[1]Supporting Information

3- and 5-Functionalized BODIPYs Via The Liebeskind-Srögl Reaction

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Contents

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1. General Procedures

All reactions were carried out under a dry nitrogen atmosphere unless otherwise mentioned. All organic tin compounds were received from commercially available sources unless otherwise mentioned. DMF was purchased from ACROS (< 50 ppm water). Et_3N was distilled from CaH_2. THF was dried over alumina. Other solvents and reagents were used as received. NMR spectra were recorded on a VXP-300 MHz and Inova-500 MHz spectrometers (^1H at 300 MHz or 500 MHz, ^{13}C at 75 or 125 MHz, and 19F at 282 MHz) at room temperature unless other mentioned. Chemical shifts of ^1H NMR spectra were recorded and reported in ppm from the solvent resonance ($CDCl_3$ 7.26 ppm, CD_3OD 3.30 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Proton decoupled ^{13}C NMR spectra were also recorded in ppm from solvent resonance ($CDCl_3$ 77.16, CD_3OD 49.00 ppm). Proton decoupled ^{19}F NMR spectra were also recorded in ppm comparing the standard $BF_3 \bullet Et_2O$ resonance (CD_3COCD_3, 0.00 ppm). Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica-gel 60-F plates, and visualized with UV light. Flash chromatography was performed using silica gel (230–600 mesh). MS were measured under ESI, MALDI or APCI conditions. Some compounds were purified using preparative HPLC (Beckman Coulter, X Terra Prep-MS-C18 Column, 5mm, 19 x 160 mm) eluting with solvents A (H_2O with 0.1 % TFA) and B (CH_3CN with 0.1 % TFA).

Determination of Quantum Yields and Extinction Coefficients.

UV/Vis absorbance spectra were recorded on a Cary 100 Bio spectrophotometer. Steady-state fluorescence spectroscopic studies were performed on a Cary Eclipse fluorometer. The slit width was 5 nm for both excitation and emission. Fluorescence spectra were corrected for detector sensitivity. The relative quantum yields of the samples were obtained by comparing the area under the corrected emission spectrum of the test sample with that of a solution of standard. The quantum efficiencies of fluorescence were obtained from multiple measurements (N=3) with the following equation:

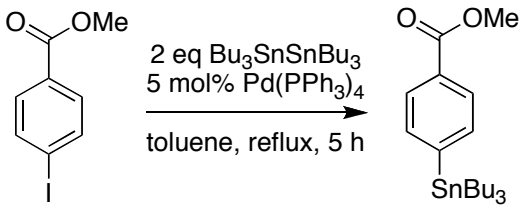
$$\mathbf{F_x = F_{st}\,(I_x/I_{st})\,(A_{st}/A_x)\,(\eta_x^2/\eta_{st}^2)}$$

Where $\mathbf{F_{st}}$ is the reported quantum yield of the standard, **I** is the area under the emission spectra, **A** is the absorbance at the excitation wavelength and $\boldsymbol{\eta}$ is the refractive index of the solvent used, measured on a pocket refractometer from ATAGO. **X** subscript denotes unknown, and **st** denotes standard. Extinction coefficients (ε) where measured from Beer's Law plots.

2. Synthesis and Characterization of Compounds 1-12

1 A mixture of **A** (310 mg, 0.75 mmol), n-butane thiol (0.17 mL, 1.55 mmol), Et_3N (0.22 mL, 1.58 mmol) was dissolved in try acetonitrile (15 mL), and then the solution was stirred at 85 ºC for 4 h. The solvent was removed under reduced pressure and the residue was purified by flash column eluting with 3:1 Hexane/ethyl acetate to afford the desired product (365 mg, 99 %) as a purple solid. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 4.5 Hz, 2H), 6.39 (d, *J* = 4.5 Hz, 2H); 3.06 (t, *J* = 7.5 Hz, 4H), 1.80-1.74 (m, 4H), 1.55-1.47 (m, 4H), 0.95 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 157.3, 146.8, 135.4, 132.9, 131.8, 131.6, 128.8, 124.2, 116.5, 32.5, 31.0, 21.9, 13.6. MS (MALDI) calcd for $C_{23}H_{26}BBrFN_2S_2^+$ (M-F), 503.08, found, 503.08. TLC (1:1 EtOAc-Hexane), R_f = 0.80.

4 A mixture of **B** (257 mg, 0.67 mmol), n-butylthiol (0.17 mL, 1.55 mmol), Et_3N (0.28 mL, 2.02 mmol) was dissolved in dry acetonitrile (15 mL), and then the solution was stirred at 85 ºC for 4 h. The solvent was removed under reduced pressure and the residue was purified by flash silica gel column eluting with 3:1 hexane/ethyl acetate to afford the desired product (326 mg, 99 %) as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 4.4 Hz, 2H), 6.41 (d, *J* = 4.4 Hz, 2H); 3.08 (t, *J* = 7.4 Hz, 4H), 1.82-1.72 (m, 4H), 1.57-1.45 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 158.3, 148.5, 140.5, 135.1, 133.3, 131.2, 128.5, 123.5, 116.8, 32.5, 30.8, 21.9, 13.6. MS (ESI) calcd for $C_{23}H_{26}BF_2N_3O_2S_2^-$ (M^-), 489.15, found 489.28.



12 Methyl 4-iodobenzoate (300 mg, 1.15 mmol), bistributyltin (1.15 mL, 2.29 mmol) and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) was degassed by vaccum/nitrogen cycles (three times), then degassed toluene (12mL) was added into the flask. The reaction mixture was heated to 120 ºC for 5 h. The solvent was removed under reduced pressure and the

product was purified by silica gel chromatography eluting with 50:1 hexane/EtOAc to afford the product as colorless oil (330 mg, 70 %). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 1.57 - 1.51 (m, 6H), 1.37 - 1.30 (m, 6H), 1.10 - 1.07 (t, *J* = 9.0 Hz, 6H), 0.88 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 167.5, 149.6, 136.4, 129.5, 128.3, 52.0, 29.0, 27.3, 13.6, 9.6. HRMS (ESI) calcd for $C_{20}H_{34}BO_2SnLi^+$ $(M+Li)^+$, 433.16, found, 433.09. TLC (1:4 EtOAc/Hexane), R_f = 0.80.

General Procedure for the Liebeskind-Srogl Coupling

The BODIPY substrate (1 eq), organotin reagent (3-6 eq), CuMeSal (4 eq) and $Pd(PPh_3)_4$ (5 mol %) were added to a round bottom flask. After 3 vacuum/nitrogen cycles, degassed THF was added into the flask. The mixture was stirred for 16 h at 55 ºC under nitrogen and the reaction was monitored by TLC. After completion, the solvent was removed under reduced pressure and ethyl acetate was added. The mixture was filtered, and the filtrate was concentrated in *vacuo*. The residue was purified by silica gel flash column.

2b Purple solid (26 %). ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 4.7 Hz, 1H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.61(d, *J* = 4.2 Hz, 1H), 6.51 (d, *J* = 4.7 Hz, 1H), 3.94 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H), 1.82-1.72 (m, 2H), 1.56-1.44 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), d 166.9, 162.5, 154.0, 138.4, 137.2, 136.1, 135.8 132.9, 131.9, 131.7, 131.4, 130.0, 129.5, 129.2, (t, J = 15.5 Hz), 127.9, 124.6, 119.3, 118.2, 52.2, 32.4, 30.9, 21.9, 13.5. MS (ESI) calcd for $C_{27}H_{25}BBrF_2N_2O_2S$ $(M+H)^+$ 568.08, found, 569.09, 571.08. ^{19}F NMR (282 MHz, $CDCl_3$), 32.1 (q, *J* = 33.6 Hz). TLC (1:1 EtoAc/Hexane) R_f = 0.50.

3a Red solid (85 %) ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.87 (dd, *J* = 7.5 Hz, 2.3Hz, 4 H), 7.69 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.44-7.41 (m, 6H), 6.86 (d, *J* = 4.3 Hz, 2H), 6.64 (d, *J* = 4.3 Hz, 2H), ^{13}C NMR (125 MHz, CDCl3), δ 159.3, 142.3, 136.2, 133.2, 132.4, 132.0, 131.6, 130.6, 129.6, 129.4 (t, *J* = 17.0 Hz), 128.2, 124.7, 121.2. ^{19}F

NMR (282 MHz, $CDCl_3$), 40.5 (q, *J* = 50.2 Hz), MS (ESI) calcd for $C_{27}H_{18}BBrF_2N_2Li^+$ $(M+Li)^+$, 505.07, found, 505.08, 507.08. TLC (1:2 EtOAc/Hexane), R_f = 0.80.

3b Red-purple solid (62%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.09 (d, *J* = 9.0 Hz, 4H), 7.92 (d, *J* = 9.0 Hz, 4H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 4.5 Hz, 2H), 6.70 (d, *J* = 4.5 Hz, 2H), 3.93 (s, 6H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 166.6, 158.1, 143.8, 136.5, 132.8, 132.0, 131.8, 131.1, 130.8, 129.5, 129.4 (t, *J* = 15.0 Hz), 125.1, 121.4, 52.2. MS (MALDI) calcd for $C_{31}H_{22}BBrF_2N_2O_4Na$ $(M + Na)^+$, 637.08 found 637.24, 639.24. TLC (1:3 EtOAc/Hexane), R_f = 0.35.

3c Purple solid (72 %) ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.88 (d, *J* = 9.0 Hz, 4 H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 4 H), 6.81 (d, *J* = 4.5 Hz, 2H), 6.62 (d, *J* = 4.5 Hz, 2H), 3.85 (s, 6H), ^{13}C NMR (125 MHz, CDCl3), δ 160.8, 158.6, 140.6, 135.9, 133.4, 132.0, 131.5, 131.1 (t, *J* = 18.0 Hz), 130.1, 125.0, 124.4, 120.7, 113.8, 55.3. ^{19}F NMR (282 MHz, $CDCl_3$), 20.1 (q, *J* = 32.5 Hz), MS (ESI) calcd for $C_{29}H_{23}BBrF_2N_2O_2^+$ $(M+H)^+$, 559.09, found, 559.15, 561.15. TLC (1:3 EtOAc/Hexane), R_f = 0.25.

5 Purple solid (17 %). ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.38 (d, *J* = 8.5 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 4.5 Hz, 1H), 6.64 (d, *J* = 4.5 Hz, 1H), 6.62 (d, *J* = 4.0 Hz, 1H), 6.55 (d, *J* = 4.5 Hz, 1H), 3.94 (s, 3H), 3.11 (t, *J* = 7.0 Hz, 2H), 1.80-1.74 (m, 2H), 1.54-1.47 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 166.8, 163.9, 154.6, 148.7, 140.4, 136.9, 136.3, 136.1, 135.4, 131.3, 131.0, 130.2, 129.5, 129.2 (t, *J* = 16.0 Hz), 127.6, 123.6, 119.7, 118.7, 52.2, 32.5, 30.9, 21.9, 13.5. MS (ESI) calcd for $C_{27}H_{24}BF_2N_3O_4SLi^+$ $(M+Li)^+$, 542.15, found, 542.15. TLC (1:3 EtOAc/Hexane), R_f = 0.45.

6 Purple solid (68%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.44 (d, *J* = 8.5 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 4H), 7.94 (d, *J* = 8.5 Hz, 4H), 7.80 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 4.3 Hz, 2H),

6.73 (d, J = 4.3 Hz, 2H), 3.94 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 166.5, 158.9, 148.9, 140.7, 140.2, 136.2, 136.1, 131.4, 131.0, 130.8, 129.5, 129.4 (t, J = 15 Hz), 123.6, 121.9, 52.3. ^{19}F NMR (282 MHz, $CDCl_3$), 40.9 (q, J = 33.6 Hz). MS (ESI) calcd for $C_{31}H_{22}BF_2N_3O_6Li^+$ $(M+Li)^+$, 588.16, found, 588.18.

7 Dimethyl ester **6** (32 mg, 0.06 mmol) was dissolved in 3 mL THF at room temperature. Then potassium trimethylsilanolate (30 mg, 0.23 mmol) was added to the reaction mixture. The reaction was complete in 6 h as indicated by TLC. Aqueous HCl (0.1 M, 10 mL) was added and the product was extracted out of water with 1:2 isopropyl alcohol/CH_2Cl_2 (10 mL x 2). The organic solvent was dried over $MgSO_4$ and then removed under reduced pressure to afford the desired product as a red solid (29 mg, 95 %). ^{1}H NMR (300 MHz, CD_3OD), δ 8.42 (d, J = 8.9 Hz, 2H), 7.98 (d, J = 8.4 Hz, 4H), 7.85 (d, J = 8.4 Hz, 4H), 7.81 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 4.5 Hz, 2H), 6.71 (d, J = 4.5 Hz, 2H). ^{19}F NMR (282 MHz, CD_3OD), 43.8 (q, J = 30.6 Hz). HRMS (ESI) calcd for $C_{29}H_{17}N_3O_6^-$ $(M-H)^-$ 552.1178, found 552.1174. This compound is not very soluble in organic solvent, so ^{13}C could not be obtained. 1:2 Hexane/EtOAc, R_f = 0.75.

8 The crude product obtained above, Pd/C (5 mg, 0.005 mmol) and hydrazine monohydrate (0.05 mL) were suspended in ethanol (2 mL). The reaction mixture was heated to 82 ºC for 25 min. The reaction solution was passed through celite, and the solvent was removed under reduced pressure to afford desired product as a dark red solid 26 mg (95 %). ^{1}H NMR (300 MHz, CD_3OD 1:2), δ 7.98 (d, J = 8.9 Hz, 4H), 7.85 (d, J = 8.9 Hz, 4H), 7.43 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 4.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 4.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 180.2, 158.1, 153.2, 137.5, 136.0, 134.2, 133.0, 131.8, 130.0, 129.9, 129.7, 123.9, 121.5, 115.1. ^{19}F NMR (282 MHz, $CDCl_3$), 43.8 (q, J = 30.5 Hz). HRMS (ESI) calcd for $C_{29}H_{19}N_3O_4^-$ $(M - H)^-$ 522.1437, found 522.1434.

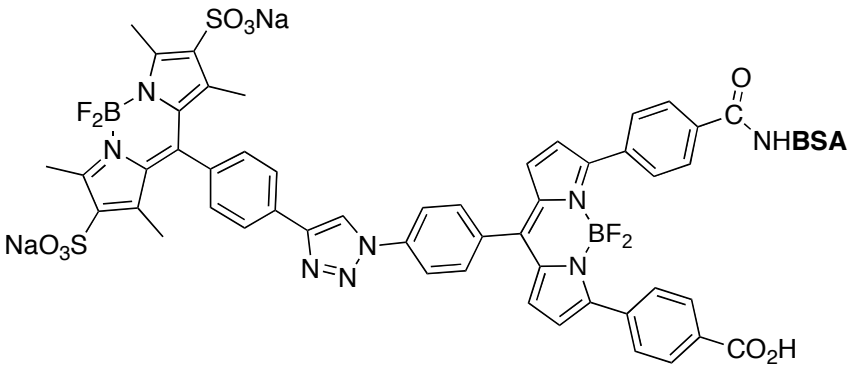
9 A solution of **8** (18 mg, 0.034 mmol) in HCl (0.1 M, 2.5 mL) and HTF (2.5 mL) was cooled to 0 ºC. A solution of $NaNO_2$ (5 mg, 0.072 mmol) in H_2O (0.25 ml) was added slowly and the mixture was kept at 0 ºC with stirring for 30 min. A solution of NaN_3 (21

mg, 0.34 mmol) in H_2O (0.35 mL) was then added dropwise to the mixture. Stirring was continued at room temperature for 16 h after completion of the addition. The reaction mixture was acidified with HCl (0.1 M) carefully, then the product was extracted out of the water using 1:2 ^{i}PrOH/CH_2Cl_2. The product was achieved after removing the solvent under reduced pressure as a red solid (14 mg, 75 %). ^{1}H NMR (500 MHz, 2:1 $CD_3OD/CDCl_3$), δ 8.06 (d, *J* = 8.5 Hz, 4H), 7.91 (d, *J* = 8.5 Hz, 4H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 4.0 Hz, 2H), 6.74 (d, *J* = 4.0 Hz, 2H), ^{19}F NMR (282 MHz, 2:1 $CD_3OD/CDCl_3$), δ 44.6 (q, *J* = 33.6 Hz). HRMS (ESI) calcd for $C_{29}H_{17}BF_2N_5O_4^-$ $(M - H)^-$, 548.1342, found 548.1339.

10 A solution of chlorosulfonic acid (23 μL, 0.35 mmol) in 2.0 mL of dry CH_2Cl_2 was added dropwise to a solution of BODIPY **C** (50 mg, 0.14 mmol) in dry CH_2Cl_2 over 10 min under N_2 at -40 ºC. The solution was slowly warmed to room temperature and an orange precipitate was formed. The disulfonic acid was neutralized with triethylamine (48 μL, 0.35 mmol) and the solvent was removed under reduced pressure. The resulting salt was purified by reverse phase preparative-HPLC (gradient: 5% solvent B to 95% solvent B, 25 min) to afford the desired product as an orange solid (45 mg, 60 %). ^{1}H NMR (500 MHz, CD_3OD), δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 3.68 (s, 1H), 3.19 (q, *J* = 7.5 Hz, 12H), 2.78 (s, 6H), 1.69 (s, 6H), 1.29 (t, *J* = 7.5 Hz, 18H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 156.9, 145.7, 143.2, 136.3, 136.1, 134.2, 131.5, 129.7, 125.3, 83.5, 80.6, 47.8, 14.5, 13.6, 9.2. MS (ESI) calcd for $C_{21}H_{17}BBrF_2O_6S_2^{2-}$ $(M - 2Et_3NH)^{2-}$, 253.02, found 253.02.

11 Cu (1 mg, 0.02 mmol) and $CuSO_4$•$5H_2O$ (2 mL, 1 M, 0.002 mmol) were added to a solution of **9** (11 mg, 0.019 mmol) and **10** (12 mg, 0.07 mmol) in 1:1 THF/H_2O (2 ml). The reaction mixture was stirred at room temperature for 48 h, and then was evaporated to dryness. The residue was purified by reverse phase prep-HPLC (gradient: 10% solvent B to 90% solvent B, 25 min) to afford a red solid with retention time at 17 min (6 mg, 30%). ^{1}H NMR (500 MHz, CD_3OD), δ 9.28 (s, 1H), 8.28-8.27 (m, 4H), 8.12 (d, *J* = 8.5 Hz, 4H), 8.03 (d, *J* = 8.5 Hz, 4H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 6.5 Hz, 2H), 7.16 (d, *J* = 4.0 Hz, 2H), 6.93 (d, *J* = 4.5 Hz, 2H), 2.83 (s, 6H), 1.81 (s, 6H). MS (ESI) calcd

for $C_{50}H_{33}B_2F_4N_7O_{10}S_2$ $(M\text{-}2Na\text{-}2H)^{4-}$, 263.25, found 263.28.



BSA-11

BSA-11 Cassette **11** (1.5 mg) was dissolved in dry DMF (0.10 mL) and *N*-hydroxysuccinimide (0.2 mg), diisopropylcarbodiimide (DIC, 1.0 μL) were added. The reaction mixture was stirred at room temperature for 24 h.

The activated cassette **11** solution (100 μL, 6 eq.) was added to the solution of BSA (13 mg, 1 eq.) in 1.5 mL freshly prepared sodium bicarbonate (0.1 M, pH 8.3). The solution was stirred at room temperature in the dark for 1 h. The desired product was purified by SephadexTM G-25 (PD-10) desalting column eluting with DI-water. The UV-vis spectra show the absorbance peak of BSA at 280 nm and the two maximum absorbance peaks of the cassettes **11** at 504 nm and 570 nm (data are shown here).

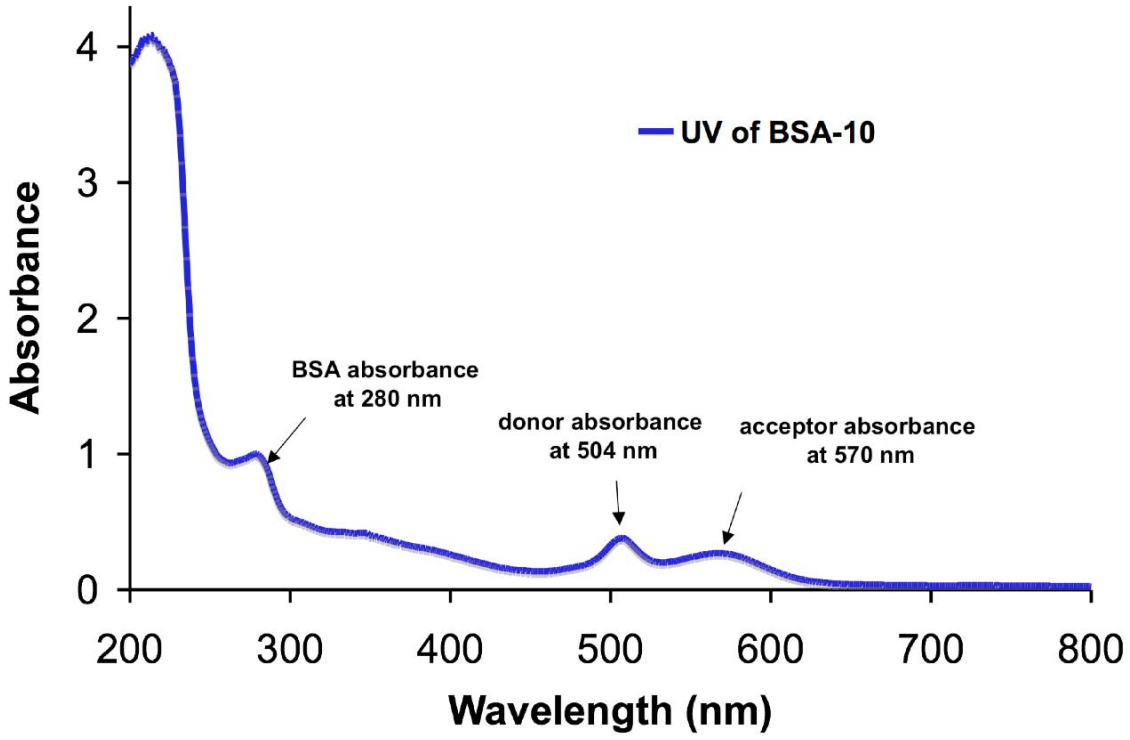
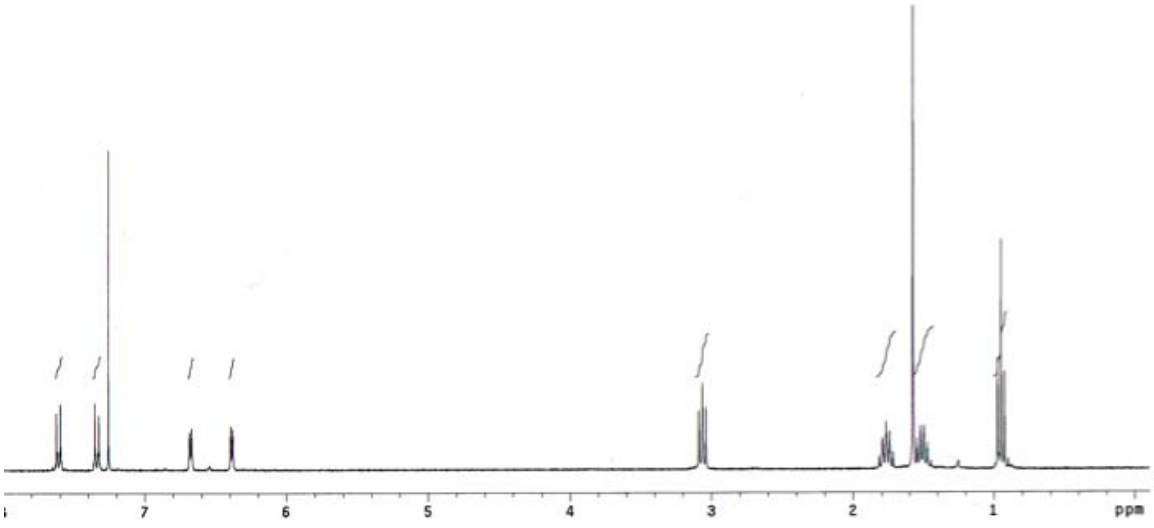


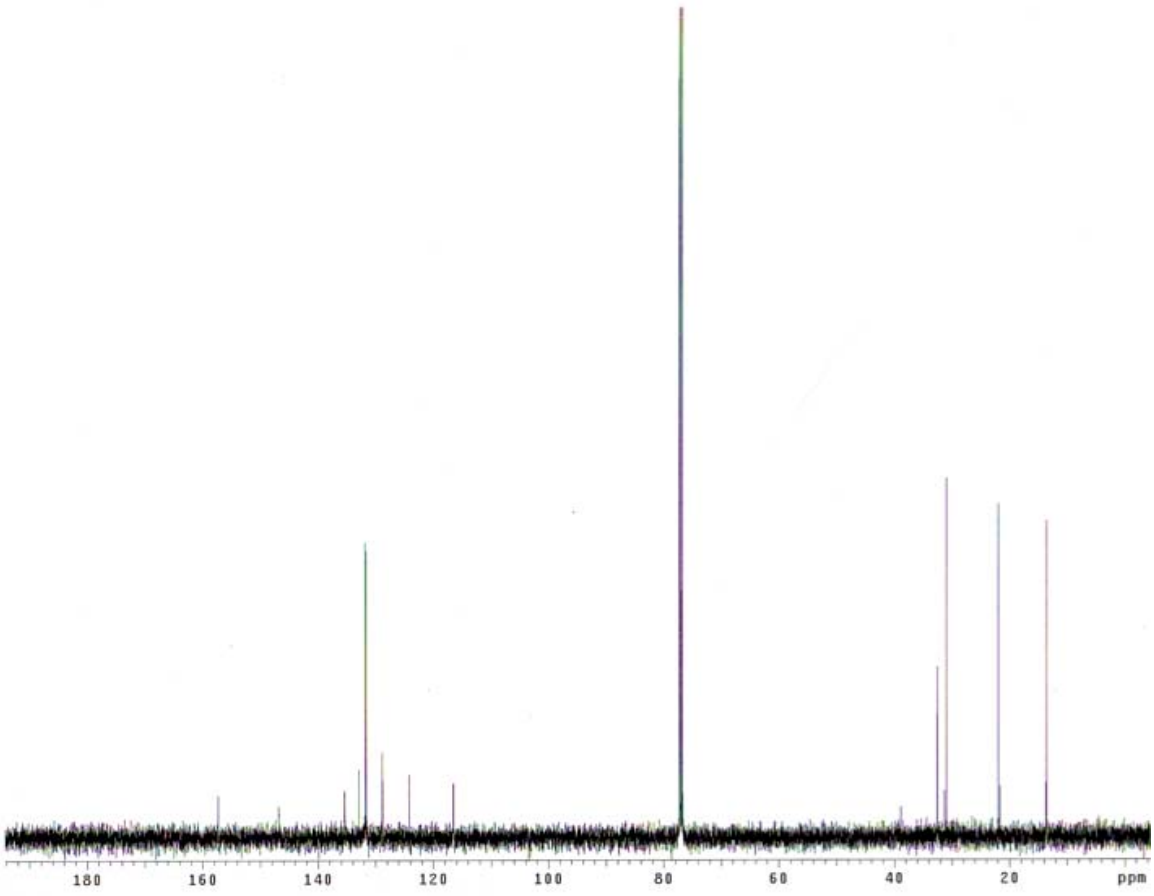
Figure S1 UV absorbance spectra of **BSA-11** conjugate in DI water.

^{1}H, ^{13}C, ^{19}F NMR or MS of compounds **1** – **12**

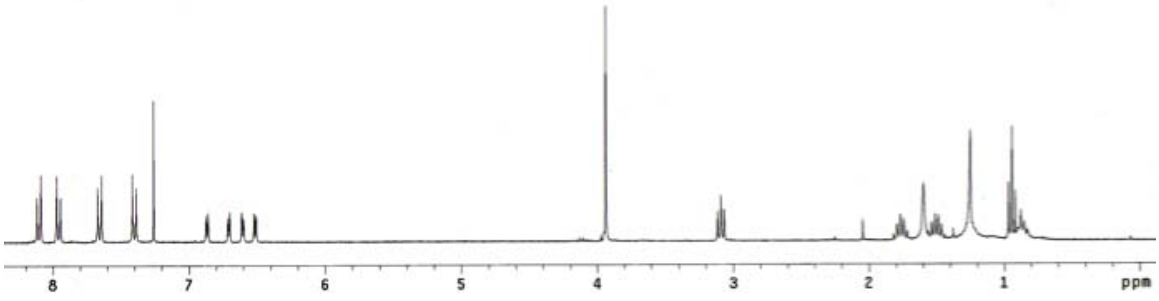
^{1}H NMR of compound **1** ($CDCl_3$, 500 MHz)



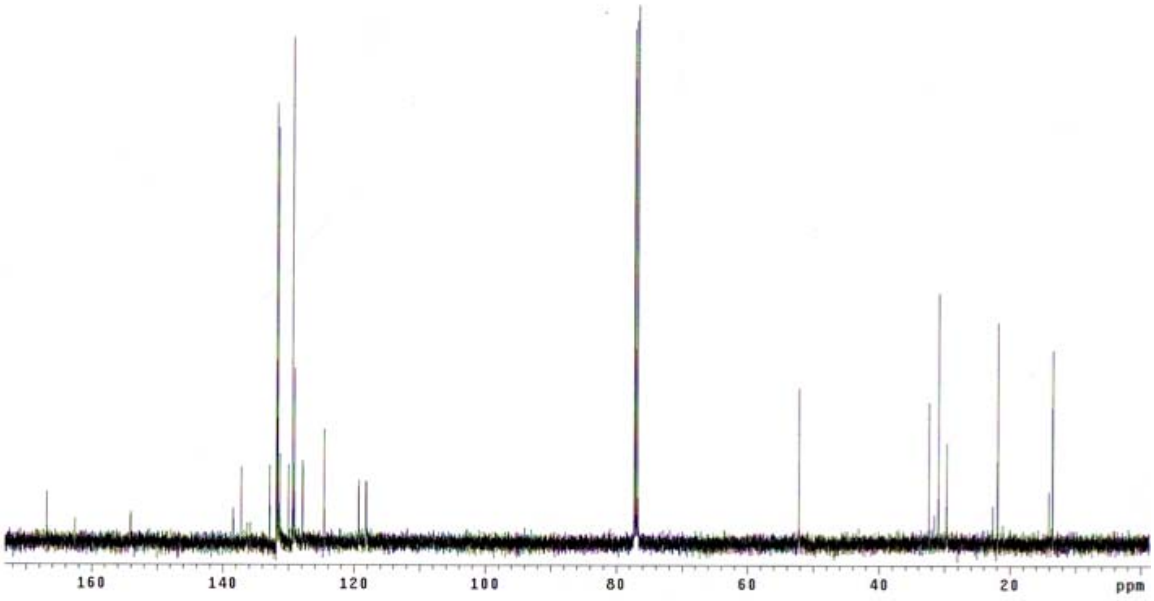
^{13}C NMR of compound **1** ($CDCl_3$, 125 MHz)



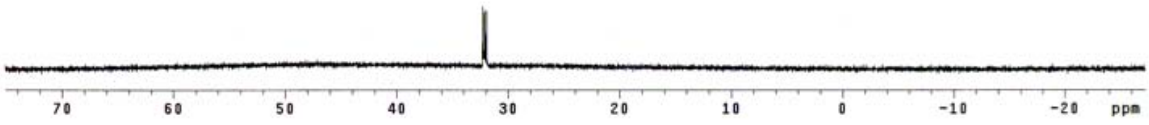
^{1}H NMR of compound **2b** ($CDCl_3$, 500 MHz)



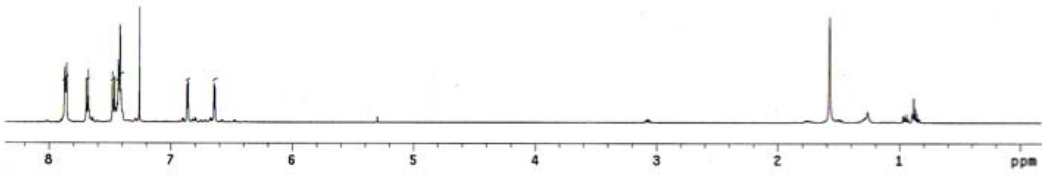
^{13}C NMR of compound **2b** ($CDCl_3$, 125 MHz)



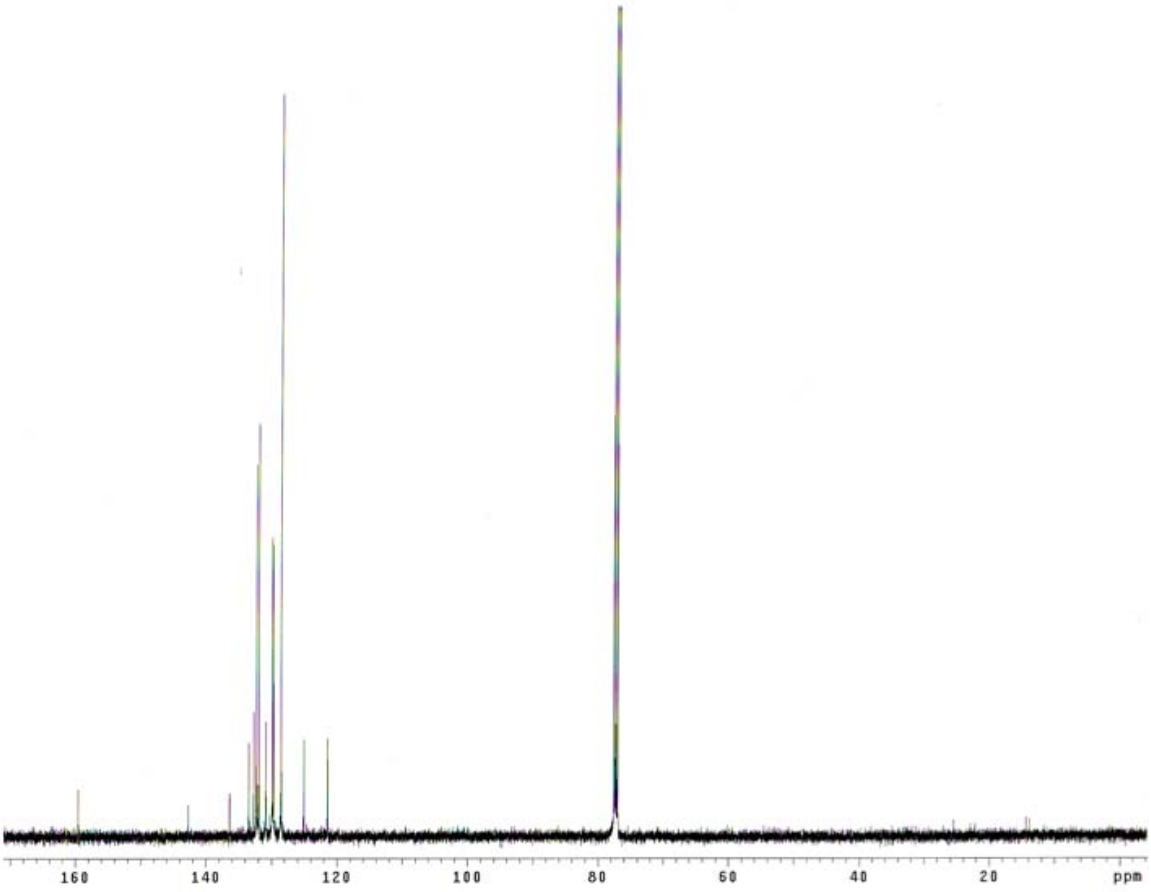
^{19}F NMR of compound **2b** ($CDCl_3$, 282 MHz)



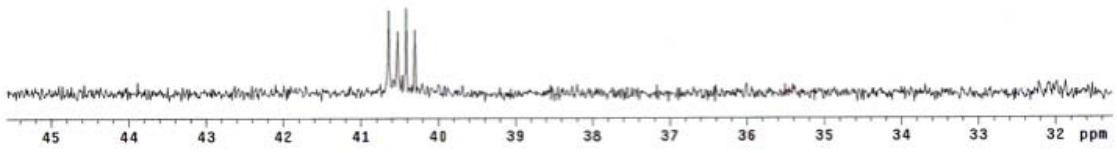
^{1}H NMR of compound **3a** ($CDCl_3$, 500 MHz)



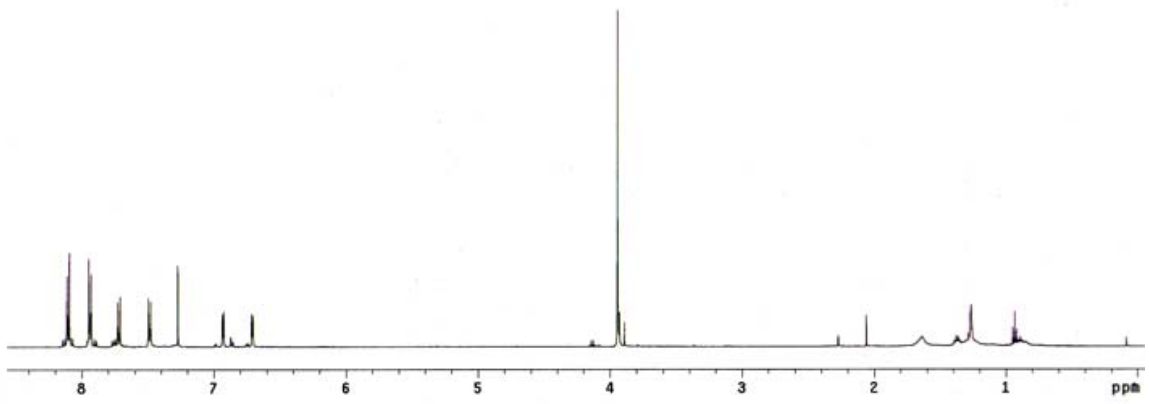
^{13}C NMR of compound **3a** ($CDCl_3$, 500 MHz)



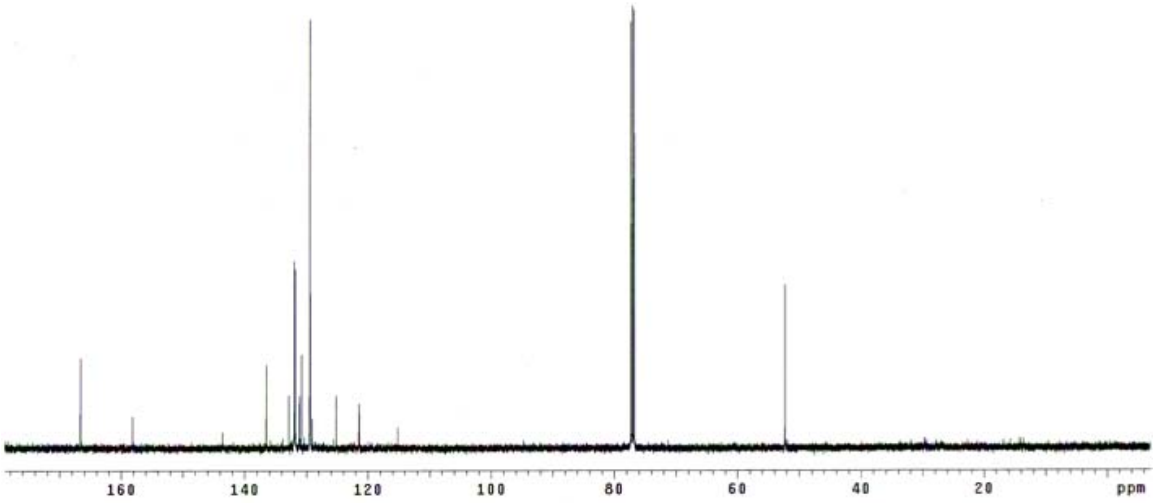
^{19}F NMR of compound **3a** ($CDCl_3$, 282 MHz)



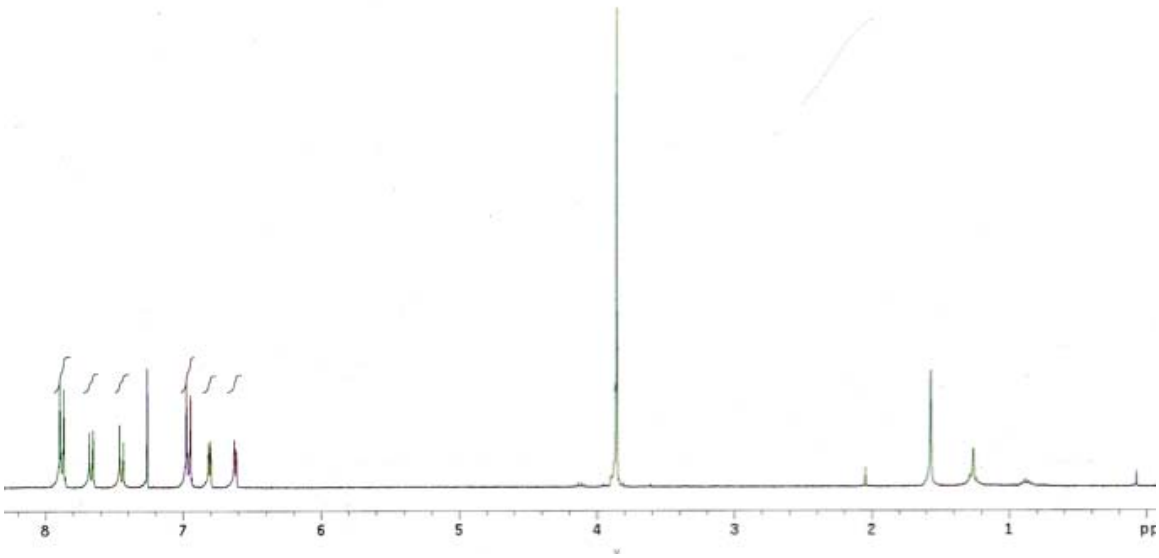
^{1}H NMR of compound **3b** ($CDCl_3$, 500 MHz)



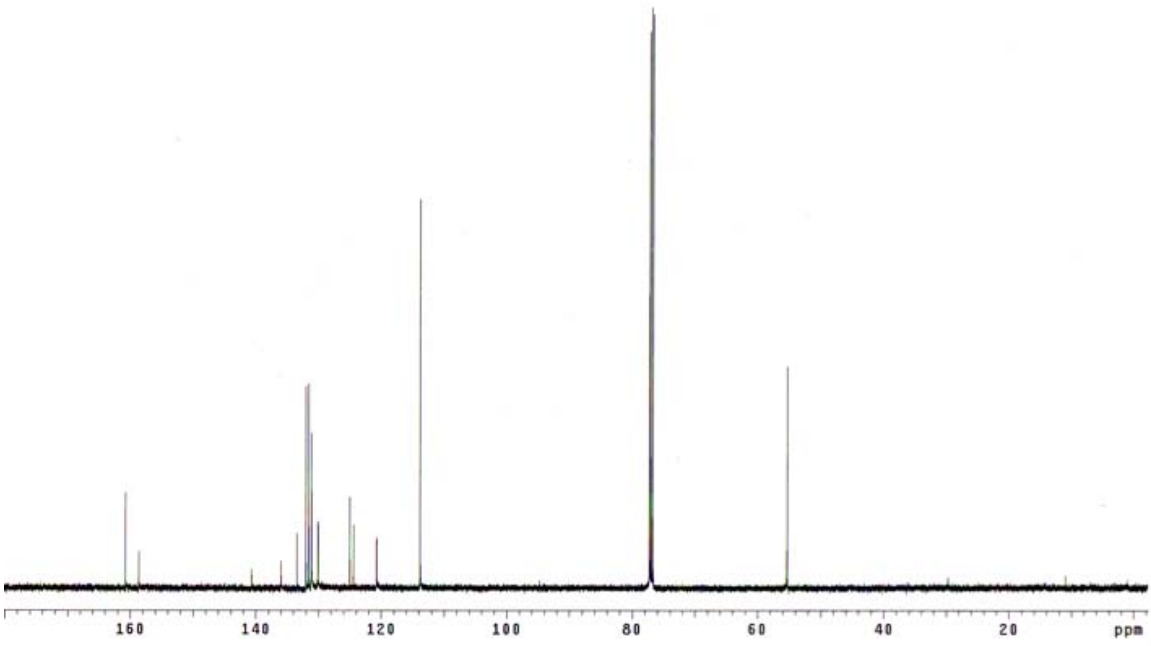
^{13}C NMR of compound **3b** ($CDCl_3$, 500 MHz)



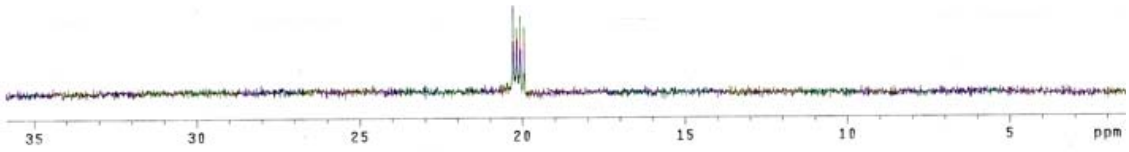
^{1}H NMR of compound **3c** ($CDCl_3$, 500 MHz)



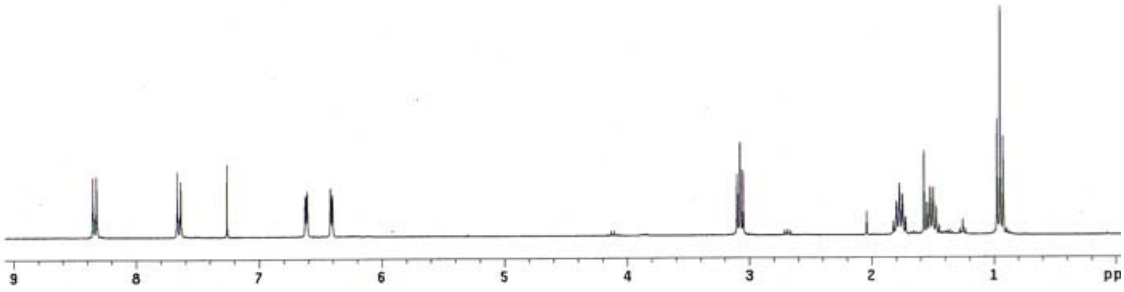
^{13}C NMR of compound **3c** ($CDCl_3$, 500 MHz)



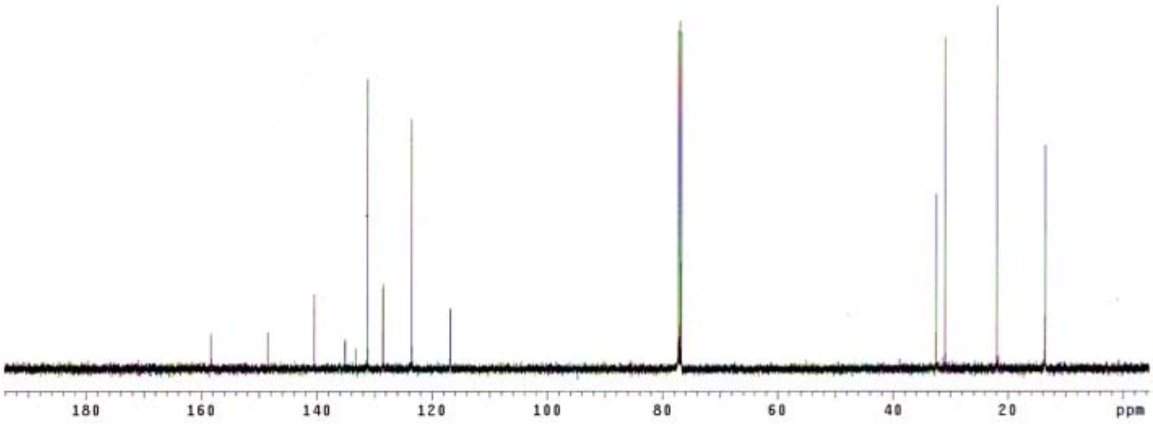
^{19}F NMR of compound **3c** ($CDCl_3$, 282 MHz)



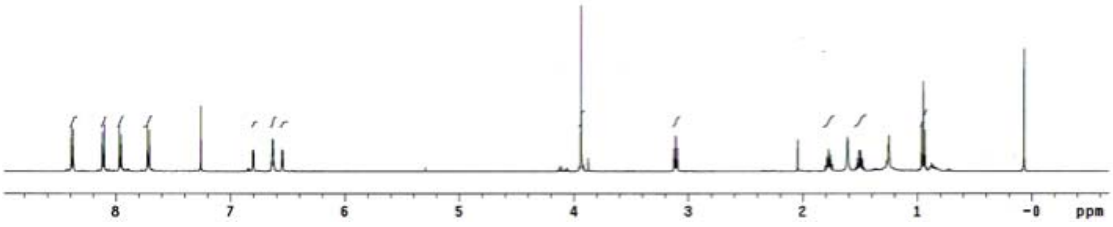
^{1}H NMR of compound **4** ($CDCl_3$, 500 MHz)



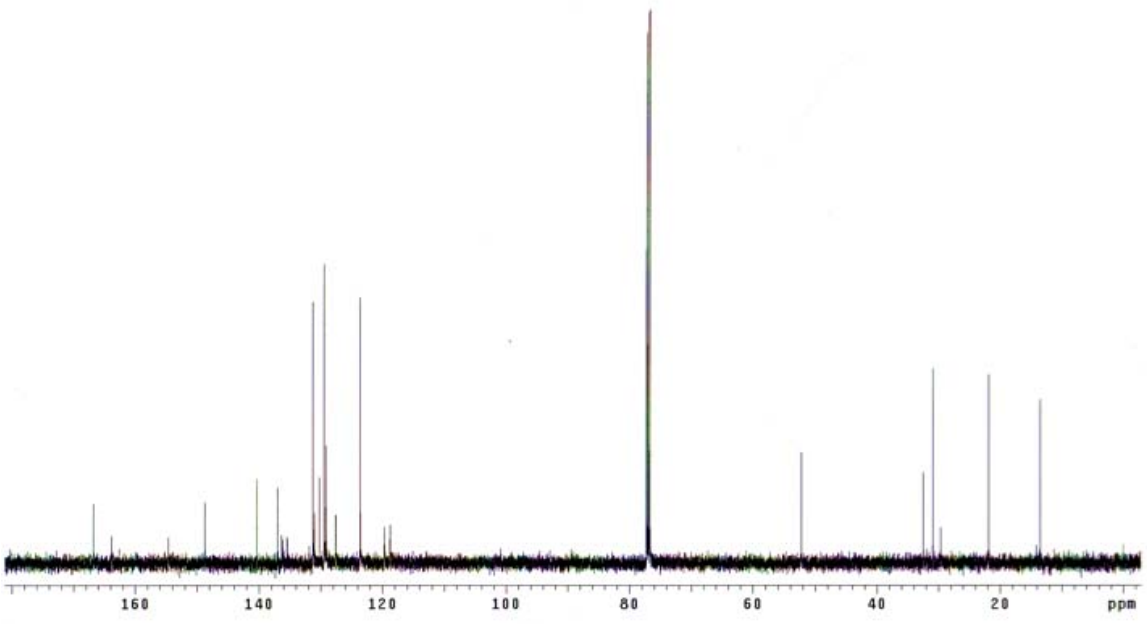
^{13}C NMR of compound **4** ($CDCl_3$, 500 MHz)



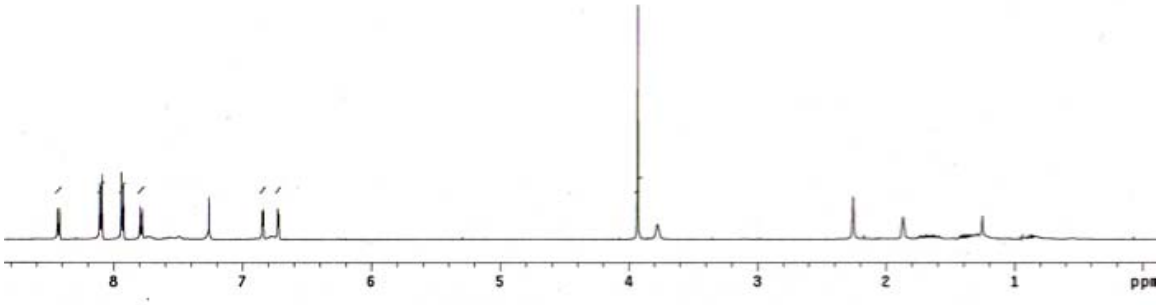
^{1}H NMR of compound **5** ($CDCl_3$, 500 MHz)



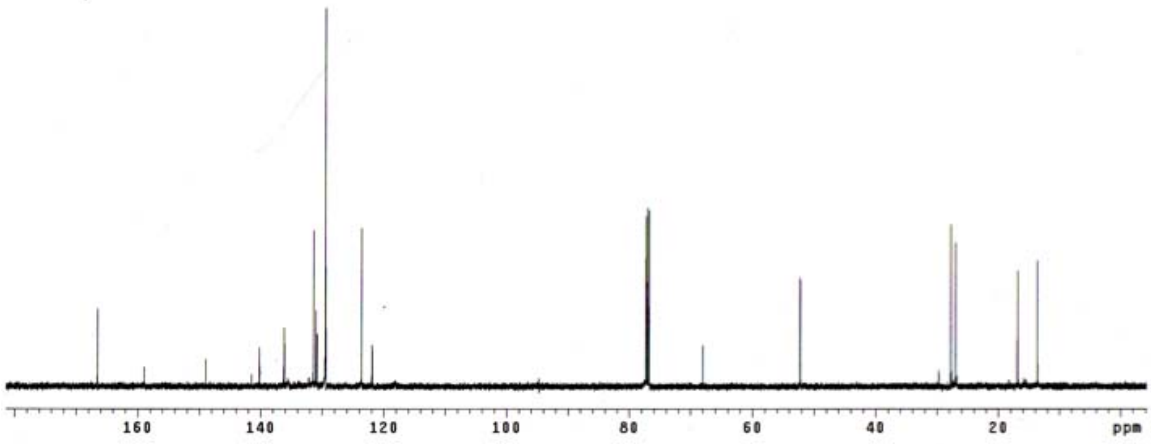
^{13}C NMR of compound **5** ($CDCl_3$, 500 MHz)



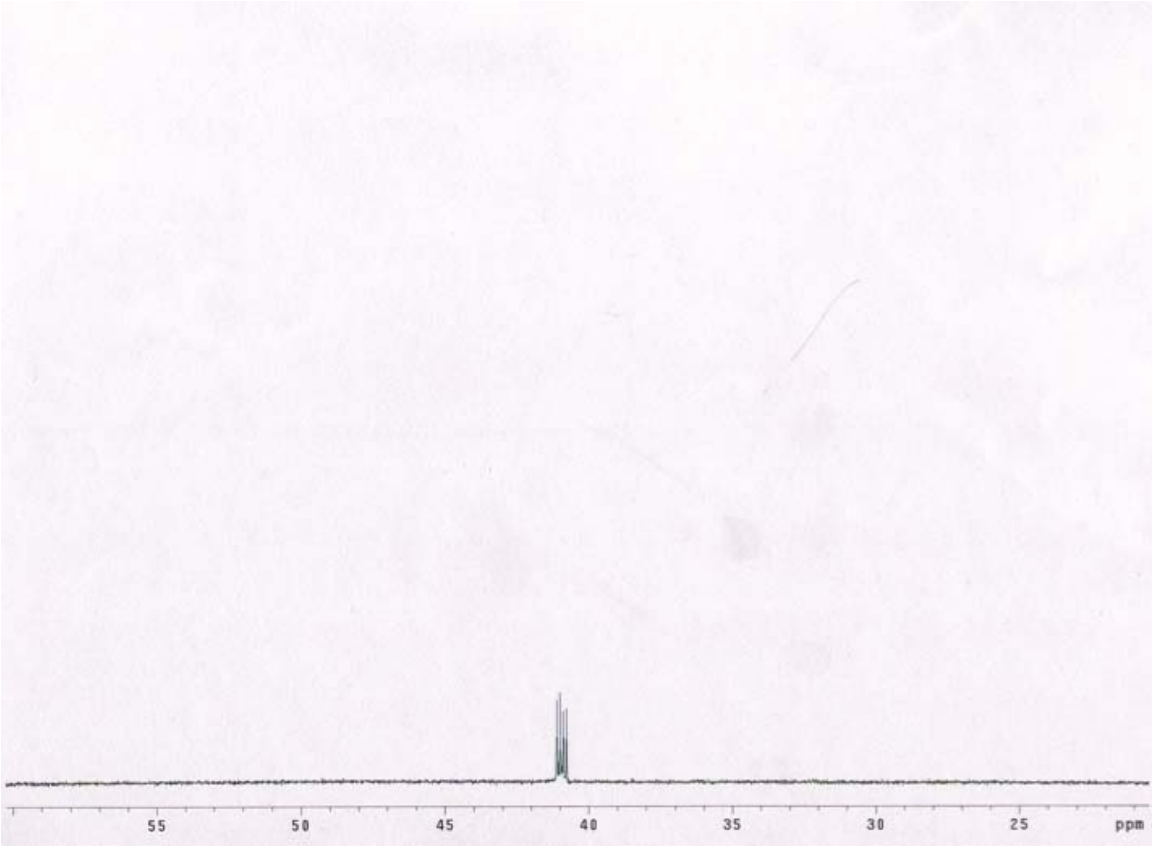
^{1}H NMR of compound **6** ($CDCl_3$, 500 MHz)



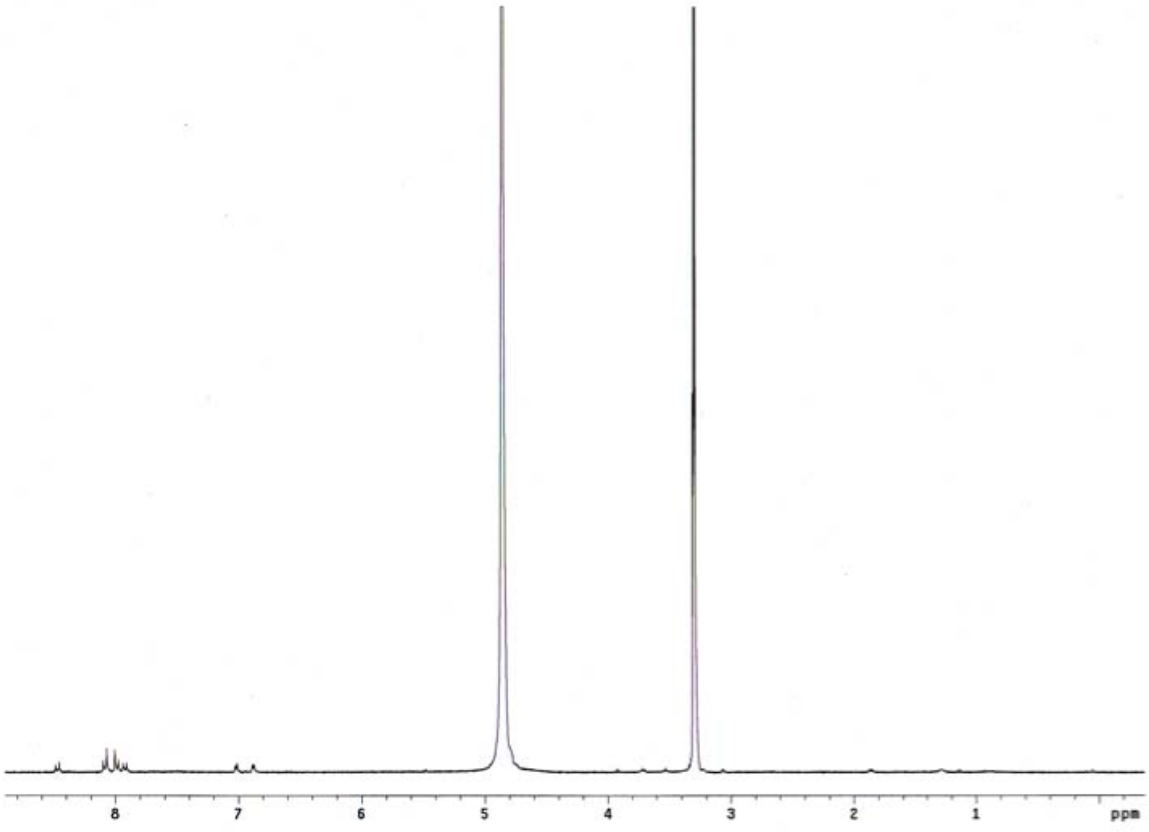
^{13}C NMR of compound **6** ($CDCl_3$, 125 MHz)



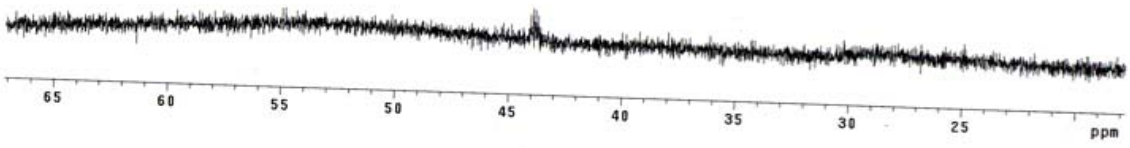
^{19}F NMR of compound **6** ($CDCl_3$, 282 MHz)



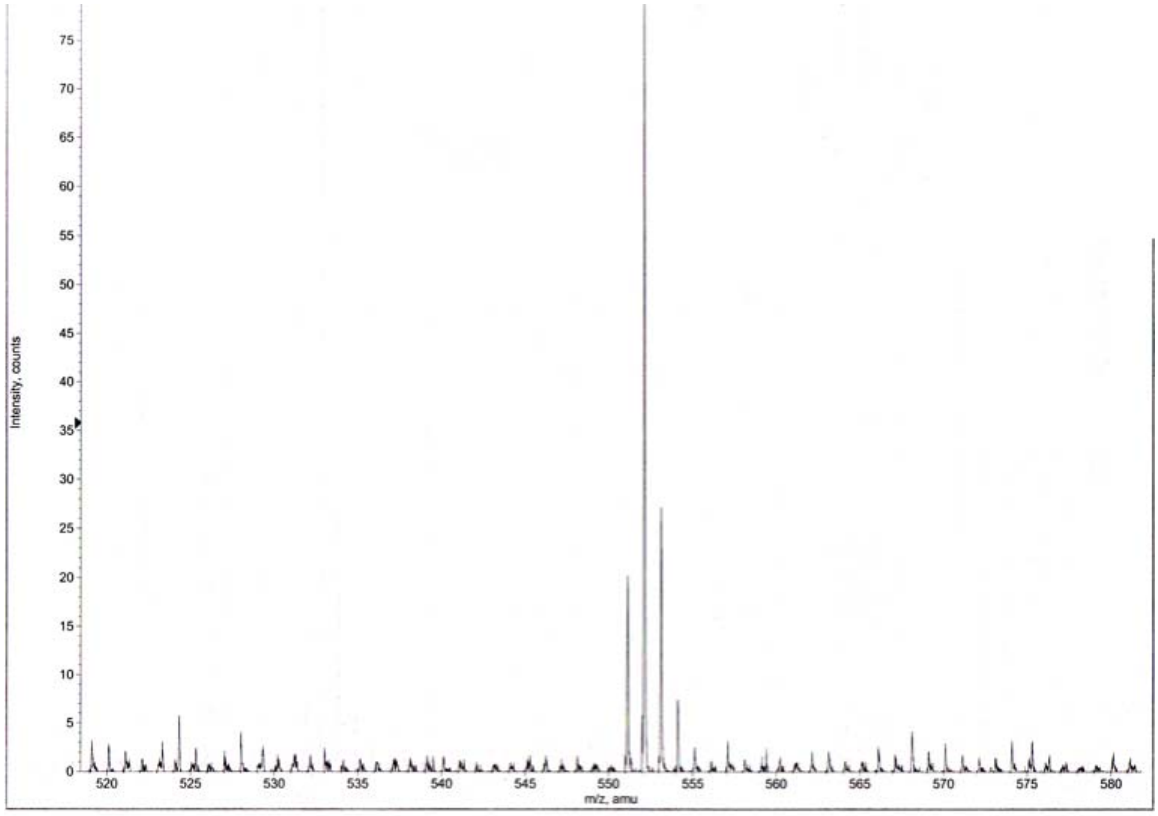
^{1}H NMR of compound **7** (CD_3OD, 500 MHz)



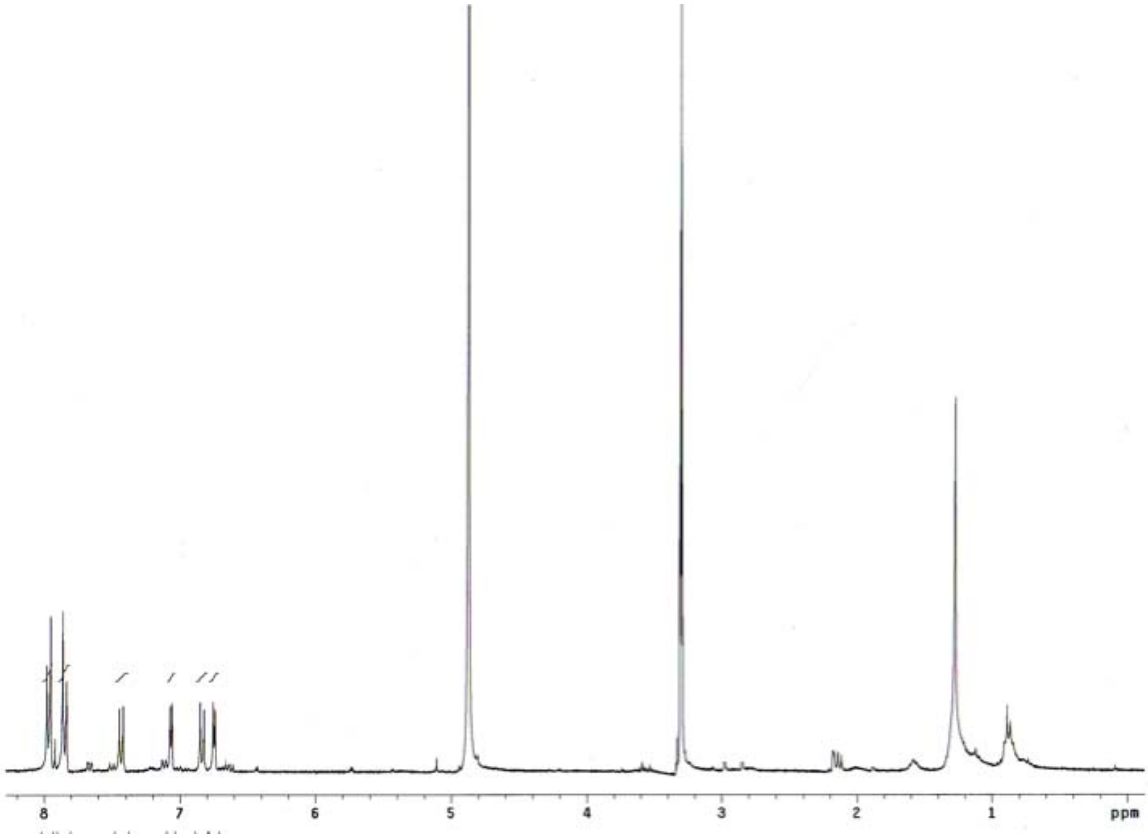
^{19}F NMR of compound **7** (CD_3OD, 282 MHz)



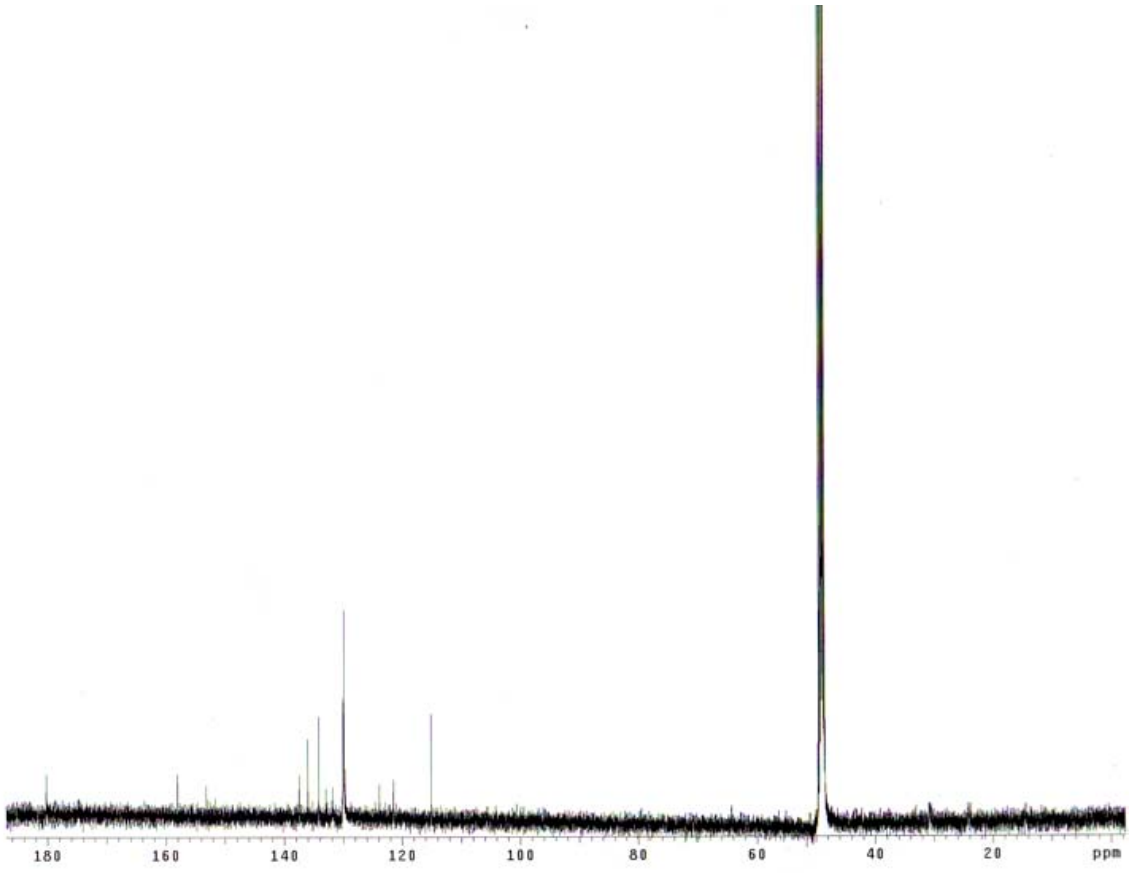
HRMS ESI of compound **7**



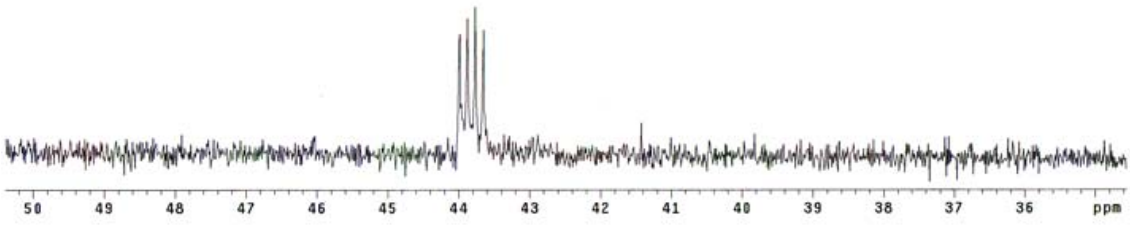
^{1}H NMR of compound **8** (CD_3OD, 500 MHz)



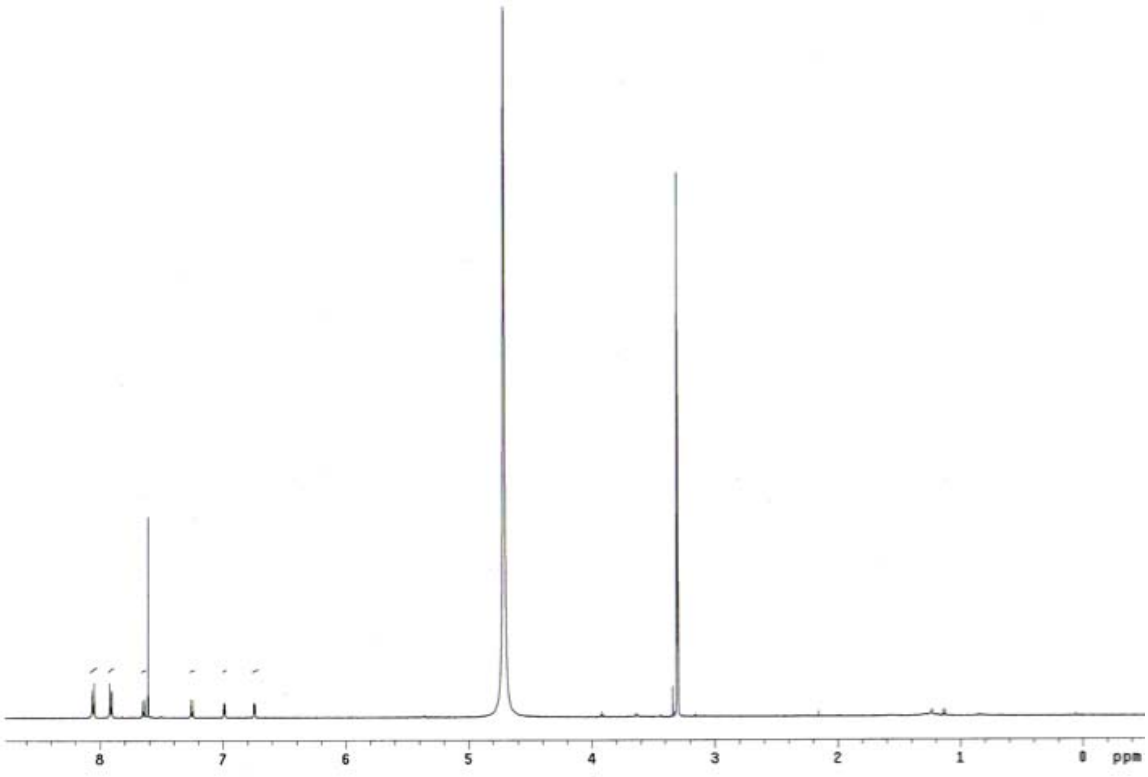
^{13}C NMR of compound **8** (CD_3OD, 500 MHz)



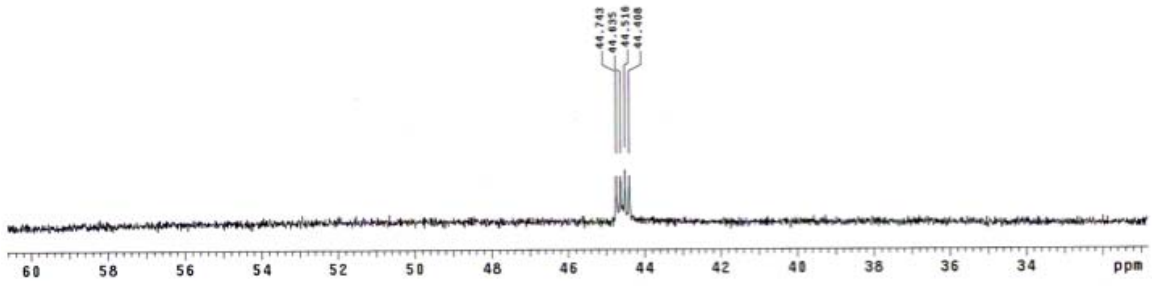
^{19}F NMR of compound **8** ($CDCl_3$, 282 MHz)



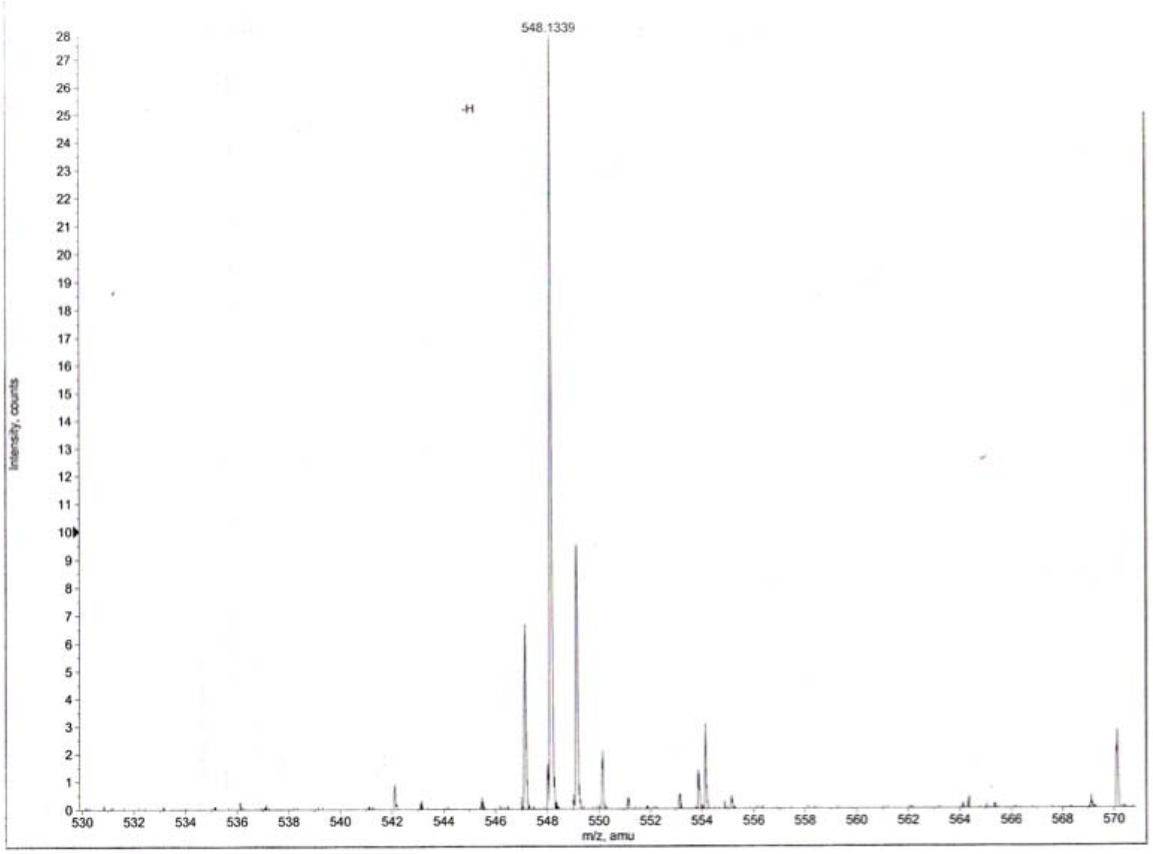
^{1}H NMR of compound **9** (1:1 $CD_3OD/CDCl_3$, 500 MHz)



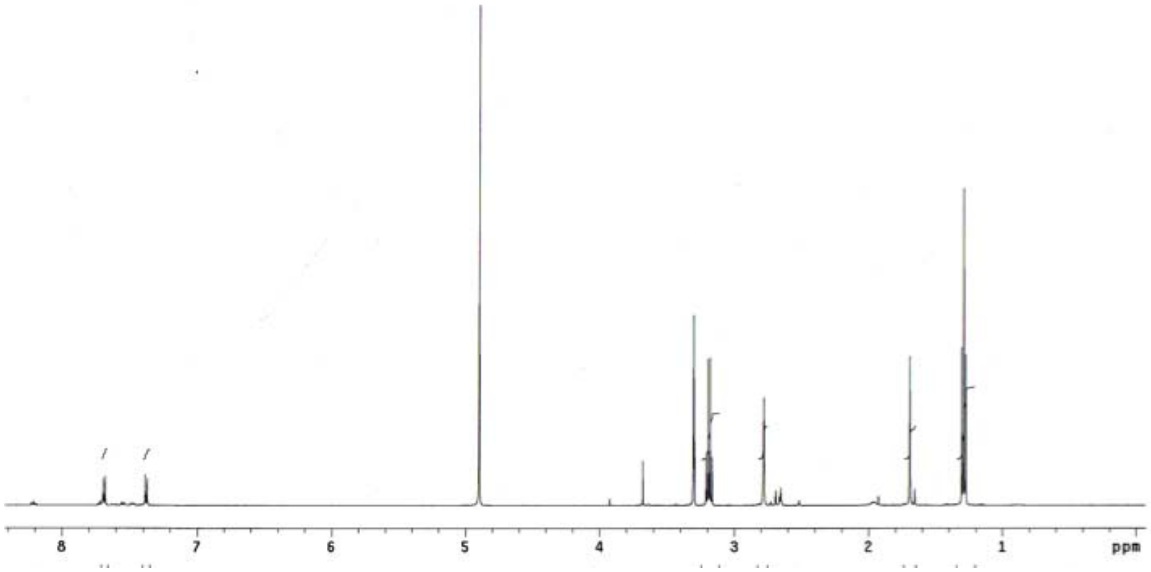
^{19}F NMR of compound **9** (1:1 $CD_3OD/CDCl_3$, 282 MHz)



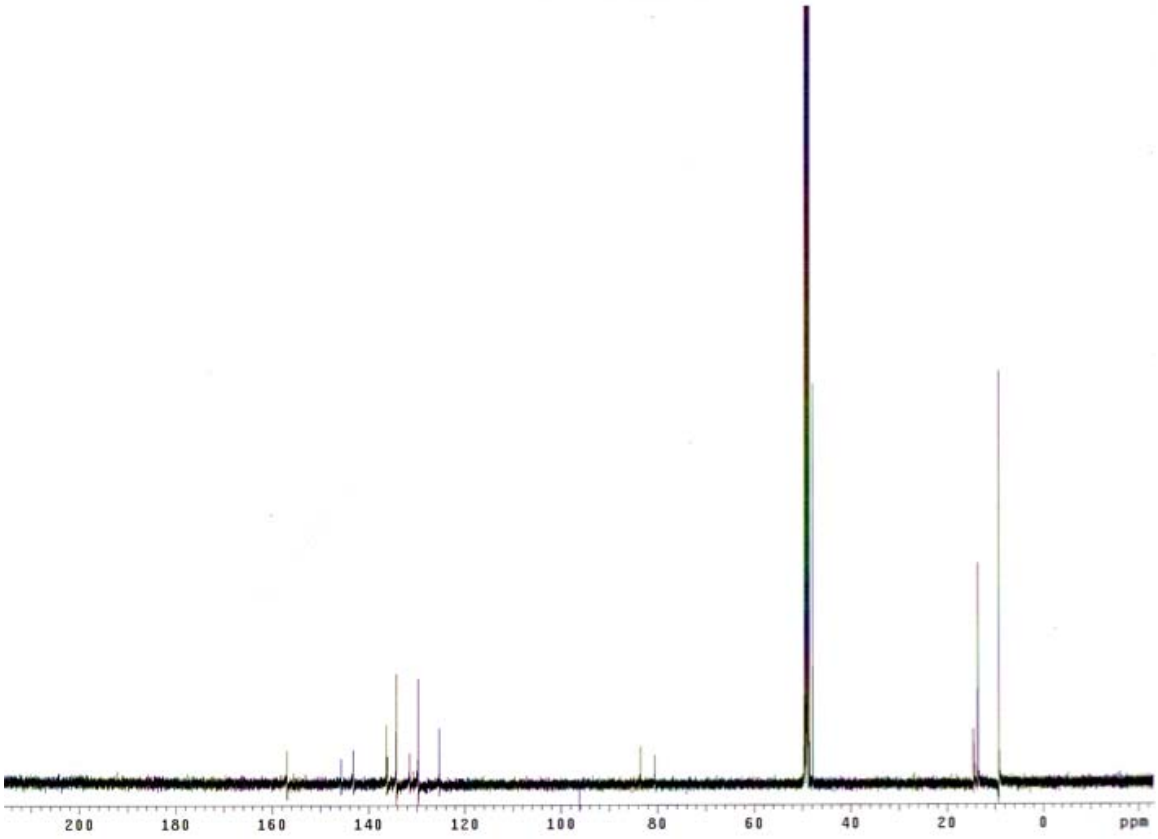
HRMS ESI of compound **9**



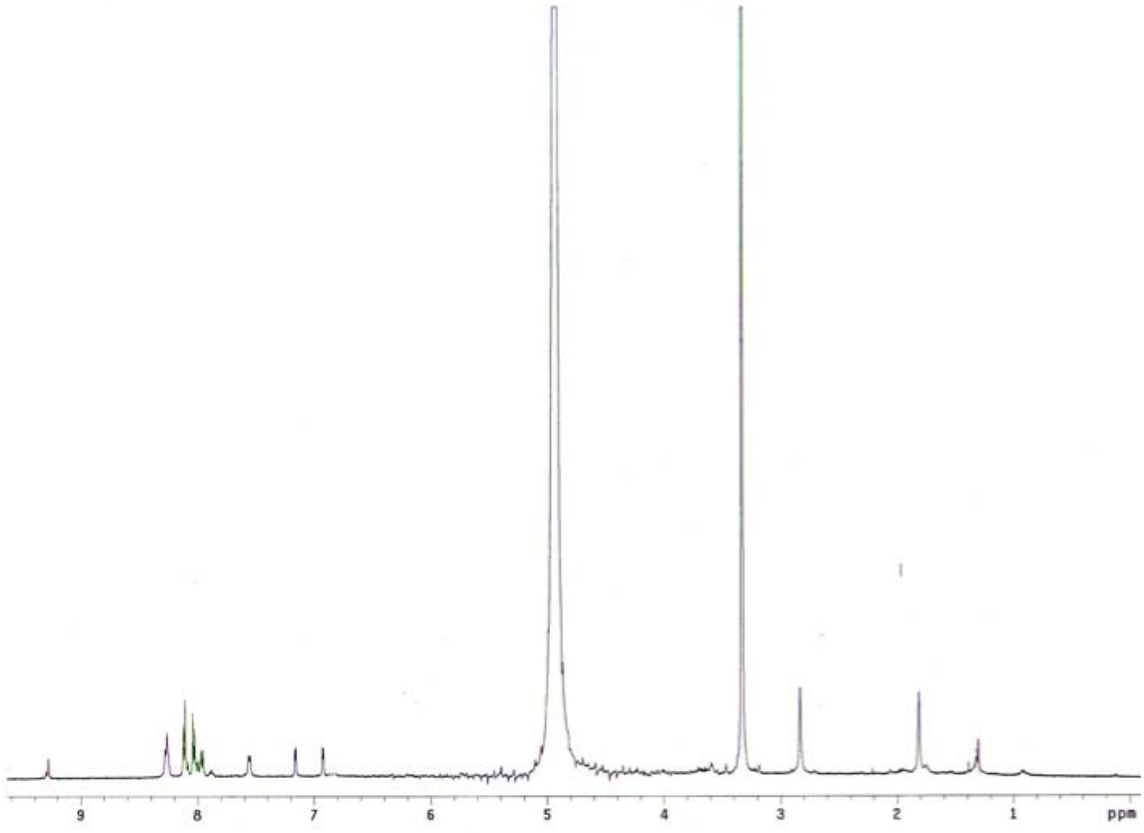
^{1}H NMR of compound **10** ($CDCl_3$, 500 MHz)



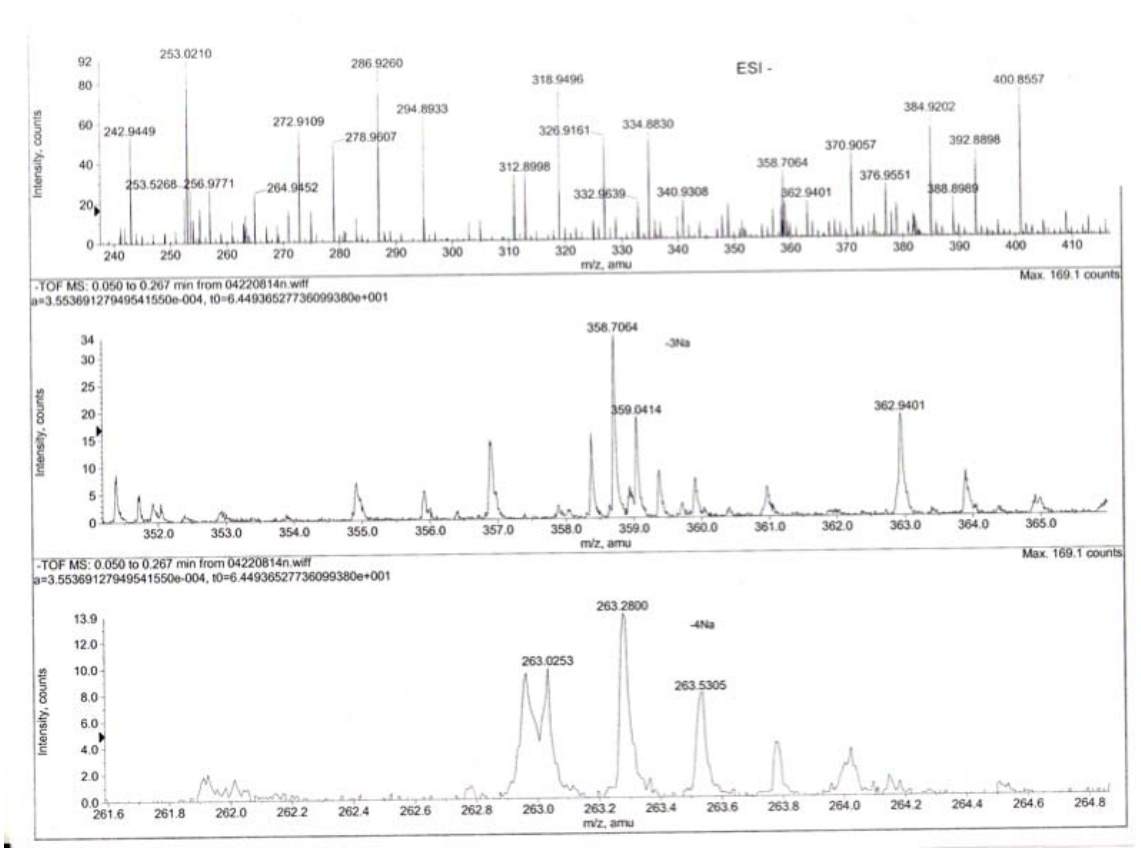
^{13}C NMR of compound **10** (CD_3OD, 500 MHz)



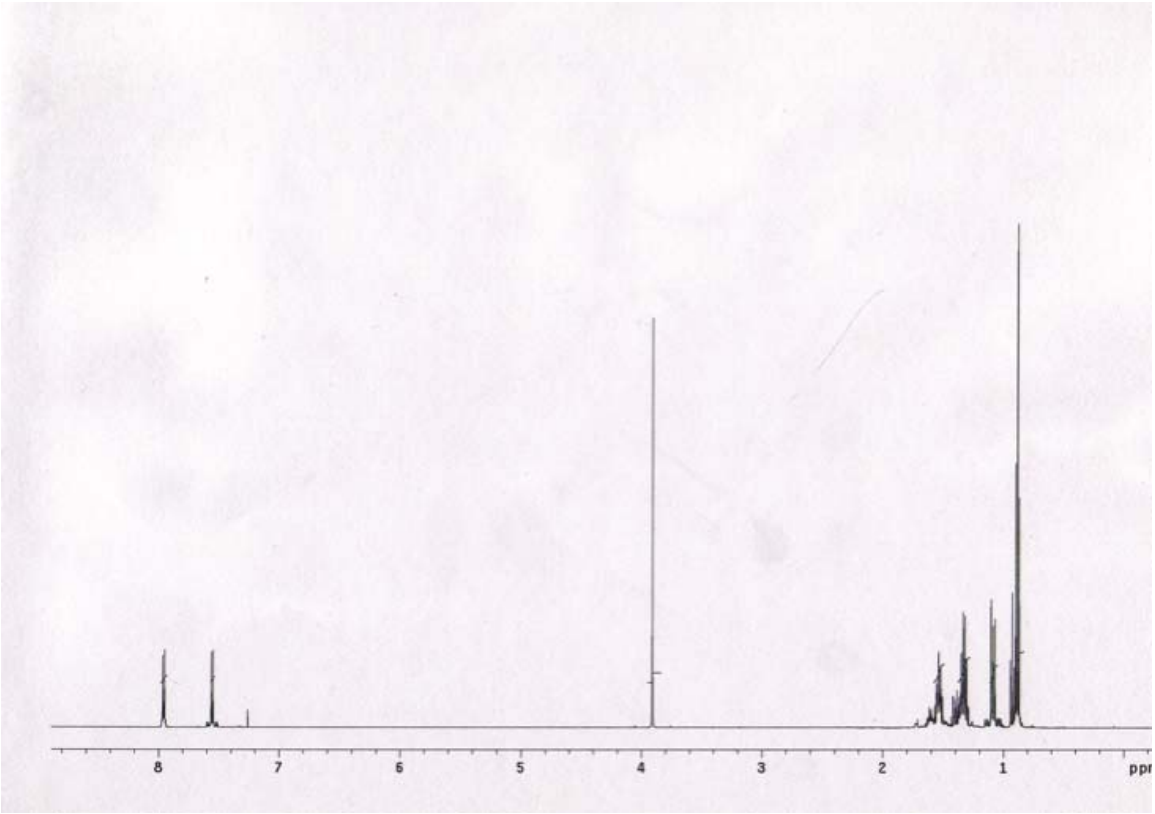
1H NMR of compound **11** (500 MHz, CD_3OD)



MS of compound **11** (MALDI)



^{1}H NMR of compound **12** ($CDCl_3$, 500 MHz)



^{13}C NMR of compound **12** ($CDCl_3$, 500 MHz)