Supporting Information

Convergent synthesis, resolution and chiroptical properties of dimethoxychromenoacridinium ions

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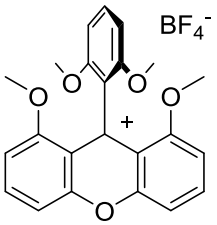
General Remarks:

Microwave reactions were performed in a Biotage® Initiator Robot with Robot Sixty set up for high absorption solvent (*eg*, NMP) with 30 seconds of previous stirring. “Biotage 2-5 ml” and “biotage 10-20 ml“ vials were used for reactions on 50 mg and 1 g scale respectively. The reactions were performed with sealed caps. NMR spectra were recorded on 300 MHz, 400 MHz and 500 MHz NMR apparatus at room temperature (20 °C). ^{1}H-NMR: chemical shifts were given in ppm relative to Me_4Si with the solvent resonance used as the internal standard (CD_2Cl_2 δ = 5.32 ppm; $CDCl_3$ δ = 7.26 ppm; DMSO δ = 2.50 ppm).^{13}C-NMR (100 MHz): chemical shifts were given in ppm relative to Me_4Si with the solvent resonance used as the internal standard (CD_2Cl_2 δ = 53.8 ppm; $CDCl_3$ = 77.1 ppm). ^{19}F RMN (282 MHz). Data were reported as follows: chemical shift (δ) in ppm on the δ scale, multiplicity (s = singulet, brs = broad singulet, d = doublet, t = triplet, dd = doublet of doublet and m = multiplet), coupling constant (Hz) and integration. IR spectra were recorded using a Universal ATR sampling and are reported in wave numbers (cm^{-1}). Melting points (M.P.) were measured in open capillary tubes and were uncorrected. Retardation factor (R_f) were measured on TLC Alumina gel 60 F_{254} plates. Electrospray high resolution mass spectra (ESI-HR-MS) were obtained by the department of Mass Spectroscopy of the University of Geneva. Absorption spectra were measured in a 1.0 cm quartz cell; λ_{max} are given in nm and molar absorption coefficient ε in $cm^{-1}\cdot dm^{3}\cdot mol^{-1}$. Optical rotations were measured in a thermostated (20 °C) 10.0 cm long microcell at 365 nm using high pressure lamps of mercury and are reported as follows: $[\alpha]_{\lambda}^{T}$ (c (g/100ml), solvent). Circular dichroism spectra were recorded in a 1.0 cm quartz cell; λ are given in nm and molar circular dichroic absorptions (Δε in $cm^{2}\cdot mmol^{-1}$). X-Ray diffraction structures were solved at the “Laboratoire de Cristallographie aux rayons X, service de Résolution Structurale par Diffraction des Rayons X” of the University of Geneva by Dr. L. Guénée. HPLC analyses were performed using a semi-preparative Chiralpak IC (0.46 cm x 25 cm). Detection was performed using UV detector at 254.4 nm. Retention times (R_t) are given in minutes (min). Photochemistry was performed using a Foba RANOO lamp with an OSRAM Ultra-Vitalux 300 W bulb.

Synthesis of salt [6][BF_4]



According to the literature,[1] a solution of tris(2,6-dimethoxyphenyl)methylium tetrafluoroborate (5.0 g., 9.8 mmol) in 800 ml of hydrochloric acid (0.1 M) was heated at reflux. After 12 hours, it was cooled to room temperature to afford a brown suspension containing a white precipitate which was filtered to yield 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthydrol in a quantitative yield. The product was then solubilized in methanol and 2 ml of tetrafluoroboric acid (50% in water) was added. The solution was stirred for 1h. The excess of methanol was evaporated and the brown residue was taken with 10 ml of dichloromethane. Upon addition of Et_2O, a brown precipitate was formed to afford, after filtration, 9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-9H-xanthen-9-ylium tetrafluoroborate salt in quantitative yield (4.5 g).

Yield: 100%, ***R_f*:** 0.20 (TLC Silica Gel 60 F_{254}, CH_2Cl_2/MeOH 95:5), **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.33 (t, J = 8.5 Hz, 2H), 7.68 (dd, J = 8.6, 1.0 Hz, 2H), 7.49 (t, J = 8.4 Hz, 1H), 7.47 (d, J = 14.8 Hz, 1H), 7.11 (dd, J = 8.4, 1.0 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 3.66 (s, 6H), 3.62 (s, 6H), **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 173.14, 162.78, 157.33, 155.68, 145.87, 132.04, 118.01, 117.20, 110.61, 108.71, 104.34, 58.04, 56.54, **^{19}F NMR** (282 MHz, C6D6) δ -152.53 (20%), -152.58 (80%).

Synthesis of dimethoxychromenoacridinium tetrafluoroborate salts [3][BF_4

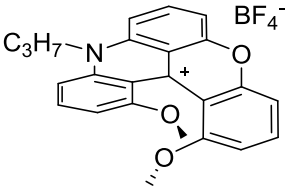
General procedure

In a microwave vial was added 9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-9H-xanthen-9-ylium tetrafluoroborate (50.0 mg, 0.108 mmol, 1 equiv) in distilled NMP (2 ml). To this dark brown solution was added, at 20 °C, the corresponding amine (3 equiv). The solution turned instantly to a pale brown color. The vial was then sealed and heated at 160 °C for 2 min under microwave irradiation. Ethyl acetate (20 ml) was then added to the residue and the organic layer was washed with brine (3x20 ml) then with a mixture of 20 ml of HBF_4 (0.5 M) or 10 ml of $NaBF_4$ (0.2M). The organic layer was then dried over Na_2SO_4, filtered, concentrated at reduced pressure to afford a dark red amorphous solid. The residue was dissolved in MeOH (just enough for its solubilization) then treated with an excess of $NaBH_3CN$ (4 equiv). The solution turned instantly to a light orange-pink color, a signature of the unreactive ADOTA byproduct. Silica (powder) was then added and the slurry was evaporated in vacuo. The adsorbed material was then deposited on top of a silica gel column which was then eluted with a 49:1 pentane:Et_2O mixture. The reduced compound **9** was obtained as a pure white amorphous solid. For the reoxidation, it was dissolved in 10 ml of MeOH to which 2 ml of HBF_4 (or 10 ml of $NaBF_4$ 0.2M) was added; the open flask being then irradiated for 1h using Foba RANOO lamp with an OSRAM Ultra-

[1] Martin, J. C.; Smith, R. G., *J. Am. Chem. Soc.* **1964,** *86,* 2252-2256.

Vitalux 300 W bulb. MeOH was evaporated. The residue was dissolved in 20 ml of dichloromethane, washed with water (1x10 ml, 2x20 ml), dried over Na_2SO_4, filtered and finally evaporated to lead to the pure product as a red solid.

1,13-dimethoxy-9-propylchromeno[2,3,4-*kl*]acridin-13b(9*H*)-ylium tetrafluoroborate [3a][BF_4]



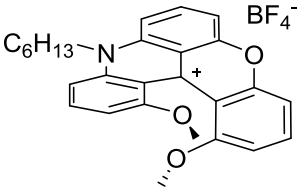
Yield: 46%, **M.P.:** 262 °C, **I.R.(neat):** υ = 2944, 1630, 1605, 1584, 1523, 1481, 1378, 1354, 1262, 1160, 1057, 815, 769, 729 cm^{-1}, ***R*$_f$:** 0.6 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 90:10),

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, J = 8.9, 8.0 Hz, 1H), 8.16 (dd, J = 9.1, 8.0 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.77 (t, J = 8.4 Hz, 1H), 7.67 (d, J = 9.1 Hz, 1H), 7.55 (d, J = 8.0, 0.6 Hz, 1H), 7.18 (dd, J = 8.5, 0.9 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.90 (dd, J = 8.5, 0.9 Hz, 1H), 4.93 (m, 1H), 4.77 (m, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 2.16 (m, 2H), 1.27 (t, J = 7.4 Hz, 3H), **^{13}C NMR** (101 MHz, CDCl3) δ 160.59(C), 159.43(C), 156.00(C), 151.06(C), 144.56(C), 143.51(C), 140.88(CH), 138.31(C), 137.88(CH), 137.86(CH), 116.65(C), 114.54(C), 111.74(C), 109.42(CH), 108.94(CH), 108.10(CH), 106.11(CH), 104.35(CH), 56.44(CH_3), 56.31(CH_3), 21.18(CH_2), 11.23(CH_3),**^{19}F NMR**: (282 MHz, CDCl3) δ -152.72 (20%), -152.75 (80%), **HRMS (ESI)** calculated for $C_{37}H_{48}NO_3^+$ (M^+): 372.1594 Found: 372.1583, **UV-Vis** (CH_3CN, C= 1×10^{-5} M) : λ_{max} (Δε in $M^{-1}.cm^{-1}$): 588 (4500), 552 (4785), 440 (6140).

(+)-[(*P*)-3a][BF_4]: CD (Acetonitrile, 1.10^{-4} M, 20 °C) λ (Δε) 273 (91.0), 301 (-137.2), 325 (-23.6), 358 (-43.2), 407 (7.01), 459 (-12.88) $[\alpha]_{365}$ + 7500 (c 10^{-4}, Acetonitrile).

(–)-[(*M*)-3a][BF_4]: CD (Acetonitrile, 1.10^{-4} M, 20 °C) λ (Δε) 273 (-91), 301 (+137.2), 325 (+23.6), 358 (+43.2), 407 (-7.01), 459 (+12.88) $[\alpha]_{365}$ – 7080 (c 10^{-4}, Acetonitrile).

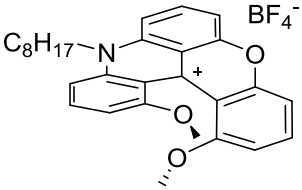
9-hexyl-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3b][BF_4]



Yield: 34%, **M.P.:** 214 °C, **I.R.(neat):** υ = 2926, 2856, 2364, 1630, 1605, 1583, 1523, 1479, 1378, 1354 1262, 1160, 1060, 816, 770, 730 cm^{-1}, ***R*$_f$:** 0.55 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 90:10),

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, J = 8.9, 8.1 Hz, 1H), 8.14 (dd, J = 9.0, 8.0 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.77 (t, J = 8.4 Hz, 1H), 7.56 (dd, J = 24.7, 8.6 Hz, 2H), 7.15 (dd, J = 8.5, 0.9 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.91 (dd, J = 8.3, 0.9 Hz, 1H), 4.91 (ddd, J = 16.2, 9.8, 6.8 Hz, 1H), 4.83 – 4.70 (m, 1H), 3.83 (d, J = 18.6 Hz, 6H), 2.20 – 1.99 (m, 2H), 1.66 (h, J = 7.5, 6.6 Hz, 2H), 1.50 – 1.15 (m, 8H), 0.95 – 0.75 (m, 5H), **^{13}C NMR** (101 MHz, CDCl3) δ 160.63(C), 159.36(C), 155.89(C), 150.99(C), 144.52(C), 143.33(C), 140.80(CH), 138.14(C), 137.97(CH), 137.93(CH), 116.53(C), 114.42(C), 111.58(C), 109.32(CH), 109.20(CH), 108.95(CH), 107.74(CH), 106.16(CH), 104.35(CH), 56.40(CH_3), 56.31(CH_3), 31.50(CH_2), 27.62(CH_2), 26.45(CH_2), 22.63(CH_2), 14.09(CH_3), **^{19}F NMR** (282 MHz, CDCl3) δ -152.71 (20%), -152.77 (80%), **HRMS (ESI)** calculated for $C_{24}H_{22}NO_3^+$ (M^+): 414.2064 Found: 414.2063.

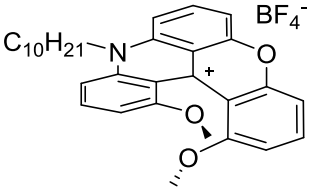
1,13-dimethoxy-9-octylchromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3c][BF_4]



Yield: 28%, **M.P.:** 230 °C, **I.R.(neat):** υ = 2927, 2855, 1630, 1603, 1583, 1523, 1477, 1377, 1353 1262, 1160, 1057, 815, 770, 730 cm^{-1}, ***R_f*:** 0.59 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 90:10),

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, J = 8.9, 8.0 Hz, 1H), 8.14 (dd, J = 9.1, 8.0 Hz, 1H), 7.89 – 7.73 (m, 2H), 7.57 (dd, J = 20.9, 8.5 Hz, 2H), 7.16 (dd, J = 8.5, 0.9 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.91 (dd, J = 8.4, 1.0 Hz, 1H), 4.98 – 4.83 (m, 1H), 4.77 (ddd, J = 15.6, 9.6, 7.2 Hz, 1H), 3.83 (d, J = 18.8 Hz, 6H), 2.17 – 2.00 (m, 2H), 1.64 (h, J = 9.8, 8.6 Hz, 2H), 1.50 – 1.12 (m, 11H), 0.93 – 0.76 (m, 4H), **^{13}C NMR** (101 MHz, CDCl3) δ 160.66(C), 159.38(C), 155.92(C), 151.03(C), 144.55(C), 143.35(C), 140.82(CH), 138.17(C), 137.98(CH), 137.91(CH), 116.56(C), 114.45(C), 111.61(C), 109.34(CH), 109.20(CH), 108.96(CH), 107.75(CH), 106.17(CH), 104.37(CH), 56.42(CH_3), 56.33(CH_3), 31.84(CH_2), 29.37(CH_2), 29.25(CH_2), 27.67(CH_2), 26.81(CH_2), 22.71(CH_2), 14.19(CH_3), **^{19}F NMR**: (282 MHz, CDCl3) δ -152.76 (20%), -152.82 (80%), **HRMS (ESI)** calculated for $C_{29}H_{32}NO_3^+$ (M^+): 442.2377 Found: 442.2373.

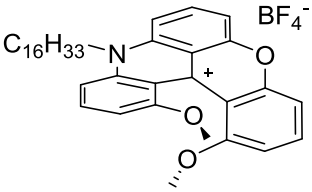
9-decyl-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3d][BF_4]



Yield: 13%, **M.P.:** 221 °C, **I.R.(neat):** υ = 2926, 2853, 1630, 1604, 1582, 1523, 1479, 1377, 1353 1262, 1160, 1057, 816, 771, 730 cm^{-1}, ***R_f*:** 0.57 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 90:10),

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, J = 8.9, 8.1 Hz, 1H), 8.15 (dd, J = 9.0, 8.0 Hz, 1H), 7.88 – 7.72 (m, 2H), 7.64 – 7.50 (m, 2H), 7.18 (dd, J = 8.5, 0.9 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.91 (dd, J = 8.4, 0.9 Hz, 1H), 4.93 (dt, J = 16.8, 7.6 Hz, 1H), 4.84 – 4.71 (m, 1H), 3.84 (d, J = 19.5 Hz, 6H), 2.17 – 2.03 (m, 2H), 1.65 (h, J = 7.3, 6.9 Hz, 3H), 1.45 (tt, J = 8.9, 6.5 Hz, 2H), 1.41 – 1.18 (m, 14H), 0.92 – 0.78 (m, 4H), **^{13}C NMR** (101 MHz, CDCl3) δ 160.68(C), 159.44(C), 155.97(C), 151.10(C), 144.59(C), 143.41(C), 140.89(CH), 138.23(C), 137.95(CH), 137.84(CH), 116.63(C), 114.52(C), 111.70(C), 109.38(CH), 109.19(CH), 108.96(CH), 107.82(CH), 106.17(CH), 104.42(CH), 56.46(CH_3), 56.35(CH_3), 31.98(CH_2), 29.83(CH_2), 29.64(CH_2), 29.63(CH_2), 29.46(CH_2), 29.41(CH_2), 27.71(CH_2), 26.87(CH_2), 22.79(CH_2), 14.25(CH_3), **^{19}F NMR** (282 MHz, CDCl3) δ -152.76 (20%), -152.82 (80%), **HRMS (ESI)** calculated for $C_{31}H_{36}NO_3^+$ (M^+): 470.2690 Found: 470.2686.

9-hexadecyl-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3e][BF_4]

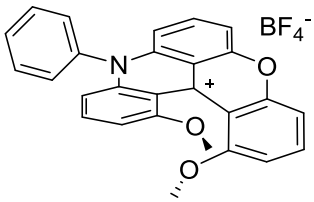


Yield: 7%, **M.P.:** 194 °C, **I.R.(neat):** υ = 2925, 2853, 2367, 1630, 1603, 1582, 1523, 1481, 1377, 1354, 1260, 1160, 1055, 816, 773, 730 cm^{-1}, ***R_f*:** 0.57 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 90:10),

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.21 (m, 1H), 8.16 (dd, J = 9.1, 8.0 Hz, 1H), 7.87 – 7.73 (m, 2H), 7.59 (dd, J = 23.3, 8.5 Hz, 2H), 7.18 (dd, J = 8.4, 0.9 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.91 (dd, J = 8.5, 0.9 Hz, 1H), 4.99 – 4.87 (m, 1H), 4.78 (dt, J = 15.8, 8.3 Hz, 1H), 3.85 (d, J = 19.8 Hz, 6H), 2.11 (h, J = 8.1, 7.1 Hz, 2H), 1.66 (q, J = 7.6 Hz, 3H), 1.45 (q, J = 7.5, 7.0 Hz, 2H),

1.25 (s, 28H), 1.14 – 1.07 (m, 2H), 0.92 – 0.80 (m, 4H), **^{13}C NMR** (101 MHz, CDCl3) δ 160.67(C), 159.47(C), 156.00(C), 151.15(C), 144.60(C), 143.44(C), 140.94(CH), 138.26(C), 137.91(CH), 137.77(CH), 116.66(C), 114.57(C), 111.75(C), 109.40(CH), 109.16(CH), 108.95(CH), 107.87(CH), 106.16(CH), 104.45(CH), 56.48(CH_3), 56.35(CH_3), 32.07(CH_2), 29.84(CH_2), 29.81(CH_2), 29.79(CH_2), 29.75(CH_2), 29.72(CH_2), 29.67(CH_2), 29.51(CH_2), 29.49(CH_2), 27.73(CH_2), 26.90(CH_2), 22.83(CH_2), 14.27(CH_3), **^{19}F NMR** (282 MHz, CDCl3) δ -152.80 (20%), -152.85 (80%), **HRMS (ESI)** calculated for $C_{37}H_{48}NO_3^+$ (M^+): 554.3629 Found: 554.3628.

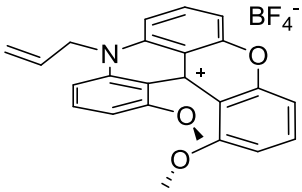
1,13-dimethoxy-9-phenylchromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3f][BF$_4$]



Yield: 15%, **M.P.:** 254 °C, **I.R.(neat):** υ = 2925, 2853, 2261, 1735, 1631, 1602, 1582, 1547, 1519, 1481, 1376, 1354, 1266, 1231, 1181, 1055, 910, 813, 770, 727, 701, 647 cm^{-1}, ***R$_f$*:** 0.59 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 90:10),

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, J = 8.4 Hz, 1H), 7.92 (t, J = 8.4 Hz, 5H), 7.89 – 7.77 (m, 4H), 7.60 – 7.50 (m, 2H), 7.43 (d, J = 7.0 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.7 Hz, 1H), 6.71 (d, J = 8.9 Hz, 1H), 3.95 (s, 6H), 3.91 (s, 3H), **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.67(C), 160.00(C), 156.57(C), 151.23(C), 146.36(C), 144.88(C), 140.73(CH), 139.60(C), 138.70(CH), 137.21(C), 137.19(CH), 132.41(CH), 131.63(CH), 131.55(CH), 128.74(CH), 127.82(CH), 116.24(C), 114.11(C), 112.00(C), 110.53(CH), 109.43(CH), 109.35(CH), 109.00(CH), 106.54(CH), 105.06(CH), 56.82(CH_3), 56.74(CH_3), **^{19}F NMR** (282 MHz, CDCl3) δ -153.25 (20%), -153.30 (80%), **HRMS (ESI)** calculated for $C_{37}H_{48}NO_3^+$ (M^+): 406.1438 Found: 406.1433.

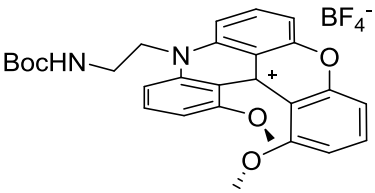
9-allyl-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3g][BF$_4$]



Yield: 27%, **M.P.:** 255 °C, **I.R.(neat):** υ = 3631, 3112, 2957, 1630, 1604, 1582, 1523, 1481, 1377, 1354, 1263, 1161, 1058, 814, 769, 730 cm^{-1}, ***R$_f$*:** 0.21 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 95:5),

1H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.8, 8.1 Hz, 2H), 8.09 (dd, J = 9.0, 8.0 Hz, 2H), 7.80 (t, J = 8.1 Hz, 2H), 7.78 (d, J = 8.73 Hz, 2H), 7.57 (d, J = 9.05 Hz, 2H), 7.57 (d, J = 8.18 Hz, 2H), 7.22 (dd, J = 8.5, 0.9 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.92 (dd, J = 8.4, 0.9 Hz, 2H), 6.42 – 6.28 (m, 2H), 5.72 – 5.61 (m, 2H), 5.49 – 5.39 (m, 4H), 5.04 (td, J = 17.3, 1.9 Hz, 2H), 3.88 (s, 12H), 3.83 (s, 6H), **^{13}C NMR** (101 MHz, CDCl3) δ 160.24(C), 159.48(C), 156.01(C), 150.81(C), 145.12(C), 143.80(C), 140.70(CH), 138.49(C), 137.92(CH), 137.70(CH), 128.93(CH), 118.55(CH_2), 116.59(C), 114.52(C), 111.74(C), 109.66(CH), 109.33(CH), 108.87(CH), 108.57(CH), 106.02(CH), 104.42(CH), 56.39(CH_3), 56.15(CH_3), 53.93(CH_2), **^{19}F NMR** (282 MHz, CDCl3) δ -152.94 (20%), -153.00 (80%), **HRMS (ESI)** calculated for $C_{37}H_{48}NO_3^+$ (M^+): 370.1438 Found: 370.1441.

9-N-Boc-ethyleneamin-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3h][BF_4]



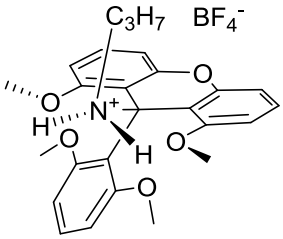
Yield: 19%, **M.P.:** 151.8 °C, **I.R.(neat):** υ = 3412, 2977, 1704, 1606, 1584, 1523, 1483, 1357, 1261, 1162, 1066, 8415, 770, 730 cm^{-1}, ***R_f*:** 0.21 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 95:5), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.8 Hz, 1H), 8.33 (t, J = 8.4 Hz, 1H), 8.27 – 8.13 (m, 2H), 7.76 (t, J = 8.3 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.20 (dd, J = 8.4, 0.9 Hz, 1H), 6.94 (d, J = 6.9 Hz, 1H), 6.85 (dd, J = 8.4, 0.9 Hz, 1H), 6.15 (brs, 1H), 5.17 – 5.03 (m, 1H), 5.03 – 4.84 (m, 1H), 3.86 (brs, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.42 (s, 9H),**^{13}C NMR** (101 MHz, CDCl3) δ 160.04(C), 159.22(C), 157.10(C), 156.02(C), 150.64(C), 144.50(C), 143.99(C), 140.94(CH), 138.62(C), 138.26(CH), 137.33(CH), 116.57(C), 114.39(C), 111.78(C), 110.26(CH), 109.47(CH), 109.10(CH), 108.79(CH), 105.60(CH), 103.88(CH), 79.54(C), 56.16(CH_3), 55.96(CH_3), 37.41(CH_2), 28.37(3xCH_3), 26.92(CH_2), **^{19}F NMR** (282 MHz, CDCl3) δ -152.20 (20%), -152.28 (80%), **HRMS (ESI)** calculated for $C_{37}H_{48}NO_3^+$ (M^+): 473.2071 Found: 473.2072.

Synthesis of salts [10][BF_4]

General procedure

In round bottom flask, to a solution of 9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-9H-xanthen-9-ylium tetrafluoroborate (50.0 mg, 0.108 mmol, 1 equiv) in CH_3CN (2 ml) was added at 20 °C the desired primary amine (1.5 equiv). The color turned instantaneously to pale yellow color. The mixture was stirred for 30 minutes. Et_2O was then added and, after cooling the solution to 4 °C, the resulting precipitate was filtered to yield salt [**10**][BF_4] as a powder.

9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-N-propyl-9H-xanthen-9-aminium tetrafluoroborate [10a][BF_4]

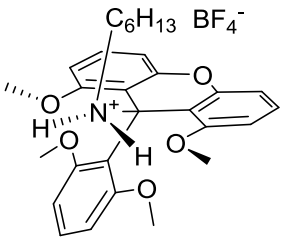


Yield: 90%, **M.P.:** 262 °C (decomposition), **I.R.(neat):** υ = 3209, 2947, 2849, 2364, 2340, 1623, 1584, 1484, 1459, 1398, 1318, 1272, 1249, 1187, 1092, 1061, 955, 781, 745, 710, 675 cm^{-1}, ***R*$_f$:** 0.36 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 95:5),

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (s, 2H), 7.39 (t, J = 8.3 Hz, 2H), 7.21 (t, J = 8.4 Hz, 1H), 6.89 (dd, J = 8.4, 1.0 Hz, 2H), 6.73 (dd, J = 8.5, 1.1 Hz, 1H), 6.67 (dd, J = 8.2, 1.0 Hz, 2H), 6.38 (d, J = 8.2 Hz, 1H), 4.15 (s, 3H), 3.74 (s, 6H), 3.18 (s, 3H), 2.56 (dd, J = 8.2, 6.9 Hz, 2H), 1.58 (h, J = 7.4 Hz, 2H), 0.78 (t, J = 7.4 Hz, 3H), **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 157.40(C), 157.03(2xC), 156.76(2xC), 152.30(C), 131.77(2xCH), 130.37(CH), 118.02(C), 109.89(2xCH), 107.35(CH), 106.92(2xC), 106.66(2xCH), 104.76(CH), 64.28(C), 57.16(CH_3), 56.98(2xCH_3), 56.21(CH_3), 46.68(CH_2), 20.86(CH_2), 11.10(CH_3),

^{19}F NMR (282 MHz, CDCl3) δ -151.82 (20%), -151.87 (80%), **HRMS (ESI)** calculated for $C_{26}H_{30}NO_5^+$ (M^+): 436.2119 Found: 436.2115.

9-(2,6-dimethoxyphenyl)-N-hexyl-1,8-dimethoxy-9H-xanthen-9-aminium tetrafluoroborate [10b][BF_4]

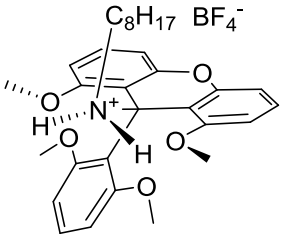


Yield: 80%, **M.P.:** 184 °C (decomposition), **I.R.(neat):** υ = 3192, 2937, 2852, 2366, 2341, 1623, 1584, 1484, 1459, 1398, 1340, 1318, 1273, 1253, 1185, 1093, 1058, 955, 783, 746, 709, 674 cm^{-1}, ***R*$_f$:** 0.37 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 95:5),

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 (t, J = 8.3 Hz, 2H), 7.21 (t, J = 8.4 Hz, 1H), 6.89 (dd, J = 8.4, 1.0 Hz, 2H), 6.73 (dd, J = 8.5, 1.1 Hz, 1H), 6.67 (dd, J = 8.3, 1.0 Hz, 2H), 6.38 (dd, J = 8.3, 1.1 Hz, 1H), 4.15 (s, 3H), 3.73 (s, 6H), 3.17 (s, 3H), 2.60 (t, J = 8.3, 7.5 Hz, 2H), 1.54 (p, J = 11.2, 8.3, 6.9 Hz, 2H), 1.23 – 1.03 (m, 6H), 0.80 (t, J = 7.2 Hz, 3H), **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 157.37(C), 157.04(2xC), 156.77(2xC), 152.30(C), 131.77(2xCH), 130.35(CH), 118.06(C), 109.89(2xCH), 107.36(CH), 106.97(2xC), 106.67(2xCH), 104.74(CH), 64.30(C), 57.15(CH_3), 56.98(2xCH_3), 56.22(CH_3), 45.11(CH_2), 31.22(CH_2), 27.24(CH_2), 26.41(CH_2), 22.80(CH_2), 14.13(CH_3),

^{19}F NMR (282 MHz, CDCl3) δ -151.86 (20%), -151.91 (80%), **HRMS (ESI)** calculated for $C_{29}H_{36}NO_5^+$ (M^+): 478.2588 Found: 478.2595.

9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-N-octyl-9H-xanthen-9-aminium tetrafluoroborate [10c][BF$_4$]

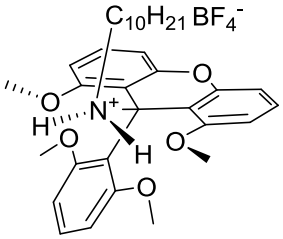


Yield: 70%, **M.P.:** 183 °C (decomposition), **I.R.(neat):** υ = 3201, 2927, 2854, 2365, 2341, 1623, 1584, 1484, 1460, 1400, 1339, 1319, 1273, 1252, 1187, 1095, 1058, 933, 785, 750, 726 cm^{-1}, ***R$_f$*:** 0.36 (TLC Silica Gel 60 F$_{254}$, CH_2Cl_2:MeOH 95:5),

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 (t, J = 8.3 Hz, 2H), 7.21 (t, J = 8.4 Hz, 1H), 6.89 (dd, J = 8.4, 1.0 Hz, 2H), 6.73 (dd, J = 8.6, 1.1 Hz, 1H), 6.66 (dd, J = 8.3, 1.0 Hz, 2H), 6.38 (dd, J = 8.3, 1.2 Hz, 1H), 4.15 (s, 3H), 3.73 (s, 6H), 3.17 (s, 3H), 2.60 (dd, J = 8.3, 7.5 Hz, 2H), 1.53 (p, J = 7.2 Hz, 2H), 1.33 – 1.03 (m, 11H), 0.85 (t, J = 7.1 Hz, 3H), **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 157.38(C), 157.05(2xC), 156.78(2xC), 152.30(C), 131.77(2xCH), 130.35(CH), 118.09(C), 109.89(2xCH), 107.37(CH), 107.00(2xC), 106.68(2xCH), 104.75(CH), 64.29(C), 57.16(CH_3), 56.98(2xCH_3), 56.23(CH_3), 45.11(CH_2), 32.15(CH_2), 29.42(CH_2), 29.05(CH_2), 27.27(CH_2), 26.73(CH_2), 23.11(CH_2), 14.38(CH_3),

^{19}F NMR (282 MHz, CDCl3) δ -151.88 (20%), -151.93 (80%), **HRMS (ESI)** calculated for $C_{31}H_{40}NO_5^+$ (M^+): 506.2901 Found: 506.2908.

N-decyl-9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-9H-xanthen-9-aminium tetrafluoroborate [10d][BF$_4$]

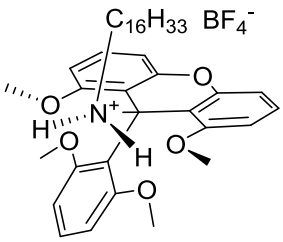


Yield: 69%, **M.P.:** 183 °C (decomposition), **I.R.(neat):** υ = 3234, 3171, 2927, 2852, 2365, 2337, 1624, 1581, 1485, 1460, 1394, 1339, 1319, 1273, 1252, 1188, 1098, 1058, 935, 787, 753, 728, 613 cm^{-1}, ***R$_f$*:** 0.37 (TLC Silica Gel 60 F$_{254}$, CH_2Cl_2:MeOH 95:5),

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 (t, J = 8.3 Hz, 2H), 7.21 (d, J = 25.1 Hz, 1H), 7.21 (t, J = 8.4 Hz, 1H), 6.89 (dd, J = 8.4, 1.0 Hz, 2H), 6.73 (dd, J = 8.6, 1.2 Hz, 1H), 6.66 (dd, J = 8.3, 1.0 Hz, 2H), 6.38 (dd, J = 8.3, 1.0 Hz, 1H), 4.15 (s, 3H), 3.73 (s, 6H), 3.17 (s, 3H), 2.60 (dd, J = 8.5, 7.5 Hz, 2H), 1.53 (p, J = 7.0 Hz, 2H), 1.34 – 1.03 (m, 14H), 0.87 (t, J = 6.9 Hz, 3H), **^{13}C NMR** (101 MHz, CD2Cl2) δ 157.38(C), 157.05(2xC), 156.78(2xC), 152.31(C), 131.77(2xCH), 130.36(CH), 118.09(C), 109.90(2xCH), 107.36(CH), 107.00(2xC), 106.67(2xCH), 104.76(CH), 64.29(C), 57.17(CH_3), 56.99(2xCH_3), 56.23(CH_3), 45.11(CH_2), 32.41(CH_2), 29.92(CH_2), 29.78(CH_2), 29.77(CH_2), 29.10(CH_2), 27.27(CH_2), 26.73(CH_2), 23.21(CH_2), 14.43(CH_3),

^{19}F NMR (282 MHz, CDCl3) δ -151.89 (20%), -151.94 (80%), **HRMS (ESI)** calculated for $C_{37}H_{44}NO_5^+$ (M^+): 534.3214 Found: 534.3217.

9-(2,6-dimethoxyphenyl)-N-hexadecyl-1,8-dimethoxy-9H-xanthen-9-aminium tetrafluoroborate [10e][BF_4]



Yield: 58%, **M.P.:** 147 °C (decomposition), **I.R.(neat):** υ = 3201, 2925, 2849, 2364, 2336, 1623, 1582, 1485, 1461, 1495, 1339, 1319, 1274, 1253, 1187, 1096, 1058, 1002, 954, 786, 749, 710 cm^{-1}, ***R_f*:** 0.34 (TLC Silica Gel 60 F_{254}, CH_2Cl_2:MeOH 95:5),

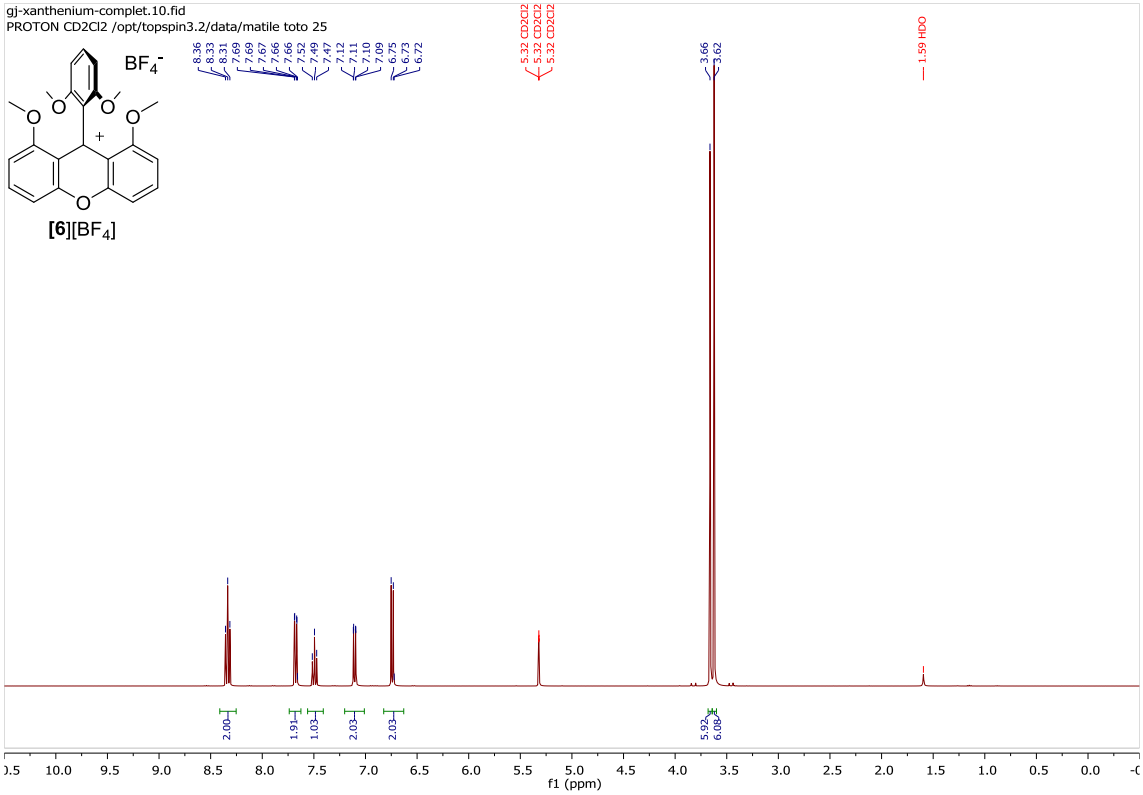
1H NMR (400 MHz, CD_2Cl_2) δ 7.39 (t, J = 8.3 Hz, 2H), 7.21 (t, J = 8.4 Hz, 1H), 7.27 – 7.16 (m, 1H), 6.89 (dd, J = 8.4, 1.0 Hz, 2H), 6.73 (dd, J = 8.5, 1.1 Hz, 1H), 6.66 (dd, J = 8.3, 1.0 Hz, 2H), 6.38 (dd, J = 8.3, 1.0 Hz, 1H), 4.15 (s, 3H), 3.73 (s, 6H), 3.17 (s, 3H), 2.60 (t, J = 8.2, 7.5 Hz, 2H), 1.53 (p, J = 7.2 Hz, 2H), 1.33 – 1.04 (m, 26H), 0.92 – 0.84 (m, 3H), **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 157.38(C), 157.06(2xC), 156.79(2xC), 152.31(C), 131.76(2xCH), 130.35(CH), 118.09(C), 109.89(2xCH), 107.36(CH), 107.01(2xC), 106.67(2xCH), 104.75(CH), 64.29(C), 57.16(CH_3), 56.98(2xCH_3), 56.23(CH_3), 45.11(CH_2), 32.49(CH_2), 30.27(CH_2), 30.25(CH_2), 30.24(CH_2), 30.22(CH_2), 30.17(CH_2), 30.14(CH_2), 29.99(CH_2), 29.92(CH_2), 29.80(CH_2), 29.11(CH_2), 27.27(CH_2), 26.73(CH_2), 23.25(CH_2), 14.45(CH_3),

^{19}F NMR (282 MHz, CDCl3) δ -149.10 (20%), -149.15 (80%), **HRMS (ESI)** calculated for $C_{39}H_{56}NO_5^+$ (M^+): 618.4153 Found: 618.4151.

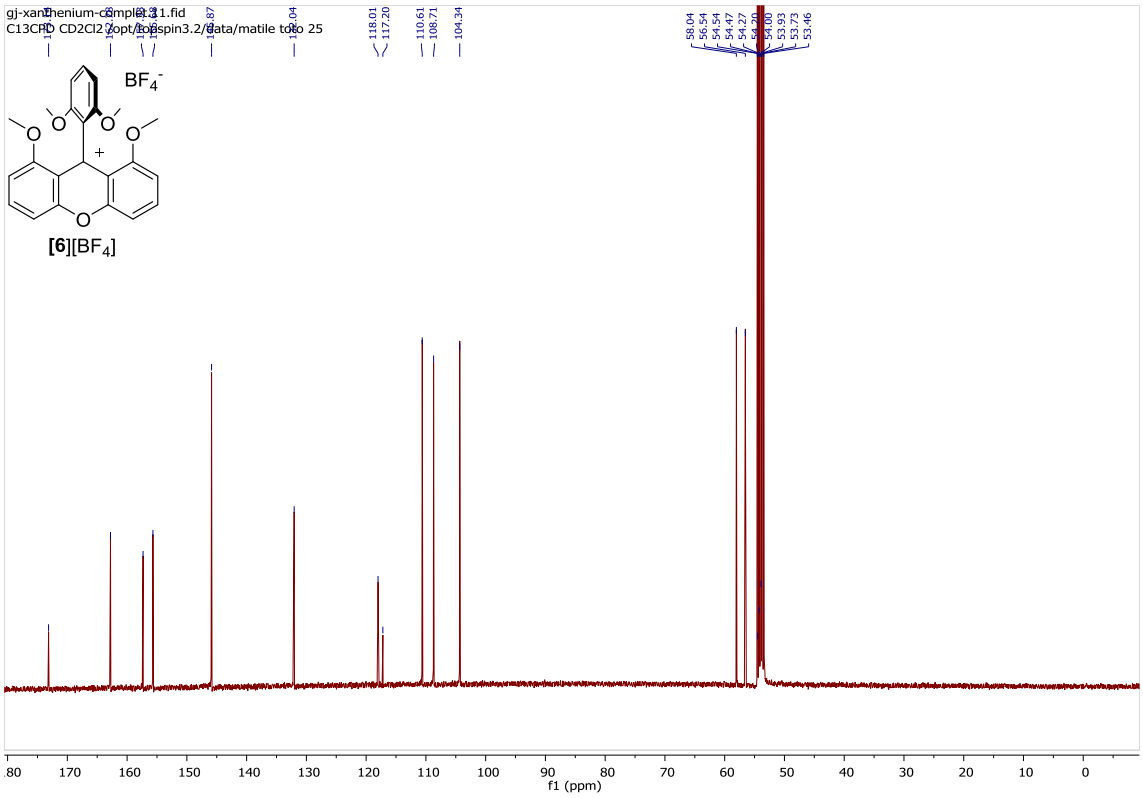
^{1}H NMR, ^{13}C NMR, ^{19}F NMR and example of Absorption/Emission spectrum

9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-9H-xanthen-9-ylium tetrafluoroborate [6][BF_4]

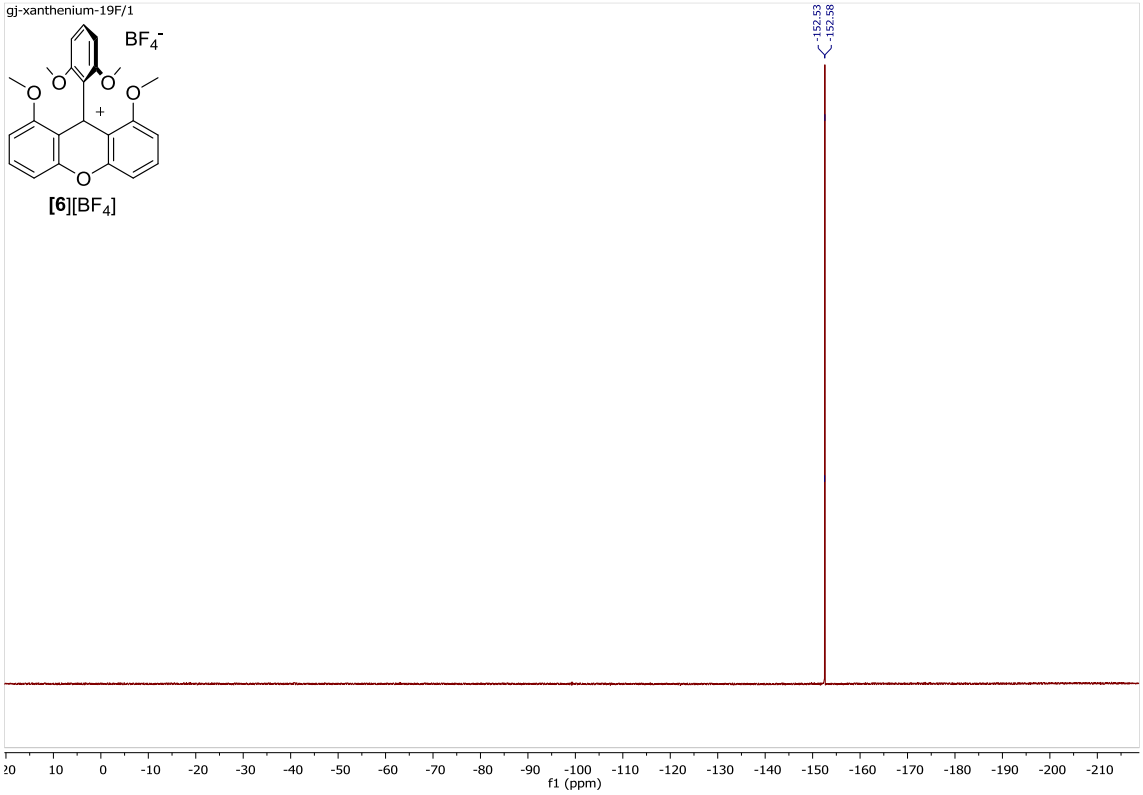
^{1}H NMR



^{13}C NMR

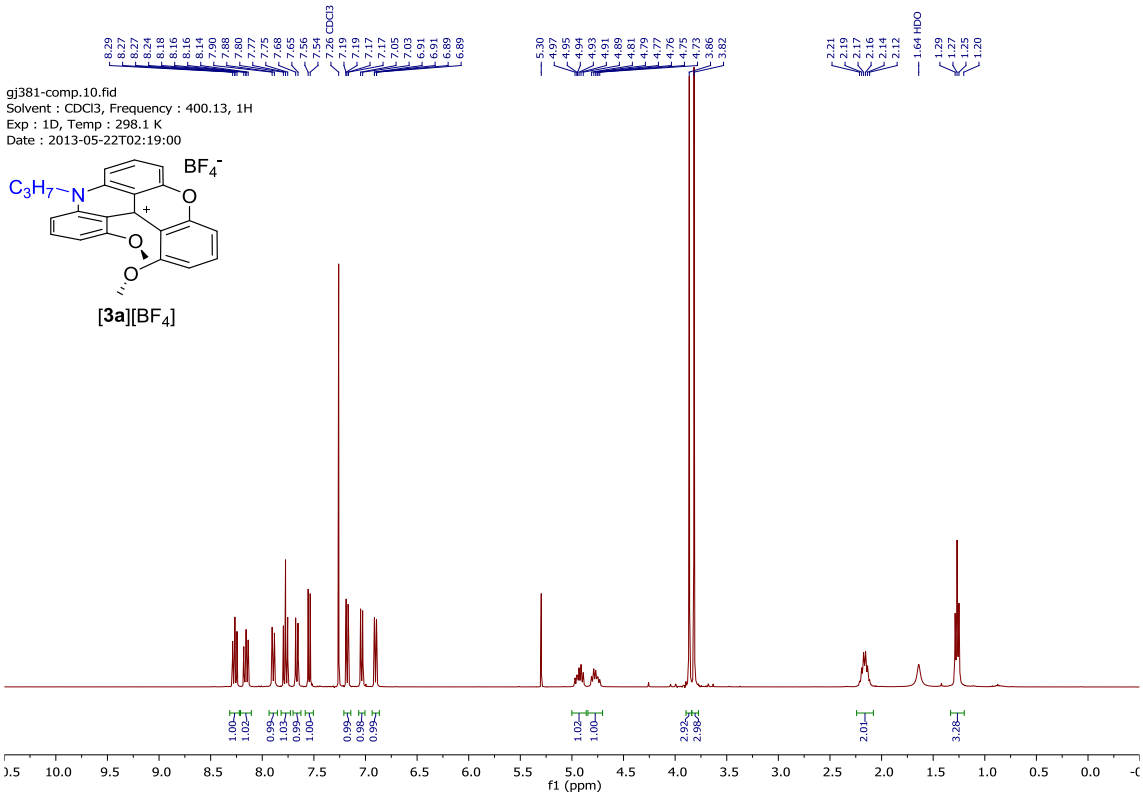


^{19}F NMR

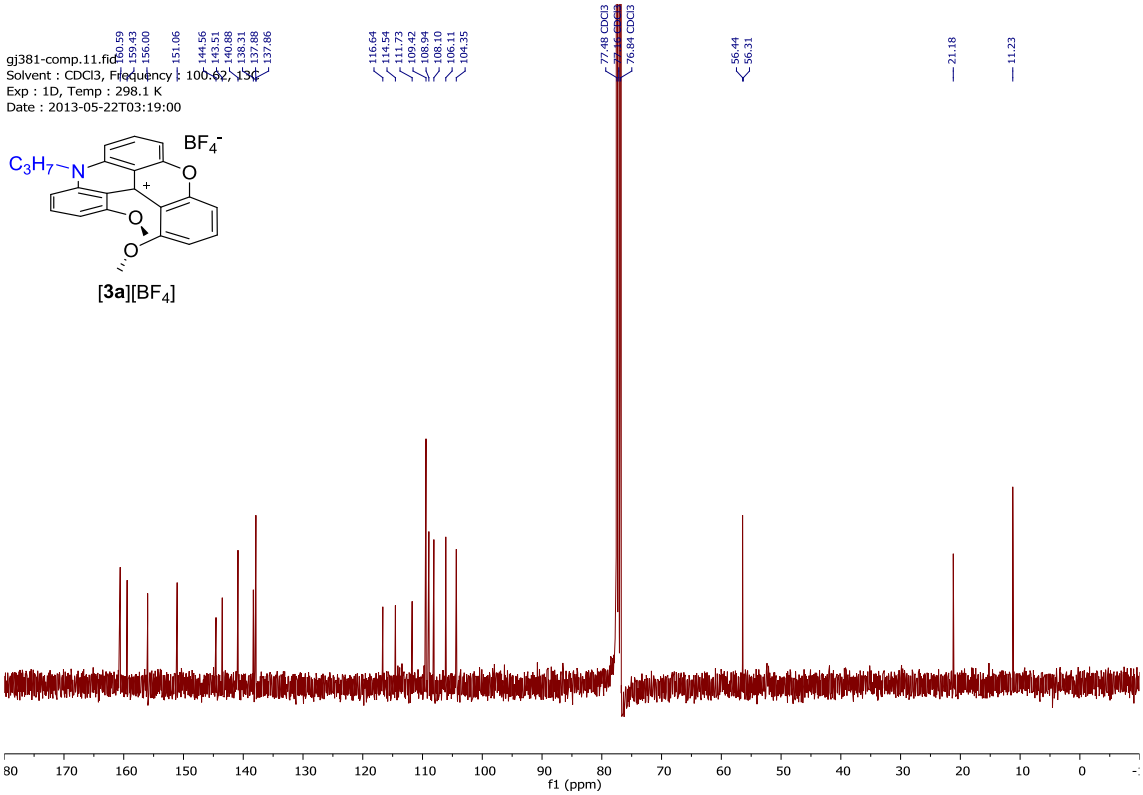


1,13-dimethoxy-9-propylchromeno[2,3,4-*kl*]acridin-13b(9*H*)-ylium tetrafluoroborate [3a][BF_4]

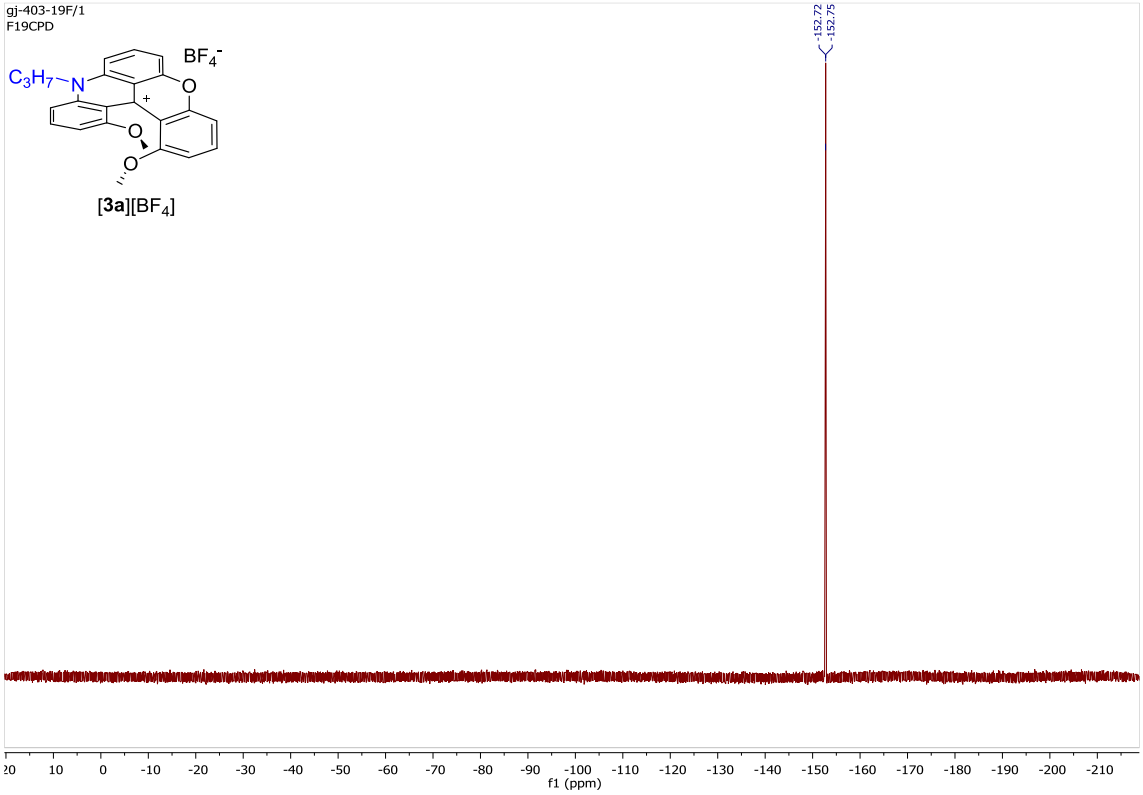
^{1}H NMR



^{13}C NMR

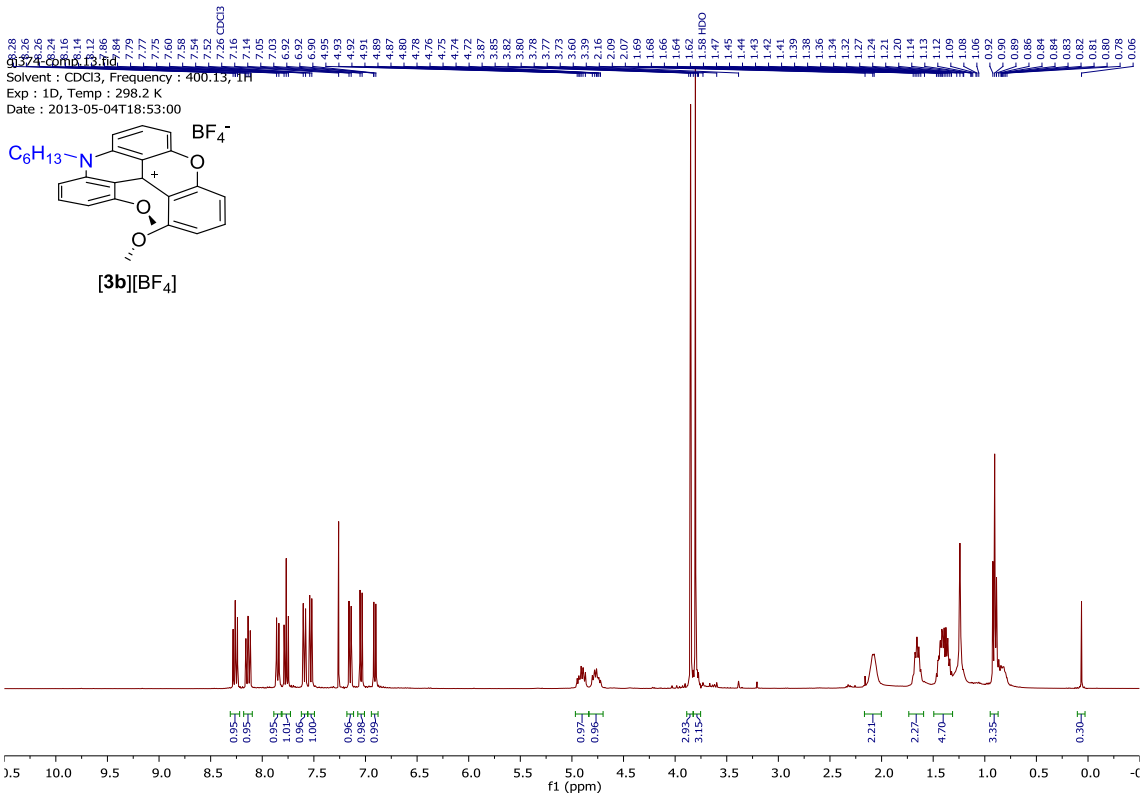


^{19}F NMR

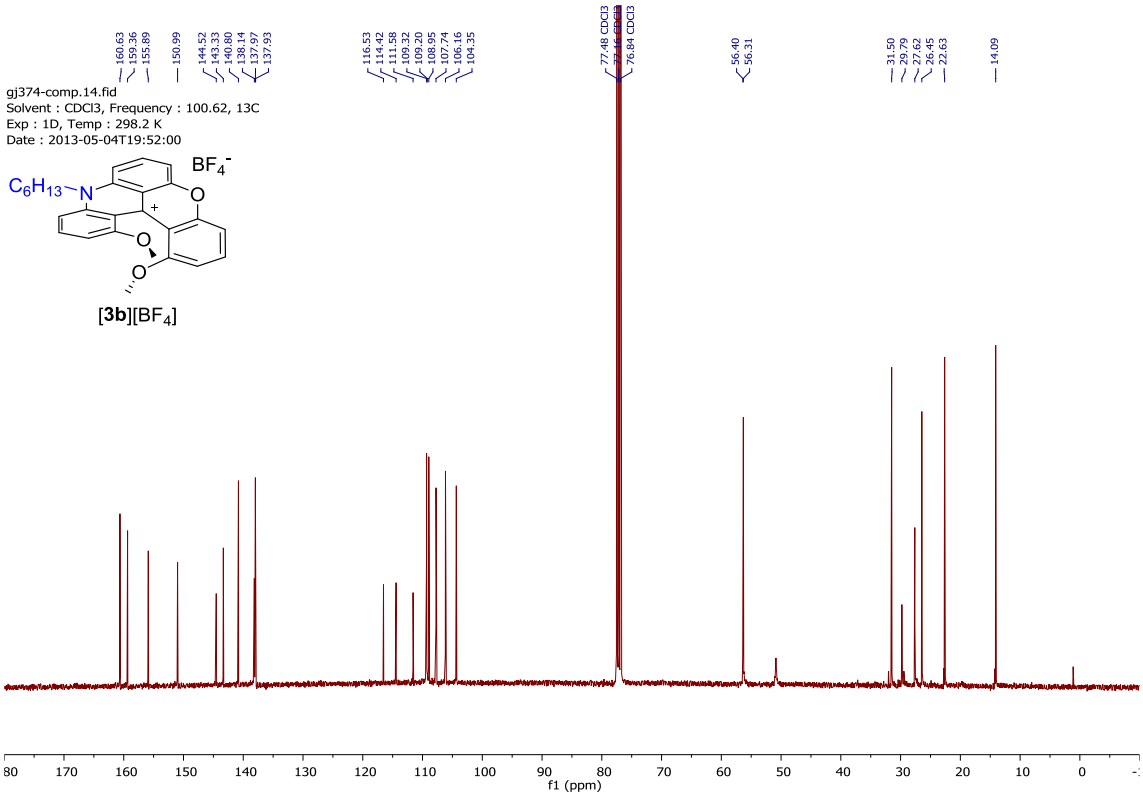


9-hexyl-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3b][BF$_4$]

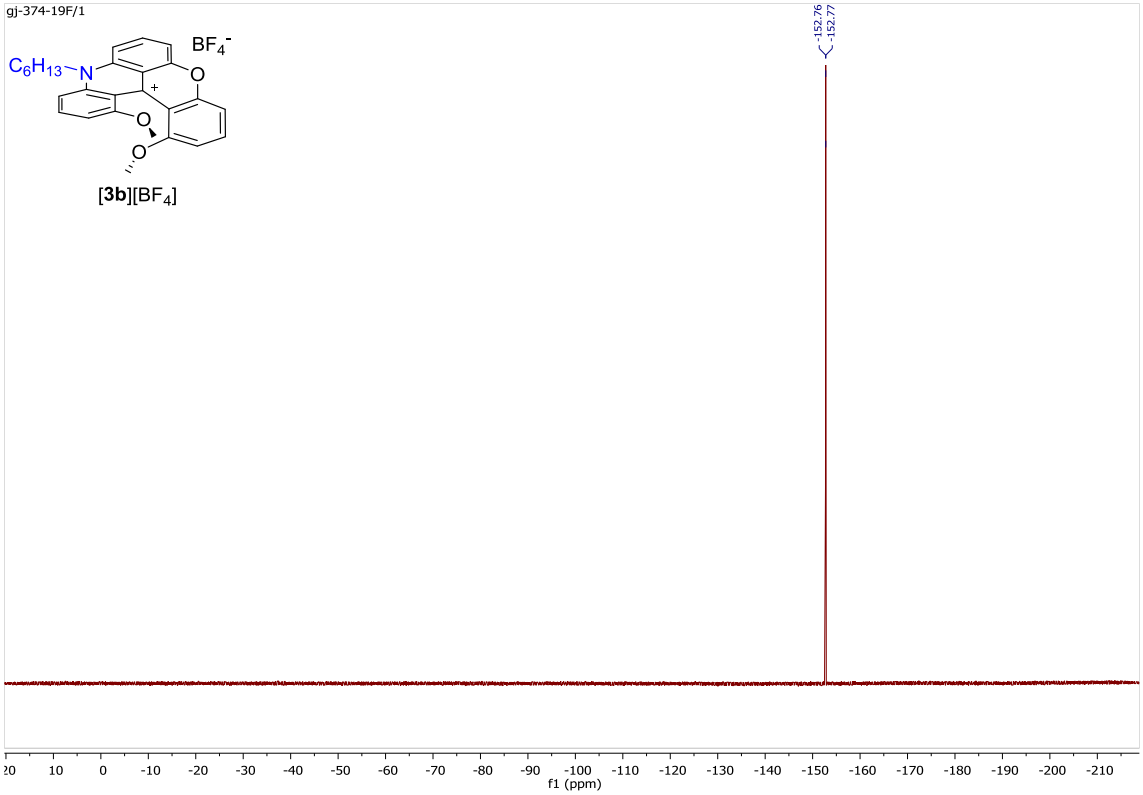
^{1}H NMR



^{13}C NMR

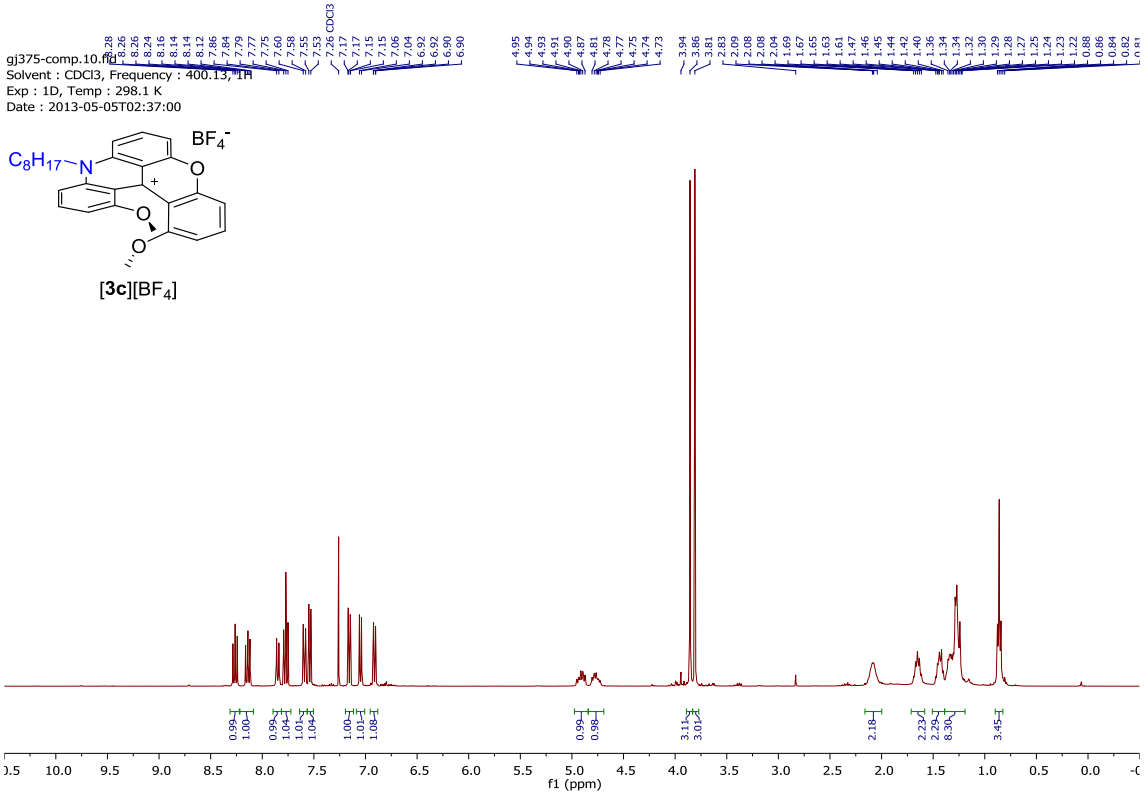


^{19}F NMR

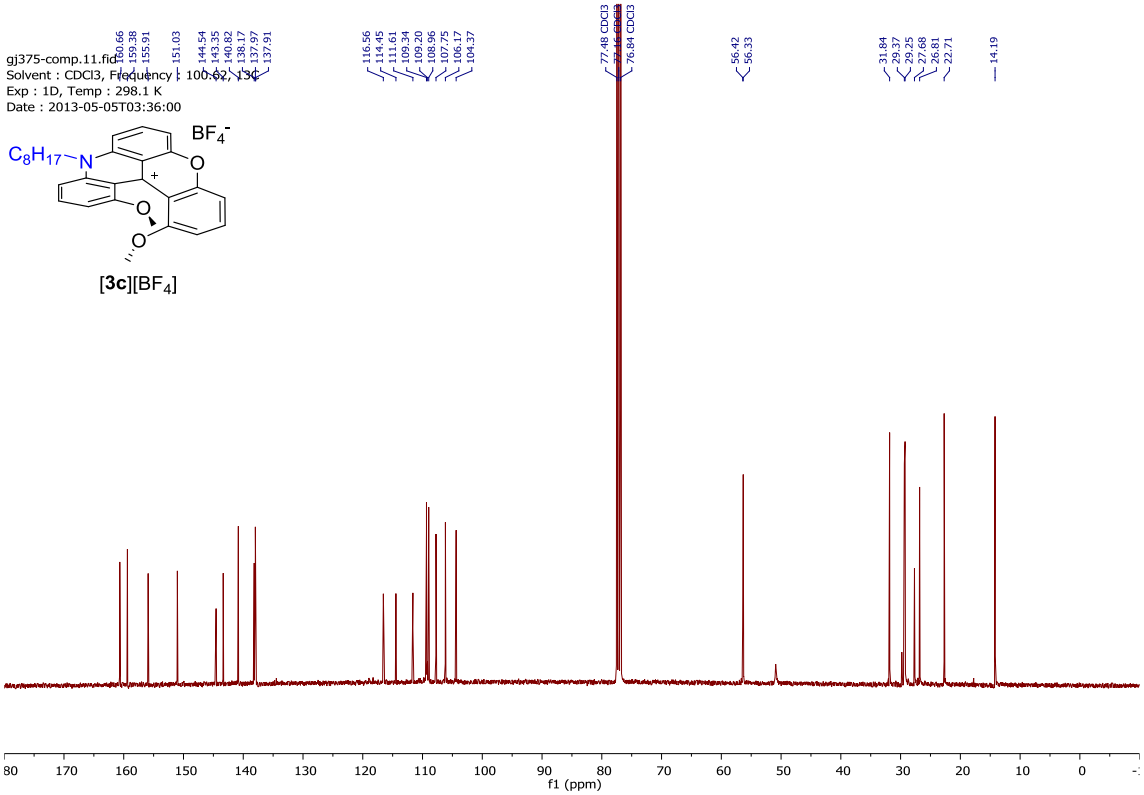


1,13-dimethoxy-9-octylchromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3c][BF_4]

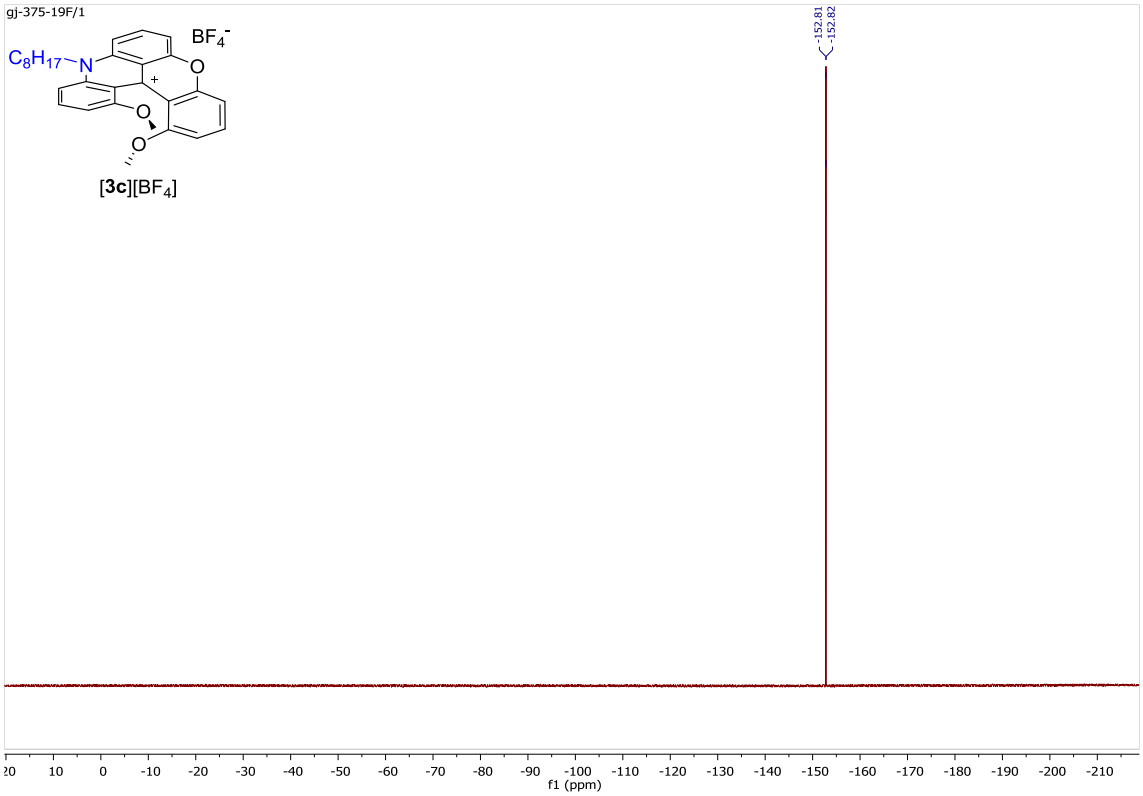
^{1}H NMR



^{13}C NMR

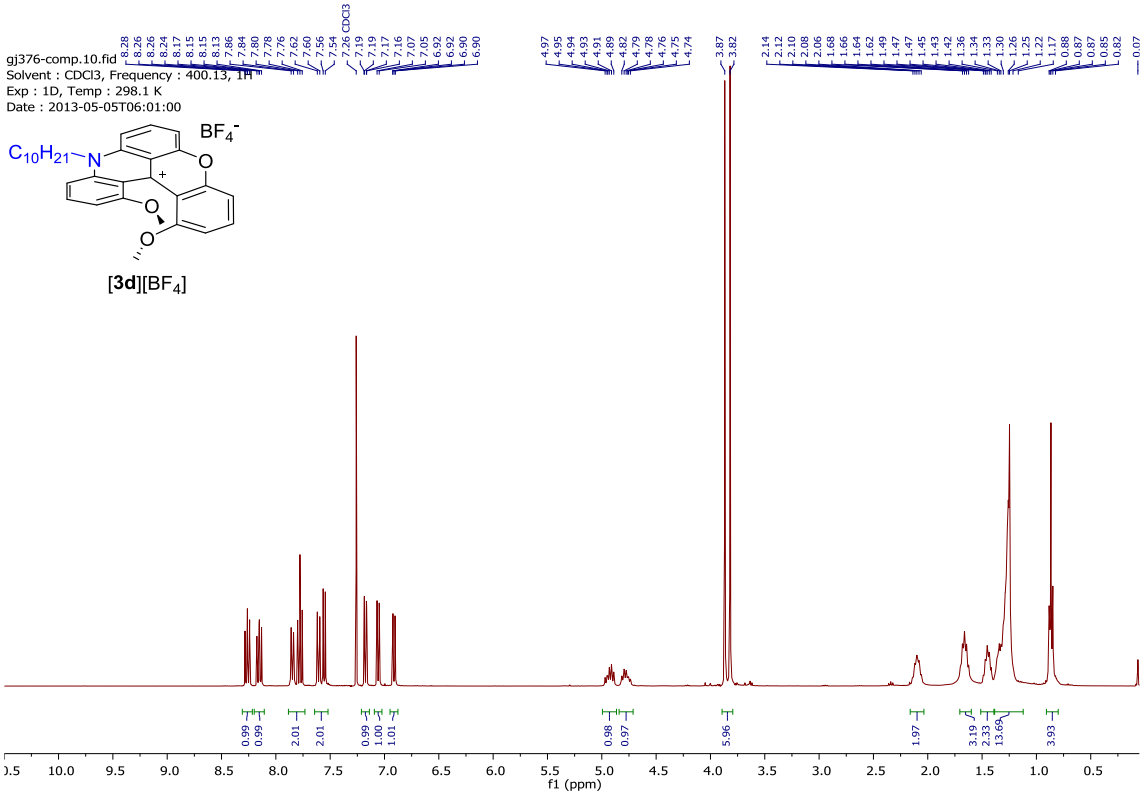


^{19}F NMR

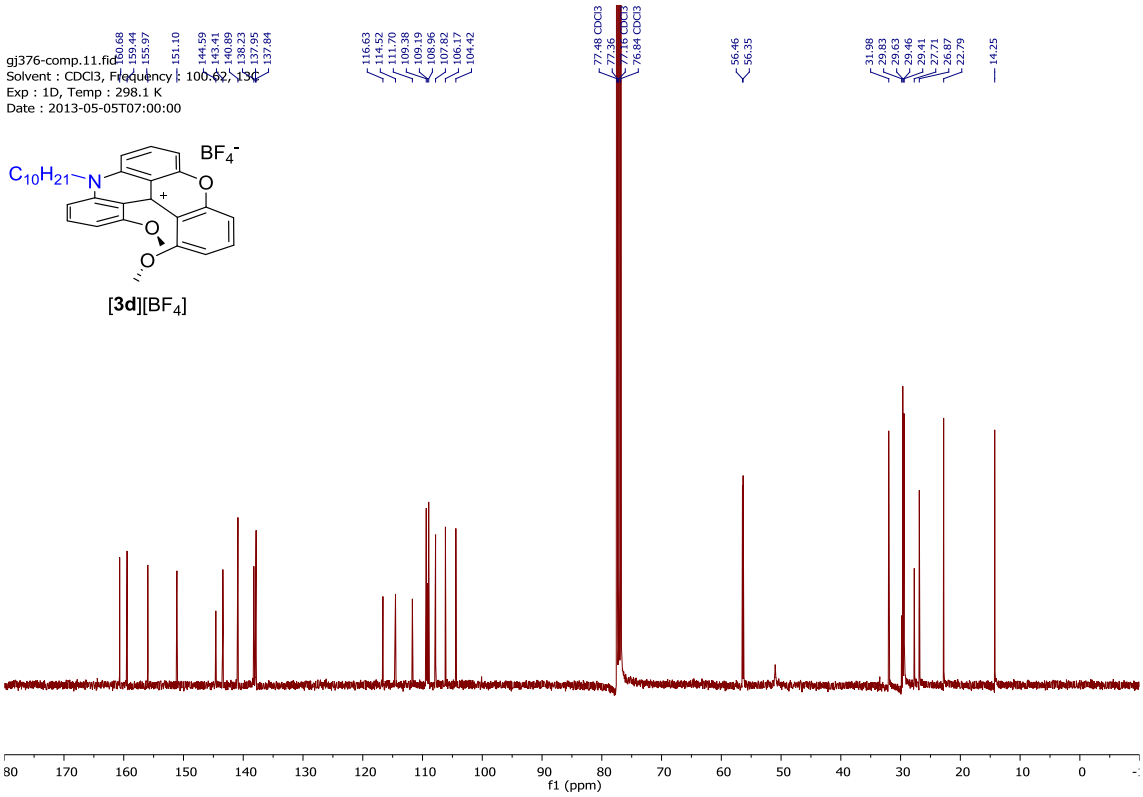


9-decyl-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3d][BF$_4$]

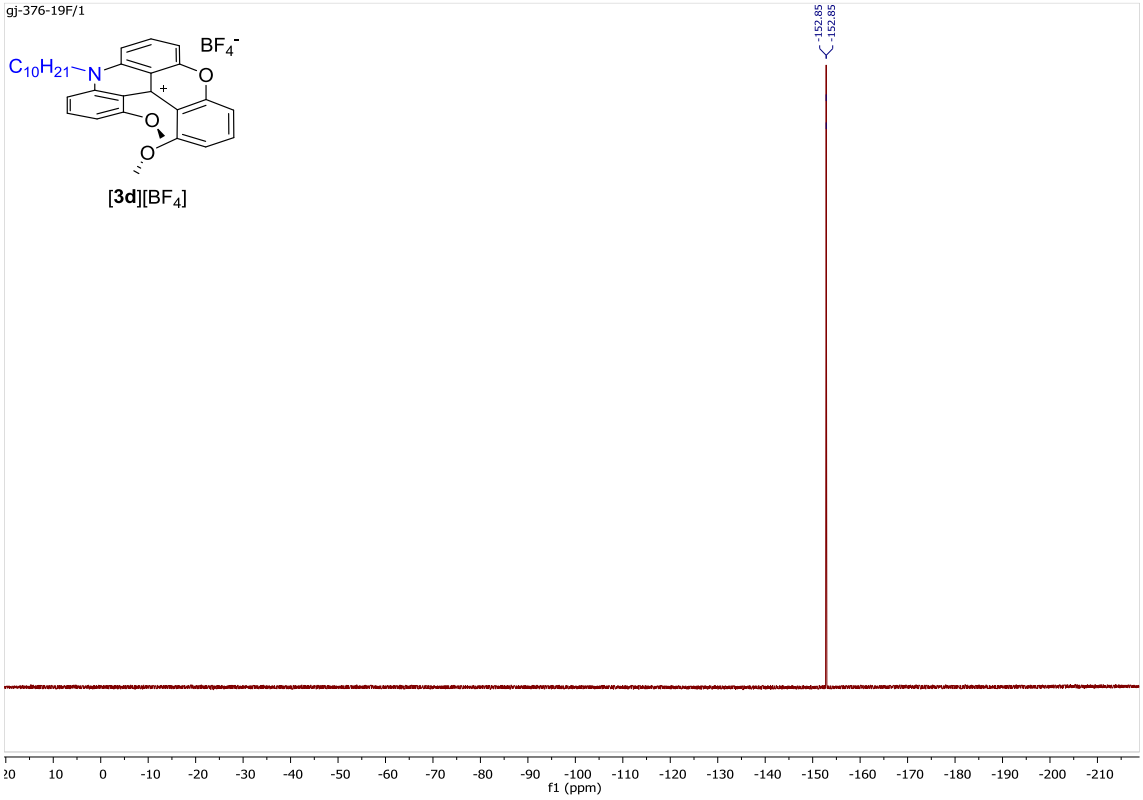
^{1}H NMR



^{13}C NMR

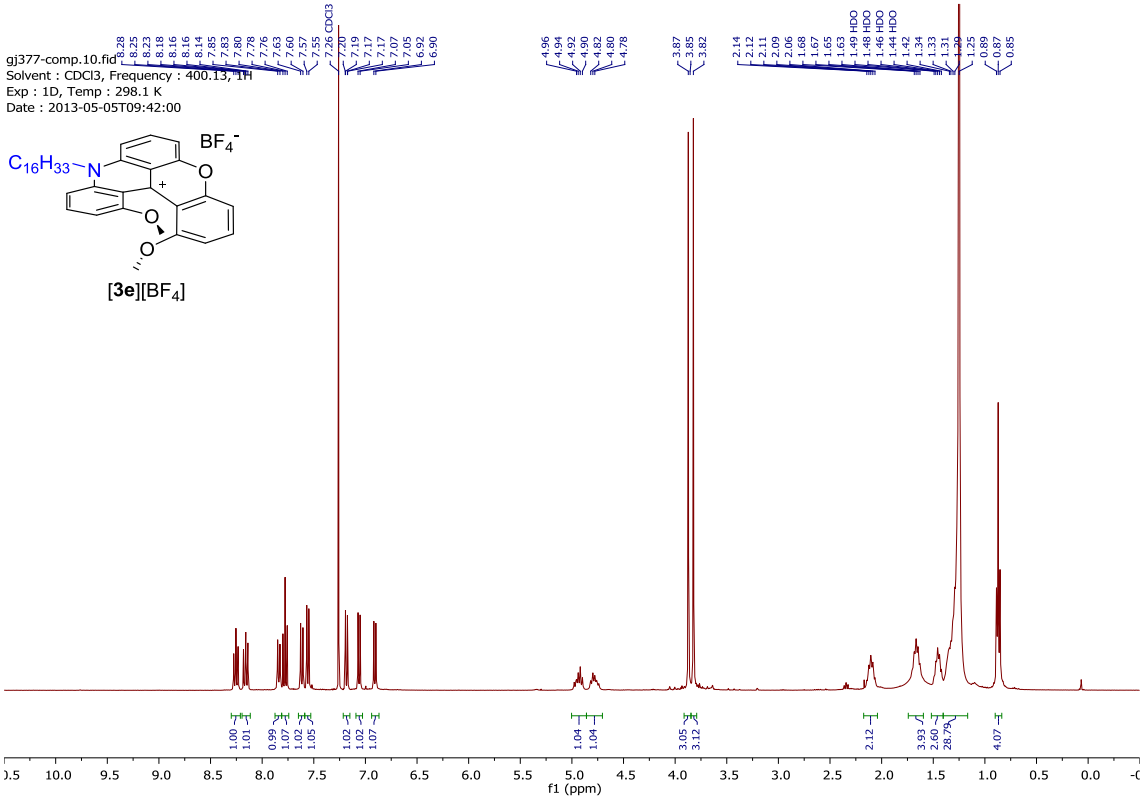


^{19}F NMR

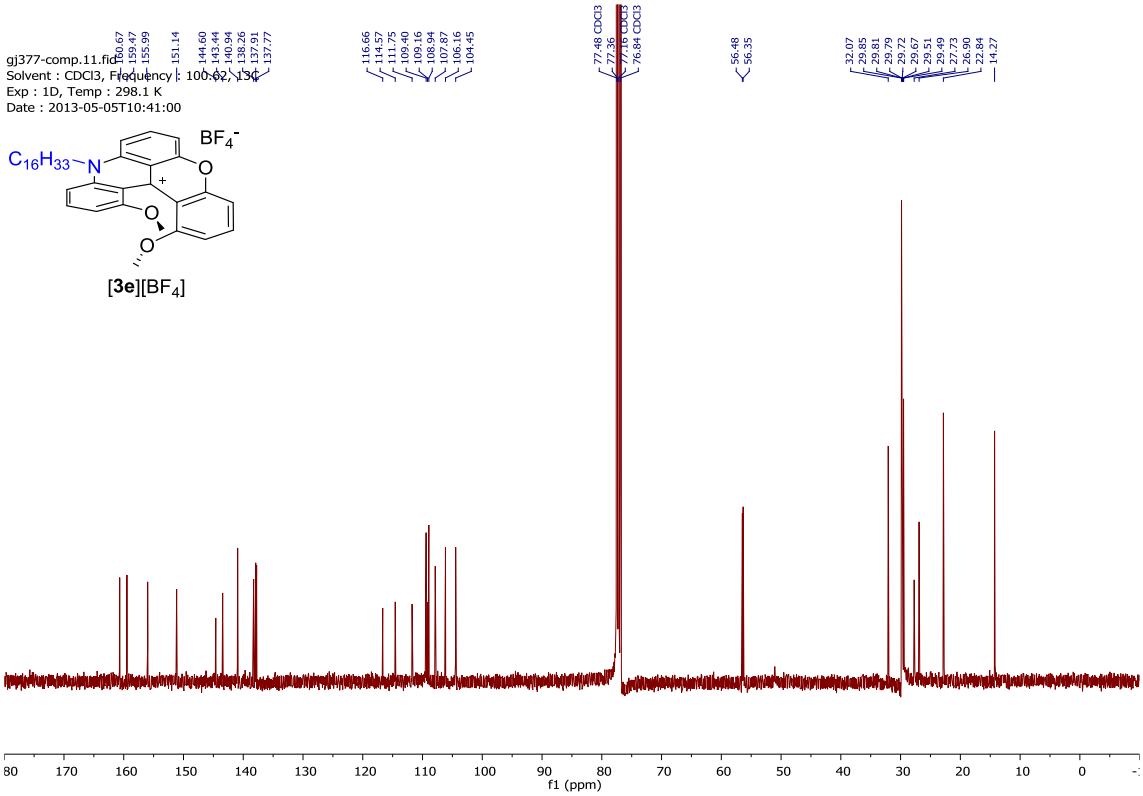


9-hexadecyl-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3e][BF_4]

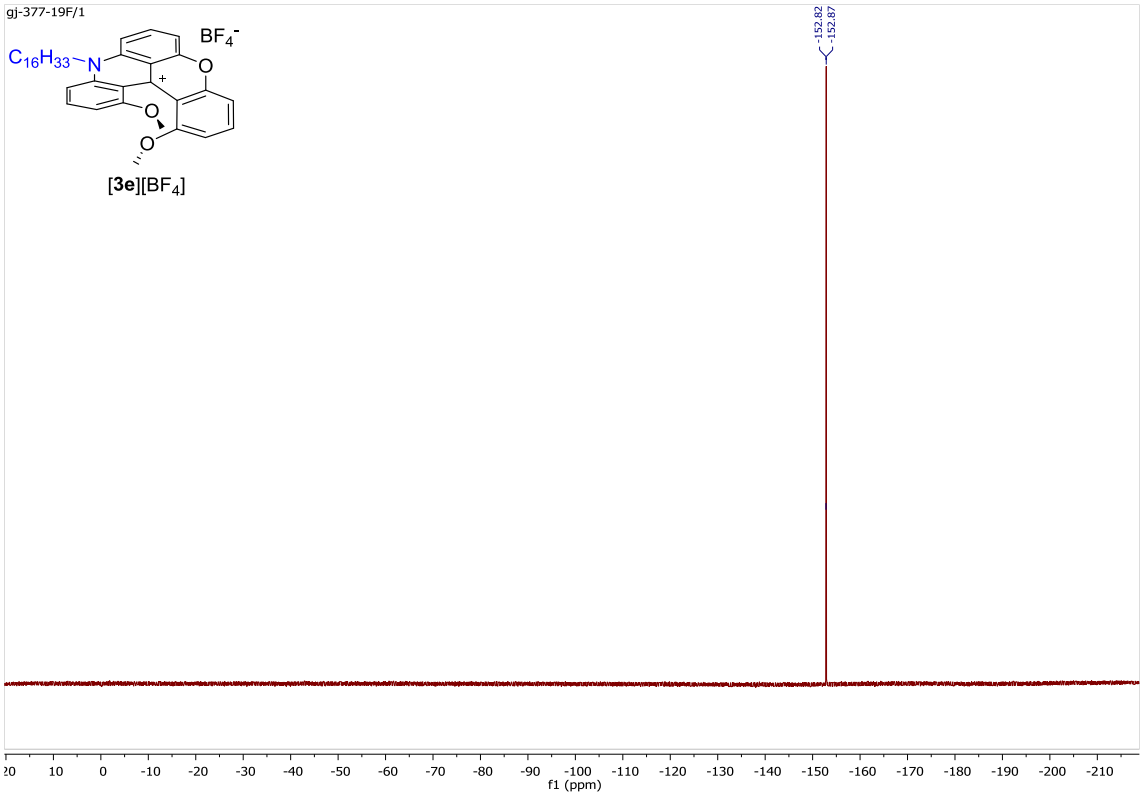
^{1}H NMR



^{13}C NMR

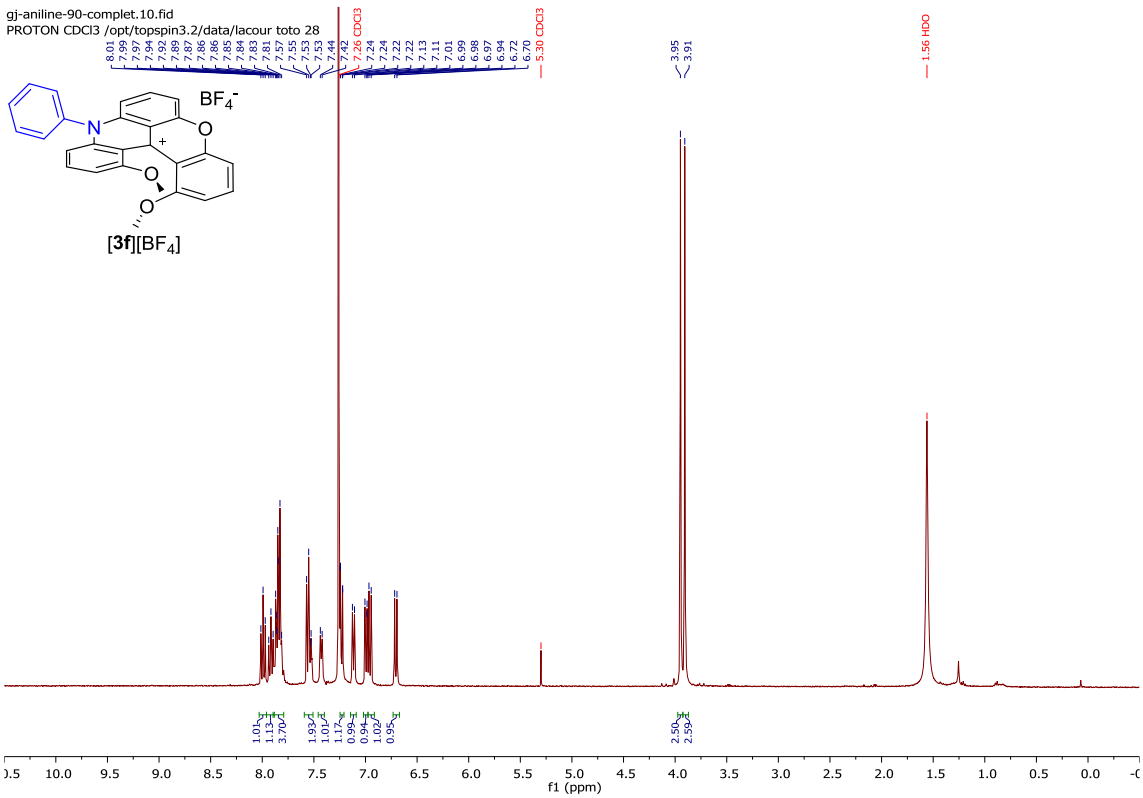


^{19}F NMR

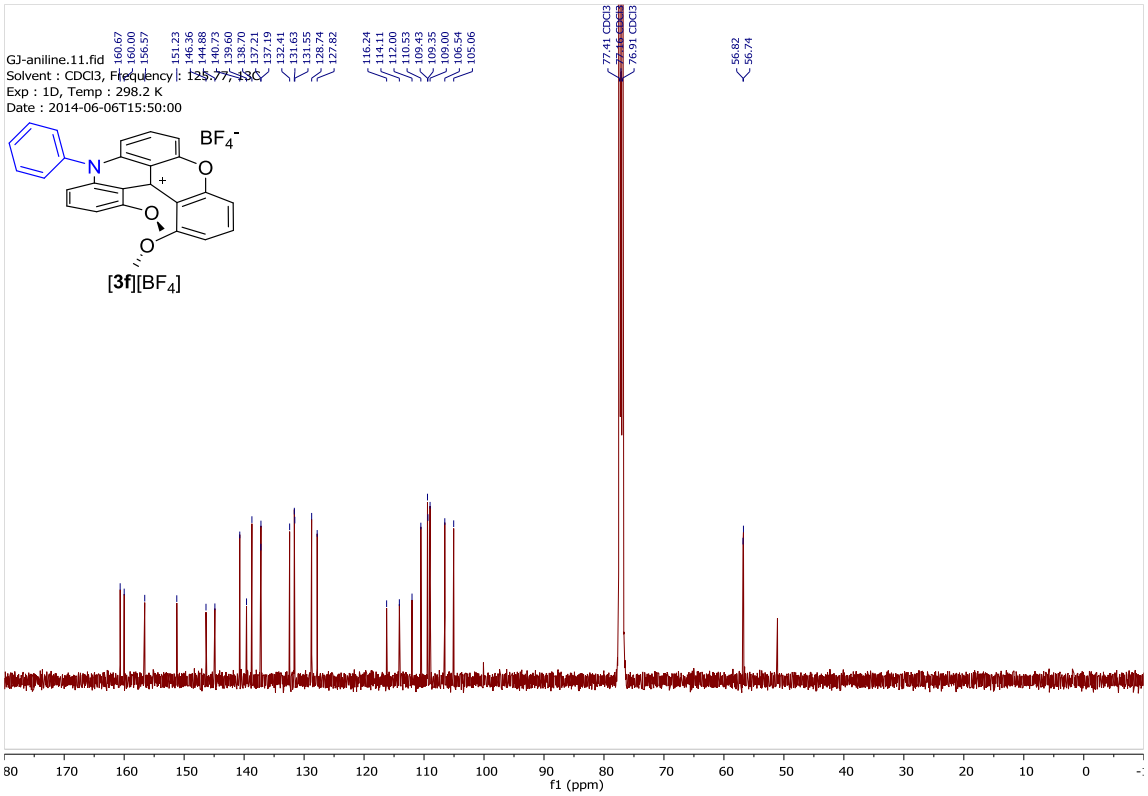


1,13-dimethoxy-9-phenylchromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3f][BF_4]

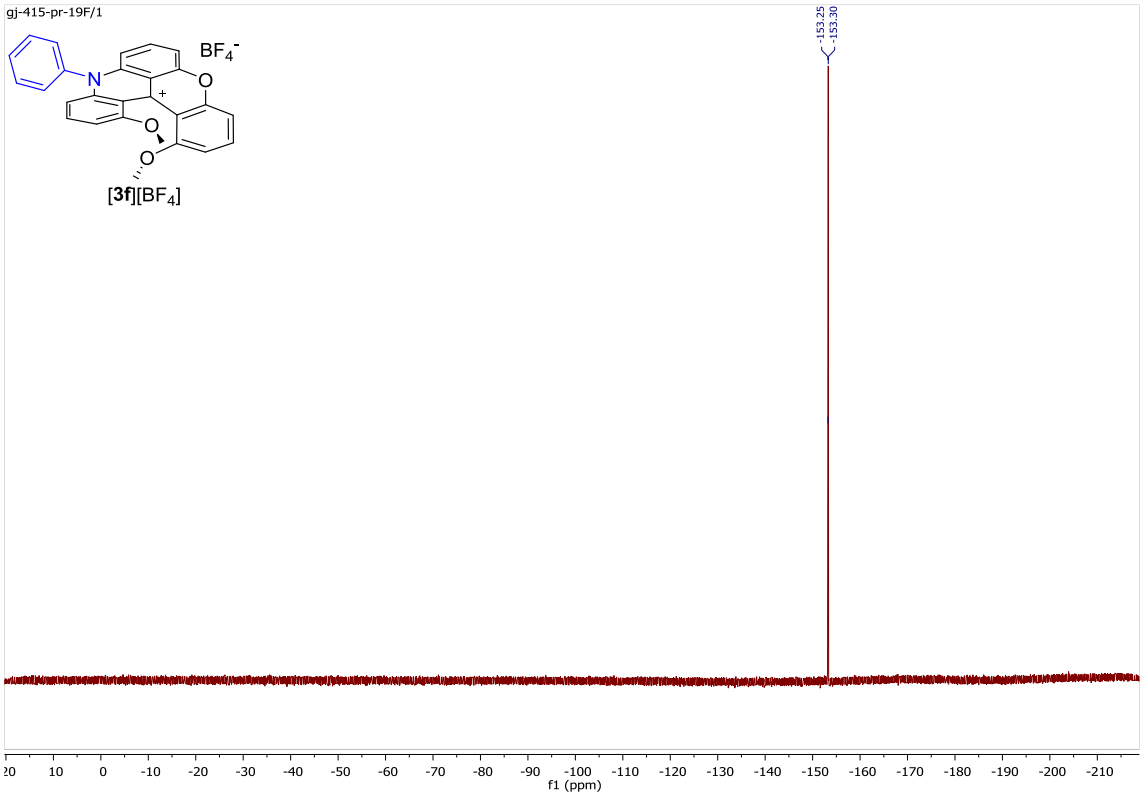
^{1}H NMR



^{13}C NMR

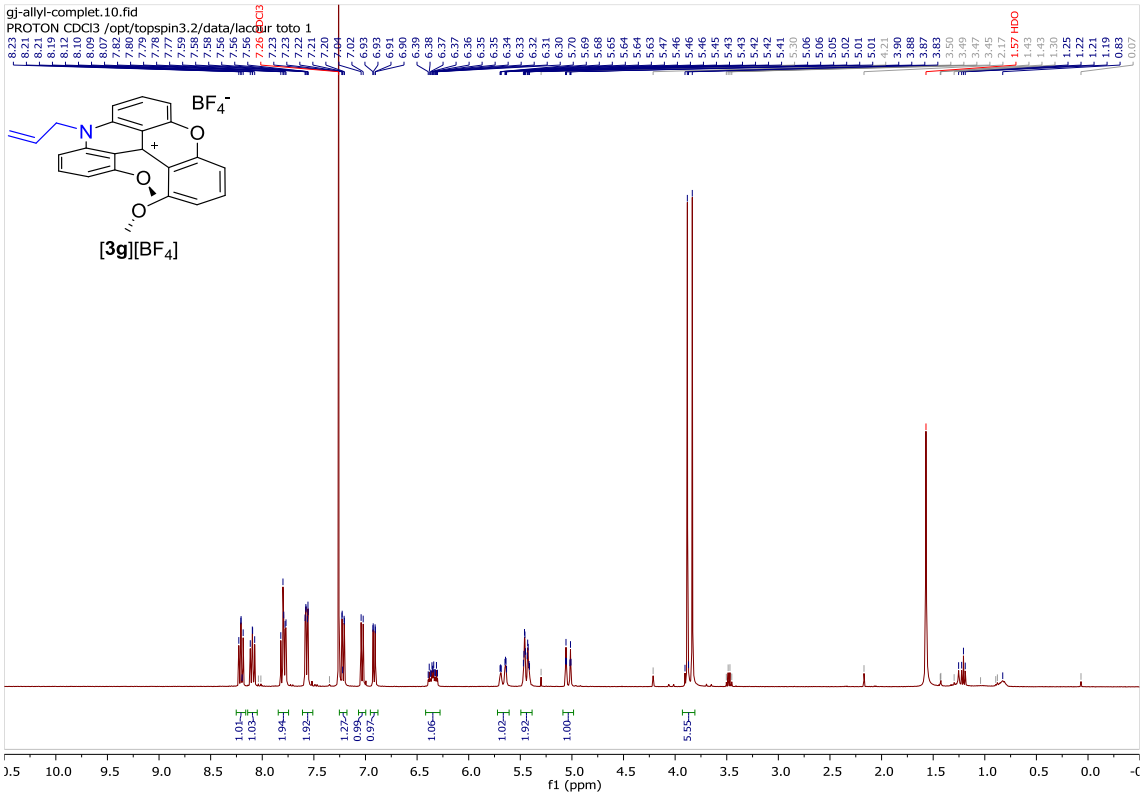


^{19}F NMR

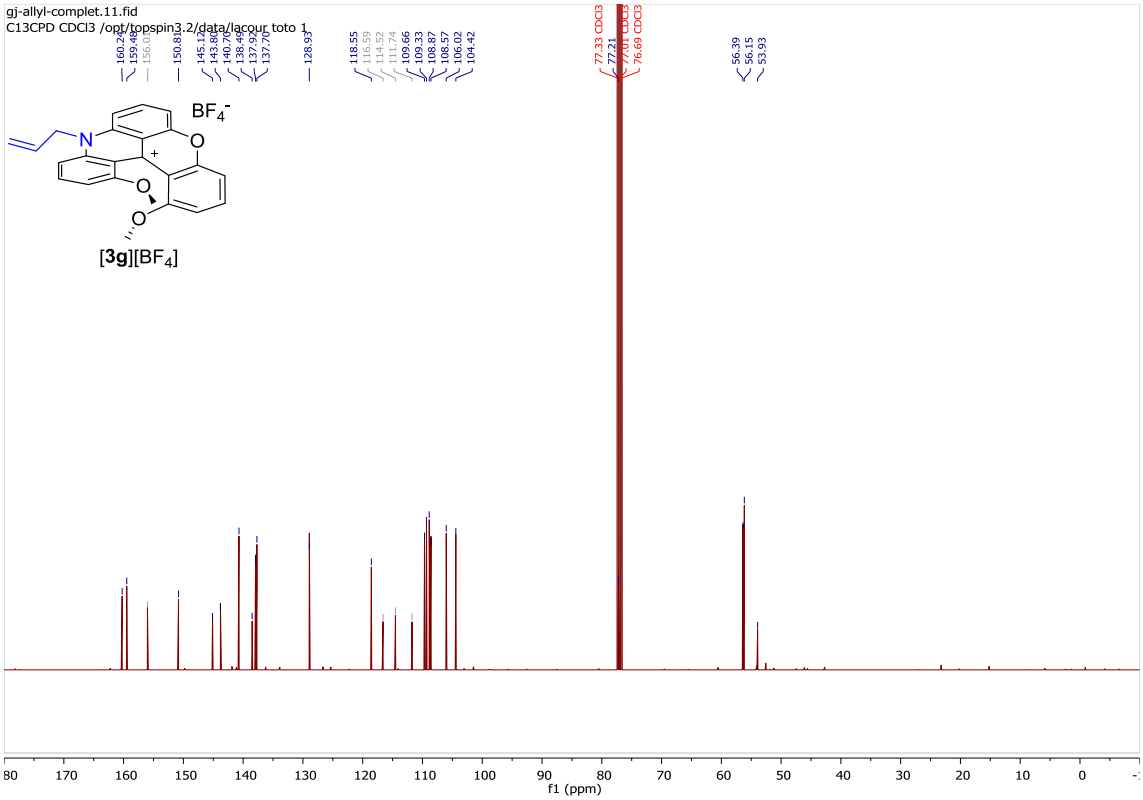


9-allyl-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3g][BF_4]

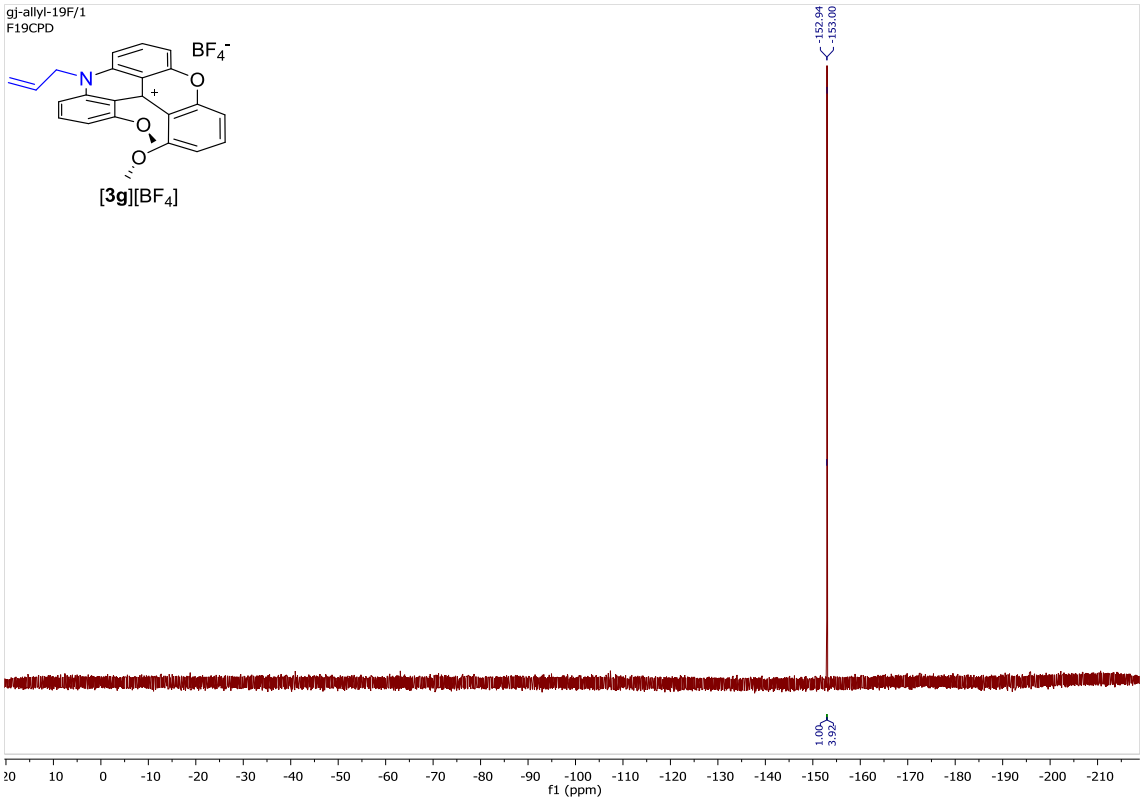
^{1}H NMR



^{13}C NMR

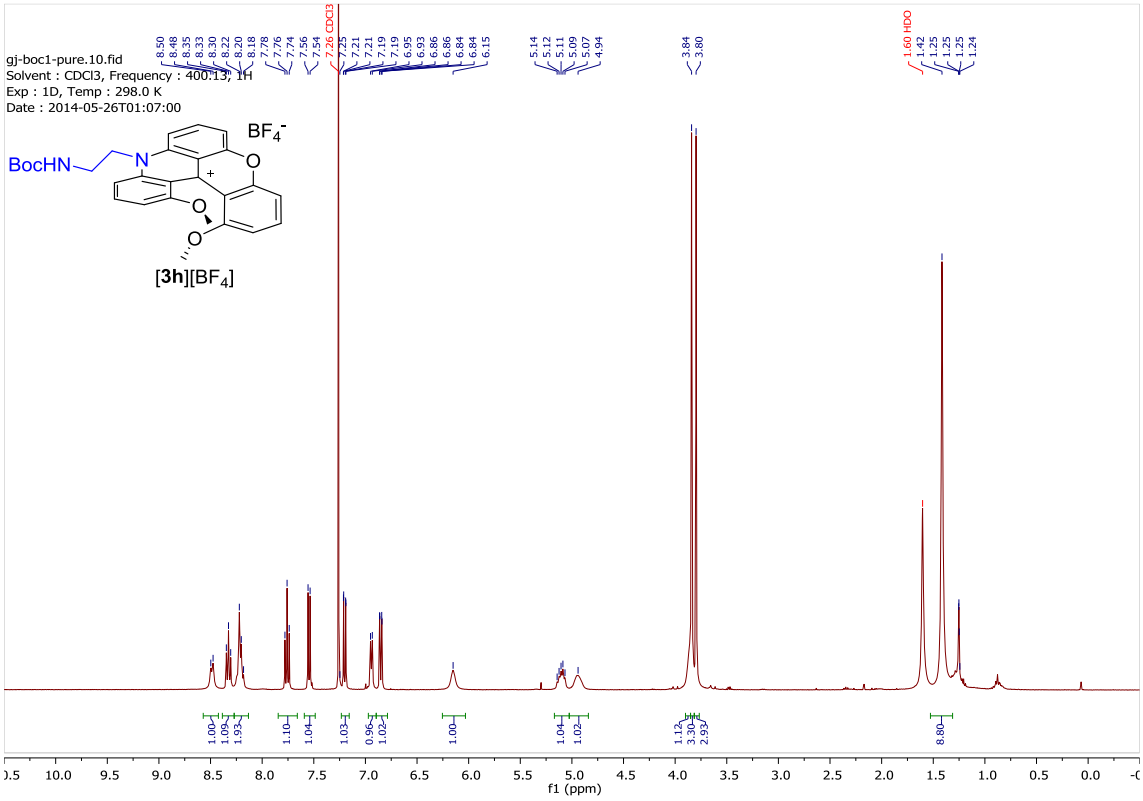


^{19}F NMR

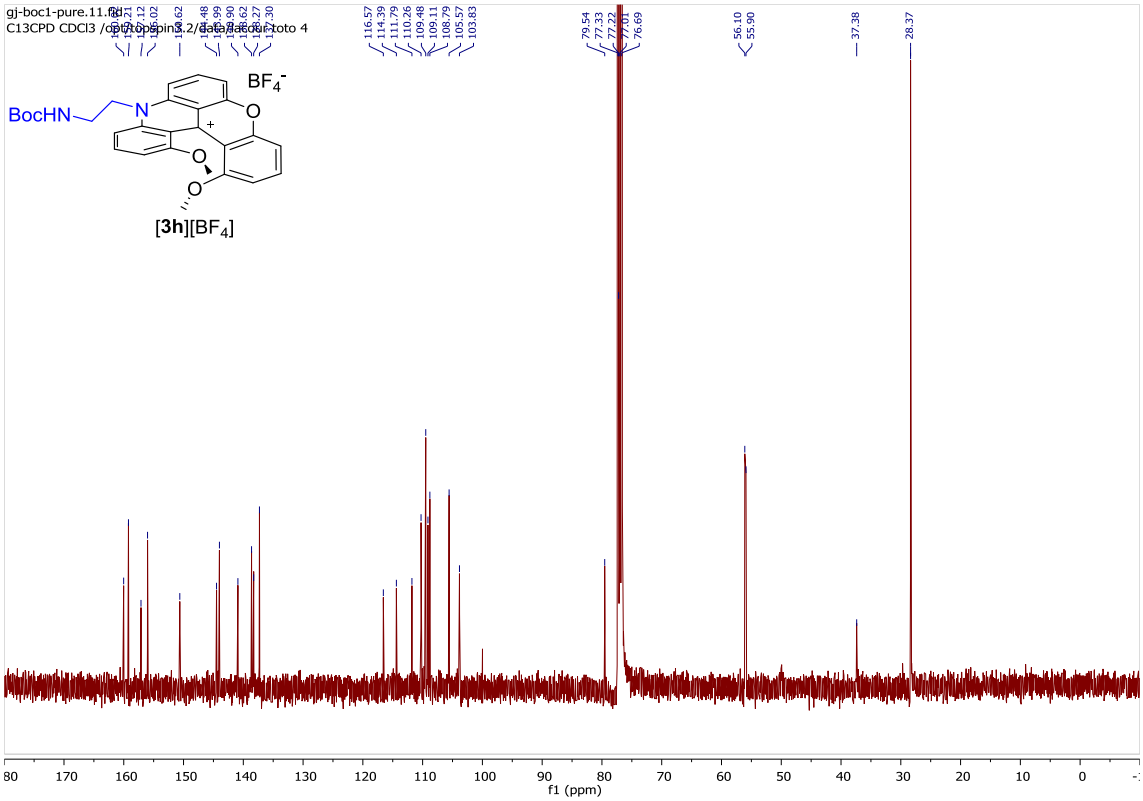


9-N-Boc-ethyleneamin-1,13-dimethoxychromeno[2,3,4-kl]acridin-13b(9H)-ylium tetrafluoroborate [3h][BF$_4$]

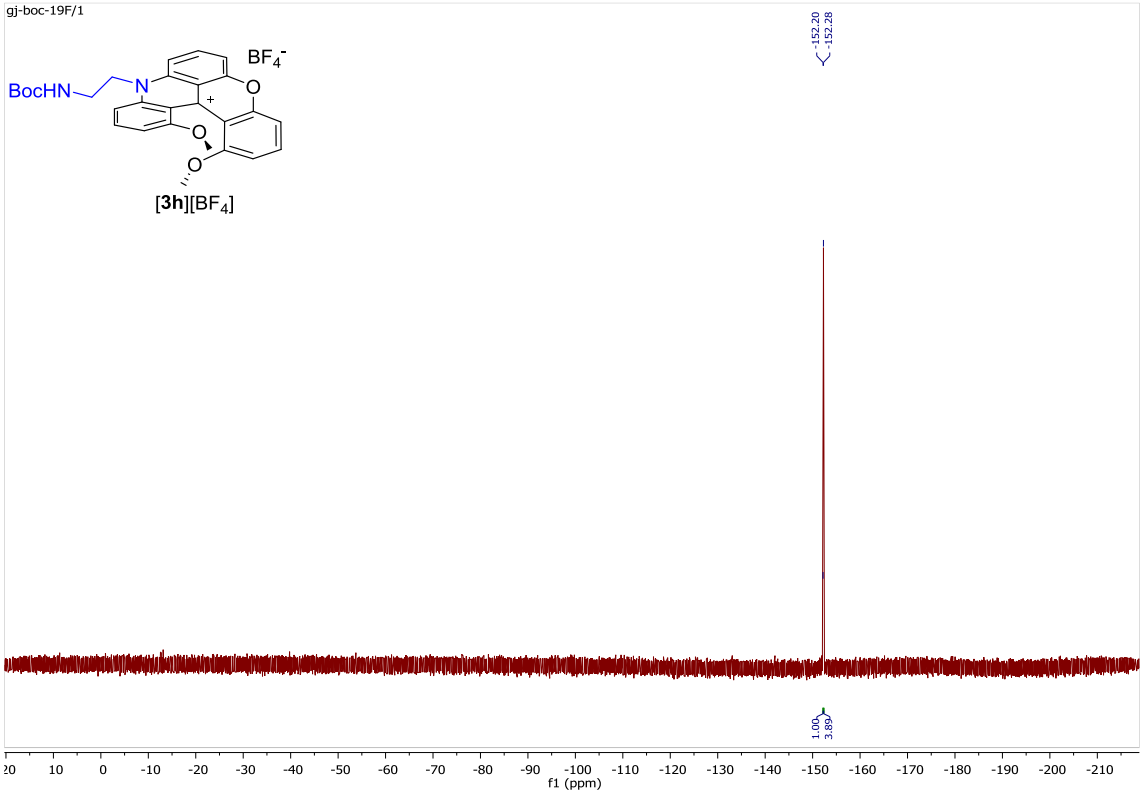
^{1}H NMR



^{13}C NMR

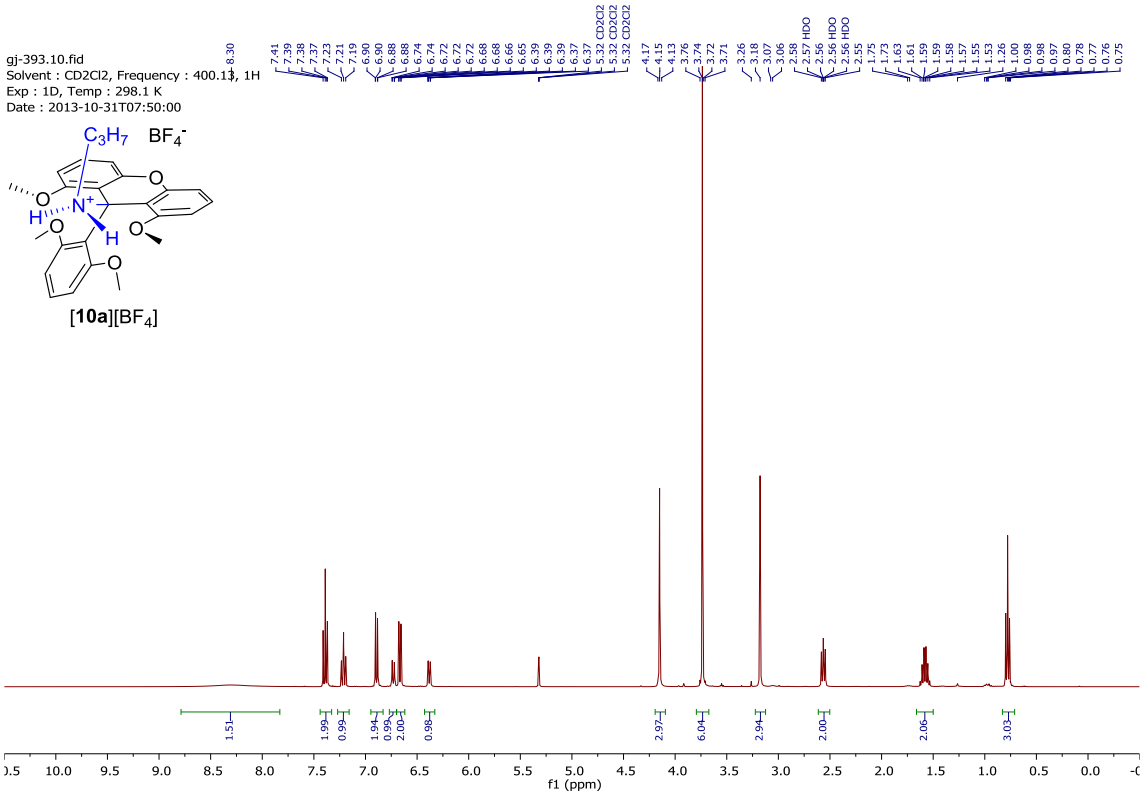


^{19}F NMR

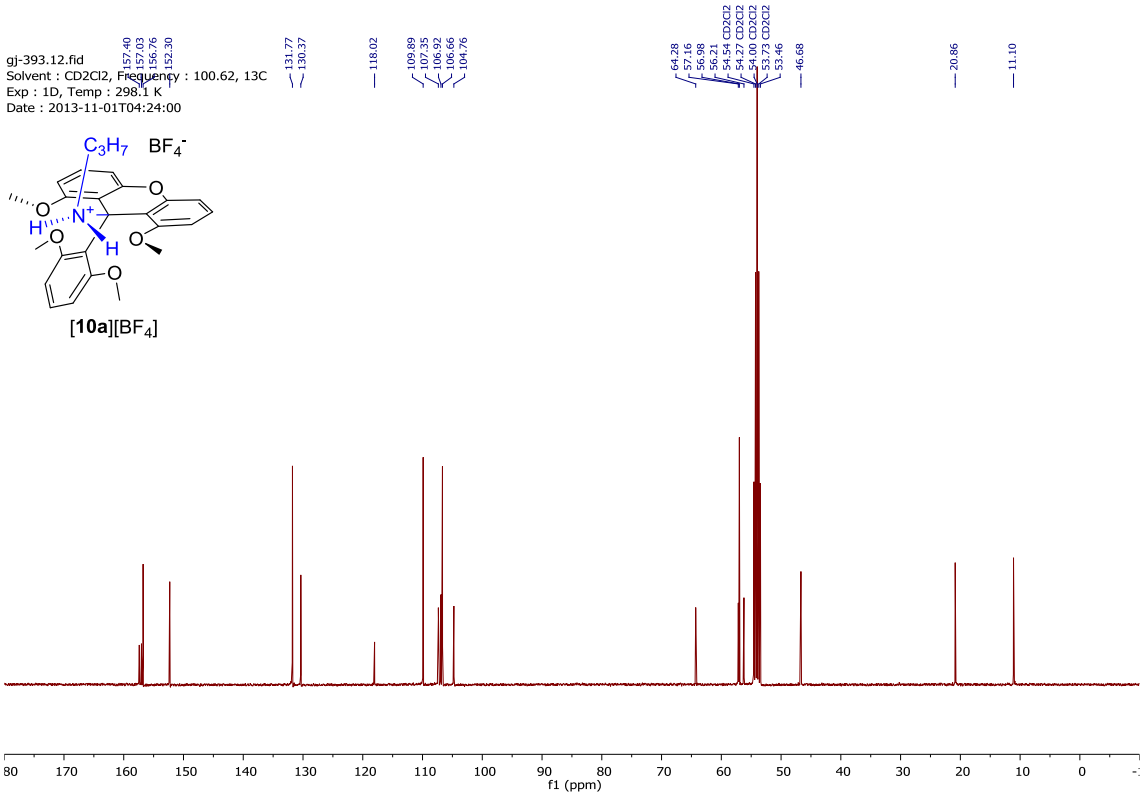


9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-N-propyl-9H-xanthen-9-aminium tetrafluoroborate [10a][BF_4]

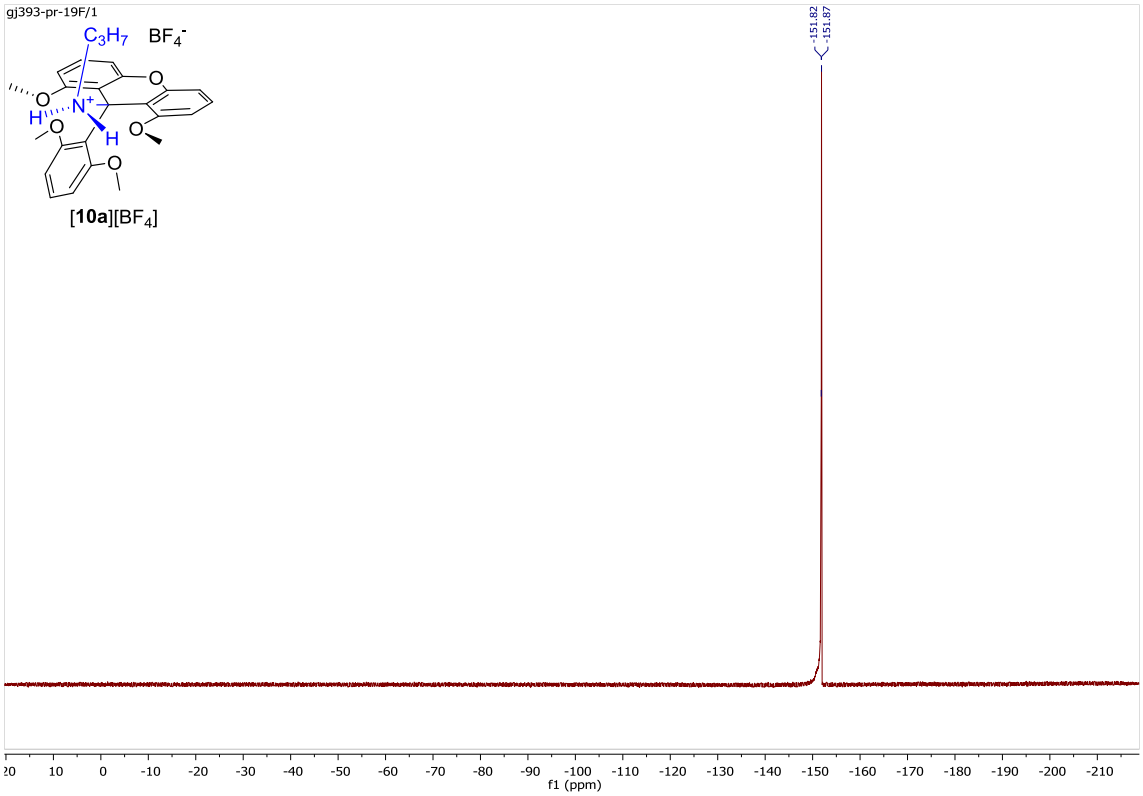
^{1}H NMR



^{13}C NMR

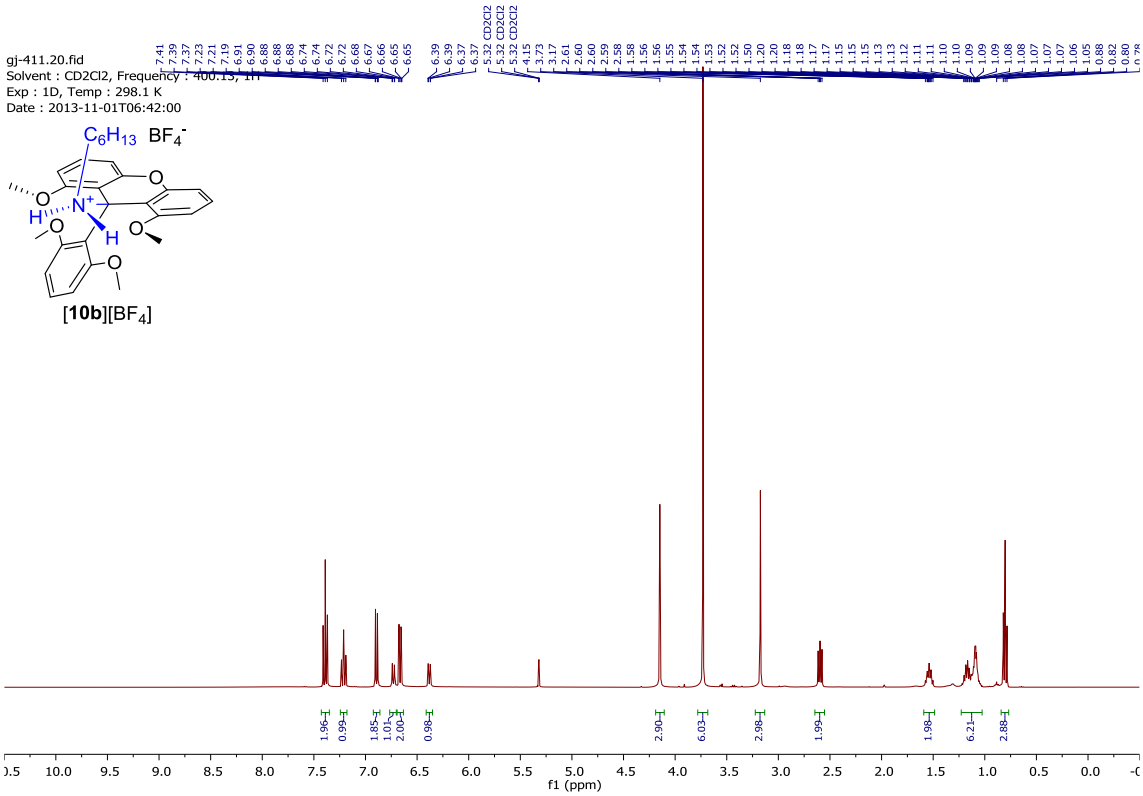


^{19}F NMR

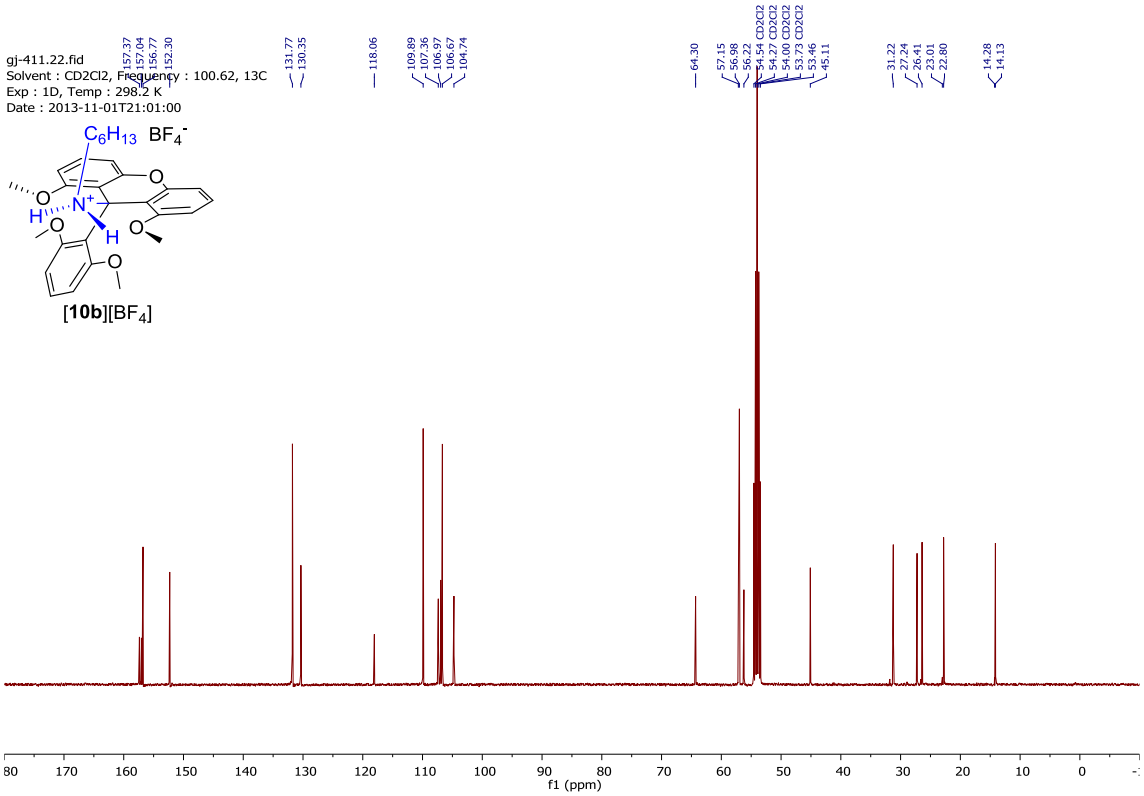


9-(2,6-dimethoxyphenyl)-N-hexyl-1,8-dimethoxy-9H-xanthen-9-aminium tetrafluoroborate [10b][BF$_4$]

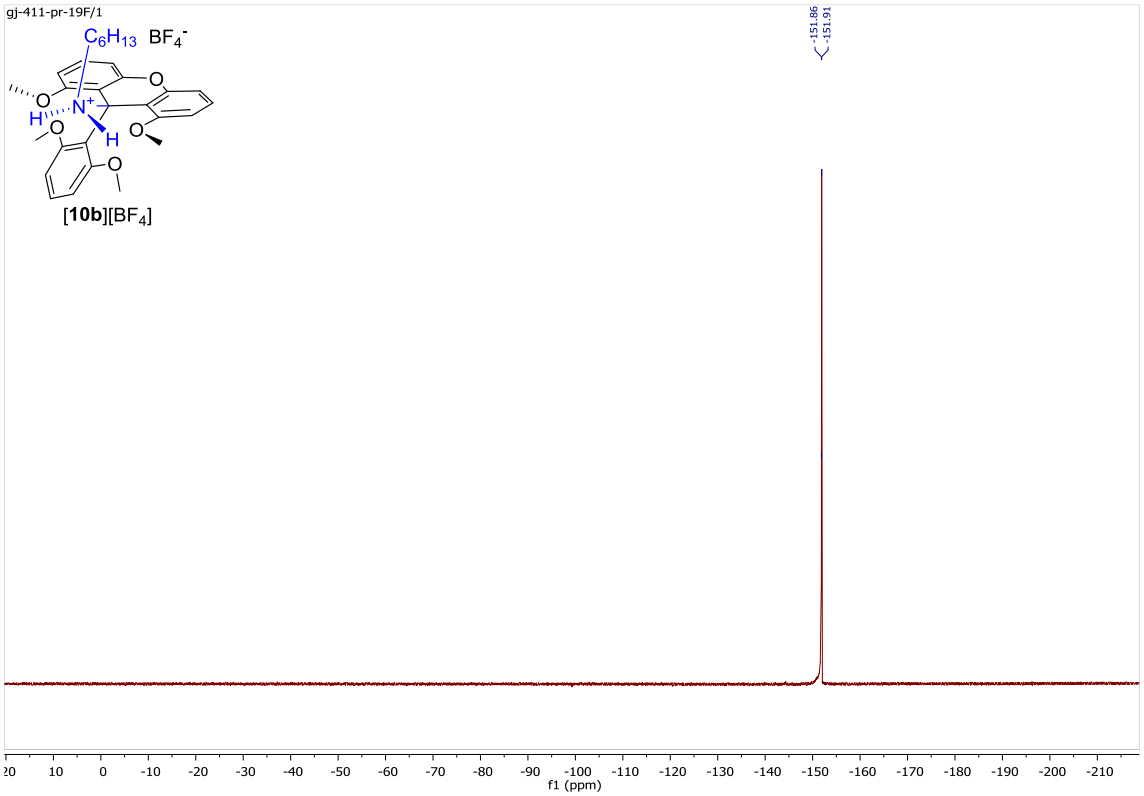
^{1}H NMR



^{13}C NMR

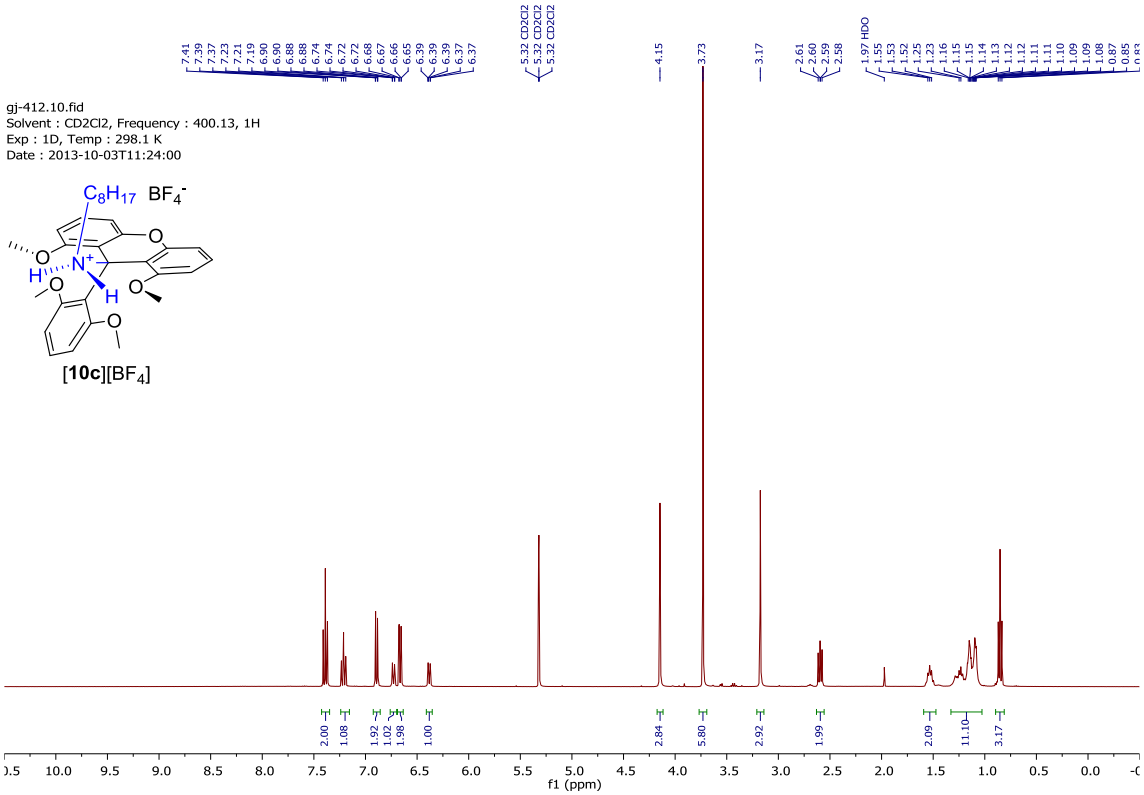


^{19}F NMR

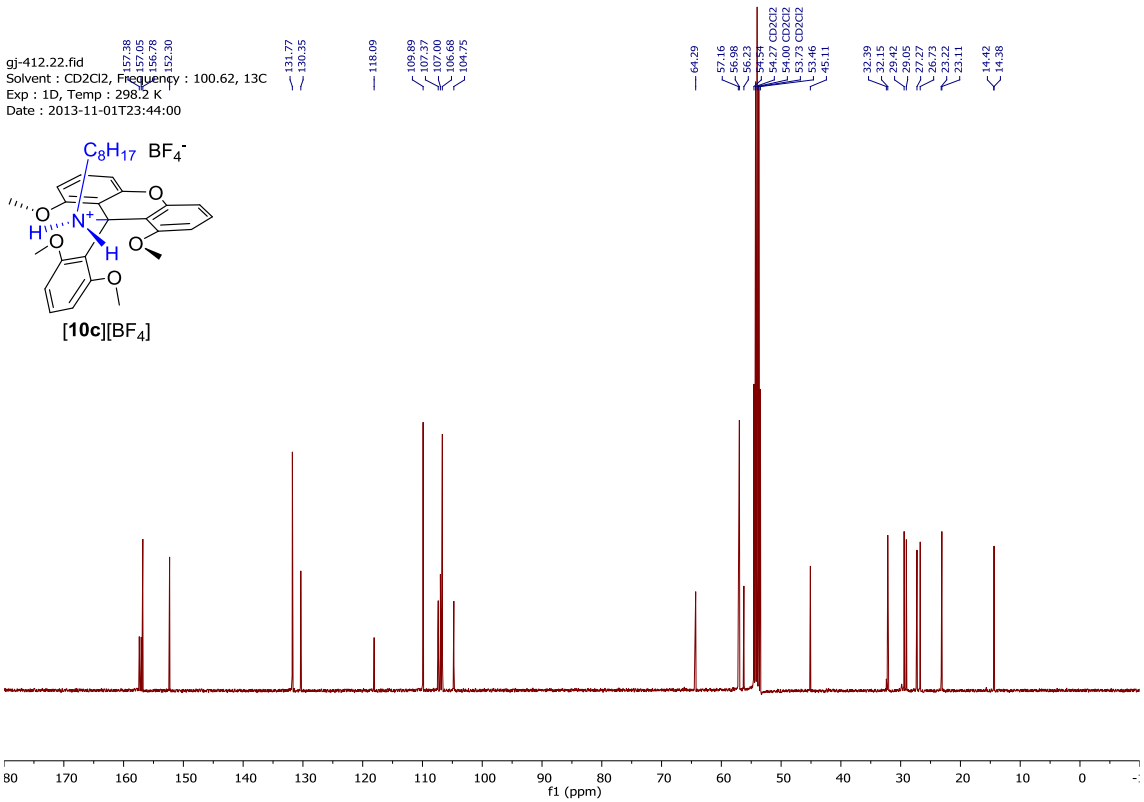


9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-N-octyl-9H-xanthen-9-aminium tetrafluoroborate [10c][BF_4]

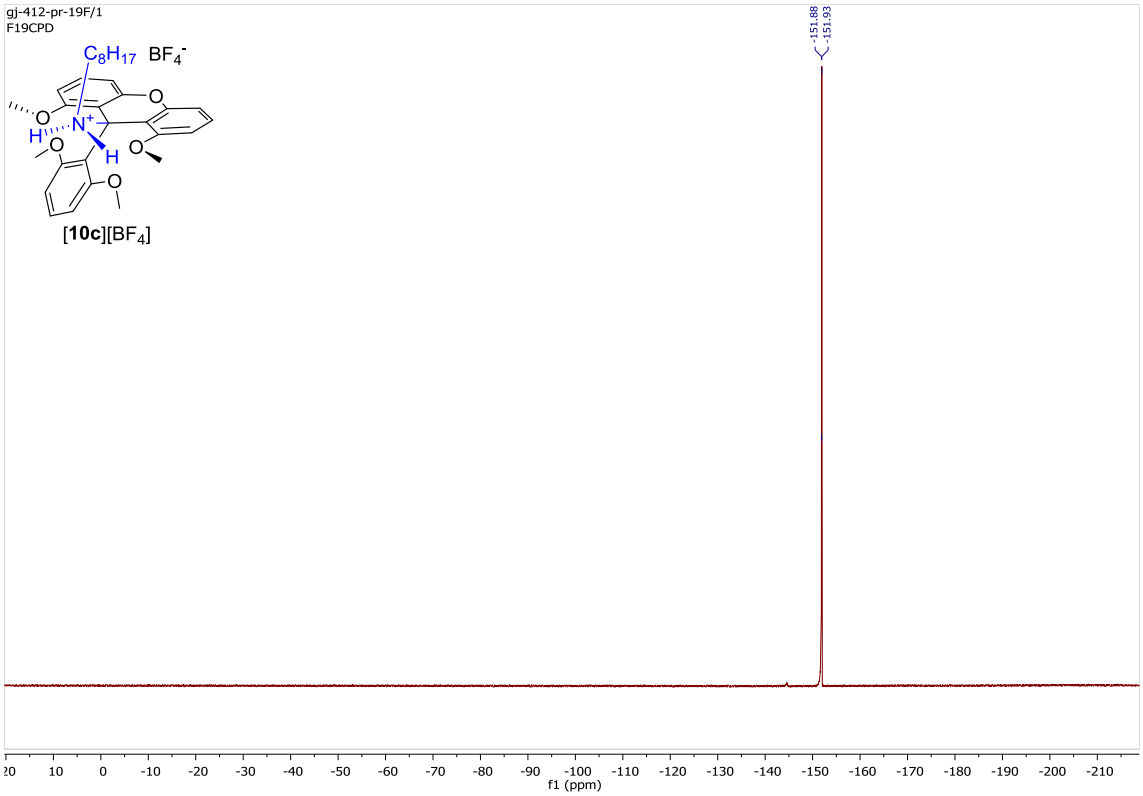
^{1}H NMR



^{13}C NMR

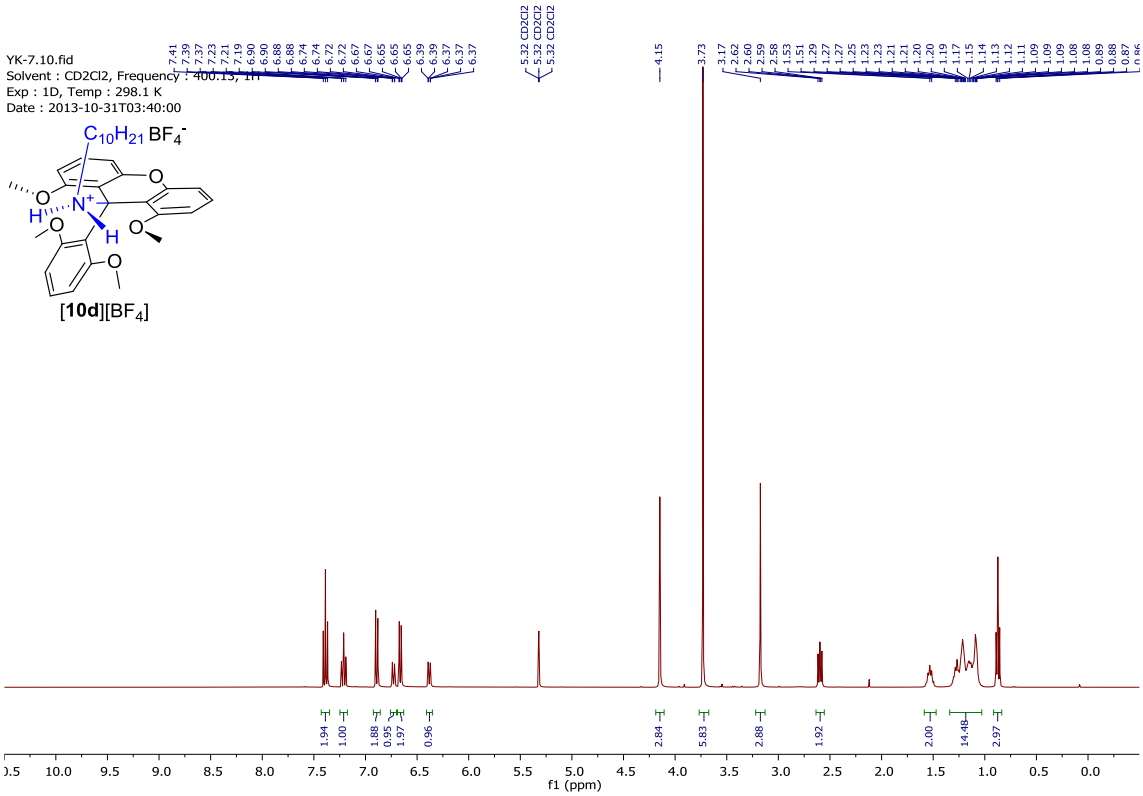


^{19}F NMR

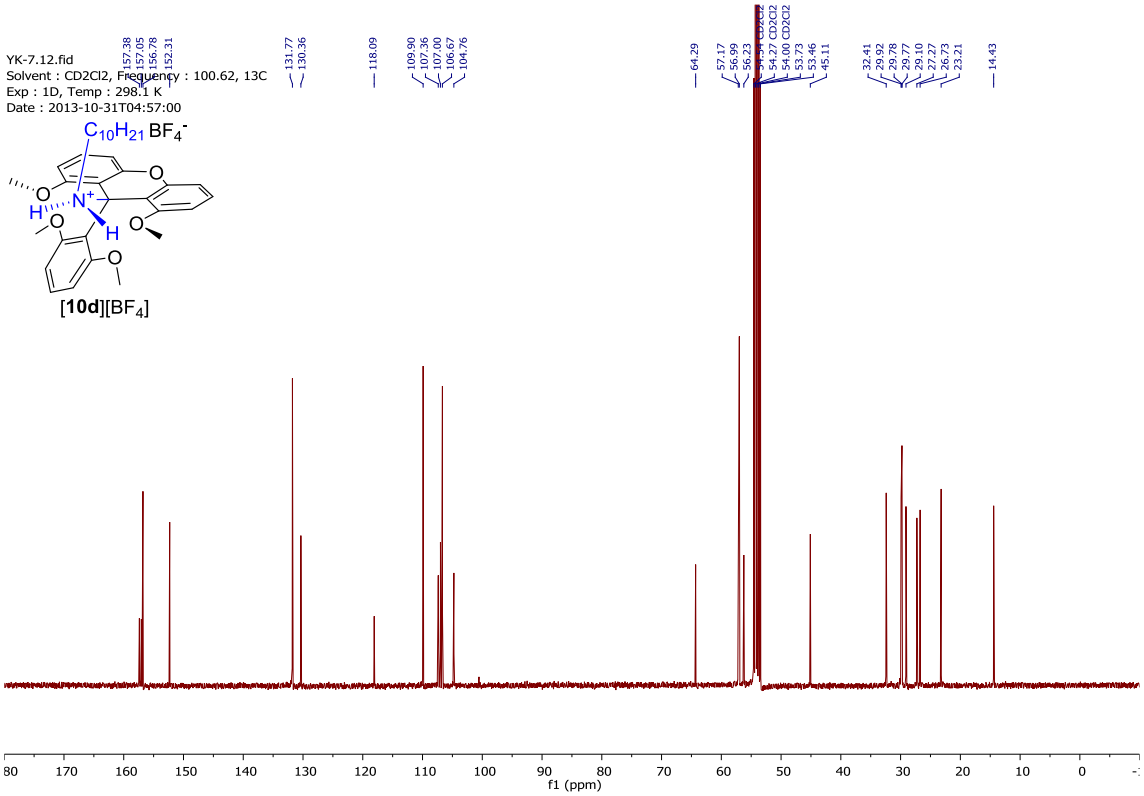


N-decyl-9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-9H-xanthen-9-aminium tetrafluoroborate [10d][BF$_4$]

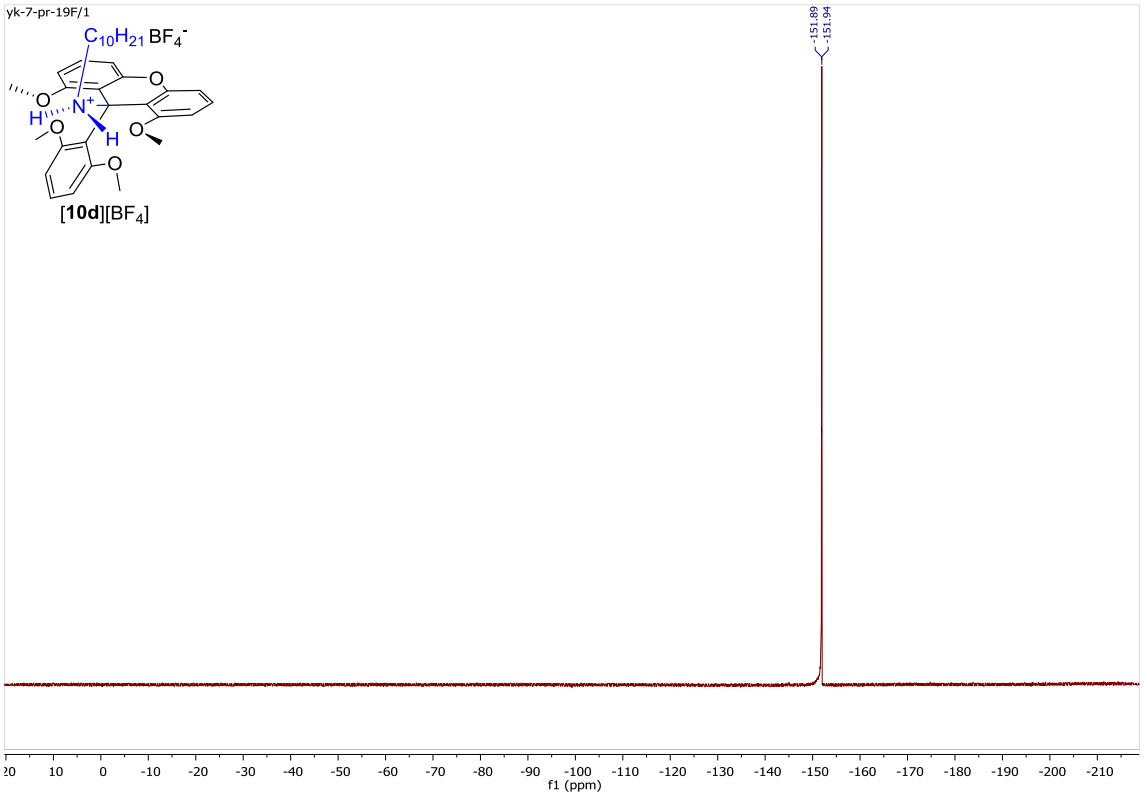
^{1}H NMR



^{13}C NMR

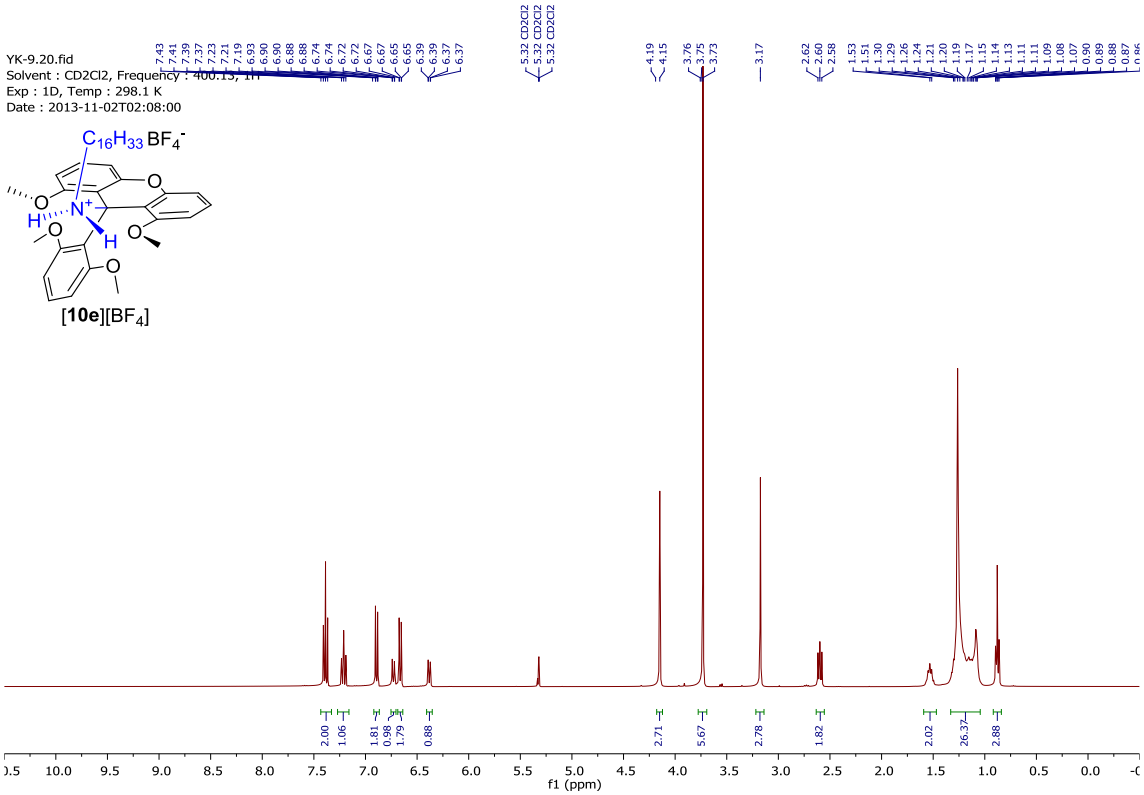


^{19}F NMR

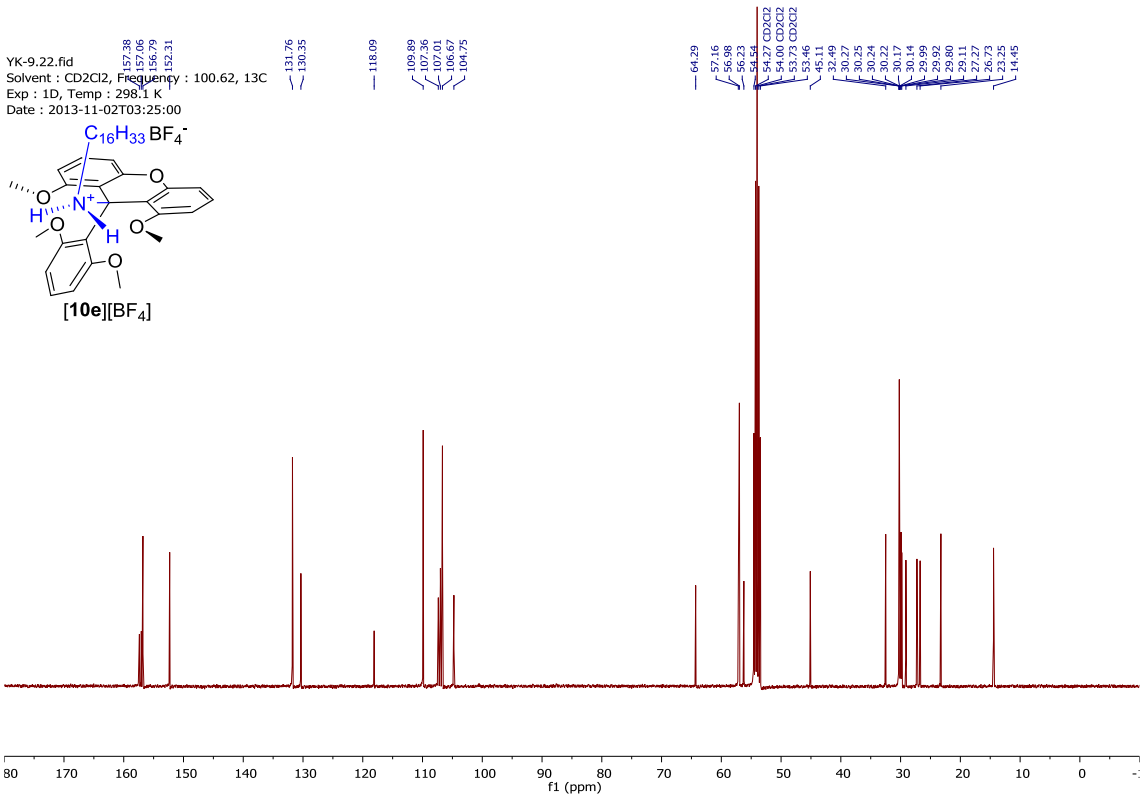


9-(2,6-dimethoxyphenyl)-N-hexadecyl-1,8-dimethoxy-9H-xanthen-9-aminium tetrafluoroborate [10e][BF_4]

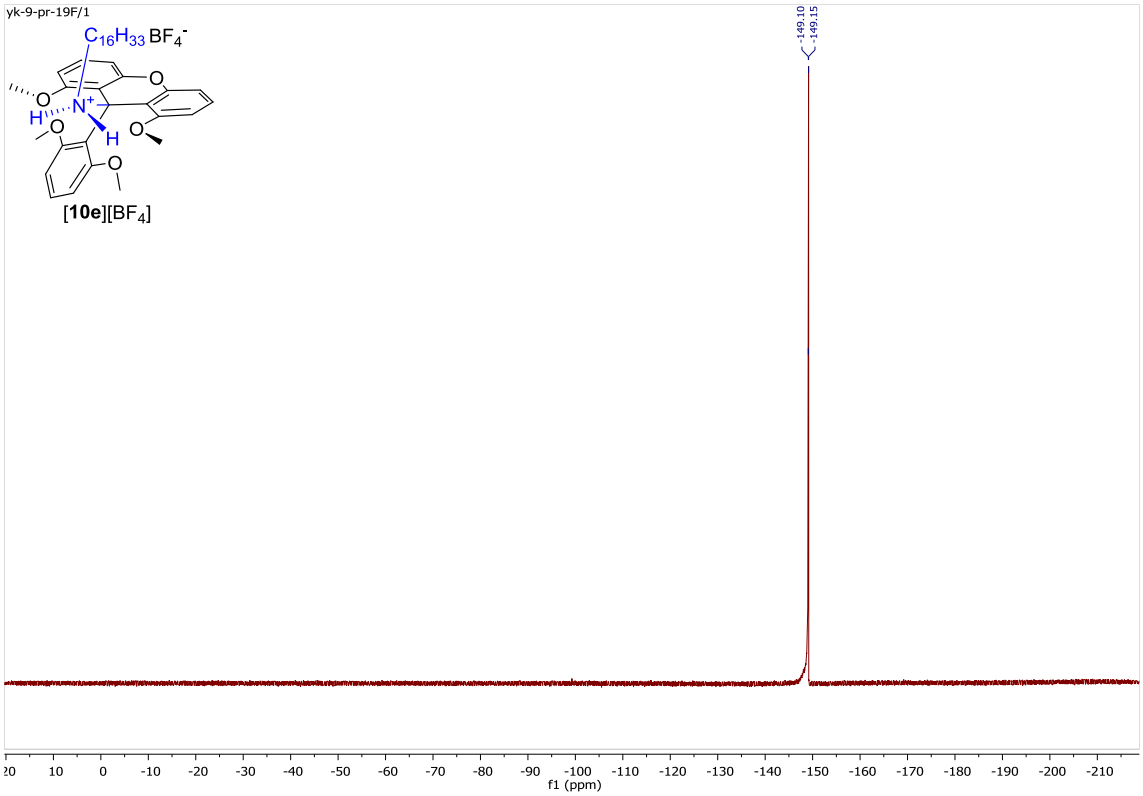
^{1}H NMR



^{13}C NMR



^{19}F NMR



UV-Vis and emission spectrum of [3a][BF_4] as an example for derivatives 3

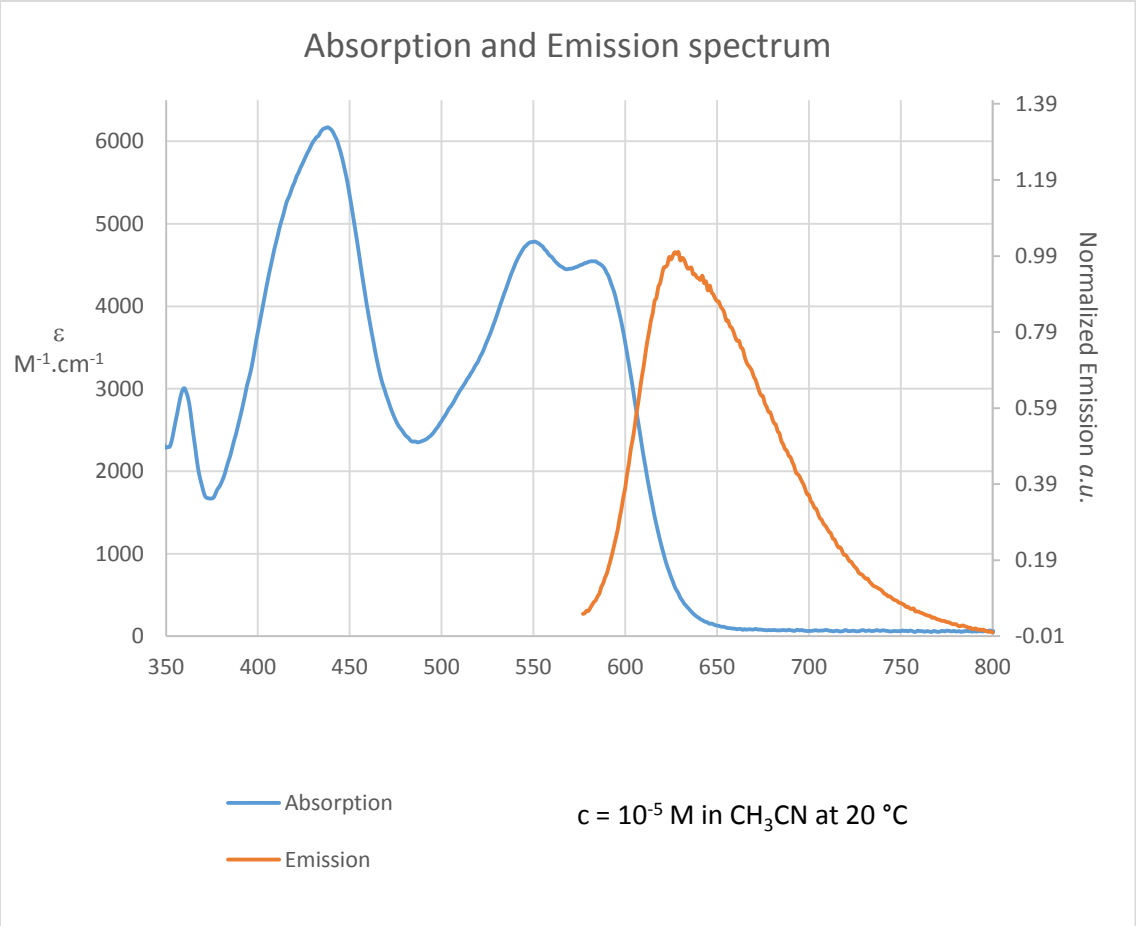


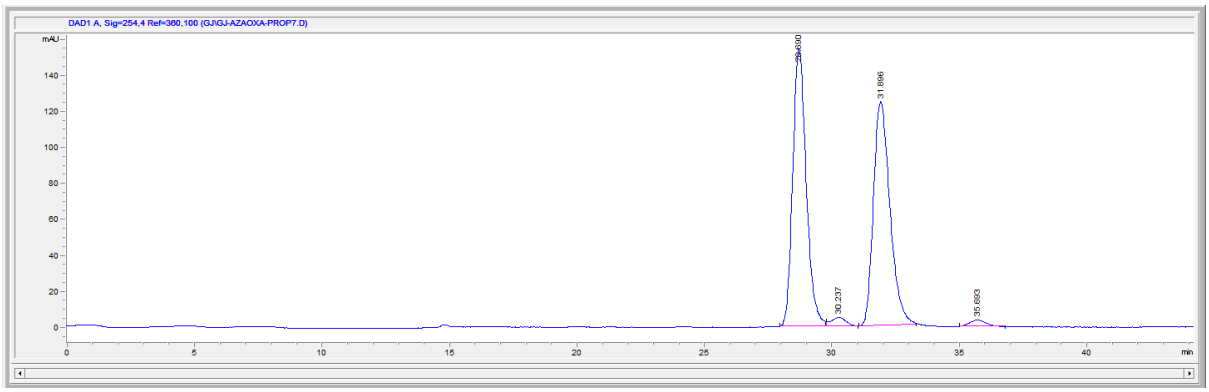
Figure S1: UV-Vis absorption spectra [**3a**][BF_4] (blue line) and Emission spectra (orange line). Solution in CH_3CN (20 °C, 10^{-5} M).

Resolution, ECD, Racemization barrier determination and Absolute configuration assignment

Resolution

Racemic **9a** (25 mg, *d.r.* 35:1) was separated into single enantiomers by repeated HPLC separations on a thermostated CHIRALPAK® IC column (1 x 25 cm, 20 °C, *n*-Hexane:*i*-PrOH 99:1, 1 ml/min flow rate, diode array detector, injections of the racemate in 100 µl of the eluent). The two major fractions (containing the predominant diastereomers) were separated to afford, after evaporation of the solvents and trituration with diethyl ether (–)-**9a** (8.5 mg, >99% ee, d.r. > 99:1) and (+)-**9a** (8.6 mg, >99% ee, d.r. > 99:1) as white amorphous solids.

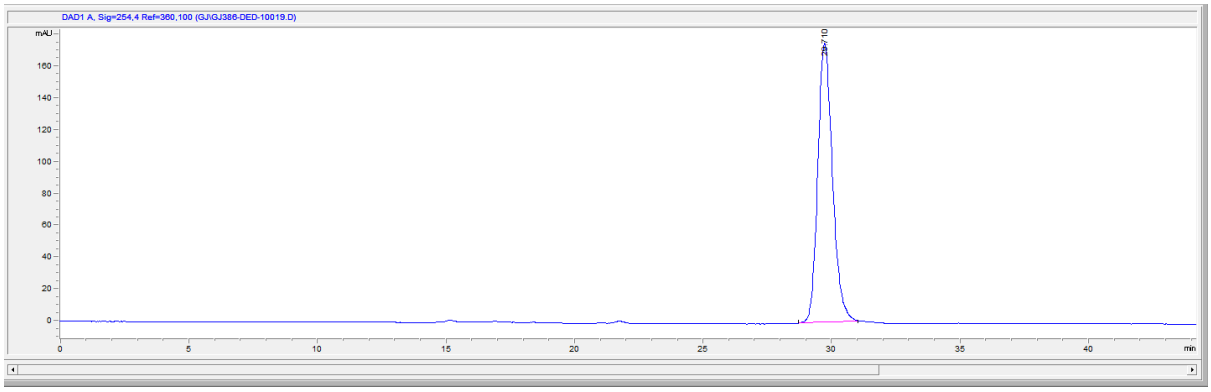
Racemic mixture (*d.r.* 35:1)



#	Time	Area	Height	Width	Area%	Symmetry
1	28.69	5683.4	154.3	0.5618	48.904	0.786
2	30.237	189.8	5	0.4656	1.633	0.94
3	31.896	5589.2	124.4	0.6901	48.094	0.719
4	35.693	159.2	3.6	0.5299	1.370	0.93

First eluted fraction:

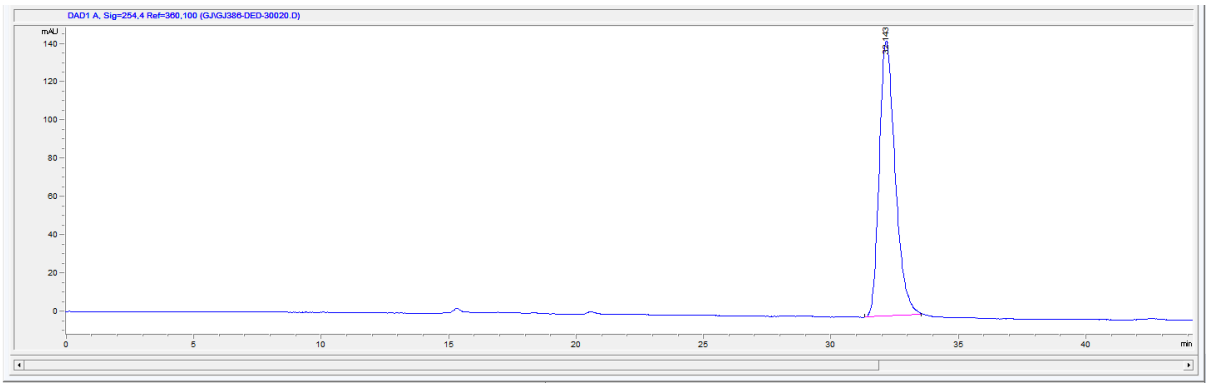
(–)-**9a**: $[\alpha]_{365}$ – 7080 (c 10^{-4} M, acetonitrile), retention time 28.69 min.



#	Time	Area	Height	Width	Area%	Symmetry
1	29.71	6984.7	175.6	0.61	100.000	0.799

Third eluted fraction:

(+)-**9a**: $[\alpha]_{365}$ + 7500 (c 10^{-4} M, acetonitrile), retention time 31.90 min.



#	Time	Area	Height	Width	Area%	Symmetry
1	32.143	6243.5	143.8	0.6584	100.000	0.709

ECD spectra of (–) and (+)-[3a][BF_4]

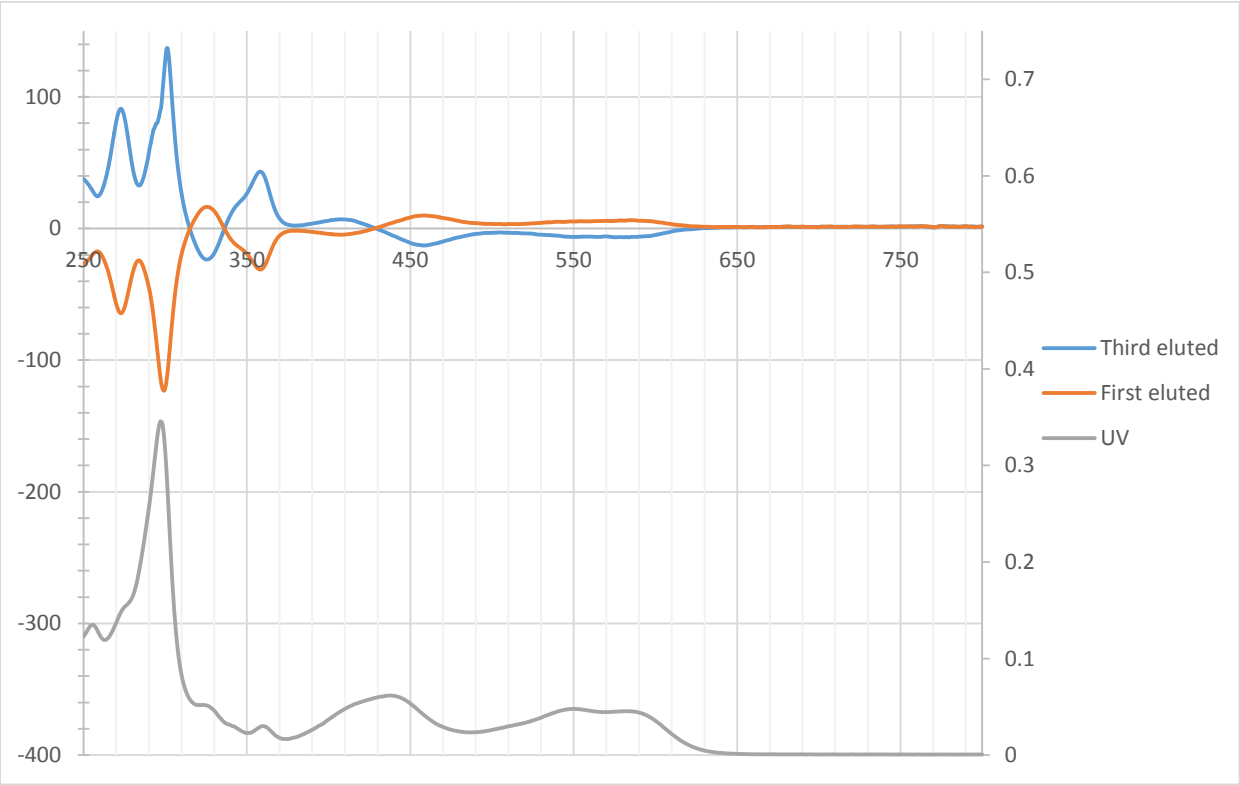


Figure S2: ECD spectra of (–)-[**3a**][BF_4] (orange solid line) and (+)-[**3a**][BF_4] (blue line) derived from (–)-**9a** and (+)-**9a** respectively. Solution in CH_3CN (20 °C, 10^{-4} M).

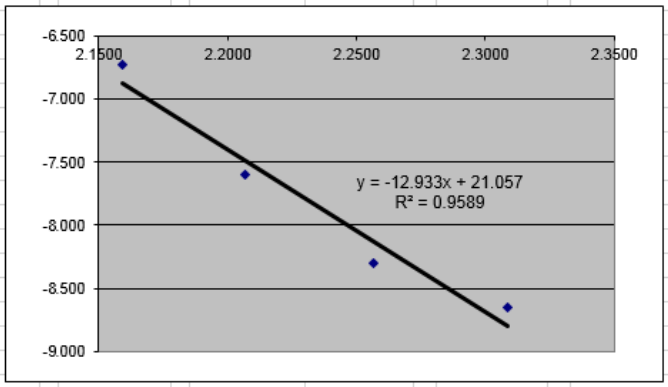
Racemization barrier determination

General procedure for the racemization of (+)-[(*P*)-3a][BF_4]

Circular dichroism “Time course” measurements were recorded at 160 °C, 170 °C, 180 °C and 190 °C during 1000 s with solutions in DMSO of (+)-[(*P*)-**3a**][BF_4] (410 nm, c 10^{-4} *M*). The kinetic constant at each of the temperature was calculated considering first order kinetics.

T [°C]	T [K]	1000/T	k	ln(k)	R-Square	DG		t1/2	
160	433.15	2.3087	1.754E-04	-8.648	0.362	138.6	kJ/mol	1.0977	h
170	443.15	2.2566	2.472E-04	-8.305	0.445	140.6	kJ/mol	0.7789	h
180	453.15	2.2068	4.997E-04	-7.601	0.667	141.2	kJ/mol	0.3853	h
190	463.15	2.1591	1.200E-03	-6.726	0.532	141.0	kJ/mol	0.1605	h

slope=	-12.93	±	1.23	- Ea/R			
intercept=	21.06	±	2.71	Ln(A)			
T	160		°C				
Ea	107.5	±	10.2	kJ/mol	25.7 ± 2.4	kcal/mol	
A	1.4E+09	±	1.8E+08				
ΔH# = Ea - RT	103.9	±	-9.8	kJ/mol	24.9 ± -2.4	kcal/mol	
ΔS# = R [ln(h*A/k*T)-1]	-81.3	±	-10.4	$J.K^{-1}.mol^{-1}$	-19.4 ± -2.5	$cal.K^{-1}.mol^{-1}$	
ΔG#	139.1	±	-5.3	kJ/mol	33.3 ± -1.3	kcal/mol	



VCD study

Calculations

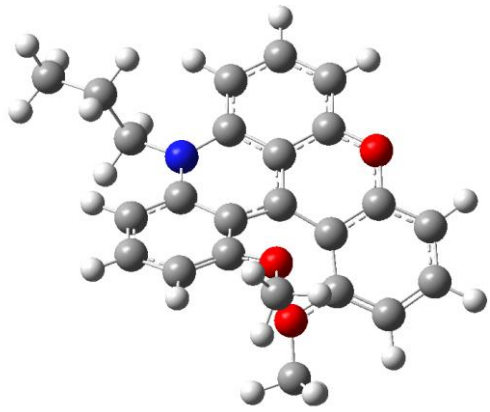
Calculations of several conformers were done at the DFT B3PW91 level using a 6-31G(d,p) basis set. Frequencies were scaled by 0.97. VCD spectra were constructed from calculated rotational strengths assuming Loretzian band shape with a half-width at half maximum of 5 cm^{-1}. All calculations were performed using Gaussian 09, Revision C.01.

Several conformers were located differing in the position of the isopropyl group. However, the conformation at this position hardly affects the IR and VCD spectra.

IR and VCD measurements

IR and vibrational circular dichroism (VCD) spectra were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (< 1800 cm-1) in front of the photoelastic modulator was used to enhance the signal/noise ratio. Spectra were recorded with a transmission cell equipped with CaF_2 windows and a 0.2 mm Teflon spacer. Solutions in CD_2Cl_2 at concentrations of 8 mg in 0.2 ml CD_2Cl_2 were measured. As the reference served the solvent measured under identical conditions. Samples were measured at a resolution of 4 cm^{-1} by averaging about 24’000 scans for both enantiomers and the solvent. Spectra are presented without further data processing.

Calculated spectra (top IR, bottom VCD) for the different conformers (*P* configuration)



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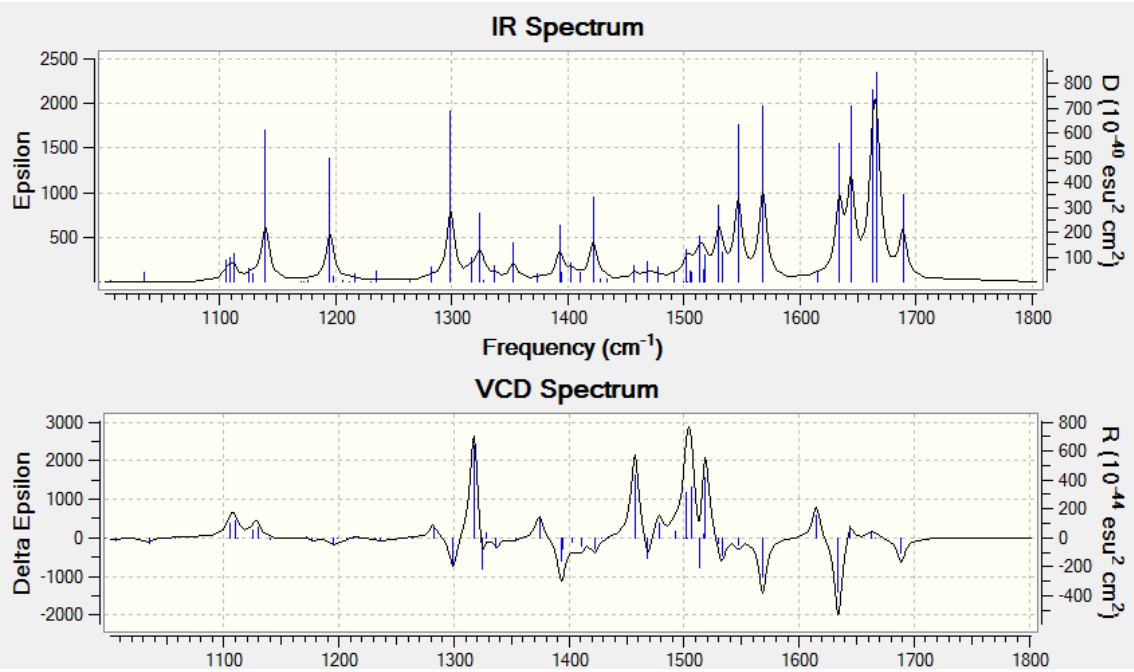
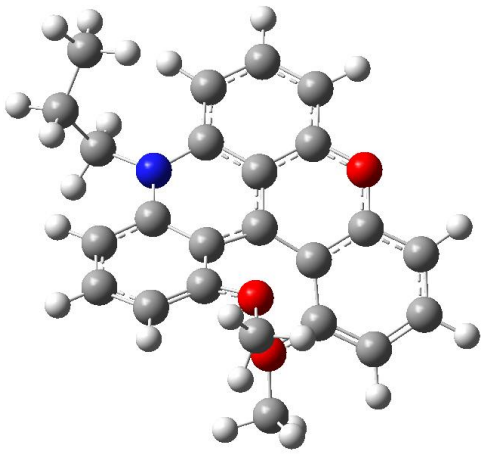
Imaginary Freq	0	
Dipole Moment	2.1208	Debye
Point Group		





Title Card Required		
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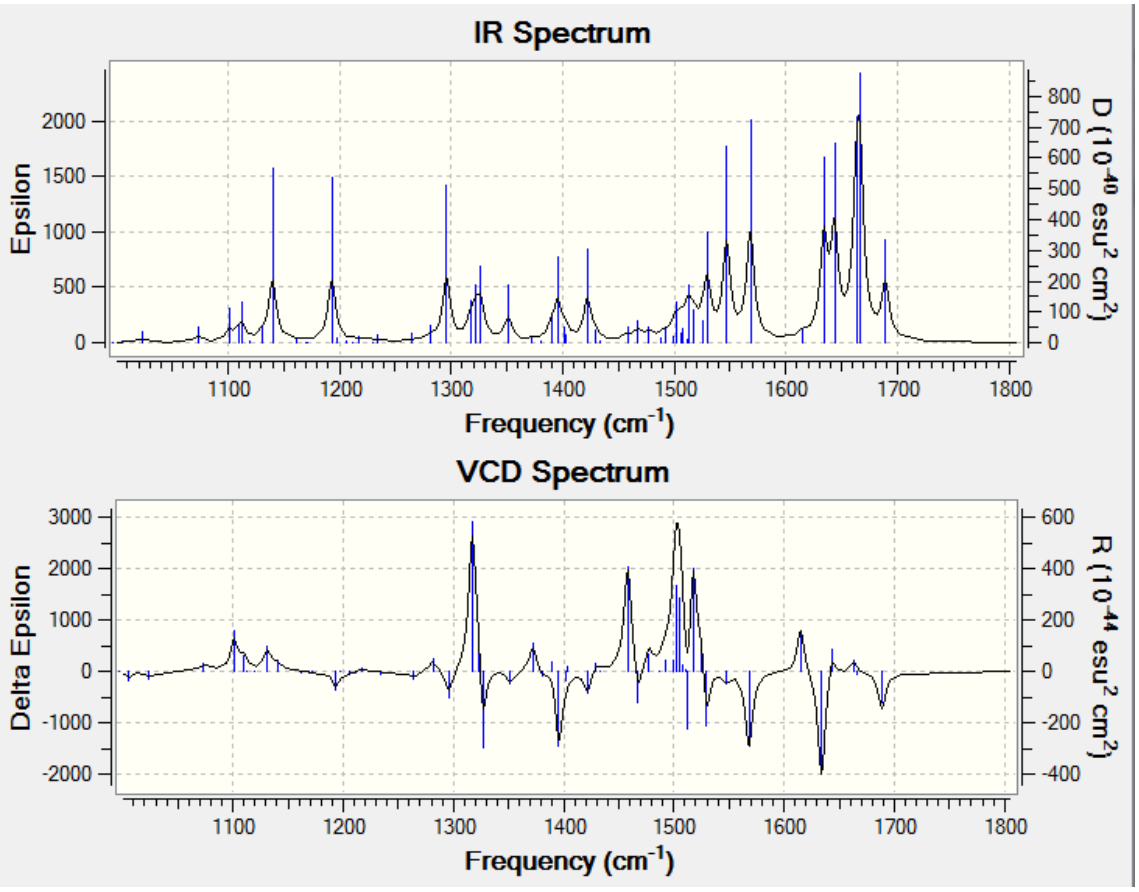
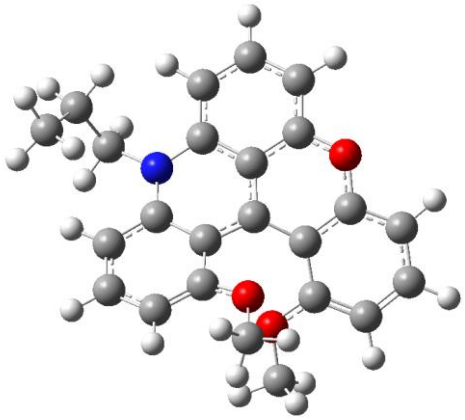
Point Group		





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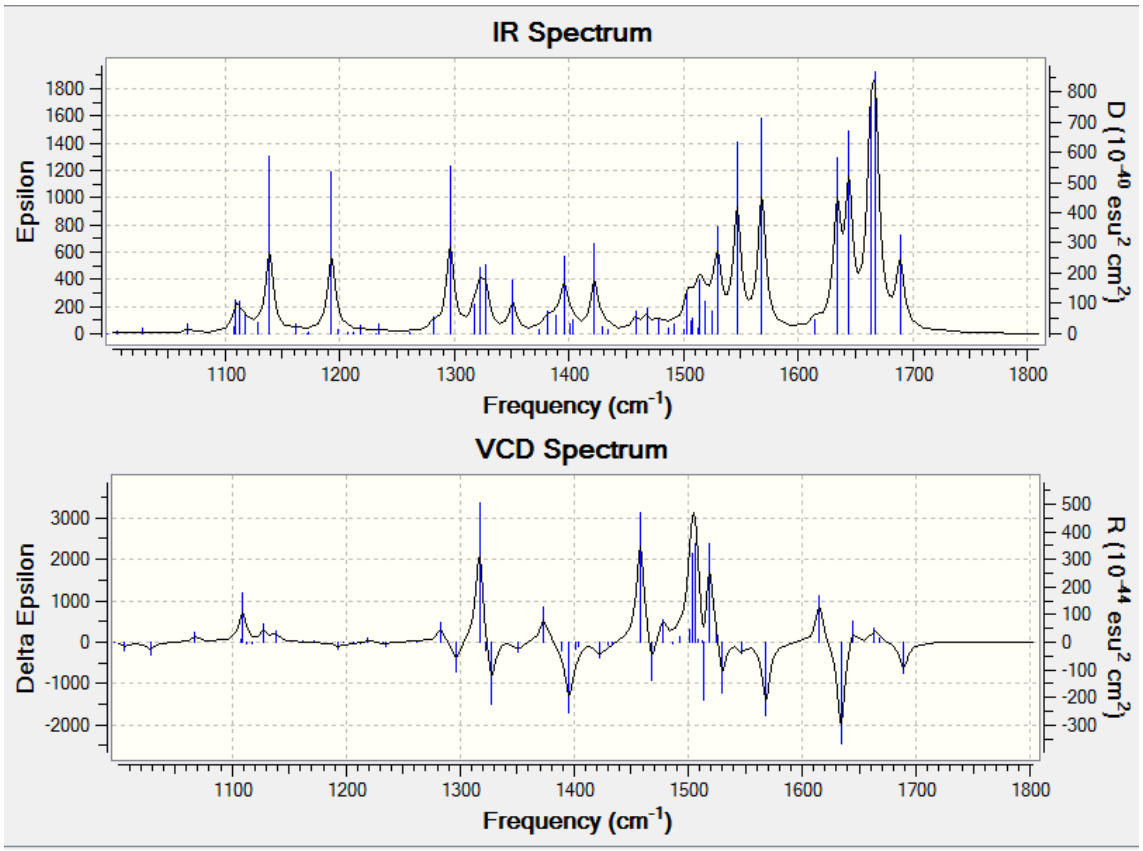
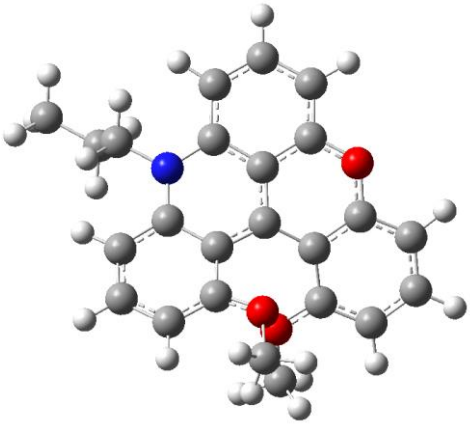
Dipole Moment	2.0789	Debye
Point Group		





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File Type	.fch	
Calculation Type	FREQ	
Calculation Method	RB3PW91	
Basis Set	6-31G(D,P)	
Charge	1	
Spin	Singlet	
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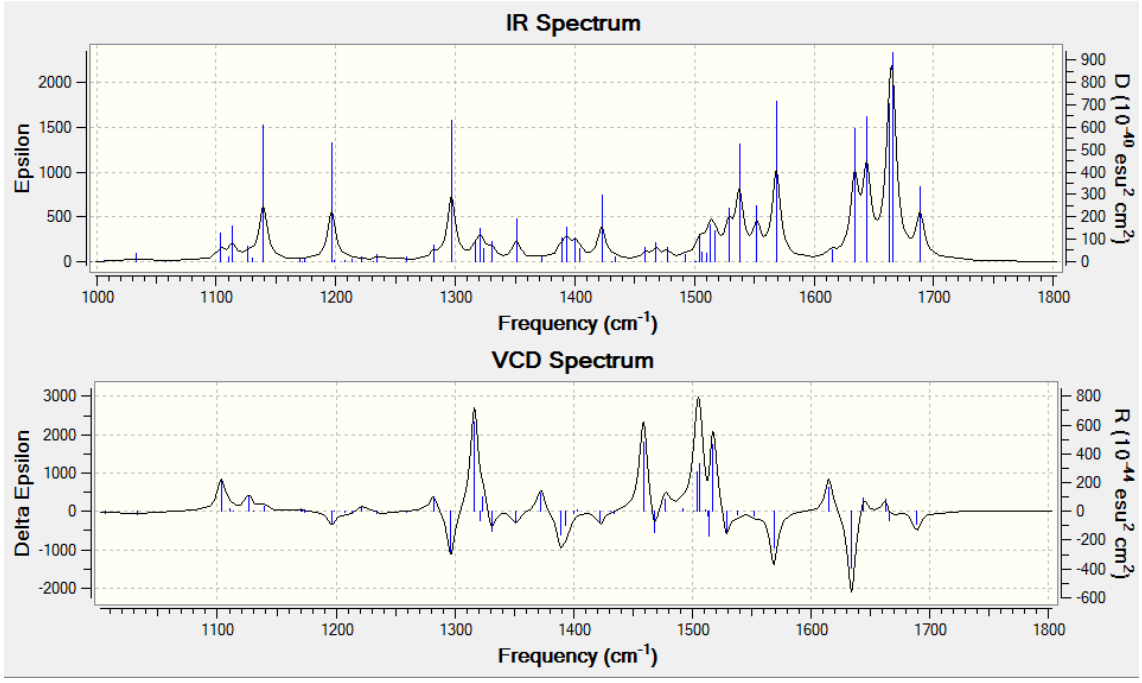
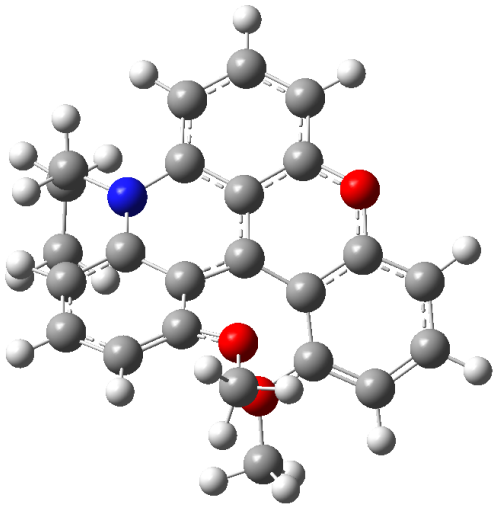
RMS Gradient Norm	0.00000425	a.u.
Imaginary Freq	0	
Dipole Moment	2.1174	Debye
Point Group		





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File Name	gouin-2-2-1-1	
File Type	.fch	
Calculation Type	FREQ	
Calculation Method	RB3PW91	
Basis Set	6-31G(D,P)	
Charge	1	
Spin	Singlet	
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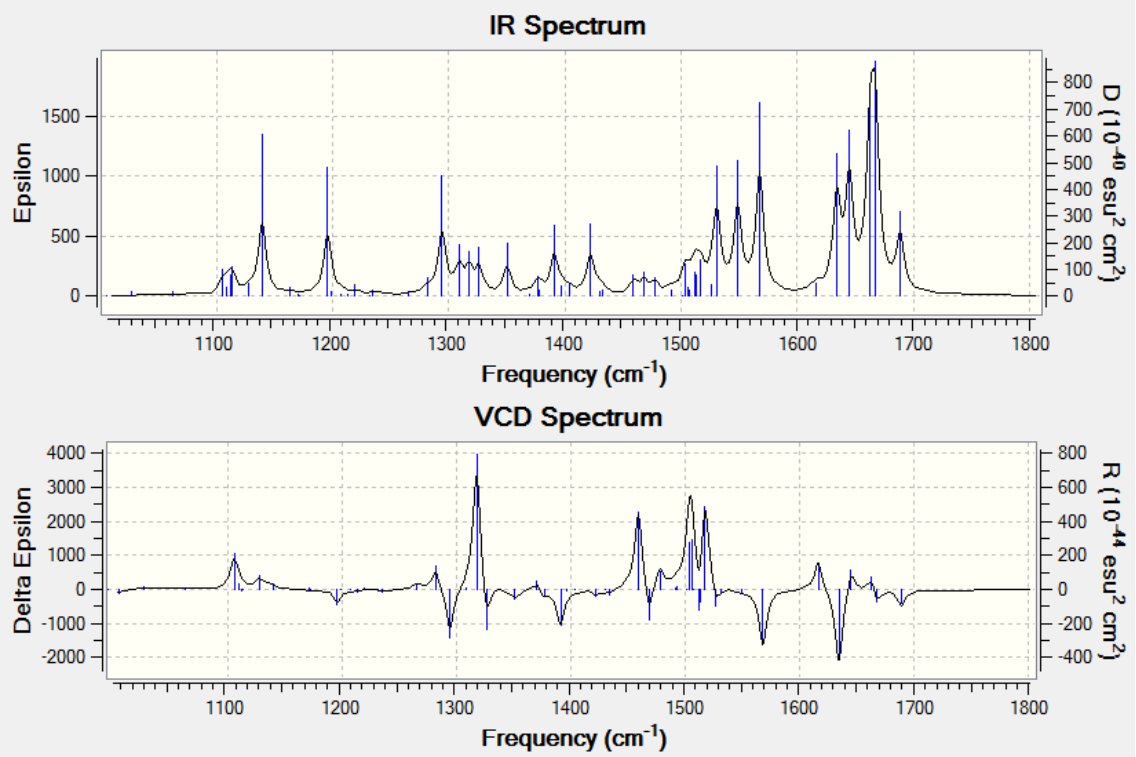
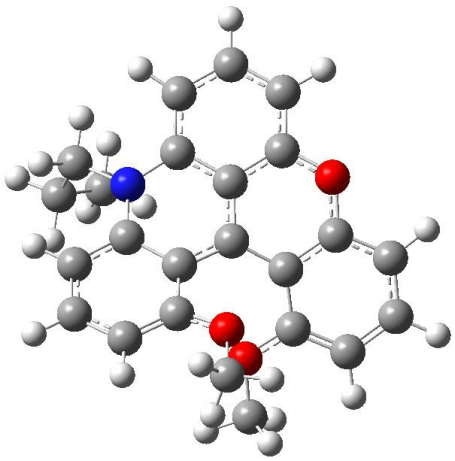
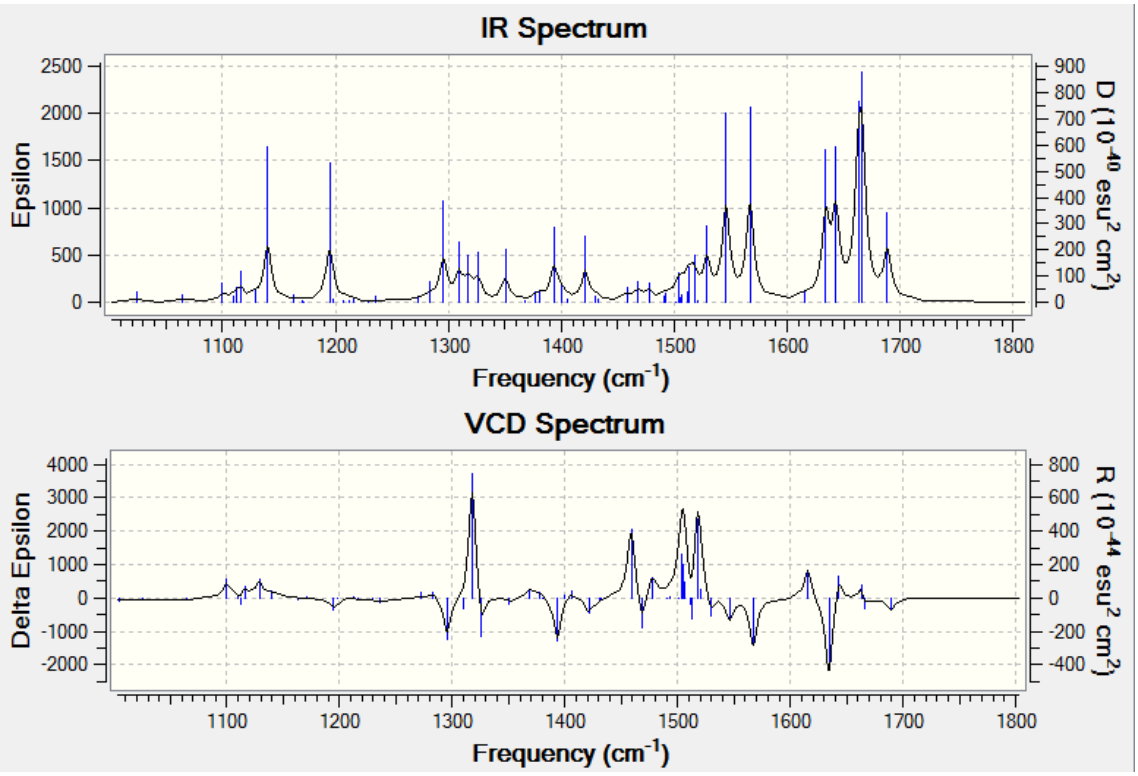
RMS Gradient Norm	0.00000223	a.u.
Imaginary Freq	0	
Dipole Moment	2.0202	Debye
Point Group		





Title Card Required		
File Name	gouin-2-3-1-1	
File Type	.fch	
Calculation Type	FREQ	
Calculation Method	RB3PW91	
Basis Set	6-31G(D,P)	
Charge	1	
Spin	Singlet	
Total Energy	-1207.59820368	a.u.
RMS Gradient Norm	0.00000214	a.u.
Imaginary Freq	0	
Dipole Moment	2.1322	Debye
Point Group		



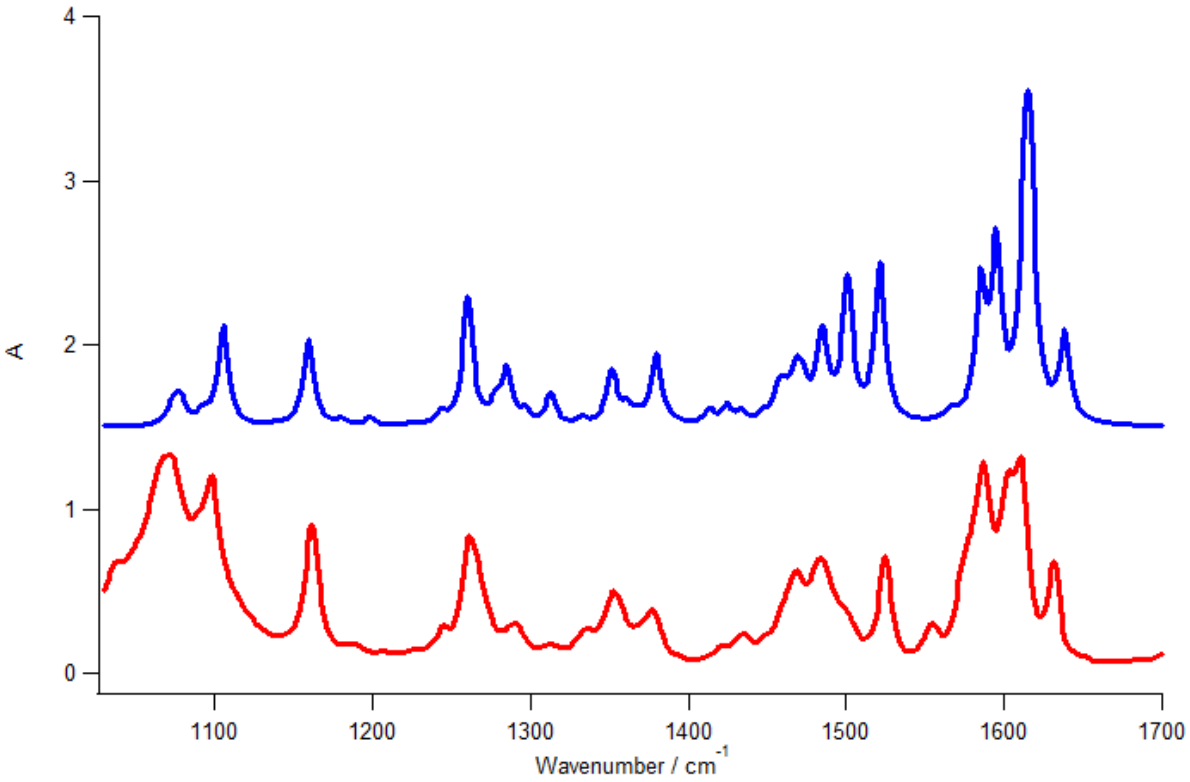


Figure S3. Resulting calculated (top, blue, most stable conformer) and experimental (bottom, red) IR spectrum of (*P*)-[**3a**][BF_4]

X-Ray data Triarylmethaneammonium [10a][BF_4]

Table S1. Crystal data and structure refinement

Empirical formula	C27 H32 B Cl2 F4 N O5	
Formula weight	608.25	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P\ 2_1/c$	
Unit cell dimensions	a = 18.1584(2) Å	α= 90°.
	b = 8.40520(10) Å	β= 129.3670(10)°.
	c = 24.4160(3) Å	γ = 90°.
Volume	2880.94(6) $Å^3$	
Z	4	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	2.590 mm^{-1}	
F(000)	1264	
Crystal size	0.6079 x 0.2777 x 0.1579 mm^3	
Theta range for data collection	3.15 to 73.26°.	
Index ranges	-22<=h<=22, -10<=k<=6, -30<=l<=30	
Reflections collected	16615	
Independent reflections	5655 [R(int) = 0.0178]	
Completeness to theta = 66.97°	100%	
Absorption correction	Analytical	
Max. and min. transmission	0.698 and 0.390	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5655 / 0 / 372	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R_1 = 0.0498, wR_2 = 0.1399	
R indices (all data)	R_1 = 0.0549, wR_2 = 0.1456	
Largest diff. peak and hole	0.733 and -0.550 $e.Å^{-3}$	

Summary of crystal data, intensity measurements and structure refinements for [**10a**][BF_4] were collected in **Table S1**. The crystal was mounted on kapton loop with protection oil. Cell dimensions and intensities were measured at 180 K on a Agilent Supernova diffractometer with mirror-monochromated Cu[Kα] radiation (λ= 1.54184 Å).

Data were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods (SIR97[1] or ShelXS-97[2]), all other calculation were performed with ShelXl[2] systems and ORTEP3[3] programs.

Ref:

[1] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115.

[2] G. M. Sheldrick (2008), Acta Cryst. A64, 112-122.

[3] ORTEP3 for Windows. L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.

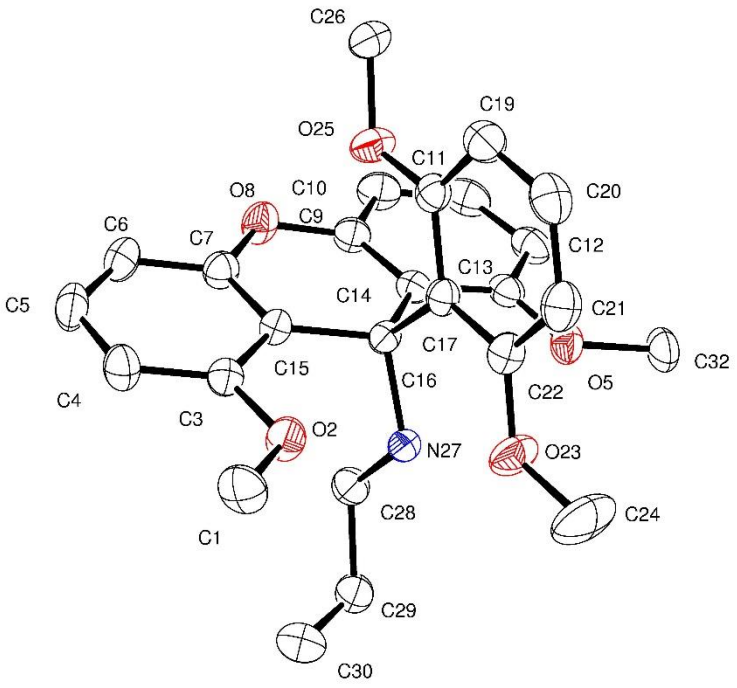


Figure S4. Ortep view of [**10a**][BF_4] (ellipsoids are drawn at 50% probability level). BF_4-, CH_2Cl_2 and all hydrogen atoms are omitted for clarity

Table S2. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(27)-H(27A)...O(5)	0.94(2)	2.15(2)	2.784(2)	123.3(17)
N(27)-H(27B)...O(2)	0.91(2)	2.08(2)	2.740(2)	129.2(19)
N(27)-H(27A)...F(1R)#1	0.94(2)	2.16(2)	2.9819(19)	145.2(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

High Resolution Mass Spectrometry (HRMS) spectra

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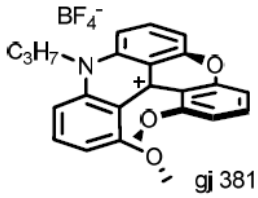
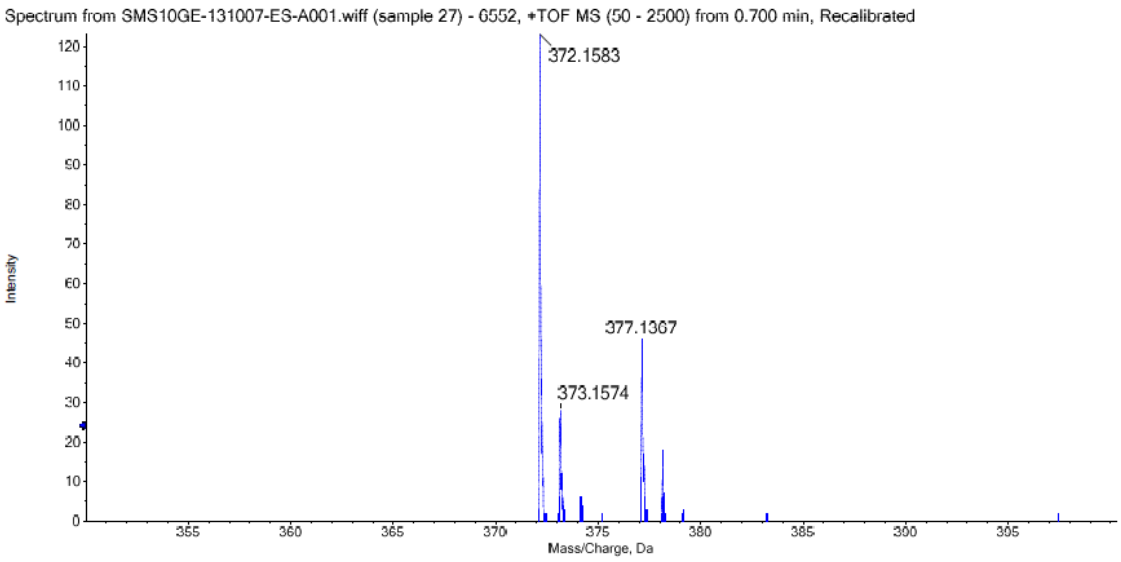
Submitter:	GOUIN	Date of reception:	04/10/13
Sample name:	gj-381	Date of certificate:	08/10/13
Sample number:	6552	Data filename:	SMS10GE-131007-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{24}H_{22}NO_3$	372.1583	372.1594	-2.9



Chemical Formula: $C_{24}H_{22}BF_4NO_3$
Exact Mass: 459.1629



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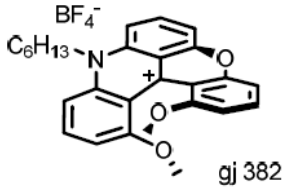
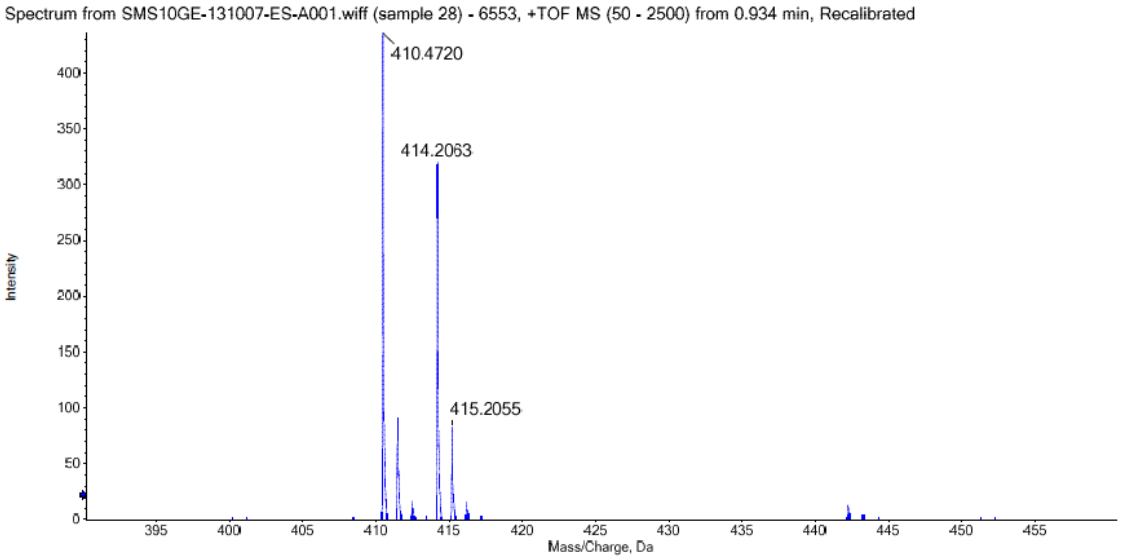
Submitter:	GOUIN	Date of reception:	04/10/13
Sample name:	gj-382	Date of certificate:	08/10/13
Sample number:	6553	Data filename:	SMS10GE-131007-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{27}H_{28}NO_3$	414.2063	414.2064	-0.3



Chemical Formula: $C_{27}H_{28}BF_4NO_3$
Exact Mass: 501.2098



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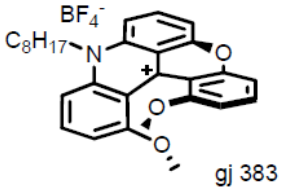
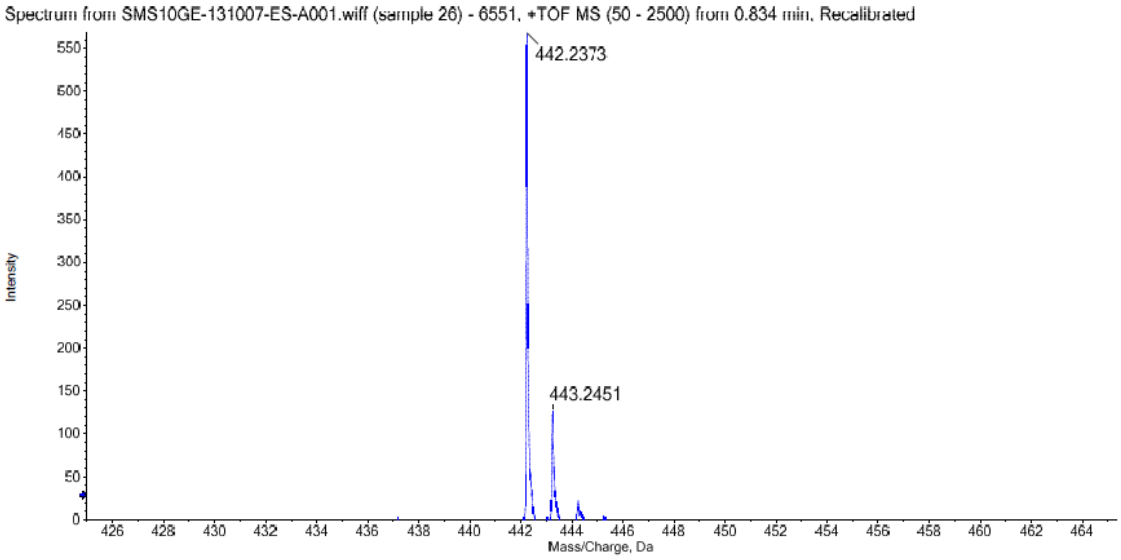
Submitter:	GOUIN	Date of reception:	04/10/13
Sample name:	gj-383	Date of certificate:	08/10/13
Sample number:	6551	Data filename:	SMS10GE-131007-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{29}H_{32}NO_3$	442.2373	442.2377	-0.7



gj 383

Chemical Formula: $C_{29}H_{32}BF_4NO_3$
Exact Mass: 529.2411



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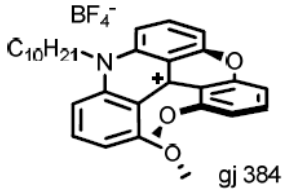
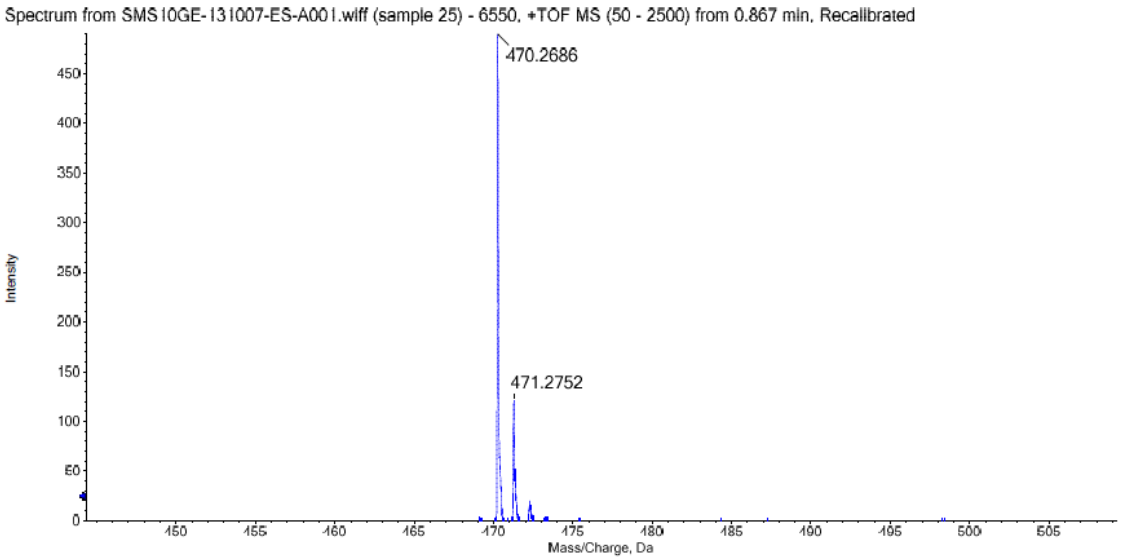
Submitter:	GOUIN	Date of reception:	04/10/13
Sample name:	gj-384	Date of certificate:	08/10/13
Sample number:	6550	Data filename:	SMS10GE-131007-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{31}H_{36}NO_3$	470.2686	470.2690	-0.7



Chemical Formula: $C_{31}H_{36}BF_4NO_3$
Exact Mass: 557.2724



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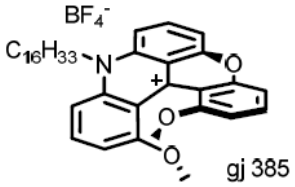
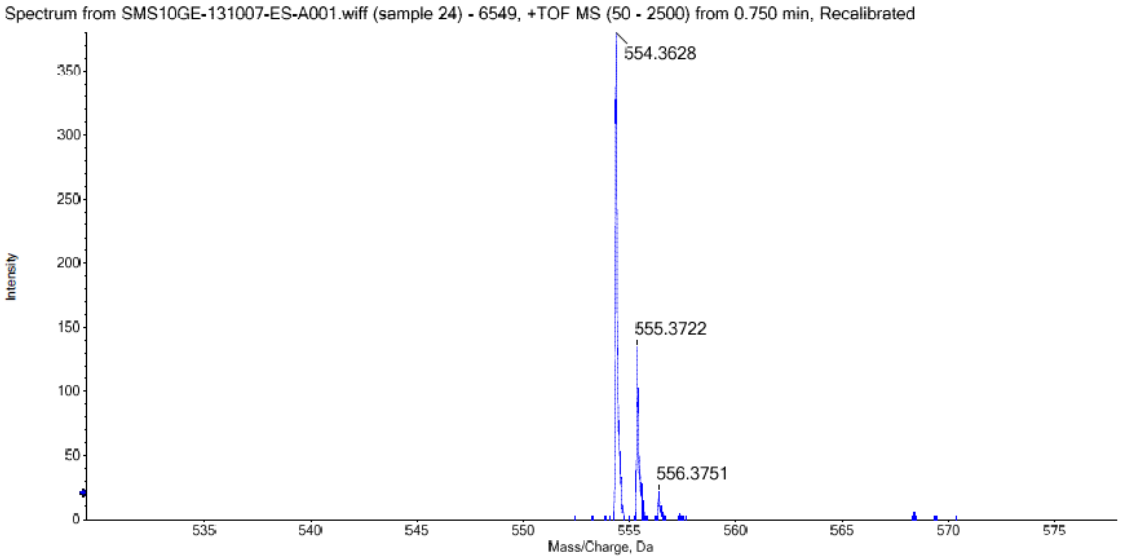
Submitter:	GOUIN	Date of reception:	04/10/13
Sample name:	gj-385	Date of certificate:	09/10/13
Sample number:	6549	Data filename:	SMS10GE-131007-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{37}H_{48}NO_3$	554.3628	554.3629	-0.1



Chemical Formula: $C_{37}H_{48}BF_4NO_3$
Exact Mass: 641.3663



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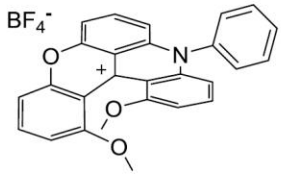
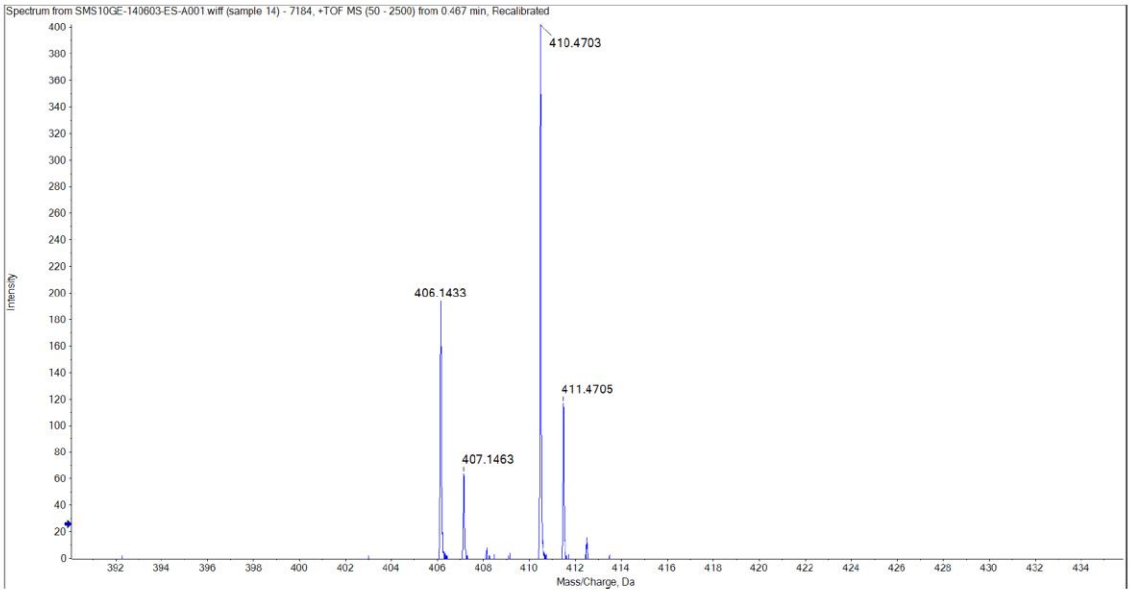
Submitter:	GOUIN	Date of reception:	03/06/14
Sample name:	gj-phenyl	Date of certificate:	04/06/14
Sample number:	7184	Data filename:	SMS10GE-140603-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{27}H_{20}O_3N$	406.1433	406.1438	-1.1



gj-phenyl



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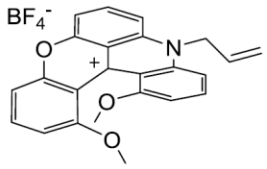
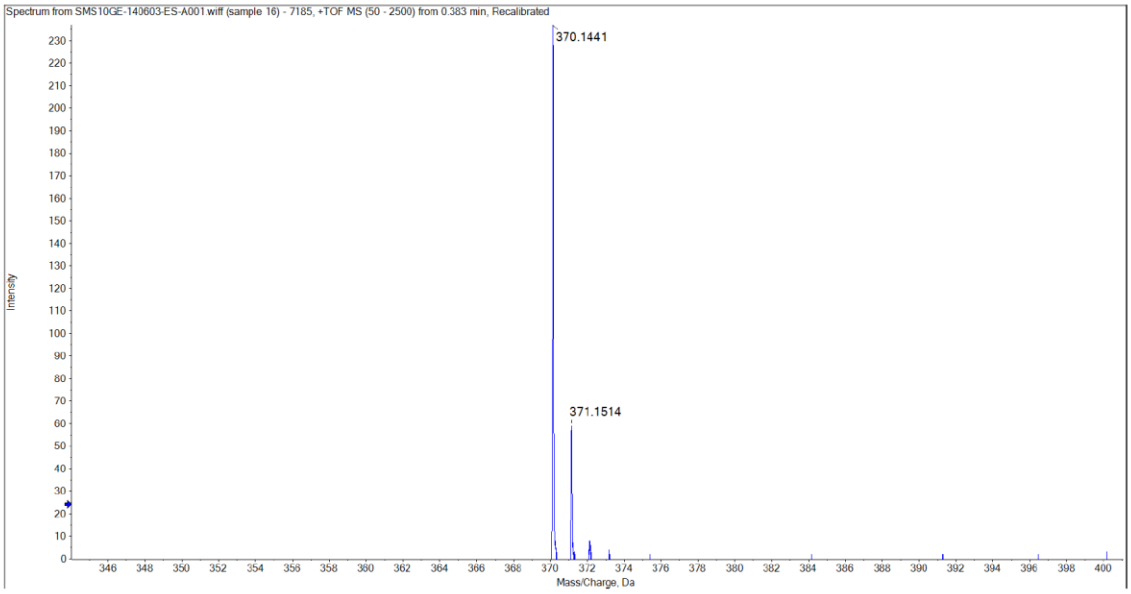
Submitter:	GOUIN	Date of reception:	03/06/14
Sample name:	gj-allyl	Date of certificate:	04/06/14
Sample number:	7185	Data filename:	SMS10GE-140603-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{24}H_{20}O_3N$	370.1441	370.1438	0.8



gj-allyle



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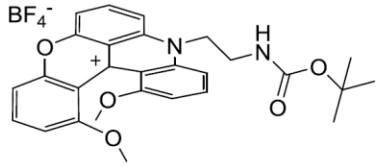
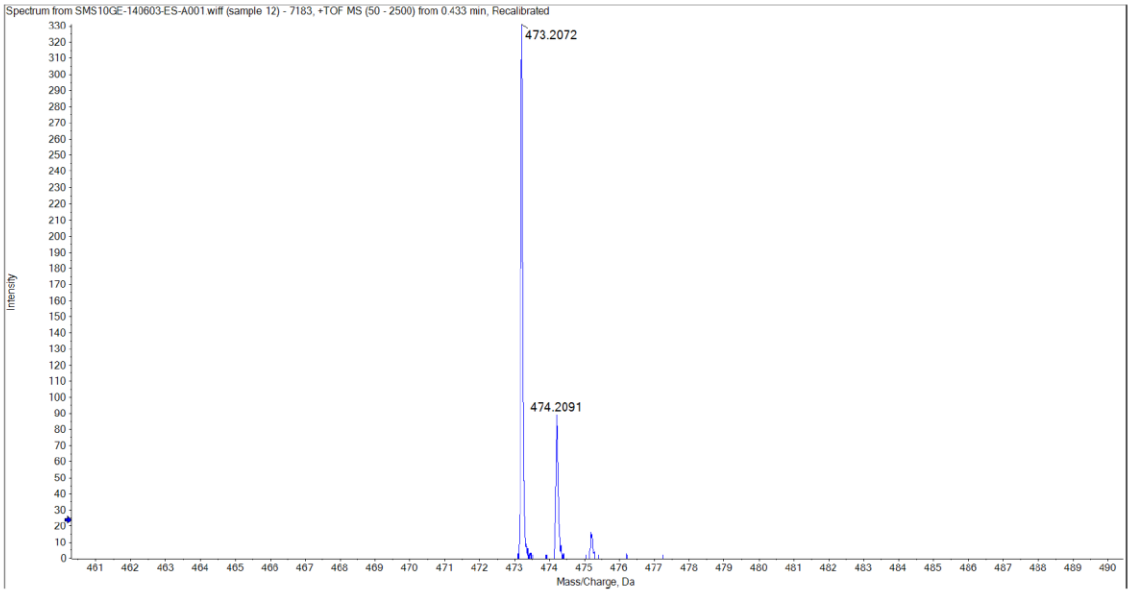
Submitter:	GOUIN	Date of reception:	03/06/14
Sample name:	gj-boc	Date of certificate:	04/06/14
Sample number:	7183	Data filename:	SMS10GE-140603-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{28}H_{29}O_5N_2$	473.2072	473.2071	0.3



gj-boc



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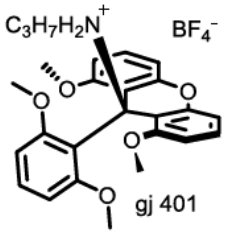
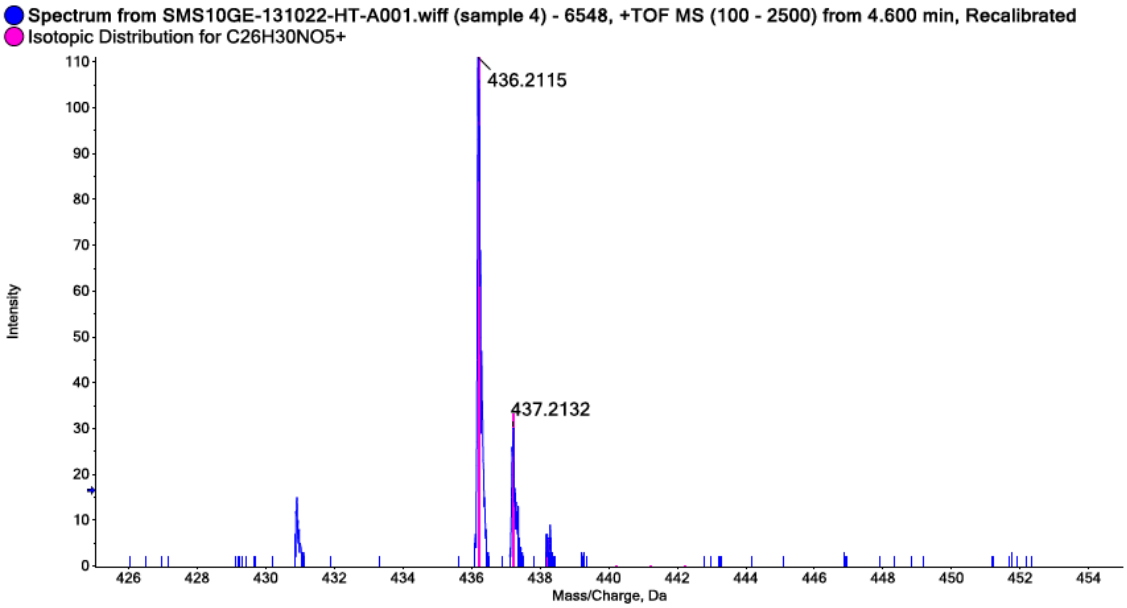
Submitter:	Gouin Jérôme	Date of reception:	03/10/13
Sample name:	gj-401	Date of certificate:	23/10/13
Sample number:	6548	Data filename:	SMS10GE-131022-HT-A001
Operators:	Harry Théraulaz – Julien Meyer	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
		Ionisation mode:	ESI (positive mode)
Principal investigator:	Dr. Sophie Michalet		

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{26}H_{30}NO_5^+$	436.2115	436.2119	-0.8





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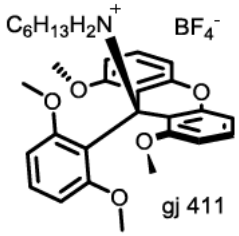
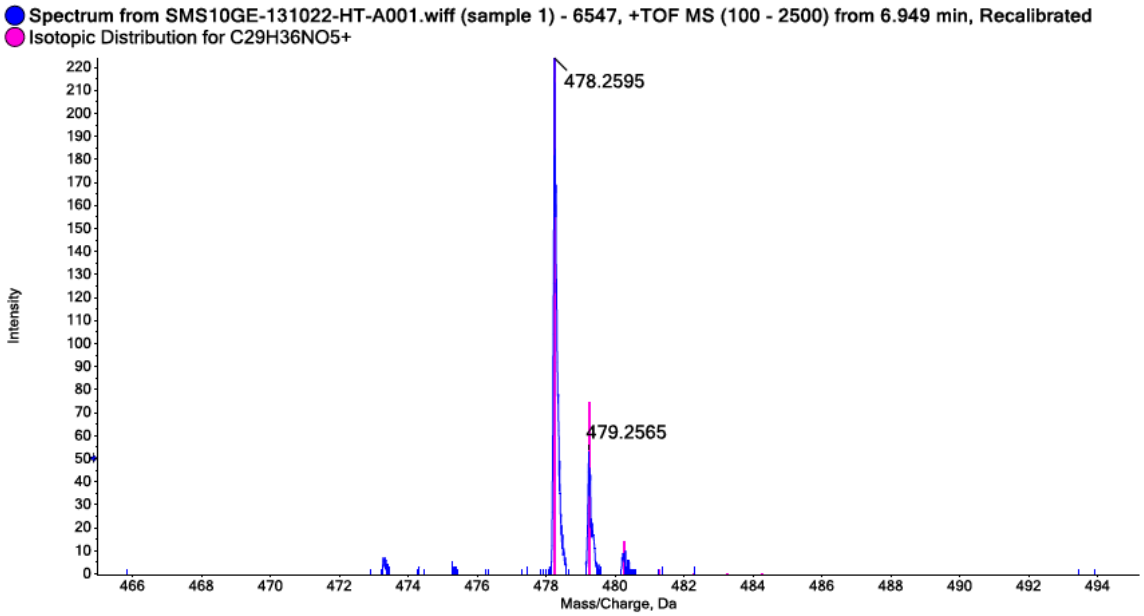
Submitter:	Gouin Jérôme	Date of reception:	03/10/13
Sample name:	gj-411	Date of certificate:	23/10/13
Sample number:	6547	Data filename:	SMS10GE-131022-HT-A001
Operators:	Harry Théraulaz – Julien Meyer	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
		Ionisation mode:	ESI (positive mode)
Principal investigator:	Dr. Sophie Michalet		

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{29}H_{36}NO_5^+$	478.2595	478.2588	1.4





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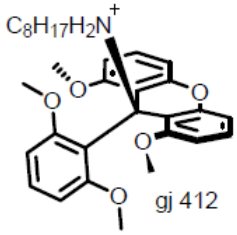
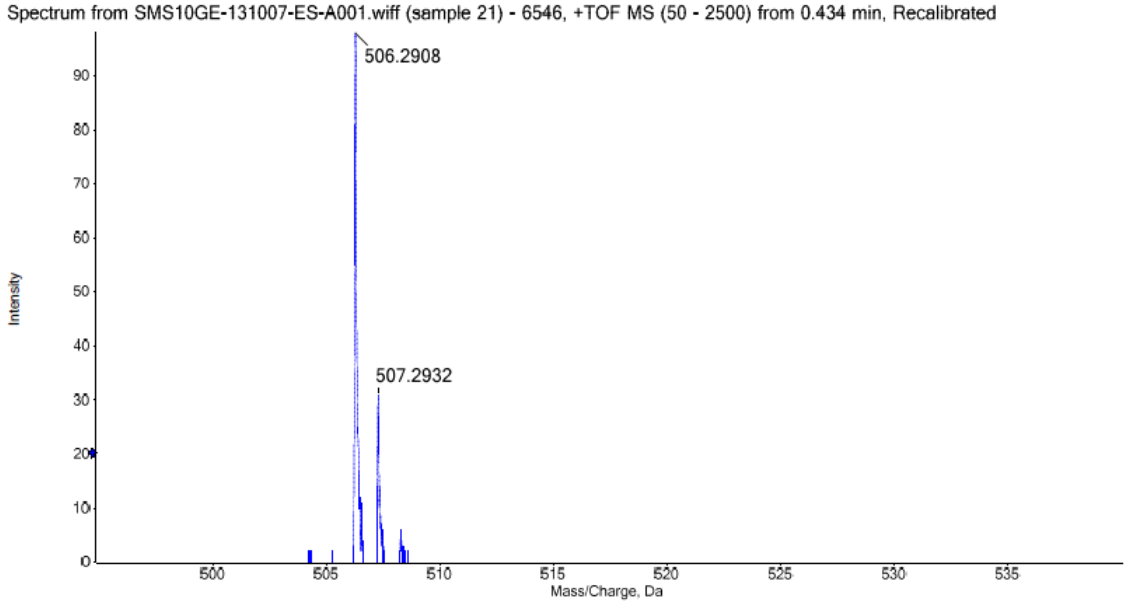
Submitter:	Gouin Jérôme	Date of reception:	03/10/13
Sample name:	gj-412	Date of certificate:	09/10/13
Sample number:	6546	Data filename:	SMS10GE-131007-ES-A001
Operators:	Eliane Sandmeier – Julien Meyer	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
		Ionisation mode:	ESI (positive mode)
Principal investigator:	Dr. Sophie Michalet		

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{31}H_{40}NO_5^+$	506.2908	506.2901	1.3



Chemical Formula: $C_{31}H_{40}NO_5^+$
Exact Mass: 506.29



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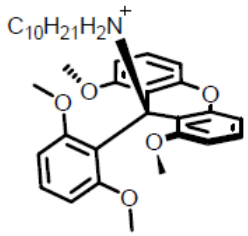
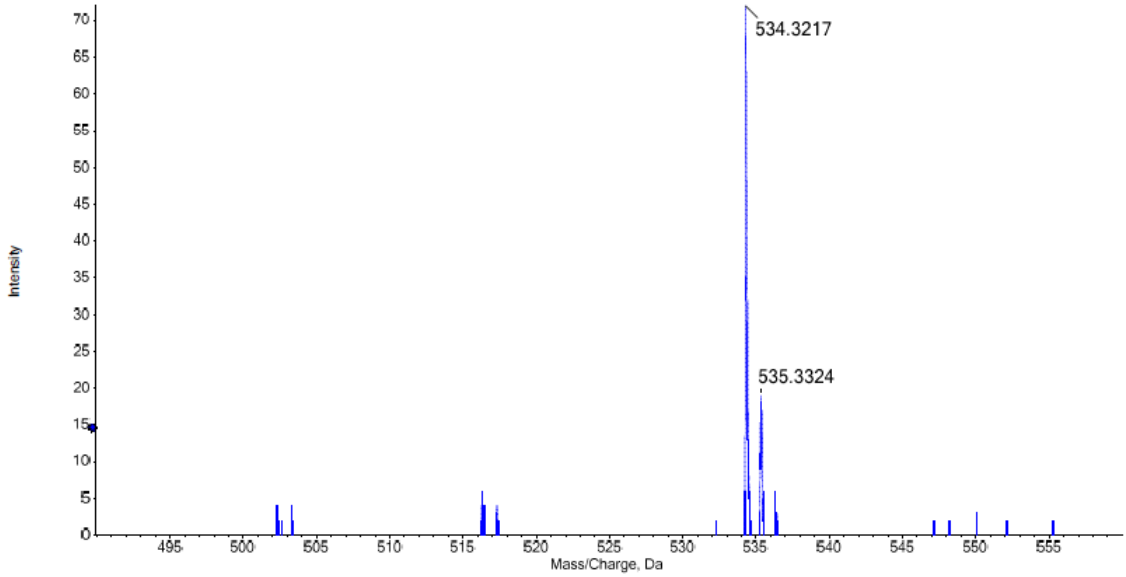
Submitter:	Gouin Jérôme	Date of reception:	03/10/13
Sample name:	YK-7	Date of certificate:	09/10/13
Sample number:	6545	Data filename:	SMS10GE-131007-ES-A001
Operators:	Eliane Sandmeier – Julien Meyer	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
		Ionisation mode:	ESI (positive mode)
Principal investigator:	Dr. Sophie Michalet		

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{33}H_{44}NO_5^+$	534.3217	534.3214	0.5



Chemical Formula: $C_{33}H_{44}NO_5^+$
Exact Mass: 534.32

Spectrum from SMS10GE-131007-ES-A001.wiff (sample 20) - 6545, +TOF MS (50 - 2500) from 0.517 min, Recalibrated



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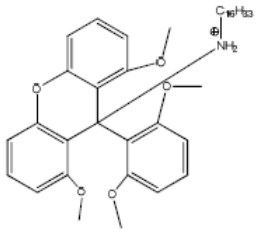
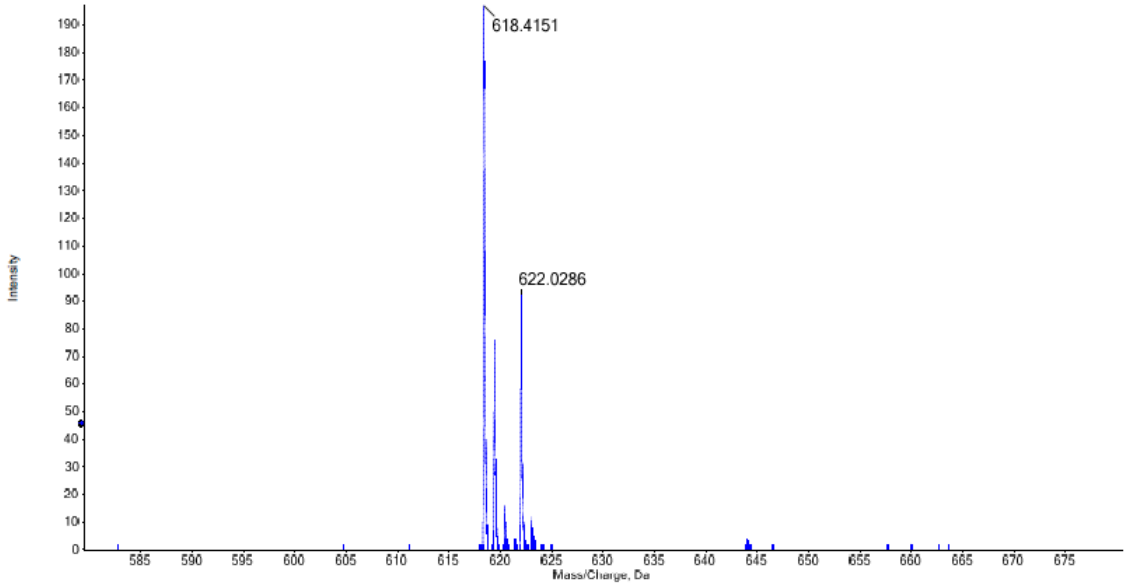
Submitter:	GOUIN	Date of reception:	04/10/13
Sample name:	YK-9	Date of certificate:	10/10/13
Sample number:	6544	Data filename:	SMS10GE-131009-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{39}H_{56}O_5N$	618.4151	618.4153	-0.2



Chemical Formula: $C_{39}H_{56}NO_5^+$
Exact Mass: 618.4153

Warning: The analyte signal is mixed with the internal standard at *m/z* 622.0286. Thus this signal was not used for calibration.

Spectrum from SMS10GE-131009-ES-A001.wiff (sample 7) - SPLE6544, +TOF MS (100 - 2500) from 0.933 min, Recalibrated