# Merging Polyacenes and Cationic Helicenes: from Weak to Intense Chiroptical Properties in the Far-Red Region

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## Supporting information

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In addition, the dataset for this article can be found at the following DOI: 10.26037/yareta:zsmeadwn3vbgpag2jqno3lj554. It will be preserved for 10 years

# 1. General remarks and analysis conditions

**Reagents**

Cationic [4]helicene **7**, **9** and [6]helicene **8** were prepared according to reported procedures.[1,2,3], Reagents were used as purchased, unless otherwise stated. Reactions were conducted under $N_2$ atmosphere using standard schlenck technics, unless otherwise stated. Column chromatography were performed using Siliaflash P60 silicagel (40-63 µm, 60 Å), Acros Brockmann I basic alumina (40-200 µm, 60 Å), or were done with a Combi*Flash*® Rf 200 on $SiO_2$ 4 g cartridge. Preparative TLC were performed using TLC Silica gel 60 F254 plates purchased from Merck.

**Analytical methods and apparatus**

**NMR spectra** were recorded on Brucker Advance II+ AMX-500 and AMX-400 spectrometers at room temperature (otherwise noted). NMR chemical shifts are given in ppm (δ) relative to $Me_4Si$ with solvent resonances used as internal standards ($CD_2Cl_2$: 5.32 ppm for $^1H$ and 53.84 for $^{13}C$; $CD_3OD$: 3.31 ppm for $^1H$ and 49.0 for $^{13}C$; DMSO-$d_6$: 2.50 ppm for $^1H$ and 39.5 for $^{13}C$). **IR spectra** were recorded on a Perkin-Elmer 1650 FT-IR spectrometer using a diamond ATR Golden Gate sampling. **Melting points** (M.P.) were measured in open capillary tubes with a Buchi B-550 melting points apparatus and are uncorrected. **R*f*** were measured on TLC Silica gel 60 F254 plates purchased from Merck. **Electrospray mass spectra** were obtained on a Finnigan SSQ 7000 spectrometer QSTAR pulsar *i* (AB / MDS Sciex) or on a ESI (TIS)/nanoESI/APCI-QqTof by the Department of Mass Spectroscopy of the University of Geneva or on a Xevo G2 Tof (TOF), ESI (positive polarity).

**(Chir)Optical properties**

**Optical rotation** were measured on a Perkin Elmer 241 polarimeter at 20 °C using a Hg lamp (365 nm). **UV-Vis-NIR absorption spectra** were recorded on a JASCO V-650 spectrophotometer at 20°C. Measurement were performed in acetonitrile analytical grade at precise concentrations *ca*. 1 $10^{-5}$ M. **Electronic Circular dichroism (ECD) spectra** were recorded on a JASCO J-815 spectrophotometer at 20°C. Measurement were performed in analytical grade acetonitrile at precise concentrations *ca*. 1 $10^{-5}$ M. **Circularly polarized luminescence measurements (CPL)** were carried out with a home-made apparatus,[4] on acetonitrile diluted solutions with an optical density lower than 0.1, under 517 nm irradiation from a LED source (90° geometry). Solid state CPL measurements were carried out on PMMA films under 365 nm irradiation (0° geometry). **Steady-state fluorescence spectra** were measured using a Varian Cary 50 Eclipse spectrofluorimeter in acetonitrile for the helical azaacenes. All fluorescence spectra were corrected for the wavelength-dependent sensitivity of the detection. Fluorescence quantum yields Φ were measured in diluted solution with an optical density lower than 0.1 using the following equation:

$$\frac{\Phi_x}{\Phi_r} = \left(\frac{\mathrm{A}_r(\lambda)}{\mathrm{A}_x(\lambda)}\right)\left(\frac{n_x^2}{n_r^2}\right)\left(\frac{\mathrm{D}_x}{D_r}\right)$$

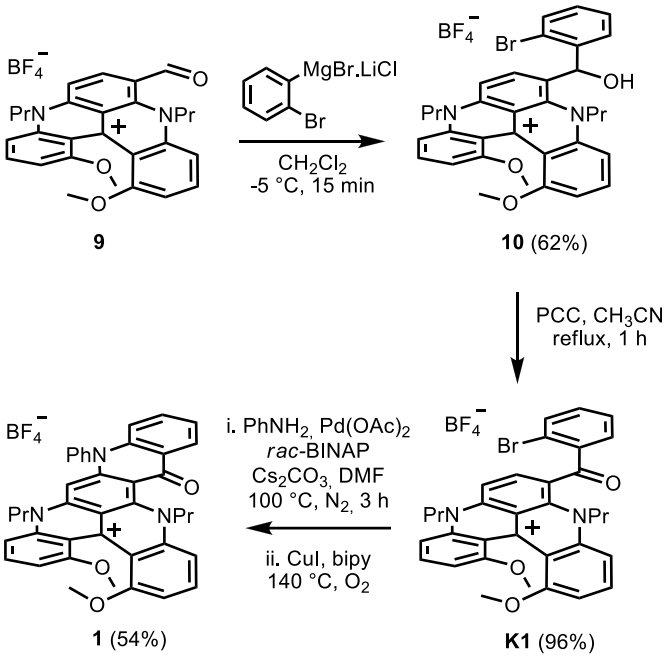
where A is the absorbance at the excitation wavelength (λ), n the refractive index and D the integrated intensity. “r” and “x” stand for reference and sample. The fluorescence quantum yields were measured relative to oxazine 725 in ethanol (Φ = 0.11). Excitations of reference and sample compounds were performed at the same wavelength.

**Crystallography**

All data were collected on an Agilent supernova dual source diffractometer equipped with an Atlas detector, using Cu Kα radiation. Data reduction was carried out in the crysalis Pro Software.[5] Structure solution was made using dual space methods (ShelxT[6]). Refinements were carried out in ShelxT[6] within the Olex2[7] software.

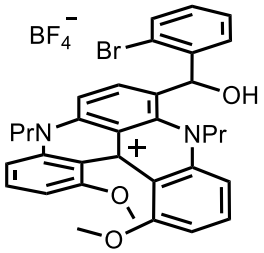
## 2. Synthetic procedures and characterizations

### Toward helical pentacene 1




Scheme S1. Access to pentacene **1** from helicene **9**.

6-((2-bromophenyl)(hydroxy)methyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate 10

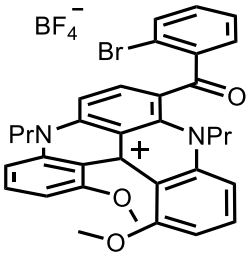



**10**

(2-bromophenyl)magnesium bromide lithium chloride was prepared following a reported procedure[8] then added to 6-formyl-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate (**9**)[2] (106 mg, 0.2 mmol, 1 equiv) in dry $CH_2Cl_2$ at – 5 °C under $N_2$. The reaction mixture was stirred for 15 minutes then hydrolyzed by addition of a 1 M aqueous solution of $HBF_4$. The organic layer was extracted then washed with a 0.2 M aqueous solution of $NaBF_4$, dried over $Na_2SO_4$ then concentrated under reduced pressure. Purification by column chromatography afforded the pure product as a green solid (85 mg, 62%).

**R*f*:** 0.43 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **M. P.:** 160 °C (decomposition). **$^1$H NMR ($CD_2Cl_2$, 500 MHz):** δ = 8.10 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.82 (t, *J* = 8.4 Hz, 1H), 7.51 (td, 8.1, 1.2 Hz,1H), 7.46 (dd, *J* = 8.7, 0.8 Hz, 1H), 7.39 (dd, *J* = 9.0, 1.4 Hz, 2H), 7.33 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.17 (td, *J* = 7.6, 1.7 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.81 (dd, *J* = 8.3, 0.7 Hz, 1H), 6.52 (s, 1H), 5.18 – 5.12 (m, 1H), 5.02 – 4.96 (m, 1H), 4.62 – 4.56 (m, 1H), 4.37 – 4.31 (m, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 2.22 – 2.07 (m, 2H), 1.84 – 1.73 (m, 2H), 1.21 (t, *J* = 7.4 Hz, 3H), 0.49 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR ($CD_2Cl_2$, 126 MHz):** δ = 160.2, 159.5, 143.9, 143.7, 142.8, 142.2, 142.0, 139.2, 137.9, 137.4, 136.7, 133.3, 130.0, 128.5, 127.7, 122.8, 122.4, 121.3, 116.8, 114.3, 110.8, 107.8, 107.2, 104.0, 103.5, 72.3, 58.5, 56.4, 56.1, 54.0, 52.9, 22.9, 20.9, 11.4, 11.0. **$^{19}$F NMR ($CD_2Cl_2$, 282 MHz):** δ = -153.40 (d, *J* = 15.4 Hz). **UV-vis:** $\lambda_{max}$ ($CH_3CN$) = 618 nm (ε = 12600 $L.mol^{-1}.cm^{-1}$). **IR (neat, $cm^{-1}$):** ν = 3493, 1963, 1877, 1597, 1580, 1499, 1466, 1340, 1261, 1168, 1124, 1044, 1021, 816, 779, 751. **HRMS (ESI+)** calculated for [M]+: 597.1747 ($C_{34}H_{34}BrN_2O_3$), Found 597.1759.

6-(2-bromobenzoyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate K1

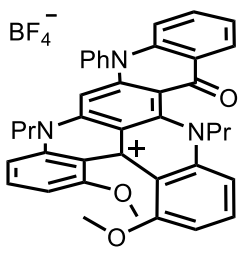



**K1**

6-((2-bromophenyl)(hydroxy)methyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate (**7**) (20 mg, 0.03 mmol, 1 equiv) and pyridinium chlorochromate (26 mg, 0,12 mmol, 4 equiv) were dissolved in $CH_3CN$. The reaction mixture was then refluxed for 1 hour. After cooling to room temperature, the organic layer was filtered through celite, washed with a 0.2 M aqueous solution of $NaBF_4$, dried over $Na_2SO_4$ then concentrated under reduced pressure. Purification by column chromatography afforded the pure product as a dark green solid (19 mg, 92%).

**R*f*:** 0.27 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **M. P.:** 156 °C (decomposition). **$^1$H NMR ($CD_2Cl_2$, 500 MHz):** δ = 8.16 (d, *J* = 9.1 Hz, 1H), 8.05 (t, *J* = 8.5 Hz, 1H), 7.94 (t, *J* = 8.4 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.57 – 7.51 (m, 4H), 7.47 – 7.42 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 4.88 – 4.82 (m, 1H), 4.78 – 4.70 (m, 1H), 4.59 – 4.48 (m, 1H), 4.14 – 4.07 (m, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.24 – 2.15 (m, 2H), 1.87 – 1.81 (m, 1H), 1.79 – 1.72 (m, 1H), 1.27 – 1.23 (m, 3H), 0.47 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR ($CD_2Cl_2$, 125 MHz):** δ = $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ 192.1, 160.2, 159.6, 141.9, 141.8, 141.5, 141.3, 141.2, 141.0, 139.7, 138.8, 137.4, 134.5, 133.4, 131.8, 128.8, 120.8, 120.7, 118.8, 116.8, 114.2, 110.6, 108.1, 105.8, 105.1, 104.7, 59.6, 56.6, 56.4, 53.1, 23.1, 21.0, 11.4, 11.0. **$^{19}$F NMR ($CD_2Cl_2$, 282 MHz):** δ = -153.32 (d, *J* = 21.2 Hz).-153.73, -153.79. **UV-vis:** $\lambda_{max}$ ($CH_3CN$) = 588 nm (ε = 12000 L.mol$^{-1}$.cm$^{-1}$). **IR (neat, cm$^{-1}$):** ν =.2952, 1652, 1584, 1506, 1468, 1345, 1275, 1238, 1172, 1126, 1080, 1026, 840. **HRMS (ESI+)** calculated for [M]+: 595.1591 ($C_{34}H_{32}BrN_2O_3$), Found 595.1597.

4,5-dimethoxy-16-oxo-11-phenyl-9,17-dipropyl-9,11,16,17-tetrahydro-4b*H*-dibenzo[*b,j*]quinolino[4,3,2-*de*][1,7]phenanthrolin-4b-ylium 1

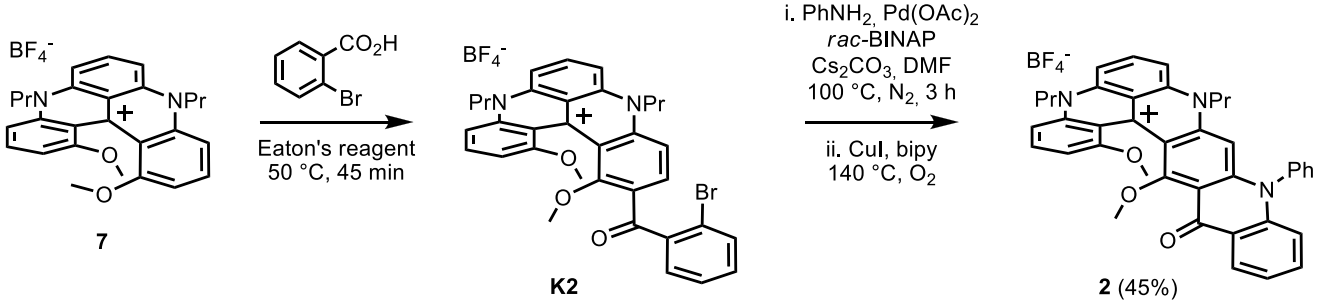



**1**

$Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%) and *rac*-BINAP (25 mg, 0.04 mmol, 20 mol%) were mixed in 0.5 mL of dry and degassed DMF under $N_2$. The reaction mixture was then warmed to 90 °C. After 15 minutes of stirring, the solution turned red. In a second round bottomed flask under $N_2$, 6-(2-bromobenzoyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate (**K1**) (80 mg, 0.12 mmol, 1 equiv), $Cs_2CO_3$ (156 mg, 0.48 mmol, 4 equiv) and aniline (33 µL, 0.36 mmol, 3 equiv) were dissolved in dry and degassed DMF (2 mL). The Pd/BINAP complex was then added to this mixture *via* a cannula and the reaction was stirred at 90 °C for 1 hour. Then, the reaction flask was opened to air and CuI (7.6 mg, 0.04 mmol, 40 mol%) and 2,2'-bipyridine (6.2 mg, 0.04 mmol, 40 mol%) were added. The reaction was warmed to 100 °C and stirred under air atmosphere for 15 minutes. The reaction was then allowed to be cooled to room temperature. The reaction was hydrolysed at 0 °C by addition of a 1 M aqueous solution of $HBF_4$. The crude mixture was extracted with $CH_2Cl_2$, washed with 0.2 M solution of $NaBF_4$, dried over $Na_2SO_4$, filtered then concentrated under vacuum. Purification by column chromatography afforded the pure product as a dark red solid (47 mg, 52%).

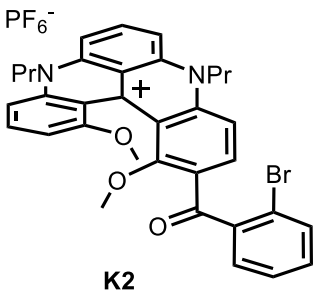
**R*f*:** 0.68 ($SiO_2$, $CH_2Cl_2$/Acetone, 95:5). **M. P.:** 295-297 °C (decomposition). **$^1$H NMR ($CD_2Cl_2$, 500 MHz):** δ = 8.49 (dd, *J*=7.9, 1.6, 1H), 8.06 – 7.93 (m, 1H), 7.93 – 7.84 (m, 3H), 7.86 – 7.79 (m, 1H), 7.69 (dd, *J*=8.8, 0.8, 1H), 7.63 – 7.55 (m, 2H), 7.53 – 7.47 (m, 0H), 7.43 (ddd, *J*=8.0, 7.0, 1.0, 1H), 7.28 (d, *J*=8.7, 1H), 7.00 (dd, *J*=8.2, 0.7, 1H), 6.92 (d, *J*=8.1, 1H), 6.87 (dd, *J*=8.4, 0.9, 1H), 6.34 (s, 1H), 5.39 – 5.31 (m, 1H), 4.39 (ddd, *J*=15.1, 11.8, 5.8, 1H), 3.88 (ddd, *J*=14.8, 9.2, 7.4, 1H), 1.98 (dddd, *J*=13.6, 12.2, 7.5, 6.1, 1H), 1.78 – 1.65 (m, 2H), 1.62 – 1.56 (m, 0H), 0.83 (t, *J*=7.4, 3H), 0.35 (t, *J*=7.3, 3H). **$^{13}$C NMR ($CD_2Cl_2$, 125 MHz):** δ = 175.3, 160.2, 159.5, 143.2, 142.7, 142.1, 141.5, 139.8, 139.1, 139.0, 137.6, 136.2, 134.3, 132.6, 132.3, 131.5, 130.3, 129.8, 127.6, 124.3, 124.2, 118.0, 117.9, 116.8, 112.4, 111.1, 107.5, 106.1, 104.9, 104.4, 93.6, 60.8, 56.4 (d, *J*=3.0), 53.0, 23.3, 19.9, 10.9, 10.8. **$^{19}$F NMR ($CD_2Cl_2$, 282 MHz):** δ = = -153.14 (d, *J* = 17.7 Hz). **UV-vis:** $\lambda_{max}$ ($CH_3CN$) = 576 nm (ε = 10100 $L.mol^{-1}.cm^{-1}$). **IR (neat, $cm^{-1}$):** ν = 2961, 1642, 1586, 1469, 1268, 840, 761. **HRMS (ESI+)** calculated for [M]+: ($C_{40}H_{36}N_3O_3$) 606.2751, Found 606.2756.

## Toward helical pentacene 2




Scheme S2. Access to helical pentacene **2** from helicene **7**.

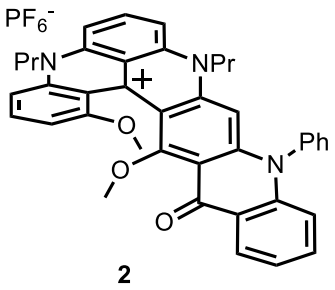
2-(2-bromobenzoyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate K2




A solution of helicene **7** (200 mg, 0.4 mmol, 1 equiv) and 2-bromobenzoic acid (161 mg, 1.6 mmol, 3 equiv) in Eaton's reagent (0.1 M) was stirred at 50 °C for 45 minutes. The reaction was cooled to 0 °C and quenched by addition of a 0.2 M solution of aqueous $NaBF_4$. The slurry was extracted with $CH_2Cl_2$, the organic layer was washed with an aqueous solution NaOH 10% then with aqueous $KPF_6$ 0.2 M, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography afforded the product as a blue solid in an acceptable purity to run the next step (traces of regioisomer not separable by flash chromatography) (255 mg, 93%).

**R*f*:** 0.57 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **M. P.:** 178 °C (decomposition). **$^1$H NMR ($CD_2Cl_2$, 400 MHz):** δ = 8.34 (t, *J* = 8.5 Hz, 1H), 8.07 (dd, *J* = 9.3, 1.3 Hz, 1H), 7.96 (t, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.58 (dd, *J* = 9.0, 6.4 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.42 – 7.33 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.77 – 4.62 (m, 2H), 4.61 – 4.40 (m, 2H), 3.78 (s, 3H), 2.81 (s, 3H), 2.25 – 2.06 (m, 4H), 1.27 – 1.21 (m, 6H). **$^{13}$C NMR ($CD_2Cl_2$, 125 MHz):** δ = 194.1, 161.9, 160.5, 144.9, 143.2, 142.7, 142.2, 139.3, 139.3, 138.9, 138.2, 138.0, 134.0, 132.4, 129.9, 128.2, 124.6, 120.1, 119.7, 115.1, 113.2, 111.2, 107.8, 106.9, 106.3, 104.5, 62.7, 56.5, 52.4, 52.3, 30.3, 20.6, 20.6, 11.4, 11.4. **$^{19}$F NMR ($CD_2Cl_2$, 282 MHz):** δ = -73.46 (d, *J* = 710.8 Hz). **IR (neat, cm$^{-1}$):** ν = 2925, 2854, 1656, 1602, 1577, 1555, 1495, 1462, 1339, 1250, 1170, 1130, 1048, 954, 918, 901, 818, 761. **HRMS (ESI+)** calculated for [M]+: ($C_{34}H_{32}BrN_2O_3$), 595.1591 Found 595.1600.

1,17-dimethoxy-16-oxo-11-phenyl-5,9-dipropyl-5,9,11,16-tetrahydro-17b*H*-pyrido[3,2-*b*:6,5,4-*k'l'*]diacridin-17b-ylium hexafluorophosphate 2

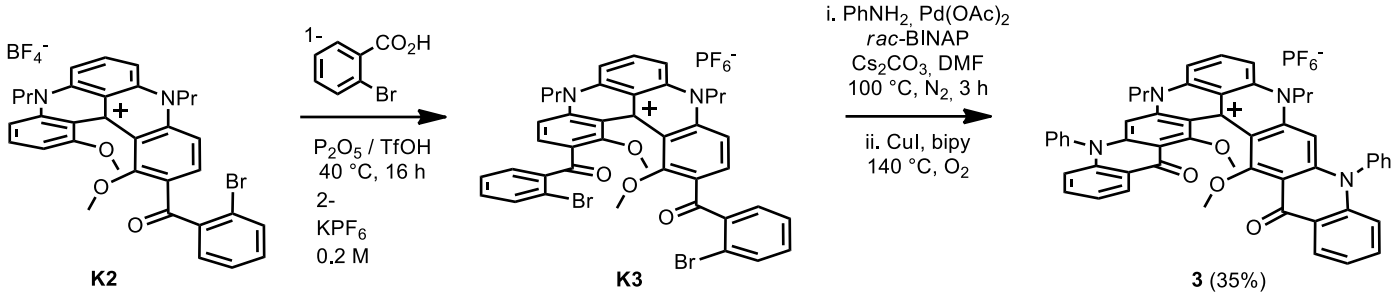


**2**

$Pd(OAc)_2$ (3,4 mg, 0,015 mmol, 10 mol%) and *rac*-BINAP (19 mg, 0,03 mmol, 20 mol%) were mixed in 0.5 mL of dry and degassed DMF under $N_2$. The reaction mixture was then warmed to 90 °C. After 15 minutes of stirring, the solution turned red. In a second round bottomed flask under $N_2$, 2-(2-bromobenzoyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate (**K2**) (50 mg, 0,07 mmol, 1 equiv), $Cs_2CO_3$ (95 mg, 0,29 mmol, 4 equiv) and aniline (20 µL, 0,22 mmol, 3 equiv) were dissolved in dry and degassed DMF (2 mL). The Pd/BINAP complex was then added to this mixture *via* a cannula and the reaction was stirred at 90 °C for 1 hour. Then, the reaction flask was opened to air and CuI (5,7 mg, 0,03 mmol, 40 mol%) and 2,2'-bipyridine (4,7 mg, 0,03 mmol, 40 mol%) were added. The reaction was warmed to 100 °C and stirred under air for 15 minutes. The reaction was then allowed to be cooled to room temperature. The reaction was hydrolysed at 0 °C by addition of a 1 M aqueous solution of $HBF_4$. The crude mixture was extracted with $CH_2Cl_2$, washed with 0.2 M solution of $KPF_6$, dried over $Na_2SO_4$, filtered then concentrated under vacuum. Purification by column chromatography afforded the pure product as a blue solid (23 mg, 45%).

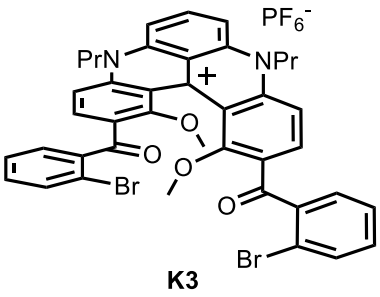
**R*f*:** 0.55 ($SiO_2$, $CH_2Cl_2$/Acetone, 95:5). **M. P.:** 294 °C (decomposition). **$^1$H NMR ($CD_2Cl_2$, 500 MHz):** δ = 8.45 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.18 (t, *J* = 8.5 Hz, 1H), 7.97 (dd, *J* = 8.9, 8.0 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.84 – 7.78 (m, 1H), 7.60 – 7.56 (m, 2H), 7.55 – 7.51 (m, 1H), 7.50 – 7.48 (m, 1H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.37 – 7.33 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.32 (s, 1H), 4.75 – 4.65 (m, 1H), 4.56 – 4.47 (m, 1H), 4.15 – 4.07 (m, 1H), 3.93 – 3.84 (m, 1H), 3.82 (s, 3H), 3.44 (s, 3H), 2.24 – 2.09 (m, 2H), 2.05 – 1.93 (m, 1H), 1.64 – 1.55 (m, 2H), 1.25 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR ($CD_2Cl_2$, 125 MHz):** δ = 176.5, 166.7, 161.1, 150.1, 143.1, 143.0, 142.5, 139.6, 139.2, 139.2, 138.4, 137.3, 134.5, 132.5, 132.3, 131.0, 130.2, 130.1, 127.8, 123.7, 123.4, 118.7, 117.5, 113.4, 111.5, 111.3, 107.5, 106.3, 105.7, 104.4, 94.9, 63.7, 56.4, 52.4, 52.1, 20.8, 19.3, 11.4, 10.9. **$^{19}$F NMR (DMSO-*d6*, 282 MHz):** δ = - 73.55 (d, *J* = 710.5 Hz). **UV-vis:** $\lambda_{max}$ ($CH_3CN$) = 620 nm (ε = 14600 $L.mol^{-1}.cm^{-1}$). **IR (neat, $cm^{-1}$):** ν = 2938, 1647, 1570, 1467, 1378, 1324, 1263, 1171, 1134, 836, 759. **HRMS (ESI+)** calculated for [M]+: ($C_{40}H_{36}N_3O_3$) 606.2751, Found 606.2756.

**Toward helical pentacene 3**




Scheme S3. Access to pentacene **3** from **K2**.

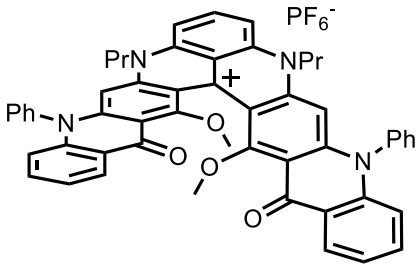
2,12-bis(2-bromobenzoyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium hexafluorophosphate K3




A solution of 2-(2-bromobenzoyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate (**K2**) (150 mg, 0.22 mmol, 1 equiv) and 2-bromobenzoic acid (133 mg, 0.66 mmol, 3 equiv) in a $P_2O_5$/TfOH mixture (0.1 M) was stirred at 40 °C for 16 hours. The reaction was cooled to 0 °C and quenched by addition of a 0.2 M solution of aqueous $NaBF_4$. The slurry was extracted with $CH_2Cl_2$, the organic layer was washed with an aqueous solution NaOH 10% then with aqueous $KPF_6$ 0.2 M, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography afforded the product as a blue solid in an acceptable purity to run the next step (traces of starting material not separable by flash chromatography) (80 mg, 40%).

**R*f*:** 0.73 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **M. P.:** 204 °C (decomposition). **$^1$H NMR ($CD_2Cl_2$, 500 MHz):** δ = 8.41 (t, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 9.3 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.68 – 7.63 (m, 2H), 7.59 (d, *J* = 9.3 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.37 – 7.32 (m, 2H), 4.78 – 4.68 (m, 2H), 4.61 – 4.47 (m, 2H), 3.04 (s, 6H), 2.26 – 2.16 (m, 2H), 2.17 – 2.05 (m, 2H), 1.25 (t, *J* = 7.4 Hz, 6H). **$^{13}$C NMR ($CD_2Cl_2$, 125 MHz):** δ = 193.4, 161.7, 144.9, 143.5, 141.2, 139.3, 138.8, 138.8, 138.7, 134.1, 132.8, 130.9, 128.3, 124.7, 120.6, 120.1, 115.1, 111.1, 107.4, 63.3, 52.5, 20.7, 11.4. **$^{19}$F NMR ($CD_2Cl_2$, 282 MHz):** δ = -73.46 (d, J = 710.7 Hz). **IR (neat, cm$^{-i1}$):** ν = 2967, 1659, 160, 1571, 1555, 1493, 1466, 1431, 1370, 1339, 1255, 1226, 1171, 1127, 1078, 1014, 979, 916, 837. **HRMS (ESI+)** calculated for [M]+: ($C_{41}H_{35}N_2Br_2O_4$) 777.0958, Found 777.0970.

Helical pentacene 3

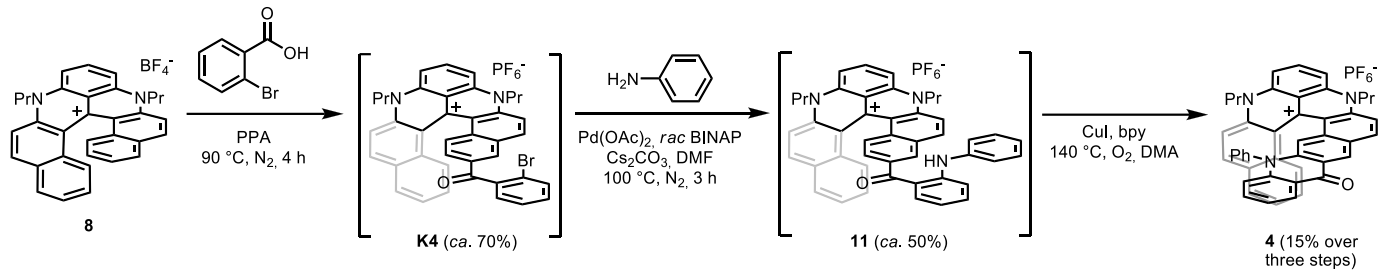



**3**

$Pd(OAc)_2$ (1.4 mg, 0.006 mmol, 10 mol%) and *rac*-BINAP (7.5 mg, 0.012 mmol, 20 mol%) were mixed in 0.5 mL of dry and degassed DMF under $N_2$. The reaction mixture was then warmed to 90 °C. After 15 minutes of stirring, the solution turned red. In a second round bottomed flask under $N_2$, 2-(2-bromobenzoyl)-1,13-dimethoxy-5,9-dipropyl-5,9-dihydro-13b*H*-quinolino[2,3,4-*kl*]acridin-13b-ylium hexafluorophosphate (**K3**) (50 mg, 0.06 mmol, 1 equiv), $Cs_2CO_3$ (139 mg, 0.42 mmol, 7 equiv) and aniline (33 µL, 0.37 mmol, 6 equiv) were dissolved in dry and degassed DMF (2 mL). The Pd/BINAP complex was then added to this mixture *via* a cannula and the reaction was stirred at 90 °C for 1 hour. Then, the reaction flask was opened to air and CuI (2.3 mg, 0.012 mmol, 20 mol%) and 2,2'-bipyridine (3.7 mg, 0.024 mmol, 40 mol%) were added. The reaction was warmed to 100 °C and stirred under air atmosphere for 15 minutes. The reaction was then allowed to be cooled to room temperature. The reaction was hydrolysed at 0 °C by addition of a 1 M aqueous solution of $HBF_4$. The crude mixture was extracted with $CH_2Cl_2$, washed with 0.2 M solution of $KBF_6$, dried over $Na_2SO_4$, filtered then concentrated under vacuum. Purification by column chromatography afforded the pure product as a purple solid (19 mg, 35%).

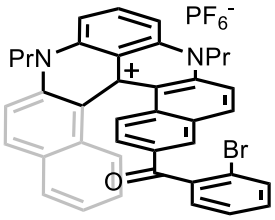
**R*f*:** 0.29 ($SiO_2$, $CH_2Cl_2$/Acetone, 95:5). **M. P.:** 291-293 °C (decomposition). **$^1$H NMR (DMSO-*d6*, 500 MHz):** δ = 8.29 (dd, *J* = 8.0, 1.7 Hz, 2H), 8.17 (t, *J* = 8.5 Hz, 1H), 7.95 – 7.88 (m, 4H), 7.88 – 7.79 (m, 5H), 7.72 – 7.66 (m, 6H), 7.39 (t, *J* = 7.4 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.32 (s, 2H), 4.33 – 4.21 (m, 2H), 3.97 – 3.87 (m, 2H), 3.35 (s, 6H), 1.90 – 1.84 (m, 2H), 1.52 – 146 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 6H). **$^{13}$C NMR (DMSO-*d6*, 125 MHz):** δ = $^{13}$C NMR (126 MHz, DMSO) δ 176.0, 165.1, 149.3, 142.4, 142.4, 138.5, 138.4, 137.0, 134.3, 131.8, 131.7, 130.2, 129. 9, 129.5, 126.7, 122.8, 122.8, 116.9, 116.7, 110.6, 106.5, 94.0, 62.8, 50.5, 18.4, 10.4, 10.4. **$^{19}$F NMR (DMSO-*d6*, 282 MHz):** δ = -70.16 (d, *J* = 710.9 Hz). **UV-vis:** $\lambda_{max}$ ($CH_3CN$) = 572 nm (ε = 16400 $L.mol^{-1}.cm^{-1}$). **IR (neat, cm$^{-1}$):** ν = 2928, 1642, 1582, 1558, 1470, 1374, 1312, 1272, 1187, 1118, 1074 969, 836, 759, 731, 700, 658. **HRMS (ESI+)** calculated for [M]+: ($C_{53}H_{43}N_4O_4$) 799.3279, Found 799.3277.

## Toward helical tetracene 4




Scheme S4. Access to helical tetracene **4** from cationic [6]helicene **8.**

3-(2-bromobenzoyl)-7,11-dipropyl-7,11-dihydro-17cH-benzo[a]phenanthro[2,3,4-kl]acridin-17c-ylium hexafluorophosphate K4.

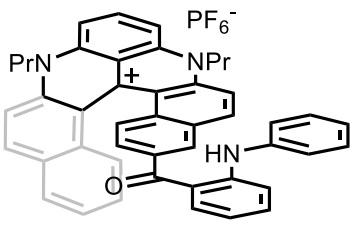



**K4**

7,11-dipropyl-7,11-dihydro-17cH-benzo[a]phenanthro[2,3,4-kl]acridin-17c-ylium tetrafluoroborate **8** (54 mg, 0.1 mmol) and 2-bromobenzoic acid (80 mg, 0.4 mmol, 4 equiv.) were charged in a round bottom flask equipped with a septum and a stirring bar that was purged with $N_2$ (x 3). PPA (4 mL) was then added and the reaction mixture was stirred at 90 °C while the evolution of the reaction was monitored by MS spectroscopy. After 4 h, the completion of the reaction was reached. At room temperature, the reaction mixture was diluted with $H_2O$. A spatula of $KPF_6$ was added to this solution that was extracted with $CH_2Cl_2$ until the aqueous layer was almost colorless. The organic layer was washed with a 1 M aqueous solution of NaOH (x 2) and then with a 0.2 M aqueous solution of $KPF_6$ (x 2). Next, the organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. This was repeated twice. The product was then purified by flash chromatography (CombiFlash, $SiO_2$ 4 g cartridge, $CH_2Cl_2$/MeOH, 100:0 to 97:03 over 60 min) followed by a selective precipitation ($CH_2Cl_2$/$Et_2O$, see above), yielding the **K4** as a blue powder and of a sufficient purity for the next step (54 mg, *ca.* 70% yield).

**R*f***: 0.43 ($SiO_2$, $CH_2Cl_2$/MeOH, 95/5). **$^1$H NMR (500 MHz, $CD_2Cl_2$):** δ = 8.41 (d, *J* = 9.5 Hz, 1H), 8.38 (d, *J* = 9.5 Hz, 1H), 8.32 (t, *J* = 8.5 Hz, 1H), 8.20 (s, 1H), 8.02 (d, *J* = 9.5 Hz, 1H), 7.97 (d, *J* = 9.4 Hz, 1H), 7.92 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.32 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.00 – 6.76 (m, 1H), 4.87 (dddd, *J* = 19.4, 15.4, 11.5, 5.6 Hz, 2H), 4.60 (dtt, *J* = 21.2, 10.6, 5.7 Hz, 1H), 2.39 – 2.07 (m, 4H), 1.32 (td, *J* = 7.3, 4.3 Hz, 6H). **$^{13}$C NMR (125 MHz, $CD_2Cl_2$):** δ = 194.9 (C), 143.8 (C), 142.8 (C), 142.0 (C), 140.4 (C), 140.1 (C*H*), 139.7 (C*H*), 138.5 (C), 138.4 (C), 136.0 (C*H*), 134.8 (C), 133.7 (C*H*), 132.7 (C), 132.1 (C*H*), 132.1 (C), 129.8 (C), 129.7 (C*H*), 129.4 (C), 129.3 (C*H*), 129.1 (C), 128.6 (C*H*), 128.3 (C*H*), 128.1 (C), 128.0 (C*H*), 127.5 (C), 127.5 (C*H*), 123.5 (C*H*), 123.1 (C), 122.1 (C), 119.8 (C), 116.9 (C), 116.7 (C*H*), 115.9 (C), 115.3 (C*H*), 107.6 (C*H*), 107.5 (C*H*), 52.4 (C$H_2$), 52.2 (C$H_2$), 21.0 (C$H_2$), 20.9 (C$H_2$), 11.3 (C$H_3$), 11.3 (C$H_3$). **$^{19}$F NMR (282 MHz, $CD_2Cl_2$):** δ -73.26 (d, *J* = 711.0 Hz). **$^{31}$P NMR (121 MHz, $CD_2Cl_2$):** δ = -132.77, -138.62, -144.47, -150.32, -156.17. **HRMS (ESI+)** calc: 635.1693; found: 635.1689.

3-(2-(phenylamino)benzoyl)-7,11-dipropyl-7,11-dihydro-17cH-benzo[a]phenanthro[2,3,4-kl]acridin-17c-ylium hexafluorophosphate 11

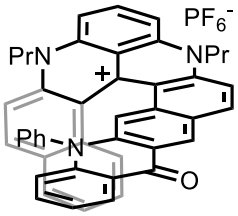


**11**

**K4** (50 mg, 0.064 mmol), $Pd(OAc)_2$ (1.4 mg, 0.0064 mmol, 0.1 equiv.), *rac* BINAP (8.2 mg, 0.013 mmol, 0.2 equiv.) and $Cs_2CO_3$ (63 mg, 0.0.192 mmol, 3 equiv.) were charged in a MW vial equipped with a stirring bar that was next sealed and purged with $N_2$ (x 3). Dry DMF (1 mL) and aniline (18 µL, 0.192 mmol, 3 equiv.) were then added and the reaction mixture was stirred at 100 °C while the evolution of the reaction was monitored by MS spectroscopy. After 3 h, the completion of the reaction was reached. At room temperature, the reaction mixture was diluted with $CH_2Cl_2$ and washed with a 1 M aqueous solution of HCl (x 5) and then with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$ and pentane. The mother liquor was separated from the precipitate by centrifugation. This was repeated two times. The product was then purified by flash chromatography (CombiFlash, $SiO_2$ 4 g cartridge, $CH_2Cl_2$/MeOH, 100:0 to 97:03 over 60 min) followed by a selective precipitation ($CH_2Cl_2$/$Et_2O$, see above), yielding the title compound as a green powder and of a sufficient purity for the next step (24 mg, *ca.* 50% yield).

**R*f***: 0.40 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **$^1$H NMR (500 MHz, $CD_2Cl_2$):** δ = 10.00 (s, 1H), 8.45 (d, *J* = 9.4 Hz, 1H), 8.42 (d, *J* = 9.4 Hz, 1H), 8.32 (t, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 1.8 Hz, 1H), 8.03 (d, *J* = 9.5 Hz, 1H), 7.98 (d, *J* = 9.5 Hz, 1H), 7.95 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.73 (t, *J* = 8.2 Hz, 2H), 7.45 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.38 – 7.33 (m, 4H), 7.29 – 7.17 (m, 5H), 7.14 – 7.06 (m, 2H), 6.94 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 6.71 (ddd, *J* = 8.1, 6.4, 1.8 Hz, 1H), 4.88 (ddt, *J* = 15.4, 11.6, 5.8 Hz, 2H), 4.60 (dtd, *J* = 15.7, 11.6, 10.5, 5.3 Hz, 2H), 2.66 – 2.00 (m, 4H), 1.40 – 1.24 (m, 6H). **$^{13}$C NMR (125 MHz, $CD_2Cl_2$):** δ = 197.7 (C), 148.5 (C), 143.3 (C), 142.8 (C), 141.9 (C), 140.8 (C), 139.8 (C*H*), 139.6 (C*H*), 138.5 (C), 138.4 (C), 138.4 (C), 135.9 (C*H*), 135.0 (C*H*), 134.9 (C*H*), 131.1 (C), 130.4 (C*H*), 129.9 (2 C*H*), 129.8 (C*H*), 129.5 (C), 129.2 (C*H*), 128.9 (C), 128.3 (C*H*), 128.1 (C*H*), 128.0 (C*H*), 124.1 (C*H*), 123.3 (C*H*), 122.9 (C*H*), 122.5 (2 C*H*), 122.3 (C), 122.0 (C), 119.8 (C), 117.1 (C*H*), 116.7 (C), 116.5 (C*H*), 116.0 (C), 115.4 (C*H*), 115.1 (C*H*), 107.4 (C*H*), 107.3 (C*H*), 52.3 (C$H_2$), 52.2 (C$H_2$), 21.0 (C$H_2$), 20.9 (C$H_2$), 11.3 (2 C$H_3$). **$^{19}$F NMR (282 MHz, $CD_2Cl_2$):** δ -73.27 (d, *J* = 710.7 Hz). **$^{31}$P NMR (121 MHz, $CD_2Cl_2$):** δ = -132.75, -138.60, -144.45, -150.30, -156.15. **HRMS (ESI+)** calc: 648.3010; found: 648.2993.

Helical tetracene 4



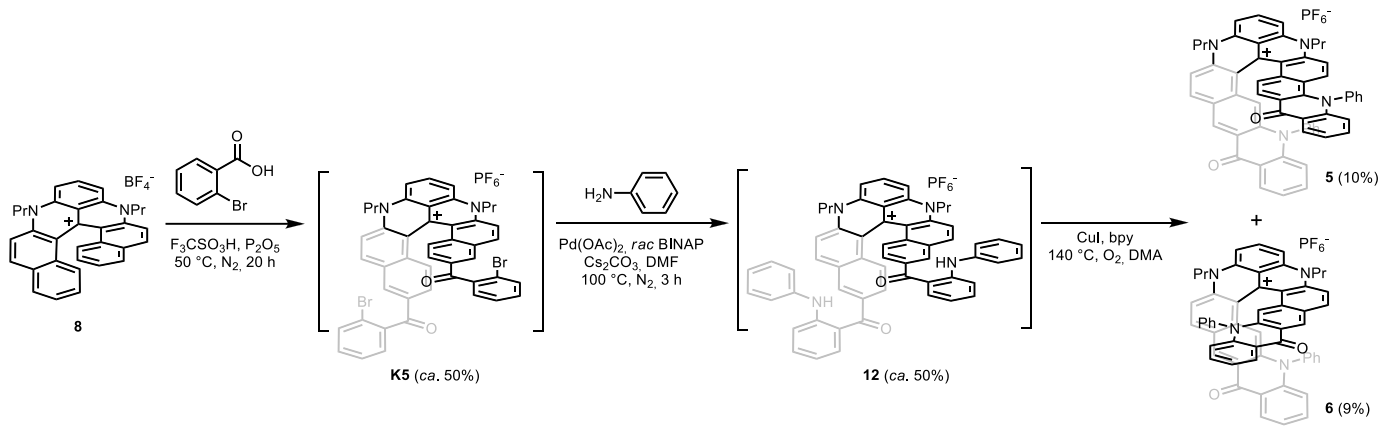
**4**

**11** (20 mg, 0.025 mmol), CuI (0.5 mg, 0.0025 mmol, 0.1 equiv.), 2,2'-bipyridine (0.4 mg, 0.0025 mmol, 0.1 equiv.) were charged in a MW vial equipped with a stirring bar. The vial was sealed, DMA (1 mL) was added and the reaction mixture was purged with a flow of $O_2$ and then heated at 140 °C. The evolution of the reaction was monitored by MS spectroscopy. After 4 h, the completion of the reaction was reached. At room temperature, the reaction mixture was diluted with $CH_2Cl_2$ and washed with a 1 M aqueous solution of HCl (x 5) and then with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with a mixture of $Et_2O$ and pentane. The mother liquor was separated from

the precipitate by centrifugation. Compound **4** was purified with a series of chromatography. First, a flash chromatography on neutral aluminum oxide (20 x 1.5 cm, $CH_2Cl_2$/MeOH, 100:0 to 97:03) allowed a substantial removal of various impurities. The fractions containing the title compound were condensed to dryness, dissolved in $CH_2Cl_2$ and washed with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. Second, a preparative thin layer chromatography ($SiO_2$ on aluminum, 20 x 20 cm, elution system: $CH_2Cl_2$/acetone 90:10, eluted twice) allowed further cleaning of the compound. The product was extracted from the silica by solid – liquid extraction with a mixture of $CH_2Cl_2$ and MeOH, 95:05. The combined liquid layers were evaporated, dissolved in $CH_2Cl_2$ and washed with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. Third, the title compound was further purified by preparative thin layer chromatography ($SiO_2$ on aluminum, 20 x 20 cm, elution system: $CH_2Cl_2$/acetone 90:10, eluted twice). The product was extracted from the silica by solid – liquid extraction with a mixture of $CH_2Cl_2$ and MeOH, 95:05. The combined liquid layers were evaporated, dissolved in $CH_2Cl_2$ and washed with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. 8 mg of clean **4** were obtained (15% yield in three steps from **8**).

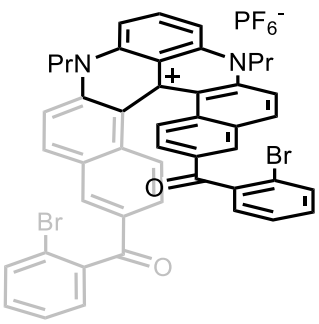
**R*f***: 0.46 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **M. P.:** 242-244 °C (decomposition). **$^1$H NMR (500 MHz, $CD_2Cl_2$):** δ = 9.09 (s, 1H), 8.52 (d, *J* = 9.1 Hz, 1H), 8.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.28 (d, *J* = 9.2 Hz, 1H), 8.23 (t, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.77 (d, *J* = 9.5 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.42 (ddd, *J* = 8.7, 6.9, 1.7 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.26 – 7.19 (m, 2H), 6.85 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 6.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.74 (s, 1H), 6.48 (ddd, *J* = 5.6, 3.6, 2.3 Hz, 1H), 6.38 (d, *J* = 8.6 Hz, 1H), 4.82 – 4.75 (m, 1H), 4.73 – 4.67 (m, 1H), 4.59 – 4.48 (m, 2H), 2.31 – 2.03 (m, 4H), 1.29 (d, *J* = 7.4 Hz, 3H), 1.22 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR (125 MHz, $CD_2Cl2$):** δ = 178.1 (C), 144.6 (C), 144.1 (C), 142.5 (C), 142.4 (C), 141.4 (C), 140.5 (C*H*), 140.3 (C*H*), 138.2 (C), 138.1 (C), 138.0 (C), 135.4 (C*H*), 134.4 (C*H*), 133.3 (C), 132.5 (C*H*), 131.1 (C*H*), 129.7 (C*H*), 129.7 (C), 129.6 (C*H*), 129.5 (C*H*), 129.2 (C*H*), 129.0 (C*H*), 128.4 (C*H*), 128.4 (C*H*), 127.9 (C), 127.2 (C*H*), 124.0 (C), 122.6 (C*H*), 122.3 (C*H*), 122.2 (C), 121.9 (C), 121.6 (C), 117.4 (C*H*), 115.9 (C), 115.5 (C), 115.4 (C*H*), 113.8 (C*H*), 109.2 (C*H*), 107.6 (C*H*), 107.1 (C*H*), 52.3 (C$H_2$), 51.8 (C$H_2$), 21.0 (C$H_2$), 21.0 (C$H_2$), 11.3 (2C$H_3$). **$^{19}$F NMR (282 MHz, $CD_2Cl_2$):** δ = -73.19 (d, *J* = 710.7 Hz). **IR (neat, cm$^{-1}$):** ν = 2962, 2929, 2875, 1646, 1606, 1526, 1512, 1492, 1470, 1407, 1337, 1322, 1264, 1217, 1180, 1166, 1142, 1104, 1056, 839, 757, 702. **UV-vis:** $\lambda_{max}$ ($CH_3CN$) = 615 nm (ε = 12600 L.mol$^{-1}$.cm$^{-1}$). **HRMS (ESI+)** calc.: 646.2853; found: 646.2853.

**Toward helical tetracenes 5 and 6.**




Scheme S5. Access to helical etracenes **5** and **6** from [6]helicene **8**.

**3,15-bis(2-bromobenzoyl)-7,11-dipropyl-7,11-dihydro-17cH-benzo[a]phenanthro[2,3,4-kl]acridin-17c-ylium hexafluorophosphate K5.**



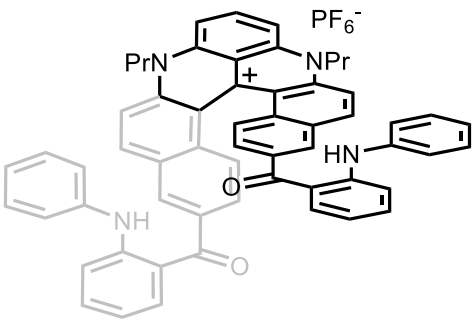
**K5**

A mixture of $F_3CSO_3H$ (2 mL) and $P_2O_5$ (600 mg) was stirred in a round bottom flask equipped with a septum and a stirring under $N_2$ atmosphere at 50 °C for 1 h. Next and still at this temperature, 7,11-dipropyl-7,11-dihydro-17cH-benzo[a]phenanthro[2,3,4-kl]acridin-17c-ylium tetrafluoroborate **8** (54 mg, 0.1 mmol, 1 equiv) and 2-bromobenzoic acid (80 mg, 0.4 mmol, 4 equiv.) were added to this mixture. The evolution of the reaction was monitored by MS spectroscopy. After 20 h, the completion of the reaction was reached. At room temperature, the reaction mixture was poured into ice. A spatula of $KPF_6$ was added to this solution that was extracted with $CH_2Cl_2$ until the aqueous layer was almost colorless. The organic layer was washed with a 1 M aqueous solution of NaOH (x 2) and then with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. This was repeated two times. The product was then purified by flash chromatography (CombiFlash, $SiO_2$ 4 g cartridge, $CH_2Cl_2$/MeOH, 100:0 to 97:03 over 60 min), repeated twice, and a flash chromatography ($SiO_2$ 25 x 1 cm, $CH_2Cl_2$/acetone, 100:0 to 98:02), followed each time by a selective precipitation ($CH_2Cl_2$ / $Et_2O$, see above). **K5** was obtained as a blue powder and of a sufficient purity for the next step (40 mg, *ca.* 50% yield).

**R*f***: 0.38 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **$^1$H NMR (500 MHz, $CD_2Cl_2$):** δ = 8.43 – 8.32 (m, 3H), 8.15 (d, *J* = 1.8 Hz, 2H), 8.02 (d, *J* = 9.5 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.49 (td, *J* = 7.4, 1.2 Hz, 2H), 7.44 (td, *J* = 7.7, 1.8 Hz, 2H), 7.38 – 7.31 (m, 4H), 7.29 – 7.27 (m, 2H), 4.87 (ddd, *J* = 15.3, 11.5, 5.6 Hz, 2H), 4.61 (ddd, *J* = 16.0, 11.4, 5.3 Hz, 2H), 2.50 – 2.04 (m, 4H), 1.32 (t, *J* = 7.4 Hz, 6H). **$^{13}$C NMR (125 MHz, $CD_2Cl_2$):** δ = 194.8 (C), 143.9 (C), 142.3 (C), 140.3 (C), 140.1 (C*H*), 138.4 (C), 136.4 (C*H*), 135.1 (C), 133.7 (C*H*), 132.7 (C), 132.5 (C*H*), 132.1 (C*H*), 129.7 (C*H*), 129.2 (C), 128.0 (C*H*), 127.5 (C*H*), 123.5 (C*H*), 122.2 (C), 119.9 (C), 116.6 (C*H*), 116.1 (C), 108.0 (C*H*), 52.4 (C$H_2$), 21.0 (C$H_2$), 11.2 (C$H_3$). **$^{19}$F**

**NMR (282 MHz, $CD_2Cl_2$):** δ -73.27 (d, *J* = 710.7 Hz). **$^{31}$P NMR (121 MHz, $CD_2Cl_2$):** δ = -132.82, -138.67, -144.52, -150.37, -156.22. **HRMS (ESI+)** calc: 819.1045; found: 819.1034.

3,15-bis(2-(phenylamino)benzoyl)-7,11-dipropyl-7,11-dihydro-17cH-benzo[a]phenanthro[2,3,4-kl]acridin-17c-ylium hexafluorophosphate 12

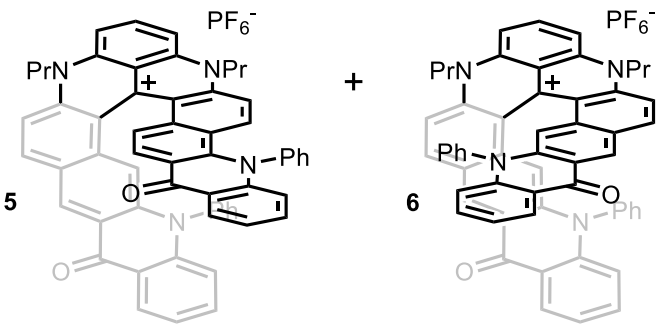



**12**

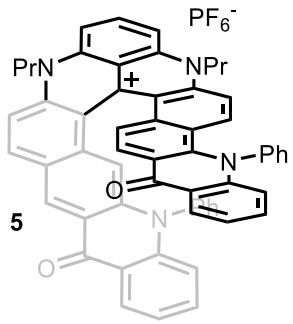
**K5** (40 mg, 0.041 mmol), $Pd(OAc)_2$ (1.9 mg, 0.0082 mmol, 0.2 equiv.), *rac* BINAP (10 mg, 0.0164 mmol, 0.4 equiv.) and $Cs_2CO_3$ (54 mg, 0.0.164 mmol, 4 equiv.) were charged in a MW vial equipped with a stirring bar that was next sealed and purged with $N_2$ (x 3). Dry DMF (1 mL) and aniline (15 µL, 0.164 mmol, 3 equiv.) were then added and the reaction mixture was stirred at 100 °C while the evolution of the reaction was monitored by MS spectroscopy. After 3 h, the completion of the reaction was reached. At room temperature, the reaction mixture was diluted with $CH_2Cl_2$ and washed with a 1 M aqueous solution of HCl (x 5) and then with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$ and pentane. The mother liquor was separated from the precipitate by centrifugation. This was repeated two times. The product was then purified by flash chromatography (CombiFlash, $SiO_2$ 4 g cartridge, $CH_2Cl_2$/MeOH, 100:0 to 97:03 over 60 min) followed by a selective precipitation ($CH_2Cl_2$ / $Et_2O$, see above), yielding the bis aniline derivative as a green powder and of a sufficient purity for the next step (25 mg, *ca.* 50% yield).

**R*f***: 0.37 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **$^1$H NMR (500 MHz, $CD_2Cl_2$):** δ = 9.95 (s, 2H), 8.48 (d, *J* = 9.5 Hz, 2H), 8.36 (t, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 1.8 Hz, 2H), 8.05 (d, *J* = 9.5 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.29 (m, 8H), 7.27 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.24 – 7.19 (m, 8H), 7.11 – 7.02 (m, 2H), 6.66 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 2H), 4.97 – 4.83 (m, 2H), 4.63 (ddd, *J* = 16.1, 11.4, 5.3 Hz, 2H), 2.41 – 2.13 (m, 4H), 1.34 (t, *J* = 7.4 Hz, 6H). **$^{13}$C NMR (125 MHz, $CD_2Cl_2$):** δ = 197.4 (2 C), 148.3 (2 C), 143.5 (2 C), 142.1 (C), 140.8 (2 C), 140.0 (2 C*H*), 138.8 (2 C), 138.5 (2 C), 136.2 (C*H*), 134.9 (2 C*H*), 134.8 (2 C*H*), 131.2 (2 C), 130. (2 C*H*), 129.8 (4 C*H*), 129.1 (2 C), 128.4 (2 C*H*), 124.0 (2 C*H*), 123.0 (2 C*H*), 122.4 (4 C*H*), 122.2 (C), 119.8 (2 C), 117.4 (2 C*H*), 116.5 (2 C*H*), 116.2 (2 C), 115.2 (2 C*H*), 107.7 (2 C*H*), 52.4 (2 C$H_2$), 21.0 (2 C$H_2$), 11.3 (2 C$H_3$). **$^{19}$F NMR (282 MHz, $CD_2Cl_2$):** δ = -73.31 (d, *J* = 711.0 Hz). **$^{31}$P NMR (121 MHz, $CD_2Cl_2$):** δ = -132.78, -138.63, -144.48, -150.34, -156.19. **HRMS (ESI+)** calc: 843.3694; found: 843.3707.

Mono tetracene 5 and bis tetracene 6

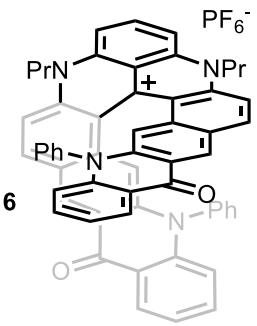



**12** (25 mg, 0.025 mmol), CuI (0.5 mg, 0.0025 mmol, 0.1 equiv.), 2,2'-bipyridine (0.4 mg, 0.0025 mmol, 0.1 equiv.) were charged in a MW vial equipped with a stirring bar. The vial was sealed, DMA (1 mL) was added and the reaction mixture was purged with a flow of $O_2$ and then heated at 140 °C. The evolution of the reaction was monitored by MS spectroscopy. After 6 h, the completion of the reaction was reached. At room temperature, the reaction mixture was diluted with $CH_2Cl_2$ and washed with a 1 M aqueous solution of HCl (x 5) and then with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. This was repeated two times. Compounds **5** and **6** were separated from impurities and isolated after a series of chromatography. The purifications were continuously monitored by MS spectroscopy as **5** and **6** display identical green colour and nearly identical $R_f$. First, a flash chromatography on neutral aluminum oxide (20 x 1.5 cm, $CH_2Cl_2$/MeOH, 100:0 to 97:03) allowed a substantial removal of various impurities. The fractions containing mixtures of **5** and **6** were combined and condensed to dryness, dissolved in $CH_2Cl_2$ and washed with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. Second, **5** and **6** were separated by preparative thin layer chromatography ($SiO_2$ on aluminum, 20 x 20 cm, elution system: $CH_2Cl_2$/acetone 90:10, eluted twice). Three fraction were isolated. The first fraction was discarded, containing mainly side produtcs. For each of the second and the third fraction, the product was extracted from the silica by solid – liquid extraction with a mixture of $CH_2Cl_2$ and MeOH, 95:05. The combined liquid layers were evaporated, dissolved in $CH_2Cl_2$ and washed with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. The second fraction afforded symmetrical **6** almost clean (10 mg). The third fraction afforded unsymmetrical **5** clean (10 mg, 10% yield in three steps from **8**). Third, symmetrical **6** was further purified by preparative thin layer chromatography ($SiO_2$ on aluminum, 20 x 20 cm, elution system: $CH_2Cl_2$/acetone 99:1, eluted five times). The product was extracted from the silica by solid – liquid extraction with a mixture of $CH_2Cl_2$ and MeOH, 95:05. The combined liquid layers were evaporated, dissolved in $CH_2Cl_2$ and washed with a 0.2 M aqueous solution of $KPF_6$ (x 2). The organic layer was dried over $Na_2SO_4$, filtered and evaporated. The resulting solid was dissolved in a minimum amount of $CH_2Cl_2$ and was precipitated with $Et_2O$. The mother liquor was separated from the precipitate by centrifugation. 9 mg of clean symmetrical **6** were obtained (9% yield in three steps from **8**).




**5**

**R*f***: 0.38 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **M. P.:** 282-284 °C (decomposition). **$^1$H NMR (500 MHz, $CD_2Cl_2$):** δ = 9.09 (s, 1H), 8.56 (d, *J* = 9.4 Hz, 1H), 8.39 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.34 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.25 – 8.18 (m, 2H), 7.94 (d, *J* = 9.1 Hz, 1H), 7.84 – 7.74 (m, 4H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.48 (m, 4H), 7.43 – 7.27 (m, 5H), 7.22 – 7.15 (m, 3H), 6.89 (s, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.41 – 6.39 (m, 2H), 4.84 – 4.78 (m, 1H), 4.58 – 4.52 (m, 2H), 4.45 – 4.29 (m, 1H), 2.26 – 2.13 (m, 2H), 2.04 – 1.84 (m, 2H), 1.30 (t, *J* = 7.4 Hz, 3H), 1.15 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (125 MHz, $CD_2Cl_2$):** δ = 177.9 (C), 177.1 (C), 145.3 (C), 144.4 (C), 144.2 (C), 144.1 (C), 142.6 (C), 142.1 (C), 142.0 (C), 141.8 (C), 141.0 (C*H*), 138.3 (C), 138.3 (C*H*), 138.0 (C), 136.3 (C), 135.8 (C*H*), 134.4 (C*H*), 134.0 (C), 133.9 (C*H*), 133.7 (C), 131.9 (2C*H*), 131.7 (C*H*), 131.6 (C*H*), 130.7 (2C*H*), 130.57 (C*H*), 129.7 (C*H*), 129.6 (C*H*), 129.5 (C*H*), 129.3 (C*H*), 127.4 (C*H*), 126.9 (C*H*), 126.3 (C*H*), 124.0 (C), 123.7 (C*H*), 123.2 (C), 122.8 (C), 122.6 (C), 122.4 (C*H*), 122.0 (C), 121.8 (C), 120.5 (C), 119.1 (C*H*), 117.3 (C*H*), 117.1 (C*H*), 117.0 (C), 116.3 (C), 113.6 (C*H*), 113.5 (C), 108.6 (C*H*), 107.8 (C), 107.5 (C*H*), 52.3 ($CH_2$), 50.9 ($CH_2$), 21.1 ($CH_2$), 20.8 ($CH_2$), 11.3 ($CH_3$), 11.2 ($CH_3$). **$^{19}$F NMR (282 MHz, $CD_2Cl_2$):** δ = -73.26 (d, *J* = 710.7 Hz). **IR (neat, cm$^{-1}$):** ν = 3032, 2970, 2929, 2875, 1740, 1644, 1605, 1525, 1490, 1470, 1400, 1366, 1283, 1217, 1159, 1107, 1025, 840, 758, 703. **UV-vis:** $\lambda_{max}$ ($CH_3CN$) = 625 nm (ε = 9000 L.mol$^{-1}$.cm$^{-1}$). **HRMS (ESI+)** calc.: 839.3381; found: 839.3421.



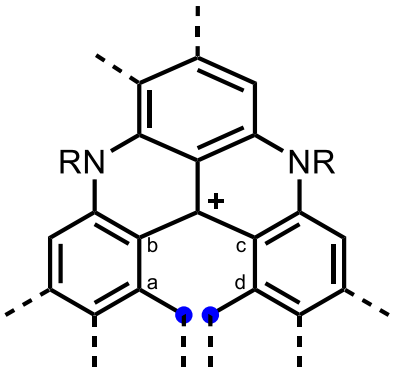

**6**

**R*f***: 0.43 ($SiO_2$, $CH_2Cl_2$/MeOH, 95:5). **M. P.:** 352 °C (decomposition). **$^1$H NMR (500 MHz, $CD_2Cl_2$):** δ = 9.06 (s, 2H), 8.38 – 8.29 (m, 4H), 8.19 (t, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.70 (tt, *J* = 7.6, 1.2 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 9.5 Hz, 2H), 7.40 – 7.34 (m, 4H), 7.18 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 2H), 6.91 (s, 2H), 6.74 (d, *J* = 2.3 Hz, 2H), 6.65 (d, *J* = 2.3 Hz, 2H), 6.32 (d, *J* = 8.6 Hz, 2H), 4.67 – 4.60 (m, 2H), 4.53 – 4.47 (m, 2H), 2.40 – 1.97 (m, 4H), 1.22 (t, *J* = 7.3 Hz, 6H). **$^{13}$C NMR (125 MHz, $CD_2Cl_2$):** δ = 178.0 (2C), 144.4 (2C), 144.2 (2C), 142.7 (2C), 141.4 (2C*H*), 141.2 (C), 138.2 (2C), 137.9 (2C), 135.3 (C*H*), 134.5 (2C*H*), 132.7 (2C*H*), 131.9 (2C), 131.2 (2C*H*), 129.8 (2C*H*), 129.7 (2C*H*), 129.6 (4C*H*), 127.1 (2C*H*), 123.8 (2C), 122.6 (2C), 122.4 (2C*H*), 121.8 (C), 121.6 (2C), 117.4 (2C*H*), 114.9 (C), 113.5 (2C*H*), 108.2 (2C*H*), 107.7 (2C*H*), 52.0 (2$CH_2$), 21.0 (2$CH_2$), 11.2 (2$CH_3$). **$^{19}$F NMR (282 MHz, $CD_2Cl_2$):** δ = -73.31 (d, *J* = 710.7 Hz). **IR (neat, cm$^{-1}$):** ν = 2975, 2924, 1740, 1646, 1604, 1524, 1469, 1408, 1367, 1280, 1223, 1178, 1030, 841, 759, 702, 638. **UV-vis:** $\lambda_{max}$ ($CH_3CN$) = 616 nm (ε = 8400 L.mol$^{-1}$.cm$^{-1}$). **HRMS (ESI+)** calc.: 839.3381; found: 839.3421.

# 3. X-ray structure determination

## Key geometrical parameters

**Table S 1. Key geometrical parameters from solid-state structures and *ab initio* calculations.**




| Helical acene | Dihedral angle[a] | Helical pitch[b] | Helical pitch[c] |
|---|---|---|---|
| **1** | | | 2.66 Å |
| **2** | 46.8° | 2.66 Å | 2.61 Å |
| **3** | | | 2.59 Å |
| **4** | 44.7° | 3.09 Å | 3.18 Å |
| **5** | | | 3.15 Å |
| **6** | 50.8° | 3.28 Å | 3.20 Å |

[a] The dihedral angle a-b-c-d defining the fjord region is a common descriptor of the [4] and the [6]helicene scaffolds.

[b] Determined from the solid-state structure

[c] Determined from *ab initio* calculations in acetonitrile (see section 6 for details)

## Compound 2 (CCDC 1960498)

**Table S 2. Crystal data and structure refinement for compound 4.**

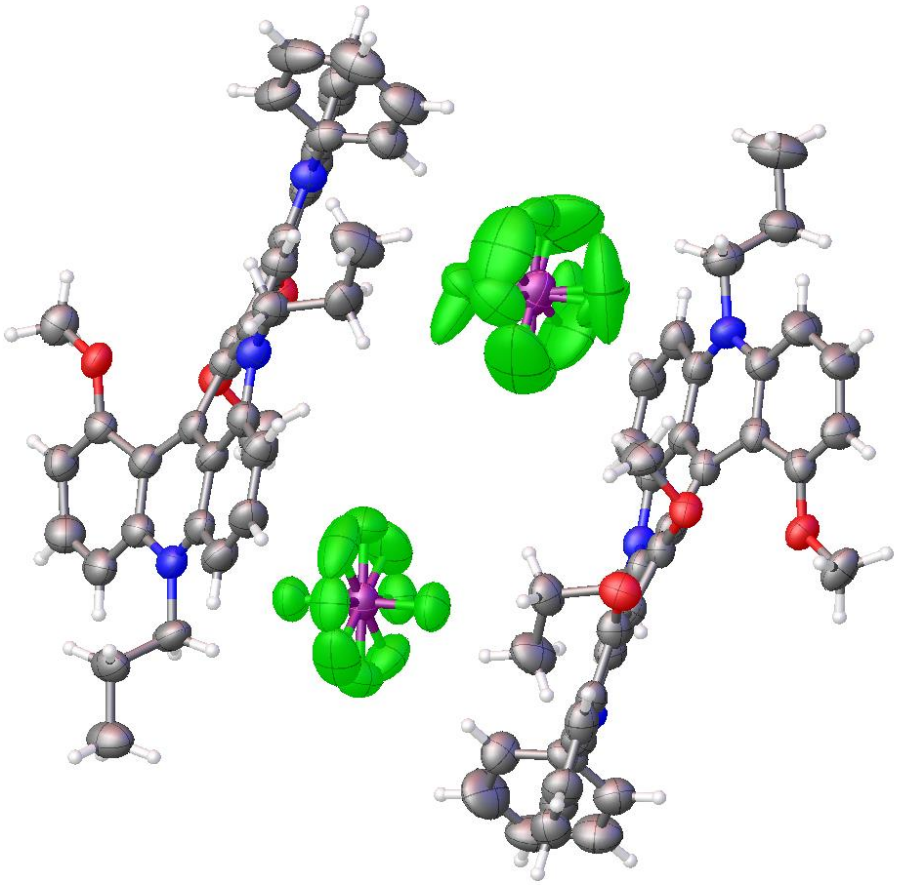
| | | |
|---|---|---|
| Empirical formula | C40 H36 F6 N3 O3 P | |
| Formula weight | 751.69 | |
| Temperature | 180.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Monoclinic | |
| Space group | P 1 21 1 | |
| Unit cell dimensions | a = 8.20579(16) Å | α= 90° |
| | b = 29.4208(8) Å | β= 93.223(2)° |
| | c = 16.5731(3) Å | γ = 90° |
| Volume | 3994.76(15) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.250 $Mg/m^3$ | |
| Absorption coefficient | 1.193 $mm^{-1}$ | |
| F(000) | 1560 | |
| Crystal size | 0.581 x 0.264 x 0.043 $mm^3$ | |
| Theta range for data collection | 3.004 to 73.588°. | |
| Index ranges | -10<=h<=9, -35<=k<=34, -17<=l<=19 | |
| Reflections collected | 14983 | |
| Independent reflections | 11054 [R(int) = 0.0241] | |
| Completeness to theta = 67.684° | 99.9 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 1.000 and 0.401 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11054 / 445 / 1056 | |
| Goodness-of-fit on $F^2$ | 1.010 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0679, wR2 = 0.1859 | |
| R indices (all data) | R1 = 0.0903, wR2 = 0.2124 | |
| Absolute structure parameter | 0.50(6) | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.594 and -0.579 $e.Å^{-3}$ | |

**Comments**

The molecule of interest is well-defined. However, the structure presents some problems:

The Flack parameter is 0.5 suggesting racemic twinning. (Data were not collected with absolute structure determination in mind so that the Friedel coverage pair is unfortunately too low for this parameter to be reliable.). In the asymmetric unit, two cations are present. They are superimposable after inversion. (there is an inversion centre at 0.29 0.5 0.29). The solvents possibly present are methanol, dichloromethane and cyclohexane. Attempts to model the solvent with disordered dichloromethane molecules were made but were still unsatisfactory so that the squeeze/bypass procedure was used. Two holes were found in the asymmetric unit, a small one (101 $A^3$) containing the equivalent of 40 electrons and a large one (50 $A^3$) containing the equivalent of 50 electron. Without using the solvent maps, the r factors were R1=15.8% and wR2=41.20 %. No suitable model for solvent could be find.

View of the asymmetric unit (Displacement Ellipsoids depicted at 50 percent probability level)



## Compound 4 (CCDC 1960499)

**Table S 3. Crystal data and structure refinement for compound 4.**

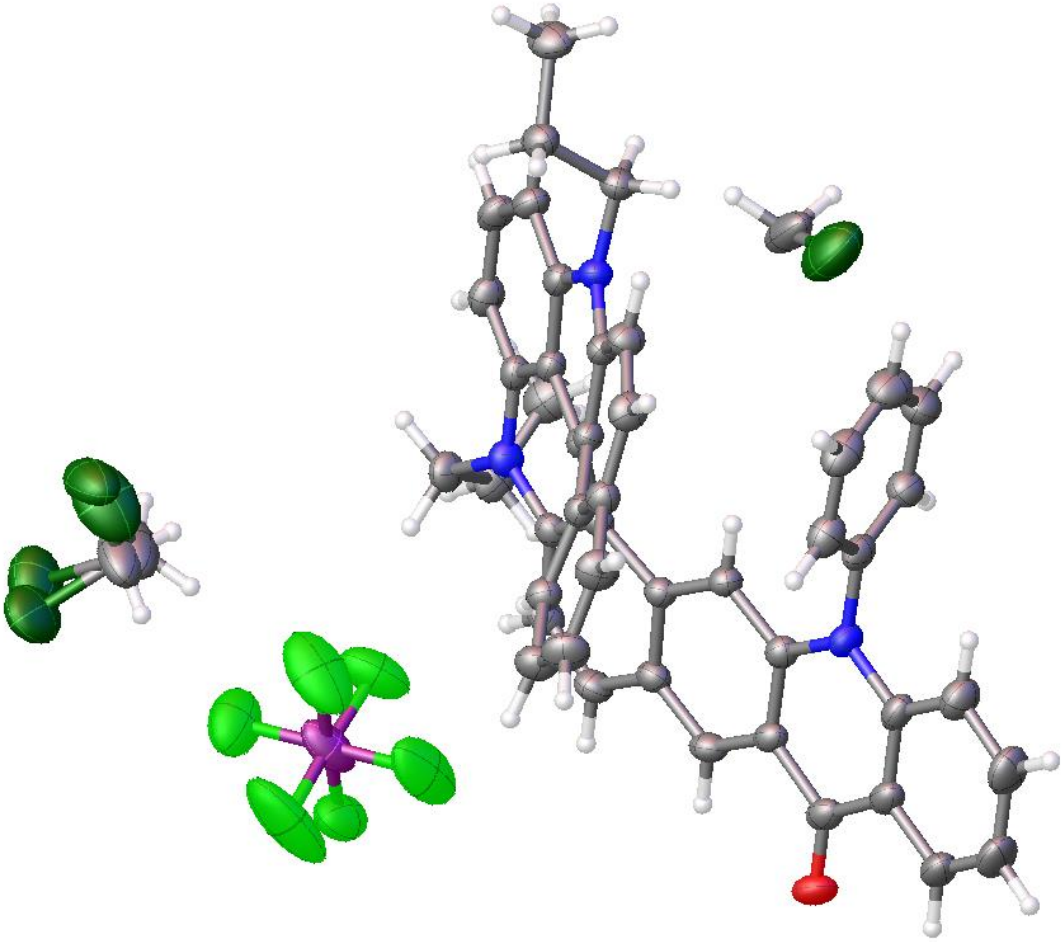
| | | |
|---|---|---|
| Empirical formula | C95 H78 Cl6 F12 N6 O2 P2 | |
| Formula weight | 1838.27 | |
| Temperature | 180.01(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 11.6780(4) Å | a= 90° |
| | b = 12.9347(5) Å | b= 90.912(8)° |
| | c = 27.785(9) Å | g = 90° |
| Volume | 4196.4(14) Å3 | |
| Z | 2 | |
| Density (calculated) | 1.455 Mg/m3 | |
| Absorption coefficient | 2.927 mm-1 | |
| F(000) | 1892 | |
| Crystal size | 0.29 x 0.142 x 0.057 mm3 | |
| Theta range for data collection | 3.770 to 72.791°. | |
| Index ranges | -13<=h<=11, -14<=k<=15, -33<=l<=29 | |
| Reflections collected | 32242 | |
| Independent reflections | 7916 [R(int) = 0.0485] | |
| Completeness to theta = 67.684° | 99.8 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 1.000 and 0.552 | |
| Refinement method | Full-matrix least-squares on F2 | |
| Data / restraints / parameters | 7916 / 0 / 583 | |
| Goodness-of-fit on F2 | 1.040 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0670, wR2 = 0.1913 | |
| R indices (all data) | R1 = 0.0822, wR2 = 0.2057 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.448 and -0.492 e.Å-3 | |

**Comments**

The crystal is split. A dichloromethane molecule was modelled using 2 components. The following restraints/constrants were used on distances and displacement parameters.

DFIX_CCL2 1.771 0.01 Cl1 C1 Cl2 C1
DFIX_CCL2 2.916 0.03 Cl1 Cl2
RIGU_CCL2 Cl2 Cl1 C1
EADP C52_1 C52_2

View of the asymmetric unit (Displacement Ellipsoids depicted at 50 percent probability level)



## Compound 6 (CCDC 1960500)

**Table S 4. Crystal data and structure refinement for compound 6.**

| | | |
|---|---|---|
| Empirical formula | C61 H46 F6 N5 O2 P | |
| Formula weight | 1026.00 | |
| Temperature | 180.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 27.6234(11) Å | a= 90° |
| | b = 16.7146(5) Å | b= 106.545(4)° |
| | c = 21.7661(9) Å | g = 90° |
| Volume | 9633.6(7) Å3 | |
| Z | 8 | |
| Density (calculated) | 1.415 Mg/m3 | |
| Absorption coefficient | 1.151 mm-1 | |
| F(000) | 4256 | |
| Crystal size | 0.127 x 0.089 x 0.009 mm3 | |
| Theta range for data collection | 4.036 to 70.175°. | |
| Index ranges | -32<=h<=33, -20<=k<=19, -24<=l<=26 | |
| Reflections collected | 20397 | |
| Independent reflections | 8977 [R(int) = 0.0359] | |
| Completeness to theta = 67.684° | 99.7 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 1.000 and 0.849 | |
| Refinement method | Full-matrix least-squares on F2 | |
| Data / restraints / parameters | 8977 / 49 / 745 | |
| Goodness-of-fit on F2 | 1.023 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0542, wR2 = 0.1332 | |
| R indices (all data) | R1 = 0.0921, wR2 = 0.1556 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.596 and -0.332 e.Å-3 | |

**Comments**

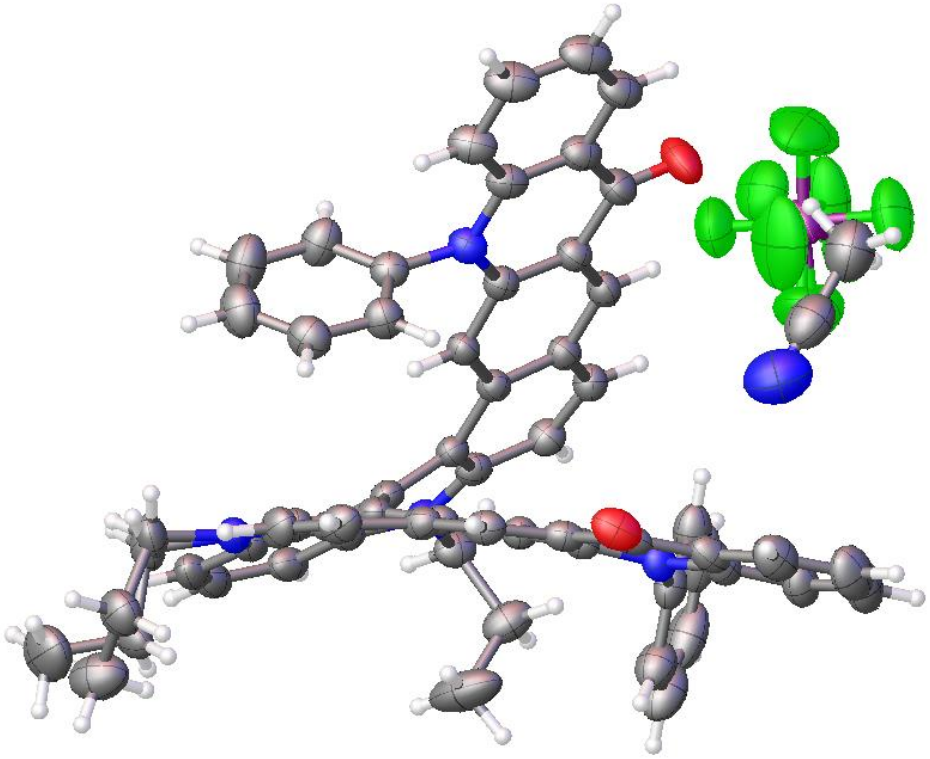
One of the side propyl chain is disordered and was refined using two component with the following restraints:

SADI C36B C35 C35 C36
SADI N34 C35B N34 C35
SADI C36 C35 C35B C36B
SADI C37 C36 C36B C37B
RIGU C36B C37B C35B
RIGU C35 C36 C37

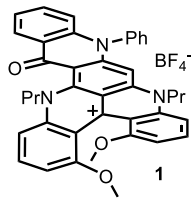
The PF6- anion is also disordered in one plane and was refined using two groups of four fluorine atom in this plane with the following restraints:

SADI C37 C36 C36B C37B
SADI P1 F6 P1 F10 P1 F5 P1 F9 P1 F4 P1 F7 P1 F11 P1 F8

View of the asymmetric unit (Displacement Ellipsoids depicted at 50 percent probability level)



# 4. HPLC resolution




## Helical pentacene 1

**Conditions:**

Chiral stationary Phase: IC semi preparative

Mobile phase: $CH_3CN$ (0.4% TEA, 0.6%TFA)/EtOH (0.4% TEA, 0.6%TFA) 80:20, 1 mL/min.

Figure S 1. First eluted (ee > 99%), $[\alpha]_{365}$ –5600

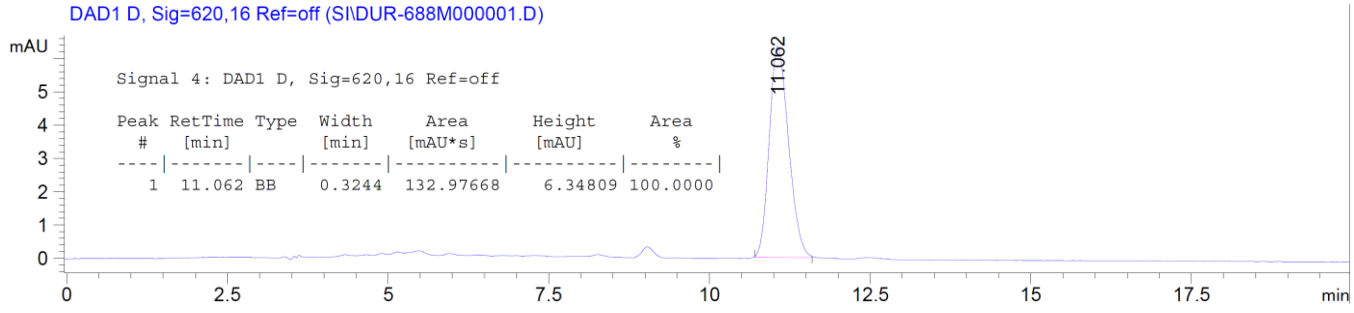
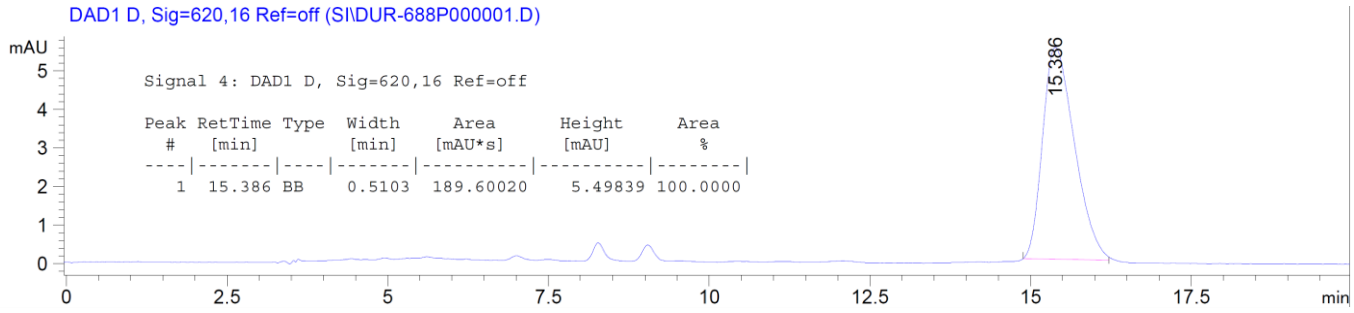
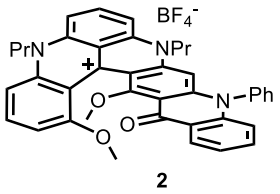



Figure S 2. Second eluted (ee >99%), $[\alpha]_{365}$ +7800



## Helical pentacene 2

**Conditions:**



2

Chiral stationary Phase: IC semi preparative

Mobile phase: $CH_3CN$ (0.4% TEA, 0.6%TFA)/EtOH (0.4% TEA, 0.6%TFA) 60:40, 1 mL/min.

Figure S 3. First eluted (ee > 99%), $[\alpha]_{365}$ –20300

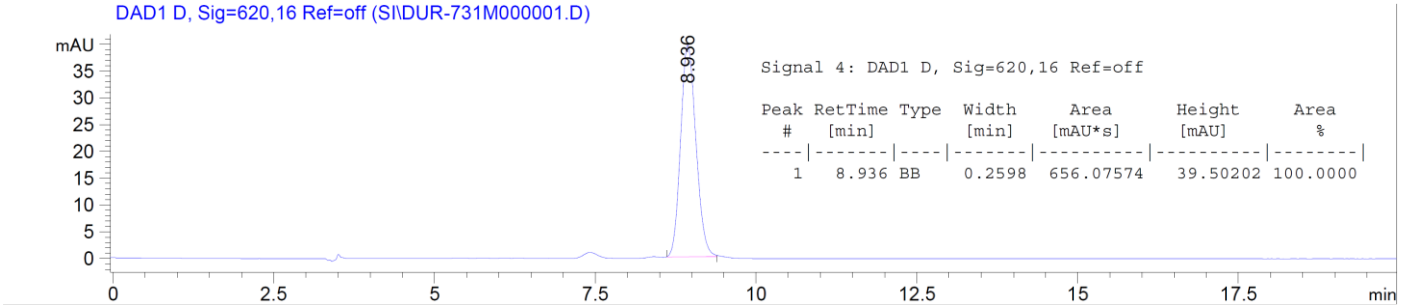
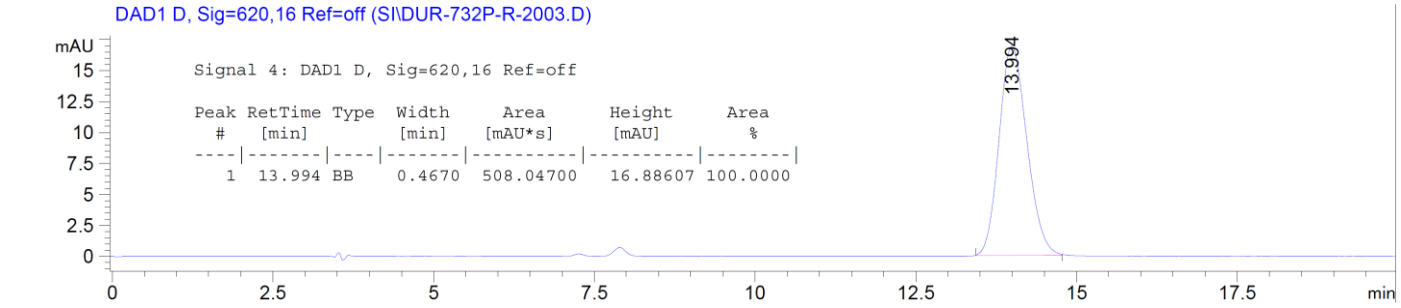
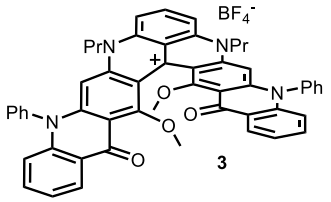



Figure S 4. Second eluted (ee >99%), $[\alpha]_{365}$ +17700



## Helical pentacene 3




**Conditions:**

Chiral stationary Phase: IC semi preparative

Mobile phase: $CH_3CN$ (0.4% TEA, 0.6%TFA)/EtOH (0.4% TEA, 0.6%TFA) 98:02, 1 mL/min.

Figure S 5. First eluted (ee > 99%), $[\alpha]_{365}$ –17200

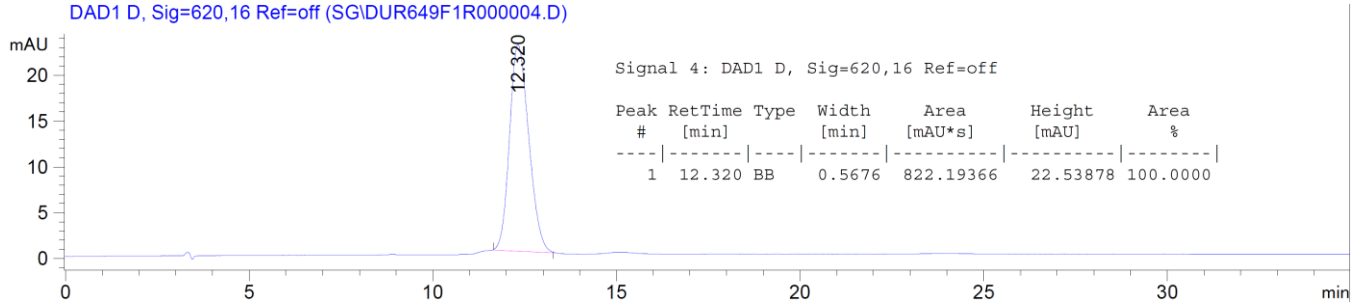
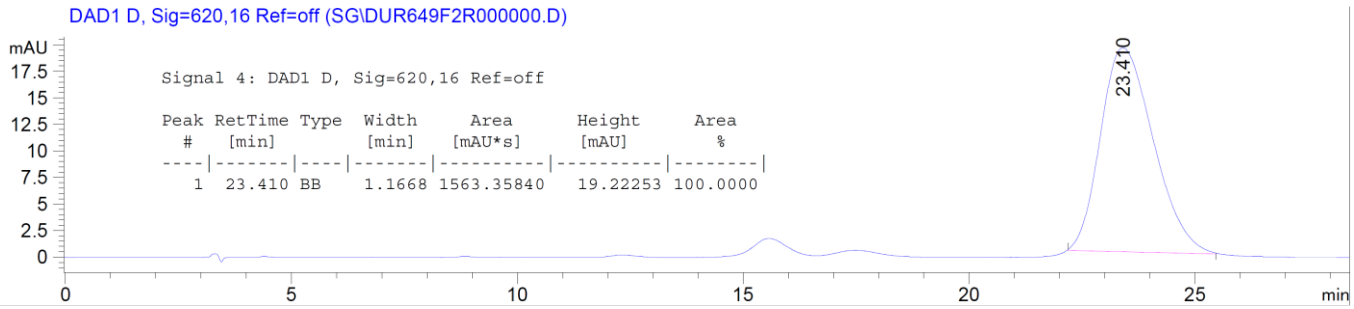
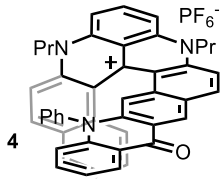



Figure S 6. Second eluted (ee >99%), $[\alpha]_{365}$ +19400



## Helical tetracene 4




4

**Conditions:**

Chiral stationary Phase: IB semi preparative

Mobile phase: $CH_3CN$ (0.4% TEA, 0.6%TFA)/EtOH (0.4% TEA, 0.6%TFA) 95:05, 3 mL/min.

Figure S 7. First eluted (ee > 99%), $[\alpha]_{365}$ +20800

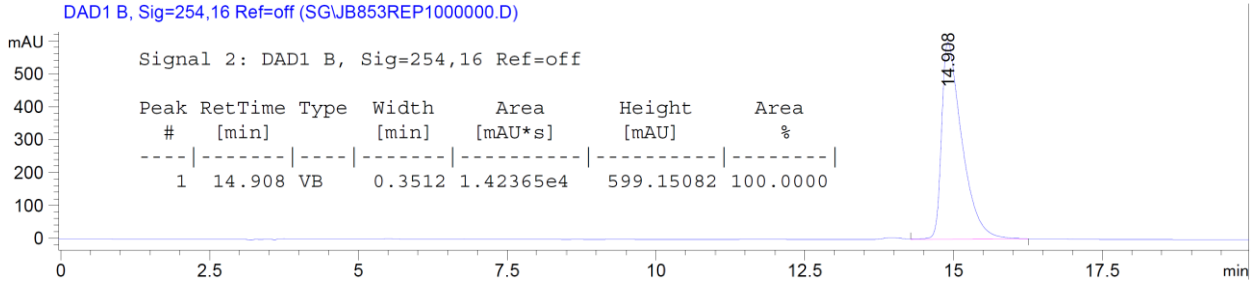
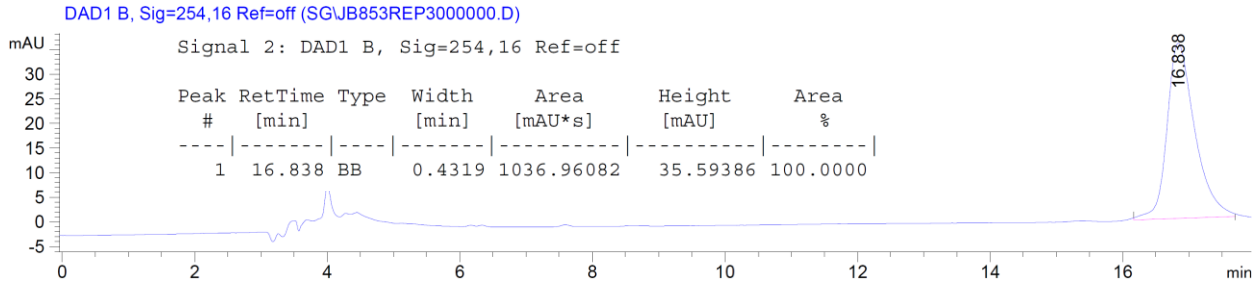
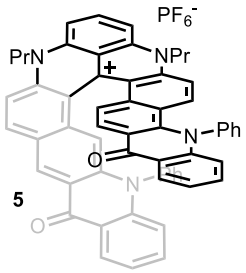



Figure S 8. Second eluted (ee >99%), $[\alpha]_{365}$ –19200



## Helical tetracene 5




**Conditions:**

Chiral stationary Phase: IB semi preparative

Mobile phase: $CH_3CN$ (0.4% TEA, 0.6%TFA)/EtOH (0.4% TEA, 0.6%TFA) 80:20, 3 mL/min.

Figure S 9. First eluted (ee > 99%), $[\alpha]_{365}$ +4400

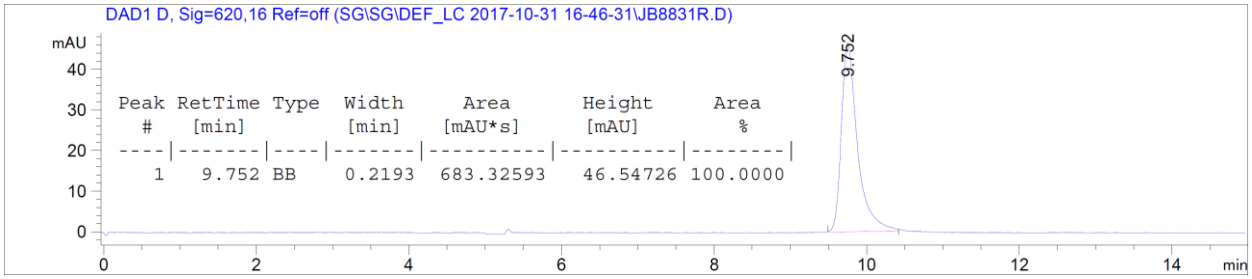
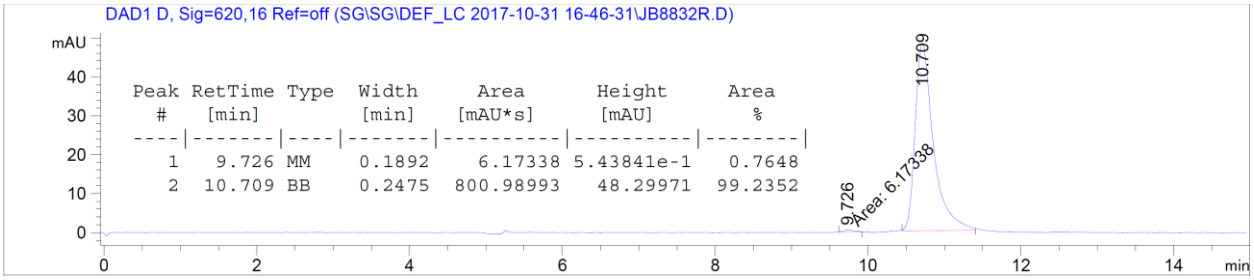
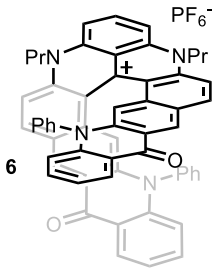



Figure S 10. Second eluted (ee 98%), $[\alpha]_{365}$ –4500



## Helical tetracene 6




6

**Conditions:**

Chiral stationary Phase: IB semi preparative

Mobile phase: $CH_3CN$ (0.4% TEA, 0.6%TFA)/EtOH (0.4% TEA, 0.6%TFA) 80:20, 3 mL/min.

Figure S 11.Firs eluted (ee > 99%), $[\alpha]_{365}$ +16300

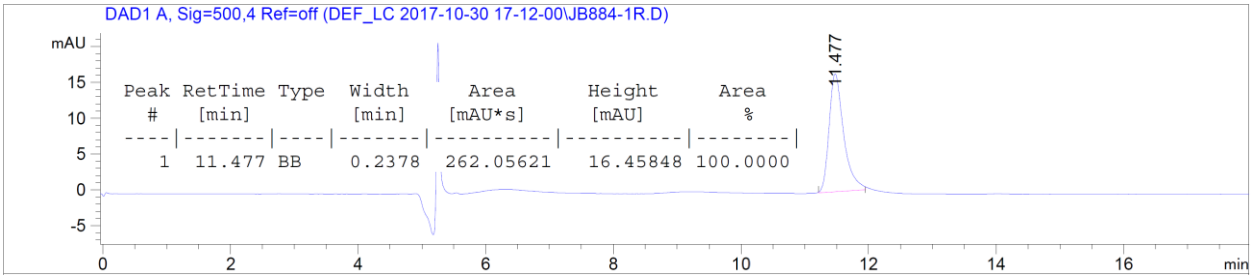
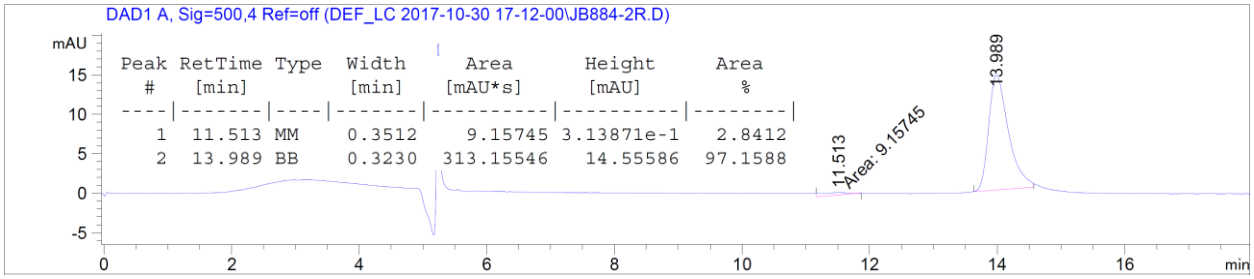



Figure S 12. Second eluted (ee 94%), $[\alpha]_{365}$ –16300



## 5. (Chir)optical properties

### Helical pentacene 1

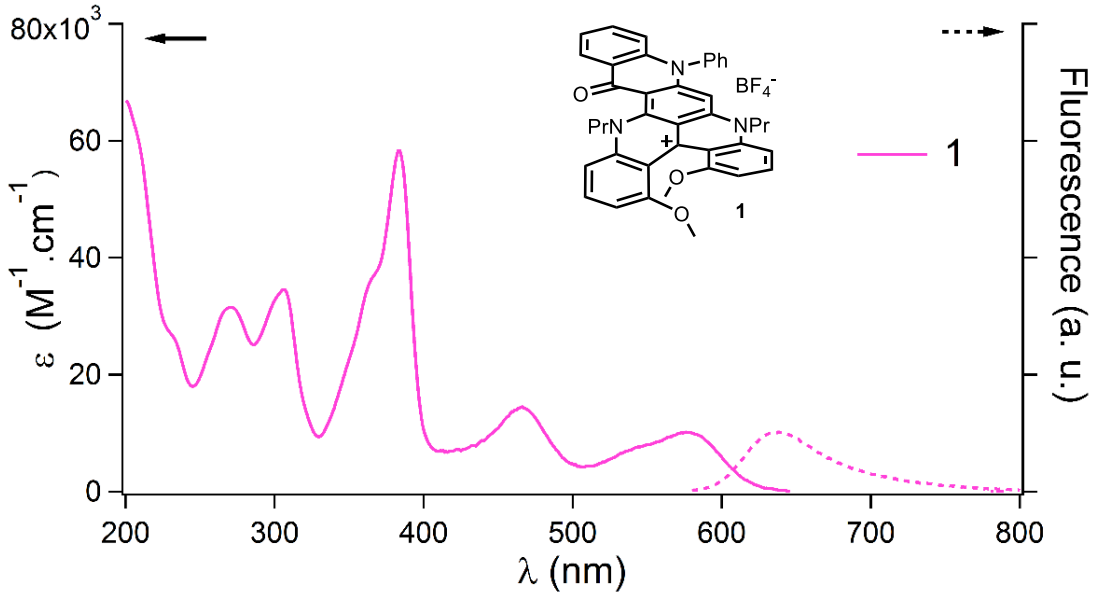



Figure S 13. Absorption (plain line) and fluorescence (dashed line) in acetonitrile.

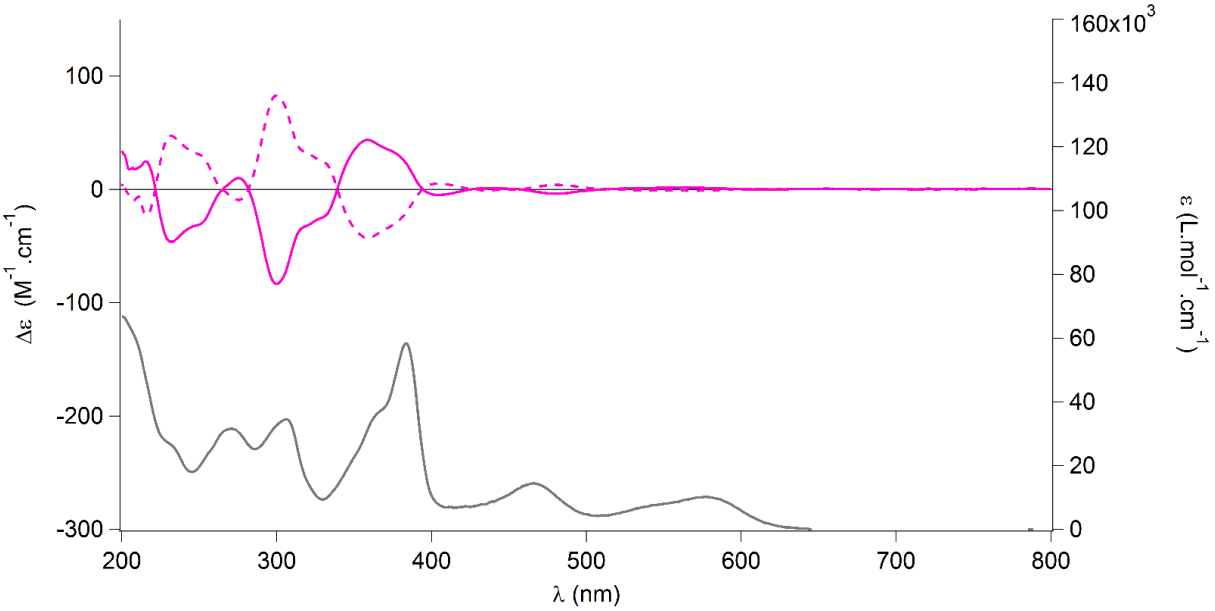



Figure S 14. Electronic circular dichroism (plain line: 1st eluted (–)-isomer, dashed line: 2nd eluted (+)-isomer) in acetonitrile.

**Helical pentacene 2**

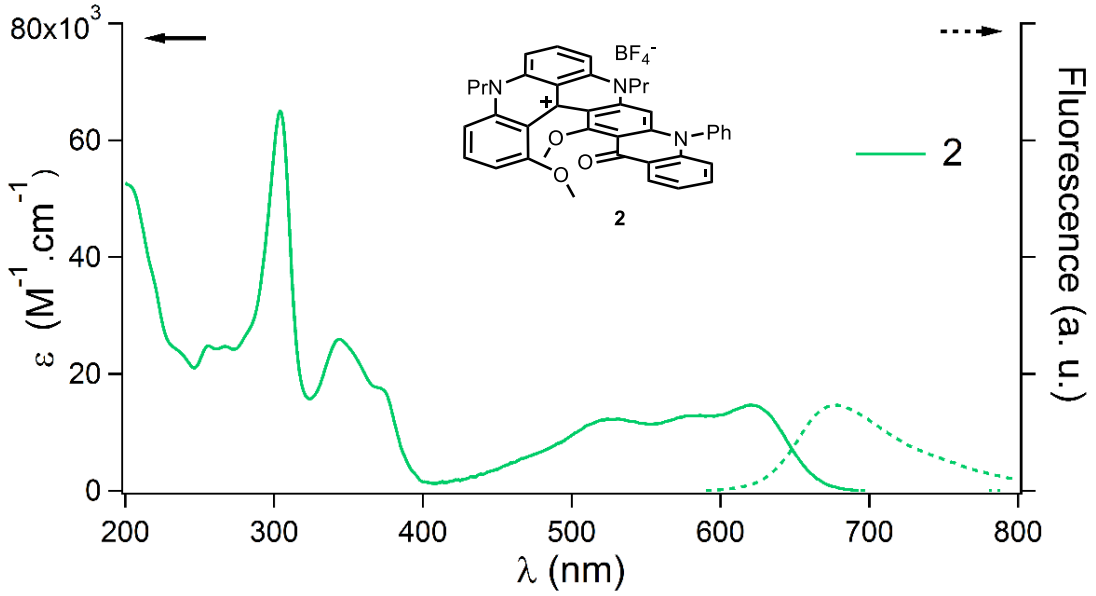



Figure S 15. Absorption (plain line) and fluorescence (dashed line) in acetonitrile.

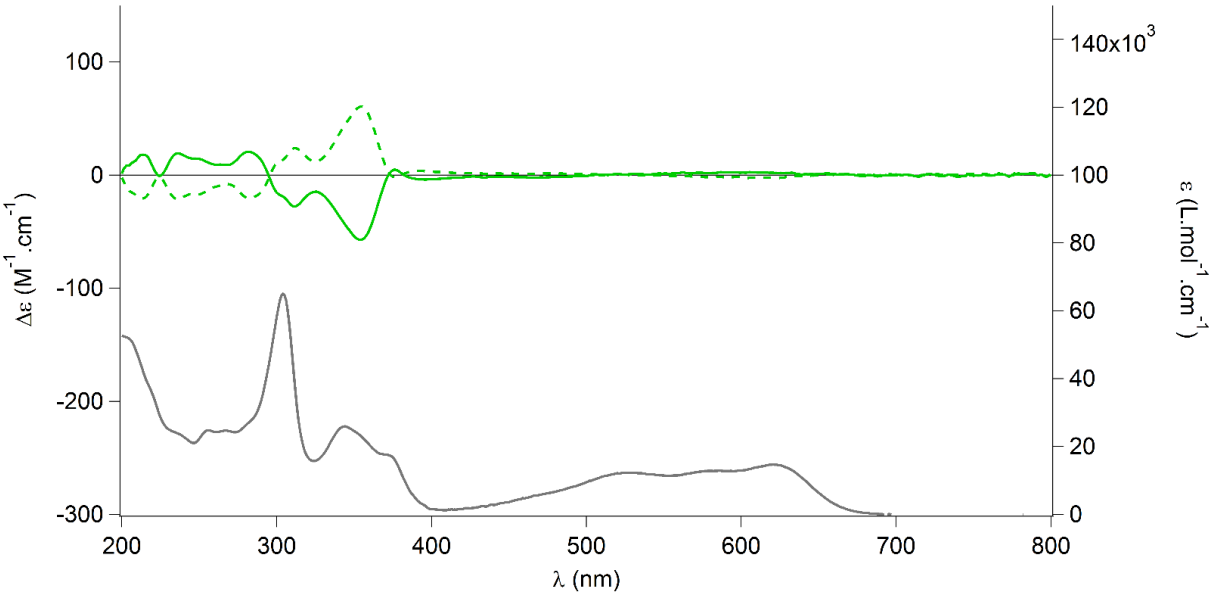



Figure S 16. Electronic circular dichroism (plain line: 1st eluted (–)-isomer, dashed line: 2nd eluted (+)-isomer) in acetonitrile.

**Helical pentacene 3**

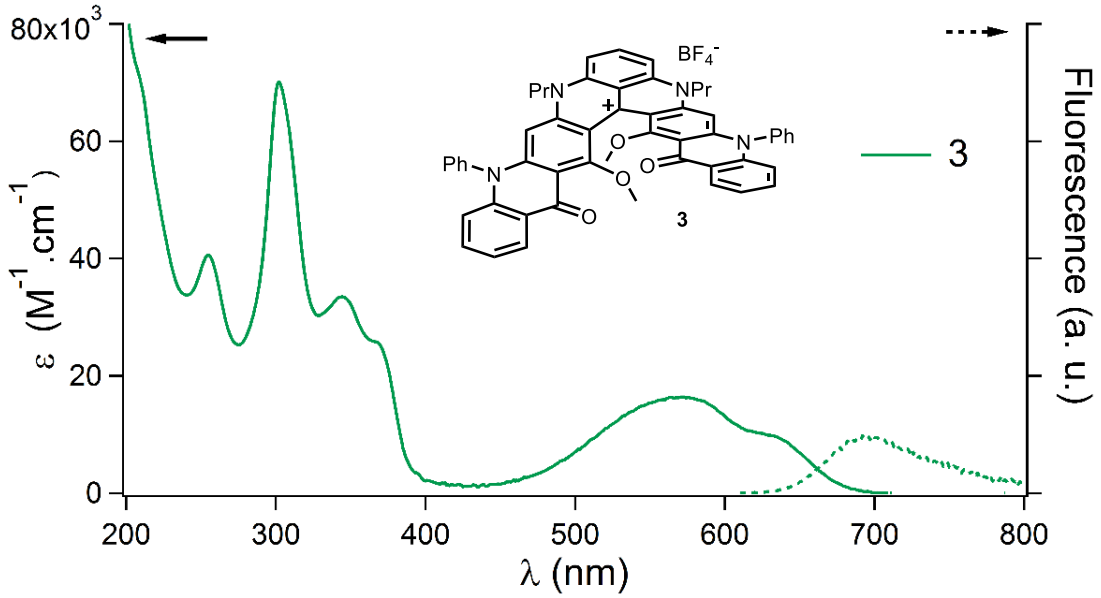



Figure S 17. Absorption (plain line) and fluorescence (dashed line) in acetonitrile.

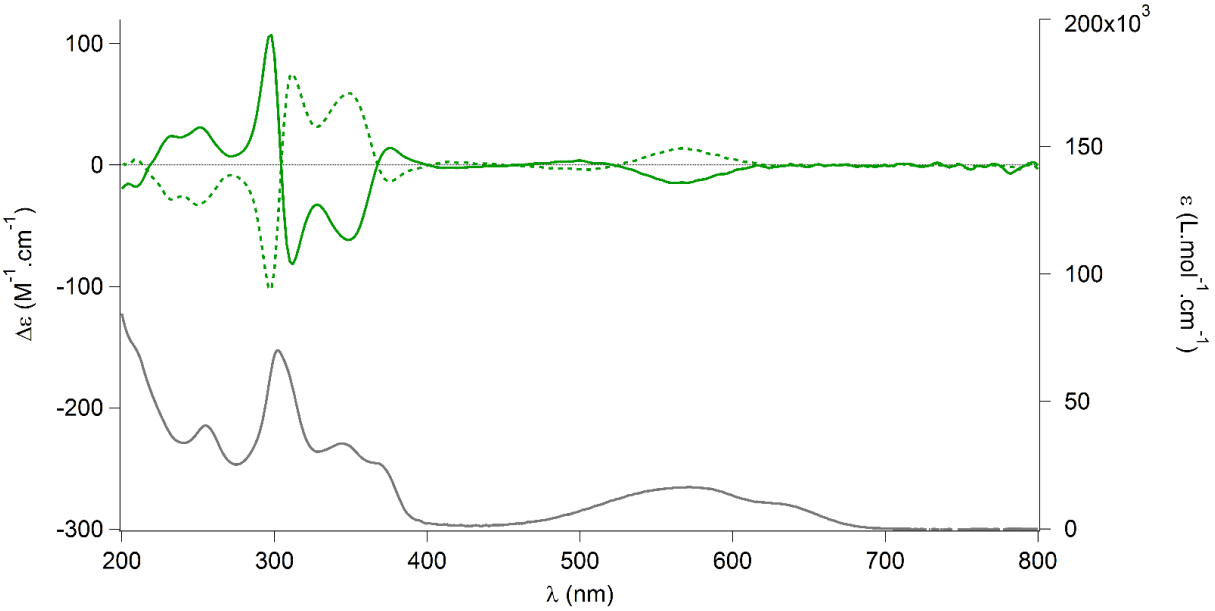



Figure S 18. Electronic circular dichroism (plain line: 1st eluted (–)-isomer, dashed line: 2nd eluted (+)-isomer) in acetonitrile.

**Helical tetracene 4**

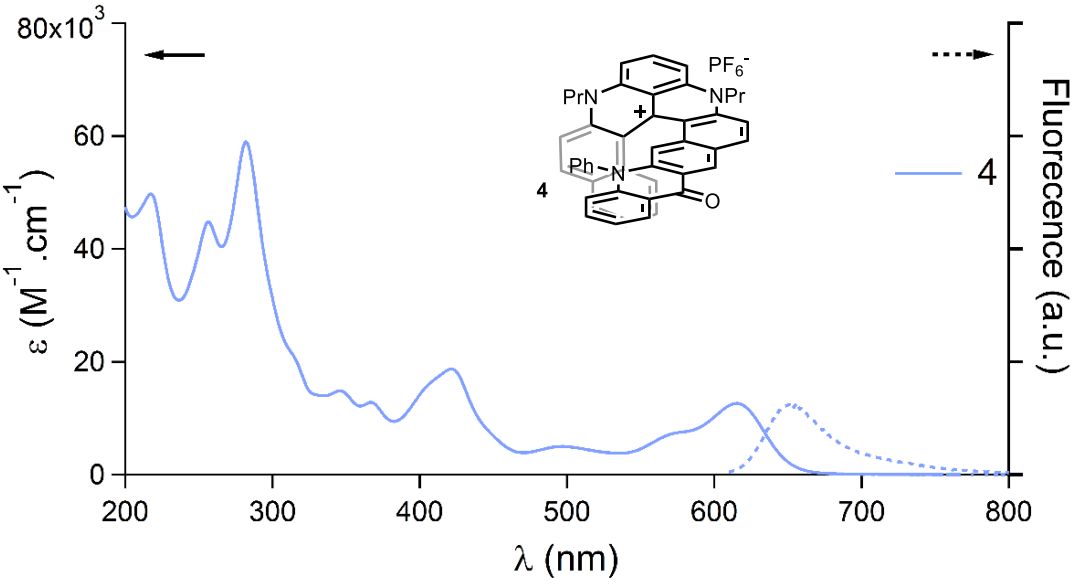



Figure S 19. Absorption (plain line) and fluorescence (dashed line) in acetonitrile.

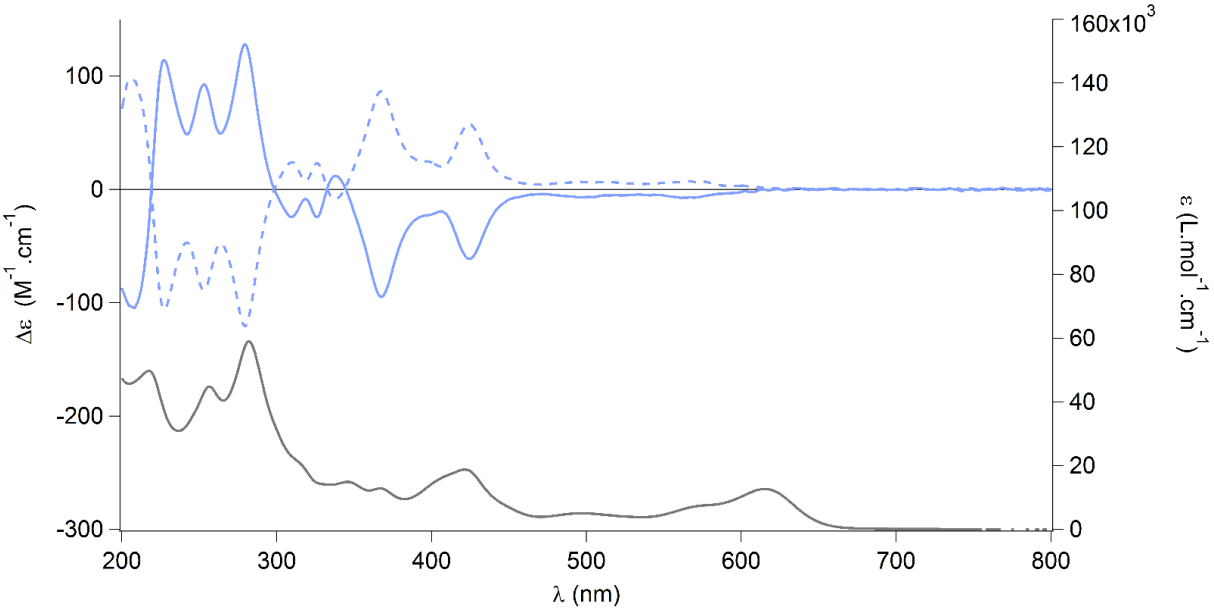



Figure S 20. Electronic circular dichroism (plain line: 1st eluted (+)-isomer, dashed line: 2nd eluted (–)-isomer) in acetonitrile.

**Helical tetracene 5**

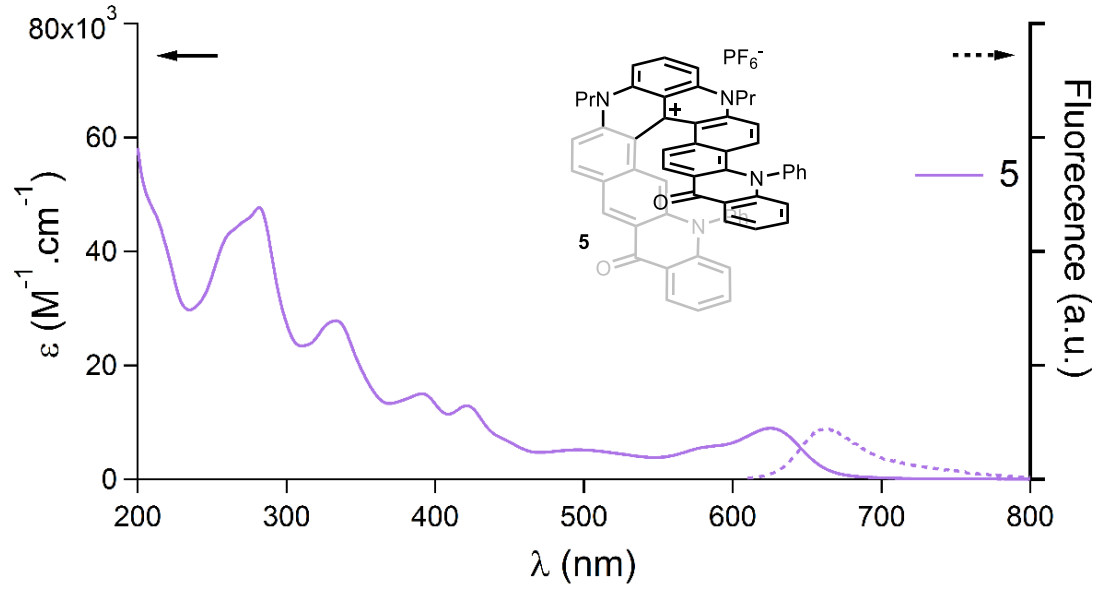



Figure S 21. Absorption (plain line) and fluorescence (dashed line) in acetonitrile.

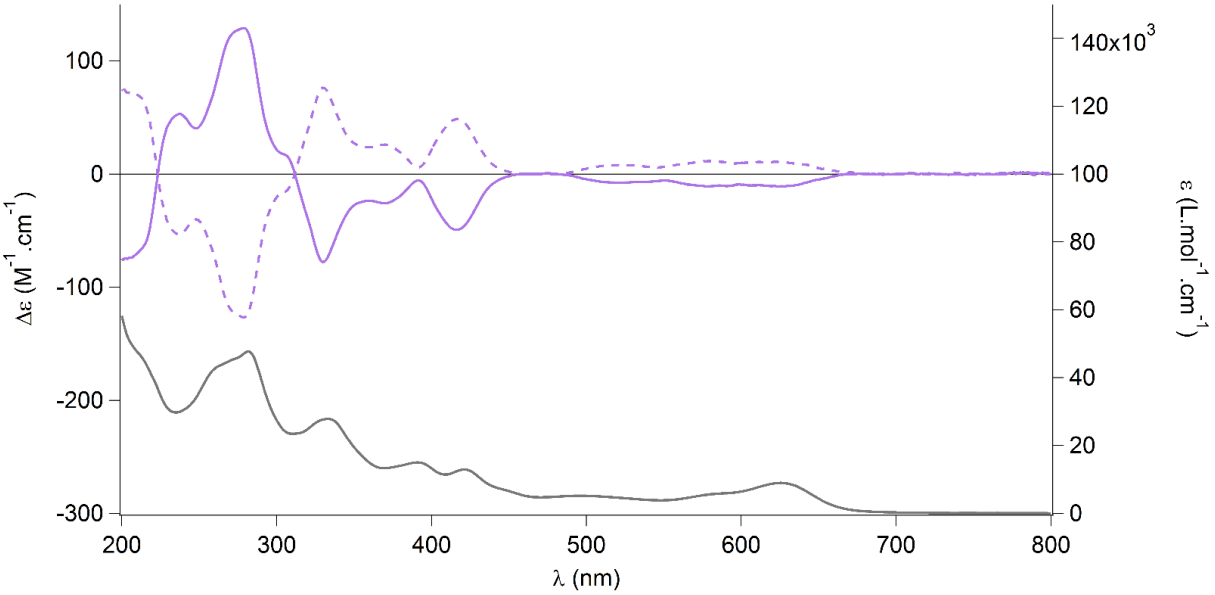



Figure S 22. Electronic circular dichroism (plain line: 1st eluted (+)-isomer, dashed line: 2nd eluted (–)-isomer) in acetonitrile.

**Helical tetracene 6**

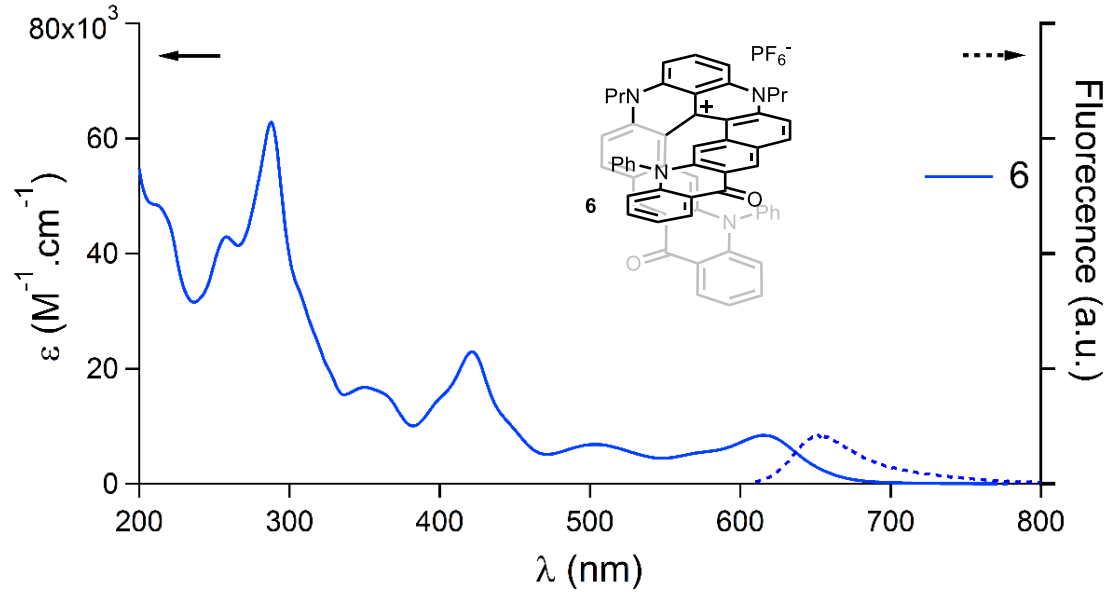



Figure S 23. Absorption (plain line) and fluorescence (dashed line) in acetonitrile.

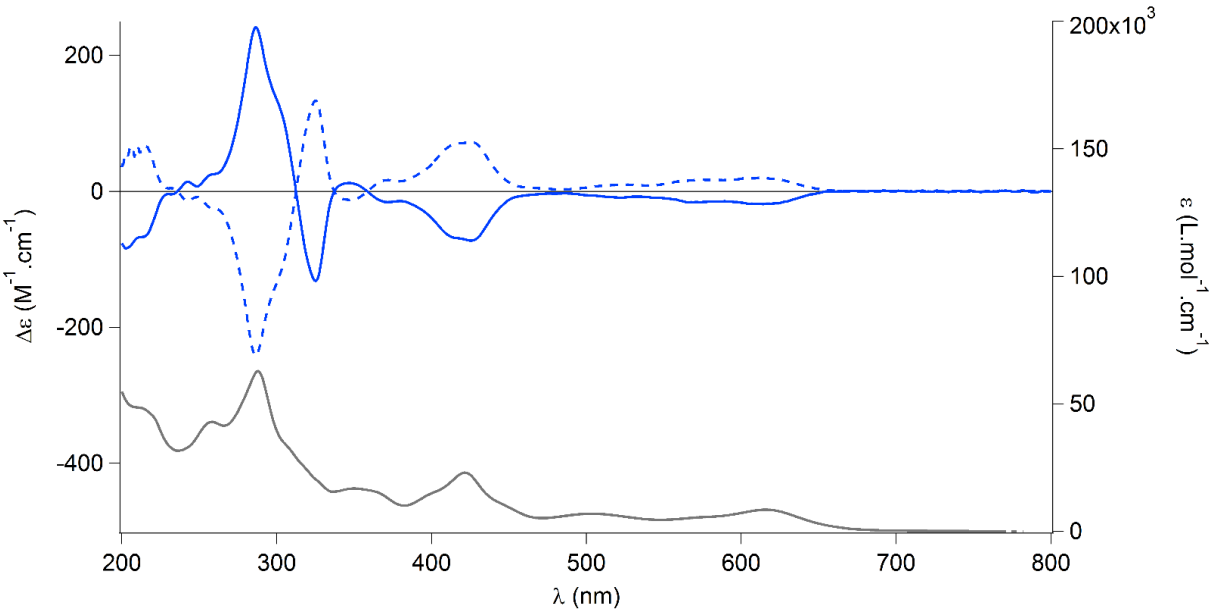



Figure S 24. Electronic circular dichroism (plain line: 1st eluted (+)-isomer, dashed line: 2nd eluted (–)-isomer) in acetonitrile.

## 6. First principle calculations

### Computational details

All (TD-)DFT calculations were performed using the Gaussian 16.A03 program,[9] whereas the wavefunction [ADC(2) and CC2] calculations were made with the Turbomole code.[10] Our calculations consisted in geometry optimization of the ground-state geometry (including conformational search) with DFT, of the excited-state geometry with TD-DFT, in Hessian calculations at the same levels of theory for both the ground- and the excited-states, as well as in calculations of the transition energies with TD-DFT, and when technically possible with ADC(2) and CC2.

For the Gaussian calculations, we used tightened self-consistent field ($10^{-10}$ a.u.) and geometry optimization ($10^{-5}$ a.u.) convergence thresholds and a large DFT integration grid (so-called *ultrafine* grid, a pruned 99 590 grid). The (TD-)DFT calculations relied on the M06-2X hybrid functional.[11] This functional is able to account for dispersion effects and is also well suited for excited-state calculations.[12] Following the basis set combination approach proposed elsewhere,[12] we used the 6-31+G(d) atomic basis set for determining the geometrical and vibrational parameters, whereas the transition energies were computed with 6-311+G(2d,p). The selection of a diffuse containing basis set for the optimization is justified by the weak interactions taking place between the different moieties in the ground-state. The nature of all stationary points, at both ground and excited-states, was confirmed by Hessian calculations that returned 0 (minima) imaginary vibrational modes. During the DFT and TD-DFT calculations, the environmental effects (herein, acetonitrile) were accounted for. We used the linear response (LR) variant of the polarizable continuum model (PCM)[13] in its equilibrium limit for optimizing the excited-state geometries, whereas the absorption and emission energies were determined adding corrections for state-specific effects using the corrected LR (cLR)[14] PCM model in its non-equilibrium limit. We indeed apply the LR+cLR model here for 0-0 energies and we refer the reader to one of our previous work for description of this model.[15] Excited-states are represented using density difference plots, in which the excited-state density was determined at the TD-DFT level. In these plots, blue and red regions, respectively, indicate decrease and increase of electron density upon photon absorption (threshold 0.001 au).

As it is well known that TD-DFT delivers rather poor estimates for cyanine-like compounds,[16] irrespective of the selected functionals, we have used ADC(2) and CC2 to correct the transition energies obtained with TD-DFT absorption, emission and 0-0 energies. Following a procedure that we recently proposed,[16] we add the difference between the gas phase wavefunction and TD-DFT transition energies to the PCM-TD-DFT values to obtain theoretical best estimates. We redirect the interested readers to previous works for discussion of the *pros* an *cons* of this approach.[15-16] both ADC(2) and CC2 calculations relied on the *aug*-cc-pVDZ atomic basis set.

### Results

Vertical spectra

In Table **S5**, we report the vertical transition energies computed for all compounds. It should be recalled that such vertical values cannot be directly compared to experimental $\lambda_{max}$,[17] they provide a good qualitative picture of the

evolutions within a homologous series of compounds. With this simple level of theory, we note that the ordering of the $\lambda_{vert}$ in the pentacene series is **3** (503 nm) > **2** (499 nm) > **7** (491 nm) > **1** (459 nm), whereas in the tetracene series one has **5** (512 nm) > **4** = **6** (507 nm) > **8** (504 nm). Whilst the values reported here are obviously all blueshifted compared to the experimental $\lambda_{max}$, the orderings of the different compounds perfectly match experiment with **3** and **5** as the most redshifted and **1** as the most blueshifted spectra.

**Table S5. Computed vertical absorption features for all compounds, considering the lowest five singlet states. All values obtained at the LR-PCM(ACN,neq)-M06-2X/6-311+G(2d,p) level of theory. We report the vertical transition wavelength (in nm), the oscillator strength (f) and the Rotatory strength (R in cgs).**

| Compound | State | $\lambda_{vert}$ | f | R |
|---|---|---|---|---|
| **1** | $S_1$ | 459 | 0.19 | 1.48 |
| | $S_2$ | 389 | 0.28 | -96.9 |
| | $S_3$ | 373 | 0.05 | 86.8 |
| | $S_4$ | 366 | 0.01 | 22.3 |
| | $S_5$ | 334 | 0.94 | -13.9 |
| **2** | $S_1$ | 499 | 0.35 | -26.9 |
| | $S_2$ | 428 | 0.16 | 68.2 |
| | $S_3$ | 396 | 0.08 | -74.4 |
| | $S_4$ | 344 | 0.04 | 13.5 |
| | $S_5$ | 319 | 0.21 | -54.2 |
| **3** | $S_1$ | 503 | 0.45 | 34.6 |
| | $S_2$ | 450 | 0.10 | 176.0 |
| | $S_3$ | 435 | 0.24 | -203.1 |
| | $S_4$ | 349 | 0.01 | 12.2 |
| | $S_5$ | 348 | 0.01 | 14.2 |
| **4** | $S_1$ | 507 | 0.21 | 56.1 |
| | $S_2$ | 406 | 0.17 | 48.3 |
| | $S_3$ | 373 | 0.10 | -35.0 |
| | $S_4$ | 360 | 0.21 | 396.8 |
| | $S_5$ | 348 | 0.25 | -76.6 |
| **5** | $S_1$ | 512 | 0.21 | 120.0 |
| | $S_2$ | 415 | 0.14 | 118.6 |
| | $S_3$ | 400 | 0.15 | -150.1 |
| | $S_4$ | 372 | 0.13 | -25.3 |
| | $S_5$ | 356 | 0.25 | 373.8 |
| **6** | $S_1$ | 507 | 0.16 | 218.8 |
| | $S_2$ | 412 | 0.09 | 282.1 |
| | $S_3$ | 405 | 0.20 | -298.1 |
| | $S_4$ | 375 | 0.13 | -235.3 |
| | $S_5$ | 373 | 0.13 | 220.6 |
| **7** | $S_1$ | 491 | 0.25 | 16.7 |
| | $S_2$ | 378 | 0.06 | 86.4 |
| | $S_3$ | 374 | 0.13 | -133.8 |
| | $S_4$ | 309 | 0.02 | 51.3 |
| | $S_5$ | 305 | 0.02 | 69.8 |
| **8** | $S_1$ | 504 | 0.28 | 24.4 |
| | $S_2$ | 352 | 0.03 | -162.2 |
| | $S_3$ | 349 | 0.10 | 43.9 |
| | $S_4$ | 327 | 0.07 | 95.9 |
| | $S_5$ | 320 | 0.09 | -650.9 |

To obtain more insights into the nature of these lowest-energy transitions, we report in **Figure S25**, the density difference plots for all investigated dyes. In this Figure the region of density loss and gain upon photo-excitation are displayed as blue and red lobes, respectively.

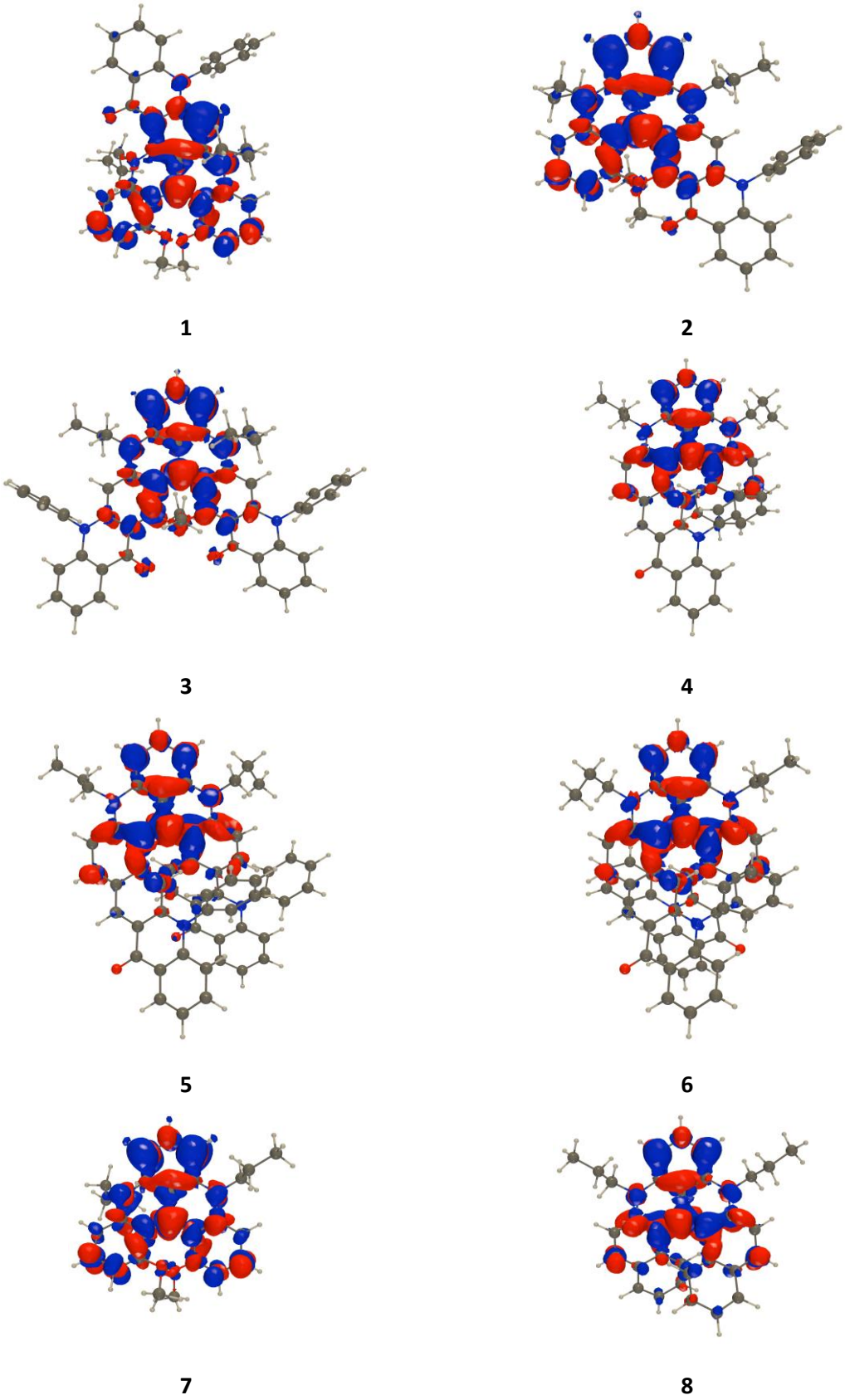



Figure S25. LR-PCM(ACN,neq)-M06-2X/6-311+G(2d,p) density difference plots for the lowest transition in all considered dyes. Blue and red regions indicate decrease and increase of electron density upon electronic excitation, respectively.

Let us start by analyzing **7**: one finds the typical pattern for such derivative, with alternating lobes of density gain and depletion, the central formally positively charge carbon atom acting has a strong acceptor (in red) and the "top" phenyl ring as an electron donor (mostly in blue). When going to **1**, the pattern of the state is globally preserved (with limited delocalization on the added moiety), but the presence of the quinone renders the donating character of the top phenyl weaker, hence explaining the blueshift. On the other hand, the density difference plots are extremely similar in **2**, **3**, and **7**, with only a very slight delocalization of the state on the quinoidal groups, hence explaining the limited, if not negligible, redshifts when going from **7** to **2** and **3**. Let us now turn to the tetracene series. Here, there is simply no noticeable variations between the density patterns of **4**-**6** and **8**, explaining their extremely similar absorption spectra (Figure 3 of the main text). We explain the slight bathochromic shift in **5** as compared to the other compounds, not by an enhanced delocalization, but in contrast by its asymmetry which induces a slightly larger change of dipole moment between the ground and the excited states (0.8 D in **5**, 0.3 D in **6**).

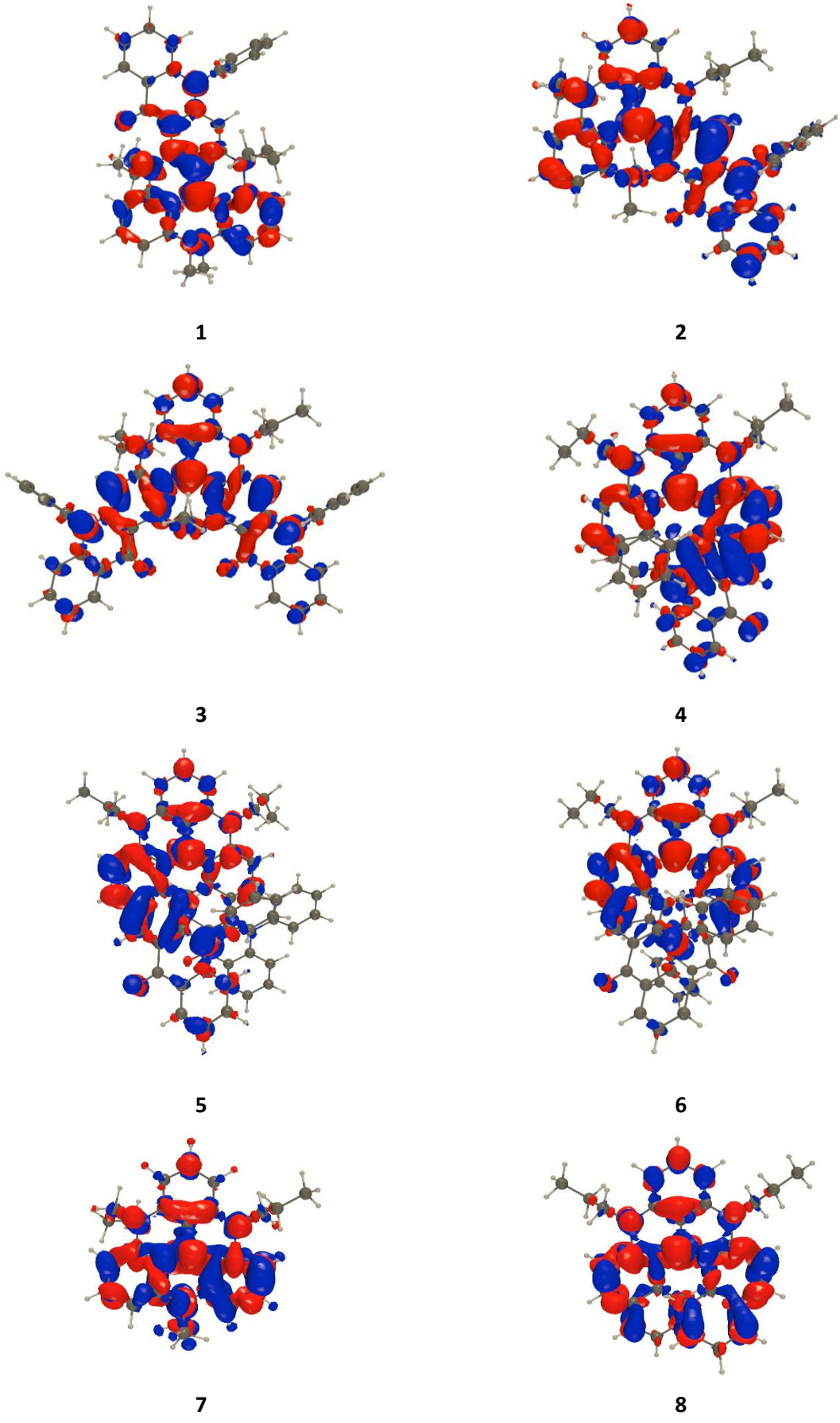



Figure S26. LR-PCM(ACN,neq)-M06-2X/6-311+G(2d,p) density difference plots for the second lowest transition in all considered dyes. Blue and red regions indicate decrease and increase of electron density upon electronic excitation, respectively.

0-0 energies

As can be seen above, the use of vertical transition values allows to qualitatively reproduce the spectral variations in the series, but falls short when quantitative comparisons are needed. There are two reasons for this outcome: *i)* the system studied have a partial cyanine nature with a positive charge delocalized on a π-conjugated path, and such systems are not very accurately determined with TD-DFT;[16] *ii*), we have neglected vibronic effects all together which is a strong approximation, and comparing 0-0 energies is more physically sound.[17] In Table S6, we present the TD-DFT 0-0 energies and compare them to their experimental counterparts. As can be seen both the linear-response and state-specific (cLR) effects are significant as they tune the transition energies significantly compare to the gas-phase case which is not surprising as the transitions are both bright (large *f*) and involve a significant density reorgeanization. Unsurprisingly, the LR+cLR values are closer to experiment, although they remain significantly larger than the experimental value due to the first point noted above. To see if this is indeed due to the limits of TD-DFT, we have carried out ADC(2) and CC2 calculations for a subset of compounds and the results are listed in Table 7. The protocol used closely follows the one published in Ref. [18]: we use adiabatic gas phase energies obtained with wavefunction approaches to correct the TD-DFT 0-0 energies in gas-phase. As can be seen, the inclusion of these corrections downshift the transition energies significantly, the expected trend for such system. With ADC(2), the 0-0 energies are significantly too small, which is a usual problem with this approach for low-lying excited-states.[18] With CC2, the 0-0 energies are now within ca. 0.2 eV of the experimental value, which is the typical error for such level of theory.

**Table S6. Comparison between experimental and theoretical 0-0 energies obtained at the TD-DFT level. The 0-0 energies have been determined using various protocols for the solvent effect. All values are in eV.**

| | Exp. | Gas | LR,eq | cLR,neq | LR+cLR,neq |
|---|---|---|---|---|---|
| **1** | 2.04 | 2.53 | 2.46 | 2.48 | 2.40 |
| **2** | 1.91 | 2.43 | 2.26 | 2.31 | 2.20 |
| **3** | 1.87 | 2.45 | 2.24 | 2.30 | 2.19 |
| **4** | 1.96 | 2.27 | 2.22 | 2.31 | 2.21 |
| **5** | 1.93 | 2.03 | 2.12 | 2.17 | 2.11 |
| **6** | 1.93 | 2.22 | 2.22 | 2.29 | 2.21 |
| **7** | 1.92 | 2.41 | 2.30 | 2.34 | 2.24 |
| **8** | 1.96 | 2.32 | 2.21 | 2.31 | 2.19 |

**Table S7. Comparison between experimental and theoretical 0-0 energies obtained with the LR+cLR,neq solvent model with TD-DFT and with additional ADC(2) or CC2 corrections. All values are in eV.**

| | Exp. | LR+cLR,neq | +ADC(2) | +CC2 |
|---|---|---|---|---|
| **1** | 2.04 | 2.40 | 1.65 | 1.84 |
| **2** | 1.91 | 2.20 | 1.45 | 1.65 |
| **7** | 1.92 | 2.24 | 1.50 | 1.71 |
| **8** | 1.96 | 2.19 | 1.64 | 1.82 |

## 7. $^{1}H$, $^{13}C$, $^{19}F$, $^{31}P$ NMR spectra, IR spectra and HRMS reports

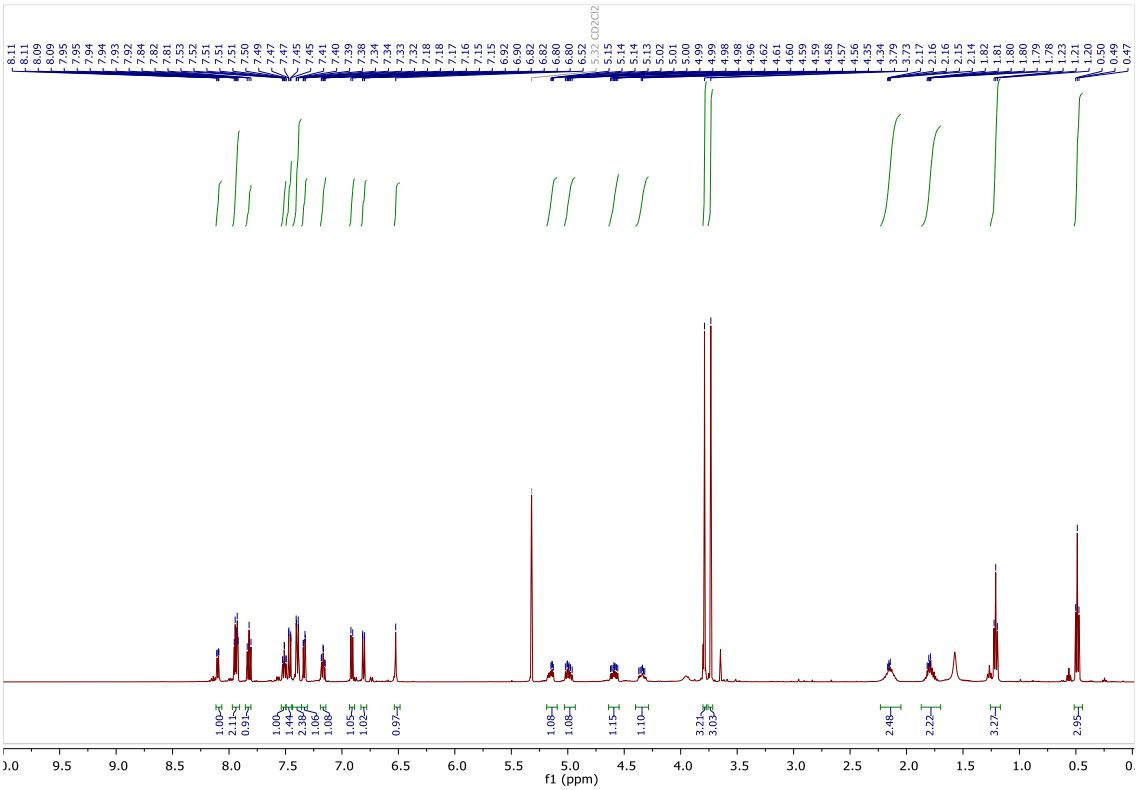



Figure S 27. $^{1}H$ NMR ($CD_2Cl_2$, 500MHz) spectrum of compound **10**.

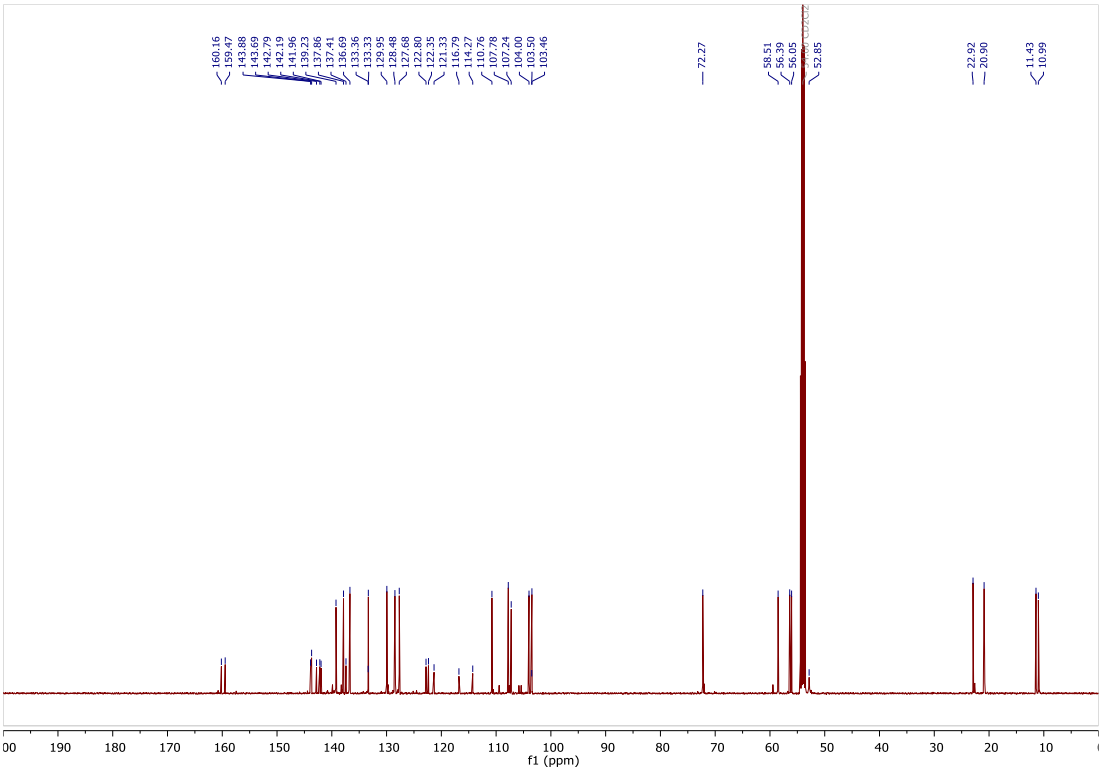



Figure S 28. $^{13}C$ NMR ($CD_2Cl_2$, 125MHz MHz) spectrum of compound **10**.

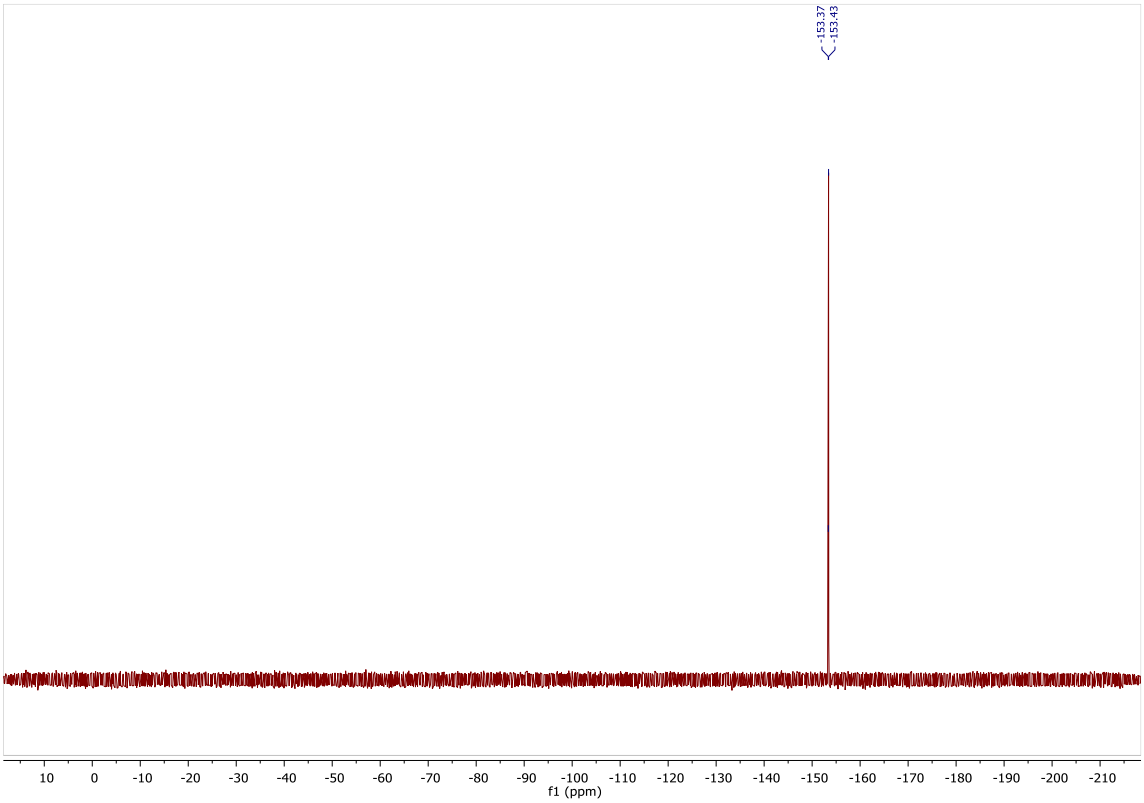



Figure S 29. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **10**.

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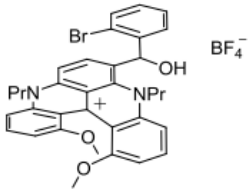
|---|---|---|---|
| Applicant: | Romain DUWALD | Date of reception: | November 16th, 2017 |
| Group/Company: | Prof. Jérôme LACOUR | Date of certificate: | November 29th, 2017 |
| Sample name: | DuR680 | Data filename: | SMS-XL-171116-HT-A012 |
| Sample number: | 9038 | Instrument: | QSTAR XL (AB/MDS Sciex) |
| **Analyst:** | **Harry THERAULAZ** | Ionisation mode: | ESI (positive polarity) |
| **Contact:** | **esi-hrms@unige.ch** | | |

| Expected Formula | Ion type | Theoretical *m/z* | Observed *m/z* | Accuracy *(ppm)* [a] |
|---|---|---|---|---|
| $C_{34}H_{34}BrN_2O_3$ | $[M]^+$ | 597.1747 | 597.1759 | 1.9 |




[a] *Mass accuracy is determined after spectrum re-calibration (internal calibration with standards added to the FIA mobile phase)*

Recalibrated mass spectrum

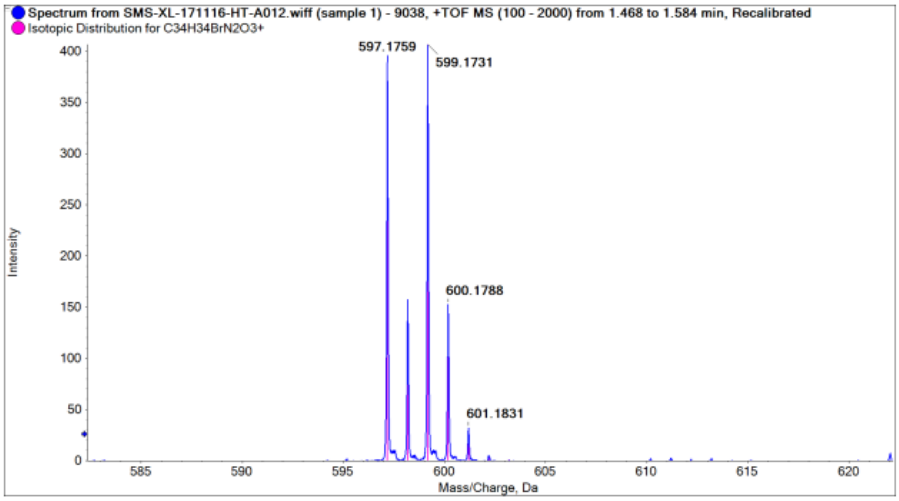



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Figure S 30. HRMS spectrum of compound **10**.

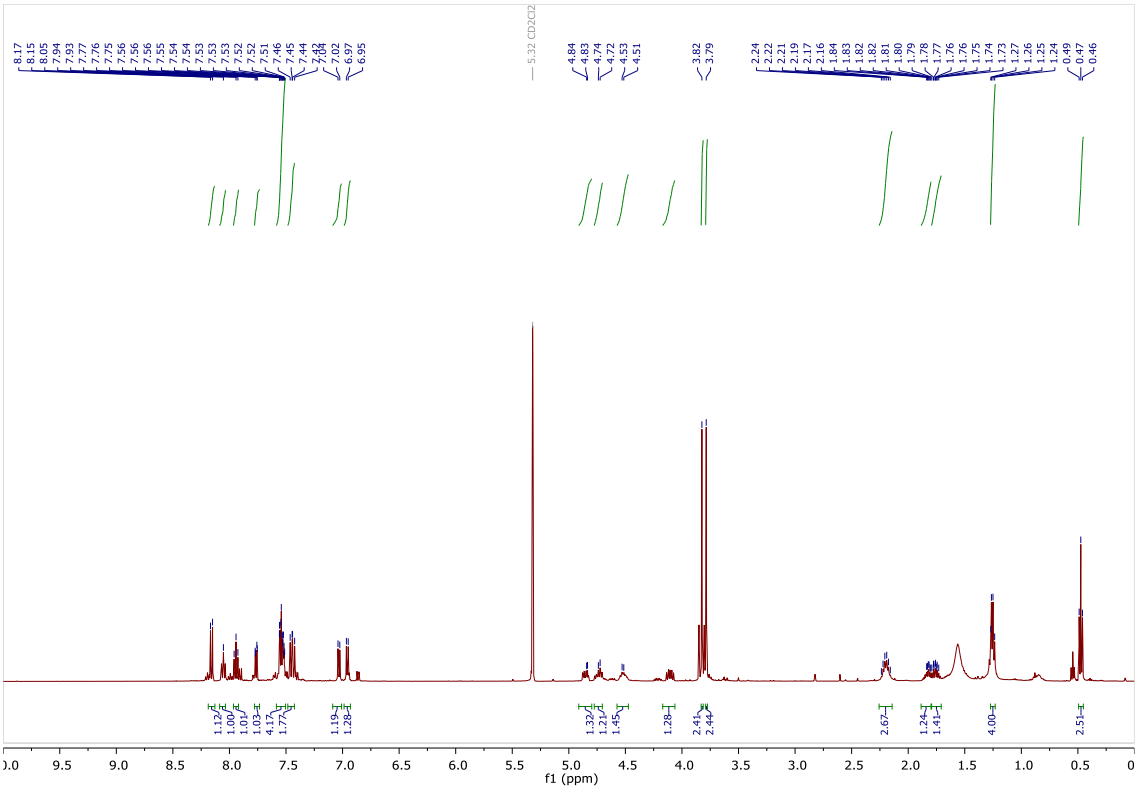


Figure S 31. $^{1}$H NMR ($CD_2Cl_2$, 500MHz MHz) spectrum of compound **K1**.

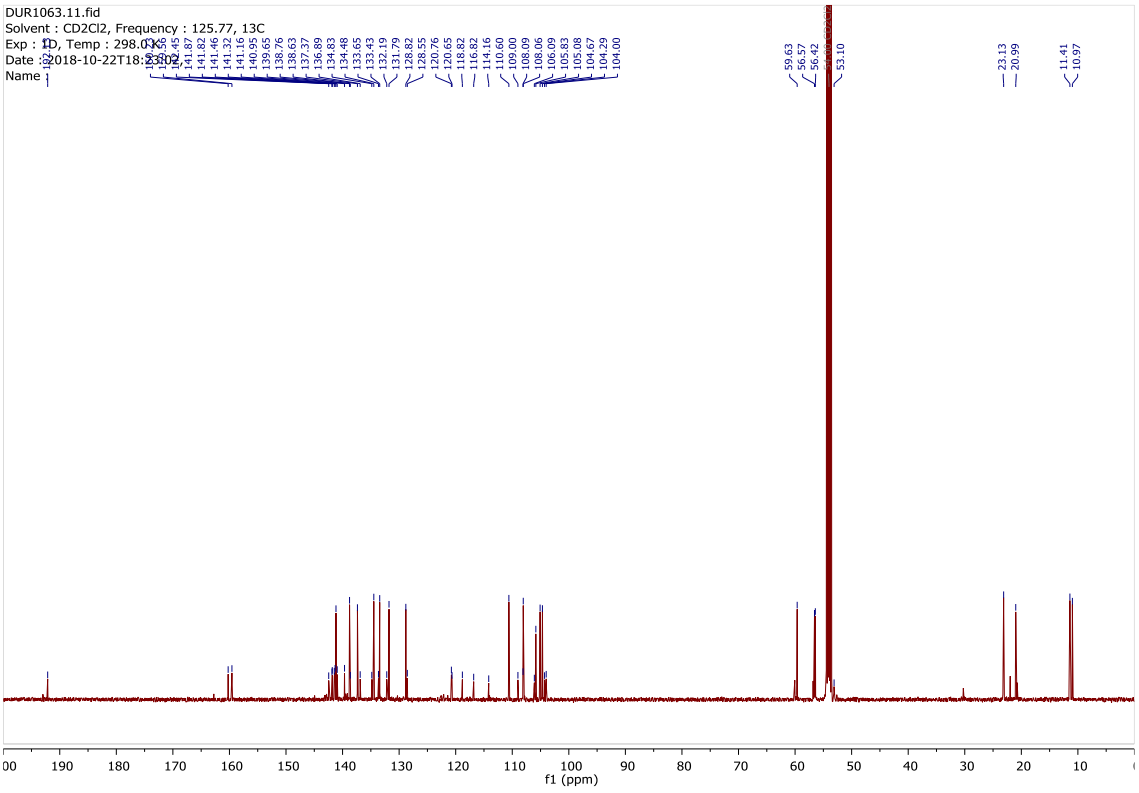


Figure S 32. $^{13}$C NMR ($CD_2Cl_2$, 125MHz MHz) spectrum of compound **K1**.

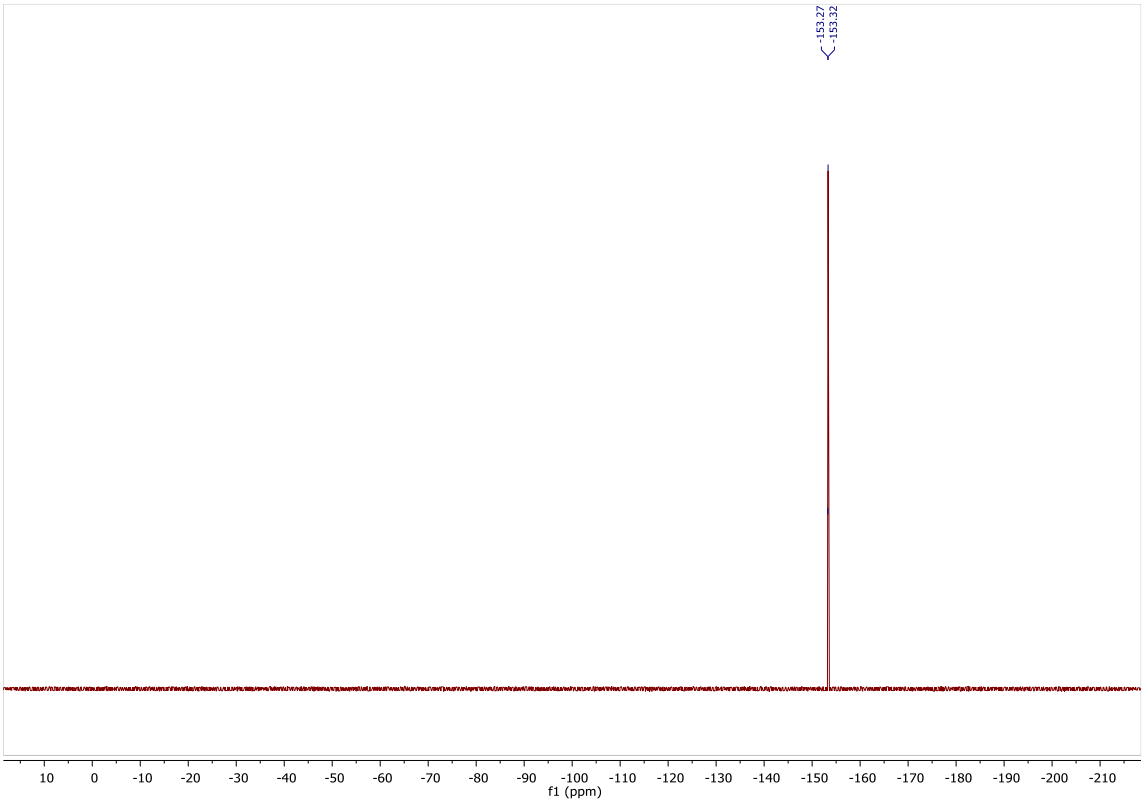


Figure S 33. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **K1**.

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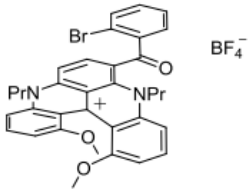
| Applicant: | Romain DUWALD | Date of reception: | November 16th, 2017 |
| Group/Company: | Prof. Jérôme LACOUR | Date of certificate: | November 28th, 2017 |
| Sample name: | SG720 | Data filename: | SMS-XL-171116-HT-A010 |
| Sample number: | 9037 | Instrument: | QSTAR XL (AB/MDS Sciex) |
| **Analyst:** | **Harry THERAULAZ** | Ionisation mode: | ESI (positive polarity) |
| **Contact:** | **esi-hrms@unige.ch** | | |

| Expected Formula | Ion type | Theoretical *m/z* | Observed *m/z* | Accuracy *(ppm)* [a] |
|---|---|---|---|---|
| $C_{34}H_{32}BrN_2O_3$ | $[M]^+$ | 595.1591 | 595.1597 | 1.1 |




$BF_4^-$

[a] *Mass accuracy is determined after spectrum re-calibration (internal calibration with standards added to the FIA mobile phase)*

Recalibrated mass spectrum

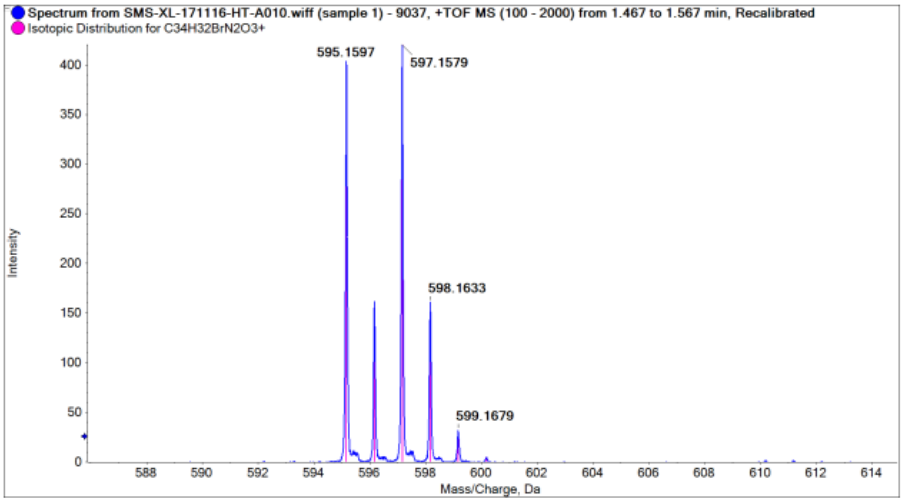



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Figure S 34. HRMS spectrum of compound **K1**.

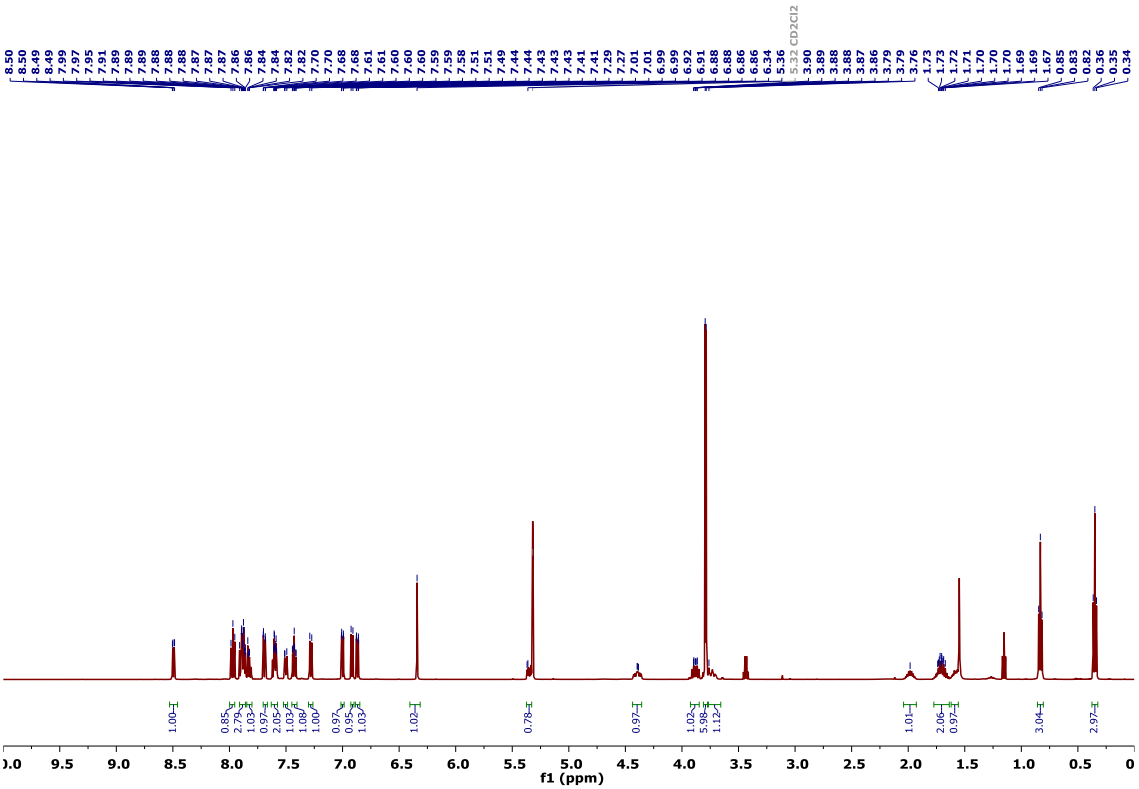

Figure S 35. $^{1}H$ NMR ($CD_2Cl_2$, 500MHz MHz) spectrum of compound **1**.

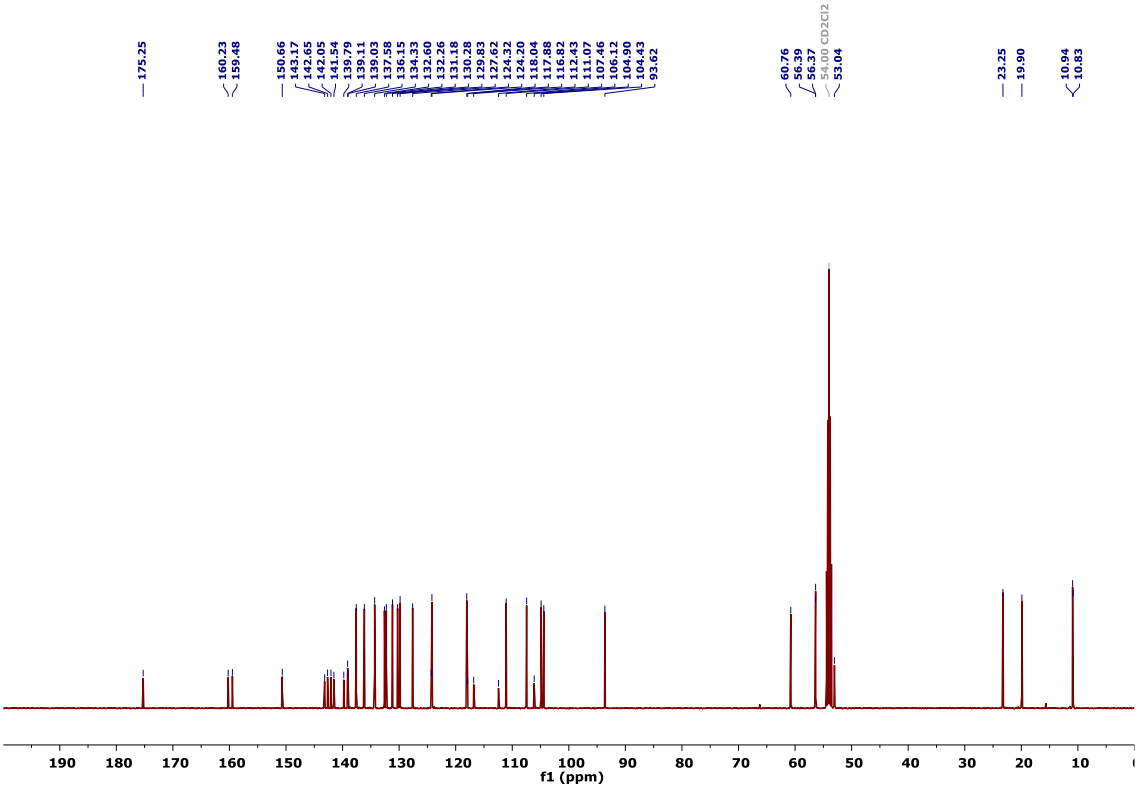

Figure S 36. $^{13}C$ NMR ($CD_2Cl_2$, 125MHz MHz) spectrum of compound **1**.

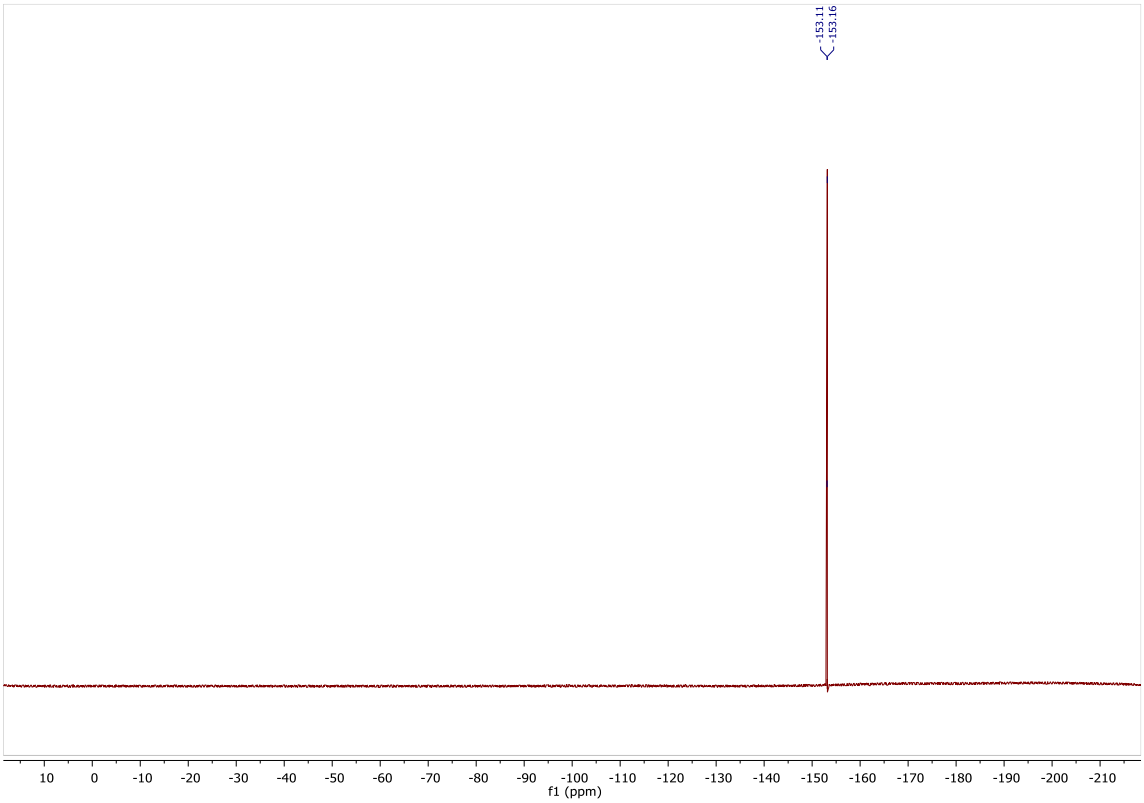


Figure S 37. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **1**.

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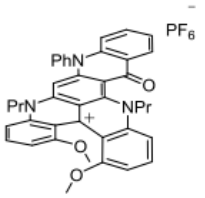
| Applicant: | Romain DUWALD | Date of reception: | October 29th, 2018 |
| Group/Company: | Prof. Lacour | Date of certificate: | October 30th, 2018 |
| Sample name: | DUR1027 | Data filename: | SMS-XL-181030-LW-A006 |
| Sample number: | 9592 | Instrument: | XL_R3 (AB/MDS Sciex) |
| **Analyst:** | **Eliane Sandmeier** | Ionisation mode: | ESI (positive polarity) |
| **Contact:** | **esi-hrms@unige.ch** | | |

| Expected Formula | Ion type | Theoretical *m/z* | Observed *m/z* | Accuracy *(ppm)* [a] |
|---|---|---|---|---|
| $C_{40}H_{36}N_3O_3$ | $[M]^+$ | 606.2751 | 606.2756 | 0.8 |

**DuR1027**




Chemical Formula: $C_{40}H_{36}N_3O_3^+$
Exact Mass: 606.28

[a] *Mass accuracy is determined after spectrum re-calibration (internal calibration with standards added to the FIA mobile phase)*

Recalibrated mass spectrum

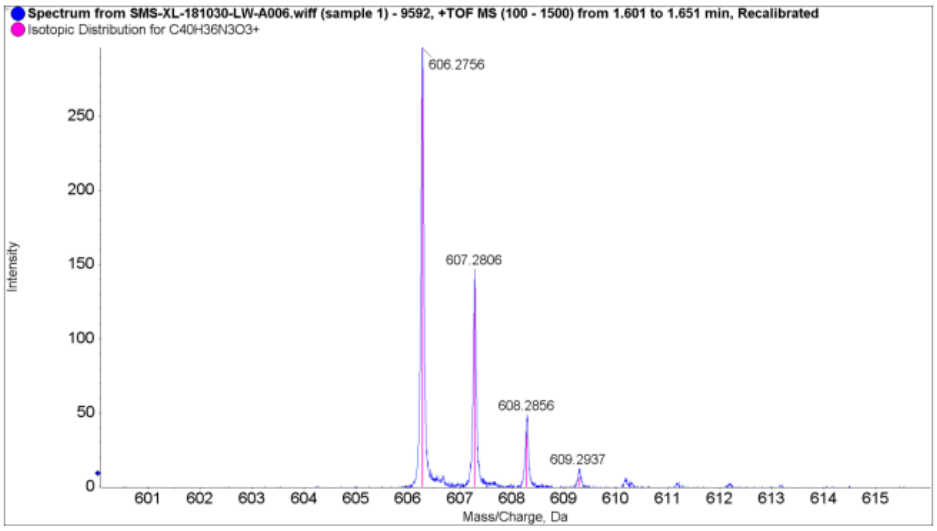



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Figure S 38. HRMS spectrum of compound **1**.

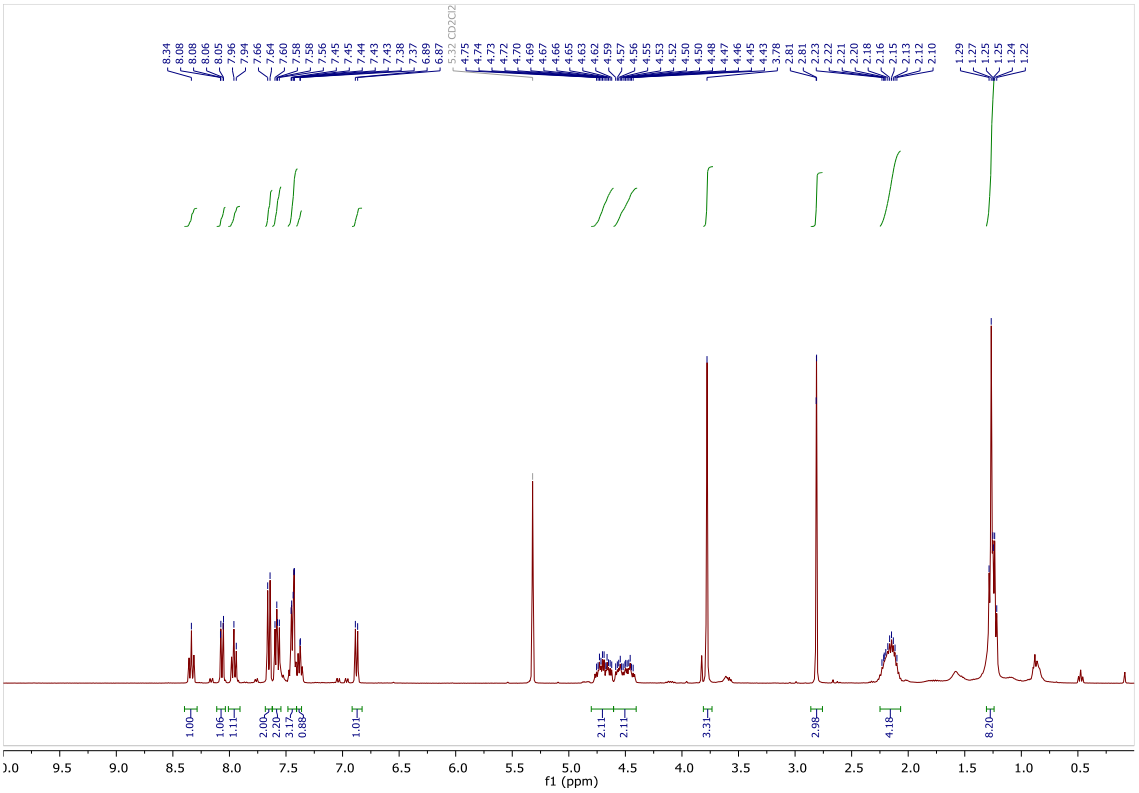


Figure S 39. $^{1}H$ NMR ($CD_2Cl_2$, 400MHz MHz) spectrum of compound **K2**.

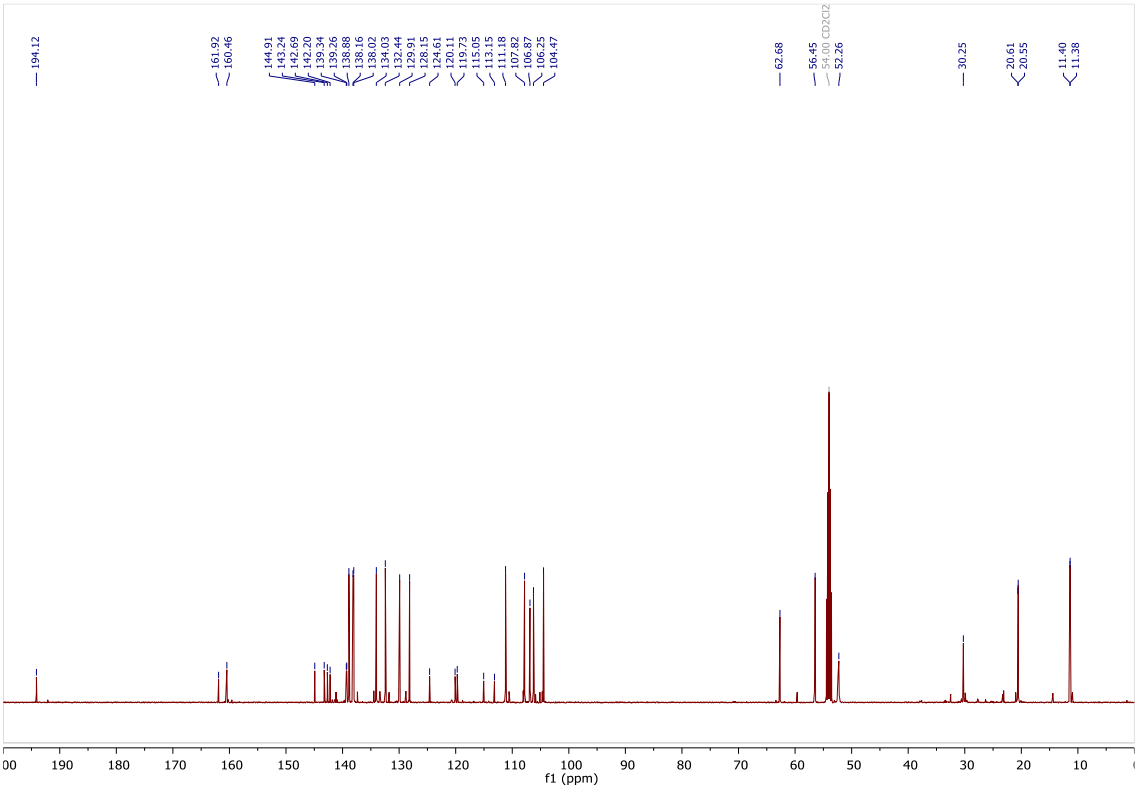


Figure S 40. $^{13}C$ NMR ($CD_2Cl_2$, 125 MHz MHz) spectrum of compound **K2**.

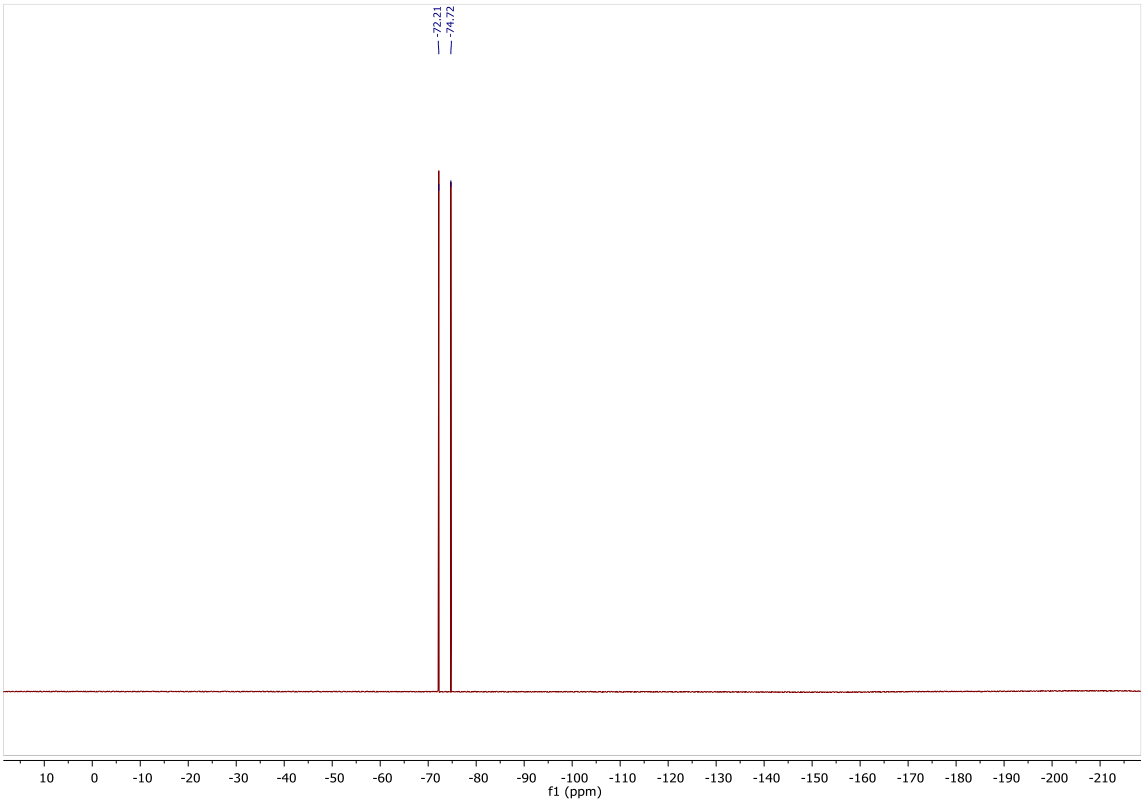


Figure S 41. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **K2**.

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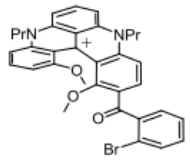
| Applicant: | Romain DUWALD | Date of reception: | October 29th, 2018 |
| Group/Company: | Prof. Lacour | Date of certificate: | October 30th, 2018 |
| Sample name: | DUR767 | Data filename: | SMS-XL-181030-LW-A004 |
| Sample number: | 9590 | Instrument: | XL_R3 (AB/MDS Sciex) |
| **Analyst:** | **Eliane Sandmeier** | Ionisation mode: | ESI (positive polarity) |
| **Contact:** | **esi-hrms@unige.ch** | | |

| Expected Formula | Ion type | Theoretical *m/z* | Observed *m/z* | Accuracy *(ppm)* [a] |
|---|---|---|---|---|
| $C_{34}H_{32}BrN_2O_3$ | $[M]^+$ | 595.1591 | 595.1600 | 1.6 |

**DuR767** $BF_4^-$




Chemical Formula: $C_{34}H_{32}BrN_2O_3^+$
Exact Mass: 595.16

[a] *Mass accuracy is determined after spectrum re-calibration (internal calibration with standards added to the FIA mobile phase)*

Recalibrated mass spectrum

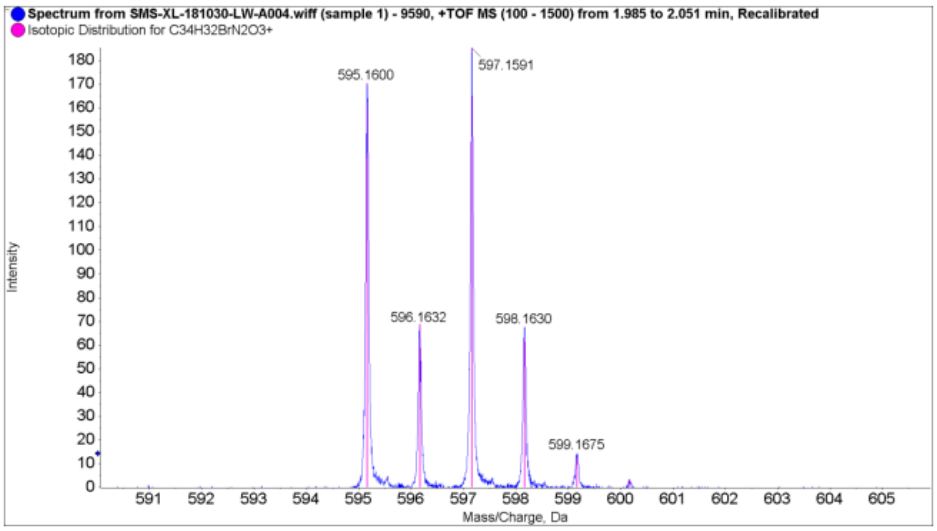



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Figure S 42. HRMS spectrum of compound **K2**.

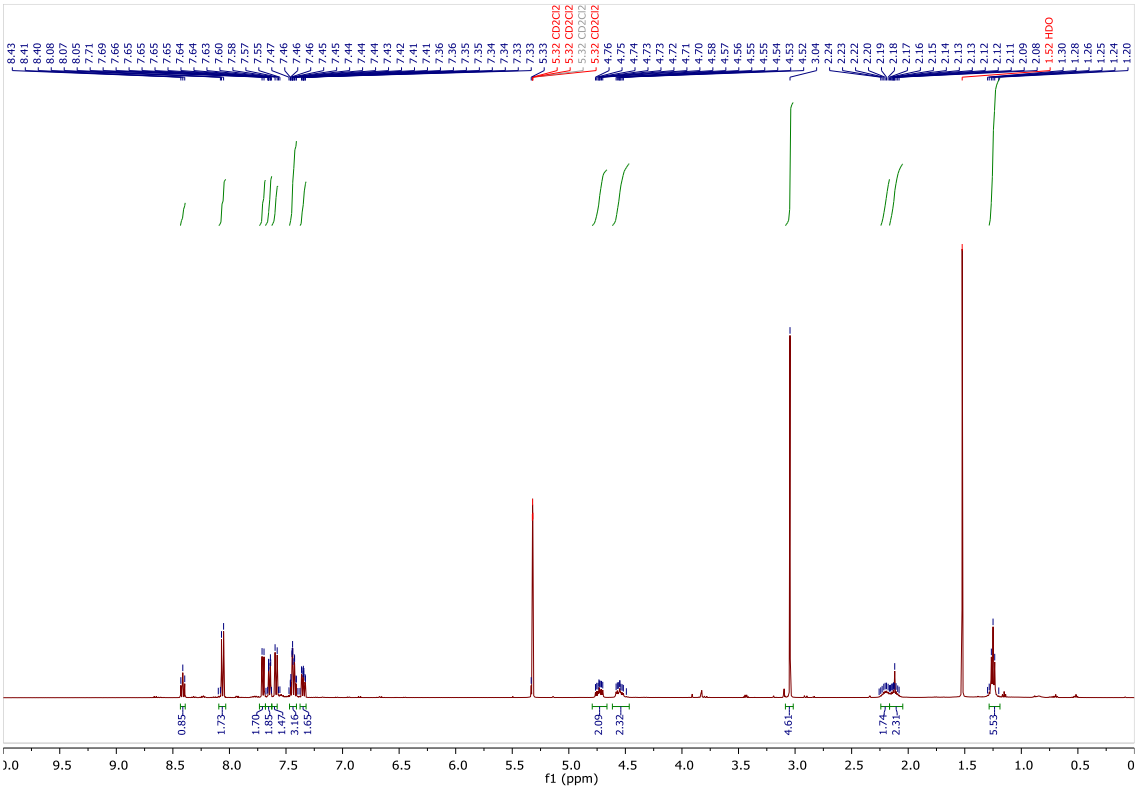


Figure S 43. $^{1}H$ NMR ($CD_2Cl_2$, 500MHz MHz) spectrum of compound **K3**.

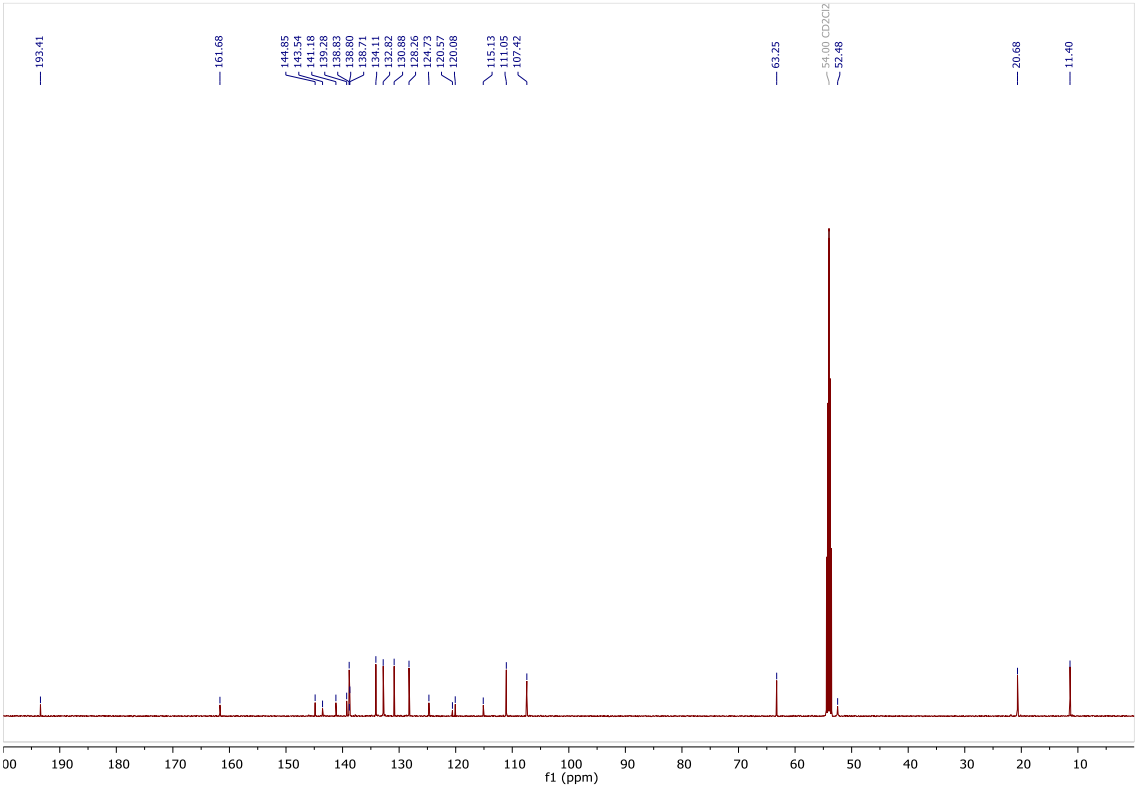


Figure S 44. $^{13}C$ NMR ($CD_2Cl_2$, 125MHz MHz) spectrum of compound **K3**.

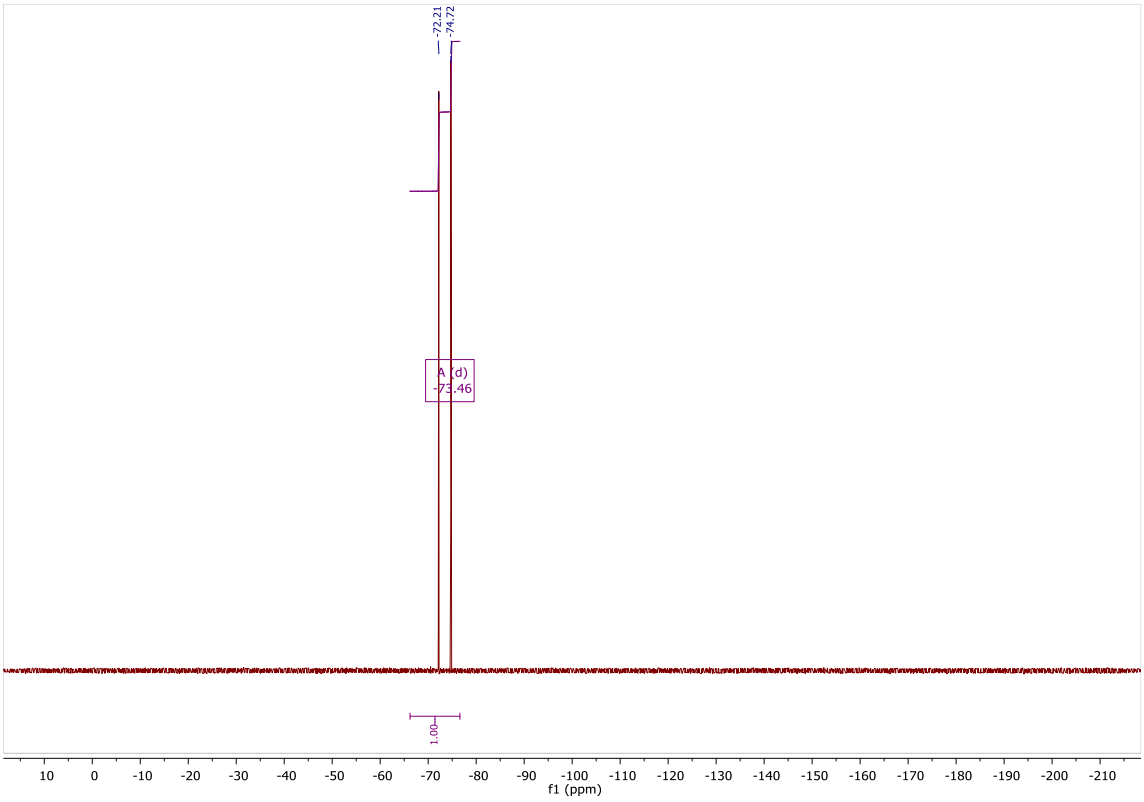


Figure S 45. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **K3**.

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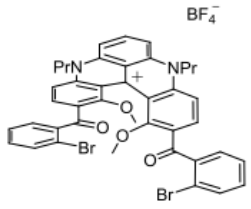
| Applicant: | Romain DUWALD | Date of reception: | October 29th, 2018 |
| Group/Company: | Prof. Lacour | Date of certificate: | October 30th, 2018 |
| Sample name: | DUR1058 | Data filename: | SMS-XL-181030-LW-A008 |
| Sample number: | 9594 | Instrument: | XL_R3 (AB/MDS Sciex) |
| **Analyst:** | **Eliane Sandmeier** | Ionisation mode: | ESI (positive polarity) |
| **Contact:** | **esi-hrms@unige.ch** | | |

| Expected Formula | Ion type | Theoretical *m/z* | Observed *m/z* | Accuracy *(ppm)* [a] |
|---|---|---|---|---|
| $C_{41}H_{35}Br_2N_2O_4$ | $[M]^+$ | 777.0958 | 777.0970 | 1.5 |

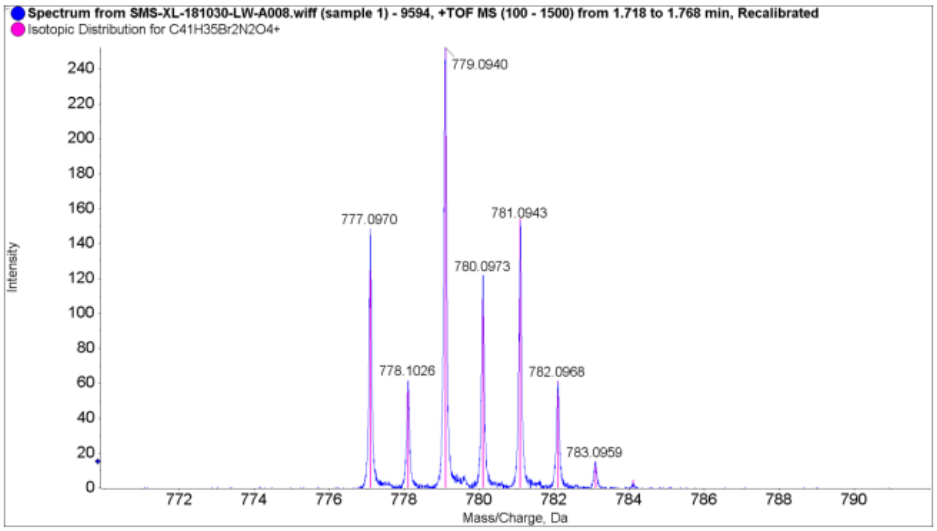
**DuR1058**




Chemical Formula: $C_{41}H_{35}Br_2N_2O_4^+$
Exact Mass: 777.10

[a] *Mass accuracy is determined after spectrum re-calibration (internal calibration with standards added to the FIA mobile phase)*

Recalibrated mass spectrum




1/1

Figure S 46. HRMS spectrum of compound **K3**.

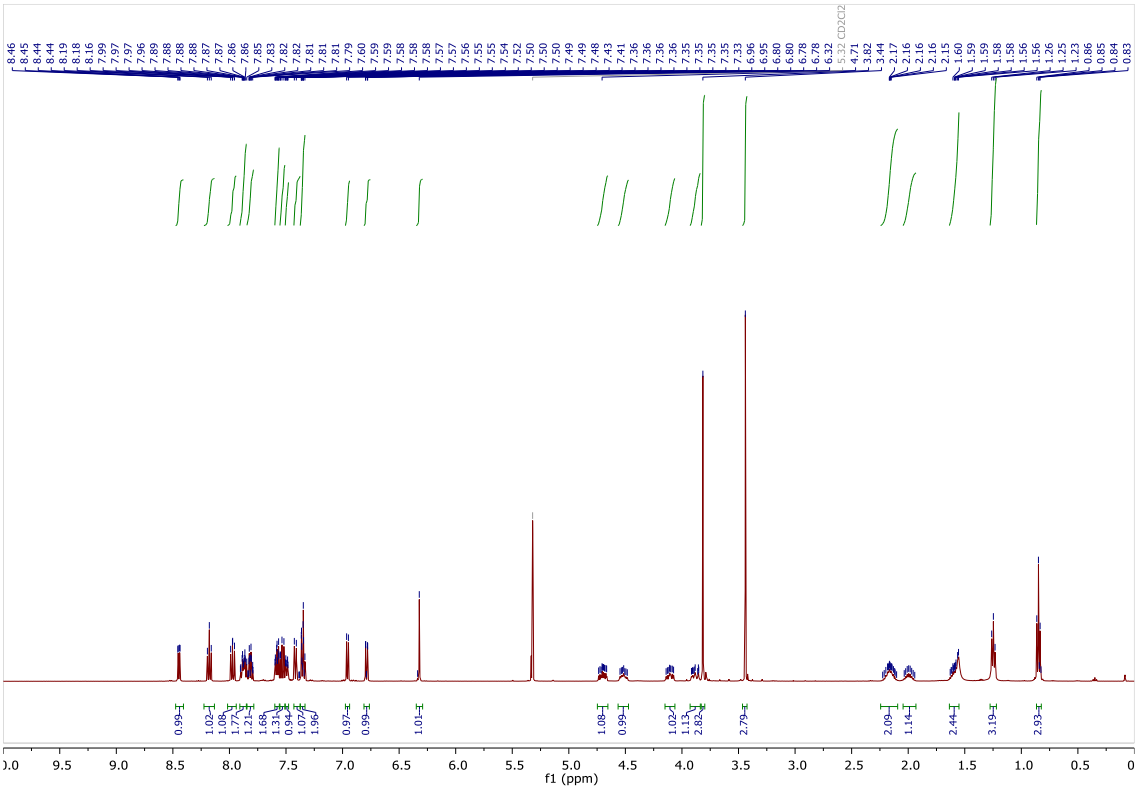


Figure S 47. $^{1}H$ NMR ($CD_2Cl_2$, 500MHz MHz) spectrum of compound **2**.

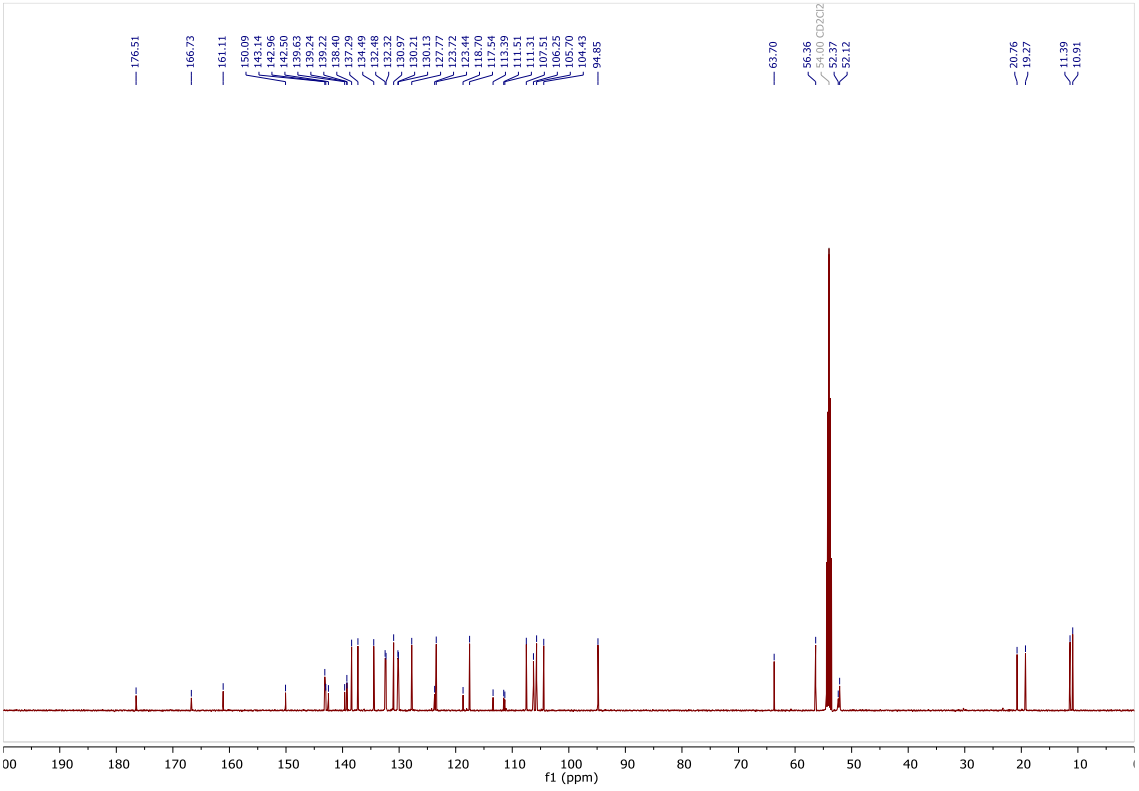


Figure S 48. $^{13}C$ NMR ($CD_2Cl_2$, 500MHz MHz) spectrum of compound **2**.

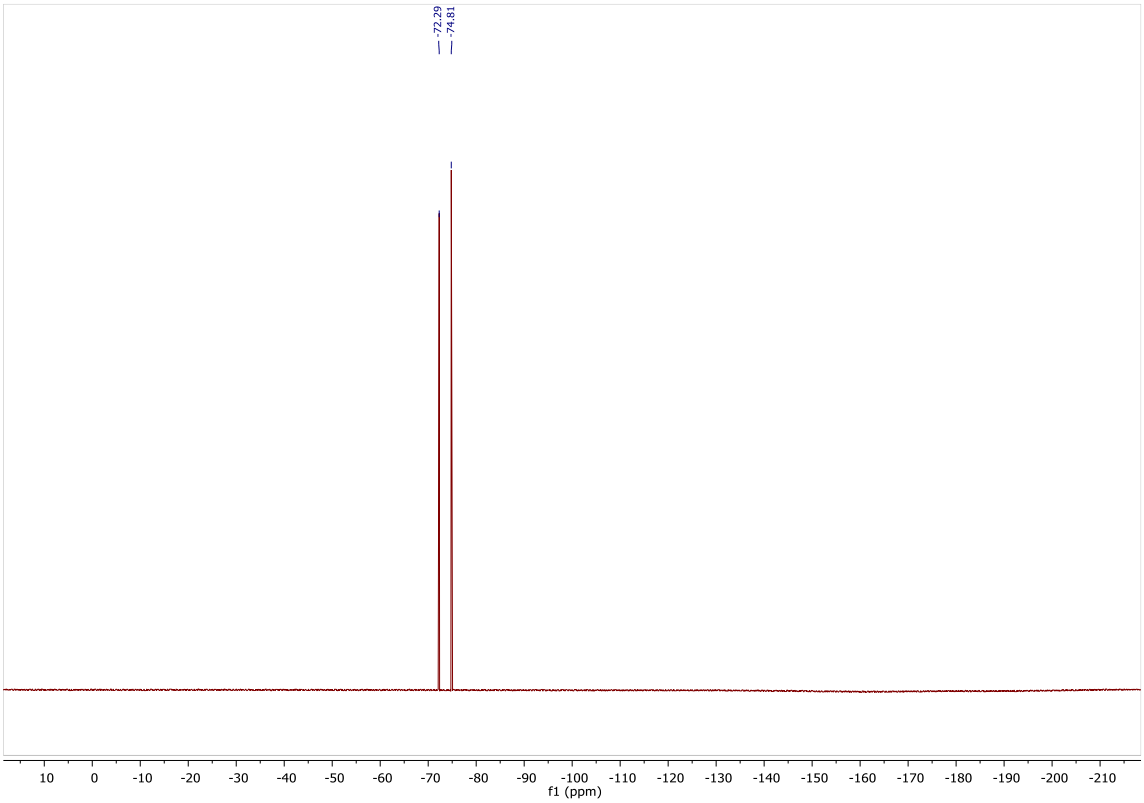



Figure S 49. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **2**.

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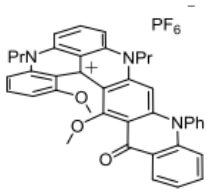
| Applicant: | Romain DUWALD | Date of reception: | October 29th, 2018 |
| Group/Company: | Prof. Lacour | Date of certificate: | October 30th, 2018 |
| Sample name: | DUR731 | Data filename: | SMS-XL-181030-LW-A006 |
| Sample number: | 9593 | Instrument: | XL_R3 (AB/MDS Sciex) |
| **Analyst:** | **Eliane Sandmeier** | Ionisation mode: | ESI (positive polarity) |
| **Contact:** | **esi-hrms@unige.ch** | | |

| Expected Formula | Ion type | Theoretical *m/z* | Observed *m/z* | Accuracy *(ppm)* [a] |
|---|---|---|---|---|
| $C_{40}H_{36}N_3O_3$ | $[M]^+$ | 606.2751 | 606.2756 | 0.8 |

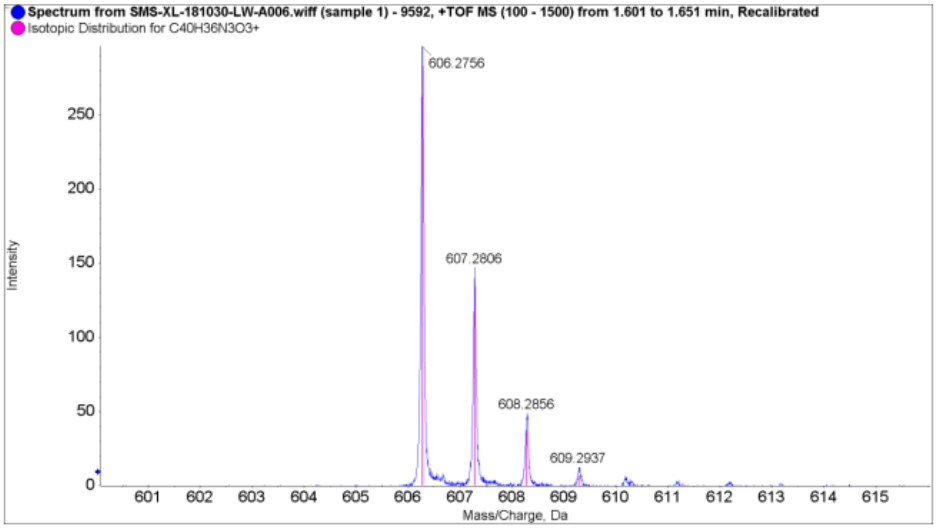
**DuR731**




Chemical Formula: $C_{40}H_{36}N_3O_3^+$
Exact Mass: 606.28

[a] *Mass accuracy is determined after spectrum re-calibration (internal calibration with standards added to the FIA mobile phase)*

Recalibrated mass spectrum




1/1

Figure S 50. HRMS spectrum of compound **2.**

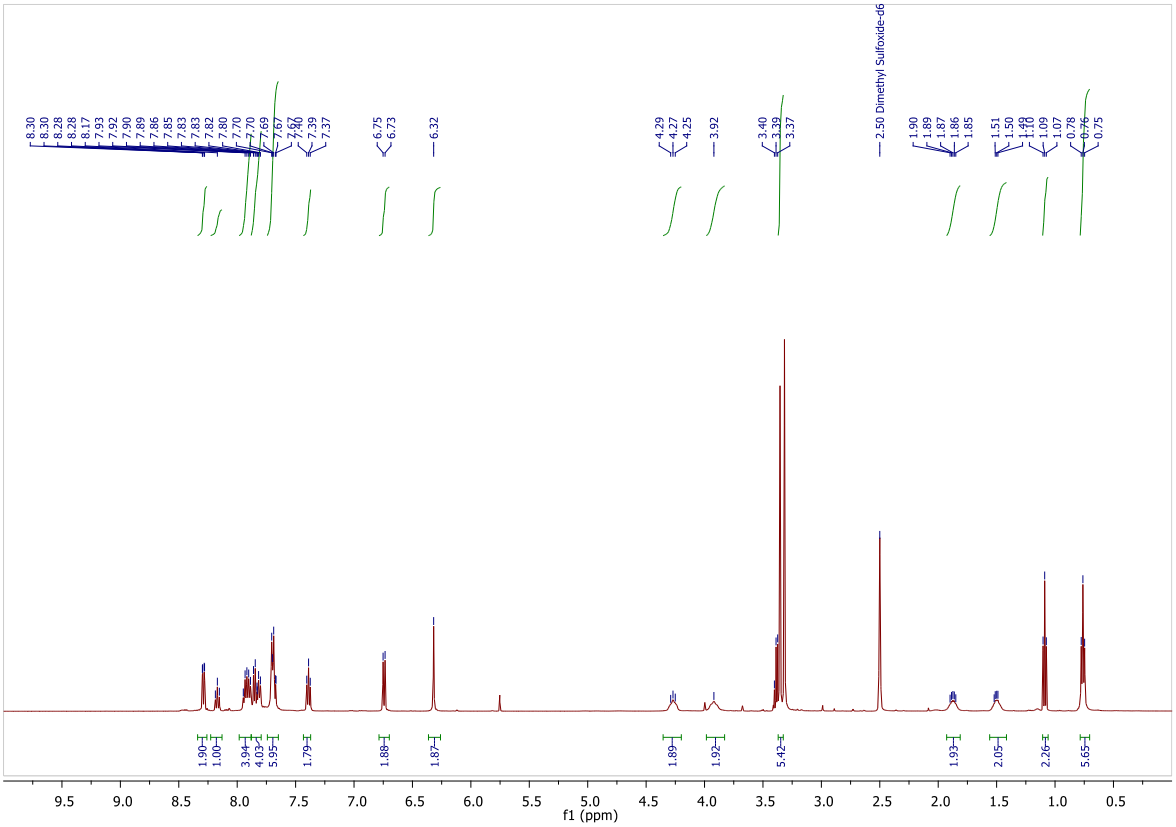



Figure S 51. $^{1}$H NMR (DMSO-*d6*, 500 MHz) spectrum of compound **3**.

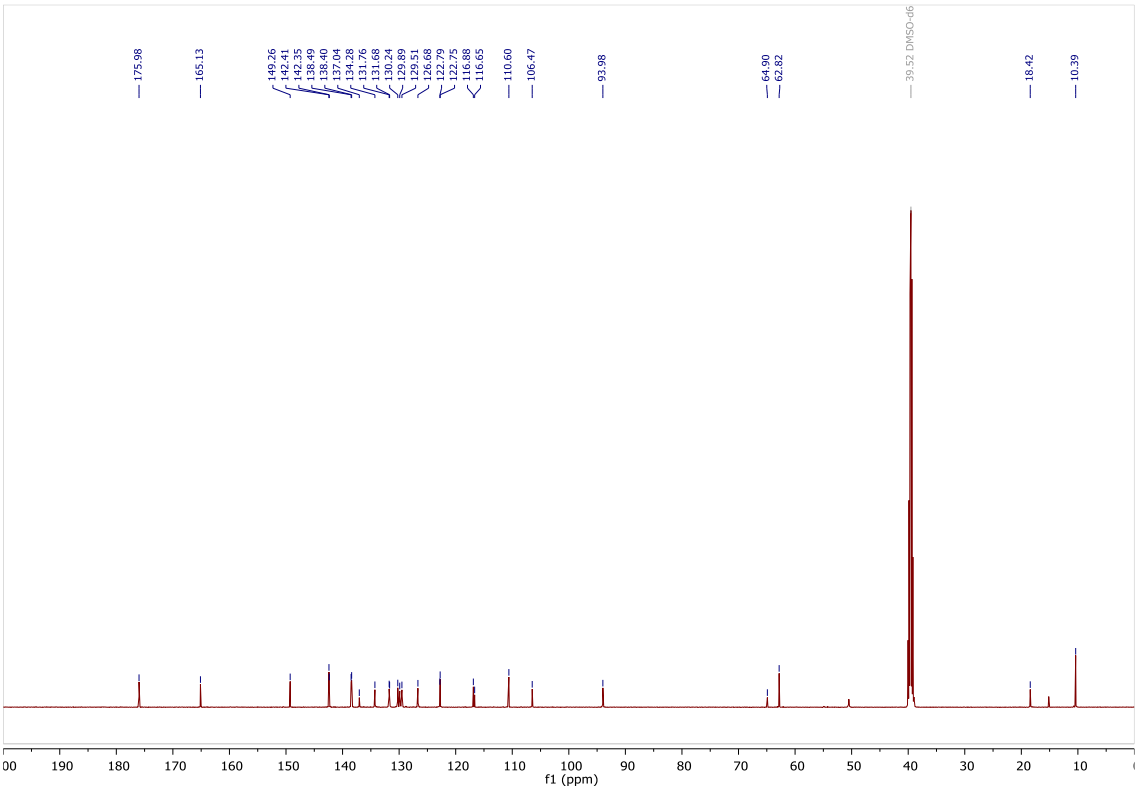



Figure S 52. $^{13}$C NMR (DMSO-*d6*, 125 MHz MHz) spectrum of compound **3.**

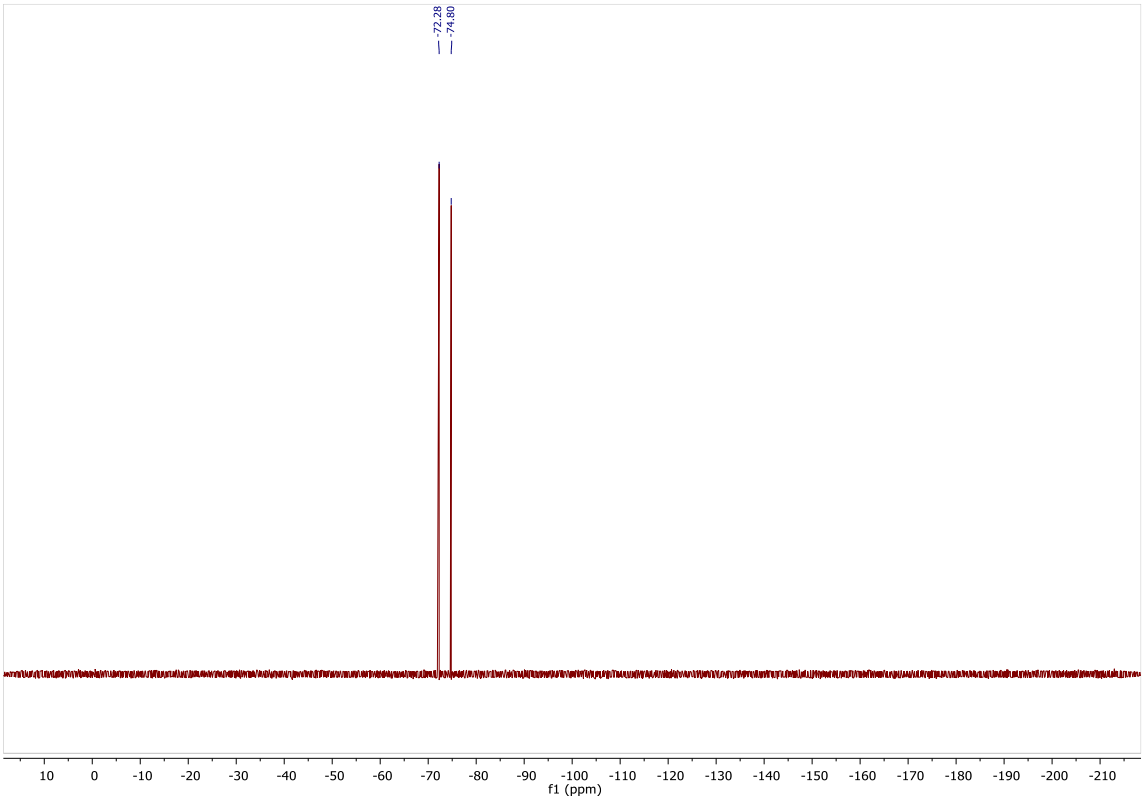



Figure S 53. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **3**.

## Mass Spectrometry Core Facility

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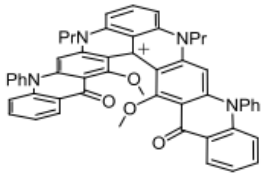
# ESI-HRMS – Certificate of Analysis

| | | | |
|---|---|---|---|
| Applicant: | Romain DUWALD | Date of reception: | October 29th, 2018 |
| Group/Company: | Prof. Lacour | Date of certificate: | October 30th, 2018 |
| Sample name: | DUR1064 | Data filename: | SMS-XL-181030-LW-A005 |
| Sample number: | 9591 | Instrument: | XL_R3 (AB/MDS Sciex) |
| **Analyst:** | **Eliane Sandmeier** | Ionisation mode: | ESI (positive polarity) |
| **Contact:** | **esi-hrms@unige.ch** | | |

| Expected Formula | Ion type | Theoretical *m/z* | Observed *m/z* | Accuracy *(ppm)* [a] |
|---|---|---|---|---|
| $C_{53}H_{43}N_4O_4$ | $[M]^+$ | 799.3279 | 799.3277 | -0.3 |

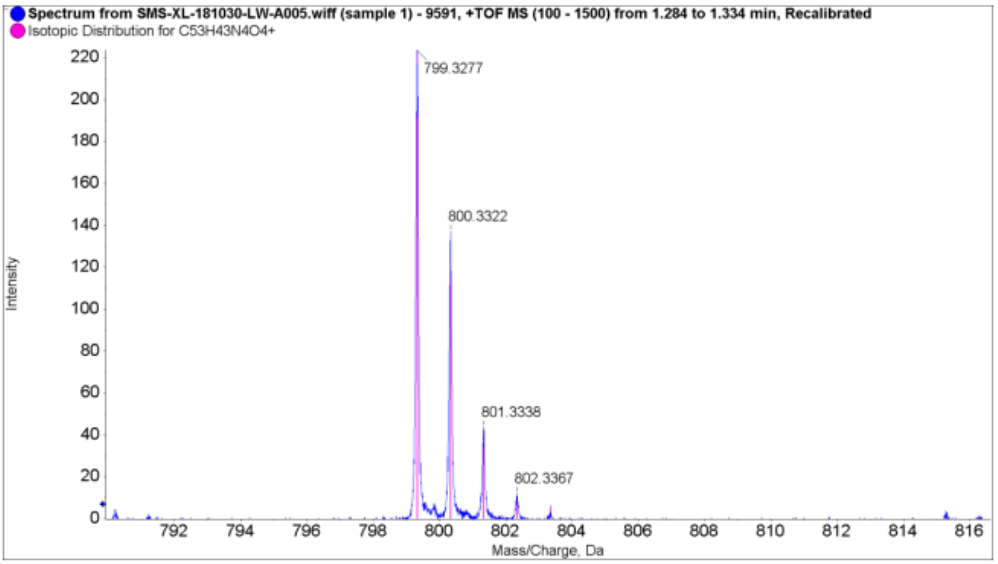
**DuR1064** $PF_6^-$




Chemical Formula: $C_{53}H_{43}N_4O_4^+$
Exact Mass: 799.33

[a] *Mass accuracy is determined after spectrum re-calibration (internal calibration with standards added to the FIA mobile phase)*

Recalibrated mass spectrum




1/1

Figure S 54. HRMS spectrum of compound **2**.

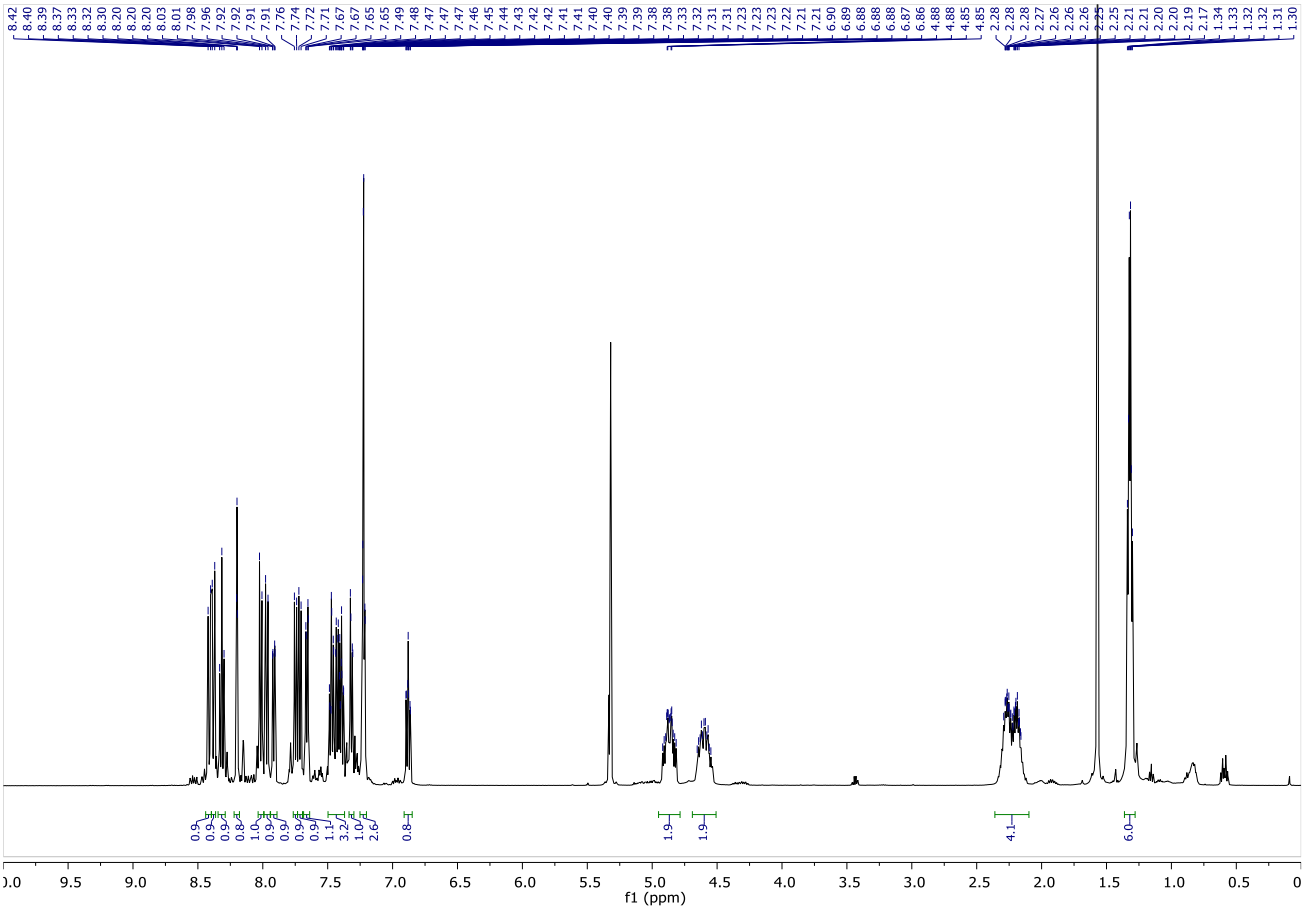



Figure S 55. $^{1}$H NMR (500 MHz, $CD_2Cl_2$) spectrum of compound **K4**

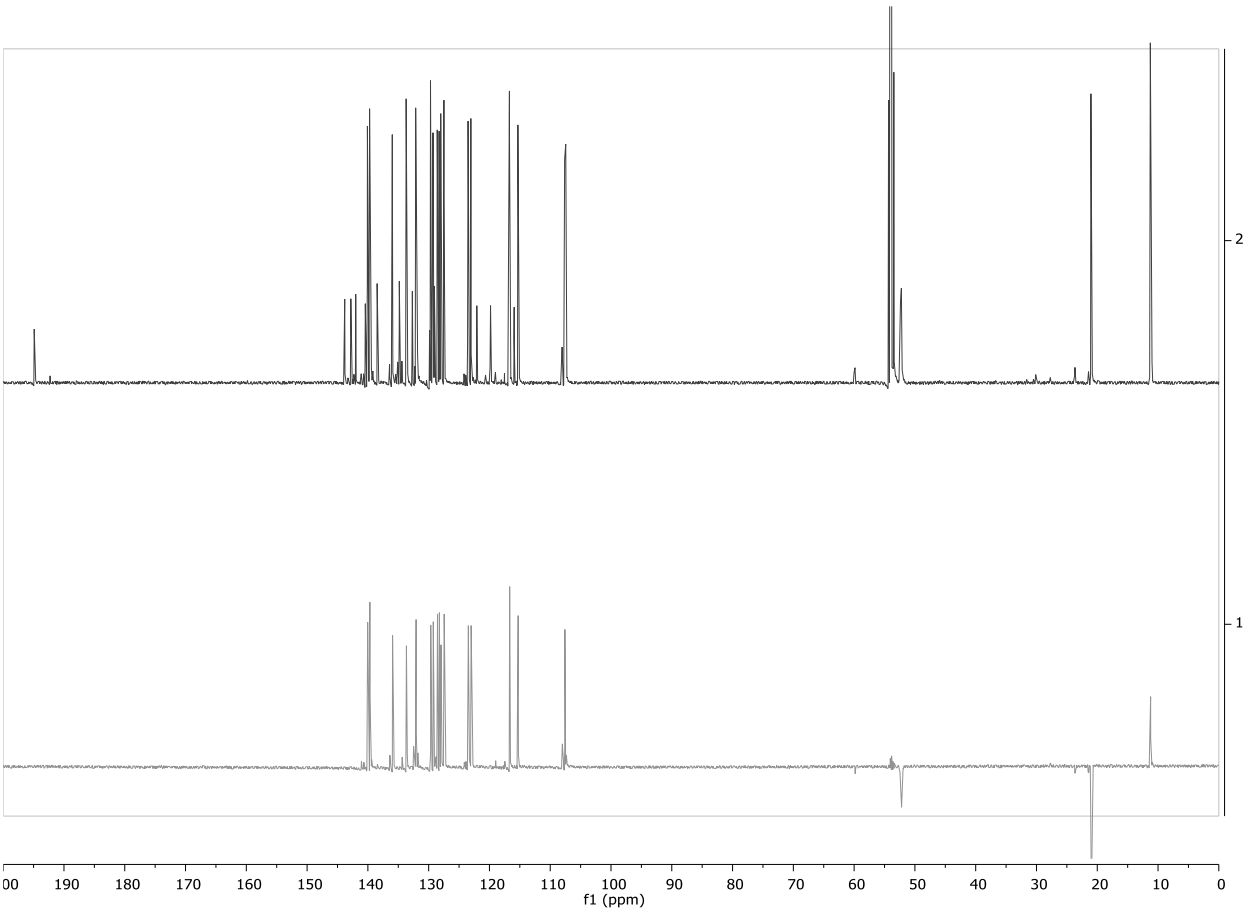



Figure S 56. $^{13}$C NMR and DEPT 135 (126 MHz, $CD_2Cl_2$) of spectrum compound **K4**

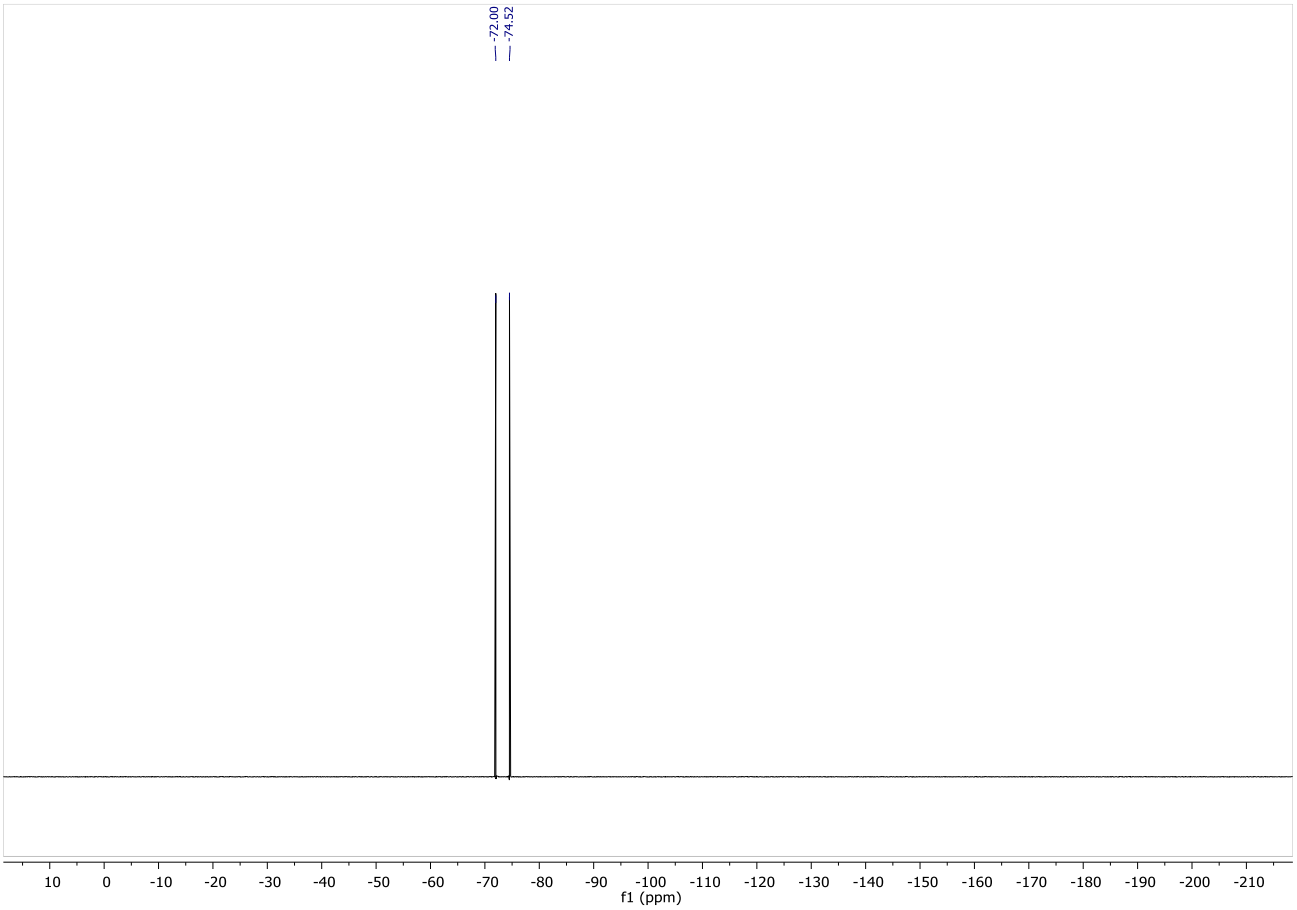



Figure S 57. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **K4**

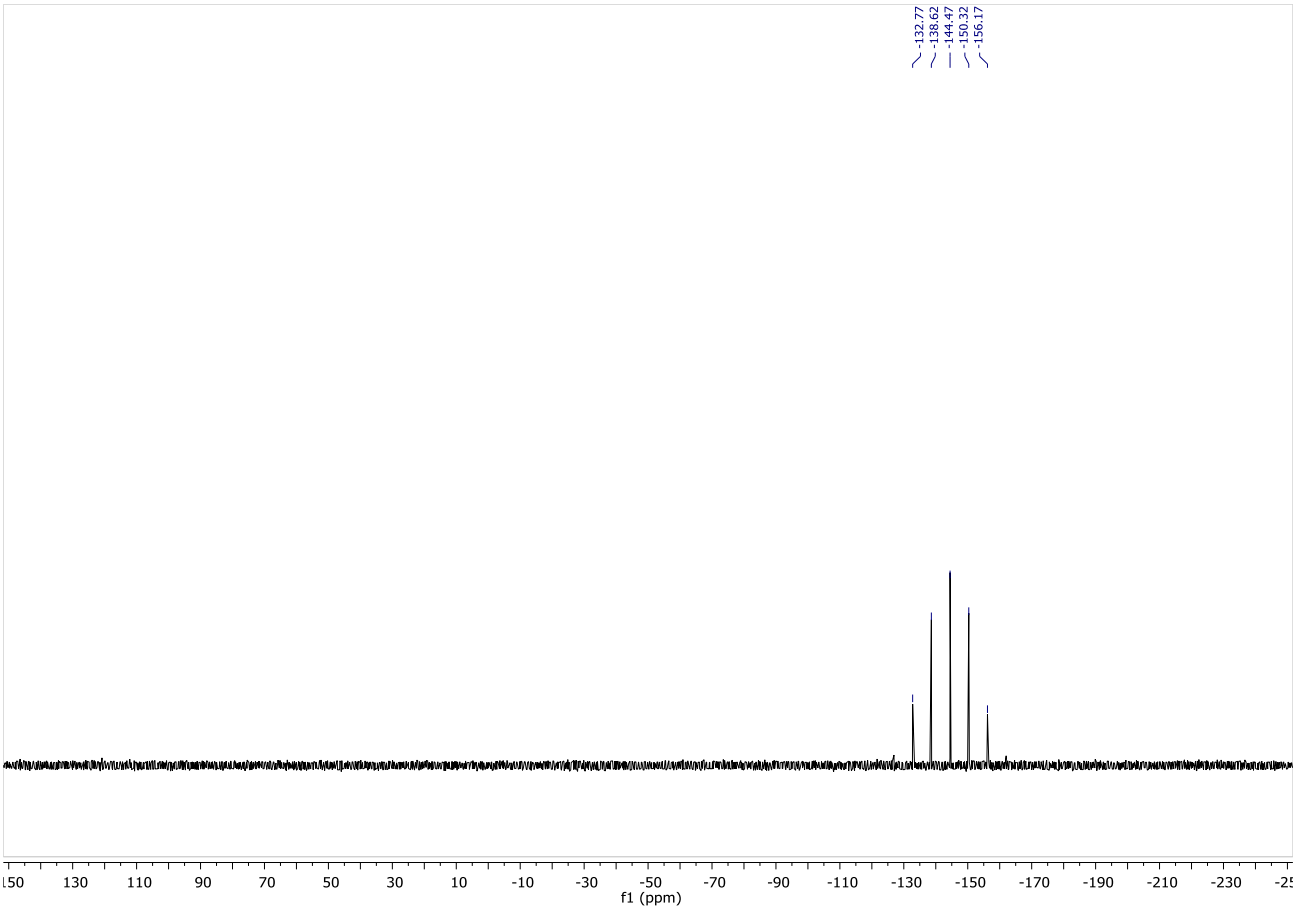



Figure S 58. $^{31}P$ NMR (121 MHz, $CD_2Cl_2$) spectrum of compound **K4**

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## ESI-HRMS – Certificate of Analysis

| | | | |
|---|---|---|---|
| Applicant: | Bosson Johann | Date of certificate: | 06/08/19 |
| Sample name: | JB1221 | Instrument: | Xevo G2 Tof (TOF) |
| Folder: | 060819.PRO | Mobile phase: | MeOH (100 µl/min) |
| Analyst: | Stéphane Grass | Ionisation mode: | ESI (positive polarity) |

| Elemental Formula | Ion type | *Masslynx values **** calc. *m/z* | *Masslynx values **** meas. *m/z* | Calc. *m/z* | Meas. *m/z* | Accuracy [a] *(ppm)* |
|---|---|---|---|---|---|---|
| $C_{40}H_{32}BrN_2O$ | $[M+H]^+$ | *635.1698* | *635.1694* | 635.1693 | 635.1689 | -0.6 |

[a] *Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution).*

**** MassLynx software does not take into account the mass of the electron for ionic species, therefore the shift of m/z 0.000459.*

Zoomed mass spectrum – Isotopic distribution.

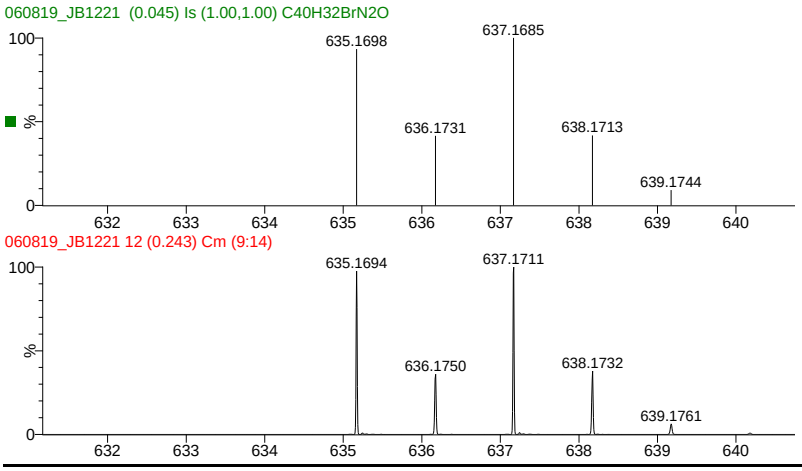


Figure S 59. HRMS (ESI) report of compound **K4**

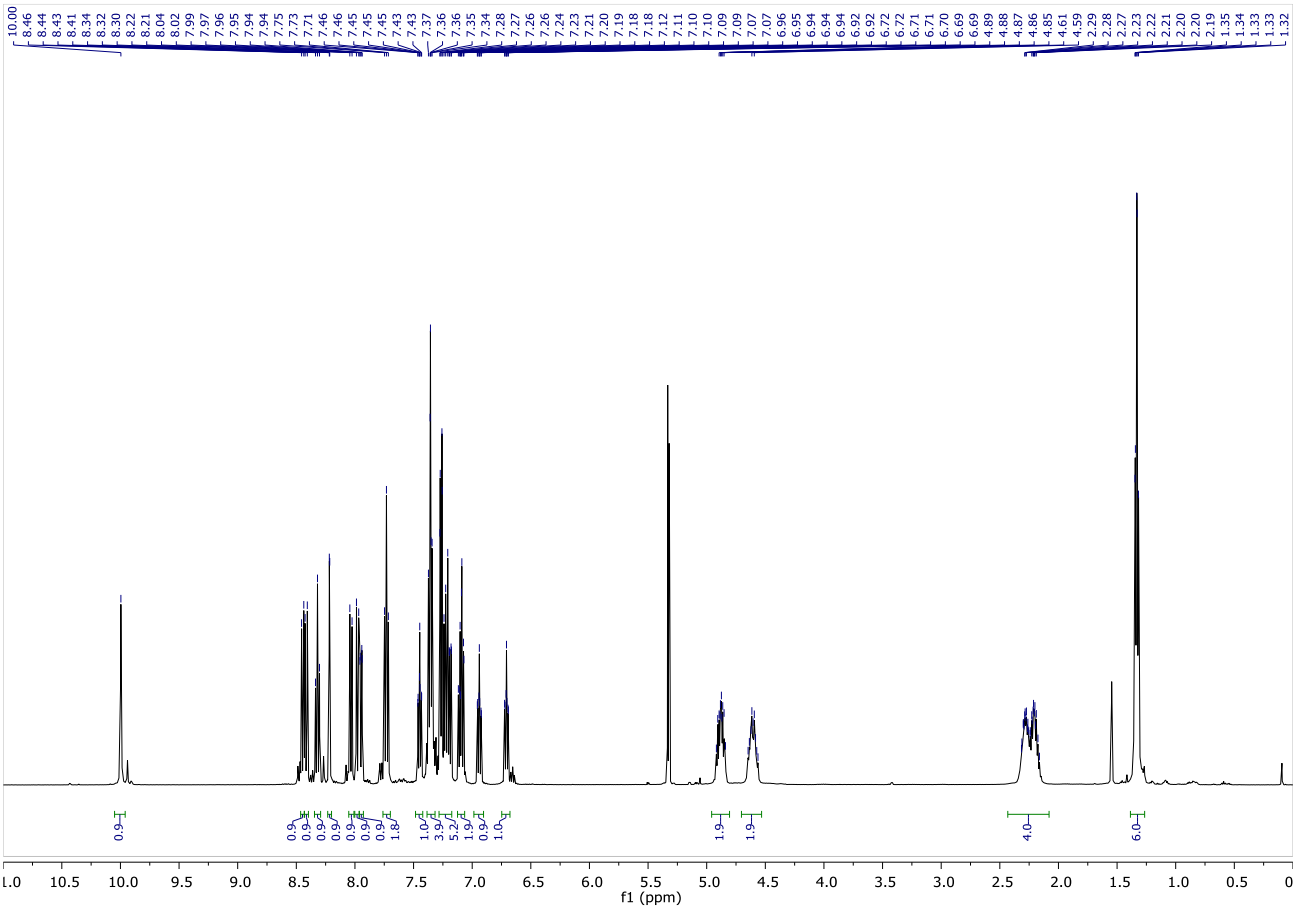


Figure S 60. $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) spectrum of compound **11**

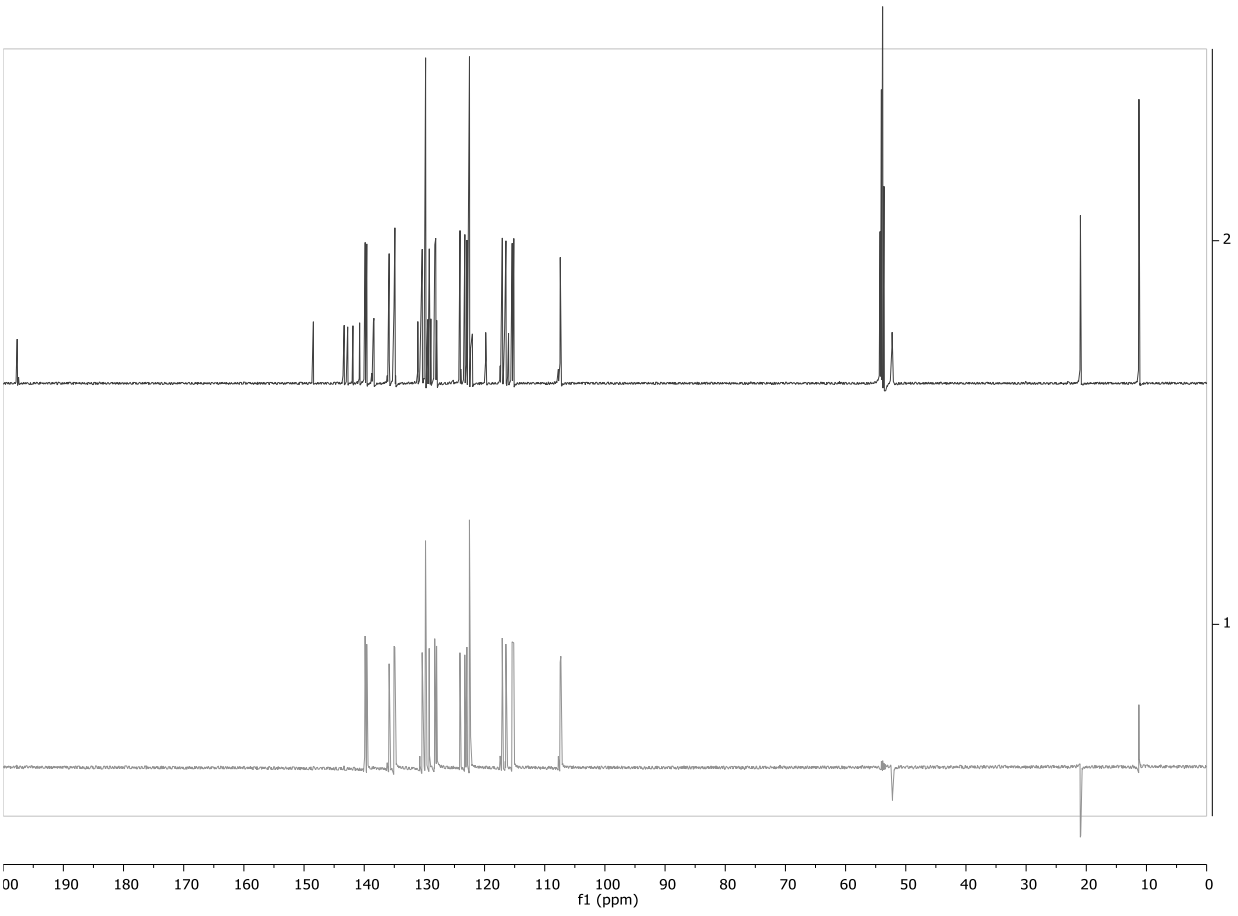


Figure S 61. $^{13}C$ NMR and DEPT 135 (126 MHz, $CD_2Cl_2$) spectrum of compound **11**

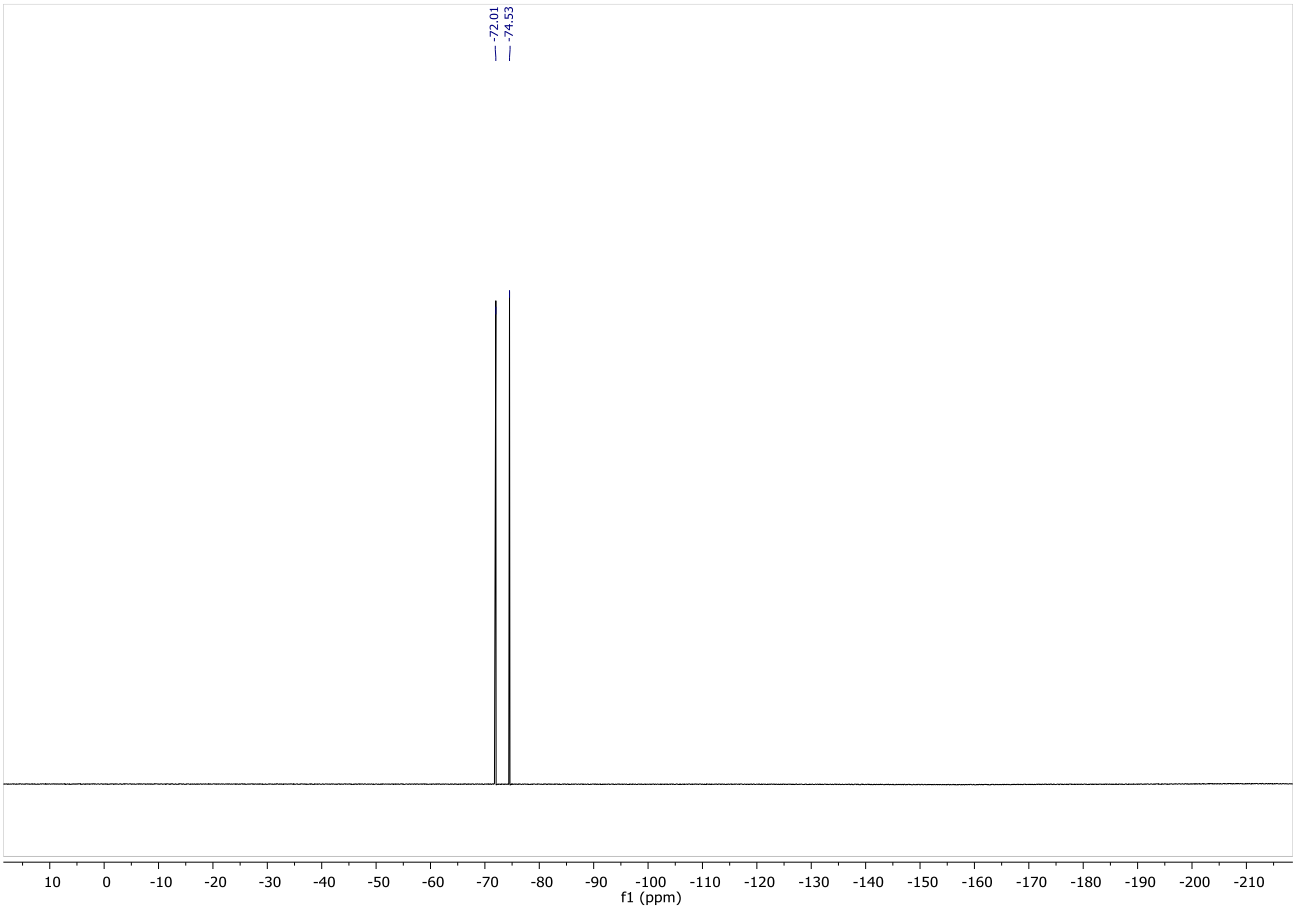


Figure S 62. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **11**

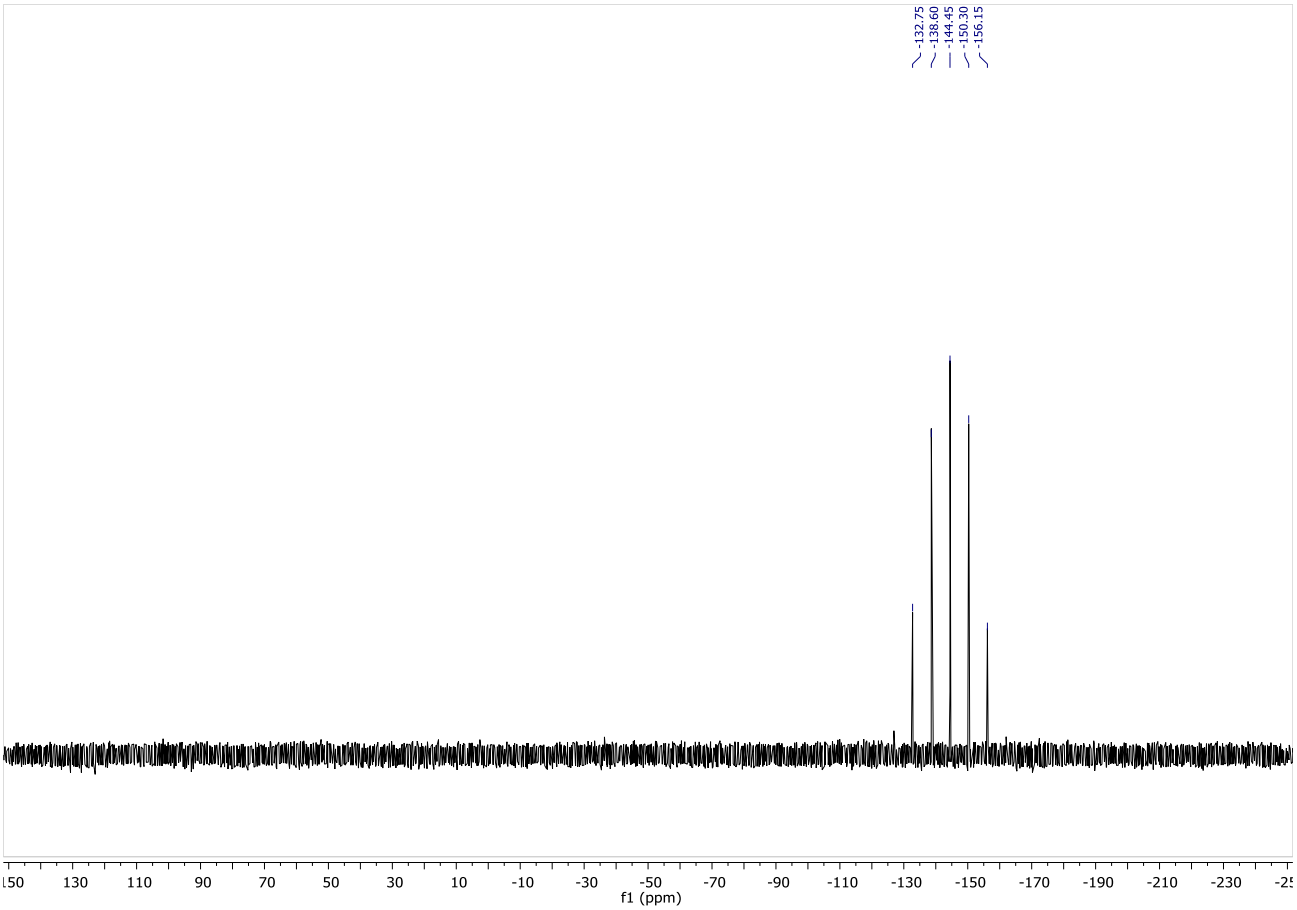


Figure S 63. $^{31}P$ NMR (121 MHz, $CD_2Cl_2$) spectrum of compound **11**

# Mass Spectrometry Core Facility

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## ESI-HRMS – Certificate of Analysis

| | | | |
|---|---|---|---|
| Applicant: | Bosson Johann | Date of certificate: | 06/08/19 |
| Sample name: | JB1228 | Instrument: | Xevo G2 Tof (TOF) |
| Folder: | 060819.PRO | Mobile phase: | MeOH (100 µl/min) |
| Analyst: | Stéphane Grass | Ionisation mode: | ESI (positive polarity) |

| Elemental Formula | Ion type | *Masslynx values **** calc. *m/z* | *Masslynx values **** meas. *m/z* | Calc. *m/z* | Meas. *m/z* | Accuracy [a] (*ppm*) |
|---|---|---|---|---|---|---|
| $C_{46}H_{38}N_3O$ | $[M+H]^+$ | *648.3015* | *648.2998* | 648.3010 | 648.2993 | -2.6 |

[a] *Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution).*

**** MassLynx software does not take into account the mass of the electron for ionic species, therefore the shift of m/z 0.000459.*

Zoomed mass spectrum – Isotopic distribution.

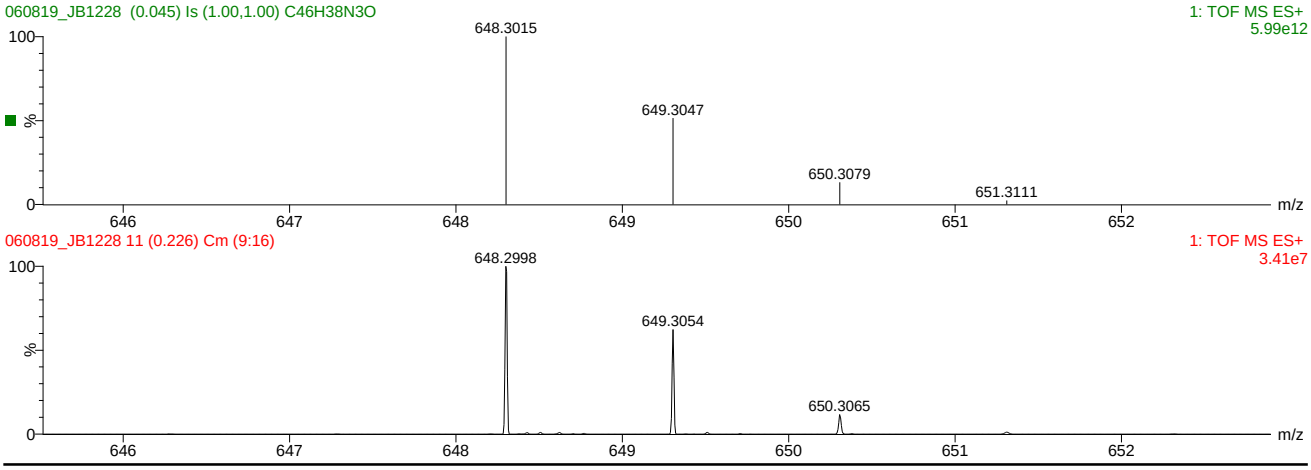


Figure S 64. HRMS (ESI) report of compound **11**

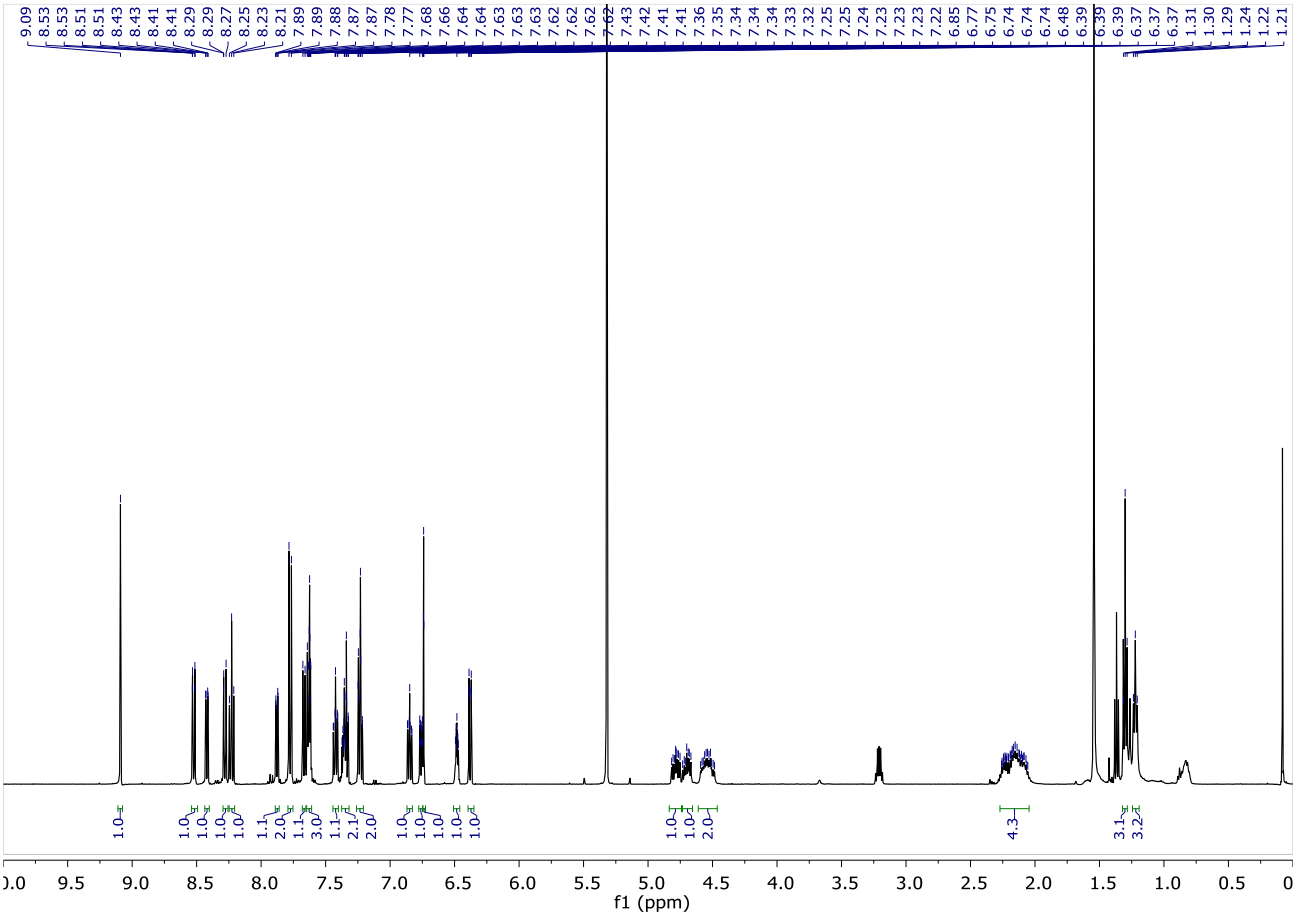


Figure S 65. $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) spectrum of compound **4**

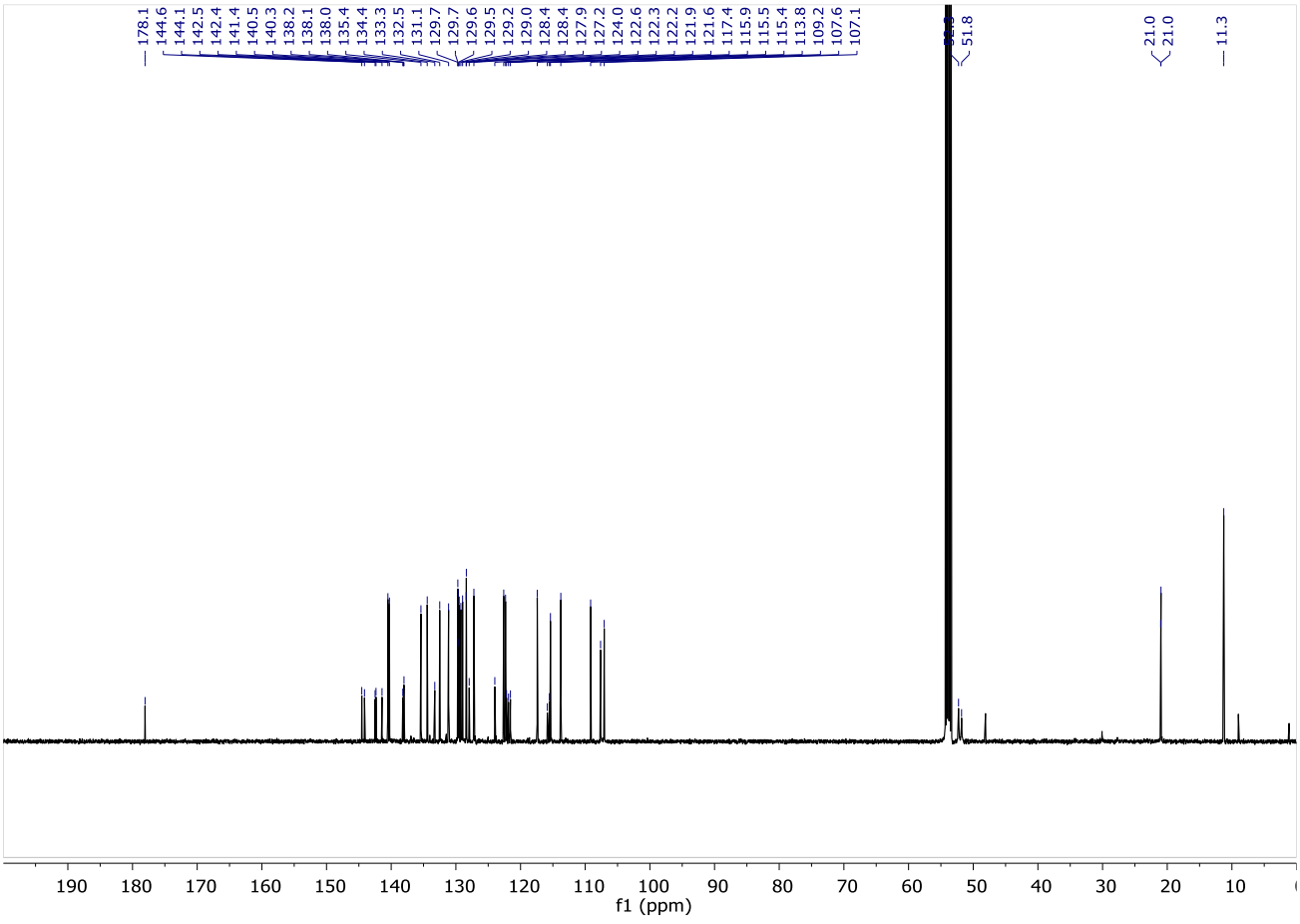


Figure S 66. $^{13}C$ NMR (126 MHz, $CD_2Cl_2$) spectrum of compound **4**

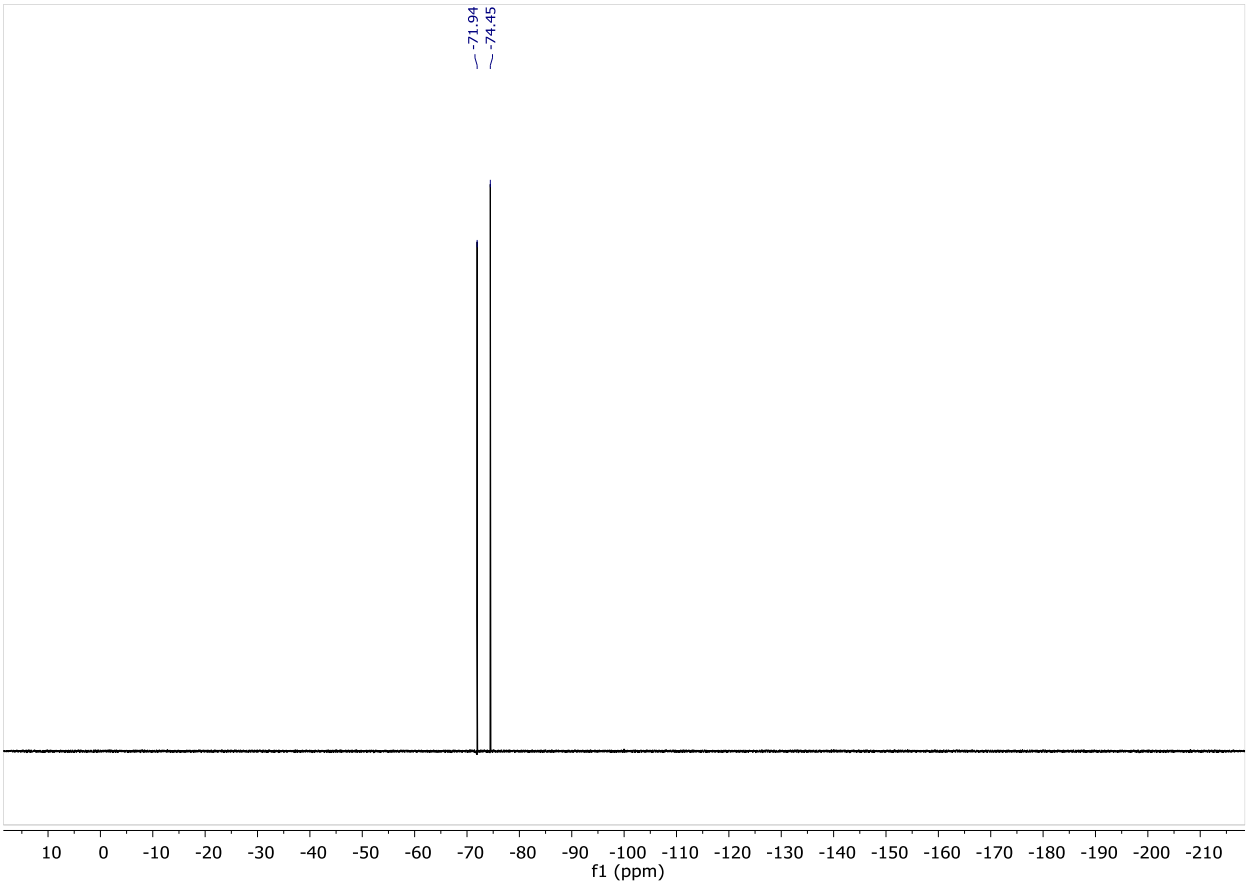


Figure S 67. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **4**

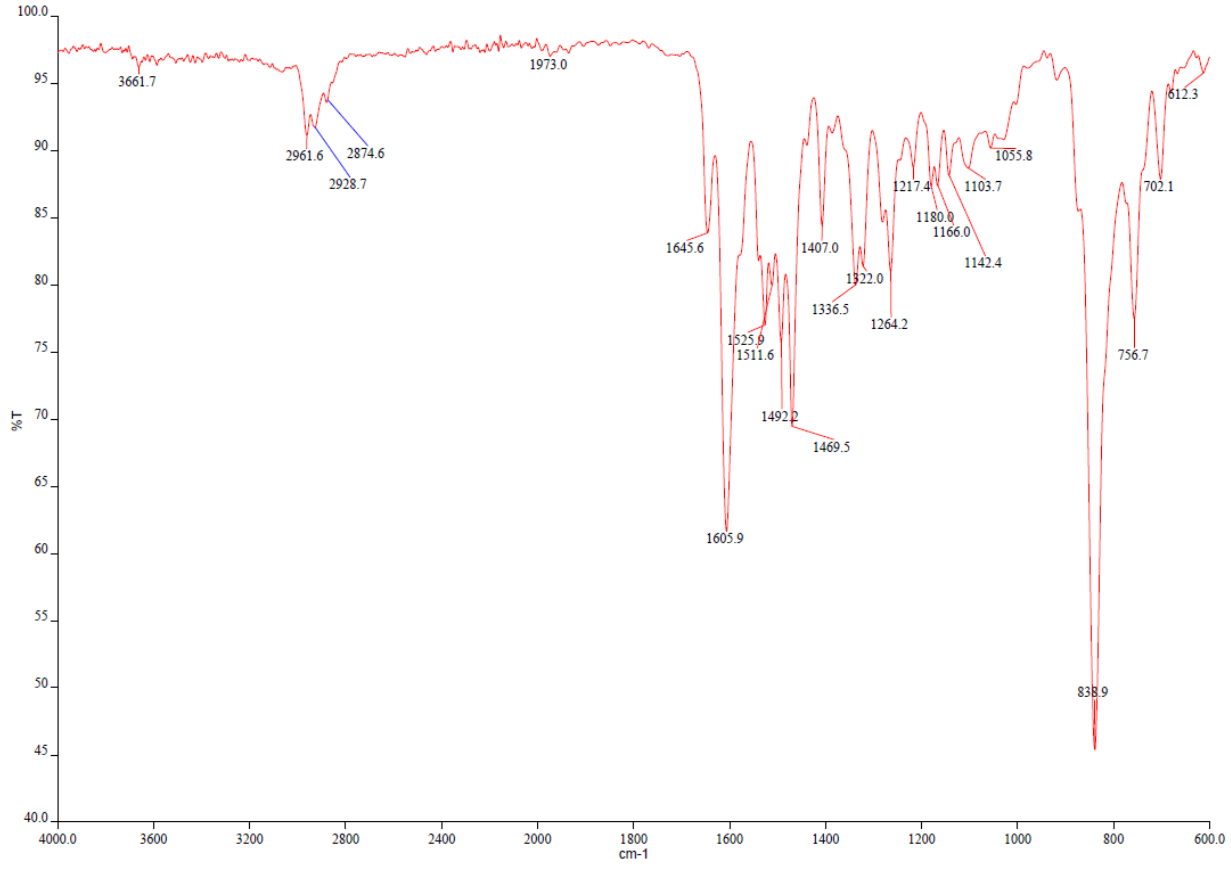


Figure S 68. IR (neat) spectrum of compound **4**

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# ESI-HRMS – Certificate of Analysis

| | | | |
|---|---|---|---|
| Applicant: | Bosson Johann | Date of certificate: | 12/06/19 |
| Sample name: | JB-853 | Instrument: | Xevo G2 Tof (TOF) |
| Folder: | 120619.PRO | Mobile phase: | MeOH (100 µl/min) |
| Analyst: | Stéphane Grass | Ionisation mode: | ESI (positive polarity) |

| Elemental Formula | Ion type | *Masslynx values **** calc. *m/z* | *Masslynx values **** meas. *m/z* | Calc. *m/z* | Meas. *m/z* | Accuracy [a] *(ppm)* |
|---|---|---|---|---|---|---|
| $C_{46}H_{36}N_3O$ | $[M+H]^+$ | *646.2858* | *646.2858* | 646.2853 | 646.2853 | 0.0 |

[a] *Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution).*

**** MassLynx software does not take into account the mass of the electron for ionic species, therefore the shift of m/z 0.000459.*

Zoomed mass spectrum – Isotopic distribution.

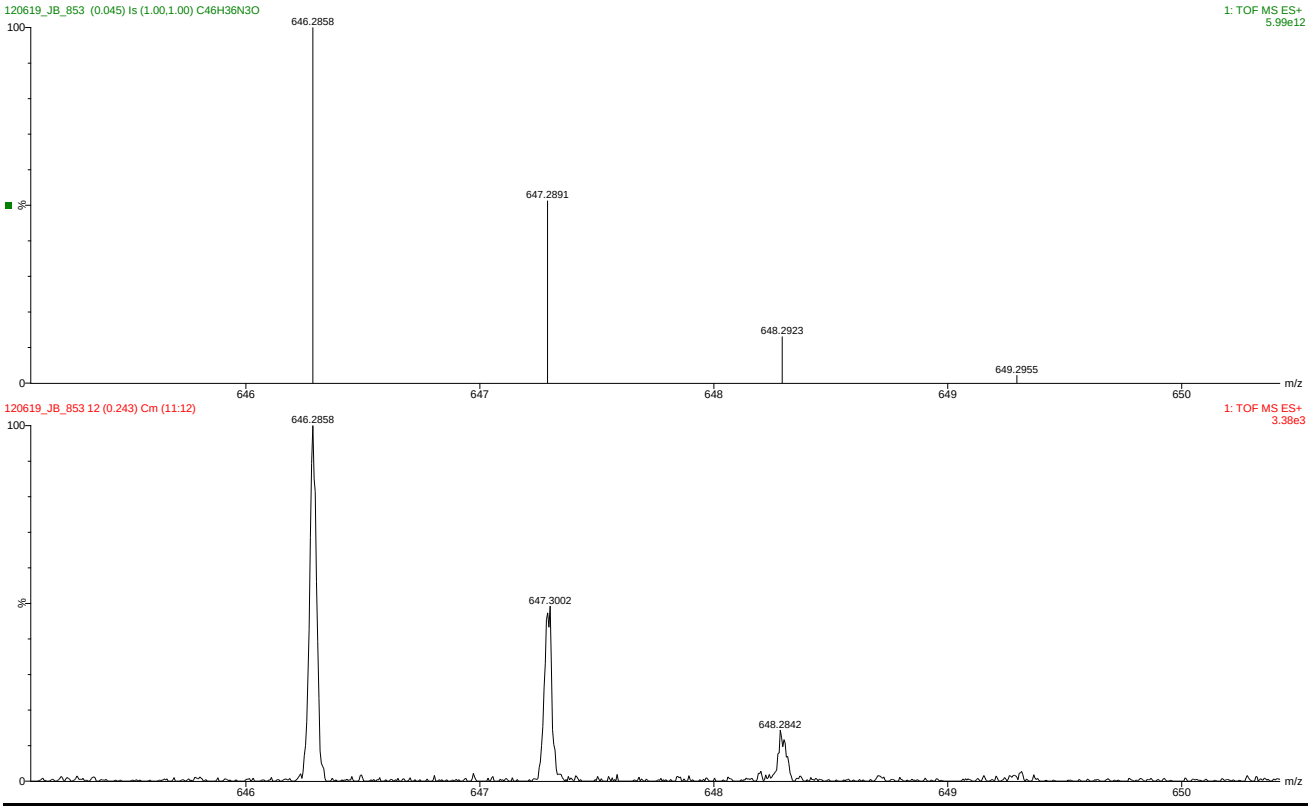


Figure S 69. HRMS (ESI) report of compound **4**

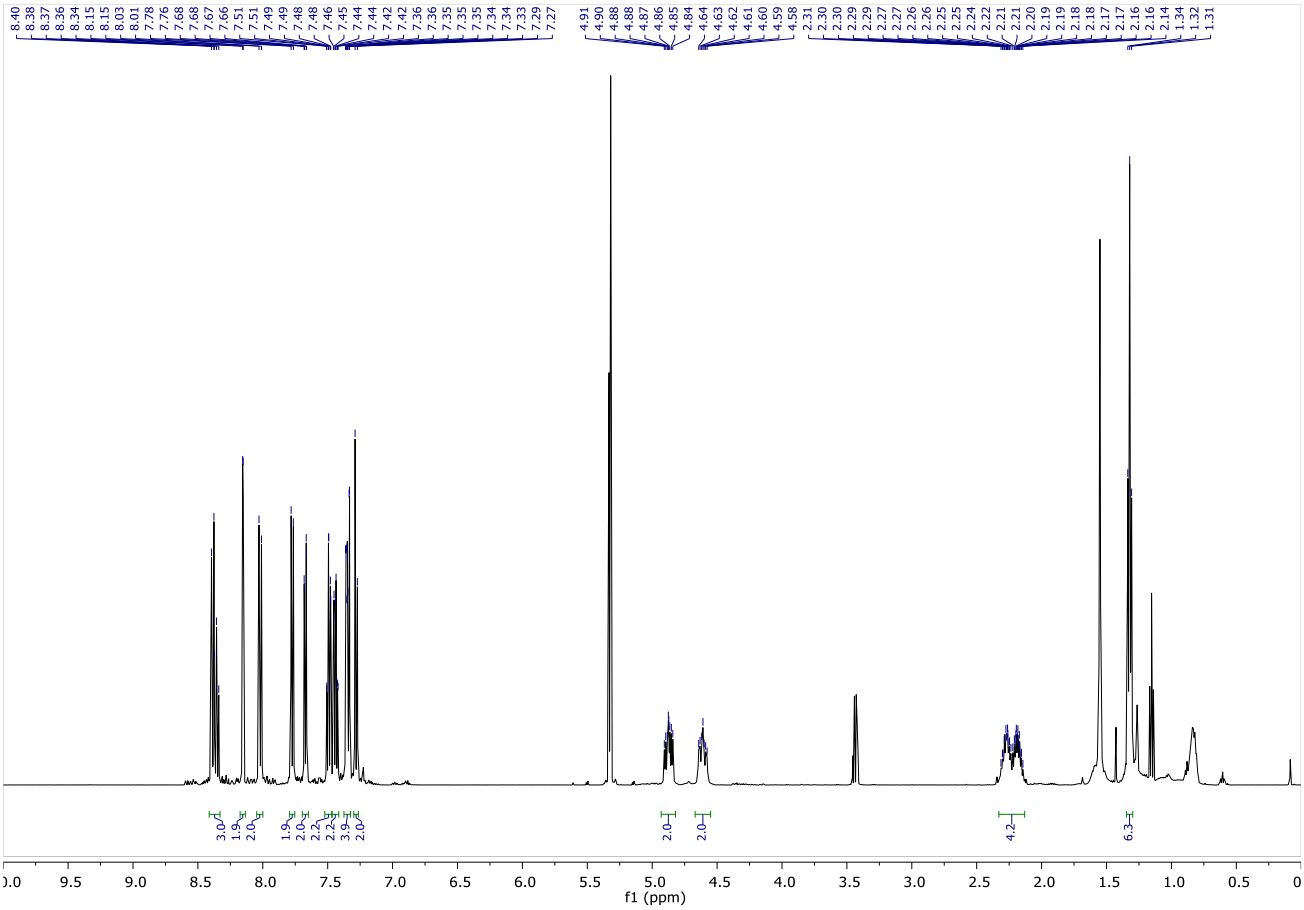


Figure S 70. $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) spectrum of compound **K5**

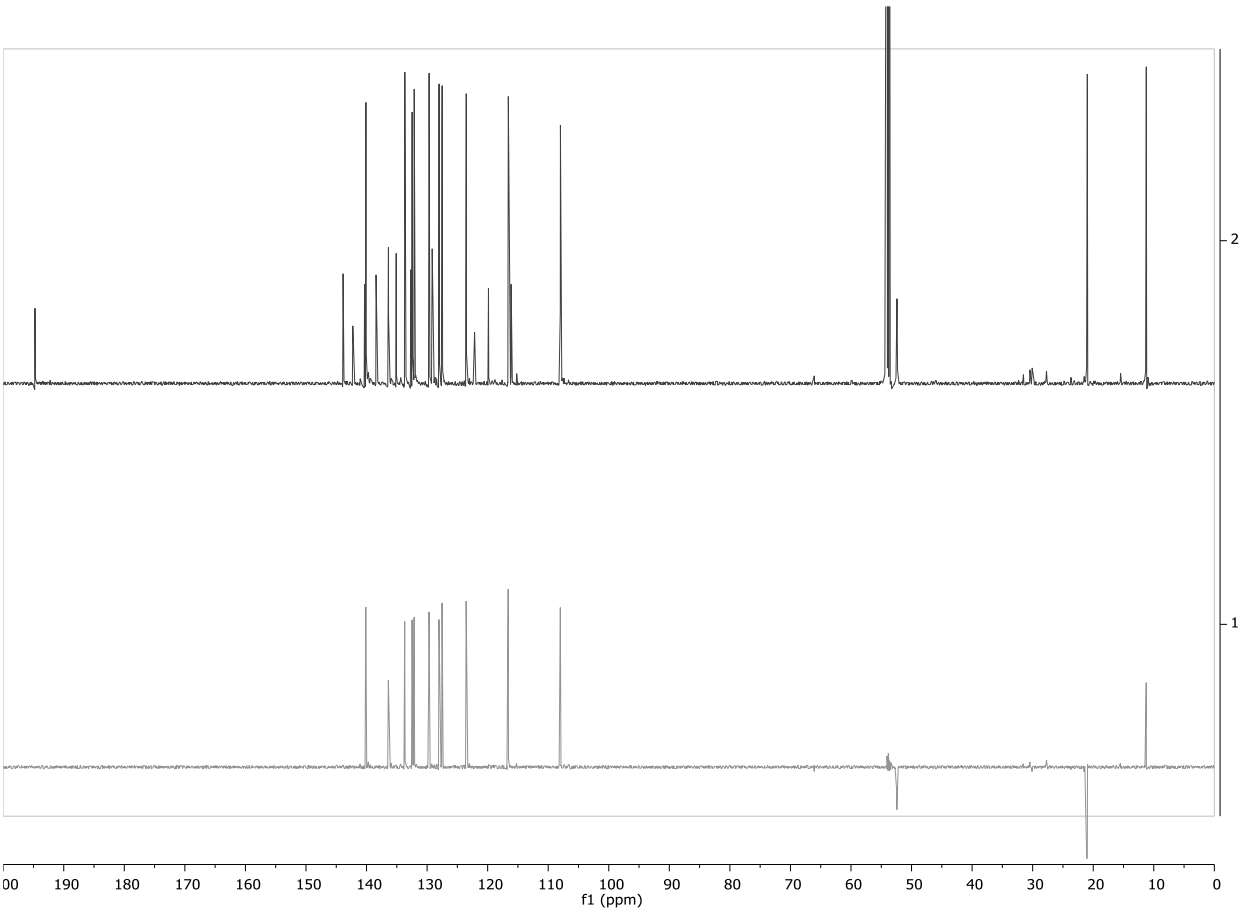


Figure S 71. $^{13}C$ NMR and DEPT 135 (126 MHz, $CD_2Cl_2$) spectrum of compound **K5**

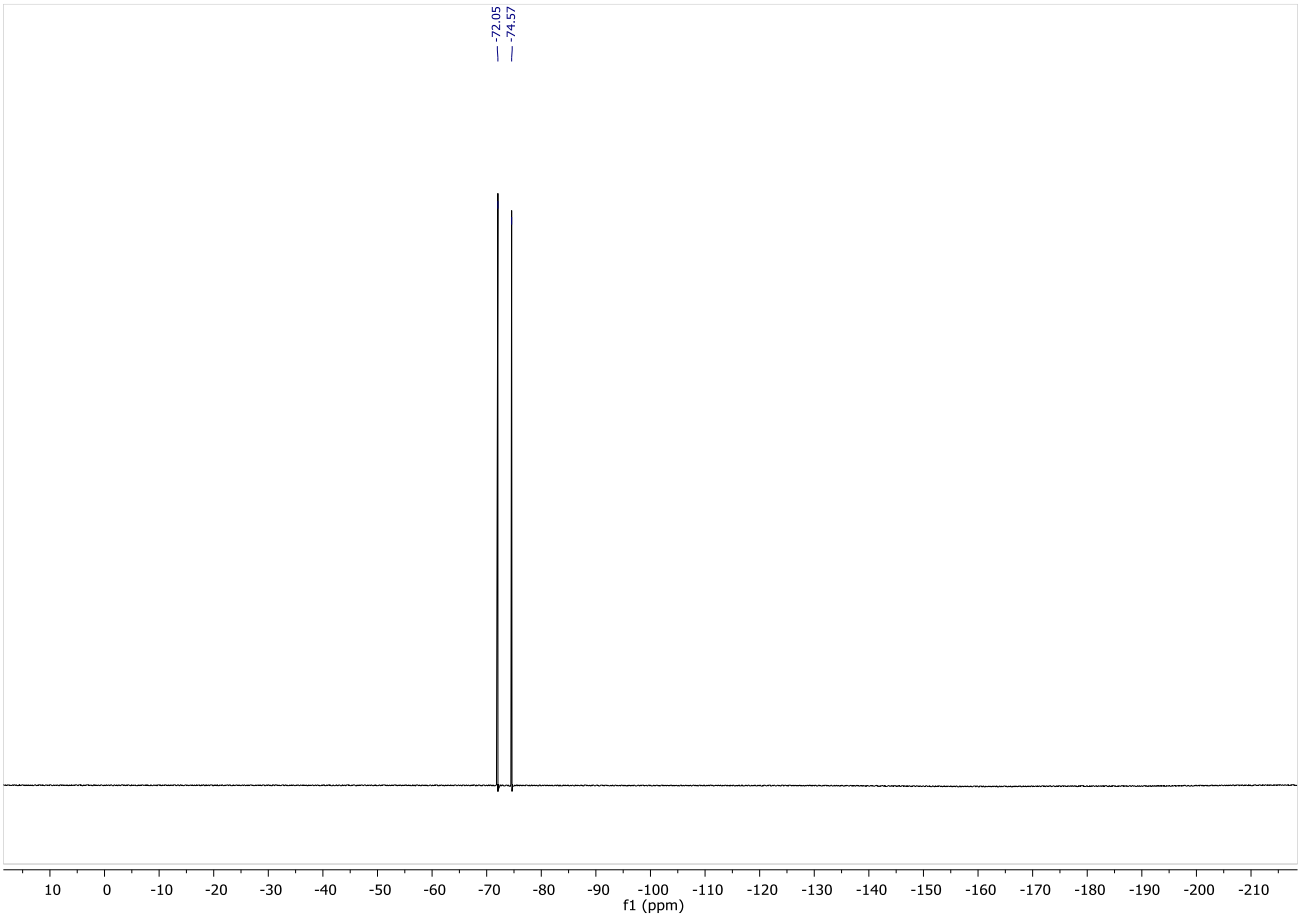


Figure S 72. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **K5**

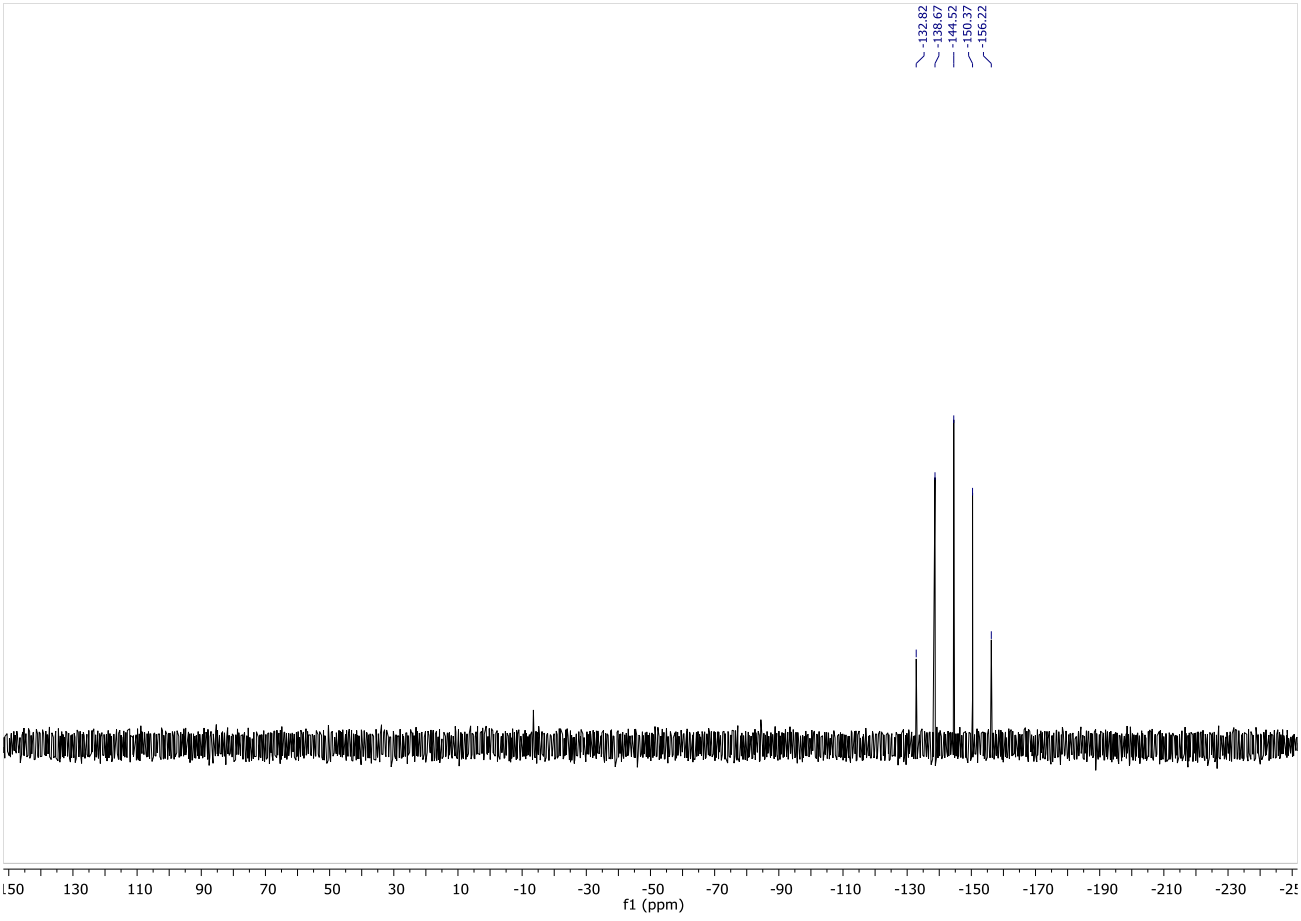


Figure S 73. $^{31}P$ NMR (121 MHz, $CD_2Cl_2$) spectrum of compound **K5**

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# ESI-HRMS – Certificate of Analysis

| | | | |
|---|---|---|---|
| Applicant: | Bosson Johann | Date of certificate: | 06/08/19 |
| Sample name: | JB1222 | Instrument: | Xevo G2 Tof (TOF) |
| Folder: | 060819.PRO | Mobile phase: | MeOH (100 µl/min) |
| Analyst: | Stéphane Grass | Ionisation mode: | ESI (positive polarity) |

| Elemental Formula | Ion type | *Masslynx values **** calc. *m/z* | *Masslynx values **** meas. *m/z* | Calc. *m/z* | Meas. *m/z* | Accuracy [a] *(ppm)* |
|---|---|---|---|---|---|---|
| $C_{47}H_{35}Br_2N_2O_2$ | $[M+H]^+$ | *819.105* | *819.1039* | 819.1045 | 819.1034 | -1.3 |

[a] *Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution).*

**** MassLynx software does not take into account the mass of the electron for ionic species, therefore the shift of m/z 0.000459.*

Zoomed mass spectrum – Isotopic distribution.

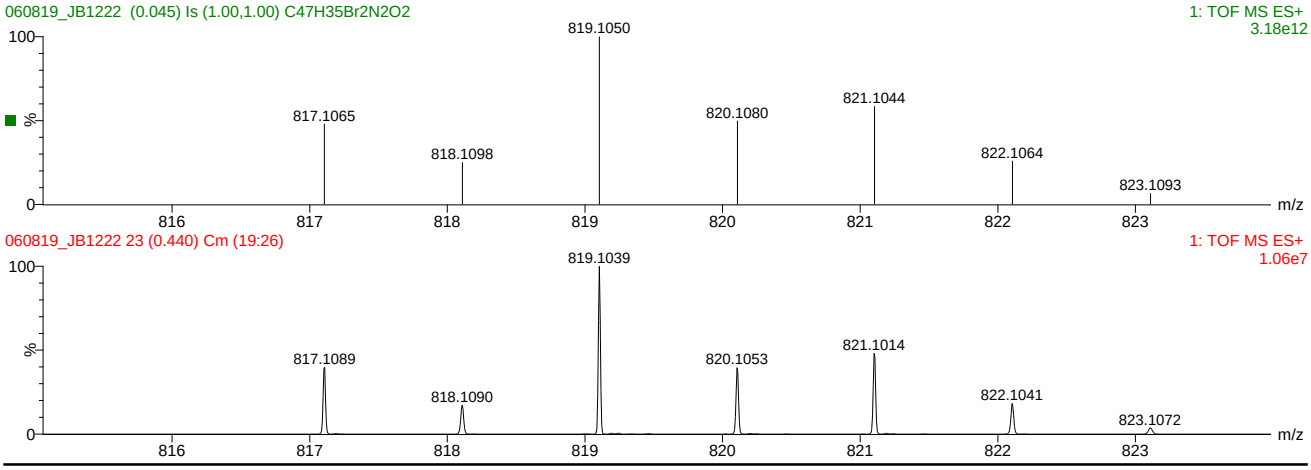


Figure S 74. HRMS (ESI) report of compound **K5**

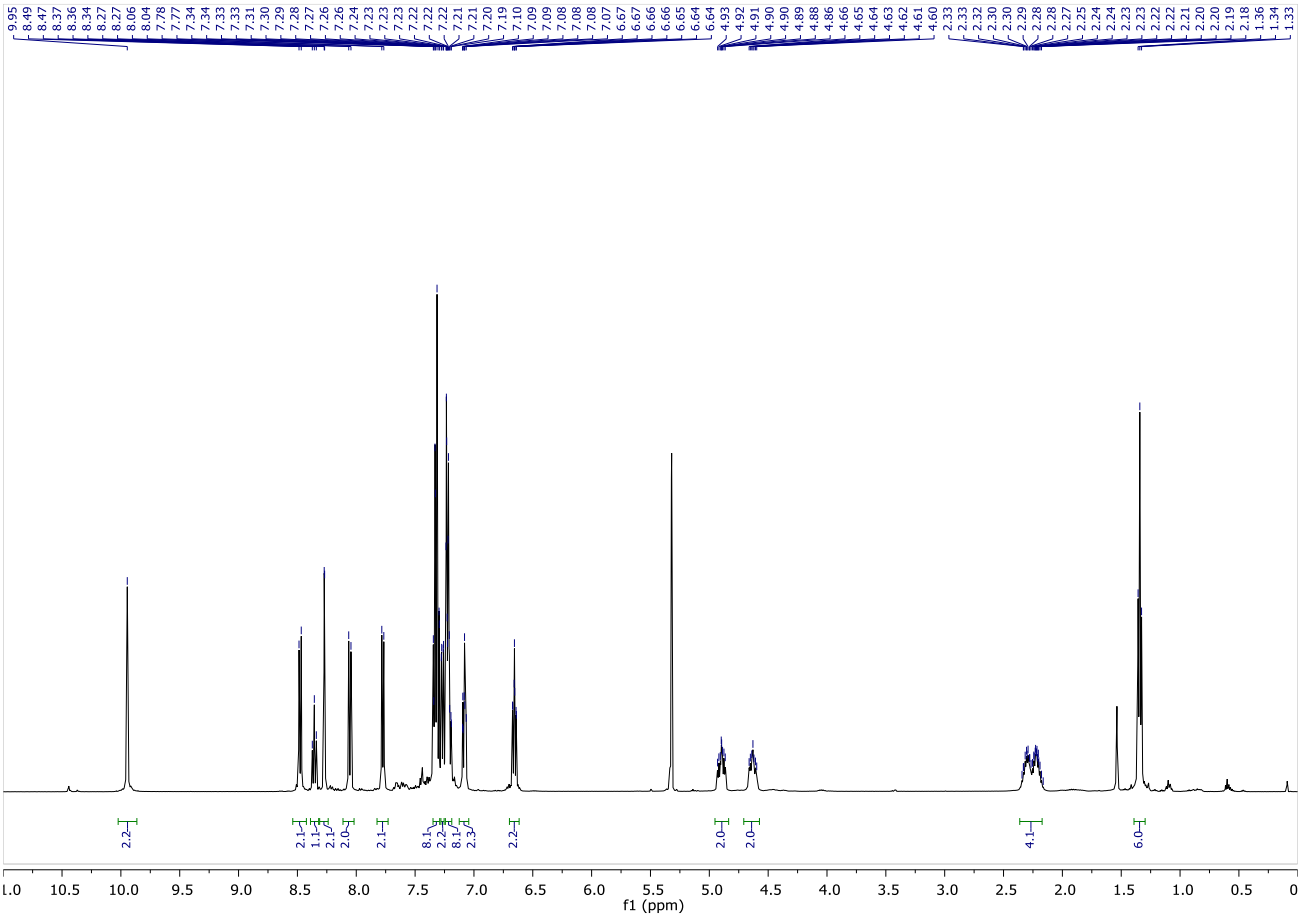


Figure S 75. $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) spectrum of compound **12**

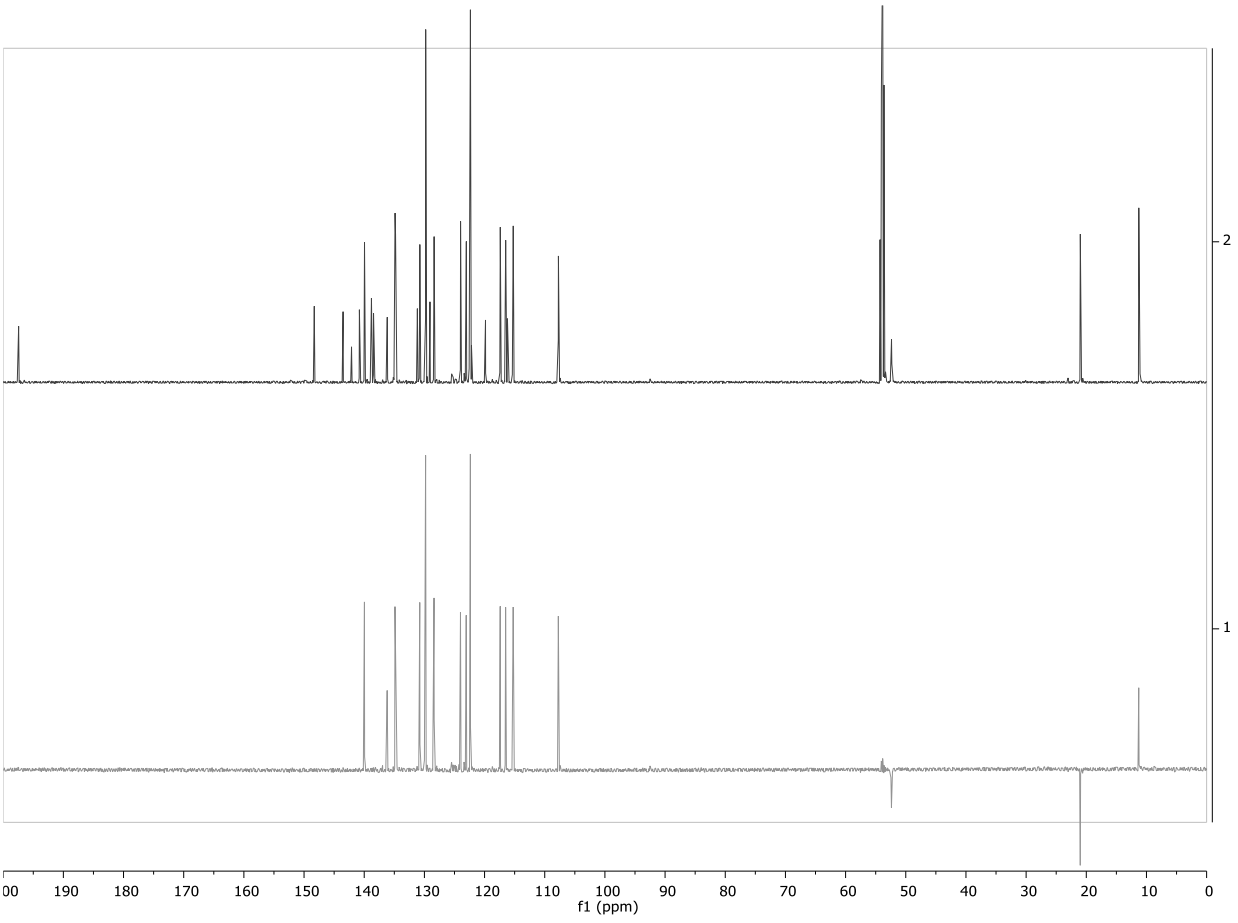


Figure S 76. $^{13}C$ NMR and DEPT 135 (126 MHz, $CD_2Cl_2$) spectrum of compound **12**

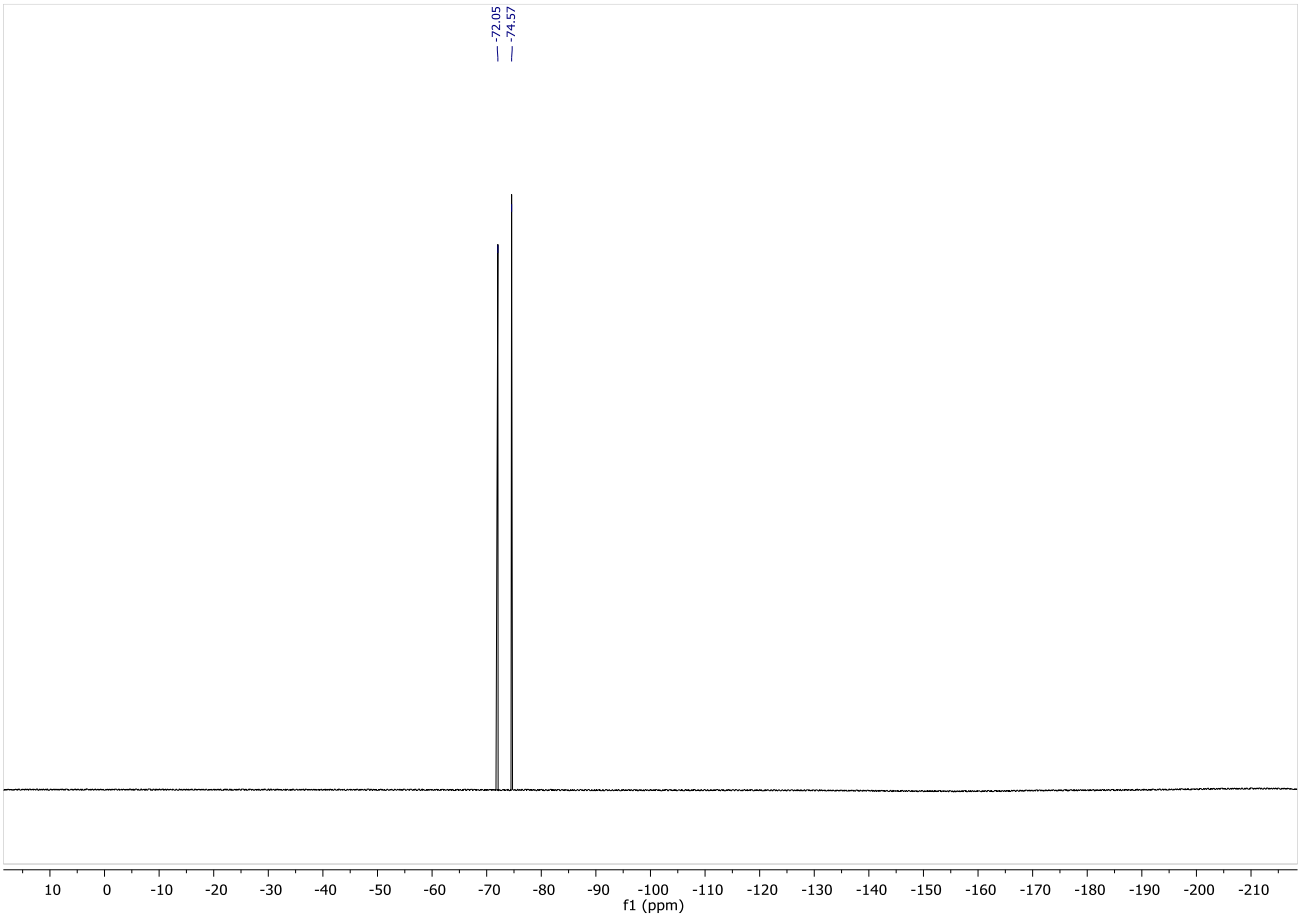


Figure S 77. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **12**

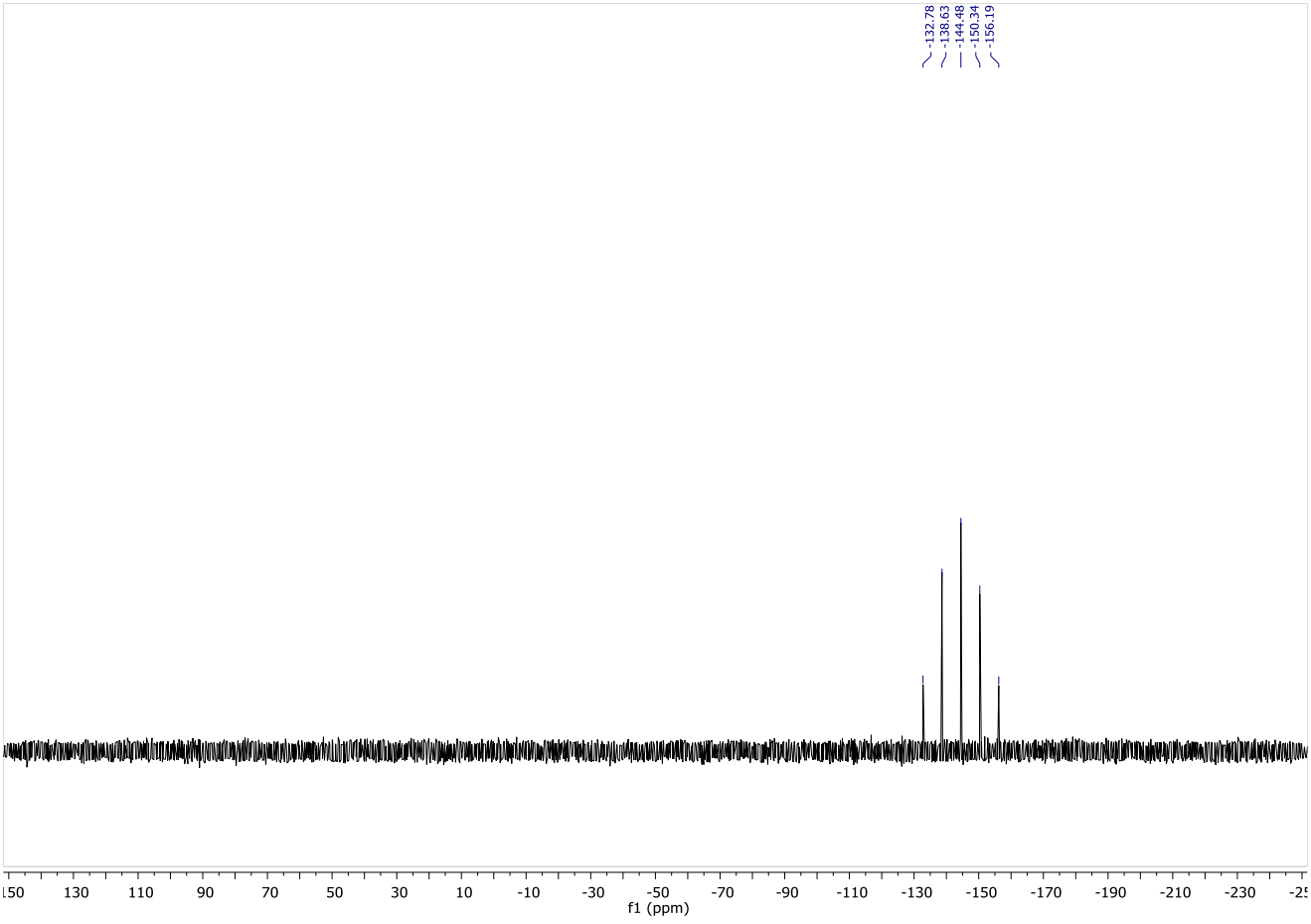


Figure S 78. $^{31}P$ NMR (121 MHz, $CD_2Cl_2$) spectrum of compound **12**

## Mass Spectrometry Core Facility

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# ESI-HRMS – Certificate of Analysis

| | | | |
|---|---|---|---|
| Applicant: | Bosson Johann | Date of certificate: | 06/08/19 |
| Sample name: | JB1229 | Instrument: | Xevo G2 Tof (TOF) |
| Folder: | 060819.PRO | Mobile phase: | MeOH (100 µl/min) |
| Analyst: | Stéphane Grass | Ionisation mode: | ESI (positive polarity) |

| Elemental Formula | Ion type | *Masslynx values **** *calc. m/z* | *Masslynx values **** *meas. m/z* | Calc. *m/z* | Meas. *m/z* | Accuracy [a] *(ppm)* |
|---|---|---|---|---|---|---|
| $C_{59}H_{47}N_4O_2$ | $[M+H]^+$ | *843.3699* | *843.3712* | 843.3694 | 843.3707 | 1.5 |

[a] *Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution).*

**** MassLynx software does not take into account the mass of the electron for ionic species, therefore the shift of m/z 0.000459.*

Zoomed mass spectrum – Isotopic distribution.

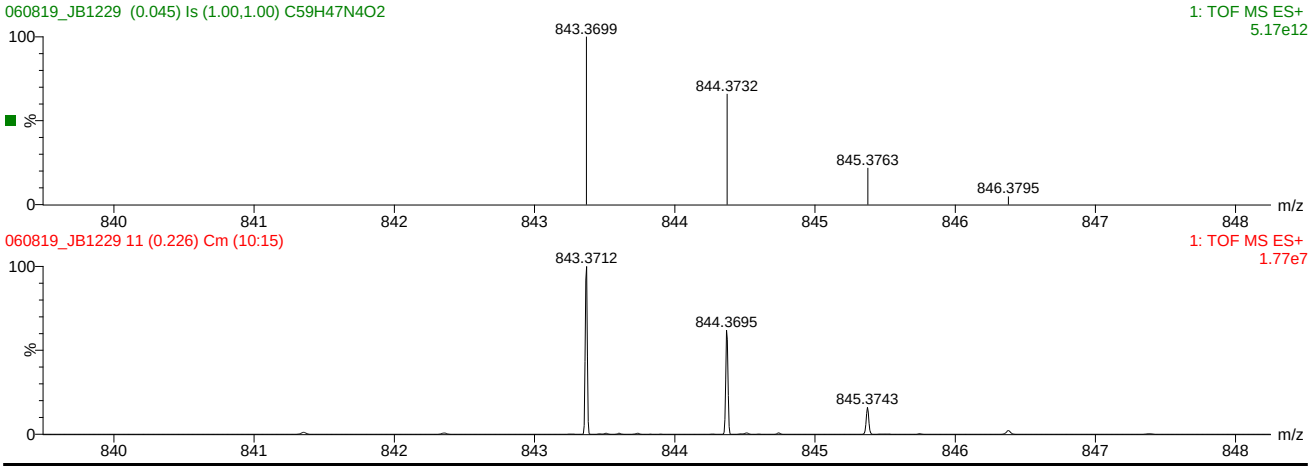


Figure S 79. HRMS (ESI) report of compound **12**

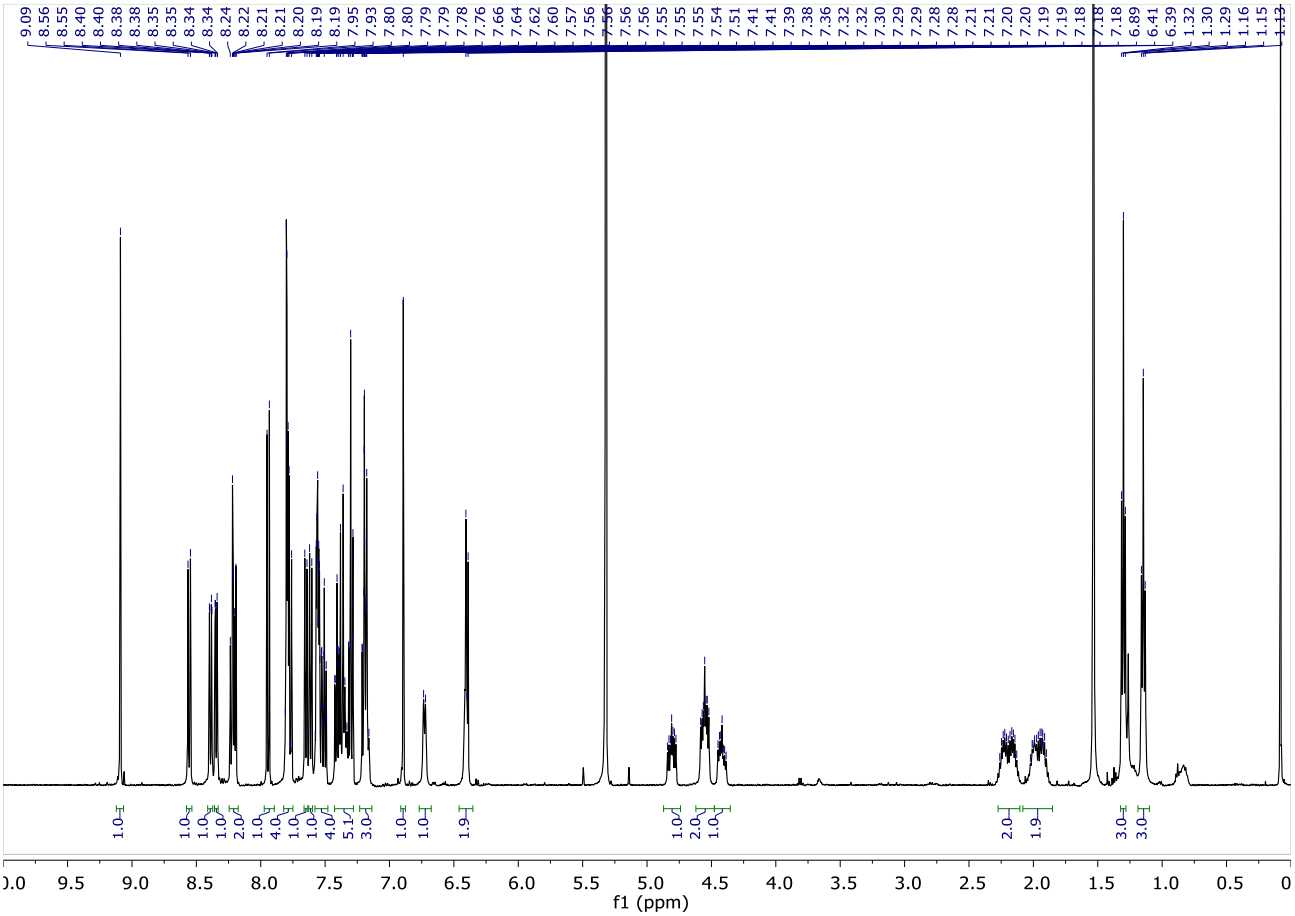


Figure S 80. $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) spectrum of compound **5**

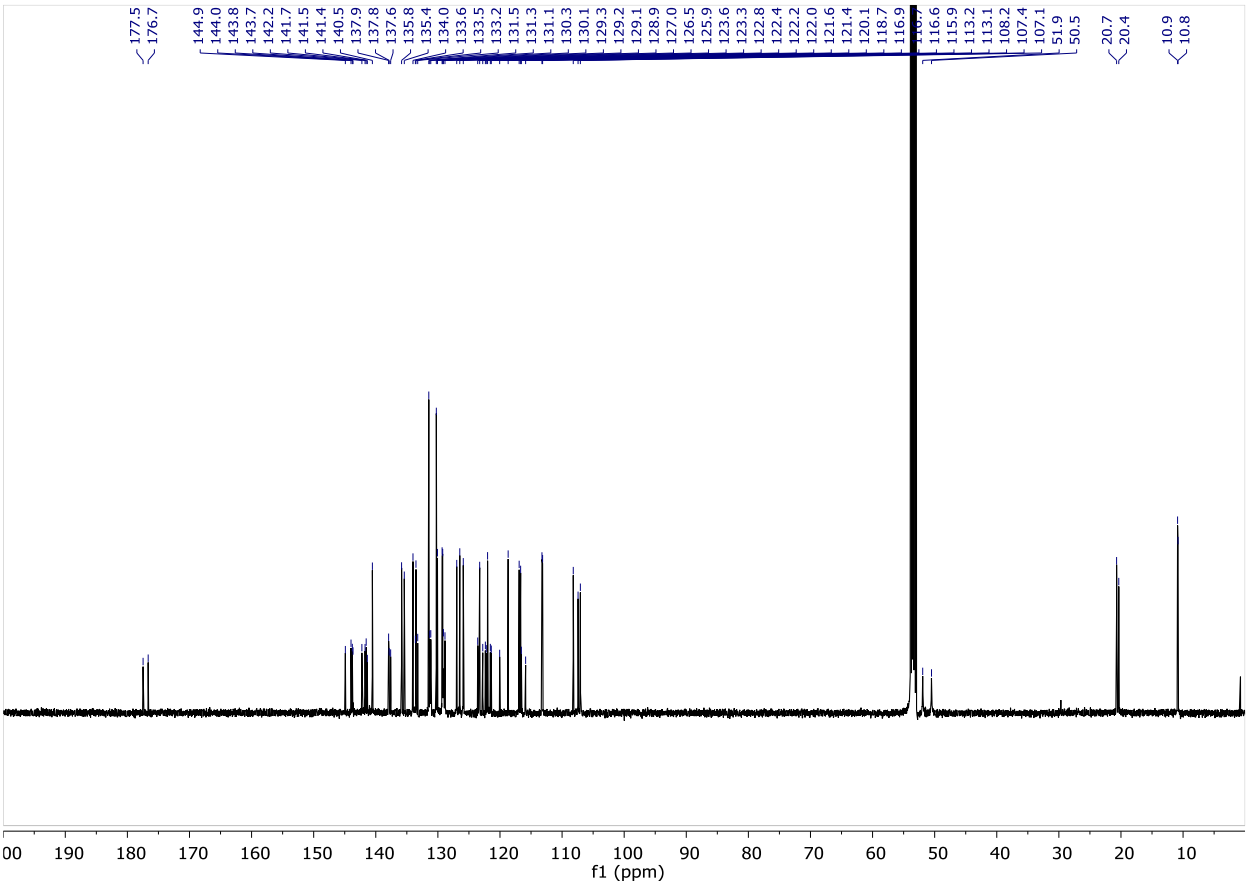


Figure S 81. $^{13}C$ NMR (126 MHz, $CD_2Cl_2$) spectrum of compound **5**

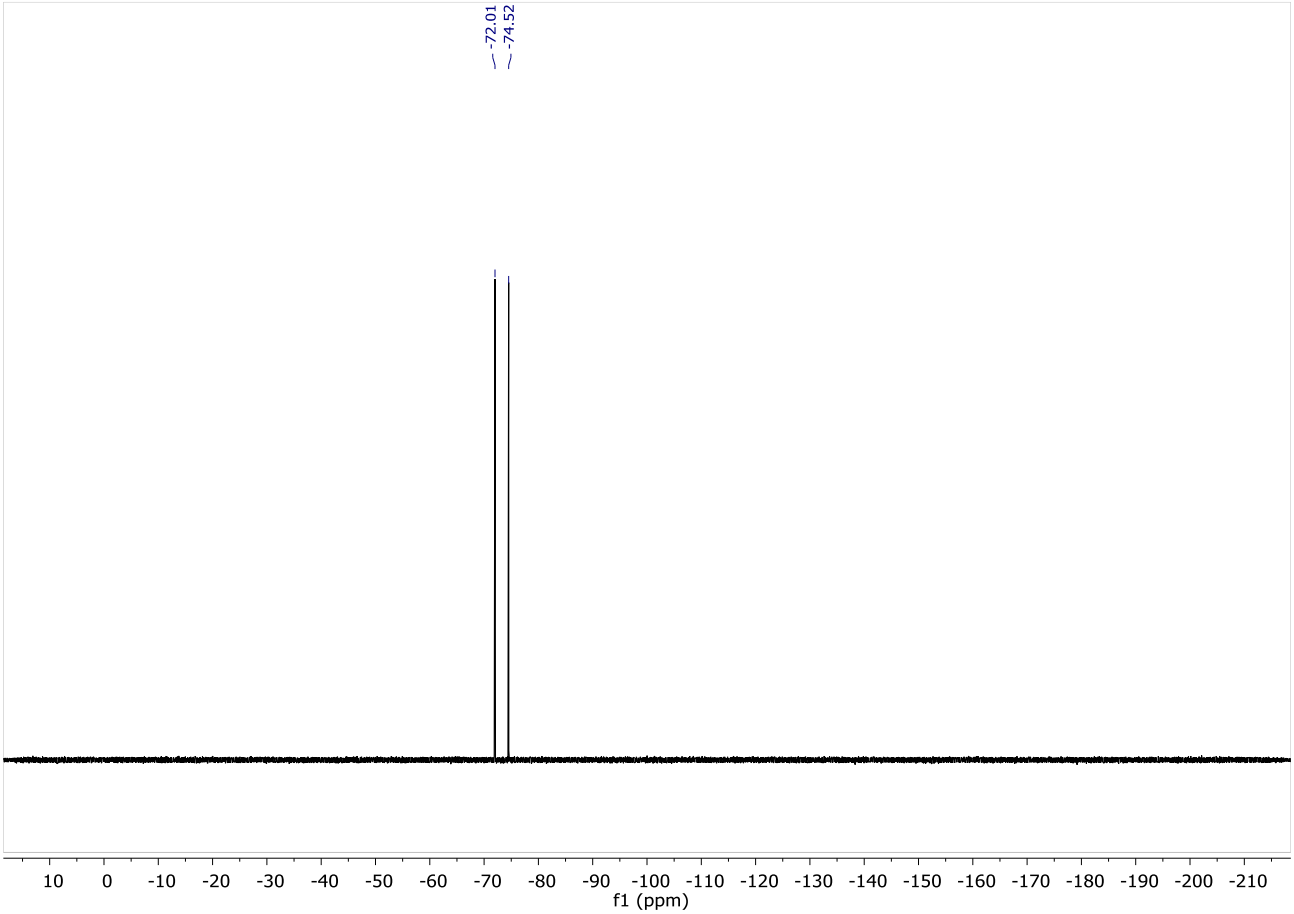


Figure S 82. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **5**

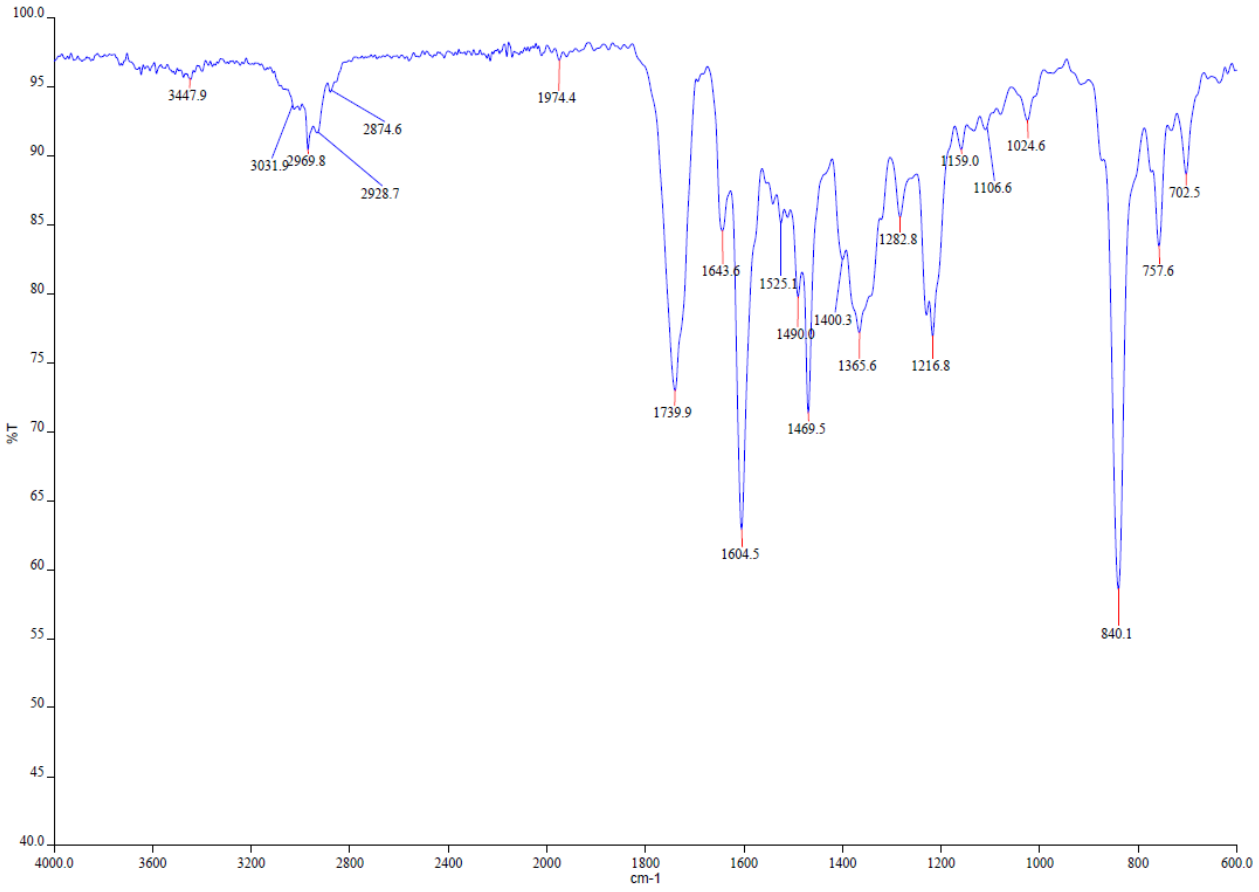


Figure S 83. IR (neat) spectrum of compound **5**

**Mass Spectrometry Core Facility**
Lacour Group – University of Geneva

# ESI-HRMS – Certificate of Analysis

| | | | |
|---|---|---|---|
| Applicant: | Bosson Johann | Date of certificate: | 12/06/19 |
| Sample name: | JB-883 | Instrument: | Xevo G2 Tof (TOF) |
| Folder: | 120619.PRO | Mobile phase: | MeOH (100 µl/min) |
| Analyst: | Stéphane Grass | Ionisation mode: | ESI (positive polarity) |

| Elemental Formula | Ion type | *Masslynx values **** calc. *m/z* | *Masslynx values **** meas. *m/z* | Calc. *m/z* | Meas. *m/z* | Accuracy [a] *(ppm)* |
|---|---|---|---|---|---|---|
| $C_{59}H_{43}N_4O_2$ | $[M+H]^+$ | *839.3386* | *839.3426* | 839.3381 | 839.3421 | 4.8 |

[a] *Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution).*

**** MassLynx software does not take into account the mass of the electron for ionic species, therefore the shift of m/z 0.000459.*

Zoomed mass spectrum – Isotopic distribution.

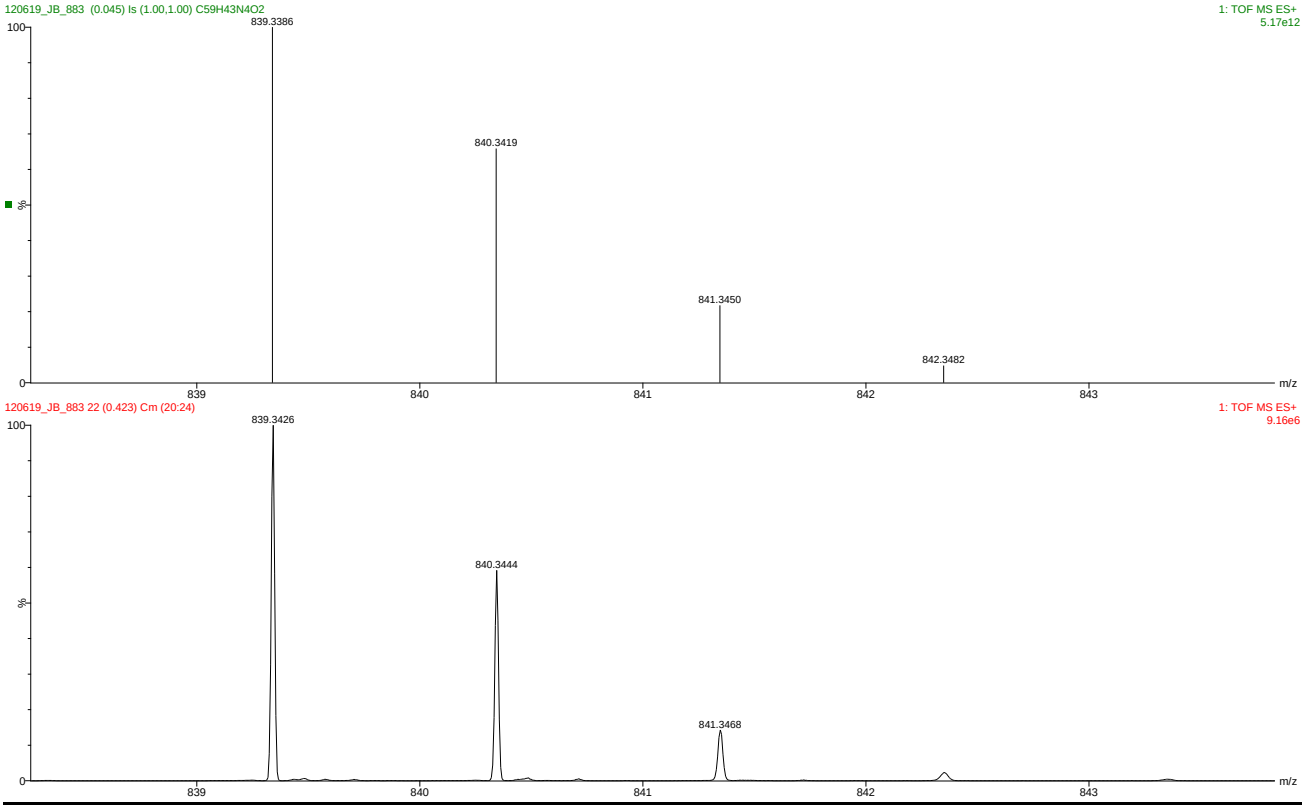


Figure S 84. HRMS (ESI) report of compound **5**

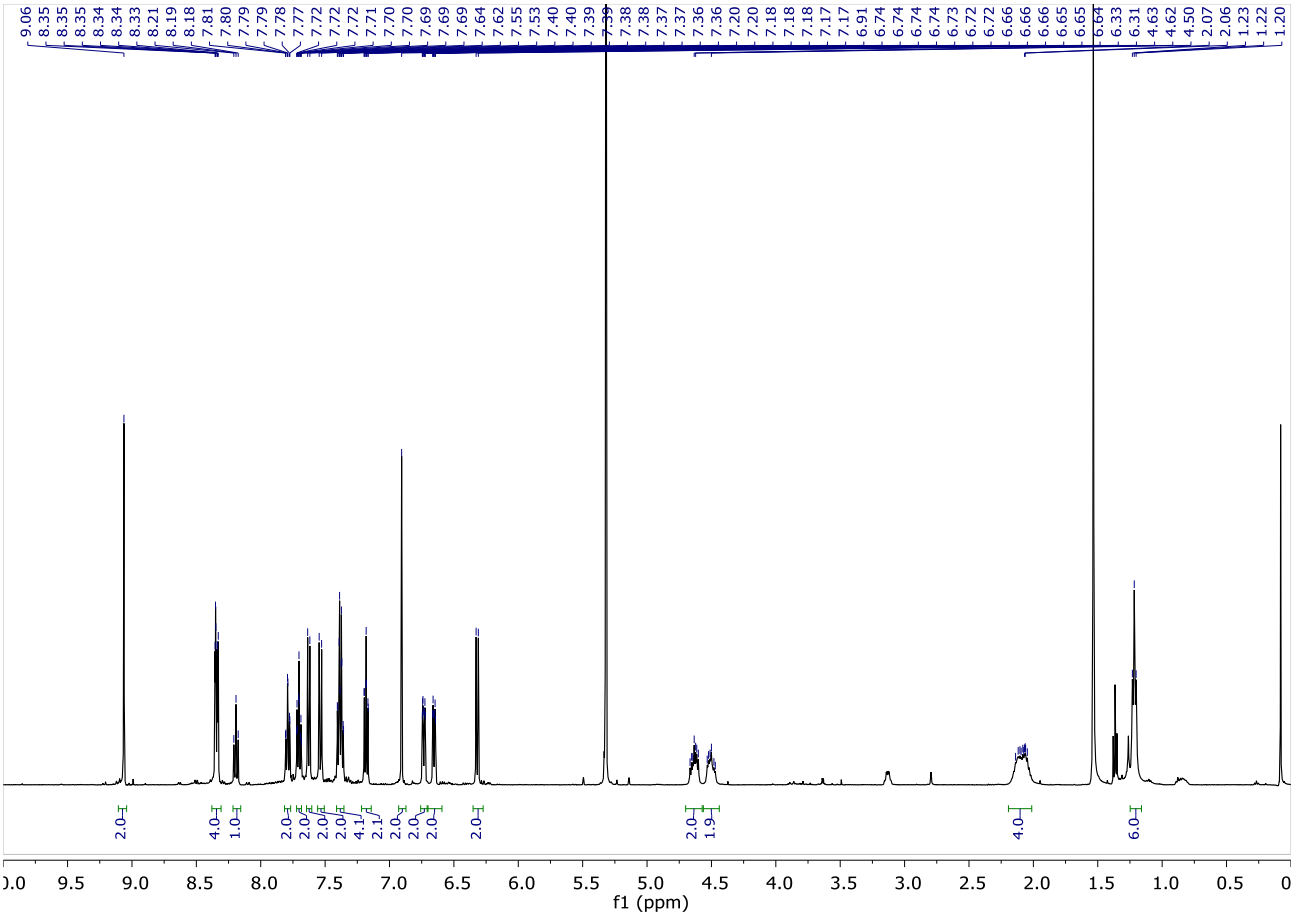


Figure S 85. $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) spectrum of compound **6**

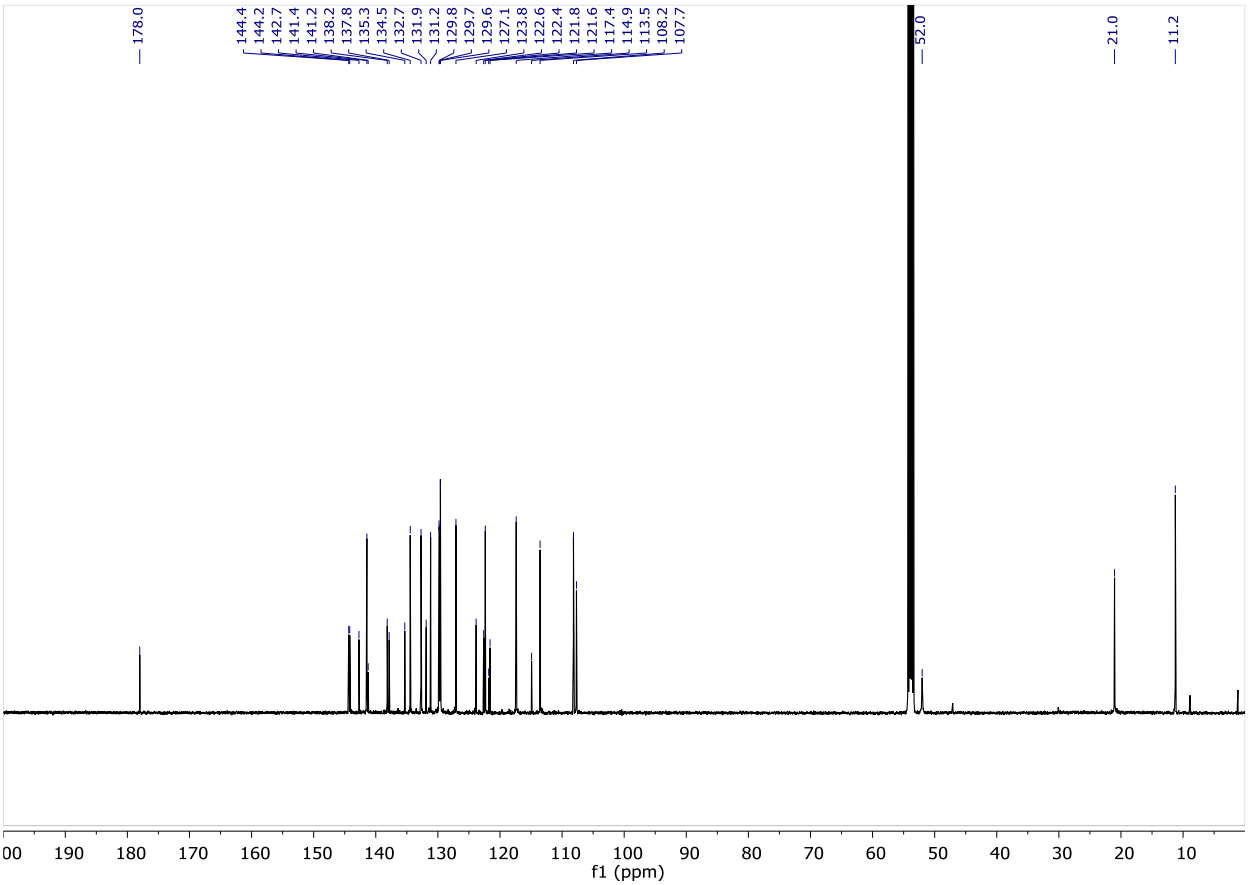


Figure S 86. $^{13}C$ NMR (126 MHz, $CD_2Cl_2$) spectrum of compound **6**

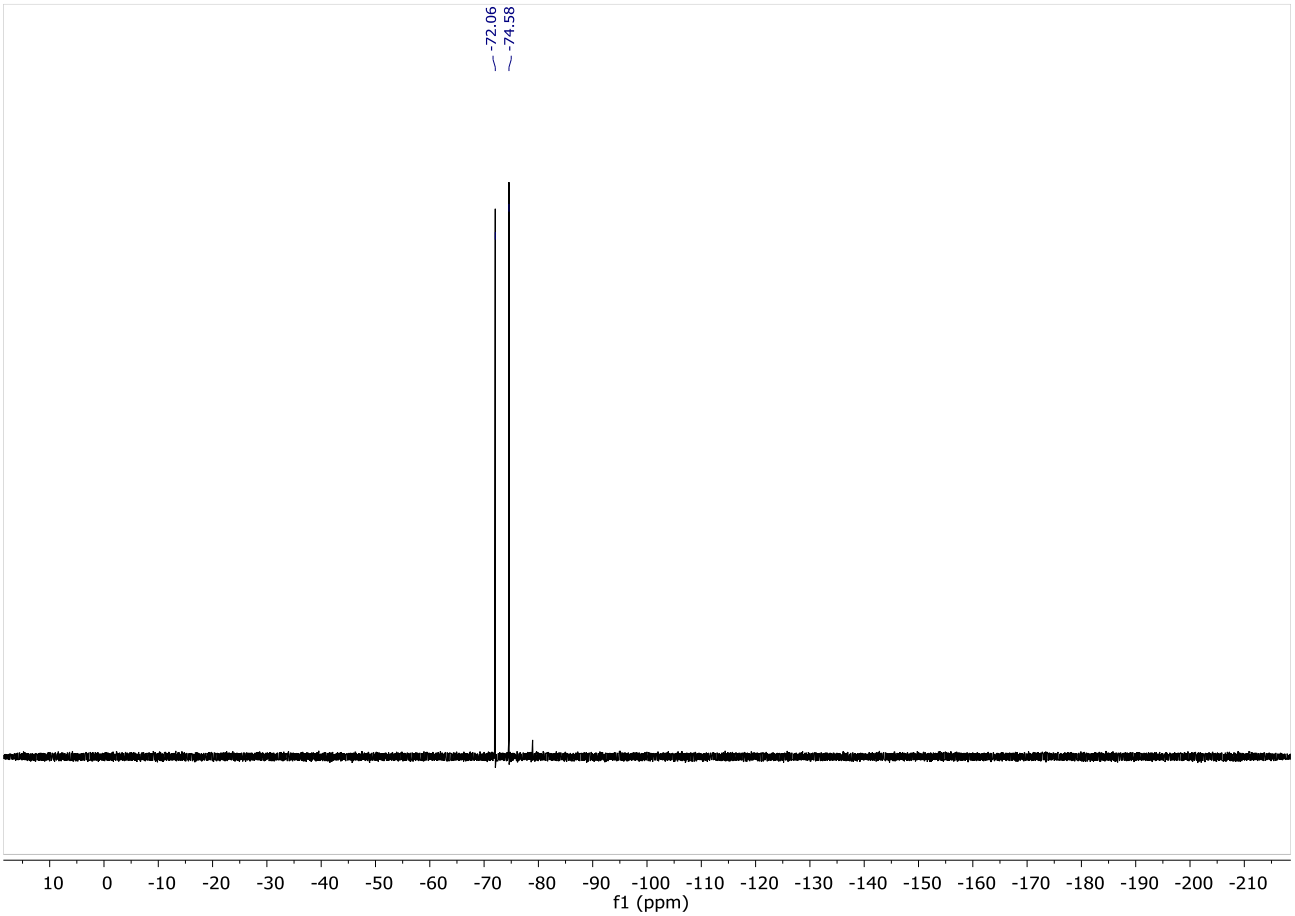


Figure S 87. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of compound **6**

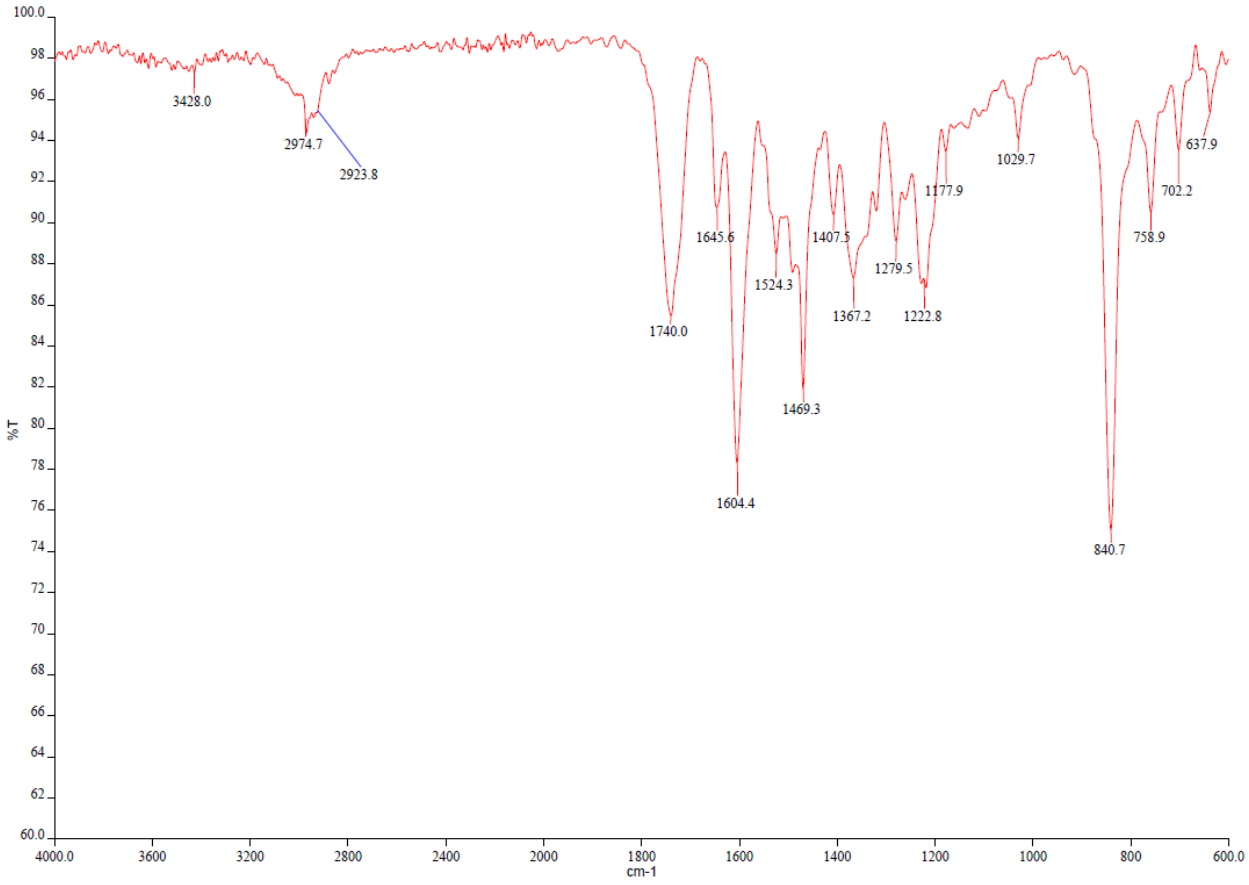


Figure S 88. IR (neat) spectrum of compound **6**

**Mass Spectrometry Core Facility**

Lacour Group – University of Geneva

UNIVERSITÉ DE GENÈVE
FACULTÉ DES SCIENCES

# ESI-HRMS – Certificate of Analysis

| | | | |
|---|---|---|---|
| Applicant: | Bosson Johann | Date of certificate: | 12/06/19 |
| Sample name: | JB-884 | Instrument: | Xevo G2 Tof (TOF) |
| Folder: | 120619.PRO | Mobile phase: | MeOH (100 µl/min) |
| Analyst: | Stéphane Grass | Ionisation mode: | ESI (positive polarity) |

| Elemental Formula | Ion type | *Masslynx values **** calc. *m/z* | *Masslynx values **** meas. *m/z* | Calc. *m/z* | Meas. *m/z* | Accuracy [a] *(ppm)* |
|---|---|---|---|---|---|---|
| $C_{59}H_{43}N_4O_2$ | $[M+H]^+$ | *839.3386* | *839.3426* | 839.3381 | 839.3421 | 4.8 |

[a] *Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution).*

**** MassLynx software does not take into account the mass of the electron for ionic species, therefore the shift of m/z 0.000459.*

Zoomed mass spectrum – Isotopic distribution.

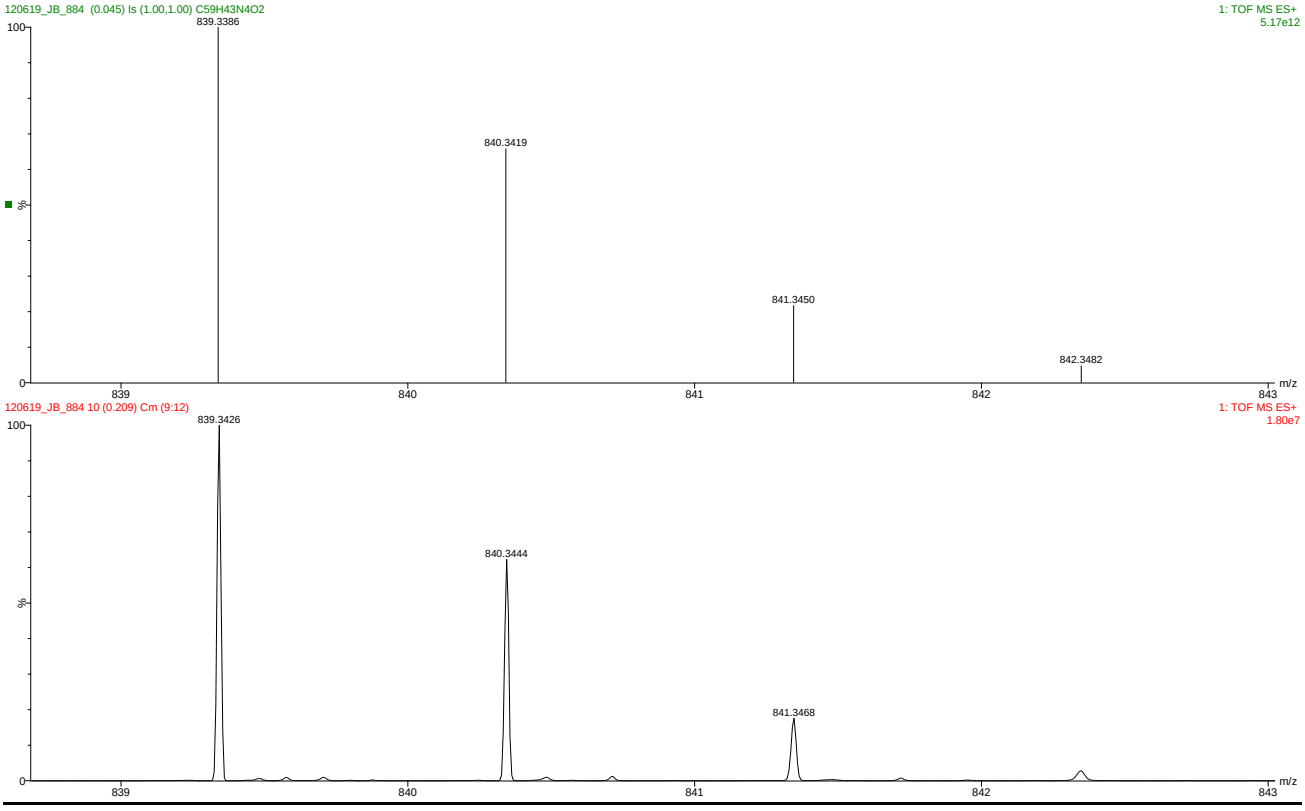


Figure S 89. HRMS (ESI) report of compound **6**

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