Design of Heavy-Atom Free Dipyridomethene Boron Complexes for Singlet Oxygen Emission with Induced Chirality

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Supplementary Information

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Materials and methods

Reactants and Solvents

Unless otherwise noted, all reactions were carried out in oven-dried glassware. Commercially available chemicals were purchased from Acros Organics, Sigma-Aldrich, Alfa Aesar and Fluorochem and used as received unless otherwise stated. The following solvents were dried by distillation over the drying agents indicated in parentheses: THF (Sodium), dichloromethane (CaH_2), NEt_3 (KOH). Solvents for spectroscopy were spectroscopic grade and were used as received.

Purifications

Flash chromatography was performed on silica gel (Merck Kieselgel 60, grading 40-63 µm) or celite (VWR Chemicals, Celite® 545).

Analysis

Reactions were monitored by TLC carried out on silica gel 0,25 mm (60 F254, Merck) using UV light as visualizing agent.

Nuclear Magnetic Resonance (NMR) spectroscopy: ^{1}H NMR (400 or 500 MHz as indicated), ^{13}C NMR (125 MHz) were measured on a Bruker Advance 400 or 500 MHz spectrometers with residual protonated solvent signals as internal references. Chemical shifts are reported in parts per million (ppm) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (br. s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m).

High-resolution mass spectra (HRMS) experiments were performed in the positive (or negative) mode on a Bruker Daltonics microTOF spectrometer (Bruker Daltonik GmgH, Bremen, Germany) equipped with an orthogonal electrospray (ESI) interface by the "Service de Spectrométrie de Masse" of the "Fédération Chimie Le Bel" in Strasbourg. Calibration was performed with a sodium formate solution, consisting of 10mM sodium hydroxide in isopropanol and 0.2% formic acid (1/1, v/v). Sample solutions were continuously infused into the pneumatically assisted electrospray ionization source by means of a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Natick, MA, USA) with a flow rate of 4 $\mu L \cdot min^{-1}$.

Spectroscopic measurements

Absorption spectra were recorded using a dual-beam grating Schimadzu UV-3000 absorption spectrometer with a quartz cell of 1 cm of optical path length. The steady-state fluorescence emission and excitation spectra were recorded by using a Horiba Jobin Yvon Fluoromax 4. Phosphorescence emission spectra were recorded by using a Horiba Jobin Yvon FluoroMax®-4P in deoxygenated methyl tetrahydrofuran (MeTHF) and shown as averaged ten acquisition scans. All emission and excitation spectra were corrected. Luminescence lifetimes were measured on a Horiba Scientific TCSPC system equipped with a nanoLED 370 and using a light-scattering solution (LUDOX) for instrument response. Lifetimes were deconvoluted with Horiba Data Station software.

Fluorescence quantum yields (ϕ_F) were measured in diluted solution with an absorption value below 0.1 at the excitation wavelength using the following equation:

$$\Phi_{exp} = \Phi_{ref} \frac{I}{I_{ref}} \frac{OD_{ref}}{OD} \frac{\eta^2}{\eta^2_{ref}}$$

I is the integral of the corrected emission spectrum, OD is the optical density at the excitation wavelength, and □ is the refractive index of the medium. The reference systems used was the Rhodamine 6G ϕ_F = 88% in ethanol (λ_{exc} = 488 nm).

For solid-state measurements, the obtained the absolute quantum yields were recorded using the given dye directly as a powder in the quartz cell and an integration sphere.

Singlet oxygen quantum yields (ϕ_Δ) were measured using a liquid nitrogen cooled, solid Indium/Gallium/Arsenic detector (850-1600 nm) on a Horiba Scientific Fluorolog-QM-75-11-C and following the same principle of the fluorescence emission except that the singlet oxygen luminescence emission band (D) is integrated for both sample and reference compounds. The measurements are set up from 1230 to 1320 nm opening the slits of both excitation and emission to 5 nm because singlet oxygen emission is observed weakly at 1270 nm. The ϕ_Δ of compounds **1a-b** and **2a-b** were calculated using phenalenone as reference (ϕ_{ref} = 0.98 in chloroform) and chloroform as solvent. Dilution of both sample and reference were adjusted to have an optical density between 0.3 and 0.2. The excitation wavelength for the ϕ_Δ is the intersection wavelength of the absorption band of the sample and the reference so that OD_{ref}/OD_{exp} is equal to 1. The reported results are the average of 3 independent measurements for both samples and reference.

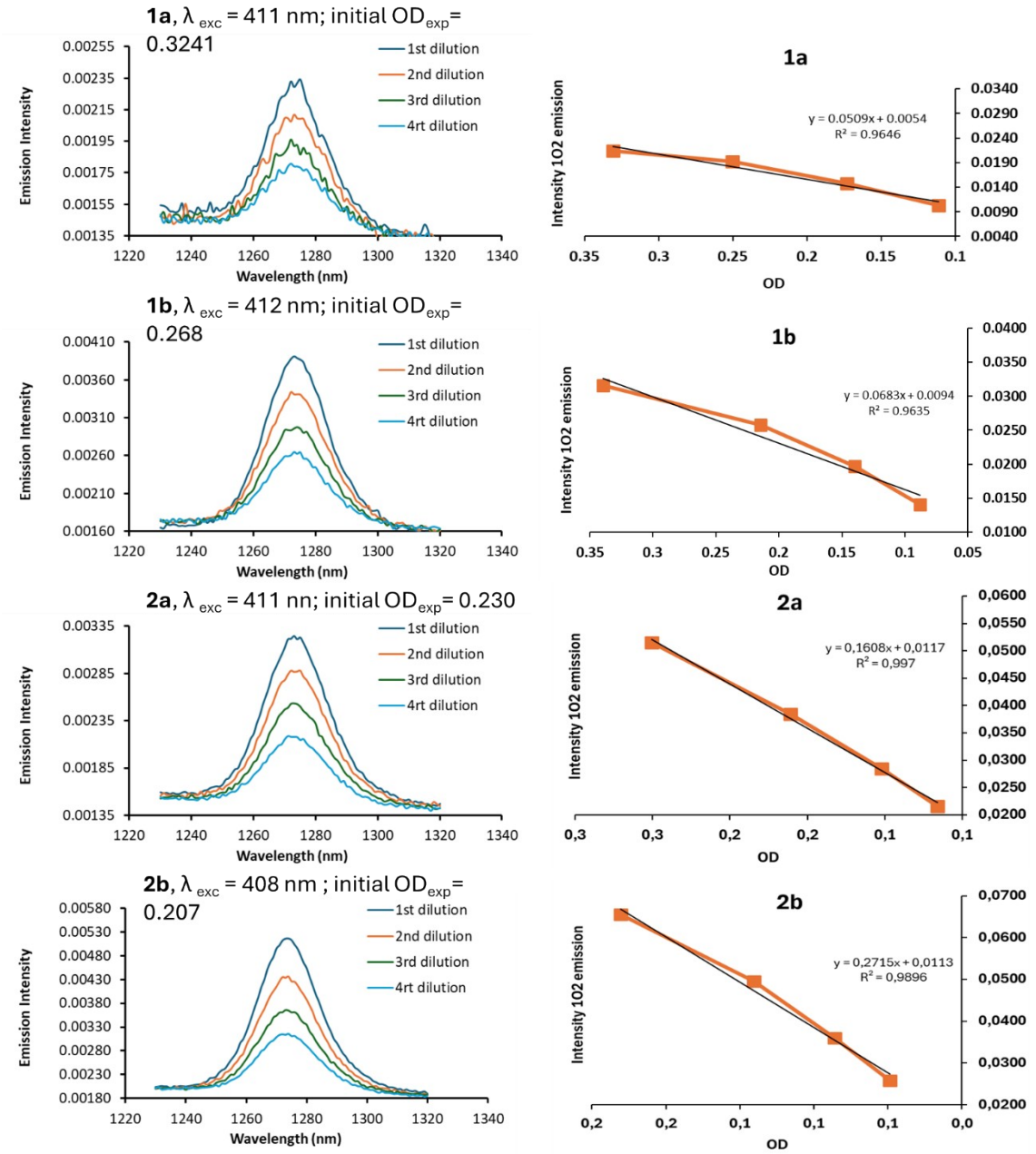


*Figure S 1. Singlet oxygen emission of four diluted solutions of compounds **1a-b** and **2a-b** in chloroform and linear correlation between the intensity of the $^1O_2$ emission and the optical density (OD) of the solution. For all samples, the excitation wavelength (λ_{exc}) and the initial averaged OD_{exp} of the sample is indicated.*

Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a halogen lamp (589, 578 and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

Electronic Circular Dichroism (ECD)

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. The spectra are presented without smoothing and further data processing.

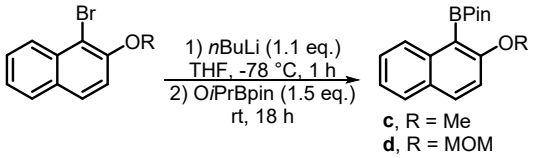
Circularly Polarized Luminescence (CPL) measurement

CPL spectra were measured on two different apparatus: preliminary results were acquired with a home-built (with the help of the JASCO company) CPL spectrofluoropolarimeter with a 90° geometry with a Xenon ozone-free lamp 150 W LS at room temperature, emission bandwidth of ∼1.0 nm, integration time of 4 sec, scan-speed of 50 nm/min. Subsequently, the results, which are presented in the article and in the SI, were acquired with a Jasco CPL-300 at room temperature in 10mm × 10mm path quartz cell. Excitation wavelength and instrument parameters were adapted for every sample. Data pitch was set at 1 nm and spectra are the mean values of a minimum of 5 accumulations.

Experimental section

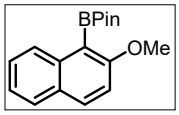
Compounds 1-bromo-2-methoxynaphthalene,[1] 1-bromo-2-(methoxymethoxy)naphthalene,[2] **3**[3] and **4**[3] were prepared according to literature procedures.

General procedure for the synthesis of 1-naphthylboronic acid pinacol esters c and d (GP1)



In a flame-dried Schlenk flask a solution of *n*BuLi (2.5 M in hexanes, 1.1 eq.) was added to a solution of the bromo derivatives (1.0 eq.) in freshly distilled THF (0.4 M) at -78 °C and, after 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.5 eq.) was added. The resulting reaction mixture was allowed to warm up to room temperature and stirred for 18 hours. Water was slowly added, and the aqueous layer was extracted with CH_2Cl_2 (x3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography on SiO_2.

2-(2-methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (c)



Boronic ester **c** was obtained according to GP1 after purification on SiO_2 (from 19:1 to 0:1, petrol ether (PET):CH_2Cl_2) in 43% yield (0.21 g, 0.74 mmol) as a pink solid.

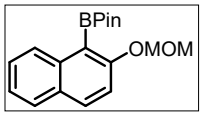
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.98 – 7.87 (m, 2H), 7.82 (d, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H), 7.48 (ddd, J = 8.3 Hz, ^3J = 6.8 Hz, ^4J = 1.5 Hz, 1H), 7.37 (ddd, J = 8.1 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 1H), 7.27 (d, ^3J = 9.0 Hz, 1H), 3.94 (s, 3H), 1.49 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 34.1 (s).

HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{17}H_{21}BNaO_3$: 307.1476; found 307.1464.

2-(2-(methoxymethoxy)naphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d)

Boronic ester **d** was obtained according to GP1 after purification on SiO_2 (from 3:7 to 2:3, petrol ether (PET):CH_2Cl_2) in 79% yield (0.79 g, 2.52 mmol) as a yellowish oil.



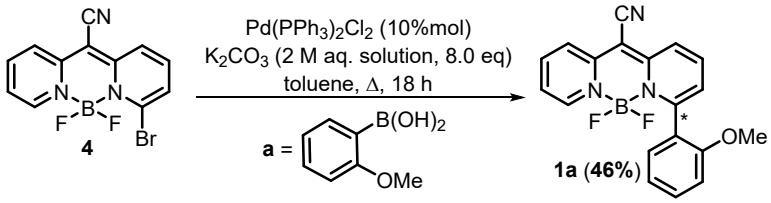
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.93-791 (m, 1H), 7.85 (d, ^3J = 9.1 Hz, 1H), 7.80 (d, ^3J = 8.2 Hz, 1H), 7.45-7.43 (m, 1H), 7.38 – 7.36 (m, 1H), 7.34 (dd, ^3J = 9.0, ^4J = 1.0 Hz, 2H), 5.25 (s, 2H), 3.53 (s, 3H), 1.46 (s, 12H).

^{13}C{H} NMR (125 MHz, $CDCl_3$): δ (ppm) 159.3, 137.3, 131.6, 130.0, 128.5, 127.4, 126.8, 124.3, 116.7, 95.8, 84.4, 78.0, 56.5, 25.2.

^{11}B NMR (160.5 MHz, $CDCl_3$): δ (ppm) 32.2 (s).

HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{18}H_{23}BKO_4$: 353.1321; found 353.1322.

Complex 1a



Boron complex **4** (0.05 g, 0.16 mmol) and 2-methoxyphenylboronic acid **a** (0.035g, 0.23 mmol) were dissolved in toluene (0.4 mL) and the resulting mixture was degassed for 20 minutes. $Pd(PPh_3)Cl_2$ (0.011 g, 0.02 mmol) and K_2CO_3 (2 M aq. solution, 0.62 mL, 1.24 mmol) were added to the reaction, which was then warmed to refluxing temperature and stirred for 18 hours. Water was added and extracted with CH_2Cl_2 (×3). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by chromatography on SiO_2 (toluene) to afford the desired complex in in 46% yield (0.025 g, 0.07 mmol) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.97 (br s, 1H), 7.62-7.70 (m, 3H), 7.51 (d, ^3J = 8.8 Hz, 1H), 7.46 (td, ^3J = 8.4, ^4J = 1.7 Hz, 1H), 7.31-7.30 (m, 1H), 7.05 (td, ^3J = 7.5, ^4J = 0.8 Hz, 1H), 6.99 (d, ^3J = 8.3 Hz, 1H), 6.78 (t, ^3J = 6.6 Hz, 1H), 6.71 (d, ^3J = 6.5 Hz, 1H), 3.76 (s, 3H).

^{13}C{H} NMR (125 MHz, $CDCl_3$): δ (ppm) 156.4, 150.9, 149.2, 138.2, 137.6, 137.2 (d, J = 4.5 Hz, 1C), 129.9 (d, J = 4.5 Hz, 1C), 129.8, 125.3, 118.8, 118.7 (2C), 118.4, 113.7, 109.7, 69.4, 54.9.

^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -120.0 (q, J = 30.2 Hz), -120.2 (q, J = 30.2 Hz), -134.7 (q, J = 28.8 Hz), 134.4 (q, J = 28.8 Hz)

^{11}B NMR (160.5 MHz, $CDCl_3$): δ (ppm) 1.37 (d, J = 29.0 Hz), 1.58 (d, J = 29.0 Hz).

HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{19}H_{15}BF_2N_3O$: 350.127075; found 350.126911.

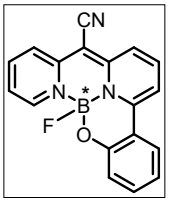
M.p: 207.8-208.3 °C.

General procedure for the Suzuki-Miyaura cross-coupling reaction (GP2)

Ligand **3** (1.0 eq.), XPhos (0.1 eq.) and 2-hydroxyphenylboronic acid **b** or boronic esters **c** and **d** (3.0 eq.) were dissolved in a mixture of *n*BuOH:H_2O (4:1, 0.08 M). The resulting mixture was degassed for 15 minutes and KOH (1.7 eq.) and $Pd(OAc)_2$ (0.1 eq.) were added to the reaction, which was then warmed to 85 °C and stirred for 18 hours. Water was added and extracted with EtOAc (x3). The combined organic layers were dried over MgSO4 and concentrated *in vacuo*. The crude product was purified by column chromatography on SiO_2.

Complex 2a

Suzuki-Miyaura cross-coupling reaction between ligand **3** (0.32 g, 1.16 mmol) and the boronic acid **b** was performed according to GP2. The crude product was used without any further purification. $BF_3{\cdot}OEt_2$ (0.25 mL, 2.03 mmol) was added to a solution of phenol (0.30 mL, 1.03 mmol) in DCE (20 mL) at room temperature and under inert atmosphere. Following stirring at reflux for 3 h, a precipitate was formed. The reaction mixture was



cooled down to room temperature and the Hunig's base (0.90 mL, 5.17 mmol) was added causing the solubilization of the precipitate and the appearance of a green fluorescence. After stirring for 10 minutes, water was added, and the organic layer is separated. The aqueous layer was extracted with CH_2Cl_2 (×3) and the combined organic solutions washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by chromatography on SiO_2 (CH_2Cl_2) in 53% yield (0.172 g, 0.55 mmol) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.44 (d, ^3J = 6.2 Hz, 1H), 7.79 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.55 (d, ^3J = 8.8 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.35 (d, ^3J = 7.7 Hz, 1H), 7.15 (dd, ^3J = 8.2, ^4J = 1.0 Hz, 1H), 7.07-7.03 (m, 1H), 6.92 (td, ^3J = 6.8, ^4J = 1.2 Hz, 1H).

^{13}C{H} NMR (125 MHz, $CDCl_3$): δ (ppm) 154.3, 150.6, 149.9, 145.3, 139.2, 139.2, 137.9, 133.2, 125.3, 121.4, 120.20, 120.15, 119.4, 117.9, 117.4, 114.9, 109.7, 70.2.

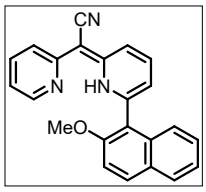
^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -127.1 (q, ^3J = 48.6 Hz).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ (ppm) 1.21 (d, ^3J = 49.0 Hz).

HRMS (ESI-TOF) m/z: [M+Na] calcd for $C_{19}H_{11}BFN_3NaO$: 337.0908; found 337.0903.

2-(6-(2-(methoxy)naphthalen-1-yl)pyridin-2(1H)-ylidene)-2-(pyridin-2-yl)acetonitrile (4-OMe)

Compound **4c** was obtained according to GP2 after purification on SiO_2 (petrol ether (PET):CH_2Cl_2, from 80:20 to 100) in 91% yield (0.113 g, 0.32 mmol) as a yellow solid.

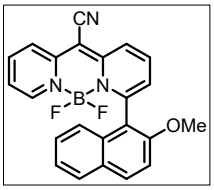


^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.99 (d, J^3 = 9.1 Hz, 1H), 7.87 (dd, J^3 = 6.8, J^4 = 2.7 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.63 (dd, J^3 = 8.7, J^4 = 7.2 Hz, 1H), 7.47 – 7.36 (m, 7H), 6.78 (dd, J^3 = 7.2, J^4 = 0.8 Hz, 1H), 6.46 (td, J^3 = 5.9, J^4 = 2.0 Hz, 1H), 3.91 (s, 3H).

^{13}C{H} NMR (126 MHz, $CDCl_3$): δ (ppm) 156.0, 155.5, 154.8, 145.8, 139.9, 136.8, 136.5, 132.8, 131.4, 129.2, 128.4, 127.5, 124.4, 124.2, 122.9, 120.1, 119.9, 118.5, 116.1, 113.5, 112.9, 68.0, 56.8.

HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{23}H_{18}BF_2N_3O$: 352.1444; found 352.1443.

Complex 1b



Freshly distilled $BF_3{\cdot}OEt_2$ (0.55 mL, 4.35 mmol) and NEt_3 (0.55 mL, 4.06 mmol) were added to a solution of **5c** (0.10 g, 0.290 mmol) in freshly distilled CH_2Cl_2 (29 mL) at room temperature and under inert atmosphere. The obtained reaction mixture was warmed at 50 °C and stirred for 2 h. Following these, additional $BF_3{\cdot}OEt_2$ (0.55 mL, 4.35 mmol) and NEt_3 (0.55 mL, 4.06 mmol) were added, and the reaction mixture was stirred at reflux for 18 h. Water was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (×3) and the combined organic solutions washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by chromatography on SiO_2 (CH_2Cl_2) in 77% yield (0.089 g, 0.22 mmol) as a yellow solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 8.01 (d, ^3J = 9.1 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.82-7-77 (m, 1H), 7.72-7.71 (m, 1H), 7.68-7.64 (m, 1H), 7.51 (d, ^3J = 8.8 Hz, 1H), 7.39 (d, ^3J = 9.1 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.36-7.33 (m, 2H), 7.27-7.25 (m, 1H), 6.79 – 6.76 (m, 2H), 3.85 (s, 3H).

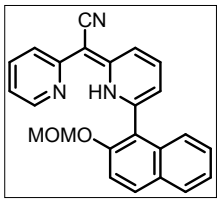
^{13}C{H} NMR (126 MHz, CD_2Cl_2): δ (ppm) 155.7 (d, J = 2.7 Hz), 152.9, 150.6, 149.4, 139.8, 139.4, 138.5 (t, J = 2.6 Hz), 134.2 (d, J = 3.2 Hz), 131.6, 128.7, 128.3, 127.2, 125.3 (d, J = 2.4 Hz), 124.2, 120.7 (br s), 120.4, 120.0, 119.8, 115.3 (br s), 113.5, 70.8 (m, Hz), 57.0.

^{19}F NMR (470 MHz, CD_2Cl_2): δ (ppm) -120.8 – -121.1 (m), -127.0 – -127.4 (m), -131.2 – -131.7 (m), -136.0 – -136.5 (m).

^{11}B NMR (160.5 MHz, CD_2Cl_2): δ (ppm) 1.40 (br t, J = 31.5 Hz).

HRMS (ESI-TOF) m/z: [M+K] calcd for $C_{23}H_{16}BF_2N_3O$: 399.1349; found 399.1326.

2-(6-(2-(methoxymethoxy)naphthalen-1-yl)pyridin-2(1H)-ylidene)-2-(pyridin-2-yl)acetonitrile (4-MOM)



Ligand **4** (0.10 g, 0.36 mmol), XPhos (0.02 g, 0.04 mmol) and boronic ester **d** (0.34 g, 1.09 mmol) are dissolved in a mixture of *n*BuOH:H_2O (4:1, 4.5 mL). The resulting mixture is degassed for 15 minutes and KOH (0.041 g, 0.73 mmol) and $Pd(OAc)_2$ (0.02 g, 0.04 mmol) are added to the reaction, which is then warmed to 85 °C and stirred for 18 hours. Water is added and extracted with EtOAc (x3). The combined organic layers are dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by chromatography on SiO_2 (CH_2Cl_2) in 62% yield (0.086 g, 0.22 mmol) as an orange oil.

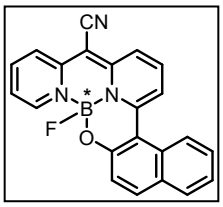
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.96 (d, ^3J = 9.0 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.73 – 7.69 (m, 1H), 7.66-7.63 (m, 1H), 7.55 (d, ^3J = 9.1 Hz, 1H), 7.46 (dd, ^3J = 8.7, ^4J = 0.9 Hz, 1H), 7.44 – 7.38 (m, 6H), 6.80 (dd, ^3J = 7.2, ^4J = 0.9 Hz, 1H), 6.46 – 6.41 (m, 1H), 5.18 (s, 2H), 3.34 (s, 3H).

^{13}C{H} NMR (125 MHz, $CDCl_3$): δ (ppm) 155.7, 152.6, 146.3, 139.3, 136.8, 136.6, 132.8, 131.2, 129.9, 128.3, 127.3, 124.7, 122.8, 122.2, 120.0, 118.4, 116.8, 116.3, 112.7, 95.6, 68.0, 56.4.

HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{24}H_{20}N_3O_2$: 382.1550; found 382.1540.

Complex 2b

HCl (6 M aq. solution, 1.0 mL) is added dropwise to a solution of ligand **5d** (0.046 g, 0.12 mmol) in THF



(1.0 mL) at room temperature. The resulting reaction mixture is stirred for 18 hours, and a yellow precipitate is obtained, which is then centrifuged. The intermediate naphthol is used directly in the next reaction step without further purification. $BF_3{\cdot}OEt_2$ (0.030 mL, 0.24 mmol) is added to a solution of naphthol (0.020 g, 0.06 mmol) in DCE (1.5 mL) at room temperature and under inert atmosphere. The resulting reaction mixture is warmed to refluxing temperature and stirred for 30 minutes. The mixture containing a white precipitate is cooled down to room temperature and the Hunig's base (0.14 mL, 0.60 mmol) is added causing the solubilization of the precipitate and a color change with green fluorescence. After stirring for 4 hours, water is added and extracted with CH_2Cl_2 (×3). The combined organic layers are washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by chromatography on SiO_2 (CH_2Cl_2) to afford **5d** in 83% yield (0.037 g, 0.10 mmol) as an orange solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.41 (d, ^3J = 8.7 Hz, 1H), 8.39 (d, ^3J = 6.4 Hz, 1H), 7.87 (d, ^3J = 8.7 Hz, 1H), 7.85 (d, ^3J = 8.4 Hz, 1H), 7.65 (m, 2H), 7.57-7.54 (m, 1H), 7.52 (d, ^3J = 8.8 Hz, 1H), 7.47 (d, ^3J = 8.4 Hz, 1H), 7.44-7.41 (m, 1H), 7.31 (d, ^3J = 8.8 Hz, 1H), 6.89-6.86 (m, 1H).

^{13}C{H} NMR (125 MHz, $CDCl_3$): δ (ppm) 156.3, 150.7, 149.6, 144.7, 139.2, 138.8, 138.5, 133.9, 130.8, 130.3, 129.3, 127.8, 124.4, 124.1, 120.3, 120.1, 119.6, 117.3, 115.3, 114.6, 113.1, 69.5.

^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -133.7 (q, J = 47.1 Hz).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ (ppm) 1.33 (d, J = 47.4 Hz).

HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{22}H_{13}BF_2N_3O$: 365.1143; found 365.1130.

M.p: degradation at T > 250 °C.

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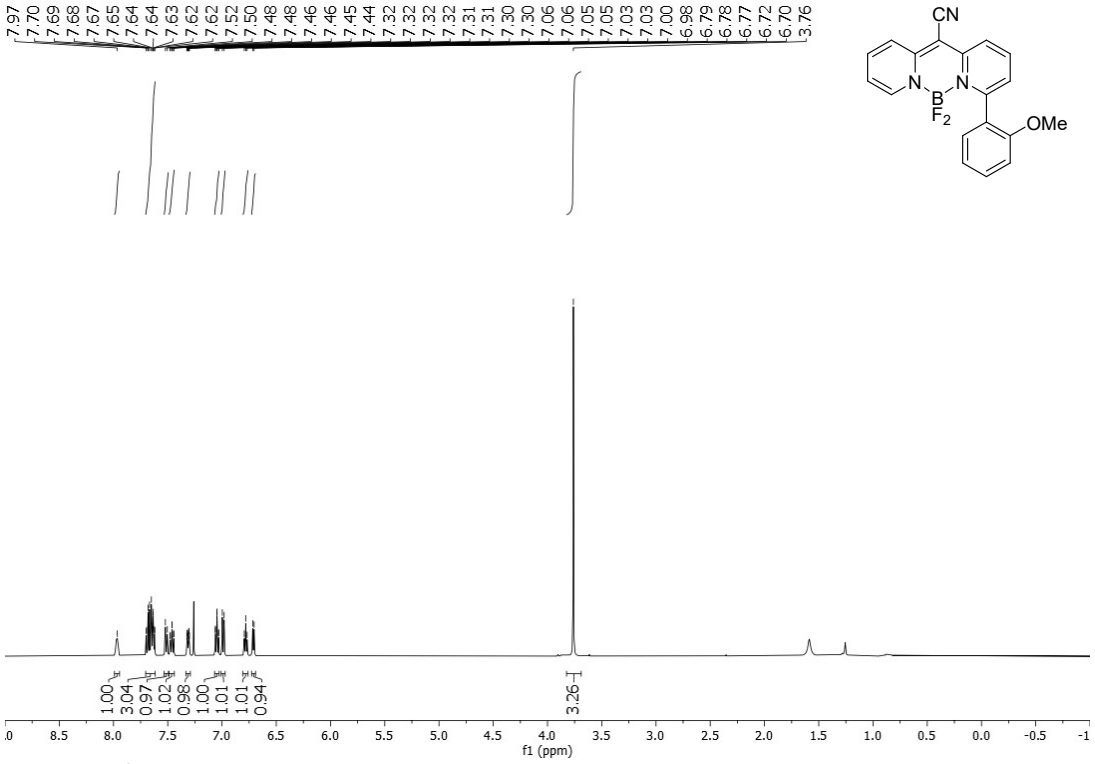
[1] Mori, K. ; Ichikawa, Y. ; Kobayashi, M.; Shibata, Y.; Yamanaka, M.; Akiyama, T. *Chem. Sci.* **2013**, *4*, 4235.

[2] Mori, K. ; Itakura, T. ; Akiyama, T. *Angew. Chem. Int. Ed.* **2016**, *55*, 11642.

[3] Figliola, C.; Sutter, A.; Papineau, T. V.; Chériaux, C.; Retailleau, P. ; Jacquemin, D. ; Ulrich, G. *J. Org. Chem.* **2024**, *89*, 3020.

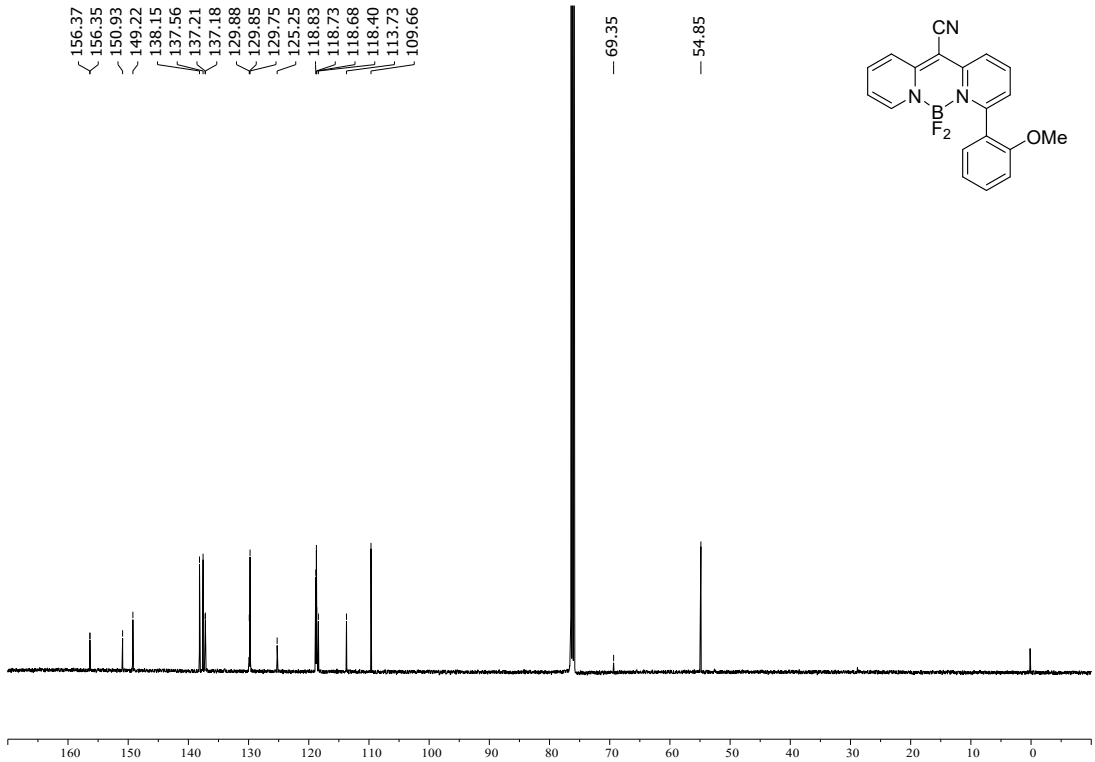
NMR and HRMS spectra

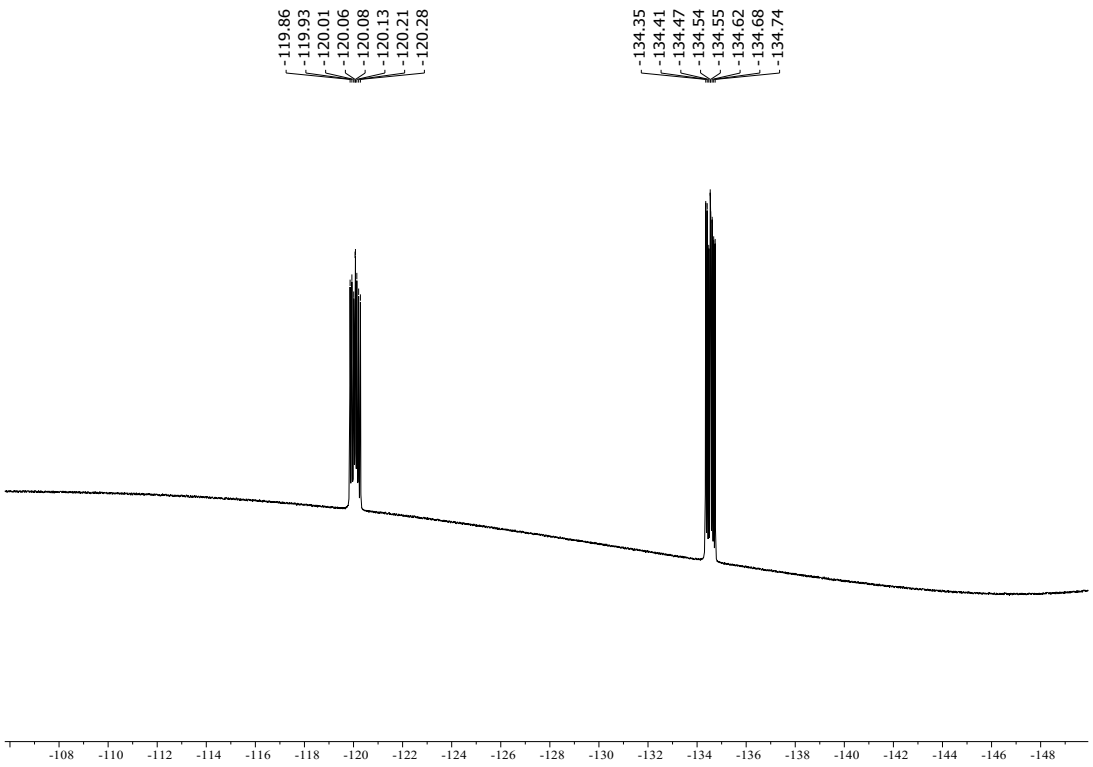
^{1}H and ^{13}C NMR spectra of **1a** in $CDCl_3$

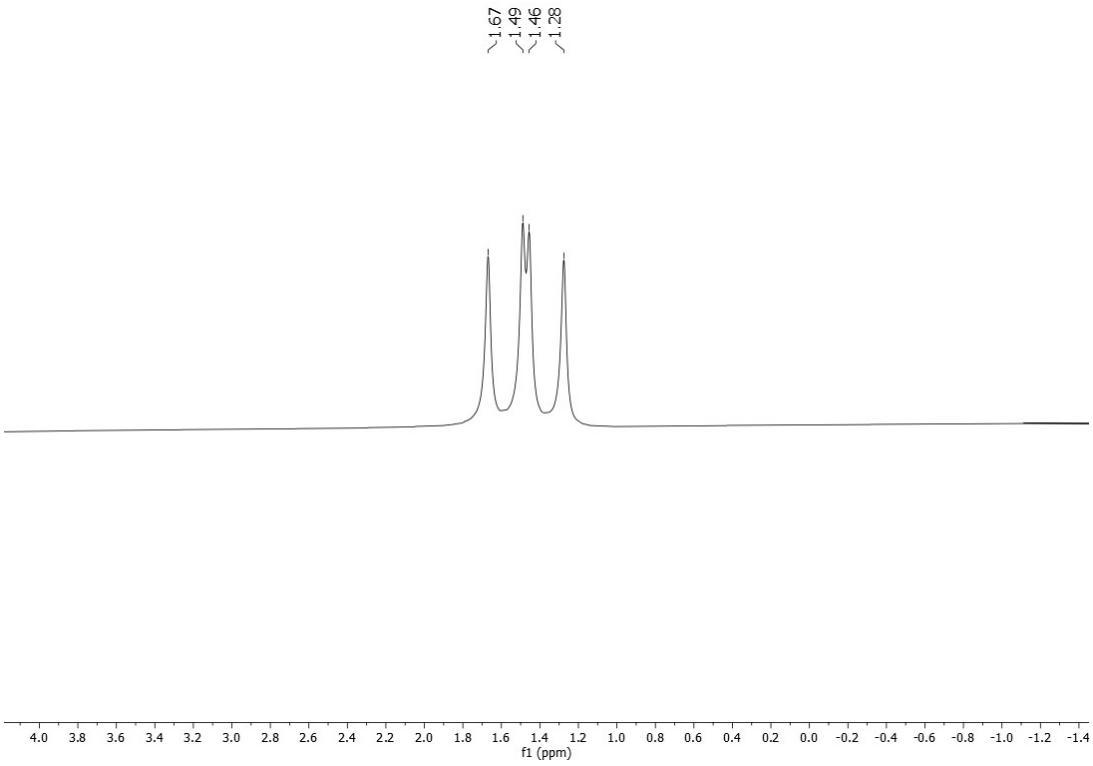


^{19}F and ^{11}B

NMR spectra of **1a** in $CDCl_3$




-119.86
-119.93
-120.01
-120.06
-120.08
-120.13
-120.21
-120.28
-134.35
-134.41
-134.47
-134.54
-134.55
-134.62
-134.68
-134.74
-108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148


1.67
1.49
1.46
1.28
4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4 -0.6 -0.8 -1.0 -1.2 -1.4
f1 (ppm)

HRMS of **1a**

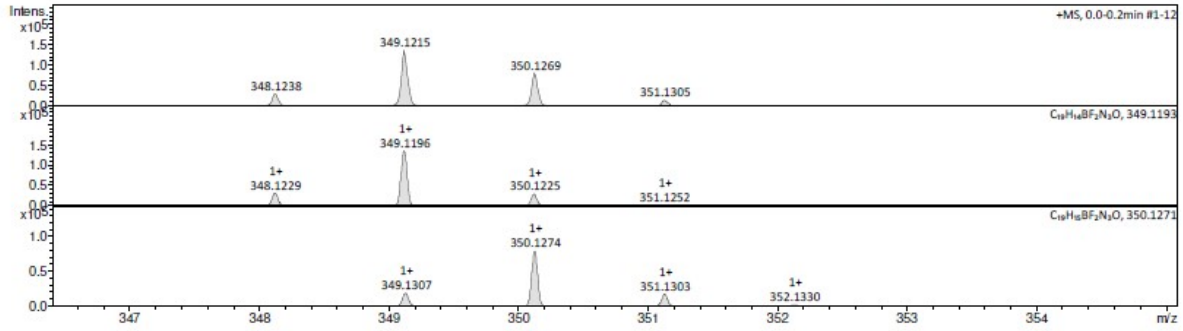
Mass Spectrum HR Report

Analysis Info

Analysis Name	Y:\2022\07_Juillet 2022\F12914SK.d	Acquisition Date	22/07/2022 11:29:52
Method	Tune_pos_Standard.m	Operator	BDAL@DE
Sample Name	CFB-68	Instrument	micrOTOF II 8213750.10451
Comment			

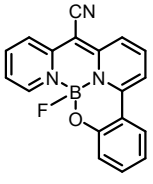
Acquisition Parameter

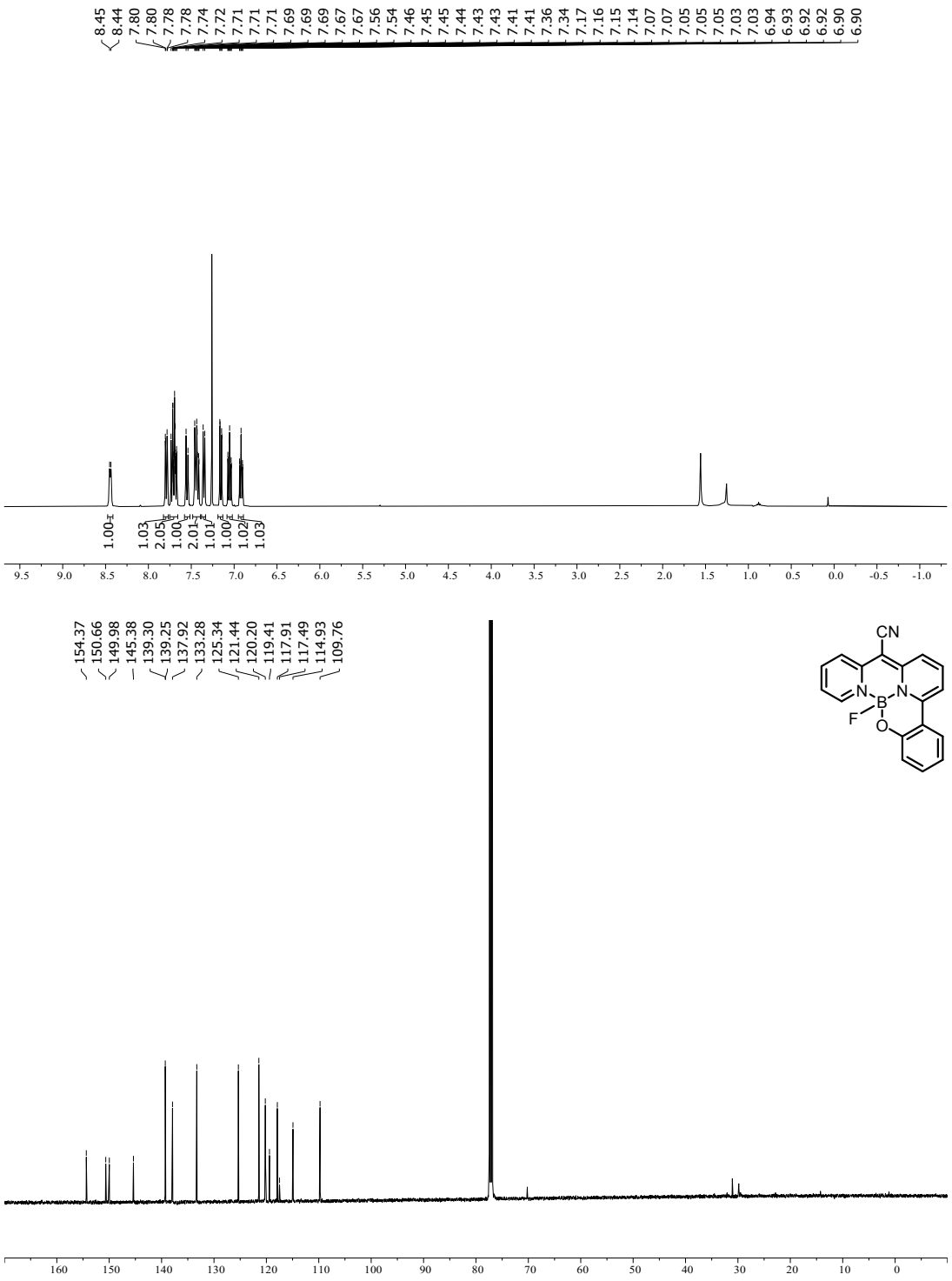
Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	49.7 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	n/a	n/a
Scan End	3000 m/z	n/a	n/a	Set Reflector	1800.0 V
		n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	2020.0 V



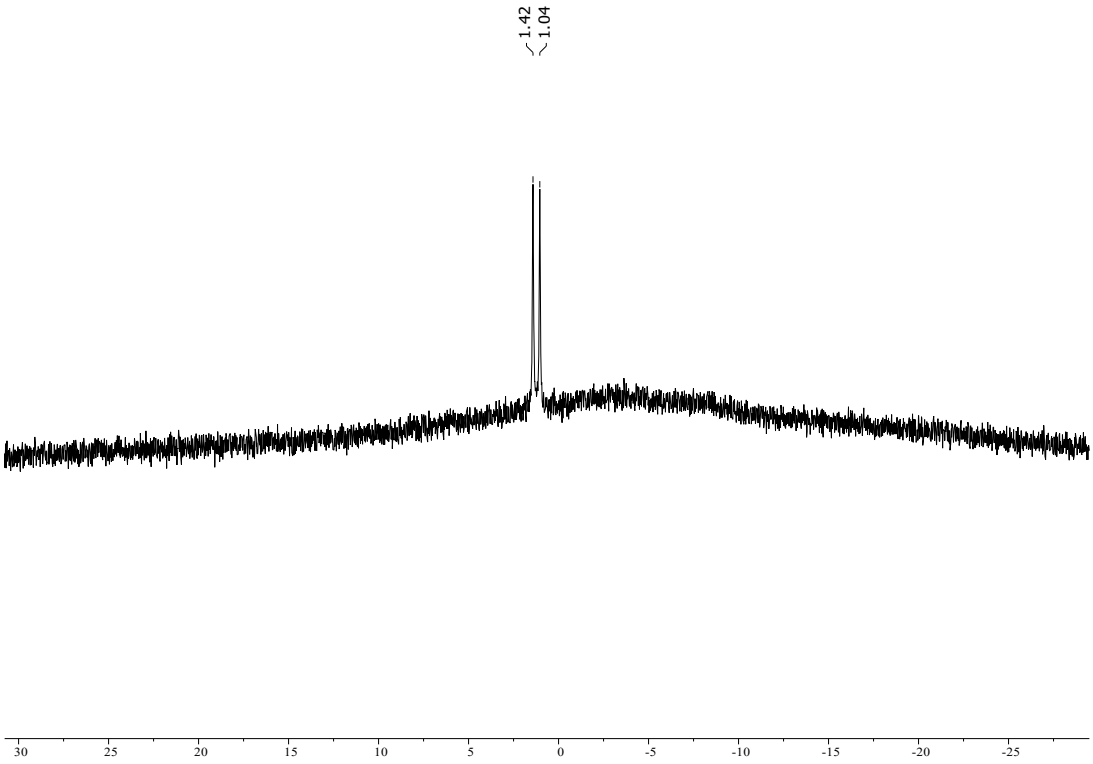
Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I	VarNorm	Std m/z	Diff	Std Comb Dev
349.121537	1	C19H14BF2N3O	349.119250	-5.6	-7.9	14.0	ok	odd	193.1	234.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
350.126911	1	C19H15BF2N3O	350.127075	1.5	5.9	13.5	ok	even	437.0	546.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

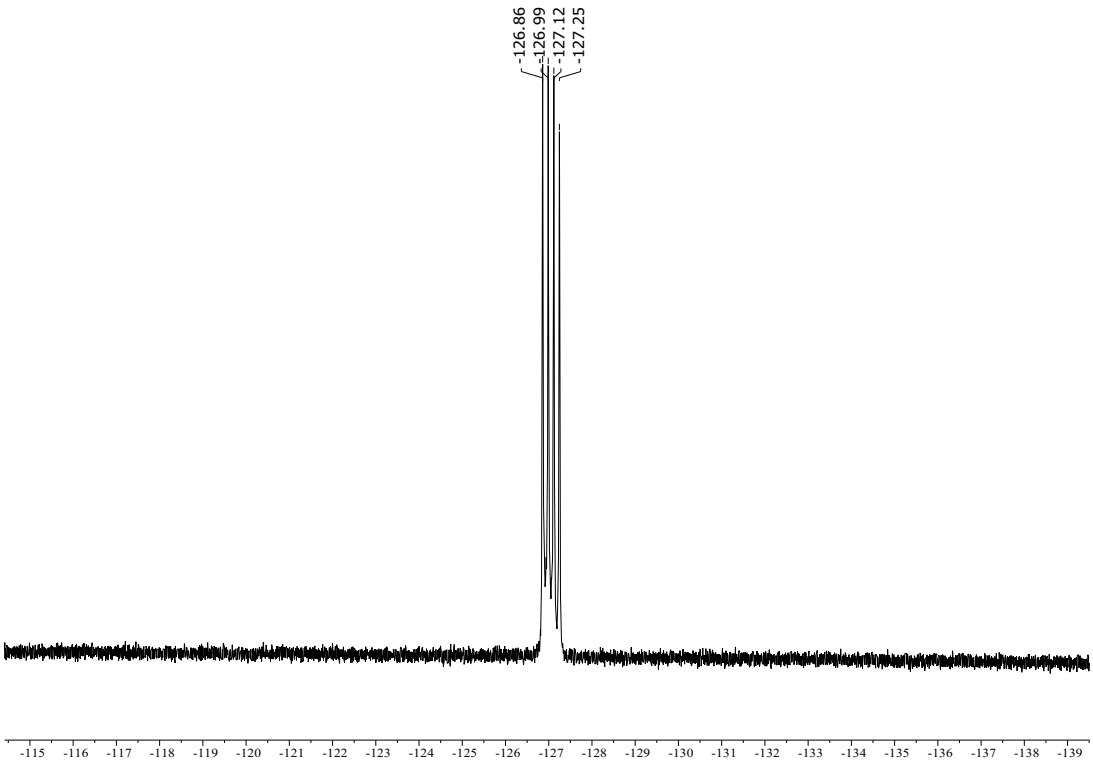
^{1}H and ^{13}C NMR spectra of **2a** in $CDCl_3$





^{19}F and ^{11}B NMR spectra of **2a** in $CDCl_3$


1.42
1.04
30
25
20
15
10
5
0
-5
-10
-15
-20
-25


-126.86
-126.99
-127.12
-127.25
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139

HRMS of **2a**

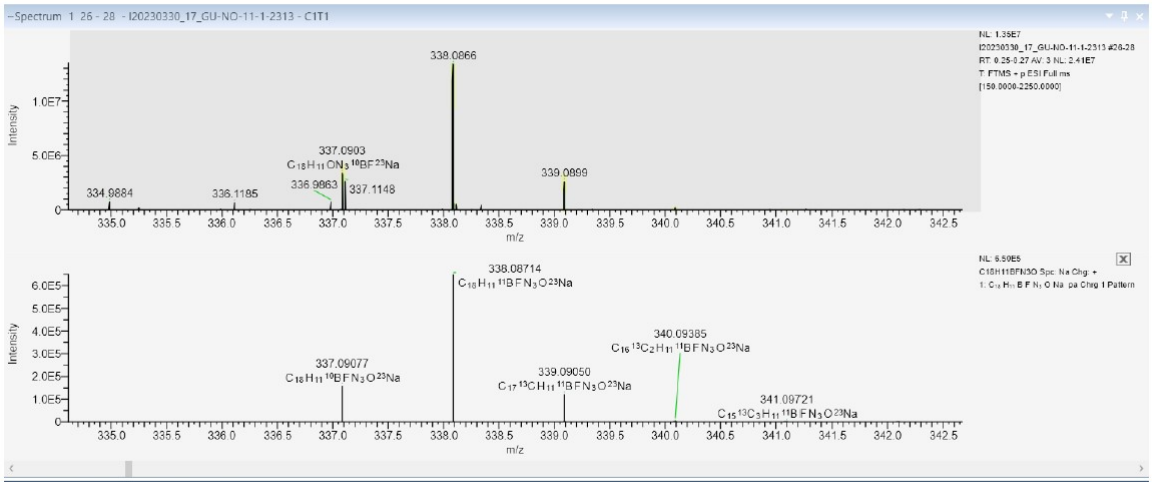
SERVICE DE SPECTROMETRIE DE MASSE - FEDERATION CHIMIE LE BEL- FR2010 - CNRS/Unistra

Sample Name: **GU.NO.11.1.2313**

Analysis Name: I20230330-17

ThermoFisher Orbitrap: Exactive Plus with Extend Mass Range: Source HESI II

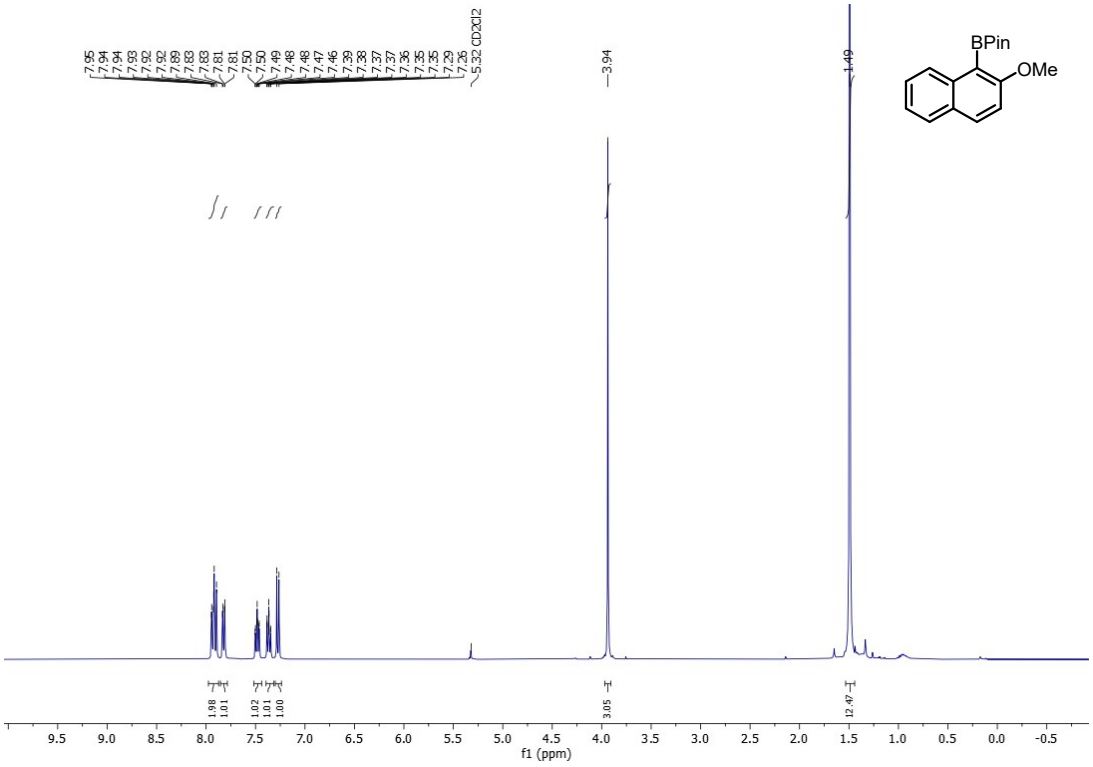
Ion Polarity: Positive

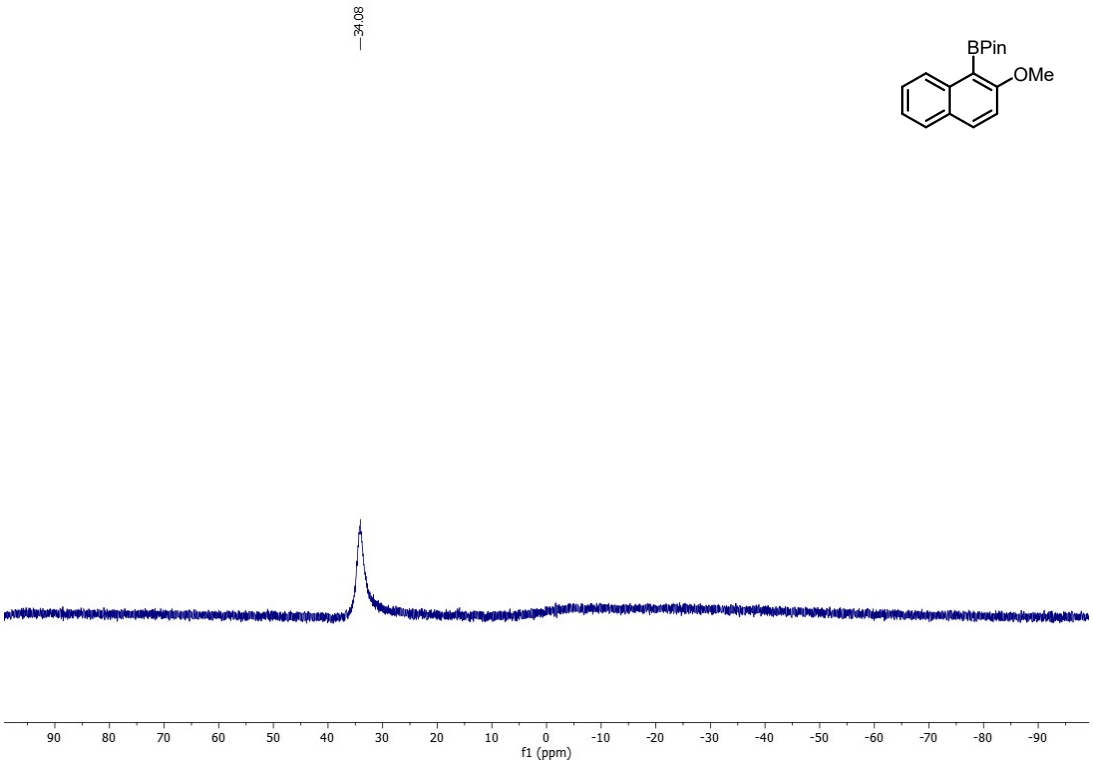


Elemental Composition Results - Spectrum 1

Peak Mass	Display Formula	S Fit	RDB	Delta [ppm]	Theo. mass	Rank	Combined Score	# Matched Iso.	# Missed Iso.	MS Cov. [%]	Pattern Cov. [%]
337.0903	$C_{18}H_{11}ON_3{}^{10}BF^{23}Na$	30.24	14.50	-1.55	337.09077	1	79.06	8	1	81.77	98.77

^{1}H and ^{11}B NMR spectra of **c** in $CDCl_3$





HRMS of **c**

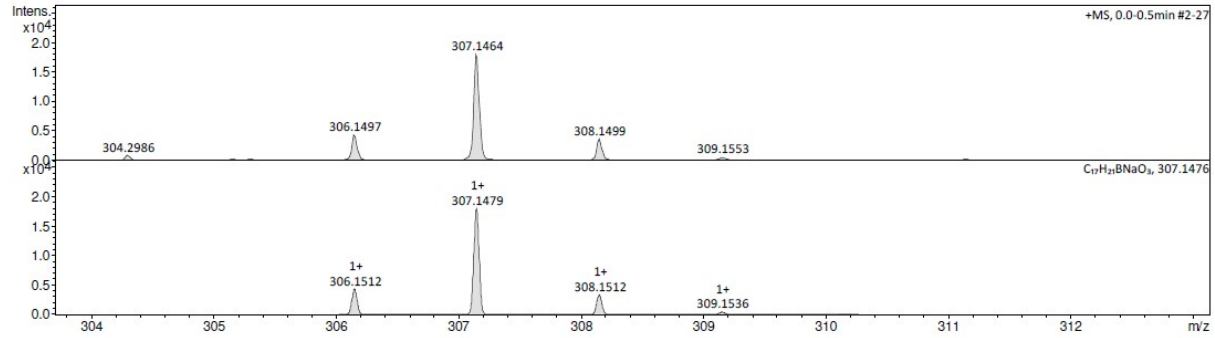
Mass Spectrum HR Report

Analysis Info

Analysis Name	Y:\2023\12_Decembre 2023\F16020SK.d	Acquisition Date	15/12/2023 10:52:48
Method	Tune_pos_Standard.m	Operator	BDAL@DE
Sample Name	CC289.F2	Instrument	micrOTOF II 8213750.10451
Comment			

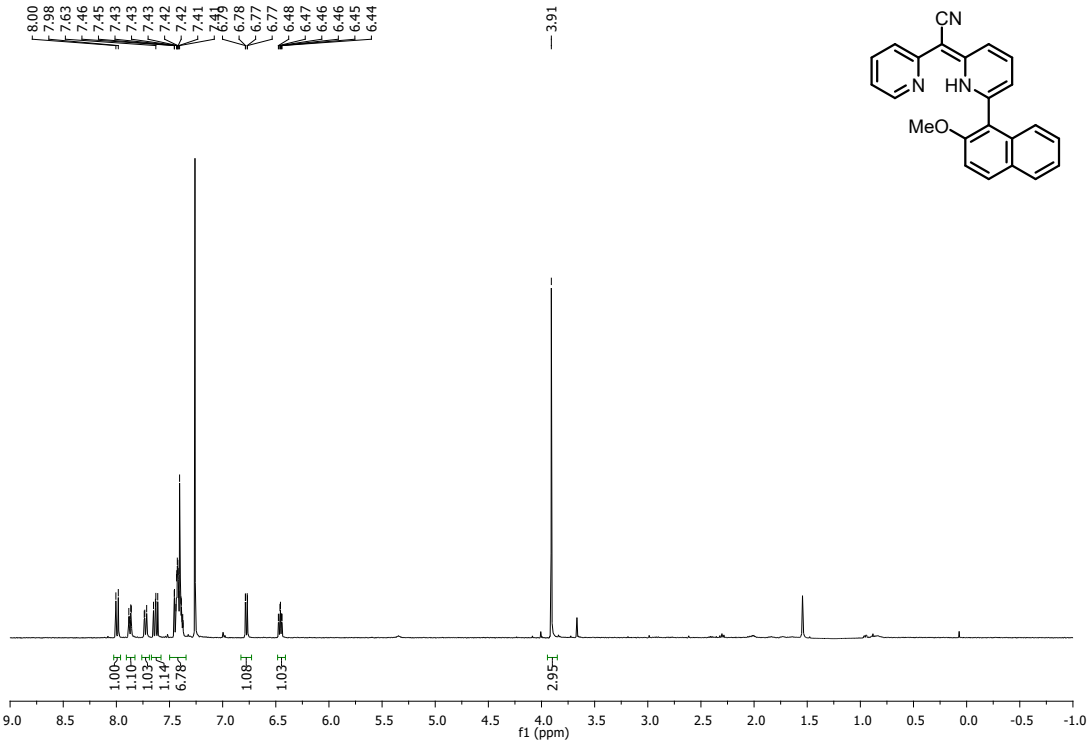
Acquisition Parameter

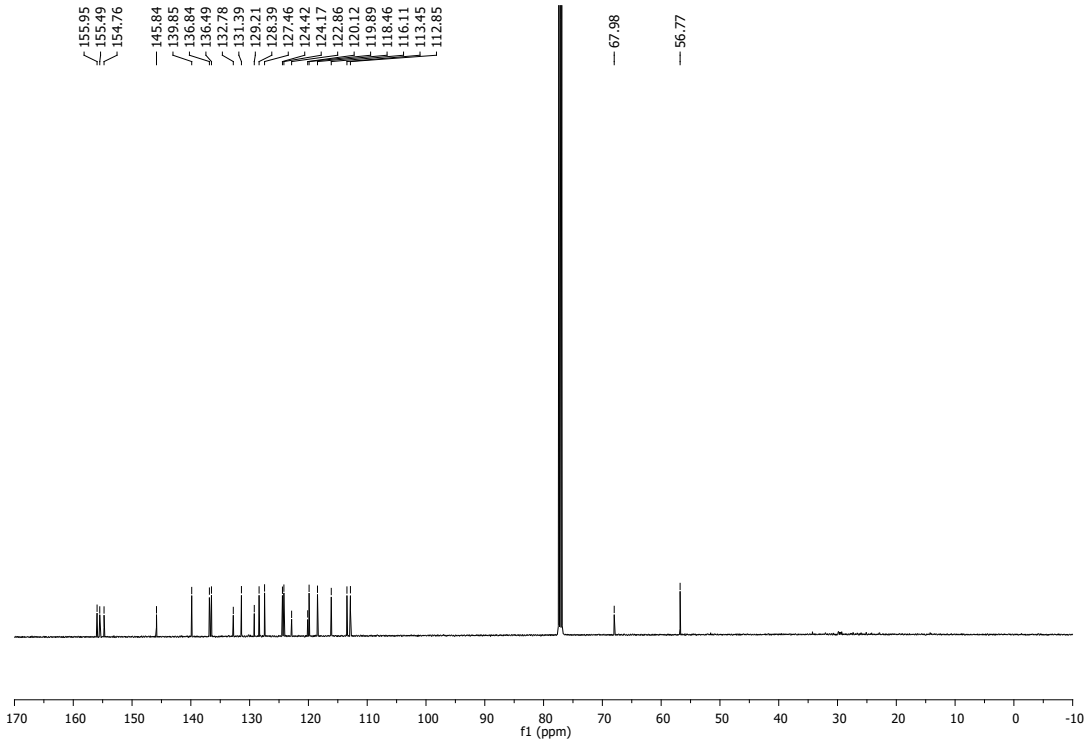
Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	48.2 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	n/a	n/a
Scan End	3000 m/z	n/a	n/a	Set Reflector	1800.0 V
		n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	2021.6 V



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
307.146436	1	C17H21BNaO3	307.147596	4.8	1711.3	7.5	ok	even	647.6	547.1	n.a.	n.a.	n.a.	n.a.

^{1}H and ^{13}C NMR spectra of **4-OMe** in $CDCl_3$





HRMS of **4-OMe**

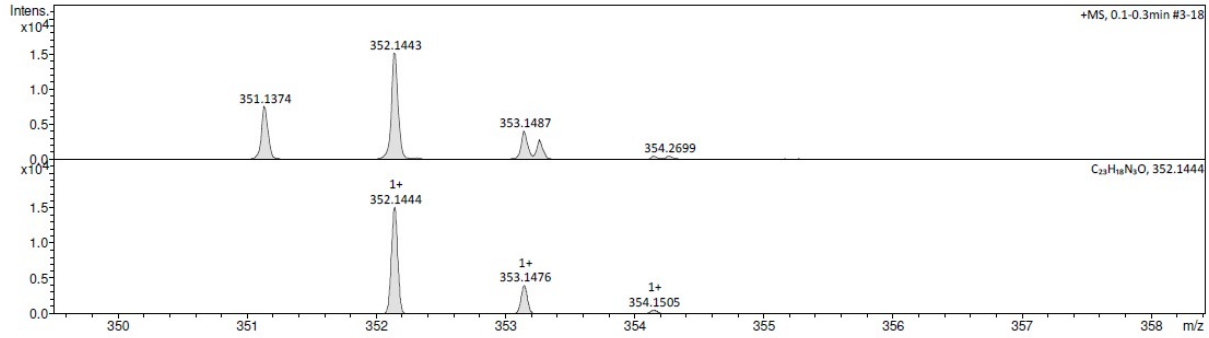
Mass Spectrum HR Report

Analysis Info

Analysis Name	Y:\2024\01_Janvier 2024\F16153SK.d	Acquisition Date	29/01/2024 15:07:04
Method	Tune_pos_Standard.m	Operator	BDAL@DE
Sample Name	CC293.F1	Instrument	micrOTOF II 8213750.10451
Comment			

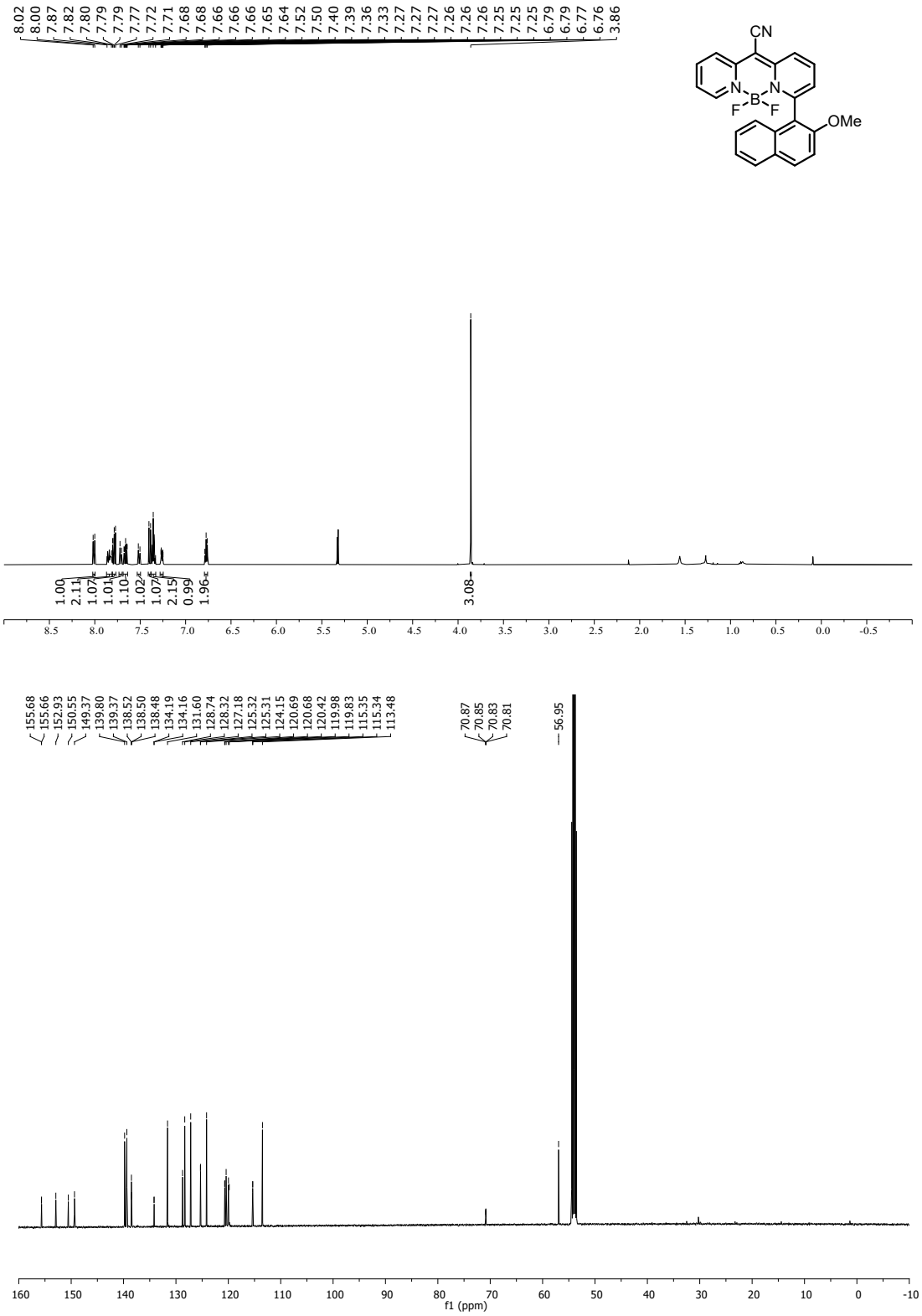
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	48.2 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	2021.6 V

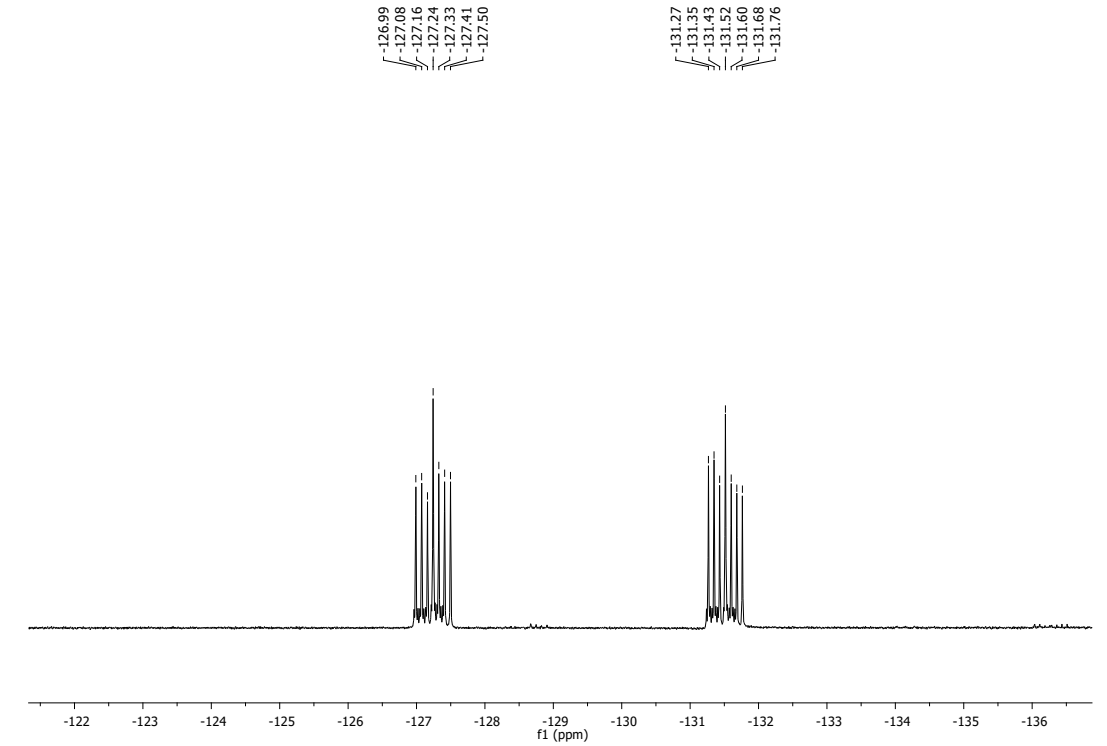


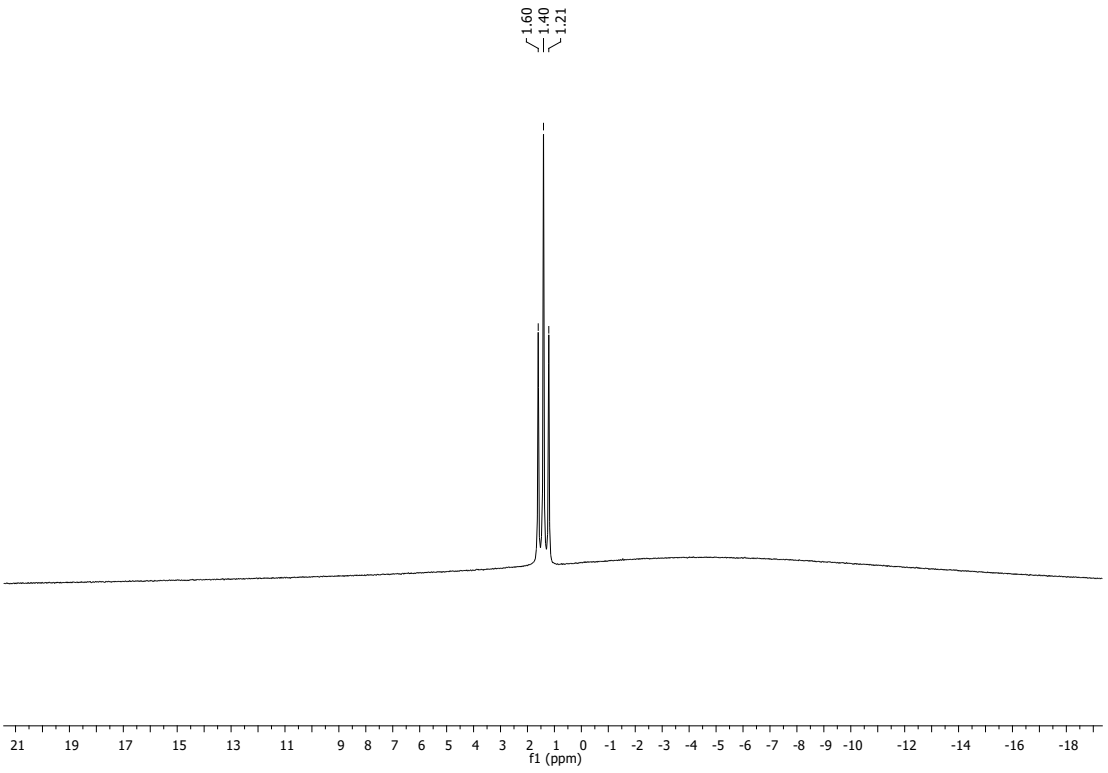
Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
352.144257	1	C23H18N3O	352.144439	0.5	-2.2	16.5	ok	even	6.3	8.7	n.a.	n.a.	n.a.	n.a.

^{1}H and ^{13}C NMR spectra of **1b** in CD_2Cl_2



^{19}F and ^{11}B NMR spectra of **1b** in CD_2Cl_2





HRMS of **1b**

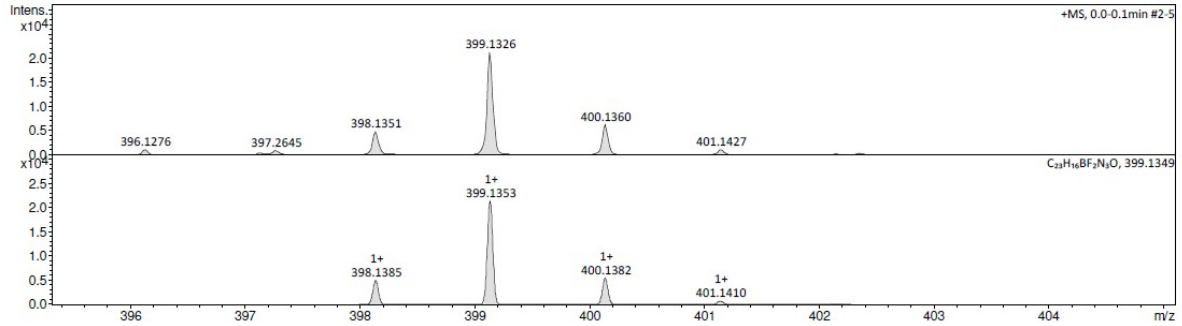
Mass Spectrum HR Report

Analysis Info

Analysis Name	Y:\2024\01_Janvier 2024\F16161SK.d	Acquisition Date	29/01/2024 15:56:00
Method	Tune_pos_Mid.m	Operator	BDAL@DE
Sample Name	CC294.P3	Instrument	micrOTOF II 8213750.10451
Comment			

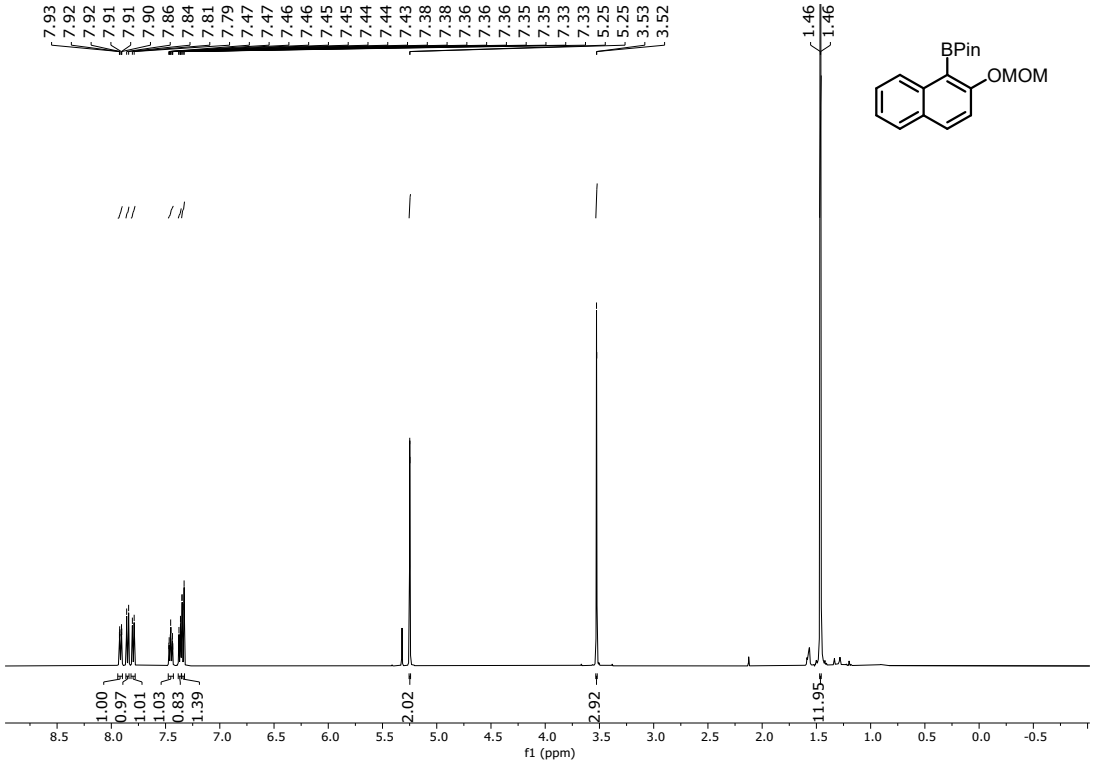
Acquisition Parameter

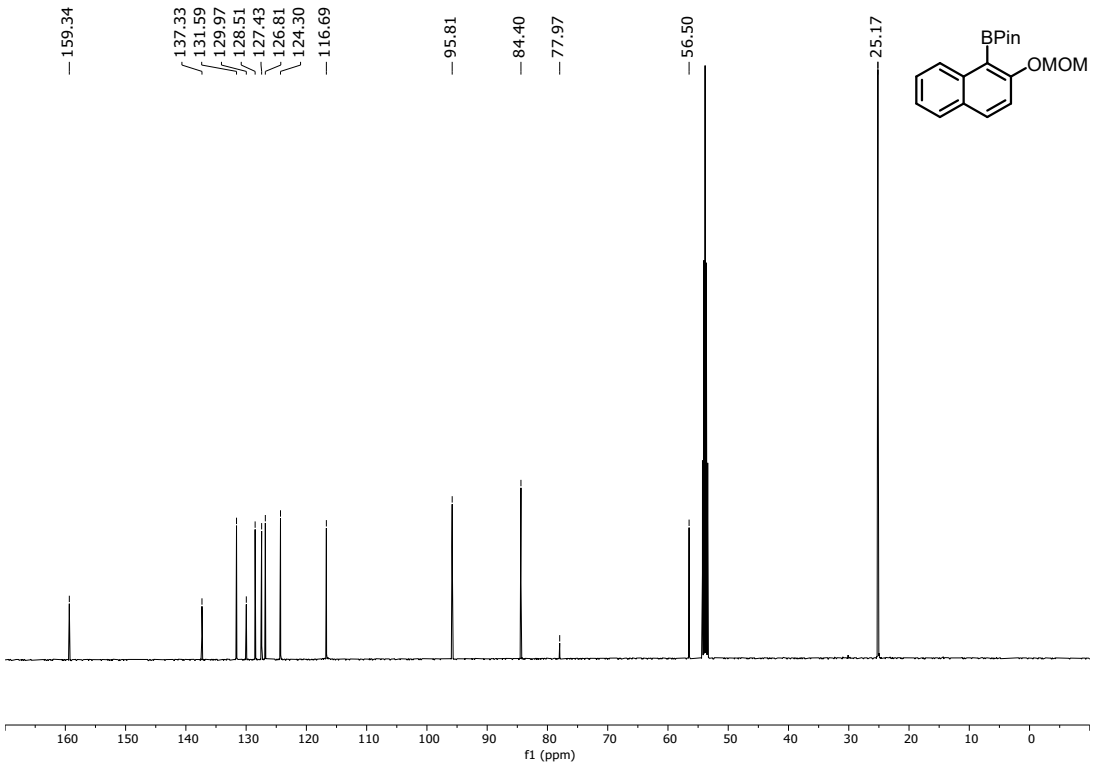
Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	48.2 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	2021.6 V



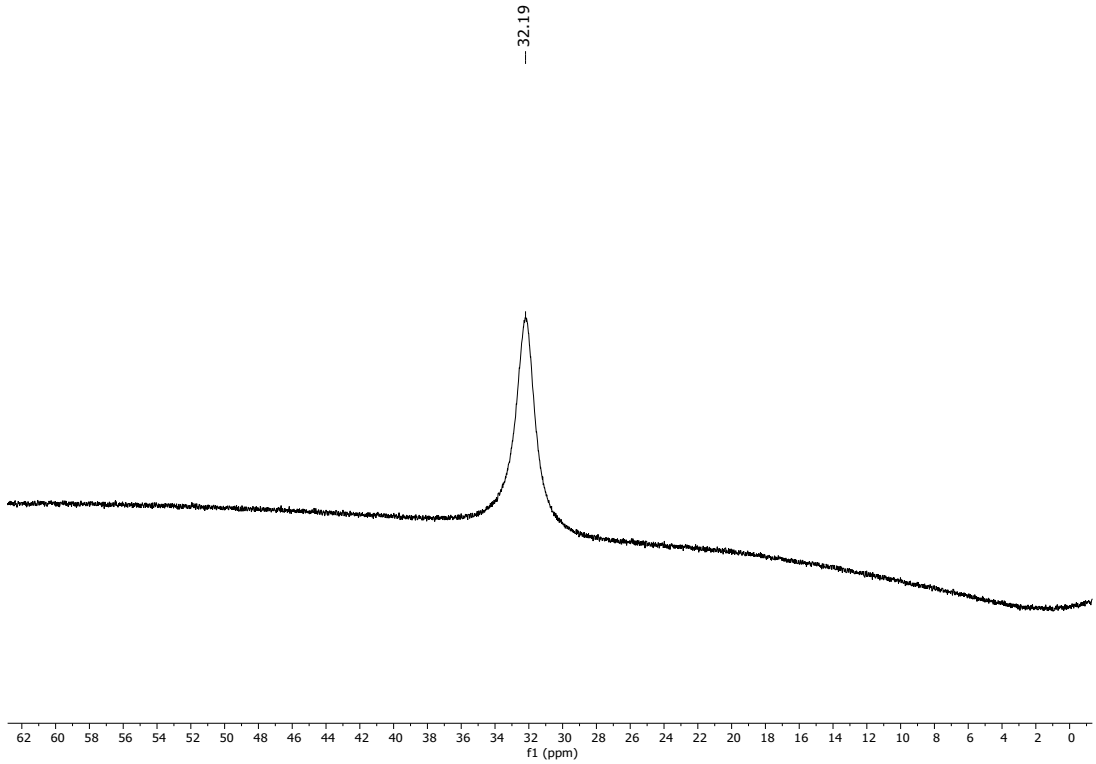
Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
399.132575	1	C23H16BF2N3O	399.134900	5.8	5.2	17.0	ok	odd	21.2	31.3	n.a.	n.a.	n.a.	n.a.

^{1}H and ^{13}C NMR spectra of **d** in $CDCl_3$





^{11}B NMR spectra of **d** in $CDCl_3$



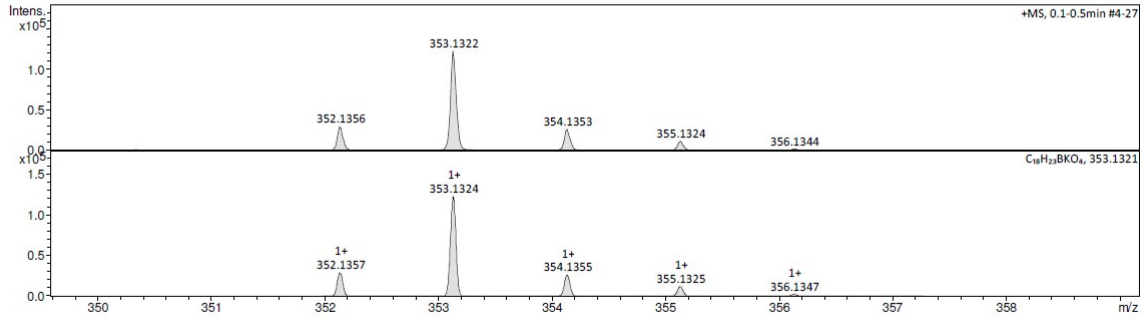
HRMS of **d**

Analysis Info

Analysis Name	Y:\2023\09_Septembre 2023\F15498SK.d	Acquisition Date	19/09/2023 14:18:56
Method	Tune_pos_Standard.m	Operator	BDAL@DE
Sample Name	CFB-76	Instrument	micrOTOF II 8213750.10451
Comment			

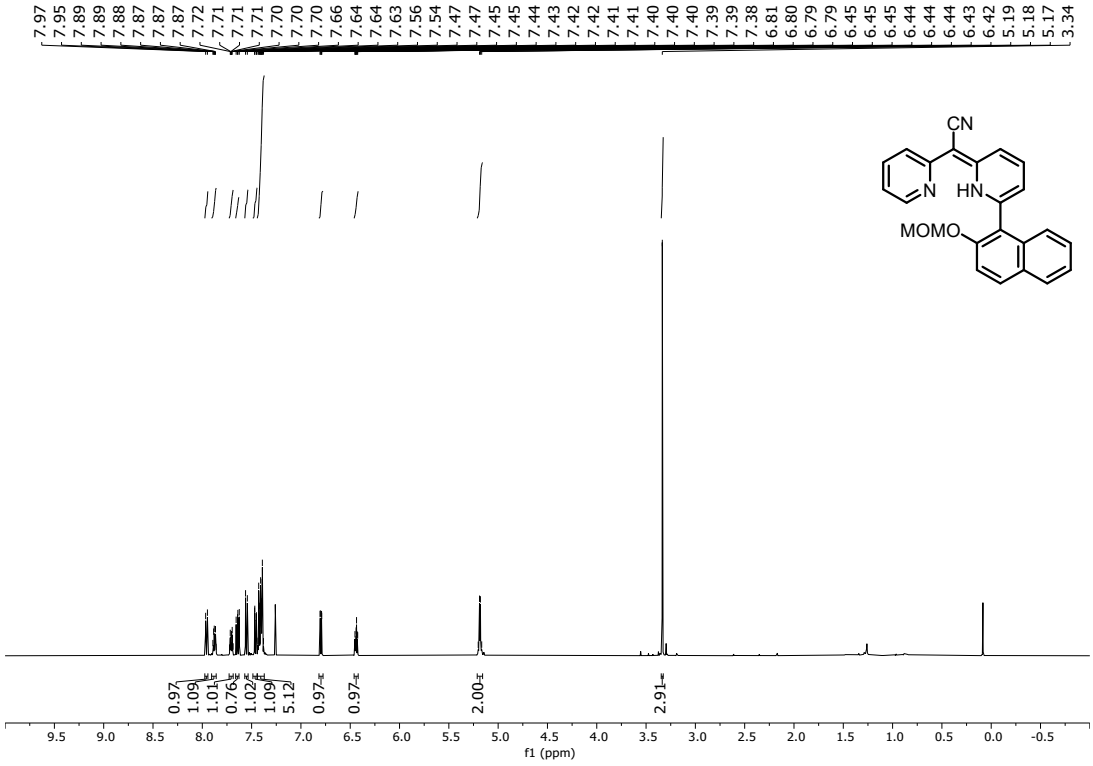
Acquisition Parameter

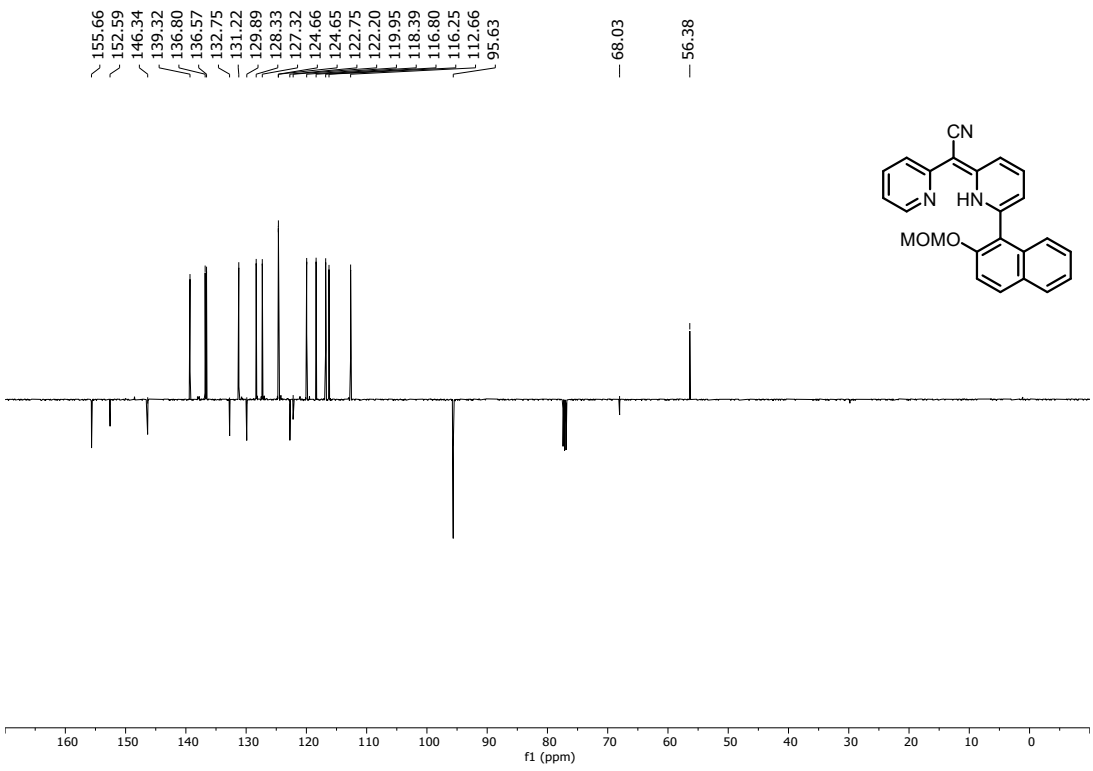
Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	48.2 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	2021.6 V



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
353.132204	1	C18H23BKO4	353.132098	0.6	0.7	7.5	ok	even	2.6	3.8	n.a.	n.a.	n.a.	n.a.

^{1}H and ^{13}C NMR spectra of **4-MOM** in $CDCl_3$





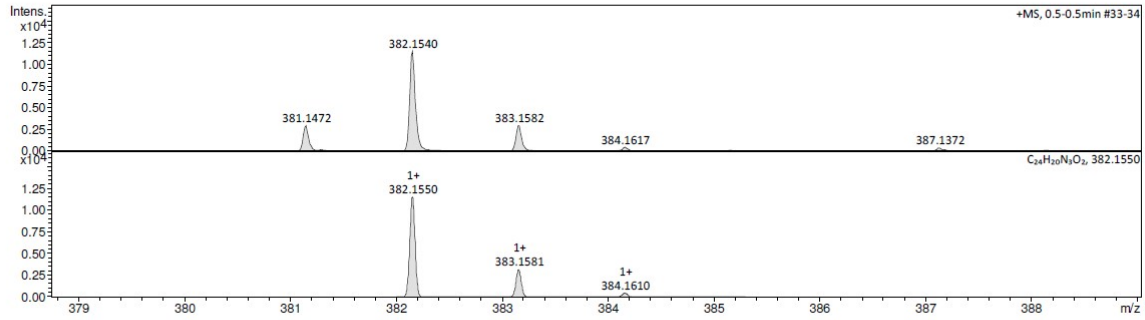
HRMS of **4-MOM**

Analysis Info

Analysis Name	Z:\Service masse 2023\11_Novembre 2023\O47201SK.d	Acquisition Date	15/11/2023 10:29:12
Method	esi low pos.m		
Sample Name	CFB-77	Operator	admin
Comment		Instrument	micrOTOF 213750.00066

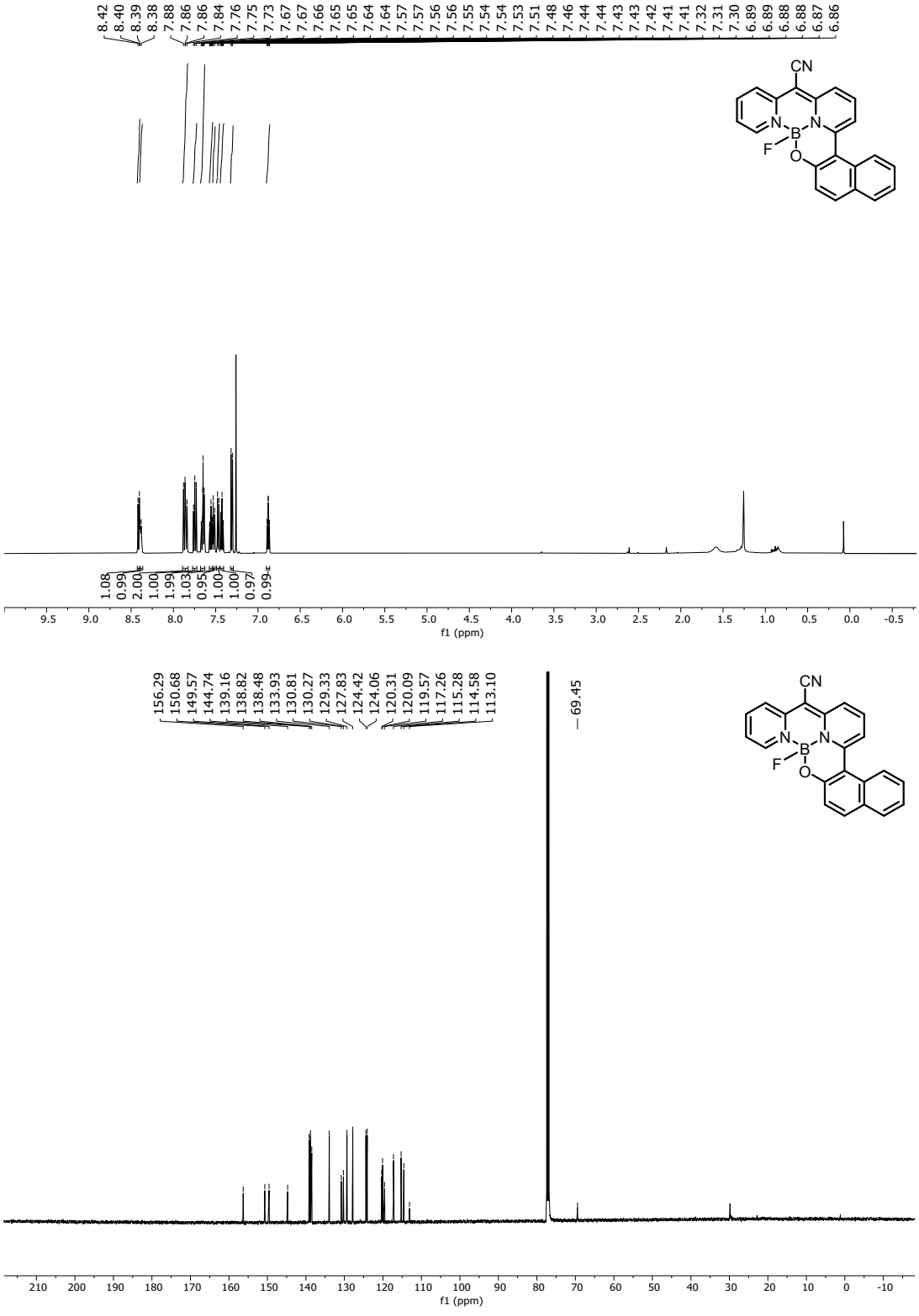
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	74 V
n/a	n/a	Set Capillary Exit	80.0 V	Set Pulsar Pull	799 V
Scan Begin	50 m/z	Set Hexapole RF	60.0 V	Set Pulsar Push	799 V
Scan End	3000 m/z	Set Skimmer 1	50.0 V	Set Reflector	1700 V
		Set Hexapole 1	24.3 V	Set Flight Tube	8600 V
				Set Detector TOF	2311 V

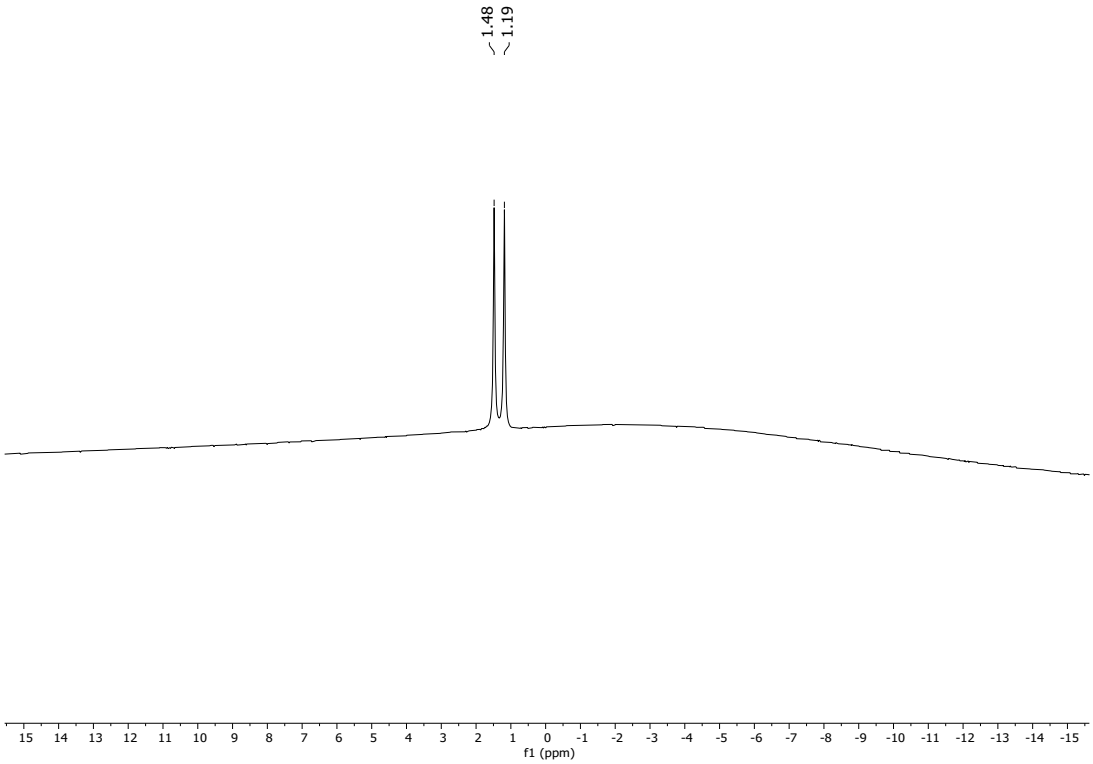


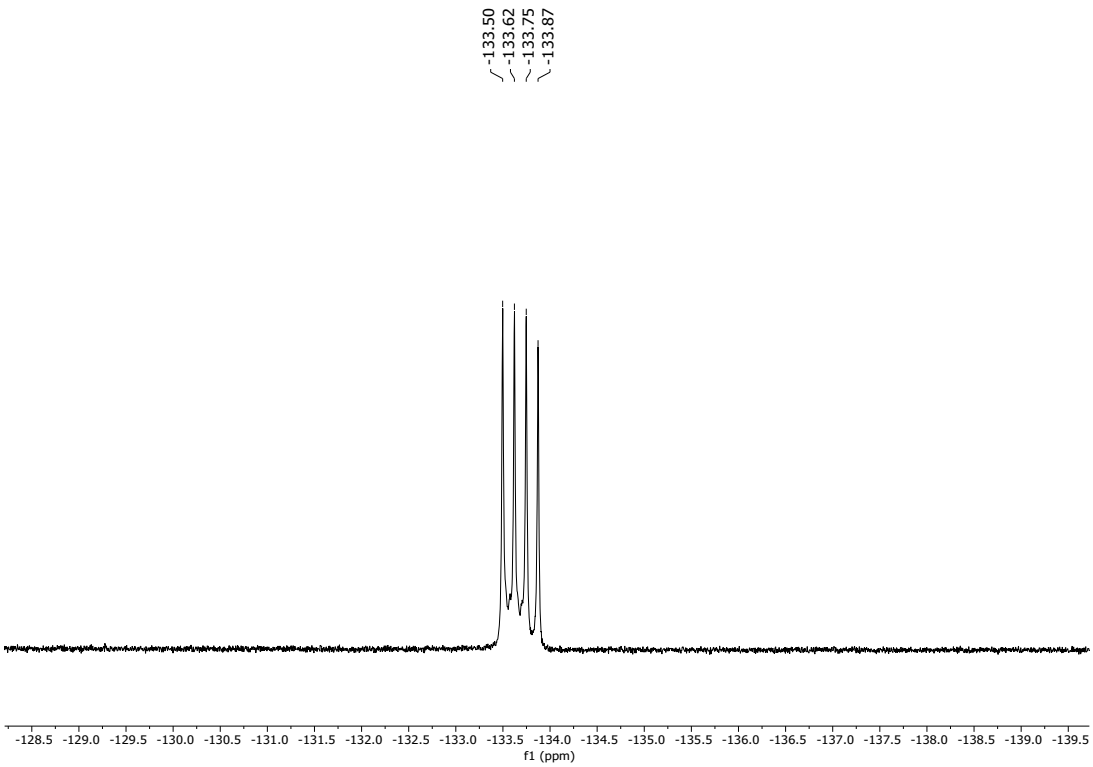
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
382.1540	1	C24H20N3O2	382.1550	2.6	9.7	1	100.00	16.5	even	ok

^{1}H and ^{13}C NMR spectra of **2b** in $CDCl_3$



^{19}F and ^{11}B NMR spectra of **2b** in $CDCl_3$





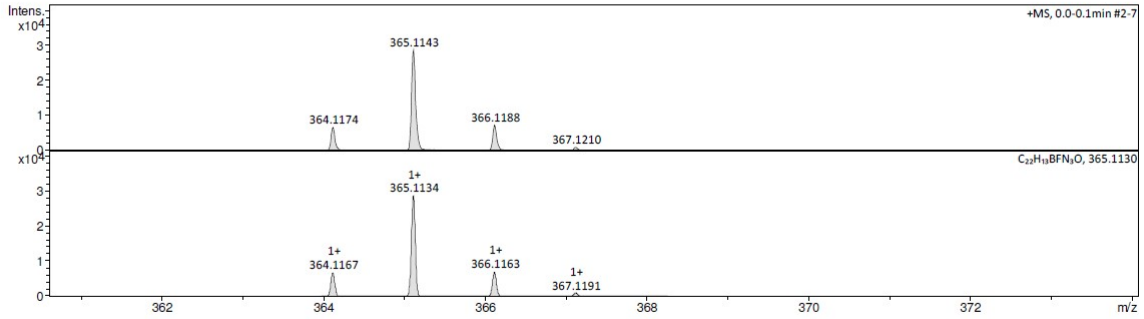
HRMS of **2b**

Analysis Info

Analysis Name	Z:\Service masse 2023\11_Novembre 2023\O47203SK.d	Acquisition Date	15/11/2023 11:15:02
Method	esi low pos.m	Operator	admin
Sample Name	CFB-85	Instrument	micrOTOF 213750.00066
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	74 V
n/a	n/a	Set Capillary Exit	80.0 V	Set Pulsar Pull	799 V
Scan Begin	50 m/z	Set Hexapole RF	60.0 V	Set Pulsar Push	799 V
Scan End	3000 m/z	Set Skimmer 1	50.0 V	Set Reflector	1700 V
		Set Hexapole 1	24.3 V	Set Flight Tube	8600 V
				Set Detector TOF	2311 V



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
365.1143	1	C22H13BFN3O	365.1130	-2.5	5.4	1	100.00	18.0	odd	ok

Analysis of the ^{1}H, ^{13}C, ^{19}F and ^{11}B spectra of **1ab**

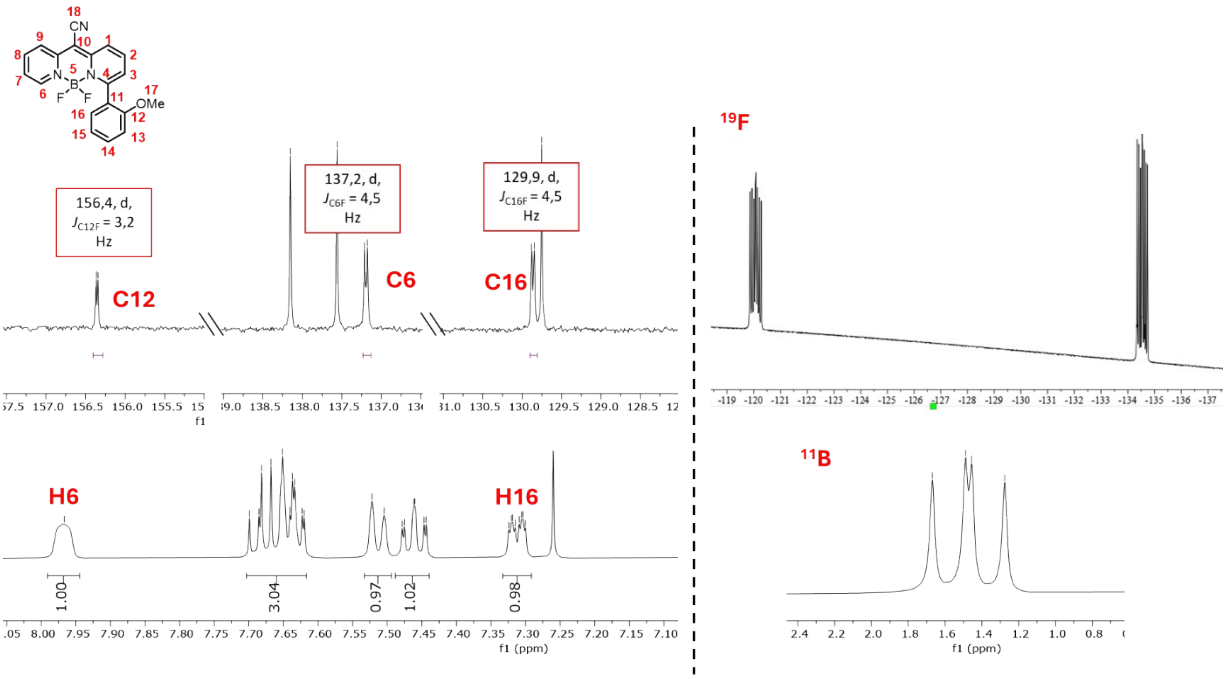


*Figure S 2. Detailed NMR spectra analysis of complexes **1a**.*

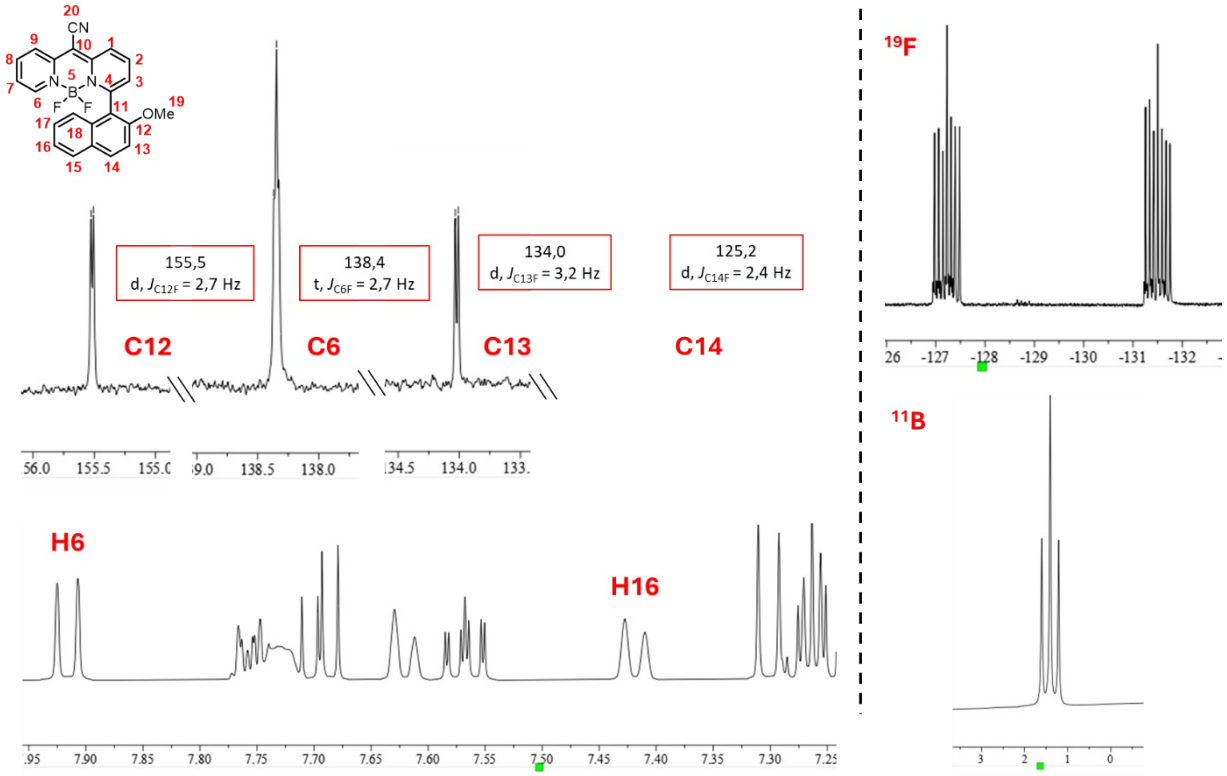
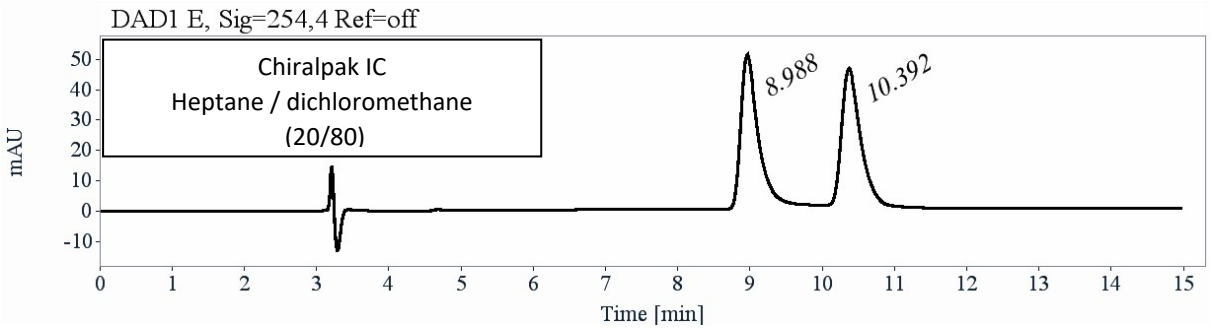


*Figure S 3. Detailed NMR spectra analysis of complexes **1c.***

Chiral HPLC separation of complexes **1ab** and **2ab**

Analytical separation for **1a**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with a UV detector at 254 nm. The flow-rate is 1 mL/min and the column is thermostated at 15°C.



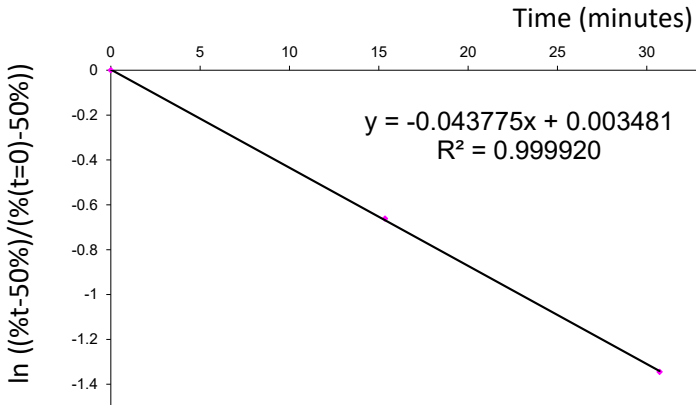
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.99	895	50.70	2.05		
10.39	870	49.30	2.52	1.23	3.17
Sum	1764	100.00			

The second eluted enantiomer was collected and its enantiomerization was followed at 25°C.

Kinetic of enantiomerization of **1a**

The second eluted enantiomer of **1a** is thermostated at 25°C in dichloromethane / heptane 8:2. 20 µL are taken and then injected on Chiralpak IC (8:2 dichloromethane / heptane, 15°C, 1 mL/min, UV 254 nm). The percentage decrease of the second eluted enantiomer of **1a** is monitored.

Time (min)	% second eluted enantiomer	ln ((%t-50%)/(%(t=0)-50%))
0	89.204	0.00000
15	70.232	-0.66151
31	60.218	-1.34463



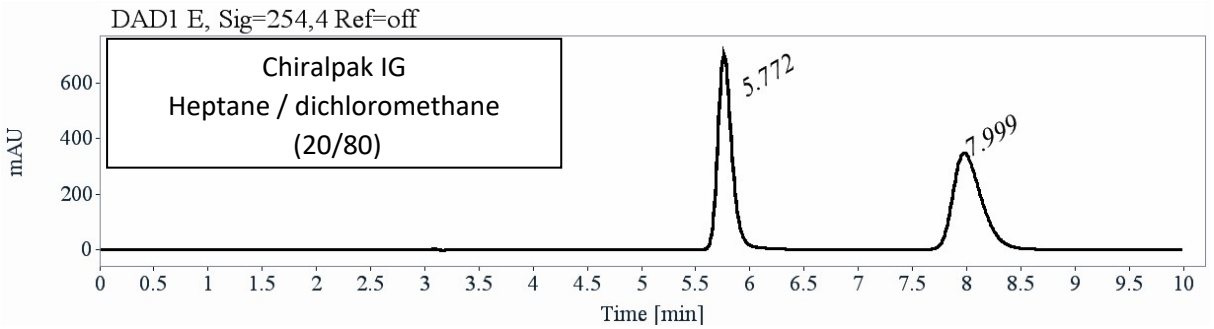
$k_{enantiomerisation}$ = 3.65 10^{-4} s^{-1} (25°C, dichloromethane / heptane 8:2)

$\Delta G^{\neq}$ = 92.7 kJ.mol^{-1} (25°C, dichloromethane / heptane 8:2)

$t_{1/2}$ = 16 minutes (25°C, dichloromethane / heptane 8:2)

Analytical chiral HPLC separation for (*rac*)-**2a**

• The sample is dissolved in a mixture of dichloromethane and heptane, injected on the chiral column, and detected with a UV detector at 254 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.77	6279	49.45	0.96		
8.00	6418	50.55	1.71	1.79	6.25
Sum	12698	100.00			

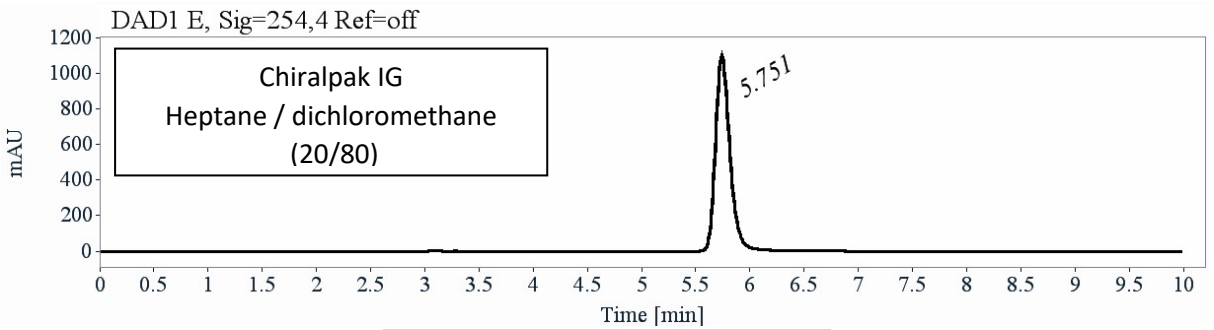
Preparative separation for (*rac*)-**2a**:

• Sample preparation: About 77 mg of compound (*rac*)-**2a** are dissolved in 20 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), hexane / dichloromethane (20/80) as mobile phase, flow-rate = 5 mL/min, UV detection at 300 nm.

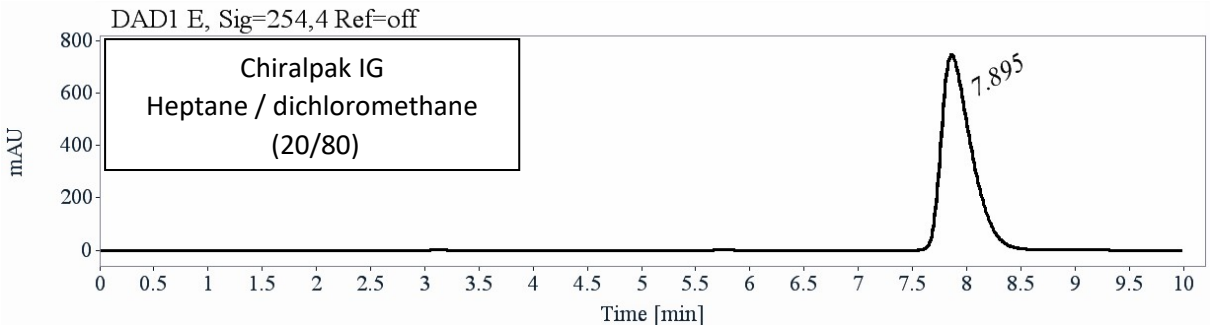
• Injections: 50 times 400 μL, every 8.2 minutes.

• First fraction: 37 mg of the first eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
5.75	10059	100.00
Sum	10059	100.00

• Second fraction: 37 mg of the second eluted enantiomer with *ee* > 99.5%



RT [min]	Area	Area%
7.89	14353	100.00
Sum	14353	100.00

λ (nm)	(*S*)-**2a** first eluted on Chiralpak IG $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c = 0.29)	(*R*)-**2a** second eluted on Chiralpak IG $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c = 0.21)
589	- 520	+ 520
578	- 590	+ 590
546	- 980	+ 980

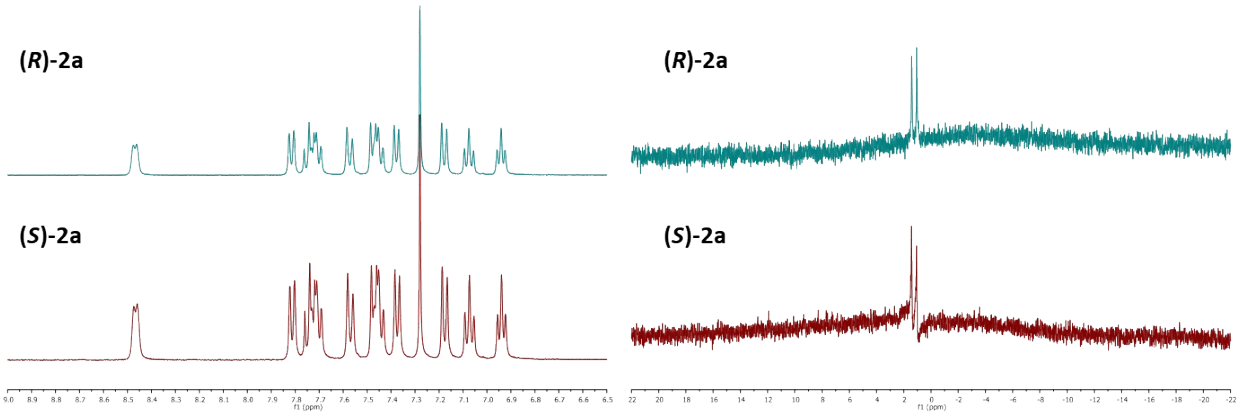
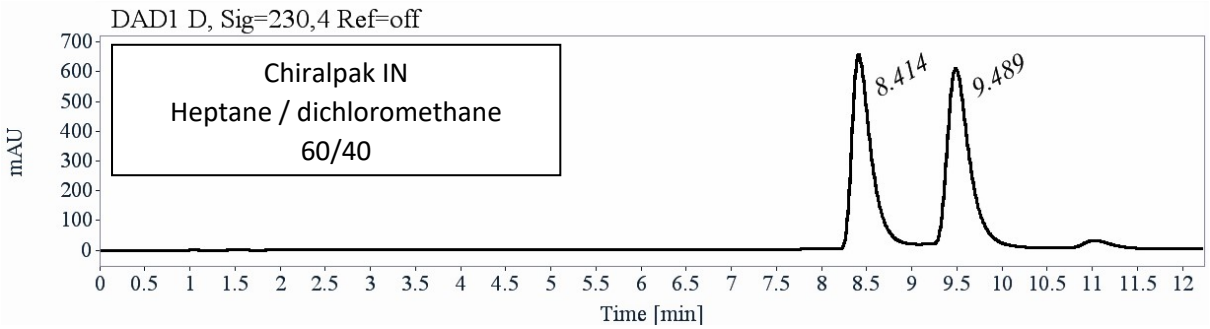
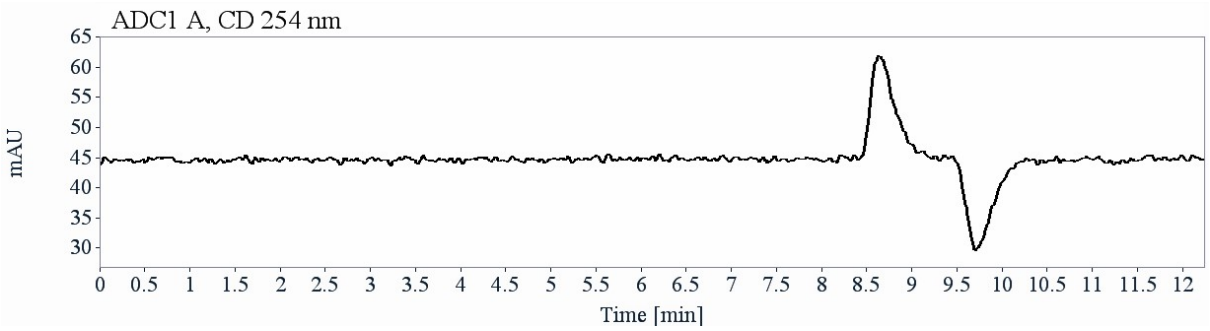


*Figure S 4. Comparison of the ^{1}H (a) and ^{11}B NMR (b) spectra of enantiomers (R)-**2a** and (S)-**2a**.*

Analytical chiral HPLC separation for (*rac*)-**1b**

• The sample is dissolved in a mixture of dichloromethane and heptane, injected on the chiral column, and detected with a UV detector at 230 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.41	9894	48.11	1.85		
9.49	10670	51.89	2.22	1.20	2.66
Sum	20563	100.00			

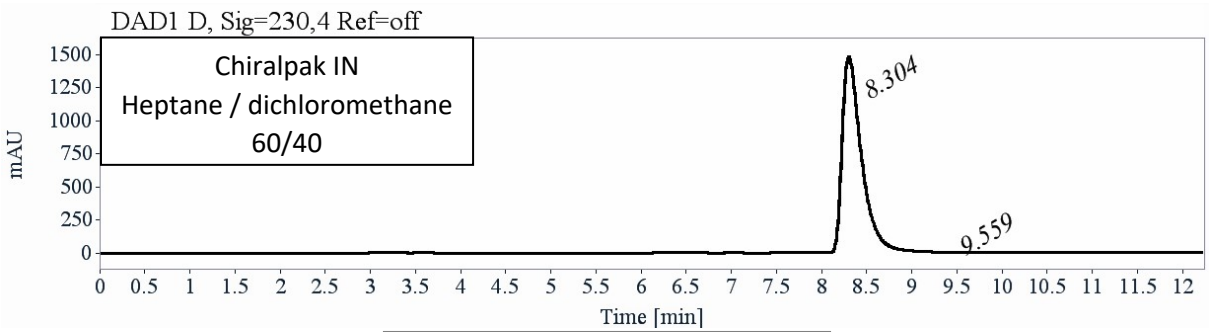
Preparative separation for compound (*rac*)-**1b**:

• Sample preparation: About 34 mg of compound (*rac*)-**1b** are dissolved in 1.9 mL of a mixture of dichloromethane and hexane (50/50).

• Chromatographic conditions: Chiralpak IN (250 x 10 mm), hexane / dichloromethane (60/40) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections: 19 times 100 µL, every 5 minutes.

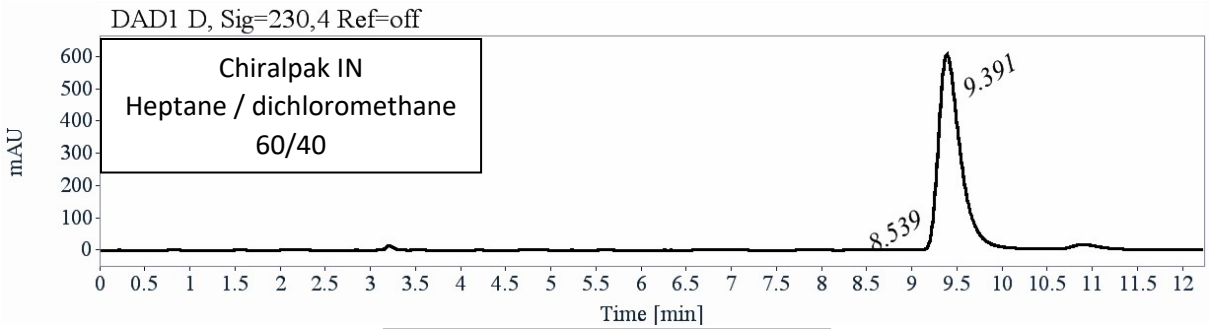
• 16 mg of the first eluted enantiomer with ee > 99 %



RT [min]	Area	Area%

8.30	22382	99.53
9.56	106	0.47
Sum	22488	100.00

• 15 mg of the second eluted enantiomer with ee > 99 %



RT [min]	Area	Area%
8.54	32	0.32
9.39	10098	99.68
Sum	10130	100.00

Optical rotations

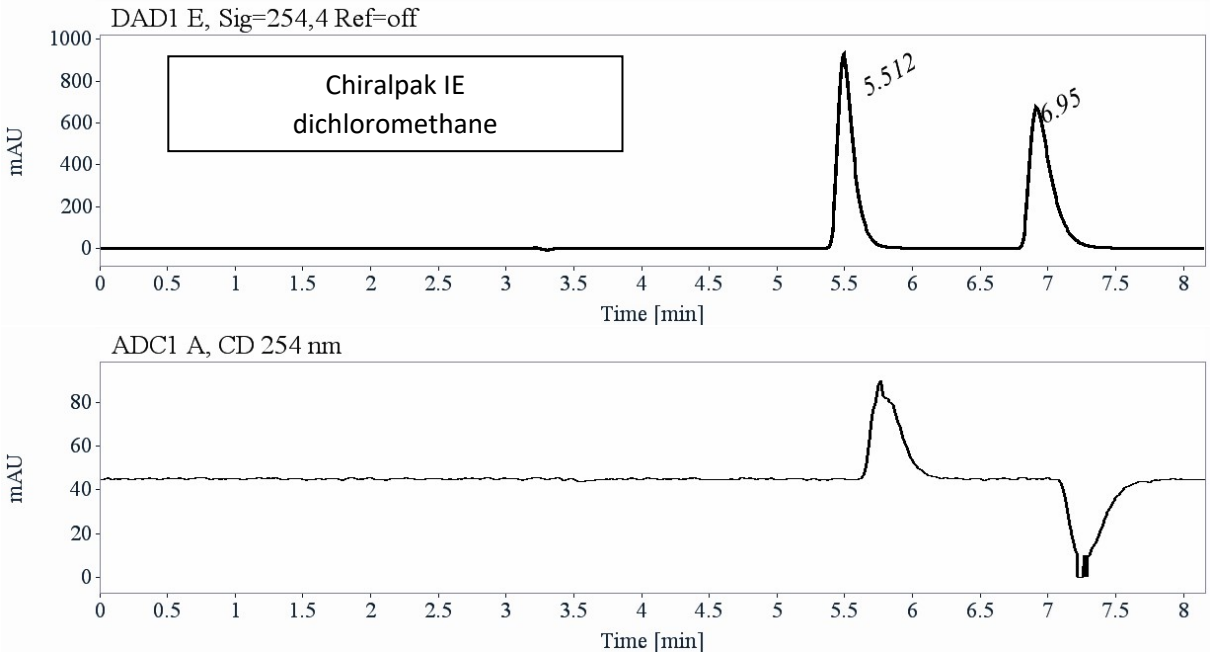
Optical rotations were measured on a Jasco P-2000 polarimeter with a halogen lamp at 589 nm, in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

For the first eluted enantiomer, (a*S*)-**1b**, $[\alpha]_D^{25}$ = - 500 (CH_2Cl_2, c = 0.10)

For the second eluted enantiomer, (a*R*)-**1b**, $[\alpha]_D^{25}$ = + 500 (CH_2Cl_2, c = 0.08)

Analytical chiral HPLC separation for (*rac*)-**2b**

• The sample is dissolved in a mixture of dichloromethane and heptane, injected on the chiral column, and detected with a UV detector at 254 nm and with a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

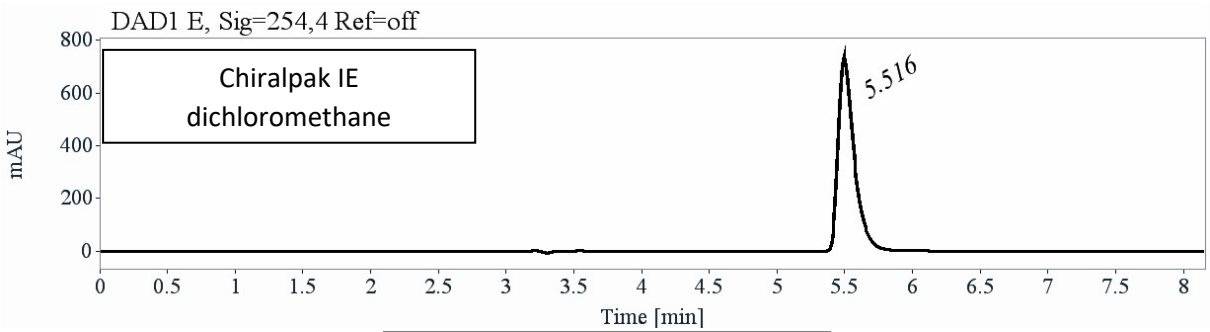


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.51	7635	49.86	0.87		
6.95	7679	50.14	1.36	1.56	5.79
Sum	15314	100.00			

Preparative separation for (*rac*)-**2b**:

• Sample preparation: About 29 mg of compound **2b** are dissolved in 5 mL of dichloromethane.
• Chromatographic conditions: Chiralpak IE (250 x 10 mm), dichloromethane as mobile phase, flow-rate = 5 mL/min, UV detection at 300 nm.
• Injections: 25 times 200 µL, every 7.8 minutes.

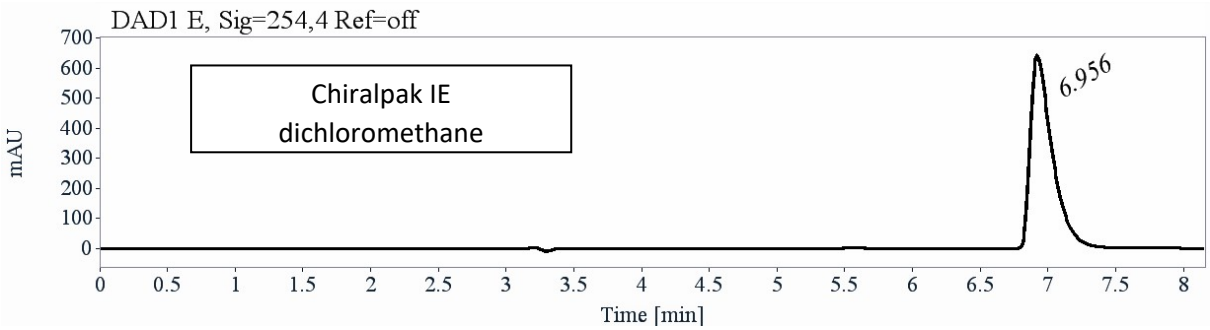
• First fraction: 11.5 mg of the first eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%

5.52	6052	100.00
Sum	6052	100.00

• Second fraction: 11.5 mg of the second eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
6.96	7288	100.00
Sum	7288	100.00

λ (nm)	(*S*)-**2b** first eluted on Chiralpak IE $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c = 0.23)	(*R*)-**2b** second eluted on Chiralpak IE $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c = 0.23)
589	+ 780	- 780
578	+ 820	- 820
546	+ 930	- 930

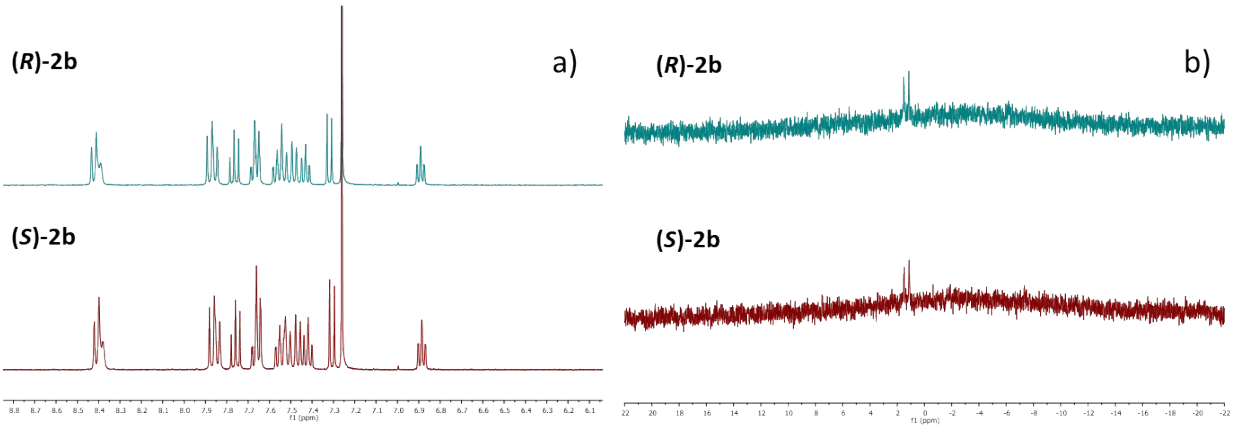


*Figure S 5. Comparison of the ^{1}H (a) and ^{11}B NMR (b) spectra of enantiomers (R)-**2b** and (S)-**2b**.*

*Table S 1. Summary of chromatographic data for enantiomers and absolute configuration of **1ab** and **2ab**.*

	Chiral stationary phase		Retention time (min)		Characterization of the 1st eluted enantiomer	
		Mobile phase	1st eluted	2nd eluted	Stereodescriptor	Specific rotation in CH_2Cl_2
2a	Chiralpak IG	Heptane / CH_2Cl_2 (2/8)	5.7	7.9	(*S*)	$[\alpha]_D^{25}$ = - 520 (c = 0.29)
1b	Chiralpak IN	Heptane / CH_2Cl_2 (6/4)	8.4	9.4	(a*S*)	$[\alpha]_D^{25}$ = - 500 (c = 0.10)
2b	Chiralpak IE	CH_2Cl_2	5.5	6.9	(*S*)	$[\alpha]_D^{25}$ = + 780 (c = 0.23)

Spectroscopic data

*Table S 2. Photophysical data of **1ab** and **2ab** (racemic mixtures) in multiple solvents at room temperature.*

	solvent	λ_{Abs} (nm)	ε_{max} ($M^{-1}\cdot cm^{-1}$)	λ_{Em} (nm)	ΔSS (cm^{-1})	ϕ_F (%)[a]	τ (ns)	k_r (s^{-1})	k_{nr} (s^{-1})	solid	
										F_{max} (nm)	ϕ_F (%)
1a	*p*-Xyl	452	2.8×10^4	516	2744	23	3.1	7.42×10^7	2.48×10^8	515	2.1 (±0.24)
	ACN	442	2.4×10^4	549	4409	5	0.9	5.26×10^7	1.00×10^9		
2a	*p*-Xyl	465	1.6×10^4	516	2126	30	5.7	5.24×10^7	1.22×10^8	551	6.3 (±0.03)
	ACN	459	1.8×10^4	530	2919	9	4.7	1.91×10^7	1.93×10^8		
1b	*p*-Xyl	454	3.1×10^4	504	2185	31	3.7	8.38×10^7	1.86×10^8	546	1.7 (±0.12)
	ACN	443	2.9×10^4	535	3881	13	3.1	4.25×10^7	2.84×10^8		
2b	*p*-Xyl	496	1.4×10^4	527	1186	32	4.3	7.29×10^7	1.55×10^8	589	0.11 (±0.02)
	ACN	479	1.4×10^4	540	2358	11	3.1	3.58×10^7	2.90×10^8		

[a] ϕ_F were calculated by using Rhodamine 6G as a reference (λ_{exc} = 488 nm, ϕ_F = 0.88 in EtOH)

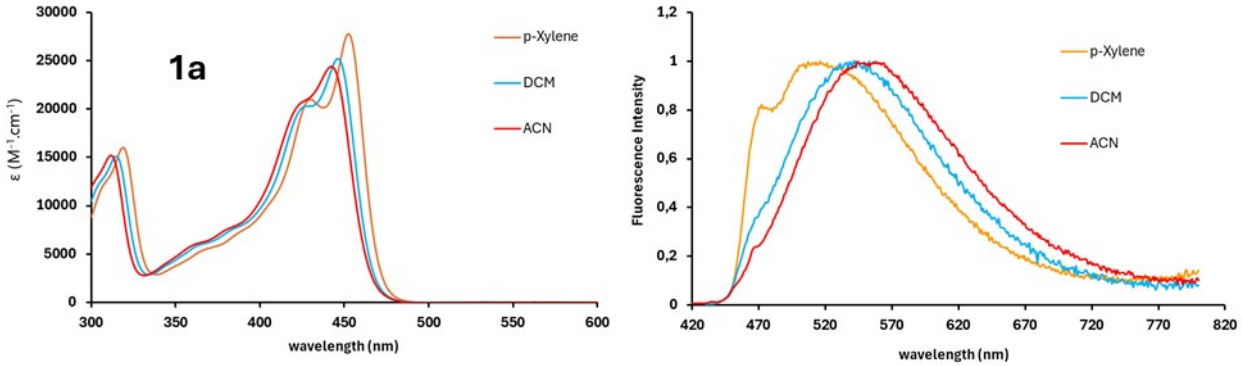


*Figure S 6. Absorption (left, conc. = x 10^{-5} M) and emission (right, λ_{exc} = 430 nm, conc. = x 10^{-6} M) spectra of dye **1a** in multiple solvents.*

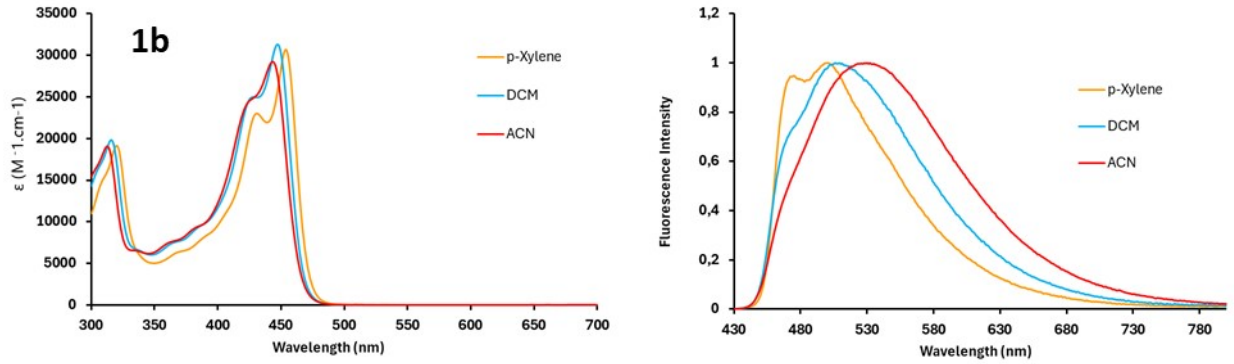


*Figure S 7. Absorption (left, conc. = x 10^{-5} M) and emission (right, λ_{exc} = 430 nm, conc. = x 10^{-6} M) spectra of dyes **1b** in multiple solvents.*

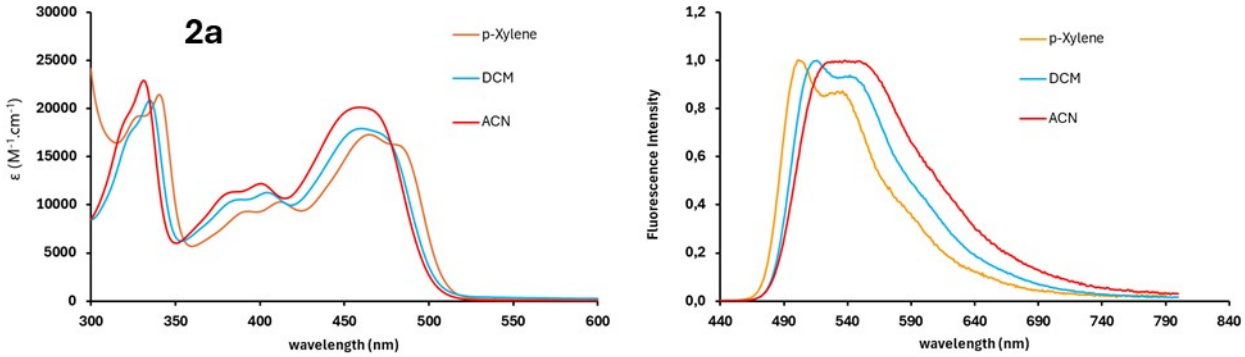


*Figure S 8. Absorption (left, conc. = x 10^{-5} M) and emission (right, λ_{exc} = 430 nm, conc. = x 10^{-6} M) spectra of dyes **2a** in multiple solvents.*

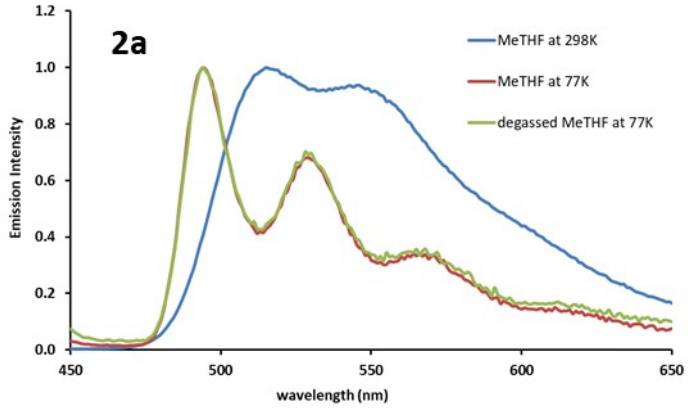


*Figure S 9. Fluorescence and phosphorescence emission (λ_{exc} = 410 nm, conc. = x 10^{-6} M) spectra of dye **2a** in MeTHF at 298K and 77K.*

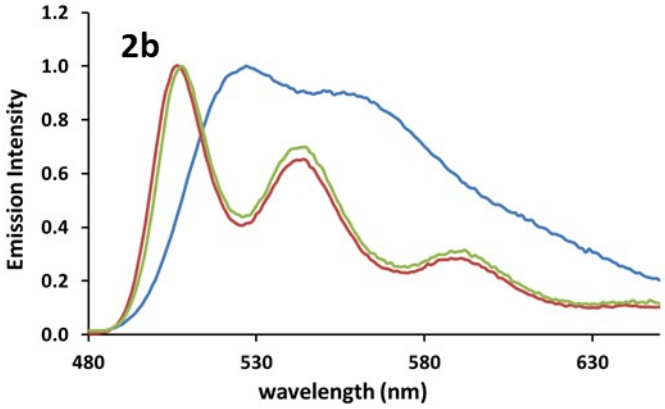


*Figure S 10. Fluorescence and phosphorescence emission (λ_{exc} = 410 nm, conc. = x 10^{-6} M) spectra of dye **2b** in MeTHF at 298k and 77K.*

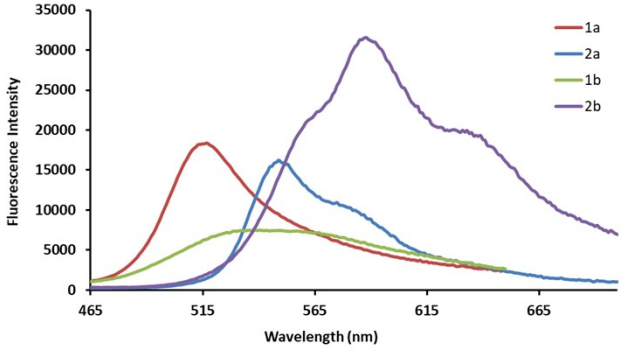


*Figure S 11. Fluorescence emission spectra in the solid state of **1ab** and **2ab**.*

*Table S 3. Photophysical data of (S)/(R)-**2a,** (S)/(R)-**1b** and (S)/(R)-**2b** in CH_2Cl_2 at room temperature.*

	λ_{Abs} (nm)	ε_{max} ($M^{-1}\cdot cm^{-1}$)	λ_{Em} (nm)	ϕ_F (%)[a]
(S)-**2a**	460	1.8×10^4	521	30
(R)-**2a**	461	2.1×10^4	519	30
(aS)-**1b**	449	2.6×10^4	507	35
(aR)-**1b**	449	2.8×10^4	507	32
(S)-**2b**	486	1.8×10^4	529	25
(R)-**2b**	486	1.9×10^4	527	23

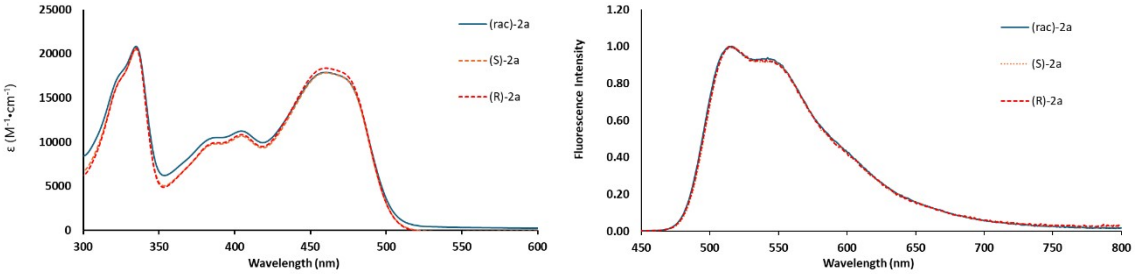


*Figure S 12. Absorption and emission spectra of (rac)-**2a**, (S)-**2a** and (R)-**2a** in CH_2Cl_2 at room temperature.*

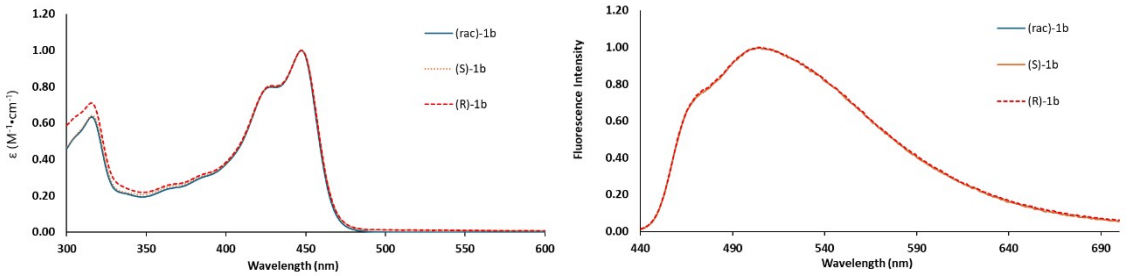


*Figure S 13. Absorption and emission spectra of (rac)-**1b**, (S)-**1b** and (R)-**1b** in CH_2Cl_2 at room temperature.*

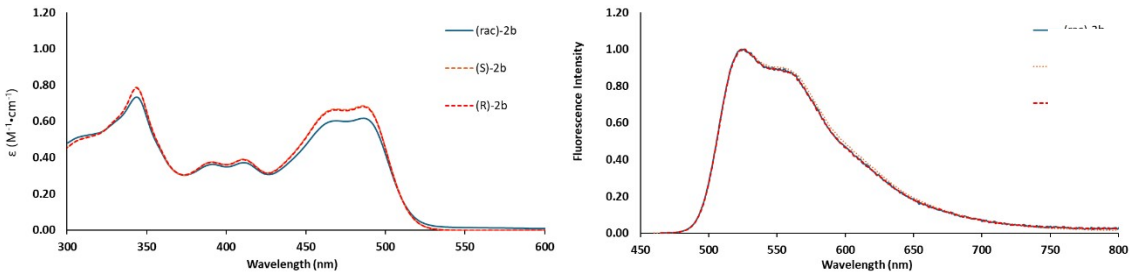


*Figure S 14. Absorption and emission spectra of (rac)-**2b**, (S)-**2b** and (R)-**2b** in CH_2Cl_2 at room temperature.*

Electronic Circular Dichroism

2a, first eluted on Chiralpak IG: green solid line, concentration = 0.440 mmol.L^{-1} in acetonitrile.
2a, second eluted on Chiralpak IG: red dotted line, concentration = 0.462 mmol.L^{-1} in acetonitrile.
Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 1 nm, and 3 accumulations per sample.

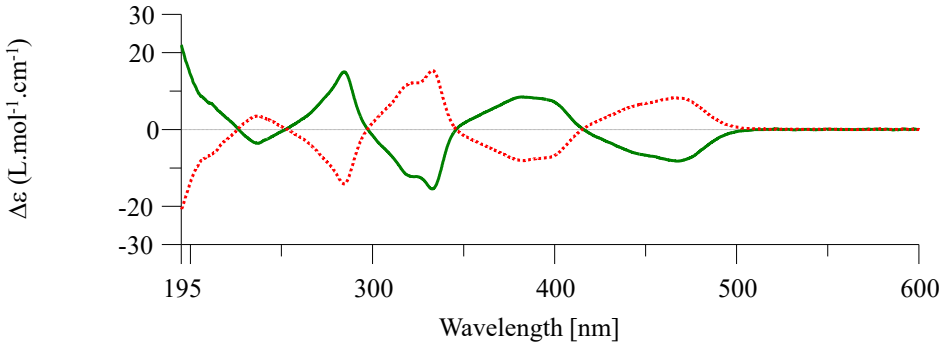


*Figure S 15. CD spectra of (S)-**2a** and (R)-**2a** in acetonitrile at room temperature.*

1b, first eluted on Chiralpak IN: green solid line, concentration = 0.228 mmol.L^{-1} in acetonitrile.
1b, second eluted on Chiralpak IN: red dotted line, concentration = 0.229 mmol.L^{-1} in acetonitrile.
Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 1 nm, and 3 accumulations per sample.

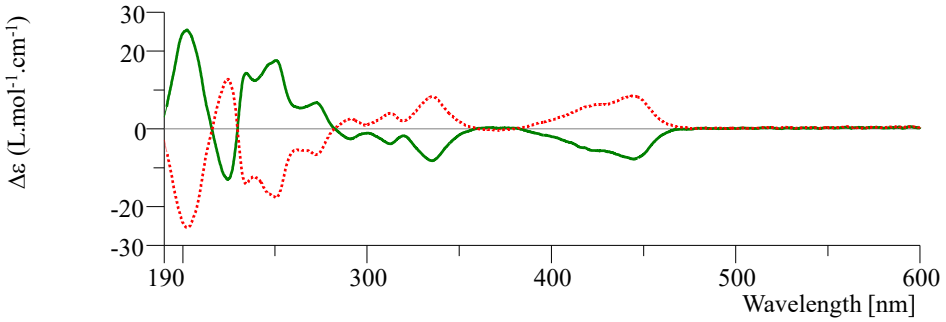


*Figure S 16. CD spectra of (S)-**1b** and (R)-**1b** in acetonitrile at room temperature.*

2b, first eluted on Chiralpak IE: green solid line, concentration = 0.321 mmol.L^{-1} in acetonitrile.
2b, second eluted on Chiralpak IE: red dotted line, concentration = 0.319 mmol.L^{-1} in acetonitrile.
Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 1 nm, and 3 accumulations per sample.

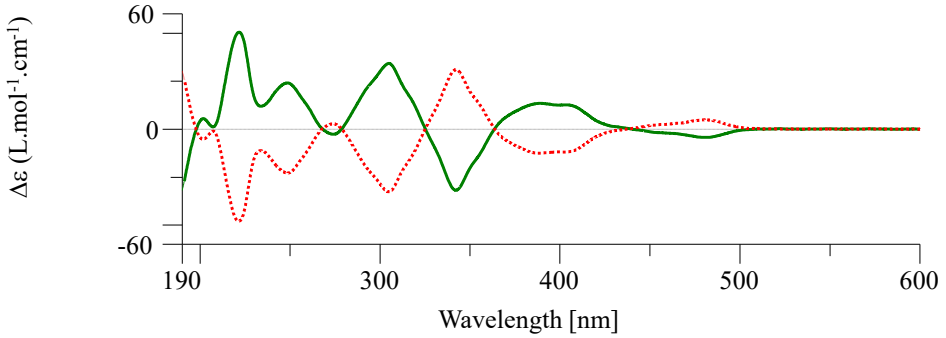


*Figure S 17. CD spectra of (S)-**2b** and (R)-**2b** in acetonitrile at room temperature.*

The ECD spectra of enantiopure samples were then measured (see SI). In the UV/vis region, enantiomer *(S)*-**2a** displays two positive bands at 284 ($\Delta\varepsilon$ = +15 M^{-1} cm^{-1}) and 382 nm ($\Delta\varepsilon$ = +8.4 M^{-1} cm^{-1}) and three negative bands, one small at 237 nm ($\Delta\varepsilon$ = -14 M^{-1} cm^{-1}), one large at 333 nm ($\Delta\varepsilon$ = -15.5 M^{-1} cm^{-1}) and one moderate at 468 nm ($\Delta\varepsilon$ = -8.3 M^{-1} cm^{-1}). Regarding *(αS)*-**1b**, the ECD spectrum features four weak negative bands at 291 ($\Delta\varepsilon$ = -2.7 M^{-1} cm^{-1}), 313 ($\Delta\varepsilon$ = -3.9 M^{-1} cm^{-1}), 336 ($\Delta\varepsilon$ = -8.3 M^{-1} cm^{-1}) and 445 nm ($\Delta\varepsilon$ = -7.8 M^{-1} cm^{-1}). Lastly, *(S)*-**2b** shows two large bands in the UV/vis region, one positive at 305 nm ($\Delta\varepsilon$ = +34.2 M^{-1} cm^{-1}) and one negative at 342 nm ($\Delta\varepsilon$ = -31.9 M^{-1} cm^{-1}) accompanied by one positive at 389 nm ($\Delta\varepsilon$ = 13.4 M^{-1} cm^{-1}) and one negative shoulder at 482 nm ($\Delta\varepsilon$ = -4.4 M^{-1} cm^{-1}).

Circularly Polarized Luminescence

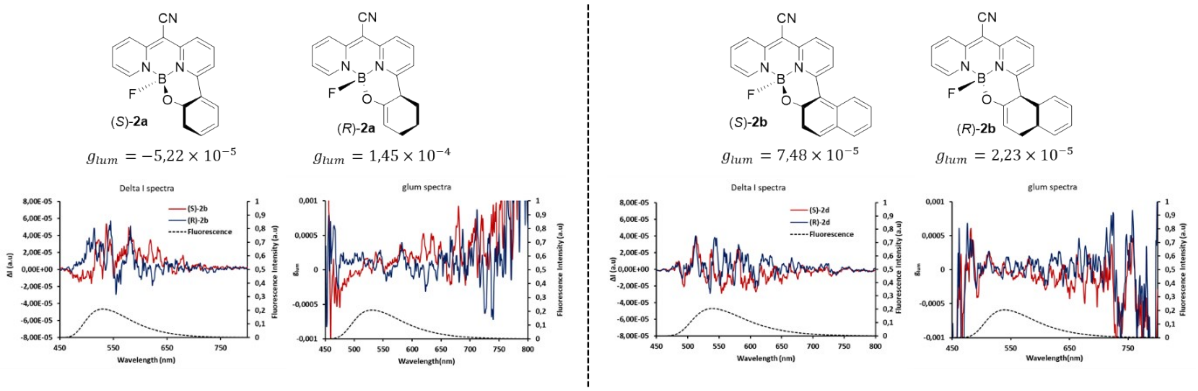


*Figure S 18. Unpolarized and circularly polarized fluorescence spectra in CH_2Cl_2 at room temperature of complexes (S)/(R)-**2a** and (S)/(R)-**2b**.*

Crystallographic data collection

Single crystals of **1a**, and **2b** suitable for X-ray diffraction analysis were obtained in saturated solutions of each compound dissolved in chloroform and dichloromethane, respectively. High resolution crystallographic data were recorded for **1a** using a Rigaku *XtaLabPro* single-crystal diffractometer equipped with a microfocus Mo K*α* radiation source and a HPAD PILATUS3 R 200K detector. *CrysAlisPro* [1] was used for the processing of these data recorded at room temperature from multiple ω scans. An absorption correction was applied, combining both empirical using spherical harmonics, implemented in the *SCALE3 ABSPACK* scaling algorithm, and a numerical approach based on Gaussian integration over a multifaceted crystal model. The second crystal, **2b**, was also measured at room temperature but a rotating mm007HF anode delivering copper Ka (λ= 1.54187 Å) radiation through an Osmic CMF optic and equipped with a Rapid II curved Image Plate detector. The data reduction process, which included a multi-scan absorption correction, was done using the *Fs_process/Abscor* [2,3] program, as implemented into the *CrystalClear 2.0* software suite.[4] Their respective structures were readily solved by intrinsic phasing methods (*SHELXT*) [5] and then refined by full-matrix least-squares methods on F^2 using *SHELXL*. [6] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms, all identified in difference Fourier maps, were first geometrically positioned and refined using a riding model with U_{iso} set to xU_{eq} of the parent atom (x= 1.2 for the aromatic ones and 1.5 for the methyl carbon in **1a**). In both cases, owing to the high resolution limit of the **1a** dataset and to the use of copper energy for **2b**, structure refinement was achieved through Hirshfeld atom refinement (HAR) [7] using aspherical scattering factors via *NoSpherA2* [8] partitioning in *Olex2*.[9] This was based on electron density obtained from iterative single-determinant SCF single-point DFT calculations using *ORCA* [10] at the *B3LYP*/def2-SVP or def2-TZVP (resp.) level of theory. The *NoSpherA2* software read any of these wavefunctions and the related electron-density was partitioned into Hirshfeld atoms. The Fourier transforms of these atoms are the non-spherical scattering factors, which were then tabulated in a .tsc file and provided to *olex2.refine* [11] for the L-M refinement. In this HAR approach, all hydrogen atoms were refined independently and anisotropically, (except one aromatic hydrogen that was kept isotropic in **2b**) providing better descriptions of their positions, and therefore more precise hydrogen-bond length and, in fine, better model statistics, as summarized in *Table S4*.

Crystallographic data for the two X-ray structures have been deposited in the Cambridge Crystallographic Data Centre database (deposition number CCDC 2247239-2473850 for **1a**, and **2b** respectively). Copies of the data can be obtained free of charge from the CCDC at www.ccdc.cam.ac.uk.

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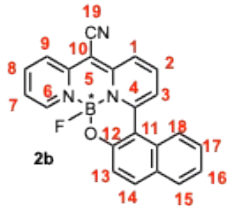
*Table S 4. Crystal data and structure refinement for **1a**, and **2b**.*

Identification code		**1a**	**2b**
2D scheme			
Empirical formula		$C_{19}H_{14}BF_2N_3O$	$C_{22}H_{13}BFN_3O$
Formula weight		349.164	365.191
Temperature	K	293 (2)	293 (2)
Diffractometer, Wavelength	Å	*Rigaku* XtaLabPro μ-Source MM003, Pilatus3 R 200K 0.71073	*Rigaku* Spider rotating anode MM007HF, Rapid 2 IP 1.54187
Crystal system, Space group		Monoclinic, P $2_1/c$	Triclinic, P -1
Unit cell dimensions	a |Å b |Å c |Å α | ° β | ° γ | °	 11.1316(4) 18.2559(6) 8.0791(3) 90 99.445(4) 90	 7.5432(4) 8.0975(5) 14.2914(10) 95.850(7) 95.816(7) 103.652(7)
Volume	Å^3	1619.56(10)	836.72(10)
Z, Z' Calculated density	Mg/m^3	4, 1 1.432	2, 1 1.449
Absorption coefficient	mm^{-1}	0.106	0.800
F(000)		720	376
Crystal size	mm	0.22 x 0.17 x 0.09	0.37 x 0.30 x 0.21
θ range for data collection	°	2.79 to 27.87	5.67 to 68.21
Limiting indices		-15 ≤ h ≤ 15, -25 ≤ k ≤ 25, -11 ≤ l ≤ 11	-9 ≤ h ≤ 9, -7 ≤ k ≤ 9, -17 ≤ l ≤ 17
Refl. collected / unique R(int)		49352 / 3868 0.035	10478 / 2981 0.0547
Completeness to θ_{full}	%	99.9 (θ_{full}=25.2°)	96.8 (θ_{full}=67.7°)
Absorption correction		Gaussian & Multi-scan	Multi-scan
Max. and min. transmission		1.000 and 0.534	1.000 and 0.846
Refinement method		HAR least squares	
Data / restraints / parameters		3868 / 0 / 361	2968 / 0 / 364
Goodness-of-fit on F^2		1.078	0.9641

Final R indices [$I>2\sigma(I)$]	R1, wR2	0.0196, 0.0382	0.0451, 0.095
R indices (all data)	R1, wR2	0.0291, 0.0411	0.0711, 0.116
Largest Δ peak and hole	e.Å^{-3}	0.141 and -0.144	0.287 and -0.289
CCDC deposit number		2247239	2473850

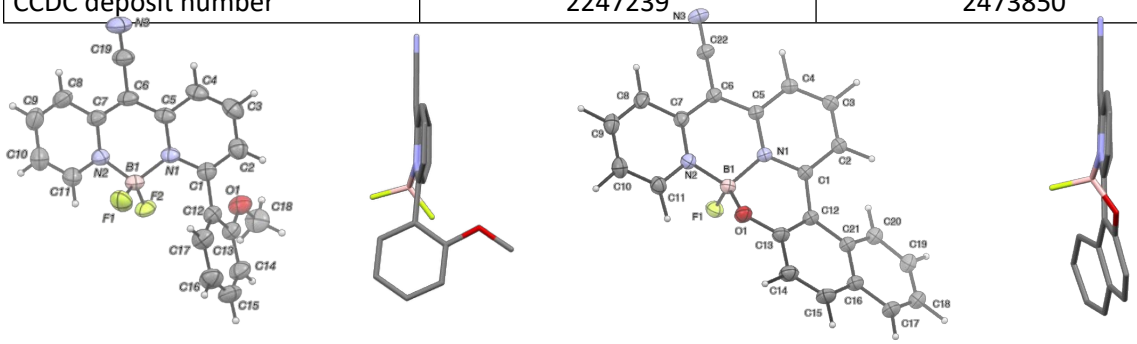


*Figure S 19. Ortep views of the molecular structure of **1a** (left) and **2b** (right), with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Adjacent to these are side views in capped stick representation.*

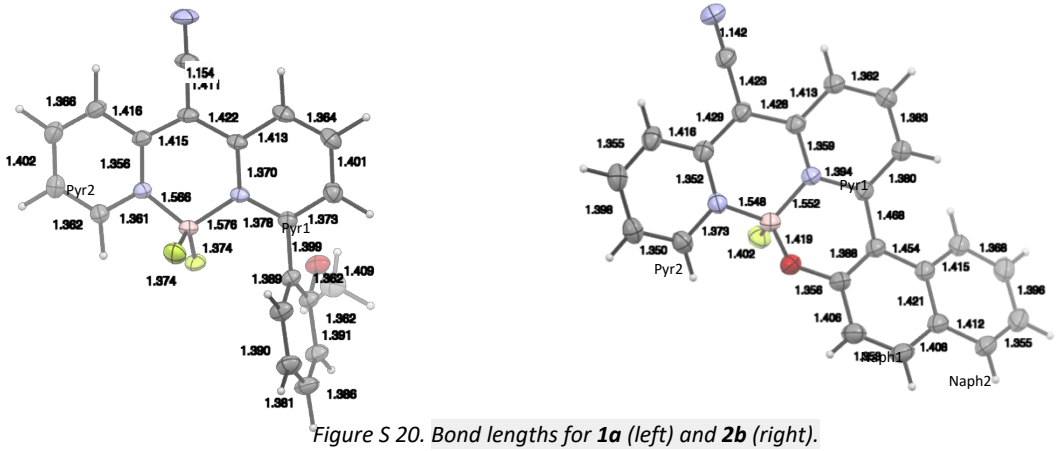


*Figure S 20. Bond lengths for **1a** (left) and **2b** (right).*

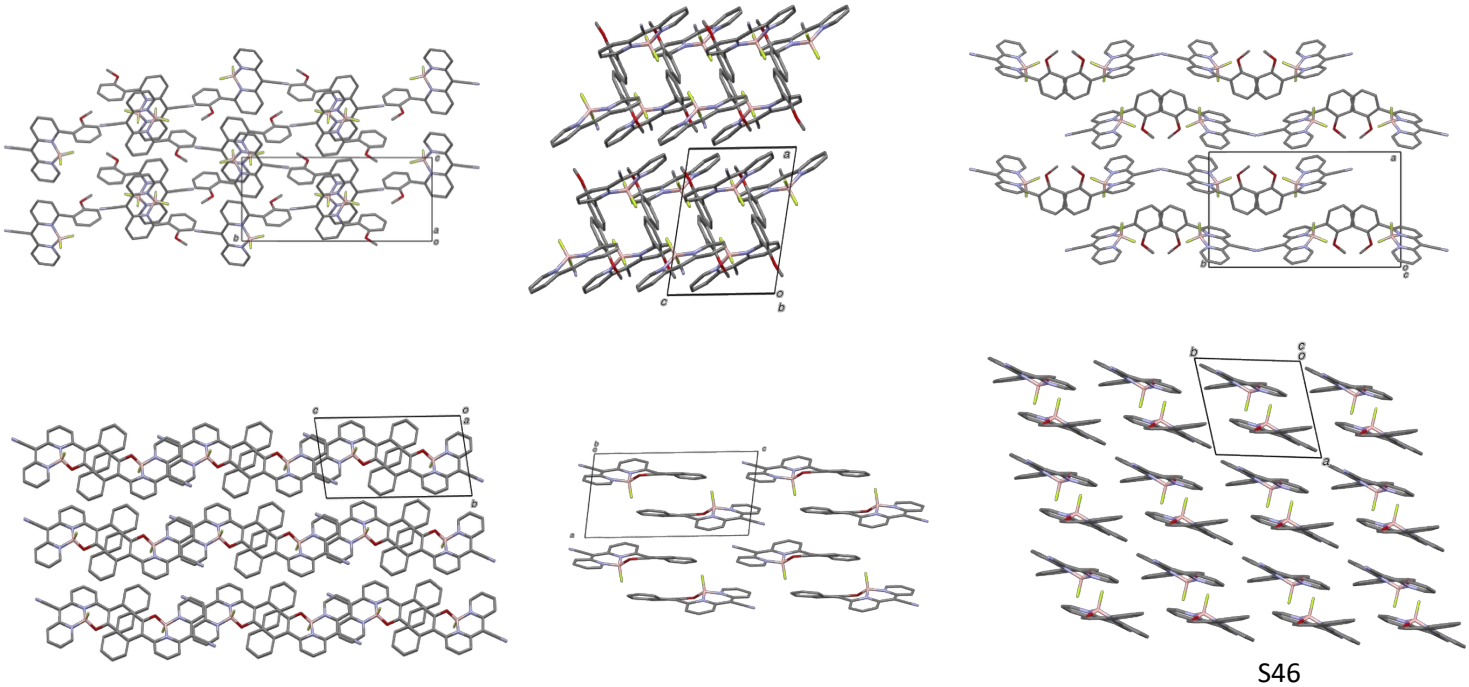
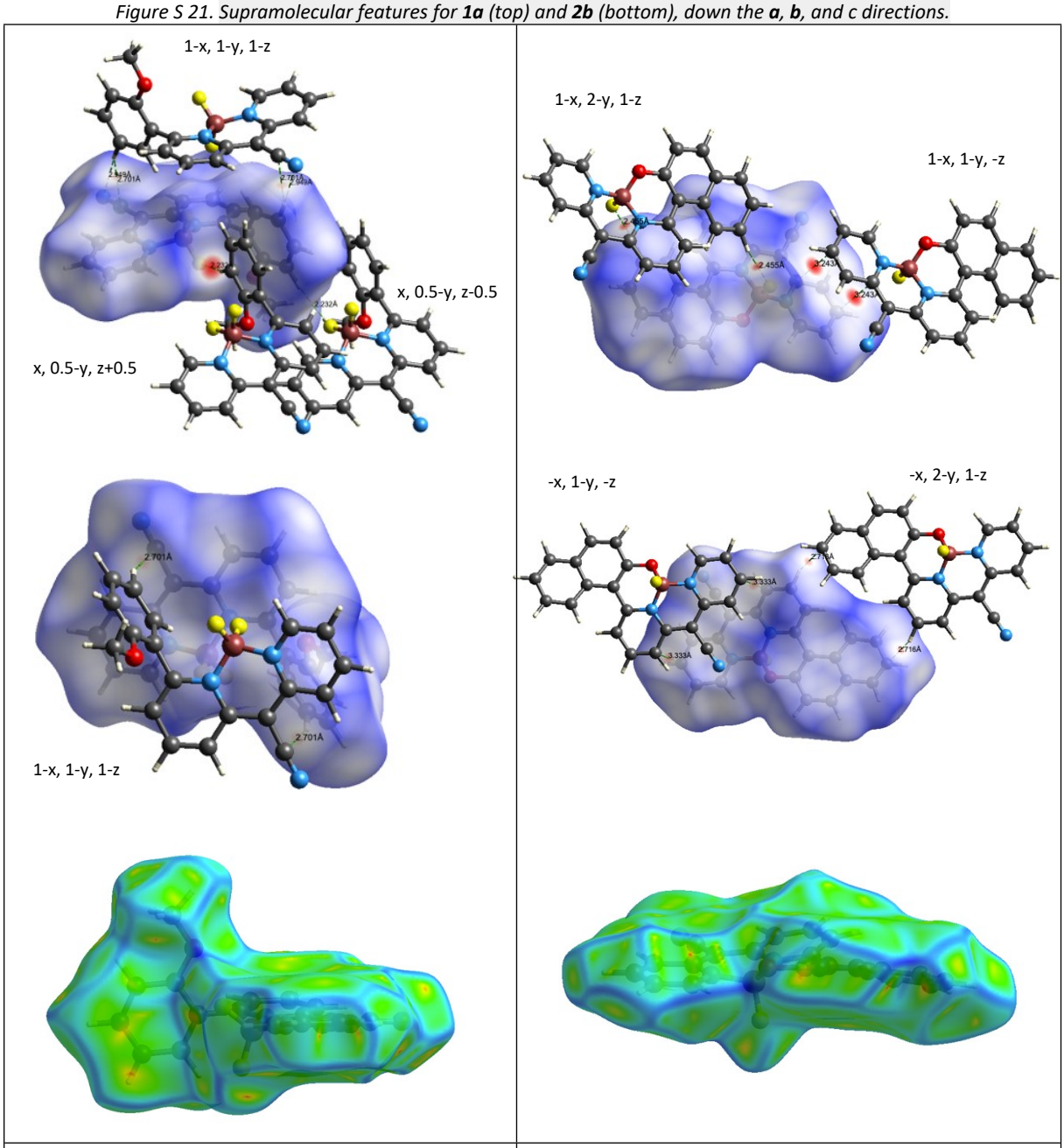


*Figure S 21. Supramolecular features for **1a** (top) and **2b** (bottom), down the **a**, **b**, and c directions.*



1a	**2b**
Volume = 397.9Å^3 Surface = 352.7Å^2 Globularity = 0.742 Asphericity = 0.110	Volume = 411.3Å^3 Surface = 359.3Å^2 Globularity = 0.745 Asphericity = 0.225

*Figure S 22. Hirshfeld surfaces for **1a** and **2b** mapped over d_{norm} in the colour range -0.2498 to 1.2274 a.u. (-0.0918 to 1.2841a.u., respectively) highlighting the short contacts (red spots), and curvedness (bottom).*

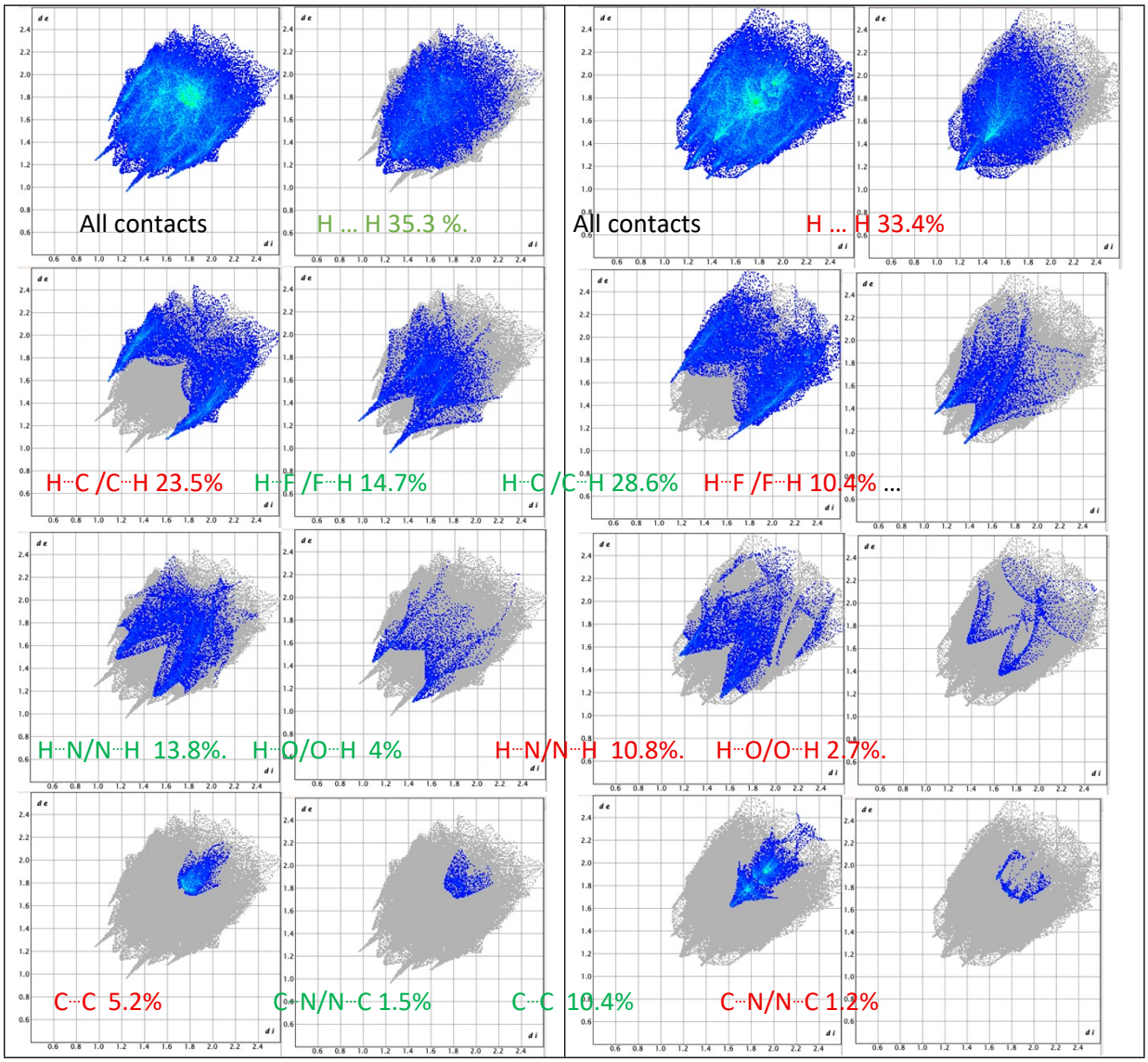
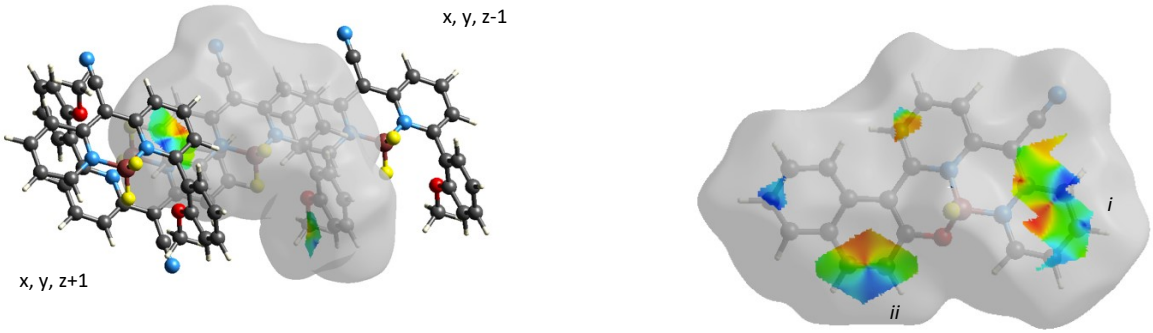


*Figure S 23. The full two-dimensional fingerprint plots for **1a** (left) and **2b** (right) and those delineated into the main contacts: H···H, C···H/H···C, F···H/H···F, N···H/H···N, O···H/H···O, C···C, and N···C/C···N, contacts. The colour of the mention (green vs red) highlights that the corresponding interaction is more significant for the related crystal packing than the other one.*



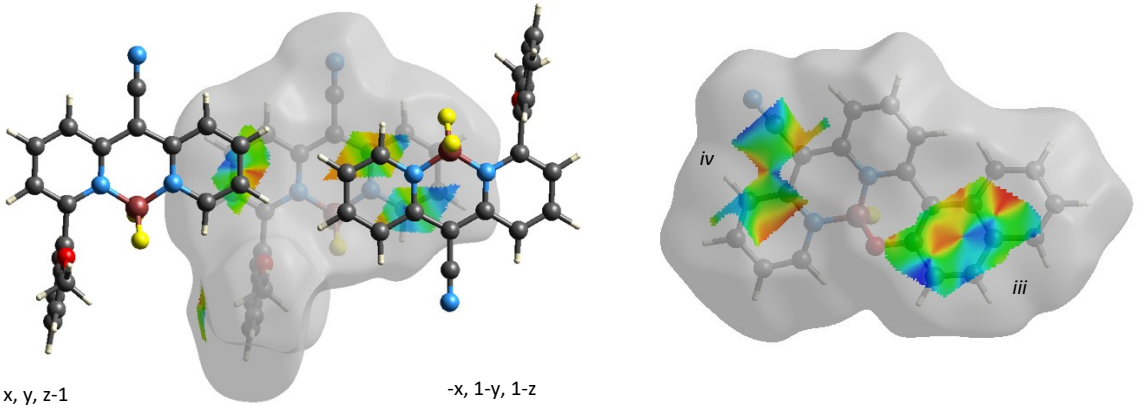


Figure S 24. 180°-rotated views of the Hirshfeld surface plotted over shape index to highlight the short π–π ring-interactions with Cg-Cg Distances < 6.0 Å and β < 60.0°. [12]

- Cg(I) = Plane number I (= ring number in () above)
- Cg-Cg = Distance between ring Centroids (Å)
- Alpha = Dihedral Angle between Planes I and J (°)
- Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (°)
- Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (°)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Å)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Å)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Å).
- P,Q,R,S = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

	Cg(I) Res(I) Cg(J) [ARU(J)]	Cg-Cg	Transformed J-Plane P, Q, R, S	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp	Slippage
1a	Cg(pyr1) -> Cg(pyr1) [-X,1-Y,1-Z]	3.5573(4)	-0.7076-0.2266-0.6693	-2.5268	0.02(3)	12.1 12.1	-3.4785(3)	-3.4785(3)	0.745
	Cg(pyr2) -> Cg(pyr1) [X, Y, Z-1]	4.2381(4)	0.7076 0.2266 0.6693	1.6097	15.38(3)	43.1 28.0	3.7408(3)	-3.0952(3)	
	Cg(pyr1) -> Cg(pyr2) [X, Y, Z+1]	4.2380(4)	0.8556 0.2584 0.4485	8.2730	15.38(3)	28.0 43.1	-3.0951(3)	3.7408(3)	
2b ***i***	Cg(pyr2) -> Cg(pyr2) [1-X,1-Y,-Z]	3.5276(12)	-0.8686-0.4954-0.0119	-6.0156	0.00(10)	23.3 23.3	3.2410(9)	3.2410(9)	1.393
ii	Cg(naph1)-> Cg(naph1) [1-X,1-Y,1-Z]	4.0226(12)	-0.9676-0.2232-0.1177	-5.3356	0.03(10)	25.9 25.9	3.6200(9)	3.6201(9)	1.754
	Cg(naph1)-> Cg(naph2) [1-X,1-Y,1-Z]	5.0520(13)	-0.9936-0.0937-0.0625	-4.8342	8.21(10)	47.2 38.9	3.9292(9)	3.4357(9)	
	Cg(naph2)-> Cg(naph1) [1-X,1-Y,1-Z]	5.0520(13)	-0.9676-0.2232-0.1177	-5.3356	8.21(10)	38.9 47.2	3.4357(9)	3.9292(9)	
iii	Cg(naph1)-> Cg(naph1) [-X,1-Y,1-Z]	3.8696(12)	-0.9676-0.2232-0.1177	1.9635	0.03(10)	18.1 18.1	-3.6791(9)	-3.6790(9)	1.199
	Cg(naph1)-> Cg(naph2) [-X,1-Y,1-Z]	4.2676(13)	-0.9936-0.0937-0.0625	2.6610	8.21(10)	25.1 33.3	-3.5660(9)	-3.8635(9)	
	Cg(naph2)-> Cg(naph1) [-X,1-Y,1-Z]	4.2675(13)	-0.9676-0.2232-0.1177	1.9635	8.21(10)	33.3 25.1	-3.8634(9)	-3.5659(9)	
	Cg(naph2)-> Cg(naph2) [-X,1-Y,1-Z]	5.7826(14)	-0.9936-0.0937-0.0625	2.6610	0.00(11)	53.6 53.6	-3.4288(9)	-3.4288(9)	4.656
	Cg(pyr1) -> Cg(naph1) [-X,1-Y,1-Z]	5.9723(12)	-0.9676-0.2232-0.1177	1.9635	25.91(10)	53.2 60.4	-2.9493(8)	-3.5816(8)	
iv	Cg(pyr1) -> Cg(pyr2) [-X,1-Y,-Z]	4.8917(12)	-0.8686-0.4954-0.0119	0.5361	12.77(10)	47.2 53.9	-2.8789(8)	-3.3206(9)	
	Cg(pyr2) -> Cg(pyr1) [-X,1-Y,-Z]	4.8918(12)	-0.7663-0.6211-0.1644	0.2744	12.77(10)	53.9 47.2	-3.3206(9)	-2.8789(8)	
	Cg(pyr2) -> Cg(pyr2) [-X,1-Y,-Z]	5.7069(13)	-0.8686-0.4954-0.0119	0.5361	0.00(10)	54.5 54.5	-3.3108(9)	-3.3107(9)	4.648

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane) 8.8770 (0.0013) x + 3.6605 (0.0054) y + 3.4780 (0.0012) z = 5.2679 (0.0028) * 0.0644 (0.0010) C1 * -0.1514 (0.0011) C2 * -0.2205 (0.0012) C3 * -0.0951 (0.0011) C4 * 0.1759 (0.0009) N1 * 0.0942 (0.0011) C5 * 0.1598 (0.0010) N2 * 0.1561 (0.0011) C6 * 0.1050 (0.0011) C7 * -0.0575 (0.0012) C8 * -0.2034 (0.0013) C9 * -0.1644 (0.0012) C10 * 0.0263 (0.0011) C11 * 0.1106 (0.0010) C19 0.4766 (0.0016) B1 Rms deviation of fitted atoms = 0.1389	Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane) 6.3439 (0.0020) x + 2.5673 (0.0040) y - 0.7050 (0.0088) z = 2.9052 (0.0018) * 0.1705 (0.0021) N1 * 0.0347 (0.0023) C1 * -0.1782 (0.0025) C2 * -0.1674 (0.0027) C3 * -0.0186 (0.0027) C4 * 0.1015 (0.0025) C5 * 0.1178 (0.0025) C6 * 0.0488 (0.0025) C7 * -0.0985 (0.0029) C8 * -0.1664 (0.0027) C9 * -0.0940 (0.0025) C10 * 0.0436 (0.0025) C11 * 0.1224 (0.0021) N2 * 0.0838 (0.0023) C22 0.4526 (0.0038) B1 Rms deviation of fitted atoms = 0.1156
6.2777 (0.0037) x + 3.0157 (0.0104) y - 7.1960 (0.0016) z = 2.0163 (0.0036) Angle to previous plane (with approximate esd) = 88.716 (0.020) * -0.0026 (0.0010) C12 * 0.0134 (0.0012) C13 * 0.0135 (0.0012) C14 * -0.0020 (0.0009) C15 * -0.0164 (0.0010) C17 * 0.0246 (0.0010) O1 * -0.0305 (0.0010) C18 0.1339 (0.0020) C1 Rms deviation of fitted atoms = 0.0176	7.4064 (0.0012) x - 0.6607 (0.0069) y - 0.1599 (0.0096) z = 1.4811 (0.0038) Angle to previous plane (with approximate esd) = 23.214 (0.058) * -0.1201 (0.0022) C12 * 0.0872 (0.0024) C13 * 0.1044 (0.0025) C14 * -0.0209 (0.0026) C15 * -0.0730 (0.0026) C16 * -0.0543 (0.0027) C17 * 0.0264 (0.0028) C18 * 0.1002 (0.0028) C19 * 0.0354 (0.0026) C20 * -0.0854 (0.0025) C21 0.2417 (0.0030) O1 -0.4847 (0.0038) C1 Rms deviation of fitted atoms = 0.0781

Analysis of Short Ring-Interactions with Cg-Cg Distances < 6.0 Angstrom and Beta < 60.0Deg.

- Cg(I) = Plane number I (= ring number in () above)
- Alpha = Dihedral Angle between Planes I and J (Deg)
- Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).
- P,Q,R,S = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I)	Res(I)	Cg(J)	[ARU(J)]	Cg-Cg	Transformed J-Plane P, Q, R, S	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp	Slippage
Cg(1)	[1] ->	Cg(1)	[3566.01]	3.5573(4)	-0.7076-0.2266-0.6693 -2.5268	0.02(3)	12.1	12.1	-3.4785(3)	-3.4785(3)	0.745
Cg(1)	[1] ->	Cg(3)	[1556.01]	4.2380(4)	0.8556 0.2584 0.4485 8.2730	15.38(3)	28.0	43.1	-3.0951(3)	3.7408(3)	
Cg(1)	[1] ->	Cg(3)	[3566.01]	5.1157(4)	-0.8556-0.2584-0.4485 -1.3239	15.38(3)	56.5	41.1	-3.8540(3)	-2.8238(3)	
Cg(1)	[1] ->	Cg(4)	[3666.01]	5.8709(5)	0.5737 0.1691-0.8014 0.2333	84.72(3)	35.1	62.6	-2.7050(3)	4.8042(3)	
Cg(3)	[1] ->	Cg(1)	[1554.01]	4.2381(4)	0.7076 0.2266 0.6693 1.6097	15.38(3)	43.1	28.0	3.7408(3)	-3.0952(3)	
Cg(3)	[1] ->	Cg(1)	[3566.01]	5.1157(4)	-0.7076-0.2266-0.6693 -2.5268	15.38(3)	41.1	56.5	-2.8238(3)	-3.8539(3)	
Cg(3)	[1] ->	Cg(4)	[2655.01]	5.9172(4)	0.5737-0.1691-0.8014 -0.8230	84.97(3)	45.0	89.1	-0.0919(3)	4.1867(3)	
Cg(4)	[1] ->	Cg(3)	[3665.01]	5.4573(4)	-0.8556-0.2584-0.4485 -8.4083	79.91(3)	23.9	64.4	2.3613(3)	-4.9890(3)	
Cg(4)	[1] ->	Cg(4)	[4554.01]	4.6698(4)	-0.5737 0.1691 0.8014 -4.1227	19.47(3)	47.1	31.8	3.9699(3)	-3.1776(3)	
Cg(4)	[1] ->	Cg(4)	[4555.01]	4.6698(4)	-0.5737 0.1691 0.8014 3.0248	19.47(3)	31.8	47.1	-3.1777(3)	3.9699(3)	
			Min or Max	3.557		0.0	12.1	89.1	-3.854	-4.989	

[3566] = -X,1-Y,1-Z
[1556] = X,Y,1+Z
[3666] = 1-X,1-Y,1-Z
[1554] = X,Y,-1+Z
[2655] = 1-X,1/2+Y,1/2-Z
[3665] = 1-X,1-Y,-Z
[4554] = X,1/2-Y,-1/2+Z
[4555] = X,1/2-Y,1/2+Z

Analysis of Short Ring-Interactions with Cg-Cg Distances < 6.0 Angstrom and Beta < 60.0Deg.

- Cg(I) = Plane number I (= ring number in () above)
- Alpha = Dihedral Angle between Planes I and J (Deg)
- Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).
- P,Q,R,S = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I)	Res(I)	Cg(J)	[ARU(J)]	Cg-Cg	Transformed J-Plane P, Q, R, S	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp	Slippage
Cg(2)	[1] ->	Cg(4)	[1565.01]	5.4577(12)	0.8686 0.4954 0.0119 5.0131	12.77(10)	59.5	60.7	-2.6703(8)	2.7718(9)	
Cg(2)	[1] ->	Cg(4)	[2565.01]	4.8917(12)	-0.8686-0.4954-0.0119 0.5361	12.77(10)	47.2	53.9	-2.8789(8)	-3.3206(9)	
Cg(4)	[1] ->	Cg(2)	[2565.01]	4.8918(12)	-0.7663-0.6211-0.1644 0.2744	12.77(10)	53.9	47.2	-3.3206(9)	-2.8789(8)	
Cg(4)	[1] ->	Cg(4)	[2565.01]	5.7069(13)	-0.8686-0.4954-0.0119 0.5361	0.00(10)	54.5	54.5	-3.3108(9)	-3.3107(9)	4.648
Cg(2)	[1] ->	Cg(6)	[2676.01]	4.8639(13)	-0.9936-0.0937-0.0625 -3.6728	33.91(10)	18.4	40.9	3.6742(8)	4.6166(10)	
Cg(4)	[1] ->	Cg(4)	[2665.01]	3.5276(12)	-0.8686-0.4954-0.0119 -6.0156	0.00(10)	23.3	23.3	3.2410(9)	3.2410(9)	1.393
Cg(5)	[1] ->	Cg(5)	[2566.01]	3.8696(12)	-0.9676-0.2232-0.1177 1.9635	0.03(10)	18.1	18.1	-3.6791(9)	-3.6790(9)	1.199
Cg(5)	[1] ->	Cg(6)	[2566.01]	4.2676(13)	-0.9936-0.0937-0.0625 2.6610	8.21(10)	25.1	33.3	-3.5660(9)	-3.8635(9)	
Cg(6)	[1] ->	Cg(5)	[2566.01]	4.2675(13)	-0.9676-0.2232-0.1177 1.9635	8.21(10)	33.3	25.1	-3.8634(9)	-3.5659(9)	
Cg(6)	[1] ->	Cg(6)	[2566.01]	5.7826(14)	-0.9936-0.0937-0.0625 2.6610	0.00(11)	53.6	53.6	-3.4288(9)	-3.4288(9)	4.656
Cg(2)	[1] ->	Cg(5)	[2566.01]	5.9723(12)	-0.9676-0.2232-0.1177 1.9635	25.91(10)	53.2	60.4	-2.9493(8)	-3.5816(8)	
Cg(5)	[1] ->	Cg(6)	[2676.01]	5.9177(14)	-0.9936-0.0937-0.0625 -3.6728	8.21(10)	55.6	62.1	2.7678(9)	3.3425(9)	
Cg(6)	[1] ->	Cg(2)	[2676.01]	4.8640(13)	-0.7663-0.6211-0.1644 -8.9868	33.91(10)	40.9	18.4	4.6166(10)	3.6742(8)	
Cg(6)	[1] ->	Cg(6)	[2676.01]	5.3696(14)	-0.9936-0.0937-0.0625 -3.6728	0.00(11)	57.2	57.2	2.9050(9)	2.9050(9)	4.516
Cg(6)	[1] ->	Cg(2)	[2576.01]	5.5555(13)	-0.7663-0.6211-0.1644 -3.2064	33.91(10)	46.5	77.9	-1.1638(10)	-3.8210(8)	
			Min or Max	3.528		0.0	18.1	77.9	-3.863	-3.864	

[1565] = X,1+Y,Z
[2565] = -X,1-Y,-Z
[2566] = -X,1-Y,1-Z
[2676] = 1-X,2-Y,1-Z
[2665] = 1-X,1-Y,-Z
[2666] = 1-X,1-Y,1-Z
[2576] = -X,2-Y,1-Z

Theoretical calculations

Methods

We have performed the DFT and TD-DFT calculations with Gaussian 16.[1] No structural simplification was performed. Default Gaussian16 thresholds and algorithms were used but for an improved optimization threshold (10^{-5} au on average residual forces), a stricter self-consistent field convergence criterion (10^{-10} a.u. for optimization/frequencies, 10^{-8} a.u. for single-point calculations), an increased two-electron accuracy level (10^{-14} a.u.) and the use of the *superfine* DFT integration grid, the largest pruned grid available in Gaussian.

Firstly, the S_0 geometries have been optimized with DFT and the vibrational frequencies have been analytically determined, using the M06-2X *meta*-GGA hybrid exchange-correlation functional.[2] These calculations were performed with the 6-311G(d,p) atomic basis set and account for solvent effects through the linear-response PCM approach considering CH_2Cl_2 (CH_3CN for ECD modelling) as solvent.[3] We selected CH_2Cl_2, since this aprotic solvent is typically the one the best modeled by the PCM approach. These ground-state optimizations have been carried out starting with a series of chemically-sound conformers and we report below only the results obtained for the most stable ones (lowest free energy). Secondly, to model the UV/Vis and ECD spectra, we used vertical TD-DFT considering 150 singlet excited states and using the LR-PCM model. These calculations have been made with PBE0[4] since this functional is generally valuable in comparison between vertical TD results and experimental spectra. The plots were performed with Specdis v. 1.71 as sum of Gaussians with σ as half the bandwidth at 1/*e* peak height taken from the "stick" vertical transitions.[5] The 6-311+G(2d,p) basis set was applied. Thirdly, starting from the optimal ground-state geometries, we have used TD-DFT with the same functional and basis set as for the S_0 state, M06-2X/6-311G(d,p), to optimize the S_1 geometry and compute the vibrational frequencies. All optimized structures correspond to true minima of the potential energy surface. Finally, the vertical transition energies to the lowest excited state were determined with TD-DFT and the same M06-2X functional, but a larger basis set, namely 6-311+G(2d,p), in gas-phase as well as in solution using the cLR^2 variant of the PCM,[6] in its *non-equilibrium* limit. The lowest triplet state (T1) structures have been optimized using a consistent level of theory, *i.e.*, PCM-M06-2X/6-311G(d,p) within the unrestricted DFT (U-DFT) formalism.

As we are aware of the significant dependency of the TD-DFT results on the selected functional,[7] the obtained absorption, fluorescence and total energies were also computed using CC2[7] with the Turbomole 7.3 code.[9] The CC2 energies were calculated in gas phase applying the resolution of identity scheme and the frozen-core approximations, and using the *aug*-cc-pVTZ atomic basis set. Combining the CC2 and TD-DFT data using a well-known protocol,[10] one can obtain accurate CC2-corrected estimates of the absorption, fluorescence and 0-0 energies that can be straightforwardly compared to experimental values. The 0-0 phosphorescence energies have been determined with the same protocol, but using the SCS-CC2 rather than CC2 energies, since SCS-CC2 provides more accurate relative energies for singlet-triplet cases.[11,12]

The vibrationally resolved spectrum was determined with the FCClasses 3.01 program.[13,14] We used the time-dependent formulation, applied the FC approximation (HT effects were neglected since the transitions are bright), and selected the so-called *Vertical Gradient* and *Vertical Hessian*[15] models for the calculations, accounting for Duschinsky rotations in the latter. We used a simulation temperature of 298K and internal coordinates, as build by default by FCClasses. The broadening function was a Gaussian with an HWM of ca. 30-50 cm^{-1}, adequate to reproduce the experimental shape.

The spin-orbit coupling elements were computed using the same M06-2X hybrid functional, the ZORA Hamiltonian and the *def2*-TVP basis set a for the calculations using ORCA 5.[16] TDA was not applied, RI used, and the so-called "1X" approach selected for estimating the SOC. Solvent effects were included through the CPCM model, with CH_2Cl_2 as solvent. The reported SOC values reported in the text have been computed as:

$$\sqrt{\frac{1}{3}S_x^2 + \frac{1}{3}S_y^2 + \frac{1}{3}S_z^2}$$

The S-T gaps determined when studying the ISC process have been computed with the same methodology (and ORCA), as well as at SCS-CC2/*aug*-cc-pVTZ level in gas-phase (with Turbomole). Both TD-M06-2X[17] and SCS-CC2[11,12] are known to provide accurate S-T gaps.

The rotational barrier in **1a** and **1b**, was evaluated by DFT at the PCM(CH_2Cl_2)-M06-2X/6-311G(d,p) level. To do so, we first performed a relaxed scan rotating the side phenyl/naphthyl ring from its optimal position by steps of 10° so has to have a full rotation profile. Then the positions in that profiles corresponding to maxima were optimized using a transition state search. The final geometries were checked for presenting a single imaginary frequency corresponding to the rotation, and we report in the text the ΔG from the corresponding minimum as the rotation barrier.

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Geometries

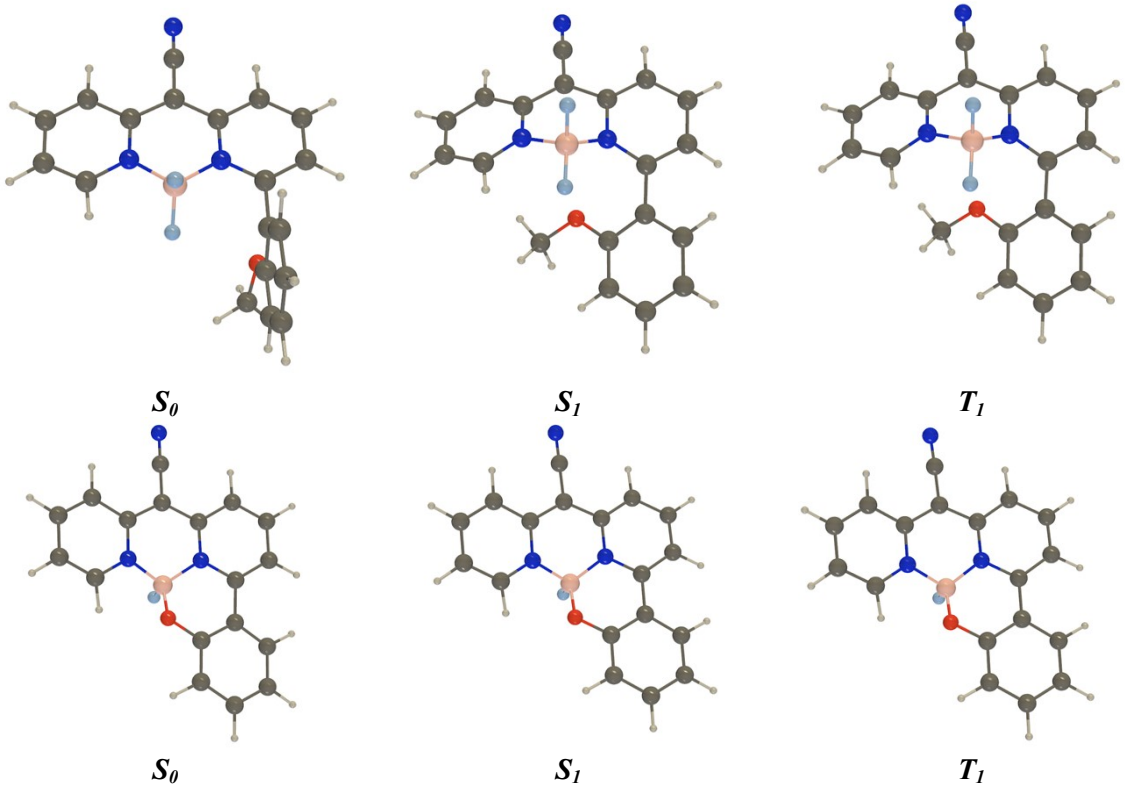

*Figure S 25. Comparison between the optimal geometries of the three states of **1a** (top) and **2a** (bottom). The Cartesian coordinates can be found at the end of this ESI.*

EDD Plots

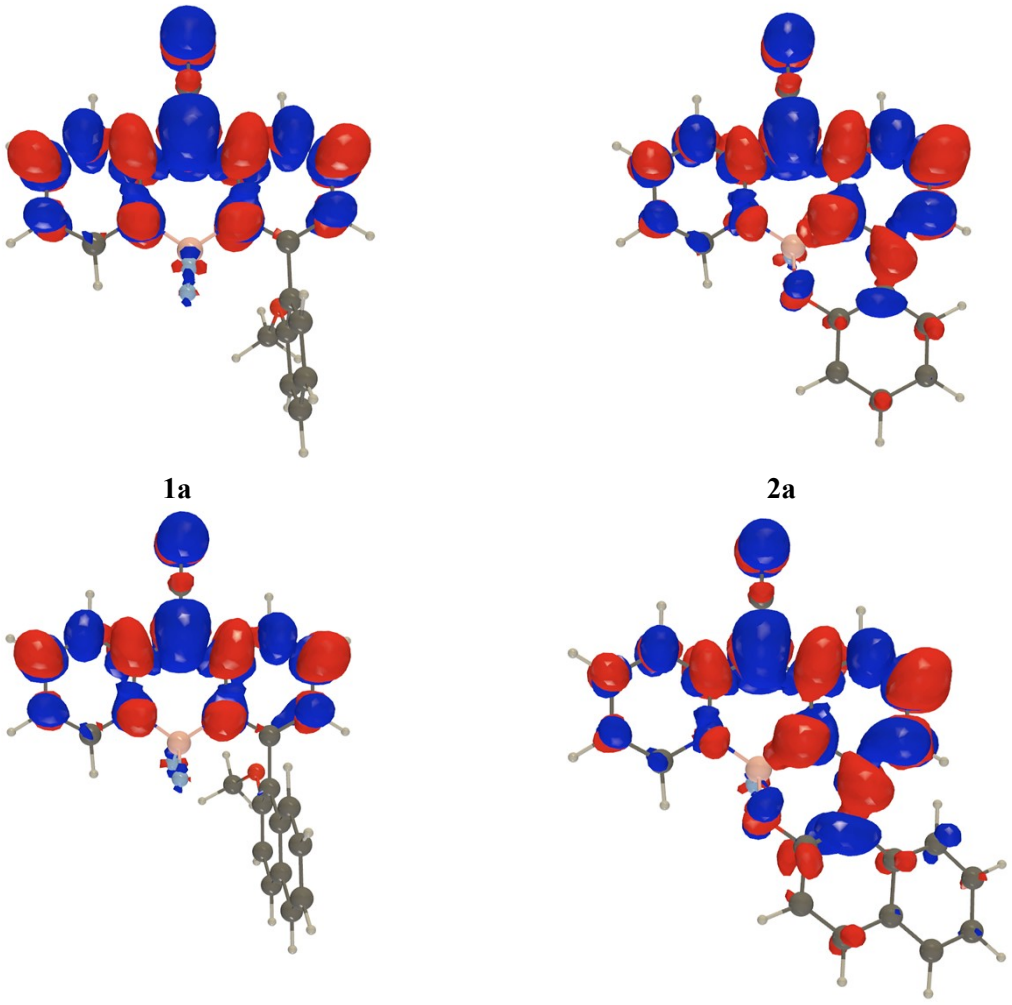

Figure S 26. *Electron density difference (EDD) plots corresponding to the absorption to the lowest singlet state of all compounds. The blue and red lobes represent regions of decrease and increase of density (threshold: 0.001 au). PCM-TD-M06-2X/6-311+G(2d,p) calculations*

UV/Vis and ECD spectrum

Absolute configuration determination by comparison of calculated and experimental ECD spectra. For complex **2a**, according to the following ECD spectra calculations, the second eluted enantiomer on Chiralpak IG, with $[\alpha]_D^{25}$ (CH_2Cl_2, c =0.21) = + 520, is the (*R*)-enantiomer.

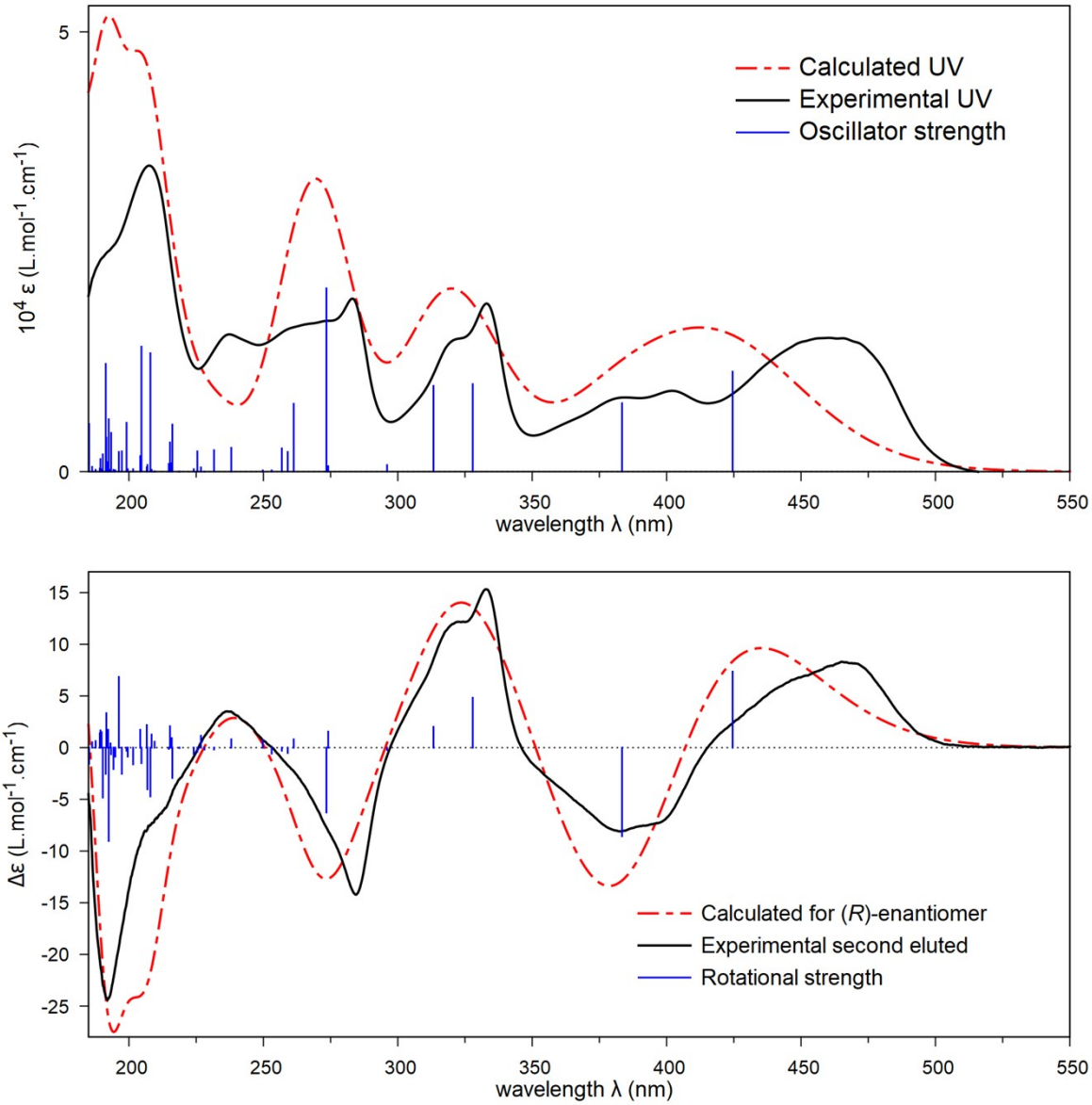

Figure S 27. Comparison of UV (top) and ECD (bottom) experimental spectra in acetonitrile for the second eluted enantiomer on Chiralpak IG and TD-DFT calculated spectra (σ = 0.28 eV, shifted by 6 nm). Vertical bars are oscillator and rotational strengths calculated with arbitrary unit.

For complex **2b**, according to the following ECD spectra calculations, the second eluted enantiomer on Chiralpak IE, with $[\alpha]_D^{25}$ (CH_2Cl_2, c =0.23) = - 780, is the (*R*)-enantiomer.

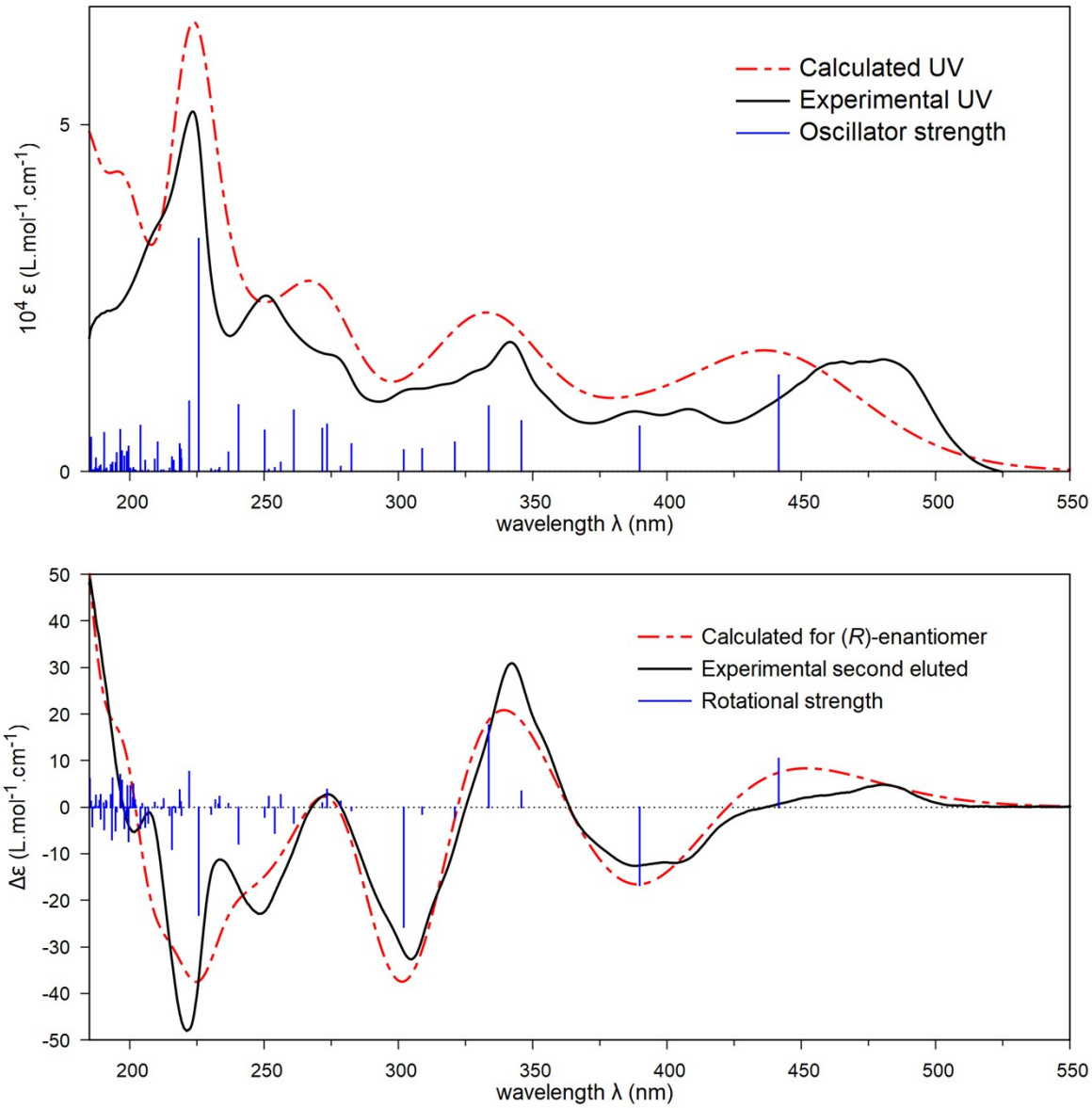

Figure S 28. Comparison of UV (top) and ECD (bottom) experimental spectra in acetonitrile for the second eluted enantiomer on Chiralpak IE and TD-DFT calculated spectra (σ = 0.28 eV, shifted by 6 nm). Vertical bars are oscillator and rotational strengths calculated with arbitrary unit.

For complex **1b**, according to the following ECD spectra calculations, the first eluted enantiomer on Chiralpak IN, with $[\alpha]_D^{25}$ (CH_2Cl_2, c =0.10) = - 500, is the (a*S*)-enantiomer.

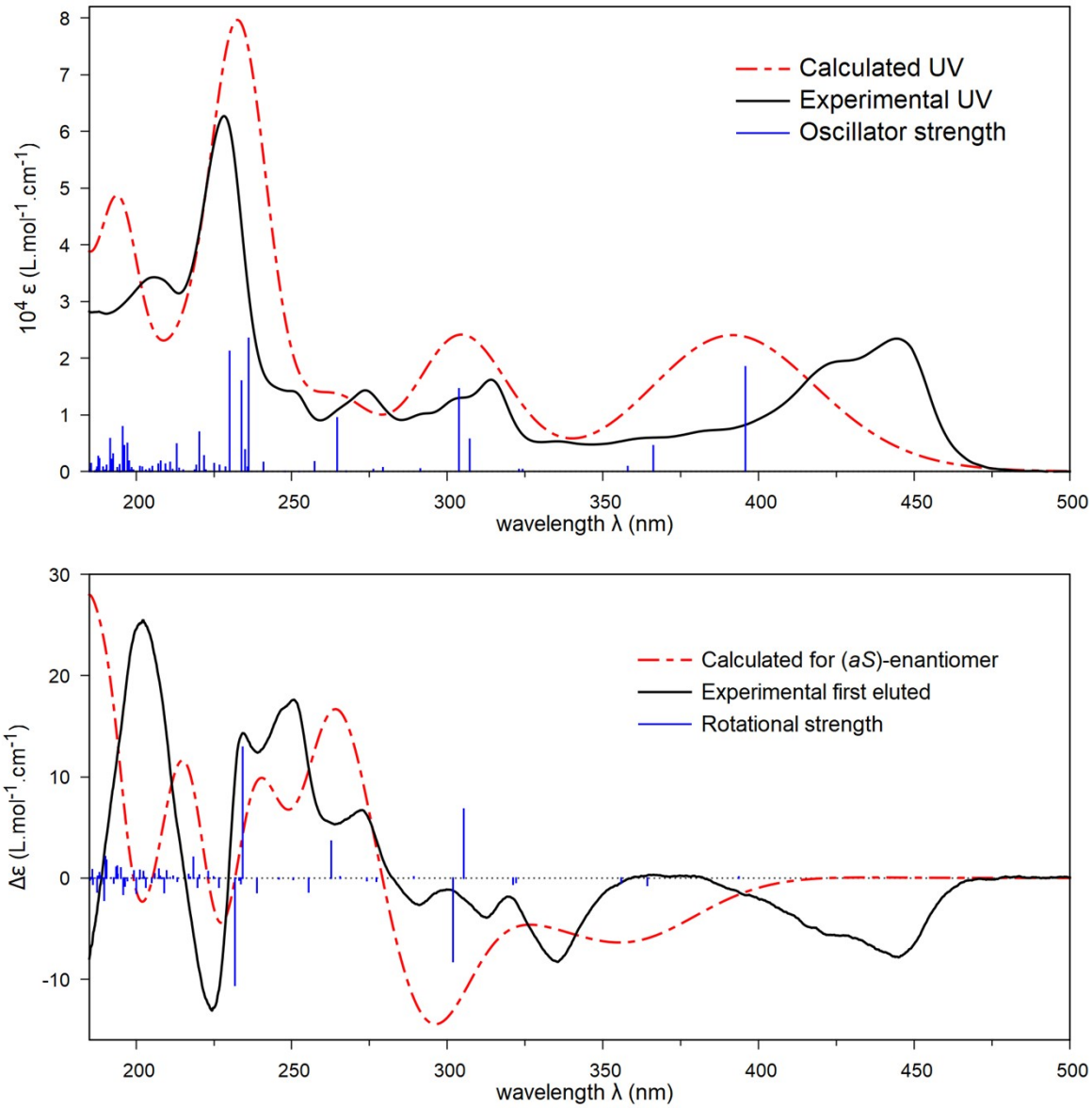

Figure S 29. Comparison of UV (top) and ECD (bottom) experimental spectra in acetonitrile for the first eluted enantiomer on Chiralpak IN and TD-DFT calculated spectra (σ = 0.28 eV, shifted by 6 nm). Vertical bars are oscillator and rotational strengths calculated with arbitrary unit.

0-0 energies and band shapes

Table S 5. Theoretical best estimates of the vertical absorption and fluorescence wavelengths (in nm) and 0-0 energies (in eV) for all compounds. In the rightmost column, we provide the experimental 0-0 energies for comparisons. These calculations correspond CC2 corrected cLR[2]-PCM-TD-M06-2X results (see computational details)

	$\lambda^{vert\text{-}abs}$ (nm)	$\lambda^{vert\text{-}flu}$ (nm)	ΔE^{0-0} (eV)	ΔE^{0-0} (eV), Exp.
1a	402	510	2.531	2.52
2a	425	503	2.524	2.59
1b	404	477	2.707	2.57
2b	437	511	2.463	2.46

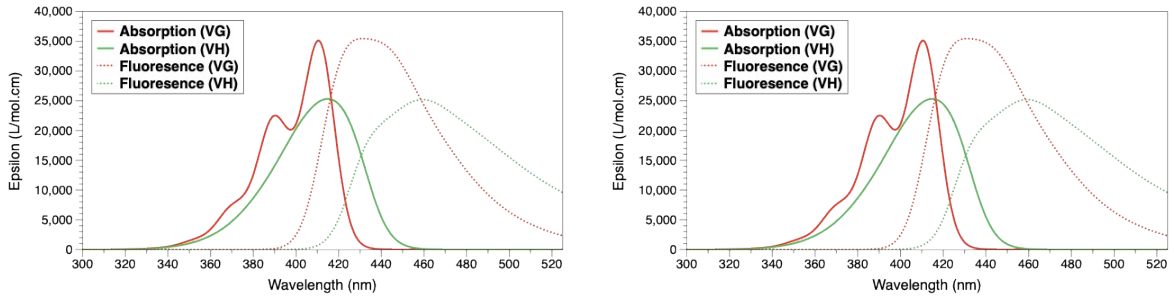

*Figure S 30. Computed vibrationally-resolved spectra for **1a** (left) and **2a** (right) for the absorption and emission using the VG and VH vibronic models. The fluorescence intensities are normalized to the absorption intensity. The radiative rates for emission computed by integrating the VH spectra are 8.2 x 10^7 s^{-1} and 7.2 x 10^7 s^{-1} for **1a** and **2a**, respectively.*

Table S 6. Theoretical best estimates of the phosphorescence 0-0 energies (in eV) for all compounds. In the rightmost column, we provide the experimental 0-0 energies for comparisons. These are SCS-CC2 and CC2 values determined on (U)DFT geometries.

	ΔE^{0-0} (eV), CC2	ΔE^{0-0} (eV), SCS-CC2	ΔE^{0-0} (eV), Exp.
1a	2.197	2.444	2.38
2a	2.188	2.371	2.54
1b	2.409	2.593	2.40
2b	2.103	2.296	2.48

Spin-orbit couplings and S-T gaps

Table S 7. Singlet-triplet gaps (eV) computed at M06-2X and SCS-CC2 levels. A negative value indicates a higher-lying triplet state. On the right-hand-side, we report M06-2X SOC matrix elements (cm^{-1}). All calculations on the optimal S_1 structures.

	M06-2X		SCS-CC2		M06-2X	
	S_1-T_1 (eV)	S_1-T_2 (eV)	S_1-T_1 (eV)	S_1-T_2 (eV)	S_1-T_1 (cm^{-1})	S_1-T_2 (cm^{-1})
1a	0.61	-0.08	0.24	-0.36	0.07	0.24
2a	0.57	0.10	0.21	-0.21	0.03	0.32
1b	0.61	0.11	0.22	-0.20	0.08	0.37
2b	0.60	0.13	0.24	-0.15	0.19	0.43

Cartesian coordinates

We produce below the Cartesian coordinates of all optimized geometries. All structures are true minima. The free energies are PCM(CH_2Cl_2)-(TD-)M06-2X/6-311G(d,p) ones.

1a – S_0 – G= -1196.253508 au.

C	4.2615080	-2.3098350	0.2106550
C	4.0829100	-0.9546120	0.1778320
C	2.7836350	-0.4095310	0.0132750
C	1.9218580	-2.6102700	-0.0744210
C	3.1536510	-3.1723090	0.0850060
C	2.5306380	0.9852310	-0.0066320
C	1.2284590	1.5495060	-0.0954260
C	1.0454570	2.9541120	-0.0468390
H	1.9168950	3.5842580	0.0632770
C	-0.2053470	3.4913080	-0.1422320
C	-1.3159740	2.6429530	-0.2843070
C	-1.1247080	1.2877090	-0.3229970
H	5.2562560	-2.7190380	0.3370860
H	4.9198290	-0.2773320	0.2797250
H	1.0192170	-3.1971980	-0.1766360
H	3.2614600	-4.2465760	0.1110940
H	-0.3405250	4.5653150	-0.1078530
H	-2.3212710	3.0318210	-0.3608080
C	3.6371080	1.8594640	0.1099580
N	4.5455460	2.5671130	0.2039540
B	0.2644690	-0.8155890	-0.3935480
N	0.1333840	0.7438790	-0.2261500
N	1.7396100	-1.2633670	-0.1150070
F	-0.0513350	-1.1589070	-1.7004870
F	-0.5398610	-1.4884020	0.5106390
C	-2.3107150	0.3993100	-0.4850730
C	-2.9592050	-0.0876670	0.6593610
C	-2.8155830	0.1079410	-1.7438280
C	-4.0950940	-0.8822360	0.5234220
C	-3.9549120	-0.6812270	-1.8847820
H	-2.2995670	0.4897620	-2.6169660
C	-4.5835470	-1.1720120	-0.7494870
H	-4.6028600	-1.2751030	1.3935640
H	-4.3398350	-0.9098110	-2.8702050
H	-5.4686290	-1.7899870	-0.8438030
O	-2.4068810	0.2662580	1.8418630
C	-2.8924450	-0.3713790	3.0121720
H	-2.8034760	-1.4574590	2.9239230
H	-2.2669470	-0.0174200	3.8274500
H	-3.9330240	-0.0996790	3.2081090

1a – S_1 – G= -1196.144026 au.

C	3.5740060	-2.5094060	0.2902040
C	3.5477310	-1.1421750	0.4557790
C	2.4420950	-0.3985280	-0.0037830
C	1.4535230	-2.3873310	-0.7999300
C	2.5001440	-3.1579080	-0.3367300
C	2.3103090	1.0115280	0.2040930
C	1.0844940	1.7357190	0.0227670
C	0.9426260	3.0844720	0.2719480
H	1.8159630	3.6722340	0.5260040
C	-0.3458410	3.6636360	0.2720060
C	-1.4407170	2.8107560	0.1846690
C	-1.2806200	1.4347340	-0.0438510
H	4.4205640	-3.0791530	0.6519300
H	4.3589440	-0.6268280	0.9531830
H	0.5991430	-2.8066710	-1.3151660
H	2.4818730	-4.2296240	-0.4715590
H	-0.4762400	4.7207280	0.4531740
H	-2.4392390	3.1859460	0.3702490
C	3.4272060	1.7052430	0.7338400
N	4.3329190	2.2796280	1.1604000
B	0.2895370	-0.1863860	-1.3136020

N	-0.0216080	0.9478130	-0.3167560
N	1.4320220	-1.0583740	-0.6477840
F	0.8487680	0.3667680	-2.4674530
F	-0.7819800	-0.9918250	-1.6188260
C	-2.4165880	0.5266730	0.0770460
C	-2.2941520	-0.7508540	0.6882500
C	-3.6856880	0.9221440	-0.3728220
C	-3.4112240	-1.5693780	0.8214700
C	-4.7956910	0.1017540	-0.2408160
H	-3.7853290	1.8808380	-0.8680810
C	-4.6553530	-1.1457650	0.3564730
H	-3.3250720	-2.5387580	1.2923440
H	-5.7585480	0.4290010	-0.6120520
H	-5.5113160	-1.8009270	0.4639280
O	-1.0680610	-1.0883200	1.1461870
C	-0.8914390	-2.3740750	1.7150420
H	-1.1426310	-3.1580350	0.9945240
H	0.1633210	-2.4406510	1.9750050
H	-1.4979830	-2.4949950	2.6165970

1a – T_1 – G= -1196.166311 au.

C	3.5027600	-2.5538710	0.3425990
C	3.5053940	-1.1797010	0.4984750
C	2.4298530	-0.4264260	0.0079650
C	1.4097240	-2.3846090	-0.7889960
C	2.4347190	-3.1759660	-0.3006750
C	2.3244990	0.9999190	0.1896480
C	1.0937800	1.7214720	0.0468060
C	0.9701000	3.0533650	0.3634670
H	1.8418350	3.6096900	0.6833660
C	-0.3279860	3.6637510	0.3481620
C	-1.4157480	2.8350150	0.2158420
C	-1.2826230	1.4527340	-0.0410130
H	4.3272330	-3.1407500	0.7268760
H	4.3165880	-0.6779980	1.0089840
H	0.5565440	-2.7864830	-1.3193050
H	2.3964210	-4.2474970	-0.4335130
H	-0.4422520	4.7167160	0.5596100
H	-2.4153090	3.2249190	0.3706350
C	3.4739570	1.6857290	0.6563310
N	4.4135710	2.2395370	1.0322700
B	0.2875470	-0.1547310	-1.3332830
N	-0.0105070	0.9644970	-0.3423910
N	1.4187520	-1.0586060	-0.6406580
F	0.8951140	0.3597260	-2.4798680
F	-0.7797430	-0.9568550	-1.6530980
C	-2.4194000	0.5447020	0.0716610
C	-2.3001470	-0.7360820	0.6719780
C	-3.6885710	0.9395820	-0.3714190
C	-3.4121430	-1.5607240	0.7942150
C	-4.8017910	0.1178830	-0.2406820
H	-3.7912080	1.9034670	-0.8567400
C	-4.6613880	-1.1351270	0.3385920
H	-3.3226430	-2.5352250	1.2542800
H	-5.7658200	0.4521580	-0.6034230
H	-5.5158670	-1.7927960	0.4417150
O	-1.0673510	-1.0739060	1.1315840
C	-0.8975030	-2.3554200	1.7069550
H	-1.1359630	-3.1454330	0.9878360
H	0.1528050	-2.4208480	1.9861800
H	-1.5172470	-2.4761930	2.5999180

2a – S_0 – G= -1056.551507 au.

C	-3.8610110	-2.3430890	0.3595960
C	-3.7273830	-0.9915320	0.1961940
C	-2.4429900	-0.4175120	0.0234880
C	-1.5036930	-2.5887370	0.1689320
C	-2.7218660	-3.1724550	0.3589380

C	-2.2335290	0.9830400	-0.0797550
C	-0.9459210	1.5855150	0.0014160
C	-0.7758300	2.9777550	0.1578880
H	-1.6498340	3.6138030	0.1744630
C	0.4844090	3.4923410	0.3129040
C	1.6023120	2.6497370	0.3093330
C	1.4262200	1.2974210	0.1083600
H	-4.8453560	-2.7734360	0.4969370
H	-4.5892160	-0.3383000	0.2102810
H	-0.5803650	-3.1497260	0.1381920
H	-2.7957560	-4.2417460	0.4914160
H	0.6178620	4.5579750	0.4530270
H	2.5895410	3.0543730	0.4681180
C	-3.3675810	1.8283750	-0.0962830
N	-4.2949320	2.5173060	-0.1131670
B	0.0321180	-0.7145460	-0.4240280
N	0.1607960	0.7910650	-0.0381260
N	-1.3666660	-1.2473920	-0.0034990
F	0.1438150	-0.8055690	-1.8150150
C	2.5470230	0.3426630	0.0639700
C	2.2932920	-1.0326700	0.1814840
C	3.8789500	0.7688780	-0.0387840
C	3.3459220	-1.9443570	0.2520470
C	4.9238170	-0.1363410	0.0121630
H	4.0999560	1.8194940	-0.1754490
C	4.6535140	-1.4968280	0.1727030
H	3.1085360	-2.9955300	0.3576730
H	5.9447660	0.2121500	-0.0742620
H	5.4674220	-2.2102040	0.2196550
O	1.0286500	-1.4957580	0.2489000

2a – S_1 – G= -1056.446902 au.

C	3.8528230	-2.3453970	-0.4328760
C	3.7046900	-0.9817320	-0.3516370
C	2.4330730	-0.4199990	-0.1052450
C	1.5152720	-2.5931430	-0.0132690
C	2.7327180	-3.1781790	-0.2697980
C	2.2149270	0.9905200	-0.0497960
C	0.9282320	1.6122480	-0.0068510
C	0.7598420	2.9810700	-0.0494500
H	1.6326930	3.6194130	-0.0874350
C	-0.5406270	3.5327520	-0.0755780
C	-1.6230180	2.6701050	-0.0895090
C	-1.4546430	1.2745200	-0.0462190
H	4.8286200	-2.7721760	-0.6264150
H	4.5516230	-0.3222320	-0.4866150
H	0.6111680	-3.1675680	0.1369220
H	2.8091580	-4.2538970	-0.3322860
H	-0.6839910	4.6031120	-0.1054910
H	-2.6232420	3.0748940	-0.1411280
C	3.3582700	1.8293490	-0.1076500
N	4.2880070	2.5103950	-0.1532120
B	-0.0132050	-0.6731310	0.5397440
N	-0.1666820	0.7524290	0.0171820
N	1.3661190	-1.2589800	0.0711050
F	-0.0111790	-0.6726120	1.9430820
C	-2.5504480	0.3412430	-0.0890310
C	-2.2868720	-1.0556860	-0.0989930
C	-3.9061800	0.7439570	-0.1751640
C	-3.3240670	-1.9773780	-0.2386000
C	-4.9246860	-0.1750920	-0.2937640
H	-4.1570030	1.7958180	-0.1524920
C	-4.6352660	-1.5468760	-0.3364850
H	-3.0684350	-3.0298210	-0.2529440
H	-5.9502480	0.1659010	-0.3588070
H	-5.4351590	-2.2704300	-0.4344640
O	-1.0356140	-1.5330570	0.0110820

2a – T_1 – G= -1056.468582 au.

C	3.8492720	-2.3432640	-0.4630850
C	3.7081530	-0.9760610	-0.3349790
C	2.4415440	-0.4290630	-0.0834790
C	1.5095170	-2.5847060	-0.0808830
C	2.7310660	-3.1679840	-0.3440140
C	2.2170610	0.9921550	0.0041070
C	0.9295010	1.5885940	-0.0102900
C	0.7812580	2.9707170	-0.1130060
H	1.6578080	3.5995430	-0.1694990
C	-0.5399750	3.5308250	-0.1661730
C	-1.6081750	2.6974850	-0.1564990
C	-1.4592600	1.2675250	-0.0785920
H	4.8249910	-2.7683490	-0.6608130
H	4.5586140	-0.3160660	-0.4387310
H	0.5984550	-3.1546560	0.0381250
H	2.8023890	-4.2414280	-0.4426510
H	-0.6690060	4.6025920	-0.2246410
H	-2.6062720	3.1091020	-0.2103660
C	3.3624120	1.8311400	-0.0016930
N	4.3038670	2.4967970	-0.0035720
B	-0.0262940	-0.6811550	0.5223180
N	-0.1564420	0.7544110	0.0283520
N	1.3756460	-1.2557960	0.0499050
F	-0.0097560	-0.7175600	1.9244020
C	-2.5489270	0.3501690	-0.1016290
C	-2.3032170	-1.0533260	-0.0923570
C	-3.9079440	0.7557000	-0.1703190
C	-3.3419910	-1.9673200	-0.1718800
C	-4.9357510	-0.1638320	-0.2434280
H	-4.1547030	1.8090450	-0.1668170
C	-4.6624430	-1.5346780	-0.2520110
H	-3.0916460	-3.0215500	-0.1666120
H	-5.9596650	0.1860520	-0.2960830
H	-5.4670640	-2.2566440	-0.3111500
O	-1.0335900	-1.5295200	-0.0304380

1b – S_0 – G= -1349.825955 au.

C	4.5751910	-2.5431290	-0.2560600
C	4.4703240	-1.1825750	-0.3430130
C	3.2029070	-0.5555920	-0.2288350
C	2.2245140	-2.6898300	0.0566860
C	3.4229160	-3.3300110	-0.0551210
C	3.0230750	0.8456450	-0.3463120
C	1.7512960	1.4813280	-0.3186930
C	1.6335650	2.8709250	-0.5716410
H	2.5327290	3.4365650	-0.7722370
C	0.4079000	3.4712700	-0.5763600
C	-0.7395490	2.7074800	-0.3058710
C	-0.6087890	1.3705630	-0.0411100
H	5.5458900	-3.0149880	-0.3458760
H	5.3420720	-0.5634290	-0.5049960
H	1.2921350	-3.2152480	0.2133690
H	3.4723290	-4.4067290	0.0125690
H	0.3219620	4.5315090	-0.7800330
H	-1.7248850	3.1511510	-0.2807930
C	4.1703570	1.6432060	-0.5690290
N	5.1119490	2.2881890	-0.7486990
B	0.6682170	-0.7900570	0.2230450
N	0.6214020	0.7574930	-0.0641290
N	2.1158220	-1.3367390	-0.0214490
F	-0.1789120	-1.4600640	-0.6443370
F	0.3413160	-1.0540440	1.5457590
C	-1.8207380	0.5804730	0.3137910
C	-2.1102270	0.4025300	1.6502210
C	-2.6985120	0.0846970	-0.6877570
C	-3.2621350	-0.3246180	2.0428420
C	-3.8632150	-0.6264700	-0.2907540

C	-4.1102640	-0.8201260	1.0911740
H	-3.4765070	-0.4758390	3.0922440
H	-4.9954650	-1.3704550	1.3908300
O	-1.2648600	0.9734410	2.5394290
C	-1.1932600	0.4040890	3.8399110
H	-1.0608940	-0.6779480	3.7739040
H	-0.3217670	0.8502470	4.3126800
H	-2.0823610	0.6422980	4.4285850
C	-2.4432210	0.2490340	-2.0760210
C	-3.3126790	-0.2495630	-3.0092260
H	-1.5476630	0.7714480	-2.3916440
H	-3.1043750	-0.1154210	-4.0641200
C	-4.7444270	-1.1304490	-1.2826820
C	-4.4805120	-0.9449910	-2.6127330
H	-5.6310370	-1.6678280	-0.9635880
H	-5.1573200	-1.3315130	-3.3648380

1b – S_1 – G= -1349.714125 au.

C	4.7729990	-2.2184450	-0.8331280
C	4.5790550	-0.9105480	-0.4556380
C	3.2724370	-0.3846280	-0.3664090
C	2.4040690	-2.4861880	-0.9879530
C	3.6600780	-3.0298610	-1.1210600
C	3.0034020	0.9797160	-0.0710340
C	1.6925000	1.5664250	-0.0992190
C	1.5137000	2.9349350	-0.2083870
H	2.3910770	3.5674200	-0.2554020
C	0.2294190	3.4930080	-0.2707700
C	-0.8559050	2.6225230	-0.1205680
C	-0.6650780	1.2600110	0.0567240
H	5.7765950	-2.6160000	-0.9124270
H	5.4192330	-0.2635560	-0.2398420
H	1.5024220	-3.0574280	-1.1683330
H	3.7706630	-4.0586130	-1.4318390
H	0.0880400	4.5592040	-0.3700500
H	-1.8708950	2.9969540	-0.0646270
C	4.1083530	1.8272740	0.1926740
N	5.0062190	2.5204370	0.4065290
B	0.7114040	-0.8260880	-0.2530440
N	0.5962230	0.6988670	-0.0348740
N	2.2074720	-1.2066520	-0.6221640
F	-0.0966670	-1.2188920	-1.3128200
F	0.4184770	-1.5803360	0.8800450
C	-1.8019340	0.4089870	0.4415690
C	-1.8137410	-0.1551210	1.7144140
C	-2.9131610	0.2096630	-0.4317000
C	-2.8982170	-0.9574730	2.1359050
C	-4.0186300	-0.5668770	0.0158510
C	-3.9730770	-1.1468440	1.3071930
H	-2.8959700	-1.3954050	3.1248210
H	-4.8124720	-1.7473670	1.6402140
O	-0.7895660	0.1708150	2.5288610
C	-0.5192360	-0.6802430	3.6334050
H	-0.4519210	-1.7190640	3.3038060
H	0.4415170	-0.3586120	4.0277900
H	-1.2798700	-0.5765690	4.4112190
C	-2.9402370	0.7172080	-1.7575270
C	-4.0305050	0.5141600	-2.5661320
H	-2.0795780	1.2563160	-2.1340210
H	-4.0320060	0.9097890	-3.5748550
C	-5.1298540	-0.7596970	-0.8434590
C	-5.1444460	-0.2225010	-2.1041810
H	-5.9673320	-1.3473580	-0.4829300
H	-5.9976230	-0.3741980	-2.7540600

1b – T_1 – G= -1349.735804 au.

C	4.6830020	-2.4141140	-0.5891390
C	4.5385340	-1.0535490	-0.4187660

C	3.2508710	-0.4966940	-0.3072990
C	2.3097710	-2.6352270	-0.5096130
C	3.5494380	-3.2274020	-0.6481120
C	3.0237030	0.9101890	-0.2076700
C	1.7245230	1.5305720	-0.2577300
C	1.6003420	2.8755710	-0.5025760
H	2.5005050	3.4649420	-0.6216300
C	0.3171310	3.4891480	-0.6096410
C	-0.7771340	2.6728350	-0.3500810
C	-0.6491290	1.3238950	-0.0567320
H	5.6718900	-2.8443320	-0.6819190
H	5.4013180	-0.4023040	-0.3839310
H	1.3883780	-3.2019840	-0.5272290
H	3.6210230	-4.2959110	-0.7897980
H	0.2143380	4.5427610	-0.8184860
H	-1.7814370	3.0822950	-0.3333280
C	4.1684940	1.7454660	-0.1436510
N	5.1065480	2.4144410	-0.0885420
B	0.6786570	-0.8211340	0.0028610
N	0.6083020	0.7013080	-0.0937230
N	2.1678870	-1.3148990	-0.3398060
F	-0.1549480	-1.4335650	-0.9229090
F	0.4365170	-1.3239450	1.2790380
C	-1.8235990	0.5328720	0.3775990
C	-1.9422580	0.1922780	1.7141620
C	-2.8464800	0.1543270	-0.5392280
C	-3.0487490	-0.5632870	2.1738230
C	-3.9728100	-0.5772710	-0.0692440
C	-4.0370720	-0.9294370	1.3005460
H	-3.1262380	-0.8318430	3.2189130
H	-4.8906920	-1.4963430	1.6559900
O	-0.9818480	0.6551800	2.5493600
C	-0.7834810	-0.0343160	3.7736860
H	-0.6884290	-1.1078140	3.5961370
H	0.1467640	0.3501850	4.1855040
H	-1.5946070	0.1616980	4.4798430
C	-2.7712690	0.4554980	-1.9272870
C	-3.7734730	0.0807020	-2.7826080
H	-1.9015760	0.9810490	-2.3027960
H	-3.6974650	0.3182440	-3.8372610
C	-4.9963340	-0.9483720	-0.9805170
C	-4.9061790	-0.6231390	-2.3067960
H	-5.8512690	-1.4989950	-0.6024400
H	-5.6913310	-0.9090550	-2.9961850

2b – S_0 – G= -1210.118150 au.

C	4.9699000	-1.9258420	0.0029180
C	4.6555150	-0.5959920	0.0457140
C	3.2991160	-0.1824150	0.0865420
C	2.6556020	-2.4649670	0.0563870
C	3.9472440	-2.8966690	-0.0016410
C	2.9114210	1.1815850	0.0664880
C	1.5609660	1.6066620	-0.0967760
C	1.2251150	2.9452960	-0.3860900
H	2.0111170	3.6862040	-0.4298180
C	-0.0782840	3.2681500	-0.6610990
C	-1.0809620	2.2937300	-0.6095600
C	-0.7556330	1.0043460	-0.2351420
H	6.0082160	-2.2318460	-0.0329860
H	5.4272140	0.1616790	0.0375710
H	1.8100410	-3.1387320	0.0700270
H	4.1651530	-3.9537500	-0.0388190
H	-0.3349480	4.2837510	-0.9366120
H	-2.0951290	2.5370130	-0.8828350
C	3.9275860	2.1653220	0.0538670
N	4.7584000	2.9682360	0.0473430
B	0.8480740	-0.7961840	0.3592750
N	0.5620100	0.6853530	-0.0134070

N	2.3375370	-1.1433000	0.1056980
F	0.5675650	-0.9805170	1.7147810
C	-1.7357230	-0.0922600	-0.1720270
C	-1.2784430	-1.3760410	-0.4373740
C	-3.1465420	0.1075430	0.0396500
C	-2.1721420	-2.4377790	-0.7148840
C	-4.0370610	-0.9658530	-0.2432620
C	-3.5151580	-2.2231470	-0.6568850
H	-1.7512650	-3.4012130	-0.9732530
H	-4.2087090	-3.0250770	-0.8840970
O	0.0370880	-1.6501890	-0.4739430
C	-5.4316710	-0.7936570	-0.0670310
C	-5.9410050	0.3805250	0.4215580
H	-6.0875790	-1.6227030	-0.3094150
H	-7.0080300	0.5026800	0.5600330
C	-3.7031030	1.2879280	0.5994890
C	-5.0577290	1.4183020	0.7829940
H	-3.0516850	2.0831110	0.9340690
H	-5.4492270	2.3253540	1.2278400

2b – S_1 – G= -1210.016361 au.

C	5.0000290	-1.8905550	-0.1078530
C	4.6625100	-0.5604450	-0.0984360
C	3.3082170	-0.1708550	0.0092990
C	2.6922790	-2.4506700	0.1155950
C	3.9928470	-2.8679430	-0.0091110
C	2.8969490	1.1942850	-0.0291730
C	1.5393530	1.6208720	-0.1143760
C	1.1915170	2.9411340	-0.3480020
H	1.9729690	3.6842250	-0.4345290
C	-0.1588470	3.2875730	-0.5478670
C	-1.1230210	2.2993730	-0.4656960
C	-0.7871950	0.9661250	-0.1462450
H	6.0386580	-2.1832890	-0.1947820
H	5.4210670	0.2060080	-0.1844600
H	1.8642480	-3.1396020	0.2152450
H	4.2211150	-3.9237000	-0.0177100
H	-0.4313800	4.3004600	-0.8086100
H	-2.1506030	2.5295250	-0.7043790
C	3.9141700	2.1829610	-0.0676720
N	4.7444470	2.9832960	-0.0973690
B	0.8761130	-0.7695030	0.4625350
N	0.5650180	0.6404910	-0.0137400
N	2.3551720	-1.1443860	0.1255200
F	0.7066900	-0.8765800	1.8494550
C	-1.7349010	-0.1004190	-0.0971780
C	-1.2677920	-1.4264160	-0.3080160
C	-3.1666690	0.0820120	0.0549780
C	-2.1498710	-2.4548500	-0.6770410
C	-4.0413630	-0.9698260	-0.3423070
C	-3.4994610	-2.2212680	-0.7470650
H	-1.7250090	-3.4239650	-0.9074820
H	-4.1766800	-3.0110750	-1.0512740
O	0.0330480	-1.7201020	-0.2345060
C	-5.4393660	-0.7800270	-0.2606990
C	-5.9696740	0.3791750	0.2570510
H	-6.0899800	-1.5814380	-0.5937290
H	-7.0431890	0.5080660	0.3211400
C	-3.7403750	1.2229040	0.6565510
C	-5.1095920	1.3745490	0.7490010
H	-3.0981580	1.9730660	1.0989930
H	-5.5191280	2.2573450	1.2245540

2b – T_1 – G= -1210.037878 au.

C	5.0056400	-1.8655860	-0.1996560
C	4.6599770	-0.5337980	-0.1472880
C	3.3117790	-0.1669630	0.0056460
C	2.7103870	-2.4426230	0.0593130

C	4.0134060	-2.8464700	-0.1036830
C	2.8786580	1.2044920	0.0058580
C	1.5240400	1.5889120	-0.0996240
C	1.1744450	2.9359650	-0.3295180
H	1.9517700	3.6836400	-0.3860650
C	-0.1808960	3.2607290	-0.5862510
C	-1.1321970	2.2929890	-0.5229530
C	-0.7998700	0.9265470	-0.1676240
H	6.0436310	-2.1485350	-0.3207290
H	5.4094200	0.2409770	-0.2346250
H	1.8861980	-3.1359950	0.1535780
H	4.2486750	-3.9000030	-0.1443580
H	-0.4442050	4.2689840	-0.8775960
H	-2.1517330	2.5129300	-0.8026370
C	3.8834880	2.2070020	-0.0080730
N	4.7132600	3.0080050	-0.0145940
B	0.8845420	-0.7780130	0.4804200
N	0.5667320	0.6253540	-0.0306840
N	2.3736000	-1.1387970	0.1170100
F	0.7766170	-0.8244630	1.8753000
C	-1.7277960	-0.1132230	-0.0837580
C	-1.2738510	-1.4704180	-0.2237240
C	-3.1720960	0.0779370	0.0455540
C	-2.1541610	-2.4964080	-0.5481720
C	-4.0468420	-0.9828550	-0.3249770
C	-3.5105810	-2.2590460	-0.6646310
H	-1.7362250	-3.4803480	-0.7245860
H	-4.1875120	-3.0575630	-0.9425720
O	0.0432370	-1.7517580	-0.1564220
C	-5.4427820	-0.7736810	-0.2690120
C	-5.9698500	0.4078530	0.2043470
H	-6.0980430	-1.5793790	-0.5824390
H	-7.0434510	0.5466560	0.2482600
C	-3.7401990	1.2382210	0.6051900
C	-5.1106830	1.4105820	0.6759290
H	-3.0951430	1.9966030	1.0306350
H	-5.5167800	2.3134560	1.1152120