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Supporting Information

Enantioselective Lewis Acid Catalyzed *ortho* Photocycloaddition of Olefins to Phenanthrene-9-carboxaldehydes

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1. General Information

All air and moisture sensitive reactions were carried out in flame-dried glassware under a positive pressure of dry argon using standard *Schlenk* techniques.

Commercially available chemicals were used without further purification unless otherwise mentioned.

For moisture sensitive reactions, tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were dried using a MBSPS 800 *MBraun* solvent purification system. The following columns were used:

THF: 2 × MB-KOL-M type 2 (3 Å molecular sieve)

CH_2Cl_2: 2 × MB-KOL-A type 2 (aluminum oxide)

Chloroform was distilled over activated basic aluminum oxide (*Merck*, aluminum oxide 90 active basic, 0.063-0.200 mm) and then stored over 4 Å activated molecular sieves prior to use.

The following dry solvents are commercially available and were used without further purification:

Acetonitrile: *Acros Organics*, 99.9% extra dry, over molecular sieves.

N,*N*-Dimethylformamide: *Acros Organics*, 99.9% extra dry, over molecular sieves.

Ethanol: *Acros Organics*, 99.5% extra dry.

Methanol: *Acros Organics*, 99.8% extra dry, over molecular sieves.

Toluene: *Acros Organics*, 99.8% extra dry, over molecular sieves.

For photochemical reactions, dry dichloromethane was degassed by four freeze-pump-thaw cycles and stored over 4 Å activated molecular sieves. 2,3-Dimethyl-2-butene (≥ 99%, *Sigma Aldrich*) was degassed by four freeze-pump-thaw cycles and stored under argon before use. All other olefins were distilled, filtered over activated, basic aluminum oxide, degassed by four freeze-pump-thaw cycles and stored under argon prior to use.

Technical solvents for column chromatography (pentane, diethyl ether, ethylacetate) were used after simple distillation.

Flash column chromatography was performed on silica 60 (*Merck*, 230-400 mesh) with the indicated eluent mixtures (v/v).

Photochemical experiments at 366 nm were carried out in flame-dried *Duran* tubes (diameter = 1 cm) in a positive geometry setup (cylindrical array of 16 UV-A lamps, *Rayonet*, 8 W nominal power, λ_{max} = 366 nm) with the sample placed in the center of the illumination chamber.

Enantioselective reactions were carried out at −78 °C in a *Schlenk* tube (diameter = 1 cm) with a polished quartz rod as an optical fiber, which was roughened by sandblasting at one end. The roughed end has to be completely submerged in the solvent during the reaction, in order to guarantee optimal and reproducible irradiation conditions.[1] The reactions were cooled by using an *Huber* TC100E immersion cooler with ethanol as coolant.

As cooling baths were used ice/water (0 °C), dry ice/ethanol (– 78 °C).

2. Analytical Methods

Melting points (M.p.) were determined using a *Kofler* heating bar designed by *Ludwig Kofler* (*Reichert*) without correction or melting points were determined using a *Büchi* M-565 melting point apparatus, with range quoted to the nearest whole number.

Thin Layer Chromatography (TLC) was performed on silica coated glass plates (*Merck*, silica 60 F254) with detection by UV-light (λ = 254 nm) and/or by staining with a potassium permanganate solution [$KMnO_4$] followed by heat treatment.

> $KMnO_4$-staining solution: potassium permanganate (3.00 g), potassium carbonate (20.0 g) and 5% aqueous sodium hydroxide solution (5.00 mL) in water (300 mL).

Infrared Spectra (IR) were recorded on a *Perkin Elmer* Frontier IR-FTR spectrometer by ATR technique. The signal intensity is assigned using the following abbreviations: vs (very strong), s (strong), m (medium), w (weak).

Nuclear Magnetic Resonance Spectra were recorded at room temperature either on a *Bruker* AVHD-300, AVHD-400, AVHD-500 or an AV-500 cryo. ^{1}H NMR spectra were calibrated to the residual proton signal of chloroform-d_1 (δ = 7.26 ppm), dimethylsulfoxide-d_6 (δ = 2.50 ppm) or benzene-d_6 (δ = 7.16 ppm). ^{13}C NMR spectra were referenced to the ^{13}C triplet of $CDCl_3$ (δ = 77.16 ppm), to the ^{13}C septet of DMSO-d_6 (δ = 39.5 ppm) or to the ^{13}C triplet of C_6D_6 (δ = 128.06 ppm). ^{19}F NMR spectra were referenced to the ^{19}F signal of CCl_3F (δ = 0 ppm) as an internal standard. ^{11}B NMR spectra were used without reference. Apparent multiplets which occur as a result of coupling constant equality between magnetically non-equivalent protons are marked as virtual (*virt.*). Following abbreviations for single multiplicities were used: *br* – broad, s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet. Assignment and multiplicity of the ^{13}C NMR signals were determined by two-dimensional NMR experiments (COSY, HSQC, HMBC). The nomenclature in the case of diastereotopic methyl-groups at quaternary carbon atoms is as following: Methyl-groups oriented *anti* to the phenanthrene core are labeled as α and those oriented *syn* to the phenanthrene core as β.

Mass Spectra (MS) and High Resolution Mass Spectra (HRMS) were measured on a *Thermo Scientific* DFS-HRMS spectrometer (EI, 70 eV).

UV/Vis Spectra were measured on a *Perkin Elmer* Lambda 35 UV/Vis spectrometer. Spectra were recorded using a *Hellma* precision cell made of quartz *Suprasil* with a pathway of 1 mm. Solvents and concentrations are given for each spectrum.

Analytical High Performance Liquid Chromatography (HPLC) was performed (*Thermo Fisher, Dionex* Ultimate 3000, LPG 3400SD Pump, WPS3000SL Autosampler, DAD 3000 photodiode array detector) using different chiral stationary phases (*Daicel*, *Chemical Industries*) and UV detection ($\lambda = 215$).

Specific Rotation was determined using a *Bellingham+Stanley* ADP440+ polarimeter using a 0.5 cm cuvette at $\lambda = 589$ nm (Na-D-line) at room temperature. Specific rotation is reported as follows: $[\alpha]_D^T$ in 10^{-1} grad cm^2 g^{-1} (c was defined as g per 100 mL solvent).

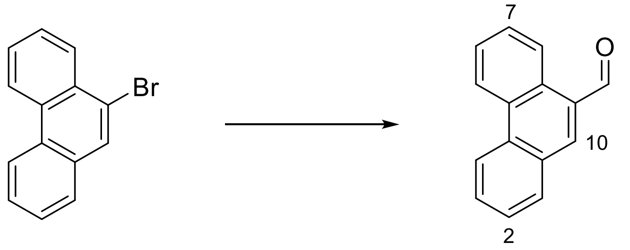
CHN analysis were performed on an *Elementar* vario EL.

Luminescence Measurements were performed on Horiba Scientific FluoroMax-4 instrument (part number J810005 rev. C) using a SUPRASIL® quartz cuvette with a 1 mm light path to record emission spectra.

pH Values were determined by the use of *Merck* universal indicator paper.

3. Synthesis of Irradiation Precursors

3.1 Phenanthrene-9-carboxaldehyde (1a)



1a

$C_{15}H_{10}O$
MW = 206.24 g/mol

At – 78 °C was added *n*-butyllithium solution (5.60 mL, 2.5 M in *n*-hexane, 14.0 mmol, 1.00 eq.) to a solution of 9-bromophenanthrene (3.00 g, 11.7 mmol, 1.00 eq.) in tetrahydrofuran (125 mL). A solution of *N*,*N*-dimethylformamide (2.70 mL, 2.57 g, 35.1 mmol, 3.00 eq.) in tetrahydrofuran (50 mL) was added dropwise after one hour and the reaction mixture was warmed to room temperature. After three hours the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (30 mL) and water (30 mL). The aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic extracts were washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. After column chromatography (silica, P/Et_2O = 100/1 → 25/1), 2.12 g aldehyde **1a** (10.3 mmol, 88%) was obtained as an off-white solid.

TLC: R_f = 0.44 (P/Et_2O = 10/1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.68 (ddd, ^3J = 8.1 Hz, ^3J = 7.1 Hz, ^4J = 1.1 Hz, 1 H, H-2), 7.71 – 7.77 (m, 2 H, H-6, H-7), 7.81 (ddd, ^3J = 8.4 Hz, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1 H, H-3), 8.03 (d, ^3J = 8.1 Hz, 1 H, H-1), 8.25 (s, 1 H, H-10), 8.64 – 8.77 (m, 2 H, H-4, H-5), 9.32 – 9.43 (m, 1 H, H-8), 10.38 (s, 1 H, CHO).

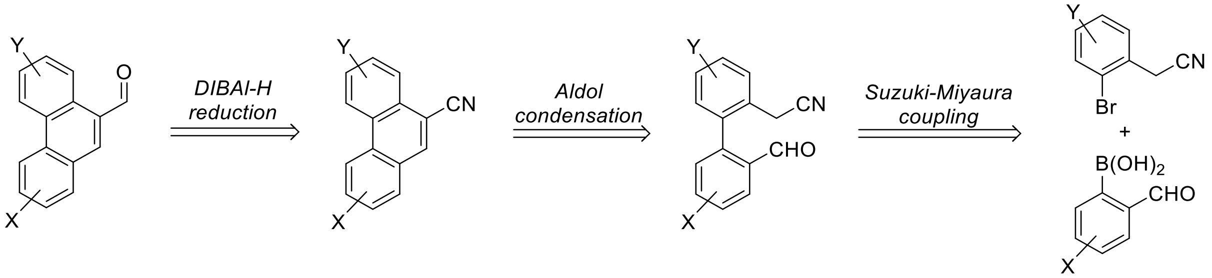
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 122.9 (d, C-5*), 123.0 (d, C-4*), 126.1 (d, C-8), 127.4 (d, C-2), 127.8 (d, C-6**), 128.4 (d, C-7**), 128.4 (s, C-9), 130.3 (s, C-8a***), 130.3 (d, C-3), 130.5 (d, C-1), 130.6 (s, C-10a***), 130.8 (s, C-4b***), 133.1 (s, C-4a), 141.3 (d, C-10), 193.7 (d, CHO).

*, **, *** assignment is interconvertible.

The analytical data obtained matched those reported in literature.[2]

3.2 Synthesis of Substituted Irradiation Precursors

Mono- and disubstituted phenanthrene-9-carboxaldehydes were synthesized from the corresponding phenanthrene-9-carbonitriles by di-*iso*-butylaluminium hydride reduction. The phenanthrene-9-carbonitriles were accessible by a *Suzuki-Miyaura* coupling/aldol condensation cascade from substituted (2-formylphenyl)boronic acids and 2-(2-bromophenyl)acetonitrile derivatives (see scheme S1).



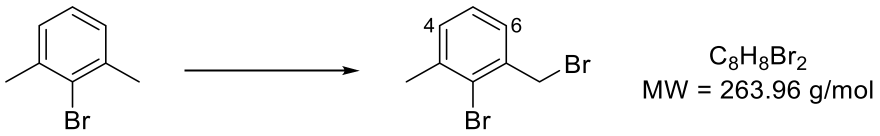
Y = Me, CF_3, F; X = Me, F, Cl

Scheme S1: Retrosynthetic disconnection for preparation of substituted phenanthrene-9-carboxaldehydes.

In the following sections, a representative procedure for the synthesis of a 2-(2-bromophenyl)acetonitrile derivative and a substituted (2-formylphenyl)boronic acid is given. Subsequently, a representative procedure for the *Suzuki-Miyaura* coupling/aldol condensation cascade is described. All other phenanthrene-9-carbonitriles were prepared analogously.

Synthesis of 2-(2’-Bromo-3’-methylphenyl)acetonitrile

2-Bromo-1-(bromomethyl)-3-methylbenzene



2-Bromo-1,3-dimethylbenzene (2.00 g, 10.8 mmol, 1.00 eq.), *N*-bromosuccinimide (2.31 g, 13.0 mmol, 1.2 eq.) and dibenzoyl peroxide (131 mg, 540 µmol, 5 mol%) were dissolved in chloroform (15 mL) and the solution was heated to reflux for 67 hours. After cooling to room temperature the reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ solution (10 mL). After separation of the layers, the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. After column chromatography (silica, P), 1.61 g of the title compound (6.10 mmol, 56%) was obtained as a colourless oil.

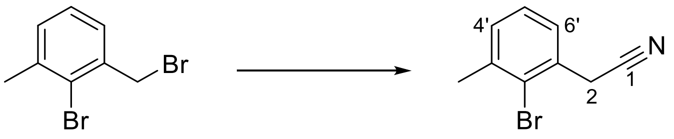
TLC: R_f = 0.65 (P) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 2.44 (s, 3 H, C-3-CH_3), 4.65 (s, 2 H, C-1-CH_2Br), 7.17 – 7.21 (m, 2 H, H-4, H-6), 7.28 – 7.31 (m, 1 H, H-5).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ [ppm] = 24.0 (q, C-3-*C*H_3), 34.8 (t, C-1-*C*H_2Br), 127.2 (s, C-2), 127.4 (d, C-6), 128.9 (d, C-5), 131.1 (d, C-4), 137.5 (s, C-1), 139.6 (s, C-3).

The analytical data obtained matched those reported in literature.[3]

2-(2’-Bromo-3’-methylphenyl)acetonitrile



C_9H_8BrN
MW = 210.07 g/mol

Trimethylsilyl cyanide (2.02 mL, 1.60 g, 16.2 mmol, 1.50 eq.) and subsequently tetra-*n*-butylammonium fluoride solution (16.2 mL, 1.0 M in tetrahydrofuran, 16.2 mmol) was added to a solution of 2-bromo-1-(bromomethyl)-3-methylbenzene (2.84 g, 10.8 mmol, 1.00 eq.) in acetonitrile (20 mL) at 0 °C. The solution was slowly warmed up to room temperature and after 25 hours all volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica, $P/Et_2O = 100/1 \rightarrow 10/1$), obtaining 2.00 g of the title compound (9.52 mmol, 88%) as a colourless solid.

M.p.: 93 °C.

TLC: $R_f = 0.25$ ($P/Et_2O = 25/1$) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 2.44 (s, 3 H, C-3’-CH_3), 3.87 (s, 2 H, H-2), 7.23 – 7.27* (m, 2 H, H-4’, H-6’), 7.35 – 7.37 (m, 1 H, H-5’).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 23.9 (q, C-3’-CH_3), 25.8 (t, C-2), 117.4 (s, C-1), 126.3 (s, C-2’), 127.2 (d, C-5’), 127.7 (d, C-6’), 130.4 (s, C-1’), 130.8 (d, C-4’), 139.6 (s, C-3’).

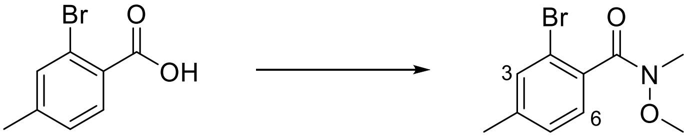
* partially overlaid with residual proton signal of chloroform.

The analytical data obtained matched those reported in literature.[4]

2-(2-Bromo-4-fluorophenyl)acetonitrile, 2-[2-bromo-4-(trifluoromethyl)phenyl]acetonitrile and 2-(2-bromophenyl)acetonitrile were commercially available and used without further purification.

Synthesis of Substituted (2-Formylphenyl)boronic acids

2-Bromo-*N*-methoxy-*N*,4-dimethylbenzamide



$C_{10}H_{12}BrNO_2$
MW = 258.12 g/mol

Oxalyl chloride (2.39 mL, 3.54 g, 27.9 mmol, 1.20 eq.) was added dropwise to a solution of 2-bromo-4-methylbenzoic acid (5.00 g, 23.3 mmol, 1.00 eq.) in dichloromethane (155 mL) at 0 °C. After addition of catalytically amounts of *N*,*N*-dimethylformamide (5 drops) the mixture was warmed to room temperature. After three hours all volatiles were removed under reduced pressure and the residue was taken up in dichloromethane (155 mL) and cooled to 0 °C. *N*,*O*-dimethylhydroxylamine hydrochloride (2.72 g, 27.9 mmol, 1.20 eq.) and triethylamine (9.72 mL, 7.06 g, 69.8 mmol, 3.00 eq.) was added and the suspension was warmed to room temperature. After 90 minutes the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ solution (200 mL). The aqueous layer was extracted with dichloromethane (3 × 150 mL). The combined organic extracts were washed with brine (200 mL), dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. After column chromatography (silica, P/EtOAc = 4/1 → 1/1), 5.90 g of the title compound (22.8 mmol, 98%) was obtained as a pale yellow oil.

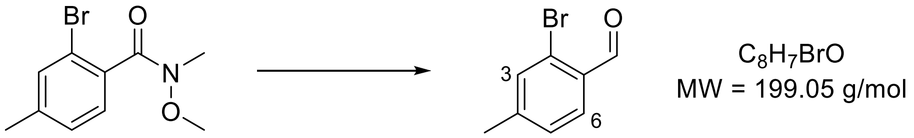
TLC: R_f = 0.47 (P/EtOAc = 2/1) [UV, $KMnO_4$].

Ratio of rotamers: R1/R2 ≈ 73/27.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 2.35 (s, 3 H, C-4-CH_3), 3.12 [*br* s, 0.81 H, O-CH_3(R2)], 3.37 [s, 2.19 H, O-CH_3(R1)], 3.47 [s, 2.19 H, N-CH_3(R1)], 3.89 [*br* s, 0.81 H, N-CH_3(R2)], 7.14 (d, ^3J = 7.2 Hz, 1 H, H-5), 7.20 (d, ^3J = 7.2 Hz, 1 H, H-6), 7.40 (s, 1 H, H-3).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ [ppm] = 21.0 (q, C-4-CH_3), 32.3 (q, N-CH_3), 61.0 (q, O-CH_3), 119.4 (s, C-2), 127.5 (d, C-6), 127.7 (d, C-5), 132.9 (d, C-3), 134.4 (s, C-1), 140.8 (s, C-4), 169.9 (s, CO). The analytical data obtained matched those reported in literature.[5]

2-Bromo-4-methylbenzaldehyde



At – 78 °C di-*iso*-butylaluminium hydride solution (28.6 mL, 1.0 M in dichloromethane, 28.6 mmol, 1.30 eq.) was added to a solution of 2-bromo-*N*-methoxy-*N*,4-dimethylbenzamide (5.67 g, 22.0 mmol, 1.00 eq.) in tetrahydrofuran (40 mL). After one hour the reaction was quenched by addition of methanol (5 mL) and saturated aqueous *Rochelle* salt (Na/K tartrate) solution (200 mL) and the mixture was vigorously stirred at room temperature for 5 h. After separation of the layers the aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. After column chromatography (silica, P/Et_2O = 50/1), 4.23 g of the title compound (21.3 mmol, 97%) was obtained as a colourless solid.

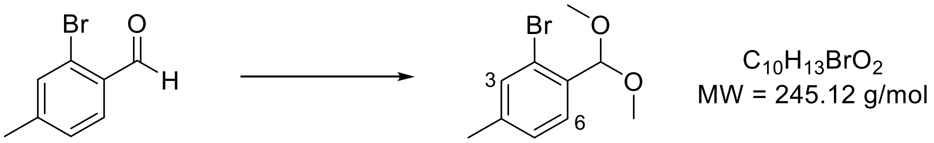
TLC: R_f = 0.65 (P/Et_2O = 10/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 2.40 (s, 3 H, C-4-CH_3), 7.22 (d, ^3J = 7.9 Hz, 1 H, H-5), 7.47 (d, ^4J = 0.9 Hz, 1 H, H-3), 7.81 (d, ^3J = 7.9 Hz, 1 H, H-6), 10.30 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ [ppm] = 20.6 (q, C-4-CH_3), 127.8 (s, C-2), 129.5 (d, C-5), 130.0 (d, C-6), 133.6 (d, C-3), 134.2 (s, C-1), 145.8 (s, C-4), 191.2 (s, CHO).

The analytical data obtained matched those reported in literature.[6]

2-Bromo-1-(dimethoxymethyl)-4-methylbenzene



p-Toluenesulfonic acid (790 mg, 4.15 mmol, 20 mol%) and trimethyl orthoformate (4.54 mL, 4.41 g, 41.5 mmol, 2.00 eq.) were added to a solution of 2-bromo-4-methylbenzaldehyde (4.13 g, 20.8 mmol, 1.00 eq.) in methanol (50 mL). After stirring the reaction mixture for 20 hours under reflux, the reaction was quenched by dropwise addition of saturated aqueous $NaHCO_3$ solution (40 mL) and water (50 mL). The aqueous layer was extracted with dichloromethane (3 × 80 mL), the combined organic layers were washed with brine (150 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. After column chromatography (silica, P/Et_2O = 100/1 → 10:1), 3.80 g of the title compound (15.5 mmol, 75%) was obtained as a colourless oil.

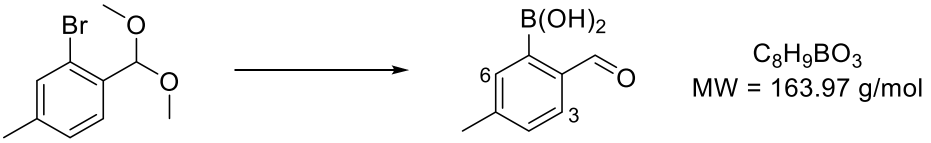
TLC: R_f = 0.50 (P/Et_2O = 10/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 2.32 (s, 3 H, C-4-CH_3), 3.37 (s, 6 H, O-CH_3), 5.53 (s, 1 H, C-1-CH), 7.13 (d, ^3J = 7.9 Hz, 1 H, H-5), 7.39 (s, 1 H, H-3), 7.47 (d, ^3J = 7.9 Hz, 1 H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.0 (q, C-4-*C*H_3), 53.9 (q, O-CH_3), 103.0 (d, C-1-*C*H), 122.8 (s, C-1), 128.1 (d, C-5, C-6), 133.4 (d, C-3), 133.9 (s, C-2), 140.5 (s, C-4).

The compound has been previously reported in the literature.[7]

(2-Formyl-5-methylphenyl)boronic acid



N-Butyllithium solution (8.83 mL, 2.5 M in *n*-hexane, 22.1 mmol, 1.50 eq.) was added dropwise to a solution of 2-bromo-1-(dimethoxymethyl)-4-methylbenzene (3.61 g, 14.7 mmol, 1.00 eq.) in tetrahydrofuran (80 mL) at – 78 °C. After 1.5 hours triethyl borate (5.01 mL, 4.30 g, 29.4 mmol, 2.00 eq.) was added, the mixture was warmed to 0 °C and stirred for 30 minutes, before warming up to room temperature. After further 3 hours the solution was cooled to 0 °C and aqueous 1 M hydrogen chloride solution was added dropwise adjusting the pH value of 3. The mixture was slowly warmed to room temperature and stirred for further 14 hours. The aqueous layer was extracted with diethyl ether (3 × 50 mL), the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude material was purified by recrystallization from water (90 mL). The precipitate was filtered, washed with precooled water (10 mL) and dried under reduced pressure, giving 1.88 g of the title compound (11.4 mmol, 78%) as colourless, crystalline needles.

M.p.: 186 °C.

^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ [ppm] = 2.38 (s, 3 H, C-5-CH_3), 7.36 (dd, ^{3}J = 7.9 Hz, ^{4}J = 1.7 Hz, 1 H, H-4), 7.41 (d, ^{4}J = 1.7 Hz, 1 H, H-6), 7.78 (d, ^{3}J = 7.9 Hz, 1 H, H-3), 8.21 [*br* s, 2 H, $B(OH)_2$], 10.06 (s, 1 H, CHO).

^{13}C NMR (126 MHz, DMSO-d_6, 300 K): δ [ppm] = 21.4 (q, C-5-CH_3), 129.3 (d, C-4), 129.8 (d, C-3), 133.7 (d, C-6), 136.9 (s, C-2), 140.4 (*br* s, C-1), 143.4 (s, C-5), 193.7 (d, CHO).

^{11}B NMR (96 MHz, DMSO-d_6, 300 K): δ [ppm] = 30.9 [*br* s, 1 B, $B(OH)_2$].

The analytical data obtained matched those reported in literature.[8]

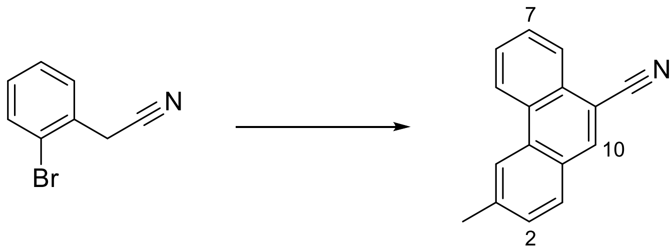
(2-Formyl-4-methylphenyl)boronic acid was synthesized similar to the (2-formyl-5-methylphenyl)boronic acid using 2-bromo-5-methylbenzoic acid as the starting material.

(4-Chloro-2-formylphenyl)boronic acid, (5-fluoro-2-formylphenyl)boronic acid and (2-formylphenyl)boronic acid were commercially available and were used without further purification.

***Suzuki-Miyaura* Coupling/Aldol Condensation Cascade**

Following, the *Suzuki-Miyaura* coupling/aldol condensation cascade is shown on one example following a modified literature procedure.[9] All other substituted phenanthrene-9-carbonitriles were synthesized in a similar manner.

3-Methylphenanthrene-9-carbonitrile



$C_{16}H_{11}N$
MW = 217.27 g/mol

Representative Procedure: Synthesis of phenanthrene-9-carbonitriles:

An Ace pressure tube (100 mL), equipped with a stirring bar, was sequentially loaded with (2-formyl-5-methylphenyl)boronic acid (502 mg, 3.06 mmol, 1.20 eq.), tetrakis(triphenylphosphine)palladium(0) (118 mg, 102 mmol, 4 mol%) and cesium carbonate (2.49 g, 7.65 mmol, 3.00 eq.). The mixture was suspended in toluene/ethanol (12 mL/6 mL) and 2-(2’-bromophenyl)acetonitrile (500 mg, 2.55 mmol, 1.00 eq.) was added. The pressure tube was placed in a pre-heated oil bath (100 °C) and was further warmed up to 125 °C. After 2 hour stirring at 125°C the reaction mixture was cooled to room temperature, diluted with ethyl acetate (15 mL) and filtered through a short Celite pad. The solution was concentrated under reduced pressure and the crude product was purified by column chromatography (silica, P/EtOAc = 25:1). The pale orange solid was further purified by addition of pentane (3 × 4 mL) and decanting the liquid after each addition. The residue was dried under reduced pressure, giving 375 mg of the title compound (1.72 mmol, 68%) as a colourless solid.

M.p.: 148 °C.

TLC: $R_f = 0.66$ (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2977 (w, sp^2-CH), 2853 (w, sp^2-CH), 2853 (w, sp^2-CH), 2218 (s, C≡N), 1620 (m, C=C), 1450 (m, sp^3-CH), 1390 (w), 1198 (w), 900 (m), 761 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 2.66 (s, 3 H, C-3-CH_3), 7.51 (dd, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 1 H, H-2), 7.72 – 7.77 (m, 2 H, H-6, H-7), 8.82 (d, ^3J = 8.1 Hz, 1 H, H-1), 8.20 (s, 1 H, H-10), 8.27 – 8.29 (m, 1 H, H-8), 8.46 (s, 1 H, H-4), 8.67 – 8.71 (m, 1 H, H-5).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 22.6 (q, C-3-$\mathit{C}H_3$), 108.4 (s, C-9), 118.3 (s, CN), 122.8 (d, C-4), 123.2 (d, C-5), 126.2 (d, C-8), 127.9 (s, C-4b*), 128.1 (d, C-6, C-7), 129.2 (s, C-10a*), 129.5 (d, C-1, C-2), 129.8 (s, C-8a*), 132.0 (s, C-4a), 135.7 (d, C-10), 140.4 (s, C-4a).

* assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 217 (100) $[M]^+$, 189 (16), 163 (3), 108 (3), 49 (4).

HRMS (EI, 70 eV): calcd for $C_{16}H_{11}N$ $[M]^+$: 217.0886; found: 217.0879.

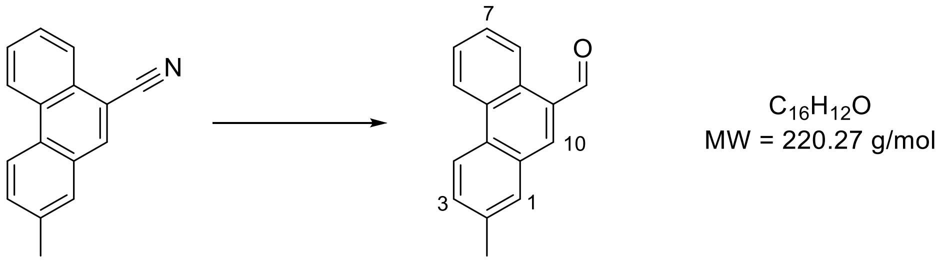
calcd for $C_{15}{}^{13}CH_{11}N$ $[M]^+$: 218.0920; found: 218.0913.

Di-*iso*-butylaluminium hydride reduction of phenanthrene-9-carbonitriles

General Procedure 1: Di-iso-butylaluminium Hydride Reduction

Di-*iso*-butylaluminium hydride solution (1.0 M in dichloromethane, 1.50 eq.) was added to a solution of phenanthrene-9-carbonitrile (1.00 eq.) in dichloromethane (c ≈ 0.03 – 0.05 M) at 0 °C. After TLC analysis showed full conversion of the starting material, saturated aqueous *Rochelle* salt (Na/K tartrate) solution was added and the mixture was warmed to room temperature and stirred for 3 hours. The aqueous layer was extracted with dichloromethane, the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography.

2-Methylphenanthrene-9-carboxaldehyde (1b)



1b

Following the general procedure 1, 2-methylphenanthrene-9-carbonitrile (375 mg, 1.72 mmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (2.59 mL, 1.0 M in dichloromethane, 2.59 mmol, 1.50 eq.) in dichloromethane (50 mL) as the solvent. After six hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (15 mL). Purification by column chromatography (silica, P/Et_2O = 15/1) gave 347 mg of aldehyde **1b** (1.57 mmol, 91%) as an off-white solid.

M.p.: 85 °C.

TLC: R_f = 0.26 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2919 (w, sp^2-CH), 2726 (w, C-HO), 1682 (vs, C=O), 1624 (w, C=C), 1454 (m), 1385 (w), 1066 (m), 758 (s, sp^2-CH), 723 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 2.59 (s, 3 H, C2-CH_3), 7.64 (dd, ^3J = 8.4 Hz, ^4J = 1.9 Hz, 1 H, H-3), 7.70 – 7.73 (m, 2 H, H-6, H-7), 7.81 (s, 1 H, H-1), 8.19 (s, 1 H, H-10), 8.58 (d, ^3J = 8.4 Hz, 1 H, H-4), 8.67 – 8.69 (m, 1 H, H-5), 9.34 – 9.36 (m, 1 H, H-8), 10.38 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.5 (q, C-2-CH_3), 122.7 (d, C-5), 123.0 (d, C-4), 126.1 (d, C-8), 127.7 (d, C-6*), 127.9 (d, C-7*), 128.1 (s, C-10a**), 130.0 (d, C-1), 130.4 (s, C-8a**), 130.7 (s, C-9**), 130.8 (s, C-4b**), 131.0 (s, C-4a**), 132.2 (d, C-3), 137.4 (s, C-2), 141.3 (d, C-10), 193.9 (d, CHO).

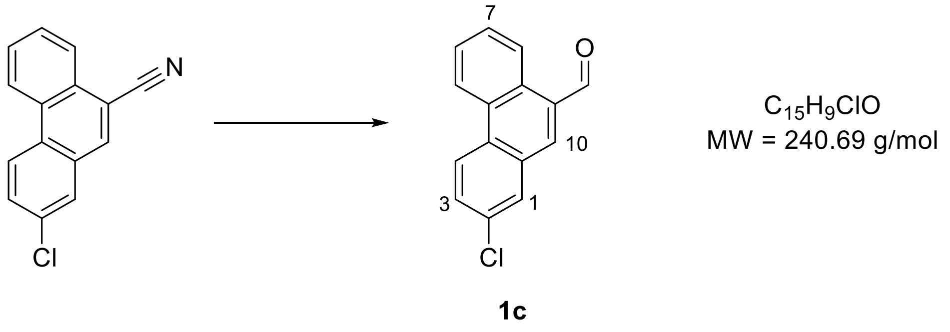
*, ** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 220 (100) [M]$^+$, 205 (18) [M-CH_3]$^+$, 191 (75) [M-CHO]$^+$, 189 (51), 176 (8) [M-C_2H_4O]$^+$, 165 (16), 109 (5), 57 (5).

HRMS (EI, 70 eV): calcd for $C_{16}H_{12}O$ [M]$^+$: 220.0883; found: 220.0881.

calcd for $C_{15}{}^{13}CH_{12}O$ [M]$^+$: 221.0916; found: 221.0912.

2-Chlorophenanthrene-9-carboxaldehyde (1c)



Following the general procedure 1, 2-chlorophenanthrene-9-carbonitrile (369 mg, 1.55 mmol, 1.00 eq.) was dissolved in dichloromethane (50 mL). di-*iso*-butylaluminium hydride solution (3.10 mL, 1.0 M in dichloromethane, 3.10 mmol, 2.00 eq.) was used in. After seven hours further di-*iso*-butylaluminium hydride solution (1.55 mL, 1.0 M in dichloromethane, 1.55 mmol, 1.00 eq.) was added. After 9 hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (20 mL). Purification by column chromatography (silica, P/EtOAc = 25/1) gave 49.8 mg of aldehyde **1c** (207 µmol, 13%) as an off-white solid.

M.p.: 144 °C.

TLC: $R_f = 0.58$ (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2923 (m, sp^2-CH), 2852 (w, sp^2-CH), 2735 (w, C-HO), 1683 (vs, C=O), 1616 (w, C=C), 1452 (m), 1384 (w), 1068 (s, C-Cl), 911 (s), 751 (s, sp^2-CH), 714 (s, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.74 – 7.78 (m, 3 H, H-3, H-6, H-7), 8.03 (d, $^4J = 2.3$ Hz, 1 H, H-1), 8.18 (s, 1 H, H-10), 8.63 (d, $^3J = 8.9$ Hz, 1 H, H-4), 8.64 – 8.68 (m, 1 H, H-5), 9.34 – 9.37 (m, 1 H, H-8), 10.40 (s, 1 H, CHO).

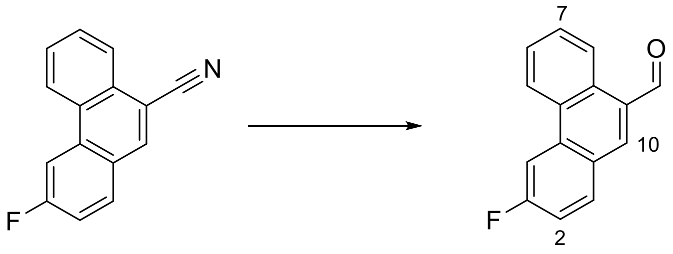
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 122.8 (d, C-5), 124.8 (d, C-4), 126.2 (d, C-8), 128.2 (d, C-6*), 128.3 (s, C-9**), 128.7 (d, C-7*), 129.1 (d, C-1), 130.5 (s, C-2**), 130.7 (d, C-3*), 131.3 (s, C-8a**), 131.4 (s, C-10a**), 131.6 (s, C-4b**), 133.3 (s, C-4a**), 139.7 (d, C-10), 193.5 (d, CHO).

*, ** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 242 (27) [M(^{37}Cl)]$^+$, 240 (84) [M(^{35}Cl)]$^+$, 214 (24) [M(^{37}Cl)-CO]$^+$, 212 (75) [M(^{35}Cl)-CO]$^+$, 176 (100) [M-CHOCl]$^+$, 150 (11), 105 (18), 84 (61), 51 (23), 49 (75).

HRMS (EI, 70 eV): calcd for $C_{15}H_9O^{35}Cl$ [M]$^+$: 240.0336; found: 240.0334.

3-Fluorophenanthrene-9-carboxaldehyde (1d)



1d

$C_{15}H_9FO$
MW = 224.23 g/mol

Following the general procedure 1, 3-fluorophenanthrene-9-carbonitrile (301 mg, 1.36 mmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (2.04 mL, 1.0 M in dichloromethane, 2.04 mmol, 1.50 eq.) in dichloromethane (30 mL) as the solvent. After five hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (10 mL). Purification by column chromatography (silica, P/Et_2O = 15/1) gave 283 mg of aldehyde **1d** (1.26 mmol, 92%) as an off-white solid.

M.p.: 135 °C.

TLC: R_f = 0.47 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3074 (w, sp^2-CH), 2853 (w, sp^2-CH), 2730 (w, C-HO), 1687 (s, C=O), 1622 (s, C=C), 1450 (m), 1233 (m), 1182 (m, C-F), 811 (w), 761 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.39 – 7.47 (m, 1 H, H-2), 7.67 – 7.80 (m, 2 H, H-6, H-7), 8.04 (ddd, ^3J = 8.4 Hz, $^4J_{HF}$ = 6.0 Hz, ^4J = 1.8 Hz, 1 H, H-1), 8.24 (d, ^4J = 1.8 Hz, 1 H, H-10), 8.29 (*virt.* dt, $^3J_{HF}$ = 11.0 Hz, $^4J \approx {}^5J$ = 2.1 Hz, 1 H, H-4), 8.57 (*virt.* dt, ^3J = 8.3 Hz, $^4J \approx {}^5J$ = 1.7 Hz, 1 H, H-8), 9.36 – 9.39 (m, 1 H, H-5), 10.37 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 108.6 (dd, $^2J_{CF}$ = 22.7 Hz, C-4), 116.7 (dd, $^2J_{CF}$ = 24.1 Hz, C-2), 123.1 (d, C-8), 126.2 (d, C-5), 127.0 (d, $^4J_{CF}$ = 2.0 Hz, C-10a), 127.9 (d, C-7), 128.6 (s, C-9), 129.1 (d, C-6), 130.0 (d, $^5J_{CF}$ = 2.5 Hz, C-8a), 130.1 (d, $^4J_{CF}$ = 4.3 Hz, C-4b), 132.9 (dd, $^3J_{CF}$ = 9.5 Hz, C-1), 135.1 (d, $^3J_{CF}$ = 9.0 Hz, C-4a), 140.6 (d, C-10), 164.0 (d, $^1J_{CF}$ = 251.0 Hz, C-3), 193.5 (d, CHO).

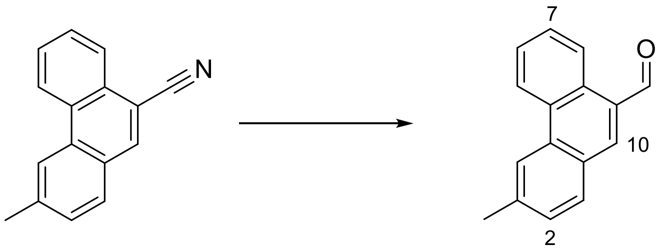
^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = – 107.6 (ddd, $^{3}J_{HF}$ = 11.0 Hz, $^{3}J_{HF}$ = 8.0 Hz, $^{4}J_{HF}$ = 6.0 Hz, 1 F, F-3).

MS (EI, 70 eV): m/z (%) = 224 (100) $[M]^+$, 196 (80) $[M\text{-}CO]^+$, 175 (22), 169 (12), 149 (2), 98 (4), 85 (2), 44 (5).

HRMS (EI, 70 eV): calcd for $C_{15}H_9OF$ $[M]^+$: 224.0632; found: 224.0637.

calcd for $C_{14}{}^{13}CH_9OF$ $[M]^+$: 225.0665; found: 225.0670.

3-Methylphenanthrene-9-carboxaldehyde (1e)



1e

$C_{16}H_{12}O$
MW = 220.27 g/mol

Following the general procedure 1, 3-methylphenanthrene-9-carbonitrile (326 mg, 1.50 mmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (2.25 mL, 1.0 M in dichloromethane, 2.25 mmol, 1.50 eq.) in dichloromethane (60 mL) as the solvent. After 5.5 hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (15 mL). Purification by column chromatography (silica, P/EtOAc = 25/1) gave 214 mg of aldehyde **1e** (1.43 mmol, 95%) as an off-white solid.

M.p.: 101 °C.

TLC: R_f = 0.68 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2981 (w, sp^2-CH), 2727 (w, C-HO), 1686 (vs, C=O), 1619 (m, C=C), 1451 (m), 1386 (w), 1066 (m), 742 (w, sp^2-CH), 724 (w, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 2.67 (s, 3 H, C3-CH_3), 7.51 (dd, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 1 H, H-2), 7.70 – 7.74 (m, 2 H, H-6, H-7), 7.94 (d, ^3J = 8.1 Hz, 1 H, H-1), 8.24 (s, 1 H, H-10), 8.49 (s, 1 H, H-4), 8.70 – 8.72 (m, 1 H, H-5), 9.37 – 9.39 (m, 1 H, H-8), 10.37 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 22.7 (q, C-3-CH_3), 122.8 (d, C-4*), 122.9 (d, C-5*), 126.1 (d, C-8), 127.5 (d, C-7**), 128.2 (s, C-10a), 128.2 (d, C-6**), 128.6 (s, C-8a), 129.2 (d, C-2), 129.8 (s, C-9), 130.4 (d, C-1), 130.4 (s, C-4b), 133.2 (s, C-4a), 140.9 (s, C-3), 141.6 (d, C-10), 193.7 (d, CHO).

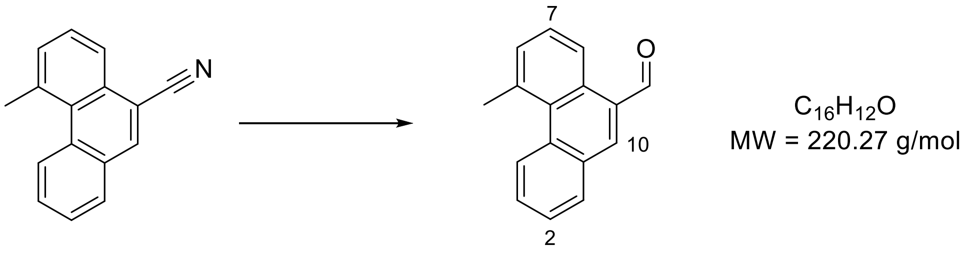
*, ** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 220 (100) $[M]^+$, 205 (4) $[M\text{-}CH_3]^+$, 191 (73) $[M\text{-}CHO]^+$, 189 (49), 176 (6) $[M\text{-}C_2H_4O]^+$, 165 (13), 84 (6), 49 (10).

HRMS (EI, 70 eV): calcd for $C_{16}H_{12}O$ $[M]^+$: 220.0883; found: 220.0880.

calcd for $C_{15}{}^{13}CH_{12}O$ $[M]^+$: 221.0916; found: 221.0913.

5-Methylphenanthrene-9-carboxaldehyde (1f)



1f

Following the general procedure 1, 5-methylphenanthrene-9-carbonitrile (950 mg, 4.37 mmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (6.56 mL, 1.0 M in dichloromethane, 6.56 mmol, 1.50 eq.) in dichloromethane (85 mL) as the solvent. After two hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (30 mL). Purification by column chromatography (silica, P/EtOAc = 30/1) gave 640 mg of aldehyde **1f** (2.91 mmol, 67%) as an off-white solid.

M.p.: 77 °C.

TLC: R_f = 0.35 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057 (w, sp^2-CH), 2877 (w, sp^2-CH), 2730 (w, C-HO), 1685 (vs, C=O), 1618 (m, C=C), 1495 (w), 1454 (m), 1097 (m), 749 (m, sp^2-CH), 722 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 3.13 (s, 3 H, C-5-CH_3), 7.58 – 7.60 (m, 1 H, H-6), 7.61 – 7.62 (m, 1 H, H-7), 7.67 (ddd, ^3J = 8.0 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1 H, H-2), 7.78 (ddd, ^3J = 8.6 Hz, ^3J = 7.0 Hz, ^4J = 1.6 Hz, 1 H, H-3), 8.06 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1 H, H-1), 8.22 (s, 1 H, H-10), 8.84 (d, ^3J = 8.6 Hz, 1 H, H-4), 9.31 (dd, ^3J = 8.0 Hz, ^4J = 1.7 Hz, 1 H, H-8), 10.38 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 27.7 (q, C-5-*C*H_3), 124.0 (d, C-8), 126.7 (d, C-2), 127.5 (d, C-7), 127.9 (d, C-4), 129.2 (d, C-3), 129.9 (s, C-8a), 130.7 (d, C-1), 130.8 (s, C-10a*), 131.0 (s, C-9*), 131.5 (s, C-4b), 132.4 (d, C-6), 134.1 (s, C-4a), 135.5 (s, C-5), 141.9 (d, C-10), 193.7 (d, CHO).

* assignment is interconvertible.

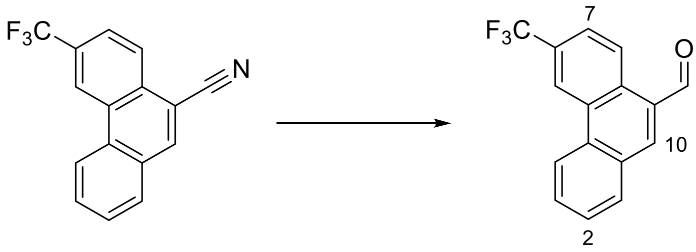
MS (EI, 70 eV): m/z (%) = 220 (100) $[M]^+$, 205 (48) $[M-CH_3]^+$, 191 (91) $[M-CHO]^+$, 189 (77), 176 (12) $[M-C_2H_4O]^+$, 165 (19), 84 (39), 49 (44).

HRMS (EI, 70 eV): calcd for $C_{16}H_{12}O$ $[M]^+$: 220.0883; found: 220.0883.

calcd for $C_{15}{}^{13}CH_{12}O$ $[M]^+$: 221.0916; found: 221.0928.

CHN: calcd for $C_{16}H_{12}O$: C 87.25, H 5.49; found C 87.03, H 5.76.

6-(Trifluoromethyl)phenanthrene-9-carboxaldehyde (1g)



1g

$C_{16}H_9F_3O$
MW = 274.24 g/mol

Following the general procedure 1, 6-(trifluoromethyl)-9-carbonitrile (200 mg, 729 µmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (1.09 mL, 1.0 M in dichloromethane, 1.09 mmol, 1.50 eq.) in dichloromethane (15 mL) as the solvent. After 90 minutes the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (10 mL). Purification by column chromatography (silica, P/EtOAc = 20/1) gave 181 mg of aldehyde **1g** (659 µmol, 90%) as an off-white solid.

M.p.: 98 – 101 °C.

TLC: R_f = 0.49 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2924 (w, sp^2-CH), 2852 (w, sp^2-CH), 2738 (w, C-HO), 1692 (vs, C=O), 1618 (w, C=C), 1388 (m), 1314 (s), 1109 (s, C-F), 830 (m), 750 (m, sp^2-CH).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.76 (ddd, ^3J = 8.1 Hz, ^3J = 7.1 Hz, ^4J = 1.1 Hz, 1 H, H-2), 7.87 – 7.89 (m, 1 H, H-3), 7.91 (dd, ^3J = 8.8 Hz, ^4J = 1.8 Hz, 1 H, H-7), 8.10 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1 H, H-1), 8.38 (s, 1 H, H-10), 8.72 (d, ^3J = 8.5 Hz, 1 H, H-4), 8.96 (d, ^4J = 1.8 Hz, 1 H, H-5), 9.53 (d, ^3J = 8.8 Hz, 1 H, H-8), 10.38 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 120.2 (qd, $^3J_{CF}$ = 4.3 Hz, C-5), 123.2 (d, C-4), 124.3 (qd, $^3J_{CF}$ = 3.4 Hz, C-7), 124.4 (q, $^1J_{CF}$ = 273.2 Hz, C-6-$\mathit{C}F_3$), 127.2 (d, C-8), 128.4 (d, C-2), 129.4 (q, $^2J_{CF}$ = 32.3 Hz, C-6), 130.0 (s, C-8a*), 130.3 (s, C-9*), 130.5 (s, C-10a*), 130.5 (s, C-4b*), 130.8 (d, C-1), 131.1 (d, C-3), 132.7 (s, C-4a), 143.4 (d, C-10), 193.3 (d, CHO).

^{19}F NMR (376 MHz, $CDCl_3$, 300 K): δ [ppm] = – 62.8 (s, 3 F, C6-CF_3).

* assignment is interconvertible.

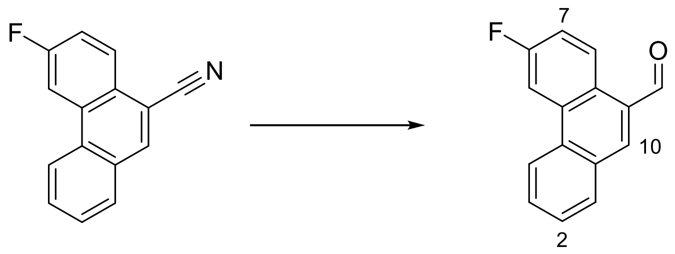
MS (EI, 70 eV): m/z (%) = 274 (100) $[M]^+$, 245 (57) $[M-CHO]^+$, 225 (23), 205 (10) $[M-CF_3]^+$, 176 (21), 150 (2), 57 (4), 43 (4).

HRMS (EI, 70 eV): calcd for $C_{16}H_9OF_3$ $[M]^+$: 274.0600; found: 274.0592.

calcd for $C_{15}{}^{13}CH_9OF_3$ $[M]^+$: 275.0634; found: 275.0639.

CHN: calcd for $C_{16}H_9OF_3$: C 70.08, H 3.31; found C 70.27, H 3.46.

6-Fluorophenanthrene-9-carboxaldehyde (1h)



1h

$C_{15}H_9FO$
MW = 224.23 g/mol

Following the general procedure 1, 6-fluorophenanthrene-9-carbonitrile (478 mg, 2.16 mmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (3.24 mL, 1.0 M in dichloromethane, 3.24 mmol, 1.50 eq.) in dichloromethane (50 mL) as the solvent. After four hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (15 mL). Purification by column chromatography (silica, P/EtOAc = 25/1 → 10/1) gave 89.7 mg of aldehyde **1h** (400 µmol, 19%) as an off-white solid.

M.p.: 114 °C.

TLC: R_f = 0.44 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2981 (w, sp^2-CH), 2853 (w, sp^2-CH), 2738 (w, C-HO), 1676 (s, C=O), 1617 (m, C=C), 1338 (w), 1209 (w), 1188 (s, C-F), 825 (m), 743 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.47 (ddd, ^3J = 9.2 Hz, $^3J_{HF}$ = 7.9 Hz, ^4J = 2.7 Hz, 1 H, H-7), 7.72 (ddd, ^3J = 8.0 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1 H, H-2), 7.83 (ddd, ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1 H, H-3), 8.06 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1 H, H-1), 8.22 (s, 1 H, H-10), 8.30 (dd, $^3J_{HF}$ = 10.9 Hz, ^4J = 2.7 Hz, 1 H, H-5), 8.56 (d, ^3J = 8.4 Hz, 1 H, H-4), 9.43 (dd, ^3J = 9.2 Hz, $^4J_{HF}$ = 6.1 Hz, 1 H, H-8), 10.33 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 108.1 (dd, $^2J_{CF}$ = 22.3 Hz, C-5), 117.1 (dd, $^2J_{CF}$ = 22.8 Hz, C-7), 123.3 (d, C-4), 124.9 (d, $^4J_{CF}$ = 1.9 Hz, C-8a), 128.1 (d, C-2), 128.8 (dd, $^3J_{CF}$ = 8.6 Hz, C-8), 130.3 (s, C-9*), 130.5 (d, C-1**), 130.5 (d, C-3**), 130.6 (s, C-10a*), 132.4 (d, $^4J_{CF}$ = 4.1 Hz, C-4a), 133.0 (d, $^3J_{CF}$ = 8.2 Hz, C-4b), 141.1 (d, C-10), 162.2 (d, $^1J_{CF}$ = 247.9 Hz, C-6), 193.7 (d, CHO).

^{19}F NMR (376 MHz, $CDCl_3$, 300 K): δ [ppm] = – 112.1 (ddd, $^3J_{HF}$ = 10.9 Hz, $^3J_{HF}$ = 7.9 Hz, $^4J_{HF}$ = 6.1 Hz, 1 F, F-6).

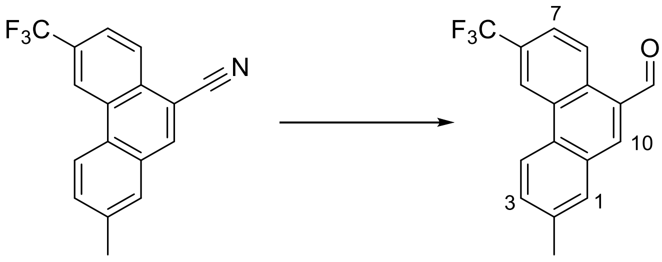
*, ** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 224 (100) $[M]^+$, 205 (2) $[M-F]^+$, 196 (65) $[M-CO]^+$, 175 (18), 169 (9), 149 (3), 98 (3), 43 (4).

HRMS (EI, 70 eV): calcd for $C_{15}H_9OF$ $[M]^+$: 224.0632; found: 224.0633.

calcd for $C_{14}{}^{13}CH_9OF$ $[M]^+$: 225.0665; found: 225.0677.

2-Methyl-6-(trifluoromethyl)phenanthrene-9-carboxaldehyde (1i)



$C_{17}H_{11}F_3O$
MW = 288.27 g/mol

1i

Following the general procedure 1, 2-methyl-6-(trifluoromethyl)phenanthrene-9-carbonitrile (203 mg, 711 µmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (1.07 mL, 1.0 M in dichloromethane, 1.07 mmol, 1.50 eq.) in dichloromethane (30 mL) as the solvent. After 5.5 hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (15 mL). Purification by column chromatography (silica, P/EtOAc = 25/1) gave 132 mg of aldehyde **1j** (457 µmol, 64%) as an off-white solid.

M.p.: 108 °C.

TLC: R_f = 0.48 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926 (w, sp^2-CH), 2857 (w, sp^2-CH), 2730 (w, C-HO), 1688 (s, C=O), 1317 (s), 1115 (vs, C-F), 836 (m), 727 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 2.61 (s, 3 H, C-2-CH_3), 7.69 (dd, ^3J = 8.5 Hz, ^4J = 1.9 Hz, 1 H, H-3), 7.83 (s, 1 H, H-1), 7.87 (dd, ^3J = 8.7 Hz, ^4J = 1.8 Hz, 1 H, H-7), 8.26 (s, 1 H, H-10), 8.56 (d, ^3J = 8.5 Hz, 1 H, H-4), 8.88 (s, 1 H, H-5), 9.48 (d, ^3J = 8.7 Hz, 1 H, H-8), 10.34 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.5 (q, C-2-*C*H_3), 119.9 (qd, $^3J_{CF}$ = 4.2 Hz, C-5), 123.0 (d, C-4), 124.8 (qd, $^3J_{CF}$ = 3.3 Hz, C-7), 124.5 (q, $^1J_{CF}$ = 272.4 Hz, C-6-*C*F_3), 127.1 (d, C-8), 129.3 (q, $^2J_{CF}$ = 32.3 Hz, C-6), 129.9 (s, C-10a*), 130.0 (s, C-4b*), 130.2 (d, C-1), 130.4 (s, C-8a*), 132.8 (s, C-4a*), 130.6 (s, C-9*), 132.8 (d, C-3), 138.4 (s, C-2), 143.2 (d, C-10), 193.3 (d, CHO).

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = – 62.7 (s, 3 F, C-6-CF_3).

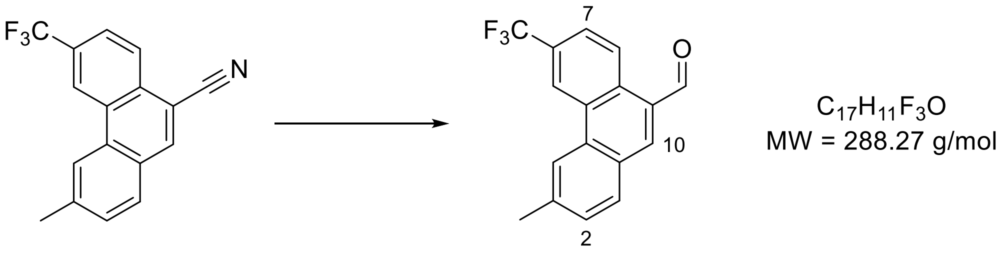
* assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 288 (100) $[M]^+$, 259 (50) $[M\text{-}CHO]^+$, 233 (8), 219 (9) $[M\text{-}CF_3]^+$, 189 (31), 173 (8), 119 (16), 57 (9), 43 (11).

HRMS (EI, 70 eV): calcd for $C_{17}H_{11}OF_3$ $[M]^+$: 288.0757; found: 288.0755.

calcd for $C_{16}{}^{13}CH_{11}OF_3$ $[M]^+$: 289.0790; found: 289.0792.

3-Methyl-6-(trifluoromethyl)phenanthrene-9-carboxaldehyde (1j)



1j

Following the general procedure 1, 3-methyl-6-(trifluoromethyl)phenanthrene-9-carbonitrile (239 mg, 836 µmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (1.25 mL, 1.0 M in dichloromethane, 1.25 mmol, 1.50 eq.) in dichloromethane (25 mL) as the solvent. After 5.5 hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (10 mL). Purification by column chromatography (silica, P/EtOAc = 25/1) gave 205 mg of aldehyde **1j** (710 µmol, 85%) as an off-white solid.

M.p.: 132 – 134 °C.

TLC: R_f = 0.37 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2924 (w, sp^2-CH), 2854 (w, sp^2-CH), 2736 (w, C-HO), 1688 (s, C=O), 1619 (m, C=C), 1317 (s), 1117 (vs, C-F), 1086 (m), 751 (w), 725 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 2.68 (s, 3 H, C-3-CH_3), 7.56 (dd, ^3J = 8.1 Hz, ^4J = 1.7 Hz, 1 H, H-2), 7.87 (dd, ^3J = 8.8 Hz, ^4J = 1.9 Hz, 1 H, H-7), 7.94 (d, ^3J = 8.1 Hz, 1 H, H-1), 8.27 (s, 1 H, H-10), 8.42 (s, 1 H, H-4), 8.88 (s, 1 H, H-5), 9.48 (d, ^3J = 8.8 Hz, 1 H, H-8), 10.31 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 22.7 (q, C-3-$\mathit{C}H_3$), 120.1 (qd, $^3J_{CF}$ = 4.3 Hz, C-5), 122.9 (d, C-4), 124.1 (qd, $^3J_{CF}$ = 3.3 Hz, C-7), 124.5 (q, $^1J_{CF}$ = 272.4 Hz, C-6-$\mathit{C}F_3$), 127.1 (d, C-8), 128.4 (s, C-10a), 129.1 (q, $^2J_{CF}$ = 32.3 Hz, C-6), 129.1 (s, C-4b), 130.0 (s, C-8a), 130.1 (d, C-2), 130.5 (s, C-9), 130.6 (d, C-1), 132.8 (s, C-4a), 141.8 (s, C-3), 143.4 (d, C-10), 193.3 (d, CHO).

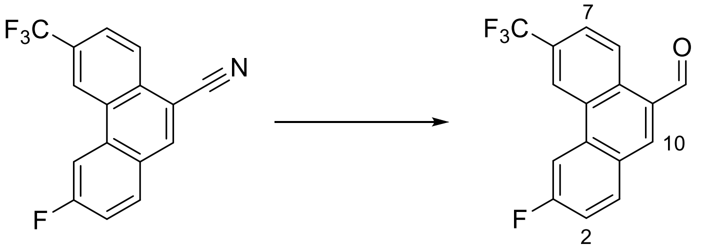
^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = – 62.6 (s, 3 F, C6-CF_3).

MS (EI, 70 eV): m/z (%) = 288 (100) $[M]^+$, 259 (51) $[M\text{-}CHO]^+$, 233 (9), 219 (9) $[M\text{-}CF_3]^+$, 189 (37), 163 (3), 84 (4) $[C_6H_{12}]^+$, 49 (4).

HRMS (EI, 70 eV): calcd for $C_{17}H_{11}OF_3$ $[M]^+$: 288.0757; found: 288.0753.

calcd for $C_{16}{}^{13}CH_{11}OF_3$ $[M]^+$: 289.0790; found: 289.0786.

3-Fluoro-6-(trifluoromethyl)phenanthrene-9-carboxaldehyde (1k)



1k

$C_{16}H_8F_4O$
MW = 292.23 g/mol

Following the general procedure 1, 3-fluoro-6-(trifluoromethyl)phenanthrene-9-carbonitrile (147 mg, 510 µmol, 1.00 eq.) was reduced using di-*iso*-butylaluminium hydride solution (764 µL, 1.0 M in dichloromethane, 764 µmol, 1.50 eq.) in dichloromethane (20 mL) as the solvent. After six hours the reaction was quenched by addition of saturated aqueous *Rochelle* salt (Na/K tartrate) solution (10 mL). Purification by column chromatography (silica, P/EtOAc = 20/1) gave 129 mg of aldehyde **1k** (441 µmol, 87%) as an off-white solid.

M.p.: 145 °C.

TLC: R_f = 0.27 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926 (w, sp^2-CH), 2865 (w, sp^2-CH), 1693 (vs, C=O), 1624 (m, C=C), 1434 (m), 1315 (s), 1145 (s, C-F), 1115 (m, C-F), 841 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.50 (ddd, ^3J = 8.7 Hz, $^3J_{HF}$ = 7.8 Hz, ^4J = 2.4 Hz, 1 H, H-2), 7.94 (dd, ^3J = 8.7 Hz, ^4J = 1.8 Hz, 1 H, H-7), 8.10 (dd, ^3J = 8.7 Hz, $^4J_{HF}$ = 5.8 Hz, 1 H, H-1), 8.30 (dd, $^3J_{HF}$ = 10.6 Hz, ^4J = 2.4 Hz, 1 H, H-4), 8.34 (s, 1 H, H-10), 8.79 (d, ^4J = 1.8 Hz, 1 H, H-5), 9.52 (d, ^3J = 8.7 Hz, 1 H, H-8), 10.35 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 108.8 (dd, $^2J_{CF}$ = 23.1 Hz, C-4), 117.7 (dd, $^2J_{CF}$ = 24.1 Hz, C-2), 120.3 (qd, $^3J_{CF}$ = 4.3 Hz, C-5), 124.3 (q, $^1J_{CF}$ = 124.3 Hz, C-6-*C*F_3), 124.9 (qd, $^3J_{CF}$ = 3.3 Hz, C-7), 127.2 (d, $^4J_{CF}$ = 1.7 Hz, C-10a), 127.3 (d, C-8), 129.4 (d, $^5J_{CF}$ = 2.5 Hz, C-8a), 129.6 (q, $^2J_{CF}$ = 32.5 Hz, C-6), 129.8 (d, $^4J_{CF}$ = 4.2 Hz, C-4b), 130.5 (s, C-9), 133.2 (dd, $^3J_{CF}$ = 9.5 Hz, C-1), 134.8 (d, $^3J_{CF}$ = 9.2 Hz, C-4a), 142.4 (d, C-10), 164.3 (d, $^1J_{CF}$ = 253.0 Hz, C-3), 193.0 (d, CHO).

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = – 106.0 (ddd, $^3J_{HF}$ = 10.6 Hz, $^3J_{HF}$ = 7.8 Hz, $^4J_{HF}$ = 5.7 Hz, 1 F, F-3), – 62.8 (s, 3 F, C-6-CF_3).

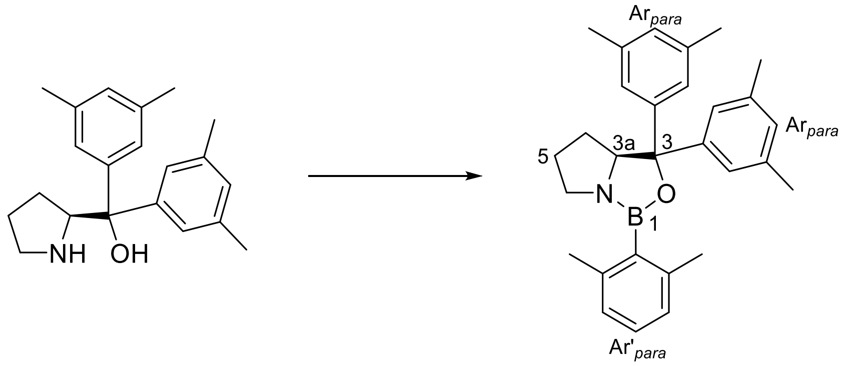
MS (EI, 70 eV): m/z (%) = 292 (100) $[M]^+$, 273 (4) $[M-F]^+$, 263 (61) $[M-CHO]^+$, 243 (24), 223 (10) $[M-CF_3]^+$, 194 (19), 84 (10), 49 (12).

HRMS (EI, 70 eV): calcd for $C_{16}H_8OF_4$ $[M]^+$: 292.0506; found: 292.0498.

calcd for $C_{15}{}^{13}CH_8OF_4$ $[M]^+$: 309.1605; found: 309.1603.

3.3 [2+2] Photocycloaddition Reactions of Irradiation Precursors

Synthesis of the Oxazaborolidine Catalyst



$C_{29}H_{34}BNO$
MW = 423.41 g/mol

In analogy to a literature procedure:[10] A *Schlenk* round-bottom flask, equipped with a *Dean-Stark* apparatus was loaded with (*S*)-bis(3,5-dimethylphenyl)(pyrrolidin-2-yl)methanol[11] (18.6 mg, 60 µmol, 1.00 eq.) and (2,6-dimethylphenyl)boronic acid (9.00 mg, 60 µmol, 1.00 eq.). The apparatus was filled with toluene (25 mL) and the solution was refluxed. After four hours toluene (around 20 mL) was removed by distillation and the flask was refilled with toluene (20 mL). This procedure was repeated a second time after further four hours. After 16 hours toluene was distilled off under argon flow. The flask was sealed and the residual solvent was removed under reduced pressure over night. The oxazaborolidine was obtained as a colourless, viscous oil and used without further purification in the next step. [*Note:* It is necessary to synthesize the oxazaborolidine freshly for every enantioselective photoreaction to avoid decomposition and ensure reproducibility of the results.]

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2918 (m, sp^3-CH), 2870 (m, sp^3-CH), 1598 (s, C=C), 1455 (vs, sp^3-CH), 1269 (s), 862 (m), 744 (m, sp^2-CH).

^{1}H NMR (500 MHz, C_6D_6, 300 K): δ [ppm] = 1.09 (*virt.* dq, ^2J = 11.9 Hz, $^3J \approx {}^3J \approx {}^3J$ = 10.1 Hz, 1 H, *H*H-4), 1.42 – 1.47 (m, 1 H, *H*H-5), 1.50 – 1.58 (m, 2 H, H*H*-4, H*H*-5), 2.14 (s, 6 H, Ar-CH_3), 2.17 (s, 6 H, Ar-CH_3), 2.43 (s, 6 H, Ar'-CH_3), 2.83 (ddd, ^2J = 10.8 Hz, ^3J = 9.7 Hz, ^3J = 5.0 Hz, 1 H, *H*H-6), 3.14 (ddd, ^2J = 10.8 Hz, ^3J = 8.8 Hz, ^4J = 5.3 Hz, 1 H, H*H*-6), 4.41 (dd, ^3J = 10.4 Hz, ^3J = 5.2 Hz, 1 H, H-3a), 6.72 – 6.74 (m, 2 H, Ar$_{para}$-H), 7.01 (d, ^3J = 7.7 Hz, 2 H, Ar'$_{meta}$-H), 7.18 (t, ^3J = 7.7 Hz, 1 H, Ar'$_{para}$-H), 7.38 (*br* s, 2 H, Ar$_{ortho}$-H), 7.54 (*br* s, 2 H, Ar$_{ortho}$-H).

^{13}C NMR (126 MHz, C_6D_6, 300 K): δ [ppm] = 21.6 (q, Ar-CH_3), 21.7 (q, Ar-CH_3), 22.6 (q, Ar'-CH_3), 25.5 (t, C-5), 31.2 (t, C-4), 43.4 (t, C-6), 73.0 (d, C-3a), 88.5 (s, C-3), 124.4 (d, Ar$_{ortho}$-C), 124.5 (d, Ar$_{ortho}$-C), 126.7 (d, Ar'$_{meta}$-C), 128.5 (d, Ar$_{para}$-C), 129.0 (d, Ar'$_{para}$-C), 129.1 (d, Ar$_{para}$-C), 134.0 (*br* s, Ar'$_{ipso}$-C), 137.4 (s, Ar$_{meta}$-C), 137.6 (s, Ar$_{meta}$-C), 141.2 (s, Ar'$_{ortho}$-C), 145.3 (s, Ar$_{ipso}$-C), 148.8 (s, Ar$_{ipso}$-C).

^{11}B NMR (128 MHz, C_6D_6, 300 K): δ [ppm] = 33.9 (*br* s, 1 B, NBO).

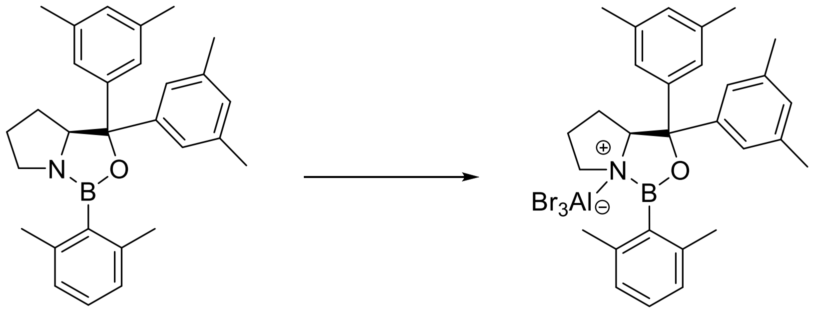
MS (EI, 70 eV): m/z (%) = 423 (34) $[M]^+$, 408 (2) $[M-CH_3]^+$, 318 (4) $[M-C_8H_9]^+$, 291 (15), 223 (100) $[C_{17}H_{19}]^+$, 207 (42), 133 (16), 105 (9) $[C_8H_9]^+$, 91 (85) $[C_7H_7]^+$.

HRMS (EI, 70 eV): calcd for $C_{29}H_{34}ON^{11}B$ $[M]^+$: 423.2728; found: 423.2729.

calcd for $C_{28}{}^{13}CH_{34}ON^{11}B$ $[M]^+$: 424.2762; found: 424.2762.

MS (EI, 70 eV): m/z (%) = 449 (10) $[M]^+$, 434 (1) $[M-CH_3]^+$, 365 (24), 276 (8), 223 (16), 207 (31), 192 (24), 133 (13), 111 (8), 97 (24), 83 (100).

Activation of the Oxazaborolidine Catalyst



$C_{29}H_{34}AlBBr_3NO$
MW = 690.10 g/mol

3c

In analogy to a literature procedure:[10] Aluminum bromide solution solution (50.0 µL, 1.0 M in dibromomethane, 50.0 µmol, 1.00 eq.) was added to a solution of oxazaborolidine (60.0 µmol, 1.20 eq.) in dichloromethane (2 mL). The solution was immediately cooled down to – 78 °C. After 5 minutes stirring an aliquot of the purple solution (0.80 mL, 20 µmol) was transferred to the phototube.

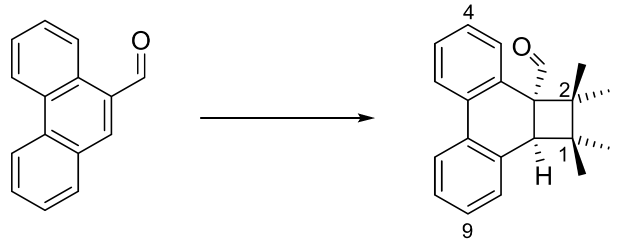
General Procedure 2: Racemic [2+2] Photocycloaddition

The respective phenanthrene-9-carboxaldehyde (100 µmol, 1.00 eq.) was dissolved in dichloromethane (5 mL, c = 20 mM) in a Duran tube and olefin (3.00 mmol, 30.0 eq.) was added. The solution was irradiated at λ = 366 nm until full conversion was observed by TLC analysis. The solvent was removed under reduced pressure and the crude product was purified by column chromatography afford the *ortho* photocycloaddition product beside the oxetane. [*Note:* In most of the cases, only the *ortho* photocycloaddition product was isolated, but TLC analysis and GC/MS analysis showed also the formation of the oxetane).

General Procedure 3: Enantioselective ortho Photocycloaddition

The respective phenanthrene-9-carboxaldehyde (100 µmol, 1.00 eq.) was dissolved in dichloromethane (4.2 mL) in a Schlenk tube and olefin (3.00 mmol, 30.0 eq.) was added. The solution was cooled to – 78 °C. An aliquot of the activated oxazaborolidine catalyst solution (0.80 mL, 20 µmol, 20 mol%, in dichloromethane) was transferred to the reaction mixture. The Schlenk tube was sealed and was irradiated at λ = 457 nm for 24 hours. The reaction was quenched by the addition of triethylamine (100 µL) and was warmed to room temperature. The solvent was removed under reduced pressure and the crude product was purified by column chromatography afford the *ortho* photocycloaddition product.

(2a*S*,10b*S*)-1,1,2,2-Tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2a)



1a **2a**

$C_{21}H_{22}O$
MW = 290.41 g/mol

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1a** (41.2 mg, 200 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (713 µL, 504 mg, 6.00 mmol, 30.0 eq.) were dissolved in dichloromethane (10 mL) and the solution was irradiated for seven hours. Purification by column chromatography (silica, P/Et_2O = 100/1) gave 18.2 mg of *ortho* photocycloaddition product *rac*-**2a** (62.7 µmol, 31%) as an off-white solid beside 4.10 mg of the oxetane *rac*-**8** (14.1 µmol, 7%) as a yellowish oil.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1a** (20.6 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (4.6 mL). An aliquot of the activated oxazaborolidine catalyst solution (0.40 mL, 10 µmol, 10 mol%, in dichloromethane) was transferred to the reaction mixture and the solution was irradiated for 26 hours. Purification by column chromatography (silica, P/Et_2O = 100/1) gave 23.4 mg of *ortho* photocycloaddition product **2a** (80.6 µmol, 81%, 94% *ee*) as a colourless, crystalline solid.

M.p.: 139 °C.

TLC: R_f = 0.51 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057 (w, sp^2-CH), 2969 (m, sp^3-CH), 2823 (w, C-HO), 2725 (w, C-HO), 1699 (s, C=O), 1501 (w), 1440 (m), 1376 (m, sp^3-CH), 755 (s, sp^2-CH), 734 (s, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.58 (s, 3 H, C-1-$CH_{3\beta}$), 0.96 (s, 3 H, C-2-$CH_{3\beta}$), 1.07 (s, 3 H, C-1-$CH_{3\alpha}$), 1.29 (s, 3 H, C-2-$CH_{3\alpha}$), 4.12 (s, 1 H, H-10b), 7.08 (d,

^3J = 7.0 Hz, 1 H, H-10), 7.21 – 7.26* (m, 2 H, H-8, H-9), 7.27 – 7.29 (m, 1 H, H-3), 7.32 – 7.37 (m, 2 H, H-4, H-5), 7.87 (d, ^3J = 7.6 Hz, 1 H, H-7), 7.96 – 7.98 (m, 1 H, H-6), 9.62 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ [ppm] = 21.8 (q, C-1-$CH_{3\beta}$, C-2-$CH_{3\beta}$), 23.9 (q, C-2-$CH_{3\alpha}$), 24.1 (q, C-1-$CH_{3\alpha}$), 42.3 (d, C-10b), 44.3 (s, C-1), 51.1 (s, C-2), 57.7 (s, C-2a), 123.1 (d, C-7), 123.6 (d, C-6), 127.2 (d, C-4**), 127.3 (d, C-5**), 127.7 (d, C-8**), 128.3 (d, C-9**), 129.3 (d, C-10), 130.9 (d, C-3), 131.1 (s, C-6b), 131.7 (s, C-2b***), 132.5 (s, C-10a***), 134.5 (s, C-6a), 200.5 (d, CHO).

* partially overlaid with residual proton signal of chloroform.

, * assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 290 (7) $[M]^+$, 273 (4) $[M-OH]^+$, 215 (6), 206 (100) $[M-C_6H_{12}]^+$, 178 (81) $[M-C_7H_{12}O]^+$, 152 (4), 84 (8) $[C_6H_{12}]^+$, 69 (6).

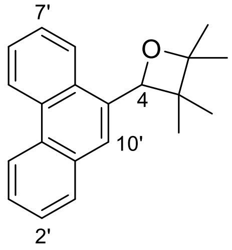
HRMS (EI, 70 eV): calcd for $C_{21}H_{22}O$ $[M]^+$: 290.1665; found: 290.1662.

calcd for $C_{20}{}^{13}CH_{22}O$ $[M]^+$: 291.1699; found: 291.1695.

Chiral HPLC: t_{R1} = 19.7 min, t_{R2} = 20.2 min, [Daicel, Chiralcel OJ-RH, 150 x 4,6 mm, 5 µm, 20 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +30.4 (c = 1.84, $CHCl_3$) [94% *ee*].

2,2,3,3-Tetramethyl-4-(phenanthren-9'-yl)oxetane (*rac*-8)



$C_{21}H_{22}O$
MW = 290.41 g/mol

rac-**8**

TLC: R_f = 0.22 (P/Et_2O = 25/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2957 (m, sp^3-CH), 2923 (m), 1370 (m, sp^3-CH), 1260 (m, C-O-C), 1070 (s, C-O-C), 1017 (s), 802 (s, sp^2-CH), 745 (s, sp^2-CH), 726 (s, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.74 (s, 3 H, C-3-CH_3), 1.41 (s, 3 H, C-2-CH_3), 1.57 (s, 3 H, C-3-CH_3), 1.64 (s, 3 H, C-2-CH_3), 6.14 (s, 1 H, H-4), 7.57 – 7.67 (m, 4 H, H-2', H-3', H-6', H-7'), 7.72 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1 H, H-8'), 7.97 (dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 1 H, H-1'), 8.10 (s, 1 H, H-10'), 8.67 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 1 H, H-4'), 8.75 (dd, ^3J = 8.3 Hz, ^4J = 1.2 Hz, 1 H, H-5').

^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ [ppm] = 19.6 (q, C-3-*C*H_3), 23.9 (q, C-3-*C*H_3), 25.5 (q, C-2-*C*H_3), 25.6 (q, C-2-*C*H_3), 43.9 (s, C-3), 85.2 (d, C-4), 85.5 (s, C-2), 122.6 (d, C-4'), 123.5 (d, C-5'), 123.7 (d, C-8'), 124.2 (d, C-10'), 126.3 (d, C-2'*), 126.5 (d, C-3'*), 126.5 (d, C-6'*), 126.9 (d, C-7'*), 129.1 (d, C-1'), 129.9 (s, C-8a'**), 130.1 (s, C-10a'**), 130.4 (s, C-4a'**), 131.9 (s, C-4b'**), 135.4 (s, C-9').

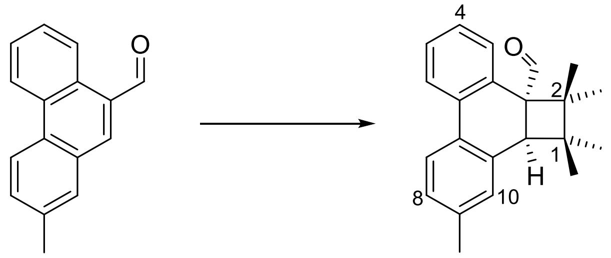
*, ** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 290 (2) $[M]^+$, 232 (14) $[M-C_3H_6O]^+$, 216 (24), 206 (100) $[M-C_6H_{12}]^+$, 178 (50) $[M-C_7H_{12}O]^+$, 151 (9), 108 (3), 84 (40) $[C_6H_{12}]^+$, 69 (29).

HRMS (EI, 70 eV): calcd for $C_{21}H_{22}O$ $[M]^+$: 290.1665; found: 290.1663.

calcd for $C_{20}{}^{13}CH_{22}O$ $[M]^+$: 291.1699; found: 291.1694.

(2a*S*,10b*S*)-1,1,2,2,9-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2b)



$C_{22}H_{24}O$
MW = 304.43 g/mol

1b **2b**

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1b** (22.0 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for eleven hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 8.40 mg of *ortho* photocycloaddition product *rac*-**2b** (27.6 µmol, 28%) as a colourless solid.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1b** (22.0 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 22.8 mg of *ortho* photocycloaddition product **2b** (74.9 µmol, 75%, 84% *ee*) as a colourless, crystalline solid.

M.p.: 142 °C.

TLC: $R_f = 0.56$ (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3059 (w, sp^2-CH), 2956 (m, sp^3-CH), 2716 (w, C-HO), 1712 (vs, C=O), 1614 (w, C=C), 1479 (m), 1377 (m), 1095 (w), 762 (m, sp^3-CH), 729 (m).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.58 (s, 3 H, C-1-$CH_{3\beta}$), 0.96 (s, 3 H, C-2-$CH_{3\beta}$), 1.06 (s, 3 H, C-1-$CH_{3\alpha}$), 1.29 (s, 3 H, C-2-$CH_{3\alpha}$), 2.33 (s, 3 H, C-9-CH_3), 4.07 (s, 1 H, H-10b), 6.89 (s, 1 H, H-10), 7.06 (d, ^3J = 8.3 Hz, 1 H, H-8), 7.27 – 7.28* (m, 1 H, H-3), 7.29 – 7.34 (m, 2 H, H-4, H-5), 7.74 (d, ^3J = 8.3 Hz, 1 H, H-7), 7.93 (dd, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 1 H, H-6), 9.62 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.3 (q, C-9-CH$_3$), 21.8 (q, C-1-CH$_{3β}$, C-2-CH$_{3β}$), 23.9 (q, C-2-CH$_{3α}$), 24.2 (q, C-1-CH$_{3α}$), 42.4 (d, C-10b), 44.3 (s, C-1), 51.1 (s, C-2), 58.0 (s, C-2a), 123.0 (d, C-7), 123.5 (d, C-6), 126.8 (d, C-5**), 127.7 (d, C-4**), 128.1 (d, C-8), 129.1 (s, C-6b), 129.9 (d, C-10), 130.7 (s, C-2b), 130.9 (d, C-3), 132.3 (s, C-10a), 134.7 (s, C-6a), 138.2 (s, C-9), 200.6 (s, CHO).

* partially overlaid with residual proton signal of chloroform.

** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 304 (4) $[M]^+$, 229 (3), 220 (98) $[M-C_6H_{12}]^+$, 192 (100) $[M-C_7H_{12}O]^+$, 165 (7), 84 (8) $[C_6H_{12}]^+$, 69 (7), 41 (4).

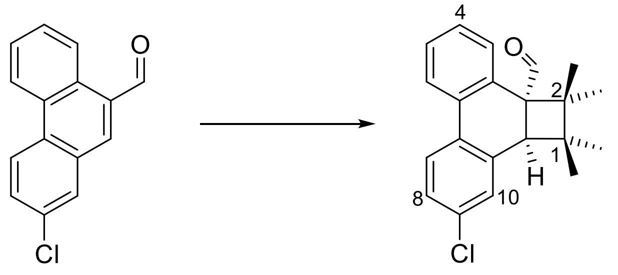
HRMS (EI, 70 eV): calcd for $C_{22}H_{24}O$ $[M]^+$: 304.1822; found: 304.1824.

calcd for $C_{21}{}^{13}CH_{24}O$ $[M]^+$: 305.1855; found: 305.1861.

Chiral HPLC: t_{R1} = 6.4 min, t_{R2} = 20.9 min, [Daicel, Chiralpak OD-RH, 150 x 4,6 mm, 5 µm, 20 °C, 80% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +57.2 (c = 1.15, $CHCl_3$) [84% *ee*].

(2a*S*,10b*S*)-9-Chloro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2c)



1c **2c**

$C_{21}H_{21}ClO$
MW = 324.85 g/mol

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1c** (24.1 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for 20 hours. Purification by column chromatography (silica, P/EtOAc = 300/1) gave 6.20 mg of *ortho* photocycloaddition product *rac*-**2c** (19.1 µmol, 19%) as a colourless solid.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1c** (24.1 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/EtOAc = 300/1) gave 27.5 mg of *ortho* photocycloaddition product **2c** (84.6 µmol, 85%, 88% *ee*) as a colourless, crystalline solid.

M.p.: 174 °C.

TLC: R_f = 0.67 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2978 (m, sp^3-CH), 2718 (w, C-HO), 1713 (vs, C=O), 1601 (m, C=C), 1477 (m), 1393 (s), 1370 (m), 1092 (m), 818 (m), 766 (vs, C-Cl).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.59 (s, 3 H, C-1-$CH_{3\beta}$), 0.96 (s, 3 H, C-2-$CH_{3\beta}$), 1.07 (s, 3 H, C-1-$CH_{3\alpha}$), 1.28 (s, 3 H, C-2-$CH_{3\alpha}$), 4.08 (s, 1 H, H-10b), 7.07 (d,

^4J = 2.3 Hz, 1 H, H-10), 7.22 (dd, ^3J = 8.6 Hz, ^4J = 2.3 Hz, 1 H, H-8), 7.27 – 7.30 (m, 1 H, H-3), 7.33 – 7.37 (m, 2 H, H-4, H-5), 7.78 (d, ^3J = 8.6 Hz, 1 H, H-7), 7.90 – 7.92 (m, 1 H, H-6), 9.61 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.7 (s, C-1-$CH_{3\beta}$, C-2-$CH_{3\beta}$), 23.8 (q, C-2-$CH_{3\alpha}$), 24.2 (q, C-1-$CH_{3\alpha}$), 42.2 (d, C-10b), 44.6 (s, C-1), 51.3 (s, C-2), 57.8 (s, C-2a), 123.8 (d, C-6), 124.6 (d, C-7), 127.4 (d, C-8), 127.6 (d, C-4*), 127.9 (d, C-5*), 128.9 (d, C-10), 130.4 (s, C-9**), 130.9 (s, C-6b**), 130.9 (d, C-3), 133.5 (s, C-2b), 134.0 (s, C-10a), 134.4 (s, C-6a), 200.1 (s, CHO).

*, ** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 326 (2) $[M(^{37}Cl)]^+$, 324 (5) $[M(^{35}Cl)]^+$, 242 (16) $[M(^{37}Cl)\text{-}C_6H_{12}]^+$, 240 (53) $[M(^{35}Cl)\text{-}C_6H_{12}]^+$, 214 (30) $[M(^{37}Cl)\text{-}C_7H_{12}O]^+$, 212 (100) $[M(^{35}Cl)\text{-}C_7H_{12}O]^+$, 176 (35) $[M\text{-}C_7H_{13}OCl]^+$, 151 (4), 84 (63) $[C_6H_{12}]^+$, 69 (28), 41 (10).

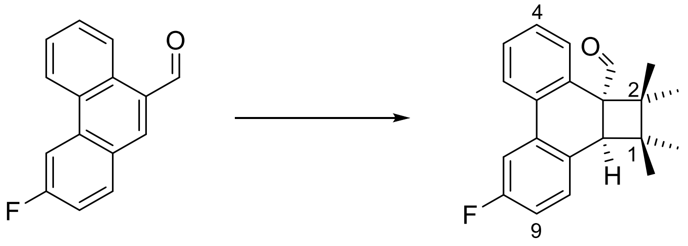
HRMS (EI, 70 eV): calcd for $C_{21}H_{21}O^{35}Cl$ $[M]^+$: 324.1275; found: 324.1287.

calcd for $C_{20}{}^{13}CH_{21}O^{35}Cl$ $[M]^+$: 325.1309; found: 325.1299.

Chiral HPLC: t_{R1} = 24.8 min, t_{R2} = 28.7 min, [Daicel, Chiralcel OD-RH, 150 x 4,6 mm, 5 µm, 20 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +39.3 (c = 2.44, $CHCl_3$) [88% *ee*].

(2a*S*,10b*S*)-8-Fluoro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2d)



1d **2d**

$C_{21}H_{21}FO$
MW = 308.40 g/mol

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1d** (22.4 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for eight hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 15.8 mg of *ortho* photocycloaddition product *rac*-**2d** (51.2 µmol, 51%) as a colourless solid.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1d** (22.4 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 24.1 mg of *ortho* photocycloaddition product **2d** (78.1 µmol, 78%, 93% *ee*) as a colourless solid.

M.p.: 134 °C.

TLC: R_f = 0.59 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2957 (w, sp^3-CH), 2869 (w, sp^3-CH), 2717 (w, C-HO), 1714 (vs, C=O), 1610 (m, C=C), 1500 (s), 1443 (m), 1164 (s, C-F), 840 (m), 770 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.56 (s, 3 H, C-1-$CH_{3\beta}$), 0.96 (s, 3 H, C-2-$CH_{3\beta}$), 1.05 (s, 3 H, C-1-$CH_{3\alpha}$), 1.29 (s, 3 H, C-2-$CH_{3\alpha}$), 4.10 (s, 1 H, H-10b), 6.94 (*virt.* td, $^3J \approx {}^3J_{HF}$ = 8.2 Hz, ^4J = 2.6 Hz, 1 H, H-9), 7.04 (dd, ^3J = 8.4 Hz, $^4J_{HF}$ = 6.0 Hz, 1 H, H-10), 7.29 – 7.31 (m, 1 H, H-3), 7.35 – 7.39 (m, 2 H, H-4, H-5), 7.54 (dd, $^3J_{HF}$ = 11.1 Hz, ^4J = 2.6 Hz, 1 H, H-7), 7.85 – 7.88 (m, 1 H, H-6), 9.62 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.7 (q, C-2-$CH_{3\beta}$*), 21.8 (q, C-1-$CH_{3\beta}$*), 23.8 (q, C-2-$CH_{3\alpha}$), 24.1 (q, C-1-$CH_{3\alpha}$), 41.8 (d, C-10b), 44.4 (s, C-1), 51.3 (s, C-2), 58.0 (s, C-2a), 109.9 (dd, $^2J_{CF}$ = 22.8 Hz, C-7), 115.2 (dd, $^2J_{CF}$ = 21.6 Hz, C-9), 124.0 (d, C-6), 127.9 (d, C-4, C-5), 128.1 (d, $^4J_{CF}$ = 2.9 Hz, C-10a**), 130.6 (dd, $^3J_{CF}$ = 8.1 Hz, C-10), 130.9 (d, C-3), 131.3 (s, C-2b), 133.6 (d, $^4J_{CF}$ = 2.5 Hz, C-6a**), 133.7 (d, $^3J_{CF}$ = 7.6 Hz, C-6b), 162.5 (d, $^1J_{CF}$ = 242.8 Hz, C-8), 200.3 (d, CHO).

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = –116.2 (ddd, $^3J_{HF}$ = 11.1 Hz, $^3J_{HF}$ = 8.1 Hz, $^4J_{HF}$ = 6.0 Hz, 1 F, F-8).

MS (EI, 70 eV): m/z (%) = 308 (2) $[M]^+$, 291 (3) $[M\text{-}OH]^+$, 224 (40) $[M\text{-}C_6H_{12}]^+$, 196 (100) $[M\text{-}C_7H_{12}O]^+$, 175 (4), 84 (24) $[C_6H_{12}]^+$, 69 (16), 41 (7).

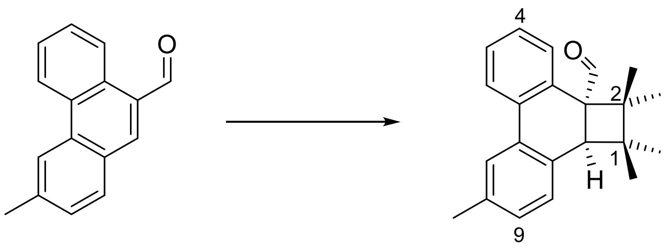
HRMS (EI, 70 eV): calcd for $C_{21}H_{21}OF$ $[M]^+$: 308.1571; found: 308.1570.

calcd for $C_{20}{}^{13}CH_{21}OF$ $[M]^+$: 309.1605; found: 309.1603.

Chiral HPLC: t_{R1} = 6.9 min, t_{R2} = 10.6 min, [Daicel, Chiralpak OD-RH, 150 x 4,6 mm, 5 µm, 20 °C, 80% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +45.5 (c = 2.33, $CHCl_3$) [93% *ee*].

(2a*S*,10b*S*)-1,1,2,2,8-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2e)



1e **2e**

$C_{22}H_{24}O$
MW = 304.43 g/mol

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1e** (22.0 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for 10 hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 17.7 mg of *ortho* photocycloaddition product *rac*-**2e** (58.1 µmol, 58%) as a colourless oil.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1e** (22.0 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 20.1 mg of *ortho* photocycloaddition product **2e** (66.0 µmol, 66%, 92% *ee*) as a colourless oil.

TLC: R_f = 0.51 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2924 (s, sp^3-CH), 2853 (m, sp^3-CH), 2715 (w, C-HO), 1714 (vs, C=O), 1600 (w, C=C), 1443 (m), 1370 (m), 1096 (m), 771 (m, sp^3-CH), 731 (m, sp^3-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.57 (s, 3 H, C-1-$CH_{3\beta}$), 0.95 (s, 3 H, C-2-$CH_{3\beta}$), 1.05 (s, 3 H, C-1-$CH_{3\alpha}$), 1.28 (s, 3 H, C-2-$CH_{3\alpha}$), 2.37 (s, 3 H, C-8-CH_3), 4.08 (s, 1 H, H-10b), 6.98 (d, ^3J = 7.7 Hz, 1 H, H-10), 7.05 (dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1 H, H-9), 7.26 – 7.28* (m, 1 H, H-3), 7.30 – 7.36 (m, 2 H, H-4, H-5), 7.68 (s, 1 H, H-7), 7.97 (dd, ^3J = 7.0 Hz, ^4J = 2.2 Hz, 1 H, H-6), 9.62 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.7 (q, C-8-*C*H_3), 21.8 (q, C-1-*C*$H_{3\beta}$, C-2-*C*$H_{3\beta}$), 23.9 (q, C-2-*C*$H_{3\alpha}$), 24.2 (q, C-1-*C*$H_{3\alpha}$), 42.1 (d, C-10b), 44.2 (s, C-1), 51.1 (s, C-2), 57.9 (s, C-2a), 123.7 (d, C-6**), 123.8 (d, C-7**), 127.1 (d, C-4***), 127.7 (d, C-5***), 129.2 (d, C-9, C-10), 129.4 (s, C-6b****), 131.0 (d, C-3), 131.2 (s, C-10a****), 131.5 (s, C-6a****), 134.6 (s, C-2b), 136.6 (s, C-8), 200.7 (d, CHO).

* partially overlaid with residual proton signal of chloroform.

, *, **** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 304 (4) $[M]^+$, 290 (18), 275 (51) [M-CHO], 259 (19), 220 (99) $[M\text{-}C_6H_{12}]^+$, 192 (100) $[M\text{-}C_7H_{12}O]^+$, 165 (12), 84 (11) $[C_6H_{12}]^+$, 69 (14), 41 (15).

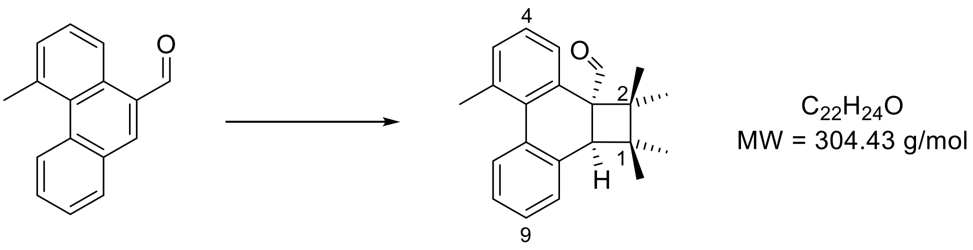
HRMS (EI, 70 eV): calcd for $C_{22}H_{24}O$ $[M]^+$: 304.1822; found: 304.1822.

calcd for $C_{21}{}^{13}CH_{24}O$ $[M]^+$: 305.1855; found: 305.1863.

Chiral HPLC: t_{R1} = 20.5 min, t_{R2} = 21.2 min, [Daicel, Chiralcel OJ-RH, 150 x 4,6 mm, 5 µm, 20 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +54.9 (c = 0.95, $CHCl_3$) [92% *ee*].

(2a*S*,10b*S*)-1,1,2,2,6-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2f)



1f **2f**

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1f** (22.0 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for 11 hours. Purification by column chromatography (silica, P/Et_2O = 100/1) gave 12.9 mg of *ortho* photocycloaddition product *rac*-**2f** (42.4 µmol, 42%) as an off-white solid.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1f** (22.0 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/Et_2O = 100/1) gave 26.0 mg of *ortho* photocycloaddition product **2f** (85.4 µmol, 85%, 86% *ee*) as a colourless solid.

M.p.:110 °C.

TLC: R_f = 0.45 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2972 (s, sp^3-CH), 2928 (s, sp^3-CH), 2716 (w, C-HO), 1712 (vs, C=O), 1594 (w, C=C), 1446 (vs), 1378 (m), 1098 (m), 757 (s, sp^3-CH), 724 (s, sp^3-CH).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.63 (s, 3 H, C-1-$CH_{3\beta}$), 0.79 (s, 3 H, C-2-$CH_{3\beta}$), 1.08 (s, 3 H, C-1-$CH_{3\alpha}$), 1.27 (s, 3 H, C-2-$CH_{3\alpha}$), 2.72 (s, 3 H, C-6-CH_3), 4.07 (s, 1 H, H-10b), 7.12 – 7.16 (m, 2 H, H-9, H-10), 7.19 – 7.24 (m, 4 H, H-3, H-4, H-5, H-8), 7.70 – 7.74 (m, 1 H, H-7), 9.72 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.8 (q, C-1-$CH_{3\beta}$, C-2-$CH_{3\beta}$), 24.1 (q, C-2-$CH_{3\alpha}$), 24.5 (q, C-1-$CH_{3\alpha}$), 25.2 (q, C-6-CH_3), 43.5 (d, C-10b), 43.6 (s, C-1), 51.8 (s, C-2), 58.4 (s, C-2a), 125.9 (d, C-4*), 126.3 (d, C-5*), 127.5 (d, C-8*), 128.9 (d, C-7, C-9**), 129.8 (d, C-10**), 131.9 (d, C-3*), 133.3 (s, C-6b***), 133.4 (s, C-10a***), 134.1 (s, C-6a***), 135.3 (s, C-2b***), 136.1 (s, C-6***), 201.1 (d, CHO).

*, **, *** assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 304 (4) $[M]^+$, 275 (6) [M-CHO], 259 (5), 220 (100) $[M-C_6H_{12}]^+$, 205 (37), 192 (81) $[M-C_7H_{12}O]^+$, 165 (11), 84 (41) $[C_6H_{12}]^+$, 69 (78), 41 (77).

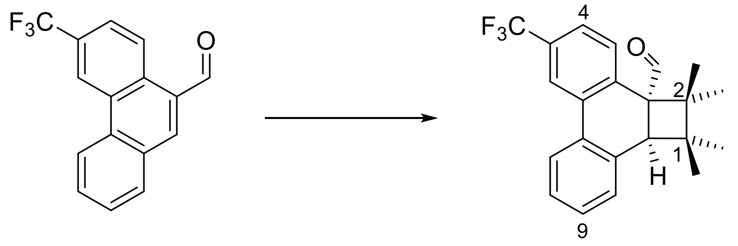
HRMS (EI, 70 eV): calcd for $C_{22}H_{24}O$ $[M]^+$: 304.1822; found: 304.1820.

calcd for $C_{21}{}^{13}CH_{24}O$ $[M]^+$: 305.1855; found: 305.1854.

Chiral HPLC: t_{R1} = 20.4 min, t_{R2} = 21.5 min, [Daicel, Chiralcel OJ-RH, 150 x 4,6 mm, 5 µm, 20 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +37.2 (c = 2.35, $CHCl_3$) [86% *ee*].

(2a*S*,10b*S*)-1,1,2,2-Tetramethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2g)



C$_{22}$H$_{21}$F$_3$O
MW = 358.40 g/mol

1g **2g**

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1g** (27.4 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for eight hours. Purification by column chromatography (silica, P/Et$_2$O = 100/1) gave 21.1 mg of *ortho* photocycloaddition product *rac*-**2g** (58.9 µmol, 59%) as an off-white solid.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1g** (27.4 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/EtOAc = 100/1) gave 32.8 mg of *ortho* photocycloaddition product **2g** (91.5 µmol, 92%, 92% *ee*) as a colourless solid.

M.p.: 112 °C.

TLC: R_f = 0.66 (P/EtOAc = 10/1) [UV, KMnO$_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2928 (m, sp^3-CH), 2720 (w, C-HO), 1718 (s, C=O), 1617 (w, C=C), 1498 (w), 1335 (vs), 1126 (s, C-F), 840 (w), 742 (m, sp^2-CH).

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ [ppm] = 0.56 (s, 3 H, C-1-CH$_{3\beta}$), 0.96 (s, 3 H, C-2-CH$_{3\beta}$), 1.09 (s, 3 H, C-1-CH$_{3\alpha}$), 1.32 (s, 3 H, C-2-CH$_{3\alpha}$), 4.16 (s, 1 H, H-10b), 7.10 – 7.12 (m, 1 H, H-10), 7.26 – 7.33 (m, 2 H, H-8, H-9), 7.40 (d, ^3J = 8.1 Hz, 1 H, H-3), 7.58 (dq,

^3J = 8.1 Hz, $^4J_{HF}$ = 0.6 Hz, 1 H, H-4), 7.87 – 7.90 (m, 1 H, H-7), 8.19 (s, 1 H, H-6), 9.64 (s, 1 H, CHO).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ [ppm] = 21.8 (q, C-2-*C*H$_{3\beta}$*), 21.9 (q, C-1-*C*H$_{3\beta}$*), 23.9 (q, C-2-*C*H$_{3\alpha}$), 24.2 (q, C-1-*C*H$_{3\alpha}$), 42.4 (d, C-10b), 44.7 (s, C-1), 52.1 (s, C-2), 58.0 (s, C-2a), 120.6 (qd, $^3J_{CF}$ = 3.7 Hz, C-6), 123.2 (d, C-7), 123.6 (qd, $^3J_{CF}$ = 3.7 Hz, C-4), 124.3 (q, $^1J_{CF}$ = 271.9 Hz, C-5-*C*F$_3$), 127.6 (d, C-8**), 129.3 (d, C-9**), 129.4 (d, C-10), 130.0 (q, $^2J_{CF}$ = 32.3 Hz, C-5), 130.4 (s, C-2b***), 131.3 (d, C-3), 132.5 (s, C-10a***), 135.1 (s, C-6b***), 135.4 (s, C-6a***), 200.0 (d, CHO).

^{19}F NMR (376 MHz, CDCl$_3$, 300 K): δ [ppm] = –63.3 (s, 3 F, C-5-CF$_3$).

MS (EI, 70 eV): m/z (%) = 358 (2) [M]$^+$, 329 (9) [M-CHO]$^+$, 274 (75) [M-C$_6$H$_{12}$]$^+$, 246 (100) [M-C$_7$H$_{12}$O]$^+$, 225 (19), 176 (17), 84 (92) [C$_6$H$_{12}$]$^+$, 69 (44) [CF$_3$]$^+$, 40 (33).

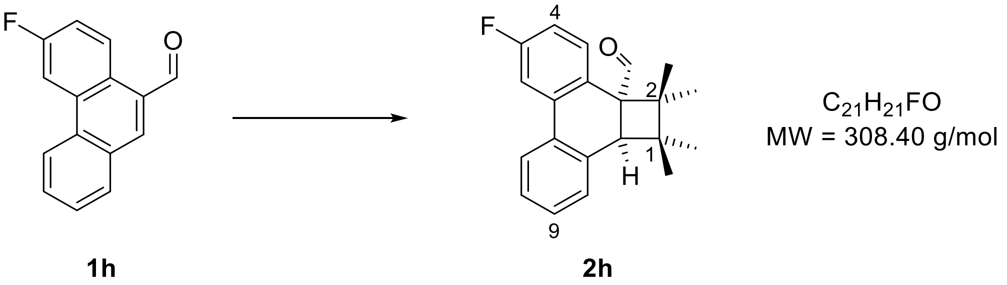
HRMS (EI, 70 eV): calcd for $C_{22}H_{21}OF_3$ [M]$^+$: 358.1539; found: 358.1538.

CHN: calcd for $C_{22}H_{21}OF_3$: C 73.73, H 5.91; found C 73.60, H 5.95.

Chiral HPLC: t_{R1} = 20.3 min, t_{R2} = 20.7 min, [Daicel, Chiralcel OJ-RH, 150 x 4,6 mm, 5 µm, 20 °C, 20% MeCN/H$_2$O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +38.9 (c = 2.01, CHCl$_3$) [92% *ee*].

(2a*S*,10b*S*)-5-Fluoro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2h)



Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1h** (22.4 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for eight hours. Purification by column chromatography (silica, P/Et_2O = 300/1) gave 16.1 mg of *ortho* photocycloaddition product *rac*-**2h** (52.2 µmol, 52%) as a colourless, crystalline solid.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1h** (22.4 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/Et_2O = 300/1) gave 23.1 mg of *ortho* photocycloaddition product **2h** (74.9 µmol, 75%, 82% *ee*) as a colourless, crystalline solid.

M.p.: 143 °C.

TLC: R_f = 0.68 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958 (m, sp^3-CH), 2927 (m, sp^3-CH), 2717 (w, C-HO), 1714 (vs, C=O), 1606 (w, C=C), 1495 (s), 1336 (w), 1193 (m, C-F), 867 (m), 770 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.57 (s, 3 H, C-1-$CH_{3\beta}$), 0.95 (s, 3 H, C-2-$CH_{3\beta}$), 1.07 (s, 3 H, C-1-$CH_{3\alpha}$), 1.29 (s, 3 H, C-2-$CH_{3\alpha}$), 4.12 (s, 1 H, H-10b), 7.04 (*virt.* td, $^3J \approx {}^3J_{HF}$ = 8.2 Hz, ^4J = 2.7 Hz, 1 H, H-4), 7.08 – 7.10 (m, 1 H, H-10**), 7.23 – 7.25* (m, 1 H, H-3), 7.26 – 7.28* (m, 2 H, H-8, H-9**), 7.64 (dd, $^3J_{HF}$ = 11.0 Hz, ^4J = 2.7 Hz, 1 H, H-6), 7.76 – 7.78 (m, 1 H, H-7), 9.60 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.8 (q, C-1-$CH_{3β}$, C-2-$CH_{3β}$), 23.8 (q, C-2-$CH_{3α}$), 24.2 (q, C-1-$CH_{3α}$), 42.5 (d, C-10b), 44.4 (s, C-1), 51.1 (s, C-2), 57.3 (s, C-2a), 110.7 (dd, $^2J_{CF}$ = 22.8 Hz, C-6), 114.2 (dd, $^2J_{CF}$ = 21.6 Hz, C-4), 123.3 (d, C-7), 126.8 (d, $^4J_{CF}$ = 3.0 Hz, C-6b**), 127.4 (d, C-9***), 129.0 (d, C-8***), 129.3 (d, C-10***), 130.9 (d, $^4J_{CF}$ = 2.3 Hz, C-2b**), 132.4 (dd, $^3J_{CF}$ = 8.4 Hz, C-3), 132.6 (s, C-10a), 136.9 (d, $^3J_{CF}$ = 7.6 Hz, C-6a), 162.7 (d, $^1J_{CF}$ = 245.4 Hz, C-5), 200.2 (d, CHO).

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = –115.1 (ddd, $^3J_{HF}$ = 11.0 Hz, $^3J_{HF}$ = 7.8 Hz, $^4J_{HF}$ = 6.0 Hz, 1 F, F-5).

* partially overlaid with residual proton signal of chloroform.

, * assignment is interconvertible.

MS (EI, 70 eV): m/z (%) = 308 (3) $[M]^+$, 263 (2), 233 (5), 224 (66) $[M-C_6H_{12}]^+$, 196 (100) $[M-C_7H_{12}O]^+$, 175 (6), 84 (28) $[C_6H_{12}]^+$, 69 (15), 40 (7).

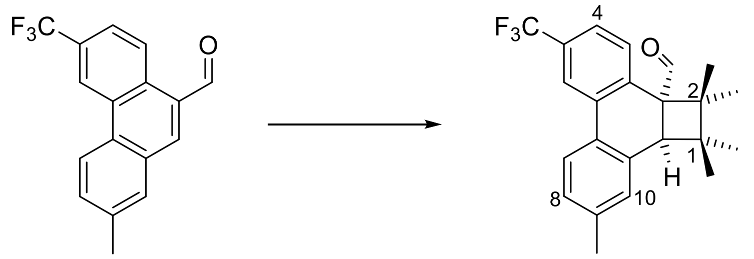
HRMS (EI, 70 eV): calcd for $C_{21}H_{21}OF$ $[M]^+$: 308.1571; found: 308.1570.

calcd for $C_{20}{}^{13}CH_{21}OF$ $[M]^+$: 309.1605; found: 309.1605.

Chiral HPLC: t_{R1} = 8.3 min, t_{R2} = 12.0 min, [Daicel, Chiralpak OD-RH, 150 x 4,6 mm, 5 µm, 20 °C, 80% $MeCN/H_2O$ (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +26.8 (c = 2.76, $CHCl_3$) [82% *ee*].

(2a*S*,10b*S*)-1,1,2,2,9-Pentamethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2i)



1i **2i**

$C_{23}H_{23}F_3O$
MW = 372.43 g/mol

<u>Racemic [2+2] Photocycloaddition</u>

Following General Procedure 2, substrate **1i** (28.8 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for eight hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 19.4 mg of *ortho* photocycloaddition product *rac*-**2i** (52.1 µmol, 52%) as a colourless solid.

<u>Enantioselective *ortho* Photocycloaddition</u>

Following General Procedure 3, substrate **1i** (28.8 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 33.0 mg of *ortho* photocycloaddition product **2i** (88.6 µmol, 89%, 90% *ee*) as a colourless solid.

M.p.: 134 °C.

TLC: R_f = 0.72 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958 (m, sp^3-CH), 2870 (w, sp^3-CH), 2718 (w, C-HO), 1716 (s, C=O), 1615 (w, C=C), 1595 (w), 1335 (s), 1124 (vs, C-F), 835 (w), 760 (w, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.57 (s, 3 H, C-1-CH$_{3\beta}$), 0.96 (s, 3 H, C-2-CH$_{3\beta}$), 1.08 (s, 3 H, C-1-CH$_{3\alpha}$), 1.30 (s, 3 H, C-2-CH$_{3\alpha}$), 2.35 (s, 3 H, C-9-CH$_3$), 4.10 (s, 1 H, H-10b), 6.91 (s, 1 H, H-10), 7.10 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1 H, H-8), 7.38 (d, ^3J = 8.1 Hz, 1 H, H-3), 7.54 (dd, ^3J = 8.1 Hz, ^4J = 0.9 Hz, 1 H, H-4), 7.76 (d, ^3J = 8.2 Hz, 1 H, H-7), 8.15 (s, 1 H, H-6), 9.62 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.3 (q, C-9-CH_3), 21.8 (q, C-1-$CH_{3\beta}$, C-2-$CH_{3\beta}$), 23.9 (q, C-2-$CH_{3\alpha}$), 24.2 (q, C-1-$CH_{3\alpha}$), 42.4 (d, C-10b), 44.6 (s, C-1), 51.9 (s, C-2), 58.1 (s, C-2a), 120.2 (qd, $^3J_{CF}$ = 3.9 Hz, C-6), 123.1 (qd, $^3J_{CF}$ = 3.7 Hz, C-4), 123.3 (d, C-7), 124.4 (q, $^1J_{CF}$ = 272.2 Hz, C-5-CF_3), 127.8 (s, C-6b), 128.5 (d, C-8), 129.9 (q, $^2J_{CF}$ = 32.3 Hz, C-5), 130.0 (d, C-10), 131.2 (d, C-3), 132.4 (s, C-10a), 134.7 (s, C-2b), 135.6 (s, C-6a), 139.3 (s, C-9), 200.0 (s, CHO).

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = –63.2 (s, 3 F, C5-CF_3).

MS (EI, 70 eV): m/z (%) = 372 (2) $[M]^+$, 343 (4) $[M\text{-}CHO]^+$, 288 (52) $[M\text{-}C_6H_{12}]^+$, 260 (43) $[M\text{-}C_7H_{12}O]^+$, 189 (10), 119 (18), 84 (100) $[C_6H_{12}]^+$, 69 (41) $[CF_3]^+$.

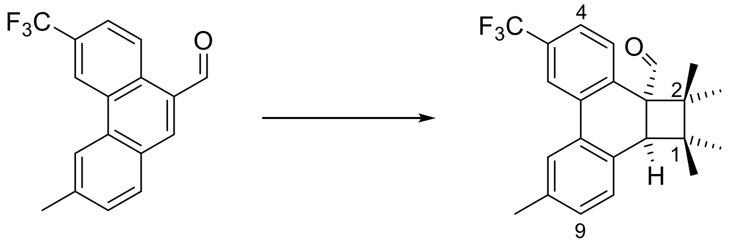
HRMS (EI, 70 eV): calcd for $C_{23}H_{23}OF_3$ $[M]^+$: 372.1696; found: 372.1689.

calcd for $C_{22}{}^{13}CH_{23}OF_3$ $[M]^+$: 373.1729; found: 373.1723.

Chiral HPLC: t_{R1} = 23.7 min, t_{R2} = 24.3 min, [Daicel, Chiralcel OD-RH, 150 x 4,6 mm, 20 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +33.6 (c = 2.20, $CHCl_3$) [90% *ee*].

(2a*S*,10b*S*)-1,1,2,2,8-Pentamethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2j)



1j **2j**

$C_{23}H_{23}F_3O$
MW = 372.43 g/mol

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1j** (28.8 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for 12 hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 17.2 mg of *ortho* photocycloaddition product *rac*-**2j** (46.2 µmol, 46%) as a colourless solid.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1j** (28.8 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 34.6 mg of *ortho* photocycloaddition product **2j** (92.9 µmol, 93%, 92% *ee*) as a colourless solid.

M.p.: 141 °C.

TLC: R_f = 0.70 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958 (m, sp^3-CH), 2718 (w, C-HO), 1714 (s, C=O), 1670 (w, C=C), 1509 (w), 1336 (m), 1126 (vs, C-F), 840 (w), 760 (w, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.55 (s, 3 H, C-1-$CH_{3\beta}$), 0.96 (s, 3 H, C-2-$CH_{3\beta}$), 1.07 (s, 3 H, C-1-$CH_{3\alpha}$), 1.31 (s, 3 H, C-2-$CH_{3\alpha}$), 2.40 (s, 3 H, C-8-CH_3), 4.12 (s, 1 H, H-10b), 7.00 (d, ^3J = 7.6 Hz, 1 H, H-10), 7.11 (dd, ^3J = 7.6 Hz, ^4J = 2.0 Hz, 1 H, H-9), 7.39 (d,

^{3}J = 8.2 Hz, 1 H, H-3), 7.56 (dd, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, 1 H, H-4), 7.68 (s, 1 H, H-7), 8.18 (s, 1 H, H-6), 9.63 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.6 (q, C-8-CH_3), 21.8 (q, C-1-$CH_{3\beta}$, C-2-$CH_{3\beta}$), 23.9 (q, C-2-$CH_{3\alpha}$), 24.2 (q, C-1-$CH_{3\alpha}$), 42.2 (d, C-10b), 44.5 (s, C-1), 51.9 (s, C-2), 58.0 (s, C-2a), 120.4 (qd, $^{3}J_{CF}$ = 4.0 Hz, C-6), 123.4 (qd, $^{3}J_{CF}$ = 3.7 Hz, C-4), 123.9 (d, C-7), 124.4 (q, $^{1}J_{CF}$ = 272.3 Hz, C-5-CF_3), 129.3 (d, C-10), 129.5 (s, C-6b), 129.9 (q, $^{2}J_{CF}$ = 32.1 Hz, C-5), 130.1 (d, C-9), 130.2 (s, C-10a), 131.3 (d, C-3), 135.2 (s, C-2b), 135.5 (s, C-6a), 137.1 (s, C-8), 200.1 (s, CHO).

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = –63.2 (s, 3 F, C5-CF_3).

MS (EI, 70 eV): m/z (%) = 372 (1) $[M]^+$, 343 (4) $[M-CHO]^+$, 288 (50) $[M-C_6H_{12}]^+$, 260 (44) $[M-C_7H_{12}O]^+$, 189 (11), 109 (3), 84 (100) $[C_6H_{12}]^+$, 69 (31) $[CF_3]^+$.

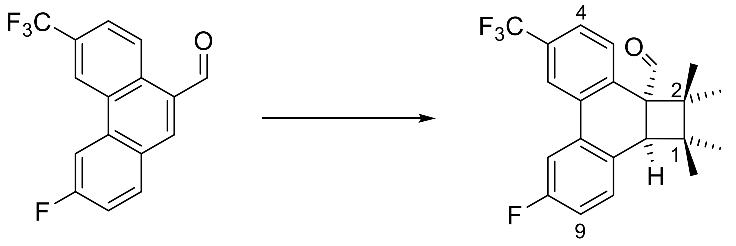
HRMS (EI, 70 eV): calcd for $C_{23}H_{23}OF_3$ $[M]^+$: 372.1696; found: 372.1684.

calcd for $C_{22}{}^{13}CH_{23}OF_3$ $[M]^+$: 373.1729; found: 373.1713.

Chiral HPLC: t_{R1} = 20.7 min, t_{R2} = 21.1 min, [Daicel, Chiralcel OJ-RH, 10 x 4,6 mm, 20 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +29.8 (c = 2.75, $CHCl_3$) [92% *ee*].

(2a*S*,10b*S*)-8-Fluoro-1,1,2,2-tetramethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2k)



1k **2k**

$C_{22}H_{20}F_4O$
MW = 376.39 g/mol

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1k** (17.0 mg, 58.1 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (207 µL, 147 mg, 1.75 mmol, 30.0 eq.) were dissolved in dichloromethane (2.91 mL) and the solution was irradiated for 11 hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 12.3 mg of *ortho* photocycloaddition product *rac*-**2k** (32.7 µmol, 56%) as a colourless solid.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1k** (29.2 mg, 100 µmol, 1.00 eq.) and 2,3-dimethyl-2-butene (357 µL, 252 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/Et_2O = 100/1) gave 31.9 mg of *ortho* photocycloaddition product **2k** (84.8 µmol, 85%, 96% *ee*) as a colourless, crystalline solid.

M.p.: 117 °C.

TLC: R_f = 0.33 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960 (m, sp^3-CH), 2872 (w, sp^3-CH), 2719 (w, C-HO), 1716 (s, C=O), 1614 (w, C=C), 1507 (w), 1335 (m), 1127 (vs, C-F), 840 (w), 760 (w, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.55 (s, 3 H, C-1-$CH_{3\beta}$), 0.96 (s, 3 H, C-2-$CH_{3\beta}$), 1.07 (s, 3 H, C-1-$CH_{3\alpha}$), 1.31 (s, 3 H, C-2-$CH_{3\alpha}$), 4.14 (s, 1 H, H-10b), 7.00 (*virt.* td,

$^3J \approx {}^3J_{HF}$ = 8.2 Hz, ^4J = 2.5 Hz, 1 H, H-9), 7.08 (dd, ^3J = 8.4 Hz, $^4J_{HF}$ = 6.0 Hz, 1 H, H-10), 7.42 (d, ^3J = 8.1 Hz, 1 H, H-3), 7.56 (dd, $^3J_{HF}$ = 10.7 Hz, ^4J = 2.5 Hz, 1 H, H-7), 7.61 (dq, ^3J = 8.1 Hz, $^4J_{HF}$ = 0.9 Hz, 1 H, H-4), 8.07 – 8.08 (m, 1 H, H-6), 9.62 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.8 (q, C-2-$\mathit{C}H_{3\beta}$*), 21.8 (q, C-1-$\mathit{C}H_{3\beta}$*), 23.8 (q, C-2-$\mathit{C}H_{3\alpha}$), 24.1 (q, C-1-$\mathit{C}H_{3\alpha}$), 41.8 (d, C-10b), 44.7 (s, C-1), 52.1 (s, C-2), 58.1 (s, C-2a), 110.2 (dd, $^2J_{CF}$ = 23.3 Hz, C-7), 116.2 (dd, $^2J_{CF}$ = 21.5 Hz, C-9), 120.8 (qd, $^3J_{CF}$ = 3.8 Hz, C-6), 124.2 (q, $^1J_{CF}$ = 272.3 Hz, C-5-$\mathit{C}F_3$), 124.3 (qd, $^3J_{CF}$ = 3.6 Hz, C-4), 128.2 (d, $^4J_{CF}$ = 2.9 Hz, C-10a), 130.2 (q, $^2J_{CF}$ = 32.5 Hz, C-5), 130.8 (dd, $^3J_{CF}$ = 8.1 Hz, C-10), 131.3 (d, C-3), 132.4 (d, $^3J_{CF}$ = 7.5 Hz, C-6b), 134.4 (d, $^4J_{CF}$ = 2.4 Hz, C-6a), 135.3 (s, C-2b), 162.6 (d, $^1J_{CF}$ = 244.1 Hz, C-8), 199.6 (s, CHO).

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ [ppm] = −115.3 (ddd, $^3J_{HF}$ = 10.7 Hz, $^3J_{HF}$ = 8.1 Hz, $^4J_{HF}$ = 6.0 Hz, 1 F, F-8), − 63.3 (s, 3 F, C-5-CF_3).

MS (EI, 70 eV): m/z (%) = 376 (1) $[M]^+$, 347 (4) $[M\text{-}CHO]^+$, 292 (38) $[M\text{-}C_6H_{12}]^+$, 264 (46) $[M\text{-}C_7H_{12}O]^+$, 243 (13), 194 (14), 84 (100) $[C_6H_{12}]^+$, 69 (41).

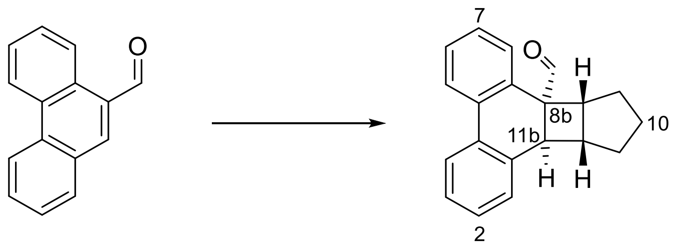
HRMS (EI, 70 eV): calcd for $C_{22}H_{20}OF_4$ $[M]^+$: 376.1445; found: 376.1443.

calcd for $C_{21}{}^{13}CH_{20}OF_4$ $[M]^+$: 377.1478; found: 377.1480.

Chiral HPLC: t_{R1} = 20.6 min, t_{R2} = 21.1 min, [Daicel, Chiralcel OJ-RH, 150 x 4,6 mm, 5 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

Specific Rotation: $[\alpha]_D^{25}$ = +34.6 (c = 2.84, $CHCl_3$) [96% *ee*].

(8b*R*,8c*R*,11a*S*,11b*S*)-8c,9,10,11,11a,11b-Hexahydro-8b*H*-cyclopenta[3,4]cyclobuta[1,2-*l*]phenanthrene-8b-carboxaldehyde (4a)



1a **4a**

$C_{20}H_{18}O$
MW = 274.36 g/mol

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1a** (20.6 mg, 100 µmol, 1.00 eq.) and cyclopentene (275 µL, 204 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for eight hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 7.6 mg of *ortho* photocycloaddition product *rac*-**4b** (27.7 µmol, 28%, d.r. 12/88) as a colourless oil.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1a** (20.6 mg, 100 µmol, 1.00 eq.) and cyclopentene (275 µL, 204 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 12.7 mg of *ortho* photocycloaddition product **4a** (46.4 µmol, 46%, 96% *ee*, d.r. 93/7) as a colourless solid.

M.p.: 106 – 108 °C.

TLC: R_f = 0.57 (P/Et_2O = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3066 (w, sp^3-CH), 2950 (m, sp^3-CH), 2854 (w, C-HO), 2720 (w, C-HO), 1713 (vs, C=O), 1489 (w), 1448 (m), 1167, 752 (s, sp^2-CH), 730 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.44 (*virt.* ddt, ^2J = 13.3 Hz, ^3J = 10.9 Hz, $^3J \approx {}^3J$ = 6.9 Hz, 1 H, *H*H-11), 1.57 – 1.66 (m, 1 H, *H*H-9), 1.81 – 1.87 (m, 2 H, *H*H-10, H*H*-11), 1.97 – 2.07 (m, 2 H, H*H*-9, H*H*-10), 2.90 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 7.0 Hz, 1 H, H-11a), 3.01

(*virt.* t, $^{3}J \approx {}^{3}J$ = 7.6 Hz, 1 H, H-8c), 3.79 (d, ^{3}J = 7.4 Hz, 1 H, H-11b), 7.10 (dd, ^{3}J = 7.4 Hz, ^{4}J = 1.6 Hz, 1 H, H-1), 7.22 (*virt.* td, $^{3}J \approx {}^{3}J$ = 7.4 Hz, ^{4}J = 1.4 Hz, 1 H, H-2), 7.25 – 7.28* (m, 1 H, H-3), 7.34 – 7.41 (m, 2 H, H-6, H-7), 7.52 (dd, ^{3}J = 7.4 Hz, ^{4}J = 1.7 Hz, 1 H, H-8), 7.87 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.4 Hz, 1 H, H-4), 7.96 (dd, ^{3}J = 7.7 Hz, ^{4}J = 1.7 Hz, 1 H, H-5), 9.72 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 25.6 (t, C-10), 27.6 (t, C-9), 31.1 (t, C-11), 37.9 (d, C-11b), 45.8 (d, C-11a), 52.6 (s, C-8b), 56.3 (d, C-8c), 123.1 (d, C-4), 123.4 (d, C-5), 127.3 (d, C-3), 127.6 (d, C-6**), 128.3 (d, C-1**), 128.4 (d, C-2**), 128.4 (d, C-7**), 129.0 (d, C-8), 130.3 (s, C-4a), 132.8 (s, C-4b), 135.1 (s, C-8a), 135.8 (s, C-11c), 200.5 (d, CHO).

* partially overlaid with residual proton signal of chloroform.

** assignment is interconvertible.

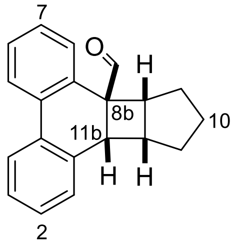
MS (EI, 70 eV): m/z (%) = 274 (11) $[M]^+$, 244 (29), 229 (33), 215 (30), 206 (83) $[M-C_5H_8]^+$, 178 (100) $[M-C_6H_8O]^+$, 152 (6), 67 (5) $[C_5H_7]^+$.

HRMS (EI, 70 eV): calcd for $C_{20}H_{18}O$ $[M]^+$: 274.1352; found: 274.1348.

calcd for $C_{19}{}^{13}CH_{18}O$ $[M]^+$: 275.1386; found: 275.1385.

Chiral HPLC: t_{D1R1} = 15.5 min, t_{D1R2} = 21.9 min; t_{D2R1} = 16.2 min, t_{D2R2} = 22.8 min [Daicel, Chiralpak OD-RH, 150 x 4,6 mm, 5 µm, 20 °C, 80% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

*(8bSR,8cRS,11aSR,11bRS)-8c,9,10,11,11a,11b-Hexahydro-8bH-cyclopenta[3,4]cyclobuta[1,2-l]phenanthrene-8b-carboxaldehyde (rac-**4b**)*



rac-**4b**

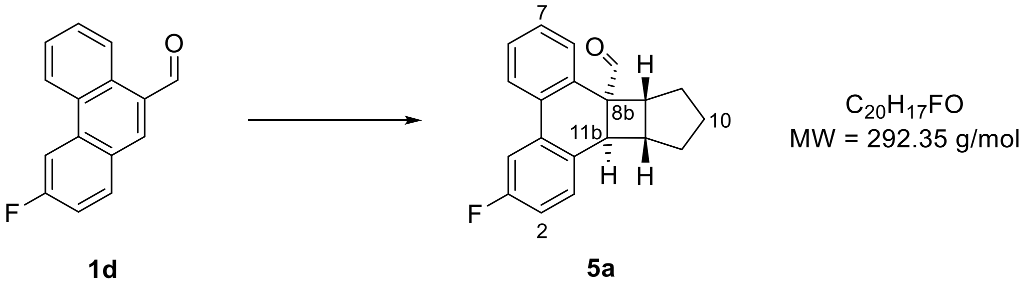
^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ [ppm] = 0.90 – 0.95 (m, 1 H, *H*H-10), 1.26 – 1.32 (m, 2 H, *H*H-9, H*H*-10), 1.33 – 1.41 (m, 1 H, *H*H-11), 1.43 – 1.48 (m, 2 H, H*H*-9, H*H*-11), 3.20 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 8.4 Hz, 1 H, H-11a), 3.51 (*virt.* t, $^3J \approx {}^3J$ = 7.4 Hz, 1 H, H-8c), 4.24 (d, ^3J = 10.2 Hz, 1 H, H-11b), 6.90 (dd, ^3J = 7.3 Hz, ^4J = 1.7 Hz, 1 H, H-8), 6.97 – 6.99 (m, 1 H, H-1), 7.24 – 7.26* (m, 2 H, H-2, H-3), 7.28* (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, ^4J = 1.5 Hz, 1 H, H-7), 7.28 (*virt.* td, $^3J \approx {}^3J$ = 7.8 Hz, ^4J = 1.7 Hz, 1 H, H-6), 7.89 – 7.91 (m, 1 H, H-4), 7.96 (d, ^3J = 7.9 Hz, 1 H, H-5), 9.76 (s, 1 H, CHO).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ [ppm] = 26.2 (t, C-10), 27.7 (t, C-9), 28.8 (t, C-11), 35.8 (d, C-11b), 42.4 (d, C-11a), 46.3 (d, C-8c), 53.6 (s, C-8b), 122.9 (d, C-4), 123.5 (d, C-5), 127.1 (d, C-3**), 128.0 (d, C-2**), 128.1 (d, C-6**), 128.2 (d, C-7**), 128.9 (s, C-11c***), 129.9 (d, C-1, C-8), 131.3 (s, C-4a), 132.5 (s, C-8a), 133.1 (s, C-4b***), 200.5 (d, CHO).

* partially overlaid with residual proton signal of chloroform.

, * assignment is interconvertible.

(8b*R*,8c*R*,11a*S*,11b*S*)-3-Fluoro-8c,9,10,11,11a,11b-hexahydro-8b*H*-cyclopenta[3,4]cyclobuta[1,2-*l*]phenanthrene-8b-carboxaldehyde (5a)



Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1d** (22.4 mg, 100 µmol, 1.00 eq.) and cyclopentene (275 µL, 204 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for 10 hours. Purification by column chromatography (silica, P/Et_2O = 200/1) gave 11.8 mg of *ortho* photocycloaddition product *rac*-**5b** (40.4 µmol, 40%, d.r. 9/91) as a colourless oil.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1d** (22.4 mg, 100 µmol, 1.00 eq.) and cyclopentene (275 µL, 204 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 17.2 mg of *ortho* photocycloaddition product **5a** (59.0 µmol, 59%, 98% *ee*, d.r. 93/7) as a colourless oil.

TLC: R_f = 0.67 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2951 (s, sp^3-CH), 2856 (m, sp^3-CH), 2716 (w, C-HO), 1714 (s, C=O), 1603 (m, C=C), 1499 (s), 1444 (m), 1185 (vs, C-F), 865 (m, sp^2-CH), 768 (vs, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.39 – 1.47 (m, 1 H, *H*H-11), 1.59 – 1.66 (m, 1 H, *H*H-9), 1.80 – 1.87 (m, 2 H, *H*H-10, H*H*-11), 1.96 – 2.05 (m, 2 H, H*H*-9, H*H*-10), 2.90 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 7.0 Hz, 1 H, H-11a), 3.01 (*virt.* t, $^3J \approx {}^3J$ = 8.0 Hz, 1 H, H-8c), 3.79 (d, ^3J = 7.4 Hz, 1 H, H-11b), 6.92 (*virt.* td, $^3J \approx {}^3J_{HF}$ = 8.4 Hz, ^4J = 2.7 Hz, 1 H, H-2), 7.05 (dd,

^3J = 8.3 Hz, $^4J_{HF}$ = 6.0 Hz, 1 H, H-1), 7.37 (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, ^4J = 1.4 Hz, 1 H, H-6), 7.42 (*virt.* td, $^3J \approx {}^3J$ = 7.5 Hz, ^4J = 1.5 Hz, 1 H, H-7), 7.51 – 7.54 (m, 2 H, H-4, H-8), 7.85 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1 H, H-5), 9.71 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 25.7 (t, C-10), 27.6 (t, C-9), 31.1 (t, C-11), 37.3 (d, C-11b), 46.0 (d, C-11a), 52.9 (s, C-8b), 56.5 (d, C-8c), 110.0 (dd, $^2J_{CF}$ = 22.9 Hz, C-4), 115.3 (dd, $^2J_{CF}$ = 21.4 Hz, C-2), 123.7 (d, C-5), 127.9 (d, C-6), 129.1 (d, C-8*), 129.2 (d, C-7*), 129.8 (dd, $^3J_{CF}$ = 8.1 Hz, C-1), 131.6 (d, $^4J_{CF}$ = 2.9 Hz, C-11c), 132.0 (d, $^4J_{CF}$ = 2.4 Hz, C-4b), 132.5 (d, $^3J_{CF}$ = 7.6 Hz, C-4a), 135.3 (s, C-8a), 162.5 (d, $^1J_{CF}$ = 243.2 Hz, C-3), 200.4 (d, CHO).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ [ppm] = –116.0 (ddd, $^3J_{\mathrm{HF}}$ = 11.0 Hz, $^3J_{\mathrm{HF}}$ = 8.1 Hz, $^4J_{\mathrm{HF}}$ = 6.0 Hz, 1 F, F-3).

* assignment is interconvertible.

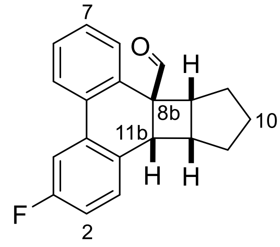
MS (EI, 70 eV): m/z (%) = 292 (9) $[M]^+$, 274 (4), 262 (8), 247 (7), 233 (12), 224 (100) $[M-C_5H_8]^+$, 196 (66), 175 (6).

HRMS (EI, 70 eV): calcd for $C_{20}H_{17}O$ $[M]^+$: 292.1258; found: 292.1262.

calcd for $C_{19}{}^{13}CH_{17}O$ $[M]^+$: 293.1291; found: 293.1296.

Chiral HPLC: t_{D1R1} = 26.5 min, t_{D1R2} = 29.5 min; t_{D2R1} = 26.8 min, t_{D2R2} = 27.1 min [Daicel, Chiralcel OD-RH, 150 x 4,6 mm, 5 µm, 20 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

*(8bSR,8cRS,11aSR,11bRS)-3-Fluoro-8c,9,10,11,11a,11b-hexahydro-8bH-cyclopenta[3,4]cyclobuta[1,2-l]phenanthrene-8b-carboxaldehyde (rac-**5b**)*



$C_{20}H_{17}FO$
MW = 292.35 g/mol

rac-**5b**

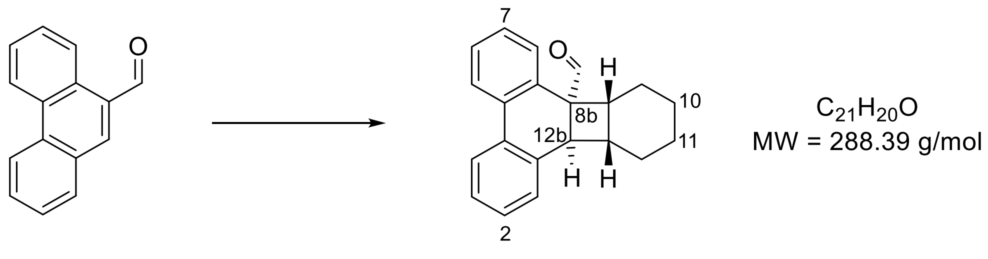
^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ [ppm] = 0.84 – 0.93 (m, 1 H, *H*H-10), 1.27 – 1.47 (m, 5 H, H-9, H*H*-10, H-11), 3.18 (*virt.* q, $^{3}J \approx {}^{3}J \approx {}^{3}J$ = 8.1 Hz, 1 H, H-11a), 3.49 (*virt.* t, $^{3}J \approx {}^{3}J$ = 7.1 Hz, 1 H, H-8c), 4.22 (d, ^{3}J = 10.1 Hz, 1 H, H-11b), 6.92 – 6.96 (m, 3 H, H-1, H-2, H-8), 7.30 – 7.36 (m, 2 H, H-6, H-7), 7.55 – 7.58 (m, 1 H, H-4), 7.84 – 7.86 (m, 1 H, H-5), 9.76 (s, 1 H, CHO).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ [ppm] = 26.2 (t, C-10), 27.6 (t, C-9*), 28.7 (t, C-11*), 35.1 (d, C-11b), 42.3 (d, C-11a), 46.6 (d, C-8c), 53.6 (s, C-8b), 109.7 (dd, $^{2}J_{CF}$ = 22.9 Hz, C-4), 115.2 (dd, $^{2}J_{CF}$ = 21.5 Hz, C-2), 123.7 (d, C-5), 128.1 (d, $^{4}J_{CF}$ = 3.1 Hz, C-11c), 128.2 (d, C-6**), 128.6 (d, C-7**), 129.2 (s, C-8a), 129.9 (d, C-8), 131.3 (dd, $^{3}J_{CF}$ = 8.1 Hz, C-1), 132.2 (d, $^{4}J_{CF}$ = 2.3 Hz, C-4b), 133.4 (d, $^{3}J_{CF}$ = 7.5 Hz, C-4a), 162.2 (d, $^{1}J_{CF}$ = 243.3 Hz, C-3), 199.5 (d, CHO).

^{19}F NMR (376 MHz, CDCl$_3$, 298 K): δ [ppm] = −116.1 – −116.0 (m, 1 F, F-3).

*,** assignment is interconvertible.

(8b*R*,8c*R*,12a*S*,12b*S*)-9,10,11,12,12a,12b-hexahydrobenzo[3,4]cyclobuta[1,2-*l*]phenanthrene-8b(8c*H*)-carbaldehyde (6a)



1a **6a**

Racemic [2+2] Photocycloaddition

Following General Procedure 2, substrate **1a** (20.6 mg, 100 µmol, 1.00 eq.) and cyclohexene (304 µL, 246 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (5 mL) and the solution was irradiated for 16 hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 8.90 mg of *ortho* photocycloaddition product *rac*-**6b**/*rac*-**6c** (30.9 µmol, 31%, d.r. *rac*-**6a**/*rac*-**6b**/*rac*-**6c** = 21/35/44) as an off-white oil.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1a** (20.6 mg, 100 µmol, 1.00 eq.) and cyclohexene (304 µL, 246 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 20.1 mg of *ortho* photocycloaddition product **6a** (69.7 µmol, 70%, 90% *ee*, d.r. 87/10/3) as a colourless oil.

TLC: R_f = 0.78 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2929 (vs, sp^3-CH), 2856 (m, sp^3-CH), 2707 (w, C-HO), 1713 (vs, C=O), 1487 (m), 1450 (s), 1085 (w), 758 (s, sp^2-CH), 735 (vs, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.95 – 1.04 (m, 1 H, *H*H-10), 1.25 – 1.33 (m, 1 H, *H*H-12), 1.53 – 1.56 (m, 1 H, *H*H-11), 1.61 – 1.71 (m, 4 H, *H*H-9, H*H*-10, H*H*-11, H*H*-12), 2.01 (ddd, ^2J = 15.9 Hz, ^3J = 8.6 Hz, ^3J = 4.5 Hz, 1 H, H*H*-9), 2.63 (*virt.* dt, ^3J = 10.8 Hz, $^3J \approx {}^3J$ = 7.2 Hz, 1 H, H-12a), 2.78 (*virt.* dt, ^3J = 11.2 Hz, $^3J \approx {}^3J$ = 7.7 Hz, 1 H, H-8c), 3.98 (d,

^3J = 10.8 Hz, 1 H, H-12b), 7.13 (dd, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 1 H, H-1), 7.23 (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, ^4J = 1.3 Hz, 1 H, H-2), 7.29* (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, ^4J = 1.5 Hz, 1 H, H-3), 7.35 – 7.41 (m, 2 H, H-6, H-7), 7.55 – 7.57 (m, 1 H, H-8), 7.84 (dd, ^3J = 7.7 Hz, ^4J = 1.3 Hz, 1 H, H-4), 7.92 (dd, ^3J = 7.4 Hz, ^4J = 1.9 Hz, 1 H, H-5), 9.67 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.8 (t, C-11), 23.1 (t, C-10), 24.2 (t, C-12), 25.4 (t, C-9), 25.8 (d, C-12a), 37.9 (d, C-12b), 49.9 (d, C-8c), 56.0 (s, C-8b), 123.7 (d, C-4, C-5), 127.6 (d, C-3), 127.9 (d, C-6**), 128.3 (d, C-2), 128.4 (d, C-1), 128.5 (d, C-7**), 129.5 (d, C-8), 131.5 (s, C-4a), 134.1 (s, C-4b***), 134.3 (s, C-8a***), 135.4 (s, C-12c), 200.8 (d, CHO).

* partially overlaid with residual proton signal of chloroform.

,* assignment is interconvertible.

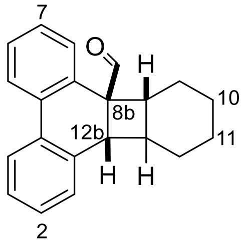
MS (EI, 70 eV): m/z (%) = 288 (5) $[M]^+$, 270 (4), 215 (3), 206 (8), 178 (9), 118 (3), 83 (100) $[C_6H_{11}]^+$, 67 (6), 47 (14).

HRMS (EI, 70 eV): calcd for $C_{21}H_{20}O$ $[M]^+$: 288.1509; found: 288.1508.

calcd for $C_{20}{}^{13}CH_{20}O$ $[M]^+$: 289.1542; found: 289.1543.

Chiral HPLC: t_{D1R1} = 12.2 min, t_{D1R2} = 25.3 min; t_{D2R1} = 16.5 min, t_{D2R2} = 20.1 min; t_{D3R1} = 10.9 min, t_{D3R2} = 17.9 min [Daicel, Chiralpak OD-RH, 150 x 4,6 mm, 5 µm, 20 °C, 80% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

*(8bSR,8cRS,12bRS)-9,10,11,12,12a,12b-hexahydrobenzo[3,4]cyclobuta[1,2-l]phenanthrene-8b(8cH)-carbaldehyde (rac-**6b**/rac-**6c**)*



$C_{21}H_{20}O$
MW = 288.39 g/mol

rac-**6b**/*rac*-**6c**

Major Diastereomer

¹H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.98 – 1.45 (m, 8 H, CH_2), 1.88 (*virt.* tdd, $^3J \approx {}^3J$ = 11.8 Hz, ^3J = 10.0 Hz, ^3J = 3.2 Hz, 1 H, H-12a), 2.41 (*virt.* td, $^3J \approx {}^3J$ = 11.9 Hz, ^3J = 3.2 Hz, 1 H, H-8c), 3.56 (d, ^3J = 10.0 Hz, 1 H, H-12b), 7.10 – 7.15 (m, 2 H, Ar-H), 7.20 – 7.39 (m, 3 H, Ar-H), 7.40 – 7.43 (m, 1 H, Ar-H), 7.88 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1 H, Ar-H), 8.00 – 8.02 (m, 1 H, Ar-H), 9.65 (s, 1 H, CHO).

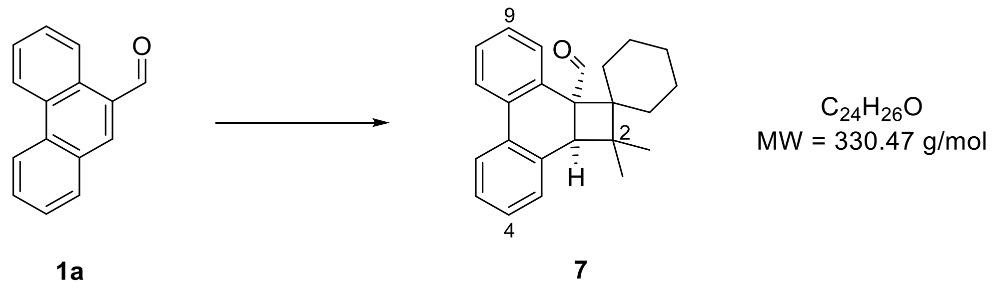
¹³C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 25.9 (t, CH_2), 26.2 (t, CH_2), 28.7 (t, CH_2), 30.4 (t, CH_2), 46.8 (d, C-12a), 46.9 (d, C-12b), 52.6 (d, C-8c), 60.3 (s, C-8b), 124.0 (d, Ar-C), 124.1 (d, Ar-C), 127.7 (d, Ar-C), 127.9 (d, Ar-C), 128.2 (d, Ar-C), 128.3 (d, Ar-C), 130.3 (s, Ar-C), 130.8 (d, Ar-C), 131.8 (s, Ar-C), 134.5 (s, Ar-C), 134.9 (s, Ar-C), 201.0 (d, CHO).

Minor Diastereomer

¹H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.55 – 0.63 (m, 1 H, C*H*H), 1.05 – 1.80 (m, 6 H, CH_2), 1.99 – 2.05 (m, 1 H, C*H*H), 2.60 – 2.68 (m, 1 H, H-12a), 3.30 (*virt.* td, $^3J \approx {}^3J$ = 8.3 Hz, ^3J = 3.8 Hz, 1 H, H-8c), 4.12 (d, ^3J = 8.9 Hz, 1 H, H-12b), 7.08 (dd, ^3J = 7.4 Hz, ^4J = 1.4 Hz, 1 H, Ar-H), 7.10 – 7.15 (m, 1 H, Ar-H), 7.20 – 7.39 (m, 4 H, Ar-H), 7.91 – 7.93 (m, 1 H, Ar-H), 8.00 – 8.02 (m, 1 H, Ar-H), 9.66 (s, 1 H, CHO).

¹³C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.5 (t, CH_2), 21.8 (t, CH_2), 23.8 (t, CH_2), 24.0 (t, CH_2), 36.7 (d, C-12a), 39.3 (d, C-12b), 40.1 (d, C-8c), 56.2 (s, C-8b), 123.1 (d, Ar-C), 124.0 (d, Ar-C), 127.4 (d, Ar-C), 127.9 (d, Ar-C), 128.2 (d, Ar-C), 129.1 (d, Ar-C), 130.0 (d, Ar-C), 131.3 (s, Ar-C), 132.7 (s, Ar-C), 133.1 (s, Ar-C), 133.9 (s, Ar-C), 200.8 (d, CHO).

(2a*S*,10b*S*)-2,2-dimethyl-2,2a-dihydro-10b*H*-spiro[cyclobuta[*l*]phenanthrene-1,1'-cyclohexane]-10b-carbaldehyde (7)



$C_{24}H_{26}O$
MW = 330.47 g/mol

Racemic [2+2] Photocycloaddition

In analogy to General Procedure 3, substrate **1a** (20.6 mg, 100 µmol, 1.00 eq.) and isopropylidenecyclohexane (373 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of $AlBr_3$ (250 µl, 0.10 M in CH_2Cl_2/CH_2Br_2, 25.0 µmol, 25 mol%) for 11 hours. Purification by column chromatography (silica, P/Et_2O = 100/1) gave 17.3 mg of *ortho* photocycloaddition product **7** (52.3 µmol, 52%, r.r. 92/8) as a colourless oil.

Enantioselective *ortho* Photocycloaddition

Following General Procedure 3, substrate **1a** (20.6 mg, 100 µmol, 1.00 eq.) and isopropylidenecyclohexane (373 mg, 3.00 mmol, 30.0 eq.) were dissolved in dichloromethane (c = 20 mM) and the solution was irradiated in presence of chiral Lewis acid **3c** (20 µmol, 20 mol%) for 24 hours. Purification by column chromatography (silica, P/EtOAc = 200/1) gave 23.1 mg of *ortho* photocycloaddition product **7** (69.9 µmol, 70%, 84% *ee*, r.r. 91/9) as a colourless oil.

TLC: R_f = 0.57 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2930 (vs, sp^3-CH), 2857 (m, sp^3-CH), 1713 (s, C=O), 1599 (m, C=C), 1502 (m), 1448 (s), 1086 (m), 754 (vs, sp^2-CH), 726 (s, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.88 – 0.93 (m, 1 H, CH_2), 1.07 – 1.15 (m, 3 H, CH_2), 1.10 (s, 3 H, C-2-CH_3), 1.23 – 1.33 (m, 3 H, CH_2), 1.32 (s, 3 H, C-2-CH_3), 1.54 – 1.65

(m, 2 H, CH_2), 1.72 – 1.74 (m, 1 H, CH_2), 4.06 (s, 3 H, H-2a), 7.18 (dd, ^3J = 7.1 Hz, ^4J = 1.9 Hz, 1 H, H-10), 7.22 – 7.28 (m, 2 H, Ar-H), 7.32 – 7.37 (m, 3 H, Ar-H), 7.84 (dd, ^3J = 7.3 Hz, ^4J = 1.7 Hz, 1 H, H-6), 7.96 – 7.98 (m, 1 H, H-7), 9.63 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 23.5 (t, CH_2), 23.6 (q, C-2-CH_3), 23.9 (q, C-2-CH_3), 24.2 (t, CH_2), 26.0 (t, CH_2), 30.9 (t, CH_2), 34.7 (t, CH_2), 43.0 (d, C-2a), 47.5 (s, C-2), 51.5 (s, C-1), 57.1 (s, C-10b), 123.2 (d, C-6), 123.6 (d, C-7), 127.1 (d, C-Ar), 127.3 (d, C-Ar), 127.7 (d, C-Ar), 128.3 (d, C-Ar), 130.2 (d, C-10), 130.9 (d, C-Ar), 131.4 (s, C-Ar), 132.1 (s, C-Ar), 132.8 (s, C-Ar), 134.9 (s, C-Ar), 200.6 (d, CHO).

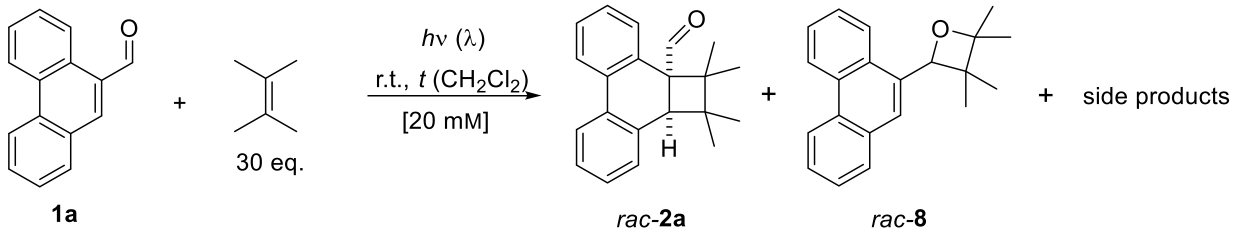
MS (EI, 70 eV): m/z (%) = 330 (3) $[M]^+$, 281 (2), 206 (100) $[C_{15}H_{10}O]^+$, 178 (85), 151 (18), 126 (2), 88 (10), 63 (2).

HRMS (EI, 70 eV): calcd for $C_{24}H_{26}O$ $[M]^+$: 330.1978; found: 330.1974.

calcd for $C_{23}{}^{13}CH_{26}O$ $[M]^+$: 331.2012; found: 331.2010.

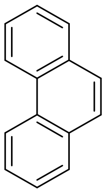
Chiral HPLC: t_{R1} = 22.0 min, t_{R2} = 22.8 min [Daicel, Chiralcel OJ-RH, 150 x 4,6 mm, 5 µm, 20 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm].

4. Additional Experiments for the Uncatalysed Photocycloaddition

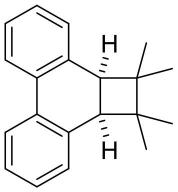


entry	λ [nm]	time [h]	*rac*-2a [%]	*rac*-8 [%]	rsm [%]
1	254 (reactor)	3.0	---	8	---
2	350 (reactor)	3.5	traces	9	---
3	366 (reactor)	7.0	30	5	---
4	398 (LED)	5.0	50	11	---
5	405 (LED)	10.5	49	9	---
6	419 (reactor)	24	traces	traces	71
7	424 (LED)	24	traces	traces	65
8	457 (LED)	13	---	---	98

Side Products from Decarbonylation:



I

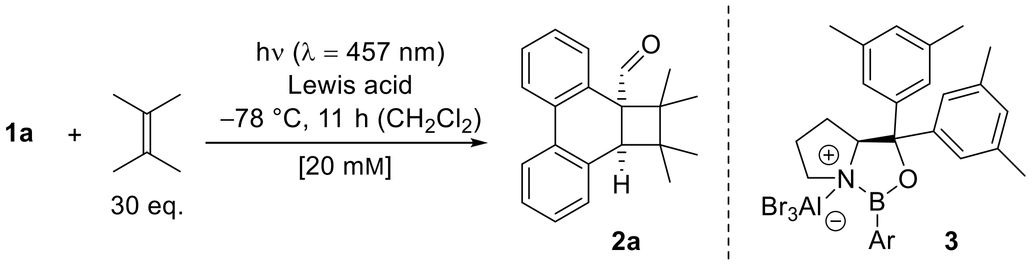


II

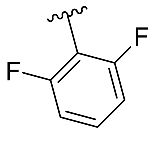
entry	λ [nm]	ratio I/II	I [%][a]	*II* [%][a]
1	350 (reactor)	41/59	25	35
2	366 (reactor)	9/91	< 5	21

[a]: Separation of side products not possible. Determination of yield by ^{1}H NMR of the mixture. Quantification was only done under these two different conditions.

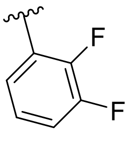
5. Additional Experiments for the Chiral Lewis Acid Screening



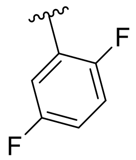
Ar =



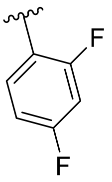
53%, 84% *ee*



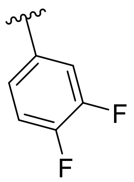
49%, 89% *ee*



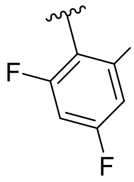
50%, 86% *ee*



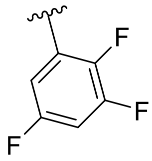
60%, 86% *ee*



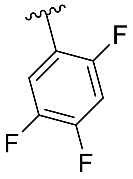
46%, 81% *ee*



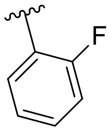
49%, 79% *ee*



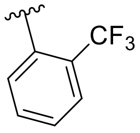
52%, 58% *ee*



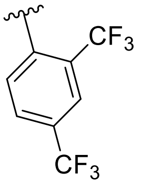
46%, 87% *ee*



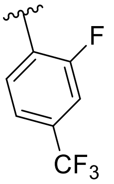
50%, 81% *ee*



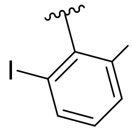
54%, 84% *ee*



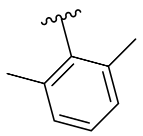
55%, 21% *ee*



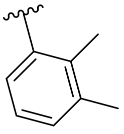
57%, 52% *ee*



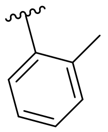
62%, 43% *ee*



62%, 97% *ee*



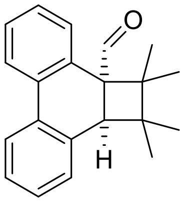
51%, 94% *ee*



41%, 94% *ee*

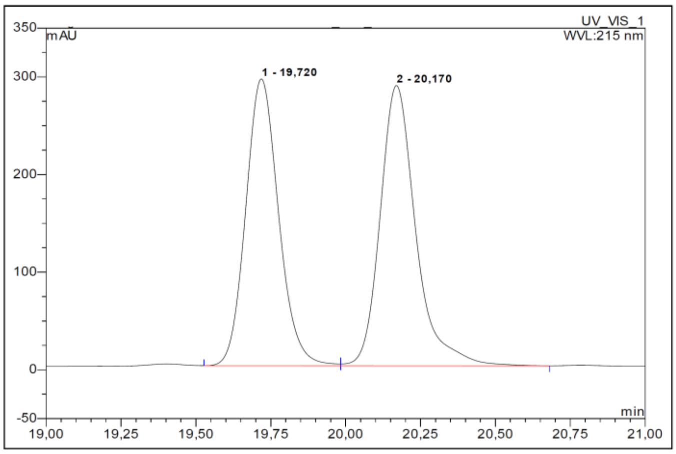
6. Chiral HPLC Traces

(2a*S*,10b*S*)-1,1,2,2-Tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2a)



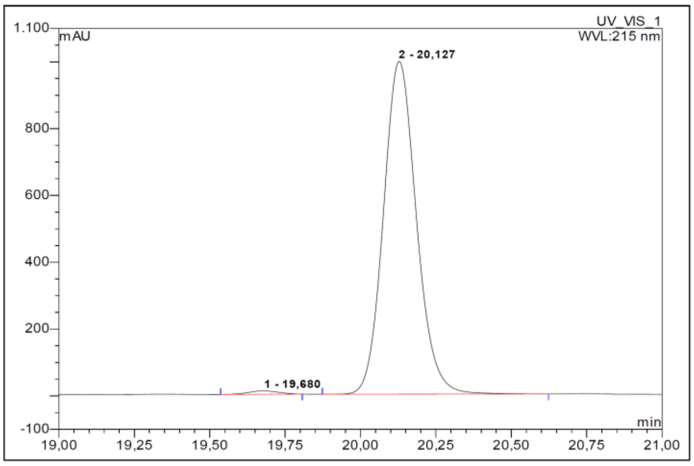
2a

Racemic product



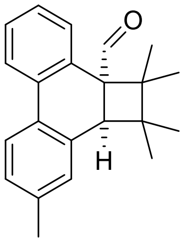
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.72	n.a.	293.690	37.363	48.57	n.a.	BM
2	20.17	n.a.	287.073	39.557	51.43	n.a.	MB
Total:			580.763	76.920	100.00	0.000	

*Enantioenriched product (*98% *ee)*



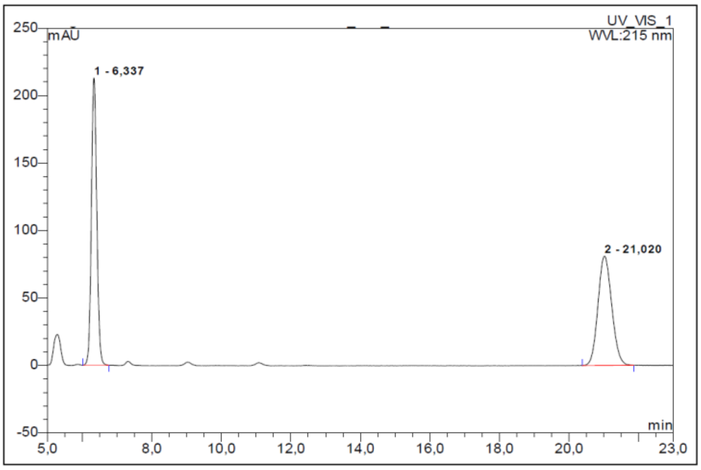
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.68	n.a.	10.154	1.165	0.91	n.a.	BMB*
2	20.13	n.a.	996.124	126.447	99.09	n.a.	BMB
Total:			1006.277	127.612	100.00	0.000	

(2a*S*,10b*S*)-1,1,2,2,9-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2b)



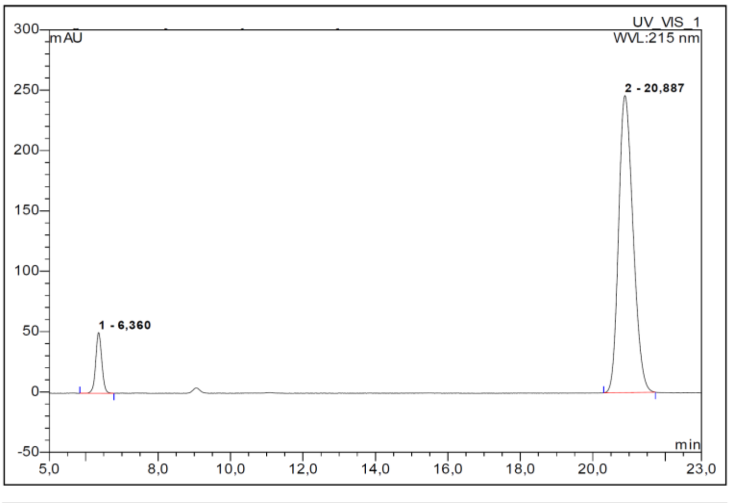
2b

Racemic product



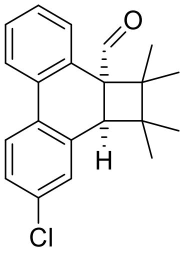
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.34	n.a.	212.900	38.186	50.70	n.a.	BMB
2	21.02	n.a.	81.015	37.131	49.30	n.a.	BMB
Total:			293.915	75.317	100.00	0.000	

*Enantioenriched product (*84% *ee)*



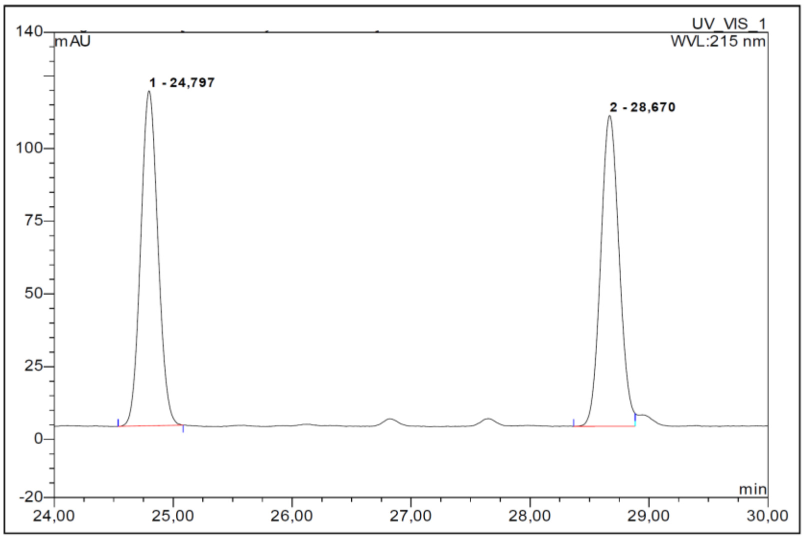
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.36	n.a.	50.366	9.806	7.93	n.a.	BMB*
2	20.89	n.a.	246.136	113.852	92.07	n.a.	BMB
Total:			296.502	123.657	100.00	0.000	

(2a*S*,10b*S*)-9-Chloro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2c)



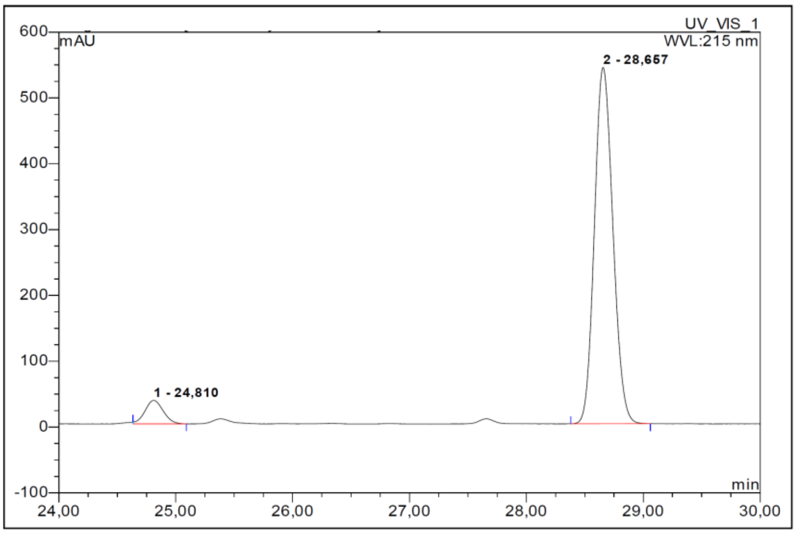
2c

Racemic product



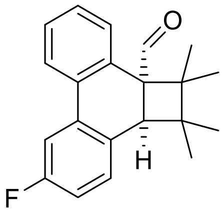
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.80	n.a.	115.195	19.316	50.14	n.a.	BMB
2	28.67	n.a.	106.913	19.204	49.86	n.a.	BM *
Total:			222.108	38.520	100.00	0.000	

*Enantioenriched product (*88% *ee)*



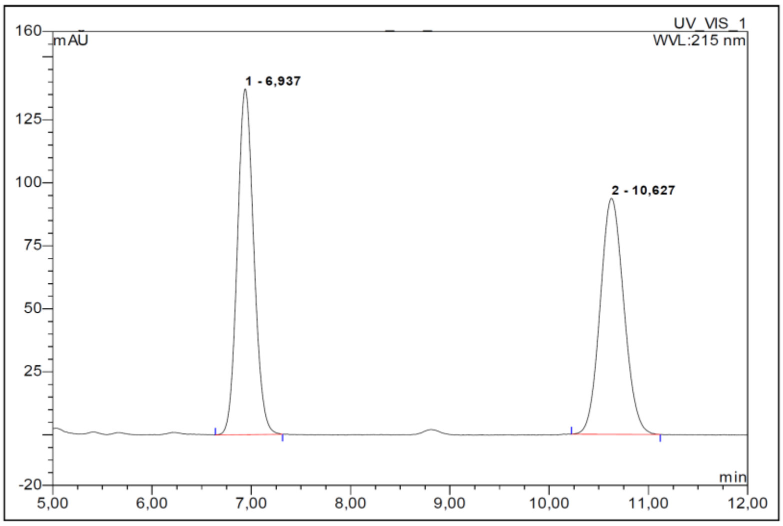
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.81	n.a.	35.643	6.467	6.12	n.a.	MB*
2	28.66	n.a.	541.260	99.177	93.88	n.a.	BMB
Total:			576.903	105.644	100.00	0.000	

(2a*S*,10b*S*)-8-Fluoro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2d)



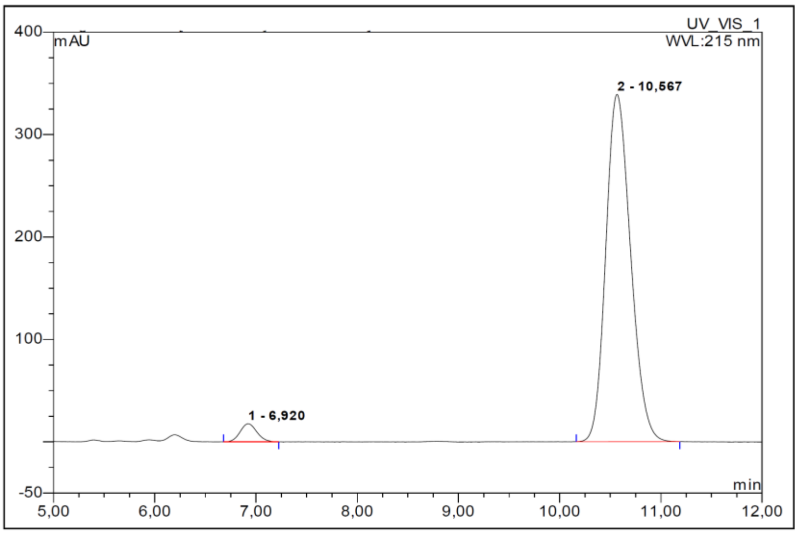
2d

Racemic product



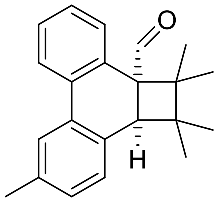
No.	Ret.Time min		Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.94	n.a.		137.159	26.342	50.43	n.a.	BMB
2	10.63	n.a.		93.619	25.896	49.57	n.a.	BMB
Total:				230.779	52.238	100.00	0.000	

Enantioenriched product (93% *ee)*



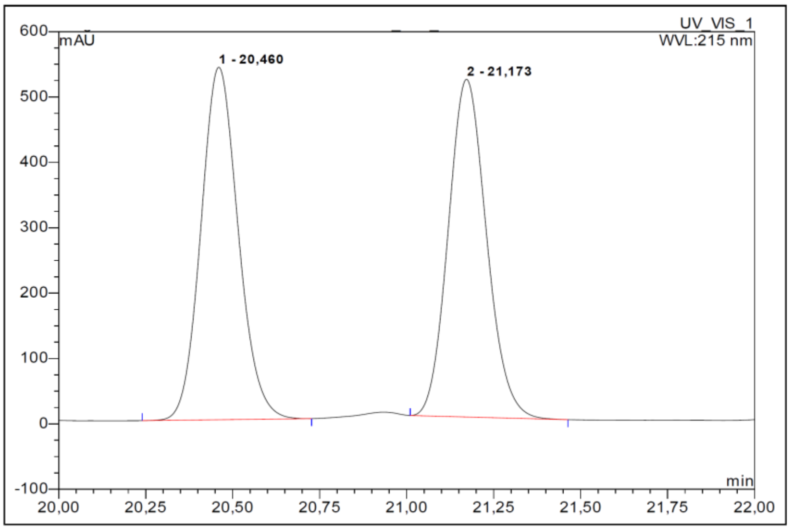
No.	Ret.Time min		Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.92	n.a.		17.621	3.387	3.40	n.a.	BMB*
2	10.57	n.a.		339.089	96.334	96.60	n.a.	BMB
Total:				356.709	99.722	100.00	0.000	

(2a*S*,10b*S*)-1,1,2,2,8-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2e)



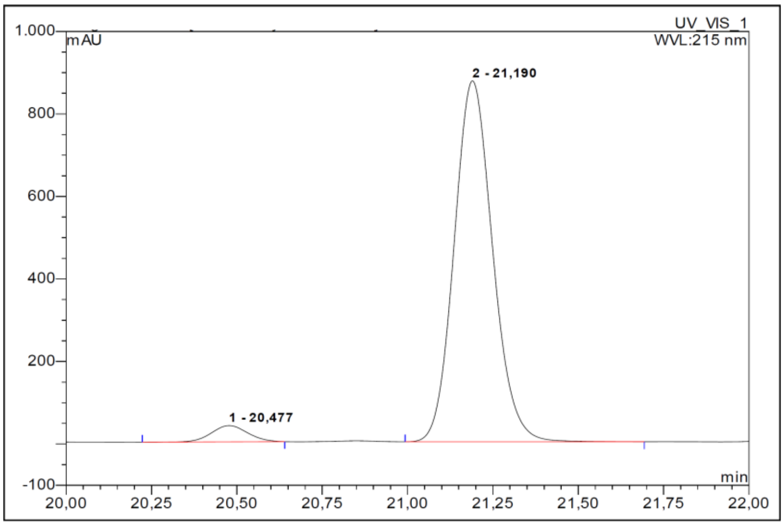
2e

Racemic product



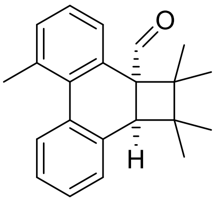
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.46	n.a.	539.421	67.069	50.42	n.a.	BMB
2	21.17	n.a.	516.621	65.959	49.58	n.a.	BMB
Total:			1056.042	133.028	100.00	0.000	

*Enantioenriched product (*92% *ee)*



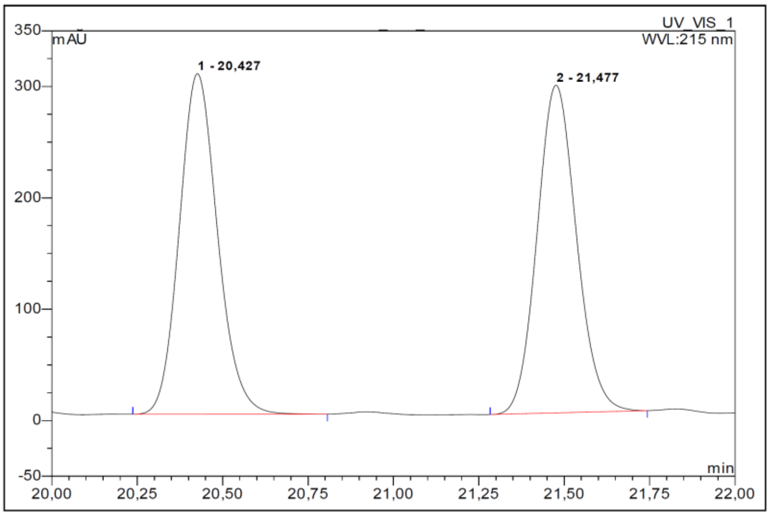
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.48	n.a.	39.433	4.860	4.08	n.a.	BMB*
2	21.19	n.a.	874.913	114.334	95.92	n.a.	BMB
Total:			914.346	119.194	100.00	0.000	

(2a*S*,10b*S*)-1,1,2,2,6-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2f)



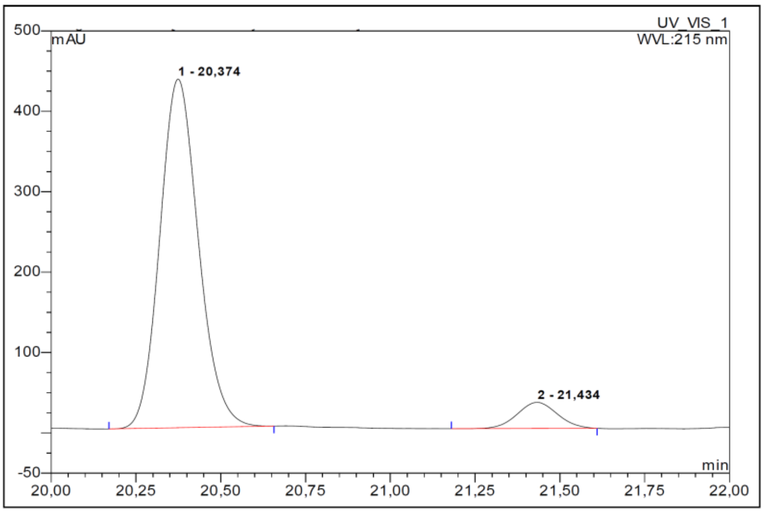
2f

Racemic product



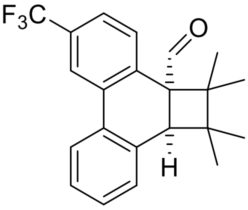
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.43	n.a.	305.830	39.693	50.24	n.a.	BMB
2	21.48	n.a.	294.301	39.314	49.76	n.a.	BMB
Total:			600.131	79.006	100.00	0.000	

Enantioenriched product (86% *ee)*



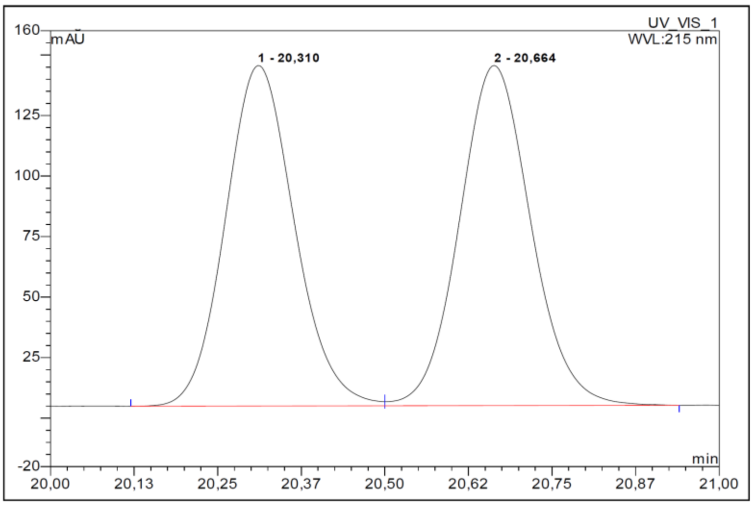
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.37	n.a.	433.617	57.202	92.77	n.a.	BMB
2	21.43	n.a.	32.494	4.455	7.23	n.a.	BMB*
Total:			466.110	61.657	100.00	0.000	

(2a*S*,10b*S*)-1,1,2,2-Tetramethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2g)



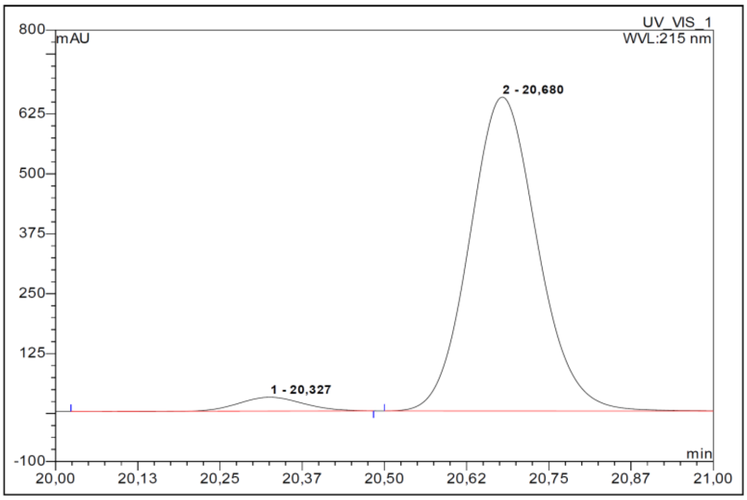
2g

Racemic product



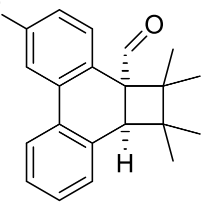
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.31	n.a.	140.608	16.823	49.14	n.a.	BM
2	20.66	n.a.	140.473	17.414	50.86	n.a.	MB
Total:			281.081	34.238	100.00	0.000	

*Enantioenriched product (*92% *ee)*



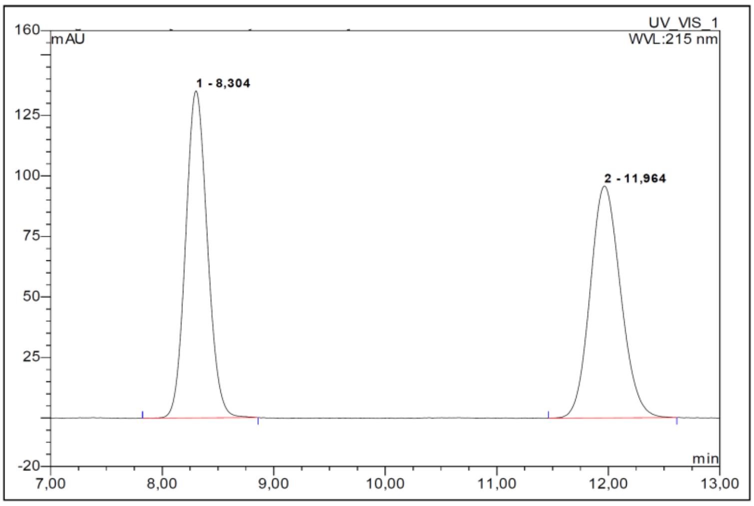
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.33	n.a.	28.917	3.228	3.95	n.a.	BMB*
2	20.68	n.a.	655.070	78.408	96.05	n.a.	BMB
Total:			683.988	81.636	100.00	0.000	

(2a*S*,10b*S*)-5-Fluoro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2h)



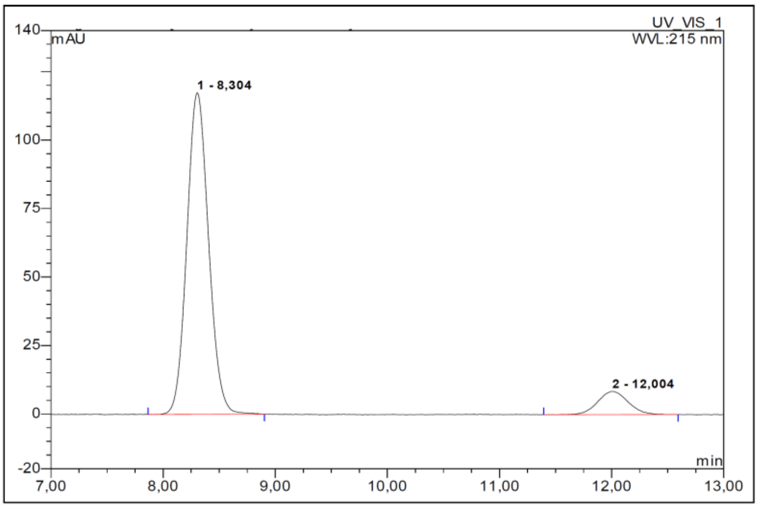
2h

Racemic product



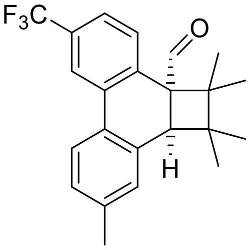
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.30	n.a.	135.073	30.486	50.07	n.a.	BMB*
2	11.96	n.a.	95.770	30.396	49.93	n.a.	BMB*
Total:			230.843	60.882	100.00	0.000	

*Enantioenriched product (*82% *ee)*



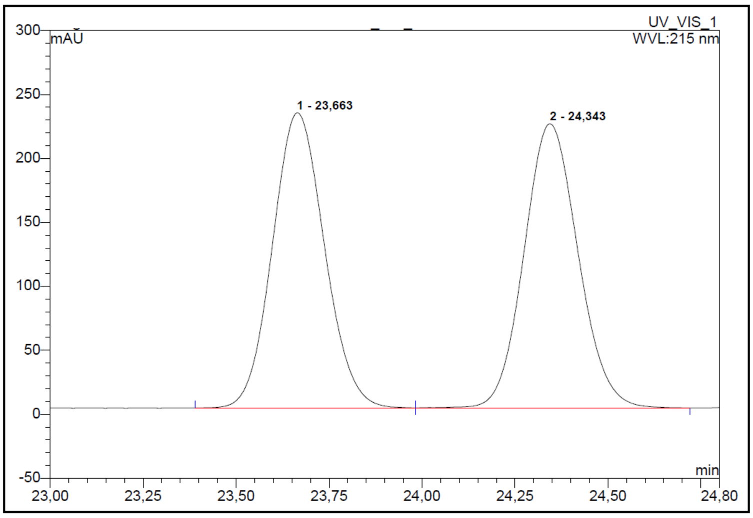
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.30	n.a.	117.352	26.343	90.79	n.a.	BMB*
2	12.00	n.a.	8.469	2.671	9.21	n.a.	BMB*
Total:			125.821	29.014	100.00	0.000	

(2a*S*,10b*S*)-1,1,2,2,9-Pentamethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2i)



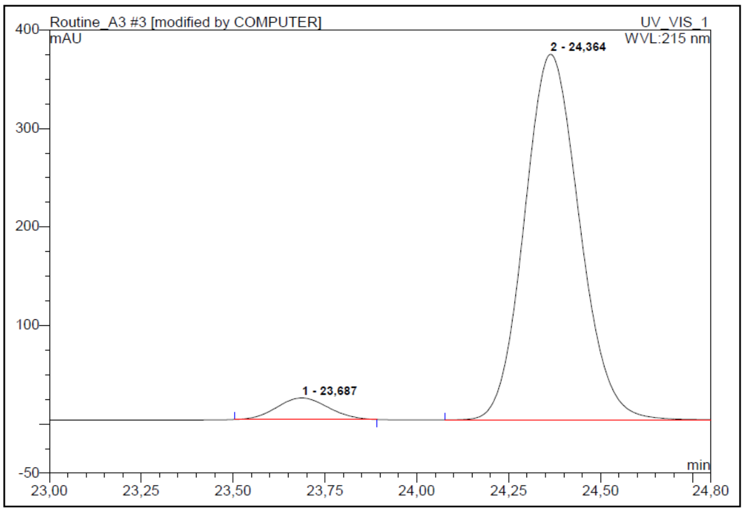
2i

Racemic product



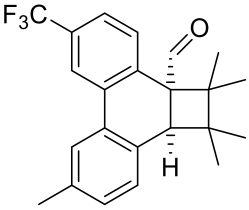
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23,66	n.a.	230,722	37,465	50,00	n.a.	BM
2	24,34	n.a.	222,204	37,470	50,00	n.a.	MB
Total:			452,926	74,934	100,00	0,000	

Enantioenriched product (90% ee)



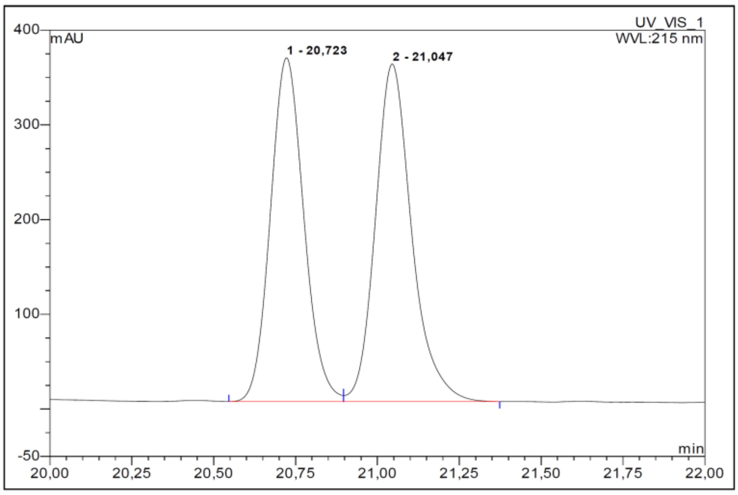
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23,69	n.a.	21,948	3,566	5,24	n.a.	BMB*
2	24,36	n.a.	371,377	64,482	94,76	n.a.	BMB
Total:			393,325	68,049	100,00	0,000	

(2a*S*,10b*S*)-1,1,2,2,8-Pentamethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2j)



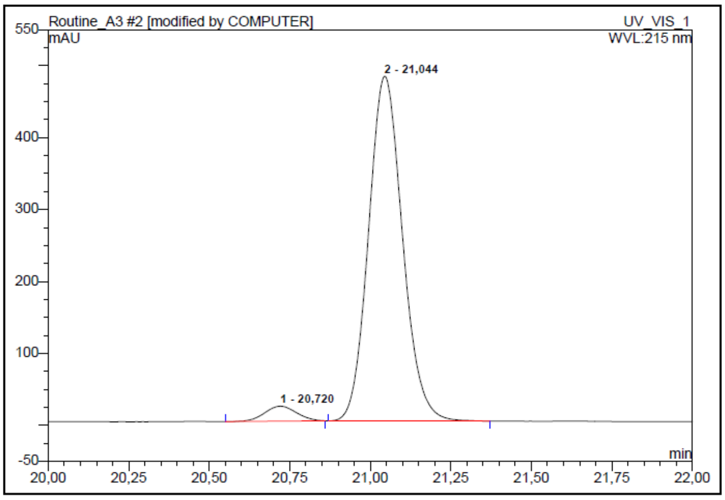
2j

Racemic product



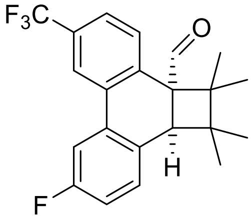
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.72	n.a.	362.932	42.896	48.37	n.a.	BM
2	21.05	n.a.	356.249	45.793	51.63	n.a.	MB
Total:			719.181	88.689	100.00	0.000	

Enantioenriched product (92% *ee)*



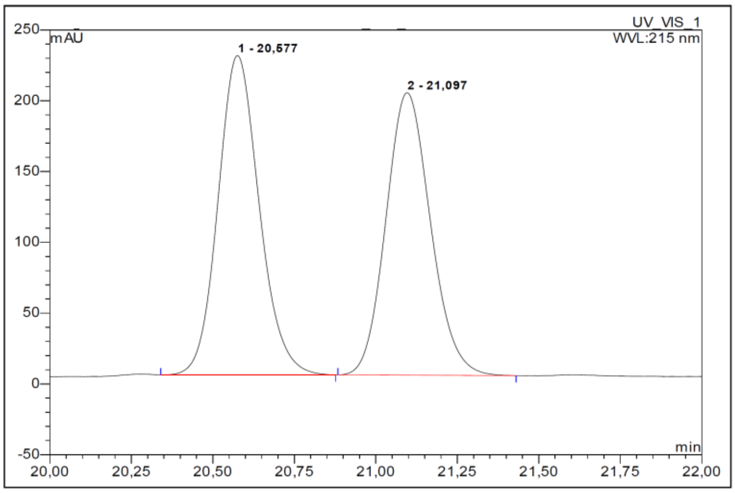
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20,72	n.a.	20,750	2,375	3,90	n.a.	BMB*
2	21,04	n.a.	479,262	58,552	96,10	n.a.	BMB
Total:			500,012	60,928	100,00	0,000	

(2a*S*,10b*S*)-8-Fluoro-1,1,2,2-tetramethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2k)



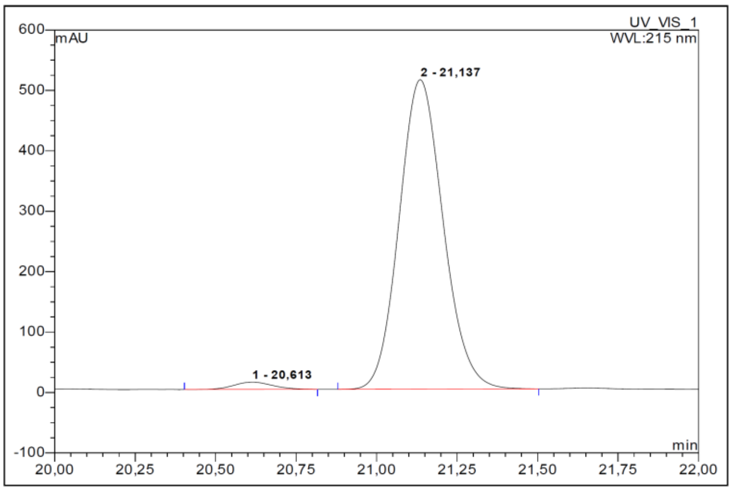
2k

Racemic product



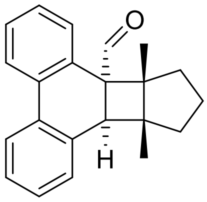
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.58	n.a.	225.488	33.091	51.12	n.a.	BMB
2	21.10	n.a.	199.472	31.638	48.88	n.a.	BMB
Total:			424.960	64.729	100.00	0.000	

Enantioenriched product (96% *ee)*



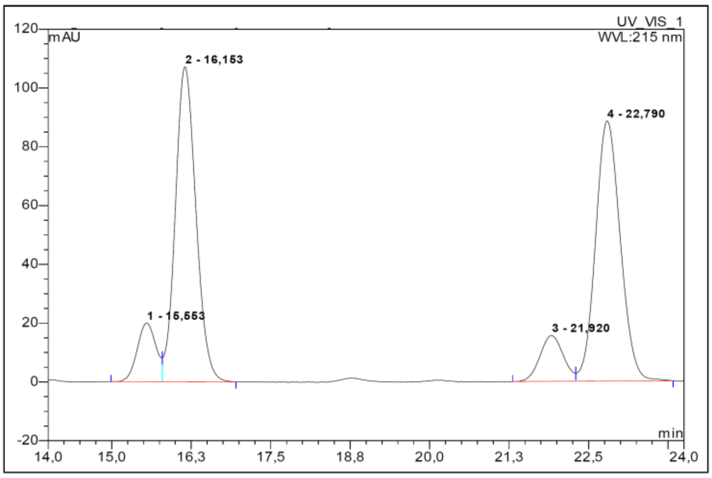
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.61	n.a.	12.058	1.680	2.02	n.a.	BMB*
2	21.14	n.a.	512.129	81.305	97.98	n.a.	BMB
Total:			524.187	82.985	100.00	0.000	

(8b*S*,8c*R*,11a*R*,11b*S*)-8c,11a-Dimethyl-8c,9,10,11,11a,11b-hexahydro-8b*H*-cyclopenta[3,4]cyclobuta[1,2-*l*]phenanthrene-8b-carboxaldehyde (4a)



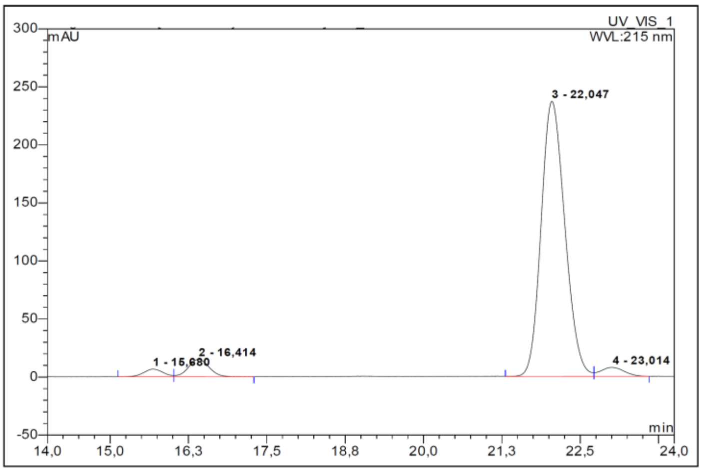
4a

Racemic product (d.r. = 12/88)



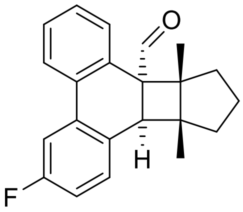
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.55	n.a.	19.936	6.850	7.31	n.a.	BM *
2	16.15	n.a.	107.182	40.362	43.05	n.a.	MB*
3	21.92	n.a.	15.638	6.631	7.07	n.a.	BM *
4	22.79	n.a.	88.512	39.918	42.57	n.a.	MB*
Total:			231.268	93.761	100.00	0.000	

*Enantioenriched product (*96% *ee*, d.r. = 93/7*)*



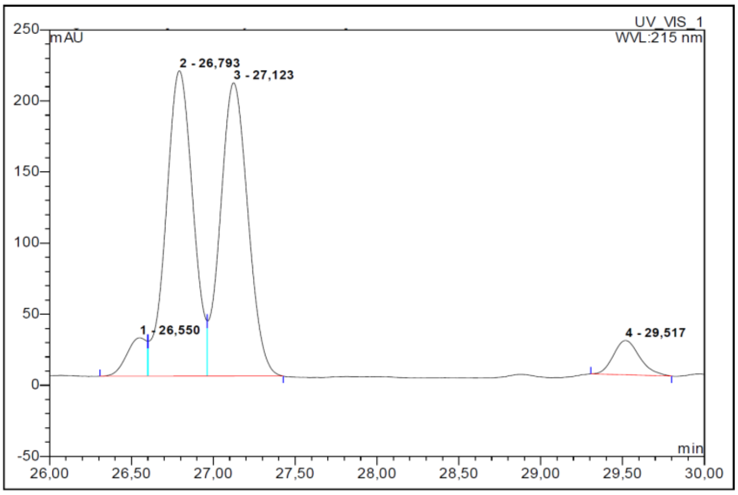
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.68	n.a.	6.518	2.305	2.00	n.a.	BM *
2	16.41	n.a.	14.943	5.672	4.92	n.a.	MB*
3	22.05	n.a.	237.021	104.081	90.21	n.a.	BM *
4	23.01	n.a.	7.688	3.322	2.88	n.a.	MB*
Total:			266.170	115.380	100.00	0.000	

(8b*S*,8c*R*,11a*R*,11b*S*)-3-Fluoro-8c,11a-dimethyl-8c,9,10,11,11a,11b-hexahydro-8b*H*-cyclopenta[3,4]cyclobuta[1,2-*l*]phenanthrene-8b-carboxaldehyde (5a)



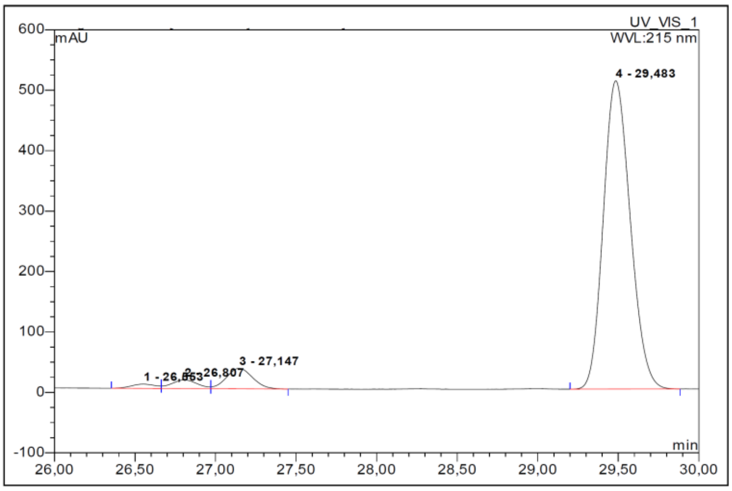
5a

Racemic product (d.r. = 9/91)



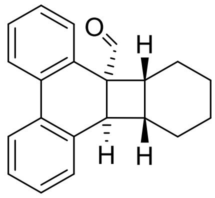
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.55	n.a.	26.962	3.744	4.18	n.a.	BM *
2	26.79	n.a.	214.784	41.059	45.81	n.a.	M *
3	27.12	n.a.	206.323	40.327	45.00	n.a.	MB*
4	29.52	n.a.	24.136	4.492	5.01	n.a.	BMB*
Total:			472.205	89.622	100.00	0.000	

*Enantioenriched product (*98% *ee*, d.r. = 93/7*)*



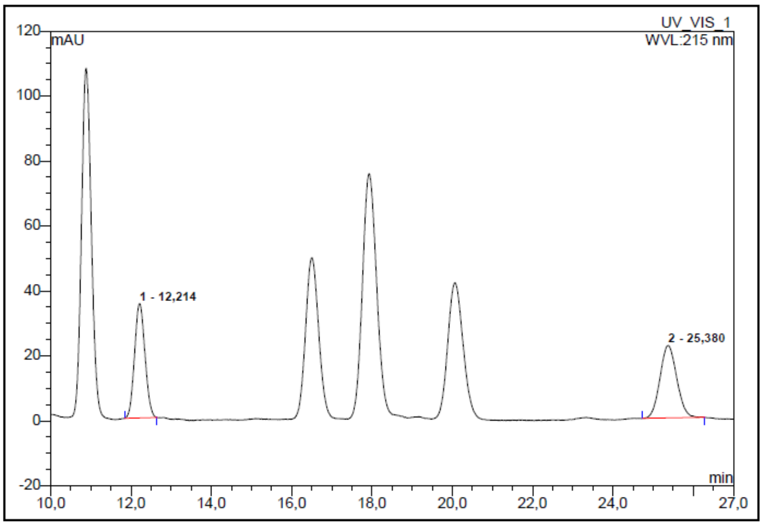
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.55	n.a.	7.051	1.212	1.11	n.a.	BM *
2	26.81	n.a.	14.242	2.625	2.40	n.a.	M *
3	27.15	n.a.	33.849	6.374	5.83	n.a.	MB*
4	29.48	n.a.	510.161	99.106	90.66	n.a.	BMB
Total:			565.303	109.316	100.00	0.000	

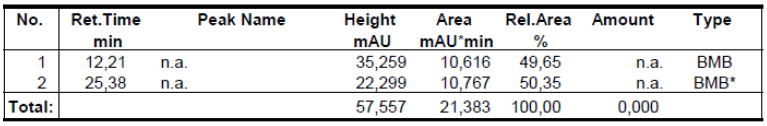
(8b*R*,8c*R*,12a*S*,12b*S*)-9,10,11,12,12a,12b-hexahydrobenzo[3,4]cyclobuta[1,2-*l*]phenanthrene-8b(8c*H*)-carbaldehyde (6a)



6a

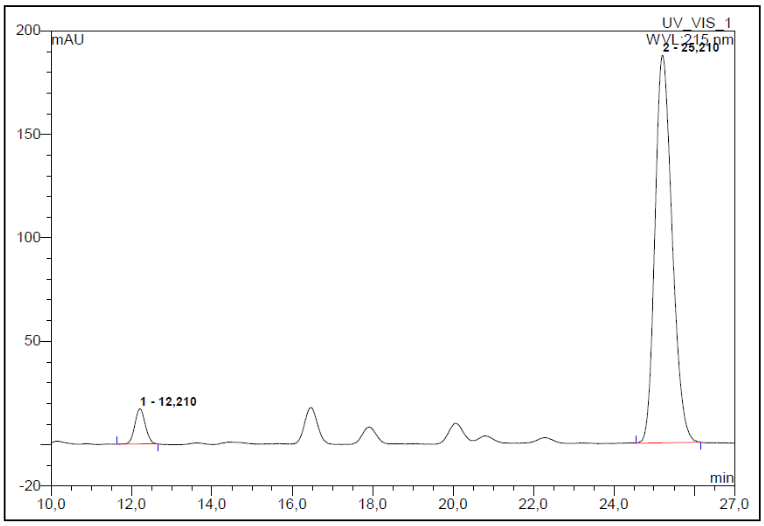
*Racemic product (*d.r. *rac*-**6a**/*rac*-**6b**/*rac*-**6c** = 21/35/44*)*

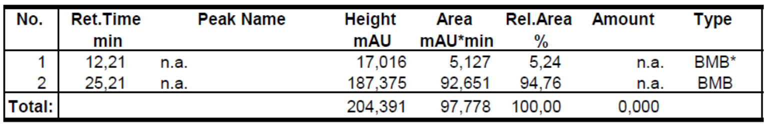




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,21	n.a.	35,259	10,616	49,65	n.a.	BMB
2	25,38	n.a.	22,299	10,767	50,35	n.a.	BMB*
Total:			57,557	21,383	100,00	0,000	

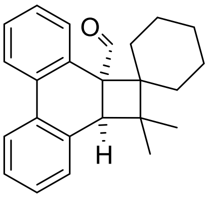
*Enantioenriched product (*90% *ee,* d.r. *rac*-**6a**/*rac*-**6b**/*rac*-**6c** = 87/10/3)





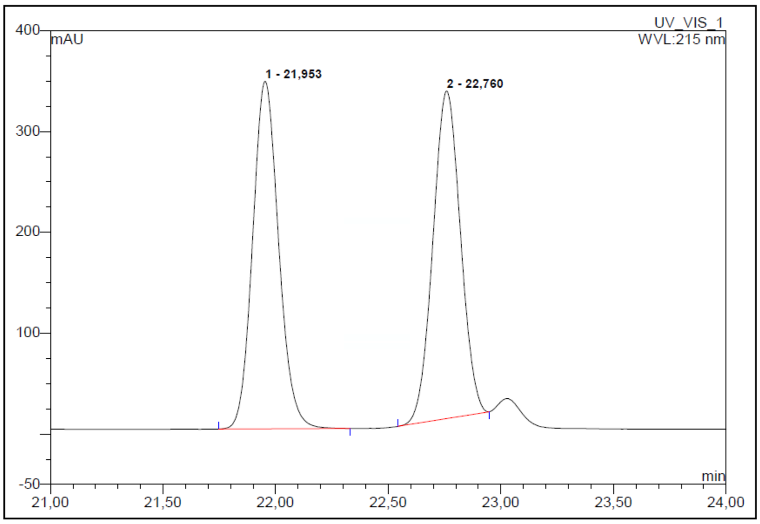
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,21	n.a.	17,016	5,127	5,24	n.a.	BMB*
2	25,21	n.a.	187,375	92,651	94,76	n.a.	BMB
Total:			204,391	97,778	100,00	0,000	

(2a*S*,10b*S*)-2,2-dimethyl-2,2a-dihydro-10b*H*-spiro[cyclobuta[*l*]phenanthrene-1,1'-cyclohexane]-10b-carbaldehyde (7)



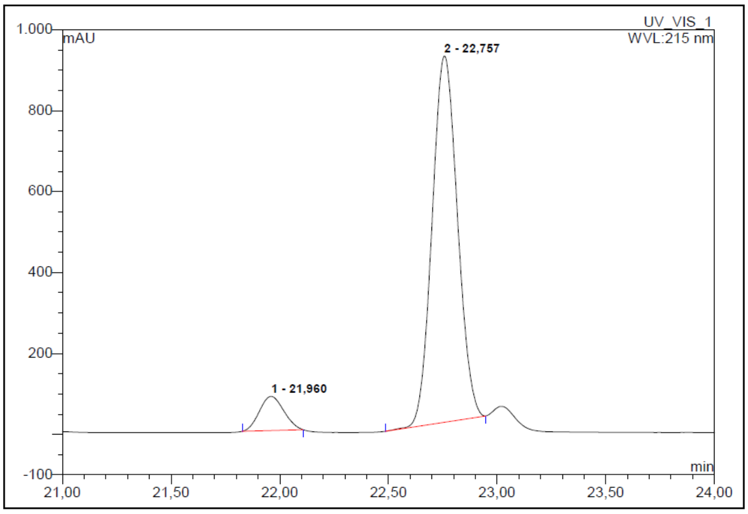
7

Racemic product



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21,95	n.a.	344,772	46,096	50,07	n.a.	BMB
2	22,76	n.a.	324,782	45,960	49,93	n.a.	BMB
Total:			669,554	92,056	100,00	0,000	

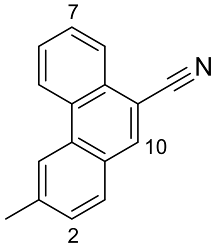
Enantioenriched product (84% *ee*)



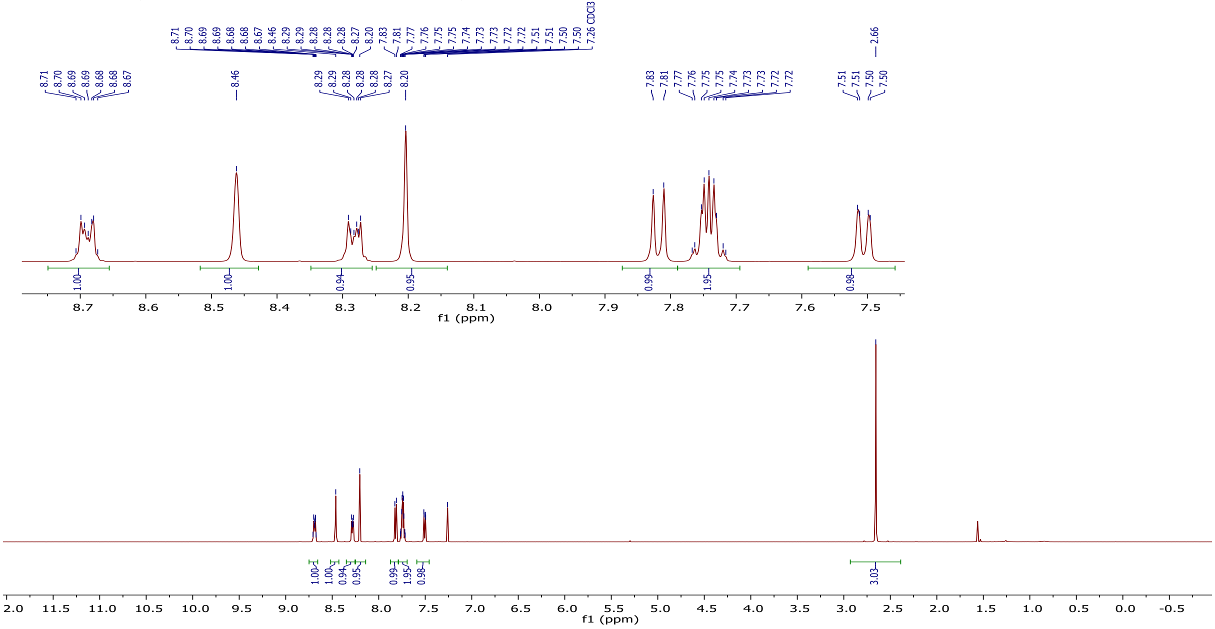
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21,96	n.a.	84,635	10,967	8,23	n.a.	BMB*
2	22,76	n.a.	905,557	122,354	91,77	n.a.	BMB
Total:			990,192	133,321	100,00	0,000	

7. NMR Spectra of New Compounds

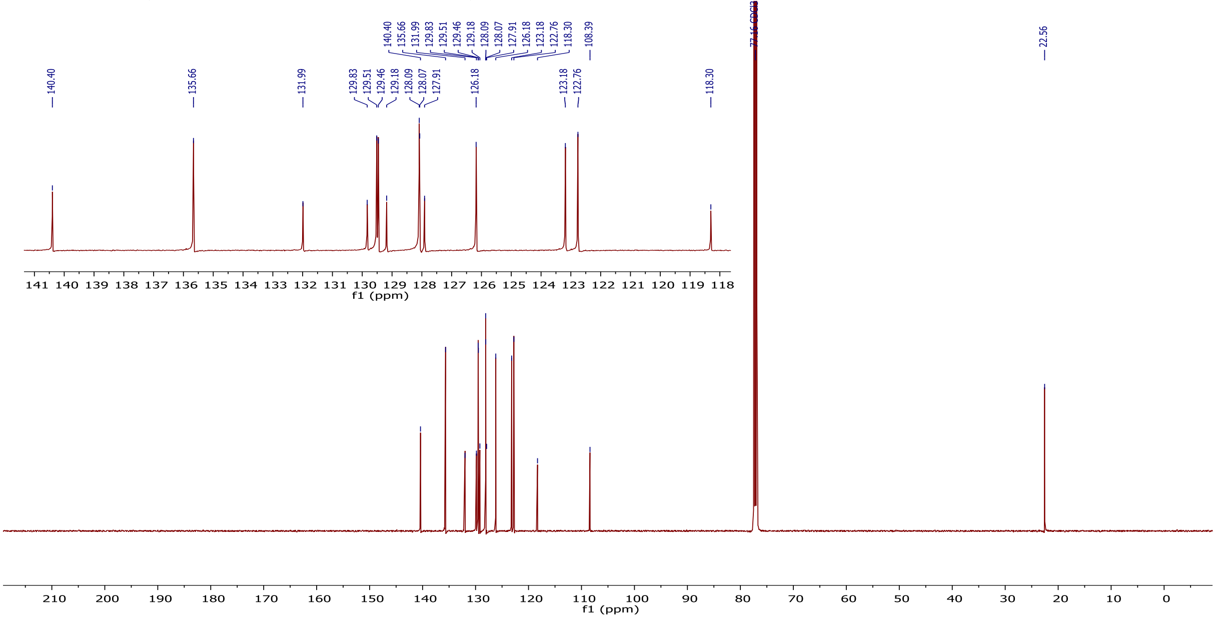
3-Methylphenanthrene-9-carbonitrile



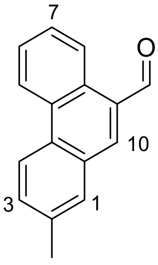
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



^{13}C NMR (126 MHz, CDCl$_3$, 300 K):

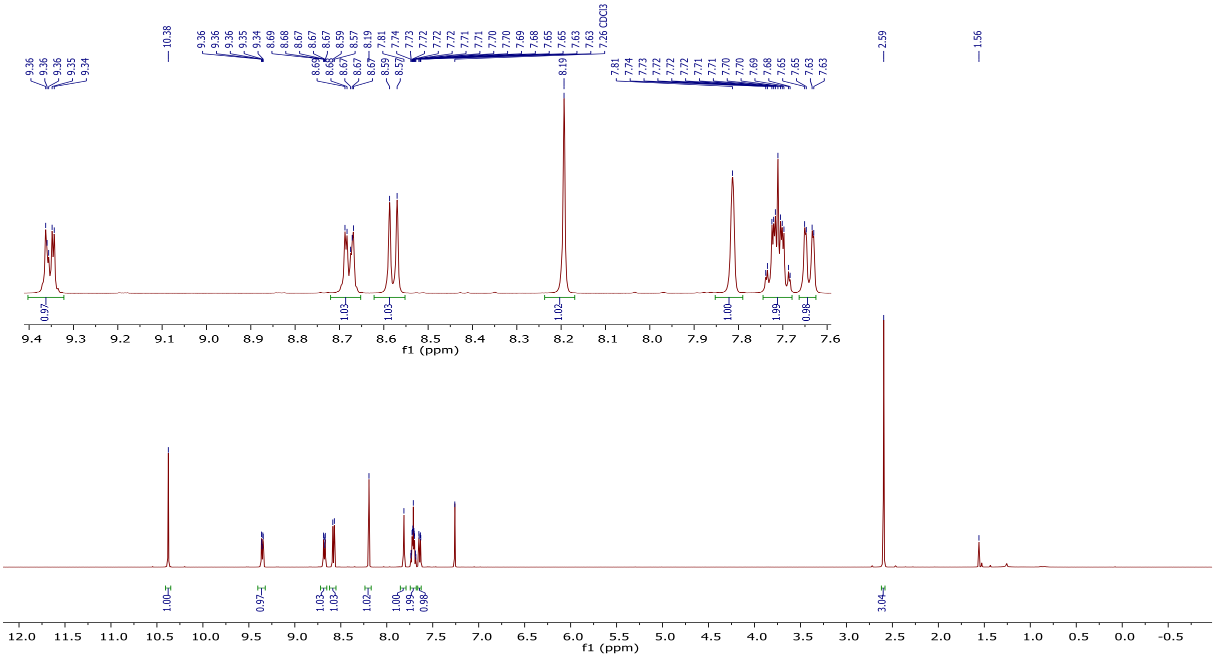


2-Methylphenanthrene-9-carboxaldehyde (1b)

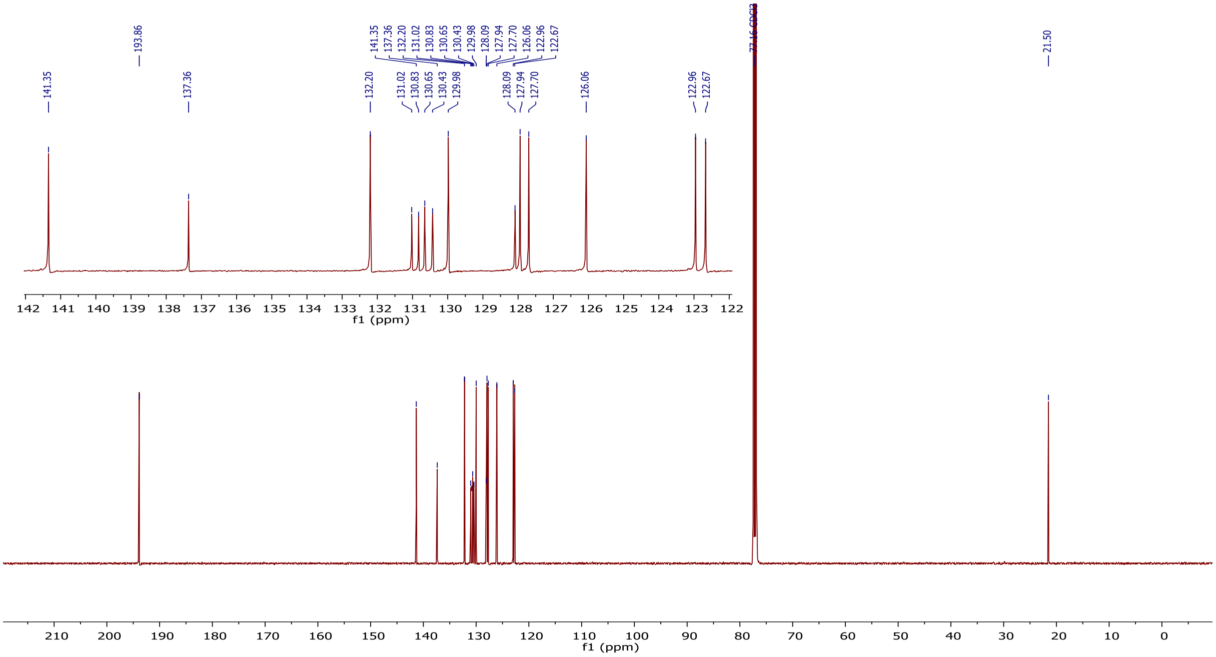


1b

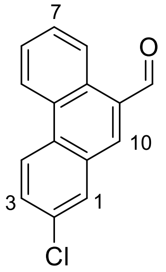
^{1}**H NMR** (500 MHz, $CDCl_3$, 298 K):



^{13}**C NMR** (126 MHz, $CDCl_3$, 300 K):

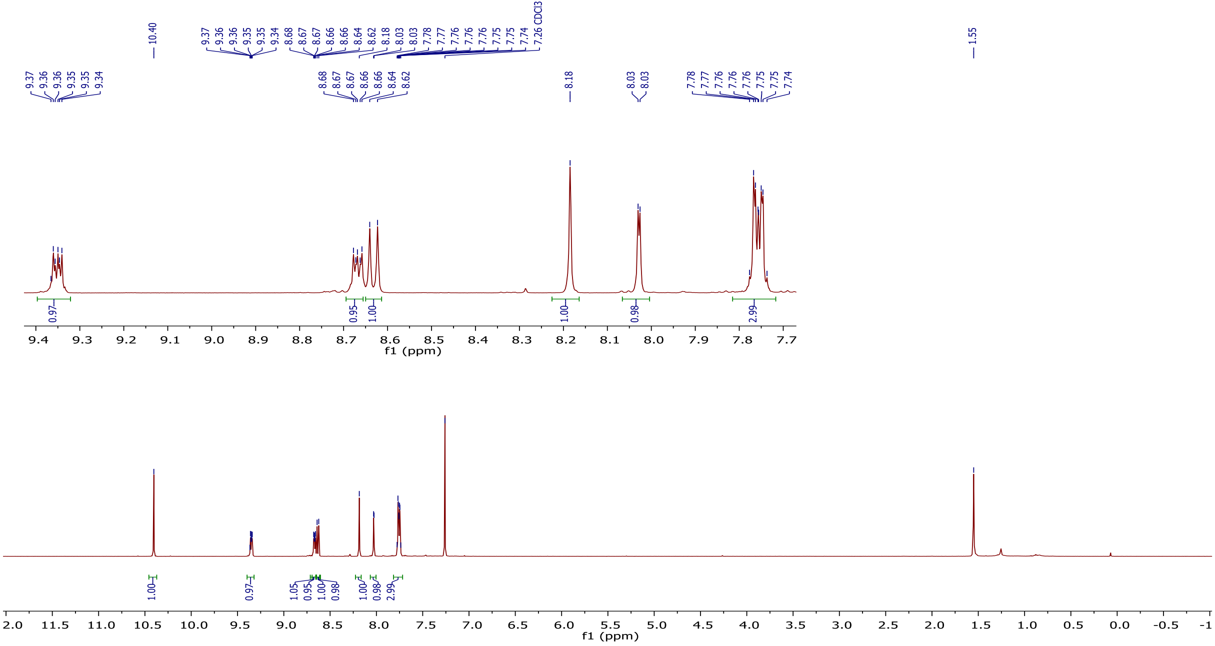


2-Chlorophenanthrene-9-carboxaldehyde (1c)

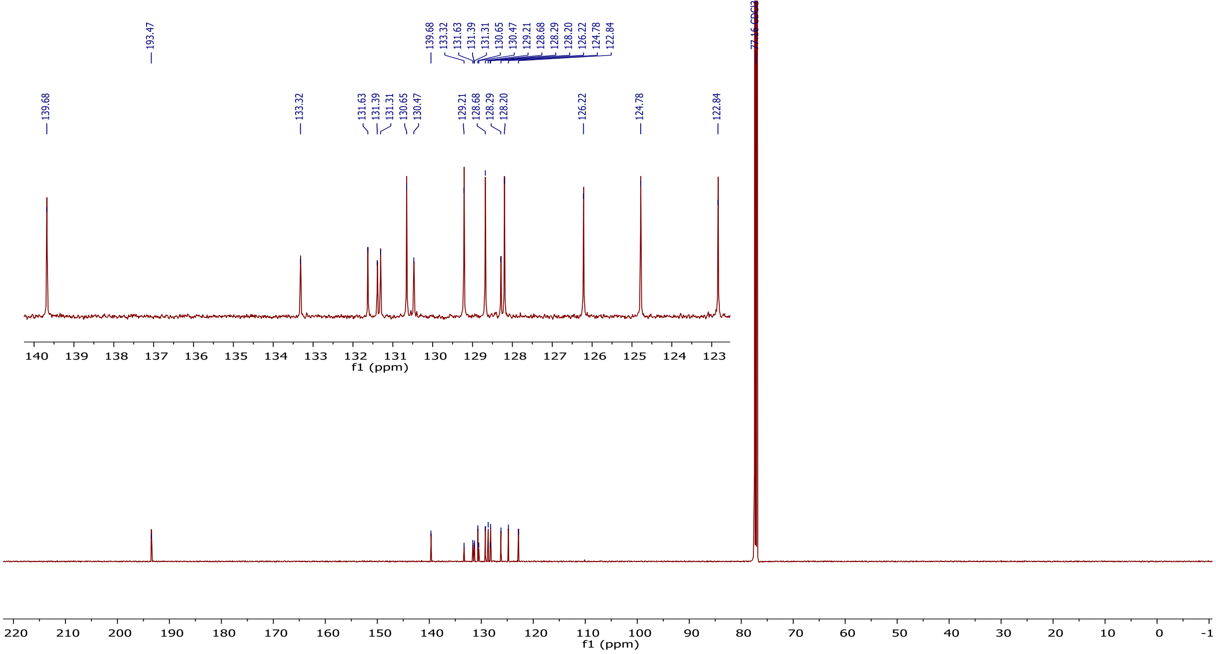


1c

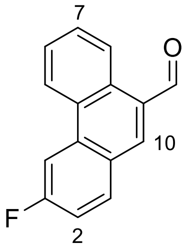
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



^{13}C NMR (126 MHz, CDCl$_3$, 300 K):

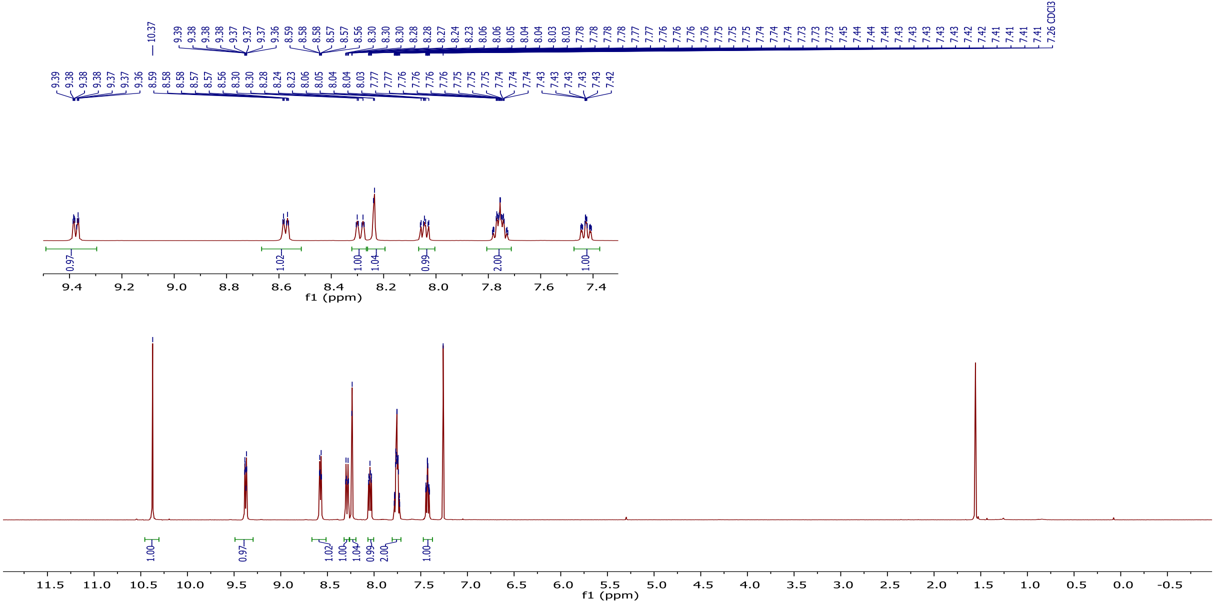


3-Fluorophenanthrene-9-carboxaldehyde (1d)

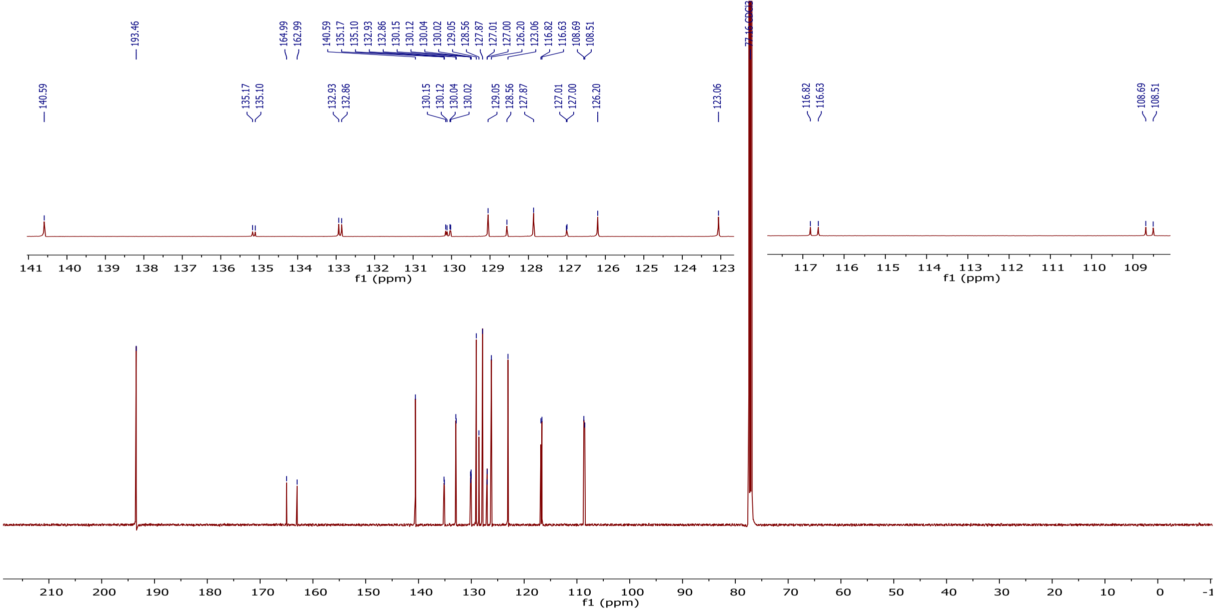


1d

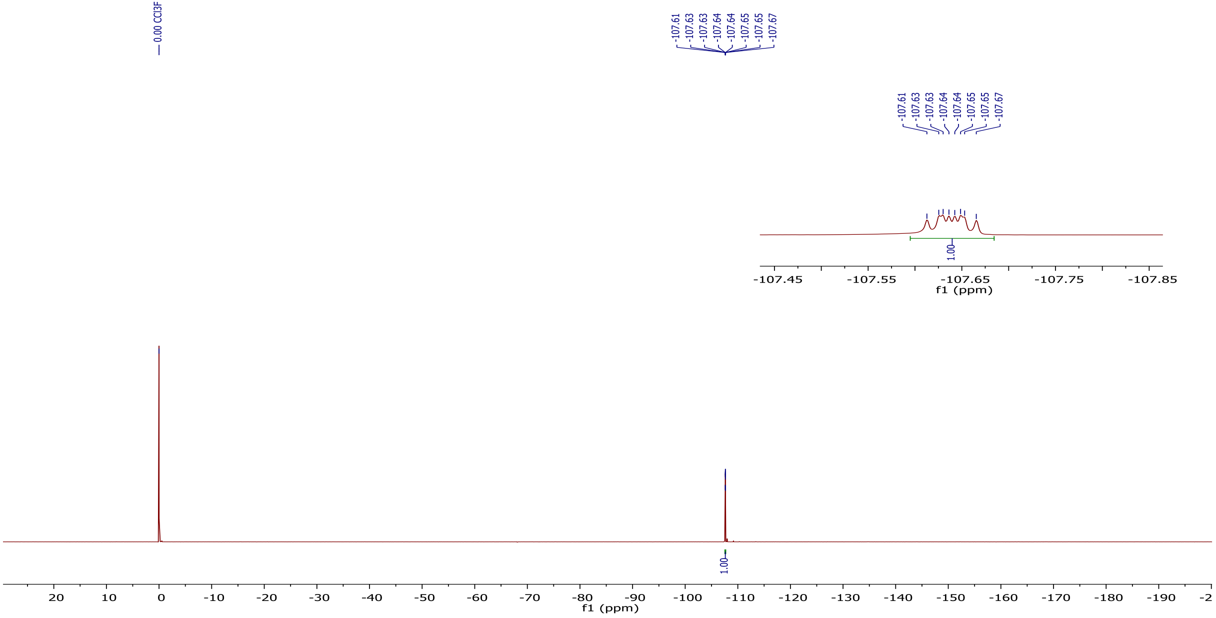
^{1}H NMR (500 MHz, CDCl$_3$, 300 K):



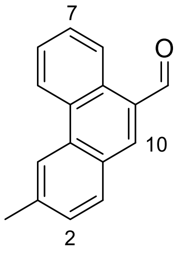
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



^{19}**F NMR** (471 MHz, $CDCl_3$, 300 K):

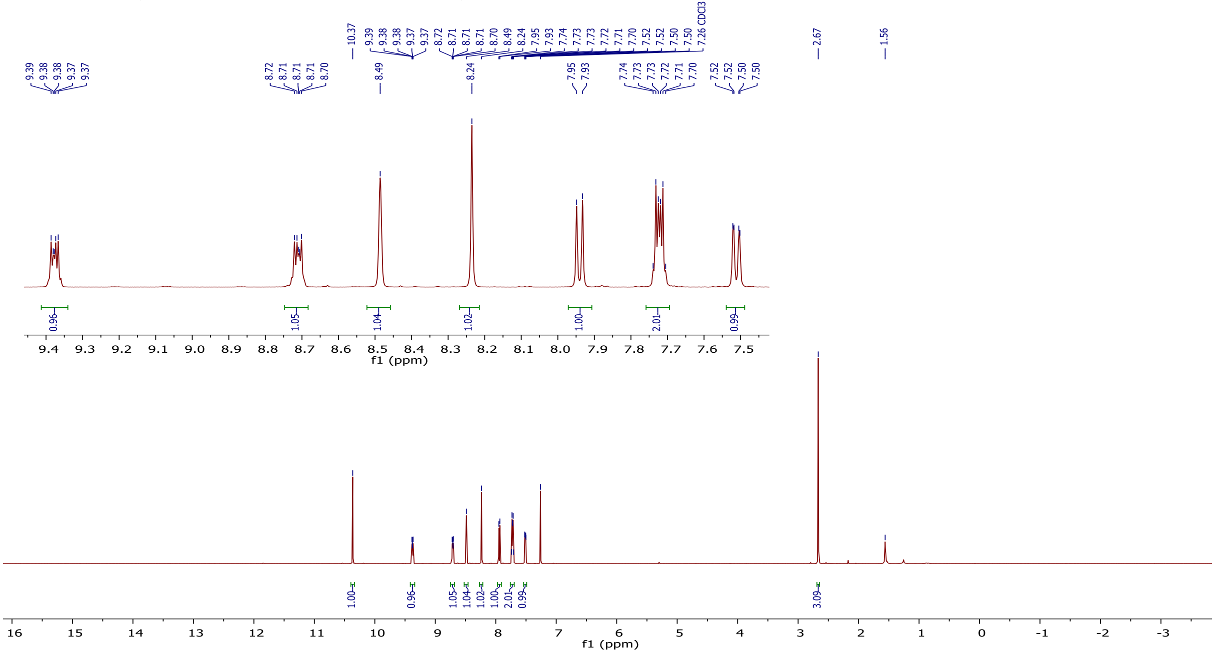


3-Methylphenanthrene-9-carboxaldehyde (1e)

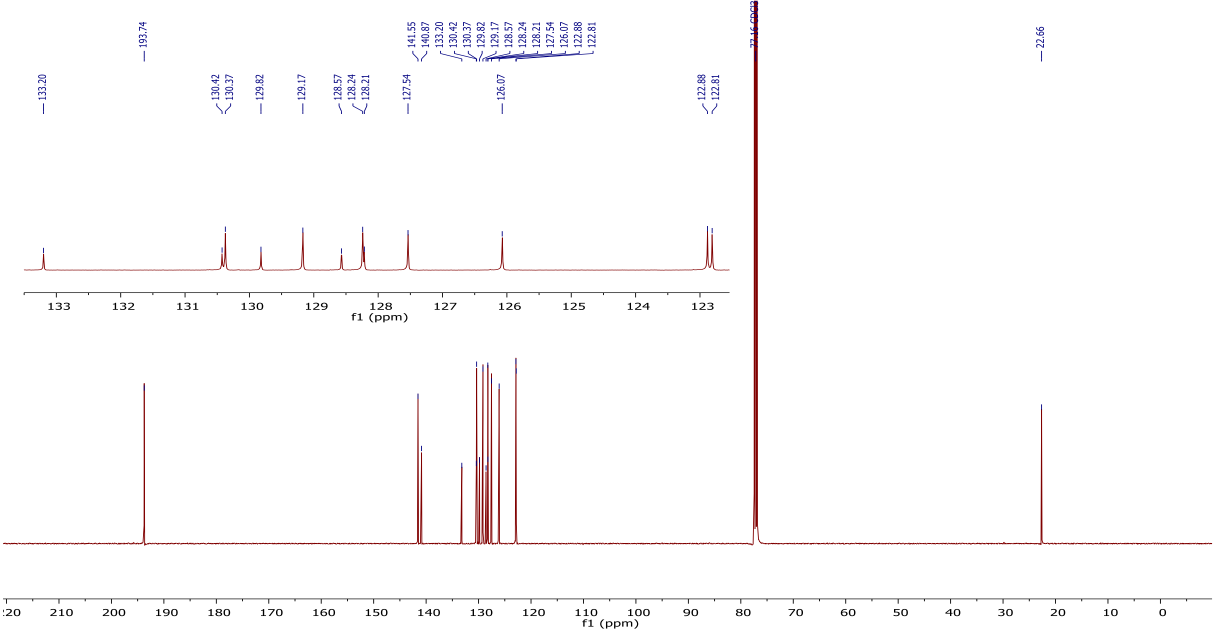


1e

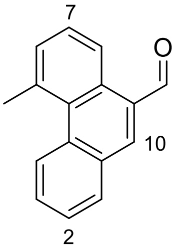
¹H NMR (500 MHz, $CDCl_3$, 298 K):



¹³C NMR (126 MHz, $CDCl_3$, 300 K):

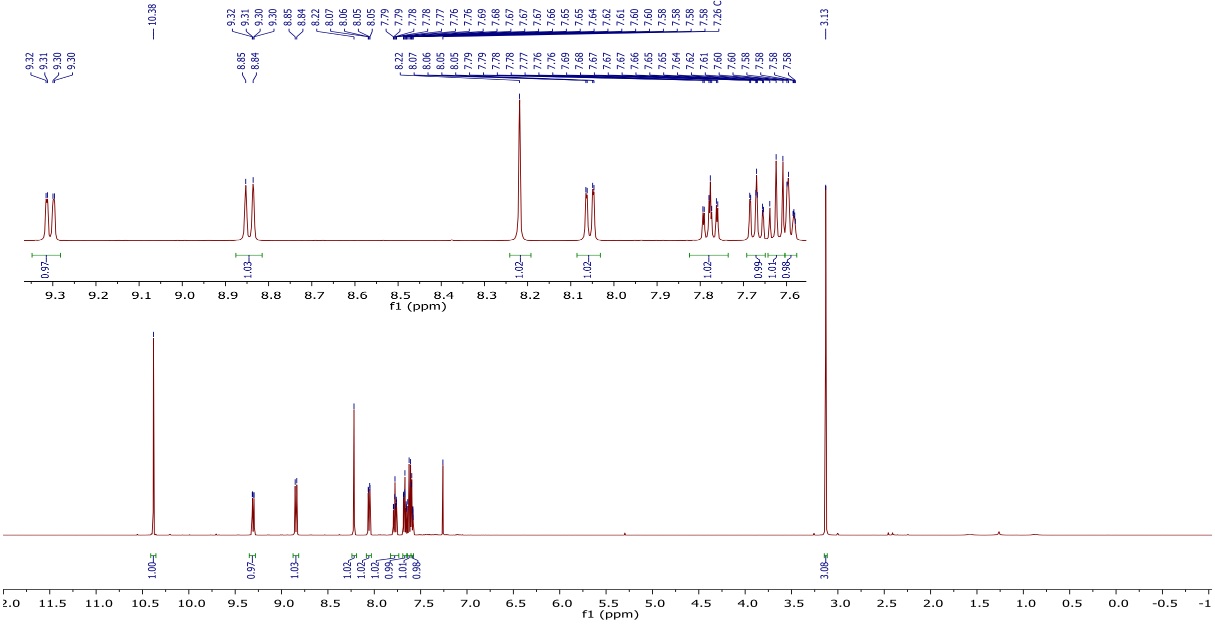


5-Methylphenanthrene-9-carboxaldehyde (1f)

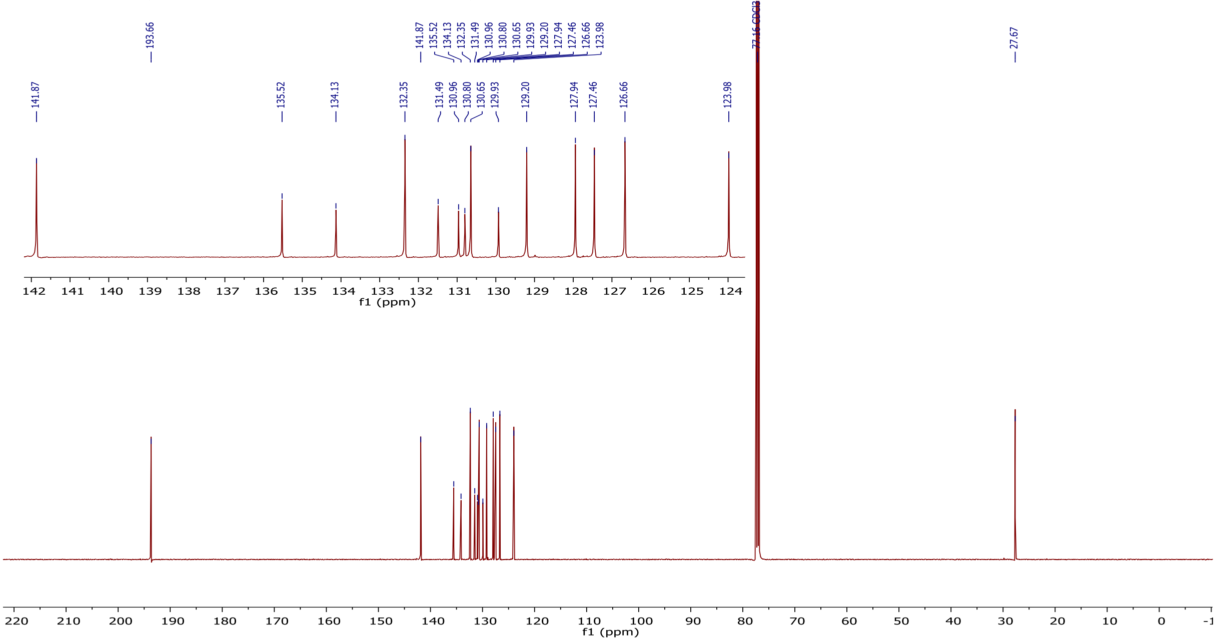


1f

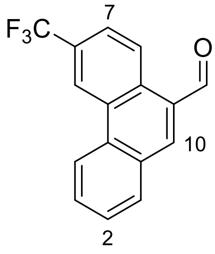
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 300 K):

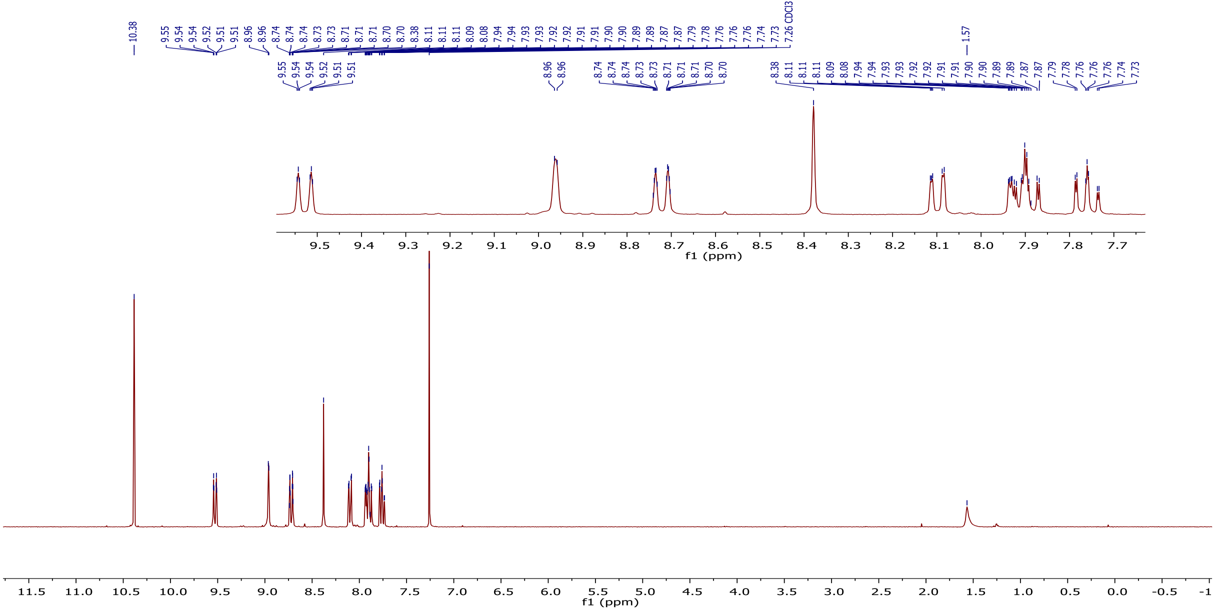


6-(Trifluoromethyl)phenanthrene-9-carboxaldehyde (1g)

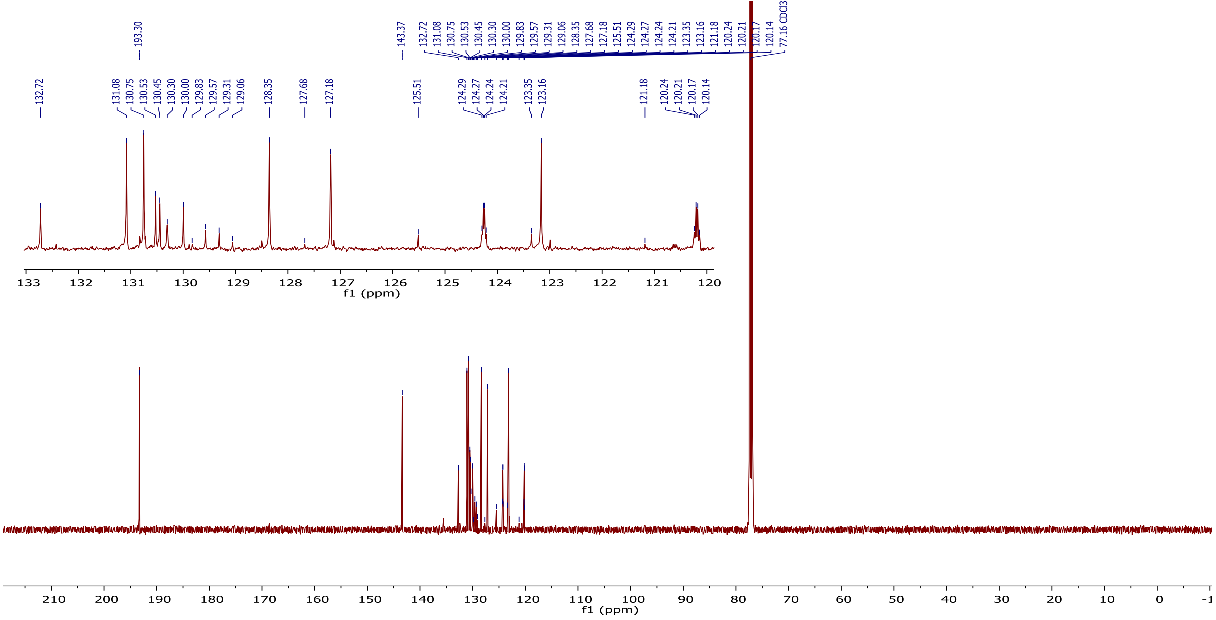


1g

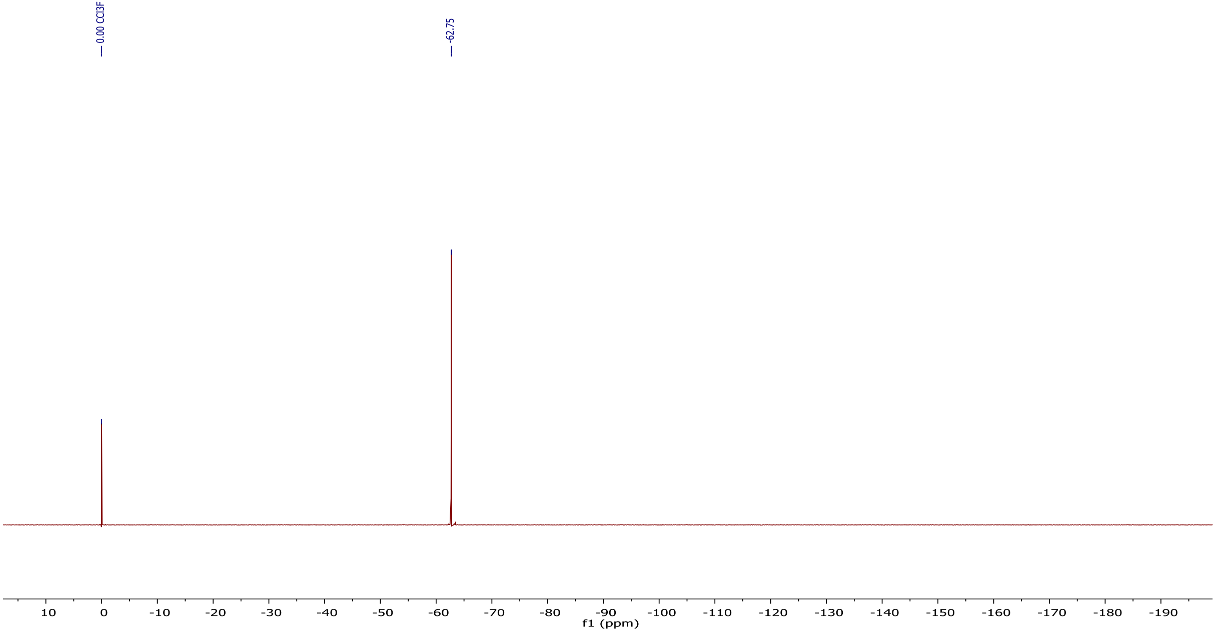
^{1}**H NMR** (300 MHz, CDCl$_3$, 298 K):



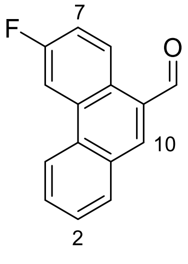
^{13}**C NMR** (126 MHz, CDCl$_3$, 300 K):



^{19}**F NMR** (376 MHz, $CDCl_3$, 300 K):

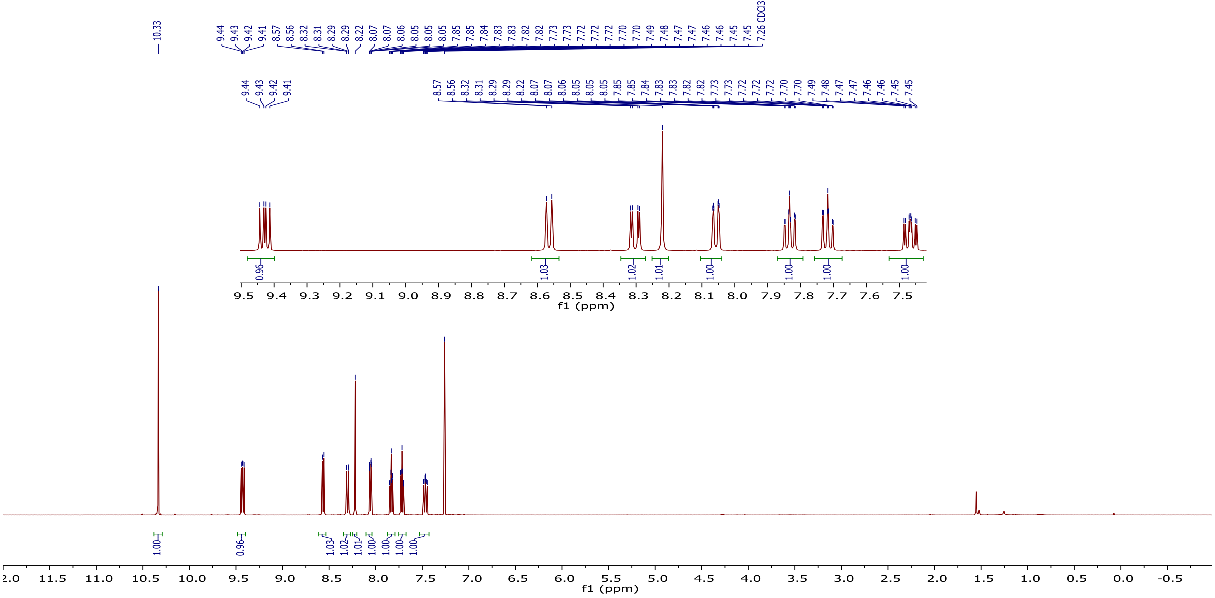


6-Fluorophenanthrene-9-carboxaldehyde (1h)

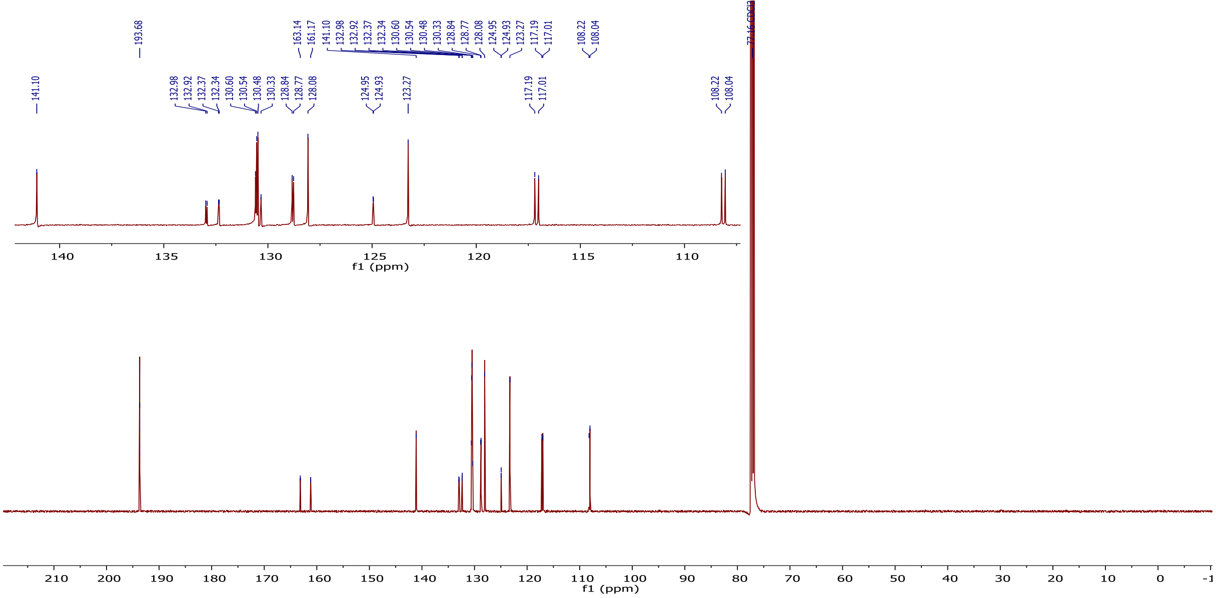


1h

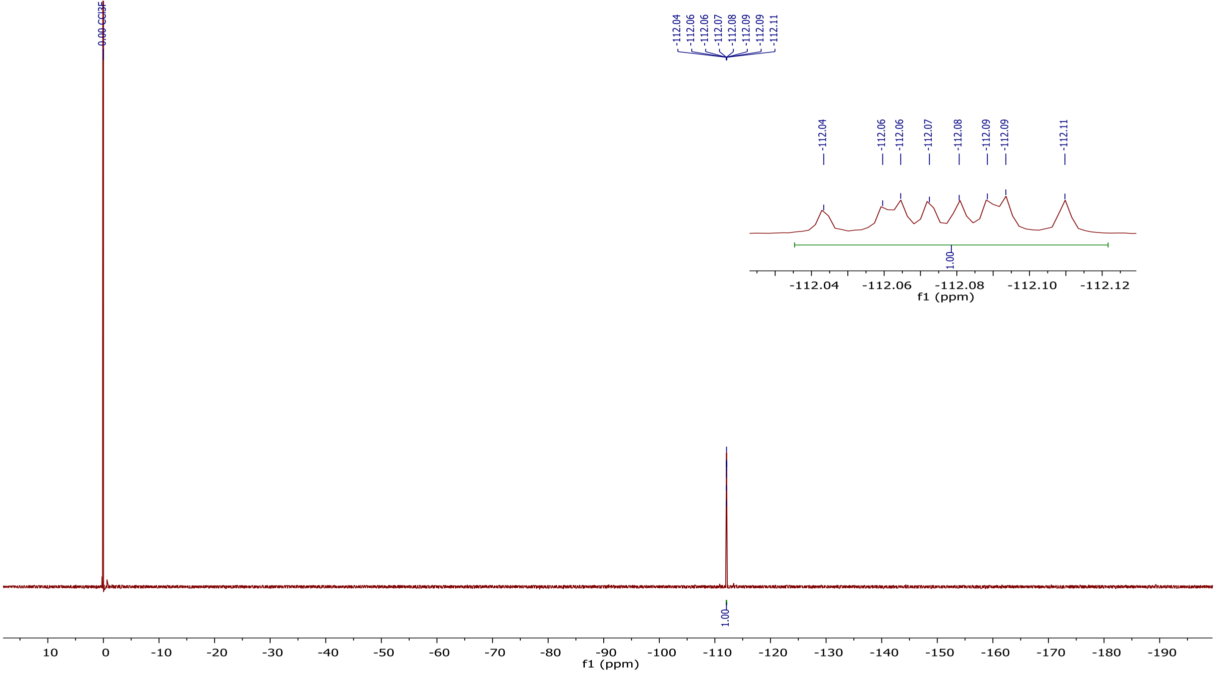
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



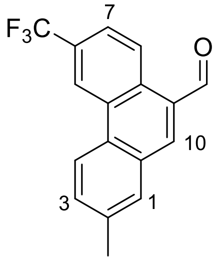
^{13}C NMR (126 MHz, $CDCl_3$, 300 K):



^{19}F NMR (376 MHz, $CDCl_3$, 300 K):

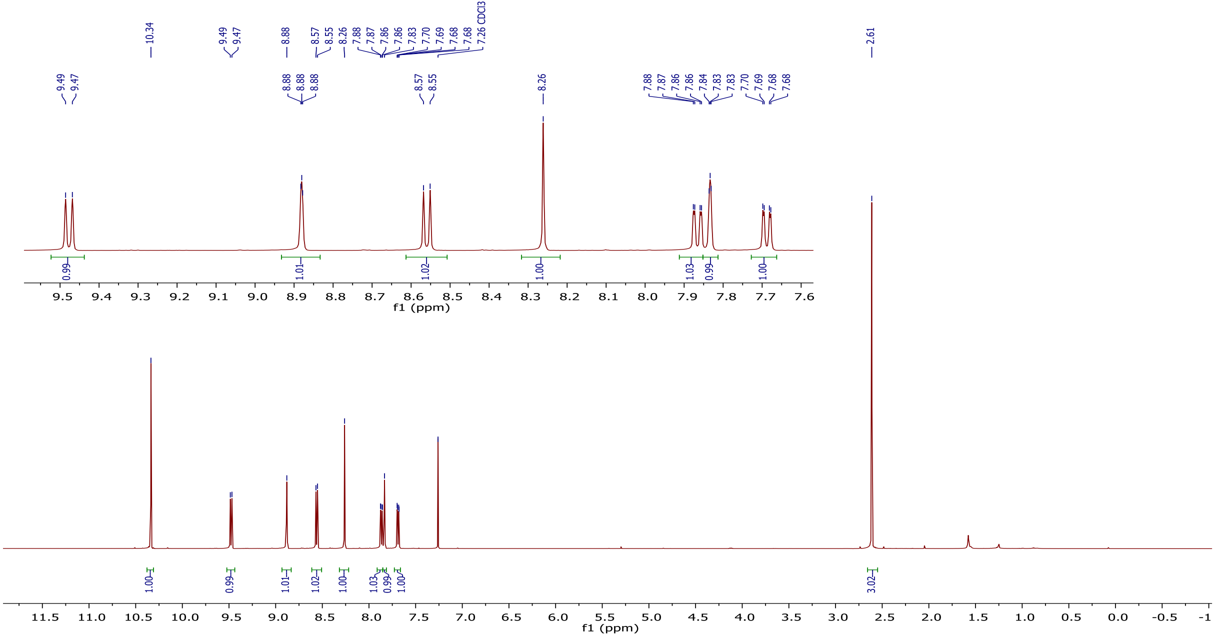


2-Methyl-6-(trifluoromethyl)phenanthrene-9-carboxaldehyde (1i)

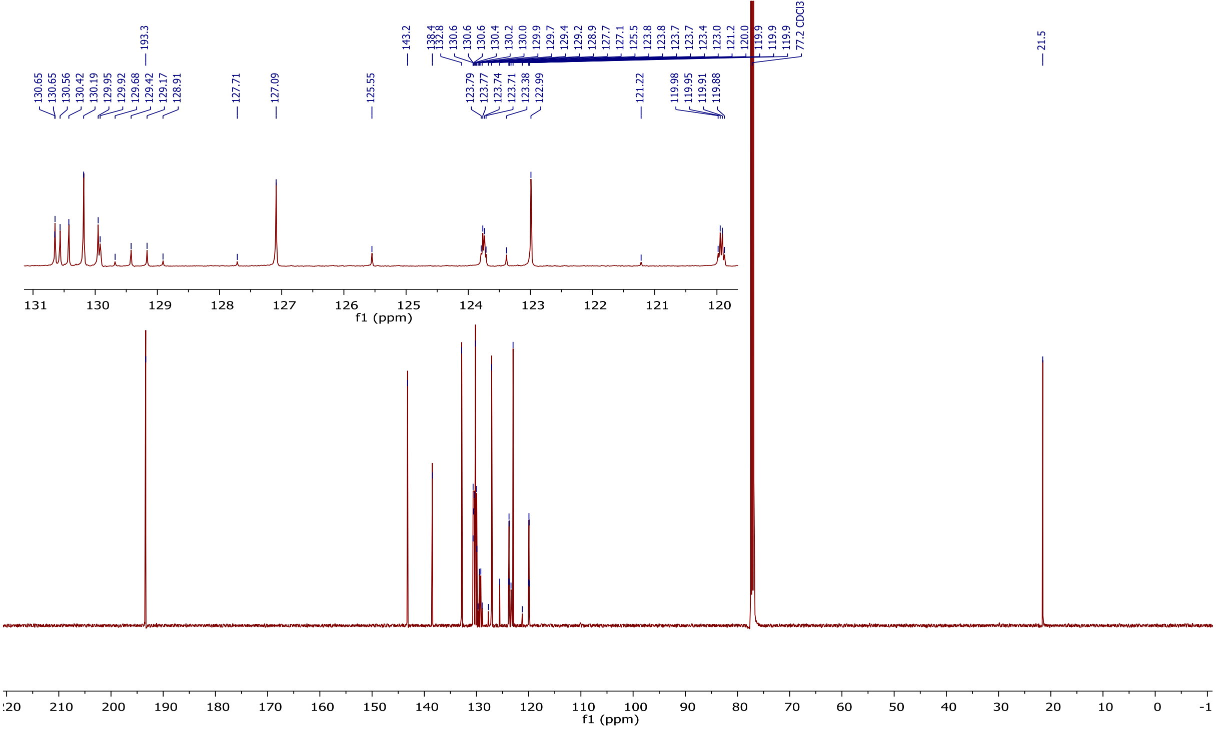


1i

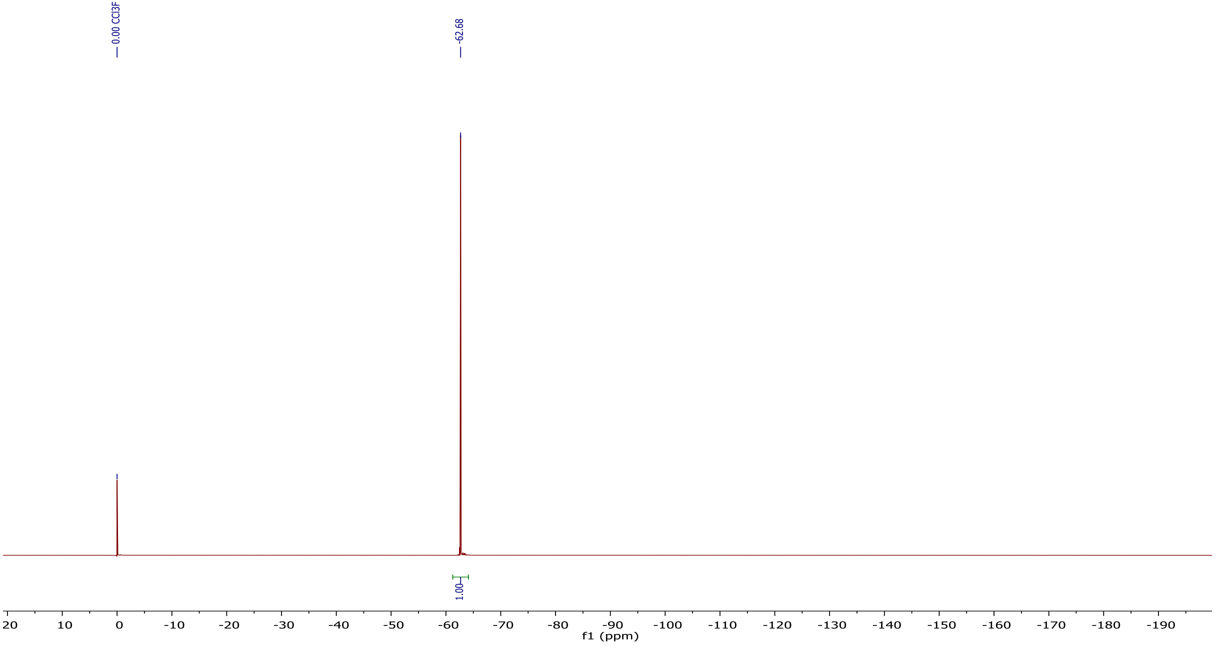
^{1}H NMR (500 MHz, $CDCl_3$, 300 K):



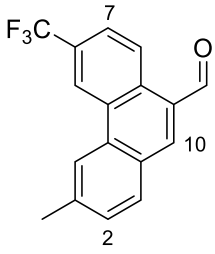
^{13}C NMR (126 MHz, $CDCl_3$, 300 K):



^{19}F NMR (471 MHz, $CDCl_3$, 300 K):

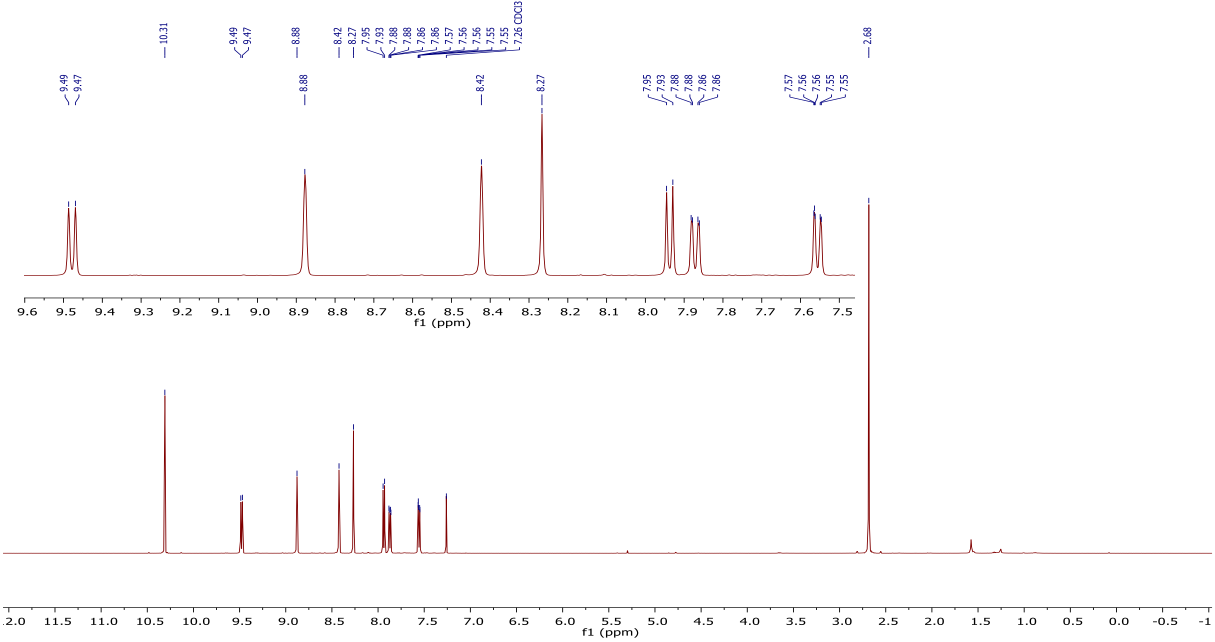


3-Methyl-6-(trifluoromethyl)phenanthrene-9-carboxaldehyde (1j)

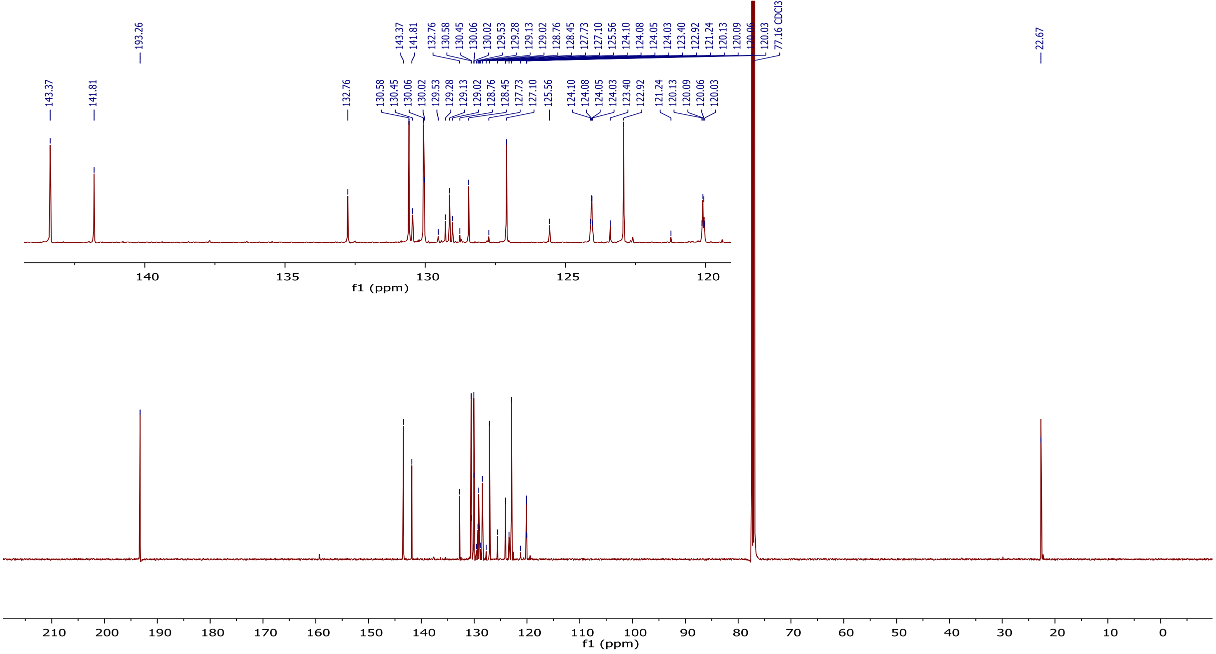


1j

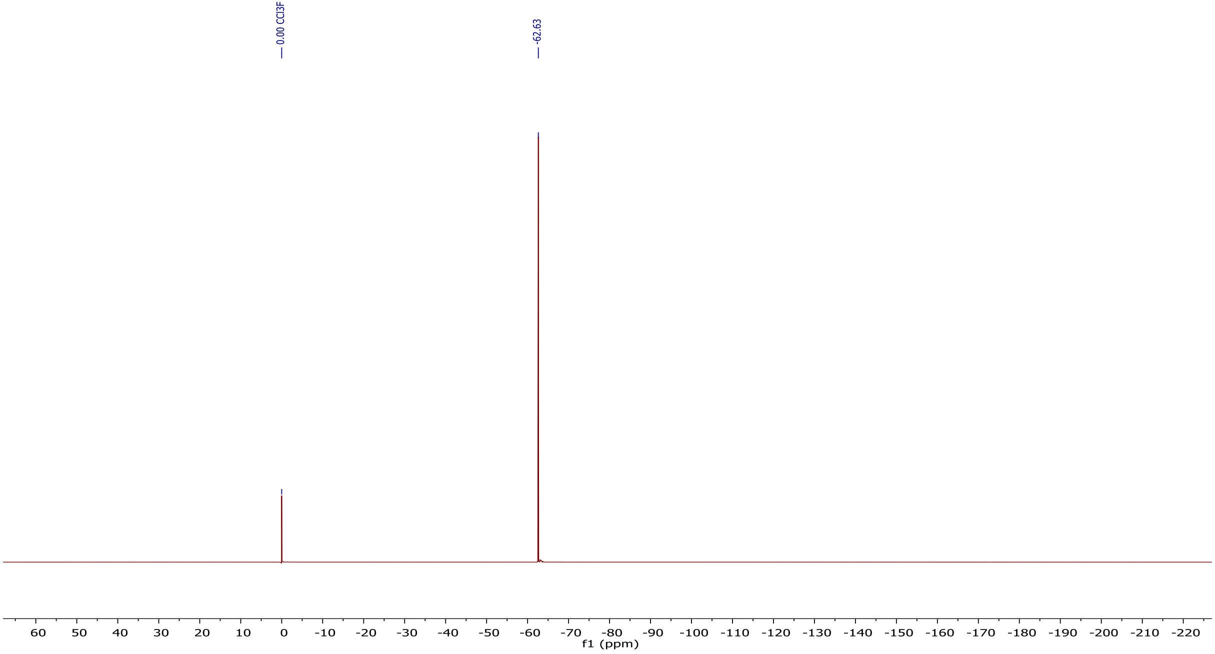
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



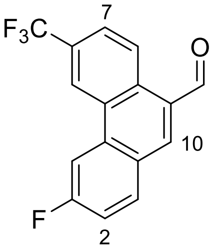
^{13}C NMR (126 MHz, $CDCl_3$, 300 K):



^{19}F NMR (471 MHz, $CDCl_3$, 300 K):

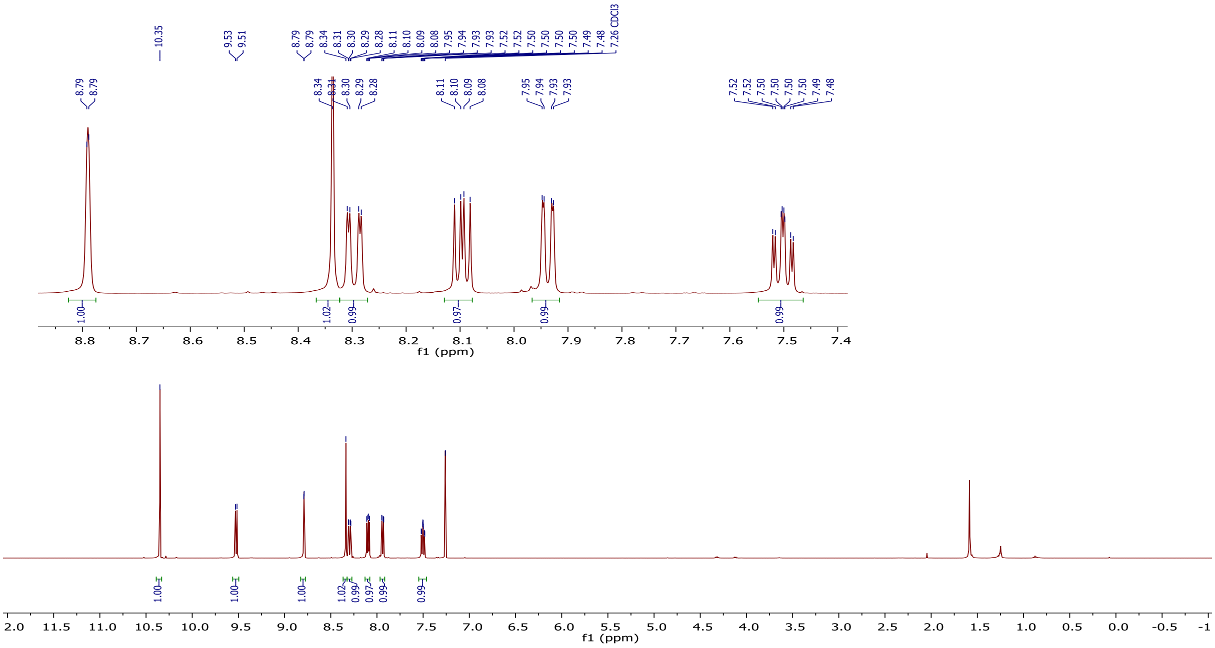


3-Fluoro-6-(trifluoromethyl)phenanthrene-9-carboxaldehyde (1k)

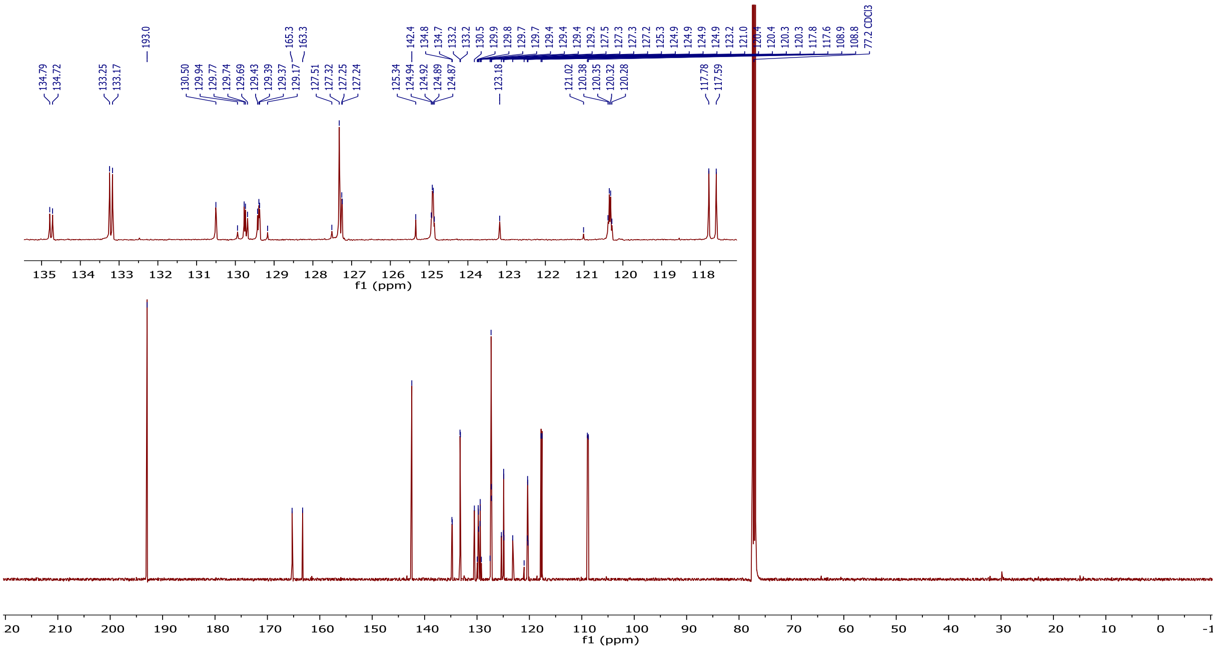


1k

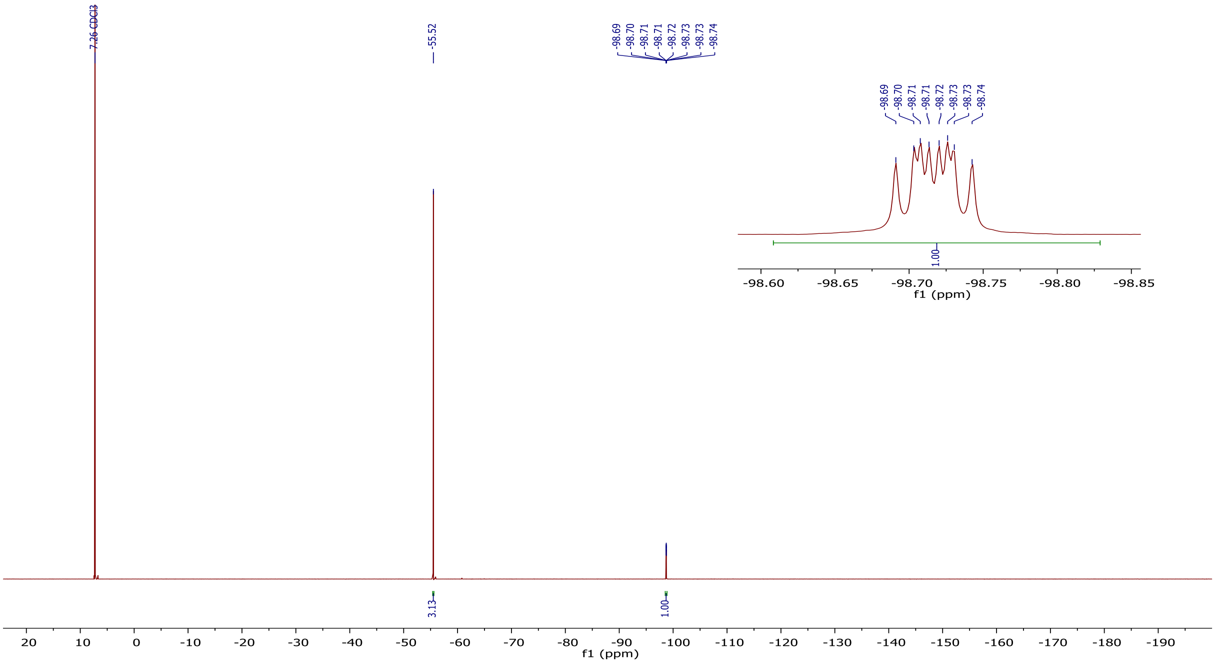
^{1}H NMR (500 MHz, CDCl$_3$, 300 K):



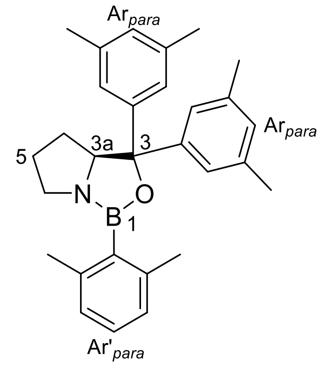
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



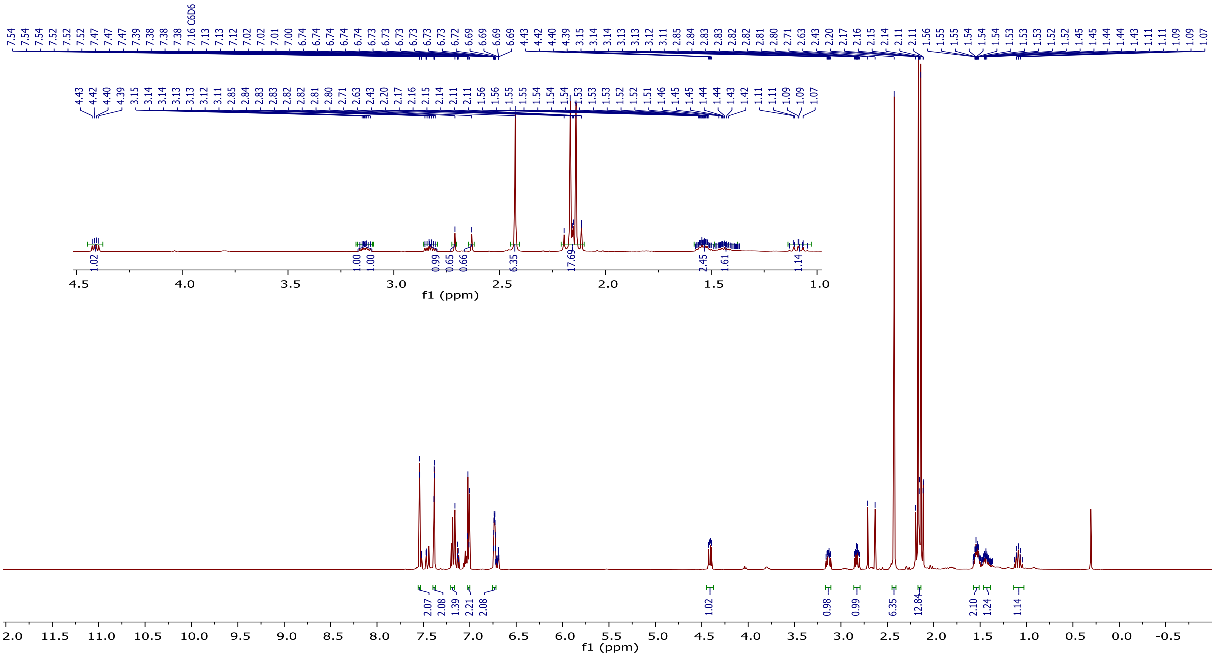
^{19}F NMR (471 MHz, $CDCl_3$, 300 K):



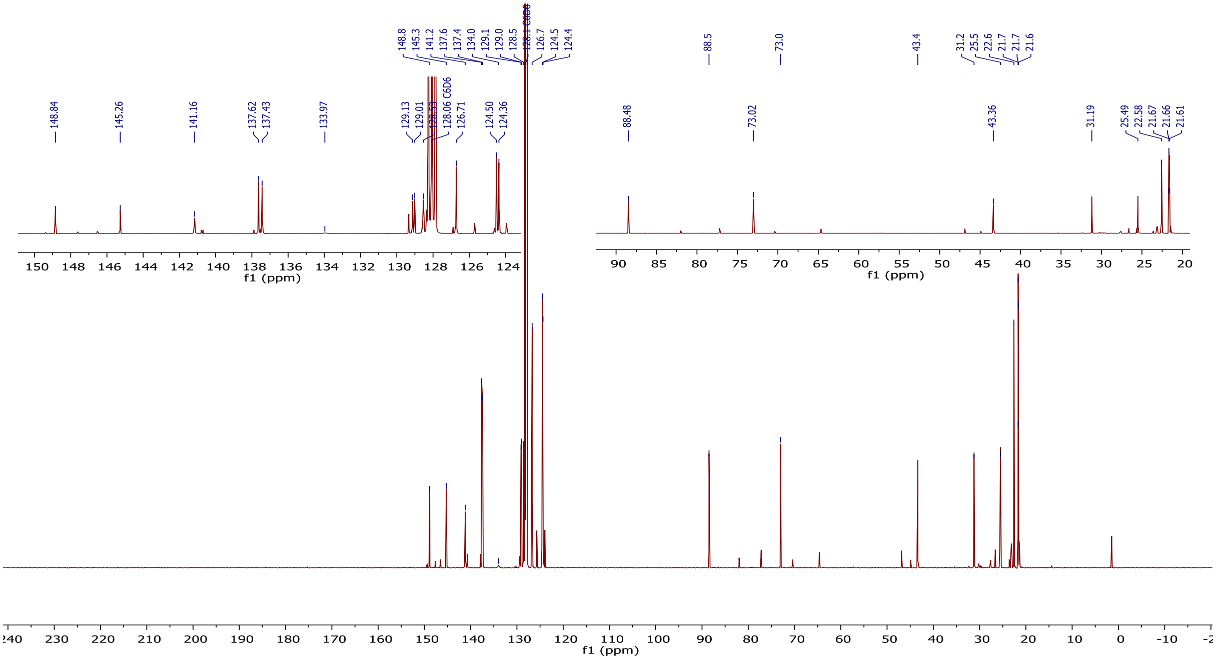
(*S*)-1-(2,6-dimethylphenyl)-3,3-bis(3,5-dimethylphenyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole



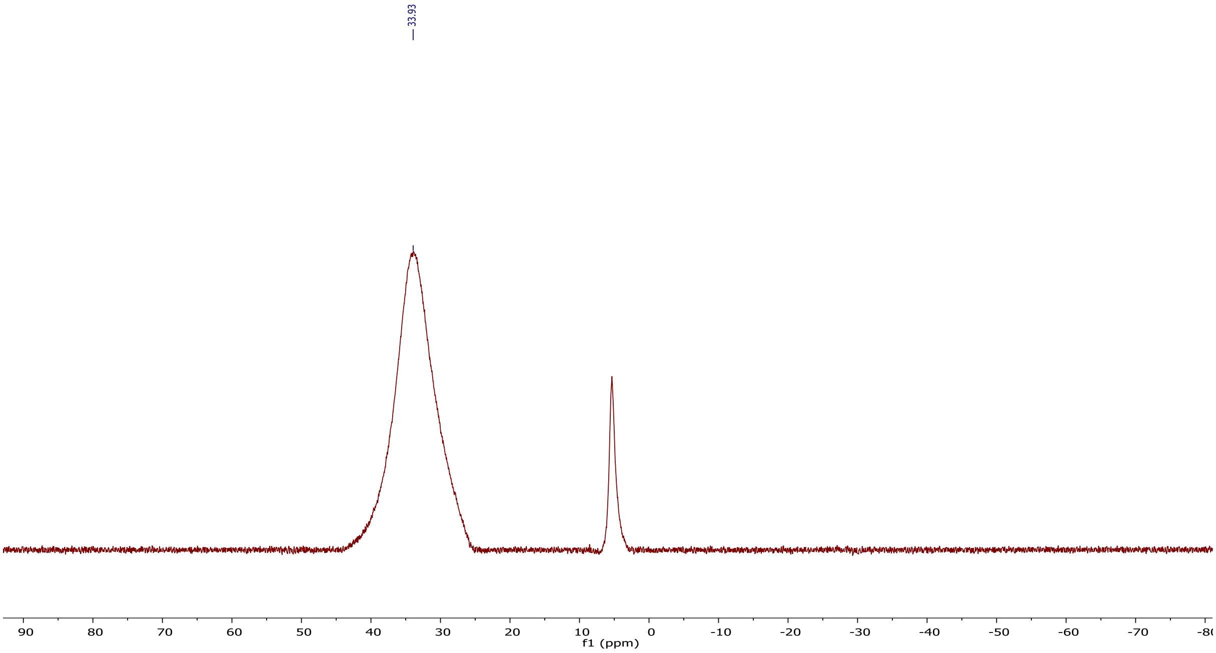
^{1}**H NMR** (500 MHz, C_6D_6, 298 K):



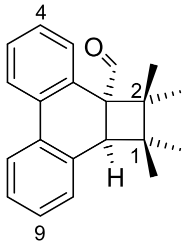
^{13}**C NMR** (126 MHz, C_6D_6, 300 K):



^{11}**B NMR** (128 MHz, C_6D_6, 300 K):

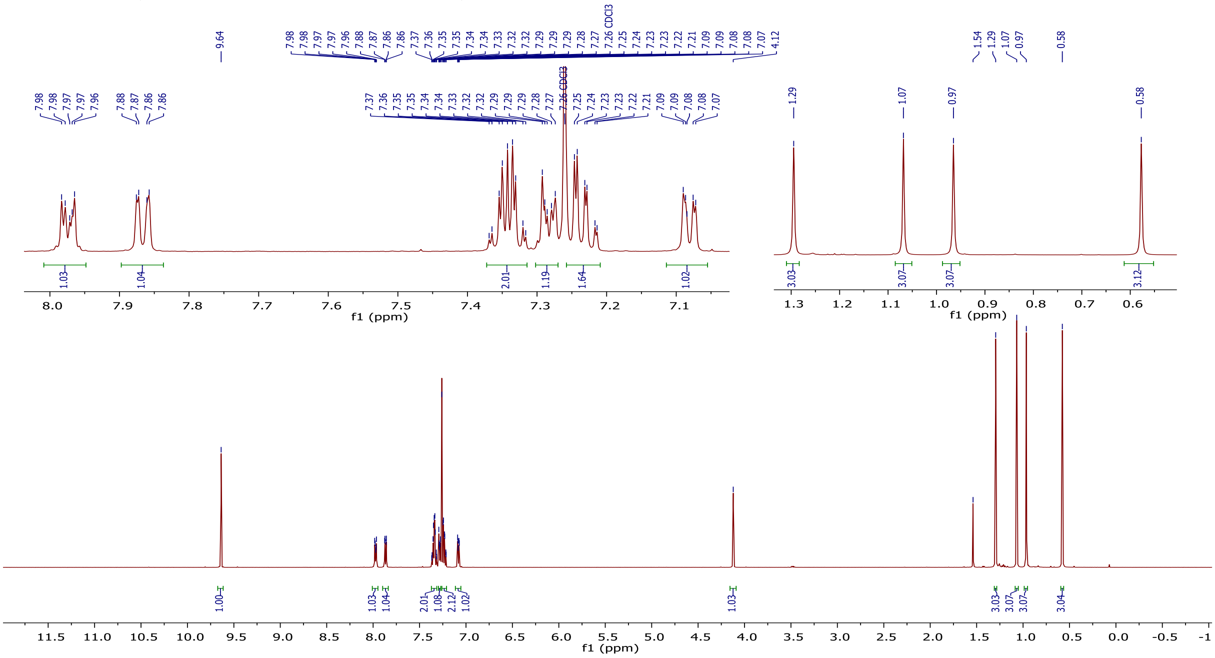


(2a*S*,10b*S*)-1,1,2,2-Tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2a)

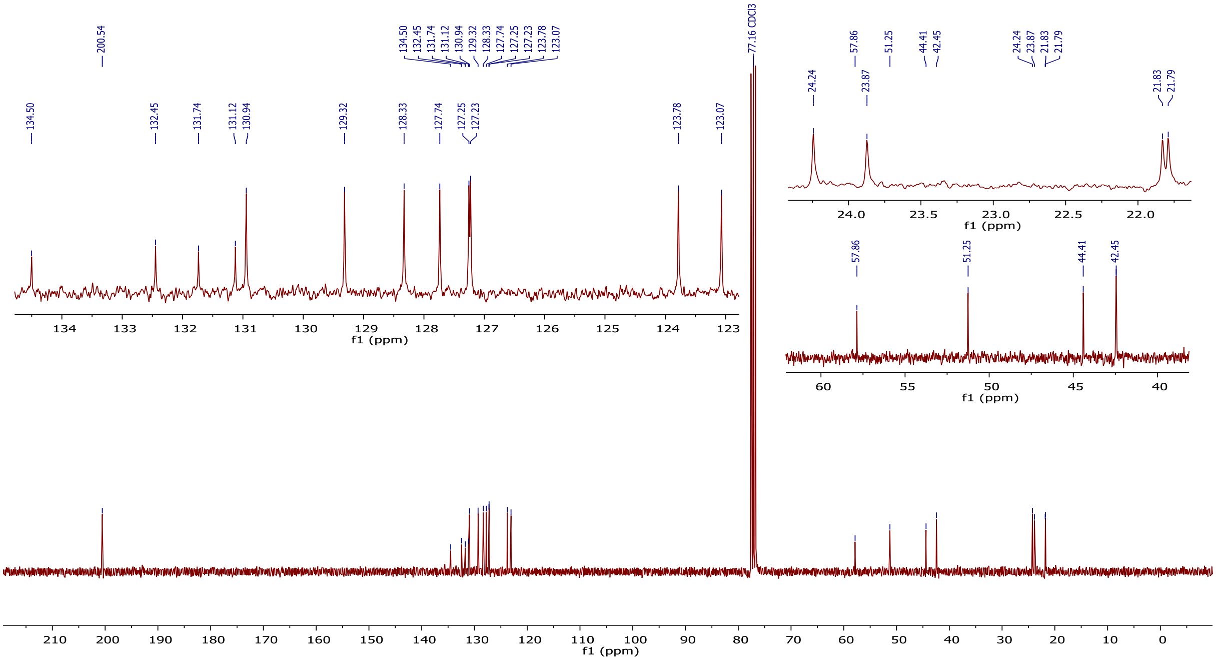


2a

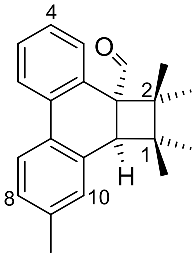
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (75 MHz, $CDCl_3$, 298 K):

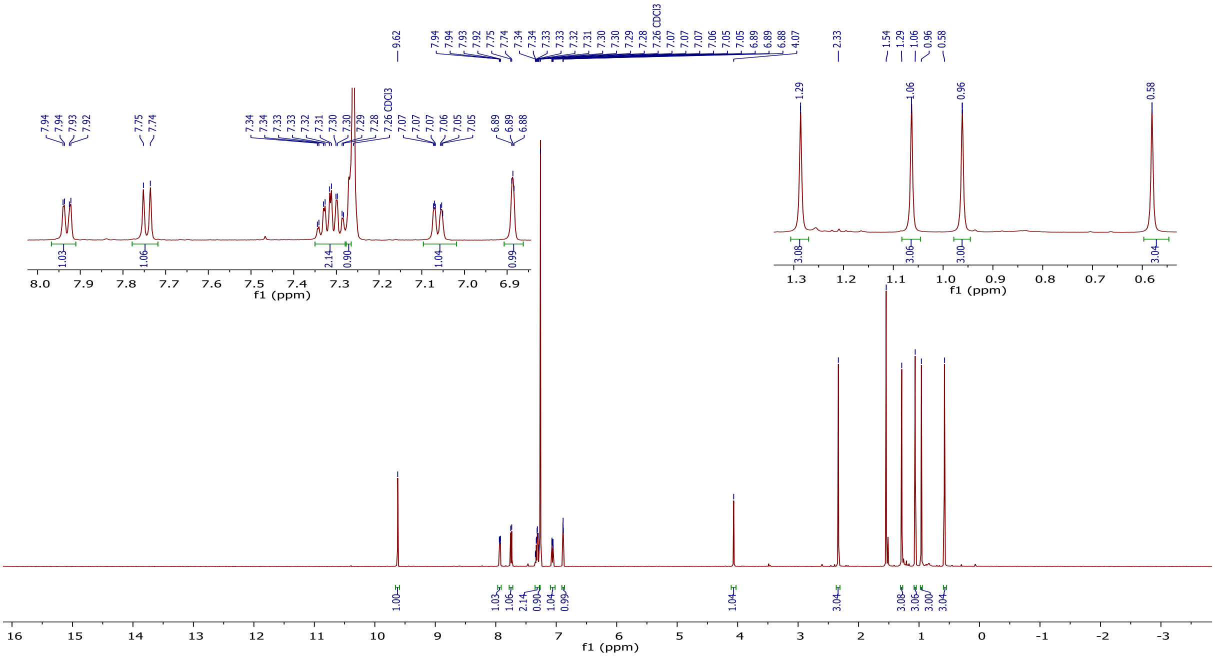


(2a*S*,10b*S*)-1,1,2,2,9-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2b)

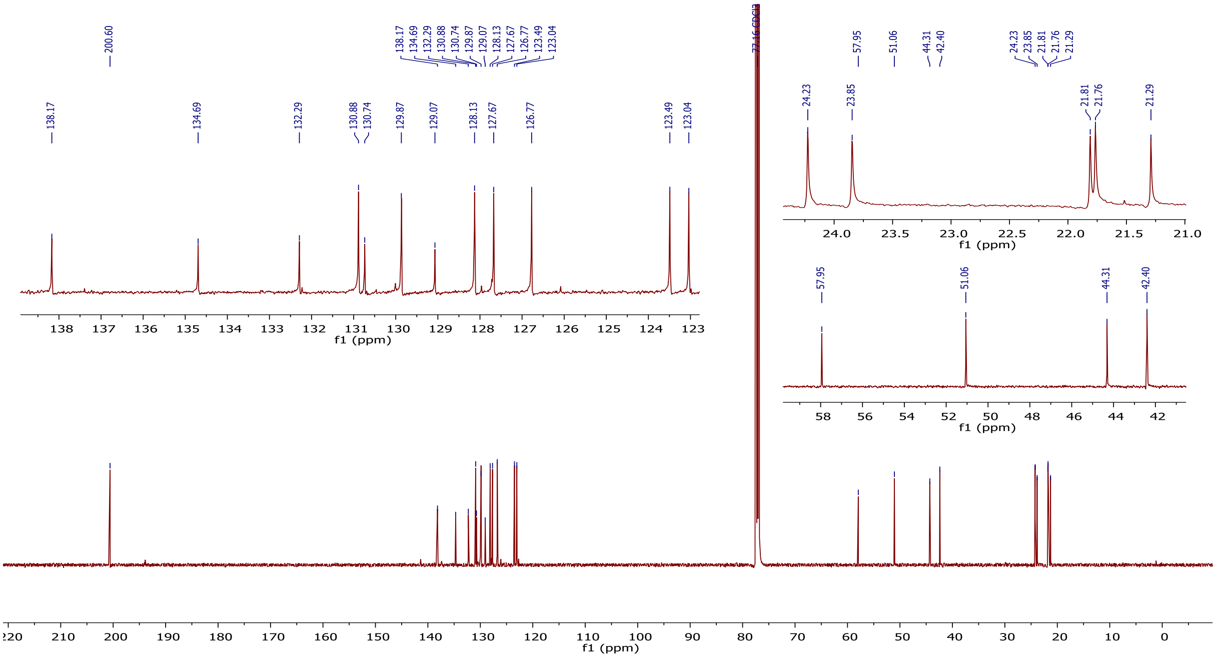


2b

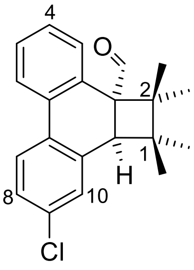
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 300 K):

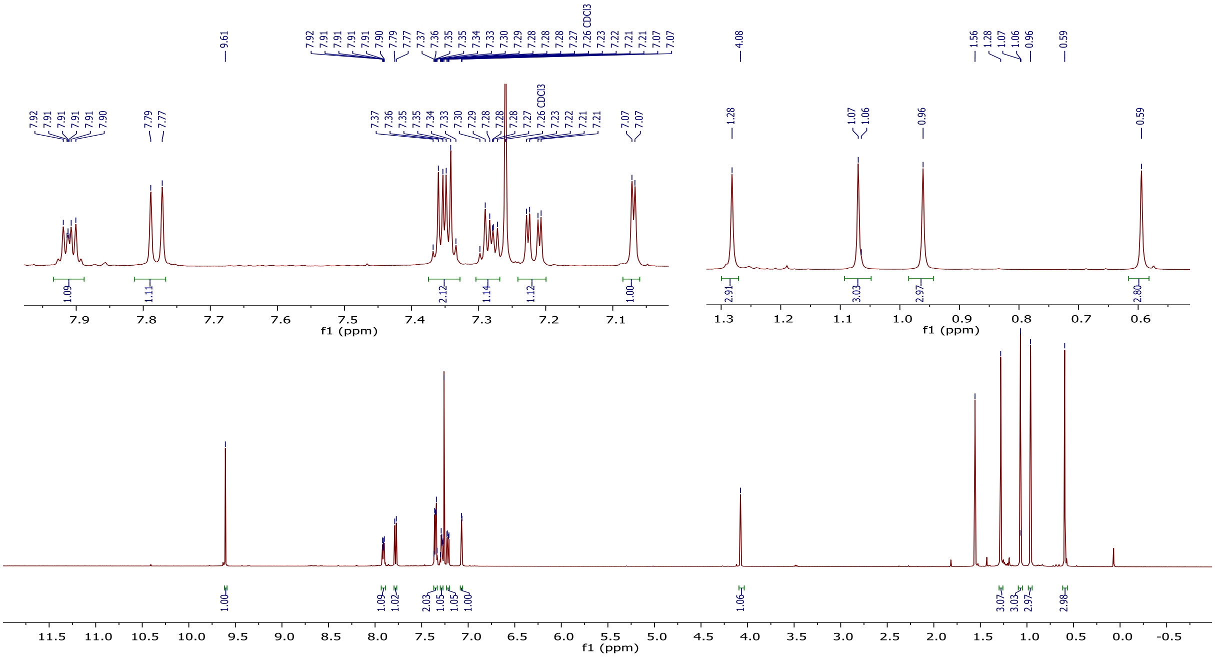


(2a*S*,10b*S*)-9-Chloro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2c)

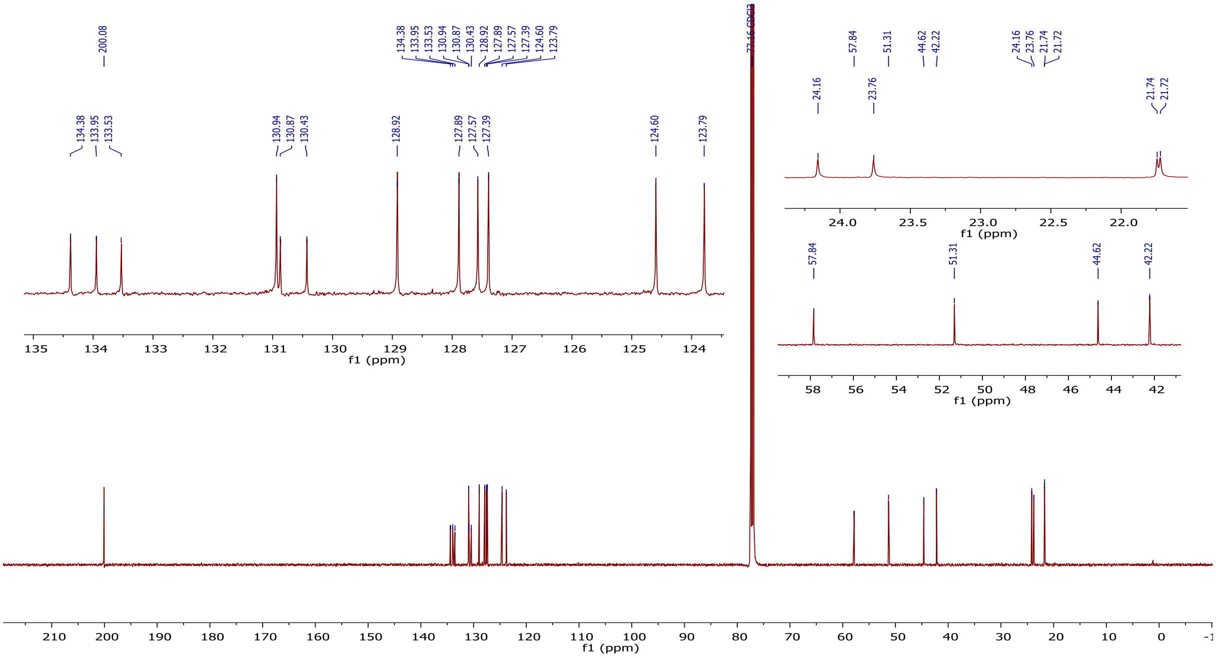


2c

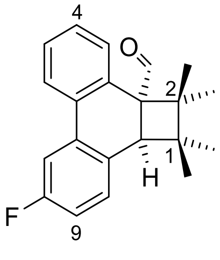
^{1}**H NMR** (500 MHz, $CDCl_3$, 300 K):



^{13}**C NMR** (126 MHz, $CDCl_3$, 300 K):

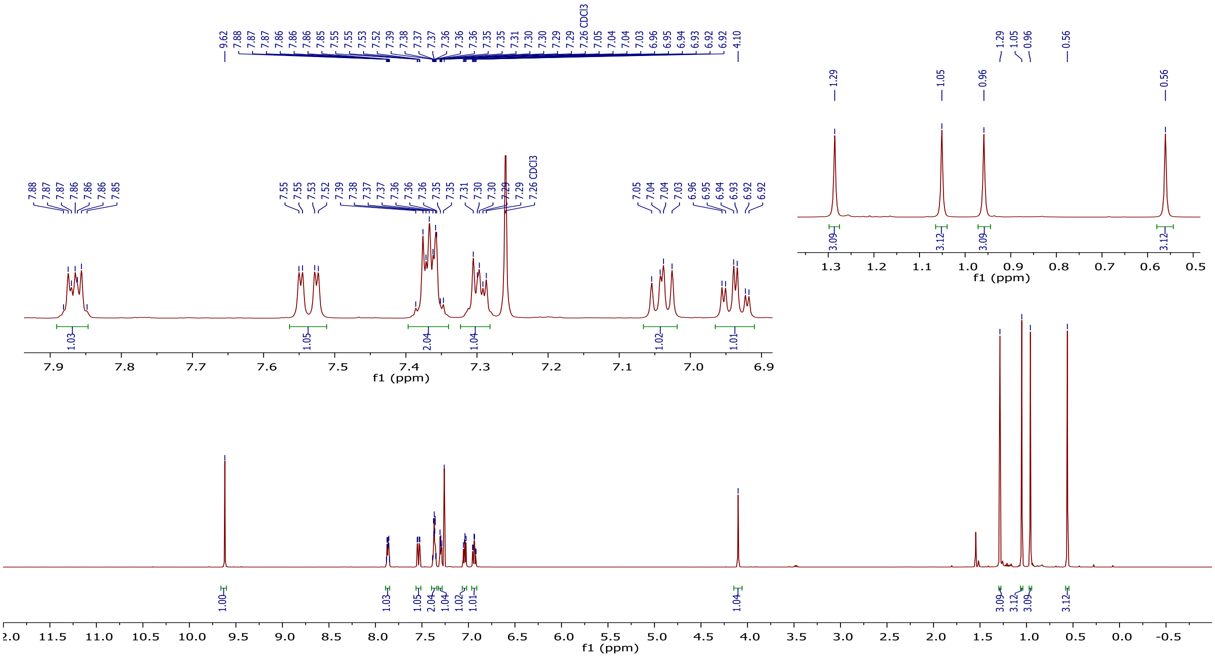


(2a*S*,10b*S*)-8-Fluoro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2d)

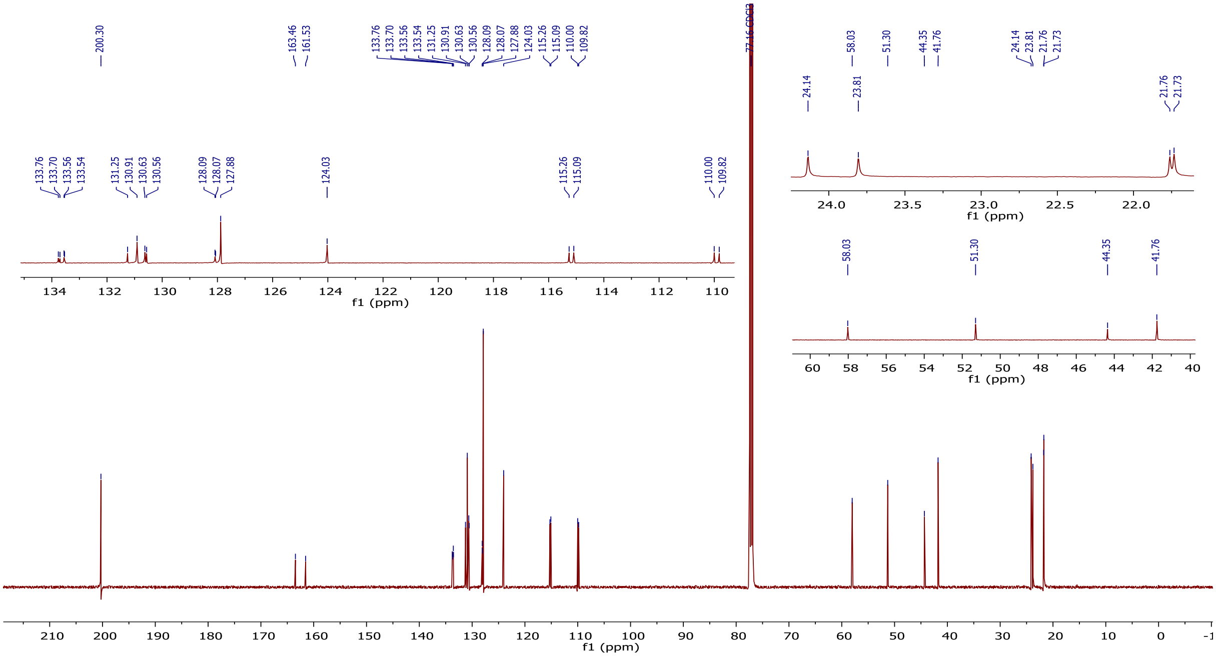


2d

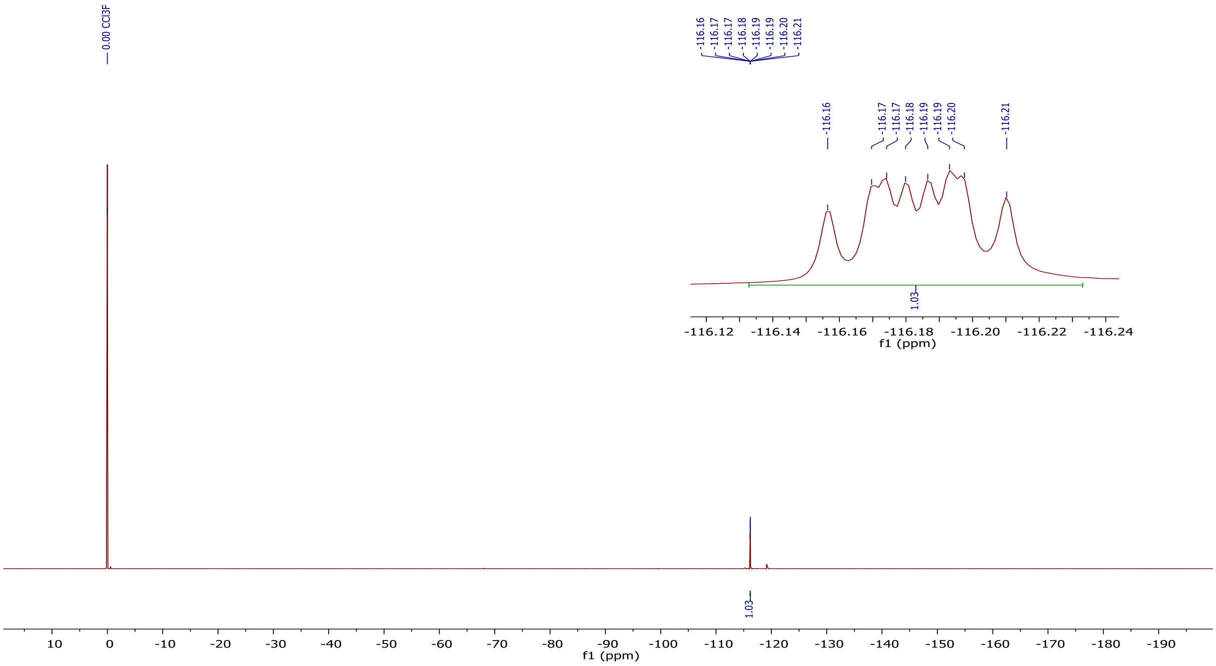
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



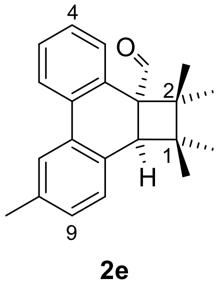
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



^{19}F NMR (471 MHz, CDCl$_3$, 300 K):

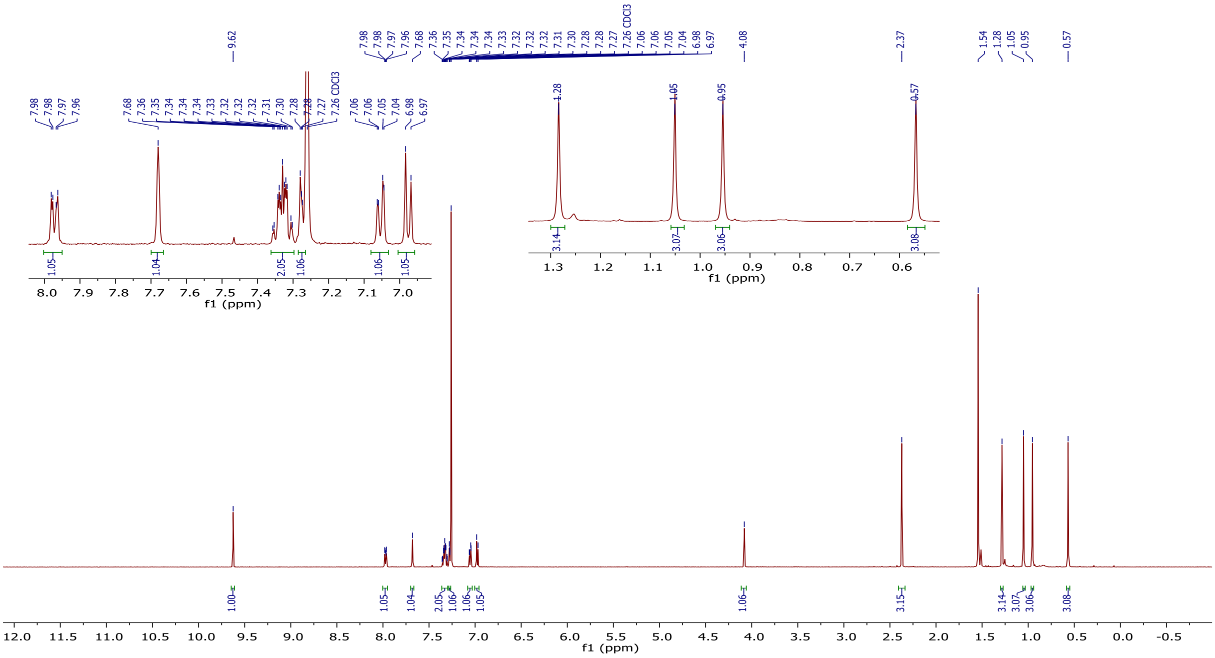


(2a*S*,10b*S*)-1,1,2,2,8-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2e)

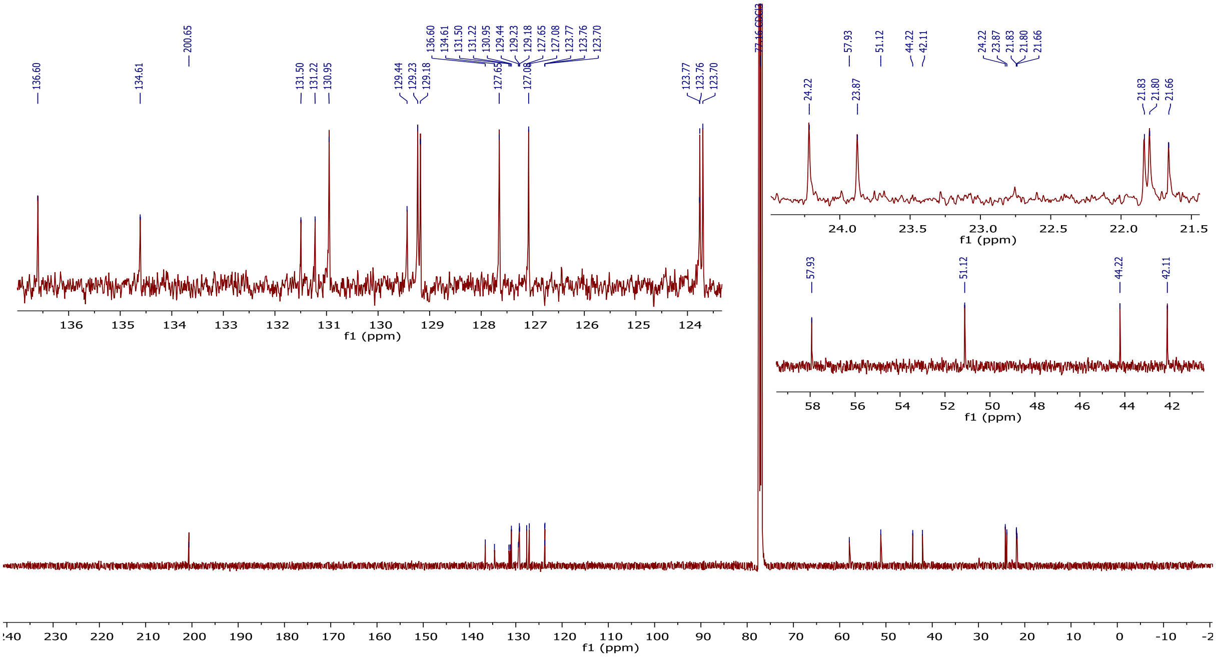


2e

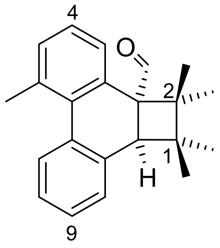
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 300 K):

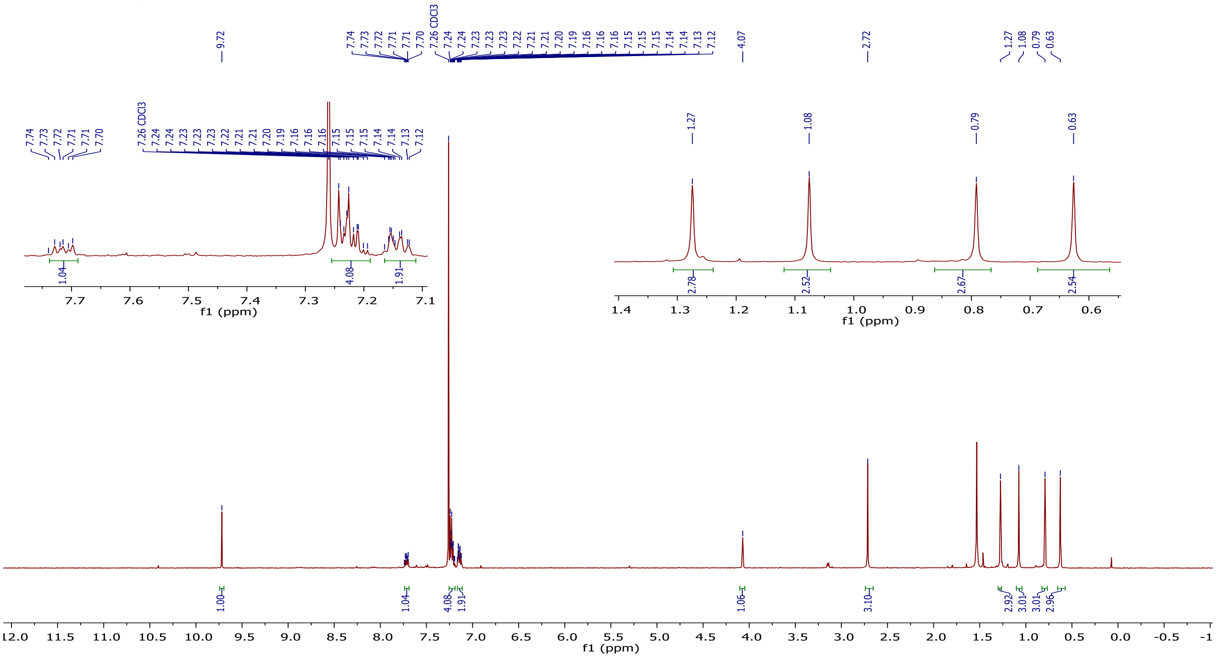


(2a*S*,10b*S*)-1,1,2,2,6-Pentamethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2f)

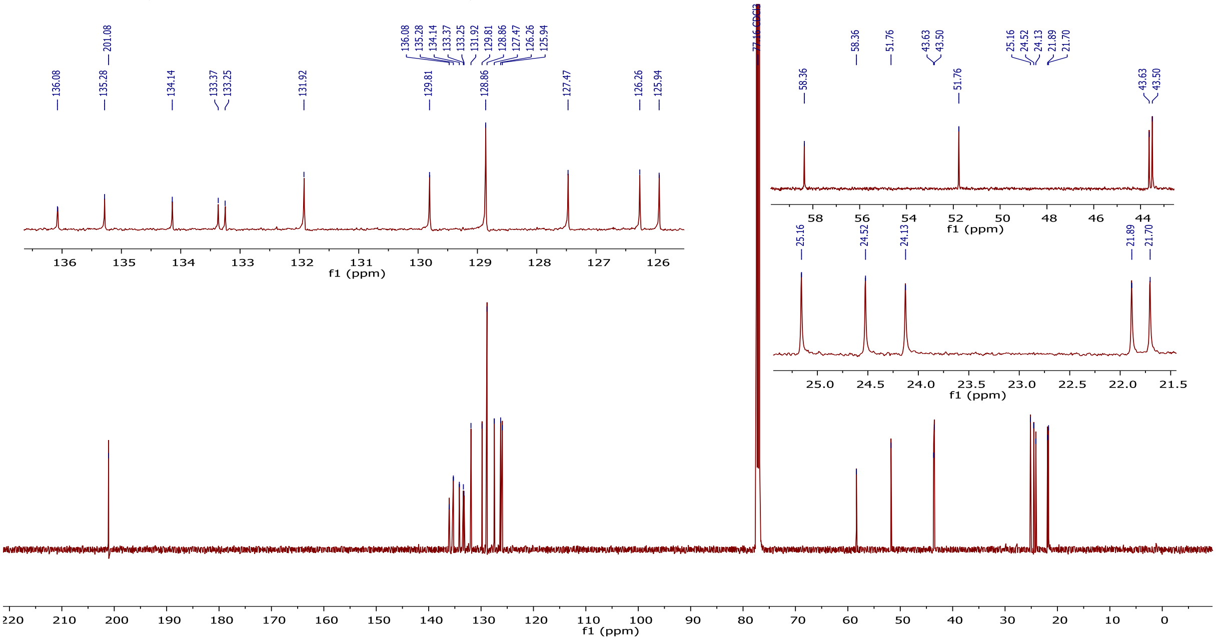


2f

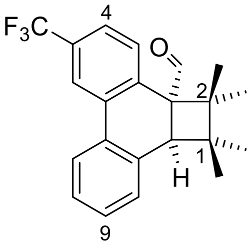
^{1}H NMR (300 MHz, CDCl$_3$, 298 K):



^{13}C NMR (126 MHz, CDCl$_3$, 300 K):

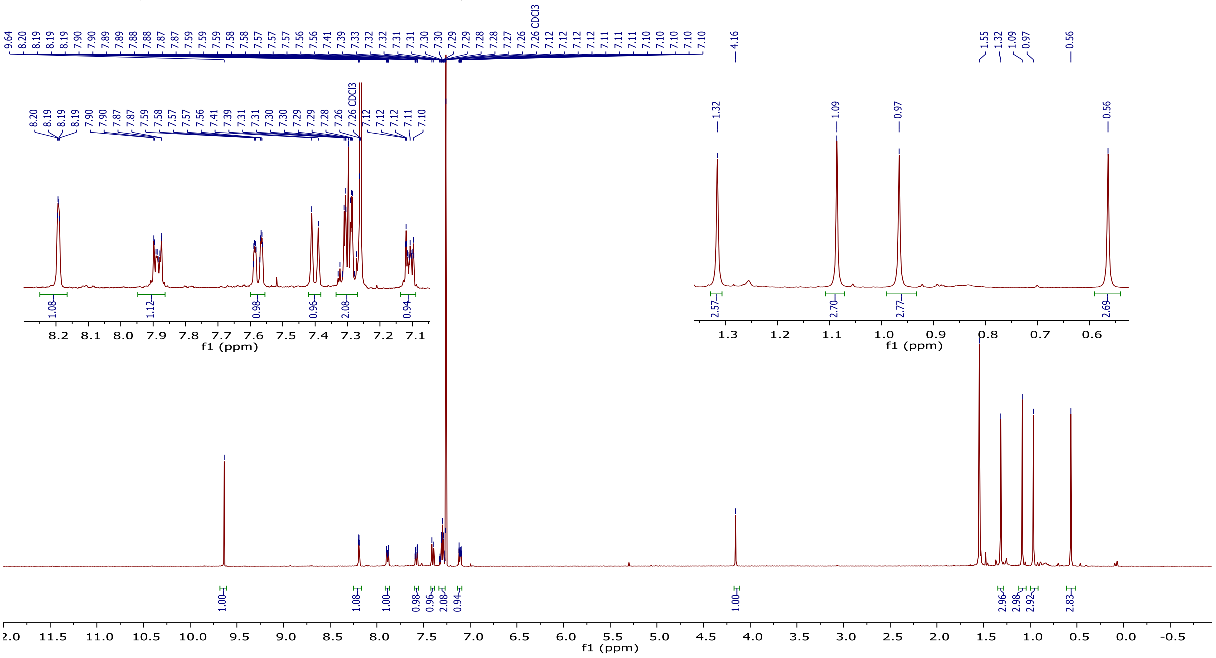


(2a*S*,10b*S*)-1,1,2,2-Tetramethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2g)

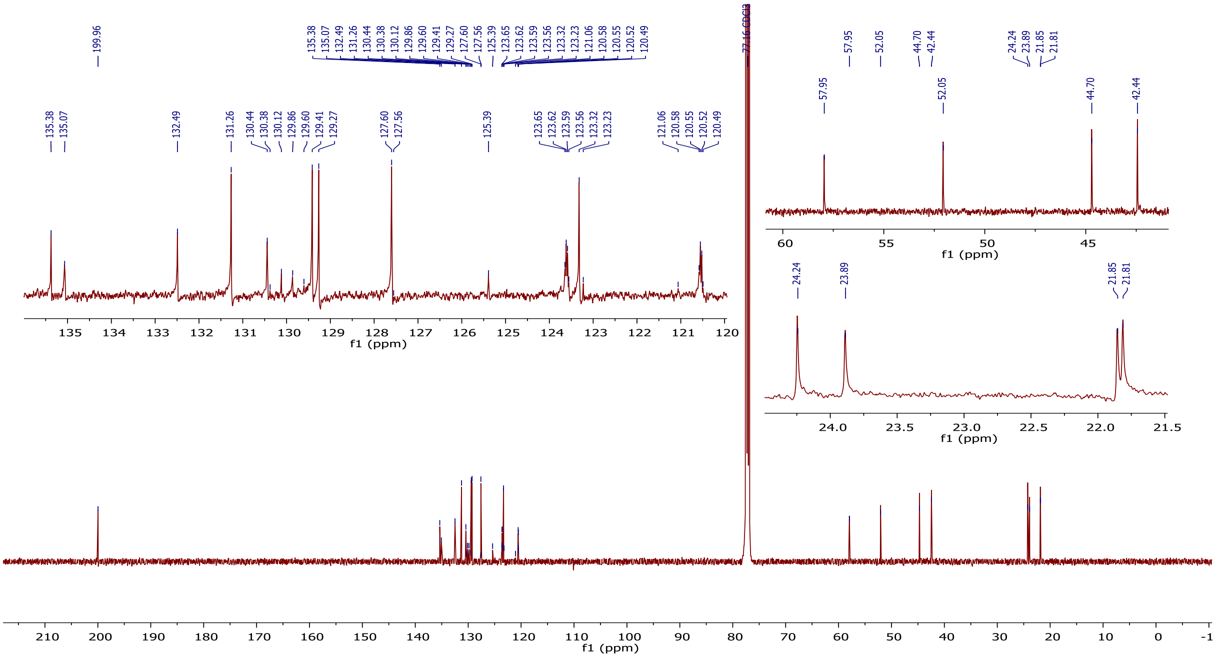


2g

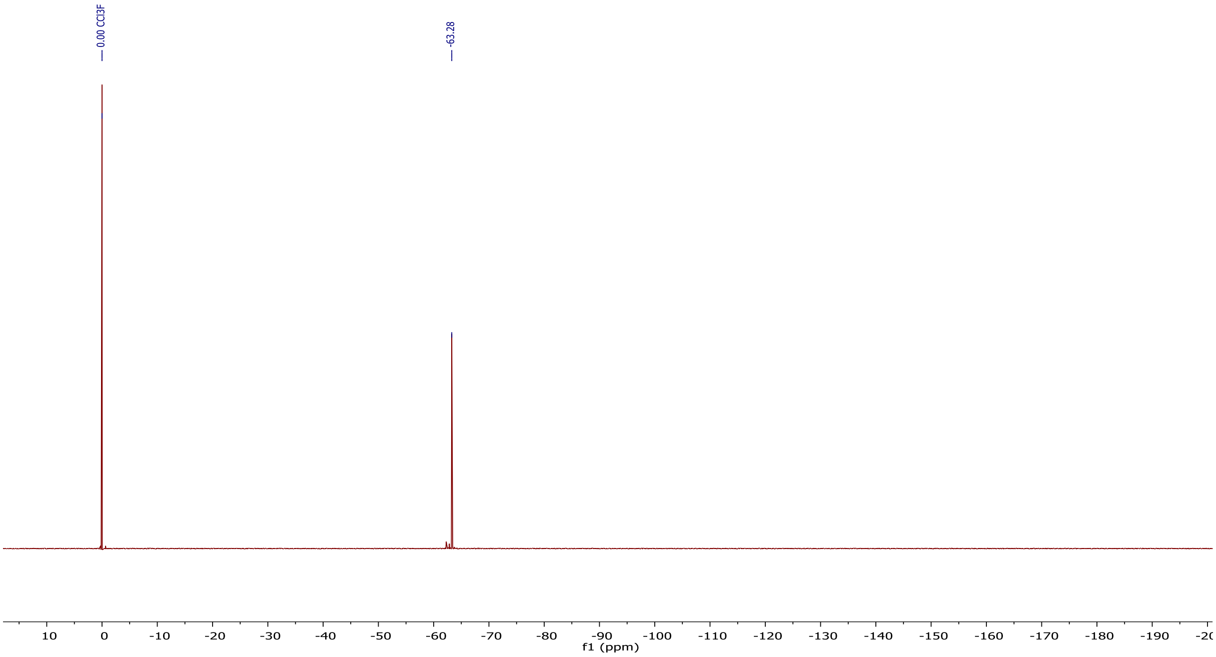
^{1}H NMR (400 MHz, CDCl$_3$, 298 K):



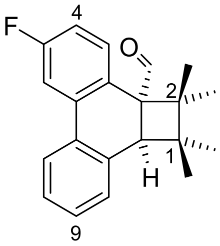
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



^{19}F NMR (376 MHz, $CDCl_3$, 300 K):

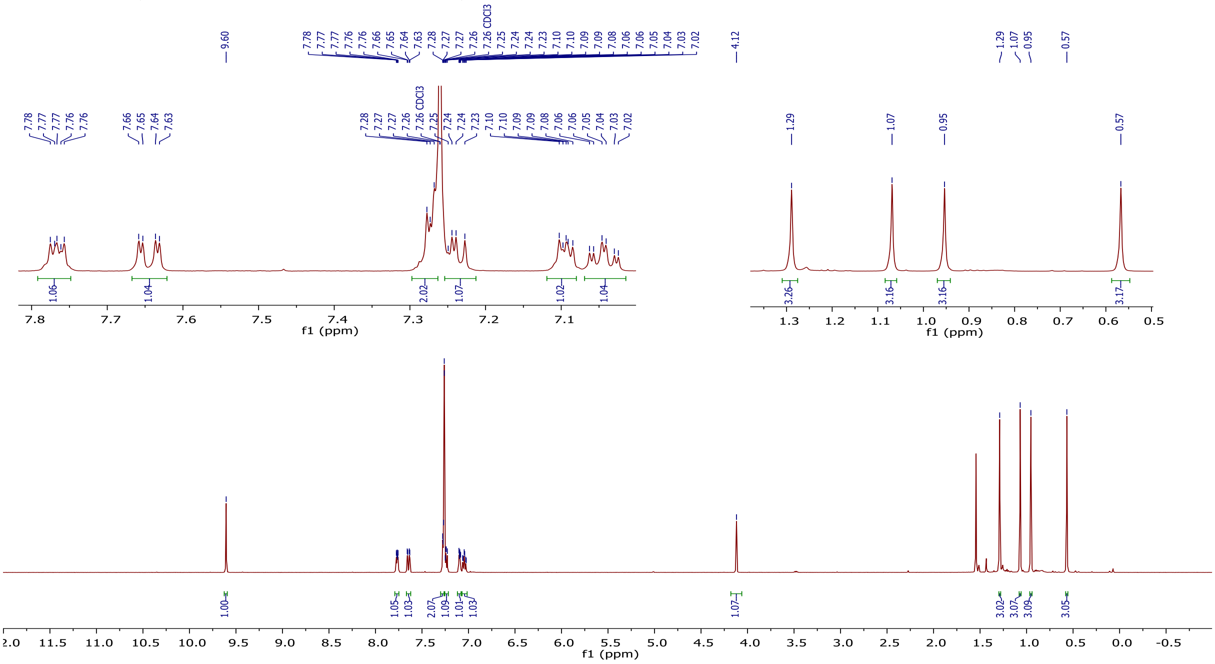


(2a*S*,10b*S*)-5-Fluoro-1,1,2,2-tetramethyl-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2h)

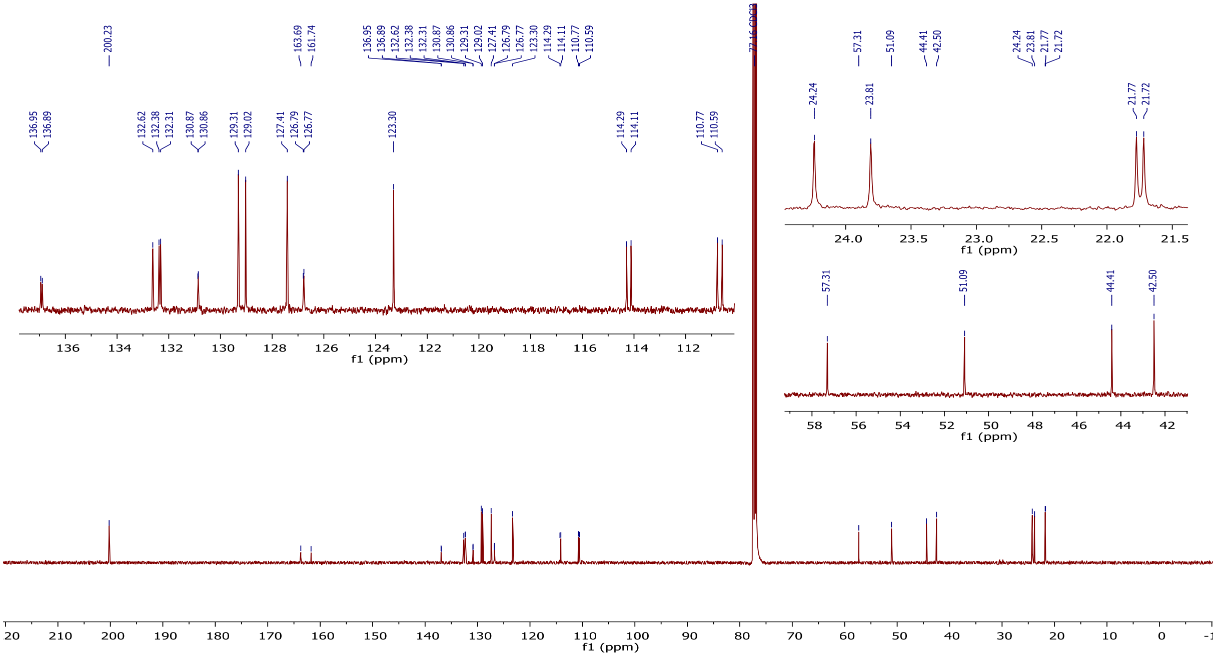


2h

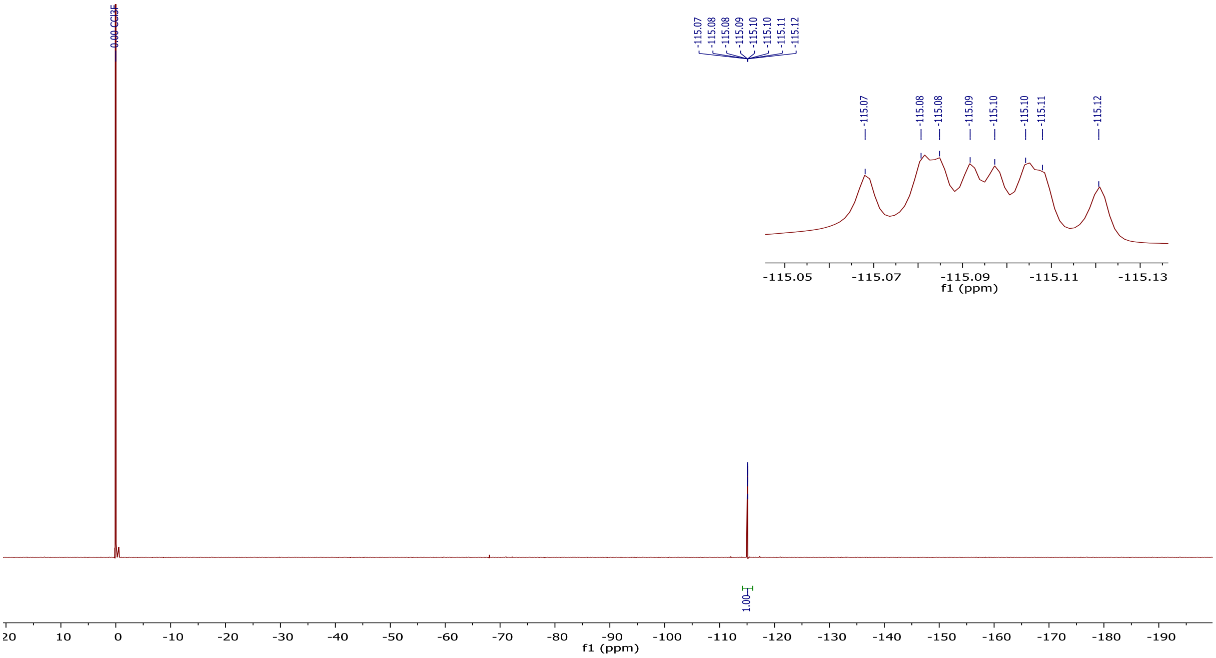
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



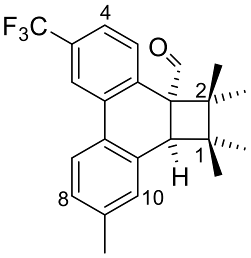
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



^{19}F NMR (471 MHz, $CDCl_3$, 300 K):

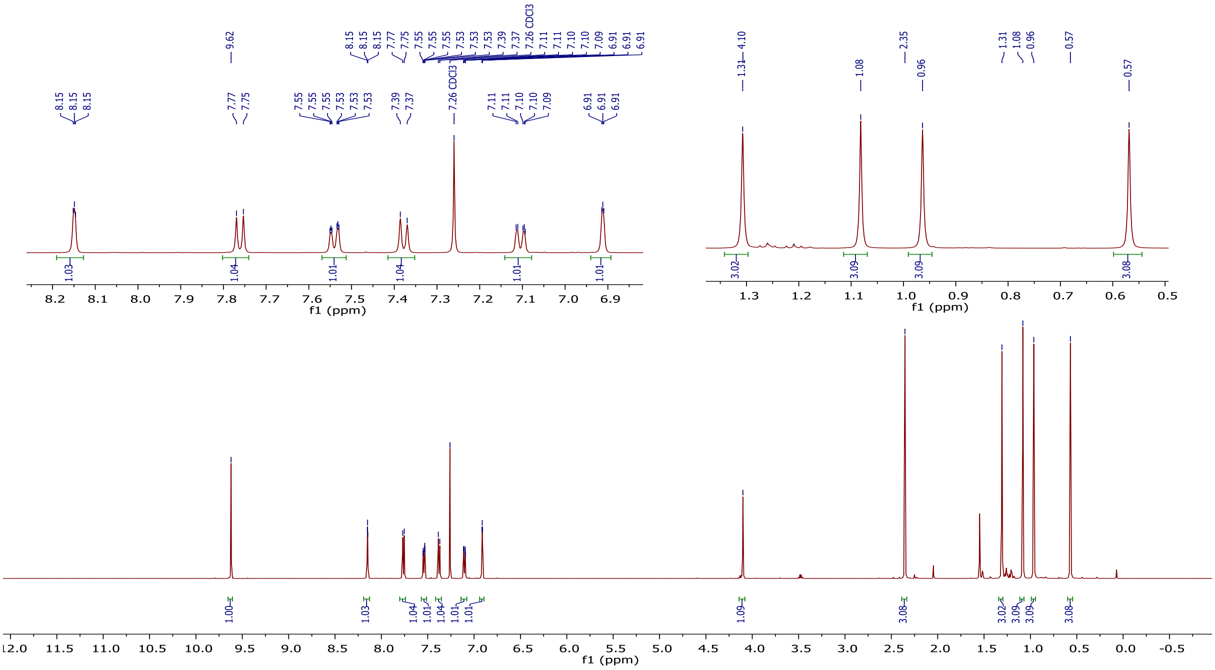


(2a*S*,10b*S*)-1,1,2,2,9-Pentamethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2i)

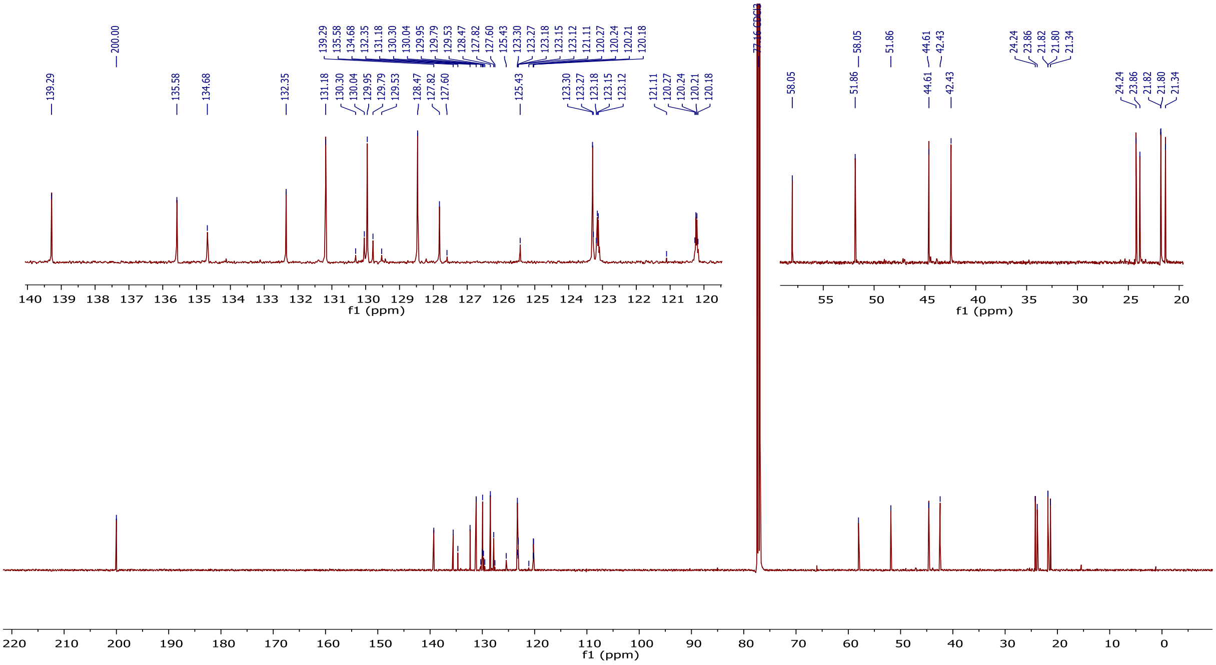


2i

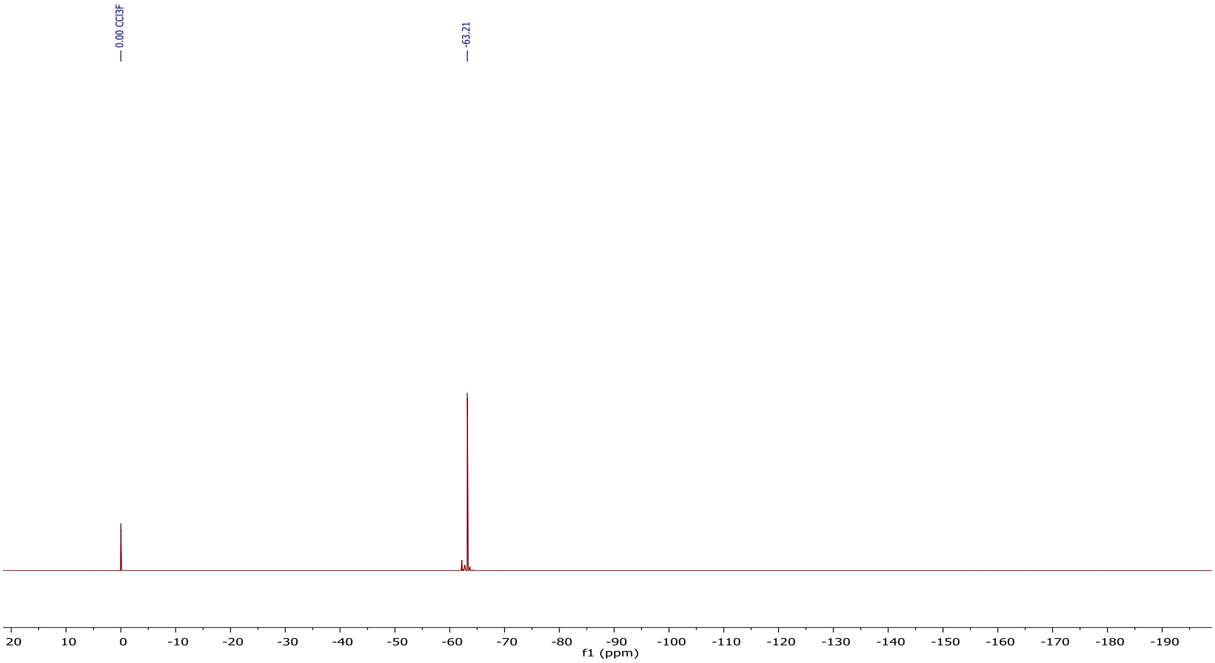
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



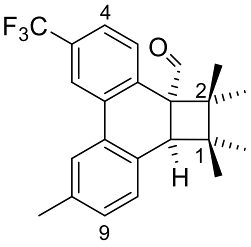
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



^{19}F NMR (471 MHz, $CDCl_3$, 300 K):

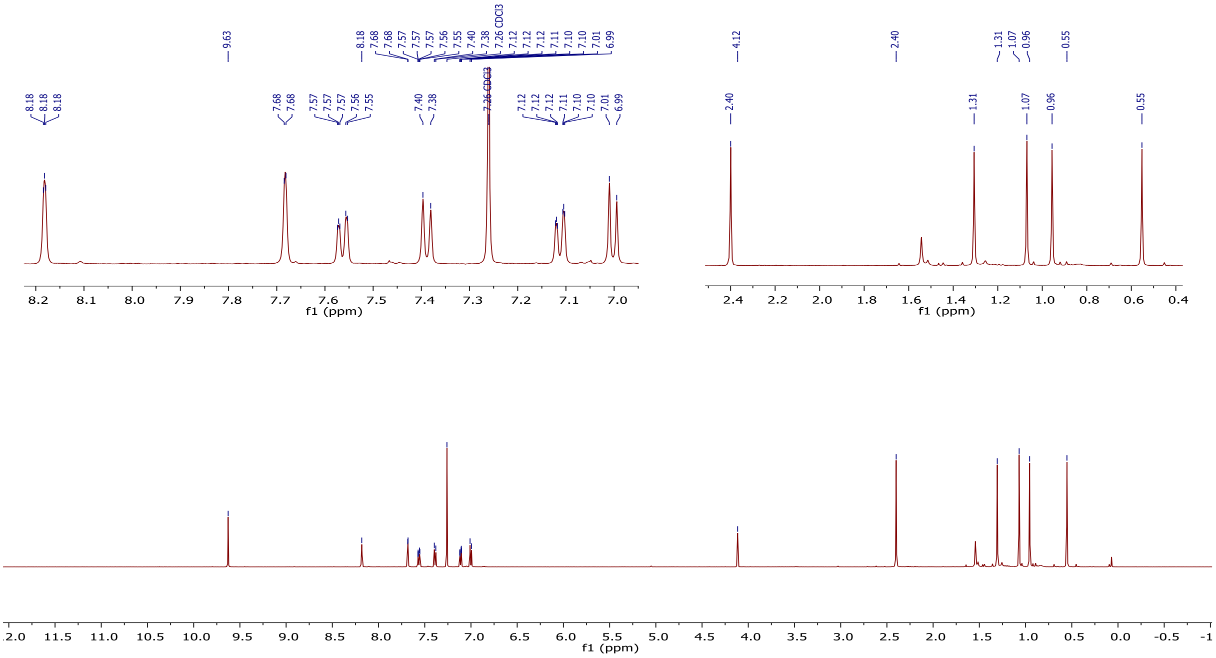


(2a*S*,10b*S*)-1,1,2,2,8-Pentamethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2j)

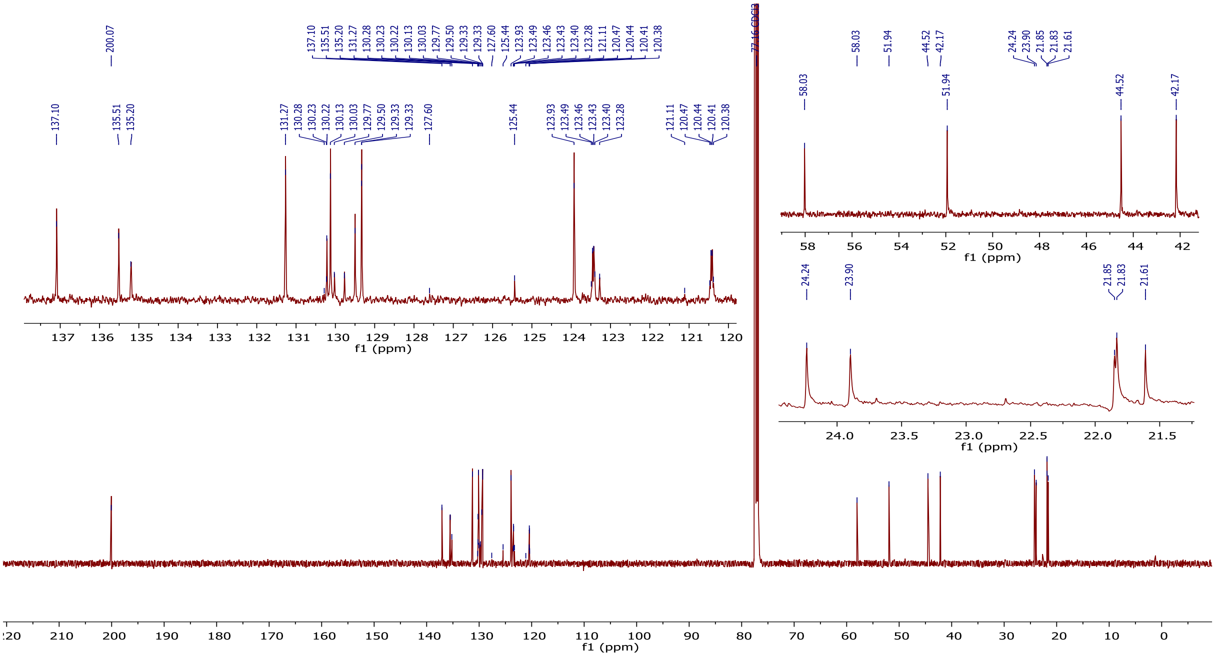


2j

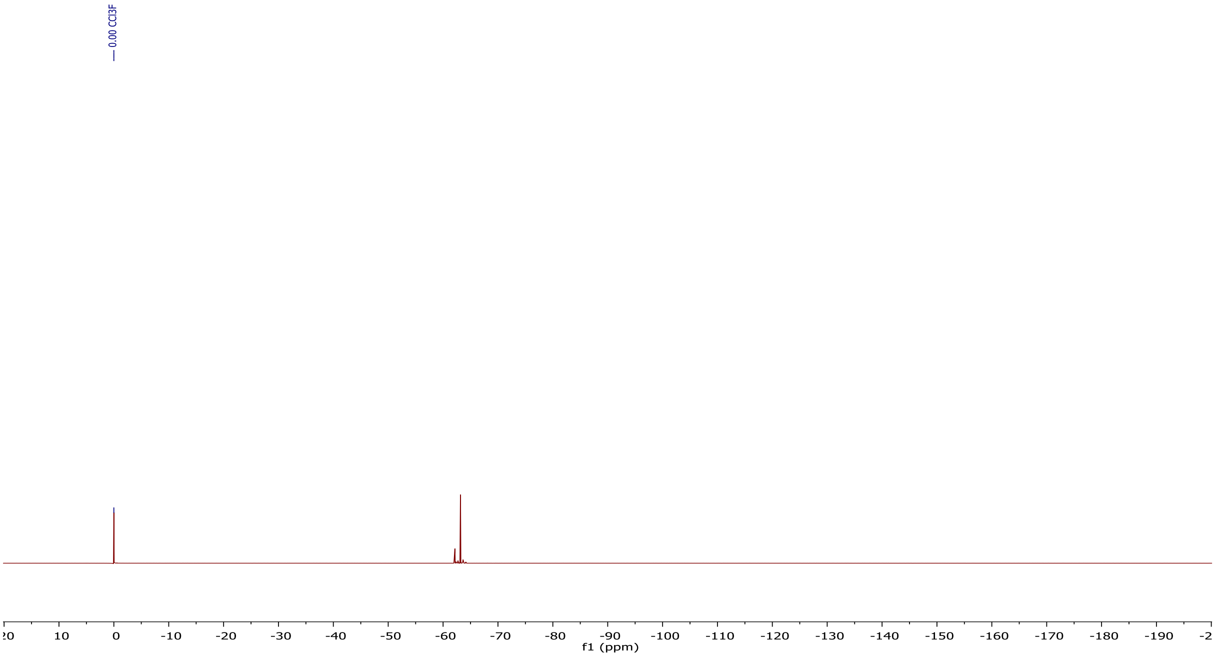
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



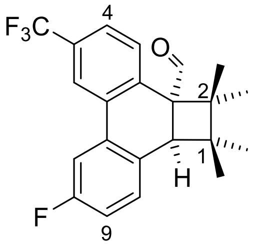
^{13}C NMR (126 MHz, $CDCl_3$, 300 K):



^{19}F NMR (471 MHz, $CDCl_3$, 300 K):

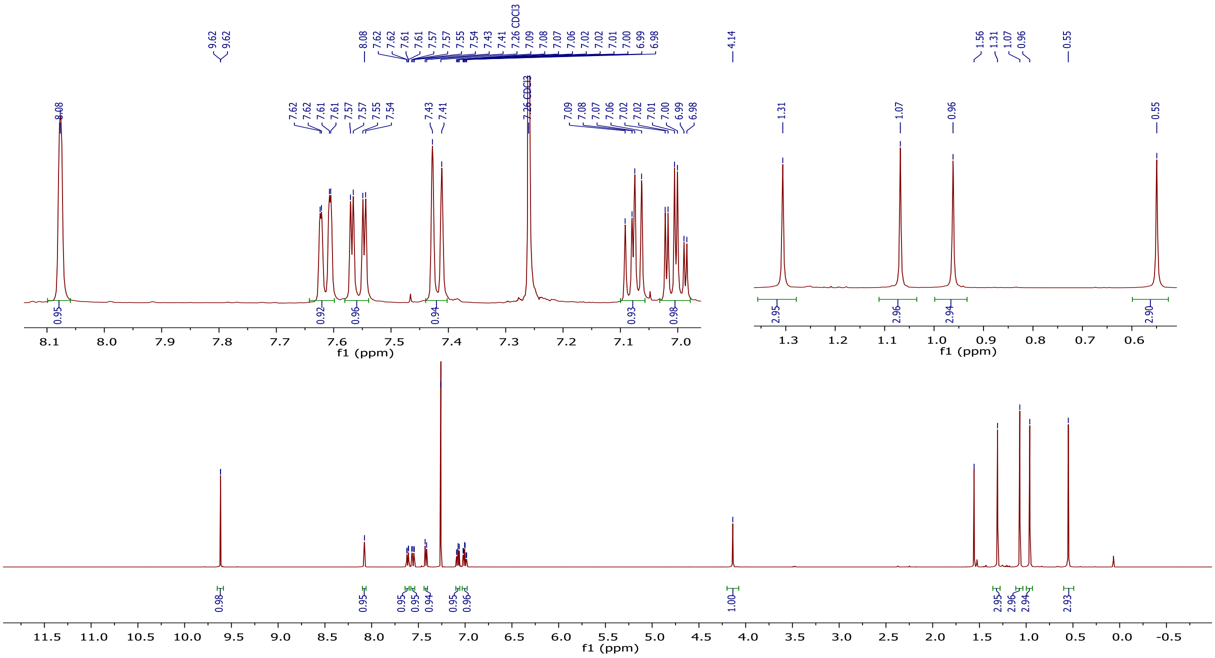


(2a*S*,10b*S*)-8-Fluoro-1,1,2,2-tetramethyl-5-(trifluoromethyl)-1,10b-dihydrocyclobuta[*l*]phenanthrene-2a(2*H*)-carboxaldehyde (2k)

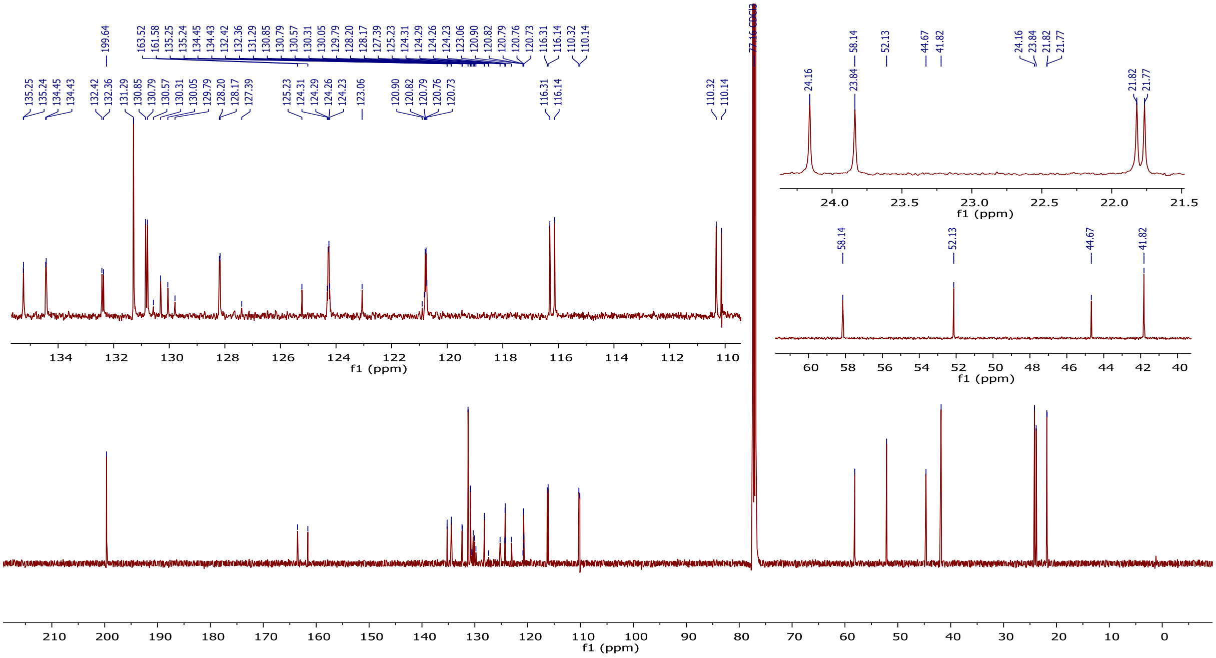


2k

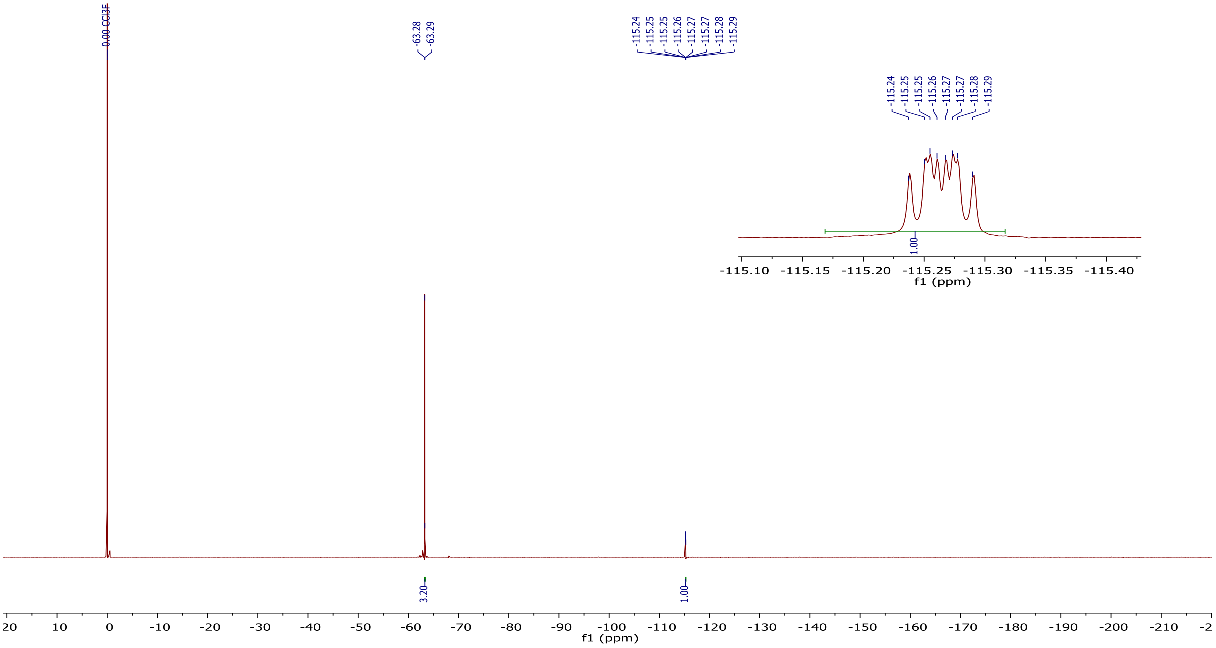
^{1}H NMR (500 MHz, CDCl$_3$, 300 K):



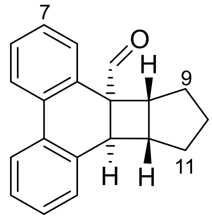
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



^{19}**F NMR** (471 MHz, CDCl$_3$, 300 K):



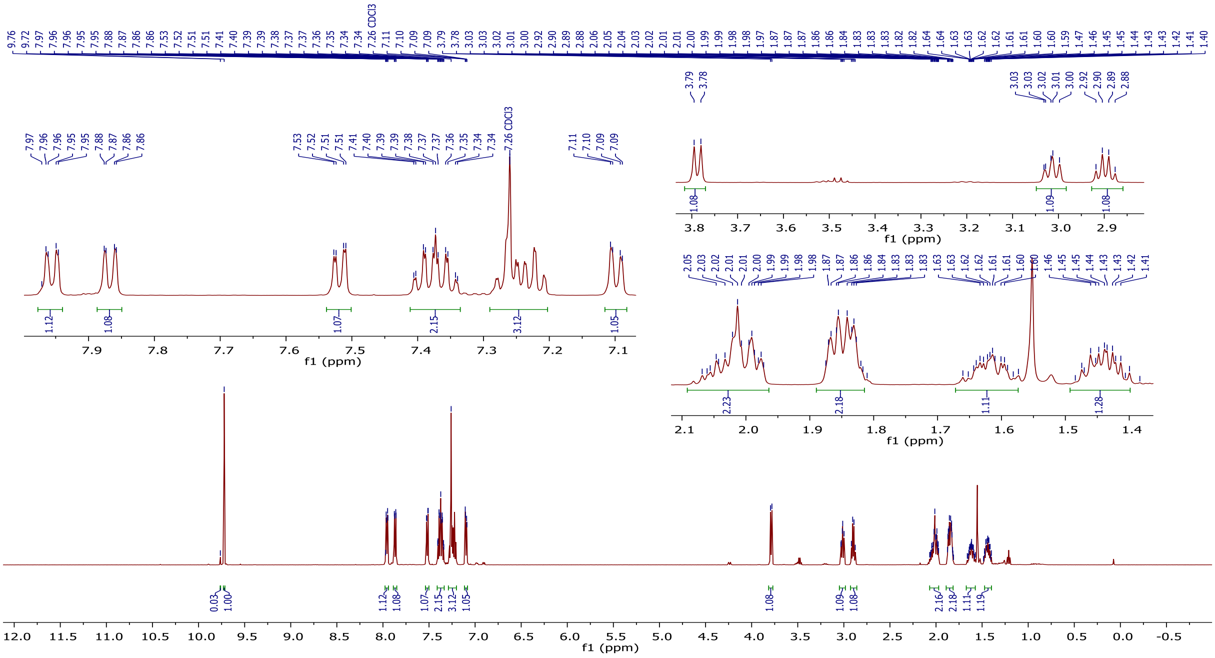
(8b*R*,8c*R*,11a*S*,11b*S*)-8c,9,10,11,11a,11b-Hexahydro-8b*H*-cyclopenta[3,4]cyclobuta[1,2-*l*]phenanthrene-8b-carboxaldehyde (4a)



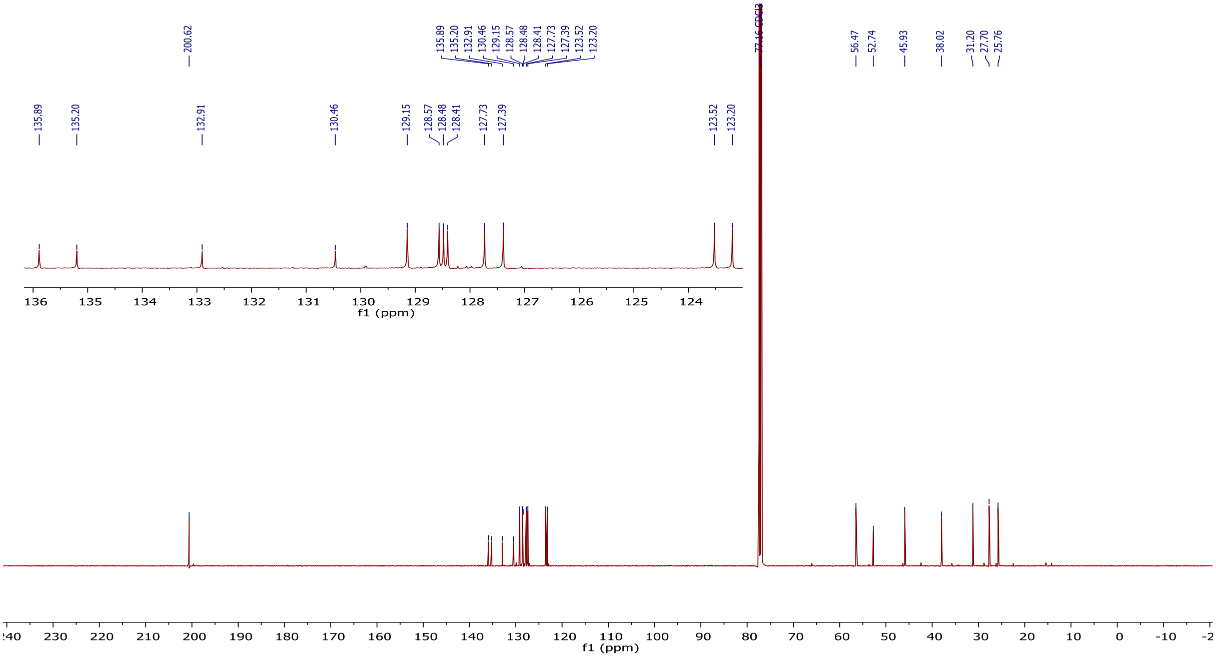
d.r. 93/7

4a

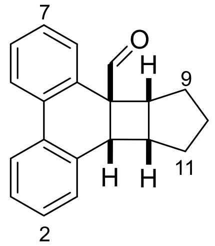
^{1}**H NMR** (500 MHz, CDCl$_3$, 298 K):



^{13}**C NMR** (126 MHz, CDCl$_3$, 300 K):



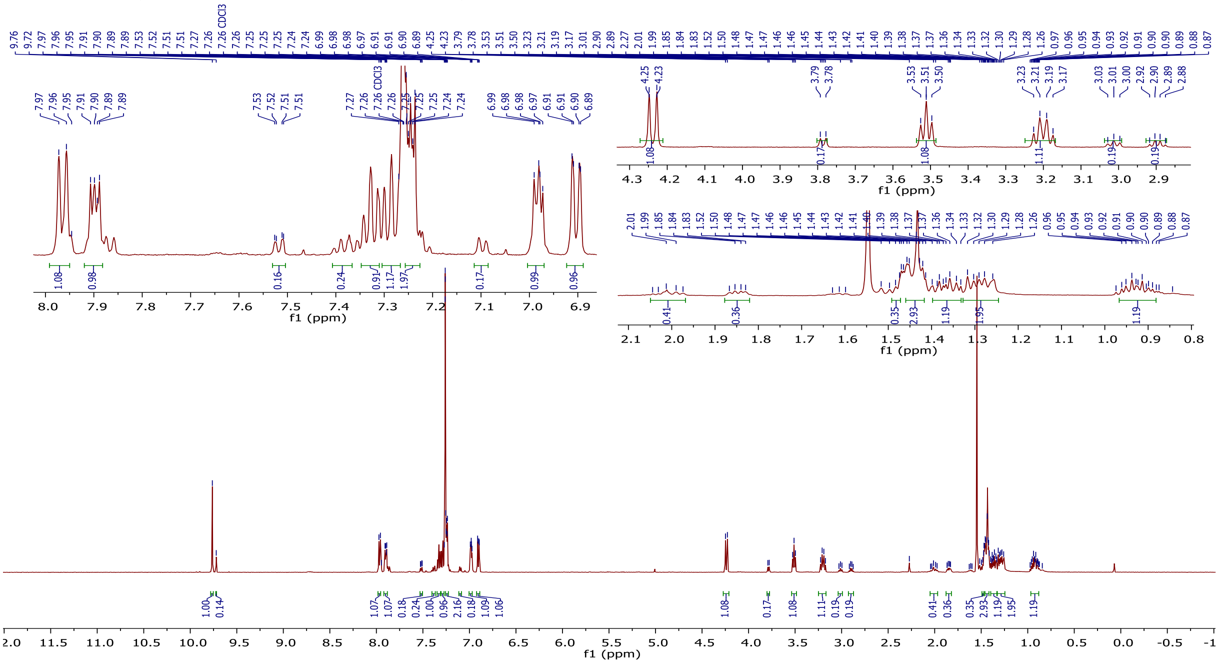
(8b*SR*,8c*RS*,11a*SR*,11b*RS*)-8c,9,10,11,11a,11b-Hexahydro-8b*H*-cyclopenta[3,4]cyclobuta[1,2-*l*]phenanthrene-8b-carboxaldehyde (*rac*-4b)



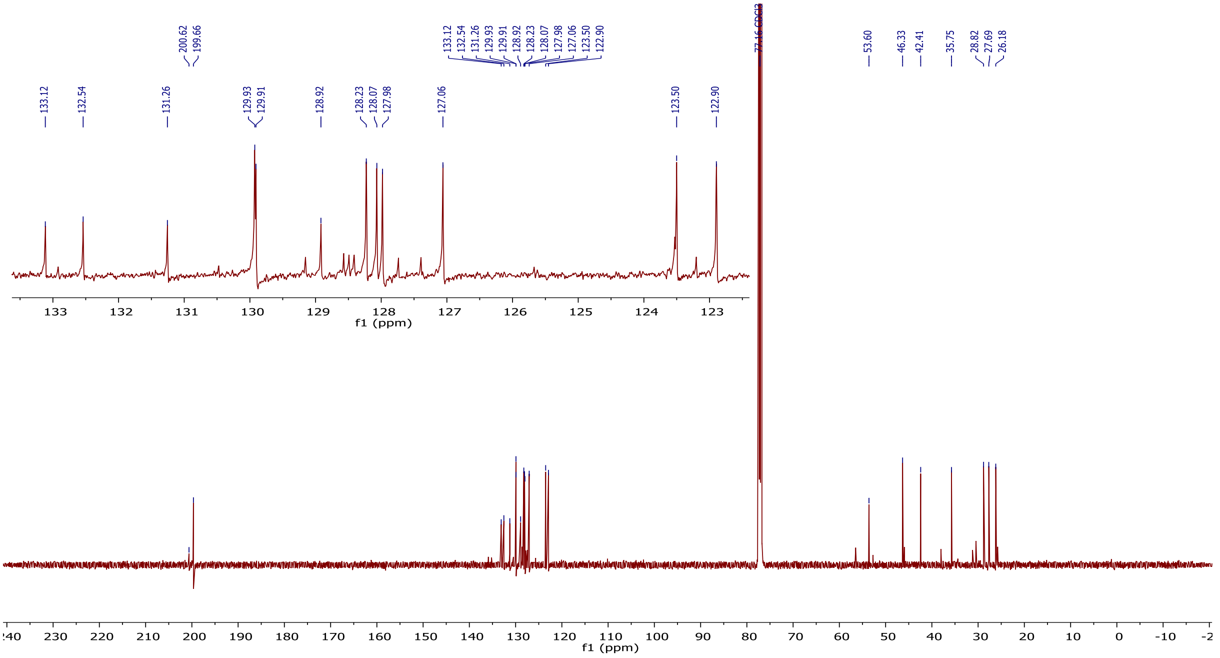
d.r. 88/12

rac-**4b**

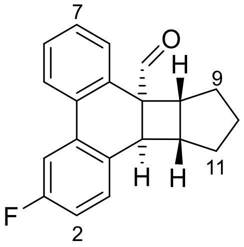
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



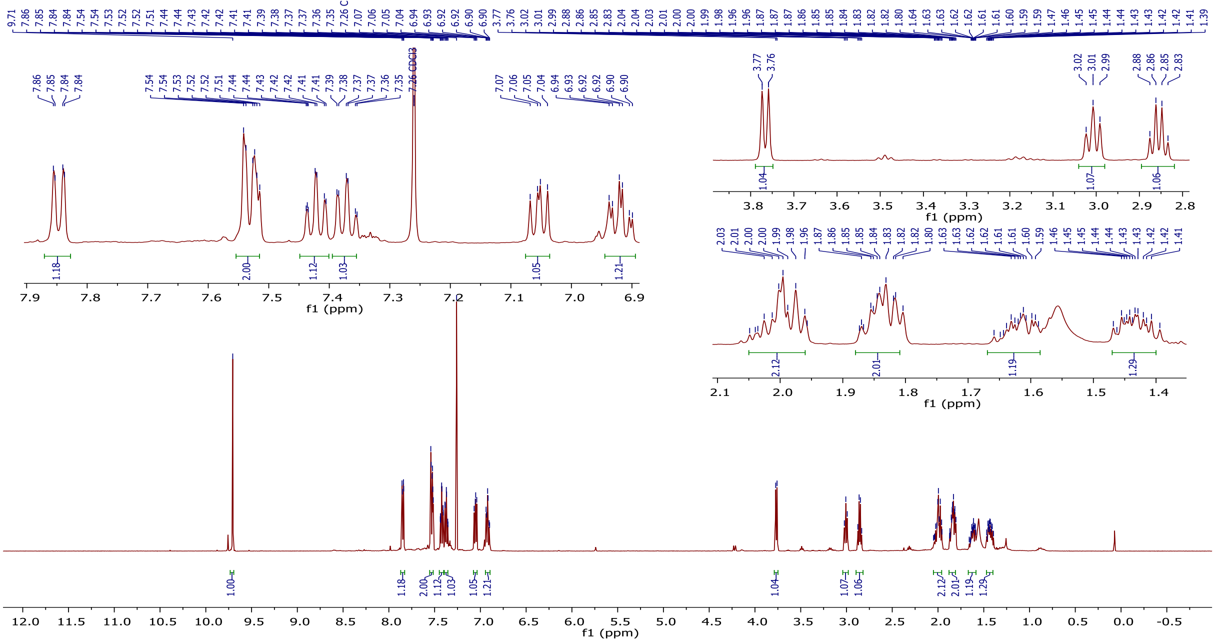
(8b*R*,8c*R*,11a*S*,11b*S*)-3-Fluoro-8c,9,10,11,11a,11b-hexahydro-8b*H*-cyclopenta[3,4]cyclobuta[1,2-*l*]phenanthrene-8b-carboxaldehyde (5a)



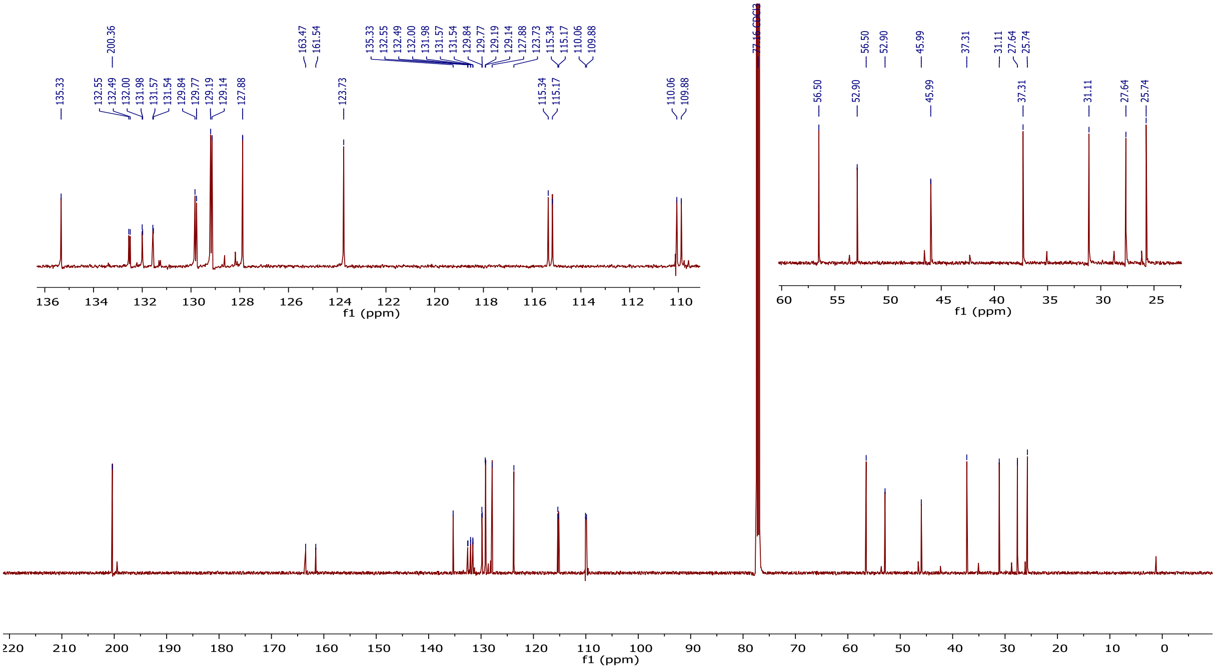
d.r. 93/7

5a

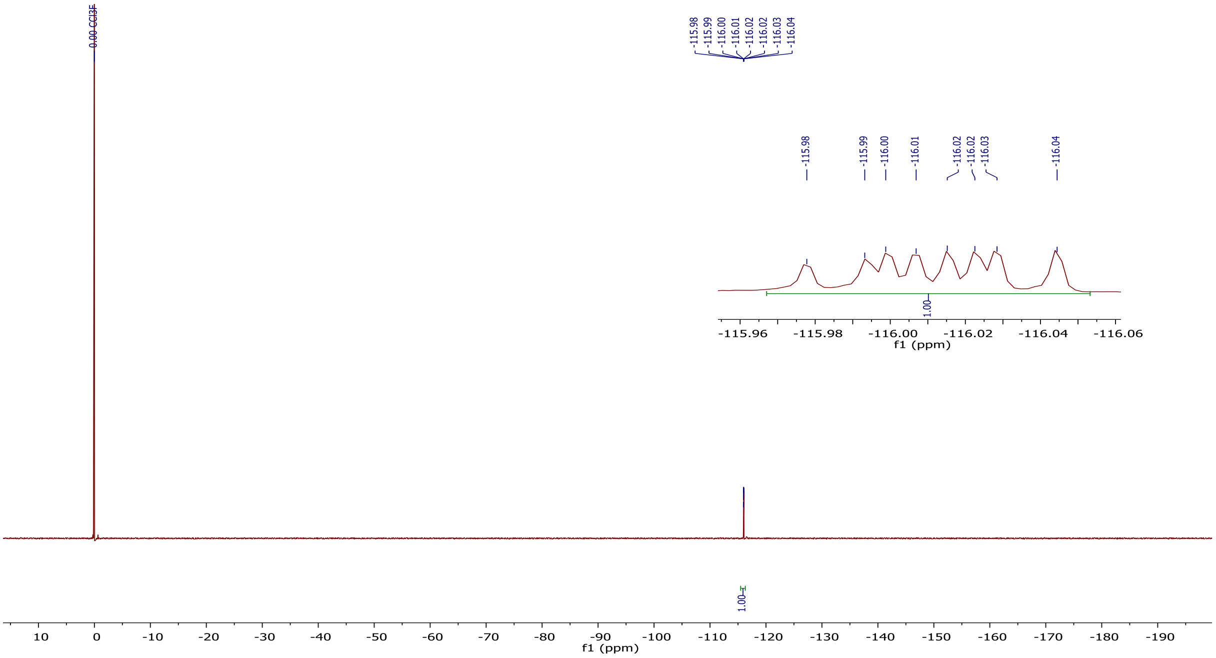
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



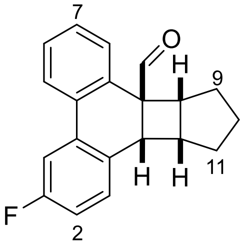
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



^{19}F NMR (376 MHz, $CDCl_3$, 298 K):



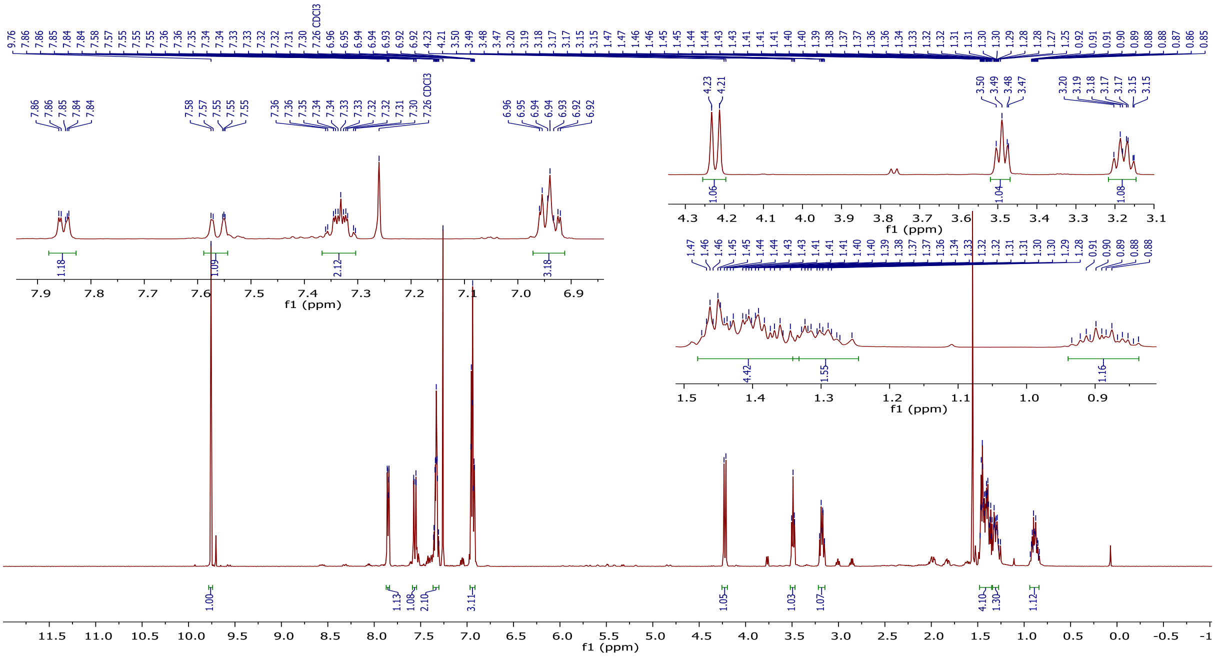
(8b*SR*,8c*RS*,11a*SR*,11b*RS*)-3-Fluoro-8c,9,10,11,11a,11b-hexahydro-8b*H*-cyclopenta[3,4]cyclobuta[1,2-*l*]phenanthrene-8b-carboxaldehyde (*rac*-5b)



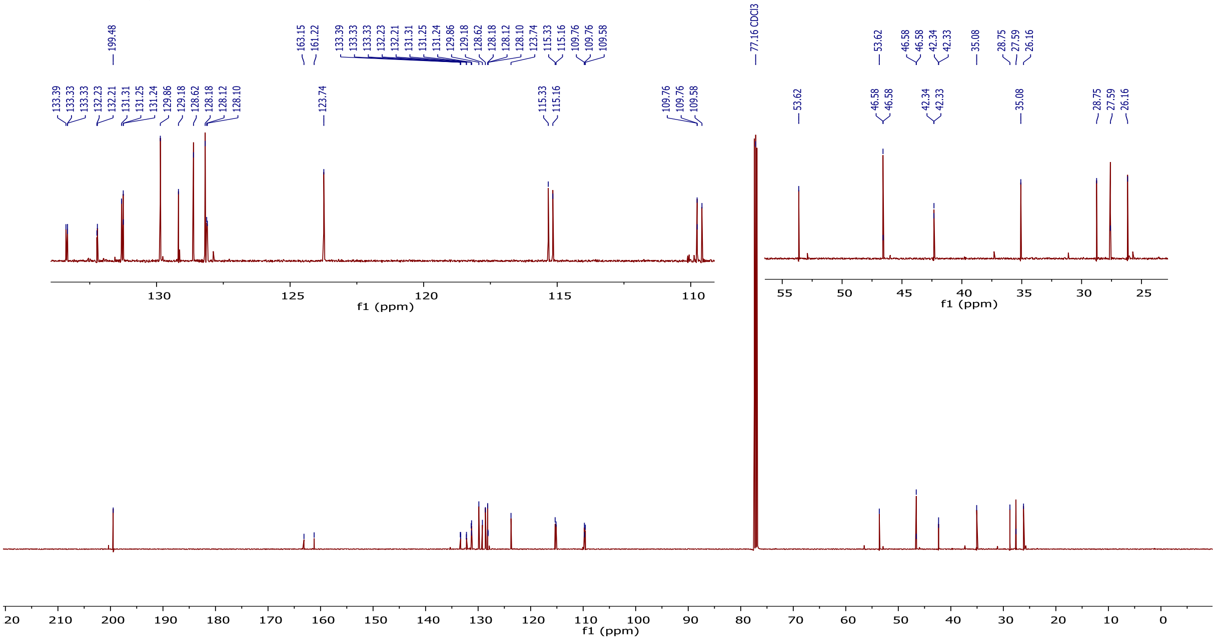
d.r. 91/9

rac-**5b**

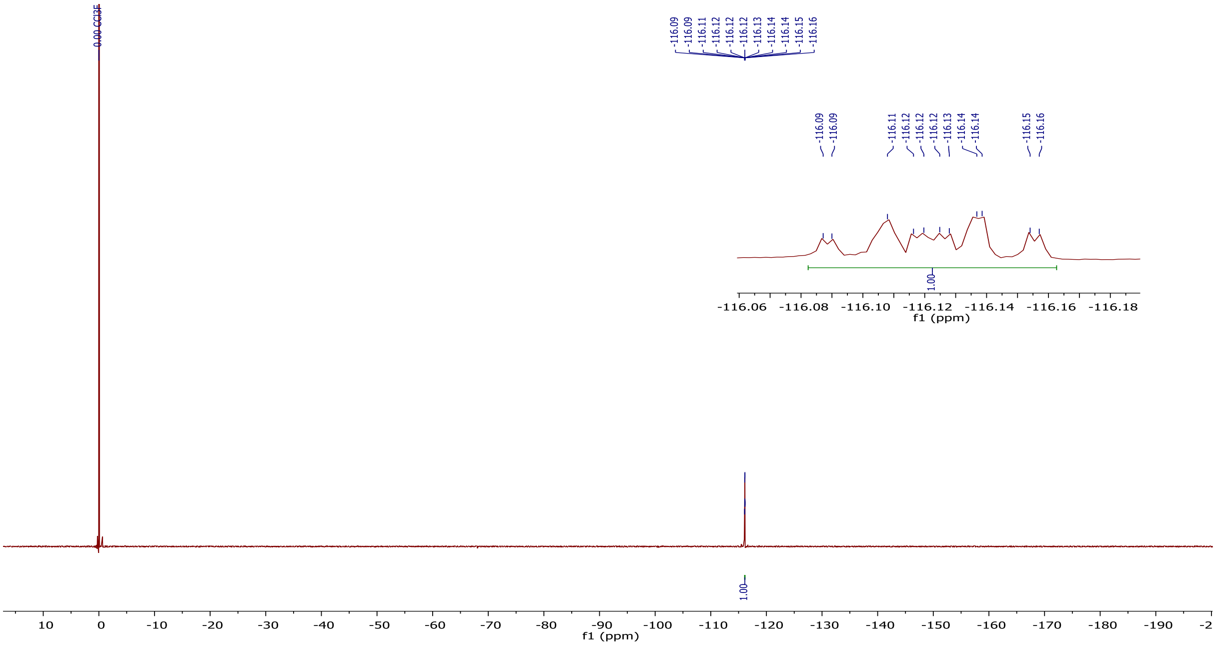
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



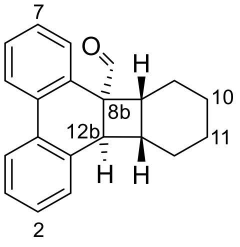
^{13}C NMR (126 MHz, CDCl$_3$, 300 K):



^{19}**F NMR** (376 MHz, $CDCl_3$, 298 K):



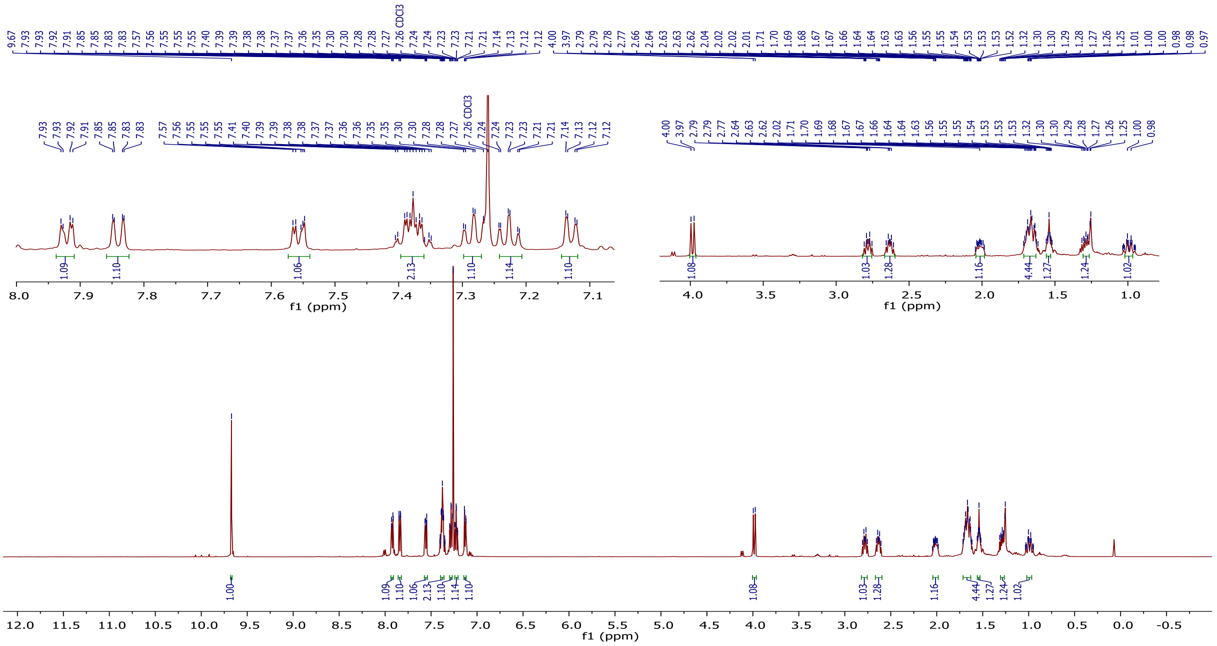
(8b*R*,8c*R*,12a*S*,12b*S*)-9,10,11,12,12a,12b-hexahydrobenzo[3,4]cyclobuta[1,2-*l*]phenanthrene-8b(8c*H*)-carbaldehyde (6a)



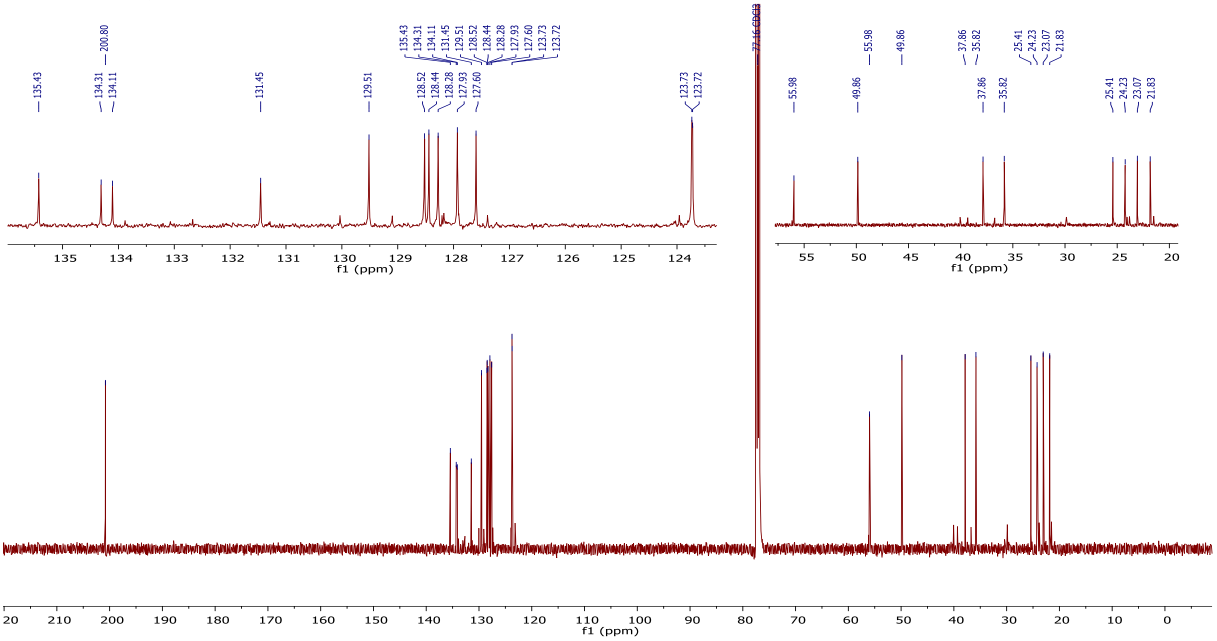
d.r. = 87/10/3

6a

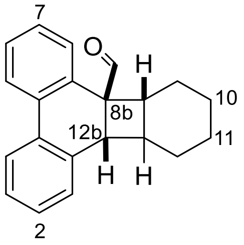
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 300 K):



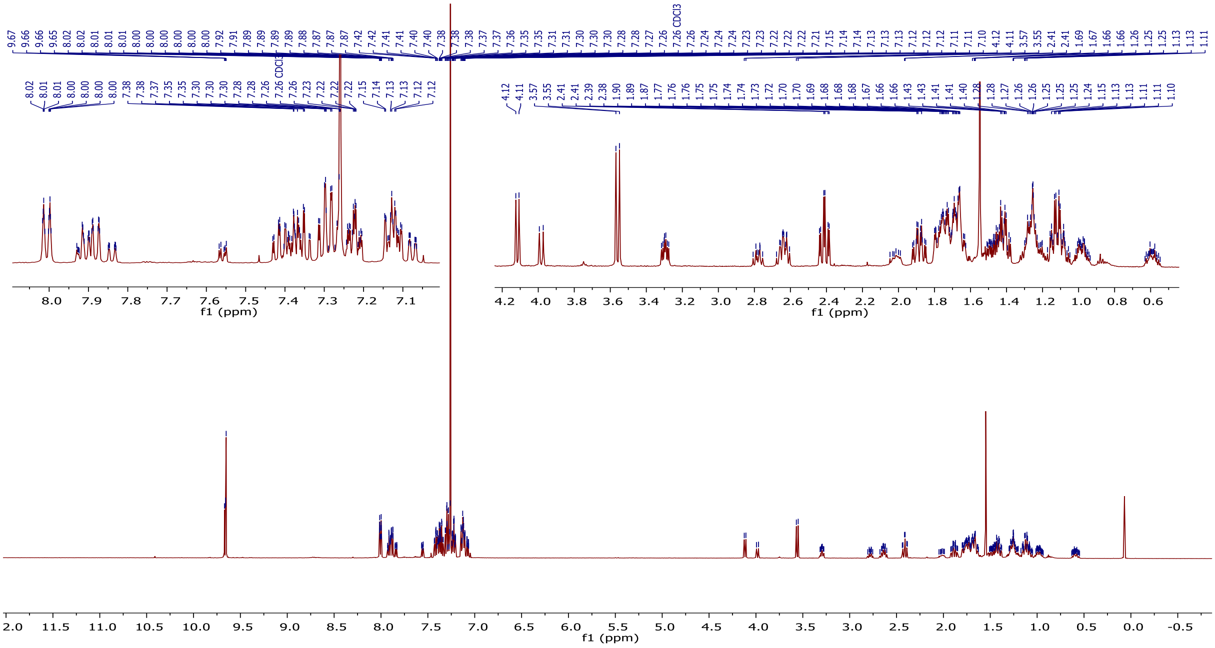
(8b*SR*,8c*RS*,12b*RS*)-9,10,11,12,12a,12b-hexahydrobenzo[3,4]cyclobuta[1,2-*l*]phenanthrene-8b(8c*H*)-carbaldehyde (*rac*-6b/*rac*-6c)



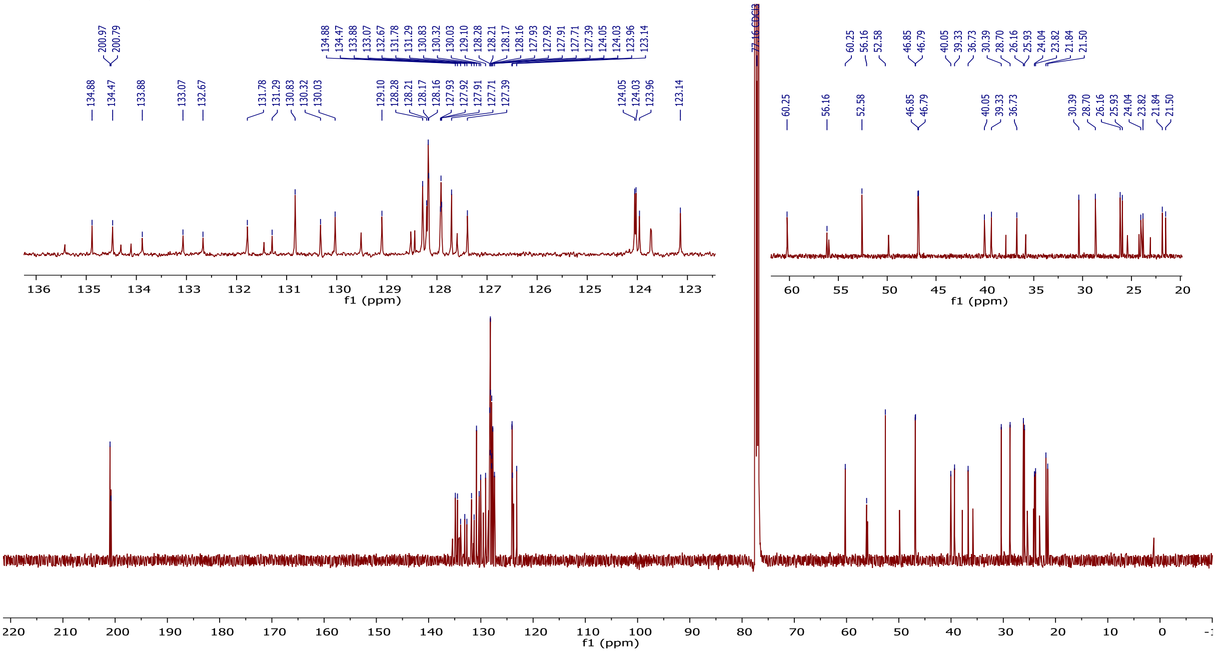
d.r. = 35/44/21

rac-**6b**/*rac*-**6c**

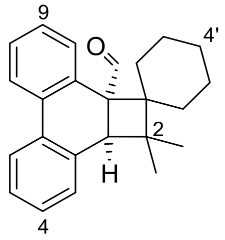
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 300 K):



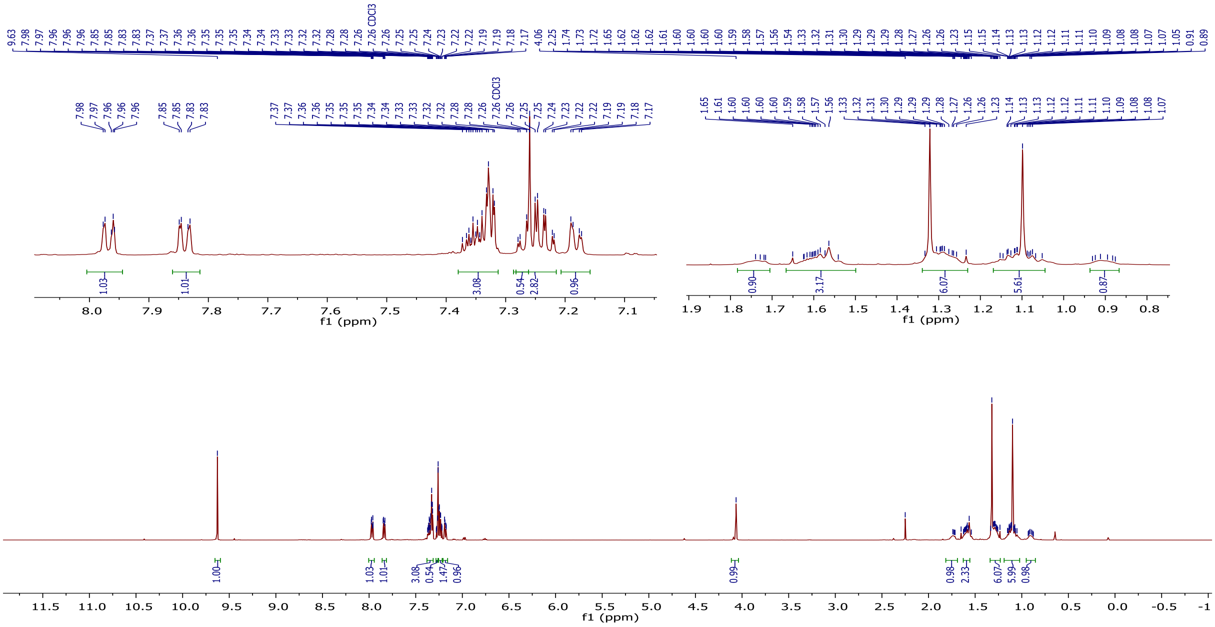
(2a*S*,10b*S*)-2,2-dimethyl-2,2a-dihydro-10b*H*-spiro[cyclobuta[*l*]phenanthrene-1,1'-cyclohexane]-10b-carbaldehyde (7)



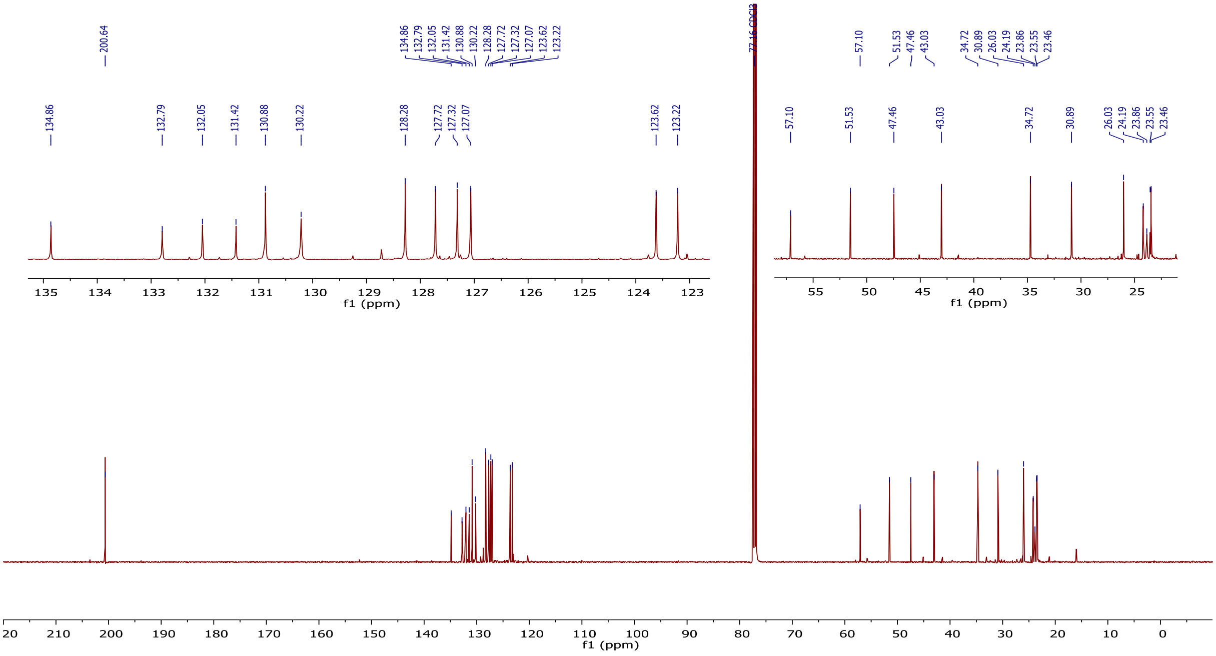
r.r = 91/9

7

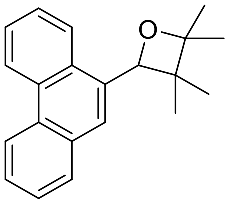
^{1}H NMR (500 MHz, CDCl$_3$, 298 K):



^{13}C NMR (126 MHz, CDCl$_3$, 300 K):

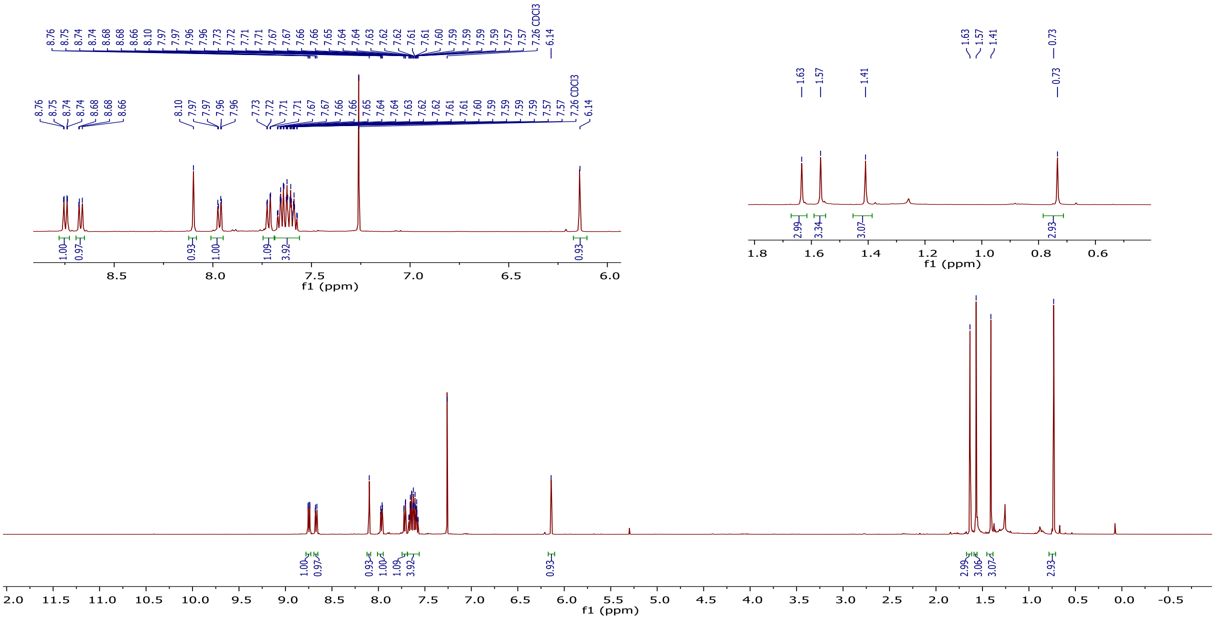


2,2,3,3-Tetramethyl-4-(phenanthren-9’-yl)oxetane (*rac*-8)

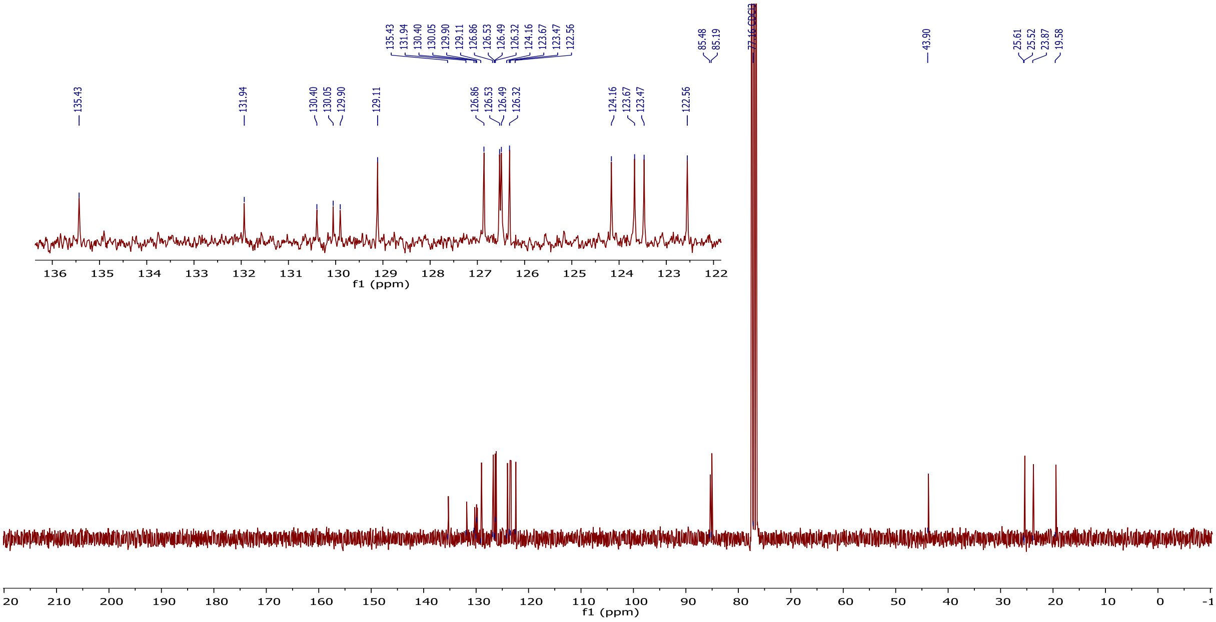


rac-**8**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

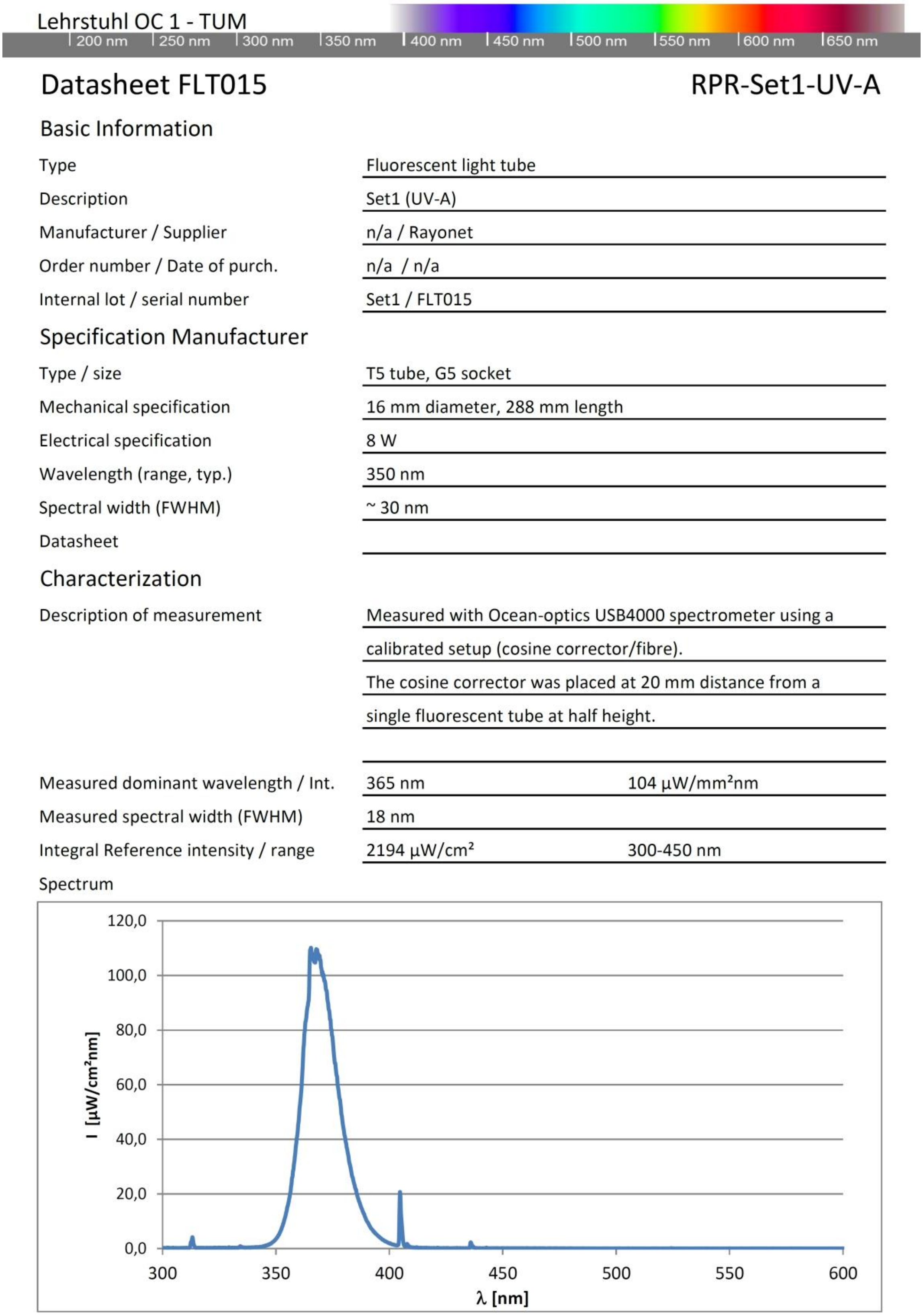


^{13}C NMR (101 MHz, $CDCl_3$, 300 K):



8. Datasheet of Flurescent Light Sources

366 nm reactor



Lehrstuhl OC 1 - TUM

Datasheet FLT015 RPR-Set1-UV-A

Basic Information

Type	Fluorescent light tube	
Description	Set1 (UV-A)	
Manufacturer / Supplier	n/a / Rayonet	
Order number / Date of purch.	n/a / n/a	
Internal lot / serial number	Set1 / FLT015	

Specification Manufacturer

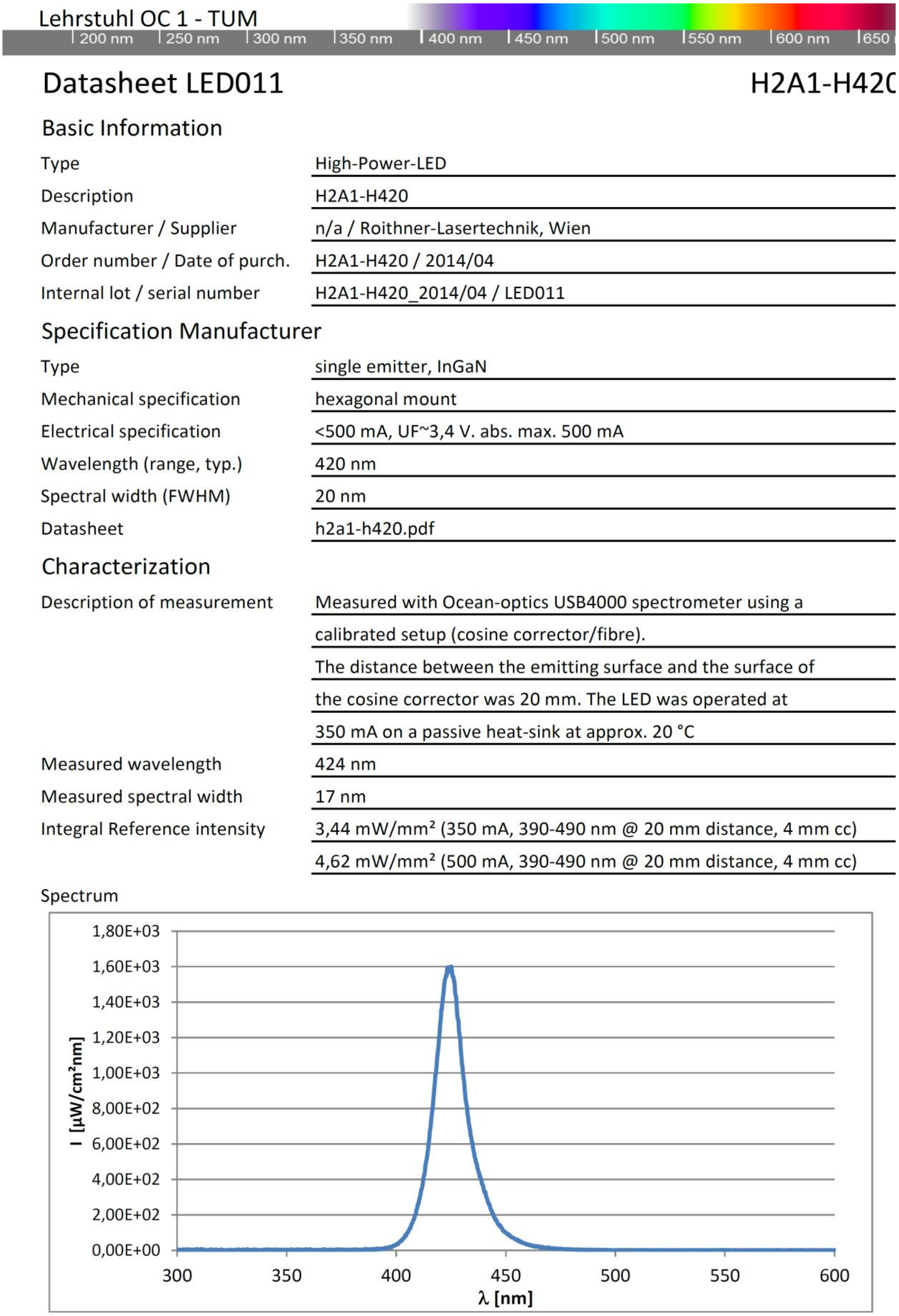
Type / size	T5 tube, G5 socket	
Mechanical specification	16 mm diameter, 288 mm length	
Electrical specification	8 W	
Wavelength (range, typ.)	350 nm	
Spectral width (FWHM)	~ 30 nm	
Datasheet		

Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The cosine corrector was placed at 20 mm distance from a single fluorescent tube at half height.	
Measured dominant wavelength / Int.	365 nm	104 µW/mm²nm
Measured spectral width (FWHM)	18 nm	
Integral Reference intensity / range	2194 µW/cm²	300-450 nm

Spectrum

424 nm LED



Lehrstuhl OC 1 - TUM

Datasheet LED011

H2A1-H42

Basic Information

Type	High-Power-LED
Description	H2A1-H420
Manufacturer / Supplier	n/a / Roithner-Lasertechnik, Wien
Order number / Date of purch.	H2A1-H420 / 2014/04
Internal lot / serial number	H2A1-H420_2014/04 / LED011

Specification Manufacturer

Type	single emitter, InGaN
Mechanical specification	hexagonal mount
Electrical specification	<500 mA, UF~3,4 V. abs. max. 500 mA
Wavelength (range, typ.)	420 nm
Spectral width (FWHM)	20 nm
Datasheet	h2a1-h420.pdf

Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 350 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	424 nm
Measured spectral width	17 nm
Integral Reference intensity	3,44 mW/mm² (350 mA, 390-490 nm @ 20 mm distance, 4 mm cc) 4,62 mW/mm² (500 mA, 390-490 nm @ 20 mm distance, 4 mm cc)

Spectrum

435 nm LED

Lehrstuhl OC 1 - TUM

200 nm 250 nm 300 nm 350 nm 400 nm 450 nm 500 nm 550 nm 600 nm 650 nm

Datasheet LED043 Av-435-5W

Basic Information

Type	High-Power-LED
Description	Avonec 435 nm / 5 W
Manufacturer / Supplier	n/a / Avonec
Order number / Date of purch.	n/a / 07/2016
Internal lot / serial number	2016-07 / LED043

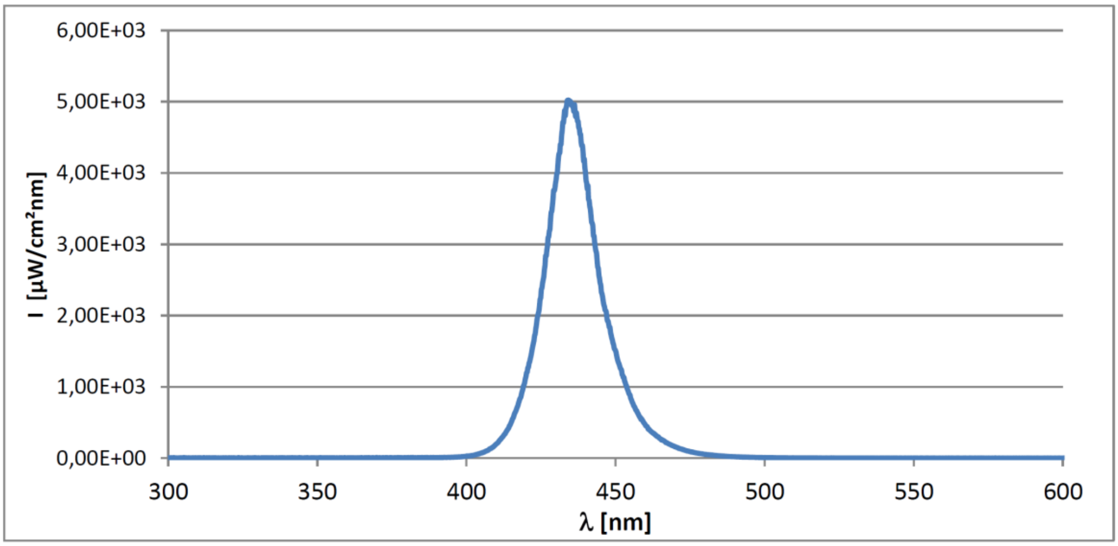
Specification Manufacturer

Type / size	dual emitter / 2 x <1 x <1 mm
Mechanical specification	
Electrical specification	700 mA, UF 6-7 V
Wavelength (range, typ.)	435-440 nm, typ. n/a
Spectral width (FWHM)	n/a
Datasheet	Avonec_435nm_5W.pdf

Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 700 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	435 nm
Measured spectral width	20 nm
Integral Reference intensity	115800 µW/cm² (350-500 nm @ 20 mm distance, 4 mmcosine corr.)

Spectrum



457 nm LED

Datasheet LED005 H2A3-H470

Basic Information

Type	High-Power-LED
Description	H2A3-H470
Manufacturer / Supplier	n/a / Roithner-Lasertechnik, Wien
Order number / Date of purch.	H2A3-H470 / 12/2011
Internal lot / serial number	2011-12 / LED005

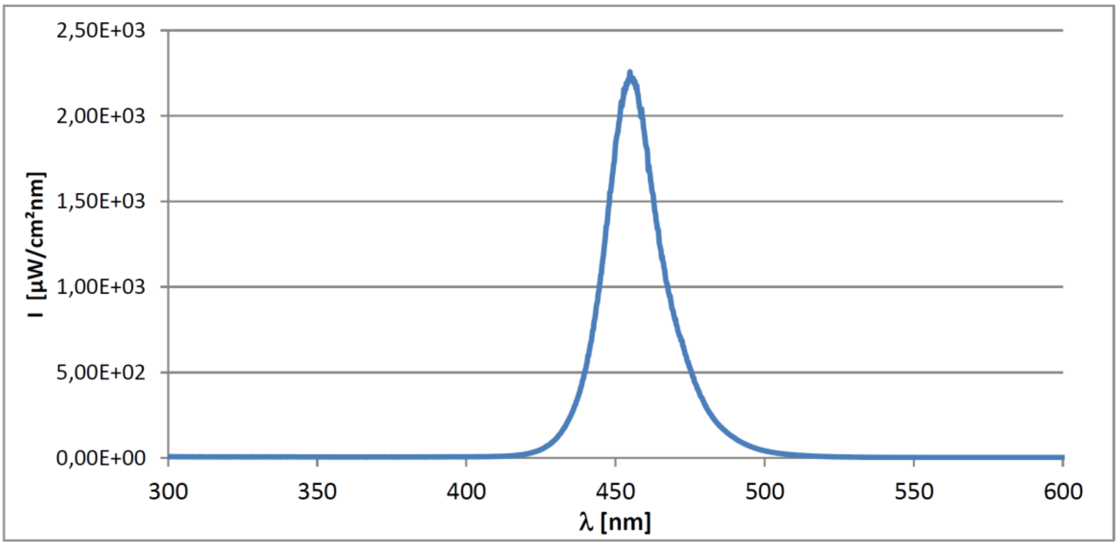
Specification Manufacturer

Type / size	single emitter / <1 x <1 mm
Mechanical specification	
Electrical specification	700 mA, UF~3.8 V
Wavelength (range, typ.)	not spec., typ. 470 nm
Spectral width (FWHM)	25 nm
Datasheet	H2A3H470.pdf (n. b. - datasheet is for H2A3H530!)

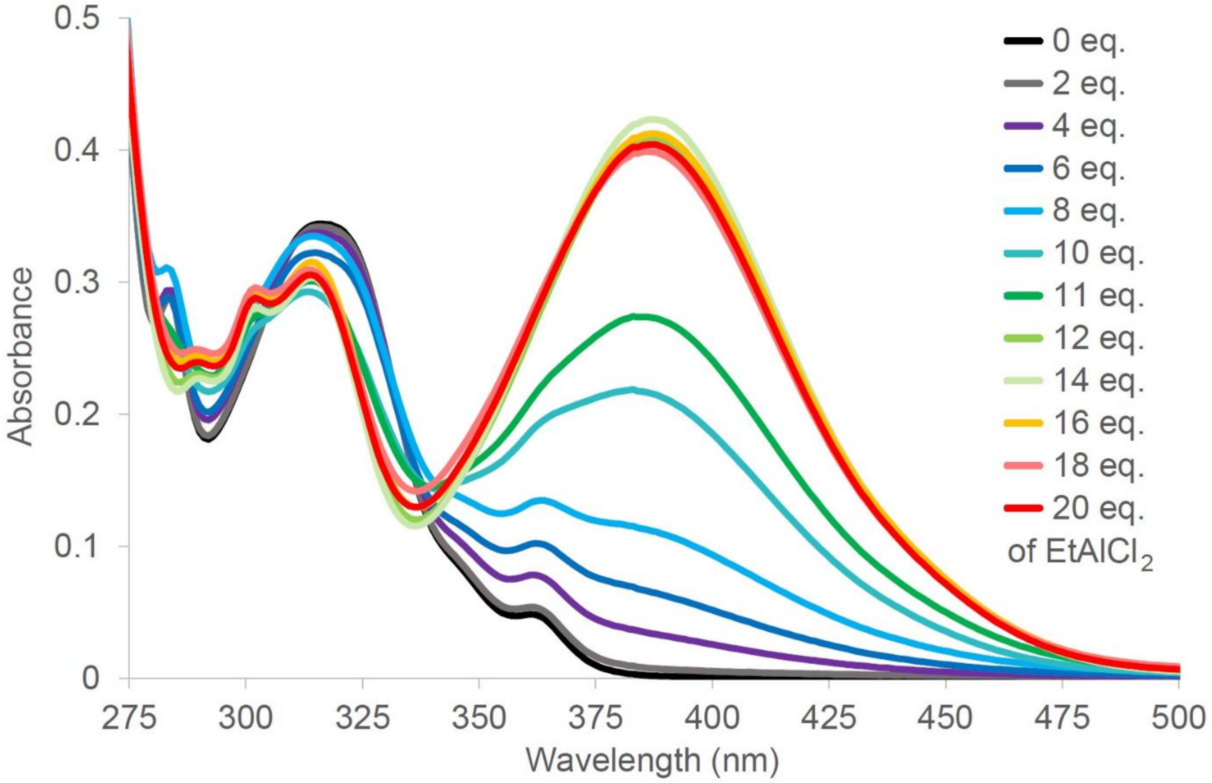
Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 700 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	457 nm
Measured spectral width	21 nm
Integral Reference intensity	56580 µW/cm² (400-550 nm @ 20 mm distance, 4 mmcosine corr.)

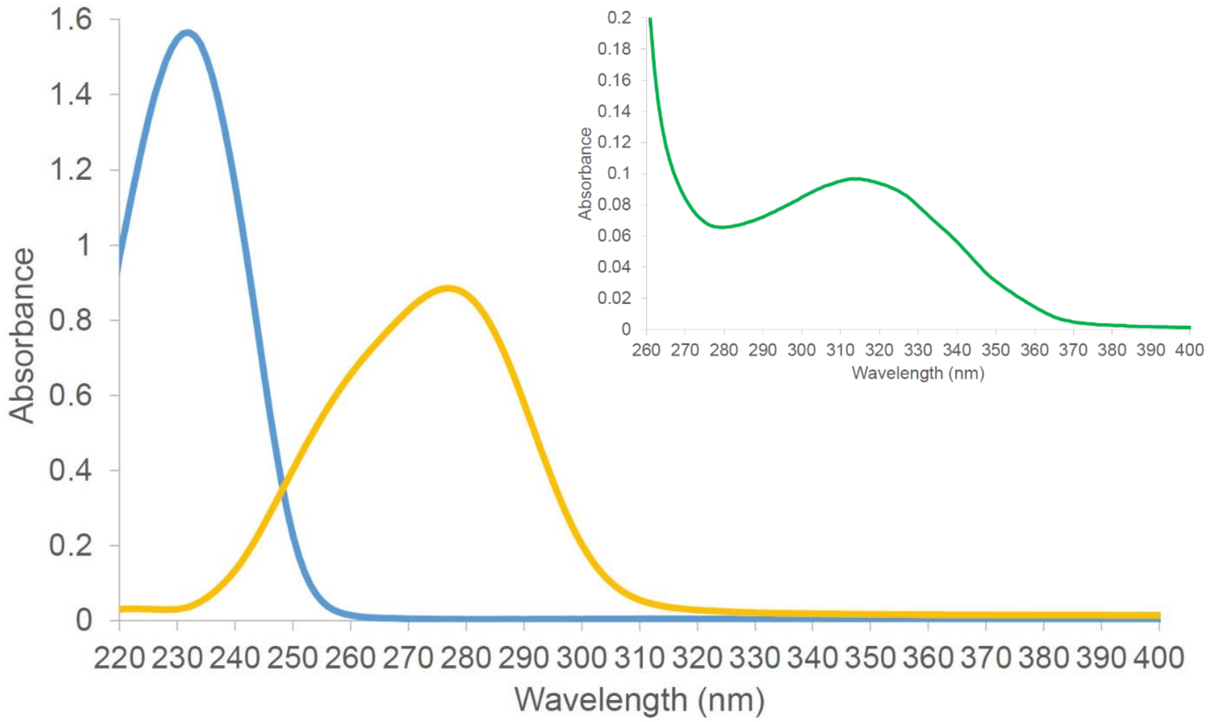
Spectrum



9. UV/Vis Spectra

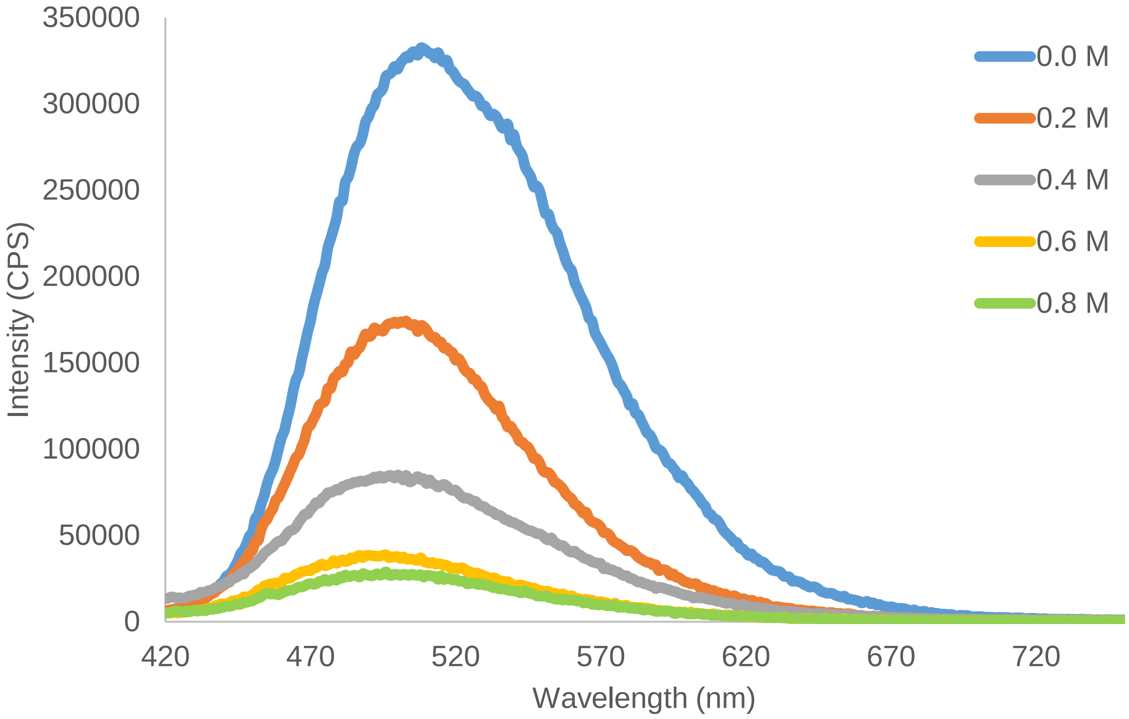


UV/Vis-spectrum of phenanthrene-9-carboxaldehyde (**1a**) in the absence of a Lewis acid (black line, $\varepsilon_{316\ \mathrm{nm}}$ = 13780 $\mathrm{M}^{-1}\mathrm{cm}^{-1}$, $\varepsilon_{361\ \mathrm{nm}}$ = 1940 $\mathrm{M}^{-1}\mathrm{cm}^{-1}$) and in the presence variable equivalents of $EtAlCl_2$ (2 eq. – 20 eq., $\varepsilon_{387\ \mathrm{nm},\ 20\ \mathrm{eq.\ L.A.}}$ = 16180 $\mathrm{M}^{-1}\mathrm{cm}^{-1}$) in dichloromethane [c = 0.25 mM].



UV/Vis-spectrum of cyclohexene-1-carbaldehyde in the absence of a Lewis acid (blue line: c = 1.00 mM, green line: c = 20.0 mM; $\varepsilon_{231\,\text{nm}} = 15640\ \text{M}^{-1}\text{cm}^{-1}$, $\varepsilon_{315\,\text{nm}} = 50\ \text{M}^{-1}\text{cm}^{-1}$) and in the presence of 20 equivalents of $EtAlCl_2$ (yellow line: c = 1.00 mM; $\varepsilon_{277\,\text{nm}} = 8850\ \text{M}^{-1}\text{cm}^{-1}$) in dichloromethane.

10. Luminescence Measurements



The emission spectrum of complex **1a**·$AlEtCl_2$ was measured (blue line) (CH_2Cl_2 as the solvent) in the presence of an excess of $EtAlCl_2$ (15 eq.). We used 400 nm as the excitation wavelength and observed the emission spectrum from 420 – 750 nm. Both excitation and emission bandwidth was set to 1.5 nm. The qualitative quenching experiment was performed by addition of varying amounts of 2,3-dimethyl-2-butene (0.0 M – 0.8 M) to a solution of **1a** (100 µM, CH_2Cl_2 as the solvent) in the presence of an excess of $EtAlCl_2$ (15 eq.).

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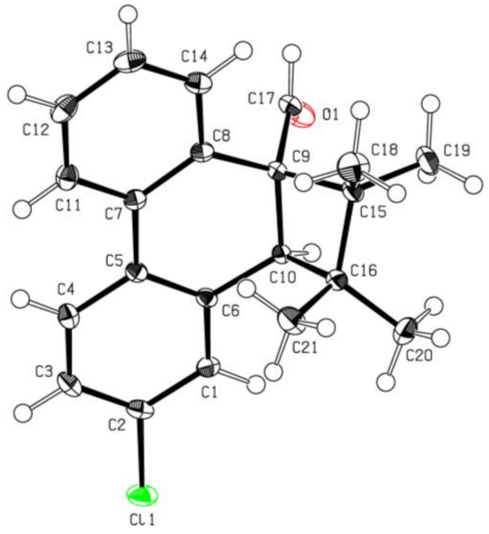
11. X-ray Crystallographic Details

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), a TXS rotating anode with MoK_α radiation (λ = 0.71073 Å) and a Helios optic using the APEX3 software package.[12] The measurement was performed on a single crystal coated with perfluorinated ether. The crystal was fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[13] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[13] Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structure was solved using SHELXT with the aid of successive difference Fourier maps, and was refined against all data using SHELXL-2014 in conjunction with SHELXLE.[14-16] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with aldehyde and aromatic C–H distances of 0.95 Å and other C–H distances of 1.00 Å, all with $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2\ F_c^2)^2$ with the SHELXL weighting scheme.[14] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[17] Images of the crystal structure were generated with PLATON.[18] CCDC 1859722 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Compound 2c (CCDC 1859722)



Diffractometer operator C. Jandl
scanspeed 1-10 s per frame
dx 60 mm
2743 frames measured in 10 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{21}H_{21}ClO$

$M_r = 324.83$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.0920 (7)$ Å

$b = 8.1128 (8)$ Å

$c = 29.514 (3)$ Å

$V = 1698.1 (3)$ Å^3

$Z = 4$

$F(000) = 688$

$D_x = 1.271$ Mg m^{-3}

Melting point: ?

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9727 reflections

$\theta = 2.6$–28.3°

$\mu = 0.23$ mm^{-1}

$T = 100$ K

Fragment, colourless

0.34 × 0.31 × 0.30 mm

Data collection

Bruker Photon CMOS diffractometer

Radiation source: TXS rotating anode

Helios optic monochromator

Detector resolution: 16 pixels mm^{-1}

phi– and ω–rotation scans

Absorption correction: multi-scan *SADABS* 2014/5, Bruker

$T_{\min}$ = 0.705, $T_{\max}$ = 0.746

47539 measured reflections

4059 independent reflections

3943 reflections with $I > 2\sigma(I)$

R_{int} = 0.030

$\theta_{\max}$ = 27.9°, $\theta_{\min}$ = 2.6°

h = −9   9

k = −10   10

l = −38   38

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.028

$wR(F^2)$ = 0.075

S = 1.07

4059 reflections

212 parameters

0 restraints

0 constraints

Primary atom site location: intrinsic phasing

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

W = $1/[\Sigma^2(F\text{O}^2) + (0.0429P)^2 + 0.4138P]$ WHERE $P = (F\text{O}^2 + 2F\text{C}^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.002

$\Delta\rho_{\max}$ = 0.25 e Å^{-3}

$\Delta\rho_{\min}$ = −0.29 e Å^{-3}

Extinction correction: none

Extinction coefficient: -

Absolute structure: Flack (1983)[19], Parsons (2013)[20]

Absolute structure parameter: 0.005 (11)

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