Chemistry–A European Journal

Supporting Information

A Thioxanthone Sensitizer with a Chiral Phosphoric Acid Binding Site: Properties and Applications in Visible Light-Mediated Cycloadditions

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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 stated. For moisture sensitive reactions, tetrahydrofuran (THF), dichloromethane and diethyl ether (Et_2O) 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 (aluminium oxide)

Et_2O: 1 × MB-KOL-A type 2 (aluminium oxide), 1 × MB-KOL-M type 2 (3 Å molecular sieves)

The following dry solvents are commercially available and were used without further purification: acetone (*Acros Organics*, 99.8% extra dry), acetonitrile (*Acros Organics*, 99.9% extra dry, over molecular sieves), *N*,*N*-dimethylformamide (*Acros Organics*, 99.9% extra dry, over molecular sieves), dioxane (*Acros Organics*, 99.5% extra dry, over molecular sieves), ethanol (*Acros Organics*, 99.5% extra dry), methanol (*Acros Organics*, 99.8% extra dry, over molecular sieves), pyridine (*Acros Organics*, 99.5% extra dry, over molecular sieves). 1,2-Dimethoxyethane (DME) was purchased from *TCI Europe* (>99%). Trifluoroethanol (TFE) (*TCI Europe*, >99%) was distilled over calcium hydride and then stored over 4 Å activated molecular sieves.

Deuterated solvents were purchased from *Deutero* or *Sigma Aldrich*. CD_2Cl_2 was freshly distilled over calcium hydride prior to use.

Technical solvents for column chromatography [cyclohexane (CyHex), hexane (Hex), pentane (P), diethyl ether (Et_2O), ethyl acetate (EtOAc), dichloromethane, methanol (MeOH), toluene (Tol), acetone] were used after simple distillation. Flash column chromatography was performed on silica 60 (*Merck*, 230-400 mesh) with the indicated eluent mixtures (v/v).

For photochemical reactions dry dichloromethane was degassed by four freeze-pump-thaw cycles and stored over 4 Å activated molecular sieves. For photochemical reactions using other dry solvents the respective solvent was degassed by purging with argon in an ultrasonic bath for 15 minutes prior to irradiation.

Photochemical experiments at 366 nm and 420 nm were carried out in flame-dried *Duran* tubes (diameter = 1 cm) in a positive geometry setup (cylindrical array of 16 UV-A lamps, 8 W nominal power, λ_{max} = 366 nm or λ_{max} = 420 nm) with the sample placed in the center of the illumination chamber.

Enantioselective reactions were carried out with an LED (λ = 437 nm) at −40 °C in a *Schlenk* tube with a polished quartz rod as an optical fiber, which was roughened by sandblasting at one end. The rough 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 either a *Julabo* FT903 or *Thermo Fisher* Haake® EK90 immersion cooler with ethanol as coolant.

In other cases ice/water (0 °C) and dry ice/acetone (−78 °C) were used as cooling baths.

3,4-Dihydro-2,2-dimethyl-4-oxo-2*H*-pyran-6-carboxylic acid (**9**) for irradiation experiments was purchased from *Sigma-Aldrich* and used without any further purification. Cyclohex-2-enone-3-carboxylic (**12**) acid was synthesized according to a known literature procedure[2] from methyl-cyclohex-1-ene-1-carboxylate which was purchased from *Sigma-Aldrich.*

Cyclopentene (*TCI Europe*) and 2,3-dimethylbut-2-ene (*Sigma-Aldrich*) are commercially available and were distilled, dried by filtration over aluminium oxide and degassed by three freeze-pump-thaw cycles prior to use. Methylidenecyclohexane (*TCI Europe*) and 2-ethylbut-1-ene (*VWR*) are commercially available and were used without further purification.

2. Analytical Methods

Melting points (M.p.) 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 ($\lambda = 254$ nm) [UV] 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: s (strong), m (medium), w (weak).

Nuclear Magnetic Resonance Spectra (NMR) were recorded at room temperature either on a *Bruker* AVHD-300, AVHD-400, AVHD-500 or an AV-III-500 (equipped with a QNP cryo sample head). ^{1}H NMR spectra were calibrated to the residual proton signal of chloroform-d_1 ($\delta = 7.26$ ppm), dimethylsulfoxide-d_6 ($\delta = 2.50$ ppm) or acetone-d_6 ($\delta = 2.05$ ppm). ^{13}C NMR spectra were referenced to the ^{13}C triplet of $CDCl_3$ ($\delta = 77.16$ ppm), to the ^{13}C septet of DMSO-d_6 ($\delta = 39.5$ ppm) or to the ^{13}C septet of acetone-d_6 ($\delta = 29.84$ ppm). ^{11}B and ^{31}P NMR spectra were measured without reference. Apparent multiplets which occur as a result of accidental 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). Signals that could not be assigned unambiguously are marked with an asterisk (*/**). For details on the conducted NMR experiments see chapter 6.

Mass Spectra (MS) and High Resolution Mass Spectra (HRMS) were measured by a *Thermo Scientific* DFS-HRMS (EI, 70 eV) or *Thermo Scientific* LTQ-FT Ultra (ESI) spectrometer.

Analytical High Performance Liquid Chromatography (HPLC) was performed (*Thermo Fisher, Dionex* Ultimate 3000, LPG 3400SD Pump, WPS3000SL Autosampler, TCC-3000 SD column thermostat, DAD 3000 photodiode array detector) using the following chiral stationary phases:

Daicel Chiralpak AD-H (250 × 4.6 mm, 5 µm).
Daicel Chiralpak AS-H (250 × 4.6 mm, 5 µm).
Daicel Chiralpak AS-RH (150 × 4.6 mm, 5 µm).
Daicel Chiralcel OJ-RH (150 × 4.6 mm, 5 µm).

Ultrapure water for HPLC was taken from a *Merck Millipore* Direct-Q 3UV with C18 Polisher LC-MS filter.

Eluent ratios, flow rate and column temperature are listed for each compound, respectively.

Specific Rotation was determined using a *Bellingham+Stanley* ADP440+ polarimeter using a 0.5 cm cuvette at λ = 589 nm (Na-D-line) at room temperature. Specific rotation is reported as follows: $[\alpha]_D^{25}$ in 10^{-1} grad·cm^2·g^{-1} (c was defined as g per 100 mL solvent).

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 pathlength of 1 mm or 10 mm (dilute samples for Fluorescence measurements). Solvents and concentrations are given for each spectrum.

Luminescence Measurements were performed on a *Horiba Scientific* FluoroMax-4P instrument equipped with a continuous Xe source for steady state measurements and a Xe flashlight source for the observation of phosphorescence spectra.

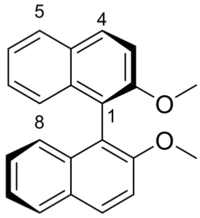
Fluorescence spectra were recorded at ambient conditions in 10×10 mm quartz cuvettes (*Hellma*, *Suprasil*). Luminescence spectra at cryogenic conditions (77 K) were recorded in quartz tubes (inner Ø = 4 mm) in a small quartz Dewar vessel which was filled with liquid nitrogen. All solutions were handled under dry nitrogen and degassed (15 min in an ultrasound bath) to exclude oxygen as triplet quencher. A longpass filter (*Schott Advanced Optics*, WG300 or *Hebo Spezialglass*, UV280) was introduced in the emission-beam path to prevent the scattered excitation light to pass the emission monochromator at higher order wavelengths where necessary.

Circular Dichroism (CD) Measurements were performed on a *JASCO* J-815 spectrometer. The spectrum was recorded using a *Hellma* precision cell made of quartz SUPRASIL® with a path length of 1 mm.

3. Experimental Procedures

3.1 Synthesis of Chiral Phosphoric Acid Catalysts

(*R*)-2,2'-Dimethoxy-1,1'-binaphthalene (S1)



S1
$C_{22}H_{18}O_2$
MW = 314.38 g/mol

According to a modified literature procedure:[3] A suspension of (*R*)-1,1'-binaphthalene-2,2'-diol (14.3 g, 50.0 mmol, 1.0 eq.) in dry acetone (50 mL) was heated to give a homogenous solution. Potassium carbonate (23.5 g, 170 mmol, 3.4 eq.) and methyl iodide (12.2 mL, 27.8 g, 196 mmol, 3.9 eq.) were added and the reaction mixture was refluxed for 24 hours. After removing the solvent in vacuo, water (20 mL) was added and the mixture was stirred at room temperature for an additional eight hours. The precipitate was filtered, washed with water and dried to afford (*R*)-2,2'-dimethoxy-1,1'-binaphthalene (**S1**) as a white solid (13.5 g, 43.0 mmol, 86%).

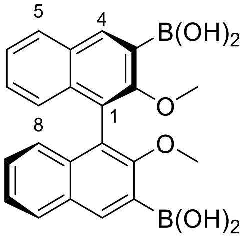
TLC: R_f = 0.62 (P:Et_2O = 2:1) [UV].

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.77 (s, 6 H, OMe), 7.12 (d, ^3J = 8.5 Hz, 2 H, H-8), 7.22 (ddd, ^3J = 8.1 Hz, ^3J = 6.6 Hz, ^4J = 1.4 Hz, 2 H, H-7), 7.32 (ddd, ^3J = 8.5 Hz, ^3J = 6.6 Hz, ^4J = 1.4 Hz, 2 H, H-6), 7.47 (d, ^3J = 9.0 Hz, 2 H, H-5), 7.88 (d, ^3J = 8.1 Hz, 2 H, H-8), 7.99 (d, ^3J = 9.0 Hz, 2 H, H-4).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 57.1 (q, 2 × OMe), 114.4 (d, 2 × C-3), 119.7 (s. 2 × C-1), 123.6 (d, 2 × C-7), 125.4 (d, 2 × C-5), 126.4 (d, 2 × C-6), 128.1 (d, 2 × C-8), 129.4 (s, 2 × C-4a), 129.5 (d, 2 × C-4), 134.1 (s, 2 × C-8a), 155.1 (s, 2 × C-2).

The analytical data are consistent with those reported in literature.[3]

(*R*)-(2,2'-Dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)diboronic acid (8)



8

$C_{22}H_{20}B_2O_6$

MW = 402.02 g/mol

According to a modified literature procedure:[4] To a solution of **S1** (2.01 g, 6.40 mmol, 1.0 eq.) in dry THF (50 mL) *n*-butyllithium (2.5 M in hexane, 10.2 mL, 25.6 mmol, 4.0 eq.) was added dropwise. The reaction mixture was stirred at room temperature for twelve hours, then cooled to –78 °C, and triethyl borate (8.85 mL, 7.59 g, 51.2 mmol, 8.0 eq.) was added dropwise. The solution was allowed to warm to room temperature and stirred for an additional twelve hours. Subsequently, the reaction mixture was cooled to 0 °C and 1 M HCl (50 mL) was added. The solution was allowed to warm to room temperature and stirred overnight. The organic phase was washed with 1 M HCl (30 mL), then brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The pale yellow foam was recrystallized from toluene to give (*R*)-(2,2'-dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)diboronic acid (**8**) as a white solid (1.50 g, 3.73 mmol, 58%).

TLC: R_f = 0.15 (CH_2Cl_2:MeOH = 50:1) [UV].

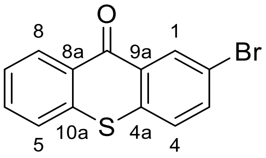
^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 3.41 (s, 6 H, OCH_3), 7.11 (d, ^3J = 8.5 Hz, 2 H, H-8), 7.29-7.38 (m, 2 H, H-7), 7.45 (dd, ^3J = 8.2 Hz, ^3J = 6.7 Hz, 2 H, H-6), 8.04 (d, ^3J = 8.2 Hz, 2 H, H-5), 8.56 (s, 2 H, H-4).

^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 61.9 (q, 2 × OCH_3), 124.3 (s, 2 × C-1), 125.8 (d, 2 × C-6), 126.5 (d, 2 × C-8), 128.3 (d, 2 × C-7), 129.8 (d, 2 × C-5), 131.6 (s, 2 × C-4a), 136.7 (s, 2 × C-8a), 139.2 (d, 2 × C-4), 161.4 (s, 2 × C-2).*

* Signal of C-3 atom is not visible in ^{13}C NMR.

The analytical data are consistent with those reported in literature.[4]

2-Bromo-9*H*-thioxanthen-9-one (S2)



S2
$C_{13}H_7BrOS$
MW = 291.16 g/mol

According to a literature procedure:[5] Thiosalicylic acid (10.0 g, 64.9 mmol, 1.0 eq.) was added slowly into a mixture of bromobenzene (13.6 mL, 20.4 g, 130 mmol, 2.0 eq.) in concentrated sulphuric acid (100 mL). The suspension was stirred for ten hours at room temperature and afterwards permitted to stand for an additional ten hours. Subsequently, the reaction mixture was stirred at 100 °C for one hour, cooled to room temperature, and then slowly poured over ice. The orange suspension was extracted with chloroform (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, P:Et_2O:Tol = 40:1:1→30:1:1) to afford 2-bromo-9*H*-thioxanthen-9-one (**S2**) as a yellow solid (7.95 g, 27.3 mmol, 42% yield).

TLC: R_f = 0.40 (P:Et_2O:Tol = 20:1:1) [UV].

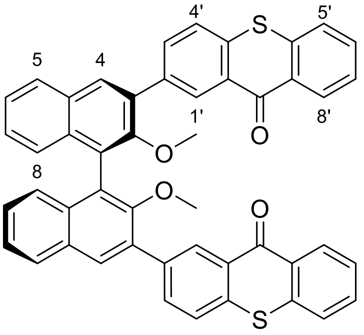
M.p.: 165.9 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.46 (d, ^3J = 8.5 Hz, 1 H, H-4), 7.50 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1 H, H-7), 7.58 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1 H, H-5), 7.64 (ddd, ^3J = 8.0 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1 H, H-6), 7.71 (dd, ^3J = 8.5 Hz, ^4J = 2.3 Hz, 1 H, H-3), 8.61 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1 H, H-8), 8.75 (d, ^3J = 2.3 Hz, 1 H, H-1).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 120.4 (s, C-2), 126.2 (d, C-5), 126.8 (d, C-7), 127.7 (d, C-4), 129.0 (s, C-8a), 130.2 (d, C-8), 130.7 (s, C-9a), 132.6 (d, C-1), 132.8 (d, C-6), 135.4 (d, C-3), 136.2 (s, C-4a), 137.0 (s, C-10a), 178.9 (s, C-9).

The analytical data are consistent with those reported in literature.[5]

(*R*)-2,2'-(2,2'-Dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)bis(9*H*-thioxanthen-9-one) (S3)



S3
$C_{48}H_{30}O_4S_2$
MW = 734.88 g/mol

2-Bromo-9*H*-thioxanthen-9-one (**S2**) (874 mg, 3.00 mmol, 3.0 eq.), $Ba(OH)_2\cdot 8\,H_2O$ (947 mg, 3.00 mmol, 3.0 eq.) and $Pd(PPh_3)_4$ (116 mg, 100 µmol, 10 mol%) were added to a solution of **8** (402 mg, 1.00 mmol. 1.0 eq.) in degassed dioxane/water (24 mL, 3:1). The reaction mixture was stirred at 80 °C for 24 hours. After cooling to room temperature, the solvent was removed in vacuo, and the crude product was dissolved in dichloromethane, washed with 1 M HCl (10 mL), brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, P:CH_2Cl_2:Et_2O = 20:1:1→10:1:1) to afford (*R*)-2,2'-(2,2'-dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)bis(9*H*-thioxanthen-9-one) (**S3**) as a yellow solid (338 mg, 0.46 mmol, 46%).

TLC: R_f = 0.15 (P:CH_2Cl_2:Et_2O = 10:1:1) [UV].

M.p.: 215.6 °C.

Specific Rotation: $[\alpha]_D^{25}$ = –96 (c = 1.00, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.21 (s, 6 H, OMe), 7.26 (d, ^3J = 8.0 Hz, 2 H, H-8), 7.32 (ddd, ^3J = 8.0 Hz, ^3J = 6.6 Hz, ^4J = 1.3 Hz, 2 H, H-7), 7.45 (ddd, ^3J = 8.2 Hz, ^3J = 6.6 Hz, ^4J = 1.3 Hz, 2 H, H-6), 7.52 (ddd, ^3J = 8.2 Hz, ^3J = 6.3 Hz, ^4J = 2.0 Hz, 2 H, H-7'), 7.63 (m, 4 H, H-5', H-6'), 7.67 (d, ^3J = 8.4 Hz, 2 H, H-4'), 7.97 (d, ^3J = 8.2 Hz, 2 H, H-5), 8.14 (s, 2 H, H-4)#, 8.15 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, H-3')#, 8.69 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 2 H, H-8'), 9.02 (d, ^4J = 2.0 Hz, 2 H, H-1').

Overlapping signals.

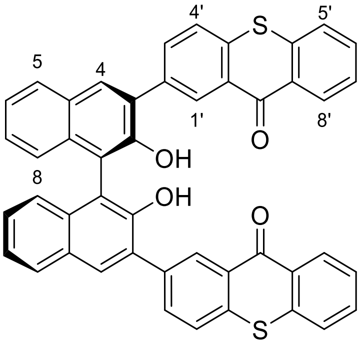
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 60.9 (q, 2 × OMe), 125.5 (d, 2 × C-6), 125.9 (s, 2 × C-Ar), 126.0 (d, 2 × C-8)*, 126.0 (d, 2 × C-4')*, 126.3 (d, 2 × C-5'), 126.5 (d, 2 × C-7'), 126.8 (d, 2 × C-7), 128.4 (d, 2 × C-5), 129.5 (s, 2 × C-Ar), 129.6 (s, 2 × C-Ar), 130.0 (d, 2 × C-1’), 130.1 (d, 2 × C-8’), 131.0 (d, 2 × C-4)**, 131.1 (s, 2 × C-4a)**, 132.5 (d, 2 × C-6’), 133.6 (s, 2 × C-Ar), 133.9 (d, 2 × C-3’), 134.1 (s, 2 × C-8a), 136.5 (s, 2 × C-Ar), 137.4 (s, 2 × C-Ar), 137.5 (s, 2 × C-Ar), 154.1 (s, 2 × C-2), 180.2 (s, 2 × CO).

*/** Assignments are interconvertible.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3058 (w, sp^2–CH), 1638 (s, C=O), 1592 (s, C=C), 1459 (m), 1438 (m), 1319 (m), 1247 (m), 746 (s, sp^2–CH).

HRMS (ESI): calc. for $C_{48}H_{31}O_4S_2^+$ $[M + H]^+$: 735.1658; found: 735.1648.

(*R*)-2,2'-(2,2'-Dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(9*H*-thioxanthen-9-one) (S4)



S4
$C_{46}H_{26}O_4S_2$
MW = 706.83 g/mol

Boron tribromide (1.0 M in CH_2Cl_2, 1.20 mL, 1.20 mmol, 6.0 eq.) was added dropwise to a solution of **S3** (147 mg, 200 µmol, 1.0 eq.) in CH_2Cl_2 (10 mL) at 0 °C and the reaction mixture was stirred at 0 °C for two hours. After quenching with methanol (5 mL), the reaction mixture was allowed to warm to room temperature and stirred overnight. Subsequently, the solvent was removed in vacuo, and the resulting solid was dissolved in methanol, which was then removed in vacuo. After repeating this step for three times, water (10 mL) was added, and the resulting suspension was stirred at 70 °C for two hours. After filtration, the precipitate was dissolved in CH_2Cl_2, dried over Na_2CO_3, filtered, and concentrated in vacuo to give the pure product (*R*)-2,2'-(2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(9*H*-thioxanthen-9-one) (**S4**) as a yellow solid (115 mg, 163 µmol, 81%).

TLC: R_f = 0.35 (P:CH_2Cl_2:Et_2O = 5:1:1) [UV].

M.p.: > 250 °C.

Specific Rotation: $[\alpha]_D^{25}$ = +32 (c = 0.10, $CHCl_3$).

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 6.98 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 2 H, H-8), 7.27 (ddd, ^3J = 8.2 Hz, ^3J = 6.8 Hz, ^4J = 1.5 Hz, 2 H, H-7), 7.33 (ddd, ^3J = 8.1 Hz, ^3J = 6.8 Hz, ^4J = 1.4 Hz, 2 H, H-6), 7.62 (ddd, ^3J = 8.2 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 2 H, H-7'), 7.81 (ddd, ^3J = 8.2 Hz, ^3J = 7.0 Hz, ^4J = 1.4 Hz, 2 H, H-6'), 7.90 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 2 H, H-5'), 7.98 (d, ^3J = 8.4 Hz, 2 H, H-4'), 8.00-8.05 (m, 2 H, H-5), 8.12 (s, H-4), 8.16 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 2 H, H-3'), 8.52 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 2 H, H-8'), 8.64 (*br* s, 2 H, OH), 8.86 (d, ^4J = 2.0 Hz, H-1').

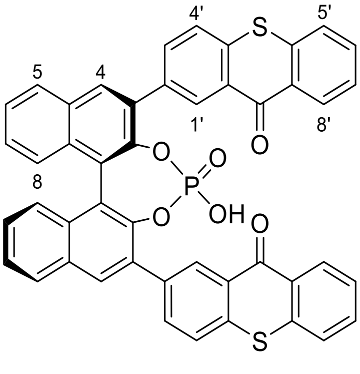
^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 115.0 (s, 2 × C-1), 123.2 (d, 2 × C-6), 124.1 (d, 2 × C-8), 126.3 (d, 2 × C-4'), 126.6 (d, 2 × C-7), 126.7 (d, 2 × C-5'), 126.9 (d, 2 × C-7'), 128.2 (s, 2 × C-8'a), 128.4 (d, 2 × C-5*), 128.4 (s, 2 × C-9'a*), 128.7 (s, 2 × C-4a), 129.2 (d, 2 × C-8'), 129.8 (d, 2 × C-1'), 130.2 (d, 2 × C-4**), 130.3 (s, 2 × C-3'**), 133.1 (d, 2 × C-6'), 133.9 (s, 2 × C-8a), 134.5 (d, 2 × C-3'), 135.2 (s, 2 × C-4'a), 136.6 (s, 2 × C-10'a), 137.5 (s, 2 × C-2'), 151.4 (s, 2 × C-2), 178.9 (s, 2 × CO).

*/** Assignments are interconvertible.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3347 (br w, O–H), 1636 (s, C=O), 1591 (vs, C=C), 1438 (m), 1123 (w), 1079 (w), 743 (vs, sp^2–CH).

HRMS (ESI): calc. for $NaC_{46}H_{26}O_4S_2^+$ [M + Na]$^+$: 729.1165; found: 729.1154.

(*R*)-2,2'-(4-Hydroxy-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-2,6-diyl)bis(9*H*-thioxanthen-9-one) (S5)



S5
$C_{46}H_{25}O_6PS_2$
MW = 768.79 g/mol

Phosphorus(V) oxychloride (18.7 µL, 30.7 mg, 200 µmol, 2.0 eq.) was added to a suspension of **S4** (70.7 mg, 100 µmol, 1.0 eq.) in pyridine (280 µL) and stirred at 95 °C for twelve hours. After cooling the reaction mixture to 0 °C water (80 µL) was added slowly and the reaction mixture was stirred at 95 °C for an additional ten hours. After dilution with CH_2Cl_2 and 1 M HCl wash, the organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification by flash column chromatography (SiO_2, CH_2Cl_2/MeOH = 30:1→20:1) yielded a yellow solid which was dissolved in CH_2Cl_2 and washed with 6 M HCl. The solvent was removed in vacuo to afford (*R*)-2,2'-(4-hydroxy-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxa phosphepine-2,6-diyl)bis(9*H*-thioxanthen-9-one) (**S5**) as a yellow solid (62.3 mg, 81.0 µmol, 81% yield).

TLC: $R_f = 0.20$ (CH_2Cl_2:MeOH = 20:1) [UV].

M.p.: > 250 °C.

Specific Rotation: $[\alpha]_D^{25} = +168$ (c = 1.00, $CHCl_3$).

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 7.16 (d, ^3J = 8.6 Hz, 2 H, H-8), 7.27-7.36 (m, 2 H, H-7), 7.48 (dd, ^3J = 8.3 Hz, ^3J = 6.7 Hz, 2 H, H-6), 7.60 (*virt*. t, $^3J \approx {}^3J$ = 7.6 Hz, 2 H, H-7’), 7.79 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 2 H, H-6’), 7.88 (d, ^3J = 8.1 Hz, 2 H, H-Ar), 7.93 (d, ^3J = 8.2 Hz, 2 H,H-Ar), 8.14 (d, ^3J = 8.3 Hz, 2 H, H-5), 8.25 (s, 2 H, H-4), 8.51 (d, ^3J = 8.1 Hz, 2 H, H-3’), 8.68 (dd, ^3J = 8.3 Hz, ^4J = 2.2 Hz, 2 H, H-8’), 8.76 (d, ^4J = 2.1 Hz, 2 H, H-1’).

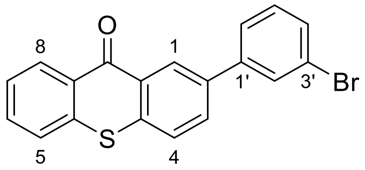
^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 122.8 (d, $^3J_{C\text{-}P}$ = 1.1 Hz, C-1), 125.1 (2 × C-Ar), 126.1 (2 × C-Ar), 126.2 (2 × C-Ar), 126.6 (2 × C-Ar), 126.8 (2 × C-Ar), 126.9 (2 × C-Ar), 128.3 (2 × C-Ar), 128.4 (2 × C-Ar), 128.7 (2 × C-Ar), 129.2 (2 × C-Ar), 130.0 (2 × C-Ar), 130.3 (2 × C-Ar), 130.6 (2 × C-Ar), 132.1 (2 × C-Ar), 133.0 (d, $^2J_{C\text{-}P}$ = 1.5 Hz, C-3), 133.1 (2 × C-Ar), 135.3 (2 × C-Ar), 135.6 (2 × C-Ar), 136.7 (2 × C-Ar), 136.8 (2 × C-Ar), 147.2 (d, $^2J_{C\text{-}P}$ = 9.2 Hz, C-2), 179.0 (2 × CO).

^{31}P NMR (203 MHz, DMSO-d_6): δ (ppm) = 2.38.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2924 (w, sp^2–CH), 1638 (s, C=O), 1592 (s, C=C), 1439 (m), 1321 (m), 1284 (m), 1080 (s, P=O), 949 (s, sp^2–CH).

HRMS (ESI): calc. for $C_{46}H_{24}O_6PS_2^-$ $[M - H]^-$: 767.0757; found: 767.0749.

2-(3-Bromophenyl)-9*H*-thioxanthen-9-one (7)



7

$C_{19}H_{11}BrOS$

MW = 367.26 g/mol

Thiosalicylic acid (**6**) (1.65 g, 10.7 mmol, 1.0 eq.) was added slowly to a mixture of concentrated sulfuric acid (15 mL) and 3-bromo-1,1'-biphenyl (**5**) (5.00 g, 21.4 mmol, 2.0 eq.) at room temperature. The suspension was stirred for ten hours and then permitted to stand for an additional ten hours. Subsequently, the reaction mixture was stirred at 100 °C for four hours, cooled to room temperature, and then poured slowly over ice. The resulting yellow suspension was extracted with chloroform (5 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, CyHex:EtOAc = 95:5→90:10) to afford 2-(3-bromo-phenyl)-9*H*-thioxanthen-9-one (**7**) as a yellow solid (1.89 g, 5.14 mmol, 48%).

TLC: R_f = 0.34 (CyHex:EtOAc = 9:1) [UV].

M.p.: 161.9 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.36 (*virt*. t, $^3J \approx {}^3J$ = 7.9 Hz, 1 H, H-5’), 7.46-7.55 (m, 2 H, H-7, H-4’), 7.62 7 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 1 H, H-5), 7.63-7.66 (m, 2 H, H-6’, H-6), 7.68 (d, ^3J = 8.4 Hz, 1 H, H-4), 7.84 (dd, ^3J = 8.4 Hz, ^4J = 2.1 Hz, 1 H, H-3), 7.86 (*virt*. t, $^4J \approx {}^4J$ = 1.8 Hz, 1 H, H-2’), 8.66 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 1 H, H-8), 8.84 (d, ^4J = 2.1 Hz, 1 H, H-1).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 123.3 (s, C-3’), 125.7 (d, C-6’), 126.2 (d, C-5), 126.5 (d, C-Ar), 126.8 (d, C-4), 128.0 (d, C-1), 129.2 (s, C-9a)*, 129.6 (s, C-8a)*, 130.1 (d, C-8), 130.2 (d, C-2’), 130.6 (d, C-Ar), 130.8 (d, C-Ar), 130.9 (d, C-Ar), 132.5 (d, C-6), 136.9 (s, C-4a)**, 137.1 (s, C-10a)**, 137.7 (s, C-2), 141.6 (s, C-1’), 179.8 (s, CO).

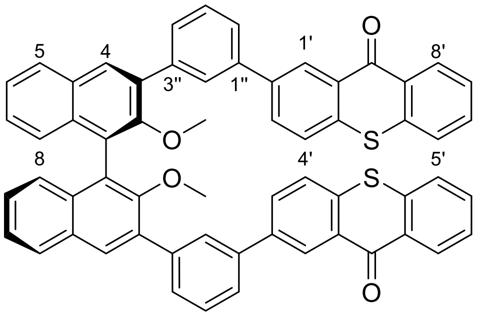
*/** Assignments are interconvertible.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1637 (vs, C=O), 1593 (vs, C=C), 1459 (m), 1438 (m), 1331 (w), 1036 (w), 743 (s, sp^2–CH).

MS (EI, 70 eV): m/z (%) = 366 (100) [^{79}Br-M]$^+$, 340 (20), 287 (9) [M-Br]$^+$, 258 (62) [$C_{13}H_7BrO$]$^+$, 129 (23), 144 (20).

HRMS (ESI): calc. for $C_{19}H_{12}{}^{79}BrOS^{+}$ $[M + H]^{+}$: 366.9787; found: 366.9784.

(*R*)-2,2'-(2,2'-Dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)bis(4-phenyl-9*H*-thioxanthen-9-one) (S6)



S6
$C_{60}H_{38}O_4S_2$
MW = 887.08 g/mol

To a solution of **8** (170 mg, 422 µmol, 1.0 eq.) in degassed 1,2-dimethoxyethane (4.0 mL) and 2 M Na_2CO_3 solution (2.11 mL, 4.22 mmol, 10 eq.) thioxanthone **7** (341 mg, 928 mmol, 2.2 eq.) and $Pd(PPh_3)_4$ (48.8 mg, 42.2 µmol, 10 mol%) were added. The mixture was stirred at 85 °C for 18 hours. After quenching with saturated NH_4Cl solution and dilution with EtOAc (5 mL), the organic layer was washed with saturated $NaHCO_3$ (5 mL), brine (5 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, Hex:Tol:EtOAc = 8:1:1→6:2:2) to afford (*R*)-2,2'-(2,2'-dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)bis(4-phenyl-9*H*-thioxanthen-9-one) (**S6**) as a yellow solid (360 mg, 406 µmol, 96%).

TLC: $R_f = 0.41$ (Hex:Tol:EtOAc = 6:2:2) [UV].

M.p.: 239.0 °C.

Specific Rotation: $[\alpha]_{D}^{25} = -34$ (c = 1.00, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.28 (s, 6 H, OMe), 7.27-7.34 (m, 4 H, H-7, H-8), 7.44 (ddd, $^{3}J = 8.1$ Hz, $^{3}J = 6.3$ Hz, $^{4}J = 1.7$ Hz, 2 H, H-6), 7.51 (ddd, $^{3}J = 8.2$ Hz, $^{3}J = 6.7$ Hz, $^{4}J = 1.3$ Hz, 2 H, H-7’), 7.56-7.66 (m, 6 H, H-5’, H-6’, H-5’’), 7.68 (d, $^{3}J = 8.4$ Hz, 2 H, H-4’), 7.75 (*virt*. dt, $^{3}J = 7.9$ Hz, $^{4}J \approx {}^{4}J = 1.4$ Hz, 2 H, H-4’’), 7.83 (dd, $^{3}J = 8.1$ Hz, $^{4}J = 1.8$ Hz, 2 H, H-6’’), 7.93-8.00 (m, 4 H, H-5, H-3’), 8.08 (s, 2 H, H-4), 8.12 (*virt*. t, $^{4}J \approx {}^{4}J = 1.8$ Hz, H-2’’), 8.65 (dd, $^{3}J = 8.2$ Hz, $^{4}J = 1.3$ Hz, 2 H, H-8’), 8.96 (d, $^{4}J = 2.1$ Hz, 2 H, H-1’).

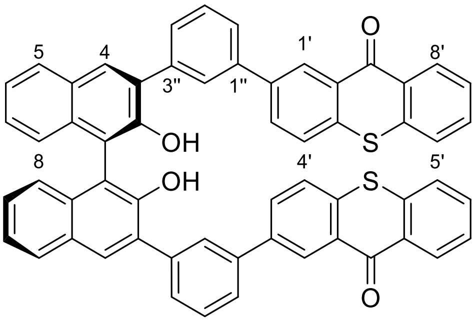
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 60.9 (q, 2 × OMe), 125.3 (d, 2 × C-6), 126.0 (2 × C-Ar), 126.1 (2 × C-Ar), 126.2 (d, 2 × C-Ar), 126.2 (d, 2 × C-4’’), 126.5 (d, 2 × C-7’), 126.6 (2 × C-Ar), 126.7 (d, 2 × C-4’), 128.1 (d, 2 × C-2’’)*, 128.1 (d, 2 × C-1’)*, 128.3 (d, 2 × C-5), 129.1 (d, 2 × C-Ar), 129.2 (d, 2 × C-Ar), 129.4 (s, 2 × C-Ar), 129.6 (s, 2 × C-Ar), 130.1 (d, 2 × C-8’), 130.8 (d, 2 × C-4), 131.0 (s, 2 × C-Ar), 131.3 (d, 2 × C-3’), 132.4 (d, 2 × C-6’), 133.9 (s, 2 × C-8a), 134.8 (s, 2 × C-Ar), 136.3 (s, 2 × C-4’a), 137.3 (s, 2 × C-10’a), 139.4 (s, 2 × C-Ar), 139.8 (s, 2 × C-1’’)**, 139.9 (s, 2 × C-3’’)**, 154.2 (s, 2 × C-2), 180.1 (s, 2 × CO).

*/** Assignments are interconvertible.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3060 (w, sp^2–CH), 1639 (vs, C=O), 1592 (s, C=C), 1460 (m), 1438 (m), 1328 (m), 1079 (w), 890 (vs, sp^2–CH).

HRMS (APCI): calc. for $C_{60}H_{39}O_4S_2^+$ $[M + H]^+$: 887.2284; found: 887.2281.

(*R*)-2,2'-{(2,2'-Dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(3,1-phenylene)}bis(9*H*-thioxanthen-9-one) (S7)



S7
$C_{58}H_{34}O_4S_2$
MW = 859.03 g/mol

Compound **S6** (358 mg, 404 µmol, 1.0 eq.) was dissolved in dichloromethane (3 mL) and cooled to 0 °C, before a 1 M solution of boron tribromide in CH_2Cl_2 (1.62 mL, 1.62 mmol, 4.0 eq.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for two hours. Water was slowly added at 0 °C to quench the reaction followed by extraction with CH_2Cl_2 (3 × 3 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, P:acetone = 5:1) to afford (*R*)-2,2'-(2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(4-phenyl-9*H*-thioxanthen-9-one) (**S7**) as a yellow solid (288 mg, 335 µmol, 83%).

TLC: R_f = 0.25 (P:acetone = 5:1) [UV].

M.p.: 243.4 °C.

Specific Rotation: $[\alpha]_D^{25}$ = –44 (c = 1.00, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.49 (*br*. s, 2 H, OH), 7.27 (d, ^3J = 8.2 Hz, 2 H, H-8), 7.36 (ddd, ^3J = 8.2 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 2 H, H-7), 7.42 (ddd, ^3J = 8.1 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 2 H, H-6), 7.49 (ddd, ^3J = 8.2 Hz, ^3J = 6.8 Hz, ^4J = 1.5 Hz, 2 H, H-7’), 7.59-7.65 (m, 6 H, H-5’, H-6’, H-5’’), 7.67 (d, ^3J = 8.4 Hz, 2 H, H-4’), 7.75 (ddd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, ^4J = 1.1 Hz, 2 H, H-4’’), 7.79 (*virt*. dt, ^3J = 7.8 Hz, $^4J \approx {}^4J$ = 1.5 Hz, 2 H, H-6’’), 7.93-7.98 (m, 4 H, H-5, H-3’), 8.10 (*virt*. t, $^4J \approx {}^4J$ = 1.8 Hz, 2 H, H-2’’), 8.13 (s, 2 H, H-4), 8.62-8.66 (m, 2 H, H-8’), 8.94 (d, ^2J = 2.1 Hz, 2 H, H-1’).

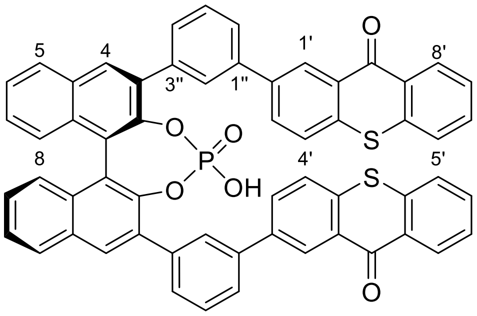
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 112.4 (s, 2 × C-Ar), 124.4 (d, 2 × C-8)*, 124.6 (d, 2 × C-6)*, 126.2 (d, 2 × C-5’), 126.5 (d, 2 × C-7’), 126.6 (d, 2 × C-4’’), 126.8 (d, 2 × C-4’), 127.7 (d, 2 × C-7), 128.1 (d, 2 × C-1’), 128.7 (d, 2 × C-2’’), 128.7 (d, 2 × C-5), 129.2 (s, 2 × C-Ar)**, 129.3 (d, 2 × C-6’’)**, 129.3 (d, 2 × C-5’’)**, 129.6 (s, 2 × C-Ar), 129.6 (s, 2 × C-Ar), 130.1 (d, 2 × C-8’), 130.5 (s, 2 × C-Ar), 131.4 (d, 2 × C-3’), 131.8 (d, 2 × C-4), 132.5 (d, 2 × C-6’), 133.2 (s, 2 × C-8a), 136.4 (s, 2 × C-4a), 137.3 (s, 2 × C-Ar), 138.4 (s, 2 × C-3’’), 139.4 (s, 2 × C-2’), 139.9 (s, 2 × C-Ar), 150.4 (s, 2 × C-2), 180.1 (s, 2 × CO).

*/** Assignments are interconvertible.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3510 (br w, O–H), 1636 (s, C=O), 1592 (s, C=C), 1439 (m), 1331 (w), 1290 (w), 1127 (w), 795 (vs, sp^2–CH).

HRMS (APCI): calc. for $C_{58}H_{35}O_4S_2^+$ $[M + H]^+$: 859.1971; found: 859.1961.

2,2'-{((11b*R*)-4-Hydroxy-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-2,6-diyl)bis(3,1-phenylene)}bis(9*H*-thioxanthen-9-one) (4)



4
$C_{58}H_{33}O_6PS_2$
MW = 920.99 g/mol

Phosphorus(V) oxychloride (46.7 µL, 76.7 mg, 500 µmol, 2.0 eq.) was added to a suspension of **S7** (215 mg, 250 µmol, 1.0 eq.) in dry pyridine (0. 8 mL) and stirred at 95 °C for twelve hours. The reaction mixture was then cooled to 0 °C, and water (220 µL) was added slowly. After stirring at 95 °C for further twelve hours, the black reaction mixture was diluted with CH_2Cl_2 and washed with 1 M HCl. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2:MeOH = 30:1→0:1), dissolved in CH_2Cl_2 and washed with 6 M HCl. Removing the solvent in vacuo yielded 2,2'-{((11b*R*)-4-hydroxy-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-2,6-diyl)bis(3,1-phenylene)}bis(9*H*-thioxanthen-9-one) (**4**) (125 mg, 136 µmol, 54%) as a yellow solid.

TLC: R_f = 0.55 (CH_2Cl_2:MeOH = 10:1) [UV].

M.p.: > 250 °C.

Specific Rotation: $[\alpha]_D^{25}$ = –402 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 7.21 (d, ^3J = 8.6 Hz, 2 H, H-8), 7.39 (ddd, ^3J = 8.6 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 2 H, H-7), 7.55 (*virt*. t, $^3J \approx {}^3J$ = 7.6 Hz, H-6), 7.60 (ddd, ^3J = 8.0 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 2 H, H-7’), 7.67 (*virt*. t, $^3J \approx {}^3J$ = 7.7 Hz, 2 H, H-5’’), 7.79 (*virt*. td, $^3J \approx {}^3J$ = 8.0 Hz, ^4J = 1.4 Hz, 2 H, H-6’), 7.87 (d, ^3J = 8.5 Hz, 2 H, H-Ar’)$^{\#}$, 7.87 (d, ^3J = 8.5 Hz, 2 H, H-Ar)$^{\#}$, 7.92 (d, ^3J = 7.7 Hz, 2 H, H-Ar), 7.96 (d, ^3J = 8.6 Hz, 2 H, H-4’), 8.17 (d, ^3J = 8.1 Hz, 2 H, H-5), 8.29 (dd, ^3J = 8.6 Hz, ^4J = 2.1 Hz, 2 H, H-3’), 8.33 (s, 2 H, H-4), 8.35 (*virt*. t, ^4J = 2.2 Hz, 2 H, H-2’’), 8.49 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 2 H, H-8’), 8.81 (d, ^2J = 2.1 Hz, 2 H, H-1’).

\# Overlapping signals.

^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 122.3 (d, $^3J_{C\text{-}P}$ = 1.2 Hz, 2 × C-1), 125.6 (d, 2 × C-6), 125.8 (d, 2 × C-Ar), 126.2 (d, 2 × C-8), 126.5 (d, 2 × C-Ar), 126.7 (d, 2 × C-1’), 126.8 (d, 2 × C-Ar), 126.9 (d, 2 × C-Ar), 127.5 (d, 2 × C-4’), 128.3 (s, 2 × C-Ar), 128.5 (d, 2 × C-2’’), 128.7 (d, 2 × C-5)*, 128.8 (s, 2 × C-Ar)*, 129.2 (d, 2 × C-8’)**, 129.2 (d, 2 × C-5’’)**, 129.7 (d, 2 × C-Ar), 130.7 (s, 2 × C-4a), 131.2 (d, 2 × C-4), 131.7 (s, 2 × C-Ar)$^{\#}$, 131.7 (d, 2 × C-3’)$^{\#}$, 133.1 (d, 2 × C-6’), 133.6 (d, $^3J_{C\text{-}P}$ = 2.1 Hz, 2 × C-3), 135.8 (s, 2 × C-4’a), 136.5 (s, 2 × C-10’a), 138.2 (s, 2 × C-2’), 138.4 (s, 2 × C-1’’), 138.5 (s, 2 × C-3’’) 145.7 (d, $^2J_{C\text{-}P}$ = 9.3 Hz, 2 × C-2), 178.8 (s, 2 × CO).

*/** Assignments are interconvertible.

$^{\#}$ Overlapping signals.

^{31}P NMR (162 MHz, DMSO-d_6): δ (ppm) = 1.81.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3056 (w, sp^2–CH), 2925 (w), 1637 (m, C=O), 1592 (s, C=C), 1439 (m), 1412 (m), 1257 (m), 1100 (s, P=O) 745 (s, sp^2–CH).

HRMS (APCI): calc. for $C_{58}H_{32}O_6PS_2^-$ [M – H]$^-$: 919.1383; found: 919.1383.

3.2 Irradiation Experiments

General Procedure 1 (GP1): Racemic [2+2] photocycloaddition of ***9***

Irradiation precursor **9** (1.0 eq.) was added to a flame-dried *Duran* phototube and dissolved in degassed dichloromethane (20 mM). Alkene (20 eq.) was added and the solution was irradiated at λ = 366 nm at room temperature. After complete conversion the solvent was removed in vacuo and the crude product was subjected to work-up procedure 1 (*WP1*).

General Procedure 2 (GP2): Racemic [2+2] photocycloaddition of ***12***

Irradiation precursor **12** (1.0 eq.) and 9*H*-thioxanthen-9-one (50 mol%) were added to a flame-dried *Duran* phototube and dissolved in degassed dichloromethane (20 mM). Alkene (20 eq.) was added and the solution was irradiated at λ = 420 nm at room temperature. After complete conversion the solvent was removed in vacuo and the crude product was subjected to work-up procedure 2 (*WP2*).

General Procedure 3 (GP3): Enantioselective [2+2] photocycloaddition of ***9*** *or* ***12***

The respective irradiation precursor (1.0 eq.) and photocatalyst **4** (10 mol%) were added to a flame-dried LED phototube and dissolved in degassed dichloromethane (10 mM). Alkene (50 eq.) was added and the solution was cooled to −40 °C for 30 min. The solution was irradiated at λ = 437 nm and −40 °C for the appropriate amount of time. After complete conversion the solvent was removed in vacuo and the crude product was subjected to work-up procedure 3 (*WP3*).

Work-up procedure 1 (WP1):

The crude product was dissolved in DMF (10 mL). After adding potassium carbonate (92.9 mg, 600 µmol, 1.5 eq.) and benzyl bromide (95.0 µL, 137 mg, 800 µmol, 2.0 eq.) the solution was stirred at room temperature for four hours. After addition of water and extraction with Et_2O (4×) the combined organic layers were washed with brine and dried over Na_2SO_4. Filtration and purification by flash column chromatography (SiO_2, P:Et_2O = 8:1→5:1) afforded the respective photoproducts.

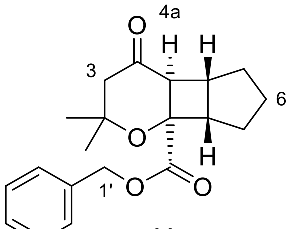
Work-up procedure 2 (WP2):

The crude product was dissolved in DMF (5 mL). After adding potassium carbonate (41.5 mg, 300 µmol, 1.5 eq.) and benzyl bromide (47.5 µL, 68.4 mg, 400 µmol, 2.0 eq.) the solution was stirred at room temperature for four hours. After addition of water and extraction with Et_2O (4×) the combined organic layers were washed with brine and dried over Na_2SO_4. Filtration and purification by flash column chromatography (SiO_2, P:Et_2O = 8:1→5:1) afforded the respective photoproducts.

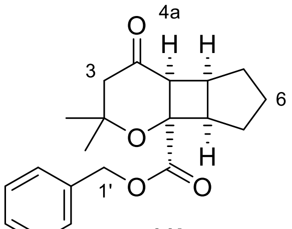
Work-up procedure 3 (WP3):

The crude product was dissolved in DMF (2 mL). After adding potassium carbonate (10.4 mg, 75.0 µmol, 1.5 eq.) and benzyl bromide (11.9 µL, 17.1 mg, 100 µmol, 2.0 eq.) the solution was stirred at room temperature for four hours. After addition of water and extraction with Et_2O (4×) the combined organic layers were washed with brine and dried over Na_2SO_4. Filtration and purification by flash column chromatography (SiO_2, P:Et_2O = 6:1→5:1) afforded the respective photoproducts.

Benzyl-(4a*S*,4b*R*,7a*S*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylate (11a) and benzyl-(4a*S*,4b*S*,7a*R*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylate (11b)



11a



11b

$C_{20}H_{24}O_4$
MW = 328.41 g/mol

Racemic [2+2] photocycloaddition:

According to *GP1* a solution of carboxylic acid **9** (68.1 mg, 400 µmol, 1.0 eq.) and cyclopentene (732 µL, 545 mg, 8.00 mmol, 20 eq.) in 20 mL degassed CH_2Cl_2 was irradiated at $\lambda = 366$ nm for eight hours. Follow-up benzylation and purification according to *WP1* afforded a mixture of diastereoisomers *rac*-**11a** and *rac*-**11b** [70.9 mg, 216 µmol, 54%, d.r. (*rac*-**11a**:*rac*-**11b**) = 71:29] over two steps as colorless oil.

Enantioselective [2+2] photocycloaddition:

According to *GP3* a solution of carboxylic acid **9** (8.51 mg, 50.0 µmol, 1.0 eq.), photocatalyst **4** (4.60 mg, 5.00 µmol, 10 mol%) and cyclopentene (229 µL, 170 mg, 2.50 mmol, 50 eq.) in 5.0 mL degassed CH_2Cl_2 was irradiated at $\lambda = 437$ nm and −40 °C for four hours. Follow-up benzylation and purification according to *WP3* afforded a mixture of diastereoisomers of **11a** and **11b** [9.10 mg, 27.7 µmol, 55%, d.r. (**11a**:**11b**) = 68:32, e.r. (**11a**) = 93:7 (85% *ee*), e.r. (**11b**) = 55:45 (10% *ee*)] over two steps as colorless oil.

Analytical data for diastereoisomer **11a**:

TLC: $R_f = 0.61$ (P:Et_2O = 2:1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{25} = +58.2$ (c = 0.50, $CHCl_3$) (85% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.89 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.36-1.38 (m, 1 H, *H*H-7), 1.41-1.52 (m, 2 H, *H*H-5, H*H*-7), 1.66-1.83 (m, 3 H, H*H*-5, H-6), 2.23 (dd, $^2J = 15.6$ Hz, $^4J = 1.4$ Hz, 1 H, *H*H-3), 2.58 (d, $^2J = 15.6$ Hz, 1 H, H*H*-3), 2.77 (*virt*. t, $^3J \approx {}^3J = 8.2$ Hz, 1 H, H-7a), 2.90 (*virt*. q, $^3J \approx {}^3J \approx {}^3J = 6.7$ Hz, 1 H, H-4b), 3.10 (dd,

${}^3J$ = 6.7 Hz, ${}^4J$ = 1.4 Hz, 1 H, H-4a), 5.13 (d, ${}^2J$ = 12.0 Hz, 1 H, *H*H-1‘), 5.25 (d, ${}^2J$ = 12.0 Hz, 1 H, H*H*-1‘), 7.29 -7.37 (m, 3 H, H-Ph), 7.37-7.42 (m, 2 H, H-Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 25.1 (q, CH_3), 25.2 (t, C-6), 27.3 (t, C-7), 30.2 (q, CH_3), 32.1 (t, C-5), 40.6 (d, C-4b), 46.2 (d, C-4a), 48.8 (d, C-7a), 50.2 (t, C-3), 67.0 (t, C-1’), 76.6 (s, C-2), 78.7 (s, C-7b), 128.6 (d, 2 × C-Ph), 128.7 (d, C-Ph_{para}), 129.1 (d, 2 × C-Ph), 135.4 (s, C-Ph_{ipso}), 171.6 (s, COO), 208.0 (s, C-4).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2958 (s, sp^3–CH), 1702 (s, C=O), 1224 (s, C–O), 1187 (s), 1039 (m), 750 (s), 697 (s).

MS (EI, 70 eV): m/z (%) = 328 (1) $[M]^+$, 262 (21), 261 (92) $[C_{15}H_{17}O_4]^+$, 125 (10), 109 (23), 91 (100) $[C_7H_7]^+$, 83 (28), 81 (14), 69 (12), 68 (5) $[C_5H_8]^+$, 67 (11).

HRMS (ESI): calc. for $C_{20}H_{25}O_4^+$ $[M + H]^+$: 329.1748; found: 329.1747.

Chiral HPLC: t_{R1} = 21.2 min, t_{R2} = 23.1 min (*Daicel* Chiralpak AS-RH, 150×4.6 mm, 5 µm, MeCN:H_2O = 30:70⟶50:50, 40 °C, 30 min, 1 mL·min^{-1}).

Analytical data for diastereoisomer **11b**:

TLC: R_f = 0.63 (P:Et_2O = 2:1) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.99 (d, ${}^4J$ = 1.1 Hz, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.41-1.50 (m, 3 H, *H*H-5, *H*H-6, *H*H-7), 1.69-1.78 (m, 2 H, H*H*-5, H*H*-6), 2.13-2.19 (m, 1 H, H*H*-7), 2.23 (dd, ${}^2J$ = 18.2 Hz, ${}^4J$ = 1.9 Hz, 1 H, *H*H-3), 2.32-2.45 (m, 1 H, H*H*-3), 2.80 (*virt.* t, ${}^3J \approx {}^3J$ = 7.6 Hz, 1 H, H-7a), 3.13 (*virt.* dt, ${}^3J$ = 11.1 Hz, ${}^3J \approx {}^3J$ = 7.0 Hz, 1 H, H-4b), 3.67 (*virt.* dt, ${}^3J$ = 11.1 Hz, ${}^4J \approx {}^4J$ = 1.3 Hz, 1 H, H-4a), 5.19 (d, ${}^2J$ = 12.1 Hz, 1 H, *H*H-1‘), 5.28 (d, ${}^2J$ = 12.1 Hz, 1 H, H*H*-1‘), 7.30-7.38 (m, 3 H, H-Ph), 7.38-7.43 (m, 2 H, H-Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 26.1 (t, C-7), 26.3 (q, CH_3), 26.9 (t, C-6), 28.6 (t, C-5), 30.2 (q, CH_3), 39.8 (d, C-4b), 44.0 (d, C-4a), 47.3 (d, C-7a), 50.9 (t, C-3), 67.3 (t, C-1’), 74.7 (s, C-2*), 74.8 (s, C-7b*), 128.6 (d, C-Ph_{para}), 128.7 (d, 2 × C-Ph), 128.7 (d, 2 × C-Ph), 135.7 (s, C-Ph_{ipso}), 175.1 (s, COO), 208.5 (s, C-4).

* Assignment is interconvertible.

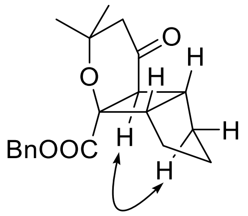
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2958 (s, sp^3–CH), 1734 (s, C=O), 1702 (s), 1371 (m), 1267 (s, C–O), 1114 (s), 1024 (m), 977 (s).

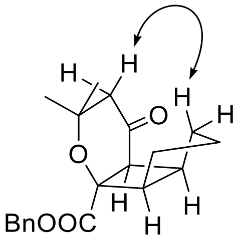
MS (EI, 70 eV): m/z (%) = 328 (1) $[M]^+$, 262 (17), 261 (84) $[C_{15}H_{17}O_4]^+$, 137 (13), 109 (25), 92 (10), 91 (100) $[C_7H_7]^+$, 83 (23), 81 (13), 69 (10), 68 (4) $[C_5H_8]^+$.

HRMS (ESI): calc. for $C_{20}H_{25}O_4^+$ $[M + H]^+$: 329.1748; found: 329.1747.

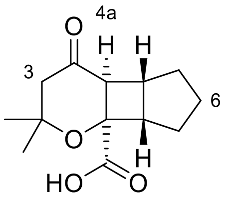
Chiral HPLC: t_{R1} = 22.2 min, t_{R2} = 32.7 min (*Daicel* Chiralpak AS-RH, 150×4.6 mm, 5 µm, MeCN:H_2O = 30:70⟶50:50, 40 °C, 30 min, 1 mL·min^{-1}).

Significant NOE contacts:

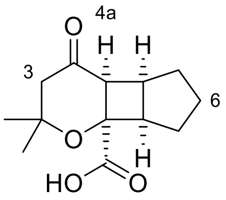




(4a*S*,4b*R*,7a*S*,7b*R*)-2,2-Dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylic acid (10a) and (4a*S*,4b*S*,7a*R*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-b]pyran-7b(2*H*)-carboxylic acid (10b)



10a



10b

$C_{13}H_{18}O_4$
MW = 238.28 g/mol

According to *GP3* a solution of carboxylic acid **9** (8.51 mg, 50.0 µmol, 1.0 eq.), photocatalyst **4** (4.60 mg, 5.00 µmol, 10 mol%) and cyclopentene (229 µL, 170 mg, 2.50 mmol, 50 eq.) in 5.0 mL degassed CH_2Cl_2 was irradiated at λ = 437 nm and −40 °C for four hours. Removal of volatile compounds and purification by flash column chromatography (SiO_2, CH_2Cl_2:MeOH = 60:1→30:1) afforded a mixture of diastereoisomers **10a** and **10b** [7.29 mg, 30.6 µmol, 61%, d.r. (**10a**:**10b**) = 69:31] as colorless solid. Diastereoisomers **10a** and **10b** could not be separated.

TLC: R_f = 0.40 (CH_2Cl_2:MeOH = 10:1) [$KMnO_4$].

HRMS (ESI): calc. for $C_{13}H_{19}O_4^+$ $[M+ H]^+$: 239.1278; found: 239.1284.

NMR data for diastereoisomer **10b**:

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.16 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.45-1.64 (m, 3 H, *H*H-5, *H*H-6, *H*H-7), 1.67-1.99 (m, 2 H, H*H*-5, H*H*-6), 2.06-2.19 (m, 1 H, H*H*-7), 2.28 (d,

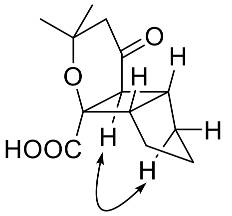
^2J = 18.2 Hz, 1 H, *H*H-3), 2.44 (d, ^2J = 18.2, 1 H, H*H*-3), 2.93[#] (m, 1 H, H-7a), 3.18 (*virt.* dt, ^3J = 11.0 Hz, $^3J \approx ^3J$ = 6.7 Hz, 1 H, H-4b), 3.67 (d, ^3J = 11.0 Hz, 1 H, H-4a), 7.39 (br. s, COOH).

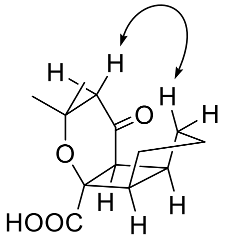
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 26.1 (t, C-7), 26.2 (q, CH_3), 26.9 (t, C-6), 28.6 (t, C-5), 30.1 (q, CH_3), 40.0 (d, C-4b), 43.6 (d, C-4a), 47.7 (d, C-7a), 50.8 (t, C-3), 74.5 (s, C-7b), 75.4 (s, C-2), 175.2 (s, COO), 208.2 (s, C-4).

[#] Signal overlapps with signal from diastereoisomer **10a**.

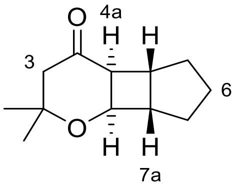
For detailed anayltical data of diastereoisomer **10a** see chapter 5.

Significant NOE contacts:





(4a*S*,4b*R*,7a*S*,7b*R*)-2,2-Dimethyloctahydrocyclopenta[3,4]cyclobuta[1,2-b]pyran-4(4a*H*)-one (S8)



S8

$C_{12}H_{18}O_2$

MW = 194.27 g/mol

A solution of carboxylic acid **9** (8.51, 50.0 µmol, 1.0 eq.), thioxanthen-9-one (1.06 mg, 5.00 µmol, 10 mol%) and cyclopentene (229 µL, 170 mg, 2.50 mmol, 50 eq.) in 5.0 mL degassed CH_2Cl_2 was irradiated at λ = 420 nm and −40 °C for four hours. Removal of volatile compounds and purification by flash column chromatography (SiO_2, CH_2Cl_2:MeOH = 10:1) afforded compound **S8** (2.15 mg, 11.1 µmol, 22%) as colorless oil.

TLC: R_f = 0.80 (CH_2Cl_2:MeOH = 5:1) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.20 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.48-1.58 (m, 2 H, *H*H-5, *H*H-7), 1.59-1.68 (m, 1 H, *H*H-6), 1.69-1.79 (m, 2 H, H*H*-5, H*H*-7), 1.80-1.91 (m, 1 H, H*H*-6), 2.31 (d, ^2J = 16.5 Hz, 1 H, *H*H-3), 2.38 (*virt.* t, $^3J \approx ^3J$ = 5.8 Hz, 1 H, H-4a), 2.50

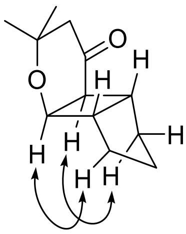
(d, ^2J = 16.5 Hz, 1 H, H*H*-3), 2.59 (ddd, ^3J = 8.5 Hz, ^3J = 7.4 Hz, ^3J = 1.6 Hz, 1 H, H-7a), 2.96 (*virt.* dt, ^3J = 7.4 Hz, $^3J \approx {}^3J$ = 6.0 Hz, 1 H, H-4b), 4.08 (dd, ^3J = 5.8 Hz, ^3J = 1.6 Hz, 1 H, H-7b).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 30.1 (q, CH_3), 25.5 (t, C-6), 25.2 (t, C-7), 30.5 (q, CH_3), 32.7 (t, C-5), 41.4 (d, C-4b), 45.0 (d, C-7a), 47.1 (d, C-4a), 51.4 (t, C-3), 73.8 (d, C-7b), 74.65 (s, C-2), 210.8 (s, C-4).

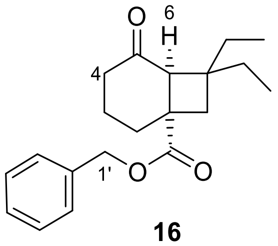
MS (ESI): m/z (%) = 253 (13) $[C_{14}H_{21}O_4]^+$, 127 (100) $[C_7H_{11}O_2]^+$, 111 (15) $[C_5H_9O_2]^+$, 95 (4) $[C_7H_{11}]^+$, 81 (33), 71 (60) $[C_5H_{11}]^+$, 67 (27).

HRMS (ESI): calc. for $C_{12}H_{19}O_2^+$ $[M + H]^+$: 195.1380; found: 195.1380.

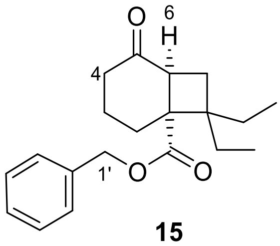
Significant NOE contacts:



Benzyl-(1*S*,6*S*)-7,7-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (16) and benzyl-(1*R*,6*S*)-8,8-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (15)



16



15

$C_{20}H_{26}O_3$
MW = 314.43 g/mol

Racemic [2+2] photocycloaddition:

According to *GP2* a solution of carboxylic acid **12** (28.0 mg, 200 µmol, 1.0 eq.), 9*H*-thioxanthen-9-one (21.2 mg, 100 µmol, 50 mol%) and 2-ethylbut-1-ene (489 µL, 337 mg, 4.00 mmol, 20 eq.) in 10 mL degassed CH_2Cl_2 was irradiated at λ = 420 nm for 15 hours. Follow-up benzylation and purification according to *WP2* afforded a mixture of regioisomers *rac*-**16** and *rac*-**15** [27.1 mg, 86.2 µmol, 43%, r.r. (*rac*-**16**:*rac*-**15**) = 65:35] as colorless oil.

Enantioselective [2+2] photocycloaddition:

According to *GP3* a solution of carboxylic acid **12** (7.01 mg, 50.0 µmol, 1.0 eq.), photocatalyst **4** (6.40 mg, 5.00 µmol, 10 mol%) and 2-ethylbut-1-ene (305 µL, 210 mg, 2.50 mmol, 50 eq.) in 5.0 mL degassed CH_2Cl_2 was irradiated at λ = 437 nm and −40 °C for 24 hours. Follow-up benzylation and purification according to *WP3* afforded a mixture of regioisomers **16** and **15** [4.27 mg, 13.6 µmol, 27%, r.r. (**16**:**15**) = 33:67, e.r. (**16**) = 89:11 (79% *ee*), e.r. (**15**) = 72:28 (44% *ee*)] as colorless oil.

Analytical data for regioisomer **16**:

TLC: R_f = 0.50 (P:Et_2O = 2:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.70 (*virt*.t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 0.82 (*virt*. t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.13 (dq, ^2J = 14.4 Hz, ^3J = 7.4 Hz, 1 H, C*H*HCH$_3$), 1.40 (dq, ^2J = 14.4 Hz, ^3J = 7.3 Hz, 1 H, C*H*HCH$_3$), 1.44-1.57 (m, 2 H, 2 × CH*H*CH$_3$), 1.80-1.94 (m, 3 H, *H*H-2, H-3), 1.97 (dd, ^2J = 12.6 Hz, ^4J = 1.1 Hz, 1 H, *H*H-8), 2.01 (dd, ^2J = 11.0 Hz, ^3J = 8.2 Hz, 1 H, H*H*-2), 2.17 (*virt.* dt, ^2J = 12.6 Hz, $^4J \approx {}^4J$ = 1.2 Hz, 1 H, H*H*-8), 2.19-2.35 (m, 2 H, H-4), 3.09 (*virt.* t, $^4J \approx {}^4J$ = 1.1 Hz, 1 H, H-6), 5.15 (d, ^2J = 12.3 Hz, 1 H, *H*H-1’), 5.18 (d, ^2J = 12.3 Hz, 1 H, H*H*-1’), 7.29-7.42 (m, 5 H, H-Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 7.2 (q, CH$_2$*C*H$_3$), 8.0 (q, CH$_2$*C*H$_3$), 19.9 (t, C-3), 26.7 (t, *C*H$_2$CH$_3$), 31.4 (t, *C*H$_2$CH$_3$), 32.0 (t, C-2), 39.9 (t, C-8), 40.6 (t, C-4), 42.0 (s, C-1), 42.5 (s, C-7), 54.3 (d, C-6), 66.9 (t, C-1’), 128.2 (d, 2 × C-Ph), 128.4 (d, C-Ph$_{para}$), 128.7 (d, 2 × C-Ph), 136.1 (s, C-Ph$_{ipso}$), 177.0 (s, COO), 210.8 (s, C-5).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2964 (m, sp^3–CH), 1720 (s, C=O), 1700 (s, C=O), 1456 (m, C=C), 1214 (s, C–O), 1150 (m), 1104 (m), 751 (s), 696 (s).

MS (EI, 70 eV): m/z (%) = 314 (1) $[M]^+$, 231 (31) $[C_{14}H_{15}O_3]^+$, 223 (20) $[M-C_7H_7]^+$, 179 (22) $[M-C_8H_7O_2]^+$, 177 (8), 149 (11), 92 (10), 91 (100) $[C_7H_7]^+$, 84 (9) $[C_6H_{12}]^+$, 69 (12), 55 (12).

HRMS (ESI): calc. for $C_{20}H_{27}O_3^+$ $[M + H]^+$: 315.1955; found: 315.1955.

Chiral HPLC: t_{R1} = 18.31 min, t_{R2} = 18.62 min (*Daicel* Chiralcel OJ-RH, 150×4.6 mm, 5 µm, MeCN:H_2O = 20:80⟶100:0, 5 °C, 30 min, 1 mL·min^{-1}).

Analytical data for regioisomer **15**:

TLC: R_f = 0.41 (P:Et_2O = 2:1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{25}$ **=** +53.3 (c = 0.60, *i*PrOH) (31% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.74 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 0.81 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 1.32-1.46 (m, 2 H, C*H*HCH$_3$), 1.49-1.62 (m, 3 H, CH*H*CH$_3$, *H*H-3), 1.67 (ddd, ^2J = 11.5 Hz, ^3J = 10.1 Hz, ^4J = 1.7 Hz, 1 H, *H*H-7), 1.90-1.95 (m, 1 H, H*H*-3), 1.95-2.00 (m, 1 H, *H*H-2), 2.03 (dd, ^2J = 11.5 Hz, ^3J = 10.4 Hz, 1 H, H*H*-7), 2.17-2.25 (m, 1 H, H*H*-2), 2.26-2.35 (m, 1 H, *H*H-4), 2.36-2.43 (m, 1 H, H*H*-4), 3.40 (*virt.* td, $^3J \approx {}^3J$ = 10.1 Hz, ^4J = 1.5 Hz, 1 H, H-6), 5.12 (d, ^2J = 12.3 Hz, 1 H, *H*H-1'), 5.19 (d, ^2J = 12.3 Hz, 1 H, H*H*-1'), 7.29-7.43 (m, 5 H, H-Ph).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.9 (q, CH_2CH_3), 8.9 (q, CH_2CH_3), 21.0 (t, C-3), 24.5 (t, CH_2CH_3), 25.6 (t, CH_2CH_3), 26.6 (t, C-2), 32.2 (t, C-7), 38.4 (t, C-4), 42.0 (d, C-6), 46.8 (s, C-8), 55.9 (s, C-1), 66.8 (t, C-1'), 128.4 (d, 2 × C-Ph), 128.4 (d, C-Ph$_{para}$), 128.7 (d, 2 × C-Ph), 135.9 (s, C-Ph$_{ipso}$), 174.4 (s, COO), 213.7 (s, C-5).

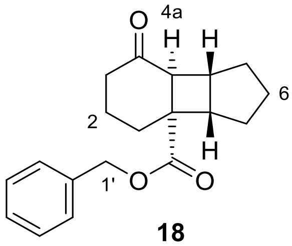
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2964 (m, sp^3–CH), 1720 (s, C=O), 1700 (s, C=O), 1456 (m, C=C), 1214 (s, C–O), 1150 (m), 1104 (m), 751 (s), 696 (s).

MS (EI, 70 eV): m/z (%) = 314 (1) $[M]^+$, 232 (8), 231 (47) $[C_{14}H_{15}O_3]^+$, 223 (2) $[M\text{-}C_7H_7]^+$, 179 (5) $[M\text{-}C_8H_7O_2]^+$, 97 (7), 92 (9), 91 (100) $[C_7H_7]^+$, 84 (10) $[C_6H_{12}]^+$, 69 (13), 55 (10).

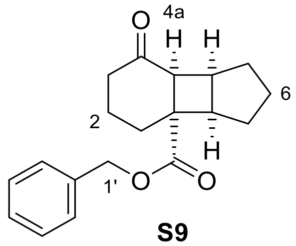
HRMS (ESI): calc. for $C_{20}H_{27}O_3^+$ $[M + H]^+$: 315.1955; found: 315.1954.

Chiral HPLC: t_{R1} = 17.6 min, t_{R2} = 17.9 min (*Daicel* Chiralcel OJ-RH, 150×4.6 mm, 5 µm, MeCN:H_2O = 20:80⟶100:0, 5 °C, 30 min, 1 mL·min^{-1}).

Benzyl-(3a*S*,3b*S*,7a*S*,7b*R*)-7-oxodecahydro-3b*H*-cyclopenta[3,4]cyclobuta[1,2]benzene-3b-carboxylate (18) and benzyl-(3a*R*,3b*S*,7a*S*,7b*S*)-7-oxodecahydro-3b*H*-cyclopenta-[3,4]cyclobuta[1,2]benzene-3b-carboxylate (S9)



18



S9

$C_{20}H_{24}O_4$
MW = 298.38 g/mol

<u>Racemic [2+2] photocycloaddition:</u>

According to *GP2* a solution of carboxylic acid **12** (28.0 mg, 200 µmol, 1.0 eq.), 9*H*-thioxanthen-9-one (21.2 mg, 100 µmol, 50 mol%) and cyclopentene (366 µL, 272 mg, 4.00 mmol, 20 eq.) in 10 mL degassed CH_2Cl_2 was irradiated at $\lambda = 420$ nm for 15 hours. Follow-up benzylation and purification according to *WP2* afforded mixture of diastereoisomers *rac*-**18** and *rac*-**S8** [36.9 mg, 124 µmol, 62%, d.r. (*rac*-**18**:*rac*-**S9**) = 84:16] as colorless oil.

<u>Enantioselective [2+2] photocycloaddition:</u>

According to *GP3* a solution of carboxylic acid **12** (7.01 mg, 50.0 µmol, 1.0 eq.), photocatalyst **4** (6.40 mg, 5.00 µmol, 10 mol%) and cyclopentene (229 µL, 170 mg, 2.50 mmol, 50 eq.) in 5.0 mL degassed CH_2Cl_2 was irradiated at $\lambda = 437$ nm and −40 °C for 24 hours. Follow-up benzylation and purification according to *WP3* afforded a mixture of diastereoisomers **18** and **S9** [6.23 mg, 20.9 µmol, 42%, d.r. (**18**:**S9**) = 59:41, e.r. (**18**) = 86:14 (73% *ee*), e.r. (**S9**) = 69:31 (38% *ee*)] as colorless oil.

Analytical data for diastereoisomer **18**:

TLC: $R_f = 0.34$ (P:Et_2O = 2:1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{25} = +32.3$ (c = 1.55, $CHCl_3$) (49% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.40-1.52 (m, 2 H, *H*H-5, *H*H-7), 1.58-1.83 (m, 5 H, *H*H-2, H*H*-5, H-6, H*H*-7), 1.87-1.98 (m, 1 H, *H*H-1), 1.99-2.11 (m, 2 H, H*H*-1, H*H*-2), 2.26 (*virt*. dt, $^2J = 18.4$ Hz, $^3J \approx {}^3J = 6.1$ Hz, 1 H, *H*H-3), 2.44 (*virt*. dt, $^2J = 18.4$ Hz, $^3J \approx {}^3J = 7.0$ Hz, 1 H, H*H*-3), 2.62 (dd, $^3J = 8.5$ Hz, $^3J = 7.1$ Hz, 1 H, H-7a), 2.73 (*virt.* q, $^3J \approx {}^3J \approx {}^3J = 6.7$ Hz, 1 H, H-4b), 3.01 (d, ^3J = 6.4 Hz, 1 H, H-4a), 5.11 (d, ^2J = 12.2 Hz, 1 H, *H*H-1'), 5.20 (d, ^2J = 12.2 Hz, 1 H, H*H*-1'), 7.29-7.43 (m, 5 H, H-Ph).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 19.8 (t, C-2), 25.4 (t, C-6), 29.2 (t, C-7), 32.6 (t, C-5*), 32.7 (t, C-1*), 38.3 (t, C-3), 40.0 (d, C-4b), 47.1 (d, C-7a), 48.5 (s, C-7b), 49.2 (d, C-4a), 66.6 (t, C-1'), 128.5 (d, C-Ph_{para})$^\#$, 128.5 (d, 2 × C-Ph)$^\#$, 128.7 (d, 2 × C-Ph), 135.9 (s, C-Ph_{ipso}), 174.2 (s, COO), 212.5 (s, C-4).

* Assignment is interconvertible. $^\#$ Overlapping signals.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2947 (m, sp^3–CH), 1720 (s, C=O), 1698 (s, C=O), 1454 (m, C=C), 1225 (s, C–O), 1174 (s), 1059 (s), 735 (s), 696 (s).

MS (EI, 70 eV): m/z (%) = 231 (37) $[M\text{-}C_5H_8]^+$, 207 (4) $[M\text{-}C_7H_7]^+$, 192 (10), 141 (7), 107 (8), 97 (9), 91 (100) $[C_7H_7]^+$, 79 (7), 68 (8) $[C_5H_8]^+$, 67 (18).

HRMS (ESI): calc. for $C_{20}H_{25}O_4^+$ $[M + H]^+$: 299.1642; found: 299.1646.

Chiral HPLC: t_{R1} = 16.5 min, t_{R2} = 17.2 min (*Daicel* Chiralcel OJ-RH, 150×4.6 mm, 5 µm, MeCN:H_2O = 20:80⟶100:0, 20 °C, 30 min, 1 mL·min^{-1}).

Analytical data for diastereoisomer **S9**:

TLC: R_f = 0.45 (P:Et_2O = 2:1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{25}$ **= +63.1** (c = 1.30, $CHCl_3$) (27% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.24-1.42 (m, 2 H, *H*H-6, *H*H-7), 1.45-1.54 (m, 1 H, H*H*-7), 1.55-1.68 (m, 1 H, *H*H-2), 1.70-1.89 (m, 4 H, *H*H-1, H*H*-2, *H*H-5, H*H*-6), 1.90-2.02 (m, 2 H, H*H*-1, H*H*-5), 2.19 (ddd, ^2J = 19.0 Hz, ^3J = 11.6 Hz, ^3J = 6.3 Hz, 1 H, *H*H-3), 2.30-2.39 (m, 1 H, H*H*-3), 2.93 (dd, ^3J = 9.1 Hz, ^3J = 7.2 Hz, 1 H, H-7a), 3.12-3.23 (m, 1 H, H-4b), 3.54 (d, ^3J = 11.1 Hz, 1 H, H-4a), 5.19 (d, ^2J = 12.3 Hz, 1 H, *H*H-1'), 5.22 (d, ^2J = 12.3 Hz, 1 H, H*H*-1'), 7.31-7.40 (m, 5 H, H-Ph).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 19.7 (t, C-2), 24.3 (t, CH_2), 26.8 (t, C-6), 27.8 (t, CH_2), 27.9 (t, CH_2), 39.6 (t, C-3), 40.7 (d, C-4b), 44.9 (d, C-7a), 45.7 (d, C-4a), 48.2 (s, C-7b), 67.1 (t, C-1'), 128.1 (d, 2 × C-Ph), 128.4 (d, C-Ph_{para}), 128.8 (d, 2 × C-Ph), 136.1 (s, C-Ph_{ispo}), 177.4 (s, COO), 212.3 (s, C-4).

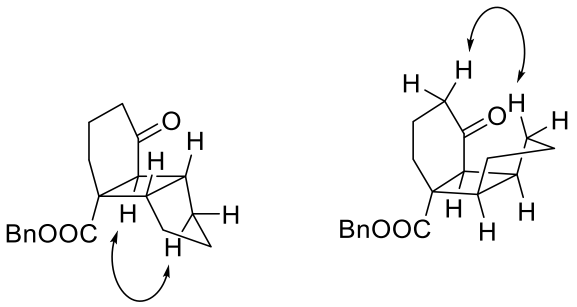
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2947 (m, sp^3–CH), 1720 (s, C=O), 1698 (s, C=O), 1454 (m, C=C), 1225 (s, C–O), 1174 (s), 1059 (s), 735 (s), 696 (s).

MS (EI, 70 eV): m/z (%) = 232 (17), 231 (100) [M-C_5H_8]$^+$, 207 (14) [M-C_7H_7]$^+$, 141 (8), 97 (12), 92 (12), 91 (91) [C_7H_7]$^+$, 79 (8), 68 (7) [C_5H_8]$^+$, 67 (18), 65 (9).

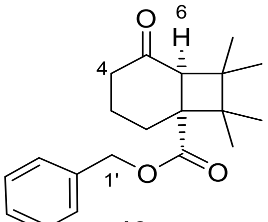
HRMS (ESI): calc. for $C_{20}H_{25}O_4^+$ [M + H]$^+$: 299.1642; found: 299.1641.

Chiral HPLC: t_{R1} = 18.9 min, t_{R2} = 19.3 min (*Daicel* Chiralcel OJ-RH, 150×4.6 mm, 5 µm, MeCN:H_2O = 20:80⟶100:0, 20 °C, 30 min, 1 mL·min^{-1}).

Significant NOE contacts:



Benzyl-(1*R*,6*S*)-7,7,8,8-tetramethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (19)



19

$C_{20}H_{26}O_3$

MW = 314.43 g/mol

Racemic [2+2] photocycloaddition:

According to *GP2* a solution of carboxylic acid **12** (28.0 mg, 200 µmol, 1.0 eq.), 9*H*-thioxanthen-9-one (21.2 mg, 100 µmol, 50 mol%) and 2,3-dimethylbut-2-ene (474 µL, 337 mg, 4.00 mmol, 20 eq.) in 10 mL degassed CH_2Cl_2 was irradiated at λ = 420 nm for 15 hours. Follow-up benzylation and purification according to *WP2* afforded *rac*-**19** (17.2 mg, 54.7 µmol, 27%) as colorless oil.

Enantioselective [2+2] photocycloaddition:

According to *GP3* a solution of carboxylic acid **12** (7.01 mg, 50.0 µmol, 1.0 eq.), photocatalyst **4** (6.40 mg, 5.00 µmol, 10 mol%) and 2,3-dimethylbut-2-ene (296 µL, 210 mg, 2.50 mmol, 50 eq.) in 5.0 mL degassed CH_2Cl_2 was irradiated at λ = 437 nm and −40 °C for 24 hours.

Follow-up benzylation and purification according to *WP3* afforded **19** [5.10 mg, 16.2 µmol, 32%, e.r. = 89:11 (77% *ee*)] as colorless oil.

TLC: R_f = 0.38 (P:Et_2O = 2:1) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.00 (s, 3 H, C-7-CH_3), 1.04 (s, 3 H, C-8-CH_3), 1.05 (s, 3 H, C-8-CH_3), 1.08 (s, 3 H, C-7-CH_3), 1.36-1.48 (m, 1 H, *H*H-3), 1.82-1.92 (m, 1 H, H*H*-3), 2.04-2.15 (m, 2 H, *H*H-2, *H*H-4), 2.29 (*virt.* ddq, ^2J = 14.2 Hz, ^3J = 3.9 Hz, $^3J \approx {}^4J \approx {}^4J$ = 2.0 Hz, 1 H, H*H*-2), 2.39-2.48 (m, 1 H, H*H*-4), 3.27 (*virt.* q, $^4J \approx {}^4J \approx {}^4J$ = 1.4 Hz, 1 H, H-6), 5.11 (d, ^2J = 12.4 Hz, 1 H, *H*H-1'), 5.18 (d, ^2J = 12.4 Hz, 1 H, H*H*-1'), 7.28-7.41 (m, 5 H, H-Ph).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 19.1 (q, C-8-*C*H_3), 20.3 (t, C-3), 23.2 (q, C-7-*C*H_3), 23.3 (q, C-7-*C*H_3), 26.8 (q, C-8-*C*H_3), 27.9 (t, C-2), 40.5 (t, C-4), 42.6 (s), 43.7 (s), 52.5 (d, C-6), 53.0 (s), 66.6 (t, C-1'), 128.3 (d, 2 × C-Ph), 128.4 (d, C-Ph_{para}), 128.7 (d, 2 × C-Ph), 36.1 (s, C-Ph_{ipso}), 175.0 (s, COO), 211.7 (s, C-5).

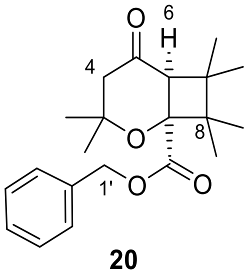
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955 (m, sp^3–CH), 2872 (w), 1720 (s, C=O), 1694 (s, C=O), 1456 (m, C=C), 1226 (s, C–O), 1167 (m), 1129 (m), 736 (m), 697 (s).

MS (EI, 70 eV): m/z (%) = 314 (1) $[M]^+$, 223 (4) $[M-C_7H_7]^+$, 205 (9), 178 (14), 91 (66) $[C_7H_7]^+$, 84 (100) $[C_6H_{12}]^+$, 83 (30), 69 (23), 65 (8), 55 (9).

HRMS (ESI): calc. for $C_{20}H_{27}O_3^+$ $[M + H]^+$: 315.1955; found: 315.1954.

Chiral HPLC: t_{R1} = 9.1 min, t_{R2} = 11.0 min (*Daicel* Chiralpak AD-H, 250×4.6 mm, 5 µm, Propan-2-ol:*n*-Heptan = 10:90, 5 °C, 30 min, 1 mL·min^{-1}).

Benzyl-(1*S*,6*S*)-3,3,7,7,8,8-hexamethyl-5-oxo-2-oxabicyclo[4.2.0]octane-1-carboxylate (20)



20

$C_{21}H_{28}O_4$

MW = 344.45 g/mol

Racemic [2+2] photocycloaddition:

According to *GP1* a solution of carboxylic acid **9** (68.1 mg, 400 µmol, 1.0 eq.) and 2,3-dimethylbut-2-ene (951 µL, 673 mg, 8.00 mmol, 20 eq.) in 20 mL degassed CH_2Cl_2 was irradiated at λ = 366 nm for eight hours. Follow-up benzylation and purification according to *WP1* afforded *rac*-**20** (44.1 mg, 128 µmol, 32%) over two steps as colorless oil.

Enantioselective [2+2] photocycloaddition:

According to *GP3* a solution of carboxylic acid **9** (8.51 mg, 50.0 µmol, 1.0 eq.), photocatalyst **4** (4.60 mg, 5.00 µmol, 10 mol%) and 2,3-dimethylbut-2-ene (297 µL, 210 mg, 2.50 mmol, 50 eq.) in 5.0 mL degassed CH_2Cl_2 was irradiated at λ = 437 nm and −40 °C for four hours. Follow-up benzylation and purification according to *WP3* afforded **20** [5.58 mg, 16.2 µmol, 32%, e.r. = 73:27 (46% *ee*)] over two steps as colorless oil.

TLC: R_f = 0.62 (P:Et_2O = 2:1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{25}$ = +11.3 (c = 1.77, CH_2Cl_2) (34% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.90 (s, 3 H, C-8-CH_3), 0.97 (s, 3 H, C-3-CH_3), 1.06 (s, 3 H, C-7-CH_3), 1.06 (s, 3 H, C-8-CH_3), 1.10 (s, 3 H, C-7-CH_3), 1.36 (s, 3 H, C-3-CH_3), 2.27 (dd, ^2J = 17.0 Hz, ^4J = 0.9 Hz, 1 H, *H*H-4), 2.32 (d, ^2J = 17.0 Hz, 1 H, H*H*-4), 3.31 (d, ^4J = 0.9 Hz, 1 H, H-6), 5.14 (d, ^2J = 12.1 Hz, 1 H, *H*H-1'), 5.20 (d, ^2J = 12.1 Hz, 1 H, H*H*-1'), 7.31-7.38 (m, 3 H, H-Ph), 7.38-7.42 (m, 2 H, H-Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 17.4 (q, C-8-*C*H_3), 21.4 (q, C-8-*C*H_3), 22.9 (q, C-7-*C*H_3), 25.7 (q, C-7-*C*H_3), 26.4 (q, C-3-*C*H_3), 30.7 (q, C-3-*C*H_3), 41.7 (s, C-7), 45.3 (s, C-8), 50.7 (d, C-6), 51.6 (t, C-4), 66.9 (t, C-1'), 76.1 (s, C-3), 80.2 (s, C-1), 128.6 (d, C-Ph_{para}), 128.7 (d, 2 × C-Ph), 129.1 (d, 2 × C-Ph), 135.5 (s, C-Ph_{ipso}), 172.7 (s, COO), 207.3 (s, C-5).

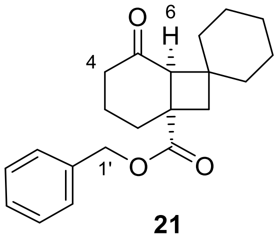
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2971 (m, sp^3–CH), 1700 (s, C=O), 1371 (m), 1266 (s, C–O), 1130 (s), 1025 (s), 751 (m), 697 (s).

MS (EI, 70 eV): m/z (%) = 344 (1) $[M]^+$, 262 (21), 261 (100) $[C_{15}H_{17}O_4]^+$, 125 (12), 109 (12), 91 (82) $[C_7H_7]^+$, 85 (9), 84 (93) $[C_6H_{12}]^+$, 83 (52), 69 (49), 55 (14).

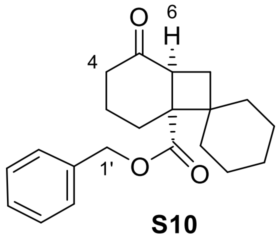
HRMS (ESI): calc. for $C_{21}H_{29}O_4^+$ $[M + H]^+$: 345.2061; found: 345.2060.

Chiral HPLC: t_{R1} = 16.3 min, t_{R2} = 23.9 min (*Daicel* Chiralpak AS-RH, 150×4.6 mm, 5 µm, MeCN:H_2O = 20:80⟶100:0, 20 °C, 30 min, 1 mL·min^{-1}).

Benzyl-(1*S*,6*S*)-5-oxospiro[bicyclo[4.2.0]octane-7,1'-cyclohexane]-1-carboxylate (21) and benzyl-(1*S*,6*R*)-2-oxospiro[bicyclo[4.2.0]octane-7,1'-cyclohexane]-6-carboxylate (S10)



21



S10

$C_{21}H_{26}O_3$
MW = 326.44 g/mol

<u>Racemic [2+2] photocycloaddition:</u>

According to *GP2* a solution of carboxylic acid **12** (28.0 mg, 200 µmol, 1.0 eq.), 9*H*-thioxanthen-9-one (21.2 mg, 100 µmol, 50 mol%) and methylidenecyclohexane (481 µL, 385 mg, 4.00 mmol, 20 eq.) in 10 mL degassed CH_2Cl_2 was irradiated at λ = 420 nm for 15 hours. Follow-up benzylation and purification according to *WP2* afforded a mixture of regioisomers *rac*-**21** and *rac*-**S10** [43.2 mg, 132 µmol, 66%, r.r. (*rac*-**21**:*rac*-**S10**) = 61:39] as colorless oil.

<u>Enantioselective [2+2] photocycloaddition:</u>

According to *GP3* a solution of carboxylic acid **12** (7.01 mg, 50.0 µmol, 1.0 eq.), photocatalyst **4** (6.40 mg, 5.00 µmol, 10 mol%) and methylidenecyclohexane (301 µL, 240 mg, 2.50 mmol, 50 eq.) in 5.0 mL degassed CH_2Cl_2 was irradiated at λ = 437 nm and −40 °C for 24 hours. Follow-up benzylation and purification according to *WP3* afforded a mixture of regioisomers **21** and **S10** [4.31 mg, 13.2 µmol, 26%, r.r. (**21**:**S10**) = 54:46, e.r. (**21**) = 73:27 (45% *ee*), e.r. (**S10**) = 58:42 (17% *ee*)] as colorless oil.

Analytical data for regioisomer **21**:

TLC: R_f = 0.35 (P:Et_2O = 2:1) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.09-1.25 (m, 3 H, CH_2), 1.32-1.42 (m, 2 H, CH_2), 1.45-1.52 (m, 4 H, CH_2), 1.58-1.64 (m, 1 H, CH_2), 1.81-1.97 (m, 3 H, *H*H-3, CH_2), 1.96 (d, ^2J = 12.5 Hz, 1 H, *H*H-8), 2.01-2.08 (m, 1 H, H*H*-3), 2.22-2.32 (m, 2 H, CH_2), 2.31 (d, ^2J = 12.5 Hz, 1 H, H*H*-8), 3.00 (s, 1 H, H-6), 5.15 (d, ^2J = 12.6 Hz, 1 H, *H*H-1’), 5.18 (d, ^2J = 12.6 Hz, 1 H, H*H*-1’), 7.28-7.47 (m, 5 H, H-Ph).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 19.9 (t, CH_2), 22.0 (t, CH_2), 22.7 (t, CH_2), 25.5 (t, CH_2), 31.7 (t, C-2), 34.7 (t, CH_2), 39.6 (s, C-7), 39.7 (t, C-8), 40.4 (t, CH_2), 40.7 (t, CH_2), 42.2 (s, C-1), 56.3 (d, C-6), 66.9 (t, C-1’), 128.1 (d, 2 × C-Ph), 128.4 (d, C-Ph_{para}), 128.7 (d, 2 × C-Ph), 136.1 (s, C-Ph_{ipso}), 176.9 (s, COO), 211.2 (s, C-5).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2928 (m, sp^3–CH), 2853 (w), 1728 (s, C=O), 1697 (m, C=O), 1450 (w, C=C), 1220 (m, C–O), 1142 (w), 698 (m).

MS (EI, 70 eV): m/z (%) = 326 (2) $[M]^+$, 282 (11), 235 (3) $[M-C_7H_7]^+$, 231 (41) $[C_{14}H_{15}O_3]^+$, 173 (14), 96 (8) $[C_7H_{12}]^+$, 92 (12), 91 (100) $[C_7H_7]^+$, 81 (23), 79 (10), 67 (12).

HRMS (ESI): calc. for $C_{21}H_{27}O_3^+$ $[M + H]^+$: 327.1955; found: 327.1955.

Chiral HPLC: t_{R1} = 5.5 min, t_{R2} = 12.3 min (*Daicel* Chiralpak AS-H, 250×4.6 mm, 5 µm, Propan-2-ol:*n*-Heptan = 30:70, 20 °C, 30 min, 1 mL·min^{-1}).

Analytical data for regioisomer **S10**:

TLC: R_f = 0.29 (P:Et_2O = 2:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.03-1.19 (m, 2 H, CH_2), 1.19-1.31 (m, 2 H, CH_2), 1.33-1.40 (m, 1 H, CH_2), 1.46-1.64 (m, 5 H, CH_2), 1.67-1.75 (m, 1 H, CH_2), 1.85 (ddd, ^2J = 12.7 Hz, ^3J = 9.7 Hz, ^4J = 1.5 Hz, 1 H, *H*H-7), 1.90-2.00 (m, 2 H, CH_2), 2.07-2.16 (m, 2 H, H*H*-7, CH_2), 2.24-2.44 (m, 2 H, CH_2), 3.39-3.45 (m, 1 H, H-6), 5.12 (d, ^2J = 12.4 Hz, 1 H, *H*H-1’), 5.21 (d, ^2J = 12.4 Hz, 1 H, H*H*-1’), 7.30-7.38 (m, 5 H, H-Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 21.1 (t, CH_2), 22.4 (t, CH_2), 22.5 (t, CH_2), 26.0 (t, CH_2), 26.0 (t, CH_2), 32.1 (t, C-7), 32.5 (t, CH_2), 32.9 (t, CH_2), 38.6 (t, CH_2), 42.1 (d, C-6), 44.0 (s, C-8), 55.6 (s, C-1), 66.5 (t, C-1’), 128.3 (d, 2 × C-Ph), 128.4 (d, C-Ph_{para}), 128.7 (d, 2 × C-Ph), 136.0 (s, C-Ph_{ipso}), 174.2 (s, COO), 213.5 (s, C-5).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2928 (m, sp^3–CH), 2852 (m), 1722 (s, C=O), 1697 (s, C=O), 1451 (m, C=C), 1218 (s, C–O), 1149 (m), 737 (m), 697 (s).

MS (EI, 70 eV): m/z (%) = 326 (1) [M]$^+$, 235 (27) [M-C_7H_7]$^+$, 231 (39) [$C_{14}H_{15}O_3$]$^+$, 191 (25), 161 (10), 96 (10) [C_7H_{12}]$^+$, 95 (16), 92 (12), 91 (100) [C_7H_7]$^+$, 81 (23), 79 (12), 67 (14).

HRMS (ESI): calc. for $C_{21}H_{27}O_3^+$ [M + H]$^+$: 327.1955; found: 327.1956.

Chiral HPLC: t_{R1} = 8.59 min, t_{R2} = 14.48 min (*Daicel* Chiralpak AS-H, 250×4.6 mm, 5 µm, Propan-2-ol:*n*-Heptan = 30:70, 20 °C, 30 min, 1 mL·min^{-1}).

4. Screening Experiments

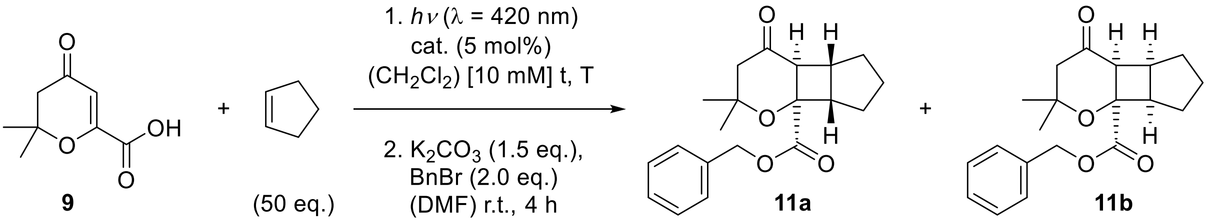


Table S1. Catalyst and reaction temperature screening.

Entry[a]	Cat.	T (°C)	t (h)	Yield (%)[b]	d.r. (**11a**:**11b**)[c]	*ee* (%, **11a**)[d]
1	**S5**	22	1	50	81:19	0
2	**4**	22	1	44	80:20	54
3	**4**	0	2	63	74:26	59
4	**4**	–20	3	55	77:23	64
5	**4**	–40	4	56	74:26	66
6	**4**	–60	4	49	83:17	65
7[e][f]	**4**	–40	4	56	74:26	72

[a] Unless otherwise noted, [2+2] photocycloaddition reactions were carried out with **9** (50.0 µmol), cyclopentene (2.50 mmol), **4** (5.00 µmol) in CH_2Cl_2 (5.0 mL). The benzylation reactions were carried out with benzyl bromide (100 µmol), K_2CO_3 (75.0 µmol) in DMF (2 mL) at room temperature for 4 h. [b] Isolated yields. [c] Determined by GC before purification. [d] Determined by chiral HPLC. [e] Reaction performed on 25.0 µmol scale. [f] Irradiation at λ = 437 nm LED.

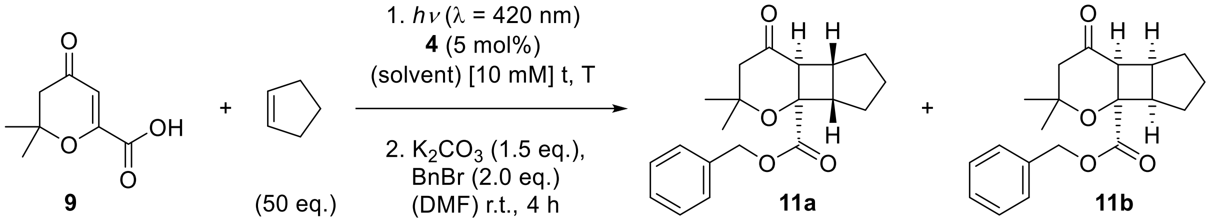


Table S2. Solvent screening.

Entry[a]	Solvent	T (°C)	t (h)	Yield (%)[b]	d.r. (**11a**:**11b**)[c]	*ee* (%, **11a**)[d]
1	CH_2Cl_2	–40	4	56	74:26	66
2	$PhCF_3$[e]	–20	10	38	84:16	42
3[f]	Et_2O	–40	--	--	--	--
4[f]	MeCN	–40	--	--	--	--

[a] Unless otherwise noted, [2+2] photocycloaddition reactions were carried out with **9** (50.0 µmol), cyclopentene (2.50 mmol), **4** (2.50 µmol) in CH_2Cl_2 (5.0 mL). The benzylation reactions were carried out with benzyl bromide (100 µmol), K_2CO_3 (75.0 µmol) in DMF (2 mL) at room temperature for 4 h. [b] Isolated yields. [c] Determined by GC before purification. [d] Determined by chiral HPLC. [e] The reaction was conducted at –20 °C as the melting point of trifluorotoluene is –29 °C. [f] Catalyst **4** can neither be dissolved in Et_2O nor MeCN very well.

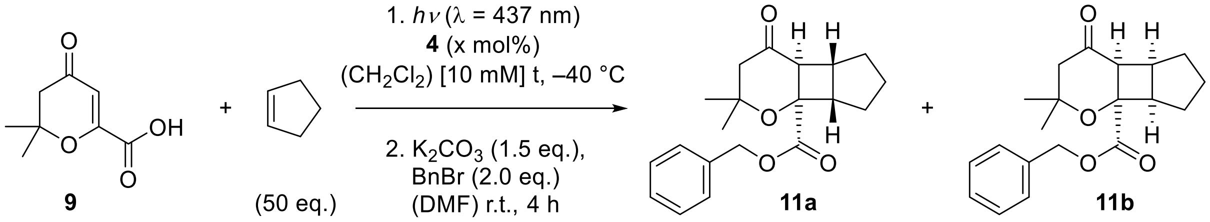


Table S3. Screening of catalyst loading.

Entry[a]	**4** (mol%)	t (h)	Yield (%)[b]	d.r. (**11a**:**11b**)[c]	*ee* (%, **11a**)[d]
1	5	4	56	74:26	72
2	10	4	55	75:25	85
3	20	2	60	73:27	86

[a] Unless otherwise noted, [2+2] photocycloaddition reactions were carried out with **9** (50.0 µmol) and cyclopentene (2.50 mmol) in CH_2Cl_2 (5.0 mL). The benzylation reactions were carried out with benzyl bromide (100 µmol), K_2CO_3 (75.0 µmol) in DMF (2 mL) at room temperature for 4 h. [b] Isolated yields. [c] Determined by GC before purification. [d] Determined by chiral HPLC.

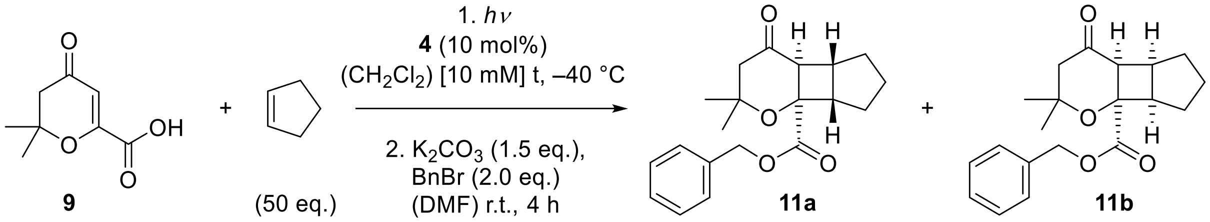


Table S4. Screening of irradiation wavelength.

Entry[a]	λ (nm)	t (h)	Yield (%)[b]	d.r. (**11a**:**11b**)[c]	*ee* (%, **11a**)[d]
1	405	1	41	74:26	51
2	415	1.5	40	77:23	69
3	420	4	56	74:26	66
4	425	2	29	79:21	72
5	437	4	55	75:25	85

[a] Unless otherwise noted, [2+2] photocycloaddition reactions were carried out with **9** (50.0 µmol), cyclopentene (2.50 mmol), **4** (5.00 µmol) in CH_2Cl_2 (5.0 mL). The benzylation reactions were carried out with benzyl bromide (100 µmol), K_2CO_3 (75.0 µmol) in DMF (2 mL) at room temperature for 4 h. [b] Isolated yields. [c] Determined by GC before purification. [d] Determined by chiral HPLC.

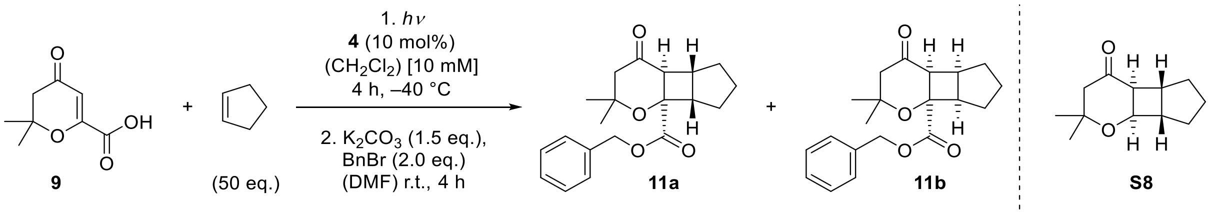


Table S5. Comparison of catalyst **4** and 9*H*-thioxanthen-9-one as sensitizers.

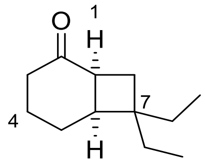
Entry[a]	Cat.	λ (nm)	**S8**:**10**[b]	Yield (%)[c]	d.r. (**11a**:**11b**)[d]
1	**4**	437	13:87	55	75:25
2	9*H*-thioxanthen-9-one	420	31:69	44	73:27

[a] Unless otherwise noted, [2+2] photocycloaddition reactions were carried out with **9** (50.0 µmol), cyclopentene (2.50 mmol), photocatalyst (5.00 µmol) in CH_2Cl_2 (5.0 mL). The benzylation reactions were carried out with benzyl bromide (100 µmol), K_2CO_3 (75.0 µmol) in DMF (2 mL) at room temperature for 4 h.[b] Determined from crude NMR by integration of product signals. [c] Isolated yields. [d] Determined by GC before purification.

5. Determination of Absolute Configuration

Determination via Decarboxylation

(1*S*,6*S*)-7,7-Diethylbicyclo[4.2.0]octan-2-one (17)



17
$C_{12}H_{20}O$
MW = 180.29 g/mol

A solution of acid **13** (31.5 mg, 140 µmol, 1.0 eq., 30% *ee*[1]), Mes-Acr-Ph (6.48 mg, 14.0 µmol, 10 mol%), diphenyl disulfide (3.07 mg, 14.0 µmol, 10 mol%) and *N*,*N*-diisopropylethylamine (4.89 µL, 3.63 mg, 28.1 µmol, 20 mol%) in degassed trifluoroethanol (2 mL) was irradiated at λ = 450 nm and room temperature for 72 hours. The reaction mixture was diluted with CH_2Cl_2 (2 mL) and washed with 1 M sodium hydroxide solution (2 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL), the combined organic layers were washed with brine (2 mL) and dried over sodium sulfate. After filtration and solvent removal in vacuo the crude product was purified by flash column chromatography (SiO_2, P:Et_2O = 7:1) and **17** was obtained as colorless oil [10.4 mg, 57.9 µmol, 41%, e.r. = 64:36 (28% *ee*)].

TLC: R_f = 0.64 (P:Et_2O = 1:1) [KMnO4].

Specific Rotation: $[\alpha]_D^{25}$ = +42.0 (c = 1.00, CH_2Cl_2) (28% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.71 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 0.77 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.32 (dq, ^2J = 14.5 Hz, ^3J = 7.4 Hz, 1 H, C*H*HCH3), 1.37-1.57 (m, 3 H, CH*H*CH3, C*H*2CH3), 1.59-1.65 (m, 1 H, *H*H-5), 1.69-1.80 (m, 2 H, *H*H-4, H*H*-5), 1.90-2.05 (m, 3 H, H*H*-4, H-8), 2.25-2.37 (m, 2 H, H-3), 2.47 (*virt*. tdd, $^3J \approx {}^3J$ = 9.4 Hz, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 1 H, H-6), 2.91 (*virt*. td, $^3J \approx {}^3J$ = 9.5 Hz, ^3J = 8.0 Hz, 1 H, H-1).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 8.0 (q, CH_2CH_3), 8.3 (q, CH_2CH_3), 22.9 (t, C-4), 23.0 (t, C-5), 24.9 (t, *C*H2CH3), 30.2 (t, *C*H2CH3), 34.6 (t, C-8), 39.5 (t, C-3), 39.6 (d, C-1), 42.8 (s, C-7), 43.8 (d, C-6), 216.5 (s, CO).

Chiral GC: t_{R1} = 106.7 min, t_{R2} = 108.8 min, [60 °C (1 min), 105 °C (30 °C/min), 105 °C (127.5 min), 135 °C (3 °C/min), 200 °C (20 °C/min), 200 °C (3 min)], Cyclosil-B.

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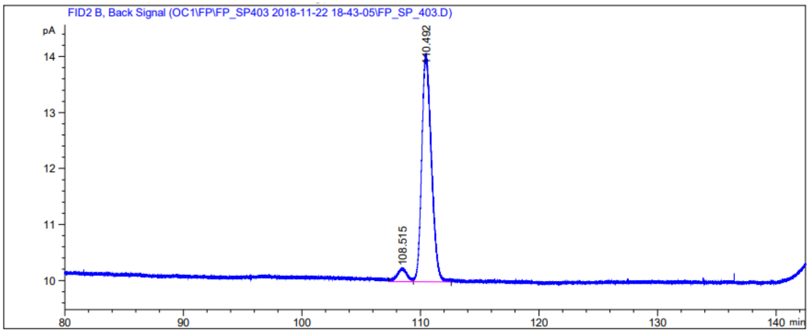
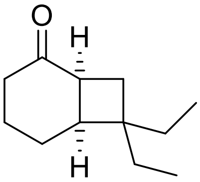
[1] The enantiomeric excess was determined by chiral HPLC analysis of the benzylated product. Benzylation was achieved following work-up procedure *WP3*.

The absolute configuration of the major enantiomer of **13** was determined by comparison of specific rotation and chiral GC signals of the decarboxylated product **17** with those of the literature known compound.[6] The results indicate that the absolute configuration of the major enantiomer of **13** is (1*R*,6*S*)-8,8-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylic acid. Accordingly, the absolute configuration of the benzylated products **15** and **16** is benzyl-(1*R*,6*S*)-8,8-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (**15**) and benzyl-(1*S*,6*S*)-7,7-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (**16**).

Chiral GC trace of **17** (89% *ee*):

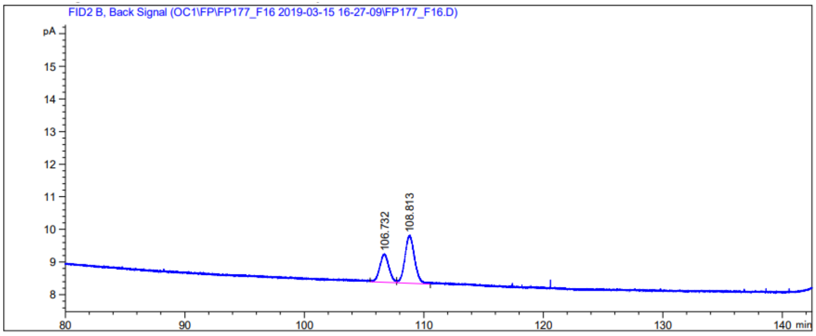


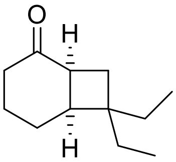


Lit.[6]: $[\alpha]_{\mathrm{D}}^{25}$ = +113
(c = 1.05, CH_2Cl_2) (90% *ee*)

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: FID2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 108.515 BV E  0.7041   13.66543 2.31710e-1  5.60121
   2 110.492 VB R  0.6838  230.30730    4.02382 94.39879
```

Chiral GC trace of **17** (28% *ee*):





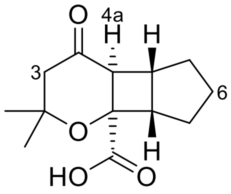
28% *ee*

$[\alpha]_{\mathrm{D}}^{25}$ = +42.0
(c = 1.00, CH_2Cl_2) (28% *ee*)

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: FID2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 106.732 BV    0.6697   46.61997 8.52911e-1 35.99688
   2 108.813 VB    0.7360   82.89117    1.45292 64.00312
```

Determination via CD Spectra

(4a*S*,4b*R*,7a*S*,7b*R*)-2,2-Dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylic acid (10a)



10a
$C_{13}H_{18}O_4$
MW = 238.28 g/mol

Compound **11a** [8.00 mg, 24.4 µmol, 1.00 eq., e.r. = 93:7 (85% *ee*)] was dissolved in EtOAc/EtOH (2 mL, v/v = 1/1). After addition of 10% Pd/C (800 µg, 10 wt%) the mixture was stirred under hydrogen atmosphere at room temperature for 15 hours. The solution was filtered through a short plug of silica (SiO_2, MeOH:CH_2Cl_2 = 1:9) to afford acid **10a** as a colorless solid [5.81 mg, 24.4 µmol, *quant*., e.r. = 93:7 (85% *ee*)].

TLC: $R_f = 0.40$ (CH_2Cl_2:MeOH = 10:1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{25} = +143$ (c = 0.35, $CHCl_3$) (85% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 1.11 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.46-1.55 (m, 1 H, *H*H-5), 1.56-1.62 (m, 2 H, H-7), 1.74-1.82 (m, 1 H, *H*H-6), 1.83-1.88 (m, 1 H, H*H*-5), 1.90-1.98 (m, 1 H, H*H*-6), 2.29 (dd, $^2J = 15.6$ Hz, $^4J = 1.2$ Hz, 1 H, H-3), 2.67 (dd, $^2J = 15.6$ Hz, $^4J = 1.2$ Hz, 1 H, H-3), 2.76-2.85 (m, 1 H, H-7a), 2.94 (*virt.* q, $^3J \approx {}^3J \approx {}^3J = 6.8$ Hz, 1 H, H-4b), 3.13 (*virt*. dt, $^3J = 6.7$ Hz, $^4J \approx {}^4J = 1.2$ Hz, 1 H, H-4a).

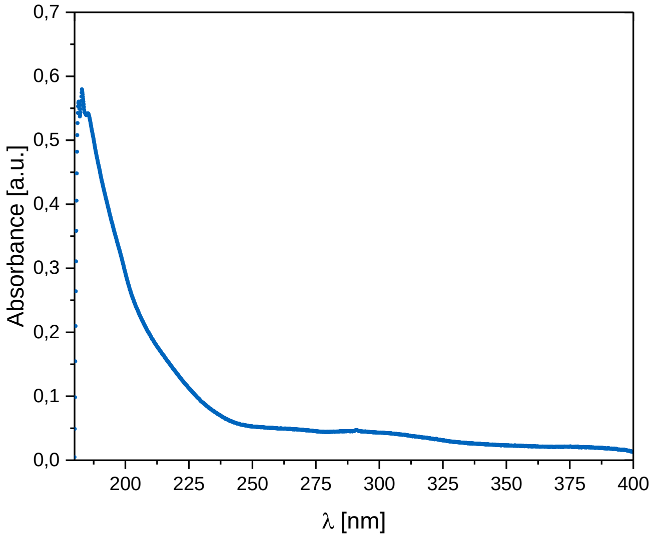
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 25.0 (q, CH_3), 25.2 (t, C-6), 27.6 (t, C-7), 30.2 (q, CH_3), 32.1 (t, C-5), 40.7 (d, C-4b), 45.3 (d, C-4a), 48.7 (d, C-7a), 50.1 (t, C-3), 77.4 (s, C-2), 78.6 (s, C-7b), 172.9 (s, COO), 207.0 (s, C-4).

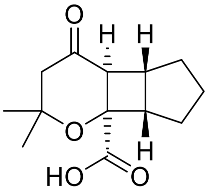
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3394 (m, O–H), 2960 (m, C–H), 1703 (s, C=O), 1373 (w, C=C), 1244 (m, C–O), 1113 (m), 849 (w).

MS (EI, 70 eV): m/z (%) = 238 (1) $[M]^+$, 172 (16), 171 (80) $[C_8H_{11}O_4]^+$, 126 (10), 125 (100) $[C_7H_9O_2]^+$, 115 (34), 109 (20), 81 (15), 69 (21), 68 (16) $[C_5H_8]^+$, 67 (19), 56 (9).

HRMS (ESI): calc. for $C_{13}H_{19}O_4^+$ $[M + H]^+$: 239.1278; found: 239.1284.

UV/VIS and CD Spectra of Compound 10a





10a

Figure S1. UV/Vis spectrum of compound **10a** (c = 1.5 mM, 85% ee) in acetonitrile.

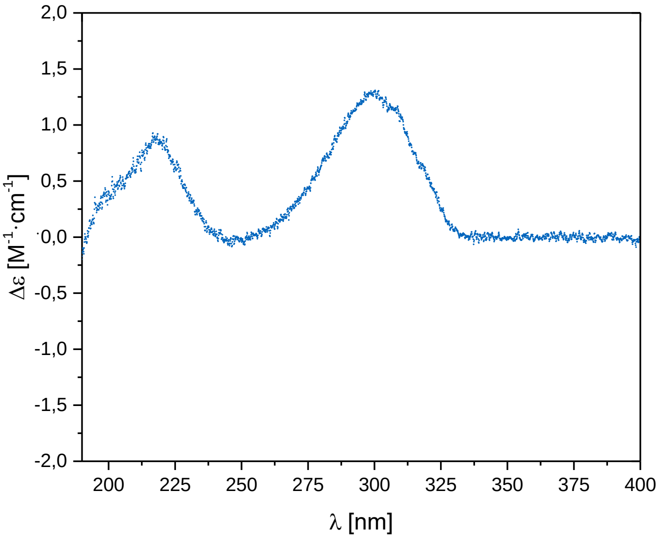


Figure S2. CD spectrum of compound **10a** (c = 1.5 mM, 20 °C, 85% ee) in acetonitrile.

Comparing the experimental (black) with the calculated CD spectrum (red) in Figure S3 one can assume that the major enantiomer is (4a*S*,4b*R*,7a*S*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta-[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylic acid (**10a**). This result is in accordance with the absolute configuration determined by decarboxylation experiments (see above). The absolute configuration of all other major enantiomers in the [2+2] photocycloaddition of **9** and **12** was assigned analogously.

Details for DFT Calculations

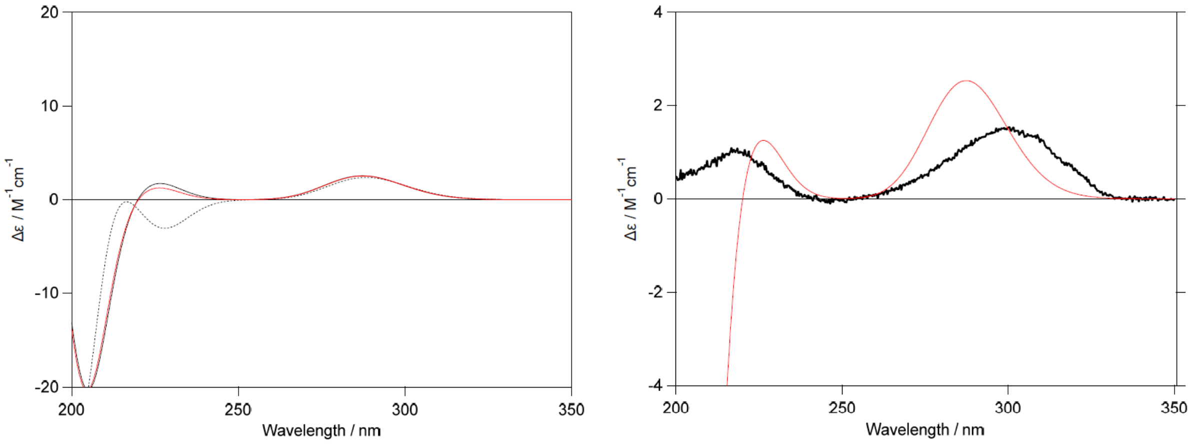


Figure S3. Left: Calculated CD spectra for (4a*S*,4b*R*,7a*S*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-b]pyran-7b(2*H*)-carboxylic acid at the RI-CC2/aug-def2-TZVPP//DFT-D3-TPSS/def2-TZVP level for major (black solid) and minor (black dotted) conformers, as well as Boltzmann weighted spectrum (red). The conformational freedom is only allowed at the orientation of carboxylic acid group (see the geometries below). The CD spectra were simulated by overlapping the individual Gaussian functions for each transition, where the bandwidth at 1/e height is fixed at 0.5 eV. Right: Comparison of experimental (black) and calculated CD spectra (red). The experimental spectrum was corrected for 100% *ee* and the calculated spectrum is that of Boltzmann weighted one.

Major conformer				Minor conformer			
Energy = -807.5893418100				Energy = -807.5872878708			
C	-2.1284228	0.8898763	-1.1007779	C	2.0991688	0.7945938	1.1080599
C	-2.2008559	0.2953015	0.3252322	C	2.2013732	0.1980382	-0.3145846
O	-1.2711388	-0.8152627	0.4395668	O	1.2329915	-0.8757941	-0.4676997
C	0.0487317	-0.6928762	-0.1032533	C	-0.1058803	-0.7102719	0.0319827
C	0.3759168	0.5295867	-1.0036266	C	-0.4126854	0.5257870	0.9275657
C	-0.7568733	1.4766492	-1.3200334	C	0.7452519	1.4335283	1.2771319
C	1.1577283	-0.2234197	0.9066756	C	-1.1487086	-0.2003963	-1.0151856
C	1.4299703	1.0415616	0.0213529	C	-1.4229526	1.0642553	-0.1244688
C	2.4829191	-1.0034312	0.9337808	C	-2.4958079	-0.9316637	-1.1185835
C	3.2487727	-0.5295724	-0.3185676	C	-3.2622687	-0.4945683	0.1431100
C	2.8983009	0.9670245	-0.4119356	C	-2.9012402	0.9960250	0.2802890
O	-0.5574875	2.6308972	-1.6587712	O	0.5745764	2.5937171	1.6107074
C	0.2917080	-2.0387991	-0.7836826	C	-0.3429195	-2.0822612	0.6604221
O	0.6250353	-2.1904435	-1.9417553	O	-0.6835422	-3.0847996	0.0747980
O	0.0928652	-3.0792738	0.0637197	O	-0.0509886	-2.0753879	1.9965704
C	-3.5654863	-0.3433777	0.5707109	C	3.5481592	-0.4926898	-0.5111912
C	-1.9018752	1.3590154	1.3895964	C	1.9797270	1.2719385	-1.3874246
H	-2.2991716	0.0746088	-1.8159969	H	2.2075258	-0.0271215	1.8275649
H	-2.8889522	1.6620099	-1.2427782	H	2.8838279	1.5361394	1.2787550
H	0.8117766	0.1973708	-1.9538394	H	-0.8864501	0.2354331	1.8722764
H	0.7299382	-0.0630020	1.8983268	H	-0.6728677	-0.0344327	-1.9834741

H	1.1637057	2.0115501	0.4464253	H	-1.1363280	2.0370857	-0.5290836
H	2.3415650	-2.0875545	0.9760353	H	-2.3882802	-2.0132938	-1.2154199
H	3.0359547	-0.7111464	1.8347593	H	-3.0191463	-0.5582049	-2.0077782
H	4.3254252	-0.7106670	-0.2477244	H	-4.3396952	-0.6703217	0.0729921
H	2.8852886	-1.0575322	-1.2072120	H	-2.9016092	-1.0545653	1.0169824
H	3.5116916	1.5384129	0.2960370	H	-3.4986277	1.5852184	-0.4263206
H	3.0612712	1.3900192	-1.4082071	H	-3.0777332	1.4011770	1.2820081
H	0.2523809	-3.8889824	-0.4599156	H	-0.1521539	-2.9986976	2.2998665
H	-3.7696529	-1.1044732	-0.1875299	H	3.6954690	-1.2601692	0.2537130
H	-3.5808405	-0.8189633	1.5559368	H	3.5807410	-0.9694724	-1.4953773
H	-4.3522277	0.4168250	0.5342652	H	4.3615211	0.2370550	-0.4463012
H	-2.6482378	2.1591837	1.3457852	H	2.7536283	2.0435686	-1.3160760
H	-1.9311922	0.9036973	2.3834739	H	2.0265464	0.8161834	-2.3803377
H	-0.9185313	1.8151871	1.2439268	H	1.0093784	1.7643680	-1.2754889

6. NMR Experiments

Sample Preparation

A 5 mm NMR tube was dried at 650 °C at vacuum (< 10^{-3} mbar) for 20 minutes. The NMR tube was brought into a glovebox under argon and pre-dried catalyst **4** and/or pre-dried carboxylic acid **9** were directly weighed into the NMR tube. Catalyst **4** and carboxylic acid **9** were pre-dried via lyophilization. Afterwards, **4** and **9** were again dried in the NMR tube at 100 °C at vacuum (<10^{-3} mbar) for 30 minutes outside of the glovebox. Dry CD_2Cl_2 (0.6 mL, less than 5 ppm H_2O) and 0.5 mL of tetramethylsilane atmosphere were added to the tube under argon flow. The NMR tube was closed and sealed with parafilm. The samples were stored in a -80 °C freezer. In case the sample contains catalyst **4**, brown-glass NMR tubes were used. For the sample with the equimolar solution of **4** and **9**, a concentration of 10 mM was used. For the sample containing only **4** or only **9**, concentrations of 4 mM or 7 mM respectively were used. To exclude thermal decomposition of the catalyst during the sample preparation, a sample of catalyst **4** was prepared as described above but dissolved in non-dried DMSO. No decomposition products were observed by NMR.

Spectrometer Data

Low temperature NMR experiments were performed on *Bruker* Avance III HD 600 MHz spectrometer, equipped with a 5 mm CPPBBO BB-1H/19F. Temperature was controlled in the VT-experiments by BVT 3000 and BVTE 3900. NMR data were processed, evaluated and plotted with TopSpin 3.2 software. Further plotting of the spectra was performed with Corel Draw X14 – X17 software. $^1H/^{13}C$ chemical shifts were referenced to TMS. The heteronucleus ^{31}P was referenced, employing Ξ (X) = Ξ (TMS) x $\Xi_{reference}$ / 100 % according to Harris *et al.*[7] The following frequency ratio and reference compound was used: Ξ (^{31}P) = 40.480742 (H_3PO_4).

Pulse Programs

All pulse programs used are standard *Bruker* NMR pulse programs. The pulse program for Diffusion Ordered Spectroscopy (DOSY) is described in the respective chapter.

Acquisition Parameters

^{1}H NMR: Pulse program: zg30; Relaxation delay = 2 – 3 s, Acquisition time = 2.48 s, SW = 22.0 ppm, TD = 64k, NS = 64 – 2048;

^{31}P NMR: Pulse program: zgpg30; Relaxation delay = 3 s, Acquisition time = 4.49 s, SW = 30.0 ppm, TD = 64k, NS = 64 – 18k;

2D-^{1}H,^{1}H NOESY: Pulse program: noesygpph; Relaxation delay = 5 - 8 s, NS = 12, mixing time (D8) = 300.00 ms; TD = 4096; increments = 1024;
2D-^{1}H,^{31}P HMBC: Pulse program: inv4gplrndqf; Relaxation delay = 4 - 8 s, NS = 8-32, TD = 4096; increments = 256 - 1k;

Content of Water

The NMR experiments revealed that careful exclusion of water is a key prerequisite to observe hydrogen bonded proton signals and complexation of acids **4** and **9**. In case **4** and **9** were not pre-dried and dried a second time prior to solvation, the hydrogen bond region of the spectra showed no signals and complexation of the carboxylic acid could not be shown by DOSY measurements (a similar hydrodynamic radius of **9** in presence and absence of **4** was observed).

Line Broadening and Chemical Shift Offsets

Line broadening and a chemical shift offset of the signals of **9** was observed in presence of **4** (see Figure S4). This shows, that **9** is involved in an exchange process fast on the NMR time scale if **4** is present. This occurring fast exchange process is the formation of a **4**·**9** complex.

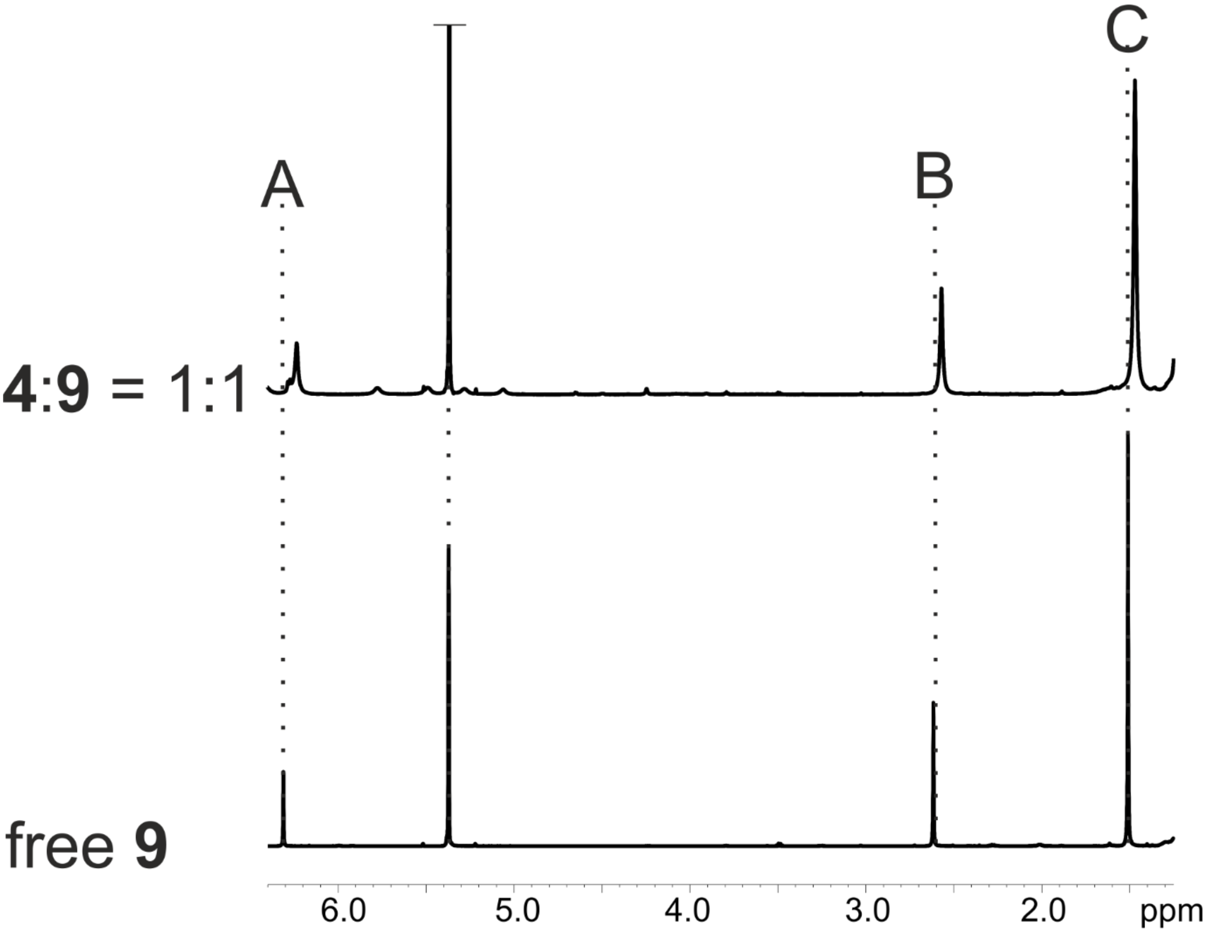


Figure S4. Comparison of the ^{1}H spectra of **9** in absence (free **9**) or presence of **4** (**4**:**9** = 1:1) at 233 K and 600 MHz in CD_2Cl_2. The spectra are referenced on TMS.

Signal A: δ(^{1}H) = 6.309 ppm, Halfline width = 2.1 Hz → δ(^{1}H) = 6.234 ppm, Halfline width = 12.5 Hz
Signal B: δ(^{1}H) = 2.616 ppm, Halfline width = 2.3 Hz → δ(^{1}H) = 2.570 ppm, Halfline width = 9.9 Hz
Signal C: δ(^{1}H) = 1.510 ppm, Halfline width = 2.3 Hz → δ(^{1}H) = 1.470 ppm, Halfline width = 10.2 Hz

Comparison of Spectra at 233 K and 180 K

Further cooling of a sample containing an equimolar solution of **4** and **9** lead to additional line broadening of the signals of **9**, indicating that the occurring fast exchange process (**4·9** complex formation) is slowed down, but still fast on the NMR time scale (see Figure S5). The offset in chemical shifts can also be caused by the temperature difference.

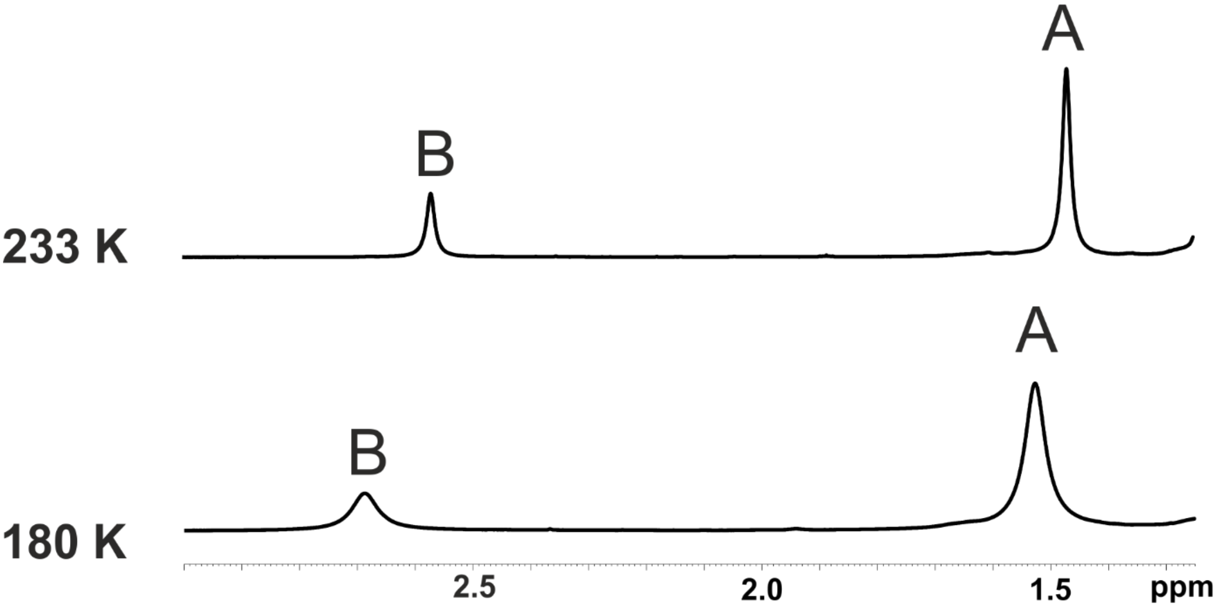


Figure S5. Excerpt of the ^{1}H spectra of an equimolar solution of **4** and **9** at 233 or 180 K at 600 MHz in CD_2Cl_2. Signals A and B belong to the carboxylic acid **9**.
Signal A: Halfline width = 10.2 Hz (233 K) → 25.9 Hz (180 K)
Signal B: Halfline width = 9.9 Hz (233 K) → 31.8 Hz (180 K)

NOE Analysis

The presence of a complex of the phosphoric acid **4** and the carboxylic acid **9** was proven by the detection of intermolecular NOE signals between **4** and **9** (see Figure S6). Besides the intramolecular (purple) NOE from protons H^a (blue) and H^b (red) to proton H^c (green) of the carboxylic acid, also two intermolecular (orange) NOE signals from protons H^a and H^b to two different protons of the phosphoric acid could be detected.

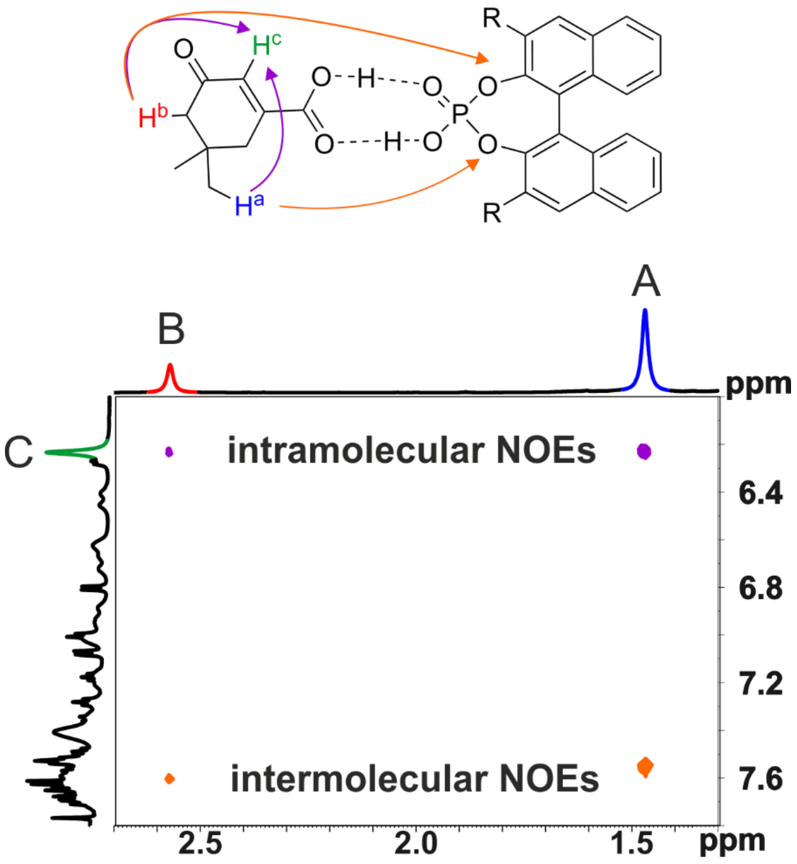


Figure S6. Excerpt of the ^{1}H^{1}H NOESY spectrum of an equimolar solution of **4** and **9** in CD_2Cl_2 at 233 K and 600 MHz. Intramolecular NOEs within the carboxylic acid are highlighted in purple, while intermolecular NOEs between **4** and **9** are highlighted in orange.

Diffusion Ordered Spectroscopy

The DOSY measurements were performed with the convection suppressing DSTE (double stimulated echo) pulse sequence developed by Jerschow and Müller in a pseudo 2D mode.[8] TMS was used to reference the viscosity of the solvent. The diffusion time delay was set to 45 ms. Gradient pulse lengths (p16, SINE.100 pulse shape) were optimized for each species to give a sigmoidal signal decay for varying gradient strengths and range between 900 to 2500 µs at 233 K. For each species, twenty spectra with linear varying gradient strength of 5%-95% have been measured. Suitable probe signals (good base line separation) for the analysis were used. The signal intensities of the respective groups were analyzed as a function of the gradient strength by *Bruker* TopSpin 3.2 software T1/T2 relaxation package by employing the Stejskal-Tanner equation.[9] The molecular radii were derived by the Stokes-Einstein equation[10] using Chens correction.[11]

$$D_i = \frac{k_B T}{6\pi\eta r_H} * \left(1 + 0.695 * \left(\frac{r_{solv}}{r_H}\right)^{2.234}\right)$$

D_i is the self-diffusion coefficient derived by the measurement, η is the viscosity of the solvent, r_H is the hydrodynamic radius of the observed molecule and r_{solv} the radius of the solvent. No form factor correction was applied. The viscosity was determined by measuring the diffusion coefficient of the reference tetramethylsilane (TMS) and solving the equation for η with the literature value[12] of the radius of 2.96 Å. The solvent radius of CD_2Cl_2 (2.46 Å) was taken from the reference.[13]

Table S6. List of parameters and results for the DOSY measurements.

Sample	**Molecule**	**Chem. shift [ppm]**	**p16 [ms]**	**D_i [m^2/s]**	**D_i [m^2/s]** (averaged)	**Hydrodynamic radius [Å]**
4:9 = 1:1	TMS	0.00	1.3	1.059E-09	1.059E-09	---
	9	6.32	1.6	5.934E-10	**5.939E-10**	**6.058**
	9	2.62	1.6	6.046E-10		
	9	1.51	1.6	5.837E-10		
4	TMS	0.00	1.6	1.040E-09	1.040E-09	---
	9	2.57	2.5	4.069E-10	**3.805E-10**	**4.329**
	9	1.47	2.5	3.541E-10		

Hydrogen Bond Region at 180 K and 233 K

At 233 K in the spectrum of the equimolar solution of **4** and **9**, proton H^3 of the catalyst is overlapped by proton H^4 of the carboxylic acid (see Figure 4 in the manuscript or Figure S7 in the SI). Further cooling to 180 K lead to a significant shift of proton H^4 and now the detection of proton H^3 is feasible (see Figure S7).

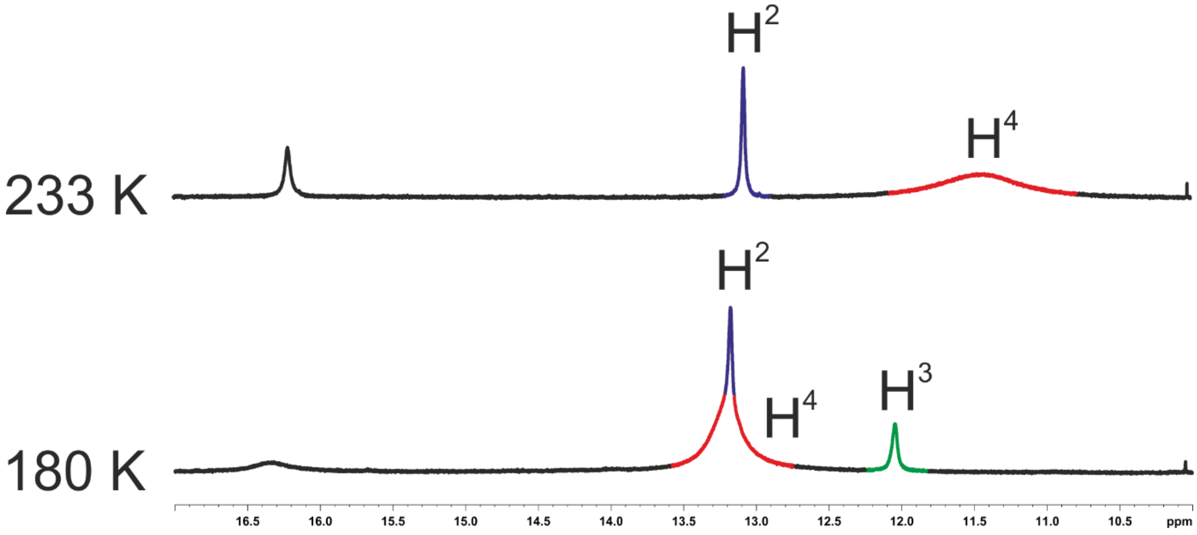


Figure S7. Hydrogen bond region of an equimolar solution of **4** and **9** at 233 K or 180 K. At lower temperatures, the detection of proton H^3 of the catalyst is again feasible.

^{1}H and ^{31}P Spectra of 4 and 4·9

The ^{1}H spectra of **4** at 180 K shows various signals in the H-bond region of the ^{1}H spectrum, as well as in the ^{31}P spectrum, corresponding to different species of the catalyst (see manuscript). In the presence of **9**, several signals in the ^{1}H and ^{31}P spectra collapse (named H^X in the manuscript). However, two signals (protons H^2 and H^3 in Figure 4 of the manuscript) and their respective ^{31}P signals remain unchanged (see Figure S8 and S9). This indicates, that the species corresponding to these ^{1}H and ^{31}P signals are dimers (or higher aggregates) of **4** und thus unaffected by the complex formation with **9**.

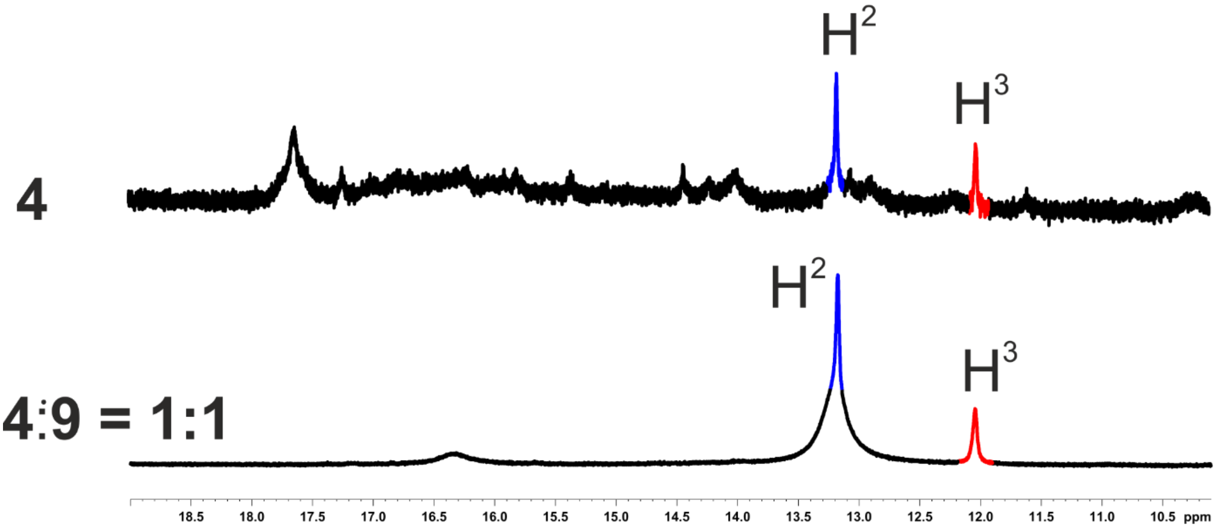


Figure S8. Section of the ^{1}H spectrum of **4** in presence or absence of **9** at 180 K and 600 MHz in CD_2Cl_2. Protons H^2 and H^3 are not affected by the presence of **9**, indicating that they correspond to dimers (or higher aggregates) of the catalyst.

4

4:9 = 1:1

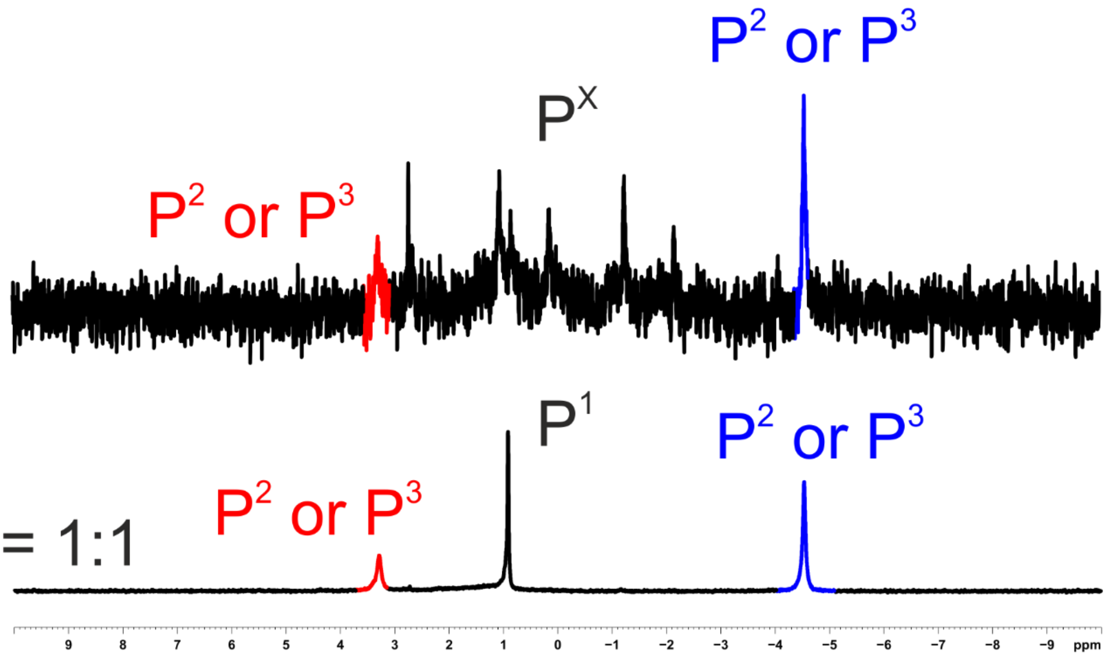


Figure S9. ^{31}P spectrum of **4** in presence or absence of **9** at 180 K and 600 MHz in CD_2Cl_2. Signals P^2 and P^3 (corresponding to protons H^2 and H^3 in Figure S8) are not affected by the presence of **9**, indicating that they correspond to dimers (or higher aggregates) of the catalyst.

Temperature Coefficients

For determination of the temperature coefficients, all spectra were referenced on the solvent signal, which was calibrated to 5.32 ppm. The following chemical shifts for protons H^X and H^1-H^4 were observed between 180 K and 233 K:

In an equimolar solution of **4** and **9**:

Proton H^1: 16.23 ppm at 180 K → 16.16 at 233 K → -1.32 ppb/K

Proton H^2: 13.08 ppm at 180 K → 13.03 at 233 K → -0.94 ppb/K

Proton H^4: 12.93 ppm at 190 K → 11.27 at 233 K → -38.6 ppb/K

In the spectra of **4**:

Proton H^X: 17.55 ppm at 180 K → 17.04 at 233 K → -9.62 ppb/K

Due to differences in the occurring signals, only the minimum temperature coefficient was determined.

Proton H^3: 11.92 ppm at 180 K → 11.87 at 233 K → -0.94 ppb/K

7. DFT Calculations for Complex 12•4

Computational Methods

Most details of the computational methods were already mentioned in the manuscript. All complexes were fully optimized in the gas phase and the absence of imaginary frequencies confirmed that minima were obtained in all cases.

Overall, eight conformers were considered in this study. Those were generated in the following fashion: first optimizations of the phosphoric acid had indicated that the structure was quite rigid, with the rotation of the thioxanthones being the most relevant option to form conformers. Upon binding, the substrate will align in a parallel fashion to one of the thioxanthones. Thus, all three groups (the two thioxanthones and the substrate) will be in one of two possible orientations, "up" or "down", which are interconverted by a rotation of approximately 180° (see blue, red, and green arrows below).

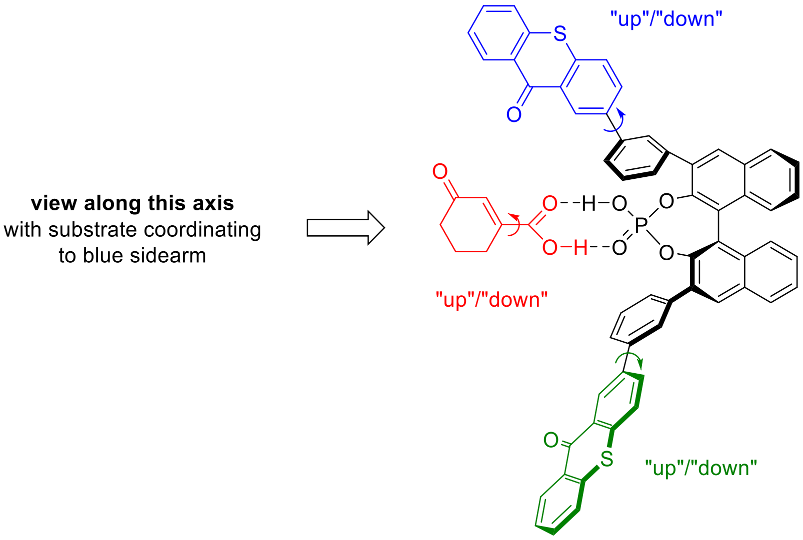


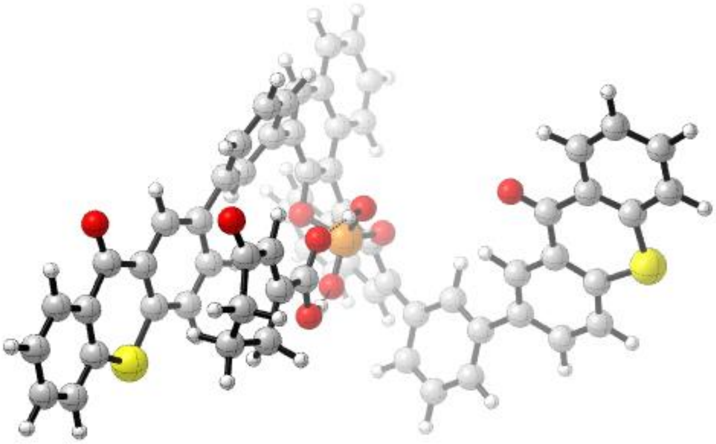
Figure S10. Model for the complex of cyclohex-2-enone-3-carboxylic acid (**12**) with chiral phosphoric acid **4**.

To differentiate the $2^3 = 8$ possible conformers, the following nomenclature will be used: the complex is viewed along the axis indicated in Figure S10. It is rotated around this axis until the substrate is coordinated to the thioxanthone which is on the left-hand side of the viewer. Then, the orientations of the three moieties (marked in color above) are assigned based on whether the respective carbonyl/ketone is pointing upwards ("up") or downwards ("down") as seen by the viewer. Molecules are then named in the order "up"/"down" – "up"/"down" – "up"/"down", e.g. up-down-up for the complex in which both thioxanthones point upward in this orientation, while the substrate points downward.

In the following, we provide the coordinates and the corrected *Gibbs* free energies (in absolute values [hartree] and relative to the most stable conformer [kJ·mol^{-1}]) for all eight conformers. We also indicate which face of the α-carbon atom of the substrate is preferentially attacked (generally, the up conformation leads to *Si* attack, while the down conformation leads to *Re* attack).

Coordinates and Free Energies

up-up-up



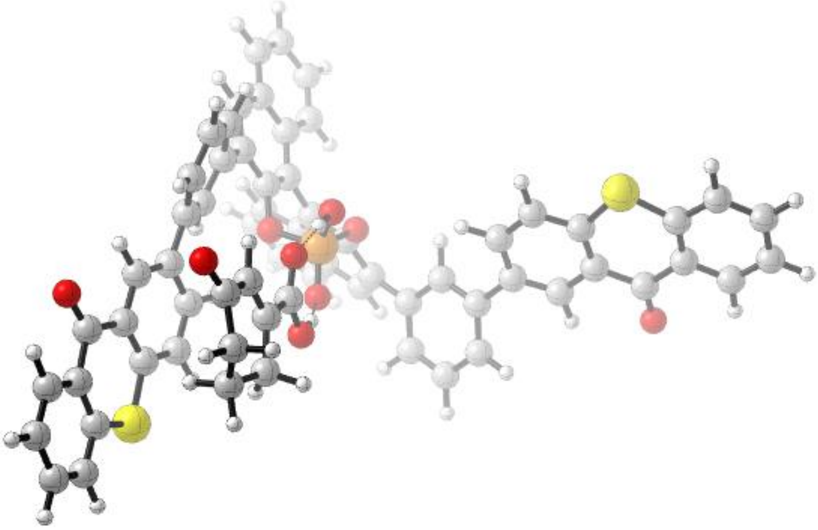
absolute free energy (ht): - 4315.762055
relative free energy (kJ·mol^{-1}): **+ 10.7**
face attacked: *Si*

C	-3.22522900	-2.52965000	-2.41377500
H	-3.95233700	-3.69506100	-4.03004900
C	-3.54421000	-3.71177800	-3.02624400
C	-2.55695600	-3.77375900	-0.39593000
C	-3.34253800	-4.95899700	-2.39537900
C	-2.72701100	-2.59901400	-1.08784500
C	-2.82268100	-5.00293600	-1.07680800
C	-3.62569600	-6.17054300	-3.07292000
H	-2.10593300	-6.32123200	0.48109600
C	-3.37287000	-7.37574600	-2.48521900
H	-4.03631100	-6.11825400	-4.07402700
H	-3.58675000	-8.29634000	-3.01196400
C	-2.81192100	-7.42153600	-1.19129000
H	-2.58600100	-8.37863600	-0.73969200
C	-2.54461000	-6.27000200	-0.50561100
C	-0.89615100	-3.06384300	1.28746300
C	-2.05544200	-3.74132700	1.00440400
C	-0.98877100	-3.61607600	3.59792100
C	-2.76851800	-4.34854700	2.08410500
C	-0.33624300	-2.95853800	2.58907600
C	-2.20124200	-4.30807000	3.38323900
C	-4.03805300	-4.95660400	1.92196800
H	-2.43021800	-4.89947400	5.44254700
H	-0.57923200	-3.58769100	4.60076100
C	-4.68003300	-5.53064200	2.98323000
H	-4.50499100	-4.95620300	0.94687000
H	-5.65187300	-5.98452400	2.83991000
C	-4.09217300	-5.53112400	4.26594700

H	-4.60928900	-5.99631300	5.09471800
C	-2.88362100	-4.92767700	4.45910800
O	-0.24541800	-2.42601500	0.23970100
O	-2.38215500	-1.40165600	-0.47215800
P	-0.84561600	-1.05683800	-0.30171900
O	-0.88485100	-0.02695400	0.84633200
O	-0.11670000	-0.65739900	-1.51348800
C	-3.36844200	-1.23618200	-3.12251600
C	-2.92710100	-1.12127000	-4.43940500
C	-3.95389000	-0.13234900	-2.50814400
C	-3.07254500	0.07545200	-5.12364500
H	-2.44386900	-1.96531300	-4.91489800
C	-4.09859400	1.07631100	-3.18333100
H	-4.32139600	-0.21896500	-1.49418000
C	-3.65274600	1.16891500	-4.50192100
H	-2.71082700	0.16189900	-6.13988300
C	0.84623500	-2.10599500	2.85834000
C	0.86863500	-1.29707600	3.99499000
C	1.92147700	-2.04487200	1.97702500
C	1.94274600	-0.45366500	4.23404800
H	0.02398800	-1.30164300	4.67193300
C	2.97422000	-1.15547000	2.17366500
H	1.93394100	-2.69389700	1.11384300
C	2.98483400	-0.36844400	3.32450900
H	1.94578500	0.17575600	5.11416700
H	3.78581000	0.34238900	3.48809600
H	-0.04766200	0.52407800	0.84706600
C	4.06967800	2.70122800	-1.48363800
C	3.34707400	2.25099000	-0.24666100
C	3.77729600	2.50398900	0.99089000
C	4.99230600	3.31314400	1.25475600
C	5.57663900	4.02611900	0.05809300
C	5.50080000	3.13786200	-1.18073000
H	3.50269300	3.52212900	-1.93758100
H	4.06284500	1.89250500	-2.21657500
H	6.59667100	4.32346600	0.29609100
H	4.98559000	4.93656300	-0.09442300
H	6.11157000	2.24976300	-1.00583600
H	5.92749000	3.64813400	-2.04450300
C	2.07418400	1.47280500	-0.37342800
O	1.40323800	1.18540100	0.60481500
O	1.76794200	1.14047700	-1.60102300
H	0.98040800	0.51460900	-1.61254000
O	5.44625700	3.40337500	2.36964500
H	3.23103100	2.13390300	1.85017300
C	3.99489700	-0.97973200	1.11813000
C	5.28606600	-0.56931700	1.39825600
C	3.63636700	-1.14569000	-0.22914100
C	6.21300300	-0.30373000	0.38575900
H	5.62340700	-0.43492900	2.41812100
C	4.53151500	-0.89422100	-1.24266400
H	2.62176500	-1.42713800	-0.48858200
C	5.82990200	-0.46556200	-0.94707300
H	4.22244300	-1.00199800	-2.27546300
C	7.56437900	0.15115800	0.80383700
C	8.51720700	0.62849500	-0.23298100
C	8.29229200	0.52495100	-1.60710200
C	9.71160500	1.20670900	0.21428400
C	9.25799000	0.98684100	-2.50961400
C	10.65741100	1.66698900	-0.67391900
H	9.85893600	1.27460900	1.28386100
C	10.42626600	1.55106500	-2.04570600

H	9.07584500	0.90001700	-3.57368800
H	11.57345800	2.11387200	-0.31230400
H	11.16345400	1.90736600	-2.75354500
S	6.85984100	-0.16685800	-2.31925200
O	7.87834300	0.15686000	1.97463600
C	-4.70273100	2.24397400	-2.50366400
C	-5.54443100	3.12529700	-3.19829900
C	-4.44952600	2.50382400	-1.16875900
C	-6.10250800	4.21591100	-2.57342800
H	-5.77741300	2.93287500	-4.23823500
C	-5.00403400	3.60632000	-0.51107700
H	-3.78970700	1.86634000	-0.59262600
C	-5.83746100	4.47012400	-1.22224500
H	-6.75797900	4.88120300	-3.12187000
C	-4.65370700	3.78729600	0.92193400
C	-5.21324100	4.94504500	1.66584500
C	-6.06534100	5.89662700	1.10339200
C	-4.85423300	5.07341800	3.01351800
C	-6.54501400	6.95443400	1.88594300
C	-5.32554600	6.11365600	3.78188600
H	-4.19251200	4.32223200	3.42344000
C	-6.17798500	7.05949300	3.20938600
H	-7.20595900	7.68779800	1.44065500
H	-5.03818700	6.19826800	4.82107400
H	-6.55542800	7.88184100	3.80332600
O	-3.92030600	2.99749200	1.47852400
S	-6.60301800	5.88210300	-0.55291300
H	-3.73085200	2.11123000	-5.02972100

up-up-down



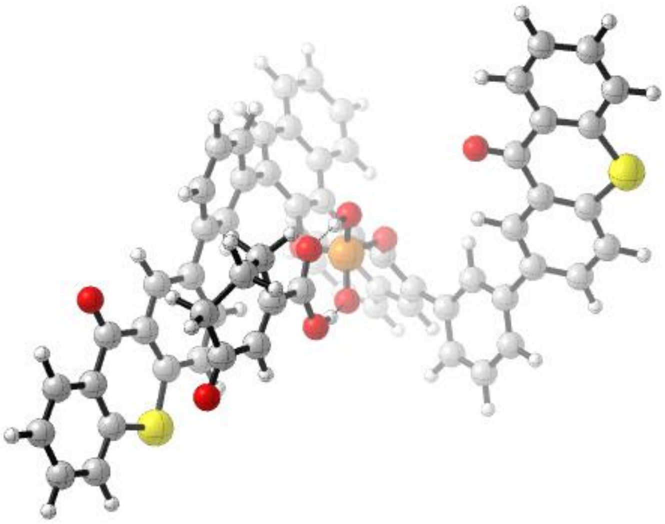
absolute free energy (ht): - 4315.762986
relative free energy (kJ·mol^{-1}): **+ 8.3**
face attacked: *Si*

C	-2.63284000	2.78719000	2.26180100
H	-3.33625000	3.72044900	4.03157000
C	-2.78505600	3.85274100	3.10796300
C	-1.42394700	4.23902400	0.68062000
C	-2.23341500	5.12091700	2.82158800
C	-1.93453400	3.01826500	1.04907400
C	-1.52664500	5.32185500	1.60883100

C	-2.35437500	6.19105700	3.74200100
H	-0.33154000	6.73556500	0.48962000
C	-1.77215600	7.39909500	3.48976800
H	-2.91008100	6.02470200	4.65685800
H	-1.86440300	8.20927000	4.20094700
C	-1.03060300	7.58715700	2.30414900
H	-0.54726000	8.53778400	2.12064400
C	-0.91088300	6.57932400	1.38893700
C	0.28370400	3.53822600	-0.96043200
C	-0.74125900	4.38960900	-0.63263300
C	0.64102300	4.57735200	-3.06879900
C	-1.15150500	5.36158800	-1.59681900
C	0.99317800	3.58691600	-2.19050500
C	-0.42312200	5.46904400	-2.80886000
C	-2.27992100	6.19854000	-1.41217200
H	-0.22666400	6.52393200	-4.67757400
H	1.17772700	4.67013800	-4.00560600
C	-2.63140200	7.11860400	-2.35971400
H	-2.87244000	6.09883100	-0.51341200
H	-3.50012700	7.74441900	-2.20266100
C	-1.87718000	7.25668500	-3.54419400
H	-2.16325200	7.99538600	-4.28117800
C	-0.80215100	6.44521400	-3.76316600
O	0.63240300	2.55842800	-0.03953200
O	-1.75054400	1.93229700	0.19783200
P	-0.30768200	1.28646600	0.10896700
O	-0.38442900	0.54468000	-1.24444900
O	0.13769200	0.48721800	1.25836500
C	-3.15815300	1.44693100	2.61198900
C	-2.97928000	0.94704800	3.90022200
C	-3.84996200	0.67699000	1.68097900
C	-3.48744900	-0.29642800	4.24383600
H	-2.41695400	1.52416700	4.62327400
C	-4.35319600	-0.57768800	2.01100900
H	-4.01941800	1.07110500	0.68781700
C	-4.16759400	-1.05764300	3.30756100
H	-3.33209400	-0.68362000	5.24228900
C	2.00586200	2.56317900	-2.54220800
C	2.03064400	2.02990800	-3.83137300
C	2.90834900	2.07448300	-1.60268200
C	2.93680500	1.03333200	-4.16007000
H	1.31330100	2.37226900	-4.56624800
C	3.77876500	1.03037400	-1.90309000
H	2.92627900	2.50796300	-0.61365000
C	3.79721800	0.52206500	-3.20140500
H	2.94271700	0.62133200	-5.16060800
H	4.45464800	-0.30169000	-3.45214900
H	0.32985100	-0.16232400	-1.28530000
C	3.54971100	-3.63855800	0.83102900
C	3.10830900	-2.79095900	-0.32745700
C	3.64846500	-2.86936100	-1.54514100
C	4.70832700	-3.85282800	-1.87784300
C	4.97575000	-4.90809800	-0.83074100
C	4.89849600	-4.30454200	0.56904300
H	2.77770500	-4.39235700	1.02391900
H	3.59541100	-3.02126800	1.72992800
H	5.94397700	-5.36201400	-1.03584300
H	4.20809800	-5.68140100	-0.95048600
H	5.68772000	-3.55605500	0.66636000
H	5.09243700	-5.06591300	1.32482100
C	2.00927900	-1.79210400	-0.14034100
O	1.54841300	-1.16844500	-1.08459100

O	1.60902900	-1.65776000	1.09665700
H	0.96530800	-0.88910100	1.18251400
O	5.28265800	-3.80712300	-2.93853600
H	3.31096500	-2.21642200	-2.34108700
C	4.58227100	0.41162500	-0.82694300
C	5.79033600	-0.21602300	-1.07312800
C	4.07792400	0.37445300	0.48283600
C	6.49207600	-0.88789600	-0.06768300
H	6.23452400	-0.21160400	-2.06041100
C	4.75213300	-0.27587500	1.48987800
H	3.11468200	0.82003100	0.70519100
C	5.96599900	-0.91894100	1.22531600
H	4.32922200	-0.31382800	2.48662400
C	7.76816600	-1.54526800	-0.45278400
C	8.44710100	-2.43170000	0.52875400
C	8.05690500	-2.56231600	1.86308100
C	9.54778400	-3.16702700	0.07181900
C	8.76975100	-3.40987800	2.71957600
C	10.24363300	-4.00579600	0.91300900
H	9.82743900	-3.04712500	-0.96632700
C	9.85040700	-4.12245400	2.24736600
H	8.46110700	-3.50290400	3.75351700
H	11.08950200	-4.56950400	0.54376900
H	10.39102800	-4.77725500	2.91845400
S	6.71101700	-1.71874800	2.58089900
O	8.23579000	-1.38239300	-1.55914600
C	-5.05728300	-1.38752700	0.99218200
C	-4.62512400	-1.38544100	-0.34342700
C	-6.14817800	-2.17000800	1.32109100
C	-5.26927800	-2.13686300	-1.29796200
H	-3.75691700	-0.80114100	-0.62456900
C	-6.81998100	-2.94349200	0.36912400
H	-6.53236800	-2.19187300	2.33283300
C	-6.37556900	-2.92343300	-0.95327900
H	-4.91731900	-2.13111700	-2.32216900
C	-7.98048800	-3.74104500	0.84094200
C	-8.73244400	-4.57397700	-0.13150700
C	-8.41642000	-4.66649600	-1.48812700
C	-9.82138200	-5.30590400	0.35900300
C	-9.18424500	-5.48112400	-2.33005600
C	-10.57534600	-6.10579300	-0.46910200
H	-10.04406700	-5.21607200	1.41370800
C	-10.25045200	-6.19117400	-1.82435300
H	-8.93130600	-5.54653200	-3.38110600
H	-11.41307000	-6.66423700	-0.07410600
H	-10.83582900	-6.81683100	-2.48567500
O	-8.30989800	-3.71413700	2.00938000
S	-7.09952600	-3.82394300	-2.25380900
H	-4.53314600	-2.04199500	3.57143300

up-down-up



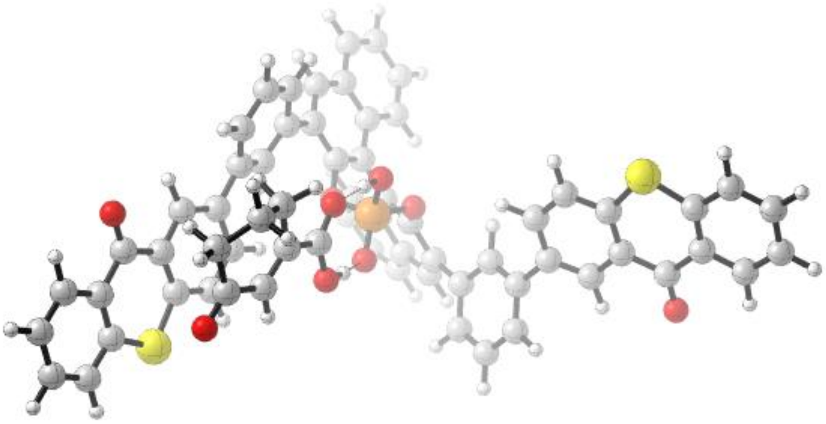
absolute free energy (ht):	- 4315.765041
relative free energy (kJ·mol^{-1}):	**+ 2.9**
face attacked:	*Re*

C	3.11453000	2.62618000	-2.40759600
H	3.76577500	3.84561100	-4.01609100
C	3.36927900	3.83002600	-3.00760900
C	2.41235400	3.81018900	-0.36551000
C	3.11606600	5.05791400	-2.35749100
C	2.62808900	2.65393800	-1.07573900
C	2.61188600	5.05953600	-1.03213400
C	3.33191300	6.29040900	-3.02184400
H	1.85389300	6.32171200	0.55269500
C	3.02954700	7.47435900	-2.41457600
H	3.73121000	6.27089000	-4.02868900
H	3.19163600	8.41096500	-2.93146900
C	2.48451900	7.47620000	-1.11307600
H	2.21920100	8.41532700	-0.64544400
C	2.28148400	6.30426400	-0.44005000
C	0.80163900	3.00394200	1.32131100
C	1.92653900	3.73668700	1.03868900
C	0.88481800	3.52962400	3.63815900
C	2.61851600	4.36209500	2.12162900
C	0.25583100	2.85725300	2.62432500
C	2.06327700	4.27869700	3.42411100
C	3.85731600	5.03016400	1.95865600
H	2.28047900	4.85372400	5.48934500
H	0.48409900	3.47016400	4.64322900
C	4.48032800	5.61924500	3.02296900
H	4.31610100	5.06378200	0.98025300
H	5.42918400	6.11924000	2.87909300
C	3.90275400	5.57603000	4.30959000
H	4.40417800	6.05381800	5.14083500
C	2.72465200	4.91517700	4.50321200
O	0.17364300	2.34801300	0.27221600
O	2.34706900	1.43330300	-0.47391600
P	0.83260600	1.01065400	-0.28217600
O	0.93952400	-0.01814900	0.86163600
O	0.10357500	0.58014200	-1.48258100
C	3.31417400	1.34982800	-3.13349700
C	2.86165400	1.22551400	-4.44560100
C	3.96488000	0.27225400	-2.53871600

C	3.06029800	0.04498000	-5.14446600
H	2.32841300	2.04774400	-4.90560000
C	4.16382100	-0.92007100	-3.22869100
H	4.34097400	0.36802800	-1.52871000
C	3.70562100	-1.02259700	-4.54229000
H	2.68930200	-0.05046000	-6.15651000
C	-0.88803000	1.95108800	2.88516200
C	-0.87040300	1.12531300	4.00859400
C	-1.96643900	1.86365900	2.00883500
C	-1.91385700	0.24306700	4.24169600
H	-0.02197100	1.15137400	4.68017800
C	-2.98702800	0.93410600	2.19395600
H	-2.00645000	2.53206200	1.16221800
C	-2.95810700	0.13661600	3.33820300
H	-1.89191700	-0.39596000	5.11464100
H	-3.73806200	-0.59275800	3.51254000
H	0.14785100	-0.63624800	0.86217000
C	-3.37864400	-3.08653000	1.30797400
C	-3.25626100	-2.39917400	-0.02034400
C	-4.22163000	-2.41431000	-0.94268400
C	-5.54035200	-3.04587500	-0.67735600
C	-5.74450400	-3.63695100	0.69812100
C	-4.43999100	-4.17866500	1.27237400
H	-3.62915400	-2.33111200	2.06115100
H	-2.40414500	-3.48068100	1.59708200
H	-6.52799400	-4.39047900	0.63031200
H	-6.12113900	-2.83292000	1.34263300
H	-4.08190600	-5.00486700	0.65198900
H	-4.60499100	-4.57597300	2.27384000
C	-2.00531000	-1.61647200	-0.24460400
O	-1.23041000	-1.43381600	0.68355600
O	-1.83543700	-1.15673000	-1.45465500
H	-1.04214100	-0.54036200	-1.50288700
O	-6.40597800	-3.04101100	-1.52175300
H	-4.10391200	-1.92036500	-1.89890100
C	-4.02543100	0.75834300	1.15205300
C	-5.27166400	0.22673600	1.43327600
C	-3.74693400	1.08981200	-0.18669200
C	-6.23495000	0.01684900	0.44006000
H	-5.55439100	-0.03533400	2.44475500
C	-4.68185500	0.91213800	-1.17637100
H	-2.76539200	1.45716000	-0.46210100
C	-5.94064500	0.37364400	-0.87812300
H	-4.43659800	1.15994700	-2.20189200
C	-7.52010200	-0.59597900	0.85917400
C	-8.57233900	-0.83953500	-0.15288900
C	-8.43325100	-0.53989400	-1.50939600
C	-9.76521600	-1.42508900	0.29057600
C	-9.47615300	-0.82651800	-2.39796500
C	-10.79022500	-1.70442300	-0.58347800
H	-9.84564700	-1.65029500	1.34541100
C	-10.63947500	-1.40190500	-1.93836500
H	-9.35574200	-0.59818000	-3.44957300
H	-11.70471900	-2.15756300	-0.22567600
H	-11.43688100	-1.62181400	-2.63636300
S	-7.01974600	0.17878500	-2.22023800
O	-7.69324000	-0.91548900	2.02130200
C	4.83756600	-2.06077200	-2.56912100
C	5.71632700	-2.88887500	-3.28302500
C	4.61555100	-2.34679100	-1.23402700
C	6.34074300	-3.95340200	-2.67608400
H	5.92497200	-2.67459500	-4.32384700

C	5.23745200	-3.42359300	-0.59430000
H	3.92927200	-1.75162200	-0.64377500
C	6.10763000	-4.23391600	-1.32429600
H	7.02396400	-4.57702400	-3.23940300
C	4.91602900	-3.63693200	0.84079900
C	5.55334200	-4.76480500	1.56799600
C	6.44852000	-5.66346700	0.98553000
C	5.22500700	-4.92058600	2.92055100
C	6.99940900	-6.69723600	1.75326000
C	5.76706900	-5.93650900	3.67451400
H	4.52919900	-4.20998500	3.34609700
C	6.66122400	-6.83013400	3.08183000
H	7.69294400	-7.38978800	1.29242400
H	5.50309900	-6.04239800	4.71796600
H	7.09414700	-7.63324700	3.66411000
O	4.14359100	-2.89720200	1.41341200
S	6.95743800	-5.60846100	-0.67870100
H	3.82526400	-1.95420900	-5.08117600

up-down-down



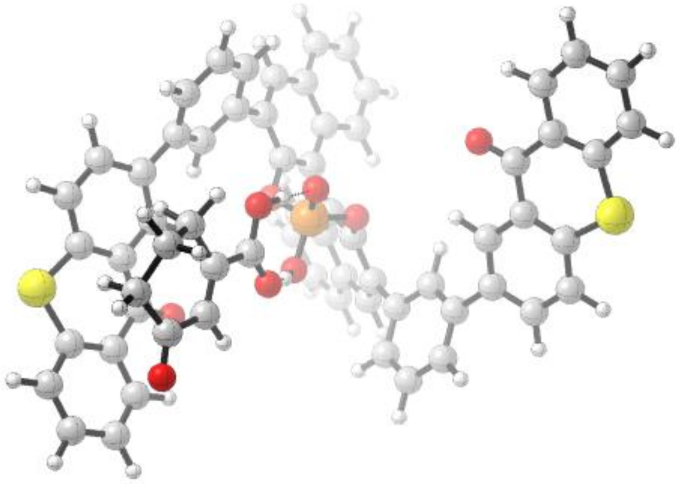
absolute free energy (ht): - 4315.766139
relative free energy (kJ·mol^{-1}): **0.0 (most stable)**
face attacked: *Re*

C	-2.60459800	2.76227100	2.26791500
H	-3.27002000	3.69837600	4.05060100
C	-2.72962500	3.82654400	3.12006200
C	-1.39510300	4.20190300	0.67644800
C	-2.16334900	5.08760500	2.83106800
C	-1.91913600	2.98722700	1.04677900
C	-1.46963100	5.28266300	1.60984100
C	-2.25616700	6.15569600	3.75710200
H	-0.26700400	6.68290800	0.48139200
C	-1.65907900	7.35585300	3.50205300
H	-2.80224700	5.99390300	4.67854000
H	-1.72979900	8.16442000	4.21751000
C	-0.93003300	7.53735100	2.30770600
H	-0.43444300	8.48116500	2.12170700
C	-0.83752500	6.53156000	1.38712000
C	0.28668000	3.48190300	-0.98101300
C	-0.72238800	4.34752500	-0.64243500
C	0.64950000	4.52520200	-3.08624000
C	-1.12251400	5.33024400	-1.59988300
C	0.99068800	3.52594900	-2.21380600
C	-0.39972300	5.43171300	-2.81594500

C	-2.23613400	6.18421200	-1.40421300
H	-0.19842300	6.49199600	-4.68113900
H	1.18265400	4.61463100	-4.02542500
C	-2.57893300	7.11396900	-2.34545000
H	-2.82400200	6.08985100	-0.50178900
H	-3.43647500	7.75292700	-2.18008800
C	-1.83012900	7.24525800	-3.53413500
H	-2.10911400	7.99167300	-4.26604300
C	-0.76938400	6.41796800	-3.76349700
O	0.62399900	2.48991400	-0.07067500
O	-1.76523400	1.90194800	0.18894500
P	-0.33620700	1.23110700	0.06758800
O	-0.44442600	0.51606700	-1.29709100
O	0.11438000	0.40491800	1.19510300
C	-3.14586500	1.42897800	2.62034600
C	-2.95194200	0.91900400	3.90240600
C	-3.86859700	0.67700000	1.69829600
C	-3.47602600	-0.31699500	4.24901100
H	-2.36589900	1.48204800	4.61768100
C	-4.38950000	-0.56946500	2.03181400
H	-4.04862700	1.07969900	0.71036200
C	-4.18827100	-1.05997300	3.32204900
H	-3.30836300	-0.71294500	5.24199300
C	1.98653000	2.48782900	-2.57161800
C	1.99785800	1.95949700	-3.86202400
C	2.88783700	1.98606900	-1.63656800
C	2.89528100	0.95755000	-4.19707300
H	1.28123300	2.31226100	-4.59253400
C	3.74802100	0.93328000	-1.93962700
H	2.91433100	2.42450400	-0.65060300
C	3.75469800	0.43739400	-3.24369600
H	2.89744900	0.55167000	-5.20016400
H	4.41373900	-0.37763700	-3.51213700
H	0.23527800	-0.22585400	-1.36078600
C	3.29552100	-3.17692400	-2.04338100
C	3.09530400	-2.78828400	-0.60768300
C	3.89267000	-3.20384000	0.37954200
C	5.10742200	-4.01665300	0.10791000
C	5.40872900	-4.32195900	-1.34068600
C	4.13067100	-4.44542800	-2.16287200
H	3.78691000	-2.34356500	-2.55783800
H	2.32258800	-3.28886100	-2.52239900
H	6.02896400	-5.21649000	-1.37679700
H	6.01239500	-3.49148600	-1.72732800
H	3.54383200	-5.29487400	-1.80272000
H	4.37178300	-4.64037100	-3.20776900
C	1.98035100	-1.83656300	-0.32923800
O	1.39347900	-1.30063100	-1.26046700
O	1.71561200	-1.62942200	0.93125600
H	1.04058300	-0.89303400	1.05066200
O	5.82481600	-4.37140200	1.01416900
H	3.71966300	-2.91993600	1.40986900
C	4.57191700	0.32031500	-0.87179500
C	5.73314800	-0.38049100	-1.14583700
C	4.16072200	0.39709500	0.47164500
C	6.48563400	-1.00010500	-0.14176900
H	6.11315400	-0.46405200	-2.15593000
C	4.89214600	-0.18446700	1.47742600
H	3.23030500	0.88979800	0.72791100
C	6.06639600	-0.89170800	1.18642700
H	4.54531300	-0.12414700	2.50178400
C	7.68972600	-1.75783600	-0.56540600

C	8.51764400	-2.43553600	0.45702500
C	8.23336500	-2.42204500	1.82390300
C	9.63832500	-3.14578600	0.00733400
C	9.06269500	-3.11118500	2.71626300
C	10.45366800	-3.82130500	0.88566800
H	9.83410600	-3.14311300	-1.05639400
C	10.15889600	-3.80191800	2.25047700
H	8.82940800	-3.10164700	3.77361600
H	11.31454300	-4.36608600	0.52270300
H	10.79014600	-4.33381600	2.95046800
S	6.88234200	-1.59787500	2.54202300
O	7.97460900	-1.83875600	-1.74646900
C	-5.12979900	-1.35986000	1.02351400
C	-4.72381000	-1.36103900	-0.32018300
C	-6.23050800	-2.12049500	1.37058400
C	-5.40217200	-2.09479000	-1.26484600
H	-3.84900100	-0.79391300	-0.61573600
C	-6.93684200	-2.87561700	0.42899400
H	-6.59527900	-2.13852800	2.38953800
C	-6.51764700	-2.85962900	-0.90165500
H	-5.07031300	-2.09207700	-2.29574400
C	-8.10493000	-3.65008000	0.92022700
C	-8.89064000	-4.46616900	-0.03982400
C	-8.60236600	-4.56076400	-1.40241400
C	-9.98338000	-5.17909900	0.46972600
C	-9.40117000	-5.35870200	-2.23141700
C	-10.76787900	-5.96254800	-0.34567700
H	-10.18402500	-5.08810200	1.52874000
C	-10.47053700	-6.05025900	-1.70704700
H	-9.16953700	-5.42608000	-3.28724200
H	-11.60808000	-6.50649100	0.06400200
H	-11.07984800	-6.66331200	-2.35849500
O	-8.41294200	-3.61865800	2.09430800
S	-7.28498300	-3.74023300	-2.19105300
H	-4.56713200	-2.03877600	3.58767700

down-down-up



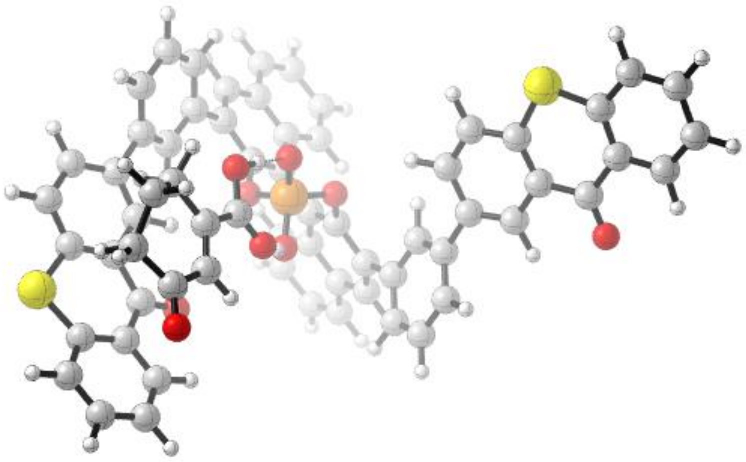
absolute free energy (ht):	- 4315.762434
relative free energy (kJ·mol^{-1}):	**+ 9.7**
face attacked:	*Re*

C	-0.20554700	3.24130600	-2.57817200
H	-0.75865200	4.19901100	-4.38946200
C	-0.94775100	4.11736300	-3.32559800
C	-1.44487400	3.94568000	-0.56994500
C	-1.98133000	4.89721500	-2.76232500
C	-0.46531400	3.20483500	-1.18342600
C	-2.26811200	4.78884300	-1.37781700
C	-2.77074800	5.75129700	-3.57149100
H	-3.64559900	5.38616700	0.17918000
C	-3.82161900	6.44168000	-3.04155800
H	-2.52970300	5.83262500	-4.62453700
H	-4.42348000	7.08672500	-3.66797900
C	-4.13842700	6.29698900	-1.67407200
H	-4.99070300	6.82279500	-1.26394800
C	-3.38505300	5.49413000	-0.86447800
C	-1.84628700	2.53932600	1.42126400
C	-1.65920900	3.79341500	0.89339600
C	-2.10717200	3.37229400	3.63572000
C	-1.62232000	4.90586000	1.79056500
C	-2.07973400	2.29106700	2.79734800
C	-1.86979700	4.68449100	3.16933500
C	-1.29744800	6.21897600	1.36767500
H	-2.05058000	5.59659100	5.11277700
H	-2.30292000	3.21984400	4.69075100
C	-1.26539000	7.25436600	2.25909000
H	-1.06205700	6.39694300	0.32758200
H	-1.00805700	8.24823500	1.91697500
C	-1.55632600	7.03953600	3.62289800
H	-1.53400900	7.87065700	4.31534500
C	-1.84601900	5.78150500	4.06515200
O	-1.77408400	1.43651000	0.57681900
O	0.29979000	2.35936300	-0.39588400
P	-0.33593800	0.98195400	0.08461500
O	0.50744300	0.62817900	1.32317100
O	-0.43310000	-0.05161400	-0.95447700
C	0.75253200	2.30857000	-3.21846000
C	0.38955300	1.68805600	-4.41403900
C	1.98721600	1.99997500	-2.65195900
C	1.24211500	0.78322800	-5.02561700

H	-0.58404000	1.88677800	-4.84286700
C	2.83784300	1.07036700	-3.24368700
H	2.29533600	2.49001100	-1.73869900
C	2.45750000	0.46773100	-4.44197300
H	0.93952800	0.29415900	-5.94219000
C	-2.25550100	0.91239100	3.31028300
C	-1.54385000	0.49714300	4.43347900
C	-3.13370500	0.02311900	2.69722200
C	-1.71093000	-0.78701400	4.92856100
H	-0.83643200	1.17373900	4.89592800
C	-3.31036300	-1.26818900	3.18616200
H	-3.70436000	0.34844800	1.83705700
C	-2.58621000	-1.66525100	4.31088200
H	-1.13864600	-1.11137800	5.78776700
H	-2.68511300	-2.67720600	4.68316200
H	1.00902800	-0.24442600	1.22315500
C	3.87768100	-3.08597400	-1.79566700
C	3.40488100	-2.75279400	-0.41031500
C	4.03513100	-3.15278400	0.69738300
C	5.29248900	-3.94177400	0.64420200
C	5.89953600	-4.12932000	-0.72637500
C	4.81822000	-4.28619000	-1.79175800
H	4.38484400	-2.20236900	-2.20594800
H	3.01576300	-3.26215100	-2.43892900
H	6.58250500	-4.97660300	-0.68613000
H	6.49460800	-3.23229800	-0.93841900
H	4.24008700	-5.19177100	-1.58832900
H	5.27237800	-4.40935200	-2.77514800
C	2.18458200	-1.89856300	-0.24591200
O	1.80228600	-1.53561700	0.85538200
O	1.60465100	-1.58955500	-1.37399000
H	0.78297300	-1.01542300	-1.23248300
O	5.79334500	-4.38257900	1.65135000
H	3.65449900	-2.89160500	1.67763600
C	-4.24733600	-2.19974000	2.51878600
C	-4.39813800	-2.20497200	1.14338100
C	-5.01288600	-3.10554900	3.26813400
C	-5.28247400	-3.07629300	0.49924800
H	-3.81446800	-1.54213100	0.51604600
C	-5.88492800	-3.97598200	2.65744400
H	-4.93348000	-3.10644400	4.34804900
C	-6.02877100	-3.97254900	1.26499300
H	-6.47334300	-4.66376000	3.25221400
C	-5.36726700	-2.98502000	-0.98167500
C	-6.27326600	-3.90630200	-1.71604100
C	-7.08501300	-4.85973000	-1.09990200
C	-6.30386000	-3.79496100	-3.11174900
C	-7.91047300	-5.68214400	-1.87709200
C	-7.11452100	-4.60419900	-3.87509800
H	-5.66477500	-3.04766800	-3.56266800
C	-7.92327000	-5.55404400	-3.24843000
H	-8.53719400	-6.41872000	-1.38957200
H	-7.12564500	-4.50540500	-4.95206300
H	-8.56530900	-6.19591400	-3.83775500
S	-7.16385400	-5.12308800	0.61936800
O	-4.70697800	-2.16621100	-1.58543500
C	4.09630600	0.67386700	-2.57665100
C	5.25201500	0.38190900	-3.31502300
C	4.15132700	0.52677400	-1.20109800
C	6.39926100	-0.06177000	-2.69562100
H	5.24526800	0.51230500	-4.39003800
C	5.29875300	0.06676400	-0.55159900

H	3.28387600	0.73536300	-0.58427700
C	6.43063100	-0.24058200	-1.30744300
H	7.28256700	-0.28475600	-3.28144300
C	5.21709400	-0.10950400	0.92318100
C	6.28244800	-0.88211700	1.60764900
C	7.48266000	-1.25554800	0.99929100
C	6.04433900	-1.27102300	2.93062500
C	8.42296500	-2.00439300	1.71303800
C	6.96684900	-2.01617700	3.62900900
H	5.10419000	-0.97184700	3.37517200
C	8.16257000	-2.38309200	3.01269800
H	9.34736800	-2.29796700	1.23136400
H	6.76048200	-2.32775700	4.64354700
H	8.88850900	-2.98064900	3.54813400
O	4.26883700	0.32515100	1.54048600
S	7.92759000	-0.83048100	-0.63572300
H	3.09499700	-0.28316300	-4.89203400

down-down-down



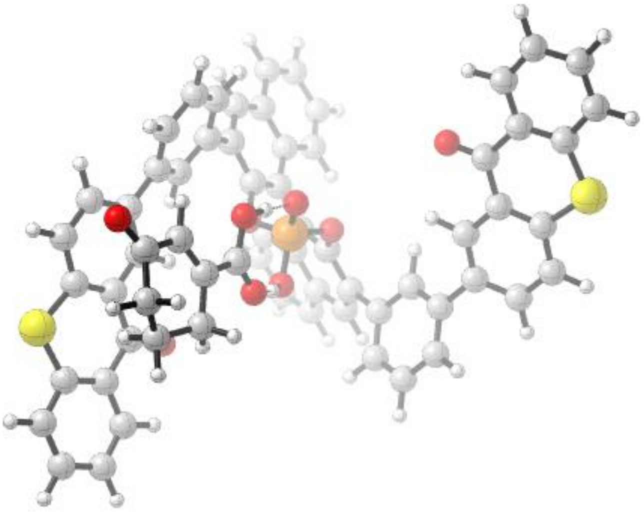
absolute free energy (ht): - 4315.764201
relative free energy (kJ·mol^{-1}): **+ 5.1**
face attacked: *Re*

C	1.59072000	3.73580700	-2.25360000
H	1.77526600	5.05899700	-3.90296800
C	1.34577000	4.90775200	-2.91969400
C	0.24504400	4.56062500	-0.36127000
C	0.51876400	5.91827400	-2.38273200
C	1.04190900	3.60994600	-0.95052200
C	-0.07646900	5.73586100	-1.10860000
C	0.23412200	7.09274900	-3.12251300
H	-1.49583500	6.56583400	0.29720500
C	-0.63211400	8.02998500	-2.63996300
H	0.70933800	7.22296000	-4.08730700
H	-0.84895400	8.92107600	-3.21409000
C	-1.26485700	7.82566800	-1.39532300

H	-1.97463300	8.55621200	-1.02988500
C	-0.99617900	6.71199900	-0.65016900
C	-0.99167800	3.14649500	1.24600800
C	-0.30839100	4.31146600	0.99677600
C	-1.45200100	3.74850900	3.49996500
C	-0.11495700	5.22617300	2.07835600
C	-1.58001100	2.82557300	2.49654700
C	-0.71869200	4.94356300	3.32993100
C	0.69412500	6.38433400	1.96723100
H	-1.02822500	5.62706900	5.34975200
H	-1.91135800	3.55250800	4.46165900
C	0.85338600	7.23173400	3.02747800
H	1.19819600	6.59048100	1.03327200
H	1.48106200	8.10717400	2.92428300
C	0.21409500	6.97294000	4.25840800
H	0.34386900	7.65718700	5.08644100
C	-0.54901100	5.85121700	4.40444500
O	-1.09887100	2.20721100	0.22515000
O	1.31263600	2.45216100	-0.23782800
P	0.18088900	1.34090700	-0.12745100
O	0.59938600	0.55076300	1.12430800
O	-0.04984700	0.55476700	-1.34865800
C	2.31352800	2.61914300	-2.90907300
C	2.04522400	2.33983500	-4.24960000
C	3.22476900	1.81467000	-2.22838400
C	2.67351800	1.28374300	-4.88943800
H	1.31083100	2.93163300	-4.78042300
C	3.83717900	0.73168600	-2.85359100
H	3.46607200	2.03241500	-1.19731300
C	3.55891000	0.47617900	-4.19553700
H	2.44277400	1.06790000	-5.92438500
C	-2.26248600	1.53005800	2.72298800
C	-2.03094800	0.82597900	3.90354600
C	-3.13267000	0.99024300	1.77948700
C	-2.66133100	-0.38788600	4.12992700
H	-1.32902000	1.21676800	4.62913000
C	-3.75286000	-0.23835500	1.98636500
H	-3.34298300	1.54103700	0.87293700
C	-3.51355700	-0.92267500	3.17755800
H	-2.46366600	-0.93397200	5.04294900
H	-3.97123300	-1.89025000	3.34062700
H	0.77587300	-0.42759600	0.93802600
C	3.10960300	-3.69824200	-2.09286400
C	2.48540300	-3.39759000	-0.76100600
C	2.69695000	-4.13351800	0.33338500
C	3.61067900	-5.30519800	0.32728400
C	4.40416300	-5.51940900	-0.94019400
C	3.58616500	-5.14457700	-2.17287200
H	3.95075300	-3.00777600	-2.24054400
H	2.39594300	-3.47418400	-2.88549100
H	4.75067100	-6.55162400	-0.95799300
H	5.28817900	-4.87273100	-0.87745900
H	2.71632200	-5.80350200	-2.24254300
H	4.17611600	-5.29477300	-3.07721200
C	1.60591400	-2.19282200	-0.62696500
O	1.12765900	-1.86427400	0.44677000
O	1.42229900	-1.54860400	-1.74941800
H	0.82674400	-0.74278700	-1.62537700
O	3.71180000	-6.01936900	1.29609700
H	2.22075400	-3.88075000	1.27329000
C	-4.62557600	-0.81274000	0.93866400
C	-5.77574600	-1.50954400	1.25743600

C	-4.29097400	-0.67282200	-0.41771300
C	-6.60176400	-2.06523500	0.27494200
H	-6.08478500	-1.63099600	2.28774100
C	-5.08775400	-1.20908300	-1.40181200
H	-3.37834300	-0.15794400	-0.69487200
C	-6.25312100	-1.90974600	-1.06713900
H	-4.81042000	-1.10118900	-2.44314300
C	-7.81197000	-2.79058800	0.73724900
C	-8.72092200	-3.40064600	-0.26660700
C	-8.51572200	-3.33687600	-1.64592600
C	-9.84740300	-4.07808300	0.21722300
C	-9.42974900	-3.94418700	-2.51660200
C	-10.74473100	-4.67461300	-0.63898800
H	-9.98172100	-4.11236600	1.29001900
C	-10.53015600	-4.60446000	-2.01688100
H	-9.26222700	-3.88915600	-3.58520600
H	-11.60933100	-5.19388900	-0.24849300
H	-11.22847200	-5.06954900	-2.70067400
S	-7.17054600	-2.53592100	-2.40643700
O	-8.05557600	-2.88724700	1.92295100
C	4.71550800	-0.17732600	-2.08637500
C	5.84436500	-0.76930000	-2.67100100
C	4.41337700	-0.51168100	-0.77740200
C	6.61549800	-1.67310800	-1.97427400
H	6.11963100	-0.50735600	-3.68505300
C	5.17241400	-1.43445900	-0.05491000
H	3.54904100	-0.08561000	-0.27957600
C	6.27907200	-2.02885900	-0.66246700
H	7.48356600	-2.12165800	-2.44162300
C	4.71216000	-1.75751700	1.32202600
C	5.29216700	-2.93709200	2.00847200
C	6.40739300	-3.63646900	1.54255500
C	4.65662800	-3.37543200	3.17563600
C	6.87137600	-4.75443100	2.24202600
C	5.10901200	-4.48136800	3.85821200
H	3.79237600	-2.81718400	3.51084300
C	6.22361600	-5.17257400	3.38495100
H	7.73108400	-5.29748900	1.86963500
H	4.59575300	-4.82126300	4.74701100
H	6.57896500	-6.05175500	3.90599600
O	3.84078200	-1.09787500	1.84651500
S	7.31252100	-3.19937000	0.11328900
H	4.00261200	-0.38326800	-4.68258800

down-up-up



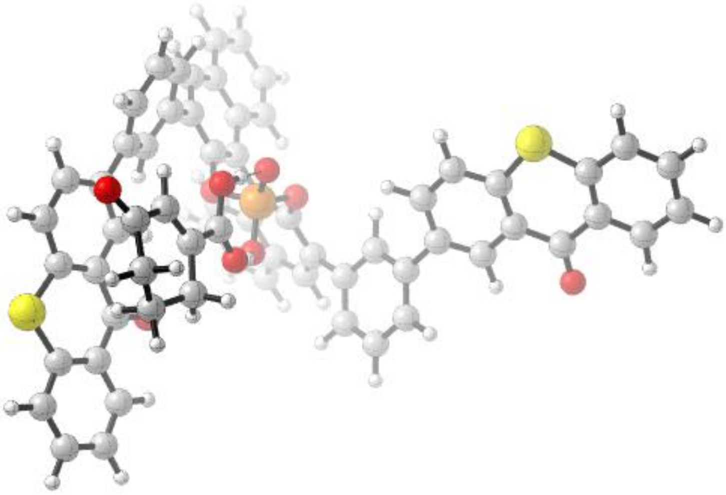
absolute free energy (ht): - 4315.762703
relative free energy (kJ·mol^{-1}): **+ 9.0**
face attacked: *Si*

C	0.05050000	2.72967200	-2.86586700
H	-0.39261700	3.45640500	-4.80925600
C	-0.60398200	3.54544300	-3.75008000
C	-1.16227800	3.80442000	-1.01175700
C	-1.57695100	4.47916600	-3.33001900
C	-0.23709100	2.91006500	-1.48843800
C	-1.89496000	4.59201300	-1.95240400
C	-2.27763100	5.27173700	-4.27238300
H	-3.24168600	5.51530000	-0.53391900
C	-3.27411200	6.11457200	-3.87410600
H	-2.01355400	5.18287100	-5.31926400
H	-3.80823400	6.71147900	-4.60152100
C	-3.62424700	6.19207300	-2.50939800
H	-4.43484200	6.83927300	-2.20098100
C	-2.95566400	5.45256900	-1.57460100
C	-1.72830400	2.71709600	1.13485600
C	-1.41964900	3.86807400	0.45121800
C	-1.97535700	3.86542800	3.20562800
C	-1.30607200	5.08497800	1.19253400
C	-2.02321000	2.68112900	2.52118700
C	-1.60688700	5.07612900	2.57823100
C	-0.85623600	6.29576100	0.60909300
H	-1.75467100	6.25776100	4.37380300
H	-2.21642300	3.87667200	4.26222400
C	-0.75465400	7.43692400	1.35405000
H	-0.58099600	6.30891100	-0.43637100
H	-0.40244900	8.34947800	0.89120700
C	-1.09683700	7.43596200	2.72295500
H	-1.01806700	8.34918900	3.29790900
C	-1.50802900	6.27941800	3.31915600
O	-1.73723300	1.50701100	0.44984900
O	0.43096000	2.11611000	-0.56812700

P	-0.34902600	0.86530600	0.03248600
O	0.43160300	0.54790200	1.32302400
O	-0.53740700	-0.24912900	-0.90465300
C	0.93918200	1.63996700	-3.33369800
C	0.52943300	0.85037100	-4.40742100
C	2.14996100	1.35069900	-2.71004200
C	1.31465800	-0.20573900	-4.84128300
H	-0.42808600	1.04152300	-4.87443900
C	2.93263500	0.27461900	-3.11974400
H	2.49019000	1.97310100	-1.89371100
C	2.50496000	-0.50003200	-4.19804300
H	0.97742000	-0.82574600	-5.66138800
C	-2.35041800	1.40962000	3.20780800
C	-1.73025100	1.09629900	4.41529100
C	-3.28806400	0.52694400	2.67879300
C	-2.04694200	-0.08014600	5.07687100
H	-0.97808500	1.76358100	4.81656600
C	-3.61431300	-0.65681800	3.33455800
H	-3.78852400	0.77567200	1.75199100
C	-2.98141400	-0.95196700	4.54261400
H	-1.54673900	-0.32782000	6.00396900
H	-3.19911100	-1.88424300	5.04854900
H	0.94359200	-0.31687800	1.25773200
C	3.87724900	-3.45357100	1.00591000
C	3.24315400	-3.02745500	-0.28498900
C	3.70024600	-3.38019800	-1.48855100
C	4.87908400	-4.26688900	-1.64648600
C	5.39243500	-4.91938100	-0.38362800
C	5.29805000	-3.96635500	0.80512100
H	3.24544500	-4.22681000	1.45848700
H	3.85524200	-2.61109400	1.69991600
H	6.40970500	-5.26324800	-0.56416600
H	4.76682000	-5.80182800	-0.20496900
H	5.95795700	-3.11571000	0.62431800
H	5.65431600	-4.45337300	1.71326400
C	2.05799700	-2.11943400	-0.17215200
O	1.76649900	-1.62722400	0.90825700
O	1.41194800	-1.91349000	-1.28439200
H	0.62932500	-1.28634500	-1.15723400
O	5.36853000	-4.46166300	-2.73422000
H	3.22792800	-3.02513800	-2.39612400
C	-4.61110700	-1.58475500	2.75466500
C	-4.69782700	-1.78386000	1.38822300
C	-5.49835300	-2.29113800	3.58037900
C	-5.63297700	-2.65870200	0.82597900
H	-4.02266500	-1.27964400	0.70734700
C	-6.42381600	-3.16008900	3.05156300
H	-5.46989100	-2.13534000	4.65159800
C	-6.49978300	-3.35650500	1.66758200
H	-7.10557400	-3.69227600	3.70349600
C	-5.63719200	-2.78709700	-0.65481100
C	-6.58128200	-3.73691800	-1.29916700
C	-7.51070900	-4.50914700	-0.60099400
C	-6.52221100	-3.84957500	-2.69377900
C	-8.36333000	-5.37498600	-1.29716300
C	-7.35911900	-4.70222300	-3.37735200
H	-5.79239500	-3.23958700	-3.20905200
C	-8.28632200	-5.46890200	-2.66922600
H	-9.08171100	-5.96979900	-0.74662500
H	-7.29945800	-4.77827300	-4.45453100
H	-8.95014500	-6.14289100	-3.19513300
S	-7.71080100	-4.48441600	1.12857000

O	-4.87900900	-2.12450600	-1.33061000
C	4.16149300	-0.08289000	-2.37870600
C	5.25504000	-0.67118500	-3.03147600
C	4.24497200	0.09506600	-1.00883300
C	6.37968300	-1.05155000	-2.33743200
H	5.22274200	-0.82366200	-4.10257300
C	5.37275500	-0.29199900	-0.27801800
H	3.41575600	0.51014500	-0.44689800
C	6.45484200	-0.85935700	-0.95338900
H	7.21060700	-1.50889500	-2.85987600
C	5.32309700	-0.10838300	1.19444900
C	6.46870600	-0.56996200	2.02130600
C	7.64596100	-1.10742800	1.49662900
C	6.34582400	-0.44121700	3.41078700
C	8.67886700	-1.49904400	2.35762500
C	7.35966800	-0.83132100	4.25606600
H	5.42369700	-0.02064800	3.78922300
C	8.53517300	-1.36148000	3.72068300
H	9.58833800	-1.91457200	1.94147100
H	7.24831400	-0.72631200	5.32668100
H	9.34021400	-1.66996200	4.37502100
O	4.35149500	0.39404600	1.72009600
S	7.94475700	-1.35635500	-0.20099100
H	3.08306500	-1.36207600	-4.50732900

down-up-down



absolute free energy (ht): - 4315.764797
relative free energy (kJ·mol^{-1}): **+ 3.5**
face attacked: *Si*

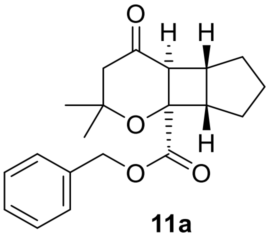
C	1.50916500	3.44834400	-2.38367700
H	1.68545700	4.66825700	-4.11095400
C	1.25620500	4.57498100	-3.12030600
C	0.15234000	4.37336500	-0.54656100
C	0.42270000	5.61099300	-2.64422600
C	0.95556400	3.39539900	-1.07813700

C	-0.17151900	5.50268100	-1.36094100
C	0.13283000	6.73818300	-3.45210700
H	-1.59164700	6.40997800	-0.00484800
C	-0.73618900	7.69961200	-3.02506500
H	0.60678800	6.81255600	-4.42338700
H	-0.95641400	8.55428800	-3.65095300
C	-1.36687700	7.56794800	-1.76971900
H	-2.07841200	8.31685600	-1.44740900
C	-1.09371900	6.50133800	-0.96004100
C	-1.08640000	3.04570300	1.13430500
C	-0.40365700	4.19606600	0.82166900
C	-1.55608600	3.77658200	3.34866000
C	-0.21240100	5.16941200	1.85106600
C	-1.68319600	2.79941100	2.39774000
C	-0.81860200	4.95802200	3.11523900
C	0.59720000	6.31933500	1.67631400
H	-1.13242100	5.75442300	5.09265400
H	-2.02289000	3.63717700	4.31659900
C	0.75507100	7.22486200	2.68763200
H	1.10306300	6.47239900	0.73316500
H	1.38332200	8.09289600	2.53648700
C	0.11327000	7.03595700	3.93000400
H	0.24146100	7.76583200	4.71838200
C	-0.65071900	5.92451900	4.13739400
O	-1.19613200	2.05036300	0.16871500
O	1.21819500	2.27643500	-0.30066400
P	0.07659000	1.17559200	-0.18188600
O	0.47922700	0.38362700	1.07620900
O	-0.15720600	0.38649300	-1.39996300
C	2.24836700	2.30011400	-2.95976400
C	1.97476500	1.90630000	-4.26956100
C	3.18243100	1.57613400	-2.22345700
C	2.62099500	0.81276000	-4.82352100
H	1.22457500	2.43816200	-4.84046500
C	3.81265100	0.45621400	-2.75916200
H	3.42545400	1.88802100	-1.21717500
C	3.52816200	0.08386200	-4.07265700
H	2.38808400	0.50530100	-5.83447100
C	-2.38511300	1.52798900	2.69156100
C	-2.17377000	0.88872700	3.91199400
C	-3.26243400	0.95304100	1.77578200
C	-2.83208200	-0.29578400	4.20502900
H	-1.46786700	1.30691400	4.61821800
C	-3.91245500	-0.24627300	2.05108400
H	-3.45681500	1.45491900	0.83776300
C	-3.69357800	-0.86512100	3.28143600
H	-2.65125100	-0.79157400	5.14973400
H	-4.17613300	-1.80964400	3.49900600
H	0.77973700	-0.55368700	0.86577800
C	2.90480900	-4.25025500	0.21668900
C	2.70717400	-3.36516900	-0.97819900
C	3.35769600	-3.52168700	-2.13326000
C	4.32543300	-4.62680300	-2.34094300
C	4.37110900	-5.68071600	-1.25882400
C	4.19414300	-5.05716700	0.12345500
H	2.03634200	-4.91434500	0.29844100
H	2.88902000	-3.63162600	1.11611100
H	5.30660500	-6.22978500	-1.35357100
H	3.55057800	-6.37928300	-1.46069600
H	5.03976900	-4.39492700	0.31930500
H	4.21238200	-5.82787900	0.89441800
C	1.75364700	-2.22406600	-0.80914400

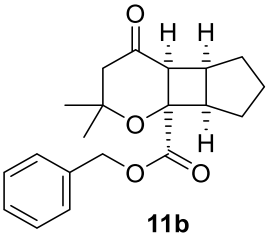
O	1.33014800	-1.93697400	0.30047900
O	1.44587500	-1.59483600	-1.90935800
H	0.80766200	-0.83229000	-1.73992200
O	5.00918000	-4.67337600	-3.33631900
H	3.20596500	-2.84058400	-2.96147700
C	-4.79854400	-0.85784200	1.03612000
C	-5.96894800	-1.50090600	1.39203300
C	-4.45886000	-0.80709500	-0.32522900
C	-6.81007700	-2.08847100	0.44141700
H	-6.28282600	-1.55206800	2.42675600
C	-5.26942800	-1.37737400	-1.27844800
H	-3.53248500	-0.33401100	-0.62985200
C	-6.45535400	-2.02277100	-0.90651100
H	-4.98813700	-1.33824100	-2.32355700
C	-8.04297000	-2.74709000	0.94199700
C	-8.97550000	-3.37569800	-0.02802400
C	-8.76634700	-3.40034900	-1.40803700
C	-10.12967000	-3.97674800	0.49031800
C	-9.70323400	-4.01988000	-2.24513400
C	-11.04991200	-4.58447600	-0.33302900
H	-10.26654100	-3.94292400	1.56280200
C	-10.83063000	-4.60406300	-1.71187000
H	-9.53242000	-4.03406500	-3.31452600
H	-11.93609400	-5.04342400	0.08377600
H	-11.54668200	-5.07892300	-2.37010900
S	-7.38861900	-2.70075400	-2.20905400
O	-8.28677100	-2.77288000	2.13138300
C	4.71168300	-0.36612300	-1.92129100
C	5.80072300	-1.05123800	-2.47975800
C	4.46301500	-0.53612900	-0.57071700
C	6.60519400	-1.85850900	-1.70961700
H	6.02227600	-0.94053800	-3.53348200
C	5.25636000	-1.36213300	0.23119500
H	3.61306800	-0.06022600	-0.09429800
C	6.34655400	-2.01801000	-0.34351700
H	7.43935800	-2.38136200	-2.16059300
C	4.85027400	-1.52131300	1.65054900
C	5.60501400	-2.46294200	2.51757800
C	6.75169900	-3.14991800	2.11328400
C	5.12780500	-2.65314800	3.82075800
C	7.40647100	-4.00338300	3.00999400
C	5.76892800	-3.49700700	4.69913700
H	4.23840600	-2.10764100	4.10690500
C	6.91899800	-4.17309400	4.28725700
H	8.29532900	-4.53173700	2.68791400
H	5.38669500	-3.63427700	5.70146300
H	7.43280900	-4.83783800	4.96954400
O	3.89924200	-0.90968500	2.09092400
S	7.45710700	-3.04136600	0.52397100
H	3.98506700	-0.80299600	-4.49451000

8. Chiral HPLC Traces

Benzyl-(4a*S*,4b*R*,7a*S*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylate (11a) and benzyl-(4a*S*,4b*S*,7a*R*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylate (11b)

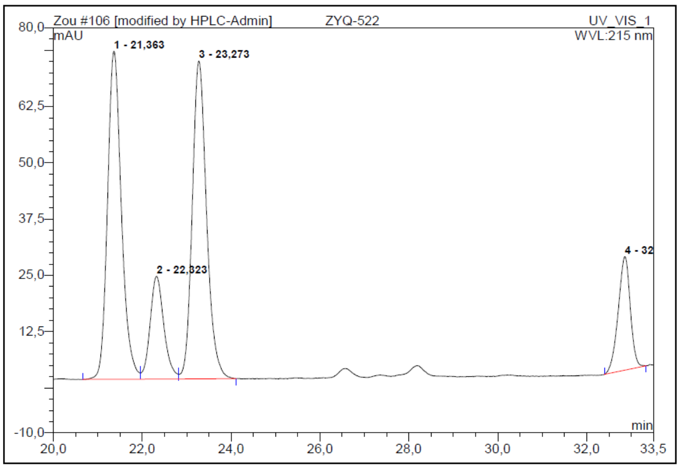


11a



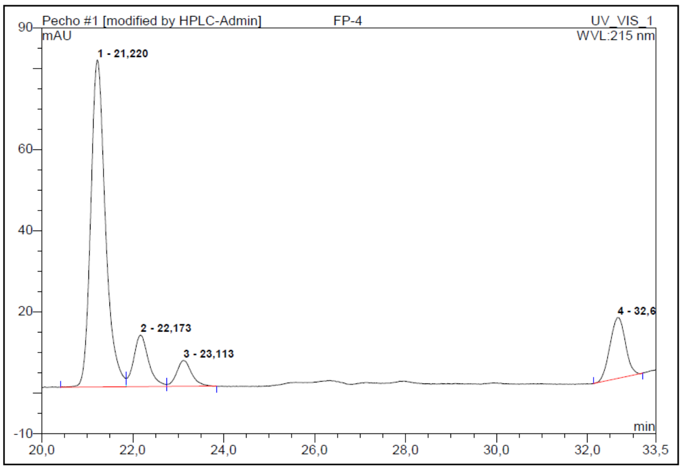
11b

*Racemic product rac-***11a** *and rac-***11b**



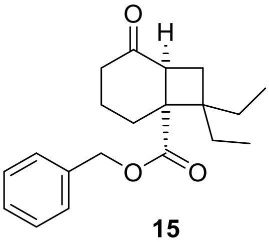
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21,36	n.a.	72,913	26,403	38,27	n.a.	BM *
2	22,32	n.a.	22,862	8,252	11,96	n.a.	M *
3	23,27	n.a.	70,635	26,399	38,27	n.a.	MB*
4	32,86	n.a.	25,220	7,929	11,49	n.a.	BMB*
Total:			191,631	68,983	100,00	0,000	

Enantioenriched product **11a** [e.r. = 93:7 (85% *ee*)] *and* **11b** [e.r. = 55:45 (10% *ee*)]

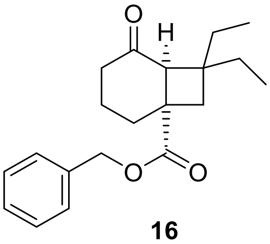


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21,22	n.a.	80,545	30,145	69,62	n.a.	BM *
2	22,17	n.a.	12,686	4,832	11,16	n.a.	M *
3	23,11	n.a.	6,371	2,425	5,60	n.a.	MB*
4	32,66	n.a.	15,003	5,899	13,62	n.a.	BMB*
Total:			114,605	43,301	100,00	0,000	

Benzyl-(1*R*,6*S*)-8,8-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (15) and benzyl-(1*S*,6*S*)-7,7-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (16)

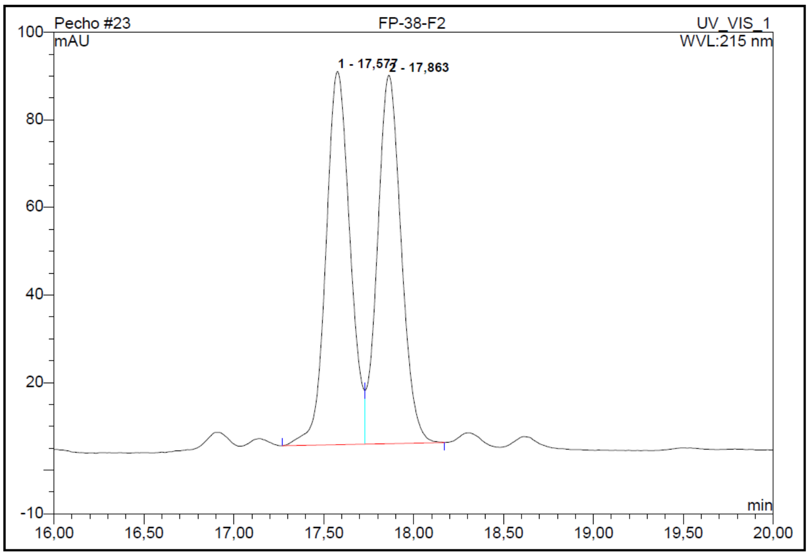


15



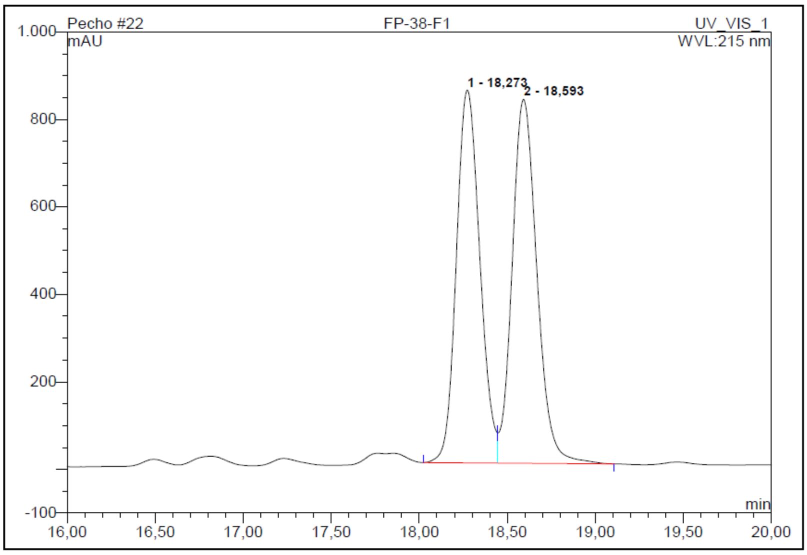
16

*Racemic product rac-***15**



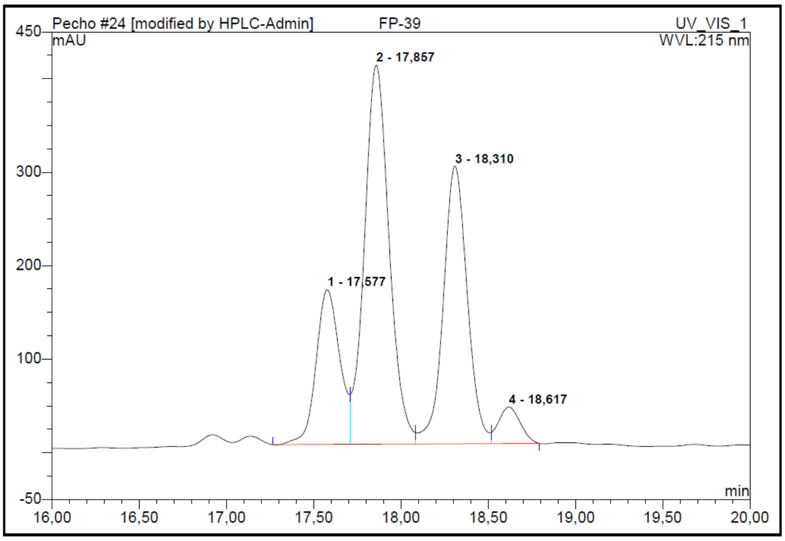
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17,58	n.a.	85,289	13,238	50,63	n.a.	BM
2	17,86	n.a.	84,168	12,908	49,37	n.a.	MB
Total:			169,457	26,146	100,00	0,000	

*Racemic product rac-***16**



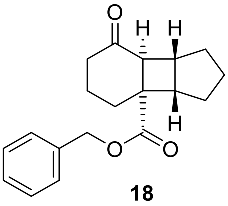
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18,27	n.a.	852,565	131,744	49,29	n.a.	BM
2	18,59	n.a.	832,156	135,540	50,71	n.a.	MB
Total:			1684,721	267,284	100,00	0,000	

Enantioenriched products **15** [e.r. = 72:28 (44% *ee*)] *and* **16** [e.r. = 89:11 (79% *ee*)]



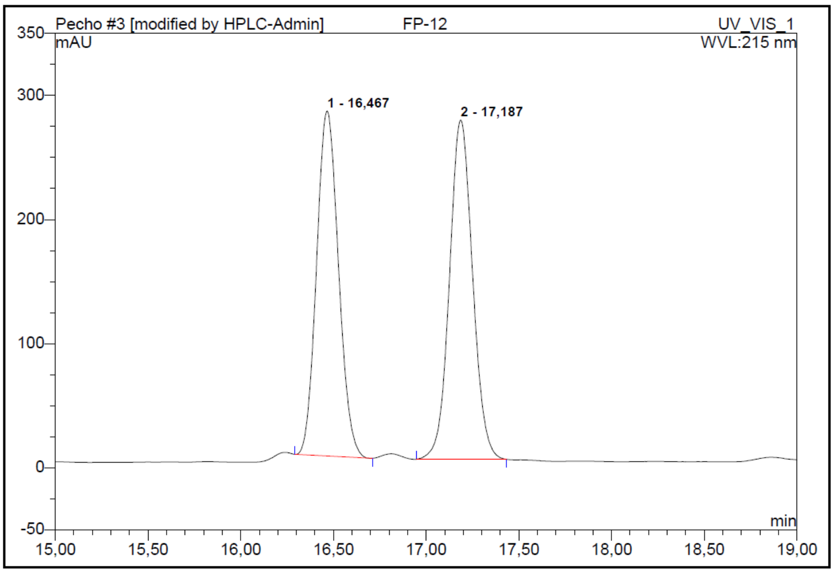
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17,58	n.a.	165,423	25,984	17,81	n.a.	BM *
2	17,86	n.a.	405,361	66,881	45,84	n.a.	M *
3	18,31	n.a.	296,891	47,394	32,48	n.a.	M *
4	18,62	n.a.	39,003	5,653	3,87	n.a.	MB*
Total:			906,678	145,912	100,00	0,000	

Benzyl-(3a*S*,3b*S*,7a*S*,7b*R*)-7-oxodecahydro-3b*H*-cyclopenta[3,4]cyclobuta[1,2]benzene-3b-carboxylate (18)



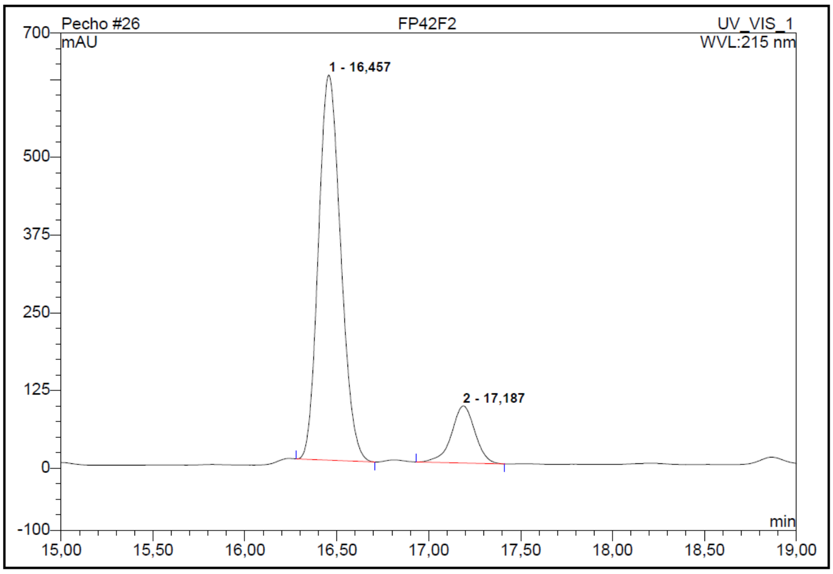
18

Racemic product rac-**18**



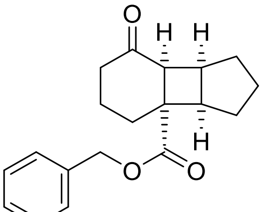
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,47	n.a.	278,128	38,104	49,09	n.a.	BMB*
2	17,19	n.a.	273,475	39,518	50,91	n.a.	BMB*
Total:			551,603	77,622	100,00	0,000	

Enantioenriched product **18** [e.r. = 86:14 (73% ee)]



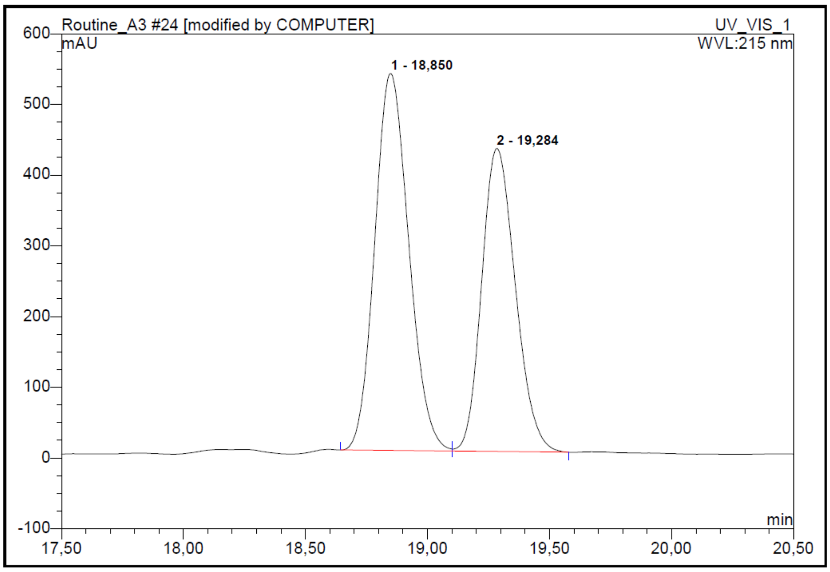
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,46	n.a.	620,203	87,301	86,48	n.a.	BMB
2	17,19	n.a.	91,739	13,645	13,52	n.a.	BMB
Total:			711,941	100,947	100,00	0,000	

Benzyl-(3a*R*,3b*S*,7a*S*,7b*S*)-7-oxodecahydro-3b*H*-cyclopenta-[3,4]cyclobuta[1,2]benzene-3b-carboxylate (S9)



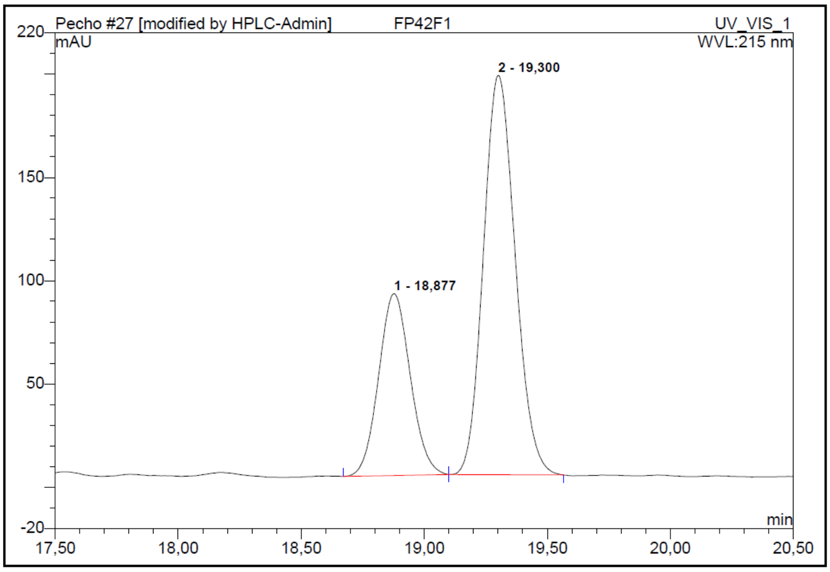
S9

*Racemic product rac-***S9**



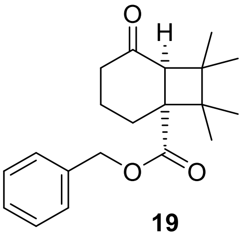
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18,85	n.a.	533,259	86,261	55,74	n.a.	BM *
2	19,28	n.a.	428,713	68,507	44,26	n.a.	MB*
Total:			961,972	154,767	100,00	0,000	

Enantioenriched product **S9** [e.r. = 69:31 (38% *ee*)]



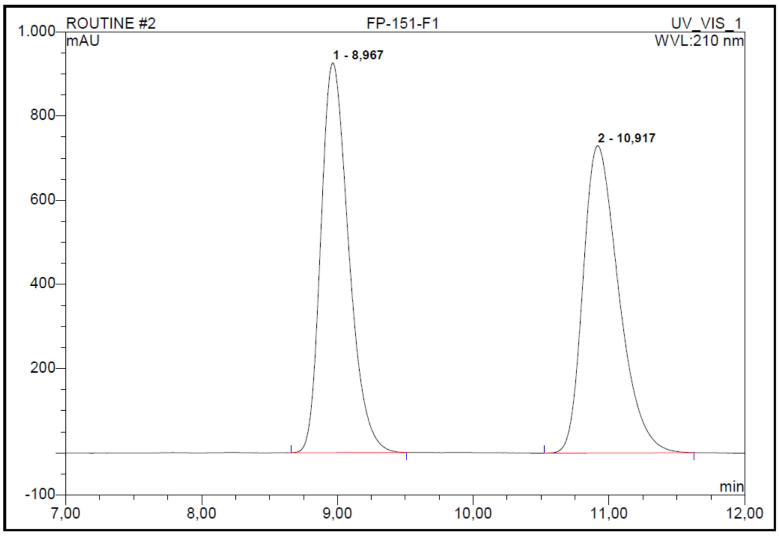
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18,88	n.a.	88,063	13,138	31,19	n.a.	BMb*
2	19,30	n.a.	193,424	28,981	68,81	n.a.	bMB*
Total:			281,487	42,118	100,00	0,000	

Benzyl-(1*R*,6*S*)-7,7,8,8-tetramethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (19)



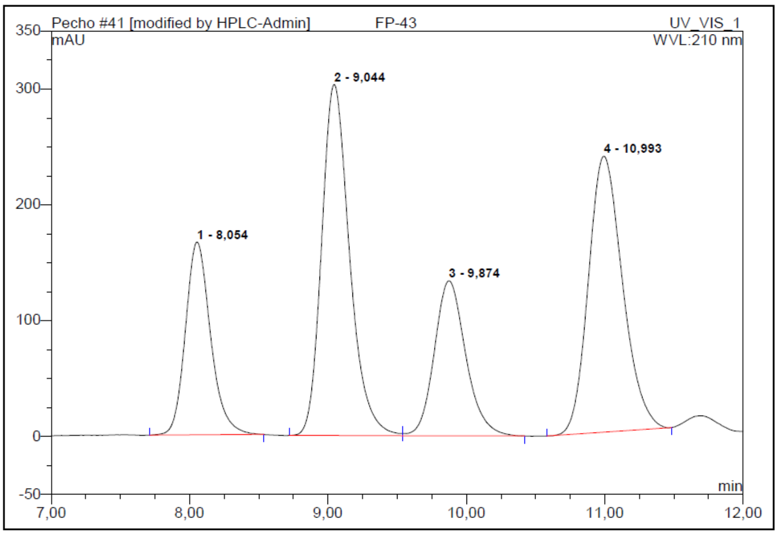
19

*Racemic product rac-**19***



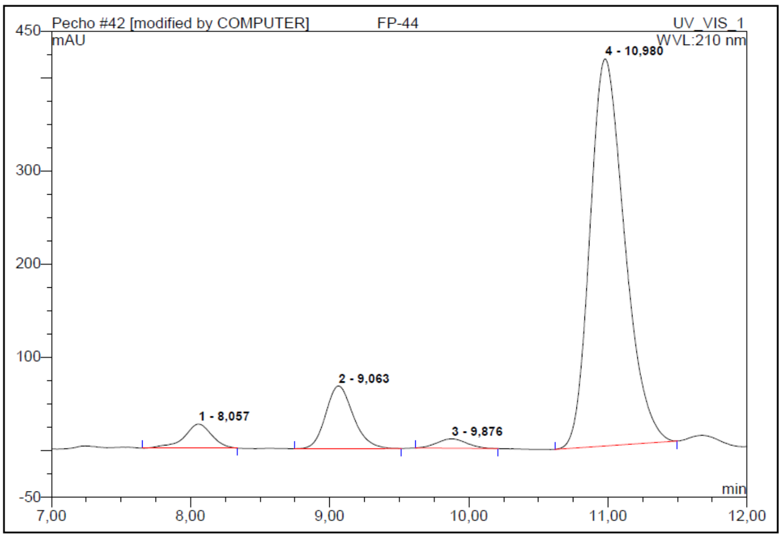
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,97	n.a.	925,292	219,611	49,71	n.a.	BMB
2	10,92	n.a.	729,483	222,133	50,29	n.a.	BMB
Total:			1654,775	441,744	100,00	0,000	

*Racemic product rac-**19** and oxetane side product*



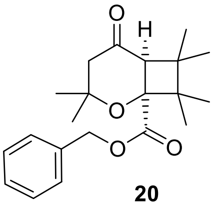
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,05	n.a.	166,453	35,111	16,75	n.a.	BMB*
2	9,04	n.a.	303,049	71,013	33,88	n.a.	BM *
3	9,87	n.a.	133,828	35,353	16,87	n.a.	MB*
4	10,99	n.a.	238,240	68,146	32,51	n.a.	BMB*
Total:			841,570	209,622	100,00	0,000	

Enantioenriched product ***19*** [e.r. = 89:11 (77% *ee*)] *and oxetane side product*



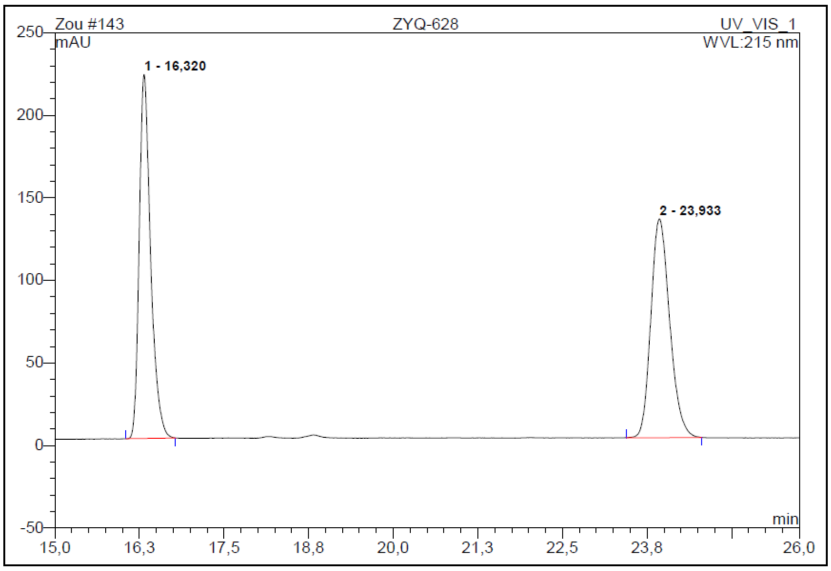
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,06	n.a.	25,683	5,929	4,11	n.a.	BMB*
2	9,06	n.a.	67,295	15,508	10,76	n.a.	BMB
3	9,88	n.a.	10,091	2,500	1,73	n.a.	BMB*
4	10,98	n.a.	415,257	120,183	83,39	n.a.	BMB
Total:			518,326	144,120	100,00	0,000	

Benzyl-(1*S*,6*S*)-3,3,7,7,8,8-hexamethyl-5-oxo-2-oxabicyclo[4.2.0]octane-1-carboxylate (20)



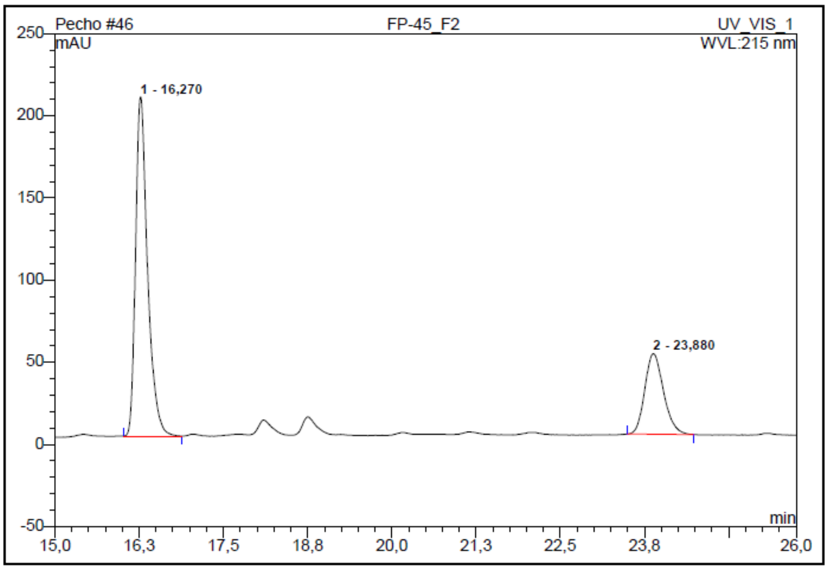
20

*Racemic product rac-***20**



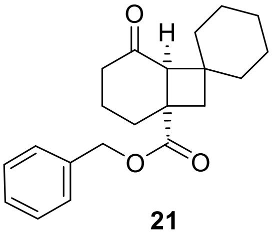
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,32	n.a.	220,495	43,112	50,20	n.a.	BMB
2	23,93	n.a.	132,501	42,777	49,80	n.a.	BMB
Total:			352,996	85,890	100,00	0,000	

Enantioenriched product **20** [e.r. = 73:27 (46% *ee*)]

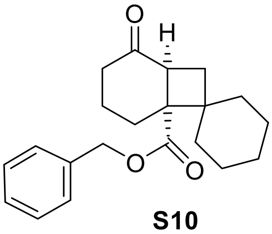


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,27	n.a.	206,404	42,436	72,82	n.a.	BMB
2	23,88	n.a.	48,915	15,842	27,18	n.a.	BMB
Total:			255,319	58,278	100,00	0,000	

Benzyl-(1*S*,6*S*)-5-oxospiro[bicyclo[4.2.0]octane-7,1'-cyclohexane]-1-carboxylate (21) and benzyl-(1*S*,6*R*)-2-oxospiro[bicyclo[4.2.0]octane-7,1'-cyclohexane]-6-carboxylate (S10)

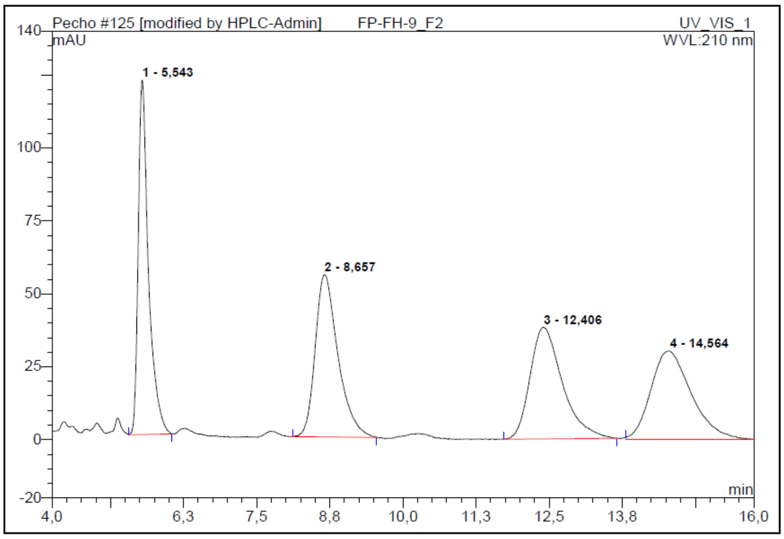


21



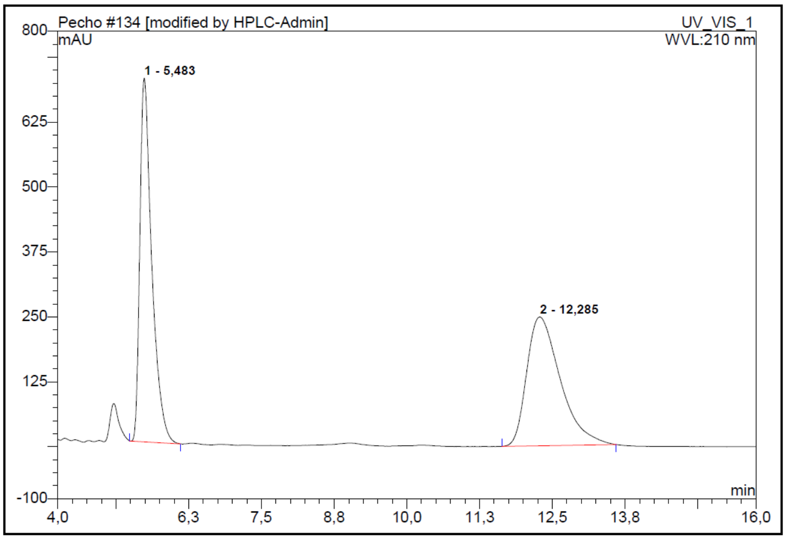
S10

*Racemic products rac-**21** and rac-**S10***



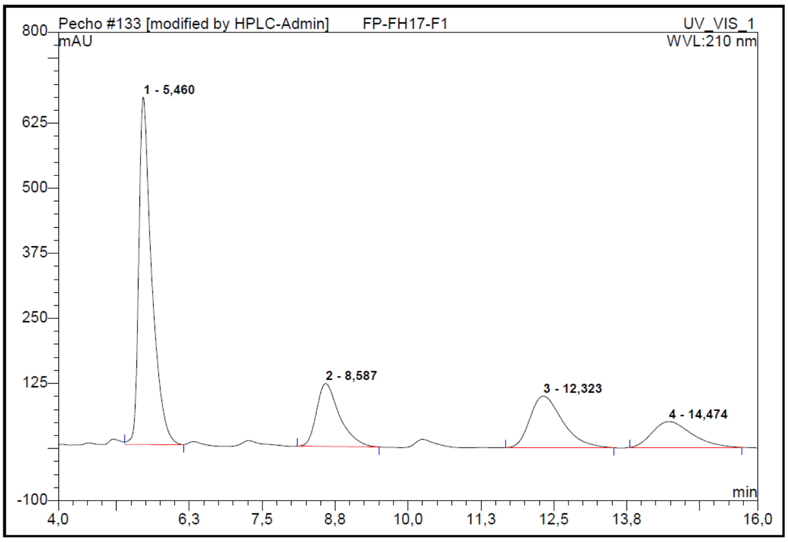
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5,54	n.a.	121,423	24,668	25,05	n.a.	BMB
2	8,66	n.a.	55,626	25,106	25,50	n.a.	BMB
3	12,41	n.a.	38,287	24,569	24,95	n.a.	BMB*
4	14,56	n.a.	30,211	24,131	24,51	n.a.	MB*
Total:			245,547	98,473	100,00	0,000	

*Racemic product rac-**21***



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5,48	n.a.	700,003	166,652	50,10	n.a.	BMB*
2	12,29	n.a.	247,917	165,956	49,90	n.a.	BMB*
Total:			947,920	332,607	100,00	0,000	

Enantioenriched products **21** [e.r. = 73:27 (45% *ee*)] *and* **S10** [e.r. = 58:42 (17% *ee*)]

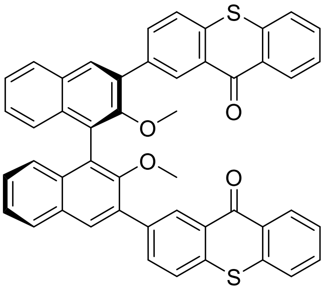


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5,46	n.a.	667,332	171,369	51,94	n.a.	MB*
2	8,59	n.a.	120,808	55,097	16,70	n.a.	BMB*
3	12,32	n.a.	99,385	64,347	19,50	n.a.	BMB
4	14,47	n.a.	49,640	39,134	11,86	n.a.	BMB
Total:			937,166	329,947	100,00	0,000	

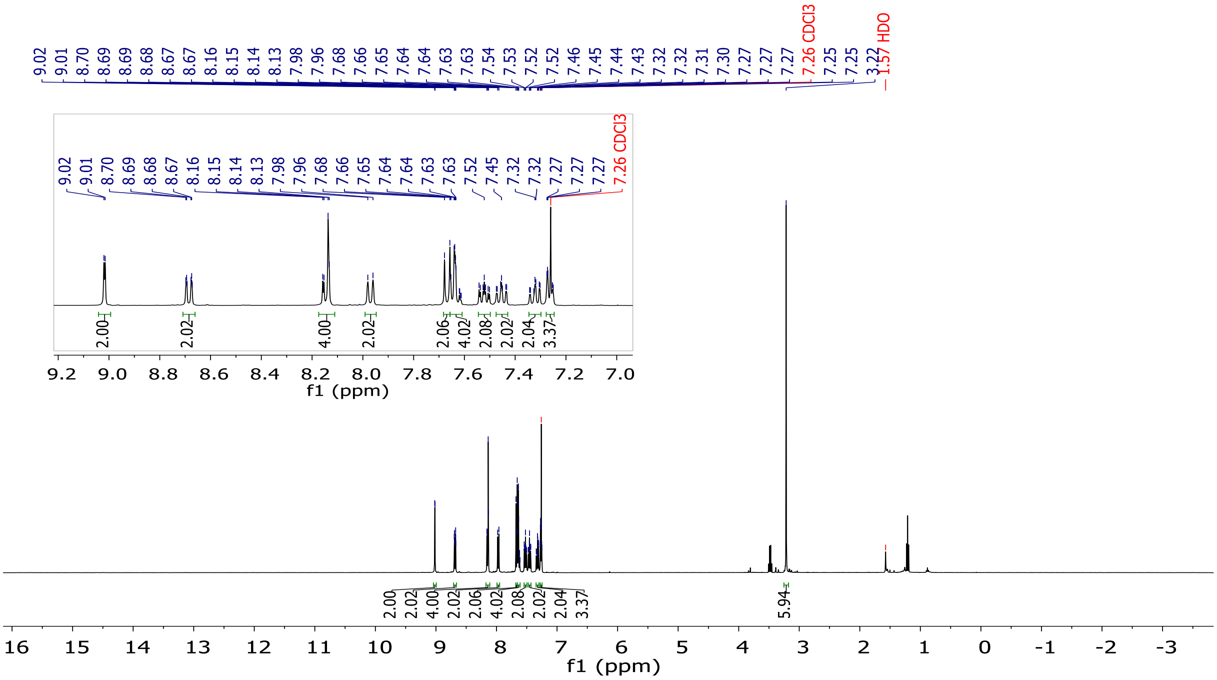
9. NMR Spectra of New Compounds

9.1. NMR Spectra of Catalysts

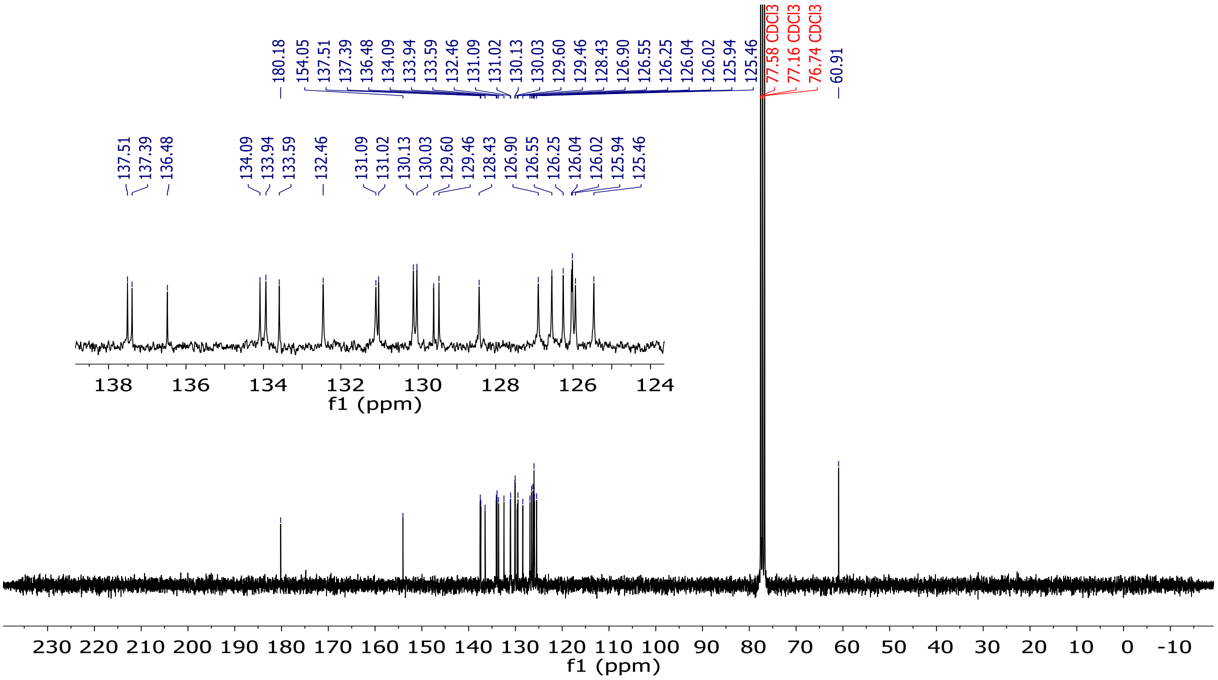
(*R*)-2,2'-(2,2'-Dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)bis(9*H*-thioxanthen-9-one) (S3)



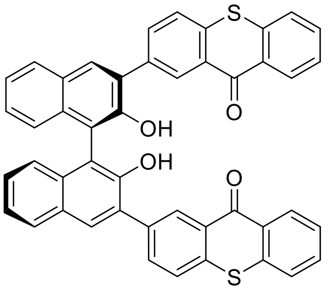
^{1}H NMR (400 MHz, CDCl$_3$):



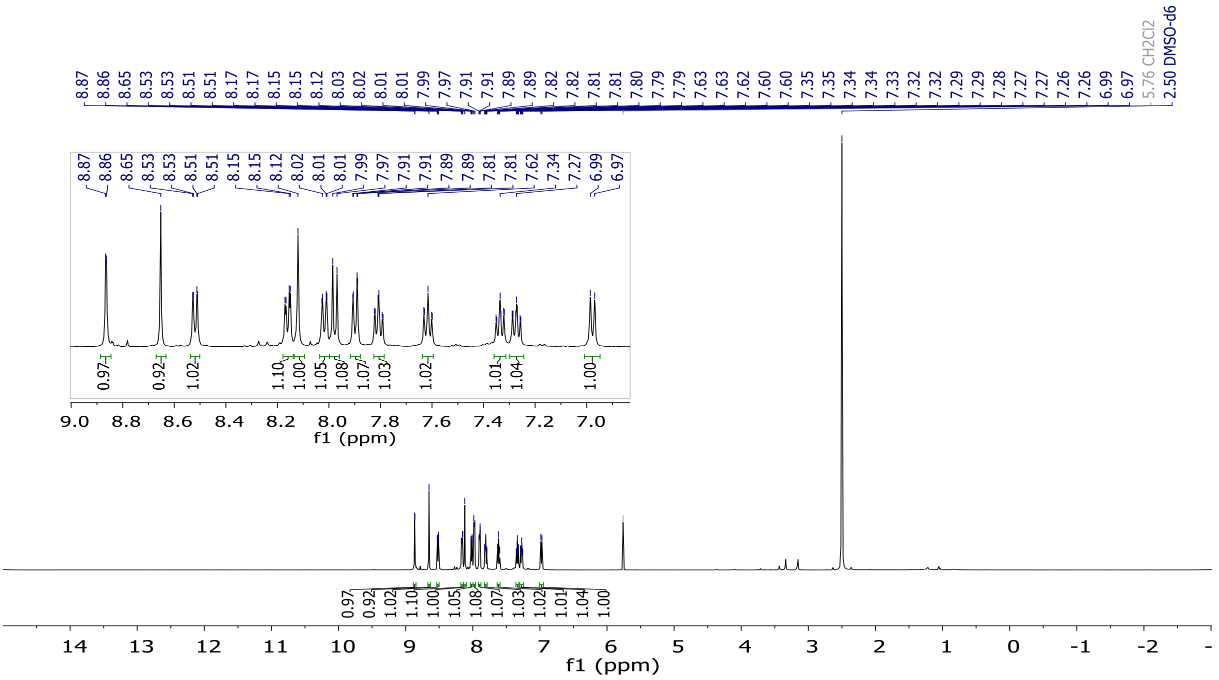
^{13}**C NMR** (75 MHz, $CDCl_3$):



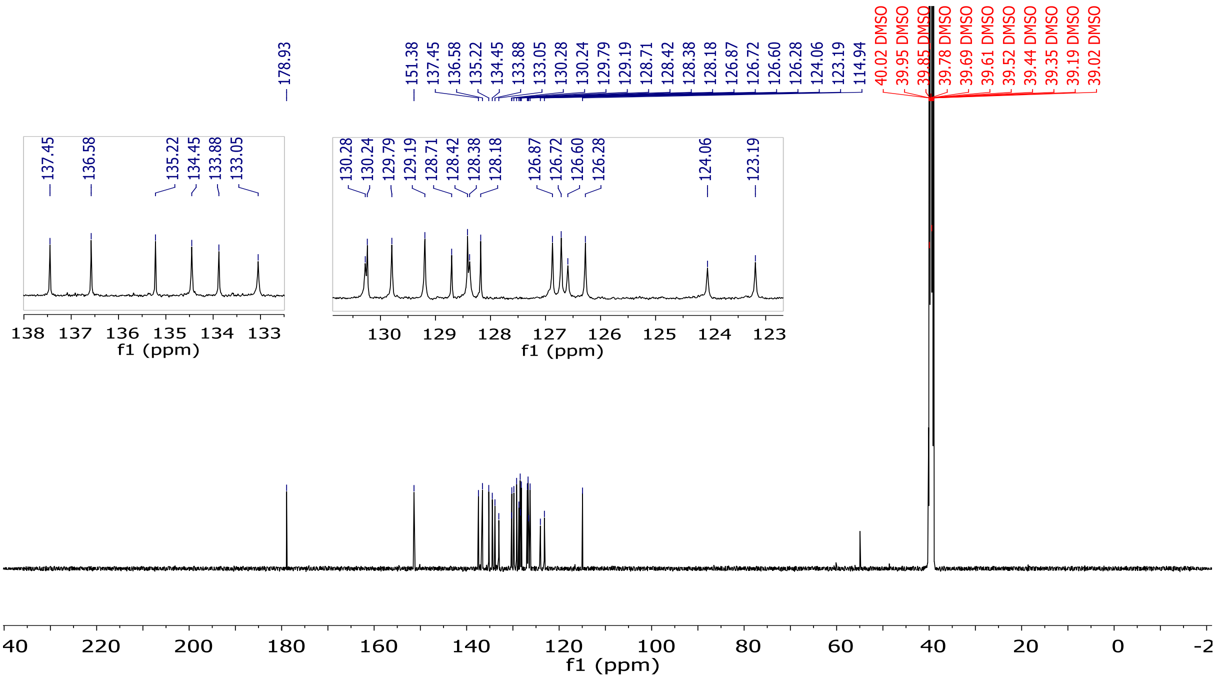
(*R*)-2,2'-(2,2'-Dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(9*H*-thioxanthen-9-one) (S4)



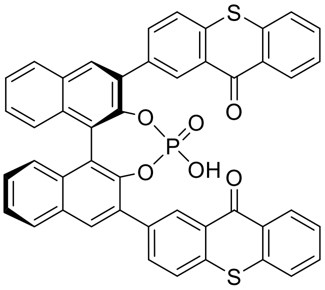
^{1}H NMR (500 MHz, DMSO-d_6):



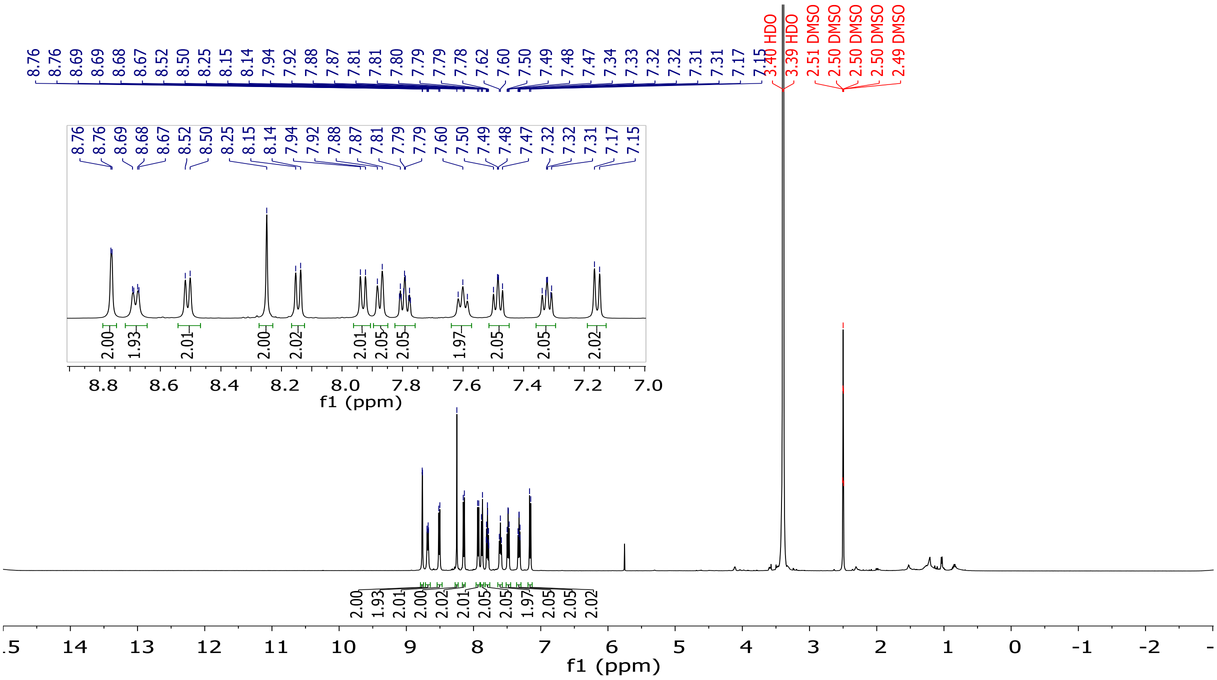
^{13}C NMR (75 MHz, DMSO-d_6):



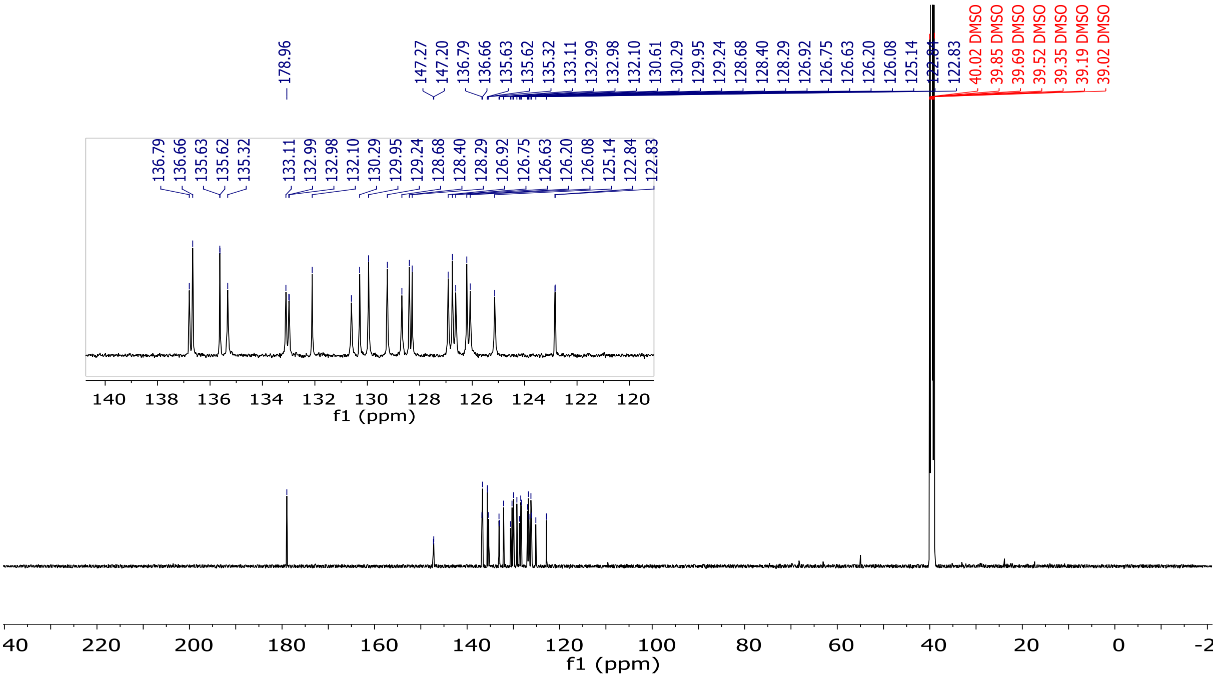
(*R*)-2,2'-(4-Hydroxy-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-2,6-diyl)bis(9*H*-thioxanthen-9-one) (S5)



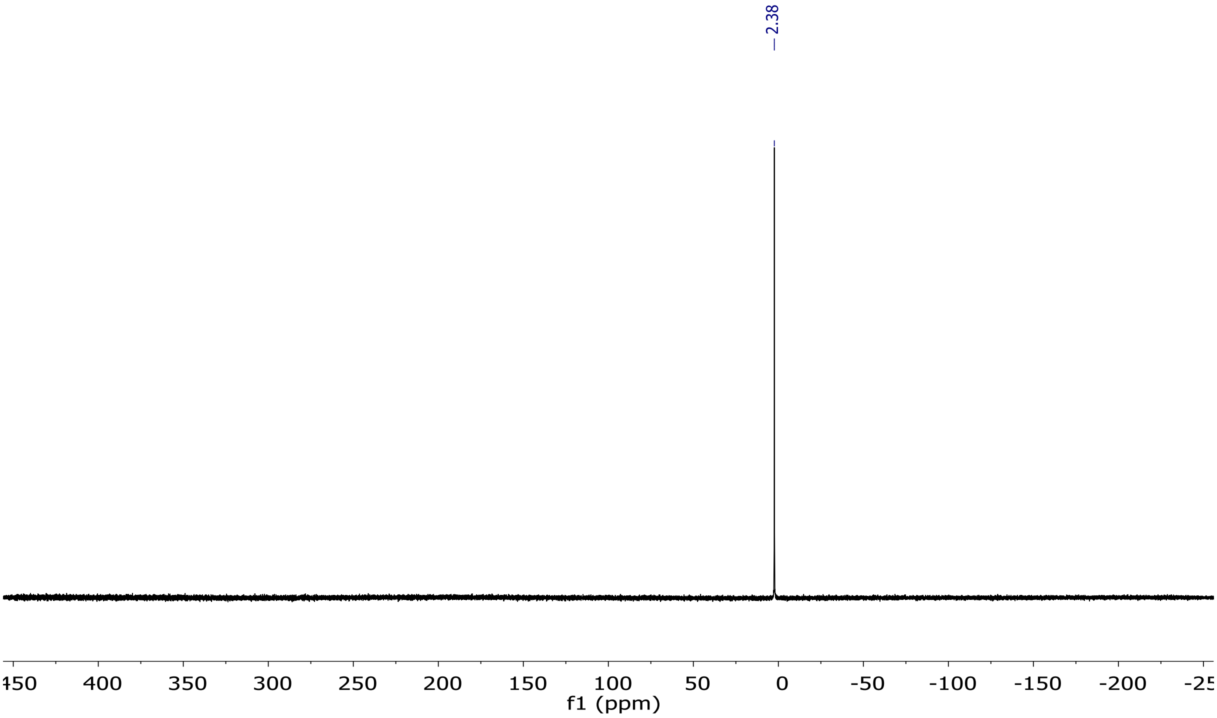
^{1}**H NMR** (500 MHz, DMSO-d_6):



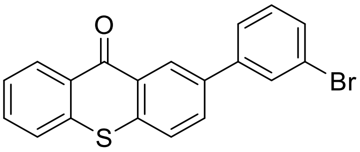
^{13}C NMR (126 MHz, DMSO-*d*$_6$):



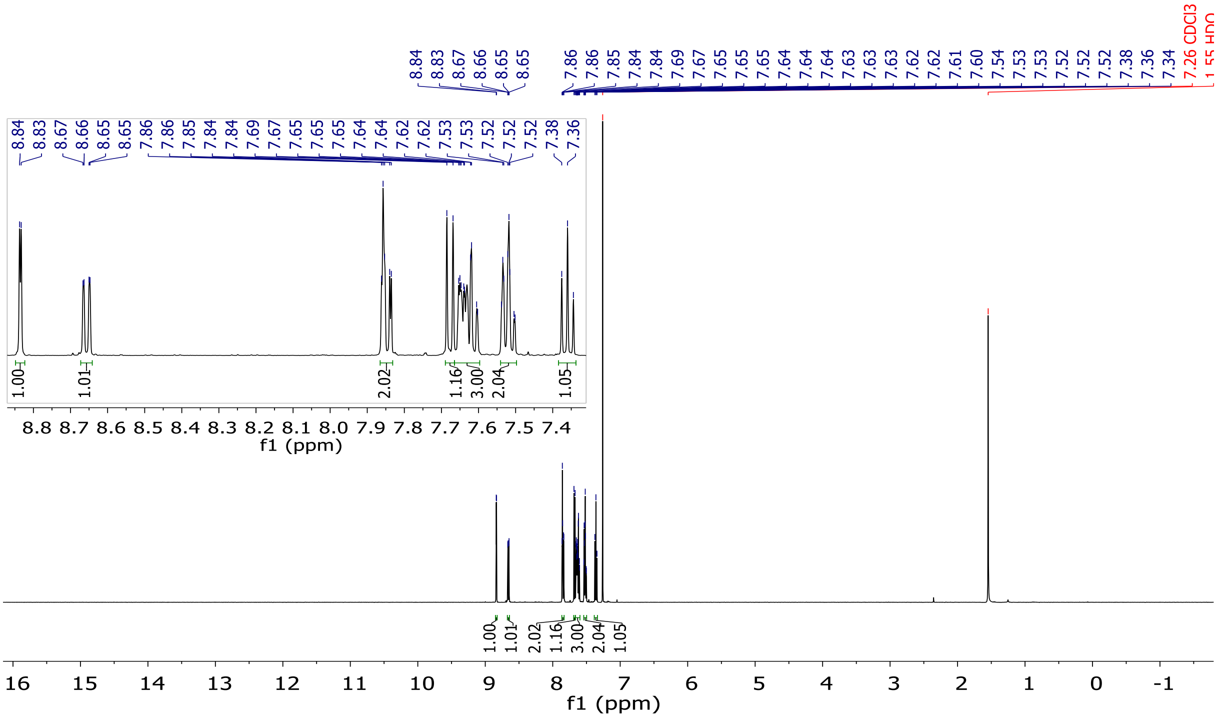
^{31}P NMR (203 MHz, DMSO-*d*$_6$):



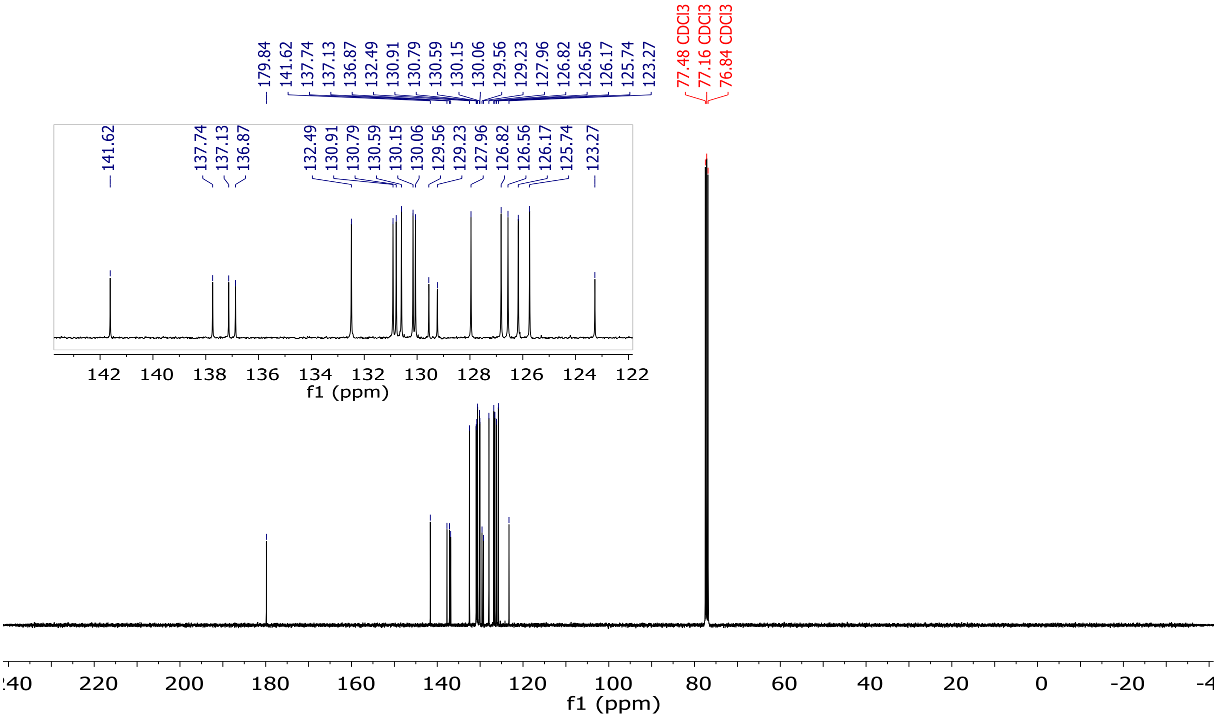
2-Bromo-4-phenyl-9*H*-thioxanthen-9-one (7)



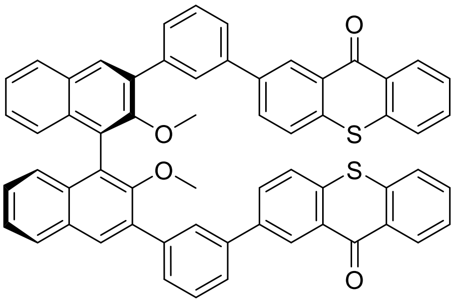
^{1}H NMR (500 MHz, CDCl$_3$):



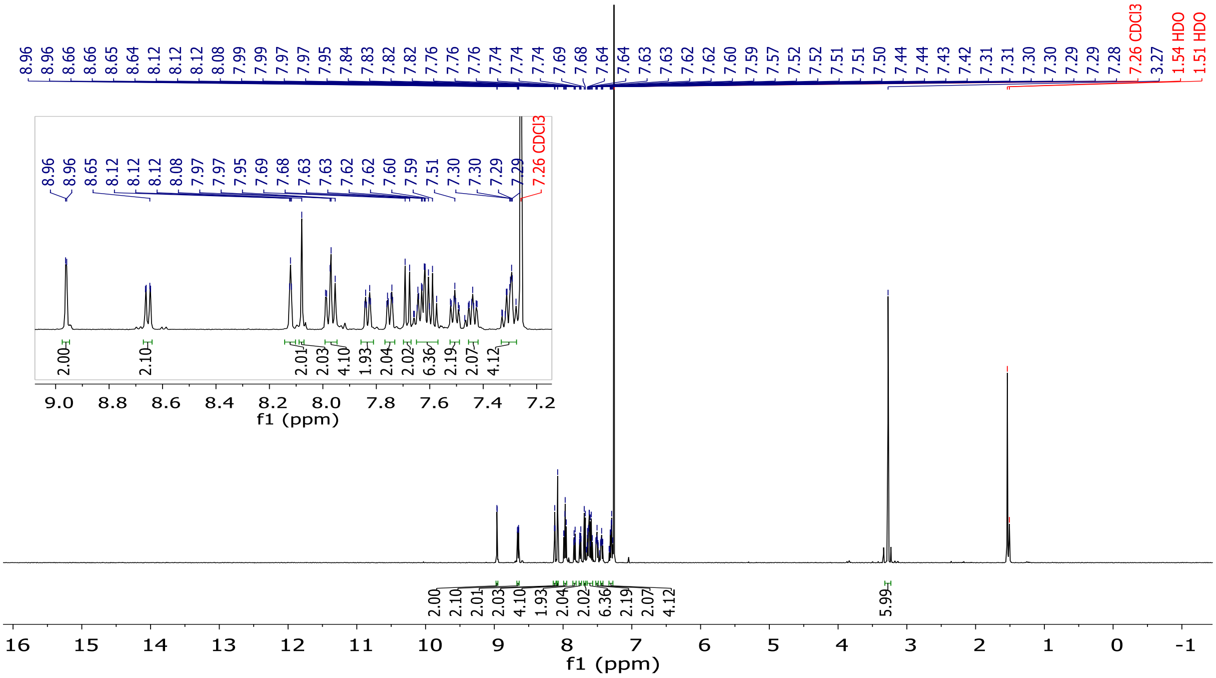
^{13}C NMR (101 MHz, CDCl$_3$):



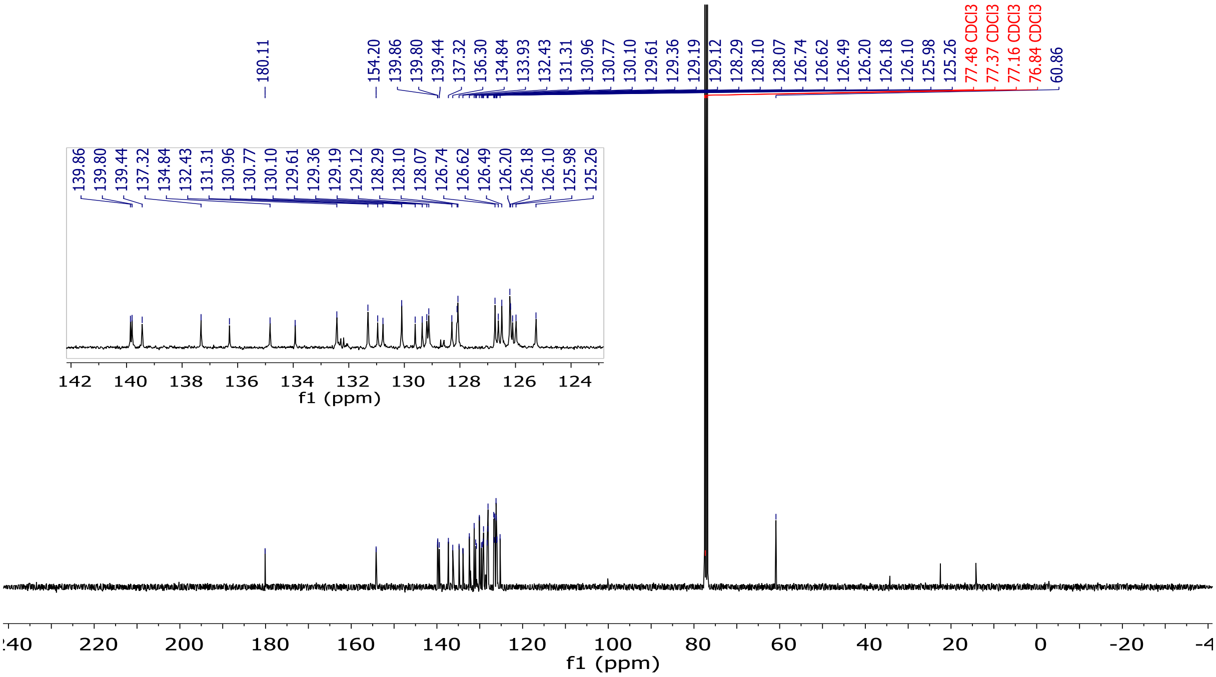
(*R*)-2,2'-((2,2'-Dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)bis(3,1-phenylene))bis(9*H*-thioxanthen-9-one) (S6)



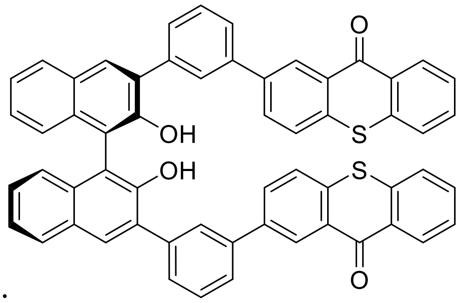
^{1}H NMR (500 MHz, CDCl$_3$):



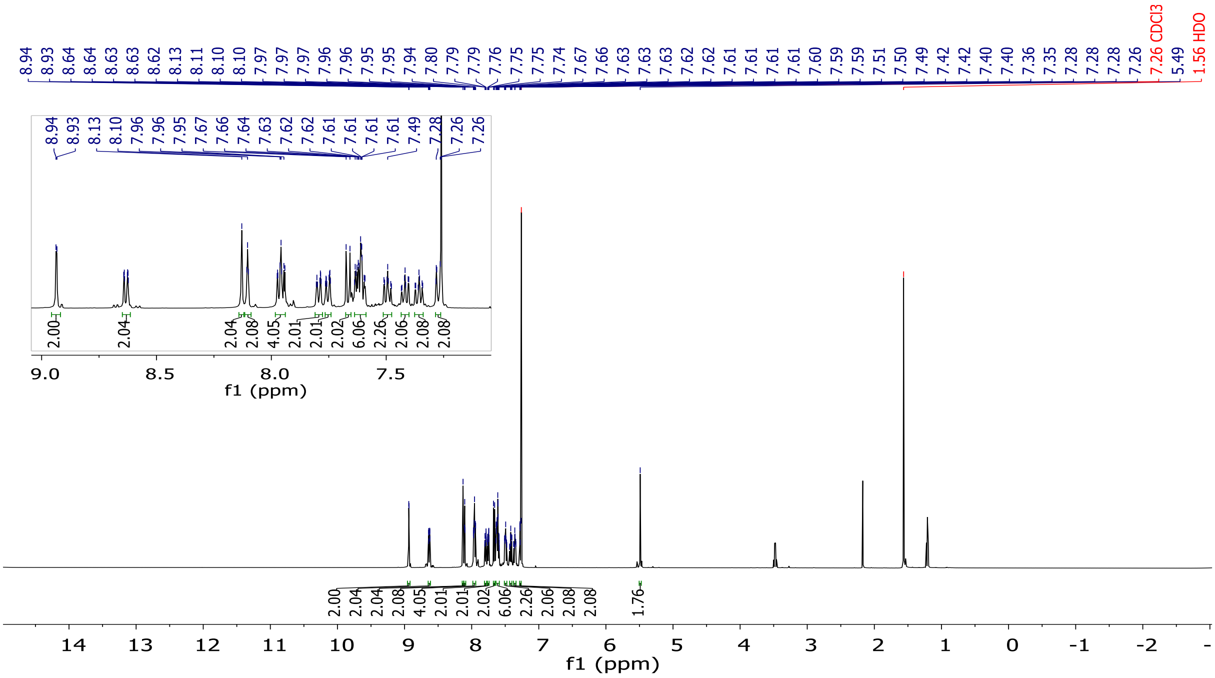
^{13}C NMR (101 MHz, CDCl$_3$):



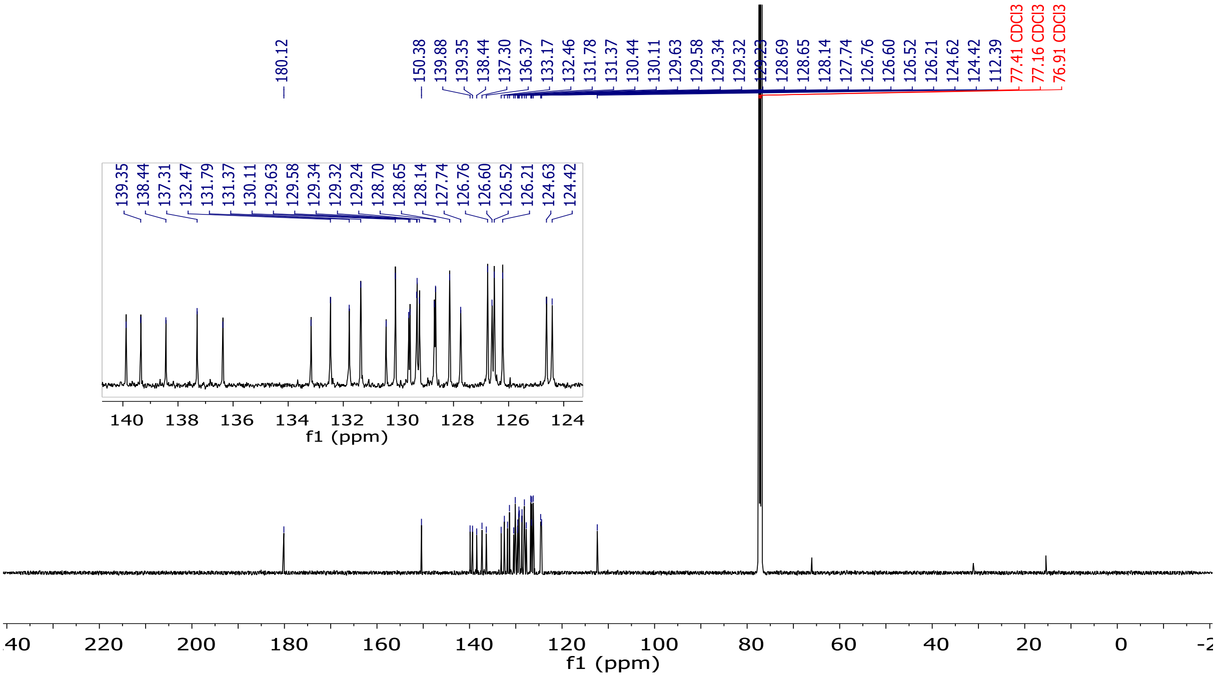
(*R*)-2,2'-((2,2'-Dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(3,1-phenylene))bis(9*H*-thioxanthen-9-one) (S7)



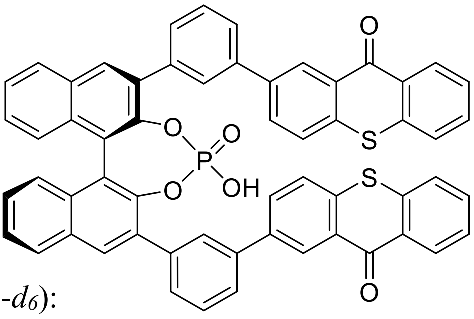
^{1}H NMR (500 MHz, CDCl$_3$):



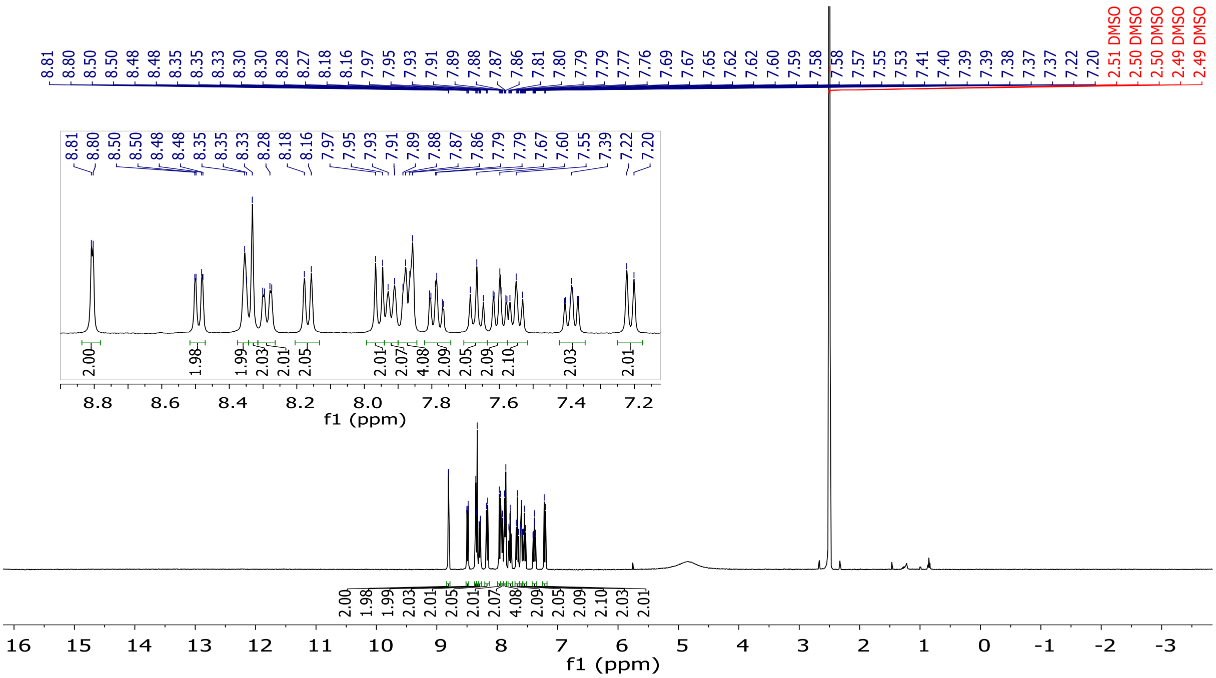
^{13}C NMR (126 MHz, CDCl$_3$):



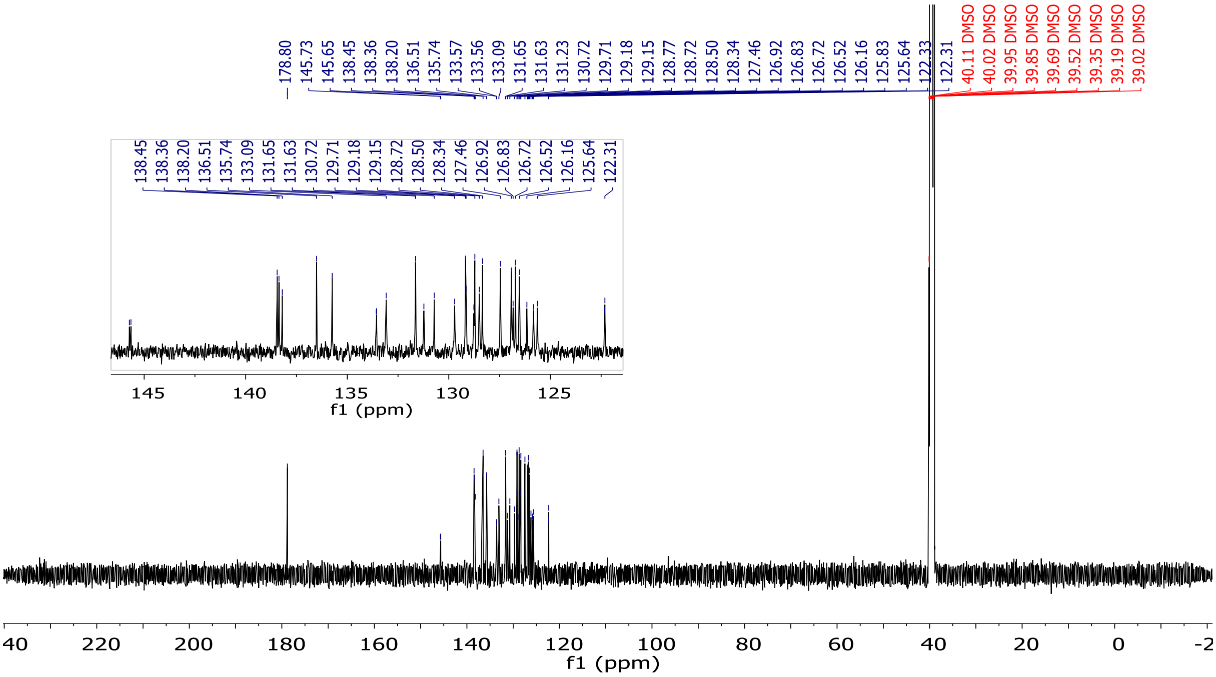
2,2'-(((11b*R*)-4-Hydroxy-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-2,6-diyl)bis(3,1-phenylene))bis(9*H*-thioxanthen-9-one) (4)



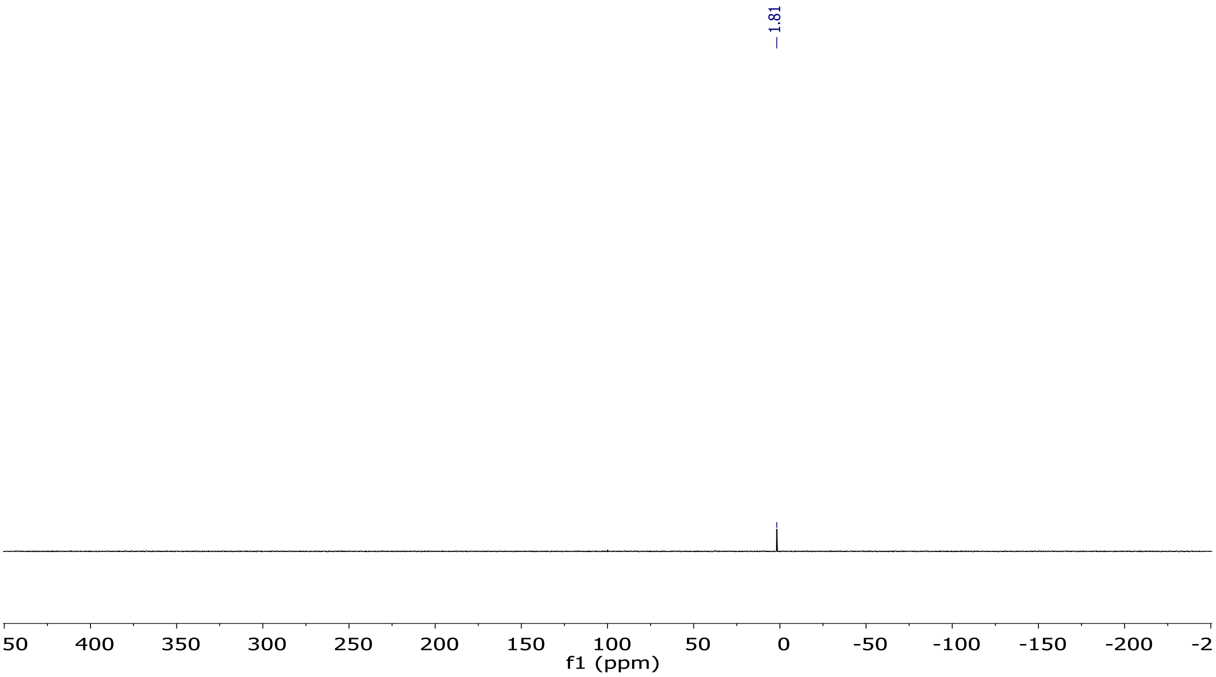
^{1}H NMR (400 MHz, DMSO-d_6):



^{13}C NMR (126 MHz, DMSO-d_6):

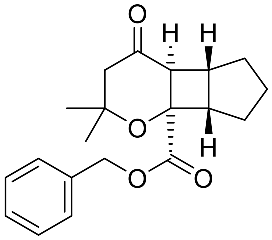


^{31}P NMR (162 MHz, DMSO-d_6):

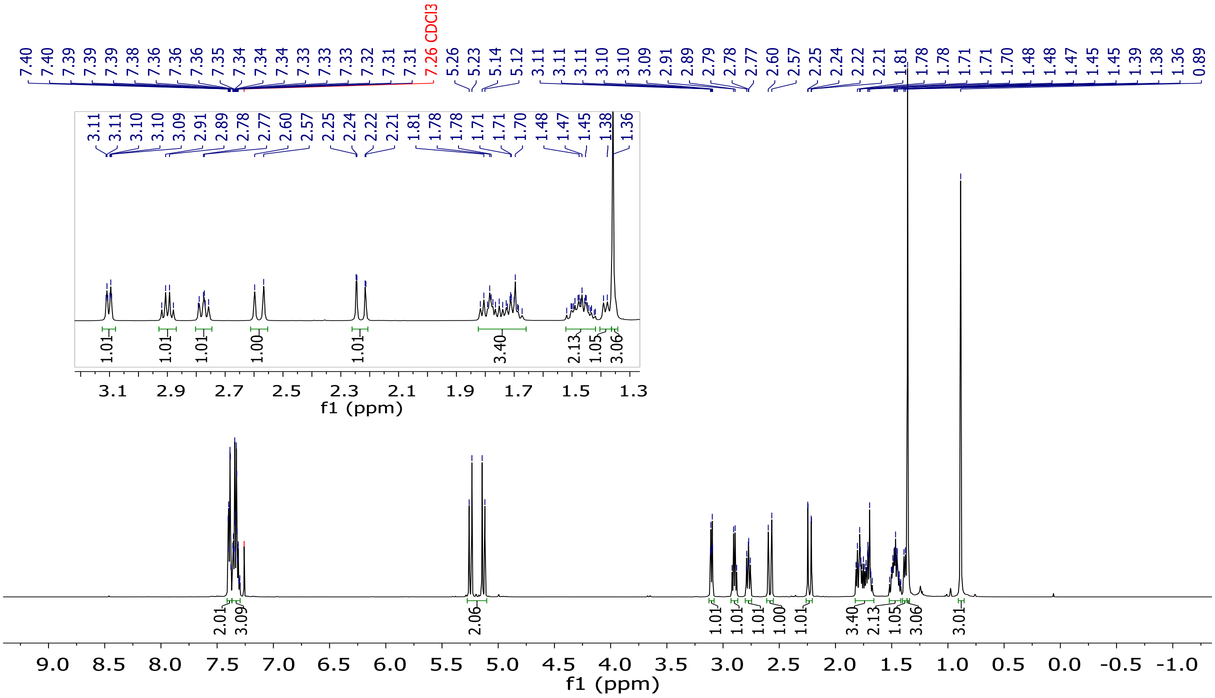


9.2. NMR Spectra of Photoproducts

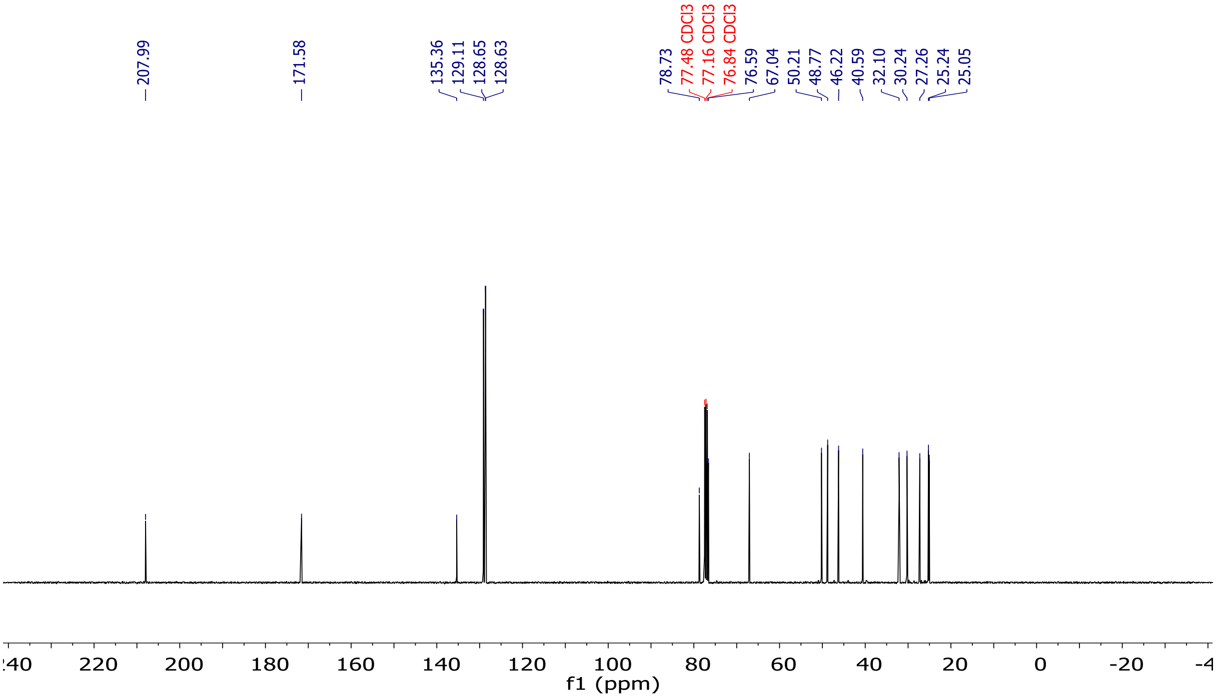
Benzyl-(4a*S*,4b*R*,7a*S*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylate (11a)



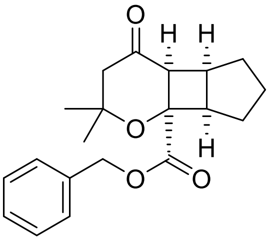
^{1}H NMR (500 MHz, CDCl$_3$):



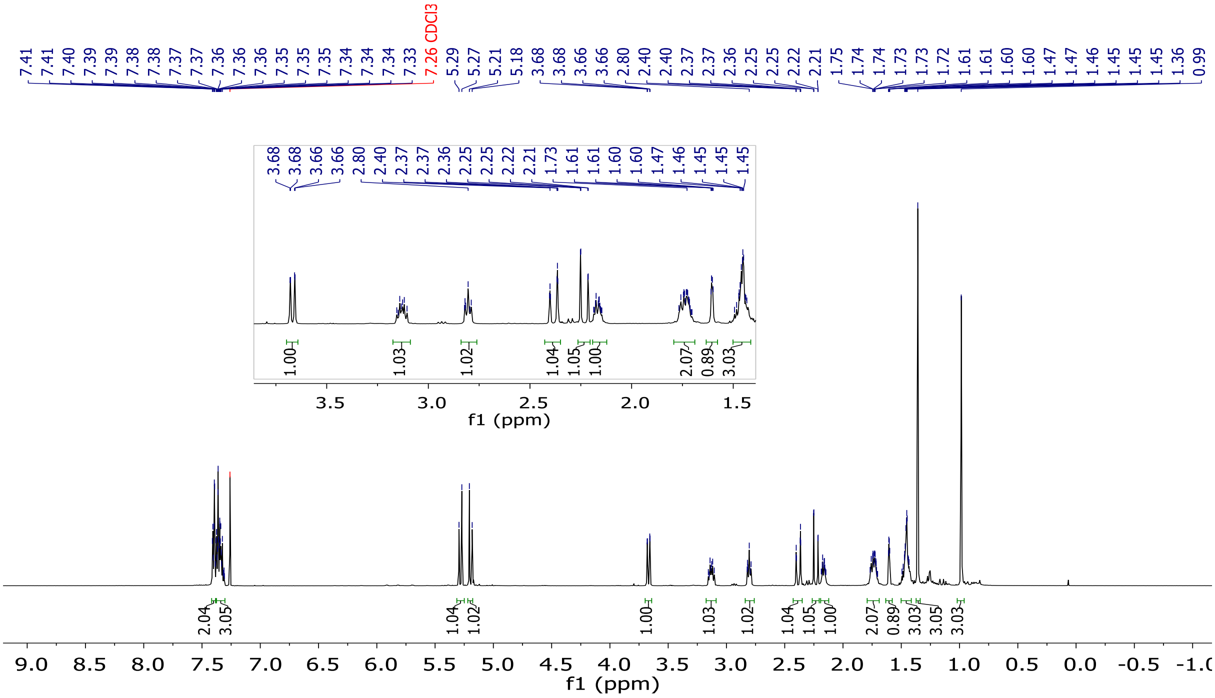
^{13}C NMR (101 MHz, CDCl$_3$):



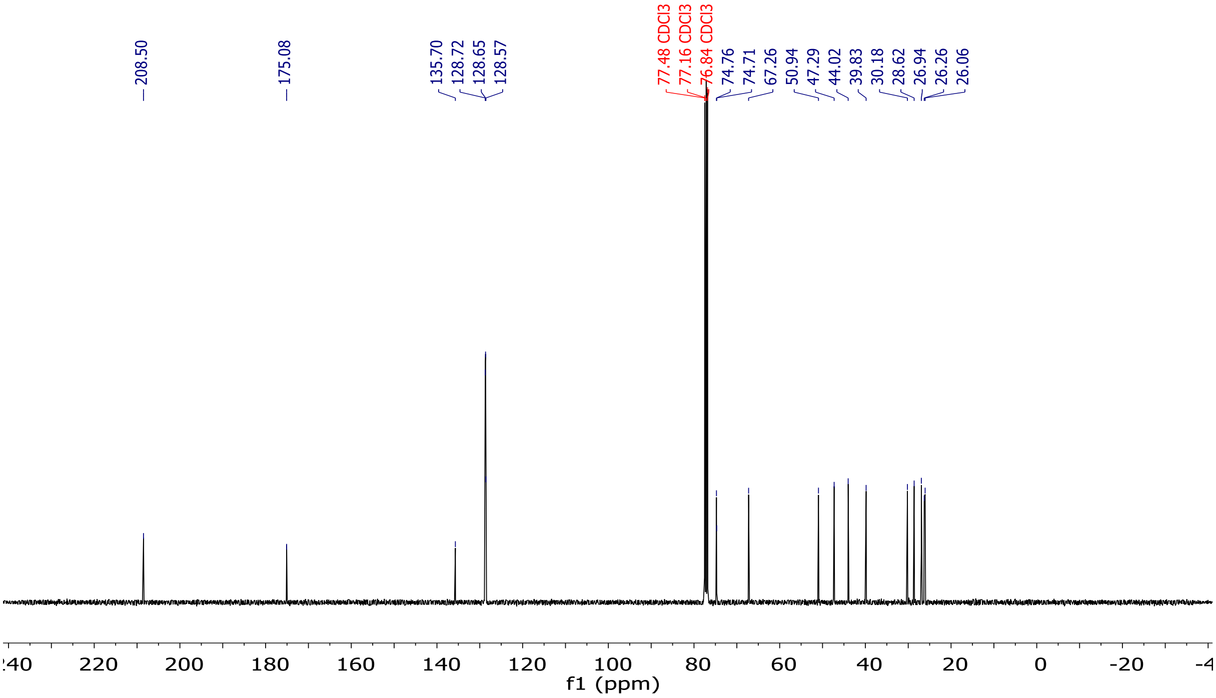
Benzyl-(4a*S*,4b*S*,7a*R*,7b*R*)-2,2-dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylate (11b)



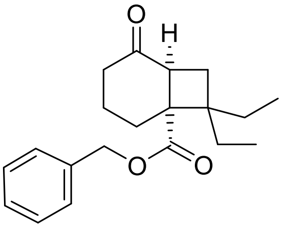
^{1}H NMR (500 MHz, $CDCl_3$):



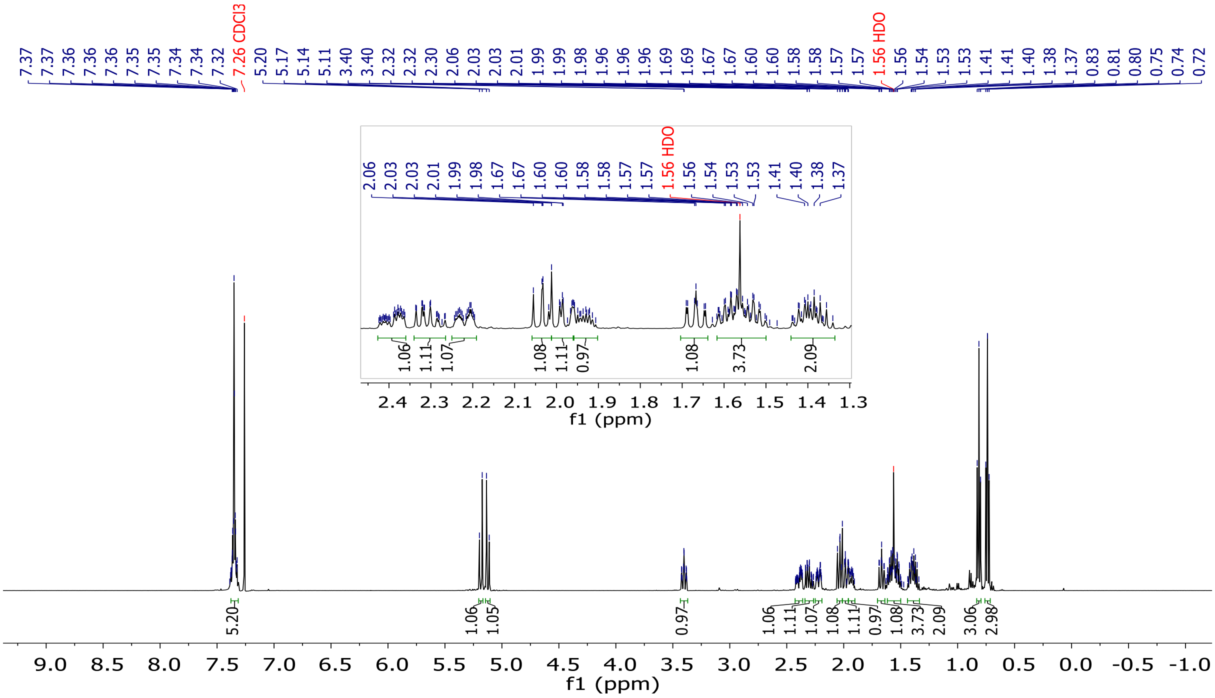
^{13}C NMR (101 MHz, $CDCl_3$):



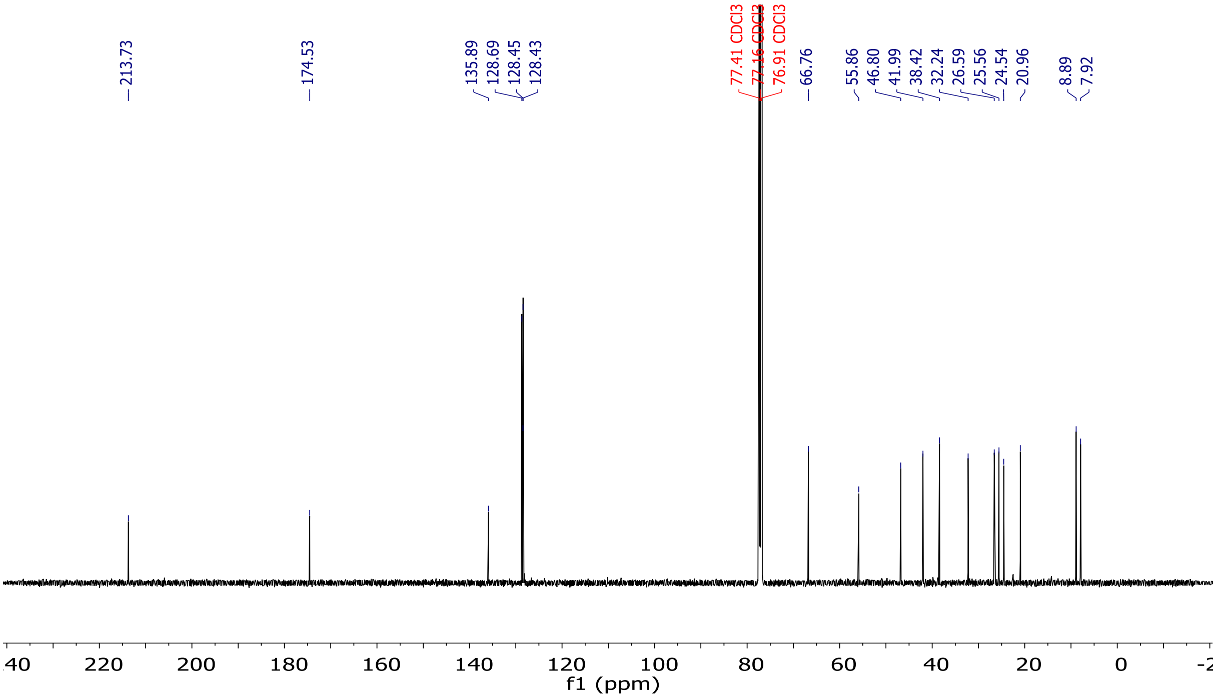
Benzyl-(1*R*,6*S*)-8,8-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (15)



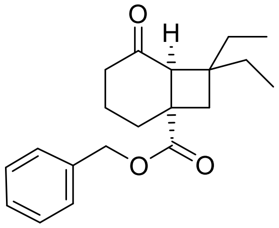
^{1}H NMR (500 MHz, CDCl$_3$):



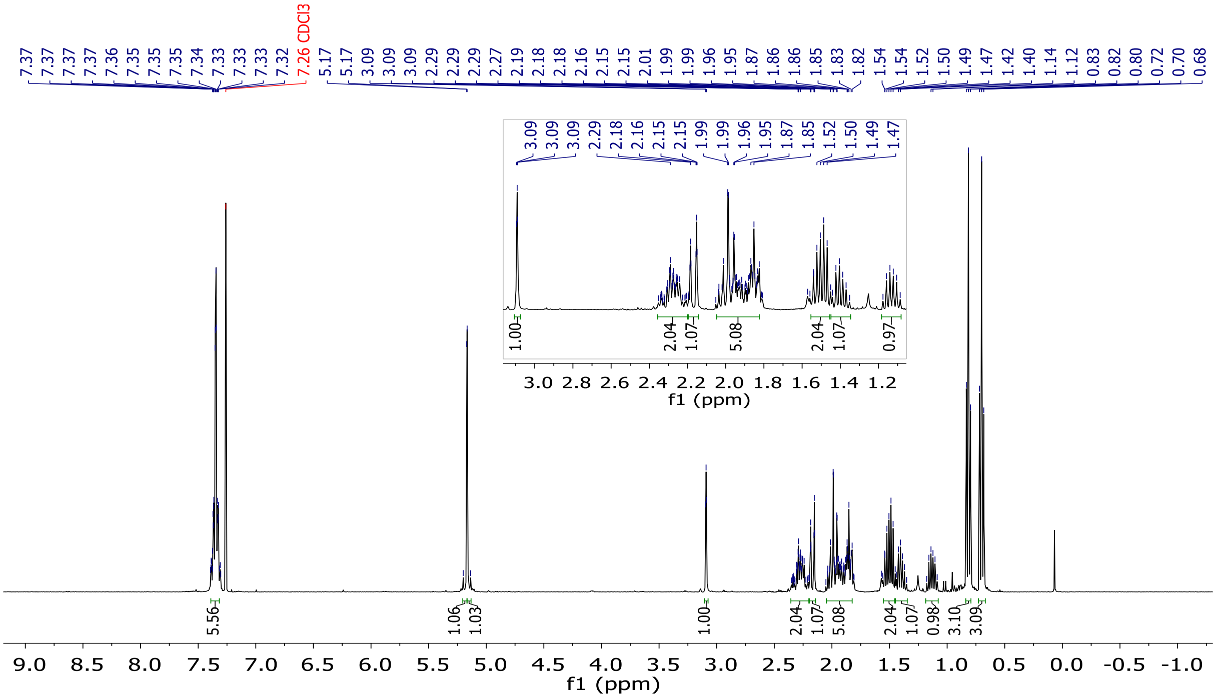
^{13}C NMR (126 MHz, CDCl$_3$):



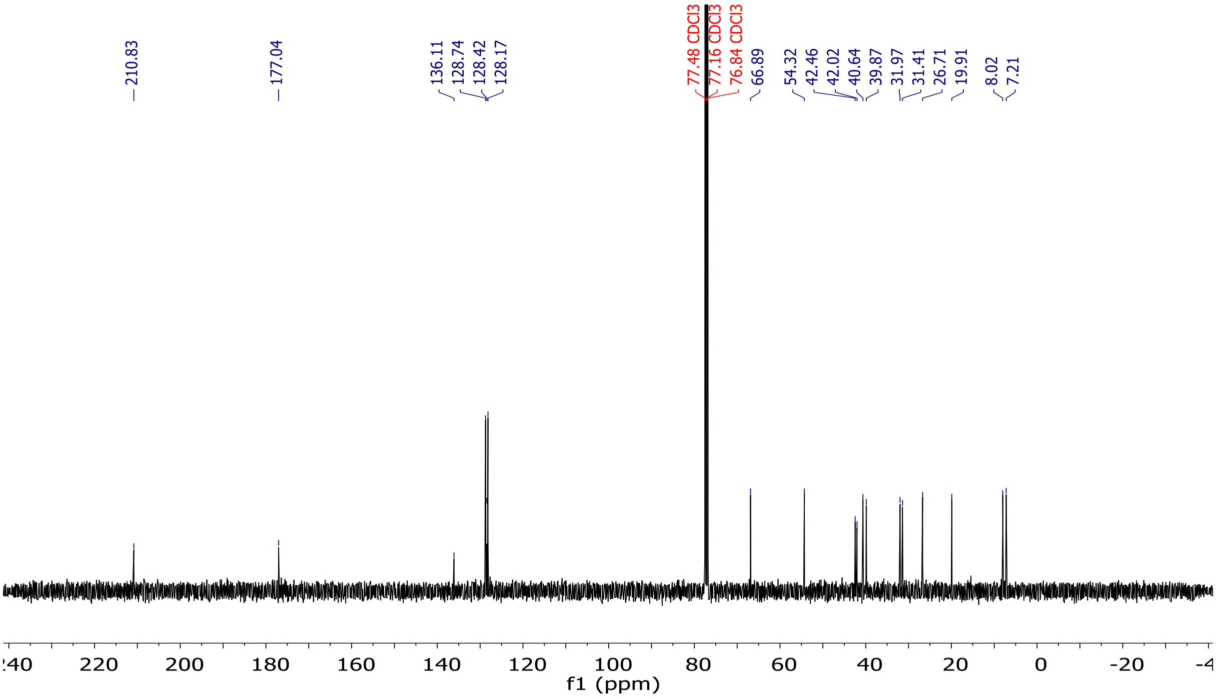
Benzyl-(1S,6*S*)-7,7-diethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (16)



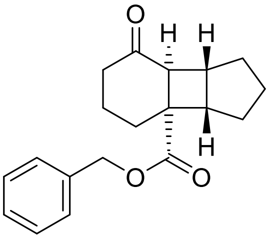
^{1}H NMR (500 MHz, $CDCl_3$):



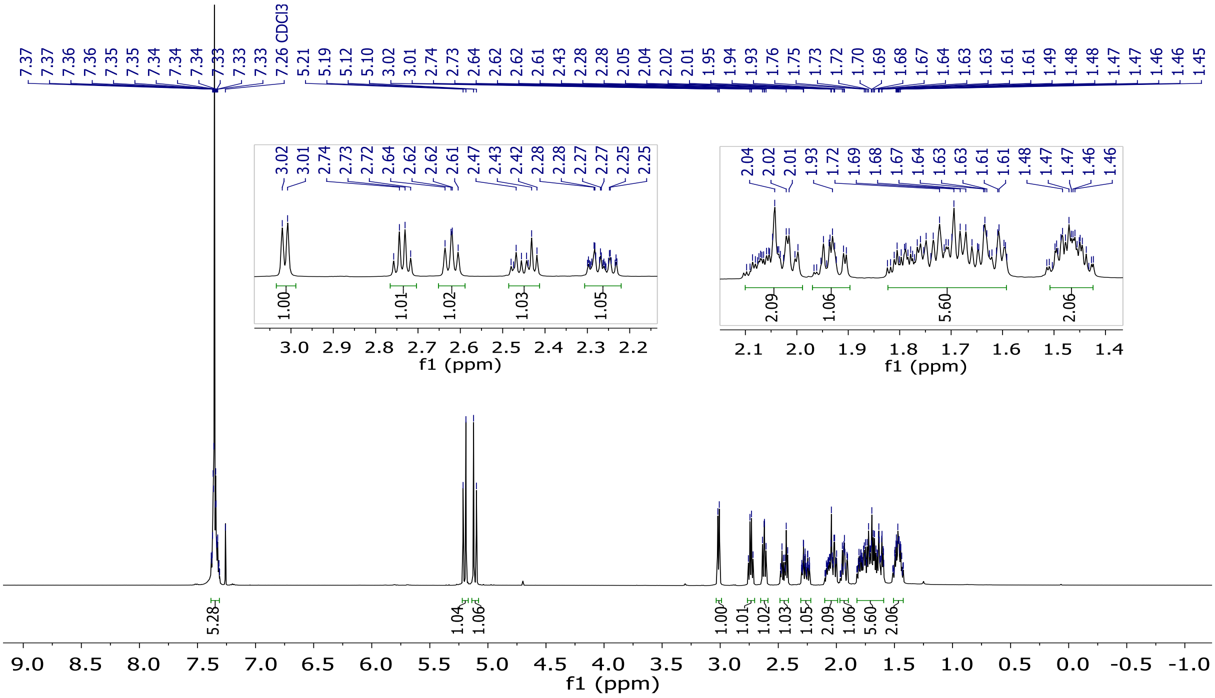
^{13}C NMR (101 MHz, $CDCl_3$):



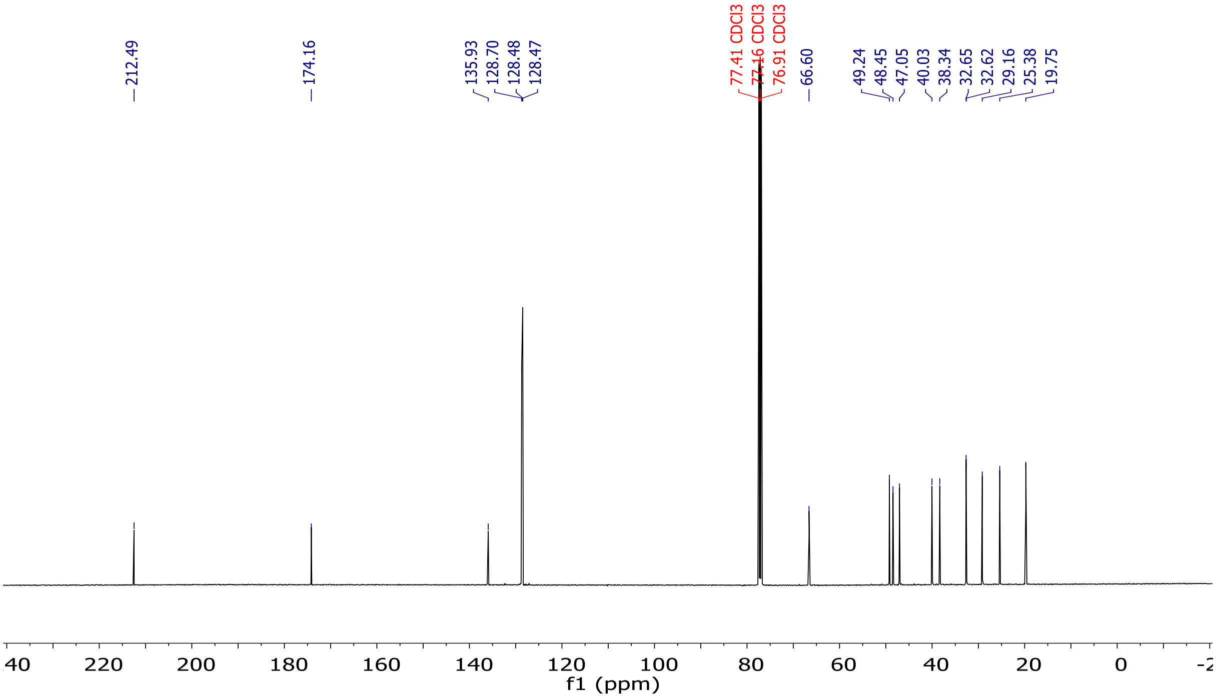
Benzyl-(3a*S*,3b*S*,7a*S*,7b*R*)-7-oxodecahydro-3b*H*-cyclopenta[3,4]cyclobuta[1,2]benzene-3b-carboxylate (18)



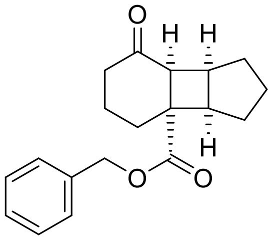
^{1}H NMR (500 MHz, CDCl$_3$):



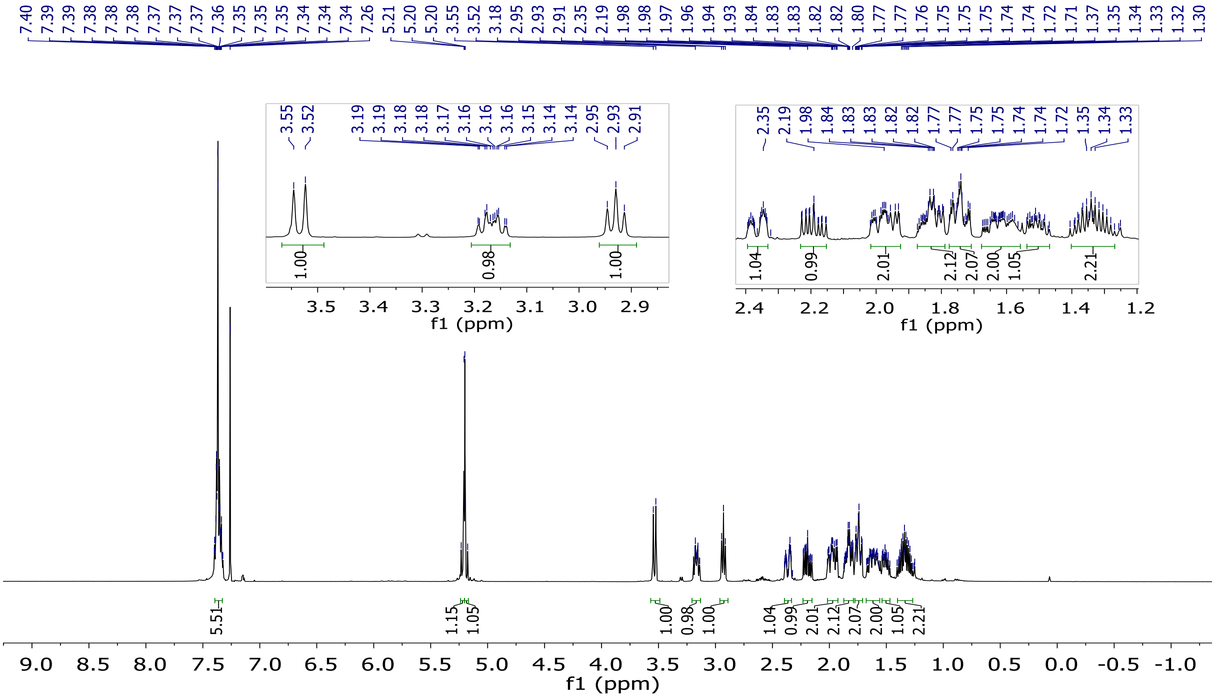
^{13}C NMR (126 MHz, CDCl$_3$):



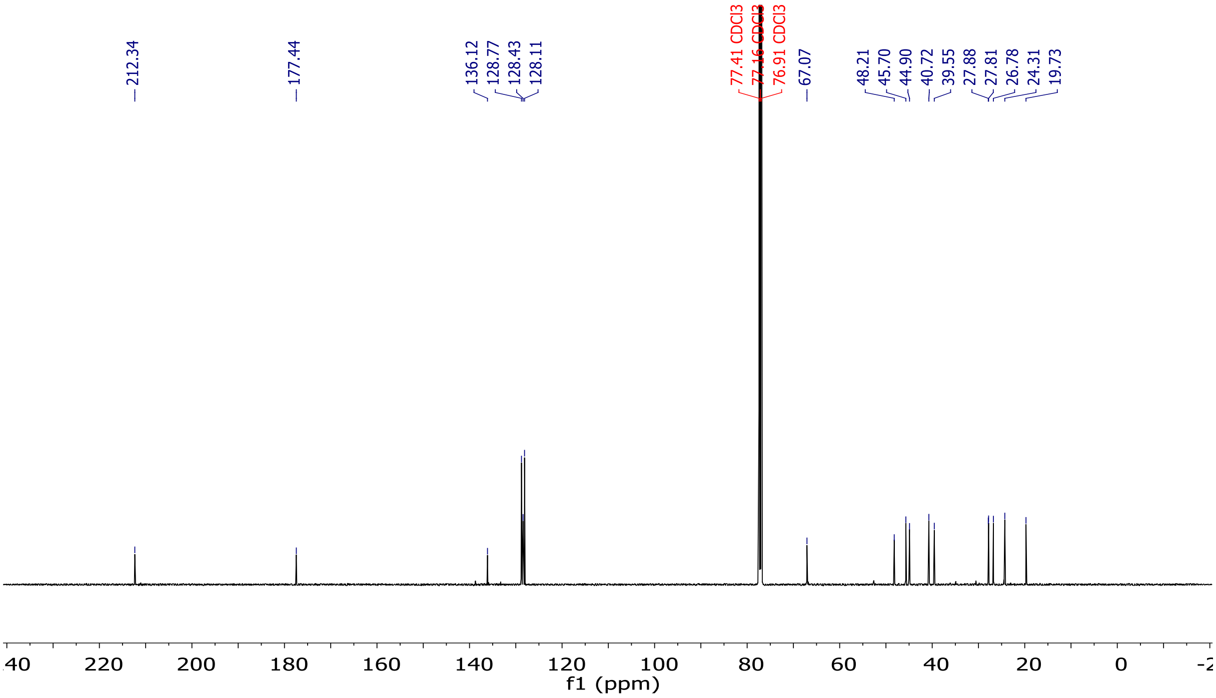
Benzyl-(3a*R*,3b*S*,7a*S*,7b*S*)-7-oxodecahydro-3b*H*-cyclopenta-[3,4]cyclobuta[1,2]benzene-3b-carboxylate (S9)



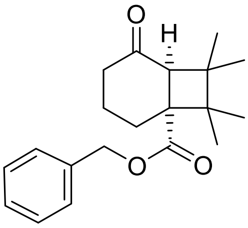
^{1}**H NMR** (500 MHz, CDCl$_3$):



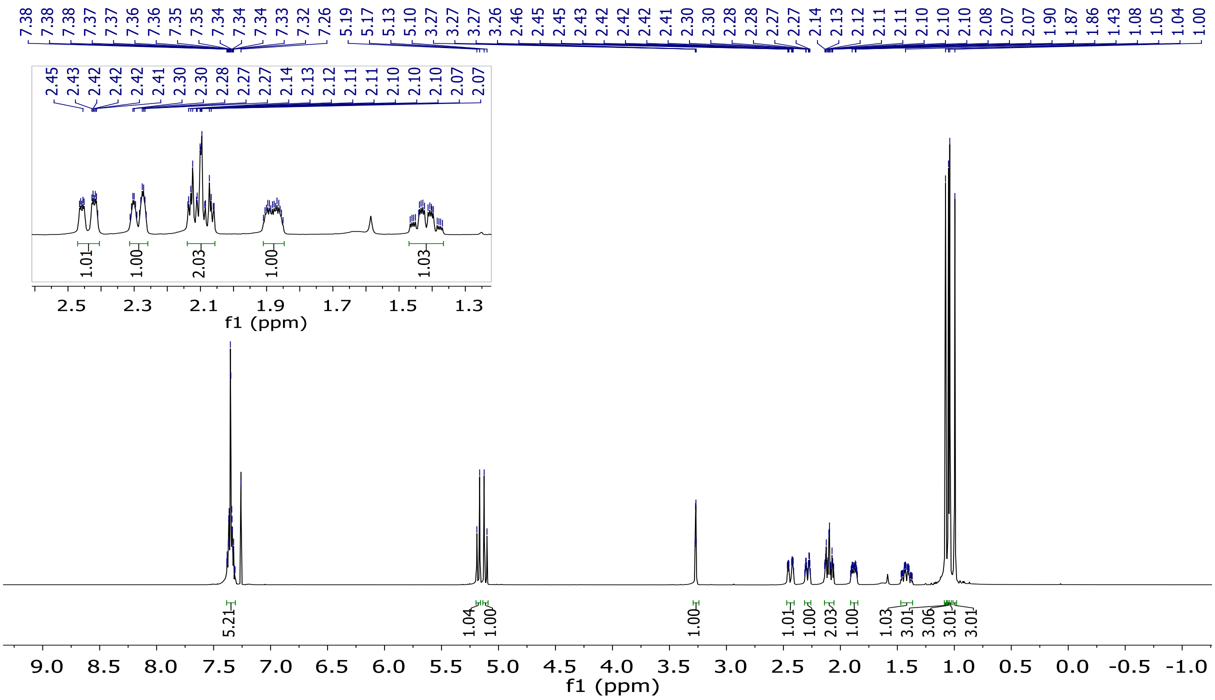
^{13}**C NMR** (126 MHz, CDCl$_3$):



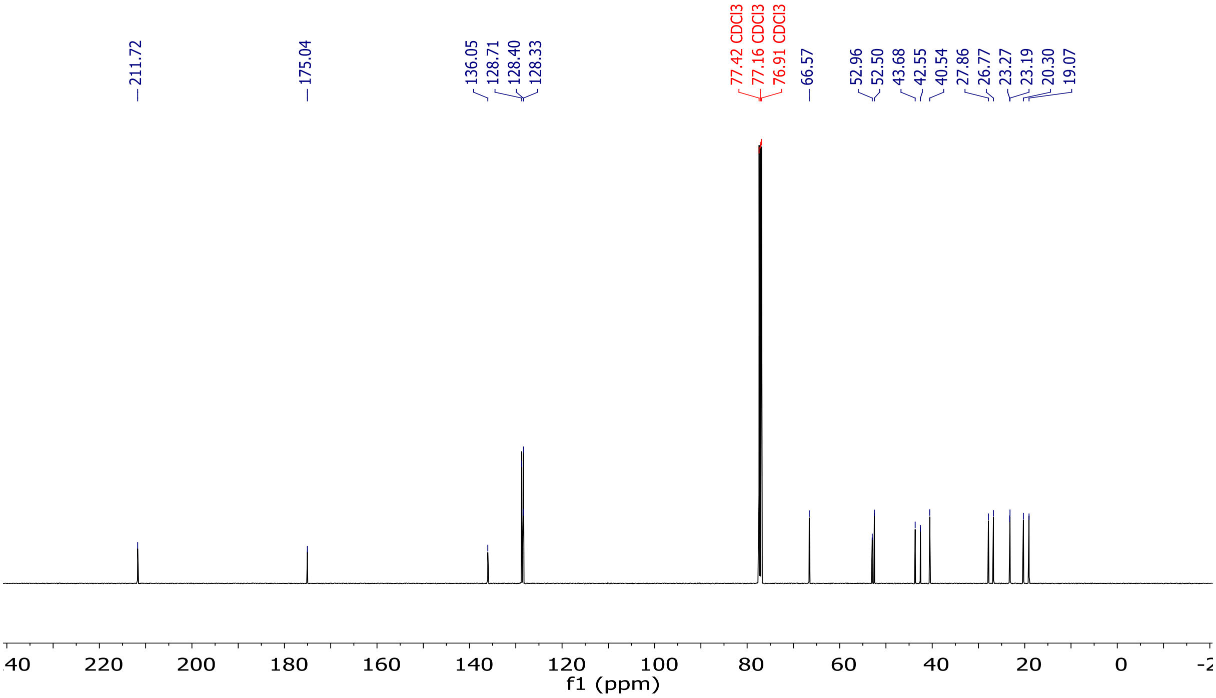
Benzyl-(1*R*,6*S*)-7,7,8,8-tetramethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (19)



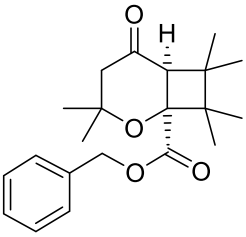
^{1}H NMR (500 MHz, $CDCl_3$):



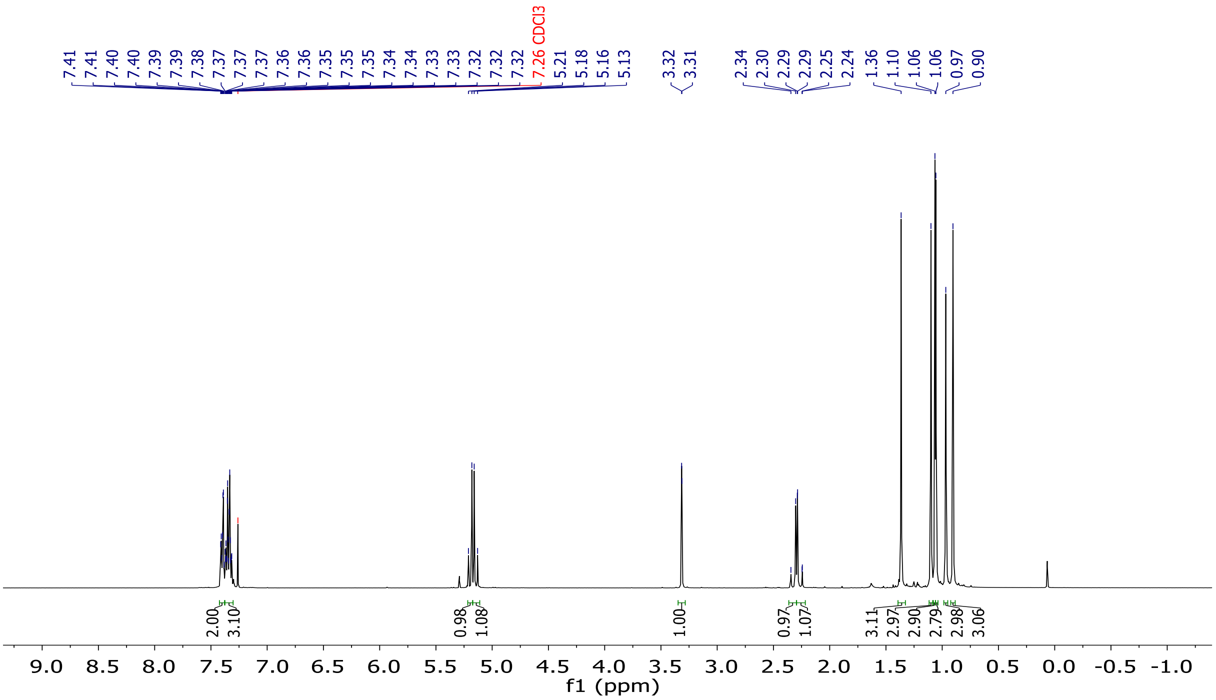
^{13}C NMR (126 MHz, $CDCl_3$):



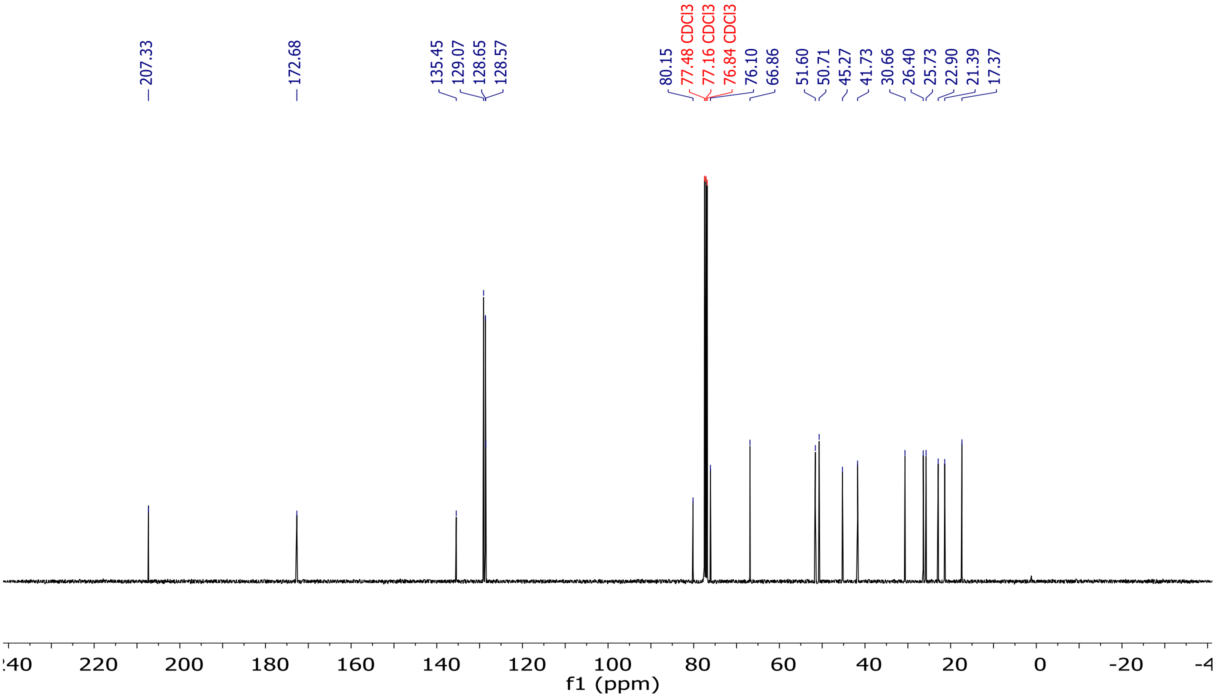
Benzyl-(1*S*,6*S*)-3,3,7,7,8,8-hexamethyl-5-oxo-2-oxabicyclo[4.2.0]octane-1-carboxylate (20)



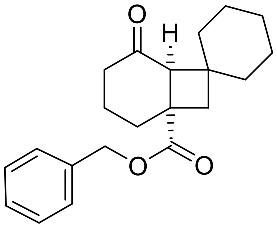
^{1}H NMR (400 MHz, $CDCl_3$):



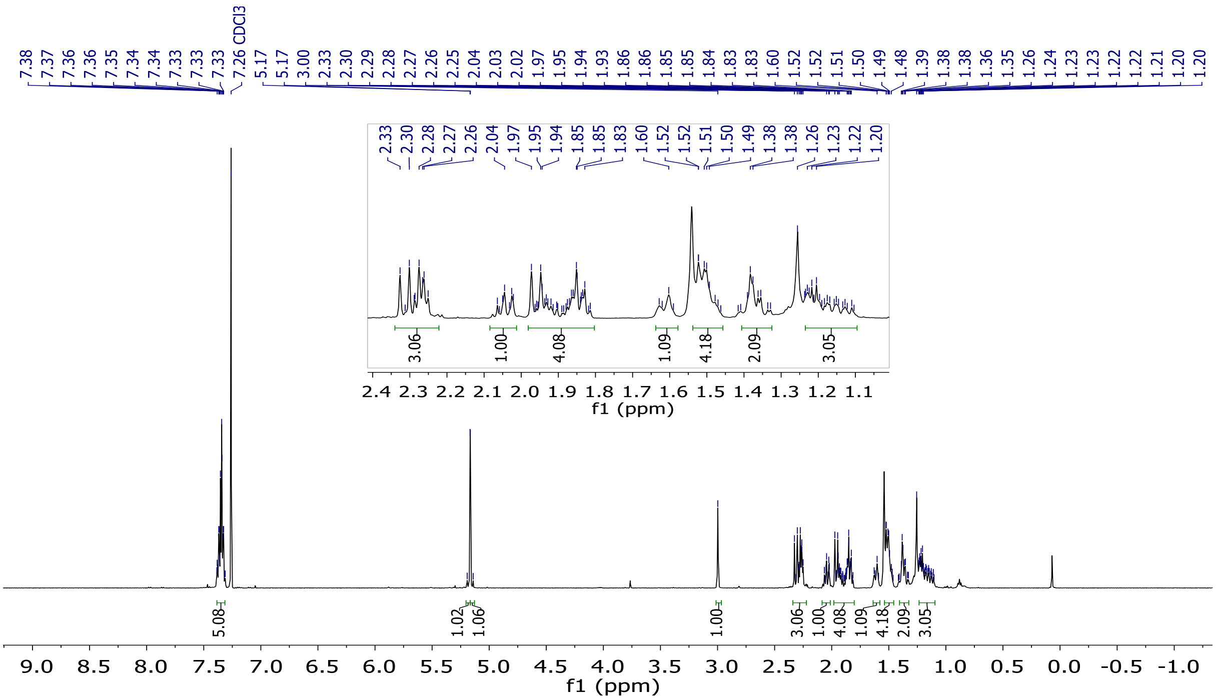
^{13}C NMR (101 MHz, $CDCl_3$):



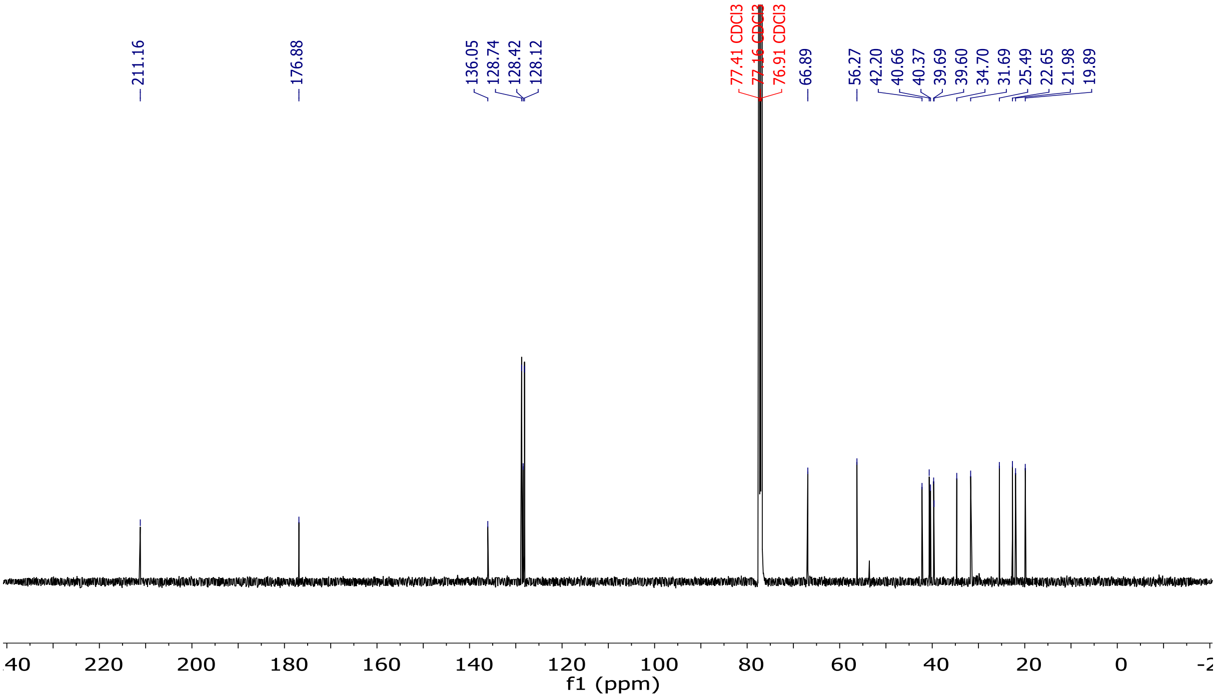
Benzyl-(1*S*,6*S*)-5-oxospiro[bicyclo[4.2.0]octane-7,1'-cyclohexane]-1-carboxylate (21)



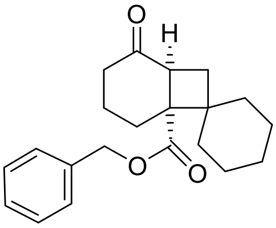
^{1}H NMR (500 MHz, $CDCl_3$):



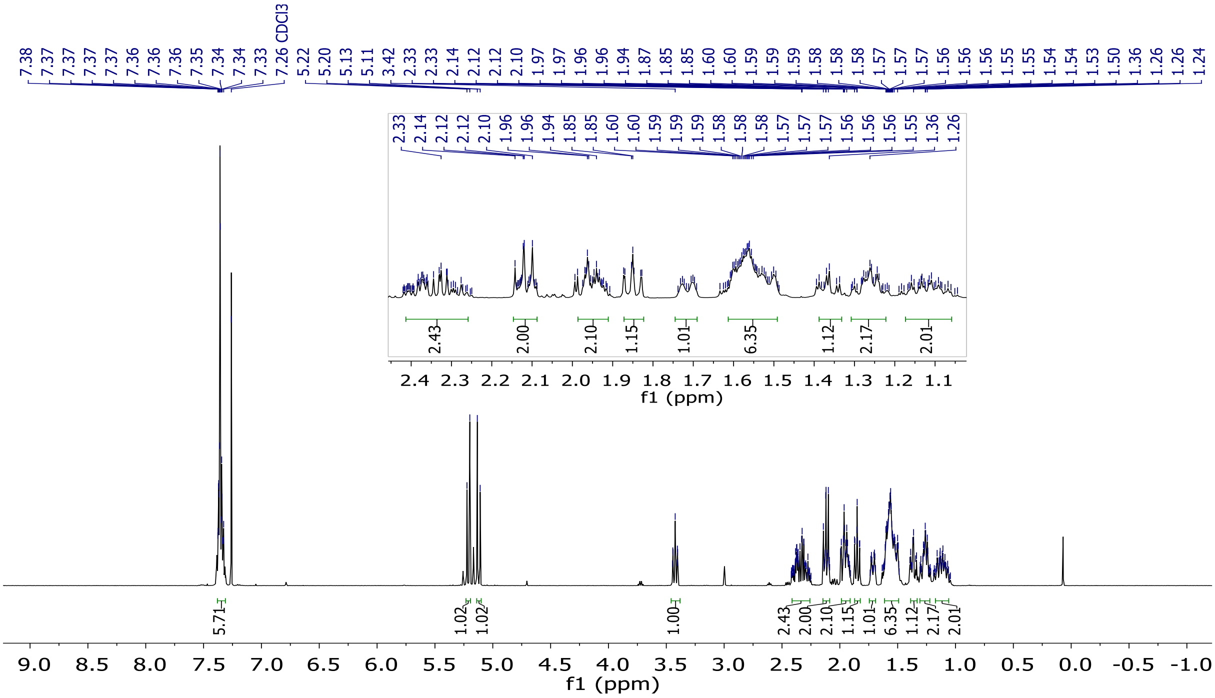
^{13}C NMR (126 MHz, $CDCl_3$):



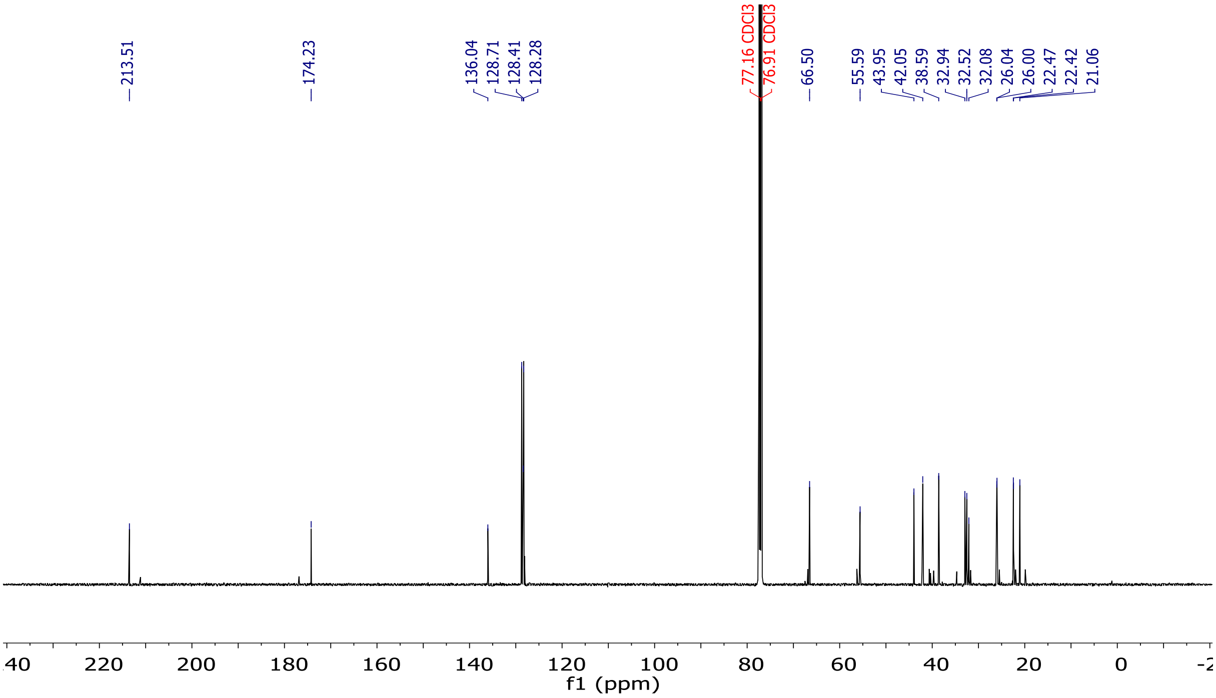
Benzyl-(1*S*,6*R*)-2-oxospiro[bicyclo[4.2.0]octane-7,1'-cyclohexane]-6-carboxylate (S10)



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

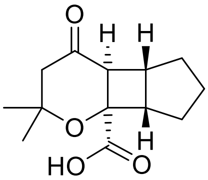


^{13}C NMR (126 MHz, $CDCl_3$)*:

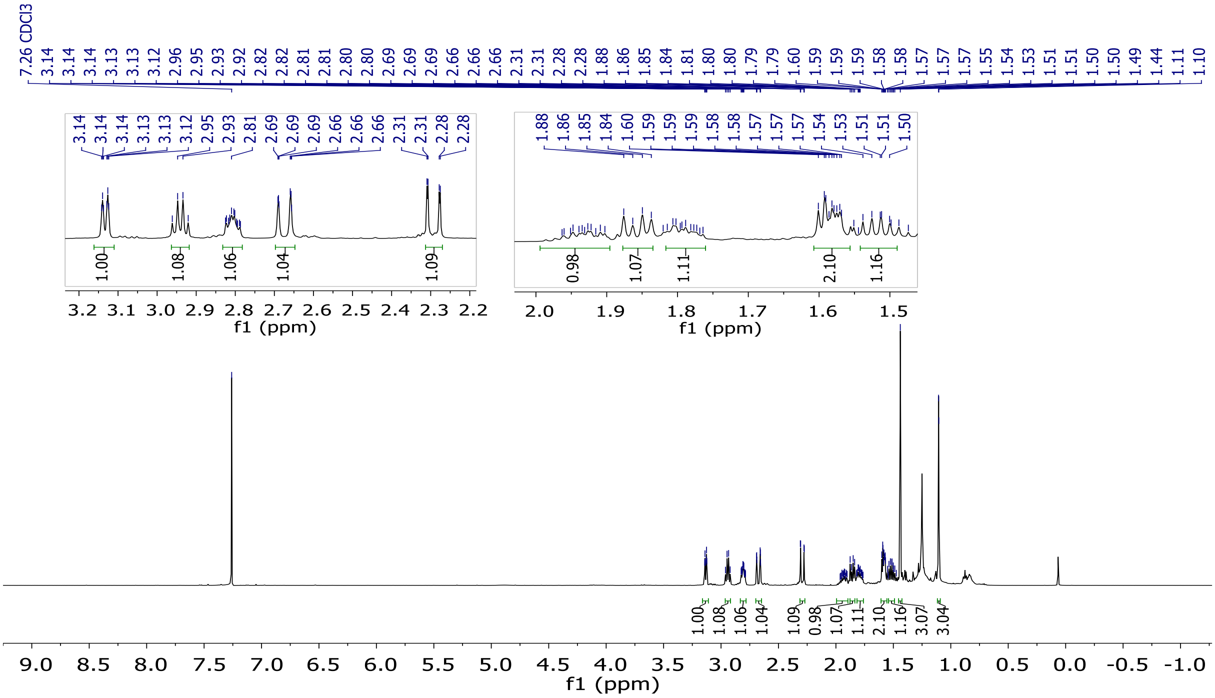


*NMR spectra show residual signals of regioisomer **21**.

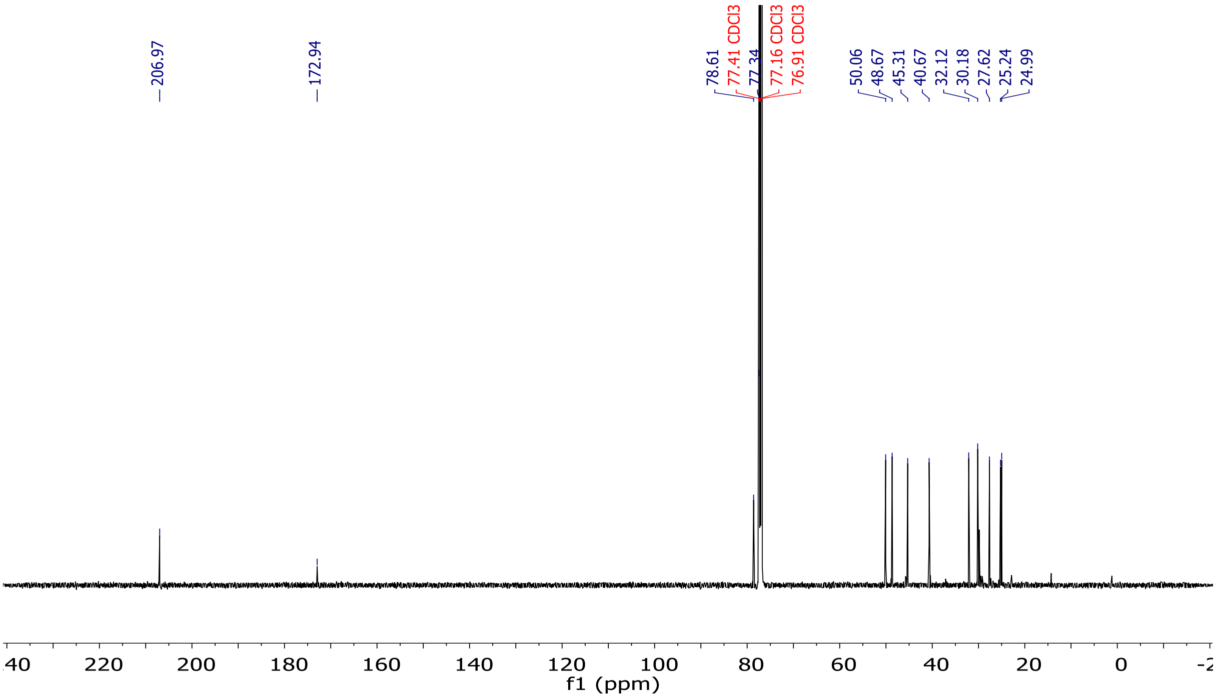
(4a*S*,4b*R*,7a*S*,7b*R*)-2,2-Dimethyl-4-oxooctahydrocyclopenta[3,4]cyclobuta[1,2-*b*]pyran-7b(2*H*)-carboxylic acid (10a)



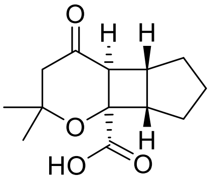
^{1}H NMR (500 MHz, CDCl$_3$):

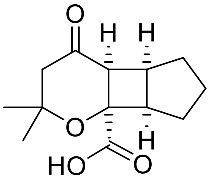


^{13}C NMR (126 MHz, CDCl$_3$):

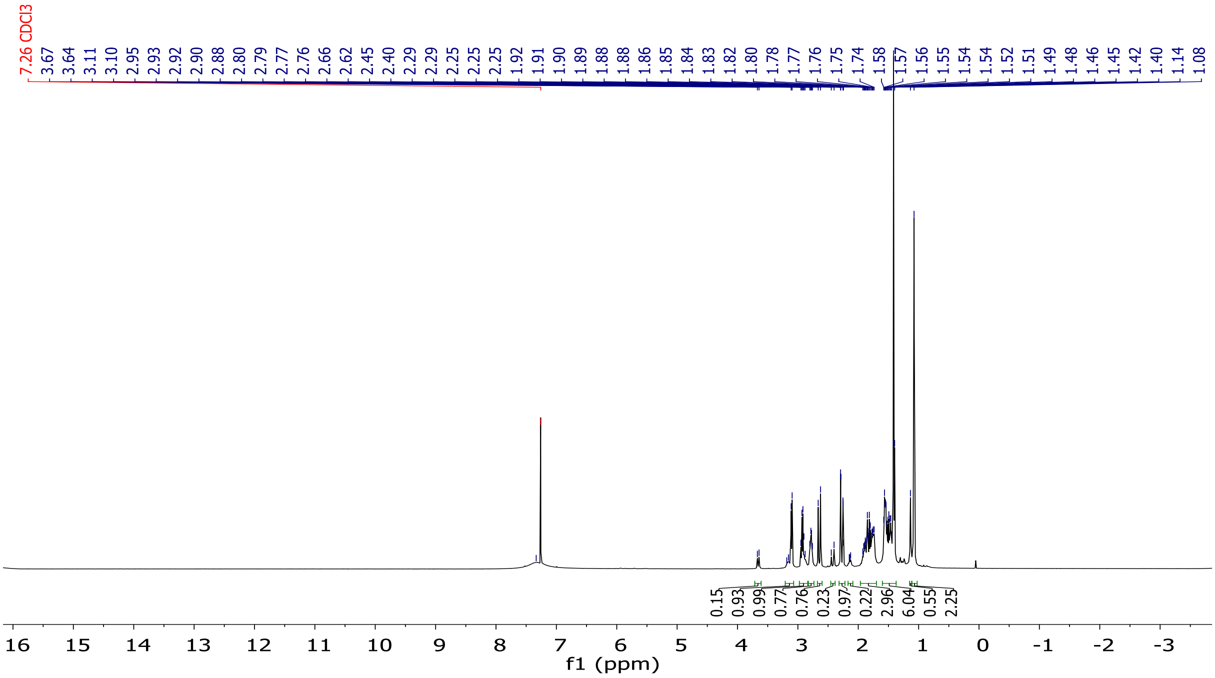


NMR spectra of a mixture of diastereoisomers 10a and 10b

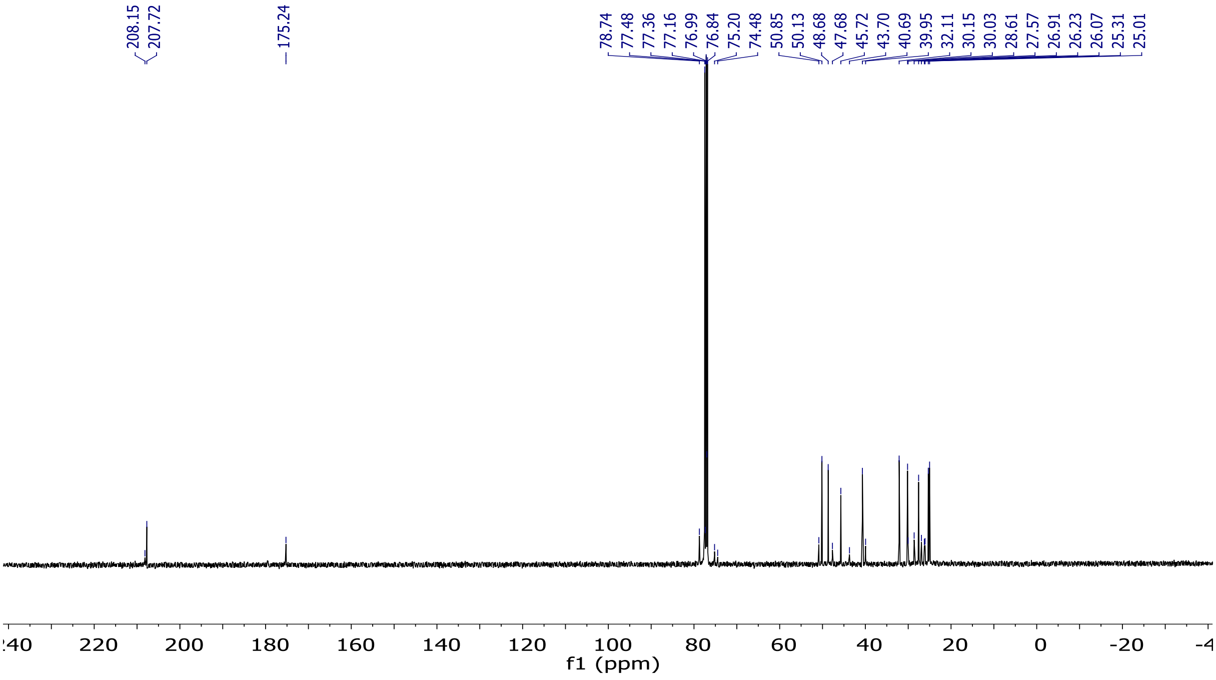




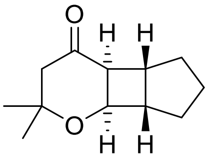
^{1}**H NMR** (500 MHz, CDCl$_3$):



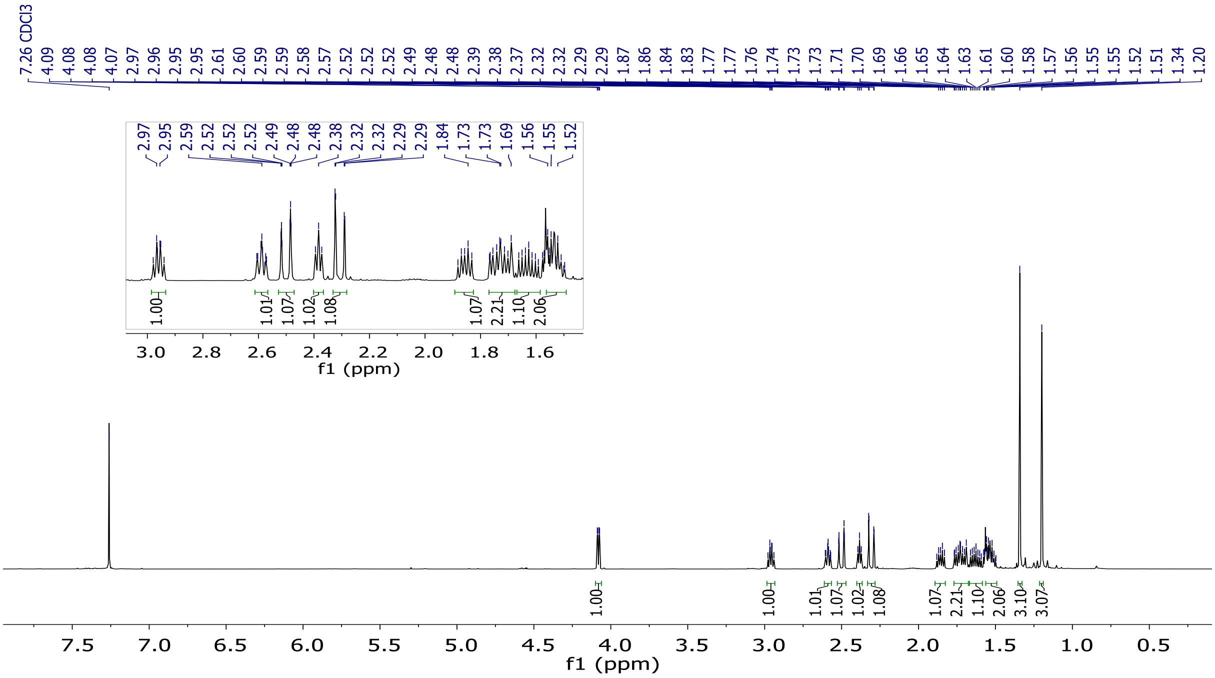
^{13}**C NMR** (101 MHz, CDCl$_3$):



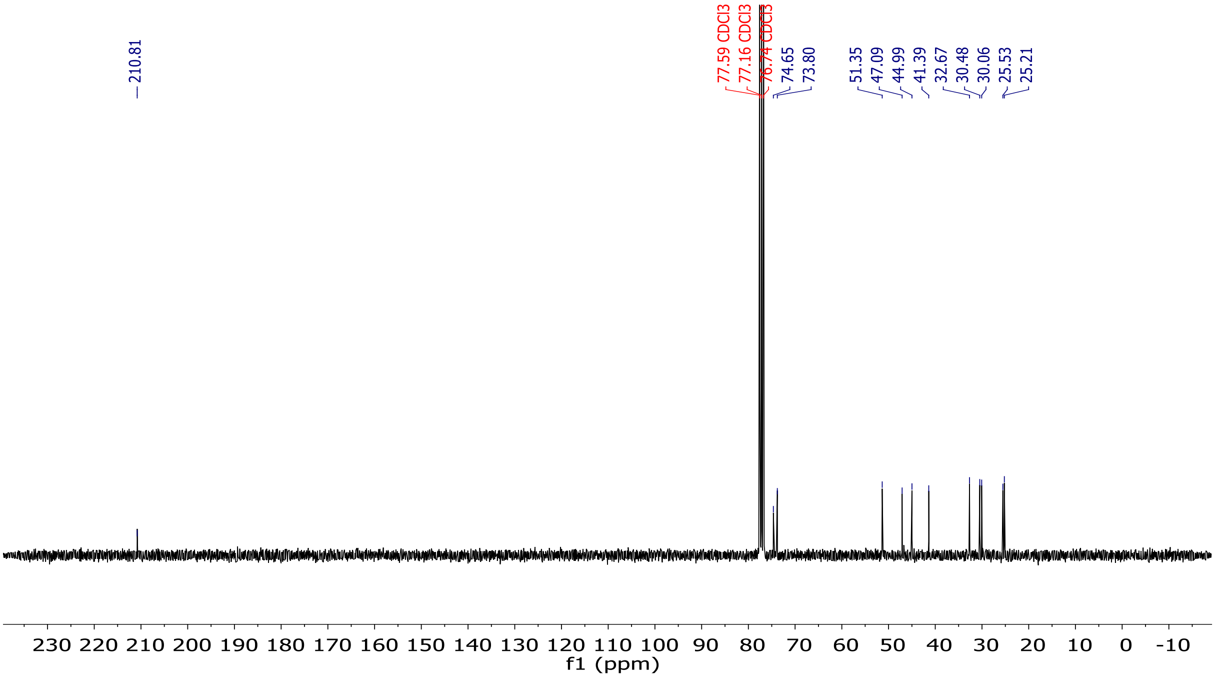
(4a*S*,4b*R*,7a*S*,7b*R*)-2,2-Dimethyloctahydrocyclopenta[3,4]cyclobuta[1,2-b]pyran-4(4a*H*)-one (S8)



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



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



10. Luminescence Measurements

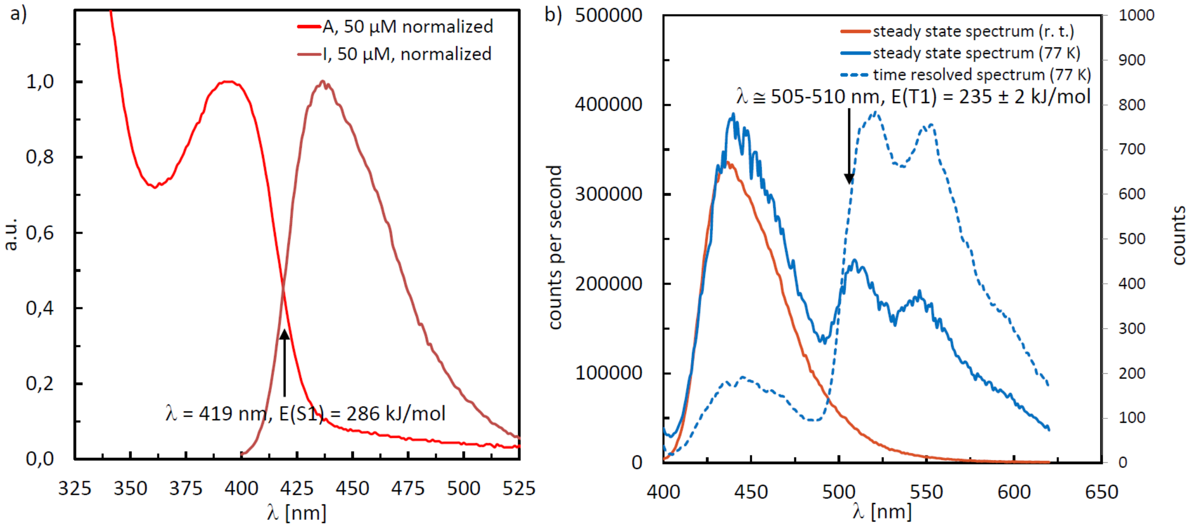


Figure S11. (a) Recorded UV/Vis of **4** in dichloromethane (c=50 µM) normalized to $A_{394\ nm}$; recorded luminescence of **4** in dichloromethane (c=50 µM) at ambient conditions, normalized to $I_{436\ nm}$. (b) Steady state spectra of **4** in dichloromethane (c=50 µM) at ambient conditions and at 77 K given in counts per second (solid lines); time resolved spectrum of **4** in dichloromethane (c=50 µM) after 50 µs delay (counts, dashed line).

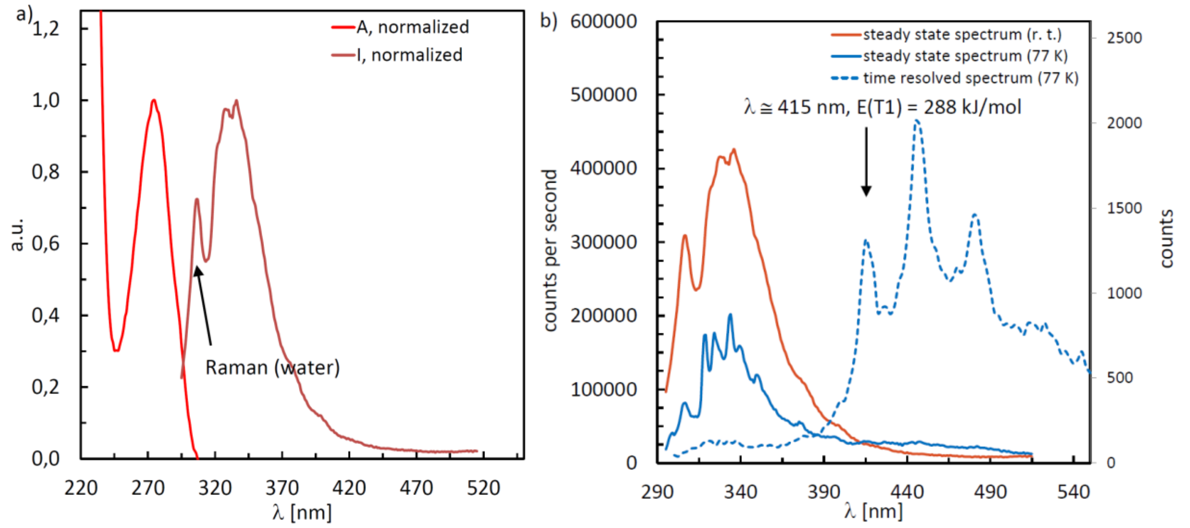


Figure S12. **(**a) Recorded UV/Vis of **9** in pentane/*iso*-pentane (c=25 µM), normalized to $A_{275\ nm}$; recorded luminescence of **9** in pentane/*iso*-pentane (c=25 µM) at ambient conditions, normalized to $I_{336\ nm}$. (b) Steady state spectra of **9** in pentane/*iso*-pentane (c=25 µM) at ambient conditions and at 77 K (WG300 filter glass applied) given in counts per second (solid lines); time resolved spectrum of **9**, sat. solution in pentane/iso-pentane, after 50 µs delay (counts, dashed line).

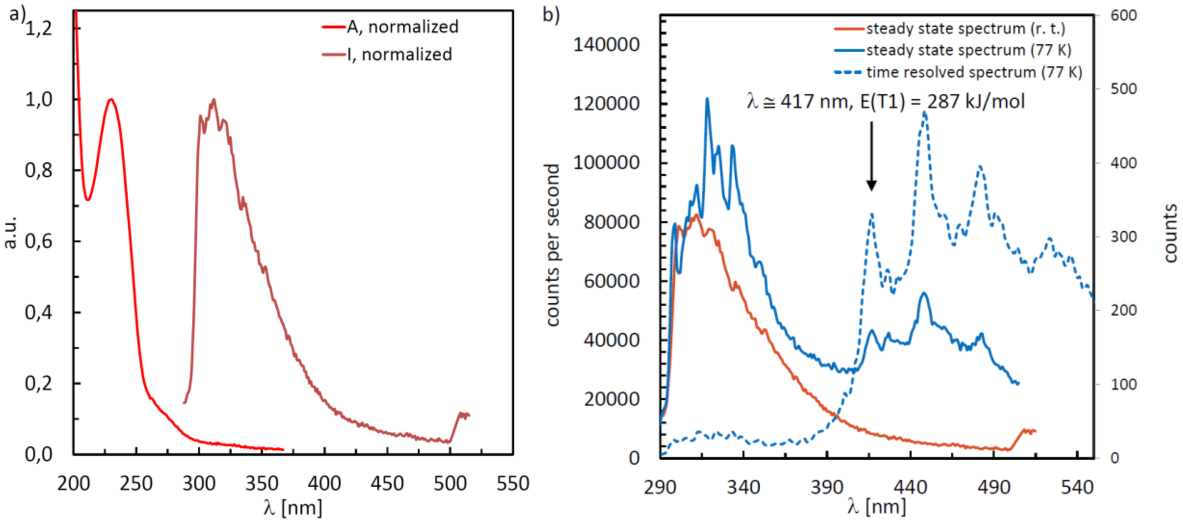
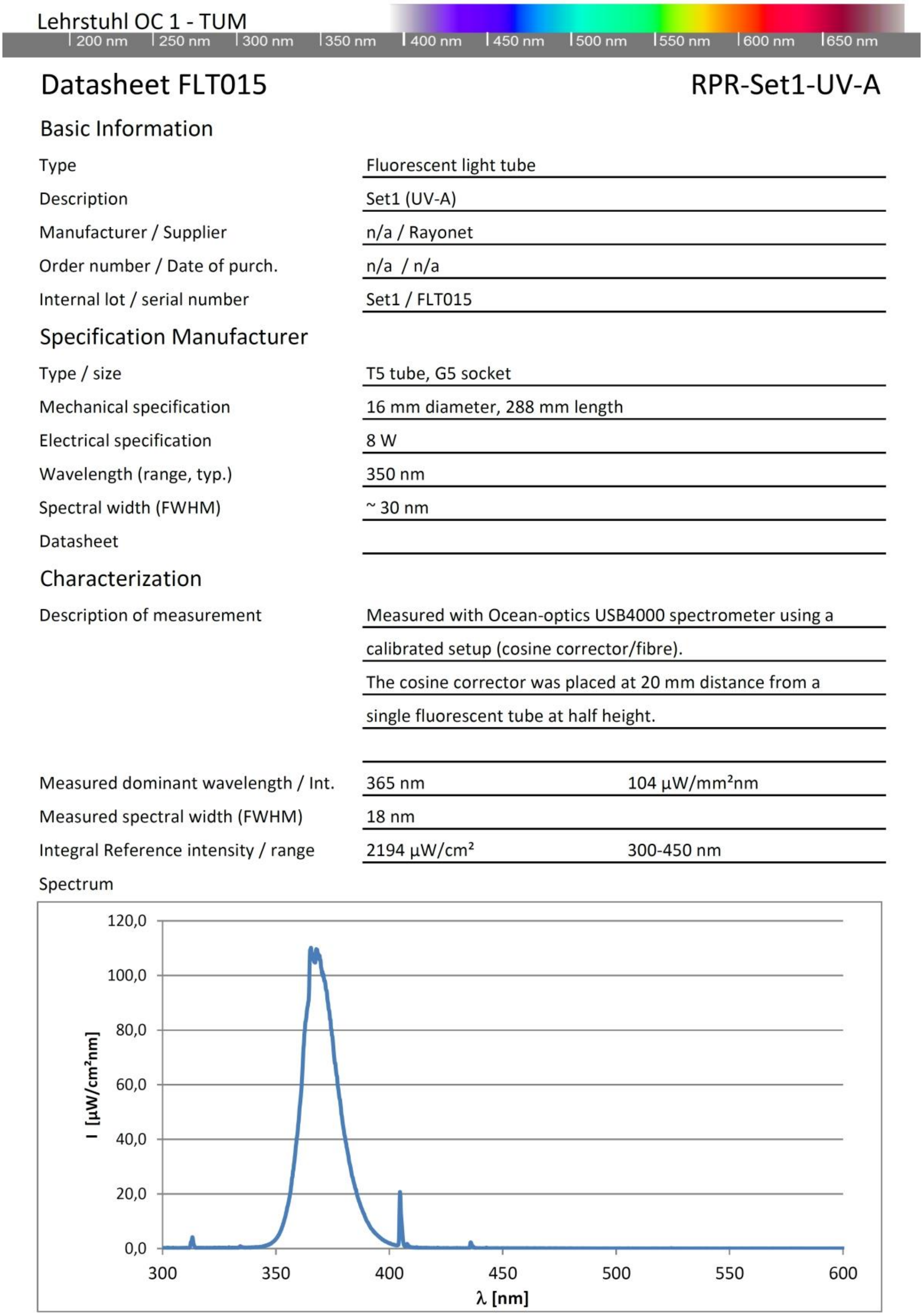


Figure S13. (a) Recorded UV/Vis of **12**, sat. solution in pentane/*iso*-pentane, normalized to $A_{230\text{ nm}}$; recorded luminescence (UV280 filter glass applied) of **12**, sat. solution in pentane/*iso*-pentane, at ambient conditions, normalized to $I_{312\text{ nm}}$. *Note: The two spectral signatures do obviously NOT belong to the same transition (no crossing at approx. half signal height, etc.). The transition, which the fluorescence originates from is most likely hidden as the shoulder of the absorption spectrum at ~260 nm*. (b) Steady state spectra of **12**, sat. solution in pentane/*iso*-pentane, at ambient conditions (UV280 filter glass applied) and at 77 K (WG300 filter glass applied) given in counts per second (solid lines); time resolved spectrum (WG300 filter glass applied) of **12**, sat. solution in pentane/*iso*-pentane, after 50 µs delay (counts, dashed line).

11. Datasheets of Fluorescent 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

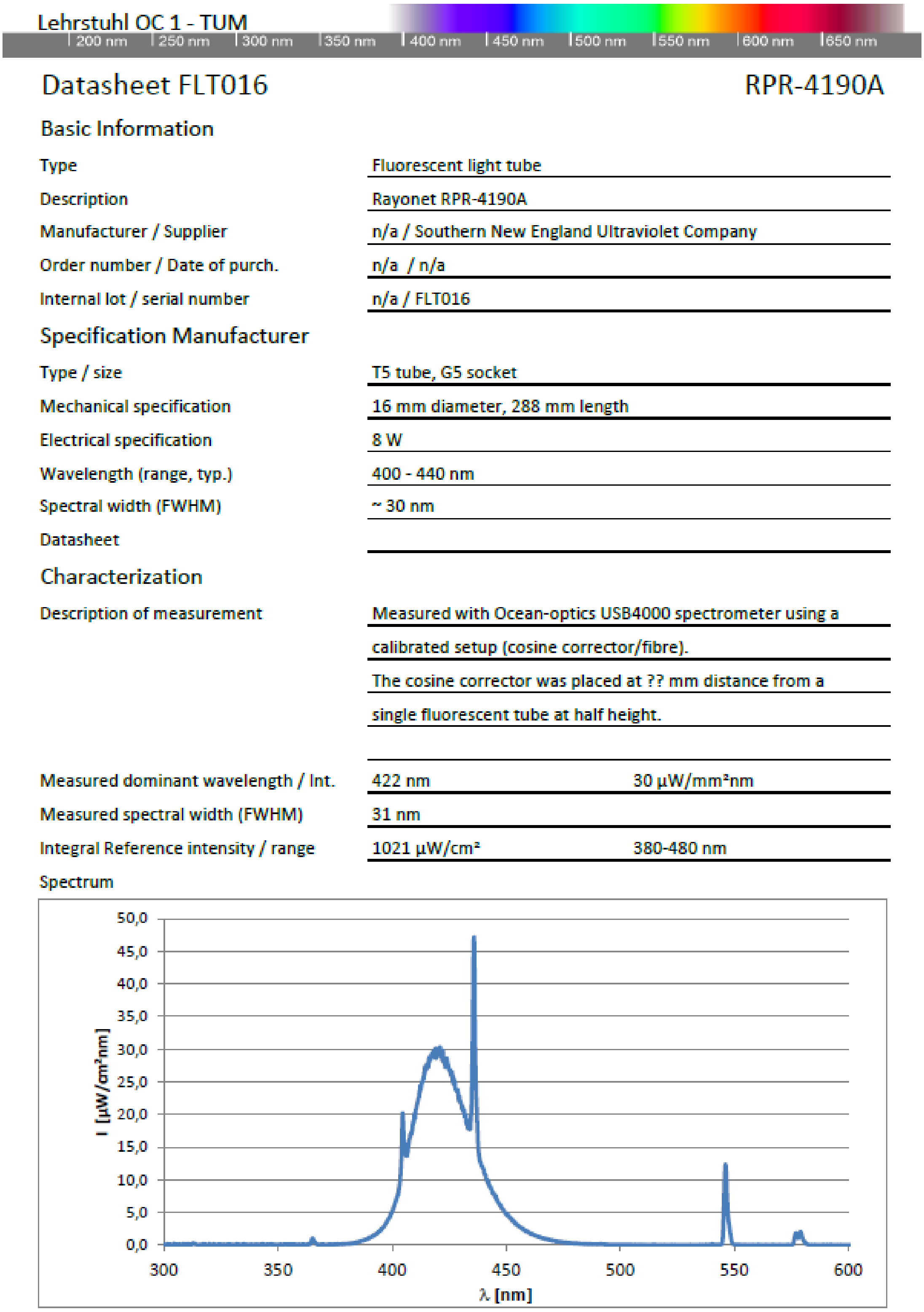
Type / size	T5 tube, G5 socket
Mechanical specification	16 mm diameter, 288 mm length
Electrical specification	8 W
Wavelength (range, typ.)	350 nm
Spectral width (FWHM)	~ 30 nm
Datasheet	

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

420 nm reactor



Lehrstuhl OC 1 - TUM

Datasheet FLT016 RPR-4190A

Basic Information

Type	Fluorescent light tube
Description	Rayonet RPR-4190A
Manufacturer / Supplier	n/a / Southern New England Ultraviolet Company
Order number / Date of purch.	n/a / n/a
Internal lot / serial number	n/a / FLT016

Specification Manufacturer

Type / size	T5 tube, G5 socket
Mechanical specification	16 mm diameter, 288 mm length
Electrical specification	8 W
Wavelength (range, typ.)	400 - 440 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 ?? mm distance from a single fluorescent tube at half height.	
Measured dominant wavelength / Int.	422 nm	30 µW/mm²nm
Measured spectral width (FWHM)	31 nm	
Integral Reference intensity / range	1021 µW/cm²	380-480 nm

Spectrum

437 nm LED

Lehrstuhl OC 1 - TUM

Datasheet LED036 Av-440-10W

Basic Information

Type	High-Power-LED
Description	Avonec 440-450 nm / 10 W
Manufacturer / Supplier	n/a / Avonec
Order number / Date of purch.	n/a / 01/2016
Internal lot / serial number	2016-01 / LED036

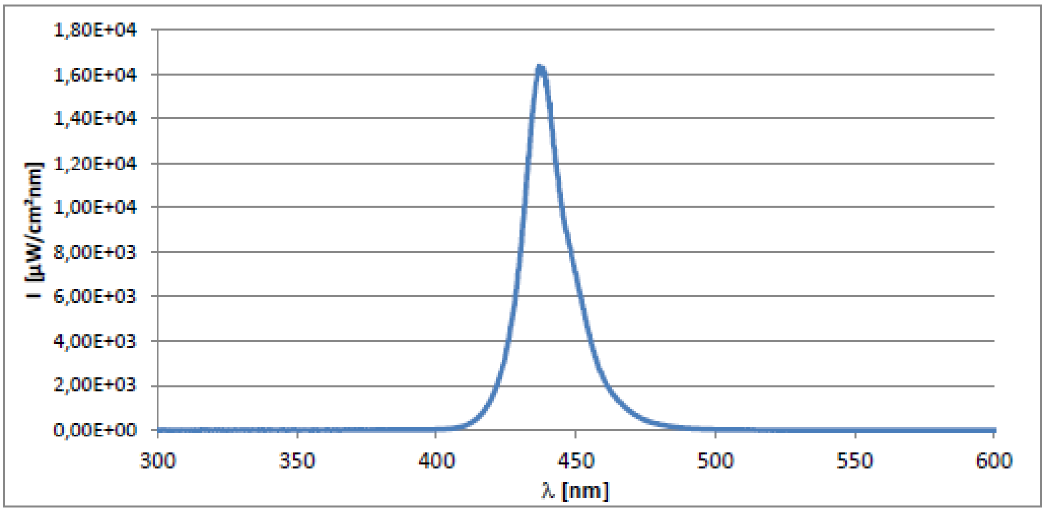
Specification Manufacturer

Type / size	10 emitter / ca. 1 x 1 mm
Mechanical specification	module, dye-area ca. 7.5 x 4 mm
Electrical specification	700 mA, UF 16 V
Wavelength (range, typ.)	440-450 nm, typ. n/a
Spectral width (FWHM)	n/a
Datasheet	n/a

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	437 nm
Measured spectral width	18 nm
Integral Reference intensity	353000 µW/cm² (380-530 nm @ 20 mm distance, 4 mm cosine corr.)

Spectrum



455 nm reactor

Decarboxylation experiments were carried out using an individually built photoreactor.[14] The interior of the photoreactor is lined with high performance mirrors. The lid and the LED with heat sink are exchangeable. The installed LEDs (10) are *Cree XLamp XP-G3* (3 W, Royal blue) lamps with a wavelength distribution of $\lambda = 455$ nm ± 10 nm at a working temperature of 25 °C (for the LED datasheet see: https://www.cree.com/led-components/media/documents/dsXPG3.pdf). The reactor chamber is cooled with two fans from each side for optimal air circulation. The LEDs are mounted on an aluminum heat sink with additional fans on top to guarantee working temperature of 25 °C.

12. References

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