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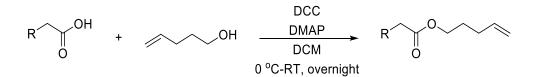
I. Supplemental Methods

1.1 General Information

All reagents were purchased from commercially available sources and used without further purification. All reactions were monitored by either ¹H NMR or thin layer chromatography (TLC) carried out on 0.25 mm pre-coated silica plates (F-254) purchased from Silicycle, Quebec, Canada, using shortwave UV light as visualizing agent and KMnO4 or phosphomolybdic acid (PMA) as developing agents. Flash column chromatography was performed using SiliaFlash-P60 silica gel (40 – 63 μ m) purchased from Silicycle, Quebec, Canada. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker DRX-600 spectrometers operating at 600 MHz for proton nuclei, 151 MHz for carbon nuclei and 565 MHz for fluorine nuclei were calibrated using residual undeuterated solvent as an internal reference (CDCl3: 7.26 ppm ¹H NMR and 77.00 ppm ¹³C NMR). PR160L 390 nm LEDs (25% intensity) from Kessil Lights were used as light source. For reporting NMR peak multiplicities, the following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet. High-resolution mass spectra (HRMS) or mass spectra (MS) were recorded on an Agilent UHPLC TOF mass spectrometer using electrospray ionization time-of-flight (ESI-TOF), chemical ionization timeof-flight (CI-TOF), atmospheric pressure chemical ionization (APCI) or gas chromatographymass spectrometry (GC-MS).

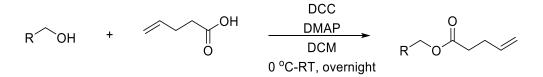
1.2 General Procedures for Substrate Synthesis

General Procedure 1 for the Synthesis of Unactivated Alkenes



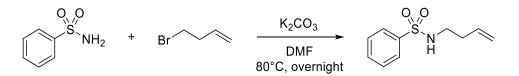
To an RB flask were added 5-pentenol (4.9 mmol, 1.96 equiv), carboxylic acid (2.5 mmol, 1.0 equiv), 4-dimethylamino pyridine (0.24 mmol, 0.097 equiv), and a stir bar. The RB flask was then evacuated and backfilled with nitrogen gas three times. Dry dichloromethane (0.225 M) was added via syringe to the RB flask, dissolving the solid components. The RB flask was then placed in an ice bath positioned on top of a stirring plate. Dicyclohexyl carbodiimide (4.85 mmol, 1.94 mmol) was added to the mixture via syringe dropwise over a period of 5 minutes. The ice bath was then removed, allowing the reaction to return to room temperature. The reaction was left to stir overnight. Following reaction, the mixture was concentrated through rotary evaporation. Subsequent flash column chromatography (hexanes/EtOAc) allowed for isolation of the ester.¹⁻²

General Procedure 2 for the Synthesis of Unactivated Alkenes



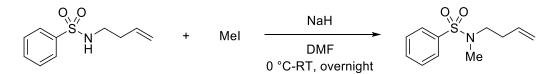
To an RB flask were added 5-pentenoic acid (2.5 mmol, 1.0 equiv), alcohol (4.9 mmol, 1.96 equiv), 4-dimethylamino pyridine (0.24 mmol, 0.097 equiv), and a stir bar. The RB flask was then evacuated and backfilled with nitrogen gas three times. Dry dichloromethane (0.225 M) was added via syringe to the RB flask, dissolving the solid components. The RB flask was then placed in an ice bath positioned on top of a stirring plate. Dicyclohexyl carbodiimide (4.85 mmol, 1.94 mmol) was added to the mixture via syringe dropwise over a period of 5 minutes. The ice bath was then removed, allowing the reaction to return to room temperature. The reaction was left to stir overnight. Following reaction, the mixture was concentrated through rotary evaporation. Subsequent flash column chromatography (hexanes/EtOAc) allowed for isolation of the ester.¹⁻²

Procedure for the Synthesis of N-(but-3-en-1-yl)benzenesulfonamide



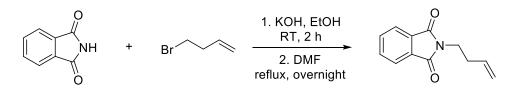
To an RB flask were added benzenesulfonamide (944 mg, 6.0 mmol), 4-bromobut-1-ene (0.8 mL, 6.0 mmol), dimethylformamide (30 mL), and a stir bar. Potassium carbonate (830 mg, 6.0 mmol) was added to the reaction mixture. After stirring overnight at 80 °C, the mixture was cooled to room temperature and quenched with water. The reaction mixture was then washed with brine and extracted with diethyl ether. The organic layer was concentrated through rotary evaporation. Subsequent flash column chromatography (hexanes/EtOAc) (3:1) allowed for isolation of *N*-(but-3-en-1-yl)benzenesulfonamide.³

Procedure for the Synthesis of N-(but-3-en-1-yl)-N-methylbenzenesulfonamide



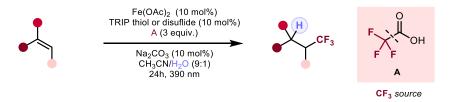
To an RB flask were added sodium hydride (60% in mineral oil, 240 mg, 6 mmol), dimethylformamide (25 mL), a solution of *N*-(but-3-en-1-yl)benzenesulfonamide (1.20 g, 5 mmol) in DMF (5 mL), and a stir bar in an ice bath at 0 °C. The reaction mixture was brought to room temperature and stirred for 30 minutes. The reaction mixture was cooled to 0 °C in an ice bath again, and a solution of methyl iodide (1.06 g, 7.5 mmol) in DMF (5 mL) was added dropwise over a period of 5 minutes by syringe. The reaction mixture was brought to room temperature and left to run overnight. The reaction mixture was quenched with a saturated aqueous solution of sodium bicarbonate. The mixture was then washed with brine and extracted with diethyl ether. The organic phase was dried over sodium sulfate and concentrated through rotary evaporation. Subsequent flash column chromatography (hexanes/EtOAc) (10:1) produced *N*-(but-3-en-1-yl)-*N*-methylbenzenesulfonamide.⁴

Procedure for the Synthesis of 2-(but-3-en-1-yl)isoindoline-1,3-dione



To an RB flask were added phthalimide (1.71 g, 11.6 mmol), potassium hydroxide (0.650 g, 11.6 mmol), ethyl alcohol (20 mL), and a stir bar. The reaction mixture was stirred at room temperature for 2 h and evaporated to remove EtOH. The resulting residue was then dissolved in dimethylformamide (15 mL) and 4-bromobut-1-ene (1.10 mL, 12.8 mmol) was added. The reaction mixture was stirred at reflux overnight. The reaction mixture was cooled, diluted with ethyl acetate, and quenched with saturated sodium bicarbonate. The mixture was then washed with brine. The extracted organic layer was dried over sodium sulfate and concentrated through rotary evaporation. Subsequent flash column chromatography (hexanes/EtOAc) (10:1) produced 2-(but-3-en-1-yl)isoindoline-1,3-dione.⁵

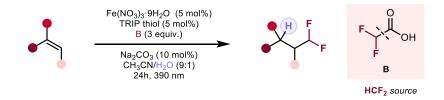
1.3 General Procedures for Photocatalytic Hydrofluoroalkylation



General Procedure A for hydrotrifluoromethylation of alkenes

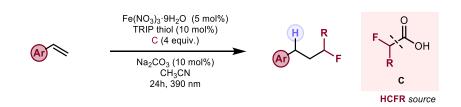
Fe(OAc)₂ (10 mol%, 0.1 equiv.), Na₂CO₃ (10 mol%, 0.1 equiv.) and TRIP disulfide (10 mol%, 0.1 equiv.) (in the case using TRIP thiol, HAT reagent was added via syringe after backfilling with N₂) was added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N₂ (repeated for 4 times), followed by addition of alkenes (0.1 mmol, 1.0 equiv.) and CF₃COOH (0.30 mmol, 3.0 equiv) in MeCN/H₂O (9:1, 0.1 M in regard to alkenes) via syringe under N₂. The reaction mixture was placed under 390nm Kessil® light after sealing the punctured holes of the vial cap with vacuum grease and electric tape/parafilm for better air-tight protection and allowed to react at room temperature for 24 h. Following this, the reaction mixture was filtered through a pad of celite which was subsequently rinsed with DCM. The filtrate was concentrated, and the residue was then purified by flash column chromatography to give the corresponding hydrotrifluoromethylated products.

General Procedure B for hydrodifluoromethylation of alkenes



Fe(NO₃)₃·9H₂O (5 mol%, 0.05 equiv.), Na₂CO₃ (10 mol%, 0.1 equiv.) was added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N₂ (repeated for 4 times), followed by addition of alkenes (0.1 mmol, 1.0 equiv.), HCF₂COOH (0.30 mmol, 3.0 equiv) and TRIP thiol (5 mol%, 0.05 equiv.) in MeCN/H₂O (9:1, 0.1 M in regard to alkenes) via syringe under N₂. The reaction mixture was placed under 390nm

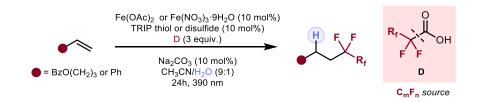
Kessil® light after sealing the punctured holes of the vial cap with vacuum grease and electric tape/parafilm for better air-tight protection and allowed to react at room temperature for 24 h. Following this, the reaction mixture was filtered through a pad of celite which was subsequently rinsed with DCM. The filtrate was concentrated, and the residue was then purified by flash column chromatography to give the corresponding hydrodifluoromethylated products.



General Procedure C for hydromonofluoromethylation of alkenes

Fe(NO₃)₃·9H₂O (5 mol%, 0.05 equiv.), Na₂CO₃ (10 mol%, 0.1 equiv.) was added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N₂ (repeated for 4 times), followed by addition of alkenes (0.1 mmol, 1.0 equiv.), H₂CFCOOH (0.40 mmol, 4.0 equiv) and TRIP thiol (10 mol%, 0.1 equiv.) in MeCN (0.1 M in regard to alkenes) via syringe under N₂. The reaction mixture was placed under 390nm Kessil® light after sealing the punctured holes of the vial cap with vacuum grease and electric tape/parafilm for better air-tight protection and allowed to react at room temperature for 24 h. Following this, the reaction mixture was filtered through a pad of celite which was subsequently rinsed with DCM. The filtrate was concentrated, and the residue was then purified by flash column chromatography to give the corresponding hydromonofluoroalkylated products.

General Procedure D for hydro(perfluoro)alkylation of alkenes



Fe salt (10 mol%, 0.1 equiv.), Na₂CO₃ (10 mol%, 0.1 equiv.) and TRIP disulfide (10 mol%, 0.1 equiv.) (in the case using TRIP thiol, HAT reagent was added via syringe after backfilling with N_2) was added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N_2 (repeated for 4 times), followed by addition of alkenes (0.1 mmol, 1.0 equiv.) and (perfluoro)alkyl carboxylic acid (0.30 mmol, 3.0 equiv) in MeCN/H2O (9:1, 0.1 M in regard to alkenes) via syringe under N_2 . The reaction mixture was placed under 390nm Kessil® light after sealing the punctured holes of the vial cap with vacuum grease and electric tape/parafilm for better air-tight protection and allowed to react at room temperature for 24 h. Following this, the reaction mixture was filtered through a pad of celite which was subsequently rinsed with DCM. The filtrate was concentrated, and the residue was then purified by flash column chromatography to give the corresponding hydroperfluoroalkylated products.

II. Supplemental Discussion

2.1 Optimization of Hydrotrifluoromethylation

BzO	metal source (5 mol%) TRIP disulfide (5 mol%) <u>A (2 equiv.)</u> Na ₂ CO ₃ (10 mol%) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h	F F F A
	GH3GN/H2G (5.1, 0.1M), 390111, 2411	CF ₃ source
entry	metal source	yield
1	Fe(acac) ₃	ND ^a
2	Fe(NO ₃) ₃ ·9H ₂ O	32
3	FeCl ₃ ·6H ₂ O	56
4	Fe(OTf) ₂	60
5	FeCl ₂	72
6	Fe(OAc) ₂	68
7	Cu(MeCN) ₄ BF ₄ ; Cu(OTf) ₂	ND ^a

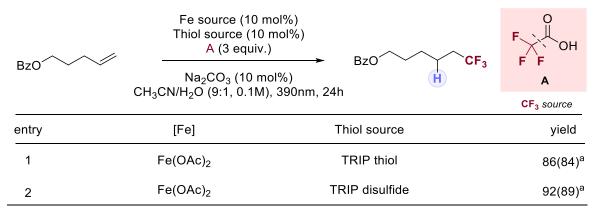
^a Almost full recovery of starting material.

Supplemental Table 1. Catalyst screening.

BzO	Fe source (5 mol%) TRIP disulfide (5 mol%) A (2 equiv.) Na ₂ CO ₃ (10 mol%) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h H BzO H $From CF_3$	
entry	[Fe]	CF ₃ source
^a 1	FeCl ₂	76
^{a,b} 2	FeCl ₂	80
ag	Fe(OAc) ₂	74
^{a,b} 4	Fe(OAc) ₂	92

^a10 mol% of [Fe] and 10 mol% of thiol/disulfide. ^bwith 3 equiv. of CF_3COOH .

Supplemental Table 2. Catalyst, TFA loading screening.



^a isolated yield in parentheses.

Supplemental Table 3. HAT reagents comparison in hydrotrifluoromethylation.

BzO	Fe(OAc) ₂ (10 mol%) TRIP thiol (10 mol%) A (3 equiv.) Na ₂ CO ₃ (10 mol%) Solvent/H ₂ O (9:1, 0.1M), 390nm, 24h	BzO CF ₃	F F A CF ₃ source
entry	Solvent		yield
1	DCM		trace
2	THF		20
3	EA		42
4	Acetone		76
BzO	Fe(OAc) ₂ (10 mol%) TRIP thiol (10 mol%) A (3 equiv.) Na ₂ CO ₃ (x quiv.)	BzO CF ₃	F F F A
BzO	TRIP thiol (10 mol%) A (3 equiv.)	Ĥ	FF
BzO	TRIP thiol (10 mol%) A (3 equiv.) Na ₂ CO ₃ (x quiv.)	Ĥ	F F A
	TRIP thiol (10 mol%) A (3 equiv.) Na ₂ CO ₃ (x quiv.) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h	Ĥ	F F A CF ₃ source
entry	TRIP thiol (10 mol%) <u>A (3 equiv.)</u> Na ₂ CO ₃ (x quiv.) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h	Ĥ	F F A CF ₃ source yield
entry 1	TRIP thiol (10 mol%) A (3 equiv.) Na ₂ CO ₃ (x quiv.) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h x no base	Ĥ	F F A CF ₃ source yield 72
entry 1 2	TRIP thiol (10 mol%) A (3 equiv.) Na ₂ CO ₃ (x quiv.) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h x no base 10 mol%	Ĥ	F F A CF ₃ source yield 72 86
entry 1 2 3	TRIP thiol (10 mol%) A (3 equiv.) Na ₂ CO ₃ (x quiv.) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h x no base 10 mol% 20 mol%	Ĥ	F F A CF ₃ source yield 72 86 80

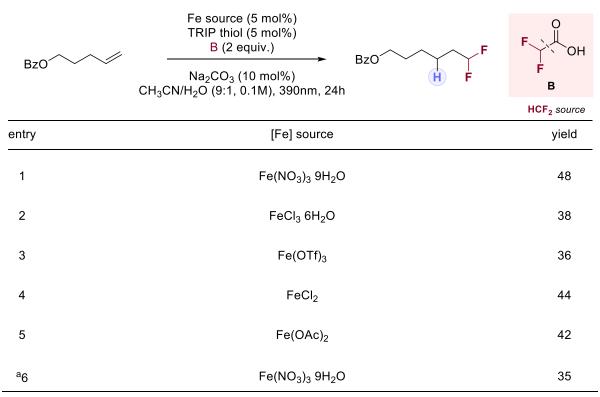
Supplemental Table 5. Base additive loading screening

BzO	Fe(OAc) ₂ (10 mol%) TRIP thiol or disulfide (10 mol%) <u>A (3 equiv.)</u> Na ₂ CO ₃ (10 mol%) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h $BzO \qquad \qquad$	F F F A $CF_3 source$
entry	Deviations from standard conditions	yield
1	no Fe	ND ^a ; ND ^b
2	no light	ND ^a ; ND ^b
3	no HAT reagent	trace ^a ; trace ^b
4	no water	18 ^a ; 24 ^b

^a with TRIP thiol. ^b with TRIP disulfide.

Supplemental Table 6. Control experiments.

2.2 Optimization of Hydrodifluoromethylation

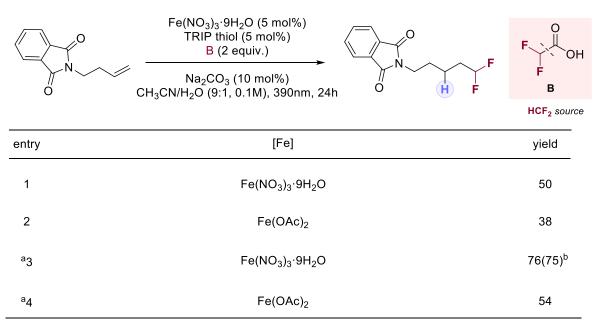


^a10 mol% of [Fe] and TRIP disulfide.

Supplemental Table 7. Iron catalyst screening

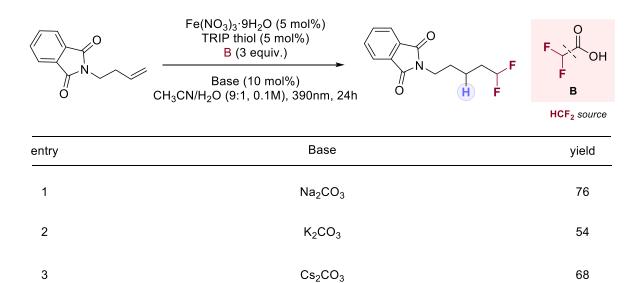
BzO	Fe source (5 mol%) TRIP thiol or disulfide (5 mol%) B (2 equiv.) Na ₂ CO ₃ (10 mol%) CH ₃ CN/H ₂ O (9:1, 0.1M), 390nm, 24h	BzO F	F B
			HCF ₂ source
entry	[Fe]	Thiol source	yield
1	Fe(NO ₃) ₃ 9H ₂ O	TRIP thiol	52
2	Fe(NO ₃) ₃ 9H ₂ O	TRIP disulfide	48
3	Fe(OAc) ₂	TRIP thiol	46
4	Fe(OAc) ₂	TRIP disulfide	42

Supplemental Table 8. The comparison between TRIP thiol and TRIP disulfide as competent HAT reagents in hydrodifluoromethylation.



2-(but-3-en-1-yl)isoindoline-1,3-dione was used as substrate due to more precise NMR integration. ^a 3 equiv. of HCF₂COOH. ^b isolated yield in parentheses.

Supplemental Table 9. Loading of difluoroacetic acid screening



Supplemental Table 10. Base additive screening

Bz0	$\begin{array}{c} Fe(NO_3)_3 \cdot 9H_2O \ (5 \ mol\%) \\ Thiol \ source \ (5 \ mol\%) \\ \hline B \ (3 \ equiv.) \\ \hline Na_2CO_3 \ (10 \ mol\%) \\ CH_3CN/H_2O \ (9:1, \ 0.1M), \ 390nm, \ 24h \end{array} BzO \begin{array}{c} F \\ \hline F \end{array}$	F F B HCF ₂ source
entry	thiol source	yield
1	4-CF3-thiolphenol	60
2	4-CI-thiolphenol	74
3	4-MeO-thiolphenol	79
4	3,5-CF3-thiolphenol	51
5	2-MeO-thiolphenol	58
6	2-CO2Me-thiolphenol	68
7	TRIP thiol	93(89) ^a

^aisolated yield in parentheses.

Supplemental Table 11. Aryl thiol screening (with pent-4-en-1-yl benzoate as substrate).

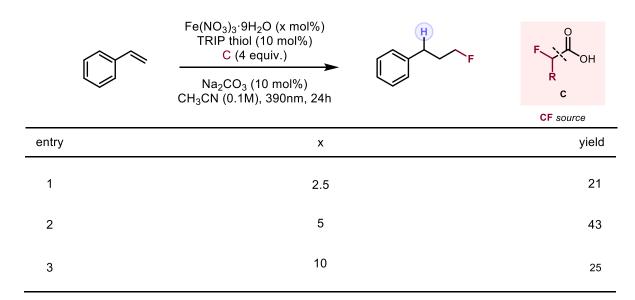
2.3 Optimization of Hydromonoluoromethylation

	$ \begin{array}{c} Fe(NO_3)_3 \cdot 9H_2O (10 \text{ mol}\%) \\ TRIP \text{ thiol (10 mol}\%) \\ C (3 \text{ equiv.}) \\ \hline Na_2CO_3 (10 \text{ mol}\%) \\ CH_3CN (0.1M), 390nm, 24h \end{array} $	F R C C F source
entry	[Fe]	yield
1	Fe(NO ₃) ₃ ·9H ₂ O	25
2	FeCl ₃ ·6H ₂ O	trace
3	Fe(OAc) ₂	13
4	Fe ₂ (C ₂ O ₄) ₃ ·6H ₂ O (5 mol%)	trace
5	Fe ₂ (SO ₄) ₃ ·5H ₂ O (5 mol%)	trace

Supplemental Table 12. Iron catalyst screening.

	Fe(NO ₃) ₃ ·9H ₂ O (10 mol%) Thiol source (10 mol%) C (3 equiv.) Na ₂ CO ₃ (10 mol%) CH ₃ CN (0.1M), 390nm, 24h	F R C C C C F source
entry	[Fe]	yield
1	TRIP thiol	25
2	2-MeO-thiolphenol	messy
3	4-F-thiolphenol	messy
4	TRIP silanethiol (5 mol%)	messy
5	TRIP disulfide (5 mol%)	messy

Supplemental Table 13. Thiol/disulfide screening.



Supplemental	Table 14.	Catalyst	loading	screening.
The second secon				

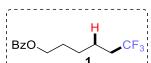
	$Fe(NO_3)_3 \cdot 9H_2O (5 \text{ mol}\%)$ $TRIP \text{ thiol (10 mol}\%)$ $C (x \text{ equiv.})$	F COH
	Na ₂ CO ₃ (10 mol%) CH ₃ CN (0.1M), 390nm, 24h	R C
		CF source
entry	X	yield
1	3	28
2	4	43
3	6	42

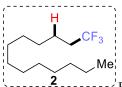
Supplemental Table 15. Monofluoroacetic acid loading screening.

	Fe(NO ₃) ₃ ·9H ₂ O (5 mol%) TRIP thiol (10 mol%) C (4 equiv.) Na ₂ CO ₃ (10 mol%) solvent (0.1M), 390nm, 24h	F R C
		CF source
entry	Solvent	yield
1	CH ₃ CN	43
2	CH ₃ CN/H ₂ O (9:1)	42
3	DCE; DCE/H ₂ O (1:1)	ND

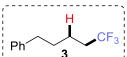
Supplemental Table 16. Solvent screening.

2.4 Characterization of Corresponding Products

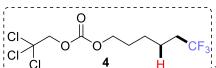




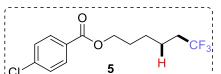
¹Chloroform-*d*) δ 2.10 – 2.00 (m, 2H), 1.59-1.50 (m, 2H), 1.41 – 1.26 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 127.35 (q, *J* = 276.2 Hz), 33.78 (q, *J* = 28.3 Hz), 31.96, 29.67, 29.63, 29.60, 29.41, 29.39, 29.23, 28.75, 22.73, 21.88 (q, *J* = 2.9 Hz)., 14.13. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.48 (t, *J* = 11.0 Hz). GC-MS: [M]+ calcd. for C13H25F3: 238.1908; Found 238



¹ Chloroform-*d*) δ 7.29 (t, J = 7.6 Hz, 2H), 7.23 – 7.14 (m, 3H), 2.64 (t, J = 7.6 Hz, 2H), 2.16 – 2.03 (m, 2H), 1.74-1.66 (m, 2H), 1.63 – 1.57 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 141.69, 128.42, 128.36, 127.18 (q, J = 276.3 Hz), 125.95, 35.50, 33.63 (q, J = 28.4 Hz), 30.47, 21.54 (q, J = 2.9 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.32 (t, J = 11.0 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.⁷

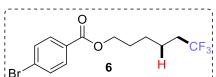


¹H NMR (600 MHz, Chloroform-*d*) δ 4.77 (s, 2H), 4.25 (t, J = 6.5 Hz, 2H), 2.15-2.03 (m, 2H), 1.81-1.70 (m, 2H), 1.66-1.58 (m, 2H), 1.55-1.44 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 154.03, 127.06 (q, J = 276.3 Hz), 94.46, 76.76, 68.74, 33.60 (q, J = 28.6 Hz), 28.22, 24.86, 21.57 (q, J = 2.9 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.39 (t, J = 10.7 Hz). HRMS APCI: [M+H]⁺ calcd. for C9H13Cl3F3O3: 330.9877; Found 330.9870

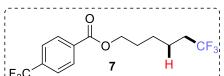


¹H NMR (600 MHz, Chloroform-*d*) δ 8.03 – 7.92 (m, 2H), 7.49 – 7.38 (m, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 2.18 – 2.03 (m, 2H), 1.87 – 1.74 (m, 2H), 1.69-1.60 (m, 2H), 1.56 – 1.48 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 165.75, 139.41, 130.94, 128.74, 127.11 (q, *J* = 276.3 Hz), 64.82, 33.64 (q, *J* = 28.4 Hz), 28.37, 25.28, 21.67 (q, *J* = 2.8 Hz). ¹⁹F NMR

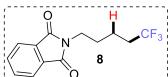
(565 MHz, Chloroform-*d*) δ -66.36 (t, *J* = 11.0 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.⁸



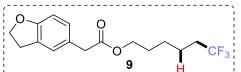
¹B¹ ¹H NMR (600 MHz, Chloroform-*d*) δ 7.94 – 7.85 (m, 2H), 7.63 – 7.55 (m, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 2.17 – 2.04 (m, 2H), 1.84 – 1.76 (m, 2H), 1.70 – 1.62 (m, 2H), 1.56 – 1.48 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 165.88, 131.74, 131.08, 129.20, 128.07, 127.10 (q, *J* = 276.2 Hz), 64.84, 33.63 (q, *J* = 28.5 Hz), 28.36, 25.27, 21.67 (q, *J* = 3.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.36 (t, *J* = 10.8 Hz). HRMS APCI: [M+H]⁺ calcd. for C13H15BrF3O2: 339.0202; Found 339.0199



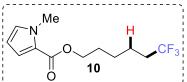
¹H NMR (600 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 4.37 (t, *J* = 6.5 Hz, 2H), 2.20 – 2.04 (m, 2H), 1.87-1.79 (m, 2H), 1.71 – 1.60 (m, 2H), 1.58-1.50 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 165.39, 134.49 (q, *J* = 32.7 Hz), 133.52, 129.96, 127.10 (q, *J* = 276.3 Hz), 125.45 (q, *J* = 3.8 Hz), 123.65 (q, *J* = 272.8 Hz), 65.14, 33.64 (q, *J* = 28.6 Hz), 28.35, 25.26, 21.68 (q, *J* = 2.8 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -63.13, -66.37 (t, *J* = 11.0 Hz). HRMS APCI: [M+H]⁺ calcd. for C13H15F6O2: 329.0971; Found 329.0967



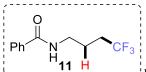
¹ Constant of the solution of the solution



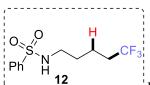
oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.14 – 7.09 (m, 1H), 6.99 (dd, J = 8.2, 1.9 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H), 4.56 (t, J = 8.7 Hz, 2H), 4.09 (t, J = 6.5 Hz, 2H), 3.53 (s, 2H), 3.19 (t, J = 8.7 Hz, 2H), 2.13 – 1.98 (m, 2H), 1.69-1.60 (m, 3H), 1.60 – 1.53 (m, 2H), 1.43-1.36 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 172.15, 159.27, 128.85, 127.39, 127.11 (q, J = 276.5 Hz), 125.91, 125.78, 109.19, 71.29, 64.35, 40.77, 33.60 (q, J = 28.4 Hz), 29.70, 28.20, 25.11, 21.56 (q, J = 3.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.36 (t, J = 11.0 Hz). HRMS APCI: [M+H]⁺ calcd. for C16H20F3O3: 317.1359; Found 317.1355



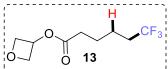
¹ Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 6.93 (dd, J = 4.0, 1.8 Hz, 1H), 6.78 (t, J = 2.2 Hz, 1H), 6.11 (dd, J = 3.9, 2.5 Hz, 1H), 4.23 (t, J = 6.5 Hz, 2H), 3.92 (s, 3H), 2.18 – 2.01 (m, 2H), 1.79 – 1.71 (m, 2H), 1.67-1.59 (m, 2H), 1.55-1.46 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 161.32, 129.52, 127.14 (q, J = 276.3 Hz), 122.51, 117.72, 107.83, 63.34, 36.81, 33.67 (q, J = 28.5 Hz), 28.52, 25.33, 21.66 (q, J = 3.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.38 (t, J = 11.0 Hz). HRMS APCI: [M+H]⁺ calcd. for C12H17F3NO2: 264.1206; Found 264.1201

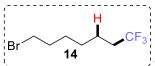


¹-------' Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.28 (s, 1H), 3.60-3.48 (m, 2H), 2.26 – 2.11 (m, 2H), 1.95-1.86 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 167.78, 134.28, 131.68, 127.90, 126.98 (q, J = 276.2 Hz), 126.85, 38.77, 31.36 (q, J = 29.1 Hz), 22.59 (q, J = 2.8 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.13 (t, J = 10.8 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.⁸

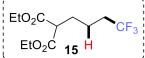


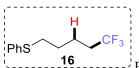
¹Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 4.61 (t, J = 6.4 Hz, 1H), 2.99 (q, J = 5.9 Hz, 2H), 2.07-1.97 (m, 2H), 1.59 – 1.53 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 139.81, 132.79, 129.21, 127.01, 126.88 (q, J = 276.3 Hz), 42.70, 33.16 (q, J = 28.7 Hz), 28.73, 19.05 (q, J = 3.2 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.34 (t, J = 11.0 Hz). HRMS APCI: [M+H]⁺ calcd. for C11H15F3NO2S: 282.0770; Found 282.0765



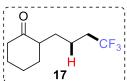


33.60, 32.44, 27.86, 27.74, 21.76 (q, J = 3.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.41 (t, J = 11.0 Hz). GC-MS: [M]+ calcd. for C7H12BrF3: 232.0074; Found 232.0

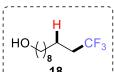




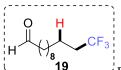
¹-------¹O</sup> Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.32 (m, 2H), 7.31-7.27 (m, 2H), 7.22 – 7.16 (m, 1H), 2.98 – 2.89 (m, 2H), 2.15 – 2.01 (m, 2H), 1.76-1.66 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 136.13, 129.44, 128.96, 127.01 (q, *J* = 276.4 Hz), 126.15, 33.34 (q, *J* = 28.8 Hz), 33.32, 28.16, 21.06 (q, *J* = 3.0 Hz). ¹⁹F NMR (565 MHz,) δ -66.35 (t, *J* = 10.8 Hz). GC-MS: [M]+ calcd. for C11H13F3S: 234.0690; Found 234.1



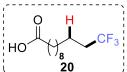
¹/₂-------¹/₂ Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 2.44-2.37 (m, 1H), 2.34 – 2.24 (m, 2H), 2.16 – 1.99 (m, 4H), 1.91 – 1.80 (m, 2H), 1.71-1.64 (m, 2H), 1.57 – 1.51 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 212.61, 127.11 (q, *J* = 276.3 Hz), 50.41, 42.14, 33.98, 33.97 (d, *J* = 28.5 Hz), 28.58, 28.00, 25.08, 19.78 (q, *J* = 3.1 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.38 (t, *J* = 10.7 Hz). GC-MS: [M+H]+ calcd. for C10H16F3O: 209.1148; Found 209.0



¹Chloroform-*d*) δ 3.57 (t, *J* = 6.7 Hz, 2H), 2.04 – 1.92 (m, 2H), 1.53-1.44 (m, 4H), 1.34-1.19 (m, 13H). ¹³C NMR (151 MHz, CDCl₃) δ 127.30 (q, *J* = 276.3 Hz), 63.04, 33.72 (q, *J* = 28.3 Hz) 32.77, 29.48, 29.37, 29.28, 29.16, 28.68, 25.72, 21.83 (q, *J* = 2.8 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.44 (t, *J* = 11.0 Hz). HRMS APCI: [M-H2O+H]⁺ calcd. for C11H20F3: 209.1512; Found 209.1507



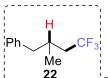
Chloroform-*d*) δ 9.77 (s, 1H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.10-2.00 (m, 2H), 1.66-1.60 (m, 2H), 1.55-1.49 (m, 2H), 1.39 – 1.26 (m, 16H). ¹³C NMR (151 MHz, CDCl₃) δ 202.91, 127.30 (d, *J* = 276.2 Hz), 43.91, 33.72 (q, *J* = 28.3 Hz), 29.30, 29.26, 29.14, 29.13, 28.67, 22.06, 21.83 (q, *J* = 2.9 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.41 (t, *J* = 11.0 Hz). GC-MS: [M+H]+ calcd. for C11H13F3S: 239.1618; Found 239.0



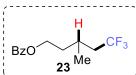
¹------² Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 2.35 (t, *J* = 7.5 Hz, 2H), 2.10-2.02 (m, 2H), 1.68-1.59 (m, 2H), 1.59-1.50 (m, 2H), 1.38 – 1.25 (m, 14H). ¹³C NMR (151 MHz, CDCl₃) δ 179.46, 127.31 (q, *J* = 276.3 Hz), 33.92, 33.73 (d, *J* = 28.3 Hz), 29.30, 29.27, 29.17, 29.14, 29.02, 28.68, 24.66, 21.83 (t, *J* = 3.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.42 (t, *J* = 11.0 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.⁸



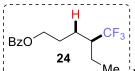
¹-----²**1**-----¹ Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 2.27-2.18 (m, 1H), 1.90-1.81 (m, 2H), 1.80 – 1.71 (m, 2H), 1.62 – 1.49 (m, 10H). ¹³C NMR (151 MHz, CDCl₃) δ 128.97 (q, *J* = 279.5 Hz), 41.92 (q, *J* = 24.4 Hz), 26.38, 26.29, 25.57 (q, *J* = 2.6 Hz), 25.11. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -73.34 (d, *J* = 9.8 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.¹⁰



¹-----² Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.30 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.5 Hz, 2H), 2.67 (dd, J = 13.6, 6.6 Hz, 1H), 2.53 (dd, J = 13.6, 7.5 Hz, 1H), 2.21 – 2.09 (m, 2H), 1.97 – 1.86 (m, 1H), 1.02 (d, J = 6.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 139.56, 129.17, 128.42, 127.19 (q, J = 277.5 Hz), 126.29, 43.22, 39.54 (q, J = 27.1 Hz), 29.65 (q, J = 2.3 Hz), 19.61. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -63.11 (t, J = 11.2 Hz). GC-MS: [M]+ calcd. for C11H13F3: 202.0969; Found 202.1

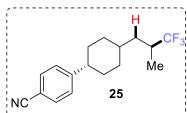


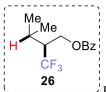
¹------- Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.59 – 7.54 (m, 1H), 7.47-7.41 (m, 2H), 4.42 – 4.34 (m, 2H), 2.26-2.15 (m, 1H), 2.15 – 2.08 (m, 1H), 2.08-1.97 (m, 1H), 1.97 – 1.88 (m, 1H), 1.76-1.66 (m, 1H), 1.12 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 164.67, 131.13, 128.30, 127.66, 126.54, 125.11 (q, *J* = 277.4 Hz), 60.59, 38.33 (q, *J* = 27.2 Hz), 33.41, 23.22 (q, *J* = 2.5 Hz), 17.75. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -63.30 (t, *J* = 11.1 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.⁶

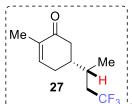


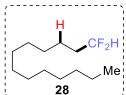
¹------<u>Me</u>-¹Prepared according to General Procedure A and obtained as colorless oil. 1.3:1 mixture of regioisomers. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.00-7.91 (m, 2H), 7.52-7.46 (m, 1H), 7.41-7.31 (m, 2H), 4.38-4.29 (m, 0.84H), 4.28-4.23 (m, 1.16H), 2.24-2.18 (m, 0.38H), 2.09 – 1.92 (m, 1.14H), 1.89 – 1.75 (m, 1.74H), 1.73 – 1.51 (m, 2.63H), 1.51 – 1.32 (m, 2.09H), 0.96-0.90 (m, 1.74H), 0.89-0.83 (m, 1.26H). ¹³C NMR (151 MHz, CDCl₃) δ 166.57, 166.41, 133.09, 132.98, 130.23, 130.03, 129.55, 129.53, 128.51 (q, J = 280.6 Hz), 128.43, 128.36 (q, J = 280.2 Hz), 128.40, 64.57, 62.35, 43.63 (q, J = 24.8 Hz), 39.69 (q, J = 25.7 Hz), 30.09 (q, J = 2.5 Hz), 27.24 (q, J = 2.6 Hz),

26.05, 23.83 (q, J = 2.6 Hz), 20.66 (q, J = 2.7 Hz), 19.95, 14.00, 11.16.¹⁹F NMR (565 MHz, Chloroform-*d*) δ -69.85 (d, J = 9.6 Hz), -70.50 (d, J = 9.7 Hz). HRMS APCI: [M+H]⁺ calcd. for C14H18F3O2: 275.1253; Found 275.1247



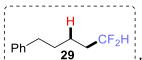


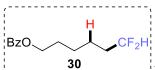


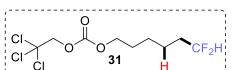


²⁰ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 5.79 (tt, *J* = 57.0, 4.6 Hz, 1H), 1.88-1.73 (m, 2H), 1.48-1.40 (m, 2H), 1.37 - 1.25 (m, 18H), 0.88 (t, 1.48-1.40 (m, 2H), 1.37 - 1.25 (m, 18H), 0.88 (t, 1.48-1.40 (m, 2H), 1.48-1.40 (m, 2H), 1.37 - 1.25 (m, 18H), 0.88 (t, 1.48-1.40 (m, 2H), 1.48-1.40 (m,

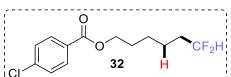
J = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 117.52 (t, J = 238.6 Hz), 34.10 (t, J = 20.6 Hz), 31.92, 29.65, 29.63, 29.59, 29.44, 29.37, 29.35, 29.07, 22.69, 22.13 (t, J = 5.4 Hz), 14.11. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.73 (dt, J = 57.1, 17.6 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.¹³



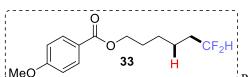




¹ H NMR (600 MHz, Chloroform-*d*) δ 5.81 (tt, *J* = 56.8, 4.4 Hz, 1H), 4.77 (s, 2H), 4.24 (t, *J* = 6.6 Hz, 2H), 1.90-1.79 (m, 2H), 1.78 – 1.72 (m, 2H), 1.54 – 1.44 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 154.04, 117.13 (t, *J* = 238.8 Hz), 94.47, 76.75, 68.90, 33.89 (t, *J* = 20.8 Hz), 28.35, 25.19, 21.69 (t, *J* = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.96 (dt, *J* = 56.8, 17.4 Hz). HRMS APCI: [M+H]⁺ calcd. for C9H14Cl3F2O3: 312.9971; Found 312.9967

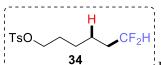


¹H NMR (600 MHz, Chloroform-*d*) δ 8.02 – 7.92 (m, 2H), 7.47 – 7.37 (m, 2H), 5.81 (tt, *J* = 56.9, 4.4 Hz, 1H), 4.32 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.76 (m, 4H), 1.57 – 1.47 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 165.77, 139.37, 130.94, 128.80, 128.73, 117.20 (t, *J* = 238.9 Hz), 64.94, 33.95 (t, *J* = 20.9 Hz), 28.51, 25.61, 21.79 (t, *J* = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.90 (dt, *J* = 57.2, 18.0 Hz). HRMS APCI: [M+H]⁺ calcd. for C13H16ClF2O2: 277.0801; Found 277.0796

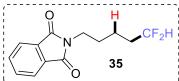


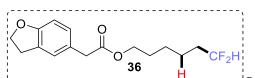
oil. ¹H NMR (600 MHz, Chloroform-d) δ 8.04 – 7.94 (m, 2H), 6.99 – 6.86 (m, 2H), 5.81 (tt, J = 56.9, 4.5 Hz, 1H),

4.30 (t, J = 6.5 Hz, 2H), 3.86 (s, 3H), 1.91-1.82 (m, 2H), 1.81 – 1.76 (m, 2H), 1.57-1.47 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 166.40, 163.34, 131.55, 122.81, 117.25 (t, J = 238.7 Hz), 113.61, 64.38, 55.44, 33.98 (t, J = 20.8 Hz), 28.60, 25.66, 21.84 (t, J = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.86 (dt, J = 56.7, 17.4 Hz). HRMS APCI: [M+H]⁺ calcd. for C14H19F2O3: 273.1297; Found 273.1293

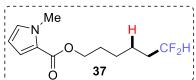


¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.83 – 7.75 (m, 2H), 7.39 – 7.32 (m, 2H), 5.76 (tt, *J* = 56.8, 4.4 Hz, 1H), 4.03 (t, *J* = 6.3 Hz, 2H), 2.45 (s, 3H), 1.82 – 1.72 (m, 2H), 1.70-1.63 (m, 2H), 1.44 – 1.34 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 144.81, 133.11, 129.89, 129.87, 127.88, 117.06 (t, *J* = 238.9 Hz), 70.14, 33.81 (t, *J* = 20.8 Hz), 28.62, 24.93, 21.63, 21.44 (t, *J* = 5.6 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -116.00 (dt, *J* = 57.0, 17.7 Hz). HRMS APCI: [M+NH4]⁺ calcd. for C13H22F2NO3S: 310.1283; Found 310.1279

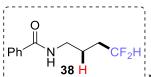




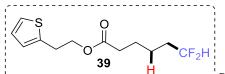
¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.11 (d, J = 2.0 Hz, 1H), 6.99 (dd, J = 8.1, 1.9 Hz, 1H), 6.72 (d, J = 8.1 Hz, 1H), 5.78 (tt, J = 56.8, 4.4 Hz, 1H), 4.55 (t, J = 8.7 Hz, 2H), 4.09 (t, J = 6.6 Hz, 2H), 3.53 (s, 2H), 3.19 (t, J = 8.7 Hz, 2H), 1.86-1.74 (m, 2H), 1.69 – 1.60 (m, 2H), 1.50 – 1.40 (m, 2H), 1.40-1.34 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 172.16, 159.26, 128.85, 127.38, 125.95, 125.78, 117.21 (t, J = 238.8 Hz), 109.17, 71.29, 64.47, 40.78, 33.92 (t, J = 20.8 Hz), 29.70, 28.35, 25.43, 21.72 (t, J = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.86 (dt, J = 56.5, 17.8 Hz). HRMS APCI: [M+H]⁺ calcd. for C16H21F2O3: 299.1453; Found 299.1448



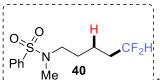
¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 6.93 (dd, J = 4.0, 1.8 Hz, 1H), 6.78 (t, J = 2.2 Hz, 1H), 6.11 (dd, J = 3.9, 2.5 Hz, 1H), 5.81 (tt, J = 56.9, 4.5 Hz, 1H), 4.22 (t, J = 6.5 Hz, 2H), 3.92 (s, 3H), 1.91 – 1.79 (m, 2H), 1.78-1.71 (m, 2H), 1.55 – 1.44 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 161.35, 129.48, 122.56, 117.70, 117.26 (t, J = 238.7 Hz), 107.82, 63.46, 36.81, 33.99 (t, J = 20.7 Hz), 28.65, 25.65, 21.83 (t, J = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.85 (dt, J = 56.8, 17.7 Hz). HRMS APCI: [M+H]⁺ calcd. for C12H18F2NO2: 246.1300; Found 242.1296

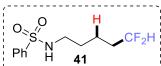


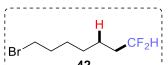
¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 2H), 7.53 – 7.48 (m, 1H), 7.48-7.40 (m, 2H), 6.23 (s, 1H), 5.88 (tt, *J* = 56.6, 4.2 Hz, 1H), 3.53 (q, *J* = 6.7 Hz, 2H), 2.00-1.86 (m, 2H), 1.86-1.76 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 167.68, 134.42, 131.58, 128.64, 126.82, 116.87 (t, *J* = 239.1 Hz), 39.21, 31.47 (t, *J* = 21.3 Hz), 22.46 (t, *J* = 5.2 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.99 (dt, *J* = 56.9, 17.6 Hz). HRMS APCI: [M+H]⁺ calcd. for C12H14F2NO: 214.1038; Found 214.1034



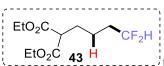
¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.16 (dd, J = 5.1, 1.2 Hz, 1H), 6.94 (dd, J = 5.1, 3.4 Hz, 1H), 6.86 (dt, J = 3.3, 1.1 Hz, 1H), 5.79 (tt, J = 56.8, 4.4 Hz, 1H), 4.31 (t, J = 6.7 Hz, 2H), 3.16 (td, J = 6.7, 0.9 Hz, 2H), 2.35 (t, J = 7.4 Hz, 2H), 1.90 – 1.76 (m, 2H), 1.74-1.64 (m, 2H), 1.52 – 1.43 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 173.07, 139.94, 126.87, 125.52, 124.03, 117.09 (t, J = 238.9 Hz), 64.59, 33.94, 33.76 (t, J = 20.8 Hz), 29.32, 21.62 (t, J = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.91 (dt, J = 57.1, 17.6 Hz). HRMS APCI: [M+H]⁺ calcd. for C12H17F2O2S: 263.0912; Found 263.0909



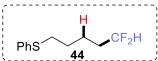




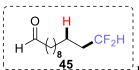
32.51, 28.21, 27.89, 21.92 (t, J = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.85 (dt, J = 56.7, 17.8 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.¹⁵



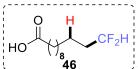
(600 MHz, Chloroform-*d*) δ 5.81 (tt, J = 56.7, 4.4 Hz, 1H), 4.25-4.16 (m, 4H), 3.33 (t, J = 7.4 Hz, 1H), 1.95 (q, J = 7.7 Hz, 2H), 1.92-1.81 (m, 2H), 1.54 – 1.47 (m, 2H), 1.27 (t, J = 7.1 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 169.16, 116.85 (t, J = 239.1 Hz), 61.50, 51.77, 33.72 (t, J = 21.1 Hz), 28.10, 19.98 (t, J = 5.6 Hz), 14.07. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -116.12 (dt, J = 56.8, 17.9 Hz). GC-MS: [M+H]⁺ calcd. for C11H19F2O4: 253.1246; Found 253



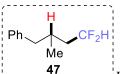
¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 2H), 7.31-7.27 (m, 2H), 7.20 – 7.16 (m, 1H), 5.79 (tt, *J* = 56.8, 4.4 Hz, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.89 – 1.78 (m, 2H), 1.73-1.66 (m, 2H), 1.64 – 1.57 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 136.35, 129.29, 128.93, 126.03, 117.09 (t, *J* = 239.0 Hz), 33.61 (t, *J* = 20.9 Hz), 33.41, 28.55, 21.25 (t, *J* = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.89 (dt, *J* = 57.2, 17.8 Hz). HRMS APCI: [M+H]⁺ calcd. for C11H15F2S: 217.0857; Found 217.0854



⁴**9**------⁴**9**-------⁴ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 5.79 (tt, *J* = 57.0, 4.6 Hz, 1H), 2.42 (t, *J* = 7.4 Hz, 2H), 1.87 – 1.76 (m, 2H), 1.66-1.60 (m, 2H), 1.47-1.39 (m, 2H), 1.36 – 1.27 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 202.93, 117.50 (t, *J* = 238.7 Hz), 43.92, 34.08 (t, *J* = 20.6 Hz), 29.33, 29.32, 29.14, 29.03, 22.10 (t, *J* = 5.4 Hz)., 22.07. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.75 (dt, *J* = 57.0, 17.6 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.¹⁶

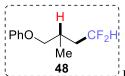


⁴⁰ MHz, Chloroform-*d*) δ 5.79 (tt, *J* = 57.0, 4.6 Hz, 1H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.89 – 1.74 (m, 2H), 1.67-1.59 (m, 2H), 1.47-1.40 (m, 2H), 1.35 – 1.27 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 180.04, 117.50 (t, *J* = 238.7 Hz), 34.08 (t, *J* = 20.7 Hz), 34.03, 29.32, 29.18, 29.03, 24.65, 22.10 (t, *J* = 5.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.73 (dt, *J* = 57.0, 17.5 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.¹⁶

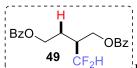


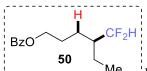
⁴⁷ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.32-7.27 (m, 2H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 2H), 5.95 – 5.72 (m, 1H), 2.64 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.51 (dd, *J* = 13.5, 7.7 Hz, 1H), 2.10-1.98 (m, 1H), 1.95-1.82 (m, 1H), 1.74-1.60 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 139.95, 129.15, 128.35, 126.16, 116.99 (t, *J* = 238.7 Hz), 43.52, 40.37 (t,

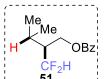
J = 20.1 Hz), 29.91 (t, J = 5.2 Hz), 19.61. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -114.61 (dt, J = 56.9, 17.5 Hz). GC-MS: [M]+ calcd. for C11H14F2: 184.1064; Found 184.1



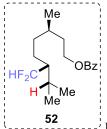
⁴⁰ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 6.98-6.92 (m, 1H), 6.91 – 6.86 (m, 2H), 5.99 (tt, *J* = 56.8, 4.8 Hz, 1H), 3.86 (dd, *J* = 9.1, 5.4 Hz, 1H), 3.79 (dd, *J* = 9.1, 6.6 Hz, 1H), 2.30 – 2.21 (m, *J* = 6.7 Hz, 1H), 2.17-2.06 (m, 1H), 1.89-1.77 (m, 1H), 1.12 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 158.79, 129.50, 120.88, 116.89 (t, *J* = 238.7 Hz), 114.47, 72.27, 38.14 (t, *J* = 20.7 Hz), 28.42 (t, *J* = 5.3 Hz), 17.16. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -113.17 – -116.09 (m). GC-MS: [M]+ calcd. for C11H14F2O: 200.1013; Found 200.0



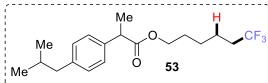


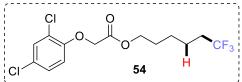


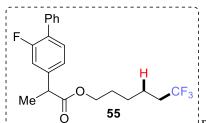
¹Chloroform-*d*) δ 8.06 – 7.99 (m, 2H), 7.59 – 7.55 (m, 1H), 7.47-7.42 (m, 2H), 6.01 (td, *J* = 55.9, 3.5 Hz, 1H), 4.55 – 4.44 (m, 2H), 2.18-2.07 (m, 2H), 1.11 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.34, 133.14, 129.93, 129.61, 128.46, 117.24 (t, *J* = 243.0 Hz), 60.72 (t, *J* = 5.7 Hz), 47.46 (t, *J* = 18.1 Hz), 25.53 (t, *J* = 3.7 Hz), 20.62, 19.77. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -117.23 – -125.25 (m). HRMS APCI: [M+H]⁺ calcd. for C13H17F2O2: 243.1191; Found 243.1188



¹ Prepared according to General Procedure B and obtained as colorless oil. 1:1 mixture of diastereomers. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.78 (td, *J* = 56.5, 3.6 Hz, 1H), 4.43 – 4.30 (m, 2H), 1.97-1.87 (m, 1H), 1.87-1.79 (m, 1H), 1.65 – 1.53 (m, 4H), 1.53 – 1.40 (m, 2H), 1.38 – 1.30 (m, 1H), 1.01-0.97 (m, 3H), 0.97-0.91 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 166.68, 132.85, 130.46, 129.54, 128.34, 119.00 (t, *J* = 242.4 Hz), 118.93 (t, *J* = 242.3 Hz), 63.40, 63.38, 47.83 (t, *J* = 17.4 Hz), 35.51, 35.45, 35.38, 30.40, 30.36, 27.11 (dd, *J* = 5.7, 3.6 Hz), 27.01 (dd, *J* = 5.8, 3.5 Hz), 21.94 (t, *J* = 4.4 Hz), 21.89 (t, *J* = 4.5 Hz)., 19.75, 19.71, 19.58, 19.41, 19.39. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -116.39 – -124.91 (m). HRMS APCI: [M+H]⁺ calcd. for C18H27F2O2: 313.1974; Found 313.1969

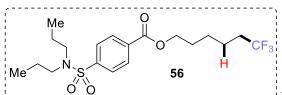




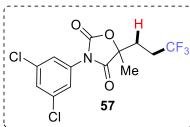


¹/₂ When the provided HTML is the provided HTML in the provided HTML in the provided HTML is the provided HTML in the provided HTML in the provided HTML is the provided HTML in the provided HTML in the provided HTML is the provided HTML in the provided HTML in the provided HTML is the provided HTML in the provided HTML in the provided HTML is the provided HTML in the provided HTML in the provided HTML is the provided HTML in the provided HTML in the provided HTML is the provided HTML in the provided HTML in the provided HTML is the provided HTML in the provided HTM

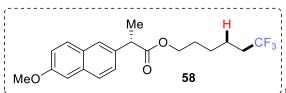
115.23 (d, J = 23.5 Hz), 64.54, 45.08, 33.59 (q, J = 28.4 Hz), 28.17, 25.06, 21.53 (q, J = 3.0 Hz), 18.28. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.36 (t, J = 11.0 Hz), -117.67 (dd, J = 13.0, 8.8 Hz). HRMS APCI: [M+H]⁺ calcd. for C21H23F4O2: 383.1629; Found 383.1623



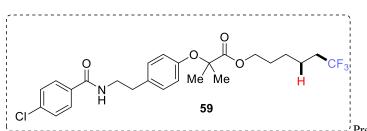
¹ Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.15 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 4.37 (t, J = 6.5 Hz, 2H), 3.16 – 3.06 (m, 4H), 2.17 – 2.06 (m, 2H), 1.86 – 1.78 (m, 2H), 1.68-1.62 (m, 2H), 1.60-1.50 (m, 6H), 0.87 (t, J = 7.4 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 165.28, 144.32, 133.59, 130.19, 127.11 (q, J = 276.3 Hz), 127.04, 65.24, 49.95, 33.62 (q, J = 28.5 Hz), 28.34, 25.26, 21.95, 21.67 (q, J = 3.0 Hz), 11.16. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.35 (t, J = 11.0 Hz). HRMS APCI: [M+H]⁺ calcd. for C19H29F3NO4S: 424.1764; Found 424.1754



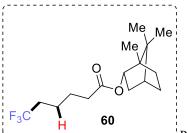
¹ Prepared according to General Procedure A and obtained as white soid. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.42-7.32 (m, 3H), 2.30 – 2.24 (m, 1H), 2.19 – 2.08 (m, 3H), 1.64 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 172.71, 151.80, 135.70, 132.29, 129.26, 126.06 (q, *J* = 276.2 Hz), 123.65, 84.08, 29.37 (q, *J* = 3.2 Hz), 28.23 (q, *J* = 30.4 Hz), 22.25. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.40 (t, *J* = 9.8 Hz). m.p.: 114-115 °C. HRMS APCI: [M+H]⁺ calcd. for C13H11Cl2F3NO2: 356.0063; Found 356.0067

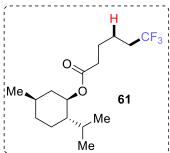


¹ Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.70 (d, J = 8.7 Hz, 2H), 7.67 – 7.64 (m, 1H), 7.39 (dd, J = 8.5, 1.8 Hz, 1H), 7.14 (dd, J = 8.9, 2.6 Hz, 1H), 7.11 (d, J = 2.5 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.91 (s, 3H), 3.84 (q, J = 7.1 Hz, 1H), 1.89 – 1.82 (m, 2H), 1.58-1.56 (m, 4H), 1.48-1.41 (m, 2H), 1.26 – 1.20 (m, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.68, 157.68, 135.76, 133.69, 129.22, 128.92, 127.11, 127.05 (q, J = 276.5 Hz) 126.20, 125.94, 119.04, 105.57, 64.25, 55.31, 45.51, 33.48 (q, J = 28.5 Hz), 28.19, 24.99, 21.48 (q, J = 3.0 Hz), 18.30. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.44 (t, J = 10.9 Hz). HRMS APCI: [M+H]⁺ calcd. for C20H24F3O3: 369.1672; Found 369.1665

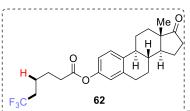


 (m, 2H), 6.89 - 6.75 (m, 2H), 6.13-6.02 (m, 1H), 5.30 (s, 6H), 4.16 (t, J = 6.5 Hz, 2H), 3.66 (q, J = 6.6 Hz, 2H), 2.85 (t, J = 6.9 Hz, 2H), 2.04 - 1.94 (m, 2H), 1.66 - 1.63 (m, 2H), 1.56 - 1.48 (m, 2H), 1.33 (p, J = 7.9 Hz, 2H). 13 C NMR (151 MHz, CDCl₃) δ 174.30, 166.37, 154.20, 137.66, 132.99, 132.29, 129.48, 128.83, 128.24, 127.05 (q, J = 276.3 Hz), 119.26, 79.12, 64.97, 53.43, 41.23, 34.72, 33.55 (q, J = 28.5 Hz), 28.09, 25.38, 25.01, 21.50 (q, J = 3.0 Hz). 19 F NMR (565 MHz, Chloroform-d) δ -66.33 (t, J = 10.9 Hz). HRMS APCI: [M+H]⁺ calcd. for C25H30NF3CIO4: 500.1816



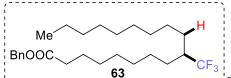


¹ Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 4.69 (td, J = 10.9, 4.4 Hz, 1H), 2.36 – 2.29 (m, 2H), 2.14 – 2.05 (m, 2H), 2.01-1.95 (m, 1H), 1.88-1.81 (m, 1H), 1.73-1.65 (m, 4H), 1.63 – 1.58 (m, 2H), 1.52-1.44 (m, 1H), 1.40-1.34 (m, 1H), 1.26 – 1.18 (m, 1H), 1.10-1.01 (m, 1H), 0.93-0.87 (m, 7H), 0.76 (d, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 172.62, 127.03 (q, J = 276.2 Hz), 74.28, 47.02, 40.94, 34.25, 34.18, 33.50 (q, J = 28.4 Hz), 31.39, 26.32, 24.13, 23.41, 22.01, 21.45 (q, J = 3.2 Hz), 20.74, 16.25. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.43 (t, J = 10.8 Hz). HRMS APCI: [M+NH4]⁺ calcd. for C16H31F3NO2: 326.2301; Found 326.2292

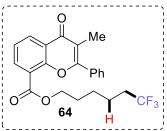


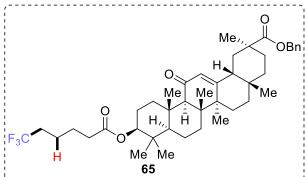
¹------- Prepared according to General Procedure A and obtained as white soid. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.24-7.20 (m, 1H), 6.79-6.75 (m, 1H), 6.75-6.71 (m, 1H), 2.88 – 2.80 (m, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.47-2.40 (m, 1H), 2.37-2.31 (m, 1H), 2.26-2.18 (m, 1H), 2.13-2.03 (m, 3H), 2.02 – 1.91 (m, 2H), 1.91-1.87 (m, 1H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.59 – 1.36 (m, 6H), 0.84 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.83, 148.47, 138.08, 137.47, 127.0 (q, *J* = 276.3 Hz), 126.45, 121.51, 118.68, 50.44, 47.96, 44.16, 38.00, 35.87, 33.85, 33.50 (q, *J* = 28.6 Hz), 31.56, 29.41, 26.34, 25.76, 23.97, 21.60, 21.47 (q, *J* = 3.1 Hz), 13.84. ¹⁹F NMR

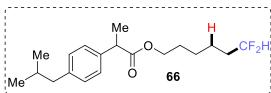
(565 MHz, Chloroform-*d*) δ -66.32 (t, J = 10.8 Hz). m.p.: 94-95 °C. HRMS APCI: [M+H]⁺ calcd. for C24H30F3O3: 423.2142; Found 423.2150



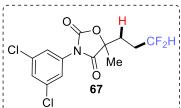
¹ Prepared according to General Procedure A and obtained as colorless oil. 1:1 mixture of regioisomers. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.30 (m, 5H), 5.11 (s, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.01 – 1.93 (m, 1H), 1.67-1.61 (m, 2H), 1.57-1.52 (m, 2H), 1.42 – 1.26 (m, 24H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.68, 173.64, 136.14, 136.13, 128.79 (q, *J* = 280.6 Hz), 128.55, 128.19, 66.10, 66.08, 42.56 (q, *J* = 24.6 Hz), 34.32, 34.29, 31.89, 31.85, 29.72, 29.65, 29.55, 29.53, 29.42, 29.38, 29.30, 29.25, 29.21, 29.18, 29.08, 29.05, 29.03, 27.85, 27.84, 27.82, 26.88, 26.86, 26.82, 24.93, 24.90, 22.68, 22.66, 14.11. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -70.05– -70.18 (m, 3F). HRMS APCI: [M+H]⁺ calcd. for C26H42F3O2: 443.3131; Found 443.3131



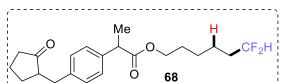




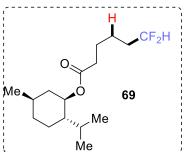
¹/₂ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.22 – 7.17 (m, 2H), 7.11 – 7.06 (m, 2H), 5.74 (tt, *J* = 56.9, 4.5 Hz, 1H), 4.13 – 4.00 (m, 2H), 3.68 (q, *J* = 7.1 Hz, 1H), 2.44 (d, *J* = 7.1 Hz, 2H), 1.90-1.80 (m, 1H), 1.80 – 1.69 (m, 2H), 1.60 – 1.57 (m, 2H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.44 – 1.35 (m, 2H), 1.30-1.25 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 174.79, 140.54, 137.85, 129.30, 127.14, 117.21 (t, *J* = 238.7 Hz), 64.27, 45.19, 45.01, 33.91 (t, *J* = 20.7 Hz), 30.19, 28.31, 25.32, 22.37, 21.68 (t, *J* = 5.5 Hz), 18.39. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.86 (dt, *J* = 57.0, 17.9 Hz). HRMS APCI: [M+H]⁺ calcd. for C19H29F2O2: 327.2130; Found 327.2125



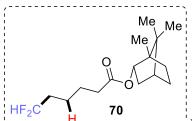
¹ (600 MHz, Chloroform-*d*) δ 7.40-7.33 (m, 3H), 5.83 (tt, J = 56.1, 3.9 Hz, 1H), 2.13 – 2.05 (m, 2H), 2.06 – 1.95 (m, 1H), 1.90 – 1.79 (m, 1H), 1.63 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.07, 152.03, 135.65, 132.41, 129.18, 123.71, 115.58 (t, J = 240.2 Hz), 84.80, 29.08 (t, J = 5.7 Hz), 28.02 (t, J = 22.2 Hz), 22.40. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -116.87 (dt, J = 56.1, 17.0 Hz). m.p.: 121-122 °C. HRMS APCI: [M+H]⁺ calcd. for C13H12Cl2F2NO3: 338.0157; Found 338.0161



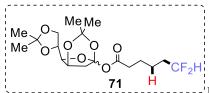
¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.21 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.75 (tt, J = 56.9, 4.4 Hz, 1H), 4.06 (tt, J = 8.1, 4.1 Hz, 2H), 3.68 (q, J = 7.2 Hz, 1H), 3.12 (dd, J = 14.0, 4.2 Hz, 1H), 2.51 (dd, J = 13.9, 9.5 Hz, 1H), 2.38 – 2.29 (m, 2H), 2.14 – 2.05 (m, 2H), 1.99-1.92 (m, 1H), 1.81 – 1.69 (m, 3H), 1.61 – 1.53 (m, 3H), 1.48 (d, J = 7.2 Hz, 3H), 1.44-1.37 (m, 2H), 1.34 – 1.27 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 220.18, 174.65, 138.87, 138.45, 129.11, 129.09, 127.52, 117.18 (t, J = 238.8 Hz), 64.35, 50.97, 45.17, 38.18, 35.19, 33.90 (t, J = 20.8 Hz), 29.24, 28.29, 25.33, 21.66 (t, J = 5.5 Hz), 20.53, 18.41. ¹⁹F NMR (565 MHz, Chloroform-d) δ -115.86 (dt, J = 56.7, 17.7 Hz). HRMS APCI: [M+H]⁺ calcd. for C21H29F2O3: 367.2079; Found 367.2075



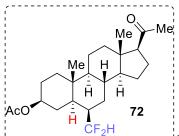
= 238.9 Hz), 74.18, 47.02, 40.95, 34.36, 34.26, 33.78 (t, J = 20.8 Hz), 31.39, 26.31, 24.50, 23.42, 22.02,21.63 (t, J = 5.6 Hz), 20.75, 16.27. ¹⁹F NMR (565 MHz, Chloroform-d) δ -115.96 (dt, J = 56.6, 17.5 Hz). HRMS APCI: [M+H]⁺ calcd. for C16H29F2O2: 291.2130; Found 291.2126

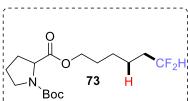


¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 5.81 (tt, *J* = 56.7, 4.5 Hz, 1H), 4.89 (dq, *J* = 10.0, 1.9 Hz, 1H), 2.39-2.31 (m, 3H), 1.94 – 1.81 (m, 3H), 1.77 – 1.67 (m, 4H), 1.55-1.47 (m, 2H), 1.34 – 1.20 (m, 3H), 0.91 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.56, 117.10 (t, *J* = 238.9 Hz), 79.89, 48.74, 47.80, 44.88, 36.84, 34.33, 33.79 (t, *J* = 21.0 Hz), 28.04, 27.12, 24.51, 21.64 (t, *J* = 5.5 Hz), 19.70, 18.84, 13.50. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.93 (dt, *J* = 57.1, 18.0 Hz). HRMS APCI: [M+H]⁺ calcd. for C16H27F2O2: 289.1974; Found 289.1972

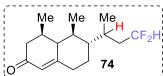


NMR (600 MHz, Chloroform-*d*) δ 6.14 (s, 1H), 5.82 (tt, J = 56.7, 4.4 Hz, 1H), 4.86 (dd, J = 5.9, 3.6 Hz, 1H), 4.69 (d, J = 5.8 Hz, 1H), 4.44-4.37 (m, 1H), 4.12-4.07 (m, 1H), 4.07-3.97 (m, 2H), 2.40-2.27 (m, 2H), 1.91-1.79 (m, 2H), 1.69 (p, J = 7.5 Hz, 1H), 1.53 – 1.47 (m, 5H), 1.46 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.61, 117.00 (t, J = 239.0 Hz), 113.32, 109.38, 100.74, 85.07, 82.28, 79.32, 72.87, 66.82, 33.90, 33.71 (t, J = 21.0 Hz), 26.99, 25.95, 25.13, 24.67, 24.08, 21.50 (t, J = 5.6 Hz). ¹⁹F NMR (564 MHz, Chloroform-*d*) δ -116.01 (dt, J = 56.8, 17.5 Hz). HRMS APCI: [M+H]⁺ calcd. for C18H29F2O7: 395.1876; Found 395.1873

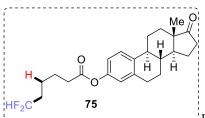




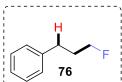
¹ Prepared according to General Procedure B and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 5.73 (tt, *J* = 57.0, 4.6 Hz, 1H), 4.28 – 3.99 (m, 3H), 3.53 – 3.29 (m, 2H), 2.20-2.07 (m, 1H), 1.93 – 1.70 (m, 5H), 1.63-1.52 (m, 2H), 1.43 – 1.32 (m, 13H). ¹³C NMR (151 MHz, CDCl₃) δ 173.30, 173.08, 154.40, 153.82, 117.25 (t, J = 238.9Hz), 117.15 (t, J = 239.0Hz), 79.84, 79.72, 64.61, 64.59, 59.18, 58.88, 46.56, 46.32, 33.91 (t, *J* = 20.8 Hz), 30.94, 29.98, 28.46, 28.43, 28.32, 25.49, 25.37, 24.32, 23.62, 21.76 (t, *J* = 5.1 Hz), 21.72 (d, *J* = 5.2 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.93 (ddt, *J* = 56.8, 26.4, 17.6 Hz). HRMS APCI: [M+H]⁺ calcd. for C16H28F2NO4: 336.1981; Found 336.1981



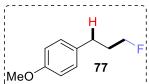
of diastereomers. ¹H NMR (600 MHz, Chloroform-*d*) δ 5.99-5.77 (m, 1H), 5.77-5.73 (m, 1H), 2.51 – 2.40 (m, 1H), 2.39-2.33 (m, 1H), 2.33 – 2.20 (m, 2H), 2.07 – 1.55 (m, 8H), 1.23 – 1.13 (m, 1H), 1.11-1.06 (m, 3H), 0.99 – 0.92 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 199.57, 170.51, 124.66, 124.63, 117.21 (t, J = 239.0 Hz), 117.17 (t, J = 239.0 Hz), 42.42, 42.04, 40.84, 40.56, 40.54, 39.27, 39.17, 38.56 (t, J = 20.1 Hz), 38.09 (t, J = 20.1 Hz), 37.62, 37.61, 32.99, 32.99, 32.22-32.18 (m), 32.16-32.13 (m), 29.77, 28.32, 16.93, 16.36, 16.00, 14.95, 14.94. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -111.43 – -119.70 (m). HRMS APCI: [M+H]⁺ calcd. for C16H25F2O: 271.1868; Found 271.1870. The compound characterization was reported in literature and the NMR data matched with previous characterization.¹



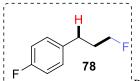
¹ Prepared according to General Procedure B and obtained as white solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.31-7.27 (m, 1H), 6.88-6.83 (m, 1H), 6.81-6.78 (m, 1H), 5.83 (tt, *J* = 56.8, 4.4 Hz, 1H), 2.94-2.88 (m, 2H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.54 – 2.48 (m, 1H), 2.44 – 2.36 (m, 1H), 2.34-2.25 (m, 1H), 2.20-2.10 (m, 1H), 2.10 – 1.98 (m, 2H), 1.98-1.94 (m, 1H), 1.94-1.84 (m, 2H), 1.94-1.79 (m, 2H), 1.69 – 1.41 (m, 9H), 0.91 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 172.01, 148.50, 138.04, 137.41, 126.42, 121.52, 118.69, 118.69, 117.03 (t, *J* = 239.0 Hz), 50.42, 47.94, 44.14, 37.99, 35.85, 34.02, 33.75 (t, *J* = 20.9 Hz), 31.54, 29.40, 26.33, 25.75, 24.35, 21.63, 21.59 (t, *J* = 5.5Hz), 21.58, 21.55, 13.82. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -115.98 (dt, *J* = 56.7, 17.6 Hz). m.p.: 95-96 °C. HRMS APCI: [M+H]⁺ calcd. for C24H31F2O3: 405.2236; Found 405.2244

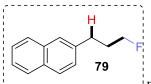


¹ Prepared according to General Procedure C and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.23-7.18 (m, 3H), 4.46 (dt, *J* = 47.2, 6.0 Hz, 2H), 2.78 – 2.70 (m, 2H), 2.06 – 1.97 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 141.11, 128.49, 128.47, 126.04, 83.15 (d, *J* = 164.8 Hz), 32.04 (d, *J* = 19.9 Hz), 31.33 (d, *J* = 5.4 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -220.01 (tt, *J* = 47.2, 25.3 Hz). GC-MS: [M]+ calcd. for C9H11F: 138.0845; Found 138

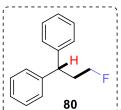


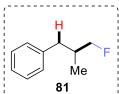
¹ Prepared according to General Procedure C and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.13 – 7.08 (m, 2H), 6.86 – 6.82 (m, 2H), 4.44 (dt, *J* = 47.2, 5.9 Hz, 2H), 3.79 (s, 3H), 2.72 – 2.66 (m, 2H), 2.04 – 1.90 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 157.93, 133.14, 129.39, 113.87, 83.14 (d, *J* = 164.6 Hz), 55.27, 32.26 (d, *J* = 19.6 Hz), 30.38 (d, *J* = 5.4 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -220.09 (tt, *J* = 47.4, 25.6 Hz). HRMS APCI:: [M-H]+ calcd. for C10H12FO: 167.0867; Found 167.0865



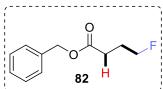


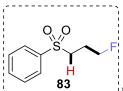
¹/₋₋₋₋₋₋ Prepared according to General Procedure C and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.75 (m, 3H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.44 (dddd, *J* = 18.4, 8.1, 6.8, 1.4 Hz, 2H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.49 (dt, *J* = 47.2, 5.9 Hz, 2H), 2.96 – 2.88 (m, 2H), 2.17 – 2.03 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 138.57, 133.60, 132.07, 128.06, 127.62, 127.43, 127.20, 126.61, 126.01, 125.29, 83.10 (d, *J* = 165.0 Hz), 31.93 (d, *J* = 19.7 Hz), 31.46 (d, *J* = 5.4 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -215.61 – -231.03 (m). GC-MS: [M]+ calcd. for C13H13F: 188.1001; Found 188



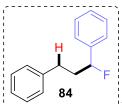


¹ Prepared according to General Procedure C and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.19 (m, 1H), 7.18 – 7.15 (m, 2H), 4.27 (dd, *J* = 47.5, 5.5 Hz, 2H), 2.77 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.47 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.18 – 1.96 (m, 1H), 0.95 (dd, *J* = 6.8, 1.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 139.88, 129.19, 128.31, 126.05, 87.42 (d, *J* = 168.8 Hz), 38.68 (d, *J* = 5.6 Hz), 36.09 (d, *J* = 18.2 Hz), 15.65 (d, *J* = 6.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -224.20 (td, *J* = 47.3, 20.4 Hz). GC-MS: [M]+ calcd. for C10H13F: 152.1001; Found 152

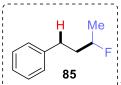




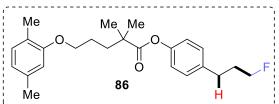
¹Chloroform-*d*) δ 7.95 – 7.89 (m, 2H), 7.71 – 7.65 (m, 1H), 7.61 – 7.57 (m, 2H), 4.52 (dt, *J* = 46.8, 5.7 Hz, 2H), 3.27 – 3.21 (m, 2H), 2.20 – 2.09 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 138.91, 133.93, 129.43, 128.05, 81.55 (d, *J* = 167.9 Hz), 52.53 (d, *J* = 4.3 Hz), 24.09 (d, *J* = 20.8 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -220.52 (tt, *J* = 46.9, 25.9 Hz). HRMS APCI: [M+H]+ calcd. for C9H12FO2S: 203.0537; Found 203.0533

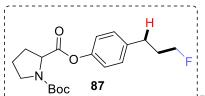


¹Chloroform-*d*) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 5.43 (ddd, J = 47.8, 8.5, 4.4 Hz, 1H), 2.87 – 2.68 (m, 2H), 2.38 – 2.24 (m, 1H), 2.18 – 2.05 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 141.13, 140.16 (d, J = 19.7 Hz), 128.48, 128.46, 128.30 (d, J = 2.0 Hz), 126.05, 125.57 (d, J = 6.8 Hz), 93.65 (d, J = 170.9 Hz), 38.82 (d, J = 23.9 Hz), 31.32 (d, J = 4.3 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -176.01 (ddd, J = 46.5, 30.0, 15.9 Hz). GC-MS: [M]+ calcd. for C15H15F: 214.1158; Found 214

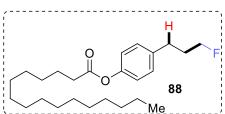


¹Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.20 (dd, *J* = 7.5, 1.4 Hz, 3H), 4.74 – 4.57 (m, 1H), 2.84-2.76 (m, 1H), 2.72-2.64 (m, 1H), 2.04-1.92 (m, 1H), 1.90 – 1.74 (m, 1H), 1.34 (dd, *J* = 23.9, 6.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 141.50, 128.44, 125.95, 90.05 (d, *J* = 165.0 Hz), 38.67 (d, *J* = 20.8 Hz), 31.37 (d, *J* = 4.9 Hz), 21.00 (d, *J* = 22.6 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -174.22 (ddqd, *J* = 47.9, 31.8, 23.7, 16.0 Hz). GC-MS: [M]+ calcd. for C10H13F: 152.1001; Found 152

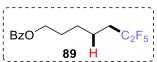




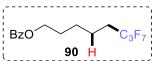
¹/₁ NMR (600 MHz, Chloroform-*d*) δ 7.23-7.16 (m, 2H), 7.06-7.00 (m, 2H), 4.55 – 4.39 (m, 3H), 3.65 – 3.41 (m, 2H), 2.78-2.69 (m, 2H), 2.44 – 2.28 (m, 1H), 2.22 – 2.12 (m, 1H), 2.08 – 1.91 (m, 4H), 1.47 (d, *J* = 7.4 Hz, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 171.74, 154.45, 153.76, 149.04, 148.83, 138.78, 138.58, 129.48, 129.33, 121.39, 121.06, 82.98 (d, *J* = 164.8 Hz), 82.95 (d, *J* = 165.4 Hz), 80.20, 79.95, 59.18, 59.06, 46.62, 46.44, 32.02 (d, *J* = 19.9 Hz), 31.99 (d, *J* = 19.6 Hz), 31.06, 30.74, 30.71, 28.43, 24.48, 23.70. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -219.84 – -220.64 (m). HRMS APCI: [M+H]+ calcd. for C19H27FNO4: 352.1919; Found 352.1916



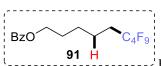
¹H NMR (600 MHz, Chloroform-*d*) δ 7.21-7.16 (m, 2H), 7.02 – 6.97 (m, 2H), 4.45 (dt, *J* = 47.2, 5.9 Hz, 2H), 2.79 – 2.67 (m, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.06 – 1.93 (m, 2H), 1.74 (p, *J* = 7.5 Hz, 2H), 1.42 – 1.25 (m, 24H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 172.49, 149.02, 138.50, 129.37, 121.51, 82.99 (d, *J* = 164.9 Hz), 34.42, 32.02 (d, *J* = 19.9 Hz), 31.94, 30.73 (d, *J* = 5.1 Hz), 29.71, 29.69, 29.67, 29.66, 29.61, 29.47, 29.37, 29.27, 29.12, 24.98, 22.70, 14.13. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -220.23 (tt, *J* = 47.5, 25.5 Hz). HRMS APCI: [M+H]+ calcd. for C25H42FO2: 393.3164; Found 393.3148

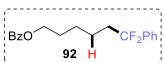


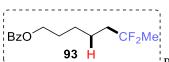
¹ Prepared according to General Procedure D and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.07 – 8.00 (m, 2H), 7.59 – 7.54 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.10-1.99 (m, 2H), 1.86-1.78 (m, 2H), 1.73-1.64 (m, 2H), 1.57 – 1.52 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 166.64, 132.97, 130.33, 129.56, 128.40, 119.24 (qt, *J* = 285.2, 36.4 Hz), 115.76 (tq, *J* = 251.5, 37.5 Hz), 64.58, 30.62 (t, *J* = 22.2 Hz), 28.47, 25.75, 20.14 (t, *J* = 3.7 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -85.45, -118.22 (t, *J* = 18.5 Hz). HRMS APCI: [M+H]⁺ calcd. for C14H16F5O2: 311.1065; Found 311.1060

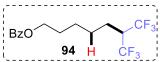


¹ Prepared according to General Procedure D and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 2H), 7.59 – 7.54 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.15 – 2.03 (m, 2H), 1.87 – 1.77 (m, 2H), 1.73-1.66 (m, 2H), 1.59 – 1.51 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 166.65, 132.98, 130.34, 129.57, 128.41, 117.93 (qt, *J* = 287.5, 34.1 Hz), 117.71 (tt, *J* = 253.2, 30.9 Hz), 108.93 (tq, *J* = 263.4, 37.0 Hz), 64.59, 30.58 (t, *J* = 22.4 Hz), 28.49, 25.77, 19.97 (t, *J* = 3.8 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -80.61 (t, *J* = 10.1 Hz), -115.36 (tdt, *J* = 20.0, 14.7, 10.0 Hz), -127.83 (d, *J* = 6.0 Hz). HRMS APCI: [M+H]⁺ calcd. for C15H16F702: 361.1003; Found 361.1029

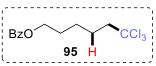




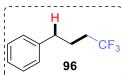


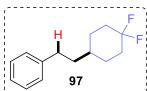


¹ Corolling to General Procedure D and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.07 – 7.98 (m, 2H), 7.59 – 7.53 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 2.90-2.79 (m, 1H), 1.90 – 1.70 (m, 4H), 1.64-1.57 (m, 2H), 1.54 – 1.47 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 166.64, 132.95, 130.32, 129.54, 128.38, 123.97 (q, *J* = 281.3 Hz), 123.95 (q, *J* = 281.6 Hz), 64.63, 47.99 (hept, *J* = 27.8 Hz), 28.35, 26.93, 25.95, 23.65 (hept, *J* = 1.9 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -67.05 (d, *J* = 8.1 Hz). HRMS APCI: [M+H]⁺ calcd. for C15H17F6O2: 343.1127; Found 343.1121

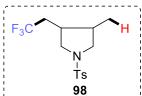


¹ Prepared according to General Procedure D and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.08 – 8.02 (m, 2H), 7.59-7.54 (m, 1H), 7.49 – 7.41 (m, 2H), 4.36 (t, *J* = 6.5 Hz, 2H), 2.76 – 2.67 (m, 2H), 1.91 – 1.79 (m, 4H), 1.60-1.55 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 166.63, 132.94, 130.29, 129.55, 128.37, 99.88, 64.64, 55.00, 28.50, 26.17, 24.99. GC-MS: [M]+ calcd. for C13H15Cl3O2: 308.0138; Found 308



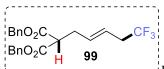


¹ Prepared according to General Procedure D and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 2.68 – 2.59 (m, 2H), 2.13 – 2.02 (m, 2H), 1.88 – 1.78 (m, 2H), 1.77 – 1.62 (m, 2H), 1.61 – 1.57 (m, 2H), 1.39 – 1.29 (m, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 142.38, 128.39, 128.29, 125.79, 123.80 (dd, *J* = 241.9, 239.5 Hz), 37.52 (d, *J* = 2.6 Hz), 35.23, 33.61, 33.45 (d, *J* = 2.9 Hz), 33.42, 33.30, 28.89 (d, *J* = 9.4 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -81.46 – -111.74 (m). GC-MS: [M]+ calcd. for C14H18F2: 224.1377; Found 224



¹ Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.67 (m, 2H), 7.34 (dd, J = 8.2, 2.3 Hz, 2H), 3.64-3.50 (m, 0.21H), 3.56-3.47 (m, 1.06H), 3.38-3.33 (m, 0.79H), 3.11 – 3.04 (m, 1.59H), 3.00-2.95 (m, 0.23H), 2.81-2.76 (m, 0.22H), 2.46-2.41 (m, 3H), 2.34 – 2.23 (m, 1.85H), 2.16 – 2.07 (m, 0.80H), 1.95 – 1.74 (m, 1.55H), 0.97 (d, J = 6.2 Hz, 0.65H), 0.77 (d, J = 6.7 Hz, 2.35H). ¹³C NMR (151 MHz, CDCl₃) δ 143.62, 143.59, 133.91, 133.67, 129.76, 129.74, 127.50, 127.40, 126.59 (q, J = 277.0 Hz), 126.35 (q, J = 276.9 Hz), 54.46, 53.96, 53.01, 50.41, 39.68 (q, J = 2.6 Hz), 38.69, 35.85 (q, J = 28.9 Hz), 35.73 (q, J = 2.6 Hz), 35.23, 32.41 (q, J = 28.8 Hz), 21.55, 21.54, 15.68, 13.25. ¹⁹F NMR (565 MHz, Chloroform-d)

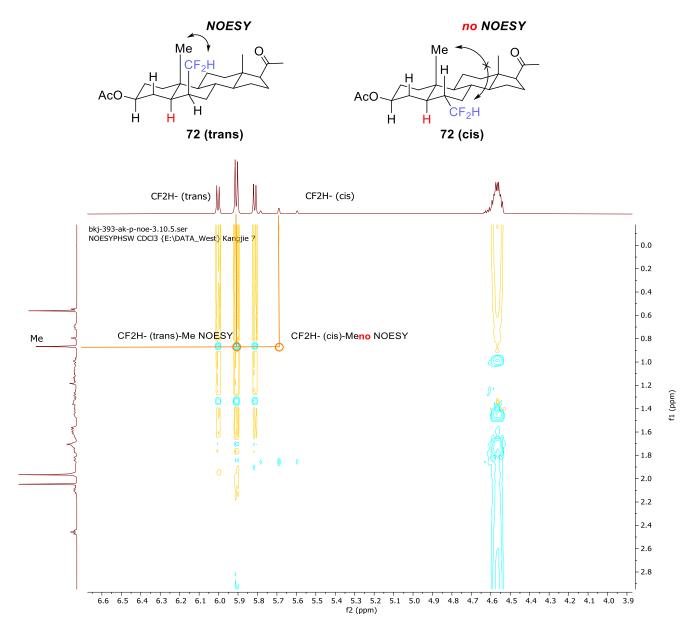
δ -64.99 (t, J = 10.9 Hz), -65.03 (t, J = 10.9 Hz). HRMS APCI: [M+H]⁺ calcd. for C14H19F3NO2S: 322.1083; Found 322.1077



¹ Prepared according to General Procedure A and obtained as colorless oil. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 7.25 (m, 10H), 5.64 (dt, *J* = 14.6, 7.0 Hz, 1H), 5.44 (dt, *J* = 14.9, 7.0 Hz, 1H), 5.20 – 5.09 (m, 4H), 3.61-3.44 (m, 1H), 2.78 – 2.59 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 168.37, 135.27, 133.06, 128.58, 128.43, 128.28, 125.75 (q, *J* = 276.5 Hz), 121.37 (q, *J* = 3.6 Hz), 67.26, 51.55, 37.19 (q, *J* = 29.7 Hz), 31.61. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -66.51 (t, *J* = 10.9 Hz). The compound characterization was reported in literature and the NMR data matched with previous characterization.¹⁸

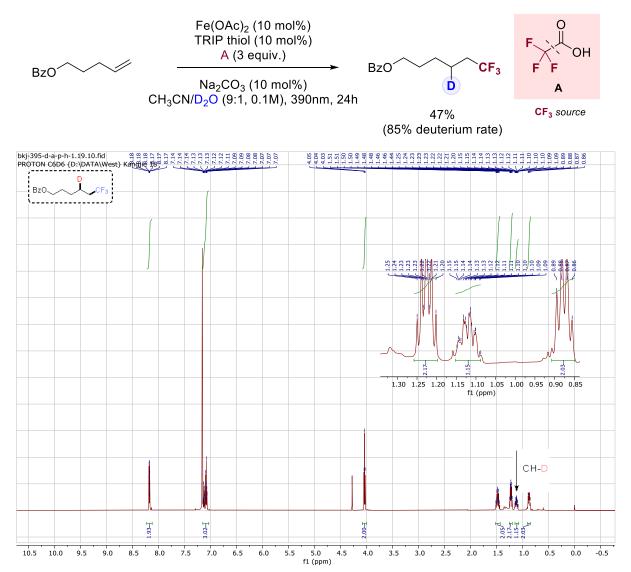
2.5 Relative configuration of compound 72

On the basis of NMR experiment, we have assigned the major diastereomers of products **72** as shown below:

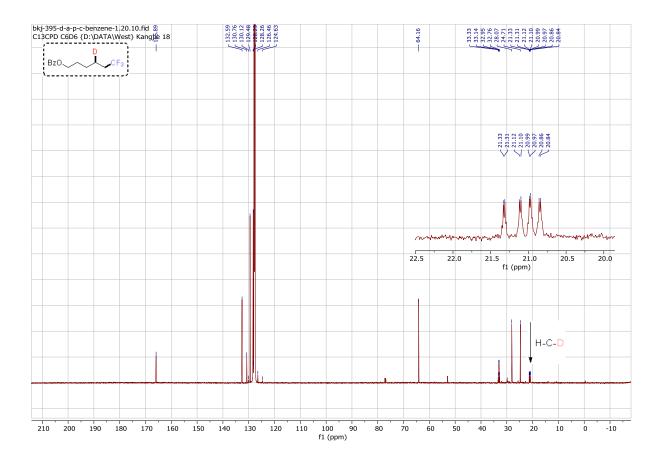


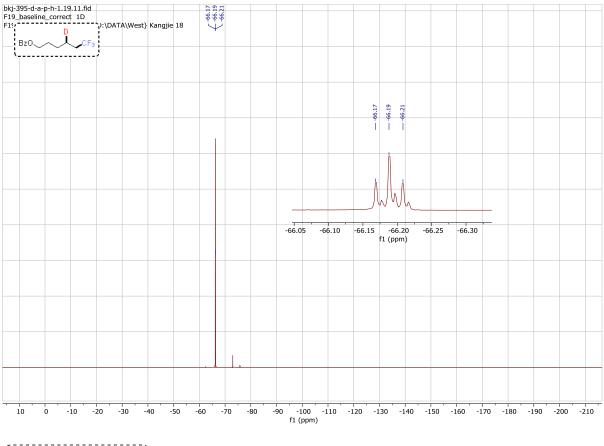
For 72-trans, a strong NOE was observed for CF_2H (trans)/Me. However, there is no significant NOE observed for CF_2H (cis)/Me of 72-cis. Therefore, major isomer of 72 should be the transproduct, which also correlates the finding by Wu and co-workers.¹⁹

2.6 Deuterium labelling and kinetic isotope effect (KIE) studies



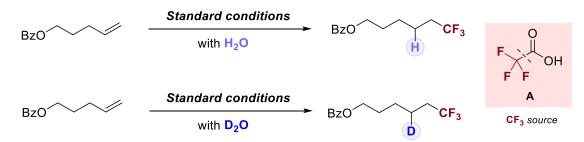
Deuterium labelling experiments





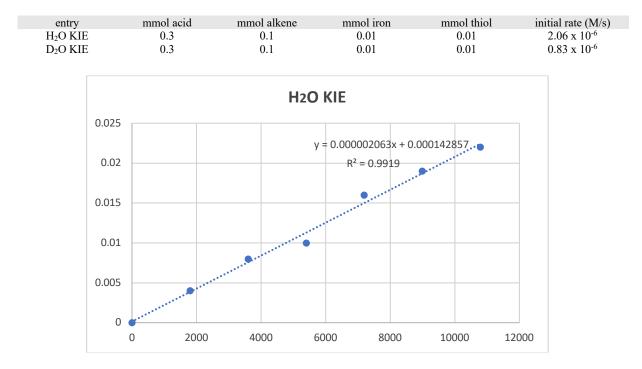
BzO CF₃

Kinetic isotope effect (KIE) experiments

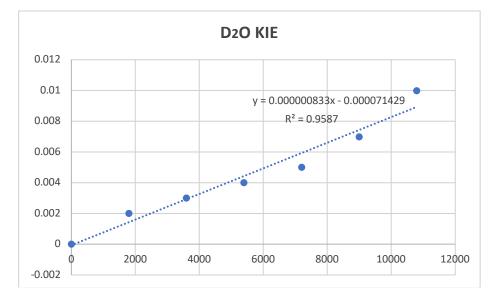


Fe(OAc)₂ and Na₂CO₃ were added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N₂ (repeated for 4 times), followed by addition of alkenes, CF₃COOH and TRIP thiol in MeCN/H₂O (9:1, 0.1 M in regard to alkenes) via syringe under N₂. Note: Both reactions were run on 0.2 mmol of the substrate and PhCF₃ was added as internal standard. The reaction mixture was placed under 390nm Kessil® light. At different time points, the aliquot of reaction mixture is directly transferred to NMR tube and reaction progress was monitored by ¹⁹F NMR.

t (s)	H ₂ O (M)	t (s)	D ₂ O (M)
0	0	0	0
1800	0.004	1800	0.002
3600	0.008	3600	0.003
5400	0.01	5400	0.004
7200	0.016	7200	0.005
9000	0.019	9000	0.007
10800	0.022	10800	0.01



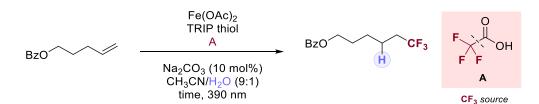
Reaction with H₂O (standard conditions): $y = (2.06 \times 10^{-6})(k_H)x + (1.4 \times 10^{-4}), R^2 = 0.9916$



Reaction with D₂O: $y = (0.83 \times 10^{-6}) (k_D)x - (7.1 \times 10^{-4}), R^2 = 0.9587$

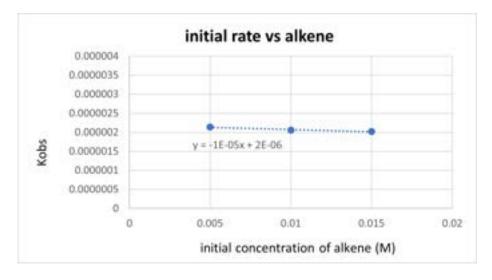
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KIE: k_H/k_D = 2.5
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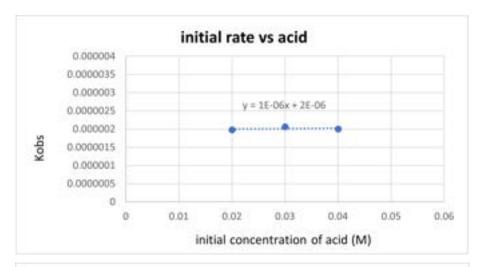
2.7 Kinetic studies to determine reaction rate law

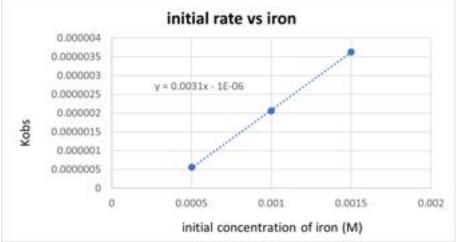


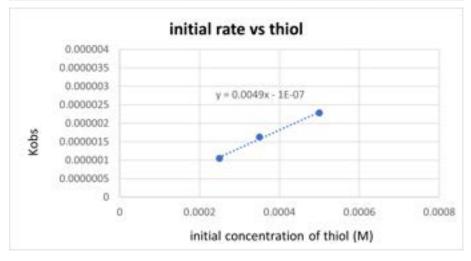
Fe(OAc)₂ and Na₂CO₃ were added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N₂ (repeated for 4 times), followed by addition of alkenes, CF₃COOH and TRIP thiol in MeCN/H₂O (9:1, 0.1 M in regard to alkenes) via syringe under N₂. Note: All reactions were run on 0.2 mmol of the substrate and PhCF₃ was added as internal standard. The reaction mixture was placed under 390nm Kessil® light. At different time points, the aliquot of reaction mixture is directly transferred to NMR tube and reaction progress was monitored by ¹⁹F NMR.

entry	mmol acid	mmol alkene	mmol iron	mmol thiol	initial rate (M/s)
1	0.3	0.1	0.01	0.01	2.06 x 10 ⁻⁶
2	0.3	0.05	0.01	0.01	2.14 x 10 ⁻⁶
3	0.3	0.15	0.01	0.01	2.02 x 10 ⁻⁶
4	0.2	0.1	0.01	0.01	1.98 x 10 ⁻⁶
5	0.4	0.1	0.01	0.01	2 x 10 ⁻⁶
6	0.3	0.1	0.005	0.01	5.6 x 10 ⁻⁷
7	0.3	0.1	0.015	0.01	3.63 x 10 ⁻⁶
8	0.3	0.1	0.01	0.0025	1.05 x 10 ⁻⁶
9	0.3	0.1	0.01	0.0035	1.63 x 10 ⁻⁶
10	0.3	0.1	0.01	0.005	2.28 x 10 ⁻⁶
11	0.3	0.1	0.01	0.0075	2.5 x 10 ⁻⁶

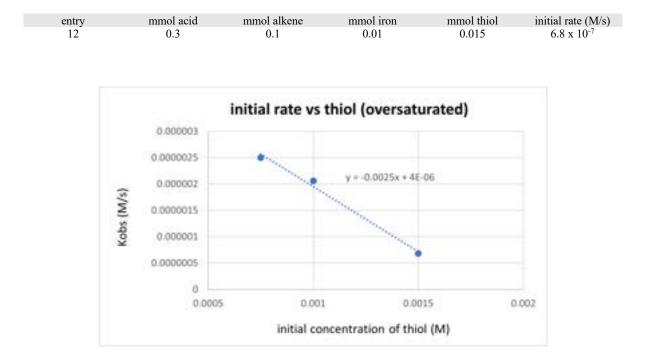








With higher loading of thiol catalyst (15 mol%), negative order of thiol is observed. The oversaturation of thiol catalyst may lead to other side reactions, consuming thiol and circumventing the following dual catalytic cycle with iron and other reactants.



Indicated by previous reports²⁰⁻²³ and our study on disulfide formation (see 2.7 Study of disulfide formation), thiol catalyst can form disulfide under light irradiation. Furthermore, TEMPO-trapping experiment demonstrates that higher concentration of disulfide could quench CF₃ radical, indicated by peak at -42.74ppm on ¹⁹F NMR, suggesting the generation of TRIP-SCF₃.²⁴

With higher concentration of TRIP thiol in the system, it is more likely to form disulfide under light irradiation, which can sequester the CF_3 radical, leading to drastically decreased rate of thiol and showing negative order when reaching oversaturation.

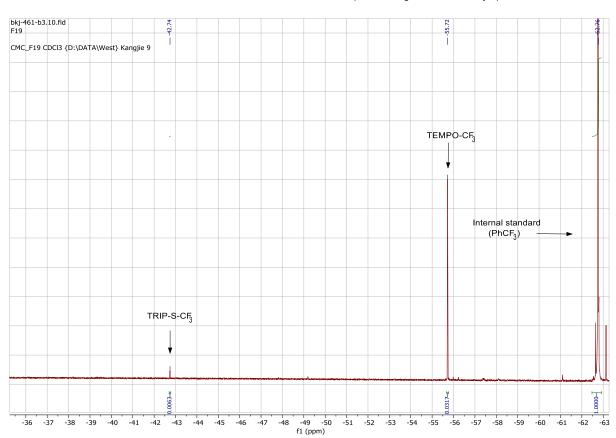


detected at -55.7 ppm on ¹⁹F NMR

3.17% (31.7% in regard to iron catalyst)

 S^{CF_3} detected at -42.7 ppm on ¹⁹F NMR

0.63% (6.3% in regard to iron catalyst)



CF₃COOH (3 equiv.)

CH₃CN/H₂O= 9:1 (0.1M) + 1equiv. TEMPO

390nm, 24h

(TRIPS)₂

0.001 mmol

10 mol%

Fe(OAc)₂ +

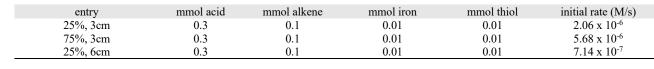
0.001 mmol

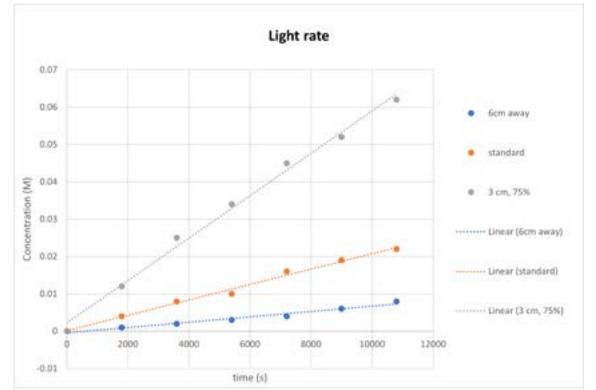
10 mol%

2.8 Light intensity impact on reaction rate

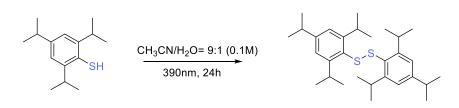


Following General Procedure A, all reactions were run on 0.2 mmol of the substrate and PhCF₃ was added as internal standard. The reaction mixture was placed under 390nm Kessil® light. At different time points, the aliquot of reaction mixture is directly transferred to NMR tube and reaction progress was monitored by ¹⁹F NMR. Reaction rate is correlated to light intensity postively, indicating a light-dependent character of the system.





2.9 Study of the disulfide formation



0.1 mmol, 1 equiv.

7.9% (with 83.8% of TRIP thiol recovery)

TRIP thiol (0.1 mmol, 1 equiv. was added to MeCN/H₂O (9:1, 0.1 M) via syringe after backfilling with N₂) was added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The reaction mixture was placed under 390nm Kessil® light after sealing the punctured holes of the vial cap with vacuum grease and electric tape/parafilm for better air-tight protection and allowed to react at room temperature for 24 h. With solid formation observed over time, crude NMR indicated the formation of TRIP disulfide in 7.9% yield with 83.8% TRIP thiol recovery. The formation of disulfide could further engage in homolysis under light irradiation, leading to generation of thiyl radical, which can oxidize Fe(II) catalyst to photoreactive Fe(III) species, initiating the fluoroalkyl radical generation.²⁰⁻²³

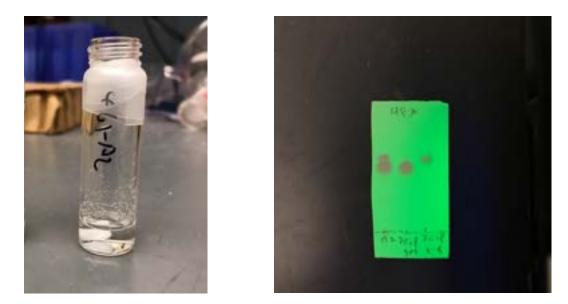
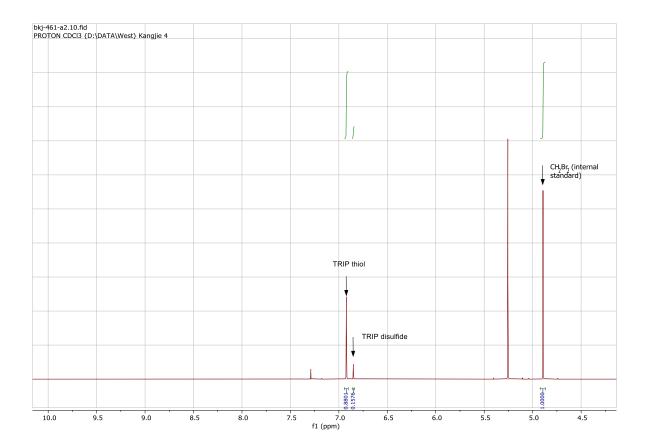


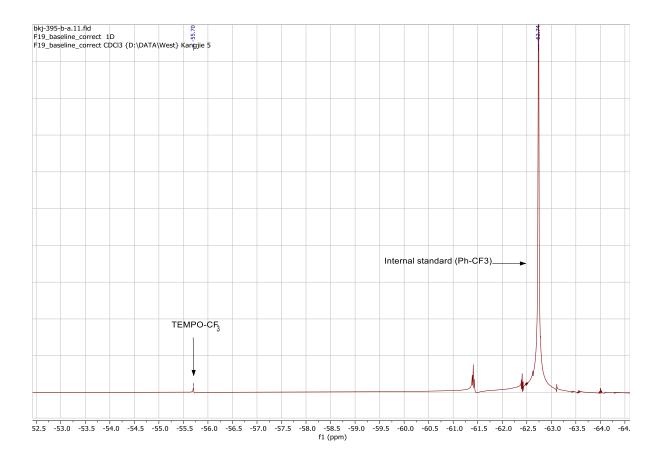
Figure S1. Left: solid formation (TRIP disulfide). Right: TLC spotting (left to right: reaction mixture, pure TRIP thiol, pure TRIP disulfide).



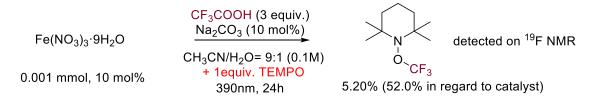
2.10 TEMPO experiment study



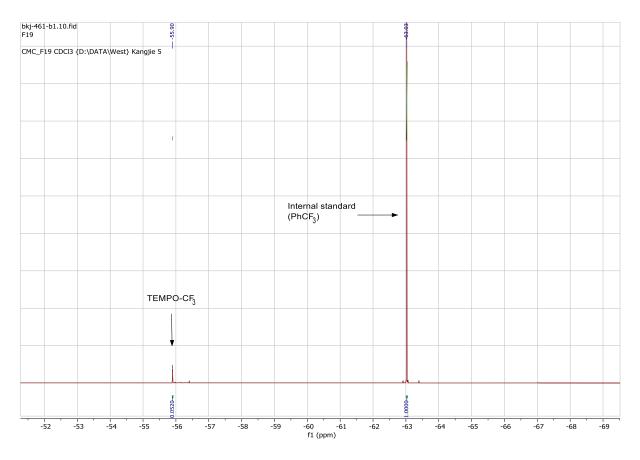
Fe(OAc)₂ (10 mol%, 0.1 equiv.), Na₂CO₃ (10 mol%, 0.1 equiv.) and TEMPO (1 equiv.) were added via syringe after backfilling with N₂) was added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N₂ (repeated for 4 times), followed by addition of alkenes (0.1 mmol, 1.0 equiv.) TRIP thiol (10 mol%, 0.1 equiv.) and CF₃COOH (0.30 mmol, 3.0 equiv) in MeCN/H₂O (9:1, 0.1 M in regard to alkenes) via syringe under N₂. The reaction mixture was placed under 390nm Kessil® light after sealing the punctured holes of the vial cap with vacuum grease and electric tape/parafilm for better air-tight protection and allowed to react at room temperature for 24 h. Following this, the reaction mixture was filtered through a pad of celite which was subsequently rinsed with DCM. The filtrate was concentrated and directly applied for crude ¹⁹F NMR (with PhCF₃ as internal standard). The detection of TEMPO-CF₃ at -55.70 ppm suggested CF₃ radical generation in the system.²⁵



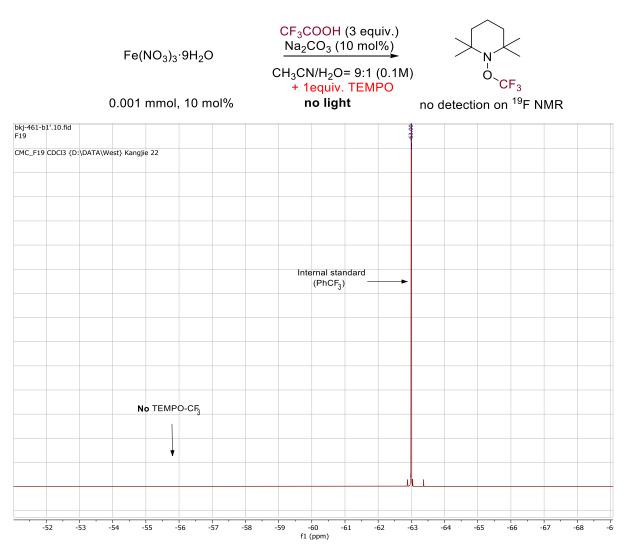
2.11 Evidence of visible-light induced homolysis of trifluoroacetic acid with iron



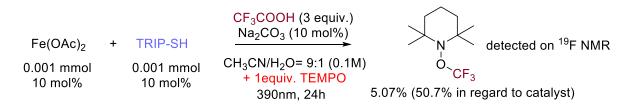
Fe(NO₃)₃·9H₂O (10 mol%, 0.1 equiv.), Na₂CO₃ (10 mol%, 0.1 equiv.) and TEMPO (1 equiv.) were added via syringe after backfilling with N₂) was added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N₂ (repeated for 4 times), followed by CF₃COOH (0.30 mmol, 3.0 equiv.) in MeCN/H₂O (9:1, 0.1M) via syringe under N₂. The reaction mixture was placed under 390nm Kessil® light after sealing the punctured holes of the vial cap with vacuum grease and electric tape/parafilm for better airtight protection and allowed to react at room temperature for 24 h. Following this, the reaction mixture was filtered through a pad of celite which was subsequently rinsed with DCM. The filtrate was concentrated and directly applied for crude ¹⁹F NMR (with PhCF₃ as internal standard).



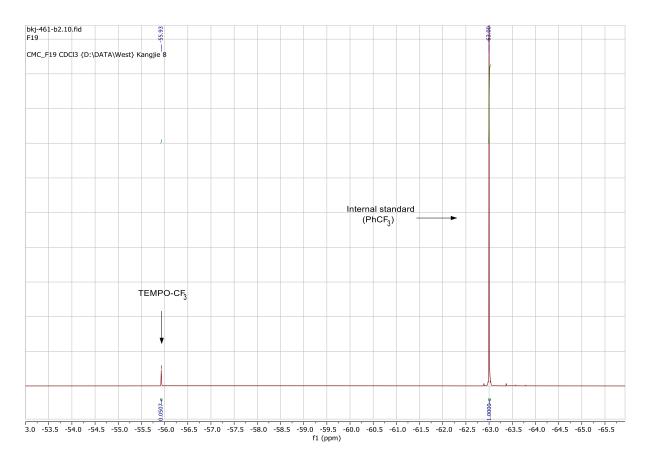
Indicated by ¹⁹F NMR, photoactive Fe(III) (Fe(NO₃)₃·9H₂O) could induce the homolysis of trifluoroacetic acid (TFA) under light irradiation, as TEMPO-CF₃ was detected at -55.9 ppm in 5.2% yield (52.0% in regard to iron).



Indicated by ¹⁹F NMR, in the absence of light irradiation, the homolysis of trifluoroacetic acid (TFA) by Fe(III) (Fe(NO₃)₃.9H₂O) is not observed, supporting light is necessary in promoting homolysis of TFA to afford CF₃ radical.

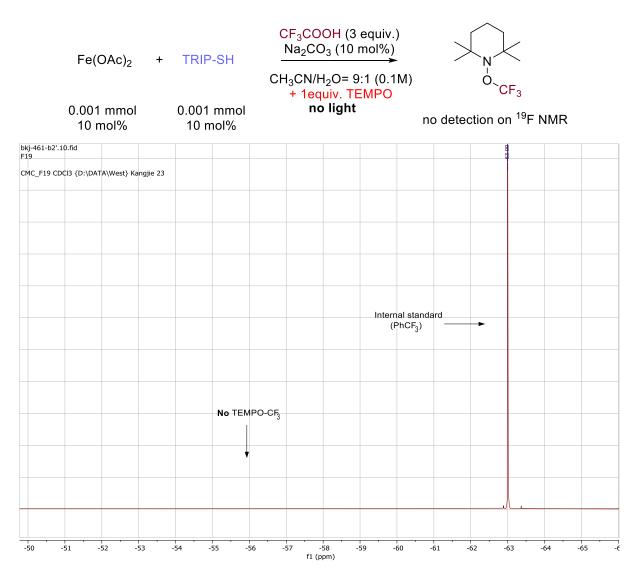


Fe(OAc)₂ (10 mol%, 0.1 equiv.), Na₂CO₃ (10 mol%, 0.1 equiv.) and TEMPO (1 equiv.) were added via syringe after backfilling with N₂) was added in an oven-dried 8-mL test vial containing a Teflon®-coated magnetic stir bar. The vial was evacuated and backfilled with N₂ (repeated for 4 times), followed by TRIPSH (10 mol%, 0.1 equiv.), CF₃COOH (0.30 mmol, 3.0 equiv.) in MeCN/H₂O (9:1, 0.1M) via syringe under N₂. The reaction mixture was placed under 390nm Kessil® light after sealing the punctured holes of the vial cap with vacuum grease and electric tape/parafilm for better air-tight protection and allowed to react at room temperature for 24 h. Following this, the reaction mixture was filtered through a pad of celite which was subsequently rinsed with DCM. The filtrate was concentrated and directly applied for crude ¹⁹F NMR (with PhCF₃ as internal standard).



As demonstrated in the section of 2.7 Study of disulfide formation and illustrated by previous reports,²⁰⁻²³ thiol or disulfide can undergo homolysis under light irradiation, which is capable of oxidizing lower-valent iron species to photoactive iron (III) species, engaging in the following photoinduced homolysis of trifluoroacetic acid.

Indicated by ¹⁹F NMR, the mixture of $Fe(OAc)_2$ and TRIP thiol could induce the homolysis of trifluoroacetic acid (TFA) under light irradiation, as TEMPO-CF₃ was detected at -55.9 ppm in 5.07% yield (50.7% in regard to iron).



Similar to Fe(III) counterpart and indicated by¹⁹F NMR, the homolysis of trifluoroacetic acid is not observed by the combination of Fe(II) (Fe(OAc)₂) and TRIP thiol in the absence of light irradiation, confirming light is necessary in inducing homolysis of trifluoroacetic acid to afford CF₃ radical.

2.12 Mass balance studies of hydrofluoroalkylation of representative examples

Mass balance studies of heterocycle-containing substrates

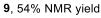
bkj-464-b1-h.12.fid PROTON CDCl3 {D:\DATA\West} Kangjie 11 o 1 1 14 Lun 0.11H 0.27-1 -00. 5.0 f1 (ppm) -0.5 10.5 10.0 9.5 9.0 8.5 7.5 6.5 6.0 5.5 4.5 3.5 2.5 2.0 1.5 1.0 0.5 8.0 7.0 4.0 3.0 0.0

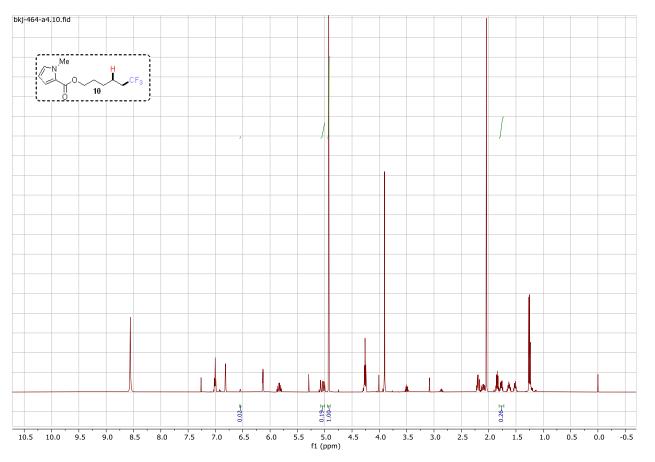
Trifluoromethylation Examples

As indicated in the crude ¹H NMR, **9** is produced in 54% NMR yield at 1.60-1.55 (m, 2H) with 44% residual starting material rat (5.75-5.66, m, 1H) (in regard to 0.1 mmol CH_2Br_2 as internal standard). The mass-balance of this reaction is 98%.



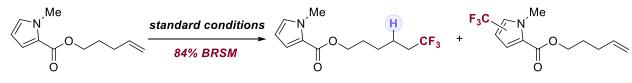
44% starting material recovery





As indicated in the crude ¹H NMR, **10** is observed in 52% NMR yield at 1.81-1.71 (m, 2H) with 38% residual starting material recovery at (5.07-5.00, m, 1H) (in regard to 0.1 mmol CH_2Br_2 as internal standard). The mass-balance is 90% from these two species.

The reduced mass balance from can be explained by slightly competitive trifluoromethylation of the pyrrole ring (diagnostic peak at 6.56-6.53 (m, 1H)) to form trifluoromethylated starting material **10'** (single isomer), accounting for 8% NMR yield. This species has been isolated and characterization is provided below. With this, the overall mass balance is 98%.

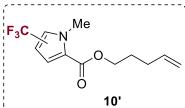


38% starting material recovery

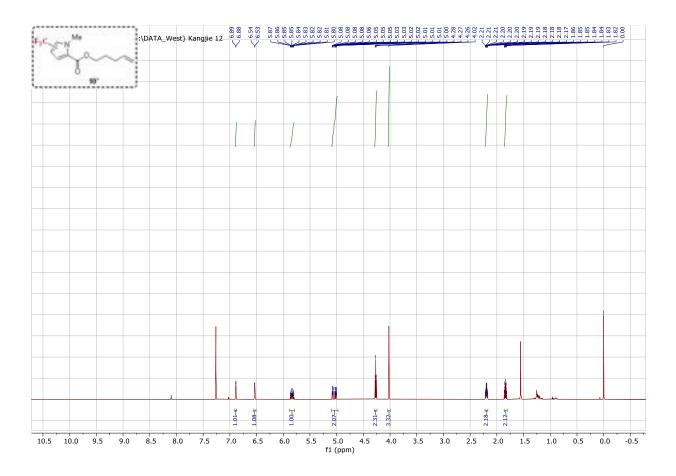
10, 52% NMR yield

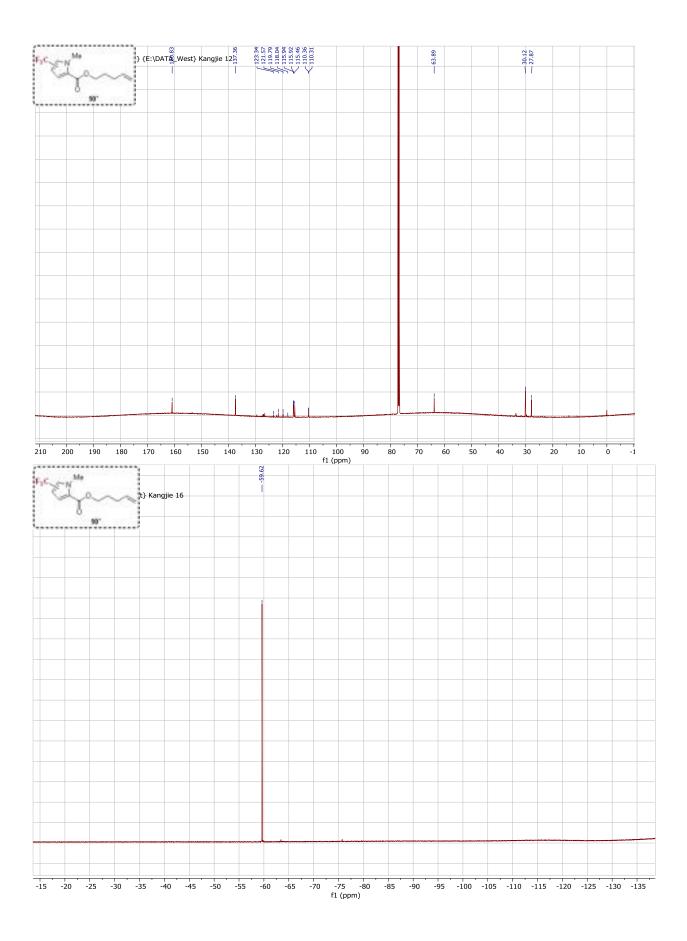
10', 8% NMR yield

The characterization data of 10' is shown below,

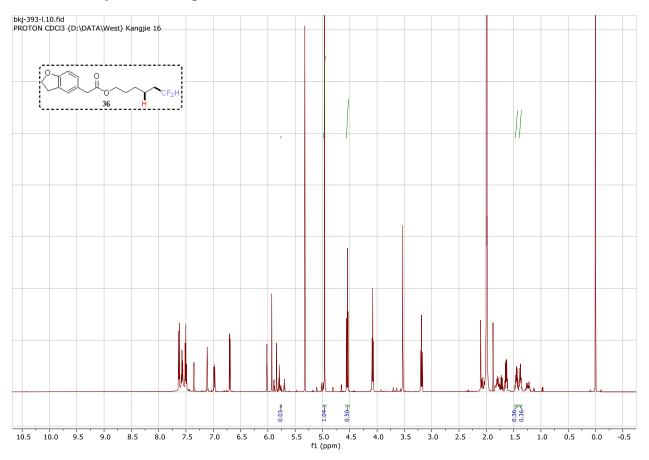


¹ H NMR (600 MHz, Chloroform-*d*) δ 6.89 (d, J = 4.1 Hz, 1H), 6.53 (d, J = 4.1 Hz, 1H), 5.89-5.79 (m, 1H), 5.10 – 4.97 (m, 2H), 4.27 (t, J = 6.6 Hz, 2H), 4.02 (s, 3H), 2.22 – 2.17 (m, 2H), 1.86 – 1.80 (m, 2H). ¹³C NMR (151 MHz, CDCl_{3_3}mm tube) δ 160.83, 137.36, 120.68 (q, J = 267.8 Hz), 115.93 (q, J = 2.4 Hz), 115.46, 110.34 (q, J = 7.6 Hz), 63.89, 30.12, 27.87. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -59.62. HRMS APCI: [M+H]⁺ calcd. for C12H15F3NO2: 262.1049; Found 262.1054

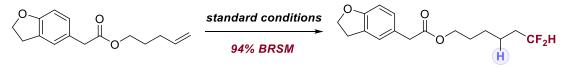




Difluoromethylation examples.

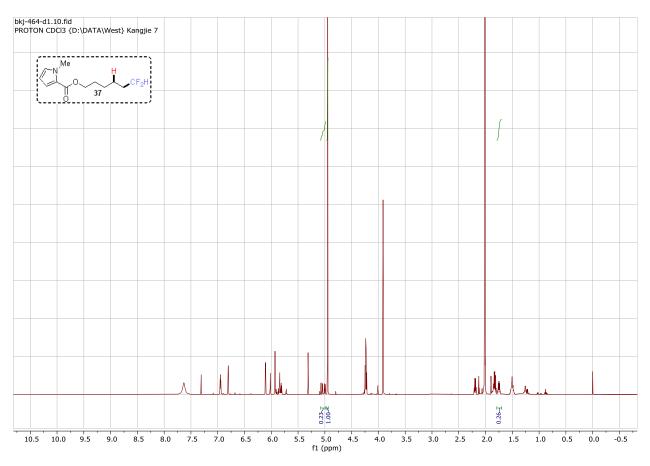


As indicated in the crude ¹H NMR, **36** is produced in 72% NMR yield (1.48-1.42, m, 2H) with 24% residual starting material at 5.81-5.74 (partially overlapped with product peak) (m, 1H) (in regard to 0.1 mmol CH_2Br_2 as internal standard). The internal standard is slightly overlapped with substrate peak which shows integration of 1.04 at 4.9 ppm. No other significant products are observed. The mass balance is approximately 96%.



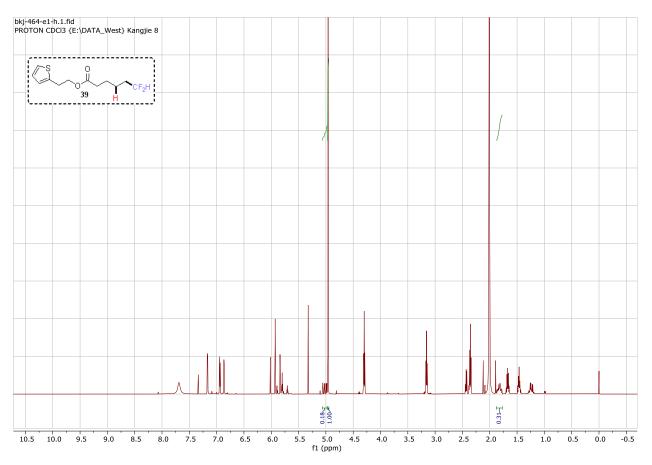
24% starting material recovery

36, 72% NMR yield



As indicated in the crude ¹H NMR, **37** is produced in 52% NMR yield (1.79-1.70, m, 2H) with 46% of starting material recovery at 5.07-4.99 (m, 1H) (in regard to 0.1 mmol CH₂Br₂ as internal standard). No other significant products are observed. The mass-balance of this reaction is 98%.





As indicated in the crude ¹H NMR, **39** is produced in 62% NMR yield (1.88-1.77, m, 2H) with 36% residual starting material at 5.07-4.98 (m, 1H) (in regard to 0.1 mmol CH₂Br₂ as internal standard). No other significant products are observed. The mass-balance of the reaction is 98%.

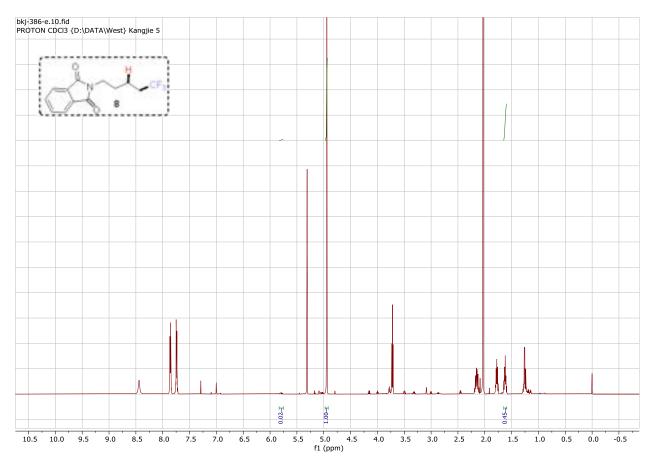


36% starting material recovery

39, 62% NMR yield

Mass balance studies of representative substrates

Hydrotrifluoromethylation of representative examples

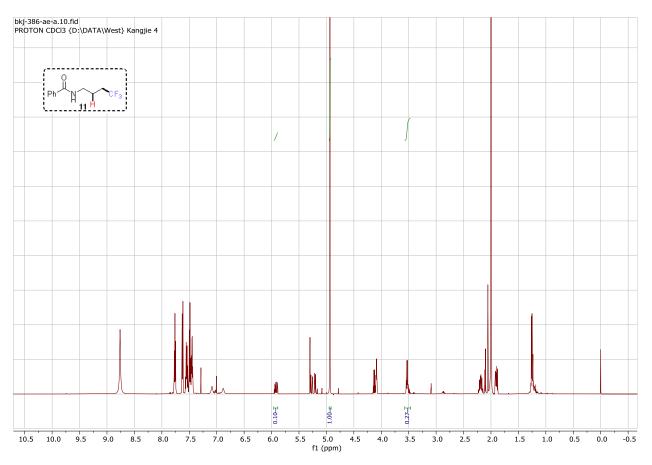


As indicated in the crude ¹H NMR, **8** is produced in 90% NMR yield (1.65-1.58, m, 2H) with 8% residual starting material at 5.84-5.74 (m, 1H) (in regard to 0.1 mmol CH₂Br₂ as internal standard). No other significant products are observed. The mass-balance is 98%



8% starting material recovery

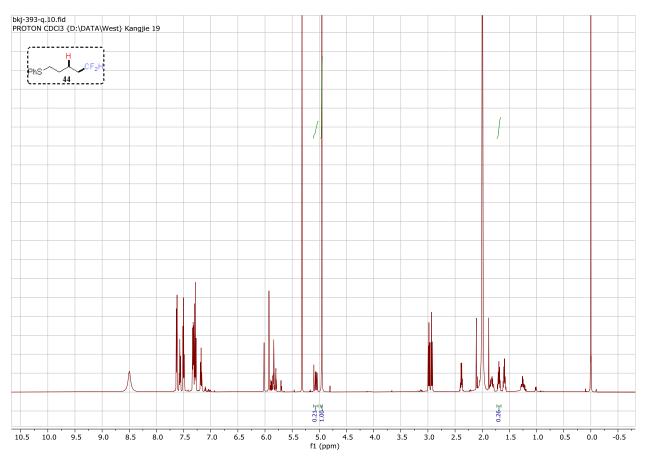
8, 90% NMR yield



As indicated in the crude ¹H NMR, **11** is produced in 54% NMR yield at 3.59-3.45 (m, 2H) with 40% residual starting material (5.97-5.87, m, 1H) (in regard to 0.1 mmol CH₂Br₂ as internal standard). No other significant products are observed. The mass-balance is 94%.

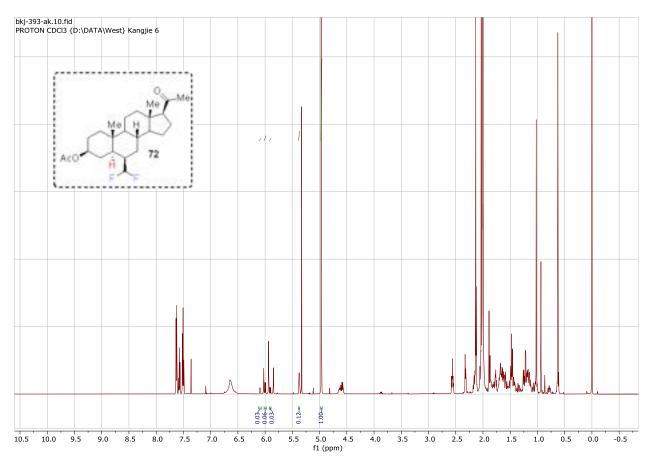


Hydrodifluoromethylation of representative examples



As indicated in the crude ¹H NMR, **44** is produced in 52% NMR yield at 1.73-1.65 (m, 2H) with 42% residual starting material at (5.11-5.803, m, 2H) (in regard to 0.1 mmol CH₂Br₂ as internal standard). No other significant products are observed. The mass-balance is 94%.

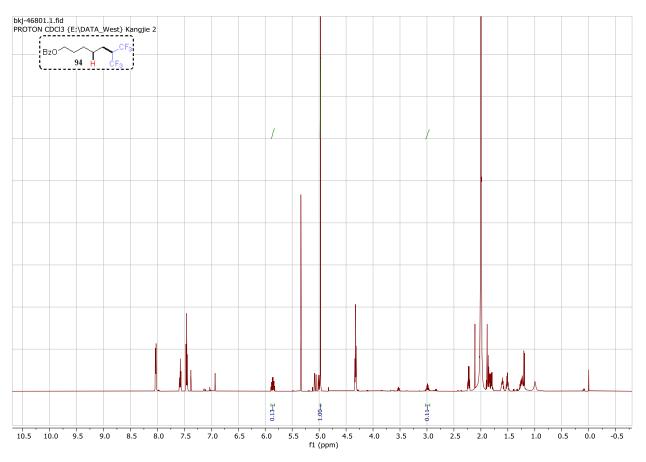




As indicated in the crude ¹H NMR, **72** is produced in 48% NMR yield at 1.73-1.65 (m, 2H) with 48% residual starting material at 5.39-5.36 (m, 1H) (in regard to 0.1 mmol CH₂Br₂ as internal standard). No other significant products are observed. The mass-balance is 96%.



Hydrofluoroalkylation of a representative substrate



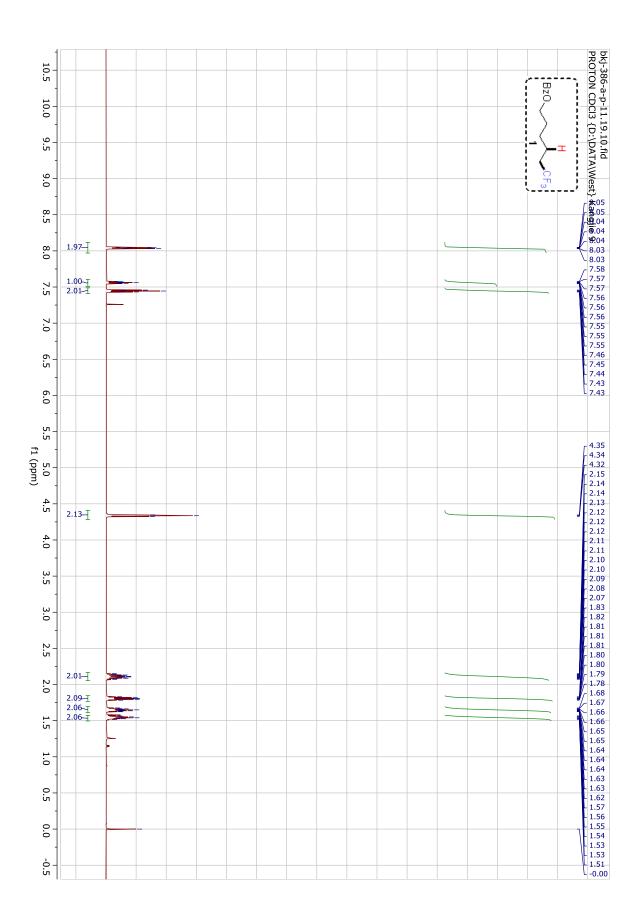
As indicated in the crude ¹H NMR, **94** is produced in 44% NMR yield at 3.03-2.95 (m, 1H) with 52% residual starting material at 5.90-5.82 (m, 1H) (in regard to 0.1 mmol CH₂Br₂ as internal standard). No other significant products are observed. The mass-balance is 96%.



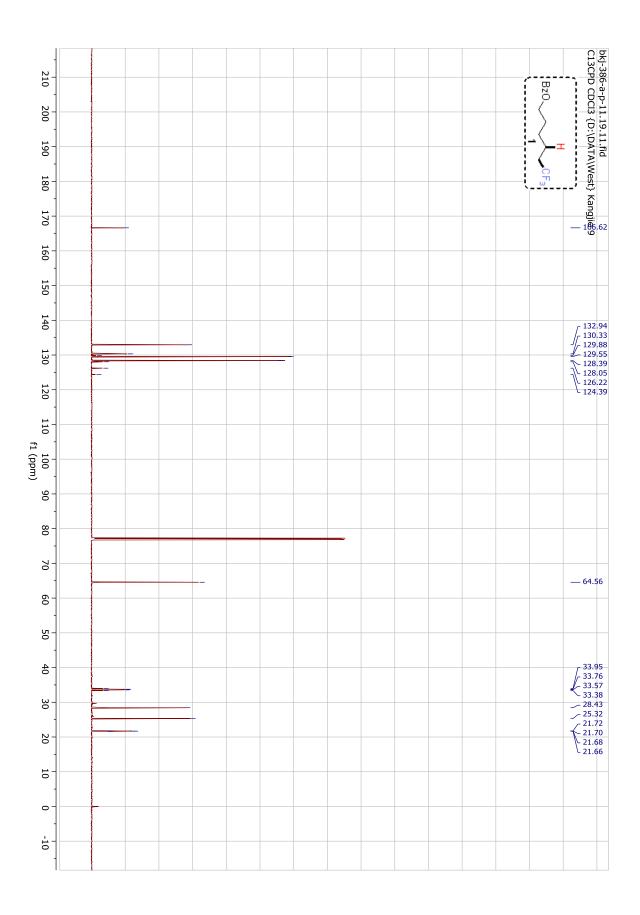
52% starting material recovery

94, 44% NMR yield

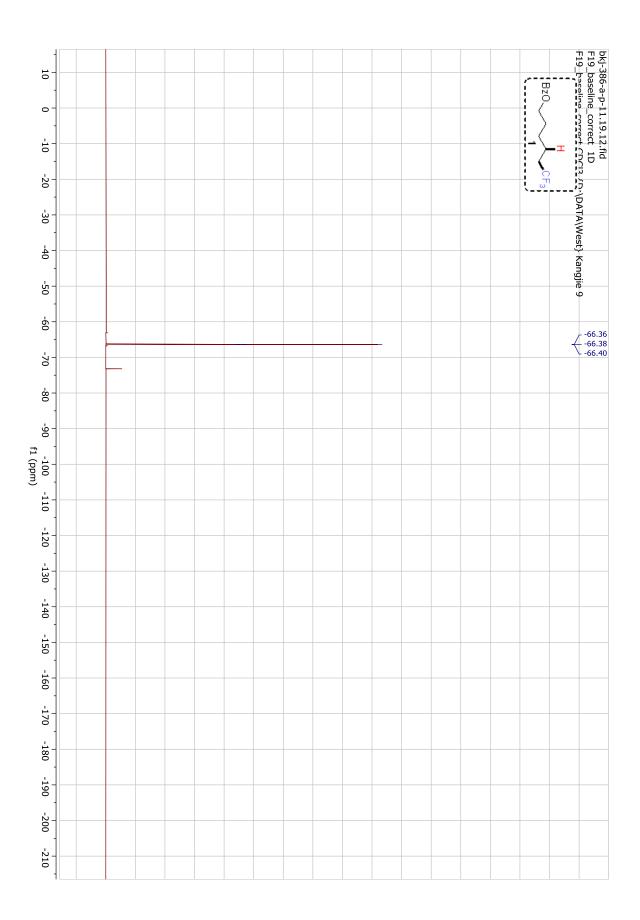
III. Supplemental Figure

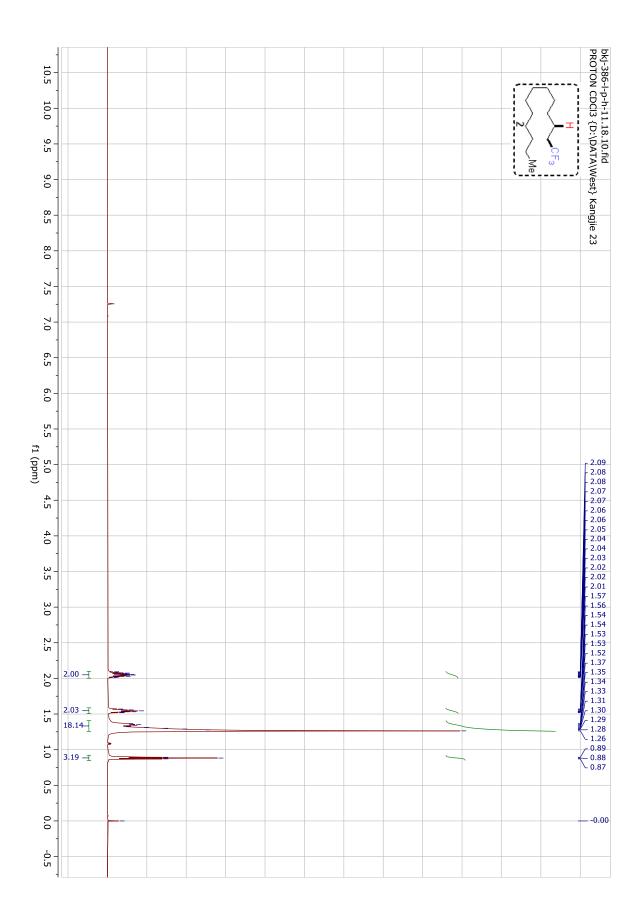




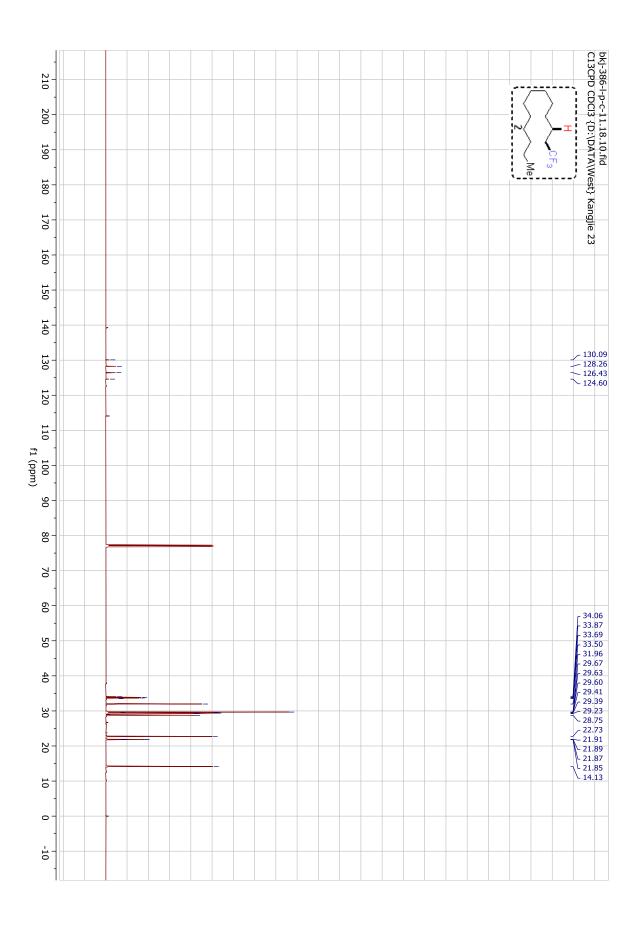


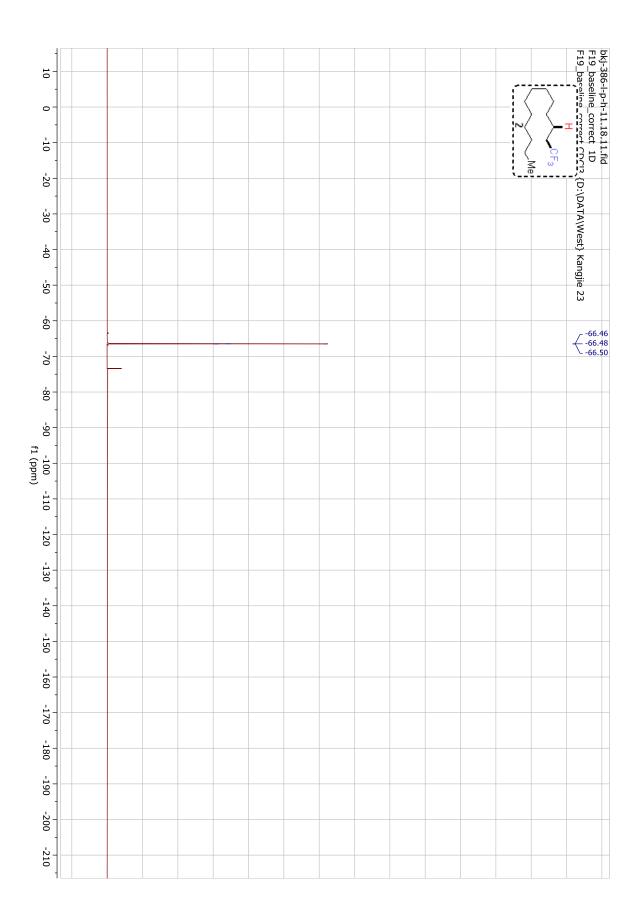


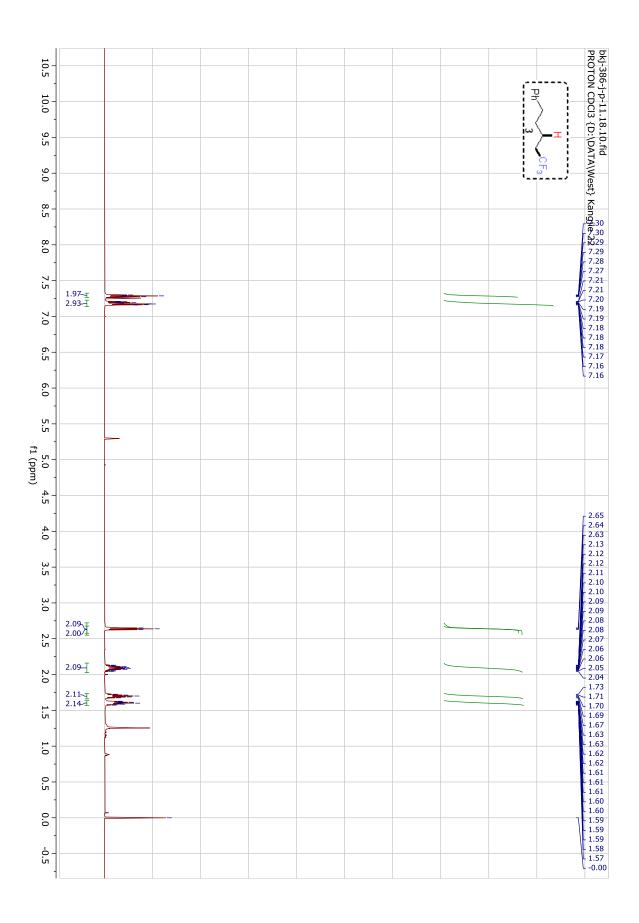




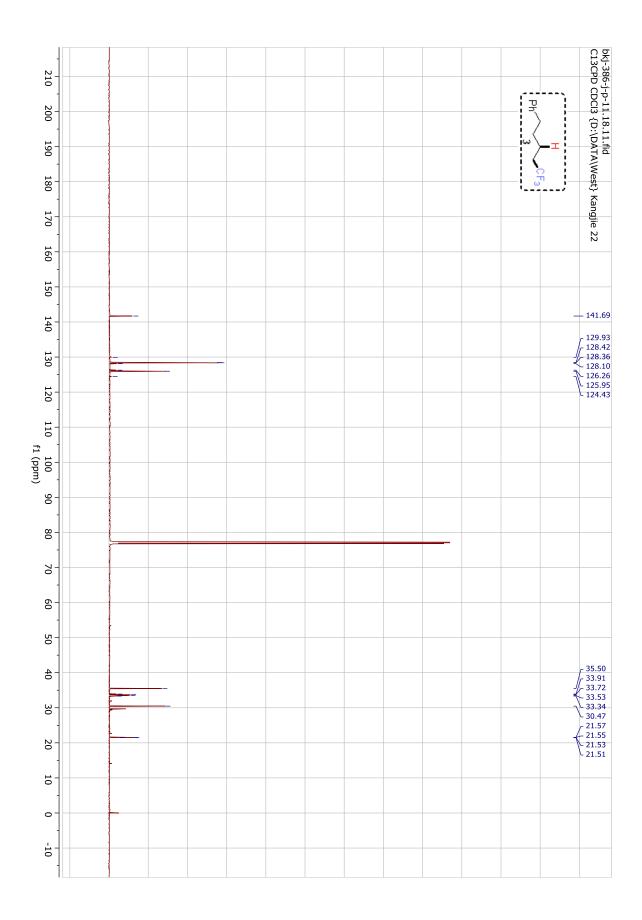




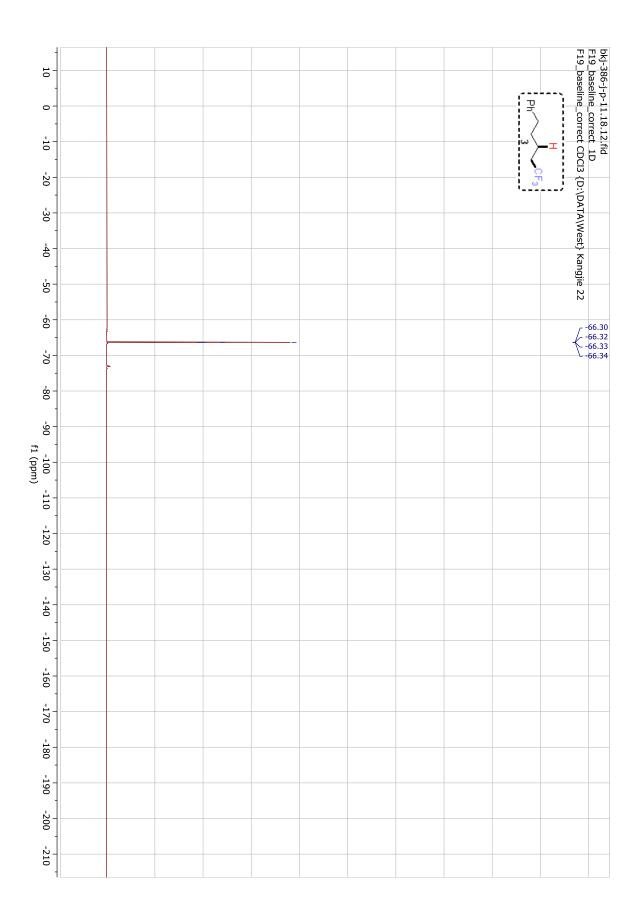




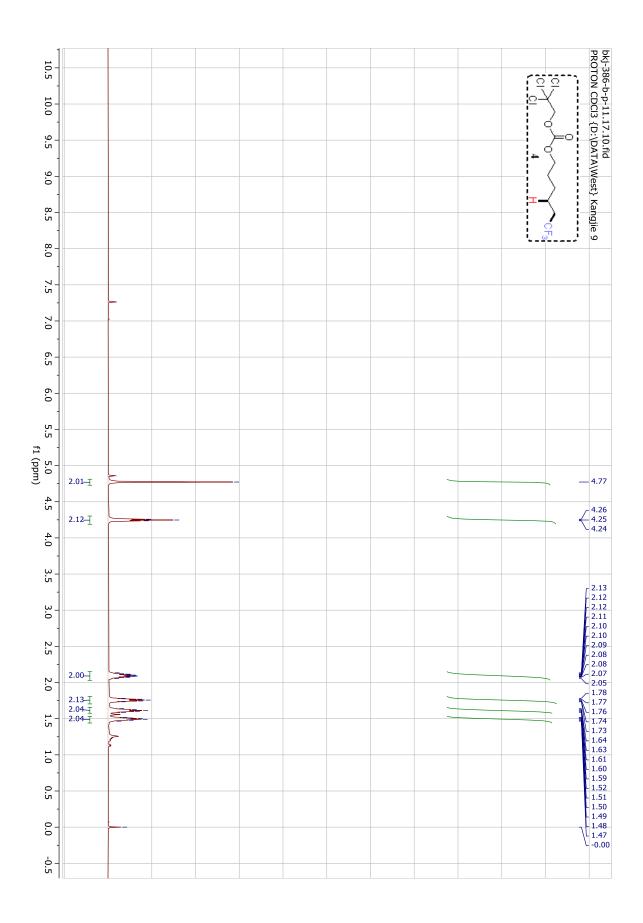




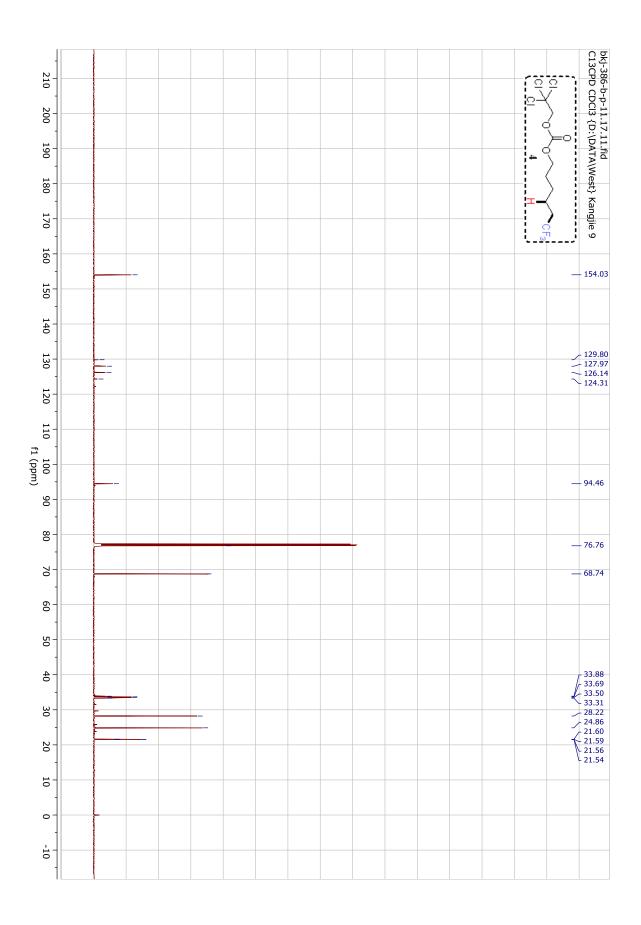


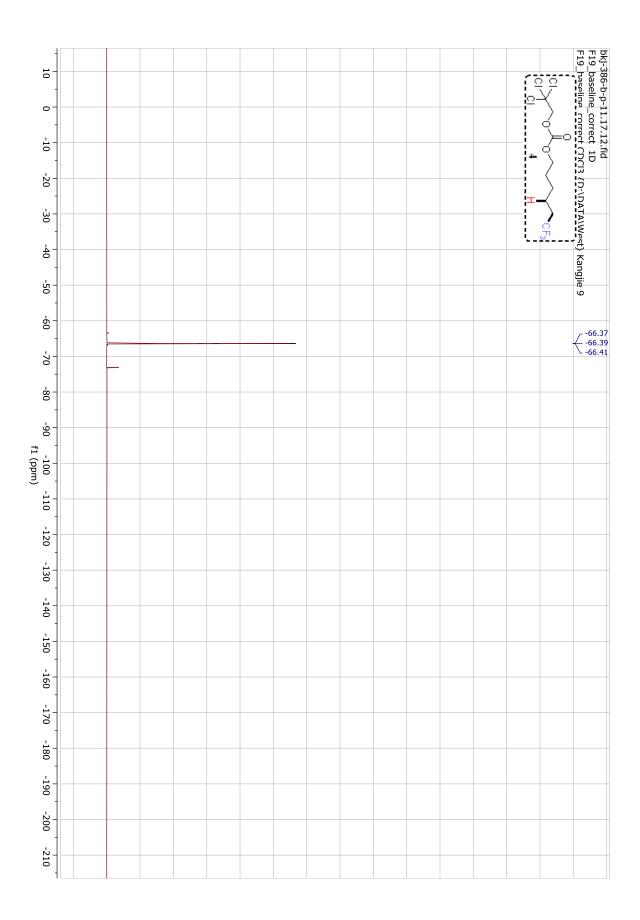




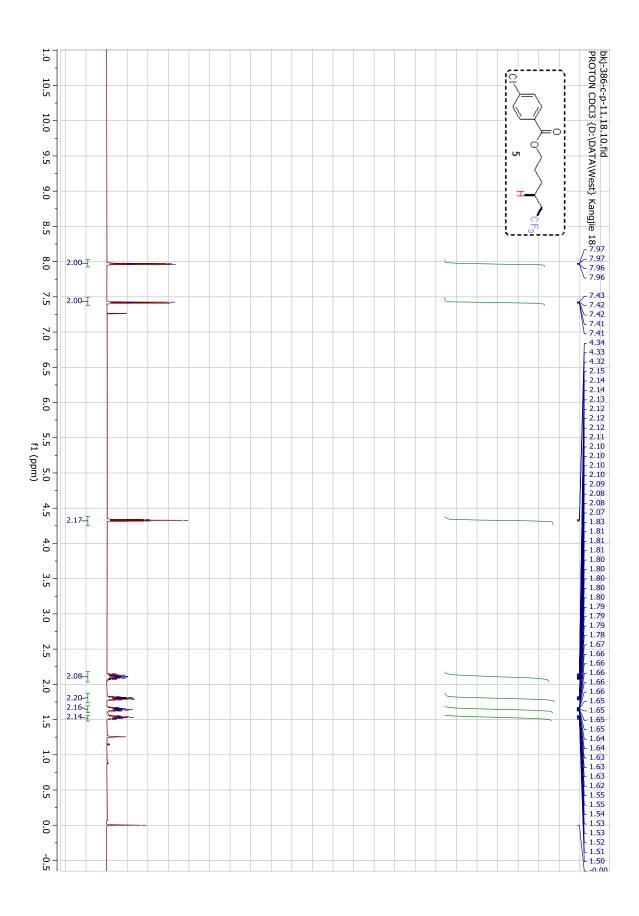




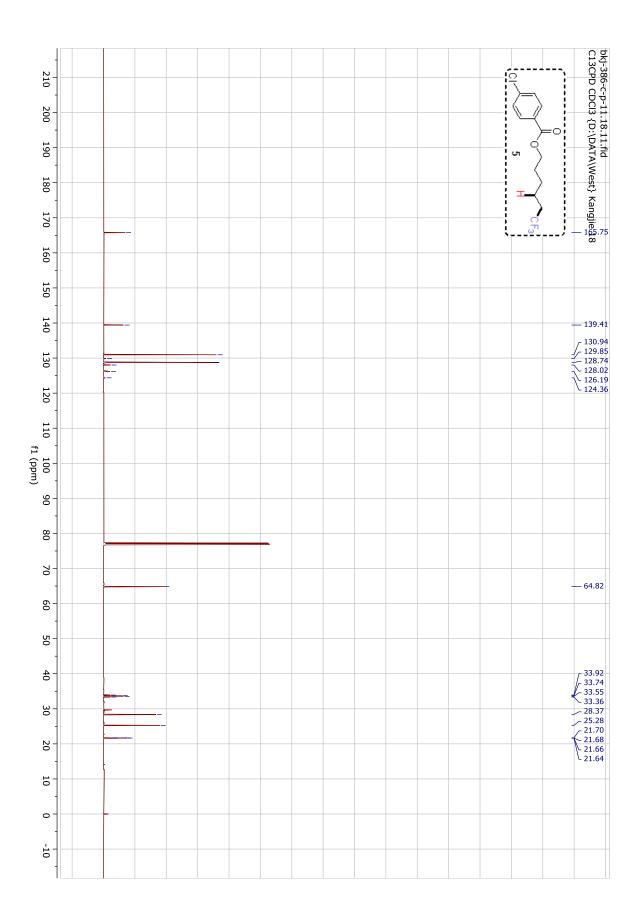


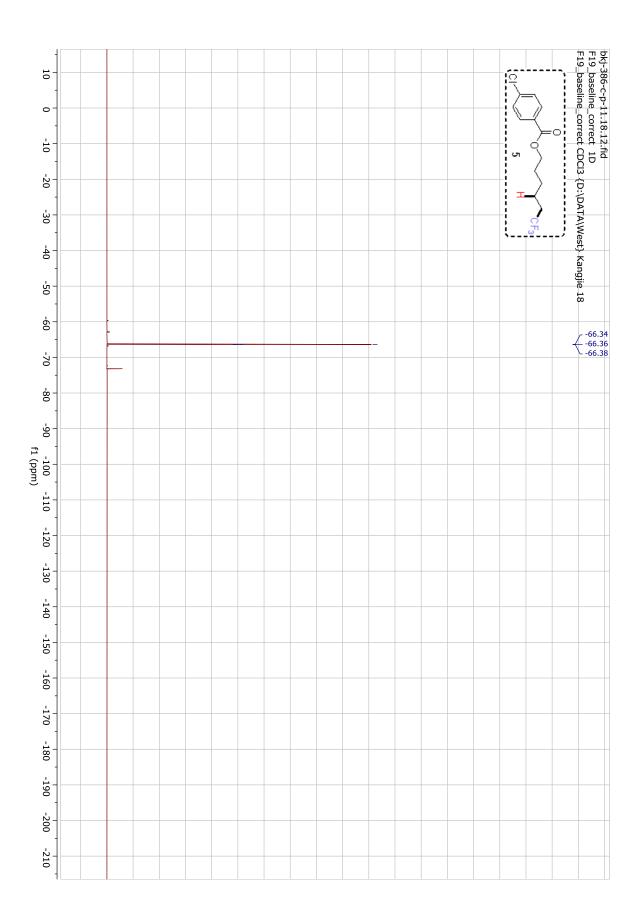




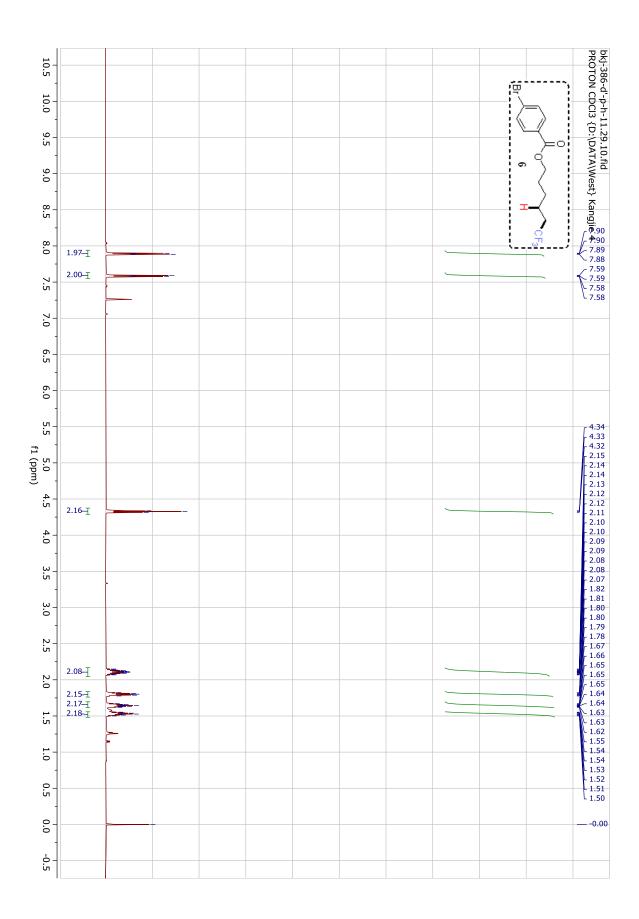


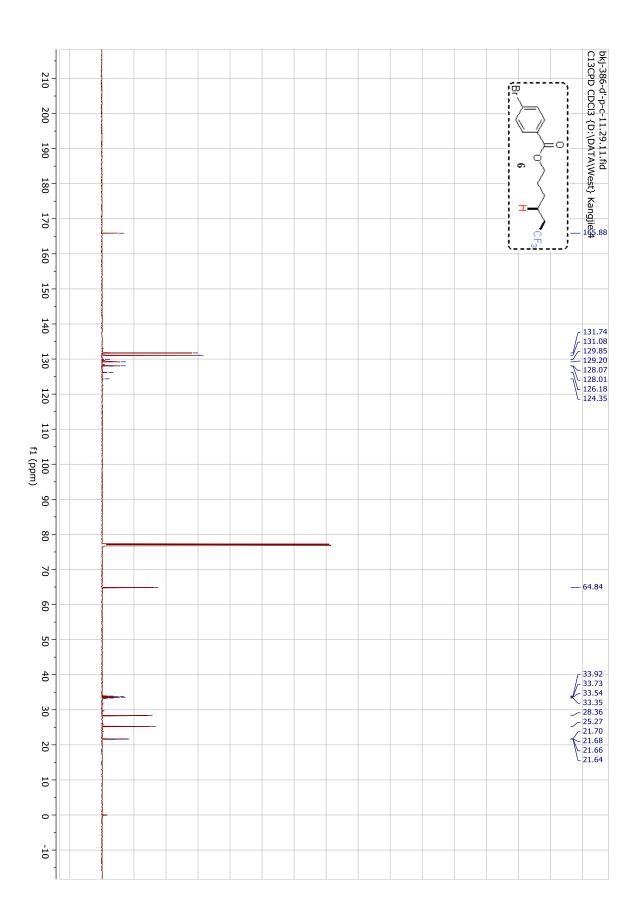




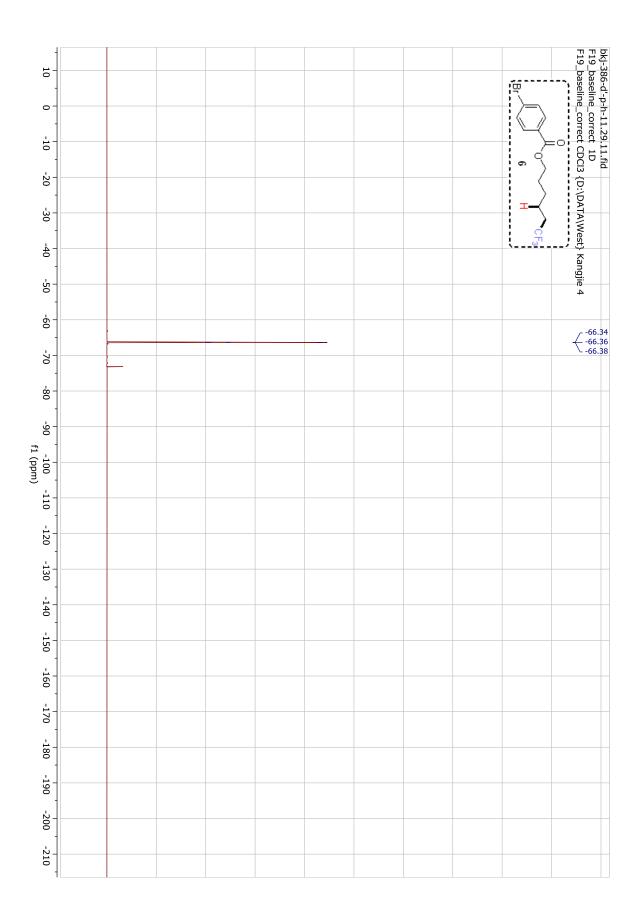




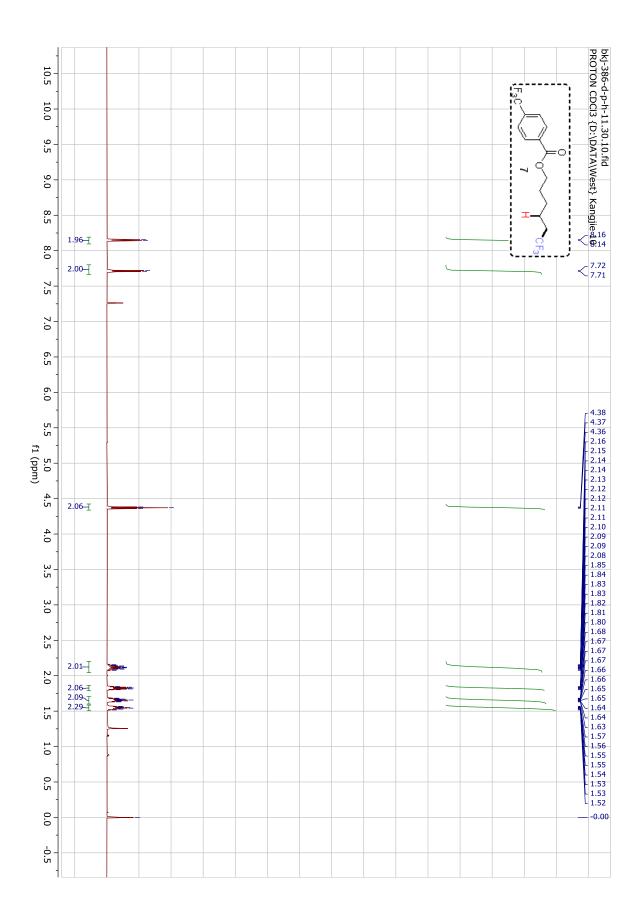


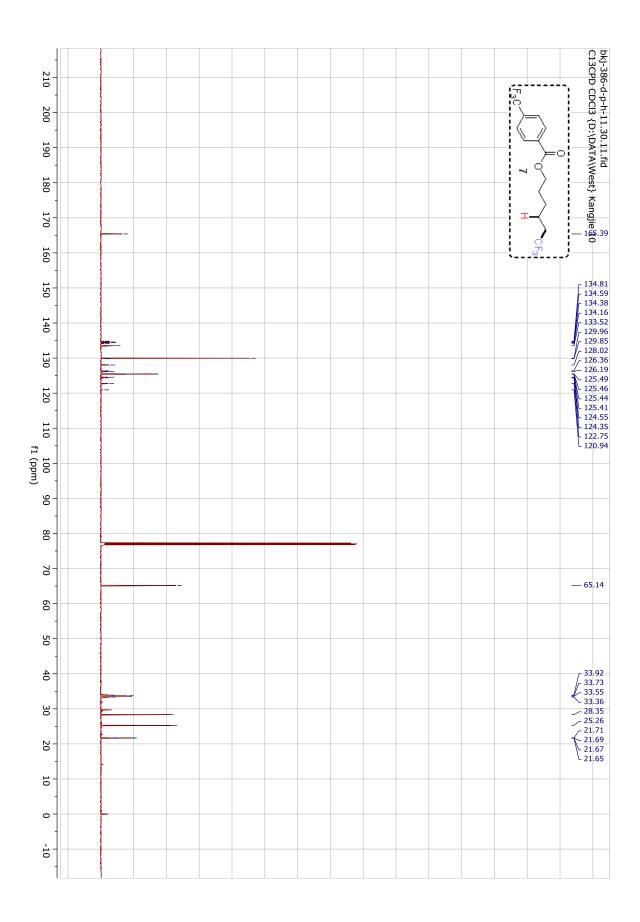


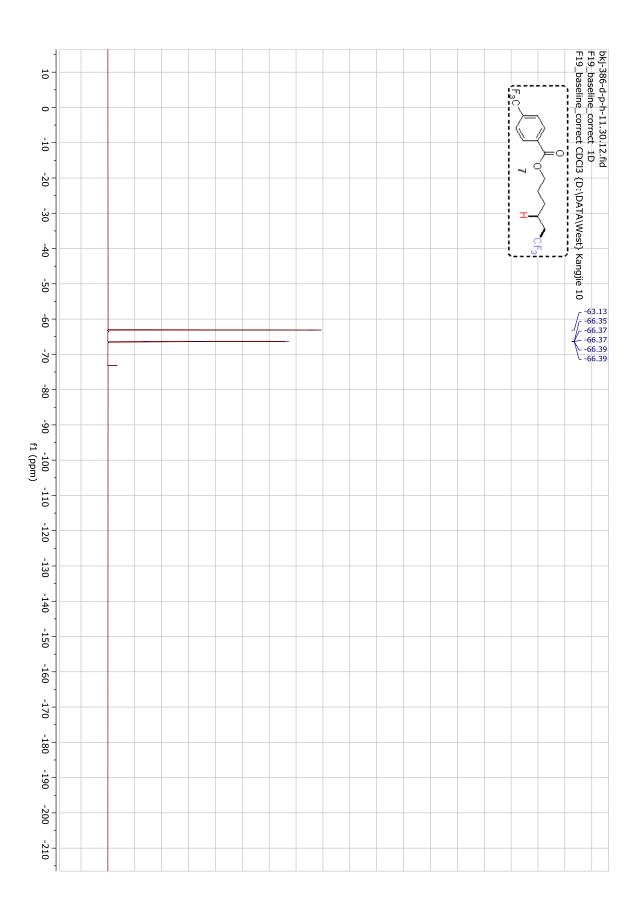


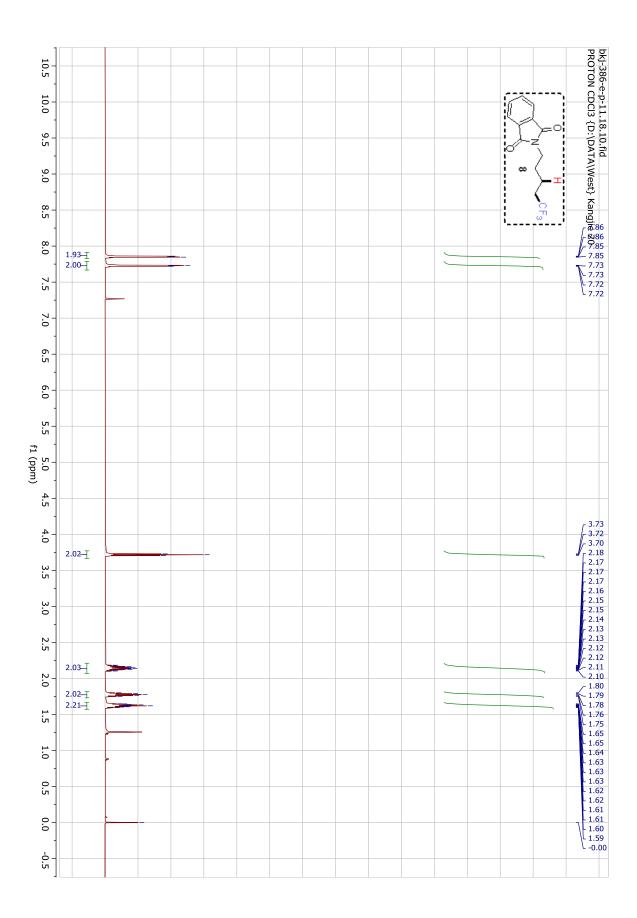


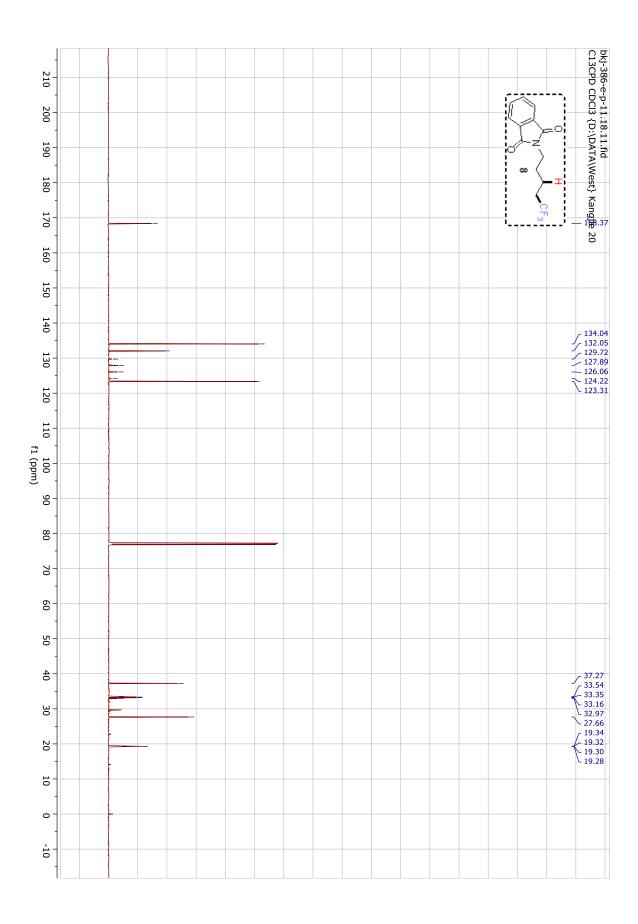


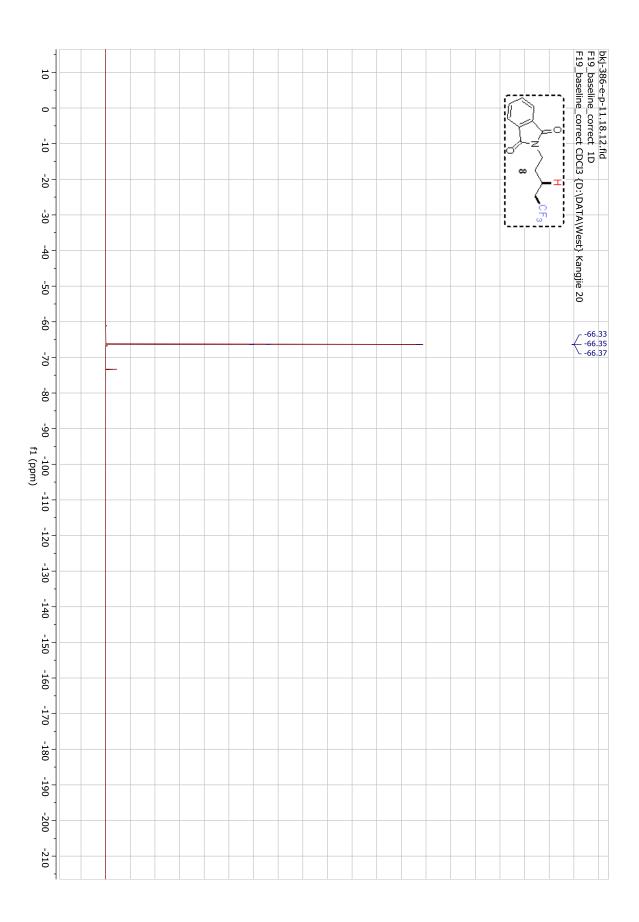




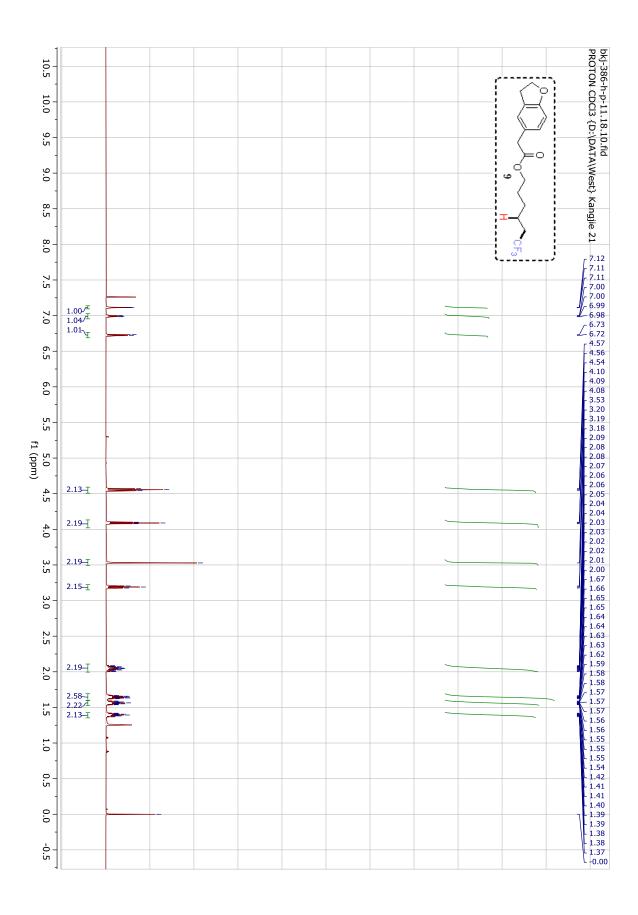




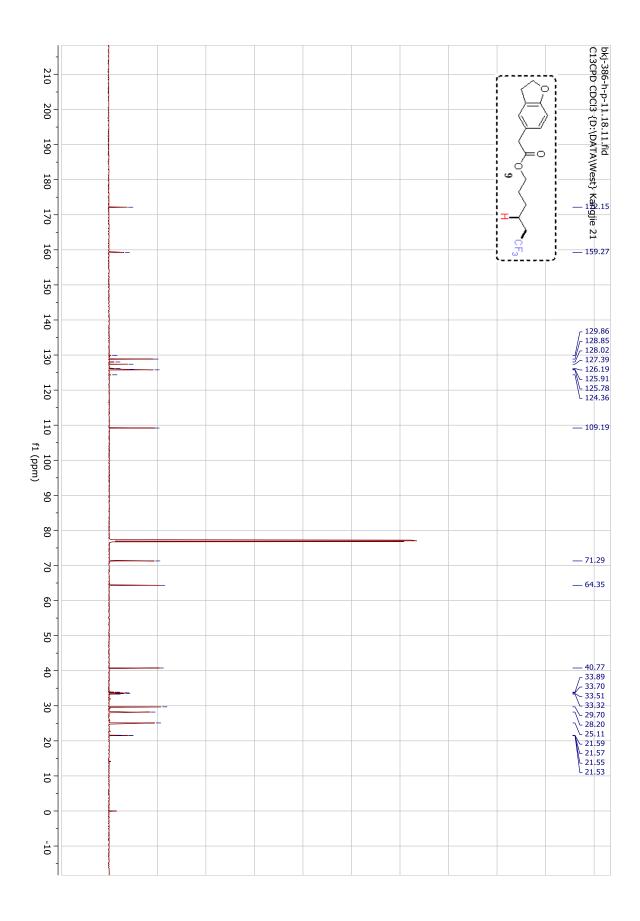


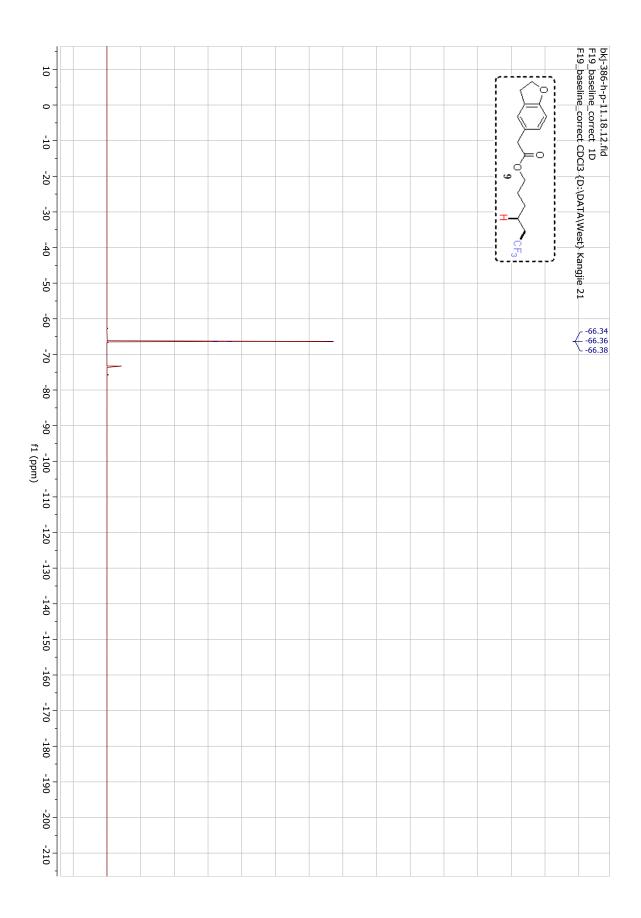




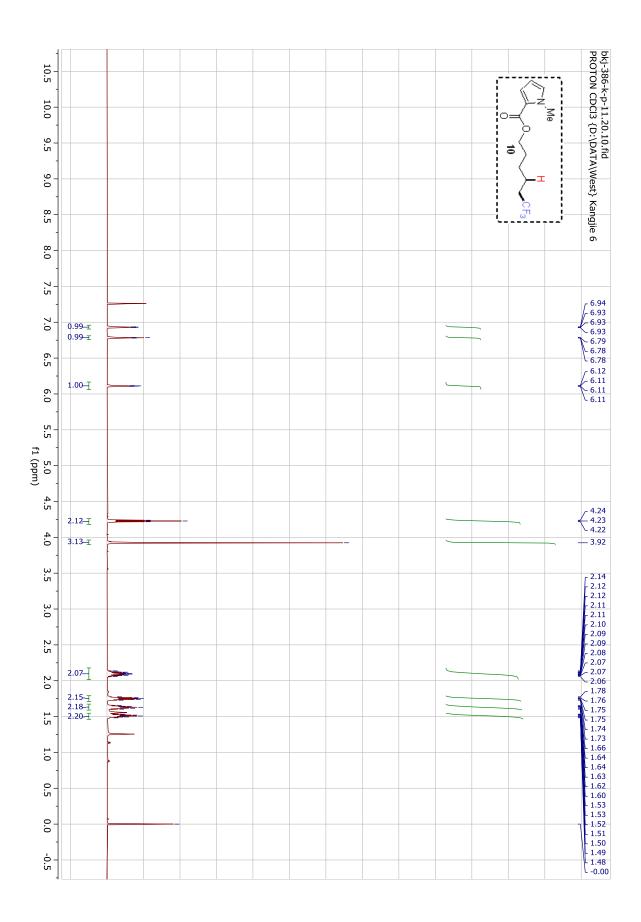




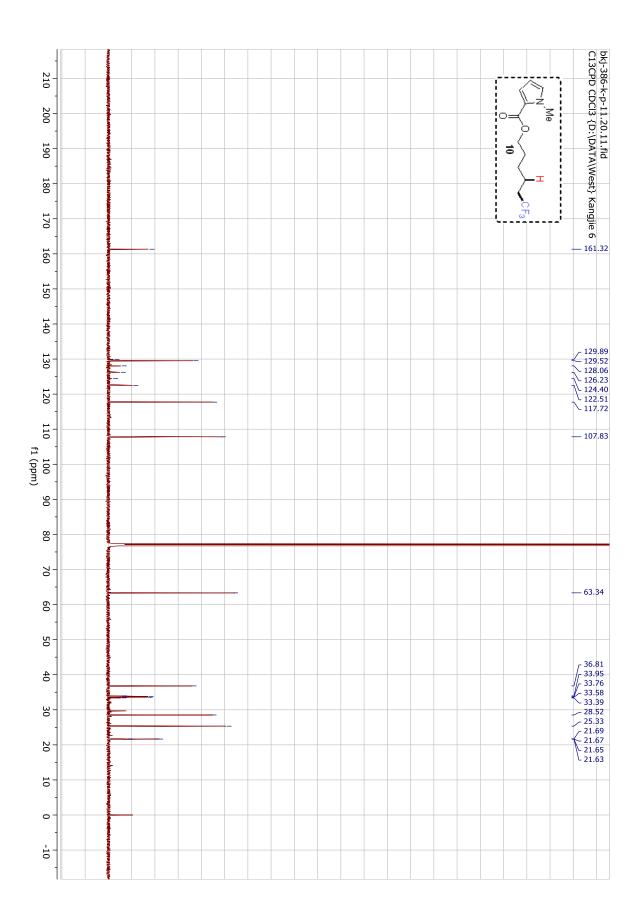


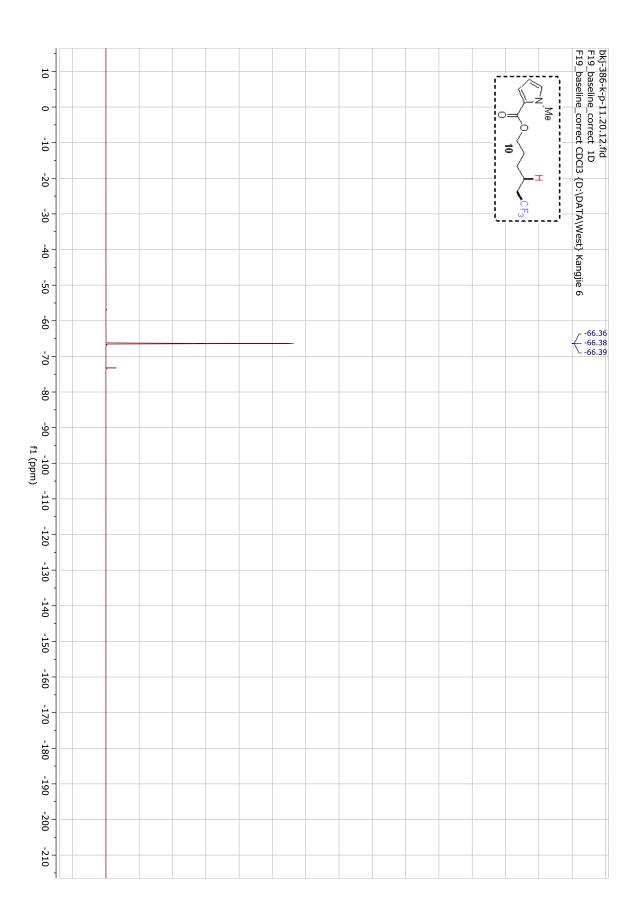




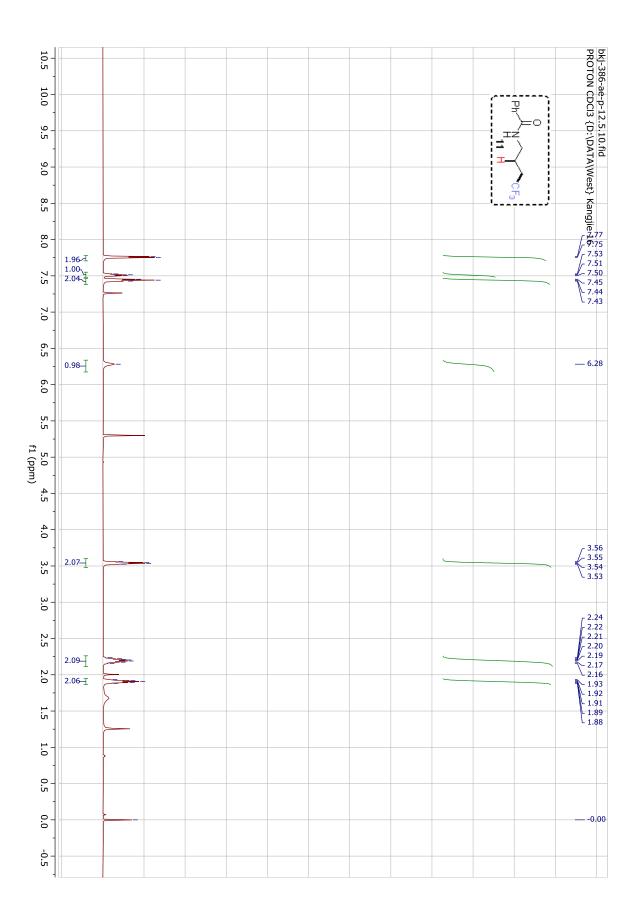


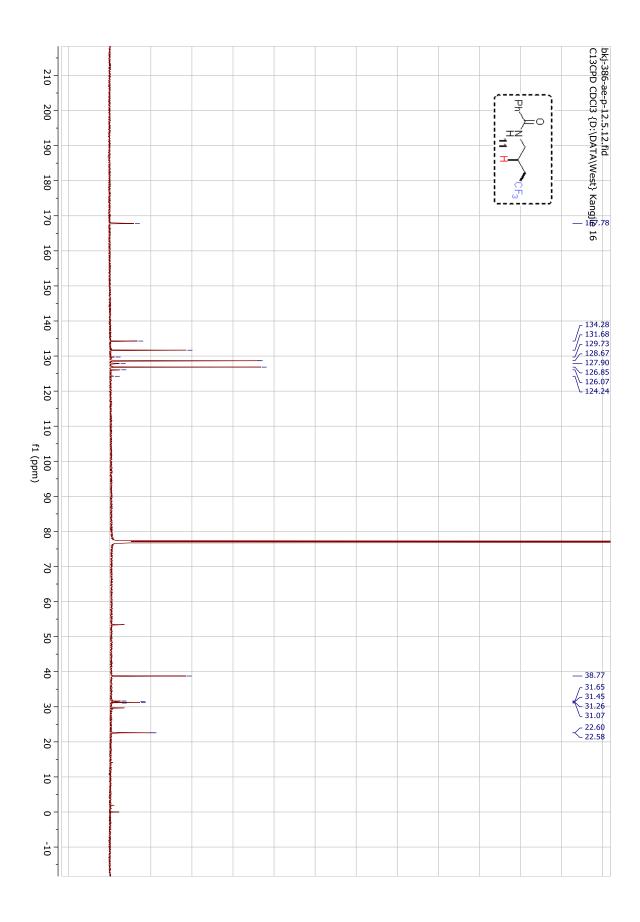




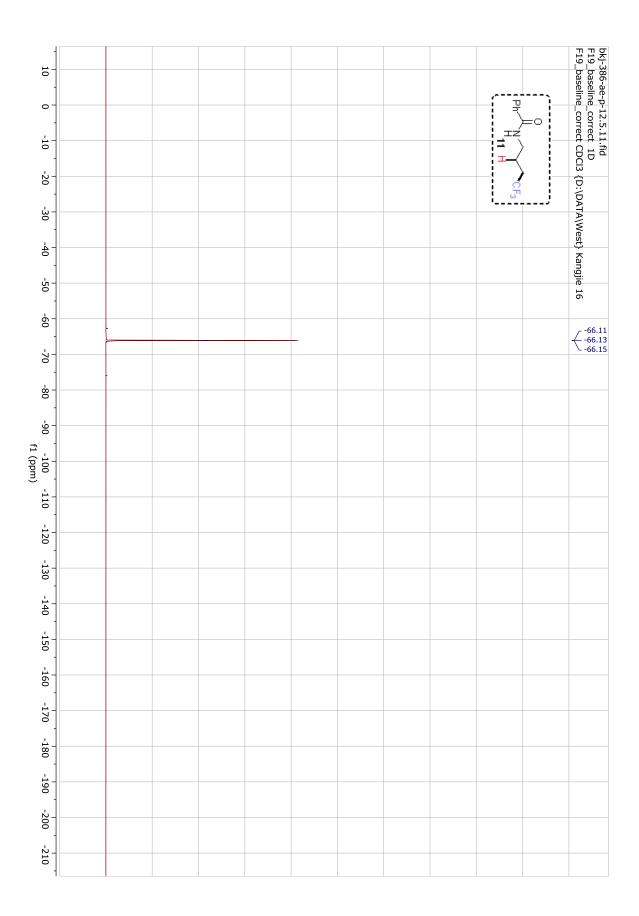




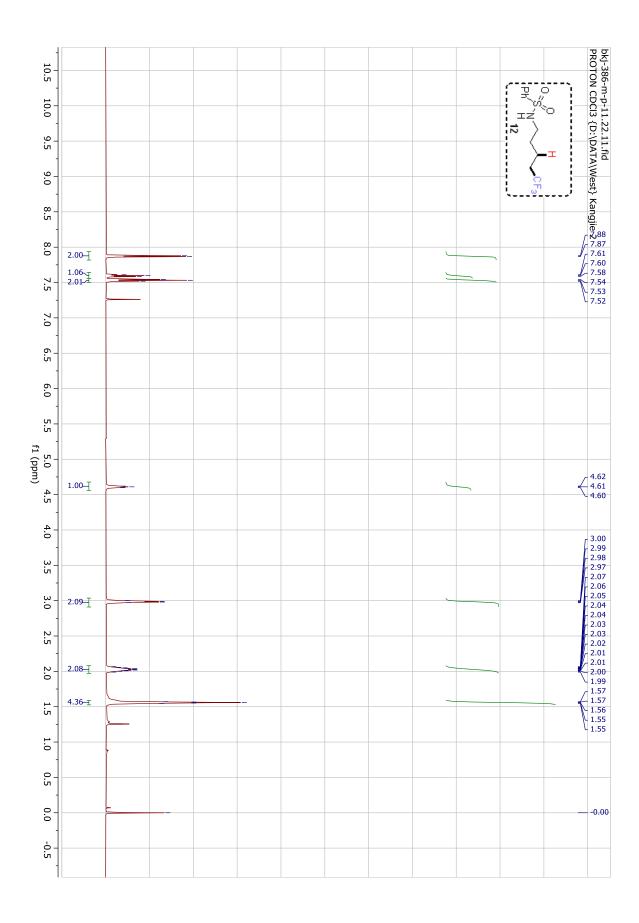




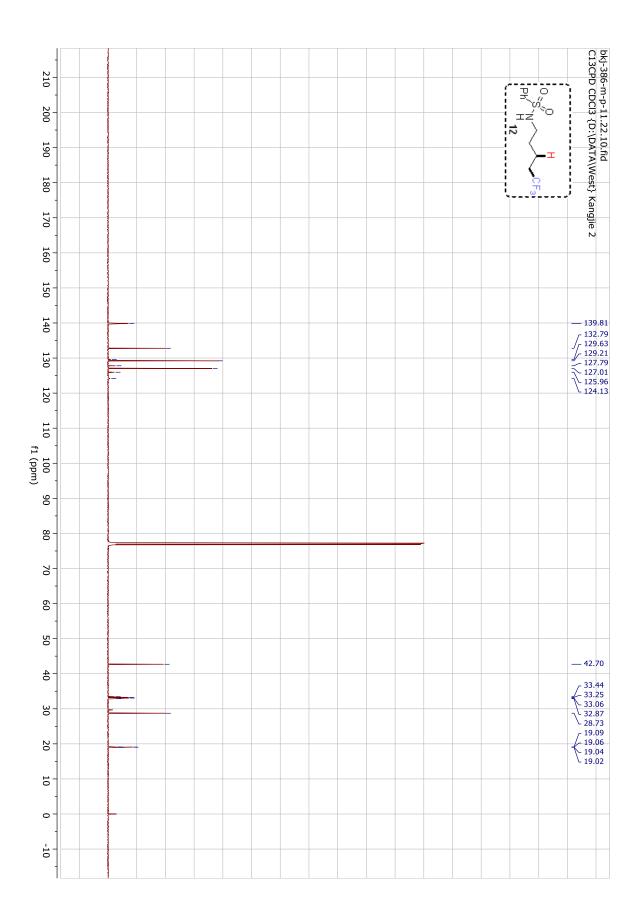




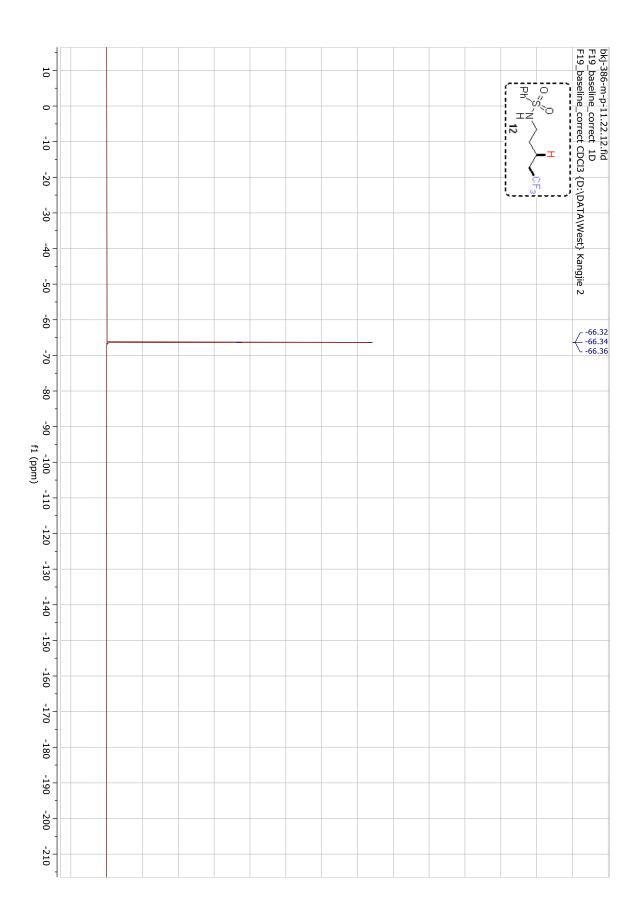


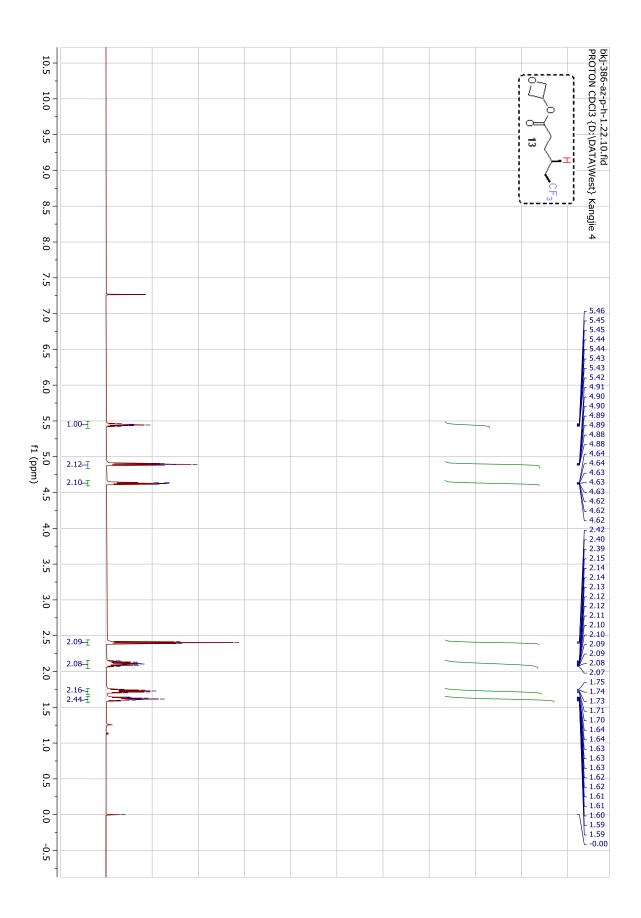




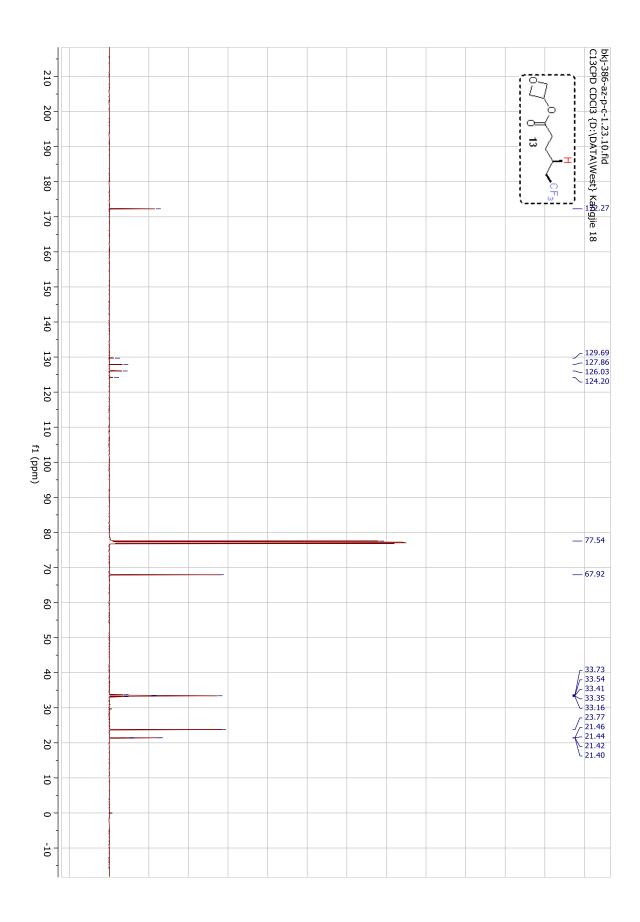




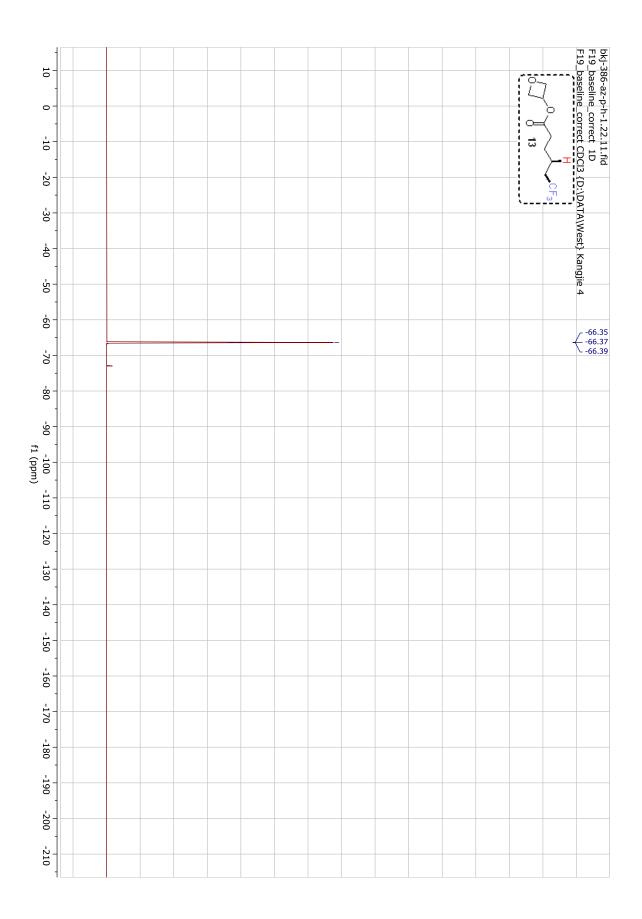


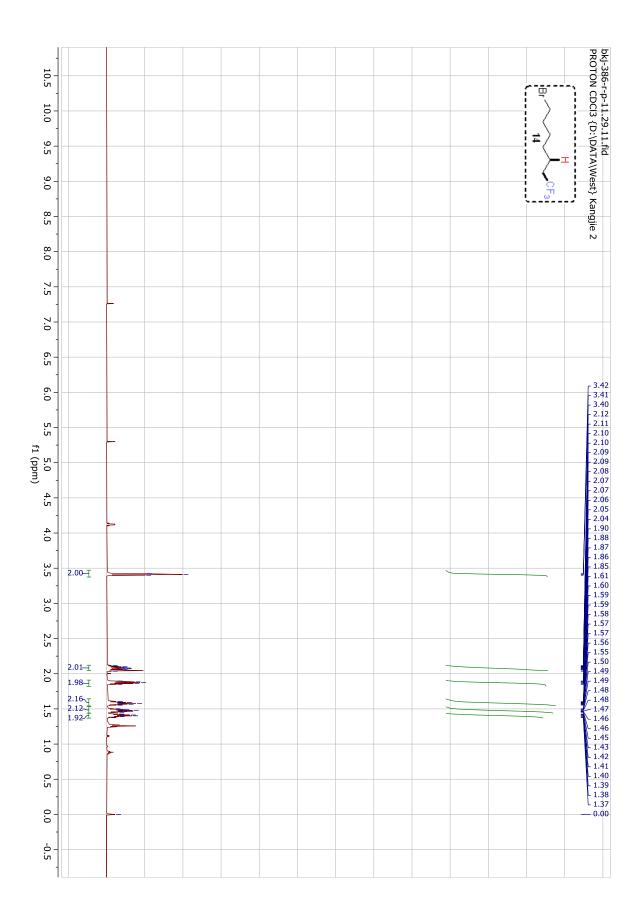




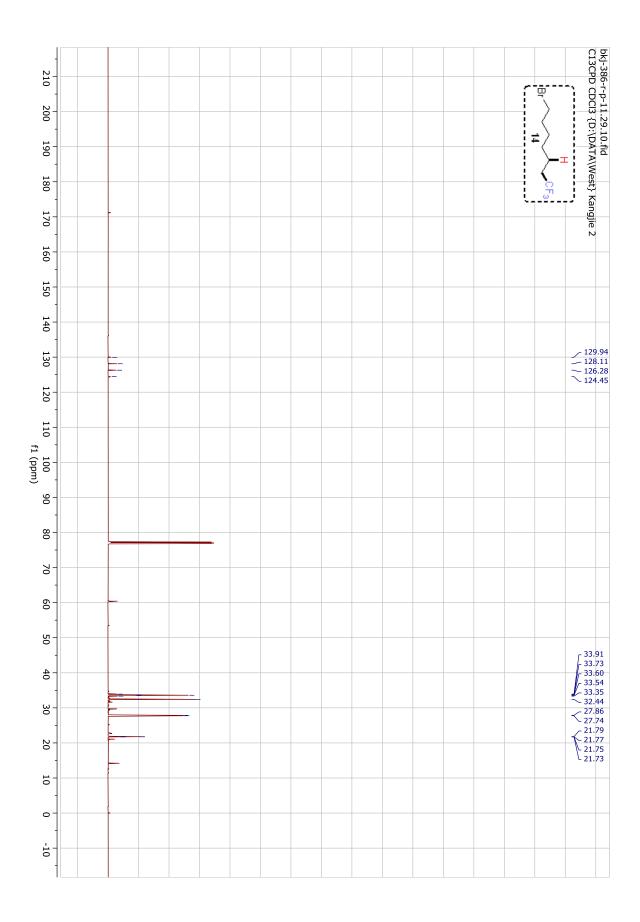




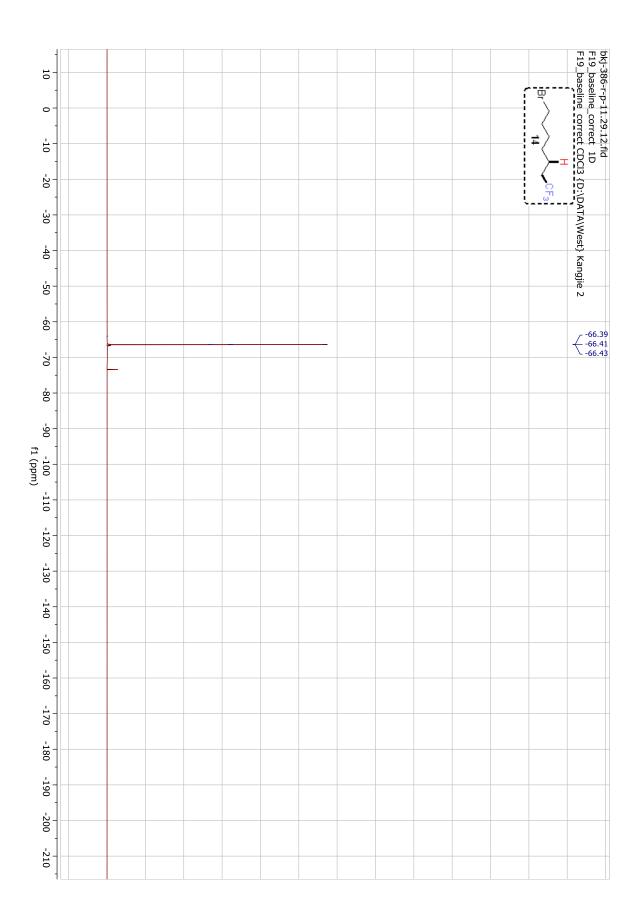


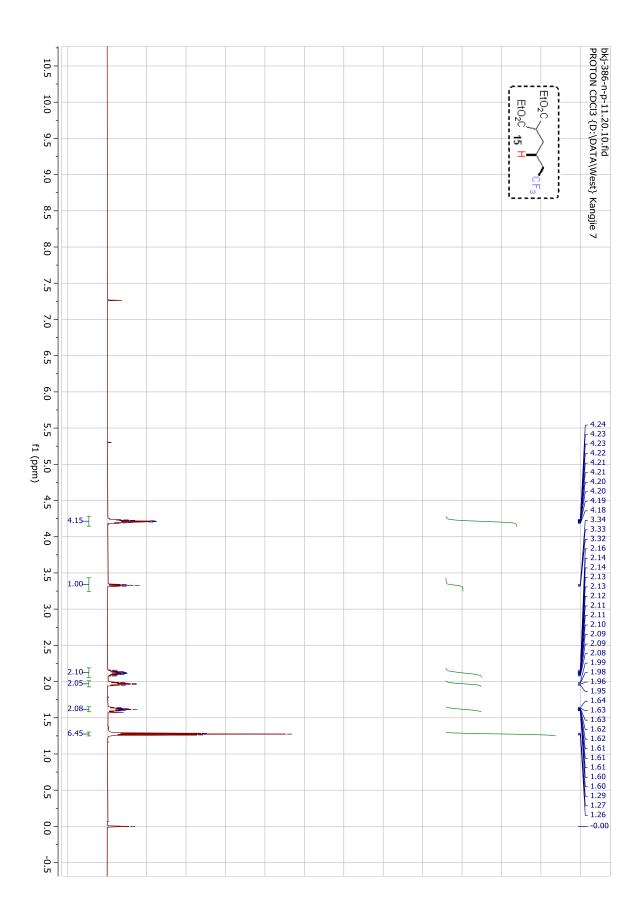


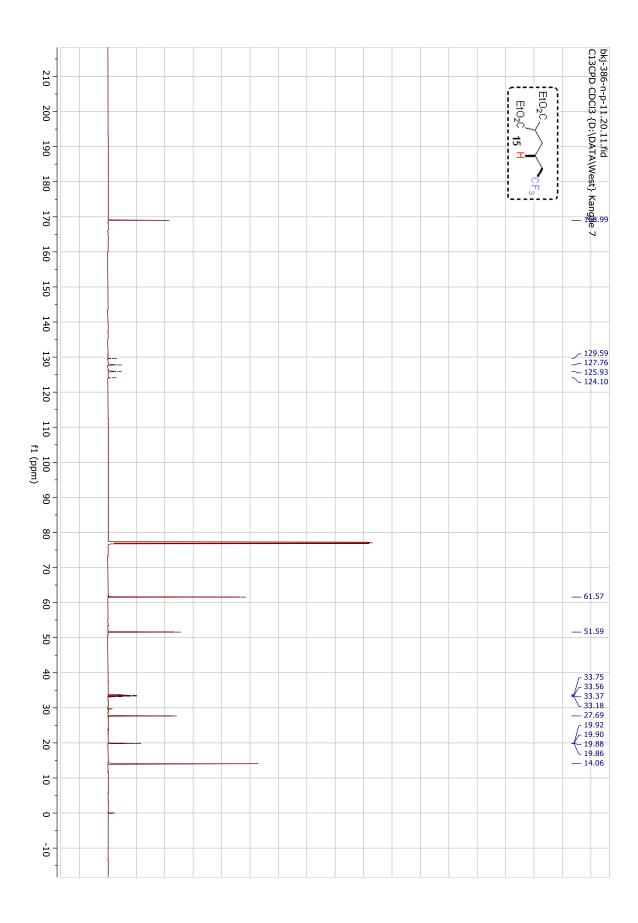


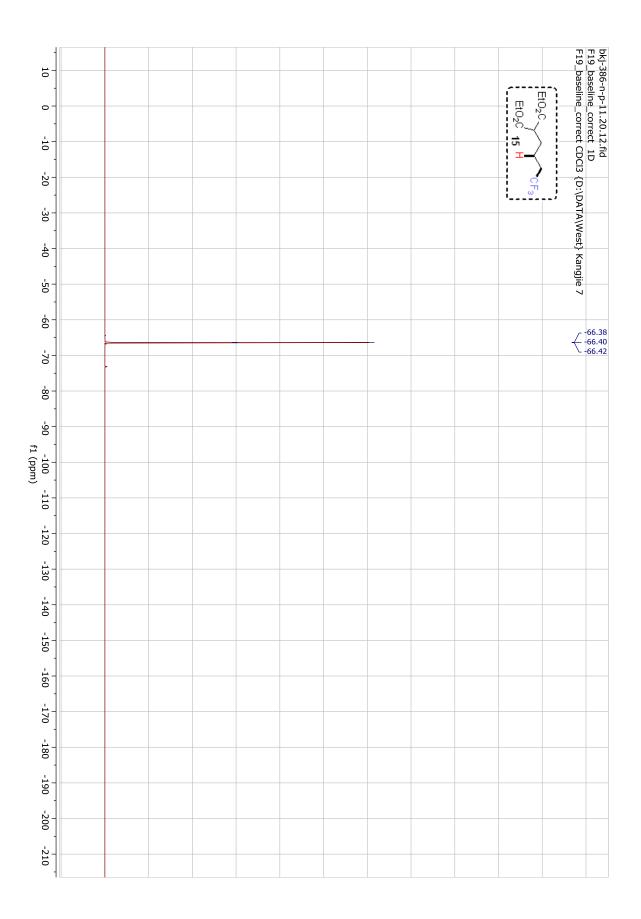




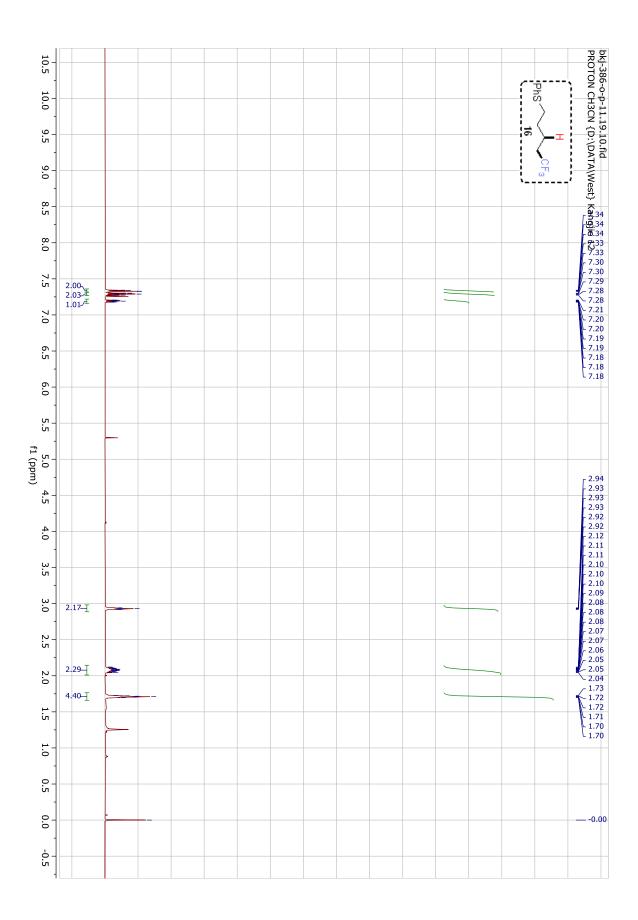




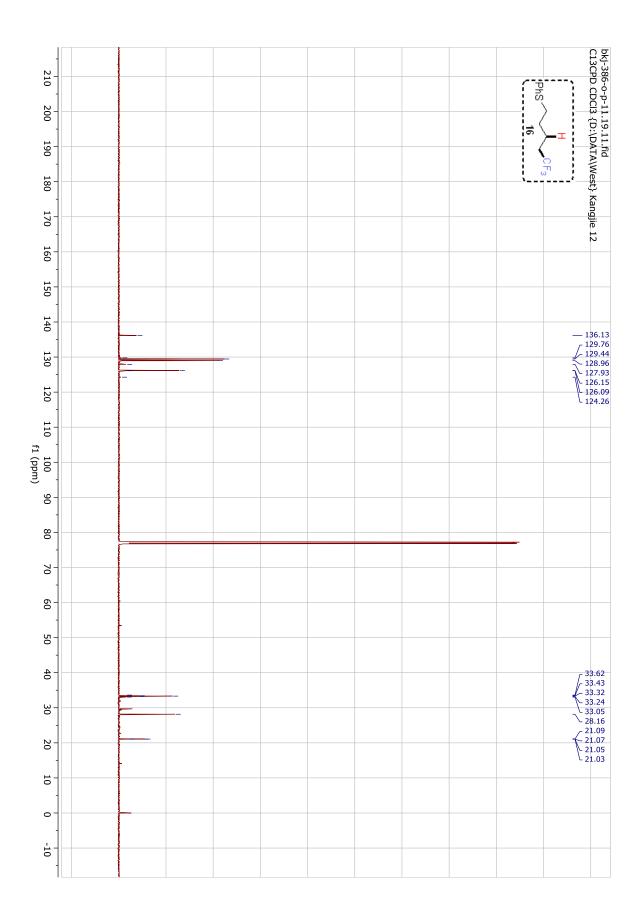


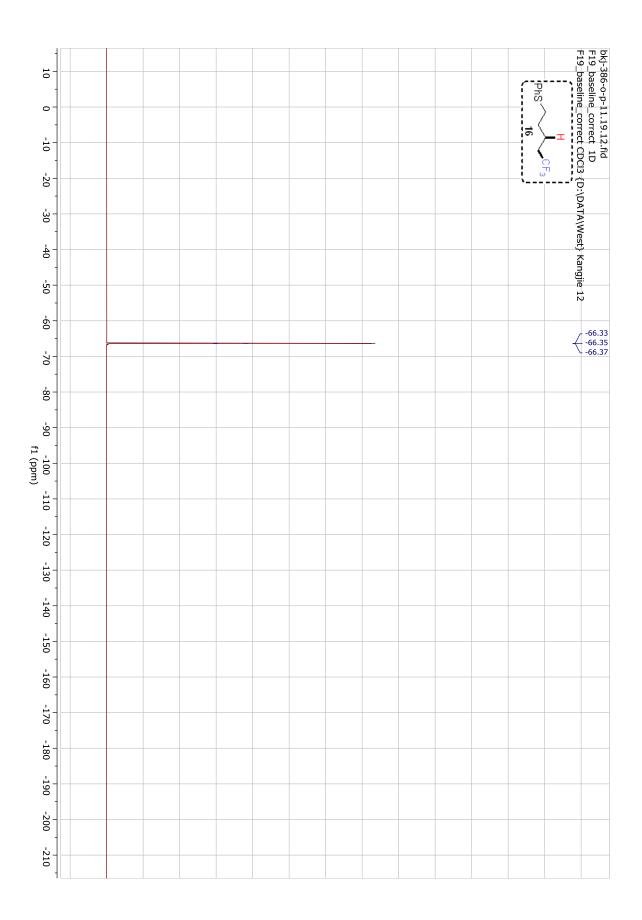




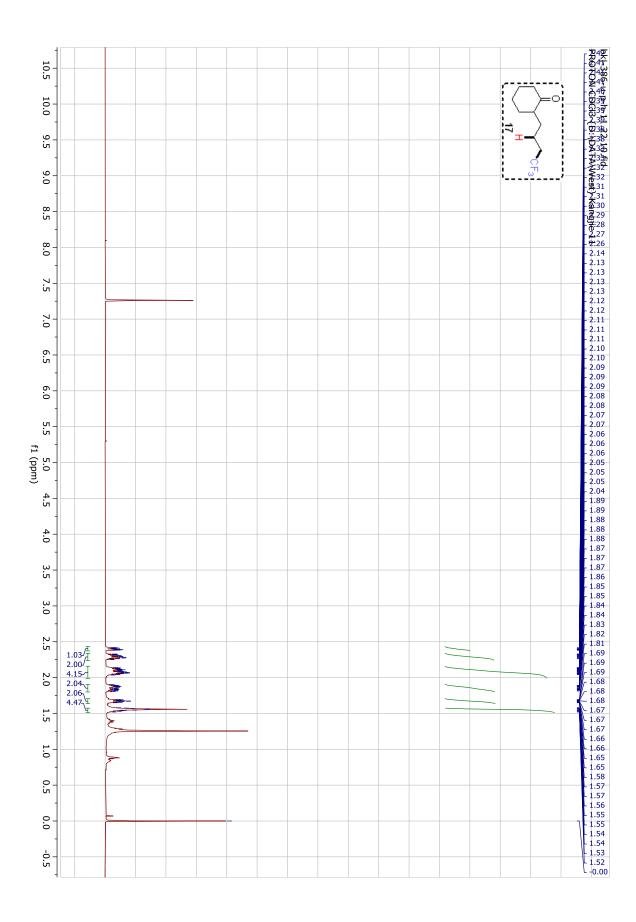


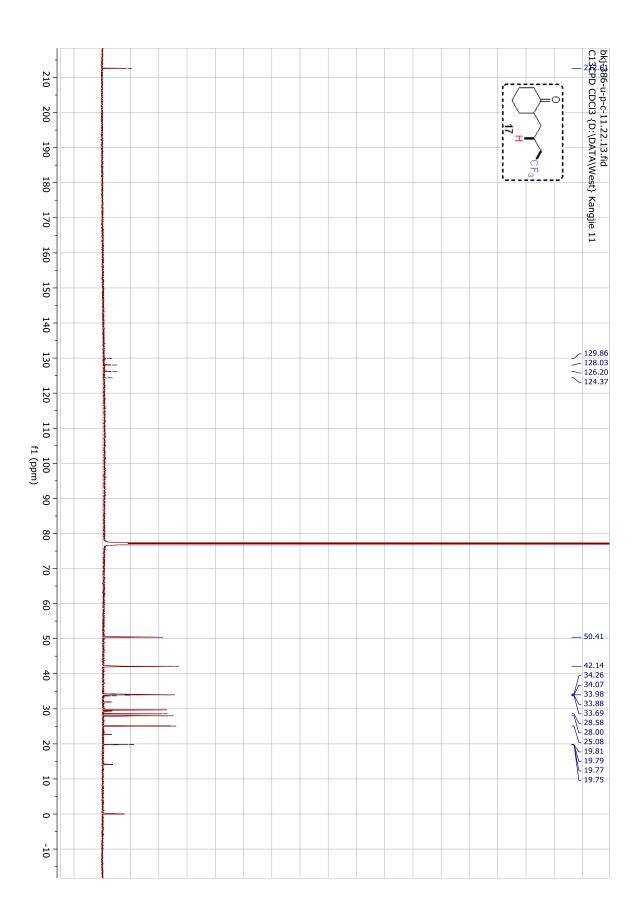


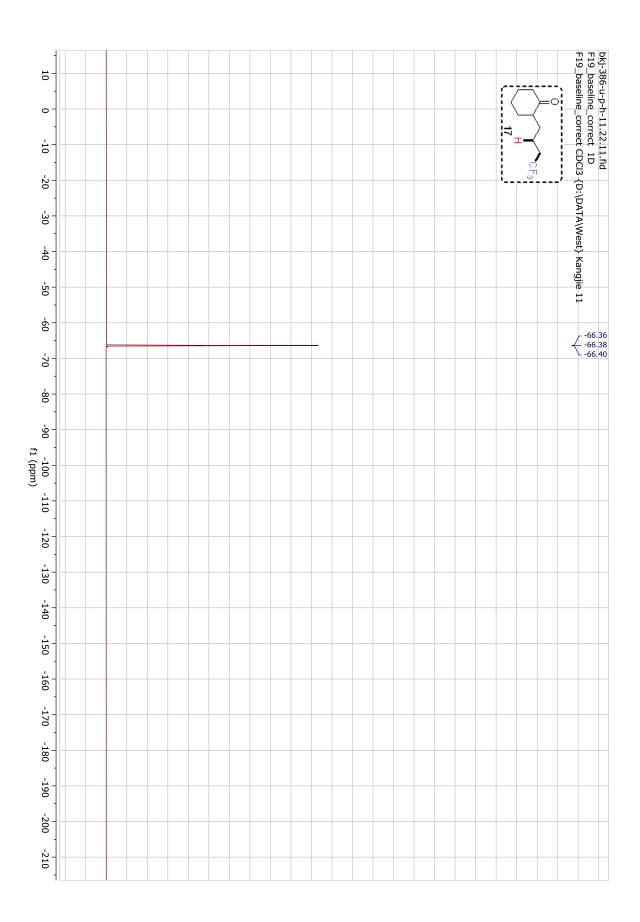


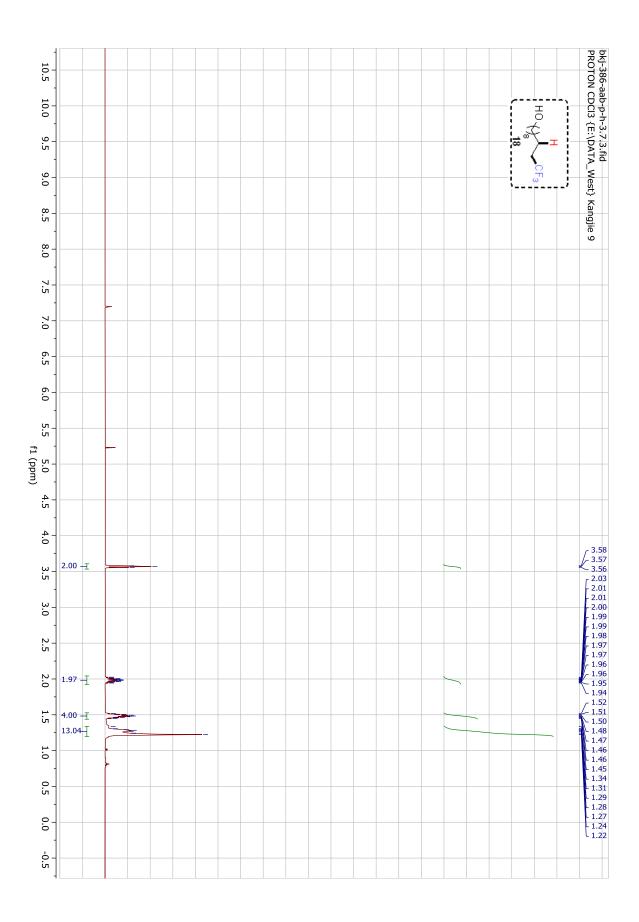




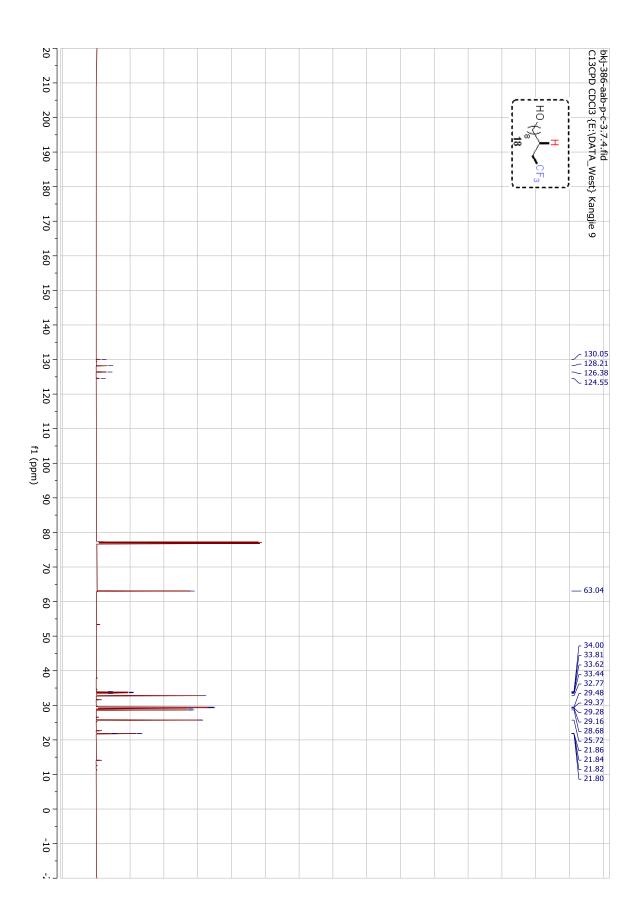




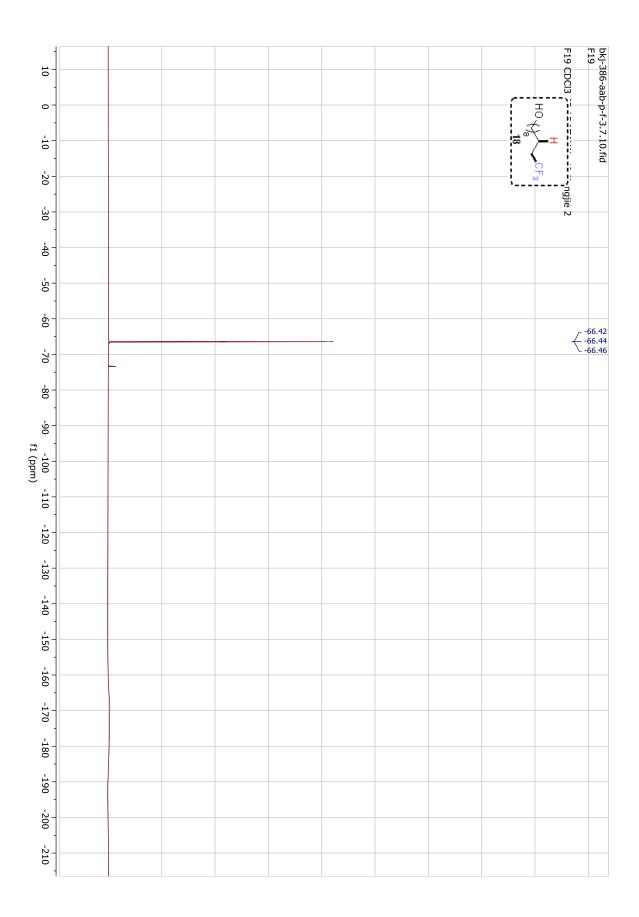




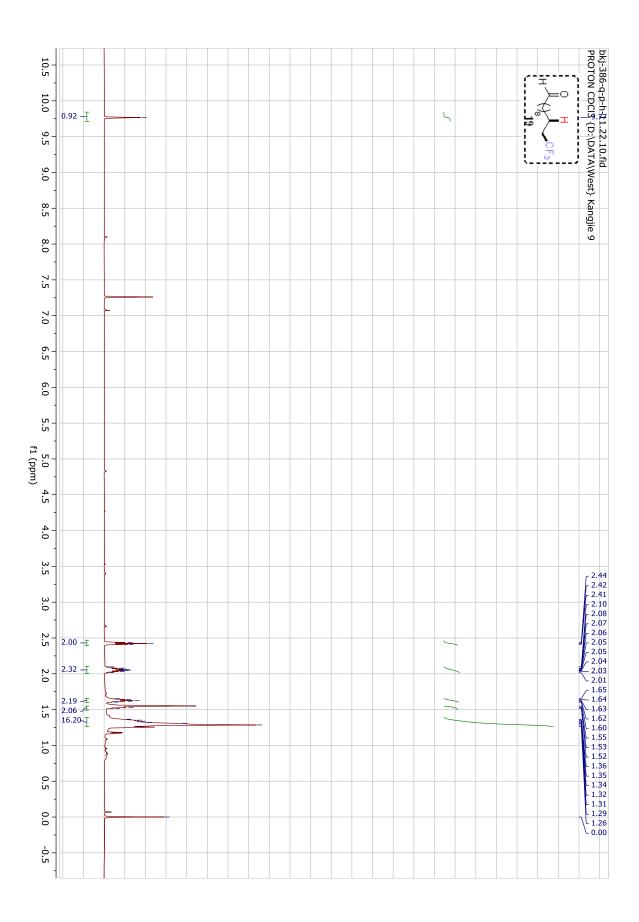




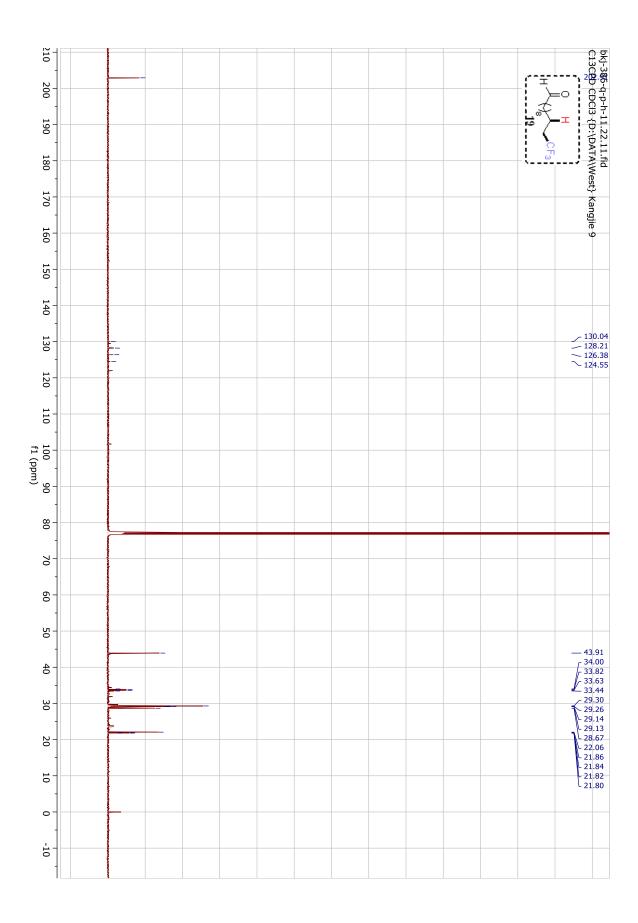




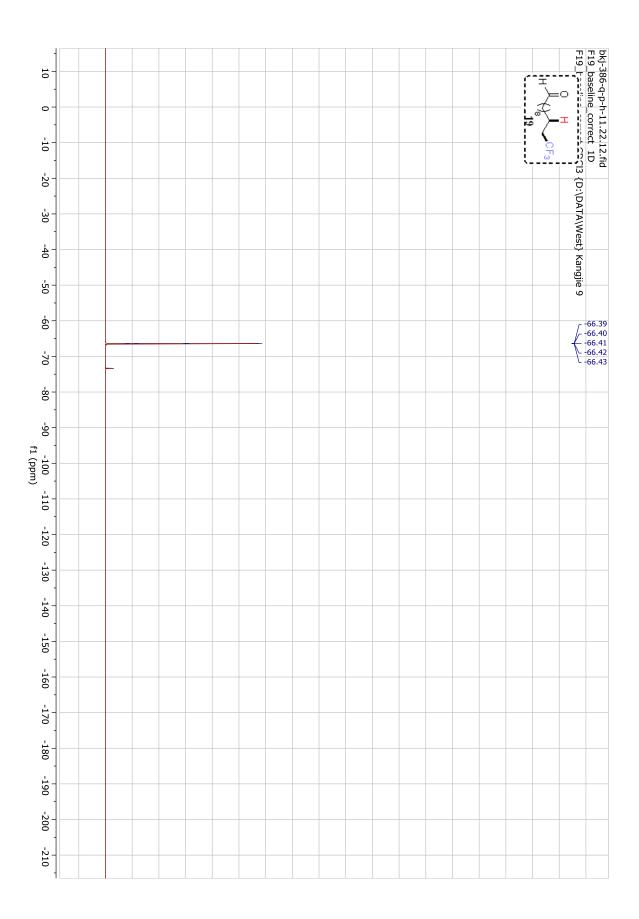


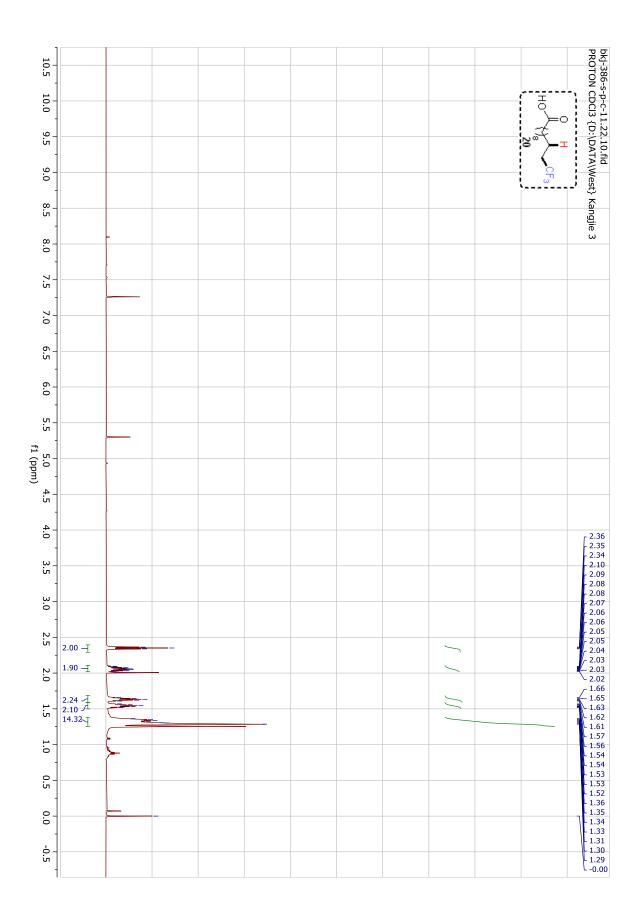




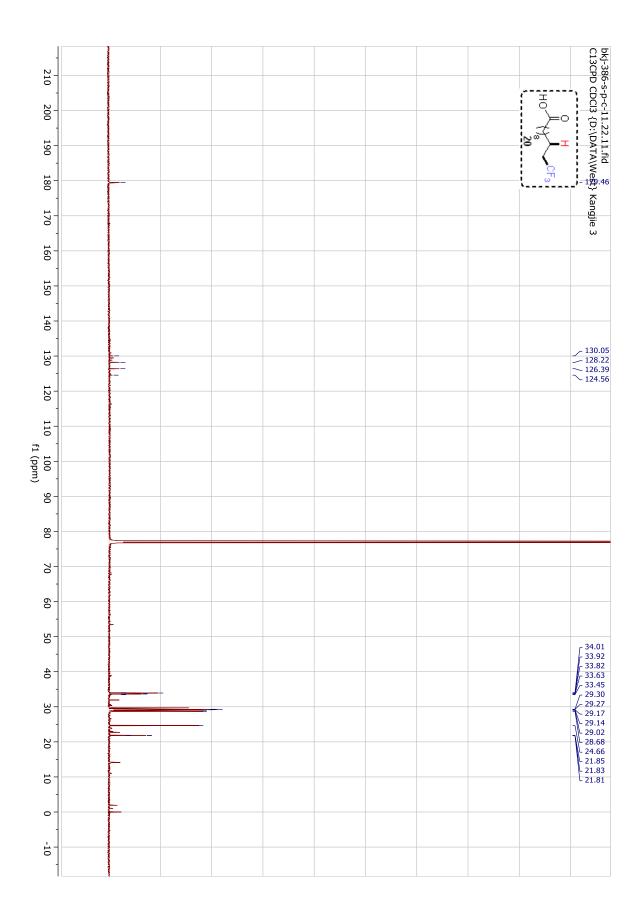




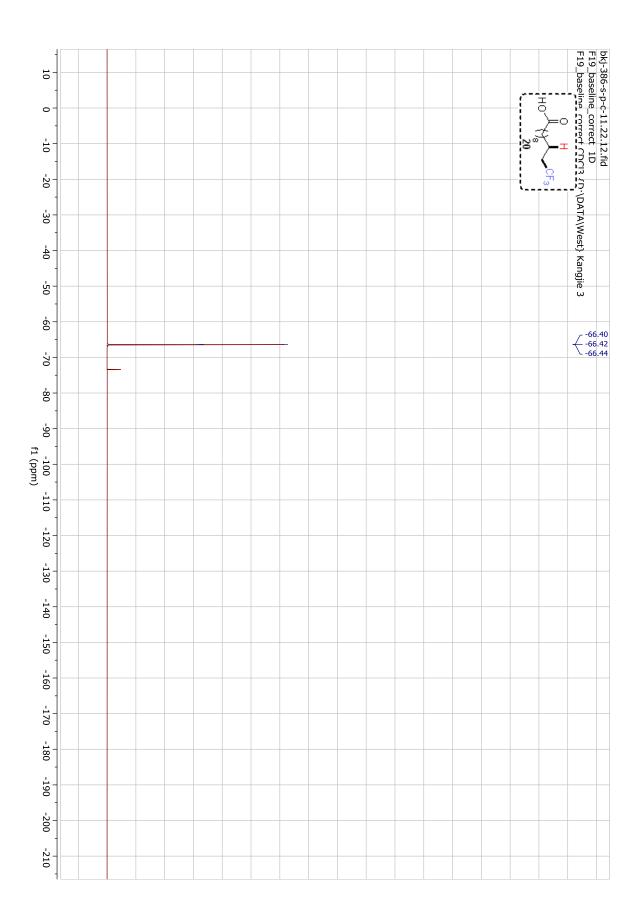


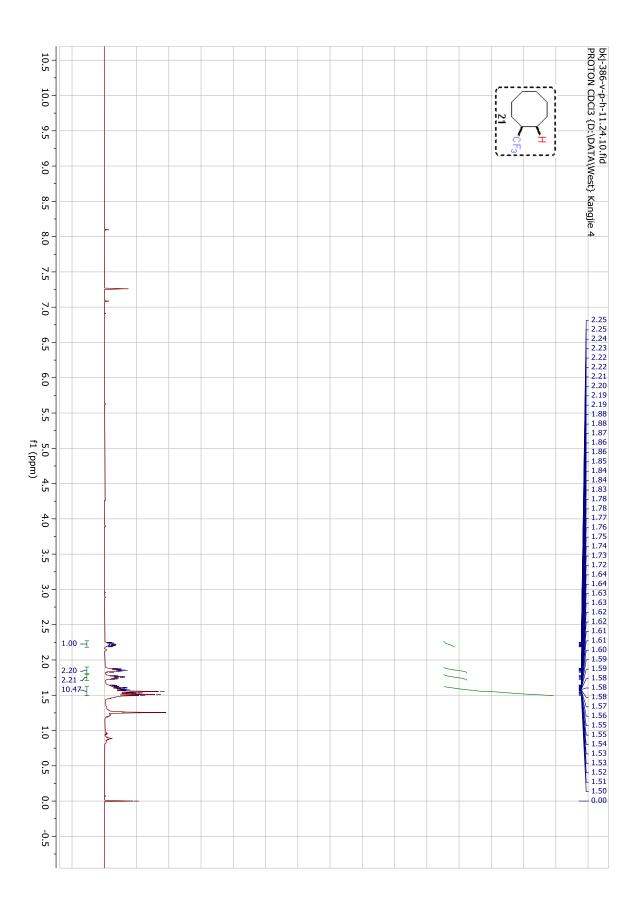


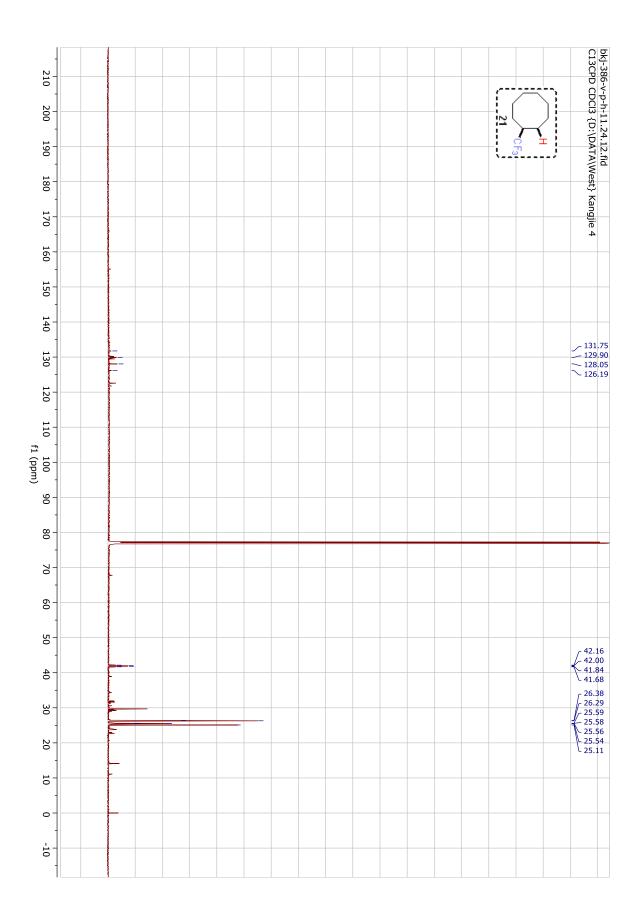




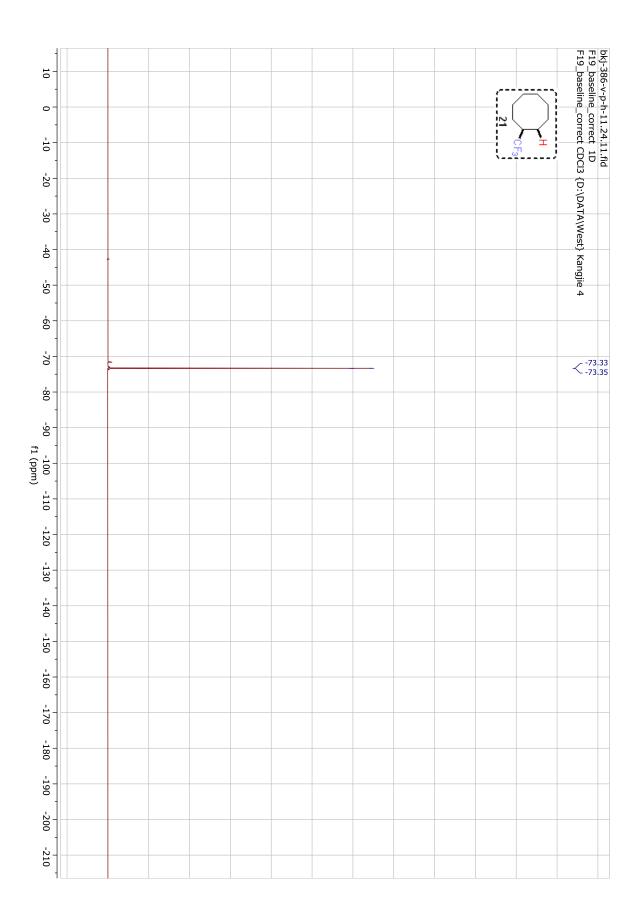




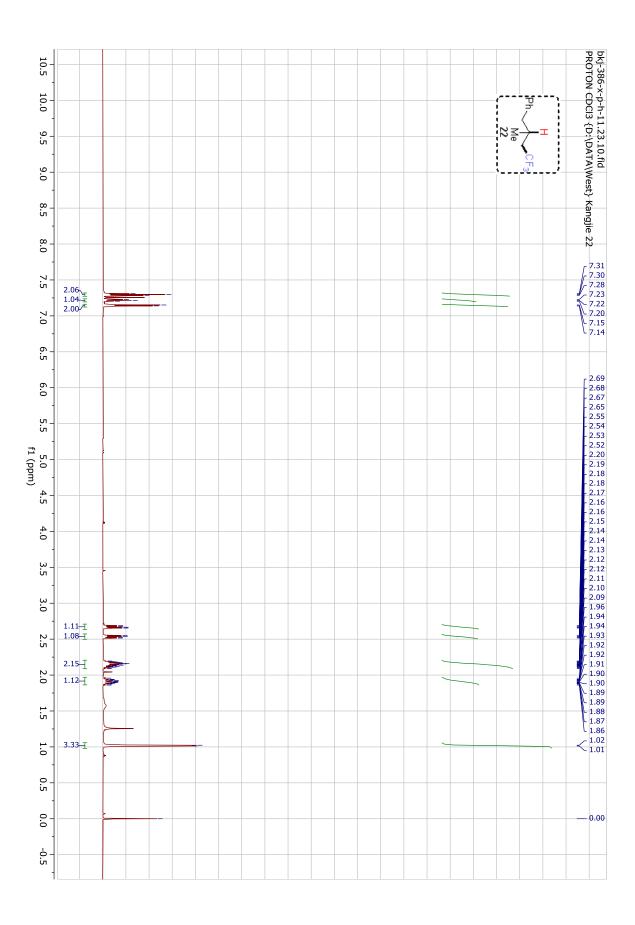


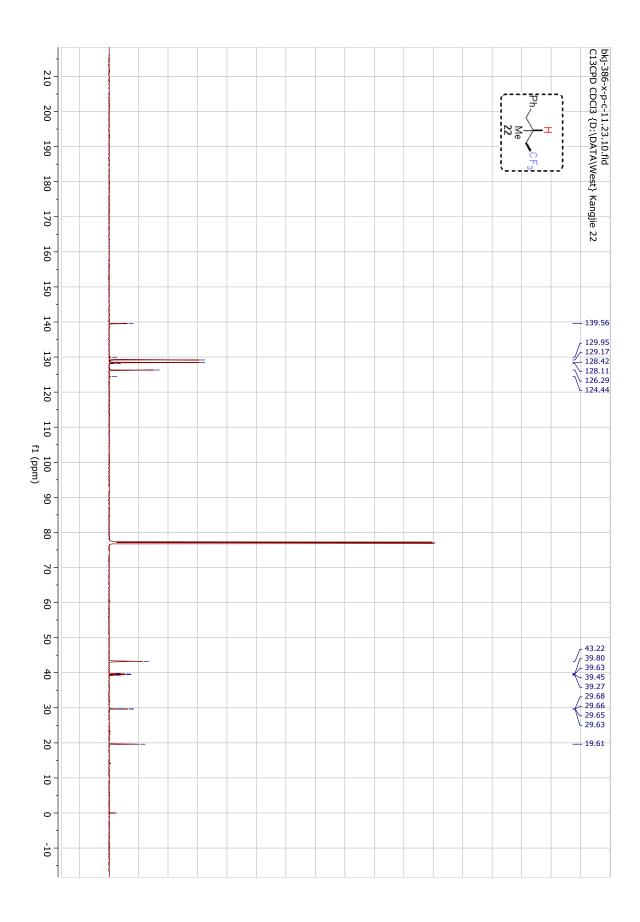


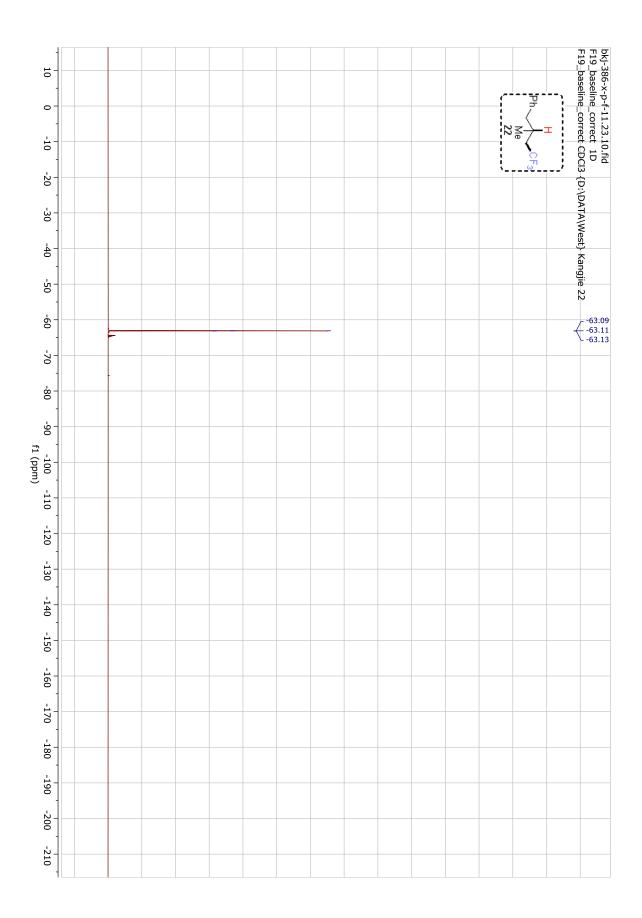




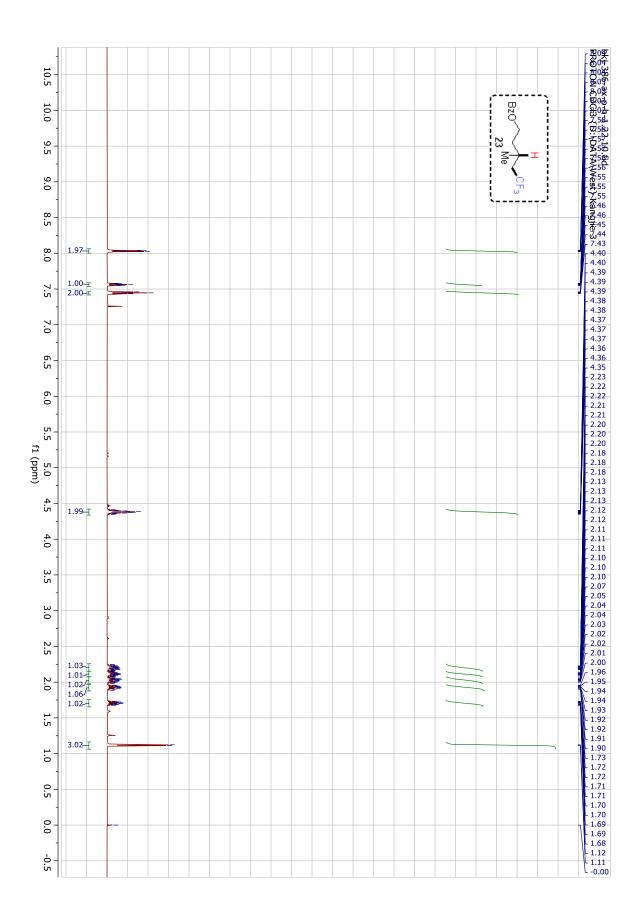


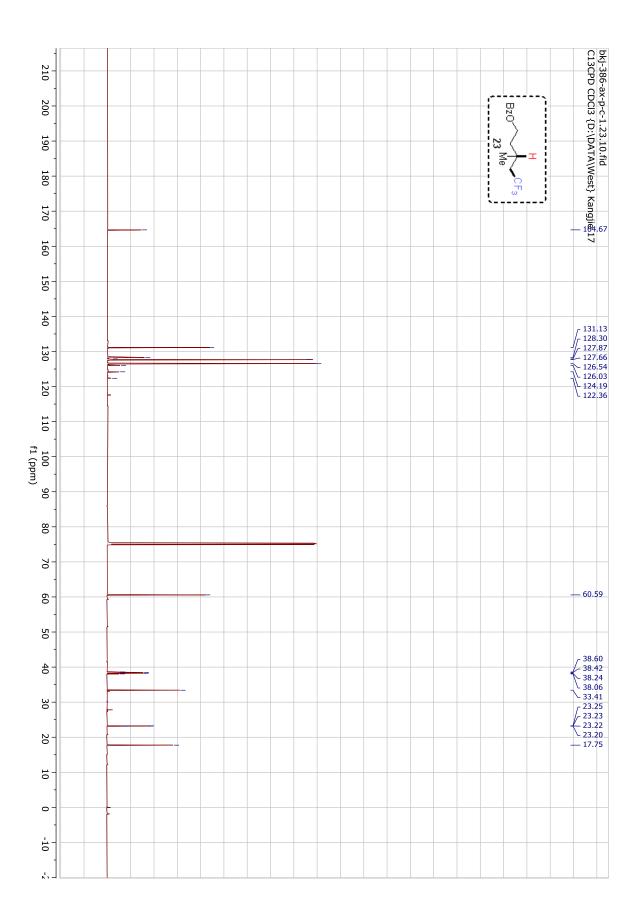


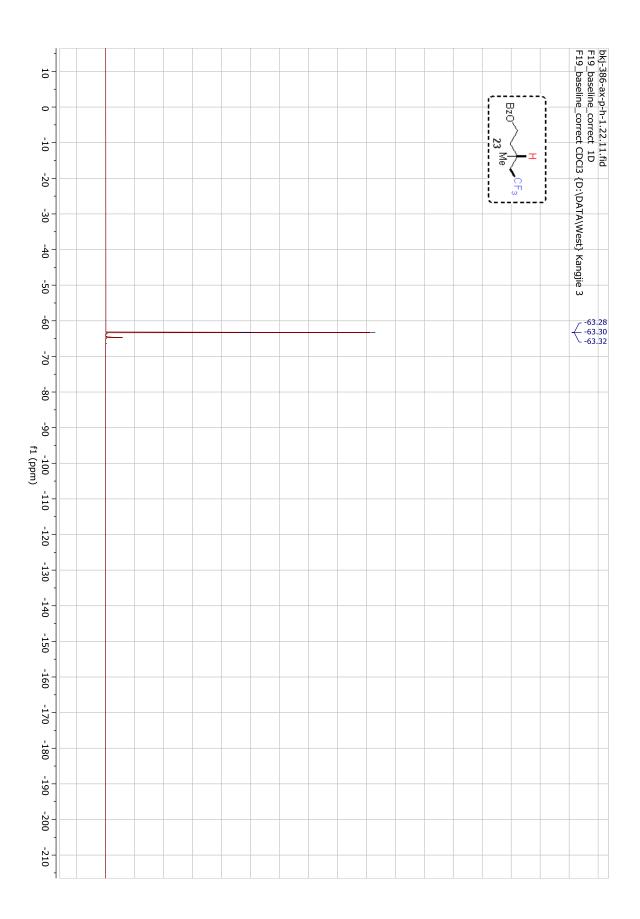




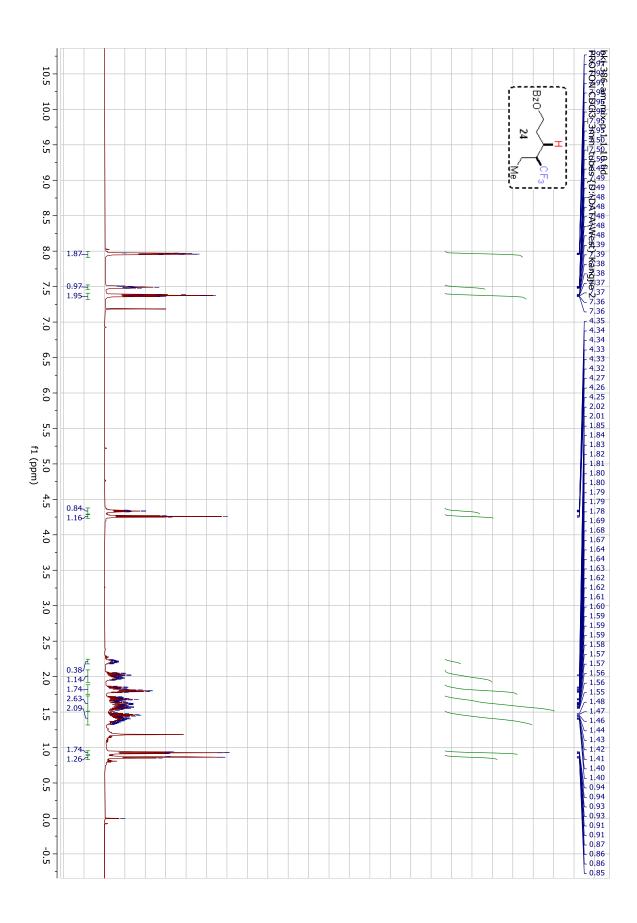


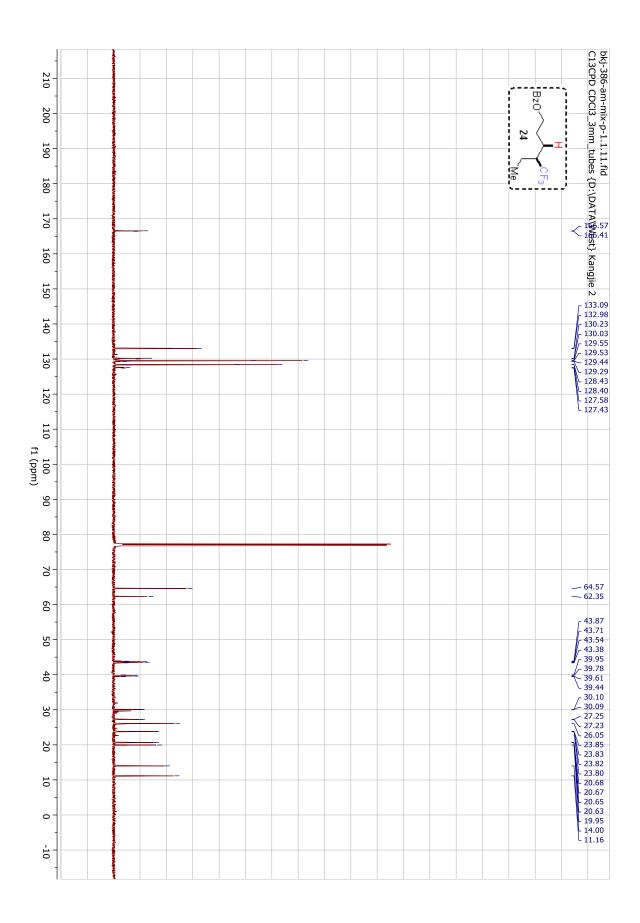




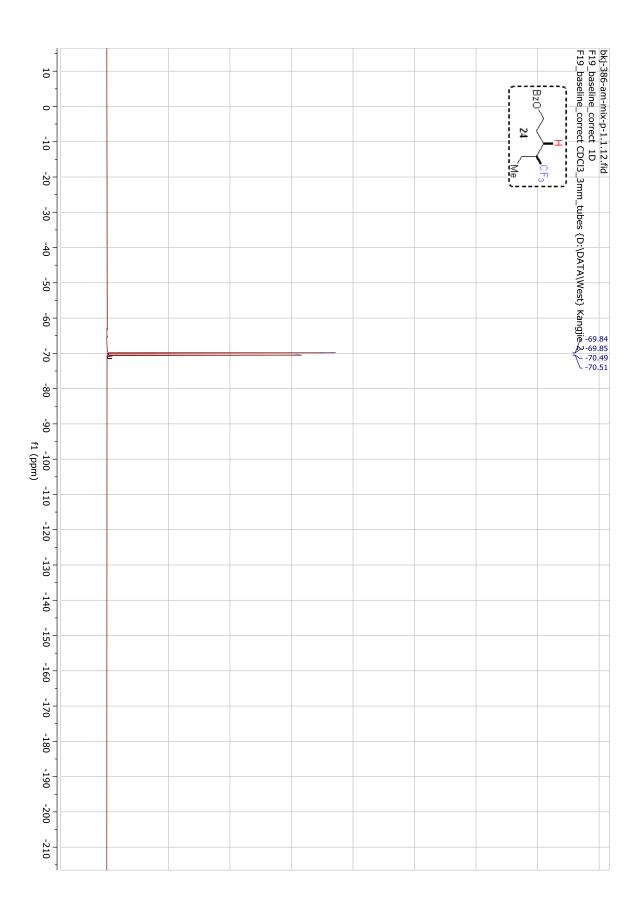




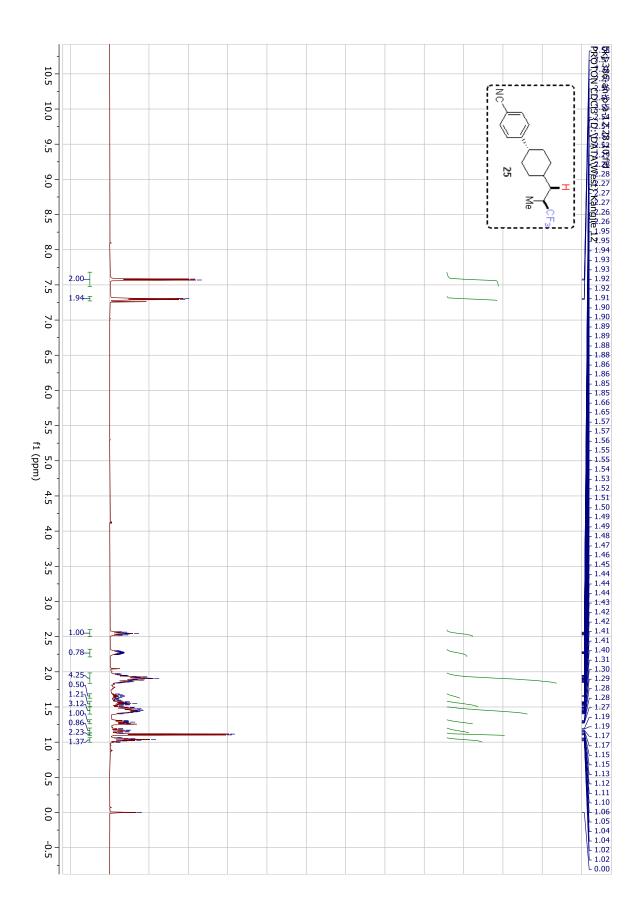


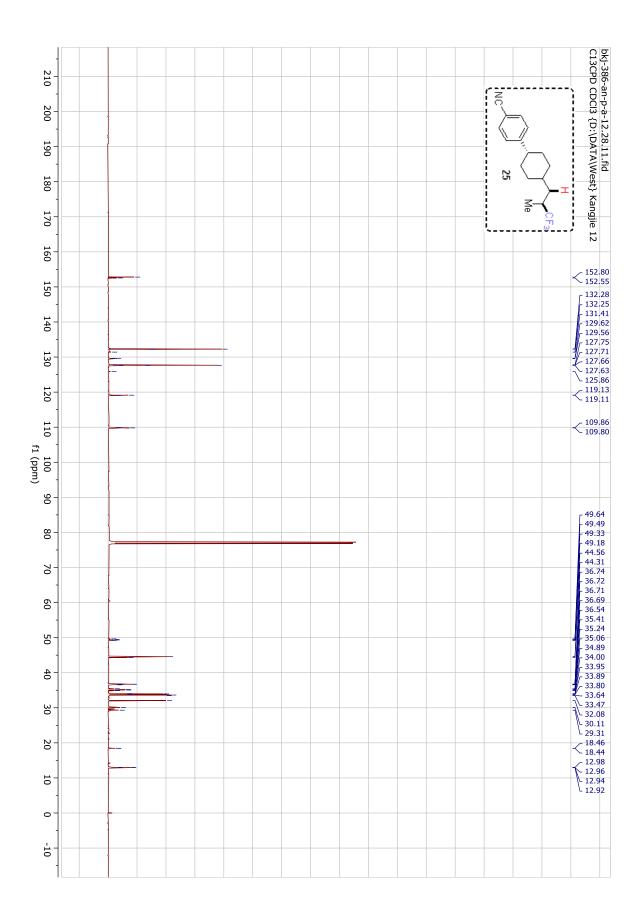




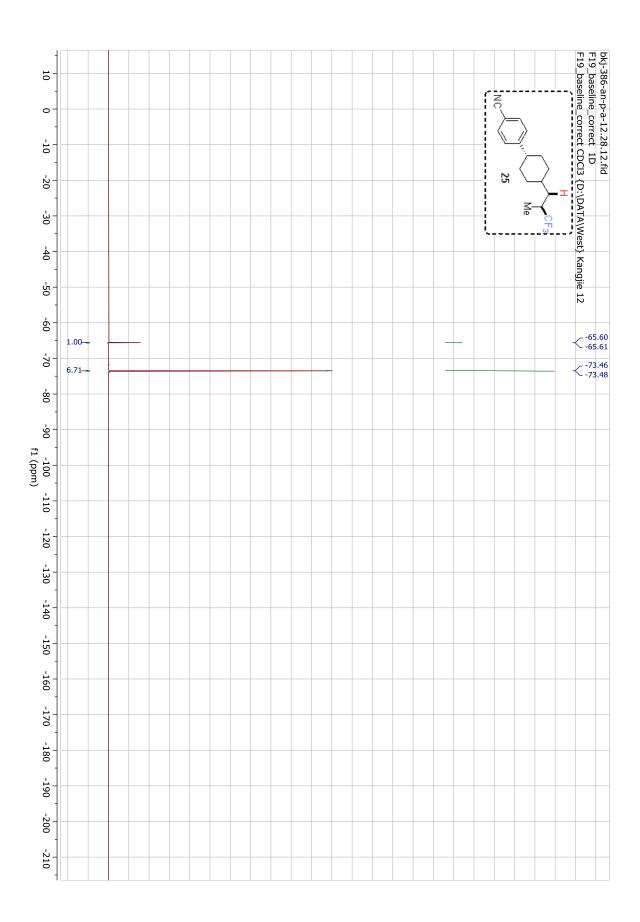


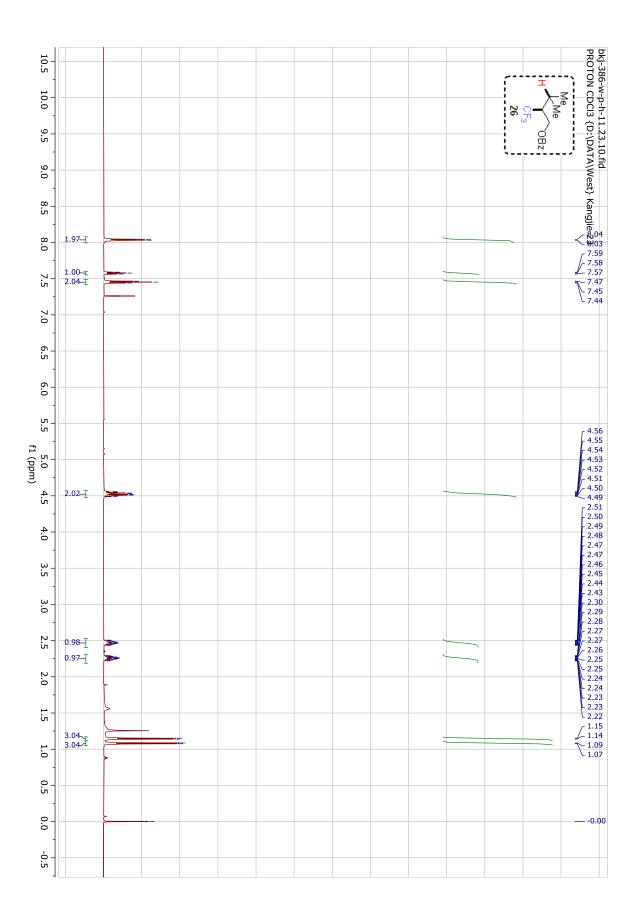




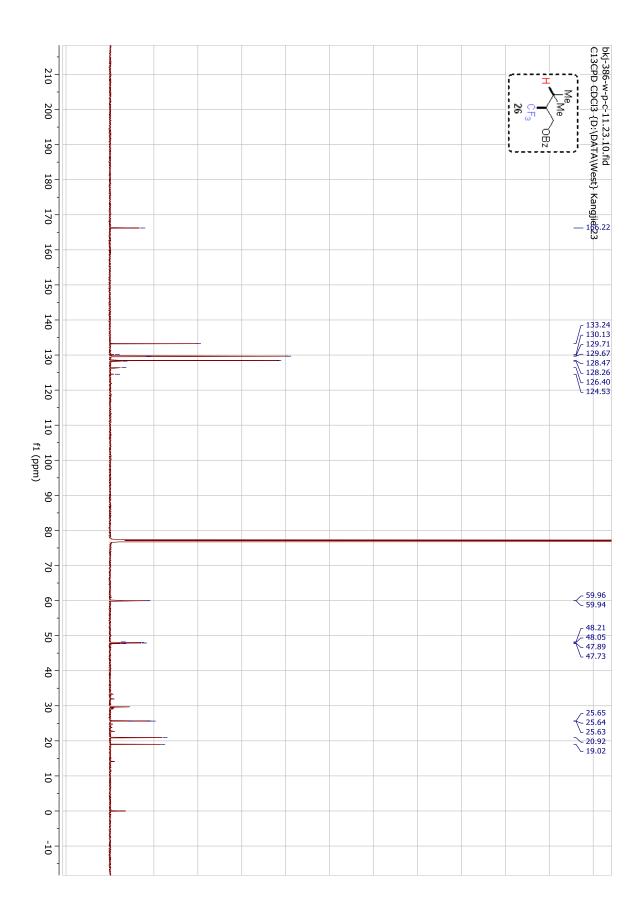


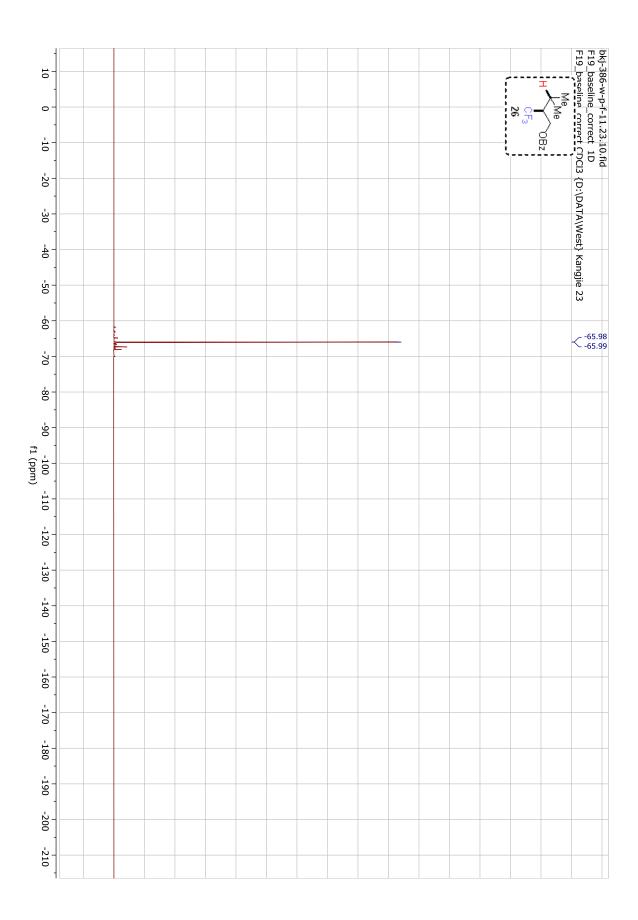




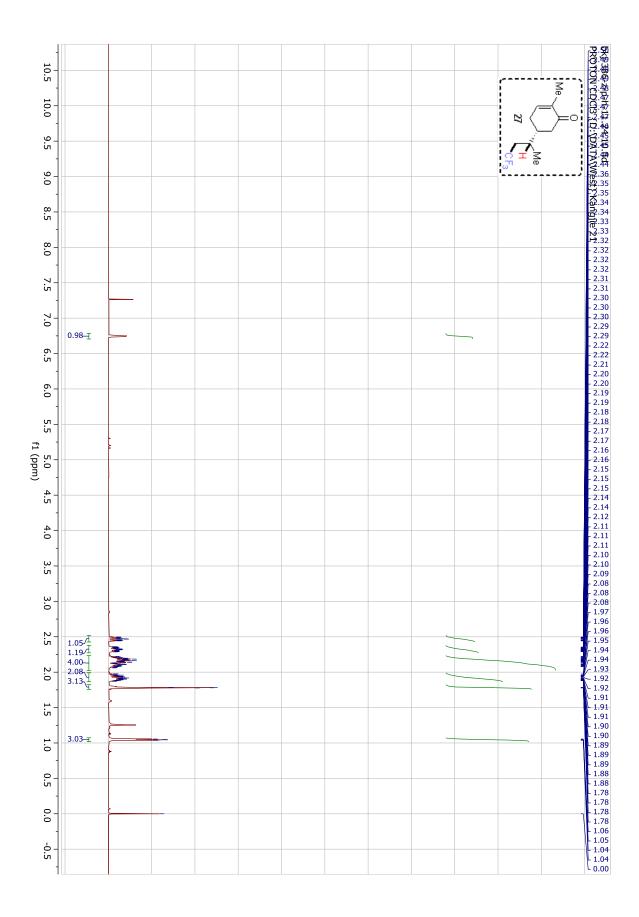




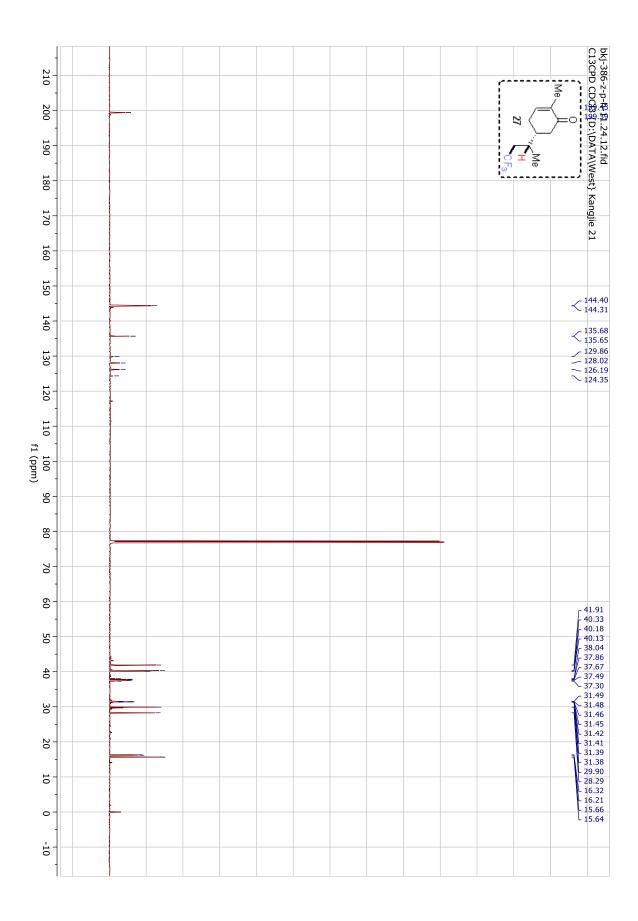




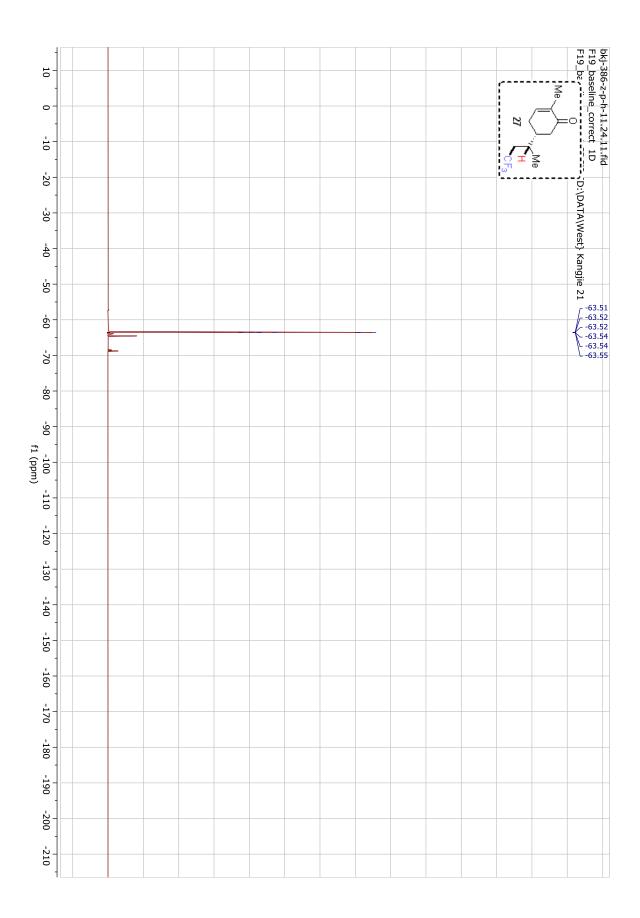




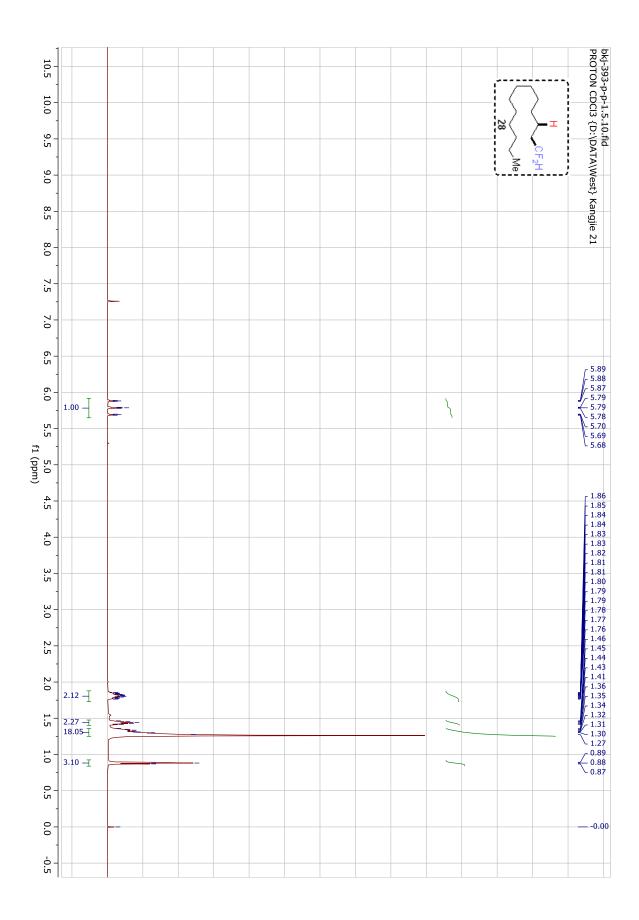




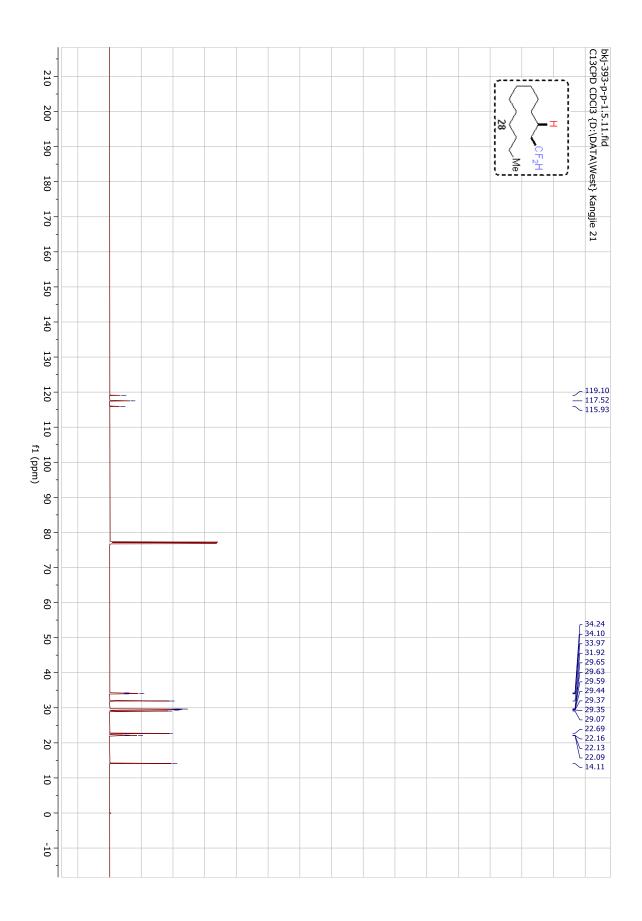


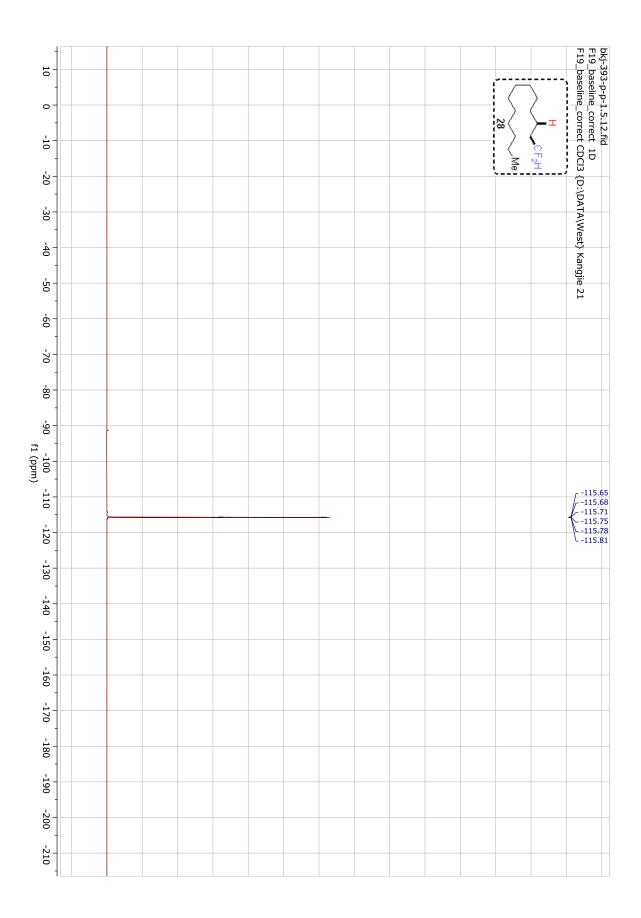


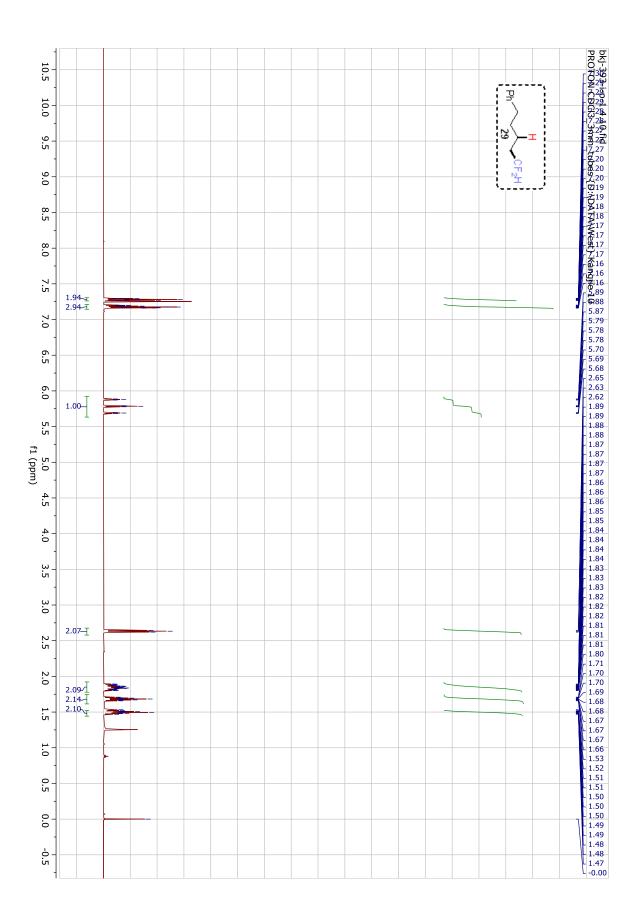


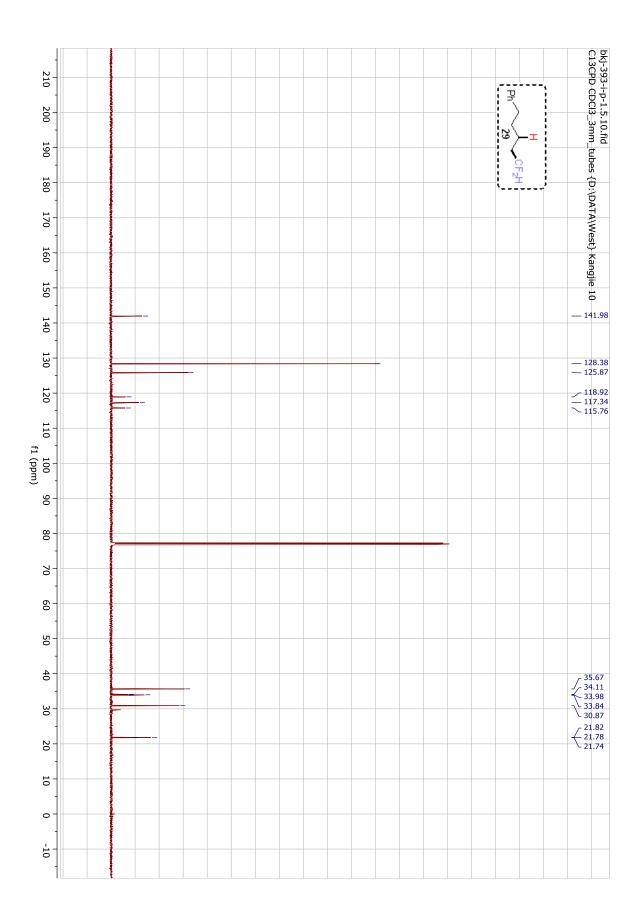


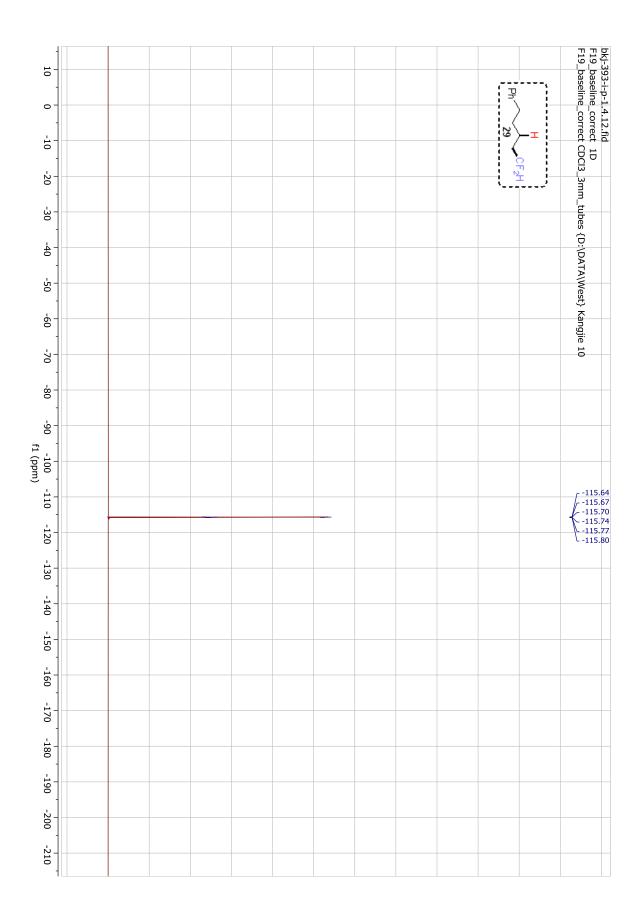


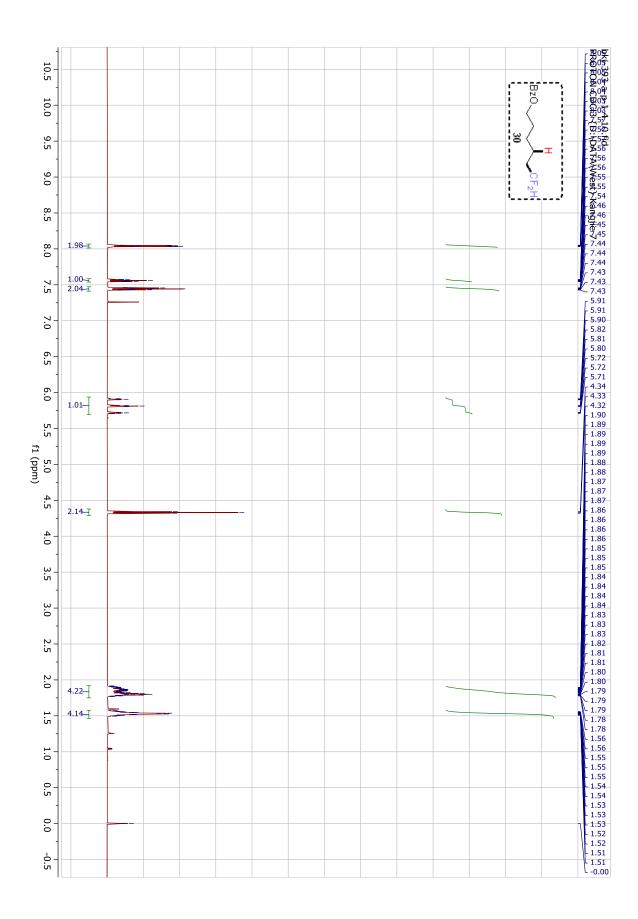




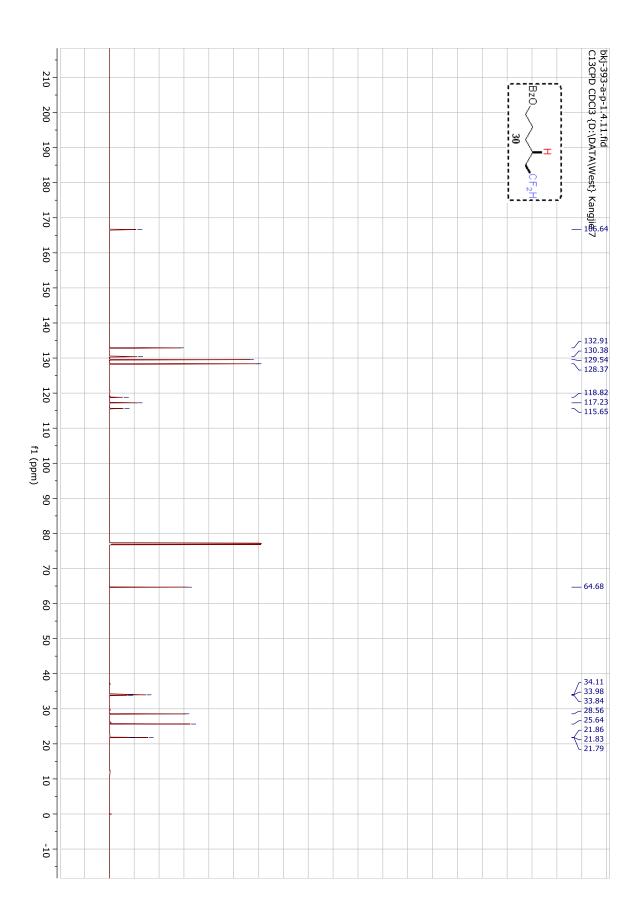


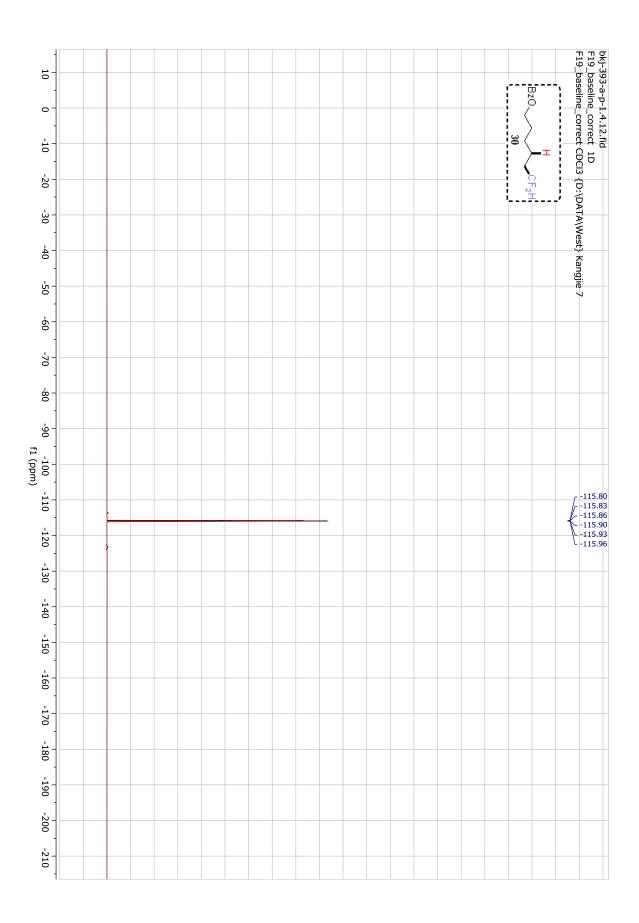


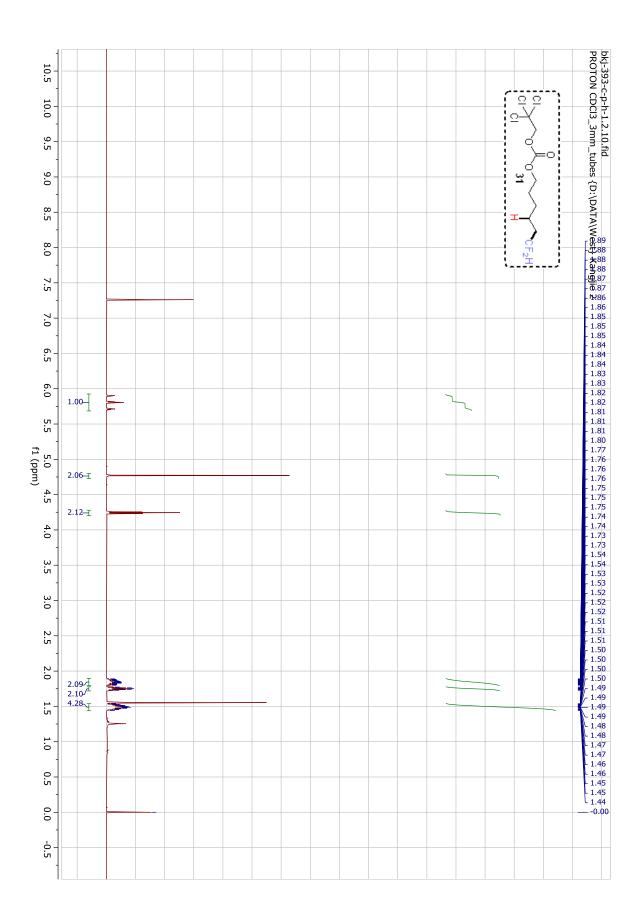


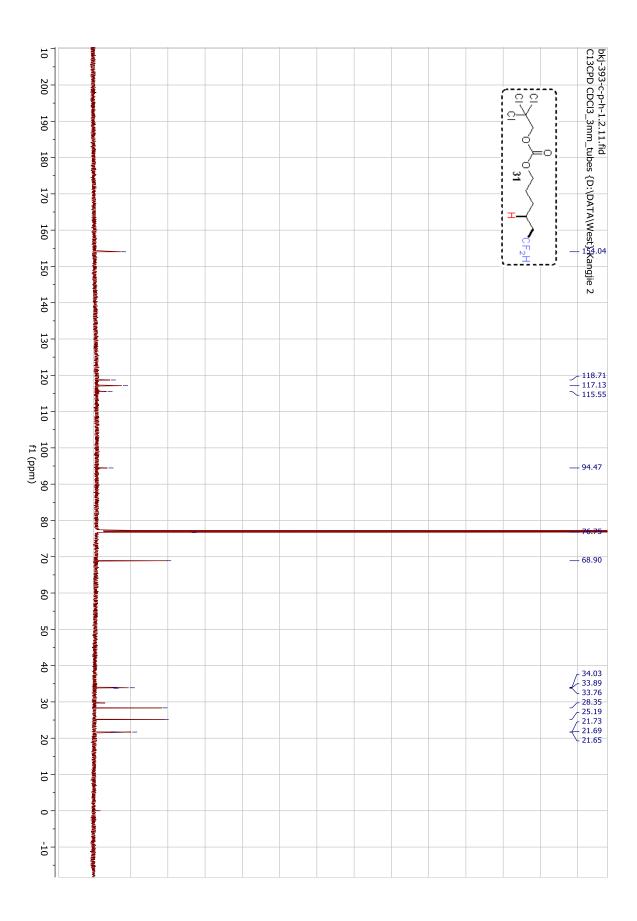




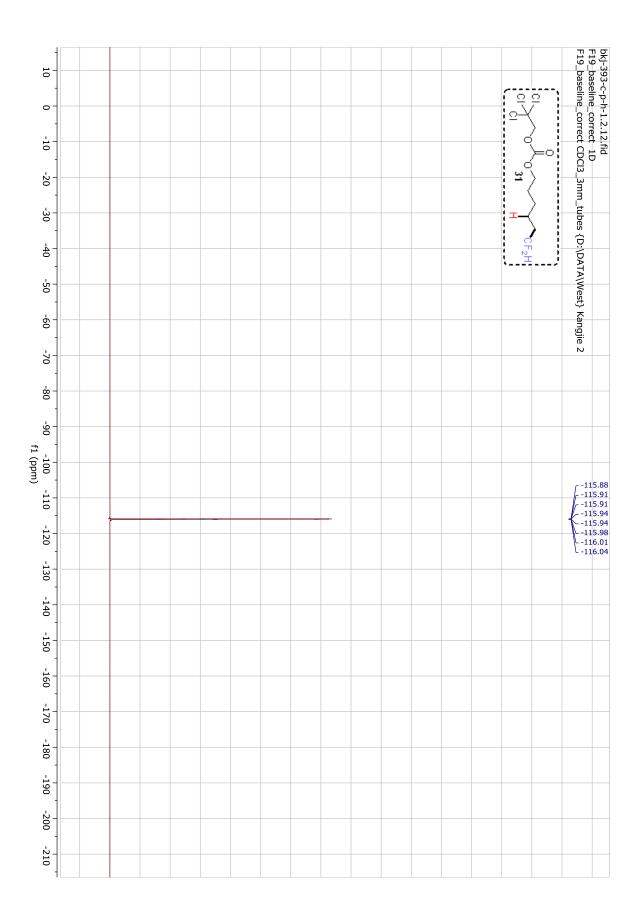




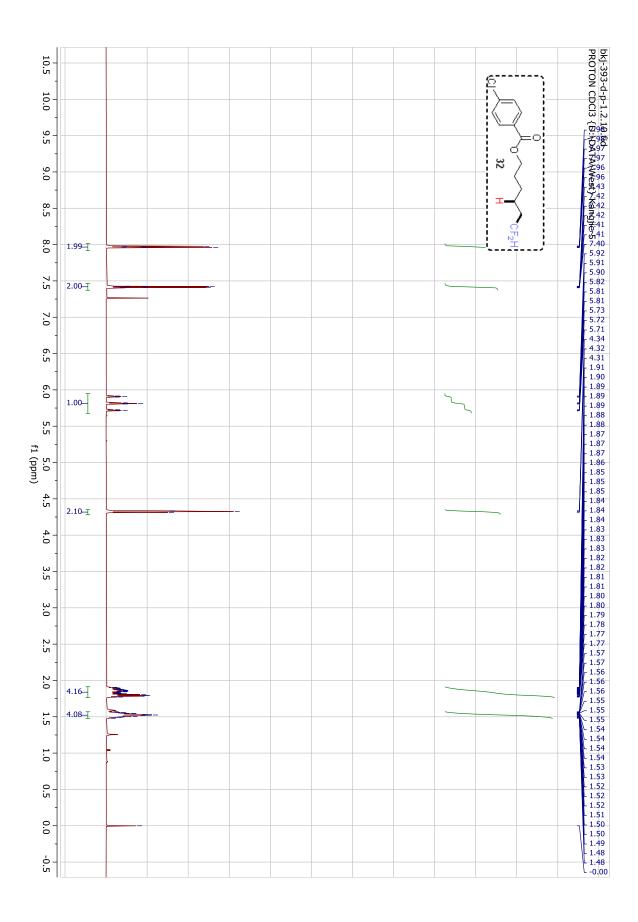




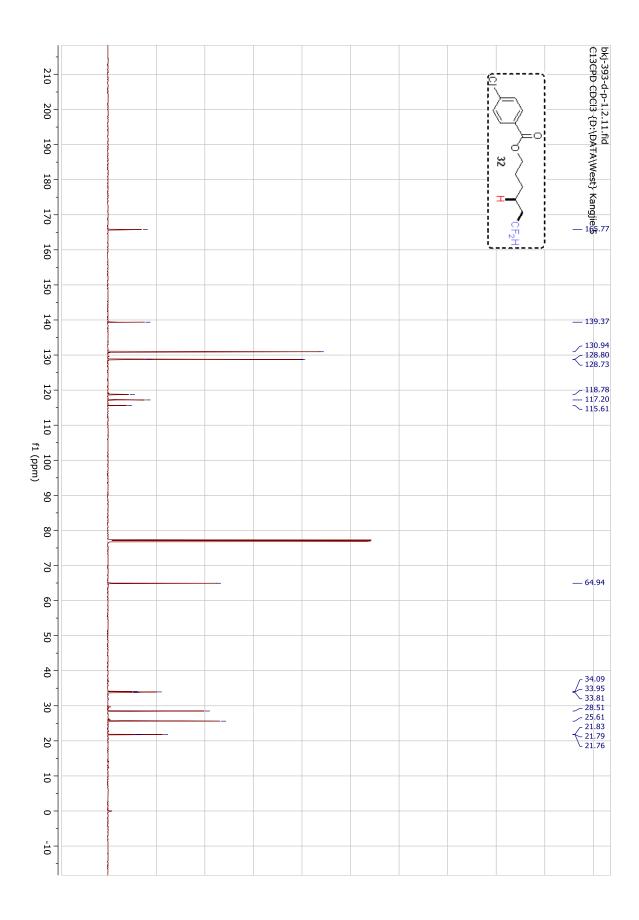


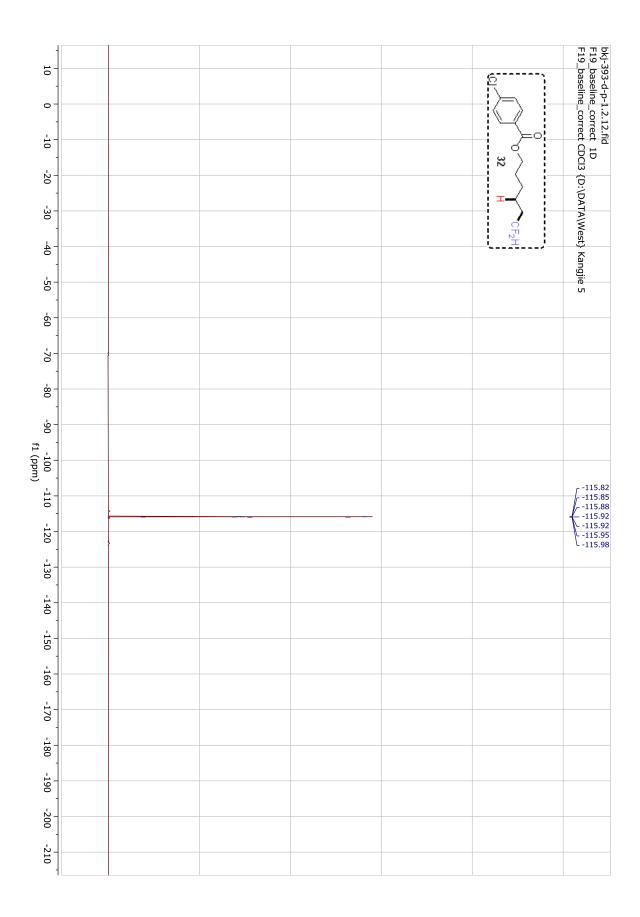


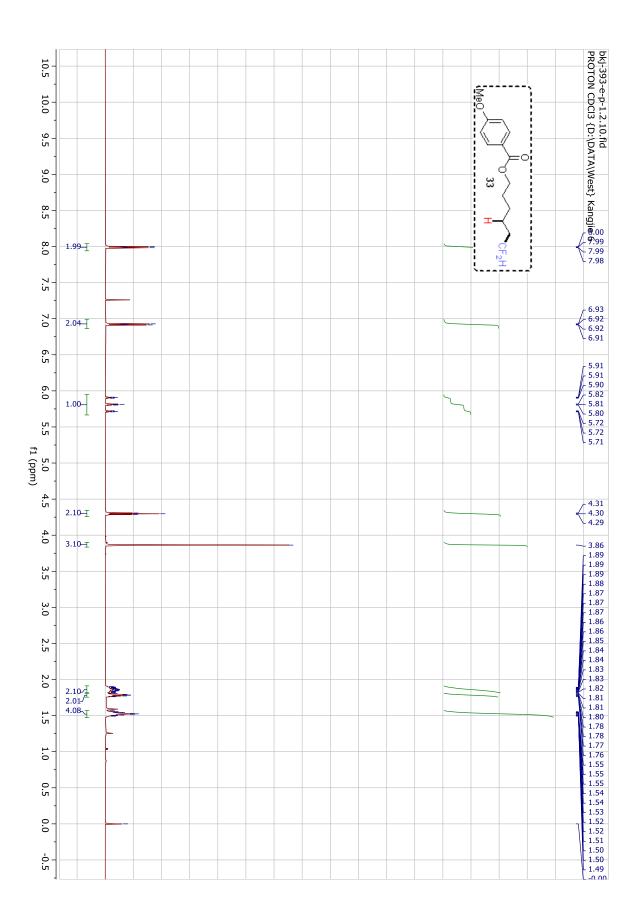


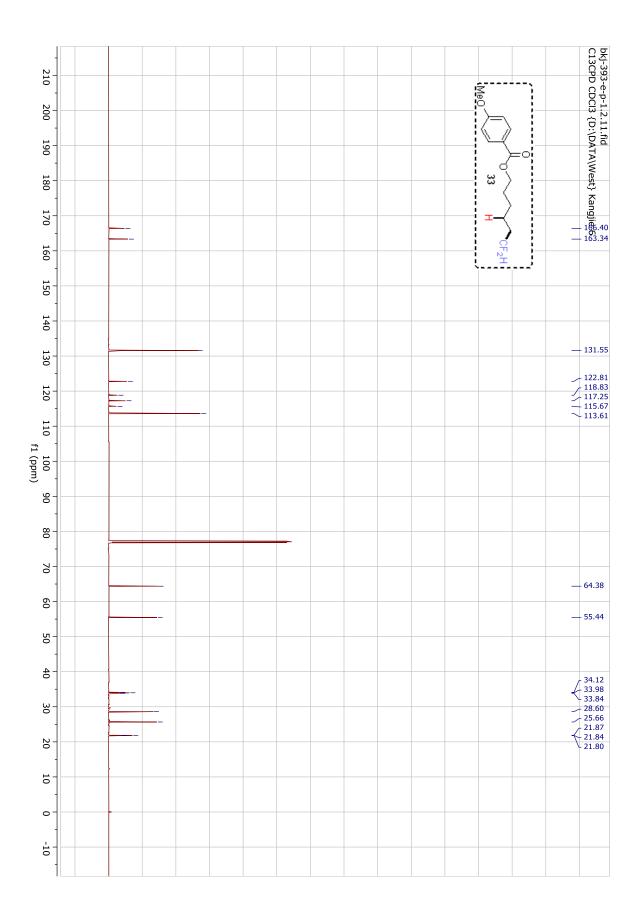


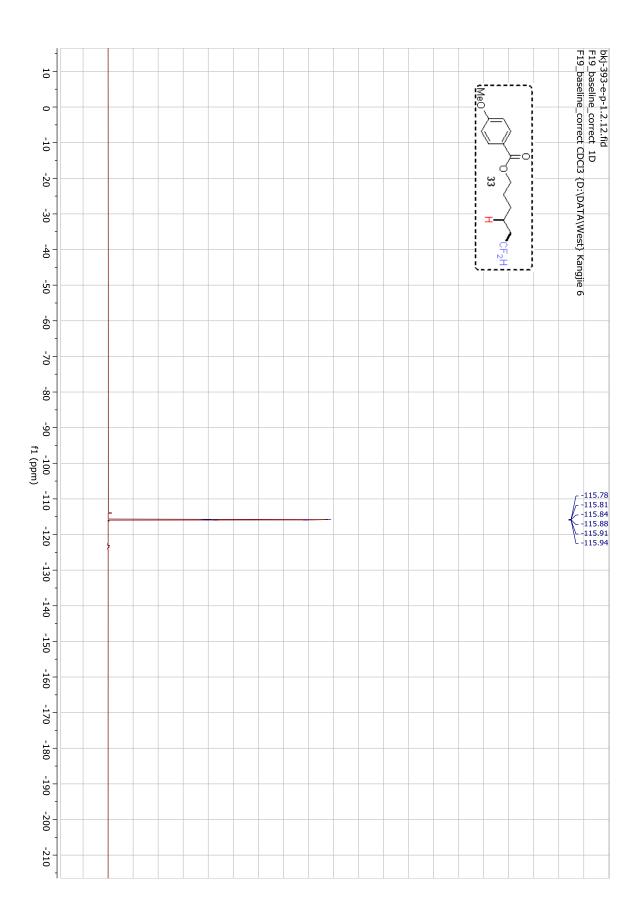




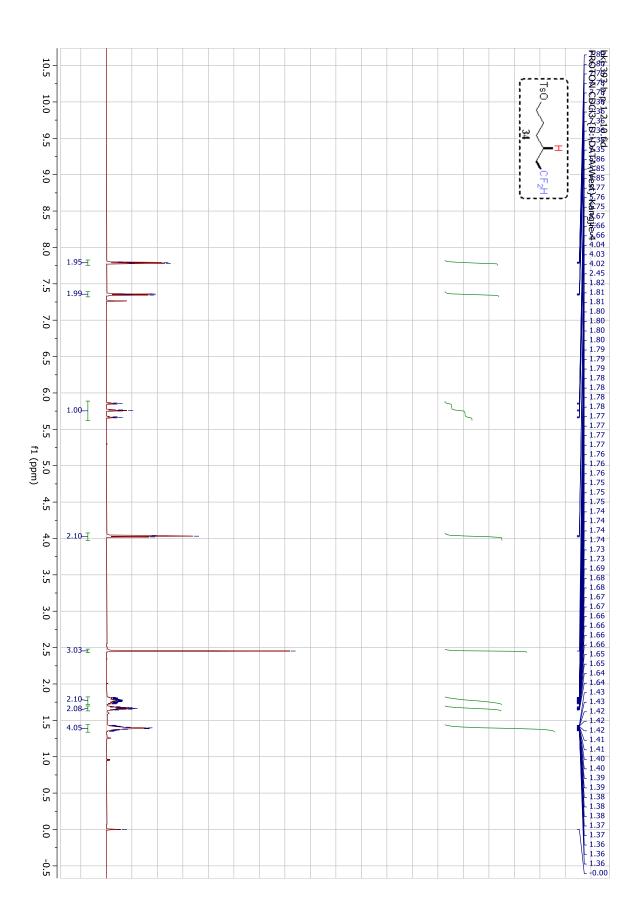


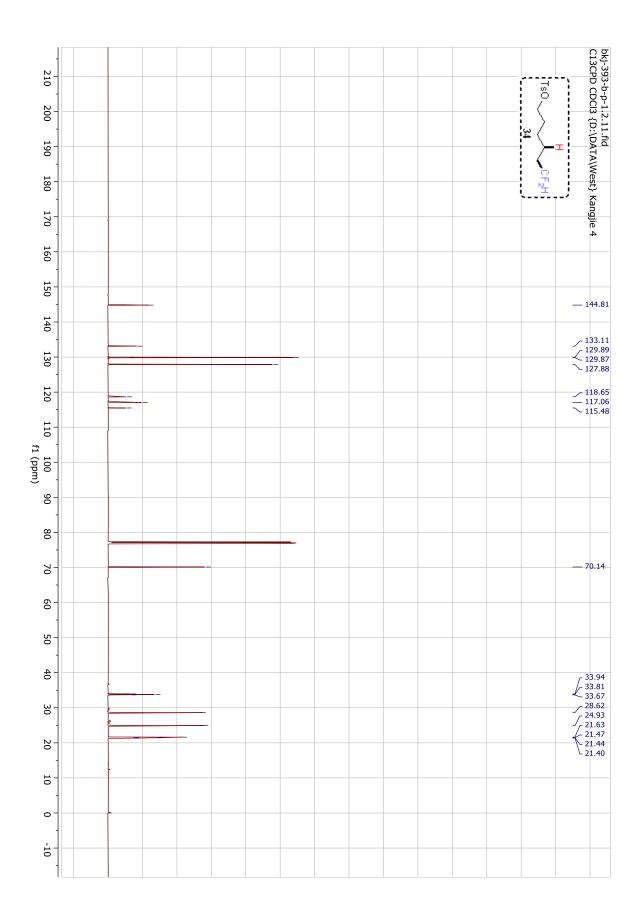


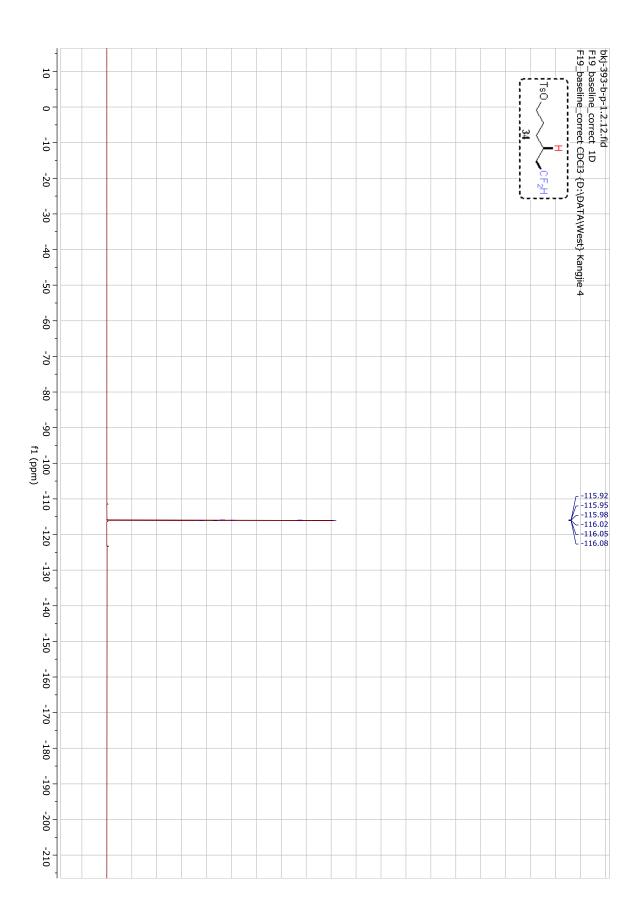


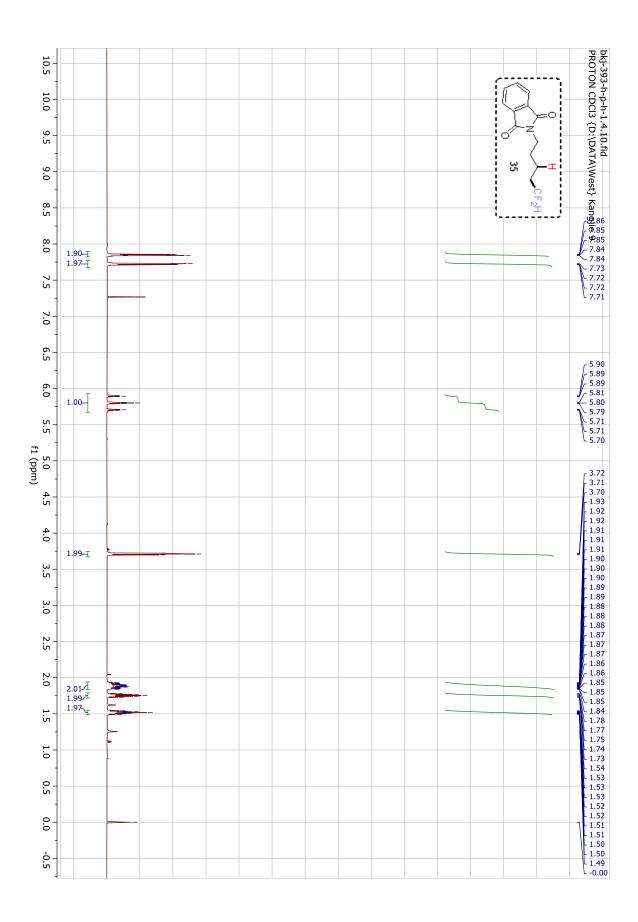




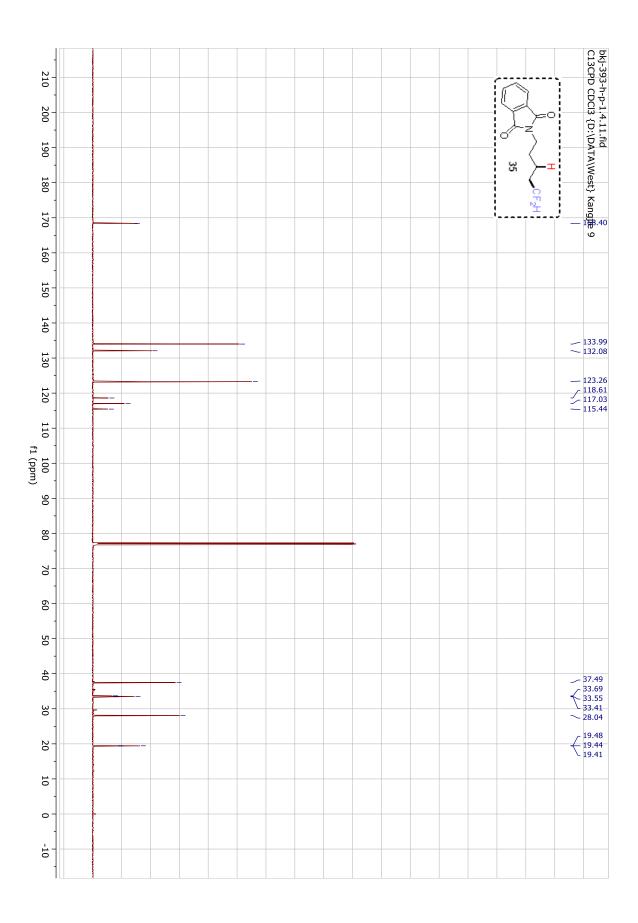


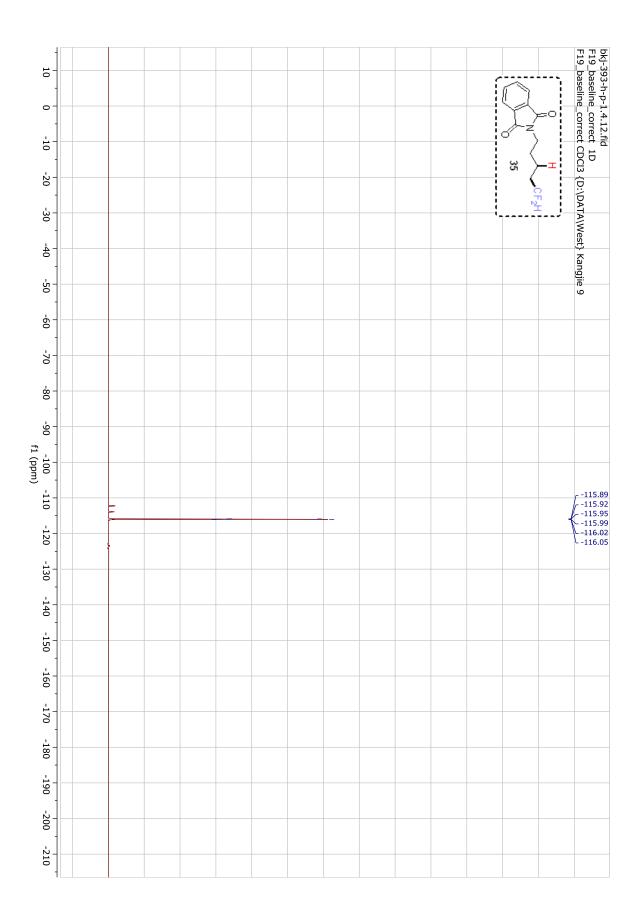


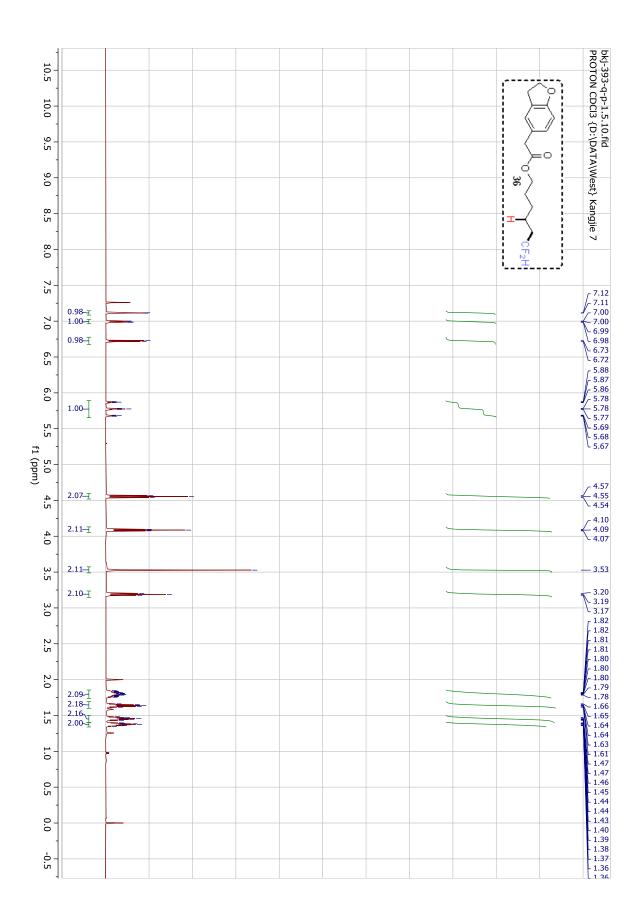




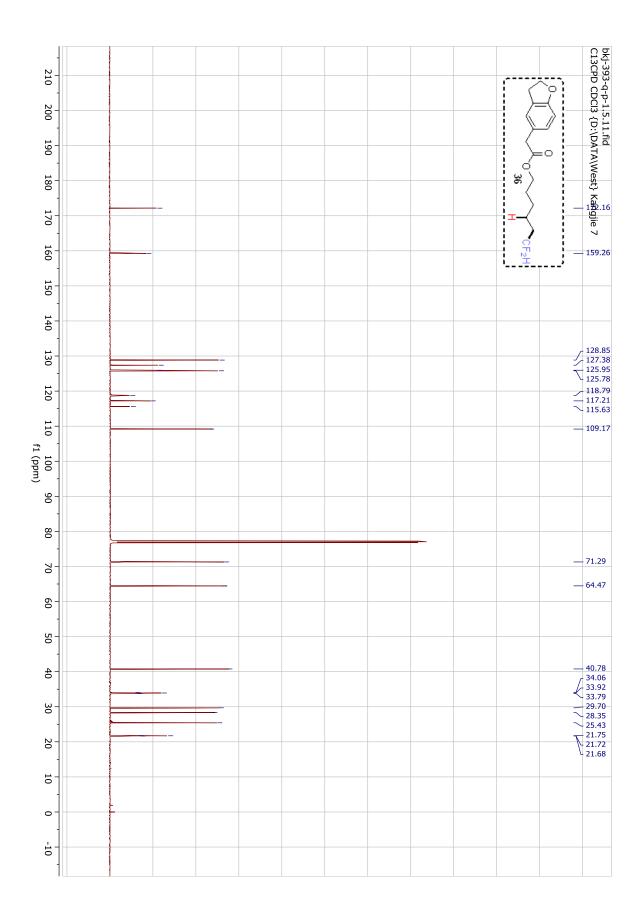


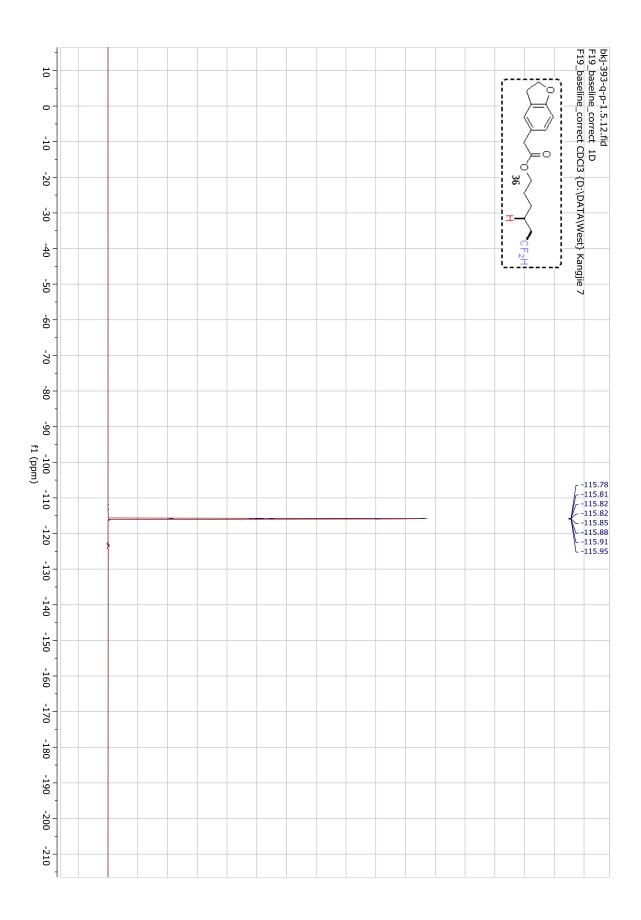




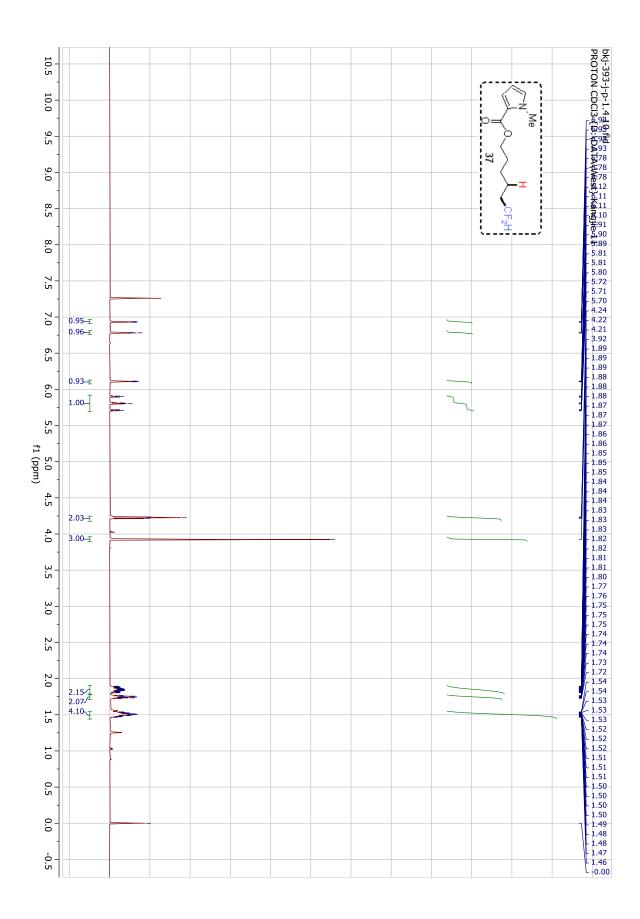




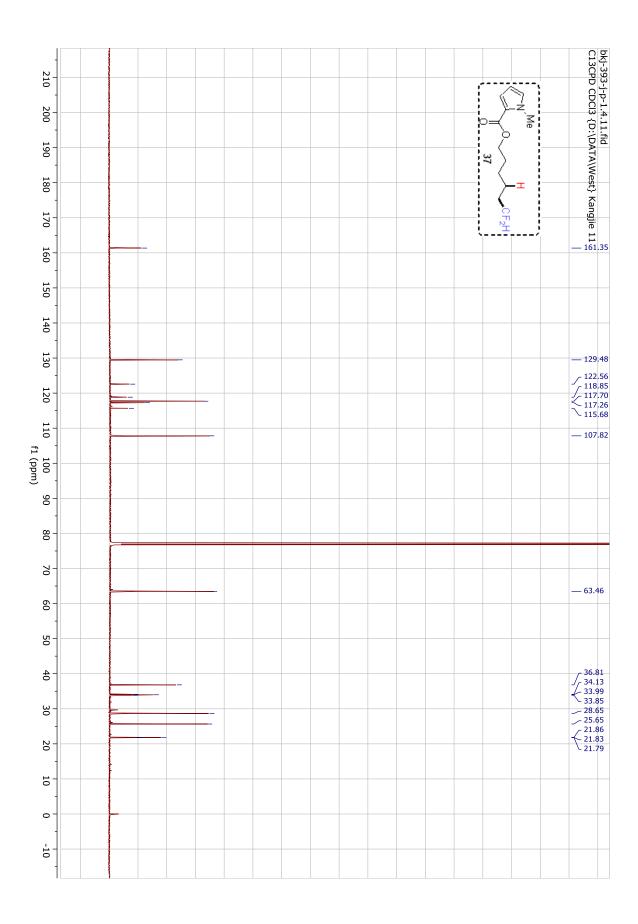


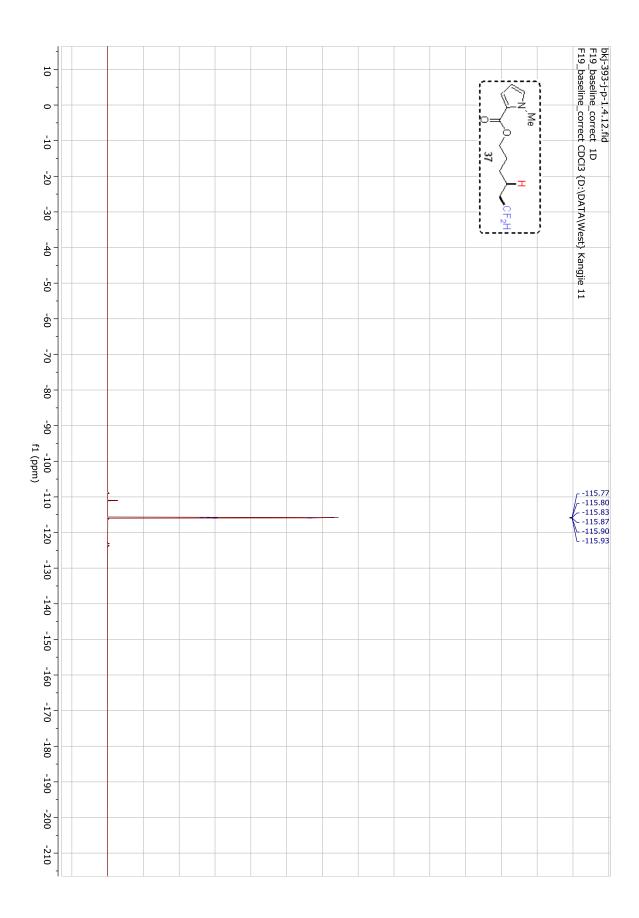




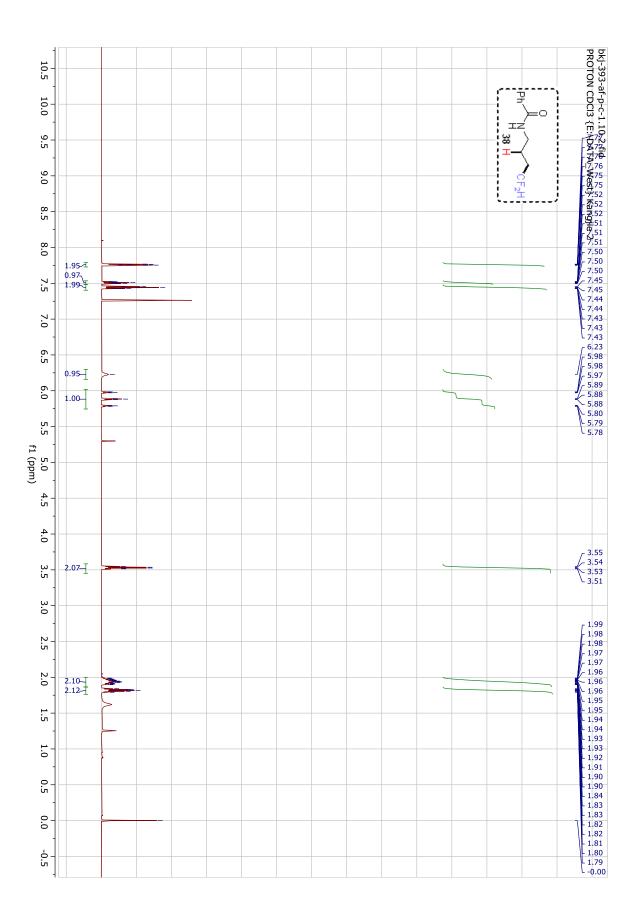


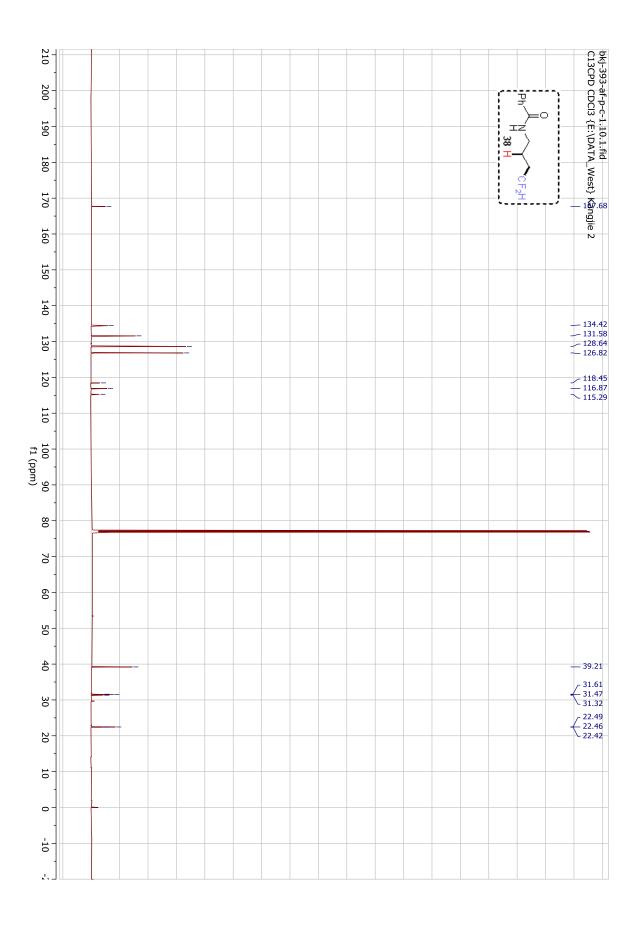


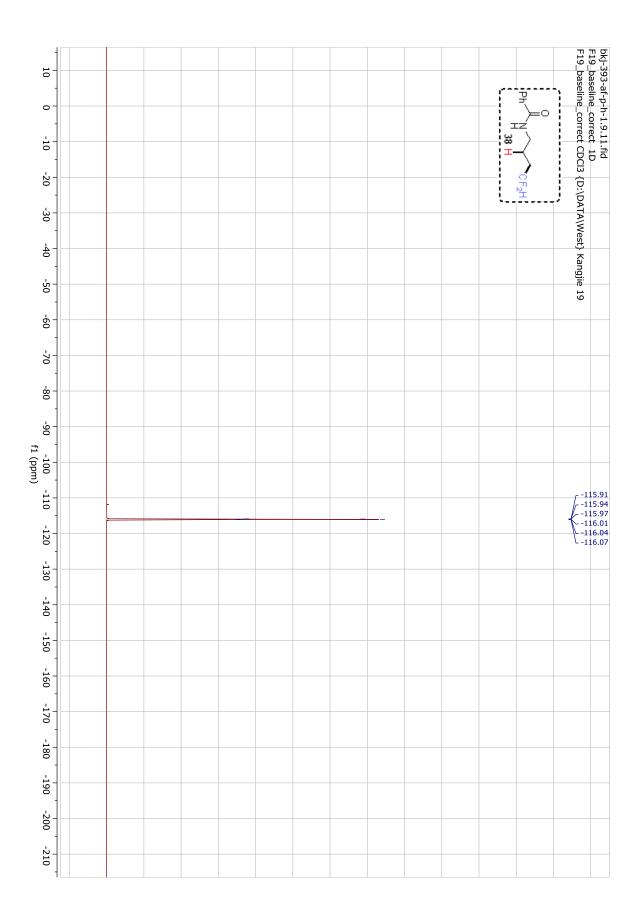


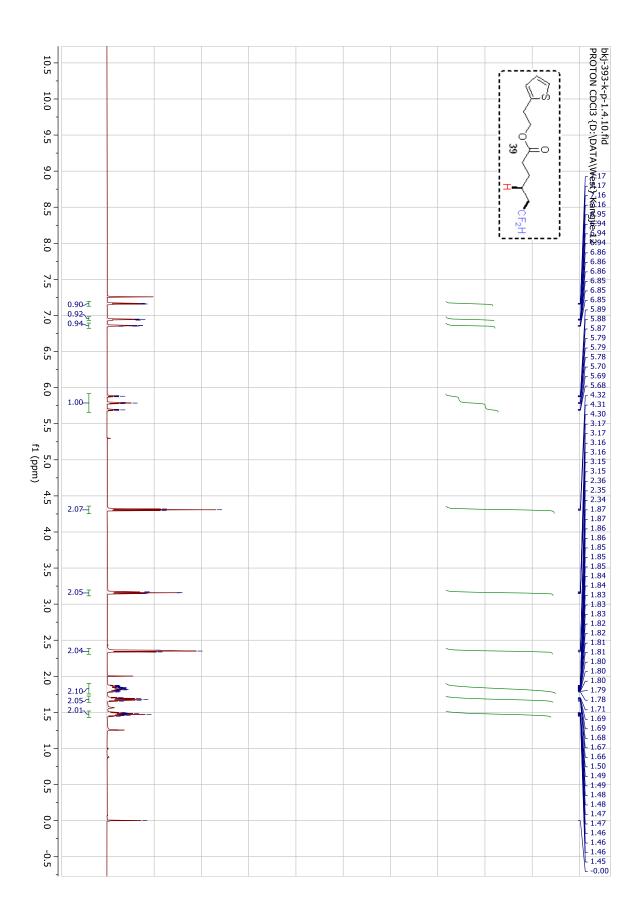




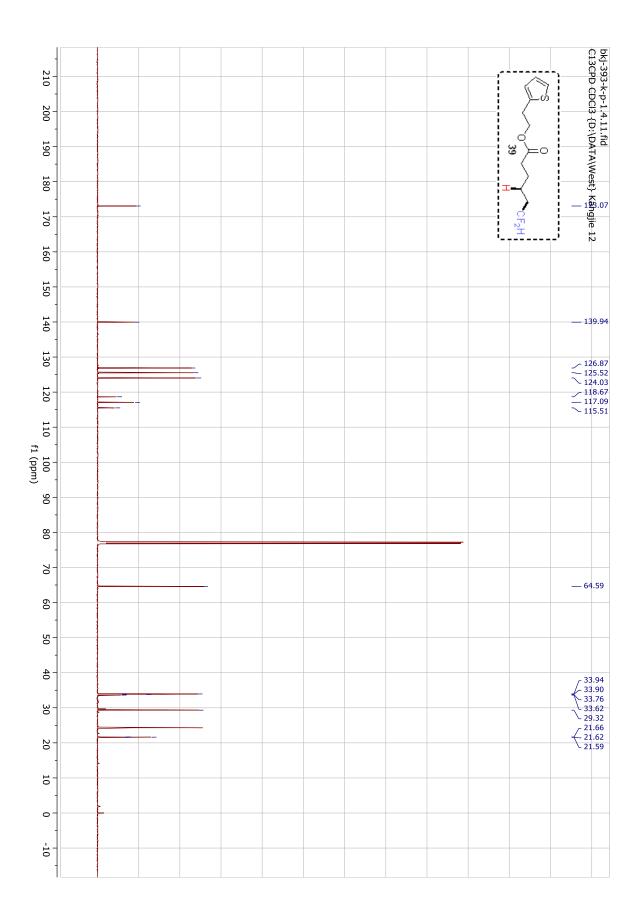




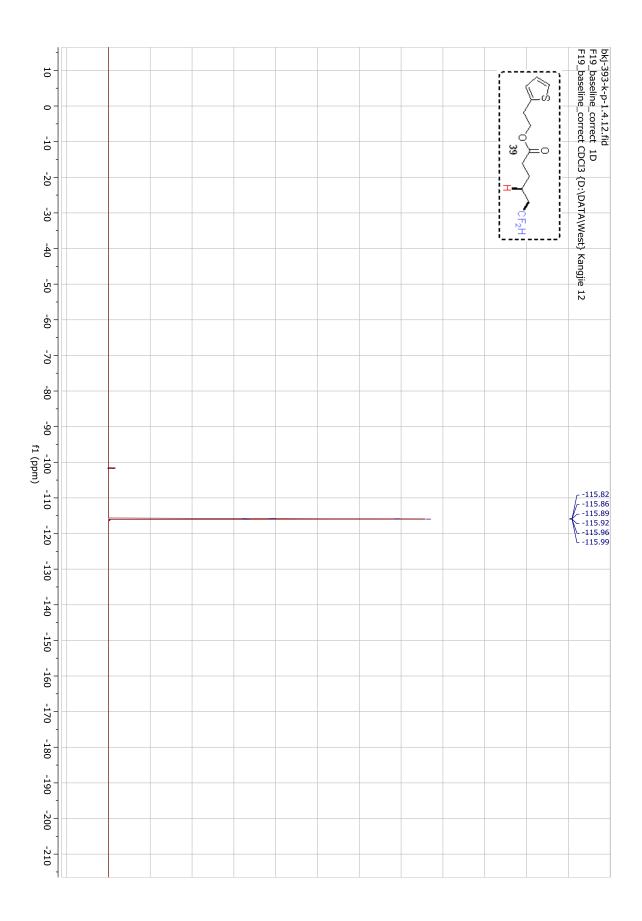




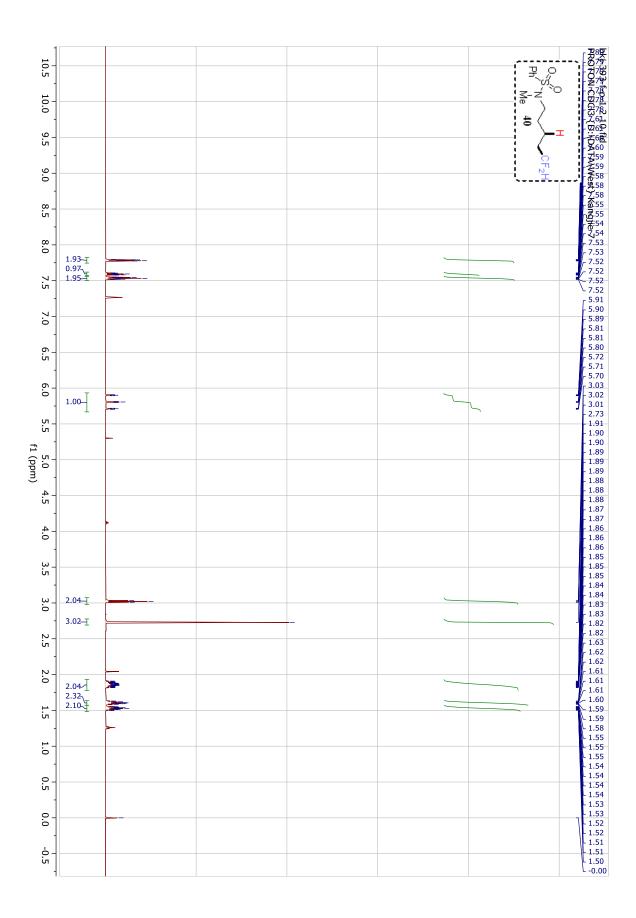


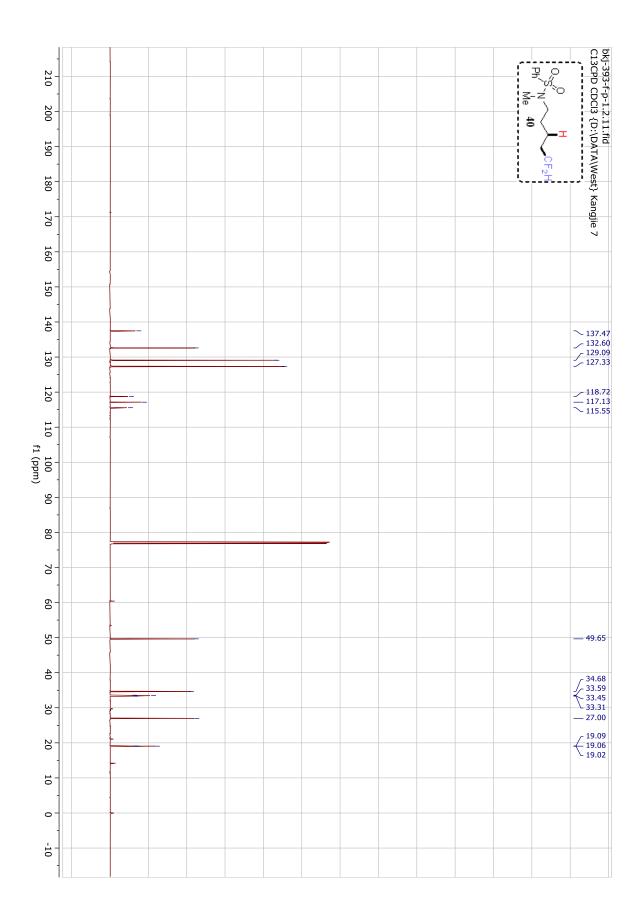




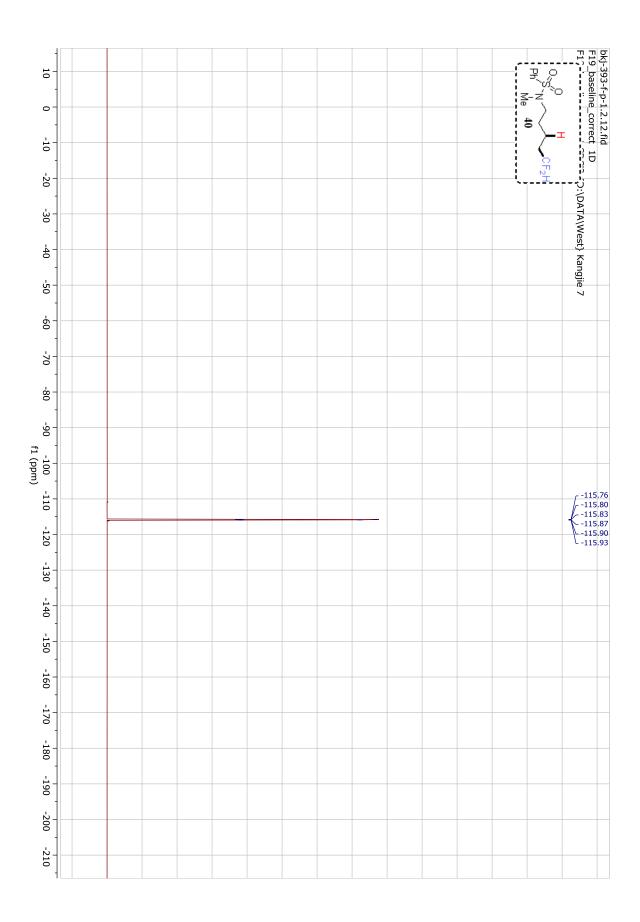




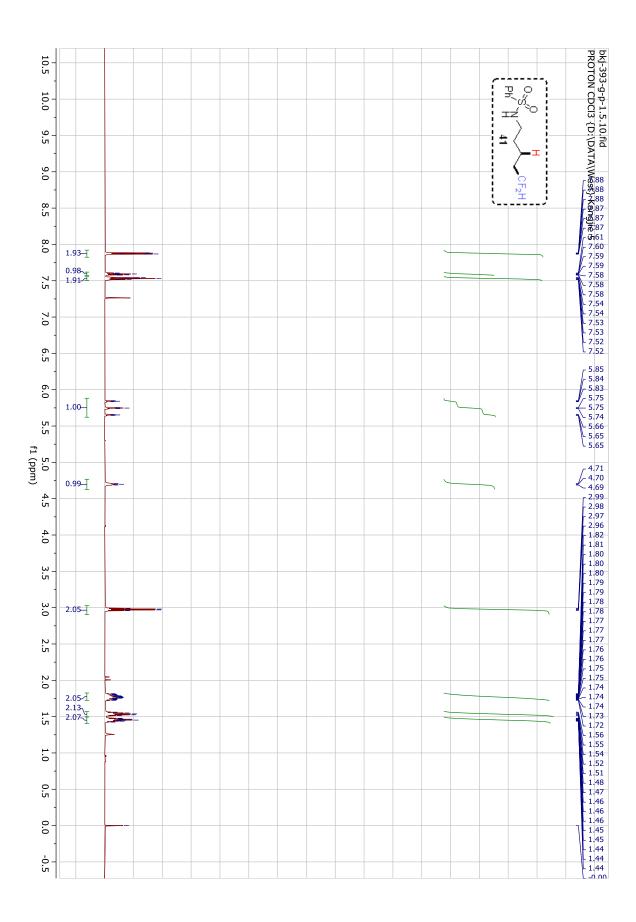




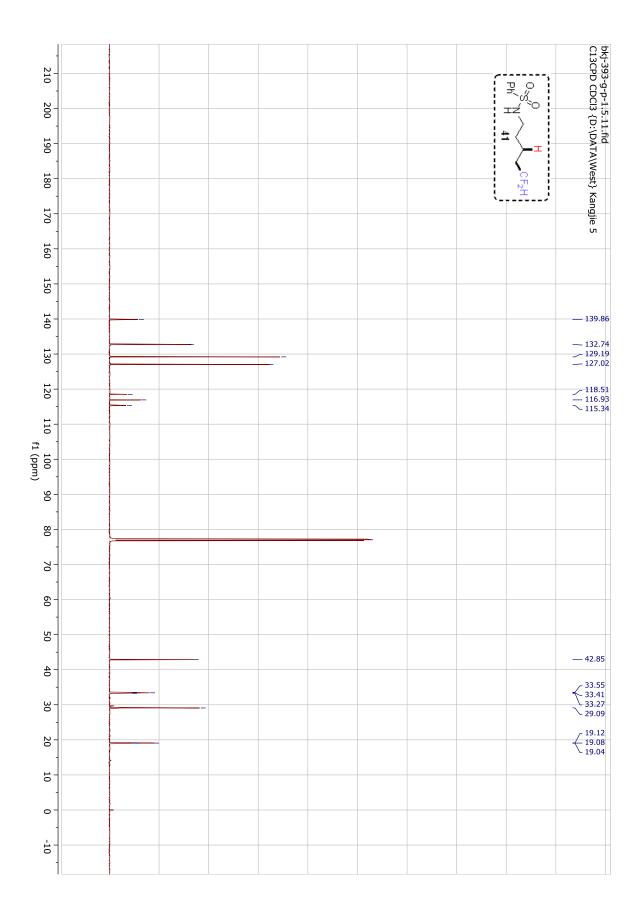


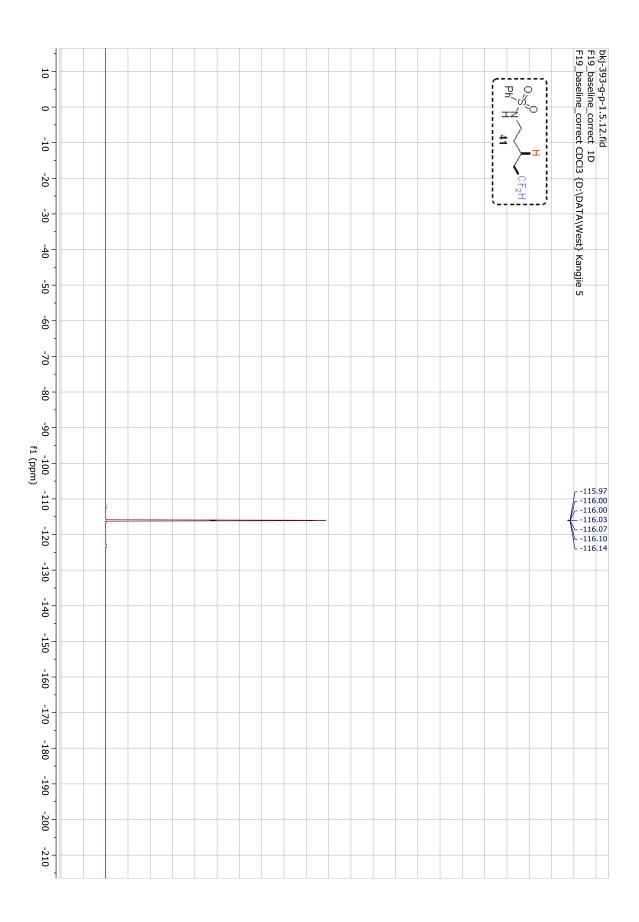




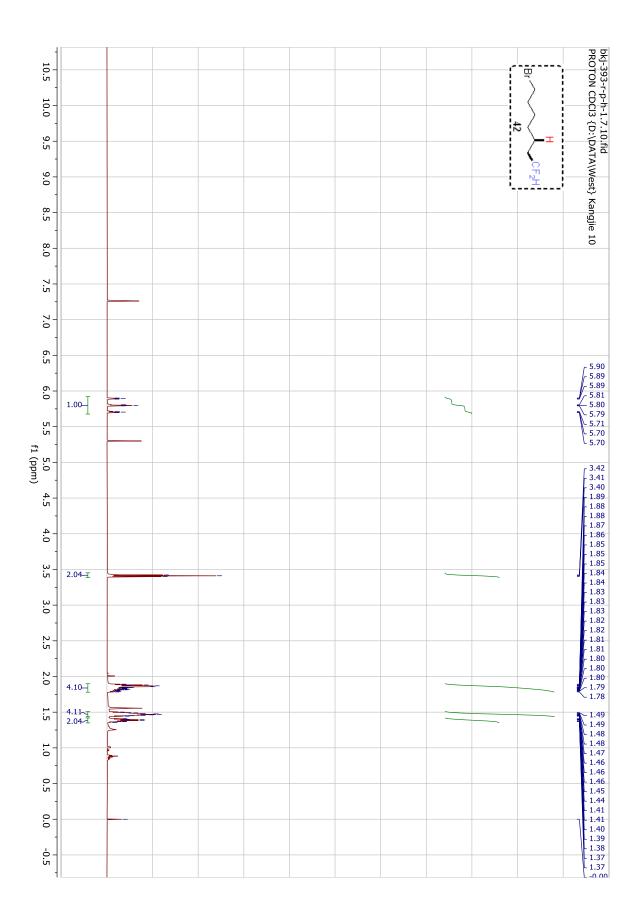




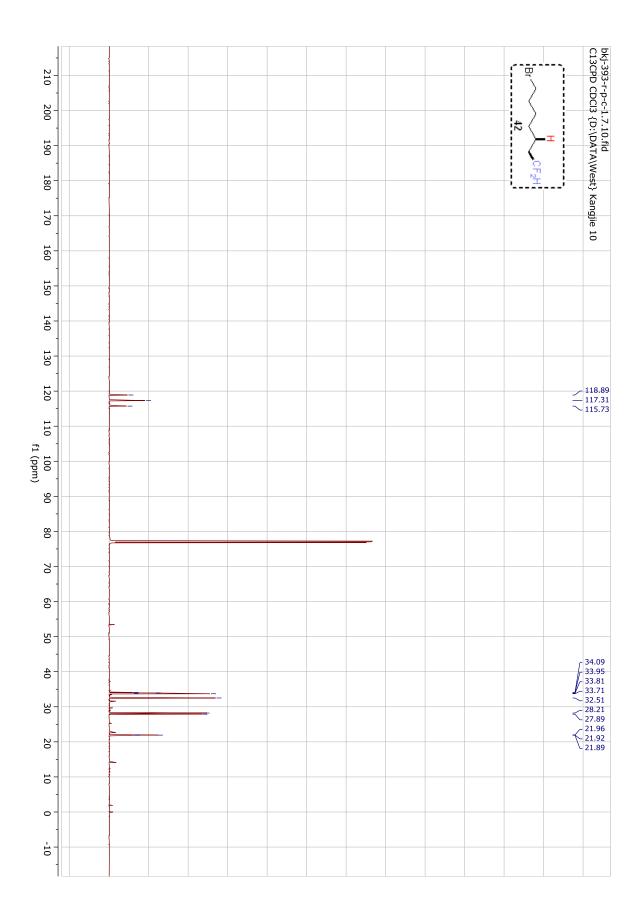


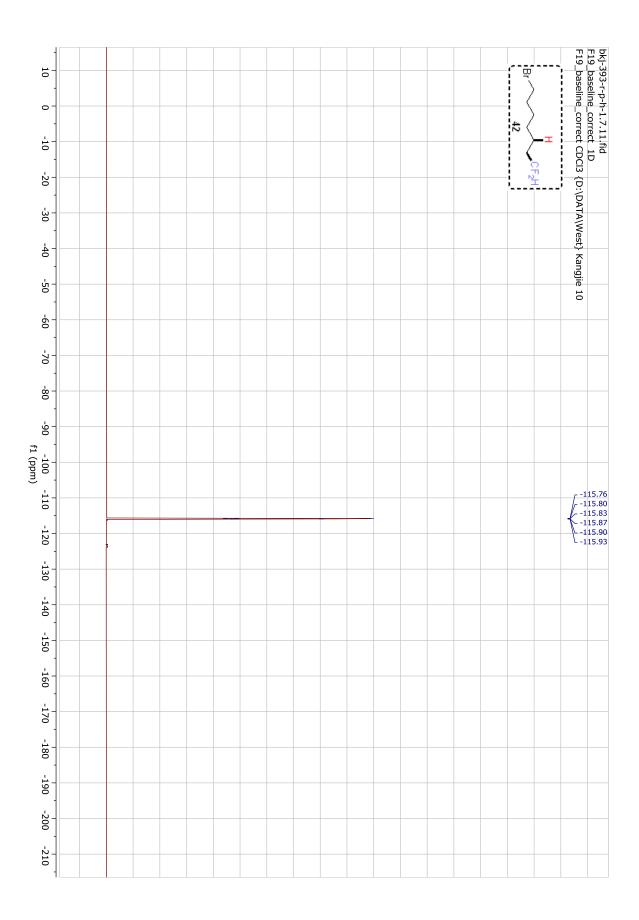




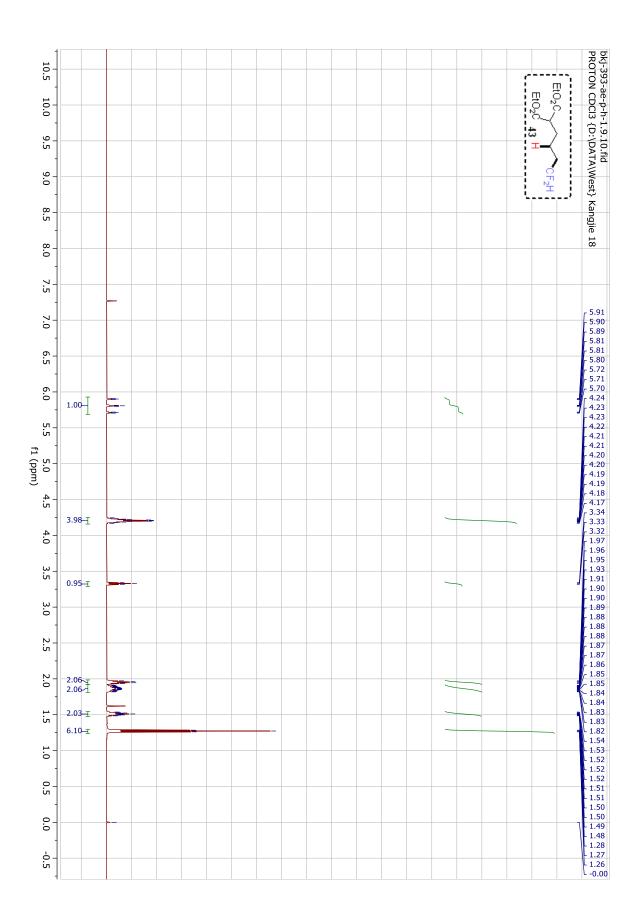


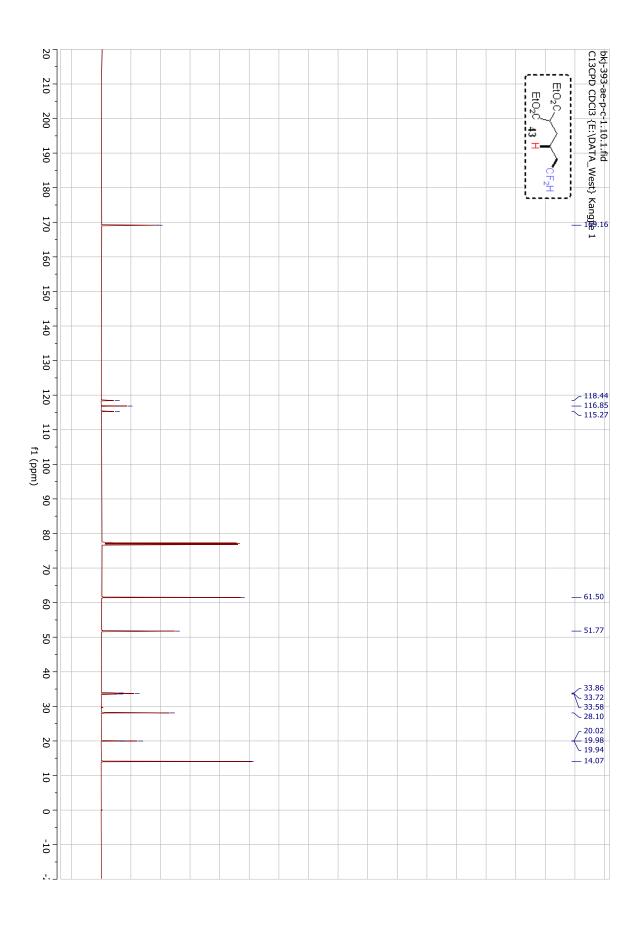




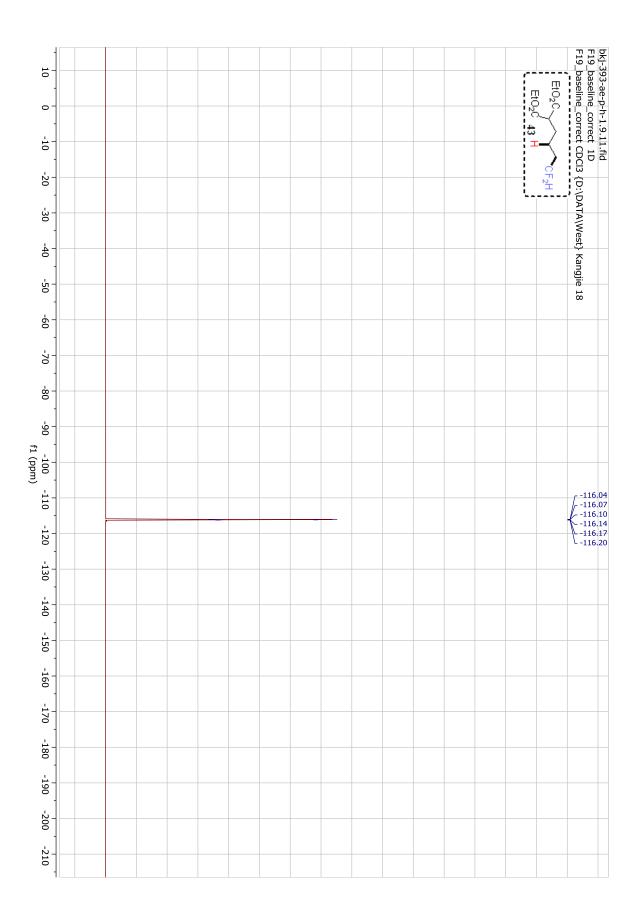


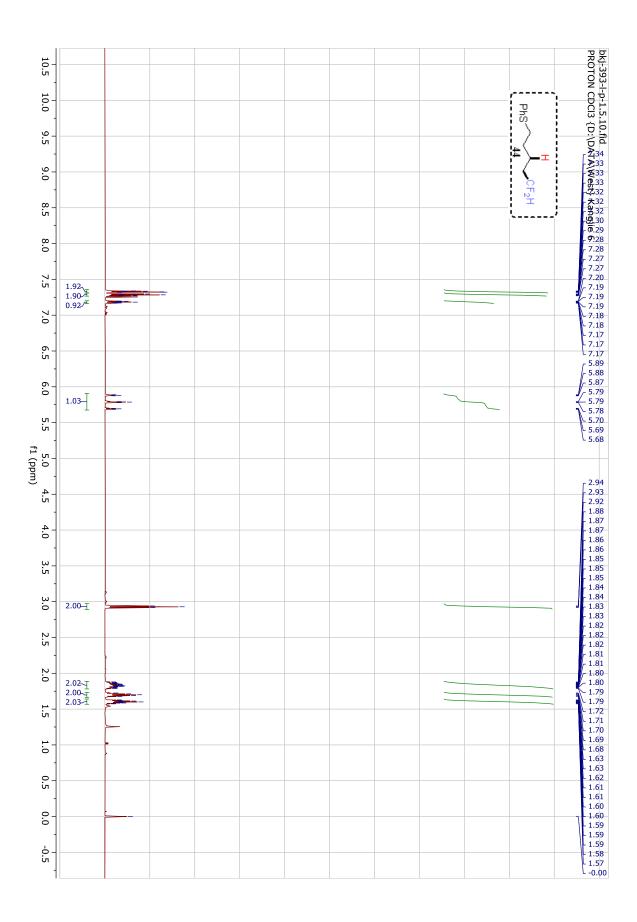


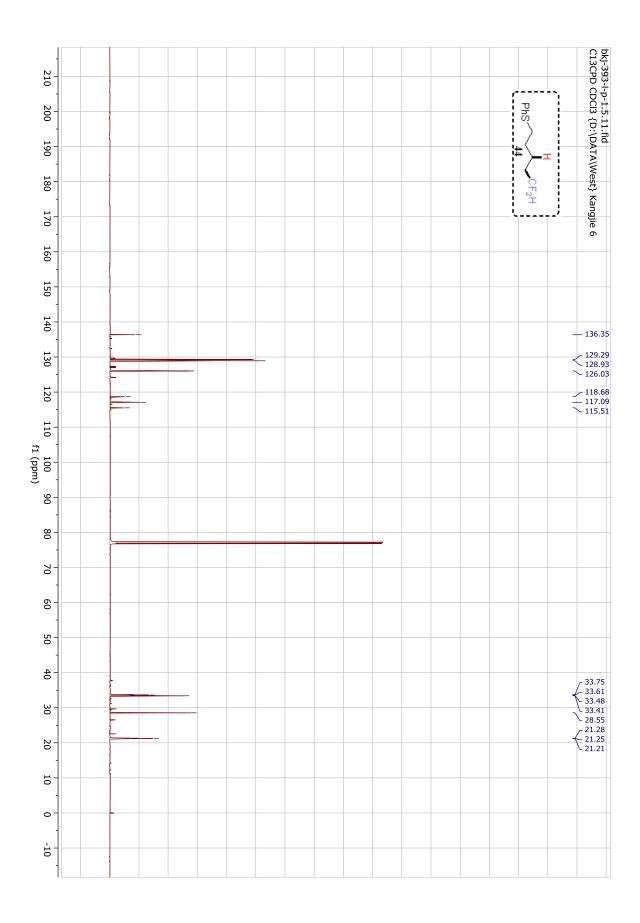


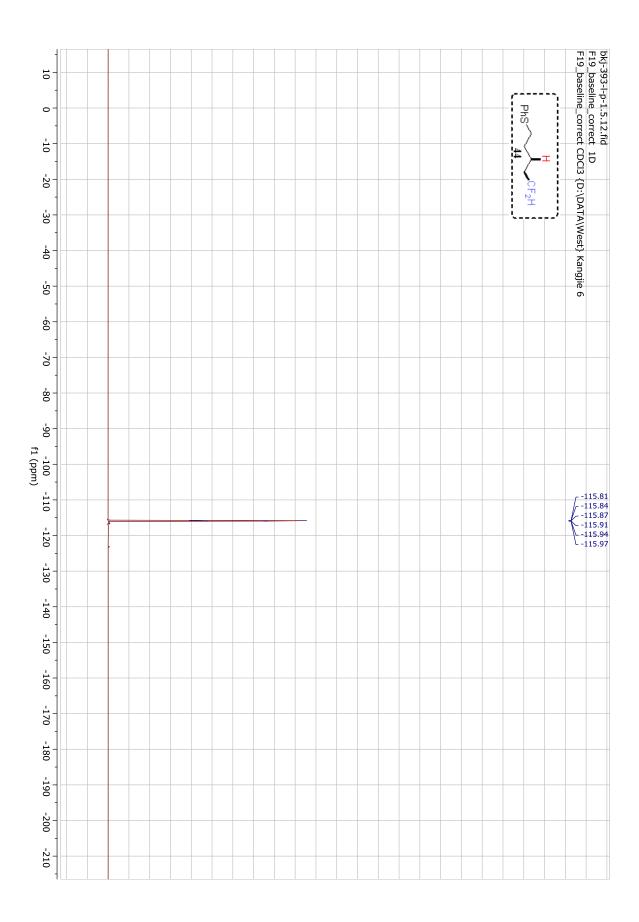




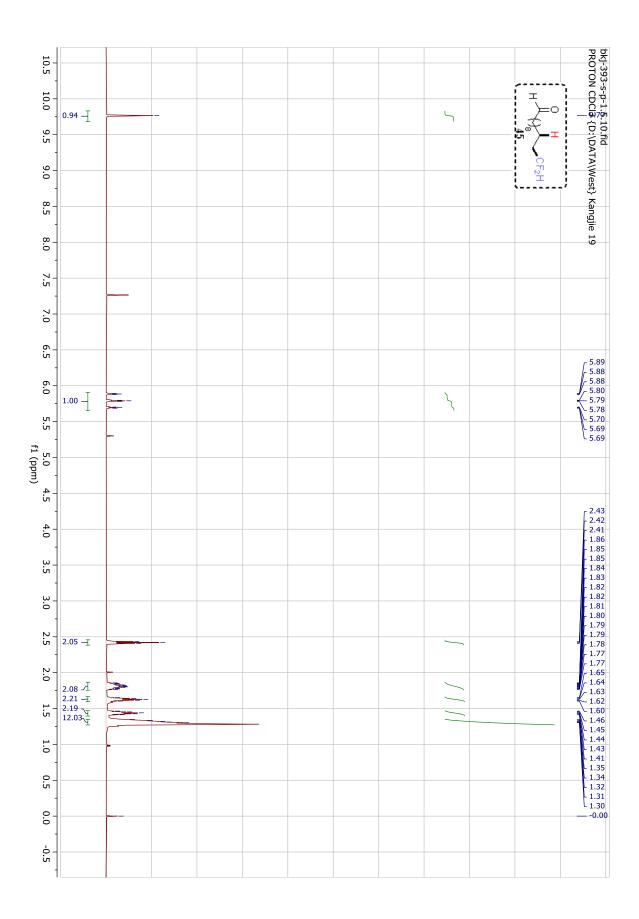


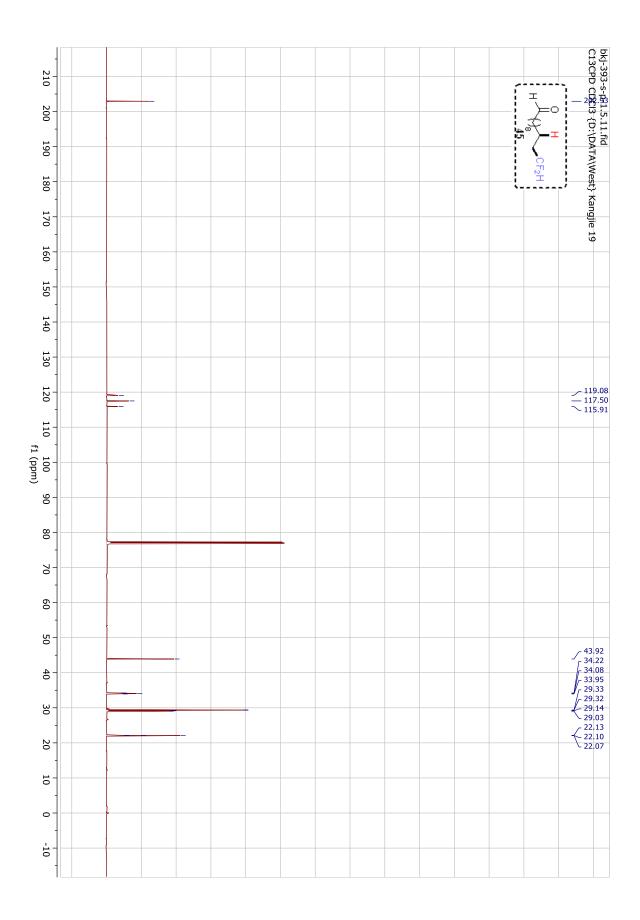




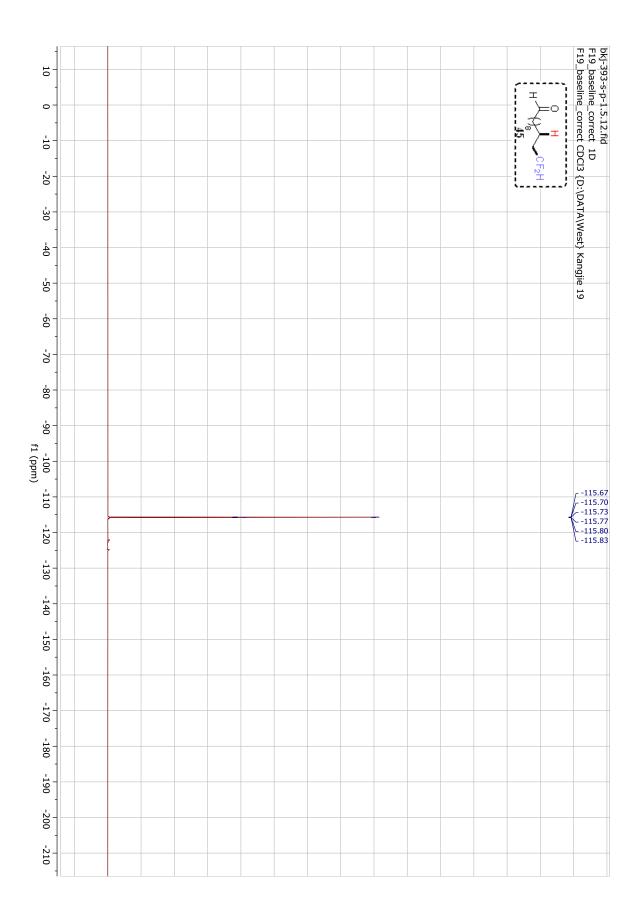




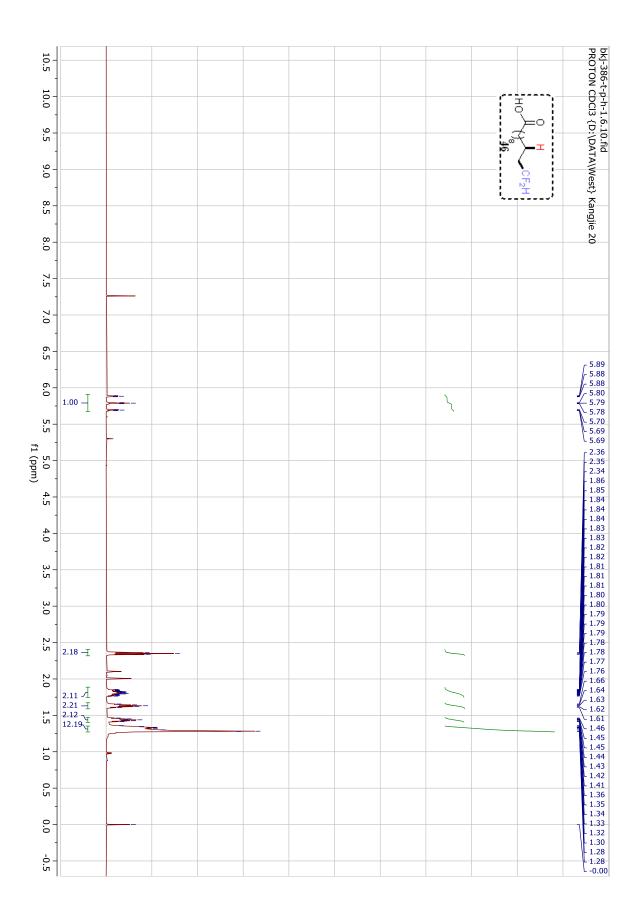




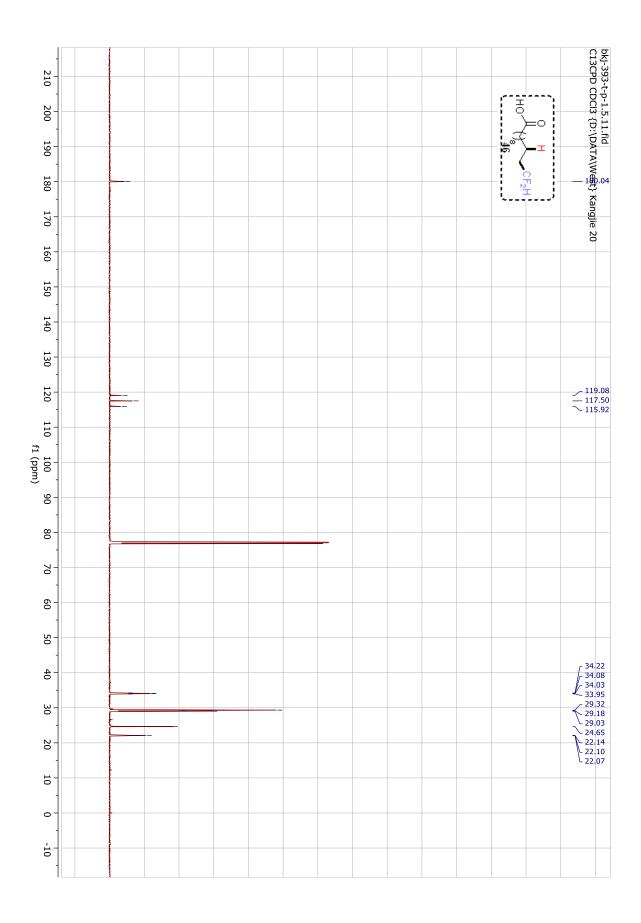


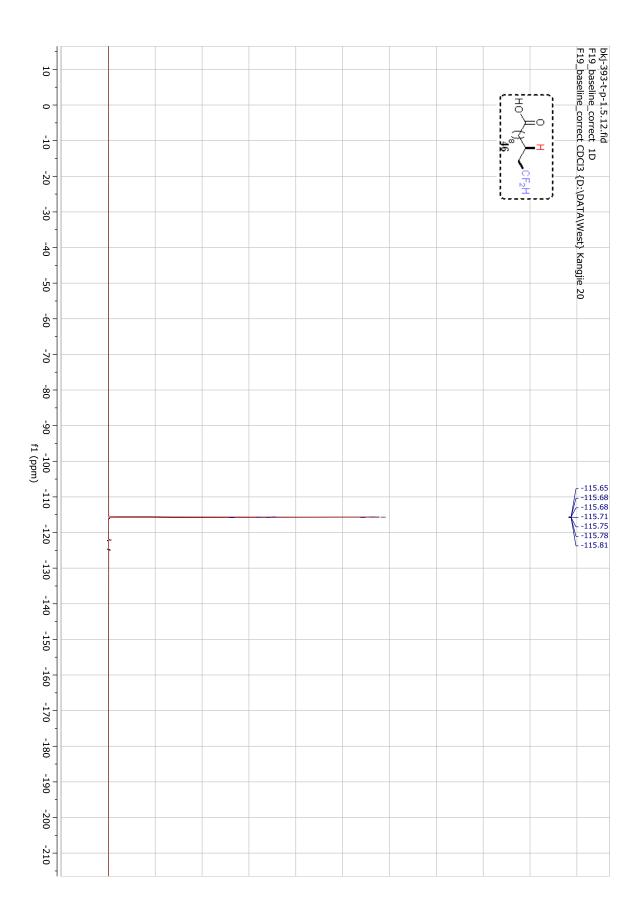




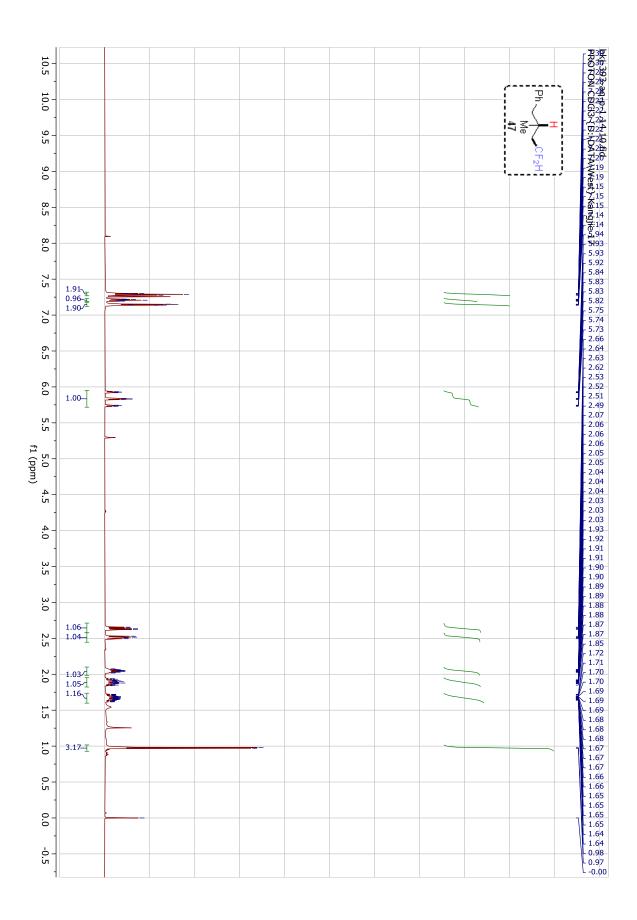


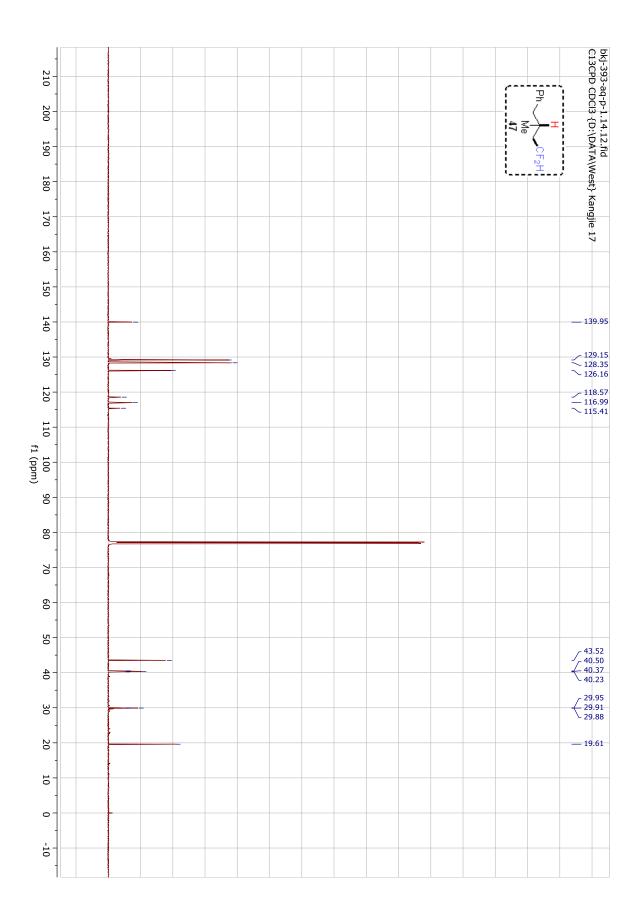


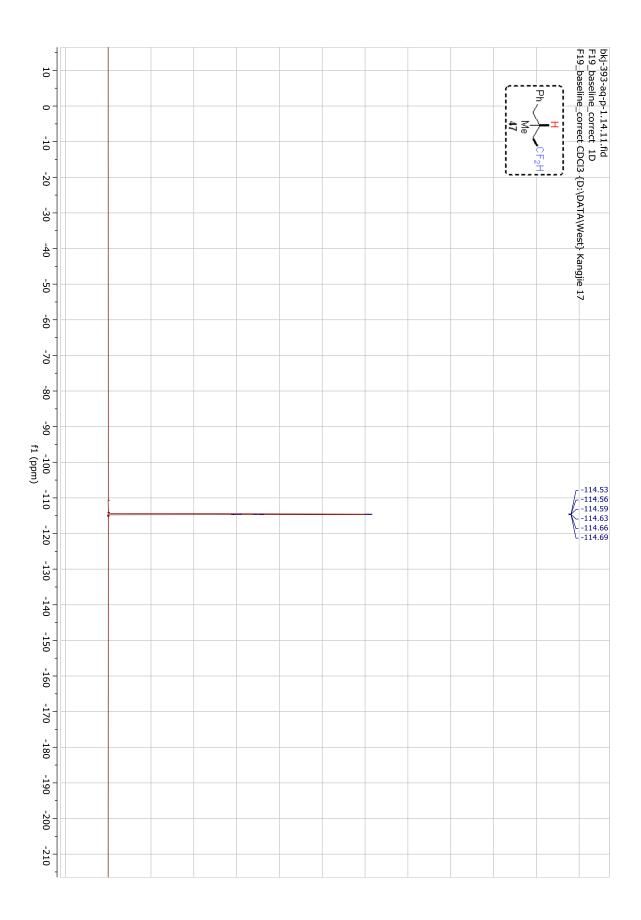




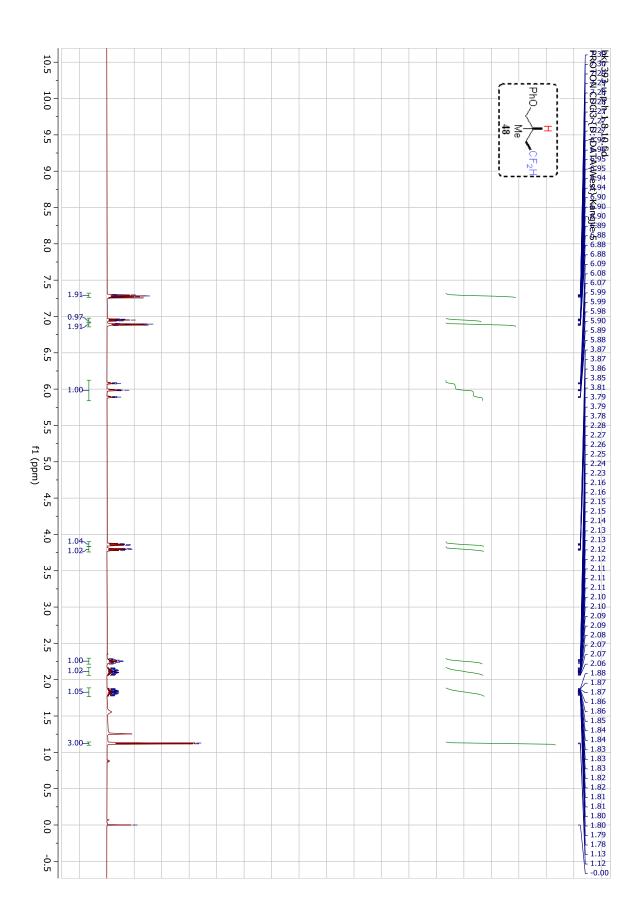




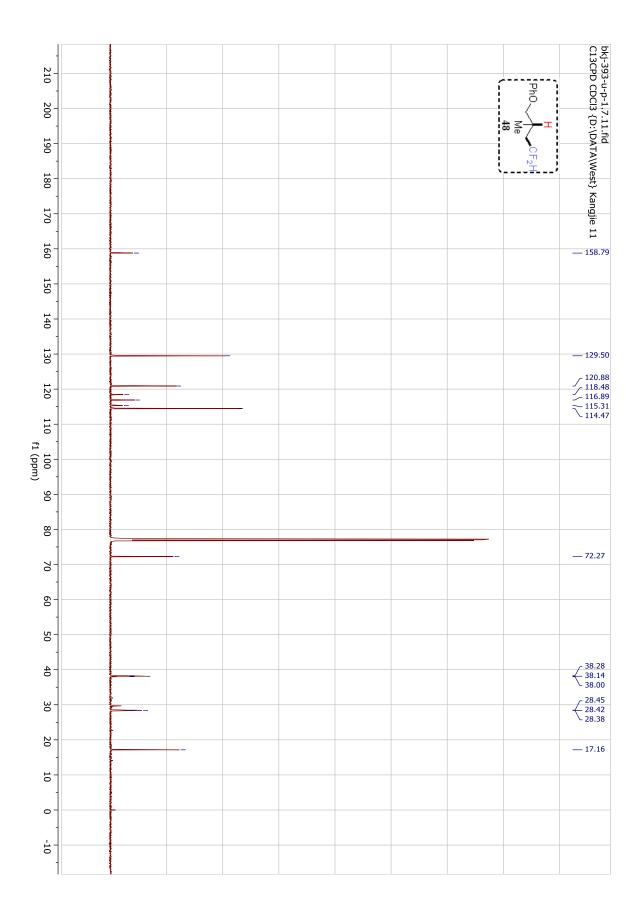


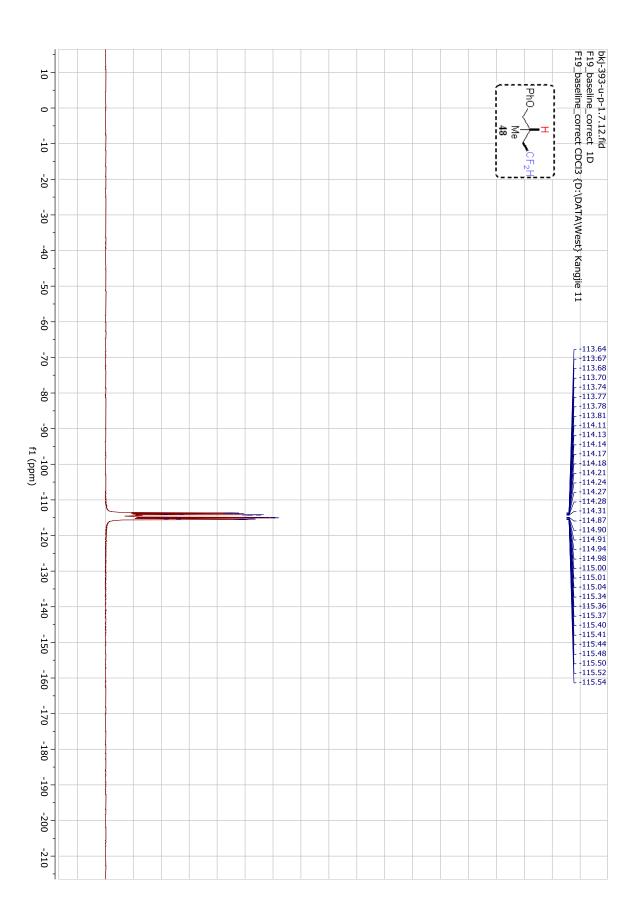




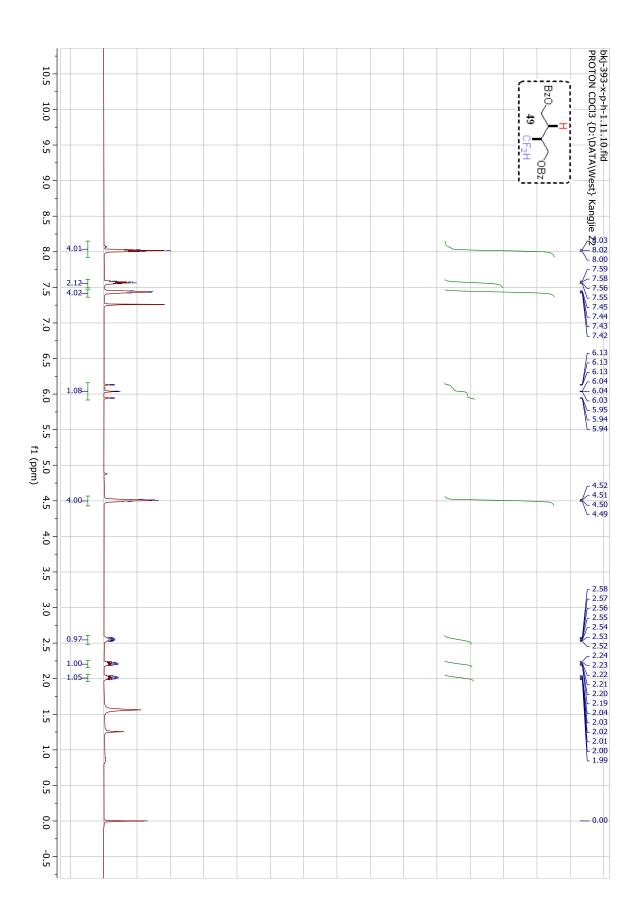




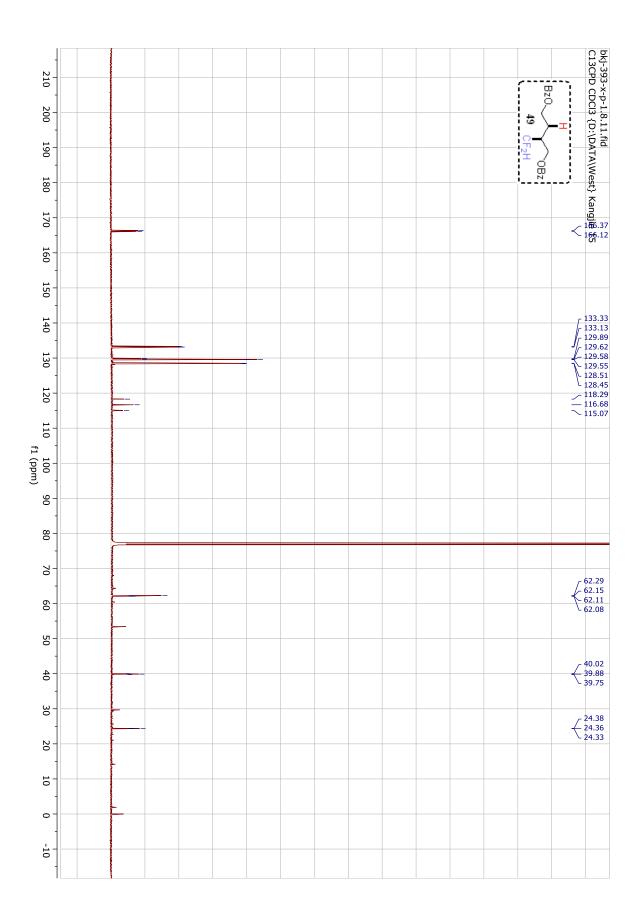




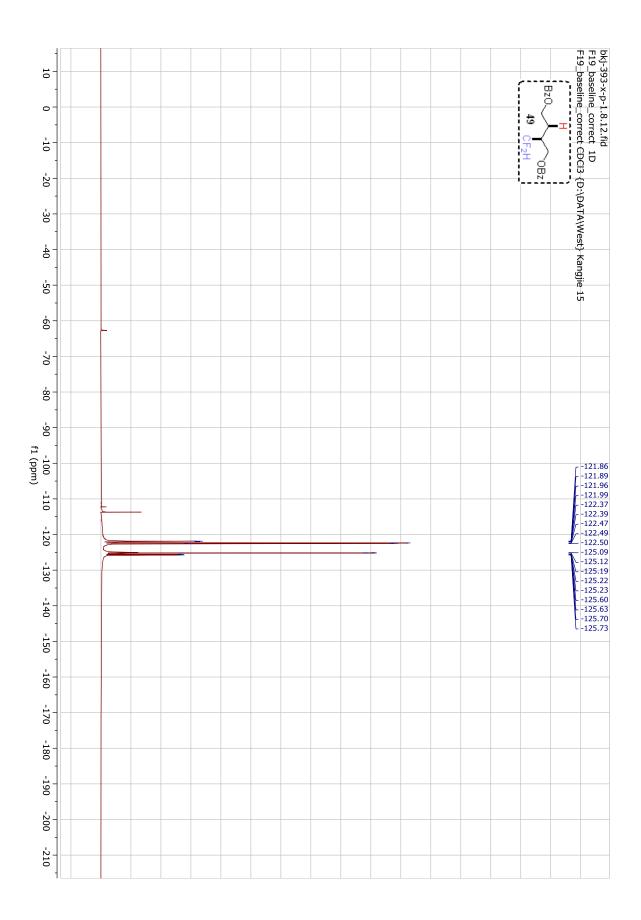




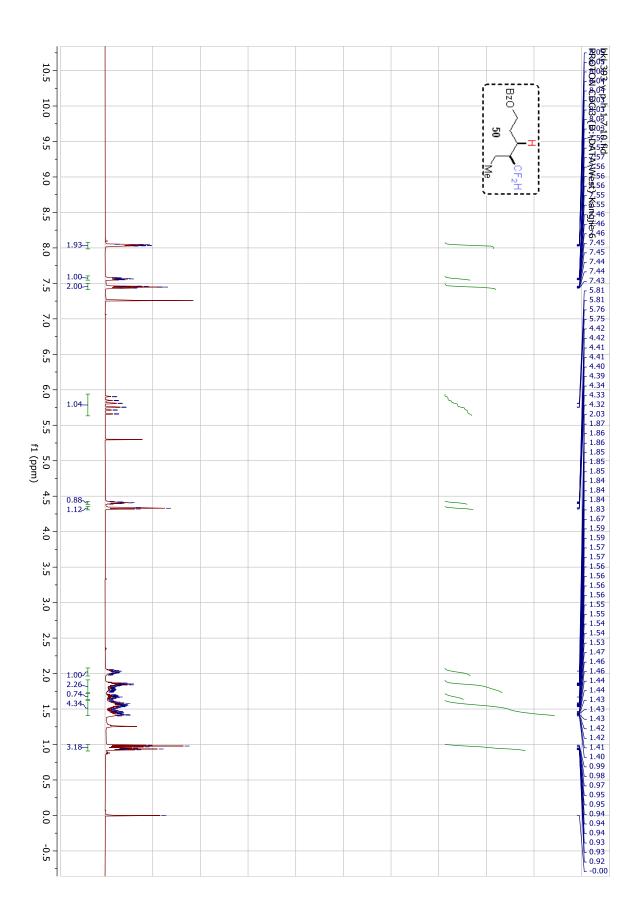


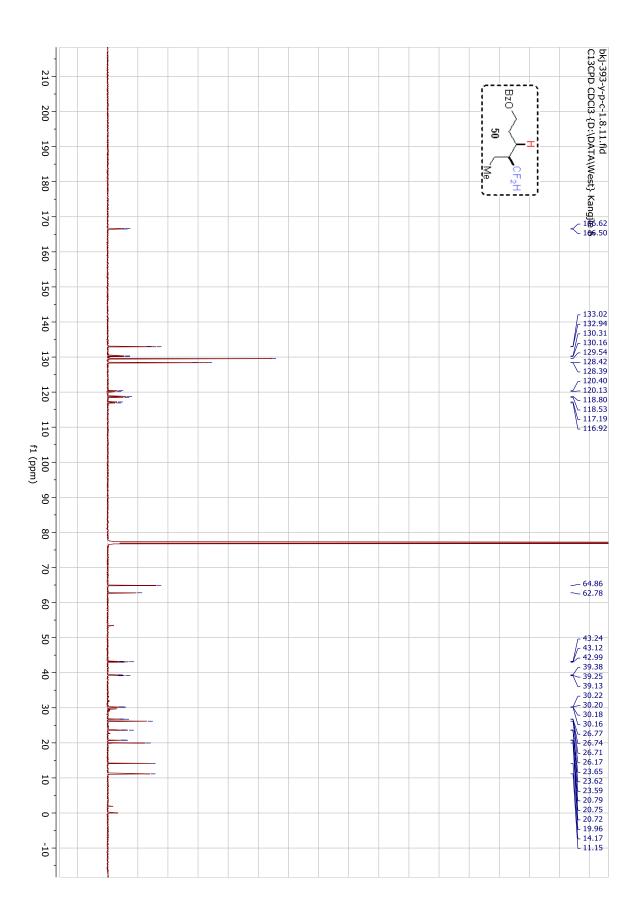




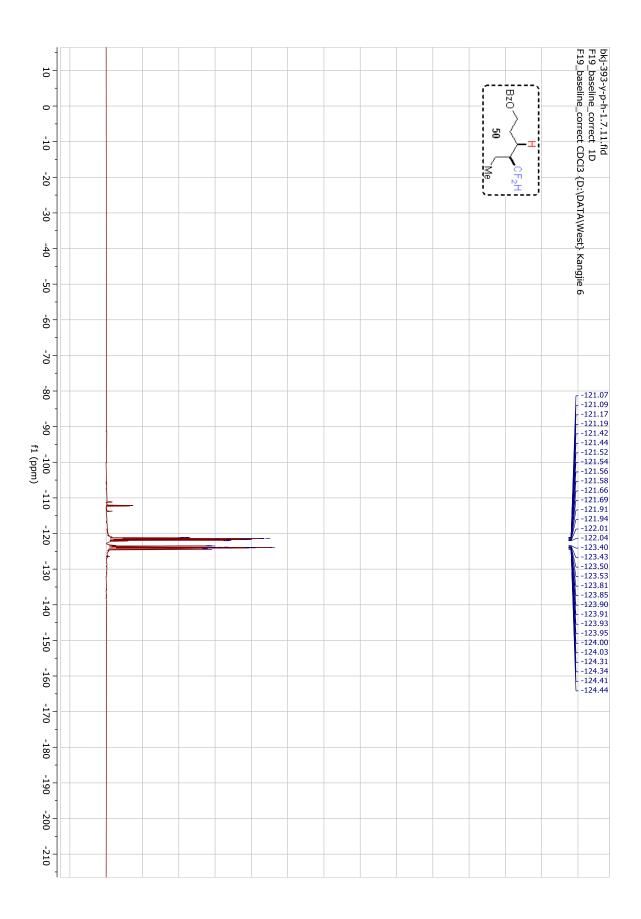




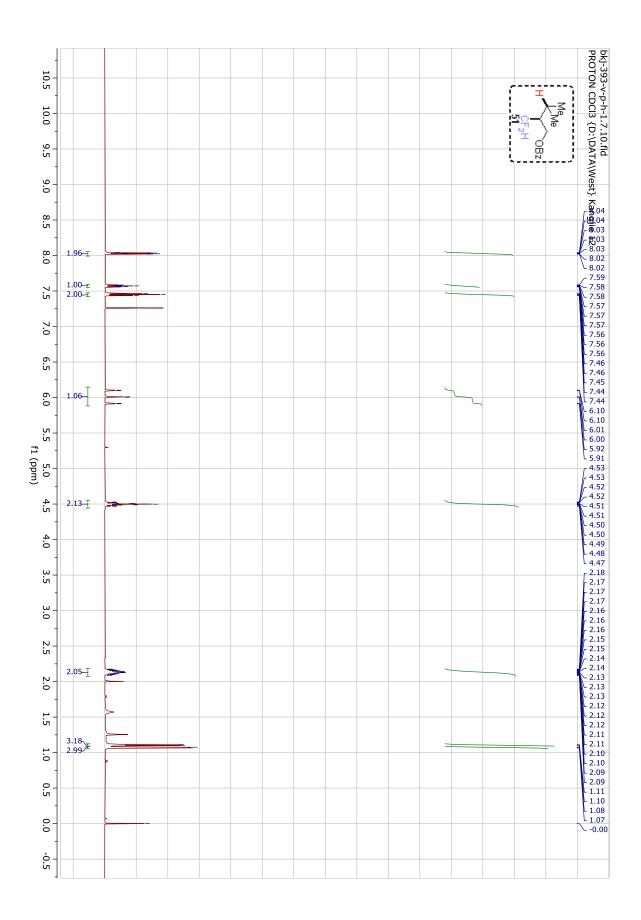




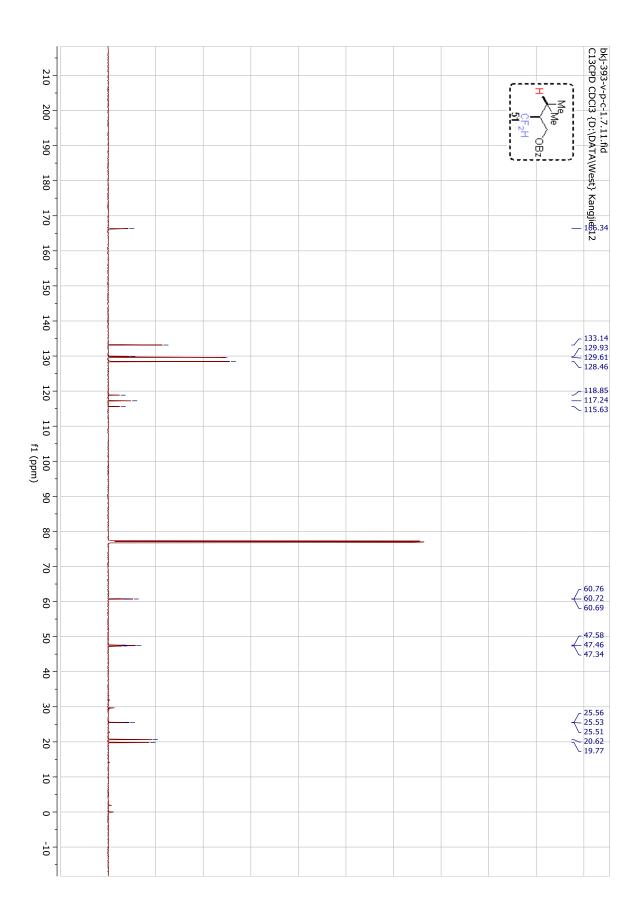




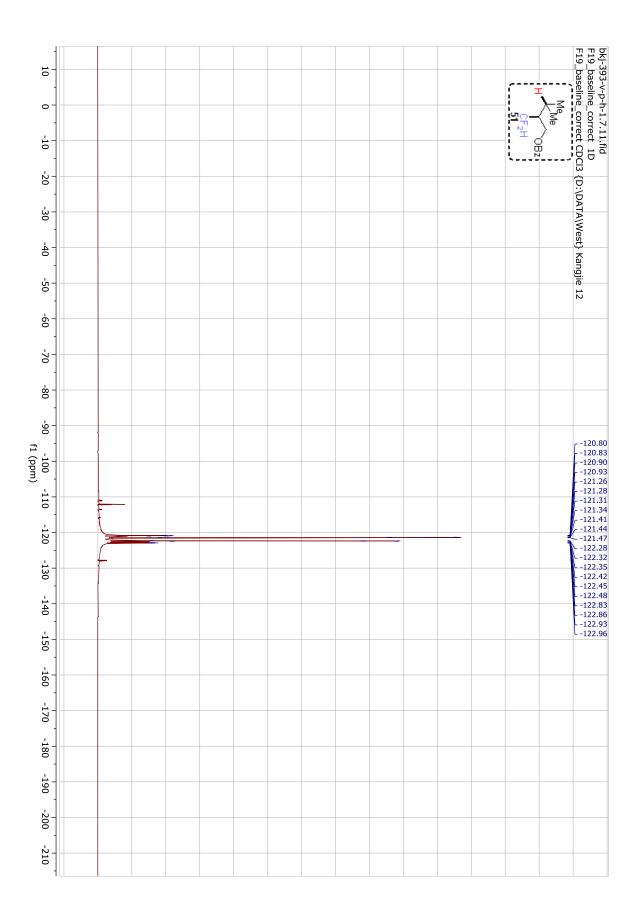




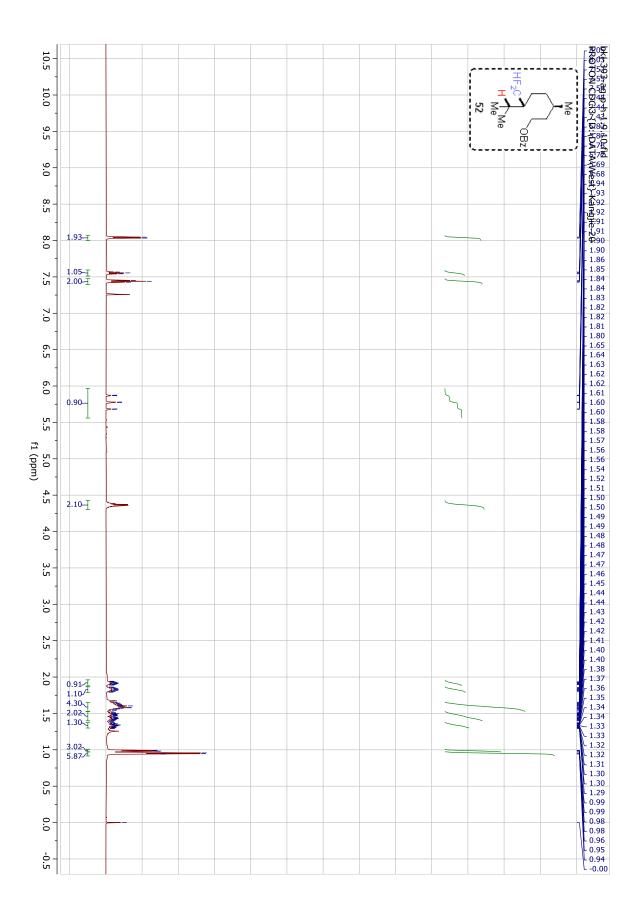


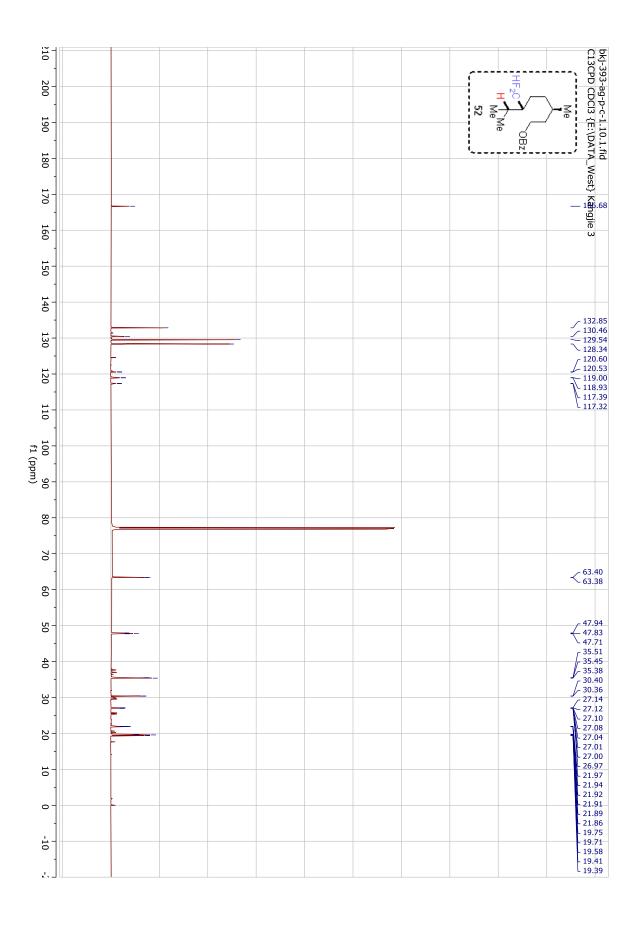


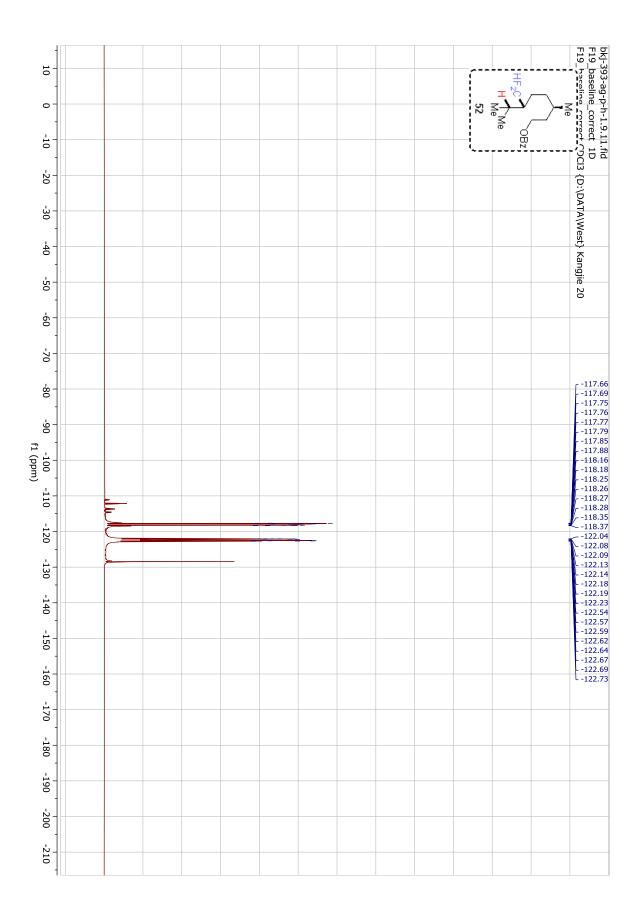




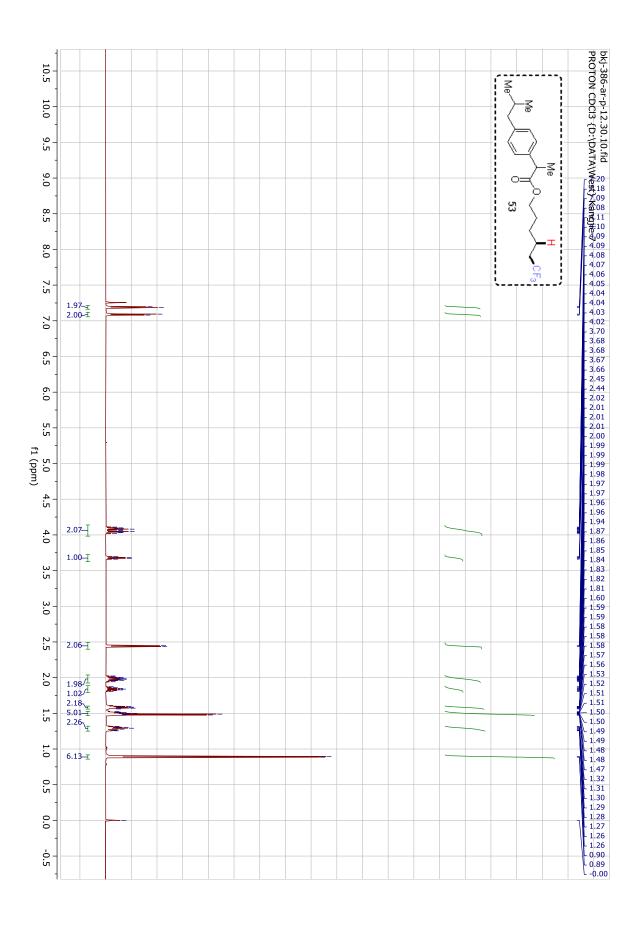




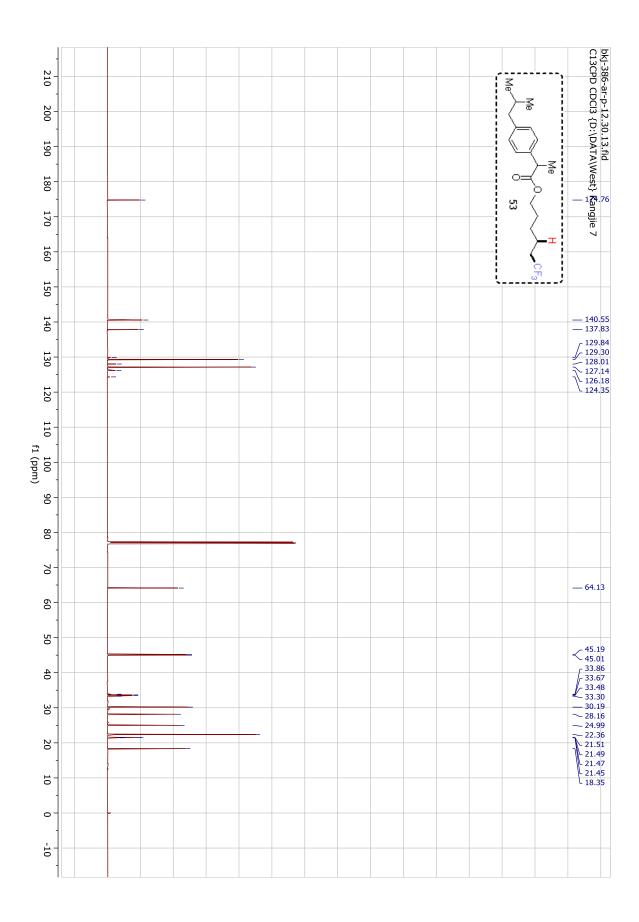




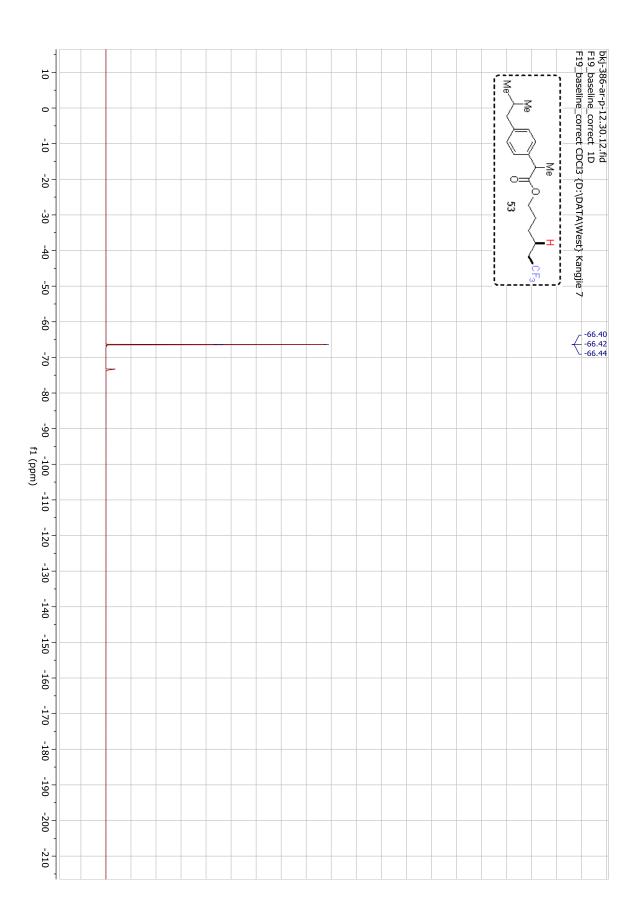




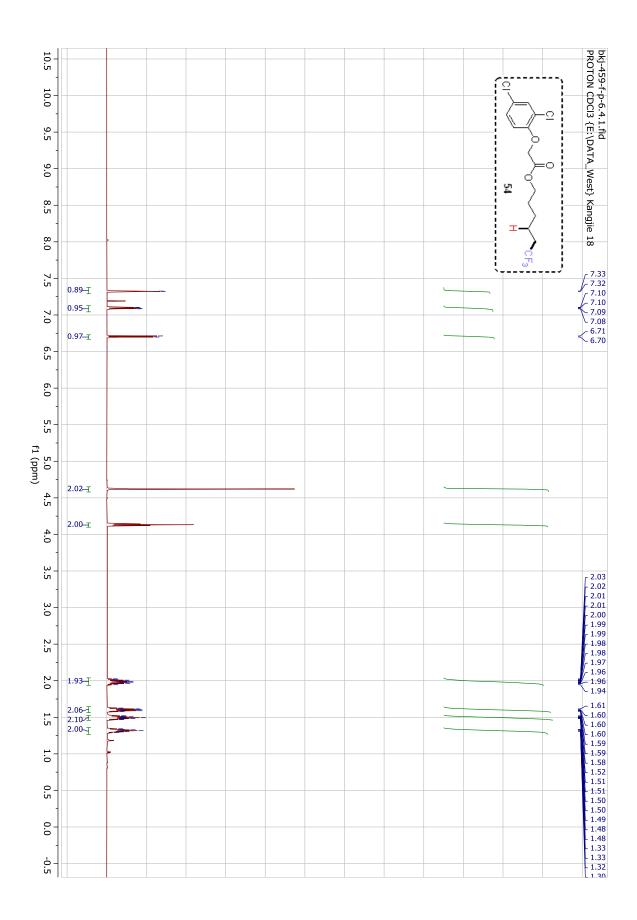




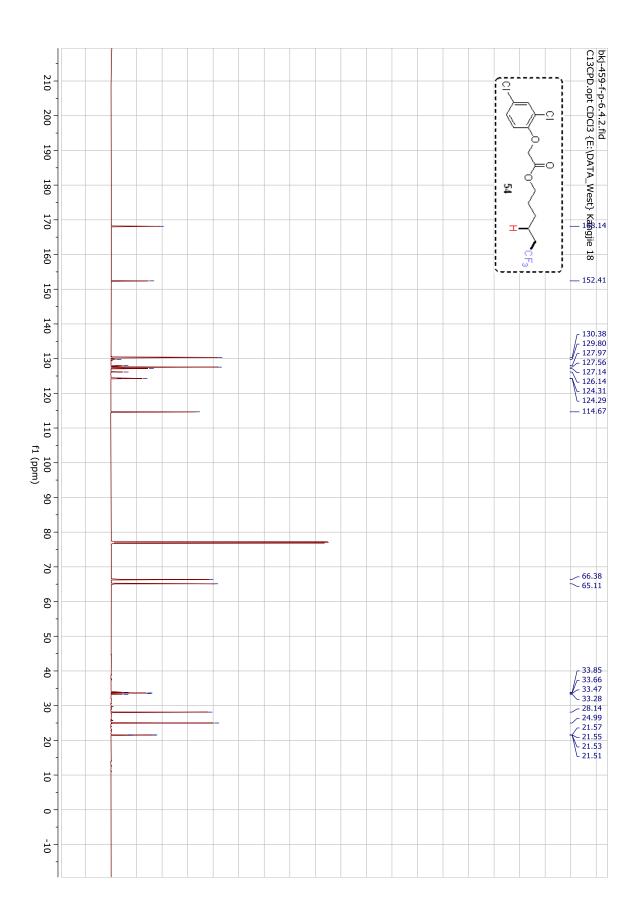




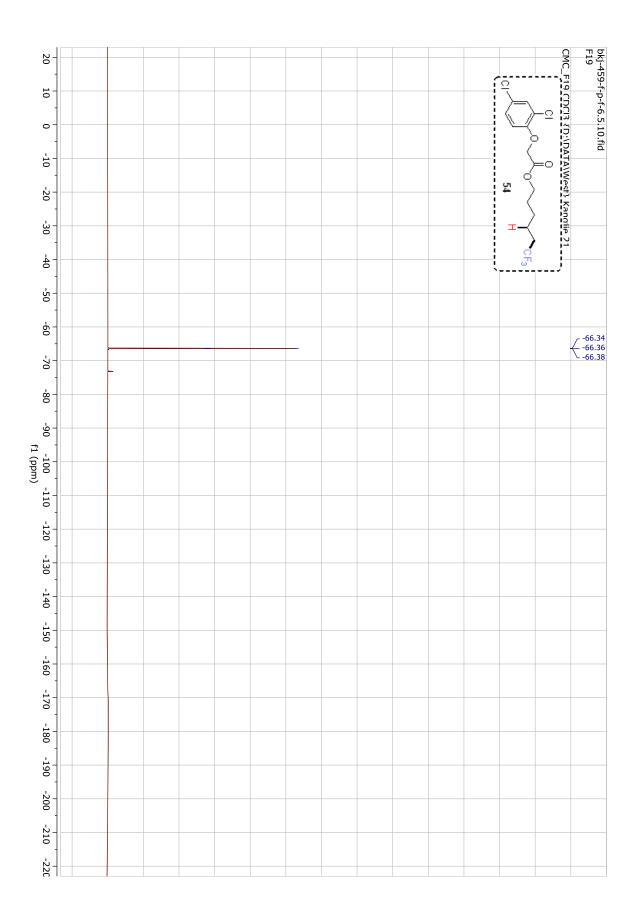




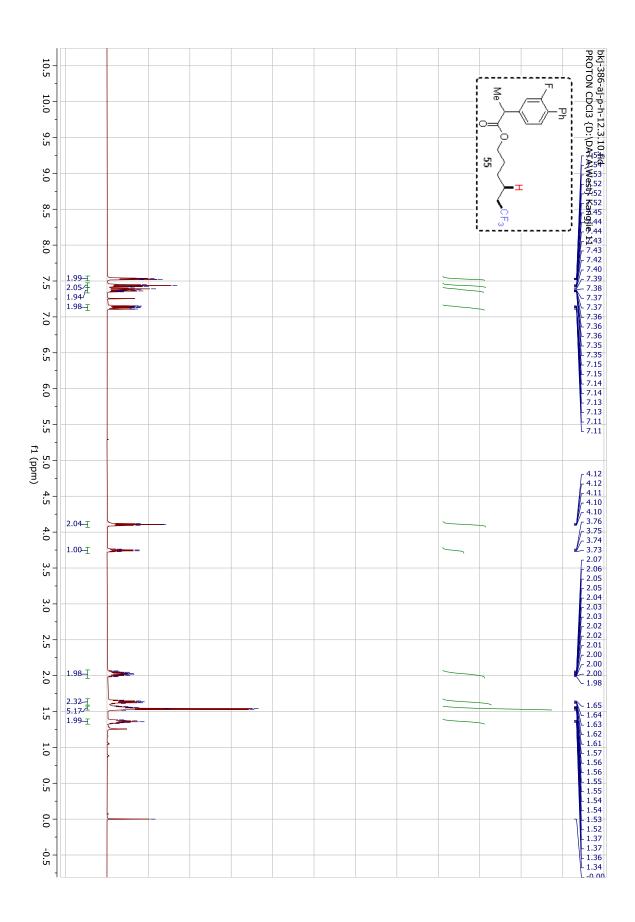


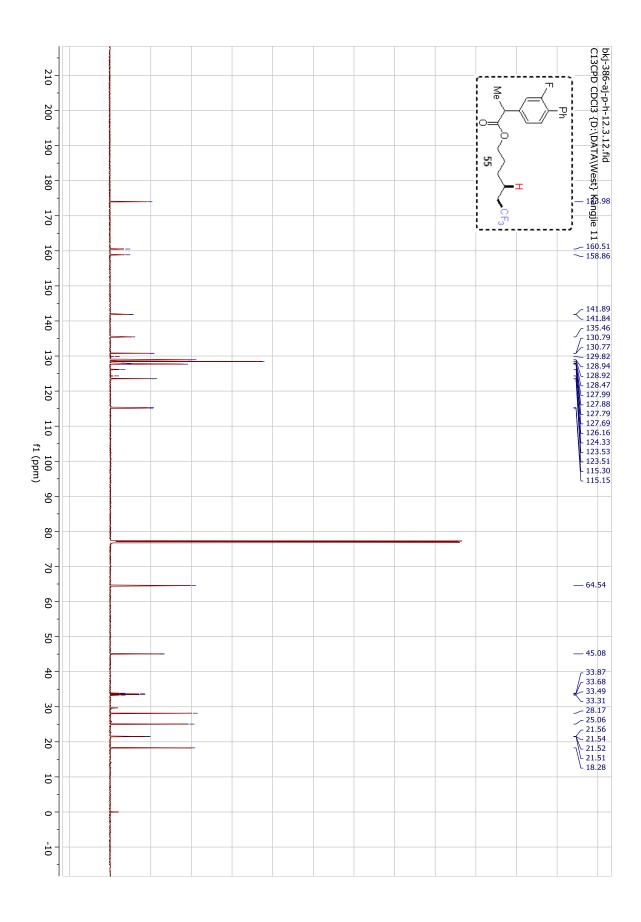


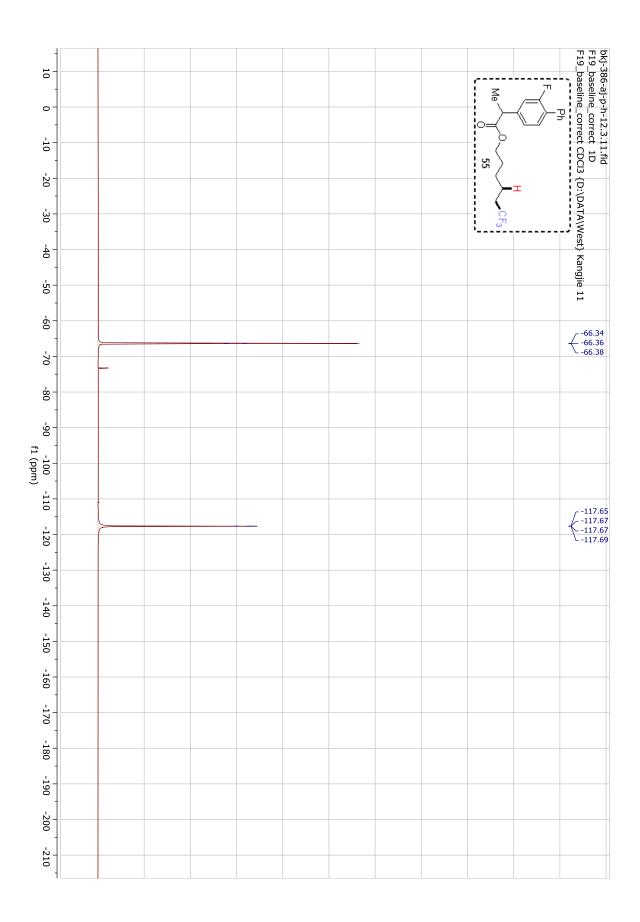




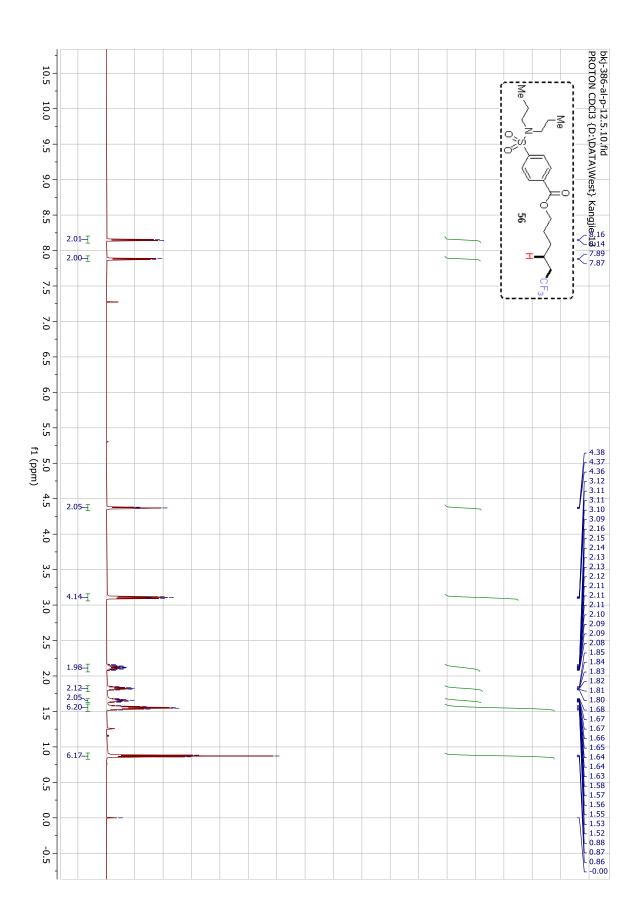


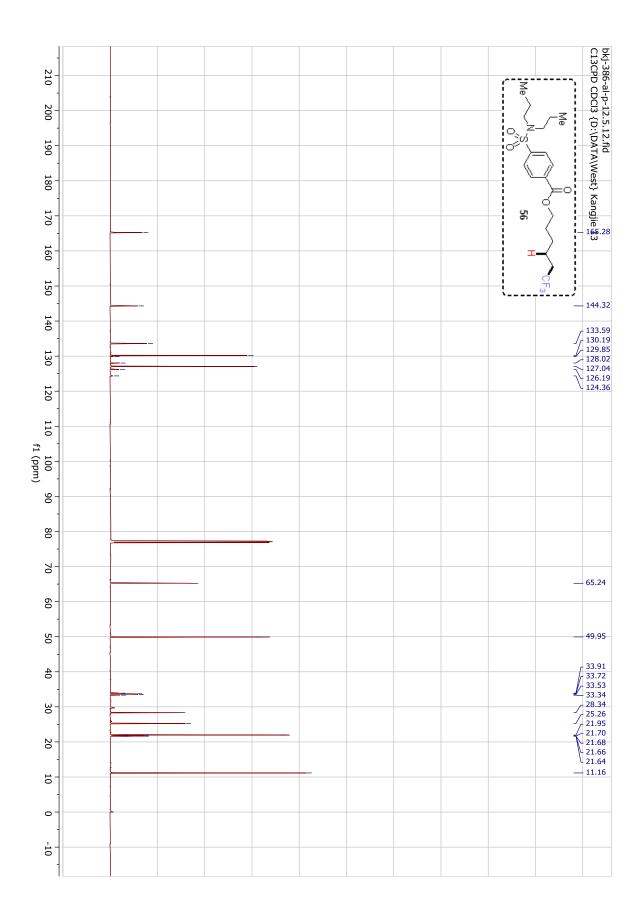


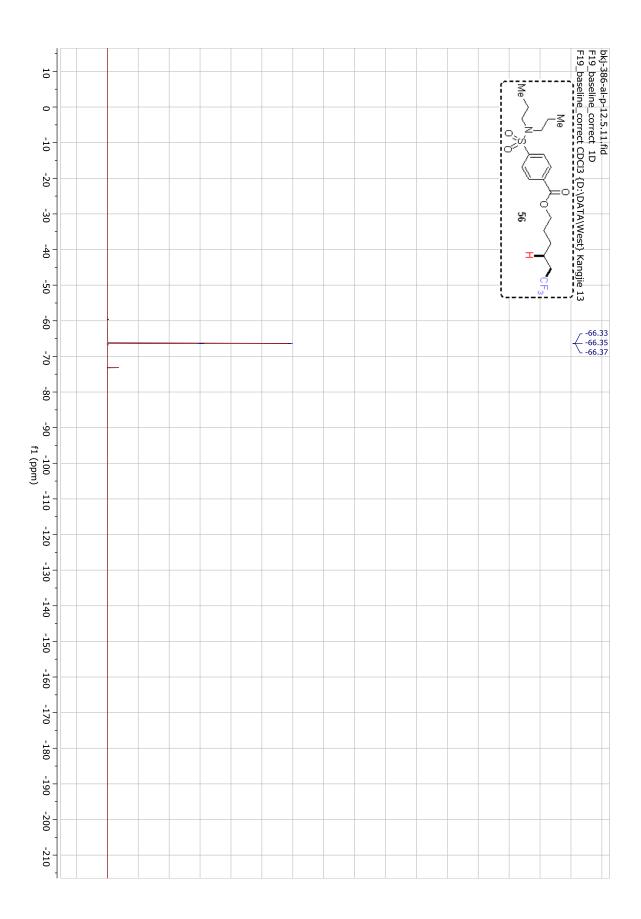


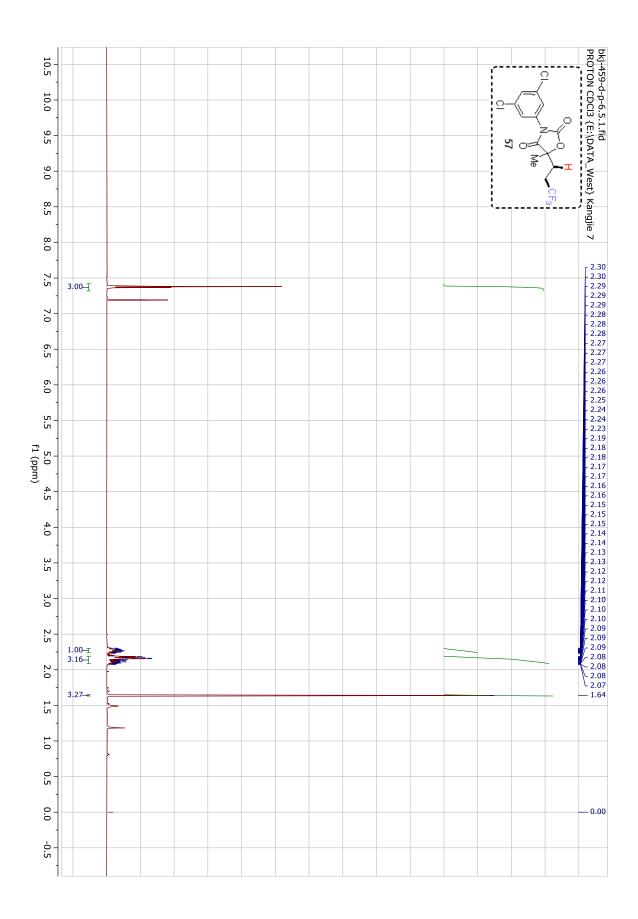




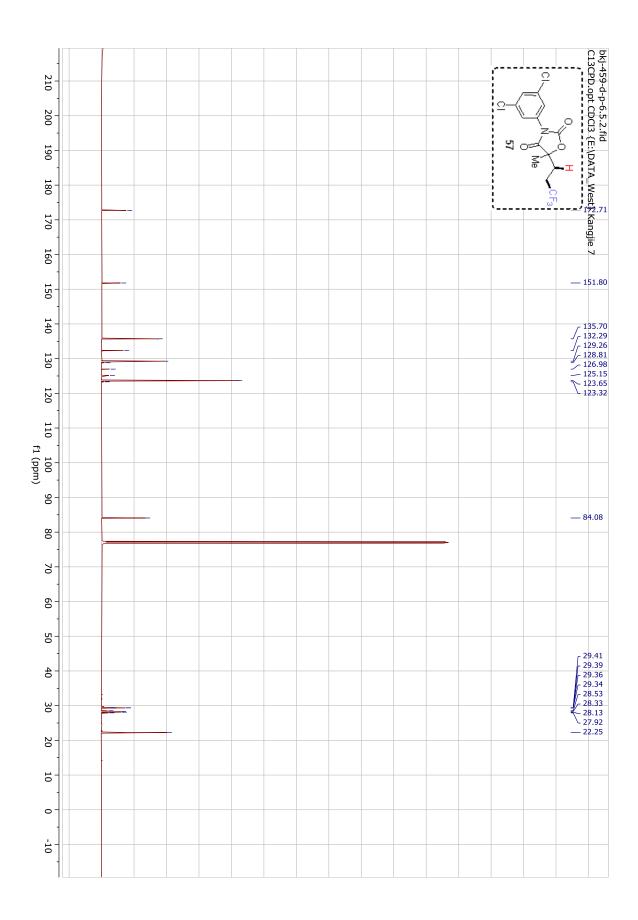




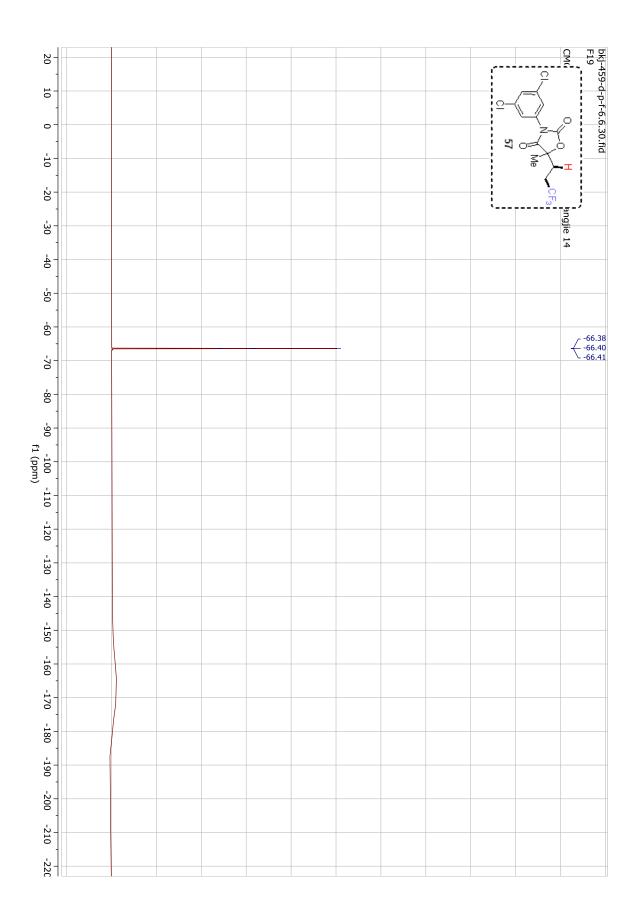


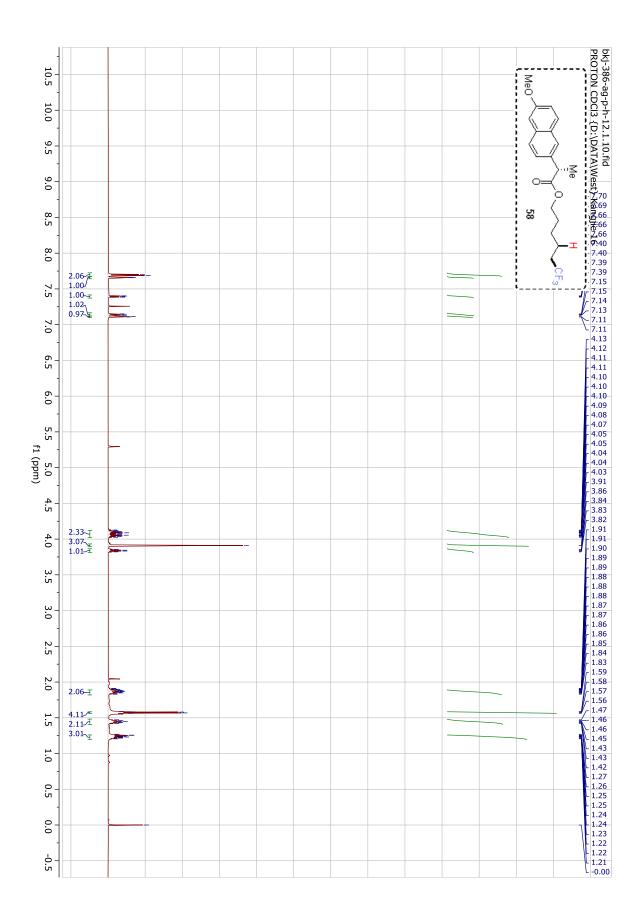




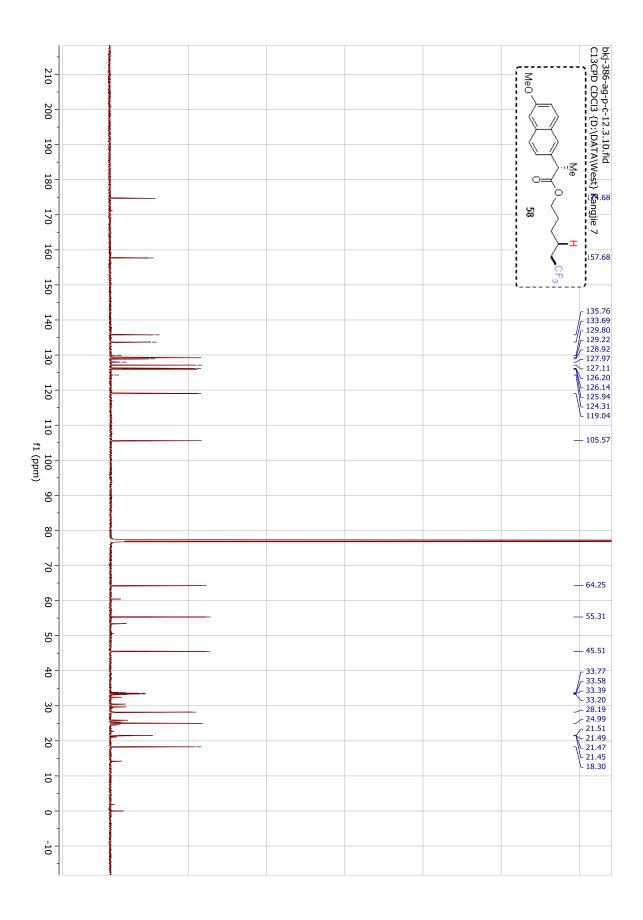


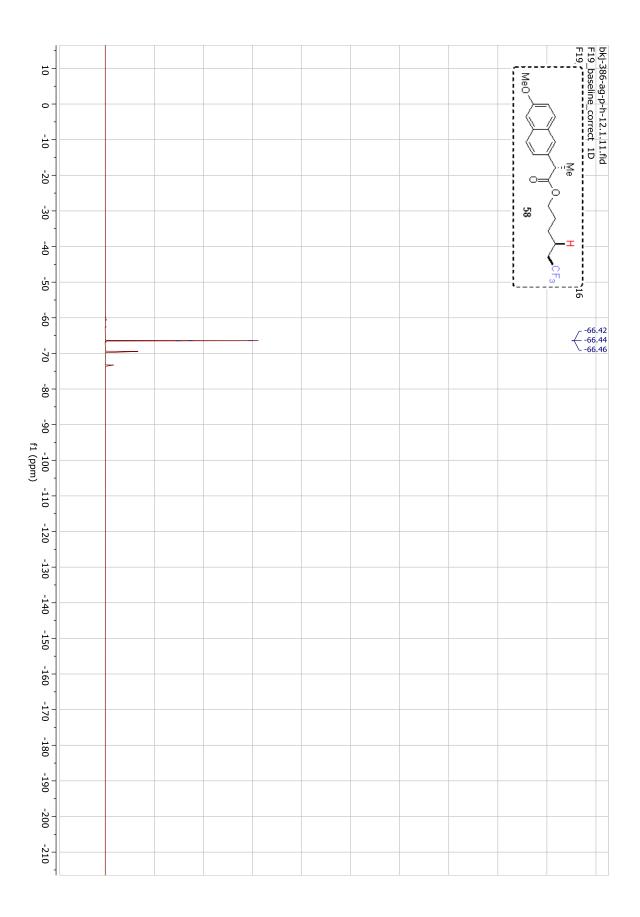




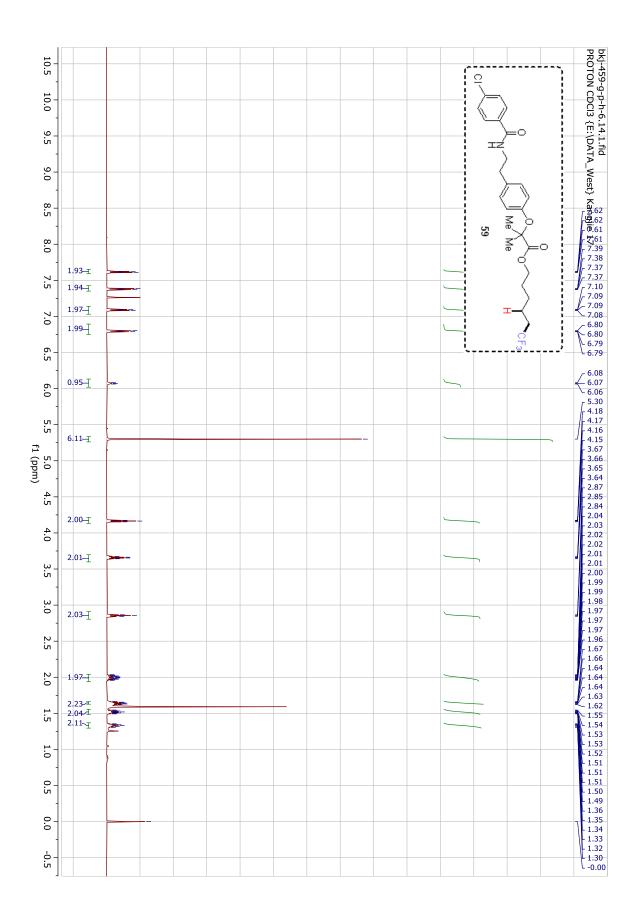




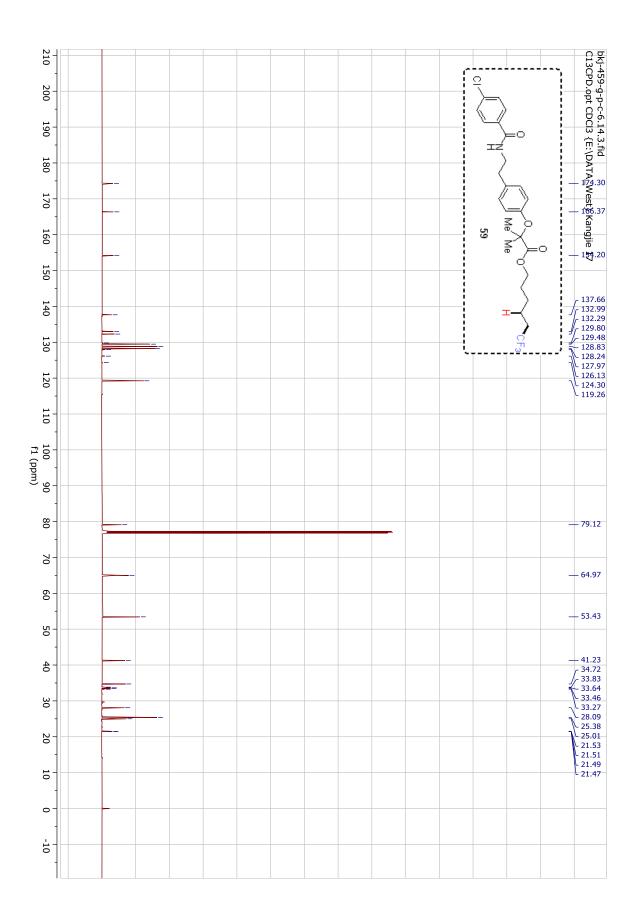




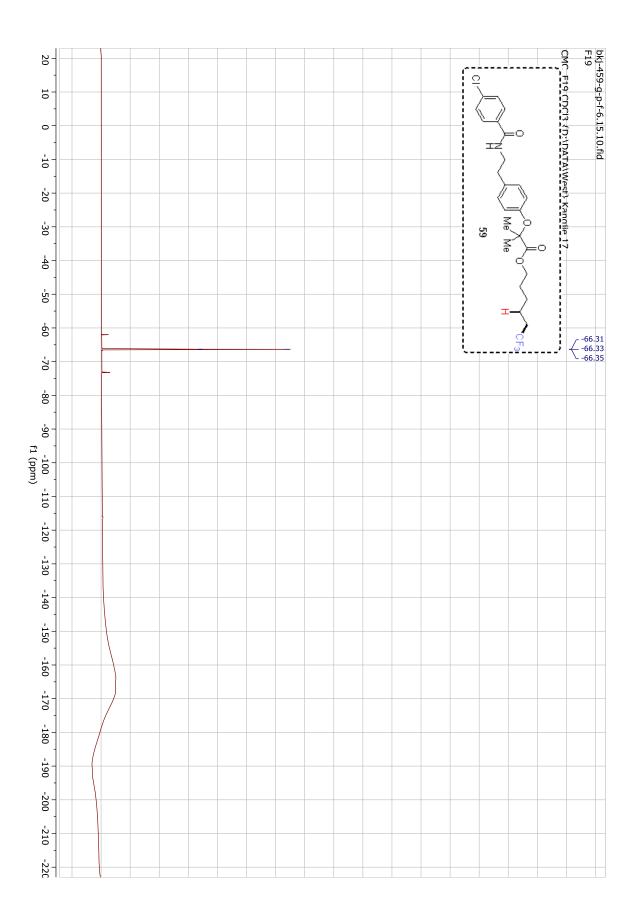




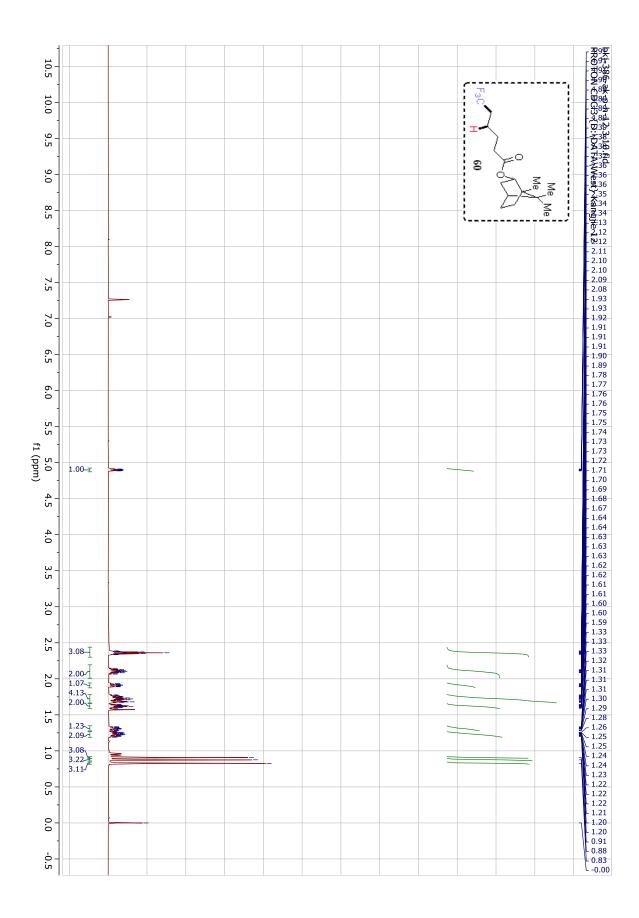


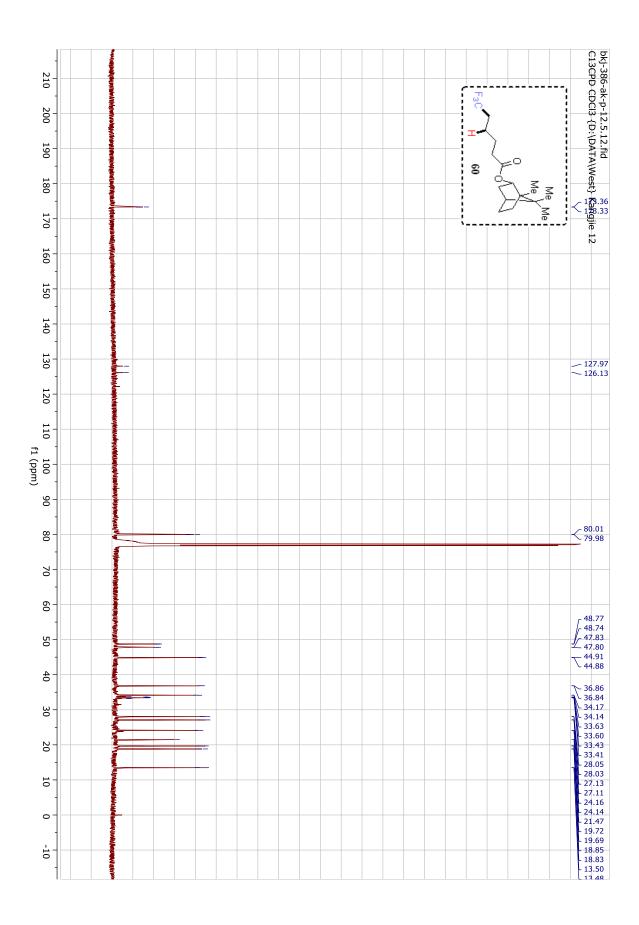




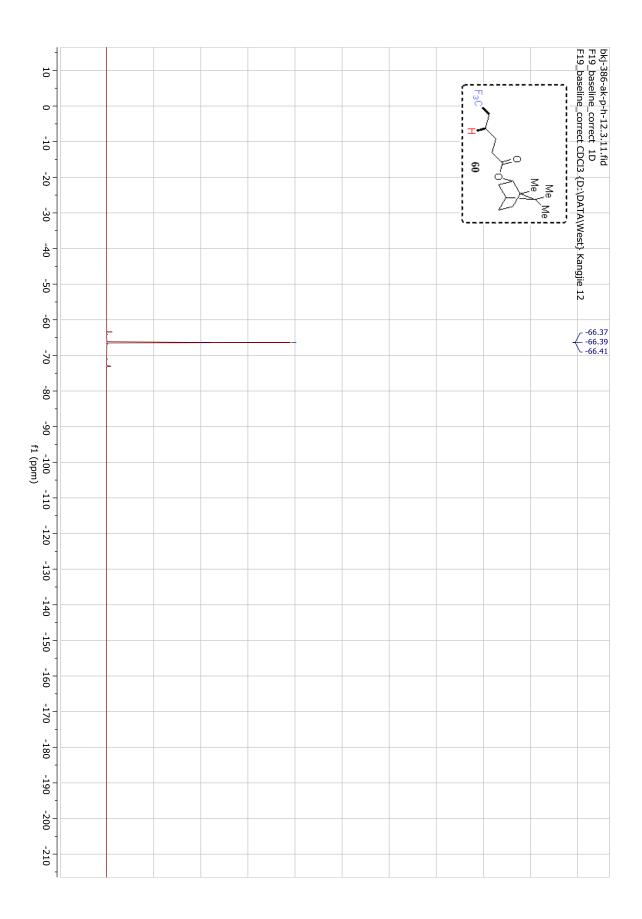




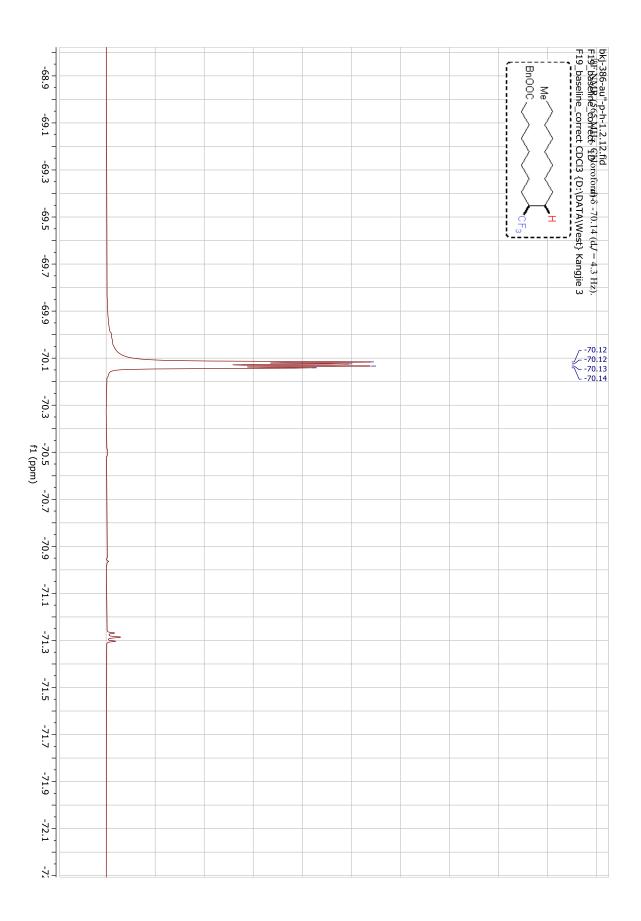




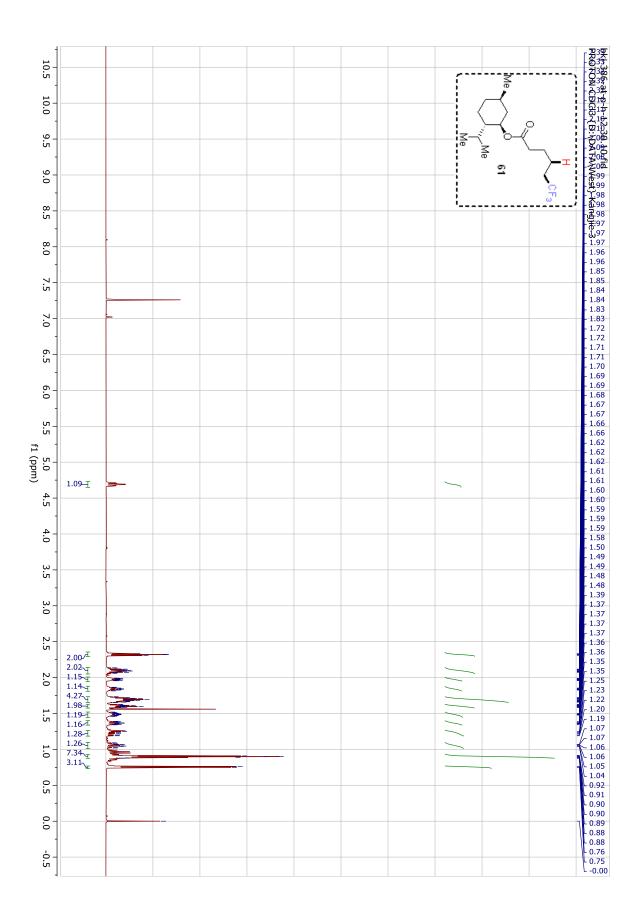


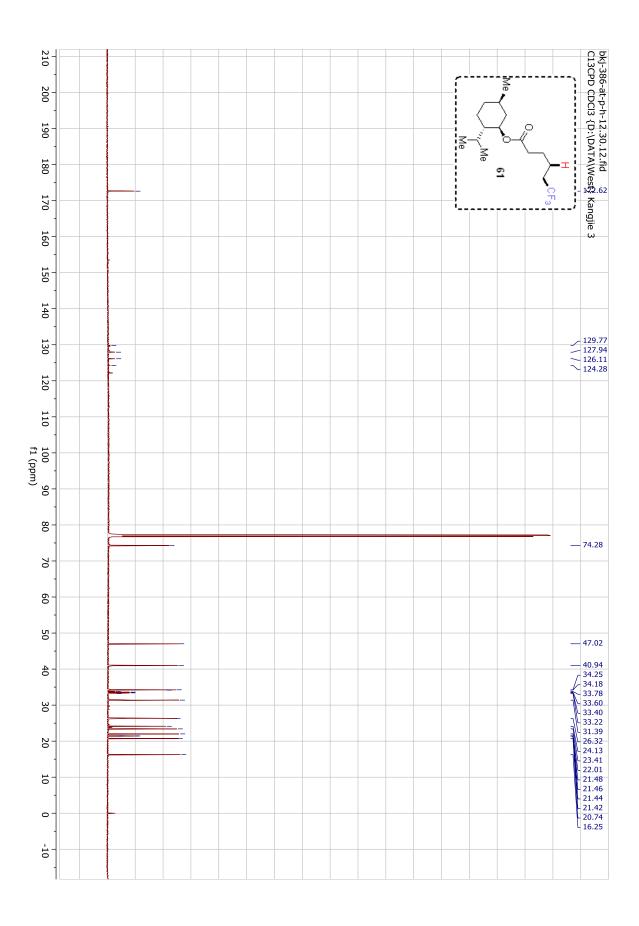




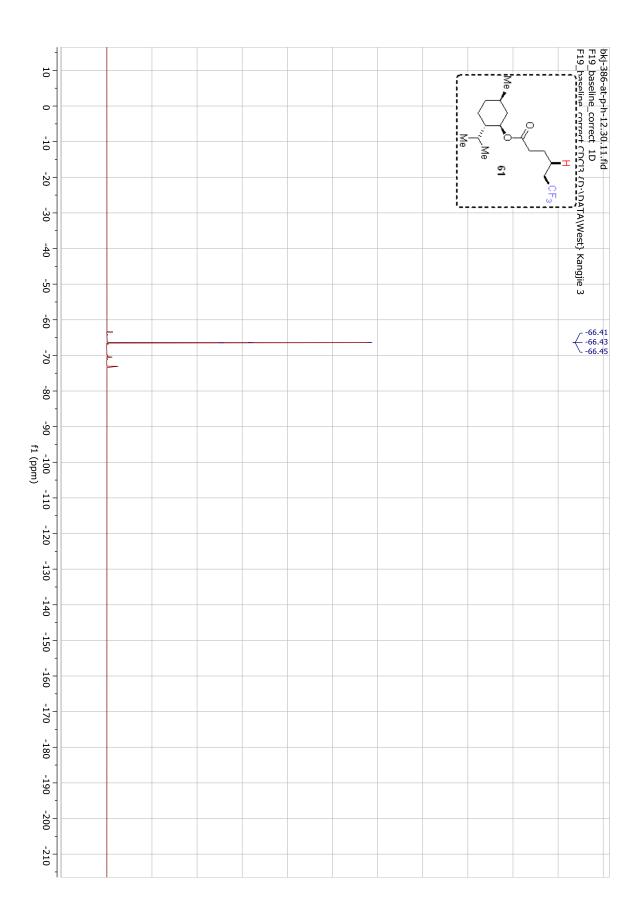




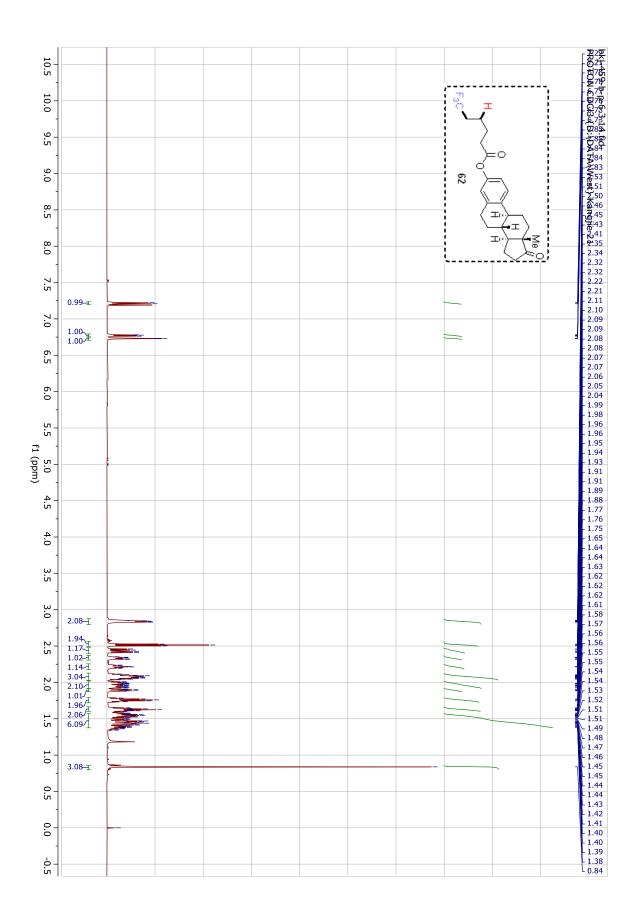


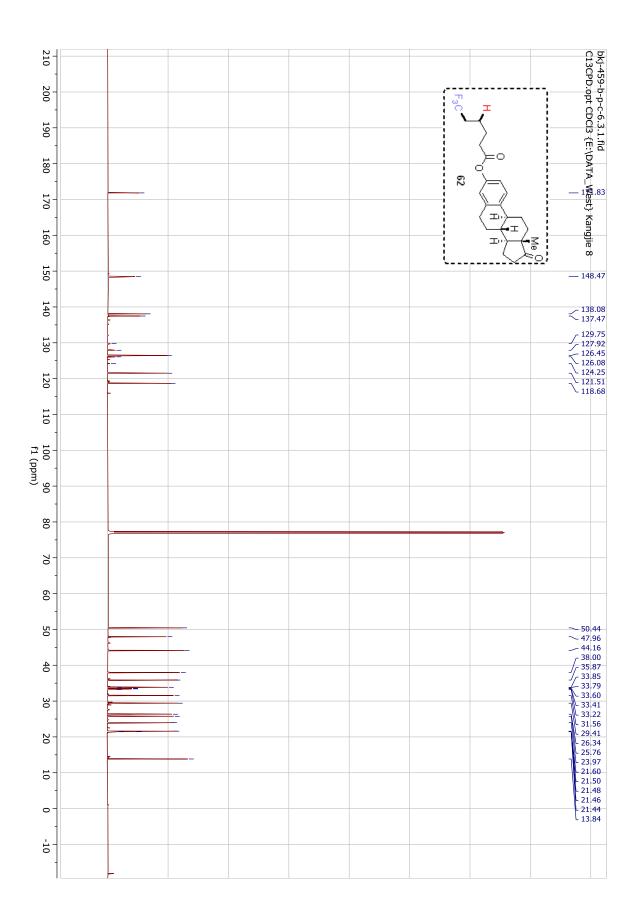




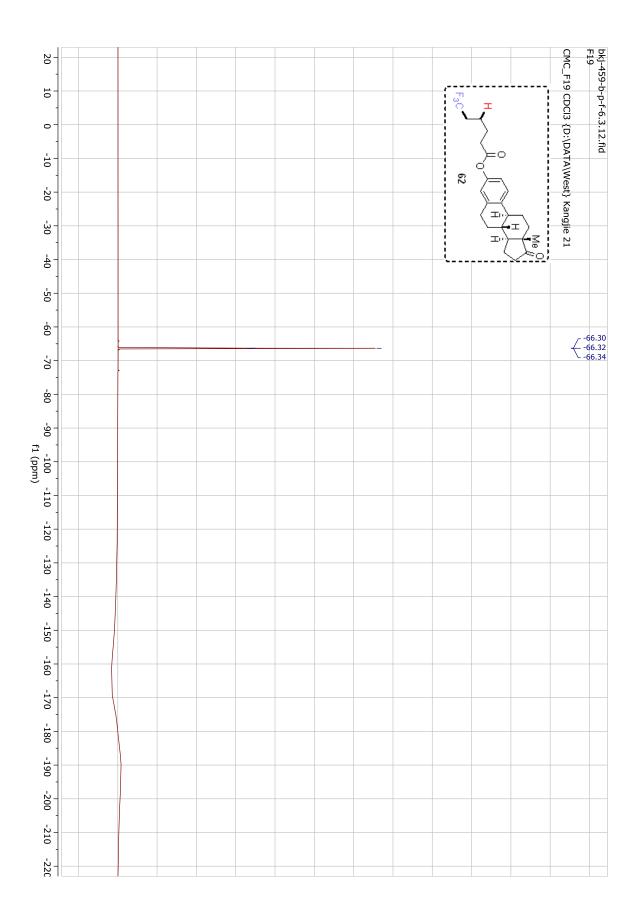


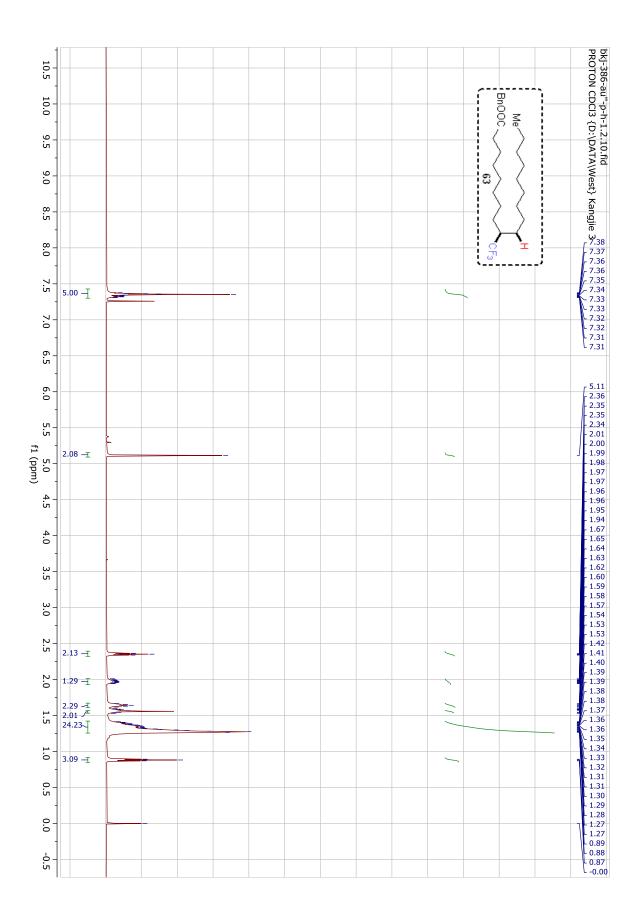




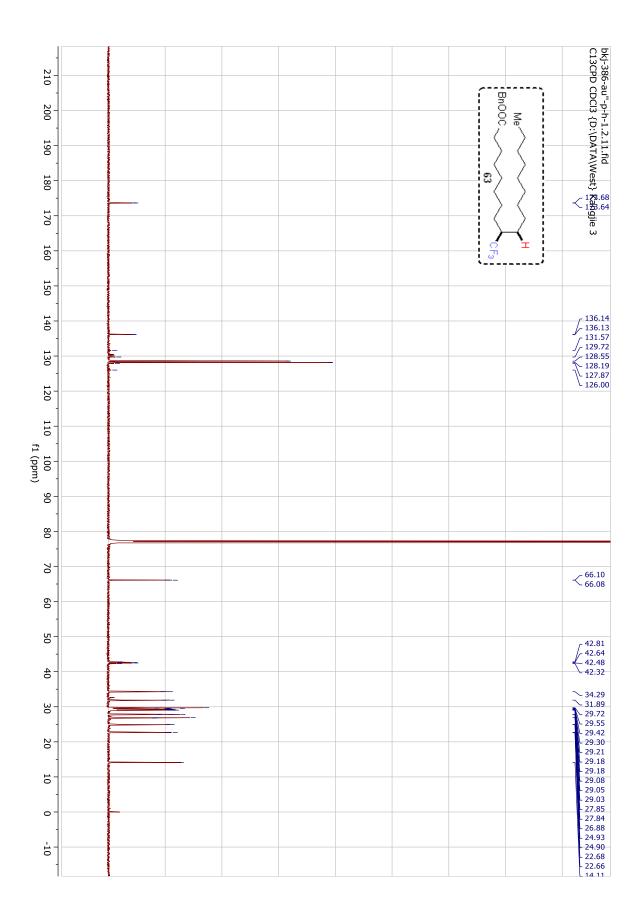




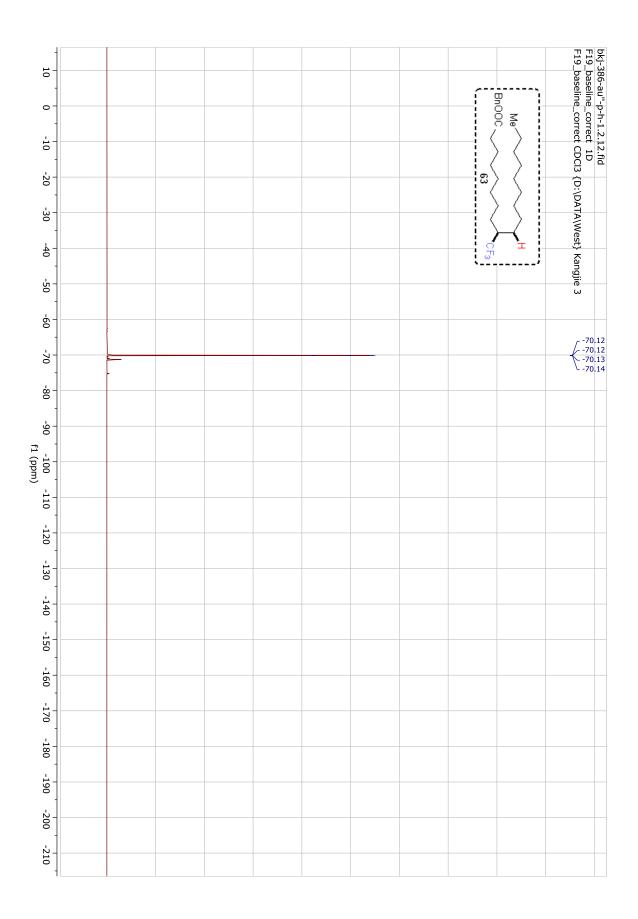




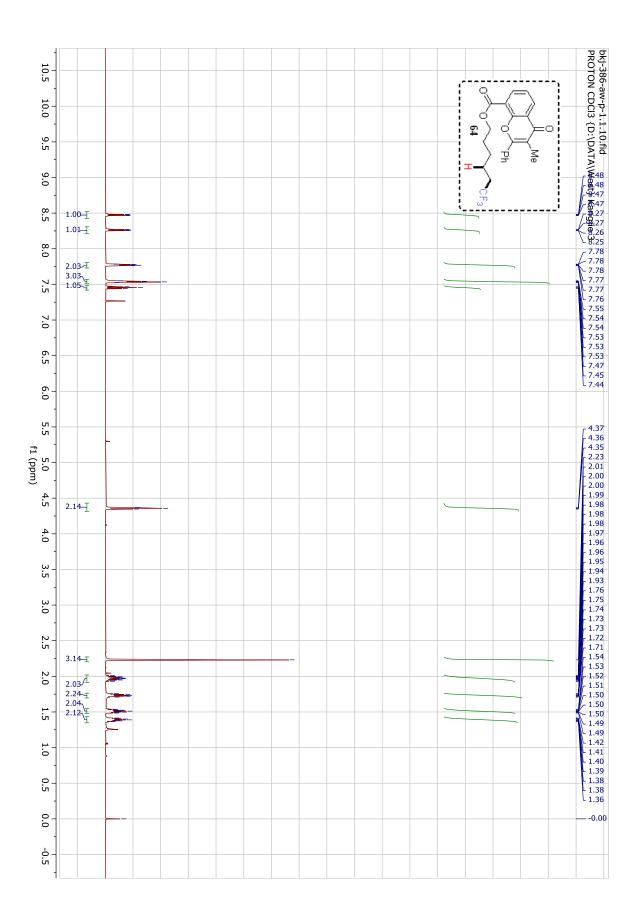




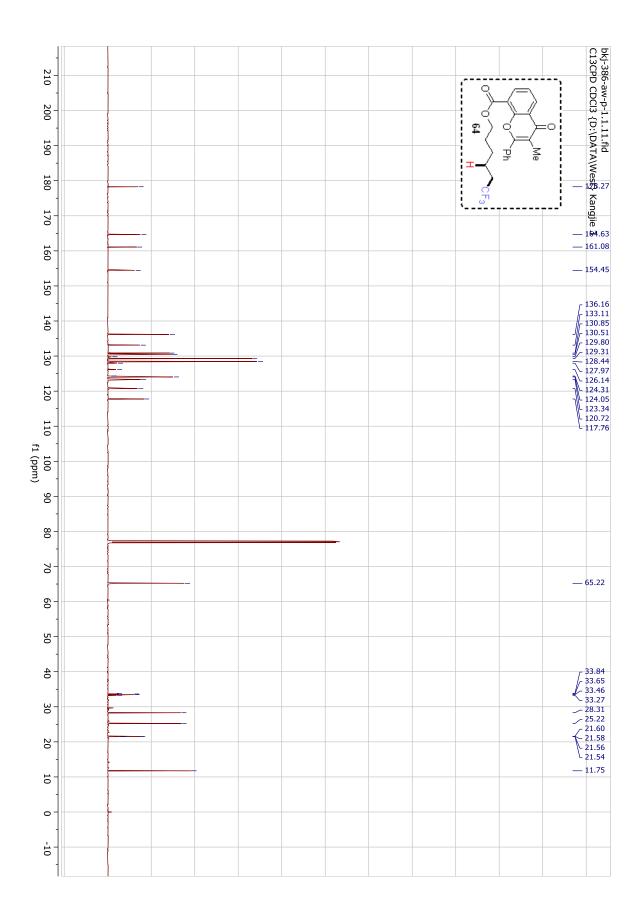


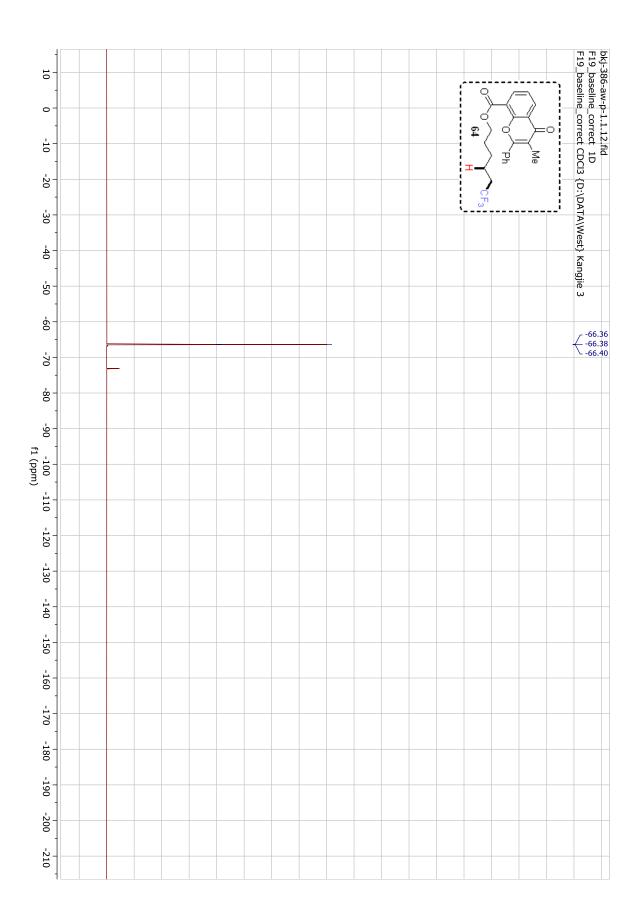


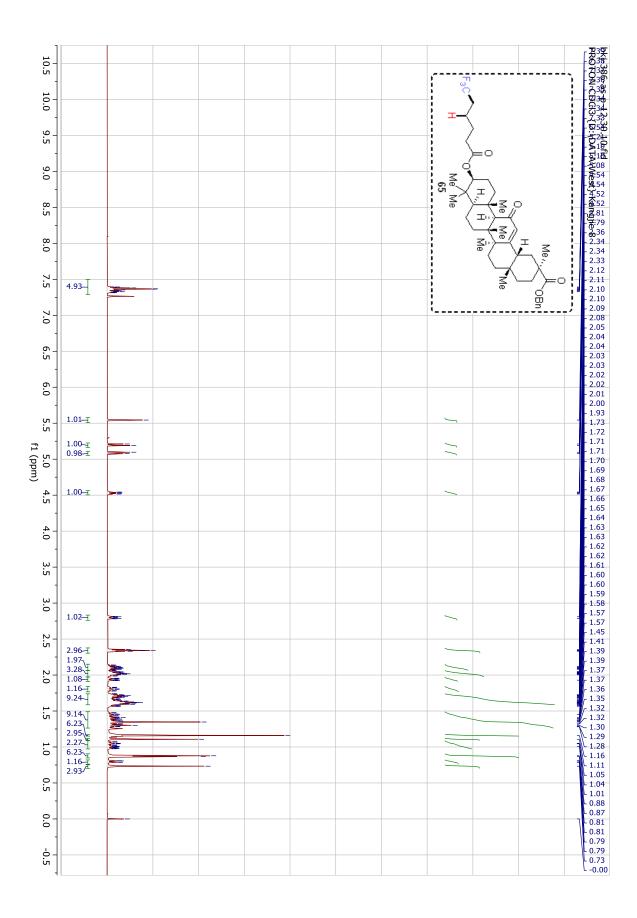


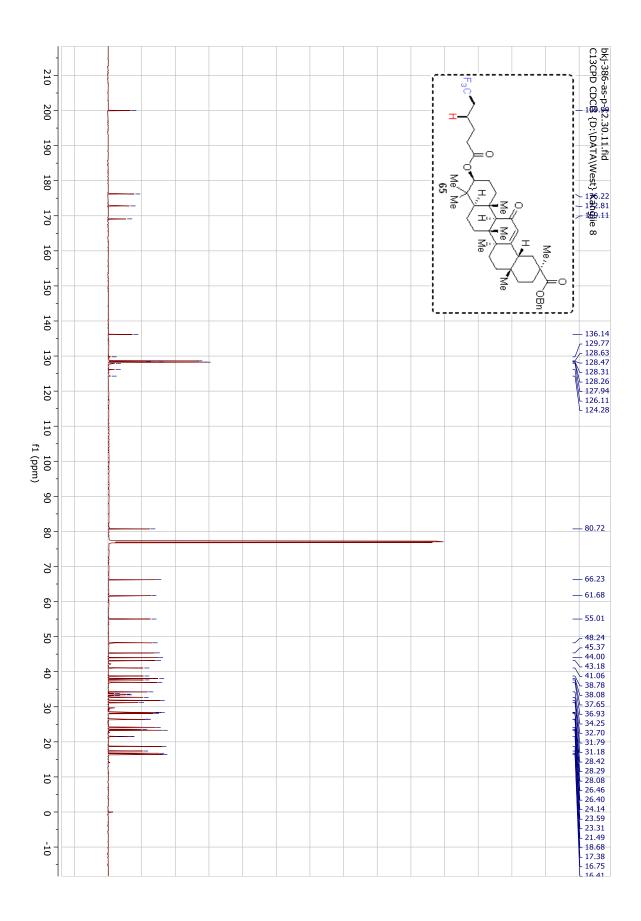


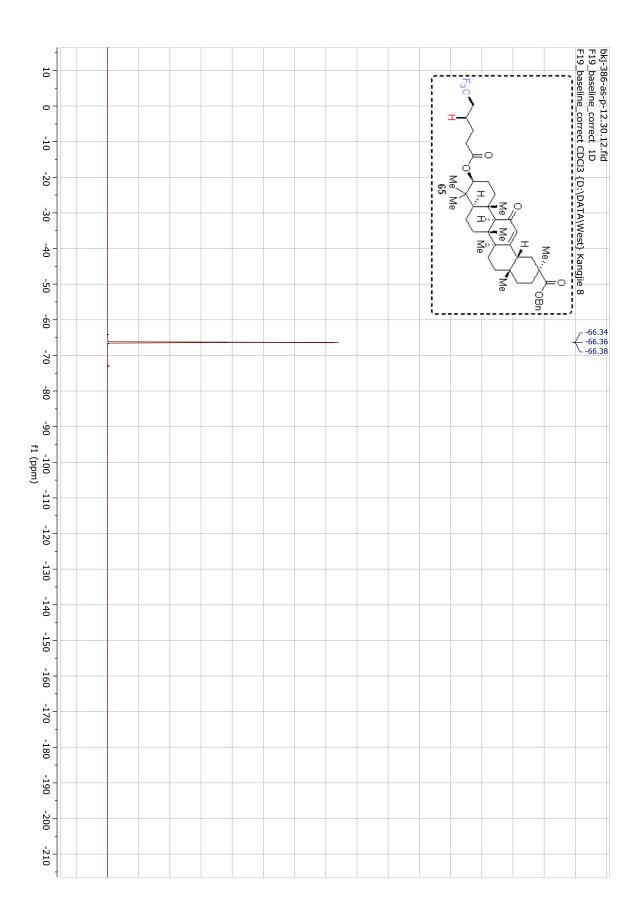




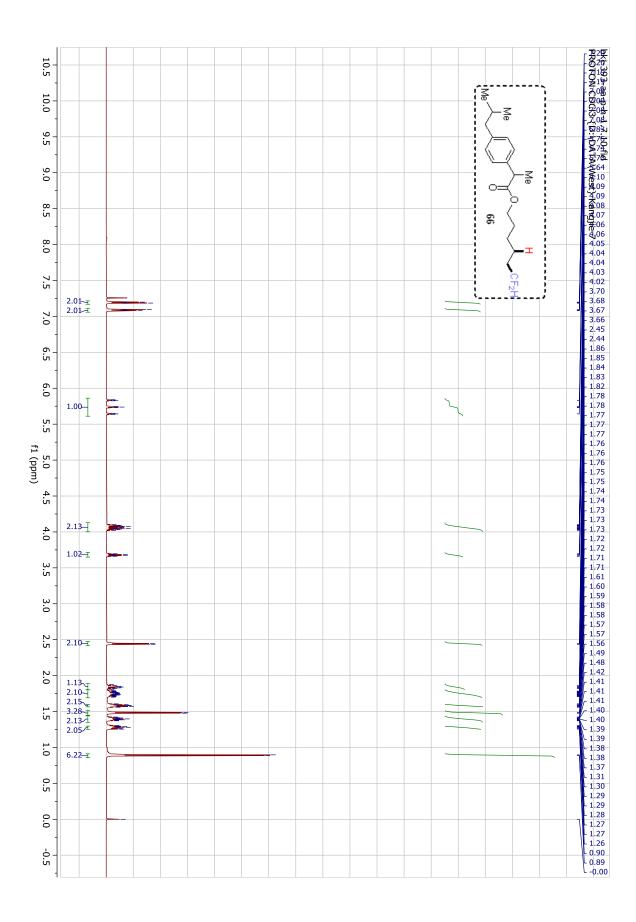


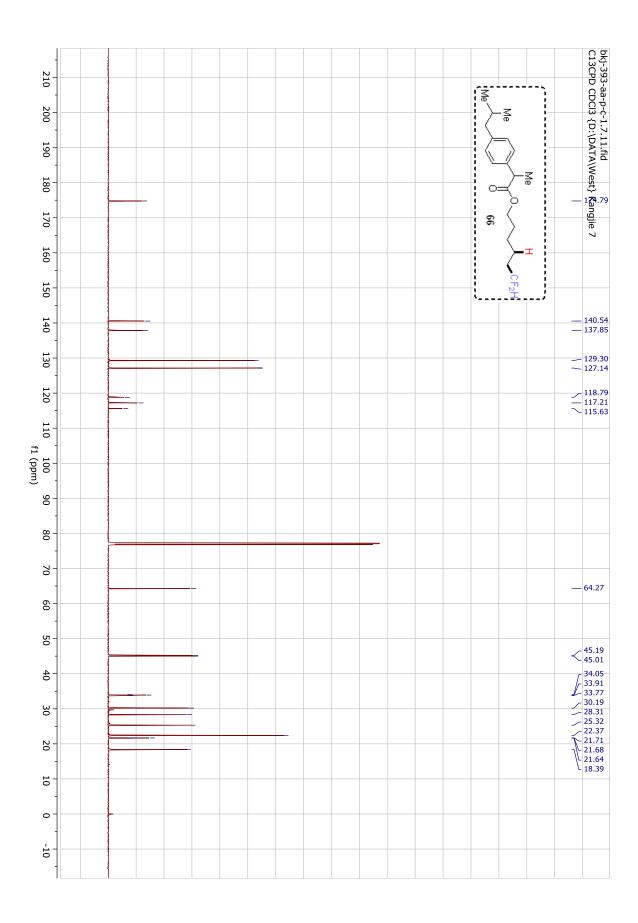


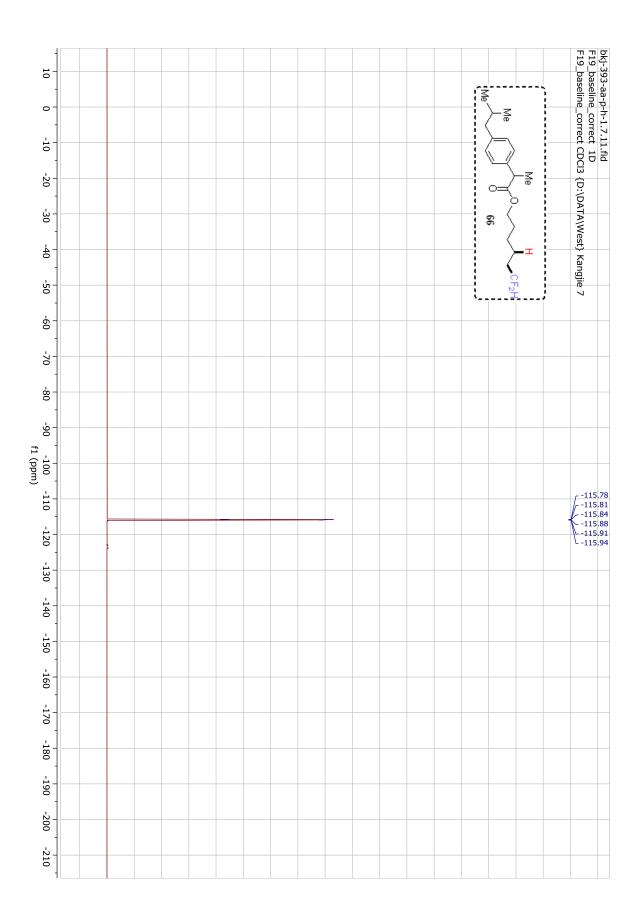




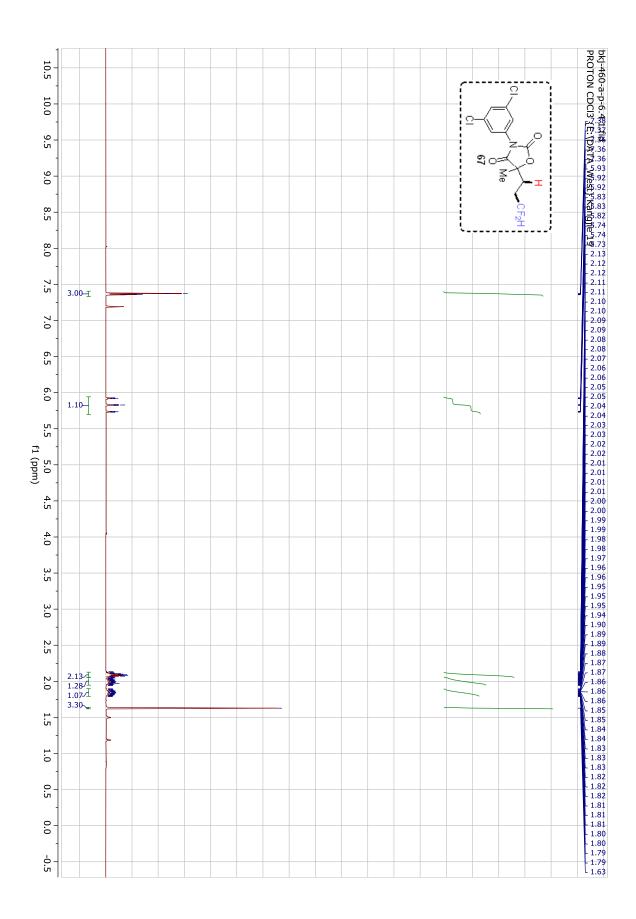


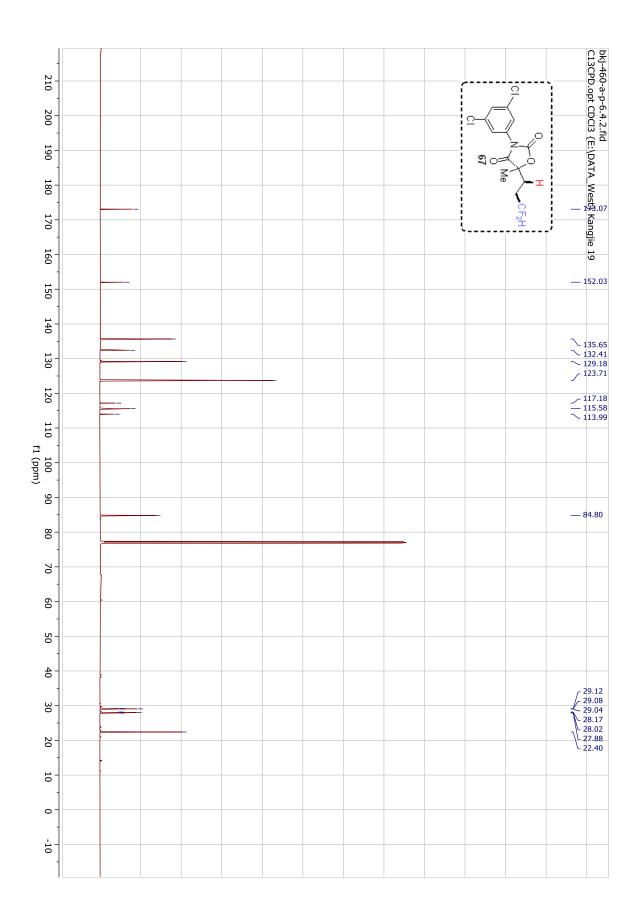


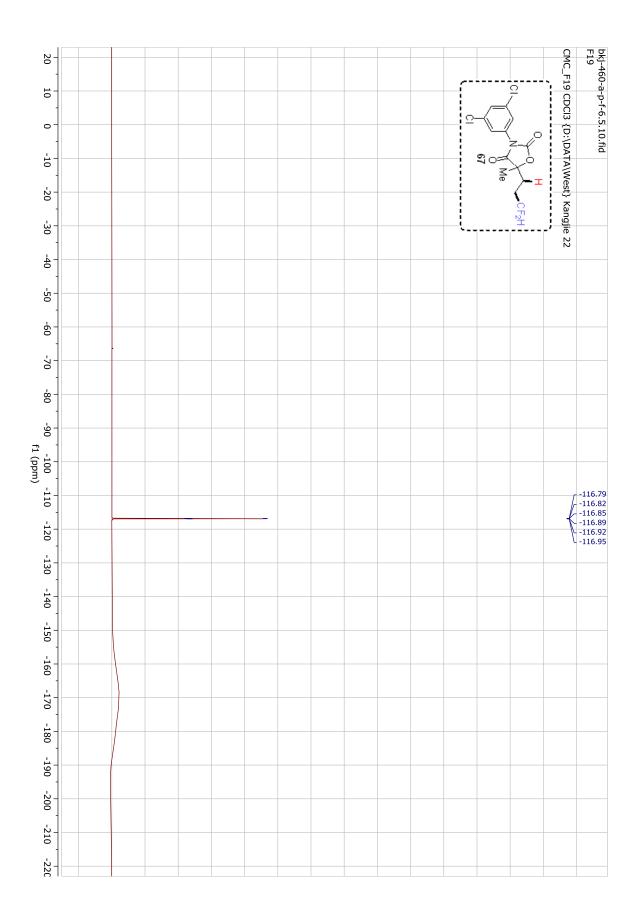


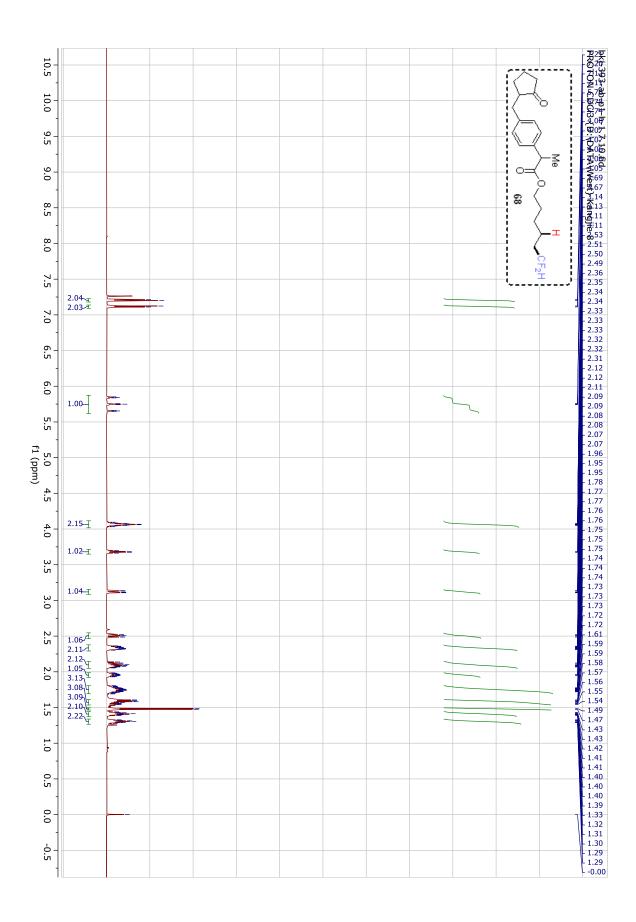


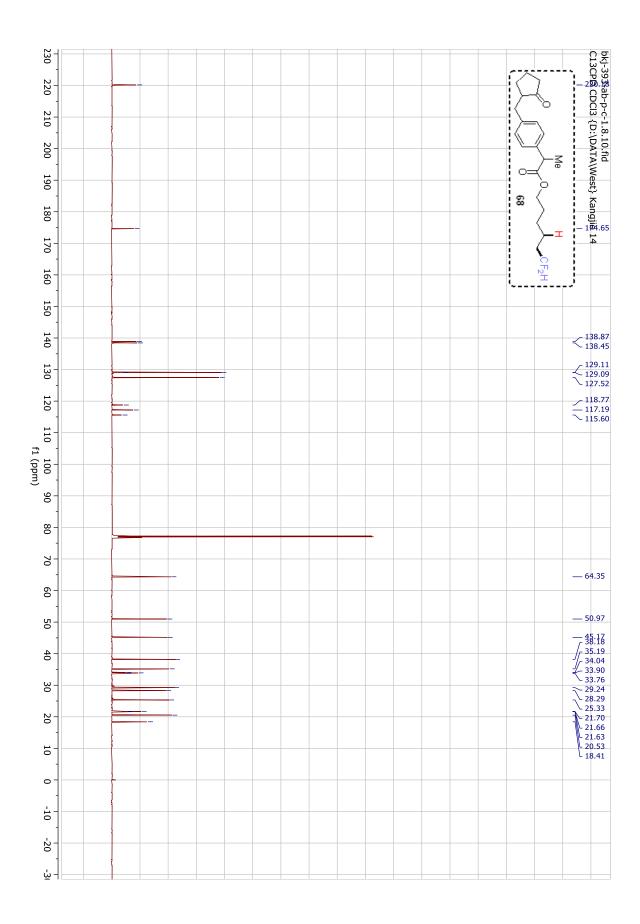


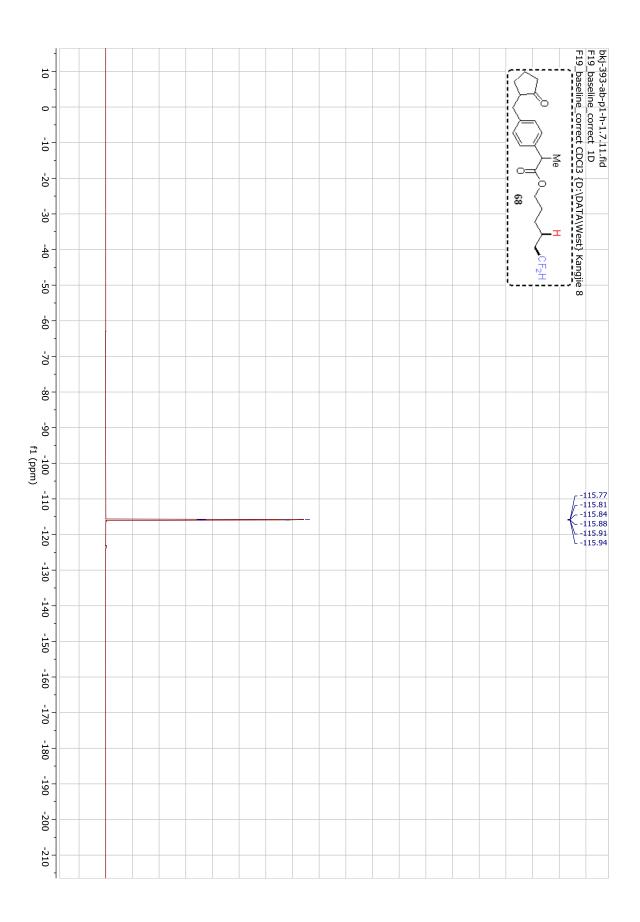




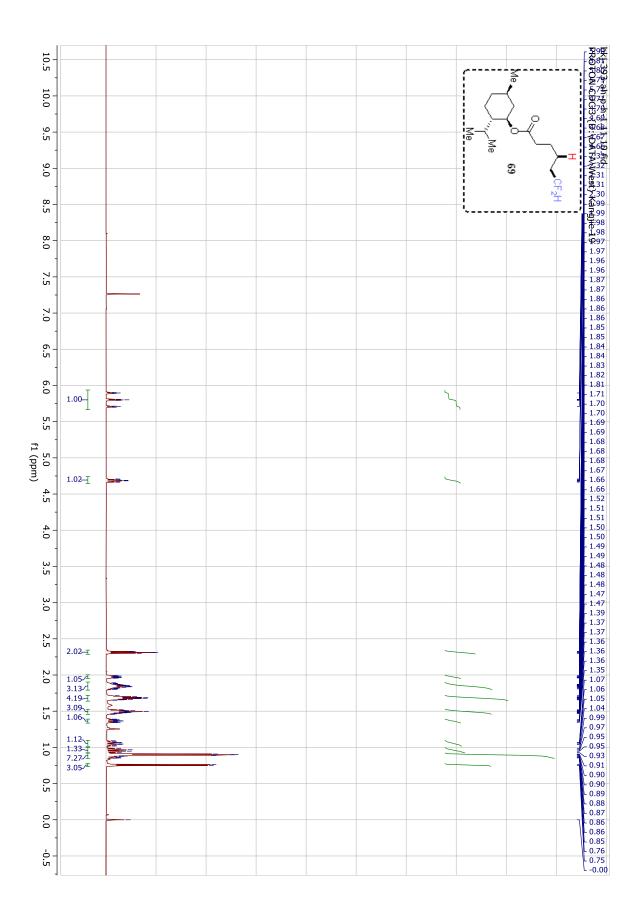


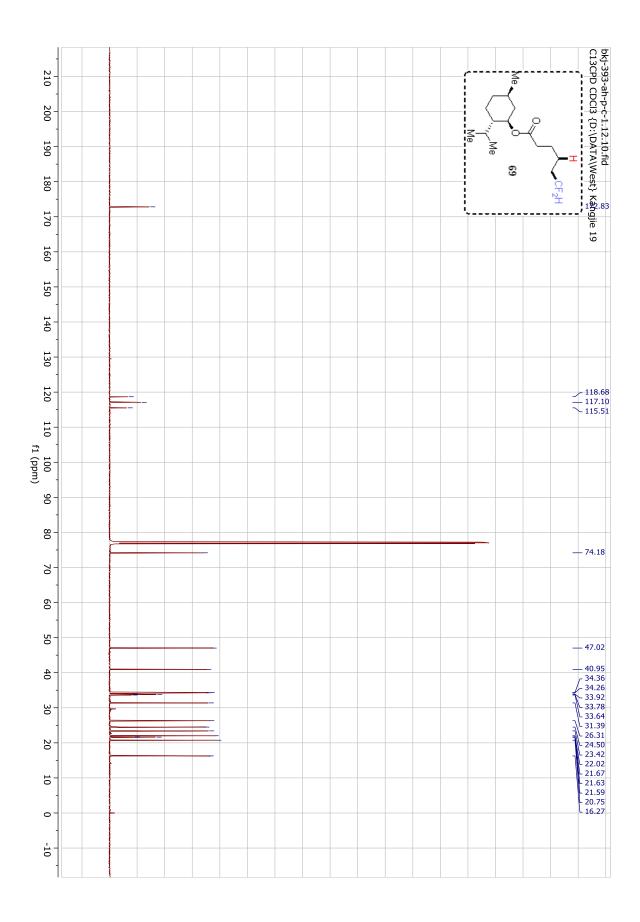




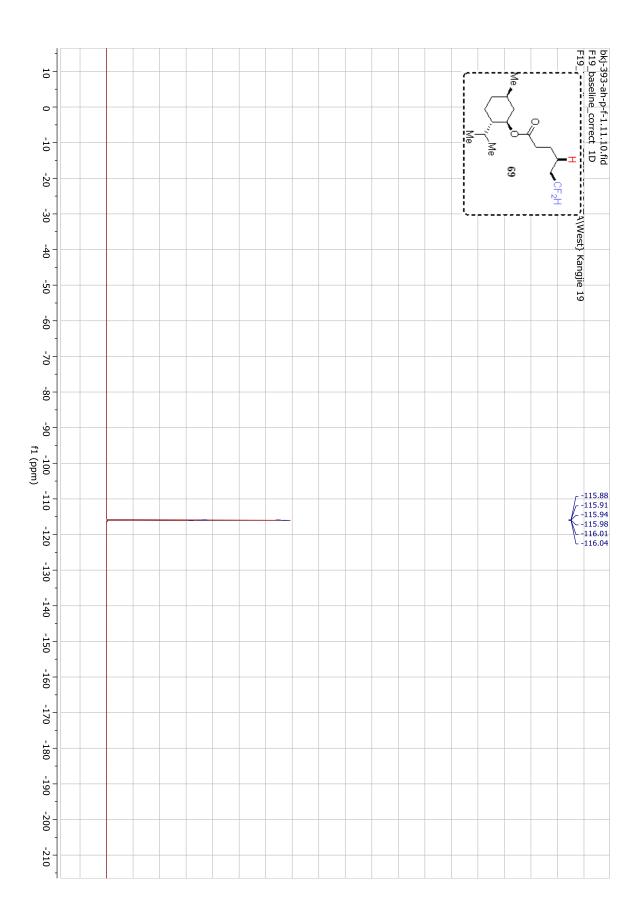




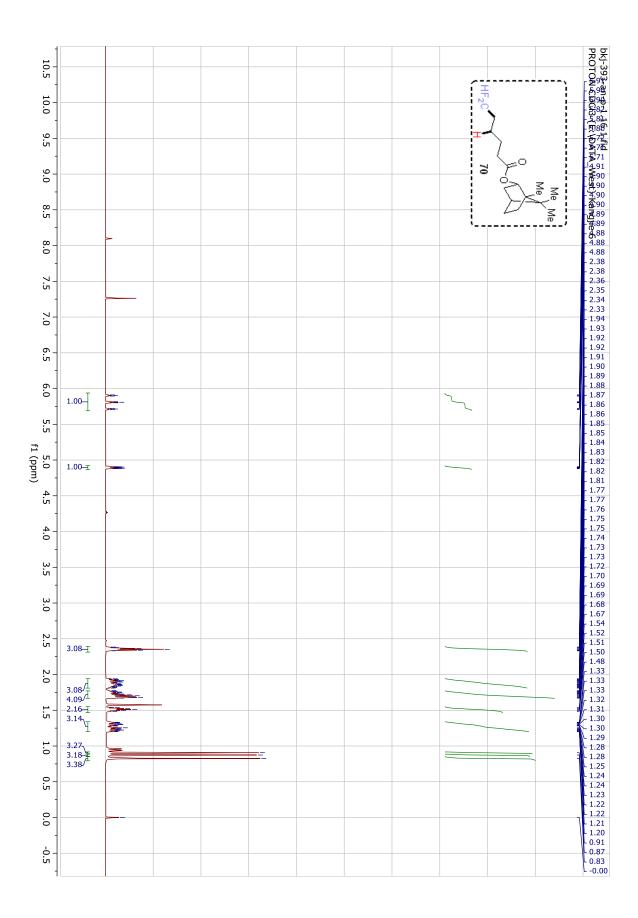


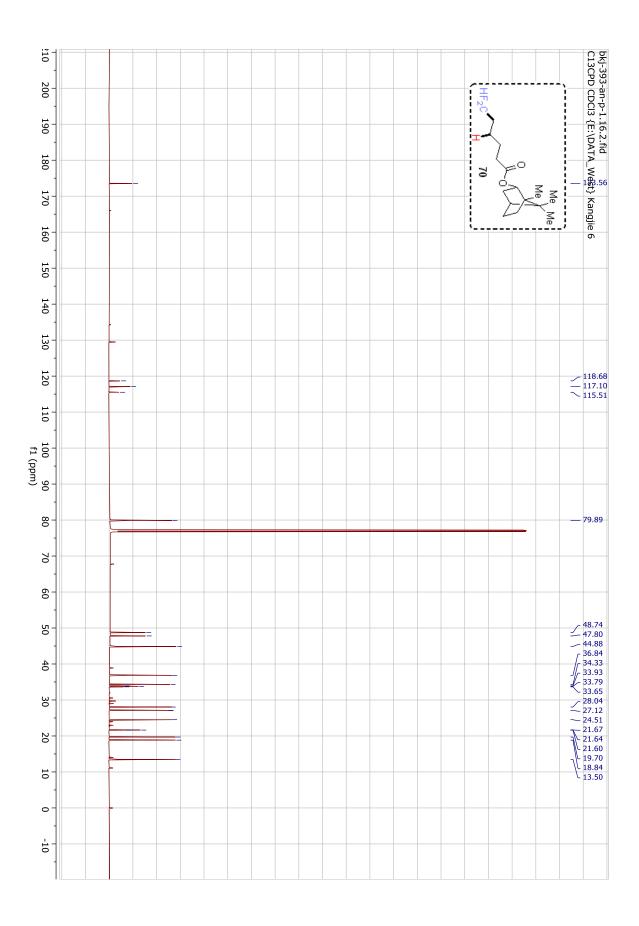




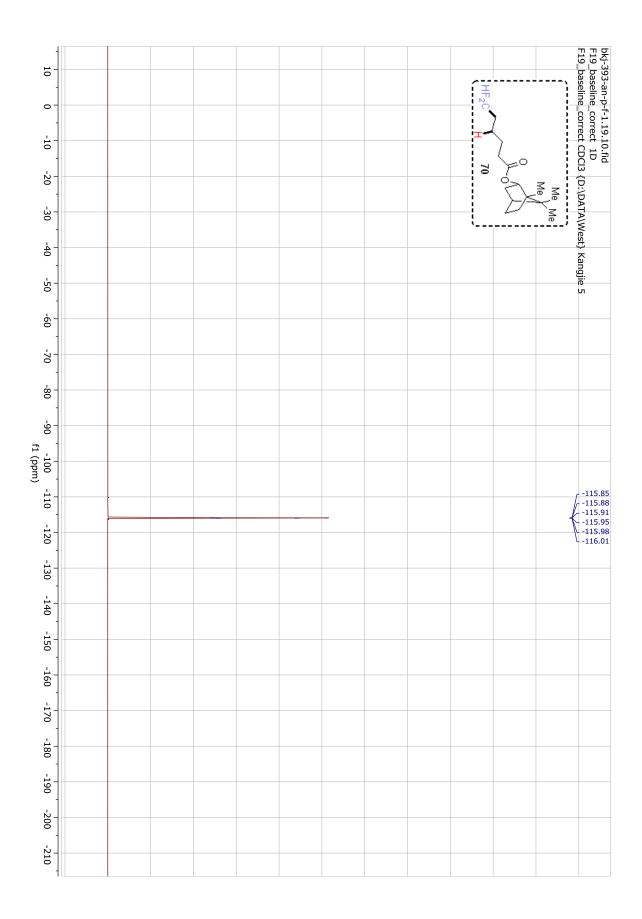


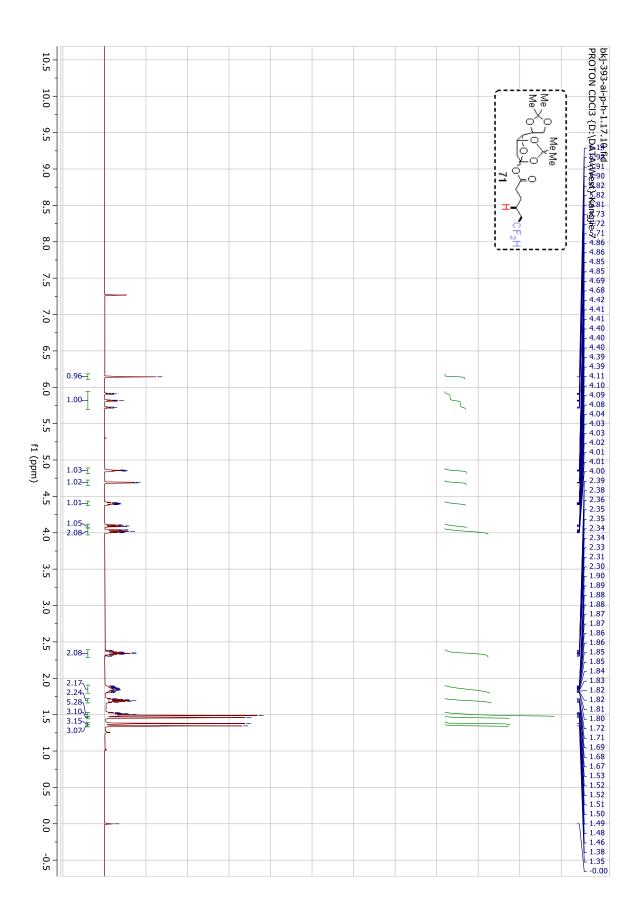


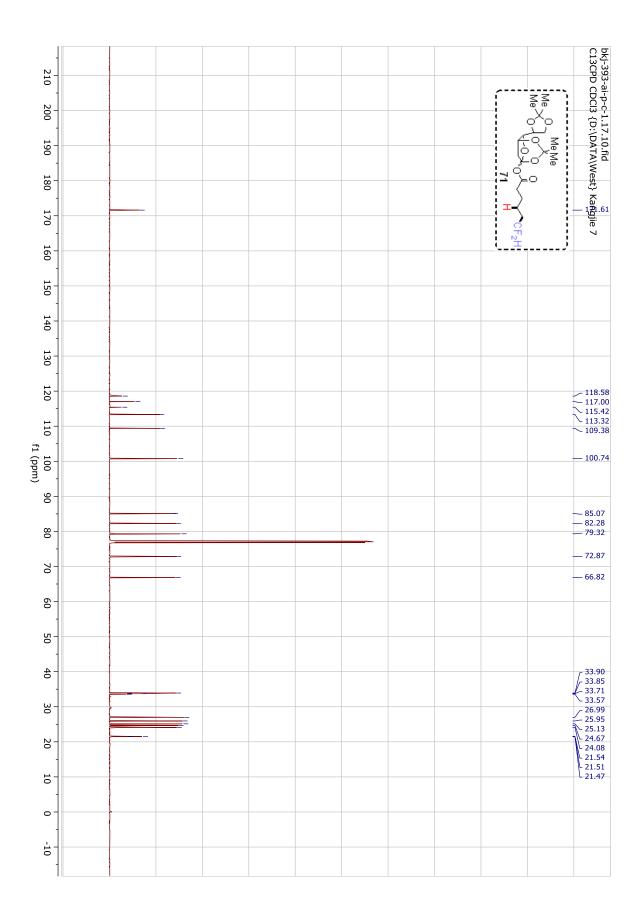




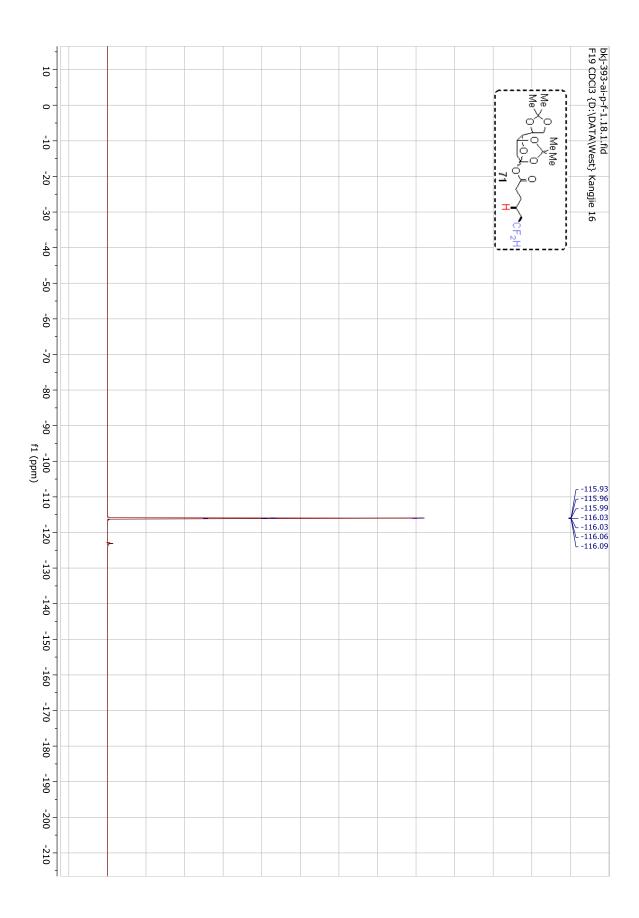




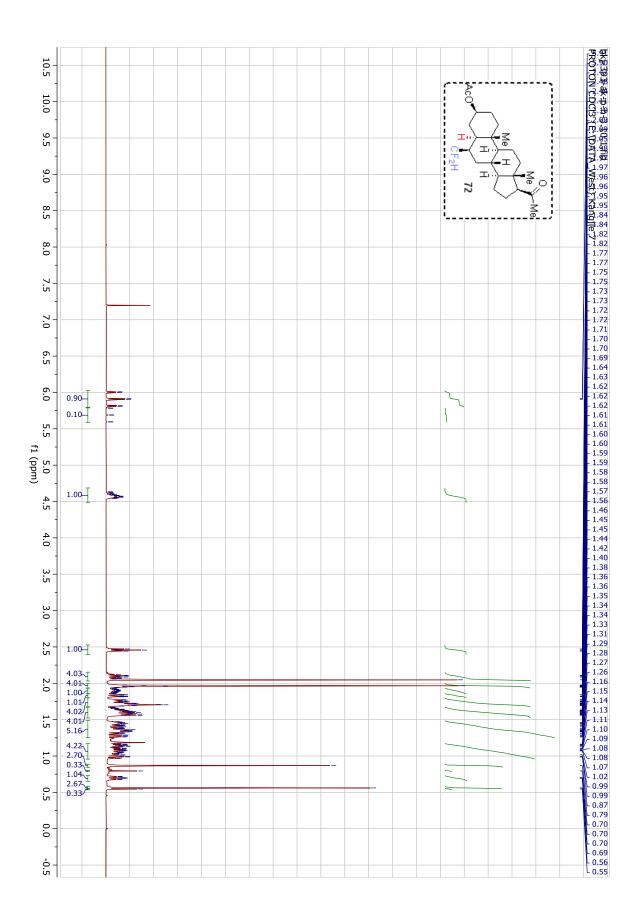




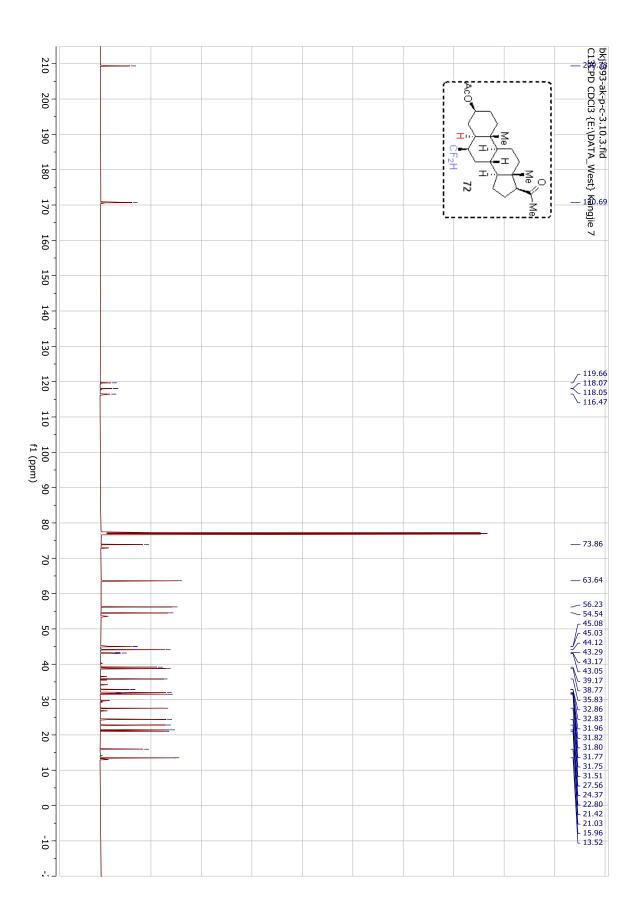




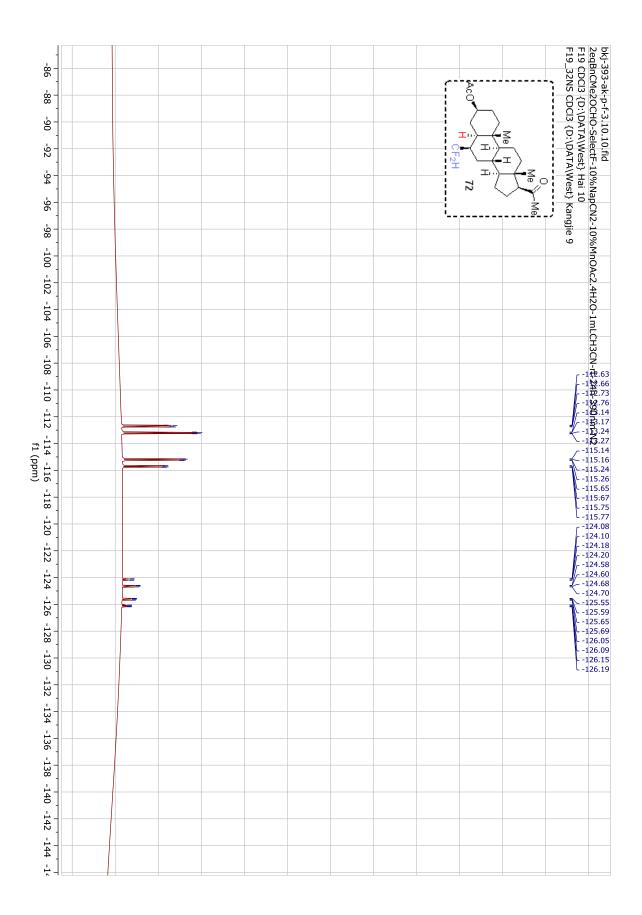


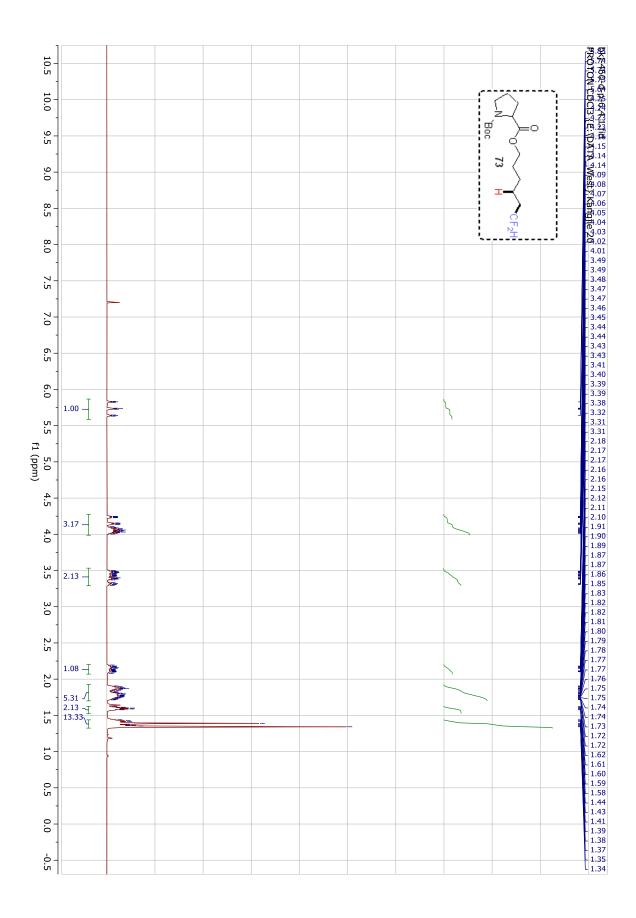


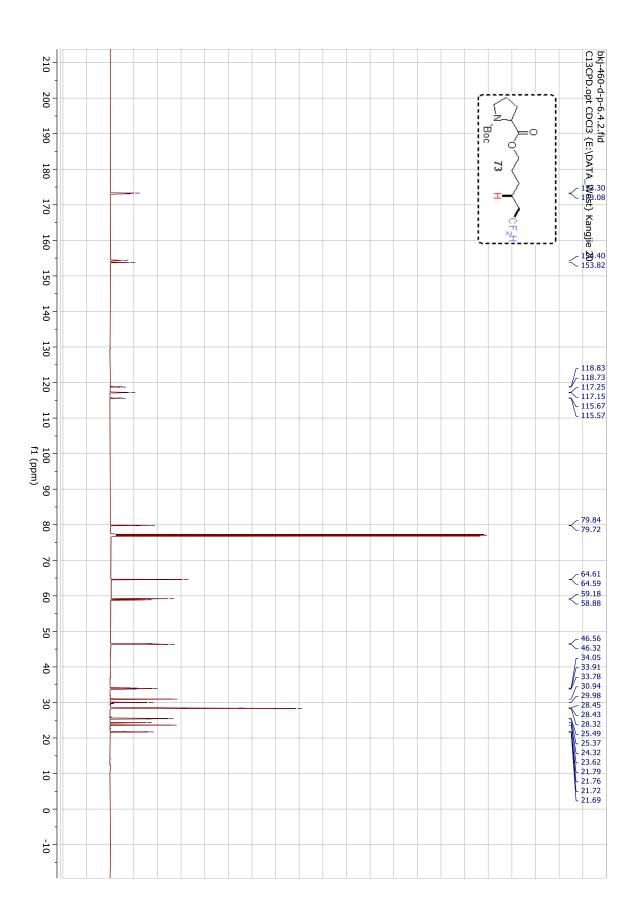


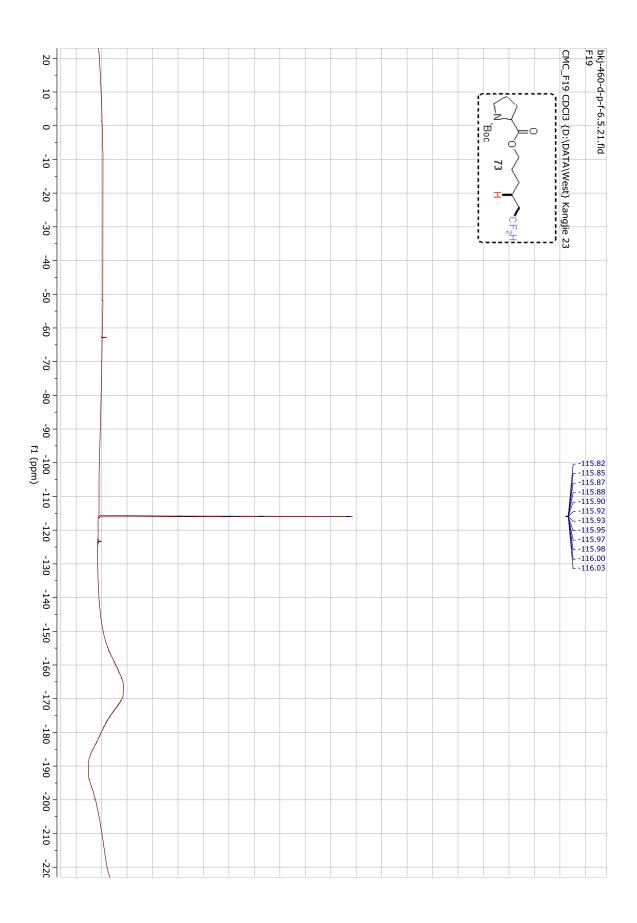




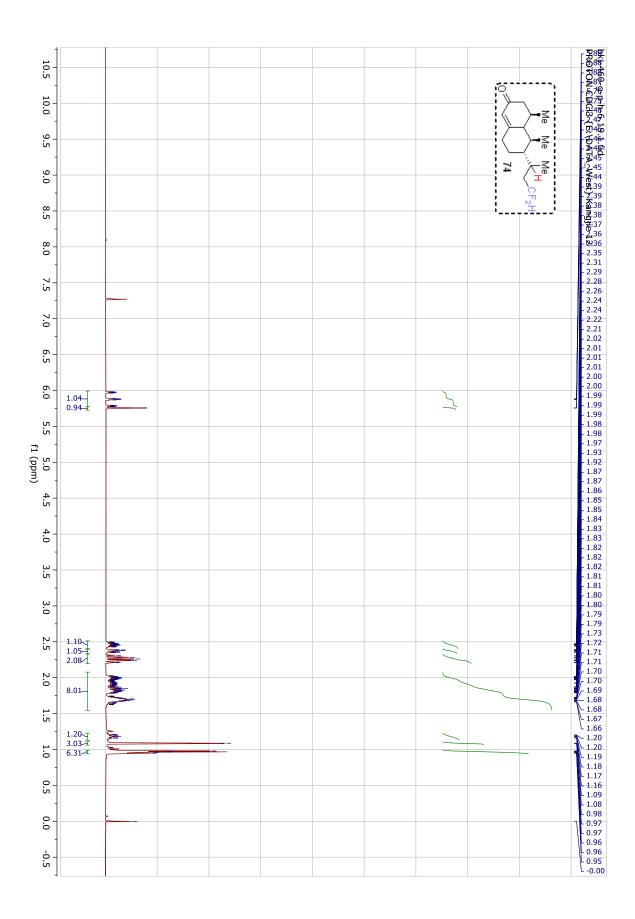


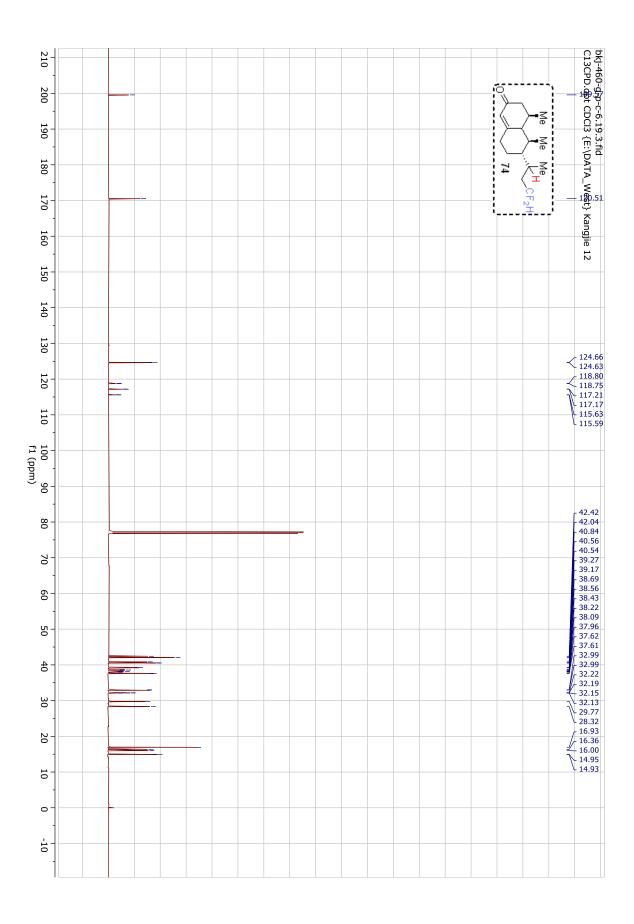


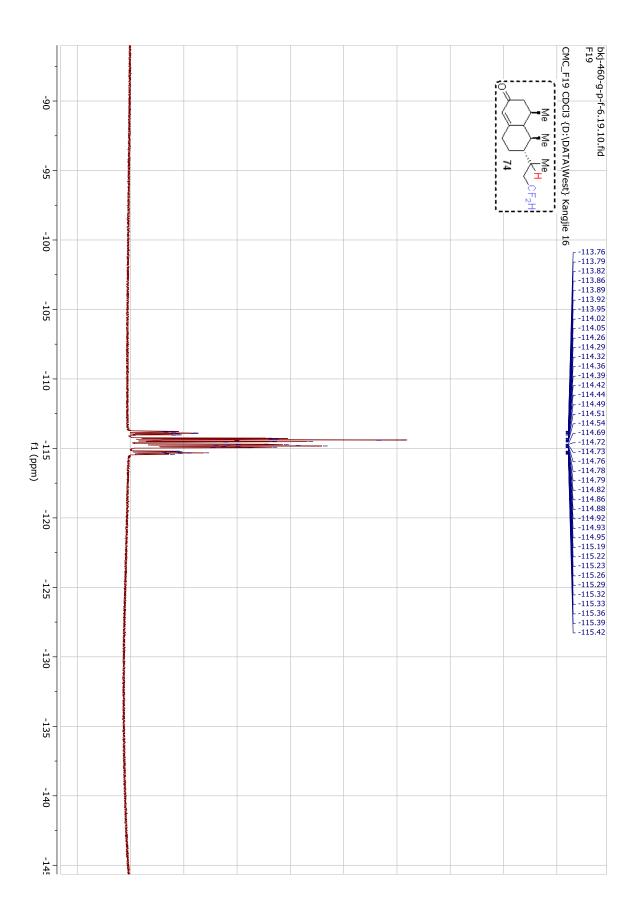




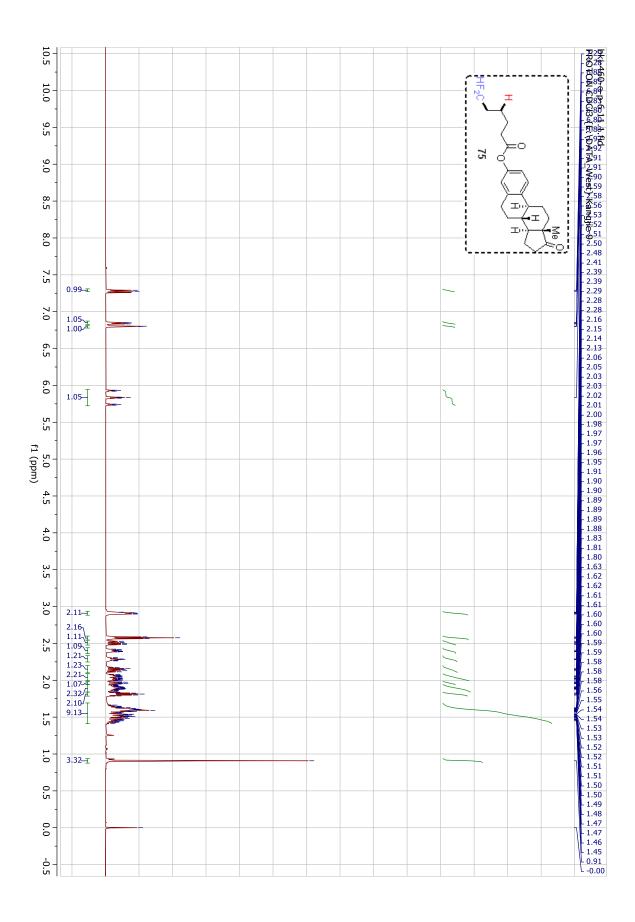




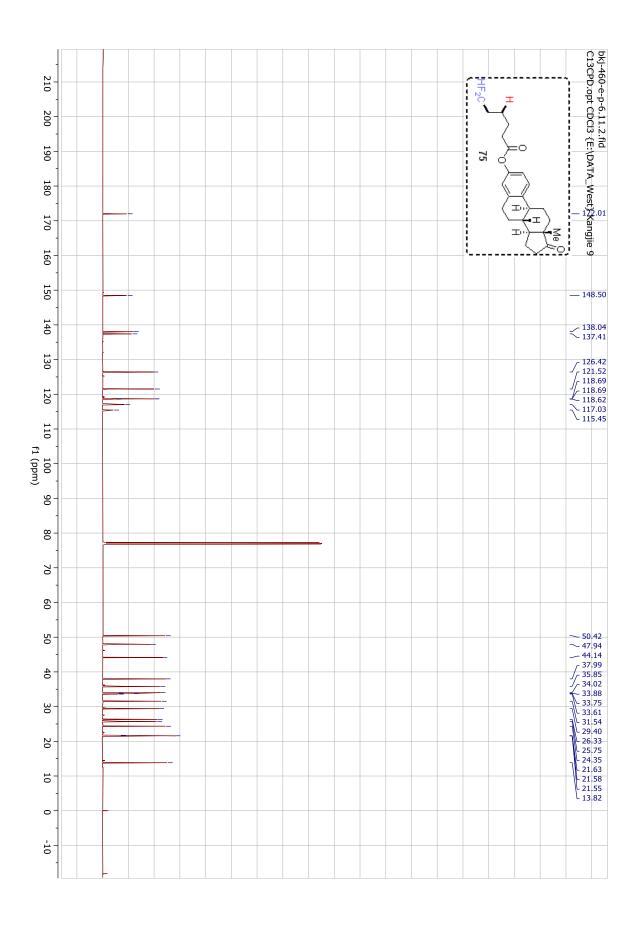


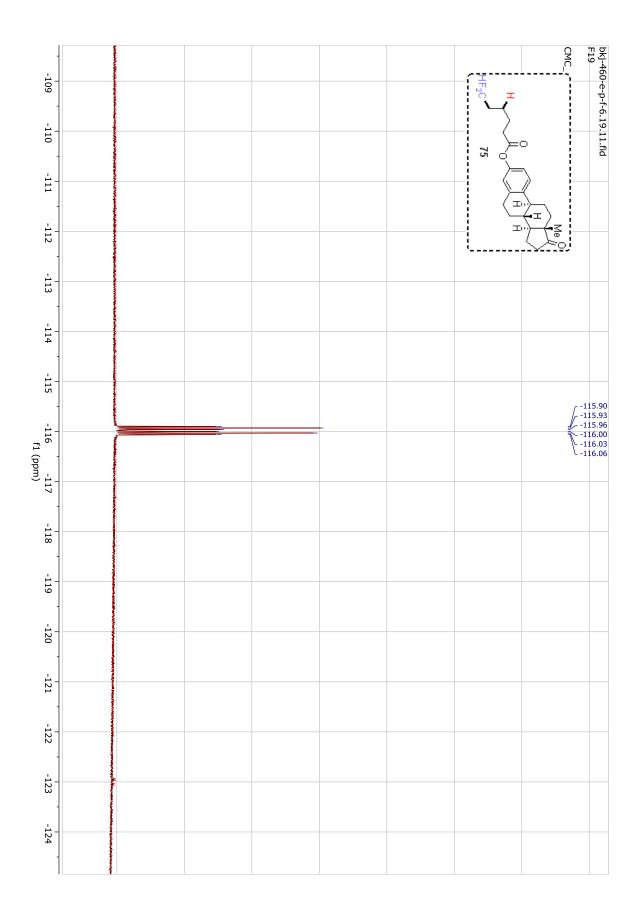


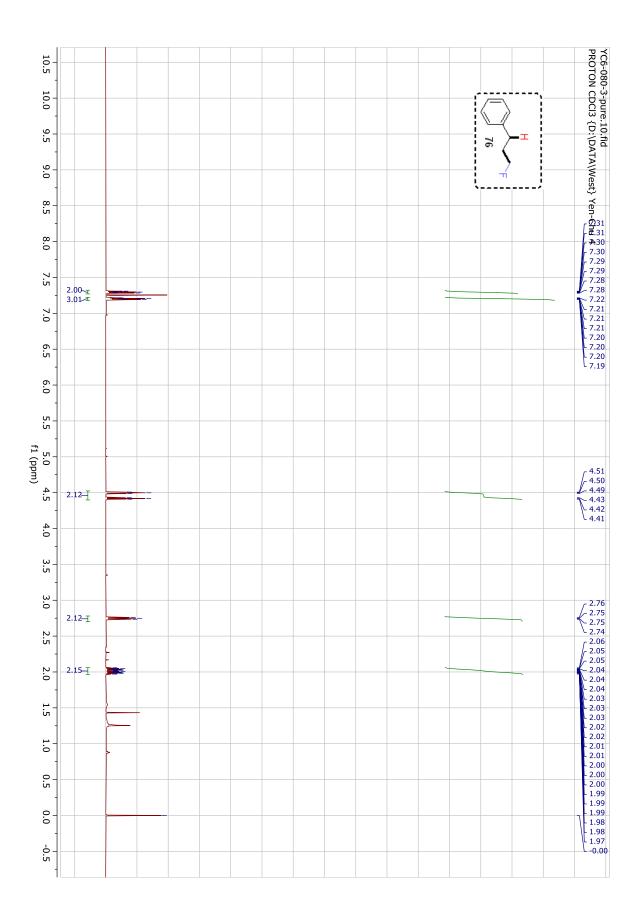




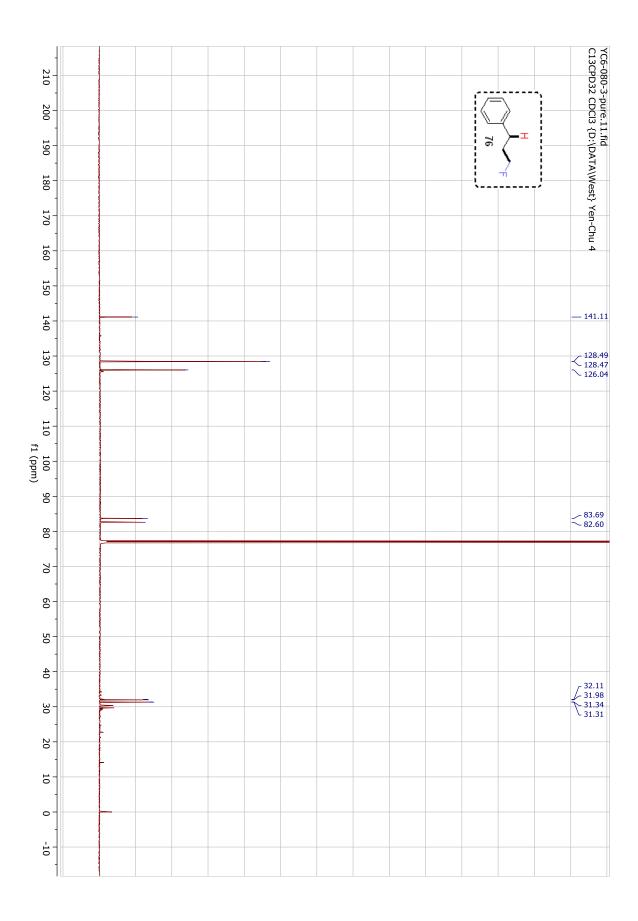


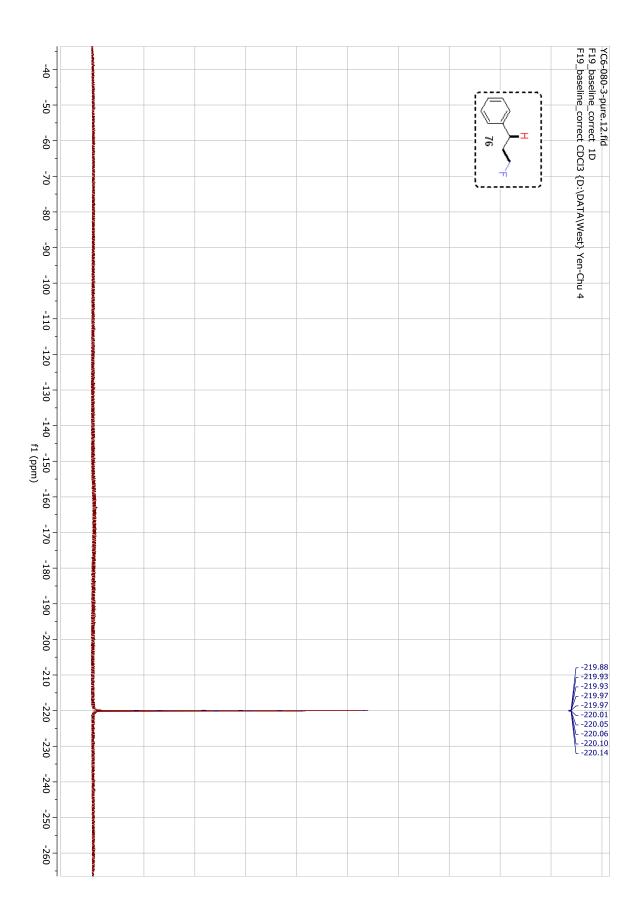


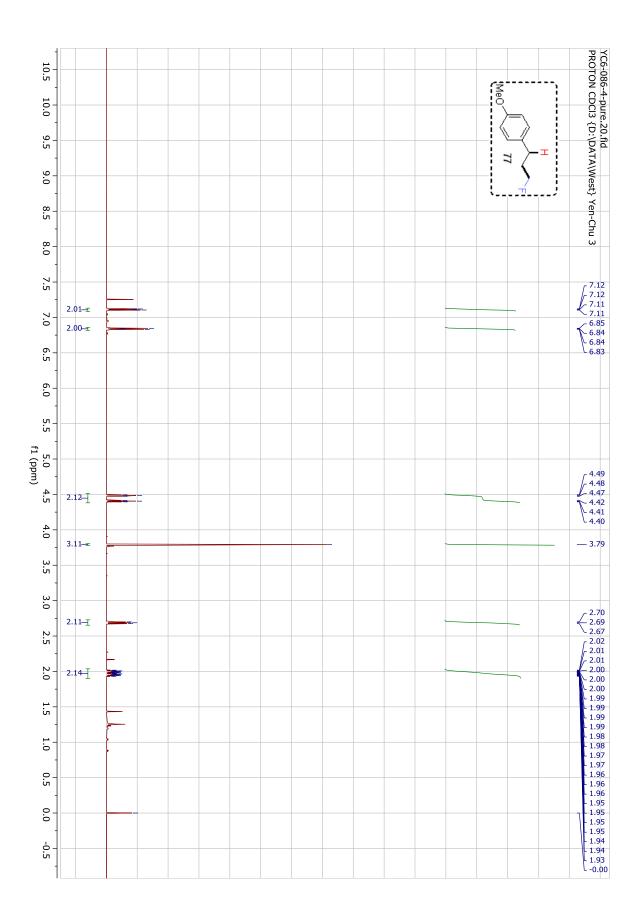


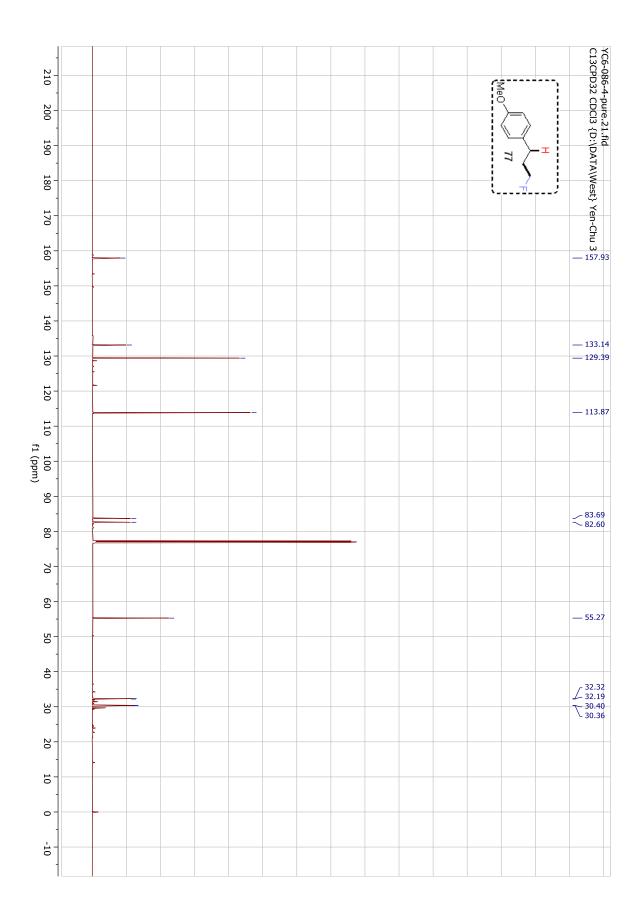


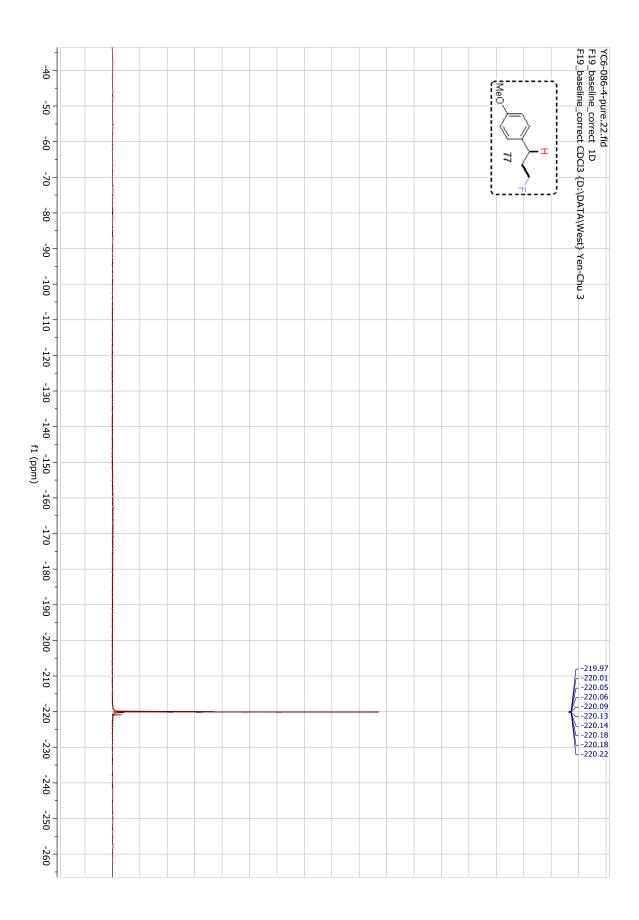




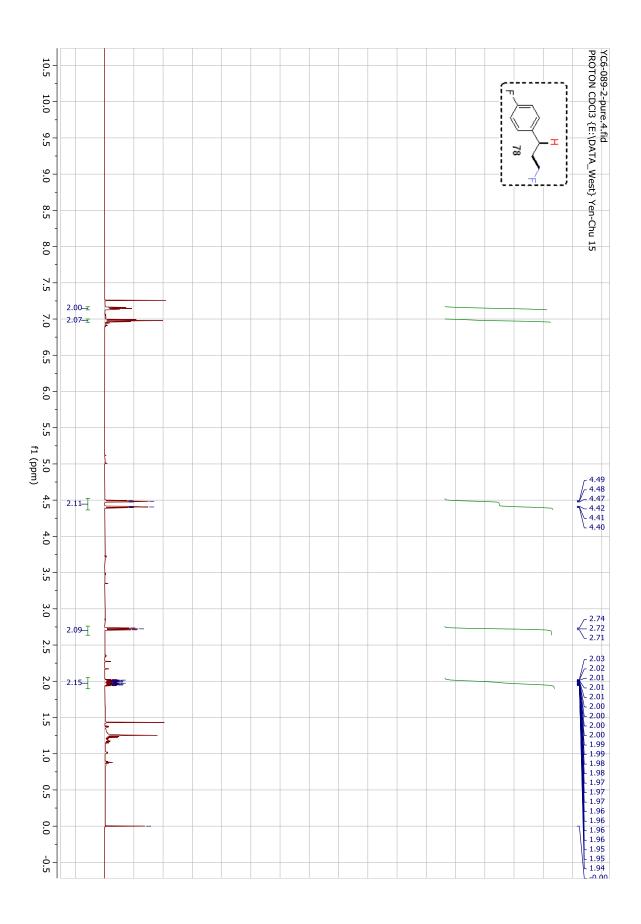




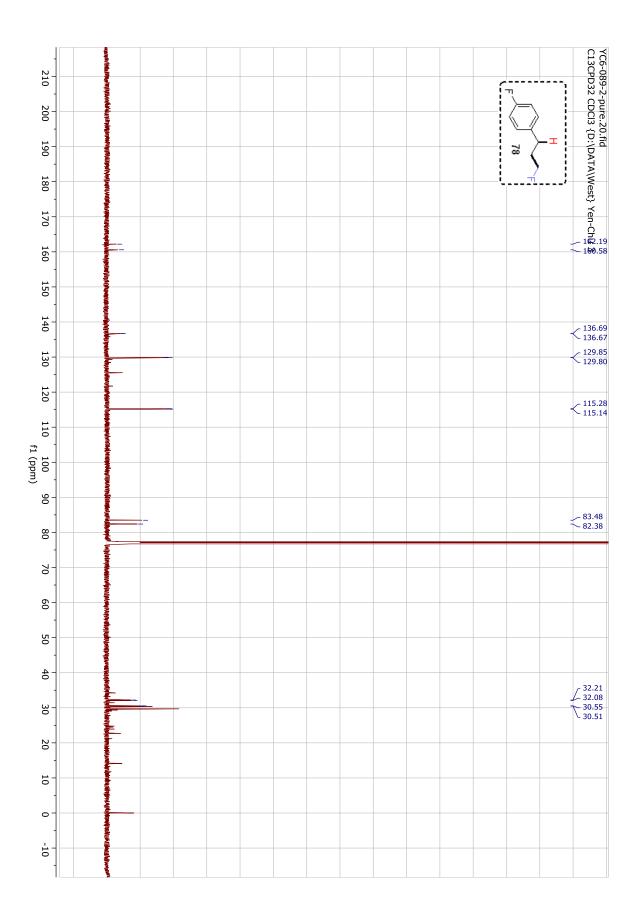


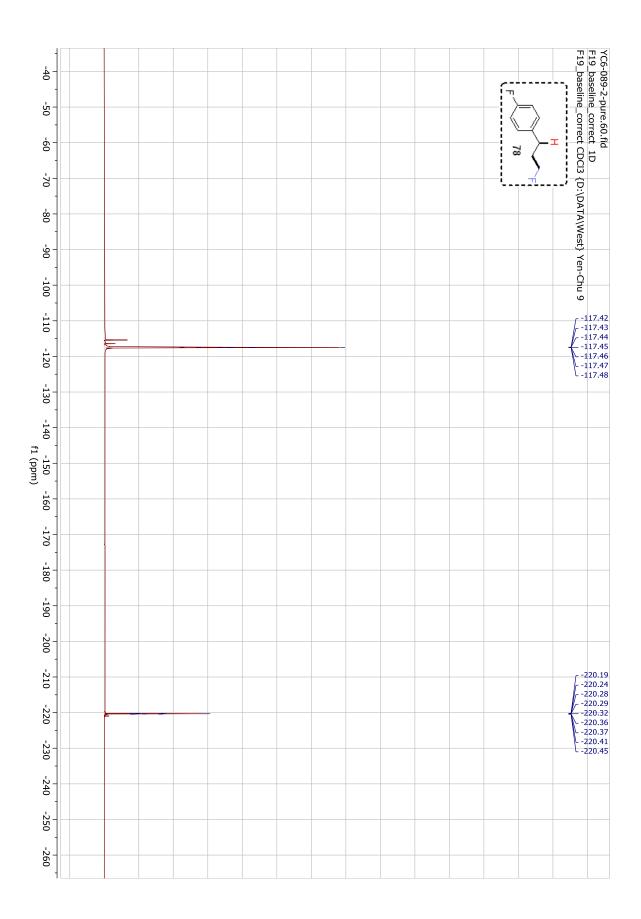


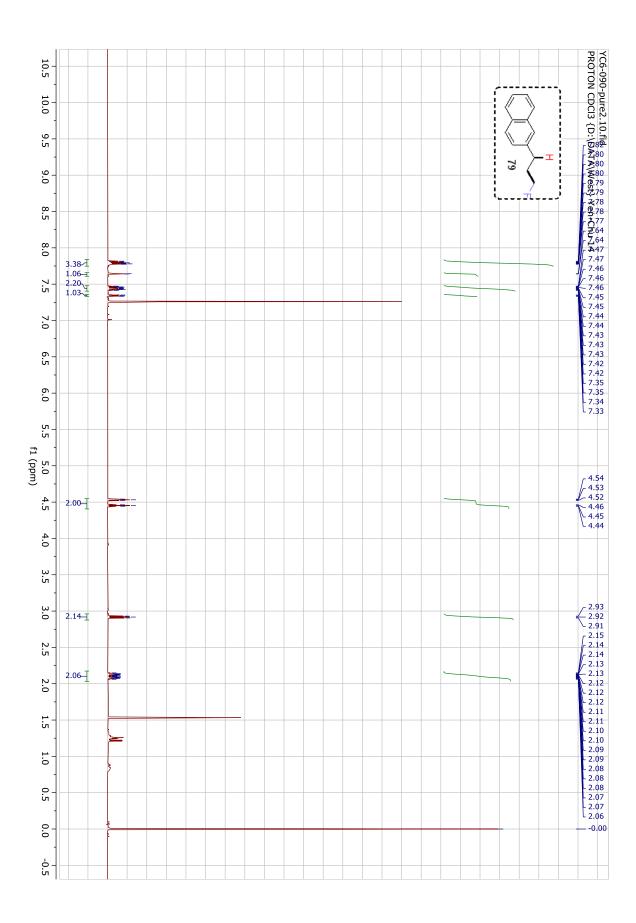


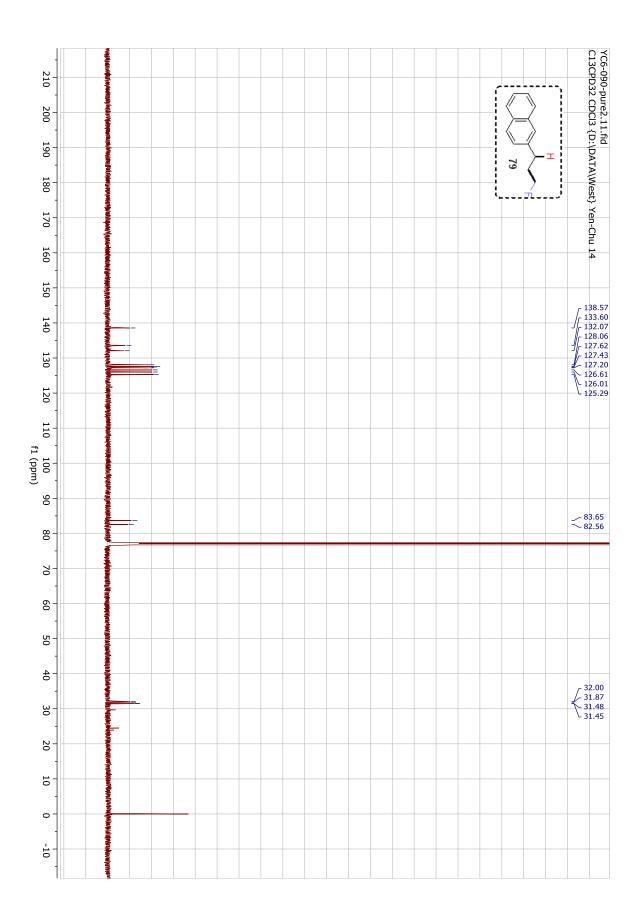


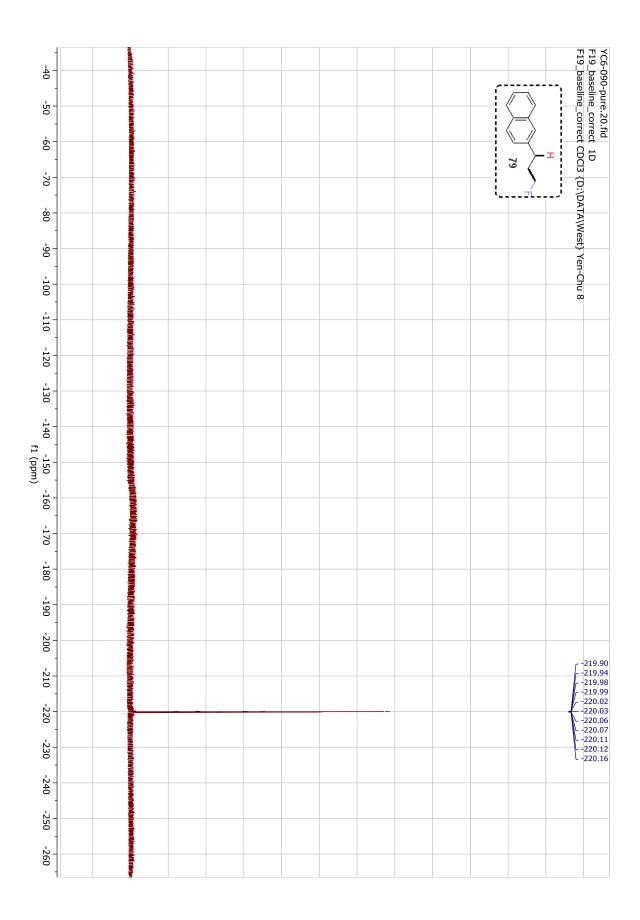




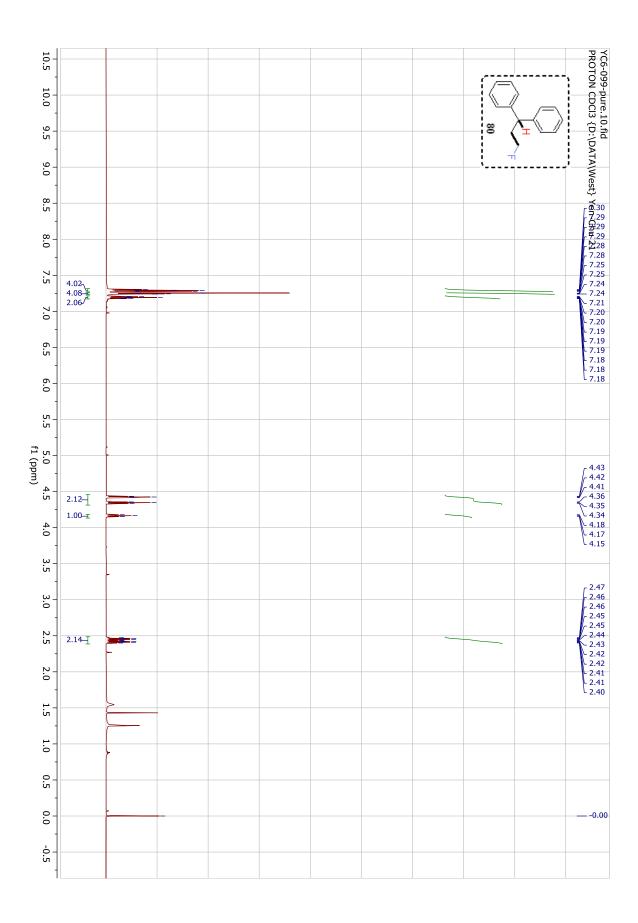


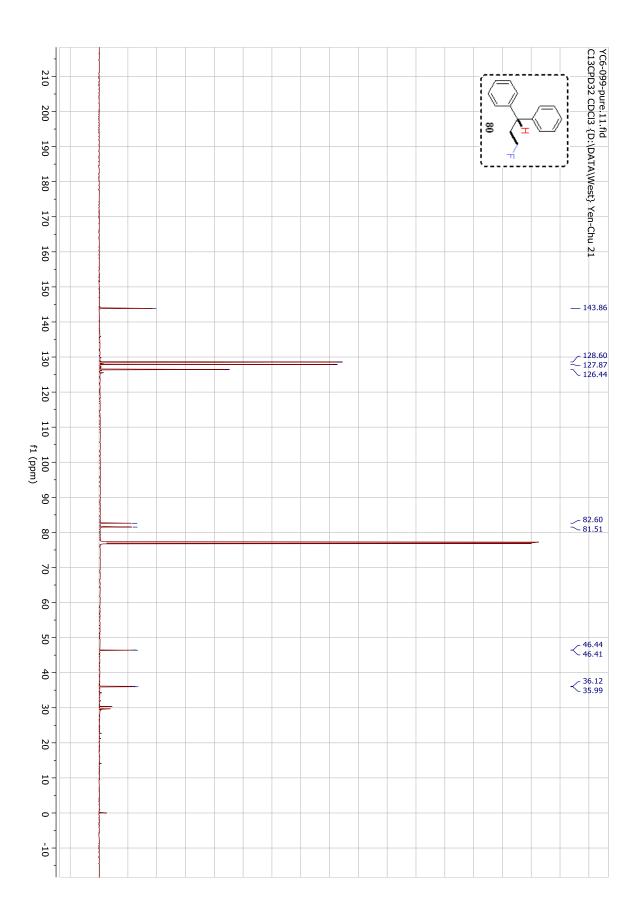




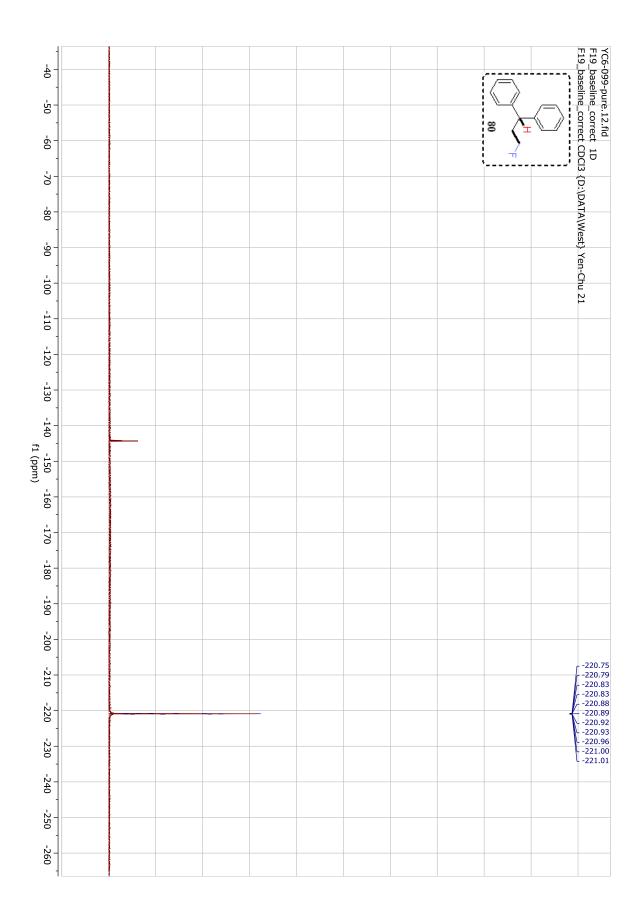


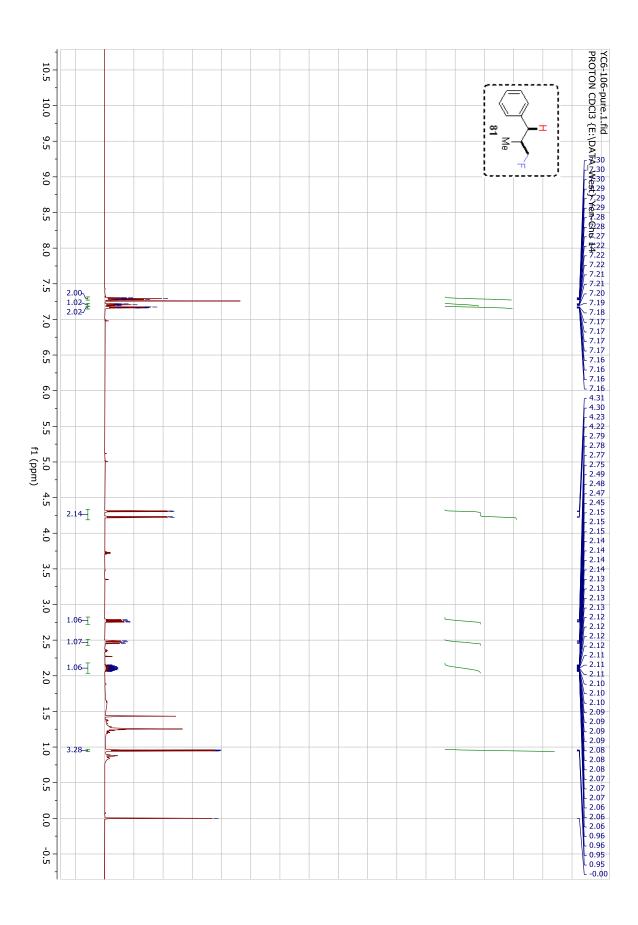


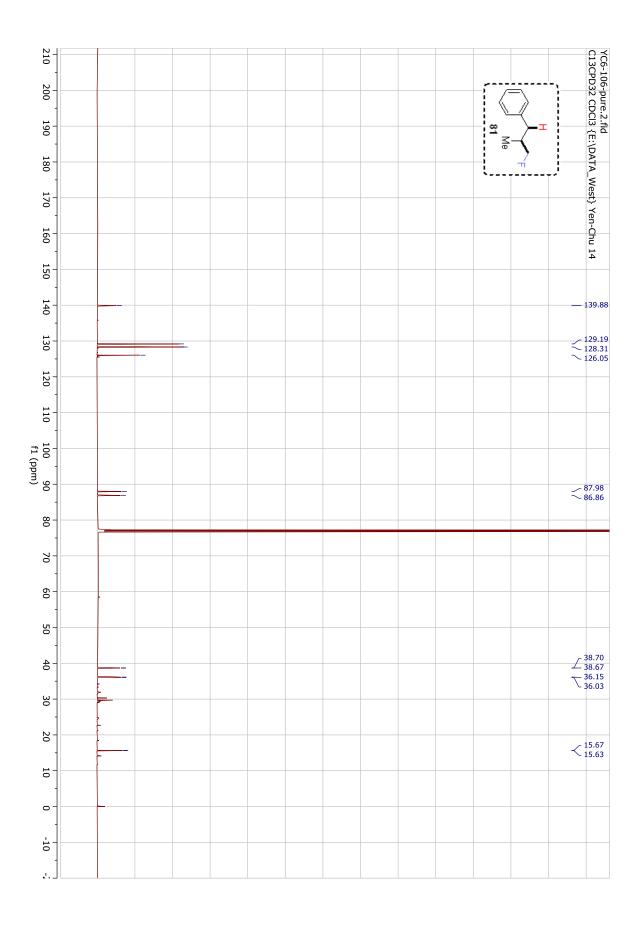




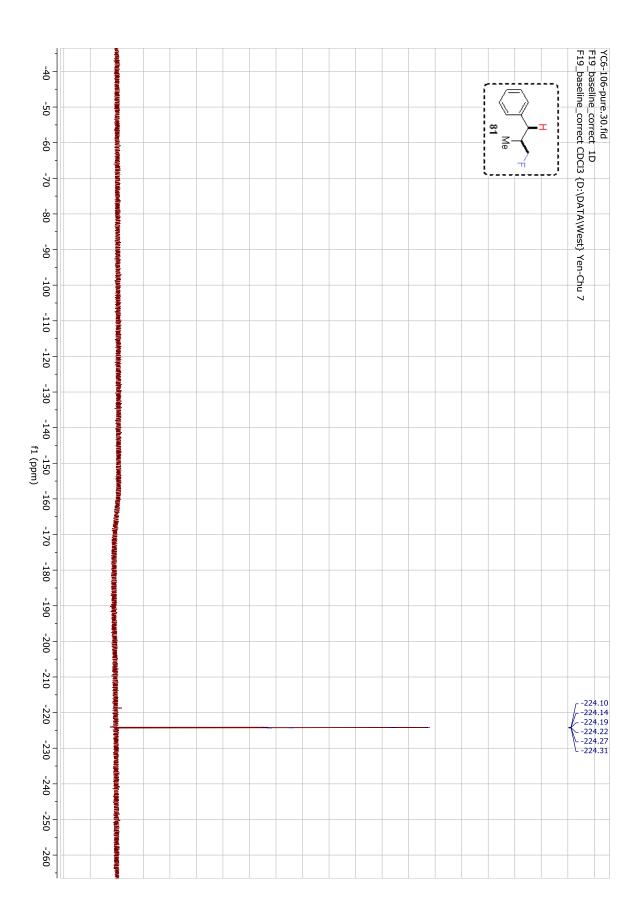




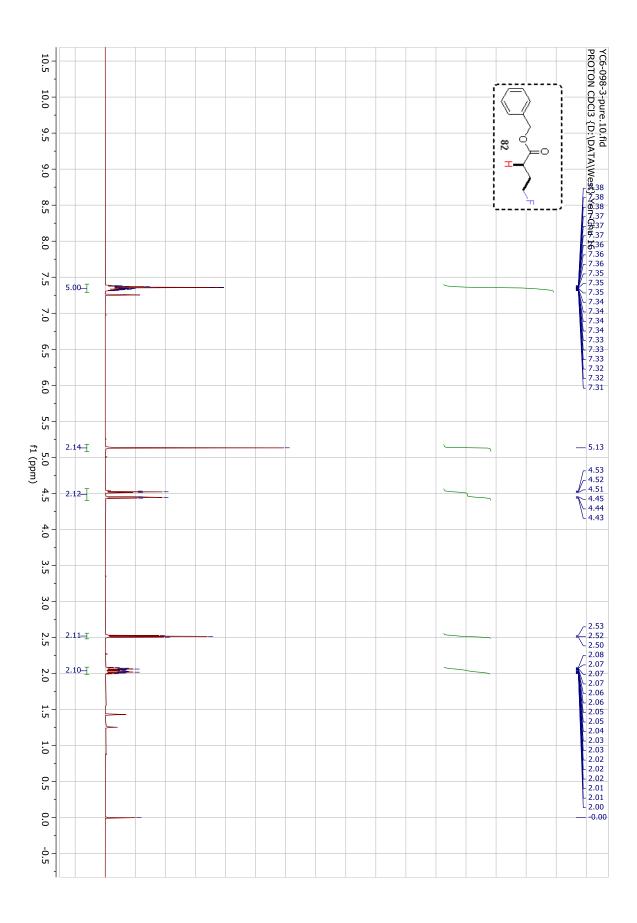




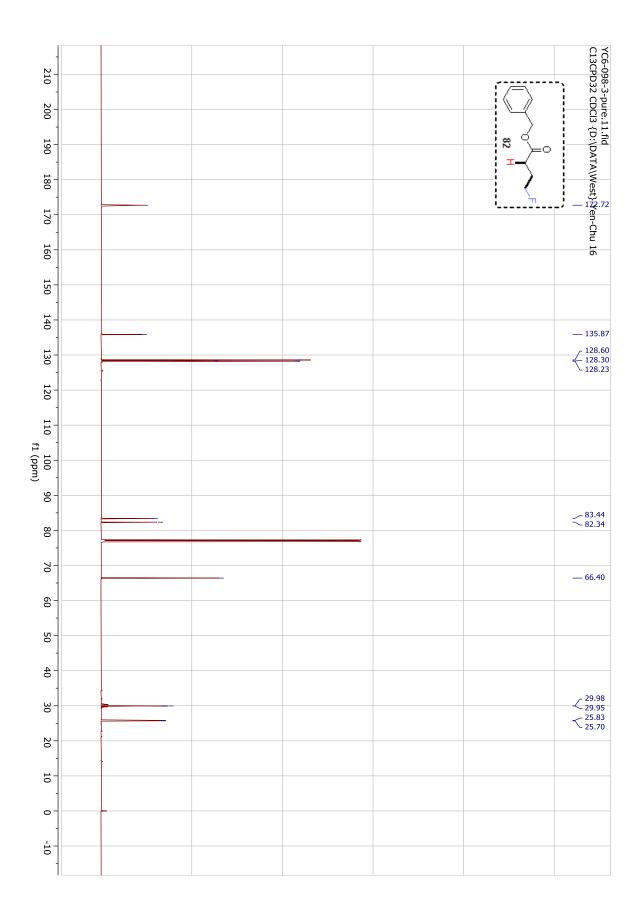


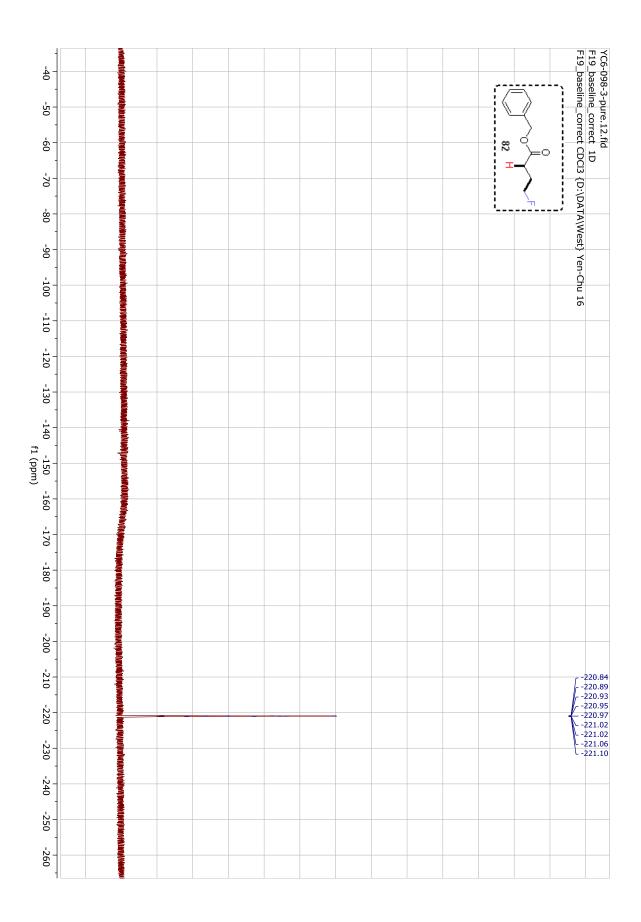


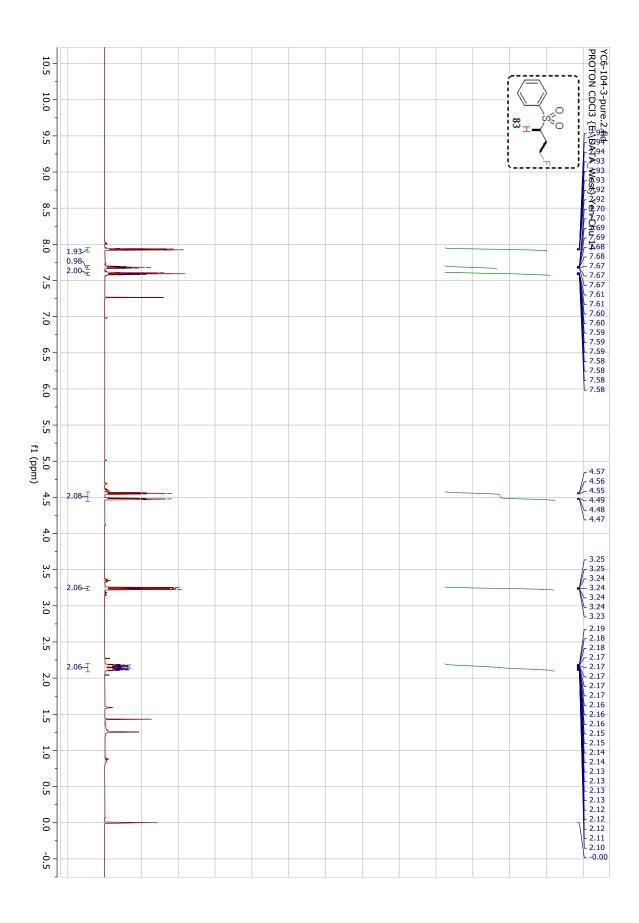




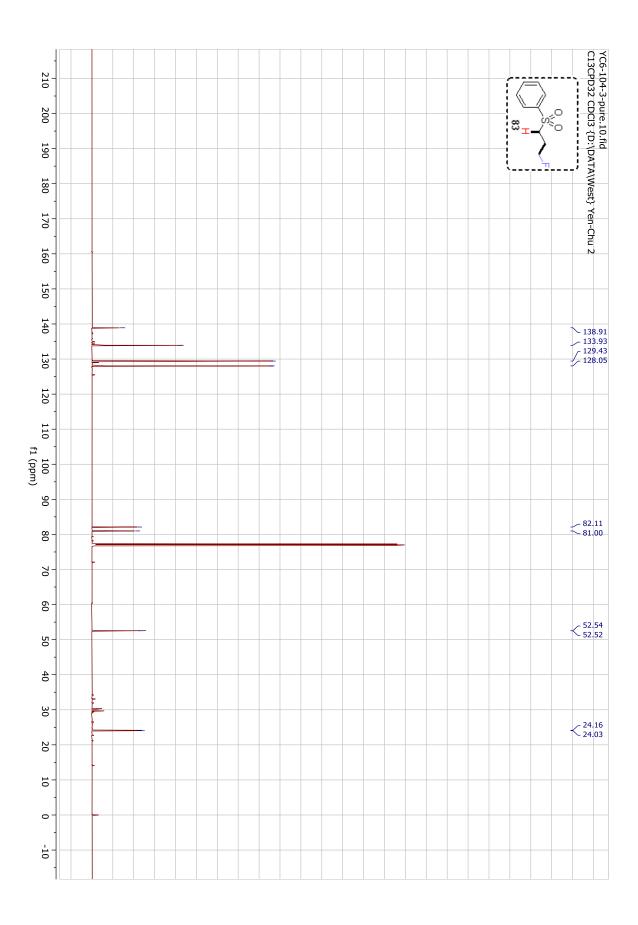


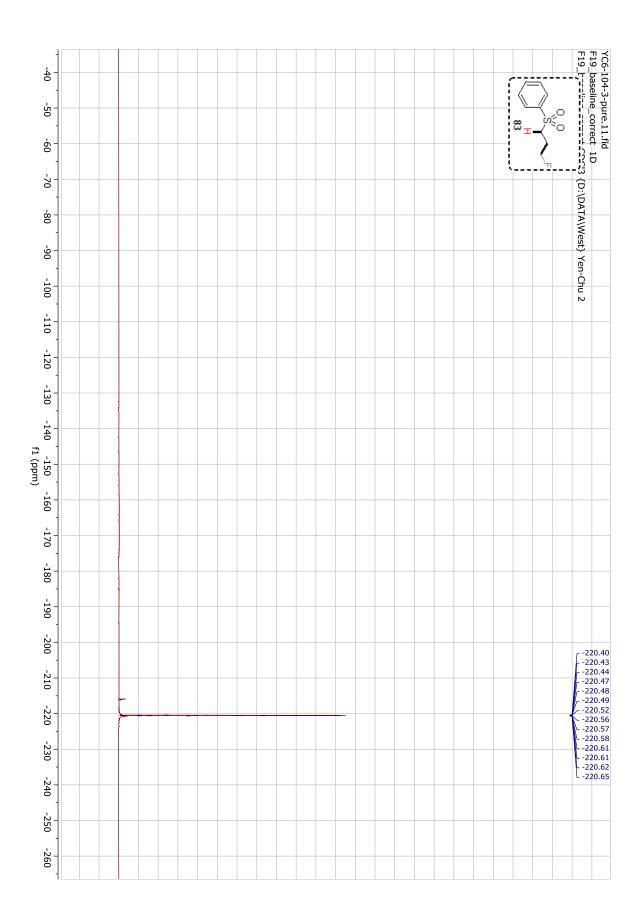


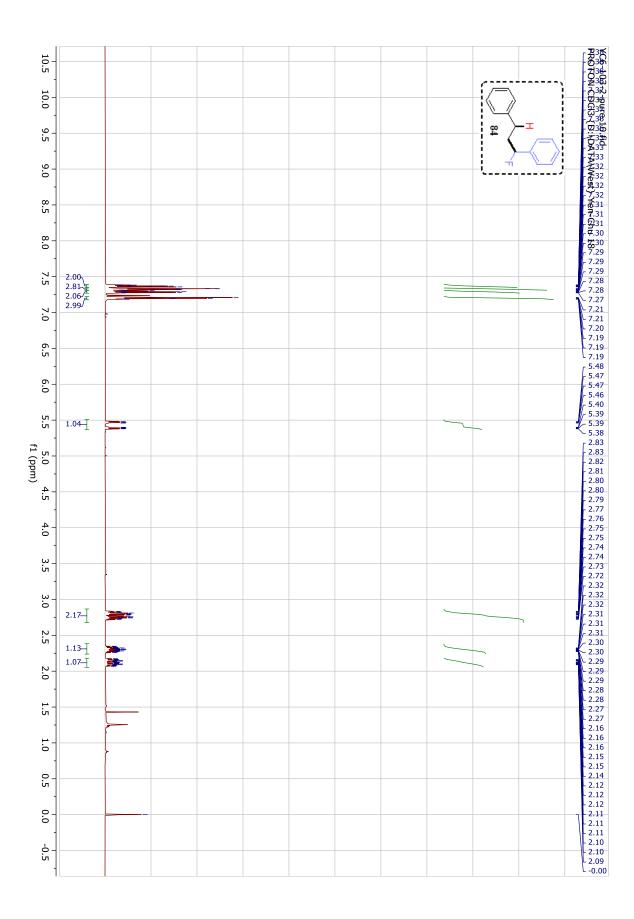




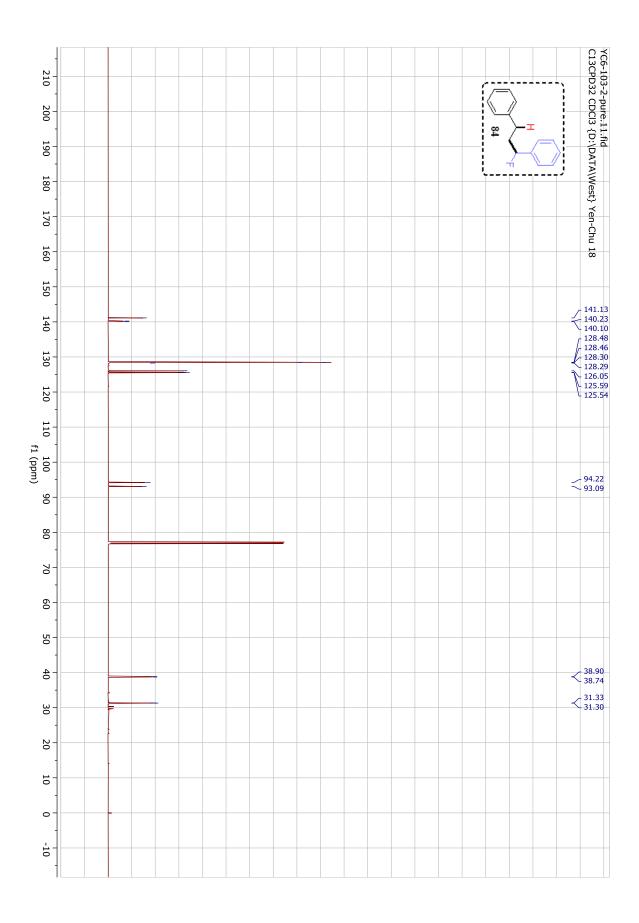


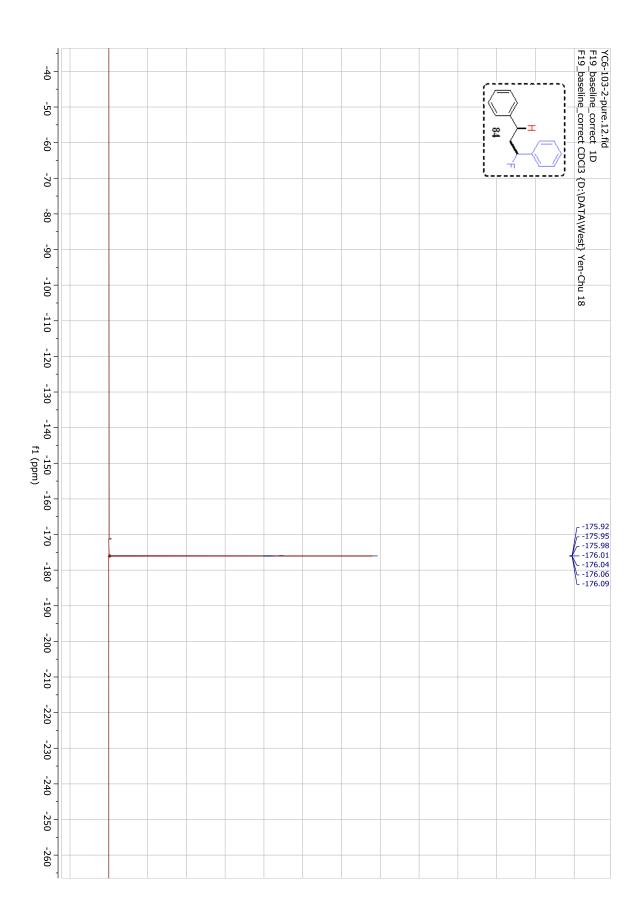


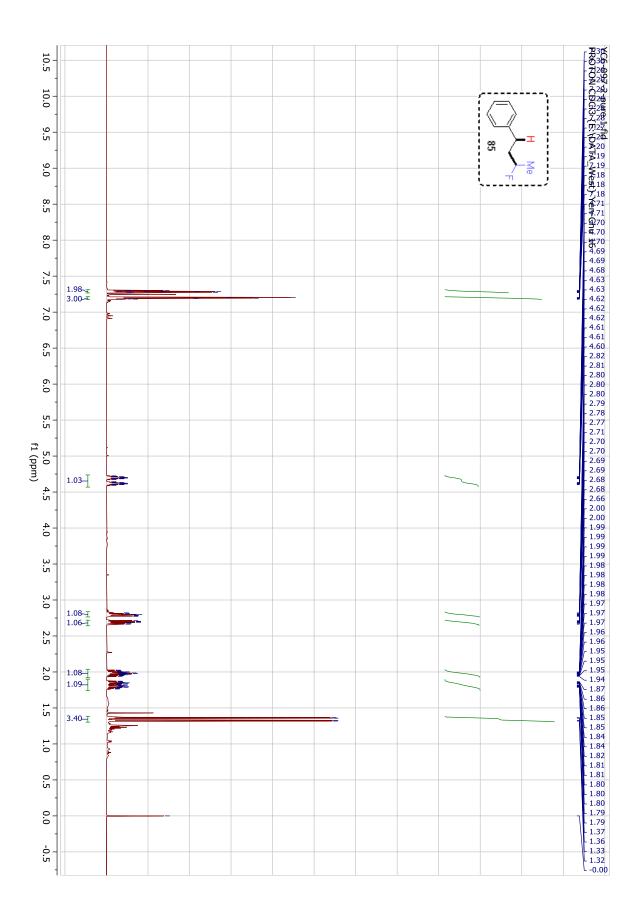


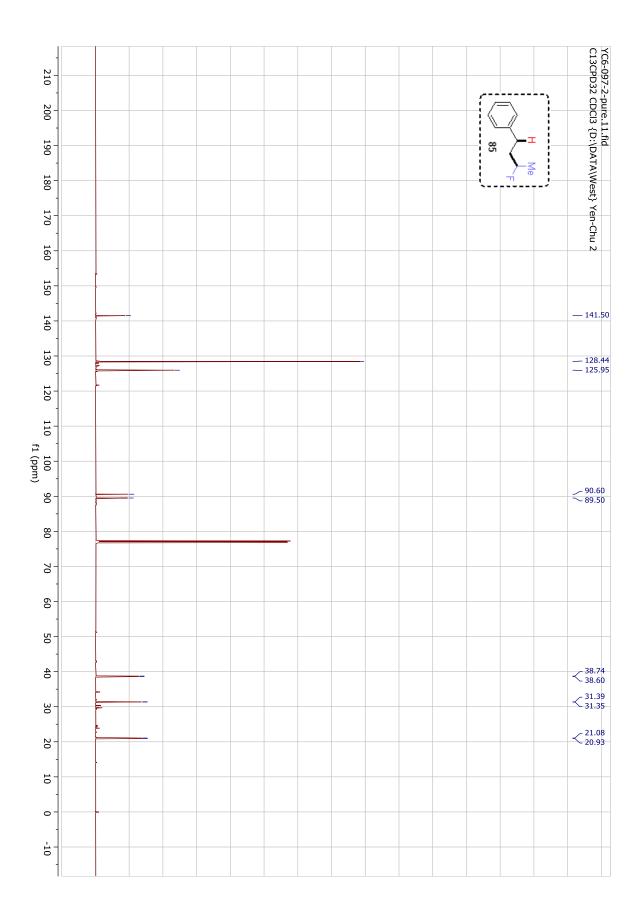




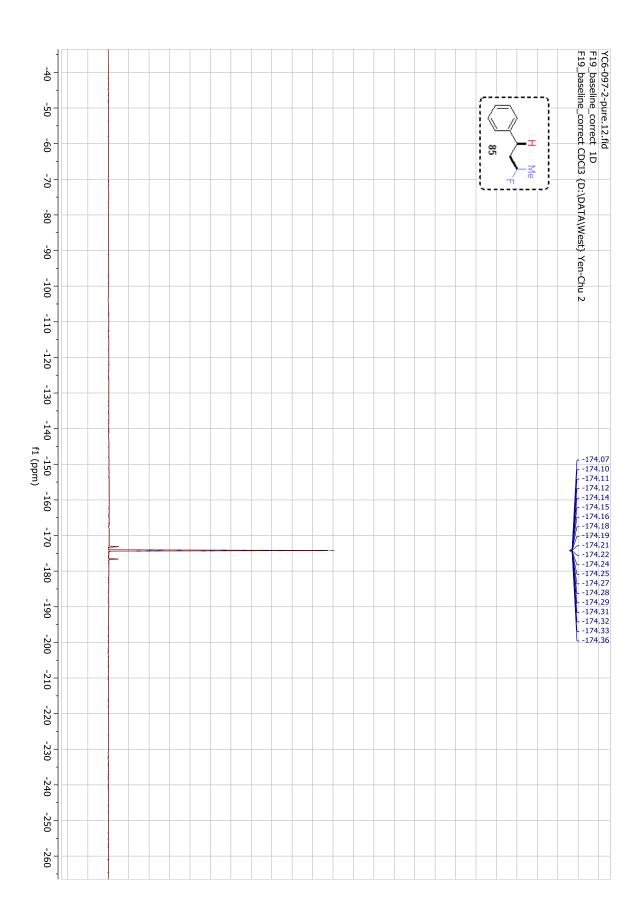


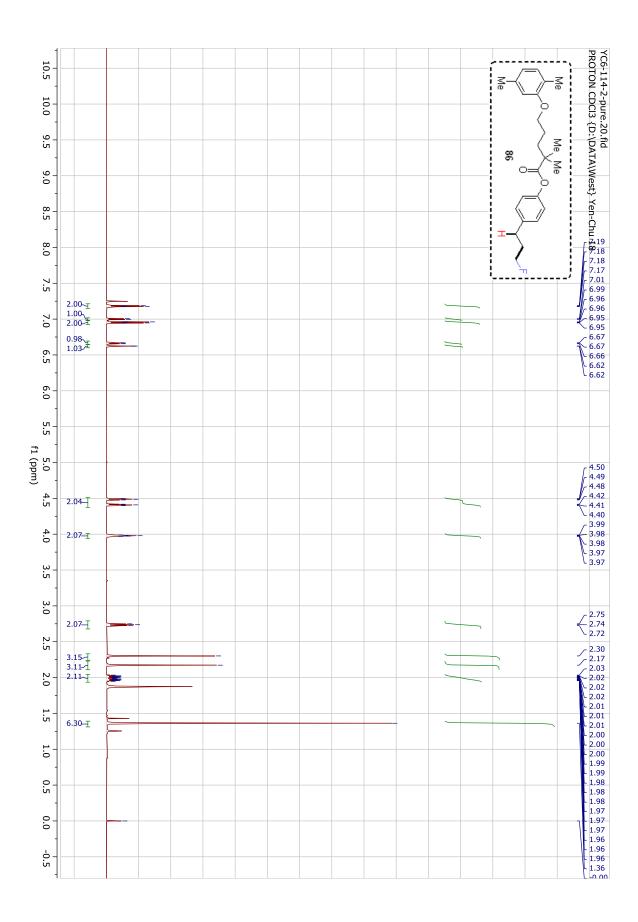




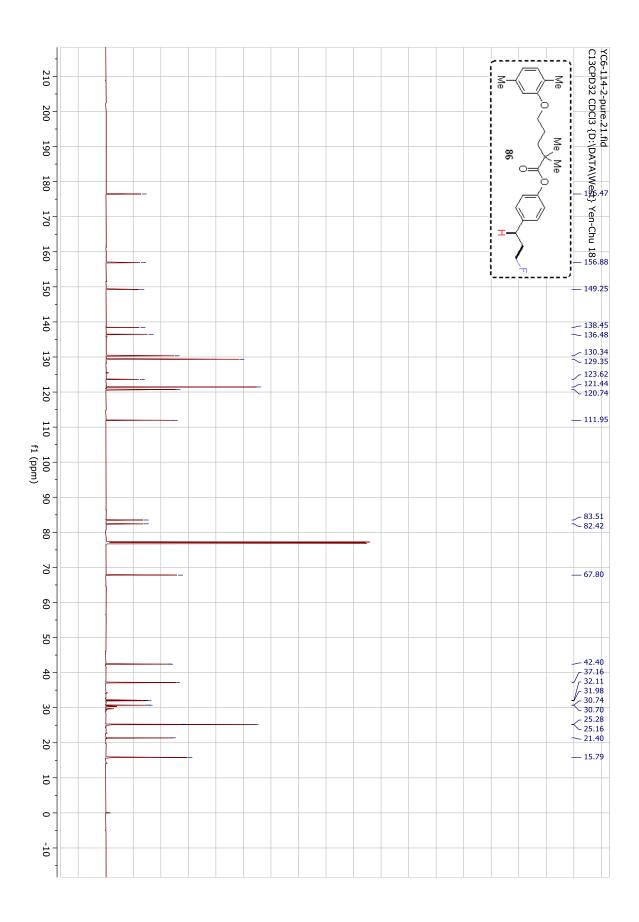




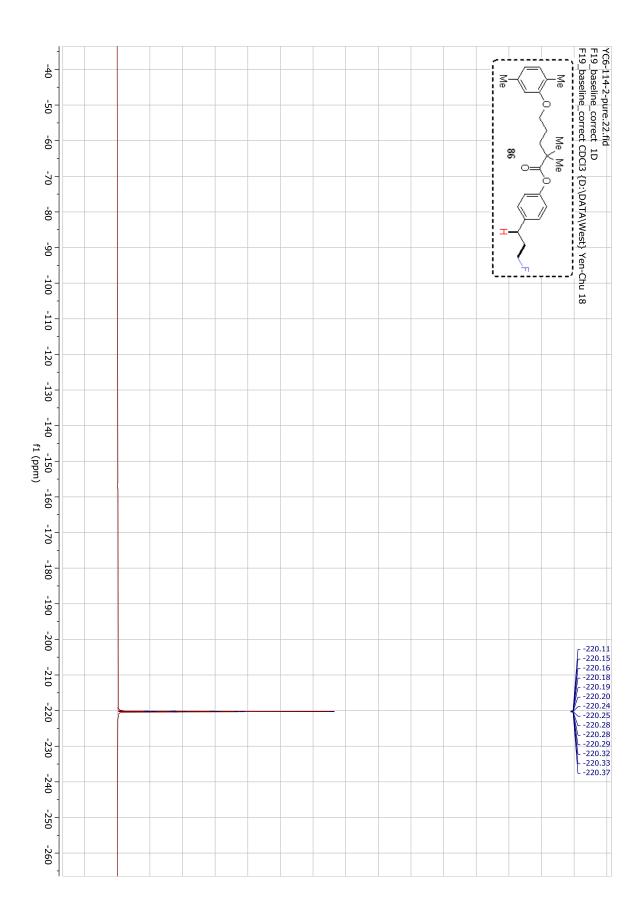


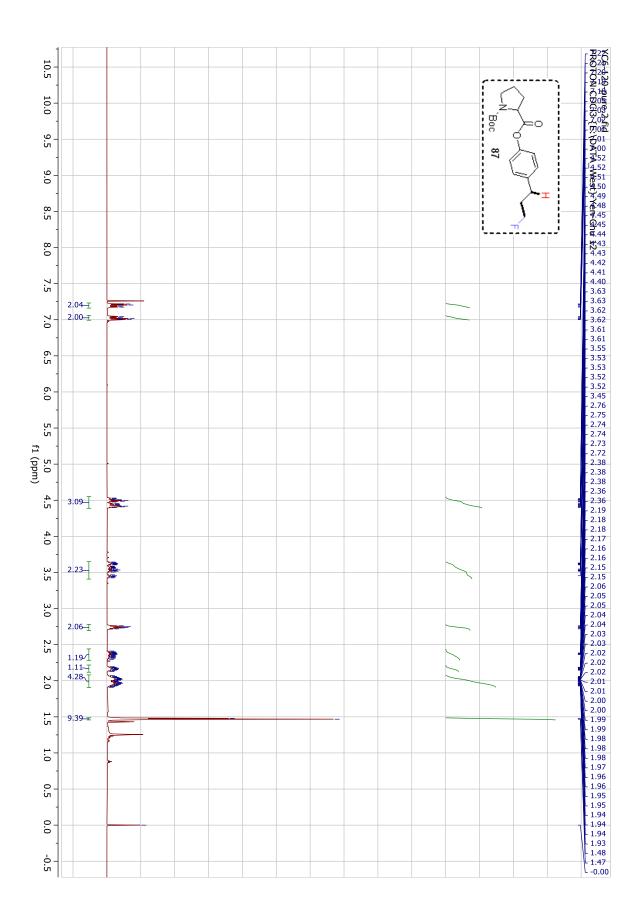




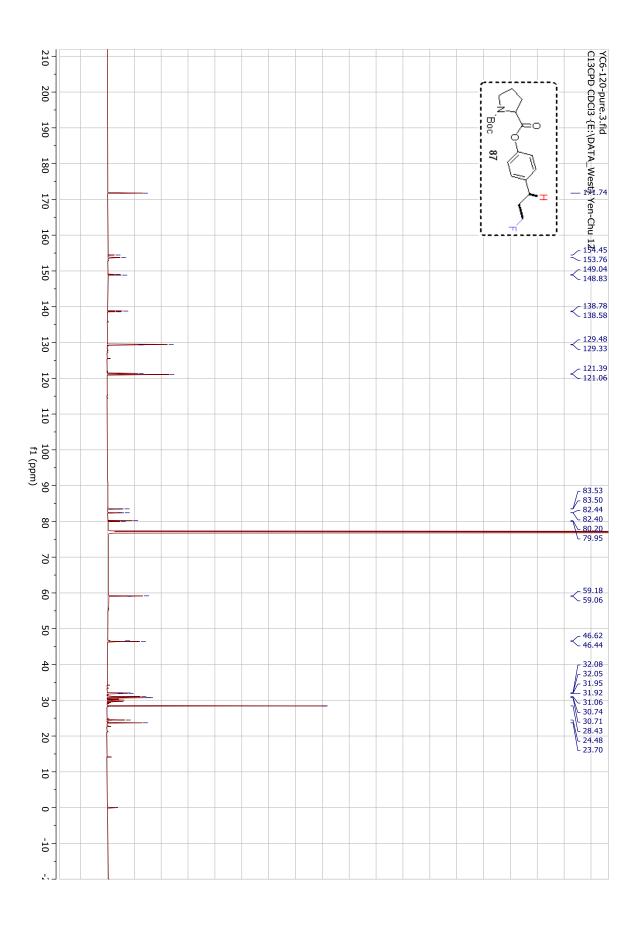


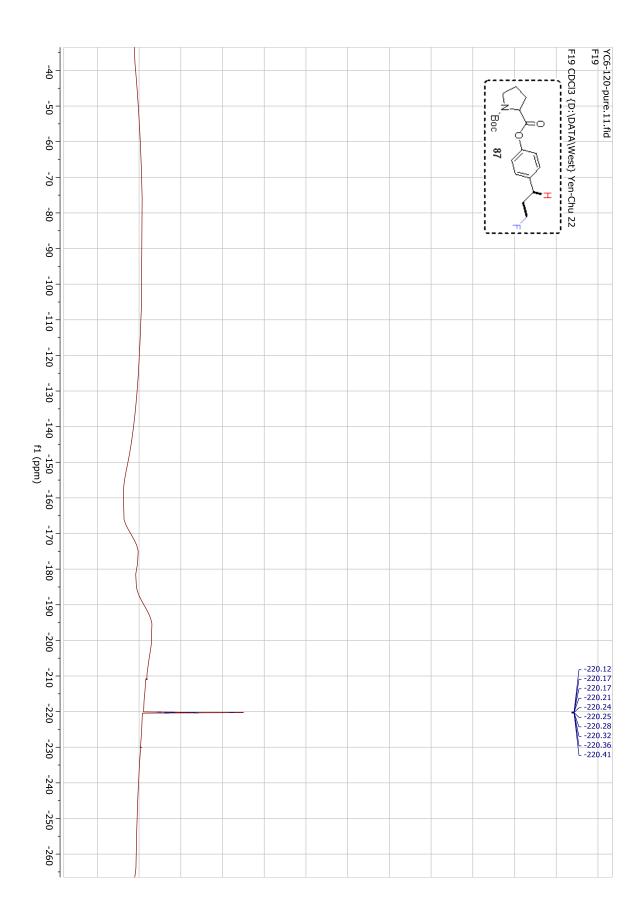


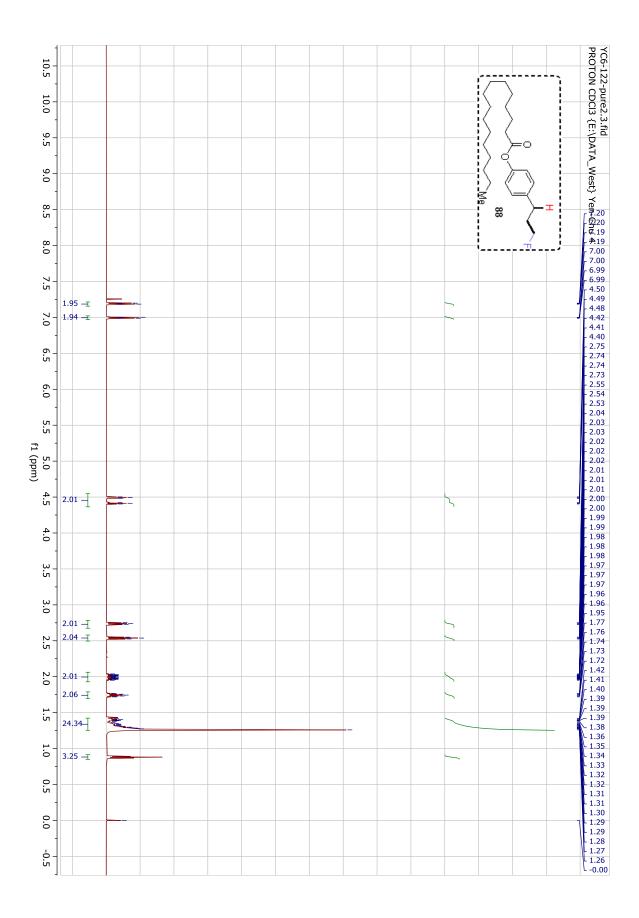




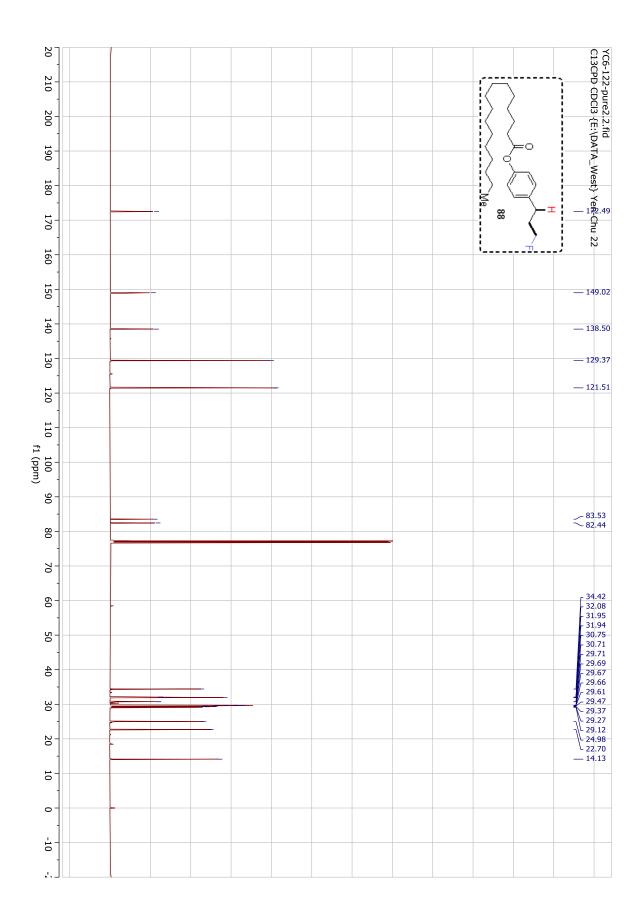




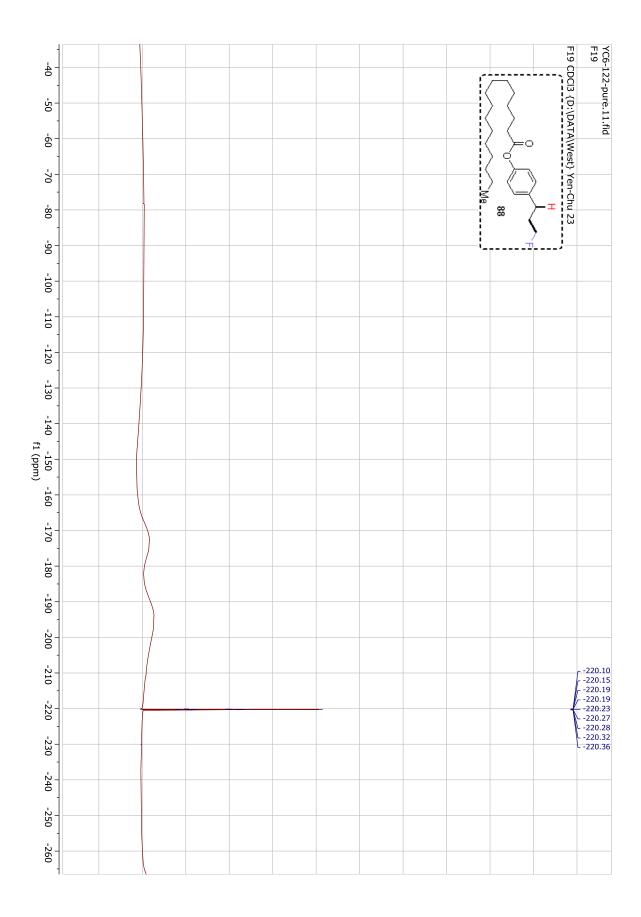


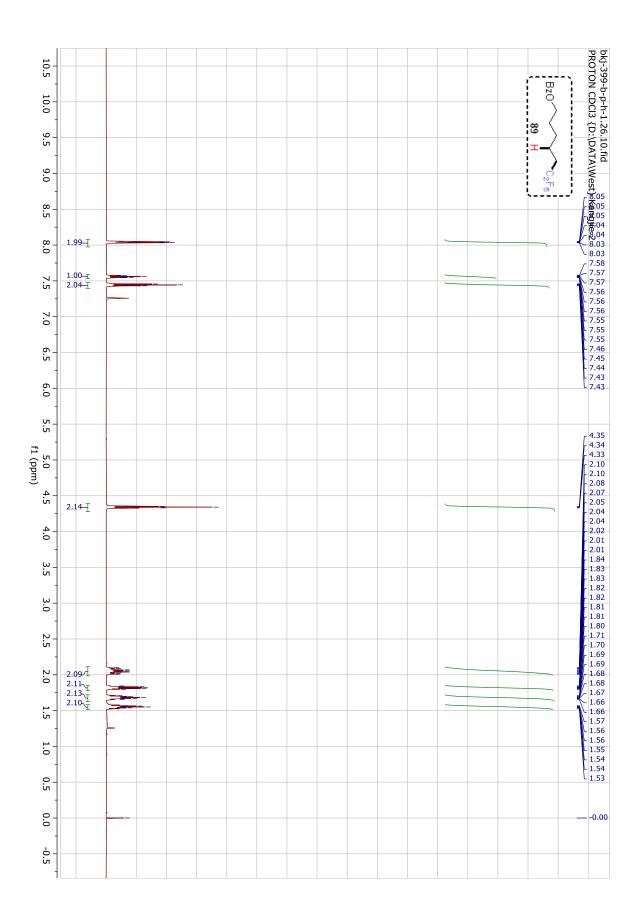




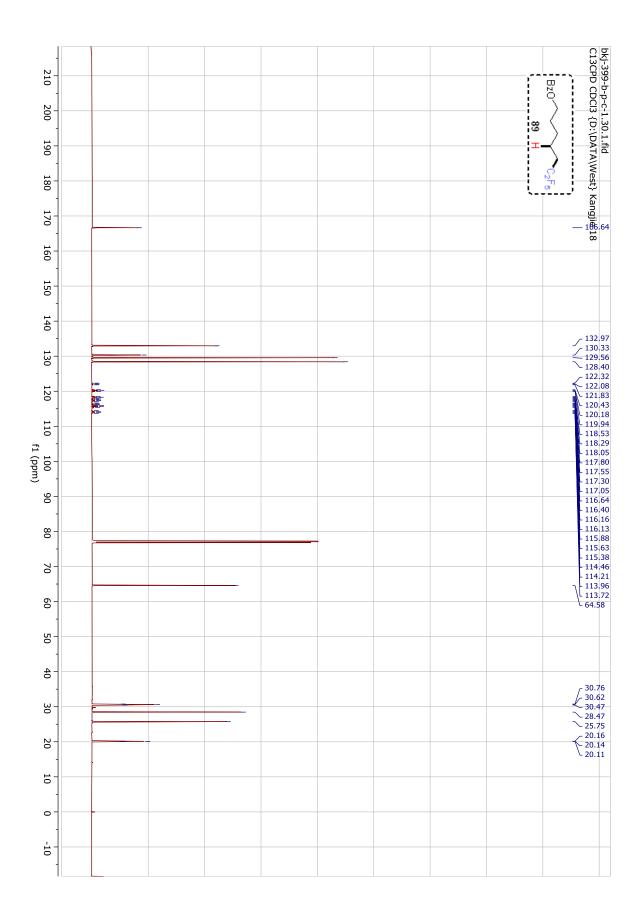


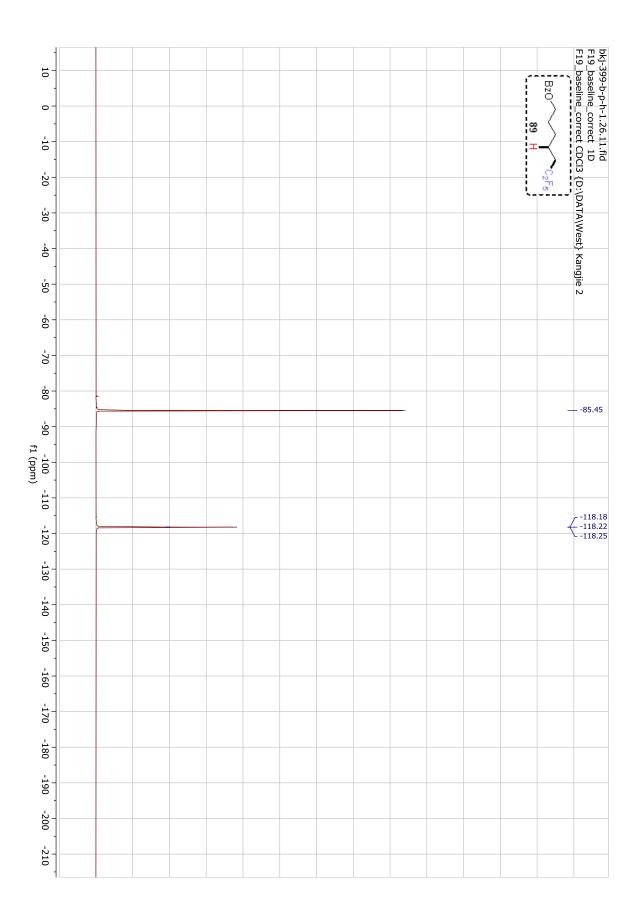




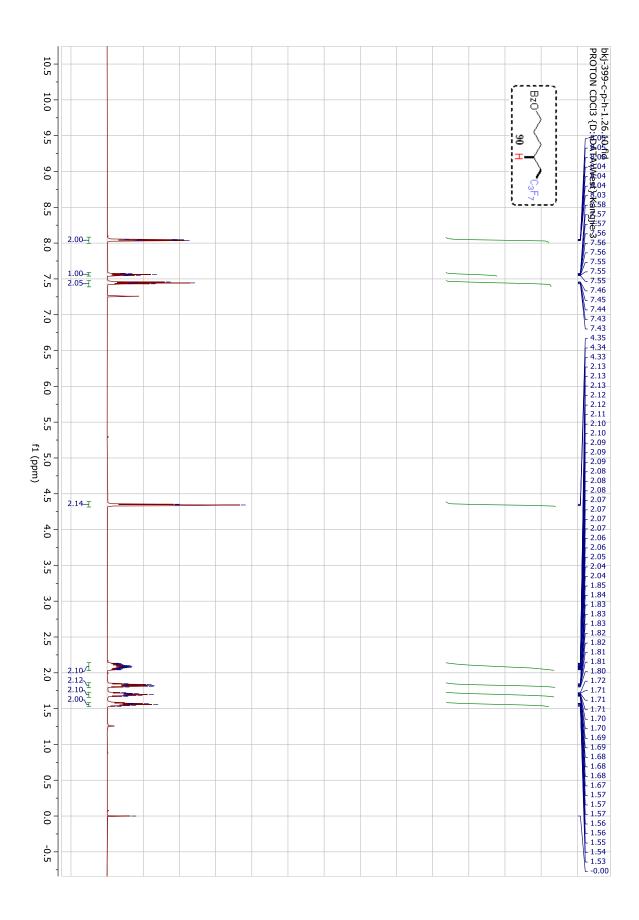




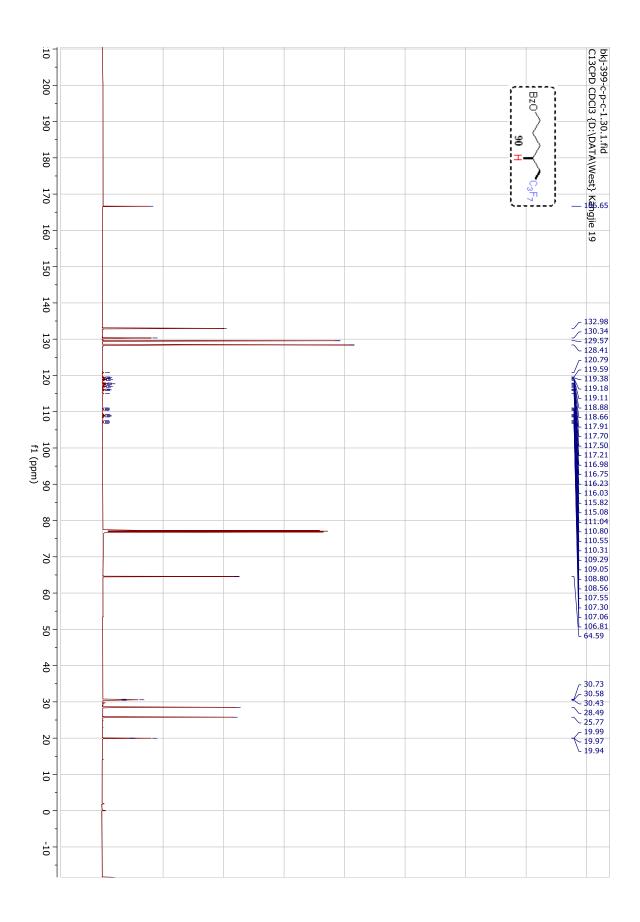




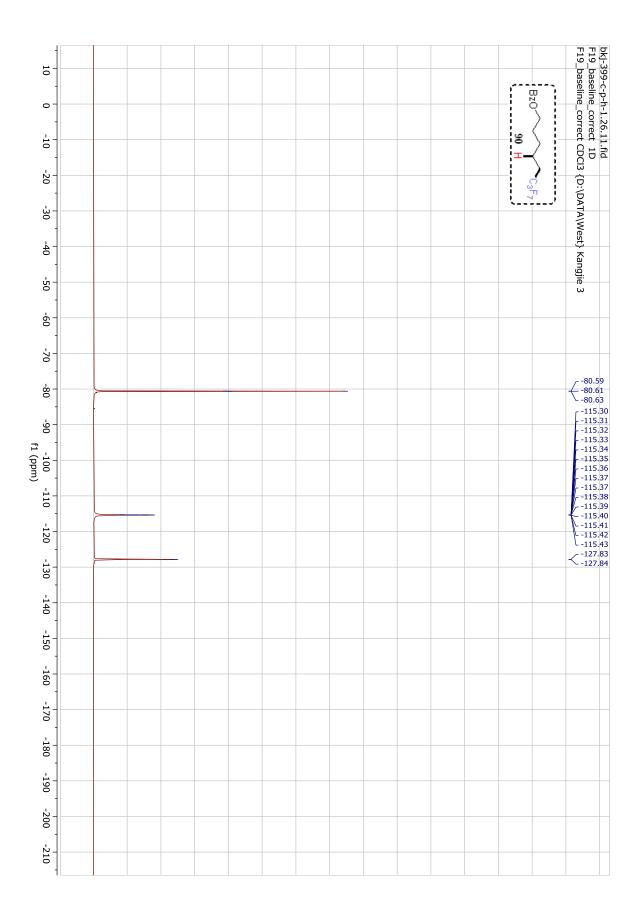


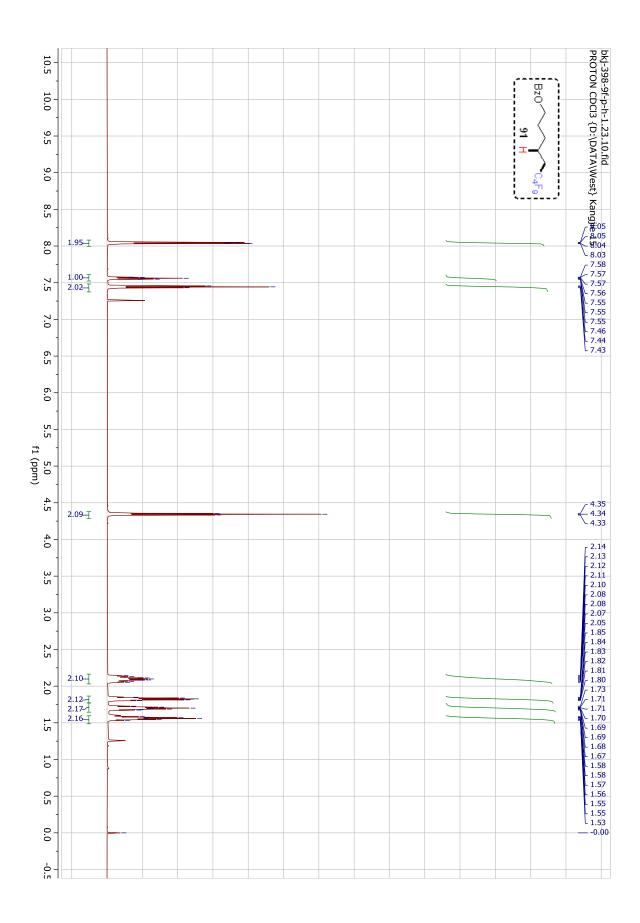




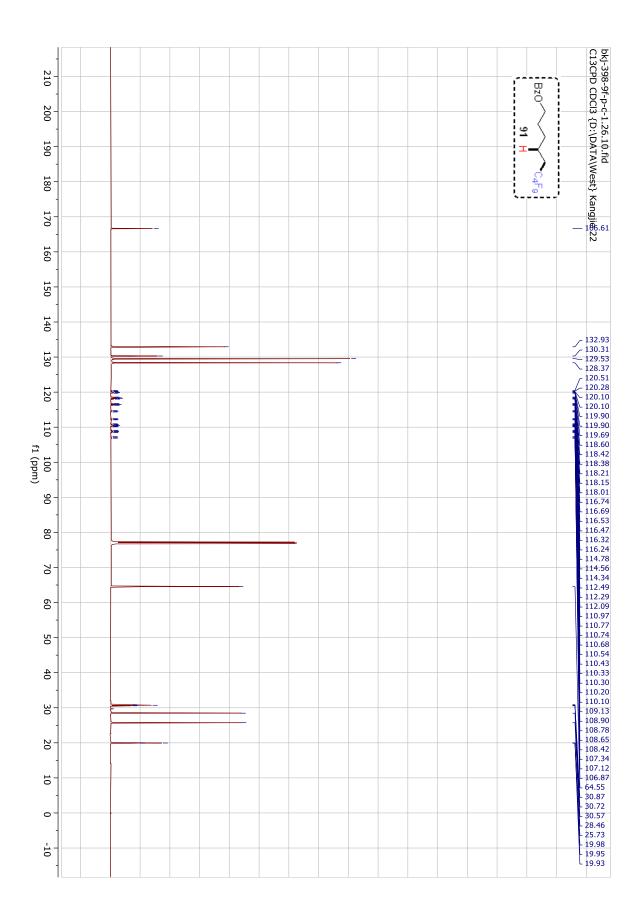




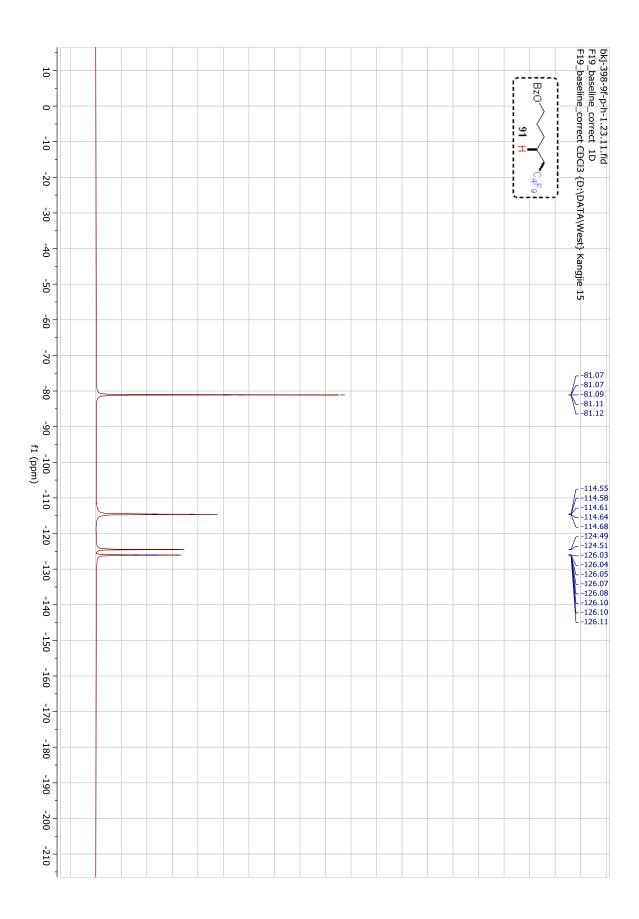


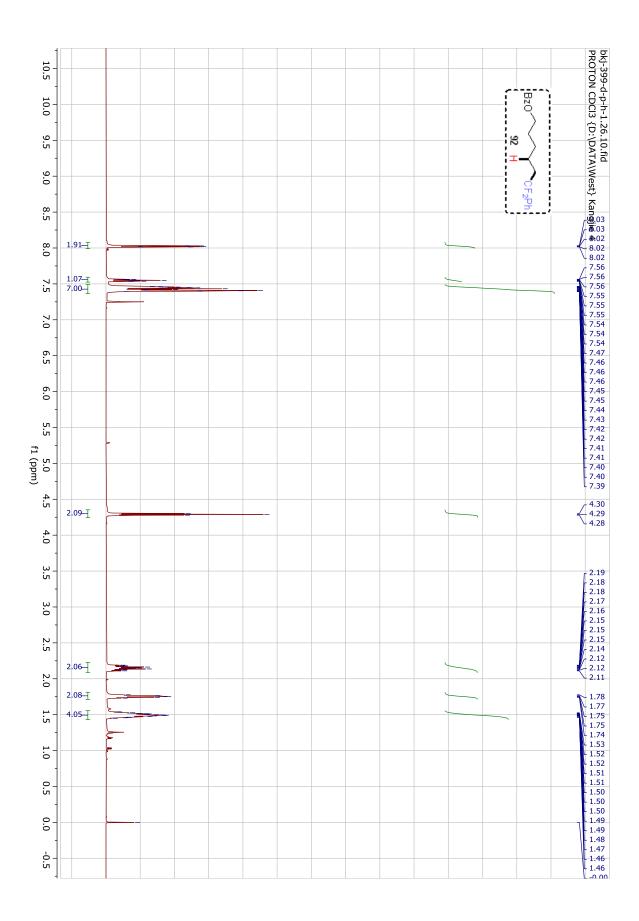




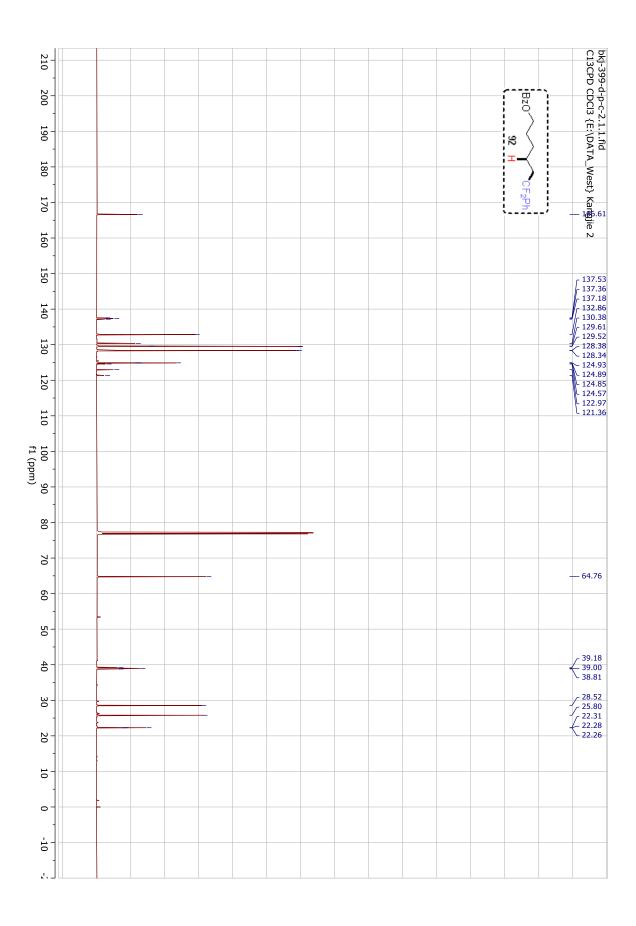


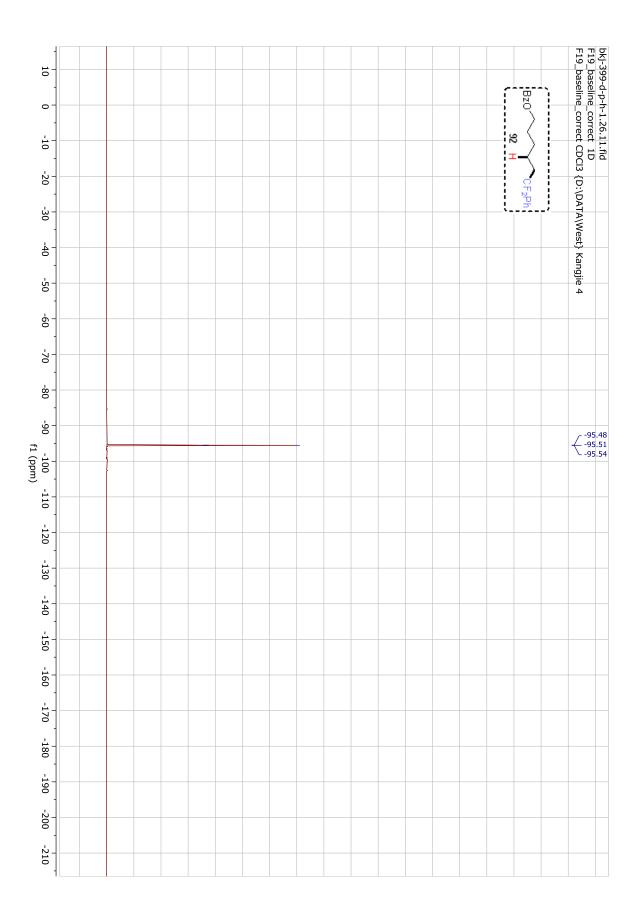




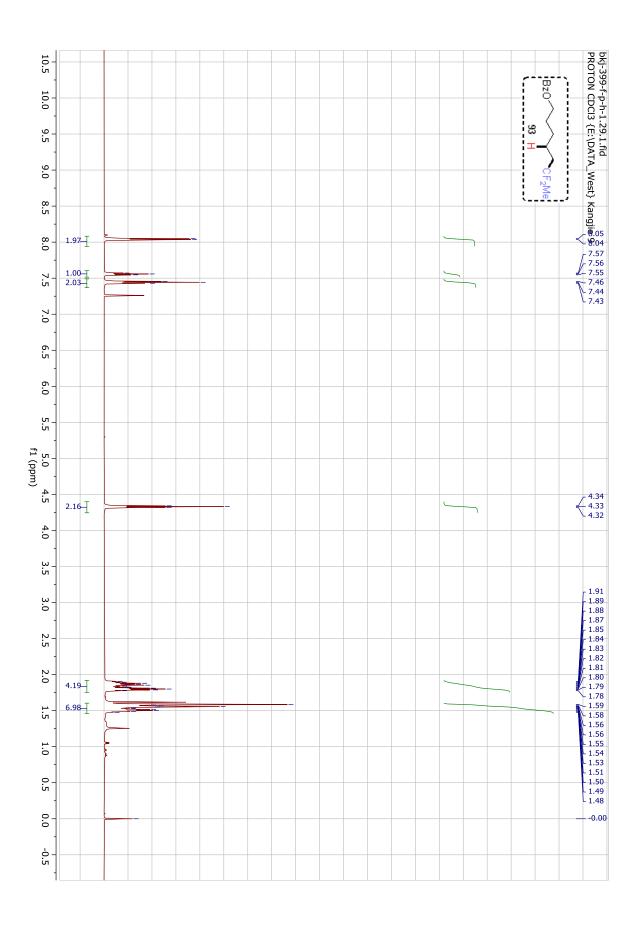




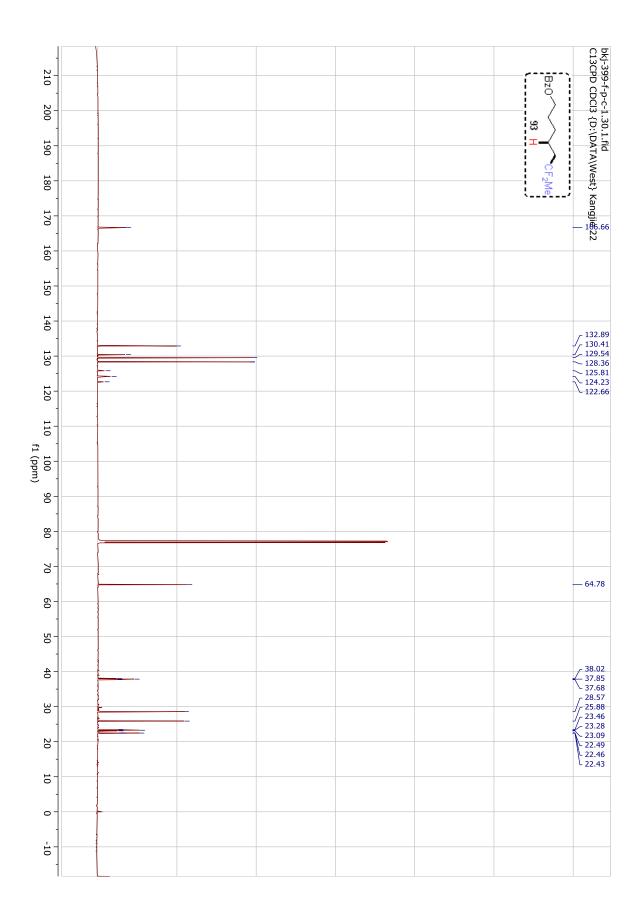


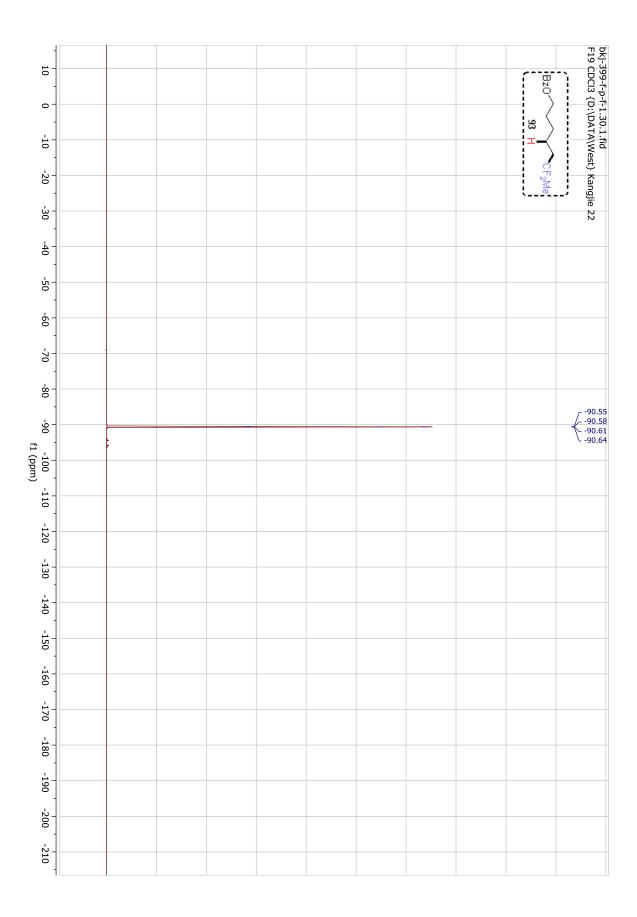




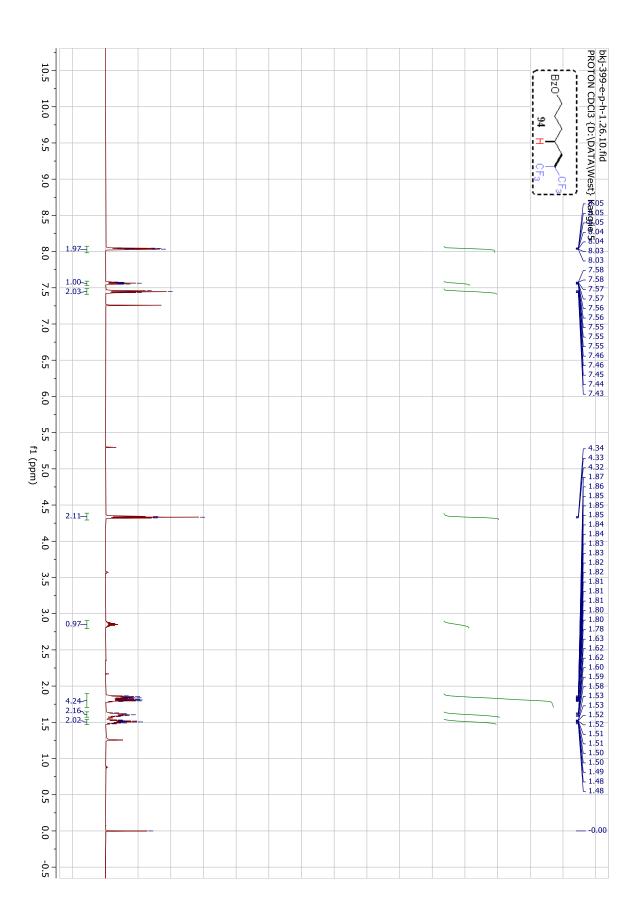




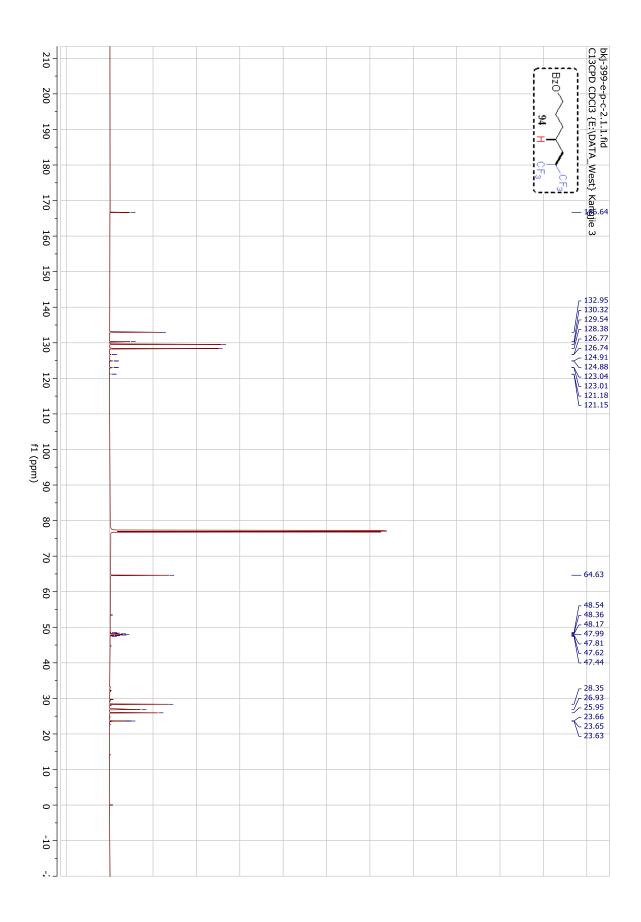


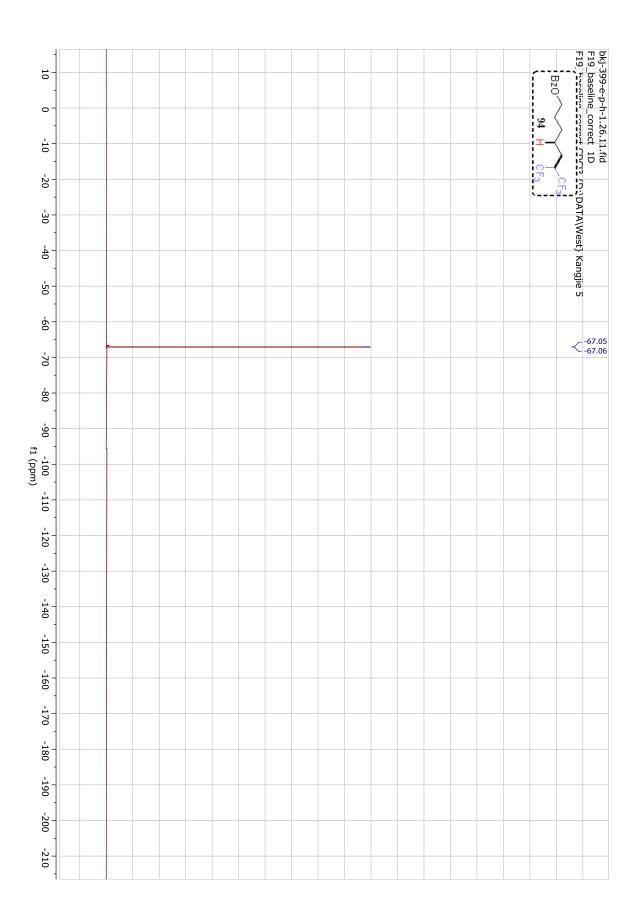


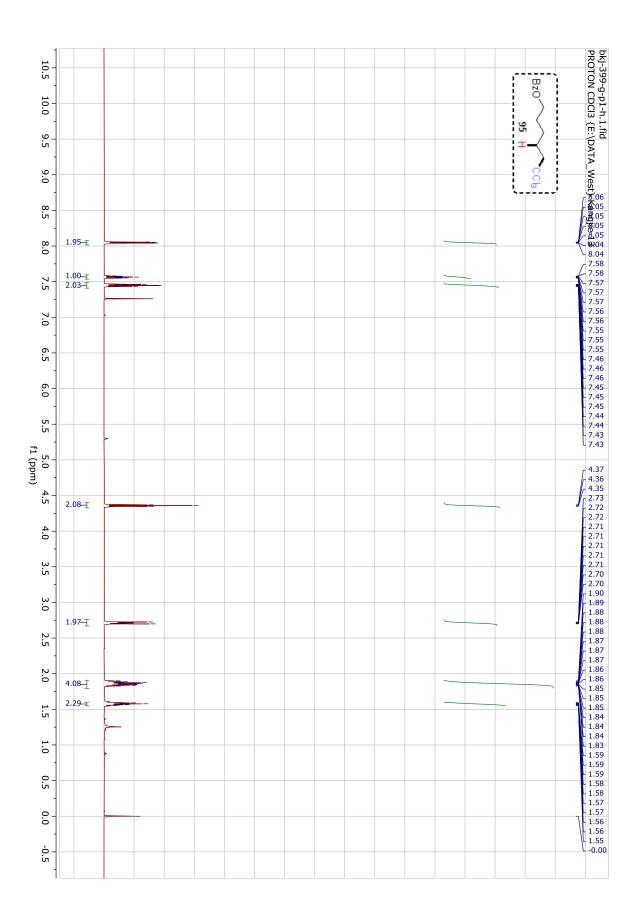


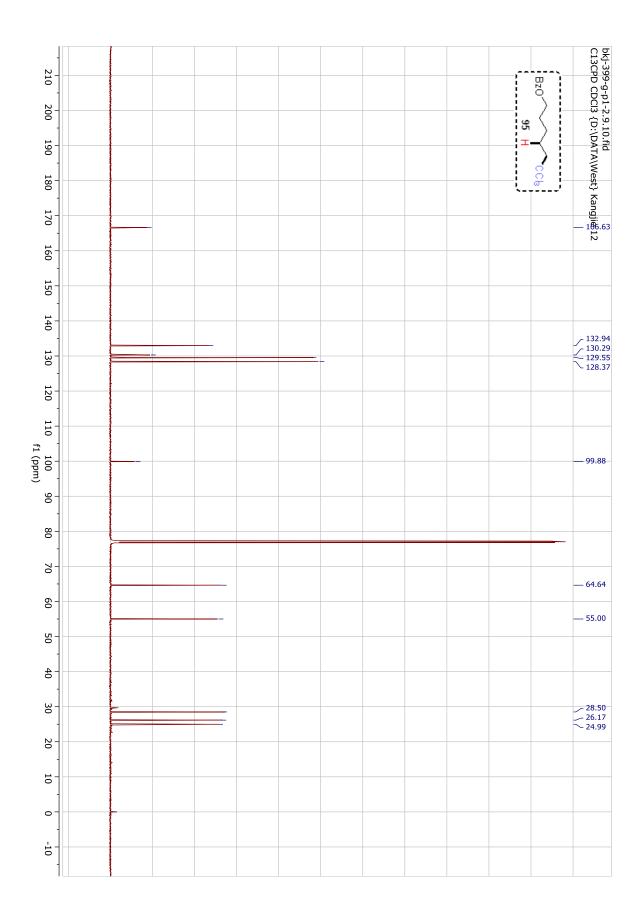


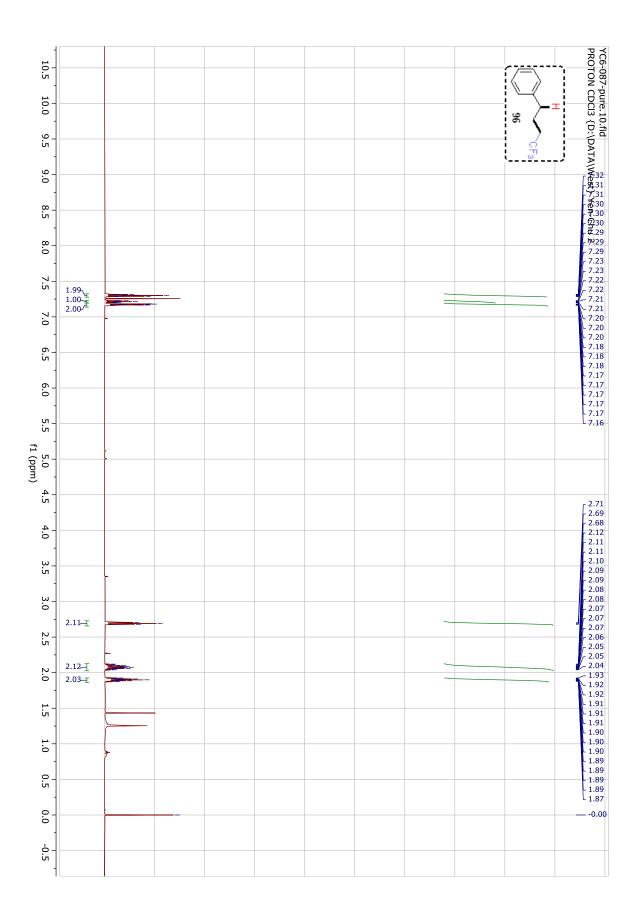


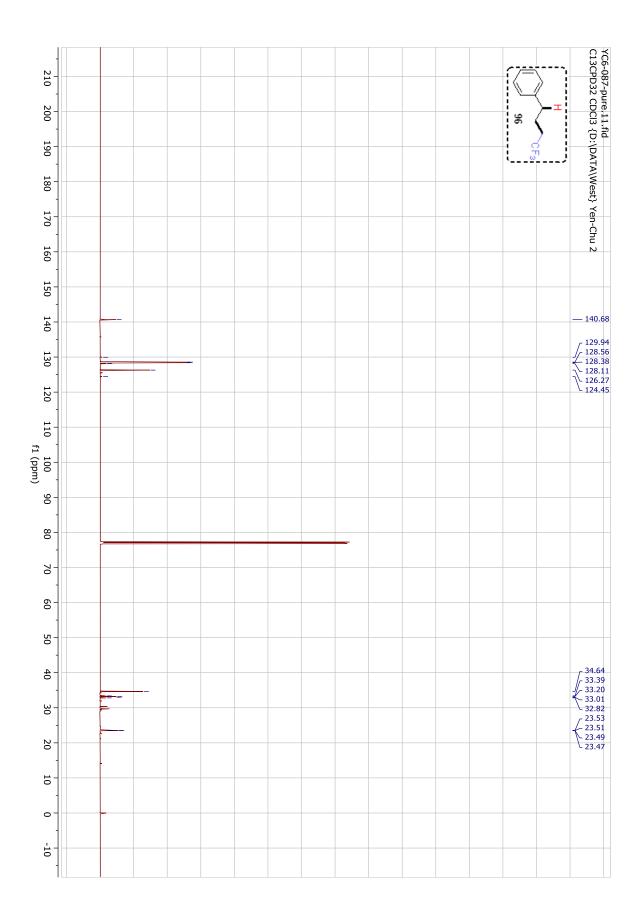


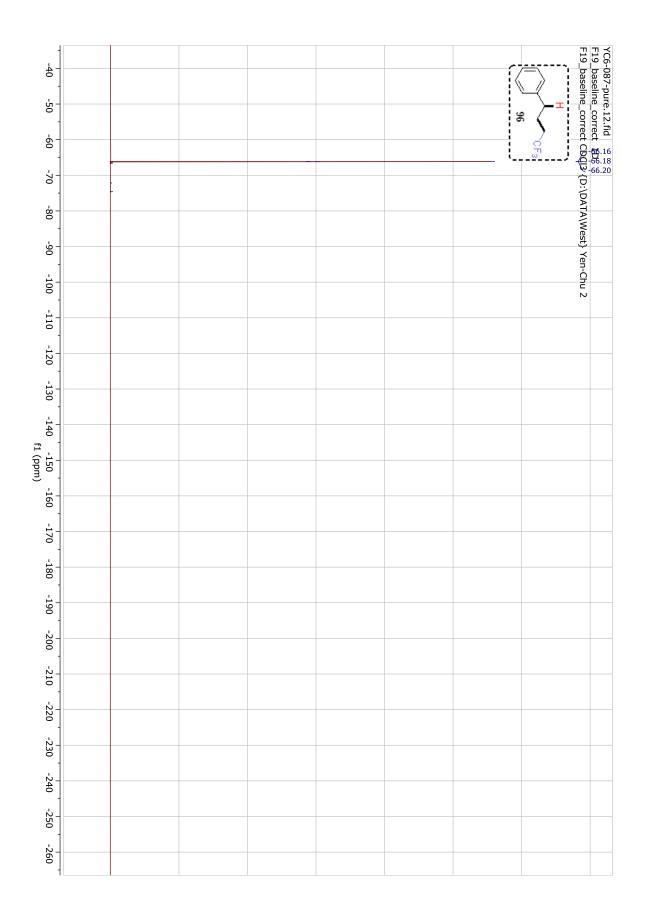


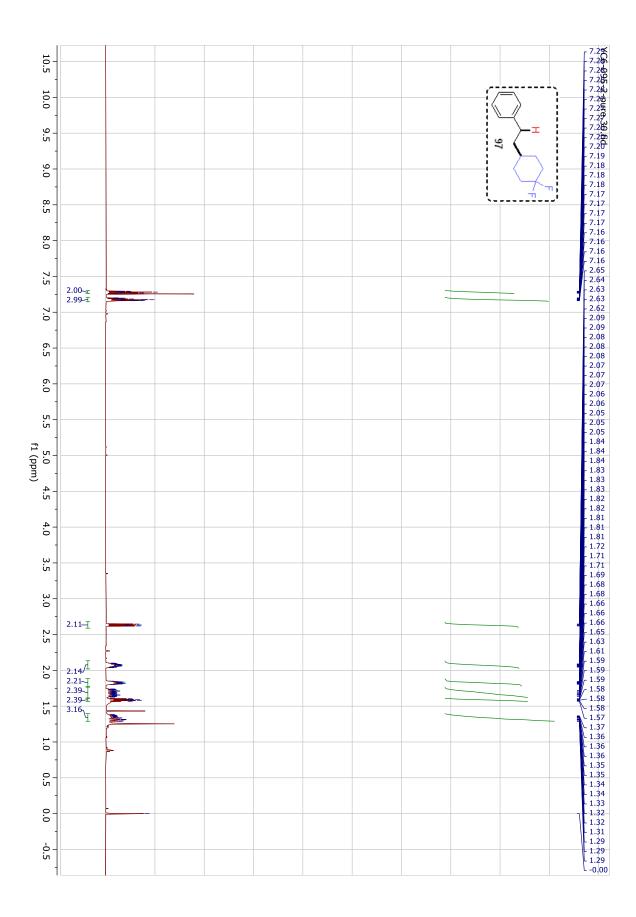


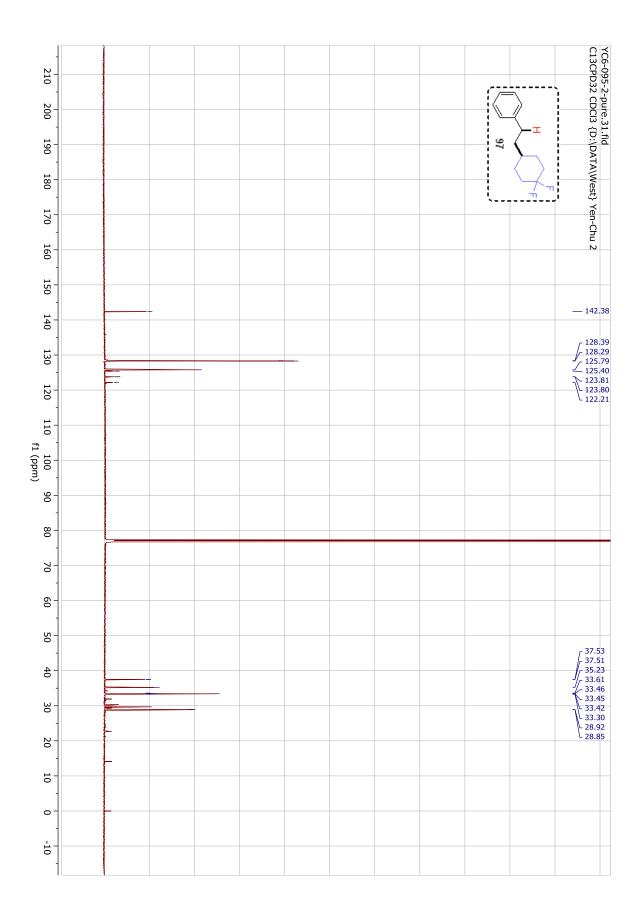


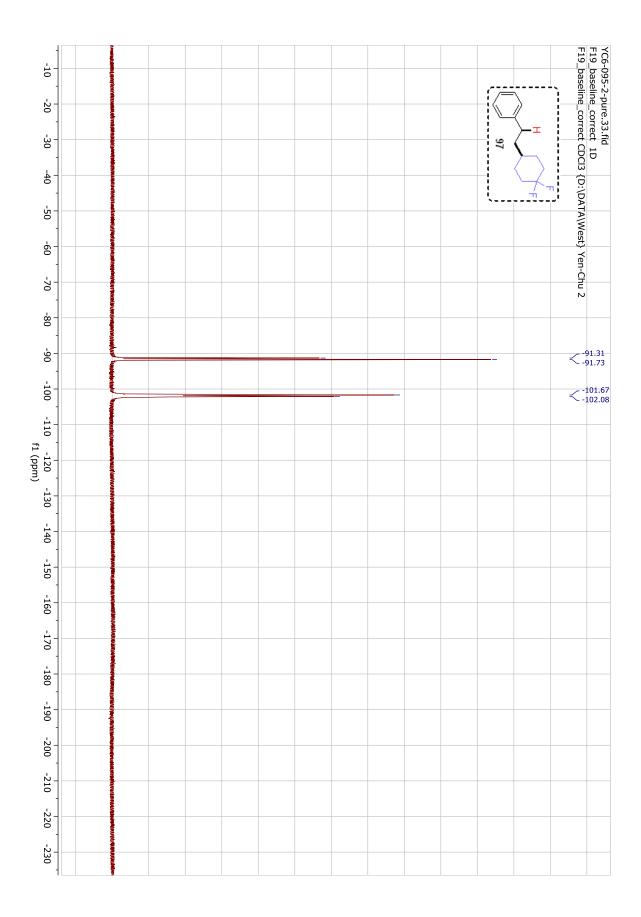


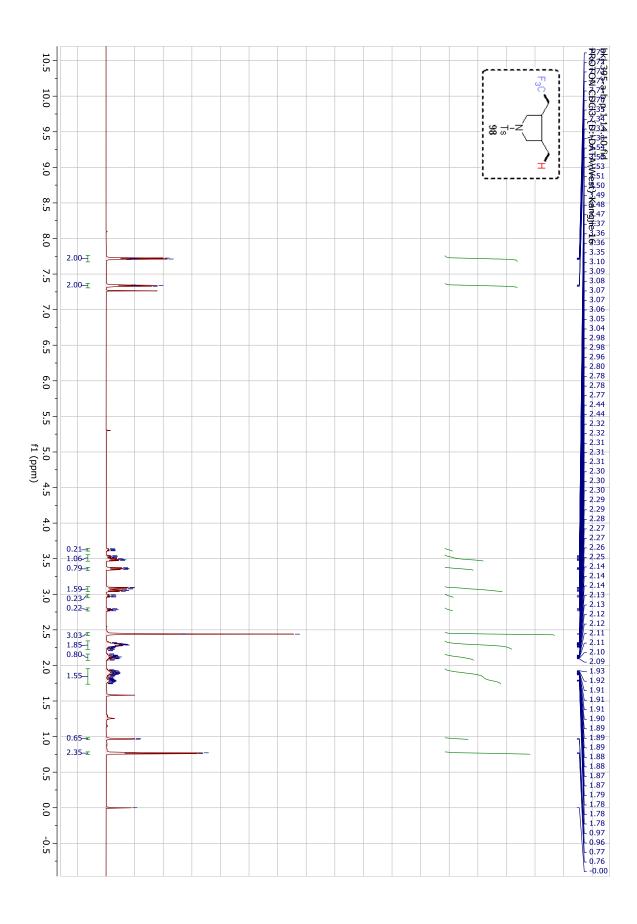


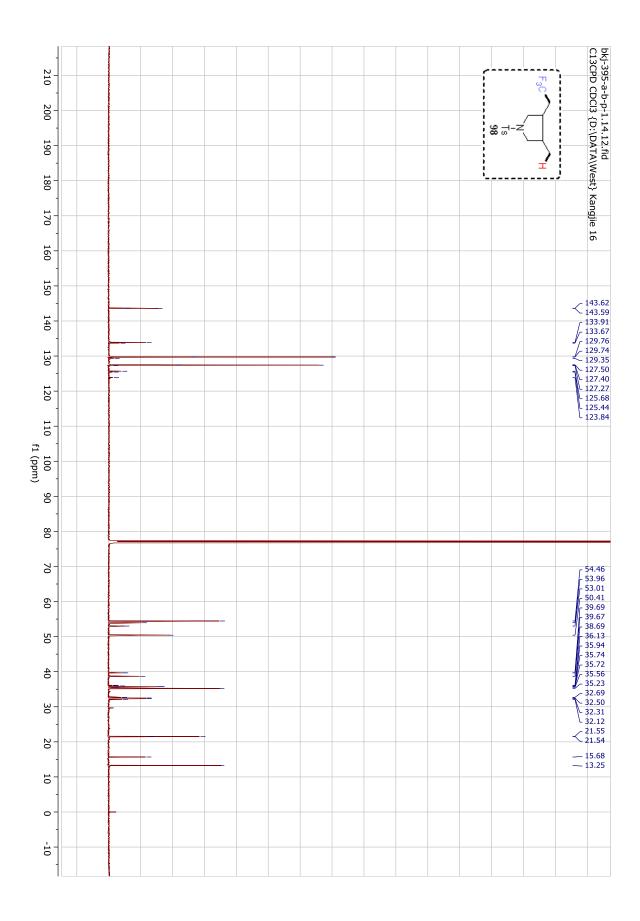


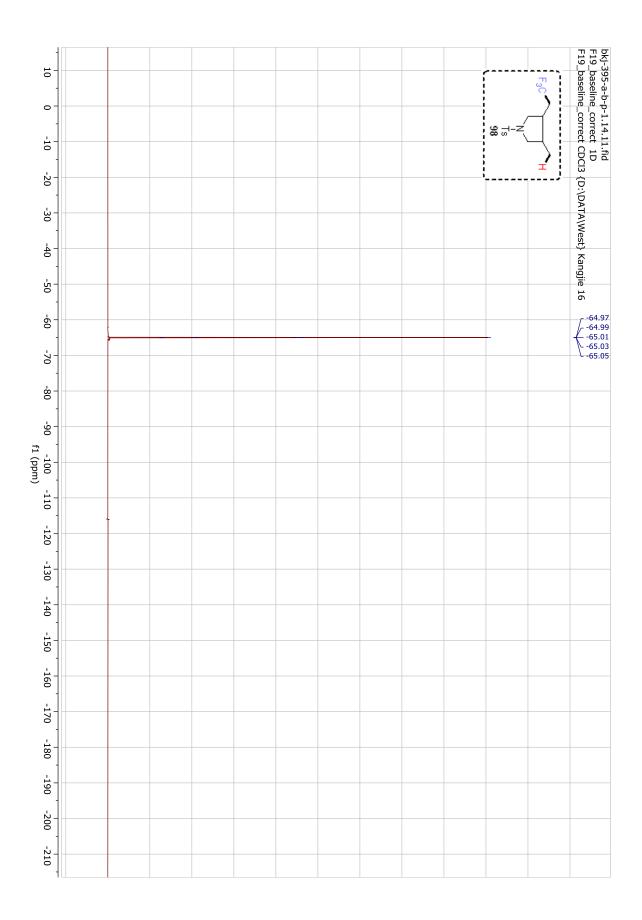




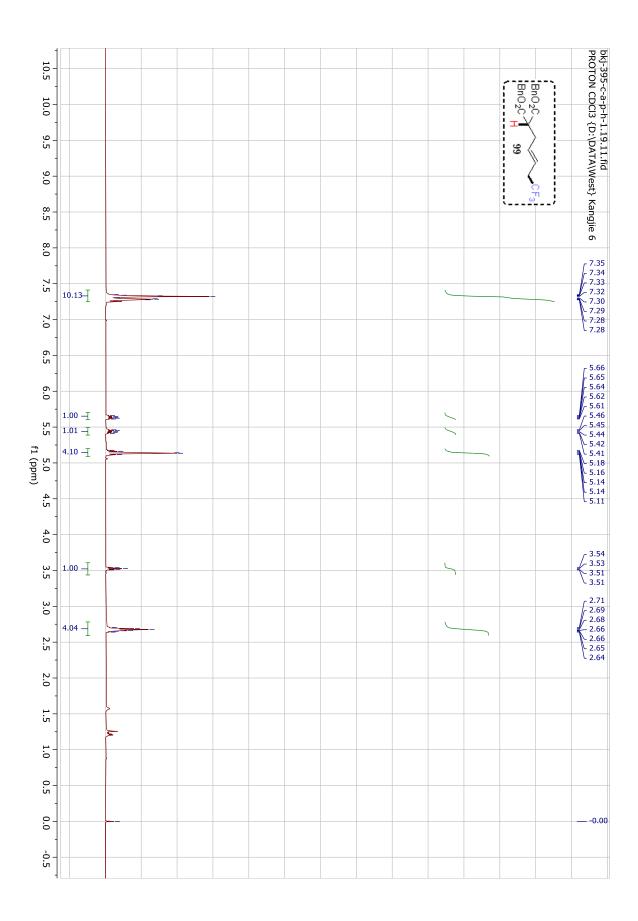




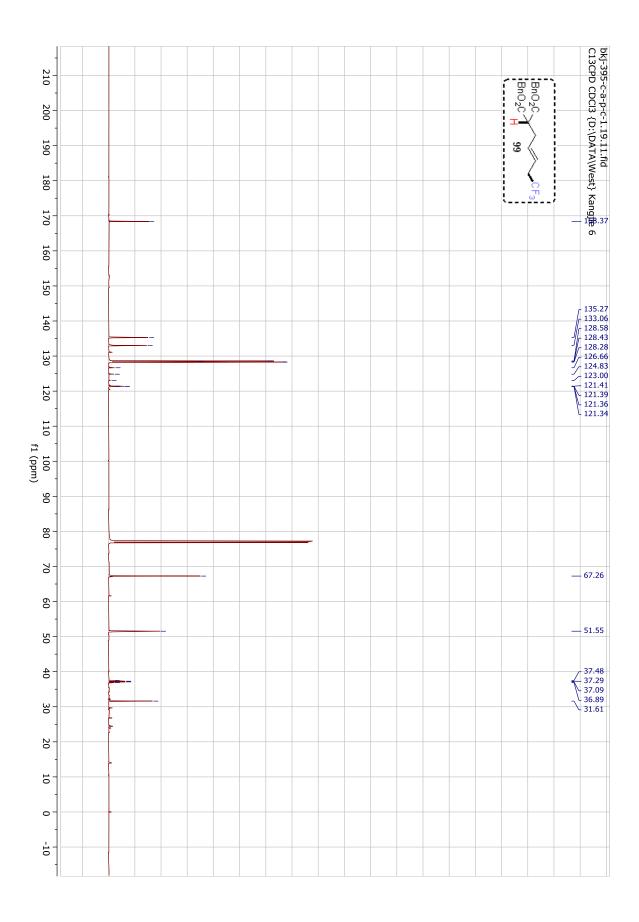




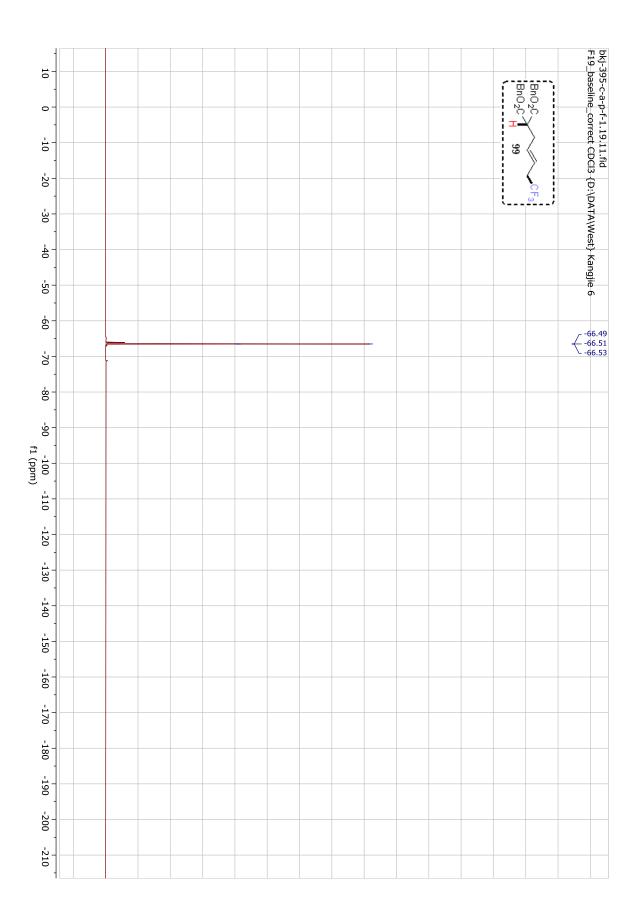












IV. Supplemental Reference

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