**Supporting Information**

# Enantioselective Intermolecular [2+2] Photocycloaddition Reactions of 2(1*H*)-Quinolones Induced by Visible Light Irradiation

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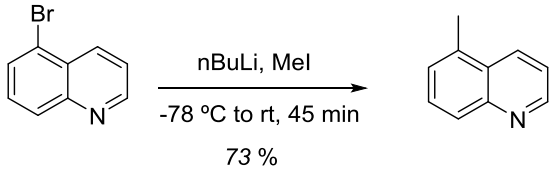
## 1. General Information

All reactions sensitive to air or moisture were carried out in flame-dried glassware under argon pressure using standard Schlenk techniques. Dry tetrahydrofuran (THF) and dichloromethane ($CH_2Cl_2$) were obtained from an MBraun MB-SPS 800 solvent purification system. Other dry solvents were obtained from Fluka and Acros in the highest purity available and used without further purification. Technical solvents used for aqueous workup and for column chromatography [*n*-pentane (pentane), ethyl acetate (EtOAc), methanol (MeOH), dichloromethane ($CH_2Cl_2$)] were distilled prior to use. Photochemical experiments were performed in pyrex tubes (∅ = 1.0 cm for racemic reactions, ∅ = 0.8 cm for enantioselective reactions and ∅ = 1.8 cm for 0.15 mmol scale reactions) in Rayonet type photochemical reactors equipped with 16 lamps [λ = 419 nm (RPR-4190 Å, Rayonet)]. Prior to irradiation, the reaction mixture was degassed by purging with argon in an ultrasonicating bath for 15 minutes. Flash chromatography was performed on silica 60 (Merck, 230-400 mesh) with the indicated eluent mixtures. Thin layer chromatography (TLC) was performed on silica coated glass plates (silica 60 F254) with detection by UV (λ = 254 and 366 nm). HPLC analyses were performed using a chiral stationary phase [ChiralPak AD-H (250 x 4.6 mm), ChiralCell OD-H (250 x 4.6 mm), Chiralcel, OJ-H, (250 x 4.6), Chiralpak AS-H (250 x 4.6 mm), Chiralpak AS-RH, 150 x 4.6 mm) Daicel Chemical Industries] with UVD 340 Photodiode Array Detector, P580 Pump and an ASI-100 Automated Sample Injector at 20 °C. Analytical gaschromatography was performed at a HP 6890 Series GC (Agilent, achiral stationary phase: HP-5 column, poly-dimethyl/diphenyl-siloxane, 95/5; chiral stationary phase: 2,3-dimethyl-6-TBDMS-β-cyclodextrine modified column) with a flame ionisation detector. The temperature method is given for the corresponding compounds. IR spectra were recorded on a JASCO IR-4100 (ATR), MS/HRMS measurements were performed on a Thermo Scientific DFS HRMS high resolution magnetic sector mass spectrometer. $^{1}H$ and $^{13}C$-NMR-spectra were recorded at 303 K either on a Bruker AVHD400 or a Bruker AVHD500 spectrometer. NMR spectra were calibrated to the respective residual solvent signals of $CDCl_3$ $\delta$ ($^{1}H$) = 7.26 ppm, $\delta$ ($^{13}C$) = 77.16 ppm (DMSO $\delta$ ($^{1}H$) = 2.50 ppm). Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (*virt.*). The relative configuration of chiral products and the multiplicity of the $^{13}C$ NMR signals were determined by two-dimensional NMR spectra (COSY, HSQC, HMBC, NOESY). UV-Vis spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis spectrometer. Melting points were measured on a Büchi 510 instrument and are not corrected. Specific rotations were determined with a ADP440+ Polarimeter.

## 2. Synthesis of Quinolones

### 5-Methylquinoline (S1)

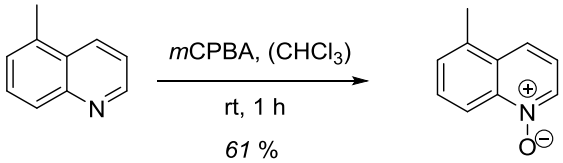



**S1**

A solution of 5-bromoquinoline (985 mg, 4.73 mmol, 1.00 eq) in dry THF (47 mL) was cooled to -78 °C under argon atmosphere and n-BuLi (2.5 M in hexane) (2.46 ml, 6.15 mmol, 1.30 eq) was added dropwise. After addition the solution was stirred at -78 °C for 15 min. Iodomethane (1.33 ml, 21.30 mmol, 4.5 eq) was added dropwise and the mixture was allowed to reach room temperature over 30 min, quenched with a solution of ammonium choride and extracted with diethyl ether. The organic phase was dried with $Na_2SO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, pentane/ethyl acetate 4:1). Quinoline **S1** (497 mg, 3.47 mmol, 73 %) was obtained as a colorless solid. The analytical data are in agreement with the literature.[*RSC Adv.* **2014**, *4*, 21456-21464.]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.91 (dd, $^3J$ = 4.2 Hz, $^4J$ = 1.6 Hz, 1H), 8.32 (*virt.* td, $^3J \approx {}^3J$ = 8.5 Hz, $^4J$ = 1.6 Hz, 1H), 7.97 (d, $^3J$ = 8.5 Hz, 1H), 7.64 - 7.57 (m, 1H), 7.42 (dd, $^3J$ = 8.5 Hz, $^3J$ = 4.2 Hz, 1H), 7.37 (d, $^3J$ = 7.1 Hz, 1H), 2.68 (s, 3H).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 150.0, 148.6, 134.7, 132.7, 129.3, 127.8, 127.8, 127.2, 120.8, 18.7.

### 5-Methylquinoline 1-oxide (S2)



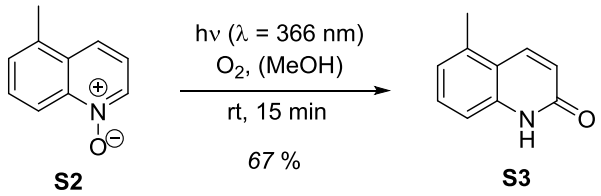

**S1** **S2**

A solution of 5-methylquinoline (**S1**) (480 mg, 3.35 mmol, 1.00 eq) in 13 mL of chloroform was treated with *meta*-chloroperbenzoic acid (1.164 g, 5.20 mmol, 1.55 eq). The mixture was stirred for 1 h at room temperature. Subsequently, saturated $NaHCO_3$ (17 mL) and 2M NaOH (17 mL) were added and the mixture was extracted with dichloromethane. The combined organic layers were dried with $Na_2SO_4$ and the solvent was removed at reduced pressure yielding the desired N-oxide **S2** (324 mg, 2.04 mmol, 61 %) as a bright yellow solid which was used in the following step without further purification. The analytical data are in agreement with the literature.[*J. Chem. Soc. B*, **1970**, 440-443.]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.74 (*virt.* td, $^3J \approx {}^3J$ = 8.9 Hz, $^4J$ = 1.0 Hz, 1H), 8.56 (dd, $^3J$ = 6.0 Hz, $^4J$ =1.0 Hz, 1H), 8.09 (dd, $^3J$ = 8.8 Hz, $^4J$ = 1.0 Hz, 1H),

7.91 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.0 Hz, 1H), 7.59 (dd, $^3J$ = 8.8 Hz, $^3J$ = 7.5 Hz, 1H), 7.39 (dd, $^3J$ = 8.8 Hz, $^3J$ = 6.0 Hz, 1H), 2.72 (s, 3H).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 142.0, 135.5, 135.4, 130.1, 130.0, 129.3, 122.9, 120.4, 117.9, 19.1.

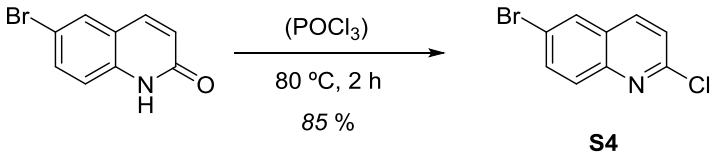
**5-Methylquinolin-2-(1*H*)-one (S3)**




5-Methylquinoline 1-oxide (**S2**) (90 mg, 0.57 mmol) was disolved in methanol (HPLC grade, 80 mL). The solution was then saturated with oxygen, transferred into 7 phototubes and irradiated at λ = 366 nm in a Rayonet photoreactor at room temperature for 15 min. Subsequently the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, pentane/ethyl acetate 1:1). Quinolone **S3** (60.4 mg, 0.38 mmol, 67 %) was isolated as a colorless solid. The analytical data are in agreement with the literature.[*PLoS ONE* **2015**, 10, e0113705]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 12.55 (br. s, 1H), 8.05 (d, $^3J$ = 9.7 Hz, 1H), 7.41 (dd, $^3J$ = 8.2 Hz, $^3J$ = 7.2 Hz, 1H), 7.33 (d, $^3J$ = 8.2 Hz, 1H), 7.06 (d, $^3J$ = 7.2 Hz, 1H), 6.76 (d, $^3J$ = 9.7 Hz, 1H), 2.64 (s, 3H).
**$^{13}$C-NMR** (400 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 164.4, 138.9, 138.0, 135.6, 130.8, 124.2, 120.7, 119.0, 114.7, 18.8.

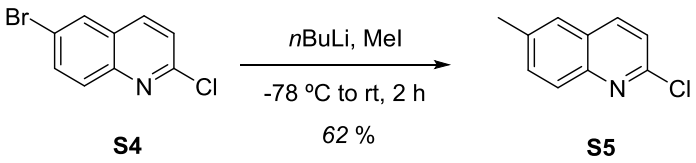
**6-Bromo-2-chloroquinoline (S4)**




6-Bromoquinolin-2(1*H*)-one (700 mg, 3.12 mmol, 1.00 eq) was suspended in $POCl_3$ (0.5 mL, 5.38 mmol, 1.72 eq) under inert atmosphere. The suspension was heated at 80 °C for 2 hours. After the mixture was cooled at room temperature, the dark red thick suspension was poured onto an ice-water mixture. The mixture was then rendered basic with 8M NaOH and extracted with dichloromethane. The organic layers were washed with water, brine, dried over $Na_2SO_4$ and concentrated in vacuo. The crude product was then purified by column chromatography (silica, pentane/ethyl acetate 9:1). Quinoline **S4** (643 mg, 2.65 mmol, 85 %) was isolated as a colorless solid. The analytical data are in agreement with the literature.[*Tetrahedron Lett.* **2014**, *55*, 7130-7132.]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.03 (d, $^3J$ = 8.6 Hz, 1H), 7.99 (d, $^4J$ = 2.1 Hz, 1H), 7.90 (d, $^3J$ = 9.0 Hz, 1H), 7.81 (dd, $^3J$ = 9.0 Hz, $^4J$ = 2.1 Hz, 1H), 7.42 (d, $^3J$ = 8.6 Hz, 1H).

**6-Methyl-2-chloroquinoline (S5)**

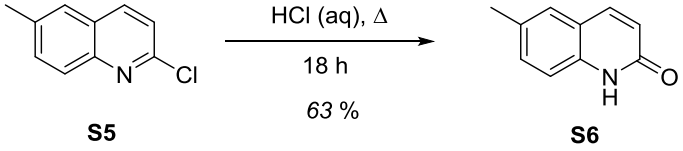



**S4** **S5**

A solution of 6-bromo-2-chloroquinoline (**S4**) (300 mg, 1.24 mmol, 1.00 eq) in dry THF (10 mL) was cooled to -78 °C under argon atmosphere and n-BuLi (2.5 M in hexane) (0.61 ml, 1.51 mmol, 1.22 eq) was added dropwise. After addition the solution was stirred at -78 °C for 1 h. Iodomethane (0.08 ml, 1.24 mmol, 1.00 eq) was added dropwise and the mixture was stirred at this temperature for 1 h, then it was quenched with water at - 20 ºC, extracted with ethyl acetate, dried with $Na_2SO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, pentane/ethyl acetate 4:1). Quinoline **S5** (137 mg, 0.77 mmol, 62 %) was obtained as a colorless solid. The analytical data are in agreement with the literature.[ *Tetrahedron Lett.* **2014**, *55*, 7130-7132]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 7.99 (d, $^3J$ =8.7 Hz, 1H), 7.91 (d, $^3J$ = 9.1 Hz, 1H), 7.61 − 7.53 (m, 2H), 7.33 (d, $^3J$ = 8.7 Hz, 1H), 2.53 (s, 3H).

**6-Methylquinolin-2-(1*H*)-one (S6)**

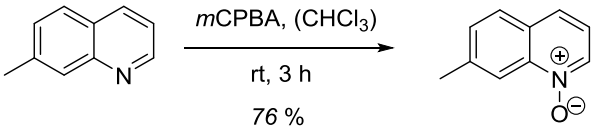



**S5** **S6**

6-Methyl-2-chloroquinoline (75 mg, 0.42 mmol, 1.00 eq) was refluxed in HCl 6M (1.5 mL) for 22 h. The reaction mixture was cooled to room temperature, and it was extracted with dichloromethane and dried with $Na_2SO_4$. The crude residue was purified by column chromatography (silica, pentane/ethyl acetate 1:1). 6-Methylquinolin-2-(1*H*)-one (**S6**) (42.1 mg, 0.26 mmol, 63 %) was obtained as a colorless solid. The analytical data are in agreement with the literature.[*Org. Lett.* **2015**, *17*, 222-225.]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 12.44 (br. s, 1H), 7.77 (d, $^3J$ = 9.4 Hz, 1H), 7.41 − 7.30 (m, 3H), 6.71 (d, $^3J$ = 9.4 Hz, 1H), 2.41 (s, 3H).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 163.9, 141.0, 136.6, 132.5, 132.3, 127.5, 121.3, 120.1, 116.2, 21.0.

**7-Methylquinoline 1-oxide (S7)**

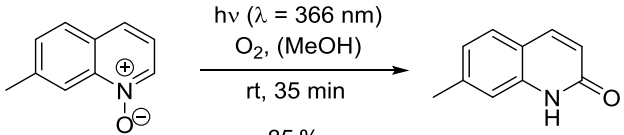



**S7**

A solution of 7-methylquinoline (1.00 g, 6.98 mmol, 1.00 eq) in 20 mL of chloroform was treated with *meta*-chloroperbenzoic acid (2.67 g, 7.57 mmol, 1.55 eq). The mixture was stirred for 3 h at room temperature. Subsequently saturated $NaHCO_3$ (25 mL) and 2M NaOH (25 mL) were added and the mixture was extracted with dichloromethane. The combined organic layers were dried with $Na_2SO_4$ and the solvent was removed at reduced pressure yielding the desired N-oxide **S7** (844 mg, 5.30 mmol, 76 %) as a yellow solid which was used in the following step without further purification. The analytical data are in agreement with the literature.[*Org. Lett.* **2015**, *17*, 3134-3137.]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.54 (s, 1H), 8.51 (d, $^3J$ = 5.9 Hz, 1H), 7.75 (d, $^3J$ = 8.4 Hz, 1H), 7.70 (d, $^3J$ = 8.4 Hz, 1H), 7.46 (d, $^3J$ = 8.4 Hz, 1H), 7.22 (dd, $^3J$ = 8.4 Hz, $^3J$ = 5.9 Hz, 1H), 2.58 (s, 3H).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 141.8, 141.6, 135.9, 131.1, 128.8, 128.0, 126.2, 120.1, 118.9, 22.2.

**7-Methylquinolin-2-(1*H*)-one (S8)**

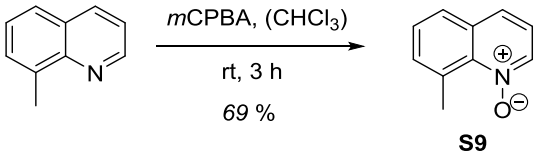



**S7** **S8**

7-Methylquinoline 1-oxide (**S7**) (250 mg, 1.57 mmol) was disolved in methanol (HPLC grade, 50 mL). The solution was then saturated with oxygen, transferred into 5 phototubes and irradiated at λ = 366 nm in a Rayonet photoreactor at room temperature for 35 min. Subsequently the solvent was removed under reduced pressure and the crude product was then purified by column chromatography (silica, pentane/ethyl acetate 1:1). Quinolone **S8** (212 mg, 1.33 mmol, 85 %) was isolated as a colorless solid. The analytical data are in agreement with the literature.[*Org. Lett.* **2015**, *17*, 222-225.]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 12.63 (br. s, 1H), 7.80 (d, $^3J$ = 9.4 Hz, 1H), 7.45 (d, $^3J$ = 7.8 Hz, 1H), 7.27 (s, 1H), 7.05 (d, $^3J$ = 7.8 Hz, 1H), 6.68 (d, $^3J$ = 9.4 Hz, 1H), 2.46 (s, 3H).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 165.0, 141.8, 141.2, 138.8, 127.6, 124.6, 120.1, 118.1, 116.3, 21.9.

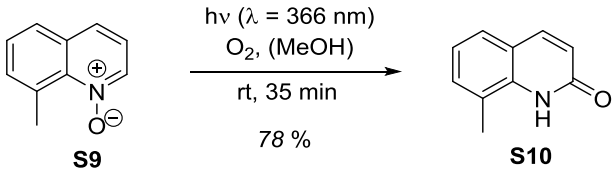
**8-Methylquinoline 1-oxide (S9)**




A solution of 8-methylquinoline (1.00 g, 6.98 mmol, 1.00 eq) in 20 mL of chloroform was treated with *meta*-chloroperbenzoic acid (2.67 g, 7.57 mmol, 1.55 eq). The mixture was stirred for 3 h at room temperature. Subsequently saturated $NaHCO_3$ (25 mL) and 2M NaOH (25 mL) were added and the mixture was extracted with dichloromethane. The combined organic layers were dried with $Na_2SO_4$ and the solvent was removed at reduced pressure yielding the desired N-oxide **S9** (767 mg, 4.81 mmol, 69 %) as a yellow solid which was used in the following step without further purification. The analytical data are in agreement with the literature.[*Org. Lett.* **2015**, *17*, 3134-3137.]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.37 (d, $^3J$ = 6.0 Hz, 1H), 7.71 − 7.53 (m, 2H), 7.46 − 7.34 (m, 2H), 7.16 (dd, $^3J$ = 7.0 Hz, $^3J$ = 5.2 Hz, 1H), 3.16 (s, 3H).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 141.5, 137.4, 133.7, 133.5, 132.6, 128.2, 126.9, 126.6, 120.7, 25.0.

**8-Methylquinolin-2-(1*H*)-one (S10)**

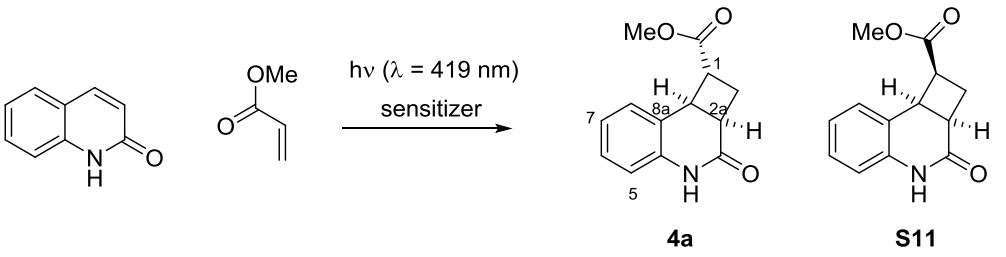



8-Methylquinoline 1-oxide (**S9**) (300 mg, 1.88 mmol) was disolved in methanol (HPLC grade, 60 mL). The solution was then saturated with oxygen, transferred into 6 phototubes and irradiated at λ = 366 nm in a Rayonet photoreactor at room temperature for 35 min. Subsequently the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, pentane/ethyl acetate 1:1). Quinolone **S10** (234 mg, 1.47 mmol, 78 %) was isolated as a colorless solid. The analytical data are in agreement with the literature.[*Org. Lett.* **2015**, *17*, 222-225.]

**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.96 (br. s, 1H), 7.77 (d, $^3J$ = 9.5 Hz, 1H), 7.41 (d, $^3J$ = 7.8 Hz, 1H), 7.35 (d, $^3J$ = 7.3 Hz, 1H), 7.12 (*virt.* t, $^3J \approx {}^3J$ = 7.6 Hz, 1H), 6.67 (d, $^3J$ = 9.5 Hz, 1H), 2.52 (s, 3H).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 163.5, 141.5, 137.0, 132.0, 126.2, 123.4, 122.5, 121.5, 119.9, 17.0.

## 3. Intermolecular [2 + 2] Photocycloaddition Reactions of Quinolones

**Methyl (1*R*,2a*R*,8b*R*)-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carboxylate (4a)** and **Methyl (1*S*,2a*R*,8b*R*)-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carboxylate (S11)**




$C_{13}H_{13}NO_3$
MW: 231,25 g/mol

*Racemic [2+2] Photocycloaddition*

2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, methyl acrylate (125 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 5 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compounds **4a** (22.4 mg, 0.10 mmol, 69 %) and **S11** (4.9 mg, 0.02 mmol, 15 %) were obtained as colorless solids.

*Enantioselective [2+2] Photocycloaddition*

2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, methyl acrylate (113 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 6 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4a** (4.4 mg, 19.0 µmol, 76 %, 81 % *ee*) was obtained as a colorless solid.

*Enantioselective [2+2] Photocycloaddition at −40 °C*

2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in a solvent mixture [1,3-bis(trifluoromethyl)benzene and α,α,α-trifluorotoluene = 2/1] (10 mL, *c* = 2.5 mmol/L). After degassing the solution, methyl acrylate (113 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 22 h at −40 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4a** (4.4 mg, 19.0 µmol, 85 %, 83 % *ee*) was obtained as a colorless solid.

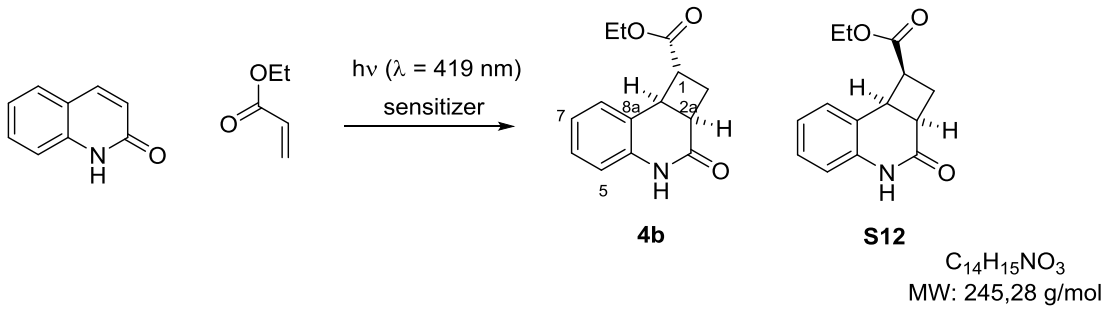
*Exo isomer (**4a**):*

**M.p.**: 156-158 °C.
**TLC**: $R_f$ = 0.66 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.36 (br. s, 1H, NH), 7.17 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, $^4J$ = 1.6 Hz, 1H, H-6), 7.10 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1H, H-8), 6.98 (*virt.* td, $^3J \approx {}^3J$ = 7.5 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.83 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 4.02 (*virt.* t, $^3J \approx {}^3J$ = 8.9 Hz, 1H, H-8b), 3.73 (s, 3H, MeO), 3.41 – 3.26 (m, 2H, H-1, H-2a), 2.87 (*virt.* dt, $^2J$ = 12.1 Hz, $^3J \approx {}^3J$ = 9.7 Hz, 1H, H-2), 2.72 – 2.58 (m, 1H, H-2).
**$^1$H-NMR** (500 MHz, DMSO, 303 K): $\delta$ (ppm) = 10.18 (br. s, 1H, NH), 7.14 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, $^4J$ = 1.5 Hz, 1H, H-6), 7.03 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1H, H-8), 6.93 – 6.85 (m, 2H, H-5, H-7), 3.86 (*virt.* t, $^3J \approx {}^3J$ = 9.0 Hz, 1H, H-8b), 3.64 (s, 3H, MeO), 3.24 (virt. qd, $^3J \approx {}^3J \approx {}^3J$ = 9.1 Hz, $^4J$ = 1.3 Hz, 1H, H-1), 3.14 (virt. tdd, $^3J \approx {}^3J$ = 9.8 Hz, 3.0, $^4J$ = 1.4 Hz, 1H, H-2a), 2.67 (virt. dt, $^2J$ = 11.8 Hz, $^3J \approx {}^3J$ = 9.8 Hz, 1H, H-2), 2.35 (ddd, $^2J$ = 11.8, $^3J$ = 8.8 Hz, $^3J$ = 3.0 Hz, 1H, H-2).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 174.0 (s, *C*OOMe), 173.0 (s, C-3), 136.8 (s, C-4a), 128.5 (d, C-6), 128.0 (d, C-8), 123.8 (d, C-7), 122.5 (s, C-8a), 116.0 (d, C-5), 52.2 (q, OMe), 45.0 (d, C-2a), 40.1 (d, C-8b), 34.9 (d, C-1), 29.4 (t, C-2).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1728, 1671, 1652, 1592, 1488, 1383, 1357, 1304, 1240, 1201, 1175, 1126, 1065, 1021, 942, 795, 766, 697, 669, 633, 620, 605.
**MS** (EI, 70 eV): *m/z* (%) = 231 (8) [$M^+$], 216 (0.4) [$M^+$–$CH_3$], 199 (4) [$M^+$–$OCH_3$], 171 (12) [$M^+$–$C_2H_3O_2$], 145 (100) [$M^+$–$C_4H_7O_2$], 117 (28), 90 (9).
**HRMS (EI)** ($C_{13}H_{13}NO_3$): calc.: 231.0895; found: 231.0890.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4a**, $t_R$ = 15.2 min; *ent*-**4a**, 16.8 min).

*Endo isomer (**S11**):*

**M.p.**: 159-161 °C.
**TLC**: $R_f$ = 0.55 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 7.96 (br. s, 1H, NH), 7.14 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, $^4J$ = 1.2 Hz, 1H, H-6), 6.98 (dd, $^3J$ = 7.3 Hz, $^4J$ = 1.2 Hz, 1H, H-8), 6.94 (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.68 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 4.25 (*virt.* t, $^3J \approx {}^3J$ = 9.7 Hz, 1H, H-8b), 3.64 (ddd, $^3J$ = 9.9 Hz, $^3J$ = 8.5 Hz, $^3J$ = 7.2 Hz, 1H, H-1), 3.45 (*virt.* td, $^3J \approx {}^3J$ = 9.9 Hz, $^3J$ = 7.0 Hz, 1H, H-2a), 3.39 (s, 3H, OMe), 2.89 (*virt.* dt, $^2J$ = 12.6 Hz, $^3J \approx {}^3J$ = 7.1 Hz, 1H, H-2), 2.72 (ddd, $^2J$ = 12.6 Hz, $^3J$ = 10.3 Hz, $^3J$ = 8.5 Hz, 1H, H-2).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 172.3 (s, *C*OOMe), 170.8 (s, C-3), 137.3 (s, C-4a), 129.0 (d, C-8), 128.6 (d, C-6), 123.3 (d, C-7), 119.5 (s, C-8a), 115.9 (d, C-5), 51.6 (q, OMe), 44.1 (d, C-1), 38.9 (d, C-8b), 34.9 (d, C-2a), 27.5 (t, C-2).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1726, 1669, 1590, 1492, 1433, 1400, 1357, 1323, 1288, 1241, 1200, 1171, 1158, 1086, 1058, 1038, 938, 874, 842, 752, 731, 709, 679, 602.
**MS** (EI, 70 eV): *m/z* (%) = 231 (9) [$M^+$], 216 (0.2) [$M^+$–$CH_3$], 199 (4) [$M^+$–$OCH_3$], 171 (14) [$M^+$–$C_2H_3O_2$], 145 (100) [$M^+$–$C_4H_7O_2$], 117 (26), 90 (10).
**HRMS (EI)** ($C_{13}H_{13}NO_3$): calc.: 231.0895; found: 231.0890.

**Ethyl (1*R*,2a*R*,8b*R*)-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carboxylate (4b) and Ethyl (1*S*,2a*R*,8b*R*)-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carboxylate (S12)**




$C_{14}H_{15}NO_3$
MW: 245,28 g/mol

*Racemic [2+2] Photocycloaddition*
2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, ethyl acrylate (150 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 5 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compounds **4b** (22.0 mg, 0.09 mmol, 64 %) and **S12** (4.1 mg, 0.02 mmol, 12 %) were obtained as colorless solids.

*Enantioselective [2+2] Photocycloaddition*
2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, ethyl acrylate (138 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 6 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4b** (5.6 mg, 23.0 µmol, 82 %, 78 % *ee*) was obtained as a colorless solid.

*Enantioselective [2+2] Photocycloaddition at −40 °C*
2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in a solvent mixture [1,3-bis(trifluoromethyl)benzene and α,α,α-trifluorotoluene = 2/1] (10 mL, *c* = 2.5 mmol/L). After degassing the solution, ethyl acrylate (138 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 45 h at −40 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4b** (4.8 mg, 19.7 µmol, 79 %, 80 % *ee*) was obtained as a colorless solid.

*Enantioselective [2+2] Photocycloaddition (0.15 mmol scale)*

2(1*H*)-Quinolone (22.0 mg, 0.15 mmol, 1.00 eq.) and enantiomerically pure **3** (6.6 mg, 15.0 μmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (60 mL, *c* = 2.5 mmol/L). After degassing the solution, methyl acrylate (807 μl, 7.50 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 8 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4b** (30.3 mg, 124 μmol, 82 %, 76 % *ee*) was obtained as a colorless solid.

*Exo isomer (**4b**):*

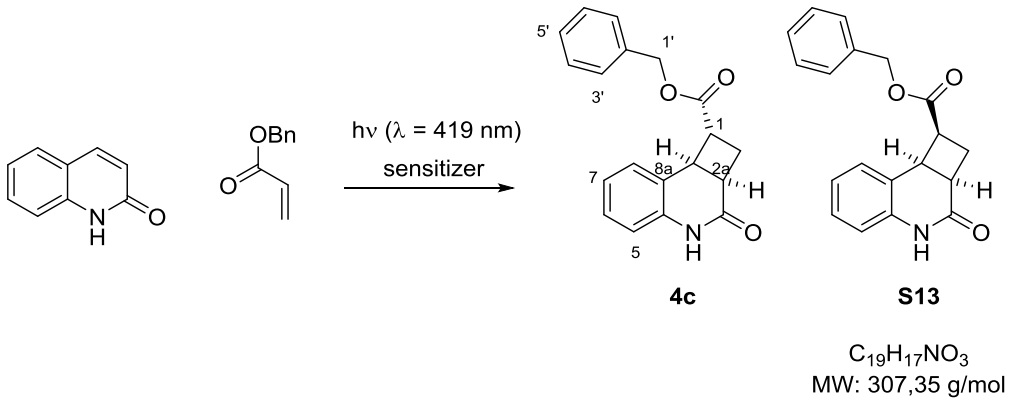
**M.p.**: 111-113 °C.
**TLC**: $R_f$ = 0.84 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.37 (br. s, 1H, NH), 7.17 (*virt.* t, $^3J \approx {}^3J$ = 7.6 Hz, 1H, H-6), 7.10 (d, $^3J$ = 7.3 Hz, 1H, H-8), 6.99 (*virt.* t, $^3J \approx {}^3J$ = 7.4 Hz, 1H, H-7), 6.84 (d, $^3J$ = 7.9 Hz, 1H, H-5), 4.27 – 4.09 (m, 2H, $OCH_2CH_3$), 4.01 (*virt.* t, $^3J \approx {}^3J$ = 8.8 Hz, 1H, H-8b), 3.48 – 3.22 (m, 2H, H-1, H-2a), 2.87 (*virt.* dt, $^2J$ = 11.9 Hz, $^3J \approx {}^3J$ = 9.8 Hz, 1H, H-2), 2.64 (ddd, $^2J$ = 11.9 Hz, $^3J$ = 9.1 Hz, $^3J$ = 3.2 Hz, 1H, H-2), 1.28 (t, 3H, $^3J$ = 7.1 Hz, $OCH_2CH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 173.5 (s, *C*OOEt), 173.0 (s, C-3), 136.7 (s, C-4a), 128.5 (d, C-6), 128.0 (d, C-8), 123.9 (d, C-7), 122.6 (s, C-8a), 116.1 (d, C-5), 61.0 (t, $OCH_2CH_3$), 45.2 (d, C-2a), 40.1 (d, C-8b), 34.8 (d, C-1), 29.3 (t, C-2), 14.4 (q, $OCH_2CH_3$).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 3204, 3062, 2982, 1726, 1666, 1593, 1491, 1374, 1350, 1301, 1239, 1198, 1166, 1063, 1035, 859, 753.
**MS** (EI, 70 eV): *m/z* (%) = 245 (7) [$M^+$], 199 (4) [$M^+–C_2H_5O$], 171 (11) [$M^+–C_3H_5O_2$], 145 (100) [$M^+–C_5H_8O_2$], 117 (23), 90 (7).
**HRMS (EI)** ($C_{14}H_{15}NO_3$): calc.: 245.1046; found: 245.1052.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4b**, $t_R$ = 12.4 min; *ent*-**4b**, 13.7 min).
**Specific rotation** $[\alpha]_D^{20}$ = –88.6 (*c* = 0.54, $CHCl_3$) [76% *ee*].

*Endo isomer (**S12**):*

**M.p.**: 131-133 °C.
**TLC**: $R_f$ = 0.54 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.21 (br. s, 1H, NH), 7.14 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, $^4J$ = 1.5 Hz, 1H, H-6), 7.00 (dd, $^3J$ = 7.6 Hz, $^4J$ = 1.5 Hz, 1H, H-8), 6.93 (*virt.* td, $^3J \approx {}^3J$ = 7.5 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.70 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 4.25 (*virt.* t, $^3J \approx {}^3J$ = 9.8 Hz, 1H, H-8b), 3.89 – 3.76 (m, 2H, $OCH_2CH_3$), 3.59 (ddd, $^3J$ = 9.9 Hz, $^3J$ = 8.5 Hz, $^3J$ = 6.8 Hz, 1H, H-1), 3.45 (*virt.* td, $^3J \approx {}^3J$ = 9.9 Hz, $^3J$ = 6.7 Hz, 1H, H-2a), 2.88 (m, 1H, H-2), 2.78 – 2.67 (m, 1H, H-2), 0.98 (t, $^3J$ = 7.1 Hz, 3H, $OCH_2CH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 174.7 (s, *C*OOEt), 172.0 (s, C-3), 137.2 (s, C-4a), 129.2 (d, C-8), 128.6 (d, C-6), 123.3 (d, C-7), 119.6 (s, C-8a), 115.9 (d, C-5), 60.7 (t, $OCH_2CH_3$), 44.2 (d, C-1), 38.8 (d, C-8b), 34.9 (d, C-2a), 27.5 (t, C-2), 14.3 (q, $OCH_2CH_3$).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 2981, 2936, 1728, 1677, 1446, 1378, 1299, 1243, 1176, 1176, 1160, 1097, 1023, 853, 757.

**HRMS (EI)** ($C_{14}H_{15}NO_3$): calc.: 245.1046; found: 245.1049.
**MS** (EI, 70 eV): *m/z* (%) = 245 (5) [$M^+$], 199 (4) [$M^+$–$C_2H_5O$], 171 (9) [$M^+$–$C_3H_5O_2$], 145 (100) [$M^+$–$C_5H_8O_2$], 117 (22), 90 (8).

**Benzyl (1*R*,2a*R*,8b*R*)-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carboxylate (4c)** and **Benzyl (1*S*,2a*R*,8b*R*)-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carboxylate (S13)**




$C_{19}H_{17}NO_3$
MW: 307,35 g/mol

*Racemic [2+2] Photocycloaddition*
2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, benzyl acrylate (207 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 3 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compounds **4c** (34.5 mg, 0.11 mmol, 79 %) and **S13** (7.4 mg, 0.02 mmol, 17 %) were obtained as colorless solids.

*Enantioselective [2+2] Photocycloaddition*
2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, benyl acrylate (188 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 6 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4c** (6.4 mg, 21.0 µmol, 83 %, 82 % *ee*) was obtained as a colorless solid.

*Enantioselective [2+2] Photocycloaddition (0.15 mmol scale)*
2(1*H*)-Quinolone (22.0 mg, 0.15 mmol, 1.00 eq.) and enantiomerically pure **3** (6.6 mg, 15.0 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (60 mL, *c* = 2.5 mmol/L). After degassing the solution, benzyl acrylate (1.16 ml, 7.50 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 8 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 7:3 → 1:1). The title compound **4c** (36.3 mg, 119 µmol, 79 %, 80 % *ee*) was obtained as a colorless solid.

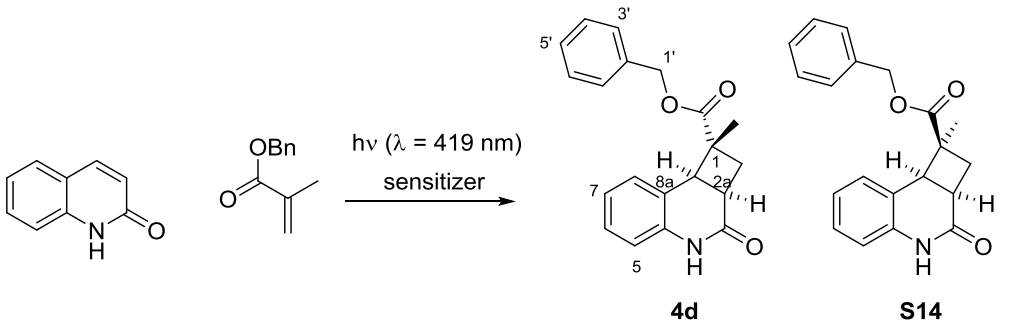
*Exo isomer (**4c**):*

**M.p.**: 119-121 °C.
**TLC**: $R_f$ = 0.73 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.36 (br. s, 1H, NH), 7.45 – 7.30 (m, 4H, Ar), 7.23 – 7.20 (m, 1H, Ar), 7.17 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, $^4J$ = 1.2 Hz, 1H, H-6), 7.01 (dd, $^3J$ = 7.1 Hz, $^4J$ = 1.2 Hz, 1H, H-8), 6.95 (*virt.* td, $^3J \approx {}^3J$ = 7.3 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.83 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 5.22 (d, $^2J$ = 12.2 Hz, 1H, H-1'), 5.13 (d, $^2J$ = 12.2 Hz, 1H, H-1'), 4.01 (*virt.* t, $^3J \approx {}^3J$ = 8.9 Hz, 1H, H-8b), 3.47 – 3.23 (m, 2H, H-1, H-2a), 2.90 (*virt.* dt, $^2J$ = 12.1 Hz, $^3J \approx {}^3J$ = 9.7 Hz, 1H, H-2), 2.65 (ddd, $^2J$ = 12.1 Hz, $^3J$ = 9.2 Hz, $^3J$ = 3.3 Hz, 1H, H-2).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 173.2 (s, *C*OOBn), 172.9 (s, C-3), 136.8 (s, C-4a), 135.8 (s, C-2'), 128.7 (d, C-4'), 128.5 (d, C-5'), 128.4 (d, C-6), 128.3 (d, C-3'), 128.0 (d, C-8), 123.8 (d, C-7), 122.4 (s, C-8a), 116.0 (d, C-5), 66.7 (t, C-1'), 45.1 (d, C-2a), 40.2 (d, C-8b), 34.9 (d, C-1), 29.2 (t, C-2).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1728, 1665, 1593, 1493, 1456, 1382, 1350, 1250, 1236, 1195, 1173, 1151, 1123, 1065, 1025, 907, 870, 854, 831, 758, 701, 679, 620.
**MS** (EI, 70 eV): *m/z* (%) = 307 (4) [$M^+$], 248 (3), 216 (3) [$M^+$–Bn], 200 (2) [$M^+$–OBn], 172 (3) [$M^+$–$C_8H_7O_2$], 159 (2) [$M^+$–$C_9H_9O_2$], 145 (100) [$M^+$–$C_{10}H_{11}O_2$], 117 (18), 91 (14).
**HRMS (EI)** ($C_{19}H_{17}NO_3$): calc.: 307.1208; found: 307.1216.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4c**, $t_R$ = 18.1 min; *ent*-**4c**, 24.2 min).
**Specific rotation** $[\alpha]_D^{20}$ = –86.8 (*c* = 0.67, $CHCl_3$) [80% *ee*].

*Endo isomer (**S13**):*

**M.p.**: 121-123 °C.
**TLC**: $R_f$ = 0.64 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.03 (br. s, 1H, NH), 7.39 – 7.26 (m, 3H, Ar), 7.26 – 7.06 (m, 3H, Ar, H-6), 6.94 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.6 Hz, 1H, H-8), 6.86 (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, $^4J$ = 1.1 Hz, 1H, H-7), 6.65 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.1 Hz, 1H, H-5), 4.85 (d, $^2J$ = 12.1 Hz, 1H, H-1'), 4.71 (d, $^2J$ = 12.1 Hz, 1H, H-1'), 4.25 (*virt.* t, $^3J \approx {}^3J$ = 9.9 Hz, 1H, H-8b), 3.66 (ddd, $^3J$ = 9.8 Hz, $^3J$ = 8.5 Hz, $^3J$ = 6.9 Hz, 1H, H-1), 3.45 (*virt.* td, $^3J \approx {}^3J$ = 9.9 Hz, $^3J$ = 6.8 Hz, 1H, H-2a), 2.91 (*virt.* dt, $^2J$ = 12.4 Hz, $^3J \approx {}^3J$ = 6.9 Hz, 1H, H-2), 2.82 – 2.64 (m, 1H, H-2).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 171.8 (s, *C*OOBn), 170.9 (s, C-3), 137.3 (s, C-4a), 135.5 (s, C-2'), 129.1 (d, C-5'), 128.7 (d, C-6), 128.6 (d, C-4'), 128.6 (d, C-3'), 128.4 (d, C-8), 123.3 (d, C-7), 119.4 (s, C-8a), 115.9 (d, C-5), 66.7 (t, C-1'), 44.2 (d, C-1), 39.0 (d, C-8b), 34.9 (d, C-2a), 27.6 (t, C-2).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1728, 1713, 1685, 1594, 1495, 1455, 1383, 1348, 1322, 1308, 1251, 1185, 1173, 1152, 1124, 1094, 1065, 1037, 1011, 946, 909, 871, 853, 810, 752, 685, 666, 648, 620.
**MS** (EI, 70 eV): *m/z* (%) = 307 (3) [$M^+$], 248 (2), 216 (2) [$M^+$–Bn], 200 (1) [$M^+$–OBn], 172 (2) [$M^+$–$C_8H_7O_2$], 159 (1) [$M^+$–$C_9H_9O_2$], 145 (100) [$M^+$–$C_{10}H_{11}O_2$], 117 (18), 91 (16).
**HRMS (EI)** ($C_{19}H_{17}NO_3$): calc.: 307.1208; found: 307.1203.

**Benzyl (1*R*,2a*R*,8b*S*)-1-methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carboxylate (4d)** and **Benzyl (1*S*,2a*R*,8b*S*)-1-methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carboxylate (S14)**




$C_{20}H_{19}NO_3$
MW: 321,38 g/mol

*Racemic [2+2] Photocycloaddition*

2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, benzyl methacrylate (234 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 6 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compounds **4d** (28.2 mg, 0.09 mmol, 64 %) and **S14** (6.8 mg, 0.02 mmol, 15 %) were obtained as colorless solids.

*Enantioselective [2+2] Photocycloaddition*

2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, benzyl methacrylate (212 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 6 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compounds **4d** (5.3 mg, 16.0 µmol, 66 %, 90 % *ee*) and **S14** (1.4 mg, 4.0 µmol, 17 %, 91 % *ee*) were obtained as colorless solids.

*Enantioselective [2+2] Photocycloaddition (0.15 mmol scale)*

2(1*H*)-Quinolone (22.0 mg, 0.15 mmol, 1.00 eq.) and enantiomerically pure **3** (6.6 mg, 15.0 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (60 mL, *c* = 2.5 mmol/L). After degassing the solution, benzyl methacrylate (1.28 ml, 7.50 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 8 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 7:3 → 1:1). The title compounds **4d** (37.2 mg, 116 µmol, 76 %, 88 % *ee*) and **S14** (7.1 mg, 22.0 µmol, 15 %, 85 % *ee*) were obtained as colorless solids.

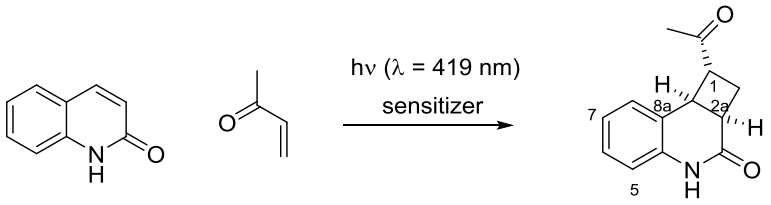
*Exo isomer (**4d**):*

**M.p.**: 157-159 °C.
**TLC**: $R_f$ = 0.78 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.11 (br. s, 1H, NH), 7.44 – 7.31 (m, 5H, Ar), 7.16 (*virt.* t, $^3J \approx {}^3J$ = 7.6 Hz, 1H, H-6), 6.99 (d, $^3J$ = 6.8 Hz, 1H, H-8), 6.95 (*virt.* t, $^3J \approx {}^3J$ = 7.1 Hz, 1H, H-7), 6.80 (d, $^3J$ = 7.9 Hz, 1H, H-5), 5.23 (d, $^2J$ = 12.4 Hz, 1H, H-1'), 5.18 (d, $^2J$ = 12.4 Hz, 1H, H-1'), 4.20 (d, $^3J$ = 10.4 Hz, 1H, H-8b), 3.33 (*virt.* td, $^3J \approx {}^3J$ = 10.6 Hz, $^3J$ = 3.9 Hz, 1H, H-2a), 3.19 (dd, $^2J$ = 12.5 Hz, $^3J$ = 10.8 Hz, 1H, H-2), 2.30 (dd, $^2J$ = 12.5 Hz, $^3J$ = 3.9 Hz, 1H, H-2), 1.16 (s, 3H, Me).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 176.4 (s, *C*OOBn), 173.2 (s, C-3), 138.0 (s, C-4a), 136.2 (s, C-2'), 129.3 (d, C-5'), 128.9 (d, C-4'), 128.6 (d, C-6), 128.6 (d, C-3'), 128.3 (d, C-8), 123.7 (d, C-7), 119.5 (s, C-8a), 115.9 (d, C-5), 66.9 (t, C-1'), 47.9 (s, C-1), 42.5 (d, C-8b), 36.4 (t, C-2), 32.5 (d, C-2a), 20.3 (q, Me).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1728, 1667, 1594, 1456, 1382, 1350, 1323, 1308, 1250, 1236, 1194, 1173, 1151, 1124, 1093, 1065, 1037, 1026, 908, 870, 830, 755, 696, 679, 667, 620.
**MS** (EI, 70 eV): *m/z* (%) = 321 (5) [$M^+$], 176 (8), 158 (8), 145 (100) [$M^+$–$C_{11}H_{12}O_2$], 131 (20), 117 (33), 91 (49), 69 (17).
**HRMS (EI)** ($C_{20}H_{19}NO_3$): calc.: 321.1359; found: 321.1361.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4d**, $t_R$ = 14.4 min; *ent*-**4d**, 19.6 min).
**Specific rotation** $[\alpha]_D^{20}$ = –74.9 (*c* = 0.67, $CHCl_3$) [88% *ee*].

*Endo isomer (**S14**):*

**M.p.**: 162-164 °C.
**TLC**: $R_f$ = 0.72 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 7.89 (br. s, 1H, NH), 7.33 – 7.26 (m, 3H, Ar), 7.14 – 7.05 (m, 3H, Ar, H-6), 6.95 (d, $^3J$ = 7.4 Hz, 1H, H-8), 6.87 (*virt.* t, $^3J \approx {}^3J$ = 7.4 Hz, 1H, H-7), 6.55 (d, $^3J$ = 7.9 Hz, 1H, H-5), 4.69 (d, $^2J$ = 12.3 Hz, 1H, H-1'), 4.65 (d, $^2J$ = 12.3 Hz, 1H, H-1'), 3.76 (d, $^3J$ = 10.1 Hz, 1H, H-8b), 3.44 (*virt.* td, $^3J \approx {}^3J$ = 10.2 Hz, $^3J$ = 5.8 Hz, 1H, H-2a), 3.17 (dd, $^2J$ = 12.5 Hz, $^3J$ = 5.8 Hz, 1H, H-2), 2.44 (*virt.* t, $^2J \approx {}^3J$ = 11.4 Hz, 1H, H-2), 1.62 (s, 3H, Me).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 173.8 (s, *C*OOBn), 171.5 (s, C-3), 137.2 (s, C-4a), 135.7 (s, C-2'), 128.9 (d, C-5'), 128.7 (d, C-6), 128.6 (d, C-4'), 128.5 (d, C-3'), 128.4 (d, C-8), 123.3 (d, C-7), 120.0 (s, C-8a), 115.8 (d, C-5), 66.8 (t, C-1'), 50.9 (s, C-1), 47.3 (d, C-8b), 35.2 (t, C-2), 32.5 (d, C-2a), 25.5 (q, Me).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1729, 1715, 1667, 1594, 1494, 1456, 1382, 1350, 1323, 1308, 1250, 1236, 1187, 173, 1153, 1124, 1065, 911, 755, 696, 678, 667, 621, 601.
**MS** (EI, 70 eV): *m/z* (%) = 321 (5) [$M^+$], 176 (7), 158 (8), 145 (100) [$M^+$–$C_{11}H_{12}O_2$], 131 (22), 117 (34), 91 (46), 69 (12).
**HRMS (EI)** ($C_{20}H_{19}NO_3$): calc.: 321.1359; found: 321.1365.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 80:20) = **S13**, $t_R$ = 13.0 min; *ent*-**S13**, 22.8 min).
**Specific rotation** $[\alpha]_D^{20}$ = –43.0 (*c* = 1.53, $CHCl_3$) [85% *ee*].

**(1*R*,2a*R*,8b*S*)-1-Acetyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4e)**




**4e**

$C_{13}H_{13}NO_2$
MW: 215,25 g/mol

*Racemic [2+2] Photocycloaddition*

2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 3-buten-2-one (115 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 3 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4e** (21.0 mg, 0.10 mmol, 70 %) was obtained as a colorless solid.

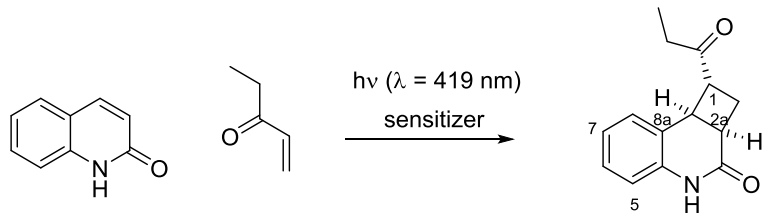
*Enantioselective [2+2] Photocycloaddition*

2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 3-buten-2-one (104 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 7 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4e** (4.3 mg, 20.0 µmol, 80 %, 91 % *ee*) was obtained as a colorless solid.

**M.p.**: 157-159°C.
**TLC**: $R_f$ = 0.62 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.52 (br. s, 1H, NH), 7.18 (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, $^4J$ = 1.6 Hz, 1H, H-6), 7.09 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1H, H-8), 6.99 (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.87 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 3.97 (*virt.* t, $^3J \approx {}^3J$ = 8.8 Hz, 1H, H-8b), 3.47 (ddd, $^3J$ = 11.6 Hz, $^3J$ = 9.2 Hz, $^3J$ = 8.5 Hz, 1H, H-1), 3.24 (ddd, $^3J$ = 9.8 Hz, $^3J$ = 9.1 Hz, $^3J$ = 3.1 Hz, 1H, H-2a), 2.80 (*virt.* td, $^2J \approx {}^3J$ = 11.8 Hz, $^3J$ = 9.8 Hz, 1H, H-2), 2.60 (ddd, $^2J$ = 12.0 Hz, $^3J$ = 9.2 Hz, $^3J$ = 3.1 Hz, 1H, H-2), 2.10 (s, 3H, Me).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 207.1 (s, *C*OMe), 173.2 (s, C-3), 136.9 (s, C-4a), 128.5 (d, C-6), 127.9 (d, C-8), 123.9 (d, C-7), 122.8 (s, C-8a), 116.1 (d, C-5), 52.8 (d, C-1), 39.1 (d, C-8b), 34.3 (d, C-2a), 28.8 (t, C-2), 28.2 (q, Me).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1699, 1662, 1592, 1492, 1440, 1388, 1363, 1317, 1302, 1250, 1237, 1189, 1175, 948, 932, 869, 833, 804, 752, 704, 607, 637, 620, 601.
**MS** (EI, 70 eV): *m/z* (%) = 215 (7) [$M^+$], 200 (1) [$M^+$–Me], 172 (55) [$M^+$–$C_2H_3O$], 154 (4), 145 (100) [$M^+$–$C_4H_6O$], 117 (37), 90 (12).

**HRMS (EI)** ($C_{13}H_{13}NO_2$): calc.: 215.0941; found: 215.0935.
**HPLC** (OJ-H, 250×4.6, *n*-hexane/*iso*-propanol = 80:20) = *ent*-**4e**, $t_R$ = 17.5 min; **4e**, 20.9 min).

**(1*R*,2a*R*,8b*S*)-1-Propionyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4f)**




$C_{14}H_{15}NO_2$
MW: 229,28 g/mol

*Racemic [2+2] Photocycloaddition*
2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 1-penten-3-one (136 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 3 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4f** (22.9 mg, 0.10 mmol, 72 %) was obtained as a colorless solid.

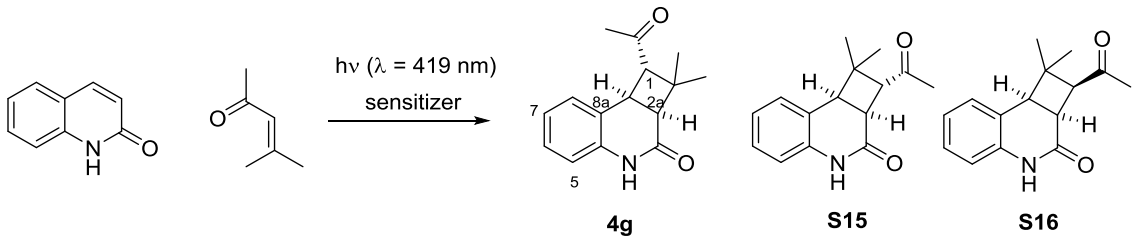
*Enantioselective [2+2] Photocycloaddition*
2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 1-penten-3-one (124 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 6 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4f** (4.0 mg, 18.0 µmol, 70 %, 92 % *ee*) was obtained as a colorless solid.

*Enantioselective [2+2] Photocycloaddition (0.15 mmol scale)*
2(1*H*)-Quinolone (22.0 mg, 0.15 mmol, 1.00 eq.) and enantiomerically pure **3** (6.6 mg, 15.0 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (60 mL, *c* = 2.5 mmol/L). After degassing the solution, 1-penten-3-one (750 µl, 7.50 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 12 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 2:1 → 1:1). The title compound **4f** (30.9 mg, 135 µmol, 89 %, 91 % *ee*) was obtained as a colorless solid.

**M.p.**: 154-156 °C.
**TLC**: $R_f$ = 0.76 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.38 (br. s, 1H, NH), 7.17 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, $^4J$ = 1.6 Hz, 1H, H-6), 7.07 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1H, H-8), 6.97 (*virt.* td, $^3J \approx {}^3J$ = 7.5 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.84 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 3.98 (*virt.* t, $^3J \approx {}^3J$ = 8.8 Hz, 1H, H-8b), 3.47 (*virt.* dt, $^3J$ = 9.8 Hz, $^3J \approx {}^3J$ = 8.0

Hz, 1H, H-1), 3.24 (ddd, $^3J$ = 9.8 Hz, $^3J$ = 9.1 Hz, $^3J$ = 3.1 Hz, 1H, H-2a), 2.78 (*virt*. td, $^2J \approx {}^3J$ = 11.9 Hz, $^3J$ = 9.8 Hz, 1H, H-2), 2.59 (ddd, $^2J$ = 12.0 Hz, $^3J$ = 9.1 Hz, $^3J$ = 3.0 Hz, 1H, H-2), 2.45 – 2.22 (m, 2H, C*H*$_2$CH$_3$), 1.05 (t, $^3J$ = 7.3 Hz, 3H, CH$_2$C*H*$_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 210.0 (s, *C*OMe), 173.2 (s, C-3), 137.1 (s, C-4a), 128.5 (d, C-6), 128.0 (d, C-8), 123.9 (d, C-7), 123.0 (s, C-8a), 116.1 (d, C-5), 51.9 (d, C-1), 39.3 (d, C-8b), 34.6 (d, C-2a), 34.4 (t, *C*H$_2$CH$_3$), 29.2 (t, C-2), 7.7 (q, CH$_2$*C*H$_3$).
**IR** (ATR): $\nu$ (cm$^{-1}$) = 1699, 1662, 1592, 1492, 1440, 1388, 1363, 1317, 1302, 1250, 1237, 1189, 1175, 948, 932, 869, 833, 804, 752, 704, 607, 637, 620, 601.
**MS** (EI, 70 eV): *m/z* (%) = 229 (8) [$M^+$], 200 (1) [$M^+$–$C_2H_5$], 172 (26) [$M^+$–$C_3H_5O$], 154 (4), 145 (100) [$M^+$–$C_5H_8O$], 128 (4), 117 (18), 90 (7), 77 (3).
**HRMS (EI)** ($C_{14}H_{15}NO_2$): calc.: 229.1097; found: 229.1096.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4f**, $t_R$ = 15.4 min; *ent*-**4f**, 16.9 min).
**Specific rotation** $[\alpha]_D^{20}$ = –93.9 (c = 0.50, MeOH) [88% *ee*].

**(1*S*,2a*S*,8b*S*)-1-Acetyl-2,2-dimethyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4g)**, **(2*R*,2a*S*,8b*R*)-2-acetyl-1,1-dimethyl-2,2a,4,8b-tetrahydrocyclobuta-[*c*]quinolin-3(1*H*)-one (S15)** and **(2*S*,2a*S*,8b*R*)-2-acetyl-1,1-dimethyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (S16)**




$C_{15}H_{17}NO_2$
MW: 243,31 g/mol

*Racemic [2+2] Photocycloaddition*
2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, mesityl oxide (158 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 22 h at room temperature (92 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compounds **4g** (14.6 mg, 0.06 mmol, 43 %), **S15** (5.2 mg, 0.02 mmol, 15 %) and **S16** (2.7 mg, 0.01 mmol, 8 %) were obtained as colorless solids.

*Enantioselective [2+2] Photocycloaddition*
2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, mesityl oxide (143 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 8 h at −25 °C (72 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4g** (2.1 mg, 8.5 µmol, 34 %, 88 % *ee*, 47 % based on recovered starting material) was obtained as a colorless solid.

*Major regioisomer (**4g**):*

**M.p.**: 151-153 °C.
**TLC**: $R_f$ = 0.76 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.88 (br. s, 1H, NH), 7.13 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, $^4J$ = 1.5 Hz, 1H, H-6), 7.08 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1H, H-8), 6.94 (*virt.* td, $^3J \approx {}^3J$ = 7.5 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.77 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 4.20 (*virt.* t, $^3J \approx {}^3J$ = 9.3 Hz, 1H, H-8b), 3.09 (d, $^3J$ = 8.7 Hz, 1H, H-1), 2.88 (d, $^3J$ = 9.8 Hz, 1H, H-2a), 2.07 (s, 3H, $COCH_3$), 1.41 (s, 3H, Me), 1.27 (s, 3H, Me).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 206.7 (s, $COCH_3$), 169.9 (s, C-3), 136.7 (s, C-4a), 128.2 (d, C-8), 127.9 (d, C-6), 123.7 (d, C-7), 123.5 (s, C-8a), 115.6 (d,

C-5), 64.4 (s, C-2), 45.2 (d, C-2a), 43.6 (d, C-1), 31.3 (d, C-8b), 30.4 (q, COC*H*$_3$), 27.1 (q, Me), 25.6 (q, Me).
**IR** (ATR): *v* (cm$^{-1}$) = 1699, 1660, 1593, 1493, 1459, 1389, 1371, 1352, 1319, 1301, 1243, 1220, 1193, 1164, 1143, 875, 832, 750, 715, 676, 624, 602.
**MS** (EI, 70 eV): *m/z* (%) = 243 (10) [M$^+$], 228 (2) [M$^+$–CH$_3$], 200 (16) [M$^+$– C$_2$H$_3$O], 186 (3), 173 (2), 158 (2), 145 (100) [M$^+$–C$_6$H$_{10}$O], 117 (16), 91 (7).
**HRMS (EI)** (C$_{15}$H$_{17}$NO$_2$): calc.: 243.1254; found: 243.1255.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = *ent*-**4g**, $t_R$ = 16.7 min; **4g**, 30.1 min).

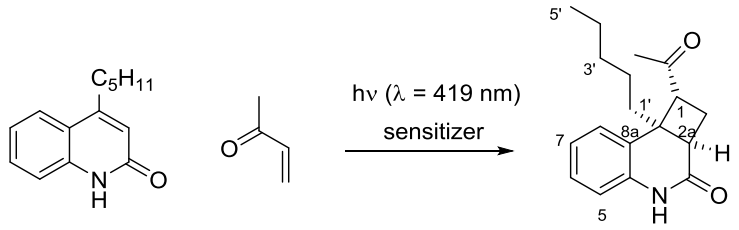
*Exo minor regioisomer (**S15**):*

**M.p.**: 176-178 °C.
**TLC**: $R_f$ = 0.69 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, CDCl$_3$, 303 K): $\delta$ (ppm) = 8.49 (br. s, 1H, NH), 7.16 (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, $^4J$ = 1.6 Hz, 1H, H-6), 6.97 (*virt.* td, $^3J \approx {}^3J$ = 7.3 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.90 (dd, $^3J$ = 7.2 Hz, $^4J$ = 1.6 Hz, 1H, H-8), 6.74 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 3.80 (dd, $^3J$ = 10.4 Hz, $^3J$ = 5.3 Hz, 1H, H-2a), 3.46 (d, $^3J$ = 10.4 Hz, 1H, H-2), 3.35 (d, $^3J$ = 5.3 Hz, 1H, H-8b), 2.17 (s, 3H, COC*H*$_3$), 1.17 (s, 3H, Me), 1.06 (s, 3H, Me).
**$^{13}$C-NMR** (100 MHz, CDCl$_3$, 303 K): $\delta$ (ppm) = 205.9 (s, *C*OCH$_3$), 171.9 (s, C-3), 137.2 (s, C-4a), 129.2 (d, C-8), 128.2 (d, C-6), 123.4 (d, C-7), 120.3 (s, C-8a), 115.8 (d, C-5), 61.0 (d, C-8b), 44.2 (d, C-2), 43.9 (s, C-1), 33.2 (d, C-2a), 31.1 (q, COC*H*$_3$), 26.4 (q, Me), 25.8 (q, Me).
**MS** (EI, 70 eV): *m/z* (%) = 243 (1) [M$^+$], 228 (1) [M$^+$–CH$_3$], 200 (4) [M$^+$– C$_2$H$_3$O], 158 (2), 145 (100) [M$^+$–C$_6$H$_{10}$O], 130 (4), 117 (15), 91 (4).
**HRMS (EI)** (C$_{15}$H$_{17}$NO$_2$): calc.: 243.1254; found: 243.1252.

*Endo minor regioisomer (**S16**):*

**TLC**: $R_f$ = 0.58 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, CDCl$_3$, 303 K): $\delta$ (ppm) = 7.67 (br. s, 1H, NH), 7.15 (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, $^4J$ = 1.6 Hz, 1H, H-6), 6.95 (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.91 (dd, $^3J$ = 7.6 Hz, $^4J$ = 1.6 Hz, 1H, H-8), 6.67 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 3.65 (*virt.* t, $^3J \approx {}^3J$ = 10.1 Hz, 1H, H-2a), 3.54 (d, $^3J$ = 10.0 Hz, 1H, H-2), 3.43 (d, $^3J$ = 10.2 Hz, 1H, H-8b), 2.20 (s, 3H, COC*H*$_3$), 1.40 (s, 3H, Me), 0.89 (s, 3H, Me).
**$^{13}$C-NMR** (100 MHz, CDCl$_3$, 303 K): $\delta$ (ppm) = 206.9 (s, *C*OCH$_3$), 169.6 (s, C-3), 137.4 (s, C-4a), 129.0 (d, C-8), 128.1 (d, C-6), 123.0 (d, C-7), 120.1 (s, C-8a), 115.5 (d, C-5), 58.0 (d, C-2), 44.7 (d, C-8b), 44.4 (s, C-1), 36.1 (d, C-2a), 32.4 (q, Me), 31.6 (q, COC*H*$_3$), 20.0 (q, Me).
**MS** (EI, 70 eV): *m/z* (%) = 243 (1) [M$^+$], 228 (1) [M$^+$–CH$_3$], 200 (4) [M$^+$– C$_2$H$_3$O], 158 (2), 145 (100) [M$^+$–C$_6$H$_{10}$O], 130 (4), 117 (15), 91 (4).

**(1*R*,2a*R*,8b*S*)-1-Acetyl-8b-pentyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4h)**




**4h** $C_{18}H_{23}NO_2$
MW: 285,39 g/mol

*Racemic [2+2] Photocycloaddition*

4-Pentylquinolin-2-(1*H*)-one[*J. Org. Chem.* **1969**, *34*, 3263–3268.] (30.1 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 3-buten-2-one (115 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 10 h at room temperature (85 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 2:1). The title compound **4h** (31.5 mg, 0.11 mmol, 79 %) was obtained as a colorless solid.

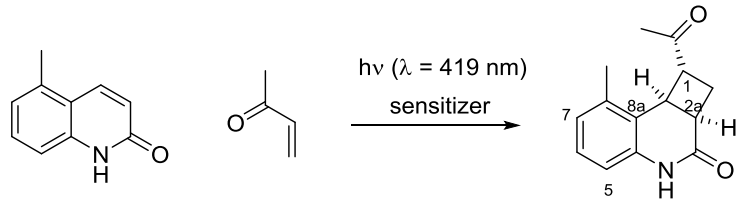
*Enantioselective [2+2] Photocycloaddition*

4-Pentylquinolin-2-(1*H*)-one (5.4 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 3-buten-2-one (104 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 18 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 2:1). The title compound **4h** (6.7 mg, 23.0 µmol, 94 %, 90 % *ee*) was obtained as a colorless solid.

**M.p.**: 88-90 °C.
**TLC**: $R_f$ = 0.82 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.27 (br. s, 1H, NH), 7.27 – 7.17 (m, 2H, H-6, H-8), 7.09 (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.86 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 3.44 (*virt.* t, $^3J \approx {}^3J$ = 7.3 Hz, 1H, H-1), 3.05 (dd, $^3J$ = 10.5 Hz, $^3J$ = 6.4 Hz, 1H, H-2a), 2.92 (ddd, $^2J$ = 12.1 Hz, $^3J$ = 10.5 Hz, $^3J$ = 6.4 Hz, 1H, H-2), 2.24 (ddd, $^2J$ = 12.1 Hz, $^3J$ = 8.8 Hz, $^3J$ = 6.4 Hz, 1H, H-2), 2.19 (s, 3H, Me), 1.81 (dt, $^2J$ = 13.4 Hz, $^3J$ = 4.3 Hz, 1H, H-1'), 1.66 (dt, $^2J$ = 13.4 Hz, $^3J$ = 3.5 Hz, 1H, H-1'), 1.21 – 1.04 (m, 6H, H-2', H-3', H-4'), 0.79 (t, $^3J$ = 6.7 Hz, 3H, H-5').
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 207.1 (s, *C*OMe), 172.2 (s, C-3), 136.9 (s, C-4a), 128.4 (d, C-8), 126.8 (s, C-8a), 126.2 (d, C-6), 124.2 (d, C-7), 116.4 (d, C-5), 56.8 (d, C-1), 48.3 (s, C-8b), 40.1 (d, C-2a), 36.0 (t, C-1'), 32.0 (t, C-2'), 31.1 (q, Me), 24.2 (t, C-2), 23.2 (t, C-3'), 22.5 (t, C-4'), 14.1 (q, C-5').
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1749, 1734, 1716, 1697, 1671, 1654, 1637, 1593, 1558, 1542, 1522, 1508, 1490, 1473, 1457, 1437, 1457, 1438, 1418, 1388, 1362, 1339, 1168, 756, 728, 707, 662, 620, 603.

**MS** (EI, 70 eV): *m/z* (%) = 285 (1) [$M^+$], 270 (1) [$M^+$–$CH_3$], 256 (1) [$M^+$–$C_2H_5$], 242 (26) [$M^+$–$C_3H_7$], 229 (9) [$M^+$–$C_4H_9$], 215 (24) [$M^+$–$C_5H_{11}$], 200 (1) [$M^+$–$C_6H_{14}$], 186 (6), 172 (9) [$M^+$–$C_7H_{14}O$], 159 (100) [$M^+$–$C_8H_{15}O$], 146 (4) [$M^+$–$C_9H_{17}O$], 130 (27).
**HRMS (EI)** ($C_{18}H_{23}NO_2$): calc.: 285.1723; found: 285.1722.
**HPLC** (OJ-H, 250×4.6, *n*-hexane/*iso*-propanol = 95:5) = *ent*-**4h**, $t_R$ = 22.5 min; **4h**, 25.0 min).

**(1*R*,2a*R*,8b*S*)-1-Acetyl-8-methyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4i)**




**S3** **4i** $C_{14}H_{15}NO_2$ MW: 229,28 g/mol

*Racemic [2+2] Photocycloaddition*

5-Methylquinolin-2(1*H*)-one (**S3**) (22.0 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 3-buten-2-one (115 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 5 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4i** (17.7 mg, 0.08 mmol, 56 %) was obtained as a colorless solid.

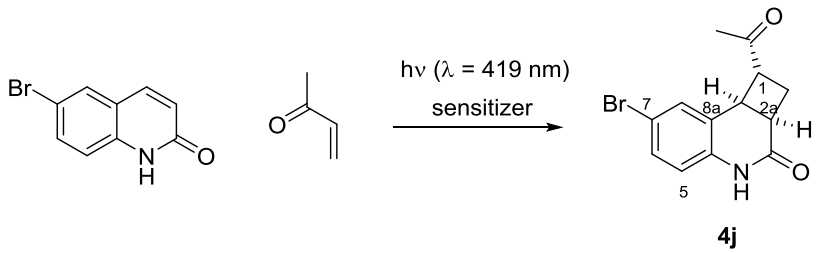
*Enantioselective [2+2] Photocycloaddition*

5-Methylquinolin-2(1*H*)-one (4.0 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 3-buten-2-one (104 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 10 h at −25 °C (73 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4i** (2.0 mg, 8.8 µmol, 35 %, 91 % *ee*, 48 % based on recovered starting material) was obtained as a colorless solid.

**M.p.**: 162-164 °C.
**TLC**: $R_f$ = 0.58 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.02 (br. s, 1H, NH), 7.07 (*virt.* t, $^3J \approx {}^3J$ = 7.7 Hz, 1H, H-6), 6.83 (d, $^3J$ = 7.5 Hz, 1H, H-7), 6.66 (d, $^3J$ = 7.9 Hz, 1H, H-5), 4.22 (*virt.* t, $^3J \approx {}^3J$ = 8.6 Hz, 1H, H-8b), 3.51 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 9.0 Hz, 1H, H-1), 3.28 (*virt.* td, $^3J \approx {}^3J$ = 9.1 Hz, $^3J$ = 4.2 Hz, 1H, H-2a), 2.77 – 2.60 (m, 2H, H-2), 2.19 (s, 3H, Me), 2.12 (s, 3H, $COCH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 207.5 (s, $COCH_3$), 172.5 (s, C-3), 137.1 (s, C-4a), 136.8 (s, C-8), 128.2 (d, C-6), 125.8 (d, C-7), 121.3 (s, C-8a), 113.9 (d, C-5), 51.9 (d, C-1), 35.7 (d, C-8b), 34.3 (d, C-2a), 30.1 (t, C-2), 28.7 (q, $COCH_3$), 19.3 (q, Me).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1699, 1667, 1590, 1558, 1542, 1521, 1507, 1489, 1474, 1457, 1437, 1418, 1396, 1362, 1340, 1314, 1233, 1200, 1177, 1162, 887, 852, 828, 804, 789, 755, 704, 668, 620.
**MS** (EI, 70 eV): *m/z* (%) = 229 (7) [$M^+$], 186 (56) [$M^+ - C_2H_3O$], 168 (4), 159 (100) [$M^+ - C_4H_6O$], 141 (2), 130 (35), 115 (4), 103 (5), 77 (8) [$C_6H_5$].

**HRMS (ESI)** ($C_{14}H_{16}NO_2^+$): calc.: 230.1176; found: 230.1174.
**Chiral GC** [60 °C (1 min), 15 °C/min → 200 °C (30 min)] = *ent*-**4i**, $t_R$ = 34.1 min; **4i**, 34.8 min).

**(1*R*,2a*R*,8b*S*)-1-Acetyl-7-bromo-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4j)**




**4j**

$C_{13}H_{12}BrNO_2$
MW: 294.15 g/mol

*Racemic [2+2] Photocycloaddition*

6-Bromoquinolin-2(1*H*)-one (31.4 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 3-buten-2-one (115 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 9 h at room temperature (78 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4j** (21.9 mg, 0.07 mmol, 54 %) was obtained as a colorless solid.

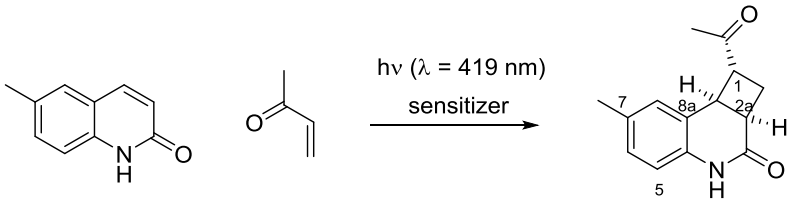
*Enantioselective [2+2] Photocycloaddition*

6-Bromoquinolin-2(1*H*)-one (5.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 3-buten-2-one (104 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 9 h at −25 °C (61 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4j** (2.7 mg, 9.0 µmol, 36 %, 94 % *ee*, 59 % based on recovered starting material) was obtained as a colorless solid.

**M.p.**: 167-169 °C.
**TLC**: $R_f$ = 0.68 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.32 (br. s, 1H, NH), 7.28 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.2 Hz, 1H, H-6), 7.24 (d, $^4J$ = 2.2 Hz, 1H, H-8), 6.72 (d, $^3J$ = 8.4 Hz, 1H, H-5), 4.00 (*virt.* t, $^3J \approx {}^3J$ = 8.9 Hz, 1H, H-8b), 3.44 (*virt.* td, $^3J \approx {}^3J$ = 10.1 Hz, $^3J$ = 8.2 Hz, 1H, H-1), 3.22 (*virt.* td, $^3J \approx {}^3J$ = 9.4 Hz, $^3J$ = 2.9 Hz, 1H, H-2a), 2.74 (*virt.* dt, $^2J$ = 12.0 Hz, $^3J \approx {}^3J$ = 9.7 Hz, 1H, H-2), 2.64 (ddd, $^2J$ = 12.0 Hz, $^3J$ = 9.3 Hz, $^3J$ = 2.9 Hz, 1H, H-2), 2.11 (s, 3H, $COCH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 206.6 (s, $COCH_3$), 172.6 (s, C-3), 136.1 (s, C-4a), 131.3 (d, C-6), 130.8 (d, C-8), 124.9 (s, C-8a), 117.5 (d, C-5), 116.1 (s, C-7), 52.6 (d, C-1), 38.2 (d, C-8b), 34.0 (d, C-2a), 29.3 (t, C-2), 27.9 (q, $COCH_3$).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1698, 1669, 1586, 1489, 1446, 1412, 1377, 1362, 1342, 1308, 1281, 1248, 1197, 1180, 1155, 1132, 1076, 1045, 986, 939, 906, 881, 851, 822, 807, 755, 725, 701, 626.

**MS** (EI, 70 eV): *m/z* (%) = 295 (8) [$M^+$ ($^{81}$Br)], 293 (9) [$M^+$ ($^{79}$Br)], 252 (42) [$M^+$ ($^{81}$Br)–$C_2H_3O$], 250 (42) [$M^+$ ($^{79}$Br)–$C_2H_3O$], 225 (93) [$M^+$ ($^{81}$Br)–$C_4H_6O$], 223 (100) [$M^+$ ($^{79}$Br)–$C_4H_6O$], 197 (19), 195 (21), 116 (27), 89 (21).
**HRMS (EI)** ($C_{13}H_{12}BrNO_2$): calc.: 295.0025; found: 295.0004.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4j**, $t_R$ = 17.7 min; *ent*-**4j**, 21.3 min).
**Specific rotation** $[\alpha]_D^{20}$ = –54.7 (*c* = 0.28, MeOH) [>99% *ee*].

**(1*R*,2a*R*,8b*S*)-1-Acetyl-7-methyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4k)**




**S6** **4k**

$C_{14}H_{15}NO_2$
MW: 229.28 g/mol

*Racemic [2+2] Photocycloaddition*
6-Methylquinolin-2(1*H*)-one (22 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 3-buten-2-one (115 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 9 h at room temperature (61 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4k** (14.2 mg, 0.06 mmol, 45 %) was obtained as a colorless solid. A second fraction was collected containing a non-characterized cyclobutane (0.9 mg, 4 µmol, 4 %, $R_f$ = 0.72 (ethyl acetate, UV)).

*Enantioselective [2+2] Photocycloaddition*
6-Methylquinolin-2(1*H*)-one (4.0 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 3-buten-2-one (104 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 7 h at −25 °C (55 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 2:1). The title compound **4k** (2.2 mg, 9.8 µmol, 39 %, 85 % *ee*, 71 % based on recovered starting material) was obtained as a colorless solid.

**M.p.**: 120-122 °C.
**TLC**: $R_f$ = 0.62 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.60 (br. s, 1H, NH), 6.98 (d, $^3J$ = 7.8 Hz, 1H, H-6), 6.91 (s, 1H, H-8), 6.68 (d, $^3J$ = 7.8 Hz, 1H, H-5), 3.95 (*virt.* t, $^3J \approx {}^3J$ = 8.8 Hz, 1H, H-8b), 3.44 (*virt.* td, $^3J \approx {}^3J$ = 10.6 Hz, $^3J$ = 8.5 Hz, 1H, H-1), 3.21 (*virt.* td, $^3J \approx {}^3J$ = 9.5 Hz, $^3J$ = 3.2 Hz, 1H, H-2a), 2.75 (*virt.* dt, $^2J$ = 12.2 Hz, $^3J \approx {}^3J$ = 9.7 Hz, 1H, H-2), 2.60 (ddd, $^2J$ = 12.2 Hz, $^3J$ = 9.5 Hz, $^3J$ = 3.2 Hz, 1H, H-2), 2.27 (s, 3H, Me), 2.11 (s, 3H, $COCH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 207.2 (s, $COCH_3$), 172.4 (s, C-3), 134.4 (s, C-4a), 133.5 (s, C-7), 128.9 (d, C-6), 128.5 (d, C-8), 122.8 (s, C-8a), 115.7 (d, C-5), 52.9 (d, C-1), 39.0 (d, C-8b), 34.3 (d, C-2a), 29.0 (t, C-2), 28.1 (q, $COCH_3$), 20.8 (q, Me).

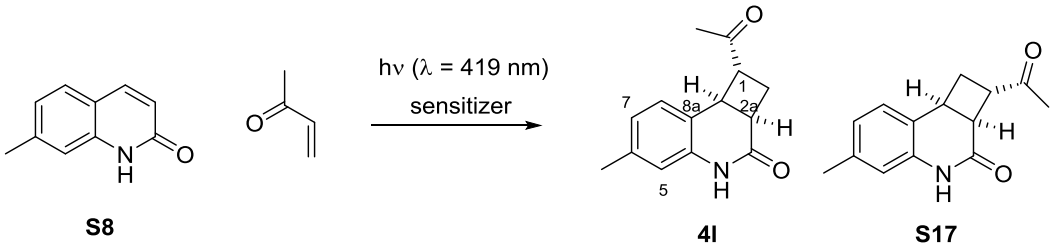
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1715, 1698, 1666, 1617, 1602, 1507, 1489, 1457, 1447, 1417, 1389, 1362, 1311, 1248, 1233, 1193, 1175, 1151, 954, 842, 818, 796, 736, 729, 703, 620.

**MS** (EI, 70 eV): *m/z* (%) = 229 (10) [$M^+$], 186 (47) [$M^+$–$C_2H_3O$], 159 (100) [$M^+$–$C_4H_6O$], 130 (22), 115 (3), 103 (4), 77 (4).

**HRMS (EI)** ($C_{14}H_{15}NO_2$): calc.: 229.1097; found: 229.1097.

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 95:5) = **4k**, $t_R$ = 35.7 min; *ent*-**4k**, 44.3 min).

**(1*R*,2a*R*,8b*S*)-1-Acetyl-6-methyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4l)** and **(2*S*,2a*S*,8b*S*)-2-acetyl-6-methyl-2,2a,4,8b-tetrahydrocyclobuta-[*c*]quinolin-3(1*H*)-one (S17)




$C_{14}H_{15}NO_2$
MW: 229.28 g/mol

*Racemic [2+2] Photocycloaddition*

7-Methylquinolin-2(1*H*)-one (22 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 3-buten-2-one (115 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 6 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compounds **4l** (21.4 mg, 0.09 mmol, 68 %) and **S17** (4.4 mg, 0.02 mmol, 14 %) were obtained as colorless solids.

*Enantioselective [2+2] Photocycloaddition*

7-Methylquinolin-2(1*H*)-one (4.0 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 3-buten-2-one (104 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 8 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 2:1). The title compound **4l** (4.1 mg, 18.0 µmol, 72 %, 95 % *ee*) was obtained as a colorless solid.

*Major regioisomer (**4l**):*

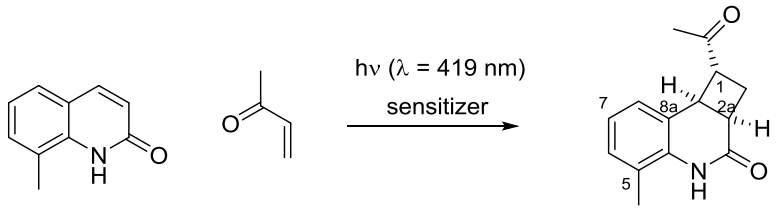
**M.p.**: 154-156 °C.
**TLC**: $R_f$ = 0.66 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.21 (br. s, 1H, NH), 6.97 (d, $^3J$ = 7.6 Hz, 1H, H-8), 6.80 (dd, $^3J$ = 7.6 Hz, $^4J$ = 2.1 Hz, 1H, H-7), 6.65 (d, $^3J$ = 2.1 Hz, 1H, H-5), 3.91 (*virt.* t, $^3J \approx {}^3J$ = 8.8 Hz, 1H, H-8b), 3.43 (*virt.* td, $^3J \approx {}^3J$ = 10.1 Hz, $^3J$ = 8.2 Hz, 1H, H-1), 3.23 (*virt.* td, $^3J \approx {}^3J$ = 8.8 Hz, $^3J$ = 2.6 Hz, 1H, H-2a), 2.79 (*virt.* dt, $^2J$ = 11.8 Hz, $^3J \approx {}^3J$ = 9.8 Hz, 1H, H-2), 2.57 (ddd, $^2J$ = 11.8 Hz, $^3J$ = 9.2 Hz, $^3J$ = 2.6 Hz, 1H, H-2), 2.30 (s, 3H, Me), 2.10 (s, 3H, $COCH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 207.2 (s, $COCH_3$), 173.2 (s, C-3), 138.7 (s, C-6), 136.9 (s, C-4a), 122.8 (d, C-8), 124.6 (d, C-7), 120.0 (s, C-8a), 116.5 (d, C-5), 53.0 (d, C-1), 39.1 (d, C-8b), 34.4 (d, C-2a), 28.6 (t, C-2), 28.2 (q, $COCH_3$), 21.3 (q, Me).

**IR** (ATR): $\nu$ ($cm^{-1}$) = 1696, 1662, 1267, 1588, 1524, 1487, 1407, 1361, 1348, 1314, 1305, 1265, 1204, 1174, 871, 835, 801, 638.
**MS** (EI, 70 eV): *m/z* (%) = 229 (6) [$M^+$], 186 (55) [$M^+$–$C_2H_3O$], 159 (100) [$M^+$–$C_4H_6O$], 130 (29), 115 (4), 103 (5), 77 (5).
**HRMS (EI)** ($C_{14}H_{15}NO_2$): calc.: 229.1097; found: 229.1097.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4l**, $t_R$ = 16.4 min; *ent*-**4l**, 21.2 min).

*Minor regioisomer (**S17**):*

**TLC**: $R_f$ = 0.72 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 7.59 (br. s, 1H, NH), 6.96 (d, $^3J$ = 7.7 Hz, 1H, H-8), 6.83 (d, $^3J$ = 7.7 Hz, 1H, H-7), 6.50 (s, 1H, H-5), 3.69 (*virt.* td, $^3J \approx {}^3J$ = 9.0 Hz, $^3J$ = 5.5 Hz, 1H, H-8b), 3.58 (*virt.* dt, $^3J$ = 9.4 Hz, $^3J \approx {}^3J$ = 7.3 Hz, 1H, H-2), 3.53 (*virt.* t, $^3J \approx {}^3J$ = 7.4 Hz, 1H, H-2a), 2.89 – 2.71 (m, 1H, H-1), 2.31 (s, 3H, Me), 2.29 – 2.24 (m, 1H, H-1), 2.23 (s, 3H, COC$H_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 207.1 (s, $C$OCH$_3$), 170.0 (s, C-3), 138.3 (s, C-6), 135.9 (s, C-4a), 128.6 (d, C-8), 125.0 (d, C-7), 121.5 (s, C-8a), 116.3 (d, C-5), 49.6 (d, C-2), 40.3 (d, C-2a), 32.5 (d, C-8b), 31.9 (t, C-1), 27.9 (q, COC$H_3$), 21.3 (q, Me).
**MS** (EI, 70 eV): *m/z* (%) = 229 (6) [$M^+$], 186 (23) [$M^+$–$C_2H_3O$], 159 (100) [$M^+$–$C_4H_6O$], 130 (19), 115 (3), 103 (3), 77 (3).
**HRMS (EI)** ($C_{14}H_{15}NO_2$): calc.: 229.1097; found: 229.1096.

**(1*R*,2a*R*,8b*S*)-1-Acetyl-5-methyl-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (4m)**




$C_{14}H_{15}NO_2$
MW: 229.28 g/mol

*Racemic [2+2] Photocycloaddition*

8-Methylquinolin-2(1*H*)-one (22.0 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 3-buten-2-one (115 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 7 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 2:1). The title compound **4m** (20.6 mg, 0.09 mmol, 65 %) was obtained as a colorless solid. A second fraction was collected containing a mixture of two non-characterized cyclobutanes (4.4 mg, 0.02 mmol, 14 %, $R_f$ = 0.74 (ethyl acetate, UV)).

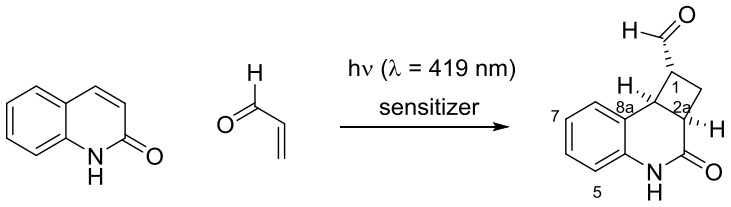
*Enantioselective [2+2] Photocycloaddition*

8-Methylquinolin-2(1*H*)-one (4.0 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 3-buten-2-one (104 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 9 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 2:1). The title compound **4m** (3.9 mg, 17 µmol, 68 %, 80 % *ee*) was obtained as a colorless solid.

**M.p.**: 146-148 °C.
**TLC**: $R_f$ = 0.68 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 7.70 (br. s, 1H, NH), 7.04 (d, $^3J$ = 7.1 Hz, 1H, H-6), 6.96 (d, $^3J$ = 7.4 Hz, 1H, H-8), 6.90 (*virt.* t, $^3J \approx {}^3J$ = 7.3 Hz, 1H, H-7), 3.94 (*virt.* t, $^3J \approx {}^3J$ = 8.9 Hz, 1H, H-8b), 3.45 (*virt.* td, $^3J \approx {}^3J$ = 9.9 Hz, $^3J$ = 7.9 Hz, 1H, H-1), 3.20 (*virt.* td, $^3J \approx {}^3J$ = 10.0 Hz, $^3J$ = 2.8 Hz, 1H, H-2a), 2.76 (*virt.* dt, $^4J$ = 11.8 Hz, $^3J \approx {}^3J$ = 9.8 Hz, 1H, H-2), 2.56 (ddd, $^3J$ = 11.8 Hz, $^3J$ = 9.0 Hz, $^3J$ = 2.8 Hz, 1H, H-2), 2.25 (s, 3H, Me), 2.09 (s, 3H, $COCH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 207.0 (s, $COCH_3$), 172.2 (s, C-3), 135.1 (s, C-4a), 130.0 (d, C-6), 125.9 (d, C-8), 123.2 (d, C-7), 122.7 (s, C-8a), 122.6 (s, C-5), 52.7 (d, C-1), 39.6 (d, C-8b), 34.3 (d, C-2a), 28.8 (t, C-2), 28.2 (q, $COCH_3$), 16.9 (q, Me).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1715, 1698, 1666, 1617, 1602, 1507, 1489, 1457, 1447, 1417, 1389, 1362, 1311, 1248, 1233, 1193, 1175, 1151, 954, 842, 818, 796, 736, 729, 703, 620.
**MS** (EI, 70 eV): *m/z* (%) = 229 (7) [$M^+$], 186 (51) [$M^+$–$C_2H_3O$], 159 (100) [$M^+$–$C_4H_6O$], 141 (14), 130 (21), 114 (5), 103 (4), 77 (4).

**HRMS (EI)** ($C_{14}H_{15}NO_2$): calc.: 229.1097; found: 229.1098.
**Chiral HPLC** (AS-H, 250×4.6, *n*-hexane/*iso*-propanol = 70:30) = **4m**, $t_R$ = 11.6 min; ent-**4m**, 14.7 min).

**(1*R*,2a*R*,8b*S*)-3-Oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[*c*]quinoline-1-carbaldehyde (4n)**



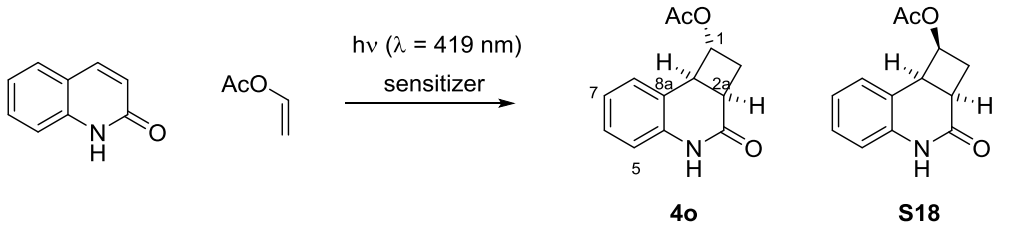

**4n** $C_{12}H_{11}NO_2$
MW: 201,23 g/mol

*Racemic [2+2] Photocycloaddition*
2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, acrolein (92 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 8 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4n** (17.6 mg, 0.07 mmol, 47 %) was obtained as a colorless solid.

*Enantioselective [2+2] Photocycloaddition*
2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, acrolein (83 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 18 h at −25 °C. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **4n** (3.0 mg, 11.0 µmol, 44 %, 91 % *ee*) was obtained as a colorless solid.

**M.p.**: Decomposition.
**TLC**: $R_f$ = 0.58 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.81 (s, 1H, C*H*O), 8.89 (br. s, 1H, NH), 7.19 (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, $^4J$ = 1.5 Hz, 1H, H-6), 7.08 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1H, H-8), 7.00 (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.81 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 4.08 (*virt.* t, $^3J \approx {}^3J$ = 8.7 Hz, 1H, H-8b), 3.45 (*virt.* td, $^3J \approx {}^3J$ = 9.2 Hz, $^3J$ = 8.0 Hz, 1H, H-1), 3.31 (*virt.* td, $^3J \approx {}^3J$ = 9.3 Hz, $^3J$ = 3.4 Hz, 1H, H-2a), 2.84 (*virt.* dt, $^2J$ = 12.0 Hz, $^3J \approx {}^3J$ = 9.8 Hz, 1H, H-2), 2.62 (ddd, $^2J$ = 12.0 Hz, $^3J$ = 9.3 Hz, $^3J$ = 3.4 Hz, 1H, H-2).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 200.1 (s, *C*HO), 172.1 (s, C-3), 136.8 (s, C-4a), 128.6 (d, C-6), 128.1 (d, C-8), 124.0 (d, C-7), 122.4 (s, C-8a), 116.0 (d, C-5), 52.4 (d, C-1), 37.4 (d, C-8b), 34.8 (d, C-2a), 27.0 (t, C-2).
**MS** (EI, 70 eV): *m/z* (%) = 201 (9) [$M^+$], 172 (44) [$M^+$–CHO], 154 (3), 145 (100) [$M^+$–$C_3H_4O$], 117 (42), 90 (14), 77 (3).
**HRMS (EI)** ($C_{12}H_{11}NO_2$): calc.: 201.0784; found: 201.0789.
**HPLC** (OJ-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = *ent*-**4n**, $t_R$ = 19.4 min; **4n**, 22.6 min).

**(1R,2aR,8bS)-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinolin-1-yl acetate (4o)** and **(1S,2aR,8bS)-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinolin-1-yl acetate (S18)**




$C_{13}H_{13}NO_3$
MW: 231,25 g/mol

*Racemic [2+2] Photocycloaddition*
2(1*H*)-Quinolone (20 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, vinyl acetate (127 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 3 h at room temperature. After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 6:4). The title compounds **4o** (14.8 mg, 64.0 µmol, 46 %) and **S18** (13.2 mg, 57.8 µmol, 40 %) were obtained as colorless solids.

*Enantioselective [2+2] Photocycloaddition*
2(1*H*)-Quinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, vinyl acetate (115 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 9 h at −25 °C (87 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 6:4). The title compounds **4o** (2.4 mg, 10.3 µmol, 42 %, 58 % *ee*, 48 % based on recovered starting material) and **S18** (2.1 mg, 9.08 µmol, 41 %, 43 % *ee*) were obtained as a colorless solid.

*Exo isomer (**4o**):*

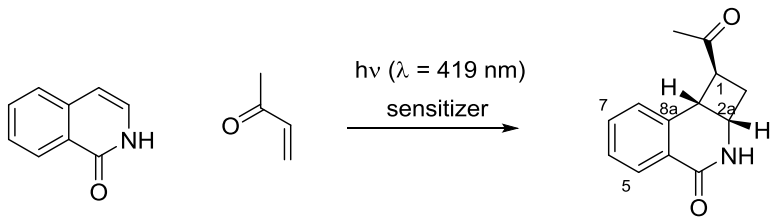
**M.p.**: 181 °C.
**TLC**: $R_f$ = 0.31 (cylohexane:ethyl acetate, 1:1, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 7.99 (br. s, 1H, NH), 7.22 – 7.12 (m, 2H, H-6, H-8), 7.00 (*virt.* td, $^3J \approx {}^3J$ = 7.5 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.72 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 5.12 (dt, $^3J$ = 7.6 Hz, $^3J \approx {}^3J$ = 6.2 Hz, 1H, H-1), 3.78 (dd, $^3J$ = 10.0 Hz, $^3J$ = 6.5 Hz, 1H, H-8b), 3.36 (dddd, $^3J$ = 11.1 Hz, $^3J$ = 9.9 Hz, , $^3J$ = 3.6 Hz, $^4J$ = 1.3 Hz, 1H, H-2a), 2.89 (dddd, $^2J$ = 12.3 Hz, $^3J$ = 7.5 Hz, $^3J$ = 3.6 Hz, $^4J$ = 1.1 Hz, 1H, H-2), 2.70 – 2.60 (m, 1H, H-2), 2.08 (s, 3H, $CH_3$).

**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 171.5 (s, C-3), 170.2 (s, O*C*OCH$_3$), 136.9 (s, C-4a), 128.7 (d, C-6), 128.5 (d, C-8), 123.8 (d, C-7), 121.2 (s, C-8a), 115.6 (d, C-5), 74.0 (d, C-1), 44.9 (d, C-8b), 35.2 (t, C-2), 31.7 (d, C-2a), 21.0 (q, $CH_3$).
**IR** (ATR): $\nu$ (cm$^{-1}$) = 3202, 3063, 1738, 1670, 1594, 1491, 1436, 1378, 1327, 1303, 1236, 1185, 1082, 1051, 815, 755, 733.
**MS** (EI, 70 eV): *m/z* (%) = 231 (5) [$M^+$], 188 (14) [$M^+$-$C_2H_3O$], 145 (100) [$M^+$-$C_4H_6O_2$], 117 (22).
**HRMS (EI)** ($C_{13}H_{13}NO_3$): calc.: 231.0890; found: 231.0892.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4o**, $t_R$ = 16.2 min; *ent*-**4o**, 30.7 min).

*Endo isomer (**S18**):*

**M.p.**: 153 °C.
**TLC**: *R*f = 0.24 (cylohexane:ethyl acetate, 1:1, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.44 (br. s, 1H, NH), 7.19 (dddd, $^3J$ = 7.8 Hz, $^3J$ = 7.0 Hz, $^4J$ = 1.8 Hz, $^4J$ = 0.7 Hz, 1H, H-6), 6.99 (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, $^4J$ = 1.2 Hz, 1H, H-7), 6.95 (ddd, $^3J$ = 7.7 Hz, $^4J$ = 1.8 Hz, $^4J$ = 0.8 Hz, H-8), 6.78 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 1H, H-5), 5.42 (*virt.* qd, $^3J \approx {}^3J \approx {}^3J$ = 7.3 Hz, $^4J$ = 0.6 Hz, 1H, H-1), 4.19 – 4.12 (m, 1H, H-8b), 3.21 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 8.6 Hz, 1H, H-2a), 2.95 (dddd, $^2J$ = 12.2 Hz, $^3J$ = 8.9 Hz, $^3J$ = 7.3 Hz, $^4J$ = 3.1 Hz, 1H, H-2), 2.53 (dddd, $^2J$ = 12.2 Hz, $^3J$ = 8.4 Hz, $^3J$ = 7.3 Hz, $^4J$ = 1.1 Hz, 1H, H-2), 1.88 (s, 3H, $CH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 170.45 (s, C-3), 170.2 (s, O*C*OCH$_3$), 137.4 (s, C-4a), 130.5 (d, C-8), 128.4 (d, C-6), 123.3 (d, C-7), 117.5 (s, C-8a), 116.0 (d, C-5), 69.4 (d, C-1), 42.5 (d, C-8b), 34.6 (t, C-2), 31.9 (d, C-2a), 20.9 (q, $CH_3$).
**IR** (ATR): $\nu$ (cm$^{-1}$) = 3202, 3064, 2987, 1735, 1671, 1593, 1559, 1507, 1490, 1436, 1388, 1324, 1296, 1235, 1087, 1014, 756, 735.
**MS** (EI, 70 eV): *m/z* (%) = 231 (5) [$M^+$], 188 (14) [$M^+$-$C_2H_3O$], 145 (100) [$M^+$-$C_4H_6O_2$], 117 (22).
**HRMS (EI)** ($C_{13}H_{13}NO_3$): calc.: 231.0890; found: 231.0893.
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 95:5) = **S17**, $t_R$ = 34.5 min; *ent*-**S17**, 36.8 min).

**(1*S*,2a*S*,8b*S*)-1-Acetyl-1,2a,3,8b-tetrahydrocyclobuta[*c*]isoquinolin-4(2*H*)-one (8)**




**8**

$C_{13}H_{13}NO_2$
MW: 215.25 g/mol

*Racemic [2+2] Photocycloaddition*
Isoquinolone (20.0 mg, 0.14 mmol, 1.00 eq.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.50 eq.) were dissolved in acetonitrile (10 mL, *c* = 14 mmol/L). After degassing the solution, 3-buten-2-one (115 µl, 1.4 mmol, 10.00 eq.) was added and the mixture was irradiated at 419 nm for 9 h at room temperature (conversion 93 %). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **8** (16.6 mg, 0.08 mmol, 56 %) was obtained as a colorless solid.

*Enantioselective [2+2] Photocycloaddition*
Isoquinolone (3.6 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). After degassing the solution, 3-buten-2-one (104 µl, 1.25 mmol, 50.00 eq.) was added and the mixture was irradiated at 419 nm for 9 h at −25 °C (86 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 1:1). The title compound **8** (4.0 mg, 19 µmol, 74 %, 91 % *ee*, 86 % based on recovered starting material) was obtained as a colorless solid.

**M.p.**: 143-145 °C.
**TLC**: $R_f$ = 0.44 (ethyl acetate, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.15 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.4 Hz, 1H, H-5), 7.47 (*virt.* td, $^3J \approx {}^3J$ = 7.5 Hz, $^4J$ = 1.4 Hz, 1H, H-7), 7.36 (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, $^4J$ = 1.2 Hz, 1H, H-6), 7.18 (dd, $^3J$ = 7.6 Hz, $^4J$ = 1.2 Hz, 1H, H-8), 6.77 (br. s, 1H, NH), 4.32 – 4.20 (m, 1H, H-2a), 3.99 (*virt.* t, $^3J \approx {}^3J$ = 7.7 Hz, 1H, H-8b), 3.52 (*virt.* td, $^3J \approx {}^3J$ = 9.0 Hz, , $^3J$ = 7.5 Hz, 1H, H-1), 2.54 (*virt*. dt, $^2J$ = 11.8 Hz, $^3J \approx {}^3J$ = 7.2 Hz, 1H, H-2), 2.37 (ddd, $^2J$ = 11.8 Hz, $^3J$ = 9.3 Hz, $^3J$ = 2.4 Hz, 1H, H-2), 2.14 (s, 3H, $COCH_3$).
**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 207.5 (s, $COCH_3$), 164.5 (s, C-4), 138.8 (s, C-8a), 133.1 (d, C-7), 128.5 (d, C-5), 127.6 (d, C-6), 127.3 (d, C-8), 126.5 (s, C-4a), 53.3 (d, C-1), 46.5 (d, C-2a), 37.1 (d, C-8b), 33.6 (t, C-2), 28.2 (q, $COCH_3$).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 3186, 2923, 1686, 1492, 1458, 1413, 1362, 1342, 1174, 1161, 811, 786, 766, 734.
**MS** (EI, 70 eV): *m/z* (%) = 215 (1) [$M^+$], 145 (100) [$M^+$–$C_4H_6O$], 118 (24), 90 (8).
**HRMS (EI)** ($C_{13}H_{13}NO_2$): calc.: 215.0946; found: 215.0949
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = ent-**8**, $t_R$ = 18.9 min; **8**, 29.4 min).

## 4. Proof of Constitution and Absolute Configuration

### Regioselectivity and Relative Configuration

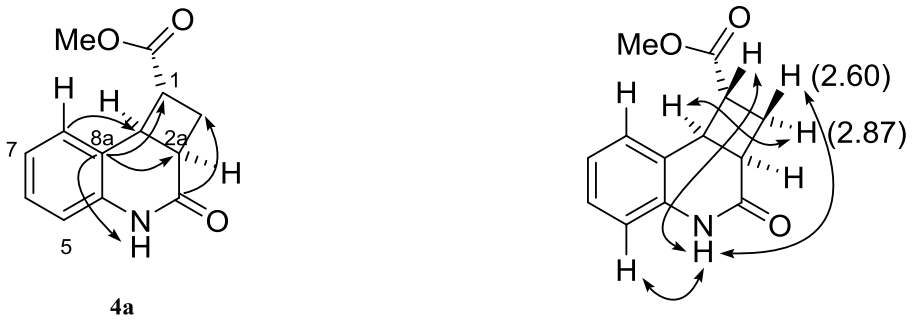
The complete set of $^{1}H$ and $^{13}C$ NMR signals was assigned by a combination of 1D and 2D NMR experiments. HMBC was used to determine the constitution of the isomers while NOESY spectra gave information about the spatial correlations between proximate protons (i.e. relative configuration). The most important HMBC and NOESY correlations for compound **4a** and **S11** are depicted in Figure S1 and Figure S2.

Important HMBC correlations (**4a**):

- C-3 → H-2, H-8b
- C-4a → H-6, H-8, H-8b
- C-8 → H-6, H-8b
- C-8a → H-1, H-2a, N-H

Important NOESY correlations (**4a**):

- N-H ↔ H-1
- N-H ↔ H-2 (2.60 ppm)
- N-H ↔ H-5
- H-8b ↔ H-2 (2.87 ppm)




**4a**

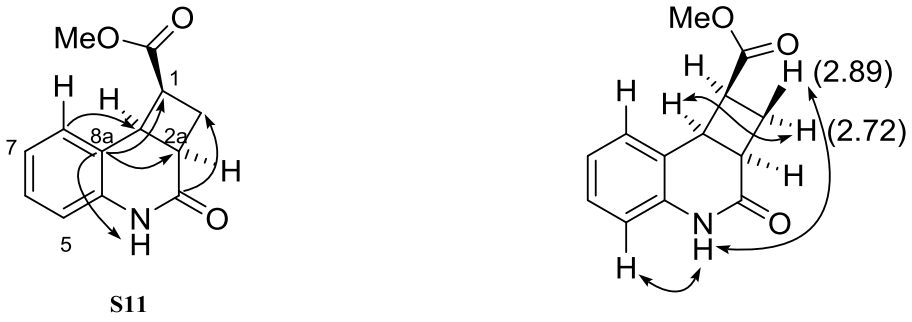
**Figure S1:** HMBC/NOESY correlations of compound **4a** (exo).

Important HMBC correlations (**S11**):

- C-3 → H-2, H-8b
- C-4a → H-6, H-8, H-8b
- C-8 → H-6, H-8b
- C-8a → H-1, H-2a, N-H

Important NOESY correlations (**S11**):

- N-H ↔ H-2 (2.89 ppm)
- N-H ↔ H-5
- H-8b ↔ H-2 (2.72 ppm)




**S11**

**Figure S2:** HMBC/NOESY correlations of compound **S11** (endo).

The most important HMBC and NOESY correlations for compound **4d** and **S14** are depicted in Figure S3 and Figure S4.

Important HMBC correlations (**4d**):

- C-3 → H-2, H-8b
- C-4a → H-6, H-8, H-8b
- C-8 → H-6, H-8b
- C-8a → H-2a, N-H

Important NOESY correlations (**4d**):

- N-H ↔ H-2 (2.33 ppm)
- N-H ↔ $CH_3$, H-5
- $CH_3$ ↔ H-2 (2.33 ppm)
- H-8b ↔ H-2 (3.21 ppm)

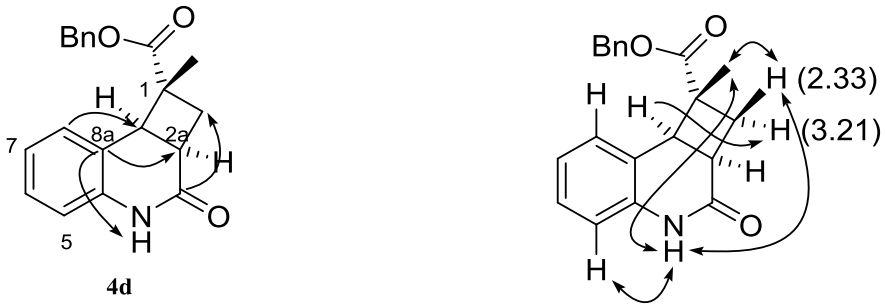



**Figure S3:** HMBC/NOESY correlations of compound **4d** (exo).

Important HMBC correlations (**S14**):

- C-3 → H-2, H-8b
- C-4a → H-6, H-8, H-8b
- C-8 → H-6, H-8b
- C-8a → H-2a, N-H

Important NOESY correlations (**S14**):

- N-H ↔ H-2 (3.17 ppm), H-5
- H-2a ↔ $CH_3$
- H-8b ↔ H-2 (2.44 ppm), $CH_3$
- $CH_3$ ↔ H-2 (2.44 ppm)

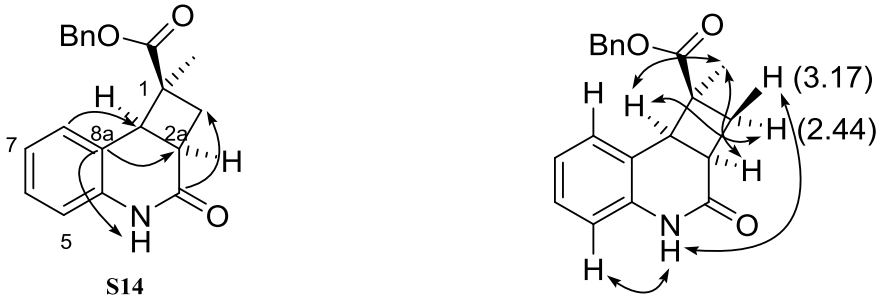
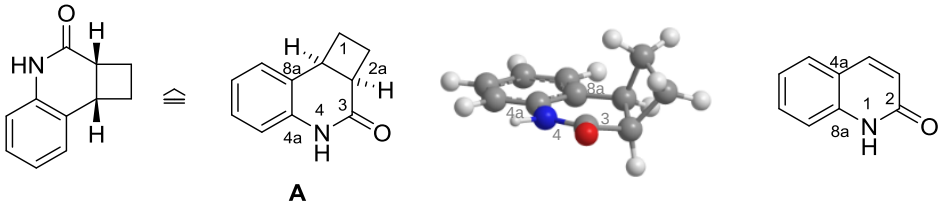



**Figure S4:** HMBC/NOESY correlations of compound **S14** (endo).

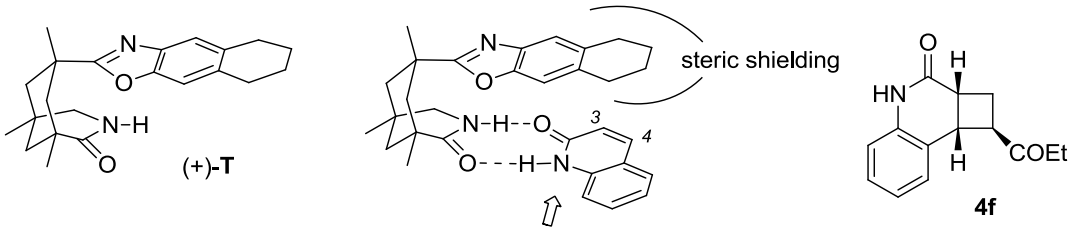
**Absolute Configuration**

In previous work [*Nature* **2005**, *436*, 1139-1140], it has been established that the dihedral angle of the dihydroquinolone chromophore is responsible for the specific rotation of a given dihydroquinolone. When applied to products of a [2+2] photocycloaddition the relevant dihedral angle relates to atoms C3-N4-C4a-C8a, which are in the precursor quinolones atoms C2-N1-C8a-C4a. In products with core **A**, the twist of the chromophore results from the annelated cyclobutane. The dihedral angle becomes negative if the cyclobutane ring and hydrogen atoms at C-2a and C-8b are positioned as shown for **A** [in **A** this would correlate to an (*R*)-configuration at C-2a]. Photocycloaddition products with this absolute configuration are levorotatory. This scenario is shown in the adjacent molecular model of **A**. In the opposite scenario, the dihedral angle is positive and the photocycloaddition products are dextrorotatory.



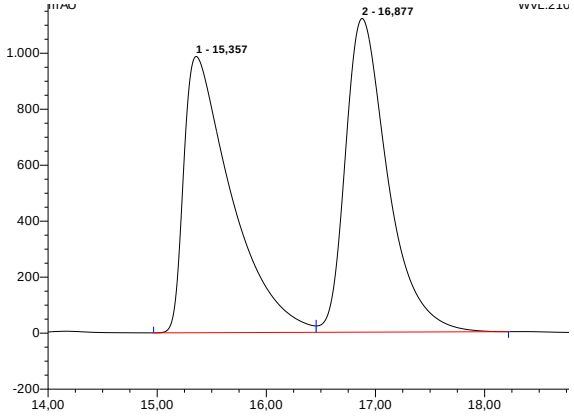

The method has been applied to assign the absolute configuration in intramolecular [2+2] photocycloaddition reactions [*J. Am. Chem. Soc.* **2011**, *133*, 16689-16697].

To substantiate further the direction of the enantioface differentiation, the reaction of 1(2*H*)-quinolone with ethyl vinyl ketone was performed under conditions of direct excitation (λ = 366 nm, –70 °C, $PhCH_3$) in the presence of stoichiometric amounts (2.5 eq.) of chiral template (+)-**T**, which has proven in the last 15 years to provide a complete enantioface differentiation according to the model shown below [Review: Bauer, A.; Alonso, R. Templated Enantioselective Photocatalysis. In *Chemical Photocatalysis*; König, B., Ed.; DeGruyter: Berlin, 2013; pp 67-90]. The product enantiomer **4f** was according to its HPLC trace identical to the product enantiomer obtained with catalyst **3**.

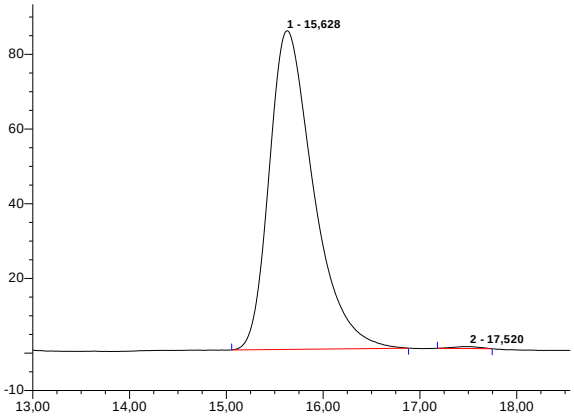


HPLC traces (for details, see section 10)

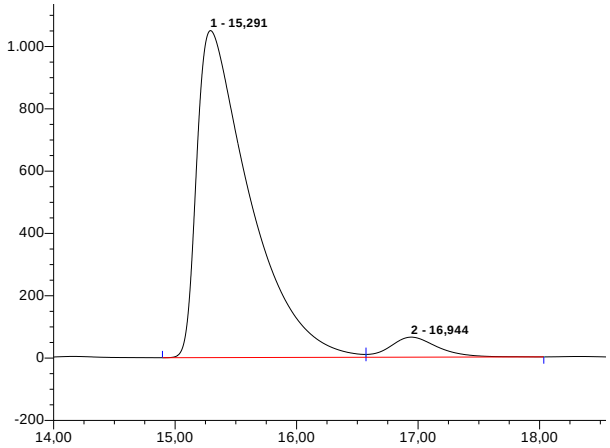
HPLC trace of *rac*-**4f**




HPLC trace of **4f** (from (+)-**T**)

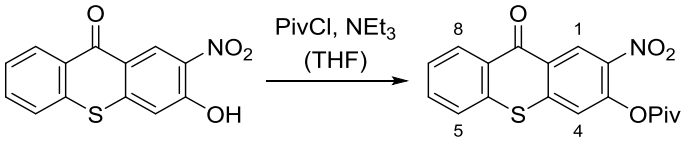



HPLC trace of **4f** (from **3**)



## 5. Synthesis of the Thioxanthone Derivative 7

### 2-Nitro-9-oxo-9*H*-thioxanthen-3-yl pivaloate (S19)

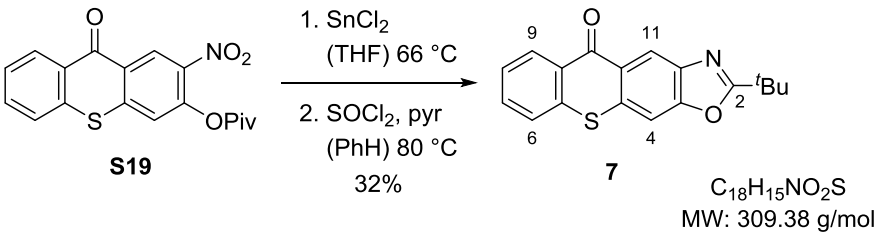



**S19** $C_{18}H_{15}NO_5S$
MW: 357.38 g/mol

PivCl (356 µL, 2.90 mmol, 1.05 eq.) was added dropwise via syringe to a solution of 3-Hydroxy-2-nitro-9*H*-thioxanth-9-one[*Angew. Chem. Int. Ed.* **2014**, *53*, 4368-4371.] (754 mg, 2.76 mmol, 1.0 eq.), $Et_3N$ (1.2 mL, 8.3 mmol, 1.15 eq.) and THF (50 mL, *c* = 50 mmol/L). The mixture was stirred at room temperature for 30 min and then poured into 0.1 M HCl (200 mL). The precipitate was filtered and dried in the desiccator to yield the desired pivaloate **S19** (980 mg, 2.74 mmol, 99 %).

**M.p.**: 233 °C.
**TLC**: $R_f$ = 0.66 (cylohexane:ethyl acetate, 1:1, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 9.30 (s, 1H, C-1-H), 8.61 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.6 Hz, 1H, C-8-H), 7.70 (ddd, $^3J$ = 8.4, 7.1 Hz, $^4J$ = 1.5 Hz, 1H, C-6-H), 7.61-7.55 (m, 2H, C-5-H, C-7-H), 7.40 (s, 1H, C-4-H), 1.42 [s, 9H, C(*C*$H_3$)$_3$].
**$^{13}$C-NMR** (126 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 178.0 (s, CO), 175.7 (s, COO), 146.6 (s, C-4a), 144.1 (s, C-2), 140.4 (s, C-3), 135.8 (s, C-5a), 133.4 (d, C-6), 130.3 (d, C-8), 128.5 (s, C-8a), 128.4 (d, C-1), 127.8 (d, C-7), 127.0 (s, C-9a), 126.3 (d, C-5), 122.1 (d, C-4), 39.5 [s, C($CH_3$)$_3$], 27.14 (q, CH3).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 1759, 1636, 1604, 1553, 1343, 1212, 1099, 929, 753, 743.
**MS** (EI, 70 eV): *m/z* (%) = 357 (18) [$M^+$], 309 (14), 294 (24), 273 (73) [M-$CO_2$tBu]$^+$, 227 (12) [M-$CO_2$tBu-$NO_2$]$^+$, 171 (9), 85 (13) [$CO_2$t$Bu^+$], 57 (100) [t$Bu^+$].
**HRMS (EI)** ($C_{18}H_{15}NO_2S$): calc.: 357.0665; found: 357.0664

**2-(*tert*-Butyl)-10*H*-thioxantheno[2,3-d]oxazol-10-one (7)**




A solution of pivaloate **S19** (910 mg, 2.55 mmol, 1.00 eq.) and dry tin(II) chloride (2.41 g, 12.7 mmol, 5.00 eq.) in anhydrous tetrahydrofuran (50 mL, *c* = 50 mmol/L) was heated to 70 °C for 20 h. The mixture was allowed to cool to room temperature and water (35 mL) was added. The resulting suspension was repeatedly extracted with chloroform until the product cannot be detected in the extract (TLC). The combined organic layers were filtered over celite. The solvent was removed in vacuo to yield 1.46 g of crude material which was used without further purification.
A solution of the crude product and pyridine (1.33 mL, 16.5 mmol, 6.50 eq.) in dry benzene (17 mL, *c* = 0.15 mol/L) was treated dropwise with thionyl chloride (0.55 mL, 7.60 mmol, 3.00 eq.) and heated to 90 °C for 20 h. The solution was allowed to cool to room temperature and some silica gel was added carefully. The solvent was removed in vacuo and the mixture was submitted to purification by column chromatography (silica gel, dichloromethane/diethyl ether = 100:0 → 95:5). Further purification by flash column chromatography (silica gel, hexane/ethyl acetate/dichloro-methane = 8:1:1) gave the pure pure benzoxazole **7** (249 mg, 0.805 mmol, 32% over two steps).

**M.p.**: 156 °C.
**TLC**: $R_f$ = 0.50 (cylohexane:ethyl acetate, 8:2, UV).
**$^1$H-NMR** (500 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 8.98 (s, 1H, C-11-H), 8.64 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.4 Hz, 1H, C-9-H), 7.67 (s, 1H, C-4-H), 7.66-7.57 (m, 2H, C-6-H, C-8-H), 7.50 (ddd, $^3J$ = 8.2, 7.0, $^4J$ = 1.3 Hz, 1H, C-7-H), 1.53 [s, 9H, C($CH_3$)$_3$].
**$^{13}$C-NMR** (126 MHz, $CDCl_3$, 303 K): $\delta$ (ppm) = 179.9 (s, CO), 175.5 (s, C-2), 153.5 (s, C-3a), 141.3 (s, C-11a), 137.2 (s, C-5a), 134.0 (s, C-10a), 132.4 (d, C-7), 130.1 (d, C-9), 128.8 (s, C-9a), 126.5 (s, C-4a), 126.5 (d, C-8), 125.8 (d, C-6), 121.9 (d, C-11), 106.7 (d, C-4) , 34.6 [s, C($CH_3$)$_3$], 28.6 (q, $CH_3$).
**IR** (ATR): $\nu$ ($cm^{-1}$) = 2973, 1635, 1617, 1589, 1436, 1412, 1289, 1246, 1112, 1101, 1043, 1032, 915, 860, 809, 744.
**MS** (EI, 70 eV): *m/z* (%) = 309 (72) [$M^+$], 294 (100) [M-$CH_3$]$^+$, 267 (14) [M-CO-$CH_3$]$^+$, 253 (7) [M-*t*Bu]$^+$, 225 (12) [M-CO-*t*Bu]$^+$.
**HRMS (EI)** ($C_{18}H_{15}NO_2S$): calc.: 309.0818; found: 309.0821

## 6. Competition Experiment

Prior to the experiment the GC calibration parameters were determined for every compound.

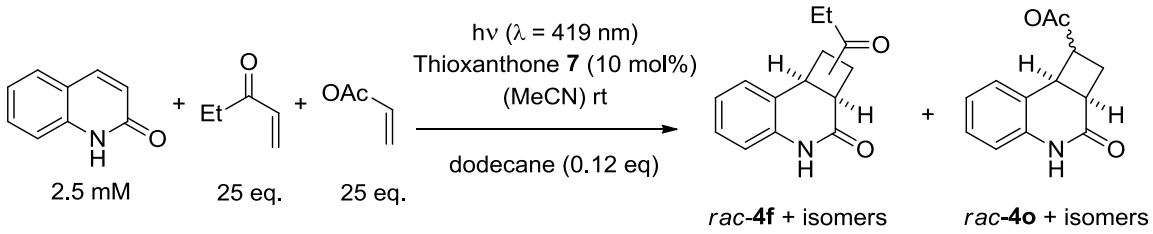
Dodecane: y = 78.12904x + 0.34781

Quinolone **S20**: y = 67.42409x - 1.17052

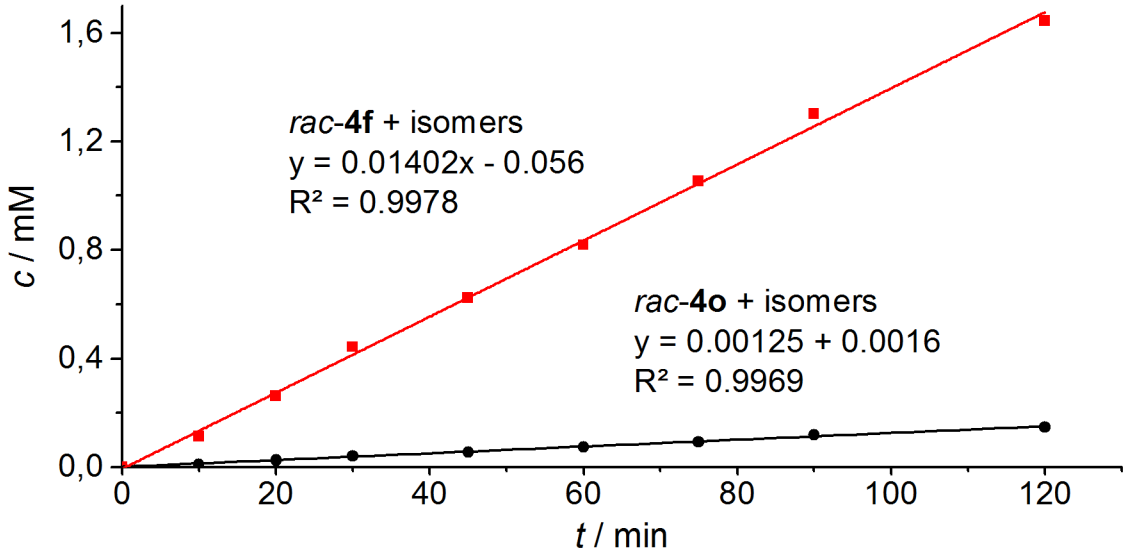
Product **4f**: y = 92.76575x - 0.25822

Product **4o**: y = 107.6437x + 0.38640

Thioxanthone **7**: y = 174.4212x - 1.56069




In the experiment 2(1*H*)-quinolone (**S20**) (7.20 mg, 50.0 µmol, 1.00 eq.) and thioxanthone **7** (1.56 mg, 5.04 µmol, 0.10 eq.) were dissolved in degassed acetonitrile (20 mL, *c* = 2.5 mmol/L). Dodecane was used as internal standard (1.36 µL, 5.99 µmol, 0.12 eq.). Subsequently, pent-1-en-3-one (123 µl, 1.24 mmol, 25 eq.) and vinyl acetate (114 µl, 1.24 mmol, 25 eq.) were added and the solution was irradiated at 419 nm at room temperature. Aliquots of 100 µL were taken from the reaction mixture after 0, 10, 20, 30, 45, 60, 75, 90 and 120 mins reaction time, and measured without dilution. GC analysis was carried using the following temperature profile: 60 ºC (hold 3 min), then 15 ºC/min to 250 ºC (hold 3 min), then 40 ºC/min to 300 ºC (hold 5 min).



## Areas measured by GC

**Table S1:** GC data (area) for Quinolone **S20** product **4f** (+isomers) and product **4o** (+isomers) at different reaction times. The conversion of quinolone **S20** was calculated as the change of the area of **S20**.

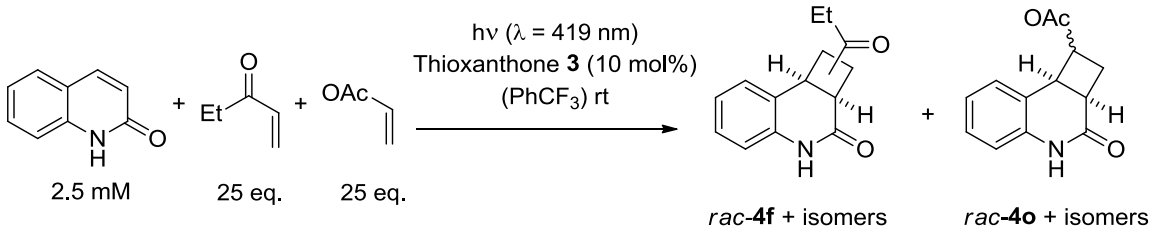
| **Time [min]** | Dodecane | Quinolone **S20** | Product **4f** + isomers | Product **4o** + isomers | Conversion (%) |
|---|---|---|---|---|---|
| 0 | 23.6 | 158.7 | 0.0 | 0.0 | 0.0 |
| 10 | 22.1 | 126.7 | 1.7 | 13.4 | 14.8 |
| 20 | 21.1 | 107.8 | 3.4 | 29.5 | 24.2 |
| 30 | 24.2 | 106.4 | 6.3 | 57.2 | 34.7 |
| 45 | 23.6 | 84.7 | 8.4 | 78.6 | 46.8 |
| 60 | 21.5 | 66.2 | 10.1 | 94.0 | 54.3 |
| 75 | 23.6 | 53.8 | 13.8 | 132.7 | 66.2 |
| 90 | 19.5 | 38.8 | 14.4 | 135.5 | 70.5 |
| 120 | 18.0 | 21.8 | 16.6 | 158.0 | 82.0 |

## Concentrations of starting material S20 and products 4f/4o

**Table S2:** Calculated concentrations for quinolone **S20,** product **4f** (+isomers) and product **4o** (+isomers).

| **Time [min]** | **0** | **10** | **20** | **30** | **45** | **60** | **75** | **90** | **120** |
|---|---|---|---|---|---|---|---|---|---|
| Quinolone **S20** (mM) | 2.74 | 2.33 | 2.08 | 1.79 | 1.46 | 1.25 | 0.93 | 0.81 | 0.49 |
| **4f** + isomers (mM) | 0.00 | 0.11 | 0.26 | 0.44 | 0.62 | 0.82 | 1.05 | 1.30 | 1.62 |
| **4o** + isomers (mM) | 0.00 | 0.01 | 0.03 | 0.04 | 0.06 | 0.08 | 0.09 | 0.12 | 0.15 |

## Competition Experiment Using Catalyst 3




In the experiment 2(1*H*)-quinolone (**S20**) (3.65 mg, 25.0 µmol, 1.00 eq.) and enantiomerically pure **3** (1.08 mg, 2.50 µmol, 0.10 eq.) were dissolved in degassed α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L). Subsequently, pent-1-en-3-one (62.2 µl, 0.63 mmol, 25 eq.) and vinyl acetate (57.6 µl, 0.63 mmol, 25 eq.) were added and the solution was irradiated at 419 nm at room temperature for 30 min. The reaction was

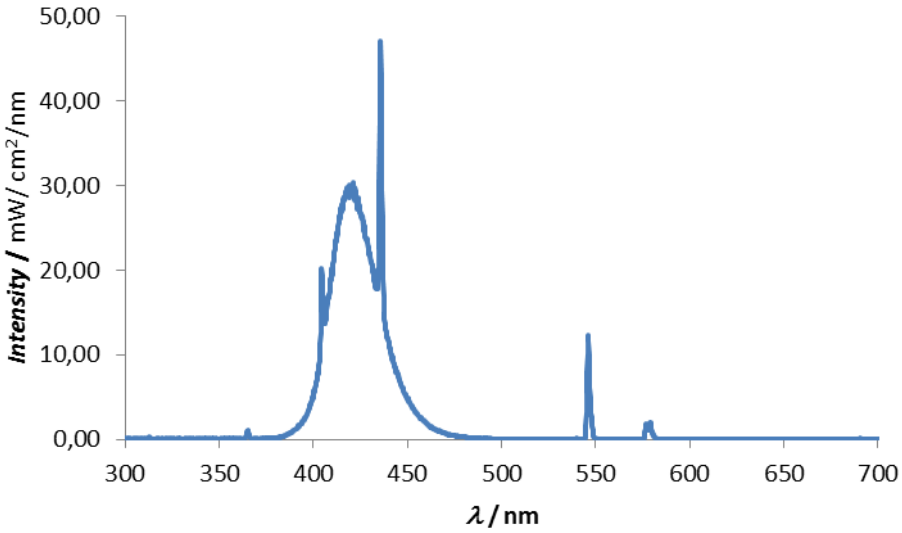
stopped and the reaction mixture was analyzed by GLC after removal of the catalyst. GC analysis was carried using the following temperature profile: 60 ºC (hold 3 min), then 15 ºC/min to 250 ºC (hold 3 min), then 40 ºC/min to 300 ºC (hold 5 min).

**Table S3:** GC data (area) and calculated concentrations for product **4f** (+isomers) and product **4o** (+isomers) after 30 min. The ratio of $k_{COEt}/k_{OAc}$ determined under these conditions was 7.7.

| **Time [min]** | Product **4f** + isomers | Product **4o** + isomers | **4f** + isomers (mM) | **4o** + isomers (mM) | $k_{COEt}/k_{OAc}$ |
|---|---|---|---|---|---|
| 30 | 73.8 | 12.1 | 0.23 | 0.03 | 7.7 |

## 7. Emission Spectra of the Light Sources.

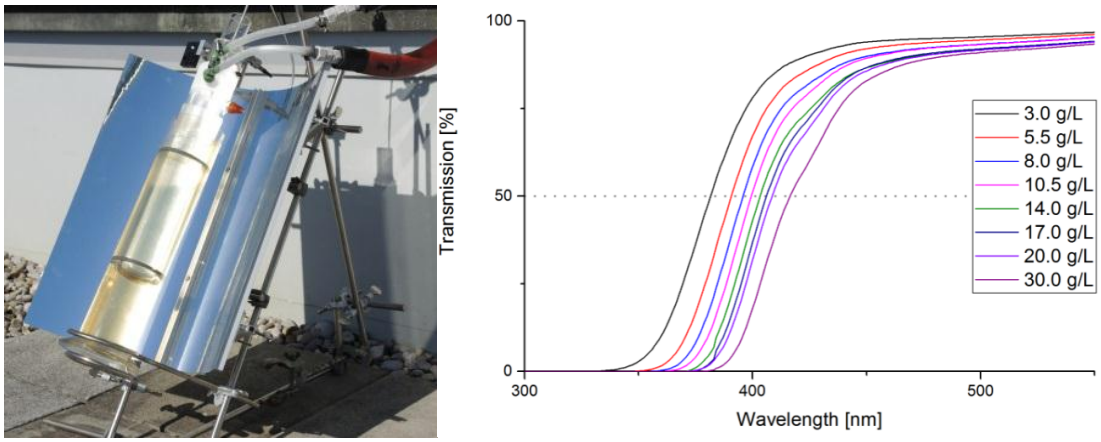
Emission spectra of the light sources used in this study (Rayonet RPR-4190A) were measured using a USB-4000 spectrometer (OceanOptics Inc. Dunedin, FL, USA; 600 lines grating blazed at 300 nm; bandwidth 200-850 nm; 10 µm slit) through a cosine corrector connected with a 400 µm fibre to the spectrometer. The light intensity was measured at the lamp centre in a distance of 10 cm and refers to a calibration of the above described setup against radiometric calibration standards (OceanOptics Inc. Dunedin, FL, USA) traceable to NIST references.



## 8. Solar Irradiation Experiment

Solar irradiation experiments were conducted in the standard low-temperature setup consisting of the irradiation tube in a vaccum-insulated cooling finger. The cooling finger was placed in a surrounding cylinder filled with a slightly acidified (0.075 mol/L HCl) iron(III) sulfate solution (c = 10.5 g/L) to cut off the UV-content of the incident light.[1] Both, cooling finger and phototube were held in place by spacers to result in a stable, concentrical setup; the resulting thickness of the filter solution was 10 mm.
The irradiation setup was placed in the focus of a parabolic mirror (see Figure S5). During prolonged irradiation, the complete device was turned and tilted, to follow the course of the sun.

**Figure S5:** Apparatus for solar irradiation and UV-Vis transmission spectra of various concentrations of a iron(III) sulfate solution (10 mm optical pathlength).

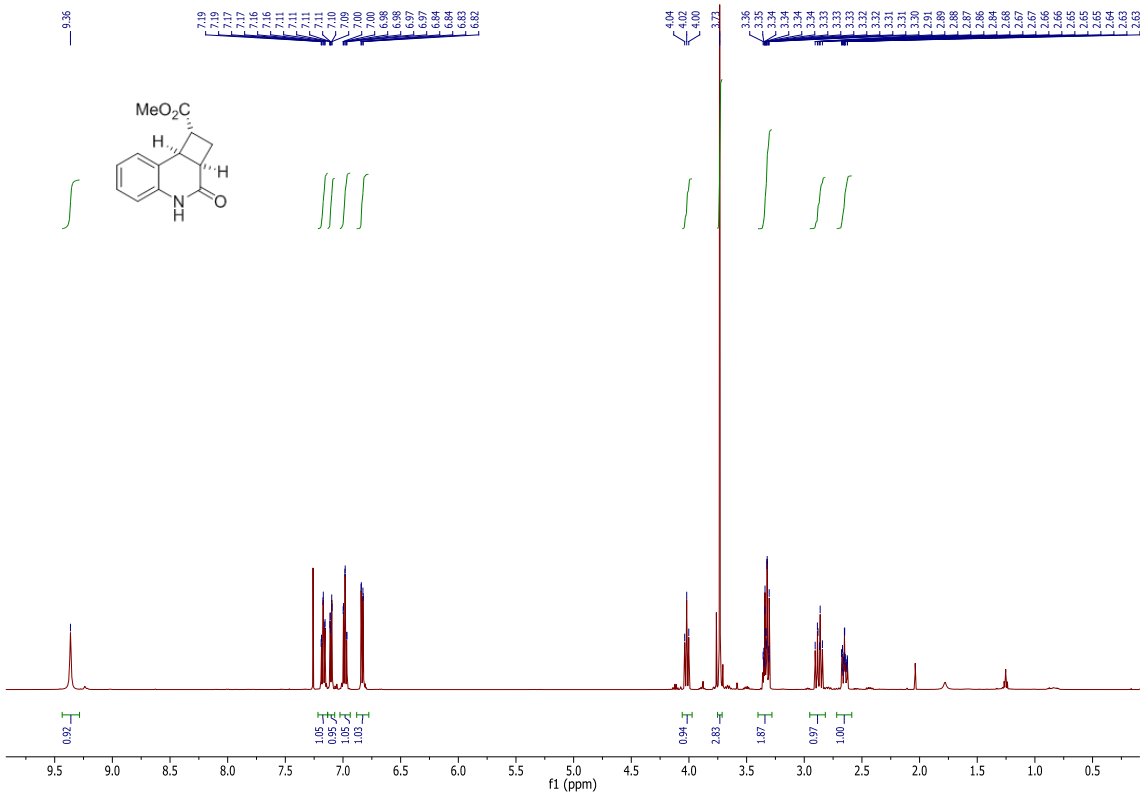


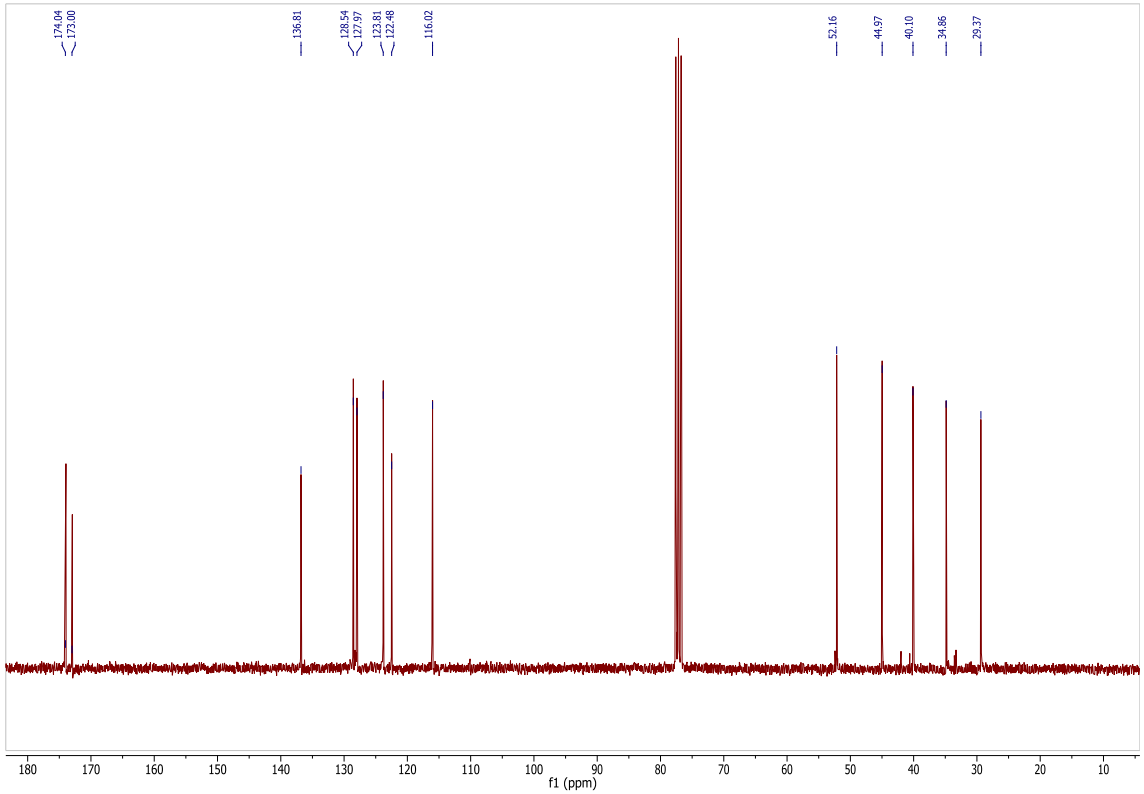

*Enantioselective [2+2] Photocycloaddition*

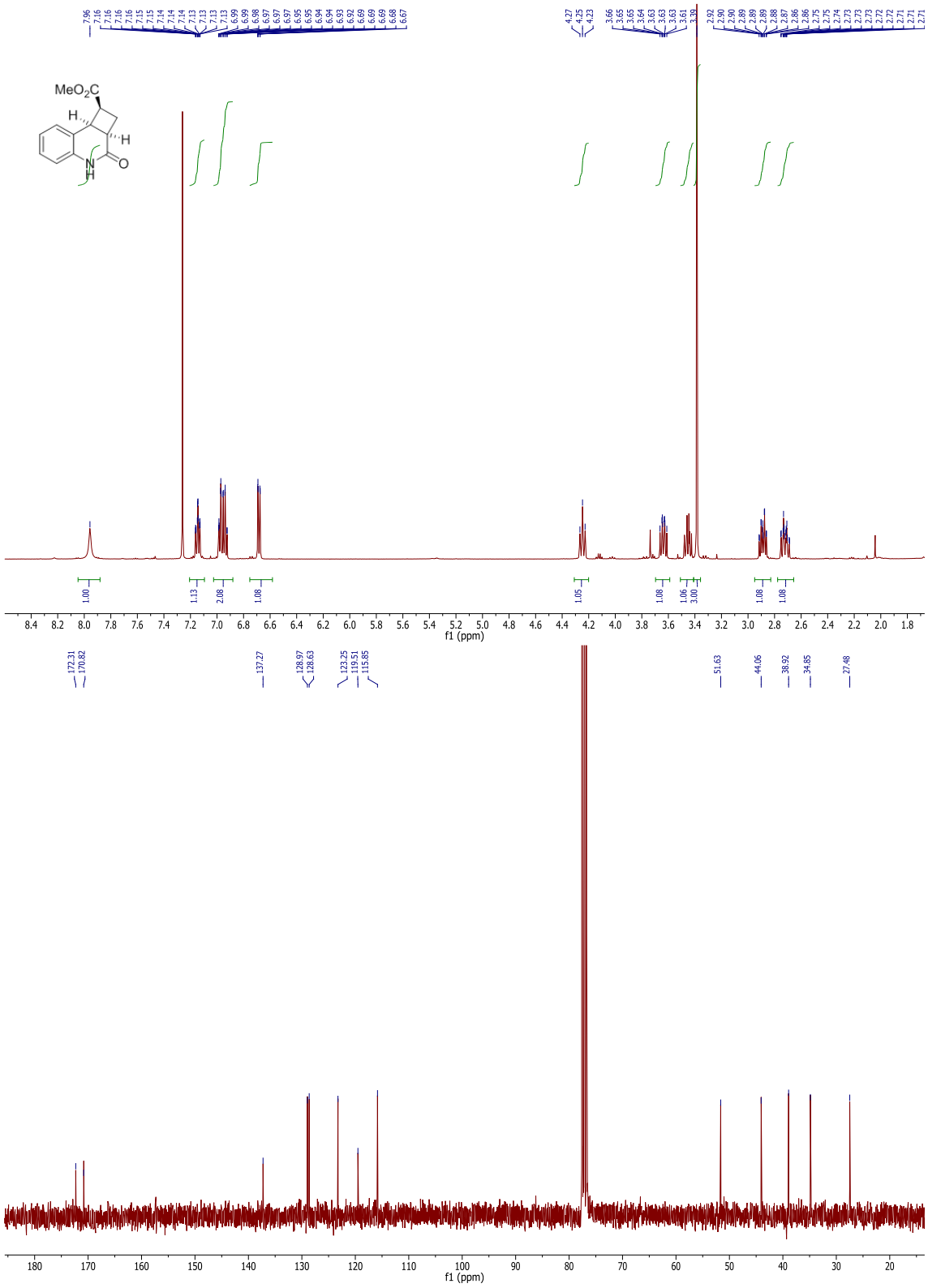
2(1*H*)-Quinolone (2.9 mg, 20.0 µmol, 1.00 eq.) and enantiomerically pure **3** (0.9 mg, 2.0 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (8 mL, *c* = 2.5 mmol/L). After degassing the solution, pent-1-en-3-one (99 µl, 1.00 mmol, 50.0 eq.) was added and the mixture was exposed to sunlight irradiation for 4 h 15 min at −25 °C (21 % conversion). After removing the solvent, purification was achieved by flash column chromatography (silica, pentane/ethyl acetate 7:3 → 1:1). The title compound **4f** (0.8 mg, 3.5 µmol, 17%, 86% *ee*, 81 % based on recovered starting material) and remaining starting material (2.3 mg, 16.0 µmol, 79 %) were obtained as a colorless solid.

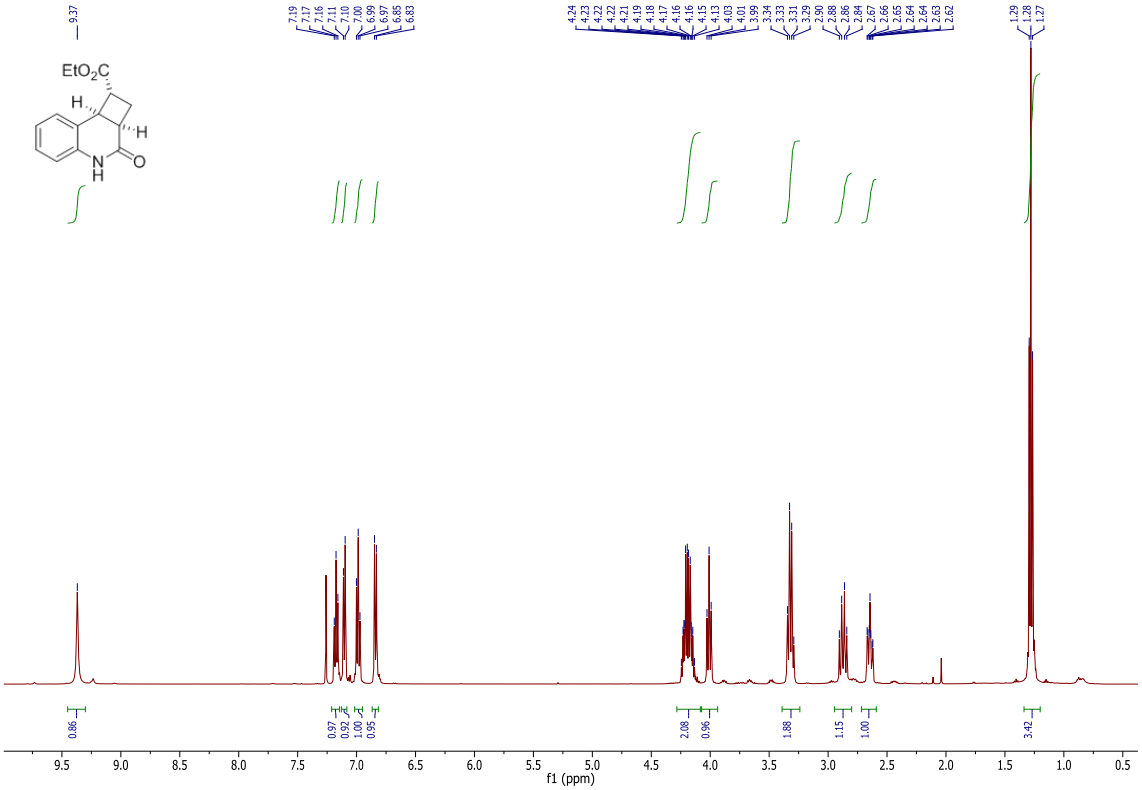
[1] The concentration needs to be optimized for different sunlight-intensities; 10.5 g/L where used for low intensity sun light (Munich, late October 2015).

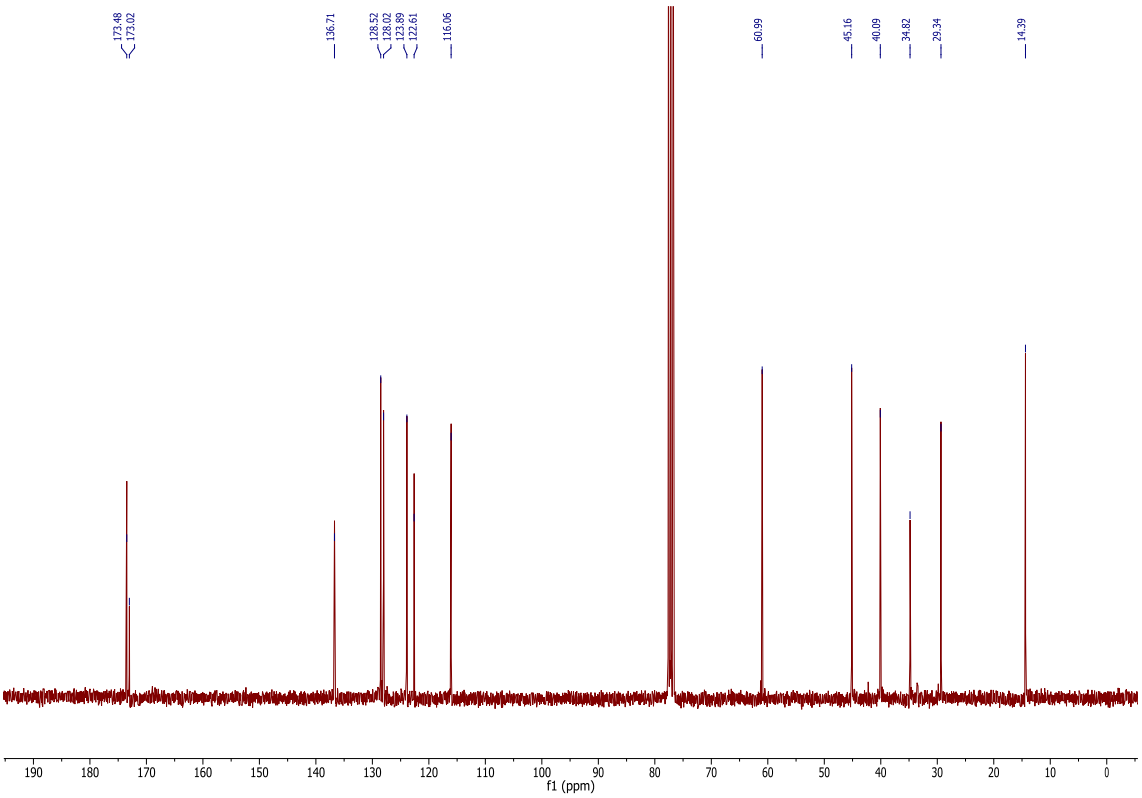
## 9. NMR-Spectra of New Compounds

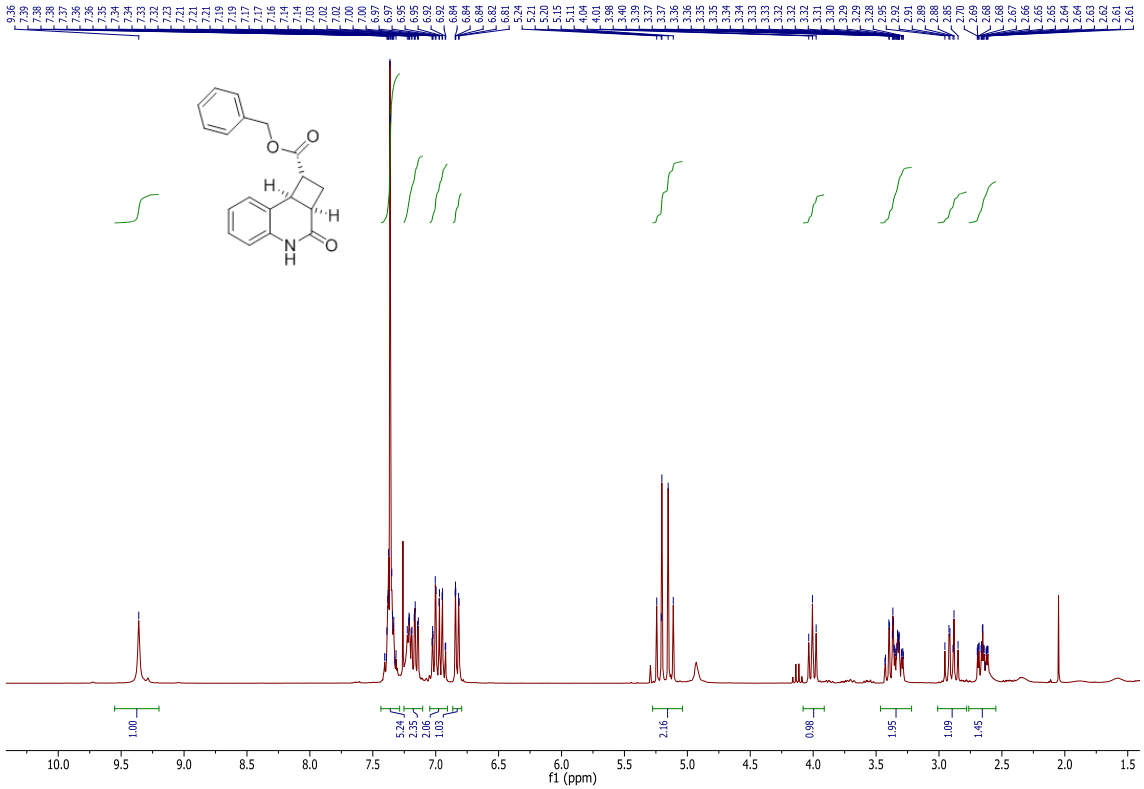


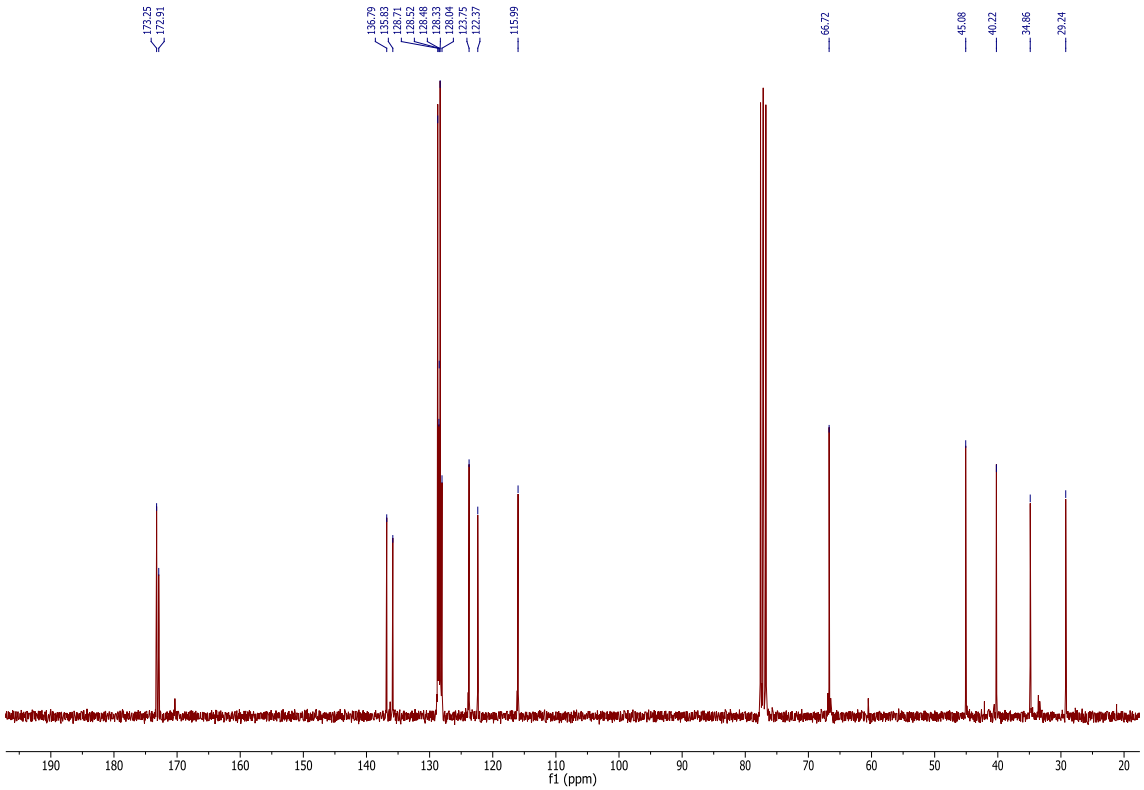



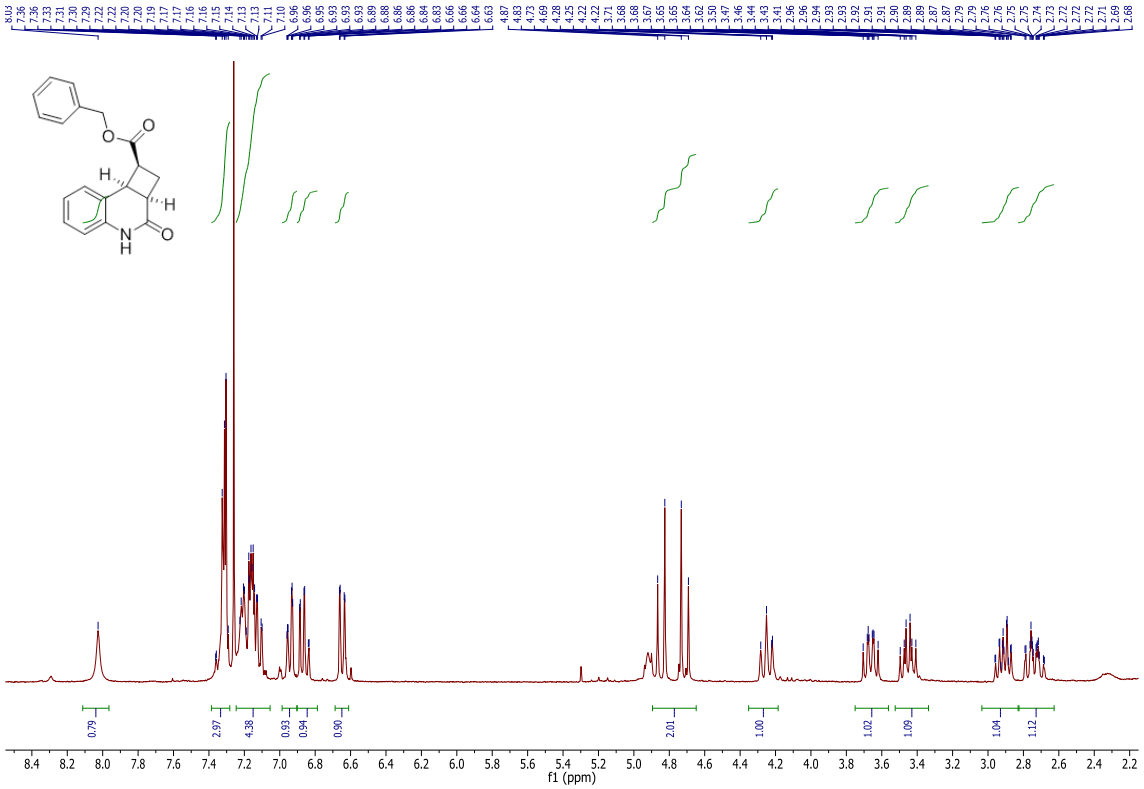

MeO2C
H
H
N
H
O
f1 (ppm)
f1 (ppm)

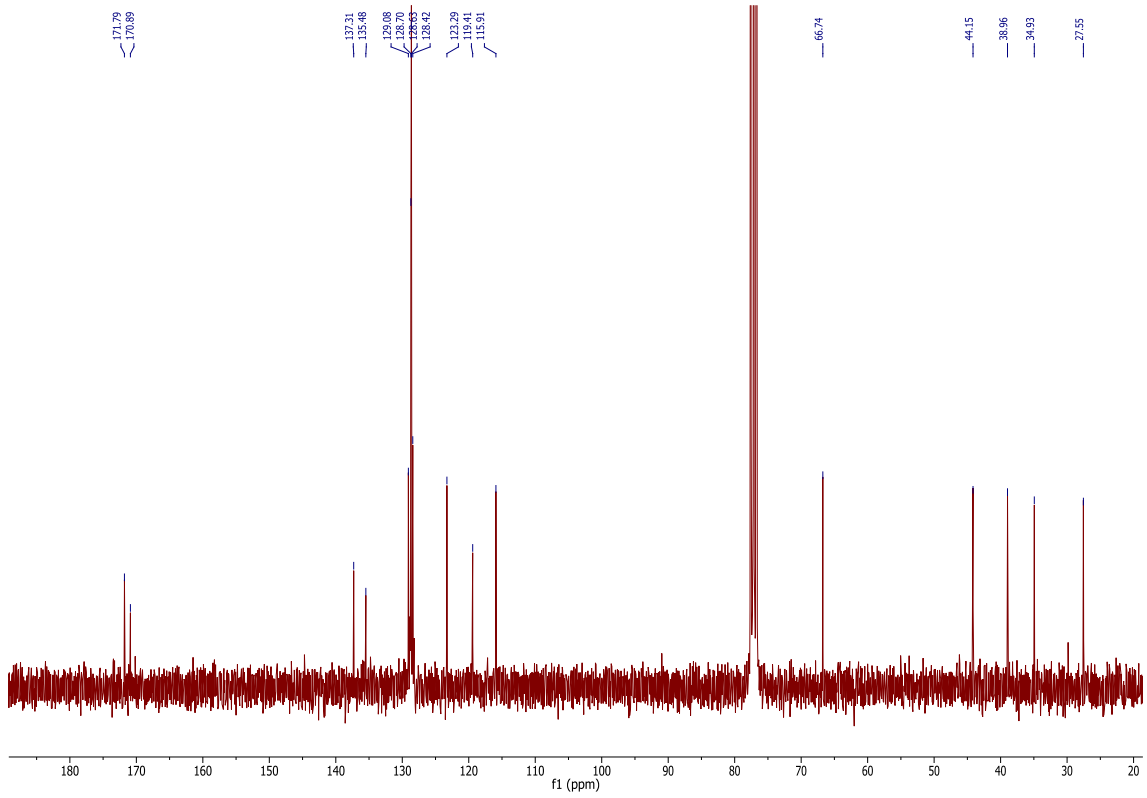

EtO2C
H
H
N
H
O
f1 (ppm)


f1 (ppm)


f1 (ppm)


f1 (ppm)


f1 (ppm)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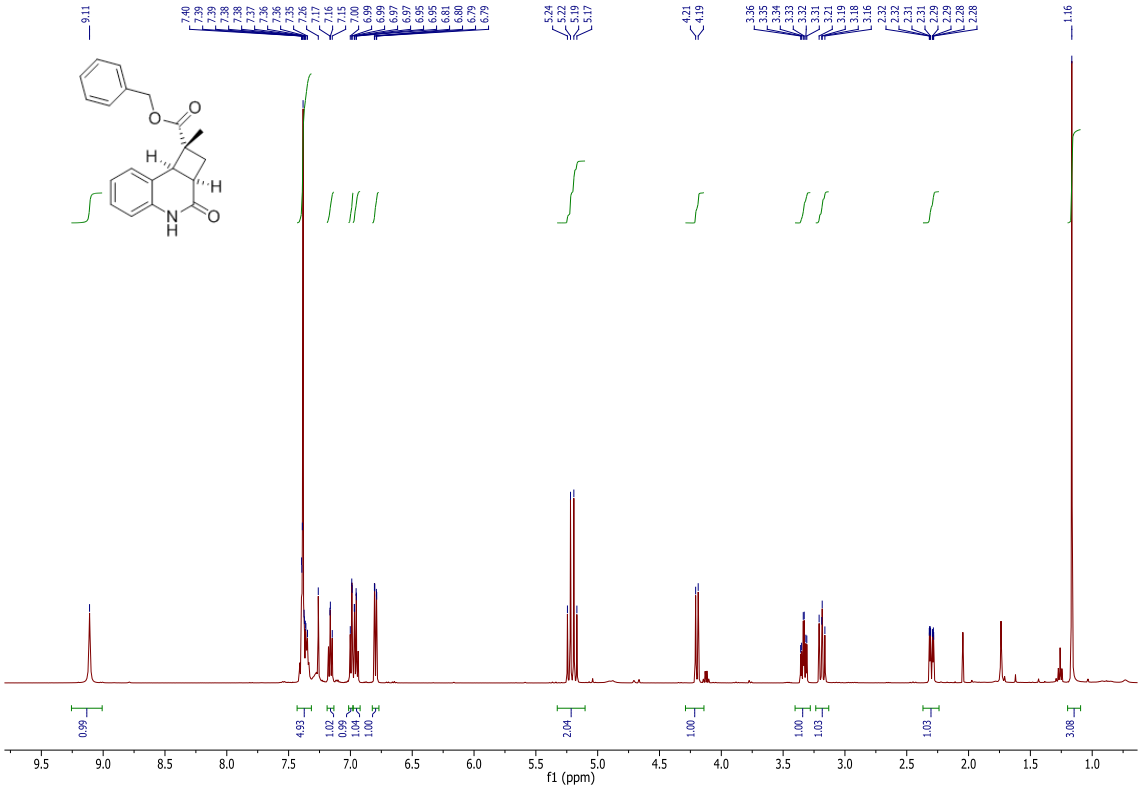
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2.29
2.28
2.28
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O
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H
N
H
O
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1.00
2.04
1.00
1.00
1.03
1.03
3.08
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9.0
8.5
8.0
7.5
7.0
6.5
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3.5
3.0
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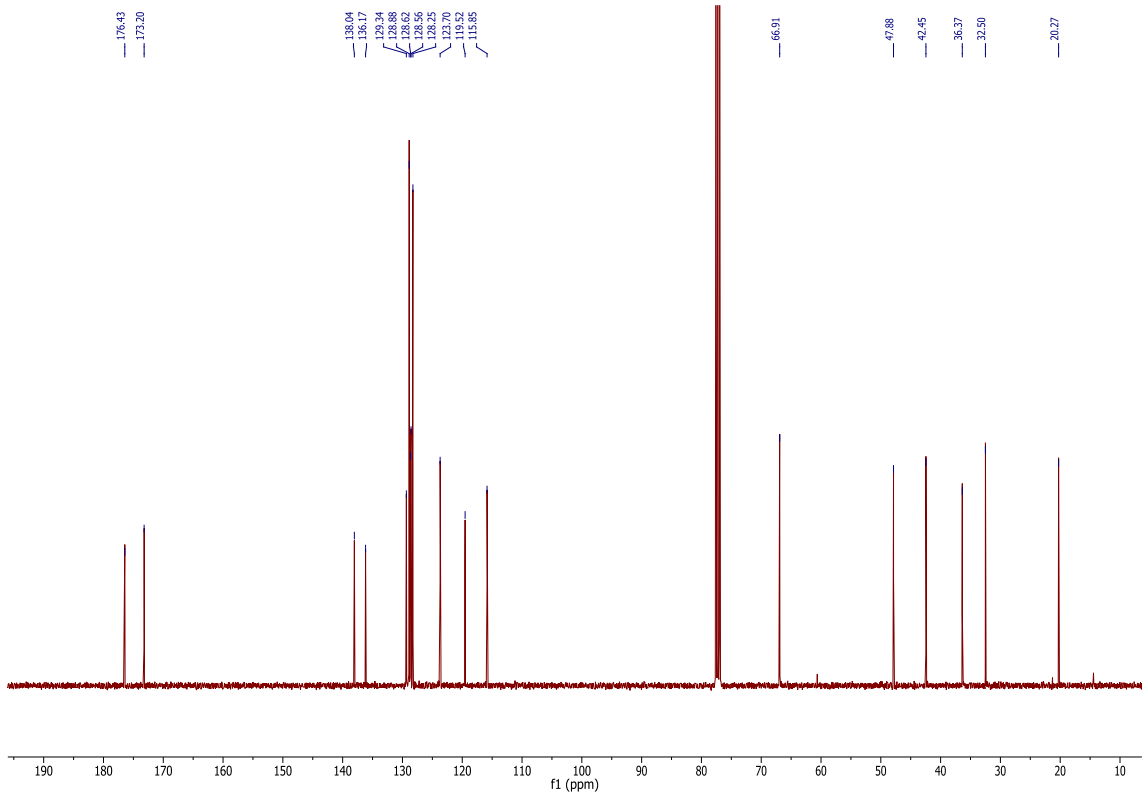
1.0
f1 (ppm)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32.50
20.27
190
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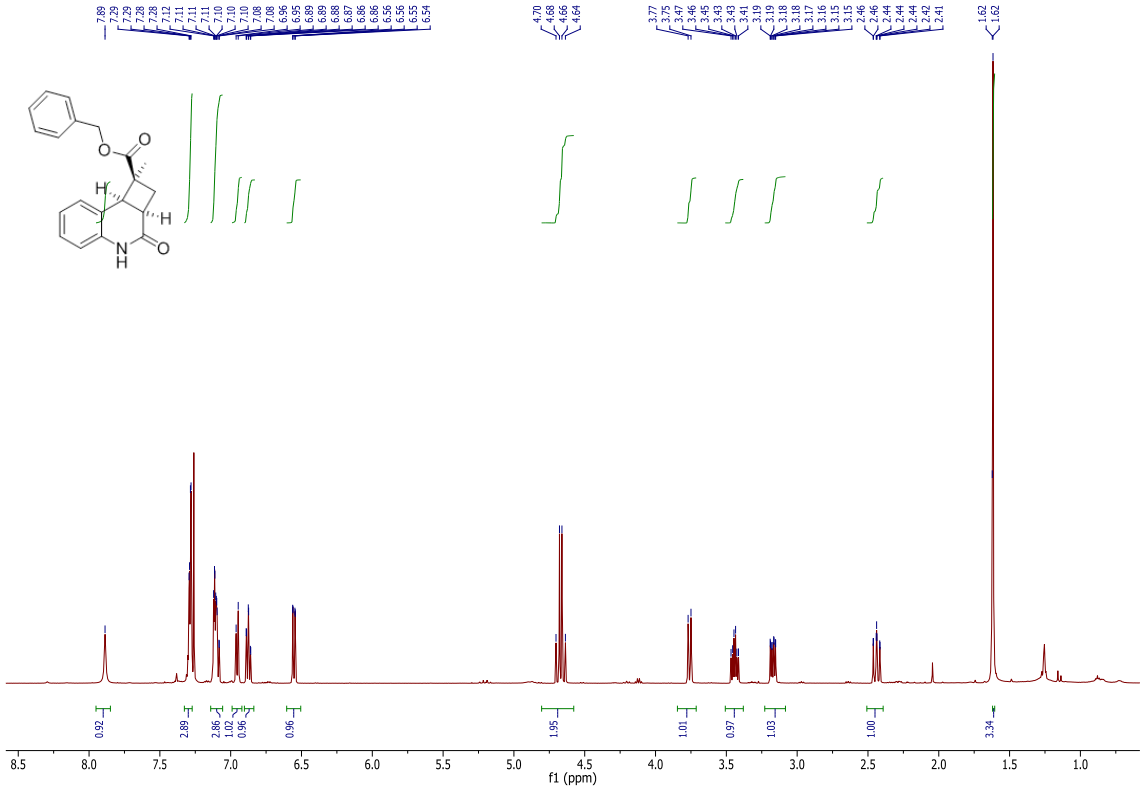
f1 (ppm)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7.08
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2.46
2.46
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2.44
2.44
2.42
2.41
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1.62
O
O
H
H
N
H
O
0.92
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2.86
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0.96
0.96
1.95
1.01
0.97
1.03
1.00
3.34
8.5
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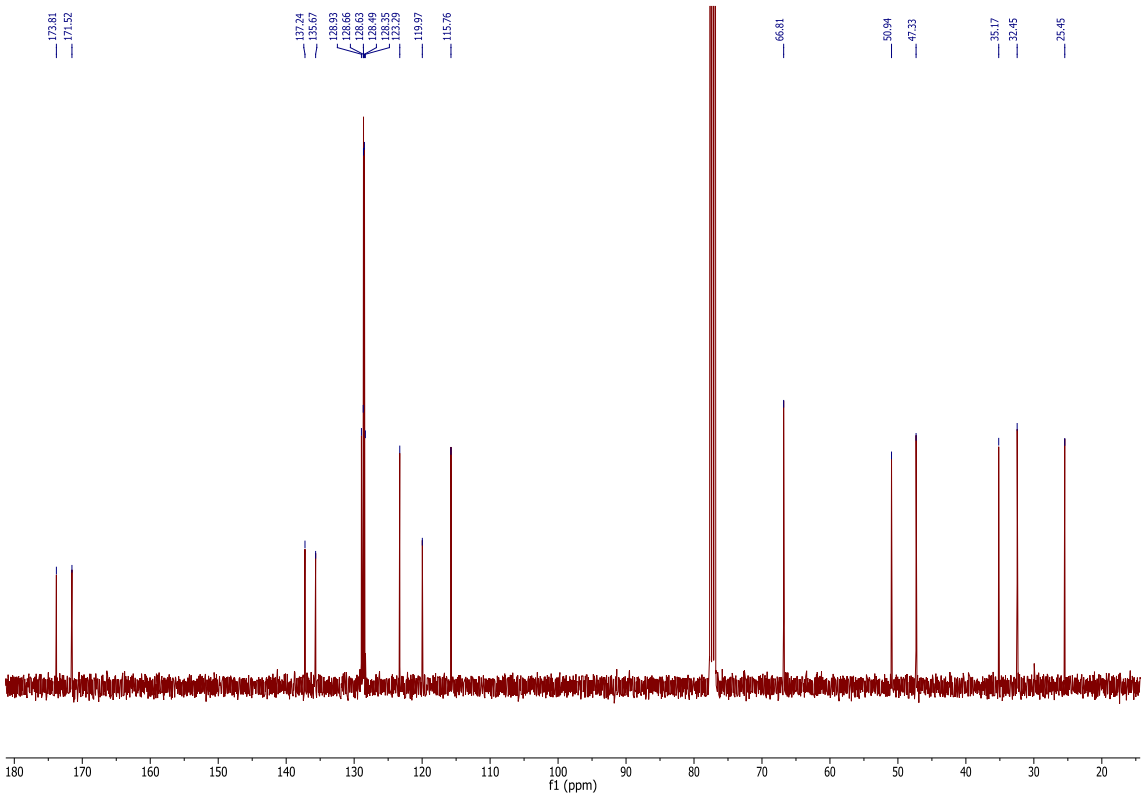
1.0
f1 (ppm)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35.17
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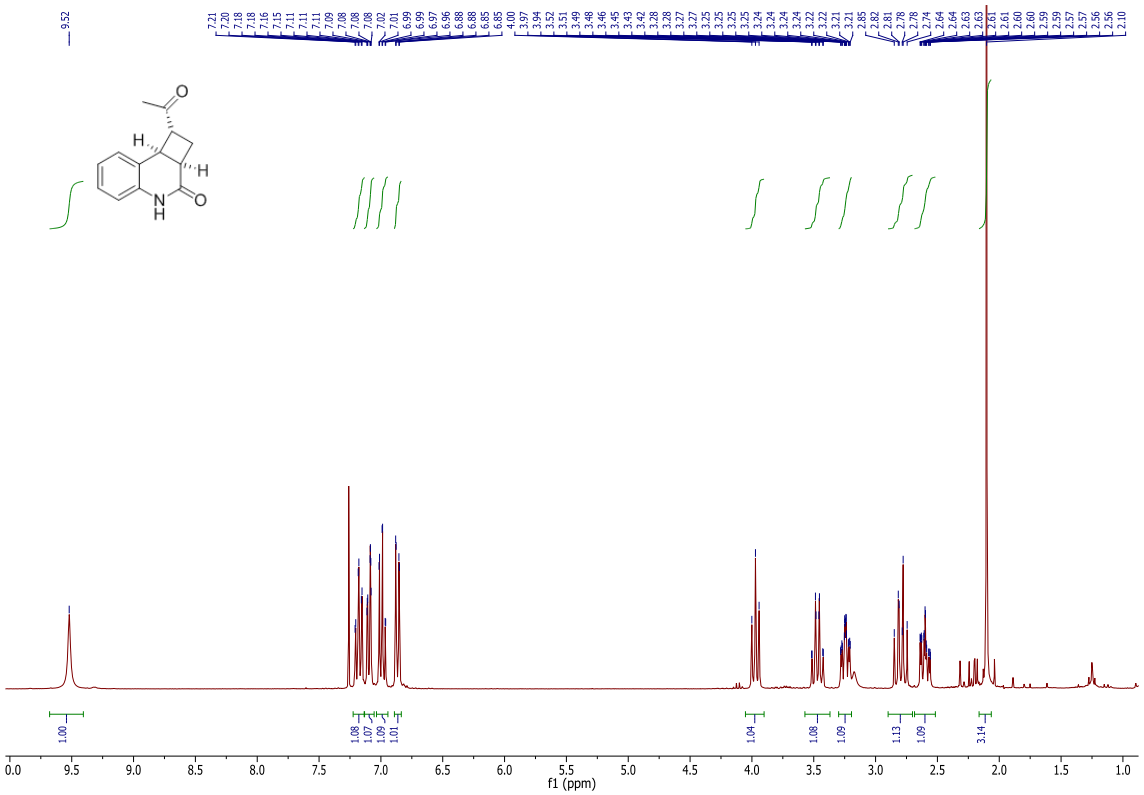
f1 (ppm)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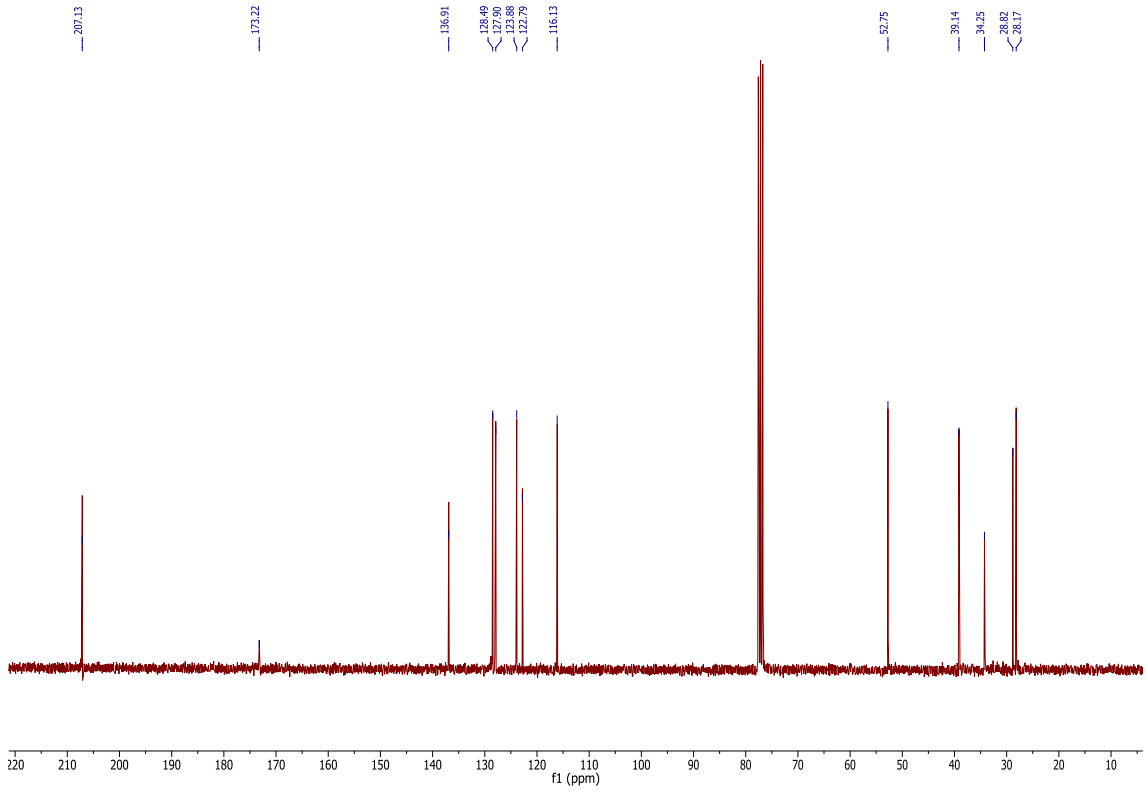
H
O
f1 (ppm)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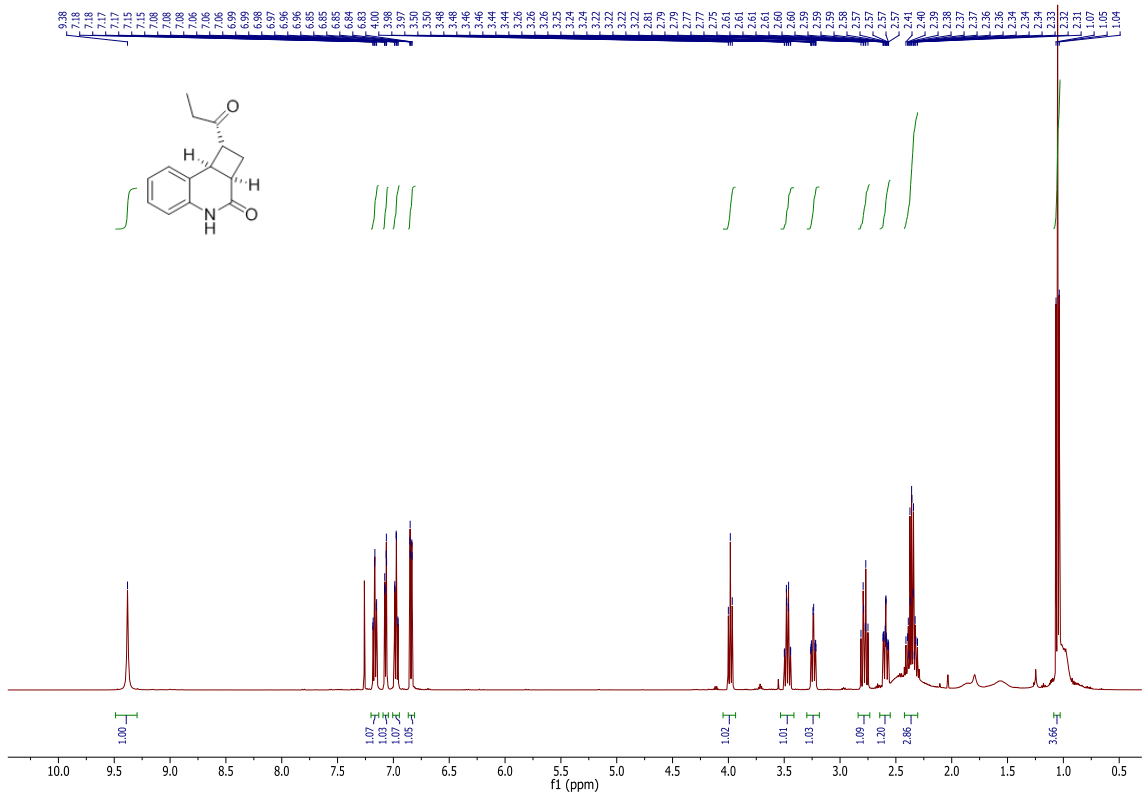
52.75
39.14
34.25
28.82
28.17
f1 (ppm)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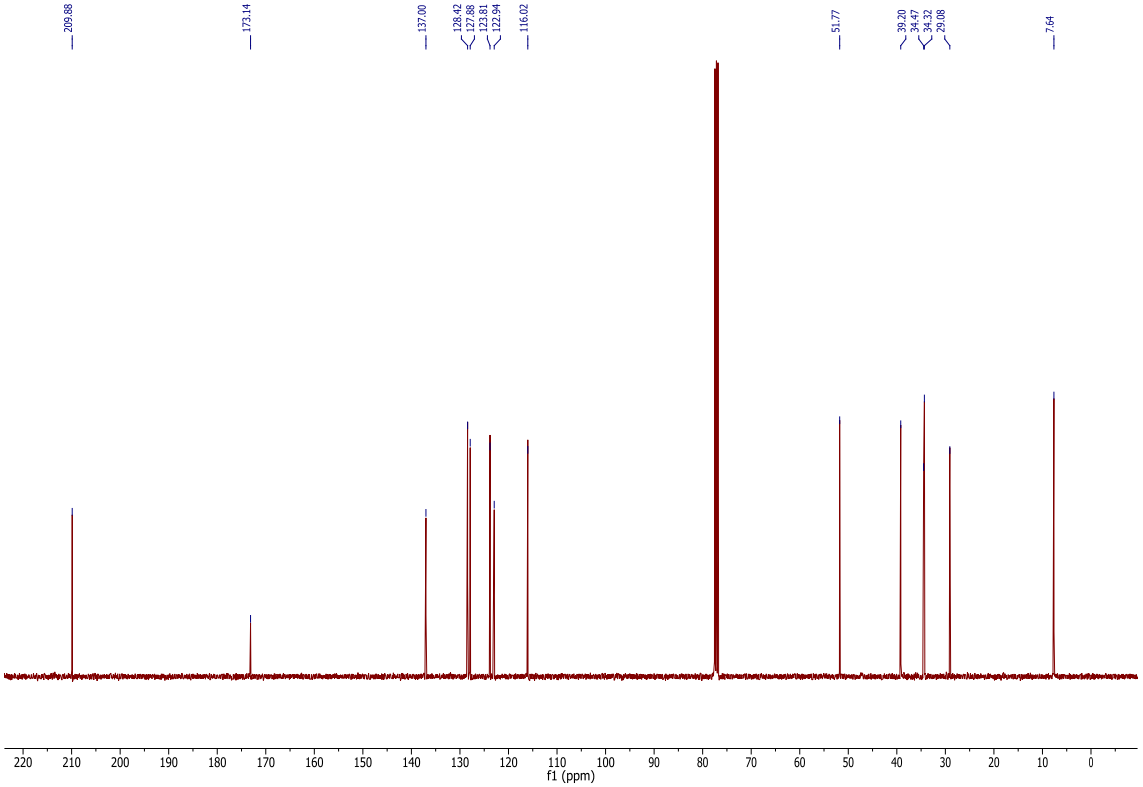
1.03
1.07
1.05
1.02
1.01
1.03
1.09
1.20
2.86
3.66
f1 (ppm)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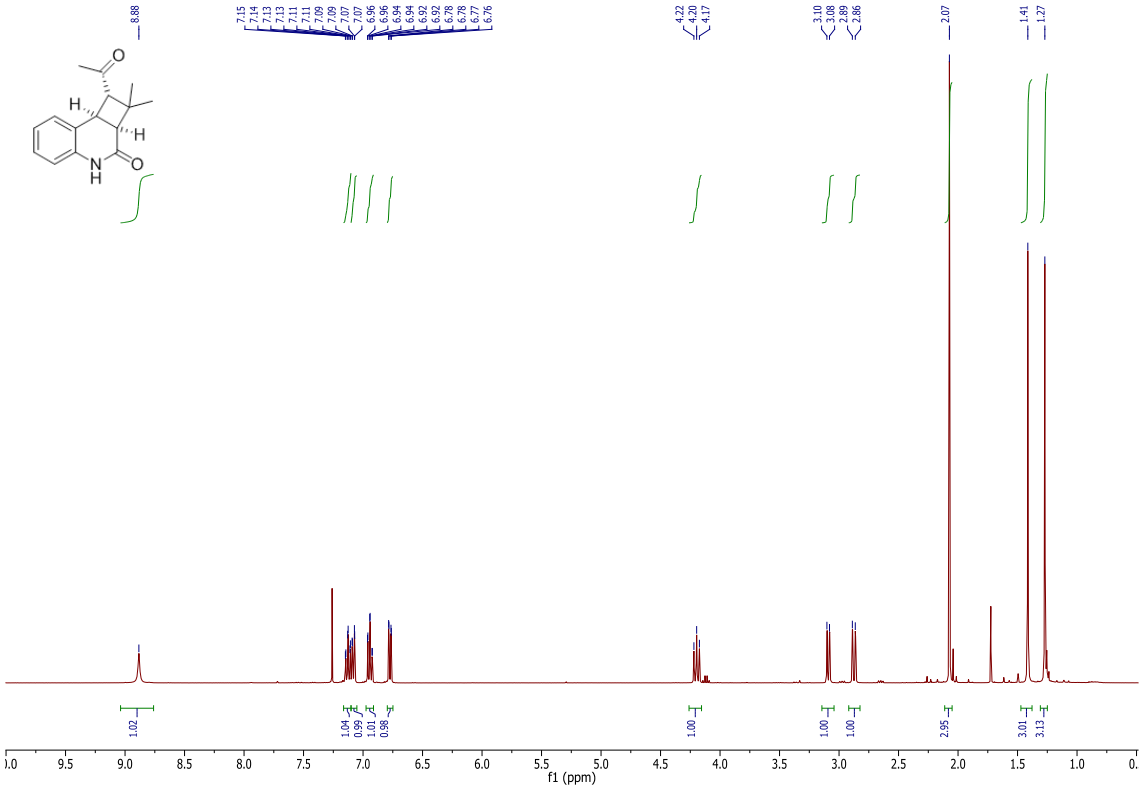
34.32
29.08
7.64
f1 (ppm)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7.09
7.09
7.07
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6.94
6.94
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6.92
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6.78
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4.22
4.20
4.17
3.10
3.08
2.89
2.86
2.07
1.41
1.27
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1.04
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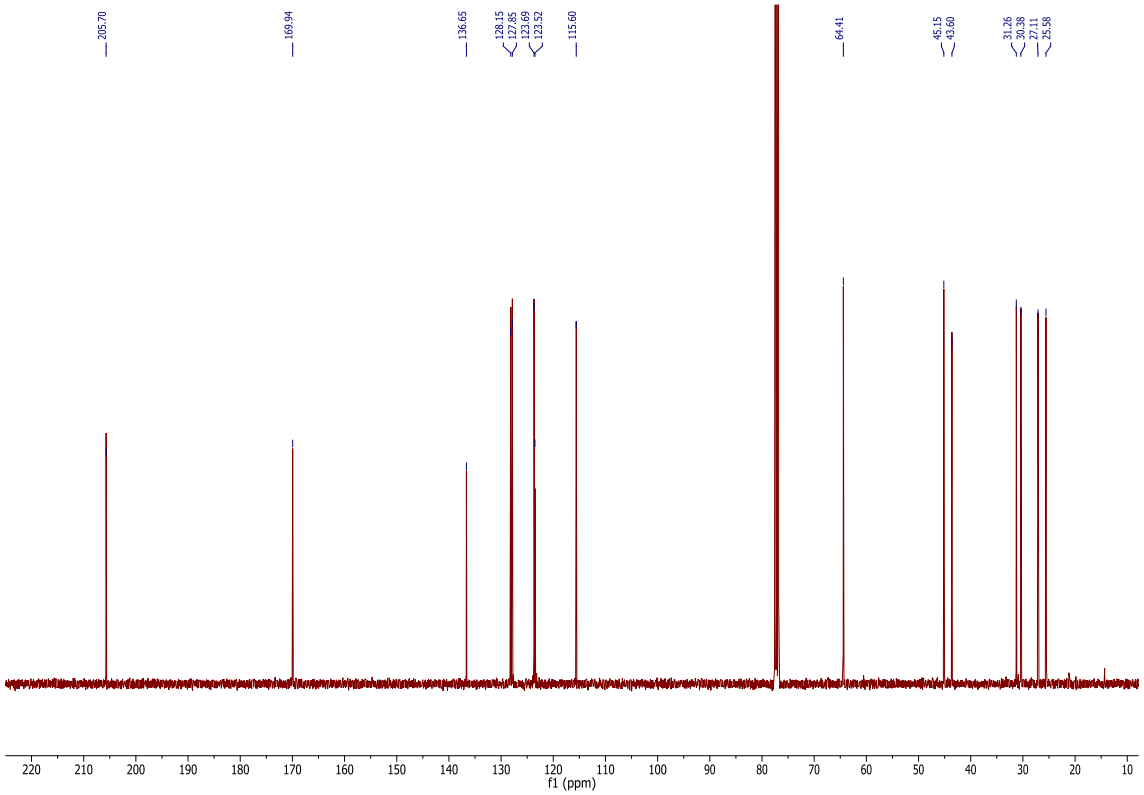
1.00
1.00
1.00
2.95
3.01
3.13
f1 (ppm)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43.60
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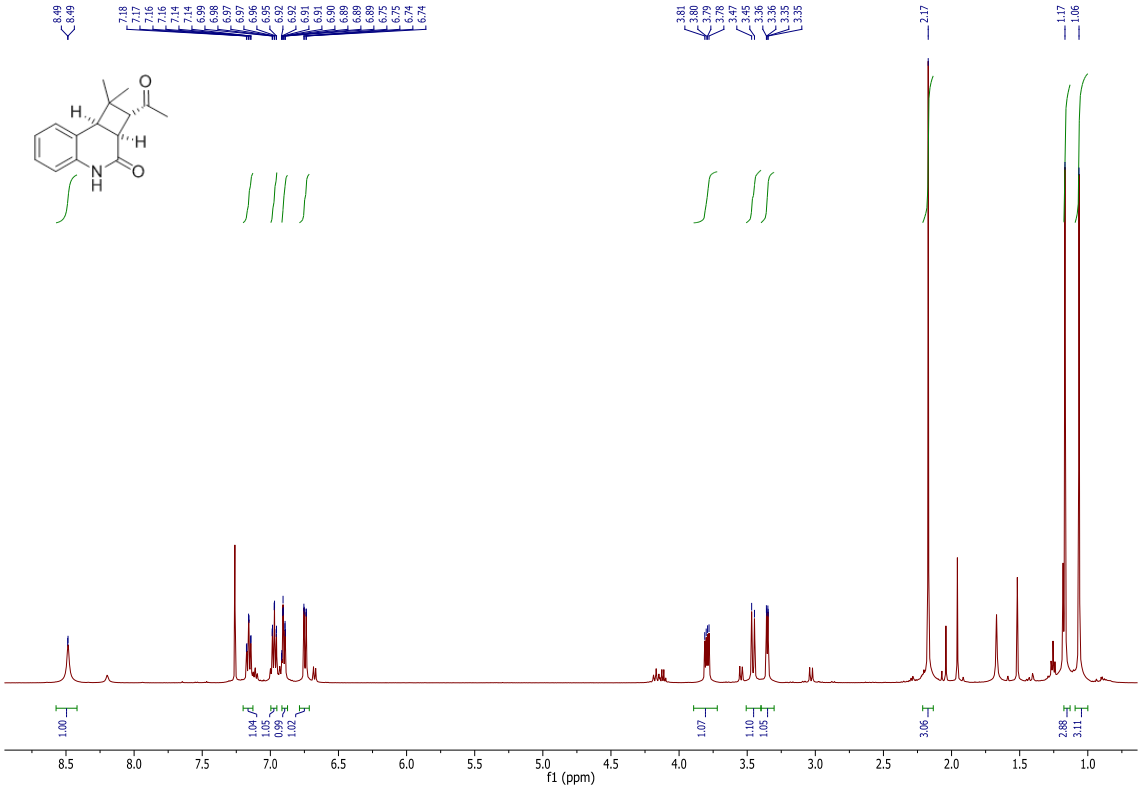
27.11
25.58
f1 (ppm)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6.91
6.90
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6.74
3.81
3.80
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3.78
3.47
3.45
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3.35
3.35
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1.17
1.06
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H
N
H
O
1.00
1.04
1.05
0.99
1.02
1.07
1.10
1.05
3.06
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3.11
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7.0
6.5
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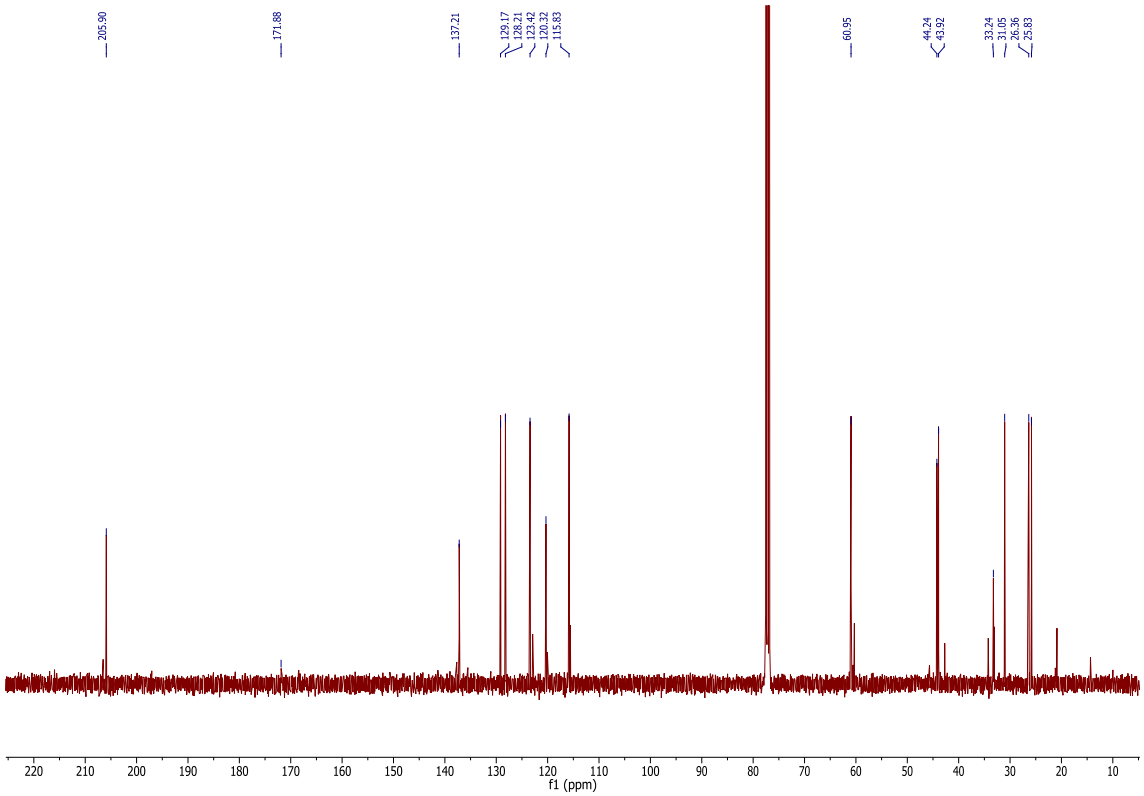
1.0
f1 (ppm)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43.92
33.24
31.05
26.36
25.83
220
210
200
190
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120
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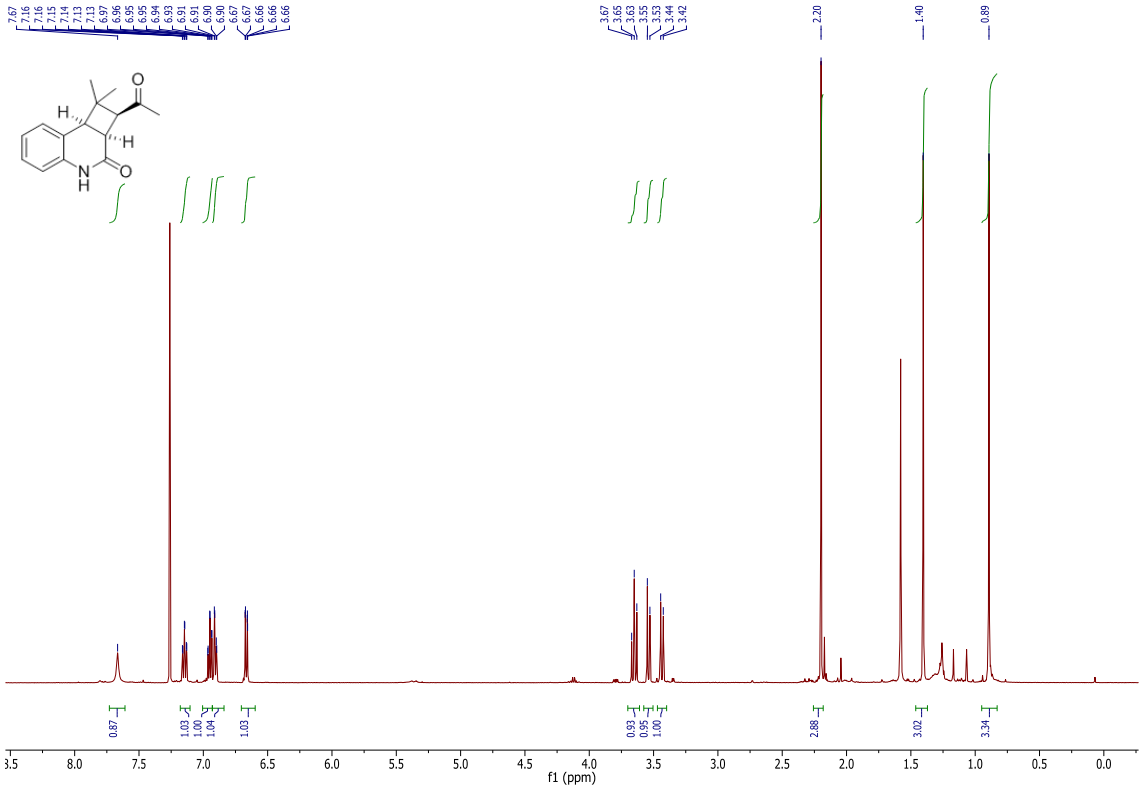
f1 (ppm)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6.94
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6.91
6.91
6.90
6.90
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6.66
6.66
6.66
3.67
3.65
3.63
3.55
3.53
3.44
3.42
2.20
1.40
0.89
O
H
H
N
H
O
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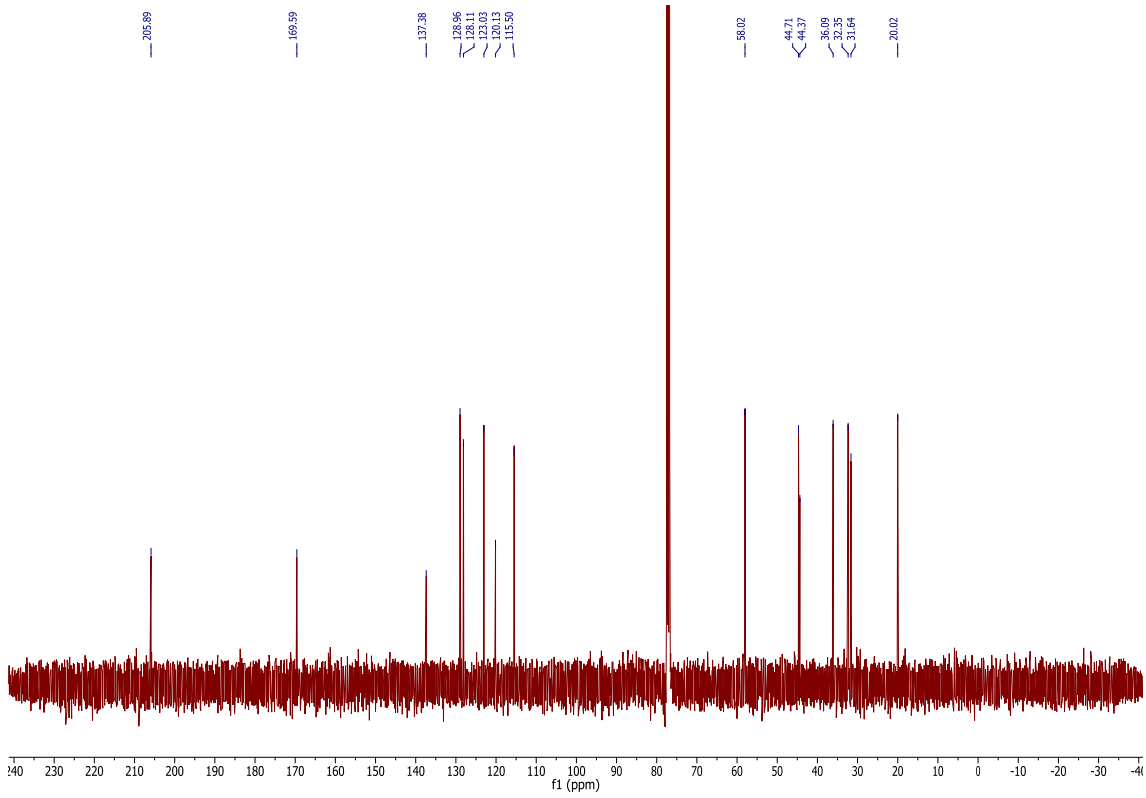
1.04
1.03
0.93
0.95
1.00
2.88
3.02
3.34
f1 (ppm)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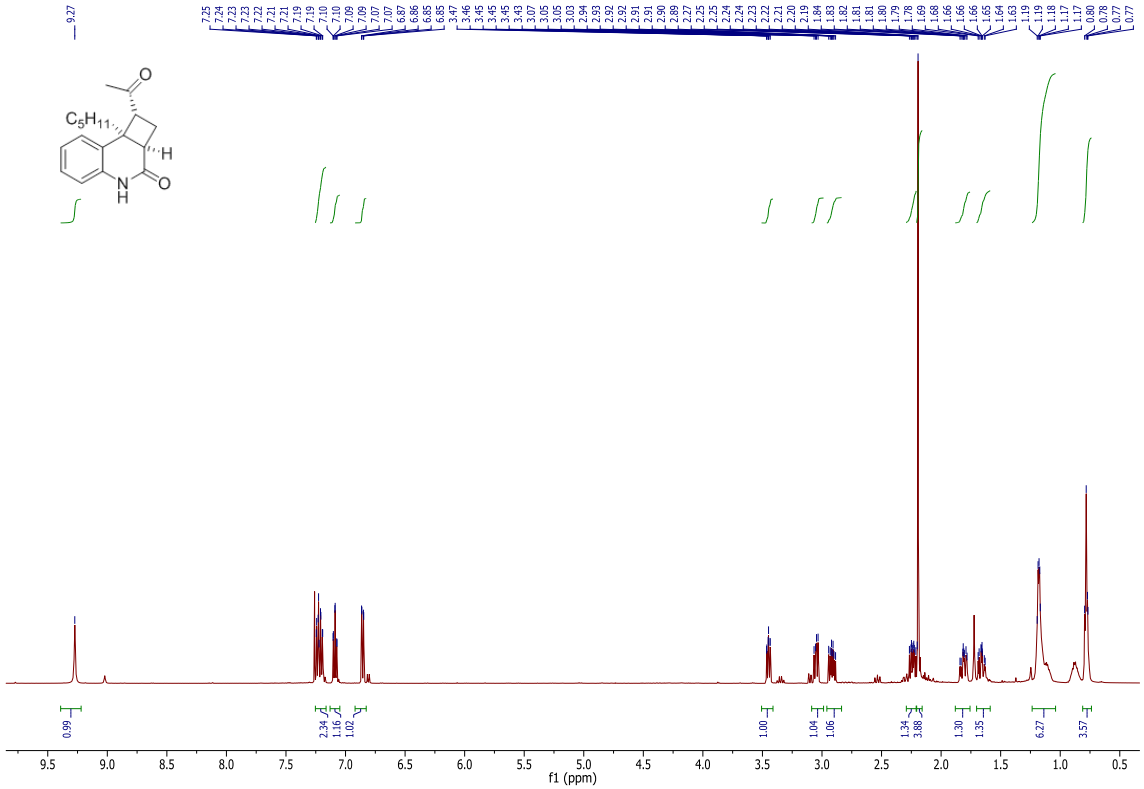
32.35
31.64
20.02
f1 (ppm)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C5H11
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H
O
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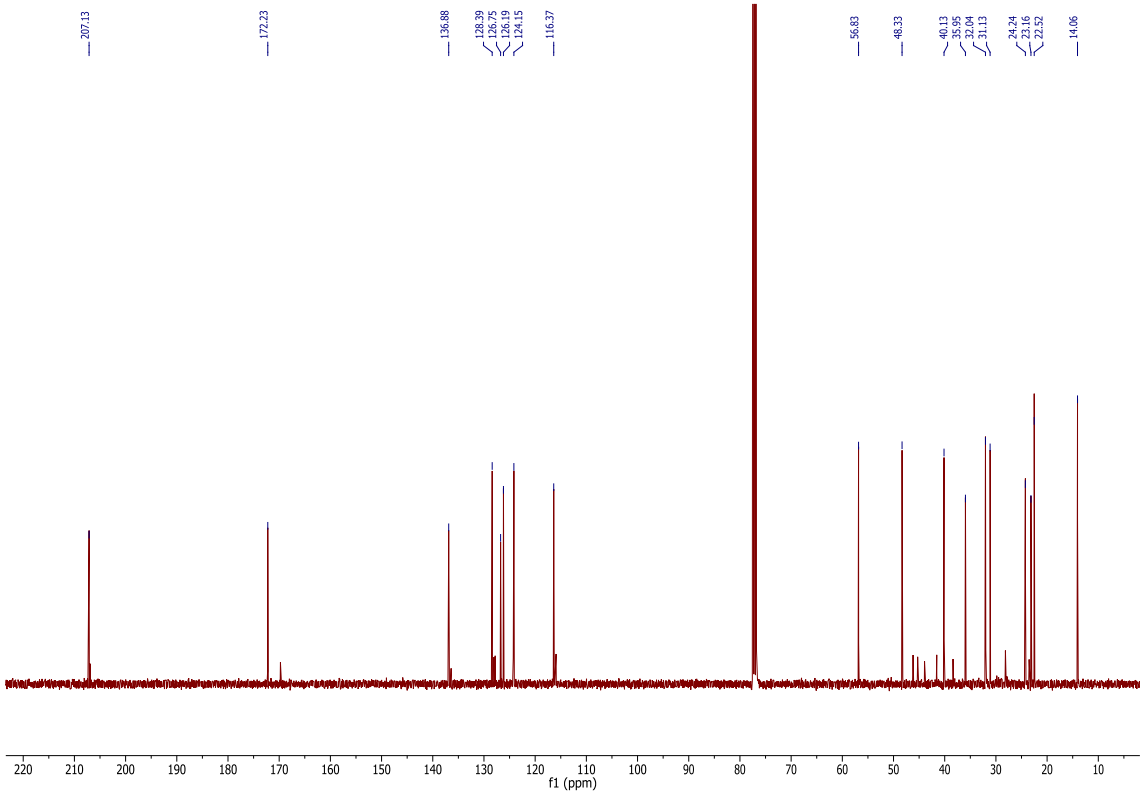
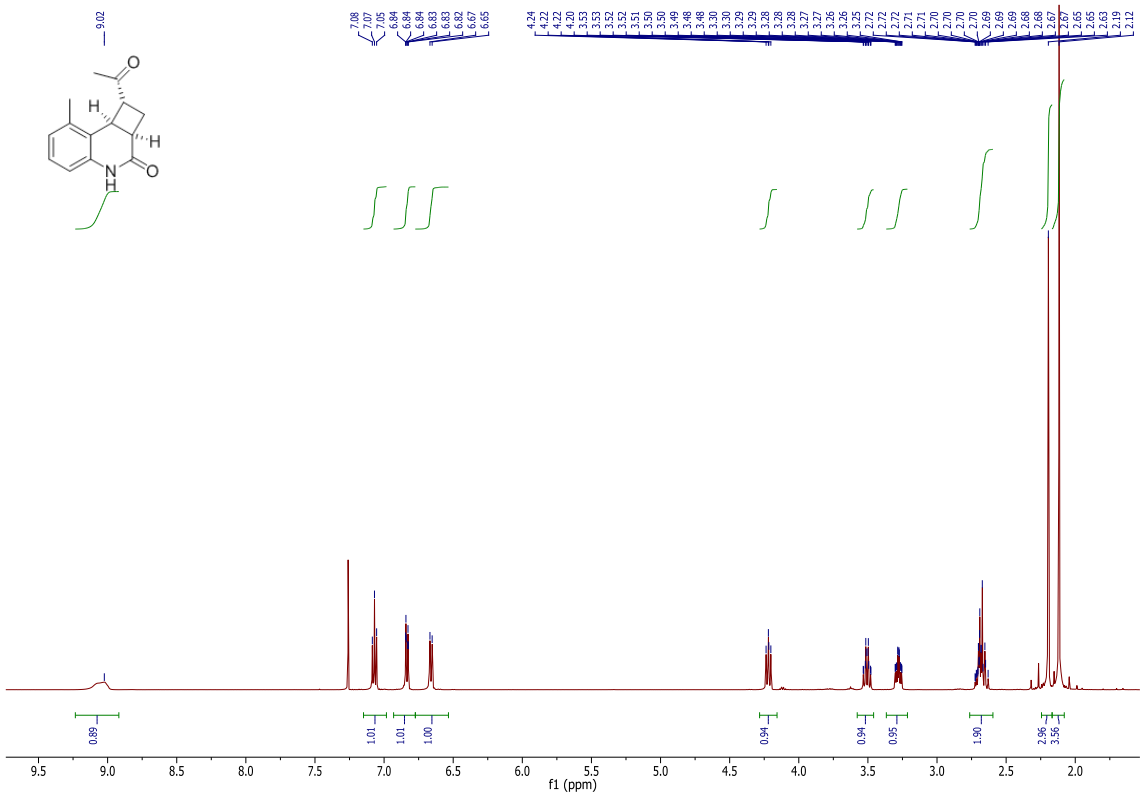

f1 (ppm)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4.22
4.20
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3.53
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3.52
3.51
3.50
3.50
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2.68
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2.63
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2.12
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H
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H
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1.01
1.00
0.94
0.94
0.95
1.90
2.96
3.56
9.5
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8.5
8.0
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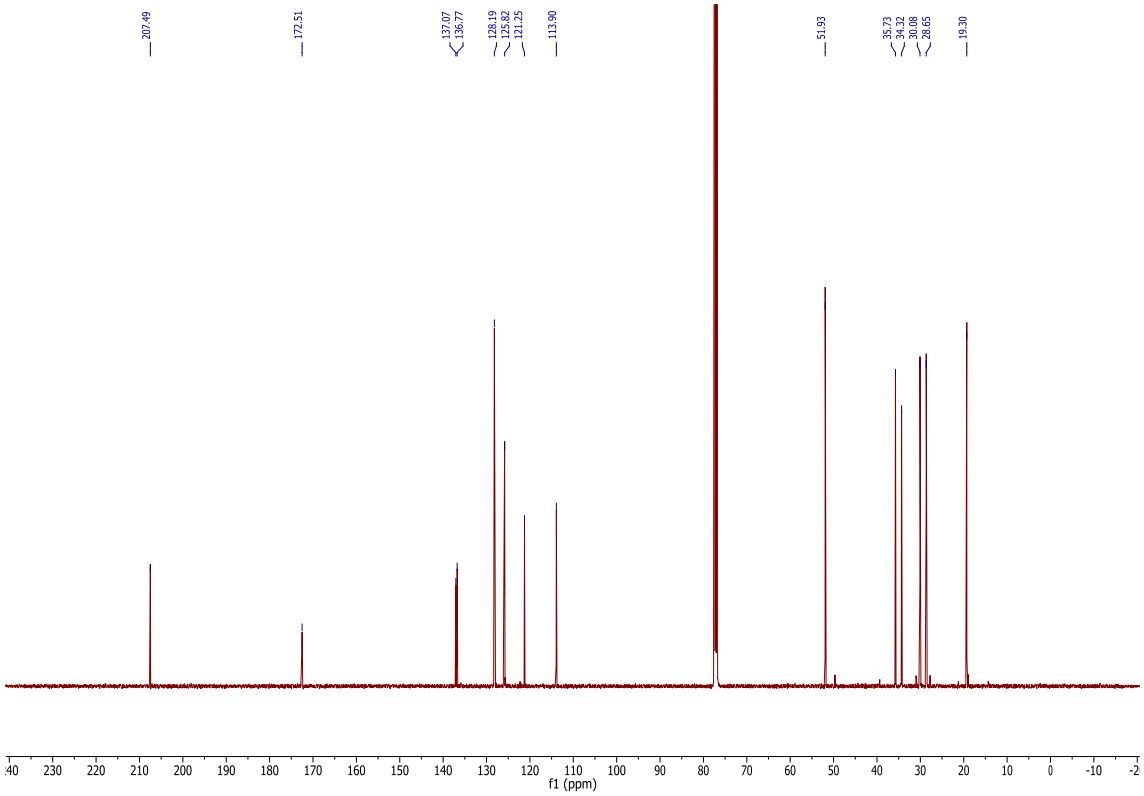
2.0
f1 (ppm)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30.08
28.65
19.30
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230
220
210
200
190
180
170
160
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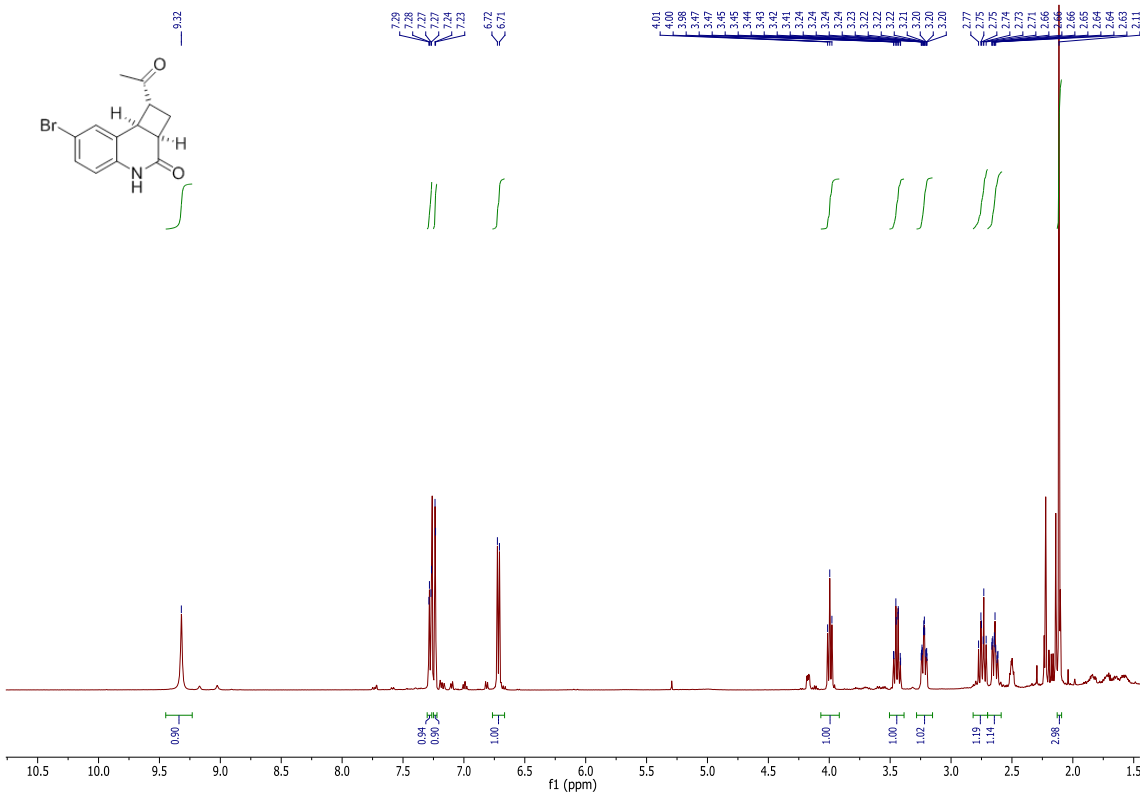
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


Br
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H
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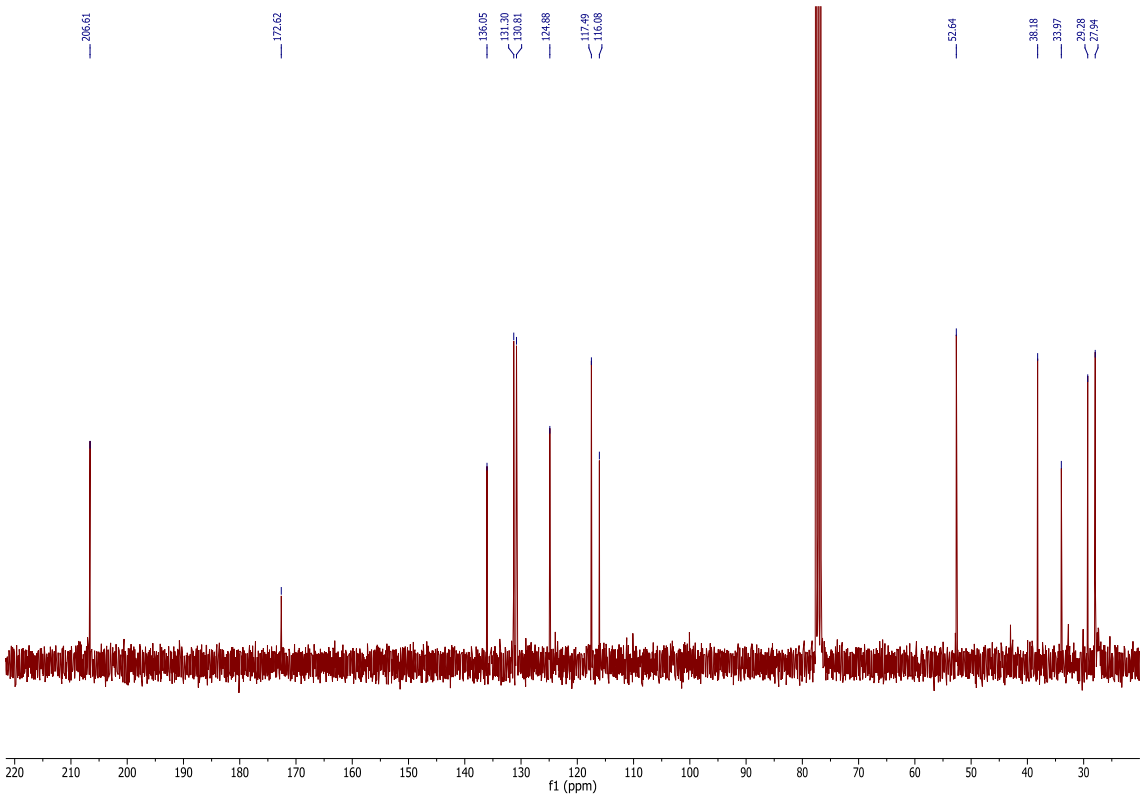
H
O
f1 (ppm)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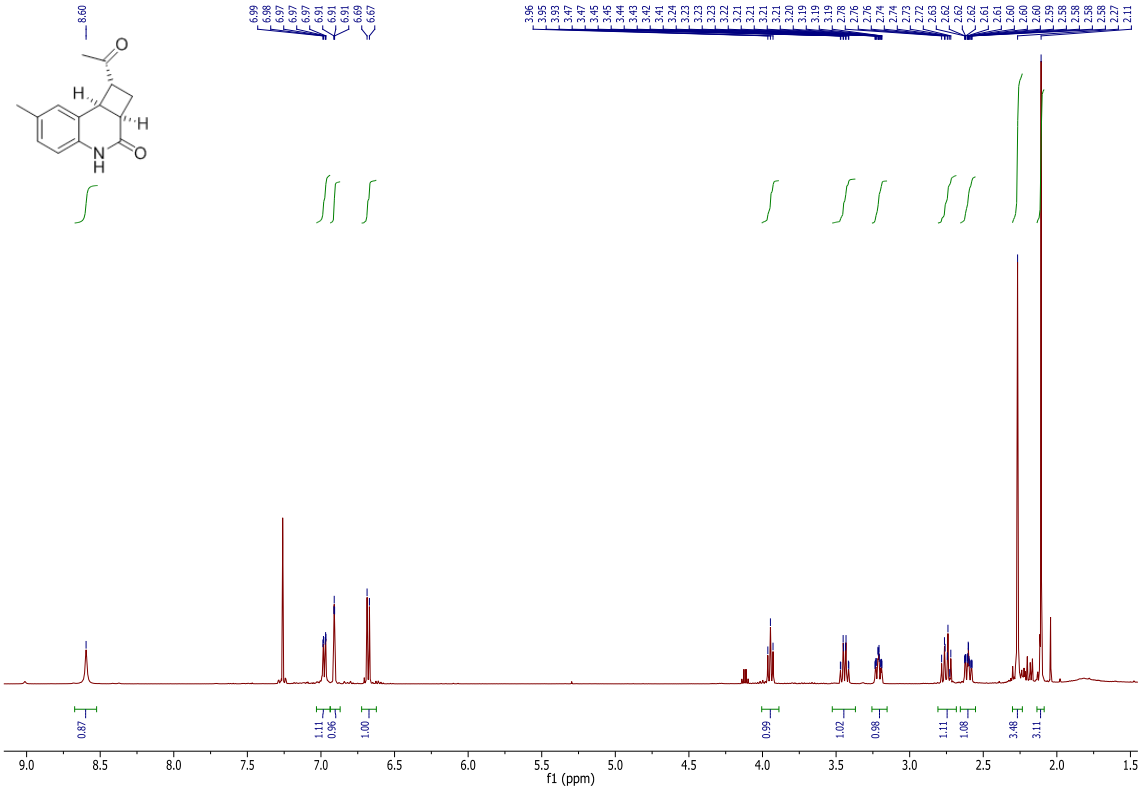
33.97
29.28
27.94
f1 (ppm)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3.43
3.42
3.41
3.24
3.23
3.23
3.22
3.21
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1.00
0.99
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1.11
1.08
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8.0
7.5
7.0
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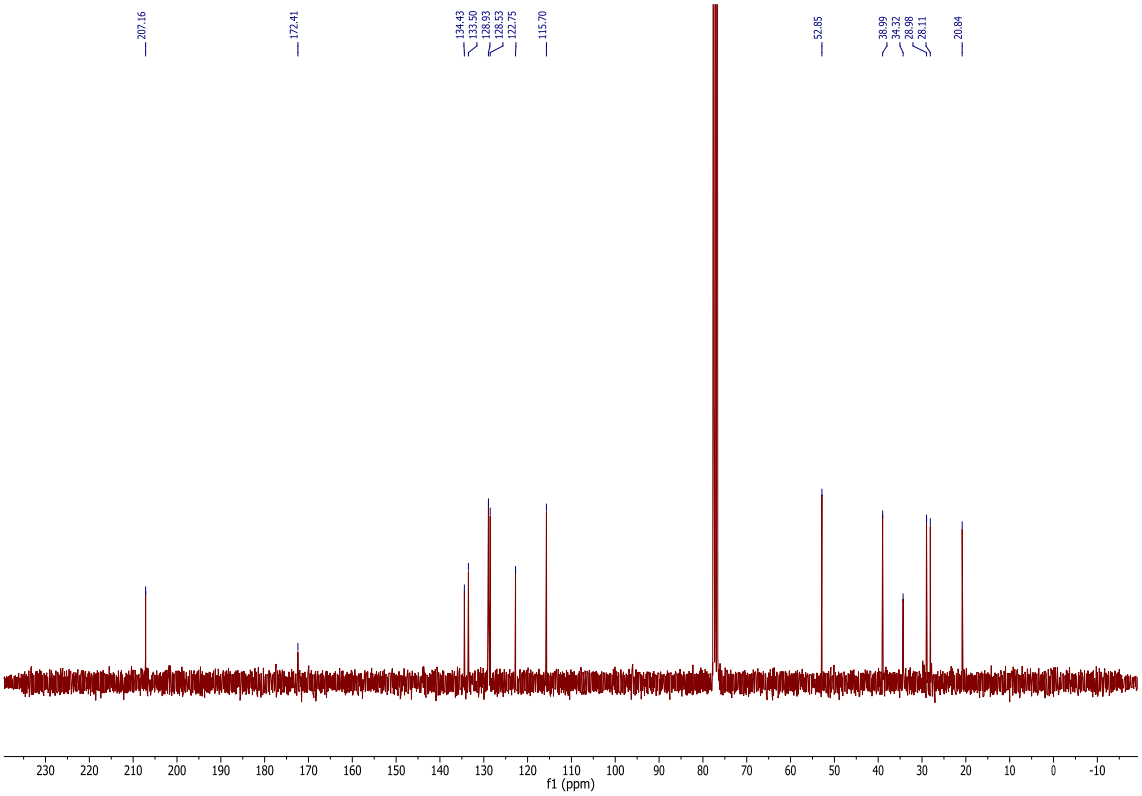
1.5
f1 (ppm)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28.11
20.84
230
220
210
200
190
180
170
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140
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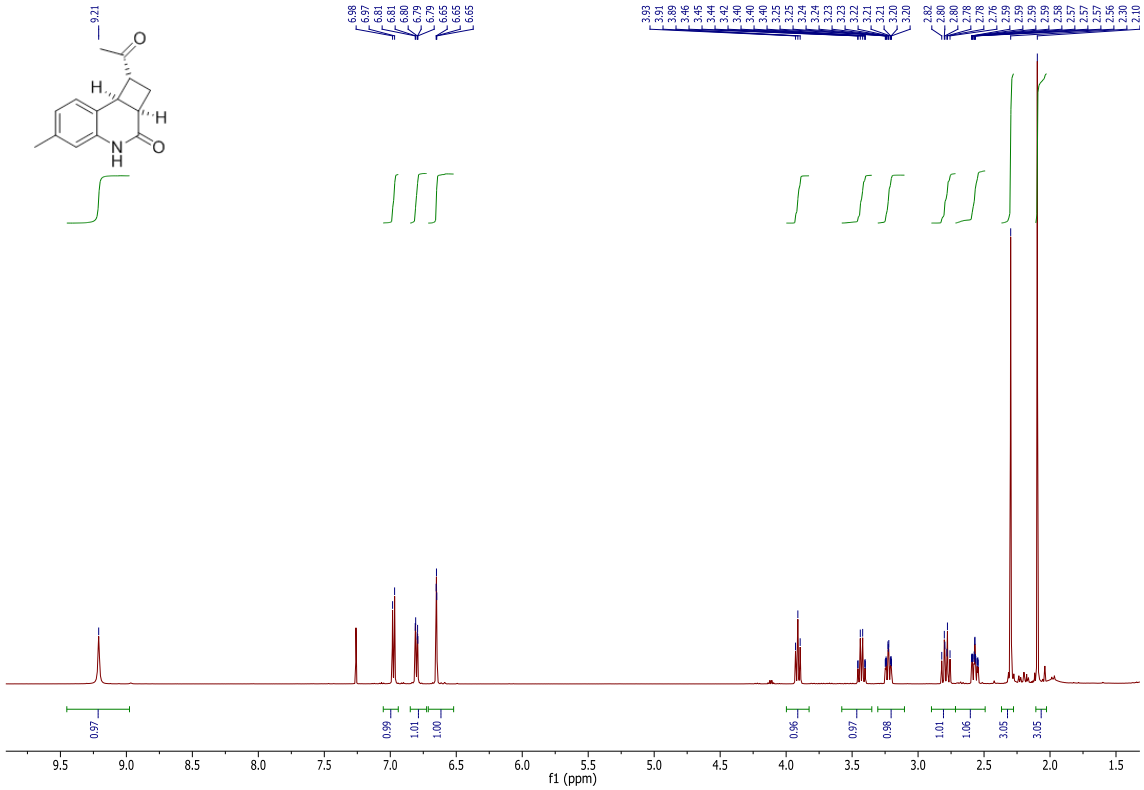
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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3.40
3.40
3.40
3.25
3.25
3.24
3.24
3.23
3.23
3.22
3.21
3.21
3.20
3.20
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2.80
2.80
2.78
2.78
2.76
2.59
2.59
2.59
2.59
2.58
2.57
2.57
2.57
2.56
2.30
2.10
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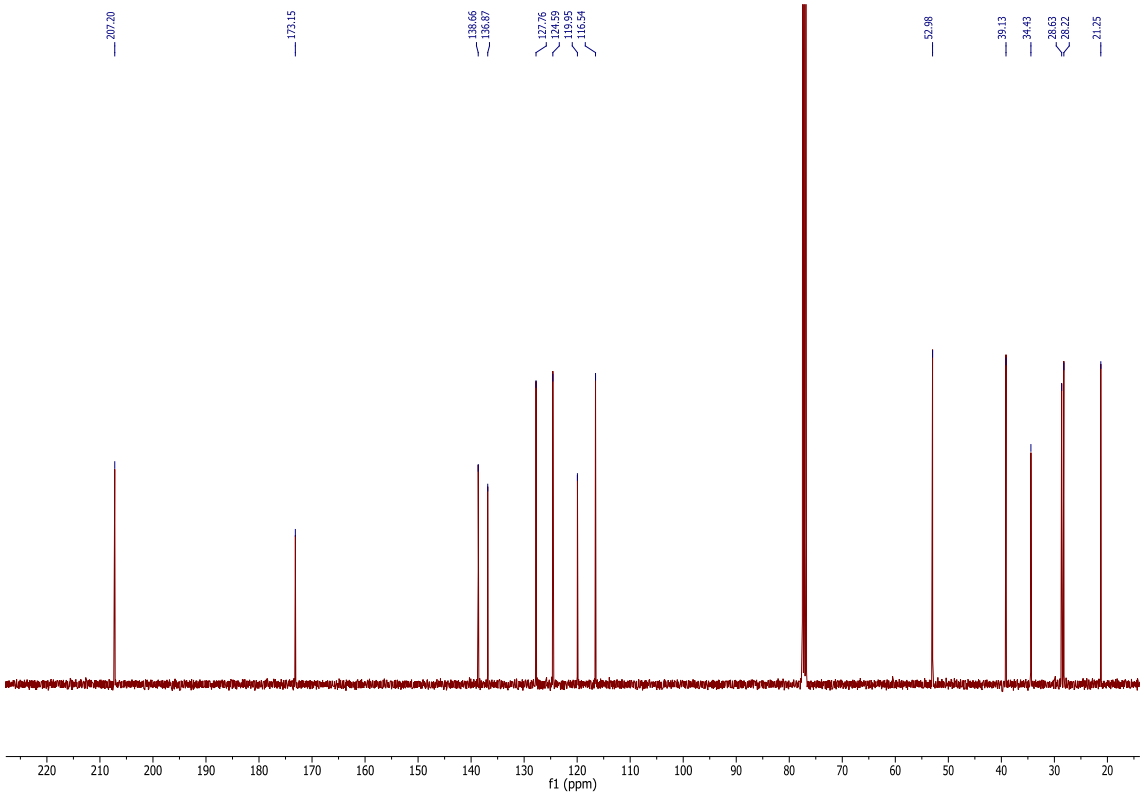
1.00
0.96
0.97
0.98
1.01
1.06
3.05
3.05
f1 (ppm)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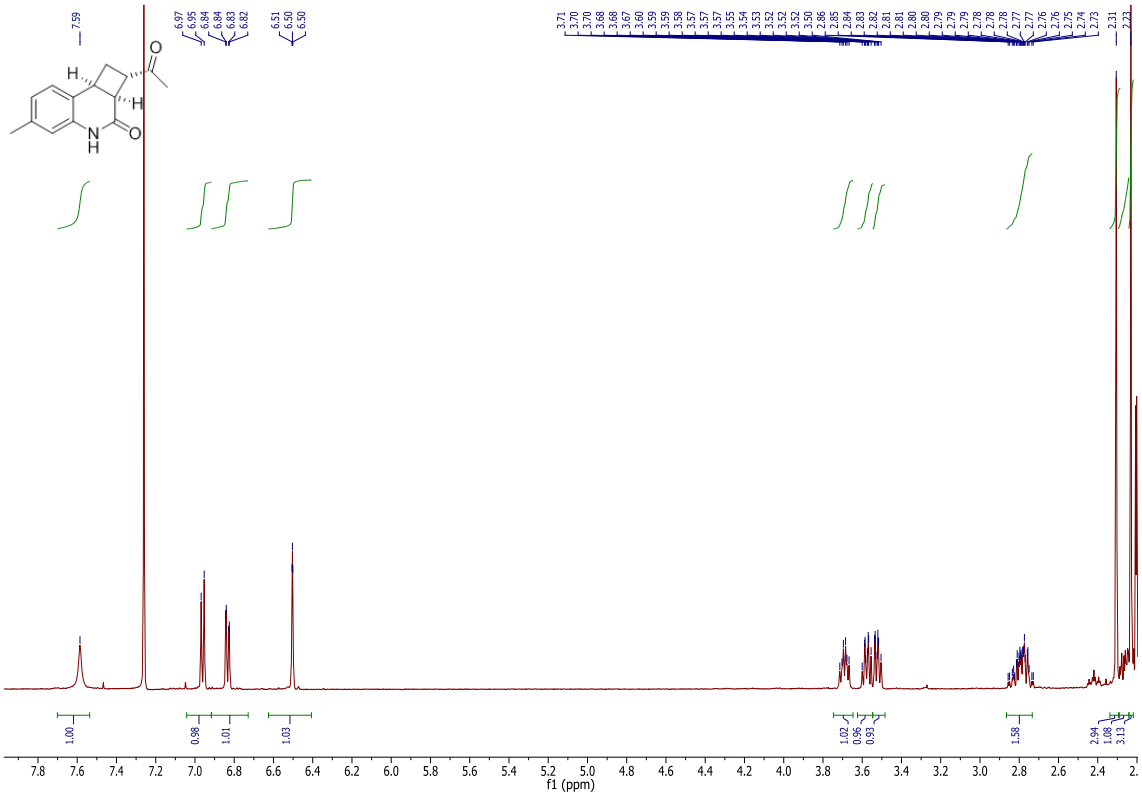
21.25
f1 (ppm)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2.76
2.75
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2.31
2.23
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N
H
O
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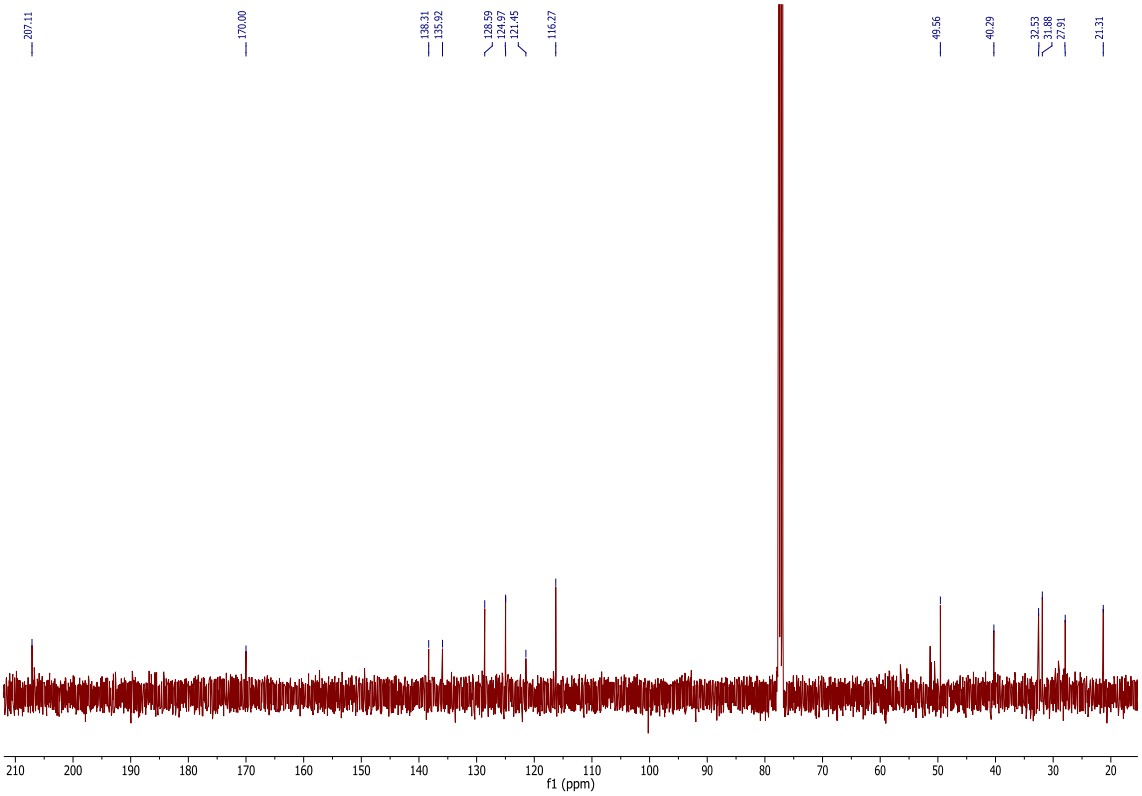
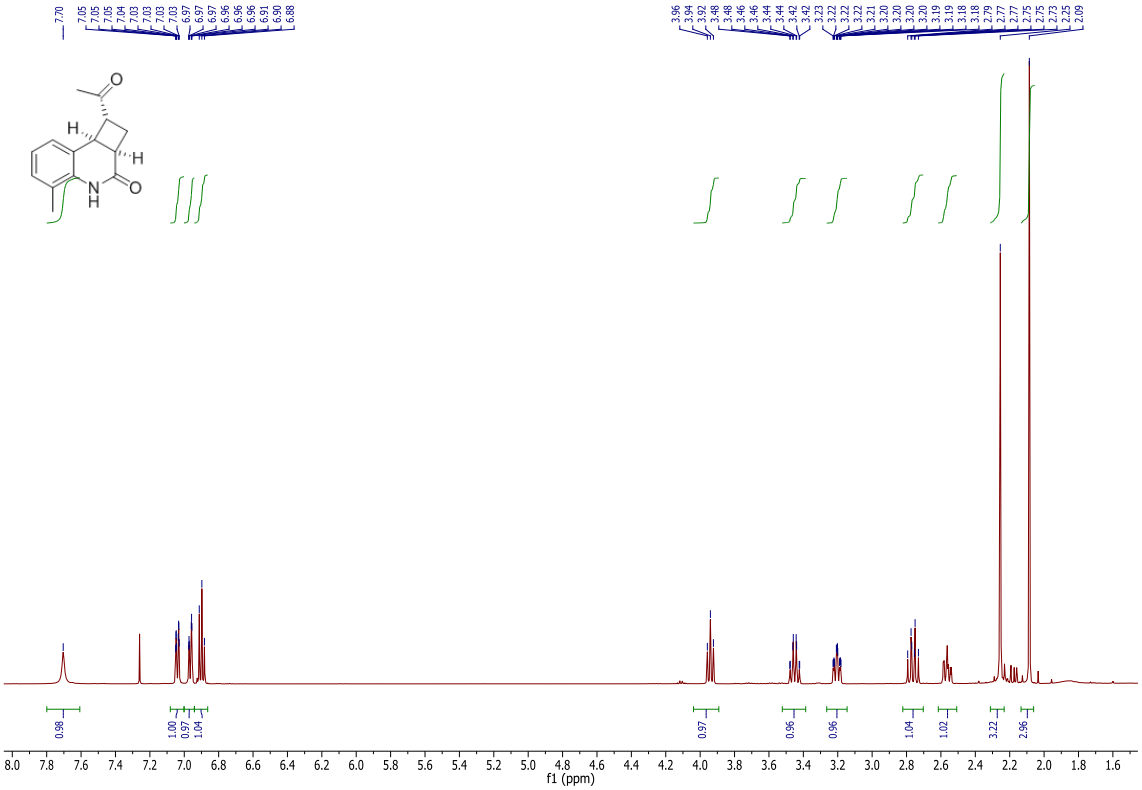
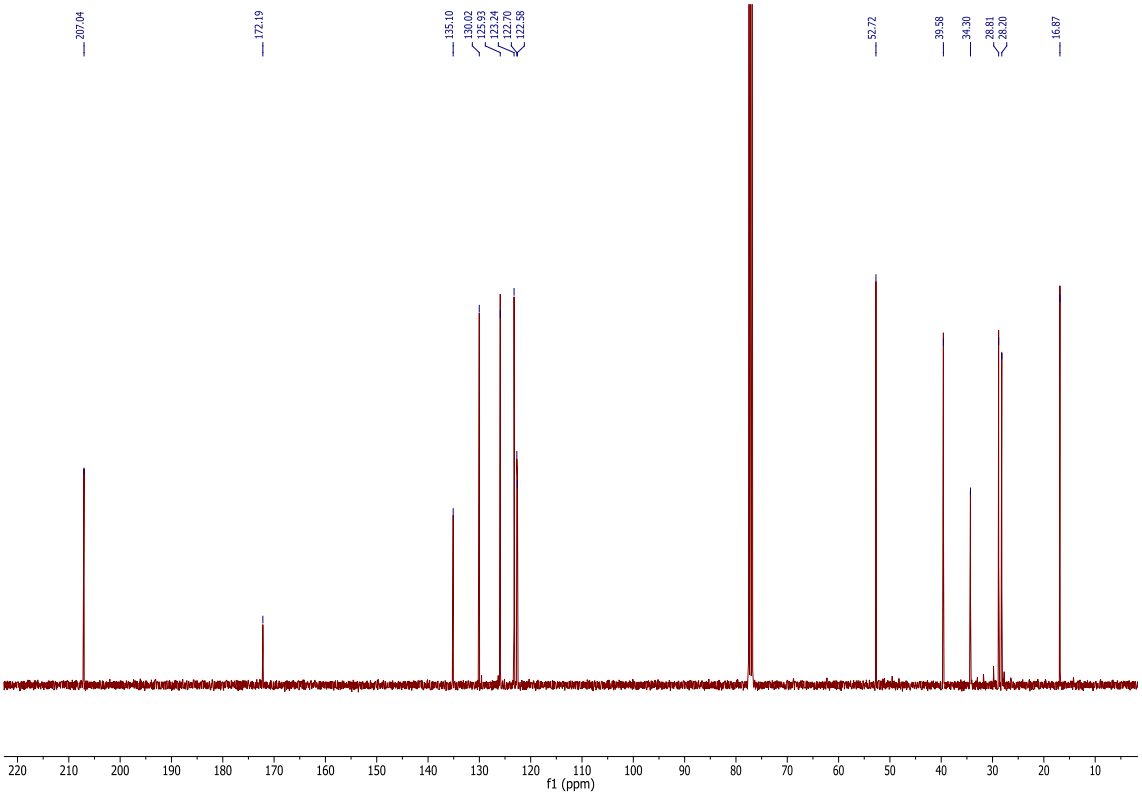
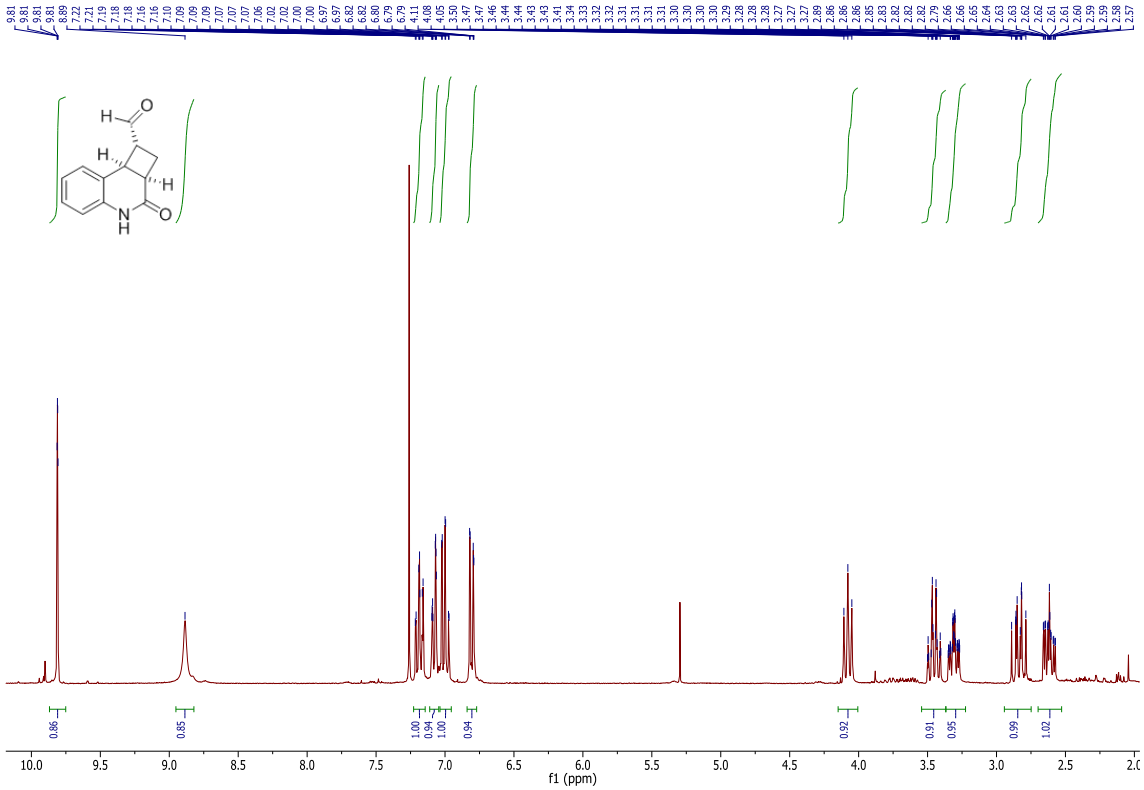
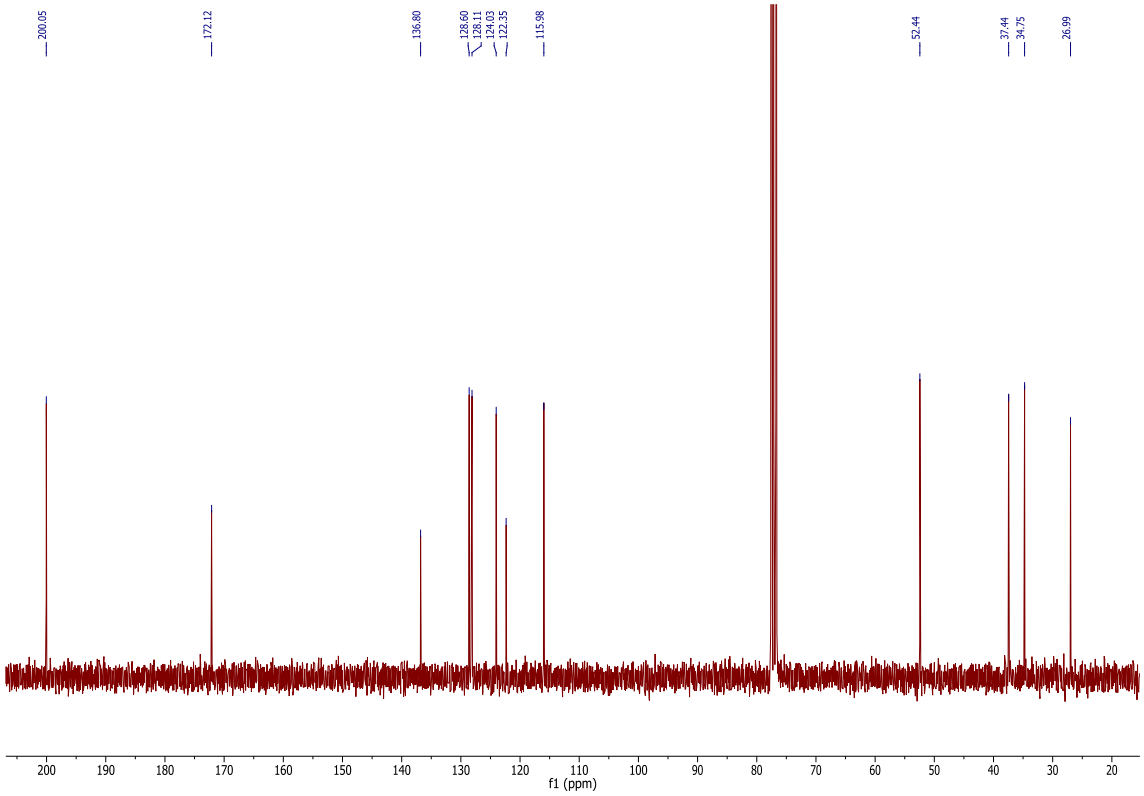
0.98
1.01
1.03
1.02
0.96
0.93
1.58
2.94
1.08
3.13
f1 (ppm)

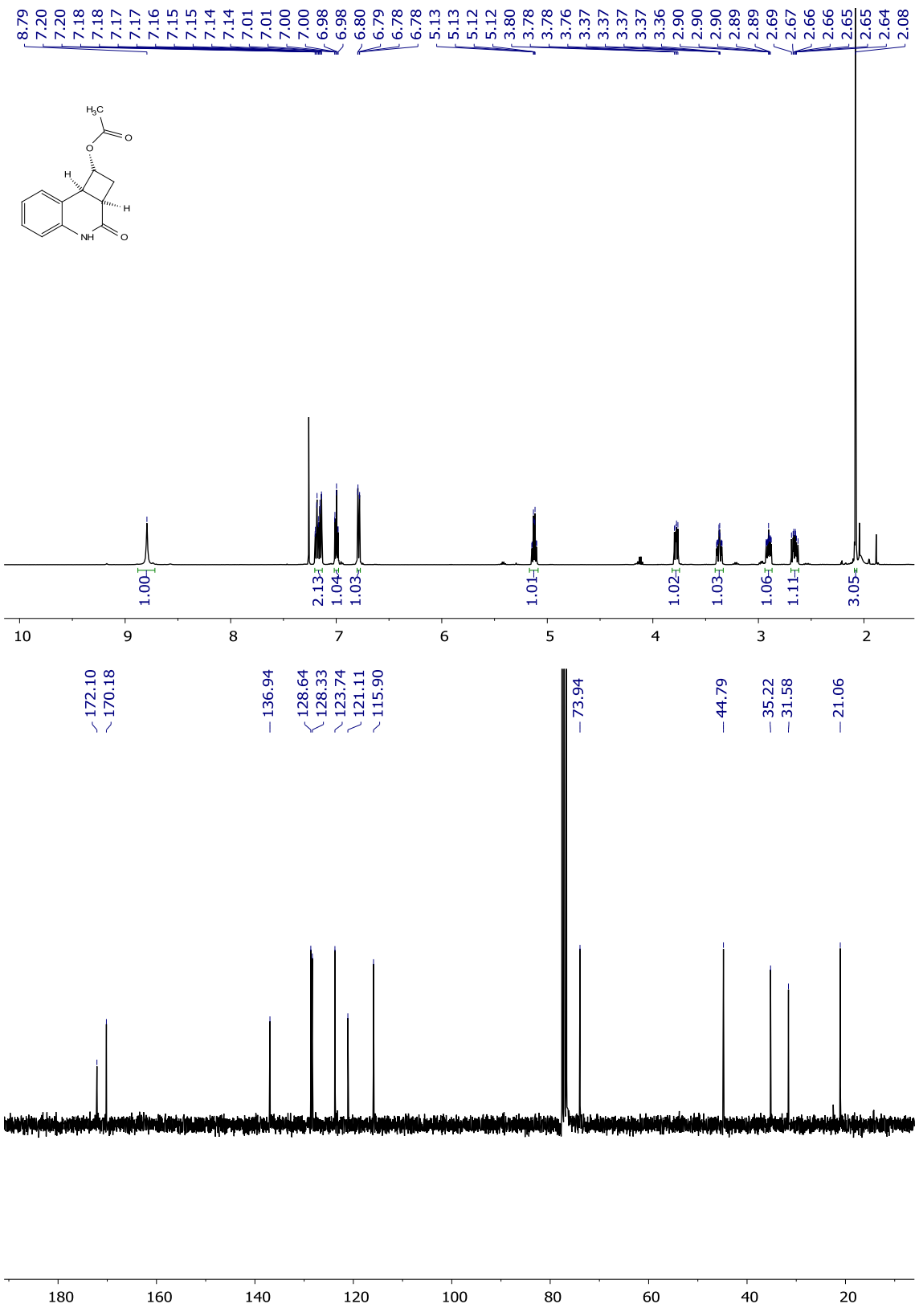

207.11
170.00
138.31
135.92
128.59
124.97
121.45
116.27
49.56
40.29
32.53
31.88
27.91
21.31
f1 (ppm)

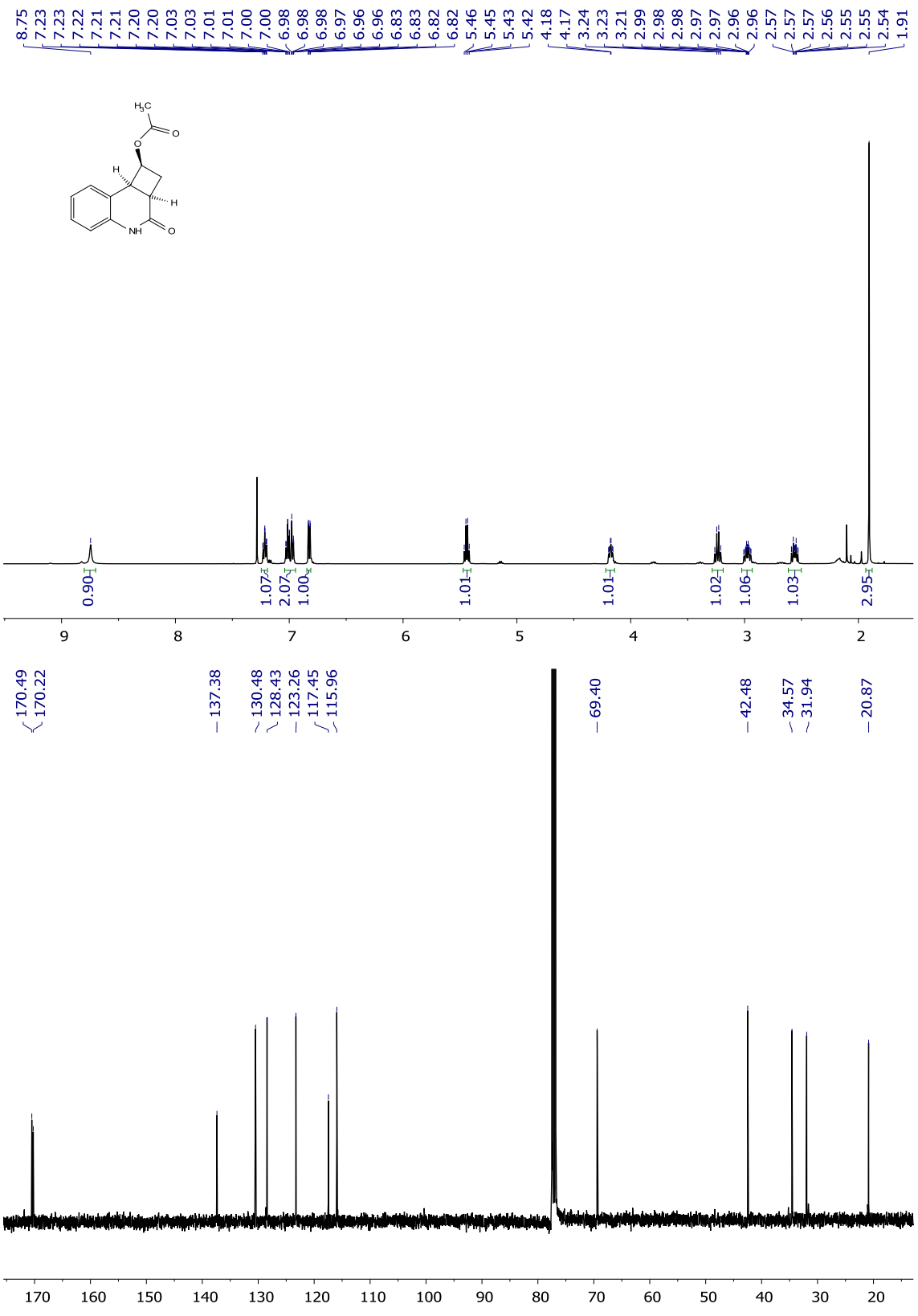

7.70
7.05
7.05
7.05
7.04
7.03
7.03
7.03
7.03
6.97
6.97
6.97
6.96
6.96
6.96
6.91
6.90
6.88
3.96
3.94
3.92
3.48
3.46
3.46
3.44
3.44
3.42
3.23
3.22
3.22
3.22
3.21
3.20
3.20
3.20
3.20
3.19
3.19
3.18
3.18
2.79
2.77
2.77
2.75
2.75
2.73
2.25
2.09
O
H
H
N
H
O
0.98
1.00
0.97
1.04
0.97
0.96
0.96
1.04
1.02
3.22
2.96
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)

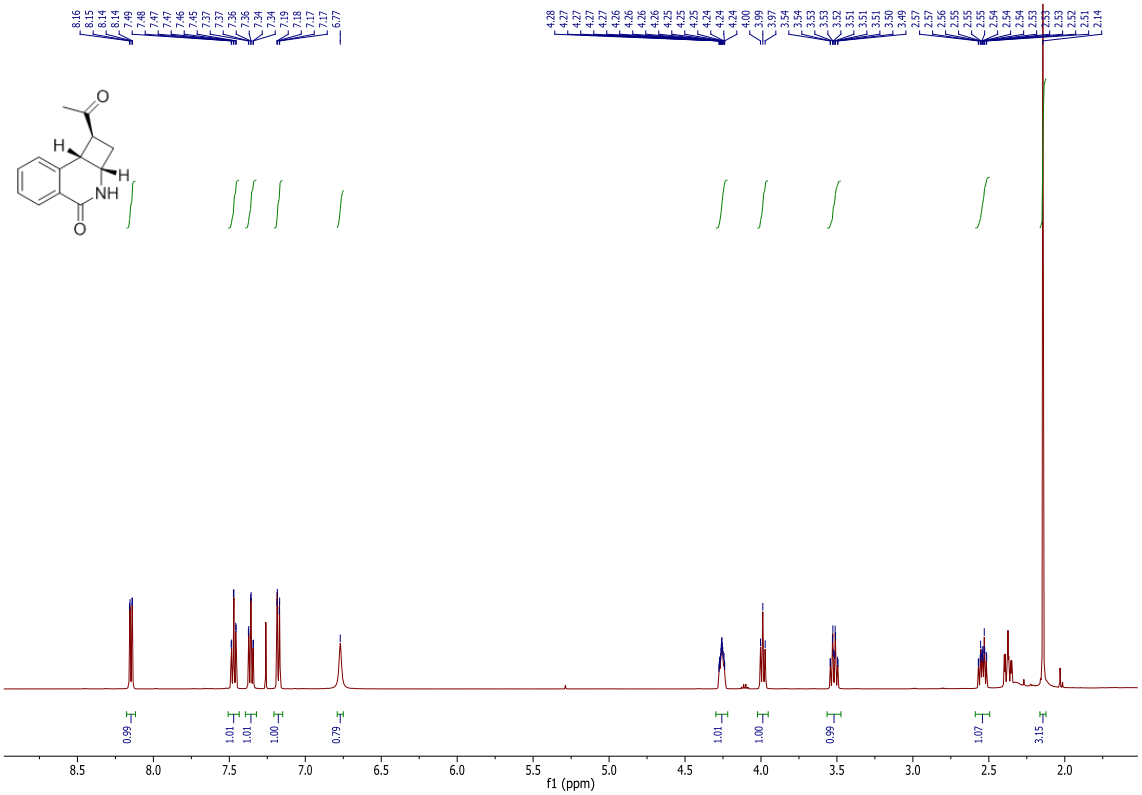

207.04
172.19
135.10
130.02
125.93
123.24
122.70
122.58
52.72
39.58
34.30
28.81
28.20
16.87
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

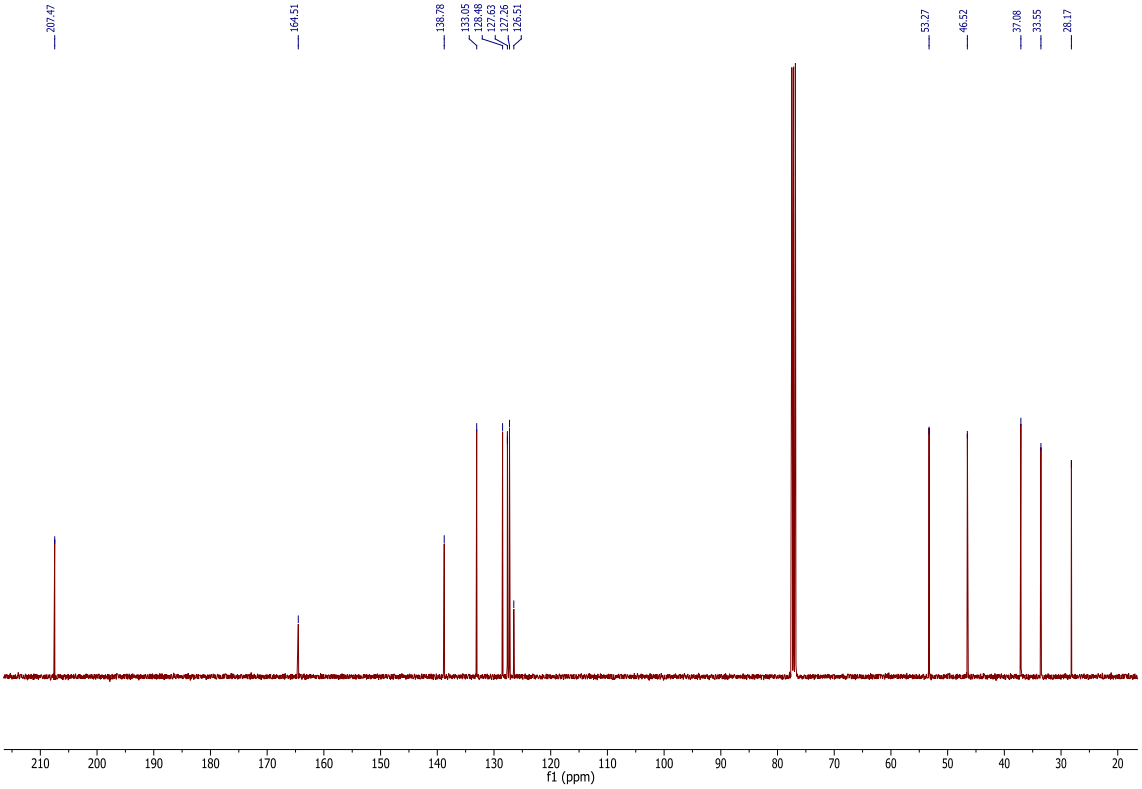

H
O
H
H
N
H
O
0.86
0.85
1.00
0.94
1.00
0.94
0.92
0.91
0.95
0.99
1.02
f1 (ppm)

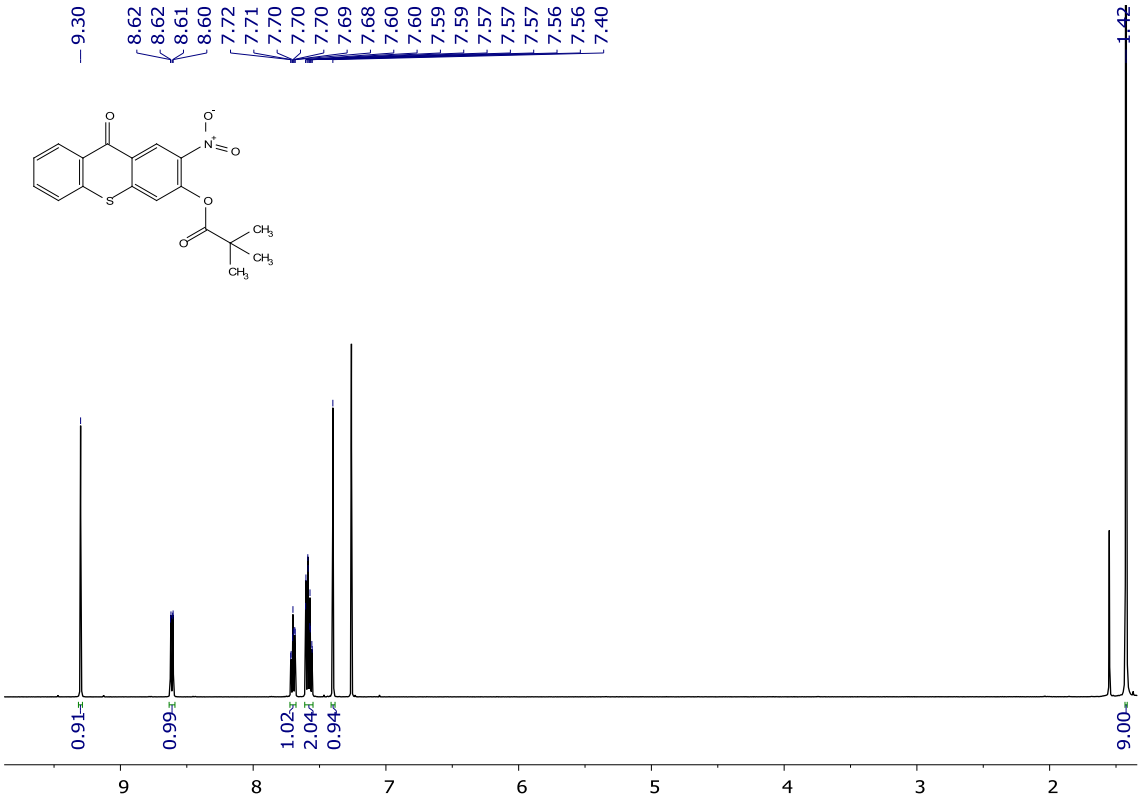

200.05
172.12
136.80
128.60
128.11
124.03
122.35
115.98
52.44
37.44
34.75
26.99
f1 (ppm)

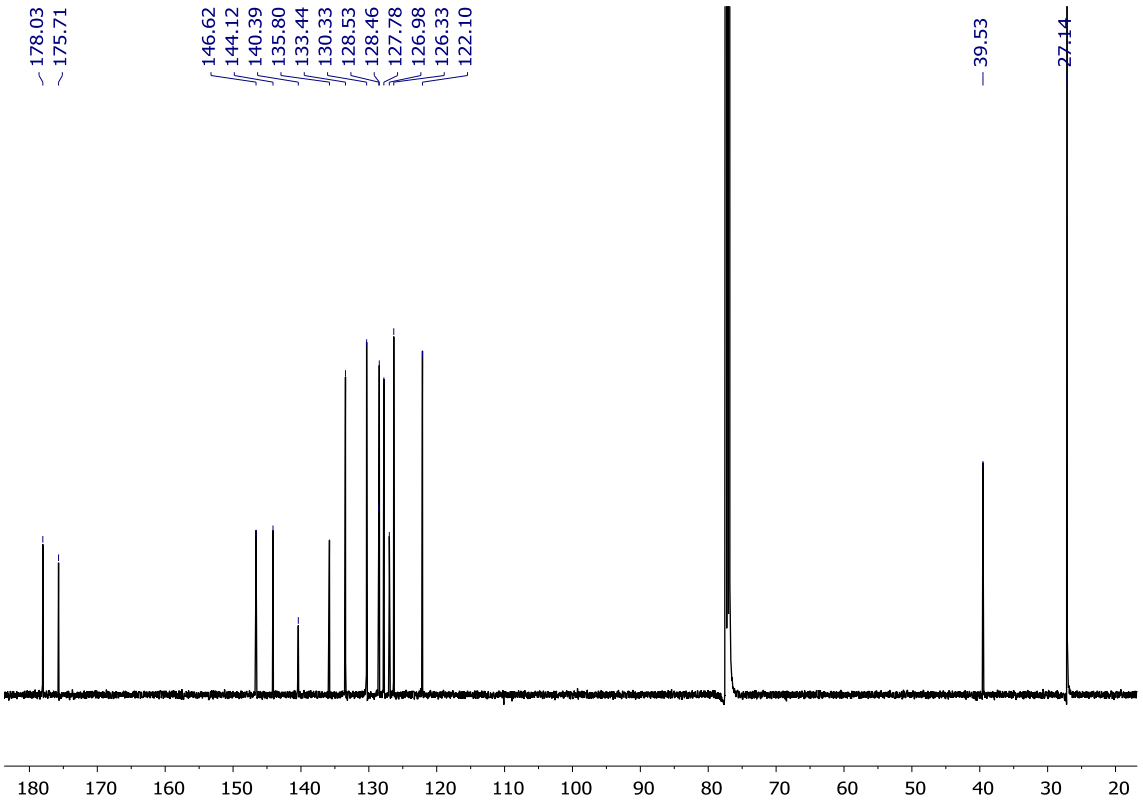

8.79
7.20
7.20
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.01
7.01
7.00
7.00
6.98
6.98
6.80
6.79
6.78
6.78
5.13
5.13
5.12
5.12
3.80
3.78
3.78
3.76
3.37
3.37
3.37
3.37
3.36
2.90
2.90
2.90
2.89
2.89
2.69
2.67
2.66
2.66
2.65
2.65
2.64
2.08
H3C
O
O
H
H
NH
O
1.00
2.13
1.04
1.03
1.01
1.02
1.03
1.06
1.11
3.05
10
9
8
7
6
5
4
3
2
172.10
170.18
136.94
128.64
128.33
123.74
121.11
115.90
73.94
44.79
35.22
31.58
21.06
180
160
140
120
100
80
60
40
20

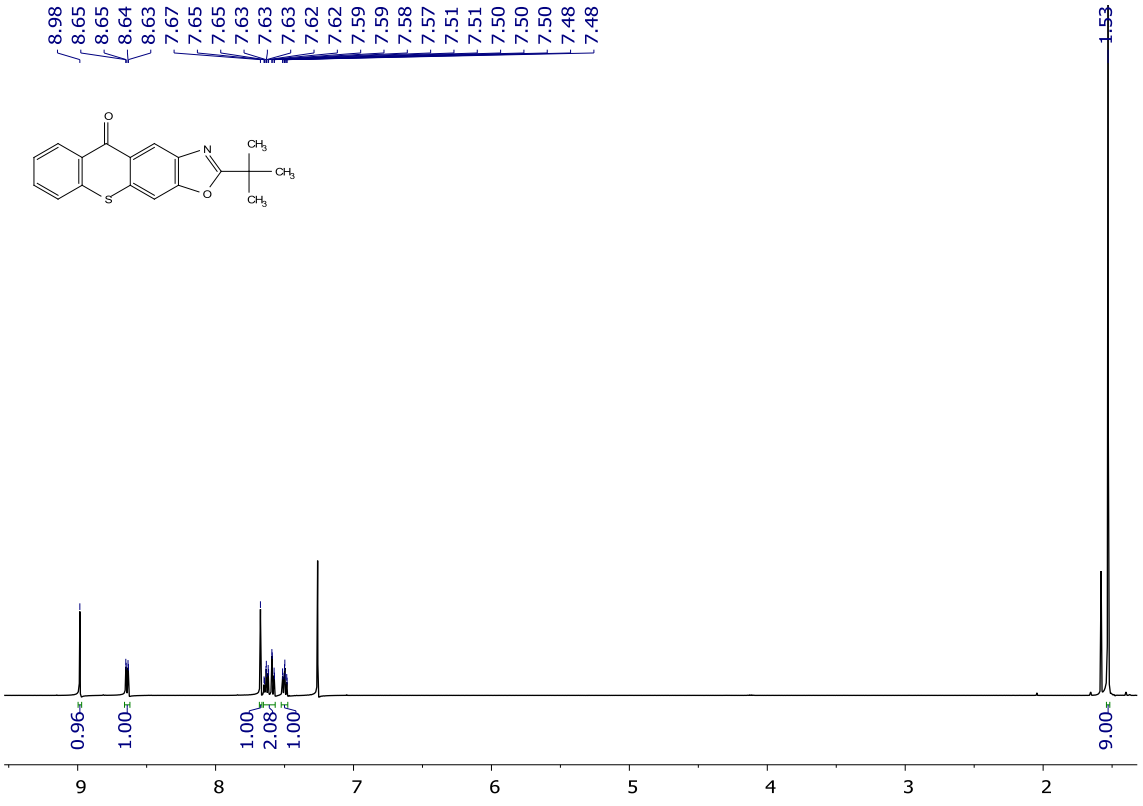

8.75 7.23 7.23 7.22 7.21 7.21 7.20 7.20 7.03 7.03 7.01 7.01 7.00 7.00 6.98 6.98 6.98 6.97 6.96 6.96 6.83 6.83 6.82 6.82 5.46 5.45 5.43 5.42 4.18 4.17 3.24 3.23 3.21 2.99 2.98 2.98 2.97 2.97 2.96 2.96 2.57 2.57 2.57 2.56 2.55 2.55 2.54 1.91
H3C
O
O
H
H
NH
O
0.90 1.07 2.07 1.00 1.01 1.01 1.02 1.06 1.03 2.95
9 8 7 6 5 4 3 2
170.49 170.22 137.38 130.48 128.43 123.26 117.45 115.96 69.40 42.48 34.57 31.94 20.87
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20


O
H
H
NH
O
f1 (ppm)


207.47
164.51
138.78
133.05
128.48
127.63
127.26
126.51
53.27
46.52
37.08
33.55
28.17
f1 (ppm)


9.30
8.62
8.62
8.61
8.60
7.72
7.71
7.70
7.70
7.70
7.69
7.68
7.60
7.60
7.59
7.59
7.57
7.57
7.57
7.56
7.56
7.40
1.42
0.91
0.99
1.02
2.04
0.94
9.00
9
8
7
6
5
4
3
2


178.03
175.71
146.62
144.12
140.39
135.80
133.44
130.33
128.53
128.46
127.78
126.98
126.33
122.10
39.53
27.14
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


8.98
8.65
8.65
8.64
8.63
7.67
7.65
7.65
7.63
7.63
7.63
7.62
7.62
7.59
7.59
7.58
7.57
7.51
7.51
7.50
7.50
7.50
7.48
7.48
1.53
O
N
O
S
CH3
CH3
CH3
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1.00
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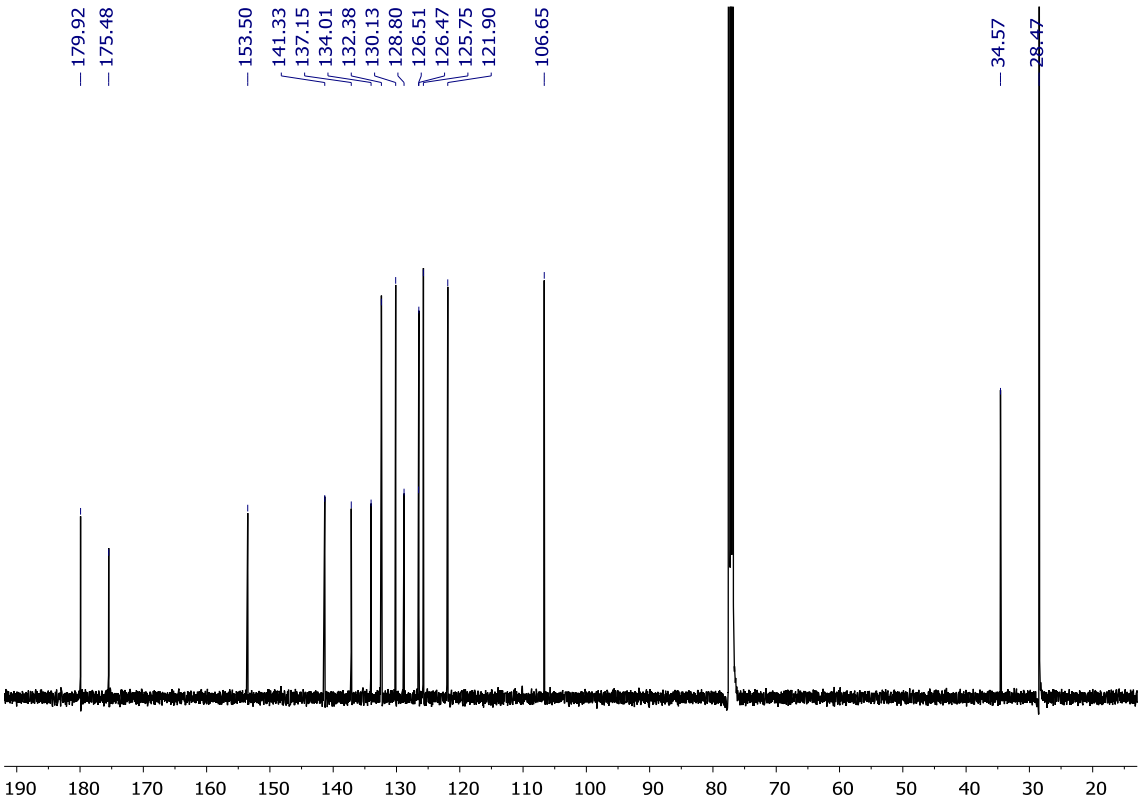
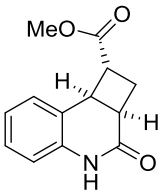
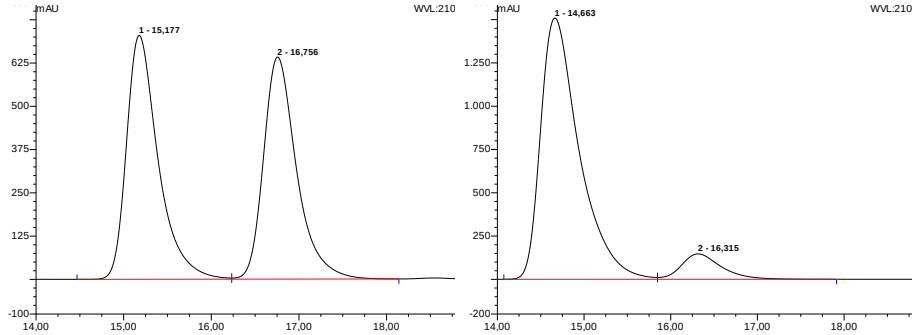
1.00
9.00
9
8
7
6
5
4
3
2


179.92
175.48
153.50
141.33
137.15
134.01
132.38
130.13
128.80
126.51
126.47
125.75
121.90
106.65
34.57
28.47
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

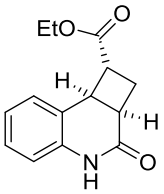
## 10. Representative HPLC/GC Traces



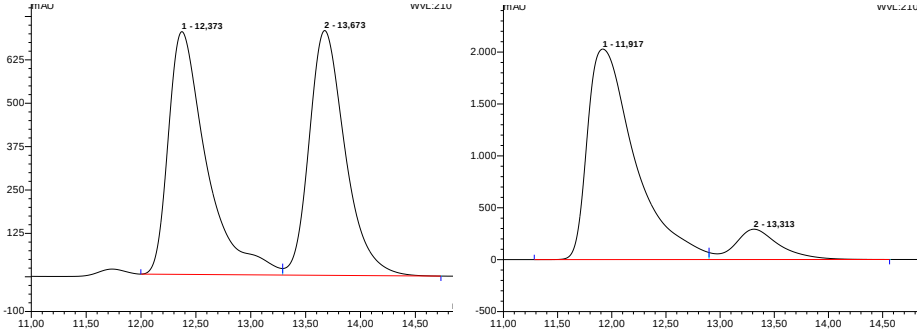

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4a**, $t_R$ = 15.2 min; *ent*-**4a**, 16.8 min).




| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 15.2 min | 295.295 | 51.33 | 777.707 | 90.89 |
| $t_R$ = 16.8 min | 279.945 | 48.67 | 77.978 | 9.11 |



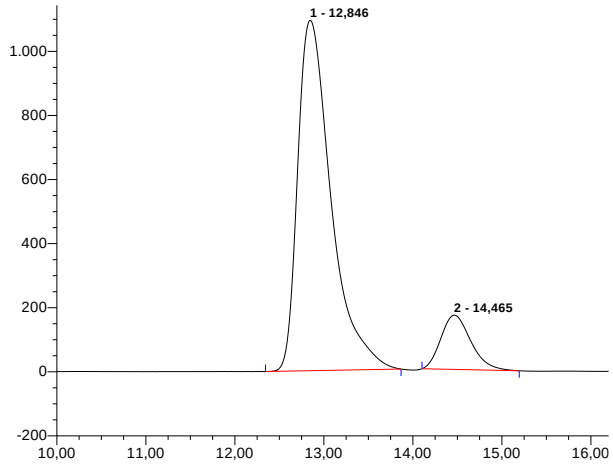

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4b**, $t_R$ = 12.4 min; *ent*-**4b**, 13.7 min).



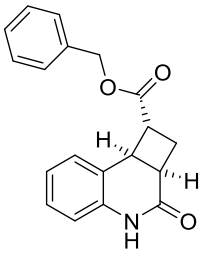

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 12.4 min | 282.609 | 51.29 | 1030.052 | 88.04 |
| $t_R$ = 13.7 min | 268.345 | 48.71 | 139.868 | 11.96 |

**HPLC trace of the 0.15 mmol scale reaction of 4b**

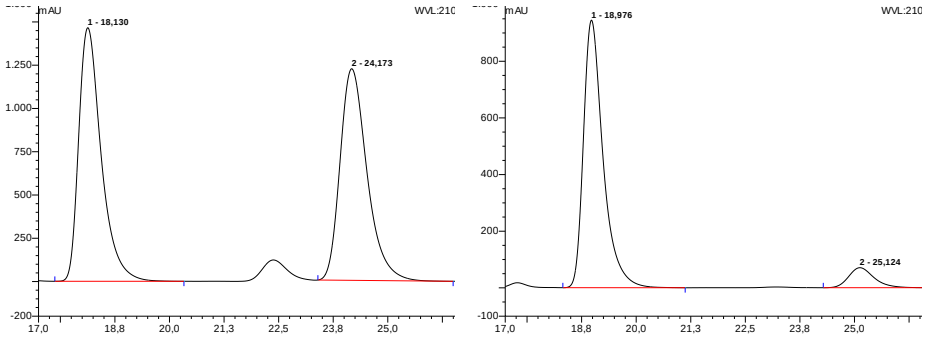
**HPLC** (AD-H, 250×4.6, *n*-heptane/*iso*-propanol = 90:10) = **4b**, $t_R$ = 12.9 min; *ent*-**4b**, 14.5 min).




| | *Area* | *Rel. Area (%)* |
|---|---|---|
| $t_R$ = 12.9 min | 1093.542 | 87.79 |
| $t_R$ = 14.5 min | 159.299 | 12.21 |



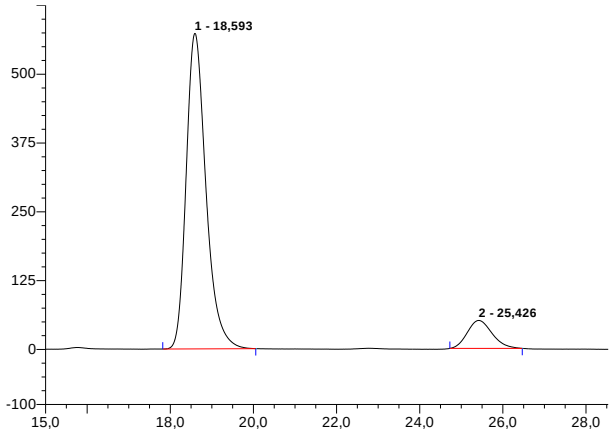

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4c**, $t_R$ = 18.1 min; *ent*-**4c**, 24.2 min).



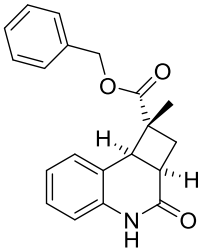

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 18.1 min | 874.215 | 50.01 | 492.605 | 91.21 |
| $t_R$ = 24.2 min | 873.870 | 49.99 | 47.473 | 8.79 |

**HPLC trace of the 0.15 mmol scale reaction of 4c**

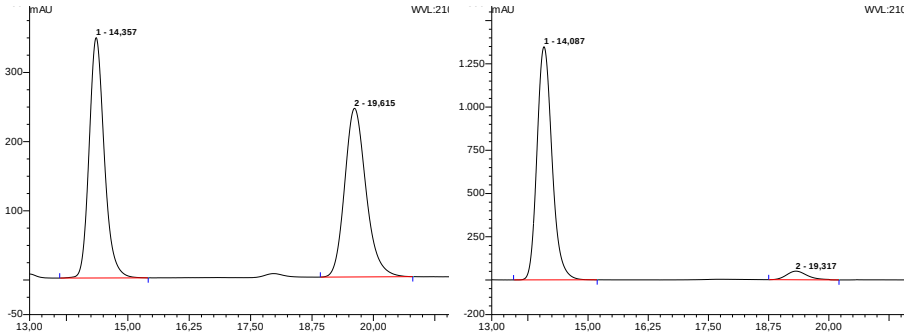
**HPLC** (AD-H, 250×4.6, *n*-heptane/*iso*-propanol = 90:10) = **4c**, $t_R$ = 18.6 min; *ent*-**4c**, 25.4 min).




| | *Area* | *Rel. Area (%)* |
|---|---|---|
| $t_R$ = 18.6 min | 573.215 | 89.99 |
| $t_R$ = 25. min | 50.792 | 10.01 |



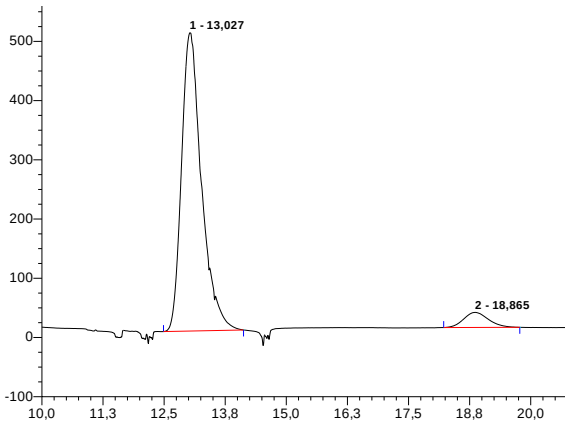

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4d**, $t_R$ = 14.4 min; *ent*-**4d**, 19.6 min).



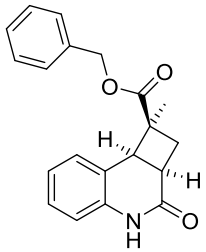

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 14.4 min | 124.001 | 50.26 | 242.833 | 92.41 |
| $t_R$ = 19.6 min | 122.735 | 49.74 | 19.931 | 7.59 |

**HPLC trace of the 0.15 mmol scale reaction of 4d**

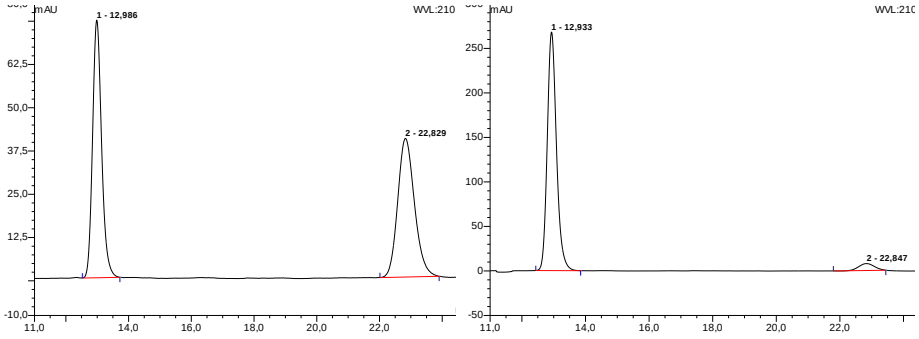
**HPLC** (AD-H, 250×4.6, *n*-heptane/*iso*-propanol = 90:10) = **4d**, $t_R$ = 13.0 min; *ent*-**4d**, 18.9 min).




| | *Area* | *Rel. Area (%)* |
|---|---|---|
| $t_R$ = 13.0 min | 238.152 | 94.11 |
| $t_R$ = 18.9 min | 14.908 | 5.89 |



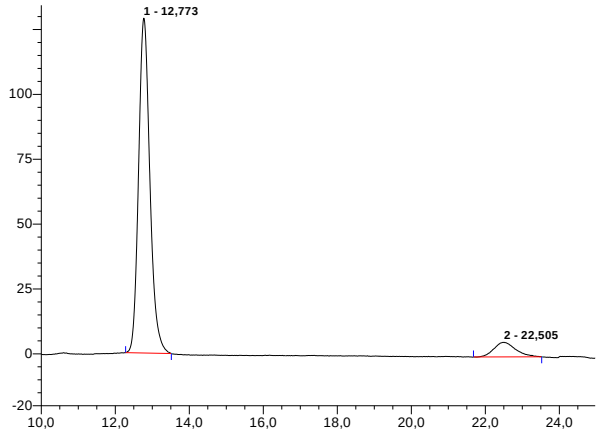

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 80:20) = **S13**, $t_R$ = 13.0 min; *ent*-**S13**, 22.8 min).



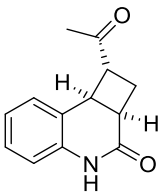

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 13.0 min | 24.877 | 50.14 | 90.037 | 95.36 |
| $t_R$ = 22.8 min | 24.743 | 49.86 | 4.377 | 4.64 |

**HPLC trace of the 0.15 mmol scale reaction of S13**

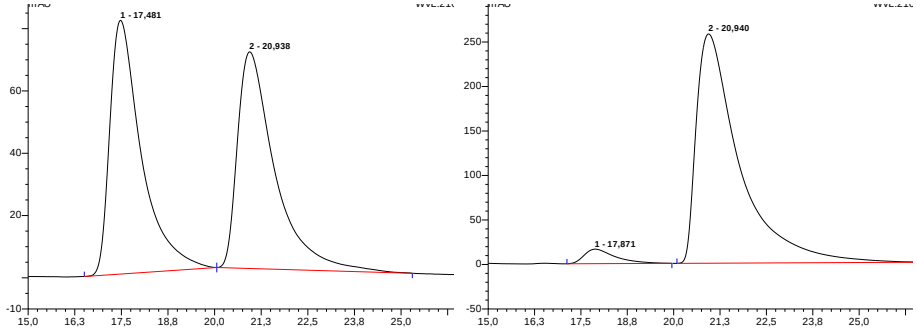
**HPLC** (AD-H, 250×4.6, *n*-heptane/*iso*-propanol = 80:20) = **S13**, $t_R$ = 12.8 min; *ent*-**S13**, 22.5 min).



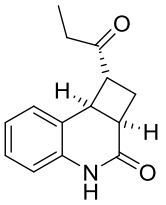

| | *Area* | *Rel. Area (%)* |
|---|---|---|
| $t_R$ = 12.8 min | 45.652 | 92.28 |
| $t_R$ = 22.5 min | 3.818 | 7.72 |



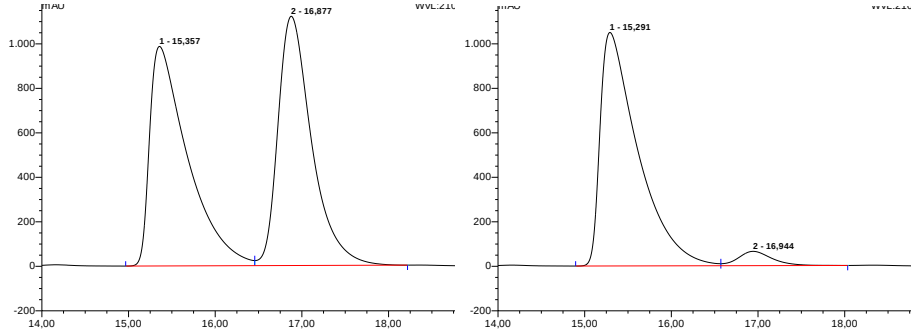

**HPLC** (OJ-H, 250×4.6, *n*-hexane/*iso*-propanol = 80:20) = *ent*-**4e**, $t_R$ = 17.5 min; **4e**, 20.9 min).




| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 17.5 min | 80.080 | 49.78 | 15.823 | 4.36 |
| $t_R$ = 20.9 min | 80.803 | 50.22 | 347.064 | 95.64 |



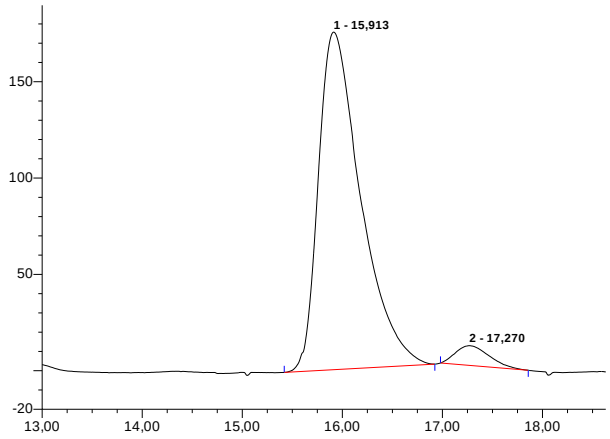

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4f**, $t_R$ = 15.4 min; *ent*-**4f**, 16.9 min).



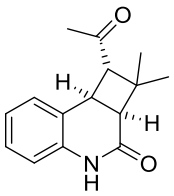

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 15.4 min | 501.803 | 49.81 | 530.416 | 94.79 |
| $t_R$ = 16.9 min | 505.639 | 50.19 | 29.149 | 5.21 |

**HPLC trace of the 0.15 mmol scale reaction of 4f**

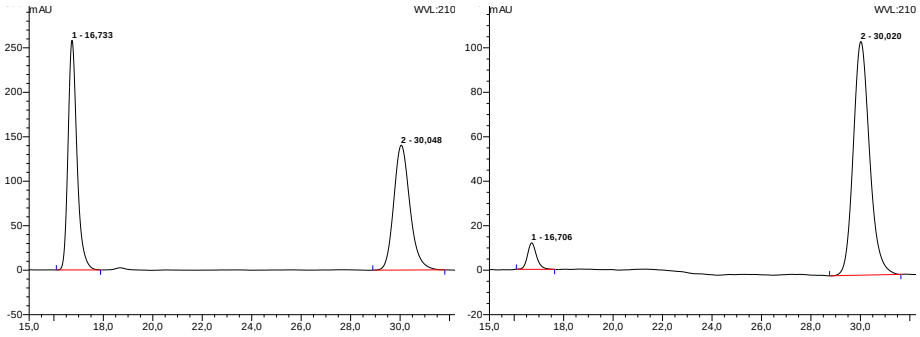
**HPLC** (AD-H, 250×4.6, *n*-heptane/*iso*-propanol = 90:10) = **4f**, $t_R$ = 15.9 min; *ent*-**4f**, 17.3 min).



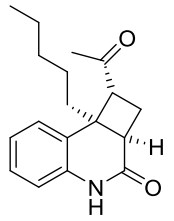

| | *Area* | *Rel. Area (%)* |
|---|---|---|
| $t_R$ = 15.9 min | 85.937 | 95.55 |
| $t_R$ = 17.3 min | 4.003 | 4.45 |



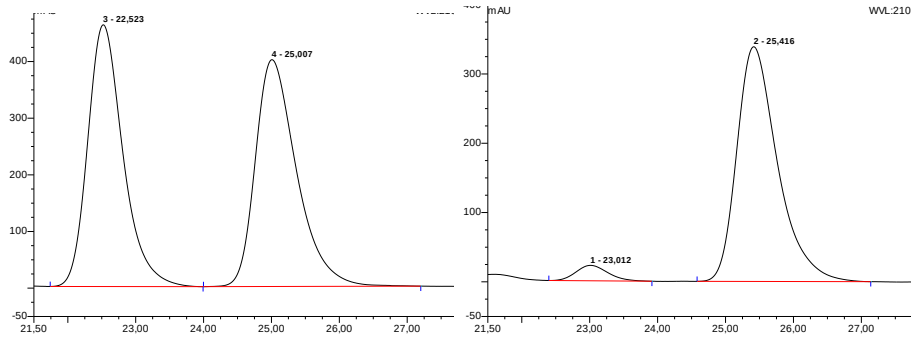
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = *ent*-**4g**, $t_R$ = 16.7 min; **4g**, 30.1 min).



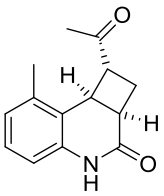

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 16.7 min | 107.983 | 50.35 | 5.046 | 5.92 |
| $t_R$ = 30.1 min | 106.463 | 49.65 | 80.256 | 94.08 |



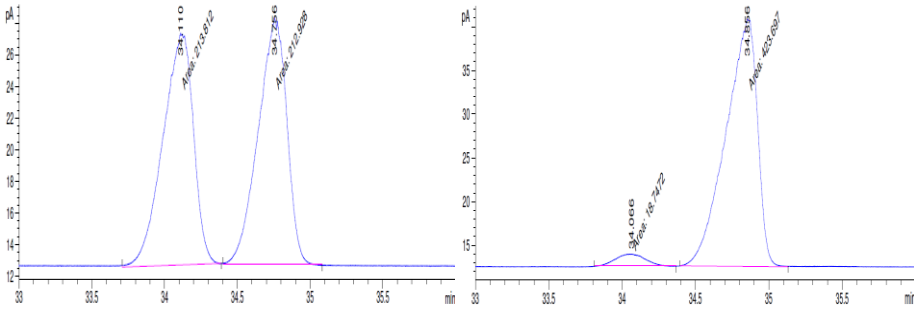
**HPLC** (OJ-H, 250×4.6, *n*-hexane/*iso*-propanol = 95:5) = *ent*-**4h**, $t_R$ = 22.5 min; **4h**, 25.0 min).



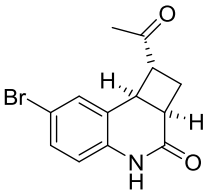

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 22.5 min | 278.239 | 49.72 | 12.102 | 4.89 |
| $t_R$ = 25.0 min | 281.343 | 50.28 | 235.231 | 95.11 |



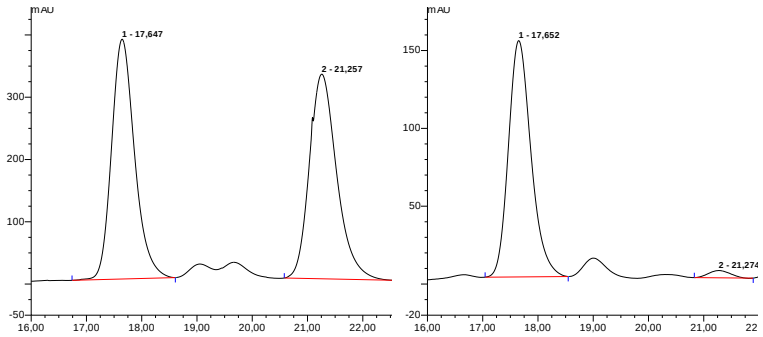
**GC** [60 °C (1 min), 15 °C/min → 200 °C (30 min)] = *ent*-**4i**, $t_R$ = 34.1 min; **4i**, 34.8 min).



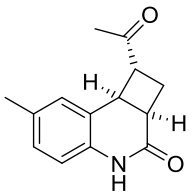
| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 34.1 min | 213.812 | 50.10 | 18.747 | 4.24 |
| $t_R$ = 34.8 min | 212.928 | 49.90 | 423.697 | 95.76 |



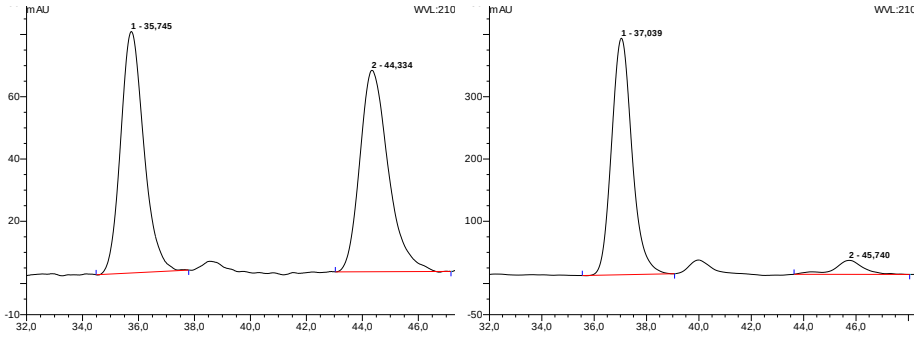
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4j**, $t_R$ = 17.7 min; *ent*-**4j**, 21.3 min).



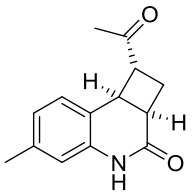
| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 17.7 min | 186.487 | 49.69 | 71.836 | 97.16 |
| $t_R$ = 21.3 min | 188.783 | 50.31 | 2.099 | 2.84 |



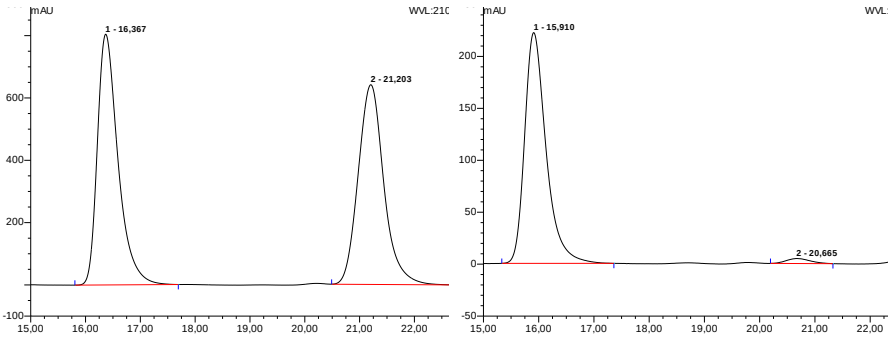
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 95:5) = **4k**, $t_R$ = 35.7 min; *ent*-**4k**, 44.3 min).



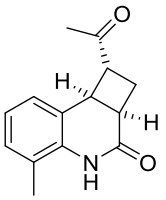

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 35.7 min | 74.674 | 49.46 | 344.454 | 92.26 |
| $t_R$ = 44.3 min | 76.317 | 50.54 | 28.908 | 7.74 |



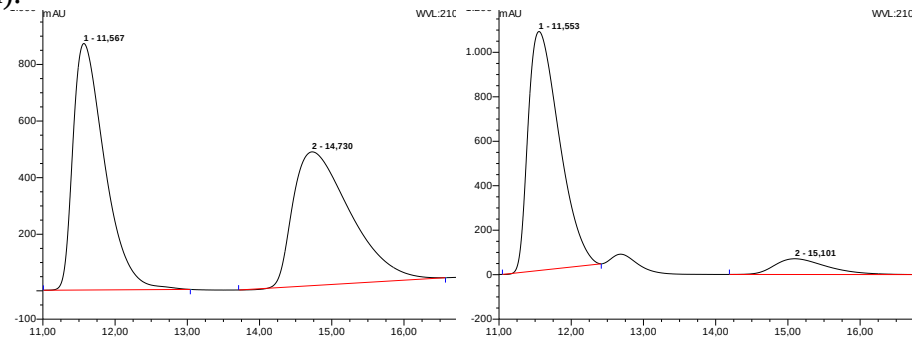
**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4l**, $t_R$ = 16.4 min; *ent*-**4l**, 21.2 min).



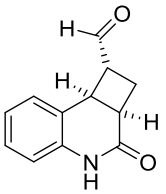

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 16.4 min | 351.037 | 50.28 | 99.933 | 97.68 |
| $t_R$ = 21.2 min | 347.185 | 49.72 | 2.377 | 2.32 |



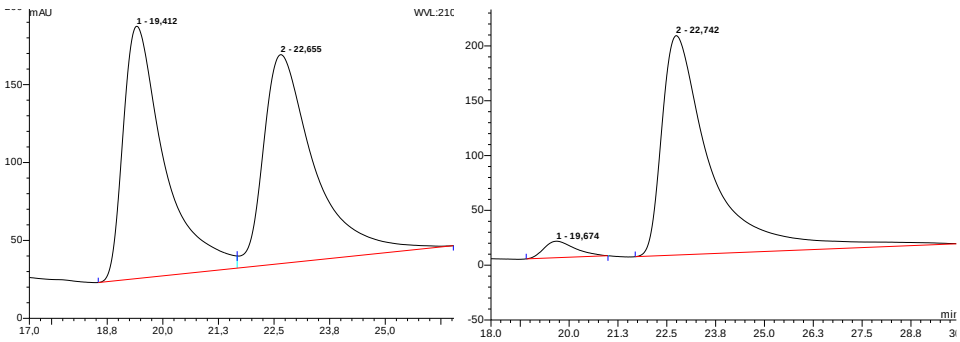
**HPLC** (AS-H, 250×4.6, *n*-hexane/*iso*-propanol = 70:30) = **4m**, $t_R$ = 11.6 min; ent-**4m**, 14.7 min).



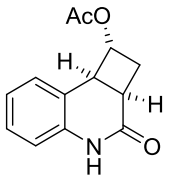

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 11.6 min | 444.509 | 50.67 | 538.649 | 90.07 |
| $t_R$ = 14.7 min | 432.785 | 49.33 | 59.403 | 9.93 |



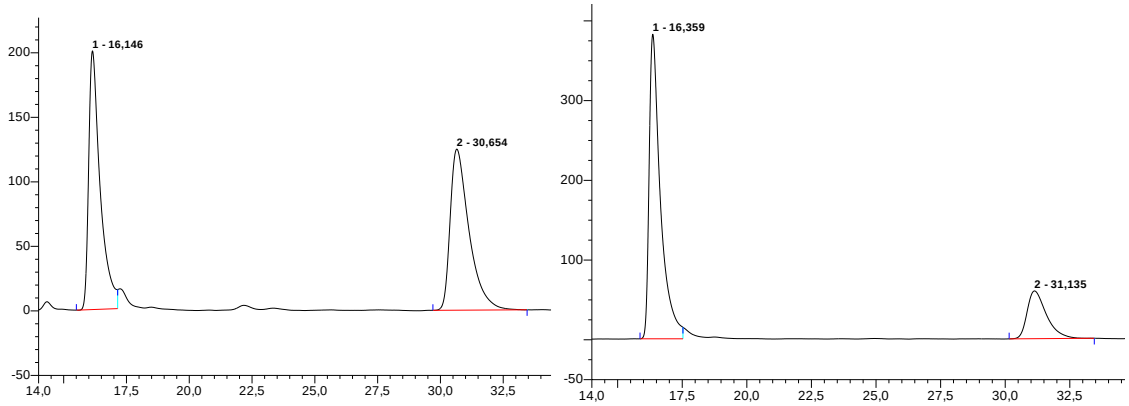
**HPLC** (OJ-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = *ent*-**4n**, $t_R$ = 19.4 min; **4n**, 22.6 min).



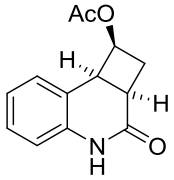

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 19.4 min | 174.665 | 49.57 | 13.879 | 4.52 |
| $t_R$ = 22.6 min | 177.728 | 50.43 | 293.261 | 95.48 |



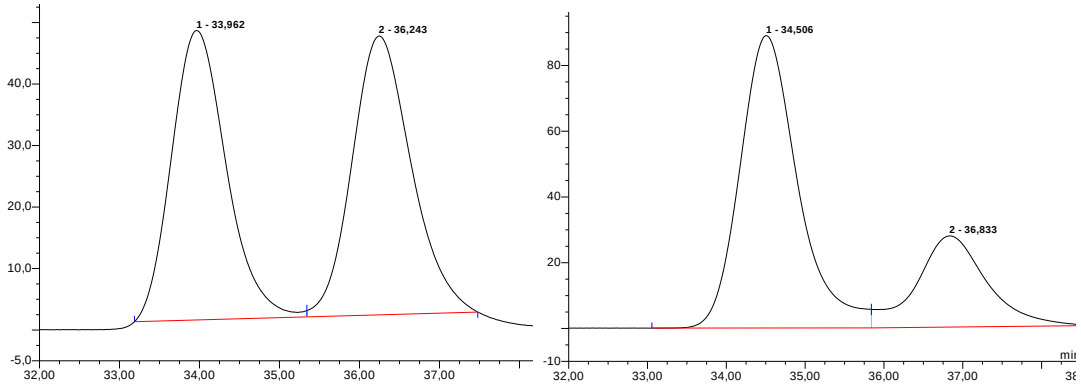

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4o**, $t_R$ = 16.1 min; *ent*-**4o**, 30.6 min).



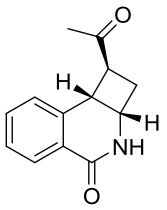

| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 16.1 min | 106.644 | 49.50 | 193.880 | 78.90 |
| $t_R$ = 30.6 min | 108.797 | 50.50 | 51.848 | 21.10 |



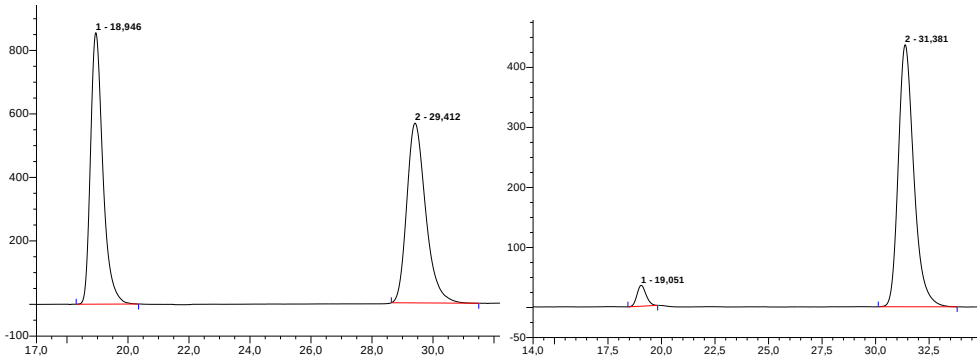

**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 95:5) = **S17**, $t_R$ = 33.9 min; *ent*-**S17**, 36.2 min).




| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 33.9 min | 37.439 | 49.02 | 75.597 | 72.52 |
| $t_R$ = 36.2 min | 38.942 | 50.98 | 28.651 | 27.48 |

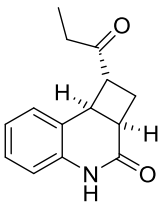



**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = ent-**8**, $t_R$ = 18.9 min; **8**, 29.4 min).

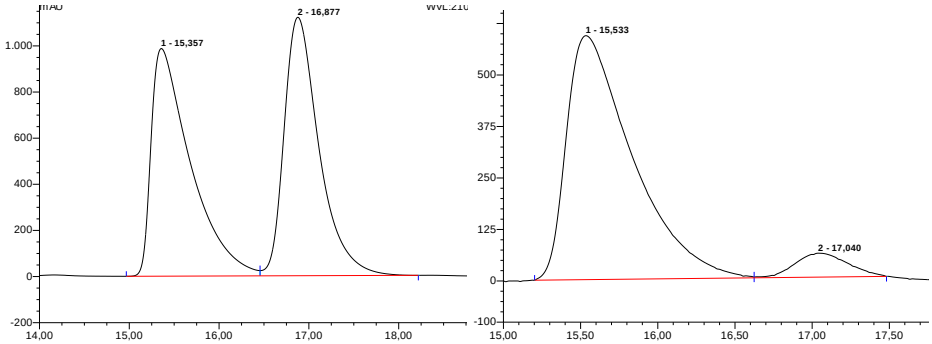



| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 18.9 min | 400.859 | 49.61 | 17.156 | 4.46 |
| $t_R$ = 29.4 min | 407.086 | 50.39 | 367.140 | 95.54 |

**HPLC traces of the solar irradiation experiment**




**HPLC** (AD-H, 250×4.6, *n*-hexane/*iso*-propanol = 90:10) = **4f**, $t_R$ = 15.4 min; *ent*-**4f**, 16.9 min).




| | *Area* | *Rel. Area (%)* | *Area* | *Rel. Area (%)* |
|---|---|---|---|---|
| $t_R$ = 15.4 min | 501.803 | 49.81 | 293.421 | 92.73 |
| $t_R$ = 16.9 min | 505.639 | 50.19 | 23.013 | 7.27 |