Supporting Information

Fluorinated Cryptophane-A and Porphyrin-based Theranostics for Multimodal Imaging-guided Photodynamic Therapy

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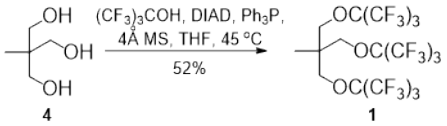
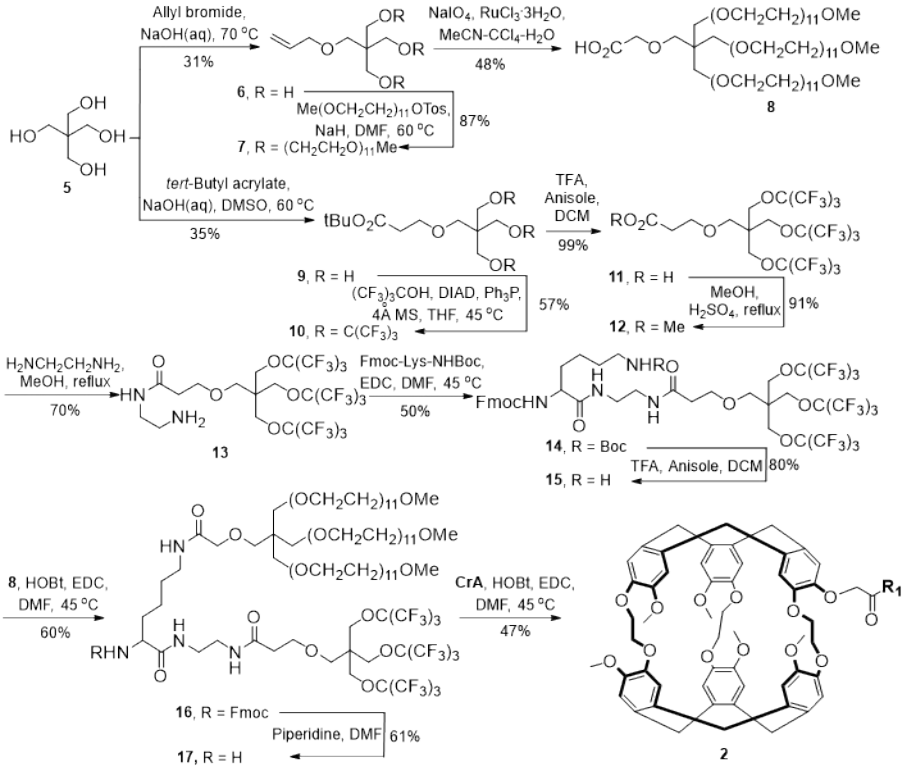
1. Chemicals and reagents

1. Phospholipid Lipoid S75 was purchased from Lipoid AG (Ludwigshafen, Germany). Pluronic F-68 (average MW = 8.4 kD) was purchased from Energy Chemical (Shanghai, China). Peptide cyclo-(Arg-Gly-Asp-D-Tyr-Cys) (c-(RGDyC)) was purchased from GL Biochem (Shanghai, China). Cholesterol-PEG_{2000} Maleimide was purchased from Shanghai Peng Sheng Biological Technology Co., Ltd. Human breast adenocarcinoma cell line MCF-7 and human lung adenocarcinoma cell line A549 were obtained from the Cell Bank of Chinese Academy of Sciences (Shanghai, China). Carboxy-H_2DCFDA was obtained from ThermoFisher Scientific (USA). The *in situ* cell death detection kit calcein-AM (CA) and Propidium Iodide (PI) were purchased from Beijing Baiao Laibo Technology (Beijing China).

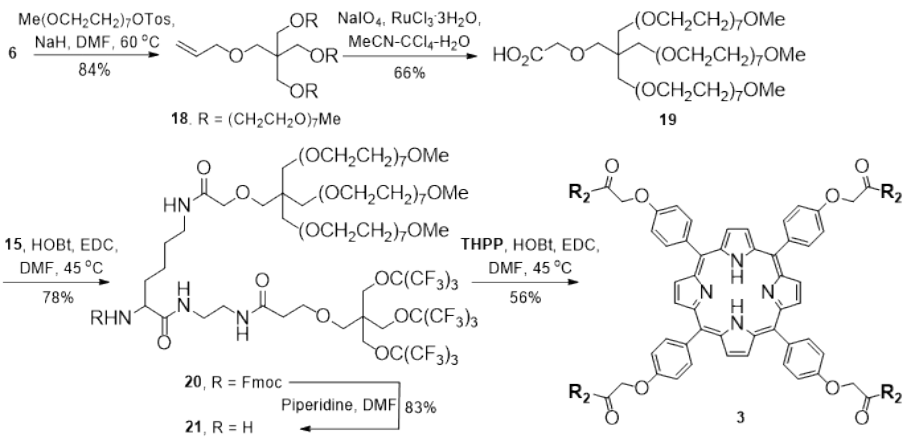
2. Synthesis scheme of compounds 1, 2, 3 and 24



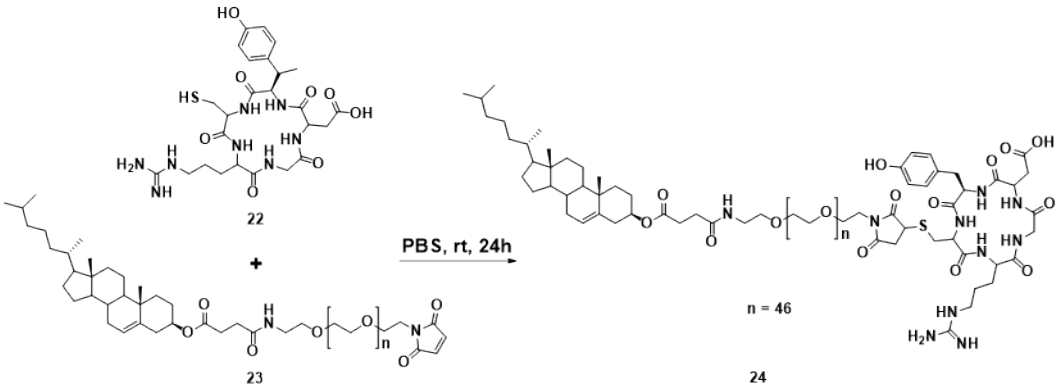
Scheme S1. Synthesis of fluorinated dendron **1**.



Scheme S2. Synthesis of fluorinated cryptophane-A **2**.



Scheme S3. Synthesis of fluorinated amphiphile F-PP **3**.



Scheme S4. Synthesis of Cls-PEG-RGDyC **24**.

3. Preparation and characterization of Eml and Eml -RGD

The nanoemulsions **Eml** were prepared with the ultrasonic emulsification method. A mixture of S-75/F 68/ F-CrA/ F-PP (40 mg/5 mg/3.2 mg/7.6 mg) was dissolved in 2.0 mL organic solvent (chloroform/methanol = 3/1). The organic solvent was removed by vacuum rotary evaporation to form a dry film. 1.0 mL of deionized water was added to the flask to dissolve the film. Then, 78 mg of fluorinated dendron **1** was added into the solution and sonicated for 10 min over an ice bath to form nanoemulsion (**Eml**), the nanoemulsion were further filtered through a 0.2 μm syringe filter for 3 times. **Eml** were incubated with compound **24** (phospholipid : **24** = 20: 1) on a rotary shaker at 25°C for 1 h to provide **Eml-RGD**. **Eml-RGD** gave a characteristic UV absorbance of c-(RGDyc) around 275 nm (Figure S1).

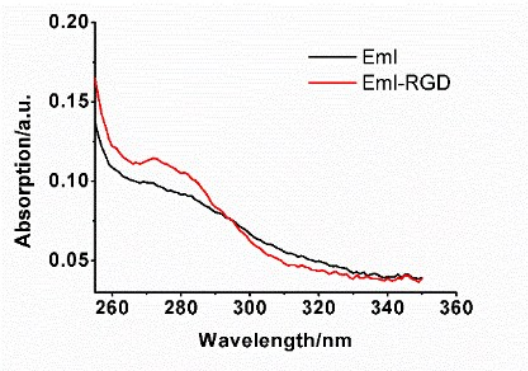


Figure S1. UV absorption of **Eml-RGD** and **Eml**.

The size distribution and ζ-potential of **Eml** and **Eml**-**RGD** were measured by DLS (Nano ZS 90, Malvern, UK) and TEM (Tecnai G20, FEI, USA, negative staining with phosphotungstic acid at 1%, w/v).

Table S1. Characterization of **EmI** and **EmI-RGD**.

	EmI	EmI-RGD
Diameter/nm	125	130
PDI	0.15	0.18
Z/mV	-13.2	-6.04

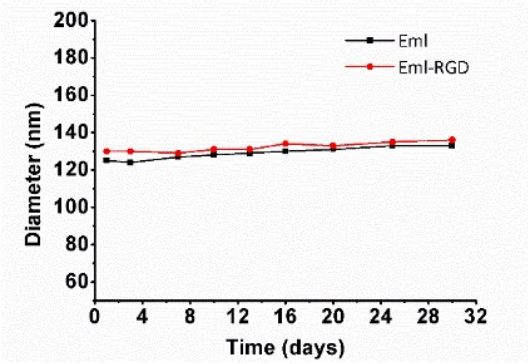


Figure S2. Stability of **EmI** and **EmI-RGD** at 4 °C by DLS.

4. *In vitro* ^{19}F NMR and MRI

The ^{19}F NMR experiments were performed on a Bruker Ascend WB 500 MHz spectrometer, the peak of trifluoroethanol (internal standard) is -76.7 ppm. The longitudinal relaxation time T_1 was measured through the inversion recovery method and the transverse relaxation time T_2 was measured through the spin-echo method. The T_1 and T_2 values of **EmI** are 504.2 ms and 265.7 ms, respectively.

In vitro ^{19}F MRI of **EmI** and **EmI-RGD**: the solution of 135 mM ^{19}F was serially diluted by 1×, 2×, 4×, 8× times with PBS, forming **EmI** and **EmI-RGD** solutions with ^{19}F concentrations of 135 mM, 67.5 mM, 33.7 mM, 16.9 mM, 8.4 mM, respectively. The ^{19}F MRI images were acquired using a RARE method (TR = 2500 ms, TE = 2.8 ms, FOV = 30 mm×30 mm, thickness = 20 mm, matrix size = 32×32, number of average = 8, RARE factor = 4, scan time = 160 s).

For *in vitro* ^{19}F MRI of cells, A549 cells and MCF-7 cells were treated with nanoemulsions (C_F=3.3 mM) in serum-free culture medium. After 2 h co-incubation, cells were washed 3 times with PBS, harvested and suspended in 2 mL PBS for ^{19}F MRI. ^{19}F MRI images were acquired through RARE method. (TR = 1500 ms, TE = 3 ms; FOV = 49 mm×49 mm, 20 mm slice thickness; matrix size = 32×32; 512 averages, RARE factor =8, 64 min of data acquisition).

5. Cellular uptake of Eml and Eml-RGD

A549 cells and MCF-7 cells were cultured in MEM (Boster, China) and DMEM-High glucose medium, respectively, with 10% fetal bovine serum and 100 units/mL penicillin and 0.1 mg/mL streptomycin under a humidified air with 5% CO_2 at 37 °C.

Cells were seeded in a 6-well chamber slide at a density of 2×10^5 /mL and incubated for 12 h before treated with nanoemulsions at 37 °C for 2 h. Washed with PBS for 3 times, the cells were fixed with 4% paraformaldehyde for 10 min and stained with DAPI for 5 min, washed with PBS for 3 times again. Finally, cells were mounted on slides in fluoromount with coverslips imaged under Confocal Laser Scanning Microscope (A1R/A1, Nikon, Japan).

6. ^{129}Xe Hyper-CEST NMR and MRI

^{129}Xe NMR and MRI measurements were performed on a 400 MHz (9.4 T) Bruker AV400 wide-bore spectrometer (Bruker Biospin, Ettlingen, Germany), equipped with microimaging gradient coils and RF pulse frequency for ^{129}Xe was 110.7 MHz. The hyperpolarized ^{129}Xe gas was obtained by a home-built continuous-flow apparatus which uses spin-exchange optical pumping method. The gas mixture consisting of 10 % N_2, 88 % He, and 2 % Xe (86 % enriched ^{129}Xe or natural abundance ^{129}Xe) and directly bubbled into a 10 mm NMR tube for 20 s, ^{129}Xe NMR spectra was obtained using a 10 mm double resonant probe (^{129}Xe and ^{1}H, PA BBO 400 W1/S2 BB-H-D-10Z) with rectangle pulse of flip angle (90°). Approximately 20% of ^{129}Xe spin polarization was achieved. The sample temperature was set at 300 K controlled by VT unit on NMR spectrometer. For the hyper-CEST NMR experiment, nanoemulsion or cells was put into NMR tube and bubbled for 20 s following a delay of 3 s to ensure the bubbles to collapse before signal acquisition. Using a RF-pulse 5 s, 6.5 μT cw saturation for varying offset frequencies, the chemical shift of ^{129}Xe range from 55 to 90 ppm in 1 ppm steps or from 50 to 250 ppm in 2 ppm steps.

For the ^{129}Xe hyper-CEST MRI, A549 cells and MCF-7 cells were treated with **Eml** and **Eml-RGD** (C_{CrA} concentration = 1.1 μM) for 2 hours at 37 °C, after washed with PBS for 3 times, the cells were collected and resuspended (5×10^6 /mL) in 2 mL PBS for the Hyper-CEST experiment (saturation: 5 s, 13 μT), respectively. MR images were acquired using RARE sequence (FOV = 30 mm x30 mm; matrix size = 32x32; slice thickness = 25 mm; echo time =

4.6 ms, repetition time = 39.7 ms, RARE factor =8). The ^{129}Xe MR images were segmented using 0.2*maximum value as threshold and interpolated into 64*64 matrix.

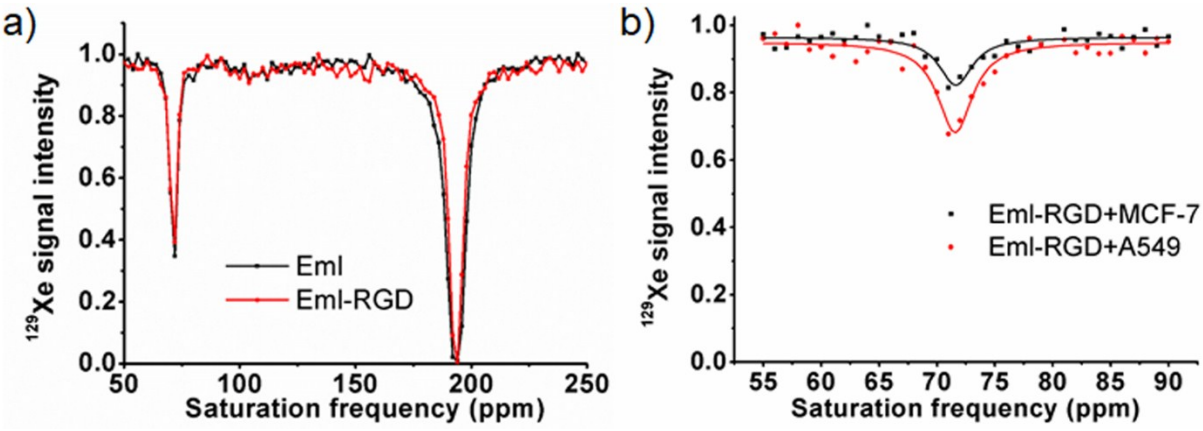


Figure S3. (a) ^{129}Xe hyper-CEST NMR of **EmI** and **EmI-RGD** from 50 to 250 ppm. (b) ^{129}Xe hyper-CEST NMR of A549 cells and MCF-7 cells after treated with **EmI-RGD**.

7. *In vitro* phototoxicity and cytotoxicity assay

A549 cells were seeded into 96-well plates and incubated with **EmI-RGD** in difference concentration (C_F= 0, 4, 8, 16, 40 and 80 mM) for 6 h, respectively. After washed with PBS, the cells were irradiated with a 650 nm laser at a power density of 100 mW/cm^2 for 5 min. The non-irradiation group was kept under same conditions except for irradiation. Methylthiazolytetrazolium (MTT) assay kit was employed to evaluate cell toxicity and cell viability was measured using ELISA plate reader (Spectra MAX 190, Molecular Devices, USA). Data are presented as mean ± SD, n = 3.

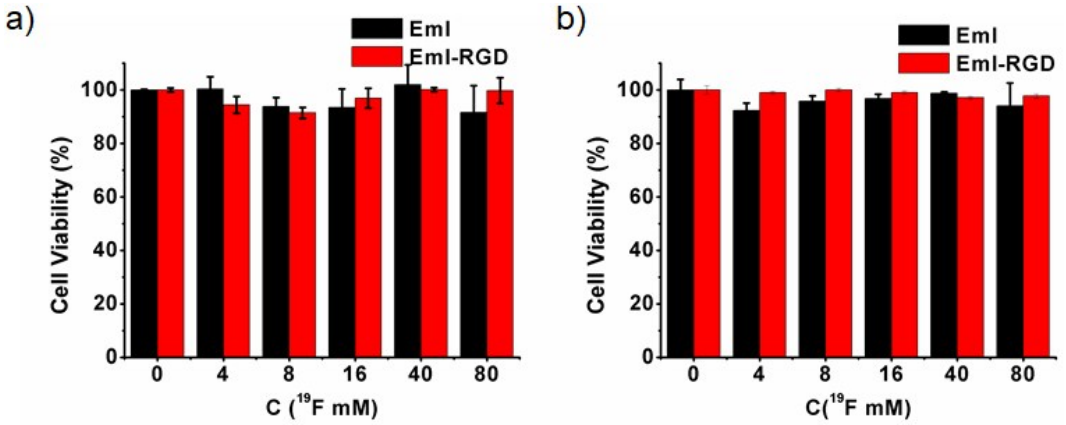


Figure S4. Cytotoxicity assay of **EmI** and **EmI-RGD** on A549 cells (a) and MCF-7 cells (b).

The live and dead cells were stained with cell death detection kit. Briefly, A549 cells were seeded in a 6-well plate and incubated with **EmI-RGD** (at a fluorinated porphyrin **3** concentration of 10 μM) at 37 °C for 2 h, washed with PBS and irradiated with a 650 nm laser

at a power density of 100 mW/cm^2 for 10 min. Then the cells were incubated with calcein AM (4 μM) and propidium iodide (4 μM) for 30 min and 5 min, respectively. Cellular fluorescence images were obtained by Confocal Laser Scanning Microscope.

8. Detection of singlet oxygen *in vitro*

A549 cells were seeded in a 6-well plate at a density of 2×10^5/mL and incubated with nanoemulsions (at a fluorinated porphyrin **3** concentration of 10 μM) at 37 °C for 2 h. After washing with PBS, the cells were incubated with carboxy-H_2DCFDA (25 μM) for 30 min, then washed again with PBS and irradiated with a 650 nm laser at a power density of 100 mW/cm^2 for 5 min per well. The cells were fixed with 4% formaldehyde polymer for 10 min and washed with PBS for 3 times. Finally, cells were imaged under Confocal Laser Scanning Microscope.

9. *In vivo* fluorescence imaging

For *in vivo* experiments, 200 μL of **EmI-RGD** (At a fluorine dose of 27 mM/kg) were intravenously injected into the A549 tumor-bearing mice. The fluorescent scans were recorded on a IVIS spectrum system. After 72 h, the mice were sacrificed and organs were collected for fluorescence imaging. Fluorescence imaging was performed using a 640 nm excitation and a 720 nm emission filter.

10. *In vivo* ^{19}F MRI

BALB/C male nude mice (6 weeks, 20 g) were purchased from Beijing Vital River Laboratory Animal Technology Co., Ltd. For the xenograft tumor mice, A549 cells (2×10^6 /100 μL) were subcutaneously injected into the right hind of the mice. The mice had free access to water and food until tumor size reached about 170 mm^3. All experimental protocols in this study were approved by Animal Care and Use Committees at the Wuhan Institute of Physics and Mathematics, the Chinese Academy of Sciences.

The A549 tumor-bearing mice were anesthetized by isoflurane, 200 μL of **EmI-RGD** (At a fluorine dose of 27 mM/kg) was intravenously injected into the tumor-bearing mice. ^{19}F MRI was performed on 400 MHz Bruker BioSpec MRI system. ^{1}H MRI scan using a RARE sequence (TR = 2500 ms, TE = 33 ms, FOV = 40 mm×30 mm, 2 mm slice thickness; 80 s of data acquisition; RARE factor =8; matrix size = 256×256), ^{19}F MRI was performed through a

RARE sequence (TR = 1600 ms, TE = 3 ms, FOV = 40 mm×40 mm, 30 mm slice thickness, 17 min of data acquisition, matrix size = 32×32, 64 averages).

11. *In vivo* phototherapy

A549 tumor-bearing mice were sorted into 4 groups with the following group treatments: 1) Saline; 2) porphyrin **3** + laser; 3) **EmI-RGD**; 4) **EmI-RGD** + laser. Mice were intravenously injected on day 0, 4, 8 with the corresponding solutions on day 0. Groups 2, 3 and 4 were injected at porphyrin **3** dose of 6 μM/kg. The mice in group 2 and 4 were irradiated with a 650nm laser at a power density of 100 w/cm^2 for 15 min on day 2, day 5, and day 8. The weight and tumor volume of mice were measured every 2 days by using of a digital caliper for a period of 17 days. The tumour volume was calculated according to the following formula: volume = (width^2 × length)/2.

12. *Ex vivo* histological staining

After group treatments, the A549 tumour-bearing mice were sacrificed on day 16. The major organs and tumors of mice in groups 1-4 were collected and fixed with paraformaldehyde or cryosectioned for hematoxylin-eosin (H&E) and TUNEL staining, respectively.

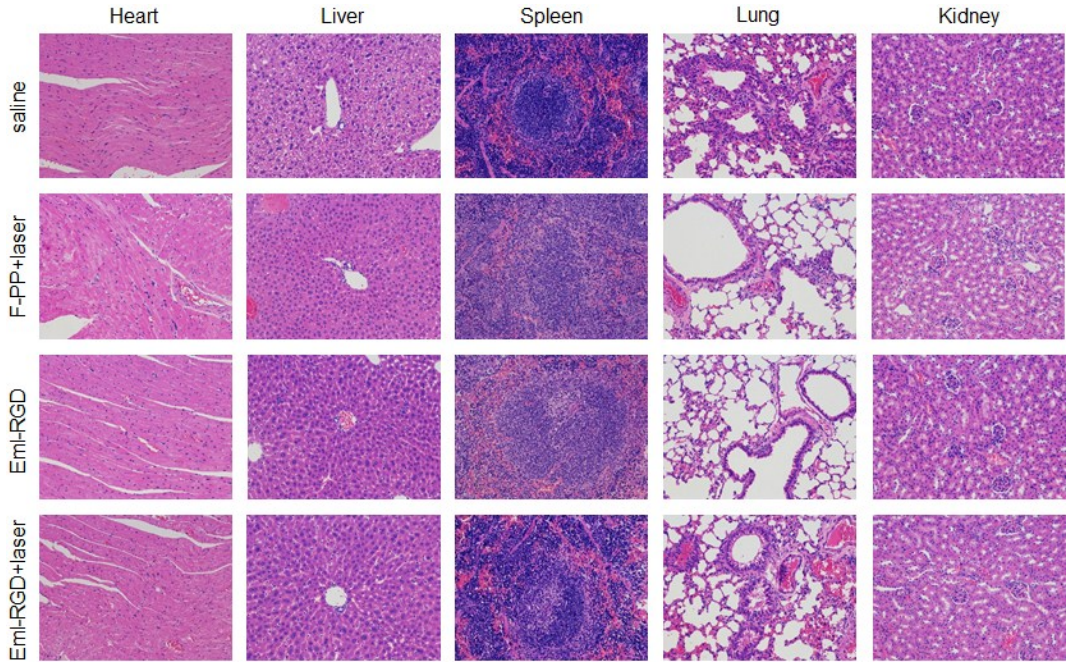


Figure S4. Representative H&E staining of major organs after group treatments.

13. Synthetic procedures of compounds 1, 2, 3 and 24

13.1 Synthesis of compound 1

Under an argon atmosphere, to a stirred suspension of compound **4** (7.2 g, 60.0 mmol), triphenylphosphine (70.8 g, 270.0 mmol) and 4 Å molecular sieves (7.0 g) in THF (300.0 mL) at 0 ºC was added dropwise diethylazodicarboxylate (54.6 g, 270.0 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 20 min. Then perfluoro-*tert*-butanol (63.7 g, 270.0 mmol) was added in one portion and the resulting mixture was stirred for 48 h at 45 ºC in a sealed vessel. Water (30.0 mL) was added to the reaction mixture and stirred for an additional 10 min. Then the mixture was transferred to a separatory funnel and the lower phase was collected. Removal of the perfluoro-*tert*-butanol under vacuum gave the product **1** as clear oil (32.5 g, 70% yield).

13.2 Synthesis of compound 7

Under an atmosphere of nitrogen, a solution of compound **6** (1.4 g, 7.7 mmol) in DMF (10 mL) was added dropwise into a suspension of NaH (1.9 g, 46.3 mmol, 60% on mineral oil) in DMF (20 mL) in an ice bath. After stirring for 30 min, a solution of $Me(OCH_2CH_2O)_{11}OTos$ (21.7 g, 32.3 mmol) in DMF (10 mL) was added to the flask, the resulting mixture was stirred at 80 ºC for 24 h. Then DMF was evaporated under reduced pressure. The crude was purified by column chromatography on a silica gel (CH_2Cl_2 /MeOH = 10/1) to give alcohol compound *7* as clear oil (11.2 g, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91-5.83 (m, 1H), 5.25 (d, *J* = 13.8 Hz, 1H), 5.15 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 2H), 3.82-3.54 (m, 134H), 3.51 (s, 4H), 3.45 (s, 2H), 3.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.9, 116.5, 72.4, 71.9, 71.6, 70.9, 70.50, 70.48, 70.34, 70.27, 70.2, 59.0, 45.1. HRMS (ESI) calcd for $C_{77}H_{154}O_{37}$ $[M+2Na]^{2+}$:858.4976, found 858.4957.

13.3 Synthesis of compound 8

Compound **7** (6.4 g, 3.8 mmol) was dissolved in $CHCl_3$: CH_3CN : H_2O (1:1:1.5, 28 mL), $NaIO_4$ (4.9 g, 22.8 mmol) and ruthenium(III) chloride hydrate (15.3 mg, 75.9 μmol) were added to the solution at 0 ºC. The mixture was stirred at room temperature for 4 h. Then 20 mL of water was added to the flask, and extracted with CH_2Cl_2 (60 mL, 3 times). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography on a silica gel (CH_2Cl_2 /MeOH = 8/1) to give compound **8** as clear oil (3.1 g, 48% yield). ^{1}H NMR (500 MHz, CD_3OD) δ 3.87 (s, 2H), 3.77-3.56 (m, 136H), 3.53 (s, 5H), 3.40 (s, 9H); ^{13}C NMR (500 MHz, CD_3OD) δ 176.0, 71.2, 71.1, 70.7, 69.9, 69.8, 69.71,

69.65, 69.6, 69.5, 69.43, 69.40, 57.8, 44.8. HRMS (ESI) calcd for $C_{76}H_{152}O_{39}$ $[M-H]^-$:1687.9838, found 1687.9867.

13.4 Synthesis of compound 16

Under an atmosphere of nitrogen, EDC (0.6 g, 3.1 mmol) was added to a stirring solution of HOBt (0.4 g, 3.1 mmol) and compound **8** (2.6 g, 1.6 mmol) in DMF (10 mL) at 0 ºC. After stirring for 30 min, a solution of compound **15** (2 g, 1.6 mmol) in DMF (5 mL) was added to the flask at room temperature, the reaction mixture was stirred at 50 °C for 12 h. Then the reaction mixture was added 10 mL of water and extracted with CH_2Cl_2 (30 mL, 3 times). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography on a silica gel (CH_2Cl_2/MeOH = 10/1) to give compound **16** as colorless oil (2.8 g, 60% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.0 Hz, 2H), 7.62 (s, 2H), 7.40 (s, 4H), 4.53-4.17 (m, 4H), 3.91 (s, 2H), 3.74 (s, 4H), 3.69-3.50 (m, 145H), 3.43 (d, *J* = 8.8 Hz, 8H), 3.37 (s, 9H), 3.28 (s, 2H), 1.86 (s, 1H), 1.74 (s, 1H), 1.54 (q, *J* = 5.3 Hz, 2H), 1.38 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 170.6, 143.8, 141.3, 127.7, 127.1, 126.5, 125.7, 125.1, 119.9, 117.7, 110.8, 71.9, 70.9, 70.6, 70.54, 70.51, 70.49, 70.45, 70.3, 70.2, 70.0, 59.0, 47.2, 45.5, 45.3, 38.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.44. HRMS (ESI) calcd for $C_{119}H_{191}F_{27}N_4O_{46}$ M^{2+}:1462.6143, found 1462.6102.

13.5 Synthesis of compound 17

1.5 mL of Piperidine was added to a solution of compound **16** (2 g, 0.7 mmol) in DMF (10 mL). The mixture was stirred at room temperature for 4 h. Then, the solvent was removed under reduced pressure. The residue was purified by column chromatography on a silica gel (CH_2Cl_2/MeOH = 20/1) to give compound **17** as a colorless oil (1.1 g, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34-8.20 (s, 1H), 7.53 (s, 1H), 7.20 (s, 1H), 4.04 (s, 6H), 3.90 (s, 2H), 3.75-3.52 (m, 142H), 3.47-3.40 (m, 11H), 3.38 (s, 9H), 2.48 (s, 1H), 2.29 (s, 1H), 1.87 (d, *J* = 6.0 Hz, 1H), 1.72 (d, *J* = 5.8 Hz, 1H), 1.57 (s, 2H), 1.41 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.4, 170.9, 121.2 (q, *J* = 1165.0 Hz), 79.6, 79.3, 71.9, 71.3, 71.0, 70.7, 70.6, 70.53, 70.51, 70.48, 70.2, 70.1, 67.8, 66.1, 65.6, 59.0, 54.3, 46.1, 45.3, 39.3, 38.3, 36.4, 31.9, 31.4, 30.2, 29.4, 22.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.42. HRMS (ESI) calcd for $C_{104}H_{181}F_{27}N_4O_{44}$ $[M+3Br]^{3-}$:979.9728, found 980.0144.

13.6 Synthesis of compound 2

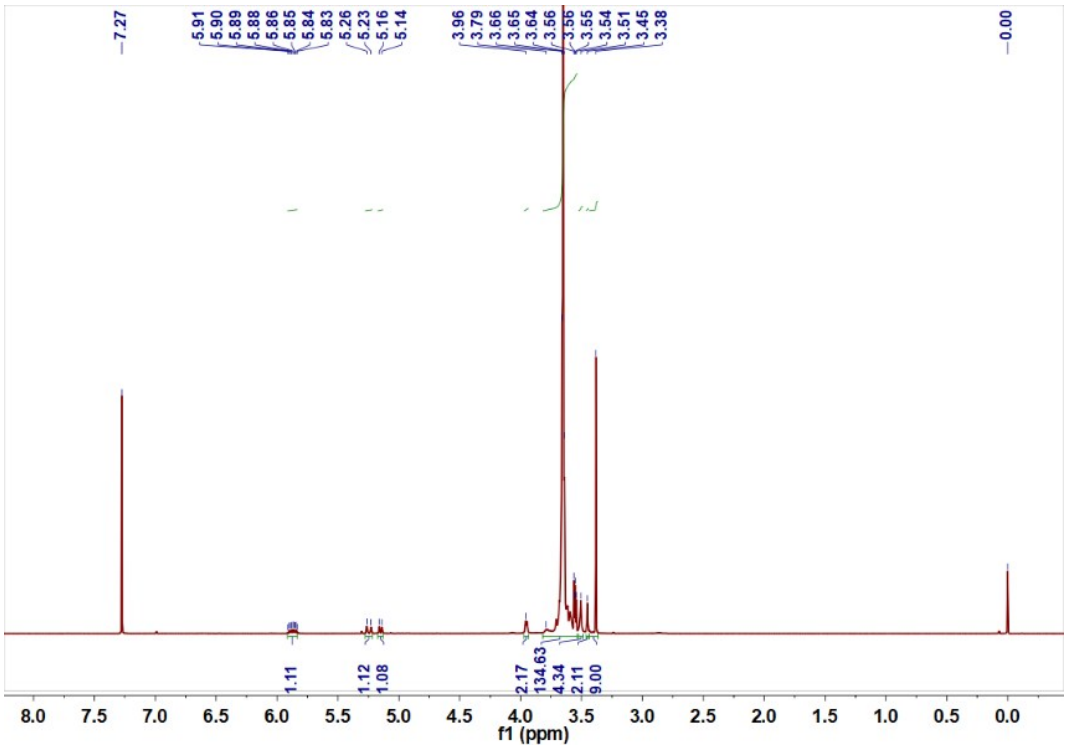
Under an atmosphere of nitrogen, to a stirring solution of HOBt (15.4 mg, 114.3 μmol) and CrA (59.6 mg, 63.5 μmol) in DMF (10 mL) was added EDC (21.9 mg, 114.3 μmol) at 0 °C. After stirring for 30 min, a solution of **17** (309.1 mg, 114.3 μmol) in DMF (2 mL) was added to the flask, and the reaction mixture was stirred at 50 °C for 12 h. Then the DMF was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to give compound **2** as purple oil (109 mg, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98-6.62 (m, 12H), 4.59 (ddd, J = 14.0, 8.8, 2.6 Hz, 6H), 4.49-4.39 (m, 2H), 4.29-4.23 (m, 2H), 4.15 (d, J = 1.9 Hz, 10H), 4.03 (s, 6H), 3.91 (s, 1H), 3.79 (d, J = 1.9 Hz, 12H), 3.75 (s, 2H), 3.69-3.52 (m, 134H), 3.35-3.46 (m, 28H), 3.32-3.27 (m, 2H), 3.15 (dt, J = 11.0, 5.9 Hz, 1H), 2.45-2.41 (m, 2H), 1.94 (s, 1H), 1.74 (ddd, J = 30.9, 11.8, 6.0 Hz, 2H), 1.55 (dt, J = 26.9, 6.0 Hz, 2H), 1.46-1.28 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 171.3, 170.9, 169.0, 149.9, 149.7, 149.4, 147.6, 146.9, 146.8, 146.5, 140.9, 134.8, 134.5, 134.2, 134.1, 134.0, 133.8, 133.6, 132.0, 131.8, 131.7, 131.4, 131.2, 128.5, 126.5, 126.0, 120.1 (q, *J* = 933.9Hz), 117.5, 115.6, 115.1, 113.7, 111.0, 71.9, 71.0, 70.53, 70.50, 70.48, 70.45, 70.2, 70.0, 69.6, 69.5, 69.44, 69.39, 69.31, 69.25, 69.2, 67.6, 66.0, 65.5, 59.0, 56.3, 55.6, 53.5, 46.1, 45.3, 39.6, 38.4, 36.5-35.7 (m), 32.1, 31.9, 31.4, 30.2, 29.3, 22.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.37. HRMS (ESI) calcd for $C_{159}H_{233}F_{27}N_4O_{57}$ $[M+2Na]^{2+}$:1834.7405, found 1834.7416.

13.7 Synthesis of compound 24

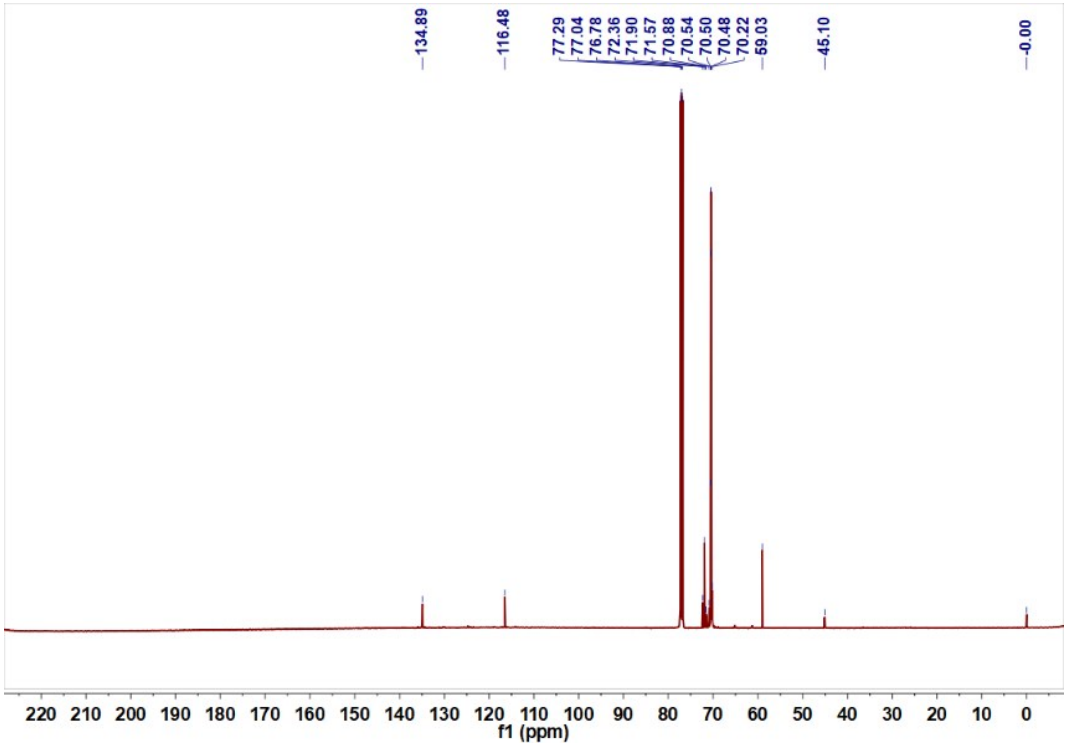
4 mg of (c-(RGDyC)) **22** and 17 mg of cholesterol-PEG_{2000}-maleimide **23** (1 eq) was dissolved in phosphate buffer (5 mM, pH = 7.4) under a nitrogen atmosphere and the resulting mixture was shaken at 25 °C for 24 h at 300 rpm. The crude product was purified by dialysis (MW cut-off = 1000 Da) in buffered water at pH = 7.4. The resulting solution was freeze-dried to give the product Cls-PEG-RGDyC (Figure S1), which was verified by mass spectroscopy, HRMS (ESI) calcd for $C_{155}H_{278}N_{10}O_{60}S$ $[M+3(CH_3OH)]^{3+}$:1122.6500, found 1122.6539.

14. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and HRMS spectra of compounds

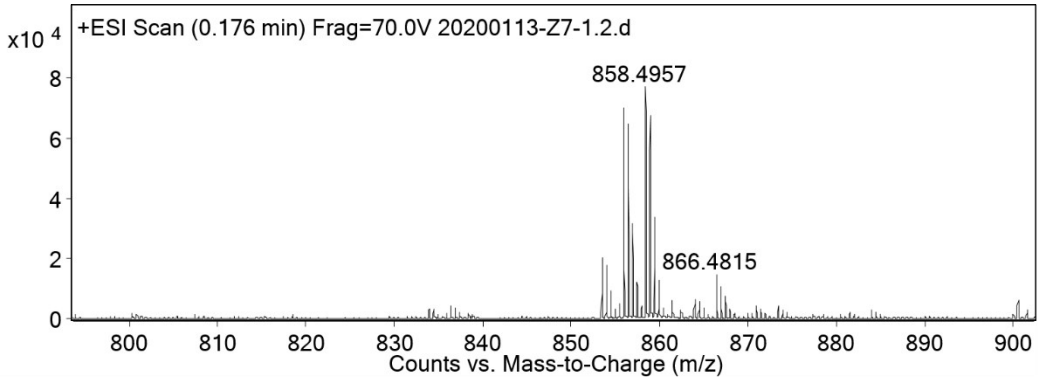
^{1}H NMR spectra of compound **7** (500 MHz, $CDCl_3$)



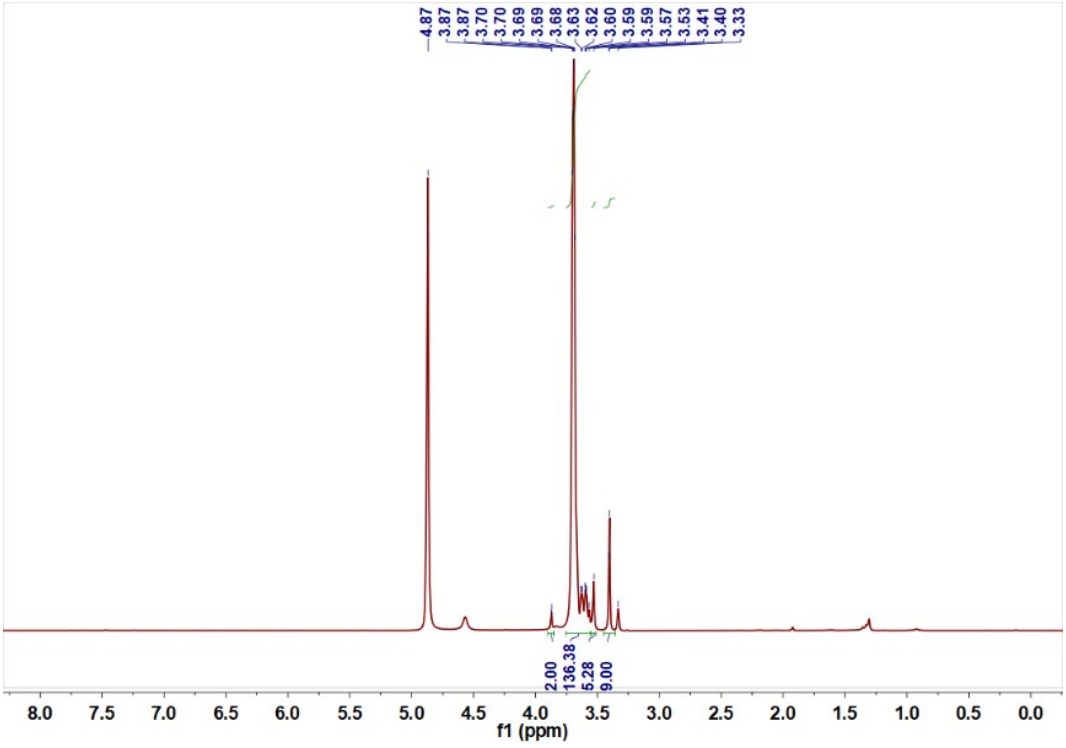
^{13}C NMR spectra of compound **7** (125 MHz, $CDCl_3$)


134.89
116.48
77.29
77.04
76.78
72.36
71.90
71.57
70.88
70.54
70.50
70.48
70.22
69.03
45.10
0.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

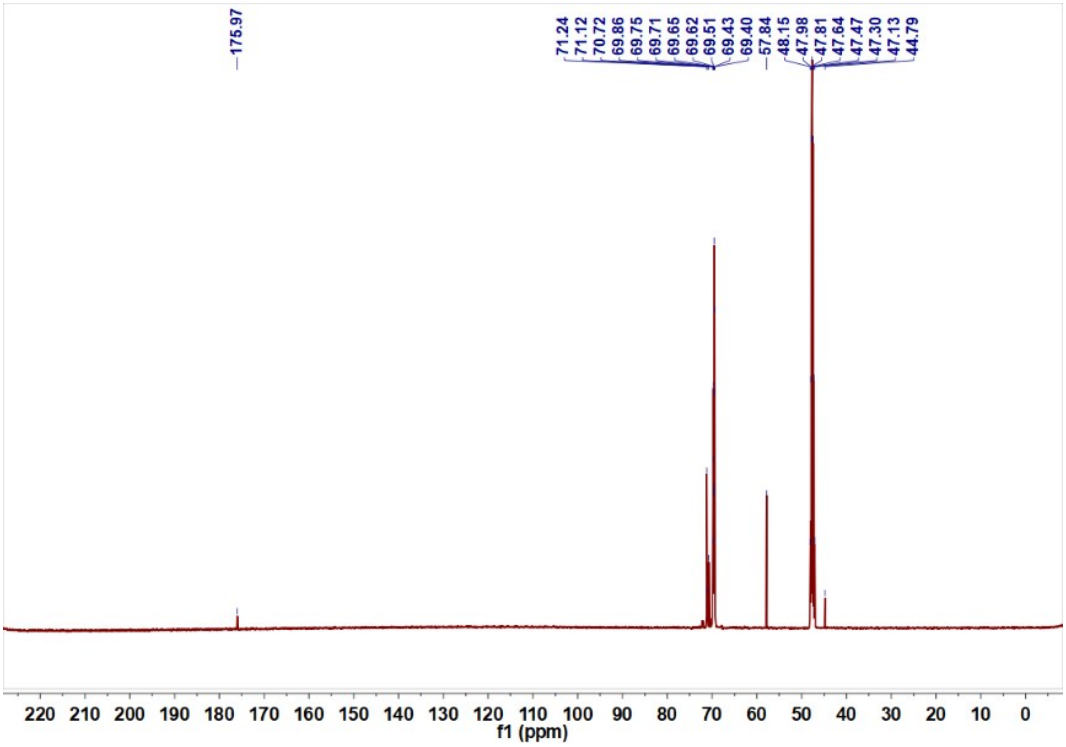
HRMS (ESI) spectra of compound **7**



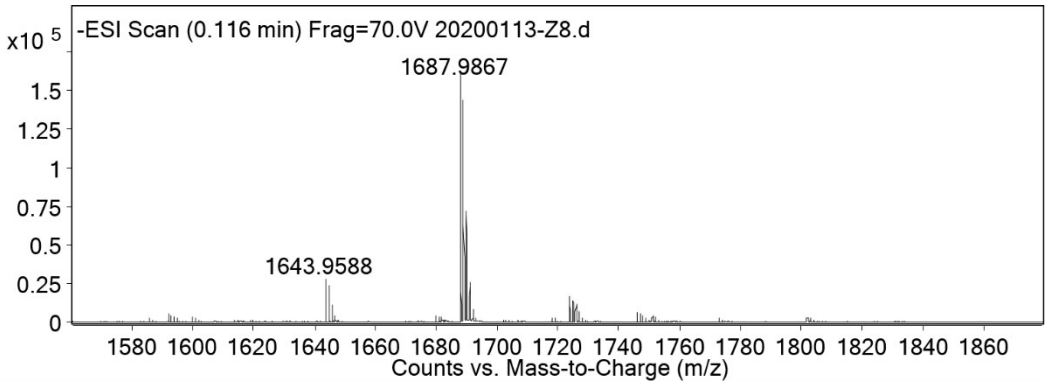
^{1}H NMR spectra of compound **8** (500 MHz, CD_3OD)



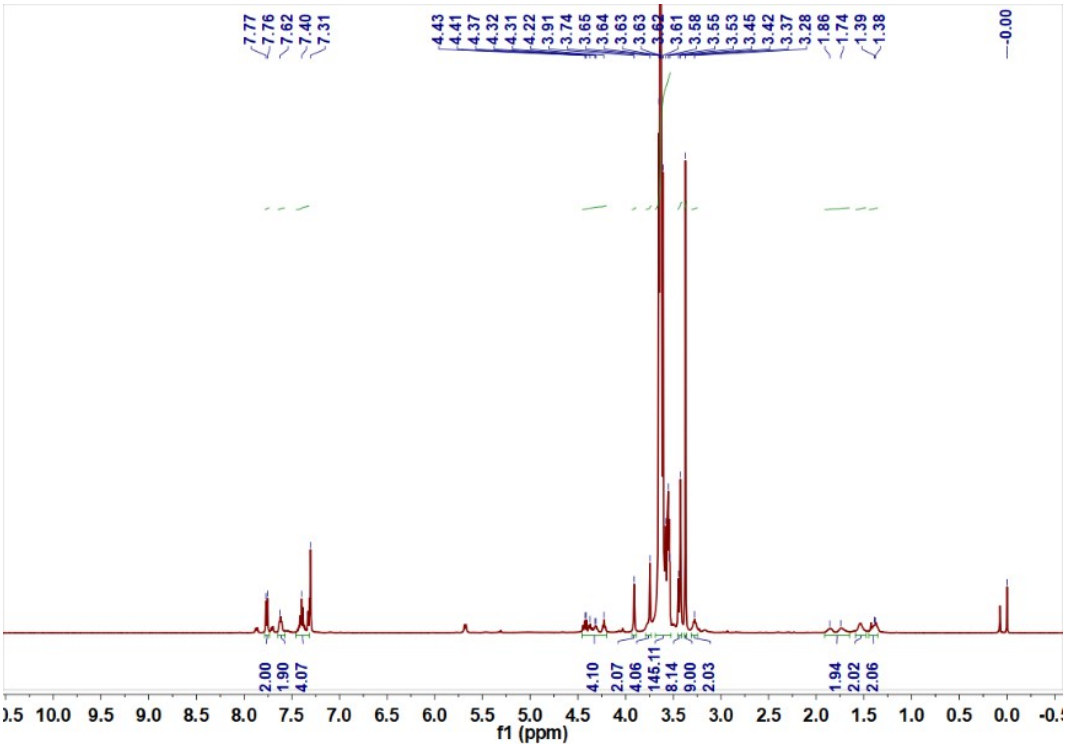
^{13}C NMR spectra of compound **8** (125 MHz, CD_3OD)



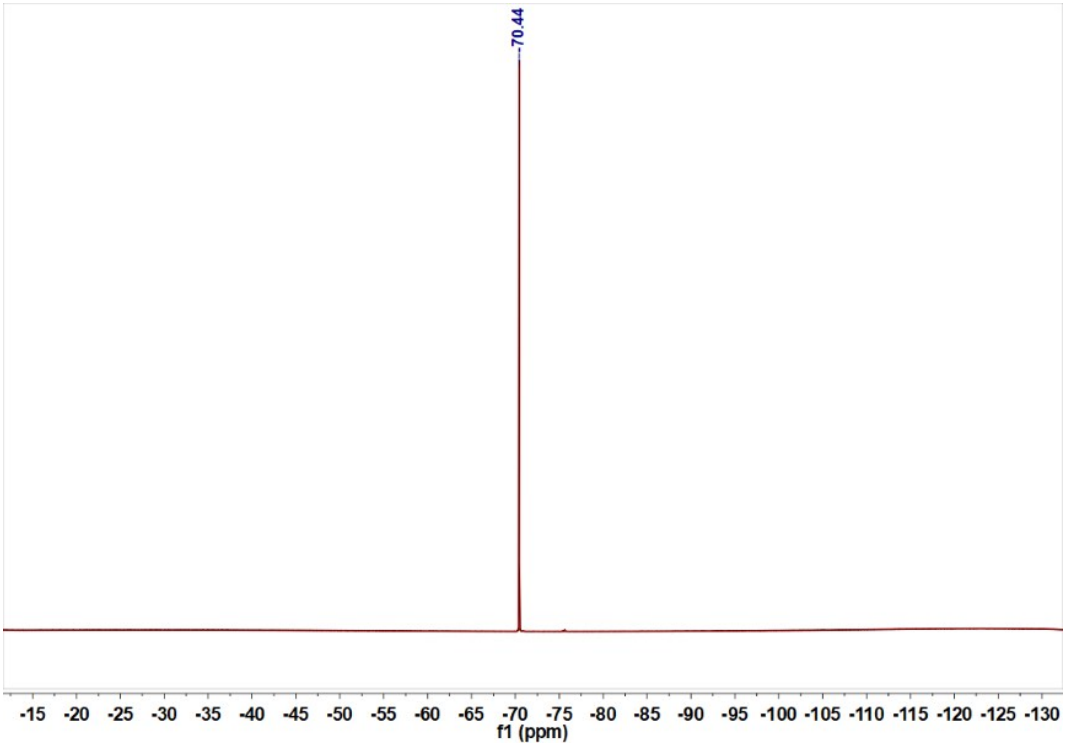
HRMS (ESI) spectra of compound **8**



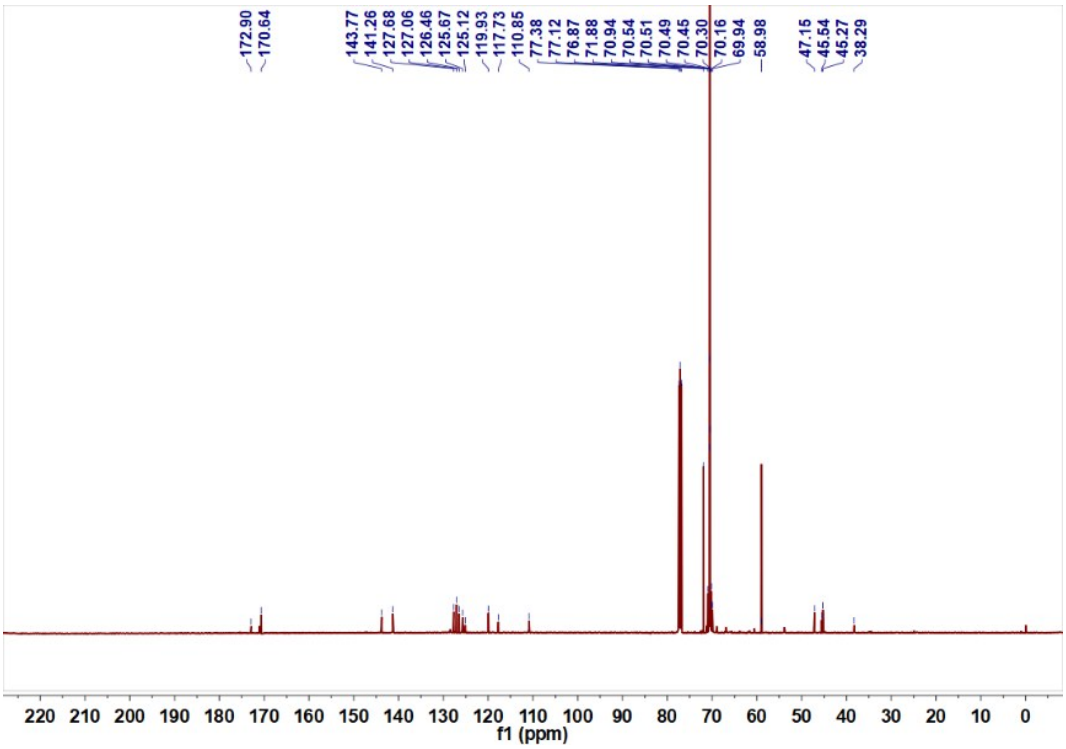
^{1}H NMR spectra of compound **16** (500 MHz, $CDCl_3$)



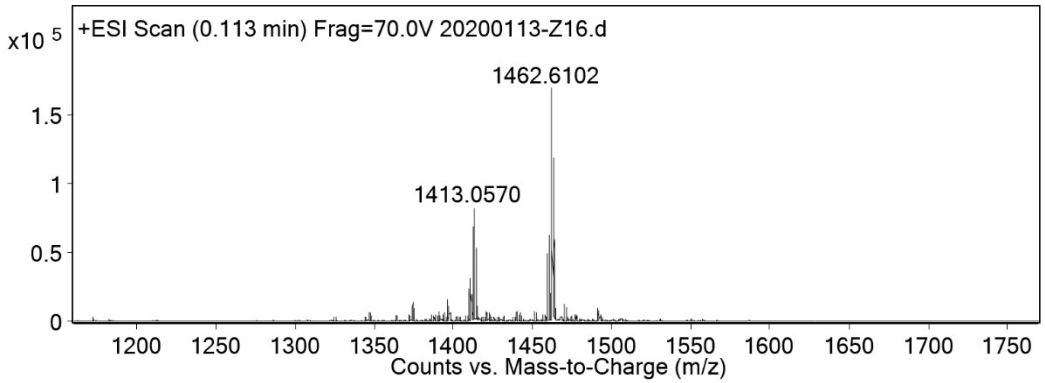
^{19}F NMR spectra of compound **16** (471 MHz, $CDCl_3$)



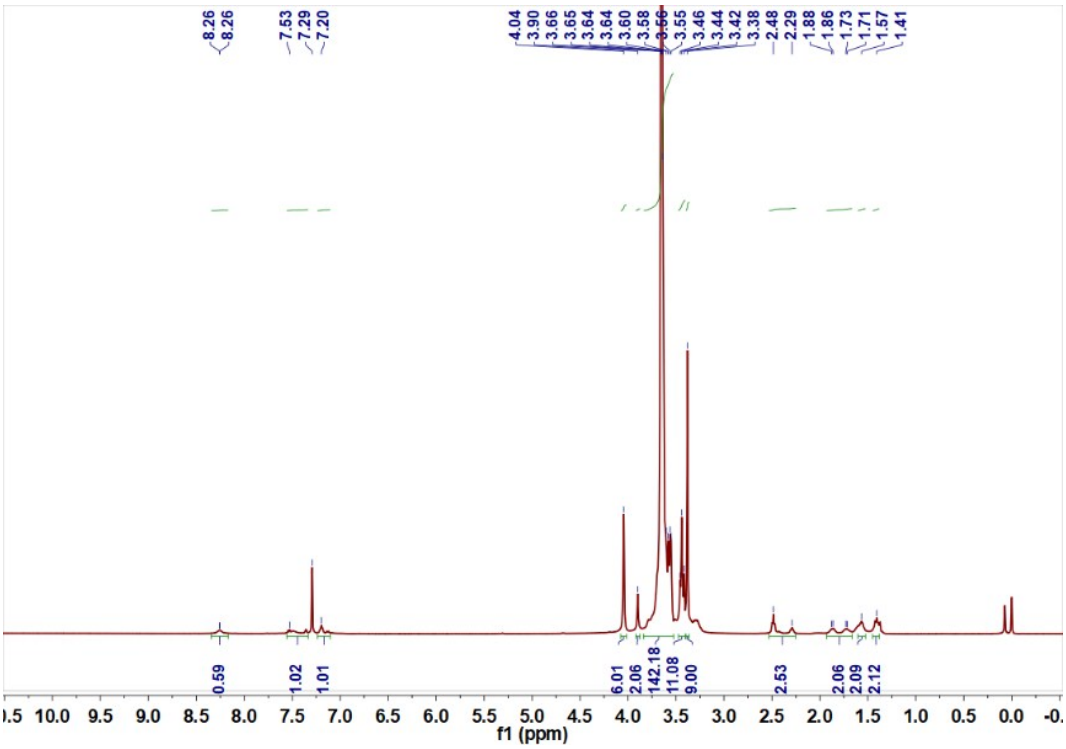
^{13}C NMR spectra of compound **16** (125 MHz, $CDCl_3$)



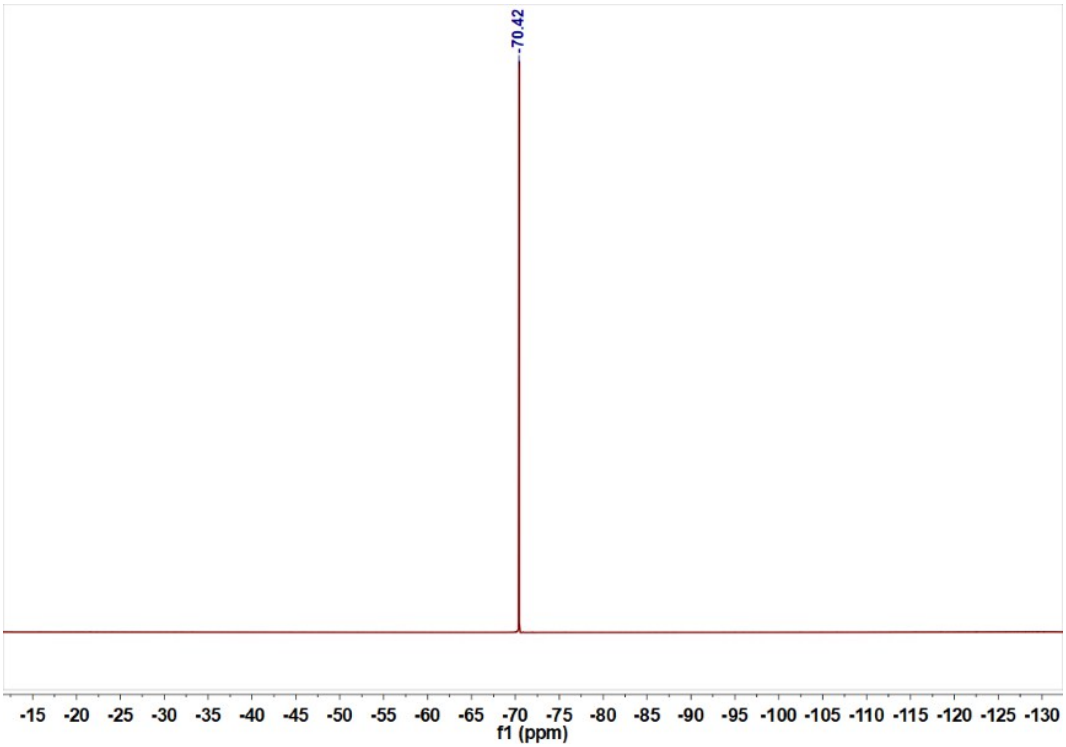
HRMS (ESI) spectra of compound **16**



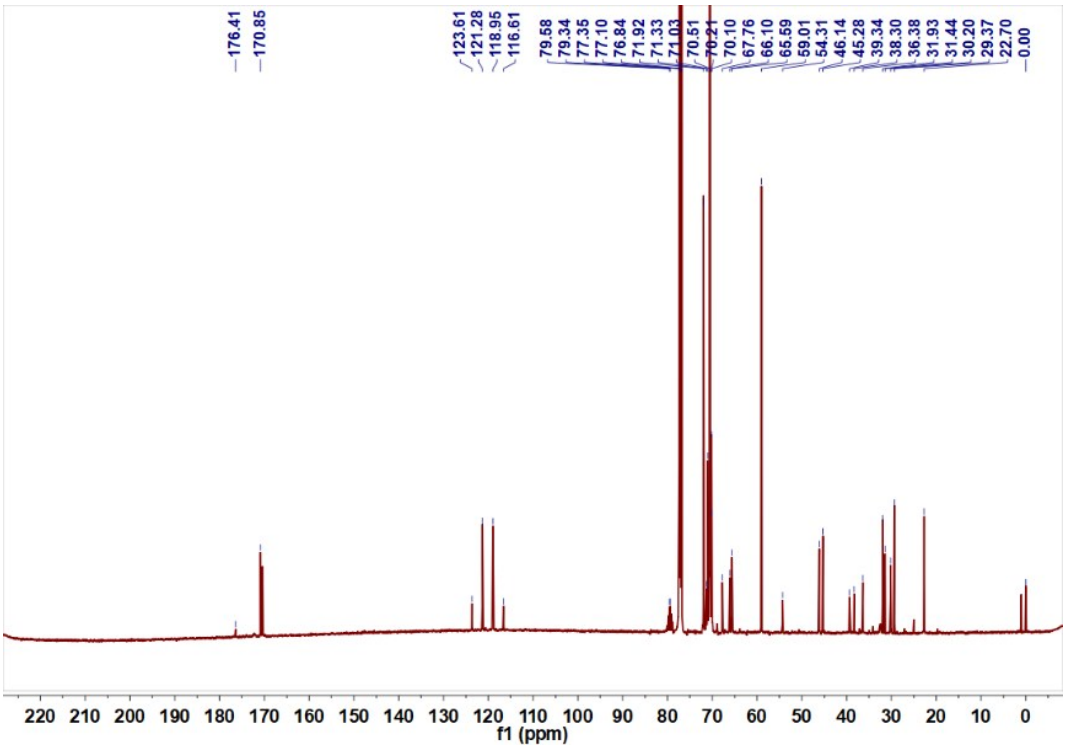
^{1}H NMR spectra of compound **17** (500 MHz, $CDCl_3$)



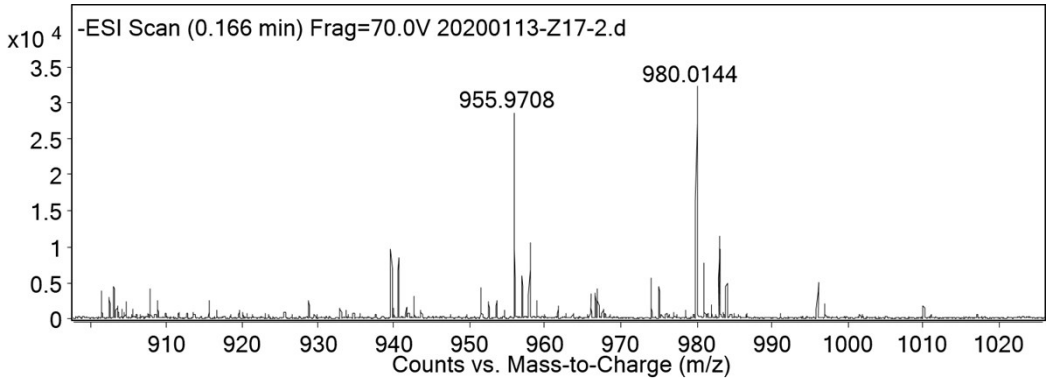
^{19}F NMR spectra of compound **17** (471 MHz, $CDCl_3$)



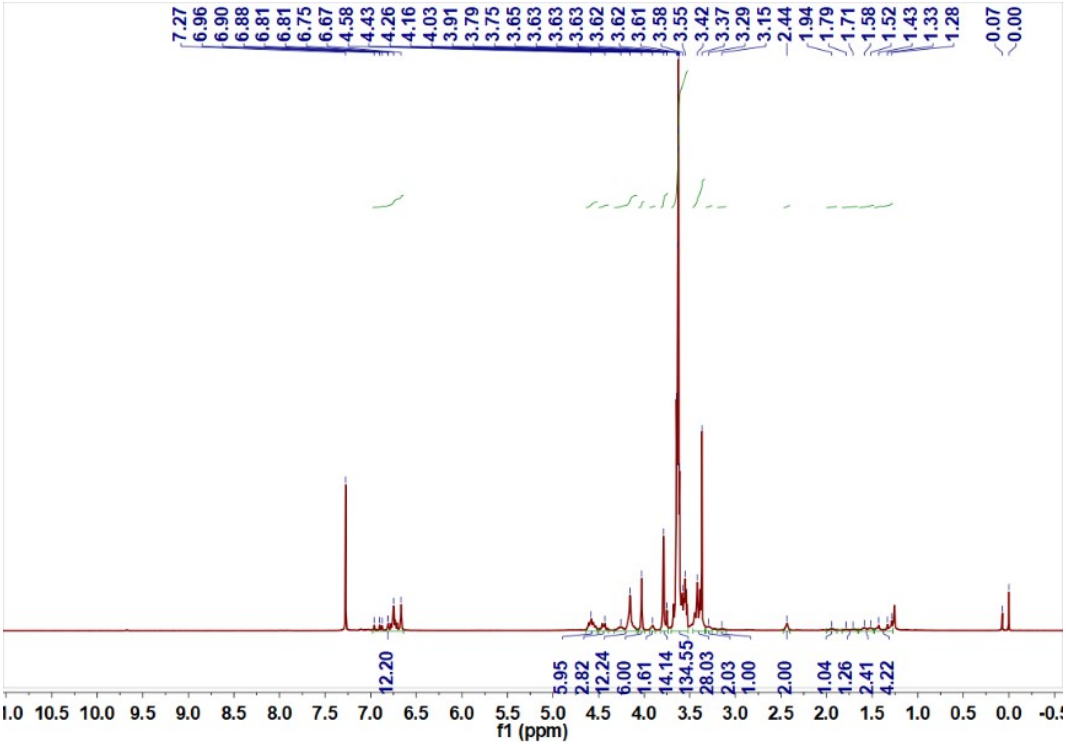
^{13}C NMR spectra of compound **17** (125 MHz, $CDCl_3$)



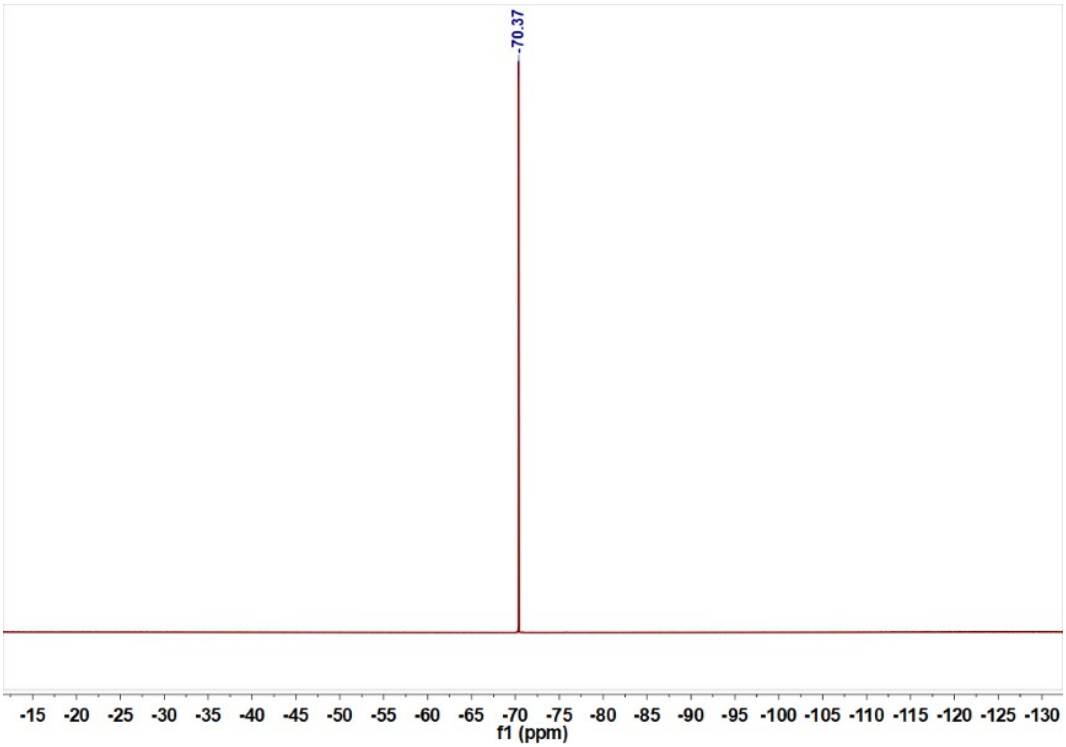
HRMS (ESI) spectra of compound **17**



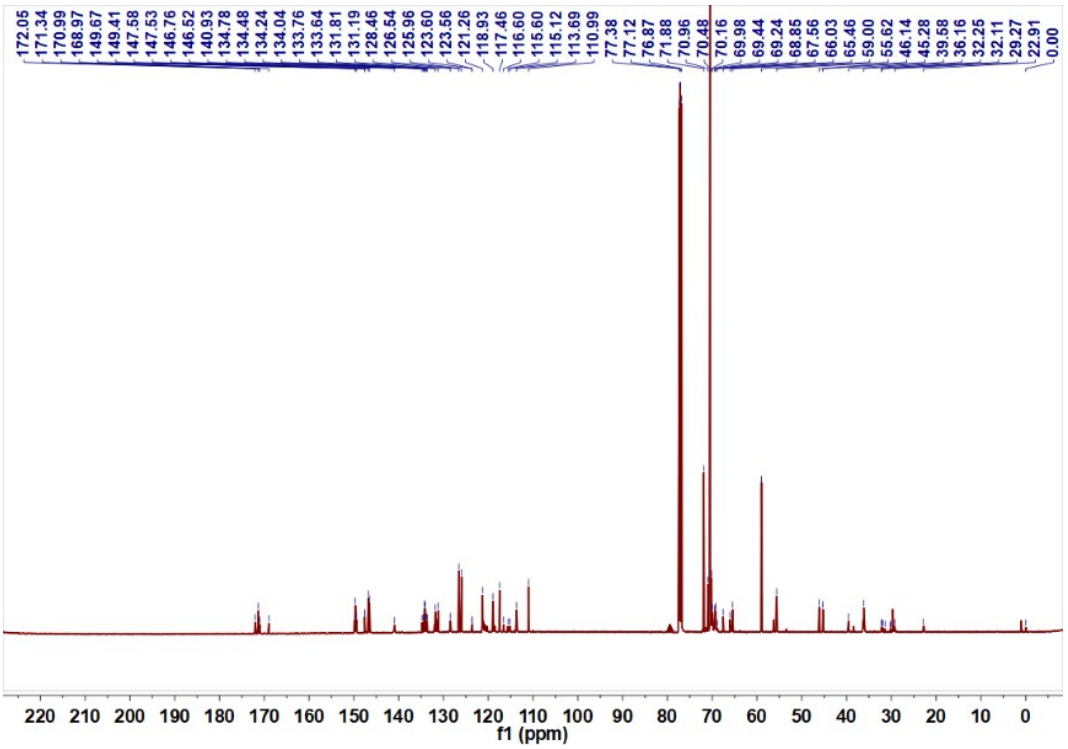
^{1}H NMR spectra of compound **2** (500 MHz, $CDCl_3$)



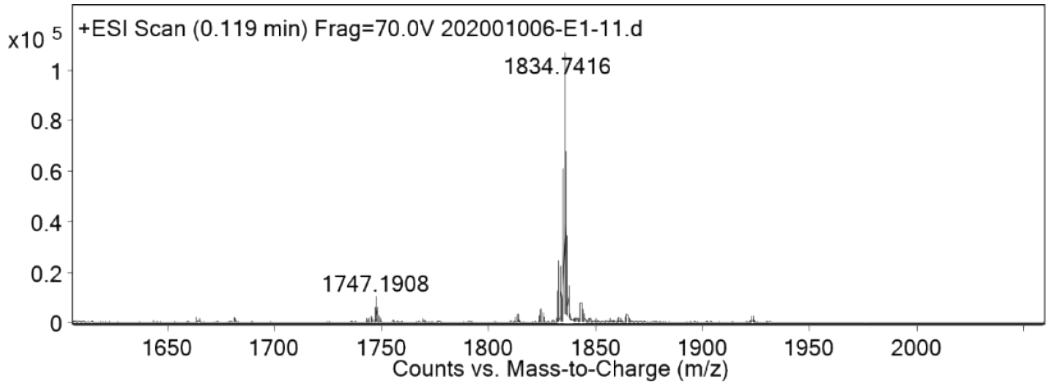
^{19}F NMR spectra of compound **2** (471 MHz, $CDCl_3$)



^{13}C NMR spectra of compound **2** (125 MHz, $CDCl_3$)



HRMS (ESI) spectra of compound **2**



HRMS (ESI) spectra of compound **24**