Supporting Information

Self-Assembly of Precisely Fluorinated Albumin for Dual Imaging-Guided Synergistic Chemo – Photothermal–Photodynamic Cancer Therapy

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1 Materials

Human breast adenocarcinoma cell line MCF-7, normal human breast epithelial cell line MCF-10A, triple-negative breast cancer MDA-MB-231 cells, human colorectal cancer HCT-116 cells, cervical cancer HeLa cells, and lung cancer A549 cells were purchased from the Cell Bank of the Chinese Academy of Sciences (Shanghai, China). MCF-7 cells, MCF-10A cells, MDA-MB-231 cells, and A549 cells were cultured in Dulbecco's Modified Eagle's Medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin. HCT-116 cells and HeLa cells were cultured in Roswell Park Memorial Institute (RPMI) 1640 supplemented with 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin. Cells were incubated at 37 ^{o}C in a humidified 5% CO_2 atmosphere.

Female BALB/c nude mice (5 weeks old) were obtained from Animal Research Center of Wuhan University (Wuhan, China). All study protocols were approved by the Institutional Animal Care and Use Committee (IACUC) of the Animal Research Center of Wuhan University (Wuhan, China). All mouse experimental procedures were carried out in agreement with the Regulations for the Administration of Affairs Concerning Experimental Animals approved by the State Council of the People's Republic of China.

2 General Information

^{1}H, ^{13}C, and ^{19}F NMR spectra of compounds were recorded on Bruker AVANCE III 400 MHz, 500 MHz or 600 MHz spectrometers. Chemical shifts are provided in ppm and coupling constants (*J*) are provided in Hertz (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane (d, 0.00 ppm) using $CDCl_3$ (s, 7.26 ppm) as solvent. ^{13}C NMR spectra were referenced to solvent carbons (77.2 ppm for $CDCl_3$). ^{19}F NMR spectra were referenced to 2% perfluorobenzene (s, -164.90 ppm) in $CDCl_3$ or 2% sodium triflate (s, -79.61 ppm) in D_2O. Multiplicities are reported as follows: s

(singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), or m (multiplet). High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Q Exactive Focus. MALDI-TOF mass spectra were recorded on an autoflex™ speed MALDI-TOF spectrometer.

The UV-vis and PL spectra were carried out by a Shimadzu UV-2600 spectrophotometer (UV-vis spectrometer) and Horiba Fluoromax-4 spectrofluorometer (PL), respectively. The size distribution, polymer dispersion index (PDI) and zeta potential of nanoparticles were determined by a dynamic light scattering (DLS) instrument (Malvern, Nano ZS 90, UK). The morphology of the nanoparticles was studied using transmission electron microscopy (TEM, Tecnai G20, FEI, USA). Small animal fluorescence imaging was carried out by IVIS imaging system (PerkinElmer). The temperature change of photothermal conversion behavior and thermal images were recorded using Hikvision H13 Thermal Imager (Hikvision, Beijing).

Compound **2** is commercially available. Compound **7**[1-3] was synthesized in this lab. Compounds **3**[4], **8a**[5], **8b**[6], **8c**[6], **9a**[7], **9b**[7], **9c**[7] are known compounds and the corresponding references were cited.

3 Synthesis and Characterization of Fluorinated Tags

Synthesis of compound 3[4]**:** Sulfuric acid (5 mL, 93.7 mmol) was added to the suspension of 4-methoxy-3,5-dimethylbenzoic acid (8.01 g, 44.4 mmol) in methanol (120 mL) and the mixture was stirred under reflux for 24 h. Then methanol was evaporated under vacuum. The residue was diluted with water (200 mL) and extracted with ethyl acetate (100 mL, 3 times). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under vacuum and purified by column chromatography on silica gel (PE/EA = 10/1) to give compound **3** as a yellowish oily liquid (8.54 g, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 2H), 3.90 (s, 3H), 3.76 (s, 3H), 2.33 (s, 6H).

Synthesis of compound 4: To a solution of compound **3** (9.29 g, 47.8 mmol) in 70 mL of carbon tetrachloride was added *N*-Bromosuccinimide (21.30 g, 119.6 mmol) and benzoyl peroxide (2.93 g, 12.0 mmol) successively. The resulting mixture was refluxed at 90 ºC for 12 h. TLC showed that the starting material was consumed completely. Then the mixture was filtered, then the filtrate was evaporated under vacuum. The residue was diluted with water (200 mL) and extracted with ethyl acetate (100 mL, 3 times). The combined organic layers were dried over anhydrous sodium

sulfate, concentrated under vacuum, and the residue was purified by silica gel column chromatography using PE/EA (20/1) as the eluent to afford compound **4** as a white solid (7.26 g, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 4.56 (s, 4H), 4.08 (d, J = 2.4 Hz, 3H), 3.93 (d, J = 2.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.8, 133.6, 132.4, 126.9, 62.5, 52.4, 26.8. HRMS (ESI) calcd for $C_{11}H_{13}Br_2O_3^+$ ([M+H]$^+$), 350.9225, found, 350.9222.

Synthesis of compound 5: Under an argon atmosphere, a solution of compound **4** (4.84 g, 13.7 mmol) in anhydrous DMF (50 mL) was added to a reaction flask containing sodium perfluoro-*tert*-butoxide (7.81 g, 30.2 mmol). The reaction mixture was stirred at room temperature for 24 h. TLC showed that the starting material was consumed completely. Then DMF was evaporated under vacuum. The residue was diluted with water (200 mL) and extracted with ethyl acetate (100 mL, 3 times). The combined organic layer was dried over anhydrous sodium sulfate, concentrated under vacuum and purified by column chromatography on silica gel (PE/EA = 20/1) to give compound **5** as a white solid (7.00 g, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 5.13 (s, 4H), 3.96 (s, 3H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.04 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 161.5, 133.5, 128.9, 127.0, 120.4 (q, J = 292.8 Hz), 80.8 – 79.0 (m), 66.2, 63.6, 52.4, 29.7. HRMS (ESI) calcd for $C_{19}H_{12}F_{18}NaO_5^+$ ([M+Na]$^+$), 685.0290, found, 685.0291.

Synthesis of compound 6: Under an argon atmosphere, anhydrous THF (30 mL) was added to the reaction flask containing lithium aluminum hydride (1.38 g, 4.2 mmol), and it was cooled to 0 ^{o}C. Then the THF (10 mL) solution of compound **5** (12.0 g, 2.1 mmol) was slowly added to it. After stirring for 0.5 h, the mixture was stirred at room temperature for 12 h. TLC showed that the starting material was consumed completely. Water (1.38 mL) and 15% NaOH solution (1.38 mL) were added successively to the mixture in an ice-water bath, and the resulting mixture was stirred for 15 min. The mixture was filtered and washed with methanol, then the filtrate was evaporated under vacuum and extracted with ethyl acetate (100 mL, 3 times). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified by silica gel column chromatography using PE/EA (20/1) as the eluent to afford compound **6** as a white solid (7.10 g, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 2H), 5.11 (s, 4H), 4.71 (s, 2H), 3.83 (s, 3H), 2.07 (d, J = 9.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.05 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 137.6, 130.4, 128.6, 120.4 (q, J = 292.8 Hz), 80.9 – 79.2 (m), 66.3, 64.3, 63.5. HRMS (ESI) calcd for $C_{18}H_{12}F_{18}NaO_4^+$ ([M+Na]$^+$), 657.0338, found, 657.0339.

Synthesis of compound 8a[5]: To a solution of compound **7** (20 g, 78.0 mmol) in 60 mL of DMF was added NaN_3 (6.6 g, 101.5 mmol). The reaction mixture was stirred at 80 °C for 12 h. TLC showed that the starting material was consumed completely. The excessive NaN_3 was removed by filtration, and the filtrate was evaporated under vacuum. Then, THF (50 mL) and H_2O (2.8 mL) were added, the pH was adjusted to 3.0 with concentrated sulfuric acid and the mixture was stirred under reflux for 12 h. After the reaction was complete, saturated $NaHCO_3$ solution was added to neutralize the reaction mixture. Then THF was evaporated under vacuum and extracted with ethyl acetate (100 mL, 3 times). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under vacuum and purified by column chromatography on silica gel (PE/EA = 1/1) to give compound **8a** as a yellow oily liquid (12.56 g, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 – 3.61 (m, 14H), 3.42 (d, J = 4.4 Hz, 2H), 2.47 (s, 1H).

Synthesis of compound 8b[6]: Under an argon atmosphere, anhydrous THF (40 mL) was added to a reaction flask containing NaH (3.50 g, 85.9 mmol). After cooling the suspension to 0 °C, anhydrous THF (10 mL) solution of compound **8a** (12.56 g, 57.3 mmol) was added slowly. The reaction mixture was stirred at 0 °C for 1 h. Then, anhydrous THF (10 mL) solution of compound **7** (17.63 g, 57.3 mmol) was added to the reaction solution, and the reaction solution was stirred at room temperature for 12 h. TLC showed that the starting material was consumed completely. The mixture was quenched with ice water. Then, the pH was adjusted to 3.0 with concentrated sulfuric acid and the mixture was stirred under reflux for 12 h. After the reaction was complete, saturated $NaHCO_3$ solution was added to neutralize the reaction mixture. Then THF was evaporated under vacuum and the residue was extracted with ethyl acetate (100 mL, 3 times). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under vacuum and purified by column chromatography on silica gel (DCM/MeOH = 20/1) to give compound **8b** as a yellow oily liquid (20.80 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 – 3.68 (m, 2H), 3.67 – 3.62 (m, 26H), 3.60 – 3.57 (m, 2H), 3.40 – 3.35 (m, 2H), 2.97 (s, 1H).

Synthesis of compound 8c[6]: Compound **8c** was prepared as a yellow oily liquid (22.26 g, 88% yield) using a procedure identical to the preparation of compound **8b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 – 3.45 (m, 46H), 3.31 – 3.26 (m, 2H), 3.06 (s, 1H).

Synthesis of compound 8d: Compound **8d** was prepared as a yellow oily liquid (12.14 g, 93% yield) using a procedure identical to the preparation of compound **8b**. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 3.76 – 3.35 (m, 62H), 3.32 – 3.27 (m, 2H), 2.87 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 72.4, 70.2, 69.9, 69.7, 61.2, 50.3. HRMS (ESI) calcd for $C_{32}H_{65}N_3NaO_{16}^+$ ([M+Na]$^+$), 770.4257, found, 770.4252.

Synthesis of compound 8e: Compound **8e** was prepared as a yellow oily liquid (8.55 g, 86% yield) using a procedure identical to the preparation of compound **8b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 – 3.71 (m, 2H), 3.67 – 3.64 (m, 74H), 3.61 – 3.59 (m, 2H), 3.39 (t, *J* = 5.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 72.7, 70.3, 70.2, 67.0, 61.6, 50.6. HRMS (ESI) calcd for $C_{40}H_{81}N_3NaO_{20}^+$ ([M+Na]$^+$), 946.5305, found, 946.5295.

Synthesis of compound 9a[7]: To a solution of compound **8a** (1 g, 4.6 mmol) in THF (20 mL) was added aqueous NaOH (0.73 g, 18.2 mmol, 2 mL), and TosCl (1.74 g, 6.8 mmol) in THF (20 mL) was slowly added at 0 °C. The reaction mixture was stirred at room temperature for 12 h. TLC showed that the starting material was consumed completely. Then THF was evaporated under vacuum and extracted with ethyl acetate (100 mL, 3 times). The combined organic layer was dried over anhydrous sodium sulfate, concentrated under vacuum and purified by column chromatography on a silica gel (PE/EA = 1/1) to give compound **9a** as a yellow oily liquid (1.50 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.16 (dd, *J* = 5.4, 4.3 Hz, 2H), 3.70 – 3.63 (m, 8H), 3.59 (s, 4H), 3.40 – 3.36 (m, 2H), 2.45 (s, 3H).

Synthesis of compound 9b[7]: Compound **9b** was prepared as a yellow oily liquid (1.35 g, 97% yield) using a procedure identical to the preparation of compound **9a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.17 – 4.14 (m, 2H), 3.69 – 3.61 (m, 26H), 3.58 (s, 4H), 3.38 (s, 2H), 2.45 (s, 3H).

Synthesis of compound 9c[7]: Compound **9c** was prepared as a yellow oily liquid (3.20 g, 93% yield) using a procedure identical to the preparation of compound **9a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.09 – 4.05 (m, 2H), 3.61 – 3.53 (m, 40H), 3.49 (s, 4H), 3.33 – 3.29 (m, 2H), 2.37 (s, 3H).

Synthesis of compound 9d: Compound **9d** was prepared as a yellow oily liquid (2.21 g, 92% yield) using a procedure identical to the preparation of compound **9a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.17 – 4.15 (m, 2H), 3.65 (d, *J* = 7.0 Hz, 56H), 3.58 (s, 4H), 3.39 (t, *J* = 5.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 133.0, 129.8, 127.9, 77.5, 77.2, 77.0, 70.5, 70.0, 69.2, 68.6, 50.6, 21.6. HRMS (ESI) calcd for

$C_{39}H_{71}N_3NaO_{18}S^+$ ([M+Na]$^+$), 924.4345, found, 924.4340.

Synthesis of compound 9e: Compound **9e** was prepared as a yellow oily liquid (1.27 g, 84% yield) using a procedure identical to the preparation of compound **9a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 2H), 4.10 (d, *J* = 4.7 Hz, 2H), 3.64 – 3.57 (m, 72H), 3.53 (s, 4H), 3.35 (d, *J* = 5.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 132.8, 129.8, 127.9, 70.7, 70.5, 69.3, 68.6, 50.6, 21.6. HRMS (ESI) calcd for $C_{47}H_{87}N_3NaO_{22}S^+$ ([M+Na]$^+$), 1100.5394, found, 1100.5391.

Synthesis of compound 10a: Under an argon atmosphere, anhydrous THF (25 mL) was added to a reaction flask containing NaH (0.15 g, 4.8 mmol). After cooling the suspension to 0 °C, anhydrous THF (10 mL) solution of compound **6** (1 g, 1.6 mmol) was added slowly. The reaction mixture was stirred at 0 ºC for 0.5 h. Then, anhydrous THF (10 mL) solution of compound **9a** (0.613 g, 1.6 mmol) was added to the reaction solution, and the mixture was stirred under reflux for 12 h. TLC showed that the starting material was consumed completely. The mixture was quenched with ice water. Then THF was evaporated under vacuum and extracted with ethyl acetate (100 mL, 3 times). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under vacuum and purified by column chromatography on a silica gel (DCM/MeOH = 20/1) to give compound **10a** as a yellow oily liquid (1.31 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 5.10 (s, 4H), 4.58 (s, 2H), 3.82 (s, 3H), 3.72 – 3.66 (m, 14H), 3.39 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.03 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 135.1, 131.2 , 128.4, 120.4 (q, *J* = 292.8 Hz), 81.0 – 78.7 (m), 72.3, 70.9, 70.7, 70.0, 69.8, 66.4, 63.5, 50.6. HRMS (ESI) calcd for $C_{26}H_{27}F_{18}N_3NaO_7^+$ ([M+Na]$^+$), 858.1453, found, 858.1450.

Synthesis of compound 10b: Compound **10b** was prepared as yellow oily liquid (1.82 g, 86% yield) using a procedure identical to the preparation of compound **10a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 5.07 (s, 4H), 4.55 (s, 2H), 3.79 (s, 3H), 3.64 (dd, *J* = 6.3, 2.0 Hz, 30H), 3.39 – 3.36 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.01 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 135.1, 131.2, 128.4, 120.4 (q, *J* = 293.5 Hz), 81.1 – 78.6 (m), 72.3, 70.9, 70.6, 70.5, 70.0, 69.7, 66.4, 63.4, 50.6. HRMS (ESI) calcd for $C_{34}H_{43}F_{18}N_3NaO_{11}^+$ ([M+Na]$^+$), 1034.2500, found, 1034.2502.

Synthesis of compound 10c: Compound **10c** was prepared as a yellow oily liquid (1.67 g, 89% yield) using a procedure identical to the preparation of compound **10a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H), 5.05 (s, 4H), 4.52 (s, 2H), 3.76 (s, 3H), 3.62 (dt, *J* = 4.2, 2.6 Hz, 46H), 3.36 – 3.33

(m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.99 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 135.1, 131.1, 128.3, 120.4 (q, J = 292.5 Hz), 80.8 – 78.8 (m), 72.2, 70.8, 70.6, 70.5, 70.0, 69.7, 66.4, 63.4, 50.6. HRMS (ESI) calcd for $C_{42}H_{59}F_{18}N_3NaO_{15}^+$ ([M+Na]$^+$), 1210.3549, found, 1210.3551.

Synthesis of compound 10d: Compound **10d** was prepared as a yellow oily liquid (1.38 g, 96% yield) using a procedure identical to the preparation of compound **10a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 10.8 Hz, 2H), 5.05 (s, 4H), 4.53 (s, 2H), 3.77 (s, 3H), 3.67 – 3.58 (m, 62H), 3.36 (t, J = 5.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.10 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 135.1, 131.2, 128.4, 120.4 (q, J = 292.9 Hz), 81.8 – 78.0 (m), 72.3, 70.5, 70.0, 69.7, 66.4, 63.5, 50.6. HRMS (ESI) calcd for $C_{50}H_{75}F_{18}N_3NaO_{19}^+$ ([M+Na]$^+$), 1386.4600, found, 1386.4607.

Synthesis of compound 10e: Compound **10e** was prepared as a yellow oily liquid (1.15 g, 81% yield) using a procedure identical to the preparation of compound **10a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 2H), 5.04 (s, 4H), 4.51 (s, 2H), 3.76 (s, 3H), 3.64 – 3.58 (m, 78H), 3.38 – 3.32 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.10 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 135.1, 131.2, 128.4, 120.4 (q, J = 292.7 Hz), 80.9 – 78.6 (m), 72.3, 70.5, 70.0, 69.7, 66.4, 63.5, 50.6. HRMS (ESI) calcd for $C_{58}H_{91}F_{18}N_3NaO_{23}^+$ ([M+Na]$^+$), 1562.5648, found, 1562.5643.

Synthesis of compound 11a: To the compound **10a** (1.21 g, 1.4 mmol) in THF (20 mL) was added Ph_3P (0.58 g, 2.2 mmol). The reaction mixture was monitored by TLC. After the starting material had been completely consumed, water (0.5 mL) was added and the reaction mixture was stirred for 5 h at room temperature. After removal of the solvent in vacuum through rotary evaporation, the residue was purified by column chromatography on a silica gel (DCM/MeOH = 20/1) to give compound **11** as a yellow oily liquid (1.00 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 2H), 5.08 (s, 4H), 4.56 (s, 2H), 3.80 (s, 3H), 3.70 – 3.62 (m, 12H), 3.50 (t, J = 5.2 Hz, 2H), 2.85 (t, J = 5.2 Hz, 2H), 1.86 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.02 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 135.0, 131.2, 128.4, 120.4 (q, J = 292.8 Hz), 80.9 – 78.6 (m), 73.2, 72.3, 70.6, 70.54, 70.52, 70.2, 69.8, 66.4, 63.4, 41.6. HRMS (ESI) calcd for $C_{26}H_{30}F_{18}NO_7^+$ ([M+H]$^+$), 810.1729, found, 810.1726.

Synthesis of compound 11b: Compound **11b** was prepared as a yellow oily liquid (1.02 g, 90% yield) using a procedure identical to the preparation of compound **11a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 2H), 5.08 (s, 4H), 4.56 (s, 2H), 3.80 (s, 3H), 3.66 (dd, J = 5.8, 2.4 Hz, 28H), 3.52 (t, J = 5.2 Hz, 2H), 2.87 (t, J = 5.2 Hz, 2H), 2.02 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.10 (s). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 157.0, 135.1, 131.2, 128.4, 120.4 (q, J = 292.8 Hz), 81.1 – 78.5 (m), 73.2, 72.3, 70.6, 70.5, 70.2, 69.8, 66.4, 63.5, 41.7. HRMS (ESI) calcd for $C_{34}H_{46}F_{18}NO_{11}^+$ ($[M+H]^+$), 986.2778, found, 986.2774.

Synthesis of compound 11c: Compound **11c** was prepared as a yellow oily liquid (1.25 g, 85% yield) using a procedure identical to the preparation of compound **11a**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 5.06 (s, 4H), 4.54 (s, 2H), 3.78 (s, 3H), 3.66 – 3.60 (m, 46H), 3.53 (t, J = 5.2 Hz, 2H), 2.88 (d, J = 4.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.06 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 135.1, 131.2, 128.4, 120.4 (q, J = 292.2 Hz), 80.6 – 78.7 (m), 72.5, 72.3, 70.6, 70.5, 70.2, 69.7, 66.4, 63.4, 41.4. HRMS (ESI) calcd for $C_{42}H_{62}F_{18}NO_{15}^+$ ($[M+H]^+$), 1162.3827, found, 1162.3826.

Synthesis of compound 11d: Compound **11d** was prepared as a yellow oily liquid (0.89 g, 91% yield) using a procedure identical to the preparation of compound **11a**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 5.06 (s, 4H), 4.54 (s, 2H), 3.78 (s, 3H), 3.67 – 3.61 (m, 60H), 3.53 (t, J = 5.1 Hz, 2H), 2.88 (t, J = 5.1 Hz, 2H), 2.25 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.14 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 135.1, 131.2, 128.4, 120.4 (q, J = 290.7 Hz), 80.4 – 77.6 (m), 72.3, 70.5, 70.2, 69.8, 66.4, 63.5, 41.6. HRMS (ESI) calcd for $C_{50}H_{78}F_{18}NO_{19}^+$ ($[M+H]^+$), 1338.4875, found, 1338.4872.

Synthesis of compound 11e: Compound **11e** was prepared as a yellow oily liquid (0.91 g, 93% yield) using a procedure identical to the preparation of compound **11a**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H), 5.04 (s, 4H), 4.52 (s, 2H), 3.98 (s, 4H), 3.76 (s, 3H), 3.61 (s, 76H), 2.99 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.09 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 135.0, 131.2, 128.4, 120.4 (q, J = 293.5 Hz), 80.8 – 78.7 (m), 72.3, 70.9, 69.9, 69.7, 66.4, 63.5, 40.8, 29.6. HRMS (ESI) calcd for $C_{58}H_{94}F_{18}NO_{23}^+$ ($[M+H]^+$), 1514.5924, found, 1514.5920.

Synthesis of compound 1a: To a solution of maleic anhydride (0.16 g, 1.5 mmol) in diethyl ether (20 mL) was added compound **11a** (1.0 g, 1.2 mmol). The reaction solution was stirred at 35 ^oC for 12 h. TLC showed that the starting material was consumed completely. After diethyl ether was evaporated under vacuum, acetic anhydride (20 mL) and NaOAc (0.041 g, 0.5 mmol) were added. The mixture was stirred and refluxed for 2 h. The mixture was quenched with ice water and extracted with ethyl acetate (100 mL, 3 times). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under vacuum and purified by column chromatography

on silica gel (DCM/MeOH = 20/1) to give compound **1a** as a yellow oily liquid (0.76 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 2H), 6.70 (s, 2H), 5.10 (s, 4H), 4.57 (s, 2H), 3.81 (s, 3H), 3.72 – 3.61 (m, 16H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.08 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 157.0, 135.1, 134.1, 131.2, 128.4, 120.4 (q, J = 293.2 Hz), 81.0 – 78.7 (m), 72.3, 70.6, 70.6, 70.5, 70.0, 69.8, 67.8, 66.4, 63.5, 37.1. HRMS (ESI) calcd for $C_{30}H_{29}F_{18}NNaO_9^+$ ([M+Na]$^+$), 912.1445, found, 912.1442.

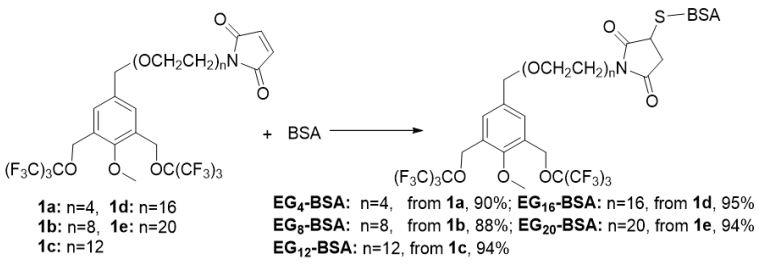
Synthesis of compound 1b: Compound **1b** was prepared as a yellow oily liquid (0.31 g, 78% yield) using a procedure identical to the preparation of compound **1a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 6.67 (s, 2H), 5.05 (s, 4H), 4.53 (s, 2H), 3.77 (s, 3H), 3.67 – 3.57 (m, 32H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.07 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 156.9, 135.1, 134.1, 131.1, 128.4, 120.4 (q, J = 292.8 Hz), 81.0 – 78.5 (m), 72.2, 70.5, 70.0, 69.7, 67.7, 66.4, 63.4, 37.0. HRMS (ESI) calcd for $C_{38}H_{45}F_{18}NNaO_{13}^+$ ([M+Na]$^+$), 1088.2493, found, 1088.2495.

Synthesis of compound 1c: Compound **1c** was prepared as a yellow oily liquid (0.88 g, 65% yield) using a procedure identical to the preparation of compound **1a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 6.70 (s, 2H), 5.07 (s, 4H), 4.55 (s, 2H), 3.79 (s, 3H), 3.66 – 3.60 (m, 48H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.08 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 157.0, 135.1, 134.2, 131.2, 128.4, 120.4 (q, J = 292.6 Hz), 80.8 – 78.7 (m), 72.3, 70.5, 70.0, 69.7, 67.8, 66.4, 63.5, 37.1. HRMS (ESI) calcd for $C_{46}H_{61}F_{18}NNaO_{17}^+$ ([M+Na]$^+$), 1264.3542, found, 1264.3546.

Synthesis of compound 1d: Compound **1d** was prepared as a yellow oily liquid (0.61 g, 67% yield) using a procedure identical to the preparation of compound **1a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 6.69 (s, 2H), 5.06 (s, 4H), 4.53 (s, 2H), 3.78 (s, 3H), 3.62 (s, 64H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.08 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 156.9, 135.1, 134.2, 131.2, 128.4, 120.4 (q, J = 292.7 Hz), 81.0 – 78.5 (m), 72.4, 70.5, 70.1, 69.7, 67.8, 66.4, 63.5, 37.1. HRMS (ESI) calcd for $C_{54}H_{77}F_{18}NNaO_{21}^+$ ([M+Na]$^+$), 1440.4593, found, 1440.4596.

Synthesis of compound 1e: Compound **1e** was prepared as a yellow oily liquid (0.52 g, 61% yield) using a procedure identical to the preparation of compound **1a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 6.70 (s, 2H), 5.07 (s, 4H), 4.54 (s, 2H), 3.79 (s, 3H), 3.63 (s, 80H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.10 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 156.9, 135.1, 134.2, 131.2, 128.4, 120.4 (q, J = 293.7 Hz), 81.2 – 78.3 (m), 72.3, 70.5, 67.8, 66.4, 63.5, 37.1. HRMS (ESI) calcd for $C_{62}H_{93}F_{18}NNaO_{25}^+$ ([M+Na]$^+$), 1616.5641, found, 1616.5641.

4 Synthesis and characterization of fluorinated BSAs



Scheme S1. Synthesis of fluorinated BSAs.

Synthesis of compound **EG$_4$-BSA**: Under an argon atmosphere, BSA (280 mg, 4.2 μmol, 1 equiv.) was dissolved in PBS buffer (7 mL, pH 7.4) and the ethanol solution (0.7 mL) of compound **1a** (15 mg, 12.6 μmol, 3 equiv.) was added in batches. The reaction mixture was shaken on an orbital shaker at 100 rpm for 36 h at 37 °C. Ellman's experiments showed that very few free sulfhydryl groups were left. Subsequently, the reaction mixture was dialyzed against PBS buffer (pH 7.4) using a dialysis membrane of 25,000 Da MWCO (molecular weight cut-off) to remove low molecular weight impurities, including excess compound **1a**. The solution was then lyophilized to yield fluorinated **EG$_4$-BSA** as a white solid (265 mg, 3.8 μmol, 90% yield). ^{19}F NMR (471 MHz, D_2O) δ -72.24 (s). MS (MALDI-TOF) m/z Calcd. for **EG$_4$-BSA**, 67335, found 66880, 0.6% of error between calcd.

Synthesis of compound **EG$_8$-BSA**: Compound **EG$_8$-BSA** was prepared as a white solid (260 mg, 88% yield) using a procedure identical to compound **EG$_4$-BSA**. ^{19}F NMR (471 MHz, D_2O) δ -72.31 (s). MS (MALDI-TOF) m/z Calcd. for **EG$_8$-BSA**, 67551, found 67117, 0.6% of error between calcd.

Synthesis of compound **EG$_{12}$-BSA**: Compound **EG$_{12}$-BSA** was prepared as a white solid (278 mg, 94% yield) using a procedure identical to compound **EG$_4$-BSA**. ^{19}F NMR (471 MHz, D_2O) δ -72.04 (s). MS (MALDI-TOF) m/z Calcd. for **EG$_{12}$-BSA**, 67688, found 67571, 0.2% of error between calcd.

Synthesis of compound **EG$_{16}$-BSA**: Compound **EG$_{16}$-BSA** was prepared as a white solid (280 mg, 95% yield) using a procedure identical to compound **EG$_4$-BSA**. ^{19}F NMR (564 MHz, D_2O) δ -72.13 (s). MS (MALDI-TOF) m/z Calcd. for **EG$_{16}$-BSA**, 67864, found 66549, 0.6% of error between calcd.

Synthesis of compound **EG_{20}-BSA**: Compound **EG_{20}-BSA** was prepared as a white solid (277 mg, 94% yield) using a procedure identical to compound **EG_4-BSA**. ^{19}F NMR (564 MHz, D_2O) δ -72.12 (s). MS (MALDI-TOF) m/z Calcd. for **EG_{20}-BSA**, 68040, found 66528, 0.7% of error between calcd.

5 Ellman's Assay of Fluorinated BSAs

5,5-dithio-bis-(2-nitrobenzoic acid) (Ellman's reagent, 20 mg, 0.05 mmol) was dissolved in 10% sodium phosphate (5 mL, pH 8.0, containing 1 mM EDTA) to prepare the Ellman's reagent solution (10 mM). 0.12 mL of free BSA (2 mM) or fluorinated BSA conjugation solution (2 mM), 50 mL of Ellman's reagent and 2.5 mL of sodium phosphate buffer were incubated for 15 min at room temperature. UV absorption spectra were acquired using a 1 cm cuvette without dilution. The content of free sulfhydryl groups in BSA or fluorinated BSA was obtained according to the standard curve measured with cysteine.

6 UV-vis Absorption Standard Curve of BSA

BSA was accurately weighed and dissolved into a series of concentration gradient samples with PBS. UV absorption spectra of the solutions were obtained. The process was repeated 3 times and the average UV absorption intensities were used. The standard curve was obtained by plotting the UV absorption intensities at 278 nm versus the corresponding BSA concentrations (Figure S1a).

7 Calibration of Fluorine Content in Fluorinated BSAs

Fluorinated BSA, **EG_{12}-BSA**, was accurately weighed and dissolved in a mixture 10% D_2O and water. The weight of **EG_{12}-BSA** was calibrated using the above UV absorption standard curve. Sodium trifluorometalesulfate solution with a ^{19}F concentration of 0.5 mM in a mixture 10% D_2O and water was used as the internal standard for ^{19}F NMR. The ^{19}F NMR signal intensity of **EG_{12}-BSA** was calibrated using the internal standard. A fluorine content standard curve of fluorinated BSA was obtained by plotting the ^{19}F NMR signal intensities with the corresponding calibrated

weight of fluorinated BSA weight using the above standard curve (Figure S1b).

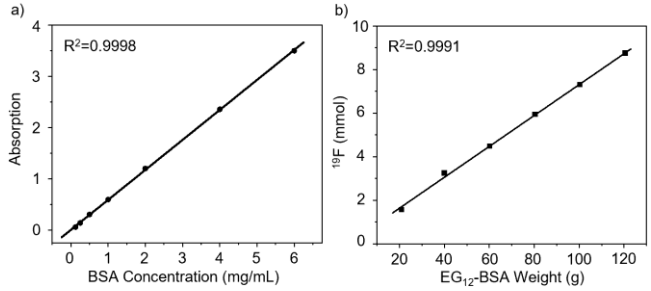


Figure S1. UV-vis absorption (a) and ^{19}F content (b) standard curves of BSA and fluorinated BSA.

8 Preparation of Nanoparticles

To prepare **PTX@BSA** nanoparticles, 15 mg of PTX and 50 mg of soybean oil were dissolved in 1 mL of dichloromethane. Then, 5 mL of 20 mg/mL BSA or fluorinated BSA solution was added. The dispersion was ultrasonicated at 250 W for 15 min, and the organic solvents were removed by rotary evaporation.

9 *In Vitro* Photothermal Capability of PTX/IR@BSA

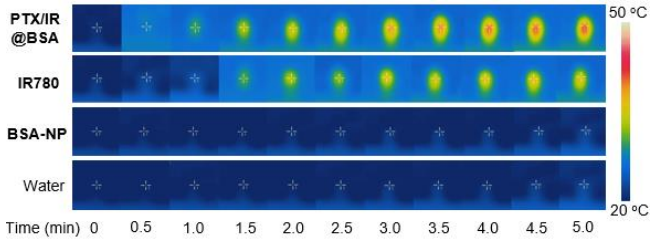


Figure S2. *In vitro* photothermal images of **PTX/IR@BSA** under 808 nm laser irradiation at 1 Wcm^{-2} for 5 min with IR-780, **BSA-NP**, and water as controls.

10 Detection of ROS Generated by PTX/IR@BSA Using ESR

TEMP was selected as a singlet oxygen capture agent. A 0.1 mM solution of **PTX/IR@BSA** in PBS was irradiated with a laser (808 nm, 1 Wcm^{-2}) for 3 minutes. TEMP was immediately added to the solution with a final concentration of 100 mM TEMP and mixture well for ESR measurements.

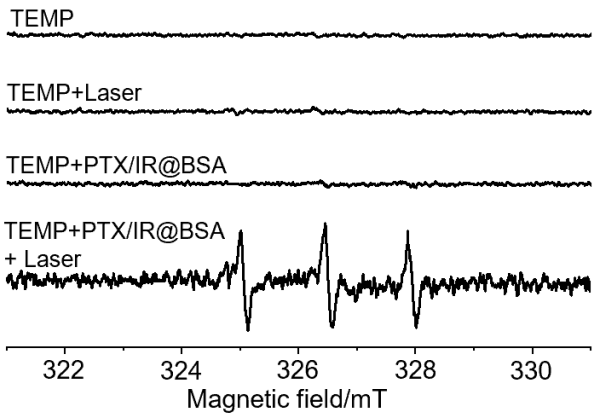


Figure S3. ESR spectra of TEMP, TEMP + Laser, TEMP + **PTX/IR@BSA**, and TEMP + **PTX/IR@BSA** + Laser.

11 Determination of Photothermal Conversion Efficiency of PTX/IR@BSA

PTX/IR@BSA ($C_{IR\text{-}780}$ = 90 μM, 1 mL) was added into a cuvette. The laser irradiated (808 nm, 1 W/cm^2) it for 600 s until the temperature remained constant. Then turned off the laser and the temperature of NPs solution was continuously recorded for another 940 s until the temperature returned to the original temperature. In the experiment, the temperature was recorded using a digital thermometer (Hikvision H13 Thermal Imager). The temperature of deionized water was investigated with the same treatment as a control. According to a reported method, the photothermal conversion efficiency (η)[8] was calculated below:

$$\eta = \frac{hS(T_{max,\ sample} - T_{surr}) - Q_{dis}}{I(1-10^{-A_\lambda})} \quad (1)$$

$$Q_{dis} = hS(T_{max,\ H_2O} - T_{surr}) \quad (2)$$

$$hS = \frac{\Sigma m_i c_i}{\tau} \quad (3)$$

$$\tau = -\frac{t}{\ln(\theta)} \quad (4)$$

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}} \quad (5)$$

in equation, h is heat transfer coefficient, S means the surface area of quartz cuvette, T_{surr} represents the temperature of surrounding environment. Besides, $T_{max,\ sample}$ reflects the final temperature of the sample solution. I is the incident laser power in W and A^{λ} represents the sample absorbance at 808 nm. Q_{dis} is the energy imputed by the deionized water system. And m and C represent the mass (1 g) and heat capacity (4.2 J/g) of water, respectively. θ is the dimensionless

driving force and t represents time. T represents the temperature of sample solution at a predetermined time point after removing the 808 nm laser irradiation.

According to the equations above, τ is equal to 631.58, m is 1 g, and C is 4.2 J/g, hS was calculated to be 0.00696 [Eq. (3)]. Through substituting $T_{max,\ H2O}$ = 25.6 ºC and T_{surr} = 25.1 ºC into Eq. (2), Q_{dis} = 0.00348 J. By substituting I = 1 W, A^{808} = 0.607, T_{max} = 48.7 ºC, and T_{surr} = 25.1 ºC into Eq. (1), the photothermal conversion efficiency was calculated to be 21.35%. The *η o*f free IR-780 was also evaluated by using the similar method and calculated to be 12.68%.

12 *In Vitro* ^{19}F MRI Study of PTX/IR@BSA

The ^{19}F MRI phantom experiments were performed on a 400 MHz Bruker BioSpec MRI system at 25 ºC. **PTX/IR@BSA** was serially diluted with PBS to give a series of ^{19}F concentrations: 20, 15, 10, 5, 2.5, and 1.25 mM, respectively. For nanoparticles, the ^{19}F density-weighted ^{19}F MRI phantom images were acquired by using a gradient-echo (GRE) pulse sequence, method = RARE, matrix size = 32 × 32, SI = 20 mm, FOV = 3.0 × 3.0 cm, TR = 4000 ms, TE = 3 ms, NS = 16, scan time = 2200 s.

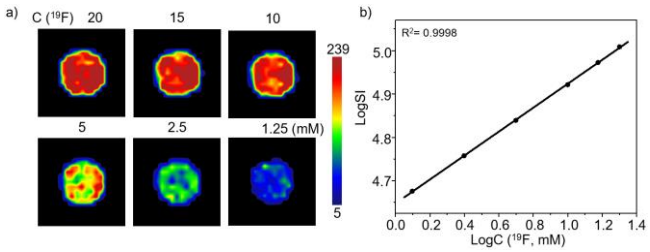


Figure S4. ^{19}F MRI phantom images (a) at the indicated ^{19}F concentrations and the logarithm plot of signal intensity (SI) versus ^{19}F concentration (b) of **PTX/IR@BSA**.

13 *In Vivo* ^{19}F MRI

The mice had free access to water and food until tumor size reached about 200 mm^3. The MCF-7 tumor-bearing mice were anesthetized by isoflurane, 0.1 mL of **EG_n-BSA NPs** were injected into the tumor of tumor-bearing mice (C_F = 0.3 mmol/kg). ^{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 = 30 mm × 30 mm, 2 mm slice thickness, RARE factor = 8, matrix size = 256 × 256), ^{19}F MRI was performed through a RARE sequence (TR = 1600 ms, TE = 3 ms, FOV = 37 mm × 37

mm, 30 mm slice thickness, matrix size = 32 × 32, 64 averages).

Table S1. The relaxation times of EG_n-BSA and EG_n-BSA NPs.

	T_1 (ms)	T_2 (ms)
EG_4-BSA	435.6	3.1
EG_4-BSA NPs	469.8	9.5
EG_8-BSA	432.7	3.6
EG_8-BSA NPs	461.6	9.0
EG_{12}-BSA	441.9	6.2
EG_{12}-BSA NPs	463.2	11.8
EG_{16}-BSA	430.9	12.8
EG_{16}-BSA NPs	463.8	16.3
EG_{20}-BSA	444.5	17.2
EG_{20}-BSA NPs	469.9	18.1

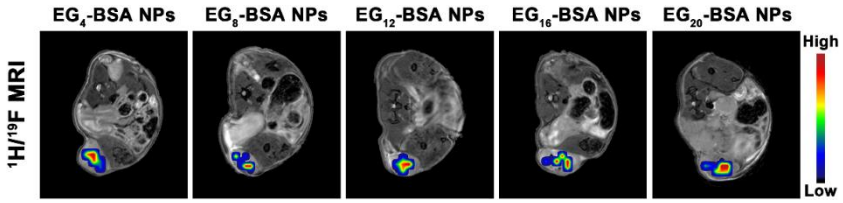


Figure S5. ^{19}F MRI of mice after intratumor injection of **EG_n-BSA NPs**.

14 H&E and Antigen Ki-67 Staining Results of Major Organs and Tumors

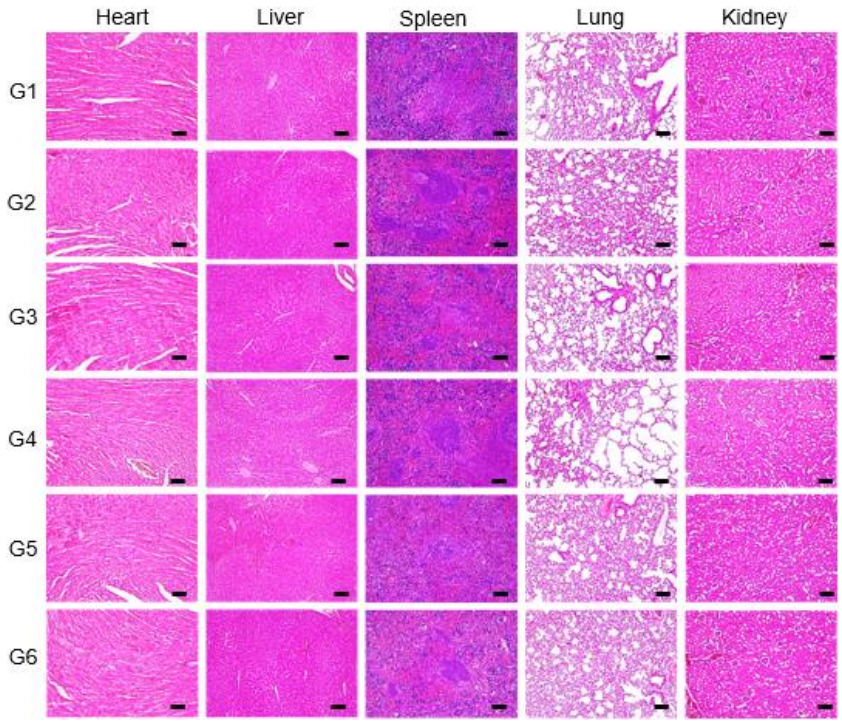


Figure S6. H&E staining assay results of major organs, scale bar: 100 μm.

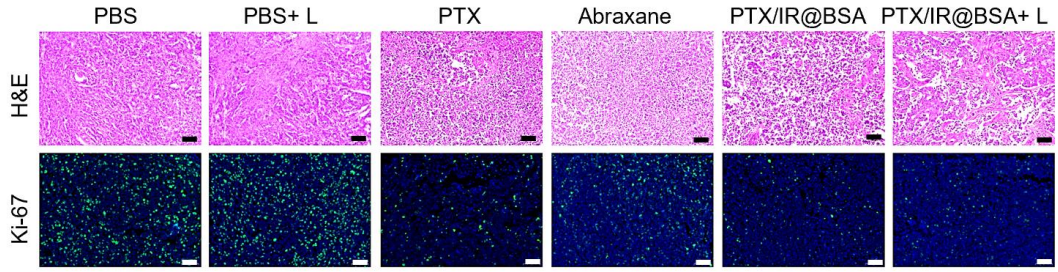


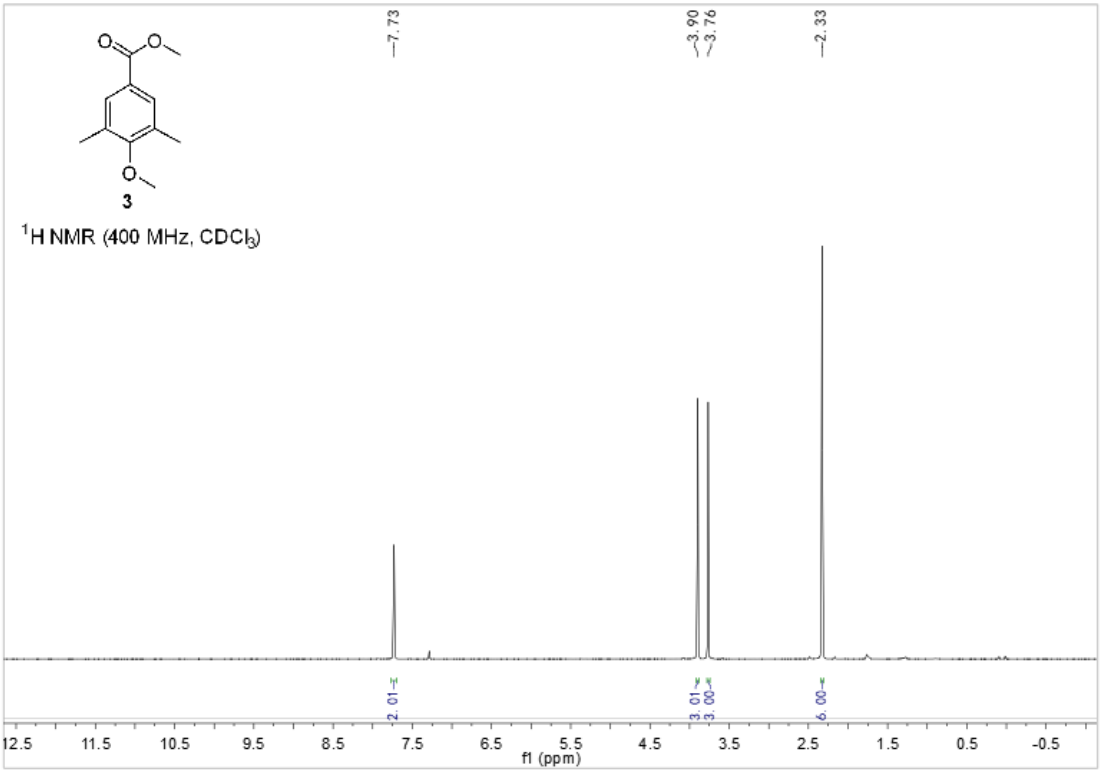
Figure S7. H&E and Antigen Ki-67 staining assay results of tumors, scale bar: 100 μm.

15 The Proposed Mechanism of the Tumor-Target Ability of PTX/IR@BSA

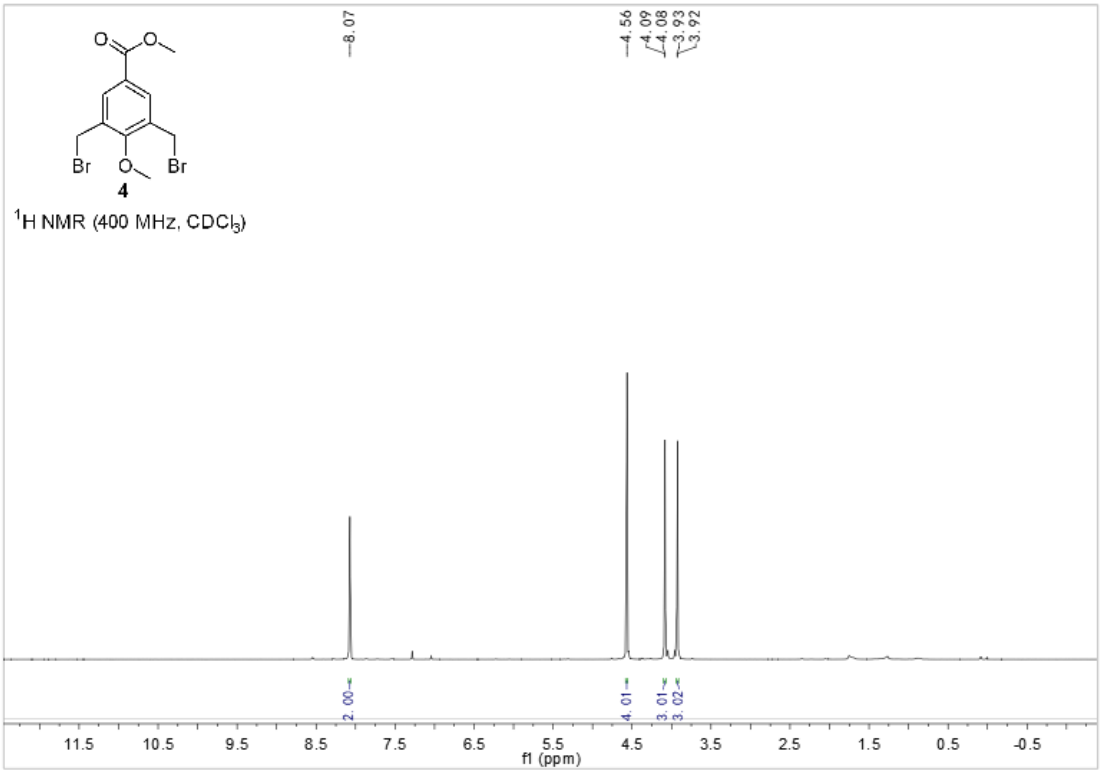
BSA can bind to the 60 kDa glycoprotein (gp60) receptor expressed on the surface of endothelial cells, allowing rapid and efficient transcytosis. Moreover, it can interact with the secreted protein acidic and rich in cysteine (SPARC), a member of matricellular proteins highly expressed in various tumor cells, thus facilitating the BSA accumulation within tumor tissues. As a result, the BSA-based nanoparticles are expected to cross the vascular endothelial barrier faster and accumulate in the tumor through the BSA-gp60-SPARC pathway.[9]

16 $^{1}H/^{13}C/^{19}F$ NMR and MS Spectra of Compounds and Fluorinated BSAs

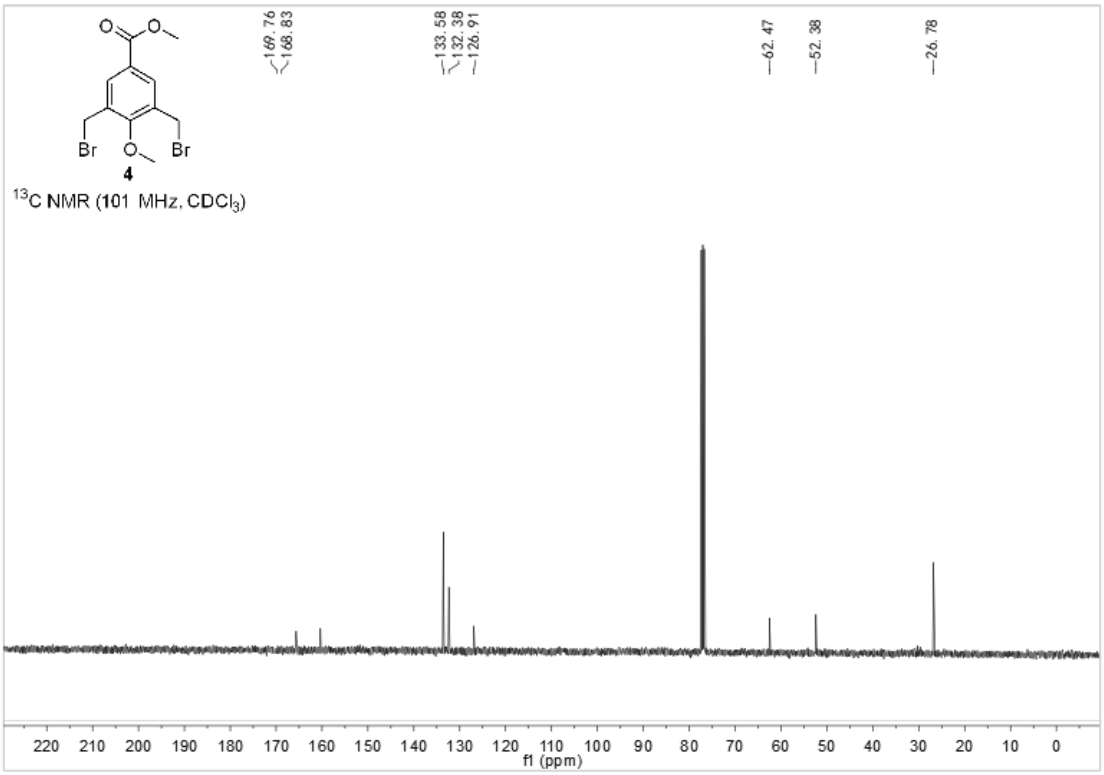
^{1}H NMR of compound **3**



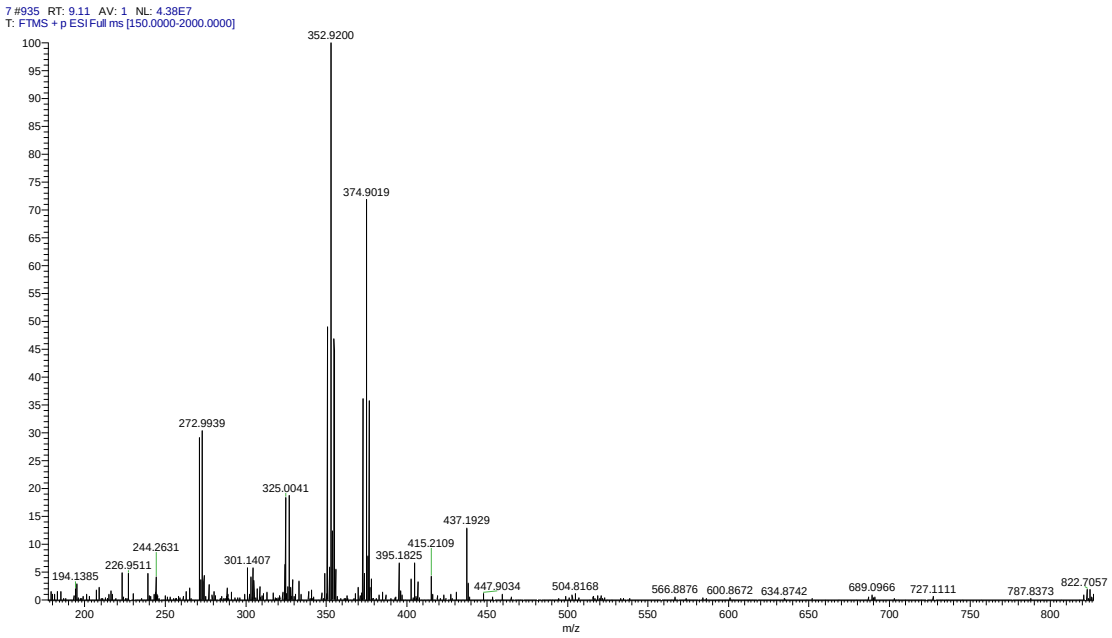
^{1}H NMR of compound **4**



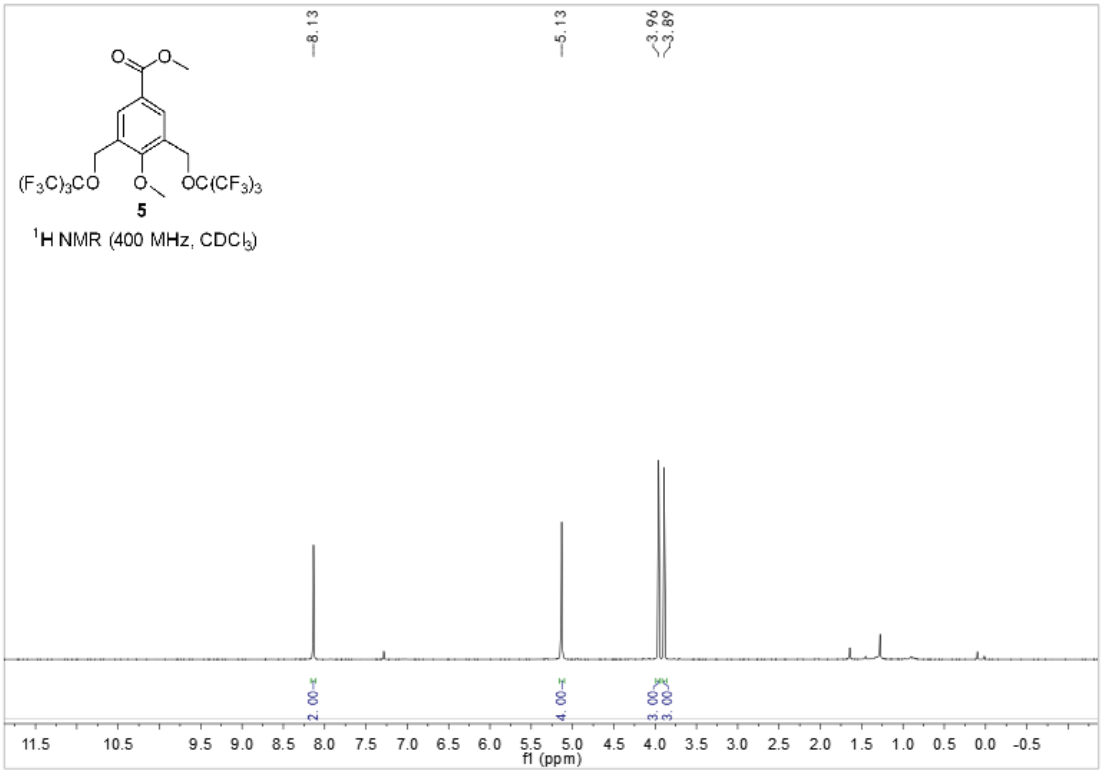
^{13}C NMR of compound **4**



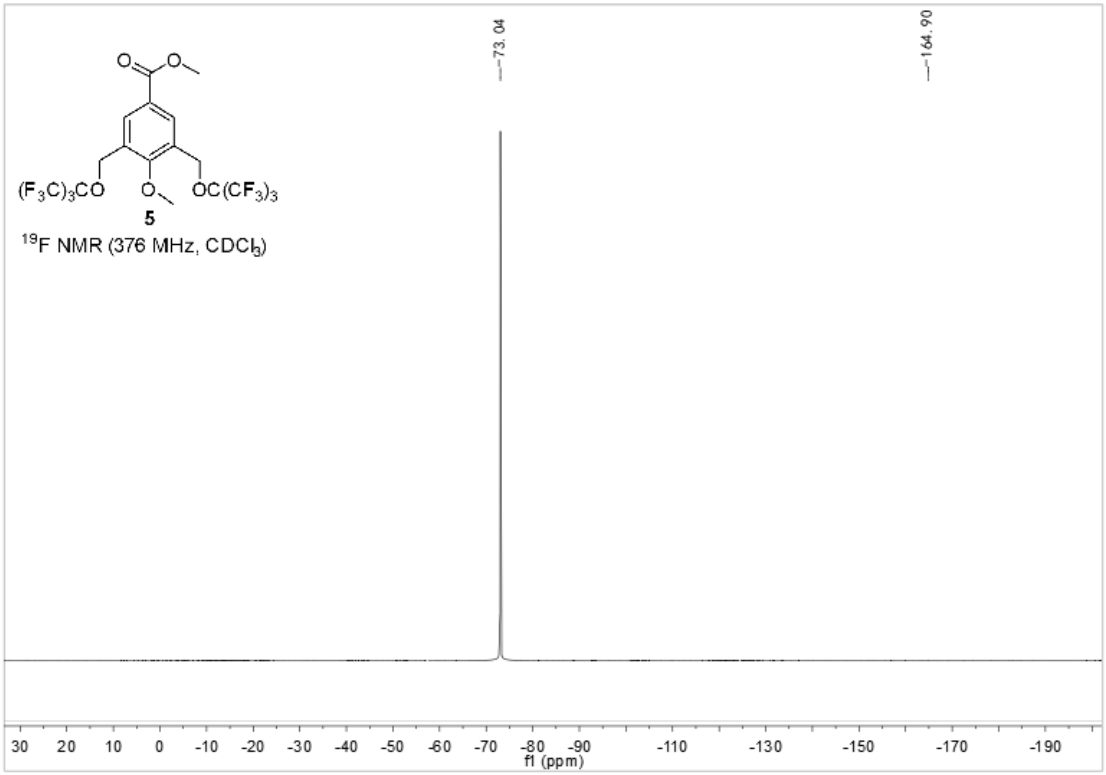
HRMS of compound **4**



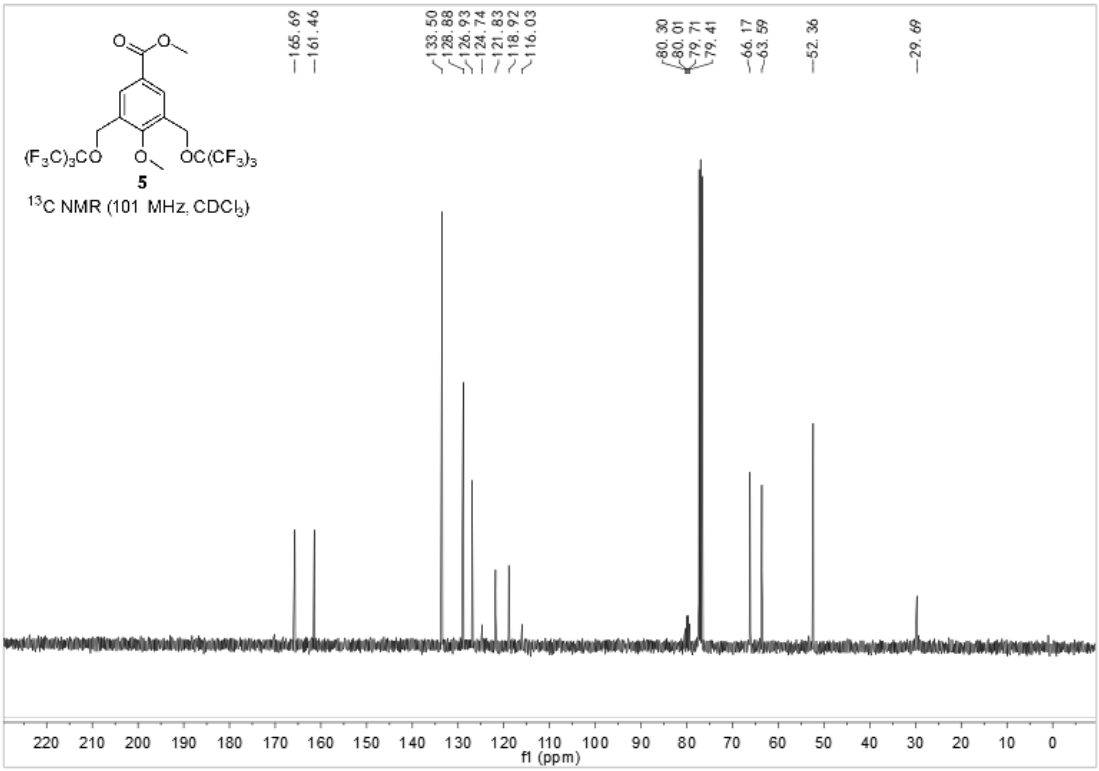
^{1}H NMR of compound **5**



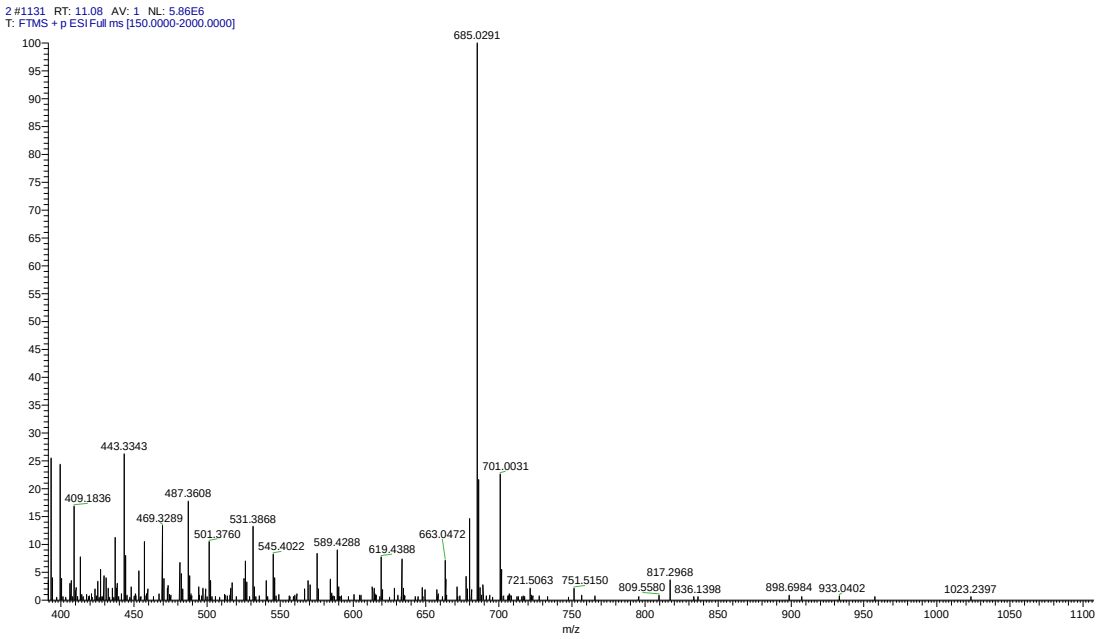
^{19}F NMR of compound **5**



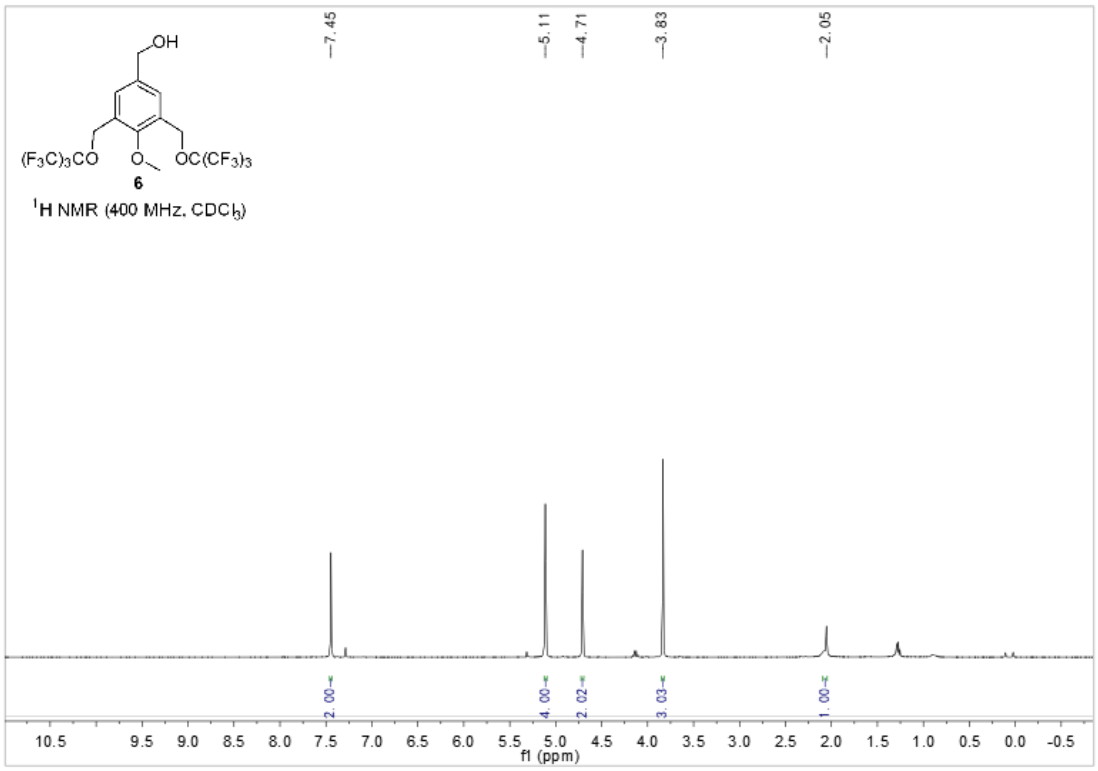
^{13}C NMR of compound **5**



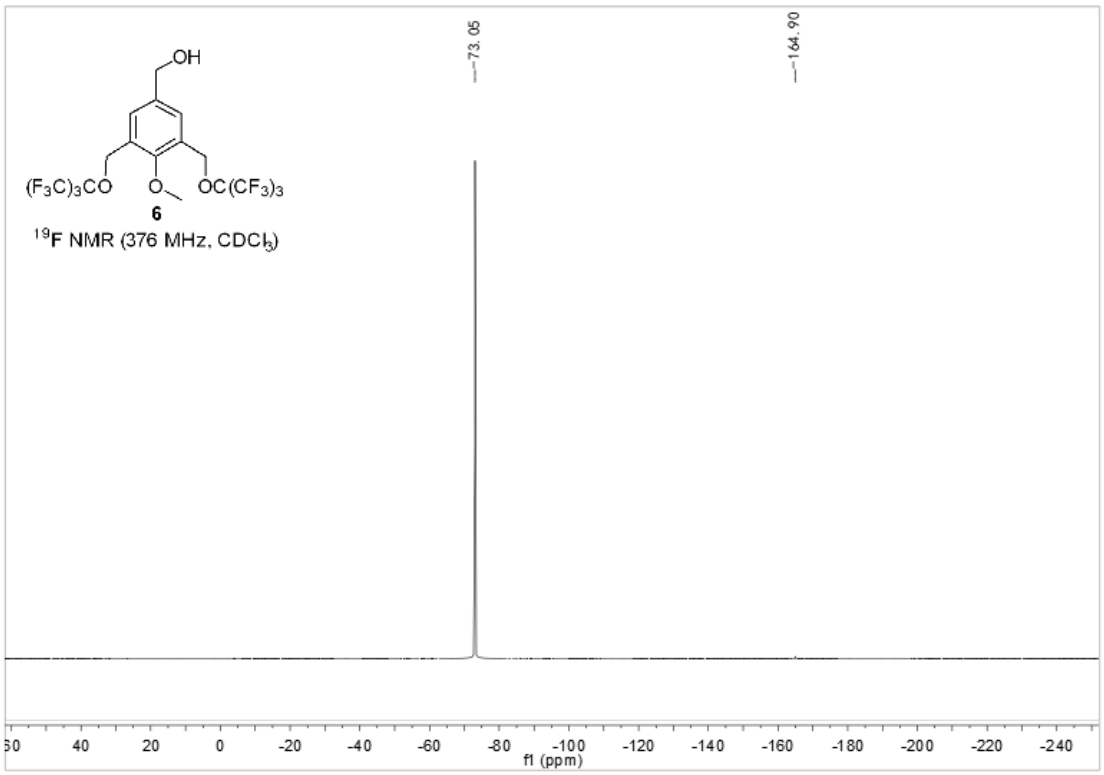
HRMS of compound **5**



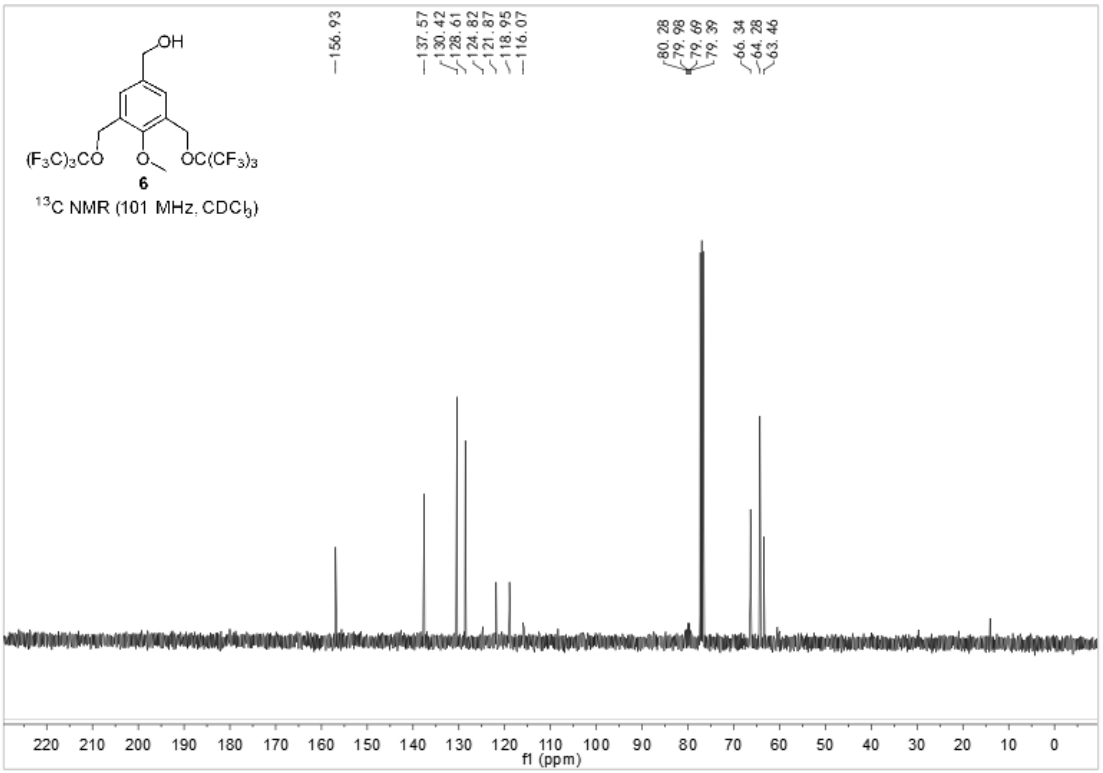
^{1}H NMR of compound **6**



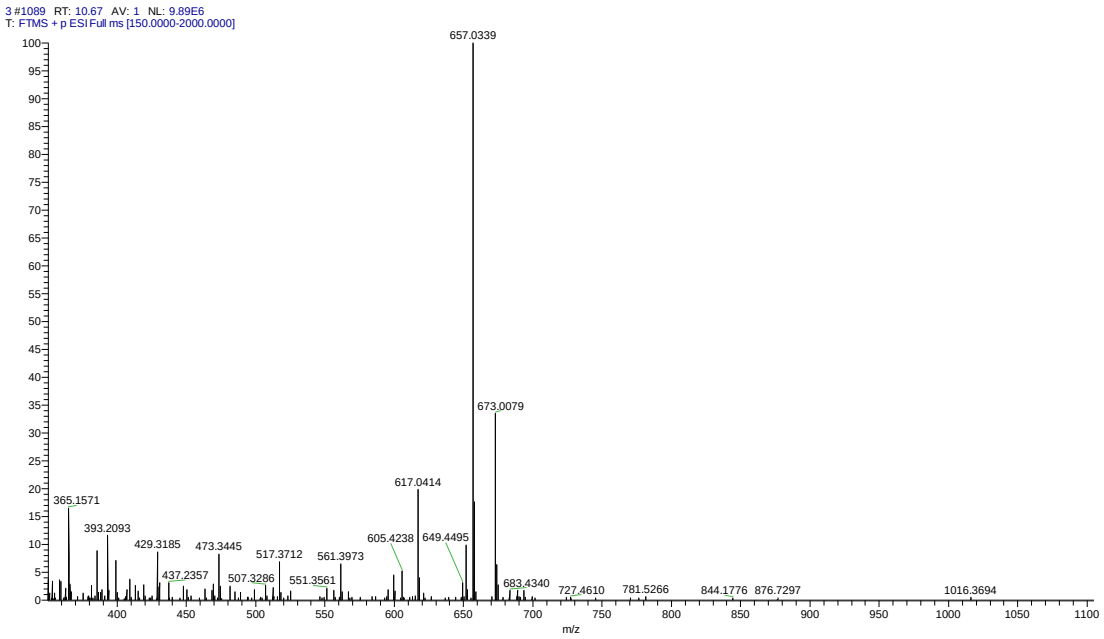
^{19}F NMR of compound **6**



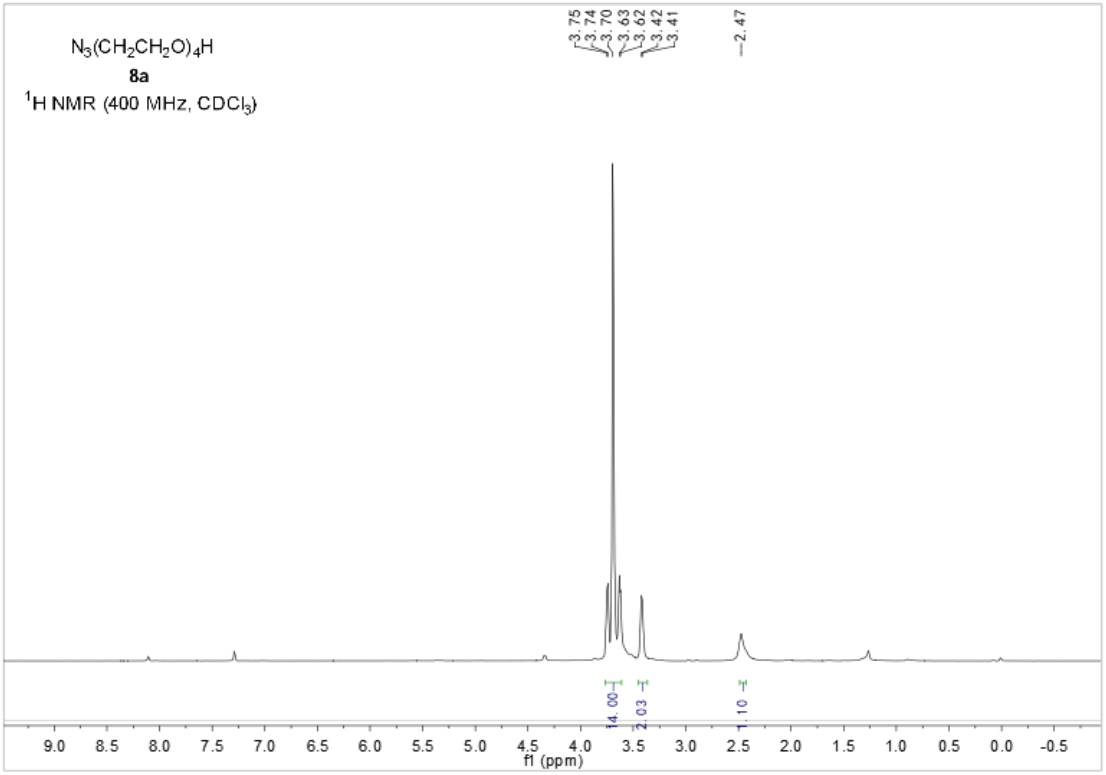
^{13}C NMR of compound **6**



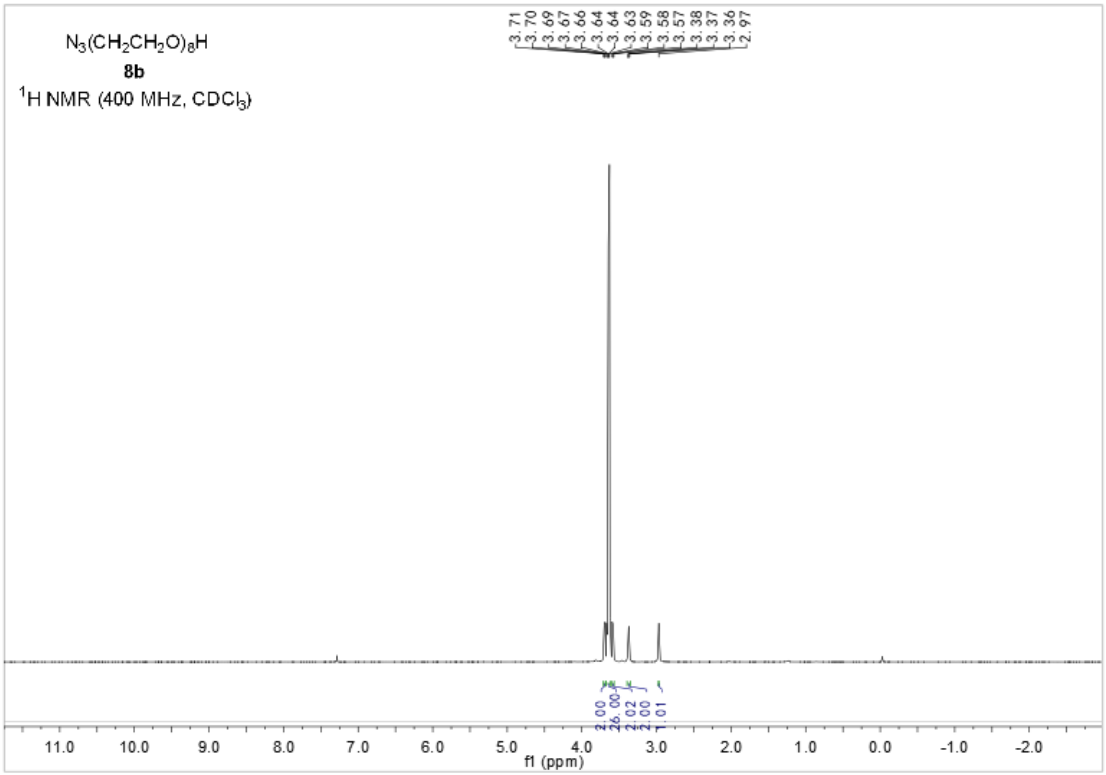
HRMS of compound **6**



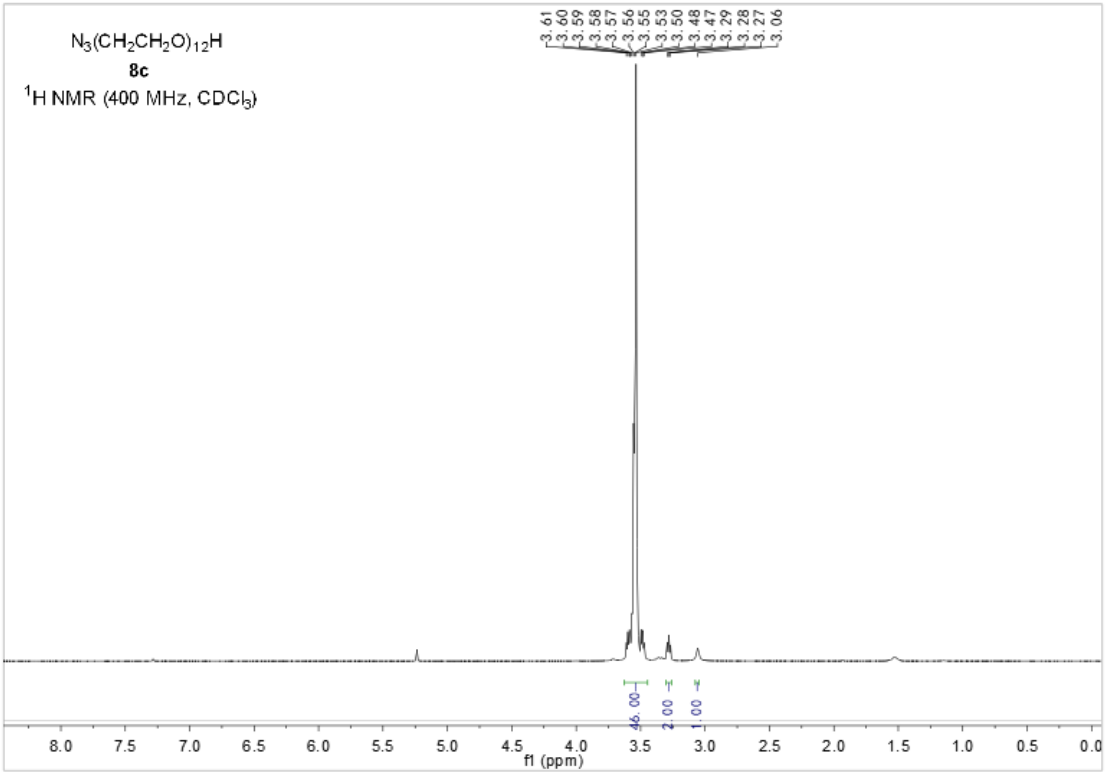
^{1}H NMR of compound **8a**



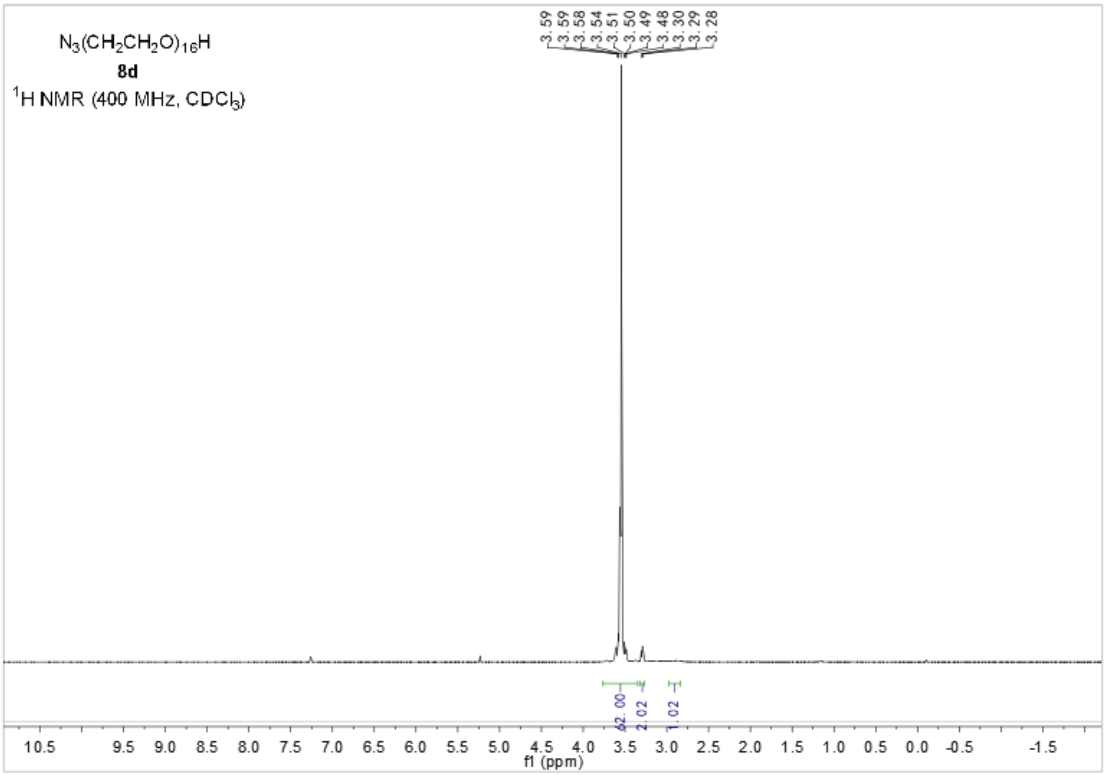
^{1}H NMR of compound **8b**



^{1}H NMR of compound **8c**



^{1}H NMR of compound **8d**



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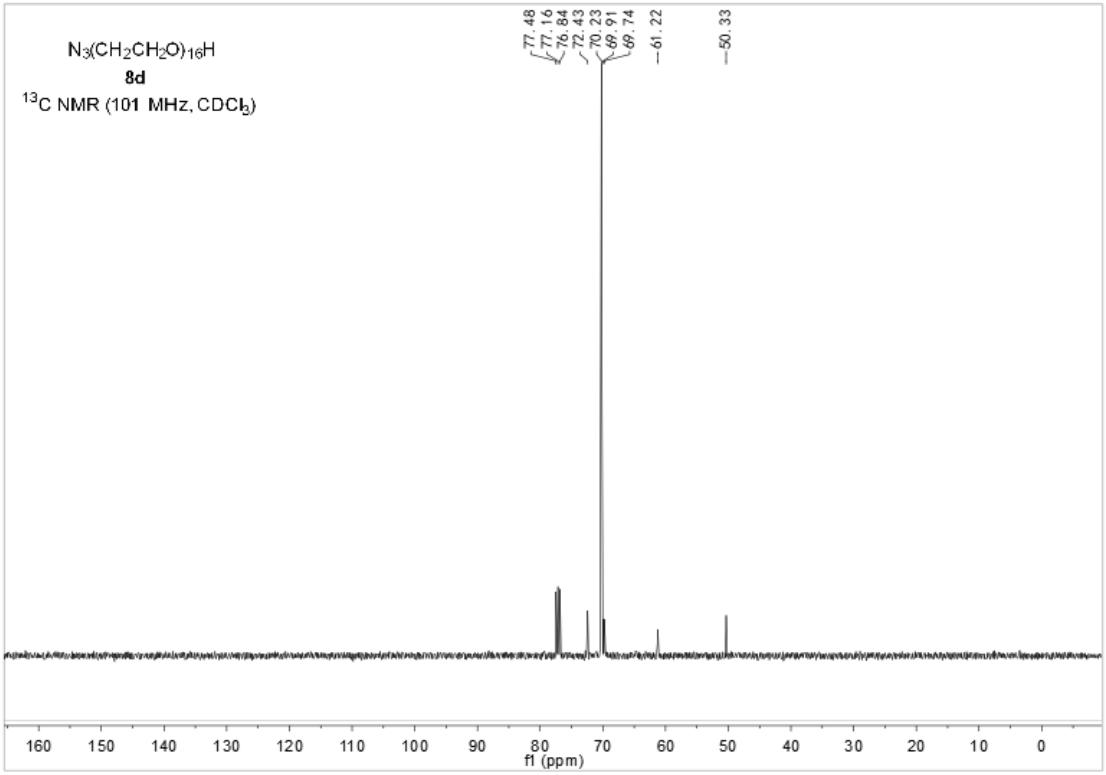
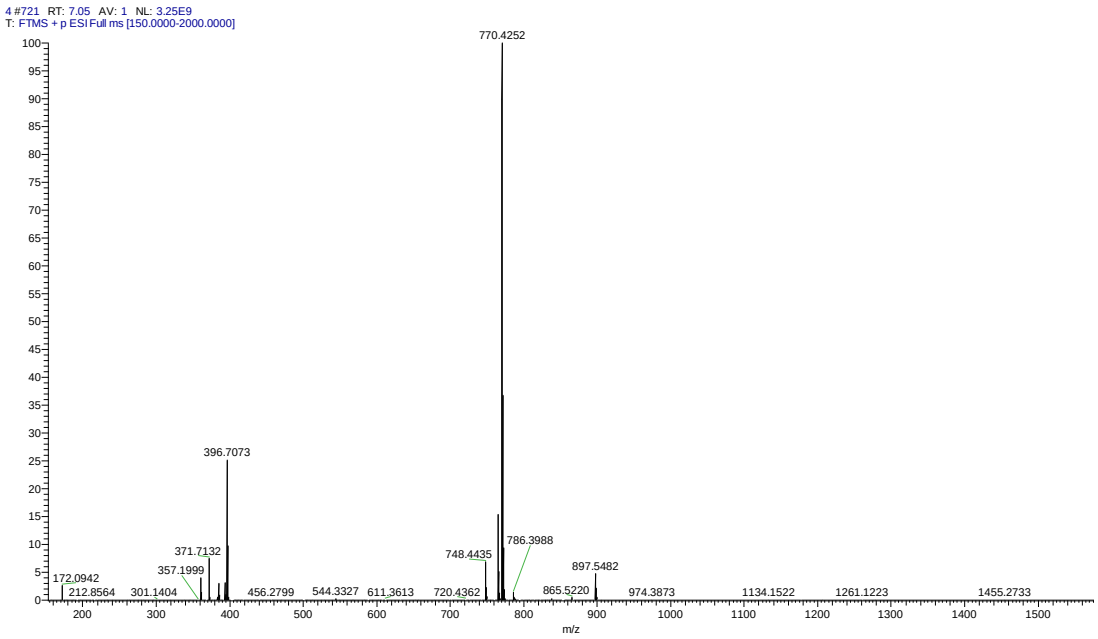
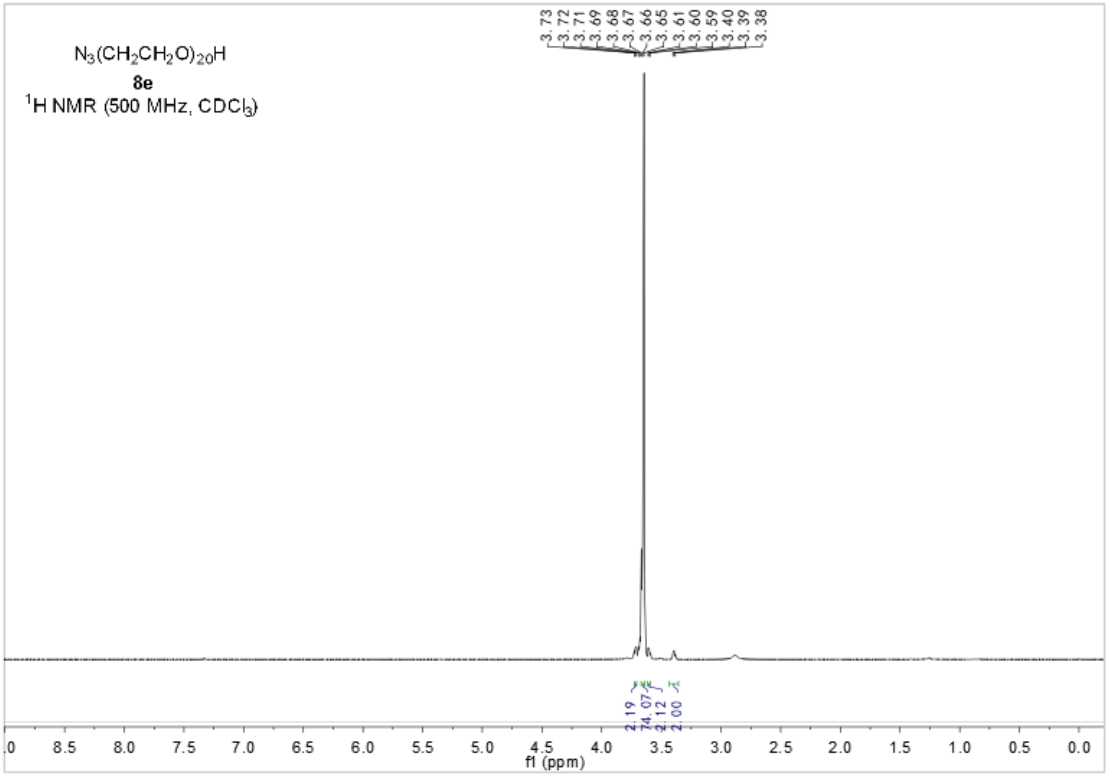


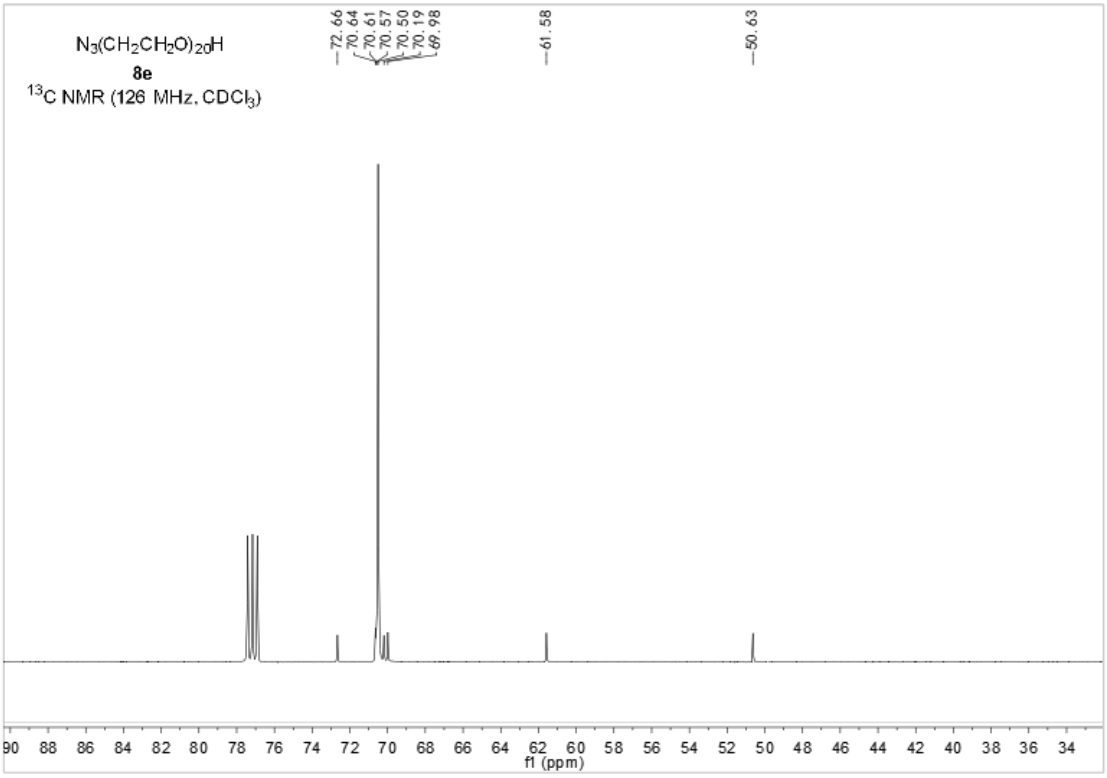
HRMS of compound **8d**



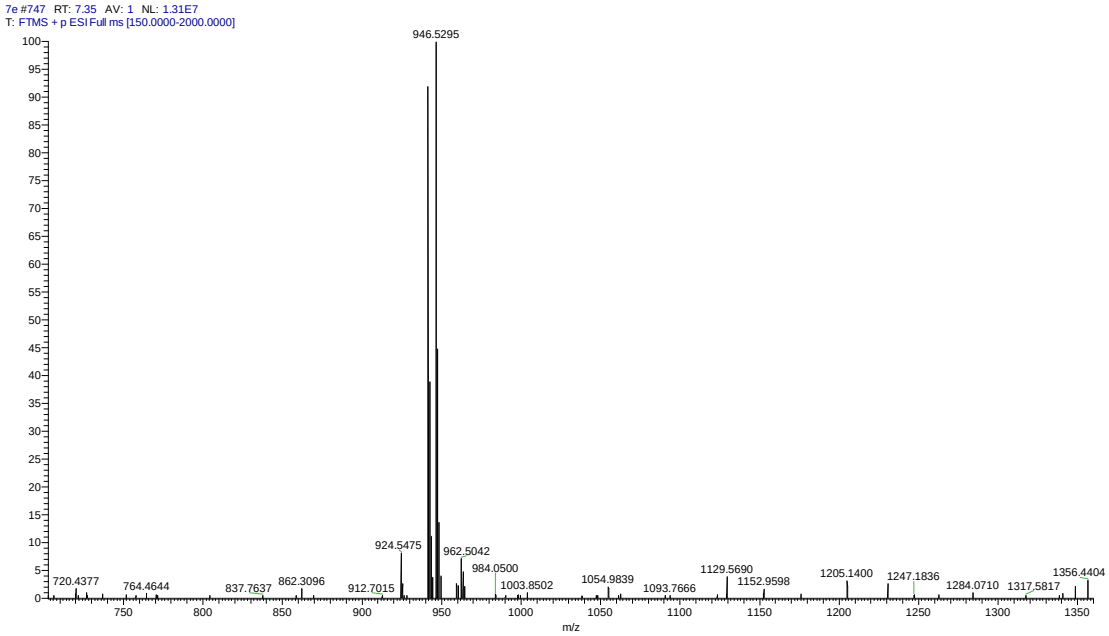
^{1}H NMR of compound **8e**



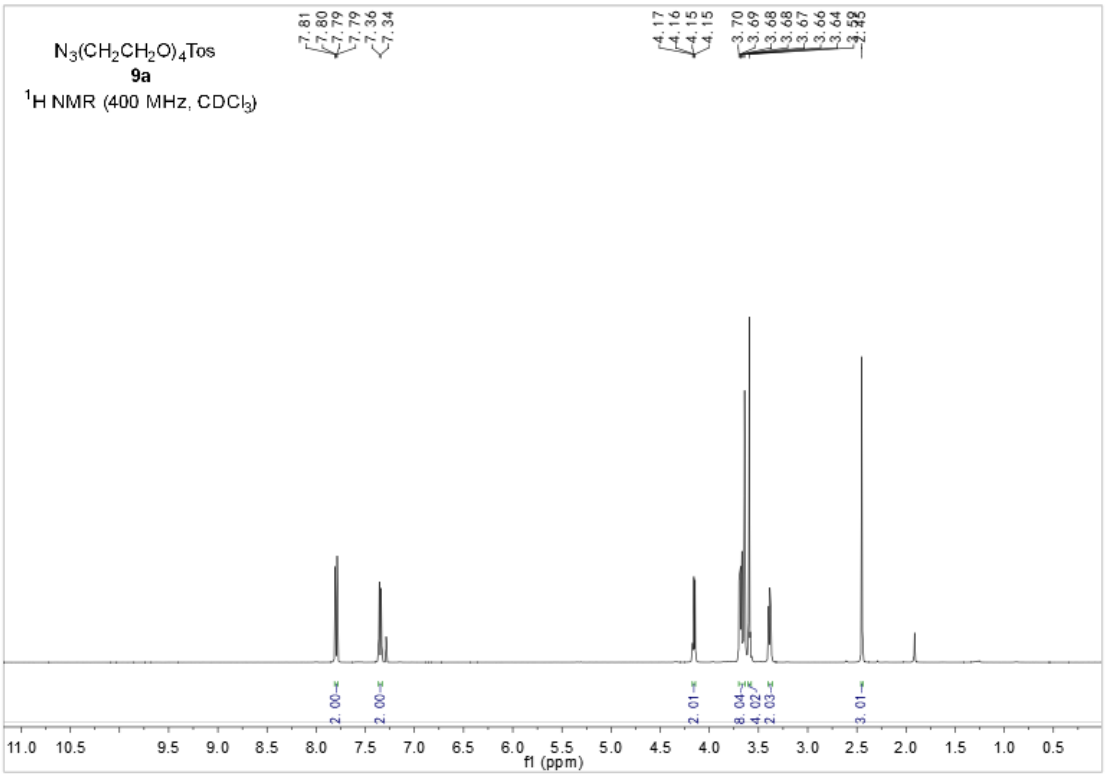
^{13}C NMR of compound **8e**



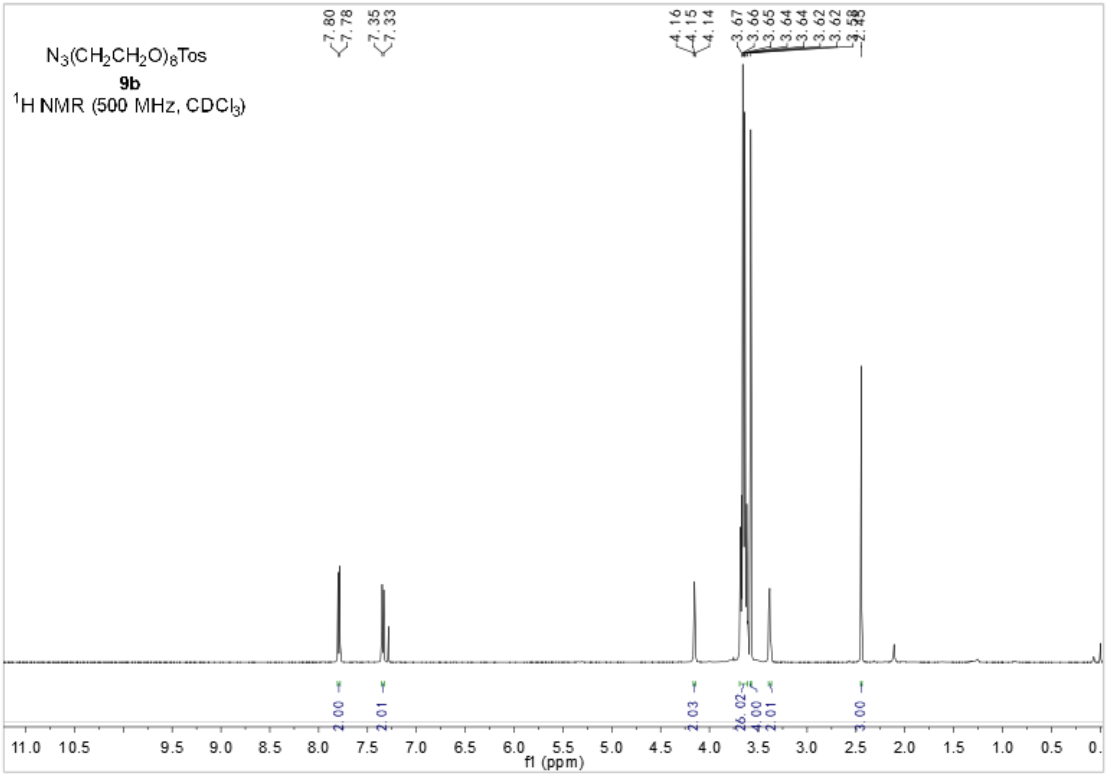
HRMS of compound **8e**



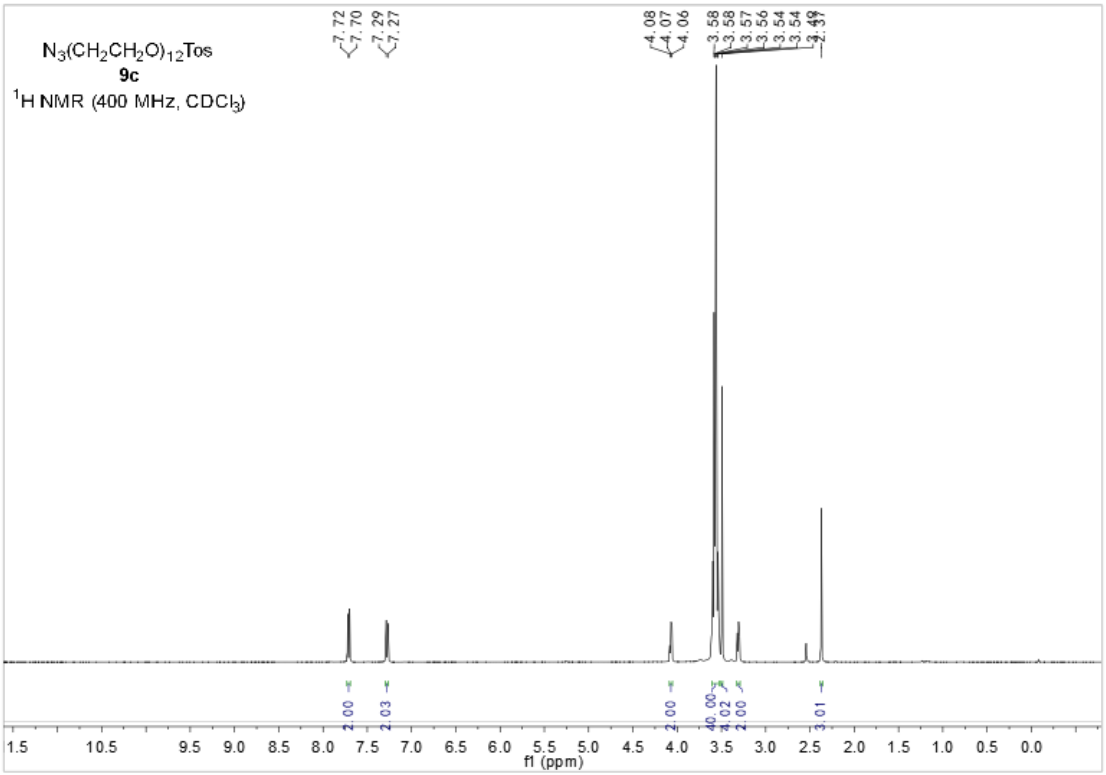
^{1}H NMR of compound **9a**



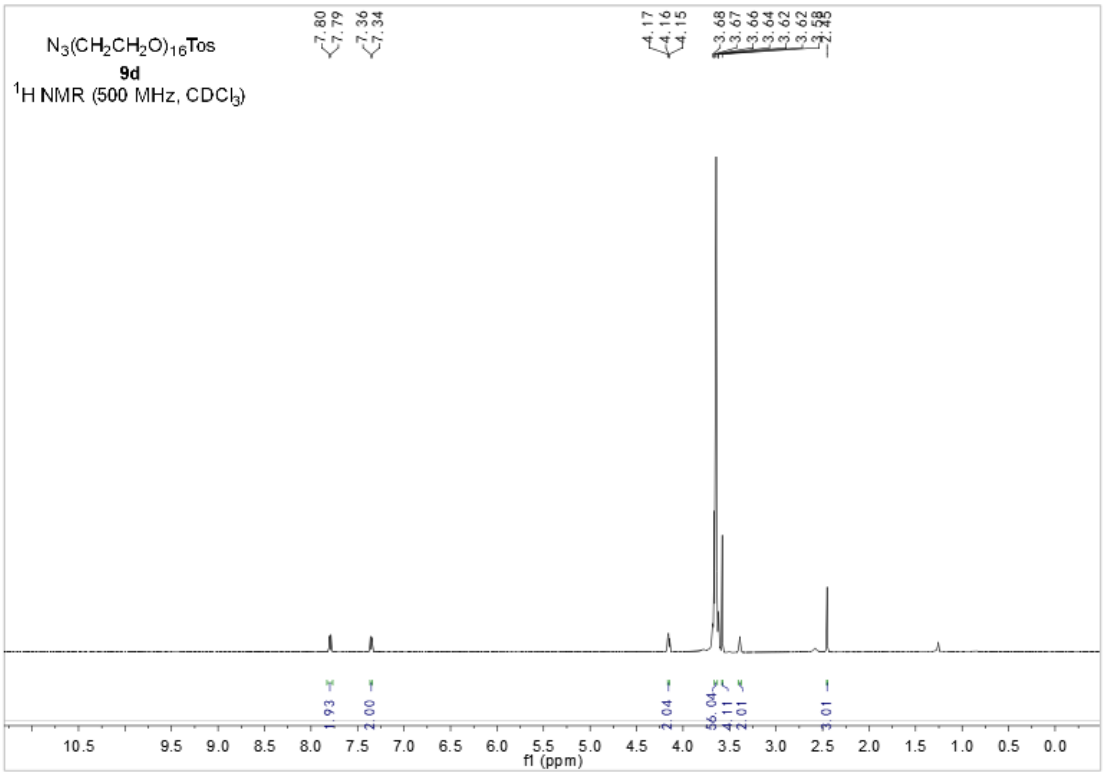
^{1}H NMR of compound **9b**



^{1}H NMR of compound **9c**



^{1}H NMR of compound **9d**



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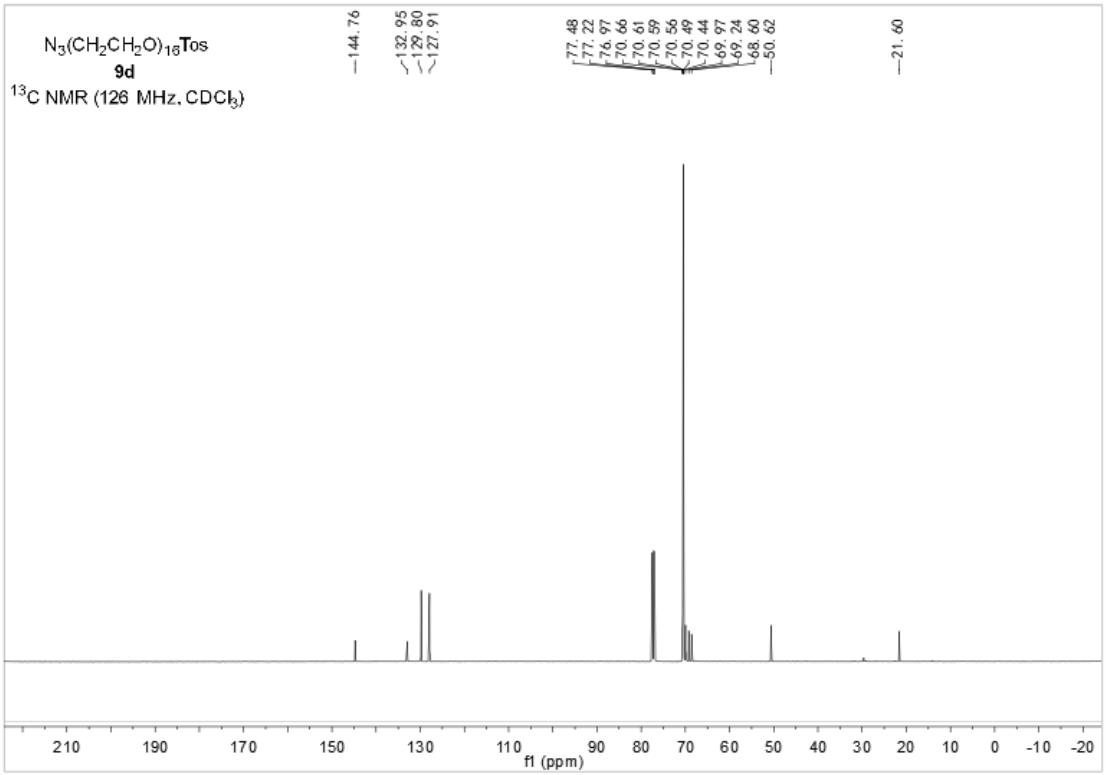
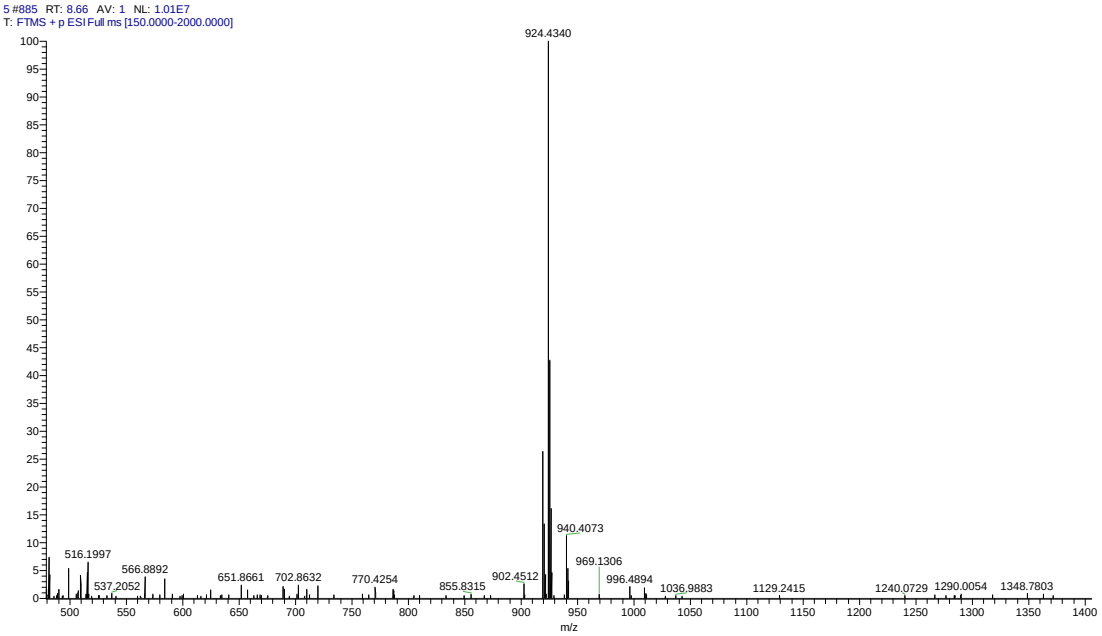
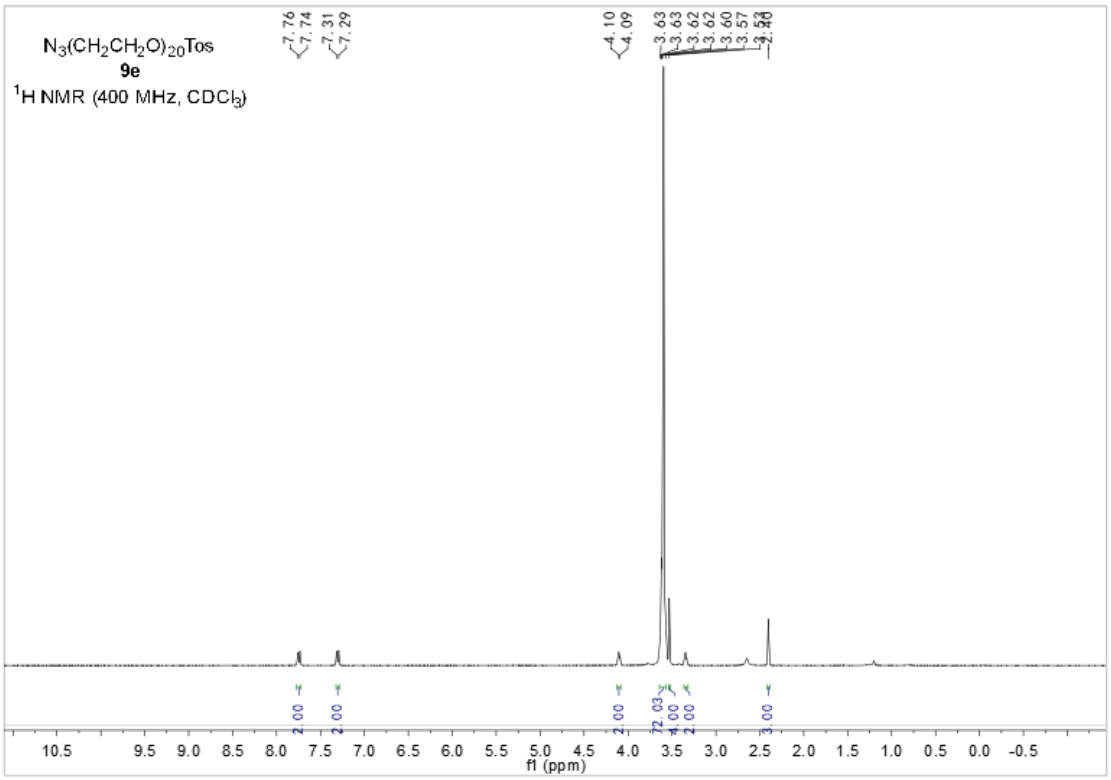


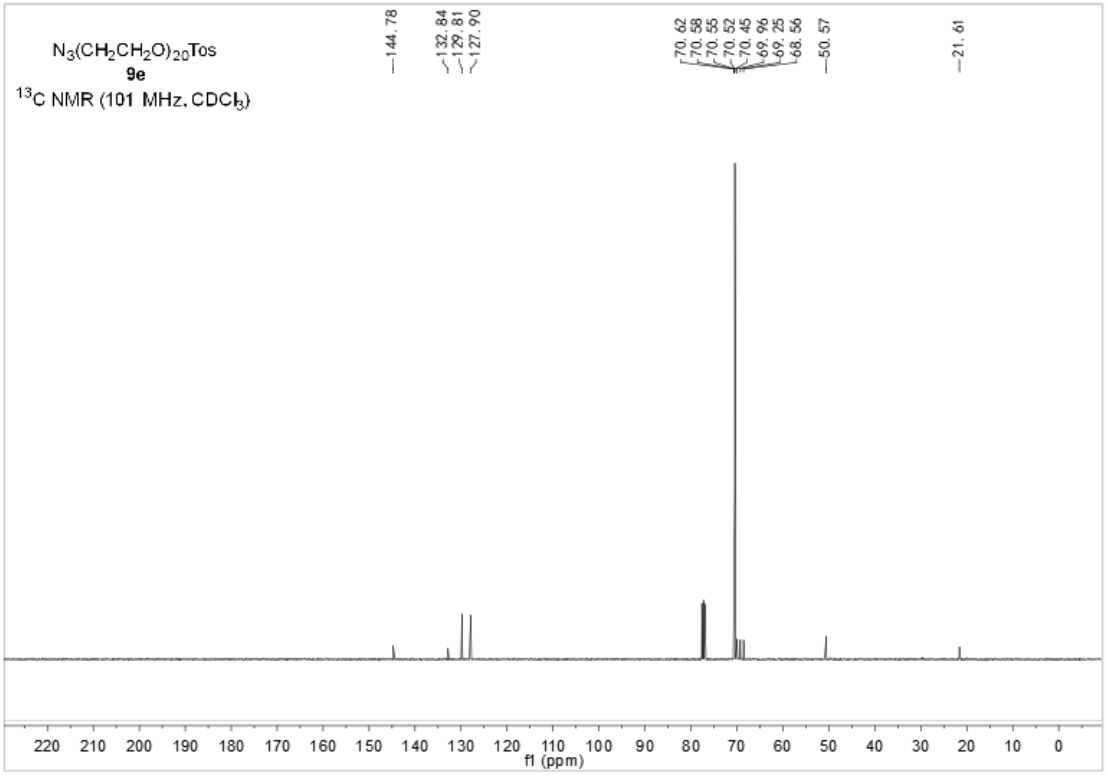
HRMS of compound **9d**



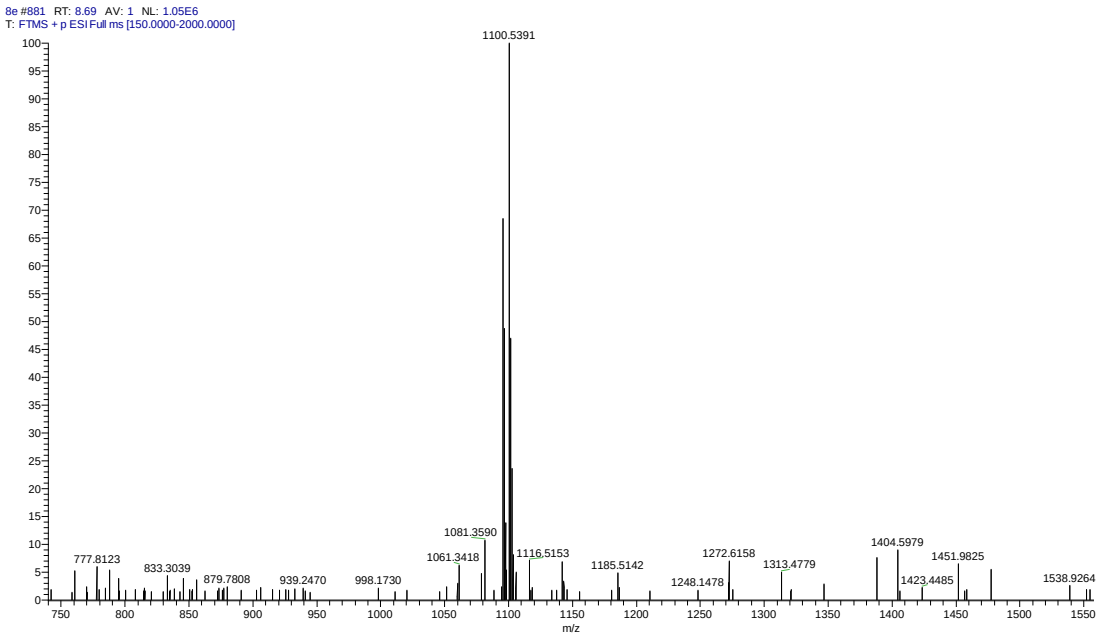
^{1}H NMR of compound **9e**



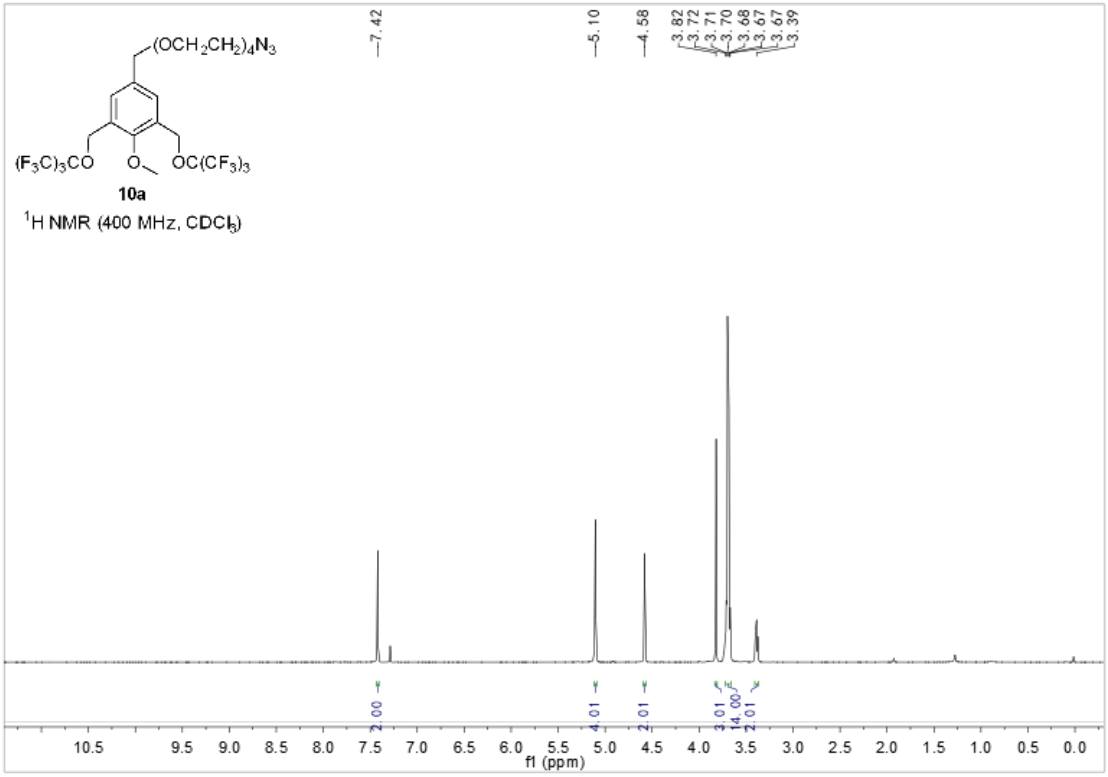
^{13}C NMR of compound **9e**



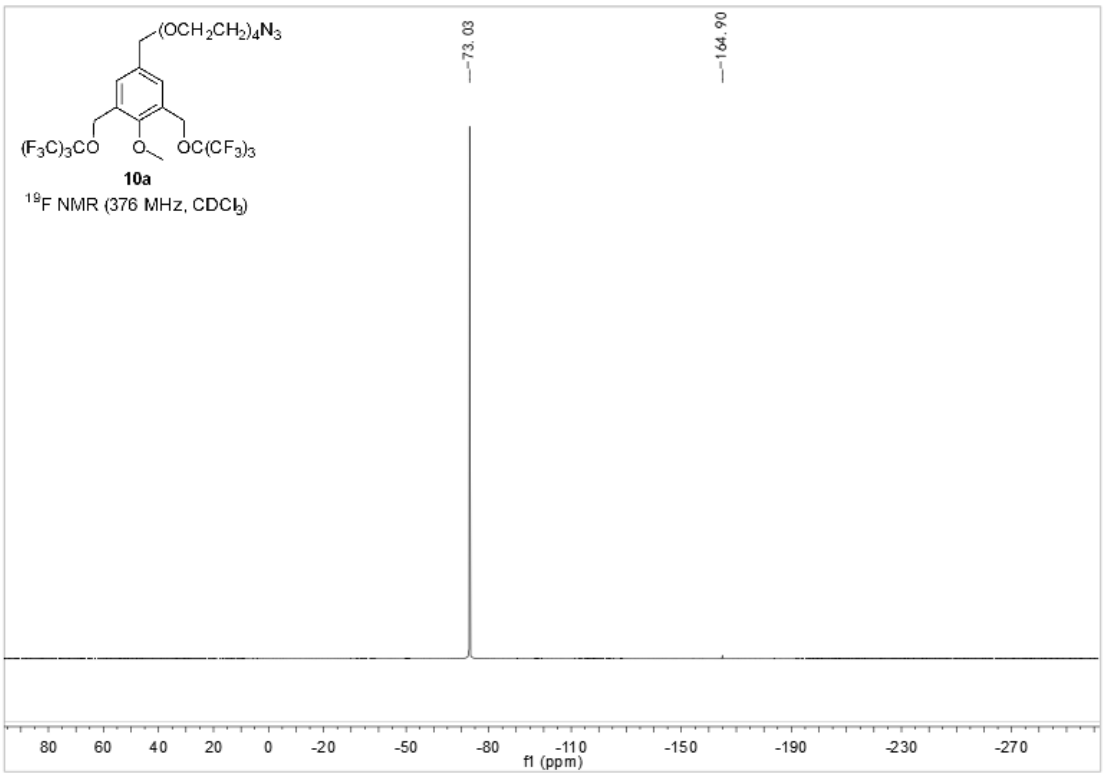
HRMS of compound **9e**



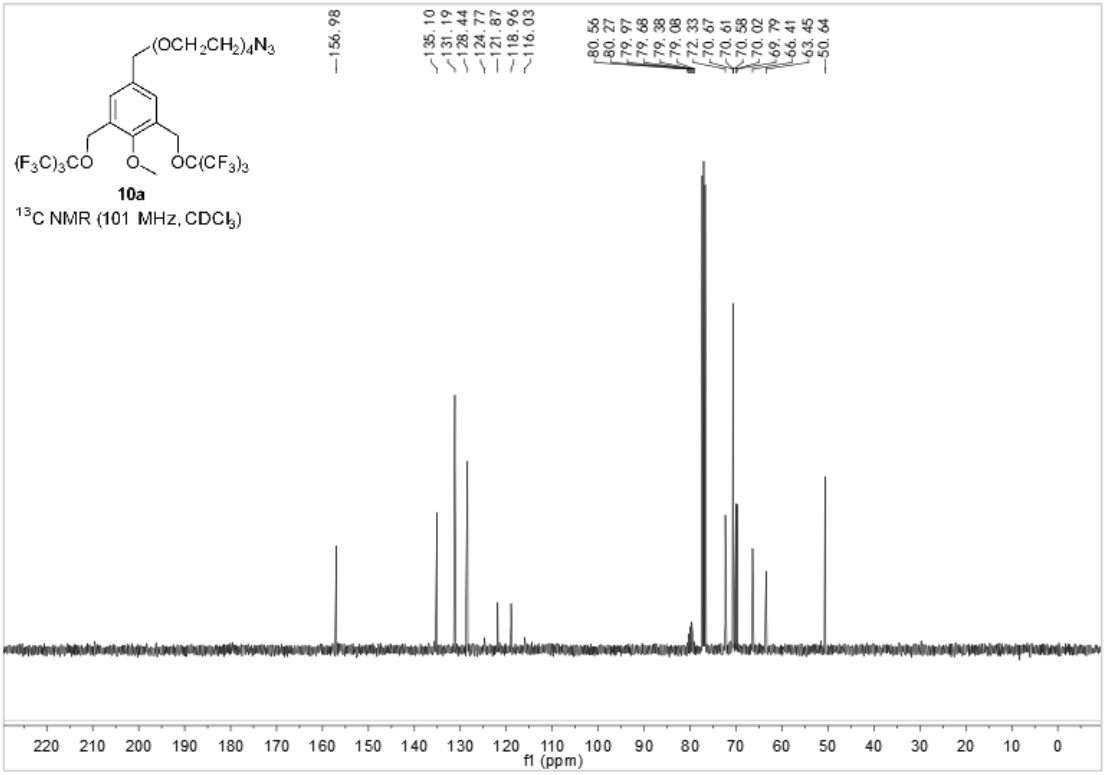
^{1}H NMR of compound **10a**



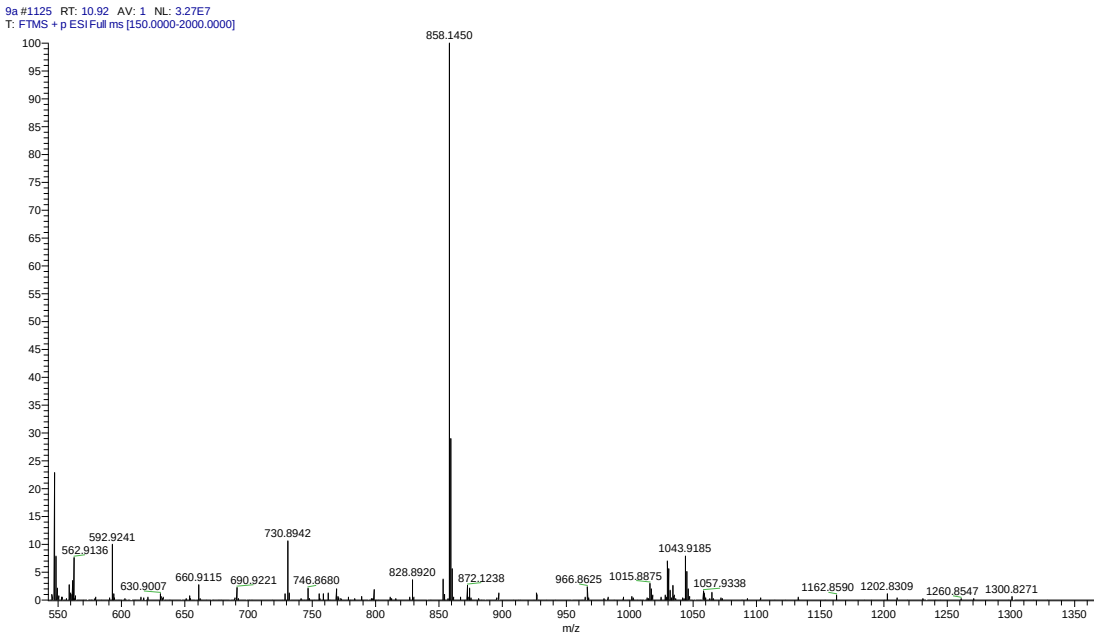
^{19}F NMR of compound **10a**



^{13}C NMR of compound **10a**



HRMS of compound **10a**



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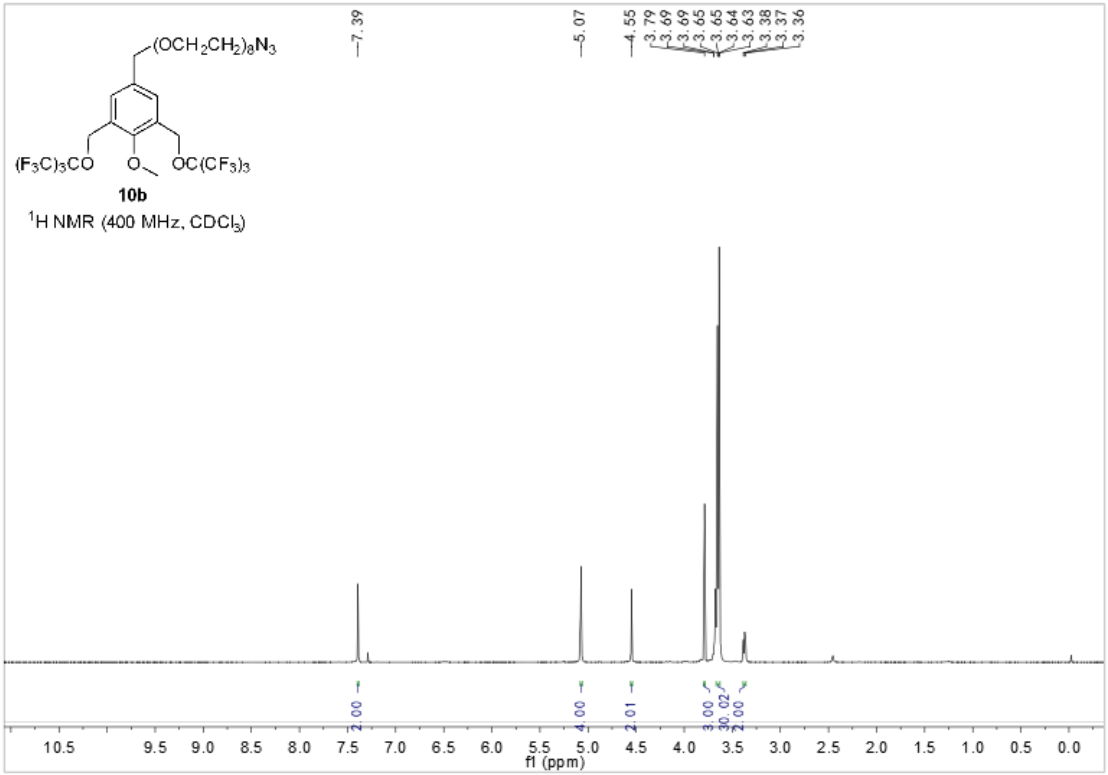

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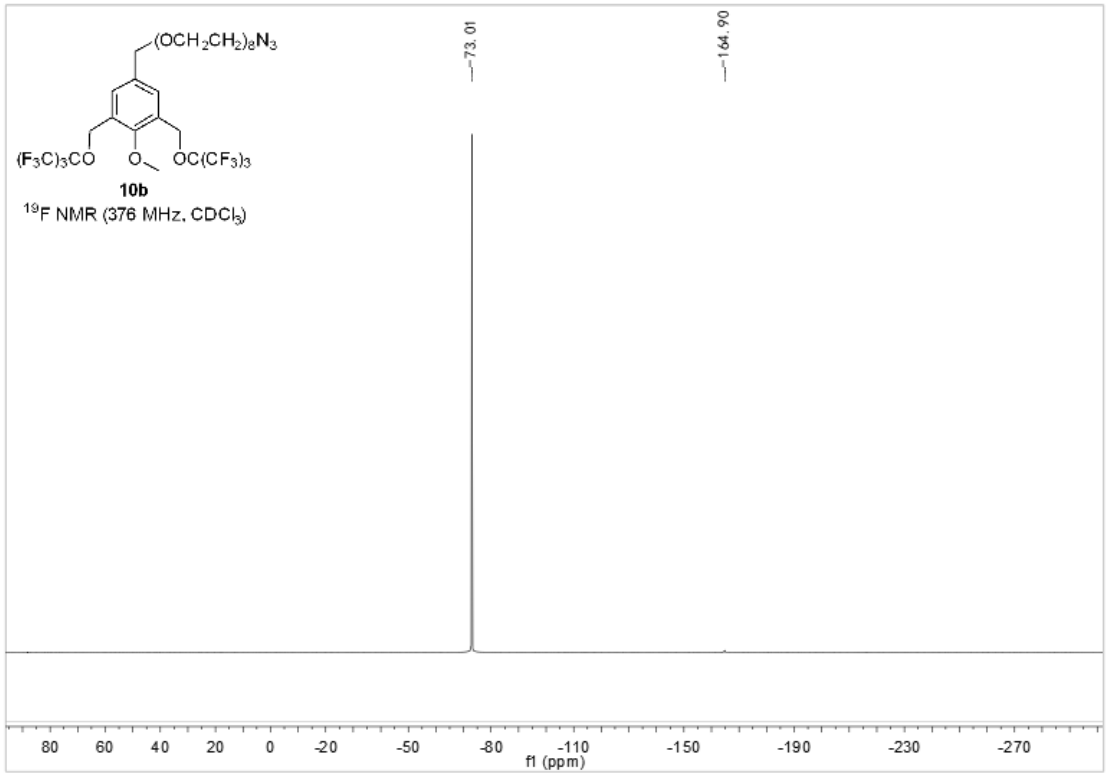
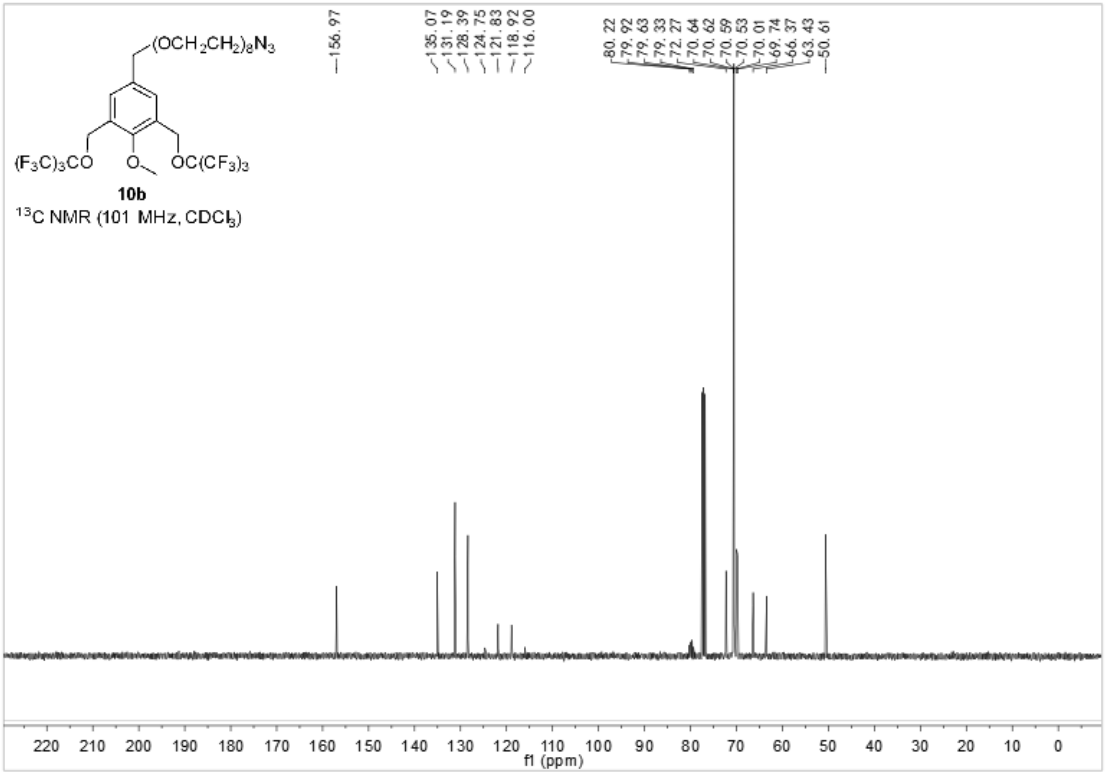


^{13}C NMR of compound **10b**



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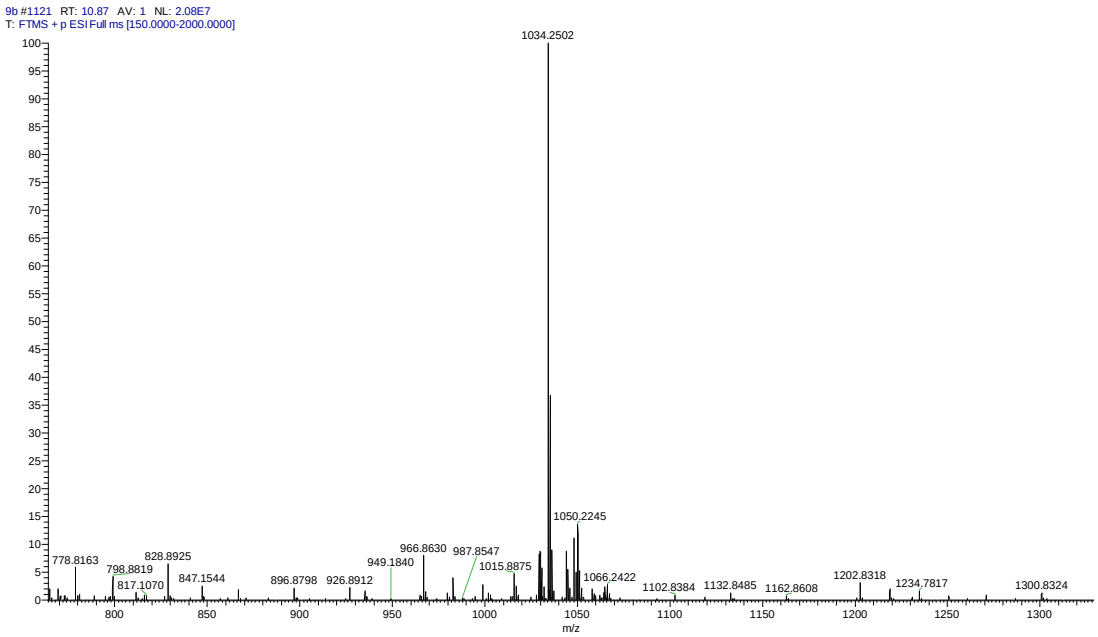

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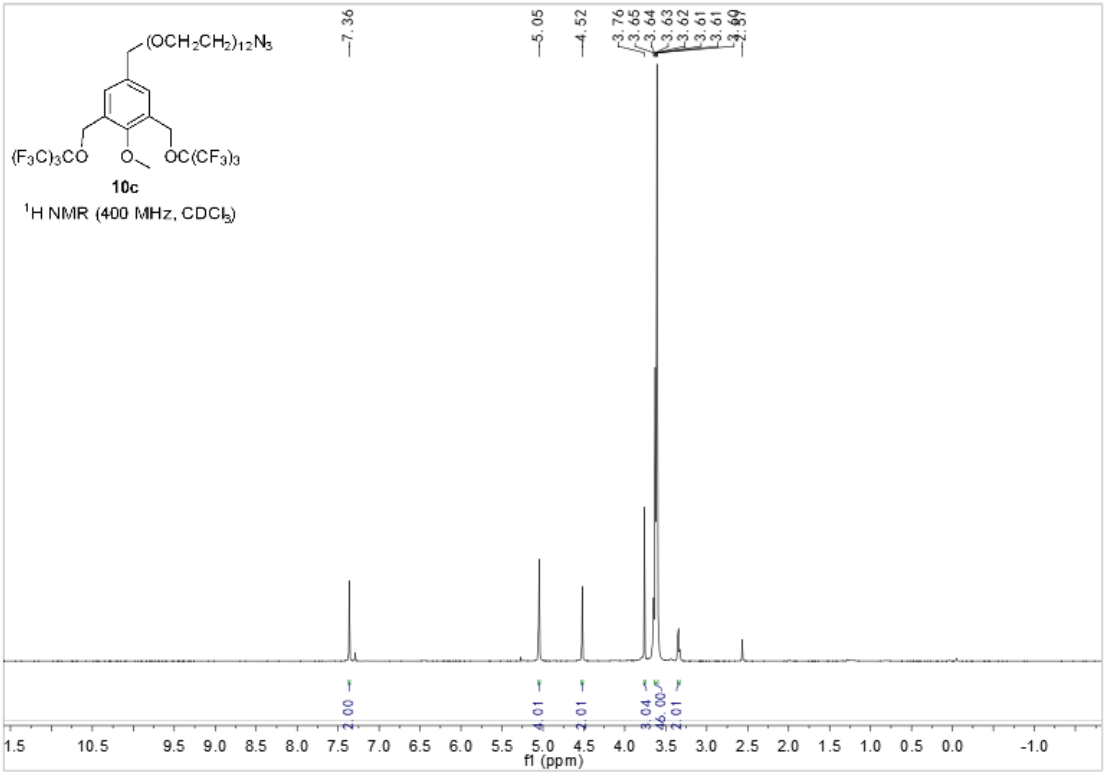

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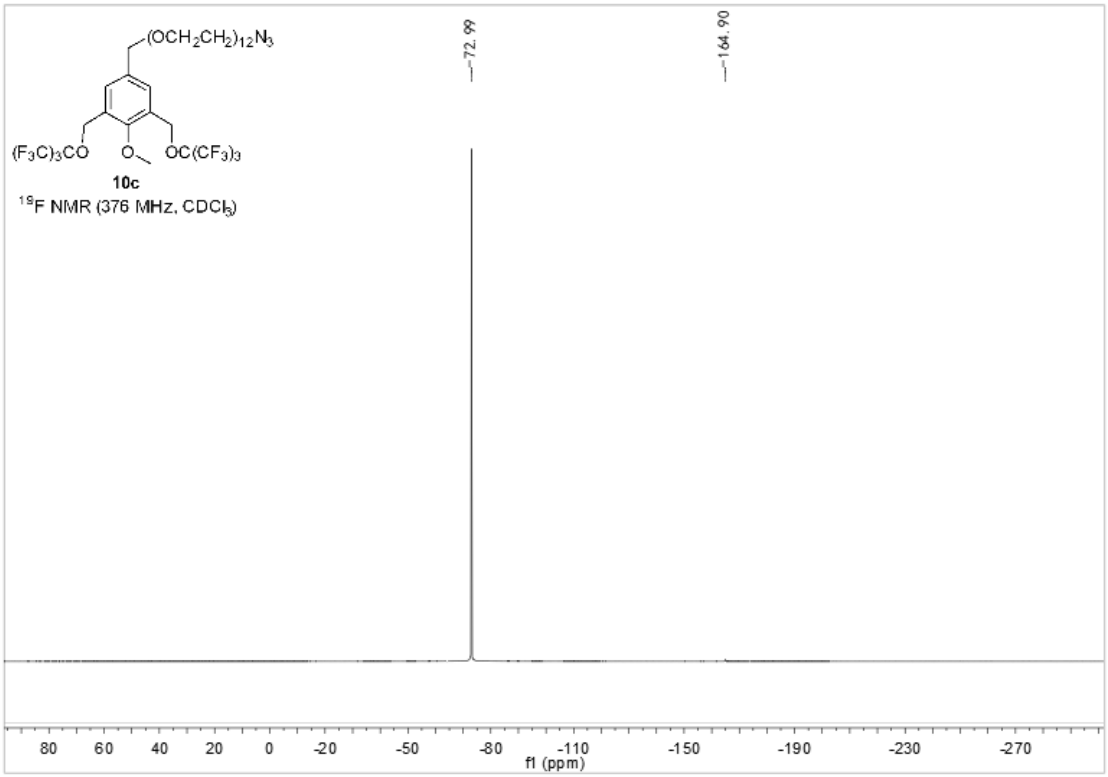

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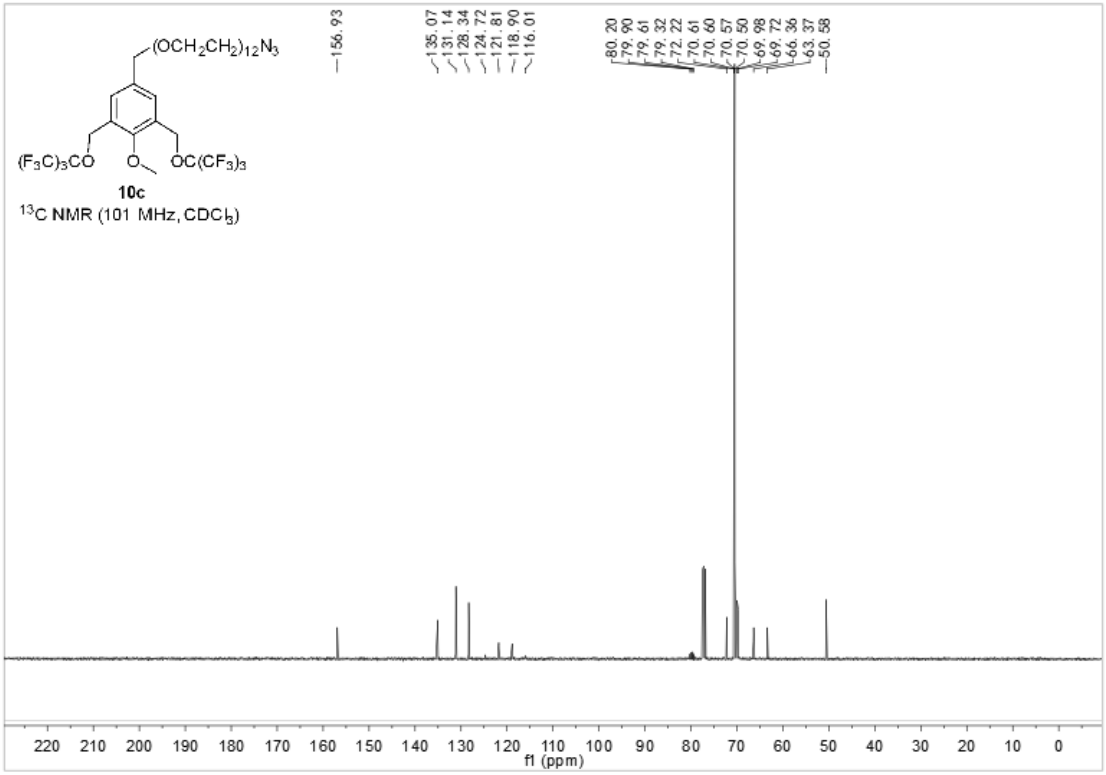

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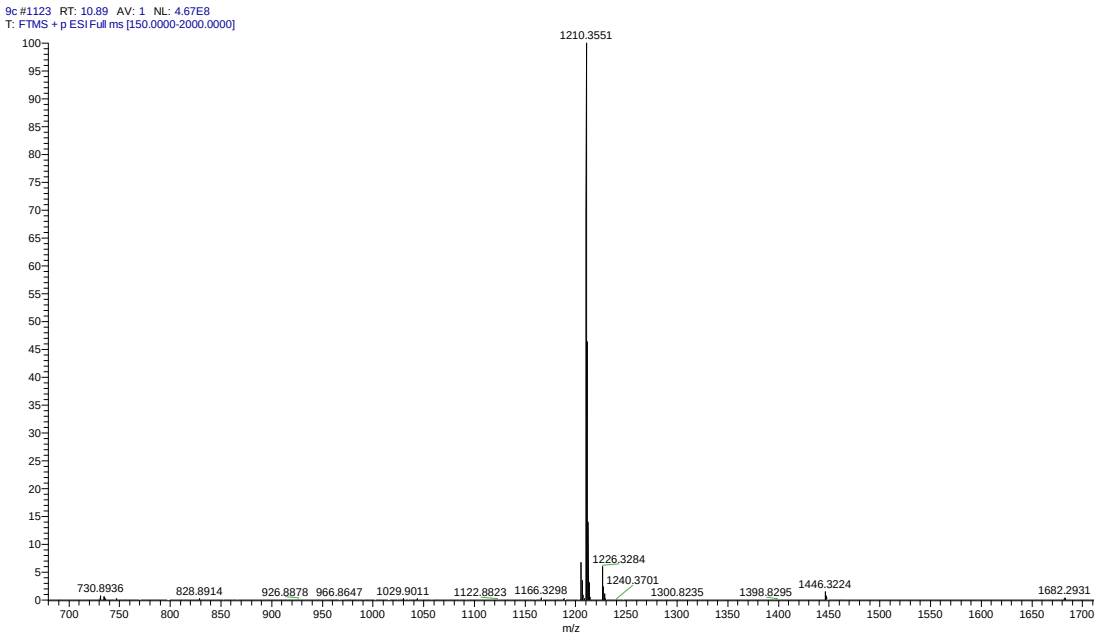
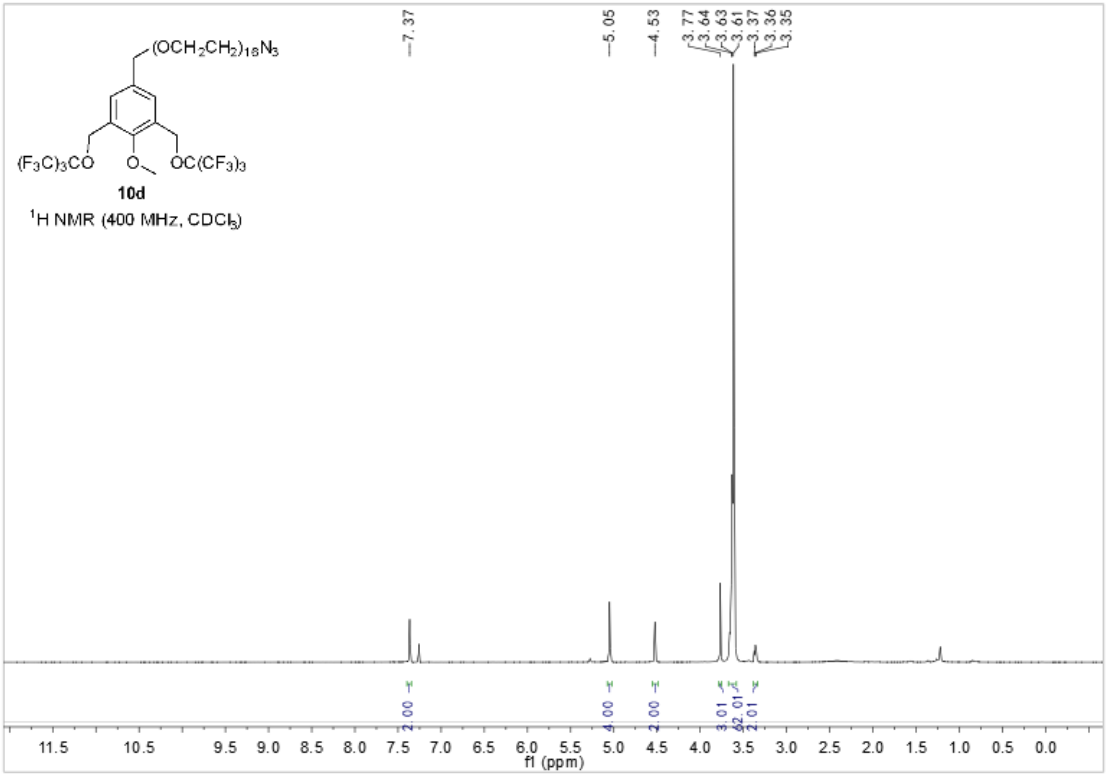


^{1}H NMR of compound **10d**



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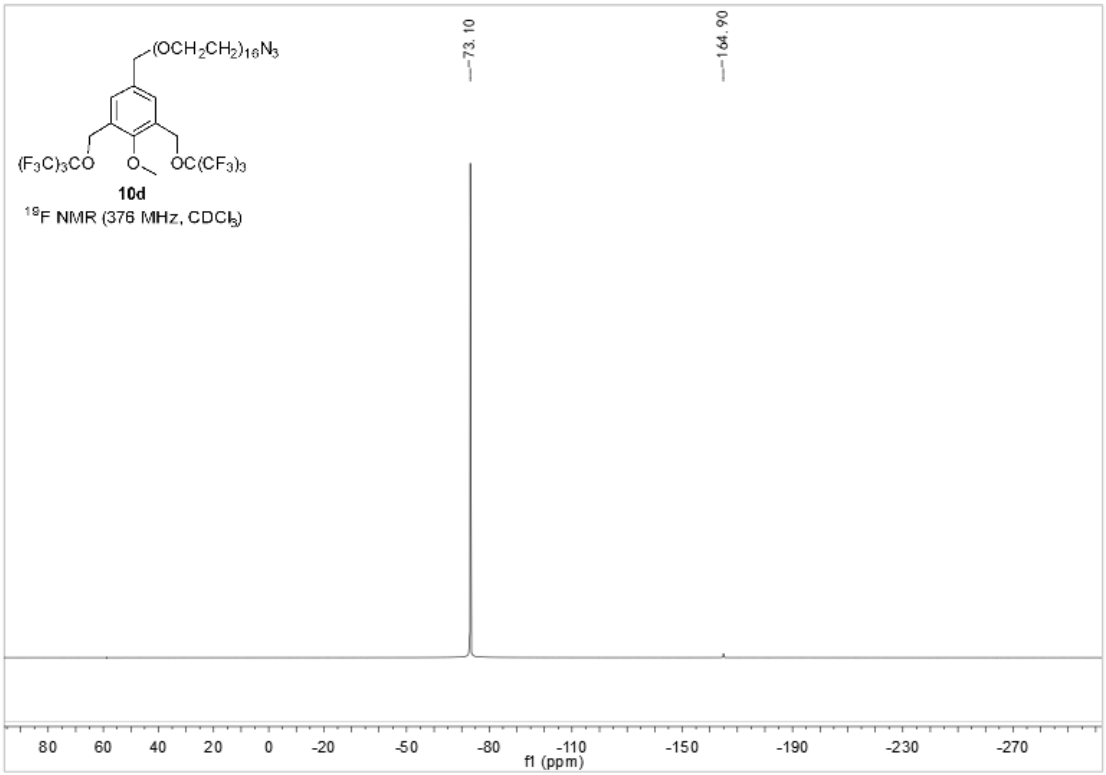

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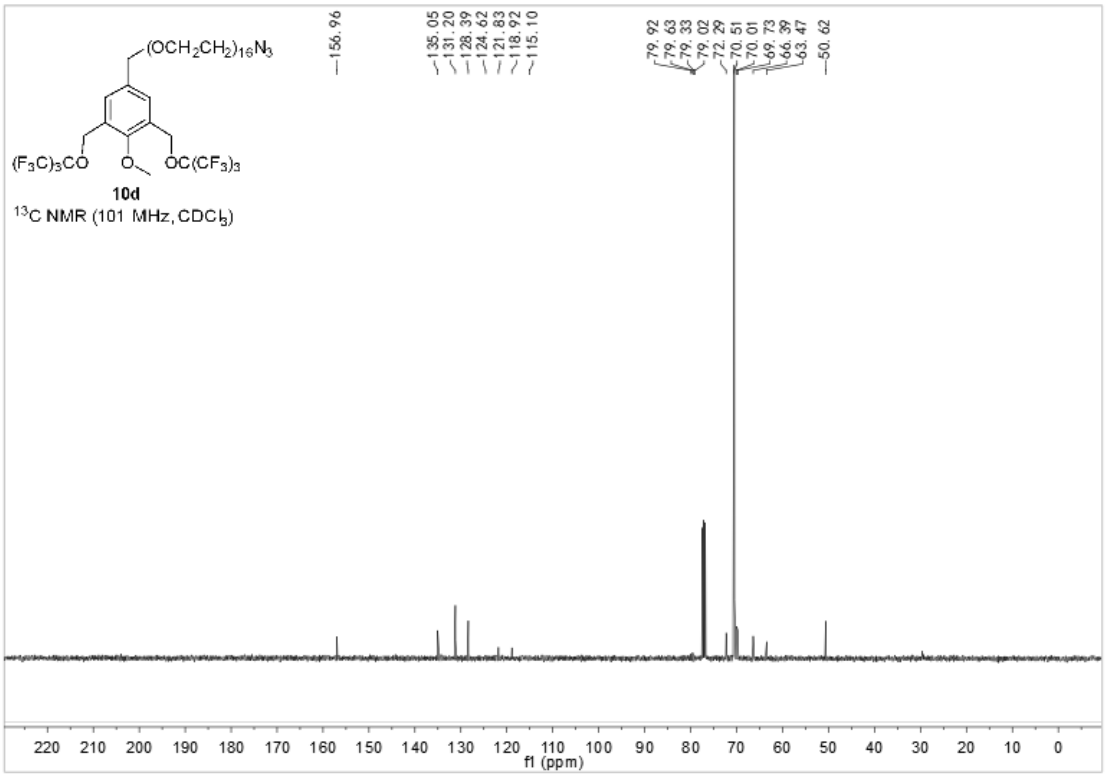

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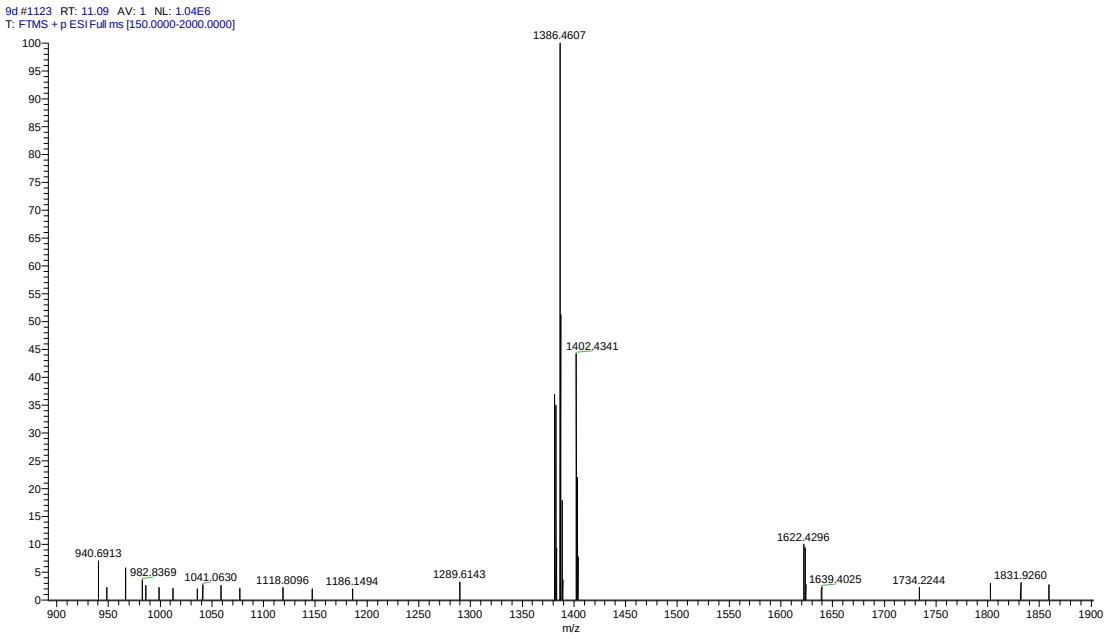

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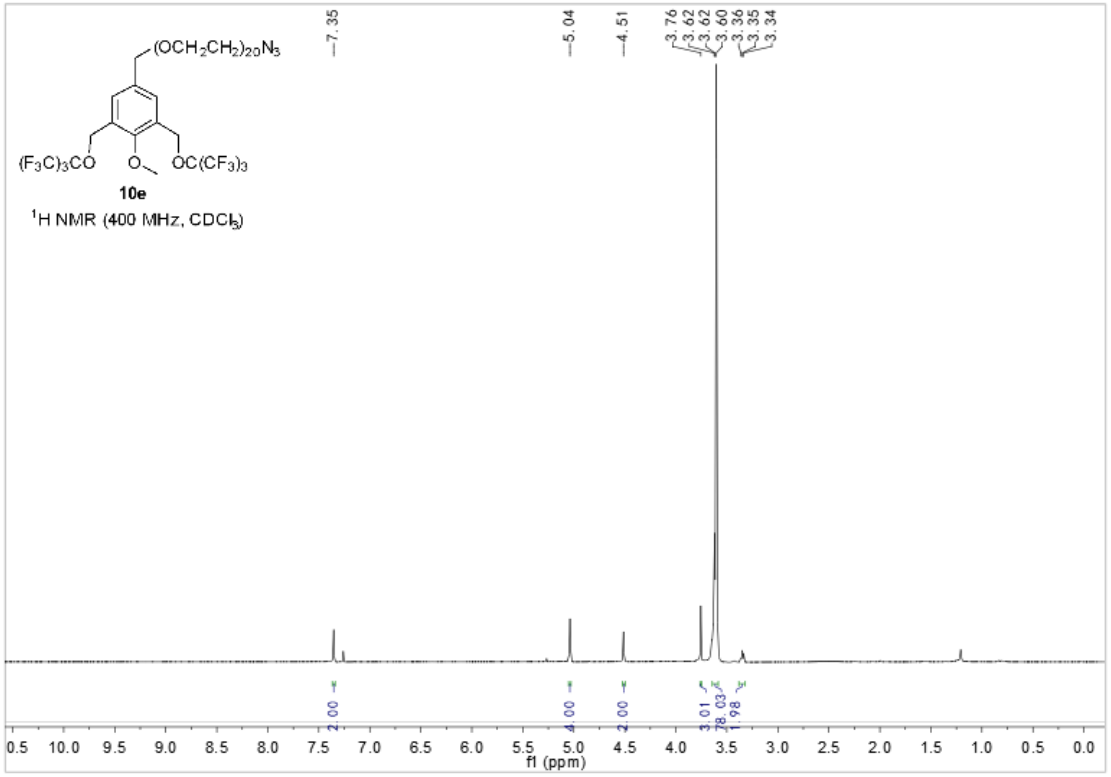

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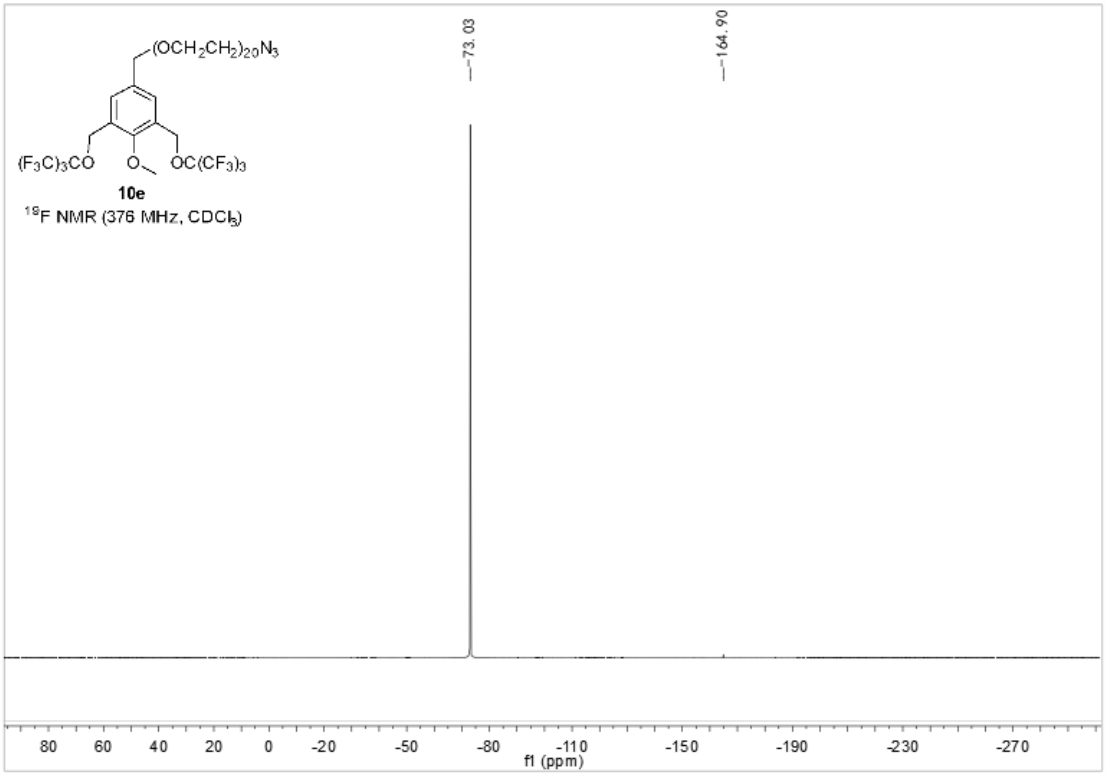

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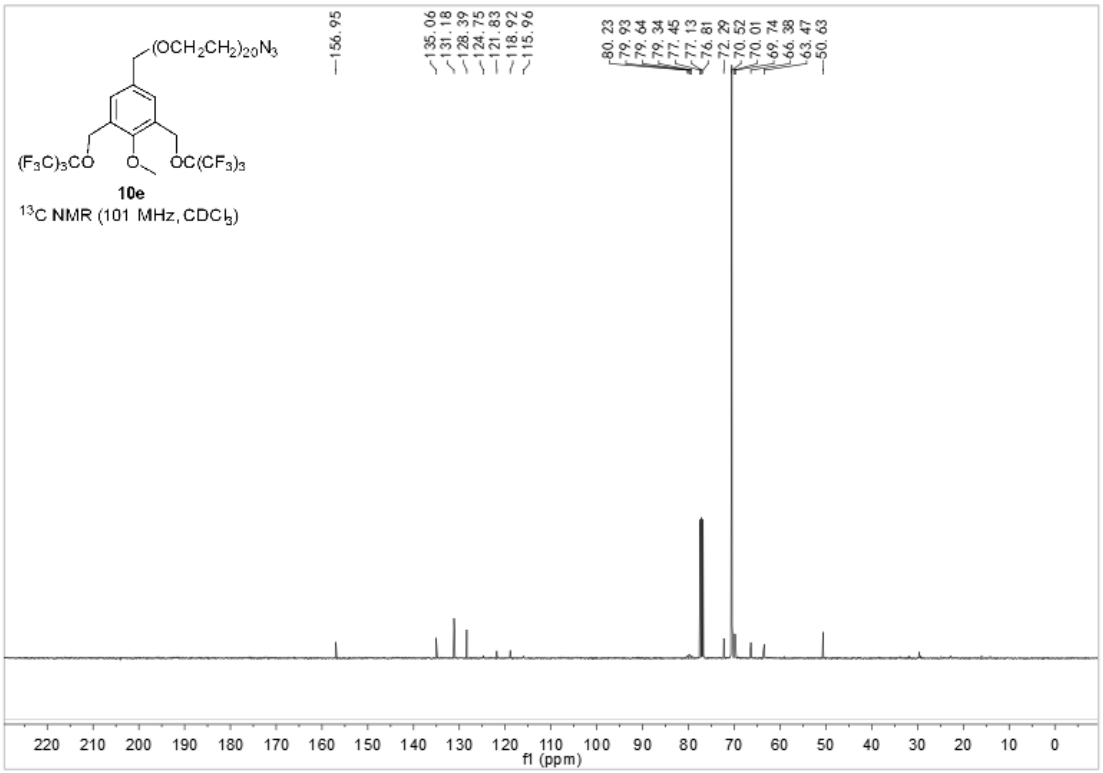

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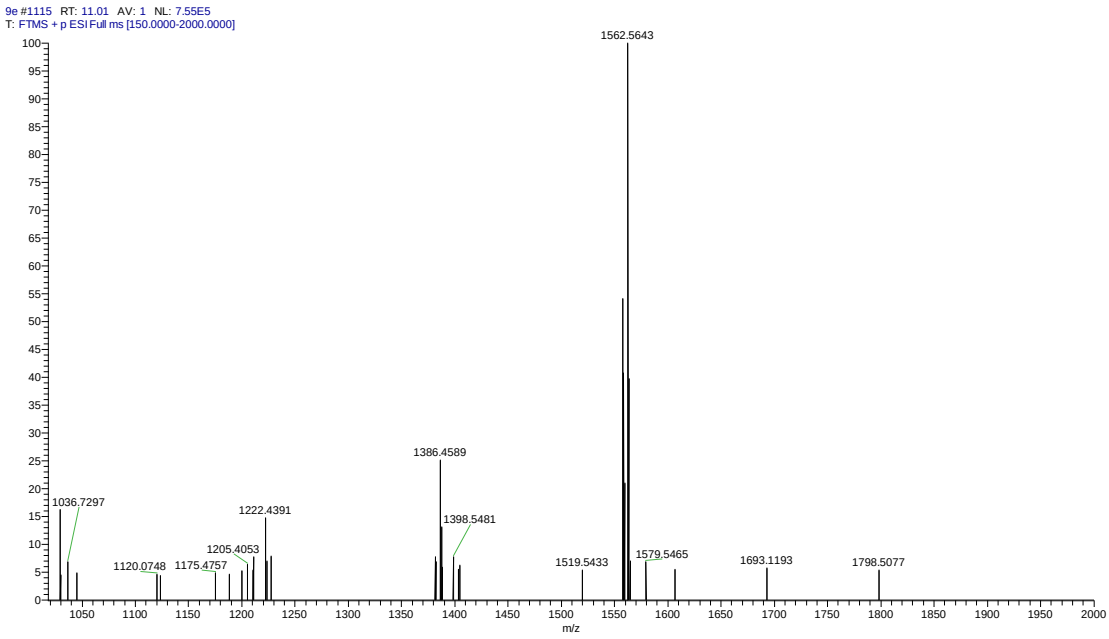
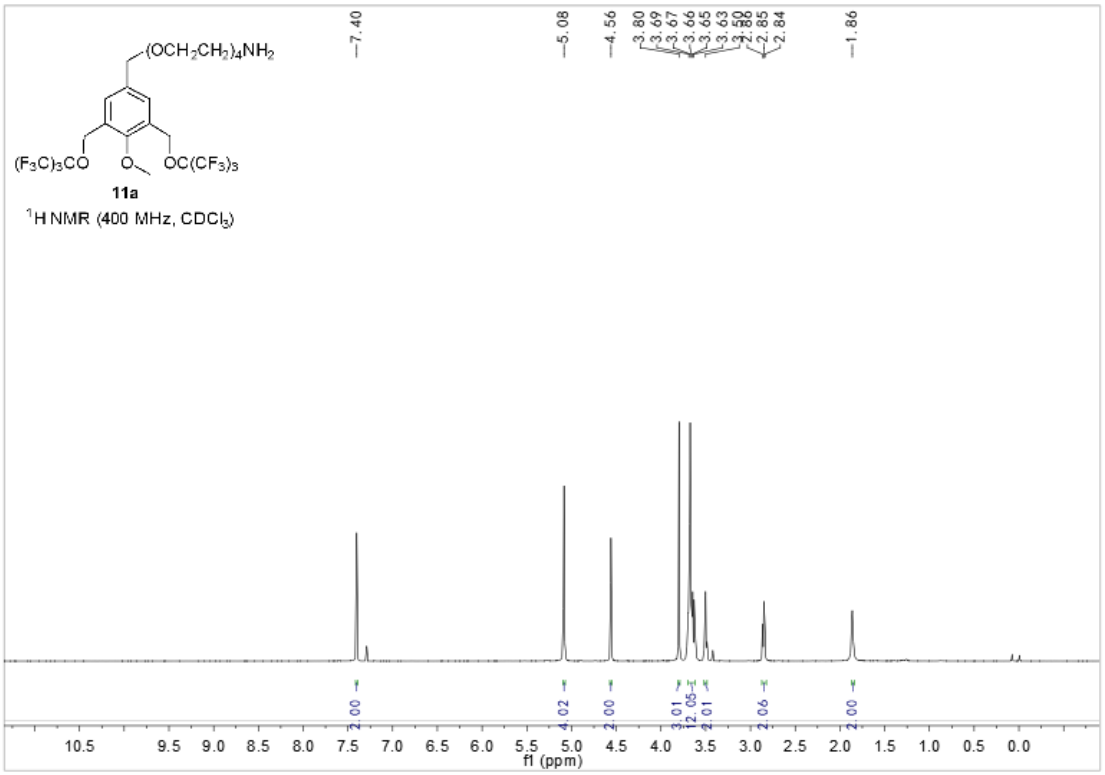


^{1}H NMR of compound **11a**



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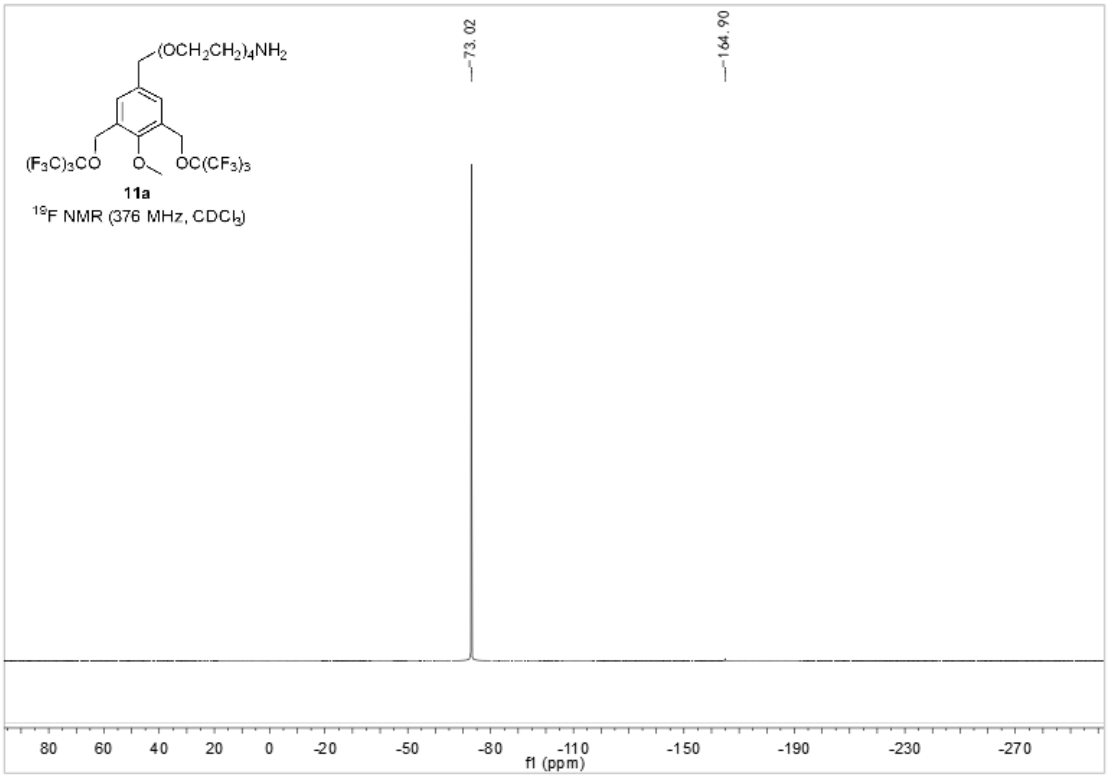
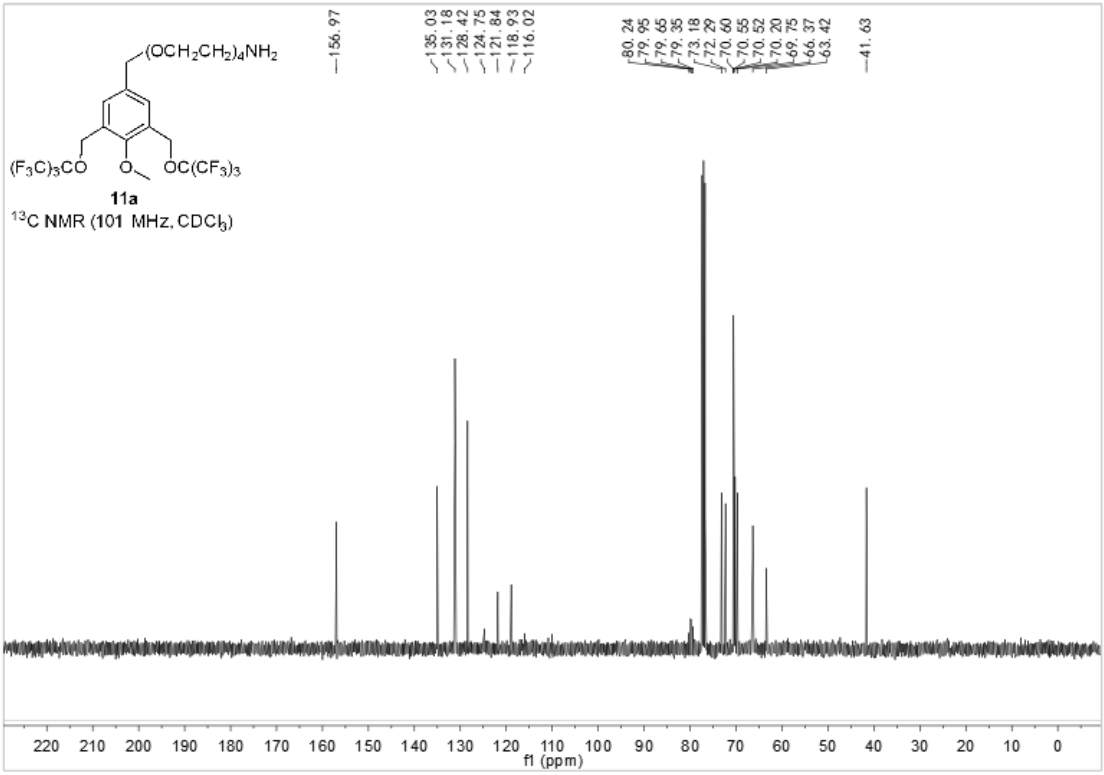


^{13}C NMR of compound **11a**



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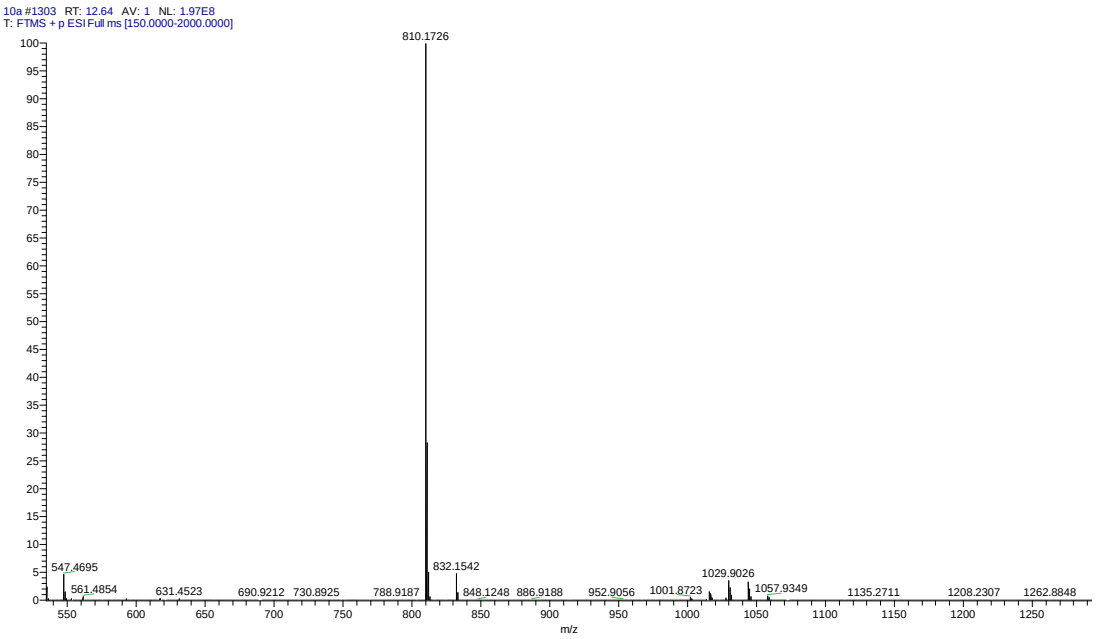

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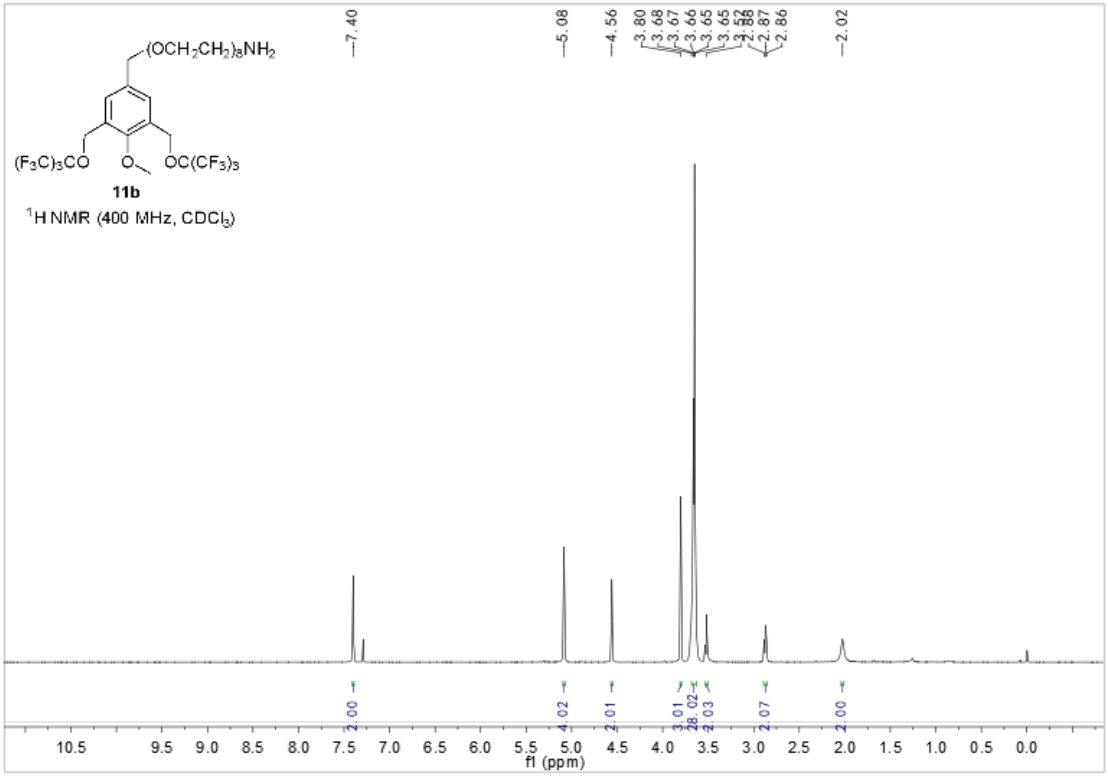
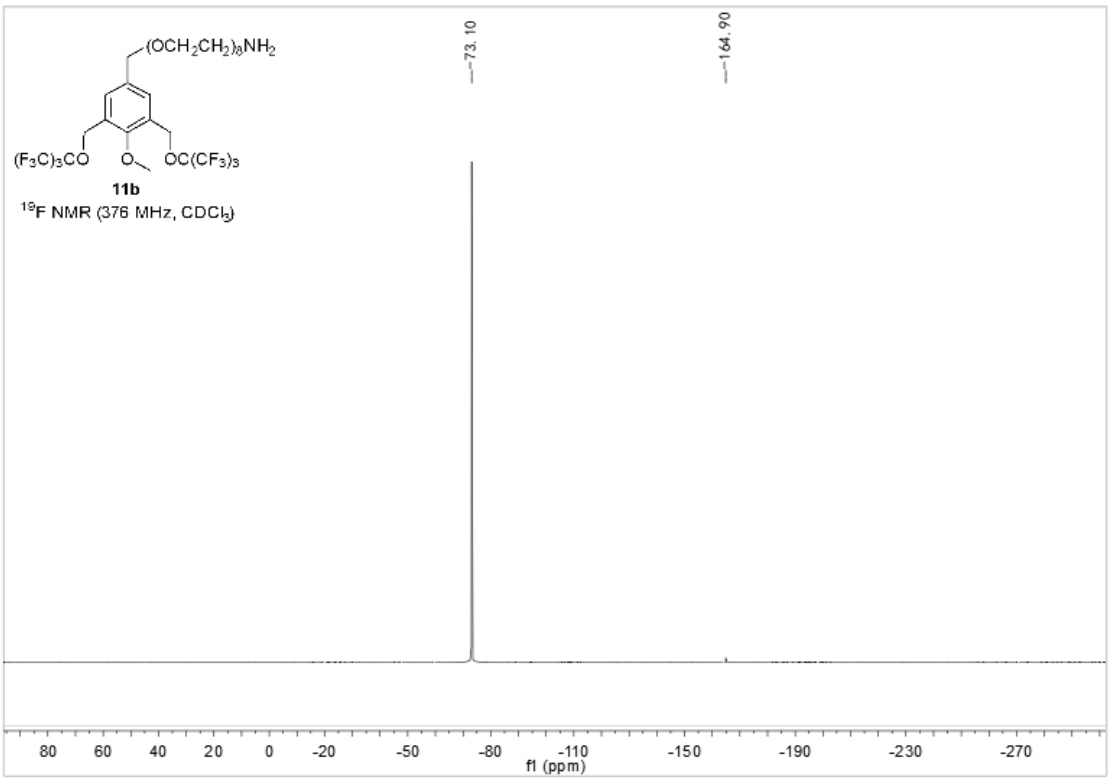


^{19}F NMR of compound **11b**



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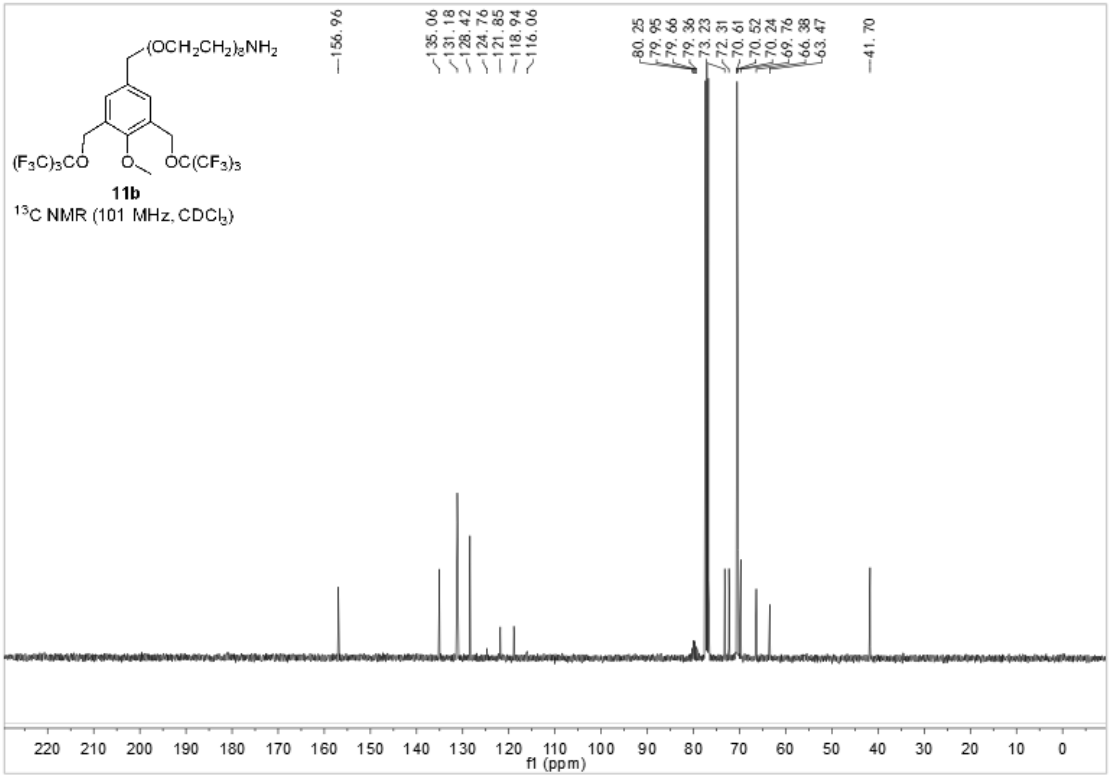
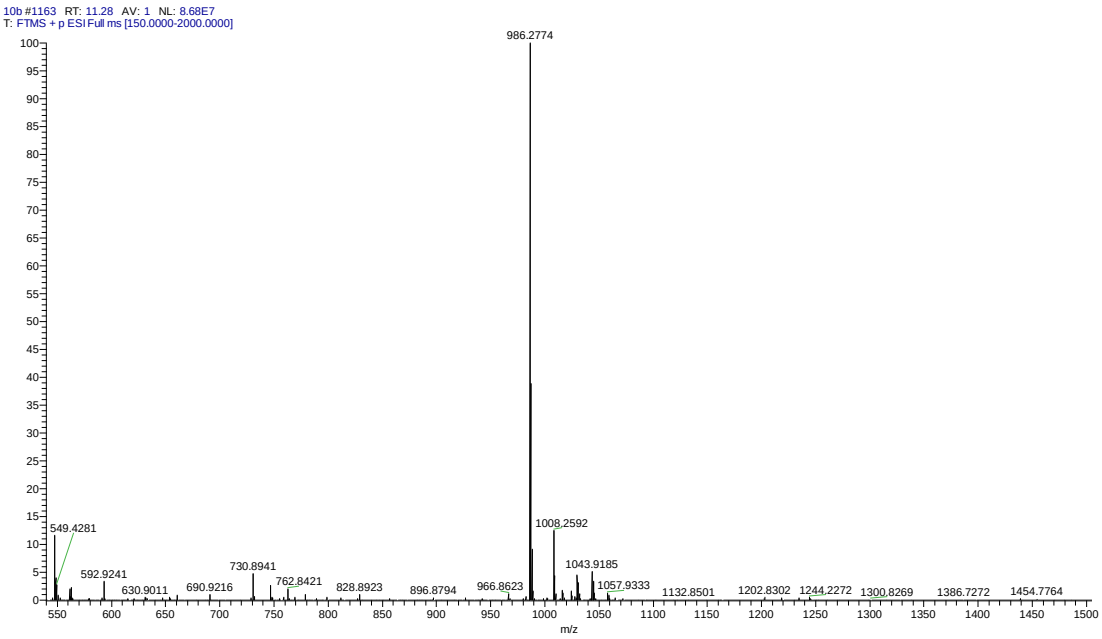


HRMS of compound **11b**



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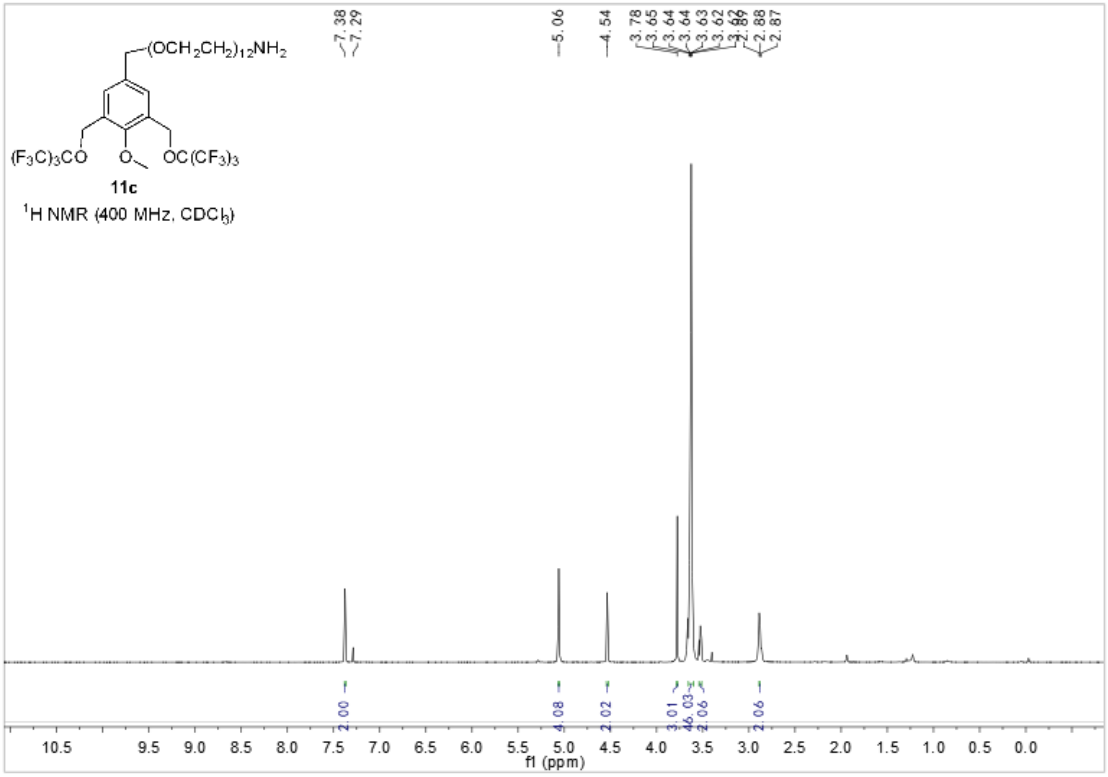

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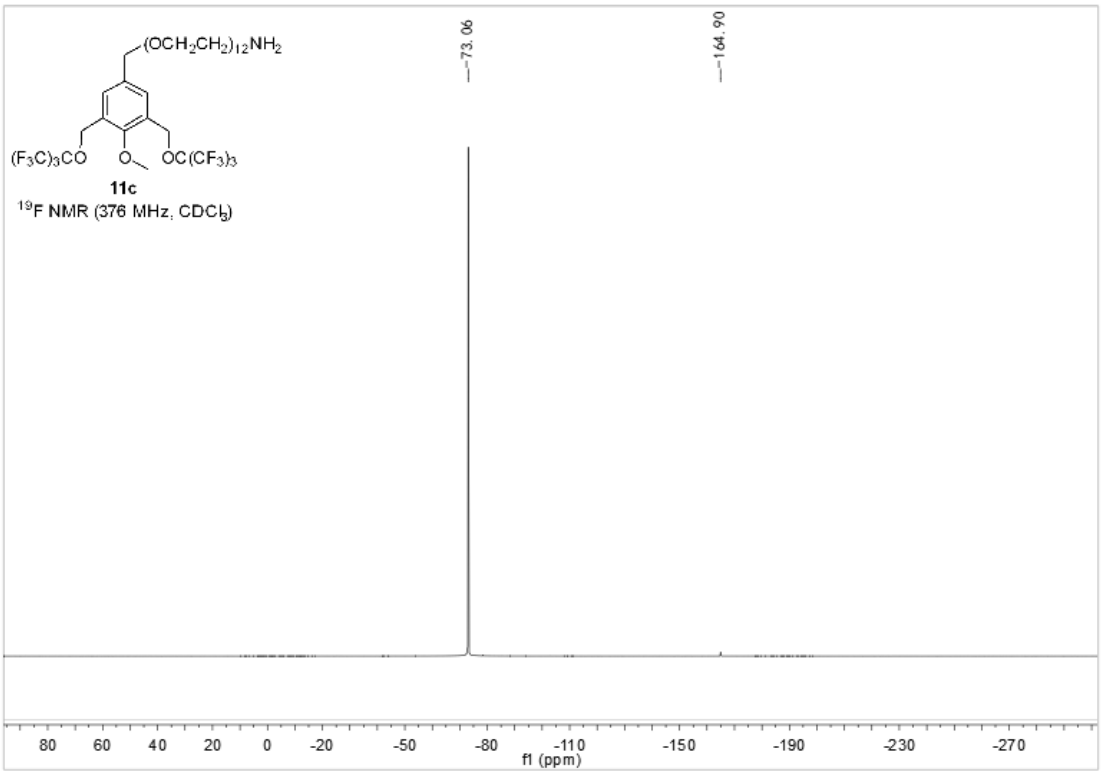
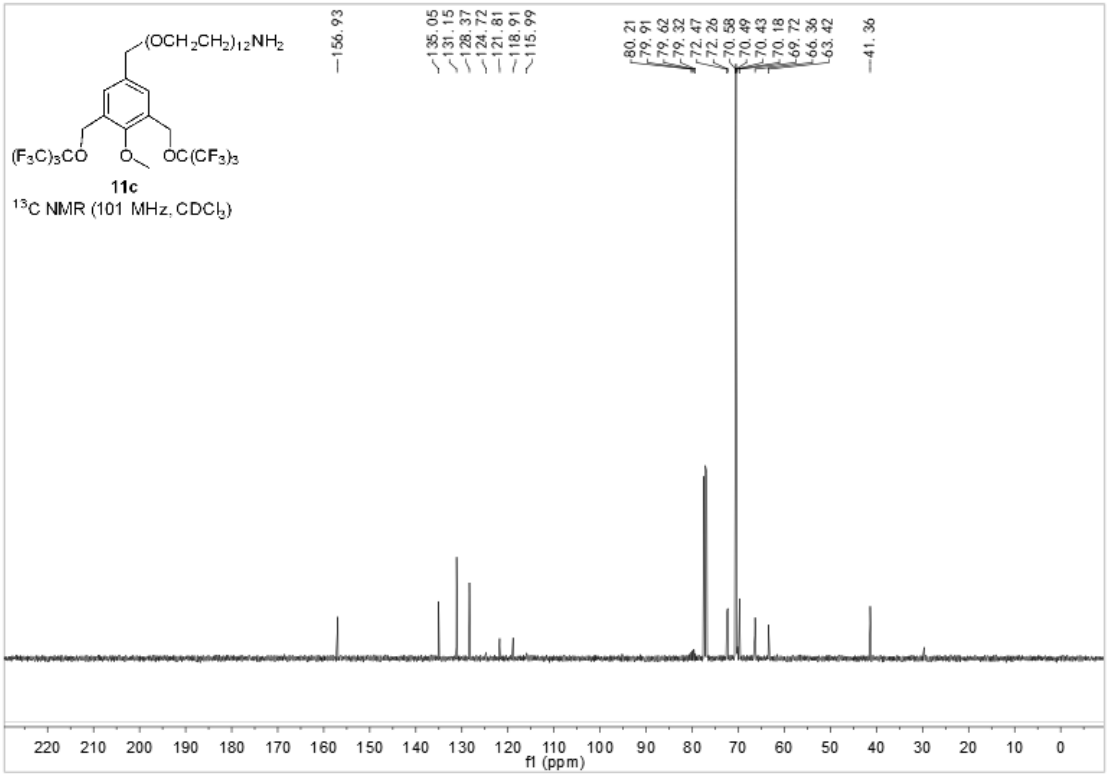
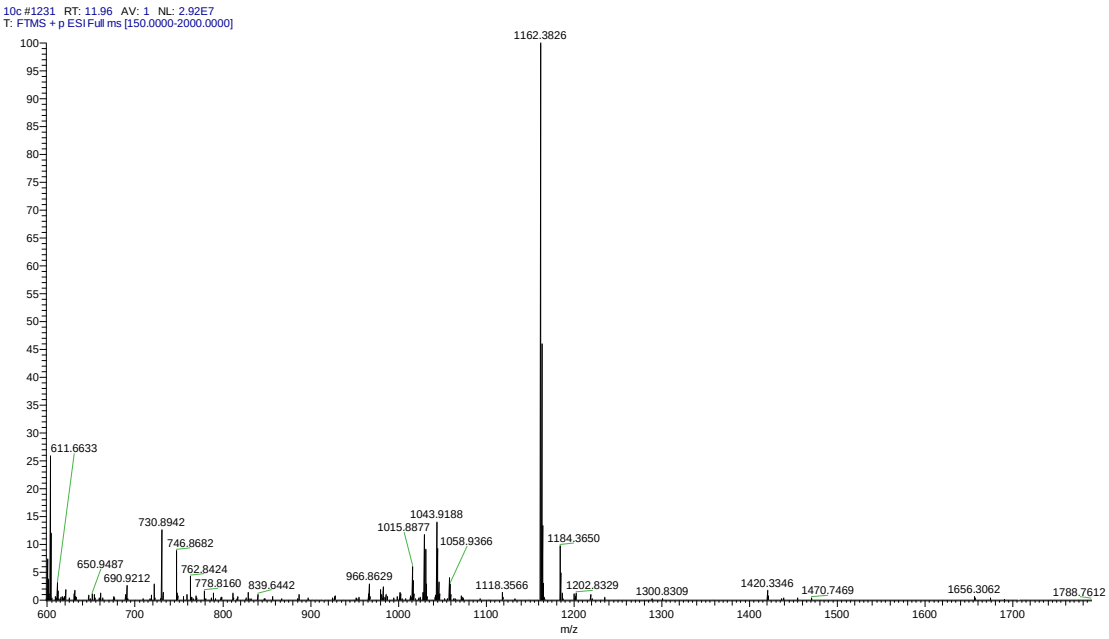


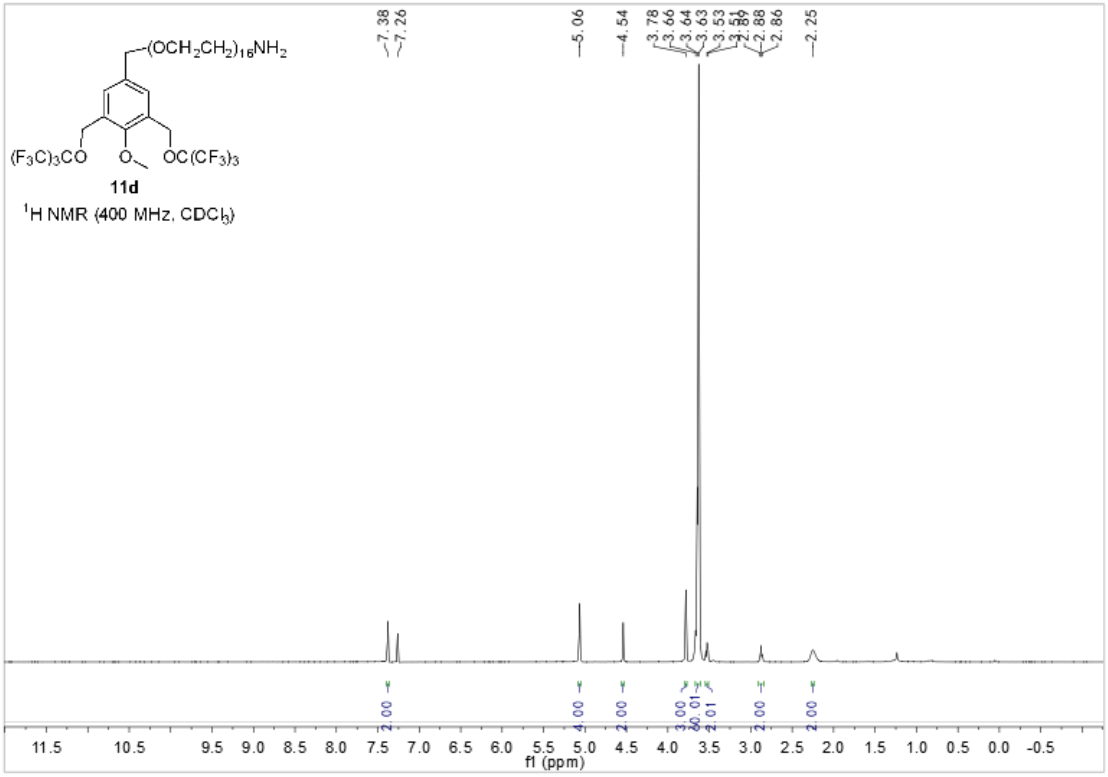
^{13}C NMR of compound **11c**



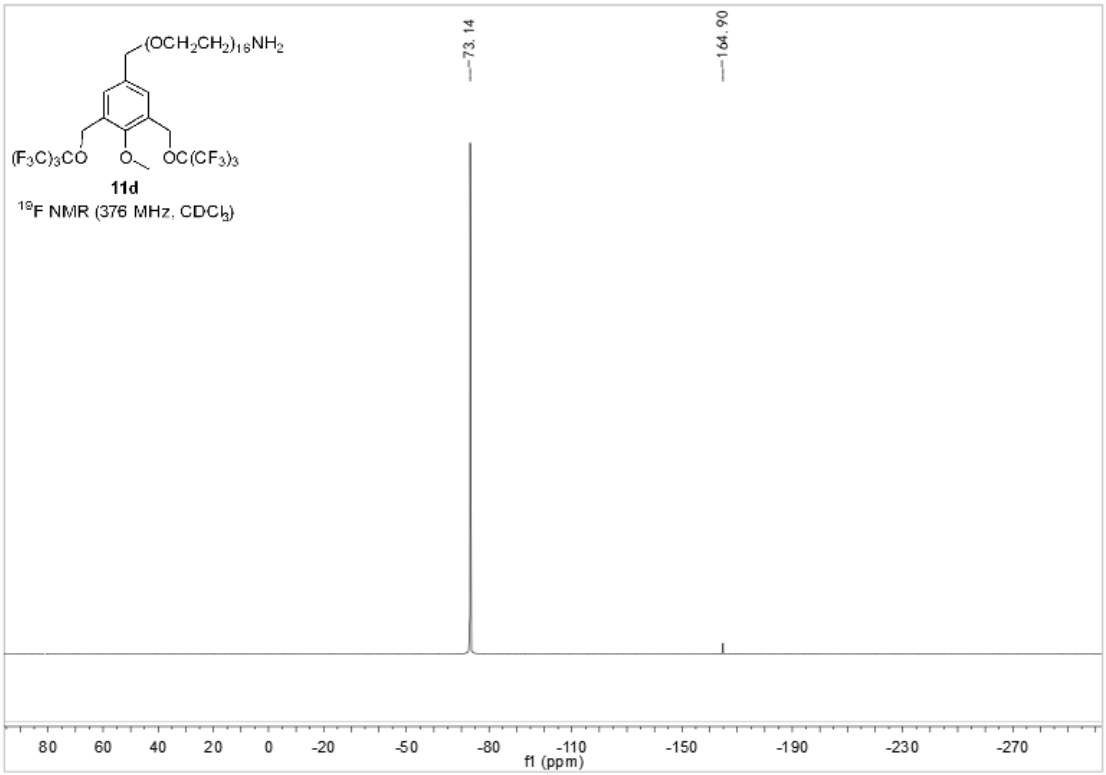
HRMS of compound **11c**



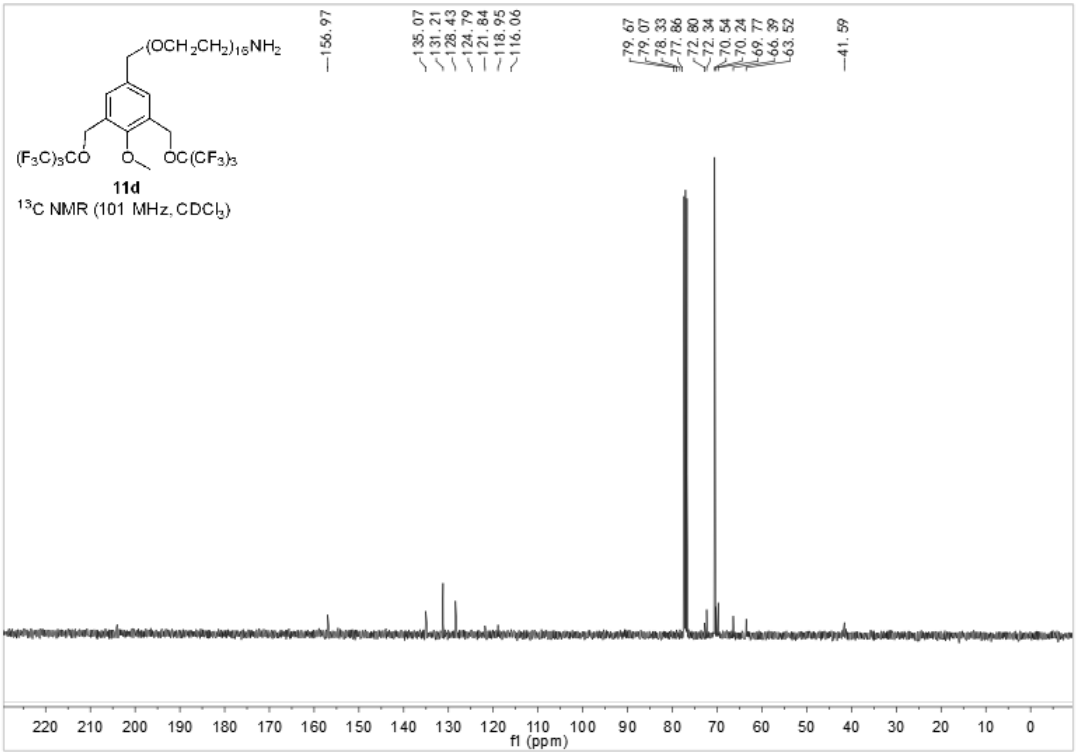
^{1}H NMR of compound **11d**



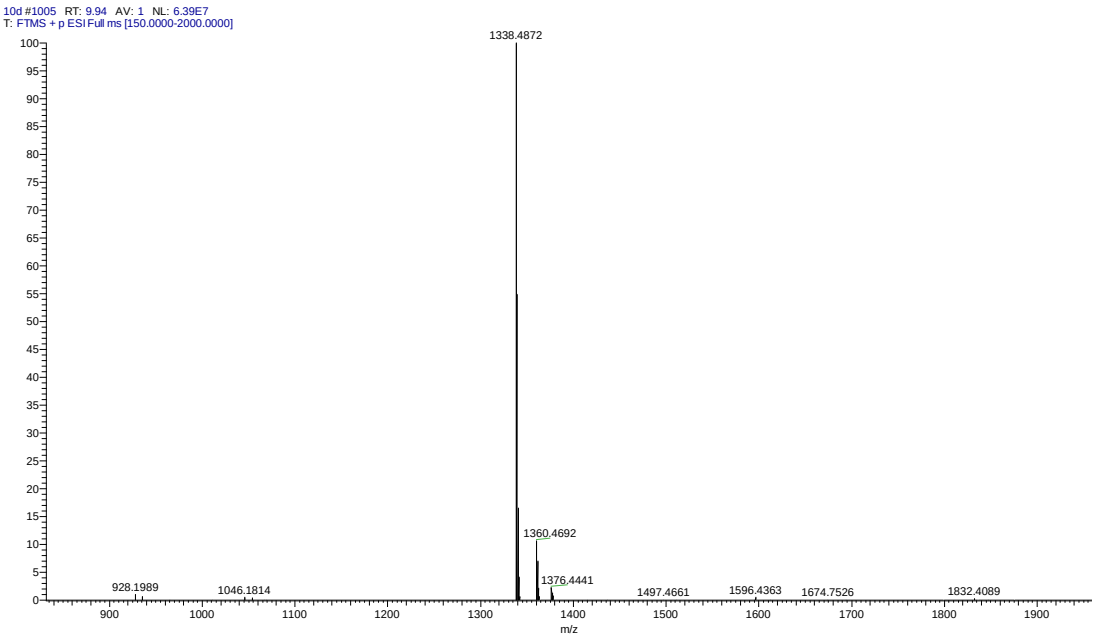
^{19}F NMR of compound **11d**



^{13}C NMR of compound **11d**



HRMS of compound **11d**



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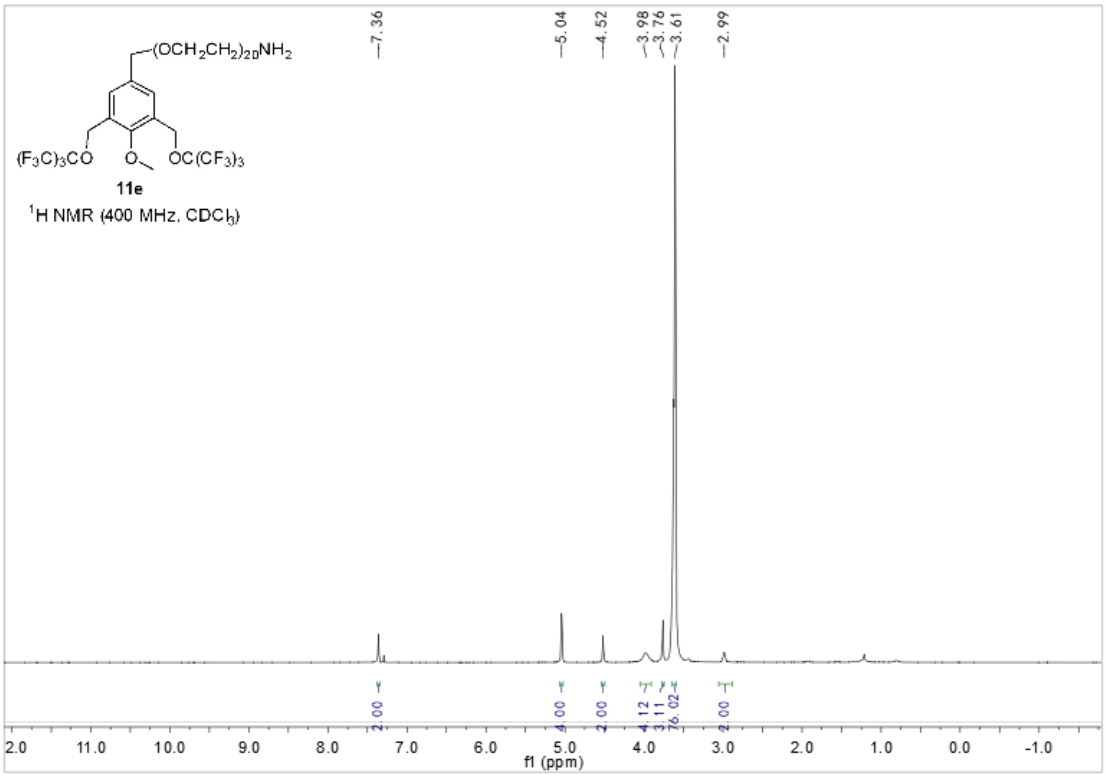
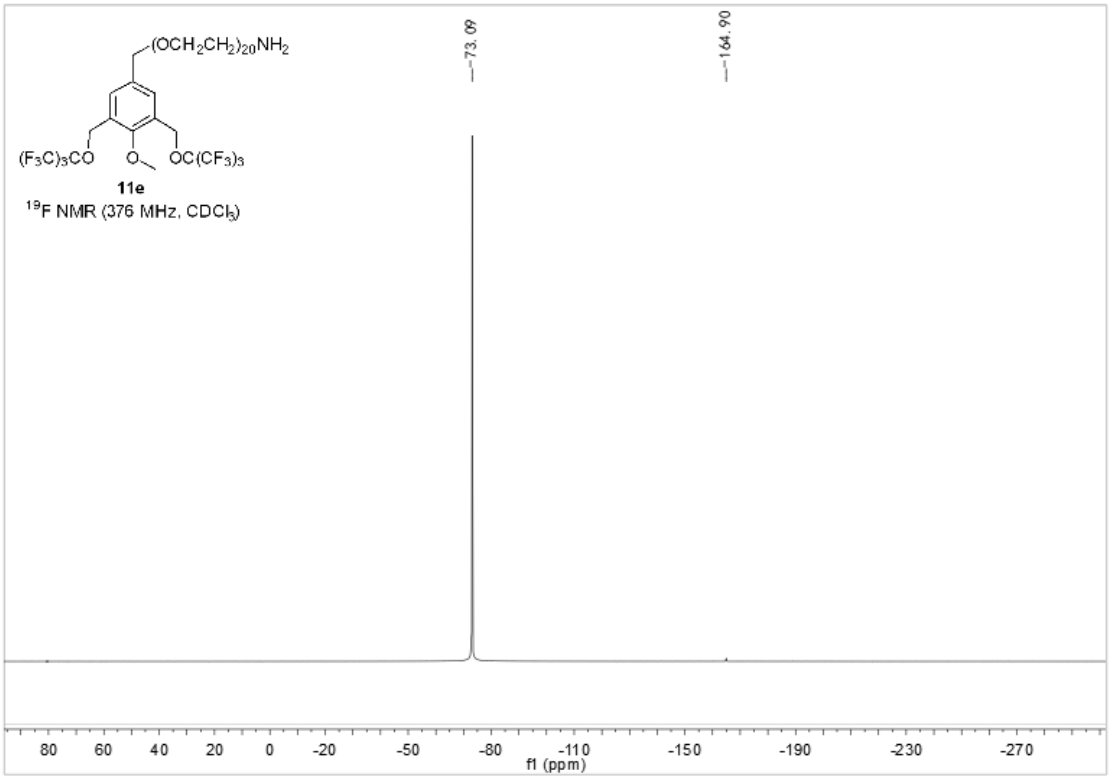
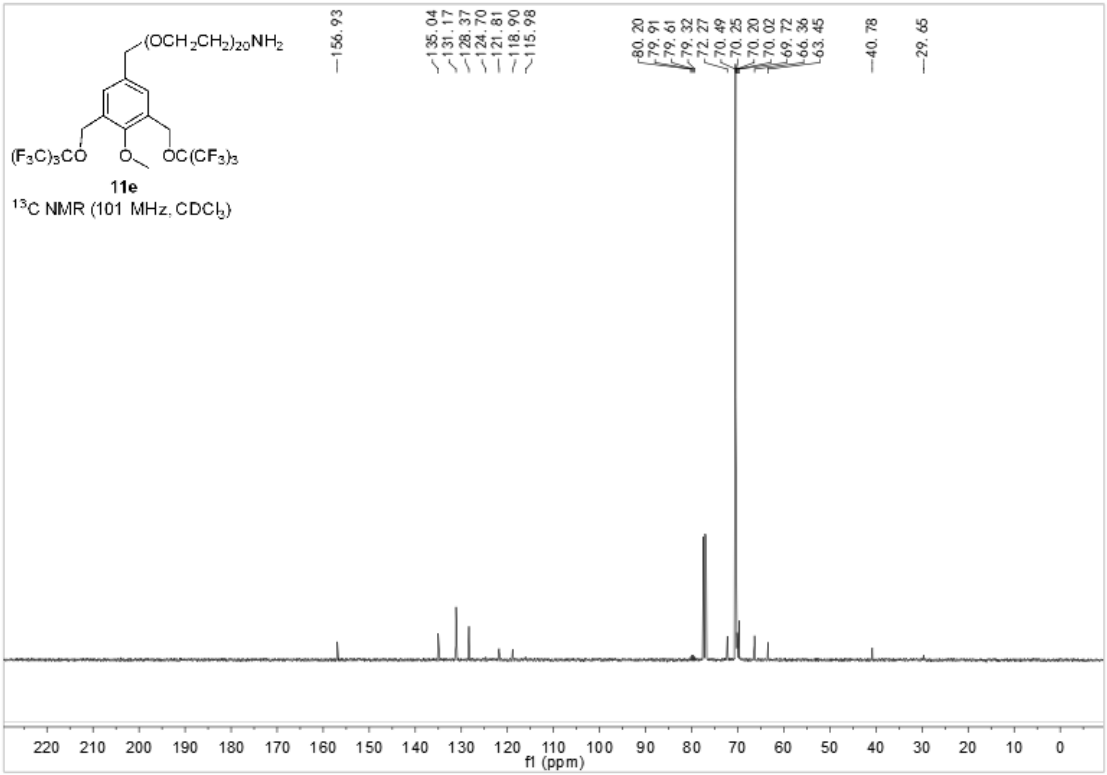


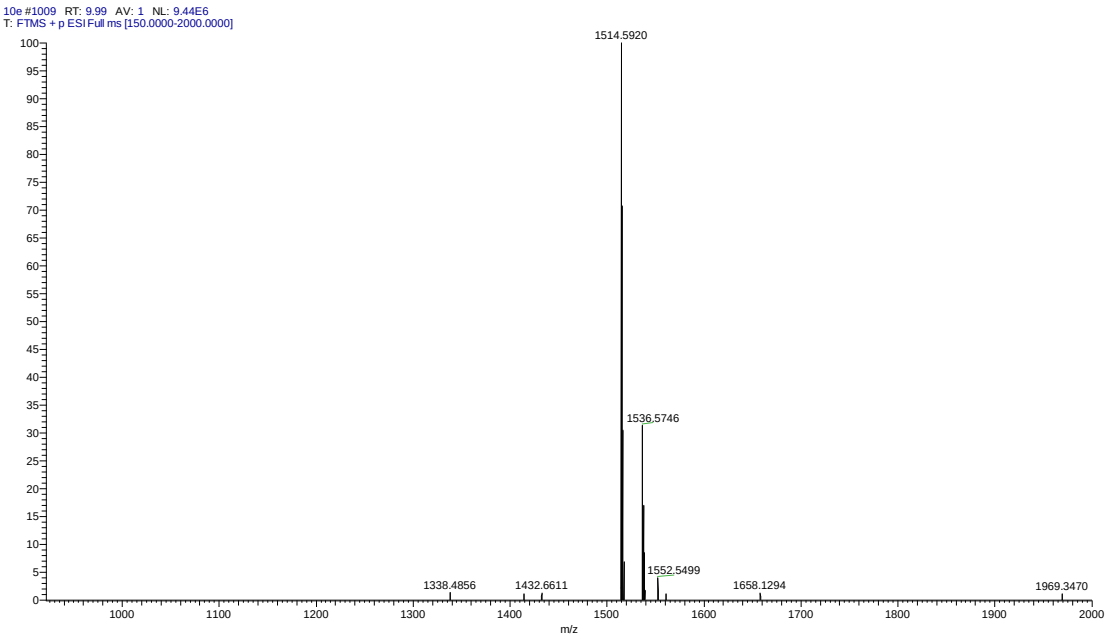
^{19}F NMR of compound **11e**



^{13}C NMR of compound **11e**



HRMS of compound **11e**



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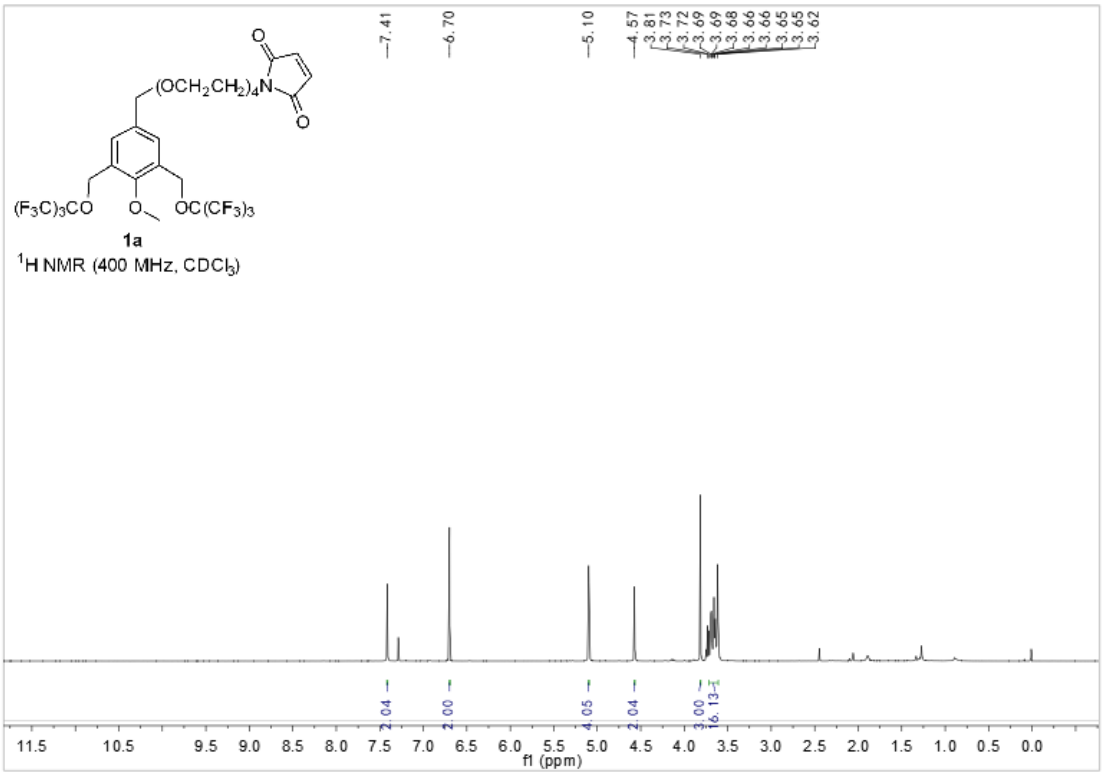

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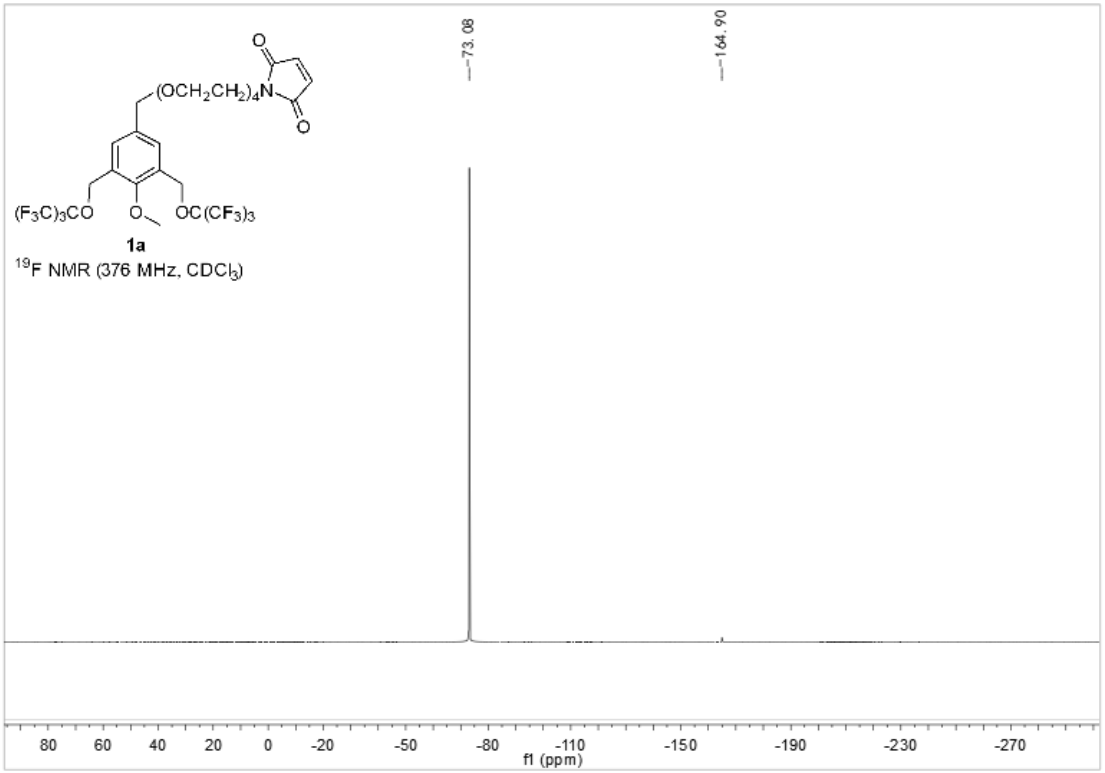

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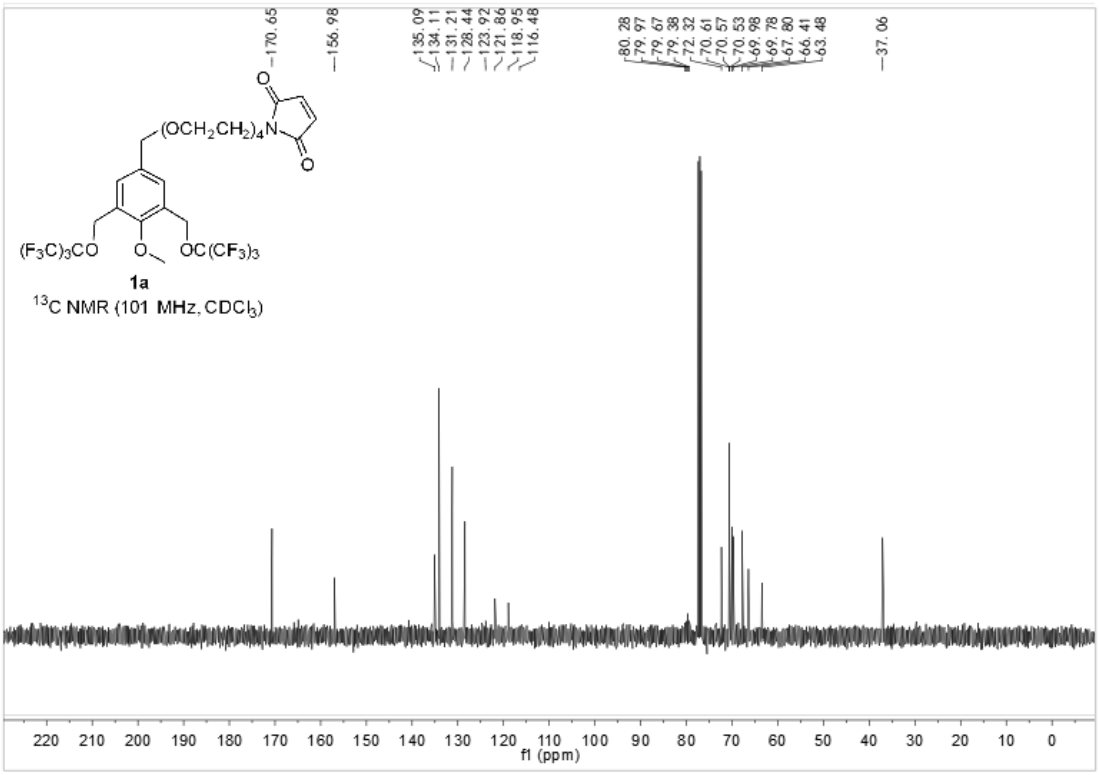
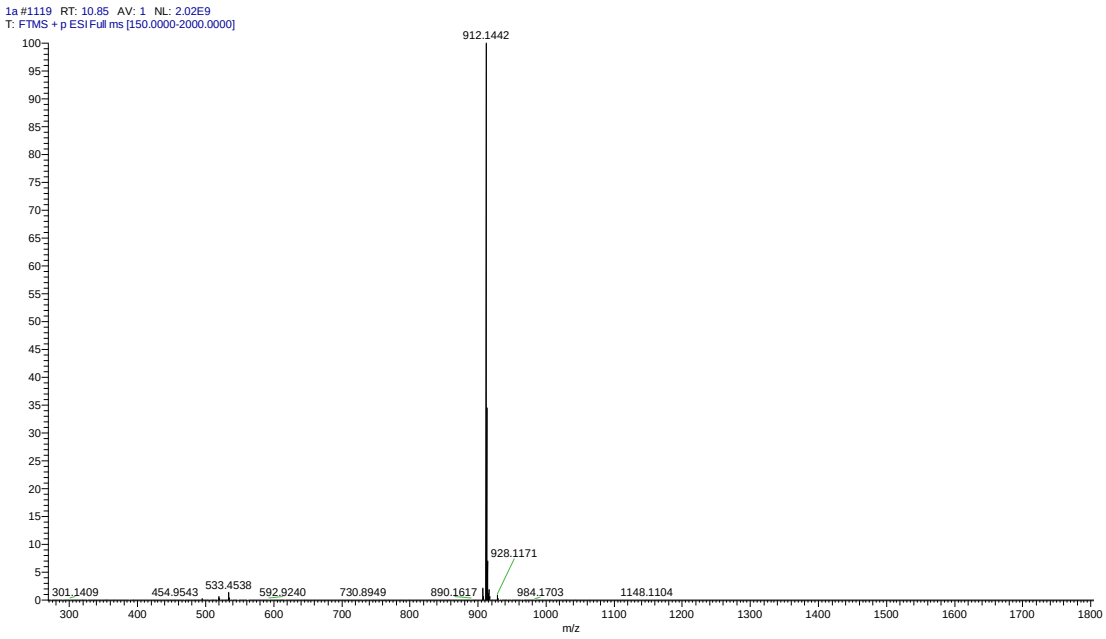
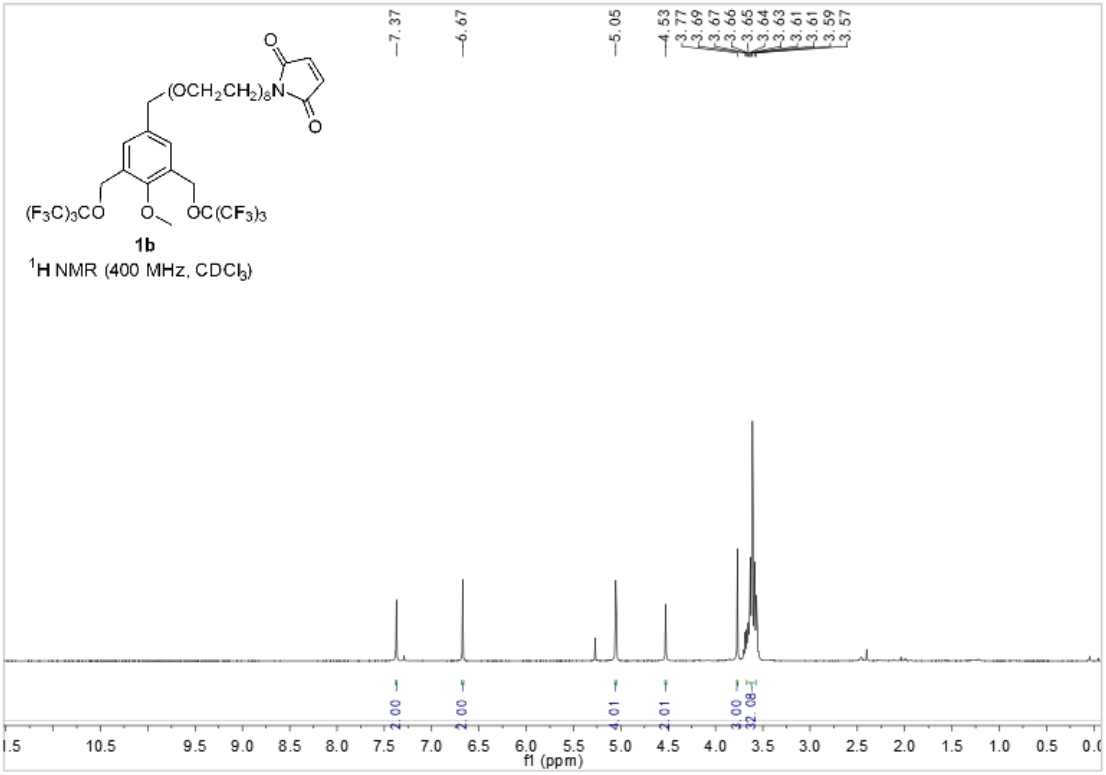


HRMS of compound **1a**



^{1}H NMR of compound **1b**



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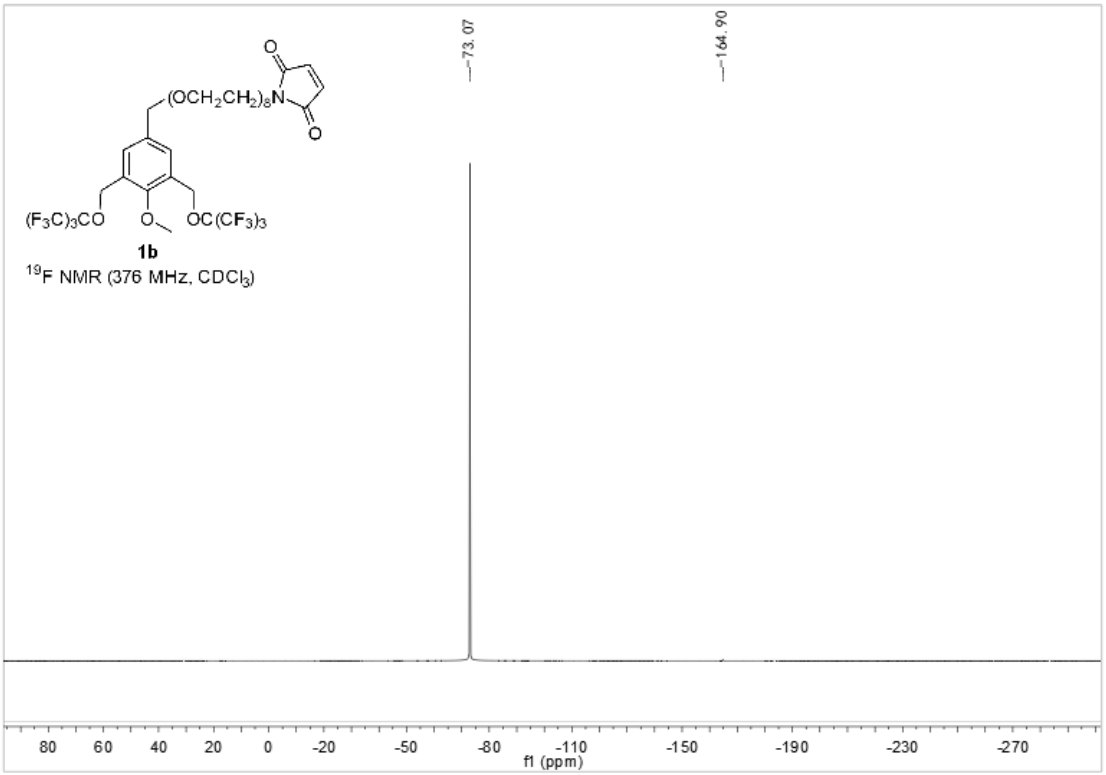

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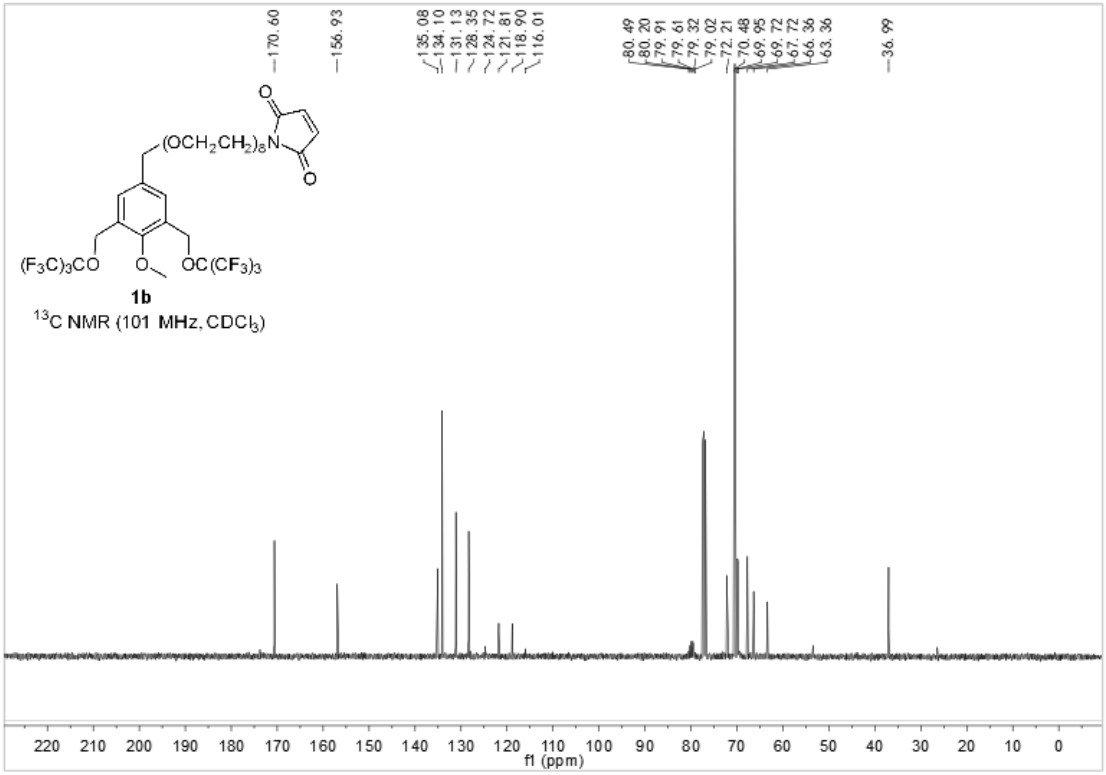
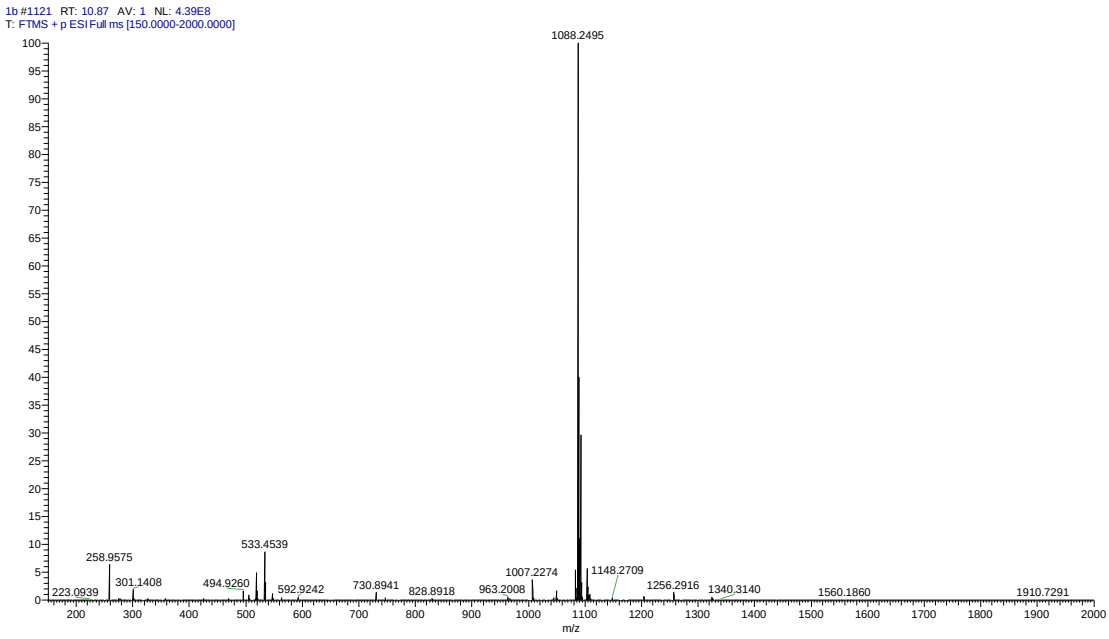


HRMS of compound **1b**



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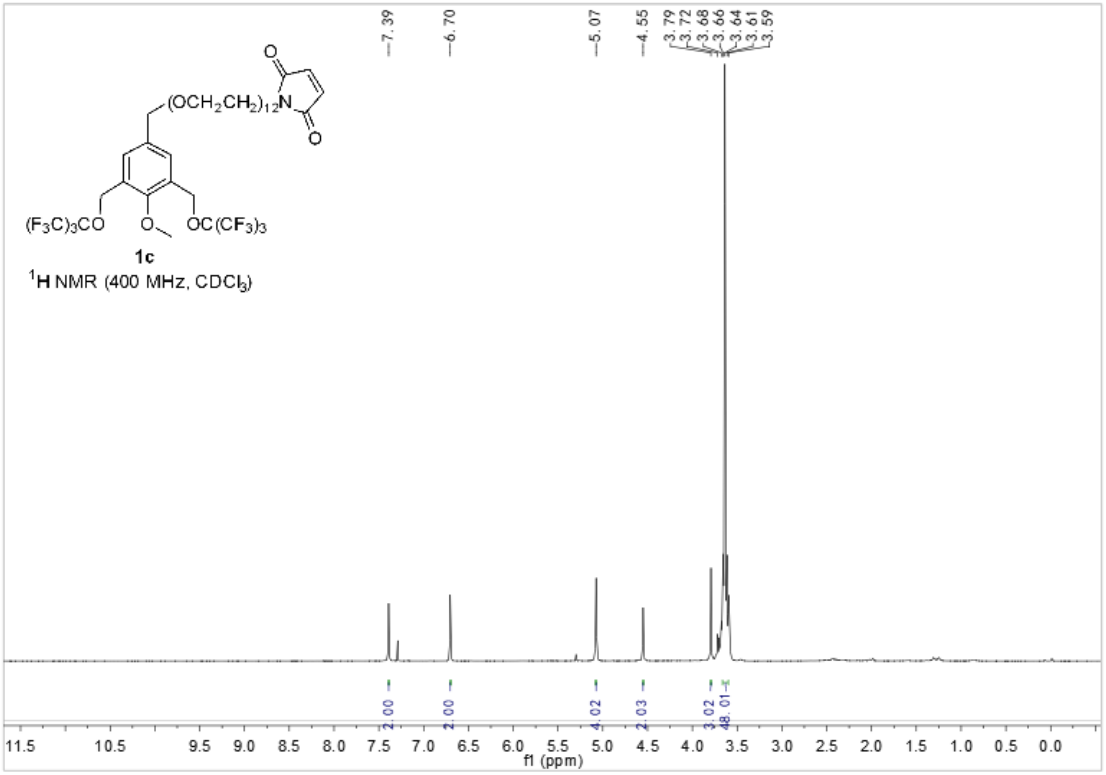

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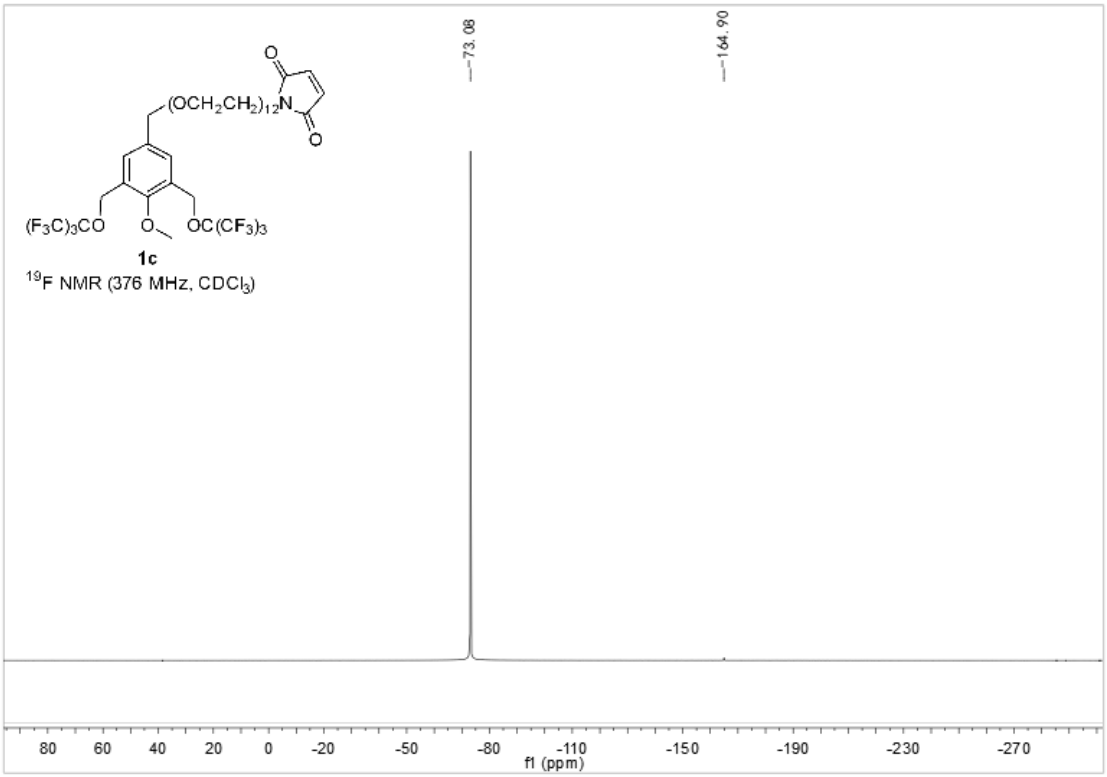

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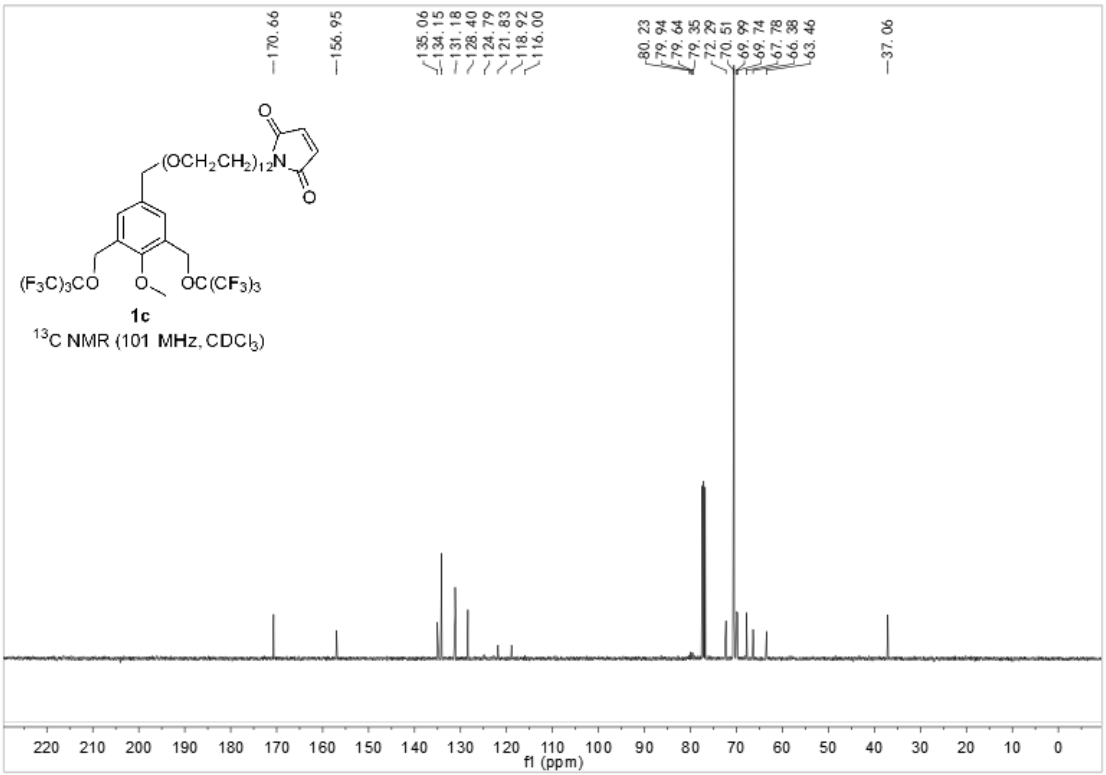

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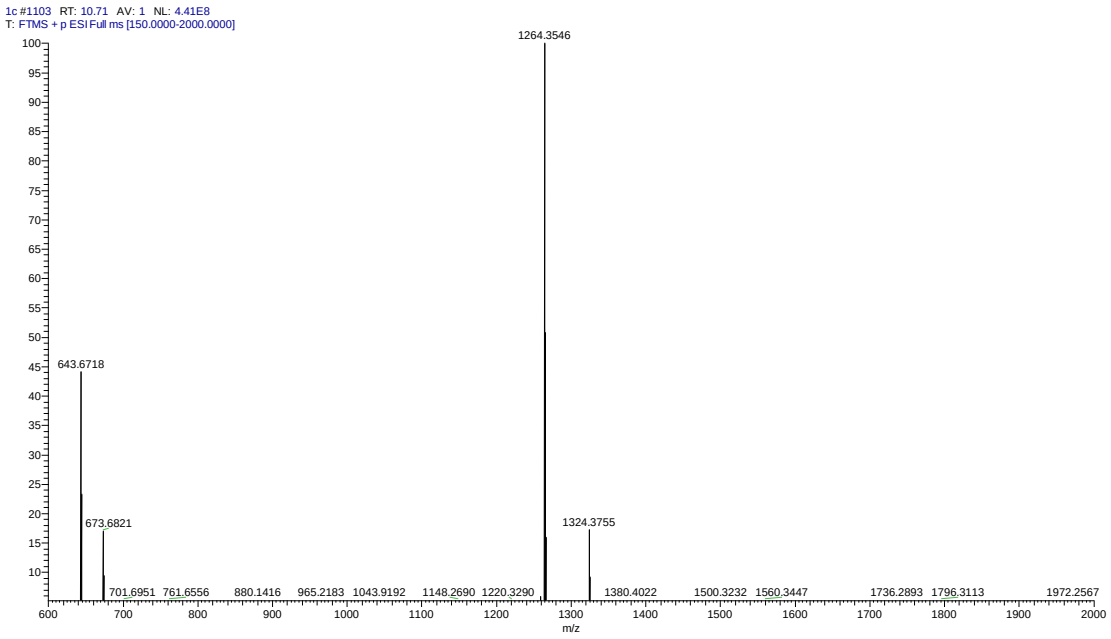
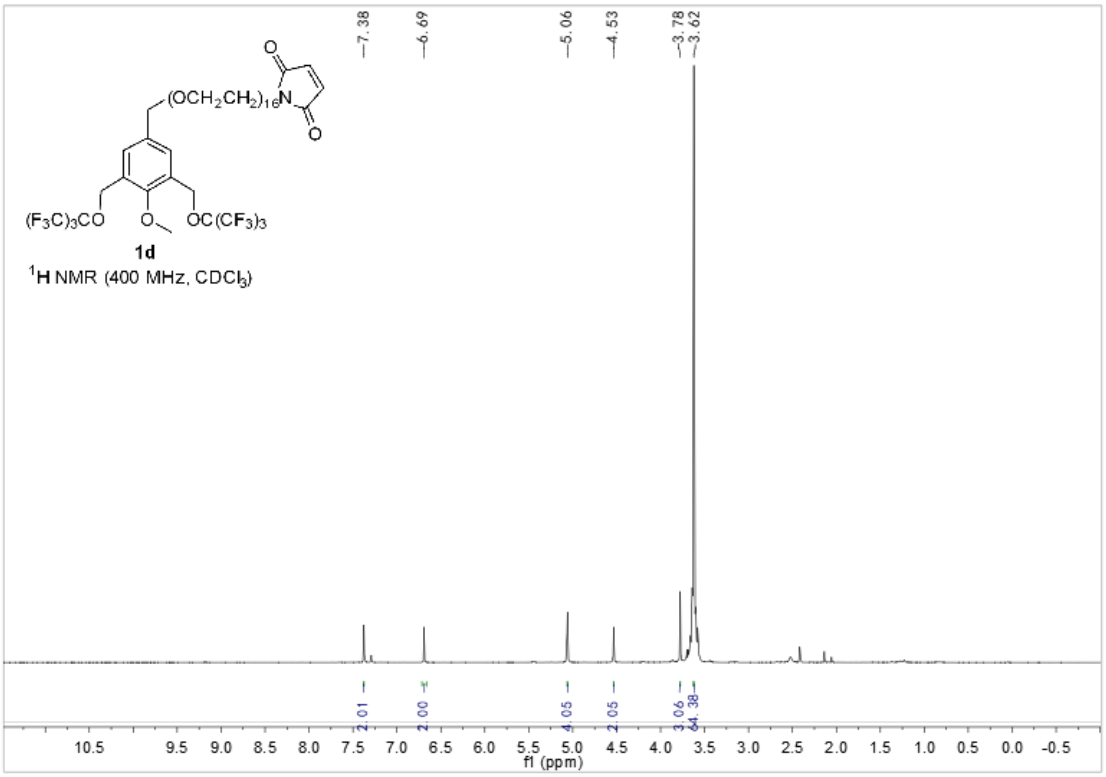


^{1}H NMR of compound **1d**



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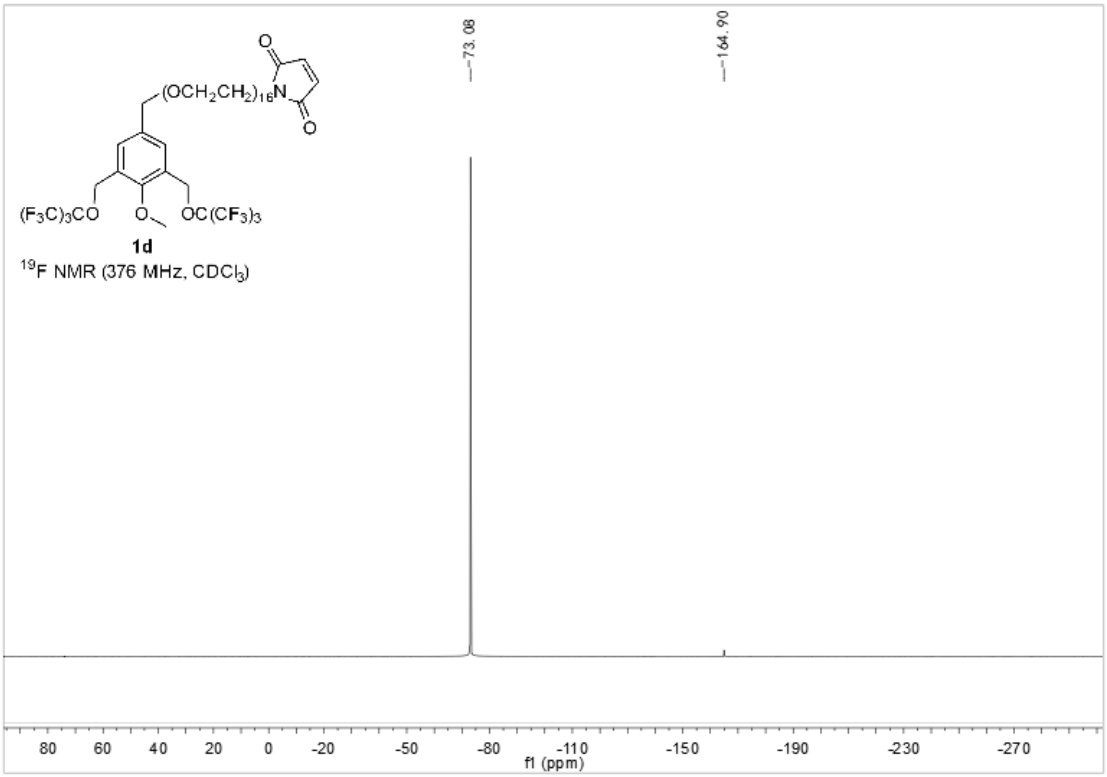

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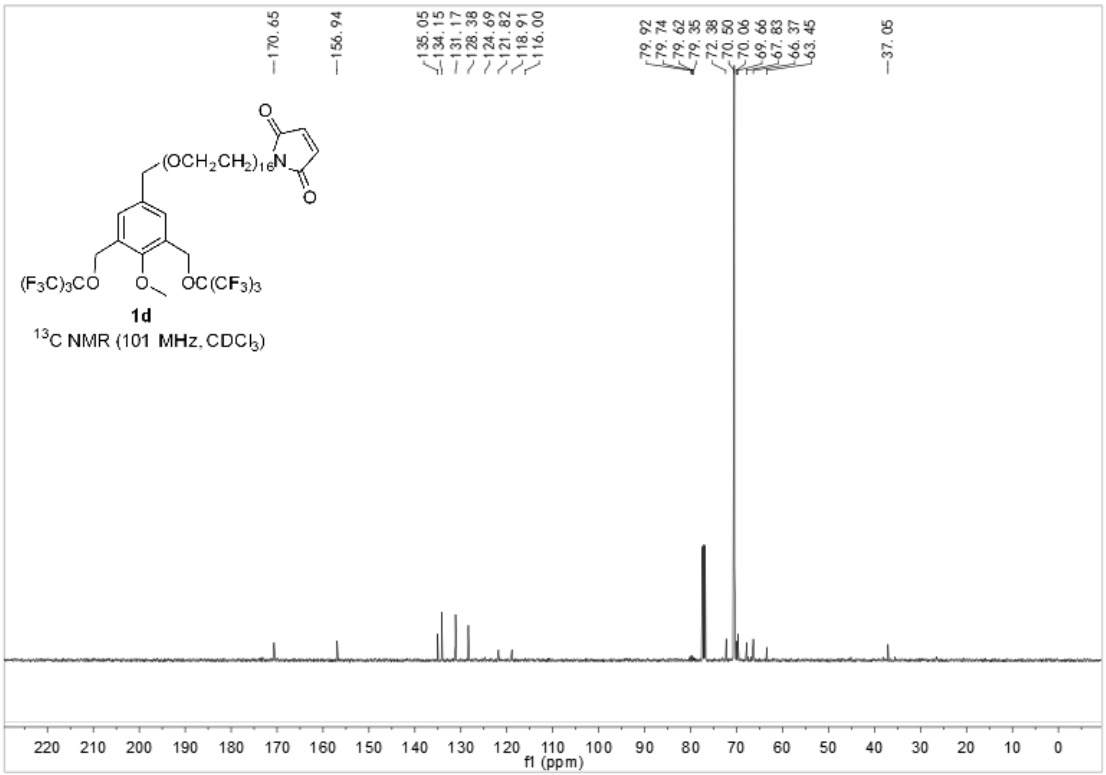
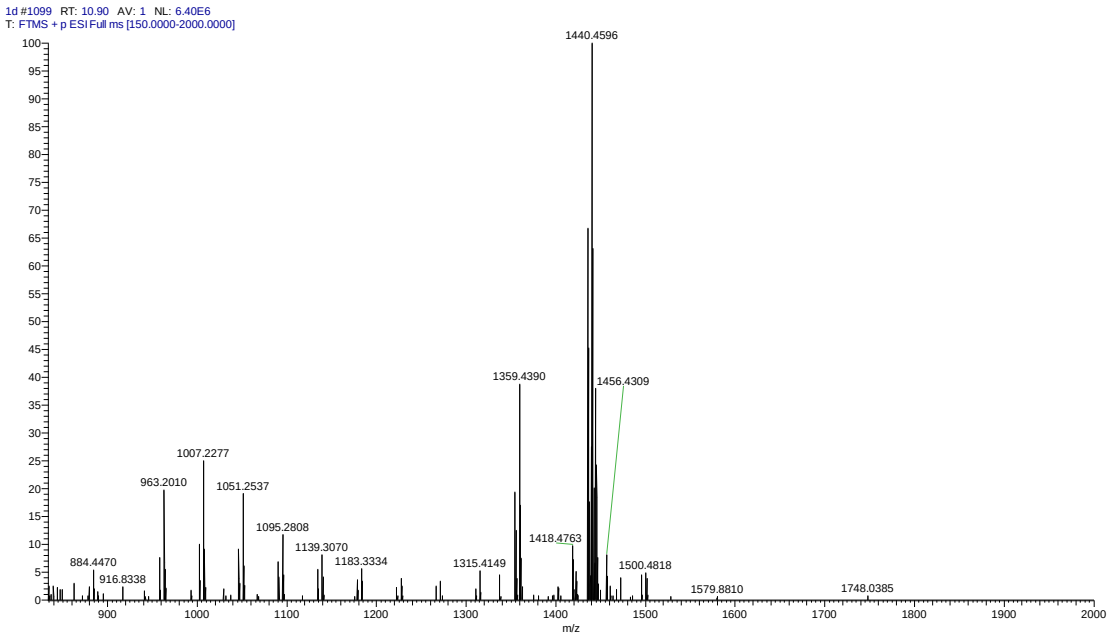
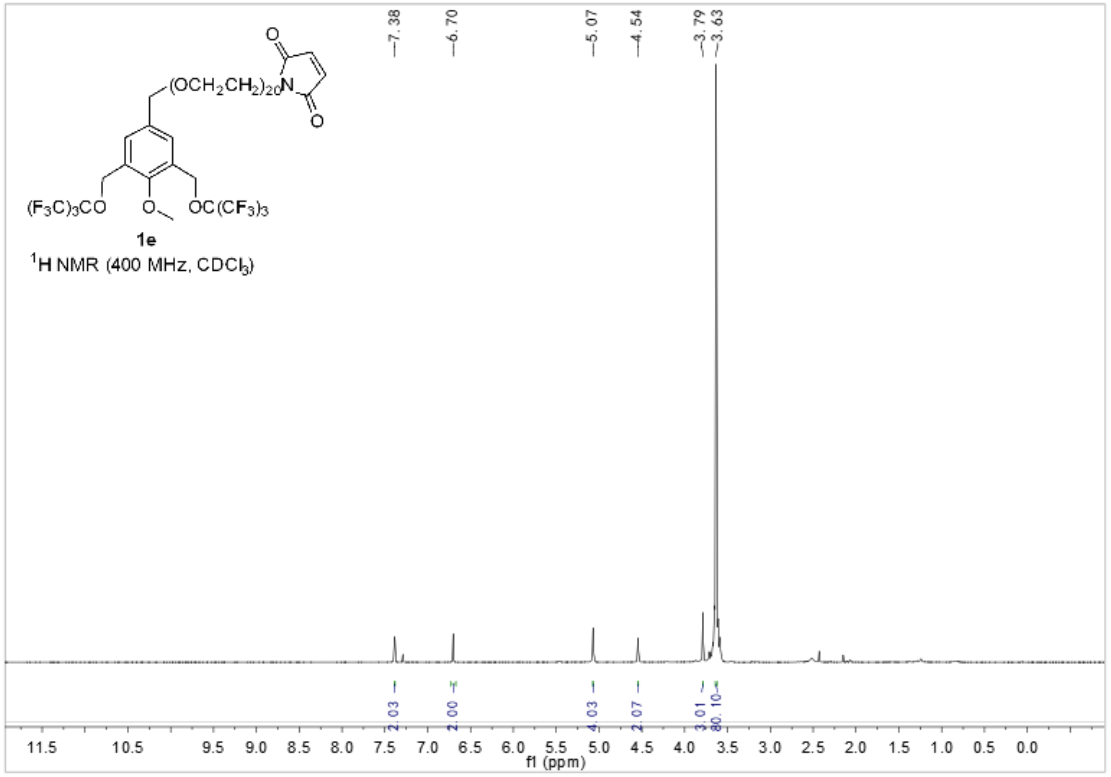


HRMS of compound **1d**



^{1}H NMR of compound **1e**



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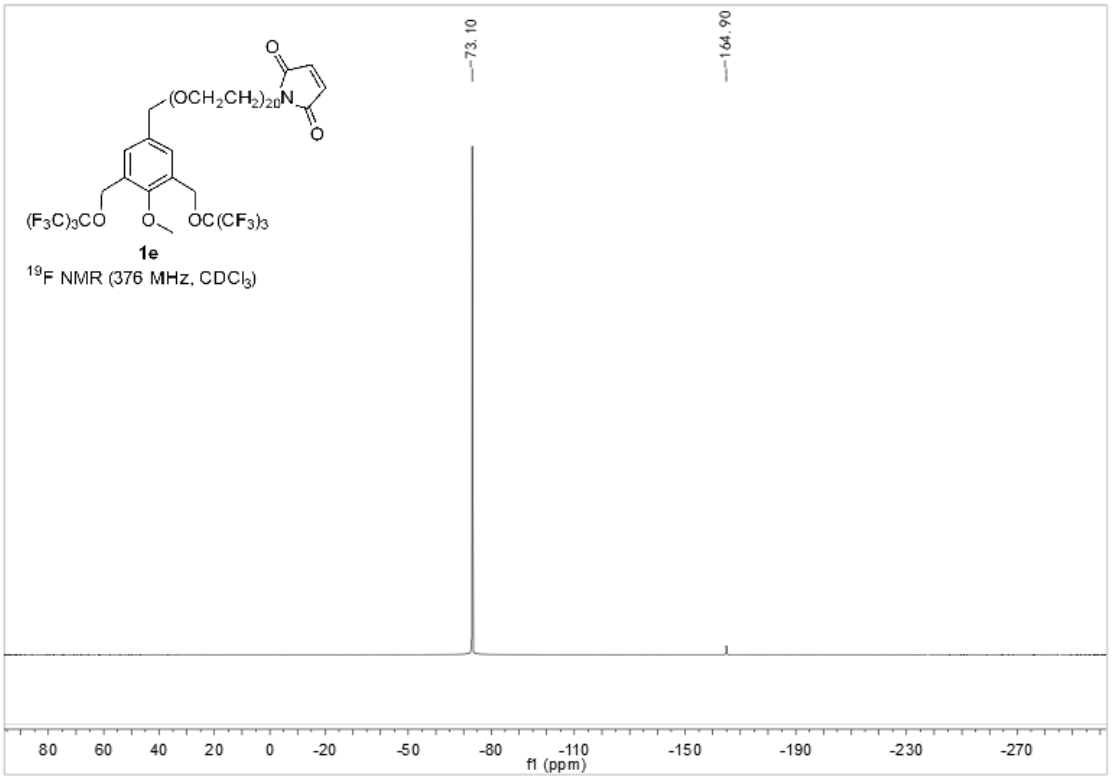

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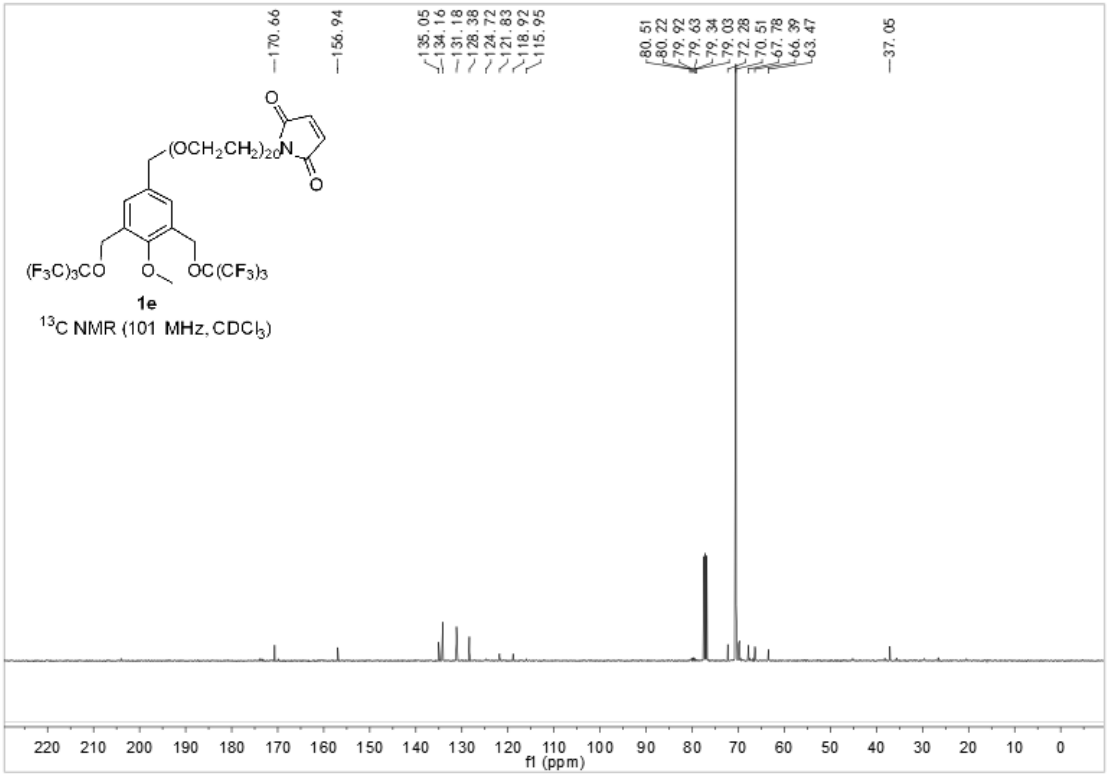

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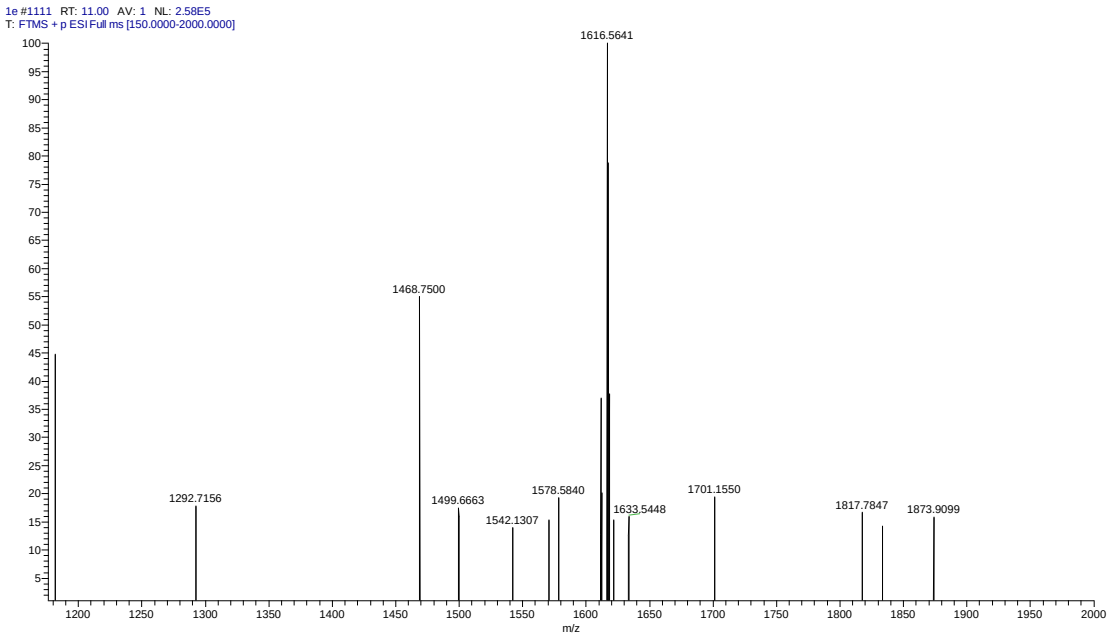
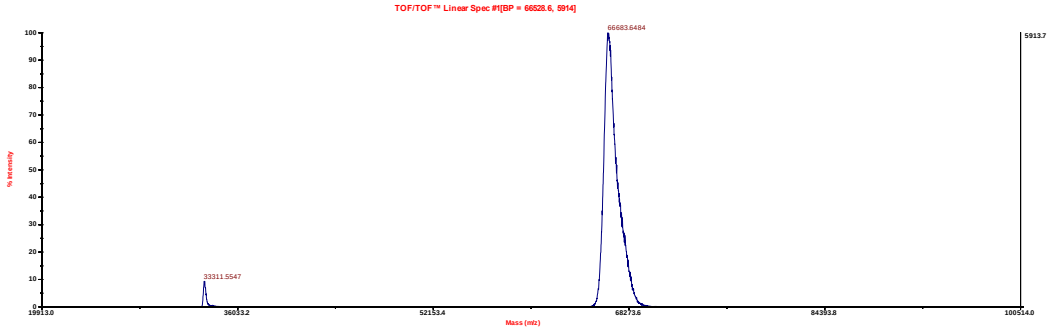
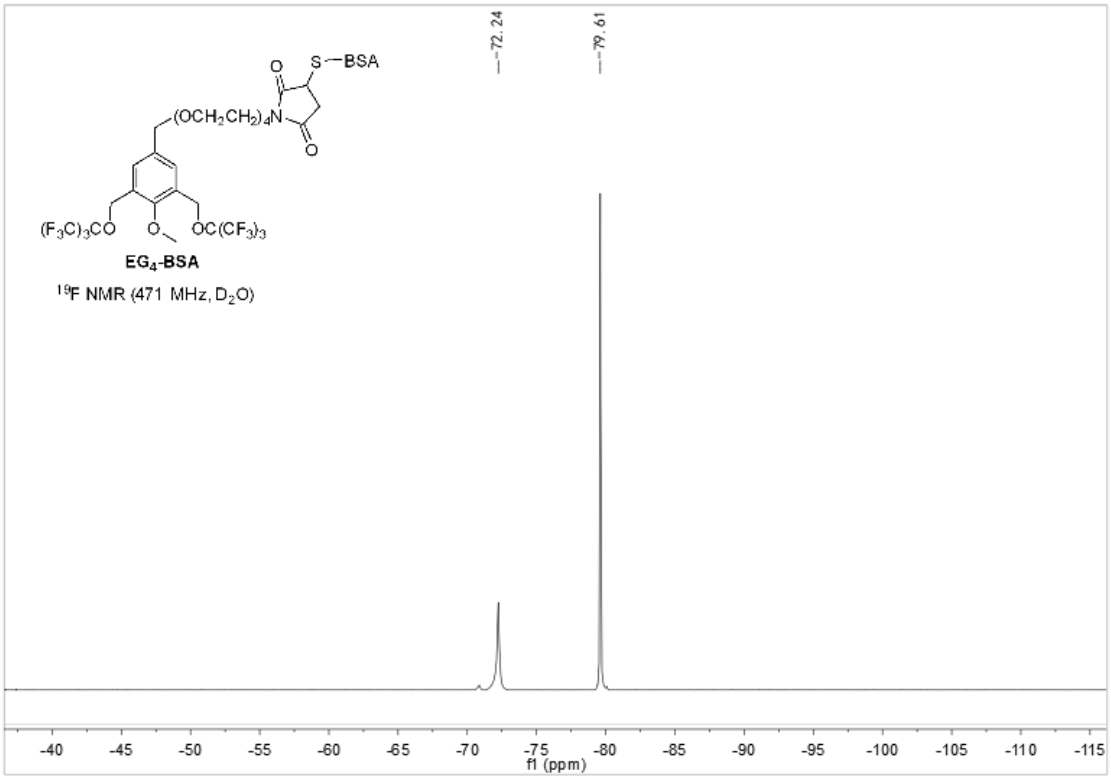


Maldi-Tof mass of BSA



^{19}F NMR of compound **EG$_4$-BSA**



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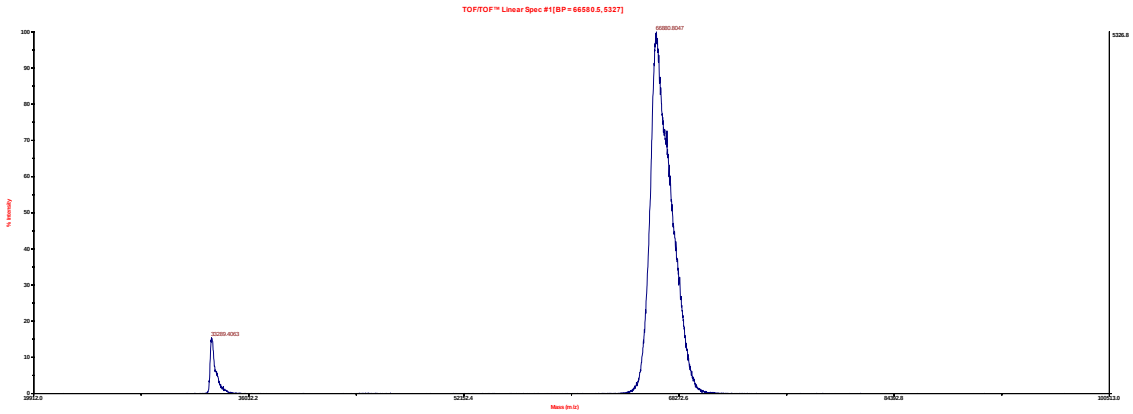
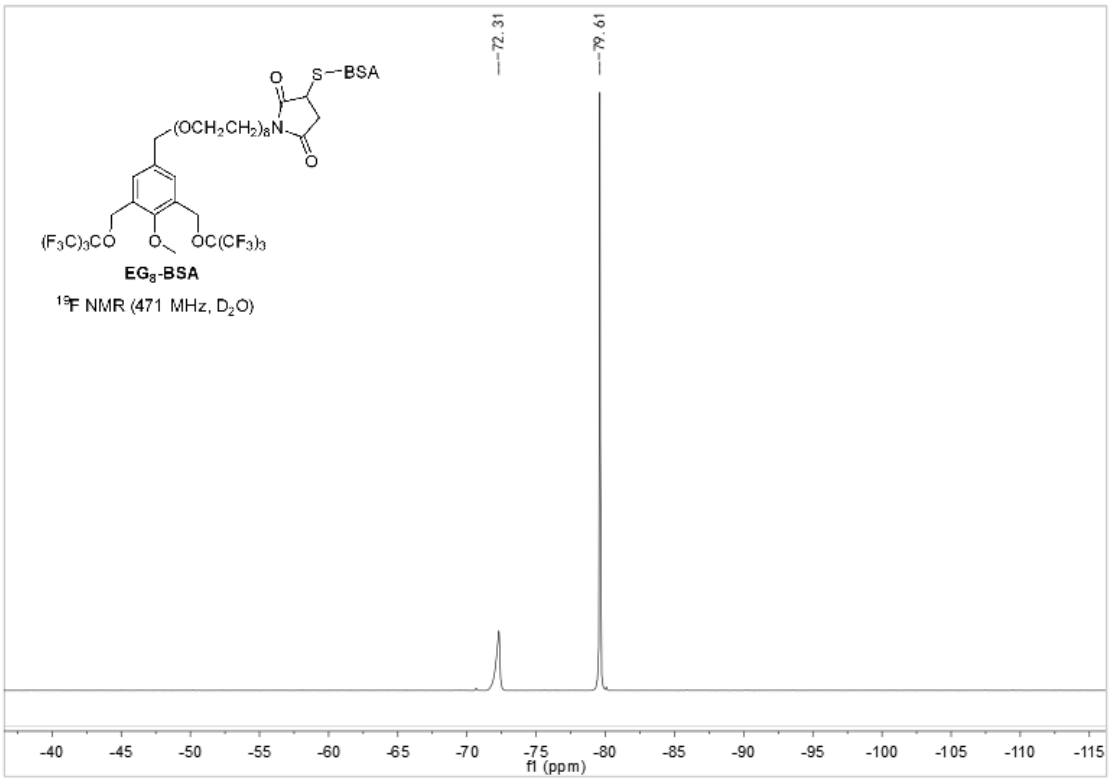
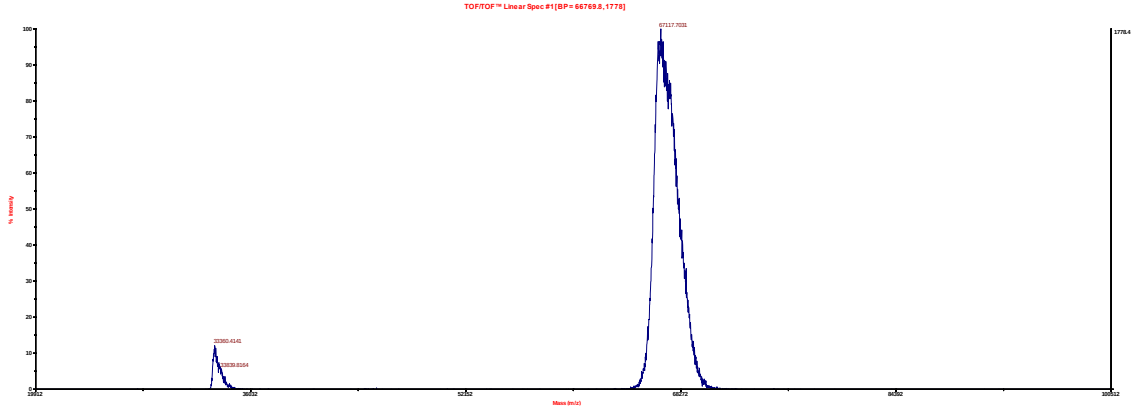


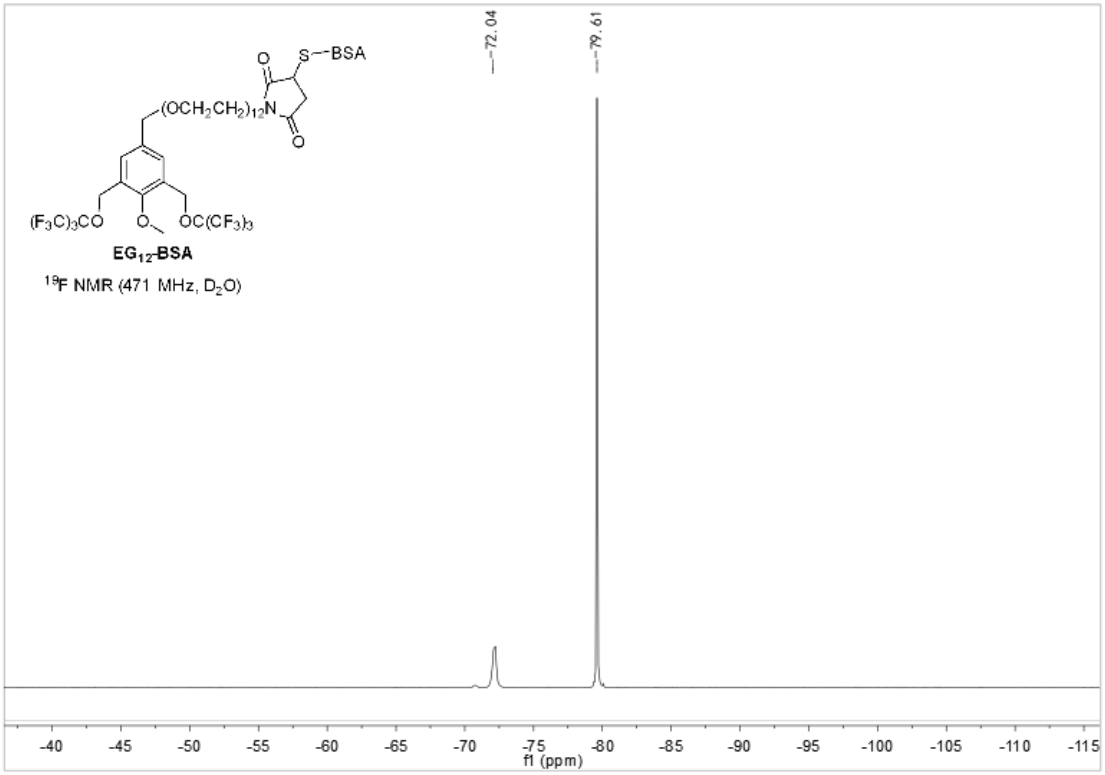
^{19}F NMR of compound **EG$_8$-BSA**



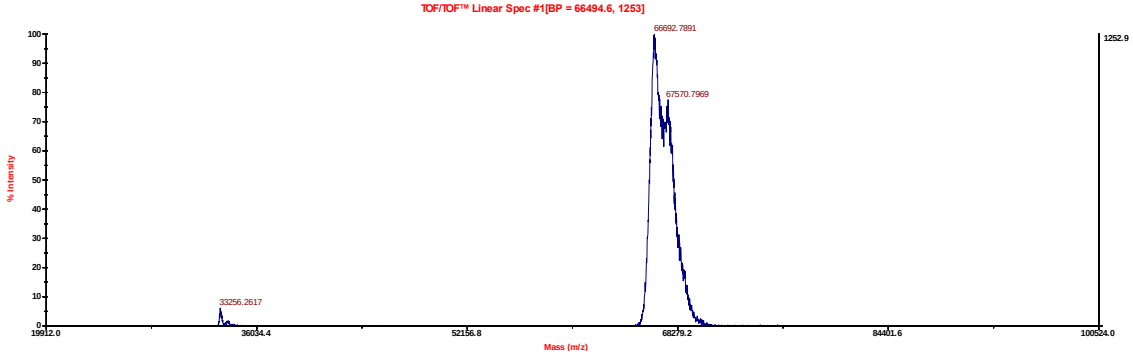
Maldi-Tof of mass compound **EG$_8$-BSA**



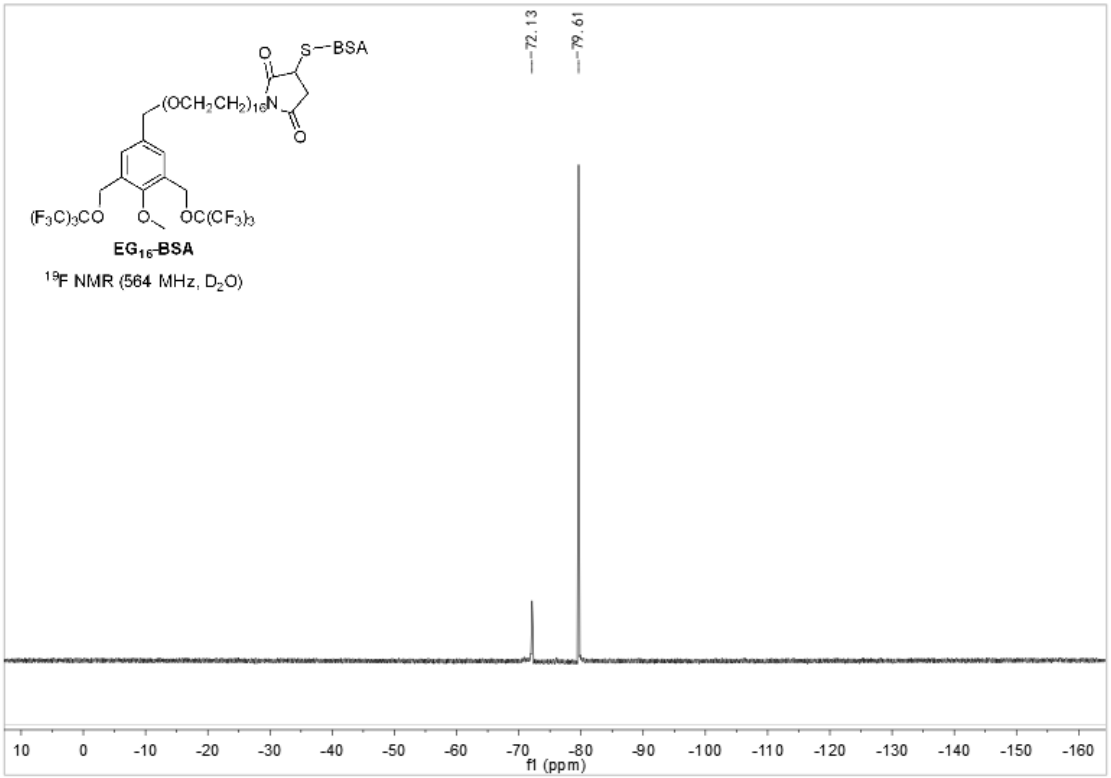
^{19}F NMR of compound **EG_{12}-BSA**



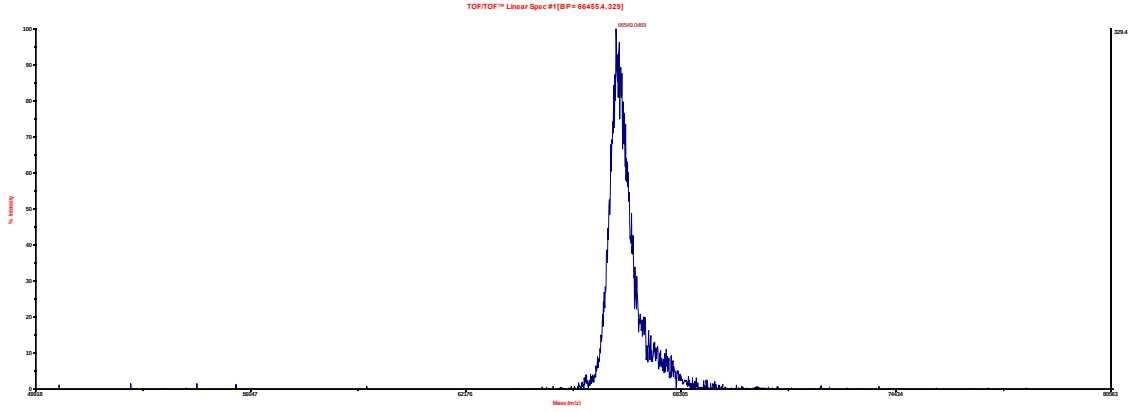
Maldi-Tof of mass compound **EG_{12}-BSA**



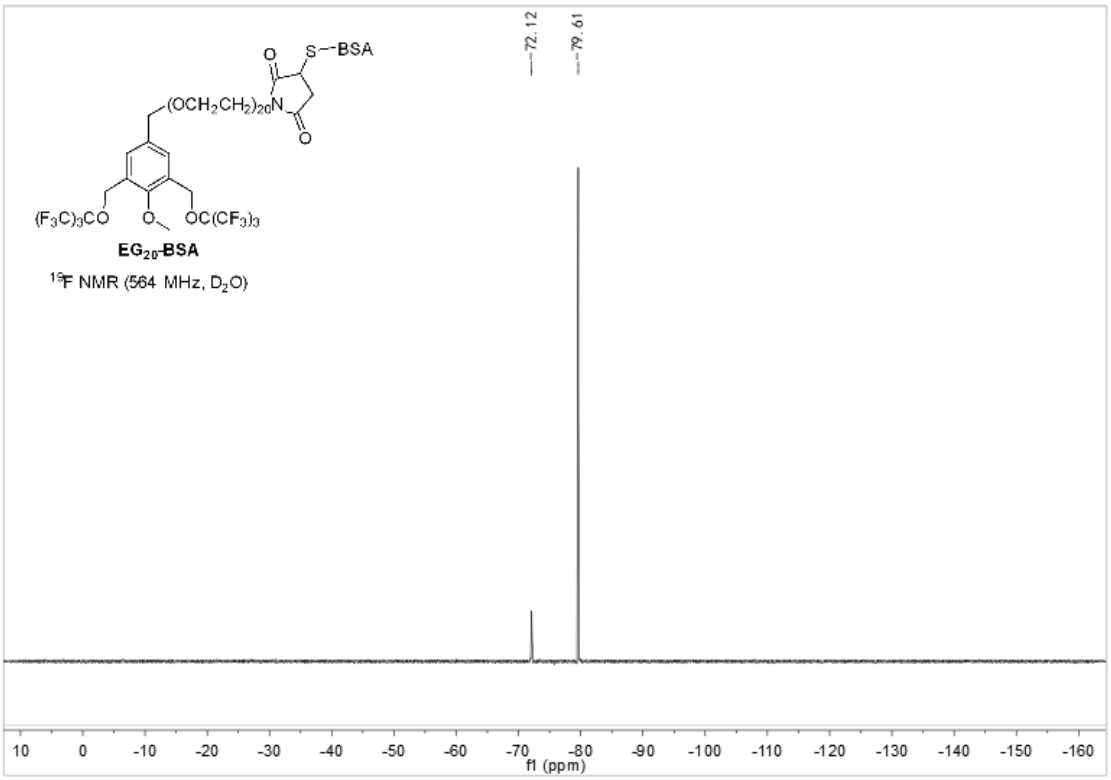
^{19}F NMR of compound **EG_{16}-BSA**



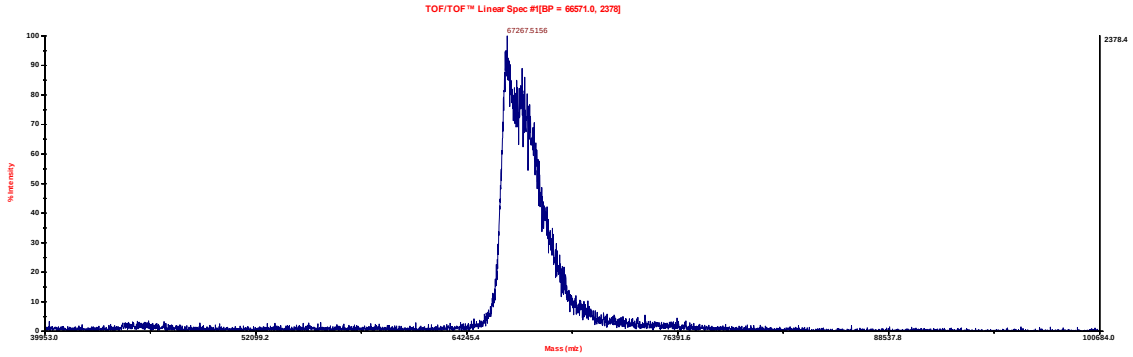
Maldi-Tof of mass compound **EG_{16}-BSA**



^{19}F NMR of compound **EG_{20}-BSA**



Maldi-Tof of mass compound **EG_{20}-BSA**



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