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of 4-(4-(*tert*-butyl)phenyl)-2,3,5,6-tetrafluoropyridine (5a)



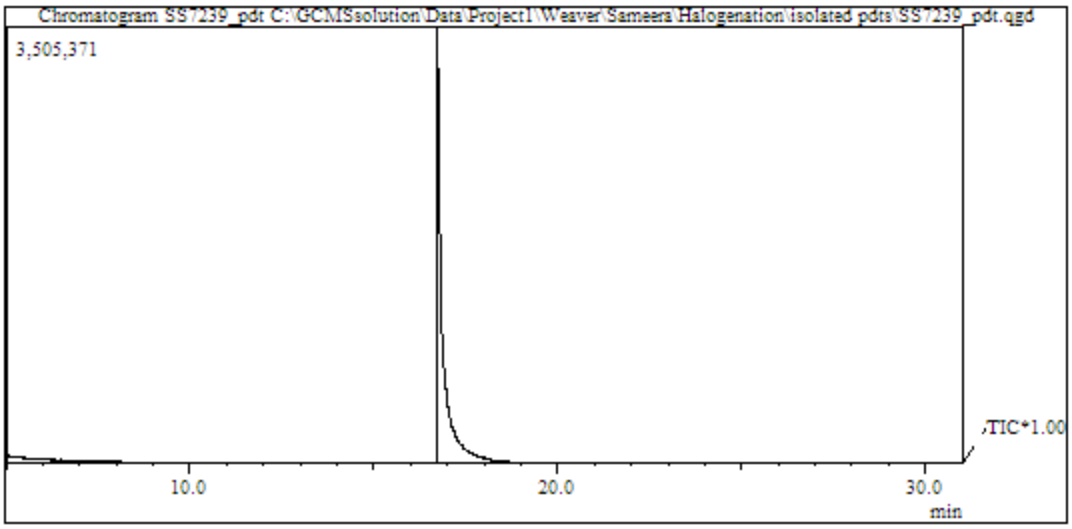
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of 4-(4-(*tert*-butyl)phenyl)-2,3,5,6-tetrafluoropyridine (5a)

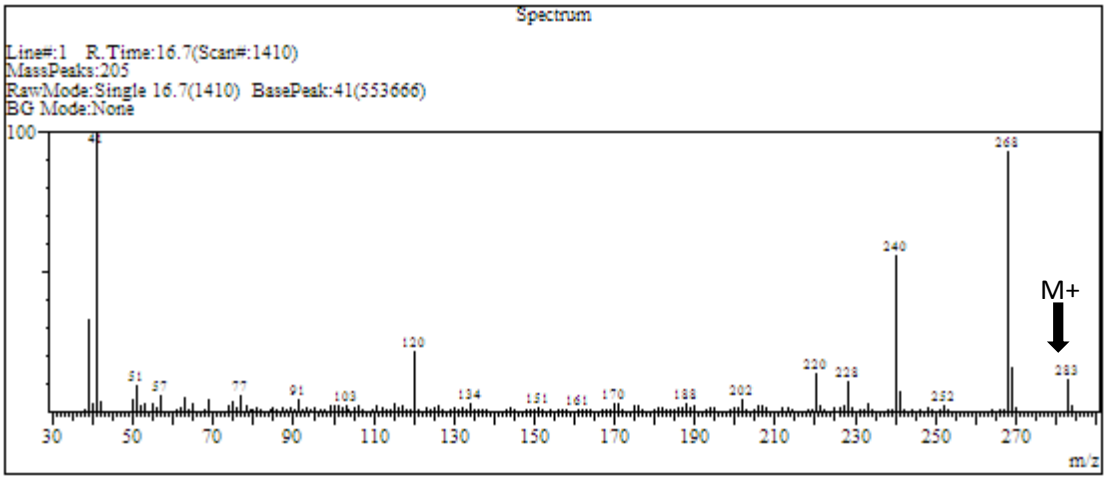


^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of 4-(4-(*tert*-butyl)phenyl)-2,3,5,6-tetrafluoropyridine (5a)

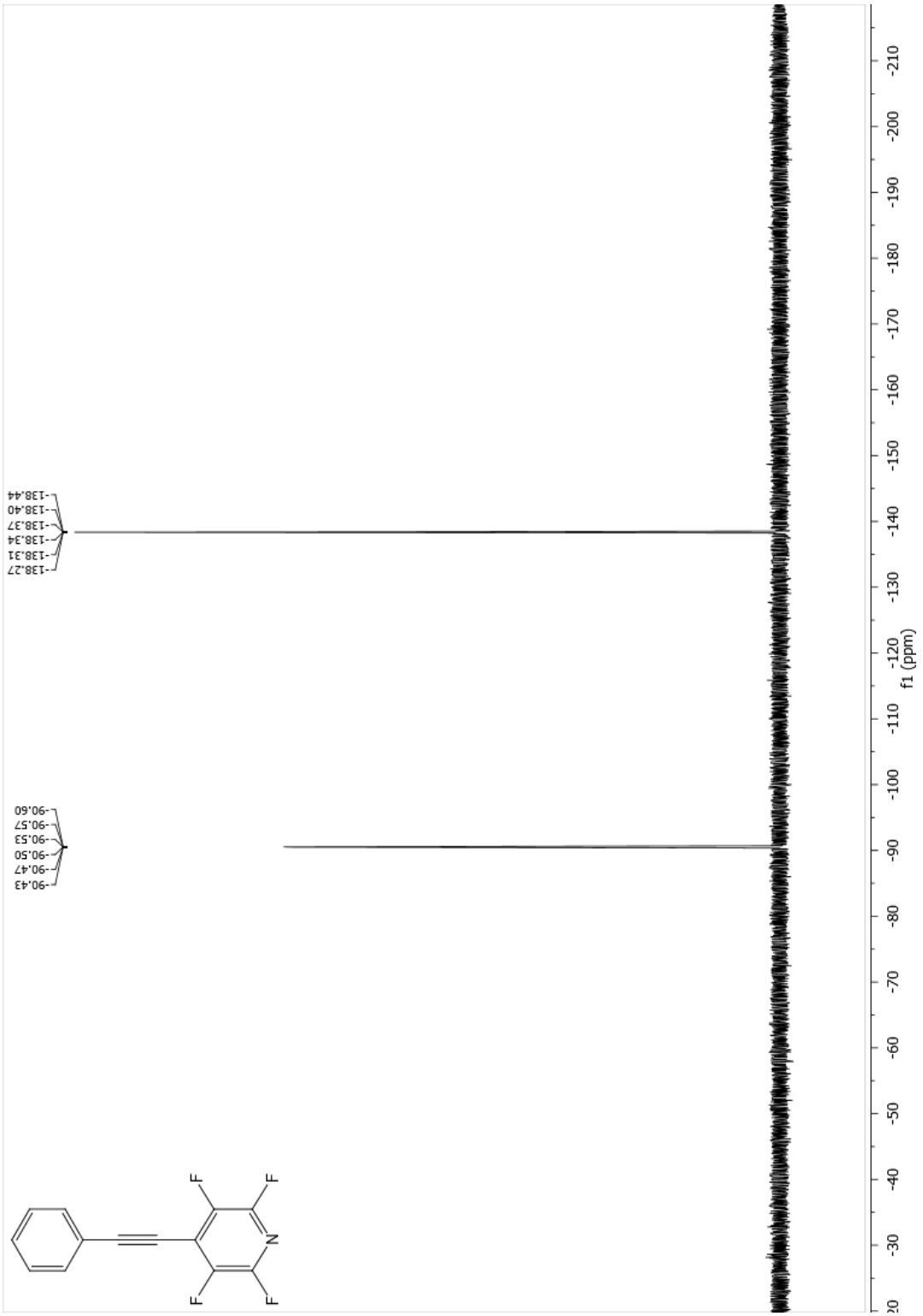


GC and MS of GC and MS of 4-(4-(*tert*-butyl)phenyl)-2,3,5,6-tetrafluoropyridine (5a)

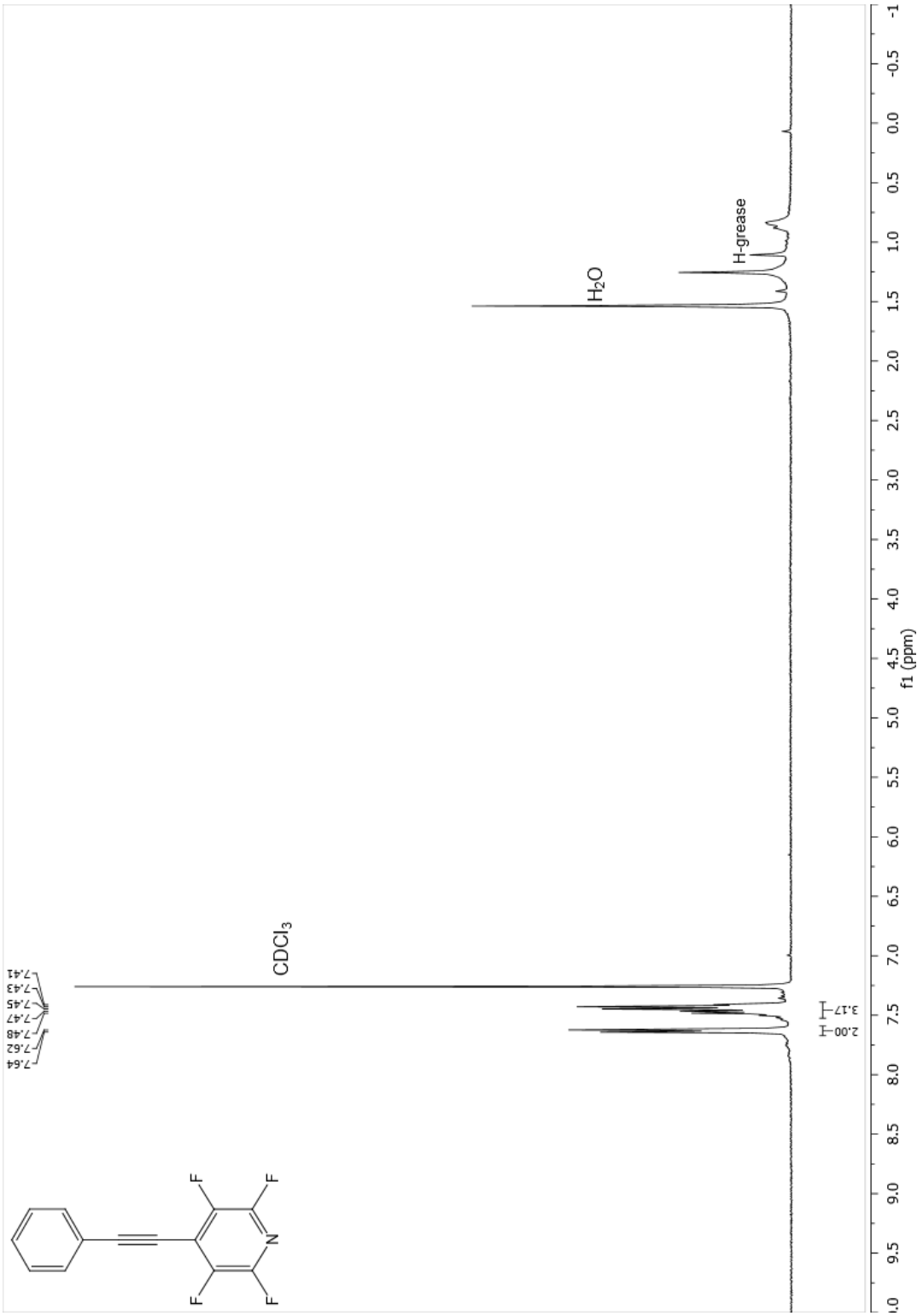




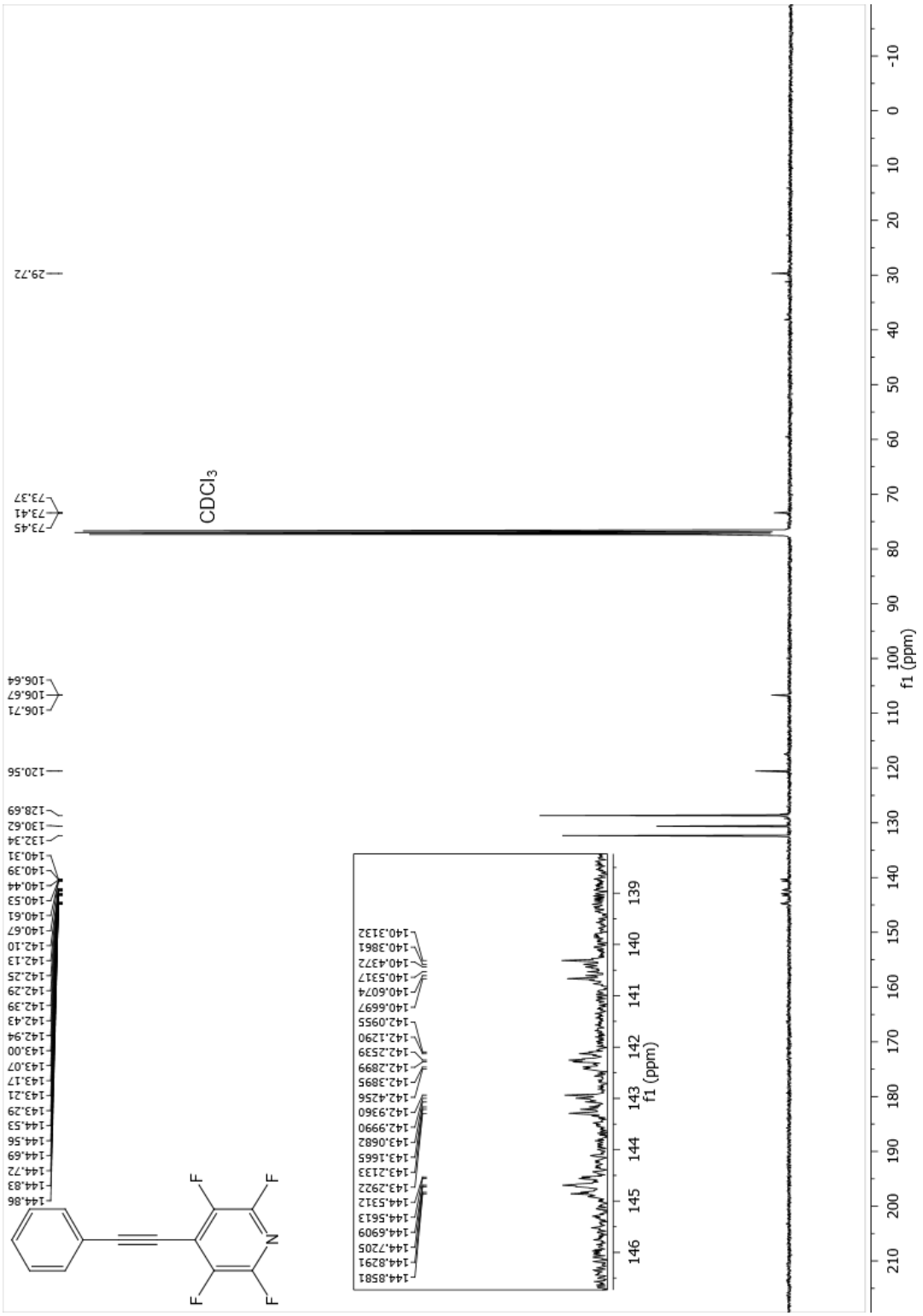
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of 2,3,5,6-tetrafluoro-4-(phenylethynyl)pyridine (5b)



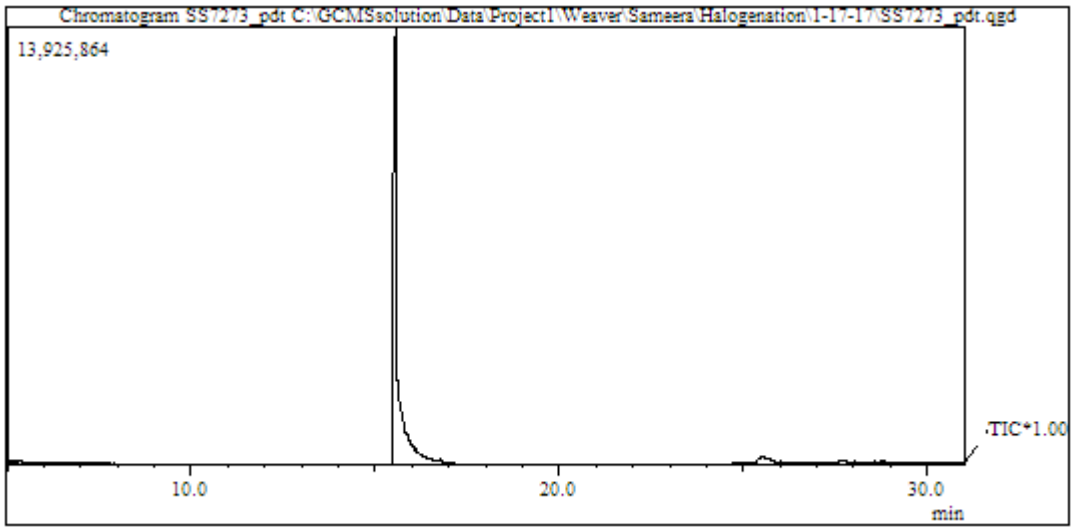
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of 2,3,5,6-tetrafluoro-4-(phenylethynyl)pyridine (5b)

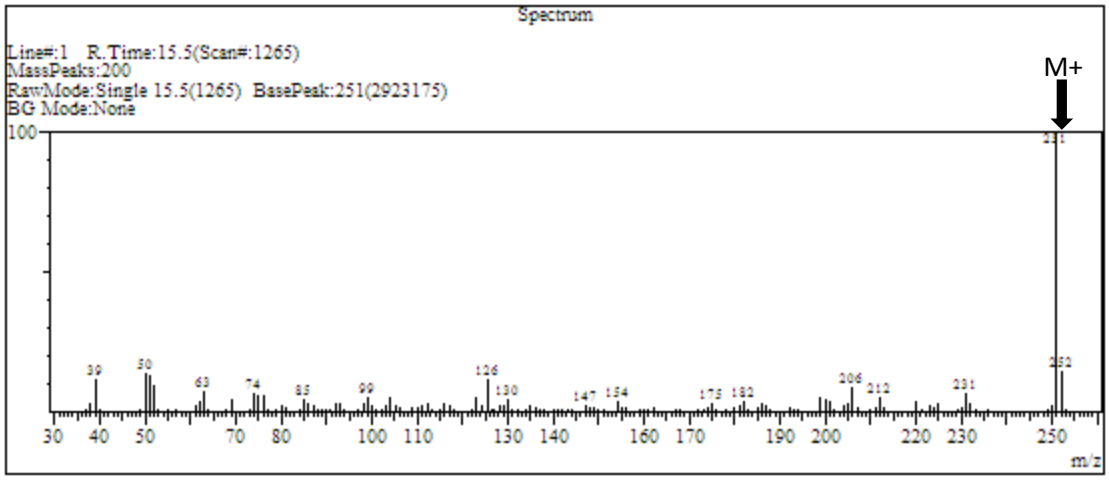


^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of 2,3,5,6-tetrafluoro-4-(phenylethynyl)pyridine (5b)

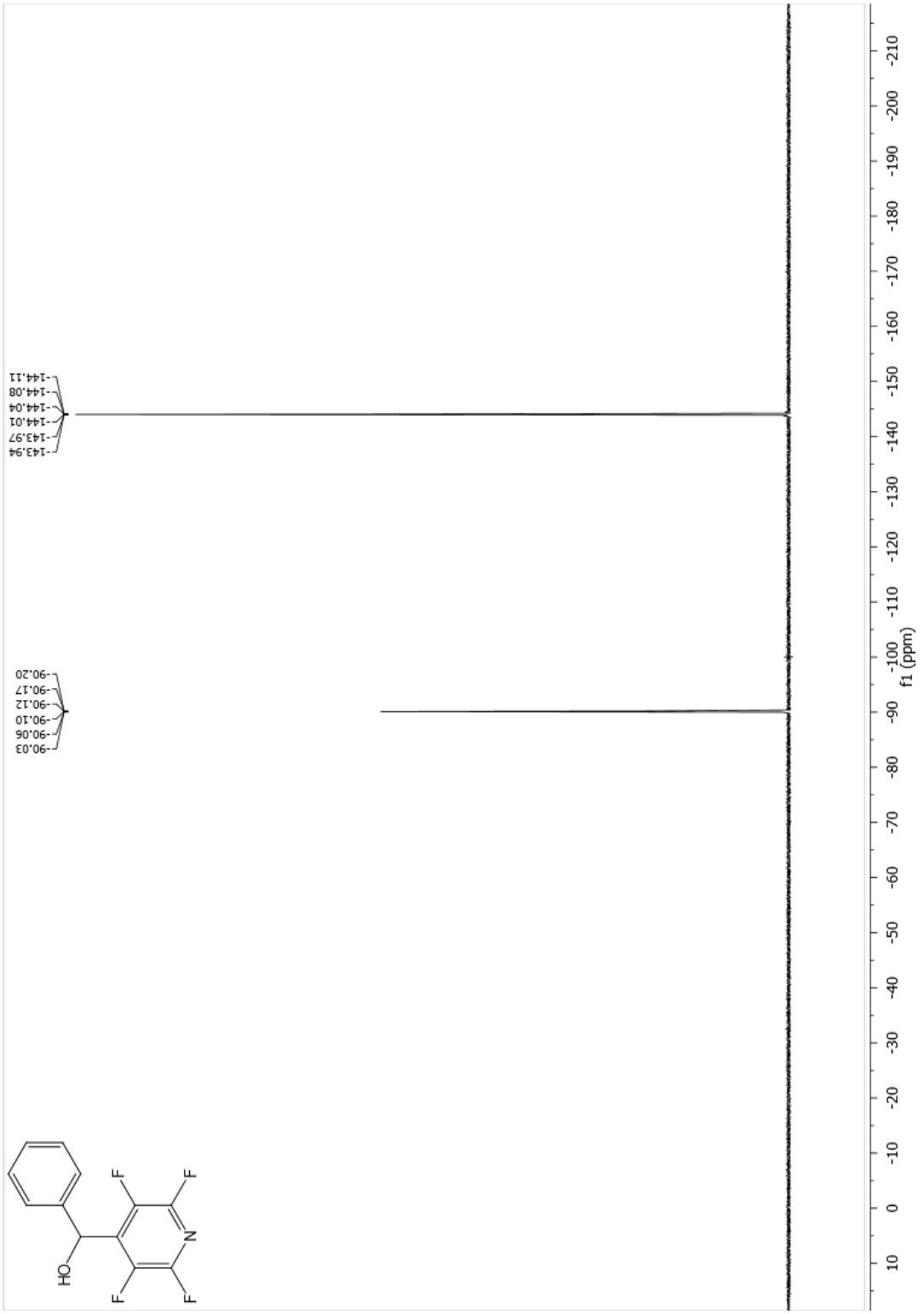


GC and MS of GC and MS of 2,3,5,6-tetrafluoro-4-(phenylethynyl)pyridine (5b)

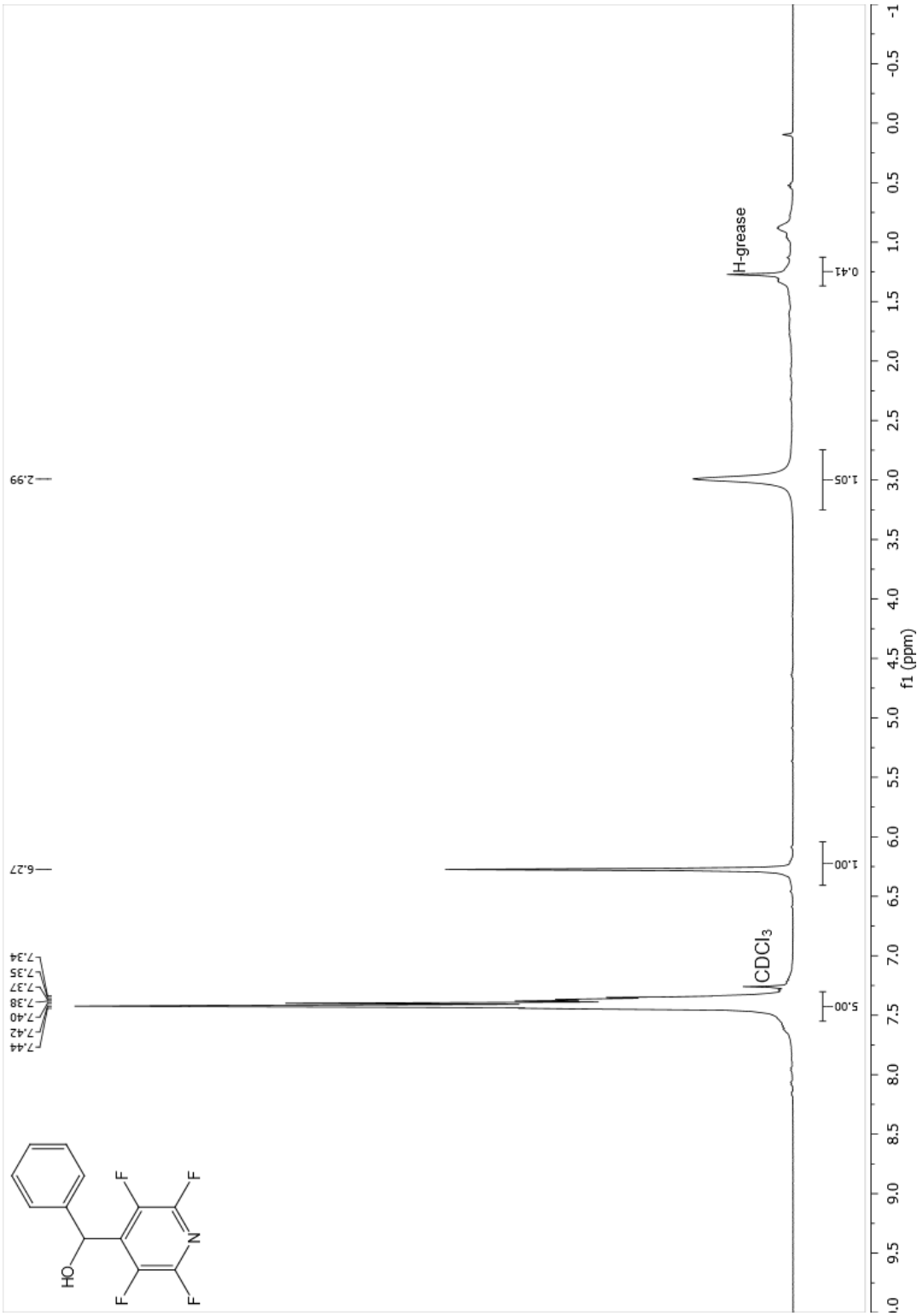




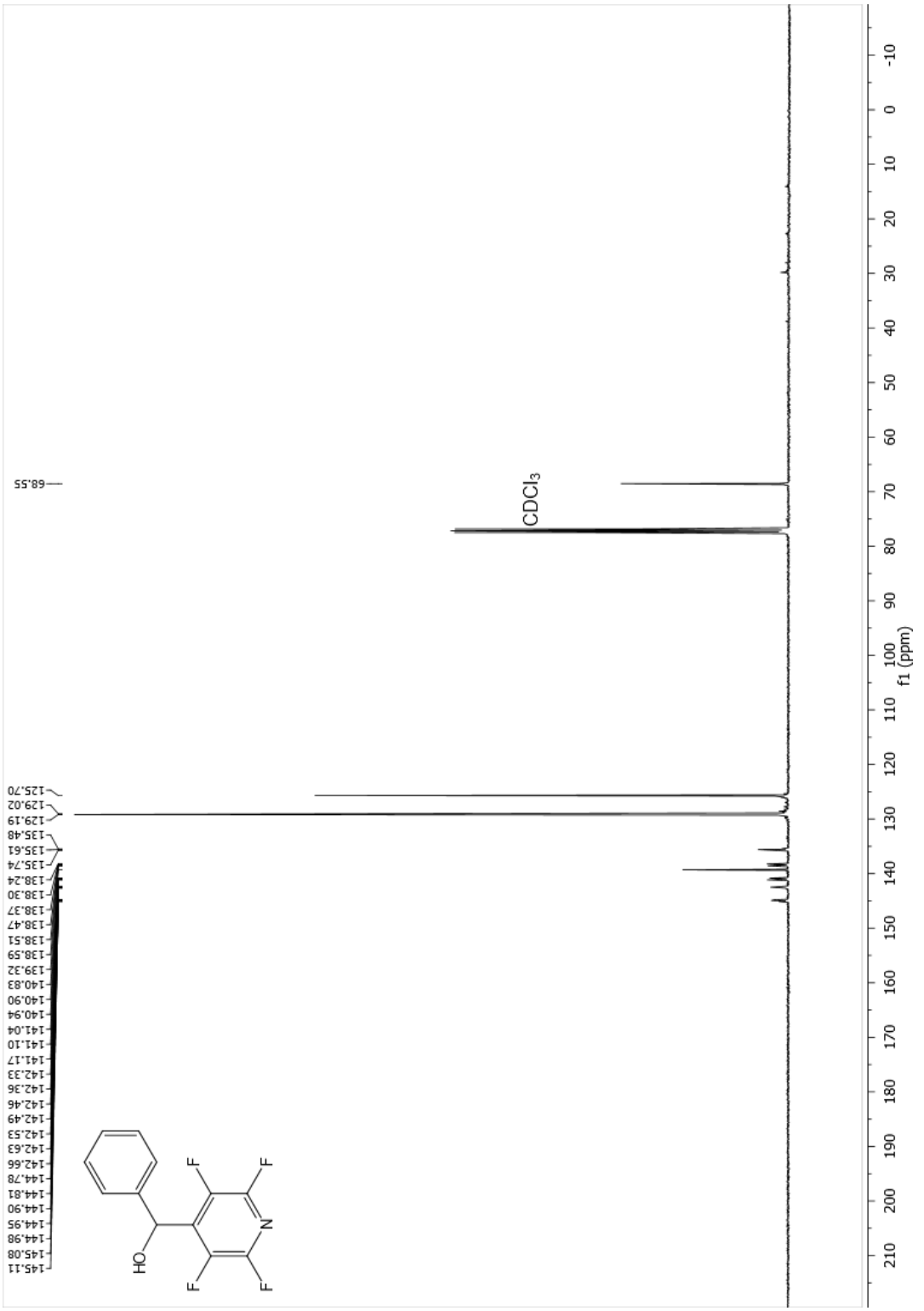
^{19}F NMR (376 MHz, Chloroform-*d* at rt) spectrum of (perfluoropyridin-4-yl)(phenyl)methanol (5c)



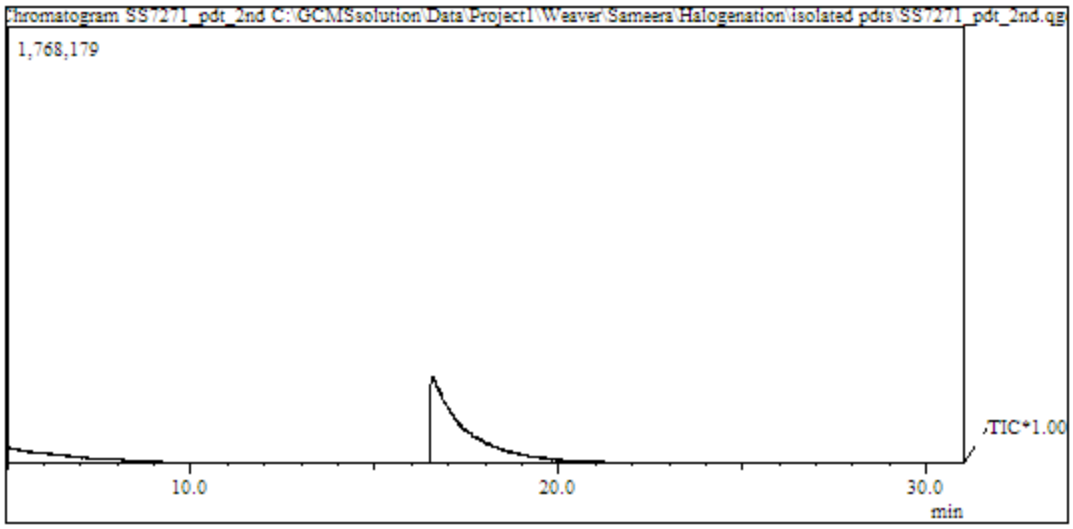
^{1}H NMR (400 MHz, Chloroform-*d* at rt) spectrum of (perfluoropyridin-4-yl)(phenyl)methanol (5c)

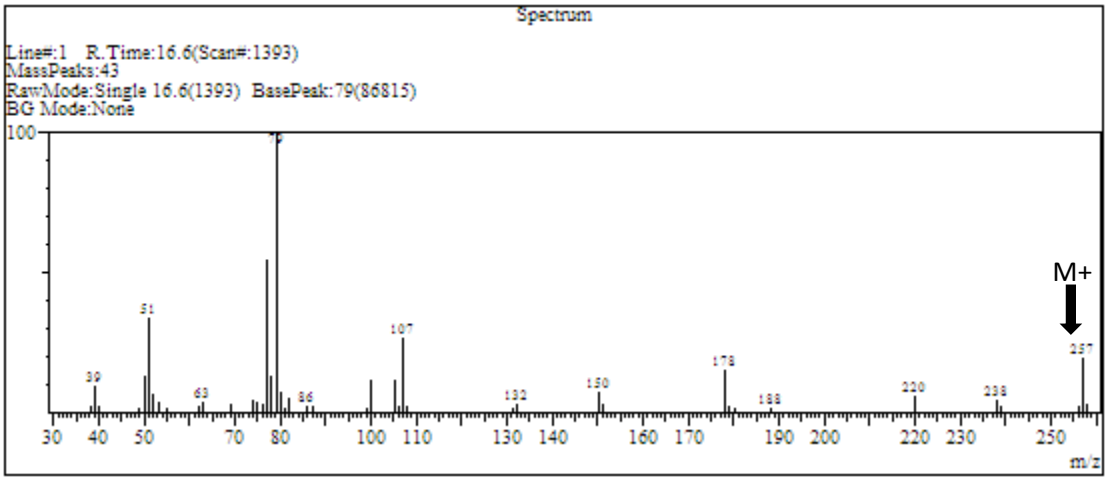


^{13}C NMR (101 MHz, Chloroform-*d* at rt) spectrum of (perfluoropyridin-4-yl)(phenyl)methanol (5c)



GC and MS of GC and MS of (perfluoropyridin-4-yl)(phenyl)methanol (5c)





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