Supporting Information for

Comparison of the effects of perfluoroalkyl and alkyl groups on cellular uptake in short peptides

Koji Kadota, Ai Kohata, Shinsuke Sando, Jumpei Morimoto, Kohsuke Aikawa, and Takashi Okazoe

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General information

Materials and instruments

Reagents were purchased from suppliers and used without further purification. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on JNM-ECZ400S (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz, ^{19}F NMR: 376 MHz) or on ECZ500R (^{1}H NMR: 500 MHz, ^{13}C NMR: 125 MHz, ^{19}F NMR: 470 MHz spectrometers (JEOL) at ambient temperature. Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral). High-resolution mass (HRMS) spectra were measured on JMS-T100LP spectrometer (JEOL) in the electron spray ionization time-of-flight (ESI-TOF) mode. IR spectra were measured on IRSpirit spectrometer (Shimadzu). Zetasizer μV (Malvern) was used for DLS measurement containing a 60 mW laser with an operating wavelength of 830 nm. Zeta-potential was measured by Zetasizer pro red (Malvern) containing a 10 mW laser with an operating wavelength of 633 nm. Leica TCS SP8 (Leica) was used for microscopic observation. MALDI-TOF MS analysis was performed on autoflex max (Bruker Daltonics).

Abbreviations

DMEM; Dulbecco's Modified Eagle Medium, D-PBS: Dulbecco's Phosphate Buffer Saline, EDTA; ethylenediaminetetraacetic acid, FBS; fetal bovine serum, GFP; green fluorescent protein, CLSM; confocal laser scanning microscope, ITC; isothermal titration calorimetry, DMSO; dimethyl sulfoxide, Et_2O; diethyl ether, $MgSO_4$; magnesium sulfate, EtOAc; ethyl acetate, $NaHCO_3$; sodium bicarbonate, CO_2 All; allyl ester, DCM; dichloromethane, MeOH; methanol THF; tetrahydrofuran, DMF; dimethylformamide, TIPS; triisopropylsilane, TFA; trifluoroacetic acid, COMU; (1-cyano-2-ethoxy-2-oxoethylidenaminooxy)dimethylamino-morpholino-carbenium hexafluorophosphate, Oxyma: ethyl 2-cyano-2-(hydroxyimino)acetate, DIPEA; *N*,*N*-diisopropylethylamine, $PhSiH_3$; phenylsilane, HCl; hydrogen chloride, DMF; *N*,*N*-

dimethylformamide, TFA; trifluoroacetic acid

Methods

Cell culture

HeLa cells were cultured in DMEM (Nacalai Tesque) supplemented with 10% FBS (v/v) heat-inactivated fetal bovine serum (FBS) and antibiotic-antimycotic mixed solution (Nacalai Tesque) at 37 °C in a humidified incubator containing 5% CO_2 respectively. A549 and HeLa cells were provided by the RIKEN BRC through the National Bio-Resource Project of the MEXT, Japan.

Evaluation of cellular uptake by flow cytometry

HeLa cells (2.0×10^4 cells) were seeded in a 96-well culture plate and incubated in DMEM (10% FBS) for 24 h at 37 °C, 5% CO_2. The cell samples were rinsed with D-PBS three times (100 μL) and incubated with 100 μL of serum-free or DMEM (10% FBS) containing 150 nM of AF_{647}-R_F/R_H-tripeptides at 37 °C or 4 °C, 5% CO_2 for 1 h. After the incubation, the cells were rinsed with D-PBS three times (500 μL) and incubated in trypsin-EDTA (30 μL) for 5 min. The cells were diluted with DMEM (10% FBS) (200 μL), and the resultant suspension was centrifuged at 200 × g for 3 min. After the removal of the supernatant, the obtained cell pellet was resuspended in PBS (400 μL) and subjected to a flow cytometer. The fluorescence was quantified by flow cytometer.

Evaluation of cellular uptake with endocytosis inhibitor

HeLa cells (1.0×10^4 cells) were seeded in a 96-well culture plate and incubated in DMEM (10% FBS) for 24 h incubation at 37 °C, 5% CO_2. The cell samples were rinsed with D-PBS three times (100 μL) and preincubated in DMEM (10% FBS) (100 μL) containing an endocytosis inhibitor; EIPA (10 μM), GEN (700 μM), CPZ (10 μM), and methyl-β-cyclodextrin (1 mM) for 30 min, 37 ºC, 5% CO_2. The cell samples were rinsed with D-PBS three times (200 μL). Then, the samples were incubated with 100 μL of serum-free DMEM containing the endocytosis inhibitor and 150

nM of AF_{647}-R_F/R_H-tripeptides at 37 °C, 5% CO_2 for 1 h. After the incubation, the cells were rinsed with D-PBS three times (500 μL) and incubated in trypsin-EDTA (30 μL) for 5 min at 37 °C. The cells were diluted with DMEM (10% FBS) (200 μL), and the resultant suspension was centrifuged at 200 × g for 3 min. After the removal of the supernatant, the obtained cell pellet was resuspended in PBS (400 μL) and subjected to a flow cytometer. The fluorescence was quantified by flow cytometry.

DLS measurement

150 nM of AF_{647}-R_F-tripeptide (R_F = C_8F_{17}) and AF_{647}-R_H-tripeptide (R_H = $C_{12}H_{25}$) in DMEM (10% FBS) were prepared. The solution was measured at 37 ºC by Zetasizer μV after 0, 60, 90, and 120 min incubation.

Observation of HeLa cells treated with AF_{647}-R_F/R_H-tripeptides under confocal laser scanning microscopy (CLSM)

HeLa cells (2.0×10^4 cells) were seeded in an 8-well glass chamber and incubated in DMEM (10% FBS) for 24 h at 37 °C, 5% CO_2. The cells were rinsed with D-PBS three times (500 μL) and incubated with serum-free DMEM (500 μL) containing 150 nM of AF_{647}-R_F/R_H-tripeptides at 37 °C, 5% CO_2 for 1 h. After the incubation, the cells were rinsed with D-PBS three times (500 μL) and stained by Hoechst 33342 for 10 min. 500 μL of DMEM (10% FBS) was added to each well. The cells were observed by CLSM. Hoechst 33342: λ_{ex} = 408 nm, λ_{obs} = 430–470 nm, $Alexa_{647}$: λ_{ex} = 638 nm, λ_{obs} = 650–700 nm.

Evaluating colocalization of AF_{647}-R_F/R_H-tripeptides with Golgi apparatus

HeLa cells (1.0×10^4 cells) were seeded in an 8-well glass chamber and incubated in DMEM (10% FBS) for 24 h at 37 °C, 5% CO_2. After washing the cell with D-PBS three times, 8 μL of

CellLight™ Golgi-GFP BacMam reagent (Invitrogen, C10592) was added to the DMEM (10% FBS) and incubated for 16 h. The cell samples were rinsed with D-PBS three times (500 μL) and incubated with serum-free DMEM (500 μL) containing 150 nM of AF_{647}-R_F/R_H-tripeptides at 37 °C, 5% CO_2 for 1 h. After the incubation, the cells were rinsed with D-PBS three times (500 μL) and stained by 500 μL of D-PBS containing 2 μg/mL Hoechst 33342 (Dojindo, H342) for 15 min. 500 μL of DMEM (10% FBS) was added to each well. The cells were observed by CLSM. GFP: λ_{ex} = 488 nm, λ_{obs} = 500–550 nm, Hoechst 33342: λ_{ex} = 408 nm, λ_{obs} = 430–470 nm, $Alexa_{647}$: λ_{ex} = 638 nm, λ_{obs} = 650–700 nm.

Evaluating colocalization of AF_{647}-R_F/R_H-tripeptides with lysosome

HeLa cells (2.0×10^4 cells) were seeded in an 8-well glass chamber and incubated in DMEM (10% FBS) for 24 h at 37 °C, 5% CO_2. The cell samples were rinsed with D-PBS three times (500 μL) and incubated with serum-free DMEM (500 μL) containing 150 nM of AF_{647}-R_F-tripeptides at 37 °C, 5% CO_2 for 1 h. After the incubation, the cells were rinsed with D-PBS three times (500 μL) and stained by 500 μL of D-PBS containing Hoechst 33342 (2 μg/mL) (Dojindo, H342), and LysoTracker Green (75 μM) (Invitrogen, L7526) for 10 min. 500 μL of DMEM (10% FBS) was added to each well. The cells were observed by CLSM. LysoTracker Green: λ_{ex} = 488 nm λ_{obs} = 500–550 nm, Hoechst 33342: λ_{ex} = 408 nm λ_{obs} = 430–470 nm, $Alexa_{647}$: λ_{ex} = 638 nm λ_{obs} = 650–700 nm.

Cytotoxicity evaluation

HeLa cells (5.0×10^3 cells) were seeded in a 96-well culture plate and incubated in DMEM (10% FBS) for 24 h incubation at 37 °C, 5% CO_2. The cell samples were rinsed with 100 μL of D-PBS three times and incubated with 100 μL of peptide sample in DMEM without 10% FBS at 37 °C,

5% CO_2 for 1h. After the incubation, the cells were rinsed with D-PBS three times (100 μL), and then 100 μ L of DMEM containing 10% FBS and 10 μL of Cell Counting Kit-8 (CCK-8) solution (Dojindo) was added to each well and incubated for 2 h. The absorbance at 450 nm of each sample was measured by a microplate reader (Infinite M200 Pro, Tecan).

Preparation of giant unilamellar vesicles (GUVs) for confocal microscopy

GUVs were prepared following the method given in reference[1]. 1 mg/mL of 2,3-dioleoyl-glycero-1-phosphocholine (DOPC) in diethyl ether and 300 mM of sucrose in distilled water were prepared. 500 μL of each solution were combined and vigorously mixed in a 1.5 mL microtube. The microtube was centrifuged at 20,000 × *g*, at 20 ºC for 1 min. The top organic phase and organic-water interface were removed. An aliquot (500 μL) of a 300 mM glucose solution was added to the bottom solution, and the microtube was repeatedly inverted for gentle mixing. The solution was gently centrifuged at 100 × *g*, at 20 ºC for 10 min. 100 μL of 300 nM peptide solution and 100 μL of liposome solution were mixed. The resultant suspension was loaded in slide glass using the edge-cut 1 mL micropipette tip, and then the cover glass was equipped. The GUVs were observed under a CLSM. $Alexa_{647}$: λ_{ex} = 638 nm, λ_{obs} = 650–700 nm.

Zeta potential measurement of liposome

To a round-bottom flask, 5 mg of DOPC and 2 mL of $CHCl_3$ were added. The solution was evaporated by a rotary evaporator and then dried in vacuo. After adding 1 mL of 300 mM sucrose solution to the flask, the flask was vigorously shaken. The resultant suspension was extruded by Avantir® Mini-extruder (Avanti) 20 times using a 100 nm polycarbonate membrane. 5 mM of liposome solution was prepared by adding 300 mM sucrose solution. The solution of AF_{647}-R_F/R_H-tripeptides (150 nM) and 50 μM of liposome solution was prepared, and the solution was equilibrated for 30 min at room temperature. Zeta potential of the liposome was measured by

Zetasizer Pro red using DTS1070 cell.

LogP measurement

Analysis was conducted on an HPLC system (Shimadzu LC20A) equipped with an octadecyl column (Shim-pack GIS C_{18} column 4.6 × 150 mm). Calibration and determination of $logP_{OW}$ were performed according to the guidelines[2]. Thiourea (t_0 standard), 2-butanone, benzonitrile, anisol, benzophenone, biphenyl. and triphenylamine were chosen as standards.[2]

Supplementary Figures and Tables

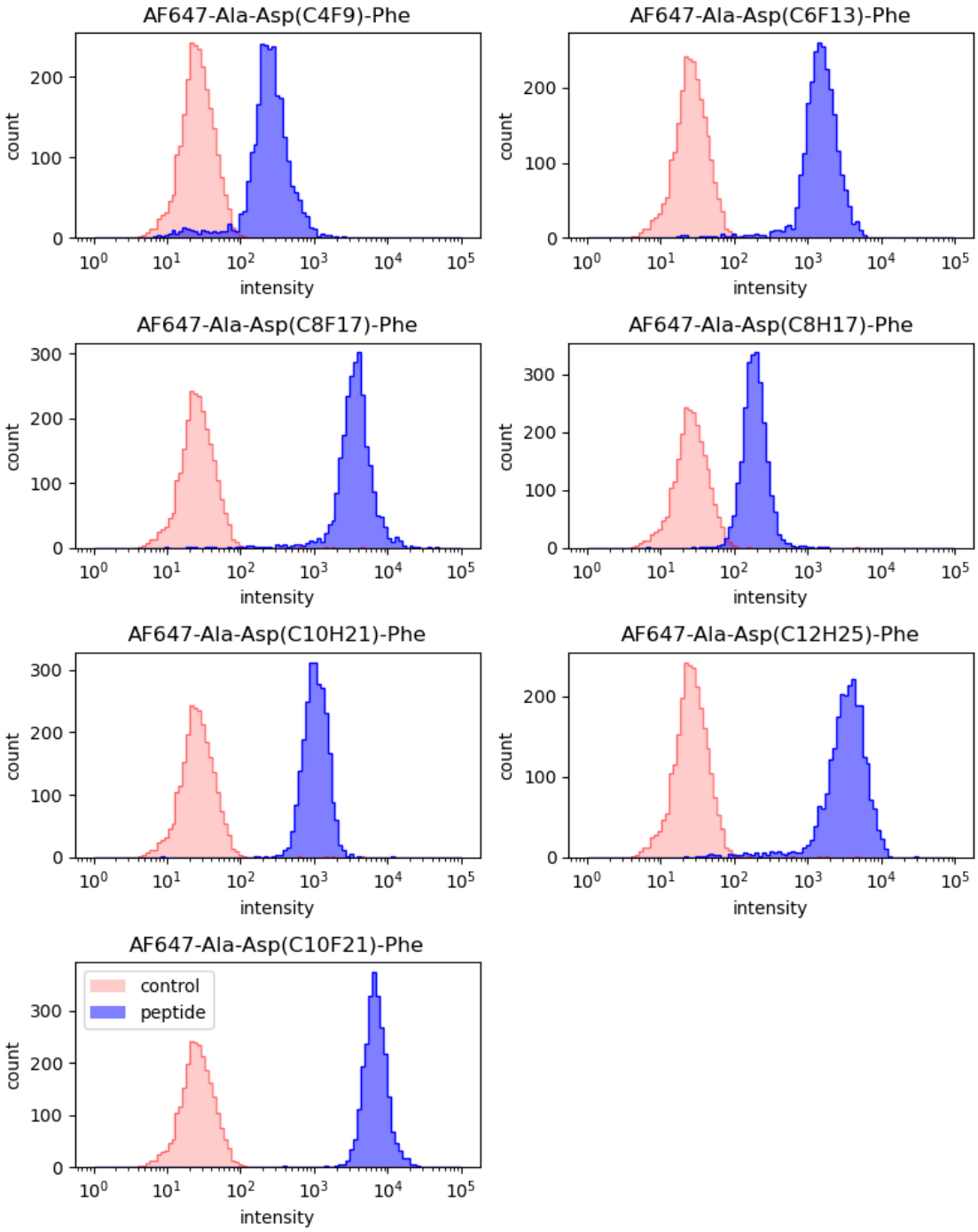


Fig. S1 Histograms of the fluorescence intensities of HeLa cells treated with AF_{647}-R_F/R_H-tripeptides. The experiment was conducted in triplicate and a representative result is shown.

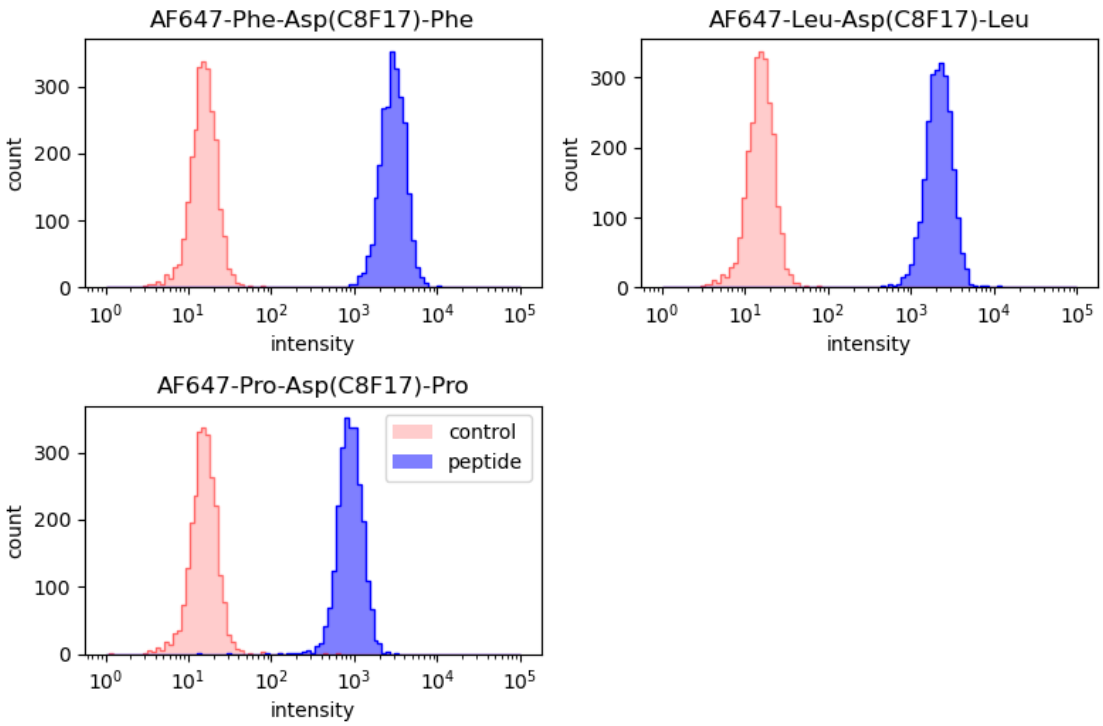


Fig. S2 Histograms of the fluorescence intensities of HeLa cells treated with AF_{647}-Z-Asp(C_8F_{17})-Z. Z represents Phe, Leu, or Pro. The experiment was conducted in triplicate and a representative result is shown.

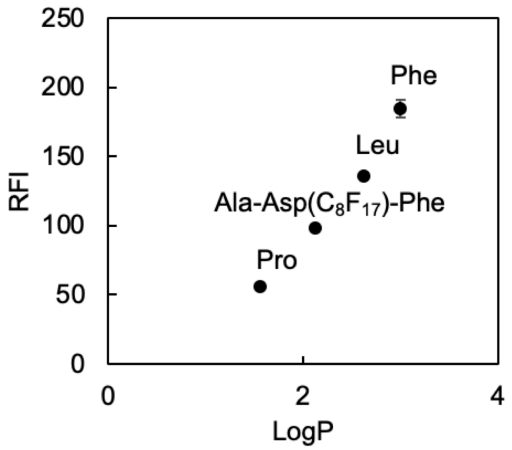


Fig. S3 Correlation between the relative fluorescence intensities of HeLa cells treated with AF_{647}-Z-Asp(C_8F_{17})-Z and LogP values of Z-Asp(C_8F_{17})-Z. Z represents Phe, Leu, or Pro. RFI = relative fluorescence intensity determined by flow cytometry. The experiment was conducted in triplicate. LogP values were determined by the HPLC method shown in Fig. S11 and S12 and Table S2 and S3.

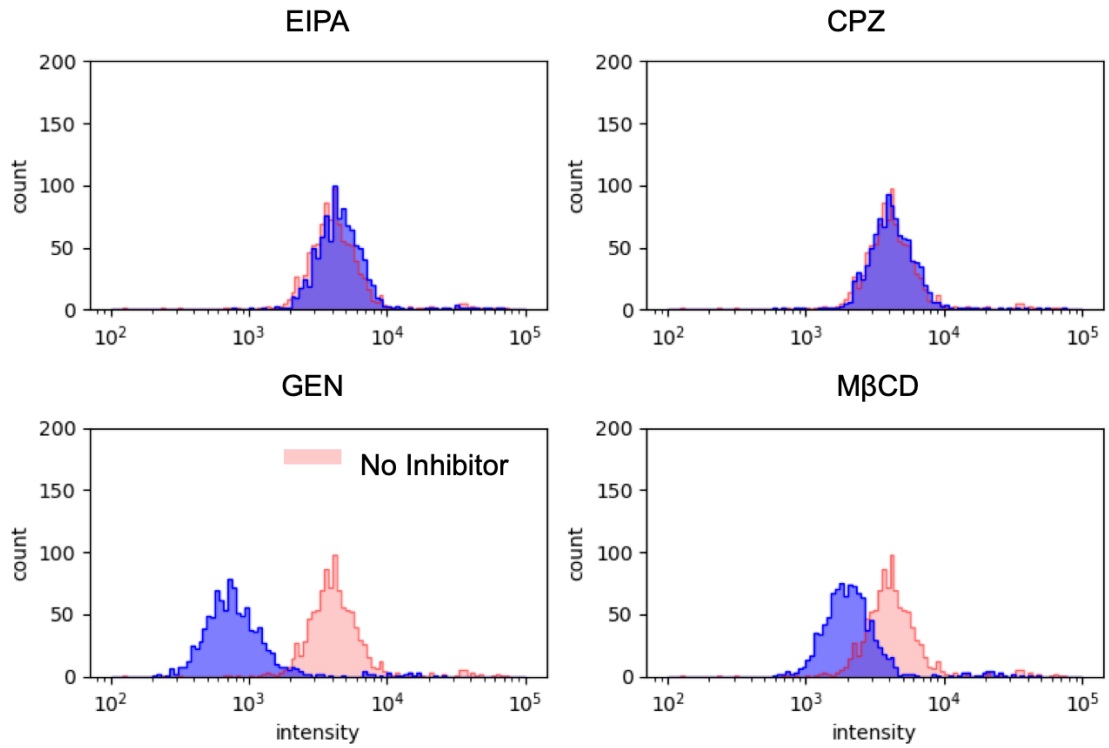


Fig. S4 Histograms of the fluorescence intensities of HeLa cells treated with AF_{647}-Ala-Asp($C_{12}H_{25}$)-Phe. The experiment was conducted in triplicate and a representative result is shown.

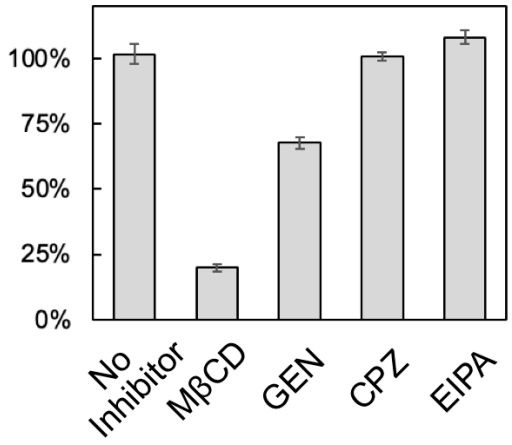


Fig. S5 Cellular uptake efficiency of AF_{647}-Ala-Asp($C_{12}H_{25}$)-Phe in the presence of endocytosis inhibitors: 1 mM methyl-β-cyclodextrin (MβCD), 10 μM 5-(*N*-ethyl-*N*-isopropyl)-amiloride (EIPA), 700 μM genistein (GEN), and 10 μM chlorpromazine (CPZ). The error bars represent the standard deviations of triplicates.

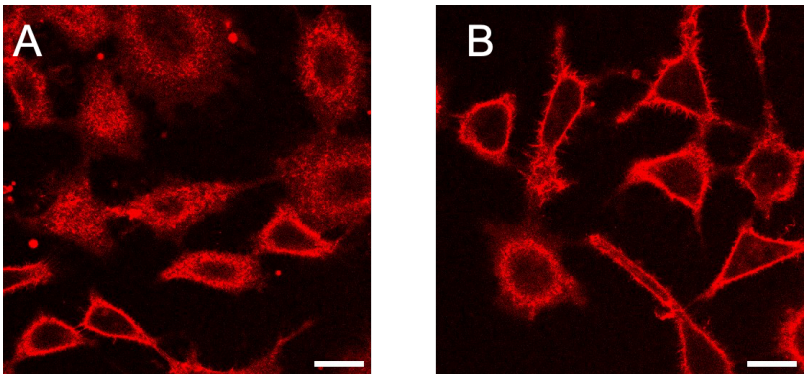


Fig. S6 The CLSM image of HeLa cells treated with AF_{647}-labeled tripeptide. The cells were visualized without D-PBS washing process. (A) AF_{647}-R_F-tripeptide ($R_F = C_8F_{17}$), (B) AF_{647}-R_H-tripeptide ($R_H = C_{12}H_{25}$). The scale bar indicates 25 μm.

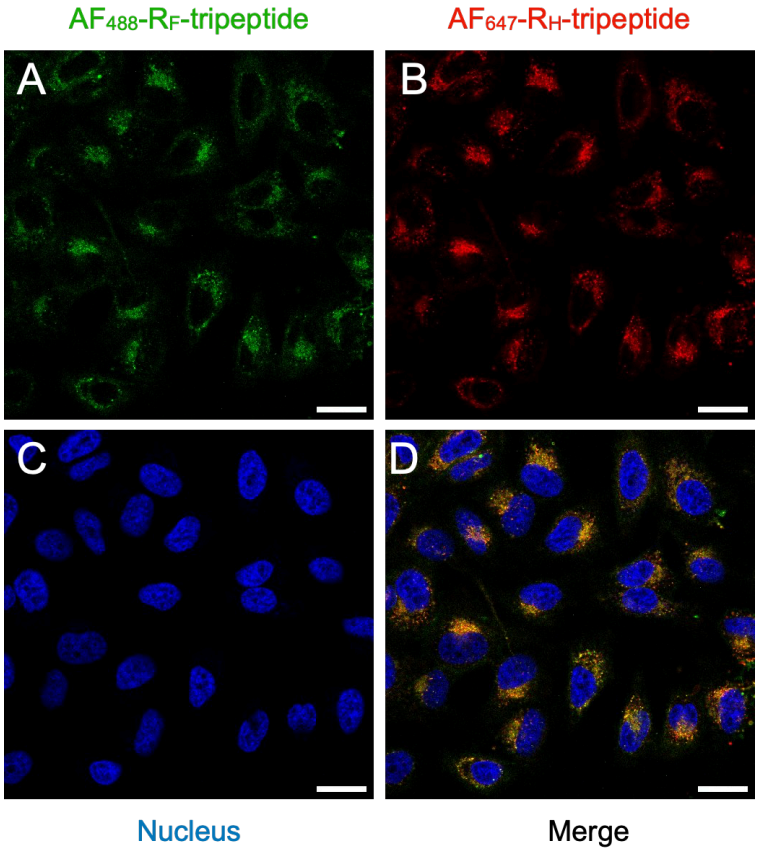
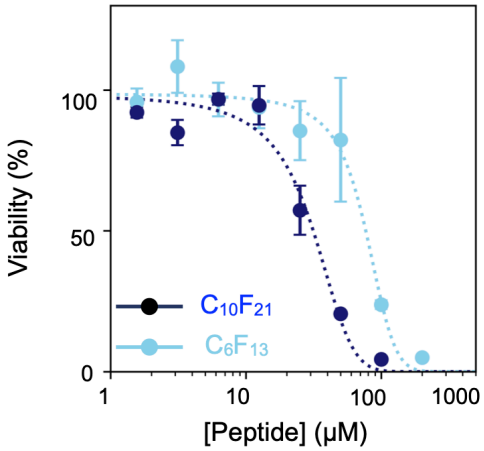


Fig. S7 The CLSM image of HeLa cells treated with 150 nM of the peptide samples (AF_{488}-R_F-tripeptide ($R_F = C_8F_{17}$) and AF_{647}-R_H-tripeptide ($R_H = C_{12}H_{25}$). To visualize R_F-tripeptide and R_H-tripeptide simultaneously, R_F-tripeptide and R_H-tripeptide were labeled with AF_{488} and AF_{647}, respectively. (A) AF_{488}-R_F-tripeptide ($R_F = C_8F_{17}$), green: λ_{ex} = 488 nm, λ_{obs} = 500–550 nm. (B) AF_{647}-R_H-tripeptide ($R_H = C_{12}H_{25}$), red: λ_{ex} = 638 nm, λ_{obs} = 650–700 nm. (C) Nucleus (Hoechst 33342), blue: λ_{ex} = 408 nm, λ_{obs} = 430–470 nm. (D) Overlay of the images in (A)–(C).



AF_{647}-R_F-tripeptide	
R_F	IC_{50} (μM)
$C_{10}F_{21}$	77 ± 7
C_6F_{13}	34 ± 2

Fig. S8 Cytotoxicity of AF_{647}-R_F-tripeptides. Cytotoxicity assay using cell-counting kit-8 (CCK-8); 5×10^3 of HeLa cells were treated with the AF_{647}-R_F -tripeptides for 1 h.

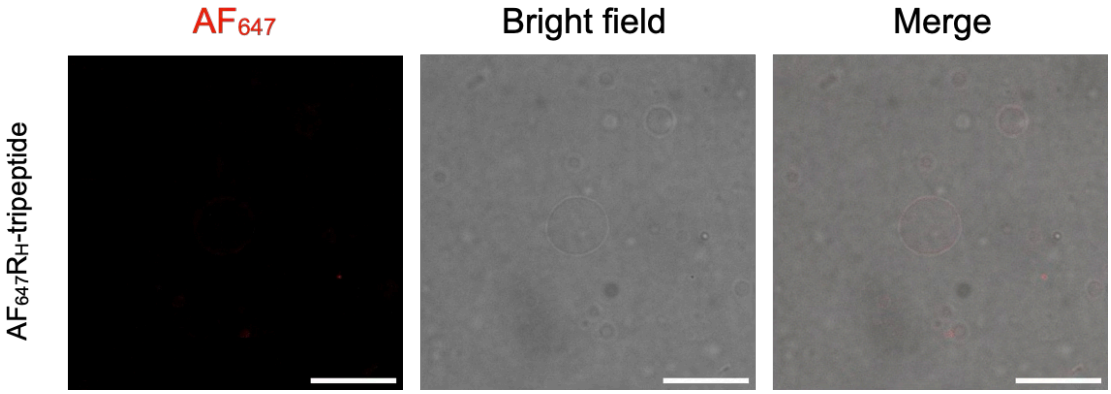


Fig. S9 The CLSM image of the lipid membrane treated with AF_{647}-R_H-tripeptide (R_H = $C_{12}H_{25}$). The interaction of AF_{647}-R_H-tripeptide (R_H = $C_{12}H_{25}$) and control against DOPC liposome membrane were evaluated. The scale bar indicates 25 μm.

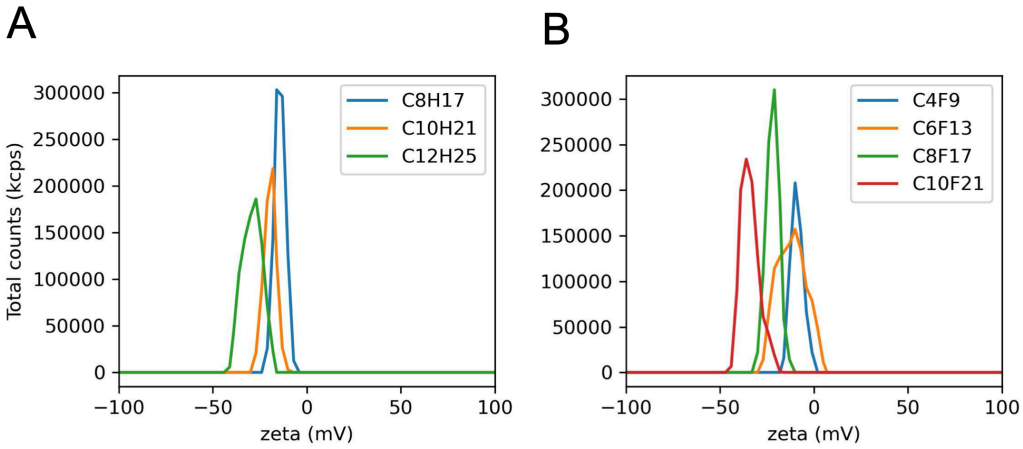


Fig. S10 Zeta potential distribution histogram of liposome surface after adding (A) AF_{647}-R_F-tripeptides and (B) AF_{647}-R_H-tripeptides.

Table S1 Zeta potential of liposome surface after adding AF_{647}-R_F/R_H-tripeptides

AF_{647}-R_H-tripeptide			AF_{647}-R_F-tripeptide		
R_H	Zeta potential (mV)	mean	R_F	Zeta potential (mV)	mean
C_8H_{17}	-12.6 -10.8 -17.8	-13.7 ± 2.9	C_4F_9	-9.6 -9.0 -8.9	-9.2 ± 0.3
$C_{10}H_{21}$	-18.5 -17.7 -21.9	-19.4 ± 1.8	C_6F_{13}	-12.1 -14.2 -15.6	-14.0 ± 1.4
$C_{12}H_{25}$	-26.7 -27.0 -27.2	-27.0 ± 0.2	C_8F_{17}	-21.9 -23.9 -22.7	-22.9 ± 0.8
			$C_{10}F_{21}$	-32.8 -33.7 -33.4	-33.3 ± 0.4

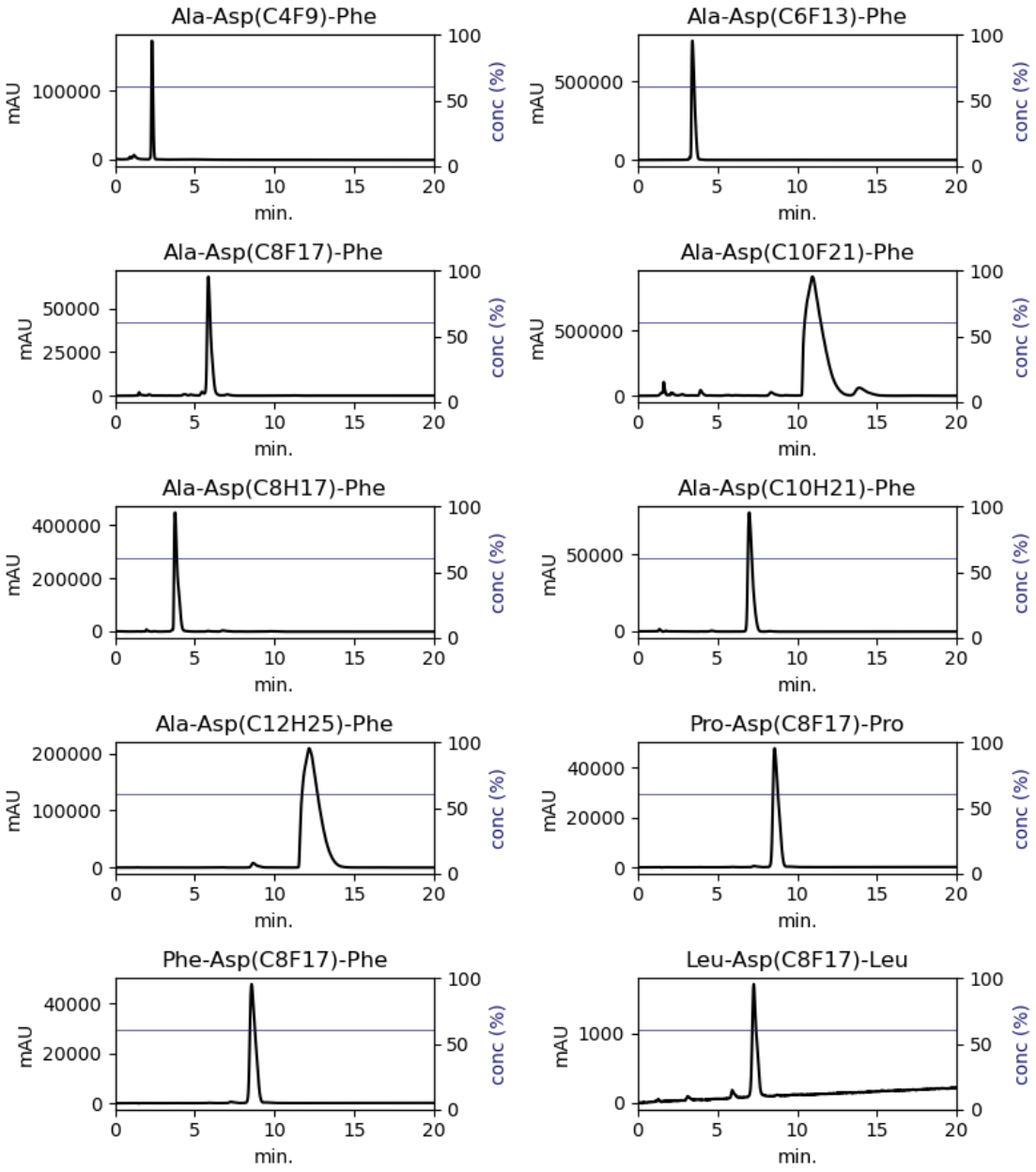


Fig. S11 HPLC chromatograms of R_F/R_H-tripeptides .

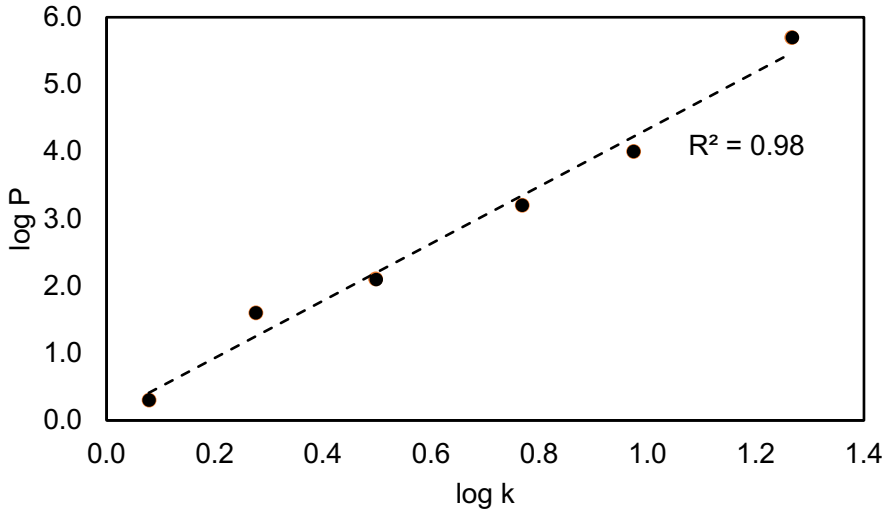


Fig. S12 Calibration curve of standard compounds used to calculate LogP values based on HPLC retention times.

Table S2 HPLC retention times of standard compounds for generating the calibration curve.

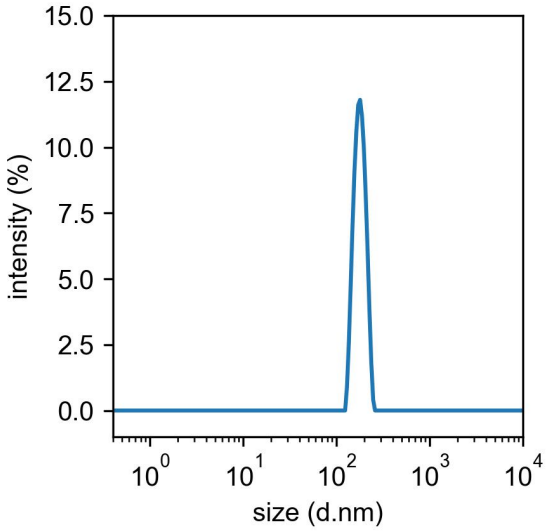
	Retention time (t) [min.]	k[a]	log k	log P_{ow}[b]
thiourea	1.4			
2-butanone	3.1	1.2	0.1	0.3
benzonitrile	4.1	1.9	0.3	1.6
anisole	5.9	3.1	0.5	2.1
benzophenone	9.8	5.9	0.8	3.2
biphenyl	14.8	9.4	1.0	4.0
triphenylamine	27.7	18.5	1.3	5.7

[a] $k = (t - t_0) / t_0$. [b] from ref. [2].

Table S3 HPLC retention times and calculated log P values of R_F/R_H-tripeptides.

	Retention time (t) [min.]	k[a]	log k	log P_{ow}
Ala-Asp(C_8H_{17})-Phe	3.8	1.6	0.2	1.0
Ala-Asp($C_{10}H_{21}$)-Phe	7.1	4.0	0.6	2.6
Ala-Asp($C_{12}H_{25}$)-Phe	12.5	7.8	0.9	3.9
Ala-Asp(C_4F_9)-Phe	2.3	0.6	-0.2	-0.8
Ala-Asp(C_6F_{13})-Phe	3.5	1.4	0.2	0.8
Ala-Asp(C_8F_{17})-Phe	5.9	3.1	0.5	2.2
Ala-Asp($C_{10}F_{21}$)-Phe	11.0	6.7	0.8	3.6
Phe-Asp(C_8F_{17})-Phe	8.6	5.0	0.7	3.1
Leu-Asp(C_8F_{17})-Leu	7.3	4.1	0.6	2.7
Pro-Asp(C_8F_{17})-Pro	4.7	2.3	0.4	1.6

[a] $k = (t - t_0) / t_0$. Note that, although the measurement of the LogP value higher than 0 is recommended by the HPLC method, the hydrophobicity of the peptide with C_4F_9 was determined by extrapolation.



Average diameter (nm)
176.9 ± 15.1

Fig. S13 DLS measurements of particle sizes formed by AF_{647}-R_F-tripeptide (R_F = C_8F_{17}). The experiment was conducted in triplicate. The top image is a representative DLS spectrum. The average diameter value and standard deviation from the triplicate is shown under the spectrum

Table S4 Mass list of AF_{647}-R_F/R_H-tripeptides

Name	Fomula	Exact mass ($[M]^+$calcd)	Observed
AF_{647}-Ala-Asp(C_8H_{17})-Phe	$C_{66}H_{88}N_7O_{17}S_4$	1378.5	1378.4
AF_{647}-Ala-Asp($C_{10}H_{21}$)-Phe	$C_{68}H_{92}N_7O_{17}S_4$	1406.5	1406.3
AF_{647}-Ala-Asp($C_{12}H_{25}$)-Phe	$C_{70}H_{96}N_7O_{17}S_4$	1434.6	1435.2
AF_{647}-Ala-Asp($C_{10}F_{21}$)-Phe	$C_{68}H_{71}F_{21}N_7O_{17}S_4$	1784.3	1784.7
AF_{647}-Ala-Asp(C_8F_{17})-Phe	$C_{66}H_{71}F_{17}N_7O_{17}S_4$	1685.4	1685.8
AF_{647}-Ala-Asp(C_6F_{13})-Phe	$C_{64}H_{71}F_{13}N_7O_{17}S_4$	1584.4	1583.8
AF_{647}-Ala-Asp(C_4F_9)-Phe	$C_{62}H_{71}F_9N_7O_{17}S_4$	1484.4	1484.0
AF_{647}-Pro-Asp(C_8F_{17})-Pro	$C_{64}H_{71}F_{17}N_7O_{17}S_4$	1660.4	1659.9
AF_{647}-Leu-Asp(C_8F_{17})-Leu	$C_{66}H_{79}F_{17}N_7O_{17}S_4$	1692.4	1692.6
AF_{647}-Phe-Asp(C_8F_{17})-Phe	$C_{72}H_{75}F_{17}N_7O_{17}S_4$	1760.4	1760.7

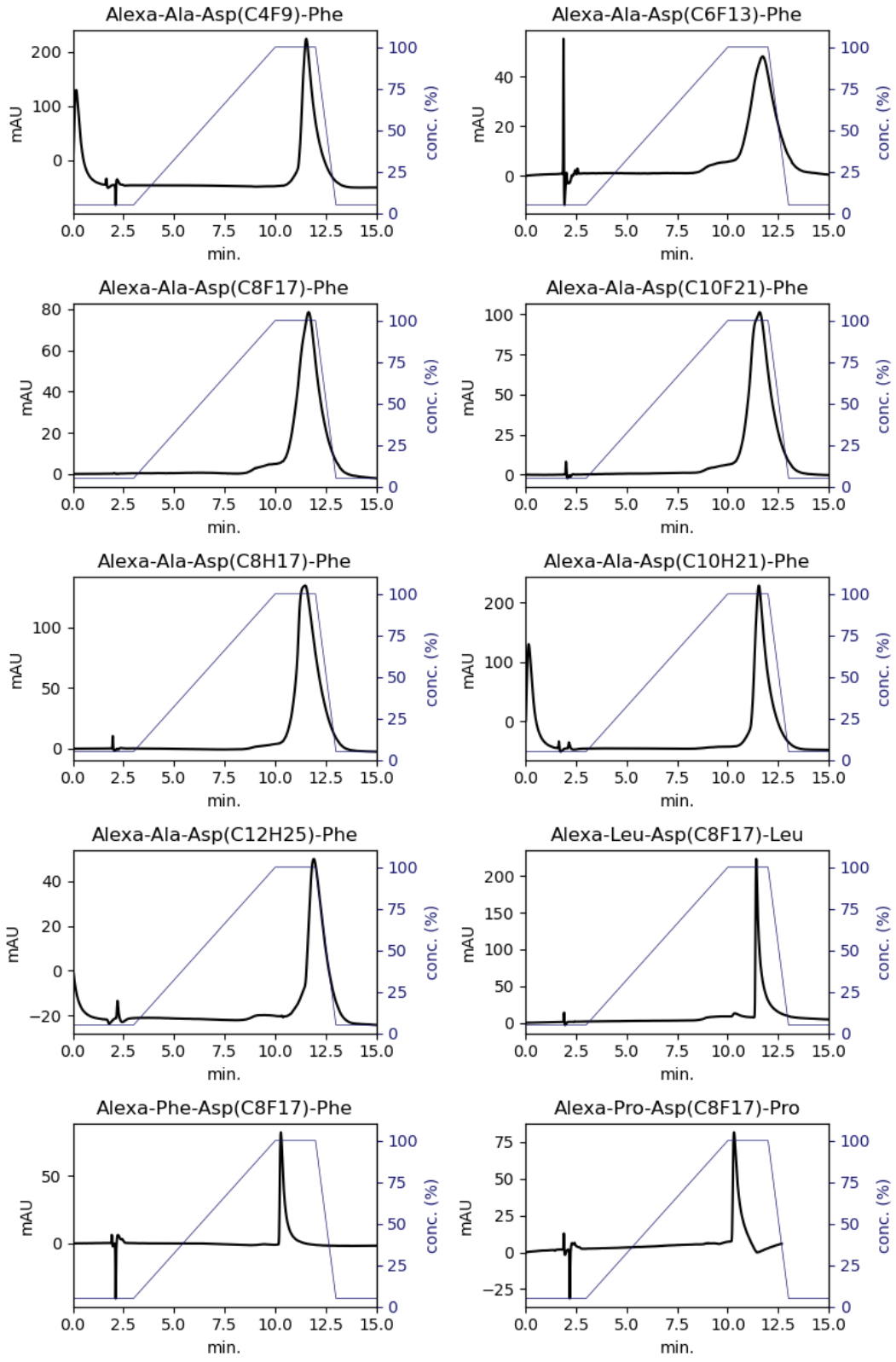
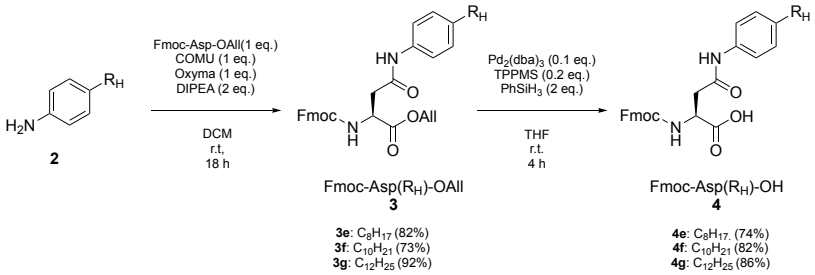


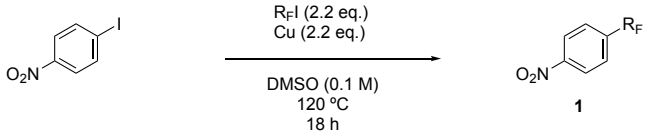
Fig. S14 HPLC chromatograms of AF_{647}-R_F/R_H-tripeptides

Synthesis of amino acids and peptides



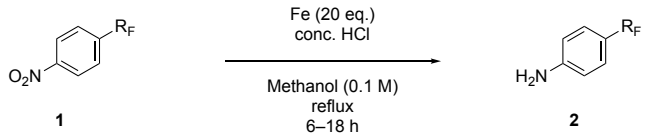
Scheme S1 Synthesis of alkyl chain (R_H)-containing amino acids

Synthesis of perfluoroalkylated nitrobenzene: synthetic procedure A



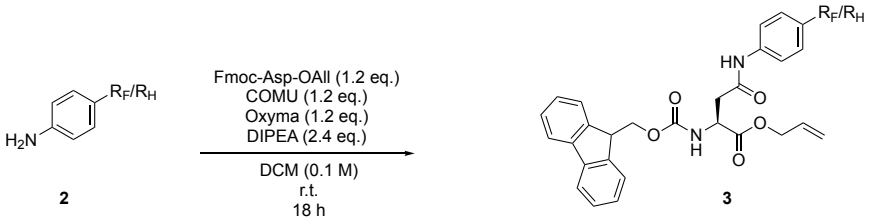
The mixture of R_FI (2.2 eq.) and Cu powder (2.2 eq.) in DMSO was stirred for 15 min at 80 °C under N_2 atmosphere. 1-Iodo-4-nitrobenzene (1.0 eq.) was added to the mixture. The reaction mixture was stirred for 18 h at 130 °C. The mixture was filtered by Celite® and washed with Et_2O and H_2O. The aqueous layer was extracted with Et_2O (100 mL×2). The organic layer was washed with H_2O and brine, and then dried over Na_2SO_4. The evaporation of the organic phase gave the crude product. The crude product was purified by silica-gel column chromatography with *n*-hexane/EtOAc (10:1) to afford the desired product **1**.

Synthesis of perfluoroalkylated aniline: synthetic procedure B



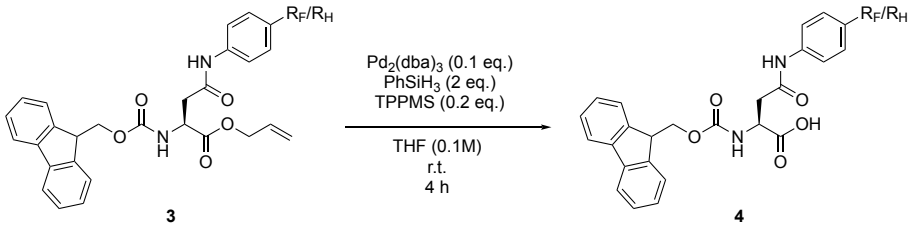
To a solution of compound **1** in methanol were added Fe (20 eq.) powder and conc. HCl (several drops) at room temperature. The solution was refluxed until the compound **1** was consumed. The reaction mixture was quenched by sat. $NaHCO_3$. DCM was added, and then the solution was filtered by a paper filter. The organic layer was washed with H_2O and brine, and dried over Na_2SO_4. The evaporation of the organic phase gave the crude product. The crude product was purified by silica-gel column chromatography with *n*-hexane/EtOAc (10:1) to afford the desired product **2**.

Synthesis of Fmoc-Asp(R_F)-OAll :synthetic procedure C



To a solution of Fmoc-Asp-OAll (1.2 eq.) and aniline **2** (1.0 eq.) in DCM (0.1M) were added DIPEA (2.4 eq), Oxyma (1.2 eq.), and COMU (1.2 eq.) at room temperature under N_2 atmosphere. After stirred for 18 h at room temperature, 1 M HCl was added and extracted with DCM. Then combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4 and filtered. The solution was concentrated under reduced pressure to give the crude product. The product was purified by silica-gel column chromatography to afford the product **3**.

Synthesis of Fmoc-Asp(R_F)-OH : synthetic procedure D



To a solution of Fmoc-Asp(R_F/R_H)-OAll (1.0 eq.) in THF (0.1 M) were added $PhSiH_3$ (2 eq.), $Pd_2(dba)_3$ (0.1 eq.), and sodium diphenylphosphinobenzene-3-sulfonate (0.2 eq.) at 0 °C under N_2 atmosphere. After stirring at room temperature for 4 h, the reaction mixture was quenched by 1 N HCl and extracted with EtOAc. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4 and concentrated in vacuo to give the crude product. The crude product was purified by silica-gel column chromatography to give the product **4**.

Synthesis of tripeptides: synthetic procedure E

Resin swelling: Rink amide resin was swelled with a minimal volume of anhydrous DMF in a syringe for 30 min.

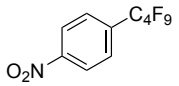
DMF was filtered off, and the resin was treated with 20% piperidine/DMF solution to remove Fmoc group.

Elongation of peptide: Fmoc-AAs-OH (1–4 eq.), COMU (4 eq.), oxyma (4 eq.), and DIPEA (8 eq.) with continuous shaking for 1–2 h. After removing the solution, the resin was washed with DMF three times. The resin was treated with 20% piperidine/DMF for 3 min twice and then

washed with DMF.

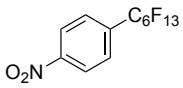
Peptide cleavage: The peptides were cleaved by treating the resin with 95/2.5/2.5 TFA/TIPS/H_2O (v/v) for 2 h. The solution was transferred to a flask and TFA solution was removed under the reduced pressure. The crude product was dissolved in 40/60 acetonitrile/water and purified by a reversed phase column (C_{18} column) on HPLC.

C_4F_9-Ar-NO_2: 1a



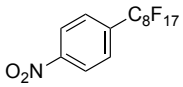
The title compound was obtained from 1-iodo-4-nitrobenzene (10.0 mmol) and perfluorobutyl iodide following the procedure **A**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave C_4F_9-Ar-NO_2 **1a** (1.1 g, 3.2 mmol, 32% yield) as a colorless solid; ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.38 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H); ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -80.8 (s, 3F), -111.5 (s, 2F), -111.5 (s, 2F), -122.5 (s, 2F), -125.4 (s, 2F).

C_6F_{13}-Ar-NO_2: 1b



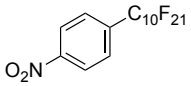
The title compound was obtained from 1-iodo-4-nitrobenzene (10.0 mmol) and perfluorohexyl iodide following the procedure **A**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave C_6F_{13}-Ar-NO_2 **1b** (1.2 g, 2.8 mmol, 28% yield) as a colorless solid; ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.38 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 2H); ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -80.8 (s, 3F), -111.2 (s, 2F), -121.4 (s, 2F), -121.6 (s, 2F), -122.8 (s, 2F), -126.2 (s, 2F).

C_8F_{17}-Ar-NO_2: 1c



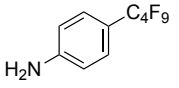
The title compound was obtained from 1-iodo-4-nitrobenzene (10.0 mmol) and perfluorooctyl iodide following the procedure **A**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave C_8F_{17}-Ar-NO_2 **1c** (1.5 g, 2.7 mmol, 27% yield) as a colorless solid; ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.39 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H); ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -80.7 (s, 3F), -111.1 (s, 2F), -121.1--122.6 (m, 10F), -126.1 (s, 2F).

$C_{10}F_{21}$-Ar-NO_2: 1d



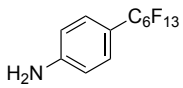
The title compound was obtained from 1-iodo-4-nitrobenzene (10.0 mmol) and perfluorodecyl iodide following the procedure **A**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave $C_{10}F_{21}$-Ar-NO_2 **1d** (3.7 g, 5.7 mmol, 57% yield) as a colorless solid; ^{1}H NMR (400 MHz, ACETONE-D_6) δ 8.56 (d, *J* = 8.9 Hz, 2H), 8.11 (d, *J* = 8.7 Hz, 2H); ^{19}F NMR (376 MHz, ACETONE-D_6) δ -81.6 (t, *J* = 10.0, Hz, 3F), -111.3 (t, *J* = 14.3 Hz, 2F), -121.6--123.2 (m, 14F), -126.7 (s, 2F).

C_4F_9-Ar-NH_2: 2a



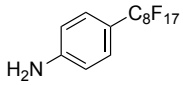
The title compound was obtained from **1a** (5.0 mmol) following procedure **B**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave C_4F_9-Ar-NH_2 **2a** (1.7 g, 4.1 mmol, 81% yield); ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 3.97 (br, 2H); ^{19}F-NMR (376 MHz, CHLOROFORM-D) δ -81.0 (s, 3F), -109.6 (s, 2F), -122.8 (s, 2F), -125.6 (s, 2F).

C_6F_{13}-Ar-NH_2: 2b



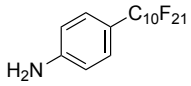
The title compound was obtained from **1b** (5.0 mmol) following procedure **B**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave C_6F_{13}-Ar-NH_2 **2b** (2.1 g, 4.1 mmol, 81% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 3.97 (s, 2H); ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -81.0 (t, *J* = 10.1 Hz, 3F), -109.5 (t, *J* = 14.4 Hz, 2F), -121.6 (s, 2F), -122.1 (s, 2F), -122.9 (s, 2F), -126.3 (s, 2F).

C_8F_{17}-Ar-NH_2: 2c



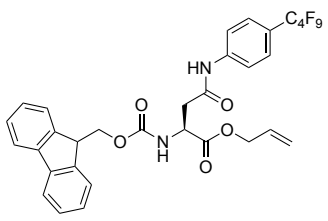
The title compound was obtained from **1c** (5.0 mmol) following procedure **B**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave C_8F_{17}-Ar-NH_2 **2c** (0.87 g, 1.6 mmol, 32% yield) as a colorless solid; ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 11.2 Hz, 2H), 3.97 (s, 2H); ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -80.8 (s, 3F), -109.4 (s, 2F), -121.2 (s, 2F), -121.9 (s, 6F), -122.9 (s, 2F), -126.1 (s, 2F).

$C_{10}F_{21}$-Ar-NH_2: 2d



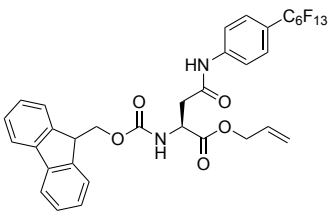
The title compound was obtained from **1d** (5.0 mmol) following the procedure **B**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave $C_{10}F_{21}$-Ar-NH_2 **2d** (0.61 g, 1.0 mmol, 20% yield) as a colorless solid; ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 3.98 (s, 2H); ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -80.7 (t, *J* = 9.9 Hz, 3F), -109.4 (t, *J* = 14.3 Hz, 2F), -121.2 (s, 2F), -121.8 (d, *J* = 76.6 Hz, 10F), -122.6 (s, 2F), -126.0 (s, 2F).

Fmoc-Asp(C_4F_9)-OAll: 3a



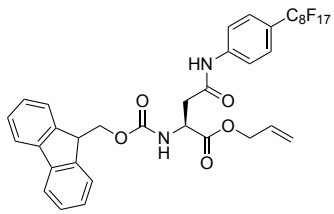
The title compound was obtained from Fmoc-L-aspartic acid 1-allyl ester and $C_4F_9ArNH_2$ **2a** (2.0 mmol) following the procedure **C**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 2/1) gave Fmoc-Asp(C_8F_{17})-OAll **3a** (867 mg, 1.22 mmol, 61% yield) as a colorless solid; ^{1}H NMR (400 MHz, ACETONE-D_6) δ 9.68 (s, 1H), 7.89-7.81 (m, 4H), 7.67-7.59 (m, 4H), 7.38-7.24 (m, 4H), 6.94 (d, *J* = 8.5 Hz, 1H), 5.89 (dq, *J* = 22.5, 5.4 Hz, 1H), 5.31 (d, *J* = 17.3 Hz, 1H), 5.13 (d, *J* = 10.5 Hz, 1H), 4.76-4.71 (m, 1H), 4.61 (d, *J* = 5.5 Hz, 2H), 4.36-4.27 (m, 2H), 4.21 (t, *J* = 7.1 Hz, 1H), 2.96-3.12 (2H); ^{19}F NMR (376 MHz, ACETONE-D_6) δ -82.0 (s, 3F), -110.6 (s, 2F), -123.2 (s, 2F), -126.3 (s, 2F); ^{13}C NMR (101 MHz, ACETONE-D_6) δ 171.6, 169.7, 156.9, 145.0, 144.9, 143.8, 142.1, 133.2, 128.5, 127.9, 126.1, 120.8, 120.0, 119.9, 118.0, 67.3, 66.3, 51.8, 47.9, 39.4; FT-IR (neat, cm^{-1}) 518, 531, 587, 621, 675, 722, 739, 757, 826, 1047, 1088, 1147, 1203, 1256, 1289, 1364, 1411, 1526, 1601, 1666, 1696, 2853, 2924, 3316; HRMS (ESI-TOF) calcd for $C_{32}H_{25}F_9N_2O_5Na$ $[M+Na]^+$: 711.1517, found: 711.1514.

Fmoc-Asp(C_6F_{13})-OAll: 3b



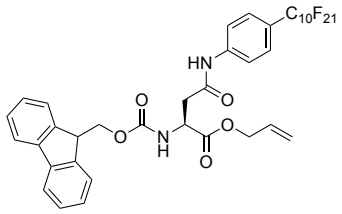
The title compound was obtained from Fmoc-L-aspartic acid 1-allyl ester and $C_6F_{13}ArNH_2$ **2b** (2.0 mmol) following the procedure **C**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 2/1) gave Fmoc-Asp(C_6F_{13})-OAll **3b** (1.24 g, 1.53 mmol, 76% yield) as a colorless solid; ^{1}H NMR (400 MHz, ACETONE-D_6) δ 9.71 (s, 1H), 7.87 (dd, *J* = 28.4, 6.9 Hz, 4H), 7.65 (dd, *J* = 18.1, 7.1 Hz, 4H), 7.39-7.26 (m, 4H), 6.96 (d, *J* = 7.1 Hz, 1H), 5.96-5.87 (m, 1H), 5.33 (d, *J* = 17.4 Hz, 1H), 5.15 (d, *J* = 9.6 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.64 (s, 2H), 4.36-4.30 (m, 2H), 4.23 (s, 1H), 3.06 (d, *J* = 14.2 Hz, 2H); ^{19}F NMR (376 MHz, ACETONE-D_6) δ -81.6 (s, 3F), -110.2 (s, 2F), -121.9 (s, 2F), -122.4 (s, 2F), -123.3 (s, 2F), -126.6 (s, 2F); ^{13}C NMR (101 MHz, ACETONE-D_6) δ 171.6, 169.7, 156.9, 145.0, 144.9, 143.8, 142.1, 133.2, 128.5, 127.9, 126.0, 120.8, 120.0, 118.0, 67.4, 66.3, 51.8, 47.9, 39.4, 29.8; FT-IR (neat, cm^{-1}) 401, 412, 418, 457, 569, 621, 696, 737, 758, 1088, 1106, 1146, 1185, 1201, 1227, 1289, 1314, 1363, 1411, 1429, 1526, 1602, 1665, 1692, 3323; HRMS (ESI-TOF) calcd for $C_{34}H_{25}F_{13}N_2NaO_5$ $[M+Na]^+$: 811.1448, found: 811.1441.

Fmoc-Asp(C_8F_{17})-OAll: 3c



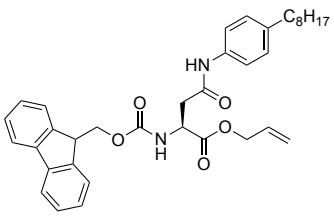
The title compound was obtained from Fmoc-L-aspartic acid 1-allyl ester and $C_8F_{17}ArNH_2$ **2c** (2.0 mmol) following the procedure **C**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 2/1) gave Fmoc-Asp(C_8F_{17})-OAll **3c** (1.49 g, 1.64 mmol, 82% yield) as a colorless solid; ^{1}H NMR (400 MHz, ACETONE-D_6) δ 9.69 (s, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 8.9 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 1H), 5.97-5.87 (m, 1H), 5.34 (dq, *J* = 17.4, 1.6 Hz, 1H), 5.17 (dd, *J* = 10.5, 1.1 Hz, 1H), 4.78-4.73 (m, 1H), 4.64 (dt, *J* = 5.5, 1.5 Hz, 2H), 4.39-4.30 (m, 2H), 4.25 (t, *J* = 7.1 Hz, 1H), 3.02-3.14 (2H); ^{19}F NMR (376 MHz, ACETONE-D_6) δ -81.5 (t, *J* = 9.9 Hz, 3F), -110.2 (t, *J* = 14.3 Hz, 2F), -121.7--123.1 (m, 10F), -126.6 (s, 2F); ^{13}C NMR (101 MHz, ACETONE-D_6) δ 171.6, 169.7, 156.9, 145.0, 145.0, 143.8, 142.1, 133.3, 128.5, 127.9, 126.1, 120.8, 120.0, 119.9, 118.0, 67.4, 66.3, 51.8, 47.9, 39.4; FT-IR (neat, cm $^{-1}$) 413, 429, 441, 458, 558, 584, 652, 738, 1049, 1088, 1110, 1147, 1196, 1411, 1605, 1694, 3322 ; FT-IR (neat, cm^{-1}): 515, 531, 554, 561, 587, 621, 643, 739, 755, 803, 847, 940, 956, 997, 1019, 1048, 1086, 1094, 1149, 1157, 1193, 1228, 1255, 1297, 1313, 1326, 1370, 1411, 1429, 1452, 1524, 1601, 1668, 1694, 1742, 3334; HRMS (ESI-TOF) calcd for $C_{36}H_{25}F_{17}N_2NaO_5$ $[M+Na]^+$: 911.1384, found: 911.1388.

Fmoc-Asp($C_{10}F_{21}$)-OAll: 3d



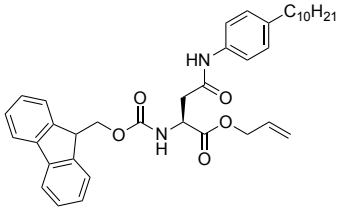
The title compound was obtained from Fmoc-L-aspartic acid 1-allyl ester and $C_{10}F_{21}ArNH_2$ **2d** (2.0 mmol) following the procedure **C**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 2/1) gave Fmoc-Asp($C_{10}F_{21}$)-OAll **3d** (1.47 g, 1.46 mmol, 73% yield) as a colorless solid; ^{1}H-NMR (400 MHz, ACETONE-D_6) δ 9.73 (s, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 5.92 (dq, *J* = 22.6, 5.3 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 4.76 (dd, *J* = 14.2, 5.7 Hz, 1H), 4.64 (d, *J* = 5.5 Hz, 2H), 4.39-4.30 (m, 2H), 4.24 (t, *J* = 7.1 Hz, 1H), 3.08 (d, *J* = 5.7 Hz, 2H); ^{19}F-NMR (376 MHz, ACETONE-D_6) δ -81.5 (t, *J* = 9.9 Hz, 3F), -110.2 (t, *J* = 14.3 Hz, 2F), -121.7--123.1 (m, 14F), -126.6 (s, 2F); ^{13}C-NMR (101 MHz, ACETONE-D_6) δ 170.7, 169.3, 156.1, 144.1, 141.3, 141.0, 132.4, 131.6, 127.7, 127.1, 125.3, 124.9, 122.2, 119.9, 117.3, 116.4, 66.5, 65.4, 50.9, 47.1, 38.6; FT-IR (neat, cm^{-1}) 418, 425, 442, 446, 457, 472, 526, 536, 553, 587, 620, 669, 737, 756, 780, 794, 821, 925, 991, 1007, 1047, 1086, 1103, 1170, 1208, 1411, 1445, 1450, 1465, 1477, 1527, 1597, 1655, 1697, 2851, 2920, 3303; HRMS (ESI-TOF) calcd for $C_{38}H_{25}F_{21}N_2NaO_5$ $[M+Na]^+$: 1011.1320, found: 1011.1720.

Fmoc-Asp(C_8H_{17})-OAll: 3e



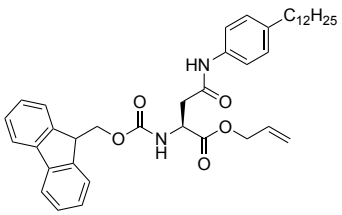
The title compound was obtained from Fmoc-L-aspartic acid 1-allyl ester (2.0 mmol) and octylaniline following the procedure **C**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 2/1) gave Fmoc-Asp(C_8H_{17})-OAll (936 mg, 1.60 mmol, 80% yield) as a colorless solid; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 7.73 (d, *J* = 7.3 Hz, 2H), 7.63-7.26 (m, 7H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.17 (d, *J* = 8.2 Hz, 1H), 5.91-5.85 (m, 1H), 5.33-5.19 (m, 2H), 4.67 (d, *J* = 5.0 Hz, 3H), 4.42-4.29 (m, 2H), 4.21 (t, *J* = 7.0 Hz, 1H), 3.03 (ddd, *J* = 85.4, 15.9, 4.1 Hz, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.55 (br, 2H), 1.26 (d, *J* = 7.8 Hz, 10H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 170.9, 168.1, 156.4, 143.9, 143.7, 141.4, 139.6, 135.0, 131.6, 129.0, 127.8, 127.2, 125.3, 120.2, 120.1, 118.9, 77.4, 77.1, 76.8, 67.4, 66.6, 51.0, 47.1, 38.8, 35.5, 32.0, 31.6, 29.6, 29.4, 29.3, 22.8, 14.2; FT-IR (neat, cm^{-1}) 404, 412, 418, 425, 447, 453, 457, 472, 476, 480, 496, 511, 518, 525, 553, 587, 620, 737, 757, 778, 926, 991, 1007, 1019, 1047, 1086, 1103, 1170, 1208, 1266, 1283, 1411, 1445, 1450, 1465, 1477, 1527, 1597, 2851, 2920, 3303; HRMS (ESI-TOF) calcd for $C_{36}H_{42}N_2NaO_5$ $[M+Na]^+$: 605.2986, found: 605.2964.

Fmoc-Asp($C_{10}H_{21}$)-OAll: 3f



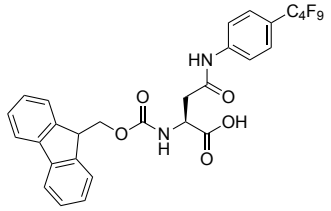
The title compound was obtained from Fmoc-L-aspartic acid 1-allyl ester (2.0 mmol) and decylaniline following the procedure **C**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 2/1) gave Fmoc-Asp($C_{10}H_{21}$)-OAll **3f** (897 mg, 1.44 mmol, 72% yield) as a colorless solid; ^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 7.73 (d, *J* = 7.1 Hz, 2H), 7.57 (d, *J* = 7.1 Hz, 2H), 7.52 (s, 1H), 7.36 (t, *J* = 8.2 Hz, 4H), 7.26 (s, 3H), 7.10 (d, *J* = 7.3 Hz, 2H), 6.16 (d, *J* = 8.0 Hz, 1H), 5.93-5.85 (m, 1H), 5.31 (d, *J* = 17.0 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 4.68 (s, 3H), 4.42-4.29 (m, 2H), 4.21 (t, *J* = 6.8 Hz, 1H), 3.15-2.90 (m, 2H), 2.54 (t, *J* = 7.4 Hz, 2H), 1.55 (t, *J* = 6.1 Hz, 2H), 1.26 (m, *J* = 10.3 Hz, 14H), 0.87 (t, *J* = 5.8 Hz, 3H); ^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 170.8, 168.1, 156.4, 143.9, 143.7, 141.4, 139.6, 135.0, 131.6, 129.0, 127.8, 127.2, 125.2, 120.2, 120.1, 118.9, 67.4, 66.6, 51.0, 47.1, 38.8, 35.5, 32.0, 31.6, 29.7, 29.7, 29.6, 29.3, 22.8, 14.2; FT-IR (neat, cm^{-1}) 406, 419, 425, 457, 472, 536, 552, 587, 620, 737, 756, 778, 821, 926, 991, 1047, 1086, 1103, 1170, 1208, 1411, 1450, 1465, 1477, 1527, 1598, 1655, 1697, 1738, 2851, 2921, 3301; HRMS (ESI-TOF) calcd for $C_{38}H_{46}N_2NaO_5$ $[M+Na]^+$: 633.3299, found: 633.3277.

Fmoc-Asp($C_{12}H_{25}$)-OAll: 3g



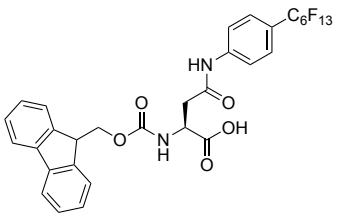
The title compound was obtained from Fmoc-L-aspartic acid 1-allyl ester (2.0 mmol) and dodecylaniline following the procedure **C**. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 2/1) gave Fmoc-Asp($C_{12}H_{25}$)-OAll **3g** (1018 mg, 1.54 mmol, 77% yield) as a colorless solid; ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 7.1 Hz, 2H), 7.47-7.26 (m, 6H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.17 (d, *J* = 8.2 Hz, 1H), 5.95-5.85 (m, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 4.69 (d, *J* = 5.0 Hz, 2H), 4.44-4.31 (m, 2H), 4.22 (t, *J* = 7.0 Hz, 1H), 3.18-2.91 (m, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.57 (t, *J* = 6.5 Hz, 2H), 1.30-1.26 (m, 18H), 0.89 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 170.8, 168.0, 156.3, 143.8, 143.7, 141.3, 139.6, 134.9, 131.5, 128.9, 127.7, 127.1, 125.2, 120.1, 120.0, 118.8, 67.4, 66.5, 50.9, 47.1, 38.8, 35.4, 31.9, 31.5, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 14.2; FT-IR (neat, cm^{-1}) 405, 418, 425, 446, 452, 457, 472, 526, 588, 620, 665, 737, 758, 776, 819, 840, 935, 991, 1007, 1045, 1088, 1102, 1170, 1259, 1363, 1411, 1451, 1598, 1658, 1697, 1737, 2849, 2917, 3309; HRMS (ESI-TOF) calcd for $C_{40}H_{50}N_2NaO_5$ $[M+Na]^+$: 661.3617, found: 661.3614.

Fmoc-Asp(C_4F_9)-OH: 4a



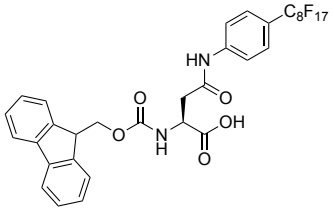
The title compound was obtained from Fmoc-Asp(C_4F_9)-OAll **3a** (711 mg, 1 mmol) following procedure **D**. Purification by silica-gel column chromatography ($CHCl_3$/MeOH = 20/1) gave Fmoc-Asp(C_4F_9)-OH **4a** (297 mg, 0.46 mmol, 46% yield) as a colorless solid; ^{1}H NMR (400 MHz, ACETONE-D_6) δ 9.83 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 1H), 4.72 (t, *J* = 6.1 Hz, 1H), 4.31 (m, 2H), 4.21 (t, *J* = 7.1 Hz, 1H), 3.06 (d, *J* = 5.3 Hz, 2H); ^{19}F NMR (376 MHz, ACETONE-D_6) δ -81.8 (t, *J* = 9.8 Hz, 3F), -110.5 (t, *J* = 13.2 Hz, 2F), -123.2 (m, 2F), -126.1--126.2 (m, 2F); ^{13}C NMR (101 MHz, ACETONE-D_6) δ 172.9, 170.0, 157.0, 145.0, 143.9, 142.1, 128.5, 127.9, 126.2, 123.2 (t, J_{FC}=24.1 Hz), 120.8, 120.0, 119.9, 67.4, 51.6, 47.9, 39.5; FT-IR (neat, cm^{-1}) 482, 535, 585, 622, 631, 691, 761, 805, 854, 880, 937, 989, 1002, 1027, 1052, 1088, 1107, 1134, 1162, 1187, 1203, 1266, 1315, 1352, 1409, 1428, 1523, 1602, 1673, 1693, 1757, 3331; HRMS (ESI-TOF) calcd for $C_{29}H_{20}F_9N_2O_5$ [M-H]$^-$: 647.1234, found: 647.1208.

Fmoc-Asp(C_6F_{13})-OH: 4b



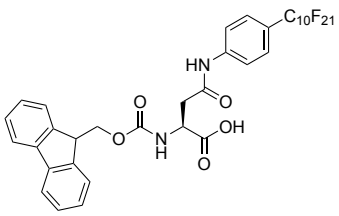
The title compound was obtained from Fmoc-Asp(C_6F_{13})-OAll **3b** (811 mg, 1.0 mmol) following procedure **D**. Purification by silica-gel column chromatography ($CHCl_3$/MeOH = 20/1) gave Fmoc-Asp(C_6F_{13})-OH **4b** (418 mg, 0.56 mmol, 56% yield) as a colorless solid; ^{1}H-NMR (400 MHz, ACETONE-D_6) δ 9.75 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.84-7.80 (m, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 1H), 4.72-4.67 (m, 1H), 4.32-4.30 (m, 2H), 4.21 (t, *J* = 6.9 Hz, 1H), 3.05 (d, *J* = 5.7 Hz, 2H); ^{19}F-NMR (376 MHz, ACETONE-D_6) δ -81.6 (t, *J* = 10.1 Hz, 3F), -110.2 (t, *J* = 14.4 Hz, 2F), -121.9--123.3 (m, 6F), -126.6--126.7 (m, 2F); ^{13}C-NMR (101 MHz, ACETONE-D_6) δ172.0, 169.2, 156.1, 144.2, 144.1, 143.0, 141.2, 127.7, 127.1, 125.3,122.8, 120.0, 119.2, 66.5, 50.7, 47.1, 38.7; FT-IR (neat, cm^{-1}) 401, 412, 418, 457, 569, 621, 696, 737, 758, 1088, 1106, 1146, 1185, 1201, 1227, 1289, 1314, 1363, 1411, 1429, 1526, 1602, 1665, 1692, 3323; HRMS (ESI-TOF) calcd for $C_{31}H_{20}F_{13}N_2O_5$ [M-H]$^-$: 747.1170, found: 747.1136.

Fmoc-Asp(C_8F_{17})-OH: 4c



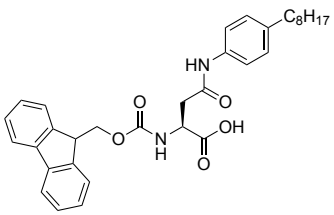
The title compound was obtained from Fmoc-Asp(C_8F_{17})-OAll **3c** (911 mg, 1.0 mmol) following procedure **D**. Purification by silica-gel column chromatography ($CHCl_3$/MeOH = 20/1) gave Fmoc-Asp(C_8F_{17})-OH **4c** (508 mg, 0.60 mmol, 60% yield) as a colorless solid; ^{1}H-NMR (400 MHz, ACETONE-D_6) δ 9.67 (s, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 7.3 Hz, 2H), 7.66 (d, J = 7.3 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.25 (t, J = 7.4 Hz, 2H), 6.83 (d, J = 8.5 Hz, 1H), 4.71-4.65 (m, 1H), 4.34-4.20 (m, 4H), 3.05 (d, J = 5.5 Hz, 2H); ^{19}F-NMR (376 MHz, ACETONE-D_6) δ -81.5 (t, *J* = 10.1 Hz, 3F), -110.2 (t, *J* = 14.3 Hz, 2F), -121.7--123.2 (m, 10F), -126.6 (s, 2F); ^{13}C-NMR (101 MHz, ACETONE-D_6) δ 171.9, 169.1, 156.1, 144.2, 144.1, 143.0, 141.2, 137.7, 127.7, 127.1, 125.3, 120.0, 119.2, 66.5, 50.6, 47.1, 38.6; FT-IR (neat, cm^{-1}) 621, 703, 735, 757, 816, 939, 1048, 1087, 1110, 1146, 1197, 1298, 1410, 1599, 1685, 3303; HRMS (ESI-TOF) calcd for $C_{33}H_{21}F_{17}N_2O_5$ [M-H]$^-$: 847.1106, found:847.1158.

Fmoc-Asp($C_{10}F_{21}$)-OH: 4d



The title compound was obtained from Fmoc-Asp($C_{10}F_{21}$)-OAll **3d** (1011 mg, 1.0 mmol) following procedure **D**. Purification by silica-gel column chromatography ($CHCl_3$/MeOH = 20/1) gave Fmoc-Asp($C_{10}F_{21}$)-OH **4d** (464 mg, 0.49 mmol, 49% yield) as a colorless solid; ^{1}H-NMR (400 MHz, ACETONE-D_6) δ 9.59 (s, 1H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 6.9 Hz, 2H), 7.66 (d, *J* = 6.4 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.37-7.34 (m, 2H), 7.27-7.24 (m, 2H), 6.67 (s, 1H), 4.69 (br, 1H), 4.34-4.22 (m, 3H), 3.04 (d, *J* = 4.6 Hz, 2H); ^{19}F-NMR (376 MHz, ACETONE-D_6) δ -81.5 (t, *J* = 9.0 Hz, 3F), -110.0 (t, *J* = 13.7 Hz, 2F), -121.4--122.9 (m, 14F), -126.4 (s, 2F); ^{13}C-NMR could not be measured due to the low solubility. FT-IR (neat, cm^{-1}) 417, 423, 510, 539, 587, 621, 736, 757, 775, 821, 938, 989, 1049, 1087, 1105, 1149, 1259, 1411, 1450, 1528, 1599, 1658, 1694, 2851, 2922, 3306; HRMS (ESI-TOF) calcd for $C_{35}H_{20}F_{21}N_2O_5$ [M-H]$^-$: 947.1042, found: 947.10315.

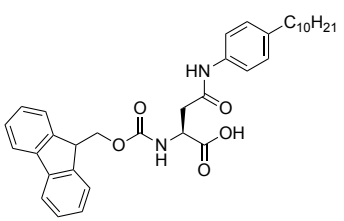
Fmoc-Asp(C_8H_{17})-OH: 4e



The title compound was obtained from Fmoc-Asp(C_8H_{17})-OAll **3e** (585 mg, 1.0 mmol) following procedure **D**. Purification by silica-gel column chromatography ($CHCl_3$/MeOH = 20/1) gave Fmoc-Asp(C_8H_{17})-OH **4e** (389 mg, 0.72 mmol, 72% yield) as a colorless solid; ^{1}H-NMR (400 MHz, ACETONE-D_6) δ 9.28 (s, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 7.3 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.28

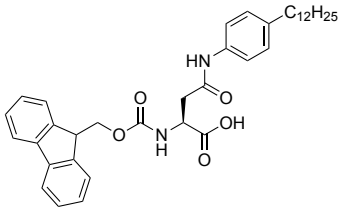
(t, J = 7.4 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 1H), 4.71-4.66 (m, 1H), 4.34-4.31 (m, 2H), 4.24 (t, J = 7.2 Hz, 1H), 3.06-2.96 (m, 2H), 2.56 (t, J = 7.7 Hz, 2H), 1.58 (t, J = 7.2 Hz, 2H), 1.29 (d, J = 16.3 Hz, 10H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C-NMR (101 MHz, ACETONE-D_6) δ 172.1, 168.3, 156.1, 144.2, 144.2, 141.2, 138.0, 136.9, 128.6, 127.7, 127.1, 125.4, 120.0, 119.4, 66.5, 50.8, 47.1, 38.4, 35.1, 31.8, 31.6, 29.4, 29.1, 22.5, 13.5; FT-IR (neat, cm^{-1}) 405, 418, 539, 587, 621, 736, 757, 777, 822, 936, 989, 1047, 1086, 1103, 1261, 1411, 1526, 1599, 1658, 1694, 2852, 2922, 3301; HRMS (ESI-TOF) calcd for $C_{35}H_{37}N_2O_5$ [M-H]$^-$: 541.2708, found: 541.2747

Fmoc-Asp($C_{10}H_{21}$)-OH: 4f



The title compound was obtained from Fmoc-Asp($C_{10}H_{17}$)-OAll **3f** (840 mg, 1.3 mmol) following procedure **D**. Purification by silica-gel column chromatography ($CHCl_3$/MeOH = 20/1) gave the compound (603 mg, 1.0 mmol, 82% yield) as a colorless solid.; ^{1}H-NMR (400 MHz, ACETONE-D_6) δ 9.28 (s, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 6.9 Hz, 2H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.25 (s, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 5.7 Hz, 1H), 4.72-4.66 (m, 1H), 4.30-4.20 (m, 3H), 3.00 (d, *J* = 17.4 Hz, 2H), 2.55-2.51 (m, 2H), 1.55 (br, 2H), 1.26 (d, *J* = 13.3 Hz, 14H), 0.84-0.82 (m, 3H); ^{13}C-NMR (101 MHz, ACETONE-D_6) δ 172.2, 168.3, 156.1, 144.2, 144.1, 141.2, 138.0, 136.9, 128.6, 127.7, 127.1, 125.4, 120.0, 119.4, 66.6, 50.8, 47.1, 38.4, 35.1, 31.8, 31.6, 29.5, 29.1, 22.5, 13.6; FT-IR (neat, cm^{-1}): 405, 411, 533, 584, 621, 736, 755, 776, 822, 936, 986, 1042, 1086, 1101, 1265, 1412, 1599, 1658, 1694, 2852, 2922; HRMS (ESI-TOF) calcd for $C_{35}H_{41}N_2O_5$ [M-H]$^-$: 569.3021, found: 569.3058.

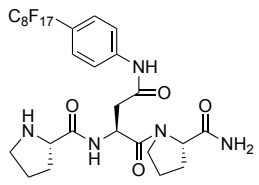
Fmoc-Asp($C_{12}H_{25}$)-OH: 4g



The title compound was obtained from Fmoc-Asp($C_{12}H_{25}$)-OAll **3g** (640 mg, 1.0 mmol) following procedure **D**. Purification by silica-gel column chromatography ($CHCl_3$/MeOH = 20/1) gave Fmoc-Asp($C_{12}H_{25}$)-OH **4g** (513 mg, 0.86 mmol, 86% yield) as a colorless solid; ^{1}H-NMR (400 MHz, ACETONE-D_6) δ 9.25 (s, 1H), 7.98 (d, *J* = 3.2 Hz, 0H), 7.81 (d, *J* = 7.1 Hz, 2H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.53 (d, *J* = 6.6 Hz, 2H), 7.37-7.34 (m, 2H), 7.25 (t, *J* = 6.8 Hz, 2H), 7.10 (d, *J* = 6.4 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.65 (d, *J* = 5.5 Hz, 1H), 4.25 (dd, *J* = 30.1, 6.8 Hz, 3H), 2.97 (d, *J* = 4.8 Hz, 2H), 2.75 (d, *J* = 3.2 Hz, 0H), 2.55-2.51 (m, 2H), 1.55 (br, 2H), 1.26 (d, *J* = 15.1 Hz, 18H), 0.84 (dd, *J* = 6.8, 3.8 Hz, 3H); ^{13}C-NMR (101 MHz, ACETONE-D_6) δ 172.1, 168.3, 156.1, 144.2, 144.2, 141.2, 138.0, 136.9, 128.6, 127.7, 127.1, 125.3, 120.0, 119.4, 66.5, 50.8, 47.1, 38.4, 35.1, 31.8, 31.6,

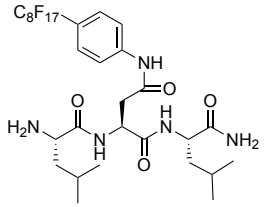
29.6, 29.5, 29.1, 22.5, 13.5; FT-IR (neat, cm^{-1}) 419, 423, 452, 457, 473, 621, 648, 736, 756, 775, 822, 936, 988, 1048, 1088, 1106, 1260, 1363, 1411, 1526, 1597, 1658, 1718, 2851, 2922, 3309; HRMS (ESI-TOF) calcd for $C_{37}H_{45}N_2O_5$ [M-H]$^-$: 597.3334, found: 597.3330.

Pro-Asp(C_8F_{17})-Pro



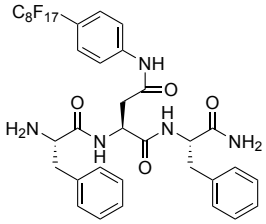
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Pro-OH (4 eq.) and Fmoc-Asp(C_8F_{17})-OH (2 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{28}H_{27}F_{17}N_5O_4$: 820.18, found: 820.18.

Leu-Asp(C_8F_{17})-Leu



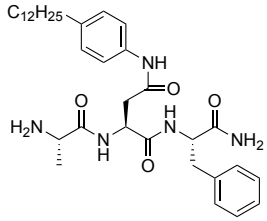
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Leu-OH (4 eq.) and Fmoc-Asp(C_8F_{17})-OH (2 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{30}H_{35}F_{17}N_5O_4$: 852.24, found: 852.55.

Phe-Asp(C_8F_{17})-Phe



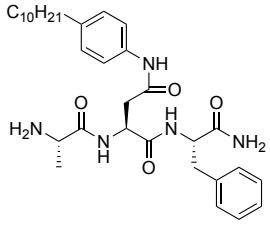
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Phe-OH (4 eq.) and Fmoc-Asp(C_8F_{17})-OH (2 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{36}H_{31}F_{17}N_5O_4$: 920.21, found: 920.17.

Ala-Asp($C_{12}H_{25}$)-Phe



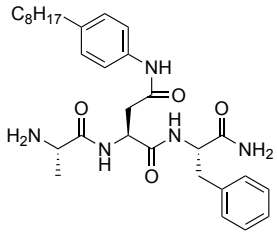
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Ala-OH (4 eq.), Fmoc-Asp($C_{12}H_{25}$)-OH (2 eq.), and Fmoc-Phe-OH (4 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{12}H_{25}C_{34}H_{52}N_5O_4$ [M+H]$^+$: 594.40, found: 594.63.

Ala-Asp($C_{10}H_{21}$)-Phe



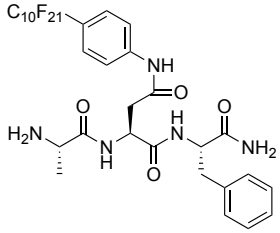
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Ala-OH (4 eq.), Fmoc-Asp($C_{10}H_{21}$)-OH (2 eq.), and Fmoc-Phe-OH (4 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{32}H_{48}N_5O_4$ $[M+H]^+$: 566.37, found: 566.56.

Ala-Asp(C_8H_{17})-Phe



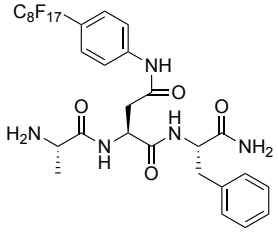
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Ala-OH (4 eq.), Fmoc-Asp(C_8H_{17})-OH (4 eq.), and Fmoc-Phe-OH (4 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{30}H_{44}N_5O_4$ $[M+H]^+$: 538.34, found: 538.53.

Ala-Asp($C_{10}F_{21}$)-Phe



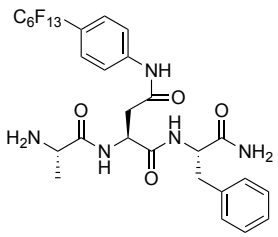
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Ala-OH (4 eq.), Fmoc-Asp($C_{10}F_{21}$)-OH (2 eq.), and Fmoc-Phe-OH (4 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{32}H_{27}F_{21}N_5O_4Na[M+Na]^+$: 966.15, found: 965.85.

Ala-Asp(C_8F_{17})-Phe



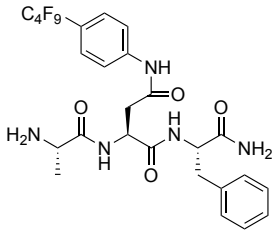
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Ala-OH (4 eq.), Fmoc-Asp(C_8F_{17})-OH (4 eq.), and Fmoc-Phe-OH (4 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{30}H_{27}F_{17}N_5O_4[M+H]^+$: 844.18, found: 844.57.

Ala-Asp(C_6F_{13})-Phe



25 μmol of Rink amide resin was used for the synthesis. Fmoc-Ala-OH (4 eq.), Fmoc-Asp(C_6F_{13})-OH (4 eq.), and Fmoc-Phe-OH (4 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{28}H_{27}F_{13}N_5O_4$ $[M+H]^+$: 744.18, found: 744.48.

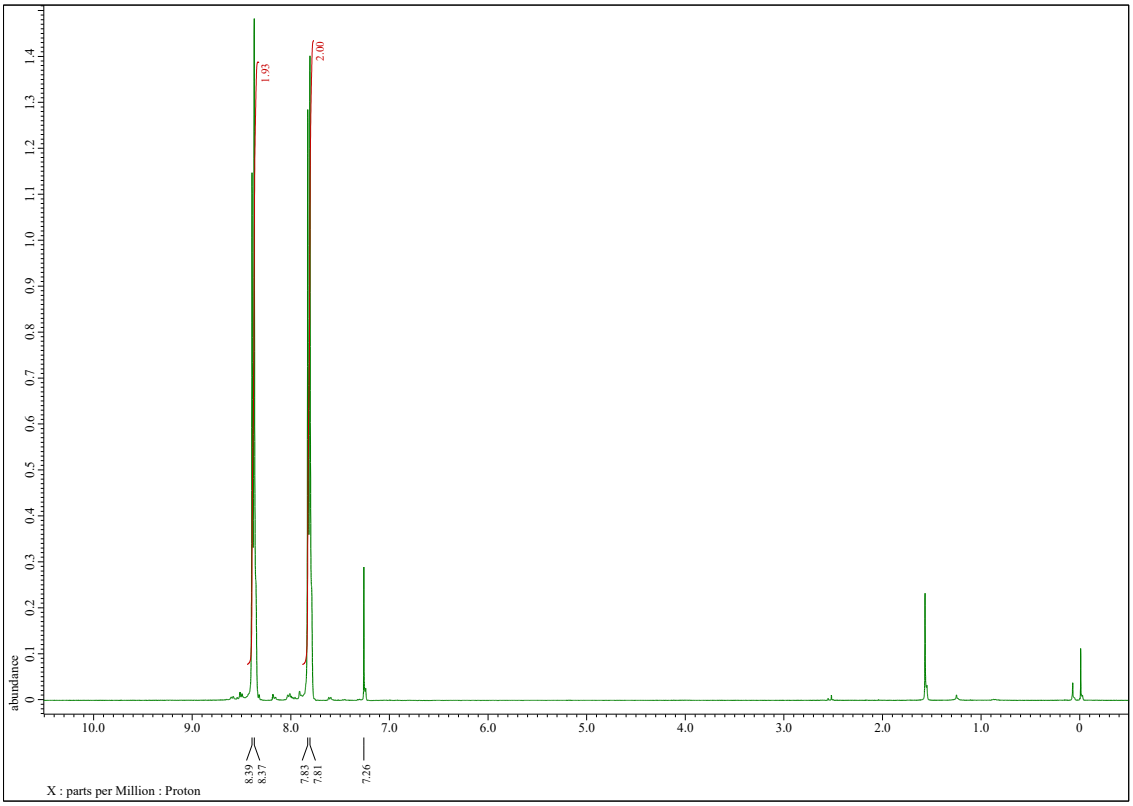
Ala-Asp(C_4F_9)-Phe

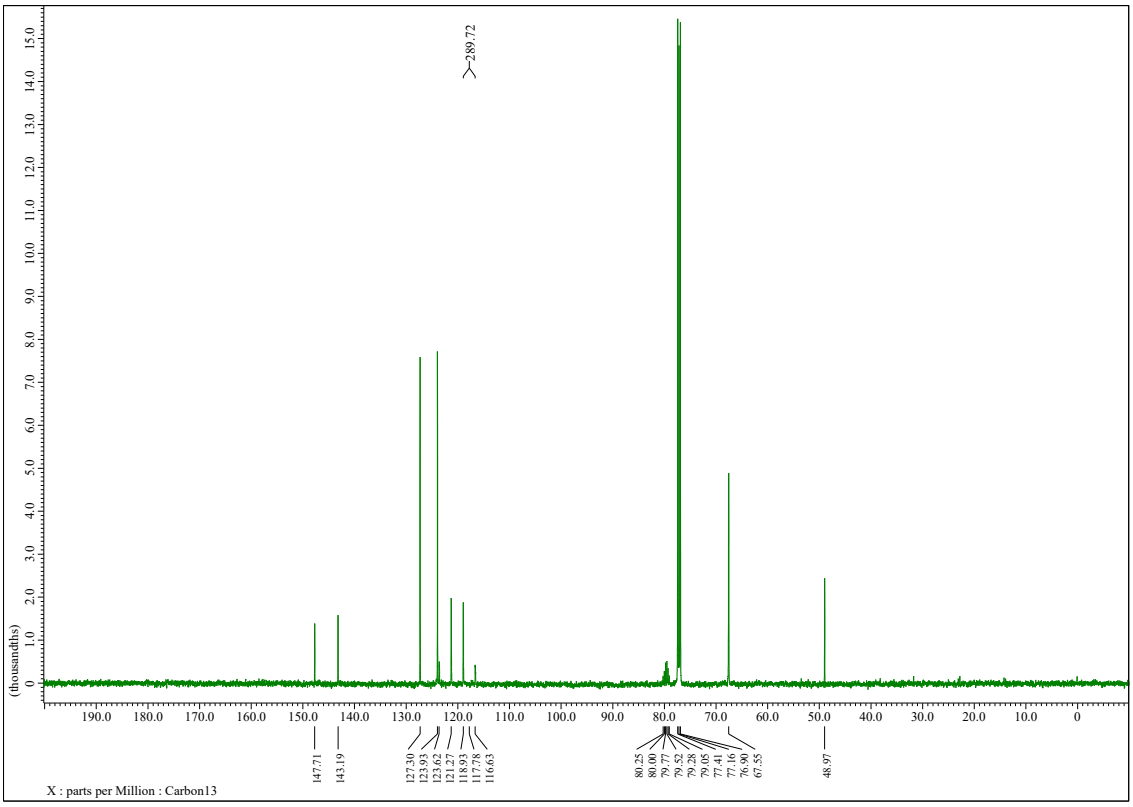


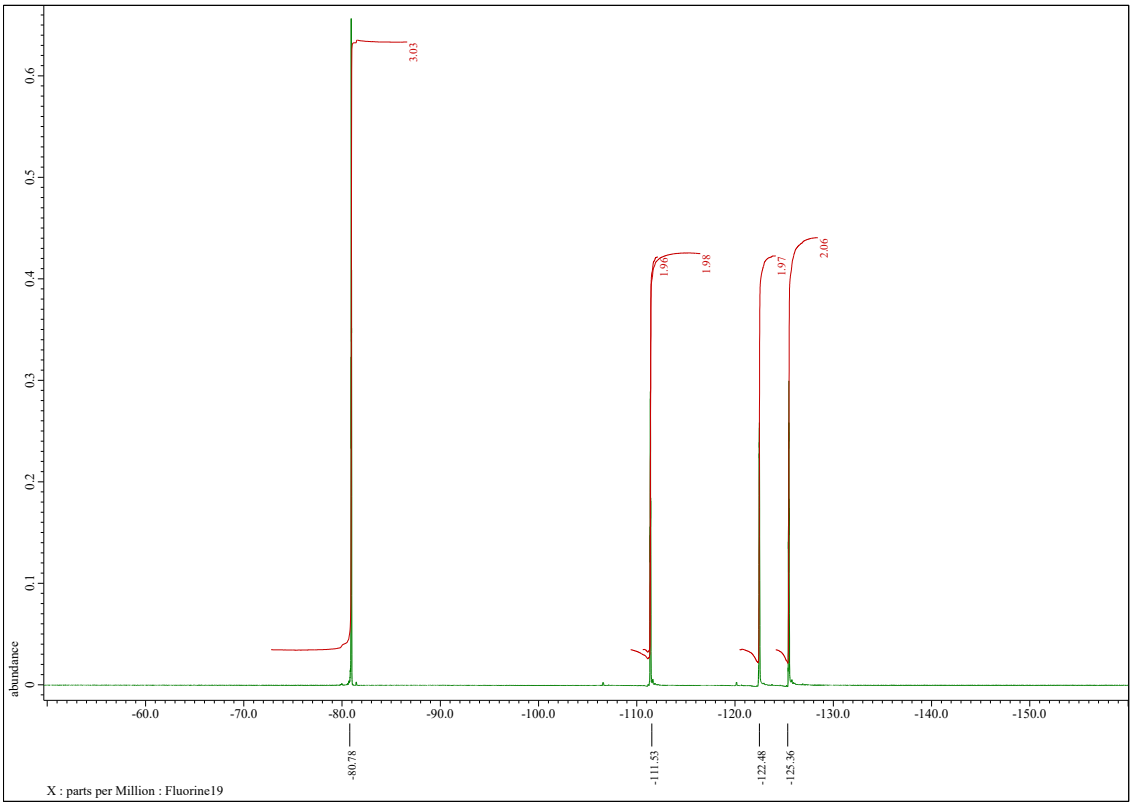
25 μmol of Rink amide resin was used for the synthesis. Fmoc-Ala-OH (4 eq.), Fmoc-Asp(C_4F_9)-OH (4 eq.), and Fmoc-Phe-OH (4 eq.) were used as building blocks. A part of the crude was purified by HPLC. LRMS (ESI-TOF) calcd for $C_{26}H_{27}F_9N_5O_4$ $[M+H]^+$: 644.19, found: 644.81.

NMR spectra

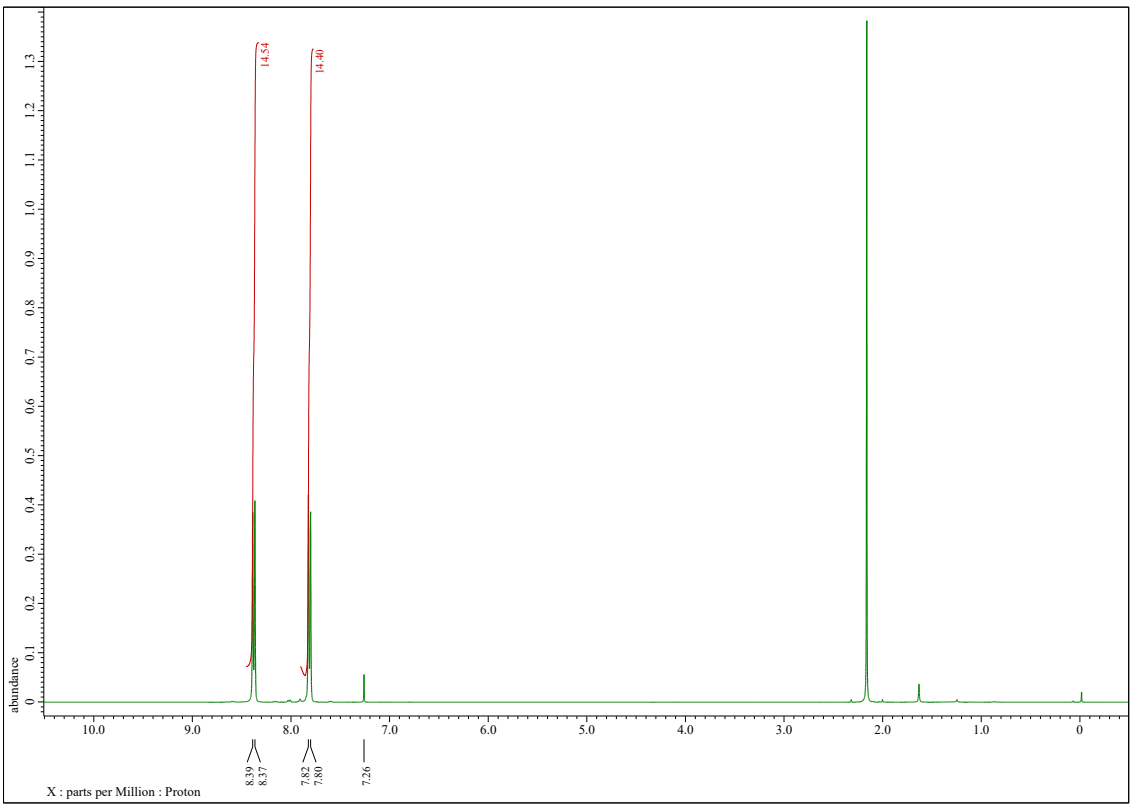
C_4F_9-Ar-NO_2 (1a)

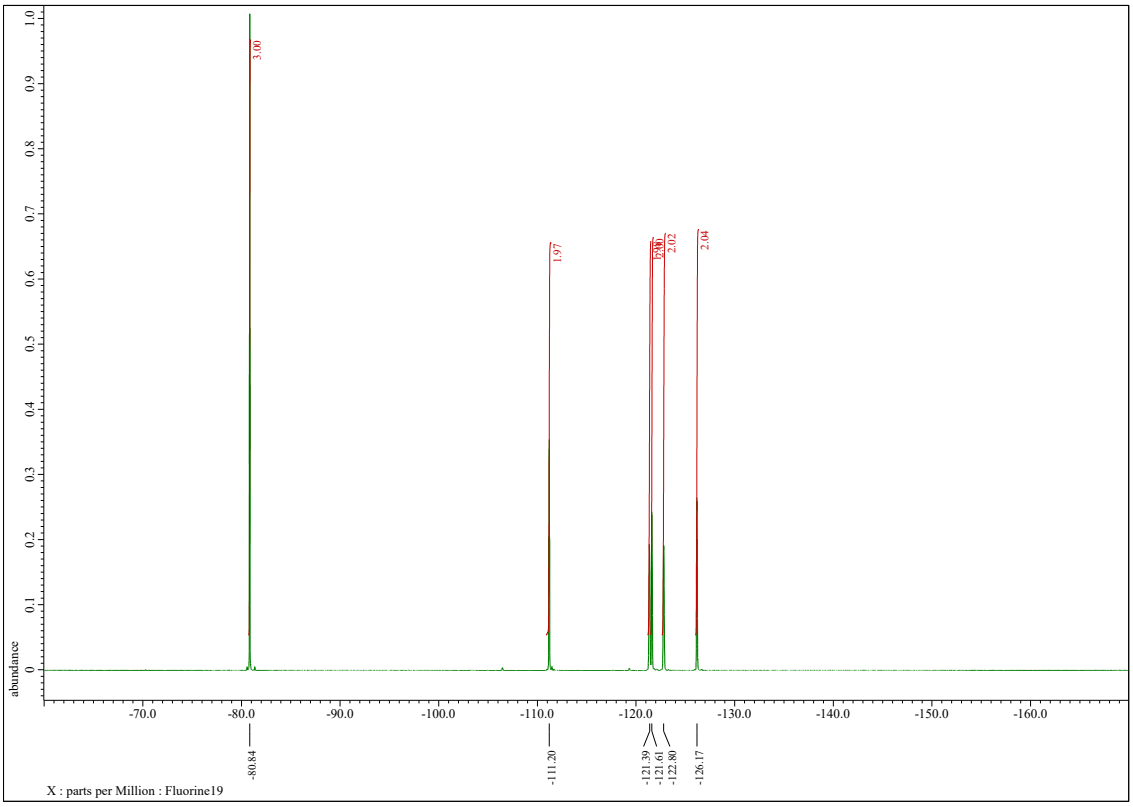


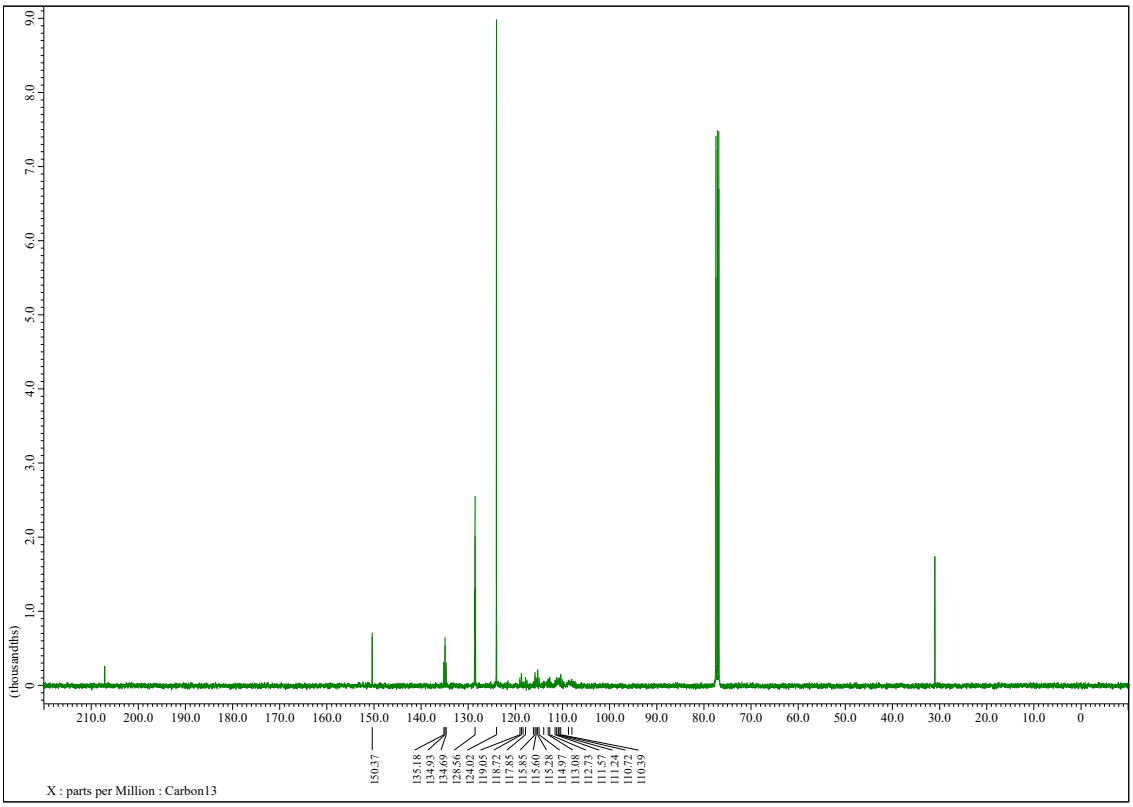

289.72
(thousandths)
X : parts per Million : Carbon13
147.71
143.19
127.30
123.93
123.62
121.27
118.93
117.78
116.63
80.25
80.00
79.77
79.52
79.28
79.05
77.41
77.16
76.90
67.55
48.97


3.03
1.96
1.98
1.97
2.06
abundance
X : parts per Million : Fluorine19
-80.78
-111.53
-122.48
-125.36

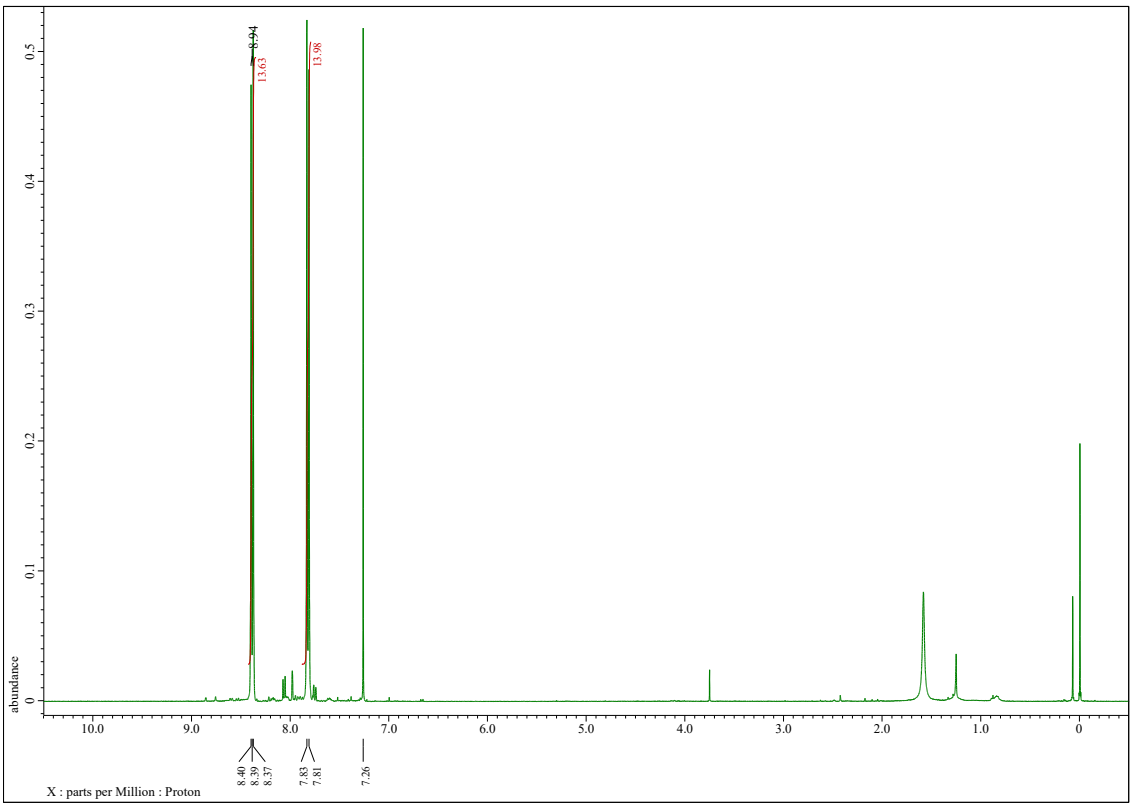
C_6F_{13}-Ar-NO_2 (1b)

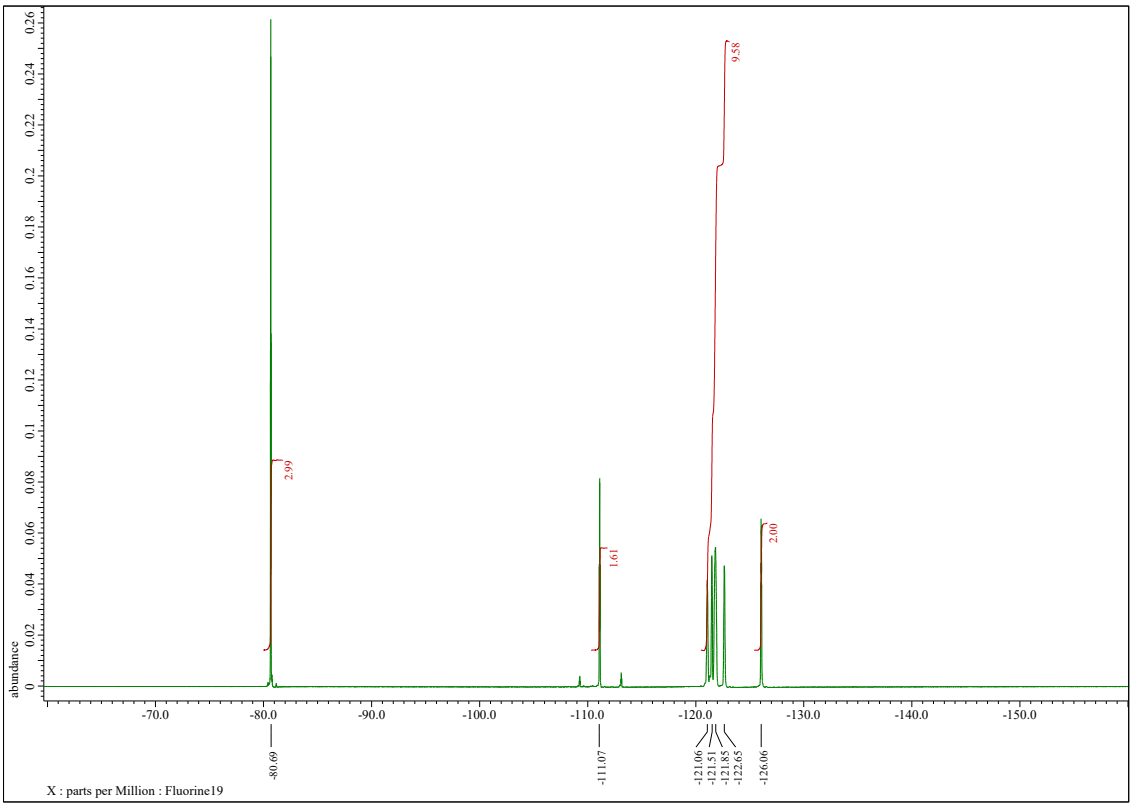


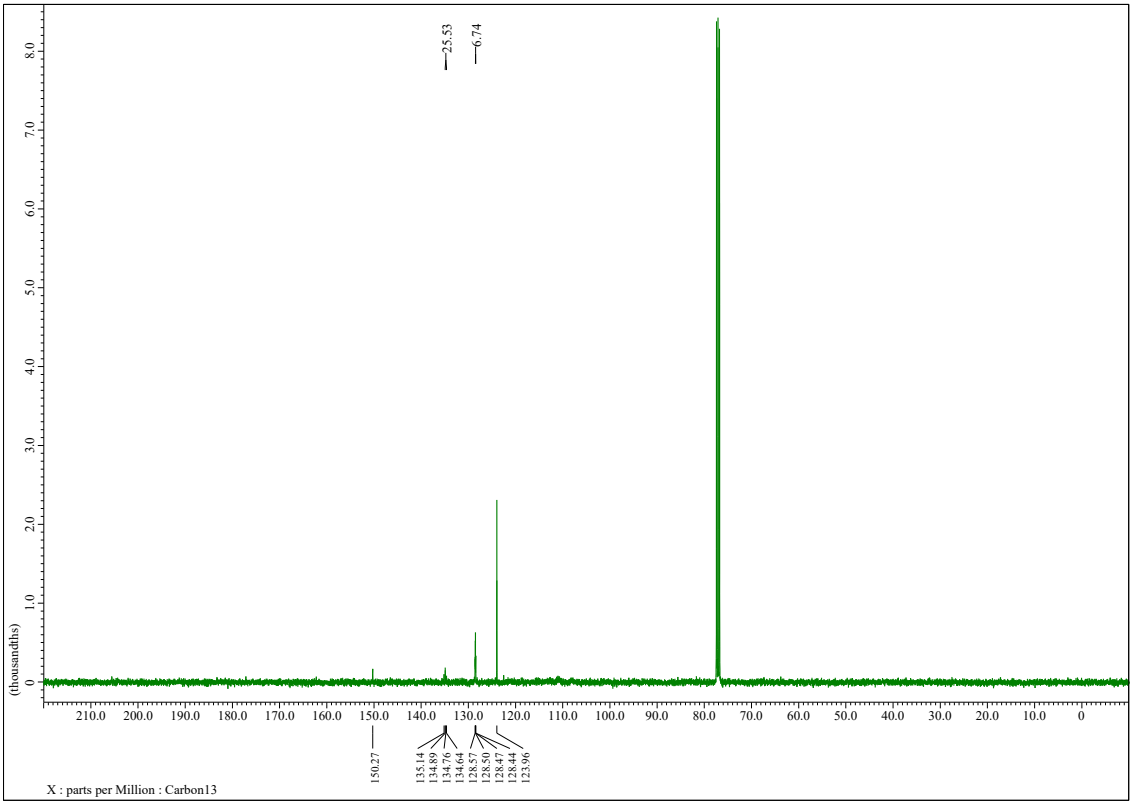




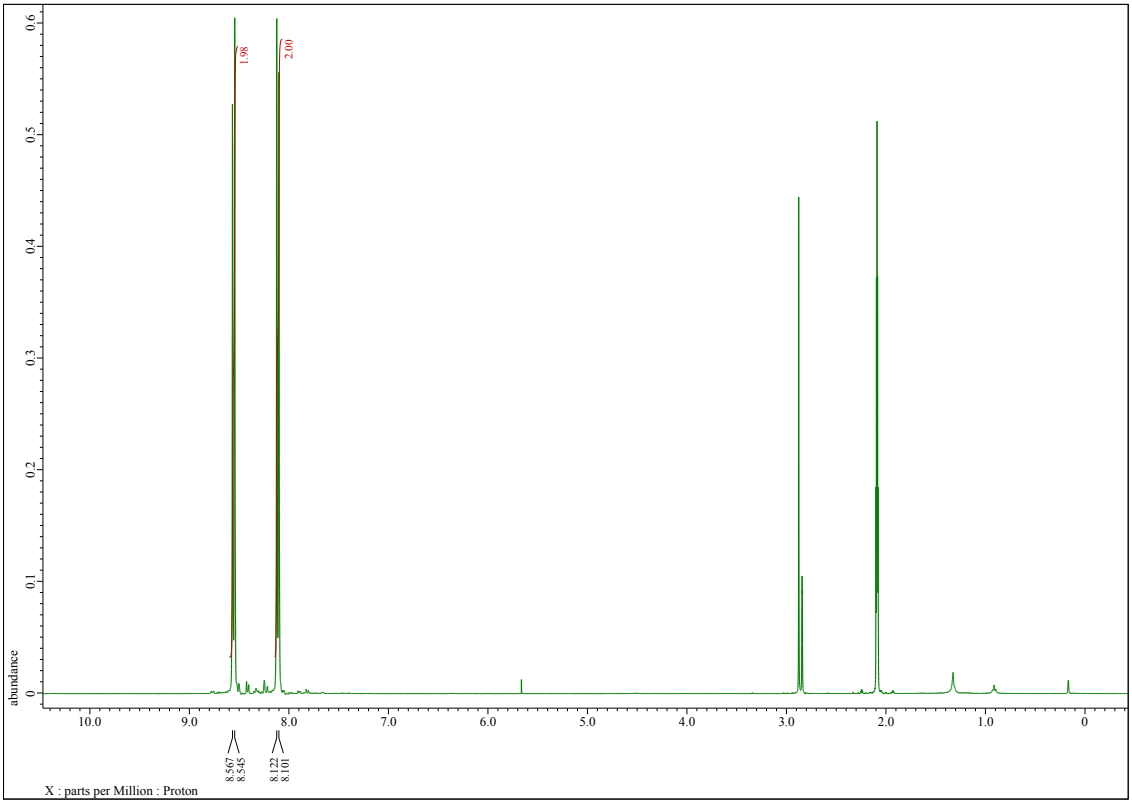
C_8F_{17}-Ar-NO_2 (1c)

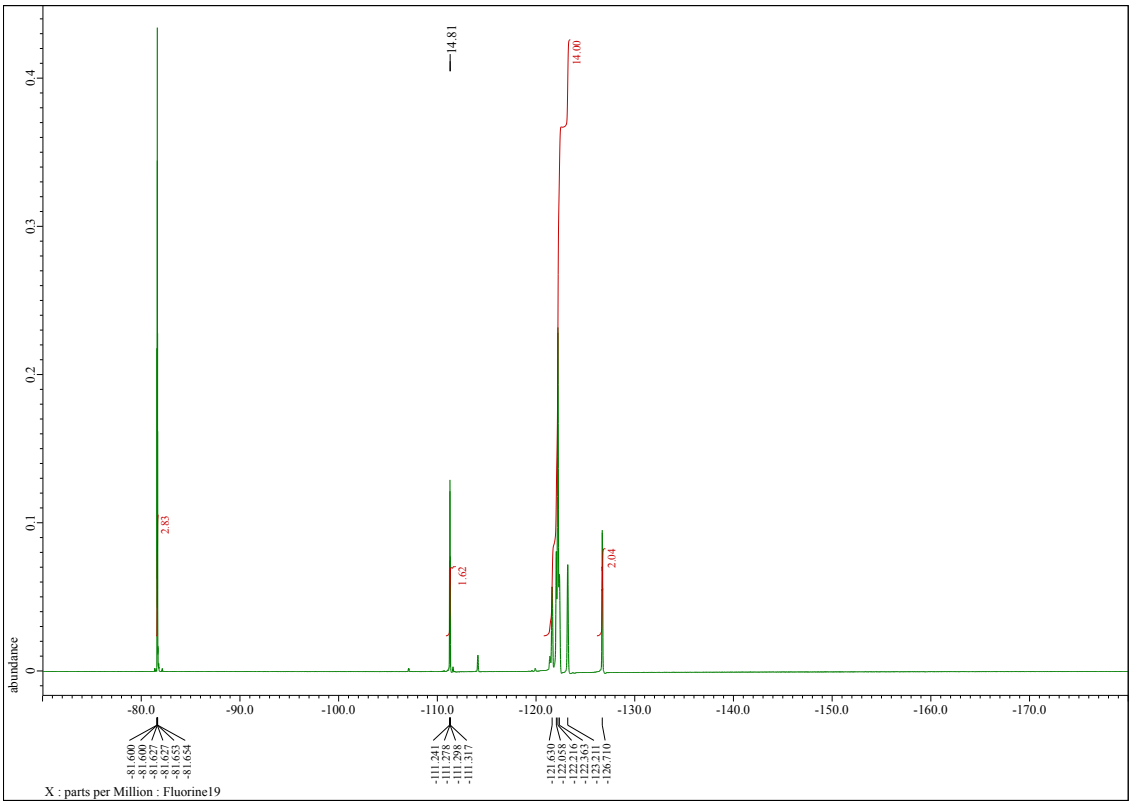


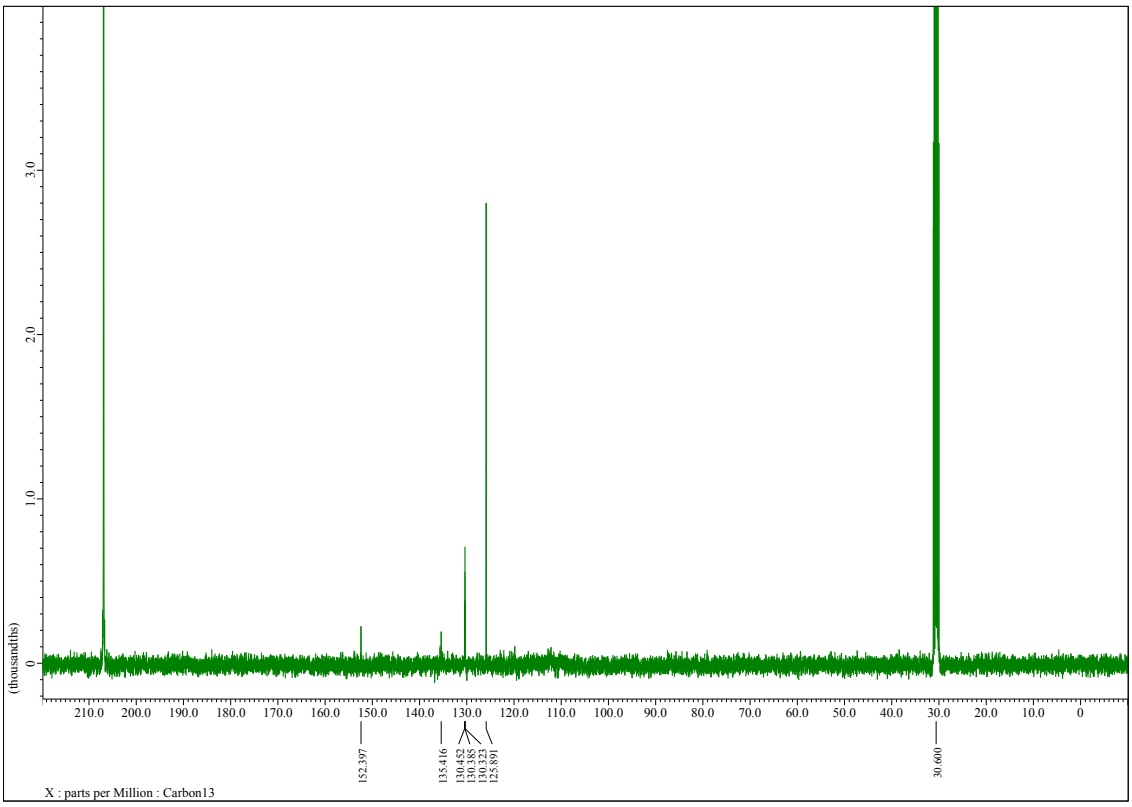

abundance
2.99
1.61
9.58
2.00
-80.69
-111.07
-121.06
-121.51
-121.85
-122.65
-126.06
X : parts per Million : Fluorine19

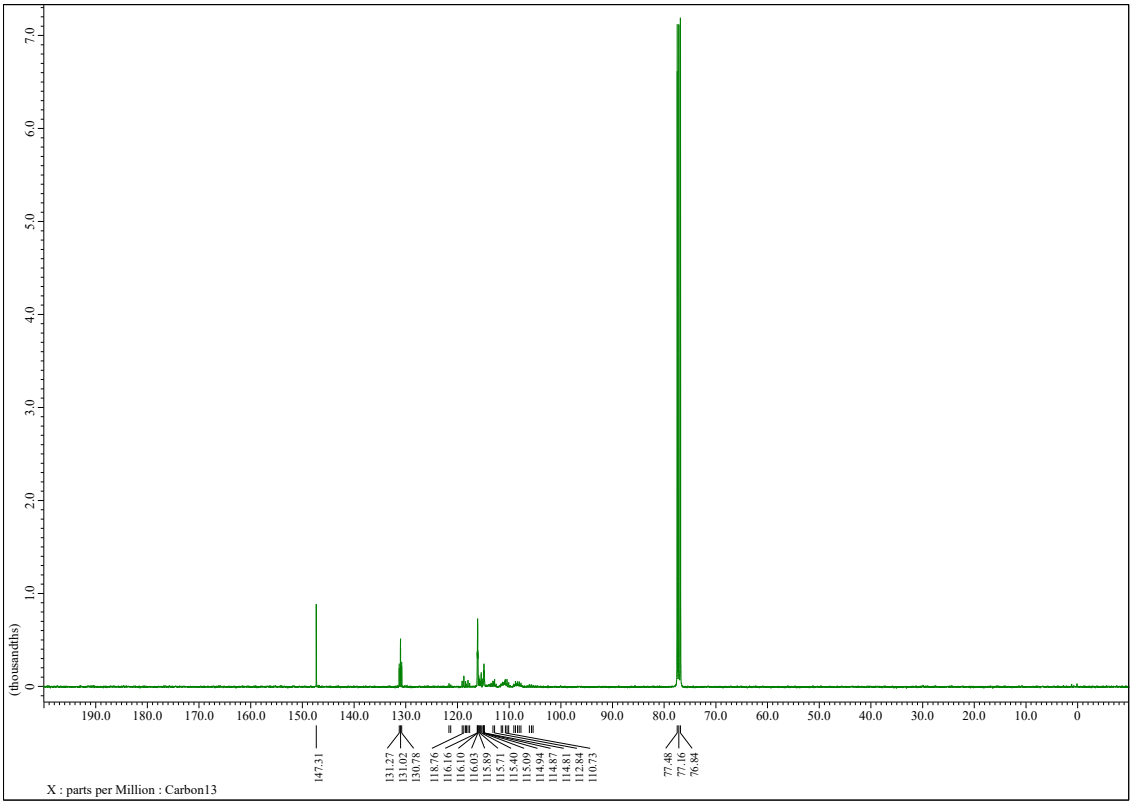

(thousandths)
25.53
6.74
150.27
135.14
134.89
134.76
134.64
128.57
128.47
128.44
123.96
X : parts per Million : Carbon13

$C_{10}F_{21}$-Ar-NO_2 (1d)

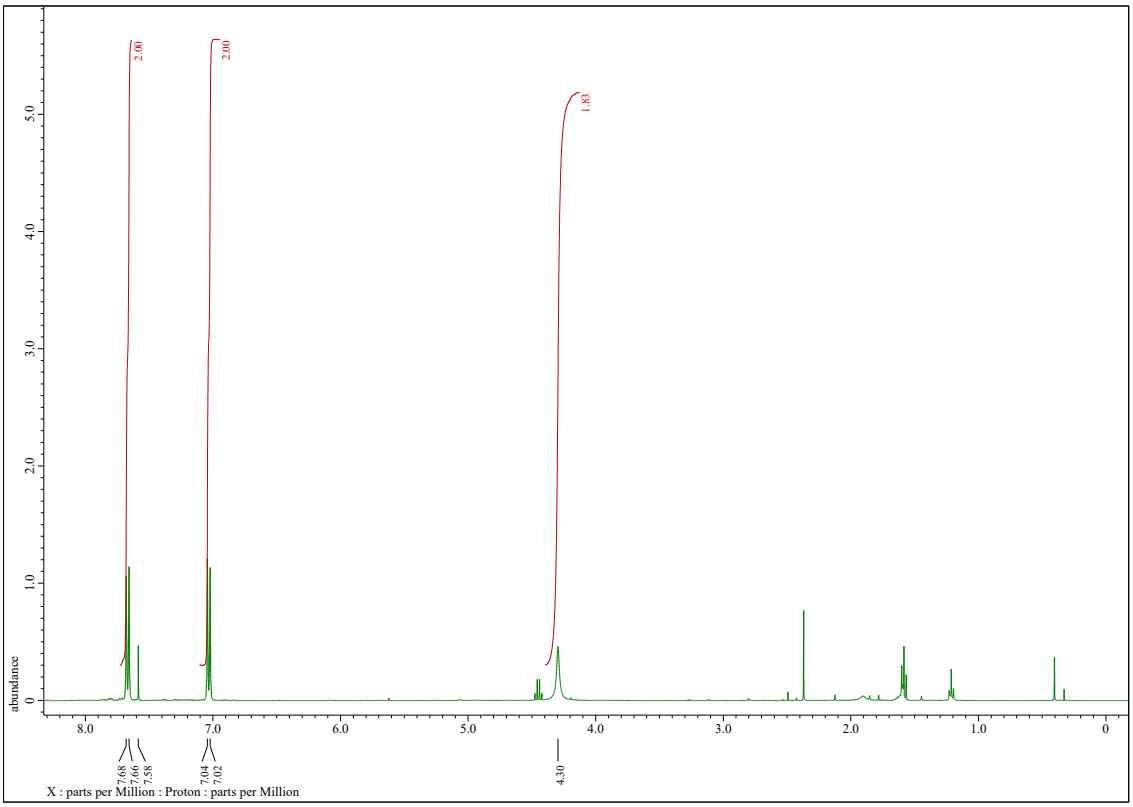


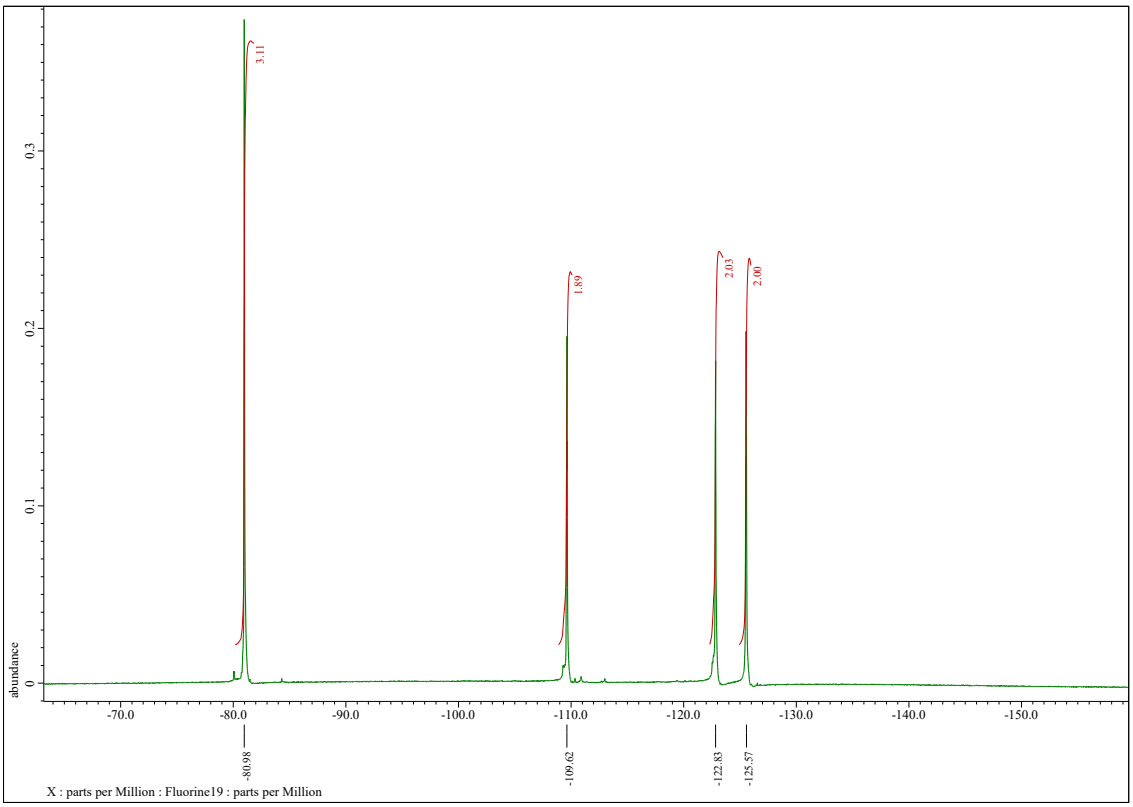



(thousandths)
3.0
2.0
1.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
152.397
135.416
130.452
130.382
130.323
125.891
30.600
X : parts per Million : Carbon13

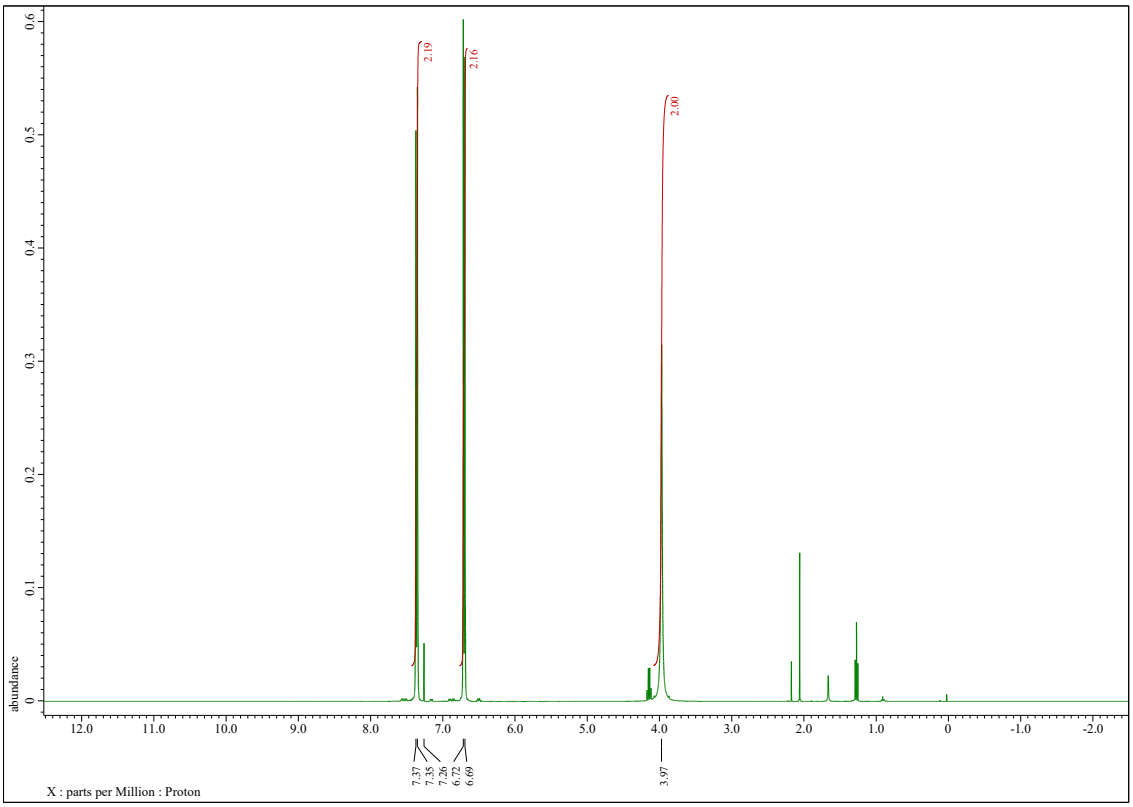

(thousandths)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
147.31
131.27
131.02
130.78
118.76
116.16
116.10
116.03
115.89
115.71
115.40
115.09
114.94
114.87
114.81
112.84
110.73
77.48
77.46
76.84
X : parts per Million : Carbon13

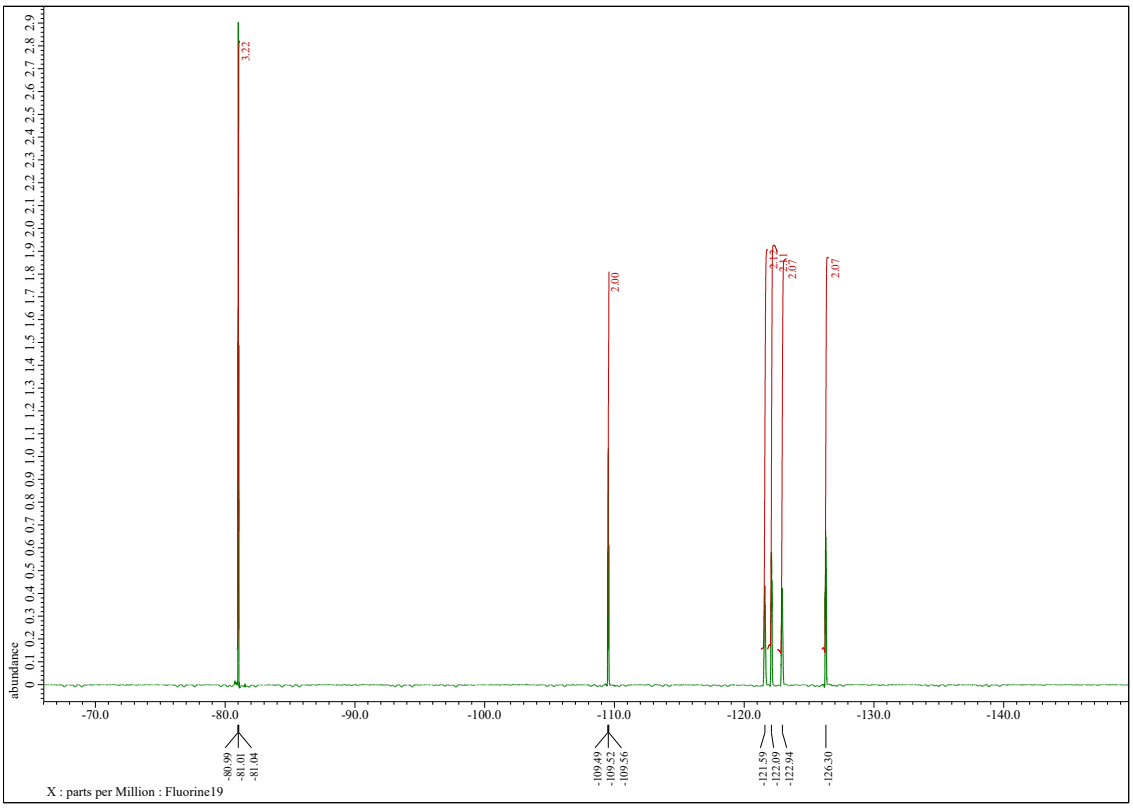
C_4F_9-Ar-NH_2 (2a)



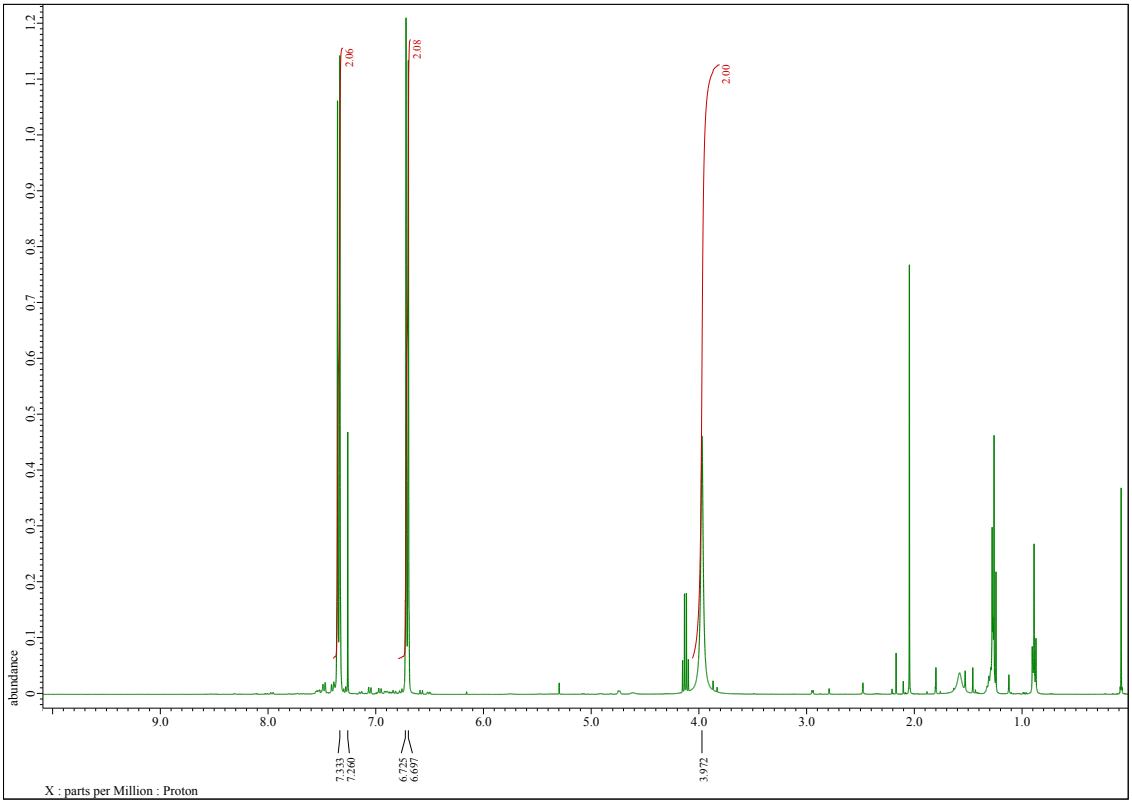


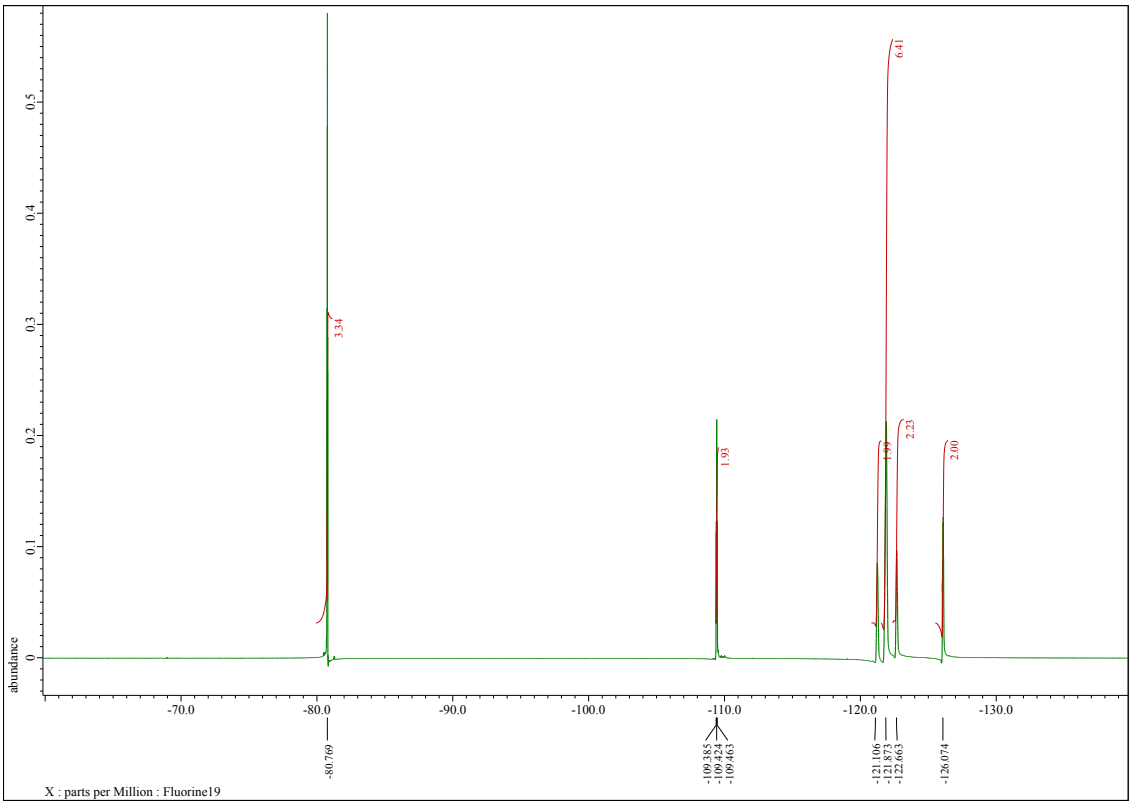
C_6F_{13}-Ar-NH_2 (2b)



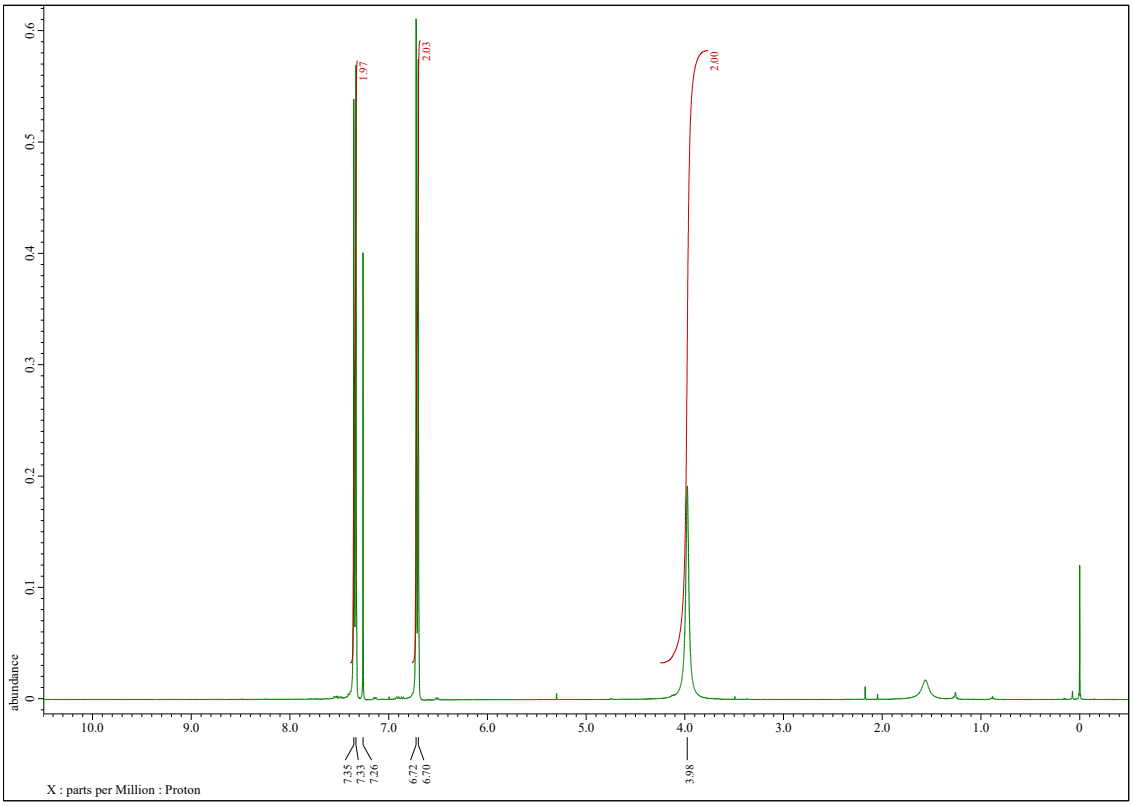


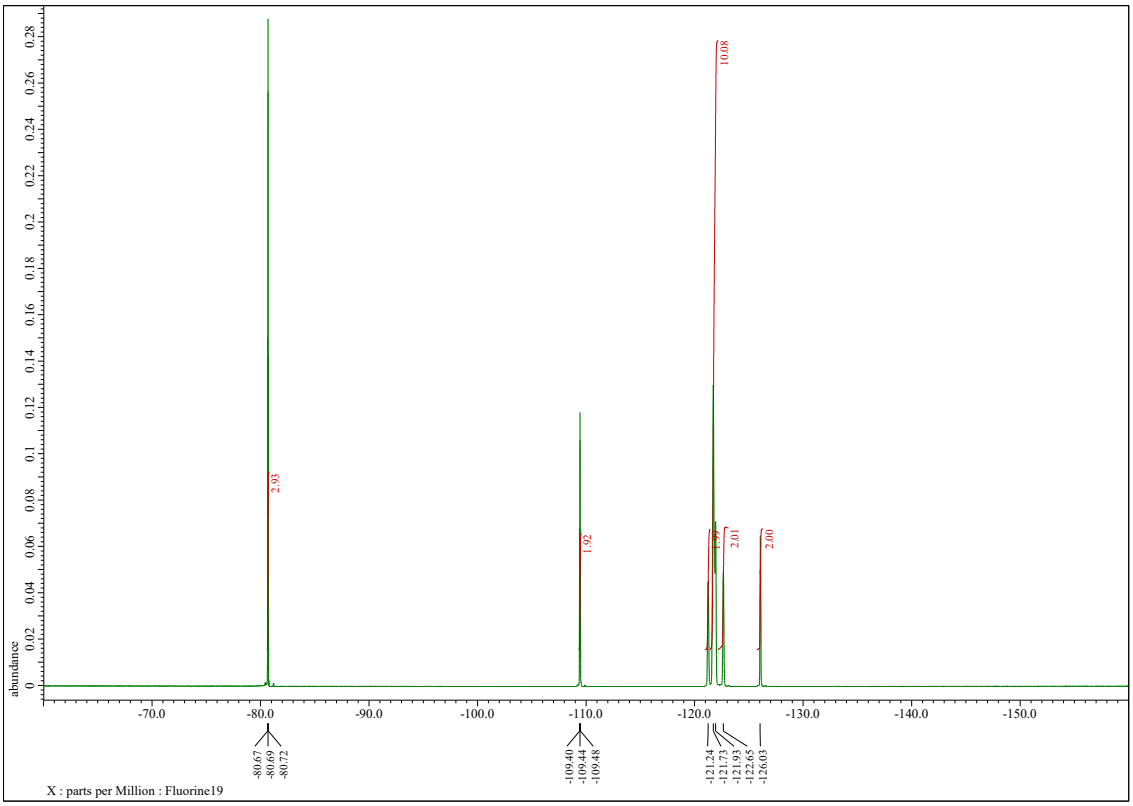
C_8F_{17}-Ar-NH_2 (2c)



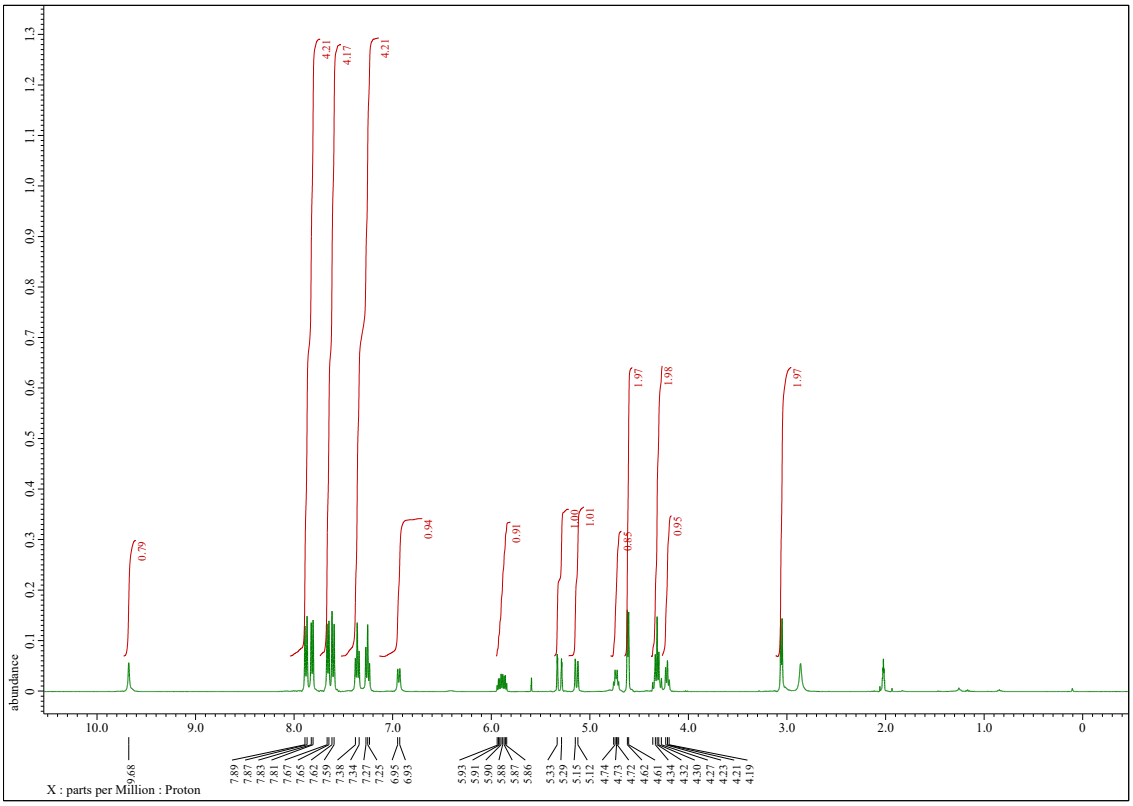


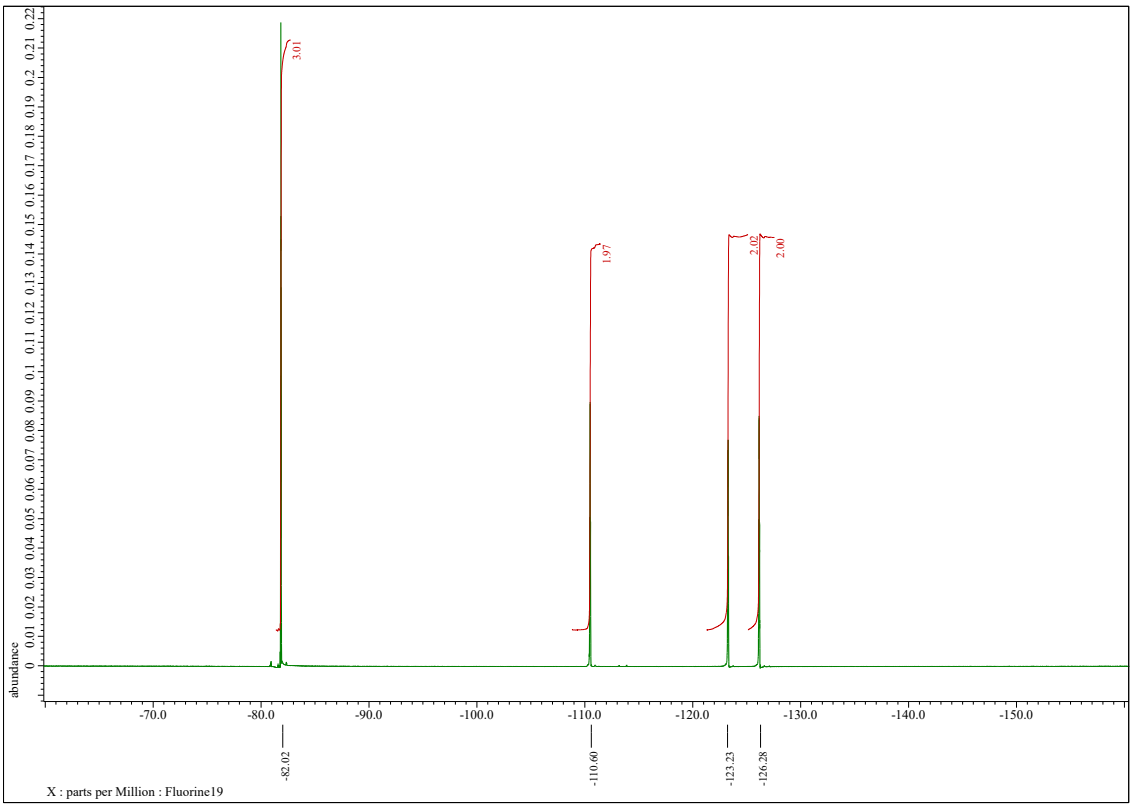
$C_{10}F_{21}$-Ar-NH_2 (2d)

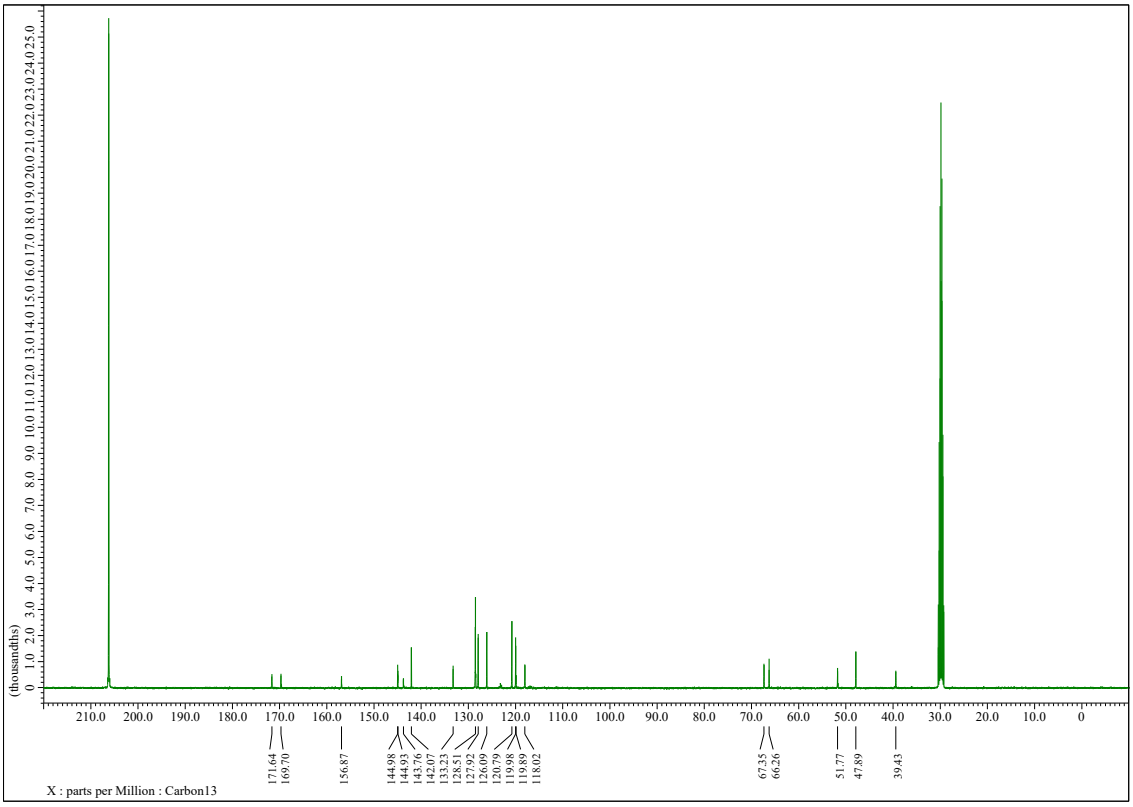




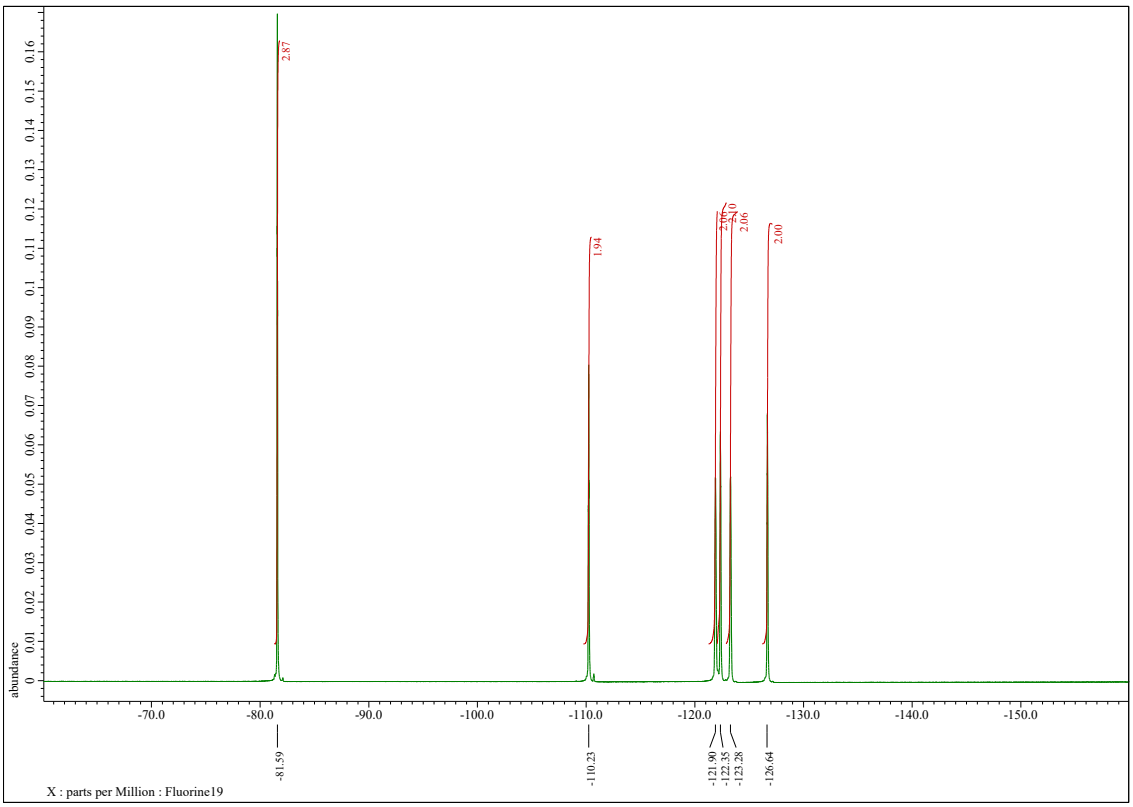
Fmoc-Asp(C_4F_9)-OAll (3a)

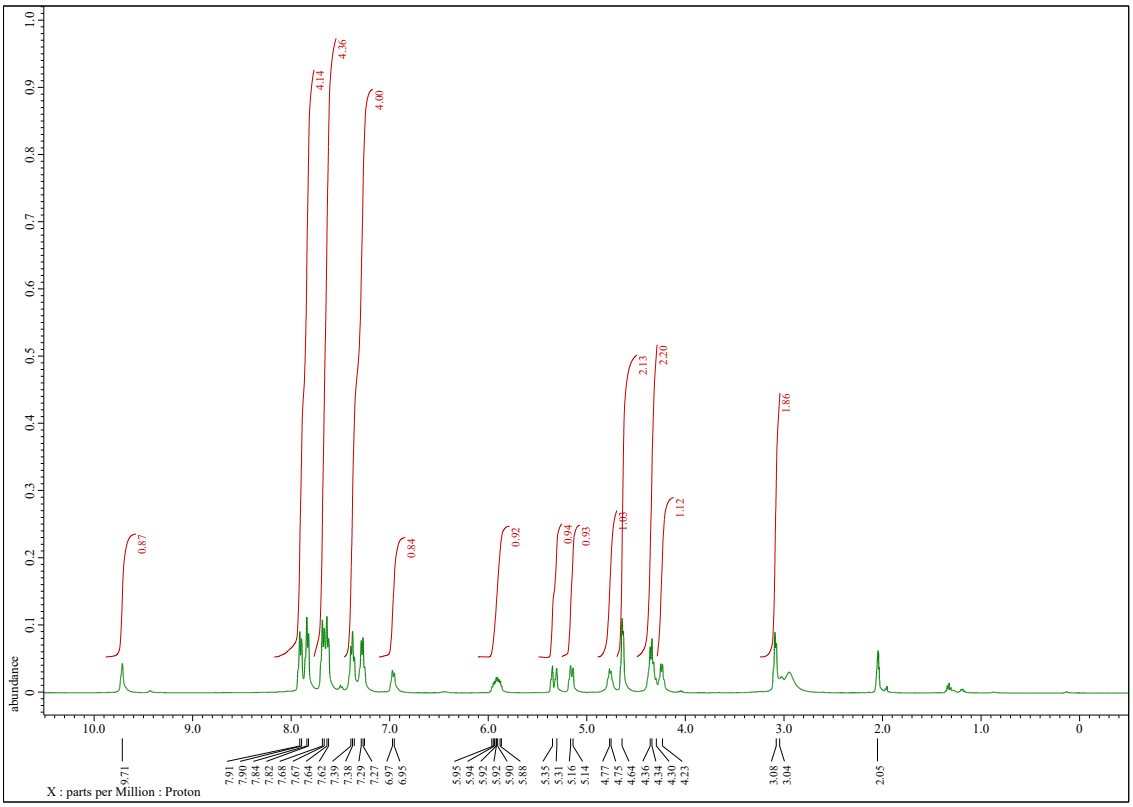


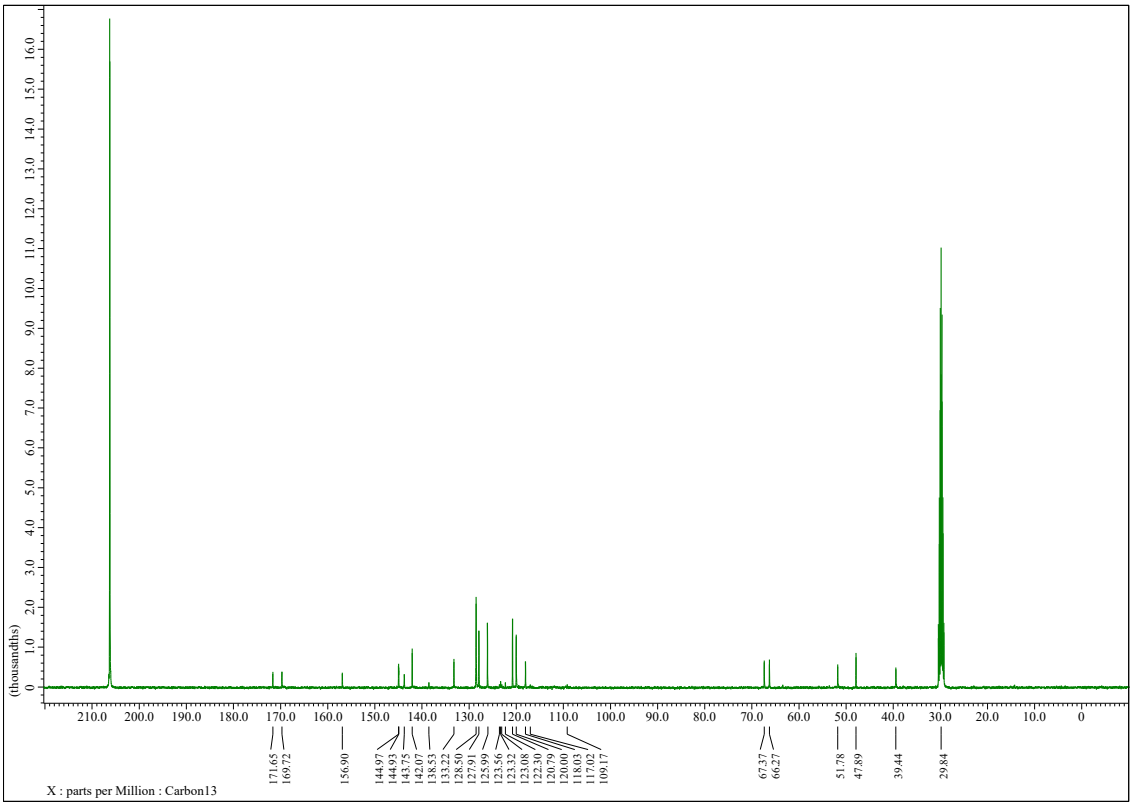




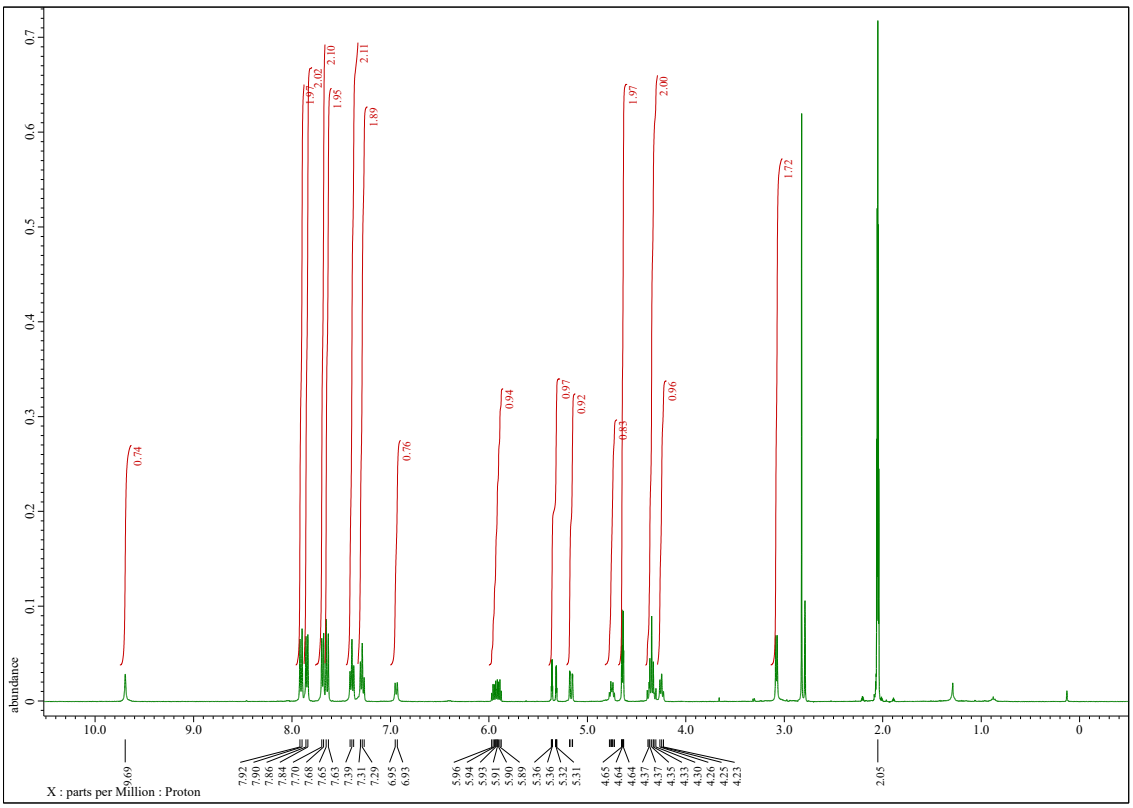
Fmoc-Asp(C_6F_{13})-OAll (3b)

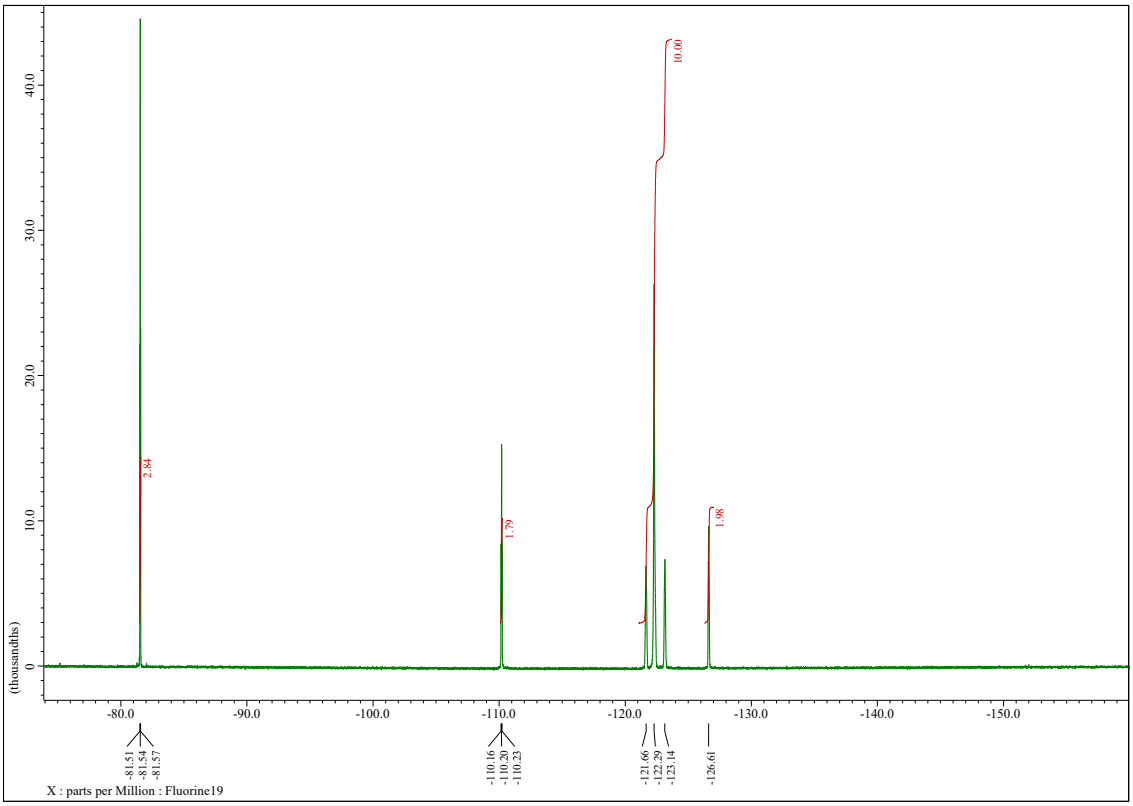


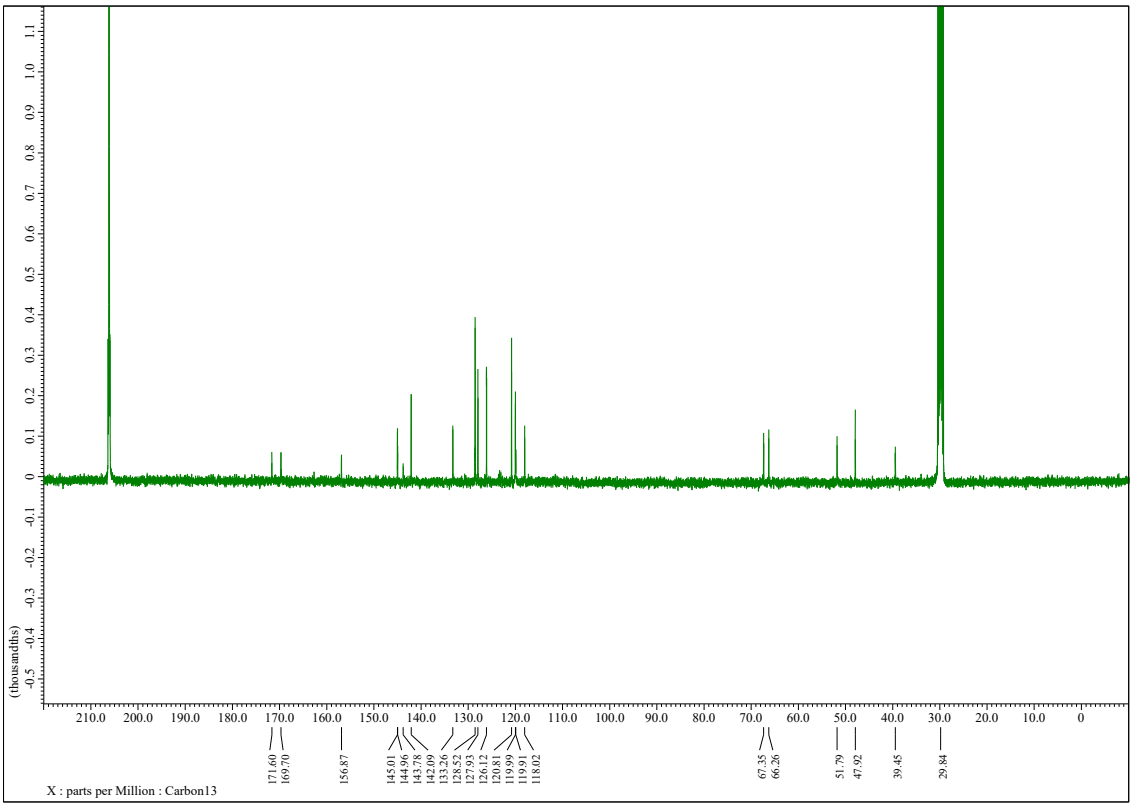

abundance
4.36
4.14
4.00
2.13
2.20
1.86
1.12
1.03
0.94
0.93
0.92
0.87
0.84
9.71
7.91
7.90
7.84
7.82
7.68
7.67
7.64
7.62
7.39
7.38
7.29
7.27
6.97
6.95
5.95
5.94
5.92
5.92
5.90
5.88
5.35
5.31
5.16
5.14
4.77
4.75
4.64
4.36
4.34
4.30
4.23
3.08
3.04
2.05
X : parts per Million : Proton


(thousandths)
171.65
169.72
156.90
144.97
144.93
143.75
142.07
138.53
133.22
131.91
127.91
125.99
123.56
123.32
123.08
122.30
120.79
120.00
118.03
117.02
109.17
67.37
66.27
51.78
47.89
39.44
29.84
X : parts per Million : Carbon13

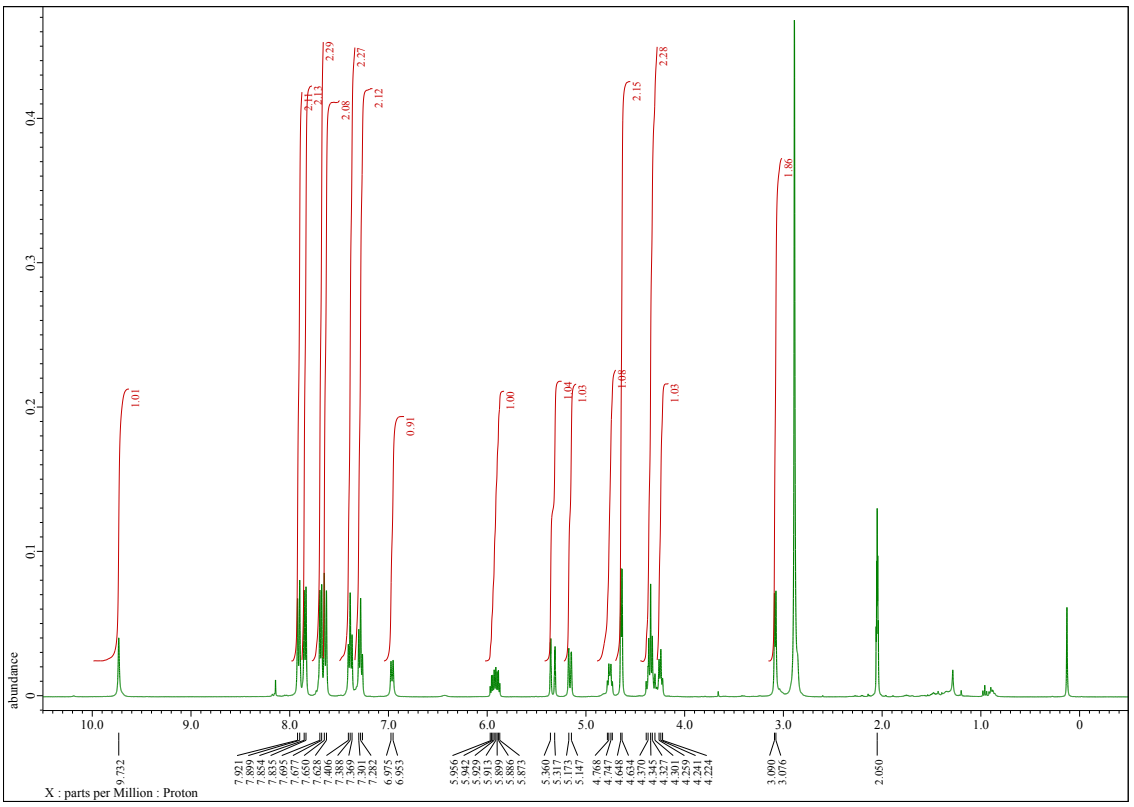
Fmoc-Asp(C_8F_{17})-OAll (3c)

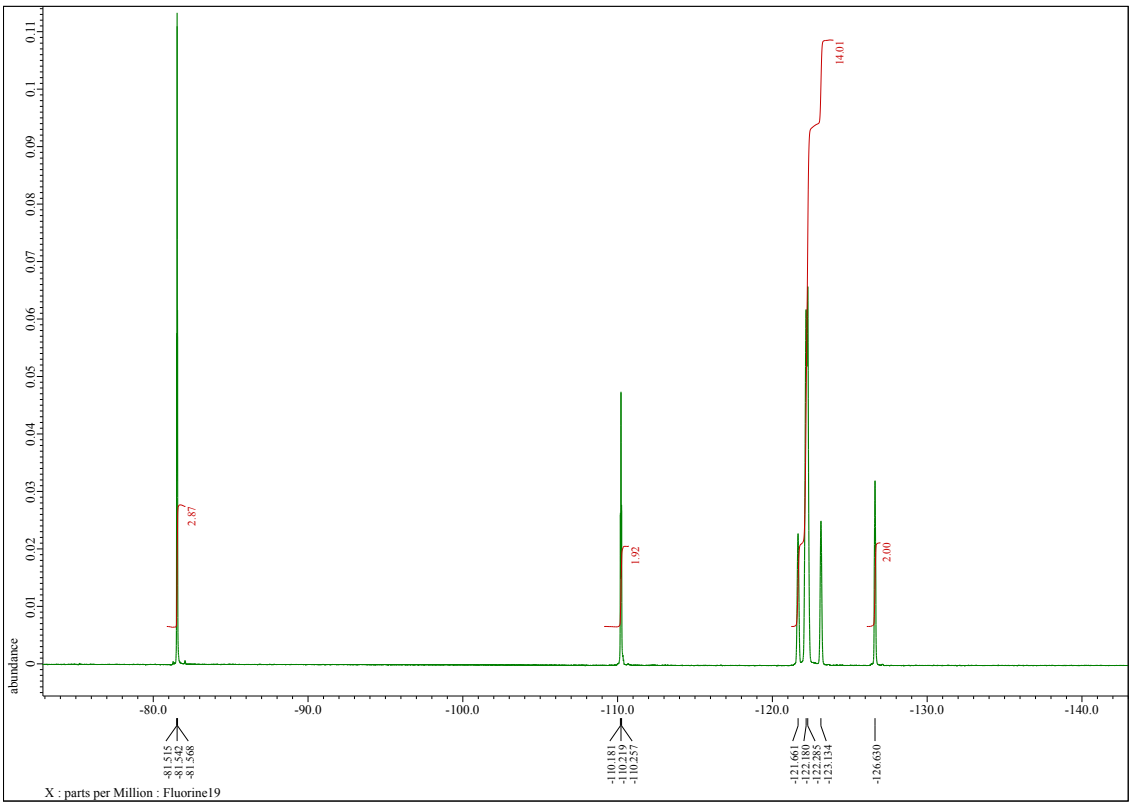


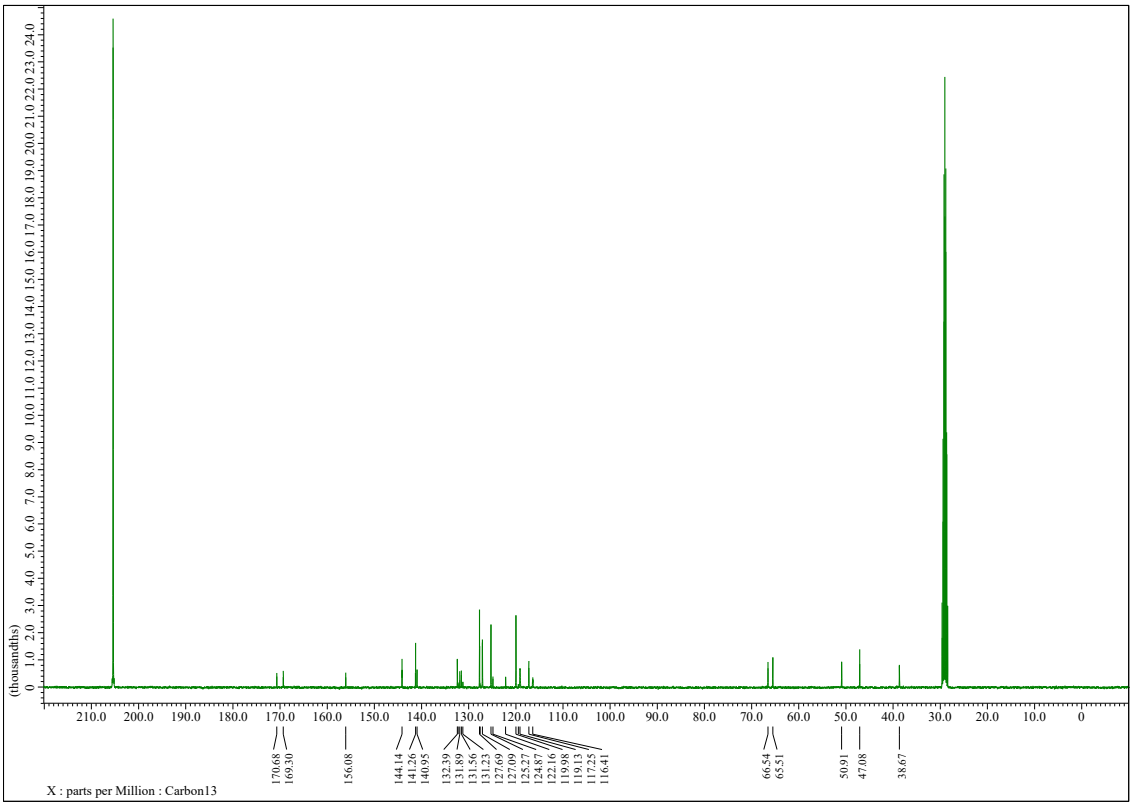




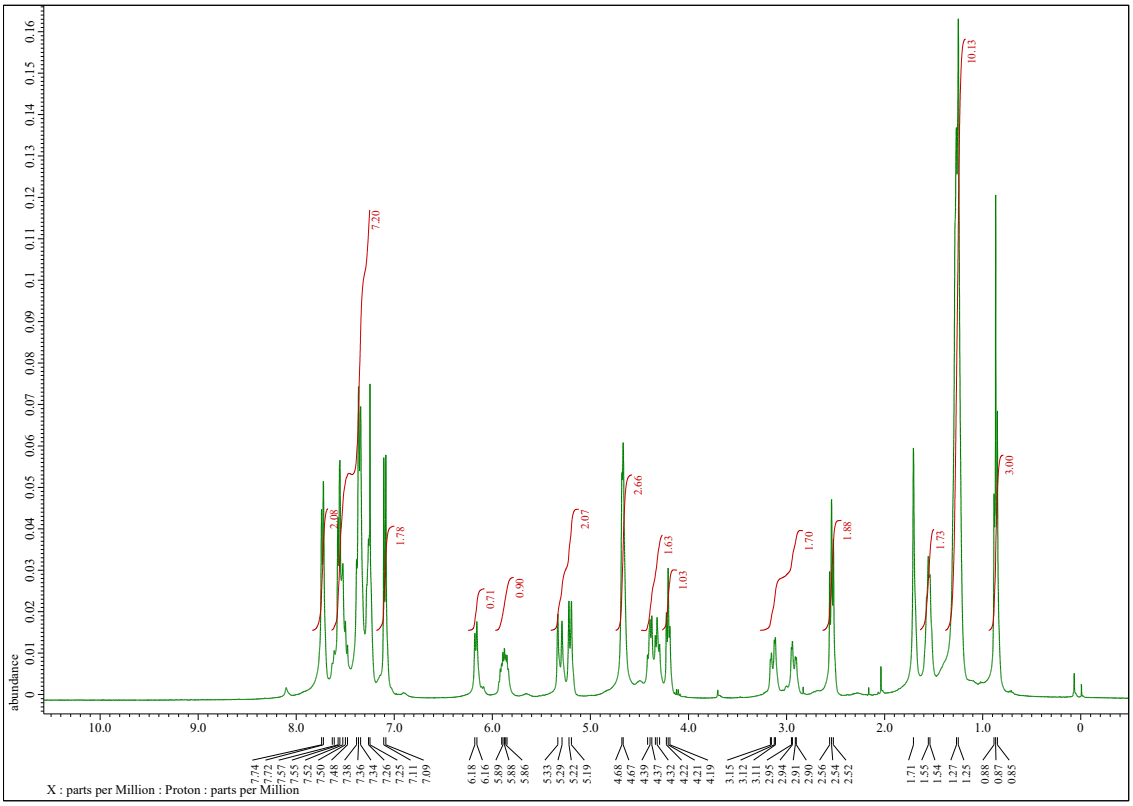
Fmoc-Asp($C_{10}F_{21}$)-OAll (3d)

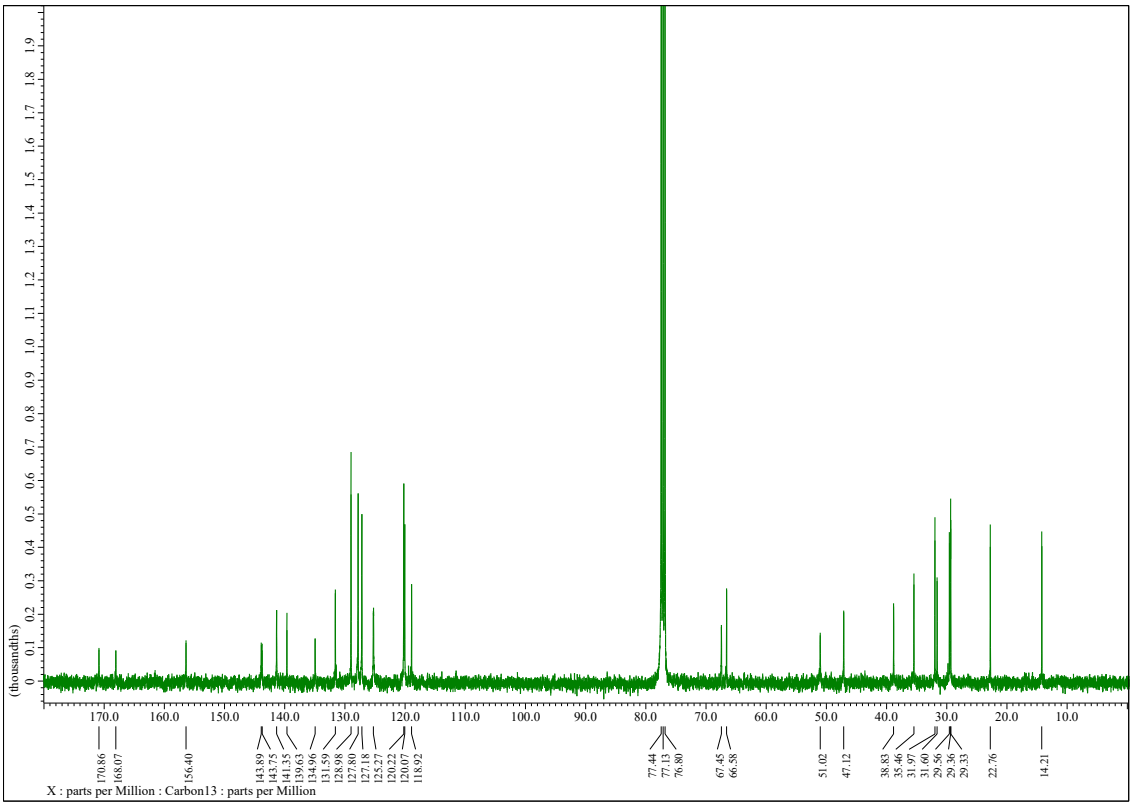



abundance
14.01
2.87
1.92
2.00
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-81.515
-81.562
-81.568
-110.181
-110.219
-110.257
-121.661
-122.180
-122.285
-123.134
-126.630
X : parts per Million : Fluorine19

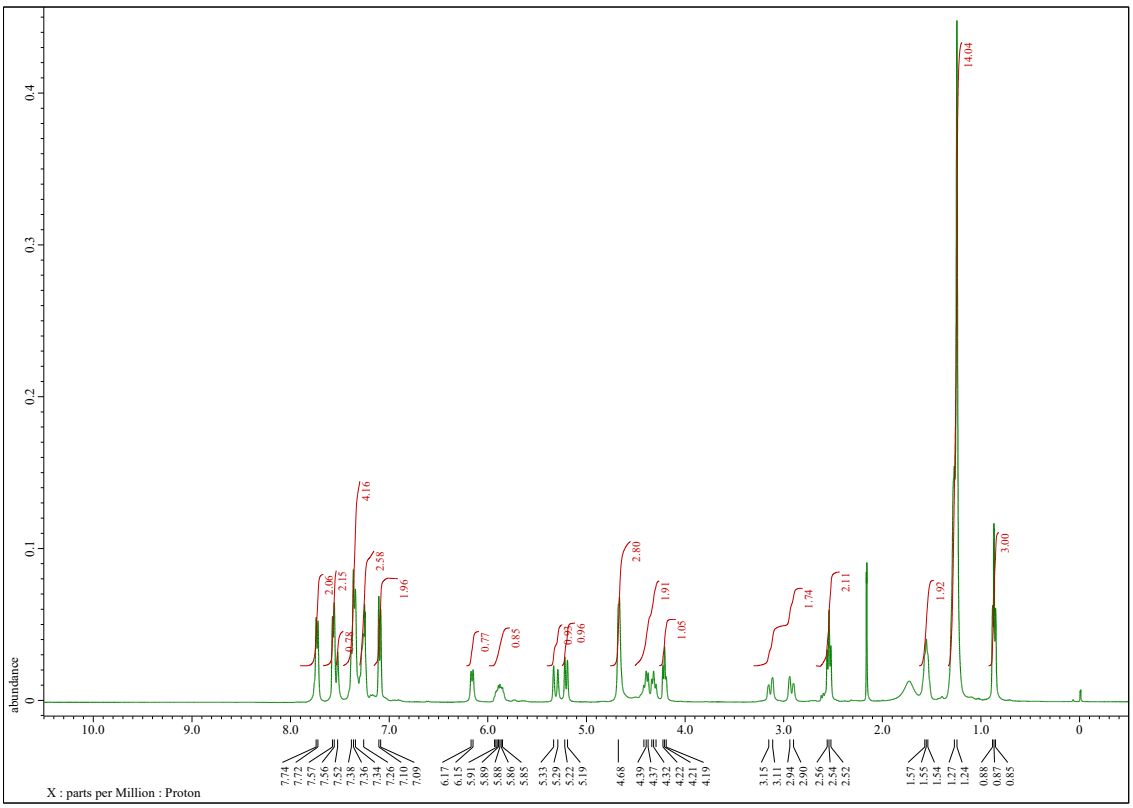

(thousandths)
170.68
169.30
156.08
144.14
141.26
140.95
132.39
131.89
131.56
131.23
127.69
127.09
125.27
124.87
122.16
119.98
119.13
117.25
116.41
66.54
65.51
50.91
47.08
38.67
X : parts per Million : Carbon13

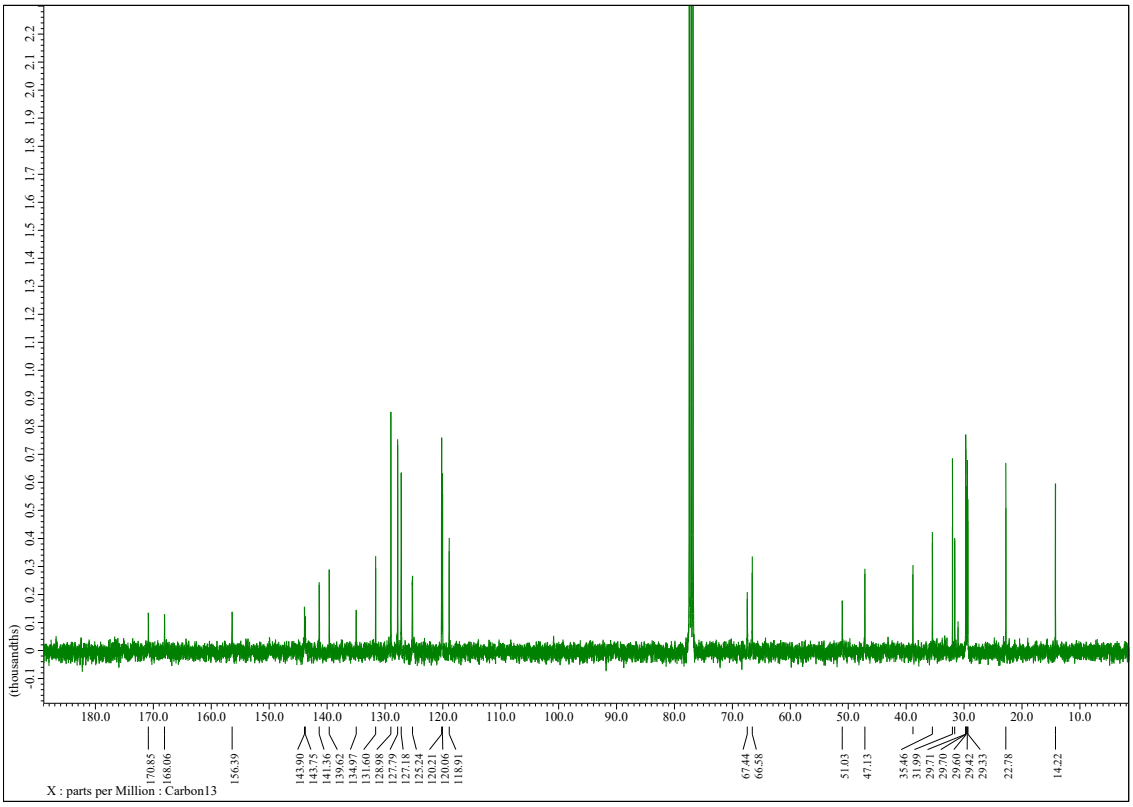
Fmoc-Asp(C_8H_{17})-OAll (3e)



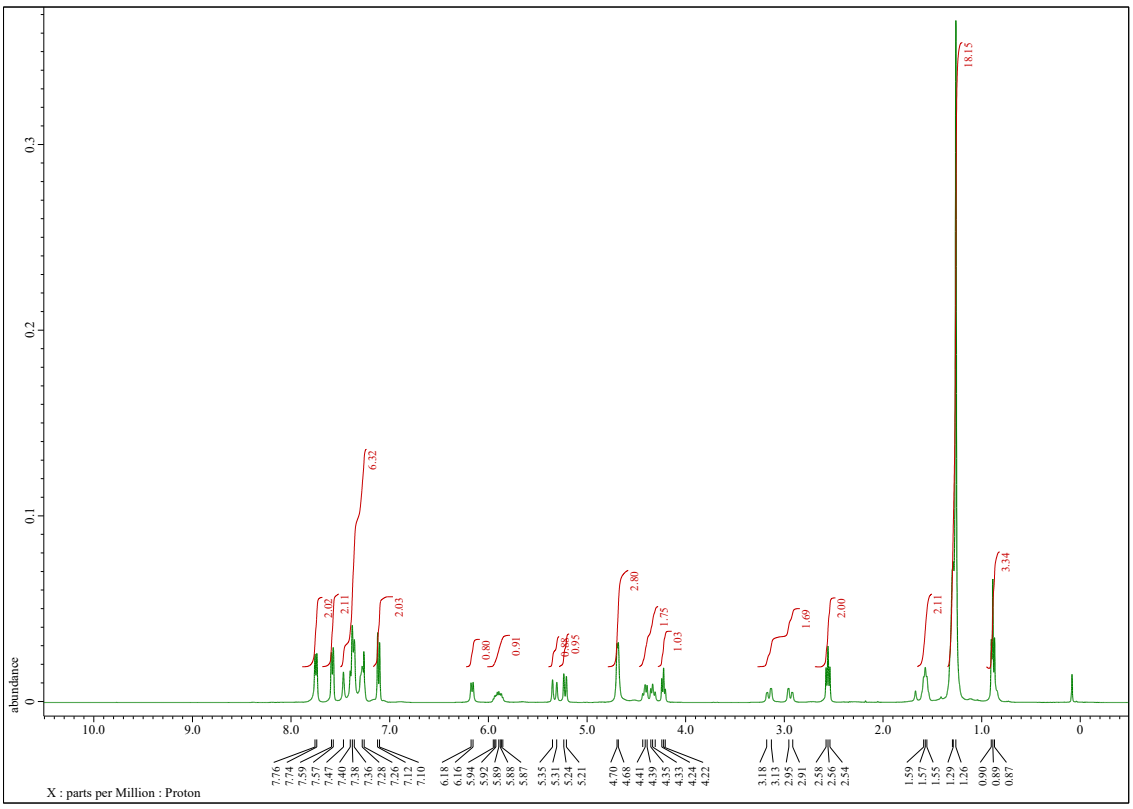


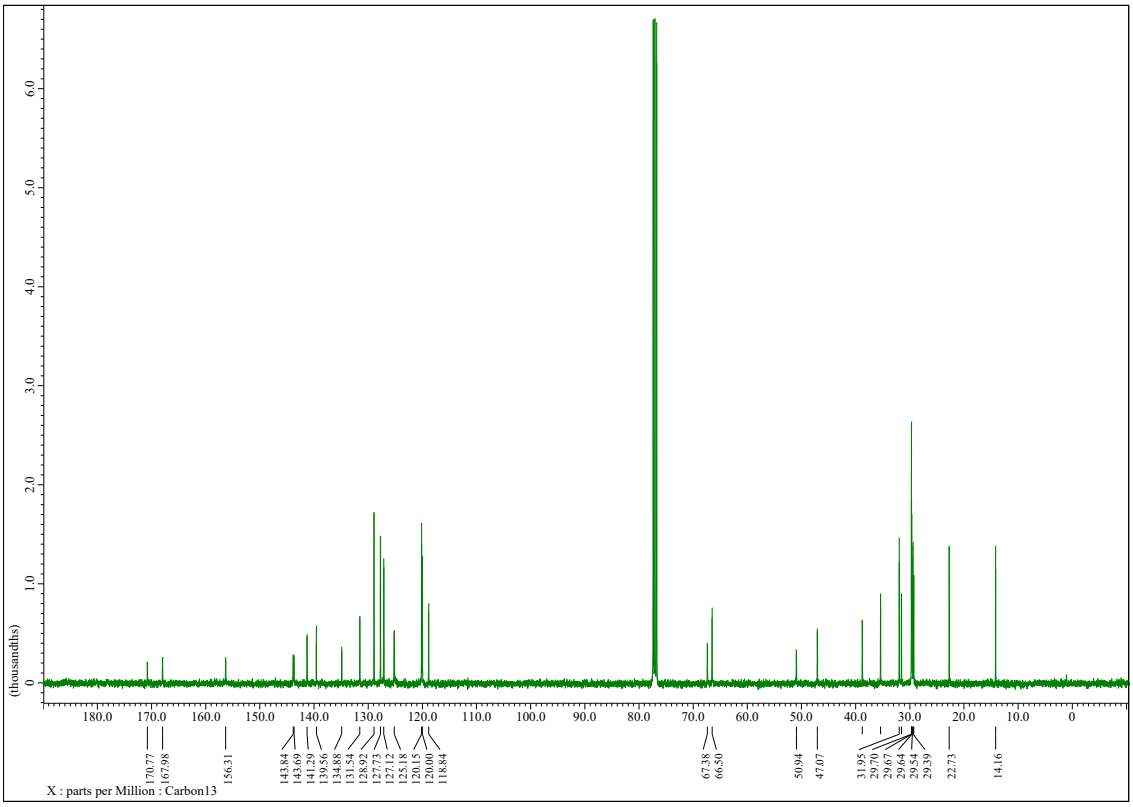
Fmoc-Asp($C_{10}H_{21}$)-OAll (3f)



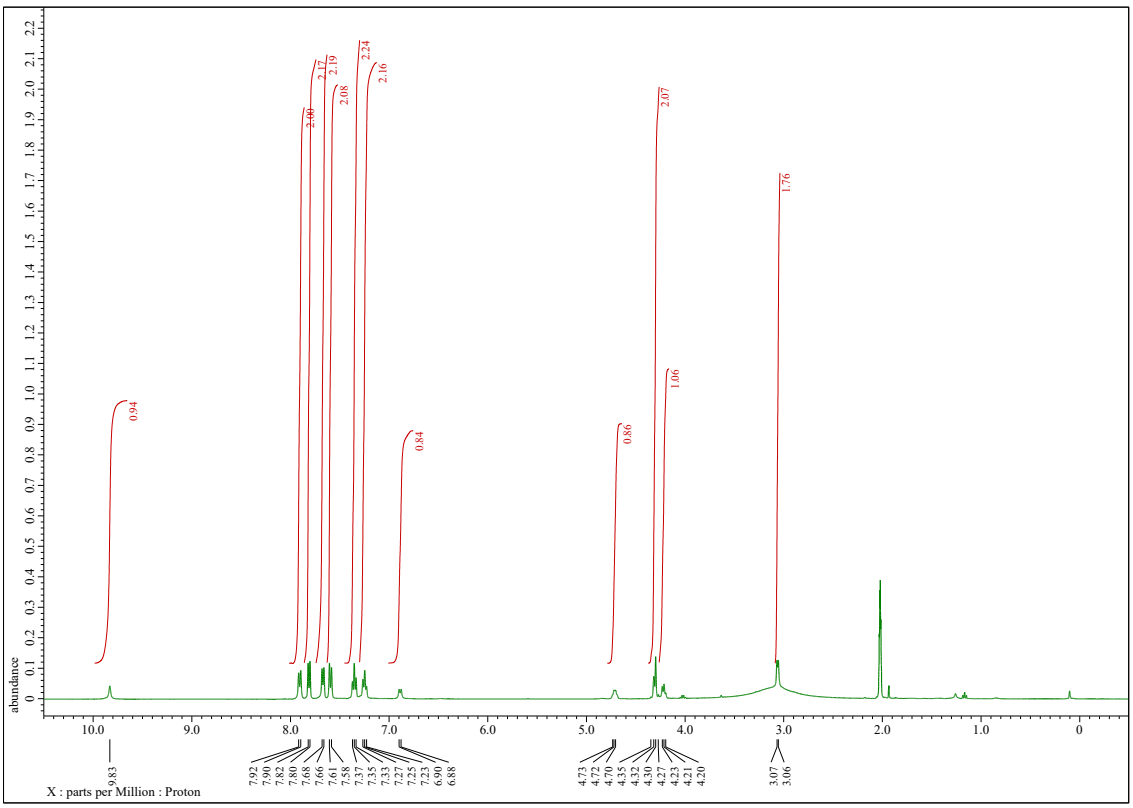


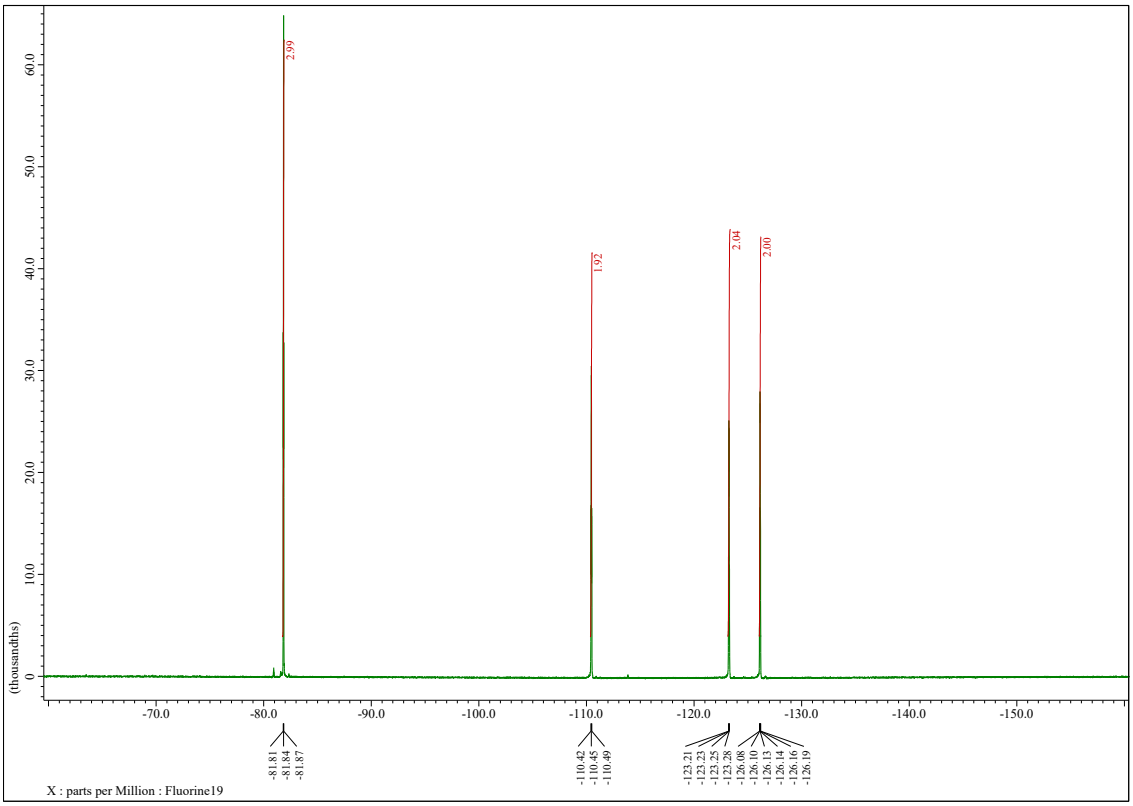
Fmoc-Asp($C_{12}H_{25}$)-OAll (3g)

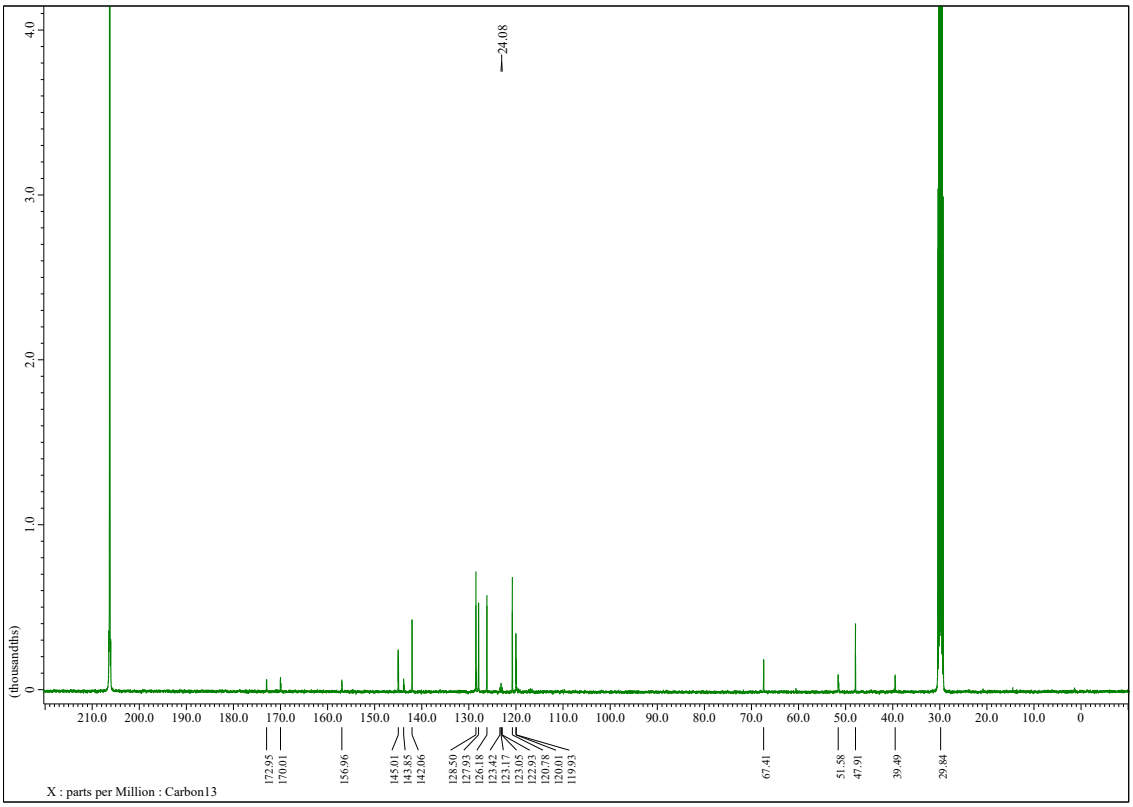




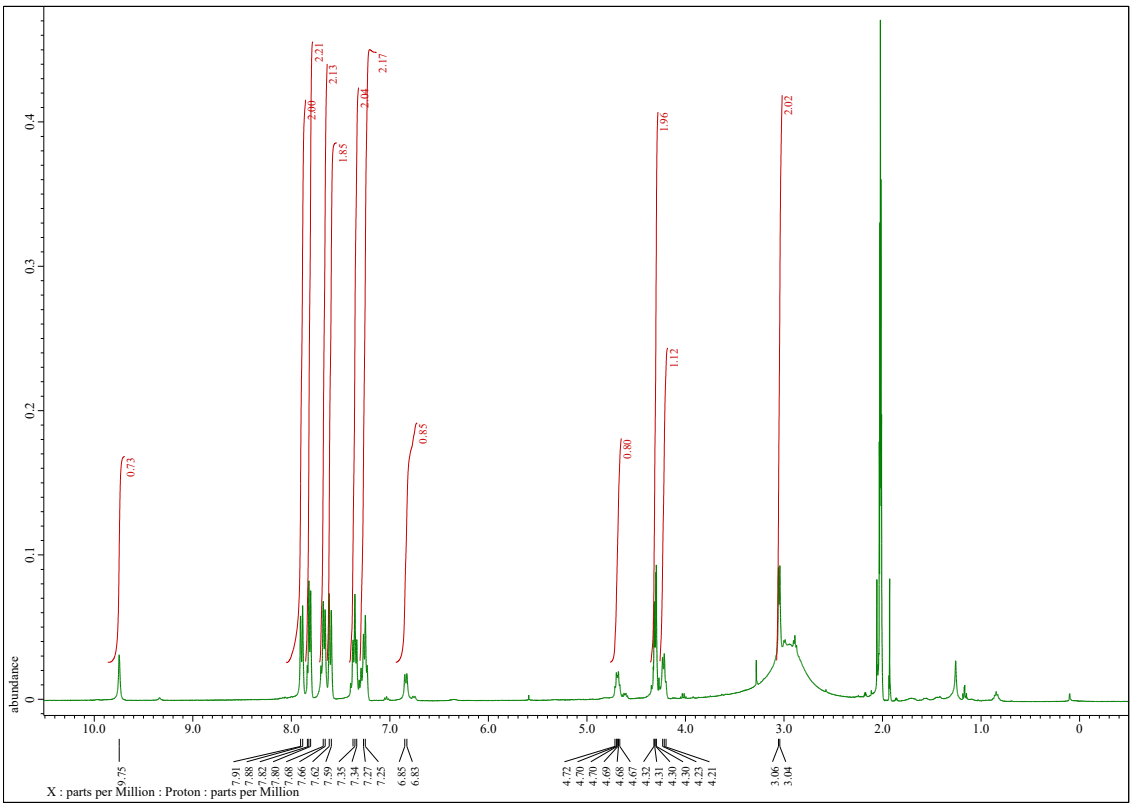
Fmoc-Asp(C_4F_9)-OH (4a)

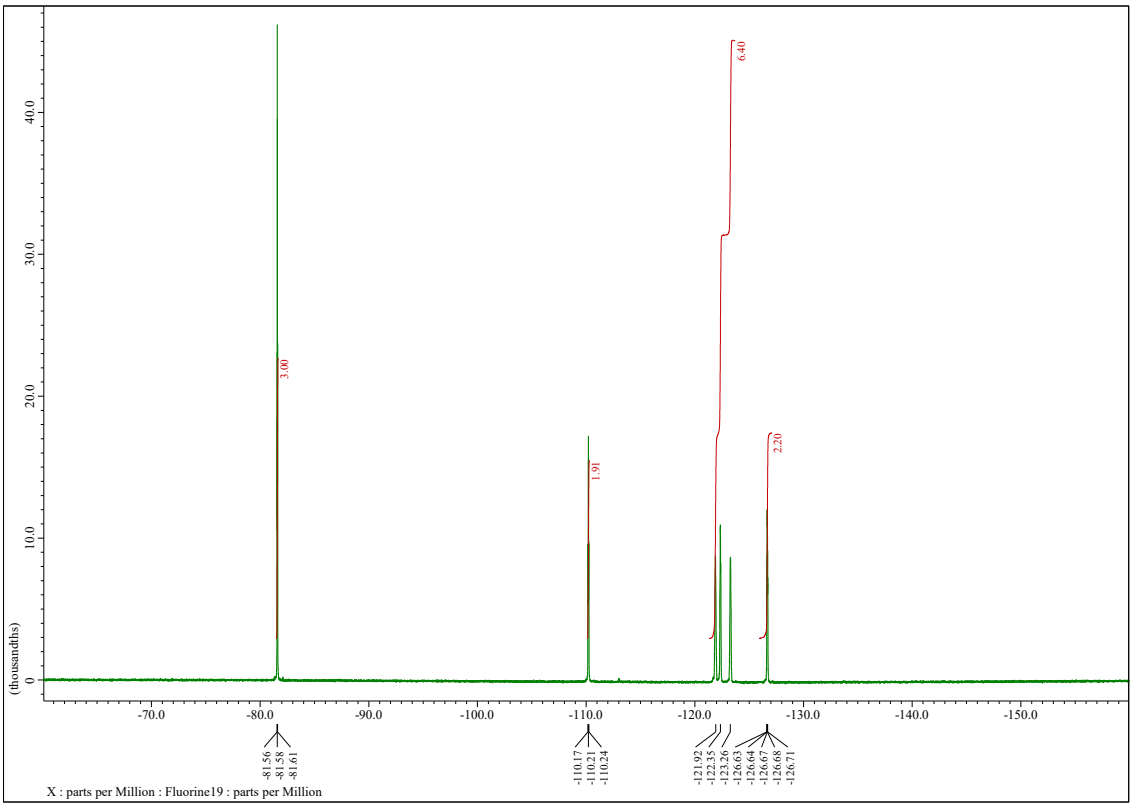


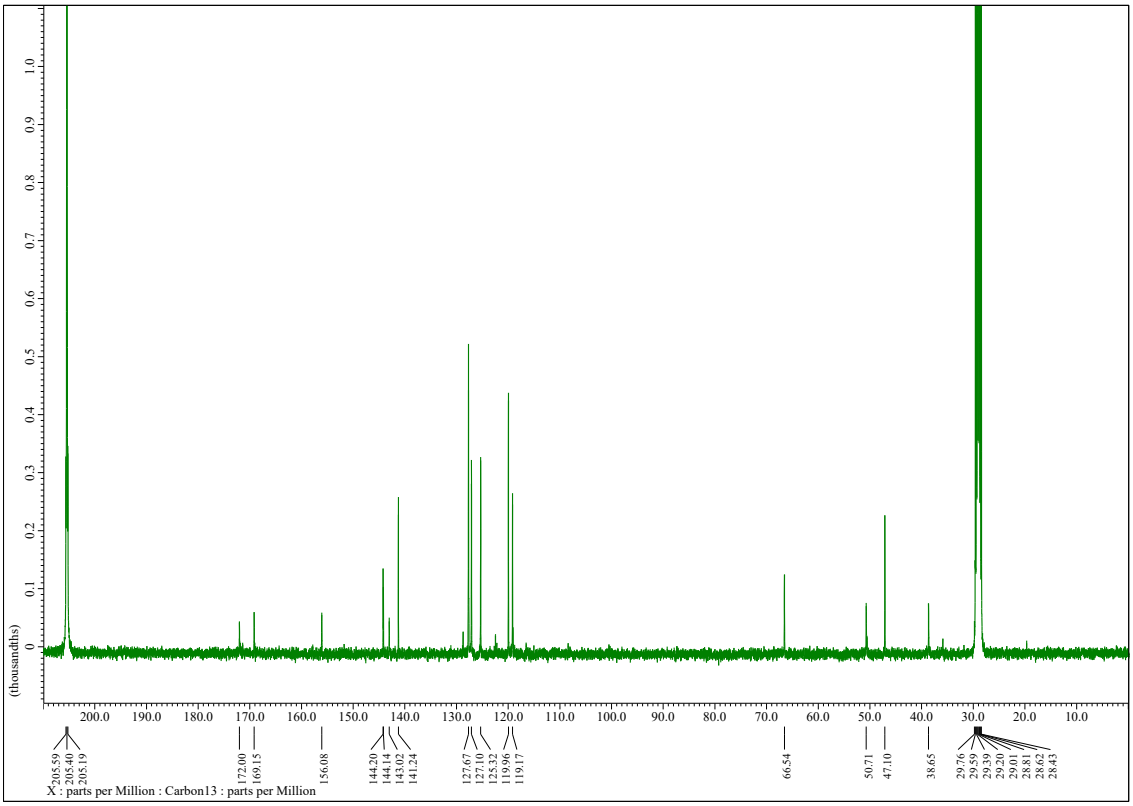




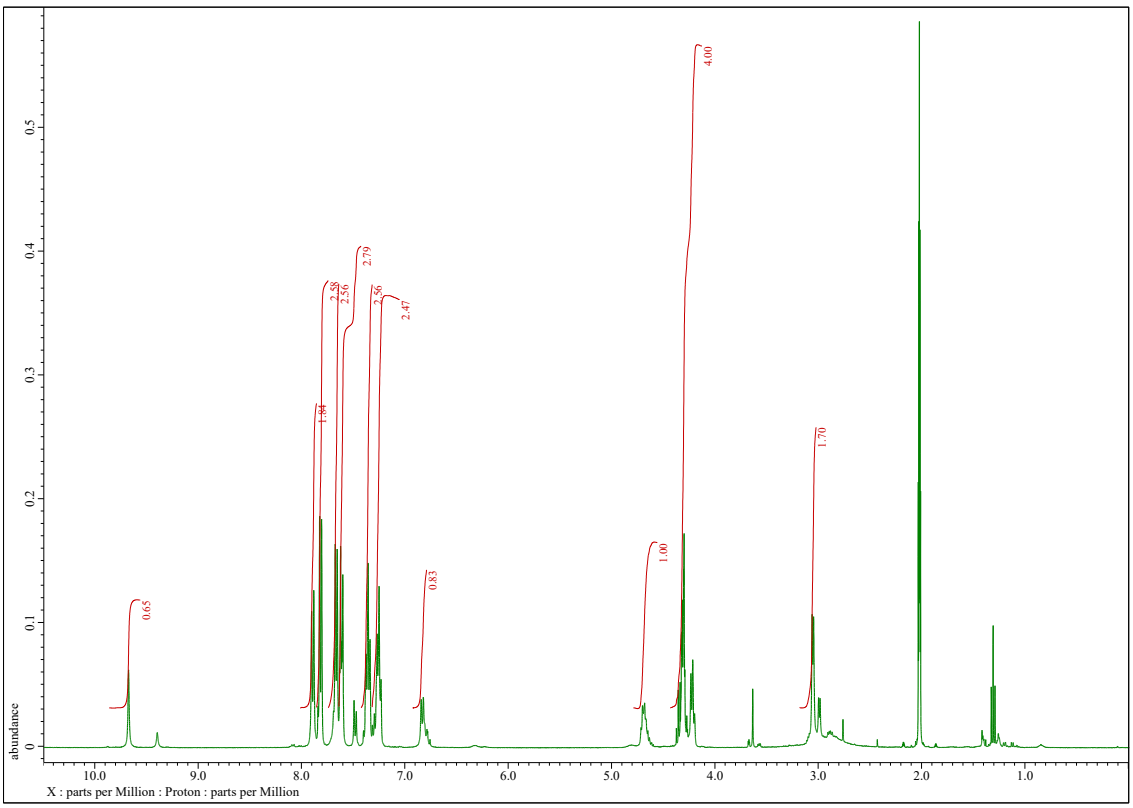
Fmoc-Asp(C_6F_{13})-OH (4b)

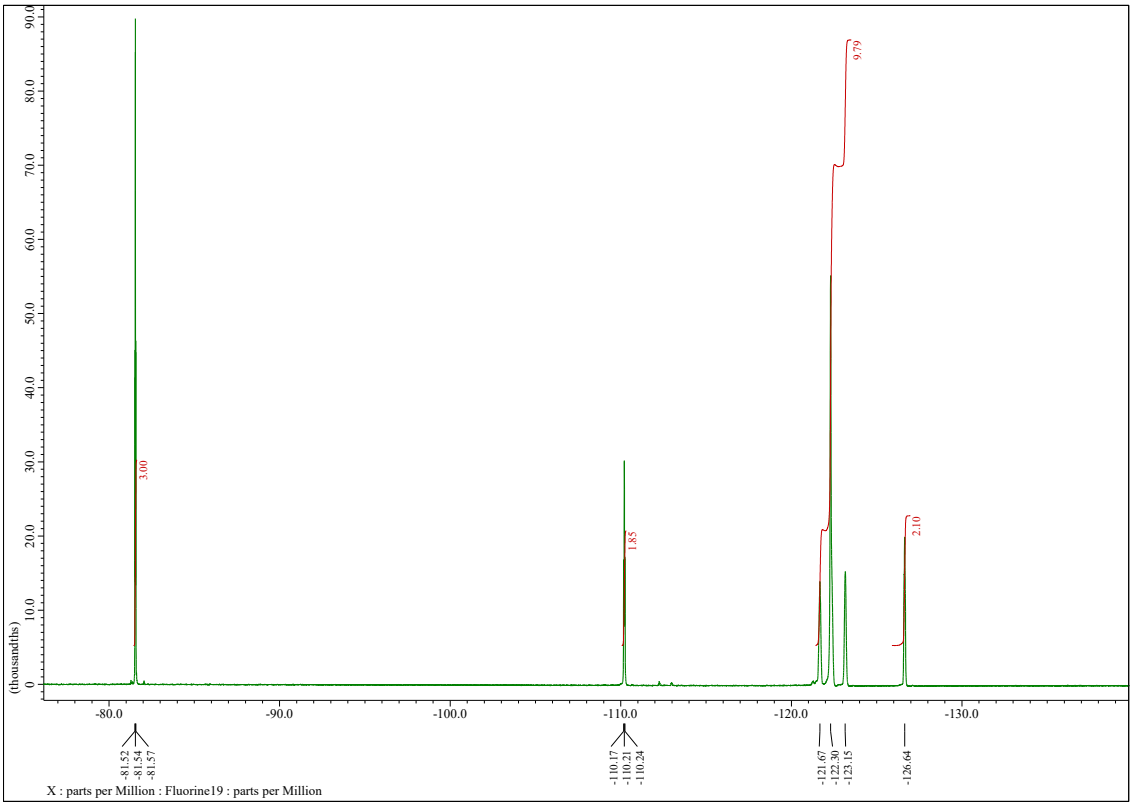


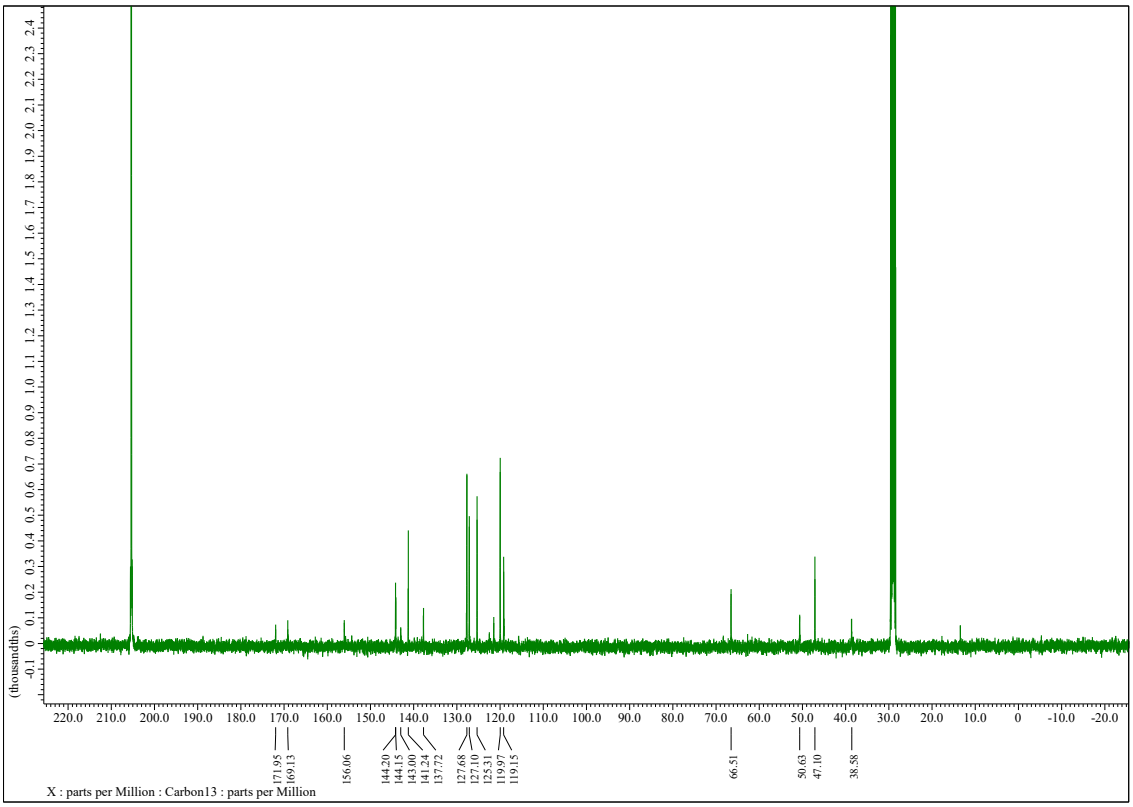

(thousandths)
40.0
30.0
20.0
10.0
0
-70.0
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-150.0
3.00
1.91
6.40
2.20
-81.56
-81.58
-81.61
-110.17
-110.21
-110.24
-121.92
-122.26
-122.35
-126.63
-126.64
-126.67
-126.68
-126.71
X : parts per Million : Fluorine19 : parts per Million


(thousandths)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
205.59
205.40
205.19
172.00
169.15
156.08
144.20
144.14
143.02
141.24
127.67
127.10
125.32
119.96
119.17
66.54
50.71
47.10
38.65
29.76
29.59
29.39
29.20
29.01
28.81
28.62
28.43
X : parts per Million : Carbon13 : parts per Million

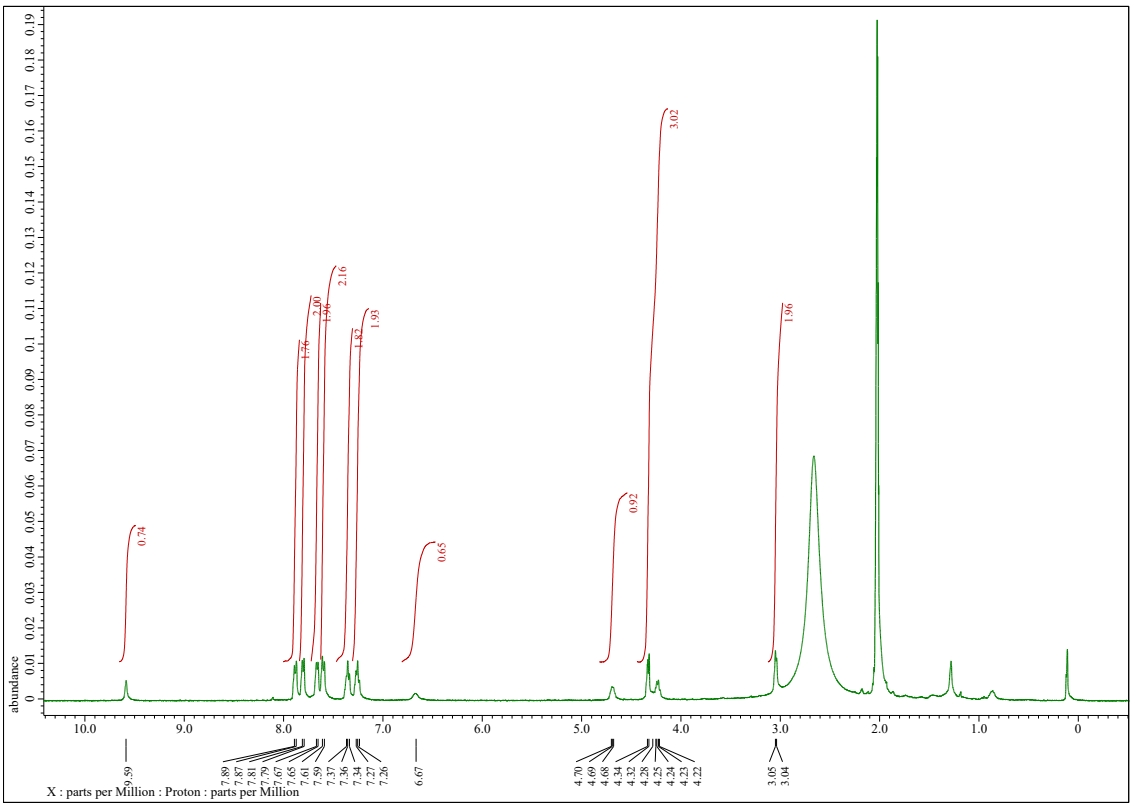
Fmoc-Asp(C_8F_{17})-OH (4c)

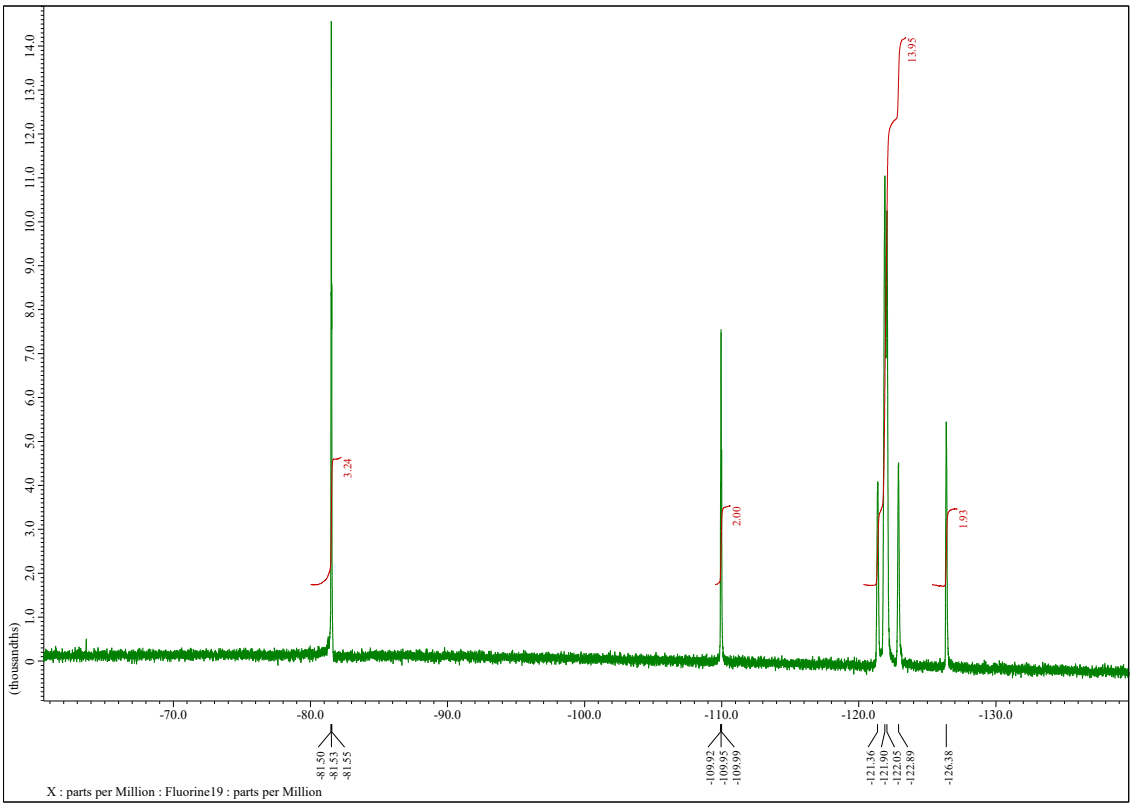




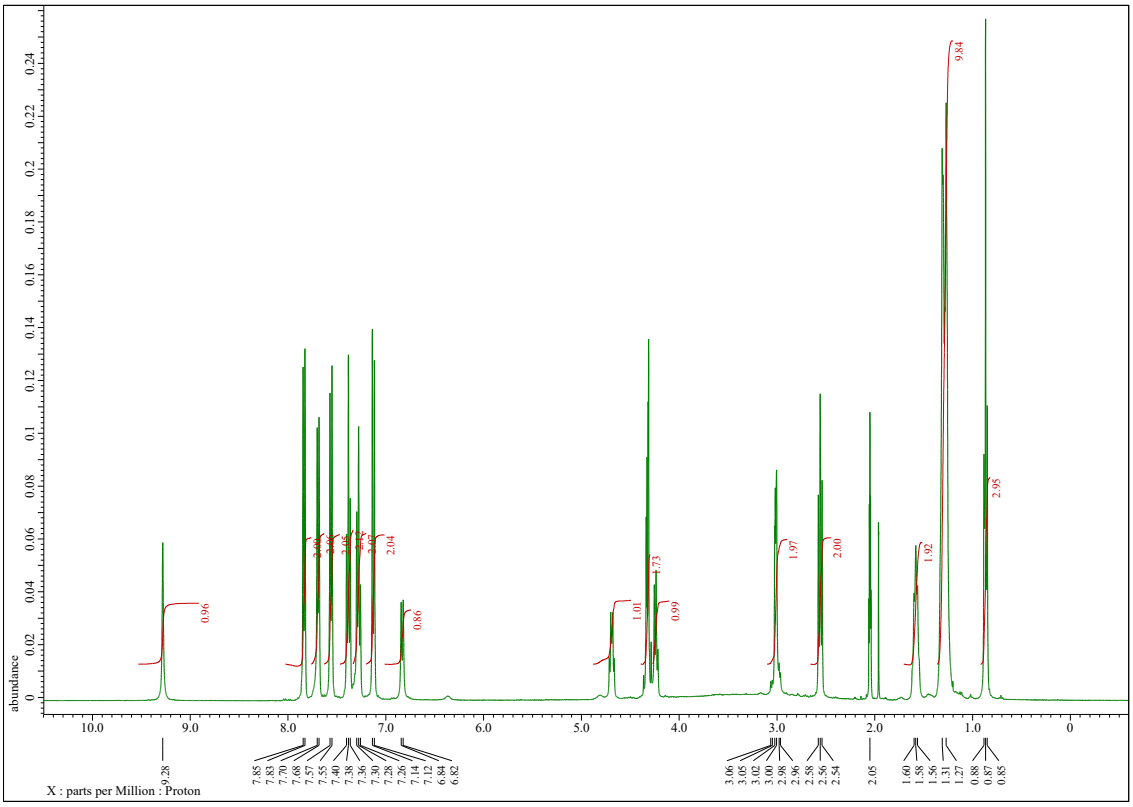


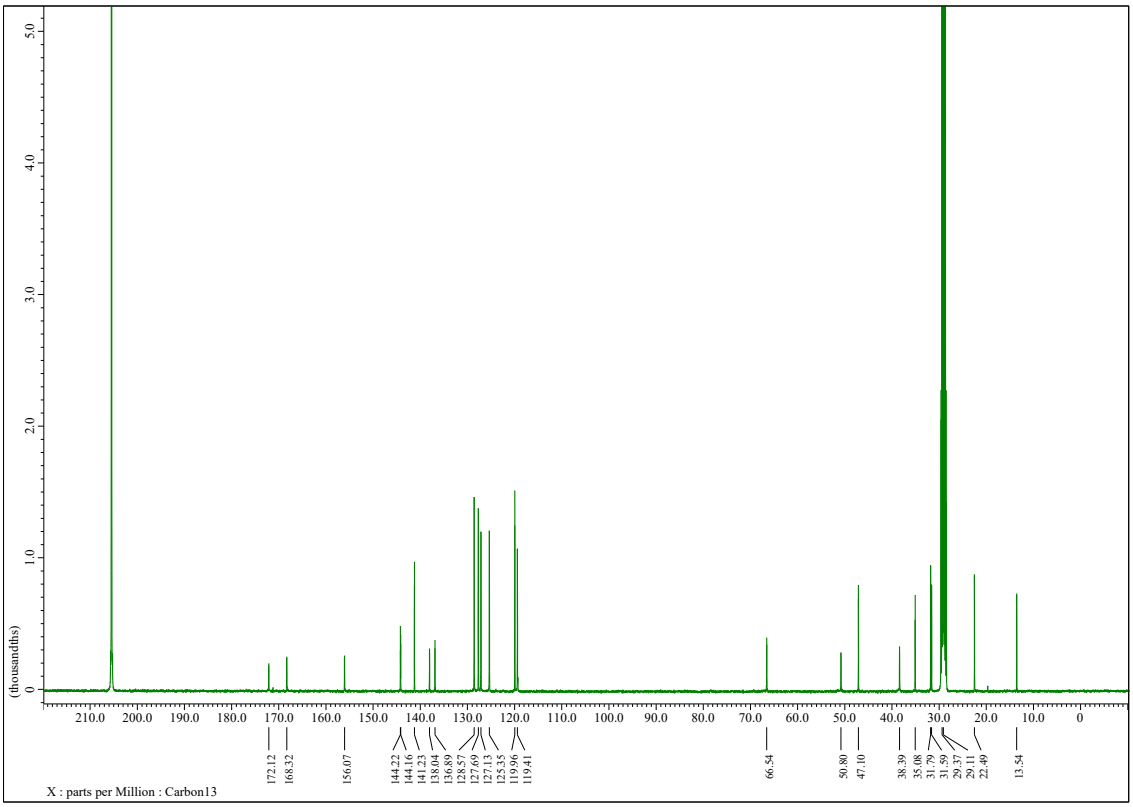
Fmoc-Asp($C_{10}F_{21}$)-OH (4d)



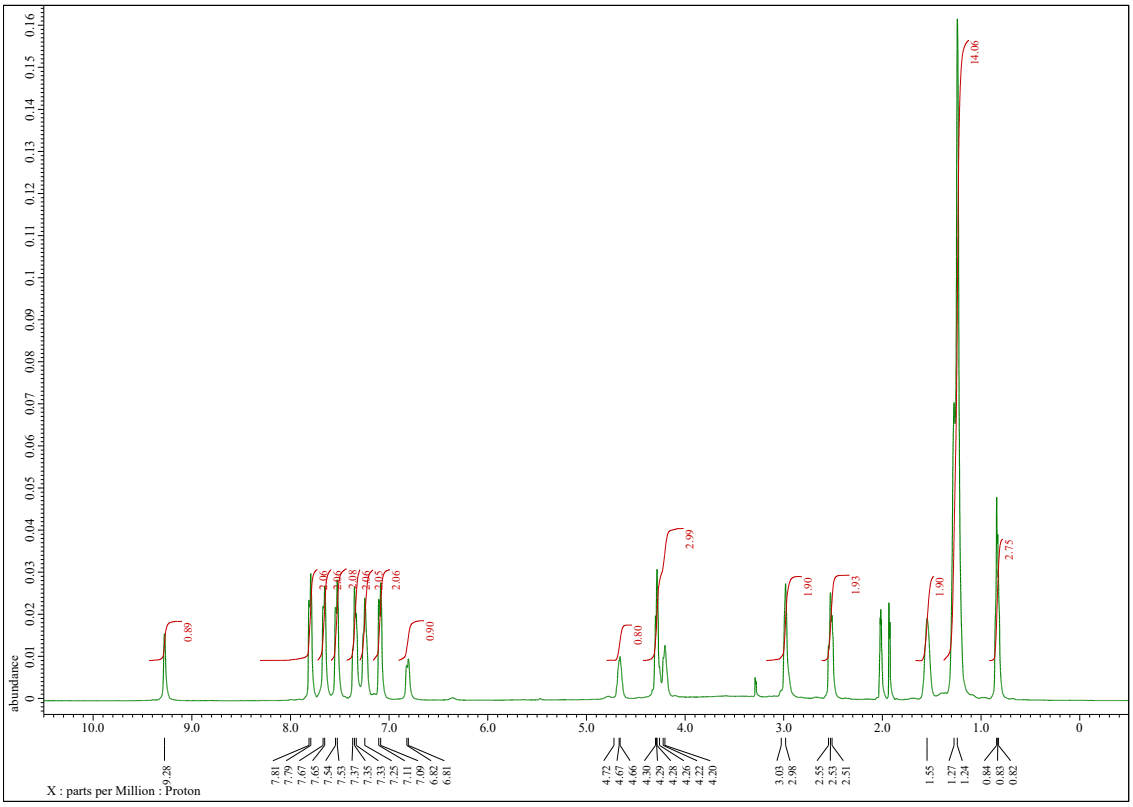


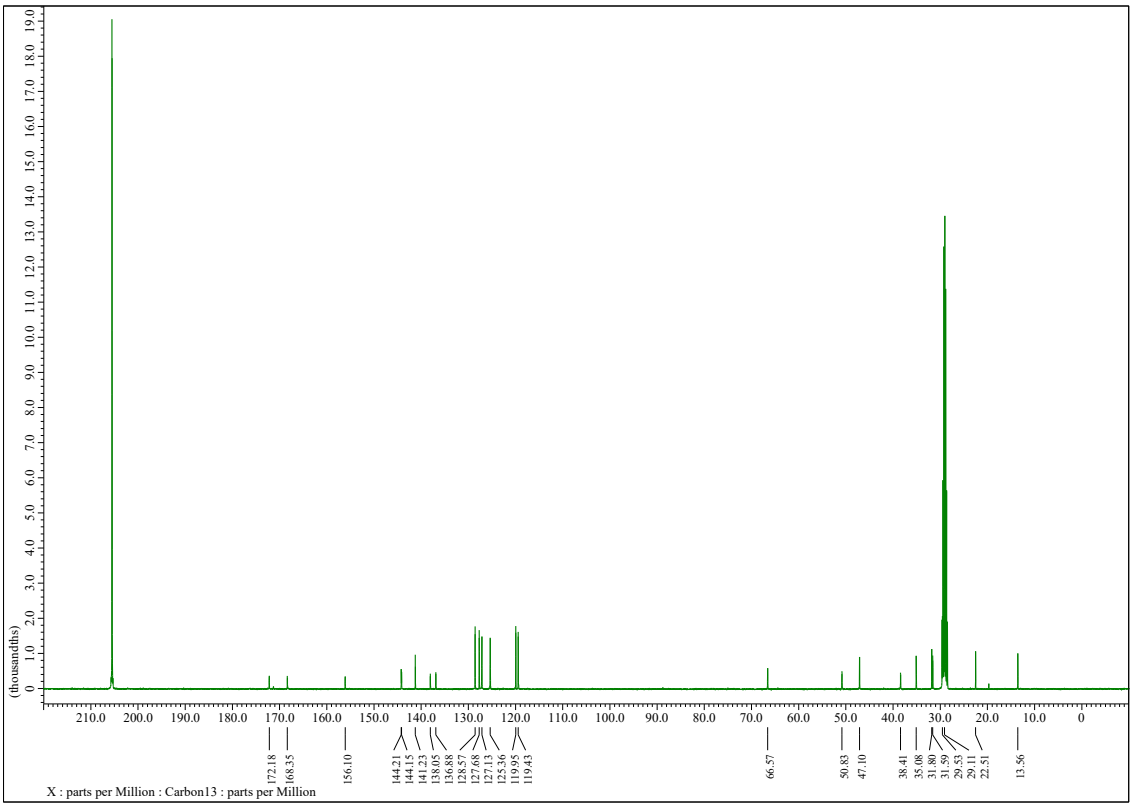
Fmoc-Asp(C_8H_{17})-OH (4e)



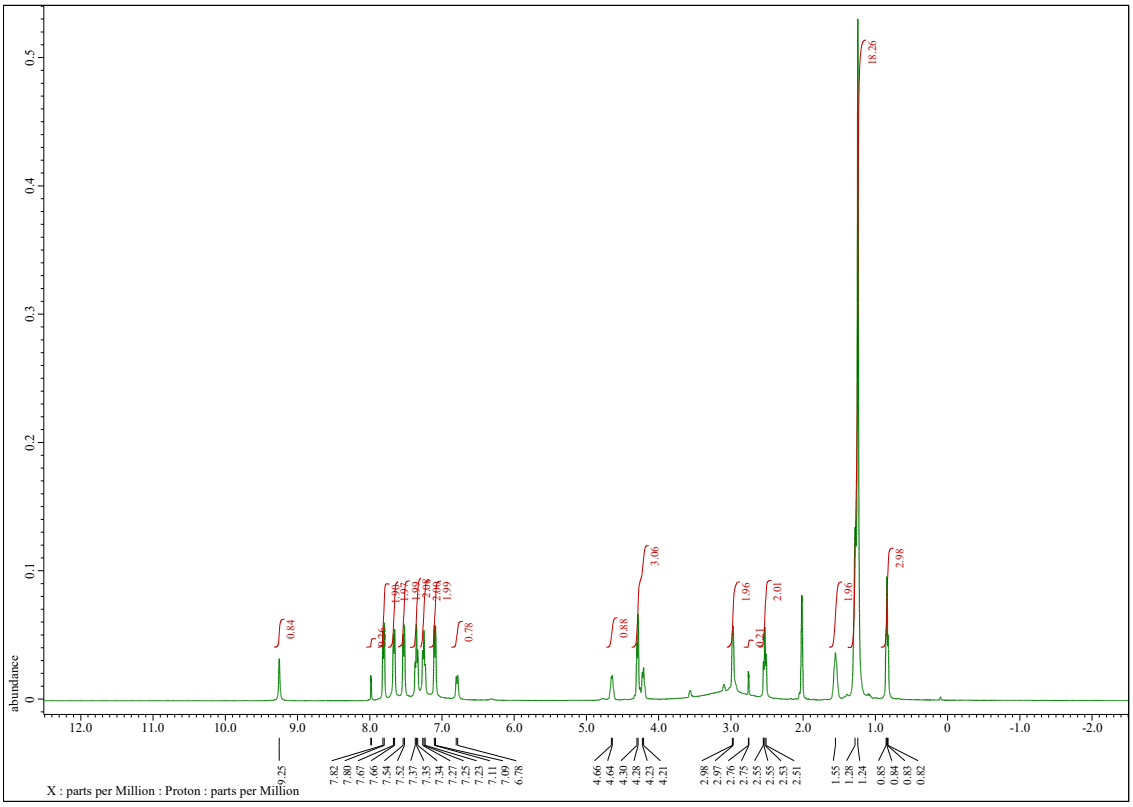


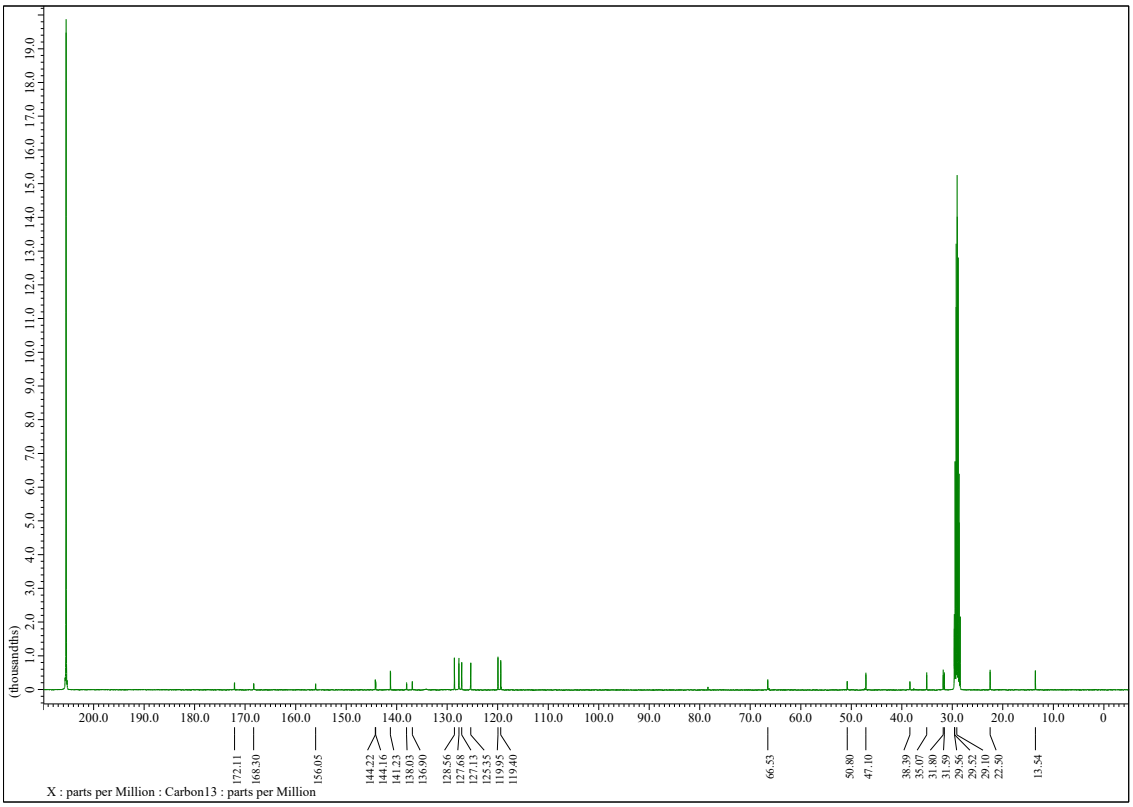
Fmoc-Asp($C_{10}H_{21}$)-OH (4f)





Fmoc-Asp($C_{12}H_{25}$)-OH (4g)




(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.11
168.30
156.05
144.22
144.16
141.23
138.03
136.90
128.56
127.68
127.13
125.15
119.95
119.40
66.53
50.80
47.10
38.39
35.07
31.80
31.59
29.56
29.52
29.10
22.50
13.54
X : parts per Million : Carbon13 : parts per Million

References

(1) K. Tsumoto, Y. Hayashi, J. Tabata, and M. Tomita, *Colloids Surf. A Physicochem. Eng. Asp*. **2018**, *546*, 74–82.

(2) OECD/OCDE, Section 1, OECD Guideline for the Testing of Chemicals, Partition Coefficient (n-octanol/water), High Performance Liquid Chromatography (HPLC) Method, **2022**.

(3) H. Osanai, T. Ikehara, S. Miyauchi, K. Shimono, J. Tamogami, T. Nara, and N. Kamo, *J. Biophys. Chem*., **2013**, *4*, 11–21.