

Straightforward chemo- and stereoselective fluorocyclopropanation of allylic alcohols: exploiting the electrophilic nature of the not so elusive fluoroiodomethylithium

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Supporting Information

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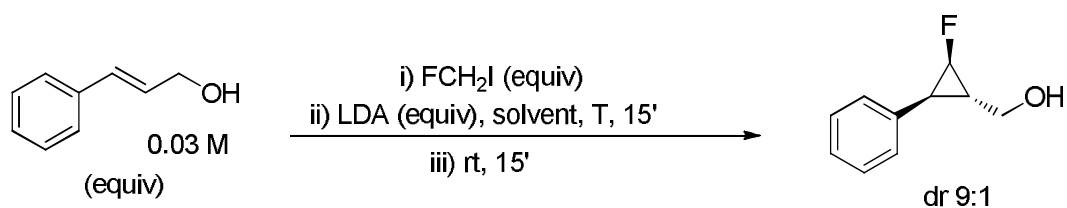
1. Instrumentation and General Analytical Methods

HRMS spectra were recorded on Agilent 6530 accurate mass Q-TOF instrument. ^1H , ^{13}C , ^{19}F NMR spectra were recorded with an Agilent 500 spectrometer (500 MHz for ^1H , 126 MHz for ^{13}C , 470 MHz for ^{19}F), and a Varian Mercury 300 spectrometer (300 MHz for ^1H , 75 MHz for ^{13}C , 282 MHz for ^{19}F). Infrared spectra of the compounds were recorded by using a PerkinElmer 283 Spectrometer or by using attenuated total reflection spectrophotometer in reciprocal centimeter (cm^{-1}). The center of the (residual) solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^1H in CDCl_3), δ 77.00 ppm (^{13}C in CDCl_3). Absolute referencing was used for the ^{19}F NMR spectra. Spin-spin coupling constants (J) are given in Hz. As far as possible, full and unambiguous assignment of all resonances was performed by combined application of standard NMR techniques, such as HSQC, COSY and NOESY experiments. The enantiomeric ratio was determined by using HPLC 1260 Infinity with DIODE detector.

THF was distilled over Na/benzophenone.

Fluoroiodomethane was purchased from ABCR GmbH Germany and it was stored at -20°C . Lithium diisopropylamide [2 M in hexane/THF/ethylbenzene] was purchased from Sigma Aldrich. Other chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Fluorochem and TCI Europe unless otherwise specified. Solutions were evaporated under reduced pressure with a rotary evaporator. TLC was carried out on aluminium sheets precoated with silica gel 60F254 (Merck); the spots were visualized under UV light ($\lambda = 254$ nm) and/or KMnO_4 (aq.) was used as revealing system.

2. Optimization of the reaction conditions



Entry	FCH ₂ I (equiv)	LDA (equiv)	Alcohol (equiv)	Solvent	T(°C)	Yield (%) ^[*]
1	4	4	1	THF : Et ₂ O=1:2	-78 °C	21
2	4	4	1	THF	-78 °C	31
3	4	4	1	Et ₂ O	-78 °C	21
4	1	3	2	CPME	-78 °C	14
5	4	4	1	Pentane	-78 °C	Traces
6	1	3	2	Toluene	-78 °C	Traces
7	1	3	2	2-MeTHF	-50 °C	<10%
8	6	6	1	THF	-78 °C	48
9 ^[a]	6	6	1	THF	-78 °C	35
10 ^[b]	1	3	2	THF	-78 °C	20
11 ^[c]	4	4	1	THF	-78 °C	28
12 ^[d]	4	4	1	THF	-78 °C	Traces
13 ^[e]	6	6	1	THF	-78 °C	/
14 ^[f]	1	3	2	THF	-78 °C	40
15 ^[f]	1	3	2	THF	-98 °C	40
16 ^[f]	1	3	2	THF	-50 °C	75
17 ^[f]	1	3	2	THF	-20 °C	33
18 ^[f,g]	1	3	2	THF	-78 °C	22
19 ^[h]	1	3	2	THF	-50 °C	80
20 ^[i]	1	3	2	THF	-50 °C	37
21	1	2	1	THF	-78 °C	38

[*] NMR yields calculated on the crude reaction mixture using mesitylene or hexafluorobenzene as internal standards; **[a]** Reaction time: 1.5 h at -78°C plus 0.25 h at rt; **[b]** Reaction quenched after 20 seconds; **[c]** Experiment performed adding FCH₂I to preformed lithium alcoholate; **[d]** Reaction carried out adding a THF solution of FCH₂I and cinnamyl alcohol to LDA; **[e]** Allylic alcohol added 1s after the LDA addition to FCH₂I; **[f]** Reaction run using 2 equivalents of allylic alcohol (FCH₂I as limiting reagent); **[g]** Reaction run using a concentration of 0.3 M for alcohol; **[h]** Reaction run using a concentration of 0.01 M for FCH₂I; **[i]** Reaction run using a concentration of 0.005 M for FCH₂I.

3. General procedures for the preparation of allylic alcohols through:

3.1 Reduction of α,β -unsaturated aldehydes and ketones

In a round bottom flask containing NaBH_4 (174 mg, 4.6 mmol, 1.15 equiv) at 0°C , a solution of aldehyde or ketone (4 mmol, 1 equiv) in absolute ethanol (10 mL) was added dropwise. After 30 min, sat. aqueous ammonium chloride and water were added. The resulting mixture was stirred at room temperature for additional 30 min, and diluted with dichloromethane (10 mL). The aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic phases were washed with water (3 x 15 mL) and dried over Na_2SO_4 . The solvent was removed under reduced pressure to afford the desired alcohol that was used without further purification.

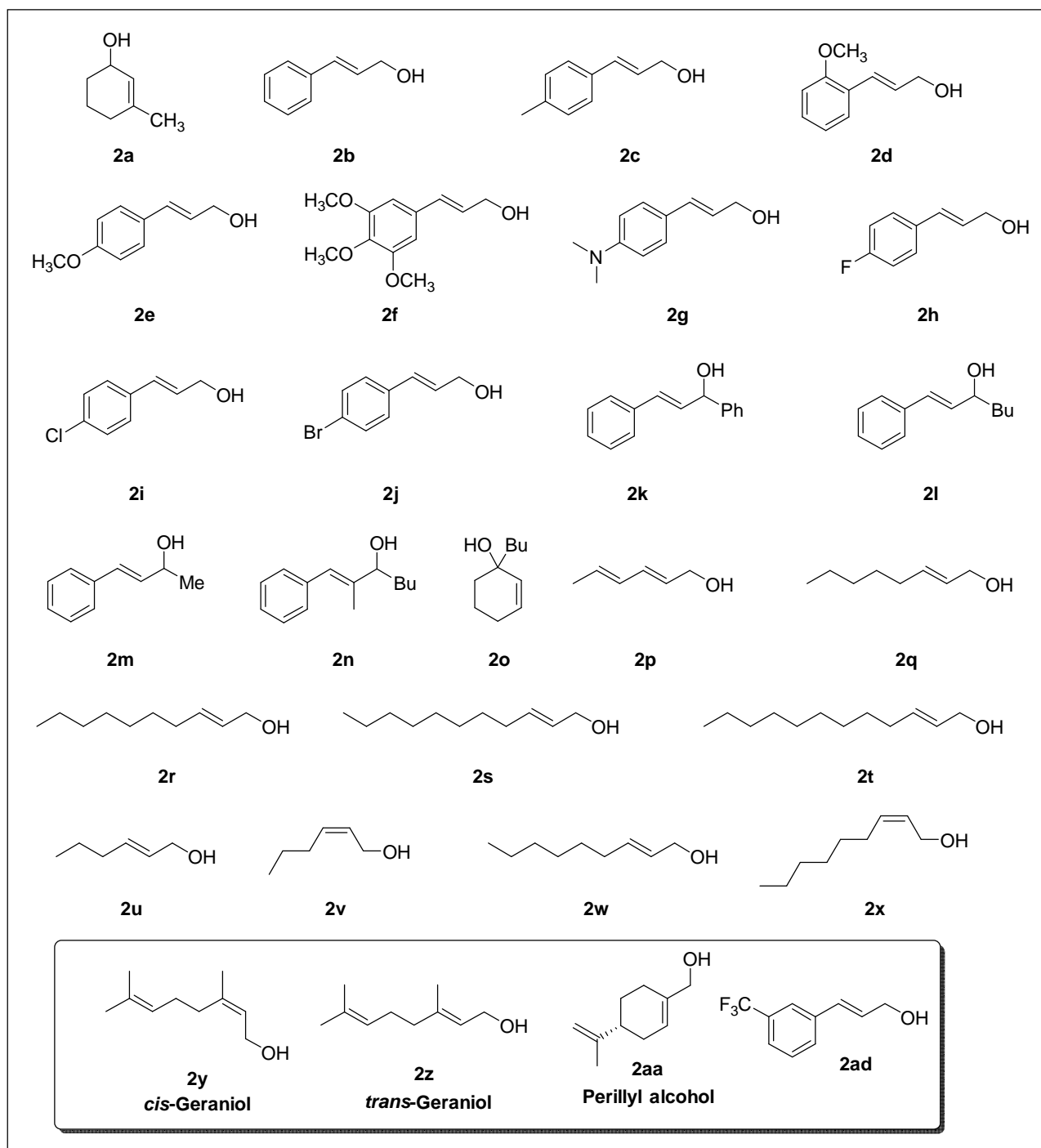
3.2 Reduction of α,β -unsaturated carboxylic acids

Cinnamyl alcohols were synthesized from the correspondent cinnamic acids following the reported procedure.¹

3.3 Nucleophilic addition of organolithiums to ketones

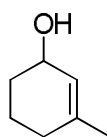
Allylic alcohols were prepared starting from corresponding ketone and alkyllithium according to the literature procedures.²

4. Collection of allylic alcohols



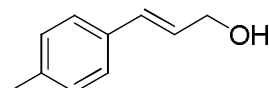
Scheme 1. Allylic alcohols

3-Methylcyclohex-2-enol (2a)



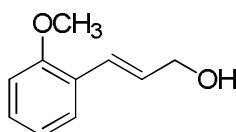
Prepared according to general procedure **3.1** to afford allylic alcohol **2a**. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.51-5.49 (m, 1H, $\text{CH}=\text{C}_\alpha$), 4.17 (m, 1H, CHOH), 1.95-1.91 (m, 2H, CH_2), 1.80-1.75 (m, 2H, CH_2), 1.68 (d, $J = 0.8$ Hz, 3H, CH_3), 1.60-1.56 (m, 2H, CH_2); the data are consistent with literature.³

(E)-3-(p-Tolyl)prop-2-en-1-ol (2c)



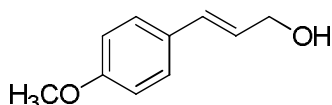
Prepared according to general procedure **3.1** to afford allylic alcohol **2c**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.29 (d, $J = 8.0$ Hz, 2H, 2 x Ar-H), 7.13 (d, $J = 8.0$ Hz, 2H, 2 x Ar-H), 6.59 (d, $J = 15.9$ Hz, 1H, $\text{ArCH}=\text{CH}$), 6.32 (dt, $J = 15.9$, 5.8 Hz, 1H, $\text{CH}=\text{CHCH}_2$), 4.31 (d, $J = 5.7$ Hz, 2H, CH_2OH), 2.34 (s, 3H, CH_3); the data are consistent with literature.⁴

(E)-3-(2-Methoxyphenyl)prop-2-en-1-ol (2d)



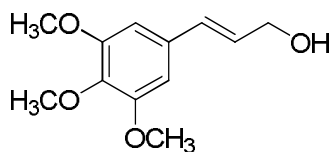
Prepared according to general procedure **3.1** to afford allylic alcohol **2d**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.44 (dd, $J = 7.6$, 1.4 Hz, 1H, Ar-H), 7.22 (dd, $J = 8.3$, 1.1 Hz, 1H, Ar-H), 6.96-6.86 (m, 3H, overlapping 2 x Ar-H and $\text{ArCH}=\text{CH}$), 6.39 (dt, $J = 16.0$, 5.9 Hz, 1H, $\text{CH}=\text{CHCH}_2$), 4.33 (d, $J = 5.9$ Hz, 2H, CH_2OH), 3.85 (s, 3H, OCH_3); the data are consistent with literature.⁵

(E)-3-(4-Methoxyphenyl)prop-2-en-1-ol (2e)



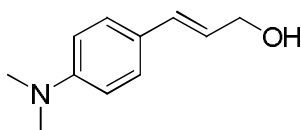
Prepared according to general procedure **3.1** to afford allylic alcohol **2e**. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.32 (d, $J = 8.7$ Hz, 2H, 2 x Ar-H), 6.86 (d, $J = 8.7$ Hz, 2H, 2 x Ar-H), 6.55 (d, $J = 15.9$ Hz, 1H, $\text{ArCH}=\text{CH}$), 6.23 (dt, $J = 15.8$, 5.9 Hz, 1H, $\text{CH}=\text{CHCH}_2$), 4.29 (d, $J = 5.9$ Hz, 2H, CH_2OH), 3.81 (s, 3H, OCH_3); the data are consistent with literature.⁴

(E)-3-(3,4,5-Trimethoxyphenyl)prop-2-en-1-ol (2f)



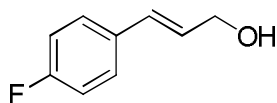
Prepared according to general procedure **3.1** to afford allylic alcohol **2f**. ^1H NMR (500 MHz, CDCl_3): δ 6.60 (s, 2H, 2 x Ar-H), 6.53 (d, $J = 15.8$ Hz, 1H, ArCH=CH), 6.28 (dt, $J = 15.8, 5.8$ Hz, 1H, CH=CHCH₂), 4.31 (dd, $J = 5.7, 1.1$ Hz, 2H, CH₂OH), 3.86 (s, 6H, 2 x OCH₃), 3.84 (s, 3H, OCH₃); the data are consistent with literature.⁶

(E)-3-(4-(Dimethylamino)phenyl)prop-2-en-1-ol (2g)



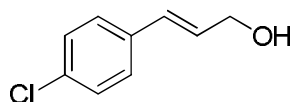
Prepared according to general procedure **3.1** to afford allylic alcohol **2g**. ^1H NMR (300 MHz, CDCl_3) δ 7.29 (d, $J = 8.8$ Hz, 2H, 2 x Ar-H), 6.68 (d, $J = 8.8$ Hz, 2H, 2 x Ar-H), 6.52 (d, $J = 15.8$ Hz, 1H, ArCH=CH), 6.18 (dt, $J = 15.8, 6.2$ Hz, 1H, CH=CHCH₂), 4.28 (m, 2H, CH₂OH), 2.96 (s, 6H, N(CH₃)₂); the data are consistent with literature.⁷

(E)-3-(4-Fluorophenyl)prop-2-en-1-ol (2h)



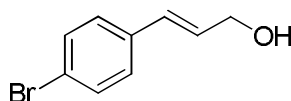
Prepared according to general procedure **3.2** to afford allylic alcohol **2h**. ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.33 (m, 2H, 2 x Ar-H), 7.04-6.98 (m, 2H, 2 x Ar-H), 6.59 (d, $J = 15.9$ Hz, 1H, ArCH=CH), 6.28 (dt, $J = 15.8, 5.6$ Hz, 1H, CH=CHCH₂), 4.33-4.31 (m, 2H, CH₂OH); the data are consistent with literature.⁴

(E)-3-(4-Chlorophenyl)prop-2-en-1-ol (2i)



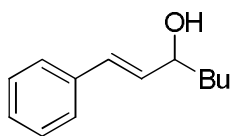
Prepared according to general procedure **3.1** to afford allylic alcohol **2i**. ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.27 (m, 4H, 4 x Ar-H), 6.58 (dt, $J = 15.9, 1.5$ Hz, 1H, ArCH=CH), 6.38-6.29 (m, 1H, CH=CHCH₂), 4.33 (d, $J = 5.4$ Hz, 2H, CH₂OH); the data are consistent with literature.⁸

(E)-3-(4-Bromophenyl)prop-2-en-1-ol (2j)



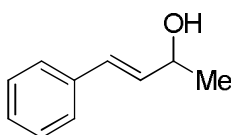
Prepared according to general procedure **3.2** to afford allylic alcohol **2j**. ^1H NMR (300 MHz, CDCl_3) δ 7.44 (d, $J = 7.8$ Hz, 2H, 2 x Ar-H), 7.24-7.23 (m, 2H, 2 x Ar-H), 6.57 (d, $J = 16.7$ Hz, 1H, ArCH=CH), 6.38-6.31 (m, 1H, CH=CHCH₂), 4.34-4.32 (m, 2H, CH₂OH); the data are consistent with literature.⁵

(E)-1-Phenylhept-1-en-3-ol (2l)



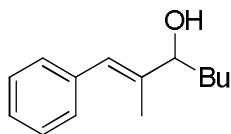
Prepared according to general procedure **3.3** to afford allylic alcohol **2l**. ^1H NMR (500 MHz, CDCl_3): δ 7.39 (d, $J = 7.3$ Hz, 2H, 2 x Ar-H), 7.32 (t, $J = 7.6$ Hz, 2H, 2 x Ar-H), 7.24 (t, $J = 7.3$ Hz, 1H, Ar-H), 6.57 (d, $J = 15.9$ Hz, 1H, ArCH=CH), 6.23 (dd, $J = 15.9, 6.8$ Hz, 1H, CH=CHCH), 4.28 (m, 1H, CHOH), 1.77 (bs, 1H, OH), 1.72-1.58 (m, 2H, CH_2), 1.45-1.34 (m, 4H, 2 x CH_2), 0.93 (t, $J = 7.0$ Hz, 3H, CH_3); the data are consistent with literature.⁹

(E)-4-Phenylbut-3-en-2-ol (2m)



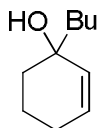
Prepared according to general procedure **3.3** to afford allylic alcohol **2m**. ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.24 (m, 5H, 5 x Ar-H), 6.56 (d, $J = 16.0$ Hz, 1H, Ar-CH=CH), 6.30-6.22 (m, 1H, Ar-CH=CH), 4.53-4.44 (m, 1H, CHOH), 1.37 (d, $J = 6.4$ Hz, 3H, CH_3); the data are consistent with literature.¹⁰

(E)-2-Methyl-1-phenylhept-1-en-3-ol (2n)



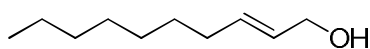
Prepared according to general procedure **3.3** to afford allylic alcohol **2n**. ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.32 (m, 2H, 2 x Ar-H), 7.29-7.27 (m, 2H, 2 x Ar-H), 7.23-7.19 (m, 1H, Ar-H), 6.48 (s, 1H, CH=Cq), 4.17 (t, $J = 6.7$ Hz, 1H, CHOH), 1.87 (d, $J = 1.3$ Hz, 3H, CH_3C_q), 1.65-1.62 (m, 2H, CHCH_2), 1.43-1.33 (m, 4H, 2 x CH_2), 0.92 (t, $J = 7.1$ Hz, 3H, CH_2CH_3); the data are consistent with literature.¹¹

1-Butylcyclohex-2-enol (2o)



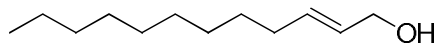
Prepared according to general procedure **3.3** to afford allylic alcohol **2o**. ^1H NMR (500 MHz, CDCl_3): δ 5.80-5.77 (m, 1H, $\text{C}_q\text{CH}=\text{CH}$), 5.61 (d, $J = 10.0$ Hz, 1H, $\text{C}_q\text{CH}=\text{CH}$), 2.05-2.01 (m, 1H, CH_aH_b), 1.95-1.89 (m, 1H, CH_aH_b), 1.73-1.45 (m, 6H, 3 x CH_2), 1.32-1.31 (m, 4H, 2 x CH_2), 0.92-0.89 (m, 3H, CH_3); the data are consistent with literature.¹²

(E)-Dec-2-en-1-ol (2r)



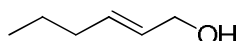
Prepared according to general procedure **3.1** to afford allylic alcohol **2r**. ^1H NMR (500 MHz, CDCl_3) δ 5.72-5.60 (m, 2H, $\text{CH}=\text{CH}$), 4.08 (d, $J = 4.9$ Hz, 2H, CH_2OH), 2.06-2.01 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}$), 1.38-1.31 (m, 10H, 5 x CH_2), 0.88 (t, $J = 6.4$ Hz, 3H, CH_3); the data are consistent with literature.¹³

(E)-Dodec-2-en-1-ol (2t)



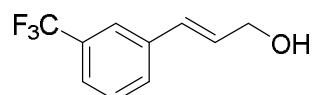
Prepared according to general procedure **3.1** to afford allylic alcohol **2t**. ^1H NMR (300 MHz, CDCl_3) δ 5.73-5.58 (m, 2H, $\text{CH}=\text{CH}$), 4.08 (d, $J = 4.9$ Hz, 2H, CH_2OH), 2.07-2.00 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}$), 1.39-1.19 (m, 14H, 7 x CH_2), 0.88 (t, $J = 6.6$ Hz, 3H, CH_3); the data are consistent with literature.¹⁴

(E)-Hex-2-en-1-ol (2u)



Prepared according to general procedure **3.1** to afford allylic alcohol **2u**. ^1H NMR (300 MHz, CDCl_3) δ 5.74-5.58 (m, 2H, $\text{CH}=\text{CH}$), 4.08 (d, $J = 4.4$ Hz, 2H, CH_2OH), 2.05-1.98 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}$), 1.41-1.36 (m, 2H, CH_2CH_3), 0.90 (t, $J = 7.3$ Hz, 3H, CH_3); the data are consistent with literature.¹⁵

(E)-3-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol (2ad)

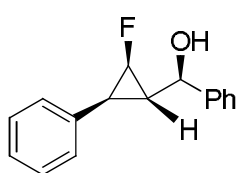
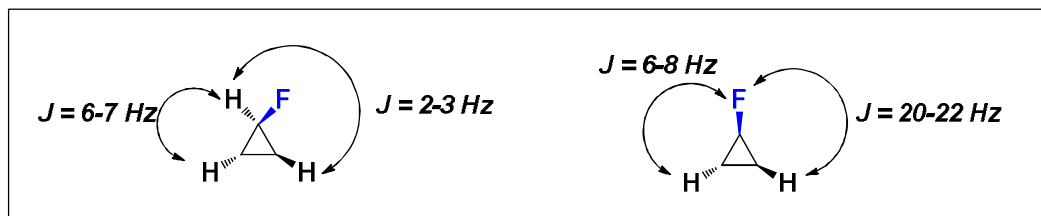


Prepared according to general procedure **3.2** to afford allylic alcohol **2ad**. ^1H NMR (500 MHz, CDCl_3) δ 7.62 (s, 1H, Ar-H), 7.55 (d, $J = 7.7$ Hz, 1H, Ar-H), 7.49 (d, $J = 7.7$ Hz, 1H, Ar-H), 7.43 (t, $J = 7.7$ Hz, 1H, Ar-H), 6.66 (d, $^3J_{\text{trans}} = 16.0$ Hz, 1H, ArCH=CH), 6.44 (dt, $J = 16.0, 5.4$ Hz, 1H, $\text{CH}=\text{CHCH}_2$), 4.36 (broad signal, 2H, CH_2OH); ^{19}F NMR (470 MHz, CDCl_3) δ 62.84 (s, 3F, CF_3); the data are consistent with literature.¹⁶

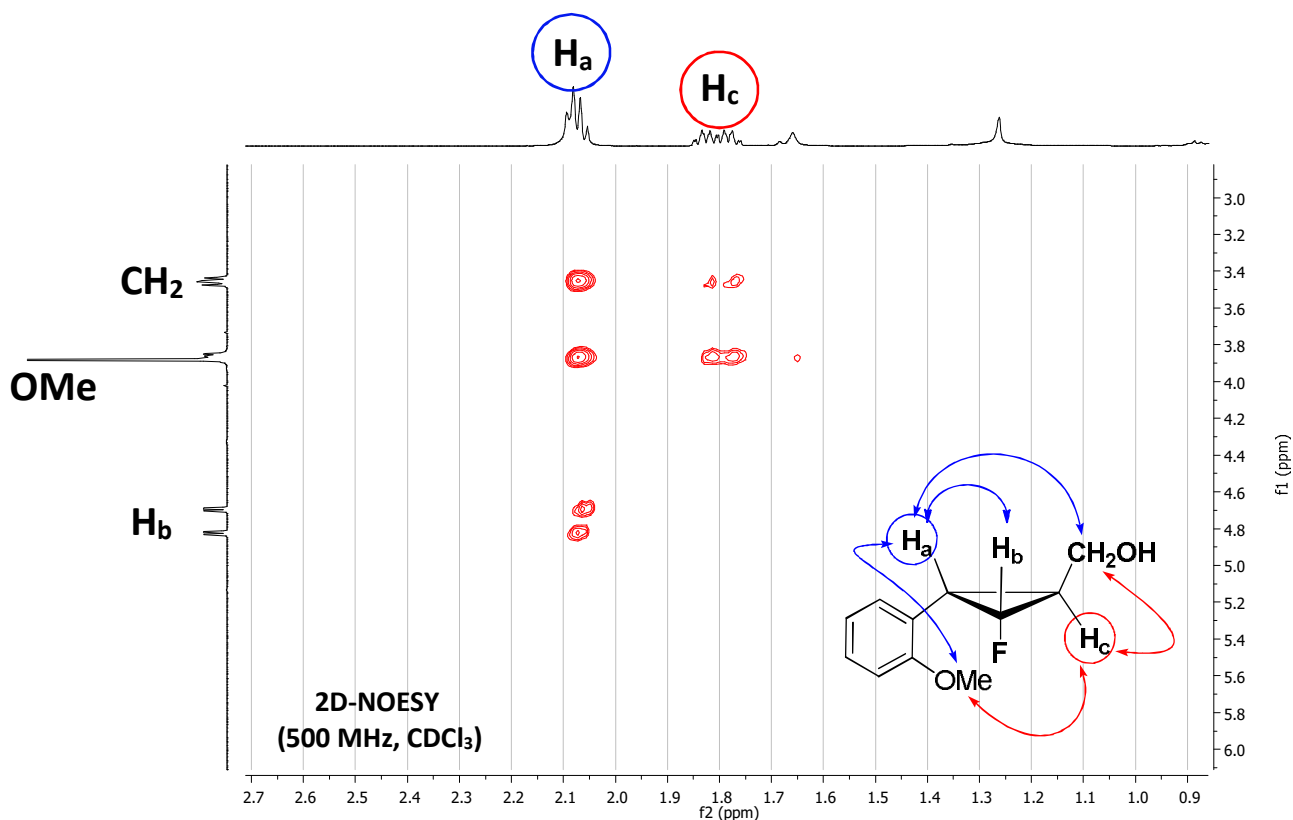
Compounds **2b**, **2k**, **2p**, **2q**, **2s**, **2v**, **2w**, **2x**, **2y**, **2z**, **2aa** are commercially available.

5. Assignment of stereochemistry for fluorocyclopropanes 4.

The stereochemistry of fluorocyclopropanes **4** was ascertained according to previous stereochemical assignments reported by Charette.¹⁷ The relative configuration of cyclopropanes was established considering the ^1H and ^{19}F coupling constants values. Typical $^3J_{\text{H-H}}$ and $^3J_{\text{H-F}}$ values for these systems are reported in the following scheme:



The stereochemical assignment is made assuming that the *trans* stereochemistry of the starting alkene is maintained in the cyclopropanation reaction, according to the proposed mechanism. For example, in cyclopropane **4d** the ^1H NMR spectrum showed H_a as a quartet, a *trans* relationship with the fluorine ($^3J_{\text{H-F}} = 6-8$ Hz), and a *cis* relationship with H_b ($^3J_{\text{H-H}} = 6-8$ Hz). The proposed stereochemistry has also been confirmed by 2D NOESY experiments (See below). Similar considerations apply to all fluorocyclopropanes.

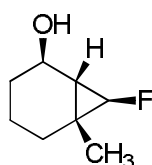


6. General procedure for the preparation of fluorocyclopropanes

To a stirred solution of allylic alcohols (2 mmol, 2 equiv) in dry THF (33 mL) cooled at -50°C , fluoroiodomethane (159.92 mg, 0.67 mL, 1 mmol, 1 equiv) was added. Then, a commercial solution of LDA (2M, in THF/hexane/ethylbenzene, 1.5 mL, 3 mmol, 3 equiv) was added dropwise. After stirring for 15 minutes at -50°C and for 10 minutes at room temperature, the reaction was quenched with water (1 mL). The mixture was poured into water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 , and concentrated under vacuum. Chromatography purification of the crude afforded the desired fluorocyclopropanes.

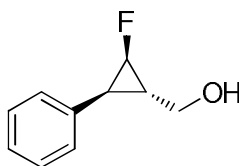
7. NMR data for fluorocyclopropanes

(1R*,2R*,6R*,7R*)-7-Fluoro-6-methylbicyclo[4.1.0]heptan-2-ol (4a)



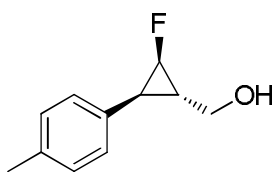
Prepared according to general procedure **6** to afford fluorocyclopropane **4a** as pale yellow oil (70 mg, 56%, *dr* = 80:20, *selected data for major*). Compound **4a** mixture with allylic alcohol **2a**. R_f = 0.3 (20% AcOEt in hexane); IR (film)/ cm^{-1} 3392, 2924, 2853, 1640, 1462, 1377, 1054; ^1H NMR (500 MHz, CDCl_3) δ 4.51 (dd, $^2J_{(\text{H-F})}$ = 65.2 Hz, $^3J_{\text{trans}(\text{H-H})}$ = 2.2 Hz, 1H, CHF), 4.17-4.16 (m, 1H, CHOH), 1.75-1.71 (m, 1H, CH_aH_b), 1.54-1.51 (m, 2H, CH_2), 1.37-1.30 (m, 1H, CHCHF), 1.27-1.24 (m, 1H, CH_aH_b), 1.21 (d, J = 1.7 Hz, 3H, C_qCH_3), 1.17-1.11 (m, 1H, CH_aH_b), 0.97-0.93 (m, 1H, CH_aH_b); ^{13}C NMR (126 MHz, CDCl_3 , *selected data for major*) δ 78.6 (d, $^1J_{(\text{C-F})}$ = 225.8 Hz, CHF), 66.0 (CHOH), 31.8 (CH_2), 31.1 (d, $^2J_{(\text{C-F})}$ = 9.1 Hz, CHCHF), 30.7 (CH_2), 23.9 (d, $^2J_{(\text{C-F})}$ = 9.5 Hz, C_qCH_3), 19.5 (d, $^3J_{(\text{C-F})}$ = 8.6 Hz, C_qCH_3), 19.1 (CH_2); ^{19}F NMR (470 MHz, CDCl_3 , *selected data for major*) δ -218.15 (dd, $^2J_{(\text{H-F})}$ = 65.2 Hz, $^3J_{\text{cis}(\text{H-F})}$ = 23.4 Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_8\text{H}_{13}\text{FNaO}$ [$\text{M}+\text{Na}$] $^+$ 167.0843; Found: 167.0842.

((1R*,2S*,3R*)-2-Fluoro-3-phenylcyclopropyl)methanol (4b)



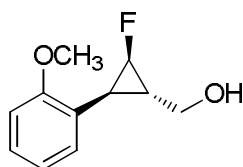
Prepared according to general procedure **6** to afford fluorocyclopropane **4b** as colorless oil (115 mg, 80%, *dr* = 90:10). R_f = 0.3 (30% EtOAc in hexane). IR (film)/ cm^{-1} 3367, 2922, 1603, 1498, 1458, 1260, 1095, 1029, 913, 799, 743; ^1H NMR (500 MHz, CDCl_3): δ 7.32-7.30 (m, 2H, 2 x Ar-H), 7.25-7.22 (m, 3H, 3 x Ar-H), 4.69 (ddd, $^2J_{(\text{H-F})}$ = 64.9 Hz, $^3J_{\text{cis}(\text{H-H})}$ = 6.7 Hz, $^3J_{\text{trans}(\text{H-H})}$ = 2.5 Hz, 1H, CHF), 3.71-3.65 (m, 2H, CH_2OH), 2.08 (q, $^3J_{\text{trans}(\text{H-H})}$ = $^3J_{(\text{H-F})}$ = 6.7 Hz, 1H, ArCHCHF), 1.98-1.89 (m, 1H, CH CH_2OH); ^{13}C NMR (126 MHz, CDCl_3): δ 135.3 (d, $^3J_{(\text{C-F})}$ = 3.0 Hz, Ar- C_q), 128.6 (d, $^4J_{(\text{C-F})}$ = 1.3 Hz, 2 x Ar-C), 128.4 (2 x Ar-C), 126.7 (Ar-C), 75.5 (d, $^1J_{(\text{C-F})}$ = 226.5 Hz, CHF), 62.4 (d, $^3J_{(\text{C-F})}$ = 0.8 Hz, CH_2OH), 27.2 (d, $^2J_{(\text{C-F})}$ = 8.8 Hz, CH CH_2), 26.5 (d, $^2J_{(\text{C-F})}$ = 11.0 Hz, ArCHCHF); ^{19}F NMR (470 MHz, CDCl_3): δ -220.75 (ddd, $^2J_{(\text{H-F})}$ = 64.9 Hz, $^3J_{\text{cis}(\text{H-F})}$ = 20.7 Hz, $^3J_{\text{trans}(\text{H-F})}$ = 5.8 Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{10}\text{H}_{10}\text{FO}$ [$\text{M}-\text{H}$] $^-$ 165.0721; Found: 165.0721.

((1R*,2S*,3S*)-2-Fluoro-3-(p-tolyl)cyclopropyl)methanol (4c)



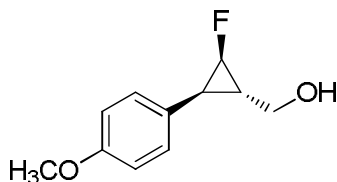
Prepared according to general procedure **6** to afford fluorocyclopropane **4c** as orange oil (121 mg, 78%, *dr* = 90:10). *R_f* = (30% EtOAc in hexane). IR (film)/cm⁻¹ 3367, 2922, 2852, 1518, 1455, 1377, 1215, 1176, 1096, 1036, 988, 817, 737; ¹H NMR (500 MHz, CDCl₃): δ 7.17-7.12 (m, 4H, 4 x Ar-H), 4.67 (ddd, ²*J*_(H-F) = 65.0 Hz, ³*J*_{cis (H-H)} = 6.7 Hz, ³*J*_{trans (H-H)} = 2.4 Hz, 1H, CHF), 3.69-3.64 (m, 2H, CH₂OH), 2.34 (s, 3H, Ar-CH₃), 2.05 (q, ³*J*_(H-F) = ³*J*_(H-H) = 6.6 Hz, 1H, ArCHCHF), 1.95-1.87 (m, 1H, CHCH₂OH), 1.77 (bs, 1H, OH); ¹³C NMR (126 MHz, CDCl₃): δ 136.3 (Ar-C_q-CH₃), 132.1 (d, ³*J*_(C-F) = 3.2 Hz, Ar-C_qCH), 129.1 (2 x Ar-C), 128.5 (d, ⁴*J*_(C-F) = 1.0 Hz, 2 x Ar-C), 75.5 (d, ¹*J*_(C-F) = 226.0 Hz, CHF), 62.4 (d, ³*J*_(C-F) = 0.6 Hz, CH₂OH), 26.9 (d, ²*J*_(C-F) = 8.8 Hz, CHCH₂OH), 26.2 (d, ²*J*_(C-F) = 11.0 Hz, Ar-CHCHF), 21.1 (Ar-CH₃); ¹⁹F NMR (470 MHz, CDCl₃): δ -220.82 (ddd, ²*J*_(H-F) = 65.0 Hz, ³*J*_{cis (H-F)} = 20.7 Hz, ³*J*_{trans (H-F)} = 6.1 Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₁H₁₂FO [M-H]⁻ 179.0878; Found: 179.0872.

((1S*,2R*,3S*)-2-Fluoro-3-(2-methoxyphenyl)cyclopropyl)methanol (4d)



Prepared according to general procedure **6** to afford fluorocyclopropane **4d** as yellow oil (82 mg, 48%, *dr* = 90:10). *R_f* = 0.4 (20% EtOAc in hexane). IR (film)/cm⁻¹ 3368, 2921, 2850, 1601, 1585, 1495, 1463, 1435, 1245, 1110, 1027, 751; ¹H NMR (500 MHz, CDCl₃): δ 7.25-7.22 (m, 2H, 2 x Ar-H), 6.94-6.89 (m, 2H, 2 x Ar-H), 4.76 (ddd, ²*J*_(H-F) = 64.2 Hz, ³*J*_{cis (H-H)} = 6.6 Hz, ³*J*_{trans (H-H)} = 2.2 Hz, 1H, CHF), 3.88 (s, 3H, Ar-OCH₃), 3.88-3.85 (m, 1H, CH_aH_b), 3.47-3.44 (m, 1H, CH_aH_b), 2.09-2.05 (m, 2H, overlapping bs OH and Ar-CHCHF), 1.85-1.76 (m, 1H, CHCH₂); ¹³C NMR (126 MHz, CDCl₃): δ 158.7 (Ar-C_q), 129.2 (d, ⁴*J*_(C-F) = 2.5 Hz, Ar-C), 128.0 (Ar-C), 123.8 (d, ³*J*_(C-F) = 2.5 Hz, Ar-C_q), 120.6 (Ar-C), 110.4 (Ar-C), 75.9 (d, ¹*J*_(C-F) = 226.2 Hz, CHF), 63.0 (d, ³*J*_(C-F) = 0.9 Hz, CH₂OH), 55.6 (OCH₃), 27.5 (d, ²*J*_(C-F) = 9.3 Hz, CHCH₂), 21.4 (d, ²*J*_(C-F) = 10.7 Hz, Ar-CHCHF); ¹⁹F NMR (470 MHz, CDCl₃): δ -219.20 (ddd, ²*J*_(H-F) = 64.2 Hz, ³*J*_{cis (H-F)} = 21.2 Hz, ³*J*_{trans (H-F)} = 5.9 Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₁H₁₂FO₂ [M-H]⁻ 195.0827; Found: 195.0820.

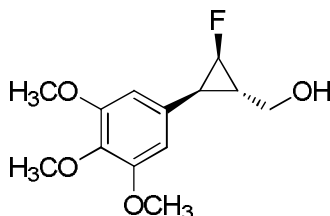
((1R*,2S*,3R*)-2-Fluoro-3-(4-methoxyphenyl)cyclopropyl)methanol (4e)



Prepared according to general procedure **6** to afford fluorocyclopropane **4e** as yellow oil (121 mg, 64%, *dr* > 95:5). *R_f* = 0.3 (60% diethyl ether in hexane); IR (film)/cm⁻¹ 3369, 2917, 1611, 1514, 1462, 1245, 1179, 1030, 830; ¹H NMR (300 MHz, CDCl₃) δ 7.18 (d, *J* = 8.2 Hz, 2H, 2 x Ar-H), 6.86 (d, *J* = 8.3 Hz, 2H, 2 x Ar-H), 4.66 (dd, ²*J*_(H-F) = 65.0 Hz, ³*J*_{cis (H-F)} = 6.5 Hz, 1H, CHF), 3.79 (s, 3H, OCH₃), 3.68 (d, *J* = 4.8 Hz, 2H, CH₂OH), 2.04 (q, ³*J*_(H-F) = ³*J*_(H-H) = 6.5 Hz, 1H, Ar-CHCHF), 1.91-1.82 (m, 1H, CHCH₂OH); ¹³C NMR (75 MHz, CDCl₃) δ 158.5 (OCH₃-Ar-

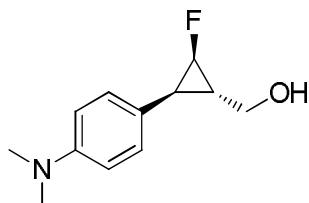
C_q), 129.7 (2 x Ar-C), 127.3 (d, ³J_(C-F) = 3.3 Hz, Ar-C_q), 113.9 (2 x Ar-C), 75.4 (d, ¹J_(C-F) = 225.4 Hz, CHF), 62.5 (CH₂OH), 55.4 (OCH₃), 27.0 (d, ²J_(C-F) = 8.8 Hz, CHCH₂OH), 25.8 (d, ²J_(C-F) = 11.1 Hz, Ar-CHCHF); ¹⁹F NMR (282 MHz, CDCl₃) δ -220.93 (ddd, ²J_(H-F) = 64.9 Hz, ³J_{cis (H-F)}} = 20.7 Hz, ³J_{trans (H-F)}} = 5.9 Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₁H₁₂FO₂ [M-H]⁻ 195.0827; Found: 195.0820.

((1*R,2*S**,3*R**)-2-Fluoro-3-(3,4,5-trimethoxyphenyl)cyclopropyl)methanol (4f)**



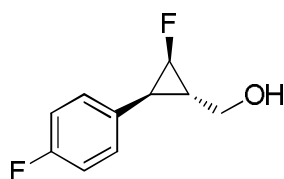
Prepared according to general procedure 6 to afford fluorocyclopropane **4f** as orange oil (112 mg, 50%, *dr* > 95:5). *R_f* = 0.2 (50% EtOAc in hexane); IR (film)/cm⁻¹ 3392, 2923, 2852, 1588, 1510, 1463, 1413, 1235, 1125, 1005; ¹H NMR (500 MHz, CDCl₃): δ 6.48 (s, 2H, 2 x Ar-H), 4.69 (ddd, ²J_(H-F) = 64.9 Hz, ³J_{cis (H-H)}} = 6.6 Hz, ³J_{trans (H-H)}} = 2.5 Hz, 1H, CHF), 3.85 (s, 6H, 2 x OCH₃), 3.83 (s, 3H, OCH₃), 3.72-3.69 (m, 2H, CH₂OH), 2.07-2.03 (m, 1H, Ar-CHCHF), 1.90 (m, 1H, CHCH₂OH); ¹³C NMR (126 MHz, CDCl₃): δ 153.2 (2 x Ar-C_q), 137.0 (Ar-C_q), 131.0 (d, ³J_(C-F) = 3.2 Hz, Ar-C_q), 105.8 (d, ⁴J_(C-F) = 1.3 Hz, 2 x Ar-C), 75.5 (d, ¹J_(C-F) = 226.5 Hz, CHF), 62.3 (d, ³J_(C-F) = 0.8 Hz, CH₂OH), 61.0 (OCH₃), 56.2 (2 x OCH₃), 27.4 (d, ²J_(C-F) = 8.8 Hz, CHCH₂OH), 26.7 (d, ²J_(C-F) = 10.9 Hz, Ar-CHCHF); ¹⁹F NMR (470 MHz, CDCl₃): δ -220.56 (ddd, ²J_(H-F) = 64.9 Hz, ³J_{cis (H-F)}} = 20.9 Hz, ³J_{trans (H-F)}} = 5.9 Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₃H₁₆FO₄ [M-H]⁻ 255.1038; Found: 255.1032

((1*R,2*R**,3*S**)-2-(4-(Dimethylamino)phenyl)-3-fluorocyclopropyl)methanol (4g)**



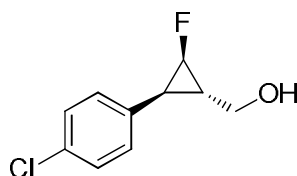
Prepared according to general procedure 6 to afford fluorocyclopropane **4g** as orange oil (108 mg, 60%, *dr* > 95:5). *R_f* = 0.4 (30% AcOEt in hexane); IR (film)/cm⁻¹ 3338, 2875, 1614, 1524, 1444, 1349, 1224, 1130, 1094, 1036, 987, 948, 818; ¹H NMR (500 MHz, CDCl₃) δ 7.14 (d, *J* = 8.6 Hz, 2H, 2 x Ar-H), 6.71 (d, *J* = 8.7 Hz, 2H, 2 x Ar-H), 4.64 (ddd, ²J_(H-F) = 65.0 Hz, ³J_{cis (H-H)}} = 6.6 Hz, ³J_{trans (H-H)}} = 2.3 Hz, 1H, CHF), 3.71-3.63 (m, 2H, CH₂OH), 2.92 (s, 6H, N(CH₃)₂), 2.01 (q, *J* = 6.6 Hz, 1H, Ar-CHCHF), 1.90-1.83 (m, 1H, CHCH₂OH); ¹³C NMR (126 MHz, CDCl₃) δ 149.6 (Ar-C_q), 129.4 (d, ⁴J_(C-F) = 1.0 Hz, 2 x Ar-C), 122.9 (Ar-C_q), 112.9 (2 x Ar-C), 75.5 (d, ¹J_(C-F) = 225.1 Hz, CHF), 62.7 (d, ³J_(C-F) = 0.7 Hz, CH₂OH), 40.9 (N(CH₃)₂), 26.8 (d, ²J_(C-F) = 8.9 Hz, CHCH₂OH), 25.8 (d, ²J_(C-F) = 11.0 Hz, Ar-CHCHF); ¹⁹F NMR (282 MHz, CDCl₃) δ -220.88 (ddd, ²J_(H-F) = 66.2 Hz, ³J_{cis (H-F)}} = 21.8 Hz, ³J_{trans (H-F)}} = 6.6 Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₂H₁₅FNO [M-H]⁻ 208.1143; Found: 208.1160.

((1*R,2*S**,3*R**)-2-Fluoro-3-(4-fluorophenyl)cyclopropyl)methanol (4h)**



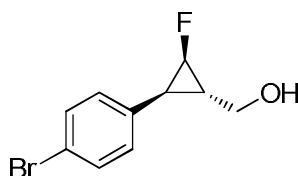
Prepared according to general procedure **6** to afford fluorocyclopropane **4h** as yellow oil (86 mg, 54%, *dr* > 95:5). R_f = 0.4 (60% diethyl ether in hexane); IR (film)/ cm^{-1} 3368, 2918, 1606, 1513, 1226, 1160, 1037, 834; ^1H NMR (500 MHz, CDCl_3) δ 7.23-7.19 (m, 2H, 2 x Ar-H), 7.01-6.98 (m, 2H, 2 x Ar-H), 4.68 (ddd, $^2J_{(\text{H-F})} = 64.8$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.6$ Hz, $^3J_{\text{trans}(\text{H-H})} = 2.4$ Hz, 1H, CHF), 3.69 (dd, $J = 6.5, 2.2$ Hz, 2H, CH_2OH), 2.06 (q, $^3J_{(\text{H-F})} = ^3J_{(\text{H-H})} = 6.6$ Hz, 1H, Ar-CHCHF), 1.91-1.82 (m, 1H, CHCH_2OH); ^{13}C NMR (75 MHz, CDCl_3) δ 161.8 (d, $^1J_{(\text{C-F})} = 244.8$ Hz, F-Ar- C_q), 130.1 (d, $^3J_{(\text{C-F})} = 7.9$ Hz, 2 x Ar-C), 115.1 (d, $^2J_{(\text{C-F})} = 21.4$ Hz, 2 x Ar-C), 75.1 (d, $^1J_{(\text{C-F})} = 227.1$ Hz, CHF), 62.0 (CH_2OH), 27.1 (d, $^2J_{(\text{C-F})} = 8.7$ Hz, CHCH_2OH), 25.5 (d, $^2J_{(\text{C-F})} = 11.0$ Hz, Ar-CHCHF); ^{19}F NMR (282 MHz, CDCl_3) δ -116.43 – -116.55 (m, Ar-F, 1F), -220.91 (ddd, $^2J_{(\text{H-F})} = 65.5$ Hz, $^2J_{\text{cis}(\text{H-F})} = 21.5$ Hz, $^2J_{\text{trans}(\text{H-F})} = 7.2$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{10}\text{H}_9\text{F}_2\text{O}$ [M-H] $^-$ 183.0627; Found: 183.0626.

((1*R,2*R**,3*S**)-2-(4-Chlorophenyl)-3-fluorocyclopropyl)methanol (4i)**



Prepared according to general procedure **6** to afford fluorocyclopropane **4i** as orange oil (70 mg, 40%, *dr* > 95:5). R_f = 0.4 (50% EtOAc in hexane); IR (film)/ cm^{-1} 3338, 2918, 1494, 1213, 1178, 1090, 1014, 913, 826, 742; ^1H NMR (500 MHz, CDCl_3): δ 7.27 (d, $J = 8.5$ Hz, 2H, 2 x Ar-H), 7.18 (d, $J = 8.5$ Hz, 2H, 2 x Ar-H), 4.69 (ddd, $^2J_{(\text{H-F})} = 64.8$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.6$ Hz, $^3J_{\text{trans}(\text{H-H})} = 2.4$ Hz, 1H, CHF), 3.70 (s, 2H, CH_2OH), 2.08-2.04 (m, 1H, Ar-CHCHF), 1.93-1.84 (m, 1H, CHCH_2OH); ^{13}C NMR (126 MHz, CDCl_3): δ 133.9 (d, $^3J_{(\text{C-F})} = 3.1$ Hz, Ar- C_q), 132.5 (Ar- C_q -Cl), 129.9 (d, $^4J_{(\text{C-F})} = 1.4$ Hz, 2 x Ar-C), 128.5 (2 x Ar-C), 75.3 (d, $^1J_{(\text{C-F})} = 226.7$ Hz, CHF), 62.1 (CH_2OH), 27.4 (d, $^2J_{(\text{C-F})} = 8.7$ Hz, CHCH_2OH), 25.8 (d, $^2J_{(\text{C-F})} = 11.0$ Hz, Ar-CHCHF); ^{19}F NMR (470 MHz, CDCl_3): δ -220.85 (ddd, $^2J_{(\text{H-F})} = 64.8$ Hz, $^3J_{\text{cis}(\text{H-F})} = 20.8$ Hz, $^3J_{\text{trans}(\text{H-F})} = 5.8$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{10}\text{H}_9\text{ClFO}$ [M-H] $^-$ 199.0331; Found: 199.0327.

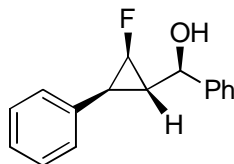
((1*R,2*R**,3*S**)-2-(4-Bromophenyl)-3-fluorocyclopropyl)methanol (4j)**



Prepared according to general procedure **6** to afford fluorocyclopropane **4j** as yellow oil (85 mg, 54%, *dr* > 95:5). R_f = 0.3 (60% diethyl ether in hexane); IR (film)/ cm^{-1} 3352, 2924, 2874, 1493, 1397, 1213, 1177, 1094, 1073, 1036, 1010, 824, 763, 717; ^1H NMR (300 MHz, CDCl_3) δ 7.42 (d, $J = 8.5$ Hz, 2H, 2 x Ar-H), 7.12 (d, $J = 8.3$ Hz, 2H, 2 x Ar-H), 4.69 (ddd, $^2J_{(\text{H-F})} = 64.8$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.6$ Hz, $^3J_{\text{trans}(\text{H-H})} = 2.5$ Hz, 1H, CHF), 3.70 (d, $J = 6.2$ Hz, 2H, CH_2OH), 2.05 (q, $^3J_{(\text{H-F})} = ^3J_{(\text{H-H})} = 6.6$ Hz, 1H, Ar-CHCHF), 1.96-1.81 (m, 1H, CHCH_2OH); ^{13}C NMR (75 MHz, CDCl_3) δ 134.6 (d, $^3J_{(\text{C-F})} = 3.1$ Hz, Ar- C_q), 131.4 (2 x Ar-C), 130.4 (2 x Ar-C), 120.5 (Ar- C_q -Br), 75.2 (d, $^1J_{(\text{C-F})}$

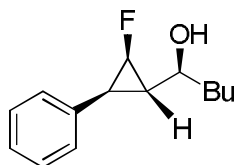
$f_J = 224.9$ Hz, CHF), 62.1 (CH₂OH), 27.4 (d, $^2J_{(C-F)} = 8.7$ Hz, CHCH₂OH), 25.9 (d, $^2J_{(C-F)} = 11.0$ Hz, Ar-CHCHF); ¹⁹F NMR (282 MHz, CDCl₃) δ -220.82 (ddd, $^2J_{(H-F)} = 64.9$ Hz, $^3J_{cis (H-F)} = 21.2$ Hz, $^3J_{trans (H-F)} = 6.7$ Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₀H₉BrFO [M-H]⁻ 242.9826; Found: 242.9840.

(R*)-((1S*,2R*,3S*)-2-Fluoro-3-phenylcyclopropyl)(phenyl)methanol (4k)



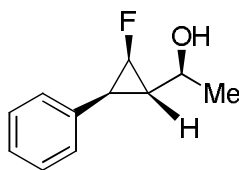
Prepared according to general procedure **6** to afford fluorocyclopropane **4k** as colorless oil (69 mg, 34%, *dr* = 80:20, *selected data for major*). *R_f* = 0.3 (30% EtOAc in hexane). IR (film)/cm⁻¹ 3400, 2923, 2852, 1496, 1455, 1178, 1072, 1028, 745, 698; ¹H NMR (500 MHz, CDCl₃, *selected data for major*) δ 7.45-7.29 (m, 8H, 8 x Ar-H), 7.22-7.19 (m, 2H, 2 x Ar-H), 4.88 (ddd, $^2J_{(H-F)} = 65.1$ Hz, $^3J_{cis (H-H)} = 6.8$ Hz, $^3J_{trans (H-H)} = 2.5$ Hz, 1H, CHF), 4.64-4.62 (m, 1H, CHOH), 2.25 (q, *J* = 6.7 Hz, 1H, Ar-CHCHF), 2.09-1.99 (m, 1H, CHCHOH); ¹³C NMR (126 MHz, CDCl₃, *selected data for major*) δ 142.7 (Ar-C_q), 135.3 (d, $^3J_{(C-F)} = 2.9$ Hz, Ar-C_q), 128.9 (2 x Ar-C), 128.7 (2 x Ar-C), 128.4 (2 x Ar-C), 128.3 (Ar-C), 126.7 (Ar-C), 126.2 (2 x Ar-C), 75.3 (d, $^1J_{(C-F)} = 227.2$ Hz, CHF), 73.0 (CHOH), 31.7 (d, $^2J_{(C-F)} = 8.6$ Hz, CHCHOH), 26.2 (d, $^2J_{(C-F)} = 11.0$ Hz, Ar-CHCHF); ¹⁹F NMR (470 MHz, CDCl₃, *selected data for major*) δ -221.24 (ddd, $^2J_{(H-F)} = 65.2$ Hz, $^3J_{cis (H-F)} = 20.7$ Hz, $^3J_{trans (H-F)} = 6.1$ Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₄FO [M-H]⁻ 241.1034; Found: 241.1031.

(R*)-1-((1R*,2S*,3R*)-2-Fluoro-3-phenylcyclopropyl)pentan-1-ol (4l)



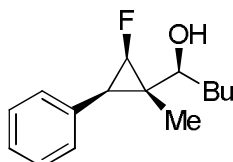
Prepared according to general procedure **6** to afford fluorocyclopropane **4l** as pale yellow oil (67 mg, 35%, *dr* > 95:5). *R_f* = 0.2 (50% EtOAc in hexane); IR (film)/cm⁻¹ 3412, 2928, 2857, 2254, 1468, 1266, 1014, 912, 742; ¹H NMR (500 MHz, CDCl₃): δ 7.33-7.30 (m, 2H, 2 x Ar-H), 7.26-7.22 (m, 3H, 3 x Ar-H), 4.76 (ddd, $^2J_{(H-F)} = 65.3$ Hz, $^3J_{cis (H-H)} = 6.7$ Hz, $^3J_{trans (H-H)} = 2.5$ Hz, 1H, CHF), 3.39-3.37 (m, 1H, CHOH), 2.11-2.05 (m, 1H, Ar-CHCHF), 1.80-1.73 (m, 1H, CHCHOH), 1.67-1.62 (m, 2H, CH₂CHOH), 1.49-1.32 (m, 4H, CH₂CH₂CH₃), 0.91 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 135.6 (Ar-C_q), 128.6 (d, $^4J_{(C-F)} = 1.3$ Hz, 2 x Ar-C), 128.4 (2 x Ar-C), 126.6 (Ar-C), 75.2 (d, $^1J_{(C-F)} = 226.3$ Hz, CHF), 71.6 (CHOH), 36.7 (CH₂CHOH), 31.2 (d, $^2J_{(C-F)} = 8.1$ Hz, CHCHOH), 27.8 (CH₂CH₂CHOH), 26.5 (d, $^2J_{(C-F)} = 11.1$ Hz, Ar-CHCHF), 22.8 (CH₂CH₃), 14.2 (CH₃); ¹⁹F NMR (470 MHz, CDCl₃): δ -217.80 (ddd, $^2J_{(H-F)} = 27.7$ Hz, $^3J_{cis (H-F)} = 22.3$ Hz, $^3J_{trans (H-F)} = 6.0$ Hz, CHF *minor*), -221.06 (ddd, $^2J_{(H-F)} = 65.3$ Hz, $^3J_{cis (H-F)} = 21.0$ Hz, $^3J_{trans (H-F)} = 6.0$ Hz, CHF *major*); HRMS (ESI-TOF) *m/z* Calcd for C₁₄H₁₈FO [M-H]⁻ 221.1347; Found: 221.1341.

(R*)-1-((1R*,2S*,3R*)-2-Fluoro-3-phenylcyclopropyl)ethanol (4m)



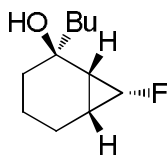
Prepared according to general procedure **6** to afford fluorocyclopropane **4m** as pale yellow oil (59 mg, 38%, *dr* = 80:20, inseparable mixture of diastereoisomers). R_f = 0.2 (20 % EtOAc in hexane). IR (film)/ cm^{-1} 3367, 2919, 2851, 1603, 1498, 1431, 1073, 945, 745, 697; ^1H NMR (500 MHz, CDCl_3): δ 7.33-7.23 (m, 5H, 5 x Ar-H, overlapping major and minor), 4.76 (ddd, $^2J_{\text{(H-F)}} = 65.2$ Hz, $^3J_{\text{cis (H-H)}} = 6.7$ Hz, $^3J_{\text{trans (H-H)}} = 2.5$ Hz, 1H, CHF major), 4.69 (ddd, $^2J_{\text{(H-F)}} = 65.1$ Hz, $^3J_{\text{cis (H-H)}} = 6.7$ Hz, $^3J_{\text{trans (H-H)}} = 2.5$ Hz, 1H, CHF minor), 3.74-3.71 (m, 1H, CHCH₃ minor), 3.61-3.58 (m, 1H, CHCH₃ major), 2.22-2.18 (m, 1H, Ar-CHCHF minor), 2.10-2.06 (m, 1H, Ar-CHCHF major), 1.82-1.74 (m, 1H, CHCHCH₃ overlapping major and minor), 1.37 (d, $J = 6.2$ Hz, 3H, CH₃ minor) 1.35 (d, $J = 6.3$ Hz, 3H, CH₃ major); ^{13}C NMR (126 MHz, CDCl_3): δ 135.7 (d, $^3J_{\text{(C-F)}} = 3.0$ Hz, Ar-C_q minor), 135.5 (d, $^3J_{\text{(C-F)}} = 3.1$ Hz, Ar-C_q major), 128.7 (d, $^4J_{\text{(C-F)}} = 1.2$ Hz, 2 x Ar-C minor), 128.6 (d, $^4J_{\text{(C-F)}} = 1.3$ Hz, 2 x Ar-C major), 128.3₉ (2 x Ar-C major) 128.3₇ (2 x Ar-C minor), 126.6 (Ar-C major), 126.5 (Ar-C minor), 76.1 (d, $^1J_{\text{(C-F)}} = 226.2$ Hz, CHF major), 74.3 (d, $^1J_{\text{(C-F)}} = 226.1$ Hz, CHF minor), 67.6 (CHCH₃ major), 67.1 (d, $^3J_{\text{(C-F)}} = 1.8$ Hz, CHCH₃ minor), 32.4 (d, $^2J_{\text{(C-F)}} = 8.1$ Hz, CHCHCH₃ minor), 32.3 (d, $^2J_{\text{(C-F)}} = 8.1$ Hz, CHCHCH₃ major), 26.2 (d, $^2J_{\text{(C-F)}} = 11.2$ Hz, Ar-CHCHF major), 26.0 (d, $^2J_{\text{(C-F)}} = 11.2$ Hz, Ar-CHCHF minor), 22.8 (CH₃ minor), 22.5 (d, $^4J_{\text{(C-F)}} = 0.8$ Hz, CH₃ major); ^{19}F NMR (282 MHz, CDCl_3) δ -220.40 (ddd, $^2J_{\text{(H-F)}} = 65.4$ Hz, $^3J_{\text{cis (H-F)}} = 21.2$ Hz, $^3J_{\text{trans (H-F)}} = 6.4$ Hz, CHF major), -221.37 (ddd, $^2J_{\text{(H-F)}} = 65.3$ Hz, $^3J_{\text{cis (H-H)}} = 21.8$ Hz, $^3J_{\text{trans (H-H)}} = 6.4$ Hz, CHF minor); HRMS (ESI-TOF) m/z Calcd for C₁₁H₁₂FO [M-H]⁻ 179.0878, Found: 179.0872.

(R*)-1-((1R*,2S*,3S*)-2-Fluoro-1-methyl-3-phenylcyclopropyl)pentan-1-ol (4n)



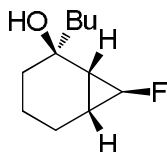
Prepared according to general procedure **6** to afford fluorocyclopropane **4n** as colorless oil (37 mg, 36%, *dr* = 90:10). R_f = 0.2 (20% EtOAc in hexane). IR (film)/ cm^{-1} 3400, 2928, 2856, 1464, 1073, 737, 698; ^1H NMR (500 MHz, CDCl_3): δ 7.35-7.28 (m, 3H, 3 x Ar-H), 7.25-7.22 (m, 2H, 2 x Ar-H), 4.74 (dd, $^2J_{\text{(H-F)}} = 65.5$ Hz, $^3J_{\text{cis (H-H)}} = 6.6$ Hz, 1H, CHF), 3.04-3.02 (m, 1H, CHO), 1.98 (t, $J = 7.1$ Hz, 1H, Ar-CHCHF), 1.65-1.62 (m, 2H, CH₂), 1.38-1.35 (m, 4H, 2 x CH₂), 0.96-0.93 (m, 6H, 2 x CH₃); ^{13}C NMR (126 MHz, CDCl_3): δ 134.5 (Ar-C_q), 128.3 (2 x Ar-C), 128.3 (2 x Ar-C), 126.5 (Ar-C), 78.3 (d, $^1J_{\text{(C-F)}} = 237.8$ Hz, CHF), 77.0 (CHO), 32.9 (d, $^4J_{\text{(C-F)}} = 1.9$ Hz, CHCH₂), 27.7 (d, $^2J_{\text{(C-F)}} = 9.4$ Hz, Ar-CHCHF), 22.9 (2 x CH₂), 22.8 (C_qCHF), 14.2 (CH₂CH₃), 7.13 (d, $J = 8.6$ Hz, C_qCH₃); ^{19}F NMR (470 MHz, CDCl_3) δ -227.51 (dd, $^2J_{\text{(H-F)}} = 65.4$ Hz, $^3J_{\text{trans (H-F)}} = 7.5$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for C₁₅H₂₀FO [M-H]⁻ 235.1504; Found: 235.1497.

(1R*,2R*,6R*,7R*)-2-Butyl-7-fluorobicyclo[4.1.0]heptan-2-ol ((4o)-minor)



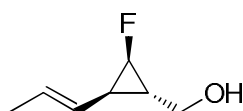
Prepared according to general procedure **6** to afford fluorocyclopropane **4o-(minor)** as yellow oil (66 mg, 41%, *dr* = 60:40). R_f = 0.4 (30% EtOAc in hexane). IR (film)/ cm^{-1} 3398, 2913, 2855, 1457, 1371, 1050; ^1H NMR (500 MHz, CDCl_3): δ 4.66 (dt, $^2J_{(\text{H-F})} = 68.2$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.4$ Hz, 1H, CHF), 1.91-1.84 (m, 1H, CH_aH_b), 1.70-1.66 (m, 2H, CH_2), 1.53-1.26 (m, 9H, overlapping CH_2), 1.18-1.11 (m, 1H, CH_2CHCHF), 1.00-0.97 (m, 1H, C_qCHCHF), 0.93 (t, $J = 7.3$ Hz, 3H, CH_3); ^{13}C NMR (126 MHz, CDCl_3): δ 76.8 (d, $^1J_{(\text{C-F})} = 219.0$ Hz, CHF), 71.3 (d, $^3J_{(\text{C-F})} = 3.3$ Hz, C_q), 42.2 (CH_2), 36.7 (d, $^3J_{(\text{C-F})} = 3.2$ Hz, CH_2), 25.6 (CH_2), 23.4 (CH_2), 22.1 (d, $^2J_{(\text{C-F})} = 8.4$ Hz, C_qCHCHF), 21.6 (CH_2), 16.2 (d, $^3J_{(\text{C-F})} = 5.8$ Hz, CH_2) 15.1 (d, $^2J_{(\text{C-F})} = 10.2$ Hz, CH_2CHCHF), 14.3 (CH_3); ^{19}F NMR (470 MHz, CDCl_3): δ -233.43 (d, $^2J_{(\text{H-F})} = 68.1$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{11}\text{H}_{18}\text{FO}$ [M-H] $^-$ 185.1342; Found: 185.1466.

(1R*,2R*,6R*,7S*)-2-Butyl-7-fluorobicyclo[4.1.0]heptan-2-ol ((4o)-major and (4o)-minor)



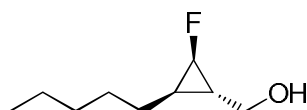
Prepared according to general procedure **6** to afford fluorocyclopropane **4o-(major)** and **4o-(minor)** as yellow oil (66 mg, 41%, *dr* = 60:40 according to ^{19}F NMR of the crude). R_f = 0.6 (30% EtOAc in hexane). IR (film)/ cm^{-1} 3442, 2932, 2870, 1662, 1458, 1408, 1378, 1162, 1137, 1088, 1029, 786, 751; ^1H NMR (500 MHz, CDCl_3 , mixture of diastereoisomers) δ 4.66 (dt, $^2J_{(\text{H-F})} = 68.2$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.4$ Hz, 1H, CHF minor) 4.58 (d, $^2J_{(\text{H-F})} = 64.3$ Hz, 1H, CHF major), 1.91-1.85 (m, 1H, CH_aH_b , overlapping major and minor), 1.79-1.65 (m, 3H, CH_2 , overlapping major and minor), 1.54-1.50 (m, 2H, CH_2 , overlapping major and minor), 1.45-1.41 (m, 2H, CH_2 , overlapping major and minor), 1.36-1.26 (m, 4H, 2 x CH_2 , overlapping major and minor), 1.18-1.11 (m, 1H, CH_2CHCHF , overlapping major and minor), 1.00-0.97 (m, 1H, C_qCHCHF , overlapping major and minor), 0.93 (t, $J = 7.5$ Hz, 3H, CH_3 , overlapping major and minor); ^{13}C NMR (126 MHz, CDCl_3 , mixture of diastereoisomers) δ 76.1 (d, $^1J_{(\text{C-F})} = 220.7$ Hz, CHF major) 75.1 (d, $^1J_{(\text{C-F})} = 219.0$ Hz, CHF minor), 71.3 (d, $^3J_{(\text{C-F})} = 3.1$ Hz, C_q minor), 69.1 (C_q major), 43.9 (CH_2 major), 42.2 (CH_2 minor), 36.7 (d, $^3J_{(\text{C-F})} = 3.1$ Hz, CH_2 minor), 35.1 (CH_2 major), 25.6 (CH_2 minor), 25.5 (CH_2 major), 23.4 (CH_2 minor), 23.3 (CH_2 major), 22.1 (d, $^2J_{(\text{C-F})} = 8.5$ Hz, C_qCHCHF overlapping major and minor), 21.6 (CH_2 minor), 20.7 (CH_2 major), 18.0 (CH_2 major), 16.2 (d, $^3J_{(\text{C-F})} = 5.8$ Hz, CH_2 minor) 15.1 (d, $^2J_{(\text{C-F})} = 10.2$ Hz, CH_2CHCHF overlapping major and minor), 14.3 (CH_3 minor), 14.2 (CH_3 major); ^{19}F NMR (470 MHz, CDCl_3 , mixture of diastereoisomers) δ -206.79 (dt, $^2J_{(\text{H-F})} = 64.5$ Hz, $^3J_{\text{cis}(\text{H-F})} = 22.5$ Hz, CHF major), -233.44 (d, $^2J_{(\text{H-F})} = 69.6$ Hz, CHF minor); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{11}\text{H}_{20}\text{FO}$ [M+Na] $^+$ 209.1312; Found: 209.1313.

((1R*,2S*,3S*)-2-Fluoro-3-((E)-prop-1-en-1-yl)cyclopropyl)methanol (4p)



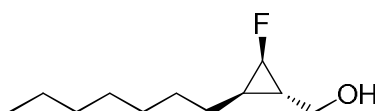
Prepared according to general procedure **6** to afford fluorocyclopropane **4p** as orange oil (82 mg, 73%, *dr* > 95:5). $R_f = 0.4$ (20% AcOEt in hexane); IR (film)/ cm^{-1} 3401, 2924, 2854, 1650, 1053; ^1H NMR (500 MHz, CDCl_3) δ 5.67 (m, 1H, $\text{CH}_3\text{CH}=\text{C}$), 5.29-5.24 (m, 1H, $\text{CH}_3\text{CH}=\text{CH}$), 4.52 (ddd, $^2J_{(\text{H-F})} = 63.9$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.4$ Hz, $^3J_{\text{trans}(\text{H-H})} = 2.4$ Hz, 1H, CHF), 3.56-3.54 (m, 2H, CH_2OH), 1.70 (d, $J = 1.7$ Hz, 3H, CH_3), 1.55-1.46 (m, 2H, overlapping CHCHF and CHCH_2OH); ^{13}C NMR (126 MHz, CDCl_3) δ 127.3 ($\text{CH}_3\text{CH}=\text{C}$), 125.5 (d, $^3J_{(\text{C-F})} = 7.7$ Hz, $\text{CH}_3\text{CH}=\text{CH}$), 75.7 (d, $^1J_{(\text{C-F})} = 224.4$ Hz, CHF), 62.2 (CH_2OH), 27.5 (d, $^2J_{(\text{C-F})} = 9.5$ Hz, CHCH_2OH), 24.9 (d, $^2J_{(\text{C-F})} = 10.6$ Hz, $\text{CHCH}=\text{CHCH}_3$); ^{19}F NMR (470 MHz, CDCl_3) δ -221.26 (ddd, $^2J_{(\text{H-F})} = 63.9$ Hz, $^3J_{\text{cis}(\text{H-F})} = 20.7$ Hz, $^3J_{\text{trans}(\text{H-F})} = 4.9$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_7\text{H}_{10}\text{FO}$ [M-H] $^-$ 129.0716; Found: 129.0919.

((1R*,2S*,3S*)-2-Fluoro-3-pentylcyclopropyl)methanol (4q)



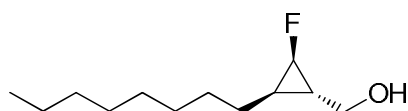
Prepared according to general procedure **6** to afford fluorocyclopropane **4q** as yellow oil (98 mg, 70%, *dr* > 95:5). $R_f = 0.4$ (20% EtOAc in hexane). IR (film)/ cm^{-1} 3370, 2925, 2855, 1457, 1073; ^1H NMR (500 MHz, CDCl_3) δ 4.54-4.39 (m, 1H, CHF), 3.48 (d, $J = 7.0$ Hz, 2H, CH_2OH), 1.52-1.31 (m, 8H, 4 x CH_2), 1.20-1.14 (m, 1H, CHCH_2OH), 0.91-0.88 (m, 3H, CH_3), 0.88-0.78 (m, 1H, $\text{CH}_3(\text{CH}_2)_4\text{CH}$); ^{13}C NMR (126 MHz, CDCl_3): δ 76.0 (d, $^1J_{(\text{C-F})} = 222.5$ Hz, CHF), 62.9 (CH_2OH), 31.7 (CH_2), 29.4 (CH_2), 26.4 (d, $^2J_{(\text{C-F})} = 9.1$ Hz, CHCH_2OH), 26.1 (d, $^3J_{(\text{C-F})} = 6.4$ Hz, $\text{CH}_3(\text{CH}_2)_3\text{CH}_2$), 22.7 (CH_2), 22.0 (d, $^2J_{(\text{C-F})} = 10.9$ Hz, $\text{CH}_3(\text{CH}_2)_4\text{CHCHF}$), 14.2 (CH_3); ^{19}F NMR (470 MHz, CDCl_3): δ -224.98 (ddd, $^2J_{(\text{H-F})} = 64.8$ Hz, $^3J_{\text{cis}(\text{H-F})} = 20.8$ Hz, $^3J_{\text{trans}(\text{H-F})} = 5.6$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_9\text{H}_{18}\text{FO}$ [M+H] $^+$ 161.1342; Found: 161.0525.

((1R*,2S*,3S*)-2-fluoro-3-heptylcyclopropyl)methanol (4r)



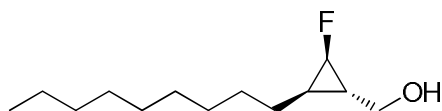
Prepared according to general procedure **6** to afford fluorocyclopropane **4r** as yellow oil (98 mg, 57%, *dr* > 95:5). $R_f = 0.3$ (50% diethyl ether in hexane); IR (film)/ cm^{-1} 3401, 2926, 2856, 1463, 1456, 1041, 1037; ^1H NMR (500 MHz, CDCl_3) δ 4.47 (ddd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.5$ Hz, $^3J_{\text{trans}(\text{H-H})} = 2.0$ Hz, 1H, CHF), 3.49 (d, $J = 6.5$ Hz, 2H, CH_2OH), 1.51-1.48 (m, 2H, CH_2CHCHF), 1.43-1.40 (m, 2H, $\text{CH}_2\text{CH}_2\text{CHCHF}$), 1.32-1.25 (m, 8H, 4 x CH_2), 1.18-1.15 (m, 1H, CHCH_2OH), 0.88 (t, $J = 6.8$ Hz, 3H, CH_3), 0.81-0.75 (m, 1H, $\text{CH}_3(\text{CH}_2)_6\text{CHCHF}$); ^{13}C NMR (126 MHz, CDCl_3) δ 76.0 (d, $^1J_{(\text{C-F})} = 226.5$ Hz, CHF), 63.0 (CH_2OH), 32.0 (CH_2), 29.7 (CH_2), 29.4₇ (CH_2), 29.4₀ (CH_2), 26.4 (d, $^2J_{(\text{C-F})} = 9.1$ Hz, CHCH_2OH), 26.1 (d, $^3J_{(\text{C-F})} = 6.3$ Hz, CH_2CHCHF), 22.8 (CH_2), 22.0 (d, $^2J_{(\text{C-F})} = 11.0$ Hz, $\text{CH}_3(\text{CH}_2)_6\text{CHCHF}$), 14.3 (CH_3); ^{19}F NMR (470 MHz, CDCl_3) δ -224.99 (ddd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-F})} = 21.0$ Hz, $^3J_{\text{trans}(\text{H-F})} = 5.4$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{11}\text{H}_{20}\text{FO}$ [M-H] $^-$ 187.1504; Found: 187.1501.

((1R*,2S*,3S*)-2-Fluoro-3-octylcyclopropyl)methanol (4s)



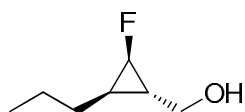
Prepared according to general procedure **6** to afford fluorocyclopropane **4s** as pale yellow oil (105 mg, 60%, *dr* > 95:5). $R_f = 0.3$ (20% EtOAc in hexane). IR (film)/ cm^{-1} 3367, 2919, 1458, 1031, 666; ^1H NMR (500 MHz, CDCl_3): δ 4.46 (ddd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.5$ Hz, $^3J_{\text{trans}(\text{H-H})} = 1.9$ Hz, 1H, CHF), 3.47 (d, $J = 7.0$ Hz, 2H, CH_2OH), 1.51-1.47 (m, 2H, CH_2), 1.45-1.39 (m, 2H, CH_2), 1.34-1.27 (m, 10H, 5 x CH_2), 1.21-1.12 (m, 1H, CHCH_2OH), 0.88 (t, $J = 6.9$ Hz, 3H, CH_3), 0.81-0.74 (m, 1H, $\text{CH}_3(\text{CH}_2)_7\text{CHCHF}$); ^{13}C NMR (126 MHz, CDCl_3): δ 76.0 (d, $^1J_{(\text{C-F})} = 222.4$ Hz, CHF), 62.9 (CH_2OH), 32.0 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.4 (d, $^2J_{(\text{C-F})} = 9.1$ Hz, CHCH_2OH), 26.1 (d, $^3J_{(\text{C-F})} = 6.3$ Hz, $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{CH}$), 22.8 (CH_2), 21.9 (d, $^2J_{(\text{C-F})} = 10.9$ Hz, $\text{CH}_3(\text{CH}_2)_7\text{CHCHF}$), 14.2 (CH_3); ^{19}F NMR (470 MHz, CDCl_3): δ -224.96 (ddd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-F})} = 20.8$ Hz, $^3J_{\text{trans}(\text{H-F})} = 5.6$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{12}\text{H}_{22}\text{FO}$ [M-H] $^-$ 201.1660; Found: 201.1653.

((1R*,2S*,3S*)-2-Fluoro-3-nonylcyclopropyl)methanol (4t)



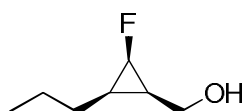
Prepared according to general procedure **6** to afford fluorocyclopropane **4t** as yellow oil (120 mg, 64%, *dr* > 95:5). $R_f = 0.3$ (50% diethyl ether in hexane); IR (film)/ cm^{-1} 3339, 2921, 2852, 1455, 1049; ^1H NMR (300 MHz, CDCl_3) δ 4.47 (ddd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.5$ Hz, $^3J_{\text{trans}(\text{H-H})} = 2.0$ Hz, 1H, CHF), 3.78-3.47 (m, 6H, overlapping 3 x CH_2), 1.77-1.43 (m, 12H, overlapping 6 x CH_2), 1.16-1.11 (m, 1H, CHCH_2OH), 0.88 (t, $J = 6.7$ Hz, 3H, CH_3), 0.82-0.74 (m, 1H, $\text{CH}_3(\text{CH}_2)_8\text{CHCHF}$); ^{13}C NMR (75 MHz, CDCl_3) δ 75.9 (d, $^1J_{(\text{C-F})} = 222.6$ Hz, CHF), 64.4 (CH_2), 63.0 (CH_2), 61.5 (CH_2), 32.1 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.5 (d, $^2J_{(\text{C-F})} = 9.0$ Hz, CHCH_2OH), 26.1 (d, $^3J_{(\text{C-F})} = 6.3$ Hz, CH_2), 22.8 (CH_2), 22.0 (d, $^2J_{(\text{C-F})} = 10.9$ Hz, $\text{CH}_3(\text{CH}_2)_8\text{CHCHF}$), 14.2 (CH_3); ^{19}F NMR (282 MHz, CDCl_3) δ -224.99 (ddd, $^2J_{(\text{H-F})} = 65.3$ Hz, $^3J_{\text{cis}(\text{H-F})} = 21.7$ Hz, $^3J_{\text{trans}(\text{H-F})} = 6.2$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{13}\text{H}_{24}\text{FO}$ [M-H] $^-$ 215.1817; Found: 215.1807.

((1R*,2S*,3S*)-2-Fluoro-3-propylcyclopropyl)methanol (4u)



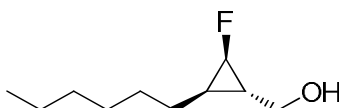
Prepared according to general procedure **6** to afford fluorocyclopropane **4u** as colorless oil (93 mg, 81%, *dr* > 95:5). $R_f = 0.4$ (60% diethyl ether in hexane); IR (film)/ cm^{-1} 3400, 2957, 2924, 2853, 1730, 1633, 1463, 1377, 1232; ^1H NMR (500 MHz, CDCl_3) δ 4.47 (ddd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.5$ Hz, $^3J_{\text{trans}(\text{H-H})} = 1.9$ Hz, 1H, CHF), 3.49 (d, $J = 7.0$ Hz, 2H, CH_2OH), 1.50-1.43 (m, 4H, 2 x CH_2), 1.23-1.14 (m, 1H, CHCH_2OH), 0.95 (t, $J = 7.0$ Hz, 3H, CH_3), 0.82-0.79 (m, 1H, $\text{CH}_3(\text{CH}_2)_2\text{CH}$); ^{13}C NMR (75 MHz, CDCl_3) δ 75.91 (d, $^1J_{(\text{C-F})} = 219.0$ Hz, CHF), 63.0 (CH_2OH), 28.2 (d, $^3J_{(\text{C-F})} = 6.3$ Hz, CH_2CHCHF), 26.4 (d, $^2J_{(\text{C-F})} = 9.1$ Hz, CHCH_2OH), 22.8 (CH_3CH_2), 21.8 (d, $^2J_{(\text{C-F})} = 10.9$ Hz, $\text{CHCH}_2\text{CH}_2\text{CH}_3$), 13.9 (CH_3); ^{19}F NMR (470 MHz, CDCl_3) δ -224.89 (ddd, $^2J_{(\text{H-F})} = 64.8$ Hz, $^3J_{\text{cis}(\text{H-F})} = 20.6$ Hz, $^3J_{\text{trans}(\text{H-F})} = 5.6$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_7\text{H}_{12}\text{FO}$ [M-H] $^-$ 131.0878; Found: 131.0848.

((1R*,2R*,3R*)-2-Fluoro-3-propylcyclopropyl)methanol (4v)



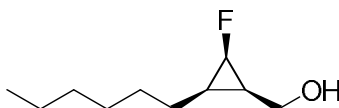
Prepared according to general procedure 6 to afford fluorocyclopropane **4v** as colorless oil (91 mg, 80%, *dr* = 80:20, *selected data for major*). R_f = 0.3 (50% diethyl ether in hexane); IR (film)/ cm^{-1} 3392, 2923, 2853, 1463, 1377, 1233, 1052; ^1H NMR (500 MHz, CDCl_3 , *selected data for major*) δ 4.69 (dt, $^2J_{(\text{H-F})} = 66.2$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.0$ Hz, 1H, CHF), 3.87 (dd, $J = 11.3, 6.8$ Hz, 1H, $\text{CH}_a\text{H}_b\text{OH}$), 3.79 (dd, $J = 11.4, 8.9$ Hz, 1H, $\text{CH}_a\text{H}_b\text{OH}$) 1.46-1.42 (m, 2H, CH_2CH_3), 1.30-1.28 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.18-1.14 (m, 1H, CHCH_2OH), 0.95 (t, $J = 7.1$ Hz, 3H, CH_3), 0.88-0.84 (m, 1H, $\text{CH}_3(\text{CH}_2)_2\text{CHCHF}$); ^{13}C NMR (126 MHz, CDCl_3 , *selected data for major*) δ 73.7 (d, $^1J_{(\text{C-F})} = 217.6$ Hz, CHF), 57.5 (d, $^3J_{(\text{C-F})} = 9.3$ Hz, CH_2OH), 29.9 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 23.2 (CH_2CH_3), 20.5 (d, $^2J_{(\text{C-F})} = 9.7$ Hz, CHCH_2OH), 19.4 (d, $^2J_{(\text{C-F})} = 10.5$ Hz, $\text{CH}_3(\text{CH}_2)_2\text{CHCHF}$), 14.0 (CH_3CH_2); ^{19}F NMR (470 MHz, CDCl_3 , *selected data for major*) δ -239.88 (dt, $^2J_{(\text{H-F})} = 66.2$ Hz, $^3J_{\text{trans}(\text{H-F})} = 7.9$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_7\text{H}_{13}\text{FNaO}$ $[\text{M}+\text{Na}]^+$ 155.0843; Found: 155.0839.

((1R*,2S*,3S*)-2-Fluoro-3-hexylcyclopropyl)methanol (4w)



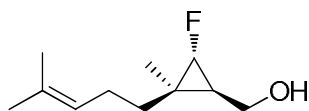
Prepared according to general procedure 6 to afford fluorocyclopropane **4w** as yellow oil (83 mg, 55%, *dr* > 95:5). R_f = 0.3 (50% diethyl ether in hexane); IR (film)/ cm^{-1} 3367, 2923, 2855, 1461, 1033; ^1H NMR (500 MHz, CDCl_3) δ 4.47 (ddd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.5$ Hz, $^3J_{\text{trans}(\text{H-H})} = 1.9$ Hz, 1H, CHF), 3.49-3.48 (m, 2H, CH_2OH), 1.53-1.48 (m, 2H, CH_2CH_3), 1.46-1.29 (m, *overlapping* 4 x CH_2), 1.21-1.14 (m, 1H, CHCH_2OH), 0.89 (t, $J = 6.9$ Hz, 3H, CH_3), 0.81-0.77 (m, 1H, $\text{CH}(\text{CH}_2)_5\text{CH}_3$); ^{13}C NMR (126 MHz, CDCl_3) δ 75.9 (d, $^1J_{(\text{C-F})} = 222.7$ Hz, CHF), 63.0 (CH_2OH), 31.9 (CH_2), 29.7 (CH_2), 29.1 (CH_2), 26.4 (d, $^2J_{(\text{C-F})} = 9.1$ Hz, CHCH_2OH), 26.1 (d, $^3J_{(\text{C-F})} = 6.4$ Hz, $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{CHCHF}$), 22.8 (CH_2), 22.0 (d, $^2J_{(\text{C-F})} = 10.9$ Hz, $\text{CH}(\text{CH}_2)_5\text{CH}_3$), 14.2 (CH_3); ^{19}F NMR (470 MHz, CDCl_3) δ -224.99 (ddd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-F})} = 20.7$ Hz, $^3J_{\text{trans}(\text{H-F})} = 5.6$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{10}\text{H}_{18}\text{FO}$ $[\text{M}-\text{H}]^-$ 173.1347; Found: 173.1350.

((1R*,2R*,3R*)-2-Fluoro-3-hexylcyclopropyl)methanol (4x)



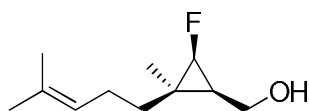
Prepared according to general procedure 6 to afford fluorocyclopropane **4x** as yellow oil (122 mg, 81%, *dr* = 70:30, *selected data for major*). R_f = 0.3 (50% diethyl ether in hexane); IR (film)/ cm^{-1} 3368, 2926, 2857, 1466, 1423, 1378, 1247, 1216, 1136, 1029; ^1H NMR (500 MHz, CDCl_3 , *selected data for major*) δ 4.67 (dt, $^2J_{(\text{H-F})} = 66.2$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.0$ Hz, 1H, CHF), 3.86 (dd, $J = 11.5, 6.7$ Hz, 1H, $\text{CH}_a\text{H}_b\text{OH}$), 3.77 (dd, $J = 11.6, 8.8$ Hz, 1H, $\text{CH}_a\text{H}_b\text{OH}$), 1.52-1.29 (m, 10H, 5 x CH_2), 1.19-1.11 (m, 1H, CHCH_2OH), 0.93-0.91 (m, 1H, $\text{CH}_3(\text{CH}_2)_5\text{CHCHF}$), 0.88 (t, $J = 6.8$ Hz, 3H, CH_3); ^{13}C NMR (126 MHz, CDCl_3 , *selected data for major*) δ 73.7 (d, $^1J_{(\text{C-F})} = 217.6$ Hz, CHF), 57.4 (d, $^3J_{(\text{C-F})} = 9.3$ Hz, CH_2OH), 31.9 (CH_2), 30.0 (CH_2), 29.2 (CH_2), 22.8 (CH_2), 21.3 (d, $^3J_{(\text{C-F})} = 6.8$ Hz, CH_2CHCHF), 20.5 (d, $^2J_{(\text{C-F})} = 9.7$ Hz, CHCH_2OH), 19.6 (d, $^2J_{(\text{C-F})} = 10.5$ Hz, $\text{CH}_3(\text{CH}_2)_5\text{CHCHF}$), 14.2 (CH_3); ^{19}F NMR (470 MHz, CDCl_3 , *selected data for major*) δ -240.00 (dt, $^2J_{(\text{H-F})} = 66.2$ Hz, $^3J_{\text{trans}(\text{H-F})} = 7.9$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{10}\text{H}_{18}\text{FO}$ $[\text{M}-\text{H}]^-$ 173.1347; Found: 173.1339.

((1R*,2R*,3R*)-3-Fluoro-2-methyl-2-(4-methylpent-3-en-1-yl)cyclopropyl)methanol (4y-(major))



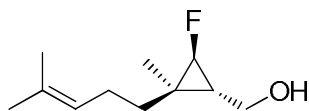
Prepared according to general procedure **6** to afford fluorocyclopropane **4y-(major)** as pale yellow oil (111 mg, 74%, *dr* = 70:30, selected data for major according to ^{19}F NMR of the crude). R_f = 0.5 (60% diethyl ether in hexane); IR (film)/ cm^{-1} 3369, 2923, 1456, 1041; ^1H NMR (500 MHz, CDCl_3 , selected data for major) δ 5.09-5.08 (m, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$), 4.18 (dd, $^2J_{(\text{H-F})} = 64.6$ Hz, $^3J_{\text{trans}(\text{H-H})} = 2.5$ Hz, 1H, CHF), 3.68-3.65 (m, 1H, $\text{CHCH}_a\text{CH}_b\text{OH}$), 3.59-3.55 (m, 1H, $\text{CHCH}_a\text{CH}_b\text{OH}$), 2.05-1.99 (m, 2H, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 1.69 (s, 3H, $(\text{CH}_3)_2\text{C}=\text{CH}$), 1.62 (s, 3H, $(\text{CH}_3)_2\text{C}=\text{CH}$), 1.37-1.33 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 1.23 (d, $J = 1.3$ Hz, 3H, $\text{CH}_3\text{C}_q\text{CHF}$), 1.21 (m, 1H, CHCHF); ^{13}C NMR (126 MHz, CDCl_3 , selected data for major) δ 132.3 ($(\text{CH}_3)_2\text{C}=\text{CH}$), 123.9 ($(\text{CH}_3)_2\text{C}=\text{CH}$), 81.0 (d, $^1J_{(\text{C-F})} = 229.8$ Hz, CHF), 60.4 (CH_2OH), 32.5 (d, $^2J_{(\text{C-F})} = 8.9$ Hz, CHCHF), 29.8 ($\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 25.8 ($\text{CH}_3\text{C}=\text{CH}$), 24.9 (d, $^3J_{(\text{C-F})} = 1.9$ Hz, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 22.8 (C_qCHF), 17.7 ($(\text{CH}_3)_2\text{C}=\text{CH}$), 17.3 (d, $^3J_{(\text{C-F})} = 8.7$ Hz, $\text{CH}_3\text{C}_q\text{CHF}$); ^{19}F NMR (470 MHz, CDCl_3 , selected data for major) δ -216.96 (dd, $^2J_{(\text{H-F})} = 64.7$ Hz, $^3J_{\text{cis}(\text{H-F})} = 22.1$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{11}\text{H}_{18}\text{FO}$ [M-H] $^-$ 185.1347; Found: 185.1333.

((1R*,2R*,3S*)-3-Fluoro-2-methyl-2-(4-methylpent-3-en-1-yl)cyclopropyl)methanol (4y-(minor))



Prepared according to general procedure **6** to afford fluorocyclopropane **4y-(minor)** as pale yellow oil (111 mg, 74%, *dr* = 70:30). R_f = 0.4 (60% diethyl ether in hexane); IR (film)/ cm^{-1} 3369, 2923, 1456, 1041; ^1H NMR (500 MHz, CDCl_3) δ 5.13 (t, $J = 7.2$ Hz, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$), 4.36 (dd, $^2J_{(\text{H-F})} = 65.8$ Hz, $^3J_{\text{cis}(\text{H-H})} = 6.1$ Hz, 1H, CHF), 3.90-3.86 (m, 1H, $\text{CHCH}_a\text{CH}_b\text{OH}$), 3.77-3.73 (m, 1H, $\text{CHCH}_a\text{CH}_b\text{OH}$), 2.14-1.99 (m, 2H, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 1.69 (s, 3H, $(\text{CH}_3)_2\text{C}=\text{CH}$), 1.62 (s, 3H, $(\text{CH}_3)_2\text{C}=\text{CH}$), 1.54-1.49 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 1.00 (t, $J = 4.9$ Hz, 3H, $\text{CH}_3\text{C}_q\text{CHF}$), 1.01-0.95 (m, 1H, CHCHF); ^{13}C NMR (126 MHz, CDCl_3) δ 132.1 ($(\text{CH}_3)_2\text{C}=\text{CH}$), 124.2 ($(\text{CH}_3)_2\text{C}=\text{CH}$), 79.4 (d, $^1J_{(\text{C-F})} = 222.0$ Hz, CHF), 57.9 (d, $^3J_{(\text{C-F})} = 9.6$ Hz, CH_2OH), 29.3 (d, $^2J_{(\text{C-F})} = 9.8$ Hz, CHCHF), 27.6 (d, $^3J_{(\text{C-F})} = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 25.8 ($\text{CH}_3\text{C}=\text{CH}$), 25.2 ($\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 22.9 (d, $^2J_{(\text{C-F})} = 9.0$ Hz, C_qCHF), 22.2 ($\text{CH}_3\text{C}_q\text{CHF}$), 17.7 ($\text{CH}_3\text{C}=\text{CH}$); ^{19}F NMR (470 MHz, CDCl_3) δ -231.11 (dd, $^2J_{(\text{H-F})} = 65.5$ Hz, $^3J_{\text{trans}(\text{H-F})} = 5.2$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{11}\text{H}_{18}\text{FO}$ [M-H] $^-$ 185.1347; Found: 185.1333.

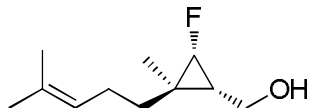
((1R*,2S*,3R*)-3-Fluoro-2-methyl-2-(4-methylpent-3-en-1-yl)cyclopropyl)methanol (4z-(major))



Prepared according to general procedure **6** to afford fluorocyclopropane **4z-(major)** as pale yellow oil (127 mg, 88%, *dr* = 55:45). R_f = 0.4 (60% diethyl ether in hexane); IR (film)/ cm^{-1} 3371, 2923, 2853, 1730, 1455, 1233, 1046; ^1H NMR (500 MHz, CDCl_3) δ 5.15 (t, $J = 7.1$ Hz, 1H, $\text{CH}=\text{C}(\text{CH}_3)_2$), 4.18 (dd, $^2J_{(\text{H-F})} = 64.3$ Hz, $^3J_{\text{trans}(\text{H-H})} = 2.4$ Hz, 1H, CHF), 3.75 (dd, $J = 11.5, 6.7$ Hz, 1H, $\text{CHCH}_a\text{CH}_b\text{OH}$), 3.47 (t, $J = 10.1$ Hz, 1H, $\text{CHCH}_a\text{CH}_b\text{OH}$), 2.18-2.10 (m, 2H, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 1.69 (s, 3H, $\text{CH}_3\text{C}=\text{CH}$), 1.63 (s, 3H, $\text{CH}_3\text{C}=\text{CH}$), 1.53-1.50 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 1.30-1.27 (m, 1H, CHCHF), 1.04 (d, $J = 3.0$ Hz, 3H, $\text{CH}_3\text{C}_q\text{CHF}$); ^{13}C NMR (126 MHz, CDCl_3) δ 131.9 ($(\text{CH}_3)_2\text{C}=\text{CH}$), 124.3 ($(\text{CH}_3)_2\text{C}=\text{CH}$), 81.6 (d, $^1J_{(\text{C-F})} = 229.5$ Hz, CHF), 60.6 (CH_2OH), 33.7 (d, $^3J_{(\text{C-F})} = 6.4$ Hz, $\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 31.6 (d, $^2J_{(\text{C-F})} = 9.4$ Hz, CHCHF), 25.8 ($\text{CH}_3\text{C}=\text{CH}$), 25.42 (d, $^2J_{(\text{C-F})} = 10.1$ Hz, C_qCHF),

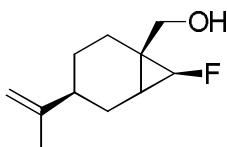
25.4 (CH₂CH=C(CH₃)₂), 17.7 (CH₃C=CH), 15.7 (d, ³J_(C-F) = 1.4 Hz, CH₃C_qCHF); ¹⁹F NMR (470 MHz, CDCl₃) δ -216.25 (dd, ²J_(H-F) = 64.3 Hz, ³J_{cis (H-F)}} = 22.6 Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₁H₁₈FO [M-H]⁻ 185.1347; Found: 185.1354.

((1R*,2S*,3S*)-3-Fluoro-2-methyl-2-(4-methylpent-3-en-1-yl)cyclopropyl)methanol (4z-(minor))



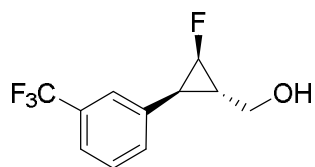
Prepared according to general procedure 6 to afford fluorocyclopropane **4z-(minor)** as pale yellow oil (127 mg, 88%, *dr* = 55:45). Compound **4z-(minor)** mixture with *trans*-geraniol **2z**. *R_f* = 0.6 (60% diethyl ether in hexane); IR (film)/cm⁻¹ 3338, 2967, 2917, 1669, 1439, 1377, 1109, 1014, 832; ¹H NMR (500 MHz, CDCl₃, *selected data for minor*) δ 5.05-5.03 (m, 1H, CH=C(CH₃)₂), 4.31 (dd, ²J_{(H-F)}} = 66.0 Hz, ³J_{cis (H-H)}} = 6.2 Hz, 1H, CHF), 3.79-3.70 (m, 2H, CH₂OH), 2.01-2.00 (m, 2H, CH₂CH=C(CH₃)₂), 1.67 (s, 6H, (CH₃)₂C=CH), 1.32-1.25 (m, 1H, CH_aH_bCH₂CH=C), 1.11 (d, *J* = 1.5 Hz, 3H, CH₃C_qCHF), 1.07-1.00 (m, 1H, CH_aH_bCH₂CH=C), 0.97-0.91 (m, 1H, CHCHF); ¹³C NMR (126 MHz, CDCl₃) δ 131.9 ((CH₃)₂C=CH), 123.8 ((CH₃)₂C=CH), 78.5 (d, ¹J_{(C-F)}} = 223.1 Hz, CHF), 57.8 (d, ³J_{(C-F)}} = 9.1 Hz, CH₂OH), 38.6 (CH₂CH₂CH=C) 27.8 (d, ²J_{(C-F)}} = 9.9 Hz, CHCHF), 24.3 (d, ⁴J_{(C-F)}} = 2.0 Hz, CH₂CH₂CH=C), 22.8 (d, ²J_{(C-F)}} = 8.7 Hz, C_qCH₃CHF), 17.7 ((CH₃)₂C=CH), 10.2 (d, ³J_{(C-F)}} = 9.3 Hz, CH₃C_qCHF); ¹⁹F NMR (470 MHz, CDCl₃) δ -230.82 (dd, ²J_{(H-F)}} = 66.0 Hz, ³J_{trans (H-F)}} = 6.7 Hz, CHF); HRMS (ESI-TOF) *m/z* Calcd for C₁₁H₁₈FO [M-H]⁻ 185.1347; Found: 185.0950.

((1R*,4R*,7R*)-7-Fluoro-4-(prop-1-en-2-yl)bicyclo[4.1.0]heptan-1-yl)methanol (4aa)



Prepared according to general procedure 6 to afford fluorocyclopropane **4aa** as yellow oil (69 mg, 36%, *dr* = 70:30, *inseparable mixture of diastereoisomers*). *R_f* = 0.2 (50% EtOAc in hexane); IR (film)/cm⁻¹ 3434, 2926, 2856, 1644, 1468, 1266, 1014; ¹H NMR (500 MHz, CDCl₃, *selected data for major*) δ 4.73-4.67 (m, 2H, C_q=CH₂), 4.37 (dd, ²J_{(H-F)}} = 67.2 Hz, ³J_{cis (H-H)}} = 6.7 Hz, 1H, CHF), 3.37-3.29 (m, 2H, CH₂OH), 2.13-2.09 (m, 1H, CH_aH_bCHC_q=CH₂), 2.00-1.96 (m, 1H, CH_aH_bCHCHF), 1.87-1.79 (m, 2H, *overlapping* CH_aH_bCHC_q=CH₂ and CHC_q=CH₂), 1.70 (s, 3H, CH₃), 1.60-1.57 (m, 1H, CH_aCH_bCH₂CHC_q=CH₂), 1.39-1.33 (m, 1H, CH_aH_bCHCHF), 1.18-1.16 (m, 1H, CH_aCH_bCH₂CHC_q=CH₂), 1.07-1.02 (m, 1H, CHCHF); ¹³C NMR (126 MHz, CDCl₃, *selected data for major*) δ 150.2 (C_q=CH₂), 108.9 (C_q=CH₂), 77.6 (d, ¹J_{(C-F)}} = 225.1 Hz, CHF), 68.8 (CH₂OH), 41.7 (CH₂=C_qCH), 27.0 (d, ⁴J_{(C-F)}} = 4.8 Hz, CH₂CH₂CHC_q=CH₂), 23.1 (d, ⁵J_{(C-F)}} = 3.6 Hz, CH₂CH₂CHC_q=CH₂), 22.1 (d, ³J_{(C-F)}} = 5.2 Hz, CH₂CHCHF), 20.9 (CH₃), 16.9 (d, ²J_{(C-F)}} = 10.1 Hz, CHCHF); ¹⁹F NMR (470 MHz, CDCl₃) δ -228.33 (dd, ²J_{(H-F)}} = 67.2 Hz, ³J_{trans (H-F)}} = 9.8 Hz, CHF *minor*), -229.73 (d, ²J_{(H-F)}} = 67.1 Hz, CHF *major*); HRMS (ESI-TOF) *m/z* Calcd for C₁₁H₁₆FO [M-H]⁻ 183.1191; Found: 183.1187.

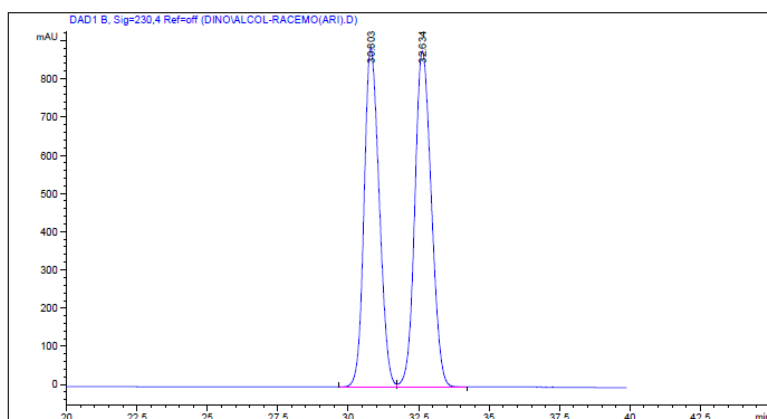
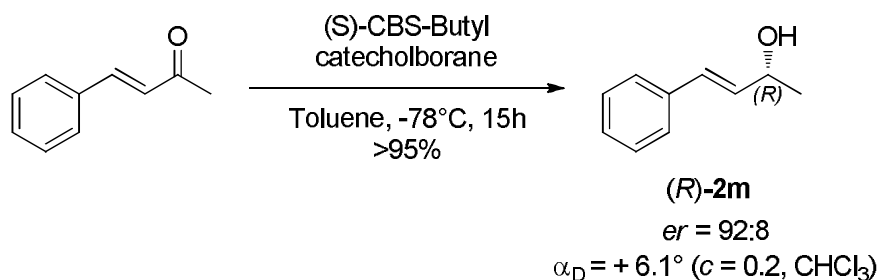
((1*S,2*R**,3*S**)-2-fluoro-3-phenylcyclopropyl)methanol (**4ad**)**



Prepared according to general procedure **6** to afford fluorocyclopropane **4ad** as colourless oil (21 mg, 15 %, *dr* > 95:5). $R_f = 0.4$ (40% EtOAc in hexane); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.51-7.49 (m, 2H, 2 x Ar-H), 7.43-7.42 (m, 2H, 2 x Ar-H), 4.75 (ddd, $^2J_{\text{(H-F)}} = 64.6$ Hz, $^3J_{\text{cis (H-H)}} = 6.6$ Hz, $^3J_{\text{trans (H-H)}} = 2.5$ Hz, 1H, CHF), 3.74 (d, $^3J_{\text{(H-H)}} = 6.1$ Hz, 2H, CH_2OH), 2.18-2.14 (m, 1H, Ar-CHCHF), 2.01-1.92 (m, 1H, CHCH $_2$ OH); $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 136.6 (d, $^4J_{\text{(C-F)}} = 2.9$ Hz, Ar-C $_q$), 131.9 (Ar-C), 128.8 (Ar-C $_q$), 125.6-125.5 (m, Ar-C), 123.4 $_5$ (q, $^3J_{\text{(C-F)}} = 3.8$ Hz, Ar-C), 75.2 (d, $^1J_{\text{(C-F)}} = 227.1$ Hz, CHF), 61.9 (CH_2OH), 27.5 $_5$ (d, $^2J_{\text{(C-F)}} = 8.7$ Hz, CHCH $_2$ OH), 26.1 $_5$ (d, $^2J_{\text{(C-F)}} = 11.0$ Hz, Ar-CHCHF); $^{19}\text{F NMR}$ (470 MHz, CDCl_3): δ 62.70 (s, 3F, CF_3), -220.77 (ddd, $^2J_{\text{(H-F)}} = 64.6$ Hz, $^3J_{\text{cis (H-F)}} = 20.8$ Hz, $^3J_{\text{trans (H-F)}} = 6.0$ Hz, CHF); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{11}\text{H}_9\text{F}_4\text{O}$ [M-H] $^-$ 233.0595; Found: 233.0591.

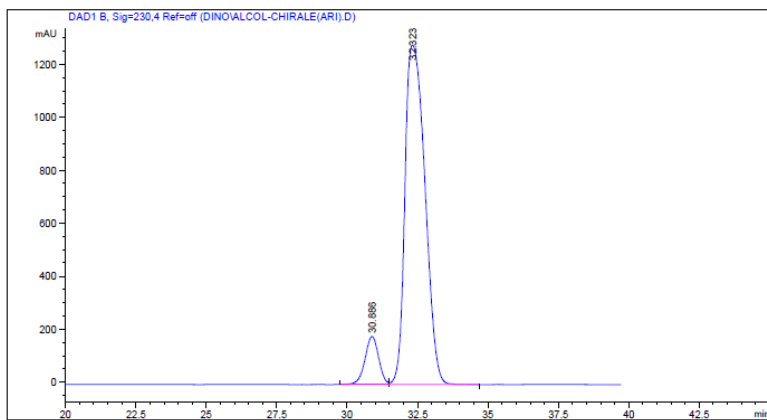
8. Synthesis of chiral allylic alcohol and fluorocyclopropane

Chiral allylic alcohol (**R**)-**2m** was prepared using the correspondent ketone, (*S*)-CBS-Butyl and catecholborane according to the literature procedure.¹⁸



Signal 1: DAD1 B, Sig=230,4 Ref=off

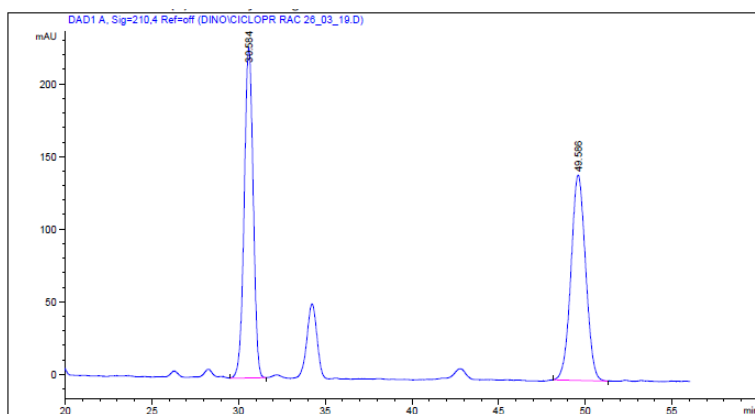
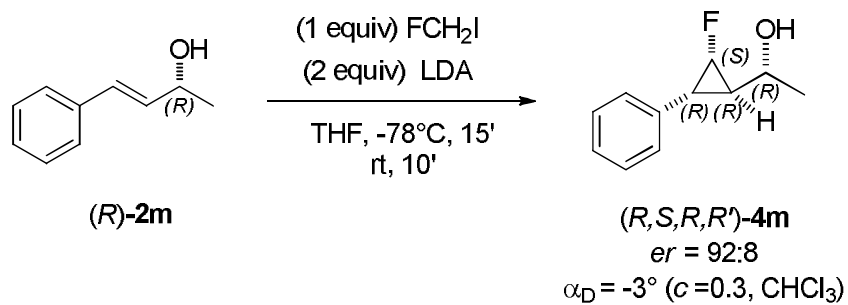
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.803	BV	0.5858	3.31313e4	886.97919	48.0282
2	32.634	VB	0.6356	3.58517e4	879.43799	51.9718



Signal 1: DAD1 B, Sig=230,4 Ref=off

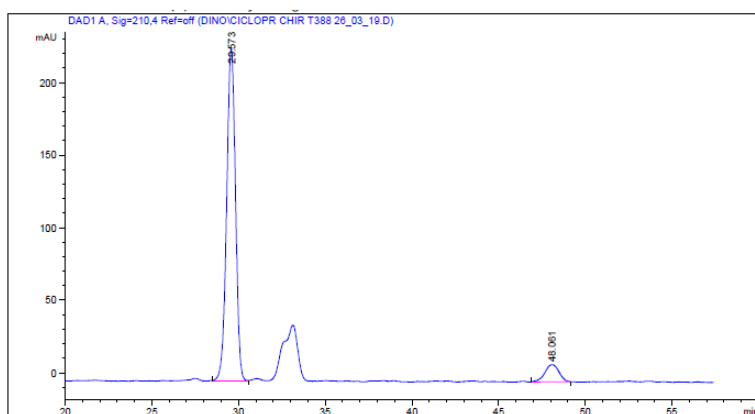
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.886	BV	0.5224	6089.12695	181.04192	8.8023
2	32.323	VB	0.7963	6.30874e4	1281.53003	91.1977

Chiralpak AD-H column; 99:1 = hexane:iPrOH, 1mL/min flux.



Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.584	BB	0.5658	8183.22168	227.40143	49.6489
2	49.586	BB	0.8465	8298.96875	141.44919	50.3511



Signal 1: DAD1 A, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.573	BB	0.5501	8081.93359	228.78384	92.4053
2	48.061	BB	0.6658	664.24219	11.89026	7.5947

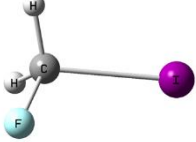
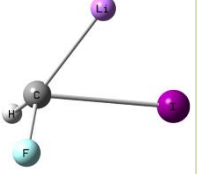
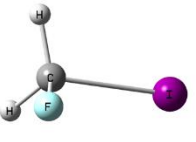
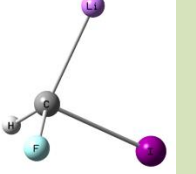
Chiralpak AD-H column; 99:1 = hexane:iPrOH, 1mL/min flux.

Computational Studies

1.1 Computational Methods

Density functional theory (DFT)¹⁹ calculations were performed using Gaussian 09 (revision E.01)²⁰ and the Gaussview²¹ was used to generate input geometries and visualize output structures. Regarding geometry optimizations and frequency calculations for fluoroiodomethane and fluoroiodomethylithium, B3LYP functional²²⁻²⁵ was used with the 6-311++G(d,p)+LANL2DZ (for I) mixed basis set.²⁶ For comparative purpose and to model solvation effect, the calculations were carried out in THF as a solvent, by applying the most commonly used integral equation formalism (IEF) version of polarized continuum model (PCM).²⁷⁻²⁸ All stationary points were characterized as minima and thermal corrections were computed from unscaled frequencies, assuming a standard state of 298.15 K and 1 atm.

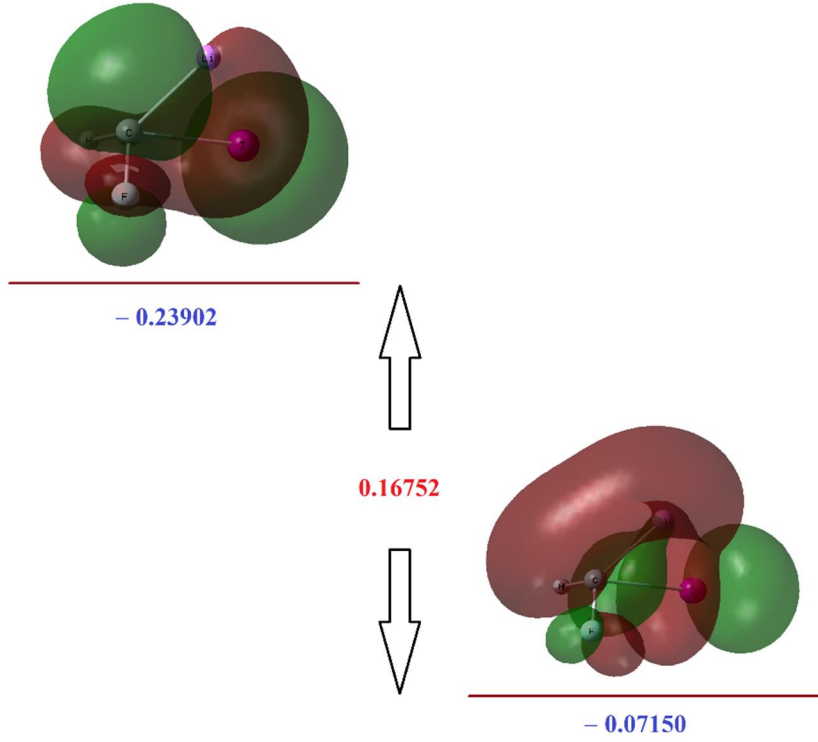
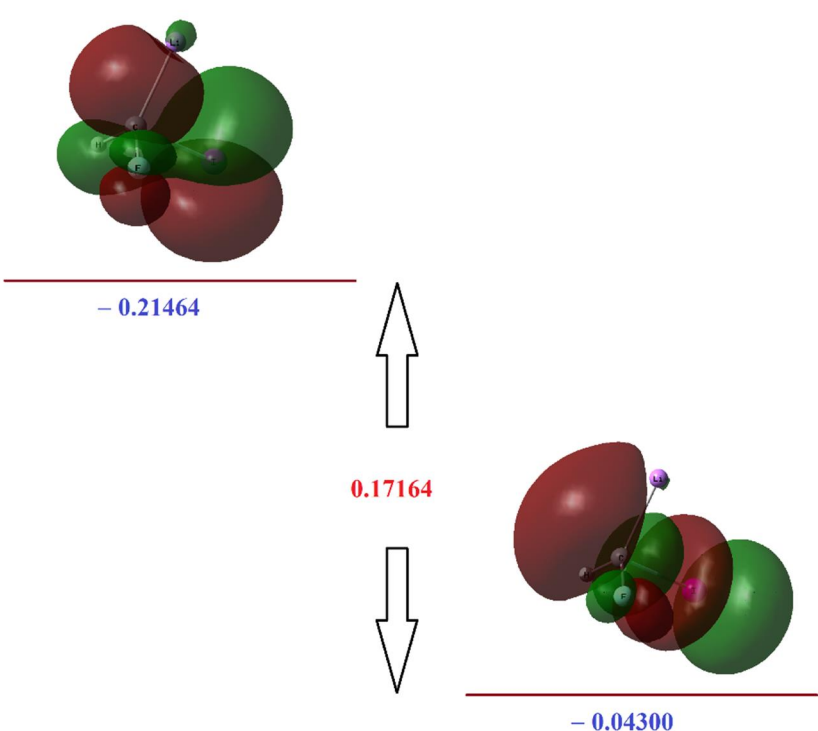
1.2 Structure optimization, bond lengths (Å) and measured bond angles (°)

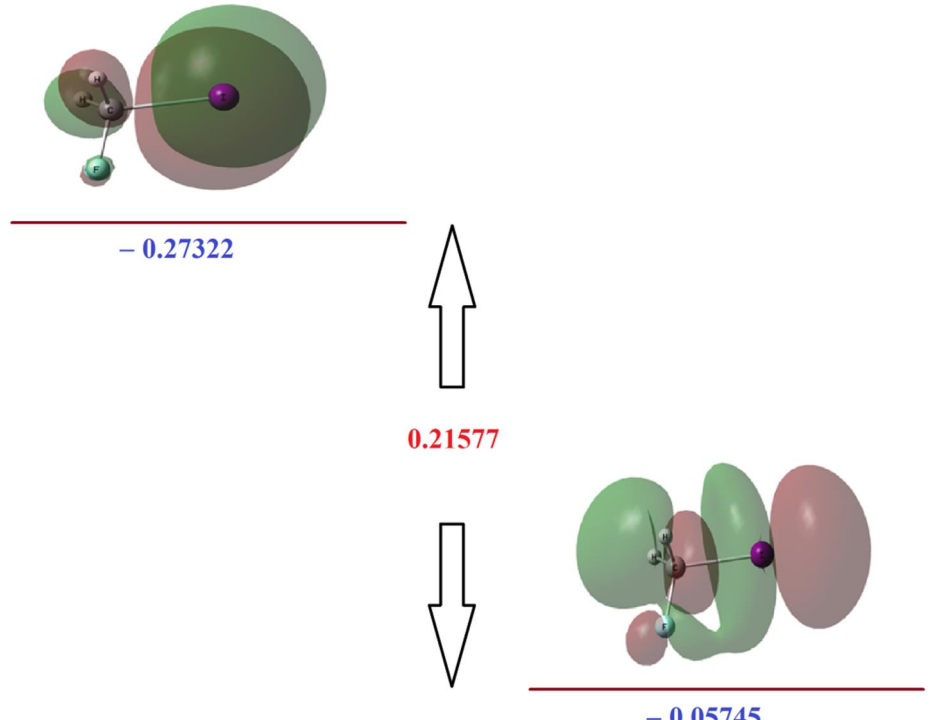
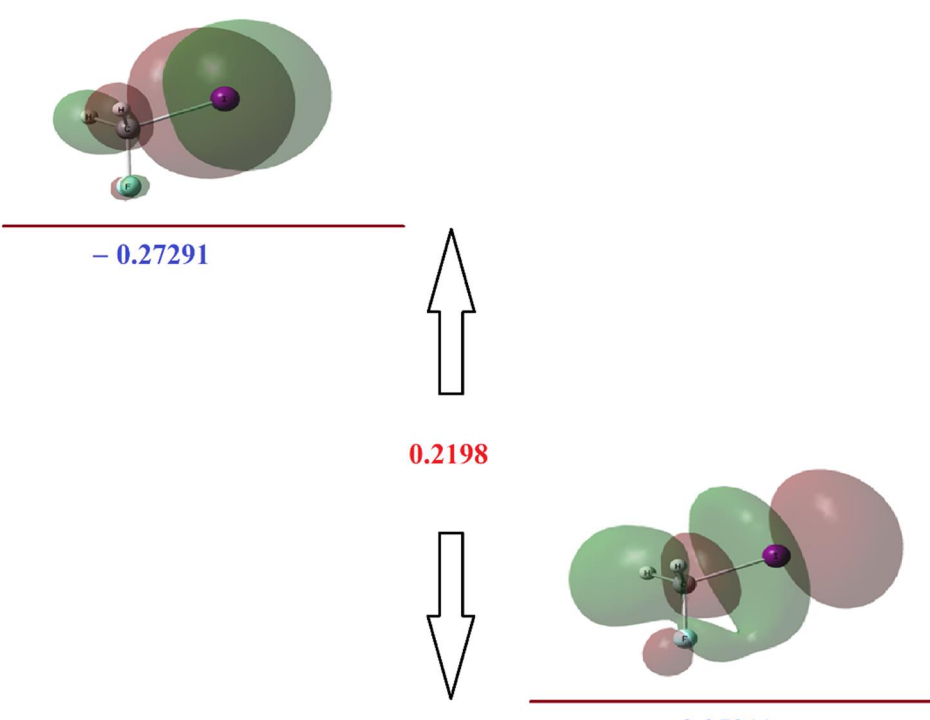
No.	Parameters	FICH ₂ – Gas Phase	FICHLi – Gas Phase	FICH ₂ – THF	FICHLi – THF
1	Optimized Structures				
2	Li–C (Å)		1.98715		2.09782
3	Li–I (Å)		2.54426		3.32028
4	Li–F (Å)		2.93467		3.03683
5	C–I (Å)	2.18567	2.59734	2.18841	2.46282
6	C–F (Å)	1.36730	1.35715	1.37357	1.39964
7	C–H (Å)	1.08609	1.10041	1.08486	1.09889
8	I–C–H (°)	106.62399	93.11711	106.73539	92.94860
9	I–C–Li (°)		65.85965		93.09497
10	C–Li–I (°)		68.68303		47.78852
11	Li–I–C (°)		45.45733		39.11651
12	F–C–Li (°)		121.54336		119.17297
13	C–Li–F (°)		23.21132		23.72995
14	Li–F–C (°)		35.24533		37.09708
15	I–C–F (°)	110.85934	106.95985	110.20028	104.53787
16	I–Li–F (°)		72.69869		58.65085

1.3 Electrostatic Potential Map

No.	Structure	Solid	Mesh	Transparent
1	FICH ₂ – Gas Phase			
2	FICH ₂ – THF			
3	FICHLi – Gas Phase			
4	FICHLi – THF			
Red: strong negative Blue: strong positive				

1.4 HOMO – LUMO Analysis

No.	Structure	HOMO – LUMO Energy Gap
1	FICH ₂ – Gas Phase	 <p style="text-align: center;"> - 0.23902 0.16752 - 0.07150 </p>
2	FICH ₂ – THF	 <p style="text-align: center;"> - 0.21464 0.17164 - 0.04300 </p>

3	FICHLi – Gas Phase	 <p>Energy level diagram for FICHLi in the gas phase. The ground state energy is -0.27322 eV. The excited state energy is -0.05745 eV. The energy difference between the two states is 0.21577 eV. Molecular models with isosurface plots are shown for both states.</p>
4	FICHLi – THF	 <p>Energy level diagram for FICHLi in THF. The ground state energy is -0.27291 eV. The excited state energy is -0.05311 eV. The energy difference between the two states is 0.2198 eV. Molecular models with isosurface plots are shown for both states.</p>

1.5 Natural and Mulliken Atomic Charges for FICH₂

Natural Atomic Charge			Mulliken Atomic Charge	
Atom	Gaseous Phase	THF (Solvent)	Gaseous Phase	THF (Solvent)
C	-0.07475	-0.06871	-0.394684	-0.391620
H	0.17727	0.18879	0.186500	0.207569
F	-0.37077	-0.38313	-0.080463	-0.104348
I	0.09098	0.07427	0.102147	0.080830
H	0.17727	0.18879	0.186500	0.207569

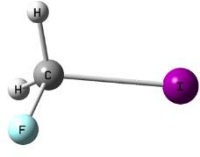
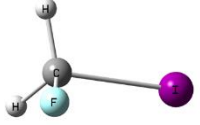
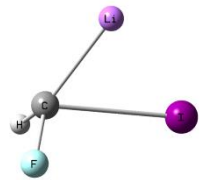
1.6 Natural and Mulliken Atomic Charges for FICHLi

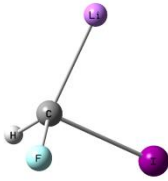
Natural Atomic Charge			Mulliken Atomic Charge	
Atom	Gaseous Phase	THF (Solvent)	Gaseous Phase	THF (Solvent)
C	-0.16466	-0.29347	-0.310173	-0.617807
H	0.12388	0.11641	0.161749	0.175419
F	-0.37211	-0.42592	-0.025295	-0.097187
I	-0.31412	-0.32845	-0.158408	-0.298543
Li	0.72701	0.93143	0.332127	0.838118

1.7 Computed Energies [values are in Hartree]

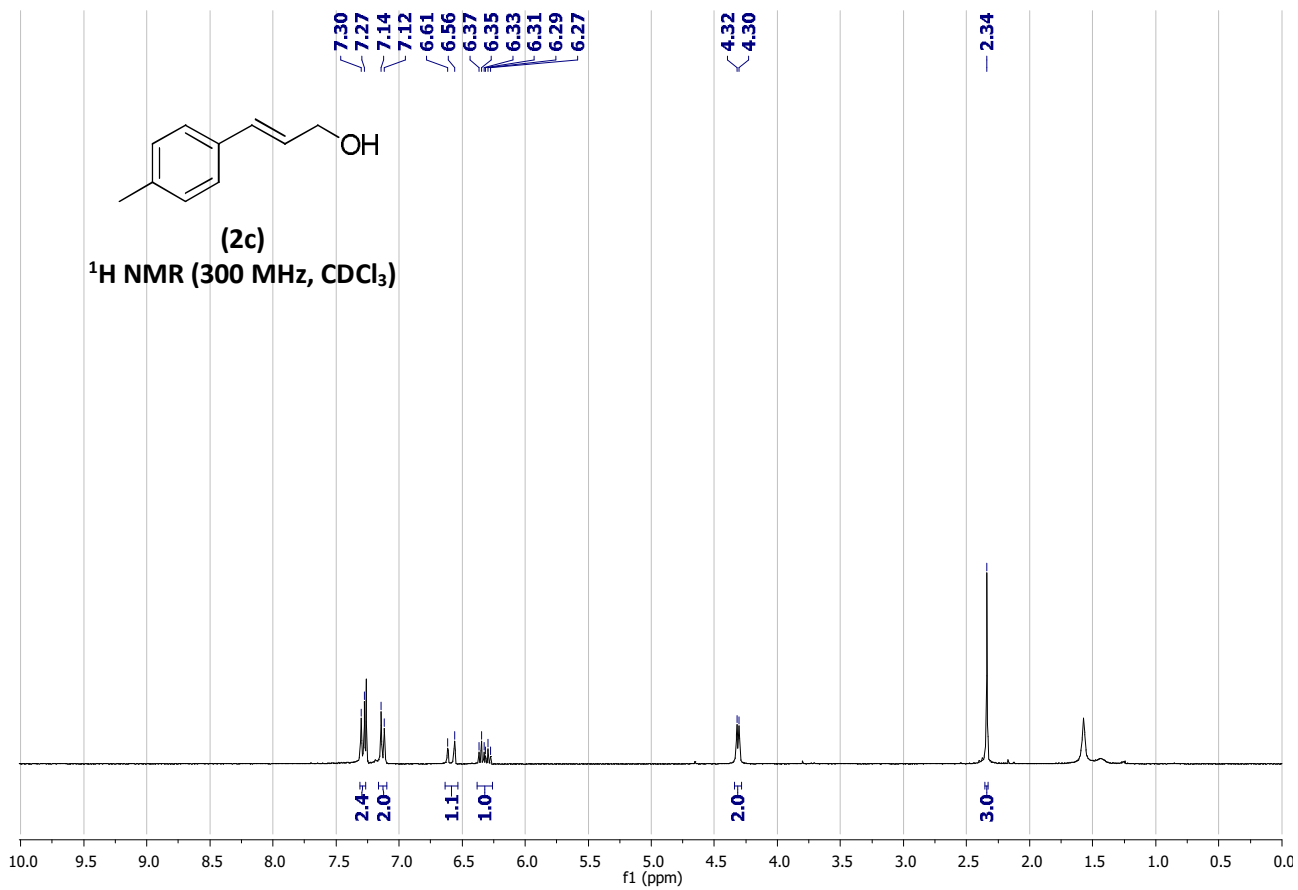
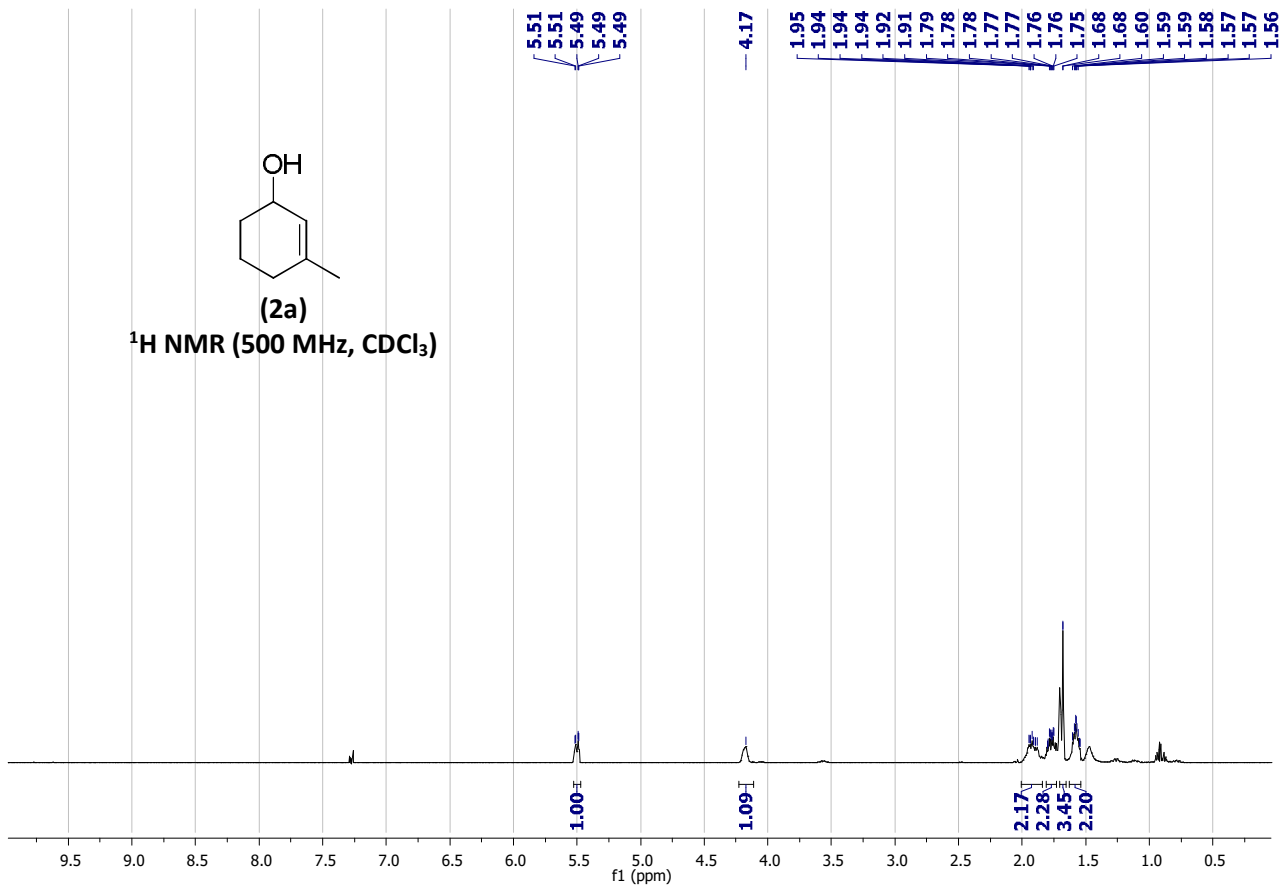
No.	Species	Total Electronic Energy	Sum of Electronic and Zero-point Energies	Sum of Electronic and Thermal Enthalpies	Gibbs Free Energy
1	FICH ₂ – Gas Phas	-150.5679248	-150.538204	-150.533635	-150.566043
2	FICH ₂ – THF	-150.5715945	-150.541926	-150.537344	-150.569778
3	FICHLi – Gas Phase	-157.4956551	-157.477551	-157.471563	-157.507425
4	FICHLi – THF	-157.5336842	-157.516485	-157.510176	-157.546843

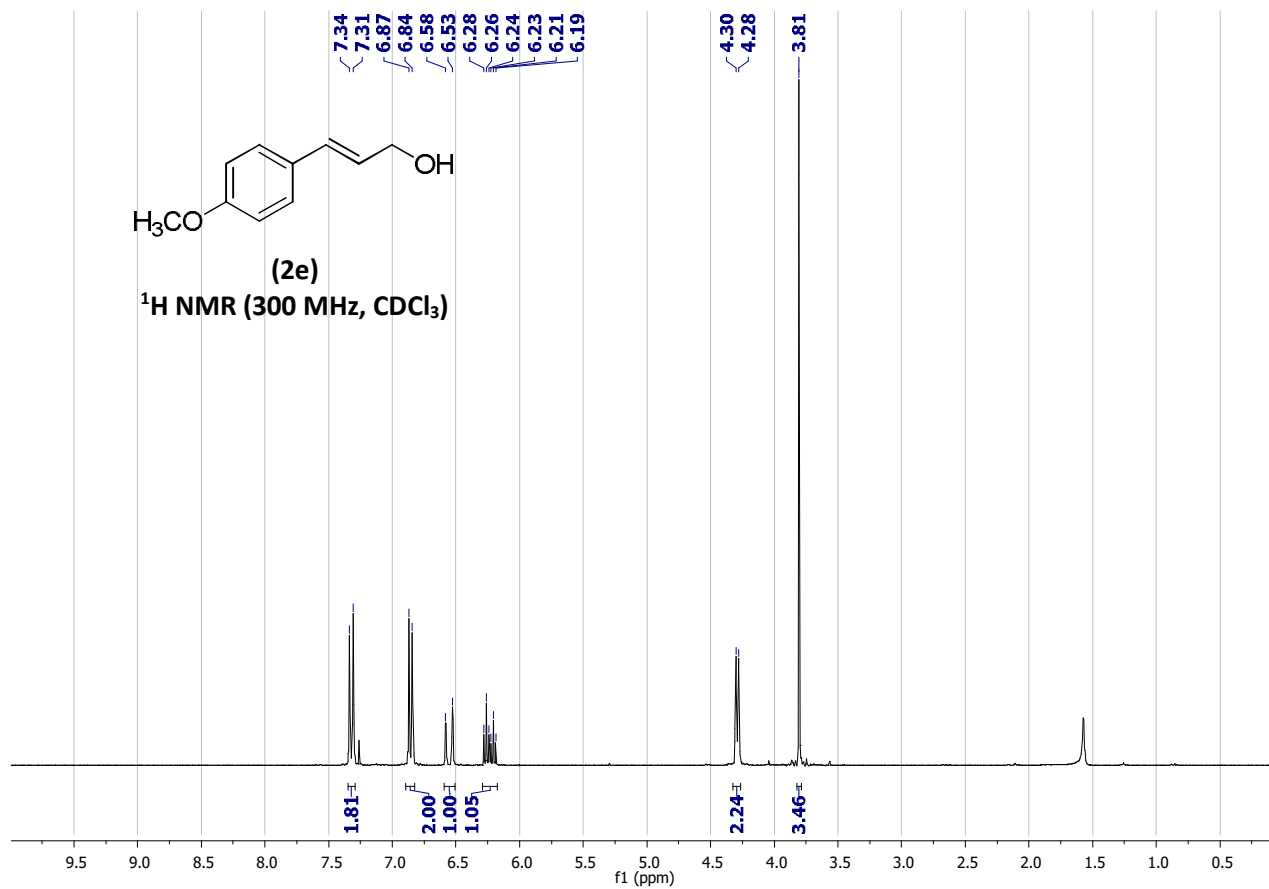
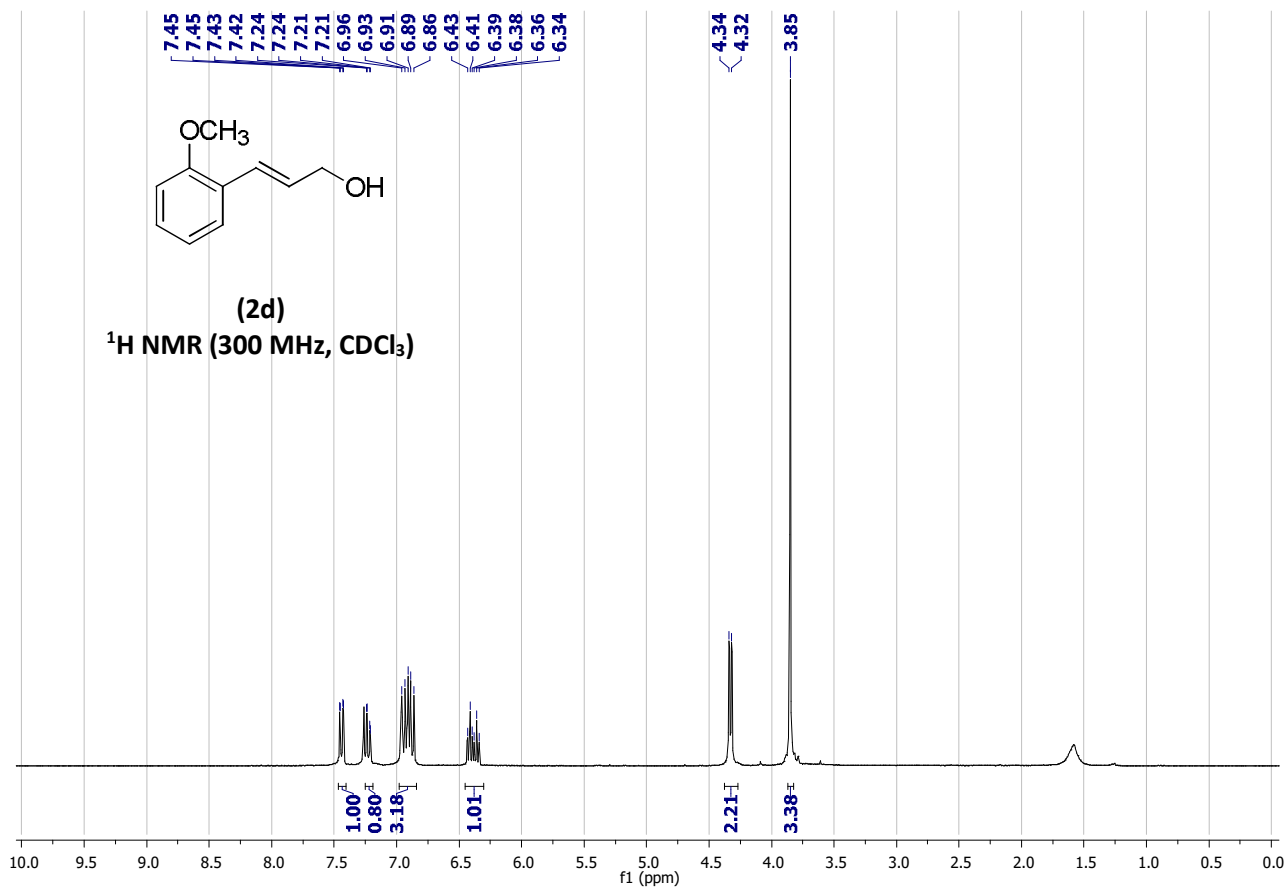
1.8 Optimized Structures and Cartesian Coordinates

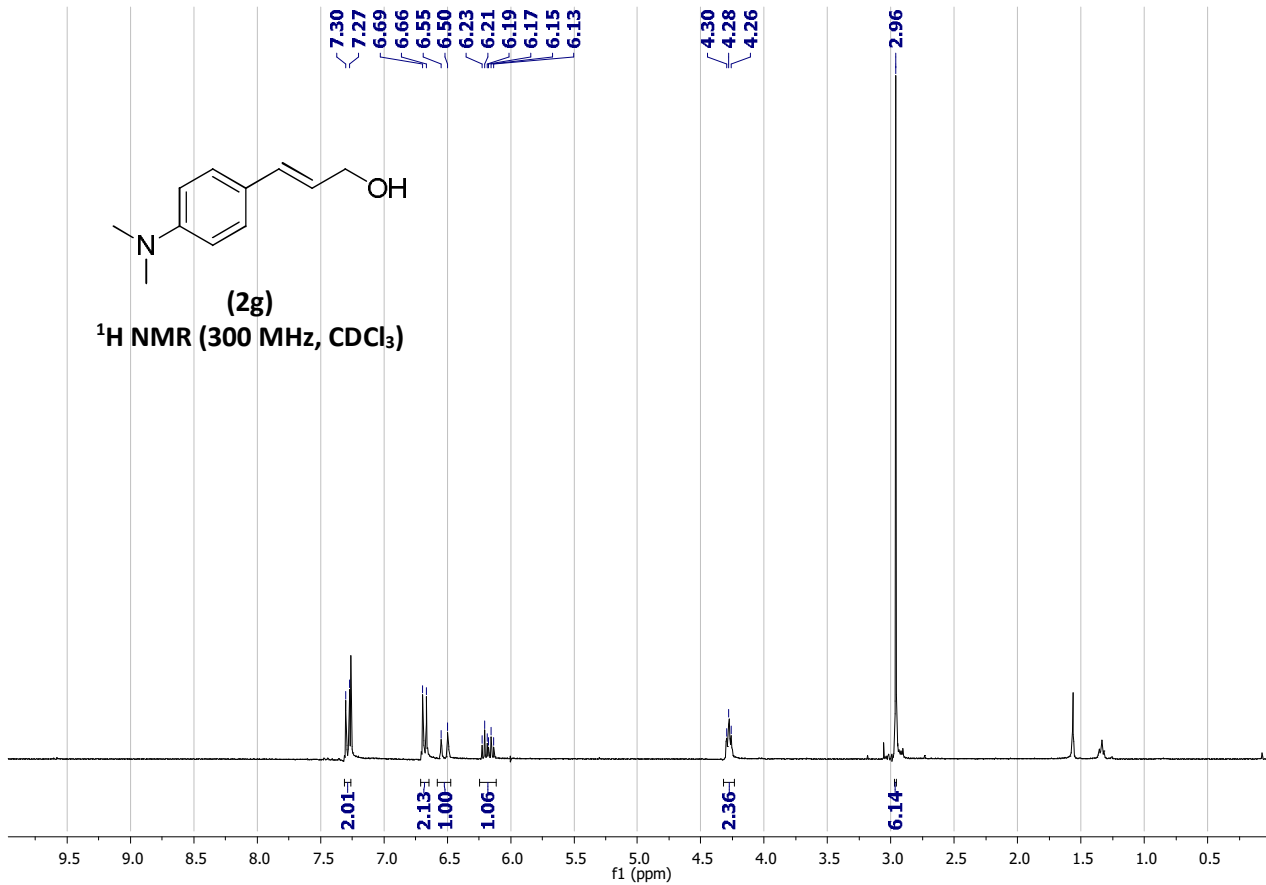
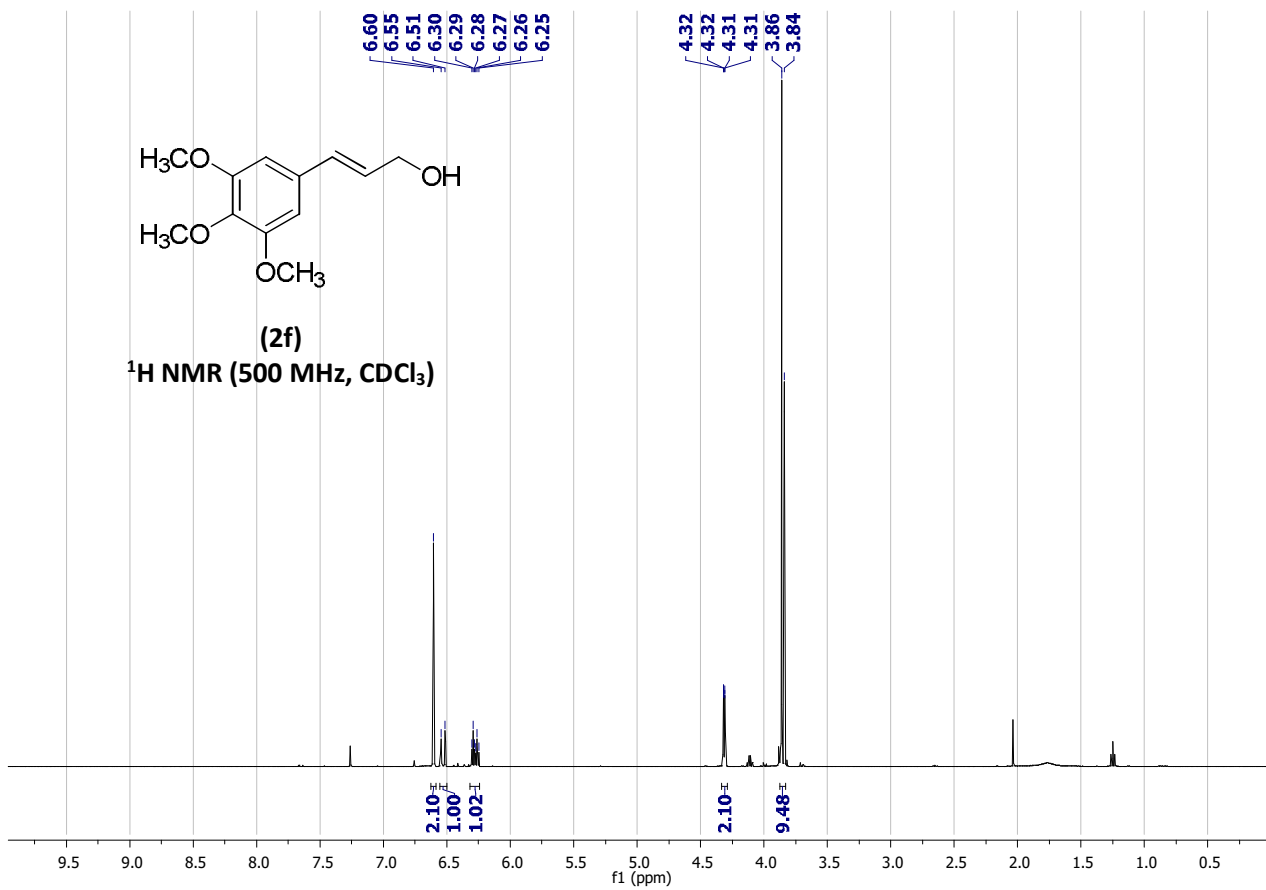
No.	Species	Optimized Structure
1	FICH ₂ – Gas Phas	
Cartesian Coordinates		
C	0.52745600 -1.50045000 0.00000000	
H	1.09500400 -1.67949700 0.90852500	
F	-0.59497200 -2.28125700 0.00000000	
I	0.00000000 0.62062300 0.00000000	
H	1.09500400 -1.67949700 -0.90852500	
2	FICH ₂ – THF	
Cartesian Coordinates		
C	0.53432300 -1.50202800 0.00000000	
H	1.09675600 -1.68255600 0.90994800	
F	-0.59993900 -2.27671300 0.00000000	
I	0.00000000 0.62014500 0.00000000	
H	1.09675600 -1.68255600 -0.90994800	
3	FICHLi – Gas Phase	
Cartesian Coordinates		
C	1.80553100 0.39081400 0.44497600	
H	1.76508600 -0.04310600 1.45541000	
F	2.50843400 -0.50721700 -0.29077000	
I	-0.71146600 -0.06526300 -0.00544200	

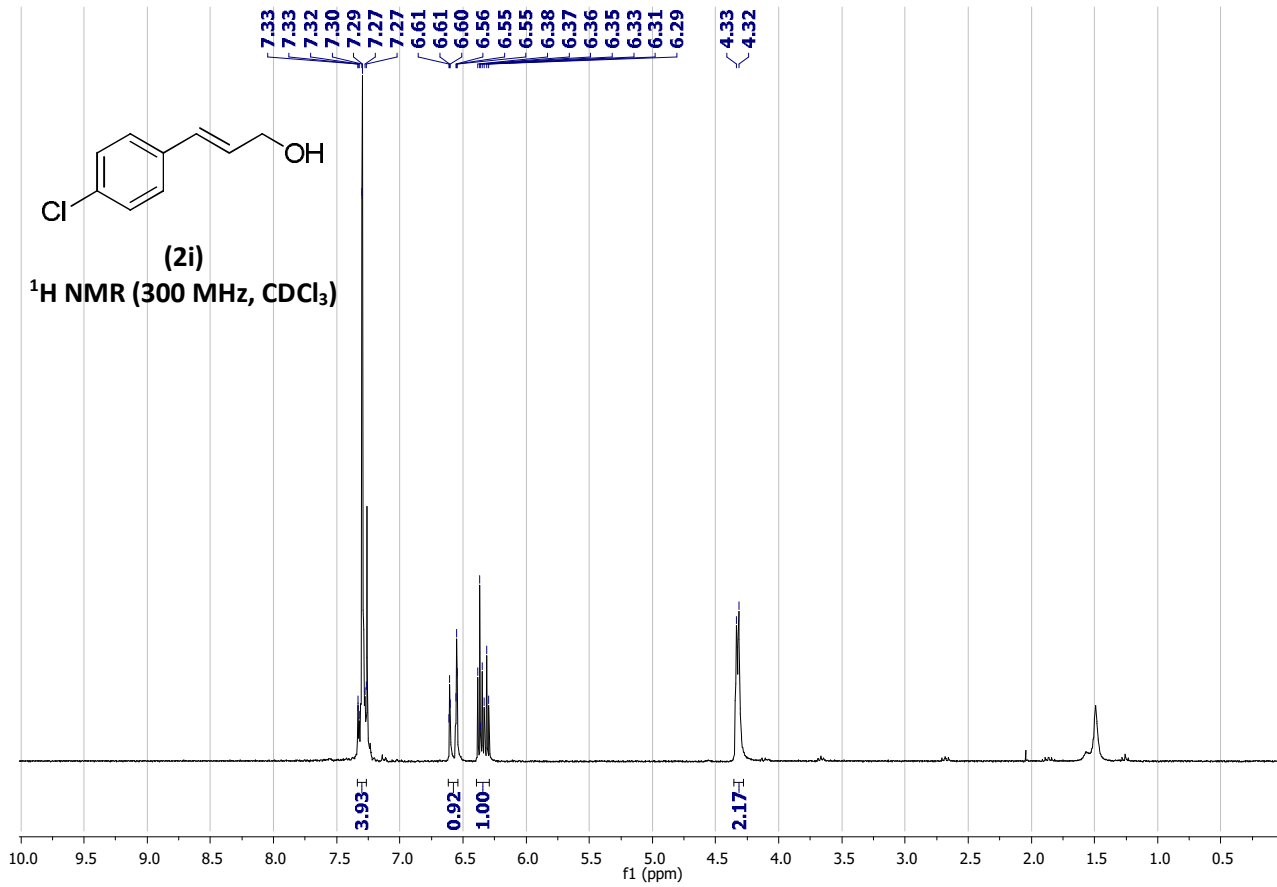
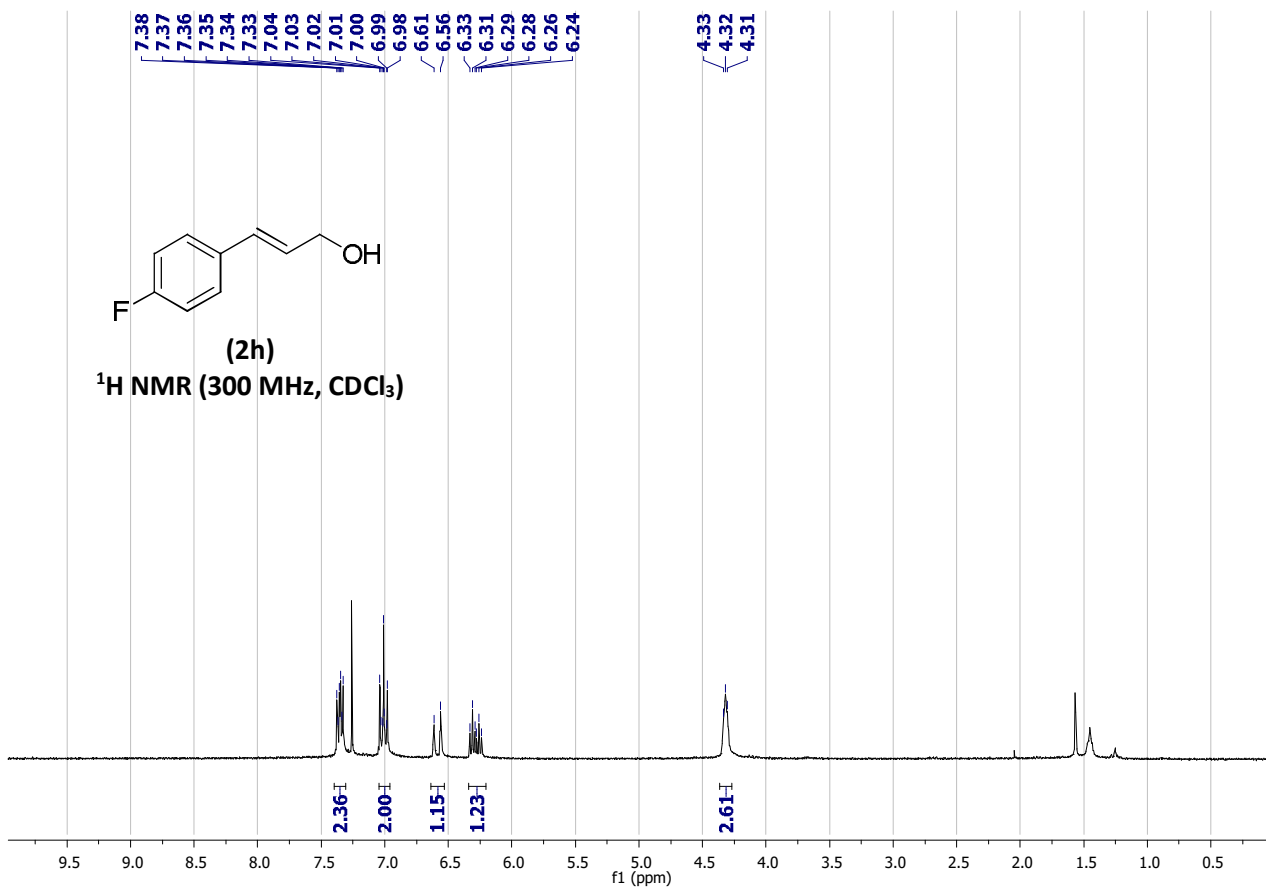
Li	0.84450100	1.90736400	-0.40664400
4	FICHLi – THF		
Cartesian Coordinates			
C	1.68705600	0.29369600	0.44219600
H	1.60703400	-0.11129000	1.46059700
F	2.32173900	-0.73506800	-0.26336900
I	-0.71125700	-0.03278000	-0.01278400
Li	1.69052700	2.23401700	-0.35529900

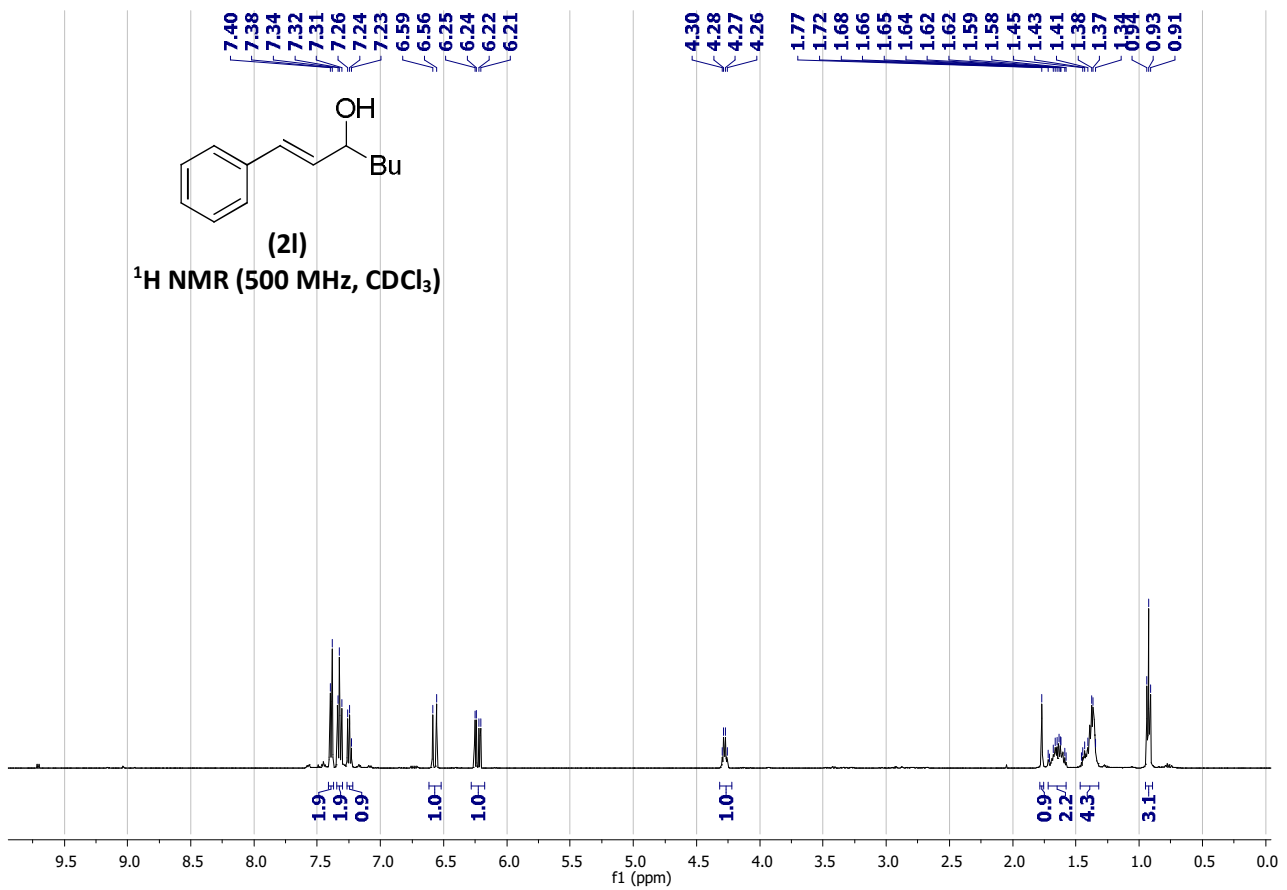
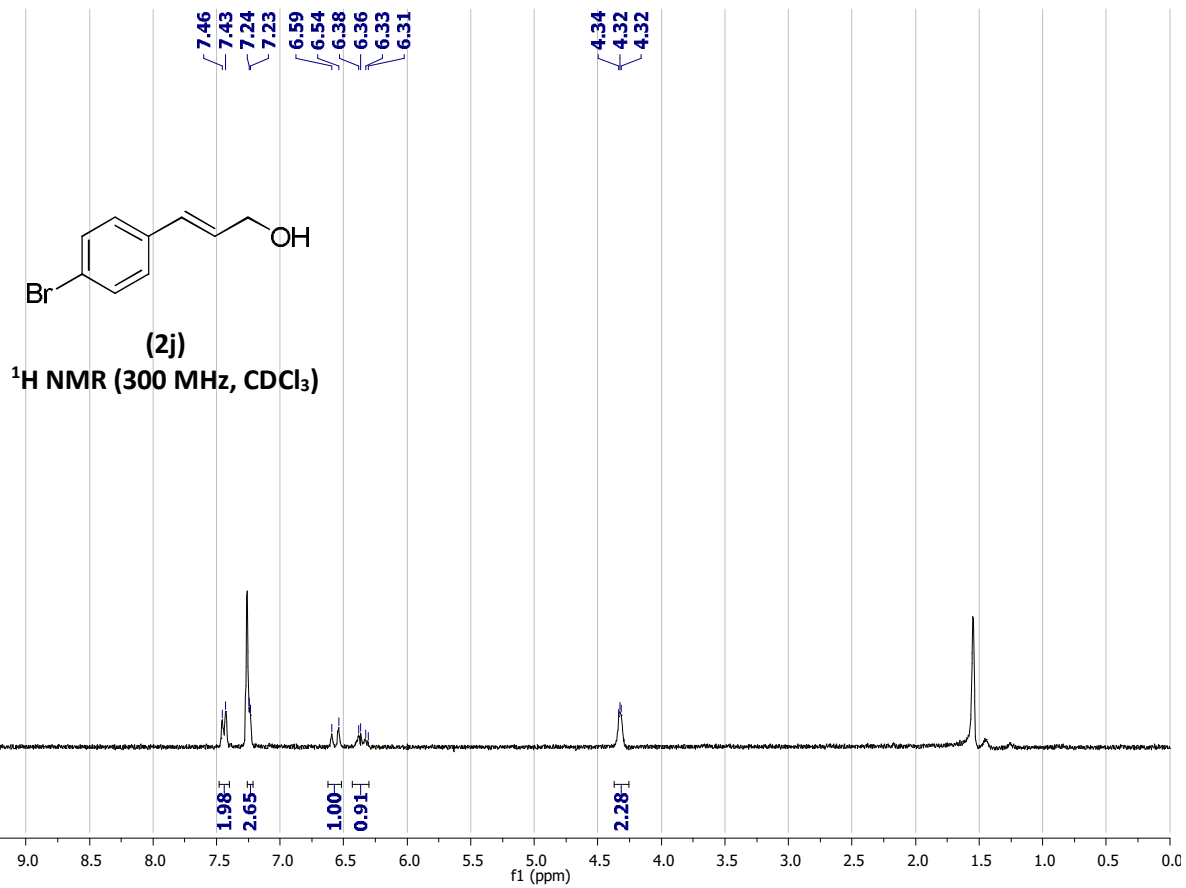
8. Copies of NMR Spectra (^1H , ^{13}C and ^{19}F) for All the Synthesized Compounds

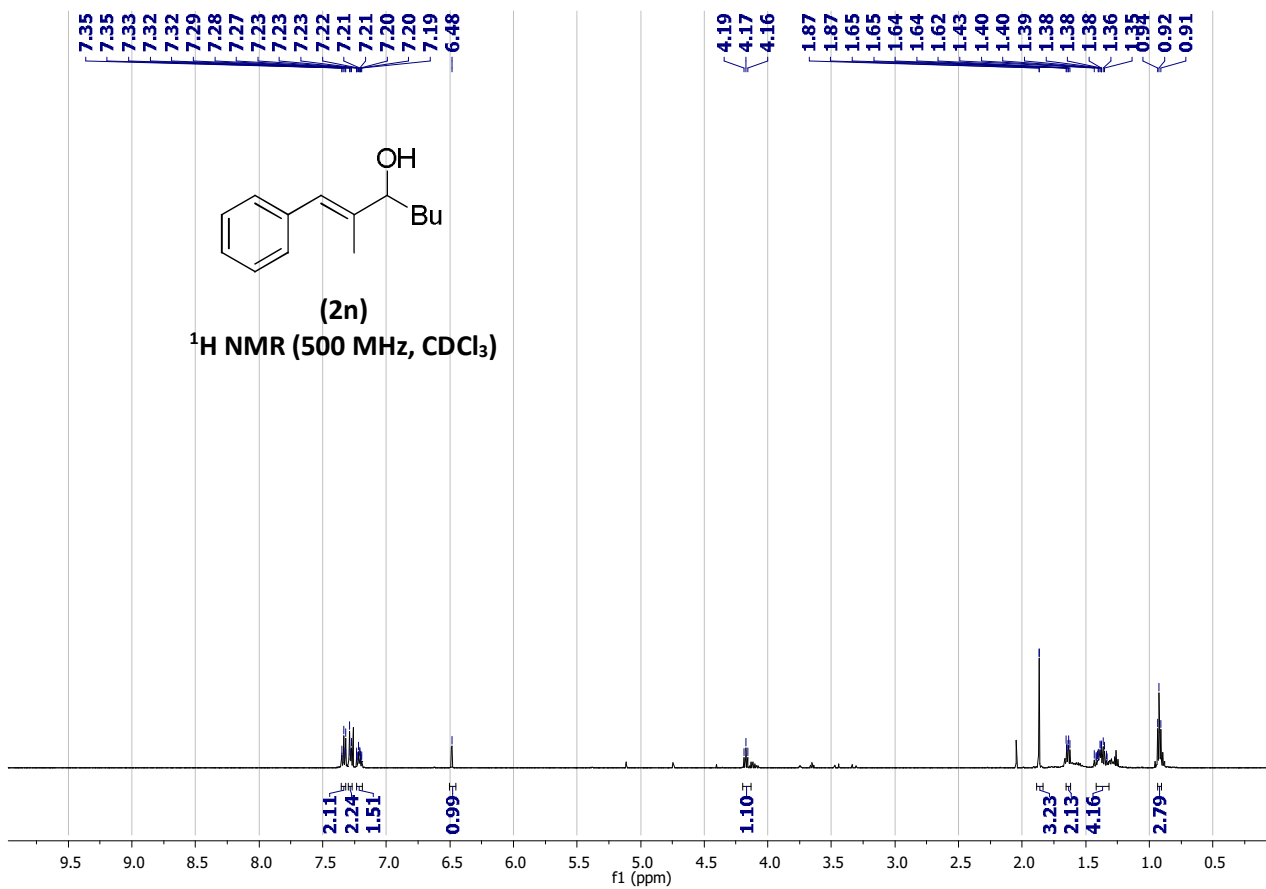
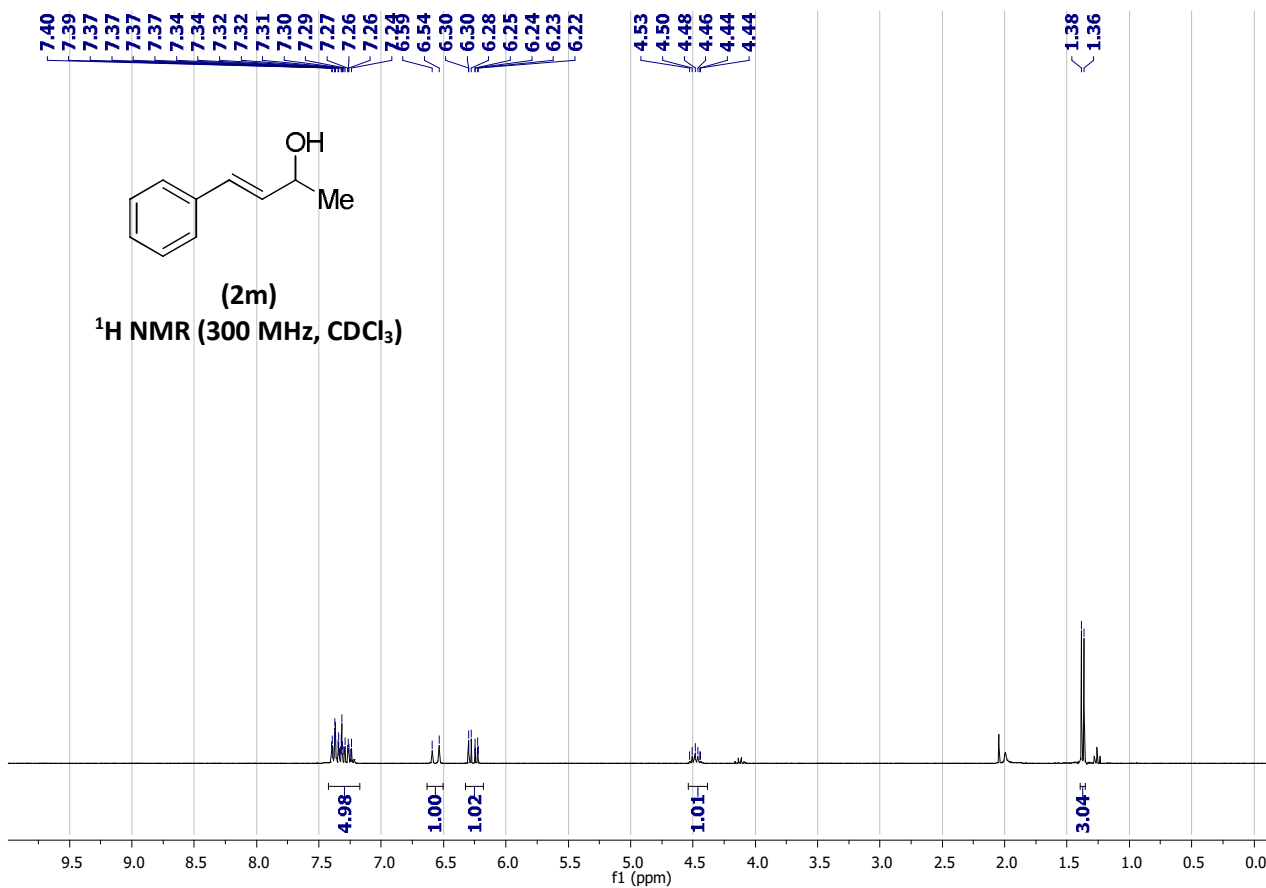




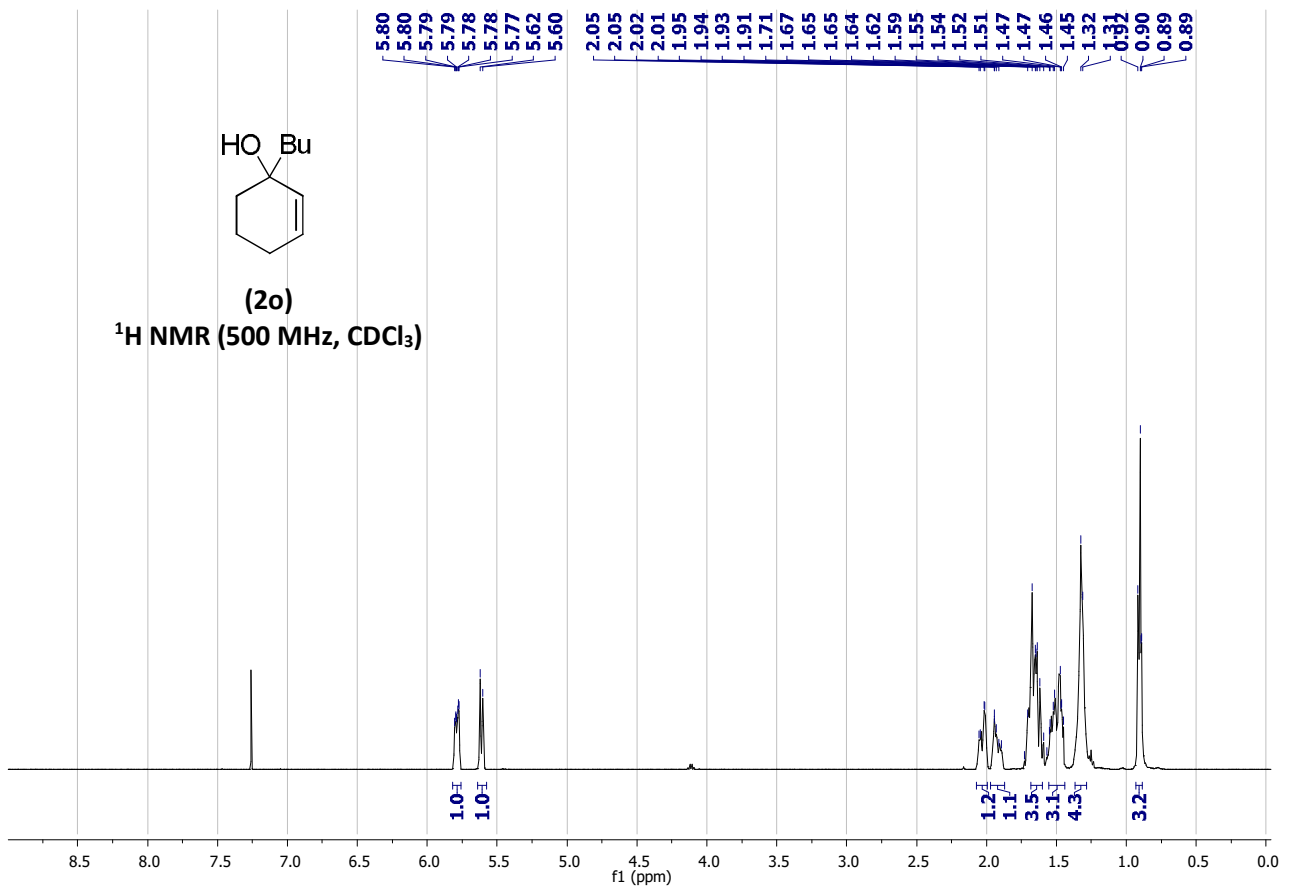




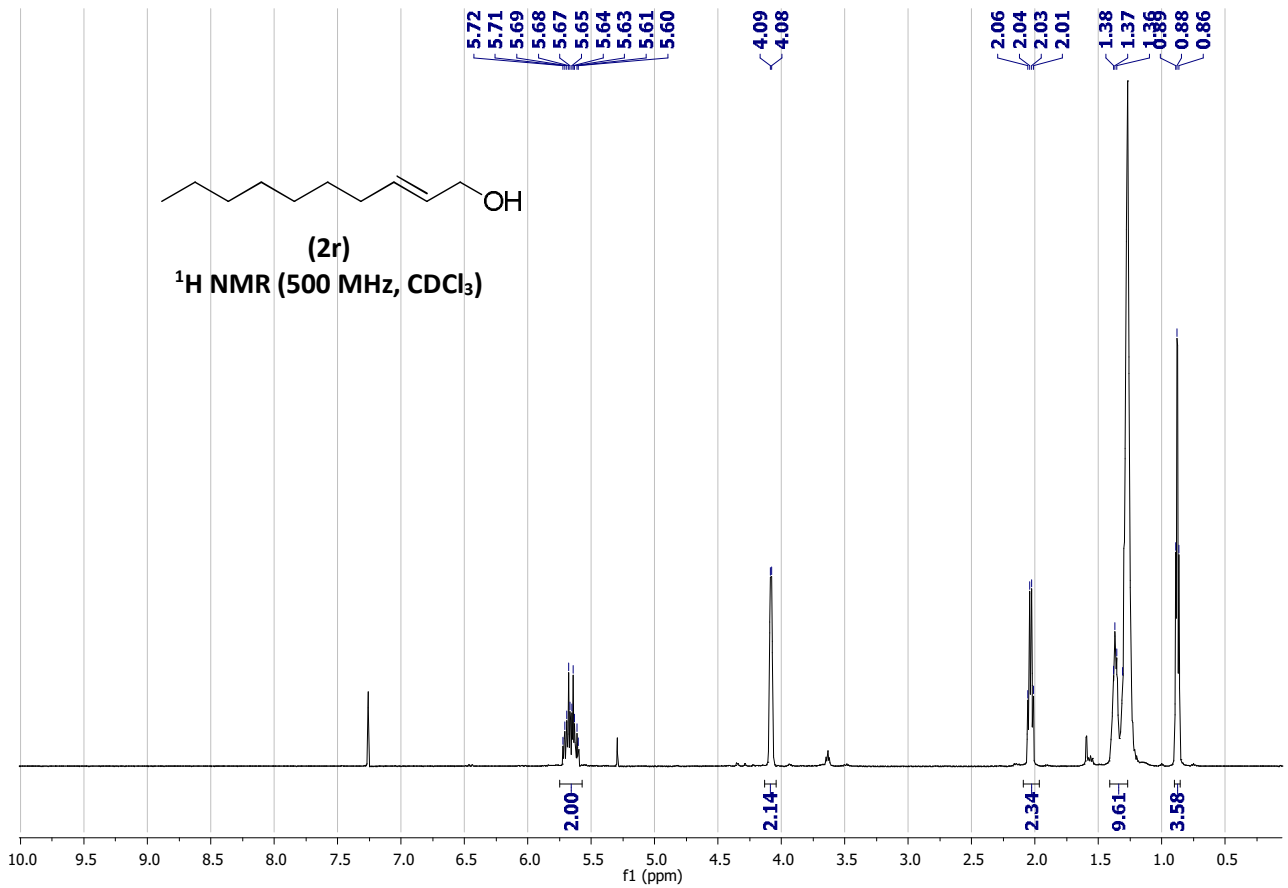


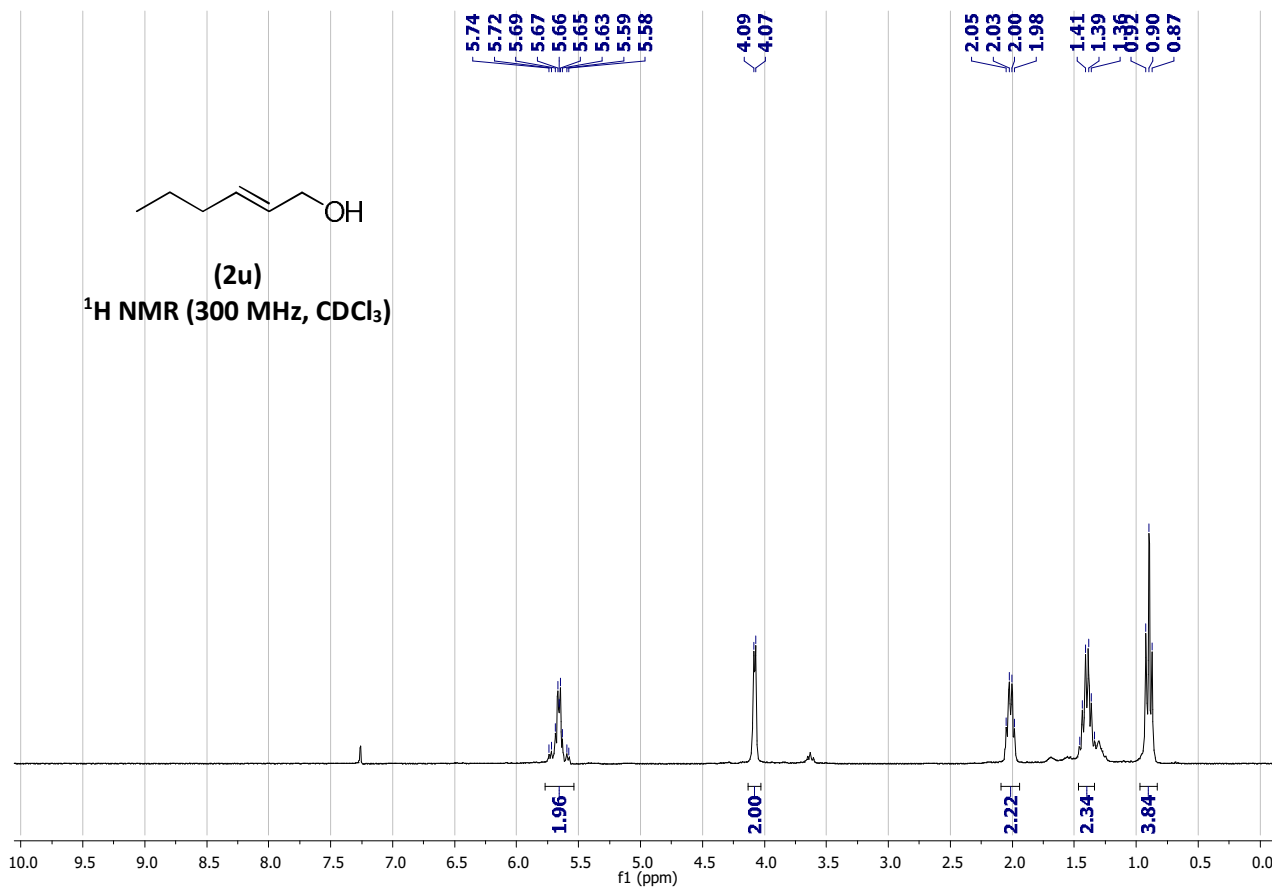
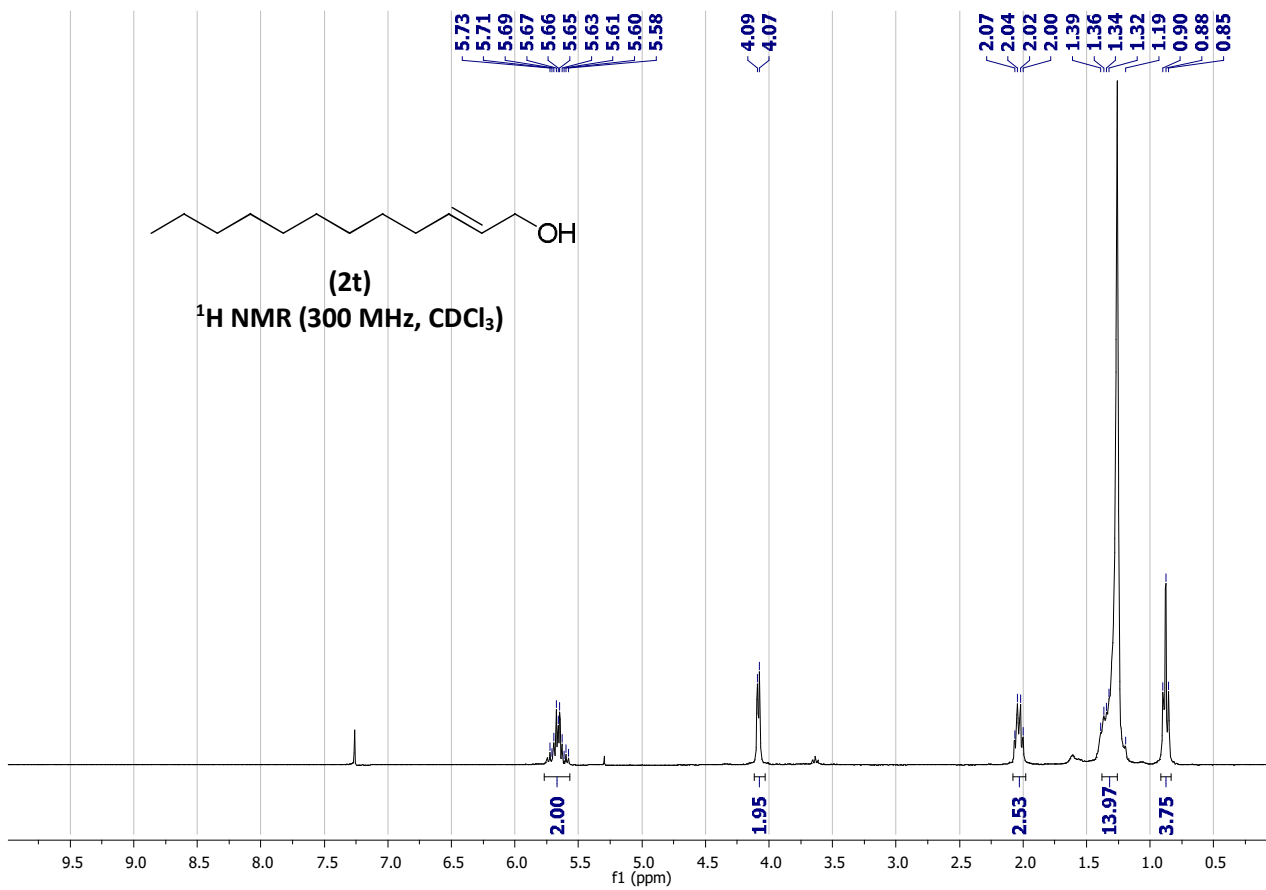


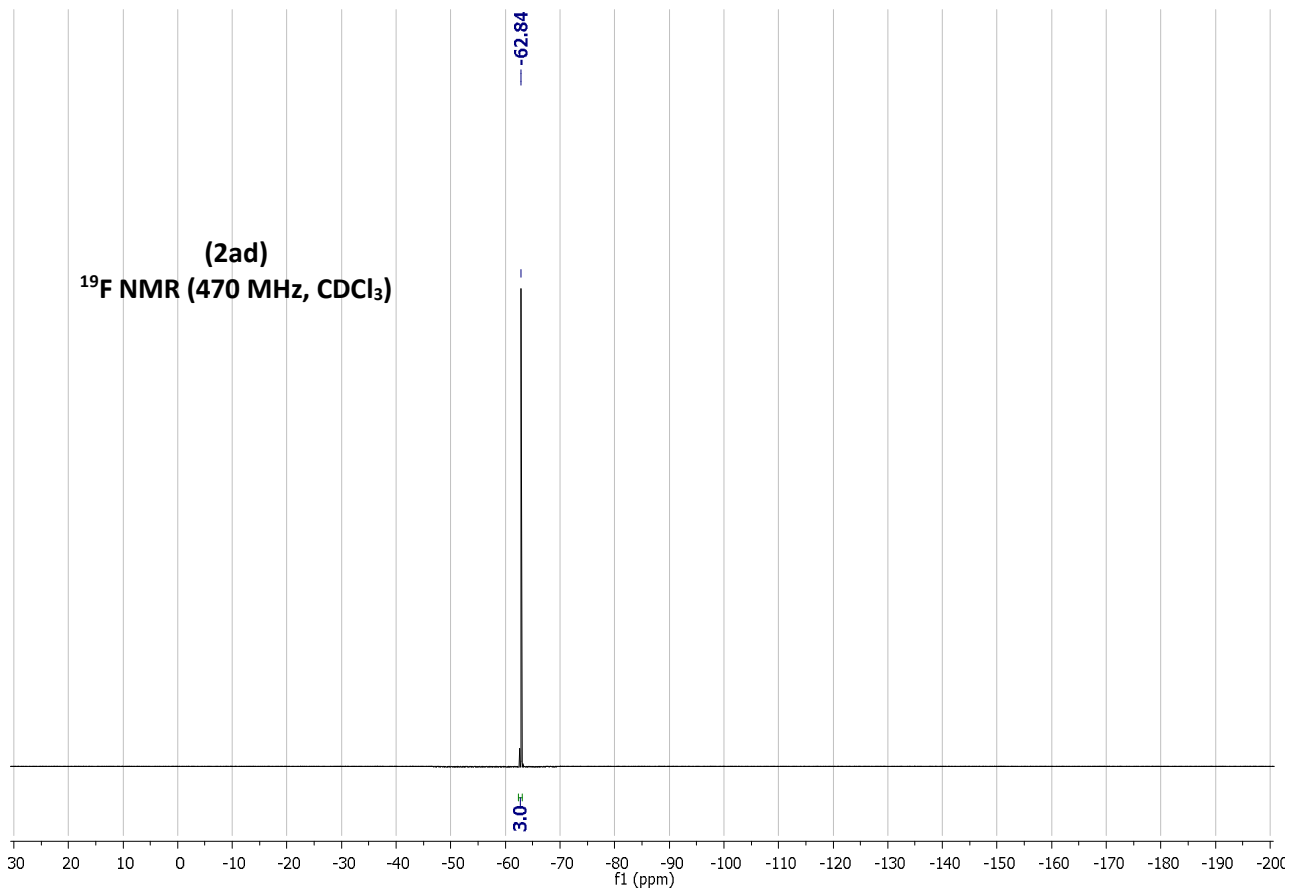
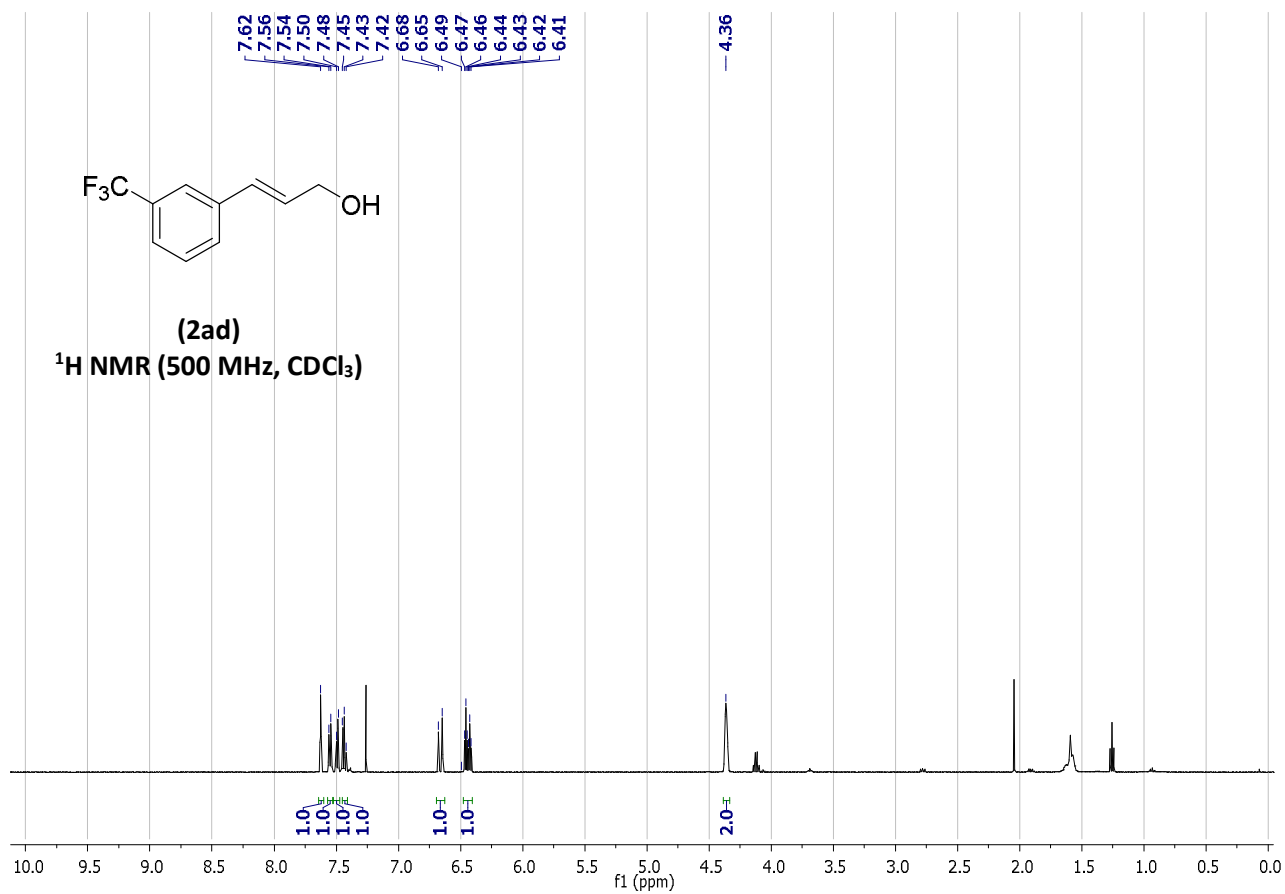
CCCC1=C(C)CCCC1O
(2o)
¹H NMR (500 MHz, CDCl₃)

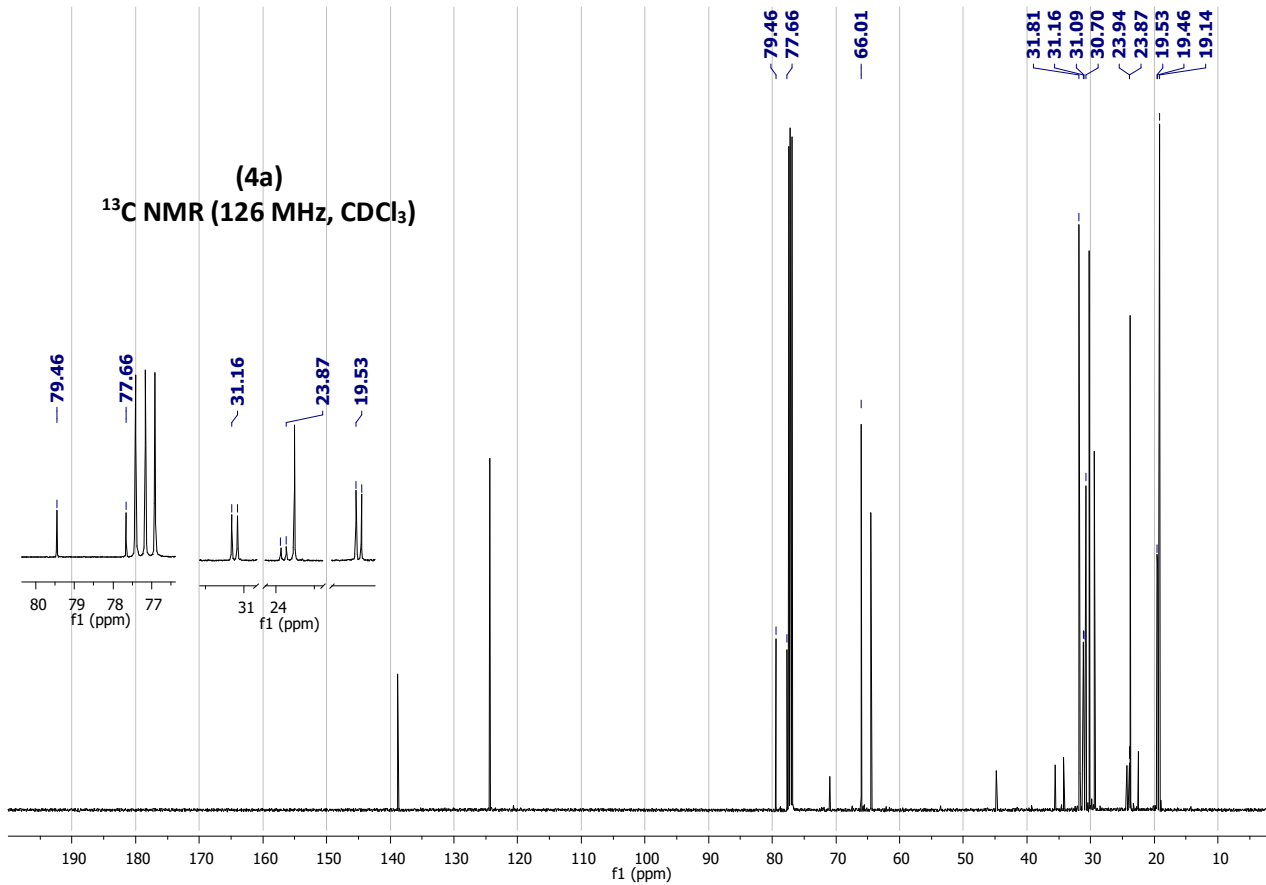
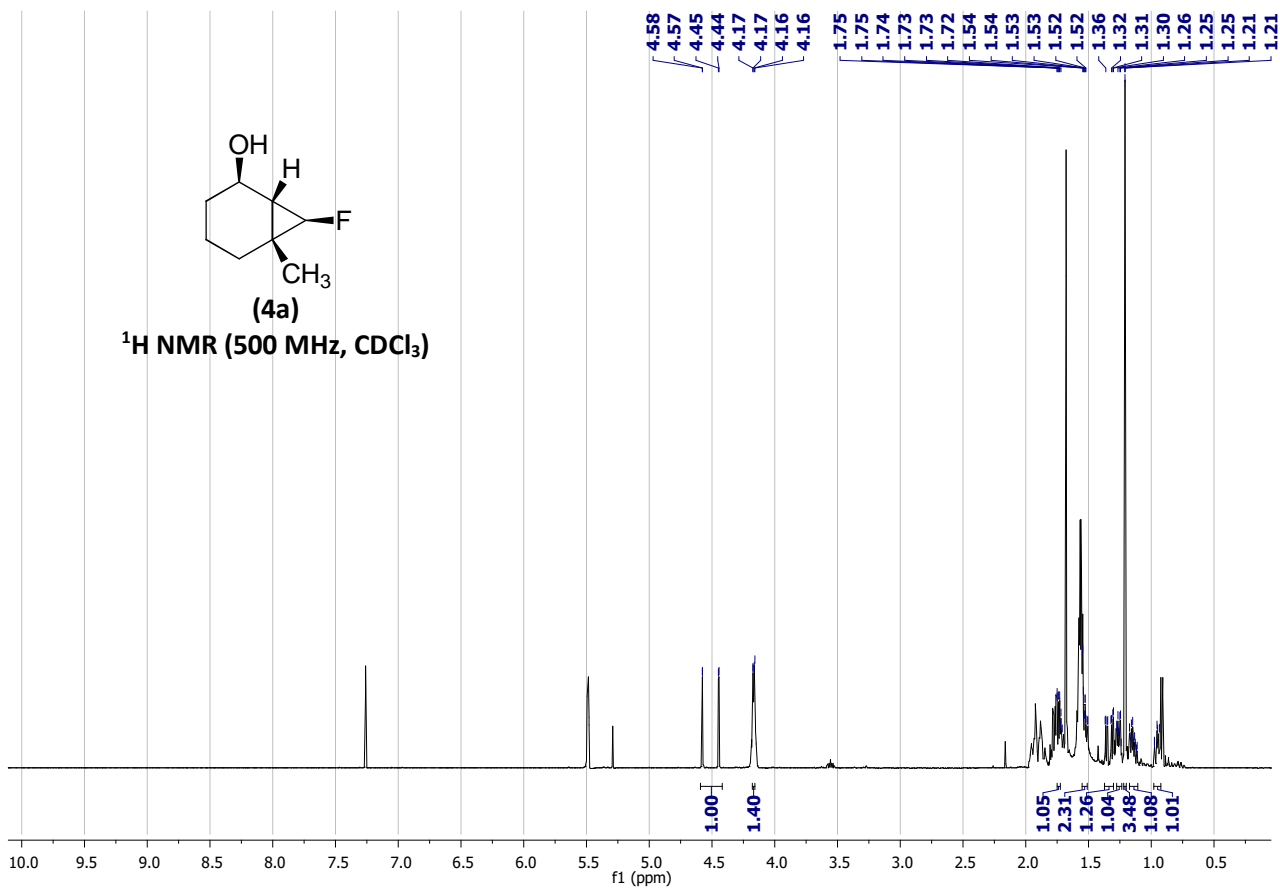


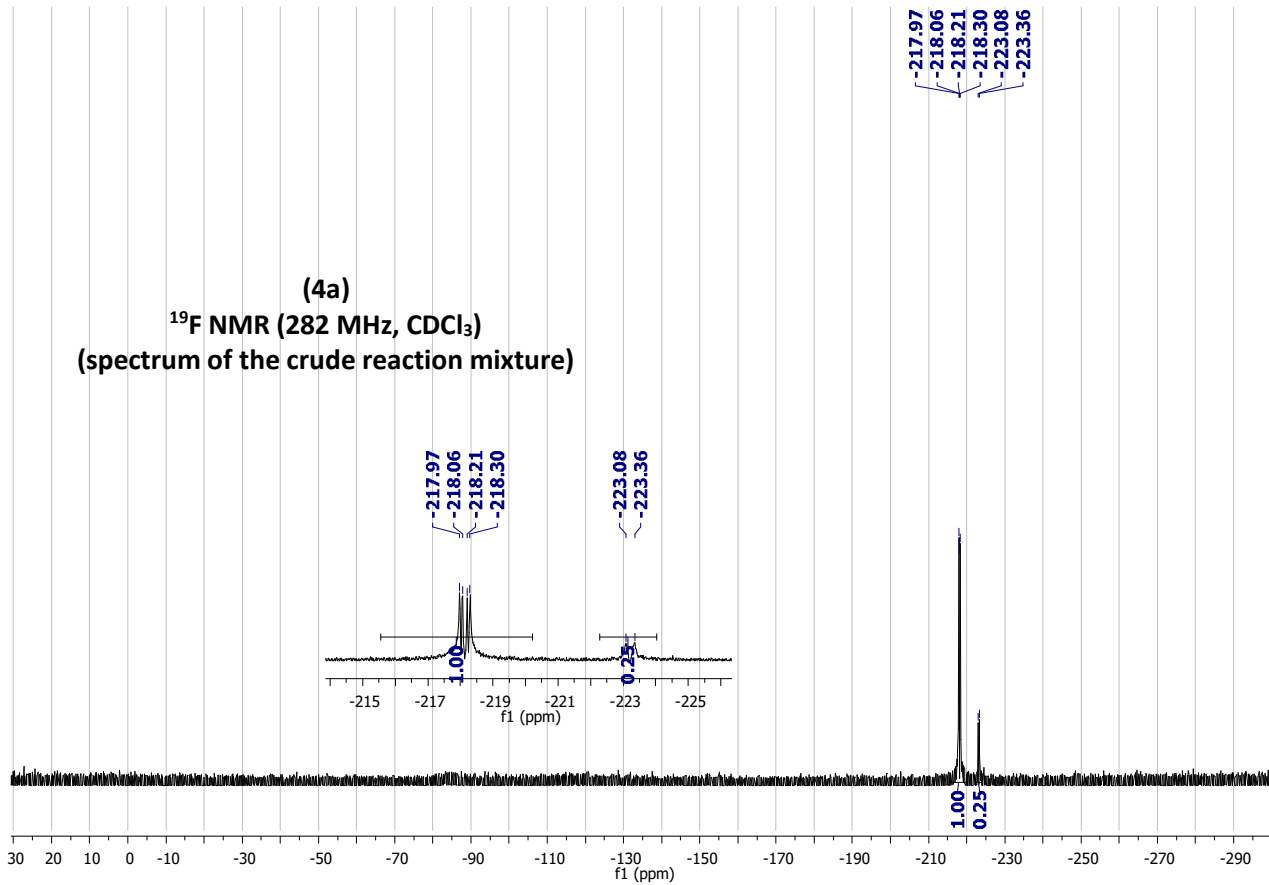
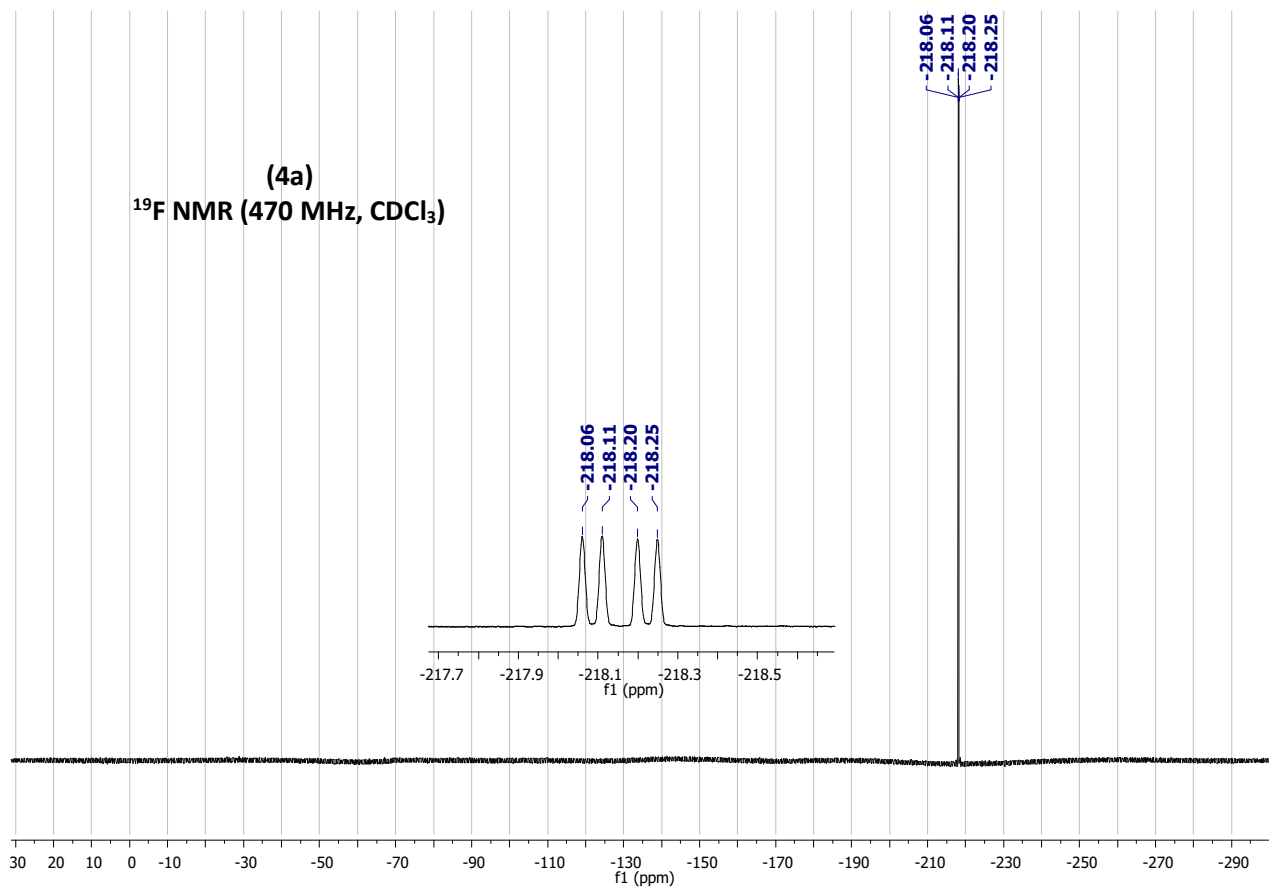
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(2r)
¹H NMR (500 MHz, CDCl₃)

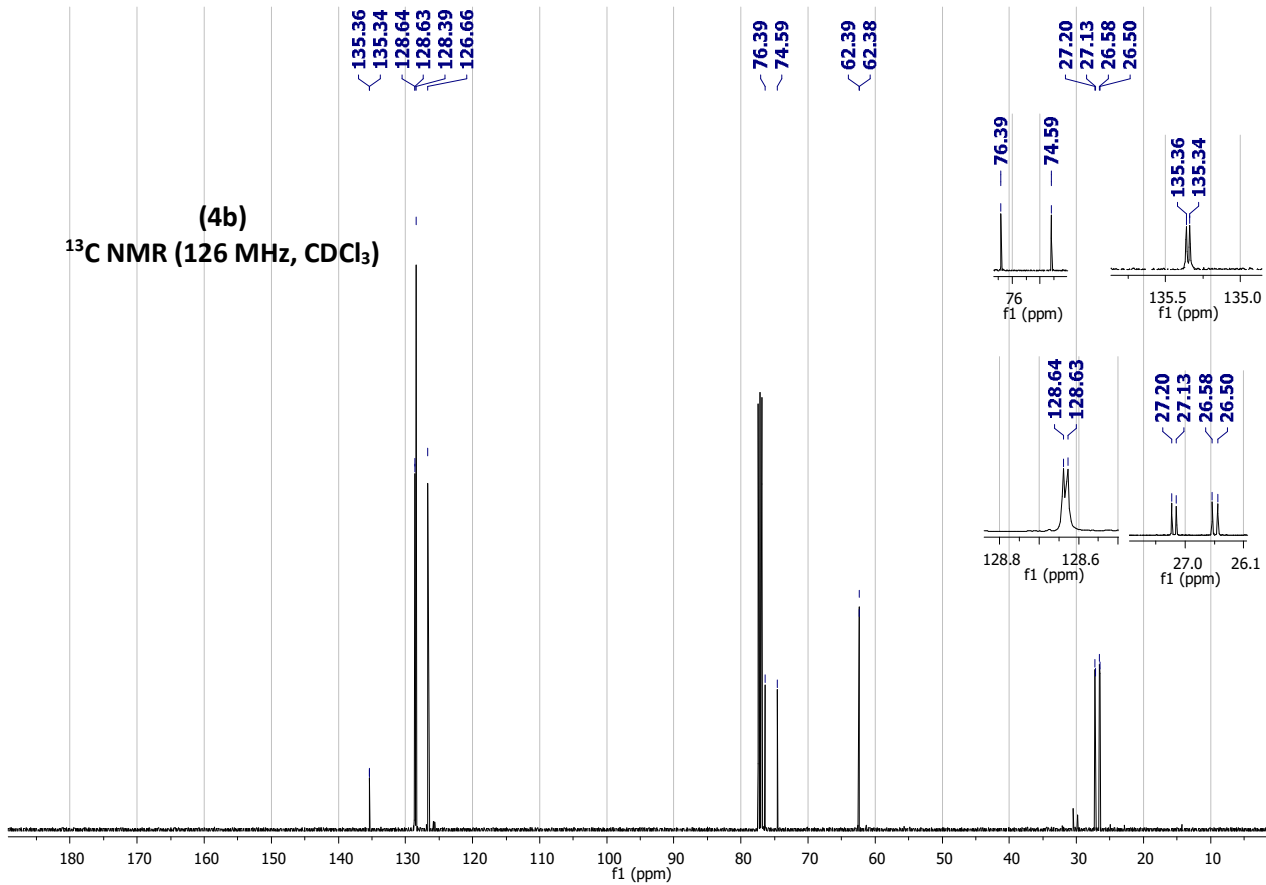
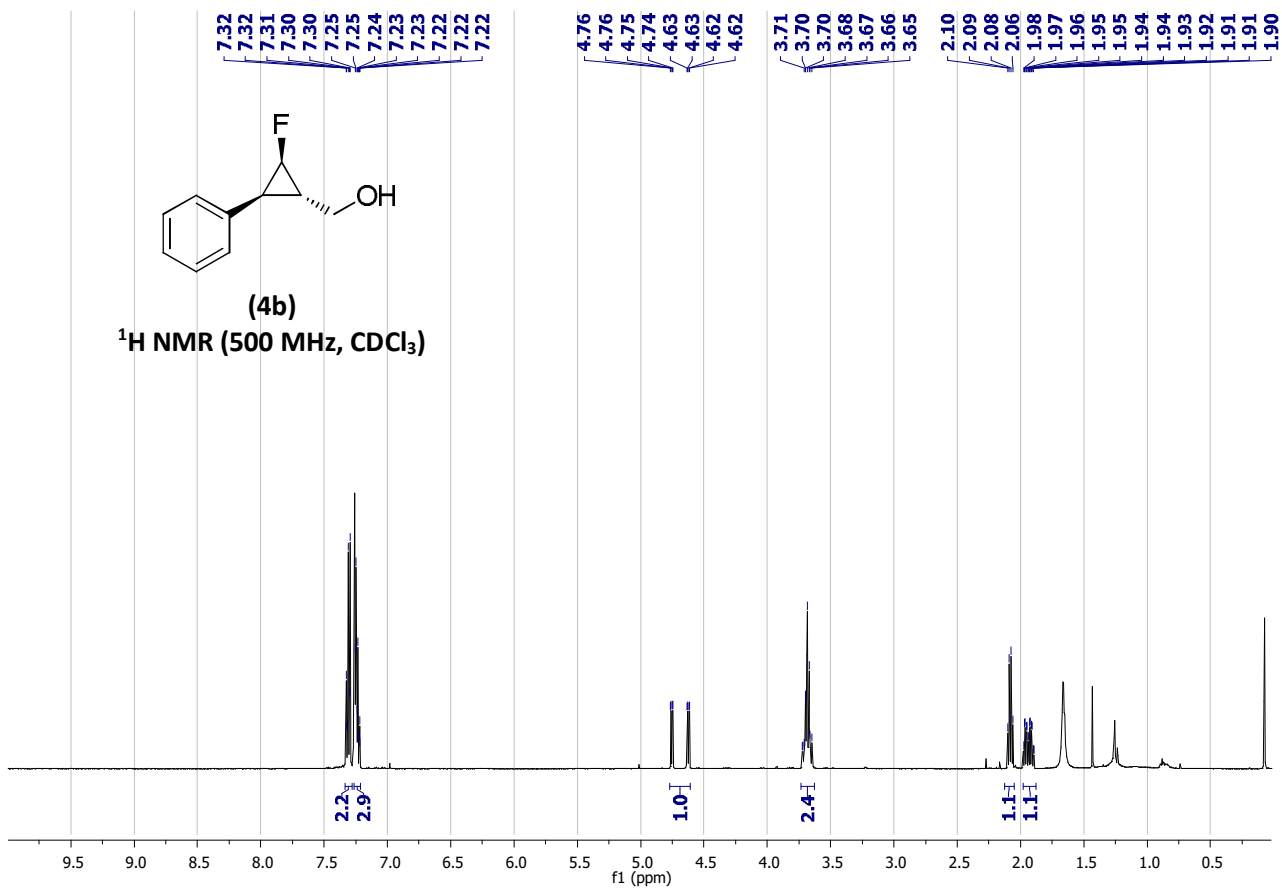


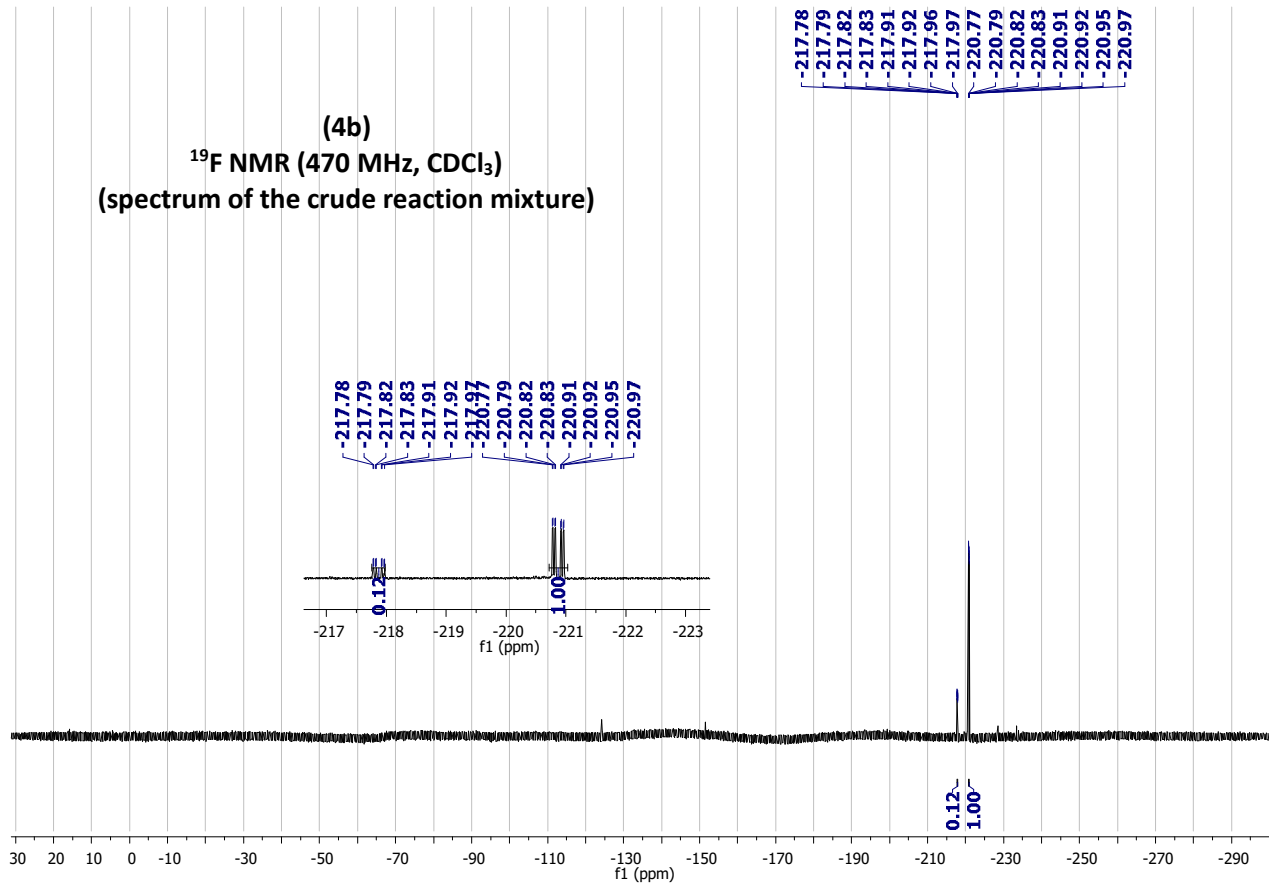
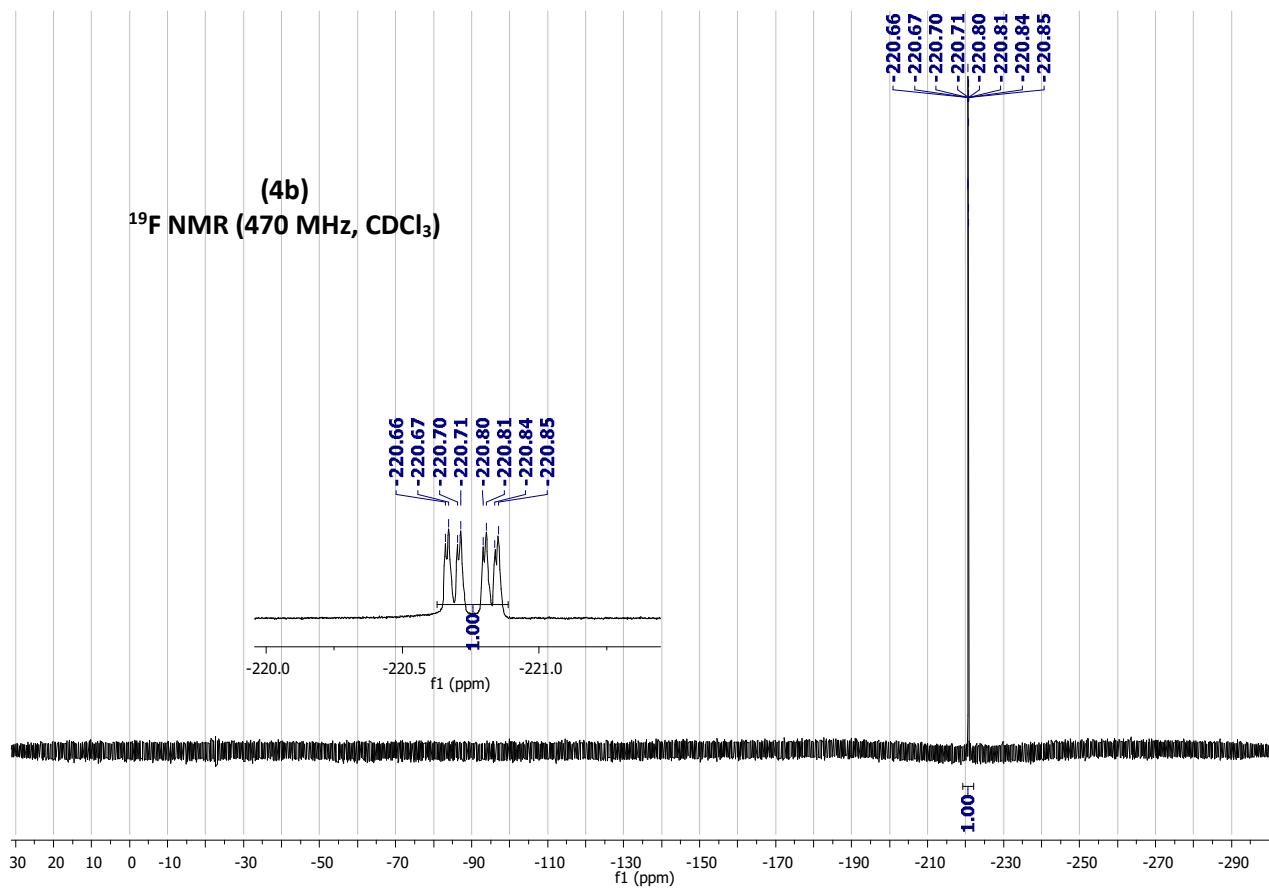


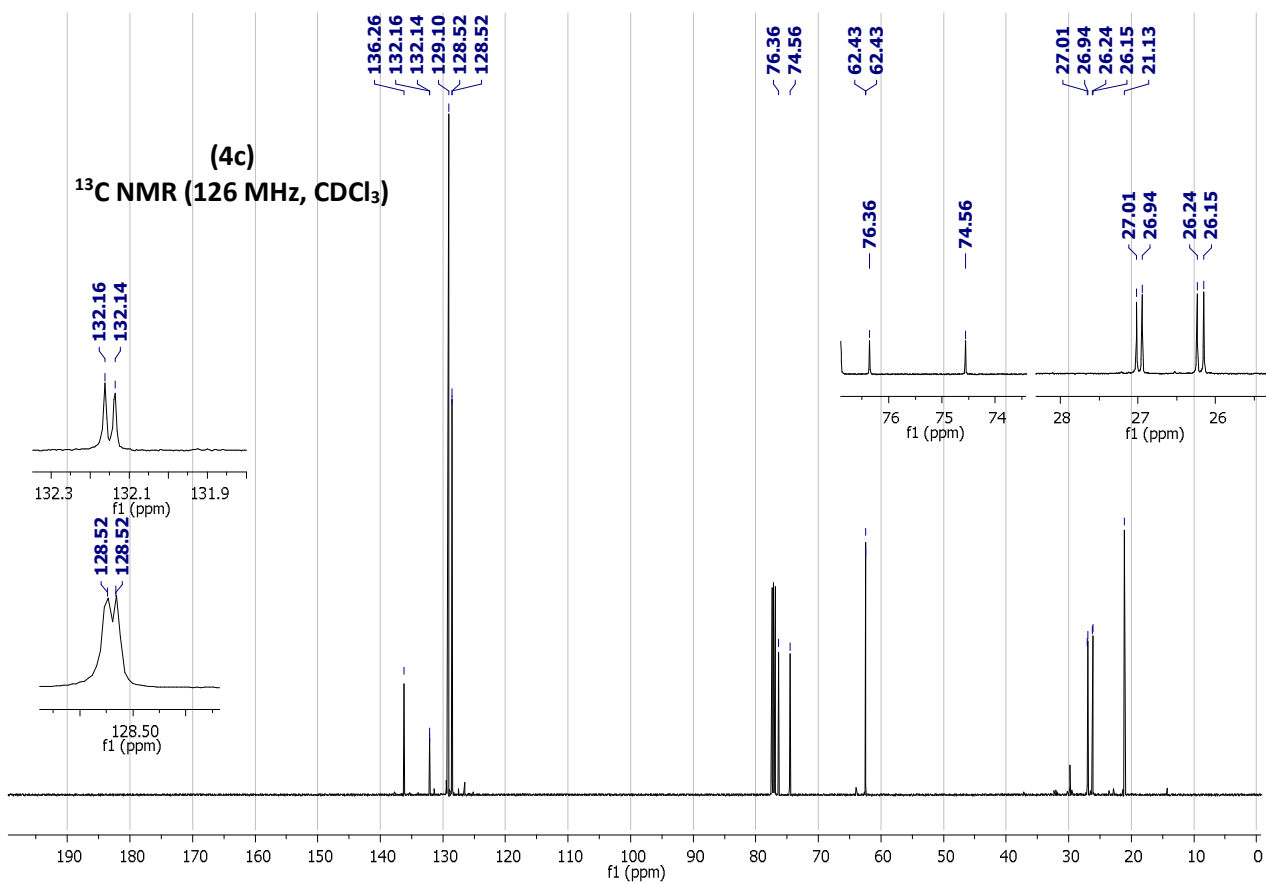
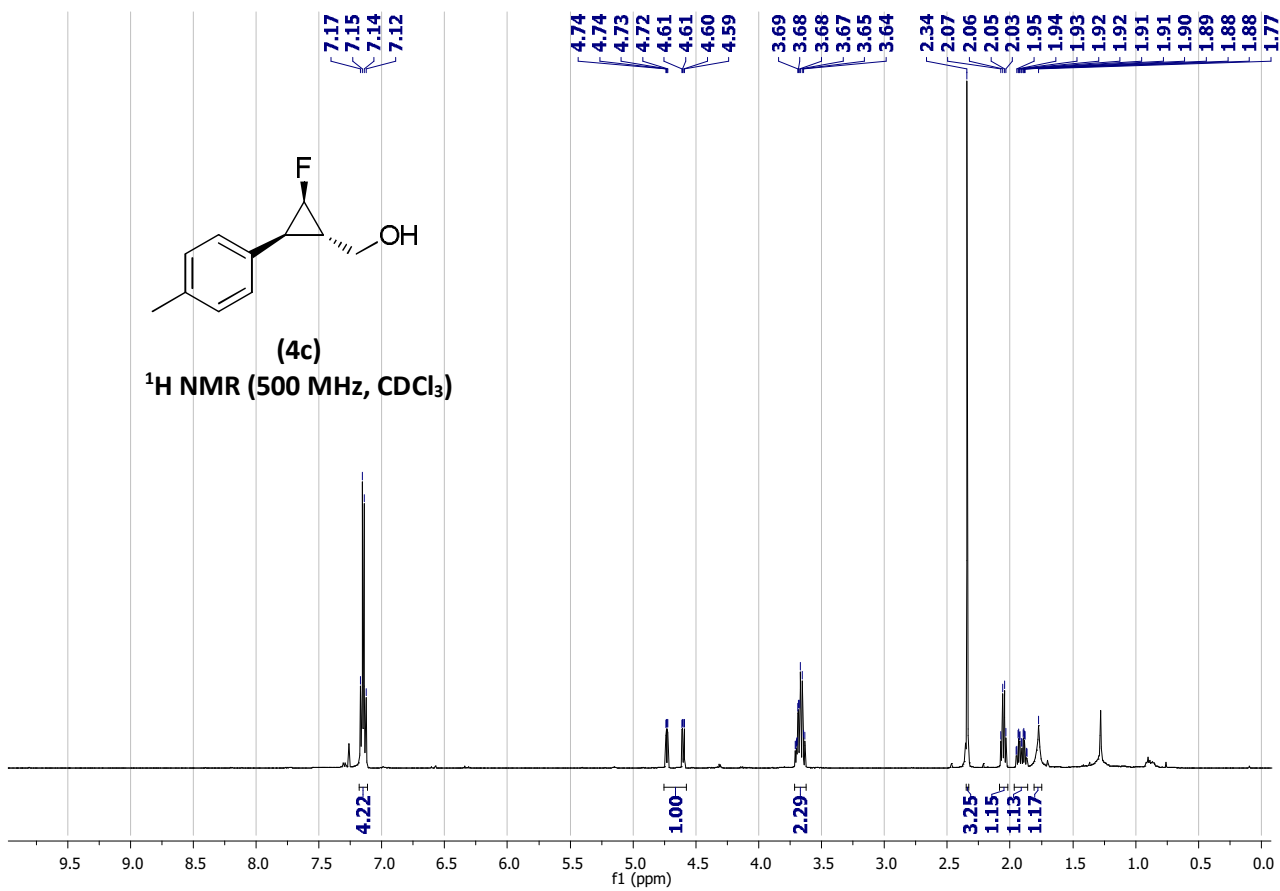


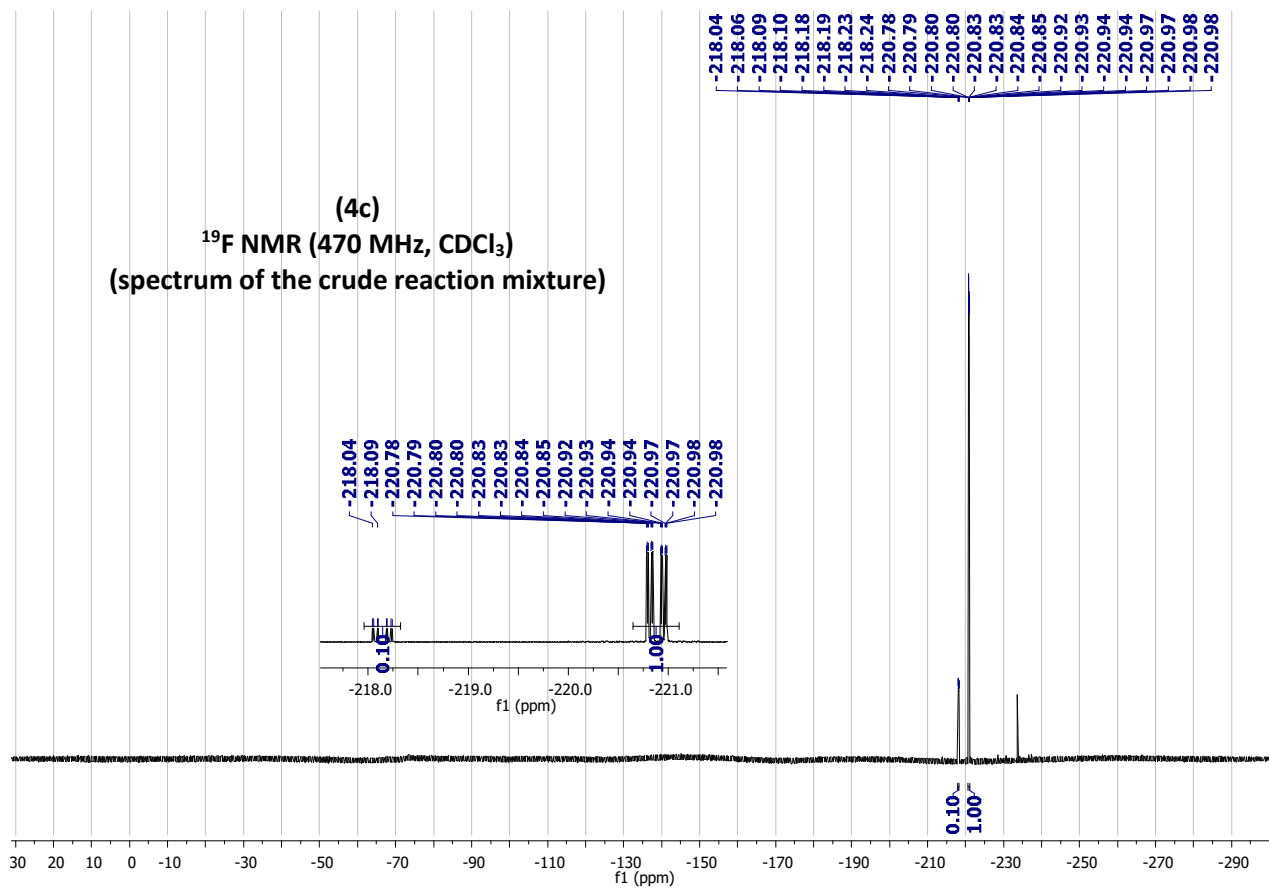
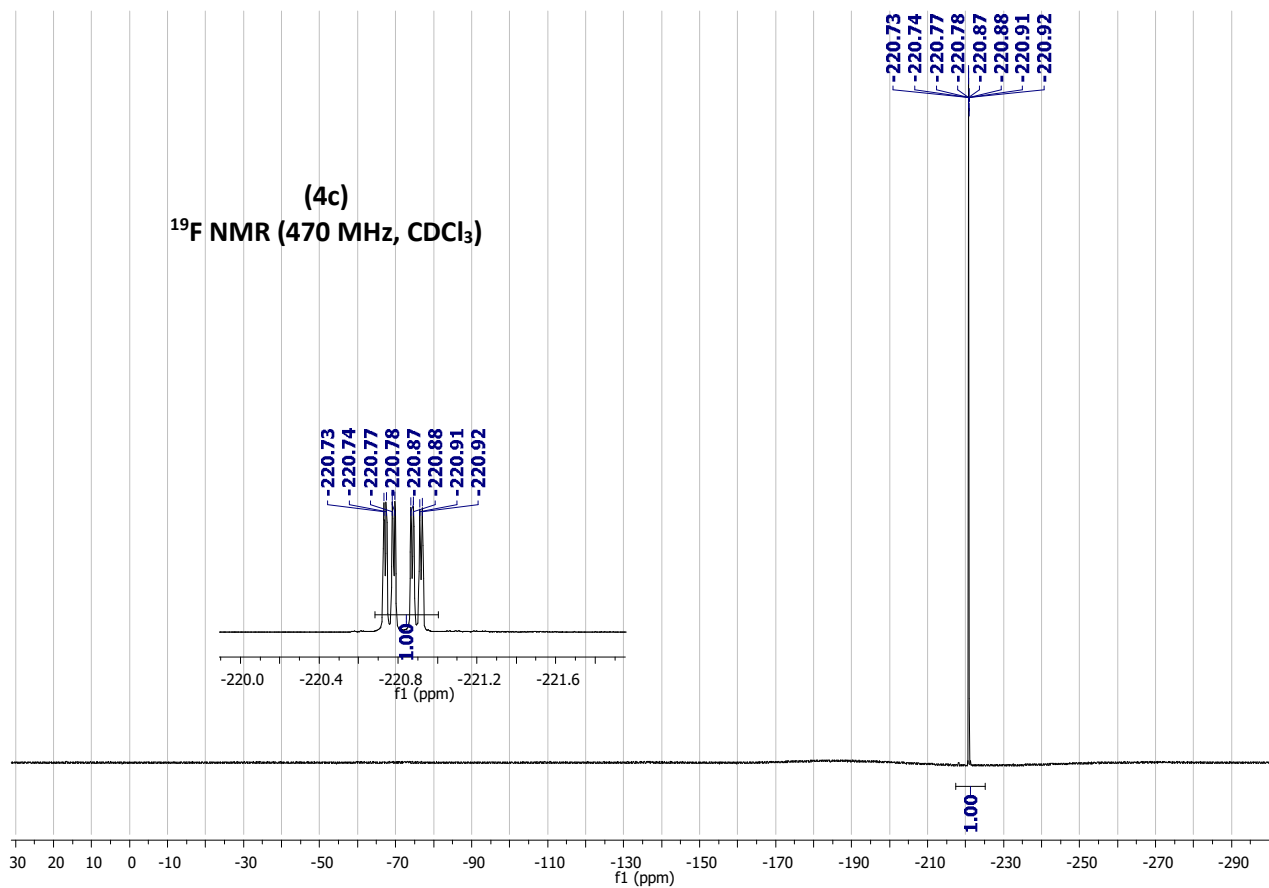


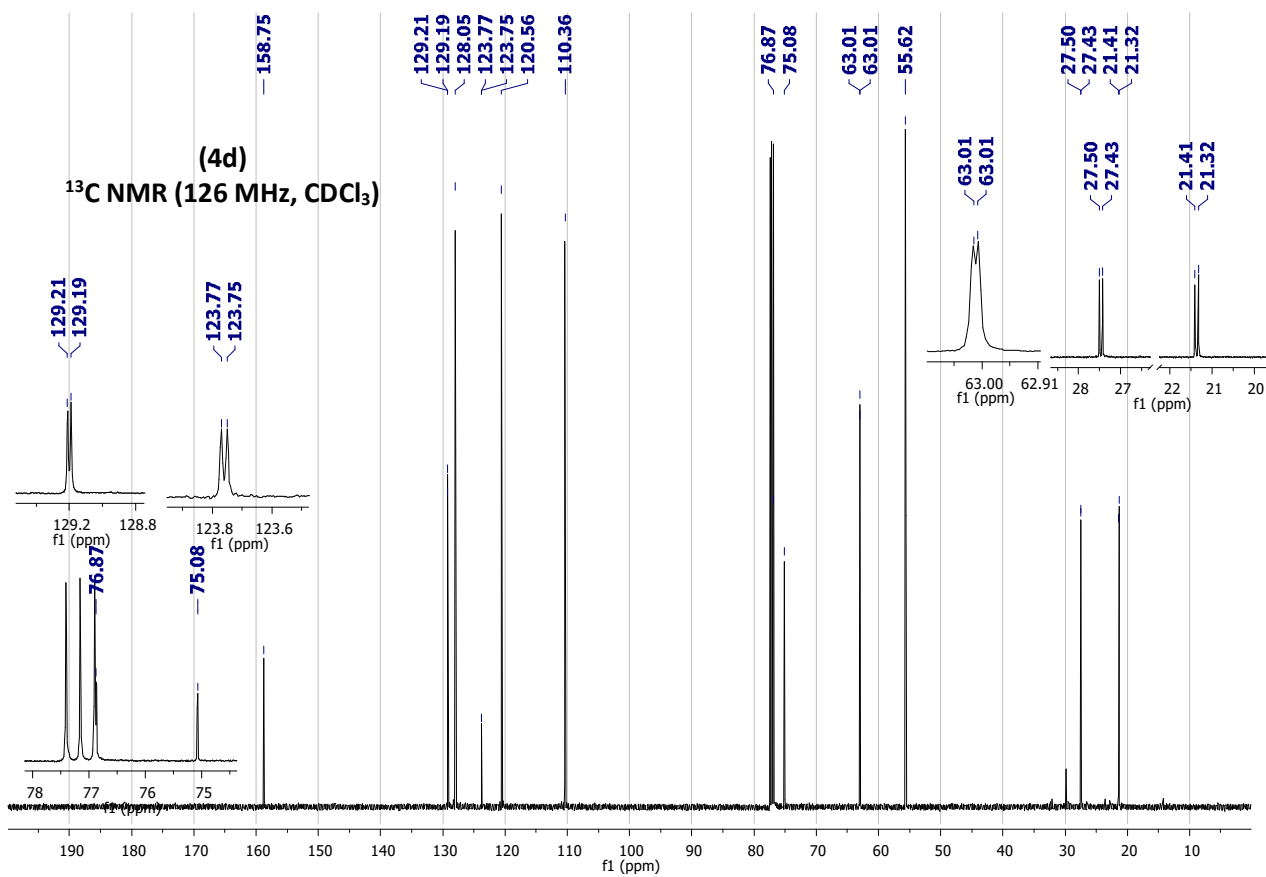
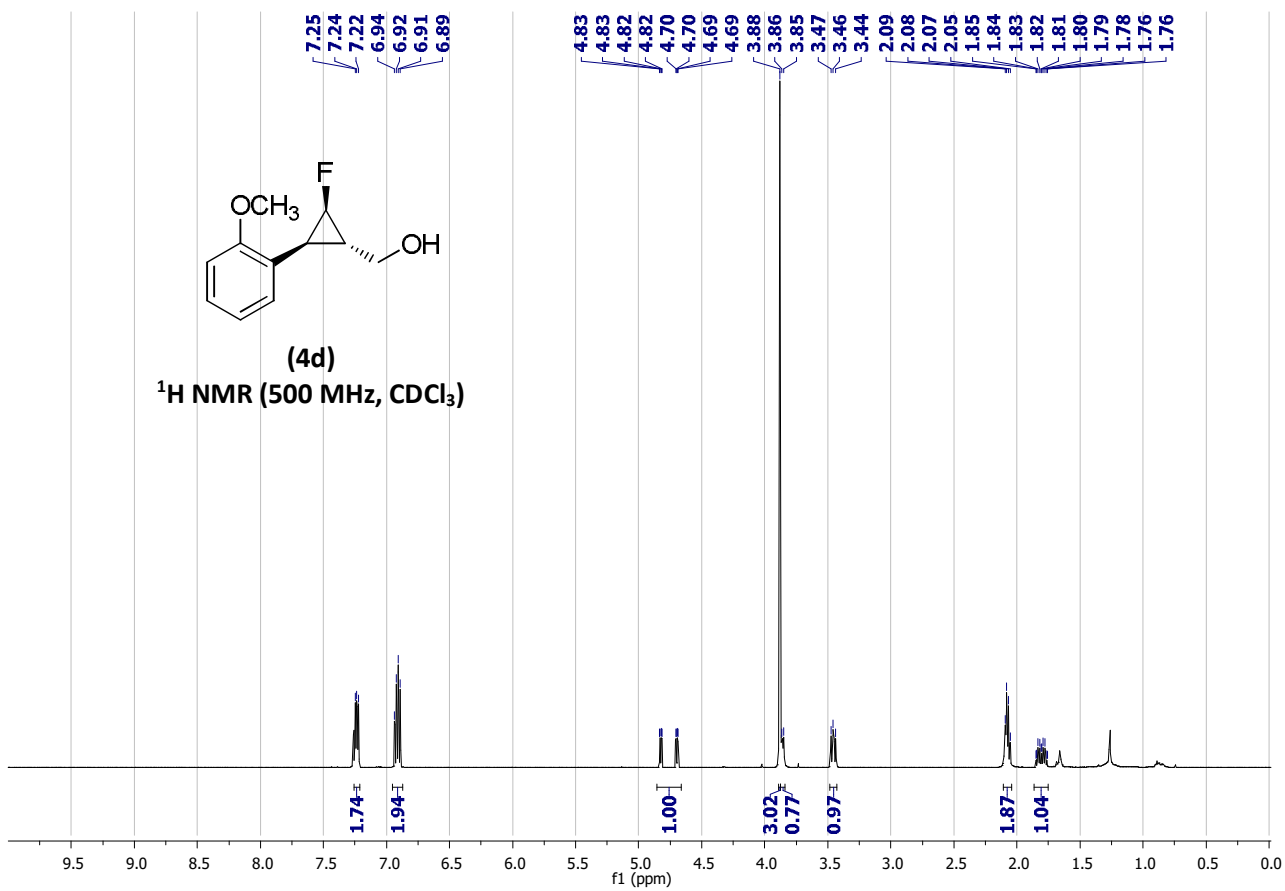


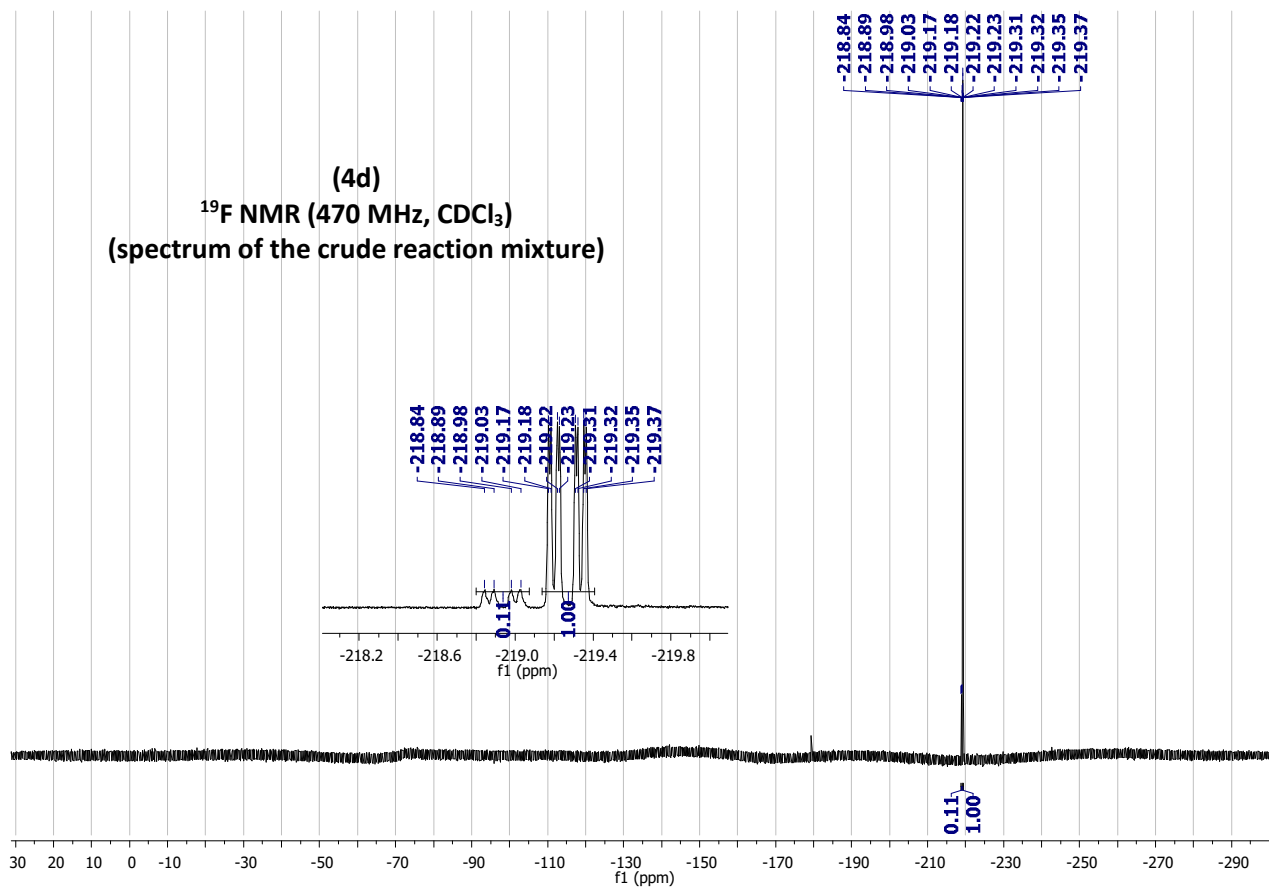
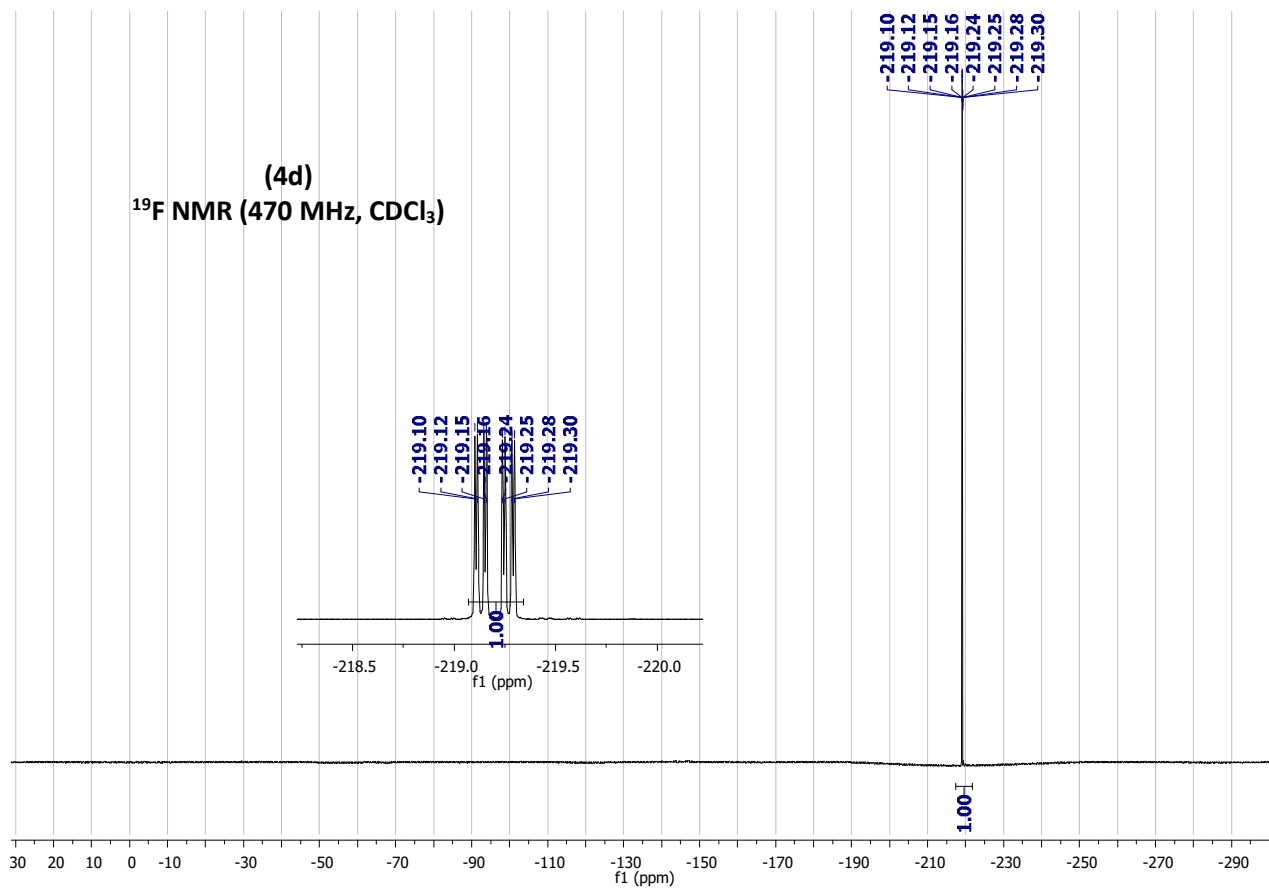


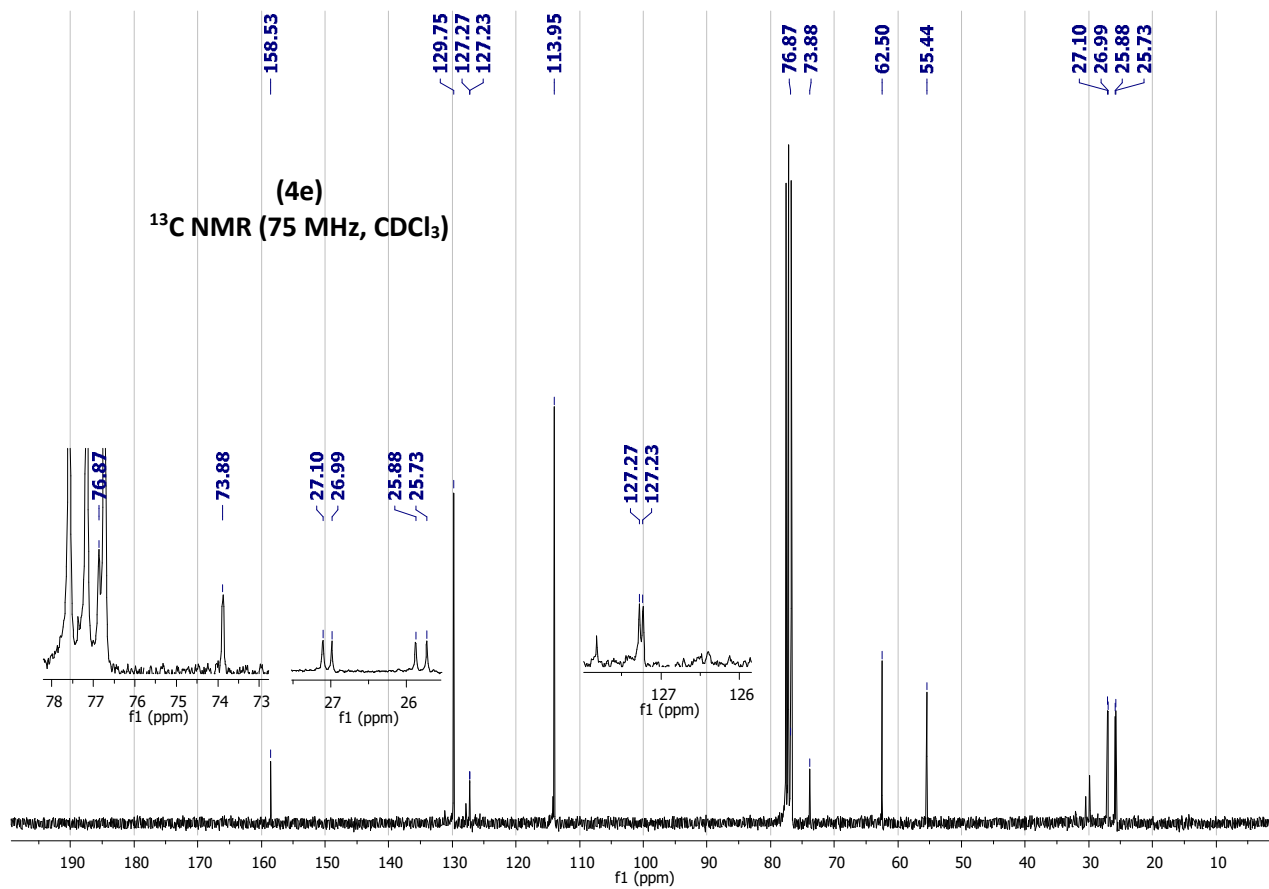
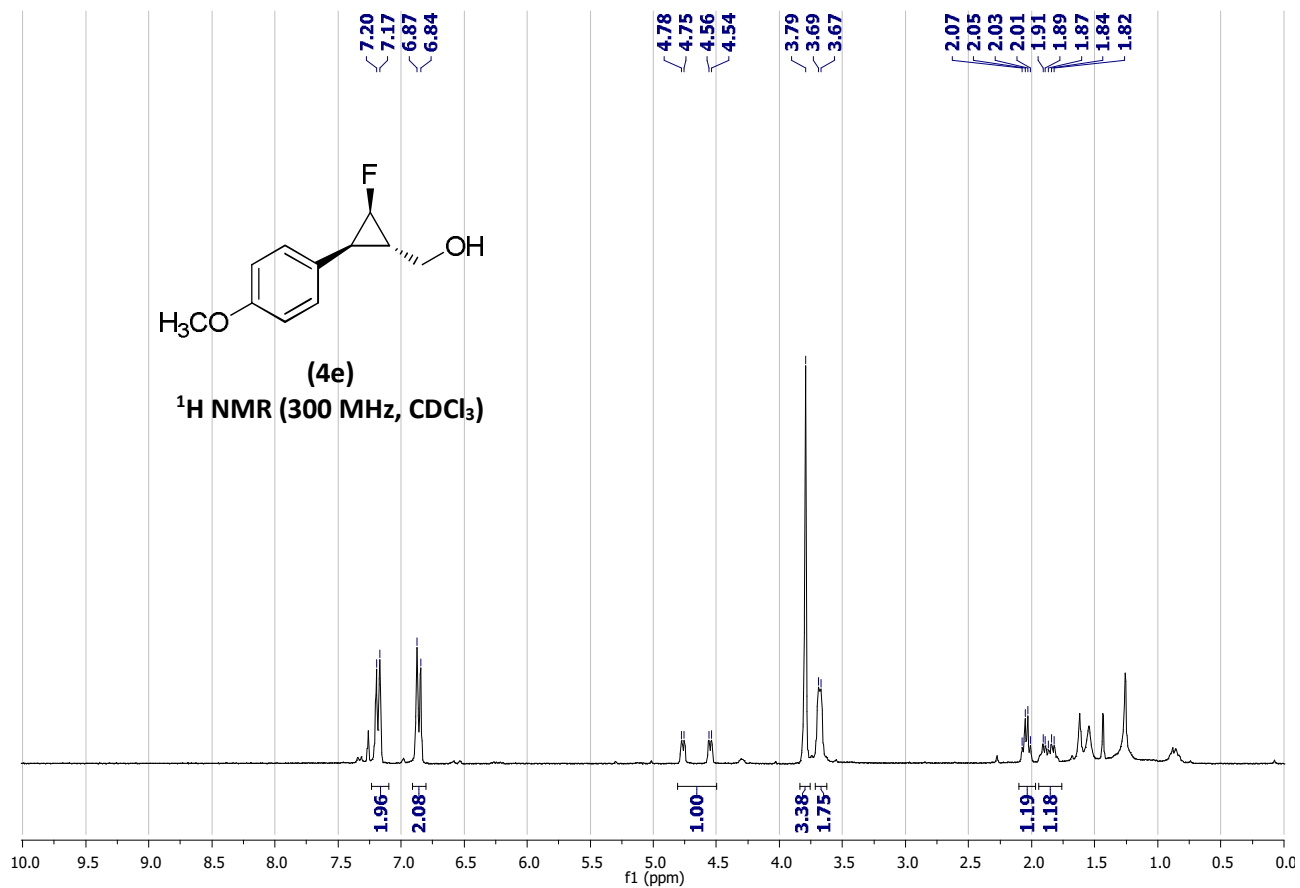


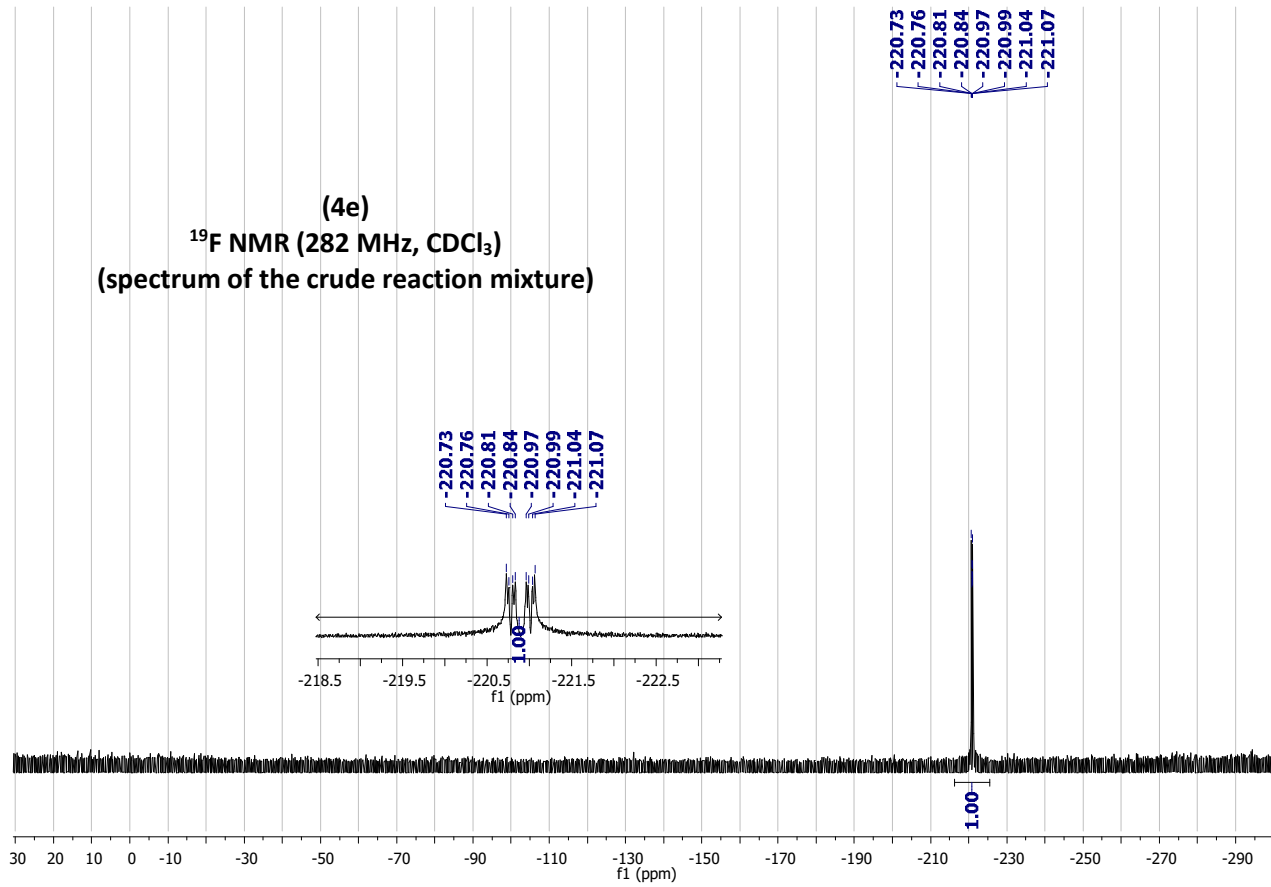
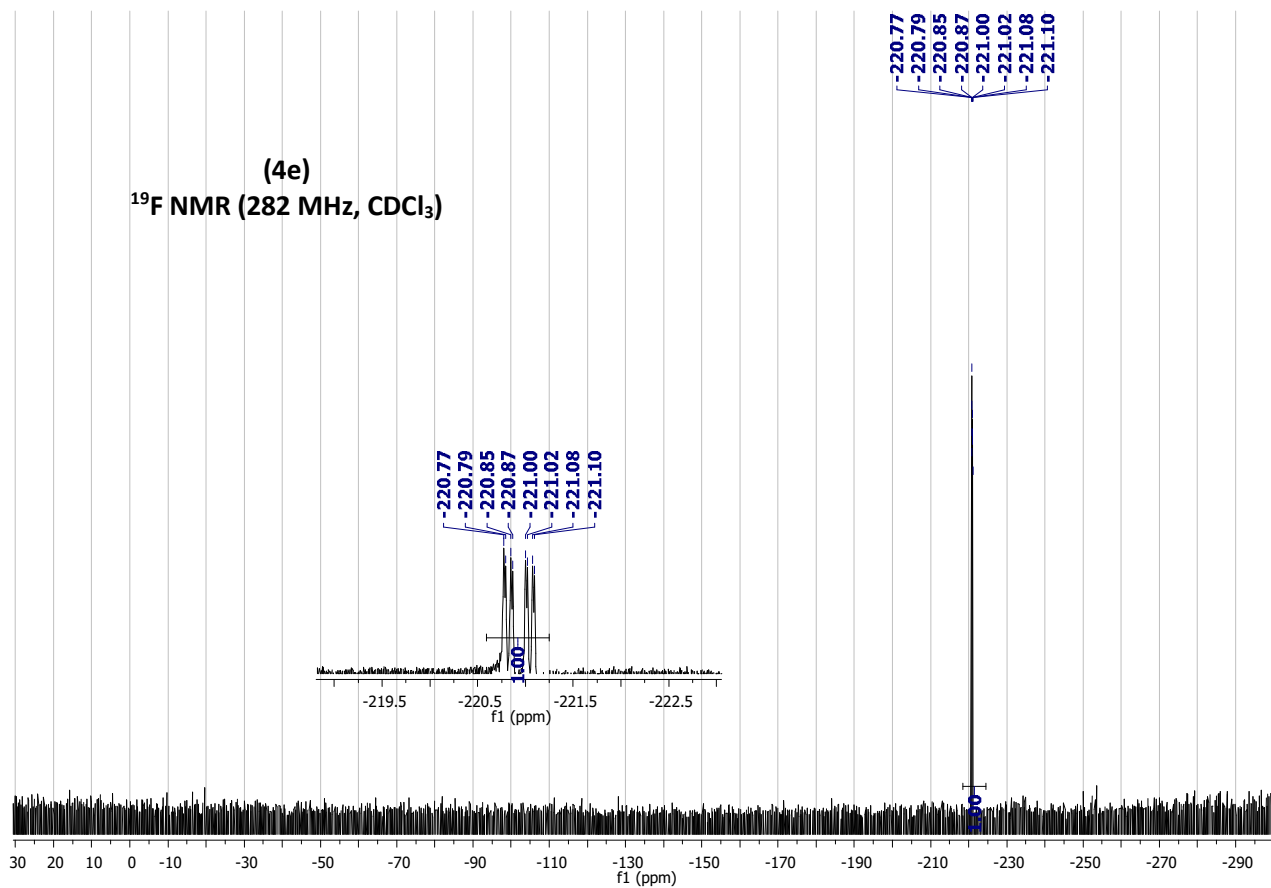


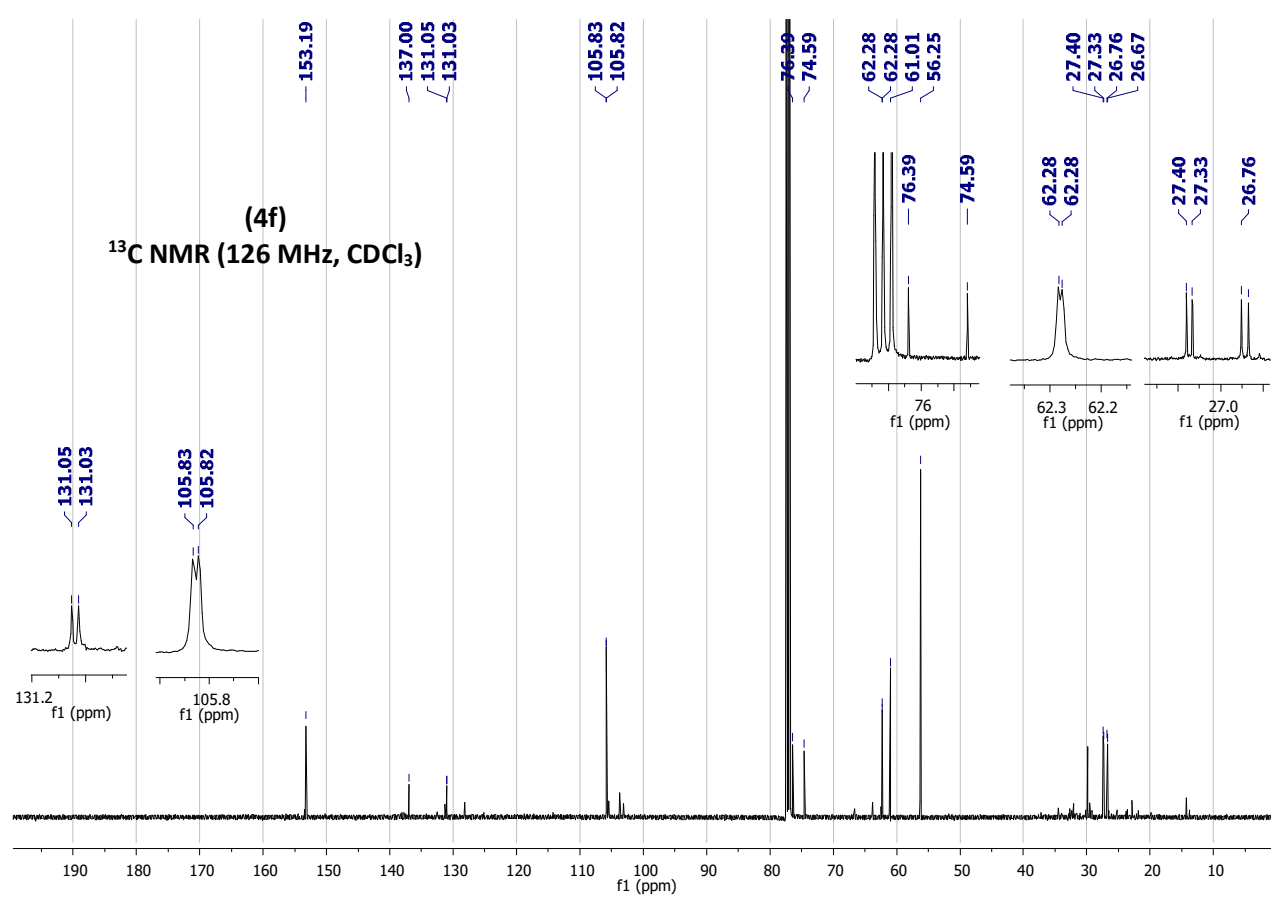
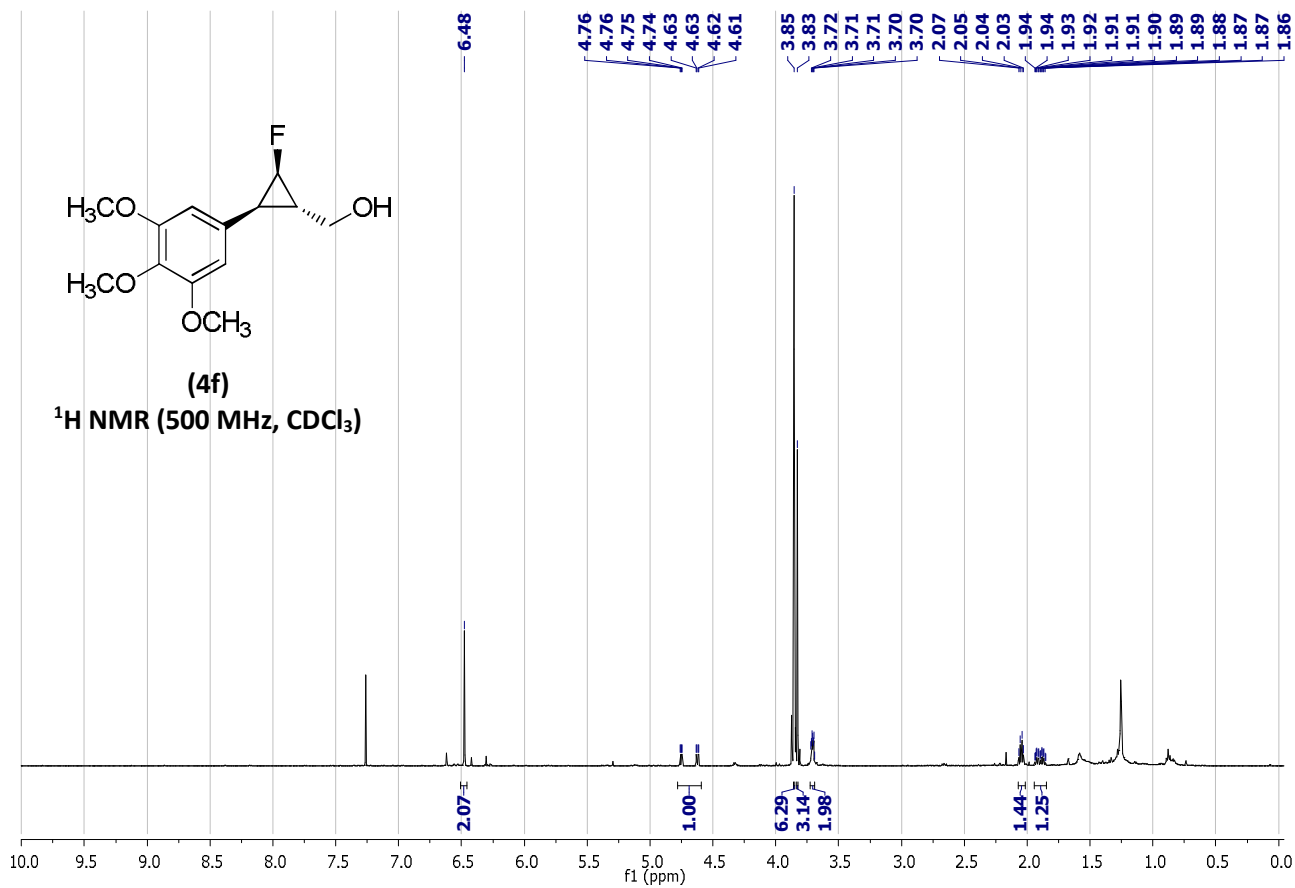


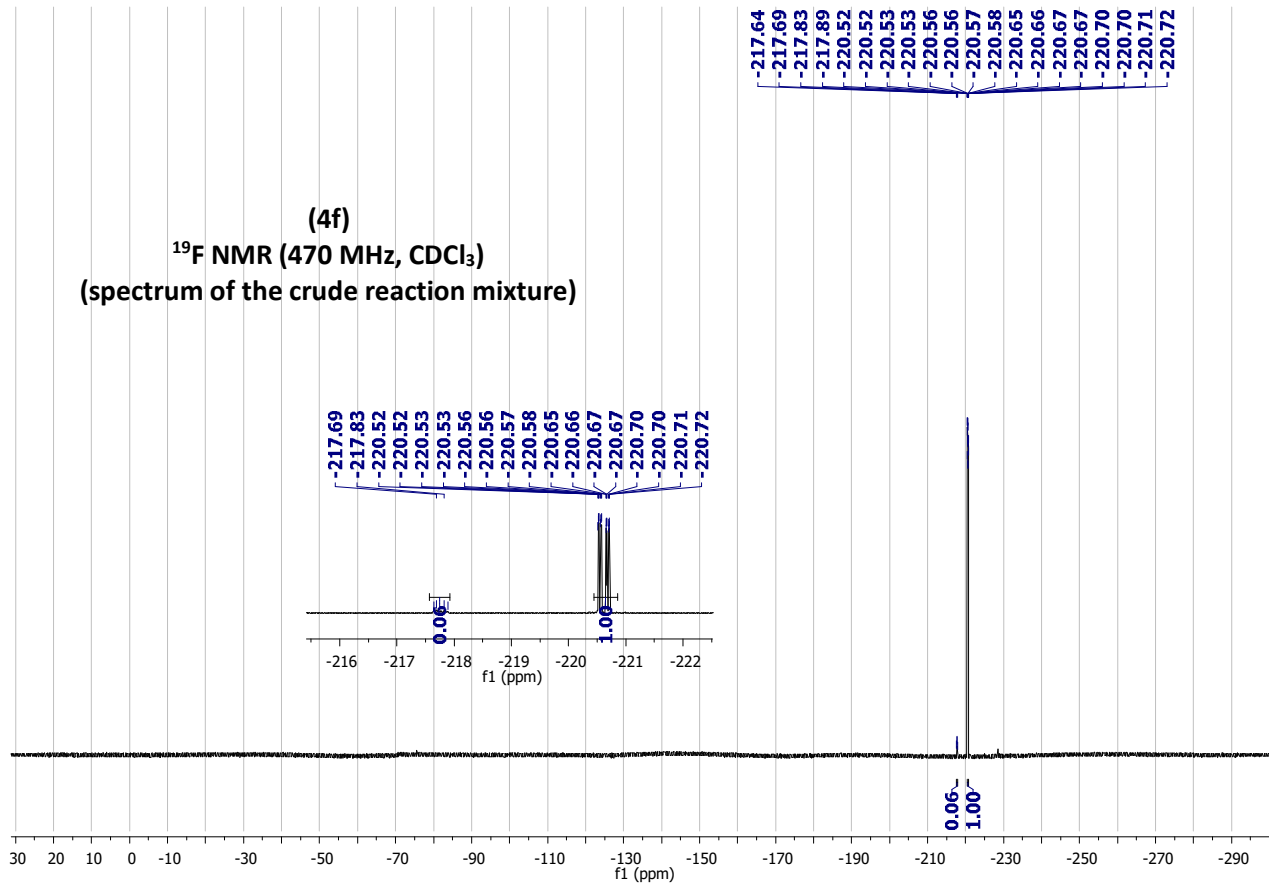
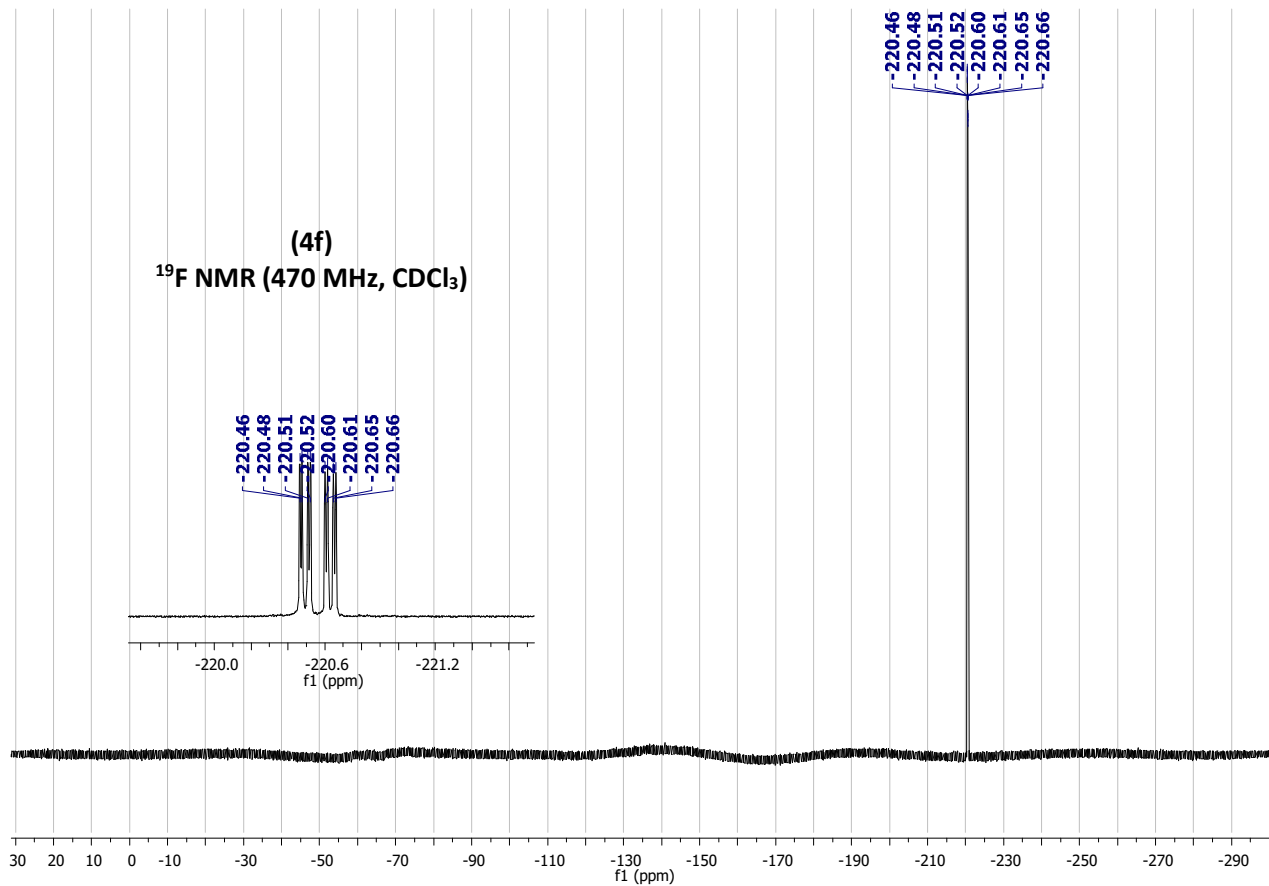


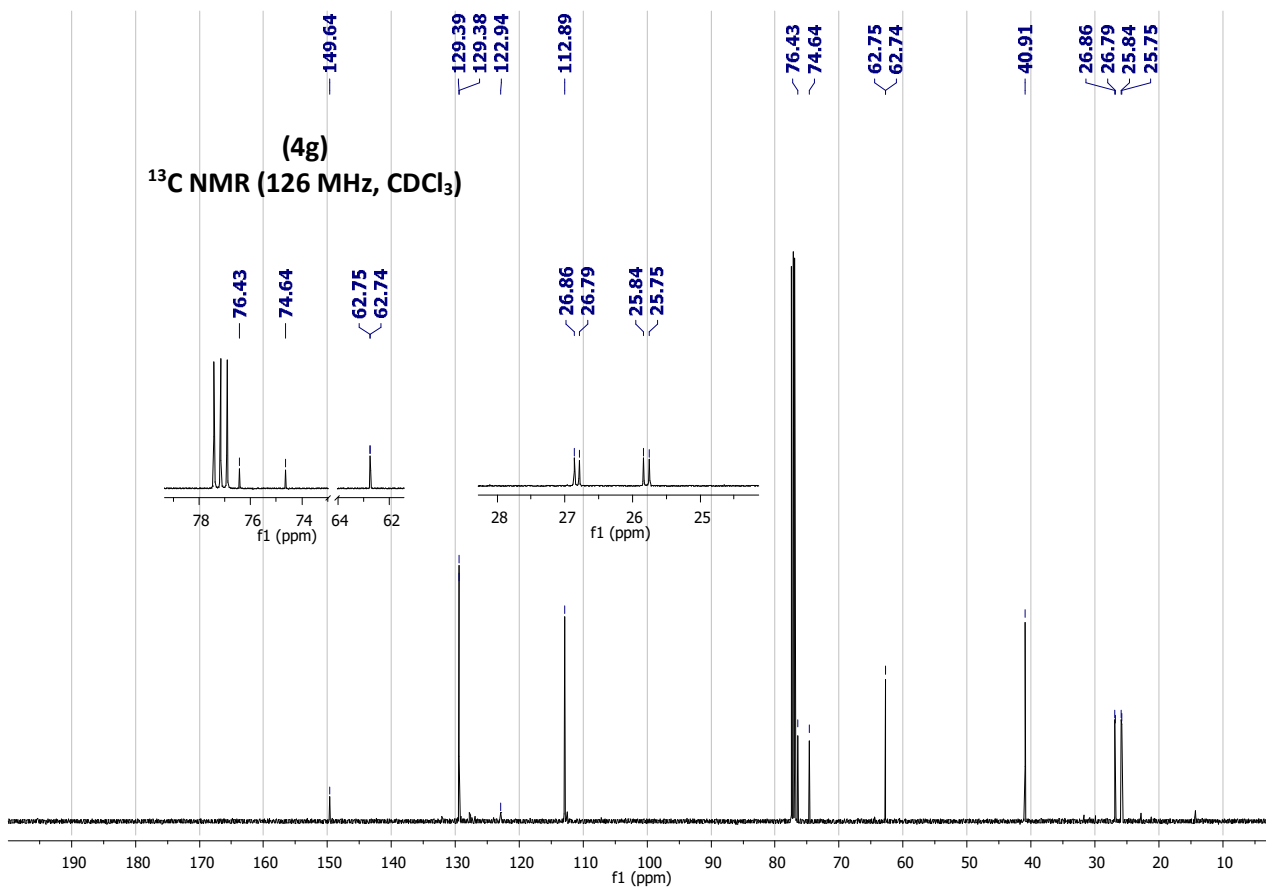
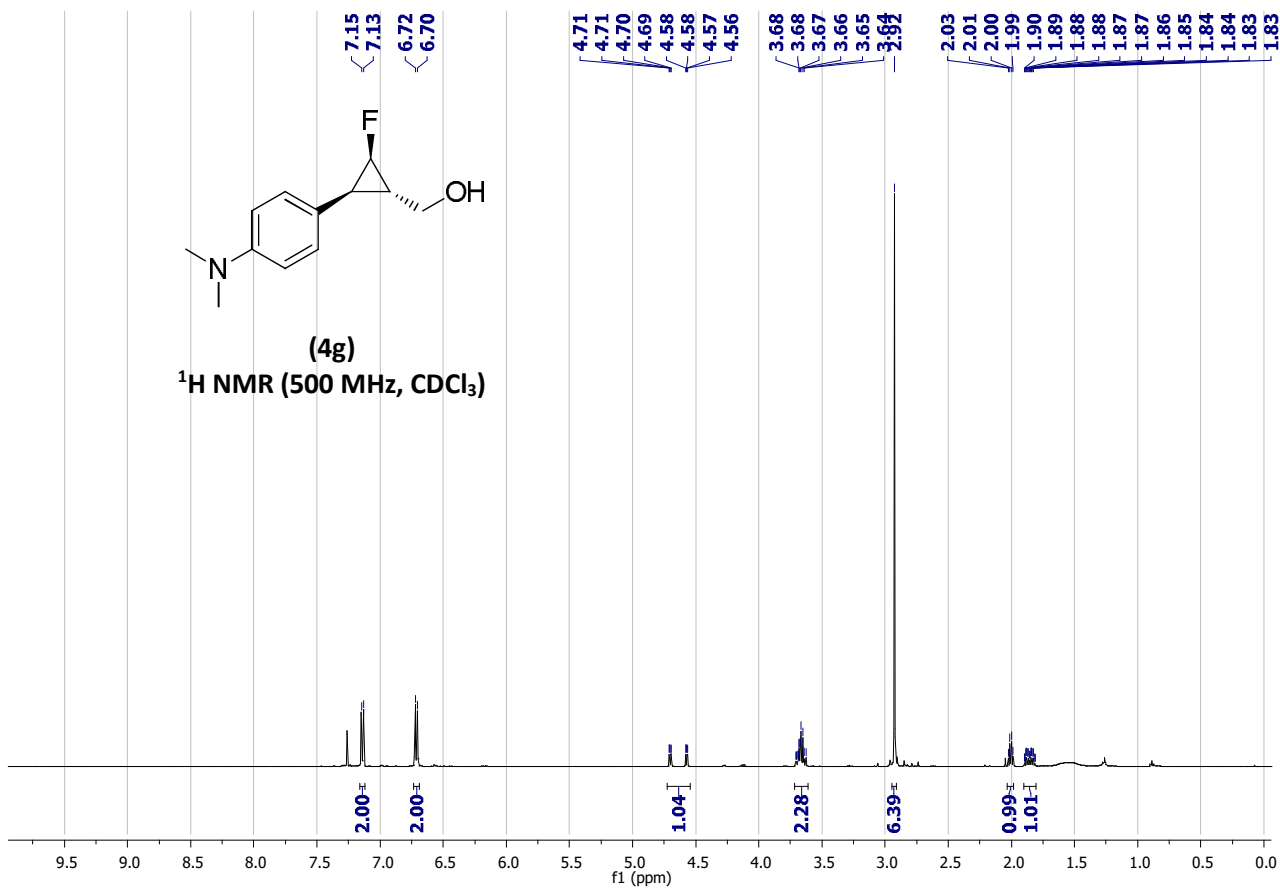


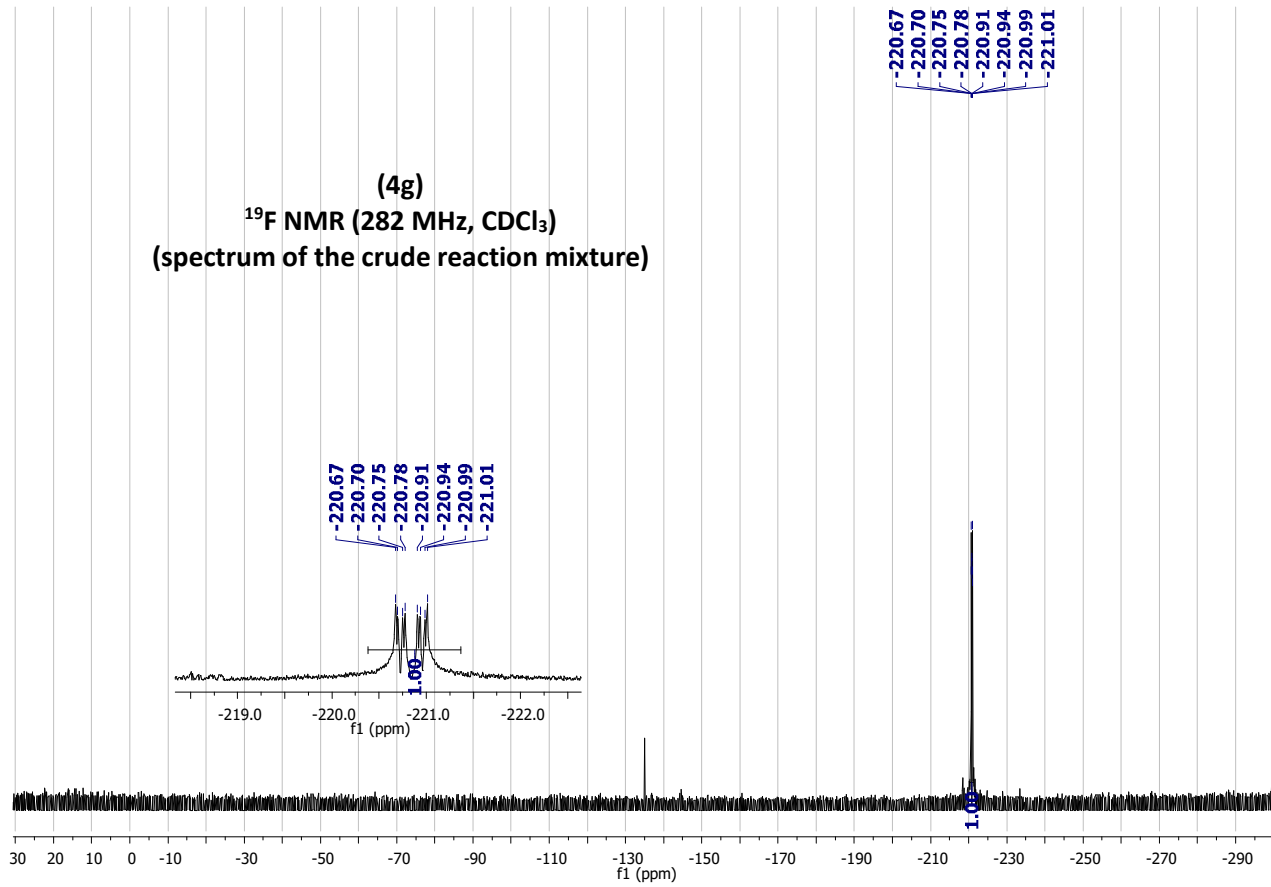
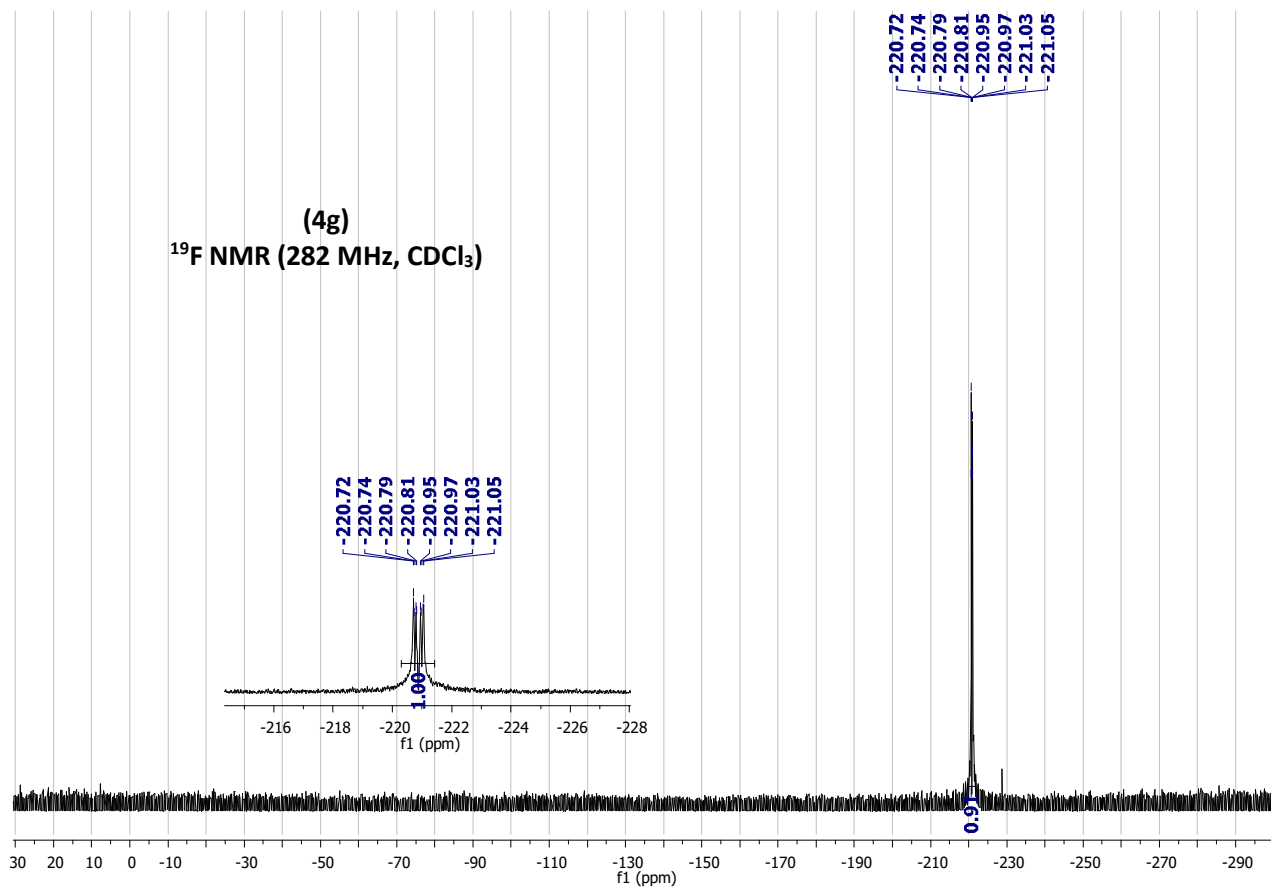


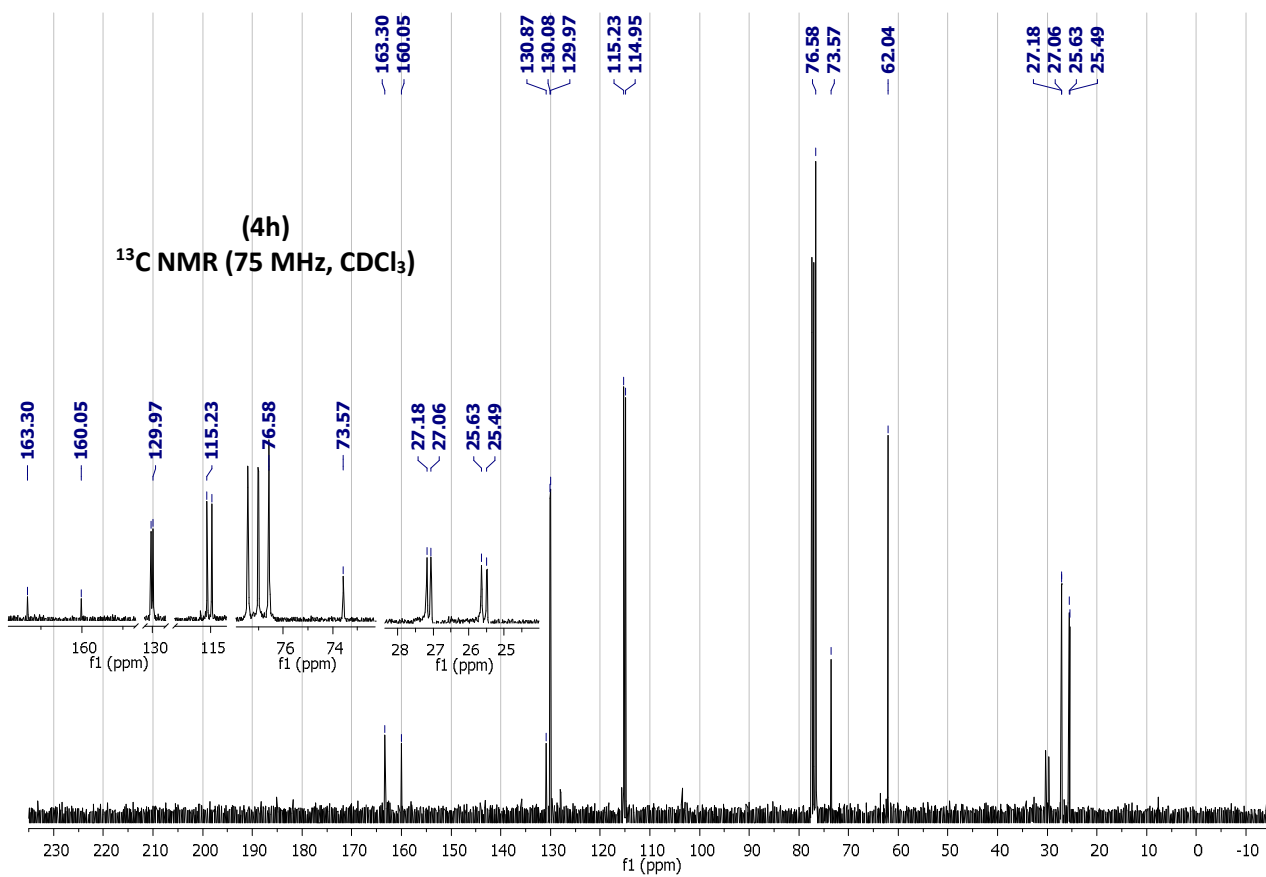
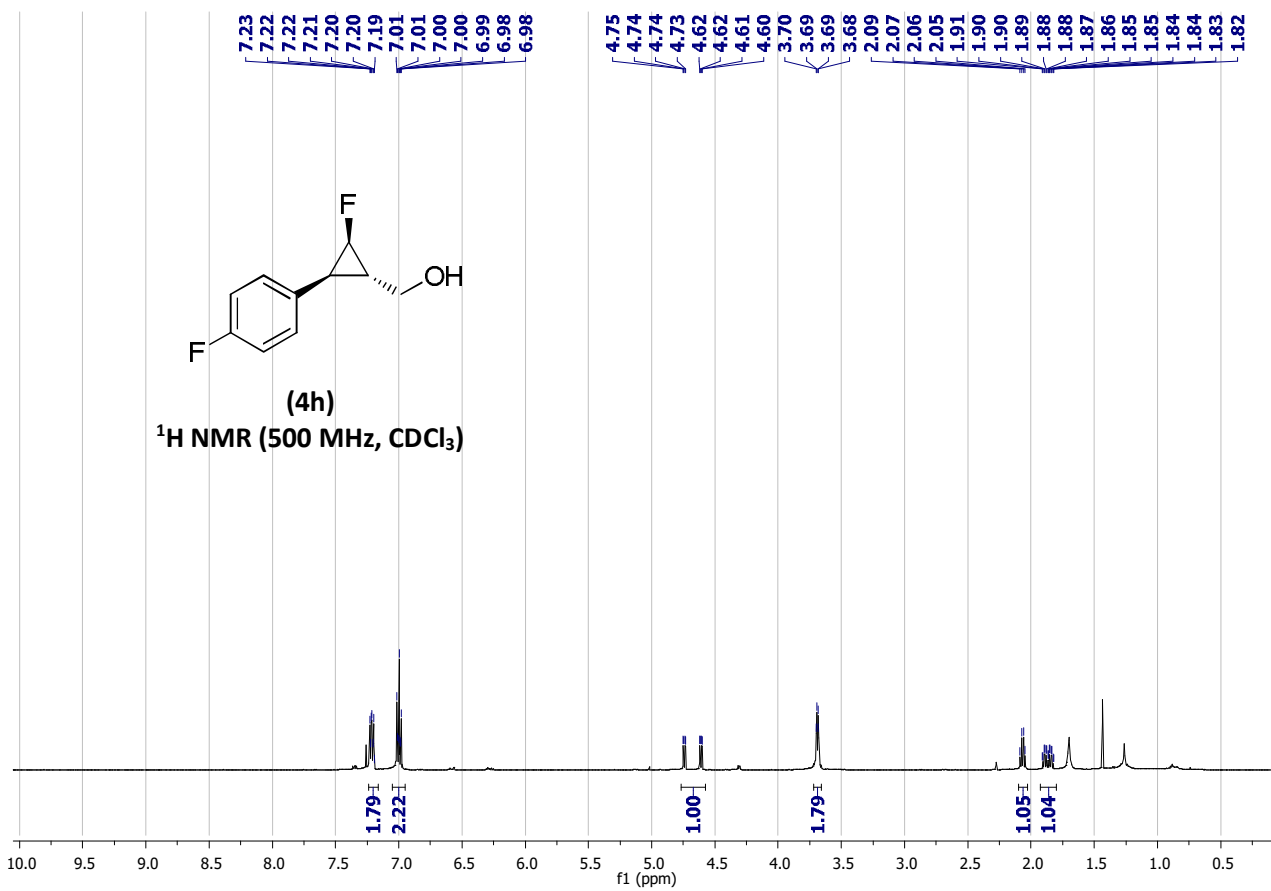


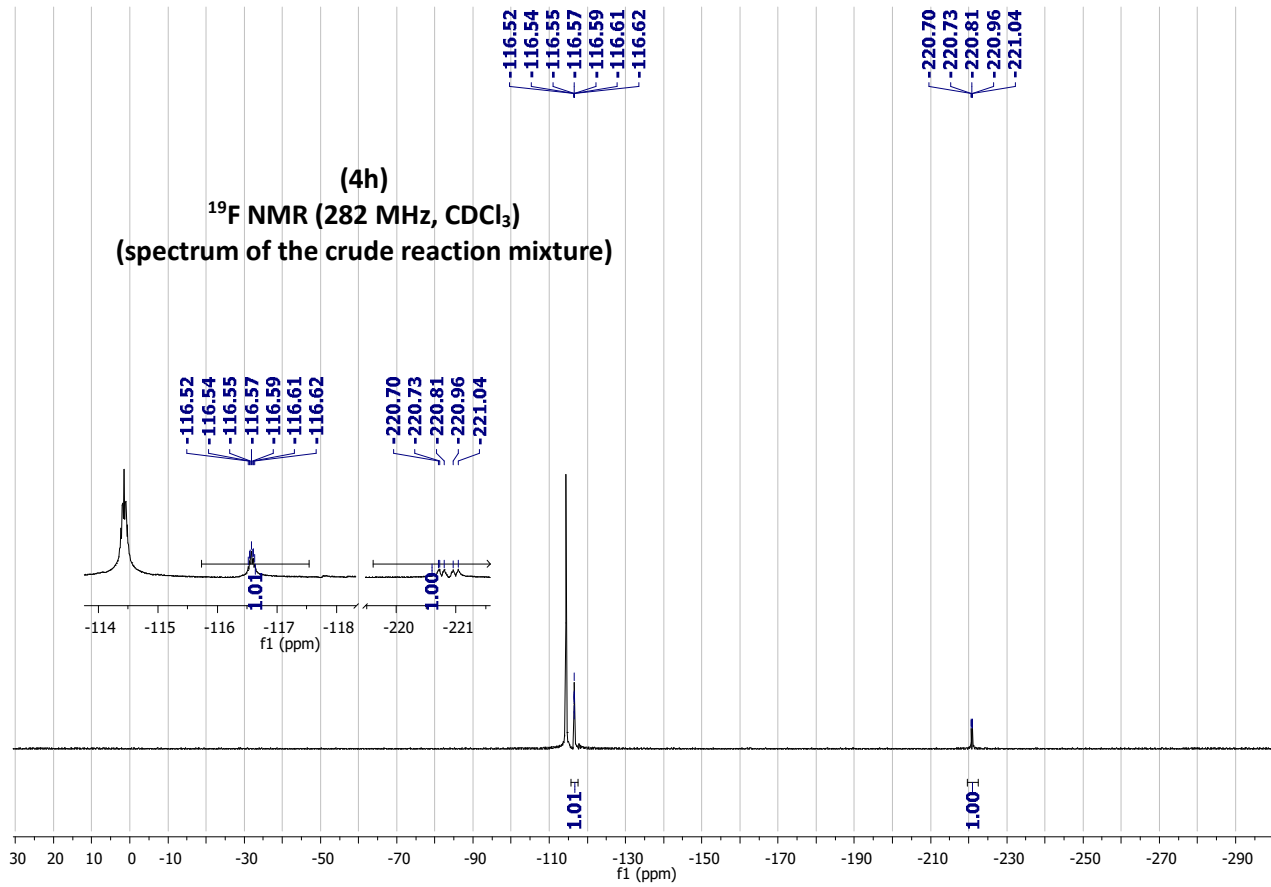
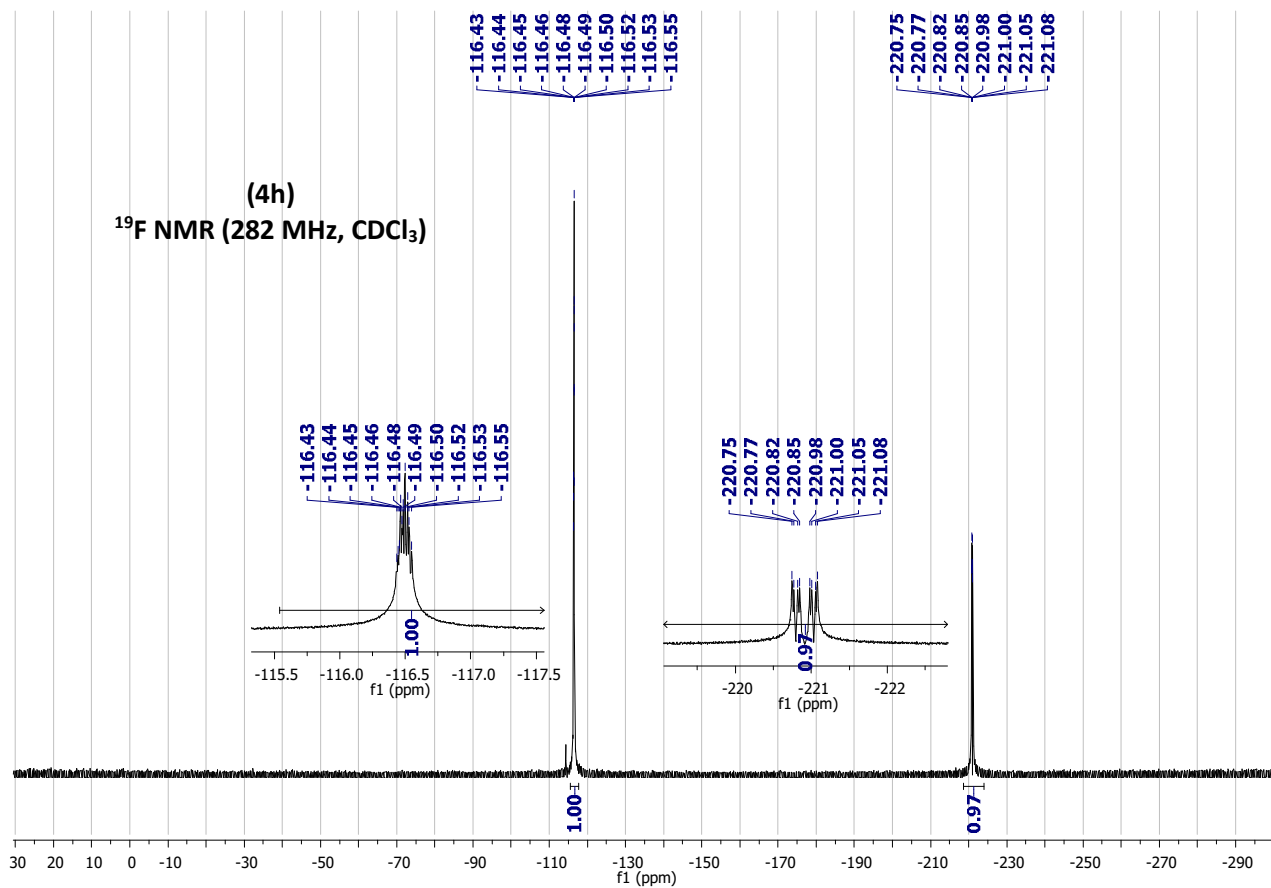


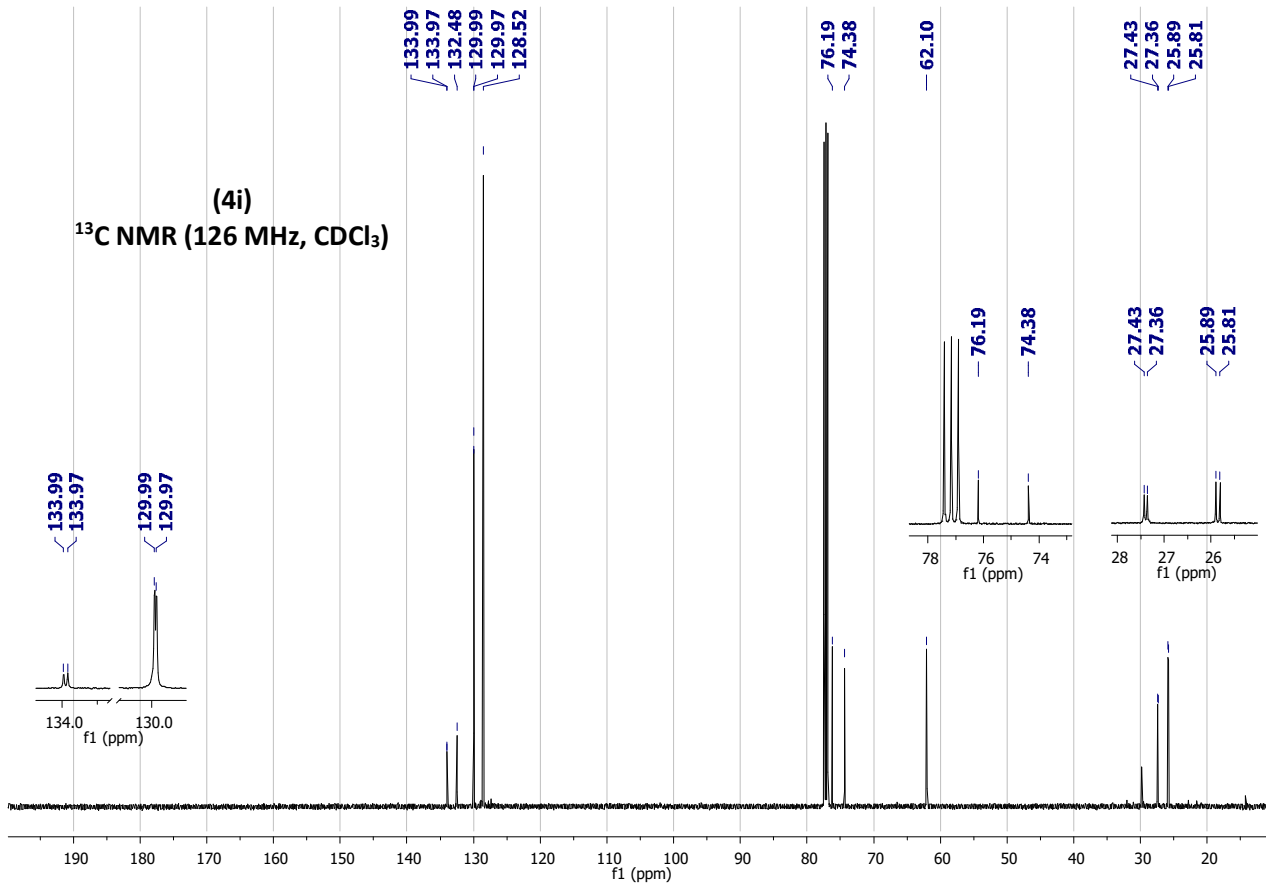
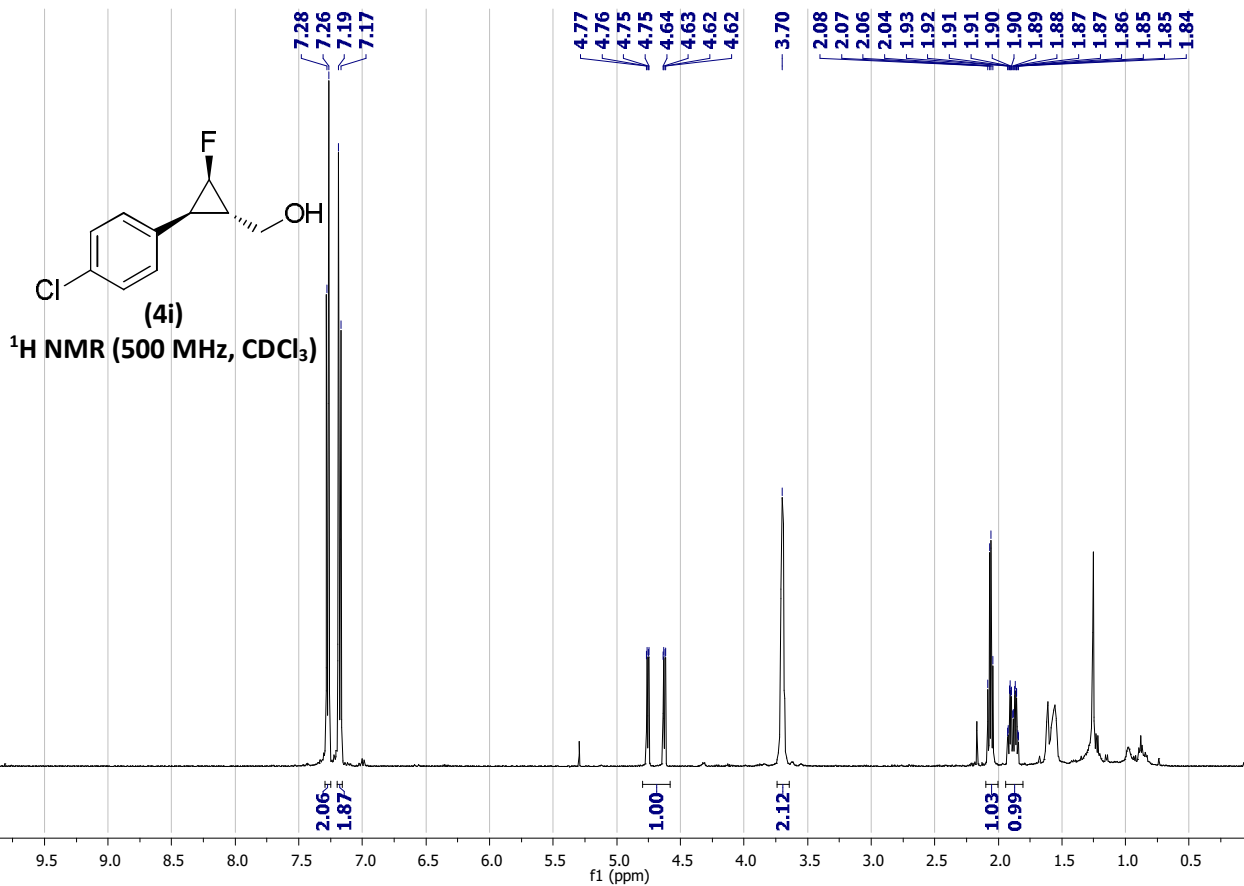


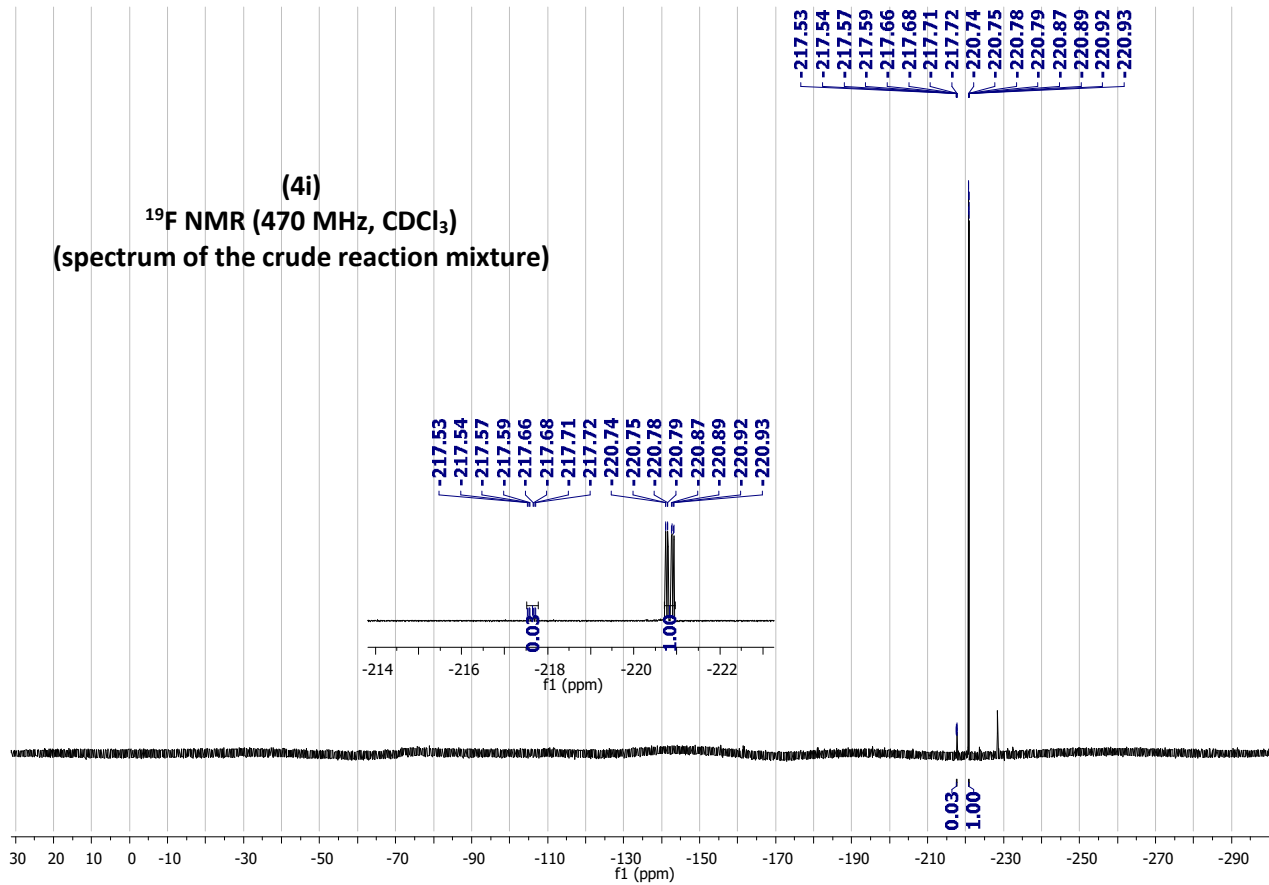
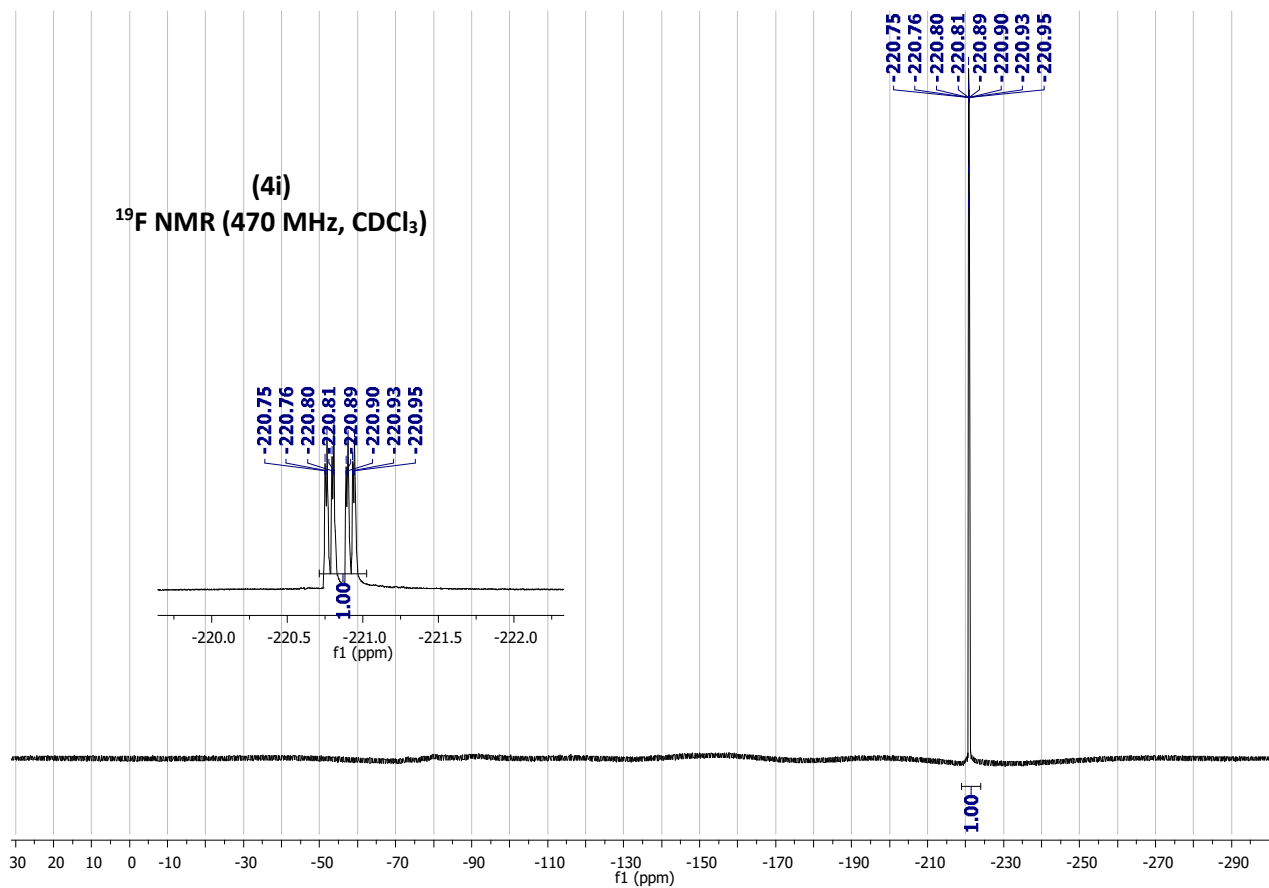


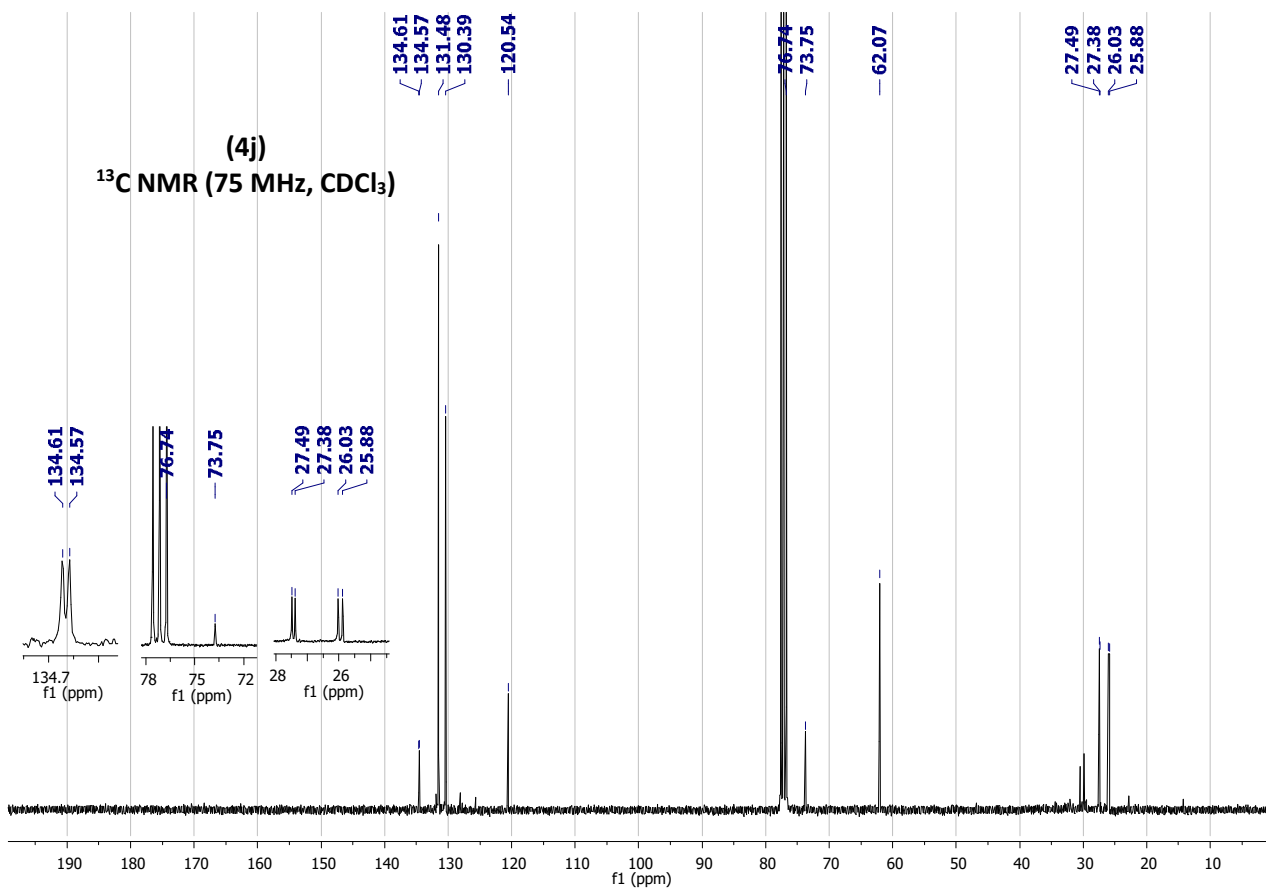
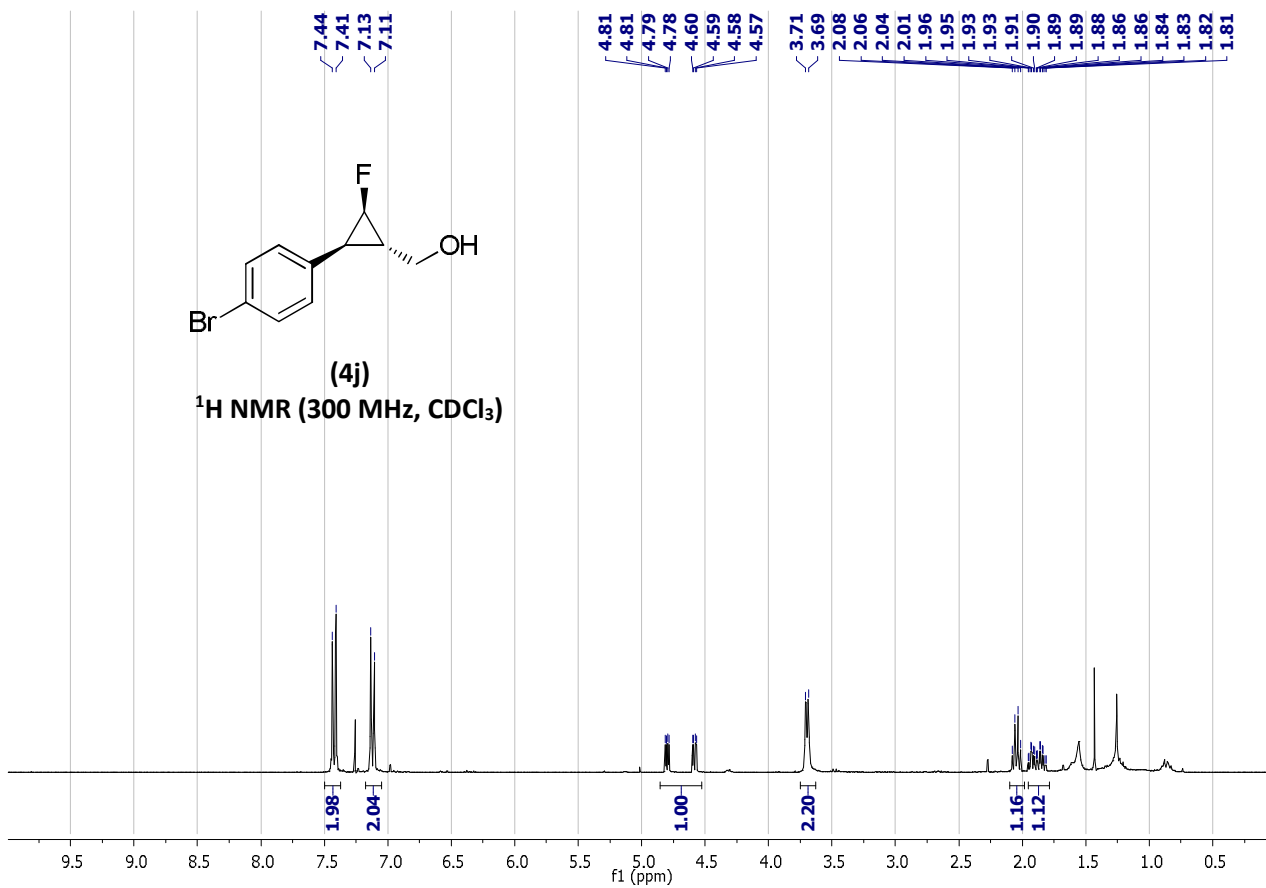


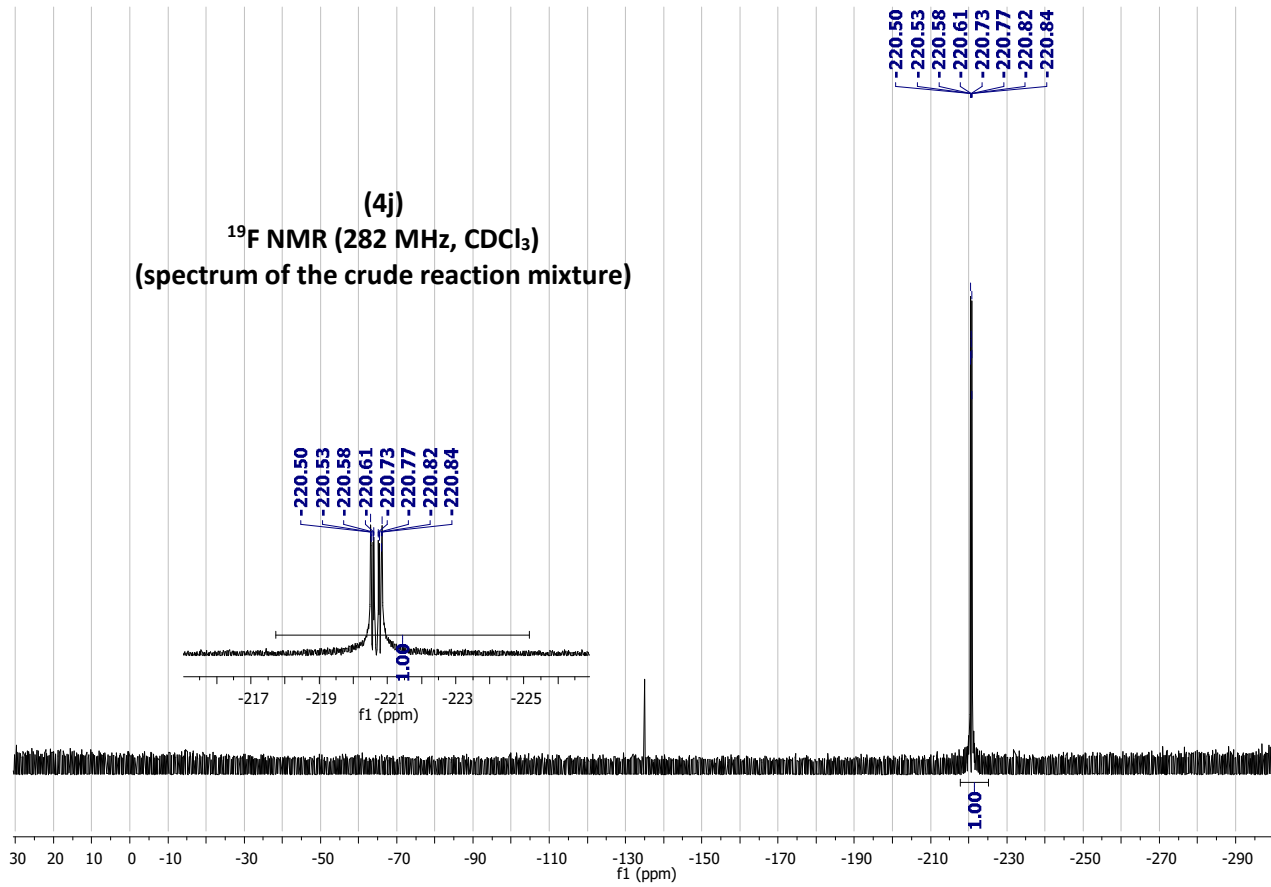
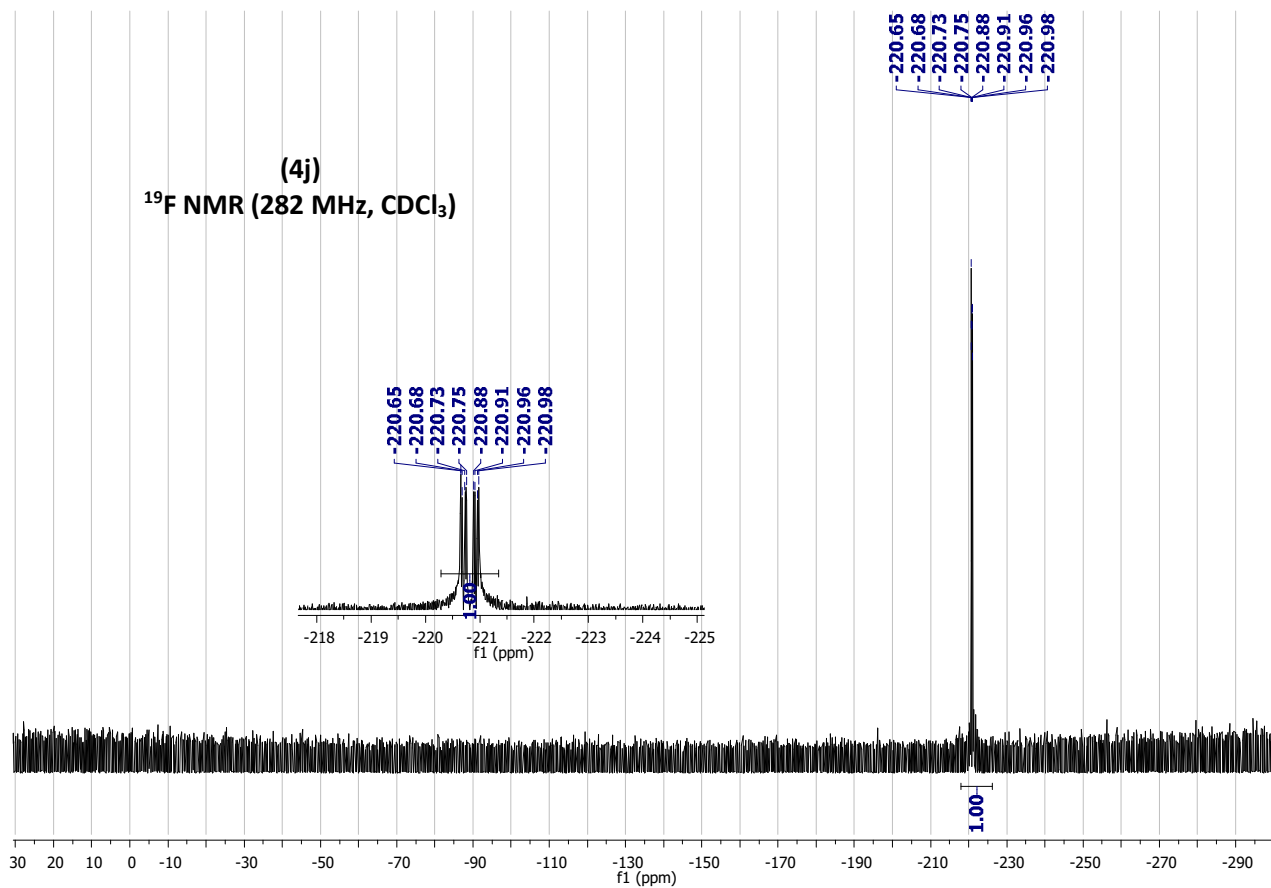


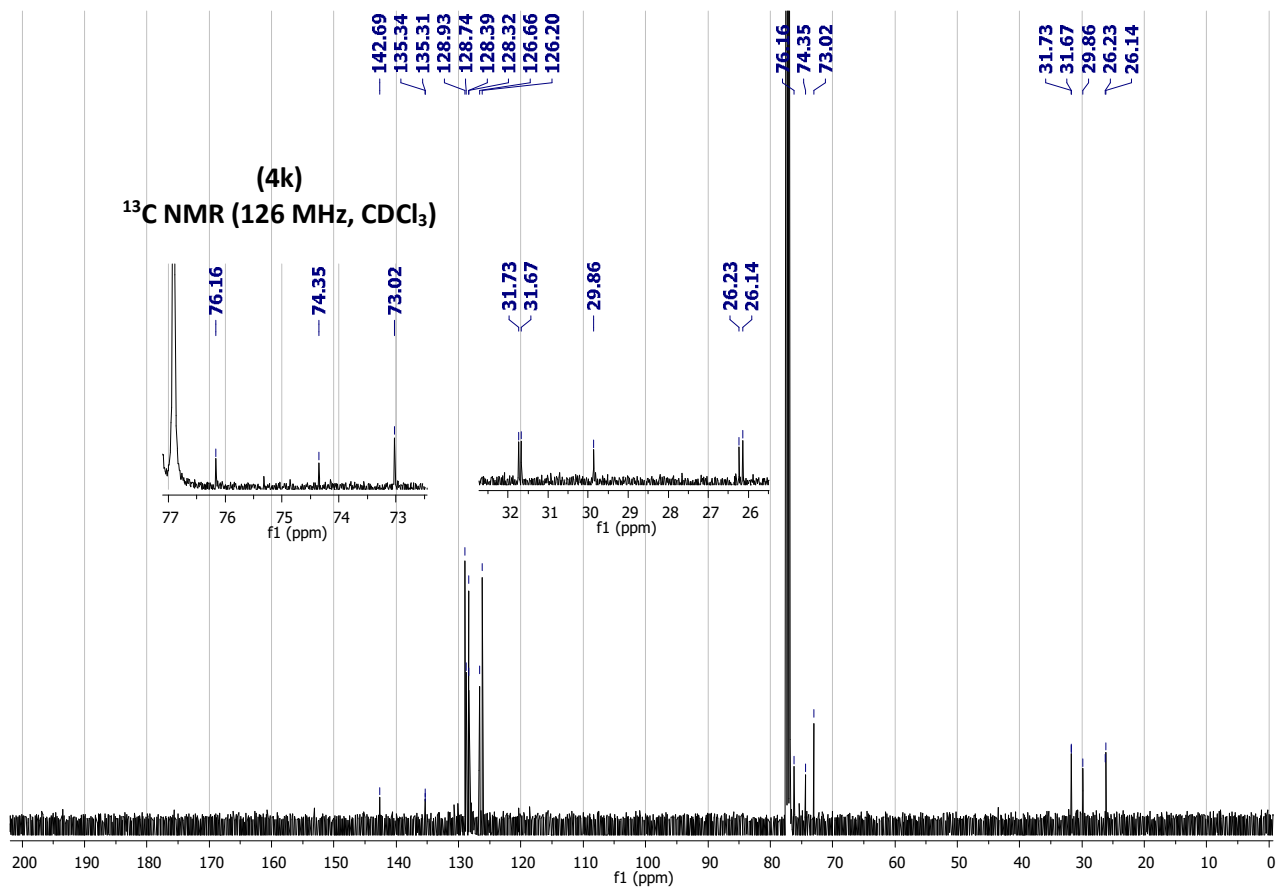
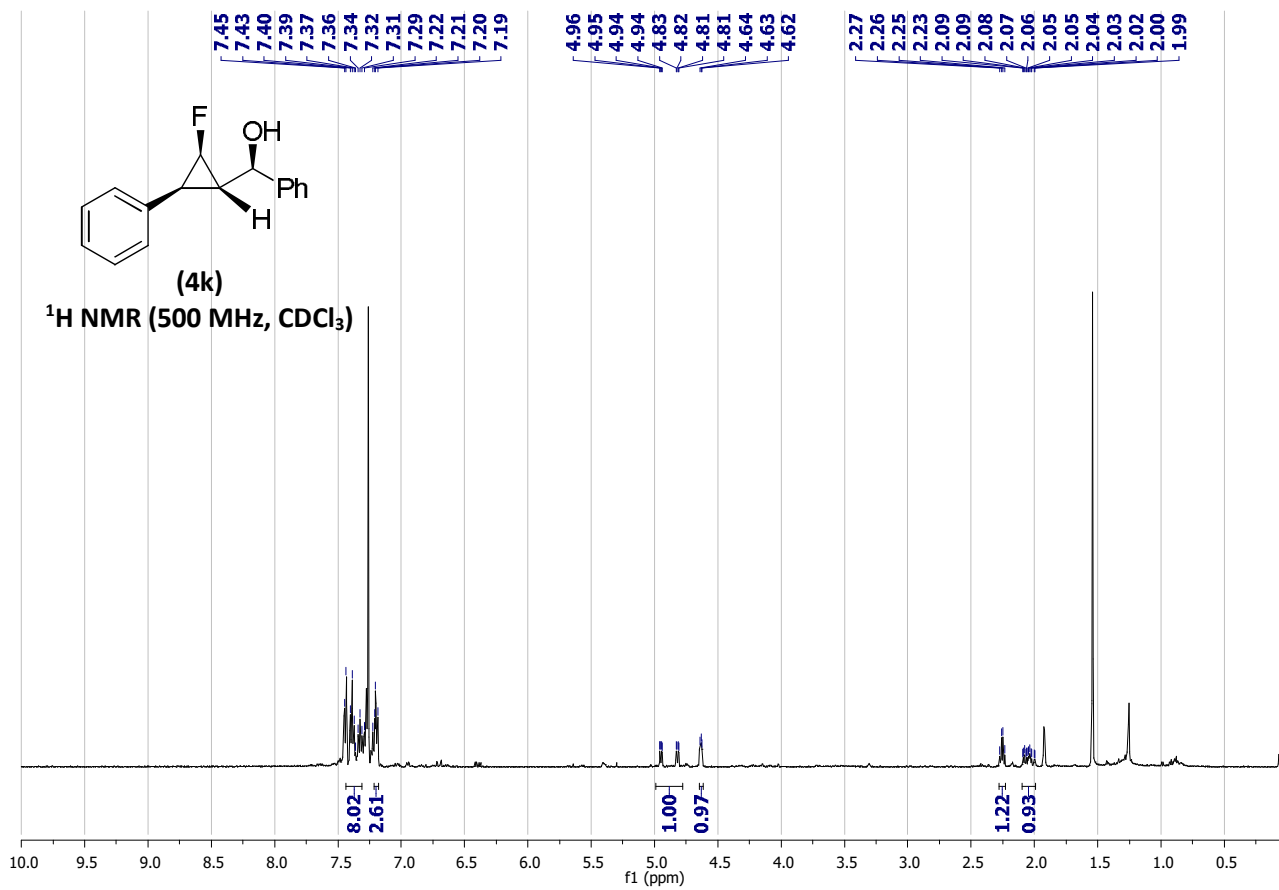


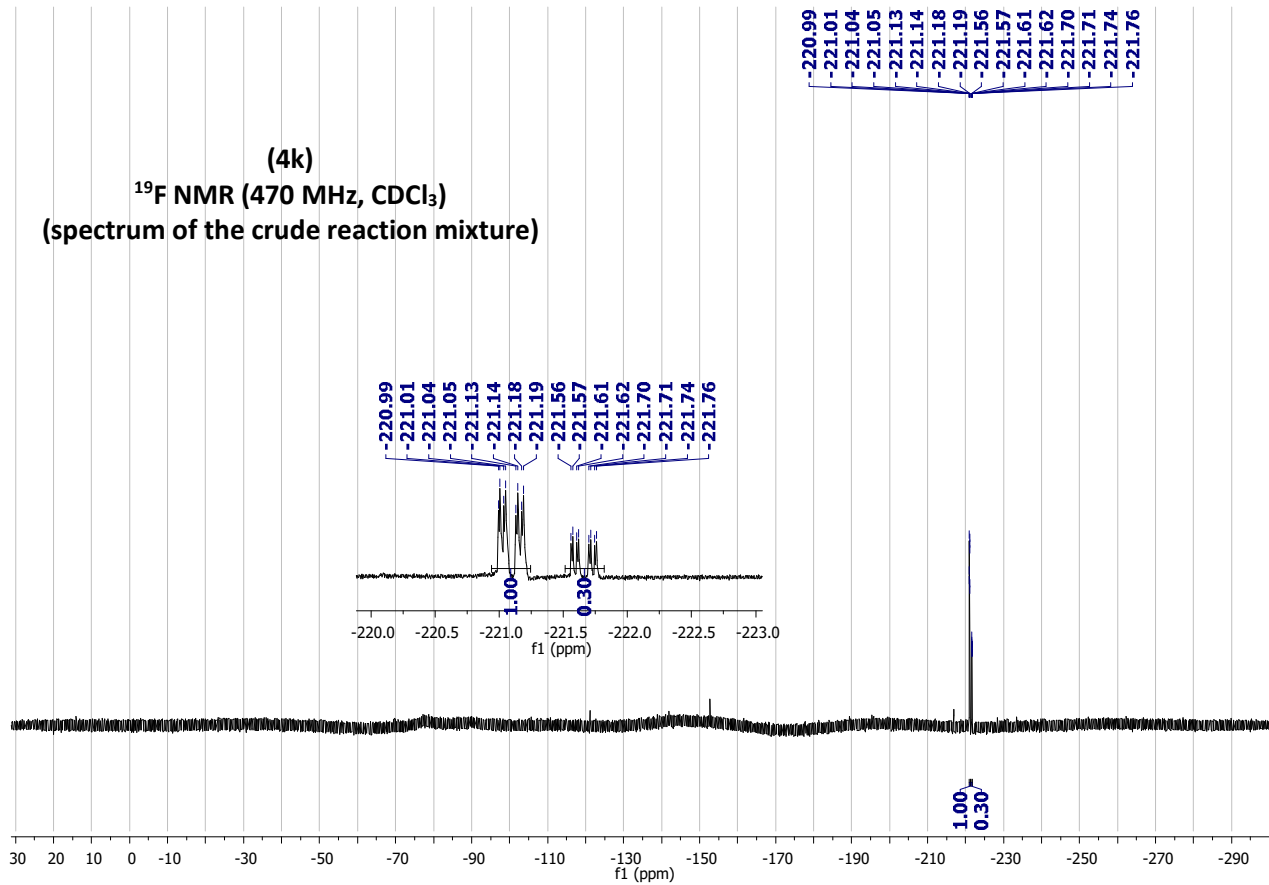
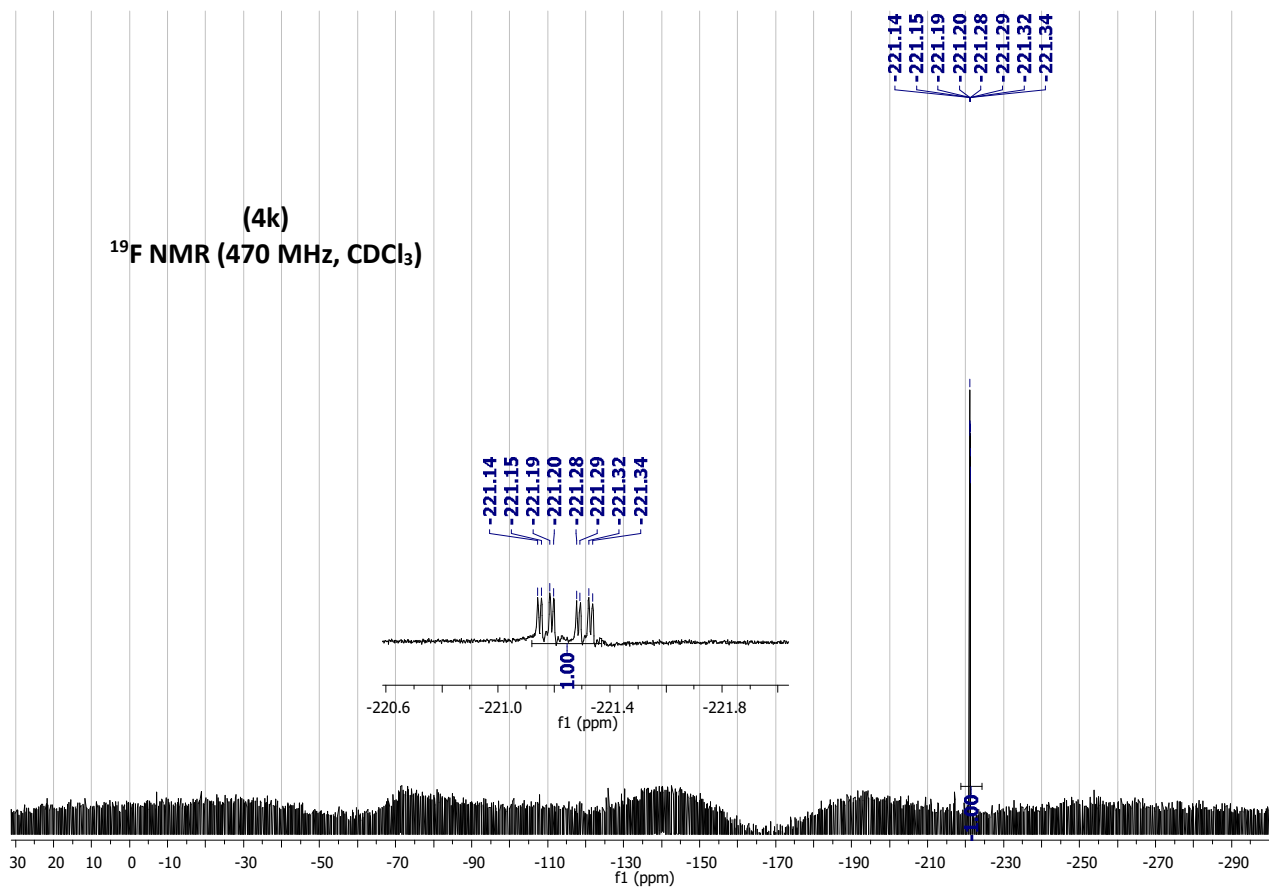


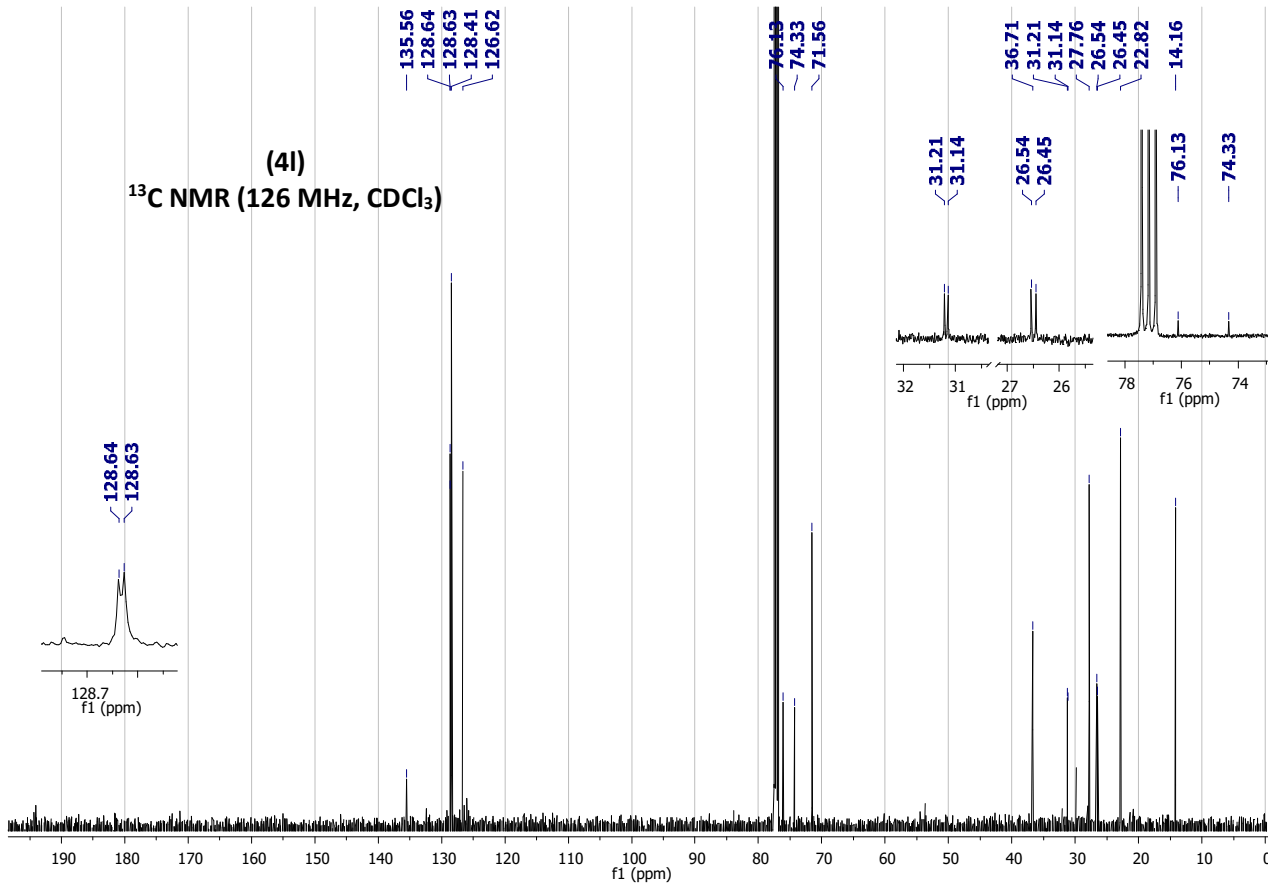
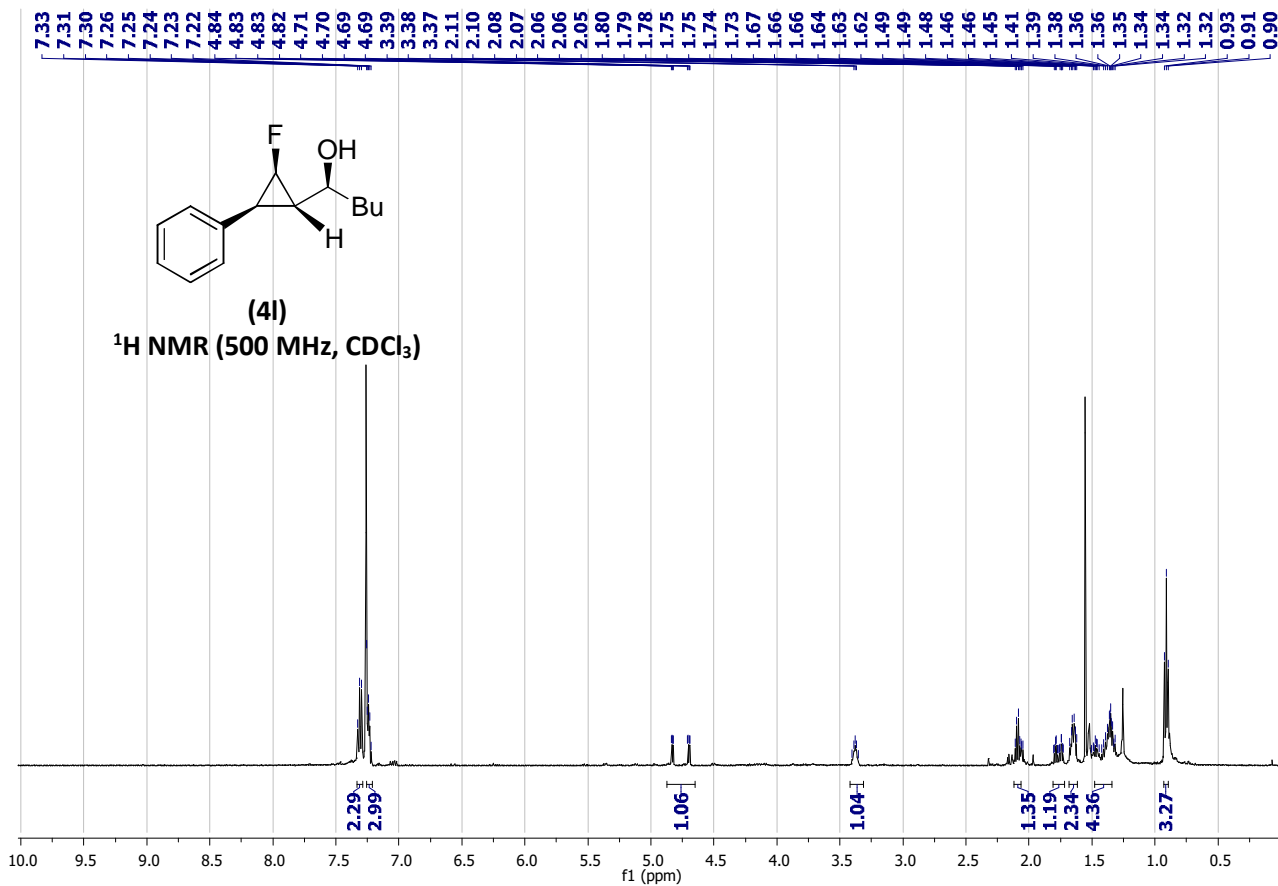


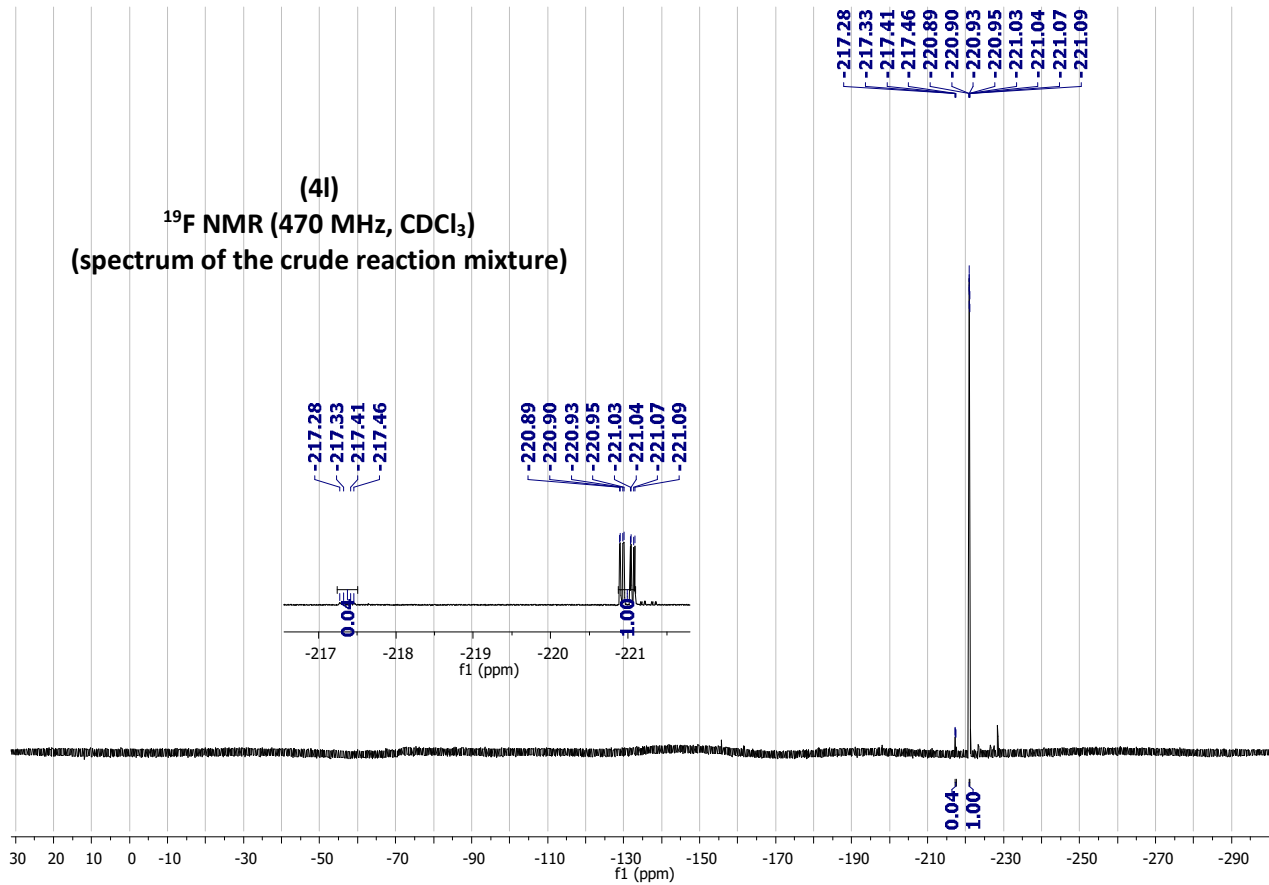
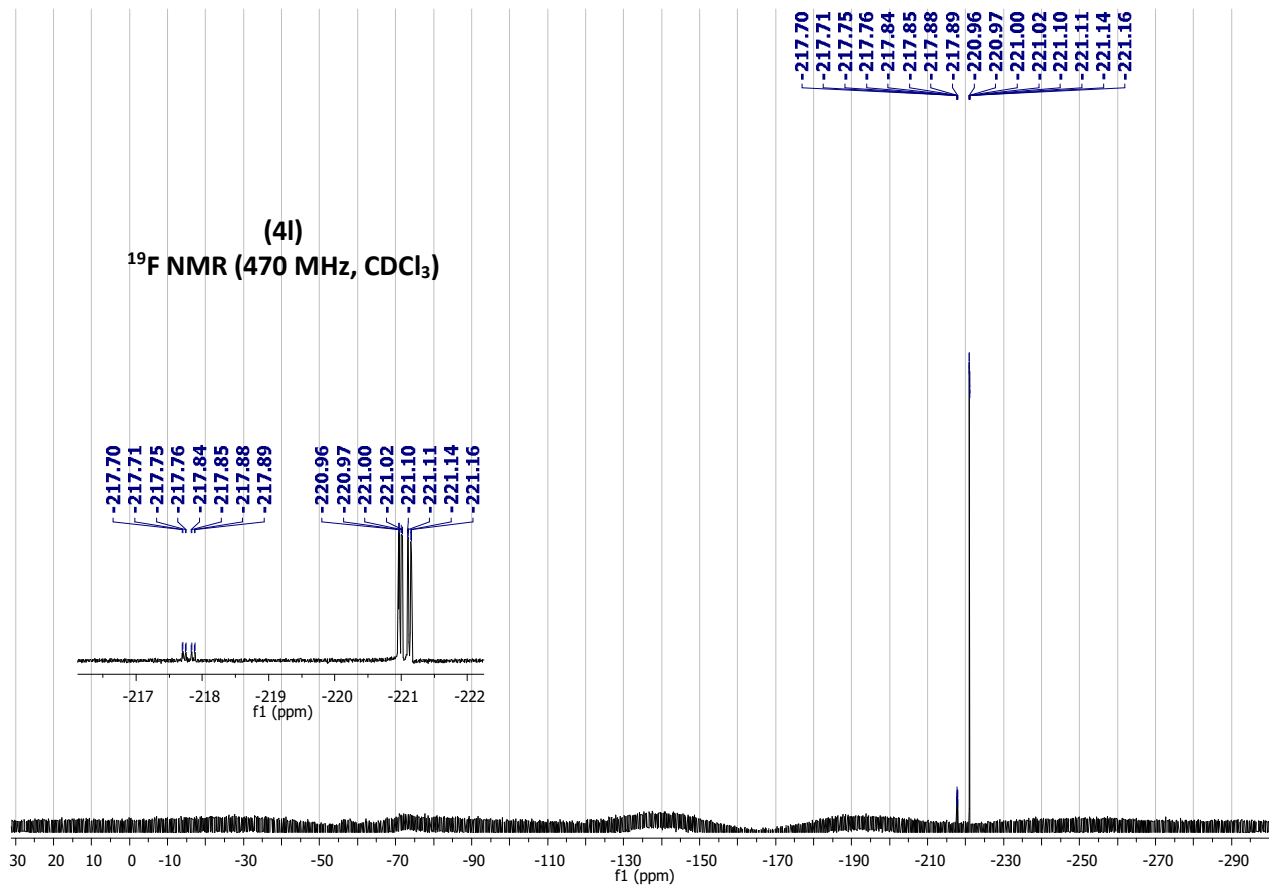


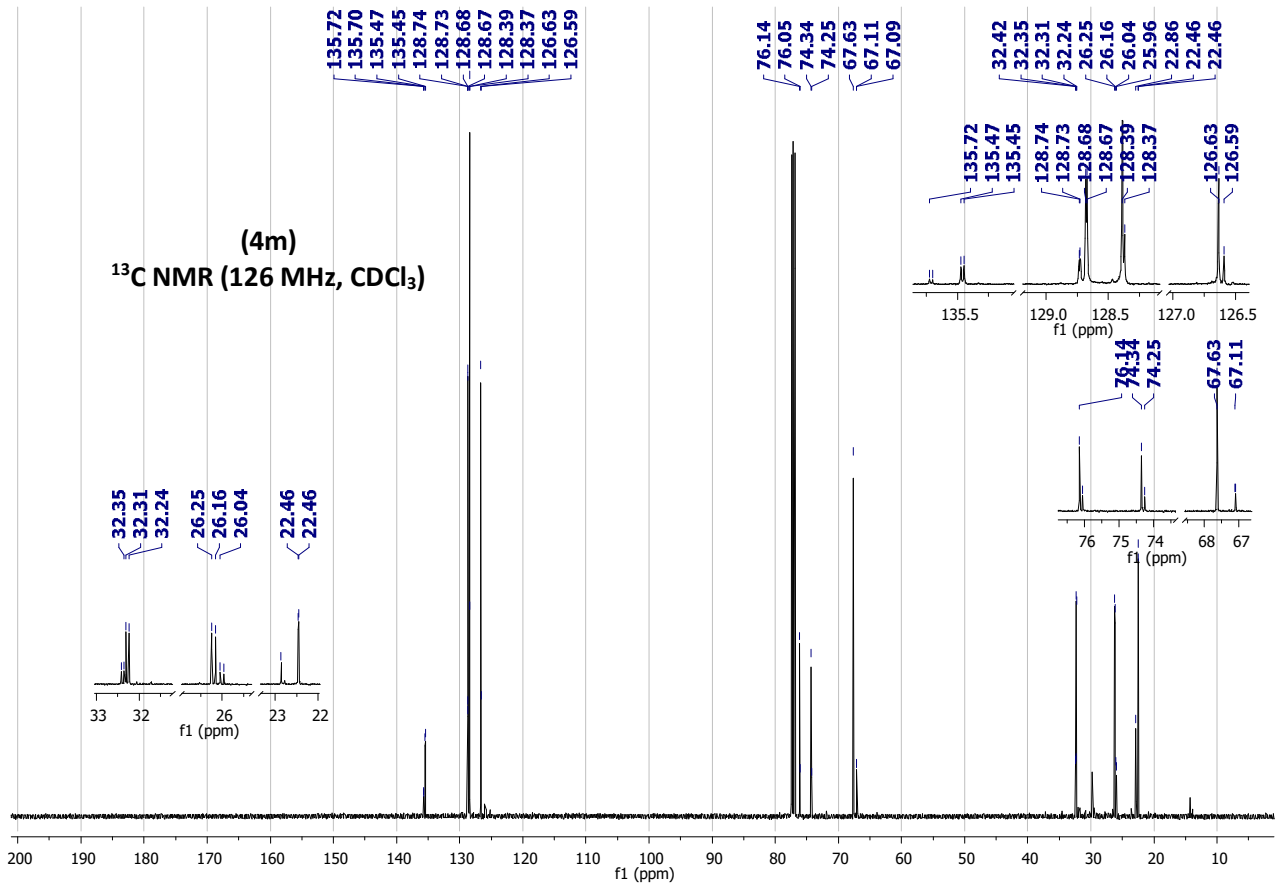
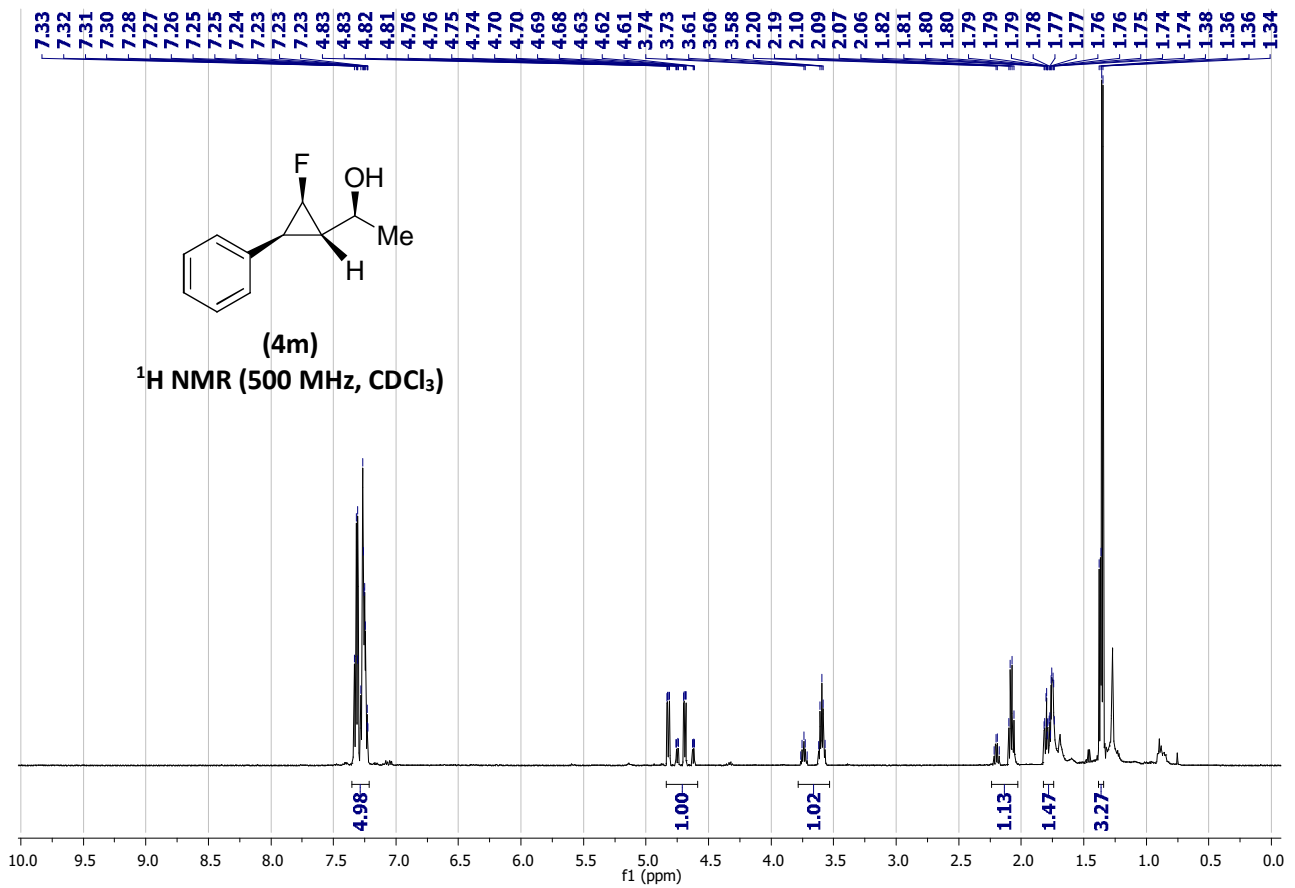


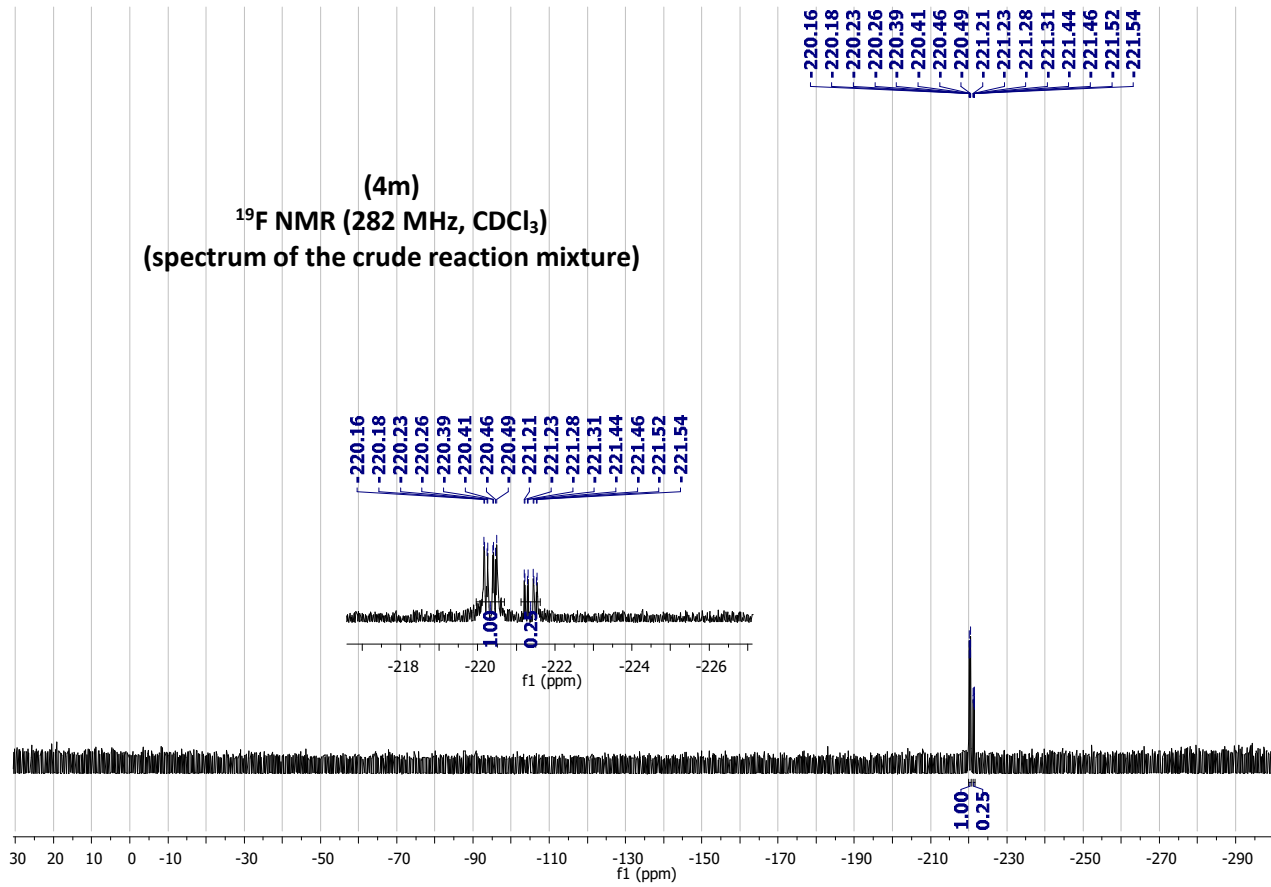
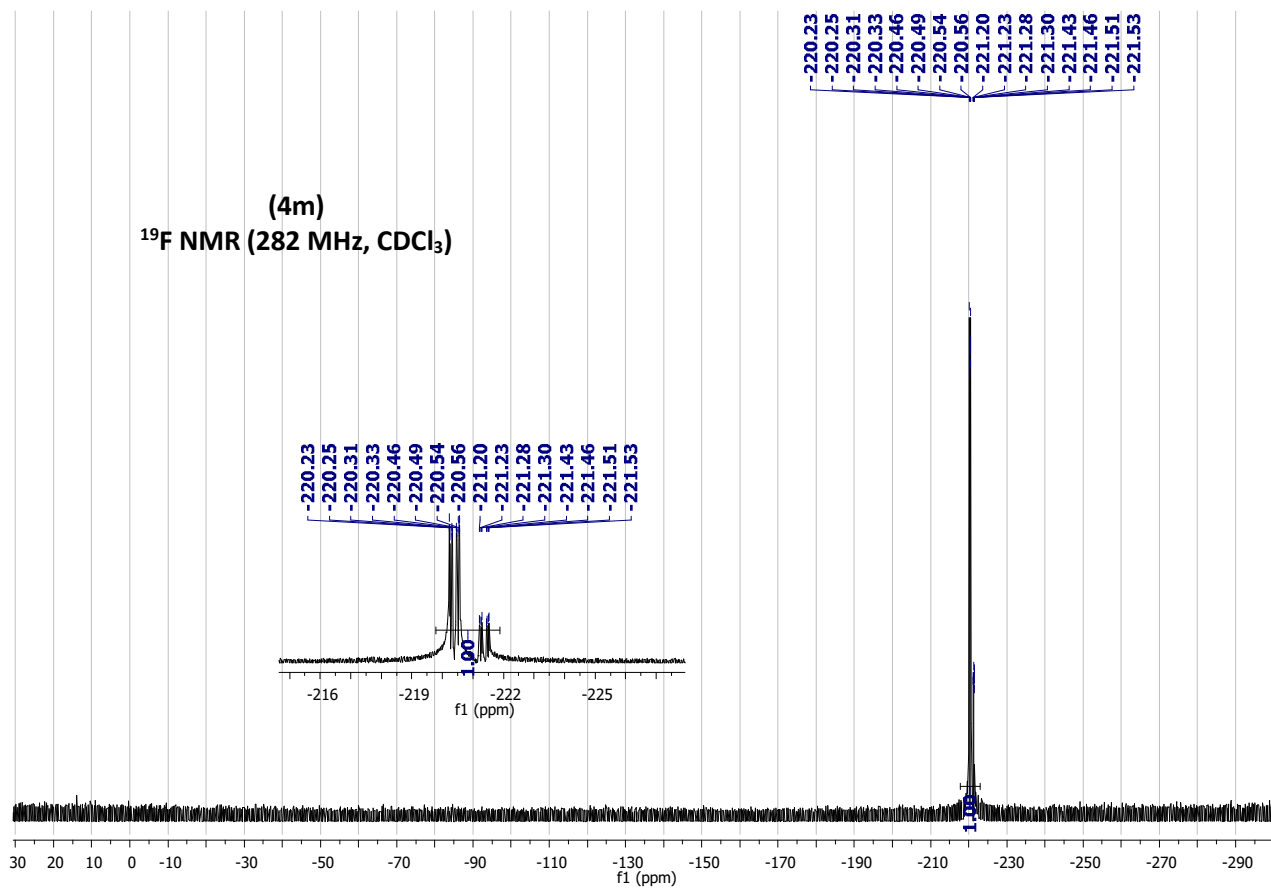


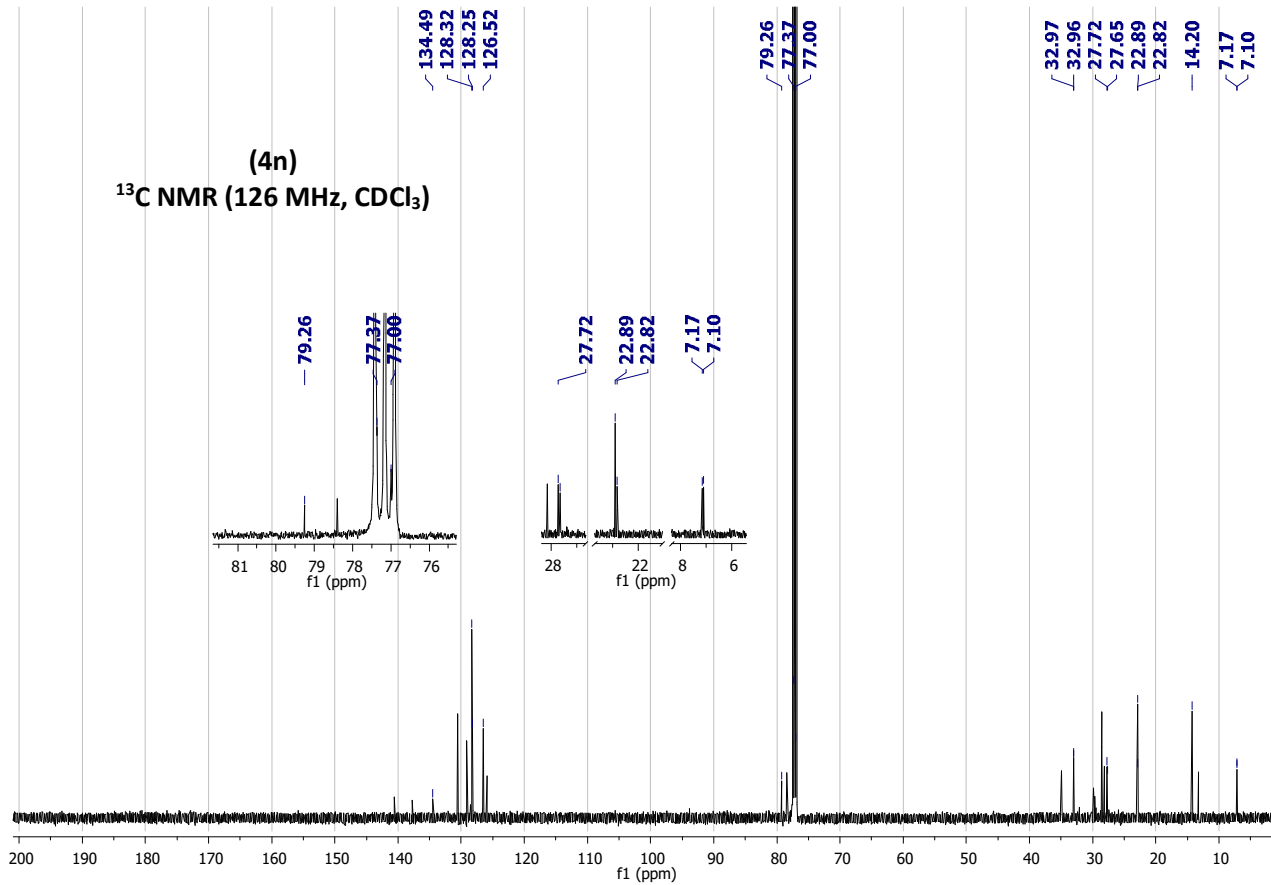
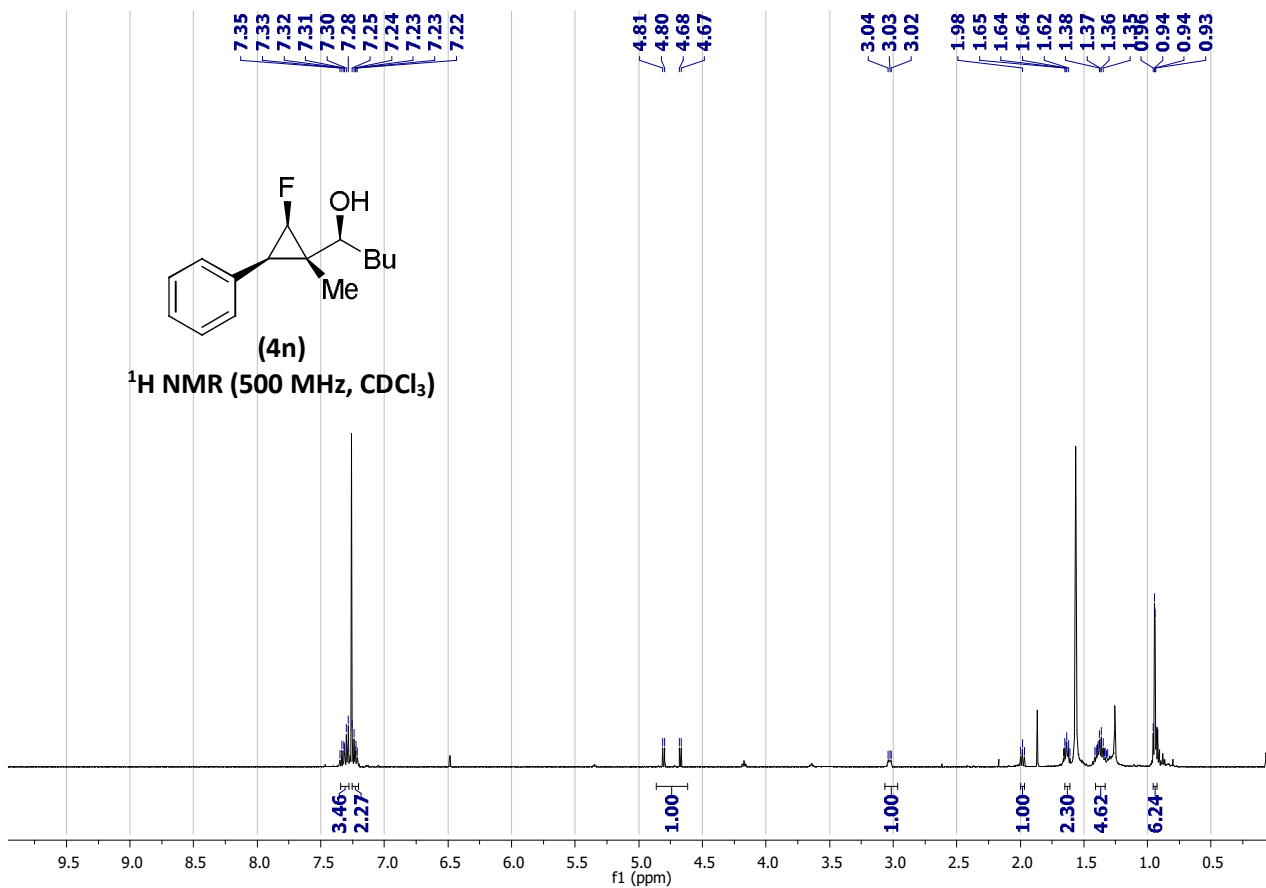


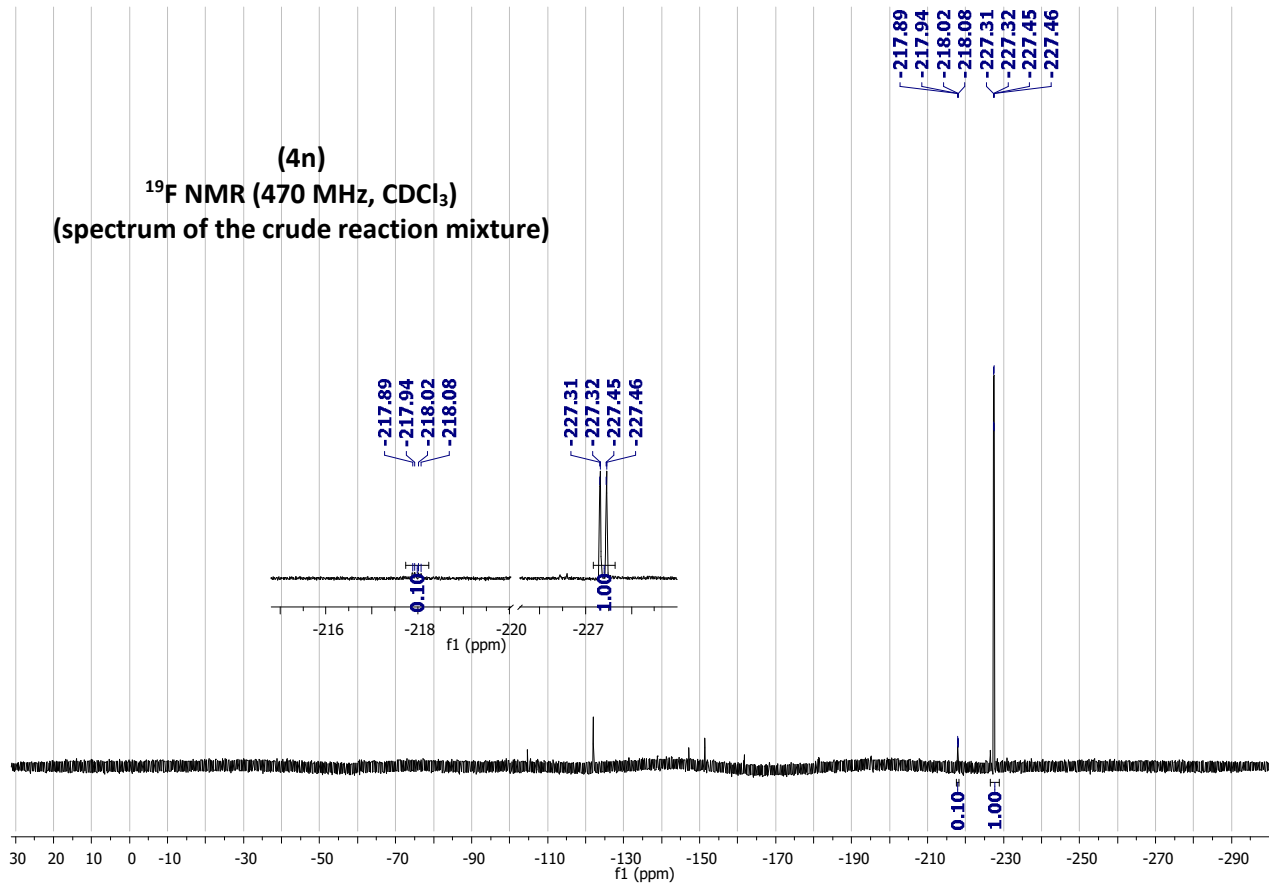
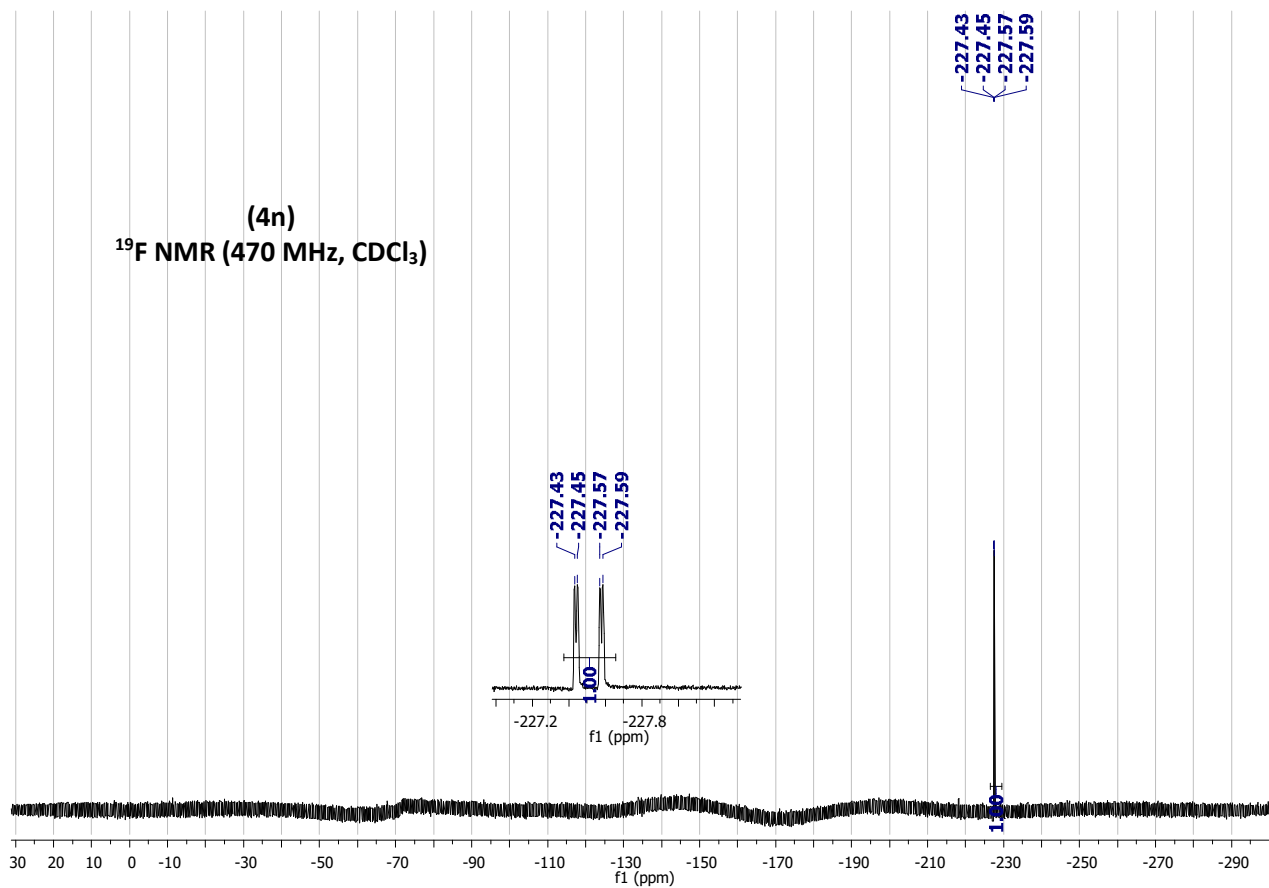


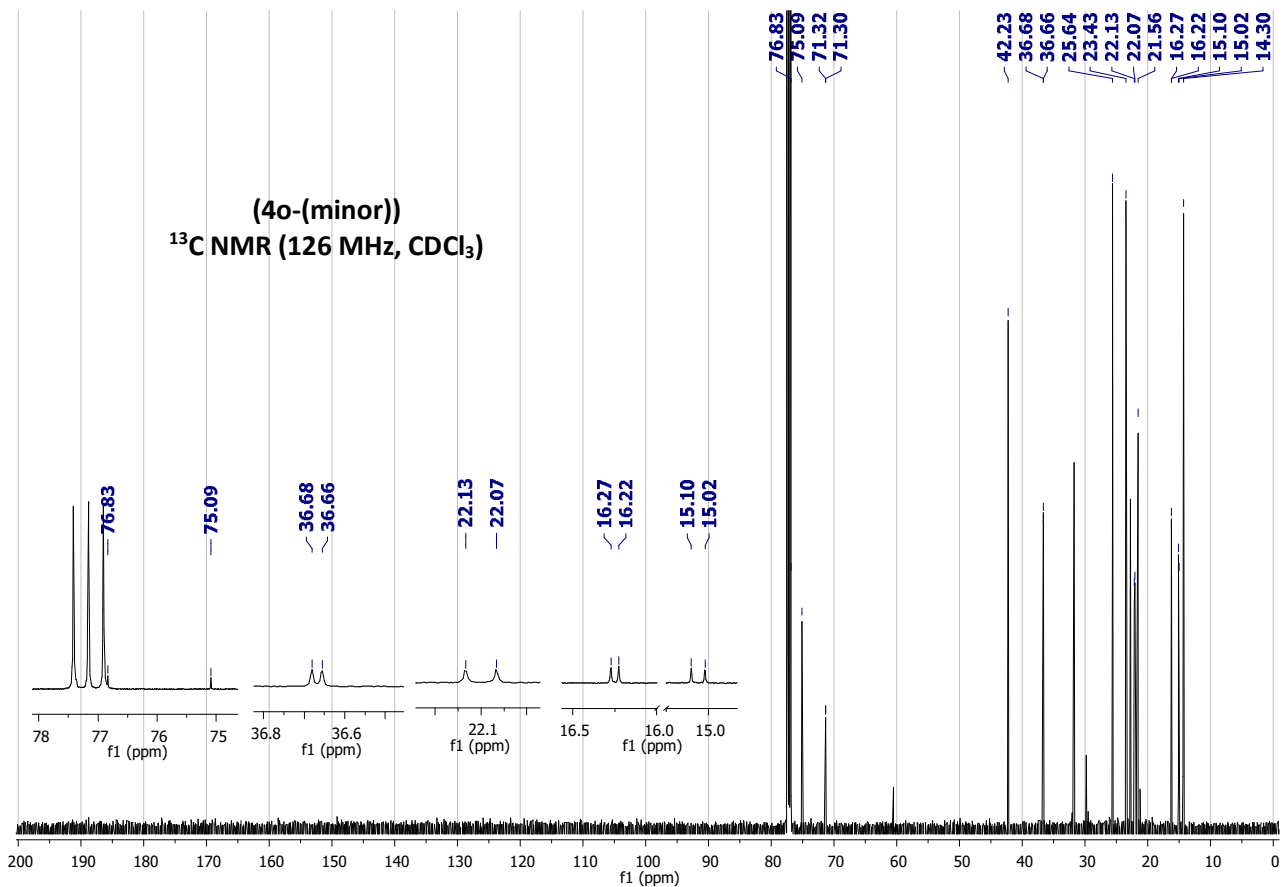
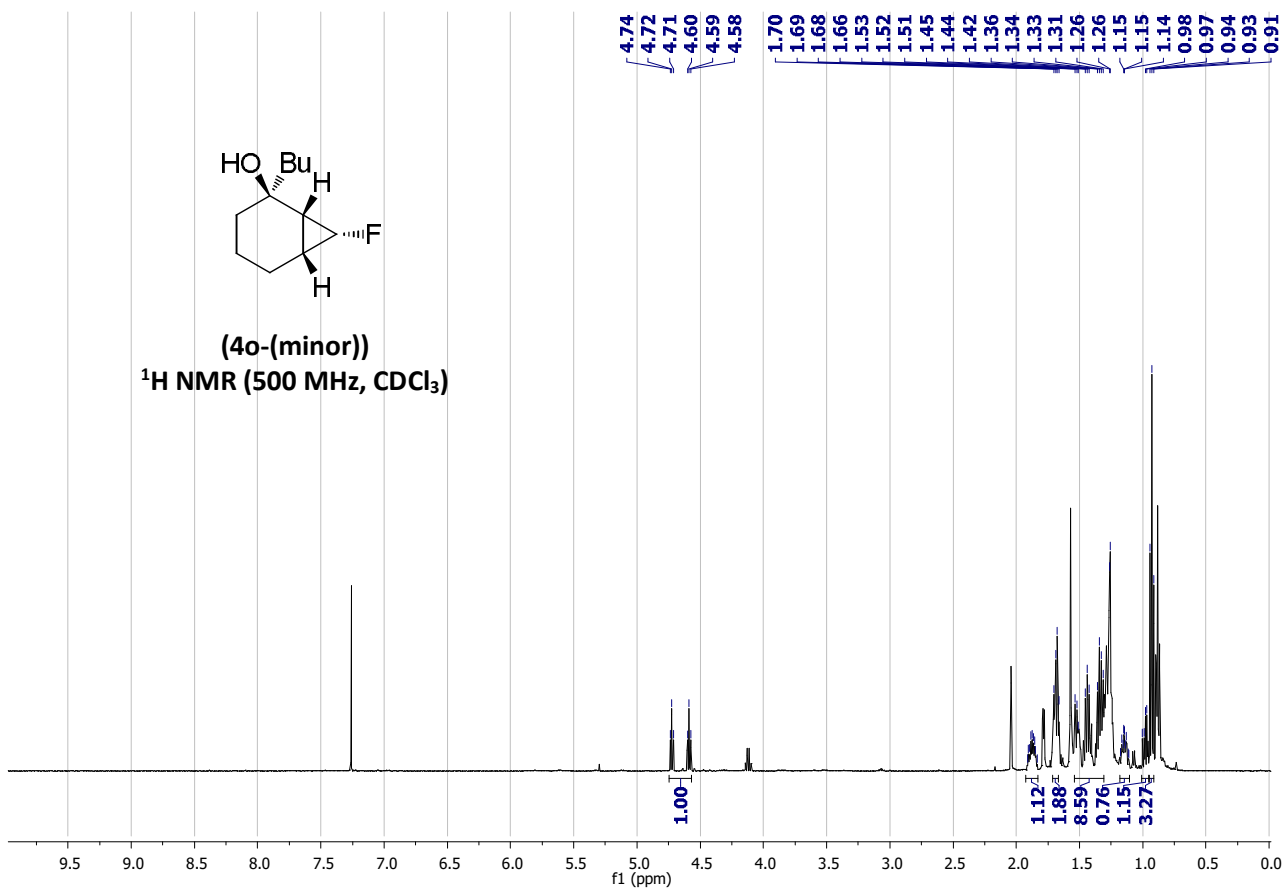


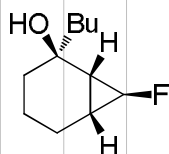
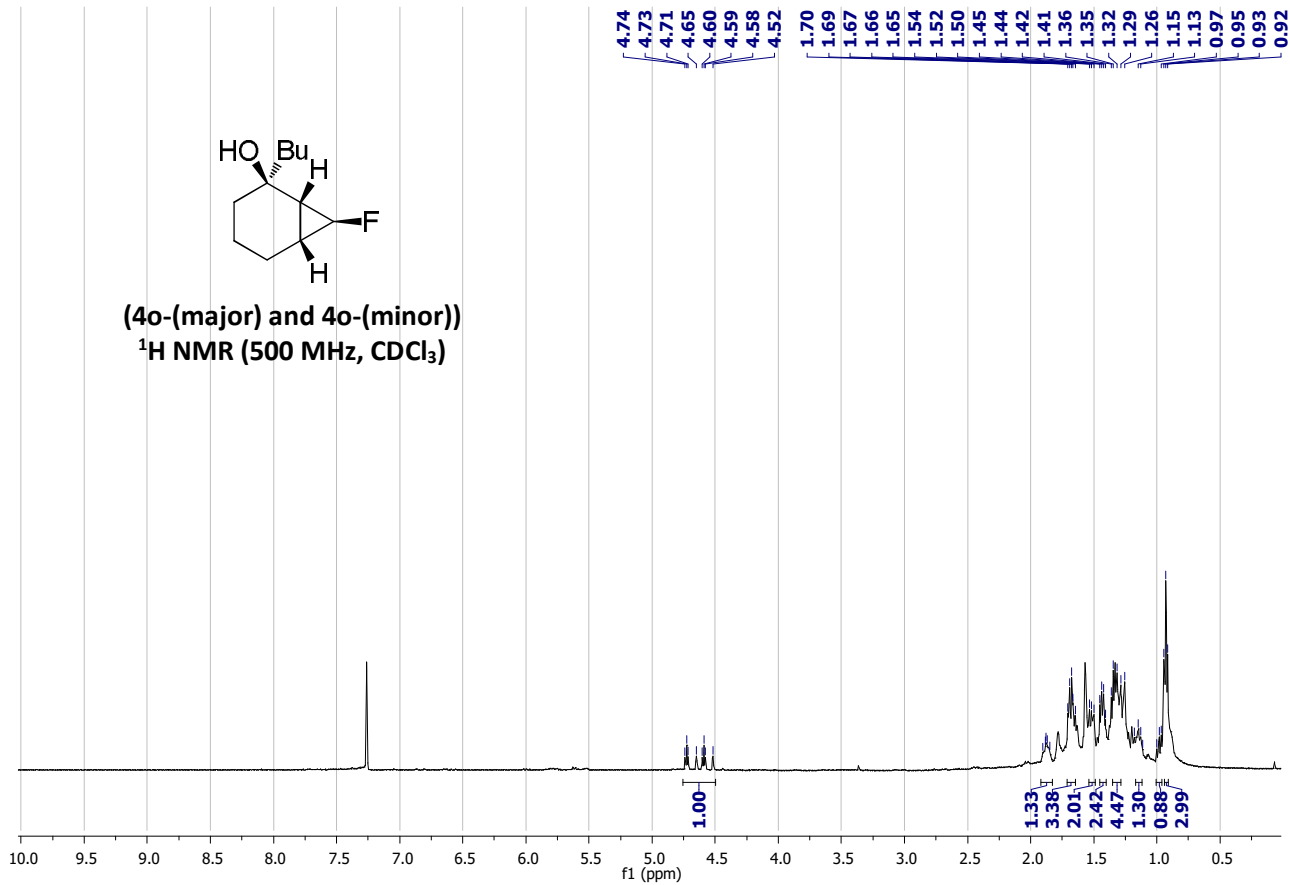
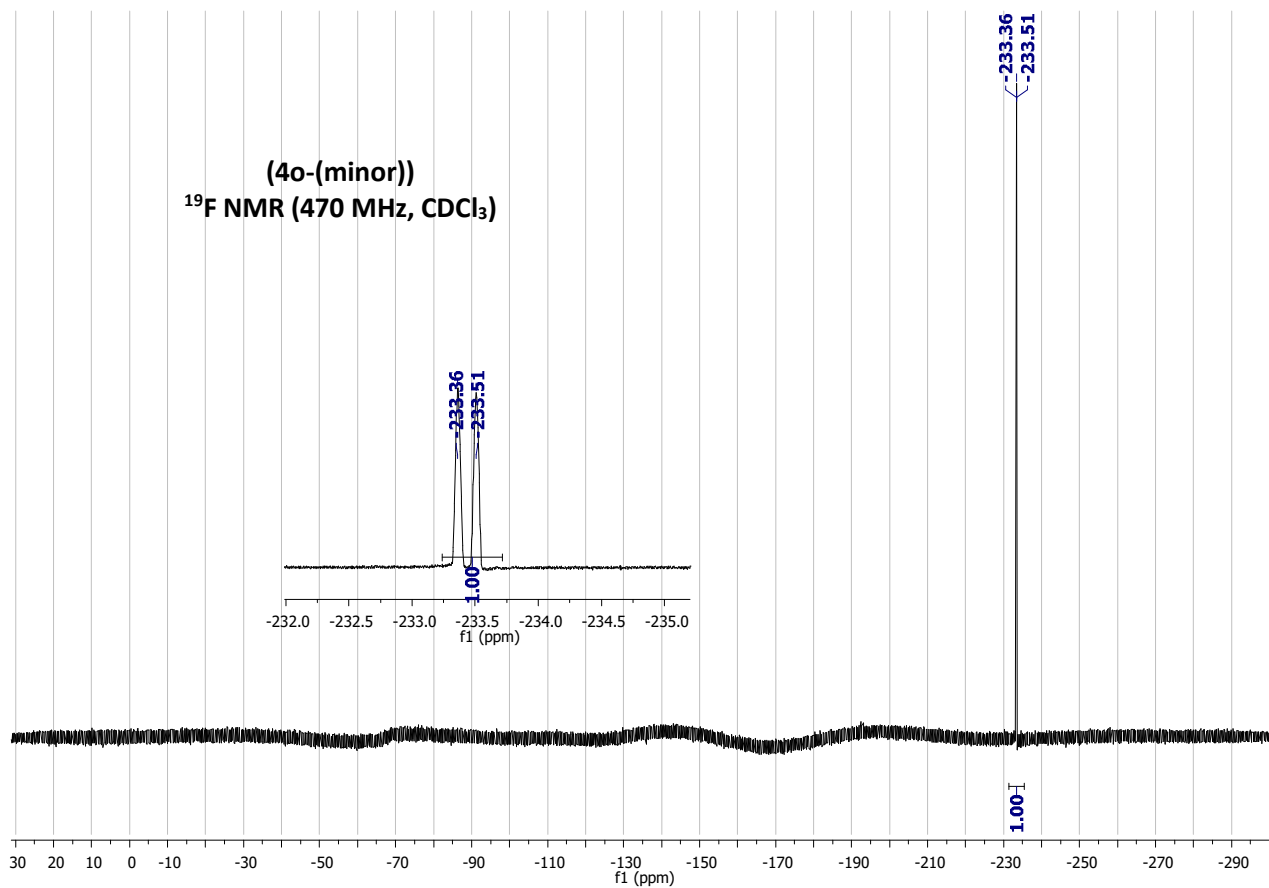


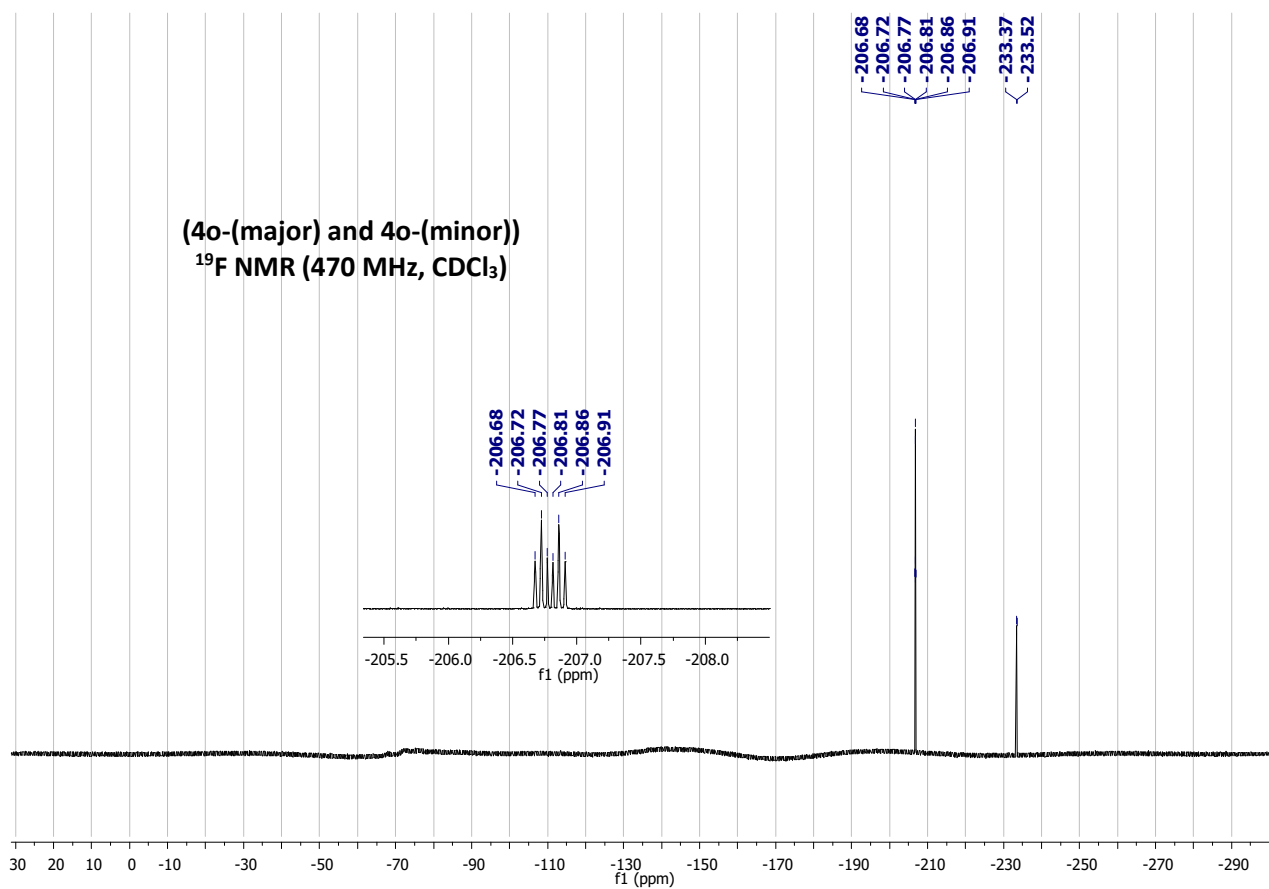
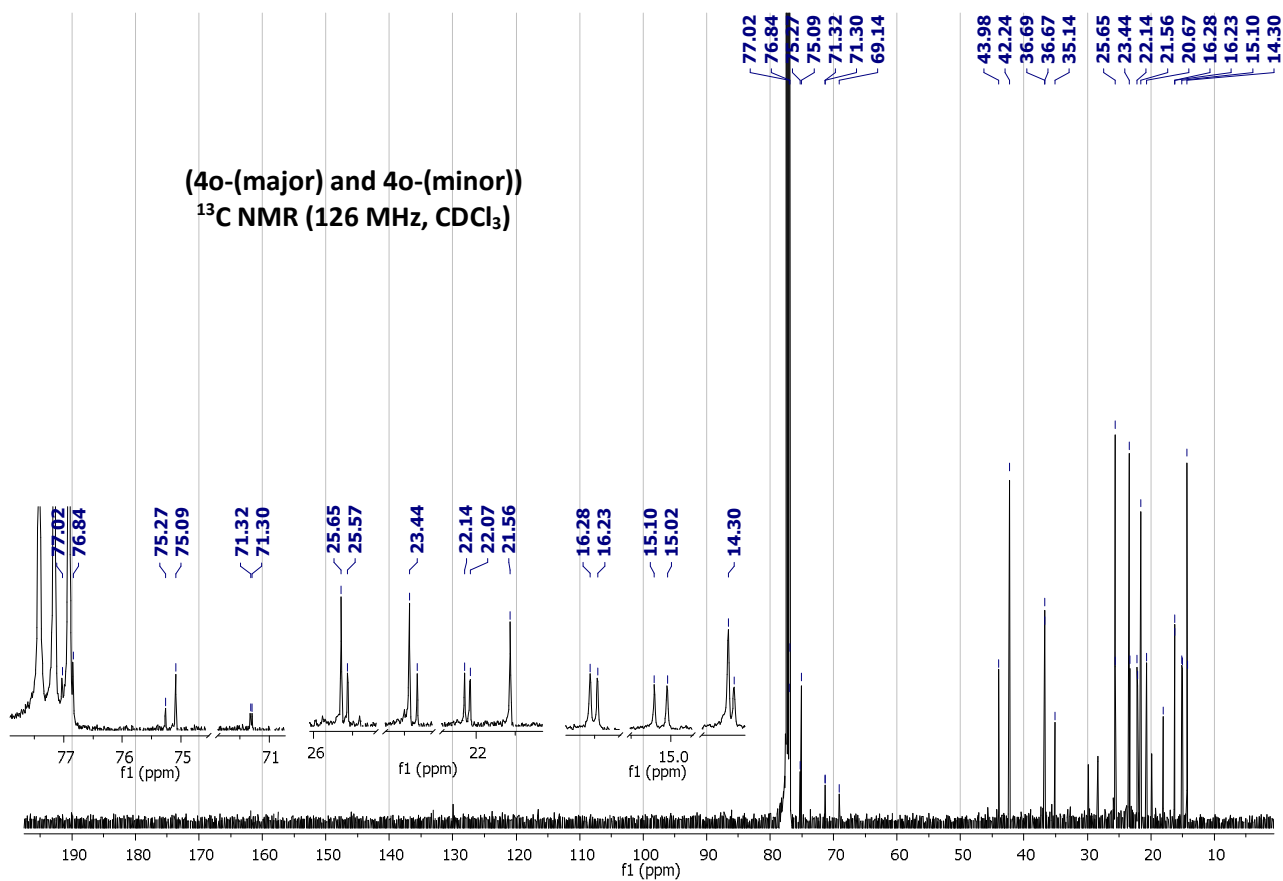


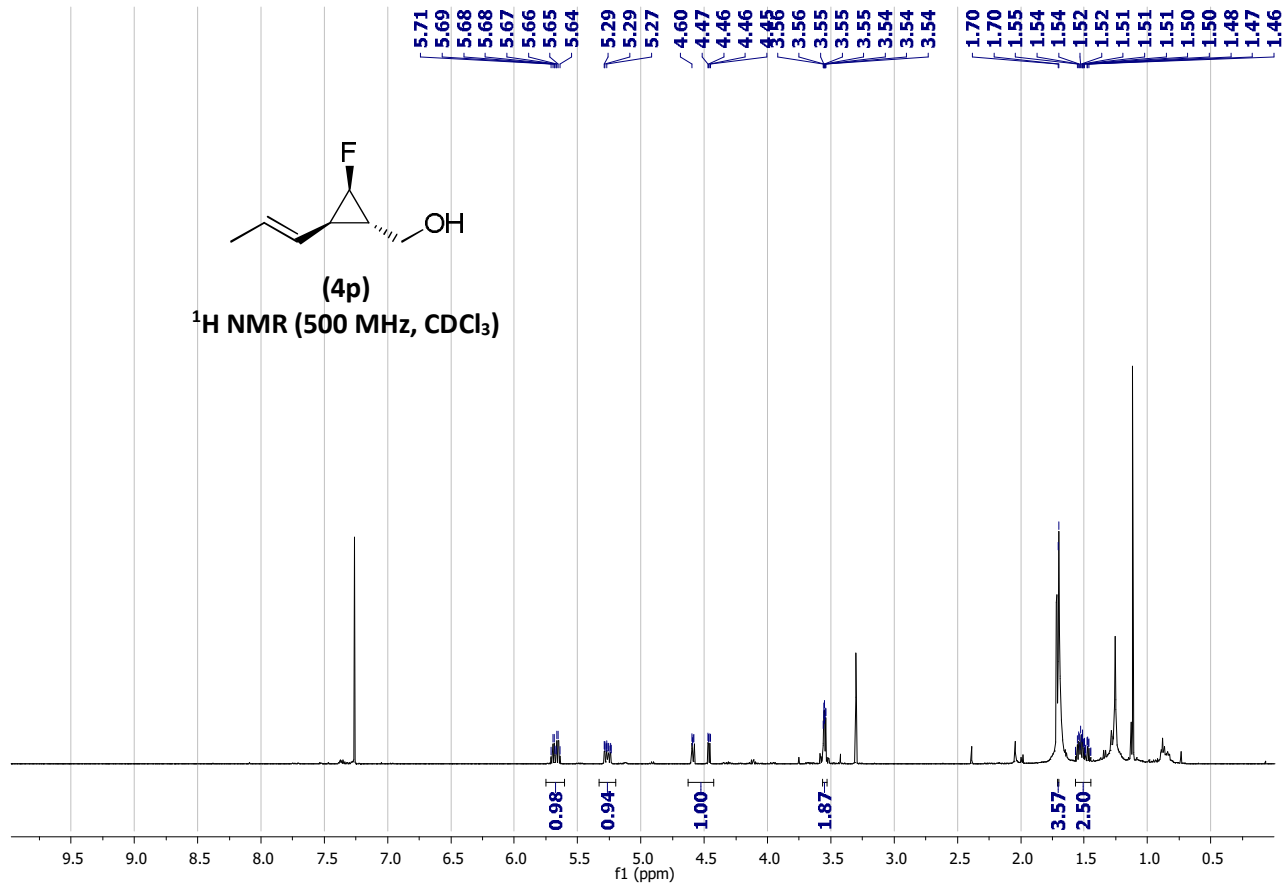
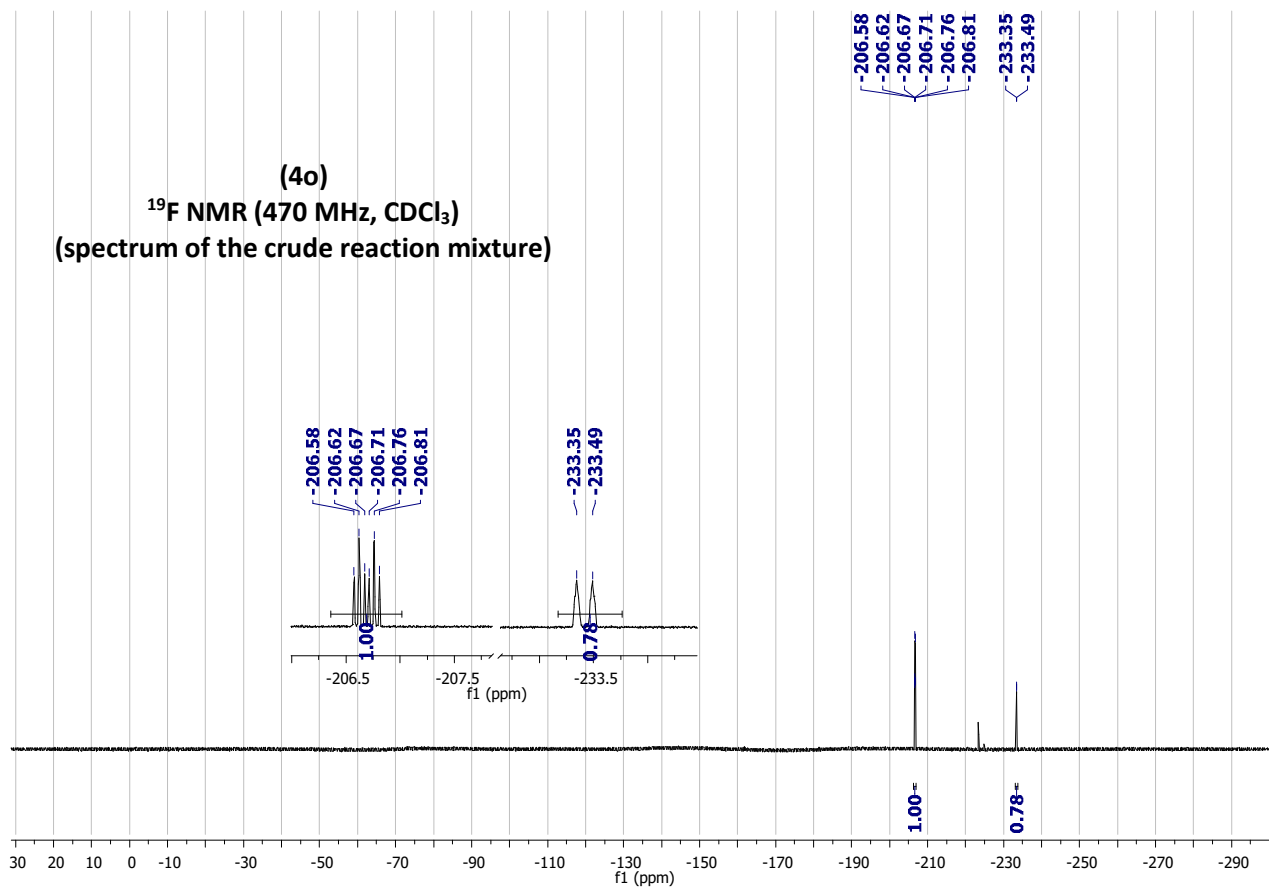


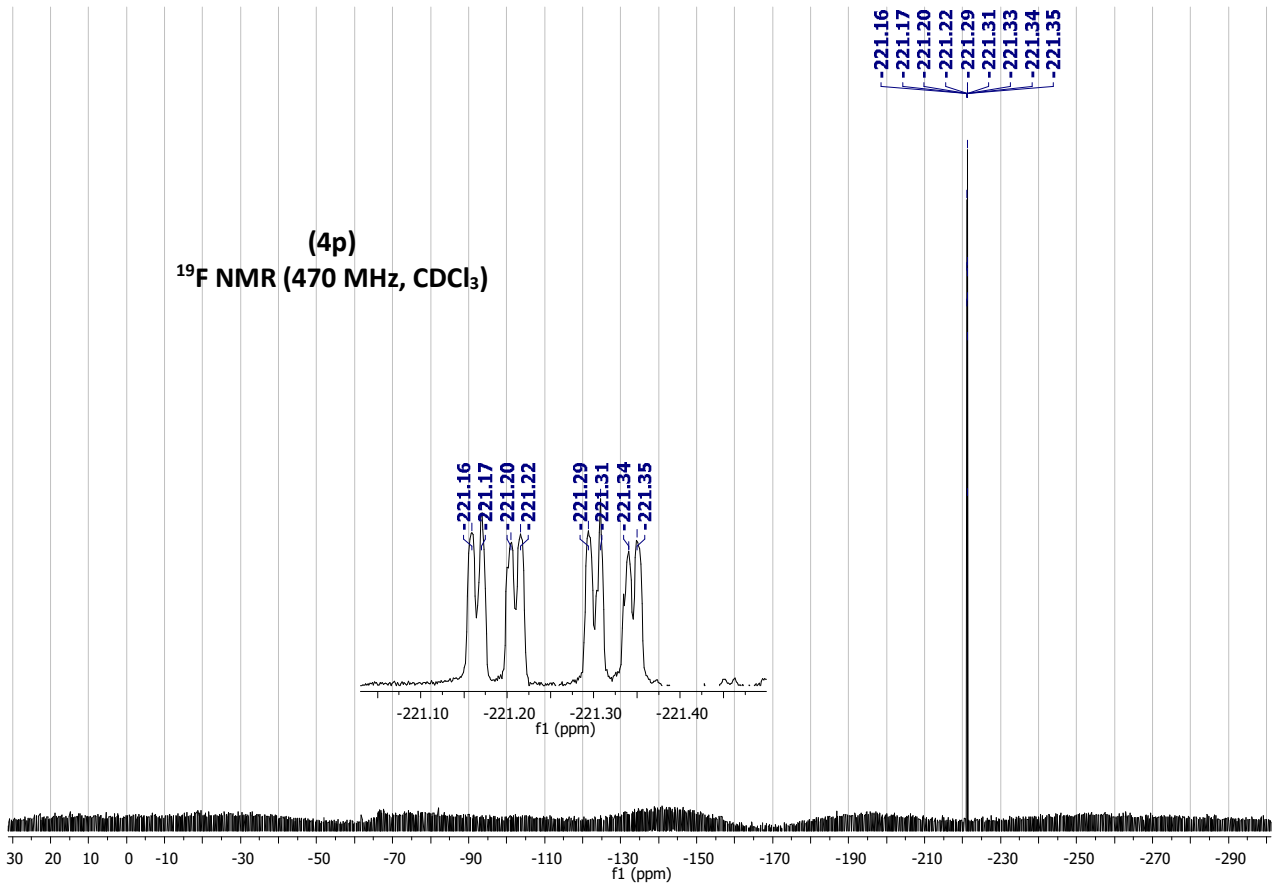
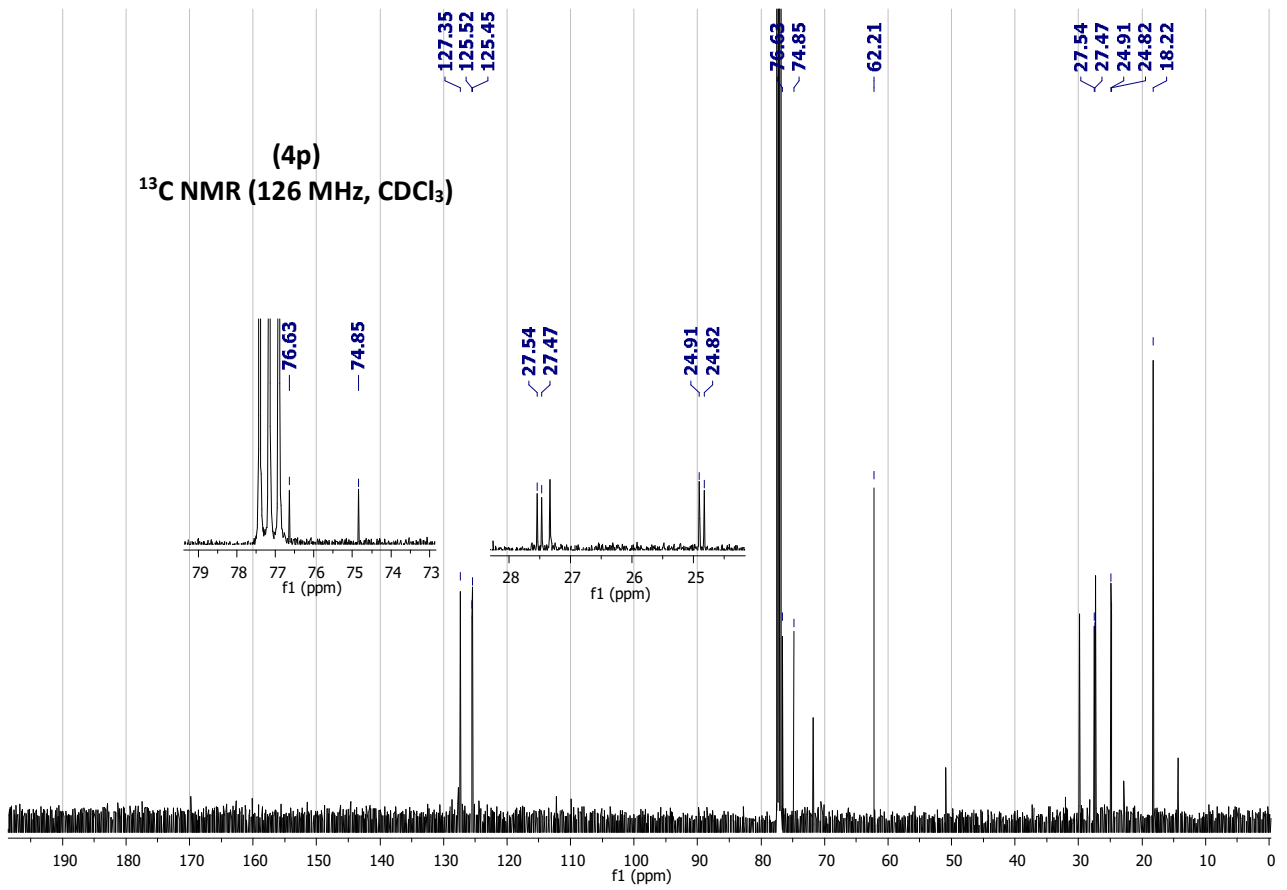


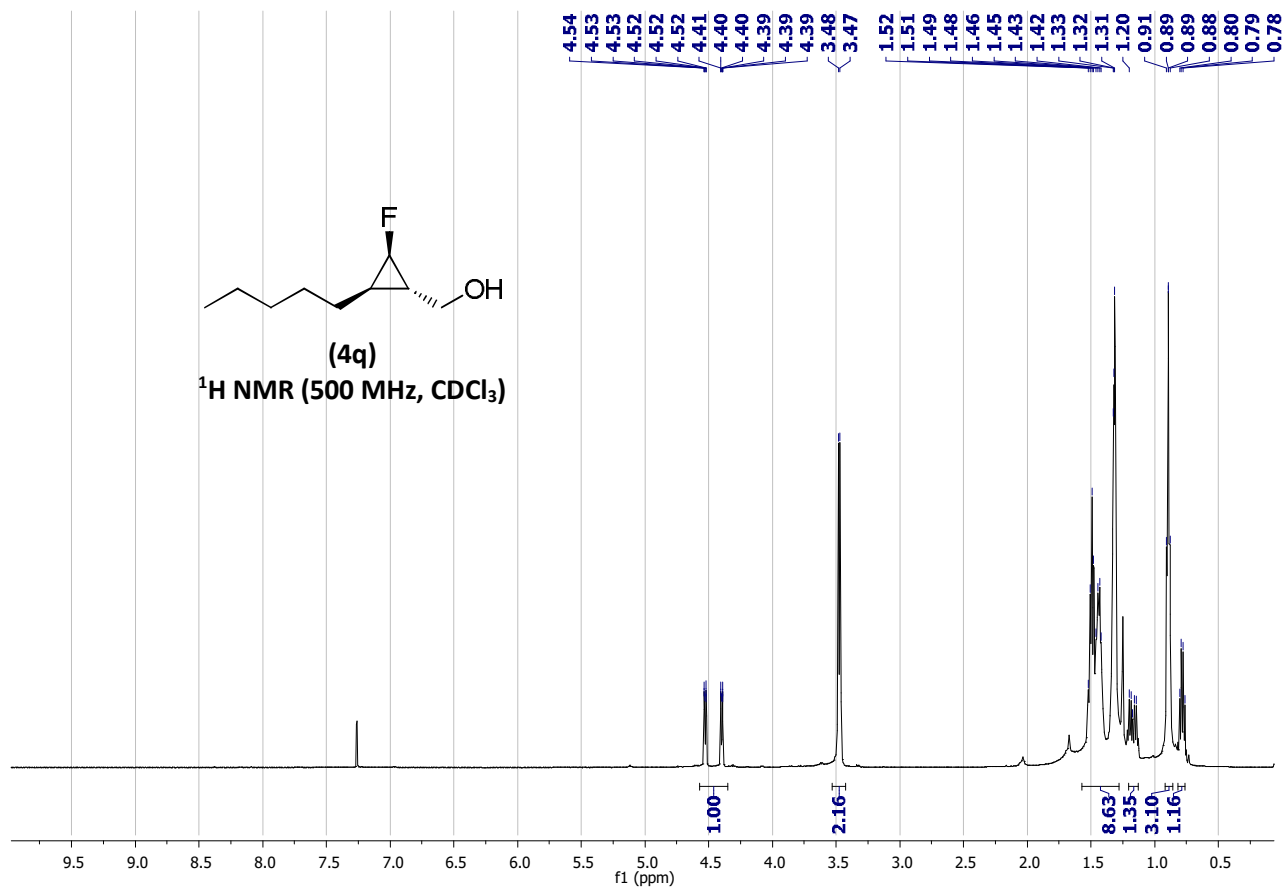
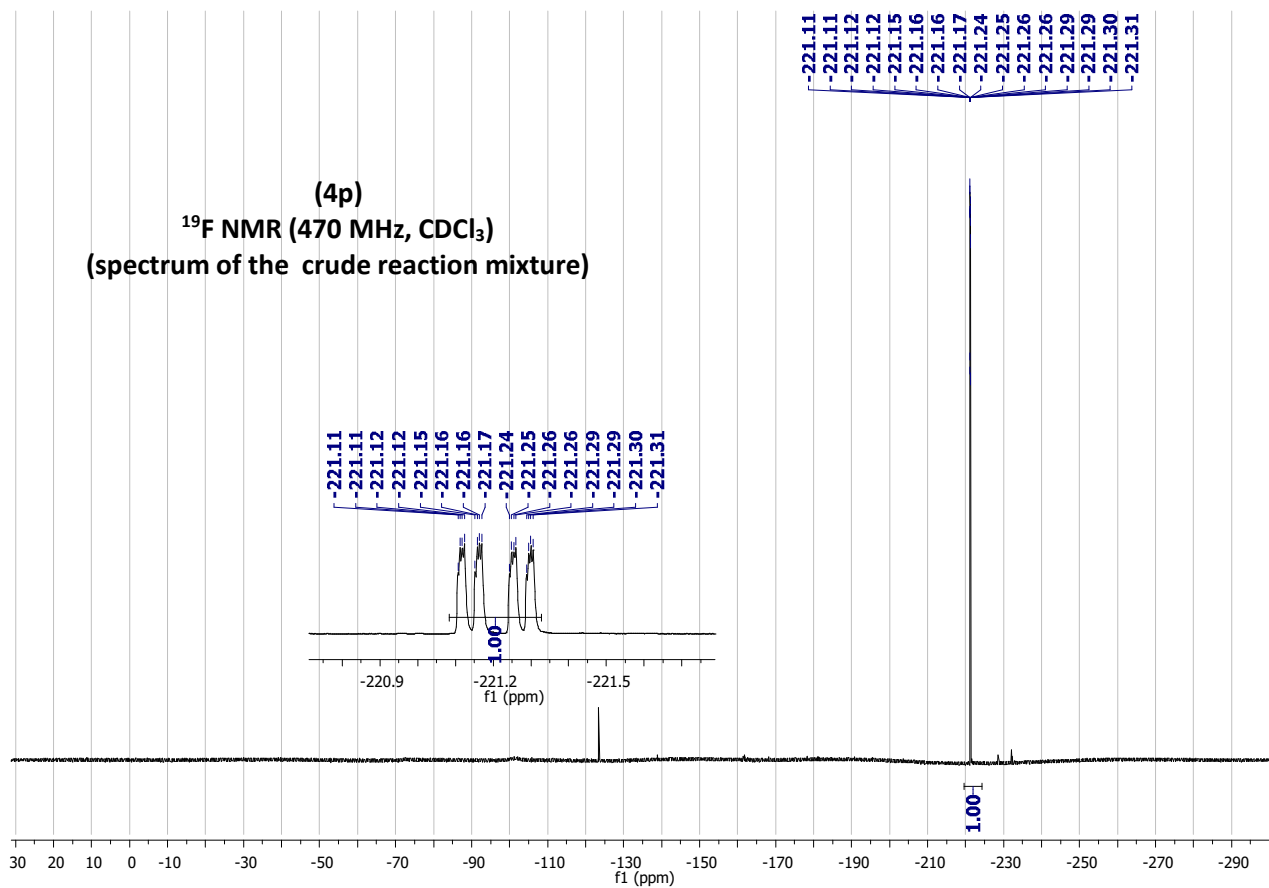


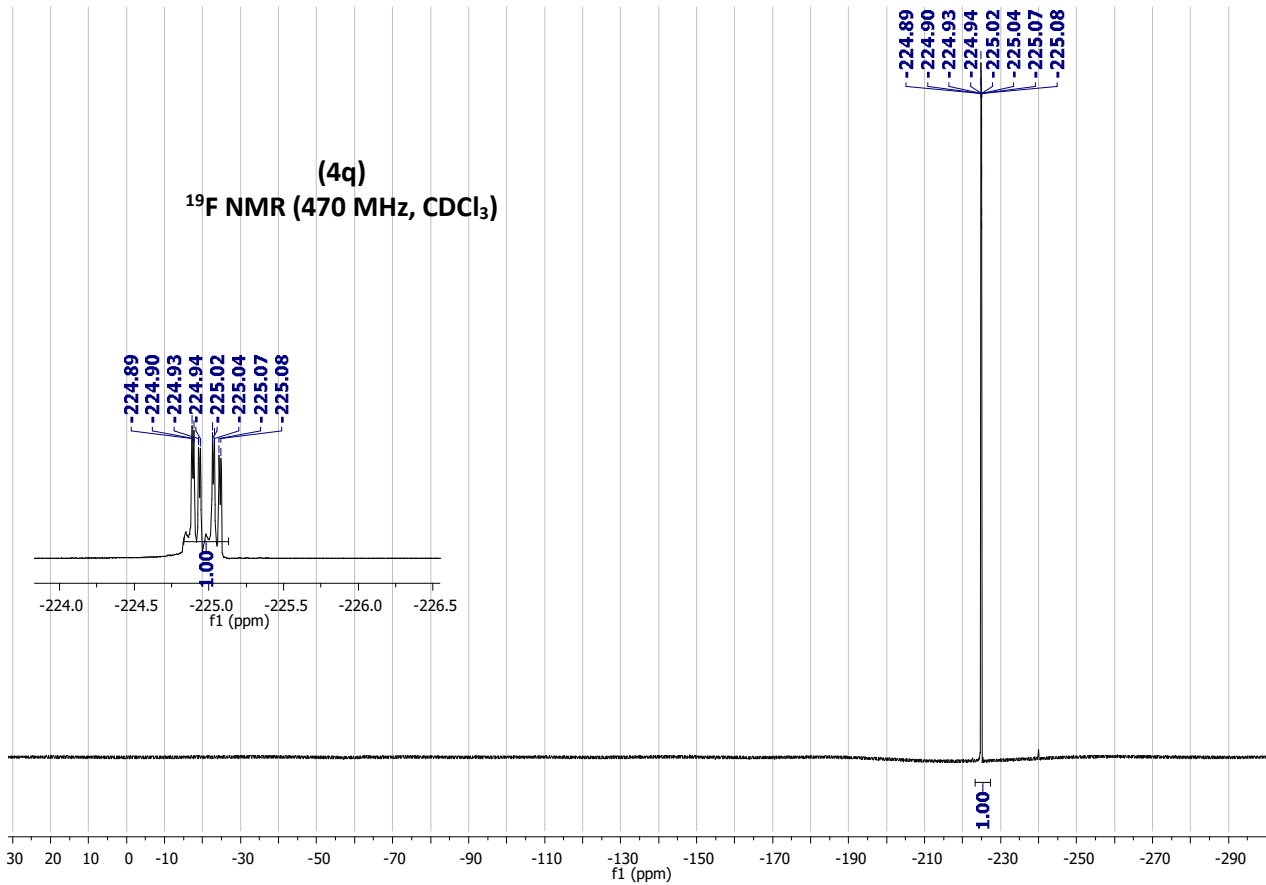
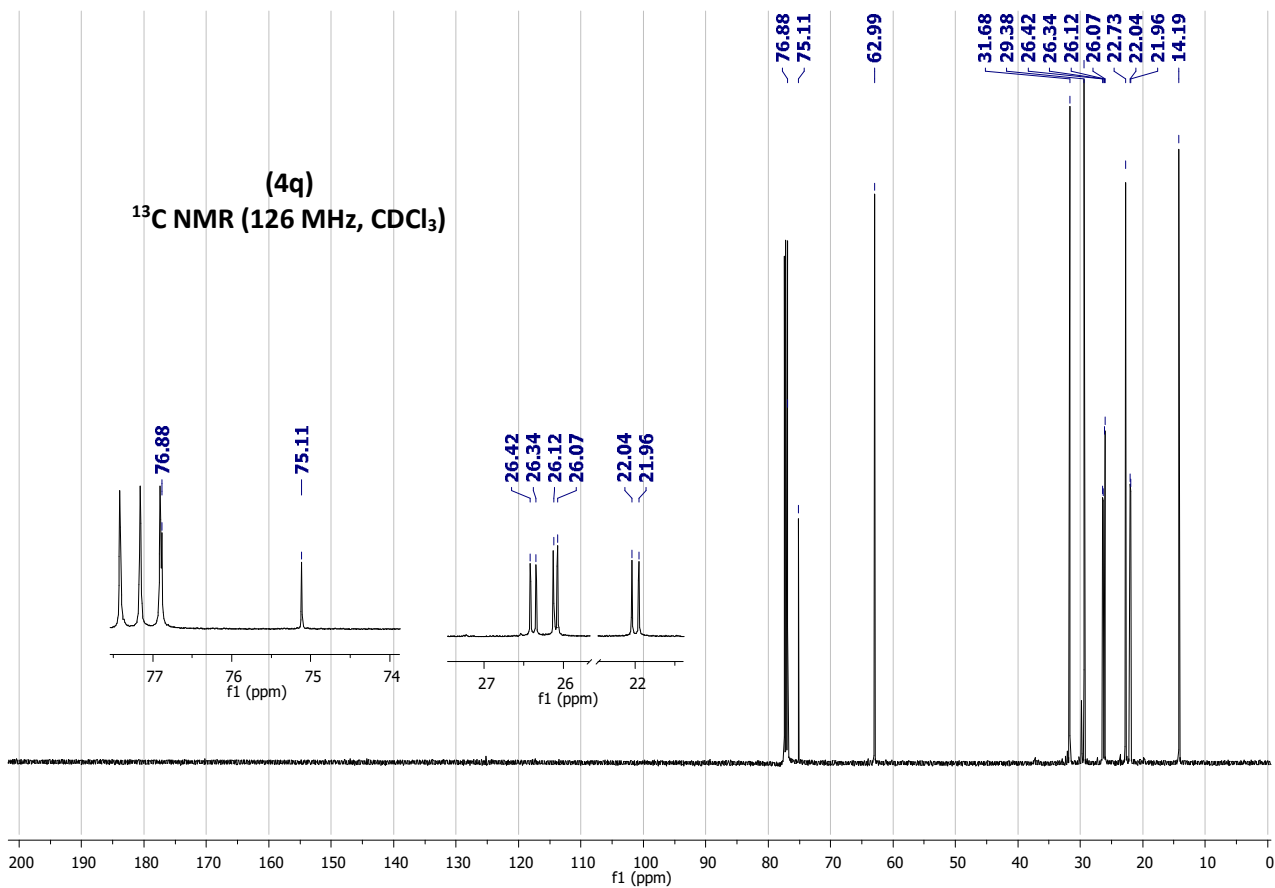


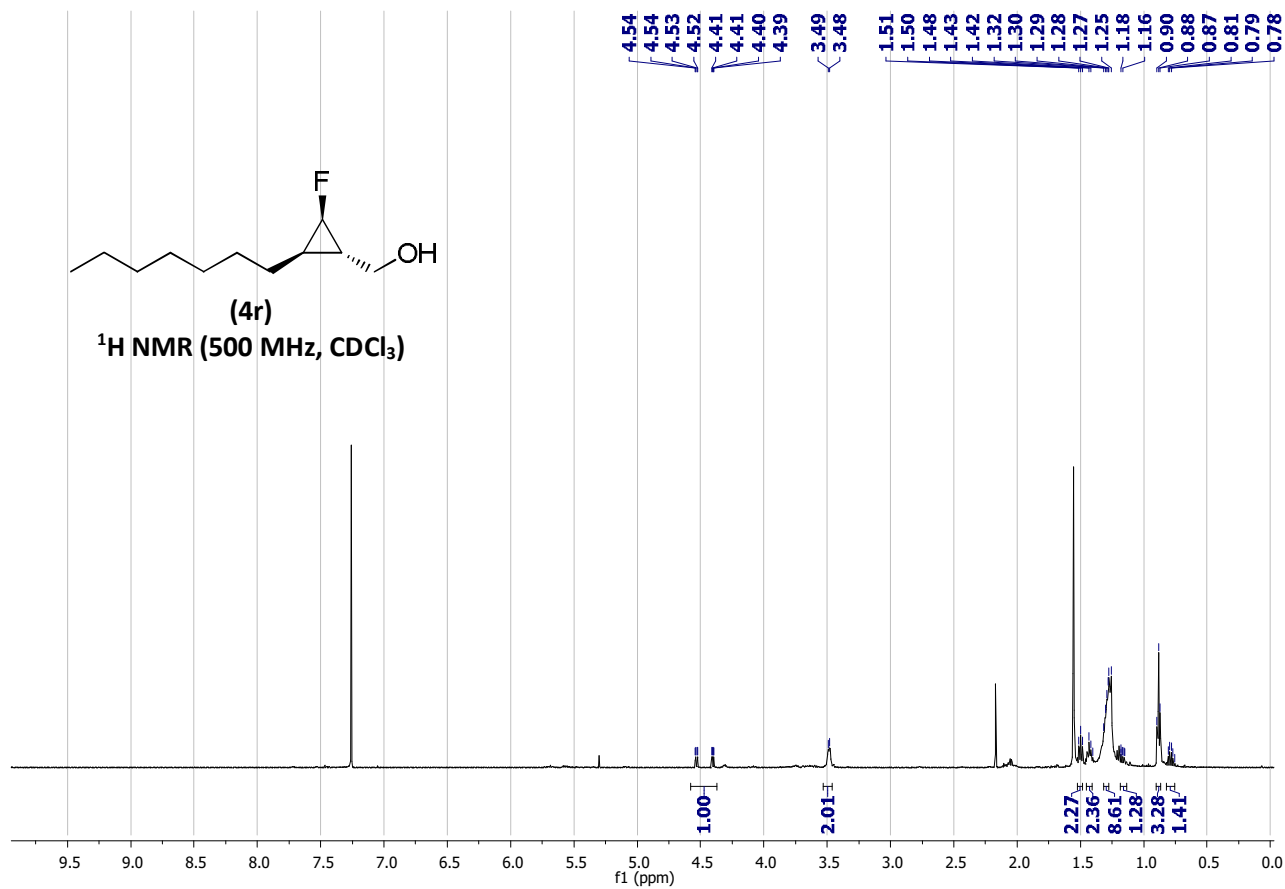
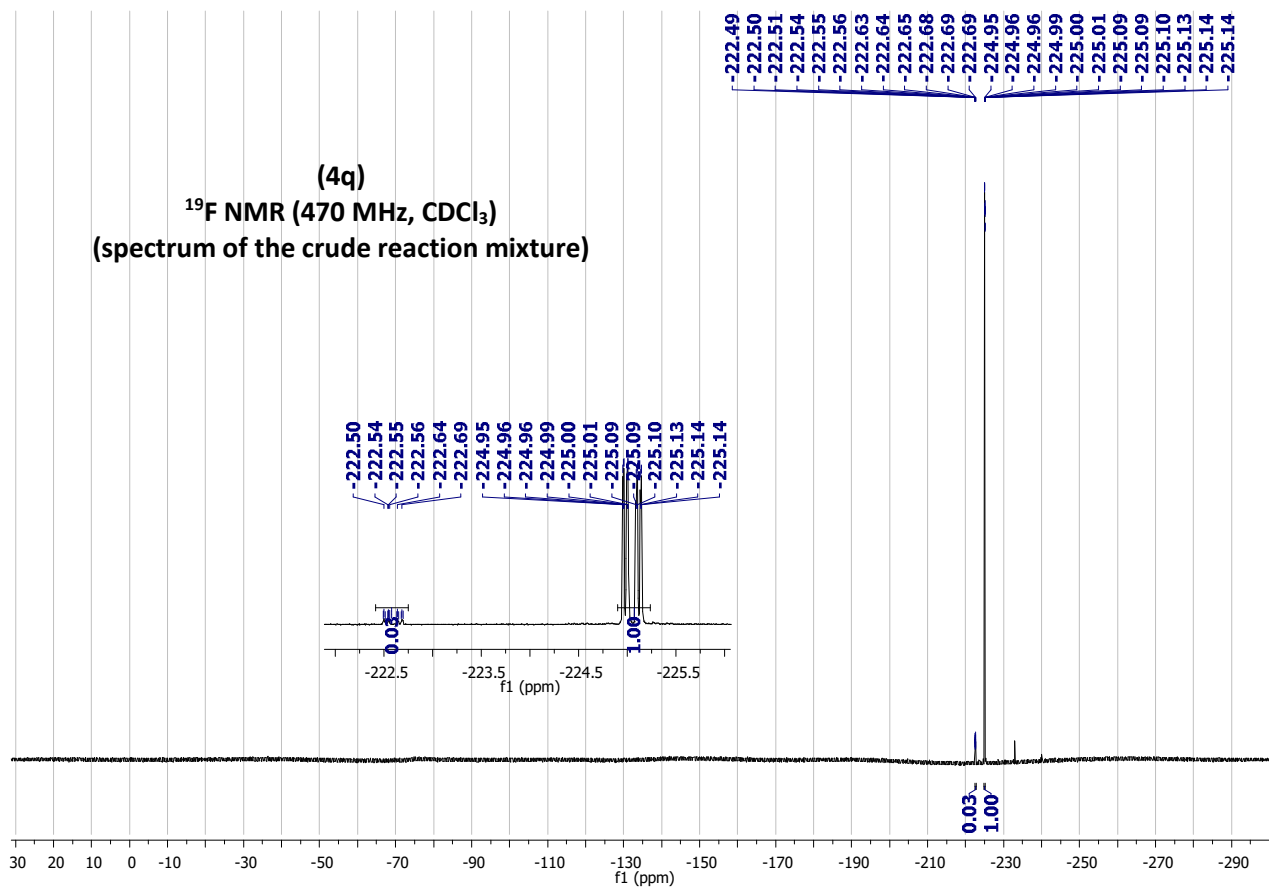


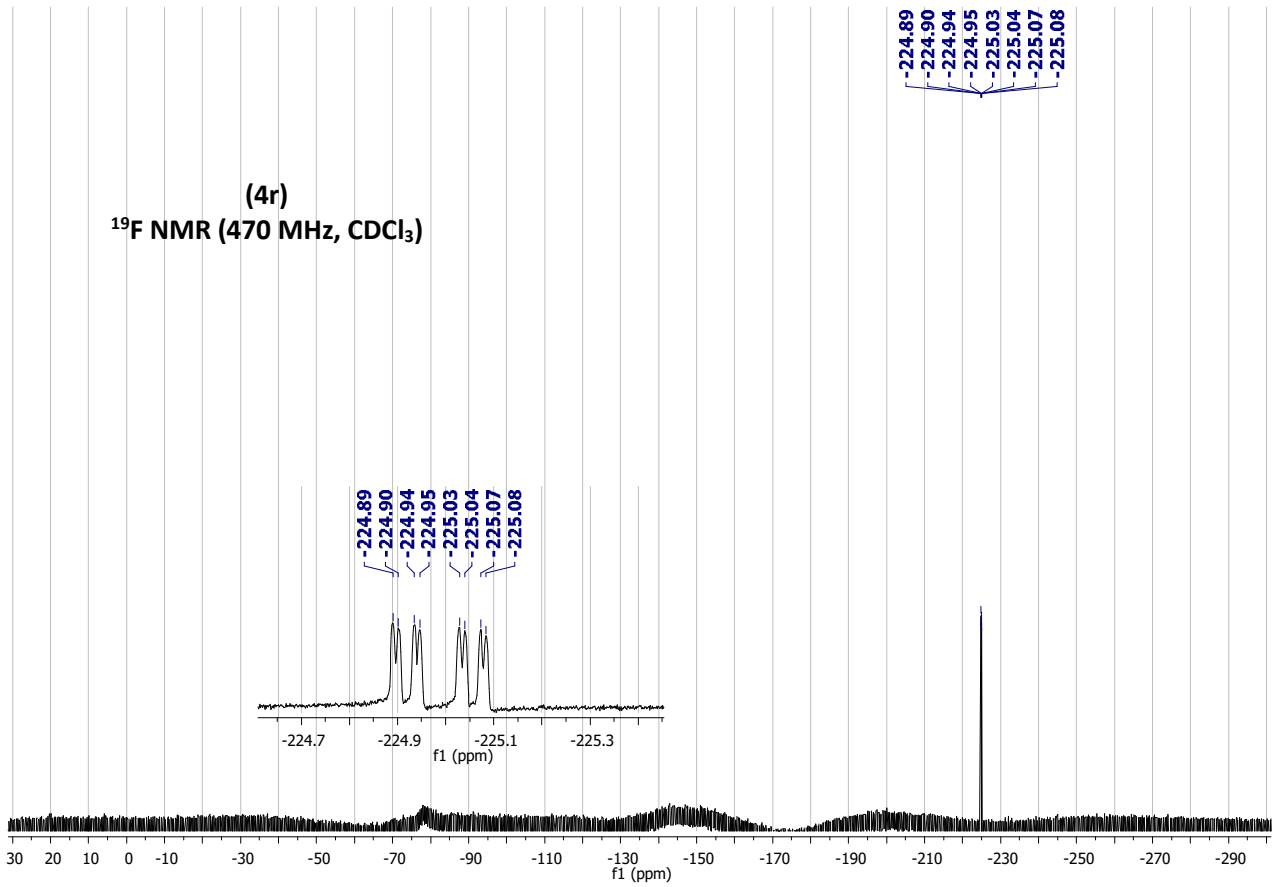
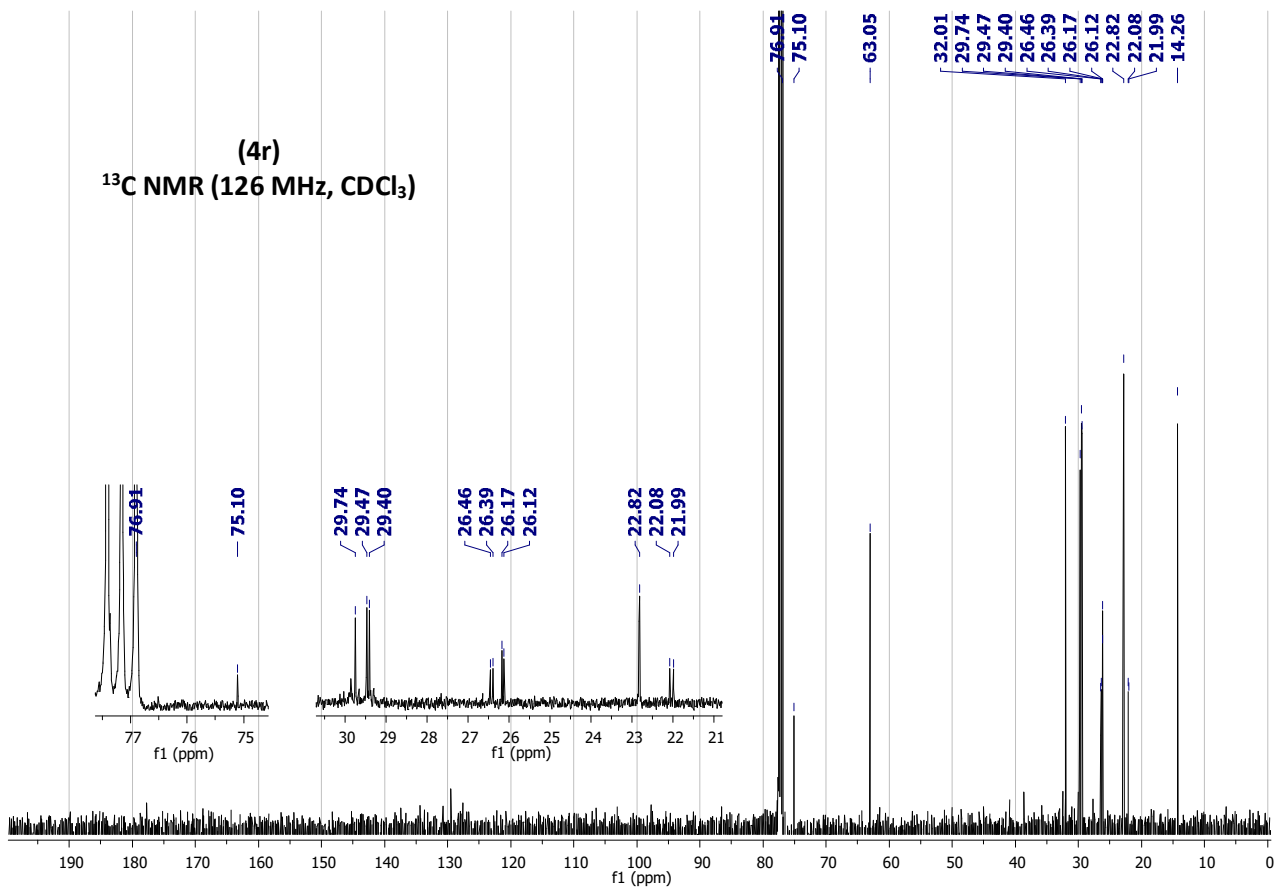


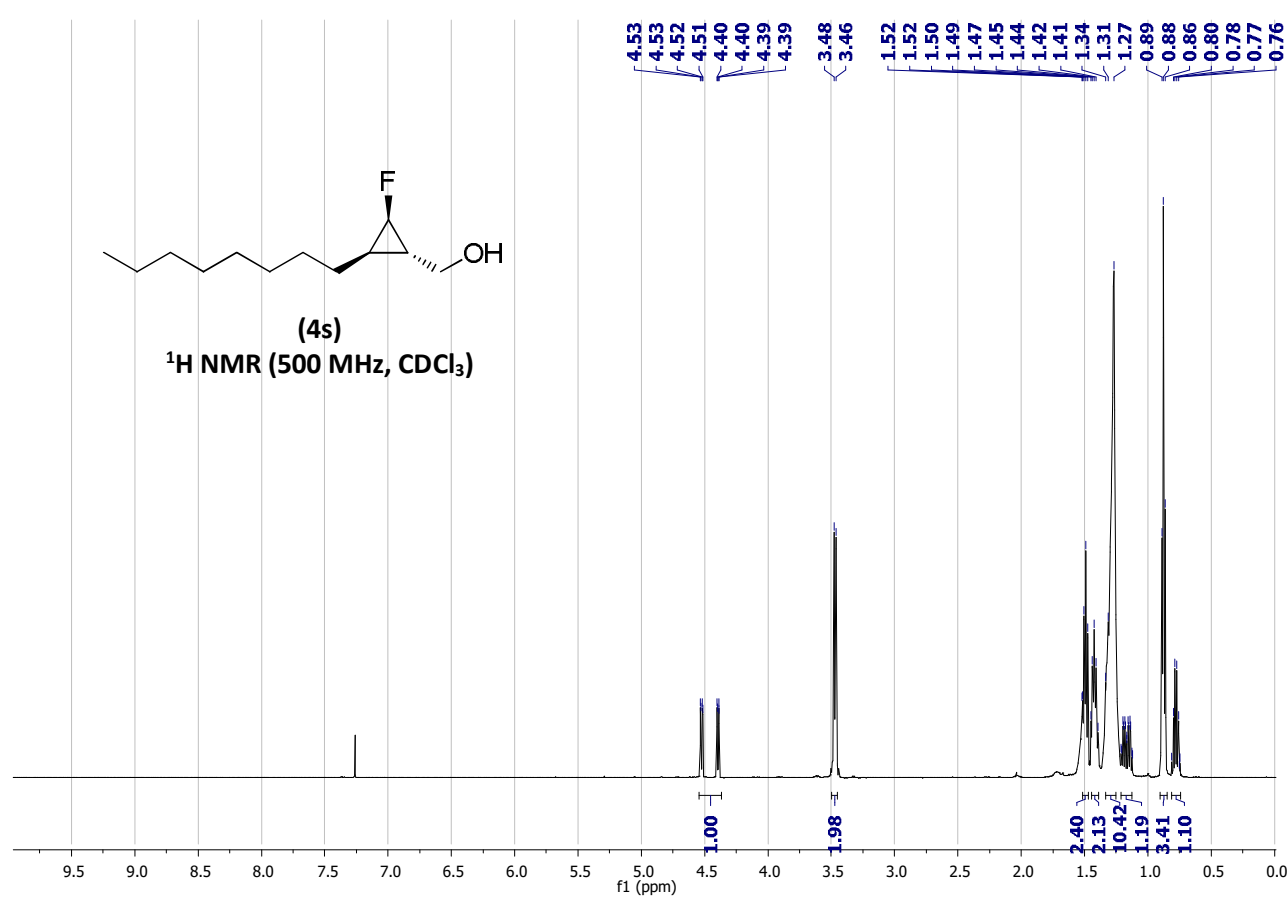
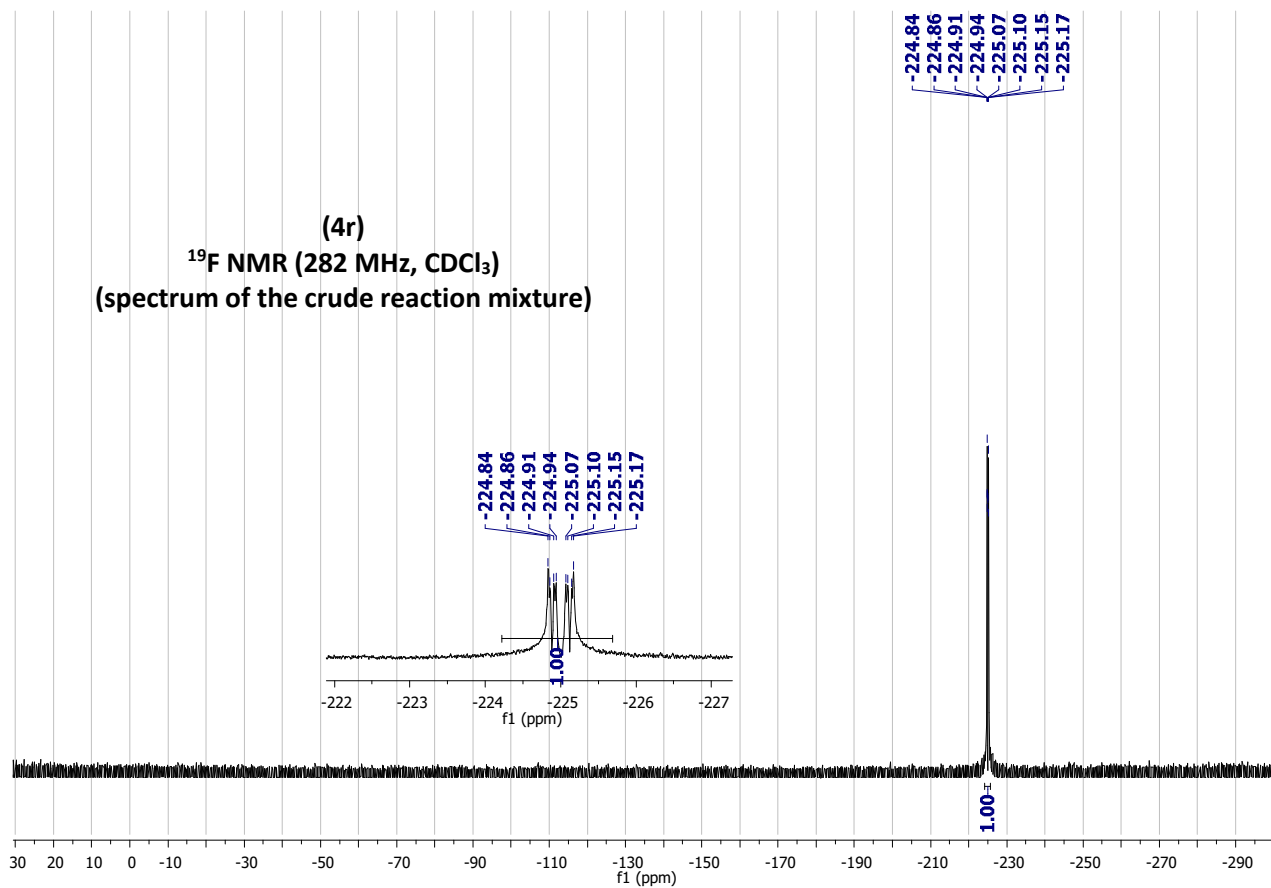


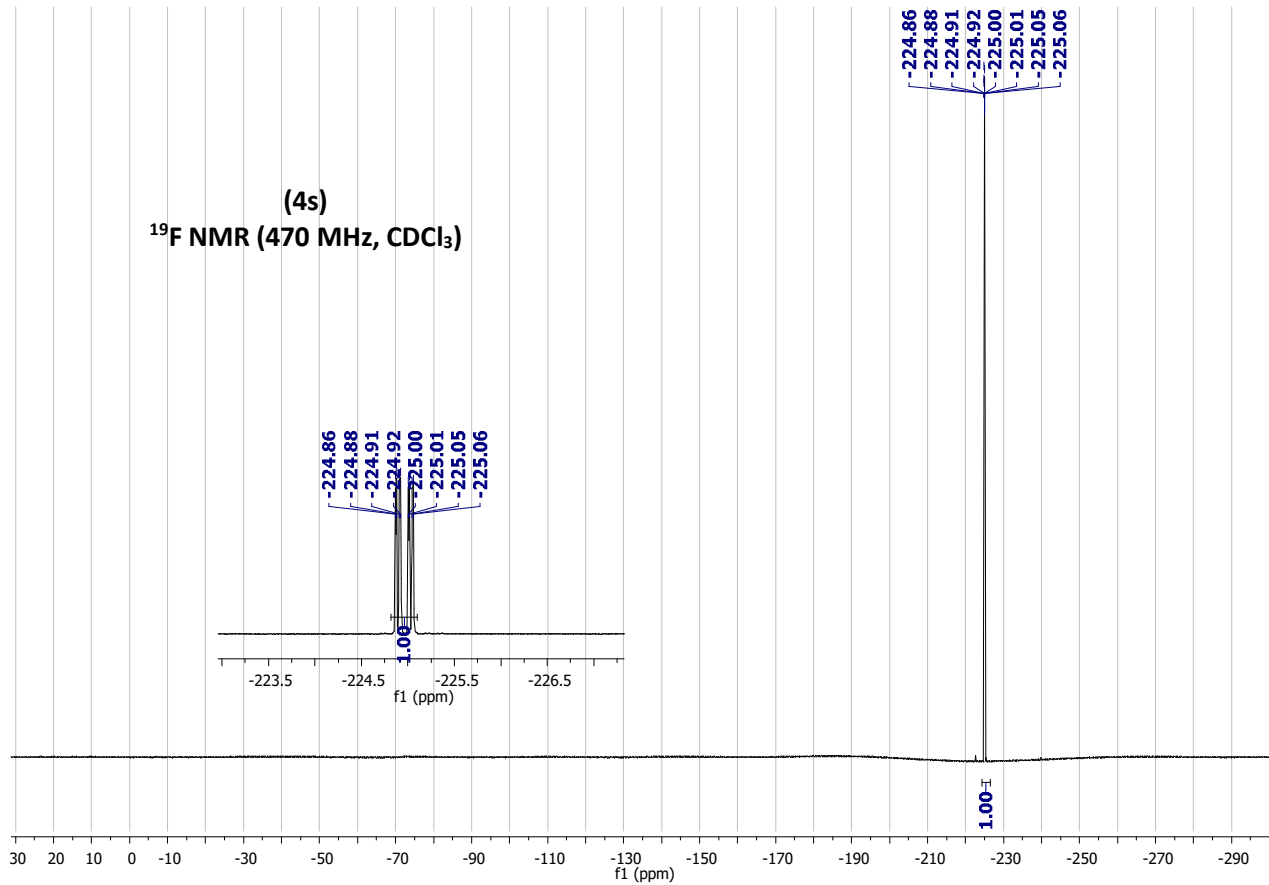
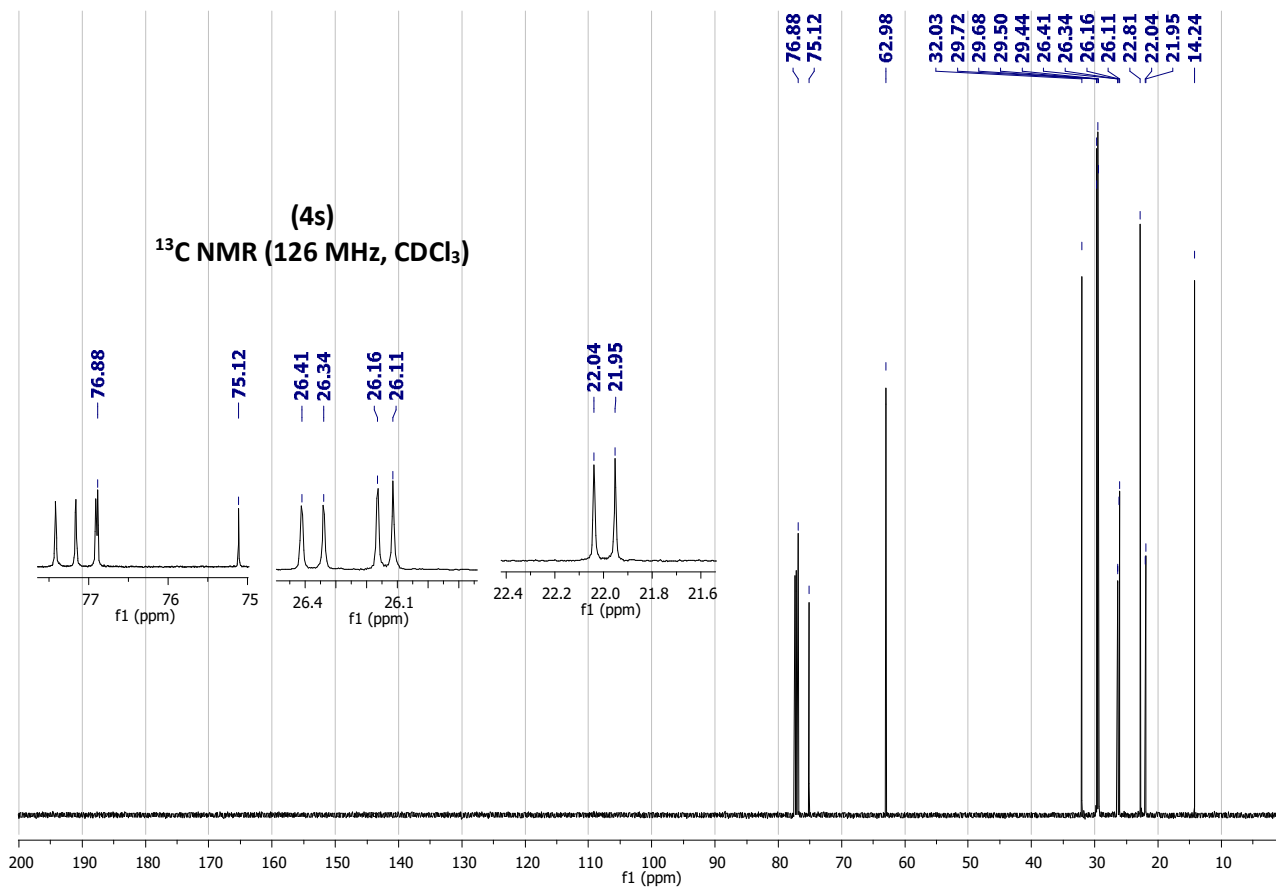


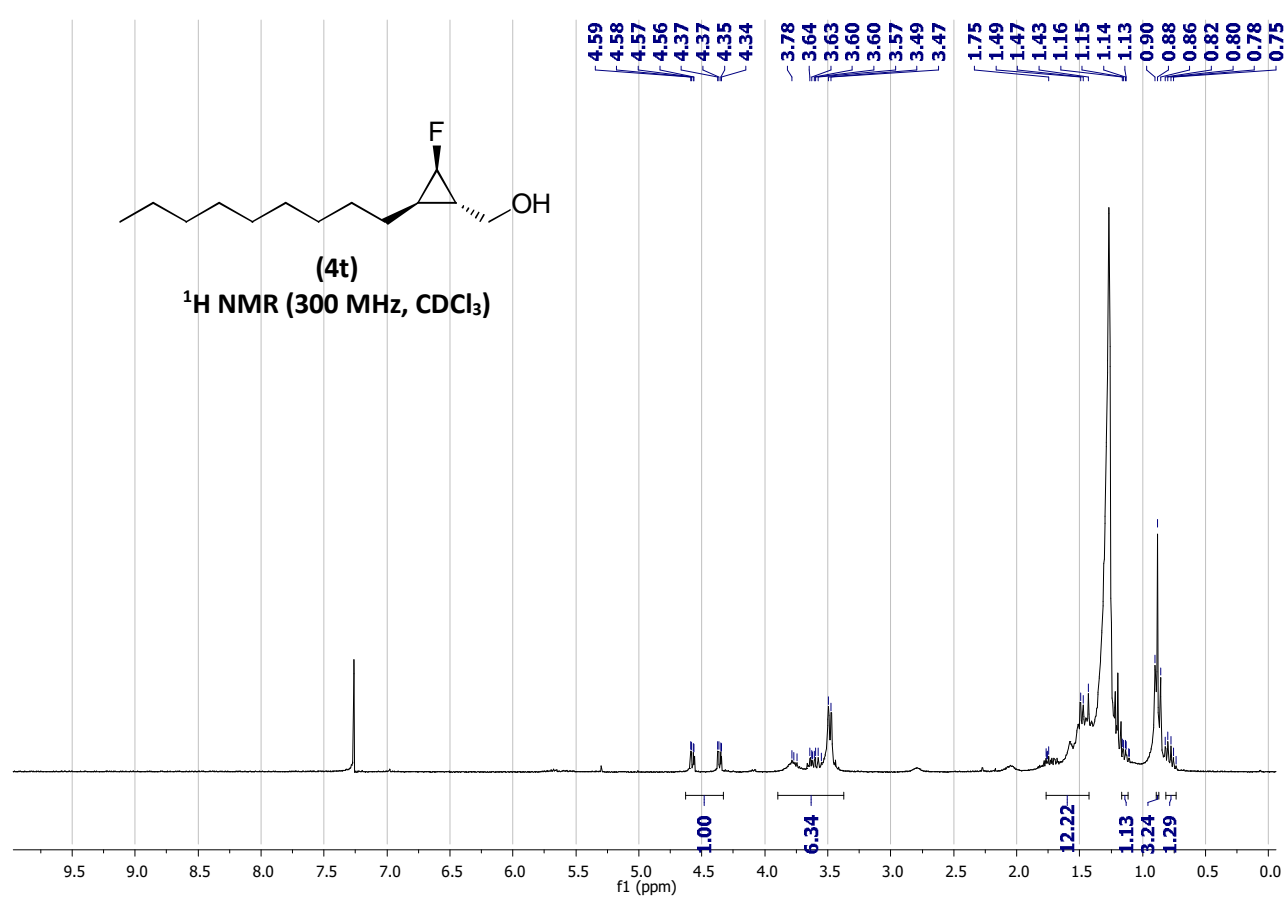
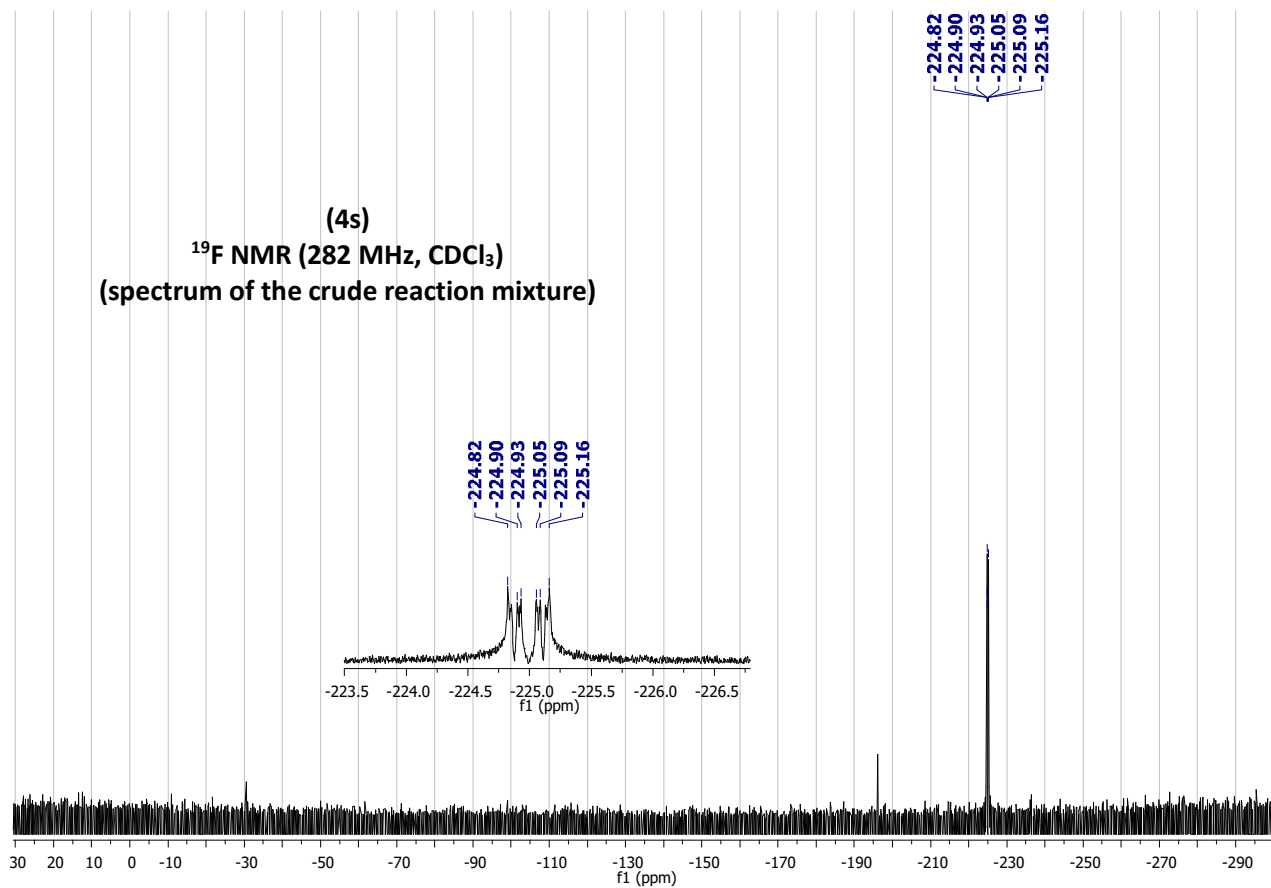


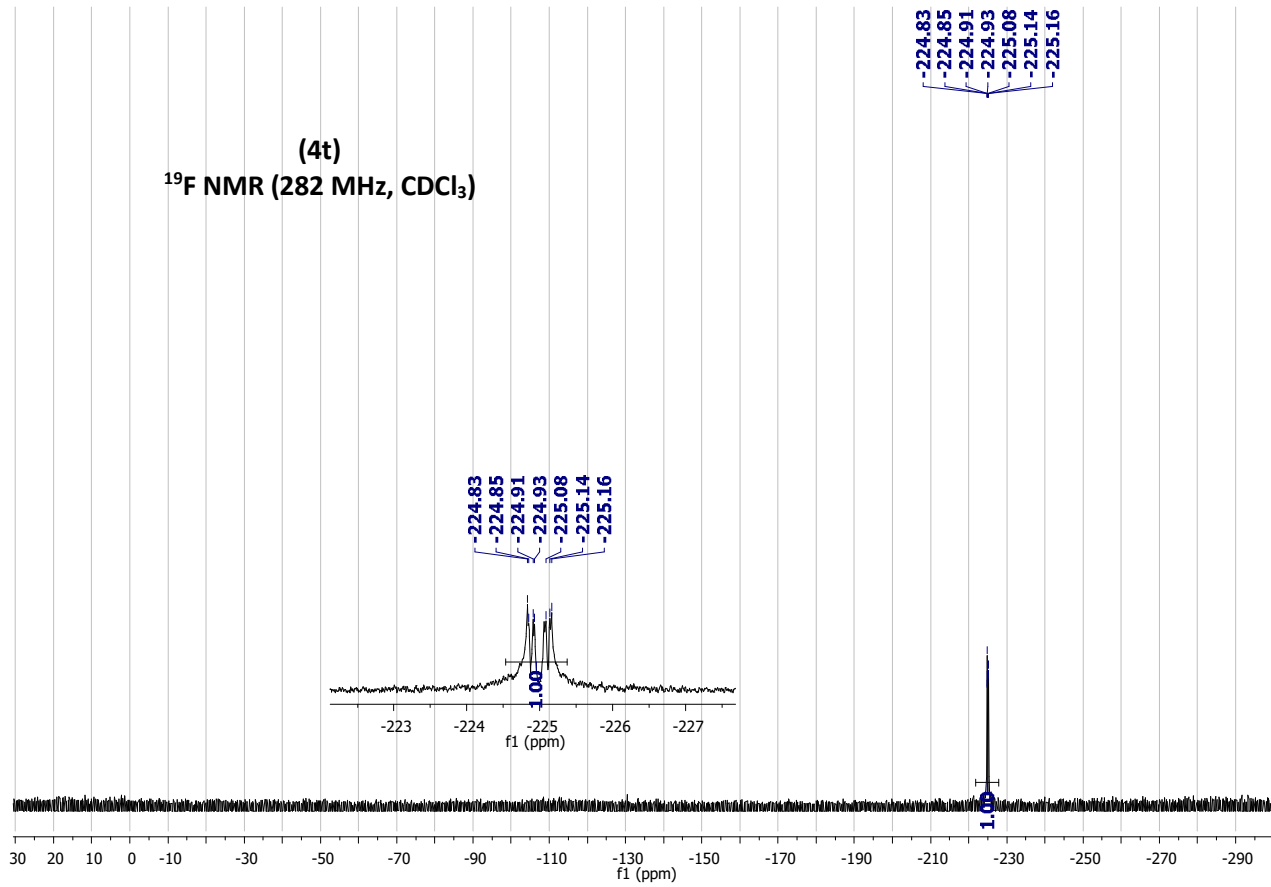
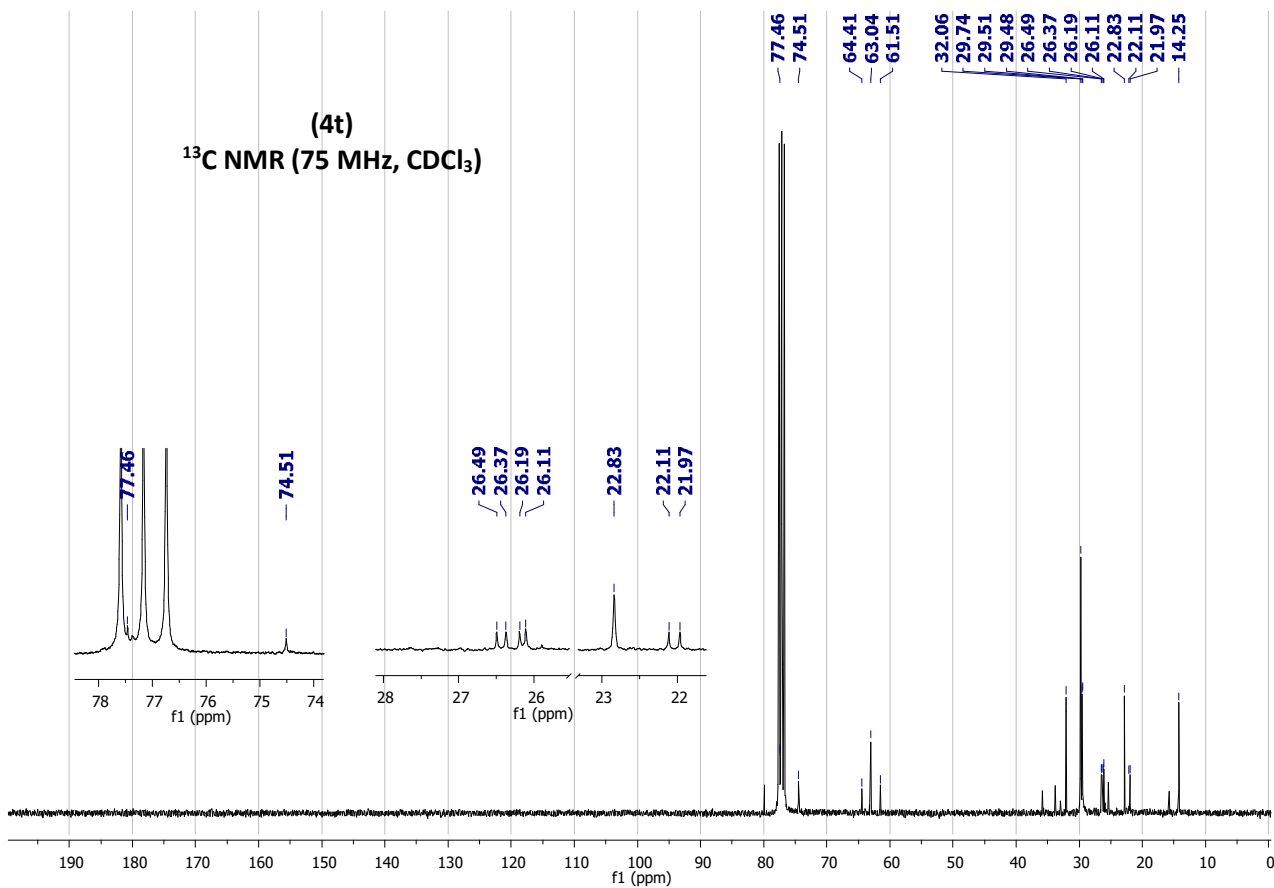


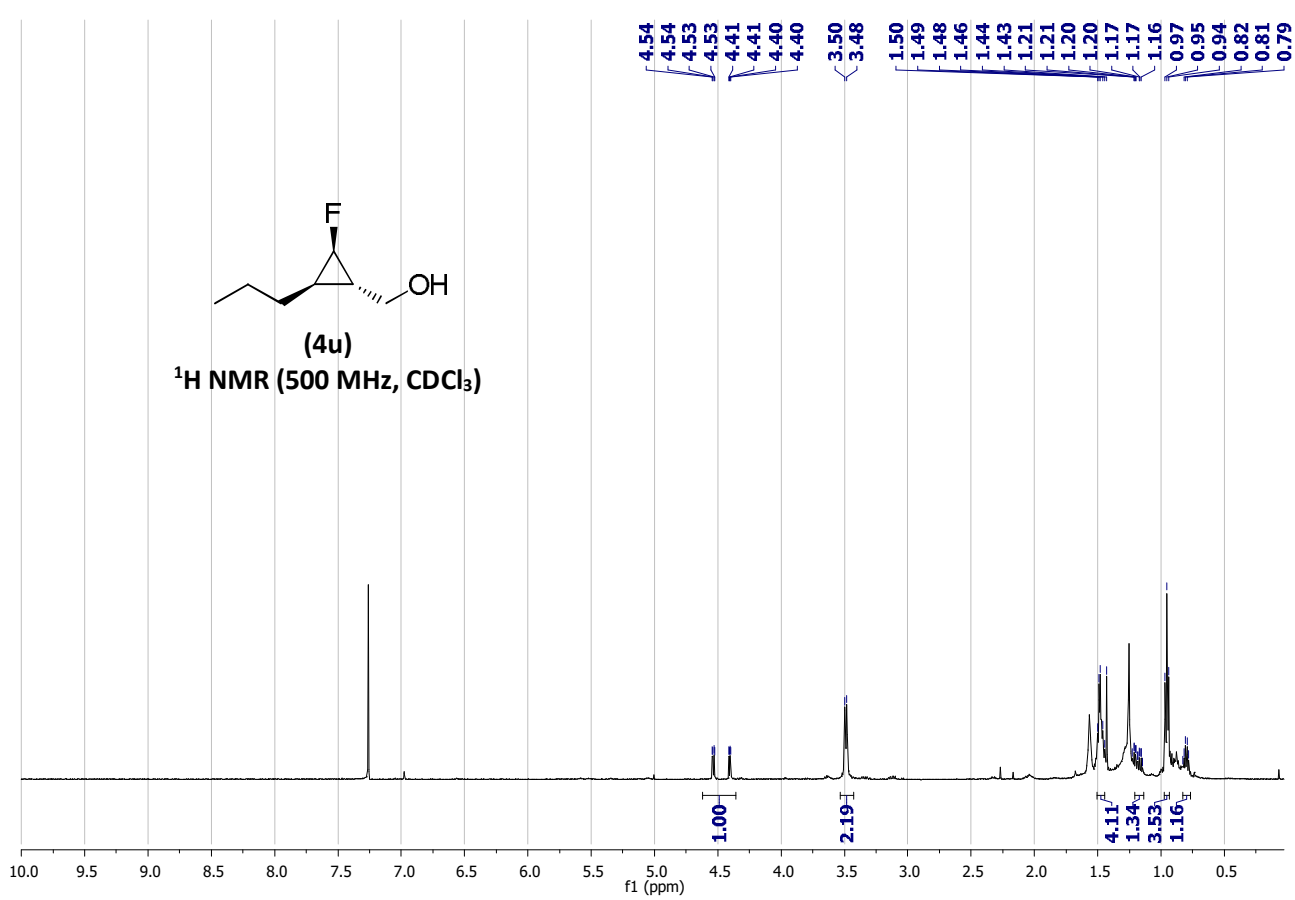
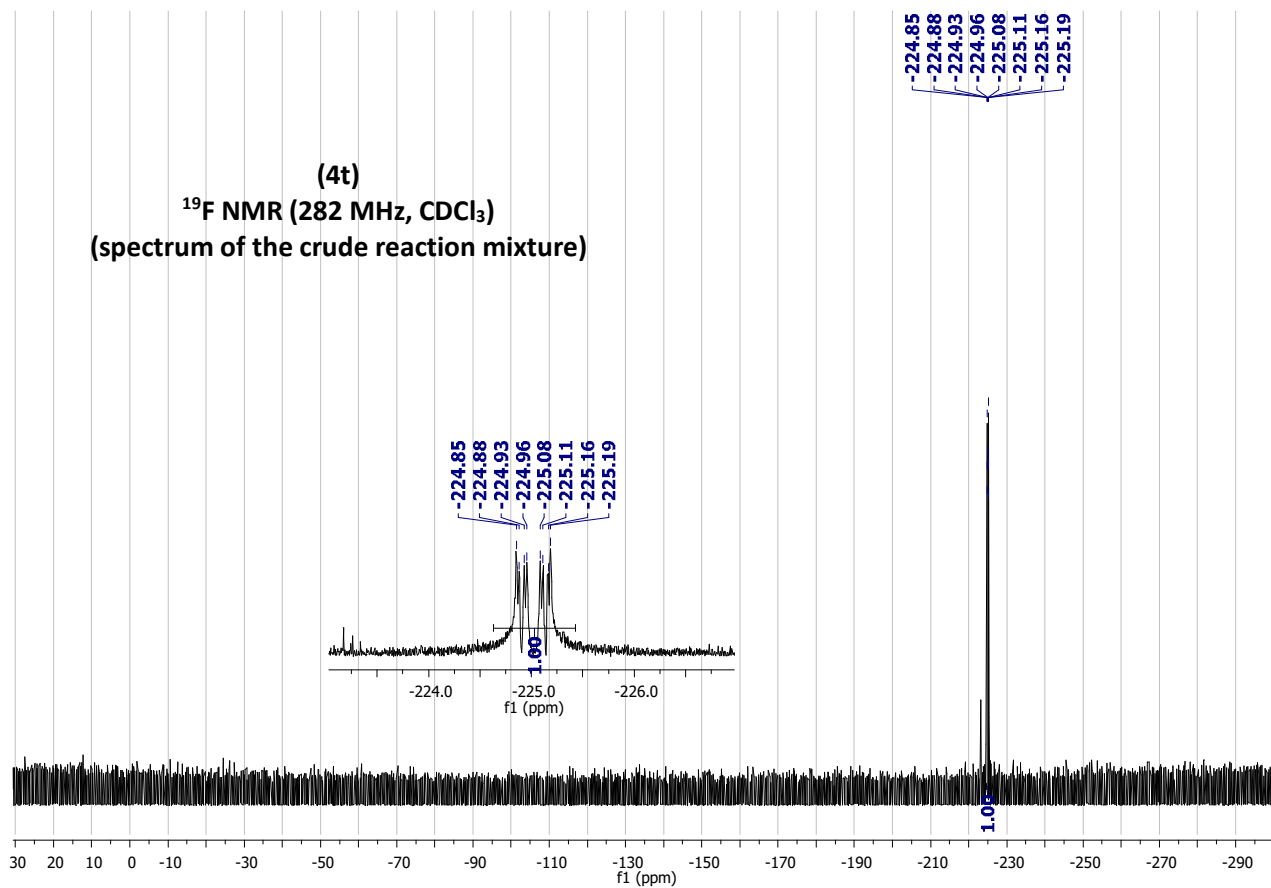


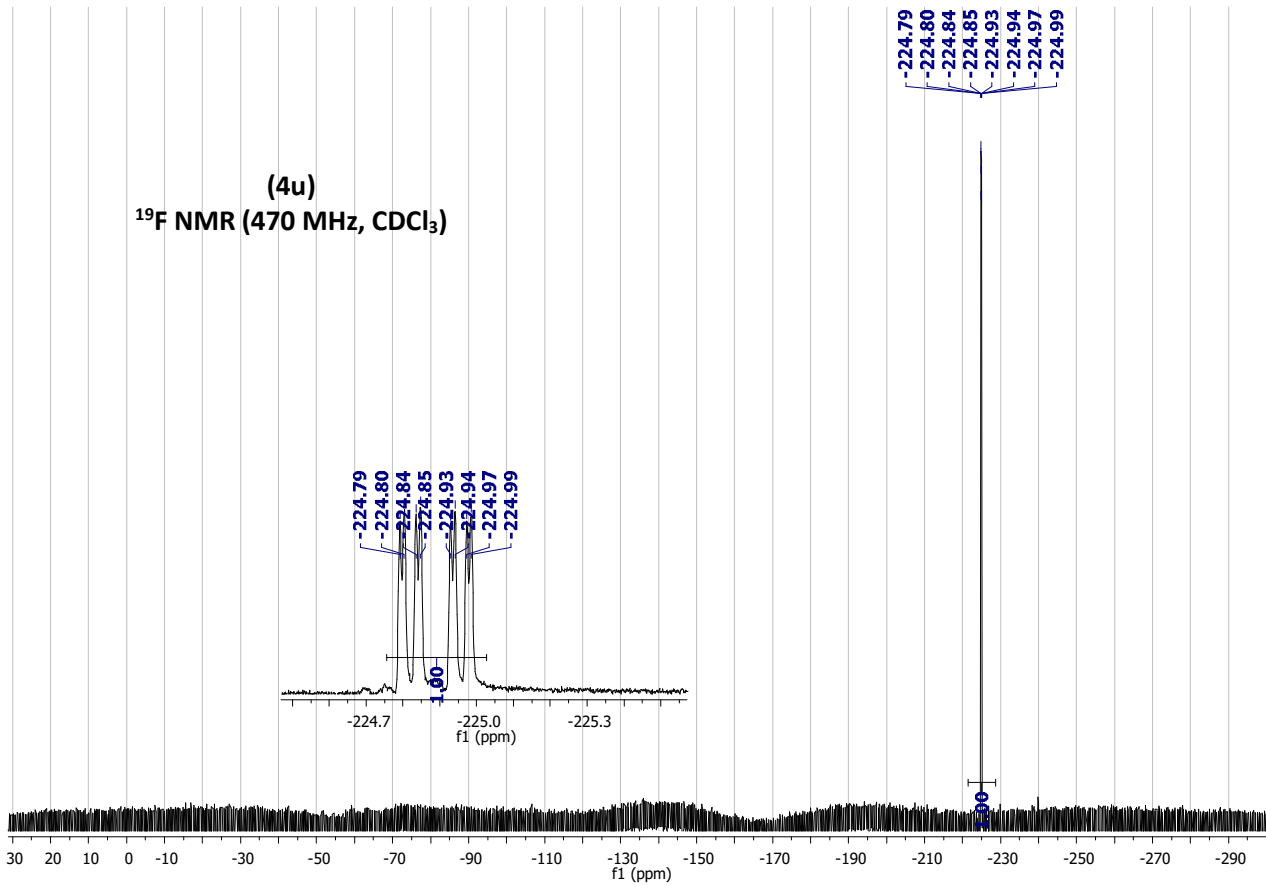
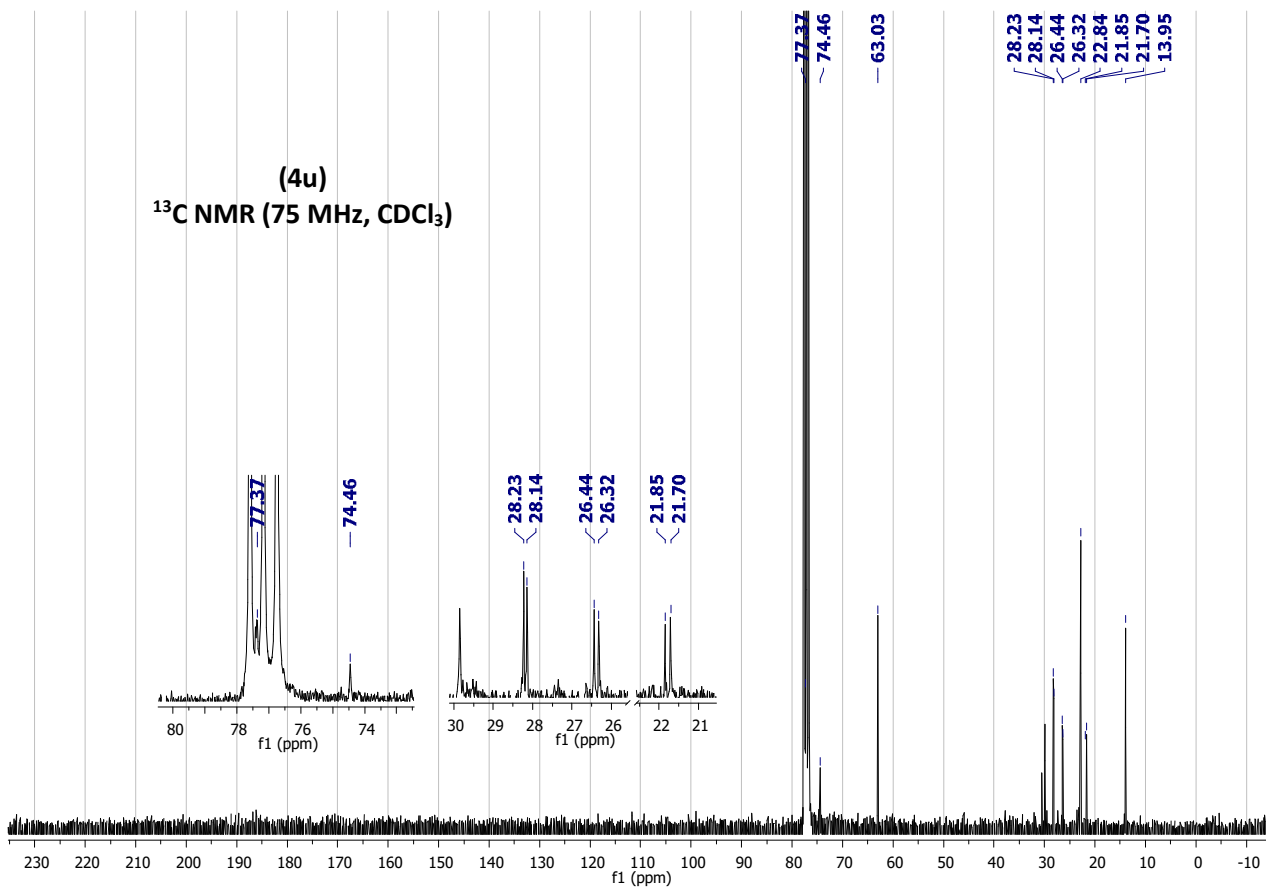


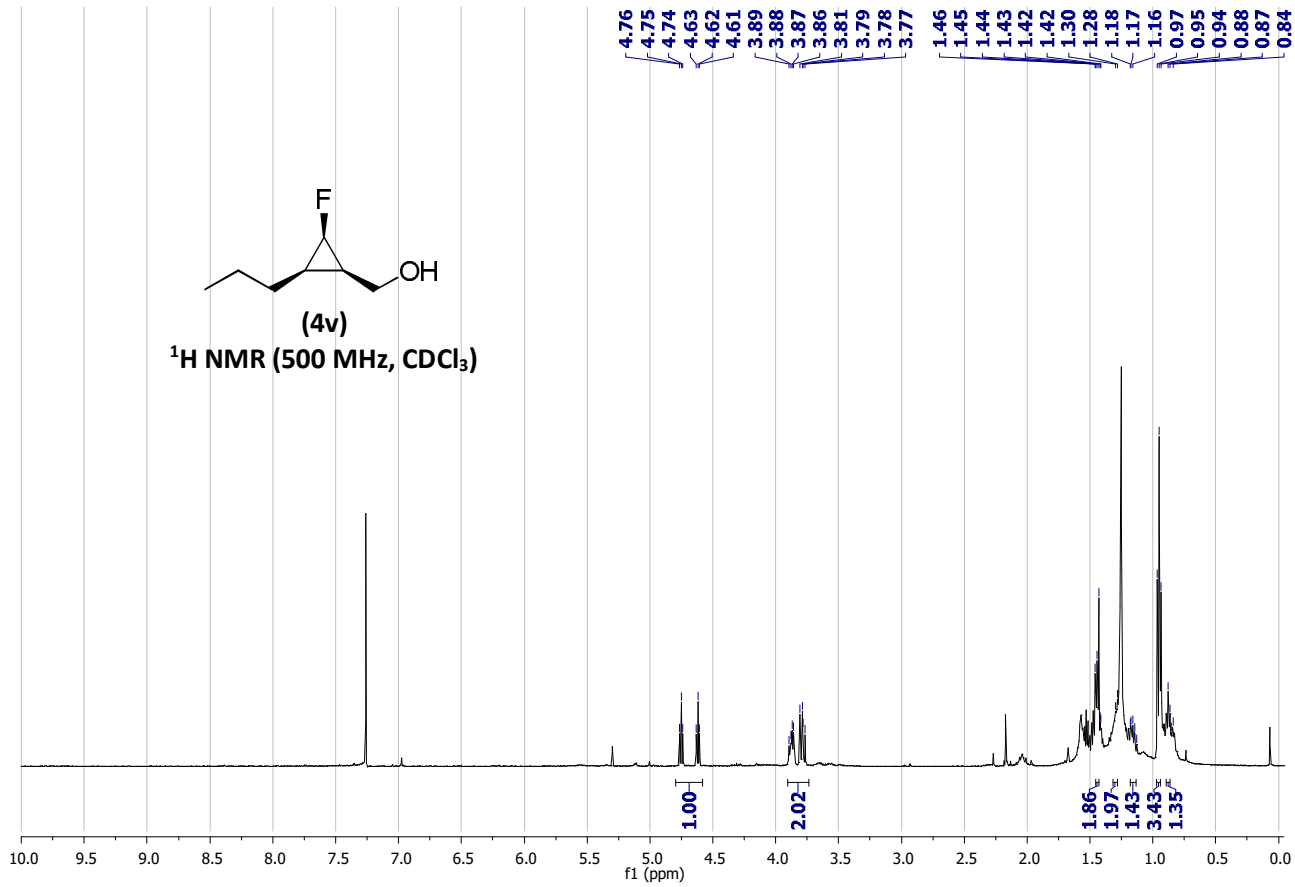
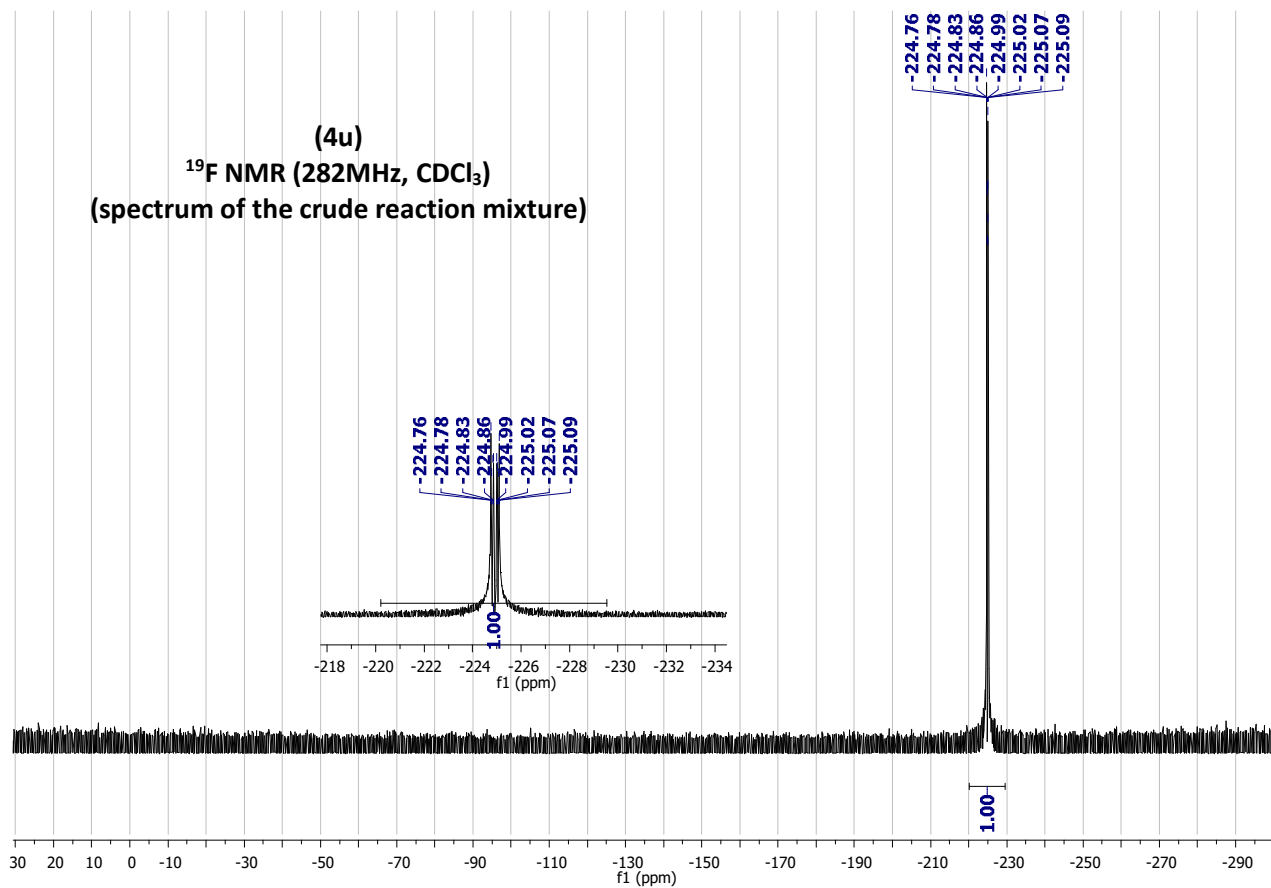


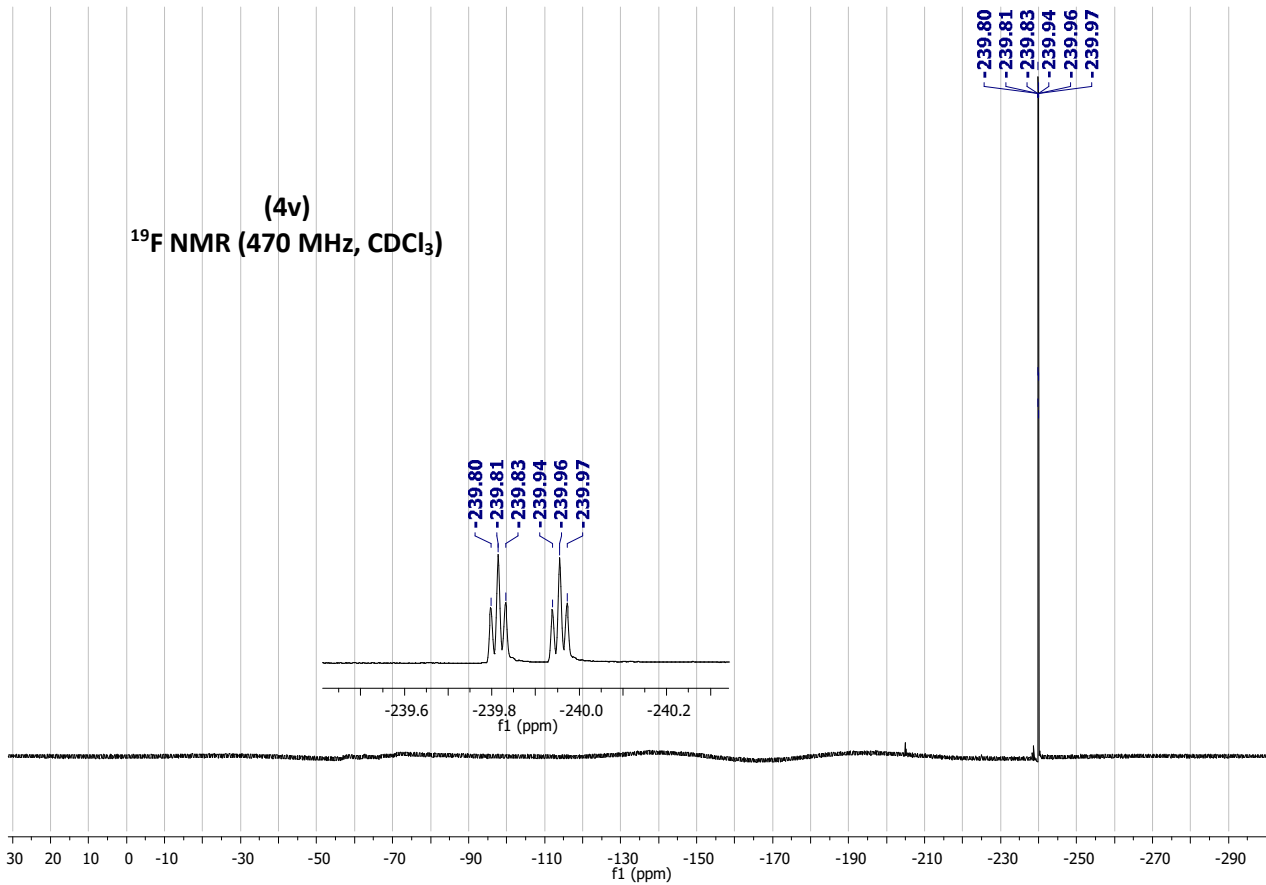
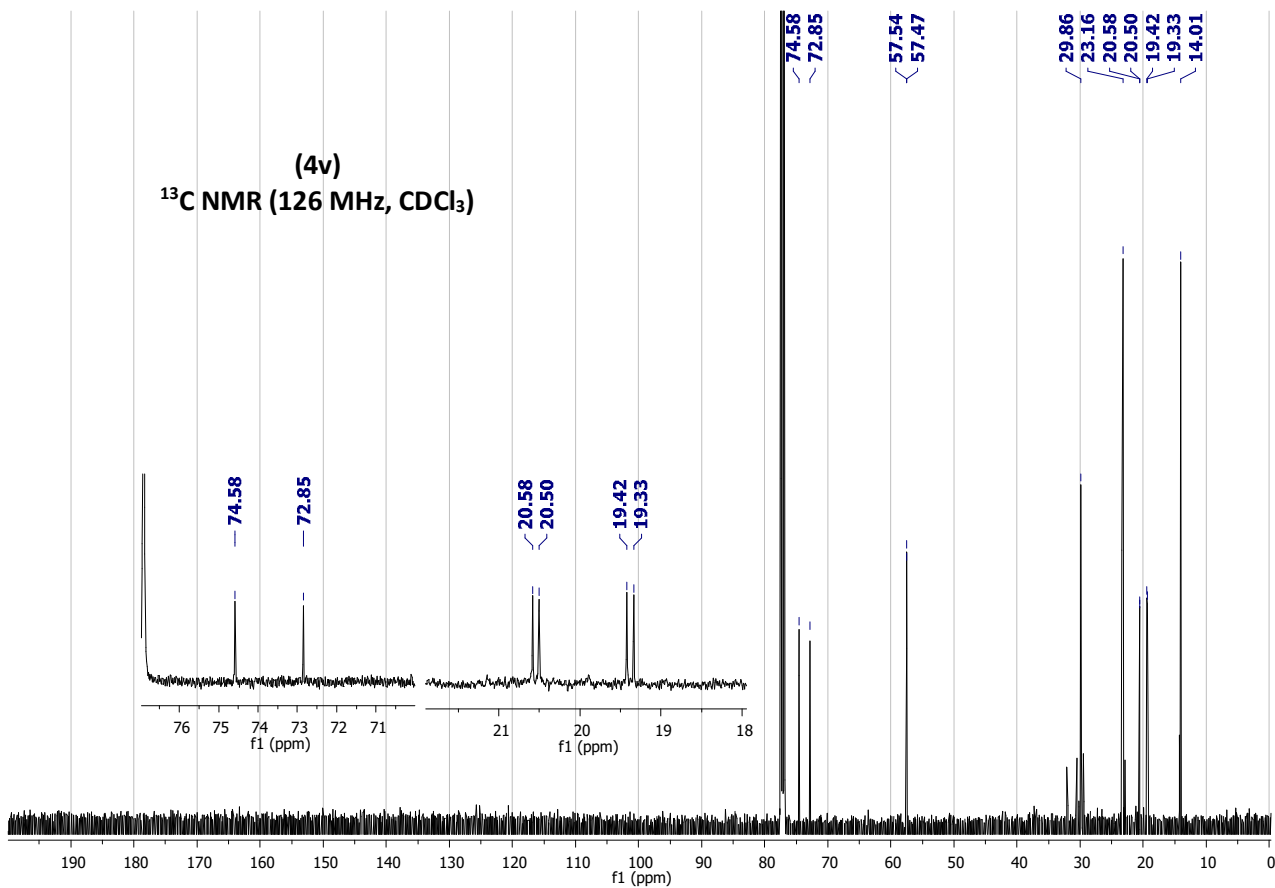


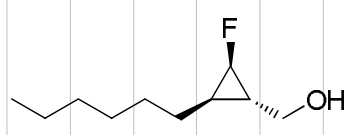
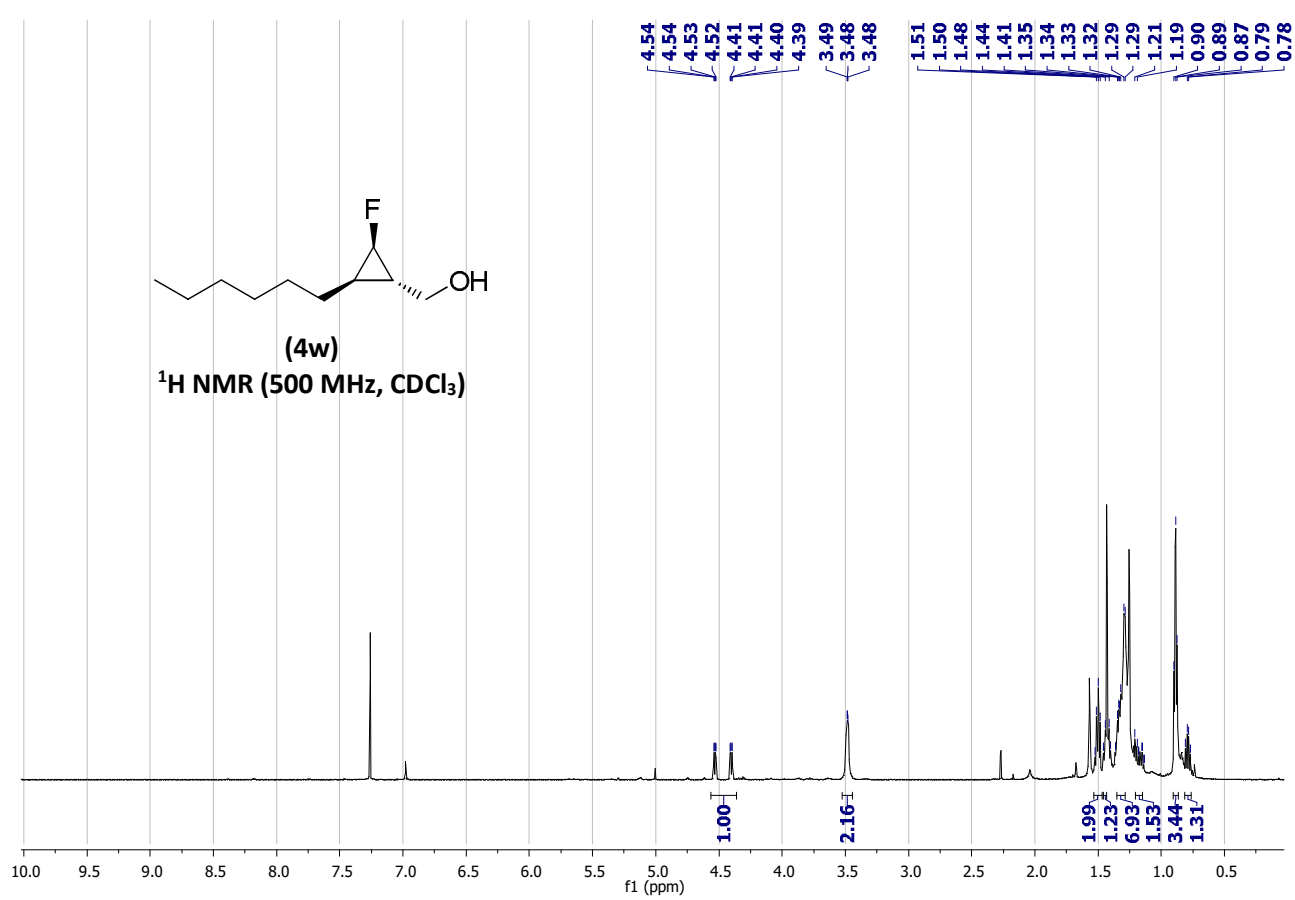
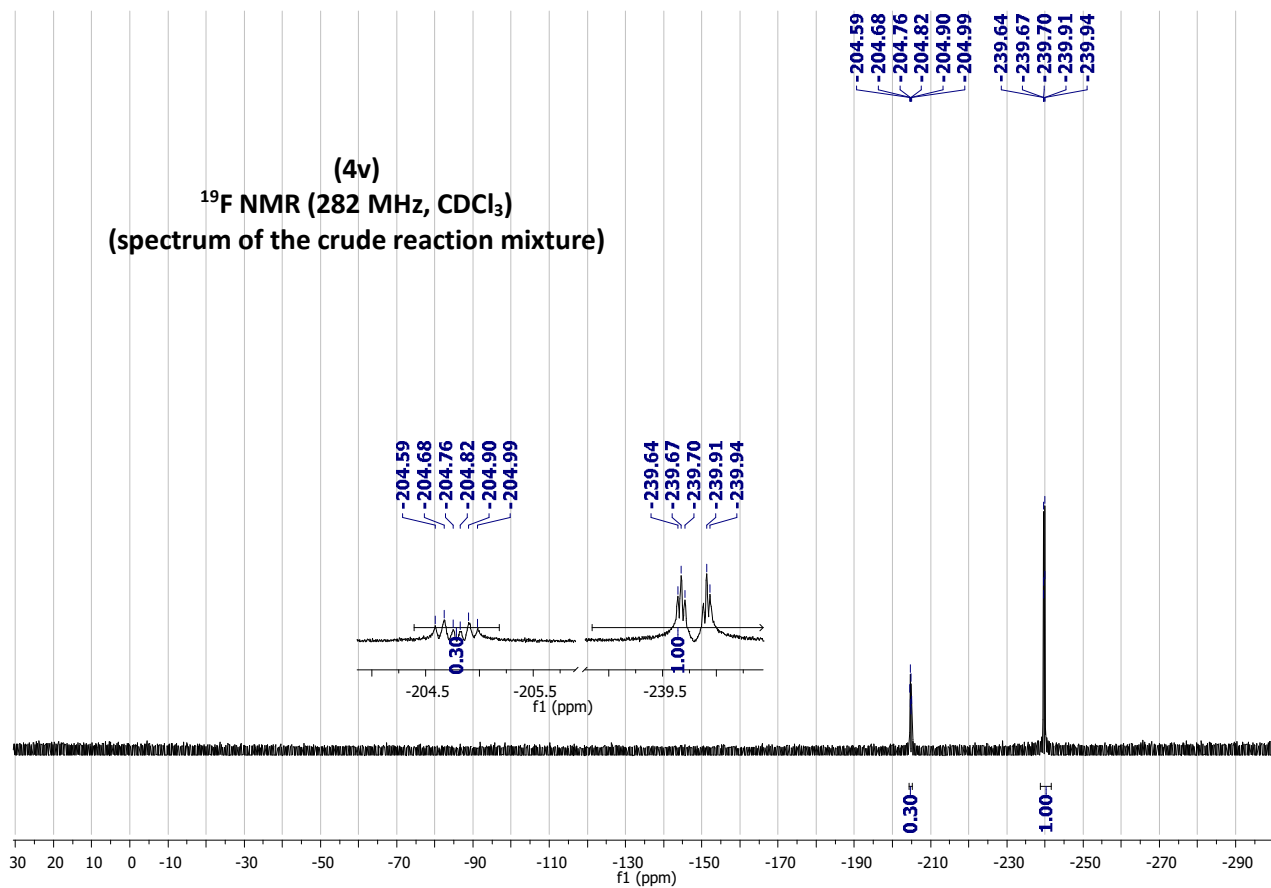




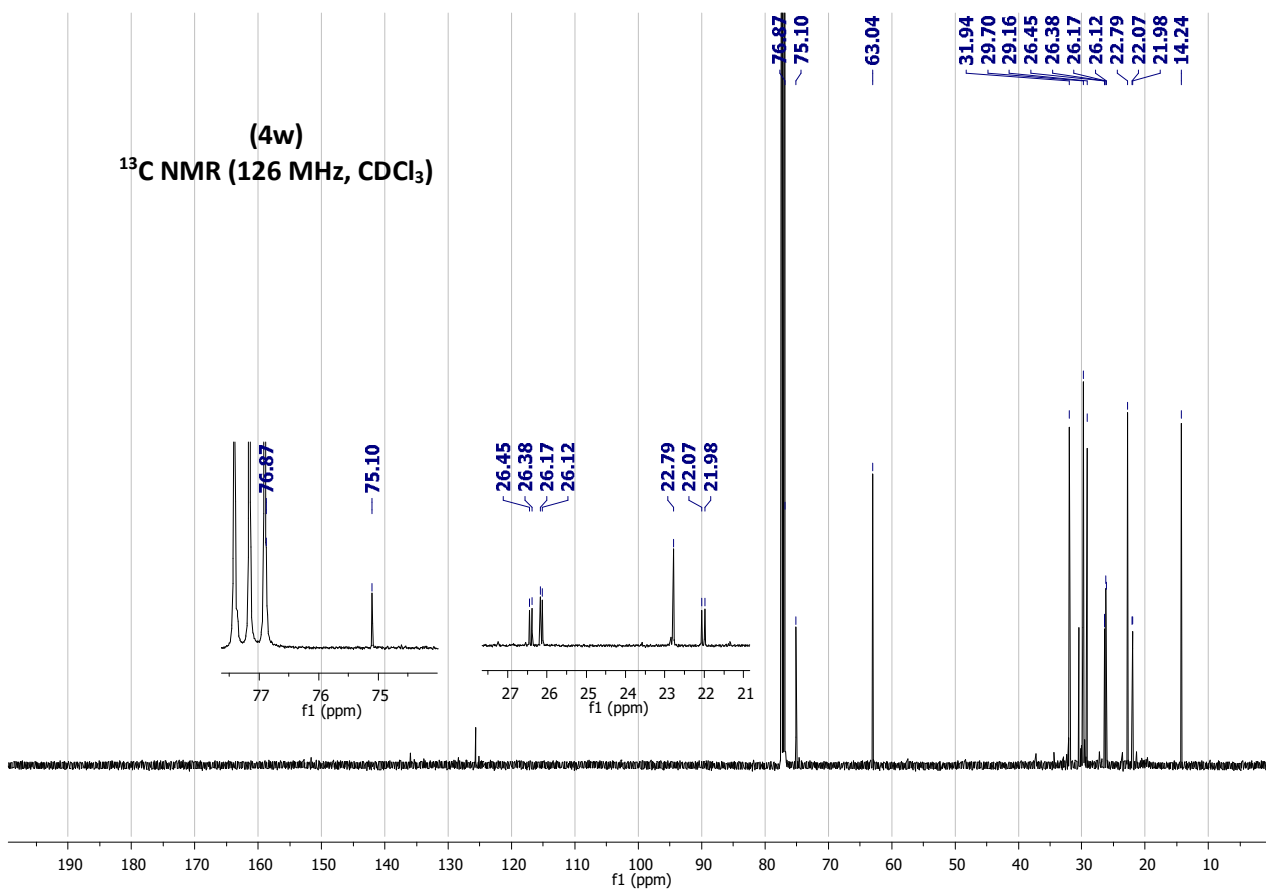




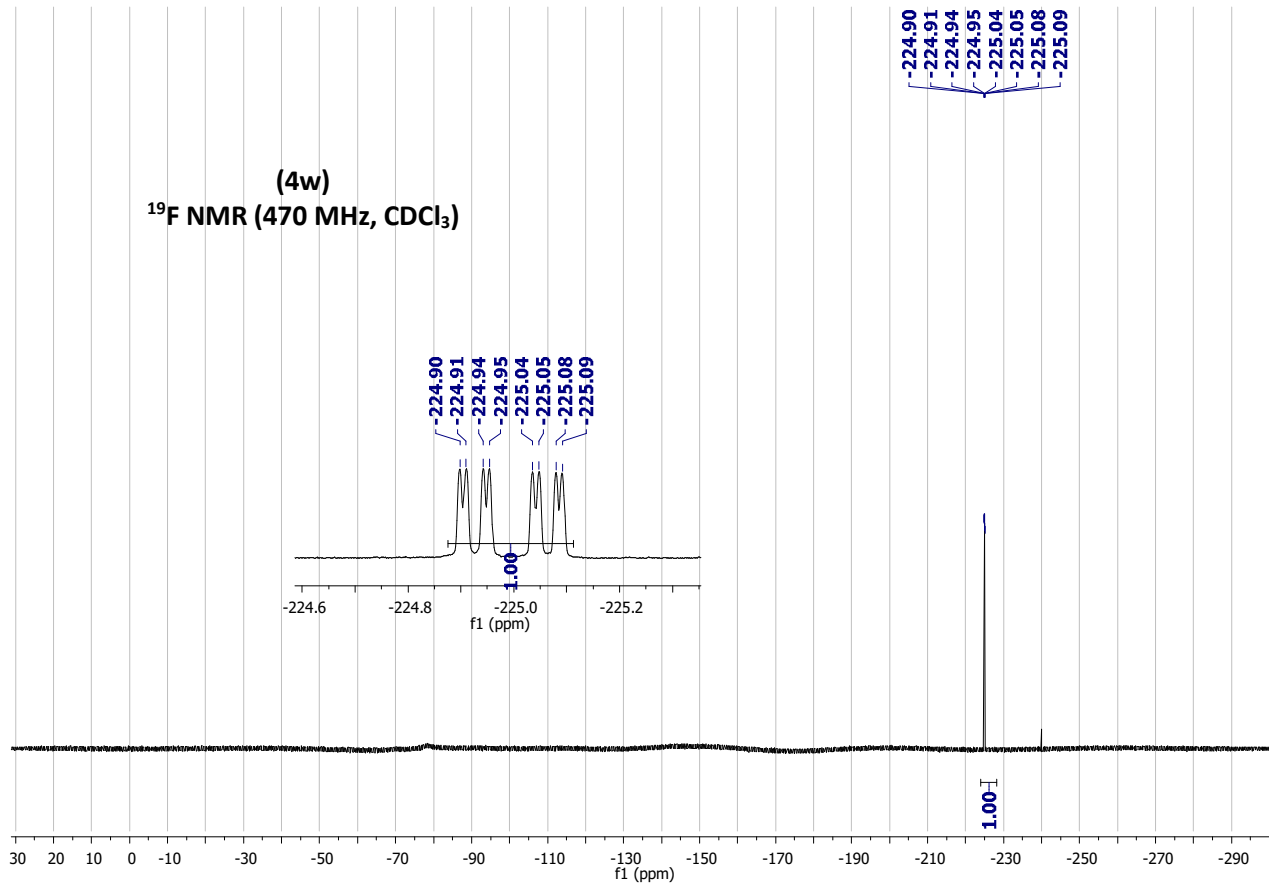


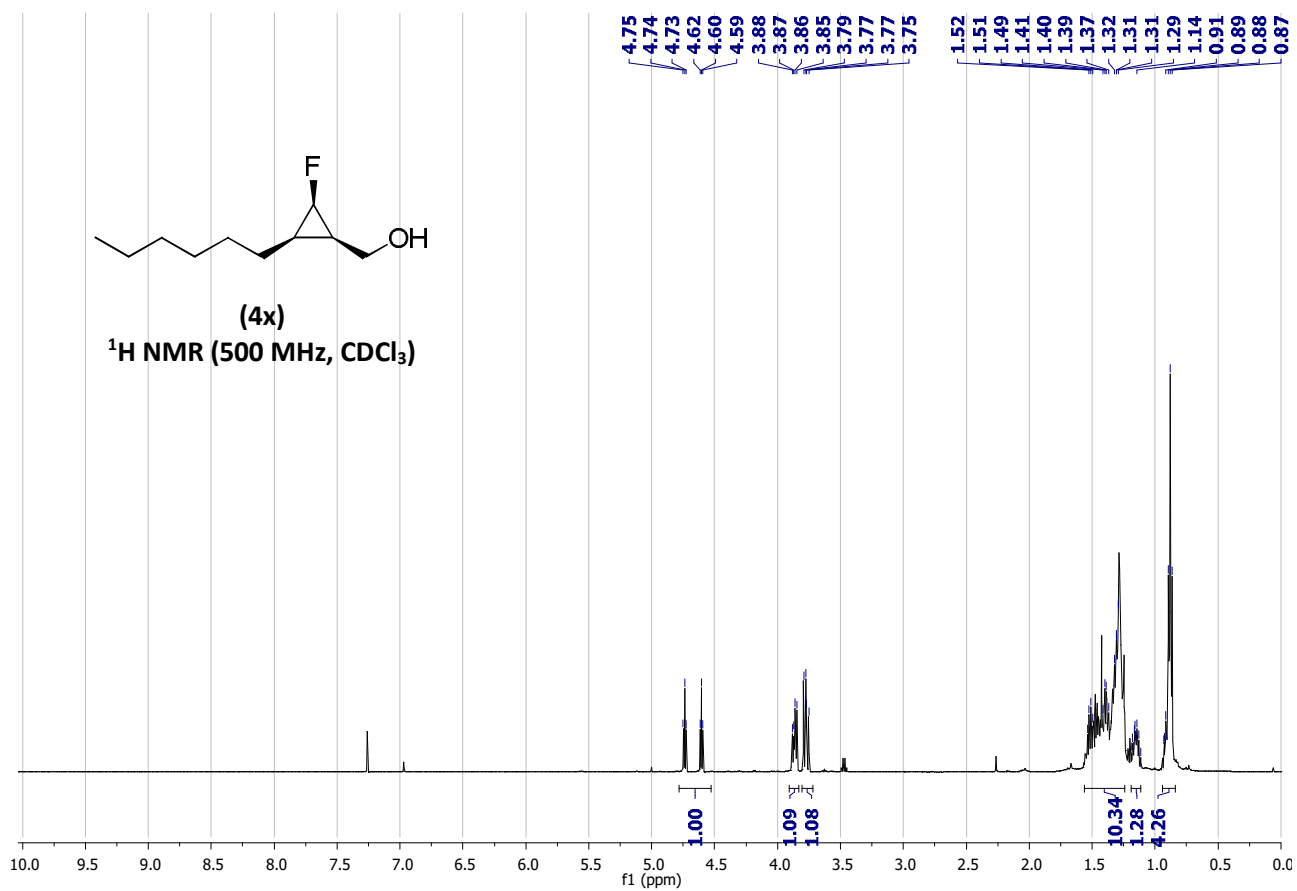
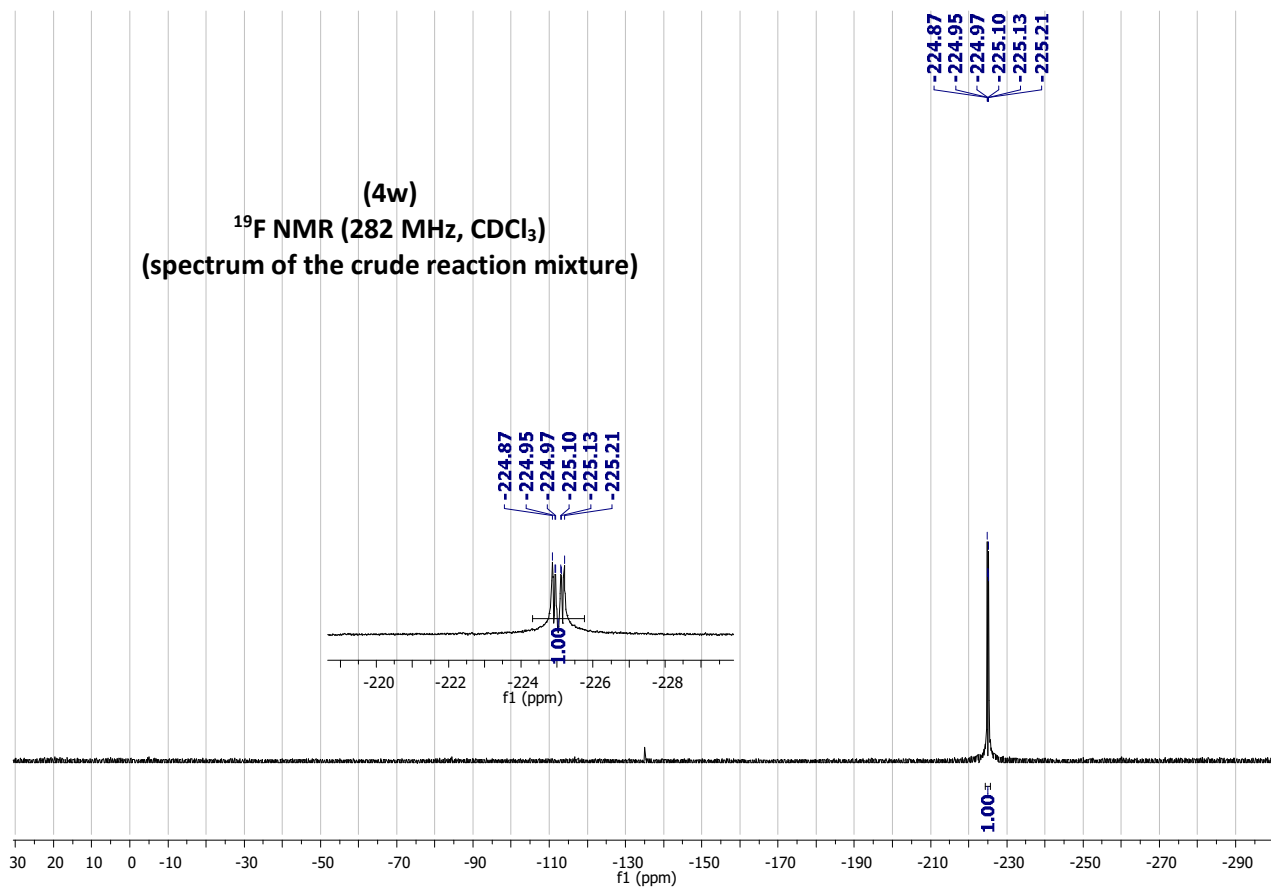


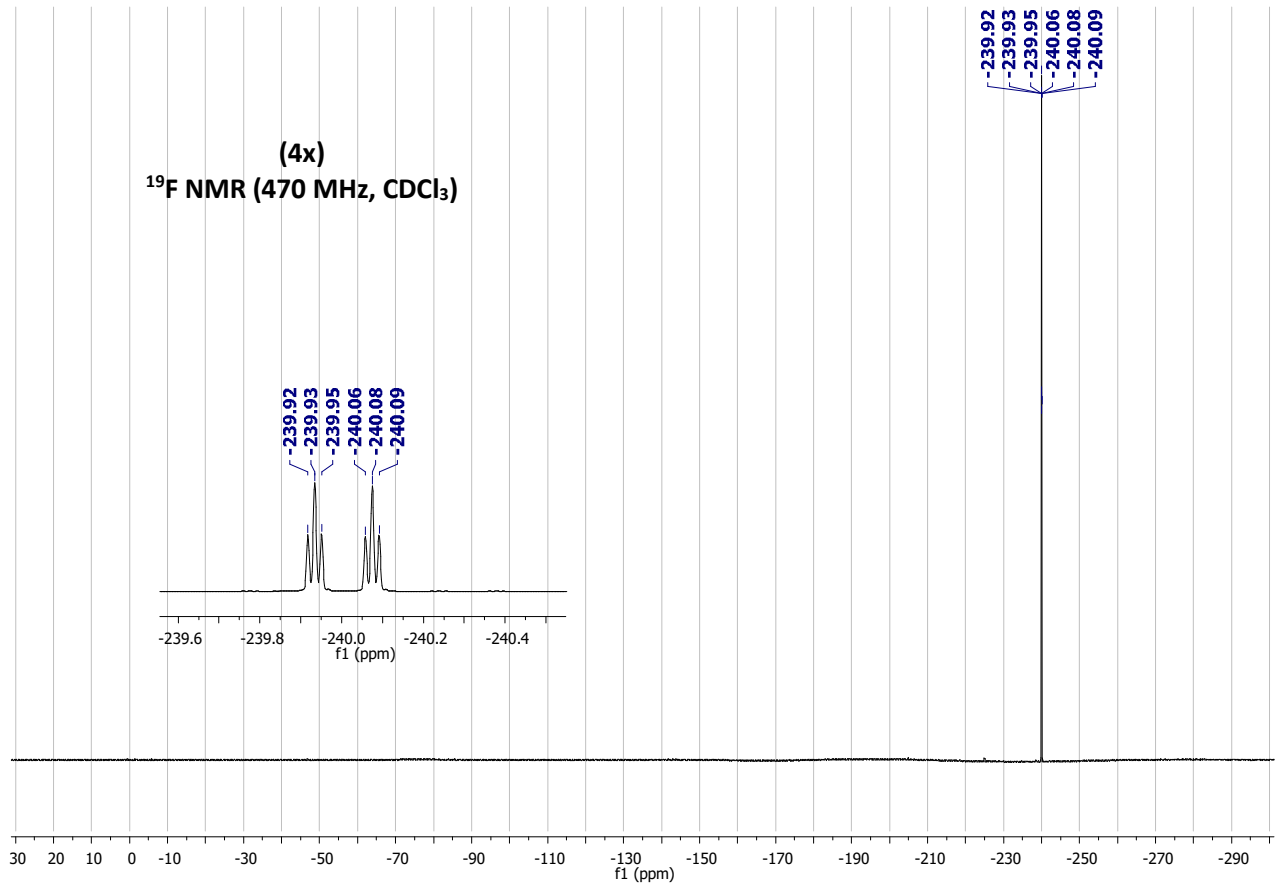
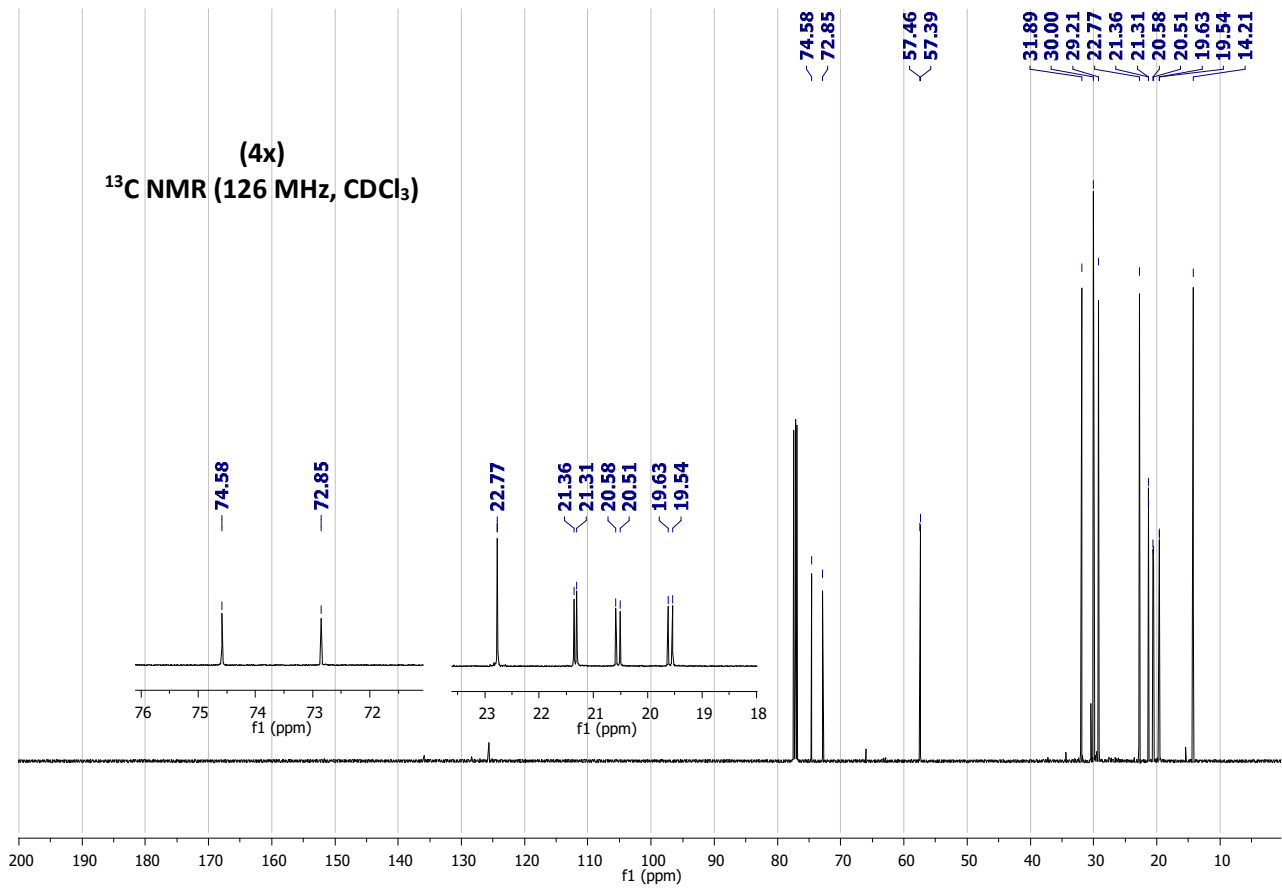
(4w)
¹³C NMR (126 MHz, CDCl₃)

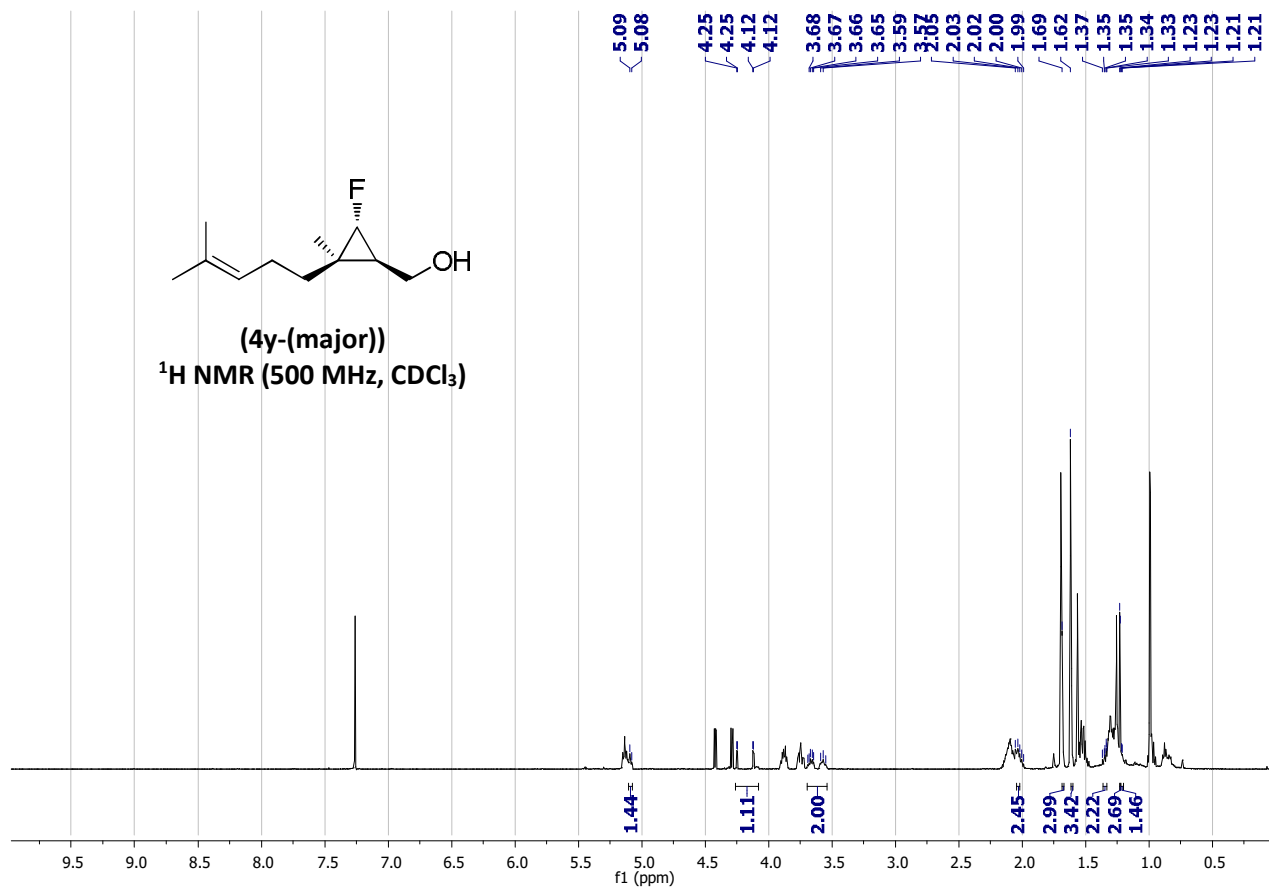
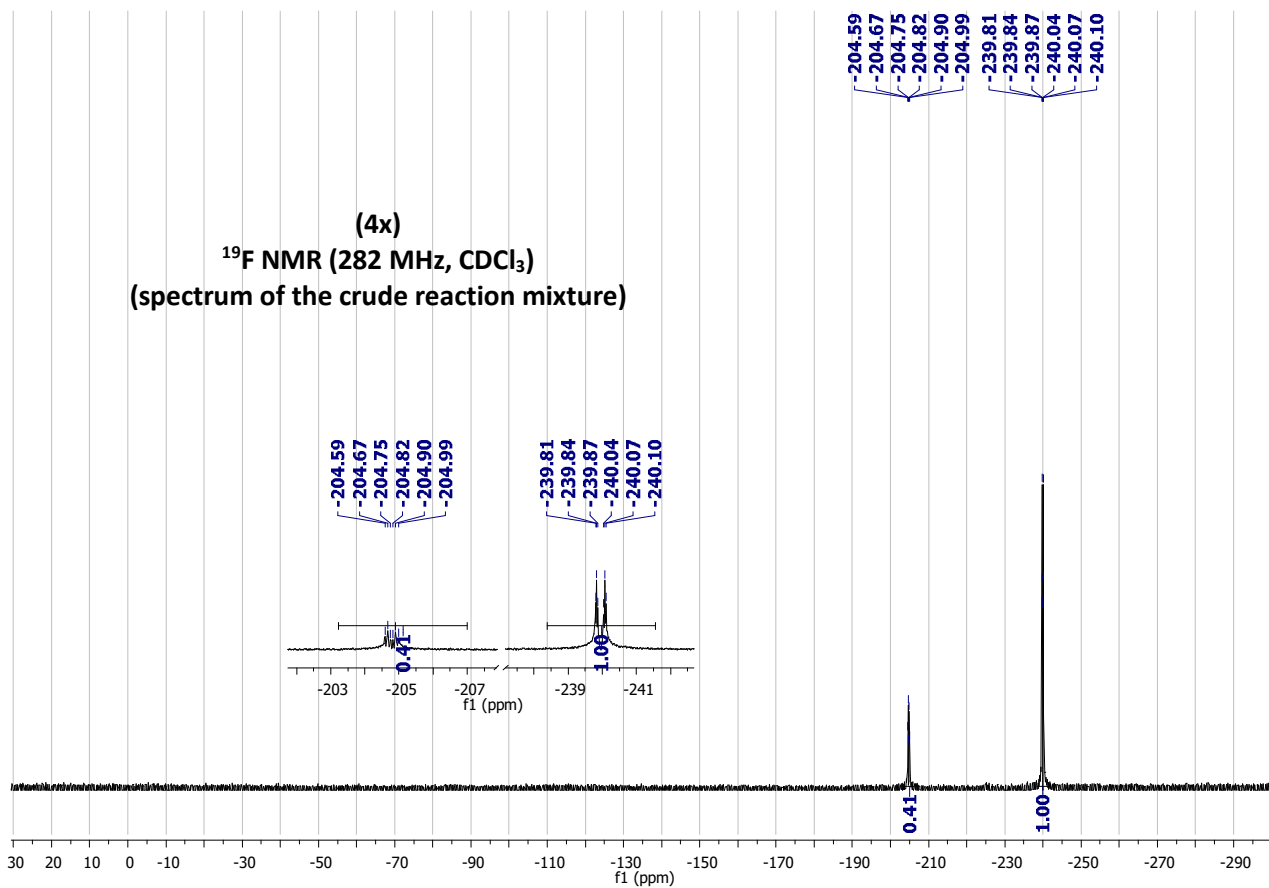


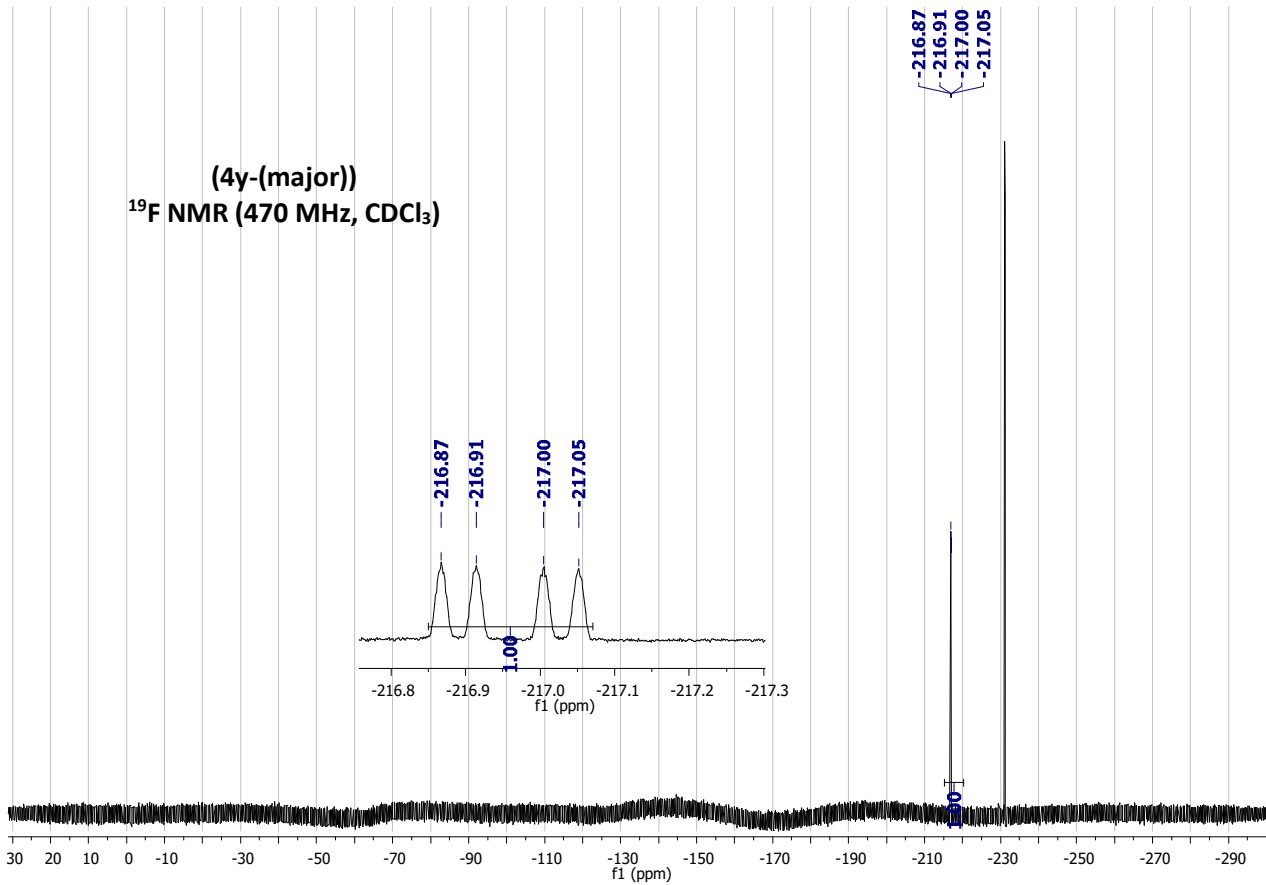
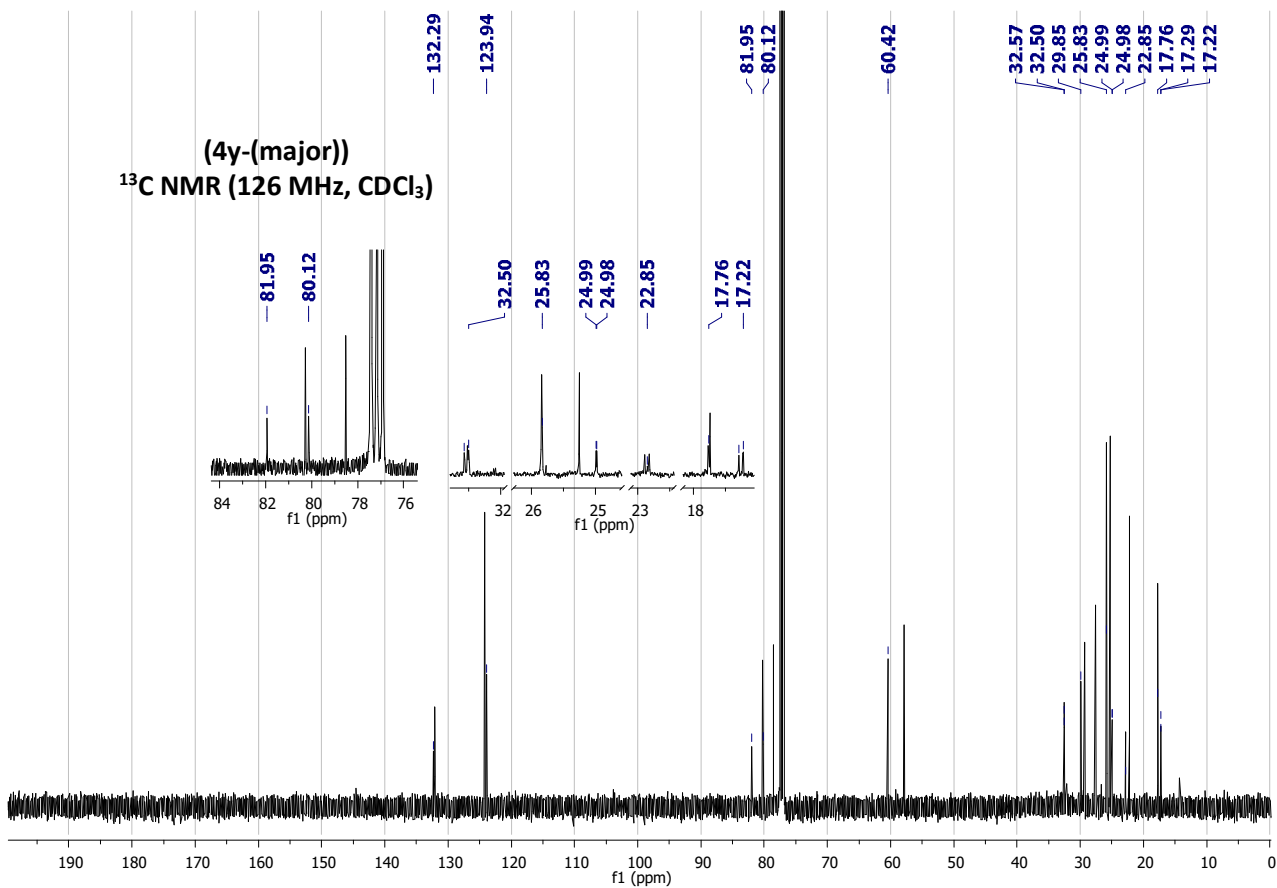
(4w)
¹⁹F NMR (470 MHz, CDCl₃)

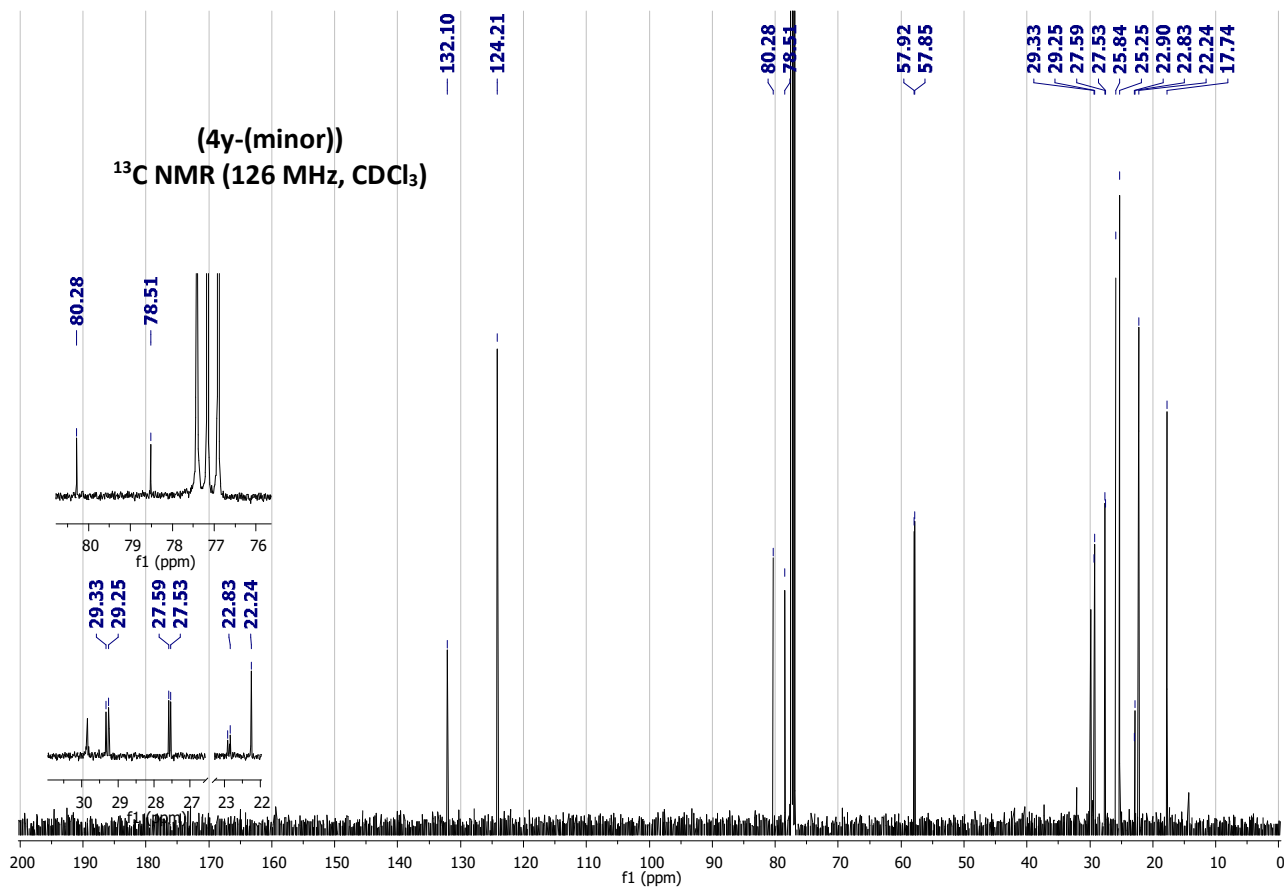
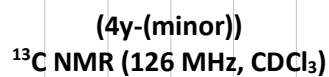
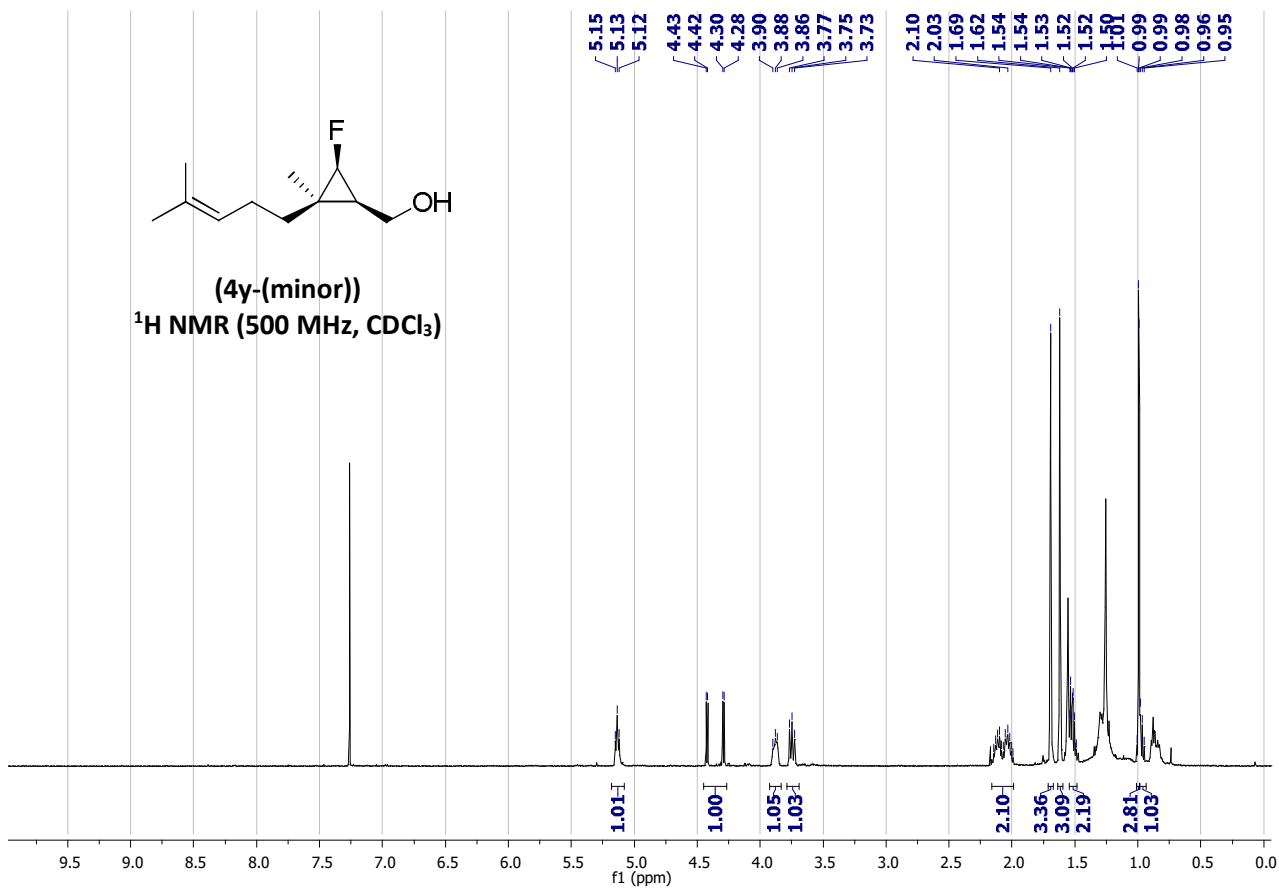
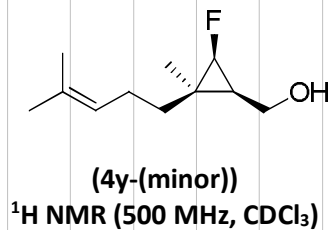


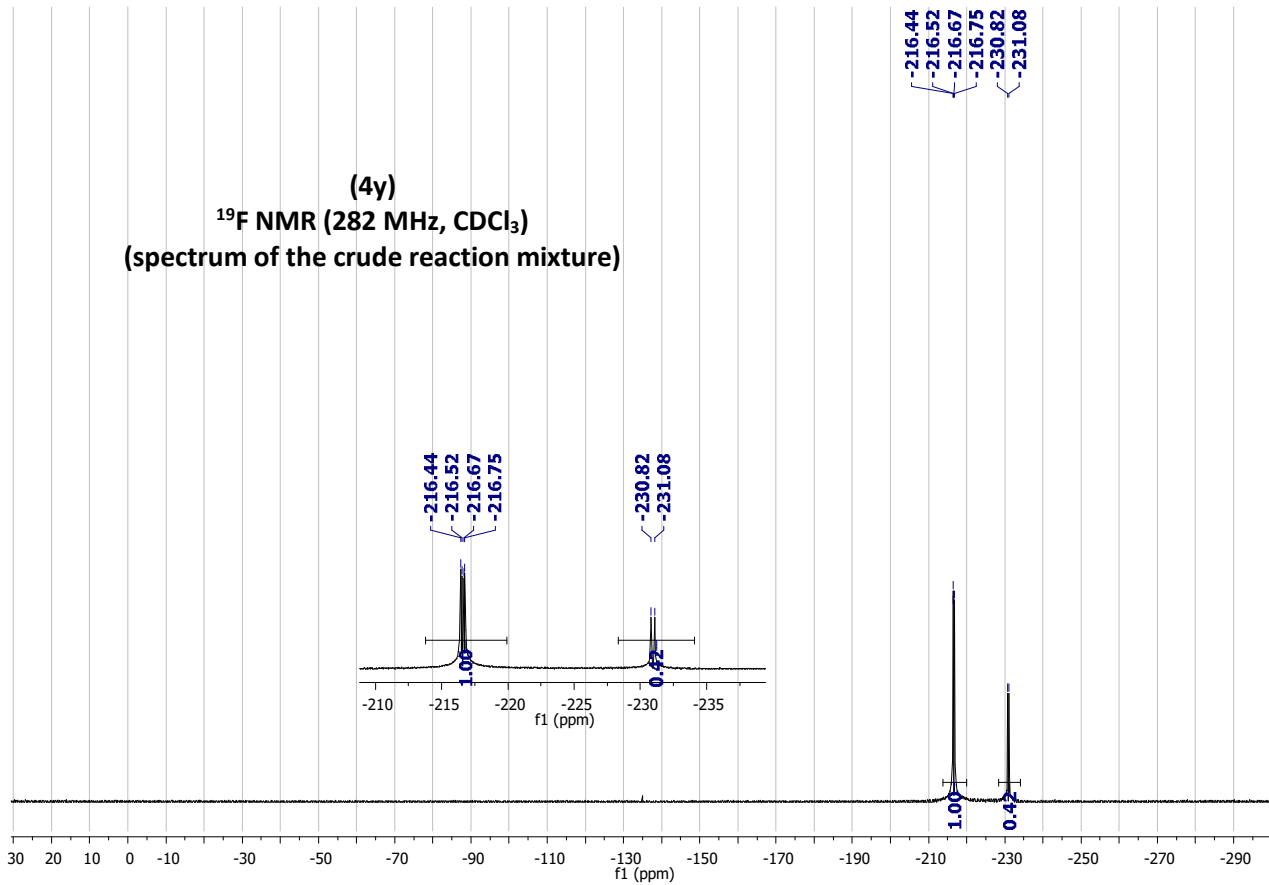
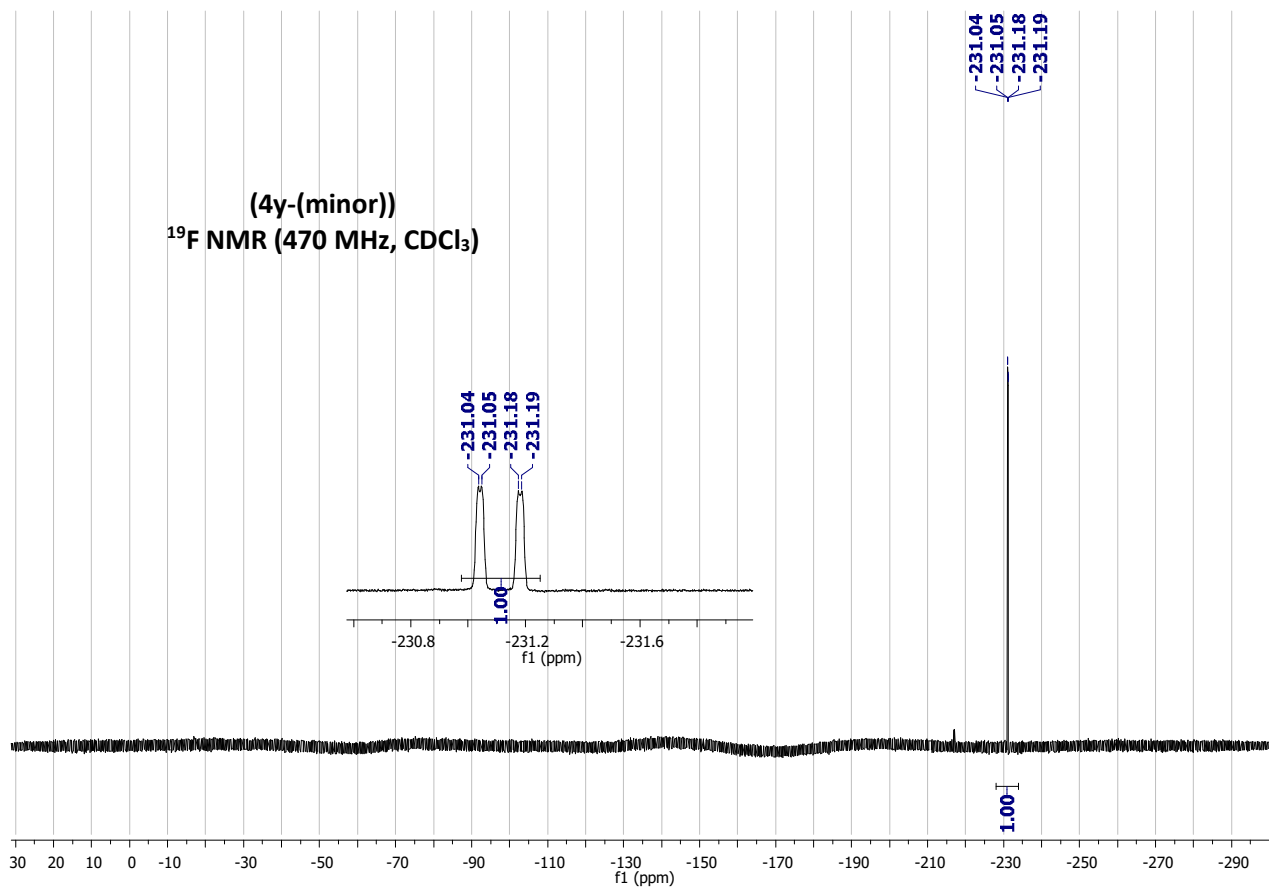


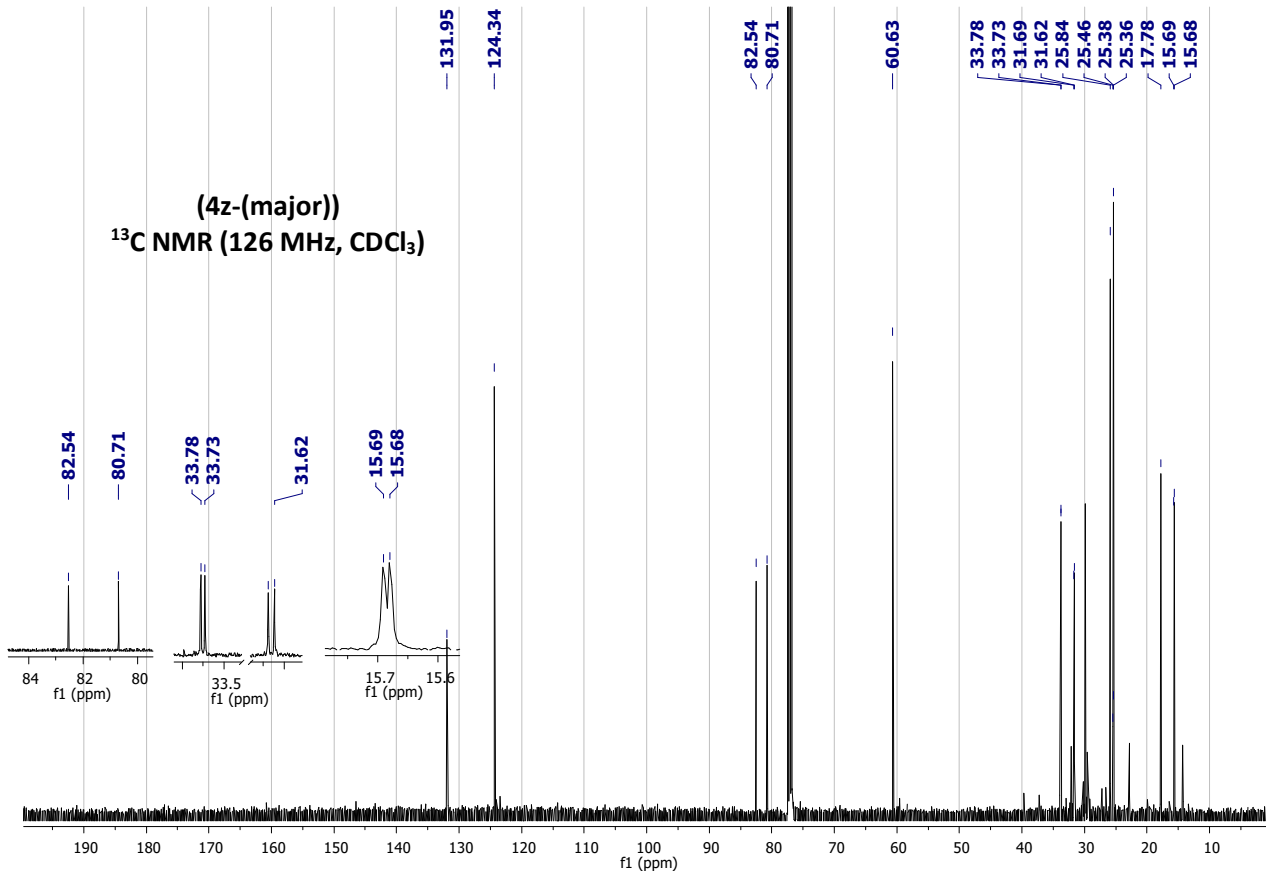
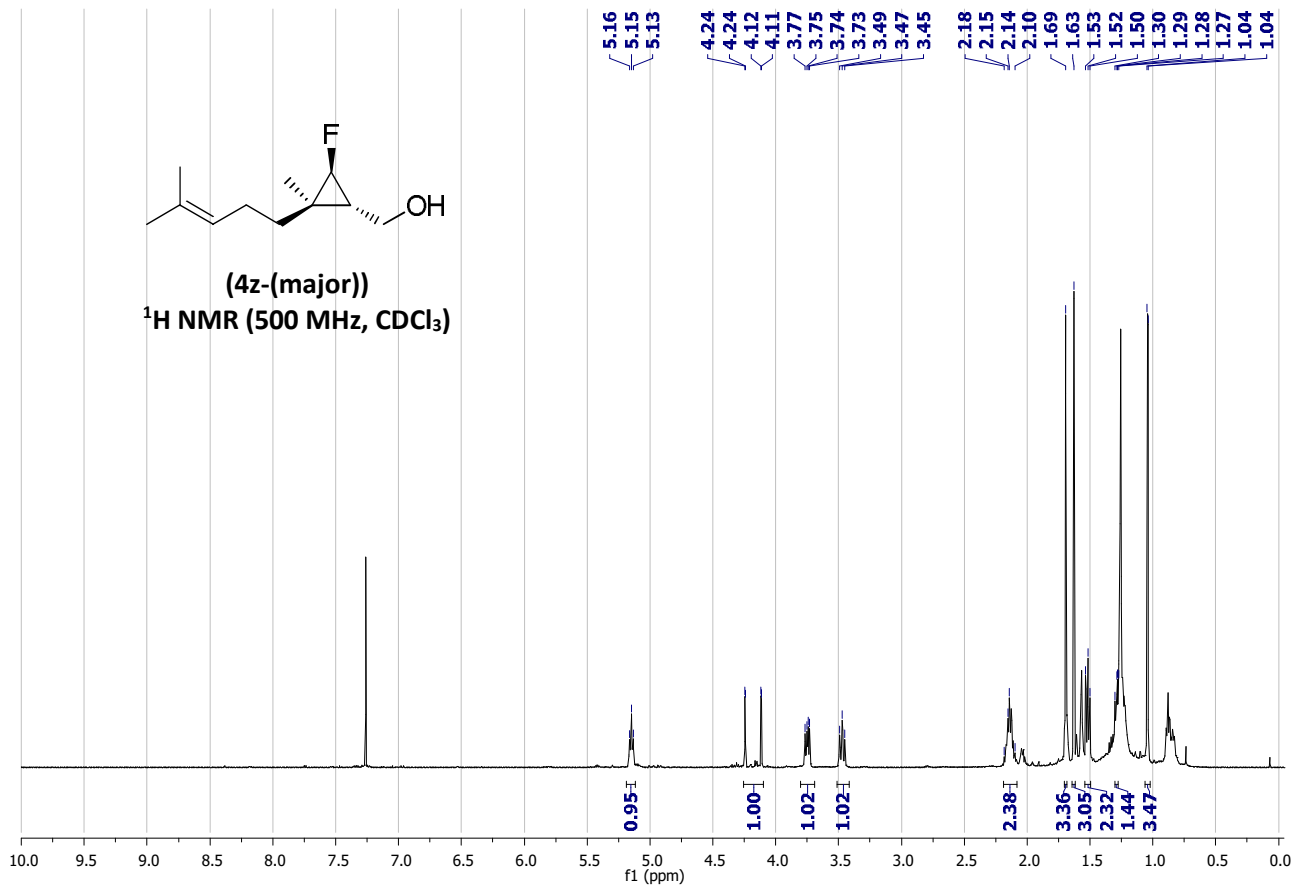


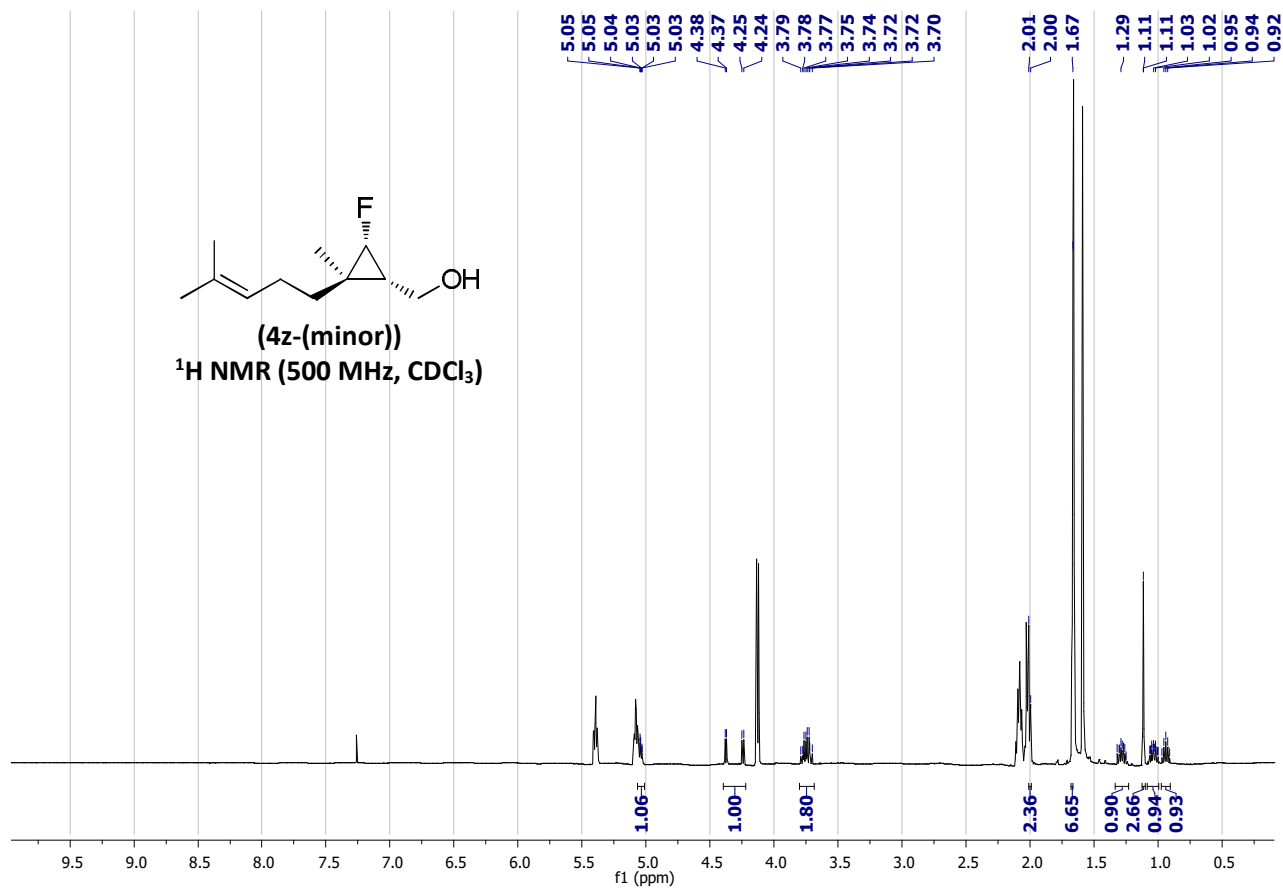
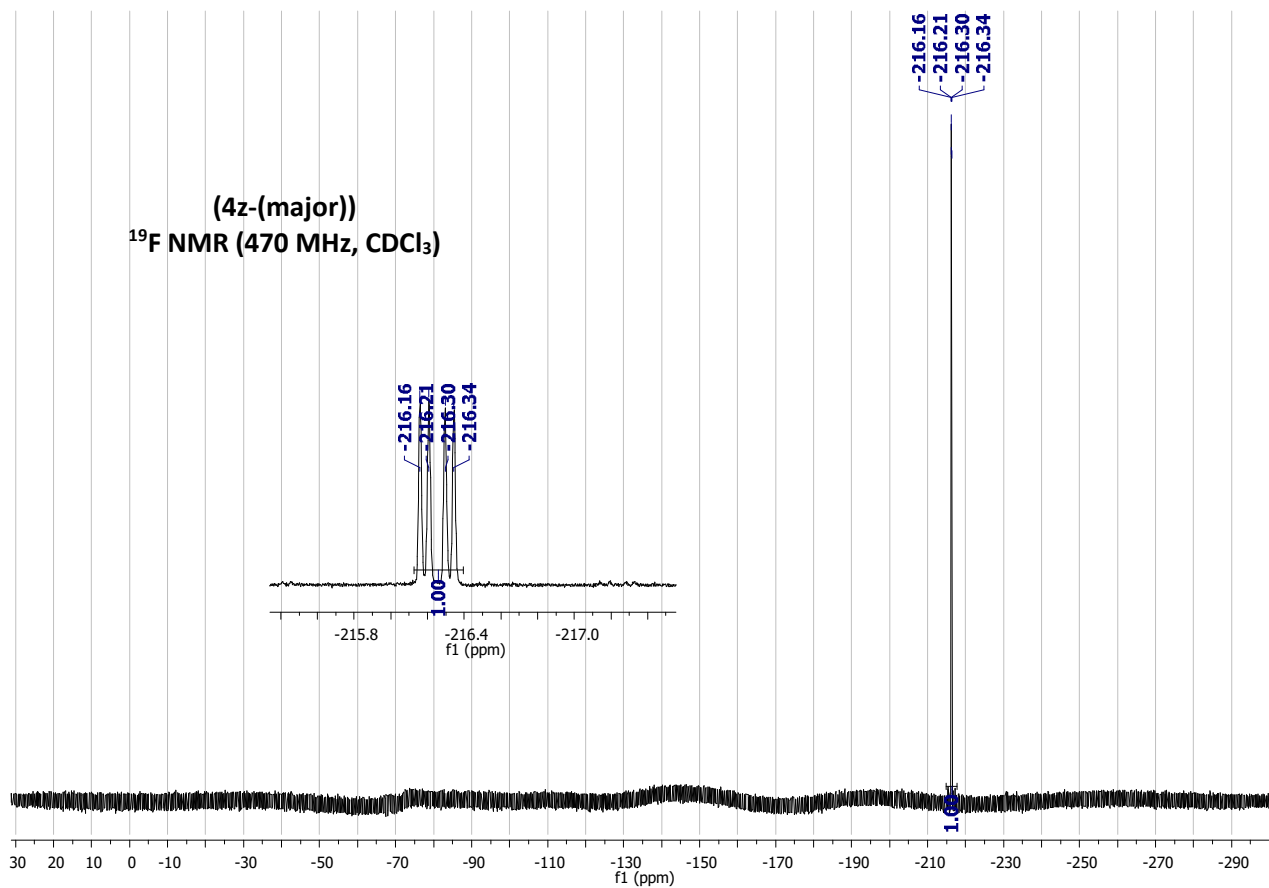


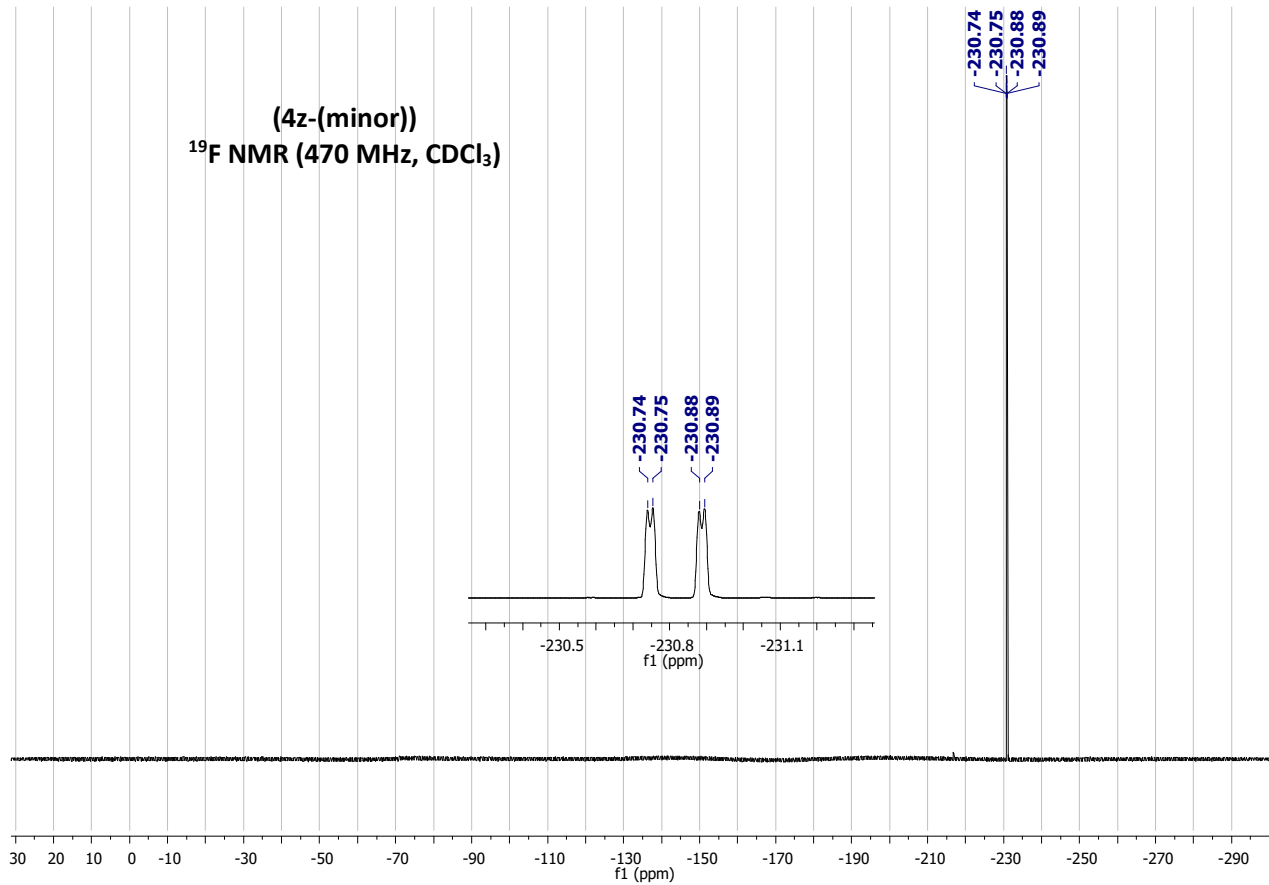
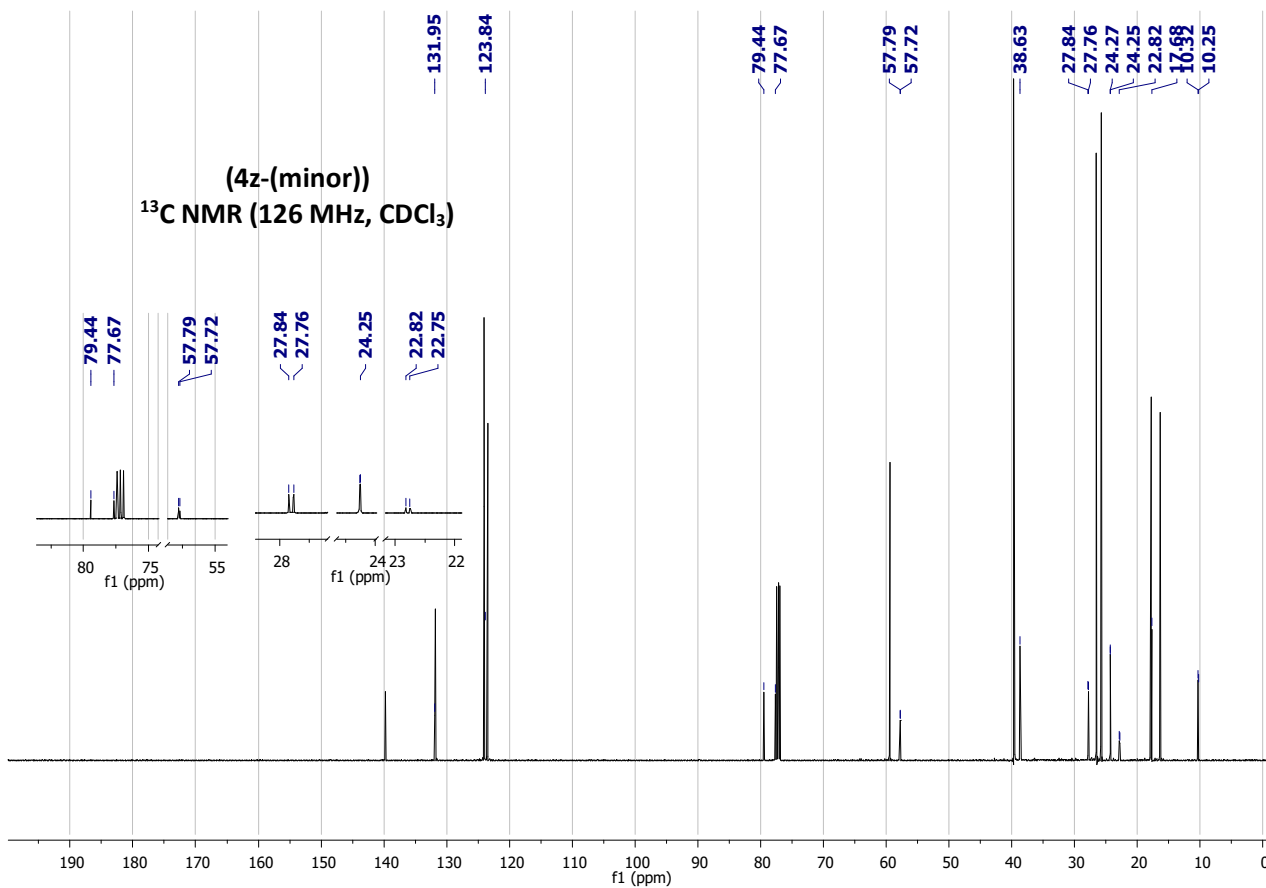


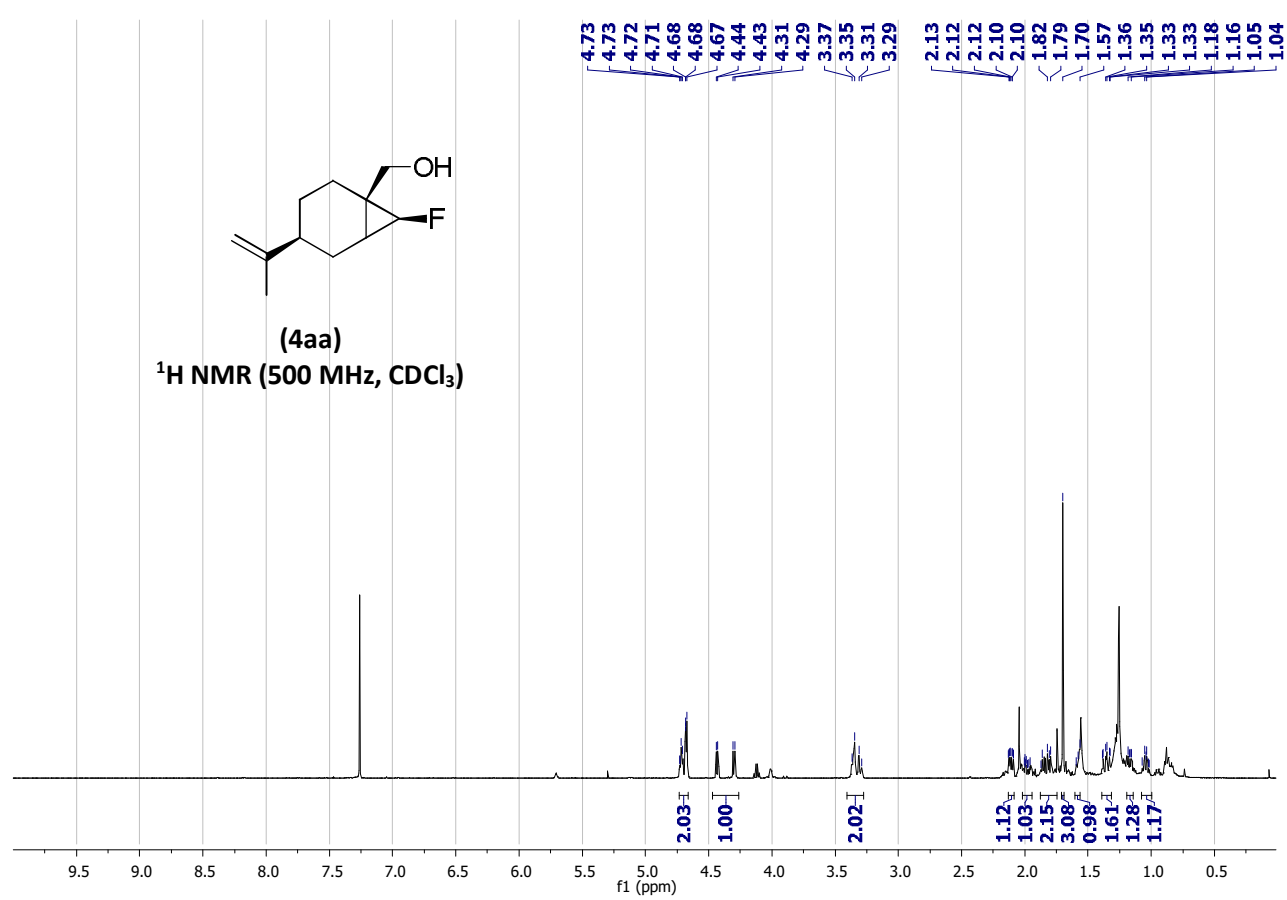
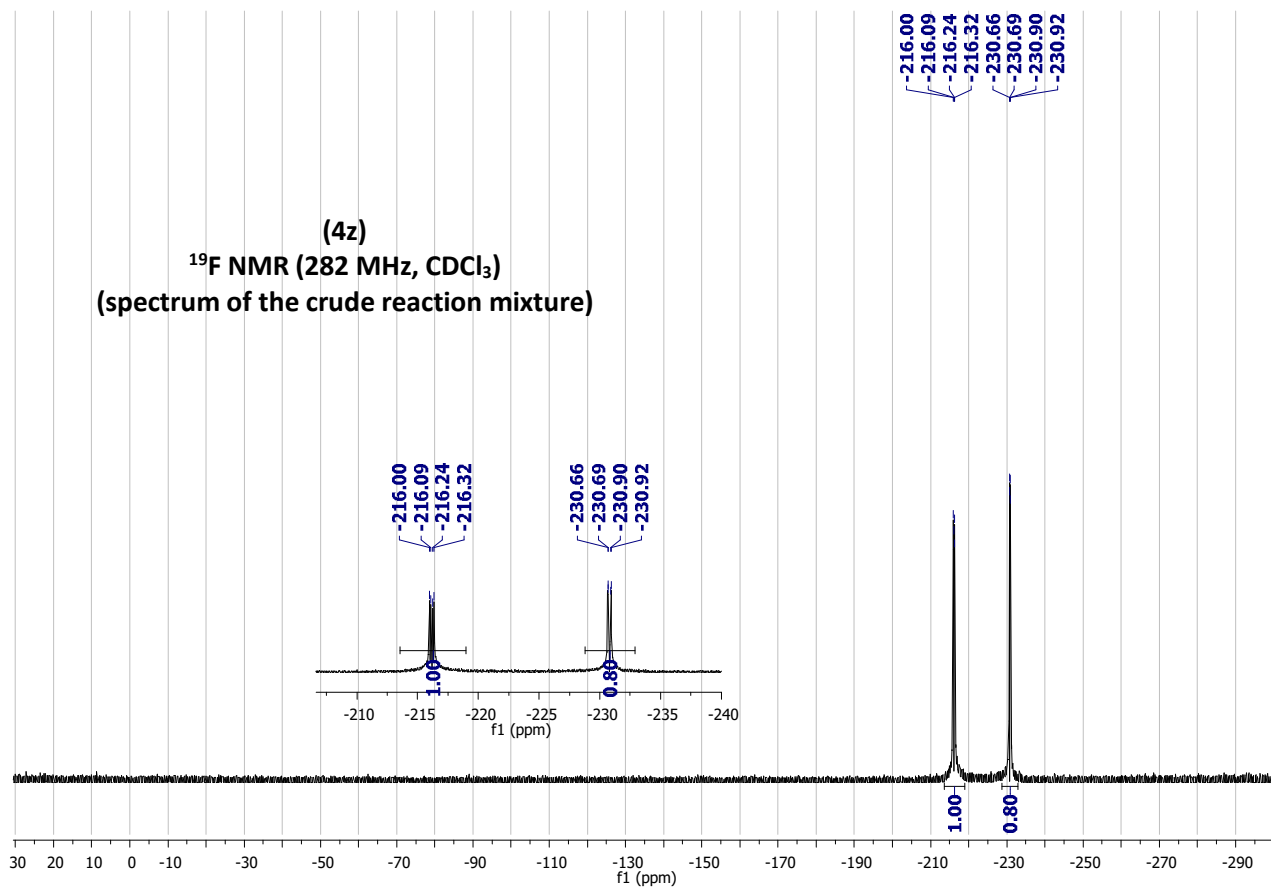


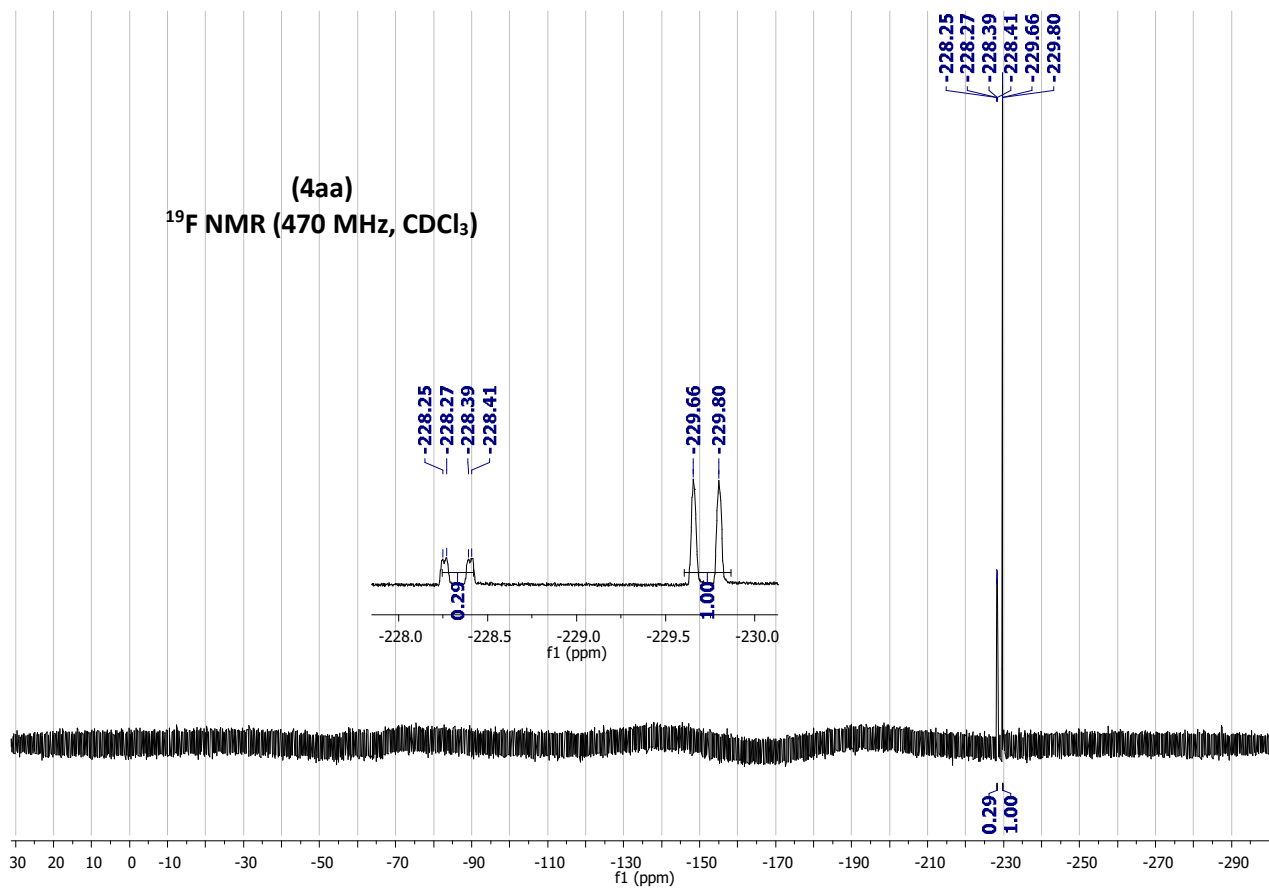
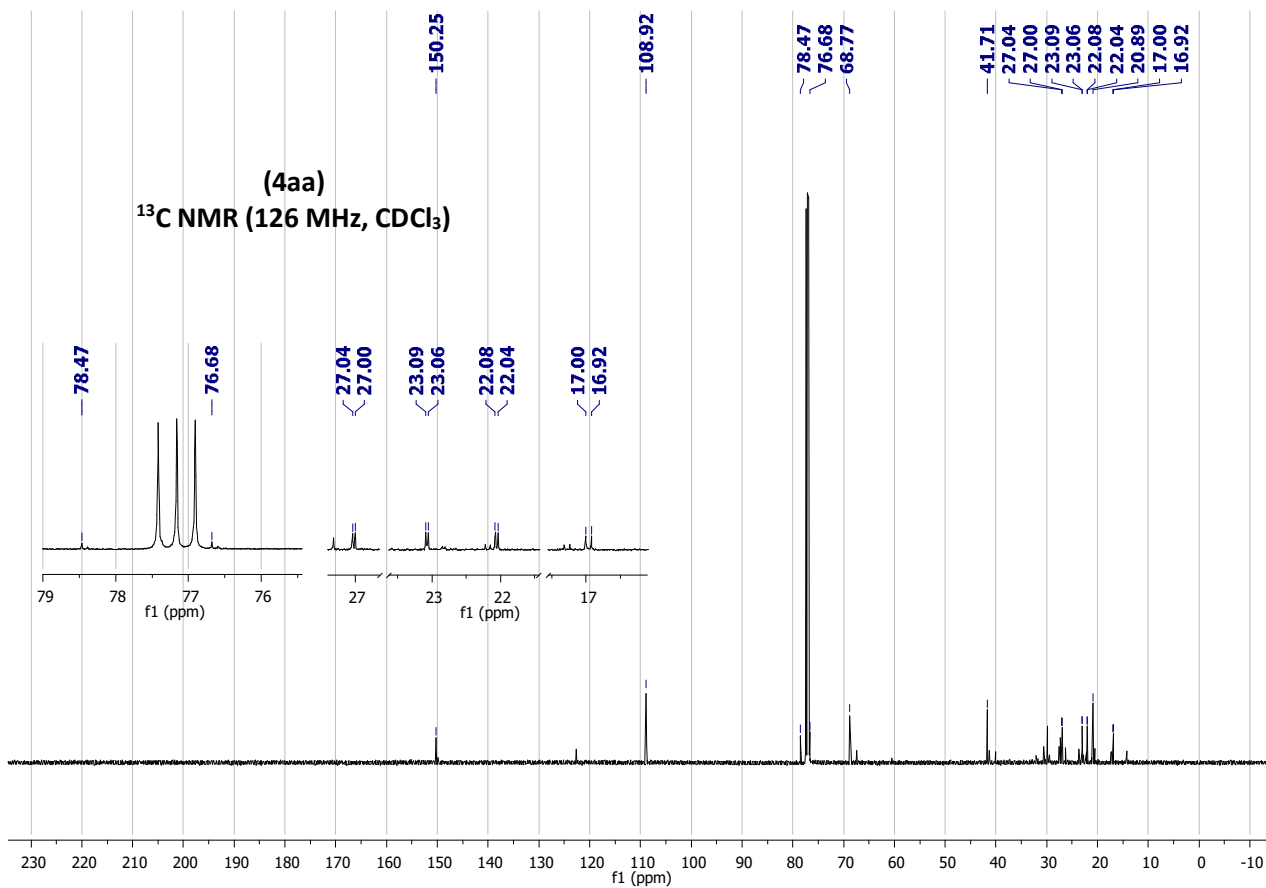


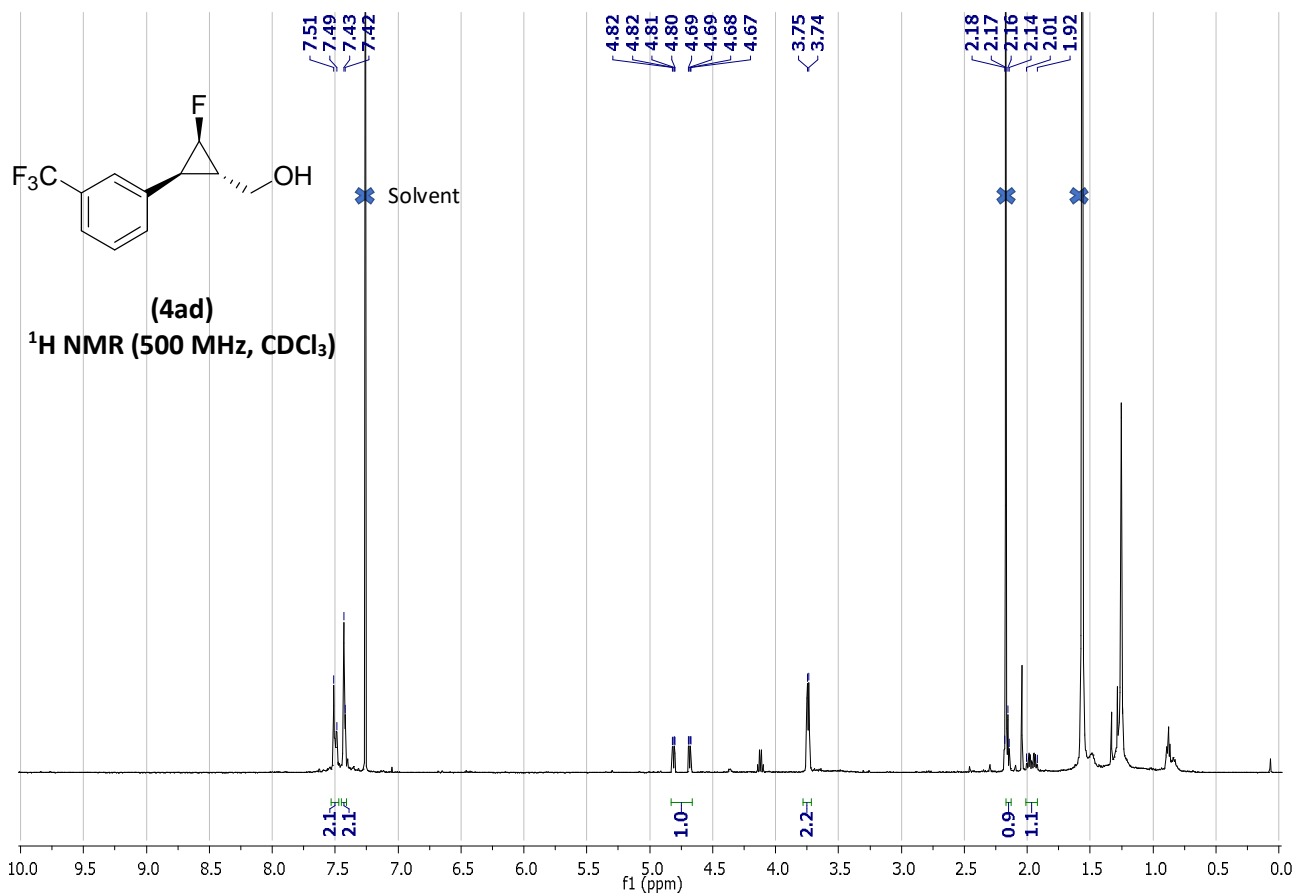
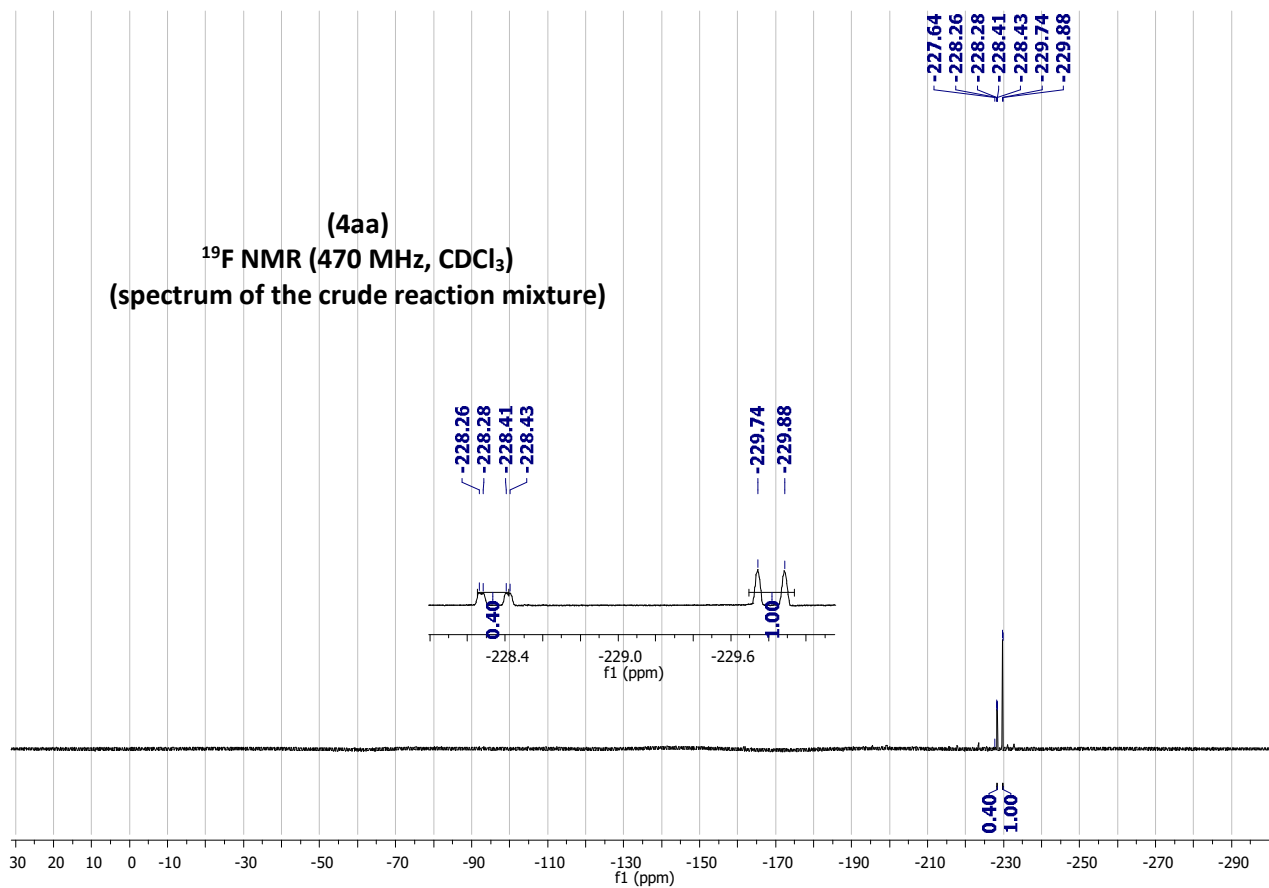


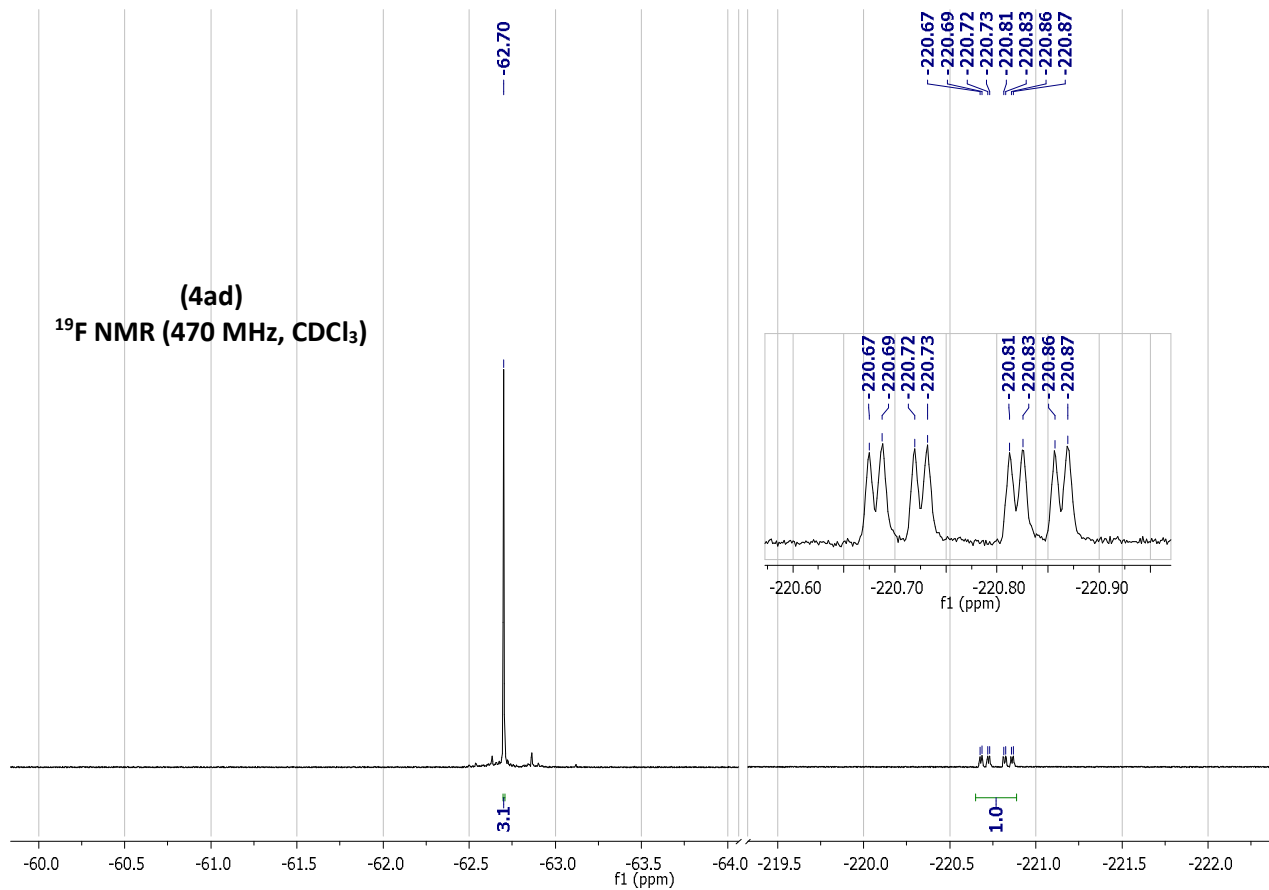
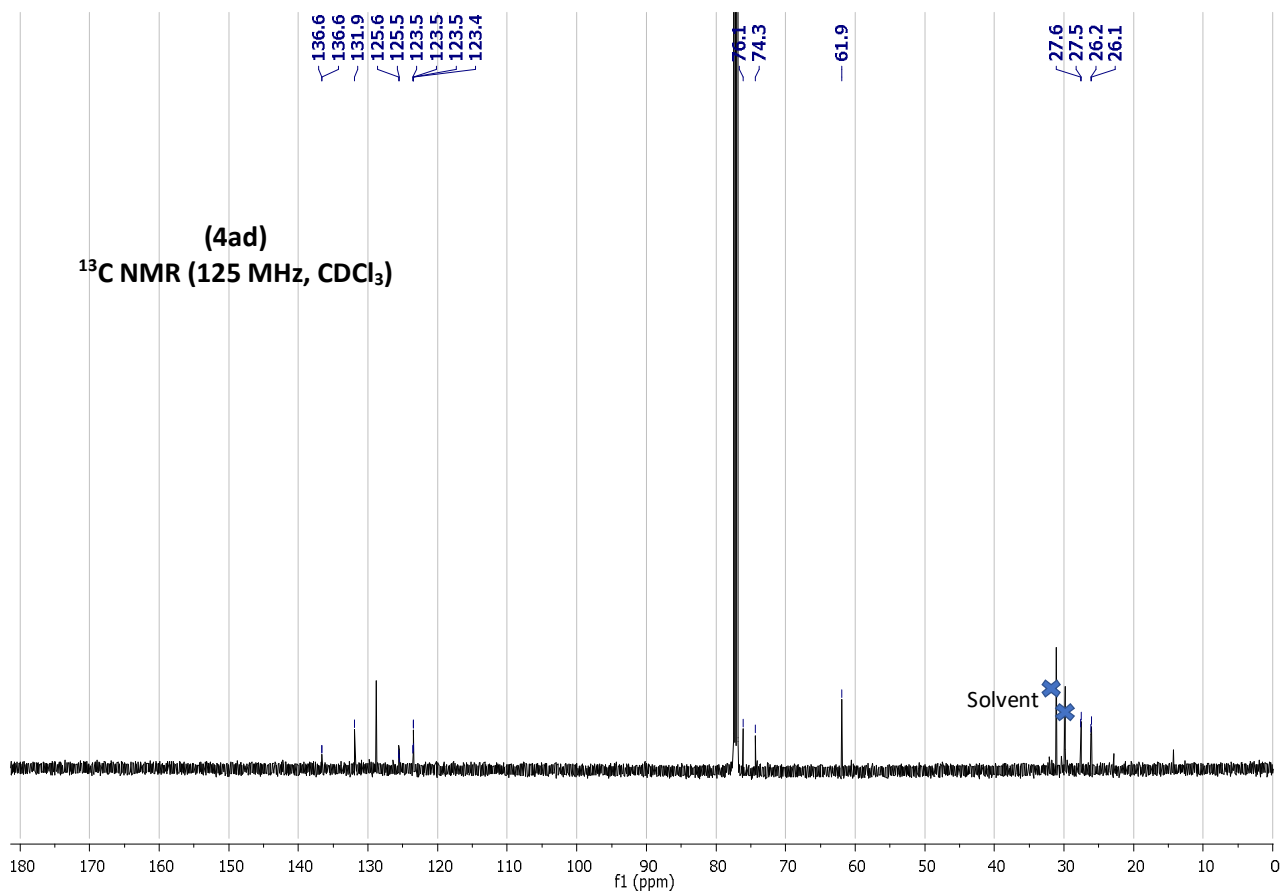












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