Electronic Supplementary Information

for

Bis-triazolyle BODIPYs: a simple dye with strong red-light emission

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Syntheses of compounds

General information

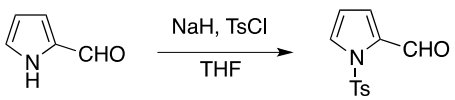
All reactions requiring inert conditions were performed under argon atmosphere using Schlenk techniques. THF was freshly distilled over sodium/benzophenone. Anhydrous dichloromethane and dimethylformamide were purchased from Sigma or Carlo Erba. Benzaldehyde was distilled before use. Other reagents and solvents were obtained from commercial suppliers (Aldrich, Sigma, Fluka, Acros Organics, Fisher Scientific) and used without further purification.

Analytical TLC was performed on ready-made plates coated with silica gel on aluminum (Merck 60 F254). Products were visualized by ultraviolet light or treatment with permanganate stain followed by gentle heating. Flash chromatography was performed using silica gel (60 Å, particle size 40-63µm).

NMR spectra were recorded on a Bruker AV 500 MHz, Bruker AV 400 MHz or Bruker DRX 300 MHz spectrometer with a QNP probe. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) downfield to tetramethylsilane using the residual solvent signal as internal standard. ^{19}F spectra are referenced to $CFCl_3$. Proton (^{1}H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad signal), coupling constant(s) (J) in Hertz (Hz), number of protons. Melting point were measured on previously calibrated Kofler bench. High resolution mass spectrometry spectra are recorded on BruckerMicrOQTOF-Q II XL.

Procedure for the preparation of the building block 1

Preparation of 1-tosyl-1H-pyrrole-2-carbaldehyde



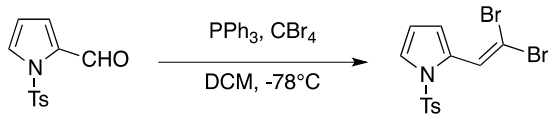
Pyrrole-2-carboxaldehyde (10.0 g, 105 mmol, 1.00 eq) was added portionwise to a stirred suspension of sodium hydride (5.30 g, 60% dispersion in oil washed three times with pentane, 1.25 eq) in 300 mL anhydrous THF under inert atmosphere. After 15 min of stirring at room temperature, a solution of tosyl chloride (22.5 g, 116 mmol, 1.10 eq) in 100 mL THF was added, and the resulting purple mixture was stirred overnight. Water (100 mL) was added to dissolve the precipitate. Then the mixture was extracted twice with dichloromethane (500 mL + 100 mL). The organic layer was washed with saturated aqueous $NaHCO_3$, NH_4Cl and brine (400 mL of each), dried over Na_2SO_4, and concentrated under vacuum to afford the tosylated compound as a brownish solid (23.4 g, 89%). The product is pure enough to be used for the next step (> 96% ^{1}H NMR).

^{1}H NMR (300 MHz, $CDCl_3$) : δ = 2.49 (s, 3H), 6.38 (dd, ^{3}J = 3.4 Hz, ^{3}J = 3.4 Hz, 1H), 7.13 (dd, ^{3}J = 3.7 Hz, ^{4}J = 1.8 Hz, 1H), 7.30 (d, ^{3}J = 8.1 Hz, 2H), 7.60 (dd, ^{3}J = 3.1 Hz, ^{4}J = 1.8 Hz, 1H), 7.78 (d, ^{3}J = 8.3 Hz, 2H), 9.95 (s, 1H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 21.7, 112.5, 124.6, 127.5, 129.5, 130.2, 133.5,

135.2, 146.0, 179.0. $[M+H]^+$ calcd. for $C_{12}H_{12}NO_2S$: 250.0538; found : 250.0534. MP (Kofler): 97°C. IR (cm^{-1}): 3125 (w), 1665 (s), 1420 (s), 1362 (s).

Spectroscopic data were in agreement with previous literature report.[1]

Preparation of 2-(2,2-dibromovinyl)-1-tosyl-1H-pyrrole



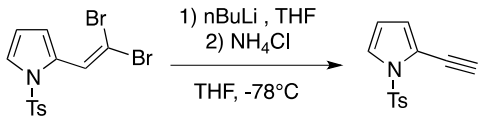
A solution of CBr_4 (58.5 g, 176 mmol, 2.0 eq) in anhydrous CH_2Cl_2 (220 mL) was cooled down to 0°C and treated with PPh_3 (92.5 g, 353 mmol, 4.0 eq) in anhydrous CH_2Cl_2 (220 mL). The orange resulting mixture was stirred for 30 min at 0°C, then cooled down to -78°C. 1-tosyl-1H-pyrrole-2-carbaldehyde (22.0 g, 88.2 mmol, 1.0 eq) in anhydrous CH_2Cl_2 (220 mL) was added dropwise. After stirring for 10 min at -78°C, the mixture was allowed to warm up over a period of 15 min and was then stirred for 1 h at 0°C. Triphenylphosphine oxide and black impurities precipitated by addition of Et_2O (2 L) were filtered off over a Celite® plug and rinsed thoroughly with Et_2O (~200 mL). The clear yellow solution was washed with water (2 L), saturated aqueous $NaHCO_3$, NH_4Cl, NaCl (1 L of each), dried over $MgSO_4$ and concentrated under reduced pressure to afford ~68 g of a crude grey solid.

Column chromatography (silica gel, cyclohexane/EtOAc 7:3) afforded an orange solid which was triturated in a small amount of Et_2O and filtered off. The dibromoalkene compound was obtained as a crystallized white-off solid (27.1 g, 76%).

^{1}H NMR (300 MHz, $CDCl_3$) : δ = 2.41 (s, 3H), 6.30 (dd, ^3J = 3.4 Hz, ^3J = 3.4 Hz, 1H), 6.88 (ddd, ^3J = 3.6 Hz, ^4J = 1.6 Hz, ^4J = 0.9 Hz, 1H), 7.31 (d, ^3J = 8.0 Hz, 2H), 7.38 (dd, ^3J = 3.3 Hz, ^4J = 1.6 Hz, 1H), 7.66 (d, ^3J = 8.4 Hz, 2H), 7.87 (s, 1H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 21.8, 90.5, 112.4, 117.1, 123.8, 126.4, 127.1, 129.4, 130.2, 135.6, 145.6. $[M+H]^+$ calcd. for $C_{13}H_{12}BrNO_2S$: 405.8935; found: 405.8924. MP (Kofler): 89°C. IR (cm^{-1}): 3063 (w), 1593 (m), 1450 (m), 1362 (m).

Spectroscopic data were in agreement with previous literature report.[2]

Preparation of 2-ethynyl-1-tosyl-1H-pyrrole 1

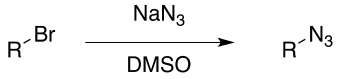


A solution of of 2-(2,2-dibromovinyl)-1-tosyl-1H-pyrrole (5.06 g, 12.5 mmol, 1.00 eq) in anhydrous THF (55 mL) was cooled down to -78°C. *n*BuLi (18.8 mL, 1.46M in hexane, 27.5 mmol, 2.20 eq) was then added dropwise over 25 min. The resulting solution was stirred for 90 min at -78°C. The reaction was quenched by a quick addition of saturated aqueous NH_4Cl solution (30 mL). The mixture was then allowed to warm to room temperature. The organic layer was washed with saturated aqueous NH_4Cl, water and brine (120 mL each), dried over Na_2SO_4 and evaporated. Column chromatography (silica gel, cyclohexane/EtOAc 95:5) yielded pyrrolylethyne **1** (1.96 g, 64%, 96% purity ^{1}H NMR) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 3.43 (s, 1H), 6.20 (dd, ^{3}J = 3.4 Hz, ^{3}J = 3.4 Hz, 1H), 6.58 (dd, ^{3}J = 3.5 Hz, ^{4}J = 1.6 Hz, 1H), 7.27-7.39 (m, 3H), 7.86 (d, ^{3}J = 8.3 Hz, 2H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 21.8, 74.0, 83.4, 111.7, 114.4, 122.6, 123.8, 128.0, 130.0, 135.4, 145.6. $[M+H]^+$ calcd. for $C_{13}H_{12}NO_2S$: 246.0589; found : 246.0584. MP (Kofler): 88°C. IR (cm^{-1}): 3306 (m), 1593 (m), 1445 (m), 1364 (m).

Spectroscopic data were in agreement with previous literature report.[2]

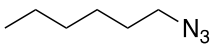
General procedure for alkyl azide synthesis



Sodium azide (1.1 eq) was dissolved in DMSO (2.2 mL/mmol alkyl bromide). 1-Alkylbromide (1.0 eq) was then added to the mixture and stirred overnight at room temperature.

Water (2 mL/mL DMSO) was added and the mixture was extracted twice with Et_2O. The organic layer was dried over Na_2SO_4 and Et_2O was carefully distilled-off under vacuum to afford 1-azidoalkane.

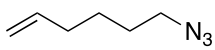
Characterization of 1-azidohexane



(60.5 mmol starting material, yellowish oil, 91% yield)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, ^{3}J = 7.0 Hz, 3H), 1.22-1.43 (m, 6H), 1.52-1.68 (m, 2H), 3.24 (t, ^{3}J = 7.0 Hz, 2H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 14.0, 22.6, 26.5, 28.9, 31.4, 51.6. IR (cm^{-1}): 2930 (w), 2087 (s).

Spectroscopic data were in agreement with previous literature report.[3]

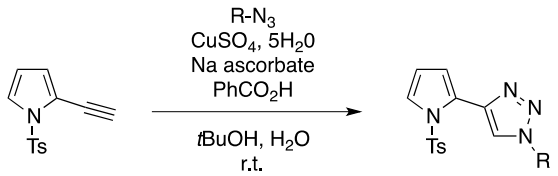
Characterization of 6-azidohex-1-ene



(30.7 mmol starting material, yellowish oil, 82% yield)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42-1.52 (m, 2H), 1.57-1.66 (m, 2H), 2.04-2.12 (m, 2H), 3.27 (t, ^{3}J = 7.2 Hz, 2H), 4.95-5.05 (m, 2H), 5.79 (ddt, ^{E}J = 17.0 Hz, ^{Z}J = 10.1 Hz, ^{3}J = 6.6 Hz, 1H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 26.0, 28.4, 33.3, 51.5, 115.1, 138.3. IR (cm^{-1}): 2936 (w), 2089 (s), 1641 (w).

Spectroscopic data were in agreement with previous literature report.[4]

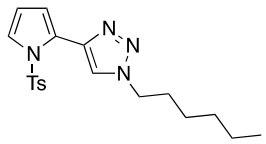
General procedure for triazoles synthesis



To a solution of $CuSO_4$. $5H_2O$ (1.0 mol%), sodium ascorbate (2.0 mol%), and benzoic acid (10 mol%) in *t*-BuOH/H_2O (1:2 v/v, 1 mL/mmol alkyne) was added a mixture of **1** (1.0 eq) and alkyl azide (1.1 eq) at room temperature.[5] The mixture was stirred vigorously for 30 min, until completion of the reaction followed by TLC (cyclohexane/EtOAc 8:2).

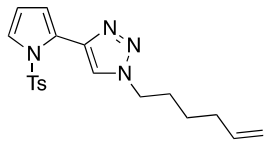
CH_2Cl_2 was then added to dissolve the crude product. The organic layer was washed 3 times with H_2O, brine and dried over anhydrous Na_2SO_4. Removal of the solvent yielded a residue, which was purified by a short chromatography (silica gel, cyclohexane/EtOAc 8:2).

Characterization of 1-hexyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-1,2,3-triazole 2a



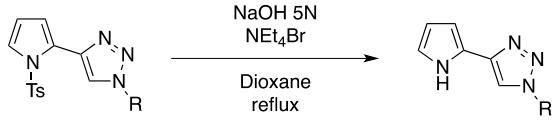
2a (12.2 mmol starting material, yellowish oil, 99% yield)
^{1}H NMR (400 MHz, $CDCl_3$) : δ = 0.85-0.92 (m, 3H), 1.23-1.41 (m, 6H), 1.88-1.99 (m, 2H), 2.31 (s, 3H), 4.39 (t, ^3J = 7.2 Hz, 2H), 6.34 (dd, ^3J = 3.3 Hz, ^3J = 3.3 Hz, 1H), 6.63 (dd, ^3J = 3.3 Hz, ^4J = 1.7 Hz, 1H), 7.10-7.17 (m, 2H), 7.35-7.40 (m, 2H), 7.42 (dd, ^3J = 3.2 Hz, ^4J = 1.7 Hz, 1H), 7.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 14.0, 21.6, 22.5, 26.2, 30.4, 31.2, 50.5, 112.6, 117.2, 124.1, 124.6, 125.4, 126.9, 129.9, 135.4, 138.3, 145.2. HR-MS (ESI^+) : $[M+H]^+$ calcd. for $C_{19}H_{25}N_4O_2S$: 373.1693; found : 373.1696. IR (cm^{-1}): 2927 (w), 1597 (w), 1366 (m), 1190 (w), 1172 (s).

Characterization of 1-(hex-5-en-1-yl)-4-(1-tosyl-1H-pyrrol-2-yl)-1H-1,2,3-triazole 2b



2b (5.19 mmol starting material, yellowish oil, 99% yield)
^{1}H NMR (400 MHz, $CDCl_3$) : δ = 1.47 (tt, ^3J = 7.6 Hz, ^3J = 7.6 Hz, 2H), 1.97 (tt, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H), 2.13 (dtt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 2H), 2.33 (s, 3H), 4.41 (t, ^3J = 7.2 Hz, 2H), 4.96-5.09 (m, 2H), 5.79 (ddt, ^EJ = 17.3 Hz, ^ZJ = 10.1 Hz, ^3J = 6.8 Hz, 1H), 6.35 (dd, ^3J = 3.4 Hz, ^3J = 3.4 Hz, 1H), 6.64 (dd, ^3J = 3.4 Hz, ^4J = 1.8 Hz, 1H), 7.12-7.19 (m, 2H), 7.34-7.41 (m, 2H), 7.43 (dd, ^3J = 3.3 Hz, ^4J = 1.8 Hz, 1H), 7.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 21.5, 25.5, 29.7, 33.0, 50.1, 112.5, 115.3, 117.1, 124.0, 124.5, 125.2, 126.8, 129.8, 135.3, 137.7, 138.2, 145.1. HR-MS (ESI^+): $[M+H]^+$ calcd. for $C_{19}H_{23}N_4O_2S$: 371.1536; found : 371.1546. IR (cm^{-1}): 2926 (w), 1639 (w), 1595 (w), 1363 (m), 1190 (m).

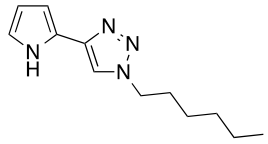
General procedure for pyrrole detosylation



To a solution of **2** (1.55 g, 4.15 mmol, 1.0 eq) in 1,4-dioxane (4 mL/mmol of **2**) were added NaOH 5N (36 eq) and tetrabutylammonium bromide (5 mol%). The biphasic solution was heated under reflux for 40 hours with vigourous stirring.

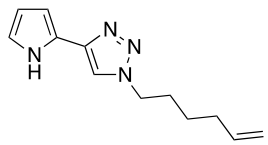
After completion of the reaction, the mixture was diluted by addition of Et_2O and water. The organic layer was collected, washed twice with aqueous $NaHCO_3$, brine, dried over Na_2SO_4 and concentrated under vacuum. The oily residue was precipitated by addition of pentane and the suspension was concentrated to dryness to afford **3** as a white partially crystallized solid which was used in the next step without further purification.

Characterization of 1-hexyl-4-(1H-pyrrol-2-yl)-1H-1,2,3-triazole 3a



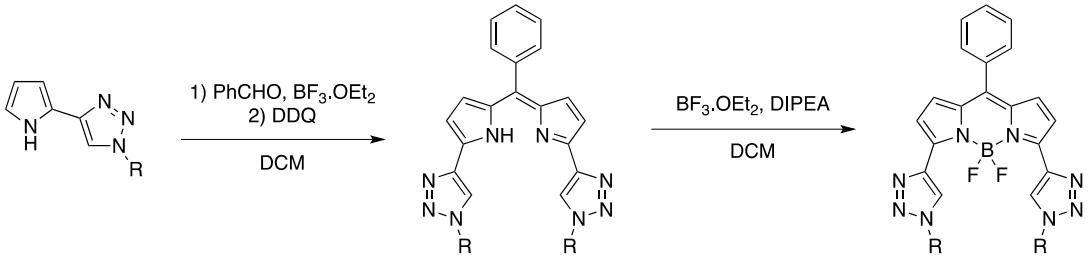
3a (4.15 mmol starting material, white-off solid, 92% yield)
^{1}H NMR (400 MHz, $CDCl_3$) : δ = 0.82-0.94 (m, 3H), 1.24-1.40 (m, 6H), 1.87-1.98 (tt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 2H), 4.35 (t, ^3J = 7.2 Hz, 2H), 6.26 (ddd, ^3J = 3.6 Hz, ^3J = 2.7 Hz, ^4J = 2.7 Hz, 1H), 6.39 (ddd, ^3J = 3.6 Hz, ^4J = 2.5 Hz, ^4J = 1.4 Hz, 1H), 6.90 (ddd, ^3J = 2.7 Hz, ^3J = 2.7 Hz, ^4J = 1.5 Hz, 1H), 7.59 (s, 1H), 9.88 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 14.1, 22.5, 26.2, 30.3, 31.3, 50.6, 105.8, 109.4, 117.9, 118.8, 122.8, 141.9. HR-MS (ESI^+) : $[M+H]^+$ calcd. for $C_{12}H_{19}N_4$: 219.1604; found : 219.1599. MP (Kofler): 97°C. IR (cm^{-1}) : 3192 (m), 2957 (m), 2930 (m), 1620 (m), 1523 (m), 1362 (m), 1215 (m).

Characterization of 1-(hex-5-en-1-yl)-4-(1H-pyrrol-2-yl)-1H-1,2,3-triazole 3b



3b (4.75 mmol starting material, white-off solid, 90% yield)
^{1}H NMR (400 MHz, $CDCl_3$) : δ = 1.44 (tt, ^3J = 7.6 Hz, ^3J = 7.6 Hz, 2H), 1.94 (tt, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H), 2.10 (dtt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 2H), 4.36 (t, ^3J = 7.2 Hz, 2H), 4.98 (ddt, ^ZJ = 10.1 Hz, ^2J = 2.0 Hz, ^4J = 1.3 Hz, 1H), 5.02 (ddt, ^EJ = 17.1 Hz, ^2J = 2.0 Hz, ^4J = 1.6 Hz, 1H), 5.76 (ddt, ^EJ = 17.1 Hz, ^ZJ = 10.3 Hz, ^3J = 6.7 Hz, 1H), 6.26 (ddd, ^3J = 3.4 Hz, ^3J = 2.7 Hz, ^4J = 2.7 Hz, 1H), 6.39 (ddd, ^3J = 3.5 Hz, ^4J = 2.5 Hz, ^4J = 1.4 Hz, 1H), 6.90 (ddd, ^3J = 2.7 Hz, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1H), 7.59 (s, 1H), 9.92 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 25.7, 29.7, 33.1, 50.3, 105.8, 109.4, 115.4, 117.8, 118.8, 122.8, 137.8, 142.0. HR-MS (ESI^+) : $[M+H]^+$ calcd. for $C_{12}H_{17}N_4$: 217.1448; found : 217.1456. MP (Kofler): 96°C. IR (cm^{-1}): 3179 (m), 3130 (m), 2938 (m), 1639 (m), 1622 (m); 1523 (m), 1356 (m), 1217 (m).

General procedure for BODIPY synthesis

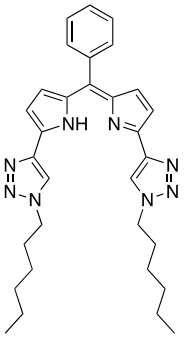


3 (2.0 eq) was dissolved in anhydrous DCM (13 mL/mmol of **3**). Benzaldehyde (1.1 eq) and few drops of $BF_3.OEt_2$ were added, and the flask was capped and stirred for 24 hours. The reaction was monitored by TLC. After full consumption of **3**, DDQ (1.2 eq) was poured into the mixture, which turned dark immediately and stirred for 2 hours. The dark purple slurry was diluted by additional DCM, and washed 3 times with saturated aqueous $NaHCO_3$. The organic layer was then washed with water, brine, dried over Na_2SO_4 and concentrated to dryness.

Crude product was purified by silica gel column chromatography using EtOAc/cyclohexane (40:60) as eluent to afford the dipyrromethene (see NMR p 8, 21, 22) which as dissolved in dry DCM (30 mL/mmol dipyrromethene) and anhydrous DIPEA (6.0 eq). $BF_3.OEt_2$ (9.0 eq) was added dropwise and the mixture was stirred under inert atmosphere at room temperature for 2 h.[6]

The fluorescent mixture was diluted by additional DCM, and neutralized by saturated aqueous $NaHCO_3$. Neutralization was repeated twice, then organic layer was collected, dried over Na_2SO_4 and concentrated to dryness. The crude was purified by silica gel column chromatography with EtOAc/cyclohexane (4:6) as eluent.

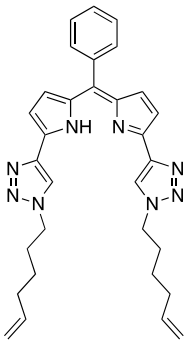
Characterization of (Z)-1-hexyl-4-(2-((5-(1-hexyl-1H-1,2,3-triazol-4-yl)-1H-pyrrol-2-yl)(phenyl) methylene)-2H-pyrrol-5-yl)-1H-1,2,3-triazole



(1.16 mmol starting material, red powder, 63% yield)

^{1}H NMR (400 MHz, Acetone-d_6) : δ = 0.80-0.94 (m, 6H), 1.24-1.49 (m, 12H), 1.94-2.10 (m, 4H), 4.55 (t, ^3J = 7.2 Hz, 4H), 6.64 (d, ^3J = 4.2 Hz, 2H), 6.89 (d, ^3J = 4.2 Hz, 2H), 7.53-7.59 (m, 5H), 8.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.3, 30.4, 31.3, 50.7, 116.1, 121.5, 127.8, 129.0, 129.5, 131.0, 137.3, 139.6, 141.7, 142.8, 146.0. HR-MS (ESI^+): $[M+H]^+$ calcd. for $C_{31}H_{39}N_8$: 523.3292; found : 523.3279. MP (Kofler): 159°C. IR (cm^{-1}): 2922 (m), 1589 (s), 1539 (s), 1319 (s), 1223 (s).

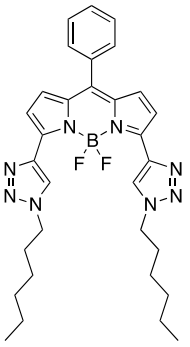
Characterization of (Z)-1-(hex-5-en-1-yl)-4-(2-((5-(1-(hex-5-en-1-yl)-1H-1,2,3-triazol-4-yl)-1H-pyrrol-2-yl) (phenyl)methylene)-2H-pyrrol-5-yl)-1H-1,2,3-triazole



(3.24 mmol starting material, red powder, 69% yield)

^{1}H NMR (400 MHz, $CDCl_3$) : δ = 1.49 (tt, ^{3}J = 7.6 Hz, ^{3}J = 7.6 Hz, 4H), 2.01 (tt, ^{3}J = 7.5 Hz, ^{3}J = 7.3 Hz, 4H), 2.13 (dtt, ^{3}J = 7.2 Hz, ^{3}J = 7.2 Hz, ^{4}J = 1.4 Hz, 4H), 4.46 (t, ^{3}J = 7.2 Hz, 4H), 4.97 (ddt, ^{Z}J = 10.2 Hz, ^{2}J = 1.9 Hz, ^{4}J = 1.2 Hz, 2H), 5.03 (ddd, ^{E}J = 17.1 Hz, ^{2}J = 1.9 Hz, ^{4}J = 1.6 Hz, 2H), 5.77 (ddt, ^{E}J = 17.1 Hz, ^{Z}J = 10.3 Hz, ^{3}J = 6.7 Hz, 2H), 6.67 (d, ^{3}J = 4.2 Hz, 2H), 6.85 (d, ^{3}J = 4.2 Hz, 2H), 7.42-7.57 (m, 5H), 8.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 25.8, 29.8, 33.1, 50.5, 115.5, 116.1, 121.5, 127.8, 129.0, 129.6, 131.0, 137.2, 137.9, 139.7, 141.8, 142.9, 146.0. HR-MS (ESI^+) : $[M+H]^+$ calcd. for $C_{31}H_{35}N_8$: 519.2979; found : 519.2957. MP (Kofler): 179°C. IR (cm^{-1}): 2937 (w), 1639 (w), 1587 (s), 1537 (s), 1312 (s), 1221 (s).

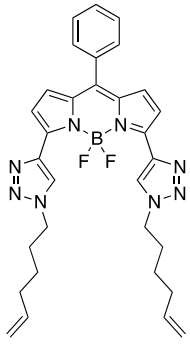
Characterization of 5,5-difluoro-3,7-bis(1-hexyl-1H-1,2,3-triazol-4-yl)-10-phenyl-5H-4λ4,5λ4-dipyrrolo[1,2-c:2',1'-f][1,3,2] diazaborinin-4-ium-5-uide 4a



4a (0.191 mmol starting material, deep purple powder, 93% yield)

^{1}H NMR (400 MHz, $CDCl_3$) : δ = 0.78-0.97 (m, 6H), 1.14-1.49 (m, 12H), 1.99 (tt, ^{3}J = 7.2 Hz, ^{3}J = 7.2 Hz, 4H), 4.44 (t, ^{3}J = 7.3 Hz, 4H), 6.90 (d, ^{3}J = 4.4 Hz, 2H), 7.35 (d, ^{3}J = 4.4 Hz, 2H) , 7.47-7.60 (m, 5H), 8.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 14.0, 22.5, 26.2, 30.3, 31.2, 50.7, 120.0, 125.0 (t, J = 11.5 Hz), 128.4, 130.4, 130.6, 131.0, 134.1, 136.6, 139.6, 143.0, 148.1. ^{19}F NMR (160 MHz, $CDCl_3$) : δ = -144.2 (q, ^{1}J = 33.6 Hz). HR-MS (ESI+) : $[M+H]^+$ calcd. for $C_{31}H_{38}BF_2N_8$: 571.3280; found : 571.3296. MP (Kofler) : 156°C. IR (cm-1): 3150 (w), 2924 (m), 1577 (s), 1543 (s), 1308 (s).

Characterization of 5,5-difluoro-3,7-bis(1-(hex-5-en-1-yl)-1H-1,2,3-triazol-4-yl)-10-phenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2] diazaborinin-4-ium-5-uide 4b



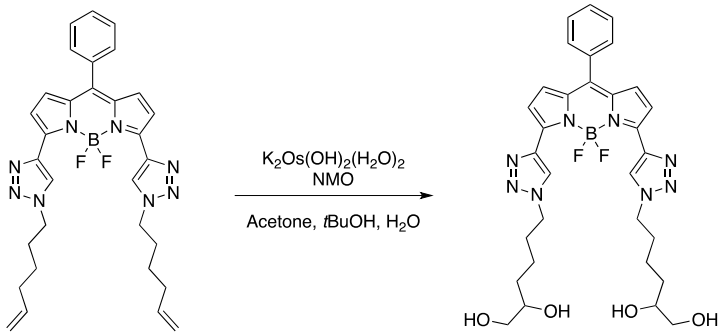
4b (0.171 mmol starting material, deep purple powder, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) : δ = 1.52 (tt, ^{3}J = 7.6 Hz, ^{3}J = 7.6 Hz, 4H), 2.03 (tt, ^{3}J = 7.5 Hz, ^{3}J = 7.5 Hz, 4H), 2.14 (dtt, ^{3}J = 7.1 Hz, ^{3}J = 7.1 Hz, ^{4}J = 1.4 Hz, 4H), 4.47 (t, ^{3}J = 7.2 Hz, 4H), 4.99 (ddt, ^{Z}J = 10.2 Hz, ^{2}J = 1.9 Hz, ^{4}J = 1.2 Hz, 2H), 5.04 (ddd, ^{E}J = 17.1 Hz, ^{2}J = 1.9 Hz, ^{4}J = 1.6 Hz, 2H), 5.79 (ddt, ^{E}J = 17.1 Hz, ^{Z}J = 10.3 Hz, ^{3}J = 6.7 Hz, 2H), 6.92 (d, ^{3}J = 4.4 Hz, 2H), 7.37 (d, ^{3}J = 4.4 Hz, 2H), 7.50-7.60 (m, 5H), 8.50 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 25.8, 29.8, 33.1, 50.5, 115.5, 120.1, 125.0 (t, J = 11.3 Hz), 128.5, 130.4, 130.7, 131.1, 134.1, 136.6, 137.8, 139.7, 143.2, 148.1. ^{19}F NMR (160 MHz, $CDCl_3$): δ = -144.2 (q, ^{1}J = 33.6 Hz). HR-MS (ESI^+): $[M+H]^+$ calcd. for

$C_{31}H_{34}BF_2N_8$: 567.2962; found : 567.2974. MP (Kofler): 142°C. IR (cm^{-1}): 3100 (w), 2940 (w), 1639 (w), 1578 (m), 1537 (s), 1313 (s).

Procedure for the preparation of the water-soluble BODIPY

Preparation of 3,7-bis(1-(5,6-dihydroxyhexyl)-1H-1,2,3-triazol-4-yl)-5,5-difluoro-10-phenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2] diazaborinin-4-ium-5-uide 5



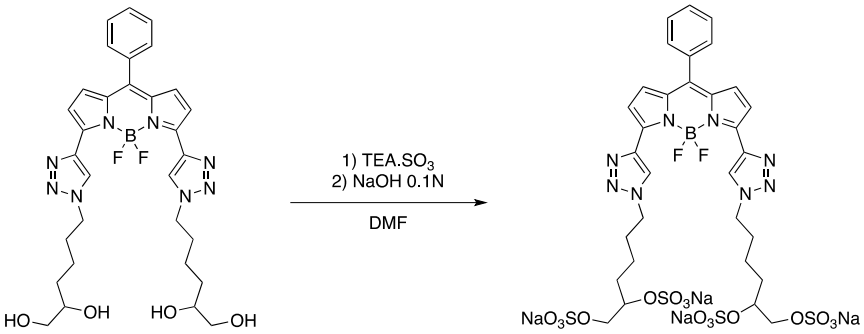
4b (380 mg, 671 µmol, 1.0 eq) was dissolved in a mixture of acetone (13 mL), *t*BuOH (720 µL) and water (720 µL). To the solution was added $K_2Os(OH)_4O_2$ (2.5 mg, 1.0 mol%) and N-methylmorpholine-N-oxide (275 mg, 3.5 eq).[7] The solution was stirred overnight at room temperature.

After full consumption of **4b**, the solvents were removed under reduced pressure and the solid was dissolved in DCM and the minimal amount of MeOH to ensure full dissolution. The organic layer was washed by aqueous $Na_2S_2O_3$, dried over $MgSO_4$ and concentrated to dryness.

The crude was purified by silica gel chromatography (9:1) DCM/MeOH followed by recrystallization in IPA/cyclohexane to get **5** as a crystallized gold solid (287 mg, 67%).

^{1}H NMR (400 MHz, DMSO-d_6) : δ = 1.25-40 (m, 4H), 1.41-1.57 (m, 4H), 1.87-2.01 (m, 4H), 3.25 (ddd, ^2J = 10.6 Hz, ^3J = 5.6 Hz, ^3J = 5.6 Hz, 2H), 3.28 (ddd, ^2J = 10.6 Hz, ^3J = 5.6 Hz, ^3J = 5.6 Hz, 2H), 3.37-3.45 (m, 2H), 4.41 (d, ^3J = 5.0 Hz, 2H), 4.45 (t, ^3J = 5.6 Hz, 2H), 4.57 (t, ^3J = 7.1 Hz, 4H), 7.00 (d, ^3J = 4.5 Hz, 2H), 7.31 (d, ^3J = 4.5 Hz, 2H), 7.60-7.70 (m, 5H), 8.82 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.2, 30.0, 32.7, 49.9, 65.9, 70.9, 119.4, 126.0 (t, J = 11.4 Hz), 128.6, 130.5, 130.6, 131.1, 133.2, 135.4, 138.0, 142.6, 147.5. ^{19}F NMR (160 MHz, DMSO-d_6): δ = -143.5 (q, ^1J = 33.2 Hz). HR-MS (ESI^+): $[M+H]^+$ calcd. for $C_{31}H_{38}BF_2N_8O_4$: 635.3072; found : 635.3085. MP (Kofler): 144°C. IR (cm^{-1}): 3325 (b), 2928 (w), 1578 (m), 1537 (s), 1325 (s).

Preparation of Sodium 3,7-bis(1-(5,6-bis(sulfonatooxy)hexyl)-1H-1,2,3-triazol-4-yl)-5,5-difluoro-10-phenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide 6



5 (50.3 mg, 79.3 µmol, 1.0 eq) was dissolved in anhydrous DMF (5 mL) under argon atmosphere. TEA.SO_3 (215 mg, 15 eq) was then poured to the solution and stirred at room temperature overnight.

The mixture was then cooled down to 0°C in an ice bath, diluted with 100 mL pure water and treated by a slow addition of NaOH 0.1 N (23.8 mL, 30 eq). The resulting mixture was then concentrated to dryness under vacuum. 100 mL of pure water was added to dissolve the solid and the solution was concentrated again. This operation was repeated at least 4 times, until DMF and TEA were fully evaporated.

The dark purple solid was then purified by dialysis to remove salts. The solid was dissolved in a minimal amount of pure water (~ 3 mL) and poured into a dialysis tube Float-A-Lyzer G2 0.1-0.5 kD. Dialysis was performed in a 500 mL pure water stirred in a beaker. The water was changed after 3, 6 and 24 hours. The solution contained into the tube was then collected, evaporated to dryness to get **6** (77 mg, 93%) as a dark solid.

^{1}H NMR (400 MHz, D_2O) : δ = 1.32-1.50 (m, 4H), 1.59-1.88 (m, 8H), 4.12 (dd, ^{2}J = 10.8 Hz, ^{3}J = 4.0 Hz, 2H), 4.23 (dd, ^{2}J = 10.8 Hz, ^{3}J = 4.0 Hz, 2H), 4.38 (t, ^{3}J = 7.1 Hz, 4H), 4.48-4.58 (m, 2H), 6.53 (d, ^{3}J = 4.4 Hz, 2H), 6.79 (d, ^{3}J = 4.4 Hz, 2H), 7.31 (d, ^{3}J = 7.4 Hz, 2H), 7.60 (t, ^{3}J = 7.4 Hz, 2H), 7.70 (t, ^{3}J = 7.4 Hz, 1H), 8.42 (s, 2H). ^{13}C NMR (100 MHz, D_2O): 21.4, 29.4, 29.9, 50.3, 68.8, 77.3, 118.8, 125.9 (*J* = 9.5 Hz), 128.5, 130.4, 130.6, 130.9, 133.4, 136.5, 138.6, 143.8, 145.7. ^{19}F NMR (160 MHz, D_2O): δ = -143.3 (m). HR-MS (ESI$^-$): [M-Na]$^-$ calcd. for $C_{31}H_{33}BF_2N_8Na_3O_{16}S_4$: 1019.0657; found : 1019.0675. MP (Kofler): >250°C. Not determined. IR (cm^{-1}): 3444 (b), 2943 (w), 1580 (m), 1549 (m), 1217 (m).

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(1) J. Waser, B. Gaspar, H. Nambu and E. M. Carreira, *J. Am. Chem. Soc.,* 2006, **128**, 11693–11712.

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Fluorescence measurements

	Solvent	λ_{max} (nm)	ε ($L.mol^{-1}.cm^{-1}$)	λ_{em} (nm)	ϕ [a] (%)	τ [b] (ns)	k_R [c] (10^6 s^{-1})	k_{NR} [c] (10^6 s^{-1})
4a	CH_2Cl_2	583	67000	598	>0.95	6.9	138	7.2
4b	CH_2Cl_2	583	83900	596	>0.95	6.5	146	7.7
5	MeOH	575	72700	590	0.86	6.8	126	20.6
6	MeOH	576	64000	595	0.93	7.8	119	8.9
6	H_2O	569	61000	590	0.81	6.9	117	27.5

[a] Standard used for quantum yield measurements: cresyl violet (ϕ = 0.55 in MeOH). [b] NanoLED excitation at 490 nm. [c] with $k_R=\phi/\tau$ and $k_{NR}=(1-\phi)/\tau$.

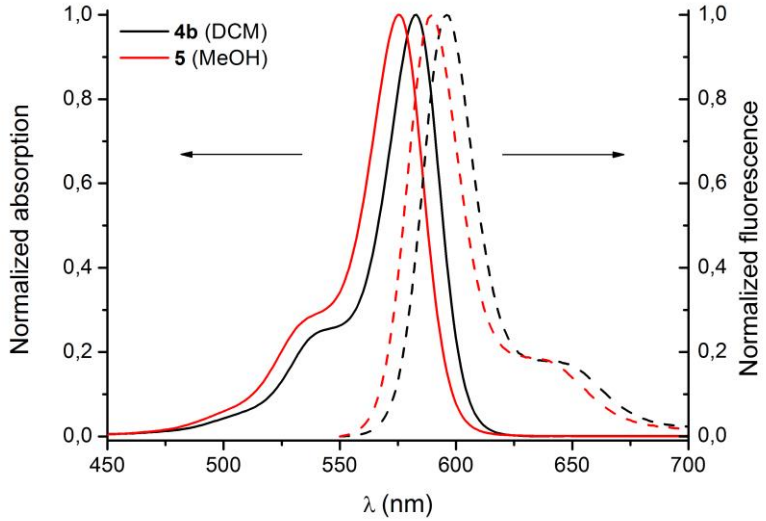

Fig 1: Normalized absorption (plain line) and normalized emission (dotted line) spectra for BODIPYs **4b** and **5**.

X-ray data

Crystal data of **4a** was collected at room temperature using a Geminini Oxford Diffractometer (MoKα radiation, λ = 0.71069 Å) equipped with a CCD camera and by using the related software.[8] An absorption correction (analytical) has been applied to all the data sets.[9] The structure was solved by direct methods using the SIR97 program [10] combined with Fourier Difference and the refined against F using the CRYSTALS program.[11] All atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms have been placed by Fourier Difference account the hybridization of the supporting atoms and for the possible presence of hydrogen bonds in the case of donor atoms. Hydrogen atoms have been finally refined using a riding mode.
CCDC 1405386 reference contains the supplementary crystallographic data for **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

In table SI1 is summarized the data collection parameters and refinement results for **4a**. Indications on B-F···H hydrogen bonds are located in Table SI2.

Table SI1. Single-crystal X-ray diffraction: data collection parameters and refinement results for **4a**.

	4a
Empirical formula	$C_{31}H_{37}B_1F_2N_8$
Molecular weight ($g.mol^{-1}$)	570.5
Crystal system	monoclinic
Space group	$P2_1/c$
Unit-cell parameters	a = 11.183(1) Å
	b = 9.737(1) Å
	c = 27.817(4) Å
	β = 94.45(1)°
	V = 3019.5(6) $Å^3$
Crystal shape	plate
Crystal color	red
Crystal size (mm^3)	0.099 × 0.279 × 0.331
Z	4
T (K)	293
Density	1.255
μ (mm^{-1})	0.086
No. ind. reflections	7122
Rint	0.087
R(F)	0.0782
$R_w(F)$	0.0839
S	1.08
$\Delta\rho_{min}$ / $\Delta\rho_{max}$ ($e^-.Å^{-3}$)	-0.40 / +0.63
No. reflections used	2901
No. refined parameters	379
Absorption correction	analytical

Table SI2. B-F···H hydrogen bonds information for **4a**.

B-F bond lengths (Å)	**F···H distances (Å)**
1.40(1)	2.287(2)
1.387(9)	2.571(3)

(8) CrysAlisPro, version 1.171.34.40 (rel. 27-08-2010, CrysAlis171.NET), Oxford Diffraction Ltd.

(9) O. D. L. CrysAlisPro, version 1.171.34.40 (rel. 27-08-2010, CrysAlis1 171.NET), (compiled Aug. 27, 2010, 11:50:40). Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by: R. C. Clark, J. S. Reid, Acta Crystallogr., Sect. A 1995, 51, 887-897.

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Cell culture, staining and epifluorescence microscopy observations

24 h prior to observation, actively growing HeLa cells were harvested and seeded in cell culture-treated 96-wells glass bottom plates, at a density of 1.10^4 cells per well, in Dulbecco's Modified Eagle Medium (DMEM) supplemented with 10% fetal calf serum, 50 $U.mL^{-1}$ penicillin/streptomycin and 1.25 $\mu g.mL^{-1}$ amphotericin B. Cells were then grown at 37°C in humidified atmosphere containing 5 % CO_2 in order to allow cellular adhesion and proliferation. After 24 h of culture, cells were stained with various concentrations (typically ranging from 5 nM to 500 µM) of **4a** or **6** in DMEM + 1% DMSO or DMEM, respectively, and then incubated for 15 min in the conditions described above. After staining, the cells were washed twice with DMEM and observed using an Olympus IX51 epifluorescence microscope. Red reflected fluorescence (Q565LP TRITC filter) and transmitted light images were obtained using an Olympus DP21 digital camera.

Cellular viability tests

24 h prior to experiment, actively growing HeLa cells were harvested and seeded in cell culture-treated 96-wells glass bottom plates, at a density of 1.10^4 cells per well, in Dulbecco's Modified Eagle Medium (DMEM) supplemented with 10% fetal calf serum, 50 $U.mL^{-1}$ penicillin/streptomycin and 1.25 $\mu g.mL^{-1}$ amphotericin B. Cells were then grown at 37°C in humidified atmosphere containing 5 % CO_2 in order to allow cellular adhesion and proliferation. After 24 h of culture, cells were treated with various concentrations of **4a** or **6** ranging from 100 nM to 100 µM in the presence of 1% DMSO, and then incubated for 1 h in the conditions described above. For viability measurements, a LIVE/DEAD® Cell Imaging Kit (488/570) (Life Technologies) was used to stain the viable cells: briefly, the cells were washed three times with DPBS (Dulbecco's Phosphate Buffered Saline : 2.7 mM KCl, 1.5 mM KH_2PO_4, 138 nM NaCl, 8 mM Na_2HPO_4-$7H_2O$) buffer and then treated with an appropriate concentration (as indicated by the manufacturer) of calcein AM. Live cells are distinguished by the presence of ubiquitous intracellular esterase activity as determined by the enzymatic conversion of the

virtually non-fluorescent cell-permeant calcein AM to the intensely fluorescent calcein, which is well-retained within live cells. The cells were then incubated for 10 min in the conditions described above, and the global fluorescence of each well was measured with an Infinite 200 PRO microplate reader (Tecan group Ltd.) at 488 nm excitation and 515 nm emission. The fluorescence of wells containing untreated cells was measured as positive control and for normalization (100% viability), and wells containing cells treated by 45% ethanol for 30 min were used as negative controls and for background fluorescence measurement. Each measurement was realized in triplicate.

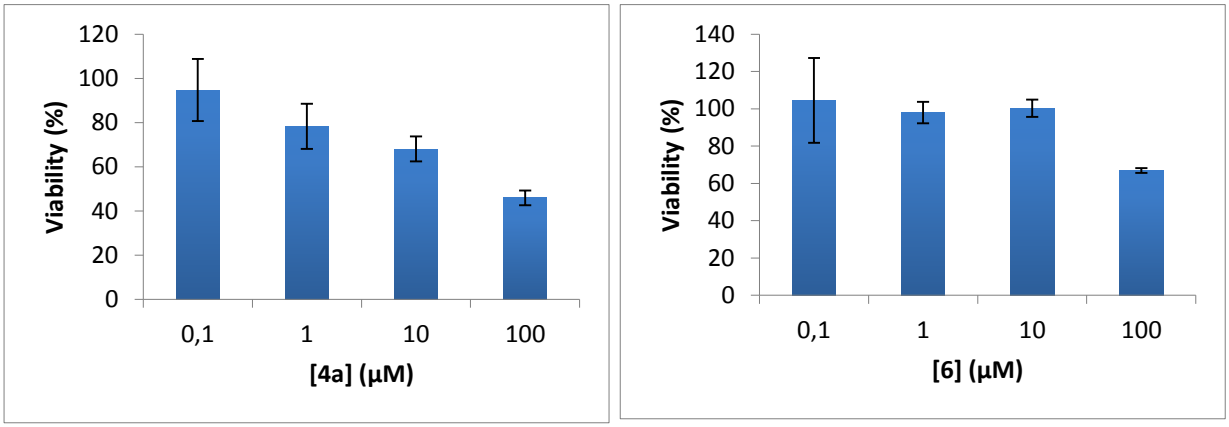
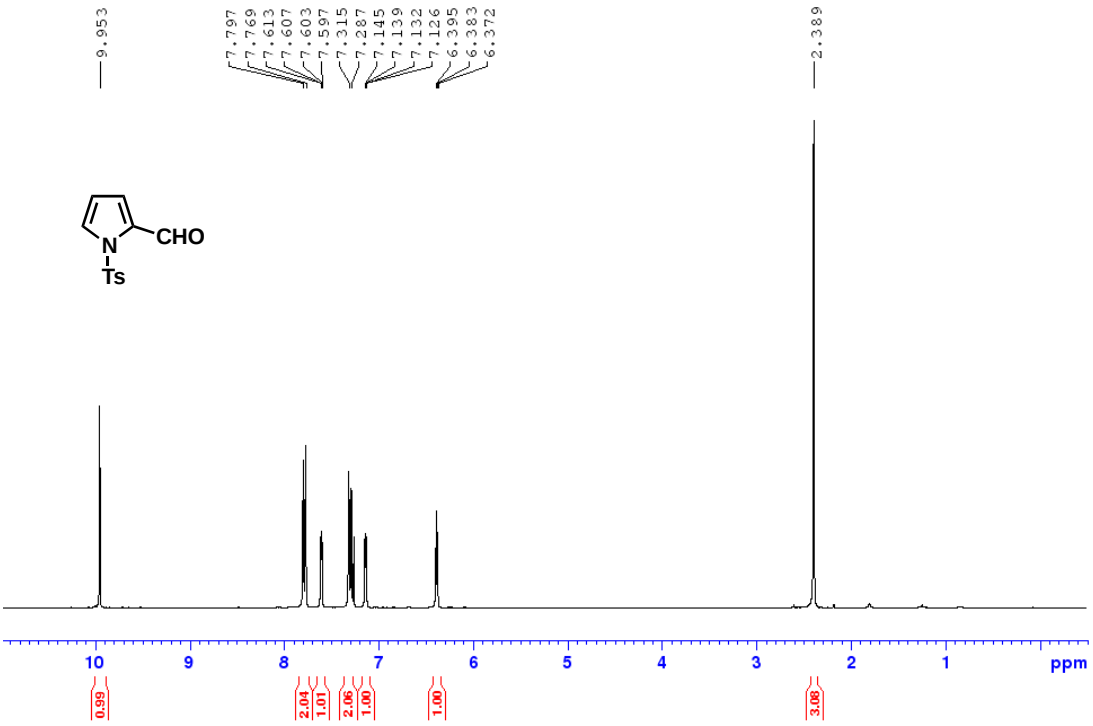


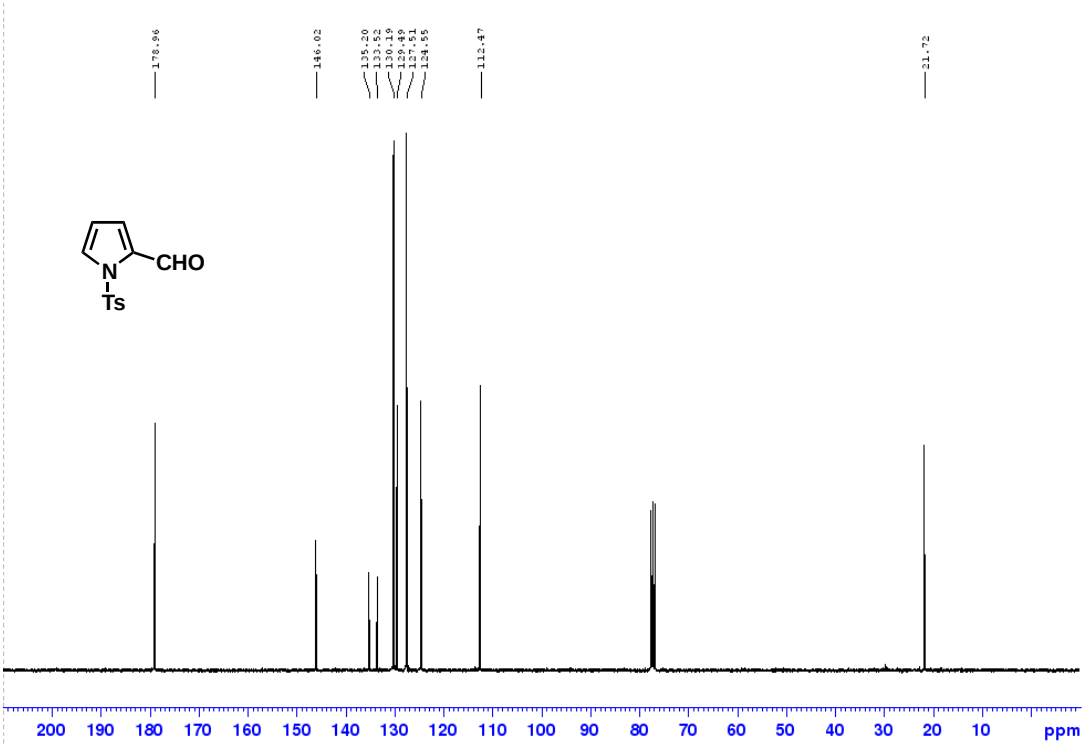
Fig. S1 Viability analysis of HeLa cells treated with **4a** and **6**. Cells were treated for 1 h with both compounds and then stained using calcein AM viability dye. The global fluorescence of wells containing untreated cells was set to 100%.

NMR Spectra

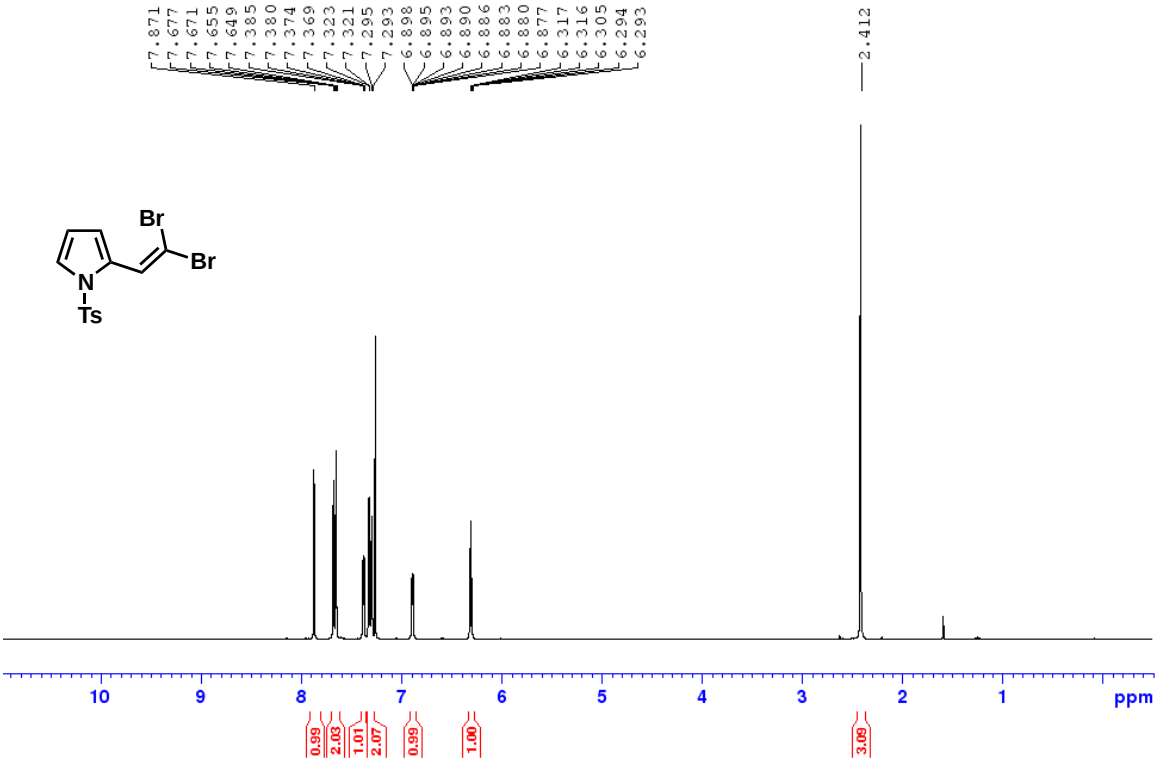
^{1}H NMR spectrum (300 MHz) of 1-tosyl-1H-pyrrole-2-carbaldehyde in $CDCl_3$



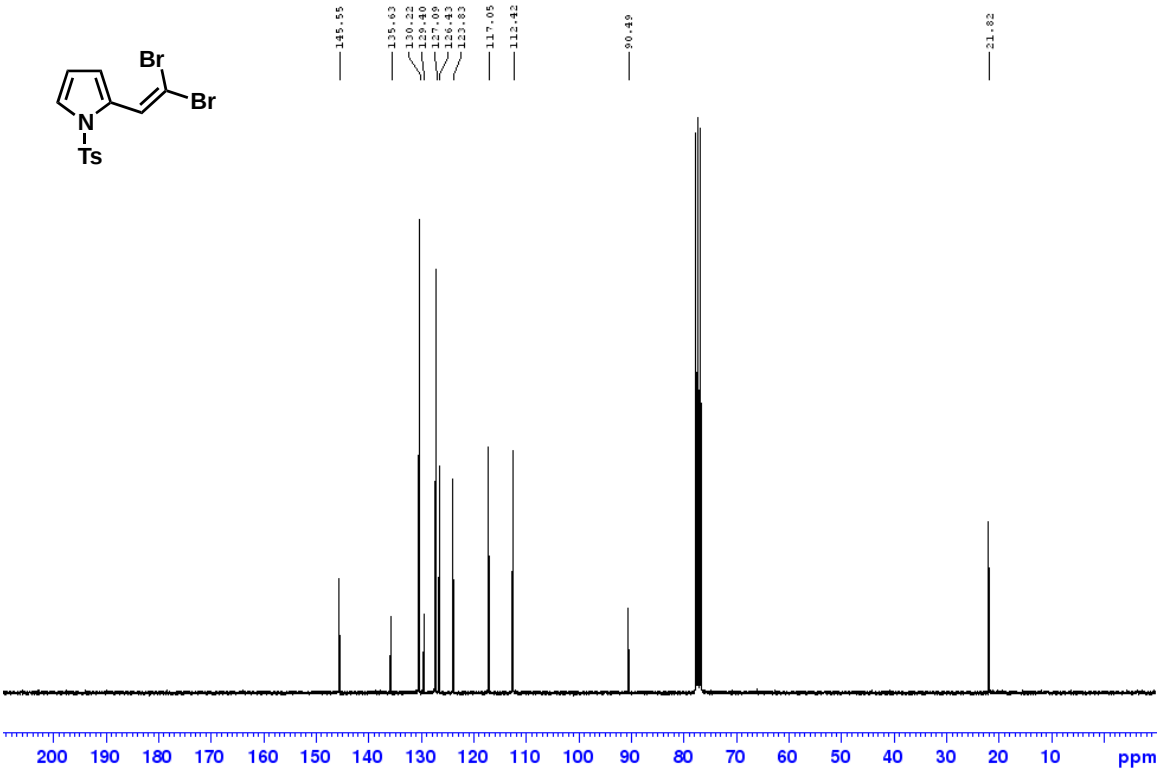
^{13}C NMR spectrum (75 MHz) of 1-tosyl-1H-pyrrole-2-carbaldehyde in $CDCl_3$



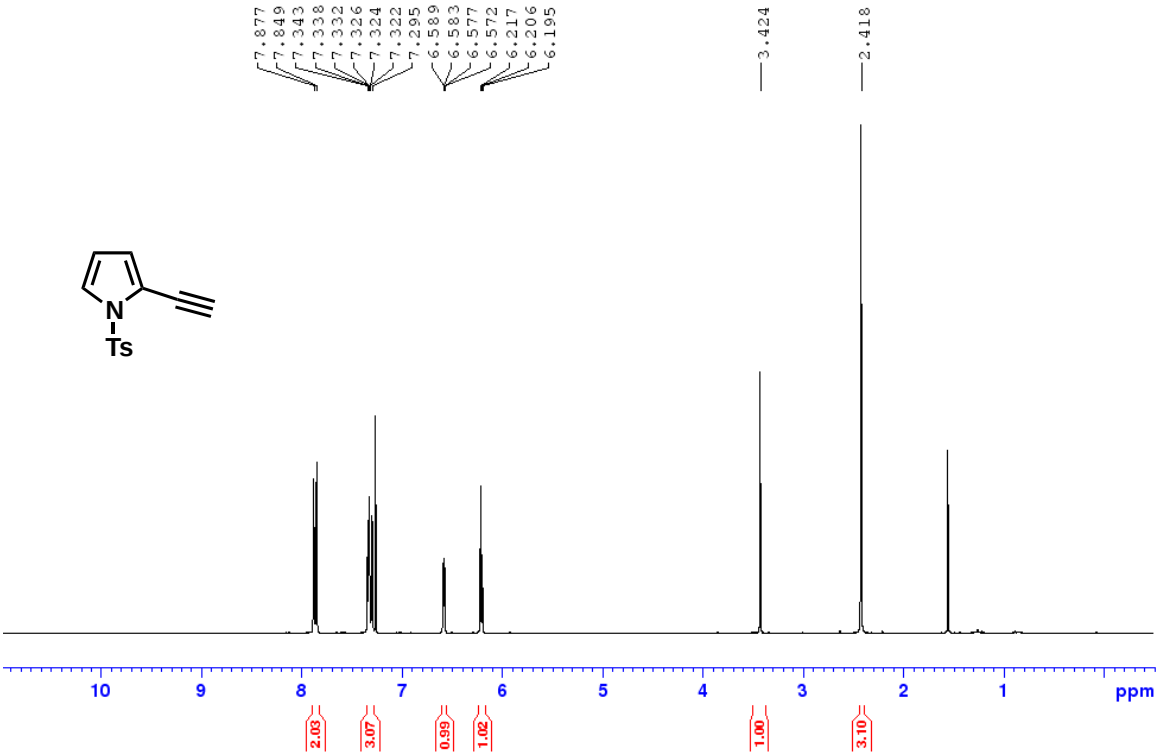
^{1}H NMR spectrum (300 MHz) of 2-(2,2-dibromovinyl)-1-tosyl-1H-pyrrole in $CDCl_3$



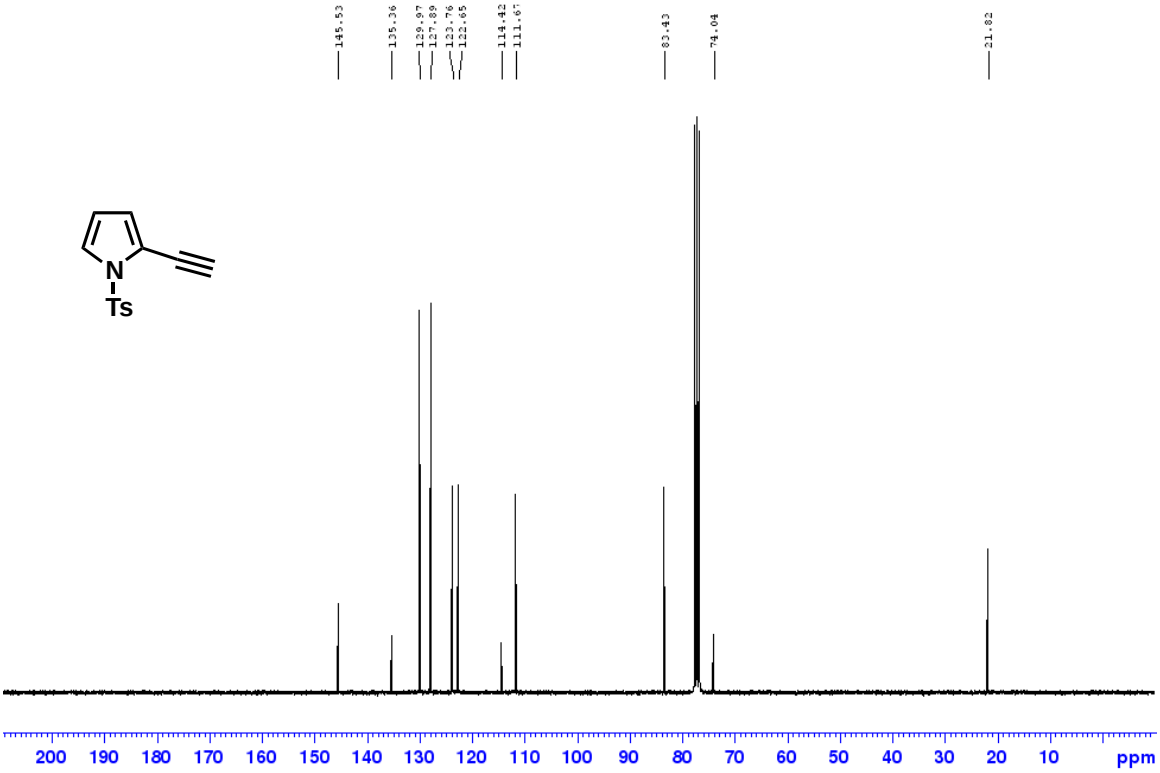
^{13}C NMR spectrum (75 MHz) of 2-(2,2-dibromovinyl)-1-tosyl-1H-pyrrole in $CDCl_3$



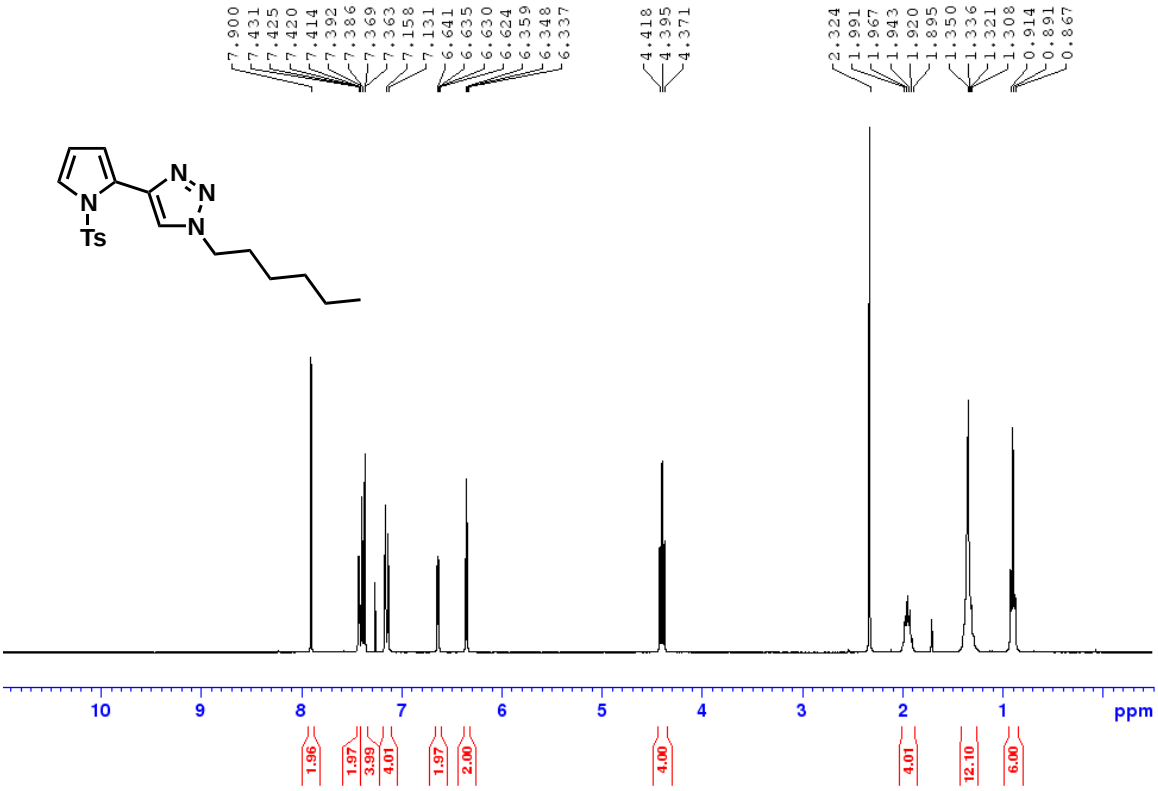
^{1}H NMR spectrum (300 MHz) of 1 in $CDCl_3$



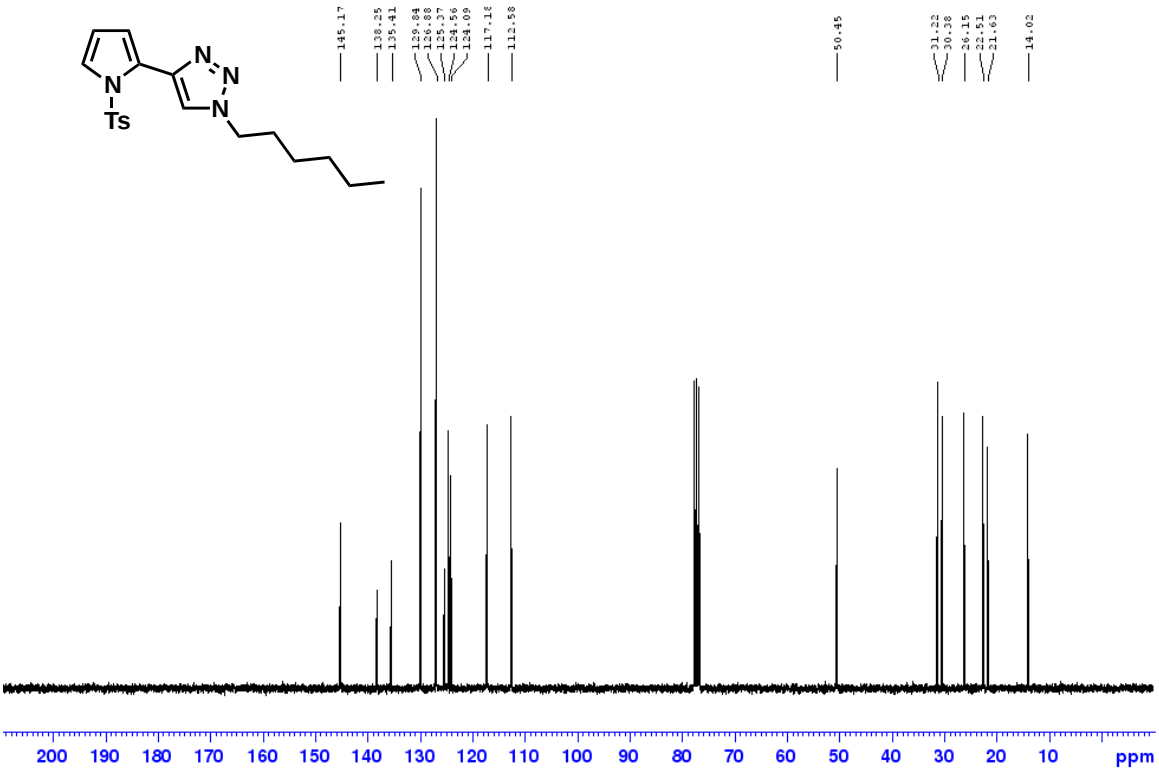
^{13}C NMR spectrum (75 MHz) of 1 in $CDCl_3$



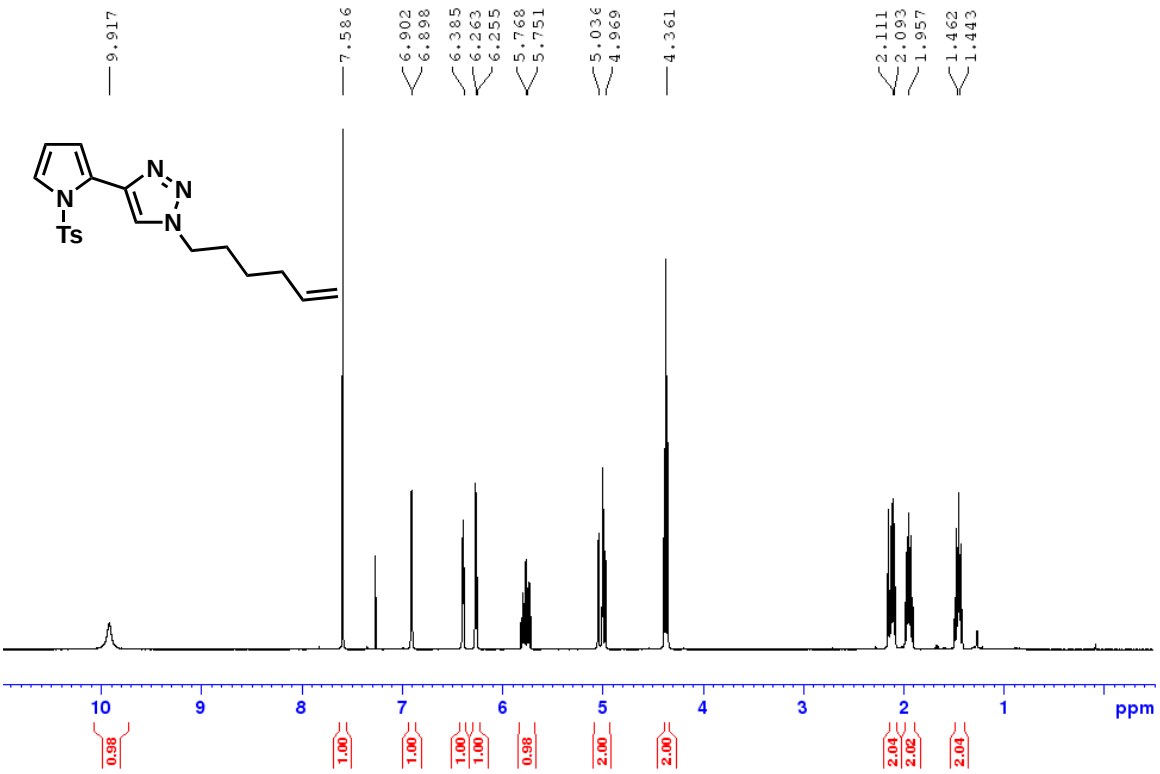
^{1}H NMR spectrum (400 MHz) of 2a in $CDCl_3$



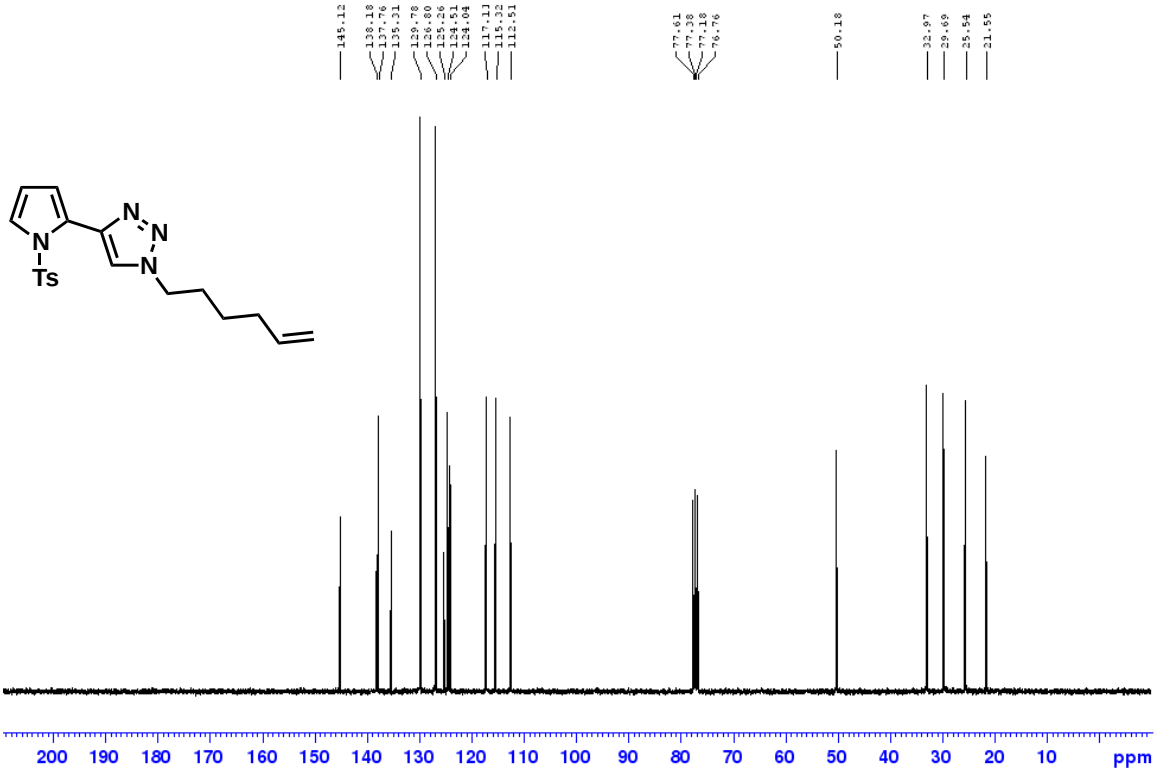
^{13}C NMR spectrum (100 MHz) of 2a in $CDCl_3$



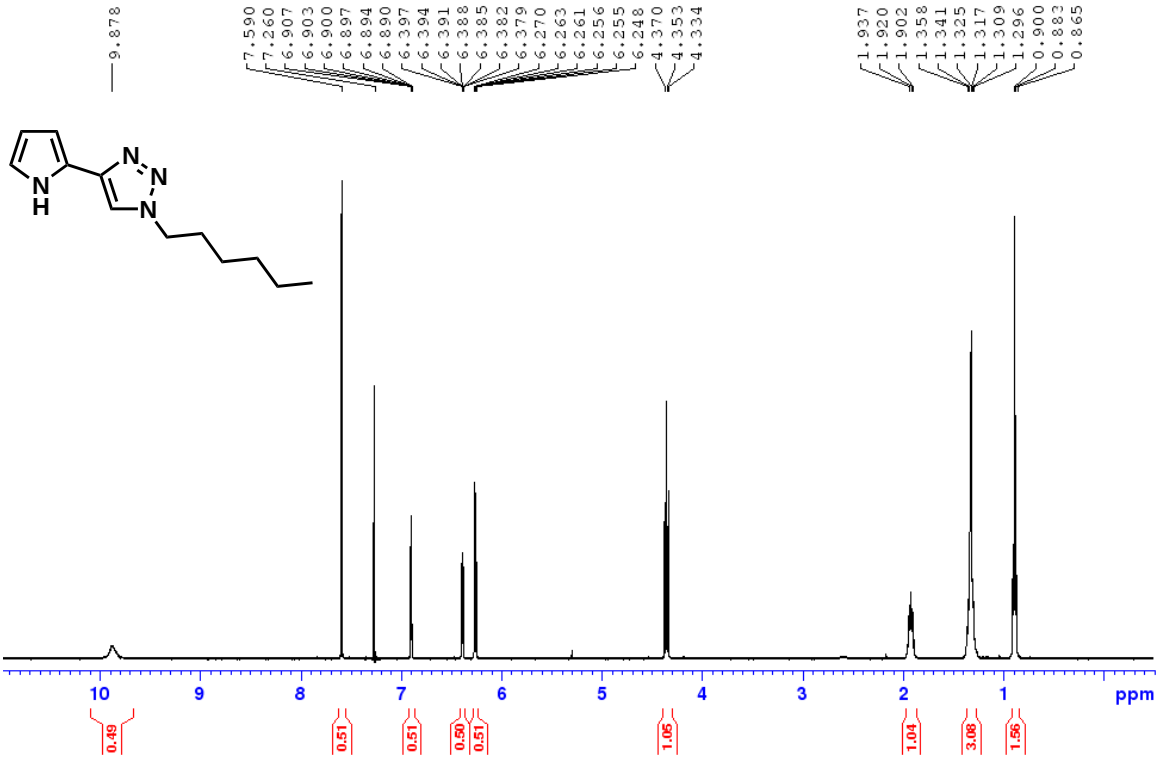
^{1}H NMR spectrum (400 MHz) of 2b in $CDCl_3$



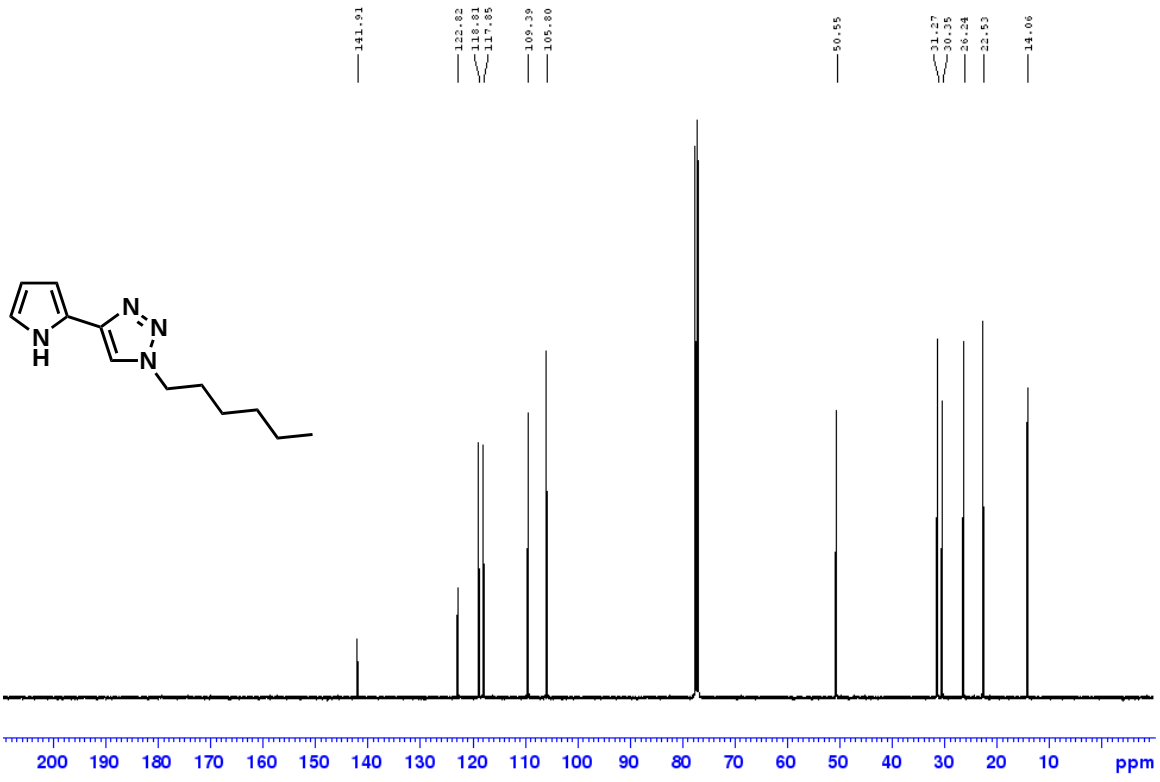
^{13}C NMR spectrum (100 MHz) of 2b in $CDCl_3$



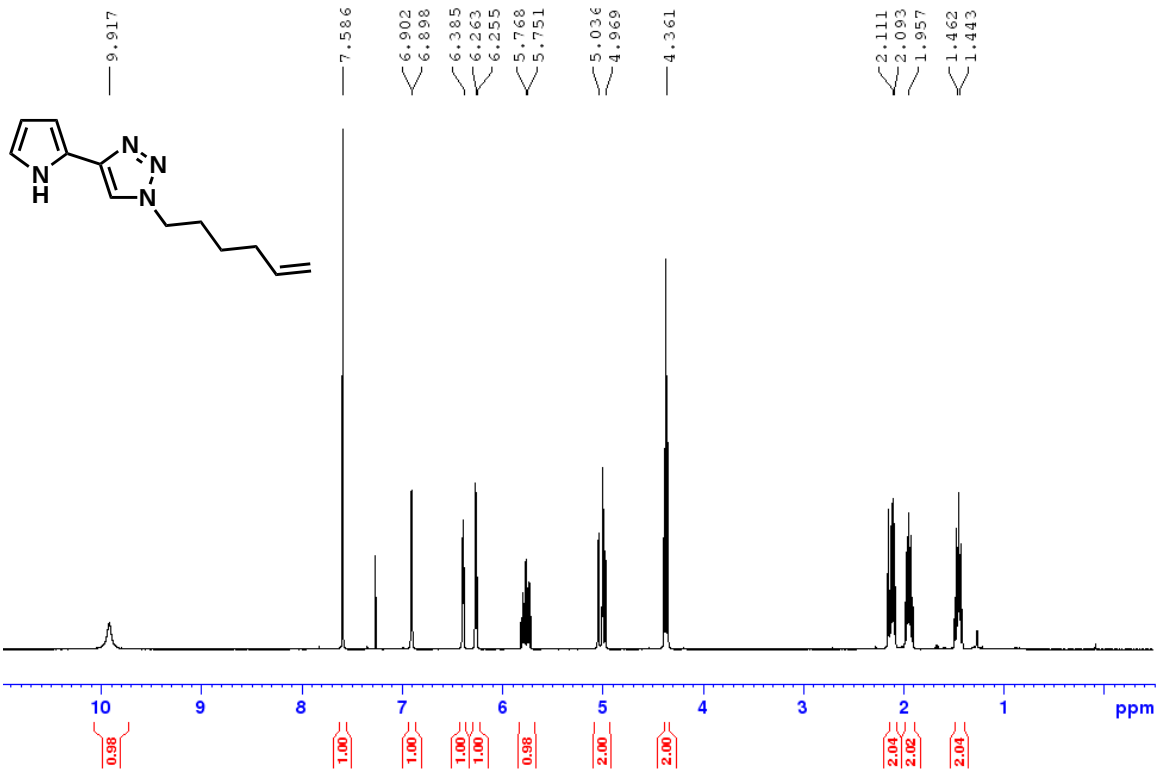
^{1}H NMR spectrum (300 MHz) of 3a in $CDCl_3$



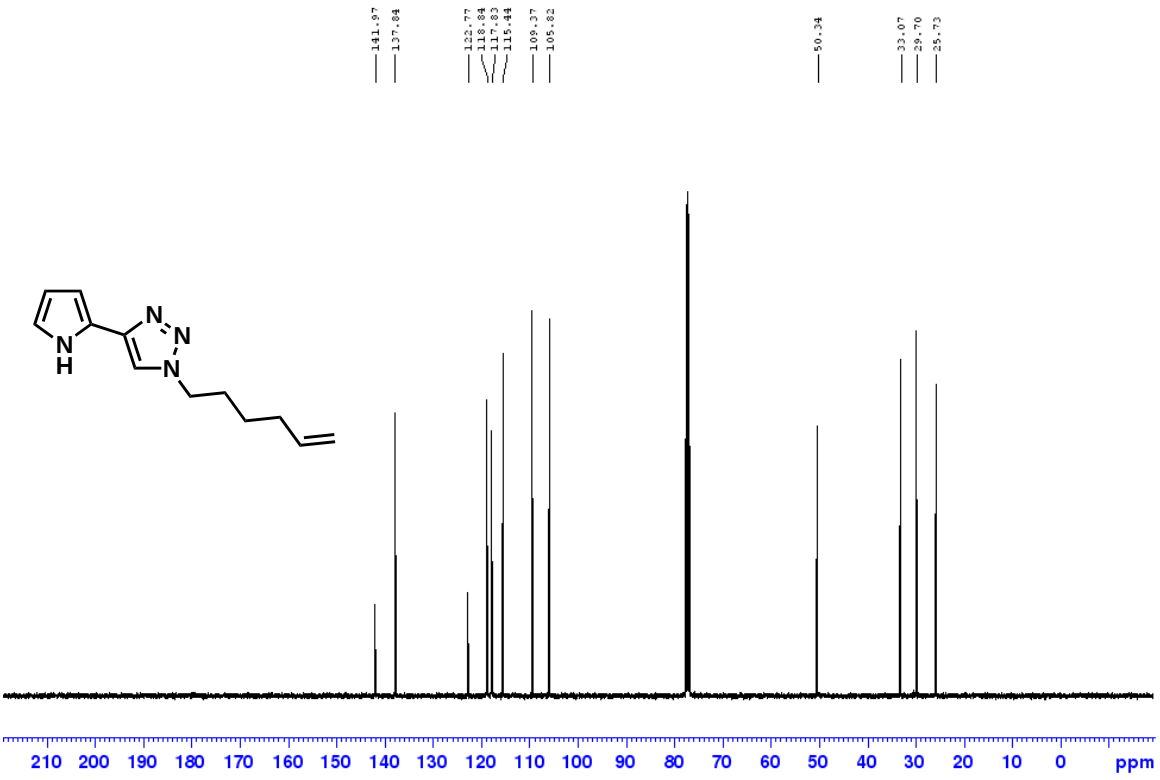
^{13}C NMR spectrum (100 MHz) of 3a in $CDCl_3$



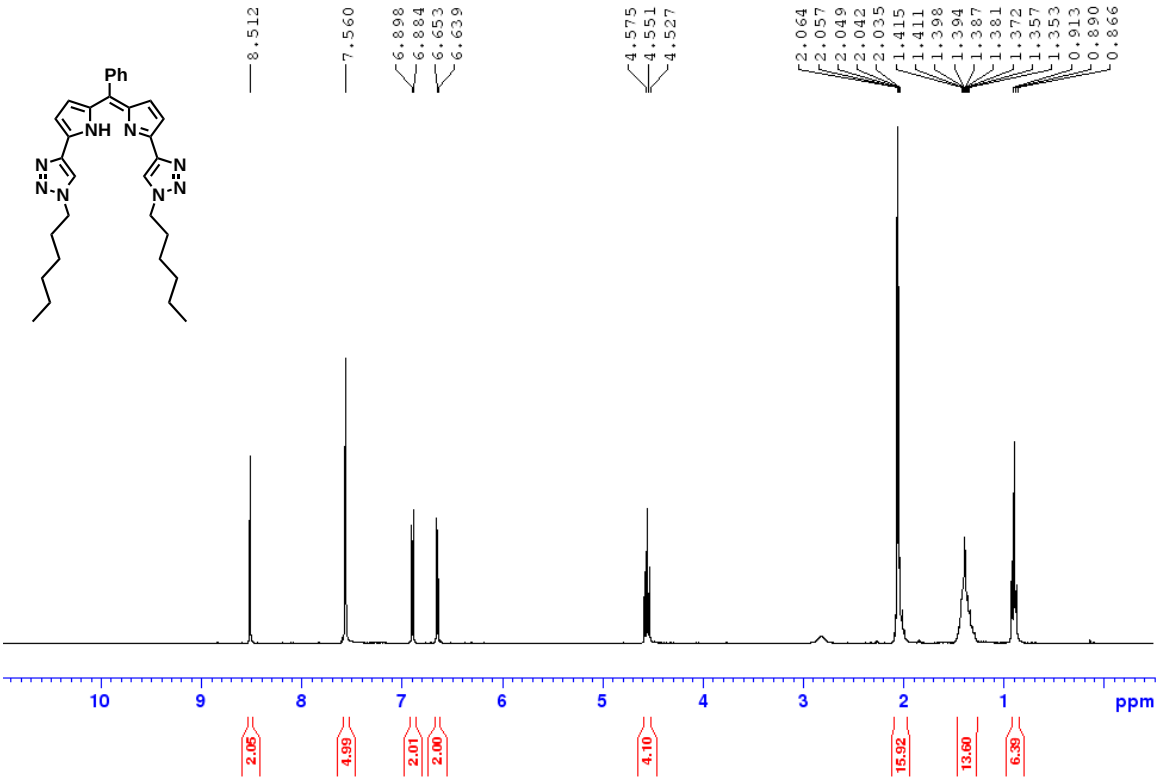
^{1}H NMR spectrum (400 MHz) of 3b in $CDCl_3$



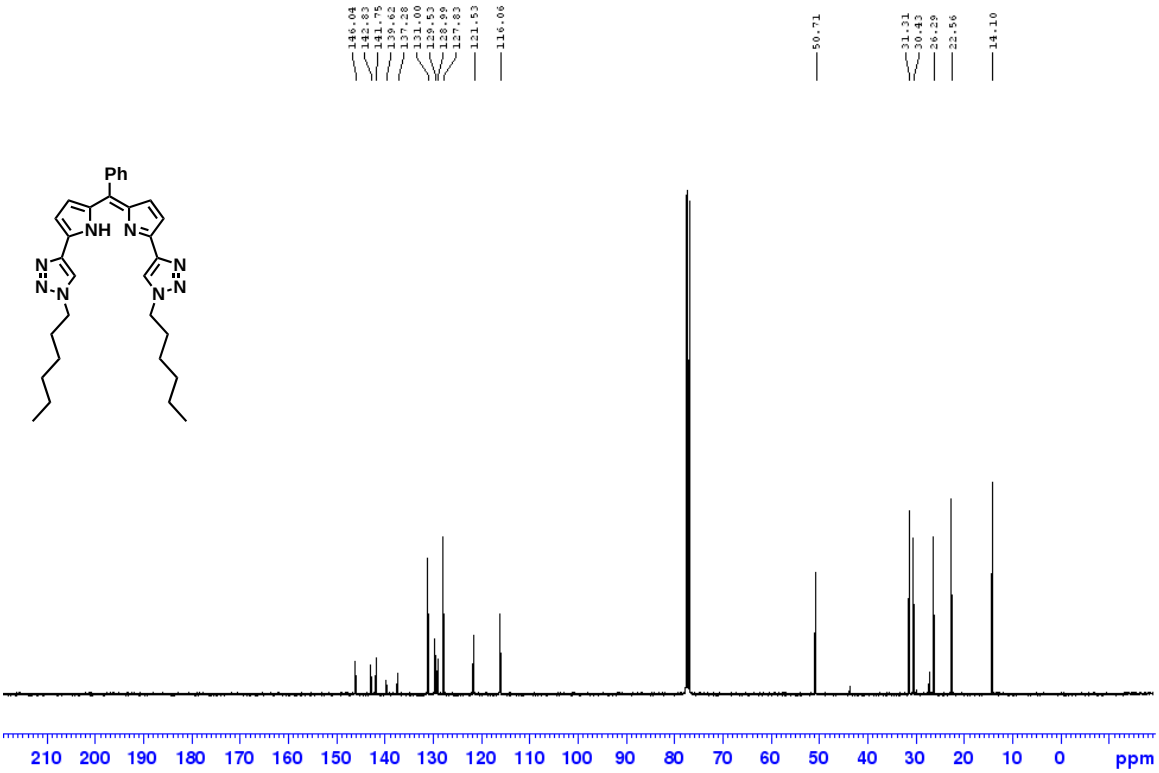
^{13}C NMR spectrum (100 MHz) of 3b in $CDCl_3$



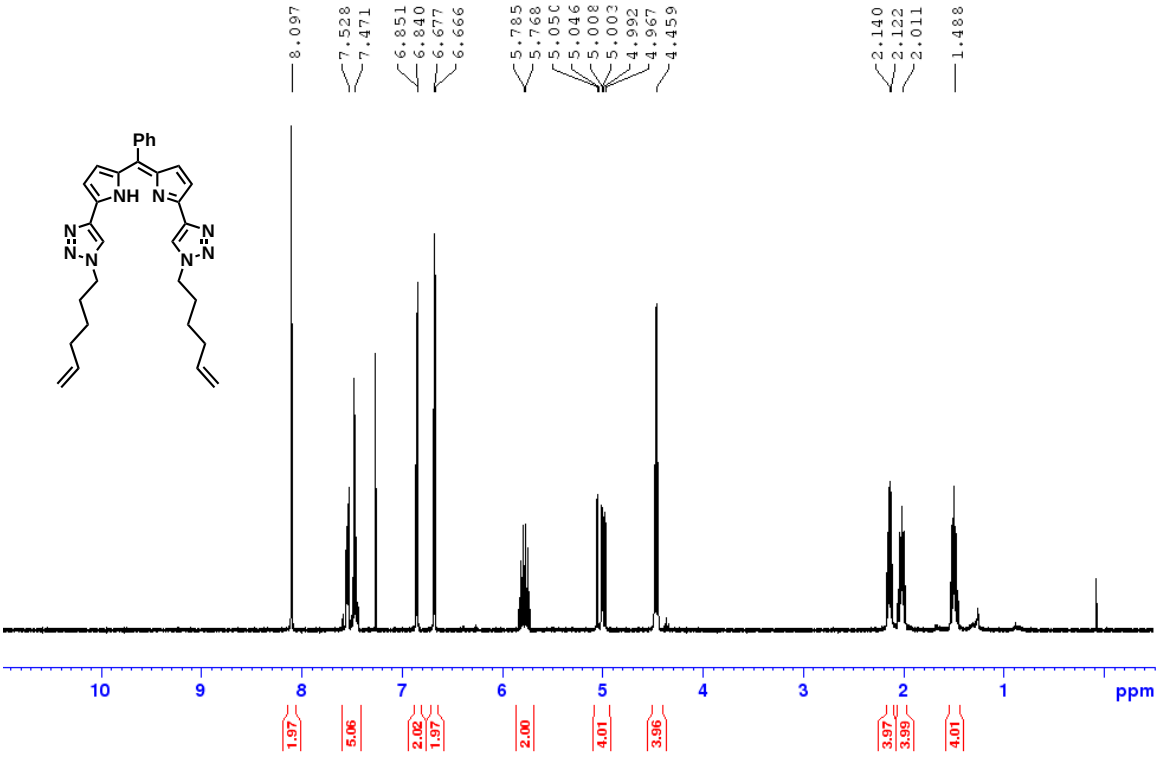
^{1}H NMR spectrum (400 MHz) of dipyrromethene derived from 3a in acetone-d_6



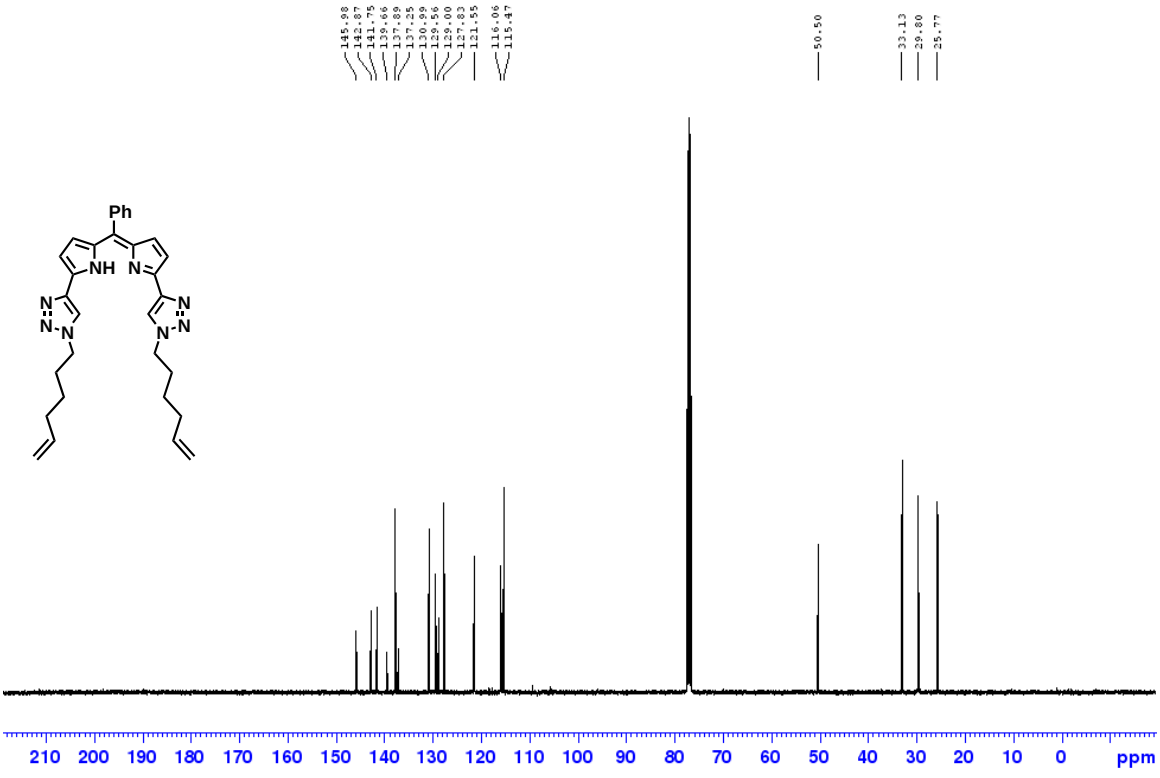
^{13}C NMR spectrum (100 MHz) of dipyrromethene derived from 3a in $CDCl_3$



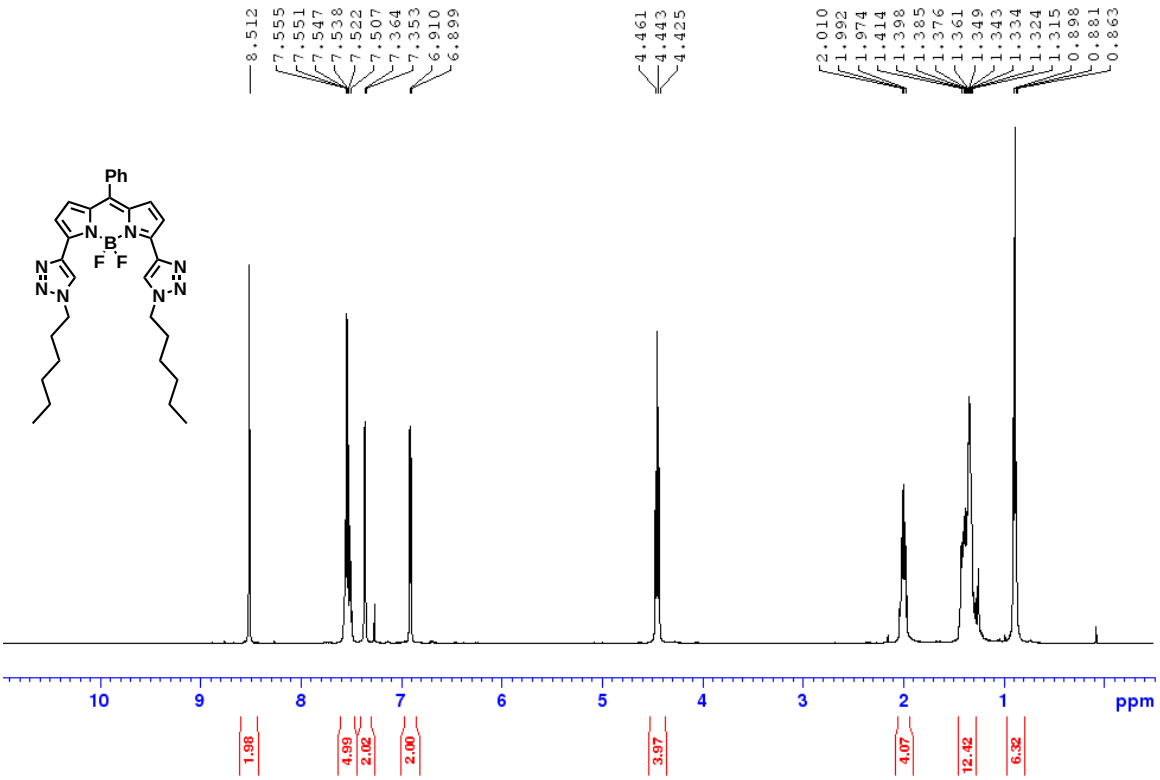
^{1}H NMR spectrum (400 MHz) of dipyrromethene derived from 3b in $CDCl_3$



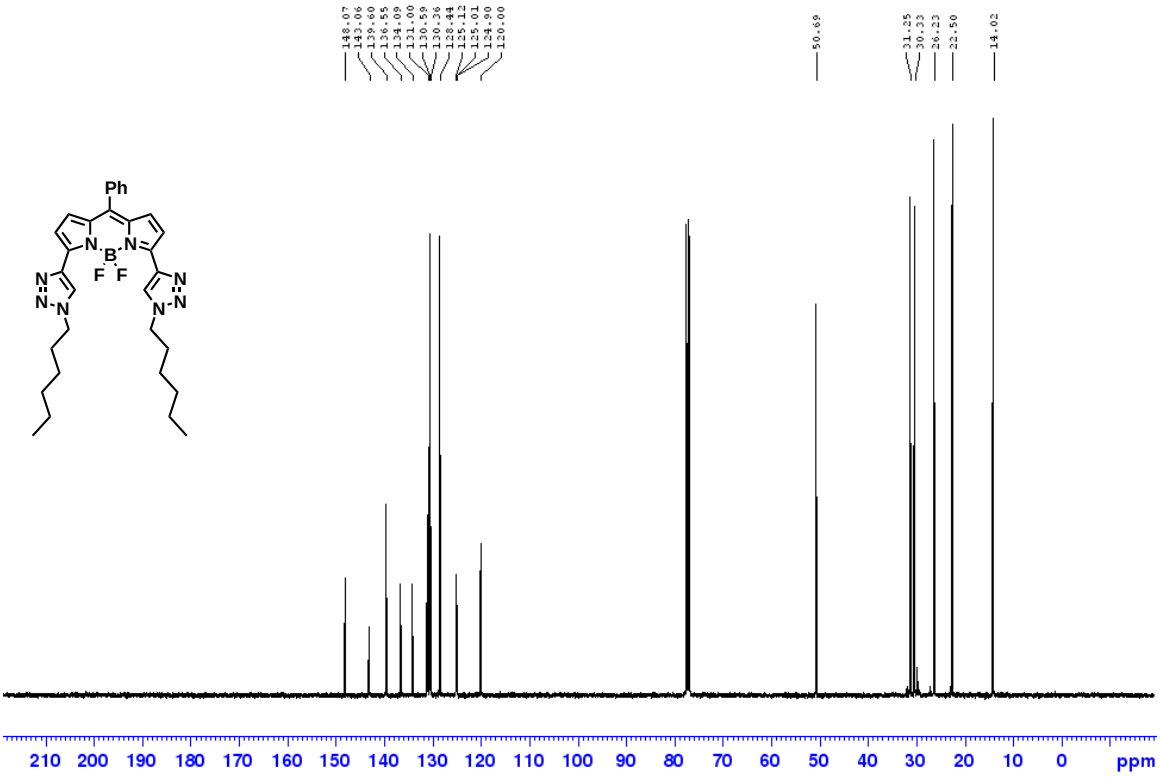
^{13}C NMR spectrum (100 MHz) of dipyrromethene derived from 3b in $CDCl_3$



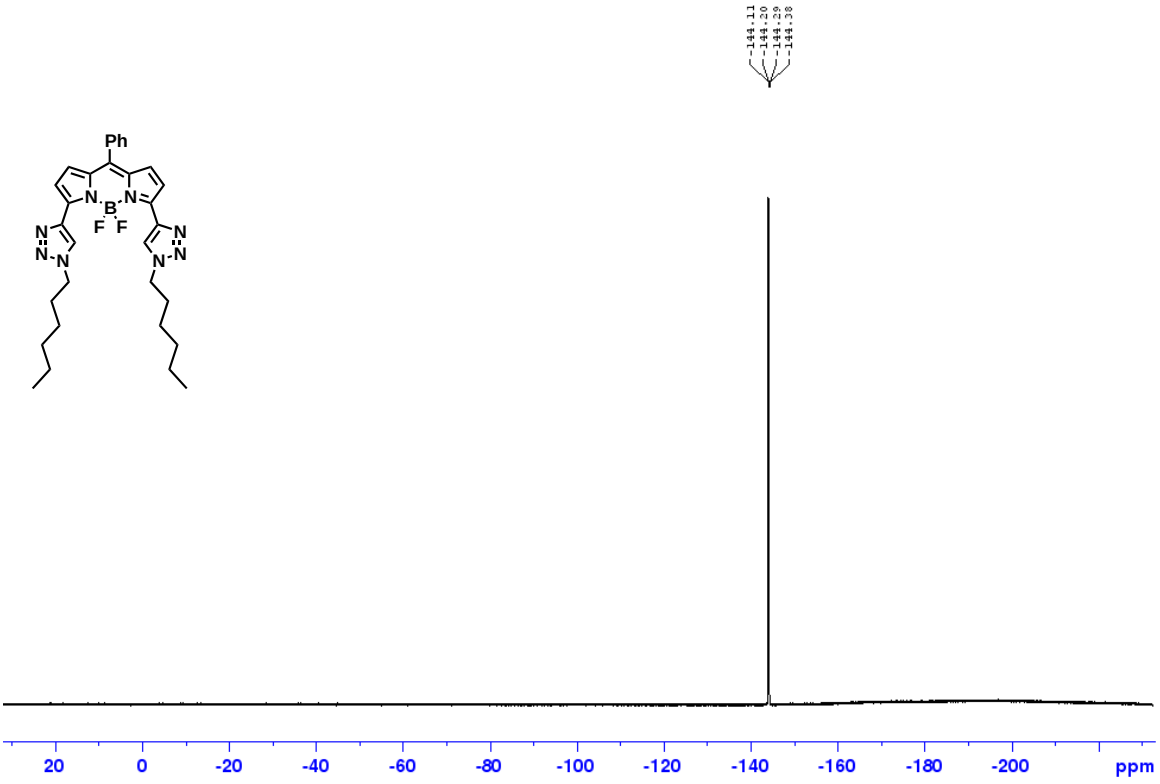
^{1}H NMR spectrum (400 MHz) of 4a in $CDCl_3$



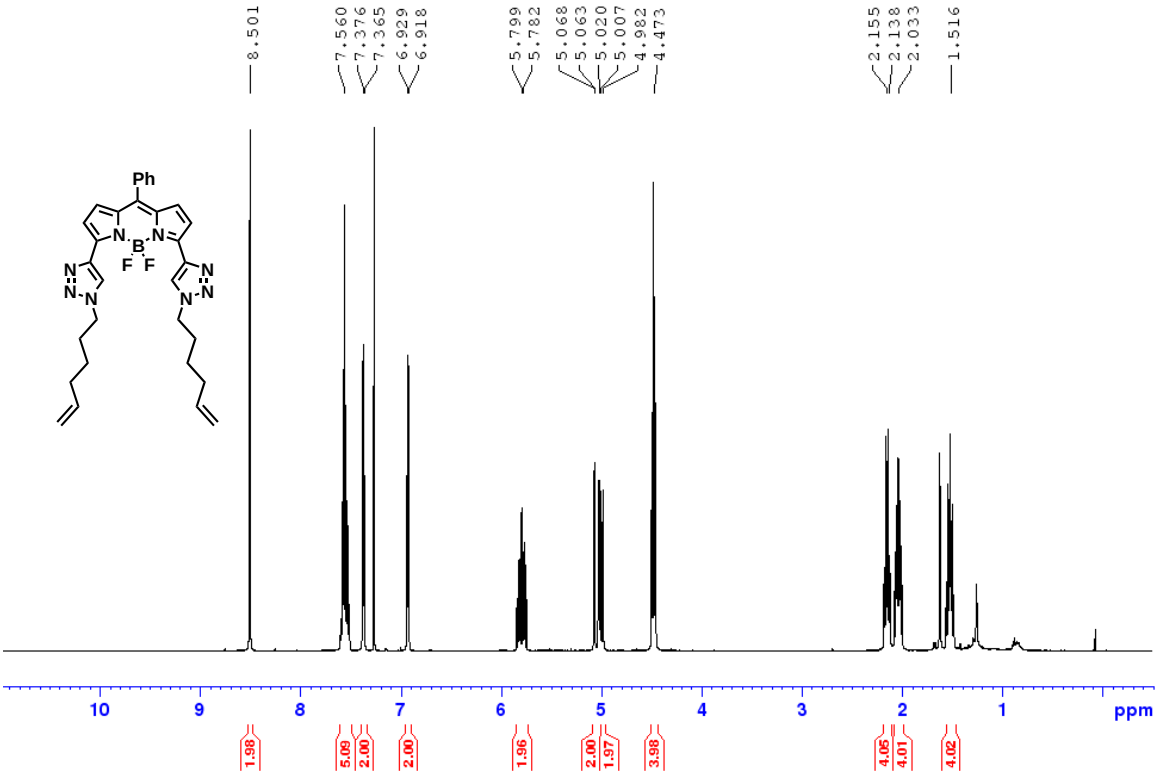
^{13}C NMR spectrum (100 MHz) of 4a in $CDCl_3$



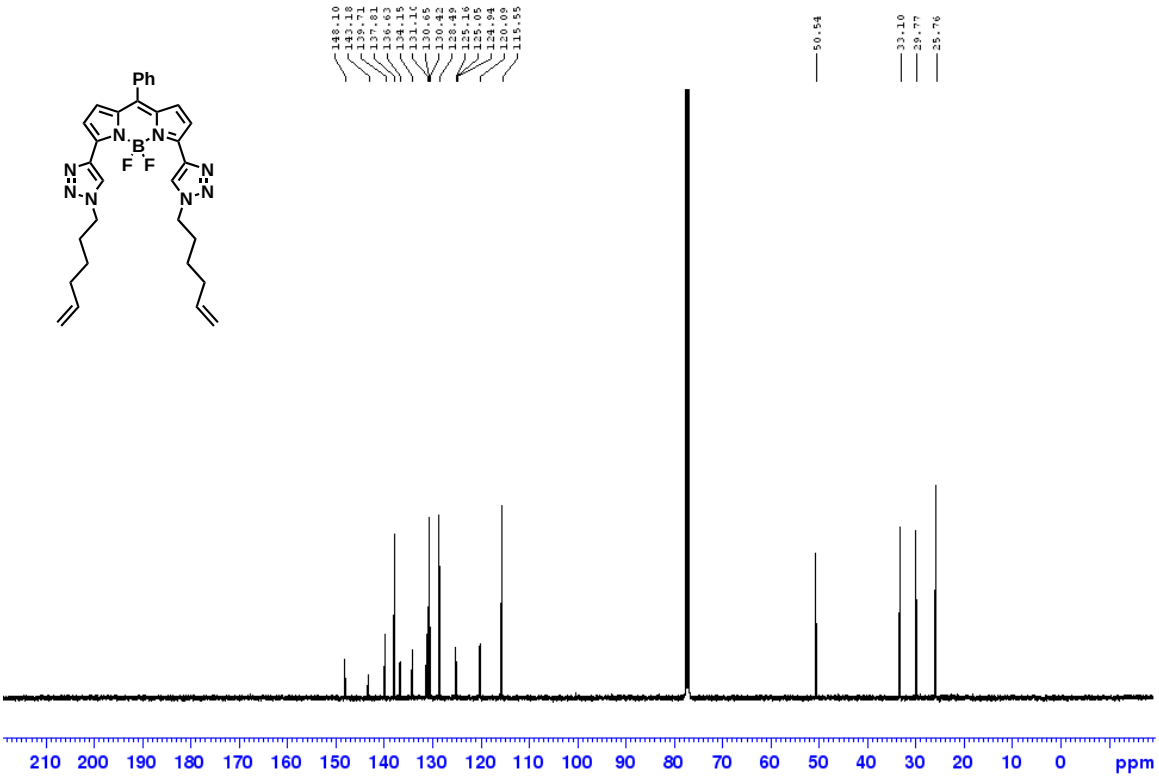
^{19}F NMR spectrum (160 MHz) of 4a in $CDCl_3$



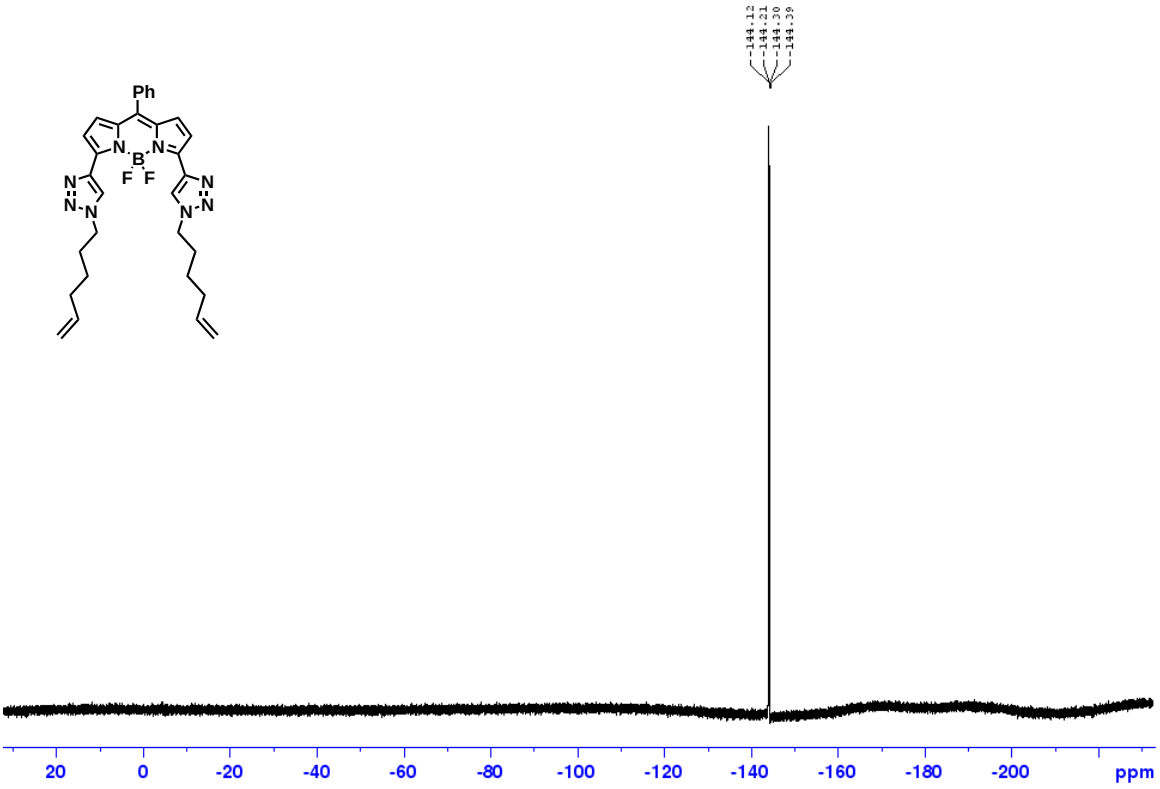
^{1}H NMR spectrum (400 MHz) of 4b in $CDCl_3$



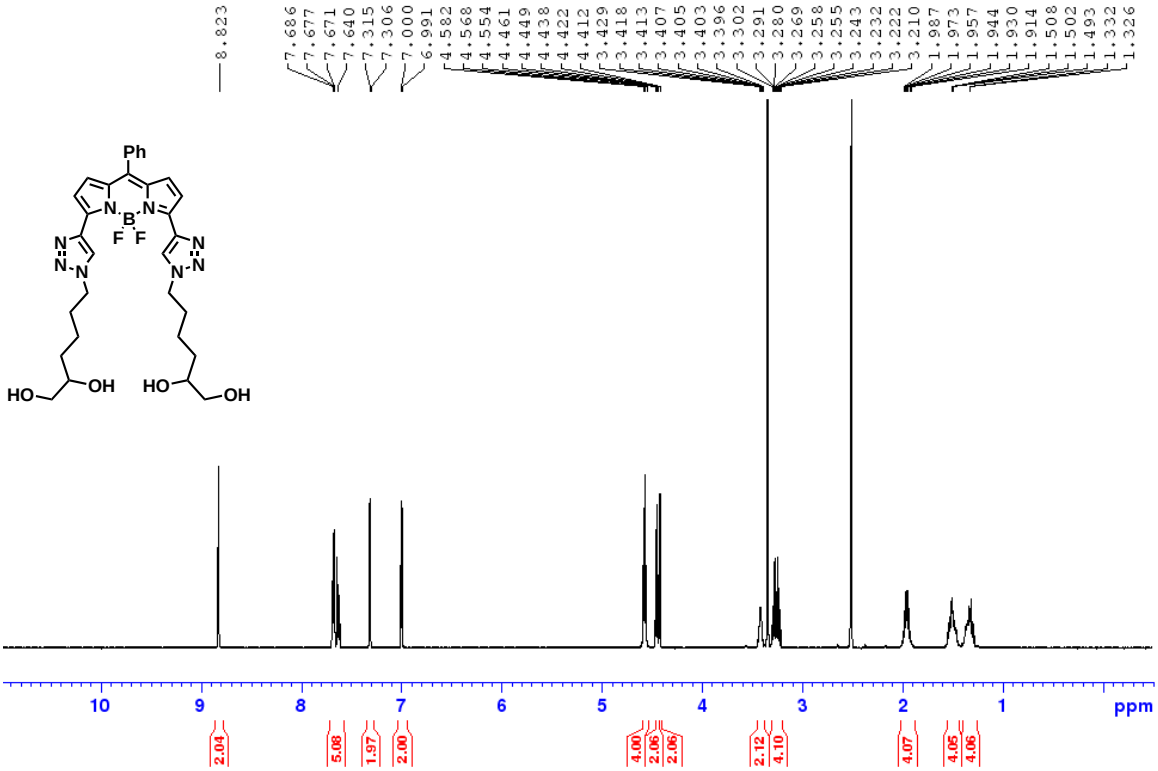
^{13}C NMR spectrum (100 MHz) of 4b in $CDCl_3$



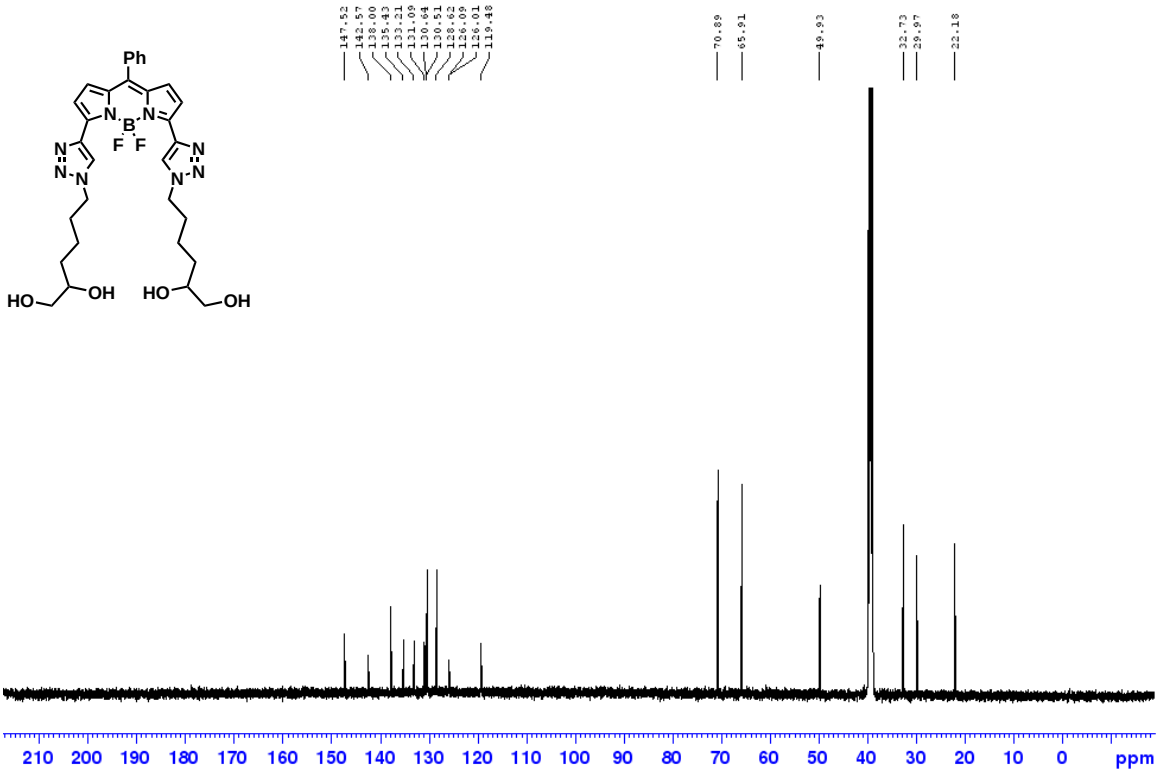
^{19}F NMR spectrum (160 MHz) of 4b in $CDCl_3$



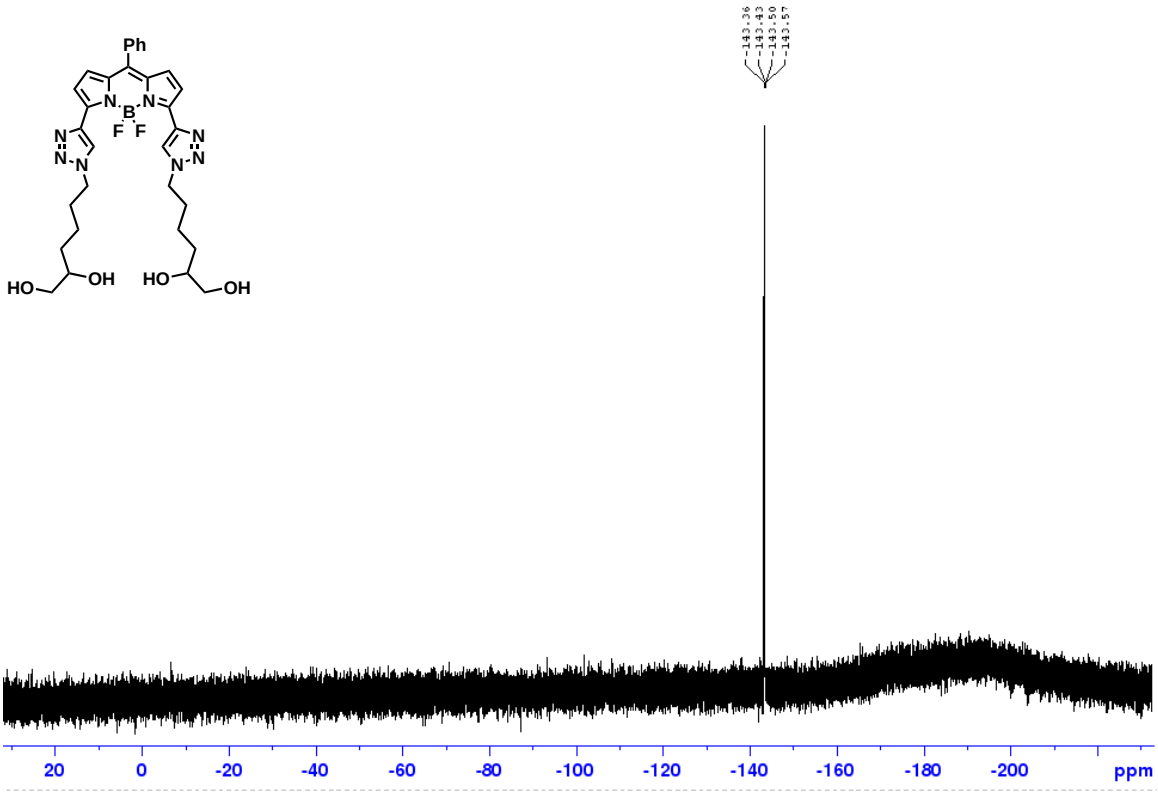
^{1}H NMR spectrum (400 MHz) of 5 in DMSO-d_6



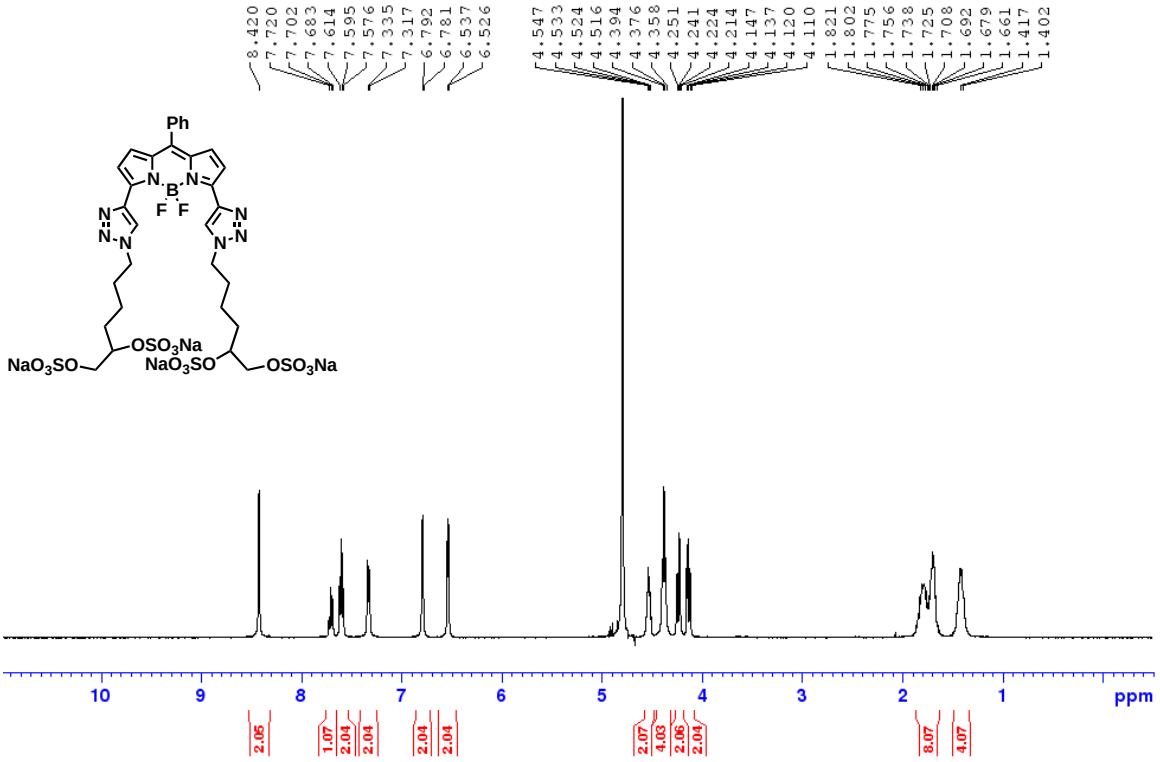
^{13}C NMR spectrum (100 MHz) of 5 in DMSO-d_6



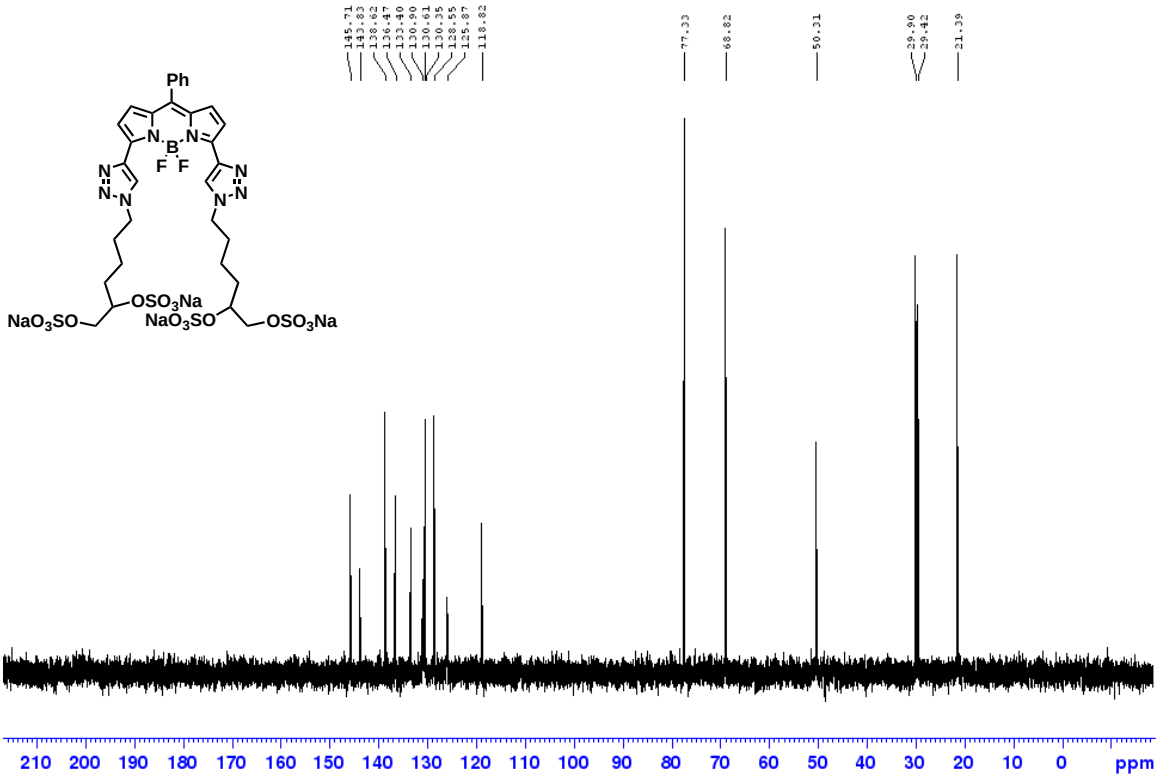
^{19}F NMR spectrum (160 MHz) of 5 in DMSO-d_6



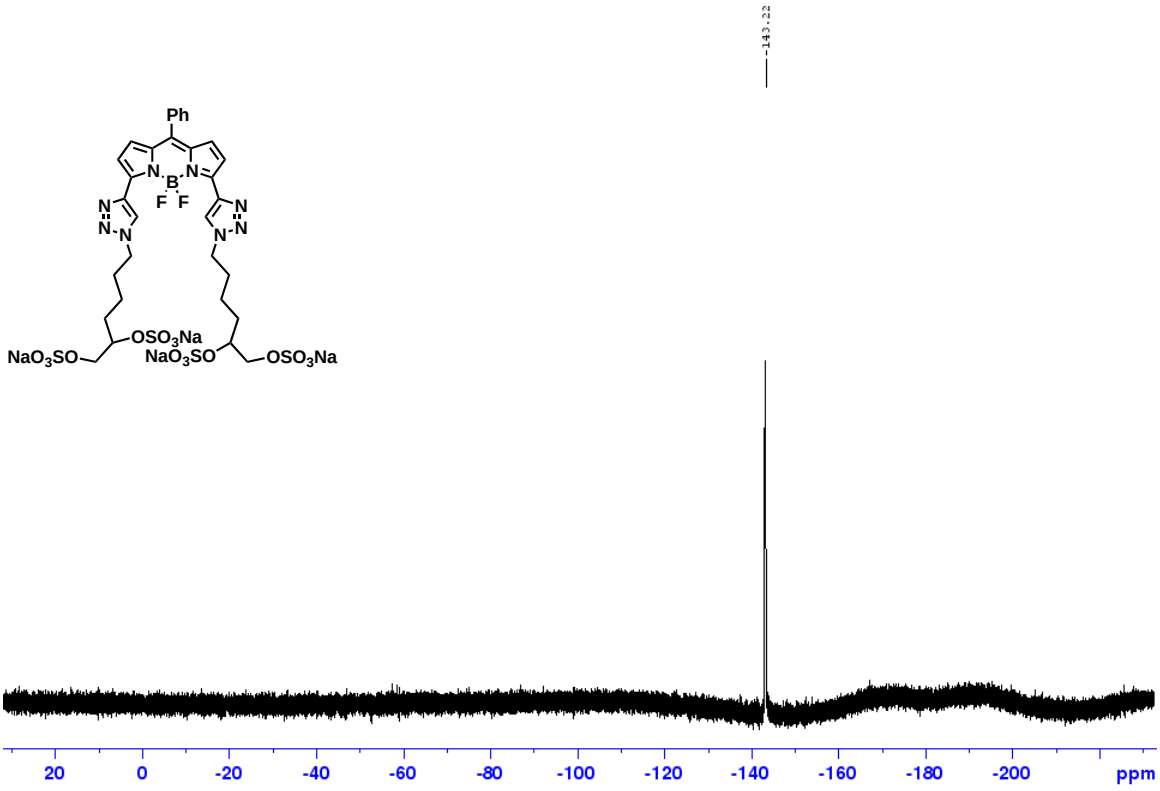
^{1}H NMR spectrum (400 MHz) of 6 in D_2O



^{13}C NMR spectrum (100 MHz) of 6 in D_2O



^{19}F NMR spectrum (160 MHz) of 6 in D_2O



HRMS Data

Std1

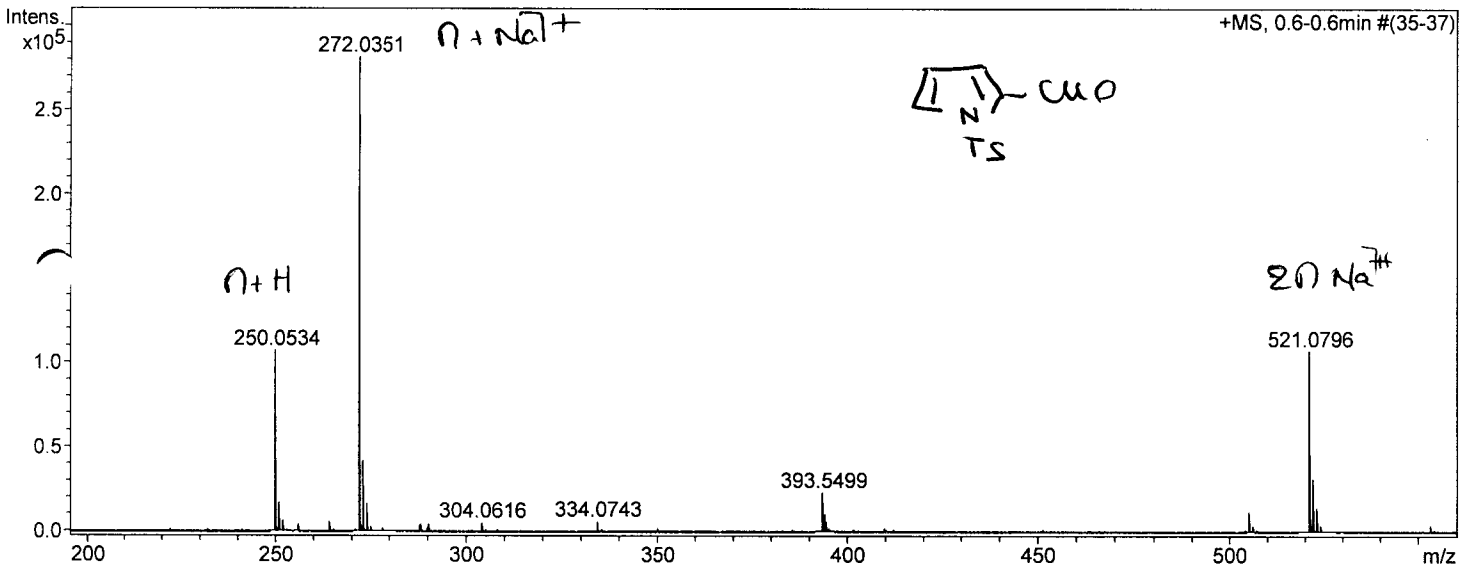
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

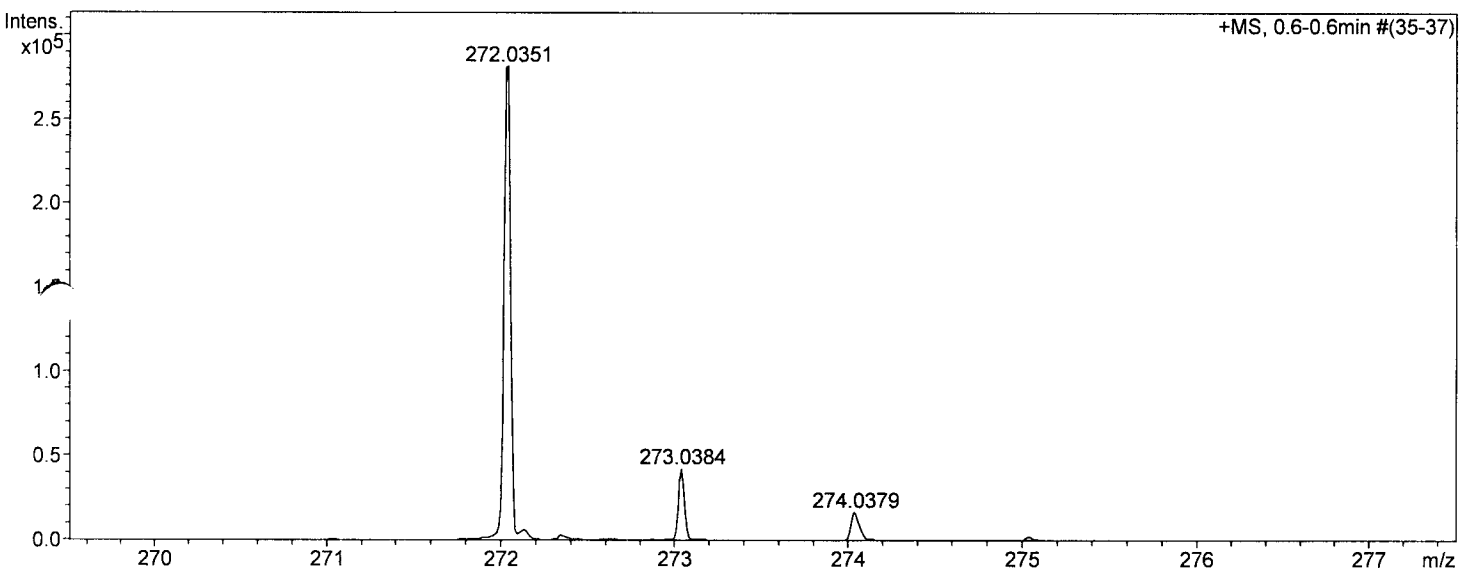
Analysis Info

Analysis Name	QTOF_150706_04_CG-Std1.d		
Method	MS_inf_TL_50_1000_2014_woCollSweep_Pos_CCSM.m	Acquisition Date	7/6/2015 11:51:08 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
272.0351	C 12 H 11 N Na O 3 S	272.0352	0.2	4.7

Std2

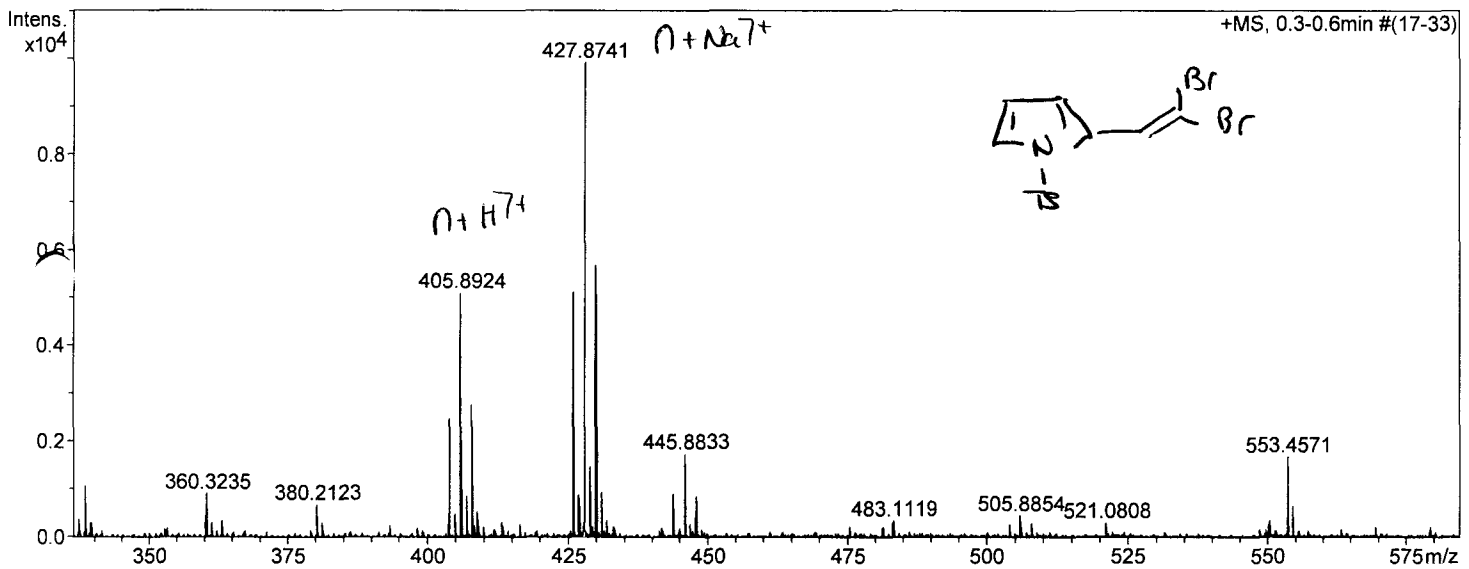
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

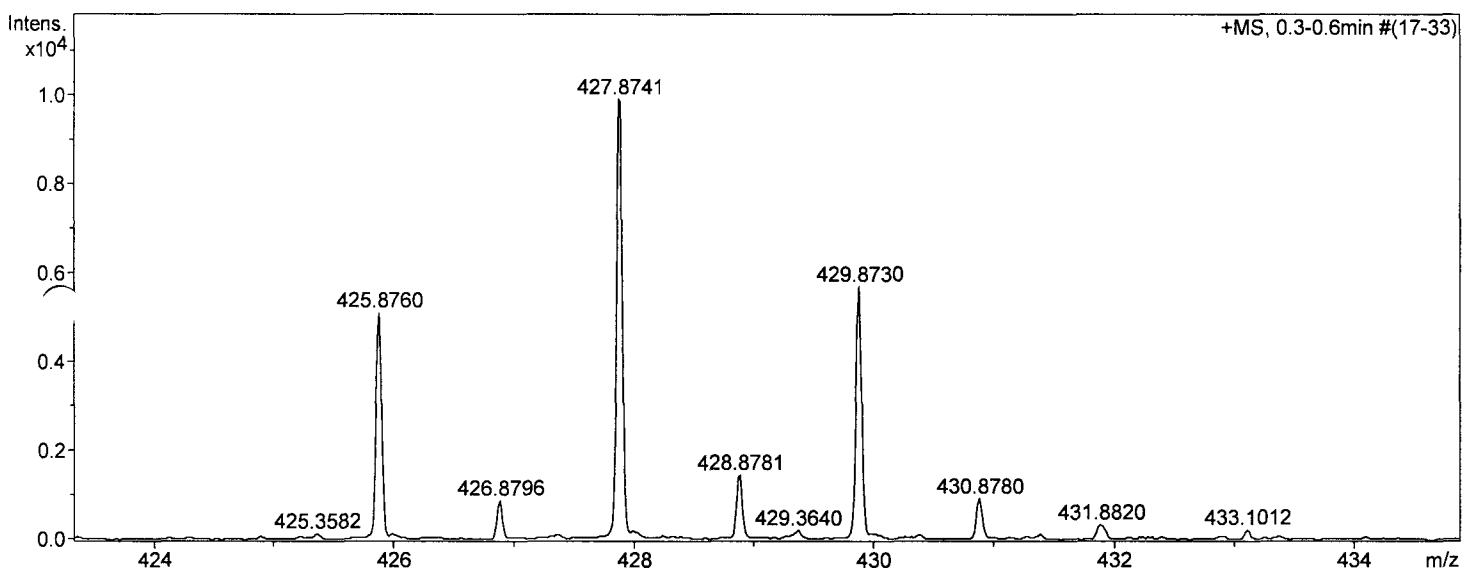
Analysis Info

Analysis Name	QTOF_150706_05_CG-Std2.d		
Method	MS_inf_TL_50_1000_2014_woCollSweep_Pos_CCSM.m	Acquisition Date	7/6/2015 11:58:05 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
425.8760	C 13 H 11 Br 2 N Na O 2 S	425.8769	2.3	19.7

Std3

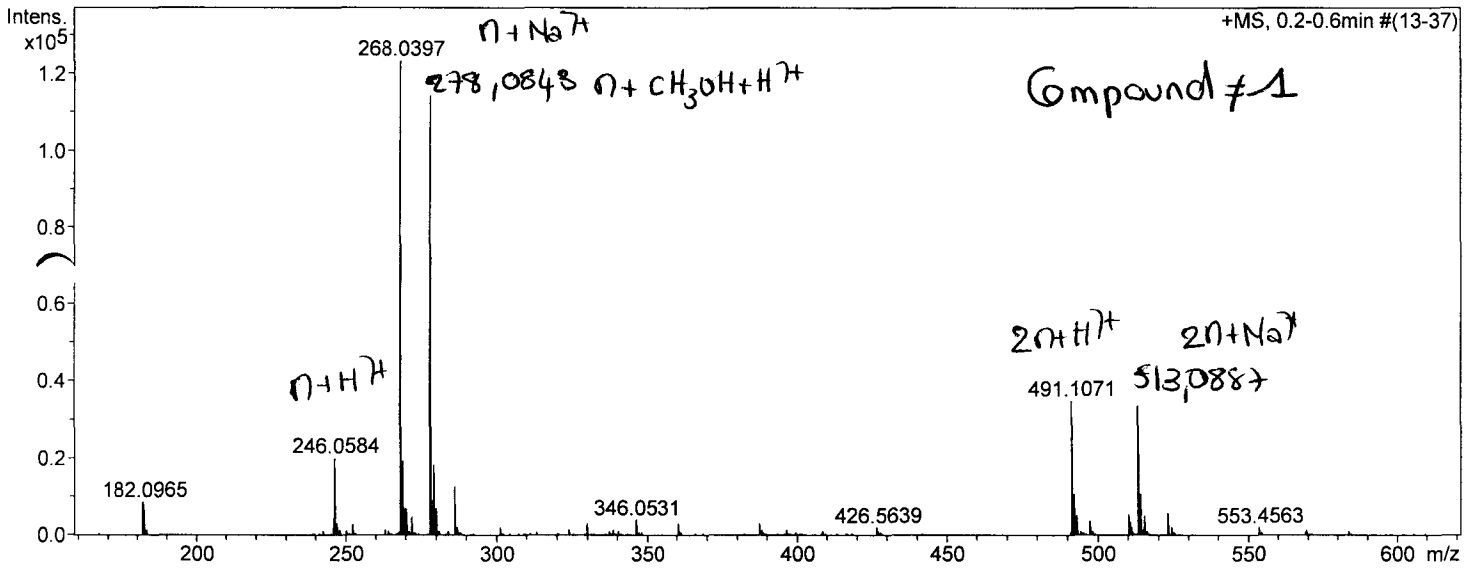
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

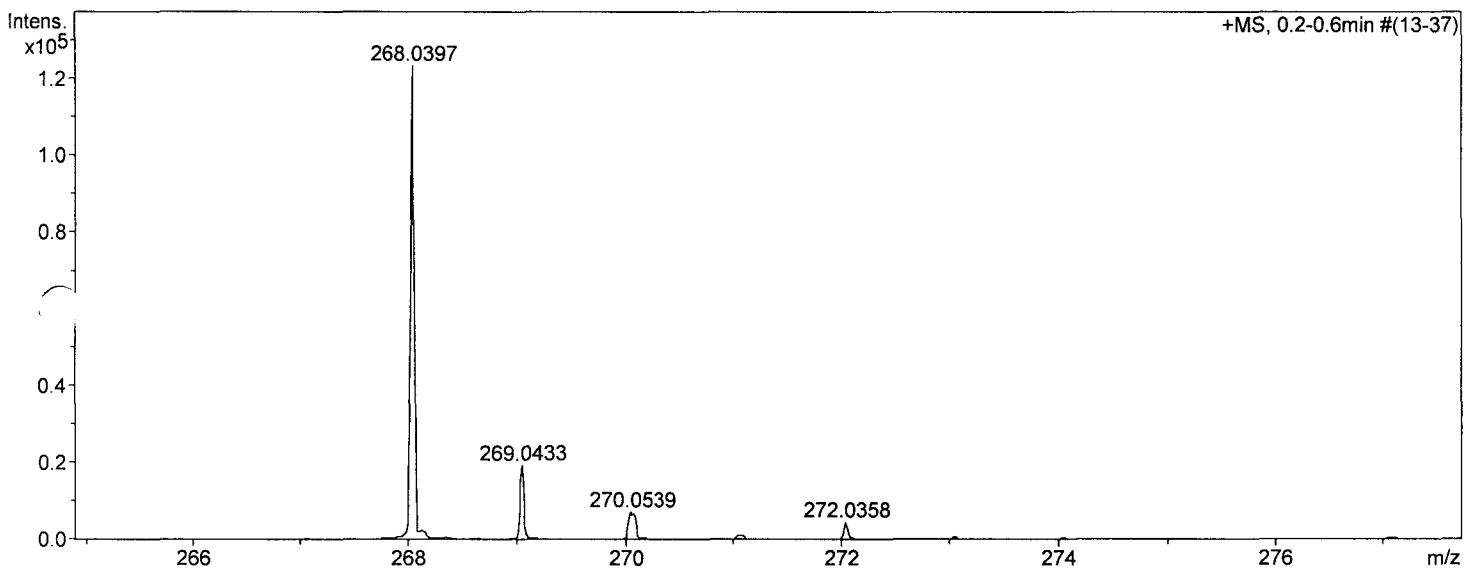
Analysis Info

Analysis Name	QTOF_150706_06_CG-Std3.d		
Method	MS_inf_TL_50_1000_2014_woCollSweep_Pos_CCSM.m	Acquisition Date	7/6/2015 12:03:57 PM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
268.0397	C 13 H 11 N Na O 2 S	268.0403	2.3	2.6

Std42

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

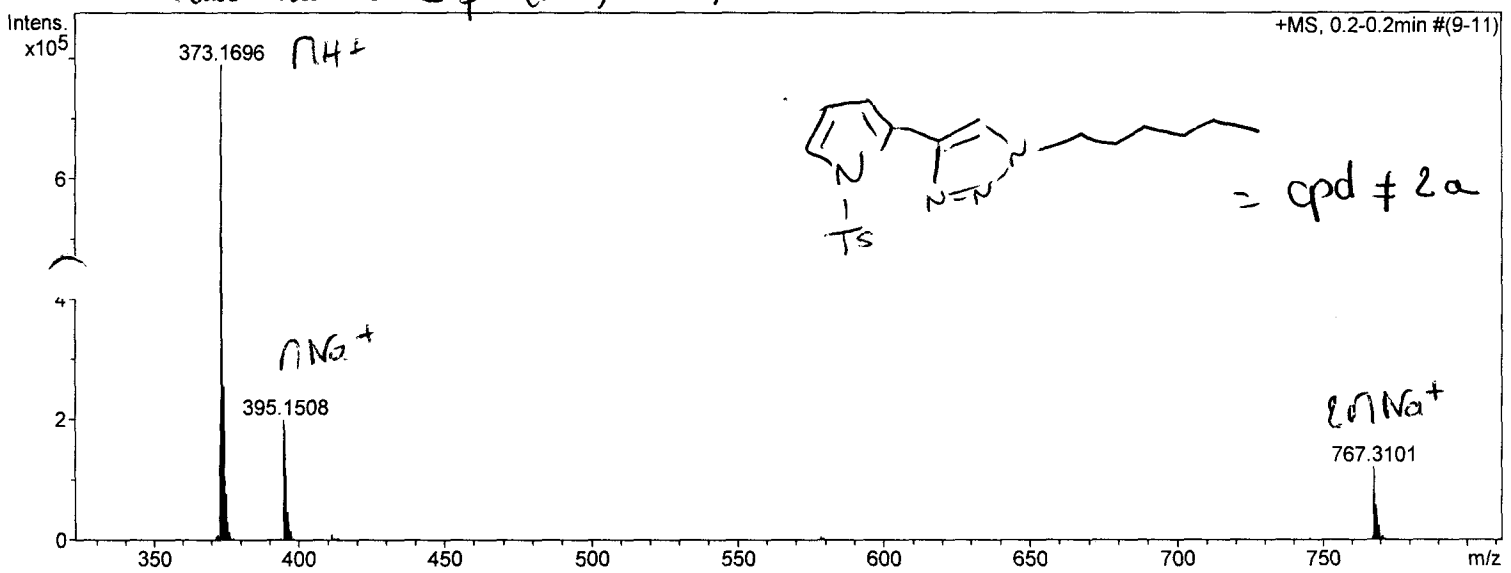
Analysis Info

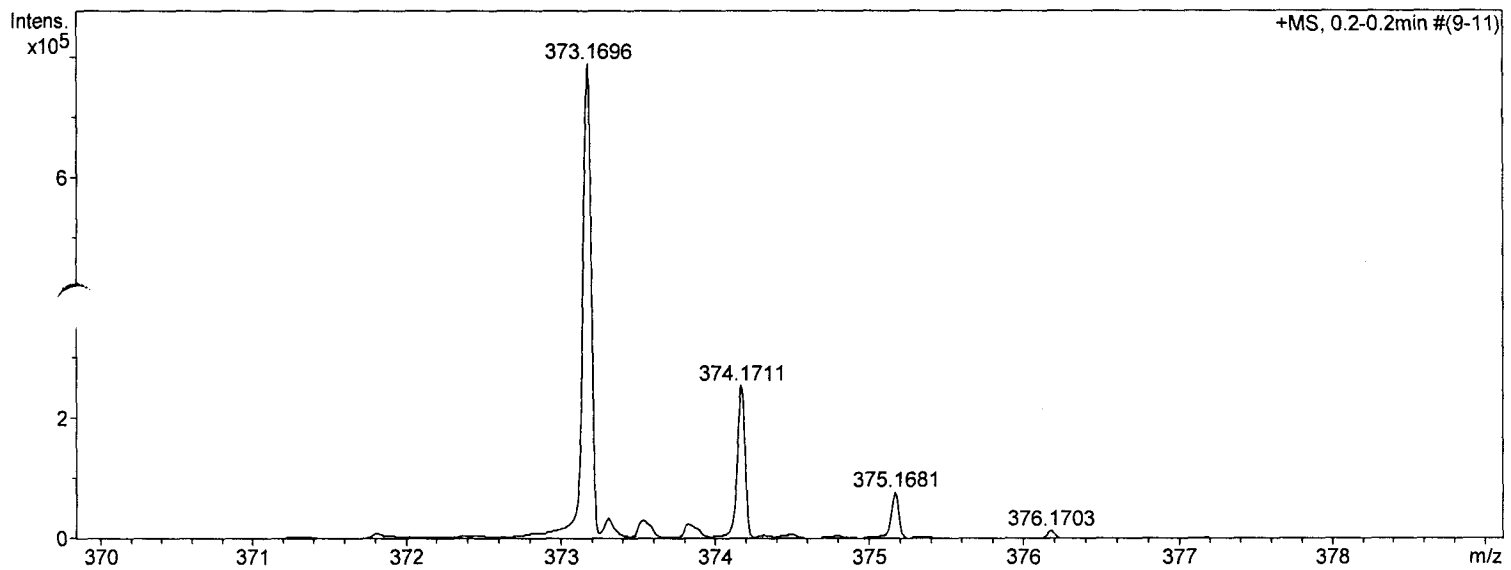
Analysis Name	QTOF_140121_03_CB1-70purif.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	1/21/2014 9:38:52 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste

masse exacte théorique (M+H) : 373,1698





Meas. m/z	Formula	m/z	err [ppm]	mSigma
373.1696	C 19 H 25 N 4 O 2 S	373.1693	-1.0	48.3

Std 52

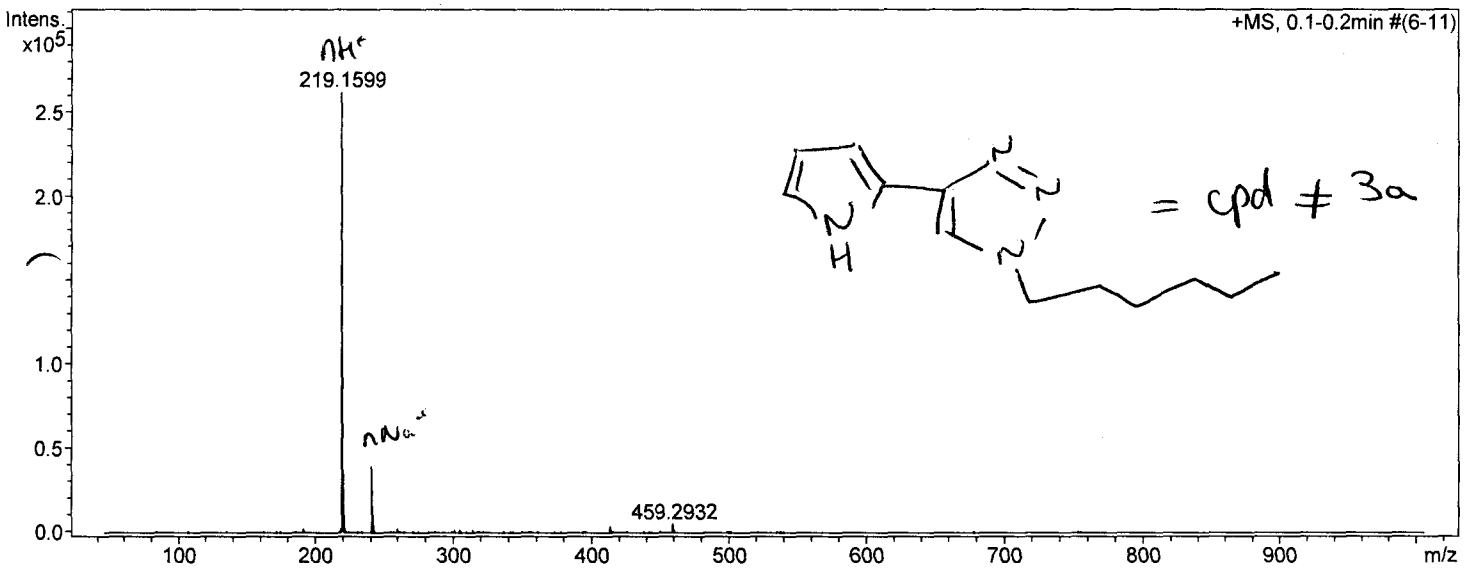
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

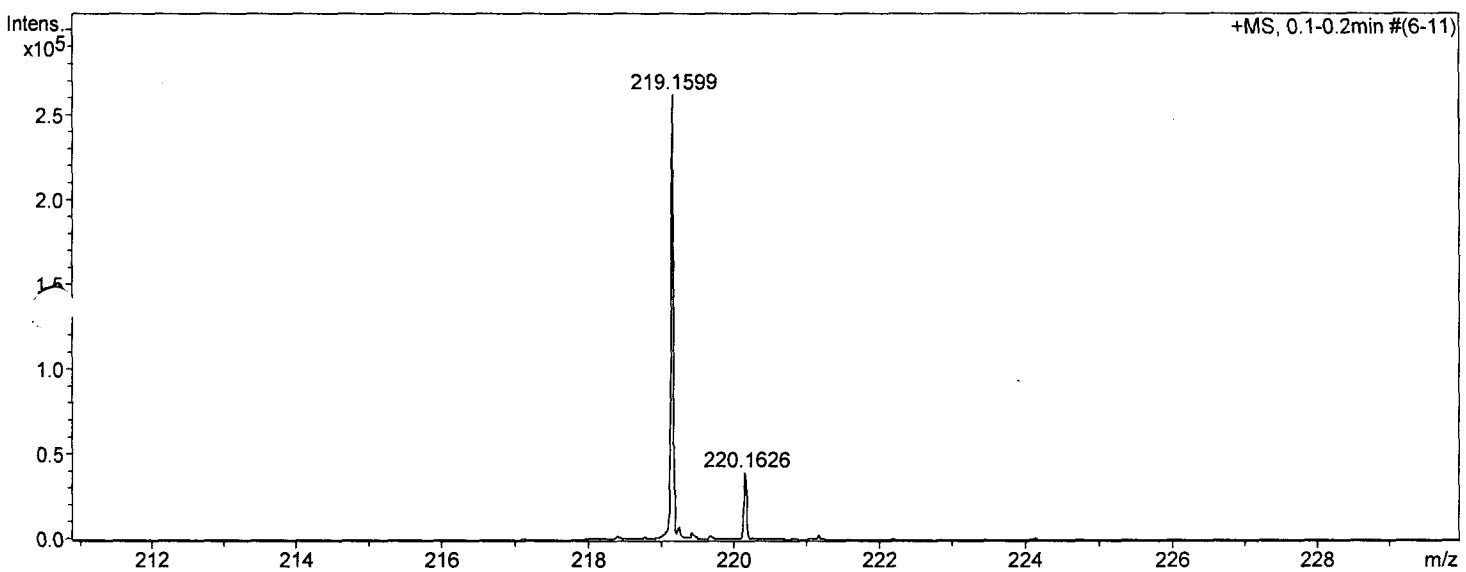
Analysis Info

Analysis Name	QTOF_140124_09_CG1-72 PURIF.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	1/24/2014 10:11:58 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1700 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
219.1599	C 12 H 19 N 4	219.1604	2.5	4.2

Std 62

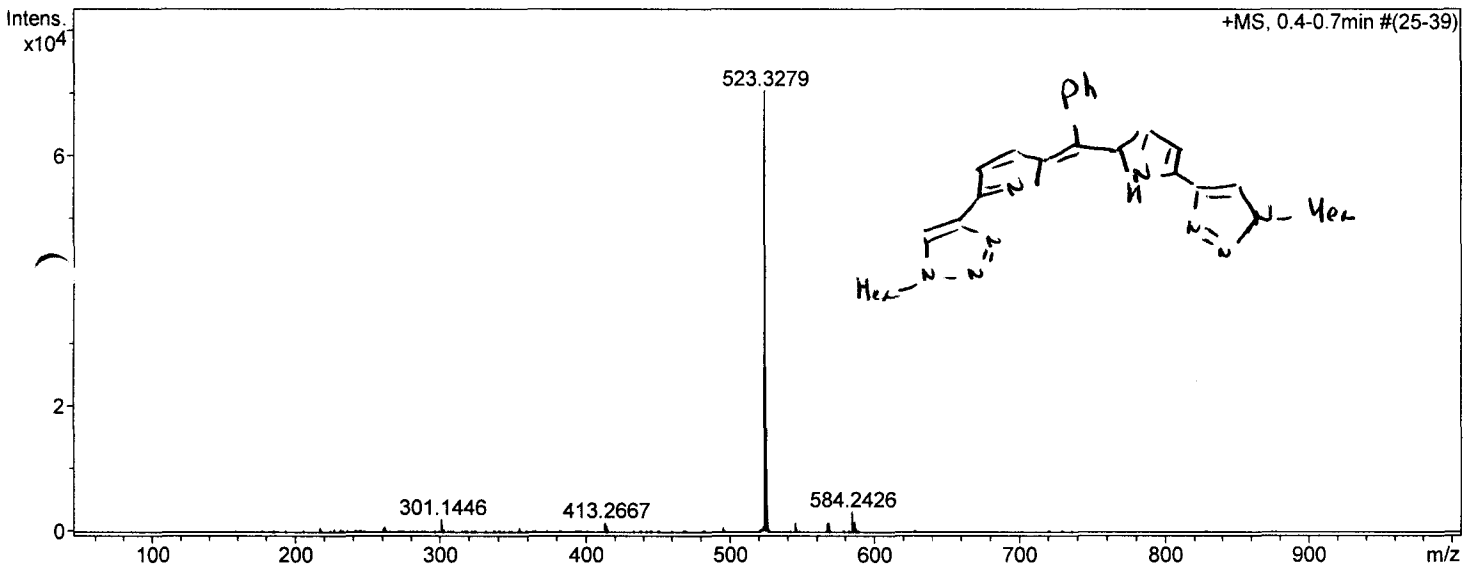
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

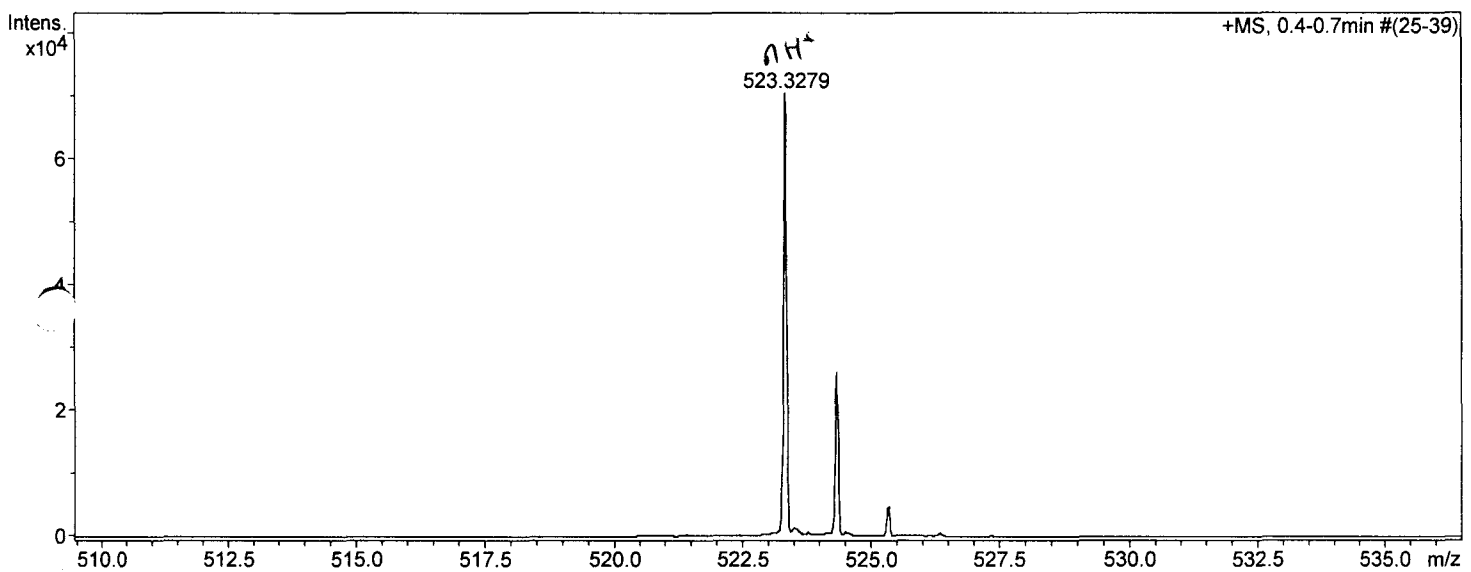
Analysis Info

Analysis Name	QTOF_140203_02_CG1-77PURIF.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	2/3/2014 8:59:46 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1200 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
523.3279	C 31 H 39 N 8	523.3292	2.6	2.1

Std 72

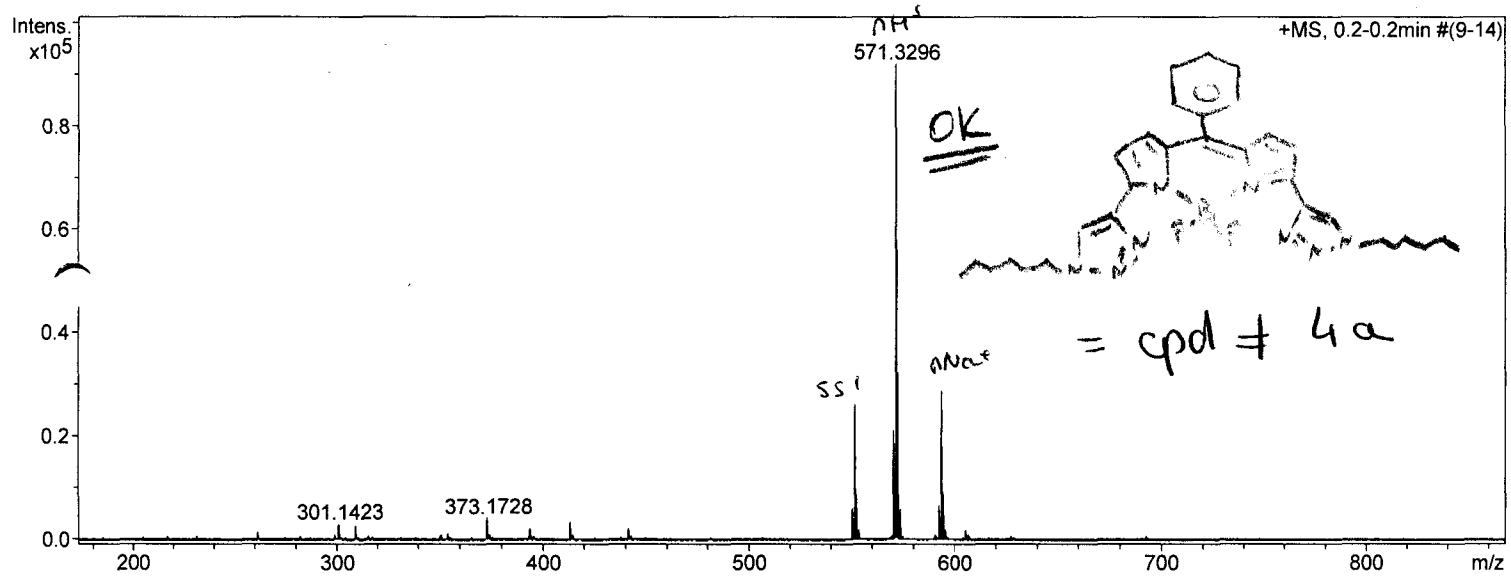
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

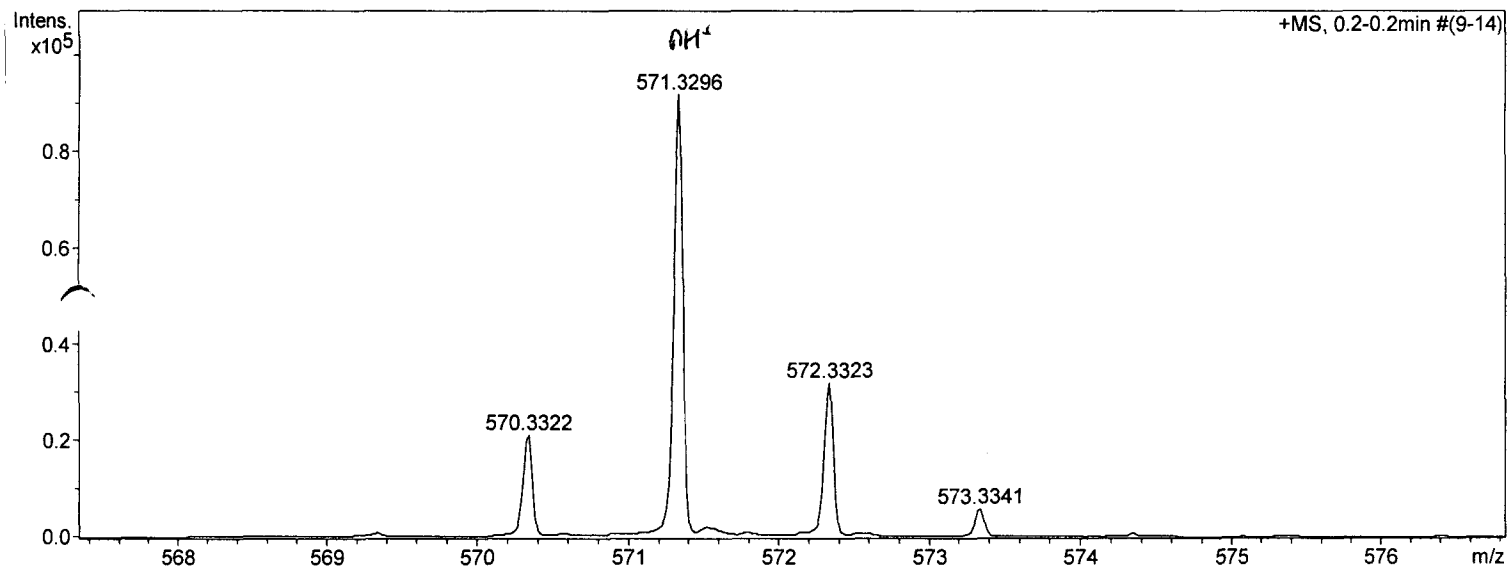
Analysis Info

Analysis Name	QTOF_140207_05_CG1-81PURIF F1.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	2/7/2014 10:20:10 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
571.3296	C 31 H 38 B F 2 N 8	571.3280	-2.7	2.4

Std45

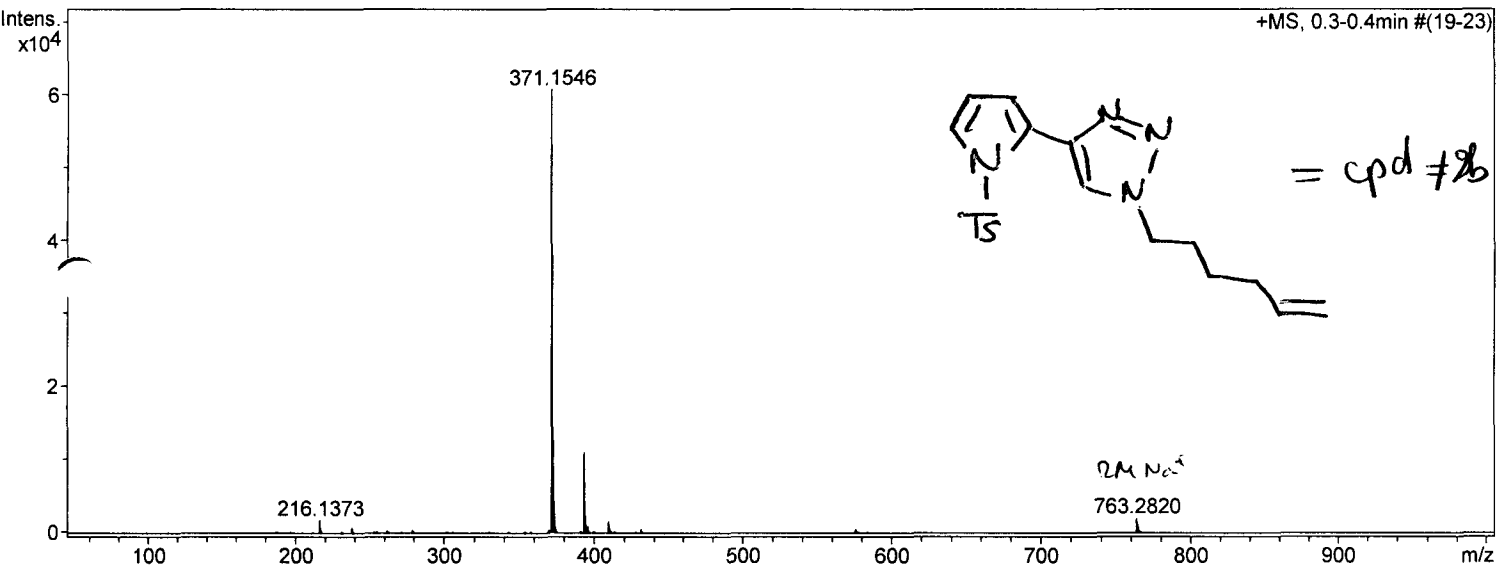
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

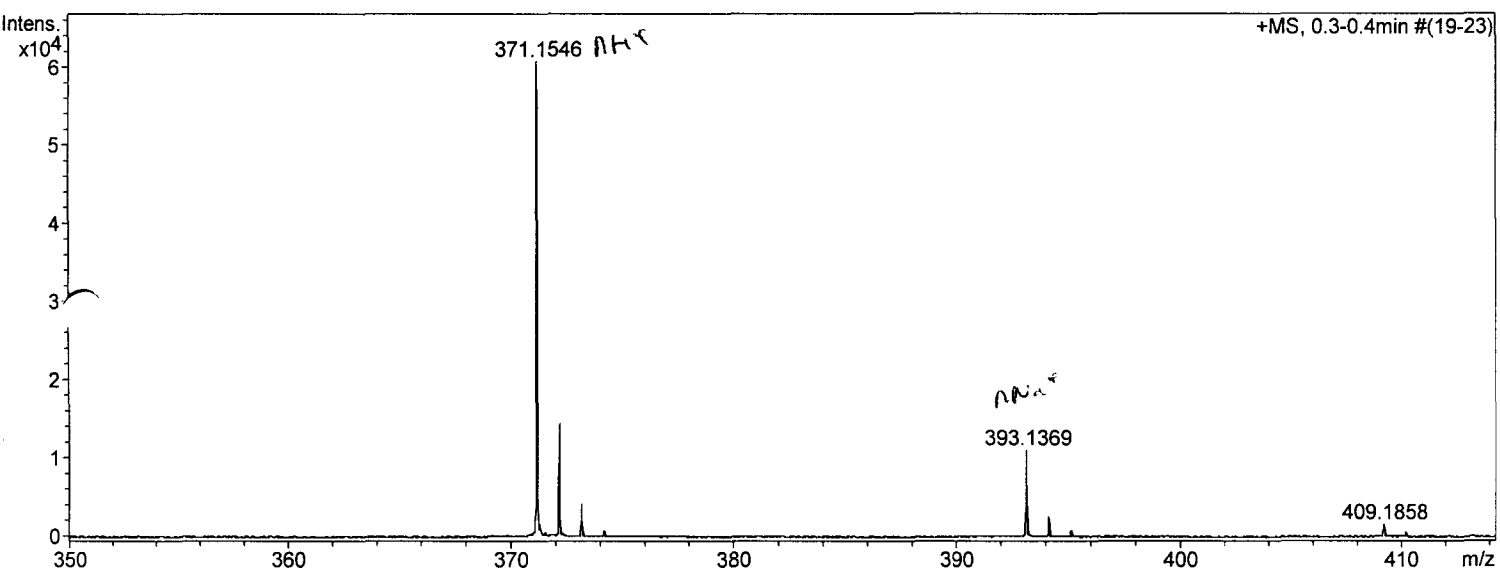
Analysis Info

Analysis Name	QTOF_140327_12_CG-STD45.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	3/27/2014 1:57:06 PM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1200 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
371.1546	C 19 H 23 N 4 O 2 S	371.1536	-2.5	5.5

Std55

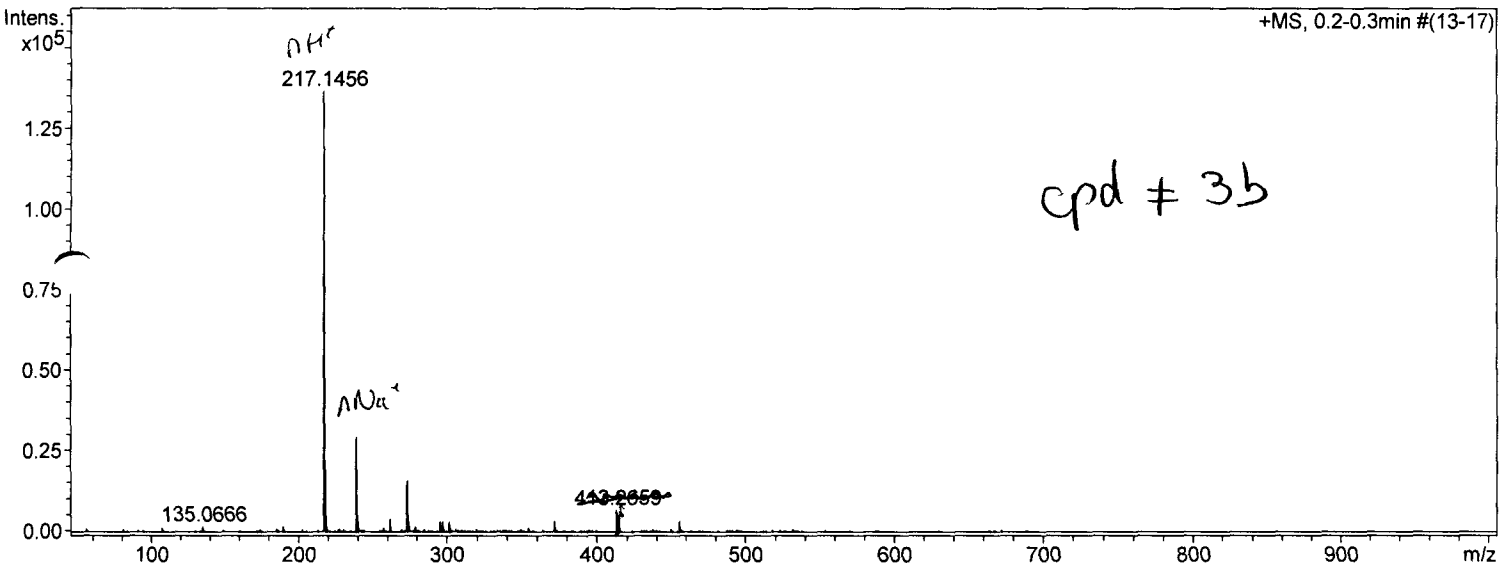
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

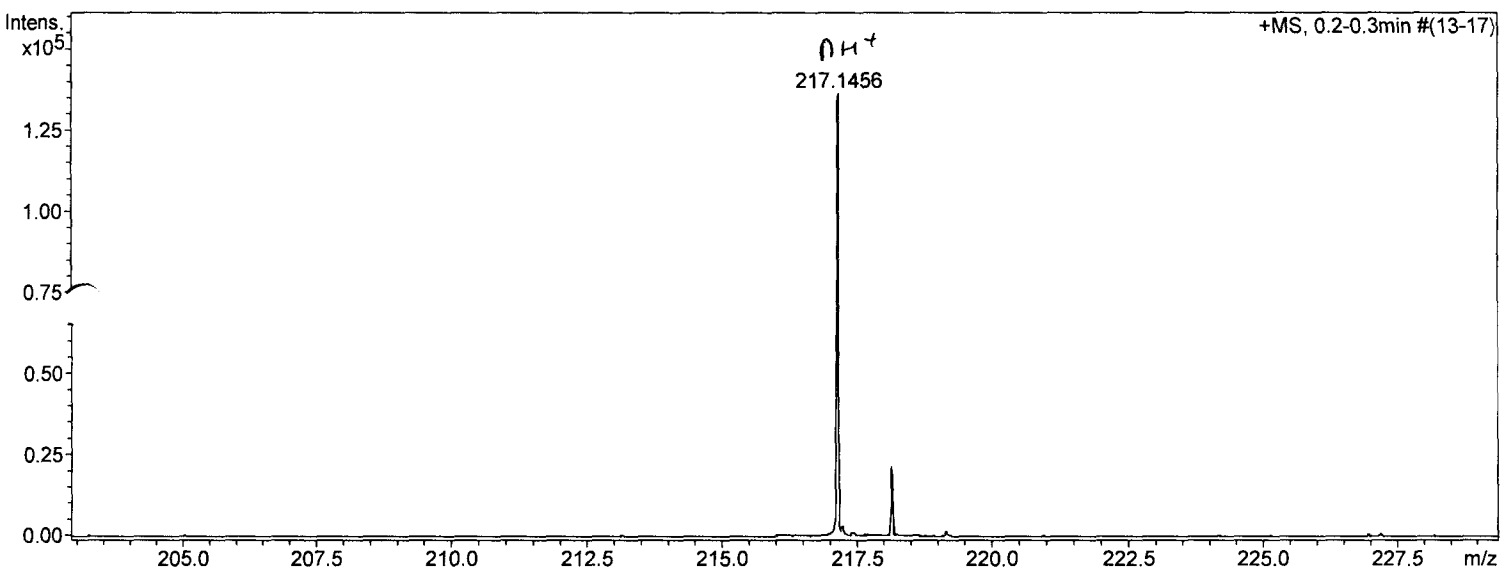
Analysis Info

Analysis Name	QTOF_140410_03_CG-STD55.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	4/10/2014 9:30:40 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
217.1456	C 12 H 17 N 4	217.1448	-3.7	7.9

Std65

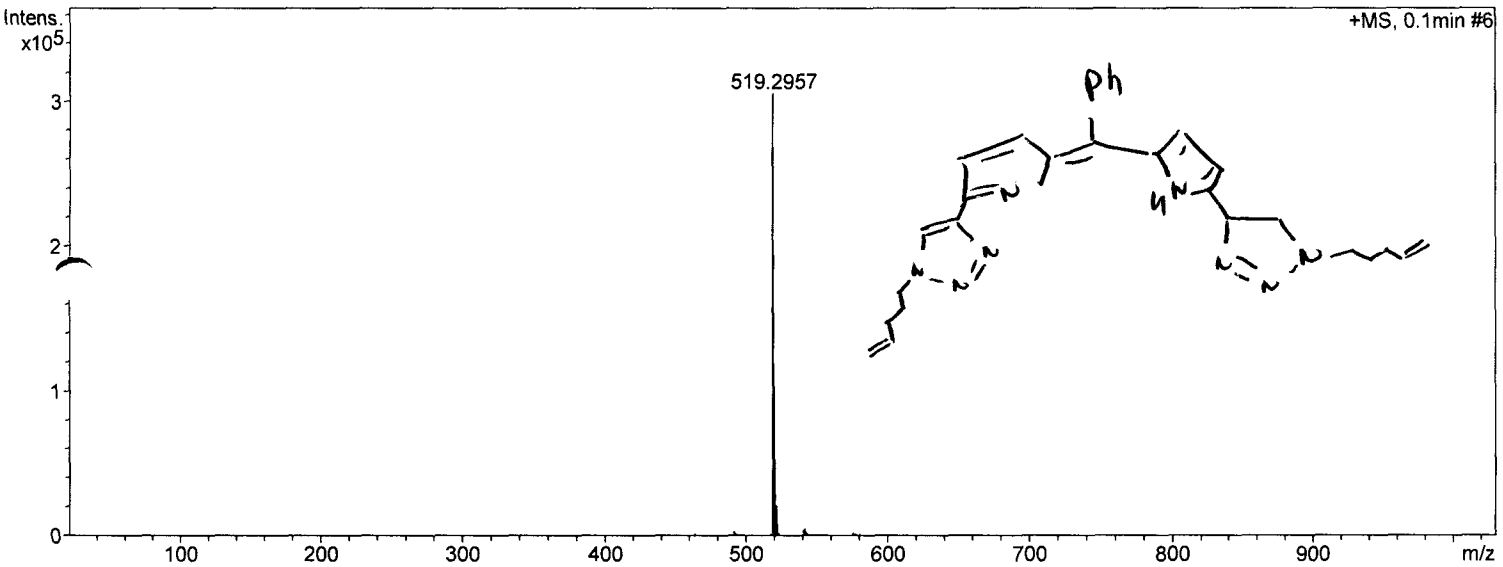
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

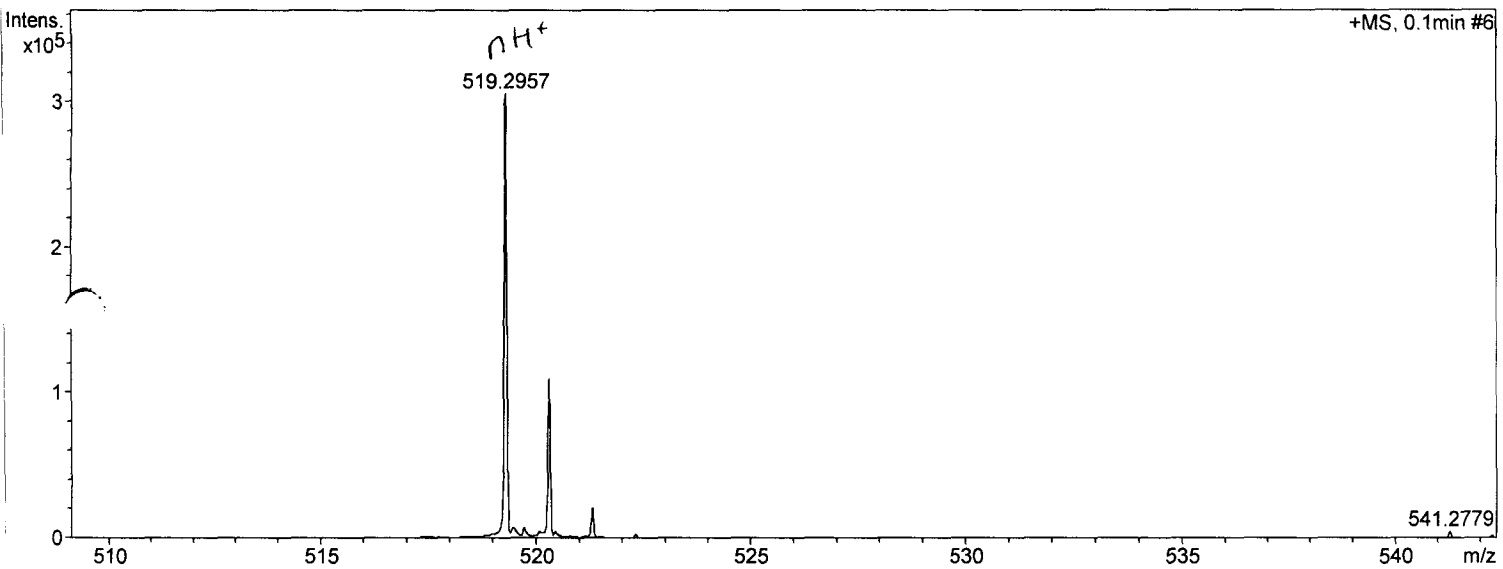
Analysis Info

Analysis Name	QTOF_140407_01_CG-STD65.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	4/7/2014 8:51:41 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
519.2957	C 31 H 35 N 8	519.2979	4.3	5.1

Std75

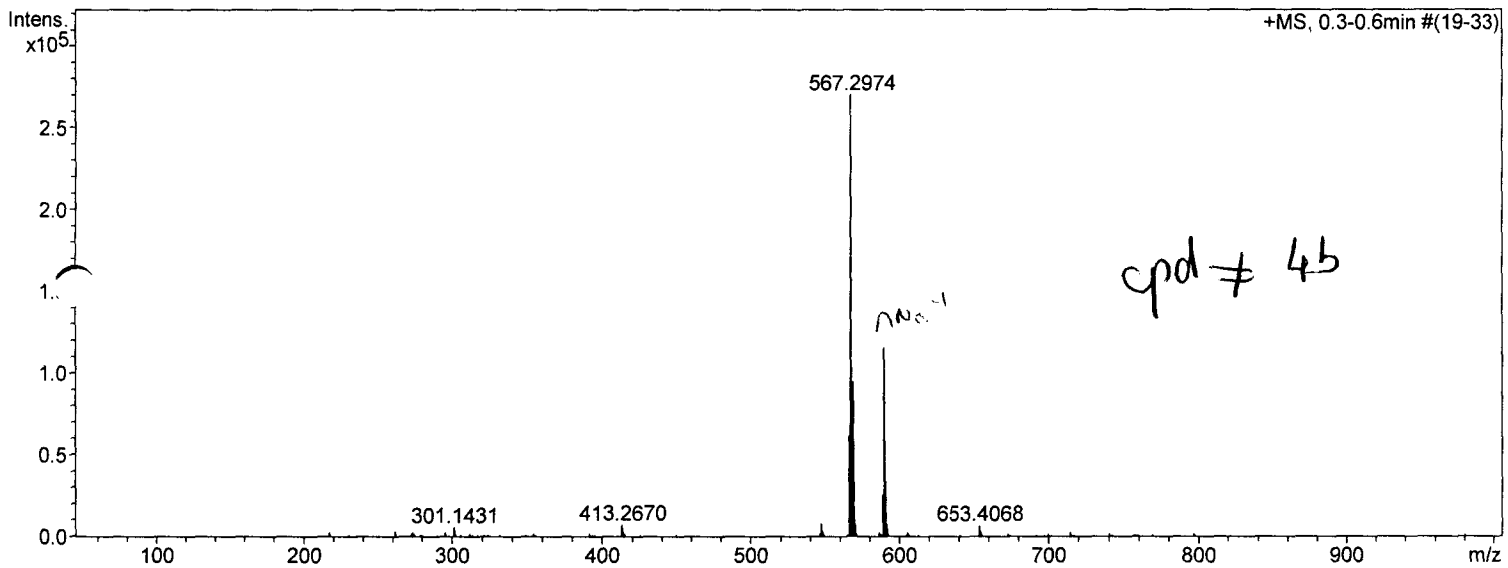
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

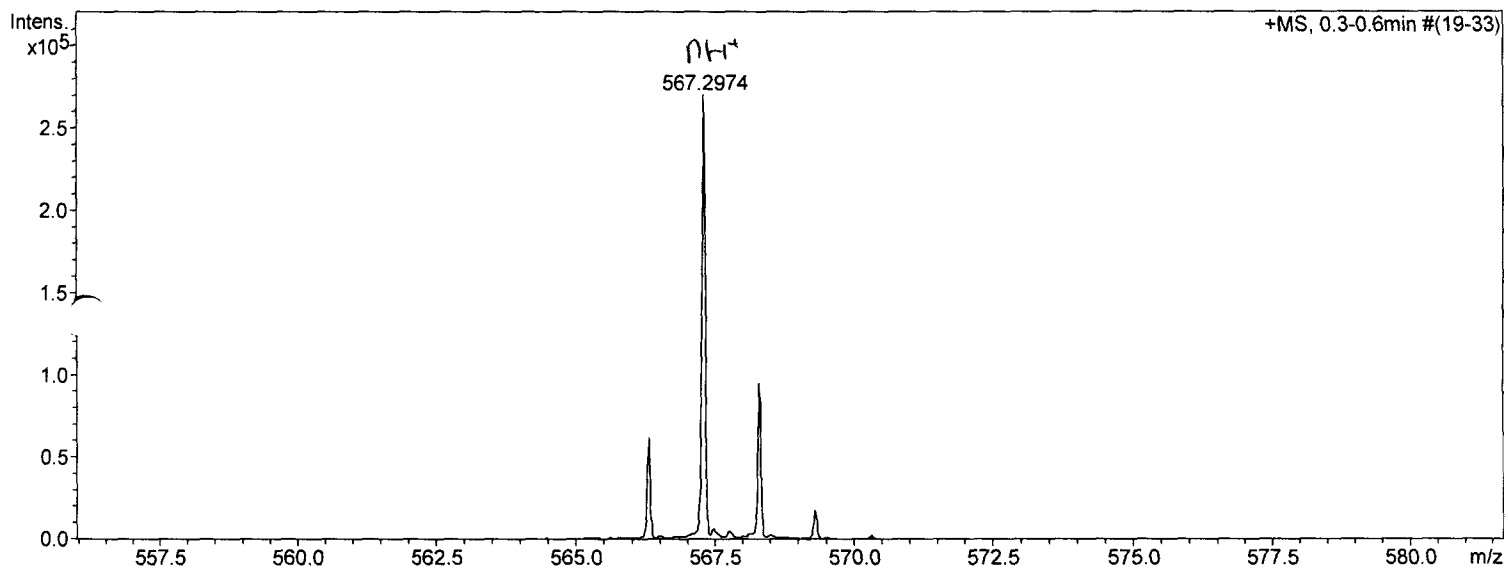
Analysis Name	QTOF_140410_06_CG-STD75.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	4/10/2014 9:40:36 AM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	2200 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste



cpd ≠ 45



Meas. m/z	Formula	m/z	err [ppm]	mSigma
567.2974	C 31 H 34 B F 2 N 8	567.2967	-1.1	1.8

propre Std 85

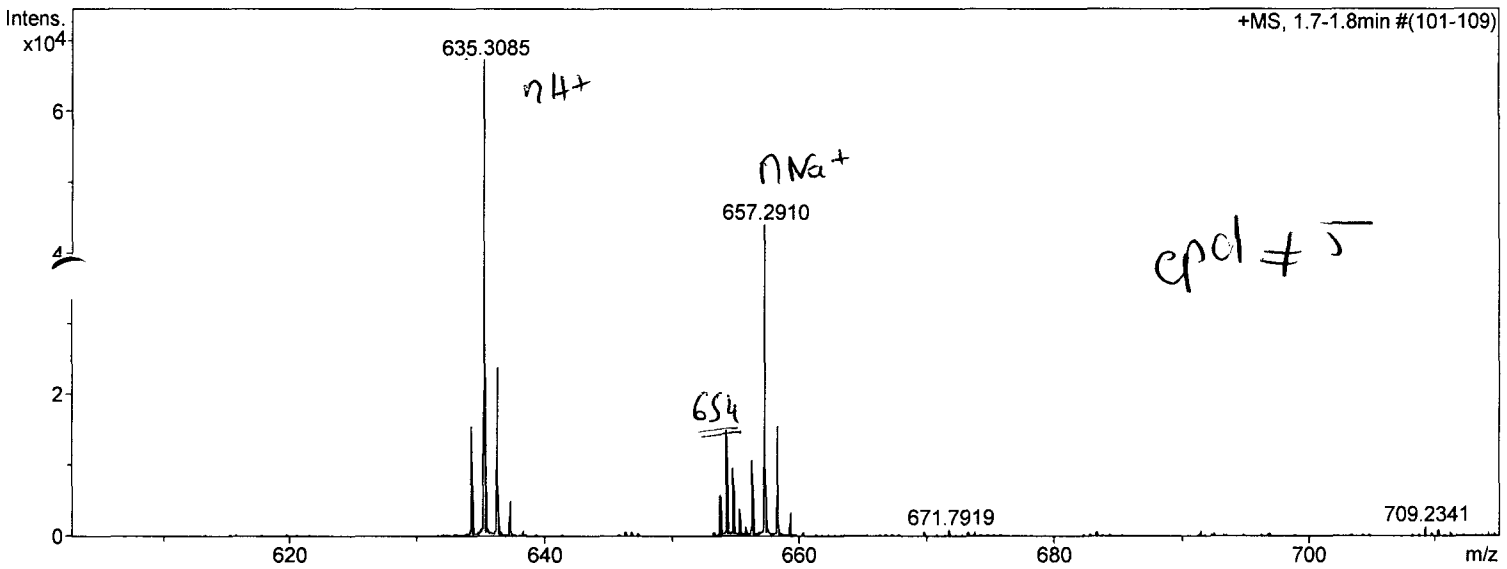
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

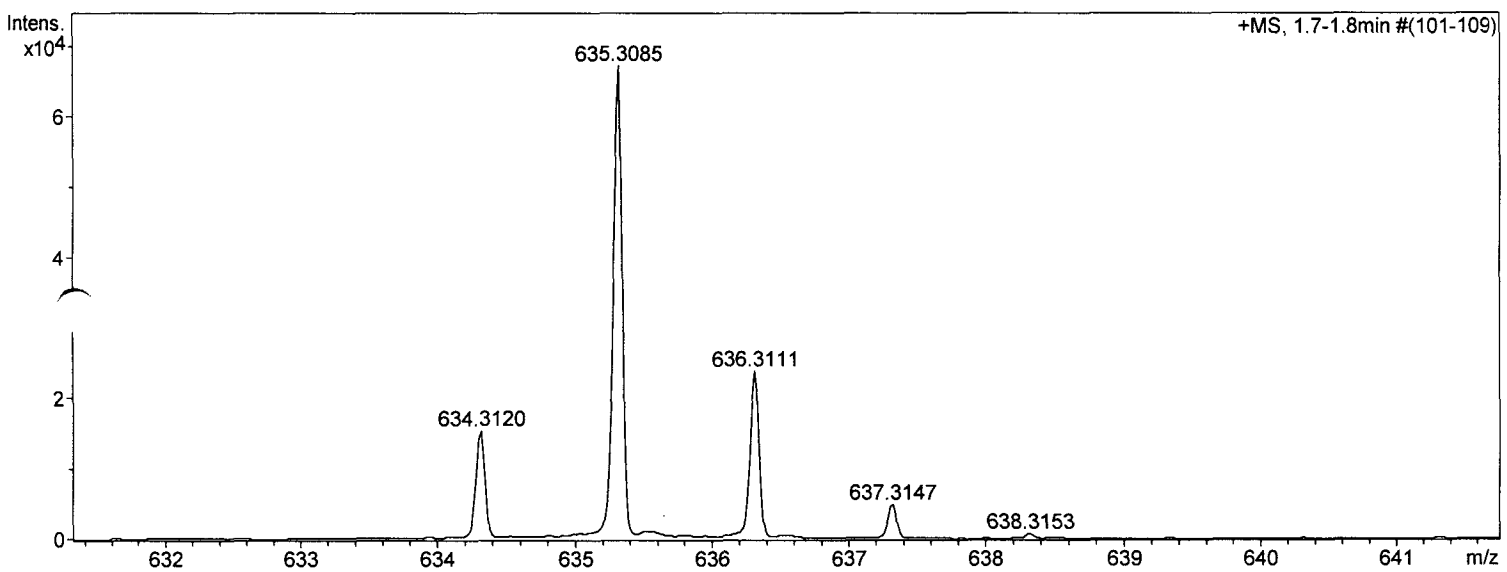
Analysis Info

Analysis Name	QTOF_140418_20_CG-Std85.d		
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m	Acquisition Date	4/18/2014 3:10:49 PM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
635.3085	C 31 H 38 B F 2 N 8 O 4	635.3077	-1.3	2.0

Std95.Na4

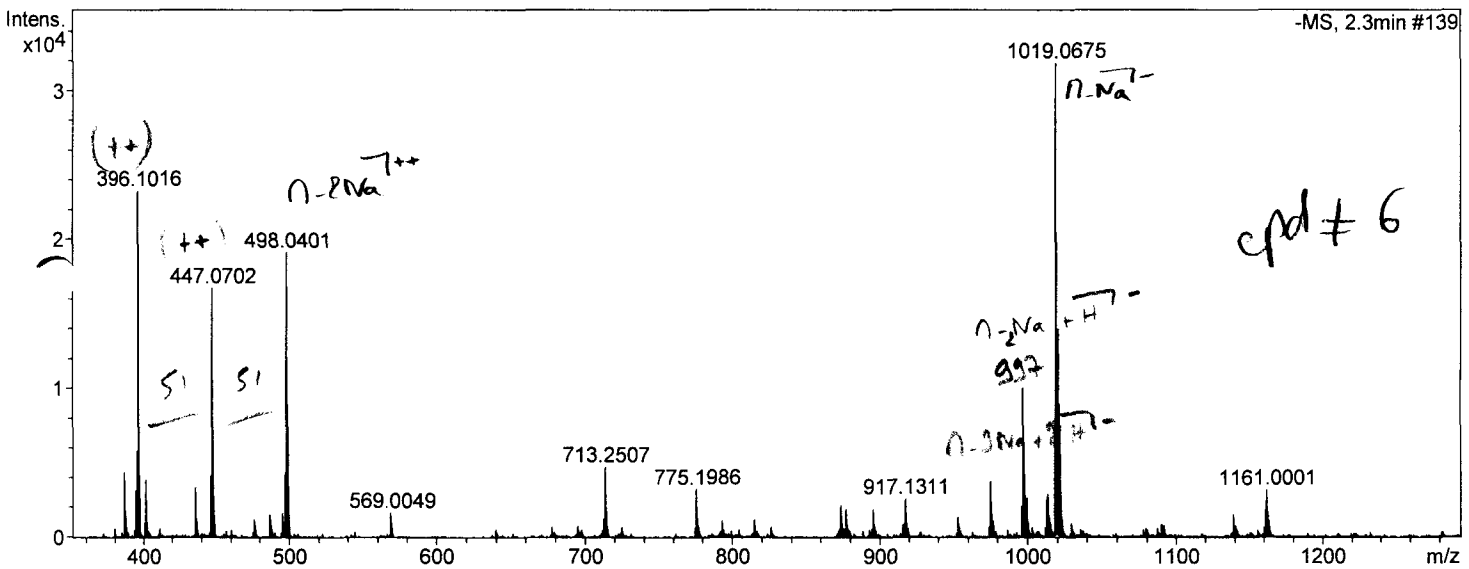
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

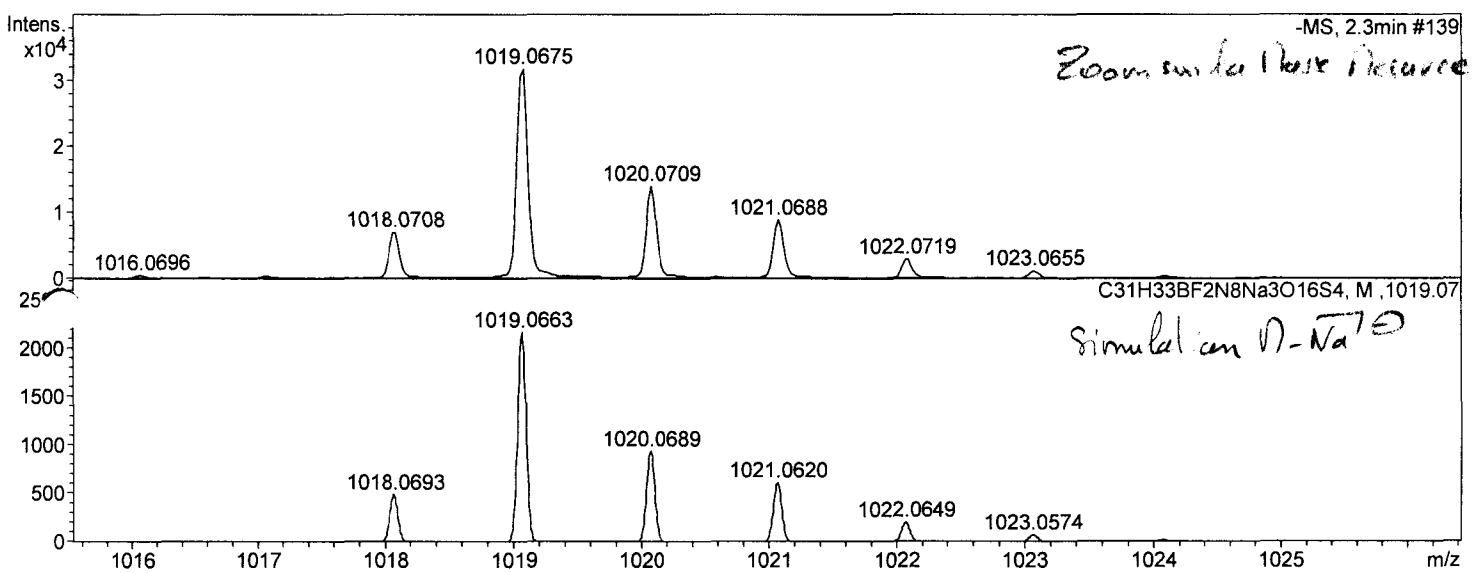
Analysis Info

Analysis Name	QTOF_150115_04_CG-Std95-Na4.d		
Method	MS_inf_TL_50_1000_2014_woCollSweep_Pos_CCSM.m	Acquisition Date	1/15/2015 12:15:21 PM
Comment		Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste





Meas. m/z	Formula	m/z	err [ppm]	mSigma
1018.0708	C 31 H 33 B F 2 N 8 Na 3 O 16 S 4	1019.0663	-1.4	5.2