Supplementary Information

Diastereoselective Rhodium-Catalyzed Hydrogenation of 2-Oxindoles and 3,4-Dihydroquinolones

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1. General remarks

All experiments were performed in oven-dried or flame-dried glassware under argon atmosphere and under anhydrous conditions using *Schlenk* techniques unless otherwise stated.

Solvents and reagents: Dry dichloromethane (CH_2Cl_2), tetrahydrofuran (THF) and diethylether (Et_2O) were obtained from a *MBraun* MB-SPS 800 solvent purification system. Dry acetonitrile (MeCN), *n*-hexane, methanol (MeOH), 2,2,2-trifluoroethanol (TFE) and toluene were obtained from either *Sigma-Aldrich*, *TCI* or *Acros Organics* in the highest available purity (>99%, extra dry over molecular sieves) and used without further purification. Technical solvents used for aqueous workup and purification by either crystallization or column chromatography [acetone, dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), ethyl acetate (EtOAc), hexane, methanol (MeOH), pentane] were distilled prior to use. All hydrogenation reactions were carried out in a high pressure autoclave using hydrogen gas. Commercially available chemicals were obtained from *Acros Organics*, *Ambeed*, *Alfa Aesar*, *ABCR, Chemical Co.*, *Chempur*, *Combi-Blocks, Sigma Aldrich*, *Strem Chemicals* and *TCI Europe* and used as received unless otherwise stated.

Catalyst synthesis: The employed ^{Cy}(CAAC) ligand salt[1] and the corresponding ^{Cy}(CAAC)Rh(cod)Cl complex[2] **1** were synthesized according procedures known from literature. All analytical data were in agreement with the reported data.[1-2]

Starting materials: Unless stated otherwise starting materials were obtained from commercial suppliers and used without further purification. The starting materials **2d**[3], **2u**[4], **4c**[5], **4f**[6], **4g**[7], **4j**[5] and **4k**[5] were synthesized according to procedures known from literature and all analytical data were in agreement with the reported ones.[3-8]

Chromatography: Thin layer chromatography (TLC) was performed on pre-coated glass-backed *Merck* silica 60 F_{254} plates with visualization effected with staining using potassium permanganate ($KMnO_4$) solution prepared from potassium permanganate (3.00 g), potassium carbonate (20.0 g) and 5% aqueous sodium hydroxide solution (5.00 mL) in water (300 mL). Flash column chromatography was performed on silica 60 (*Merck*, 230–400 mesh) with the indicated eluent mixtures.

NMR spectroscopy: ^{1}H NMR spectra were recorded on *Bruker* AVHD-300, AVHD-400 or AVHD-500 spectrometers at 303 K operating at 300 MHz, 400 MHz and 500 MHz, respectively. Data are reported in the following manner: chemical shift [in parts per million (ppm) relative to residual $CHCl_3$ (δ_H = 7.26 ppm), benzene-d_6 (δ_H = 7.16 ppm), acetone-d_6 (δ_H = 2.05 ppm) or DMSO-d_6 (δ_H = 2.50 ppm), number of protons, multiplicity and coupling constant *J* (measured in Hz to the nearest 0.1 Hz). The multiplicity of a signal is indicated as: s-singlet, bs-broad singlet, d-doublet, t-triplet, q-quartet, hept-heptet, m-multiplet, or combinations of these. ^{13}C NMR spectra were recorded on the same AVHD-500 spectrometers at 303 K operating at 126 MHz respectively with proton decoupling. The chemical shift in [parts per million (ppm)] is reported relative to residual solvent signal of $CHCl_3$ (δ_C = 77.16 ppm), Benzene-d_6 (δ_C = 49.00 ppm), acetone-d_6 (δ_H = 29.8 ppm) or DMSO-d_6 (δ_C = 39.52 ppm). ^{19}F NMR spectra with proton decoupling were recorded on a *Bruker* AVHD-500 (471 MHz) spectrometer and used without reference. ^{29}Si NMR spectra with proton decoupling were recorded on a *Bruker* AVHD-500 (99 MHz) spectrometer and used

without reference. ^{11}B NMR spectra with proton decoupling were recorded on a *Bruker* AVHD-400 (128 MHz) spectrometer and used without reference. All spectra were recorded at room temperature. Spectra are reported based on appearance, not on theoretical multiplicities derived from structural information. Apparent multiplets which occur as a result of coupling constant equality between magnetically non-equivalent protons are marked as virtual (*virt*). Only the signals of the major diastereomer are listed. Signals assigned to the minor diastereoisomer are marked (#) in the shown spectra.

Mass Spectroscopy (MS) and High-resolution mass spectra (HRMS): MS and HRMS were recorded on a *Thermo Fischer Scientific* DFS High Resolution MS employing electron ionization (EI, 70 eV).

Gas Chromatography (GCL): GC analysis for reaction optimization studies was performed on an *Agilent Technologies* 7890B with a DB-5ht column (15 m, 0.32 mm, 0.10 µM) equipped with a flame ionization detector (FID). Standard method used for separation of all the compounds **2a** and **3a**: 60 °C [1 min], 15 °C/min → 300 °C, 300 °C [5 min].

Melting points (m.p.): Determined using a *Büchi* M-510 melting point apparatus, with range quoted to the nearest whole number.

Infrared Spectroscopy (IR): Spectra were recorded on a *Perkin Elmer Frontier* Optica+SP10 spectrometer by ATR technique. The signal intensity is assigned using the following abbreviations: s (strong), m (medium), w (weak).

Chiral HPLC: Analytical HPLC (*Thermo Fisher, Dionex* Ultimate 3000 pump, *Dionex* Ultimate 3000, LPG 3400SD Pump, WPS3000SL Autosampler, DAD 3000 photodiode array detector) was performed using different chiral stationary phases (*Daicel ChiralCel*, *Chemical Industries*, flow rate, type and eluent is given for the corresponding compounds) and UV detection (λ = 210 or 254 nm) at 303 K or 323K. Semi-preparative HPLC was performed on a *Thermo Fisher* Ultimate 3000 equipped with a MWD 3000-RS detector using a Chiralpak AD-H column with a flowrate of 1 mL/min and *n*-heptane/ *iso*-propanol as eluent.

Chiral GC: Analytical chiral GC measurements were perfoment on an *Agilent* 7890 B gas chromatograph using an *Agilent* CycloSil-B column (30 m x 0.25 mm x 0.25 µm, SN: USF620714H) with a flame ionization detector. The temperature method is given for the corresponding compounds.

2. Optimization of the reaction conditions

Individual stock solutions of the two compounds oxindole **2a** and the corresponding product **3a** with *n*-dodecane in CH_2Cl_2 (c = 10 mM) were prepared and diluted to the following concentrations: 10.0 mM, 6.0 mM, 3.0 mM, 1.0 mM and 0.5 mM. The samples were submitted to GC analysis and the method for quantification of the compounds was calibrated according to the corresponding instrument response factors from the initial measurements. A correlation of $R^2 \geq 0.9999$ was obtained for each compound.

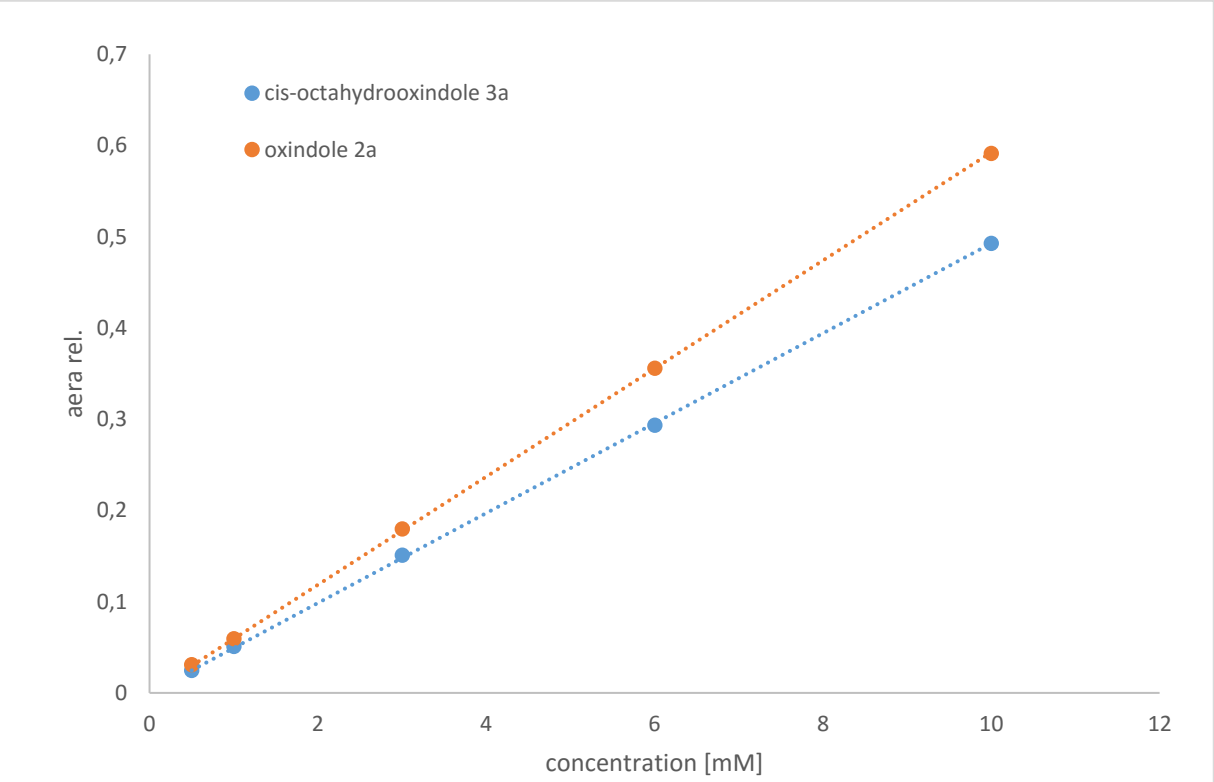
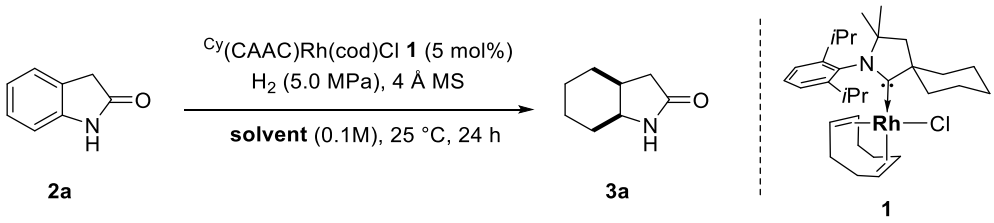


Figure S1. Instrument response for *n*-dodecane (10 mM) and starting material **2a** and product **3a** at different concentrations (0.5, 1.0, 3.0, 6.0 and 10 mM) in CH_2Cl_2 (Area rel. = relative to internal standard *n*-dodecane).

2.1. General Procedure 1 (GP1): Evaluation of the reaction conditions

Rhodium catalyst **1** (1.46 mg, 2.5 μmol, 2.5 mol%) was filled in an oven-dried 4 mL screw-cap vial equipped with a stirring bar. Solvent (as indicated), 2-oxindole **2a** (13.32 mg, 100 μmol, 1.0 equiv.) and powdered 4 Å molecular sieves (MS) (10 mg) were added under argon atmosphere. The glass vial was placed in a 60 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the indicated pressure was set. The reaction mixture was stirred at the indicated temperature for the indicated time. After the autoclave was carefully depressurized, *n*-dodecane (17.0 mg, 100 μmol, 22 μL) as internal standard was added and the vial was stirred vigorously for 5 min. After filtration over *whatman* filter, an aliquot (100 μL) was taken and diluted with CH_2Cl_2 (900 μL). Conversion, yields and diastereomeric ratio (*dr*) were determined by GC-FID analysis.

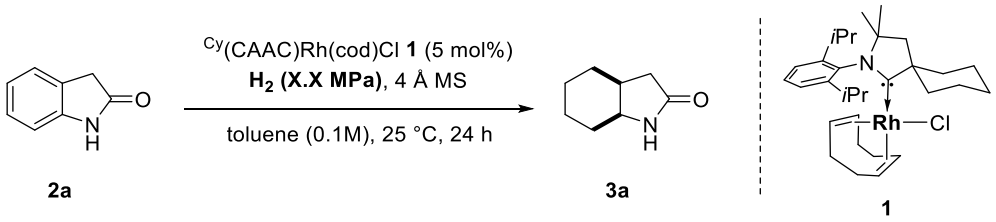
2.2. Evaluation of different solvents



Entry	Solvent	Conversion [%]	Yield [%] (*dr*)
1	MeOH	>99	98 (>99:1)
2	TFE	>99	97 (>99:1)
3	MeCN	92	n.d.[#]
4	DCM	59	10 (>99:1)[#]
5	THF	<5	n.d.
6	Et_2O	<5	n.d.
7	toluene	98	99 (>99:1)
8*	*n*-hexane	<5	>5

The reaction was carried out according to the general procedure on 0.1 mmol scale. n.d.: not determined. [#]uncharacterized site-product was formed. *Low conversion due to solubility problems of the substrate.

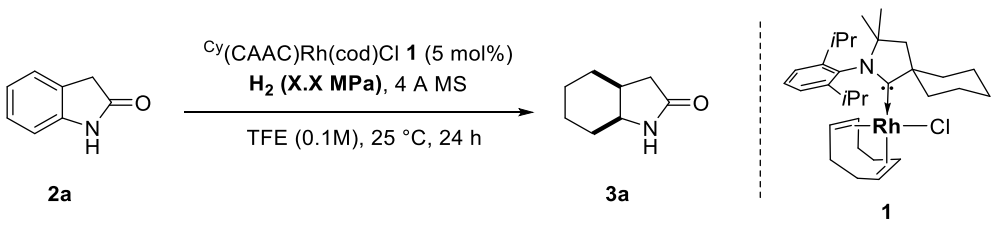
2.3. Evaluation of the hydrogen pressure



2a **3a** **1**

Entry	Pressure [MPa]	Conversion [%]	Yield [%] (*dr*)
1	1.0	<5	n.d.
2	3.0	50	48 (>99:1)
3	5.0	>99	99 (>99:1)
4	8.0	>99	98 (>99:1)

The reaction was carried out according to the general procedure on 0.1 mmol scale. n.d.: not determined.

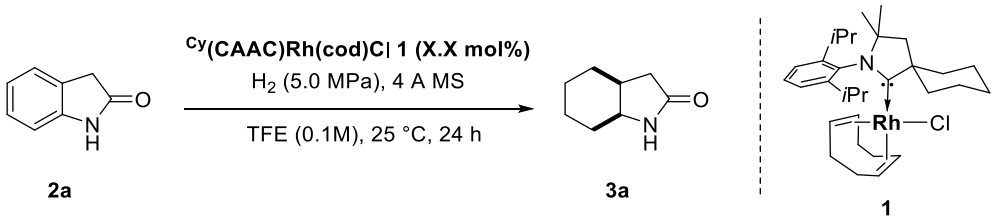


2a **3a** **1**

Entry	Pressure [MPa]	Conversion [%]	Yield [%] (*dr*)
1	1.0	90	87 (>99:1)
2	3.0	>99	99 (>99:1)
3	5.0	>99	98 (>99:1)
4	8.0	>99	97 (>99:1)

The reaction was carried out according to the general procedure on 0.1 mmol scale.

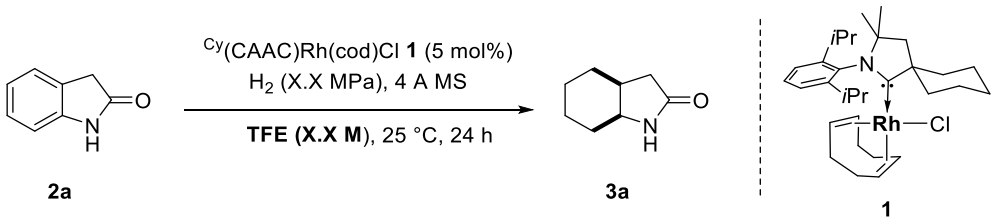
2.4. Evaluation of the catalyst loading



Entry	Catalyst Loading [mol%]	Conversion [%]	Yield [%] (*dr*)
1	5.0	100	98 (>99:1)
2	2.5	84	83 (>99:1)
3	1.0	20	19 (>99:1)
4	0.5	7	5 (>99:1)
5	0.1	<2	n.d.
6	0.05	0	n.d.

The reaction was carried out according to the general procedure on 0.1 mmol scale. n.d.: not determined.

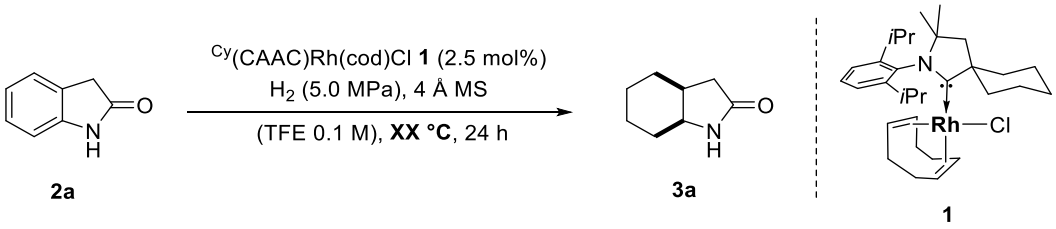
2.5. Evaluation of the reaction concentration



Entry	Concentration [M]	Conversion [%]	Yield [%] (*dr*)
1*	1.0	100	99 (>99:1)
2*	0.5	100	99 (>99:1)
3	0.25	100	99 (>99:1)
4	0.1	100	99 (>99:1)
5	0.05	78	75 (>99:1)

The reaction was carried out according to the general procedure on 0.1 mmol scale. *The reaction was carried out according to the general procedure on 1.0 mmol scale.

2.6. Evaluation of the reaction temperature



Entry	Temperature [°C]	Conversion [%]	Yield [%] (*dr*)
1	25	84	83 (> 99:1)
2	50	100	99 (> 99:1)
3	75	100	99 (> 99:1)
4*	50	0	n.d.

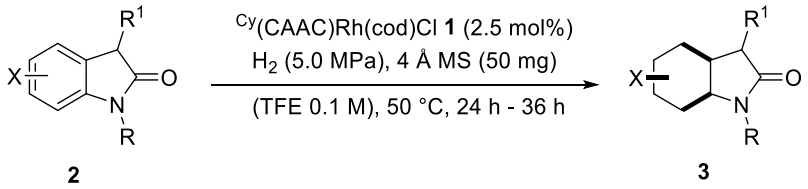
The reaction was carried out according to the general procedure on 0.1 mmol scale. n.d.: not determined.* Reaction was performed without the addition of 4 Å MS.

2.7. Filtration experiment

Rhodium catalyst **1** (7.31 mg, 12.5 μmol, 2.5 mol%), 2-oxindole **2a** (500 μmol, 1.0 equiv.) and powdered 4 Å MS (50 mg) were filled in an oven-dried 10 mL screw-cap vial equipped with a stirring bar. 2,2,2-Trifluoroethanol (5.0 mL) was added under argon atmosphere. The glass vial was placed in a 60 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the hydrogen pressure was set to 5.0 MPa. The reaction mixture was stirred at 50 °C for 24 h. Afterwards, the autoclave was carefully depressurized. The reaction mixture was filtered. The resulting precipitate **1'** was washed with TFE (3 × 2 ml) and dried *in vacuo*. Subsequently, the precipitate **1'** and 2-Oxindole **2a** (500 μmol, 1.0 equiv.) were filled in an oven-dried 10 mL screw-cap vial equipped with a stirring bar. 2,2,2-Trifluoroethanol (5.0 mL) was added under argon atmosphere. The glass vial was placed in a 60 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the hydrogen pressure was set to 5.0 MPa. The reaction mixture was stirred at 50 °C for 24 h. The crude mixture was filtered over *Celite* (eluent: ethyl acetate). After removal of all volatiles *in vacuo* the diastereomeric ratio (*dr*) was determined by NMR analysis of the crude product. Subsequently, the crude material was purified by flash column chromatography (SiO_2, pentane/ethyl acetate = 4:1→ 1:1 → 0:1) yielding the entitled hydrogenated heterocycle **3a** (53.9 mg, 387 μmol, 77%, *dr* > 99:1).

3. Catalysis

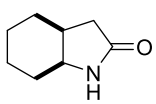
3.1. General Procedure 2 (GP2): Hydrogenation of 2-oxindole derivatives



2 **3**

Rhodium catalyst **1** (7.31 mg, 12.5 μmol, 2.5 mol%), the respective oxindole derivative **2** (500 μmol, 1.0 equiv.) and powdered 4 Å MS (50 mg) were filled in an oven-dried 10 mL screw-cap vial equipped with a stirring bar. 2,2,2-Trifluoroethanol (5.0 mL) was added under argon atmosphere. The glass vial was placed in a 60 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the hydrogen pressure was set to 5.0 MPa. The reaction mixture was stirred at 50 °C for 24 h to 36 h. Afterwards, the autoclave was carefully depressurized. The crude mixture was filtered over *Celite* (eluent: ethyl acetate). After removal of all volatiles *in vacuo* the diastereomeric ratio (*dr*) was determined by NMR analysis of the crude product. Subsequently, the crude material was purified by flash column chromatography (SiO_2, pentane/ethyl acetate = 4:1→ 1:1 → 0:1) yielding the entitled hydrogenated heterocycle **3**.

*3.1.1. (*3a*SR,*7a*SR)-Octahydroindol-2-one (***3a***)*



Following GP2 the entitled compound **3a** was obtained as a yellow oil (64.3 mg, 462 μmol, 95%).

dr > 99:1.

***R*f** (75% EtOAc/Pentane): 0.21.

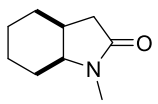
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.78 (s, 1H, NH), 3.68 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 5.1 Hz, 1H, H-7a), 2.35-2.21 (m, 2H, H-3), 2.05-1.91 (m, 1H, H-3a), 1.69-1.24 (m, 8H, CH_2).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.6 (CO), 53.2 (C-7a), 37.8 (C-3), 34.4 (C-3a), 28.8 (C-7), 27.2 (C-4), 22.6 (C-5*), 20.5 (C-6*).

*assignment is interconvertible.

Spectral data match those reported in the literature.[2, 9]

*3.1.2. (*3a*SR,*7a*SR)-1-Methyloctahydroindol-2-one (***3b***)*



Following GP2 the entitled compound **3b** was obtained as a yellow oil (71.5 mg, 467 μmol, 93%).

dr > 99:1.

***R*f** (75% EtOAc/Pentane): 0.24.

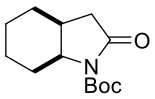
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.44 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 5.6 Hz, 1H, H-7a), 2.78 (s, 3H, CH_3), 2.38 – 2.25 (m, 2H, H-3a *H*H-3), 2.13 – 2.08 (m, 1H, H*H*-3), 1.80 – 1.56 (m, 3H, H-4, *H*H-7), 1.52 – 1.45 (m, 1H, *H*H-5*), 1.41 – 1.29 (m, 4H, H*H*-5*, H-6*, H*H*-7).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 175.8 (CO), 58.7 (C-7a), 37.6 (C-3), 32.4 (C-3a), 27.5 (C-7), 27.1 (C-4), 26.8 (N–CH_3), 22.8 (C-5), 21.0 (C-6).

*assignment is interconvertible

Spectral data match those reported in the literature.[10]

*3.1.3. (*3a*SR,*7a*SR)-N-(tert-Butoxycarbonyl)octahydroindol-2-one* (**3c**)



Following GP2 the entitled compound **3c** was obtained as a colorless solid (102 mg, 426 μmol, 85%).

dr > 99:1.

***R*$_f$** (20% EtOAc/Pentane): 0.21.

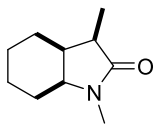
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.99 (*virt.* dt, ^3J = 10.2 Hz, $^3J \approx {}^3J$ = 5.9 Hz, 1H, H-7a), 2.56 – 2.41 (m, 2H, *H*H-3, H-3a), 2.34 – 2.25 (m, 1H, H*H*-3), 2.23 – 2.15 (m, 1H, *H*H-7), 1.78 – 1.65 (m, 2H, *H*H-4, *H*H-5*), 1.65 – 1.58 (m, 1H, H*H*-4), 1.58 – 1.54 (m, 1H, *H*H-6*), 1.51 [s, 9H, C(*C*H_3)$_3$], 1.36 – 1.18 (m, 3H, H*H*-5*), H*H*-6*), H*H*-7).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 174.4 (CO), 150.1 (COO*t*Bu), 82.6 (Me_3C), 57.9 (C-7a), 35.8 (C-3), 31.7 (C-3a), 28.3 [C(*C*H_3)$_3$], 28.2 (C-7), 25.9 (C-4), 22.9 (C-5*), 20.4 (C-6*).

*assignment is interconvertible

Spectral data match those reported in the literature.[11]

*3.1.4. (3RS,*3a*SR,*7a*SR)-1,3-Dimethyloctahydroindol-2-one* (**3d**)



Following GP2 the entitled compound **3d** was obtained as a colorless oil (77.1 mg, 461 μmol, 92%).

dr = 85:15.

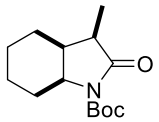
***R*$_f$** (EtOAc): 0.62.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.40 (*virt.* dt, ^3J = 7.1 Hz, $^3J \approx {}^3J$ = 3.3 Hz, 1H, H-7a), 2.75 (s, 3H, N-CH_3), 2.43 (*virt.* p, $^3J \approx {}^3J$ = 7.1 Hz, 1H, H-3), 2.15 (*virt.* dq, ^3J = 11.2 Hz, $^3J \approx {}^3J \approx {}^3J$ = 5.8 Hz, 1H, H-3a), 2.04 – 1.94 (m, 1H, *H*H-7), 1.70 – 1.46 (m, 4H, H-4, *H*H-5, *H*H-6), 1.25 – 1.09 (m, 2H, H*H*-5, H*H*-6), 1.07 (d, ^3J = 7.3 Hz, 3H, CH_3), 1.04 – 0.97 (m, 1H, H*H*-7).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.4 (CO), 56.7 (C-7a), 42.5 (C-3), 37.5 (C-3a), 26.8 (C-7), 26.2 (N-CH_3), 24.0 (C-4), 23.2 (C-6*), 20.6 (C-5*), 9.4 (CH_3).

Spectral data match those reported in the literature.[12]

*3.1.5. (3RS,*3a*SR,*7a*SR)-tert-Butyl-3-methyl-2-oxooctahydroindole-1-carboxylate (***3e***)*



Following GP2 the entitled compound **3e** was obtained as a colorless oil (116 mg, 458 μmol, 91%).

dr = 86:14.

***R*$_f$** (80% EtOAc/Pentane): 0.38.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.93 (*virt*. q, $^3J \approx {}^3J \approx {}^3J$ = 4.4 Hz, 1H, H-7a), 2.55 (*virt.* p, $^3J \approx {}^3J$ = 7.2 Hz, 1H, H-3), 2.45 – 2.35 (m, 1H, *H*H-7), 2.20 (*virt.* ddt, ^3J = 10.4 Hz, ^3J = 7.2 Hz, $^3J \approx {}^3J$ = 5.3 Hz, 1H, H-3a), 1.70 – 1.56 (m, 4H, H-4, *H*H-6, H*H*-7), 1.53 [s, 9H, $C(CH_3)_3$], 1.45 (*virt.* dp, ^2J = 10.3 Hz, $^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 5.7 Hz, 1H, *H*H-5), 1.36 – 1.21 (m, 2H, H*H*-5, H*H*-6), 1.13 (d, ^3J = 7.2 Hz, 3H, CH_3).

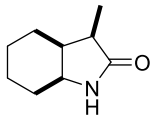
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 177.8 (CO), 151.1 (COO*t*Bu), 82.7 (Me_3C), 56.7 (C-7a), 43.6 (C-3), 35.7 (C-3a), 28.3 [$C(CH_3)_3$], 27.3 (C-7), 24.0 (C-4), 23.4 (C-6), 20.5 (C-5), 10.2 (CH_3).

HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{23}NO_3$ 253.1672; Found 253.1675.

MS (EI^+, 70 eV): m/z (%) = 253 (5) $[M]^+$, 197 (50) $[M-C_4H_9]^+$, 180 (35), 154 (100) $[M-C_5H_9O_2]^+$, 110 (55), 81 (15).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2997 (s, C_{sp3}–H), 2935 (s, C_{sp3}–H), 2862 (m), 1730 (s, C=O), 1681 (s, C=O), 1450 (w), 1359 (s), 1318 (s), 1162 (m), 992 (m), 837 (w), 780 (w).

*3.1.6. (3RS,*3a*SR,*7a*SR)-3-Methyloctahydroindol-2-one* (**3f**)



Following GP2 the entitled compound **3f** was obtained as a colorless solid (72.3 mg, 472 μmol, 94%).

dr = 87:13.

***R*$_f$** (80% EtOAc/Pentane): 0.21.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.26 (s, 1H, NH), 3.79 – 3.67 (m, 1H, H-7a), 2.55 (*virt.* p, $^3J \approx {}^3J$ = 7.2 Hz, 1H, H-3), 2.25 – 2.17 (m, 1H, H-3a), 1.89 – 1.79 (m, 1H, *H*H-4), 1.73 – 1.65 (m, 1H, H*H*-4), 1.64 – 1.45 (m, 3H, *H*H-5, *H*H-6, *H*H-7), 1.38 – 1.27 (m, 1H, H*H*-7), 1.23 – 1.14 (m, 2H, H*H*-5, H*H*-6), 1.07 (d, ^3J = 7.2 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 180.5 (CO), 51.7 (C-7a), 43.1 (C-3), 39.4 (C-3a), 27.8 (C-7), 23.8 (C-4), 22.7 (C-6), 20.1 (C-5), 8.9 (CH_3).

HRMS (EI) m/z: $[M]^+$ calcd for $C_9H_{15}NO$ 153.1148; Found 153.1146.

MS (EI$^+$, 70 eV): m/z (%) = 153 (45) [M]$^+$, 124 (5), 110 (100) [M-CHNO]$^+$, 96 (13), 81 (10).

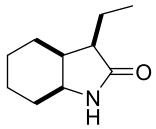
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3224 (m, N–H), 2969 (m), 2926 (s, C_{sp3}–H), 2851 (m), 1686 (s, C=O), 1444 (s), 1353 (w), 1298 (w), 1134 (w), 1027 (w), 831 (w), 743 (w).

m.p. = 138-141 °C.

Chiral GC [CycloSil-B, 60 °C (0 min), 150 °C (10 °C/min), 150 °C (50 min), 250 °C (10 °C/min), 250 °C (3 min)], t_{R1} = 44.1 min (minor), t_{R2} = 44.6 min (minor); t_{R1} = 48.1 min (major), t_{R2} = 49.1 min (major).

Relative configuration of the methyl group was determined by *N*-methylation of product **3f**. The obtained *N*-methylated product is in alignment with the previous reported product **3d**.

*3.1.7. (3RS,*3a*SR,*7a*SR)-3-Ethyloctahydroindol-2-one* (**3g**)



Following GP2 the entitled compound **3g** was obtained as a colorless solid (77.5 mg, 464 µmol, 93%).

dr = 86:14.

***R*$_f$** (80% EtOAc/Pentane): 0.21.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.38 (s, 1H, NH), 3.68 (*virt.* td, $^3J \approx {}^3J$ = 4.1 Hz, ^3J = 2.2 Hz, 1H, H-7a), 2.35 – 2.22 (m, 2H, H-3, H-3a), 1.91 – 1.84 (m, 1H, *H*H-7), 1.84 – 1.75 (m, 1H, H*H*-7), 1.75 – 1.65 (m, 1H, *H*H-6), 1.63 – 1.46 (m, 3H, *H*H-4, H*H*-6,), 1.42 – 1.28 (m, 2H, H-5), 1.17 – 1.10 (m, 2H, CH_2), 0.96 (t, ^3J = 7.5 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 180.0 (CO), 51.9 (C-7a), 50.7 (C-3), 37.8 (C-3a), 27.9 (C-7), 24.0 (C-6), 22.2 (C-4), 20.2 (C-5), 17.0 (CH_2), 12.6 (CH_3).

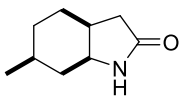
HRMS (EI) m/z: [M]$^+$ calcd for $C_{10}H_{17}NO$ 167.1305; Found 167.1302.

MS (EI$^+$, 70 eV): m/z (%) = 167 (45) [M]$^+$, 152 (10), 139 (100) [M-C_2H_5]$^+$, 124 (45), 96 (65), 84 (20).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3194 (m, N–H), 2929 (s, C_{sp3}–H), 2852 (m), 1685 (s, C=O), 1444 (w), 1356 (w), 1299 (w), 1134 (w), 1097 (w), 912 (w), 759 (w).

m.p. = 147-149 °C.

*3.1.8. (*3a*SR,*6*SR,*7a*SR)-6-Methyloctahydroindol-2-one* (**3h**)



Following GP2 the entitled compound **3h** was obtained as an off-white solid (538 mg, 3.51 µmol, 70%).

dr = 83:17.

***R*$_f$** (80% EtOAc/Pentane): 0.20.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.99 (s, 1H, NH), 3.48 (*virt.* dt, ^3J = 9.6 Hz, $^3J \approx {}^3J$ = 5.8 Hz, 1H, H-7a), 2.62 – 2.51 (m**,** 1H, *H*H-3), 2.33 – 2.21 (m, 1H, H-3a), 2.19 – 2.11 (m, 1H, H*H*-3), 1.90 – 1.81 (m, 1H, *H*H-7), 1.79 – 1.71 (m, 1H, *H*H-4), 1.67 – 1.56 (m, 1H, *H*H-4), 1.56 – 1.49 (m, 1H, *H*H-5), 1.40 – 1.27 (m, 1H, H-6), 1.10 – 0.98 (m, 1H, H*H*-5), 0.99 – 0.95 (m, 1H, H*H*-7), 0.92 (d, ^3J = 6.6 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.6 (CO), 54.0 (C-7a), 39.6 (C-7), 33.9 (C-3), 33.3 (C-3a), 29.2 (C-5, C-6), 25.8 (C-4), 22.3 (CH_3).

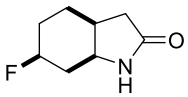
HRMS (EI) m/z: $[M]^+$ calcd for $C_9H_{15}NO$ 153.1148; Found 153.1149.

MS (EI^+, 70 eV): m/z (%) = 153 (20) $[M]^+$, 125 (5), 109 (5), 96 (100) $[M\text{-}C_2H_3NO]^+$, 83 (7).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3228 (m, N–H), 2924 (s, C_{sp3}–H), 2853 (m), 1697 (s, C=O), 1455 (s), 1381 (w), 1263 (w), 1146 (w), 1028 (w), 903 (w), 721 (w).

m.p. = 95-98 °C.

*3.1.9. (*3a*SR,*6*SR,*7a*SR)-6-Fluoroloctahydroindol-2-one* (**3i**)



Following GP2 the entitled compound **3i** was obtained as a colorless solid (60.5 mg, 385 μmol, 77%).

dr > 99:1.

***R*$_f$** (EtOAc): 0.23.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.56 (s, 1H, NH), 4.68 (*virt.* dtt, $^2J_{HF}$ = 48.1 Hz, $^3J \approx {}^3J$ = 6.8 Hz, $^3J \approx {}^3J$ = 3.3 Hz, 1H, H-6), 3.75 (*virt*. q, $^3J \approx {}^3J \approx {}^3J$ = 5.7 Hz, 1H, H-7a), 2.48 – 2.34 (m, 2H, *H*H-3, H-3a), 2.19 – 2.10 (m, 1H, H*H*-3), 2.08 – 1.58 (m, 6H, H-4, H-5, H-7).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 177.4 (CO), 88.0 (d, $^1J_{CF}$ = 172.3 Hz, C-6), 51.9 (d, $^3J_{CF}$ = 6.0 Hz, C-7a), 36.7 (C-3), 34.2 (d, $^2J_{CF}$ = 19.3 Hz, C-7), 33.9 (C-3a), 27.9 (d, $^2J_{CF}$ = 20.1 Hz, C-5), 21.8 (d, $^3J_{CF}$ = 6.7 Hz, C-4).

^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = −177.8.

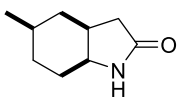
HRMS (EI) m/z: $[M]^+$ calcd for $C_8H_{12}NOF$ 157.0897; Found 157.0890.

MS (EI^+, 70 eV): m/z (%) = 157 (15) $[M]^+$, 137 (20), 96 (100) $[M\text{-}CHNOF]^+$, 83 (20).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3255 (m, N–H), 2929 (s, C_{sp3}–H), 2866 (m), 1685 (s, C=O), 1421 (s), 1370 (w), 1281 (w), 1109 (w), 1017 (m), 934 (m), 709 (w).

m.p. = 154-156 °C.

*3.1.10. (*3a*SR,*5*SR,*7a*SR)-5-Methyloctahydroindol-2-one* (**3k**)



Following GP2 the entitled compound **3k** was obtained as an off-white solid (66.3 mg, 433 μmol, 87%).

dr = 90:10.

***R*f** (80% EtOAc/Pentane): 0.21.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.26 (s, 1H, NH), 3.78 (*virt.* td, $^3J \approx {}^3J$ = 4.6 Hz, ^3J = 2.3 Hz, 1H, H-7a), 2.51 (dd, ^2J = 16.1 Hz, ^3J = 6.7 Hz, 1H, *H*H-3), 2.33 – 2.23 (m, 1H, H-3a), 1.96 – 1.85 (m, 2H, *H*H-3, *H*H-7), 1.64 – 1.55 (m, 2H, *H*H-4, H*H*-7), 1.51 – 1.42 (m, 1H, *H*H-6), 1.39 – 1.27 (m, 1H, H-5), 1.07 (*virt.* ddt, ^2J = 13.3 Hz, ^3J = 11.5 Hz, $^3J \approx {}^3J$ = 3.8 Hz, 1H, H*H*-6), 1.00 – 0.91 (m, 1H, H*H*-4), 0.89 (d, ^3J = 6.5 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 179.2 (CO), 53.0 (C-7a), 40.5 (C-3), 36.8 (C-4), 35.0 (C-3a), 30.4 (C-5), 28.3 (C-7), 27.8 (C-6), 22.6 (CH_3).

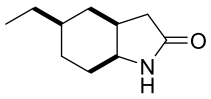
HRMS (EI) m/z: $[M]^+$ calcd for $C_9H_{15}NO$ 153.1148; Found 153.1147.

MS (EI^+, 70 eV): m/z (%) = 153 (20) $[M]^+$, 125 (5), 109 (5), 96 (100) $[M\text{-}C_2H_3NO]^+$, 84 (7).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3228 (m, N–H), 2924 (s, C_{sp3}–H), 2853 (m), 1697 (s, C=O), 1455 (s), 1372 (w), 1279 (w), 1131 (w), 1048 (w), 891 (w), 711 (w).

m.p. = 96-98 °C.

*3.1.11. (*3a*SR,*5*RS,*7a*SR)-5-Ethyloctahydroindol-2-one* (**3l**)



Following GP2 the entitled compound **3l** was obtained as an off-white solid (74.9 mg, 448 μmol, 90%).

dr = 85:15.

***R*f** (80% EtOAc/Pentane): 0.23.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.15 (s, 1H, NH), 3.65 (*virt.* dt, ^3J = 8.6 Hz, $^3J \approx {}^3J$ = 6.0 Hz, 1H, H-7a), 3.32 (t, ^3J = 6.7 Hz, 3H, CH_3), 3.23 – 3.18 (m, 1H, H-5), 2.78 – 2.46 (m, 2H, CH_2), 2.32 – 2-22 (m, 1H, *H*H-3), 2.15 – 2.05 (m, 2H, H*H*-3, H-3a), 1.85 – 1.72 (m, 2H, H-4), 1.62 – 0.78 (m, 4H, H-7, H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.0 (CO), 75.4 (C-5), 56.0 (C-7a), 53.3 (CH_3), 35.0 (C-3), 34.8 (C-4, CH_2), 34.1 (C-3a), 26.3 (C-7), 23.0 (C-6).

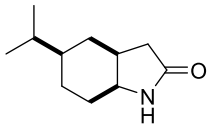
HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{17}NO$ 167.1305; Found 167.1311.

MS (EI^+, 70 eV): m/z (%) = 167 (25) $[M]^+$, 139 (95) $[M\text{-}C_2H_5]^+$, 96 (80) $[M\text{-}C_3H_5NO]^+$, 83 (100) $[M\text{-}C_4H_6NO]^+$.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3255 (m, N–H) 2936 (s, C_{sp3}–H), 2861 (m), 1686 (s, C=O), 1450 (m), 1372 (w), 1283 (w), 1147 (w), 1058 (w), 932 (w), 659 (w).

m.p. = 78-79 °C.

*3.1.12. (*3a*SR,*5*RS,*7a*SR)-5-Isopropyloctahydroindol-2-one* (**3m**)



Following GP2 the entitled compound **3m** was obtained as an off-white solid (83.7 mg, 462 μmol, 93%).

dr = 87:13.

***R*f** (80% EtOAc/Pentane): 0.25.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.31 (s, 1H, NH), 3.78 (*virt.* td, $^3J \approx {}^3J$ = 4.6 Hz, ^3J = 2.3 Hz, 1H, H-7a), 2.52 (dd, ^2J = 16.2 Hz, ^3J = 6.8 Hz, 1H, *H*H-3), 2.28 (*virt.* dp, ^3J = 11.7 Hz, $^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 6.1 Hz, 1H, H-3a), 2.01 – 1.83 (m, 2H, H*H*-3, *H*H-7), 1.60 – 1.34 (m, 4H, *H*H-4, H-5, *H*H-6 H*H*-7), 1.24 – 0.92 [m, 3H, H*H*-4, H*H*-6, C*H*$(CH_3)_2$], 0.87 [d, ^3J = 6.7 Hz, 6H, CH(C*H*$_3)_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 179.0 (CO), 53.5 (C-7a), 41.8 [*C*H$(CH_3)_2$], 40.5 (C-3), 35.4 (C-3a), 32.7 (C-5), 31.6 (C-4), 28.2 (C-7), 23.0 (C-6), 19.7 [CH(*C*H$_3)_2$], 19.6 [CH(*C*H$_3)_2$].

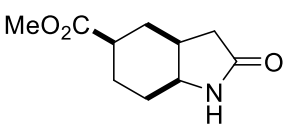
HRMS (EI) m/z: $[M]^+$ calcd for $C_{11}H_{19}ON$ 181.1461; Found 181.1460.

MS (EI^+, 70 eV): m/z (%) = 181 (22) $[M]^+$, 153 (3), 138 (5) $[M\text{-}C_2H_5]^+$, 96 (100) $[M\text{-}C_4H_8NO]^+$, 83 (10).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3210 (m, N–H), 2929 (s, C_{sp3}–H), 2868 (m), 1690 (s, C=O), 1441 (m), 1385 (w), 1271 (w), 1187 (w), 1025 (w), 967 (w), 715 (w).

m.p. = 94-96 °C.

*3.1.13. (*3a*SR,*5*RS,*7a*SR)-5-Methylcarboxy-octahydroindol-2-one* (**3n**)



Following GP2 the entitled compound **3n** was obtained as a colorless solid (95.6 mg, 436 μmol, 93%).

dr = 95:5.

***R*f** (EtOAc): 0.17.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.15 (s, 1H, NH), 3.87 – 3.77 (m, 1H, H-7a), 3.67 (s, 3H, $COOCH_3$), 2.56 (dd, ^2J = 16.5 Hz, ^3J = 6.7 Hz, 1H, *H*H-3), 2.34 (*virt.* dp, ^3J = 11.9 Hz, $^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 6.2 Hz, 1H, H-3a), 2.27 (*virt.* ddt, ^3J = 14.5 Hz, ^3J = 11.1 Hz, $^3J \approx {}^3J$ = 3.2 Hz, 1H, H-5), 2.07 – 1.96 (m, 2H, H*H*-3, *H*H-7), 1.95 – 1.75 (m, 2H, *H*H-4, *H*H-6), 1.71 – 1.52 (m, 2H, H*H*-6, H*H*-7), 1.46 (*virt.* dt, ^2J = 13.6 Hz, $^3J \approx {}^3J$ = 12.2 Hz, 1H, H*H*-4).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.7 (CO), 175.5 (*C*OOCH_3), 52.6 (C-7a), 51.9 (COO*C*H_3), 41.1 (C-5), 40.0 (C-3), 34.2 (C-3a), 30.0 (C-4), 27.0 (C-7), 22.6 (C-6).

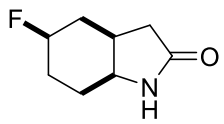
HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{15}NO_3$ 197.1046; Found 197.1044.

MS (EI$^+$, 70 eV): m/z (%) = 197 (40) [M]$^+$, 165 (30) [M-CH_3O]$^+$, 138 (25) [M-$C_2H_3O_2$]$^+$, 96 (100) [M-$C_3H_4NO_3$]$^+$, 83 (25).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3179 (m, N–H), 3079 (m, O-CH_3), 2935 (s, C_{sp3}–H), 2865 (m), 1722 (s, C=O), 1686 (s, C=O), 1431 (m), 1379 (w), 1289 (w), 1173 (w), 1035 (w), 988 (w), 752 (w).

m.p. = 147-149 °C.

*3.1.14. (*3a*RS,*5*RS,*7a*SR)-5-Fluorooctahydroindol-2-one* (**3o**)



Following GP2 the entitled compound **3o** was obtained as a colorless solid (67.9 mg, 432 μmol, 86%).

dr > 99:1.

***R*$_f$** (EtOAc): 0.18.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.16 (s, 1H, NH), 4.59 (*virt.* dtt, $^2J_{HF}$ = 51.8 Hz, $^3J \approx {}^3J$ = 9.1 Hz, $^3J \approx {}^3J$ = 4.0 Hz, 1H, H-5), 3.66 (*virt.* dt, ^3J = 8.7 Hz, $^3J \approx {}^3J$ = 4.8 Hz, 1H, H-7a), 2.52 – 2.43 (m, 2H, *H*H-3, H-3a), 2.20 (dd, ^2J = 12.0 Hz, ^3J = 7.4 Hz, 1H, H*H*-3), 2.03 – 1.90 (m, 2H, *H*H-4, *H*H-7), 1.85 – 0.93 (m, 4H, H*H*-4, H-6, H*H*-7).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.3 (CO), 89.6 (d, $^1J_{CF}$ = 171.8 Hz, C-5), 52.1 (C-7a), 38.6 (C-3), 33.9 (d, $^3J_{CF}$ = 7.6 Hz, C-3a), 33.0 (d, $^2J_{CF}$ = 19.2 Hz, C-4), 26.7 (d, $^2J_{CF}$ = 19.9 Hz, C-6), 25.2 (d, $^3J_{CF}$ = 8.9 Hz, C-7).

^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = −173.7.

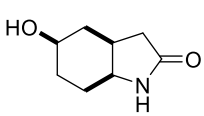
HRMS (EI) m/z: [M]$^+$ calcd for $C_9H_{12}NOF$ 157.0897; Found 157.0893.

MS (EI$^+$, 70 eV): m/z (%) = 157 (30) [M]$^+$, 126 (5), 96 (100) [M-CHNOF]$^+$, 83 (20).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3235 (m, N–H), 2945 (s, C_{sp3}–H), 2871 (m), 1687 (s, C=O), 1428 (m), 1371 (m), 1286 (s, C–F), 1132 (s), 1033 (m), 834 (w), 729 (w).

m.p. = 98-100 °C.

*3.1.15. (*3a*SR,*5*RS,*7a*SR)-5-Hydroxyoctahydroindol-2-one* (**3p**)



Following GP2 the entitled compound **3p** was obtained as a colorless oil (70.6 mg, 455 μmol, 86%).

dr = 93:7.

***R*$_f$** (EtOAc): 0.05.

^{1}H NMR (500 MHz, DMSO-d_6): δ [ppm] = 7.39 (s, 1H, NH), 4.50 (d, ^3J = 4.1 Hz, 1H, OH), 3.51 (*virt.* td, $^3J \approx {}^3J$ = 4.6 Hz, ^3J = 2.9 Hz, 1H, H-7a), 3.40 – 3.32 (m, 1H, H-5), 2.34 (dd, ^2J =15.7 Hz, ^3J = 6.8 Hz, 1H, *H*H-3), 2.27 – 2.19 (m, 1H,

H-3a), 1.82 (*virt.* dq, ^{2}J = 14.5 Hz, $^{3}J \approx {}^{3}J \approx {}^{3}J$ = 3.5 Hz, 1H, *H*H-7), 1.76 – 1.64 (m, 2H, H*H*-3, *H*H-4), 1.58 – 1.43 (m, 2H, *H*H-6, H*H*-7), 1.25 – 1.18 (m, 1H, H*H*-6), 1.01 (*virt.* dt, ^{2}J = 12.9 Hz, $^{3}J \approx {}^{3}J$ = 11.0 Hz, 1H, H*H*-4).

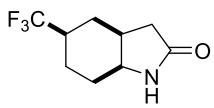
^{13}C NMR (126 MHz, DMSO-d_6): δ [ppm] = 176.8 (CO), 66.7 (C-5), 51.4 (C-7a), 39.8 (C-3), 37.0 (C-4), 34.1 (C-3a), 29.1 (C-6), 25.5 (C-7).

HRMS (EI) m/z: $[M]^+$ calcd for $C_8H_{13}NO_2$ 155.0939; Found 155.0936.

MS (EI^+, 70 eV): m/z (%) = 155 (44) $[M]^+$, 137 (40) $[M\text{-}OH_2]^+$, 96 (100) $[M\text{-}CH_2NO_2]^+$, 83 (40).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3361 (O–H) , 3189 (m, N–H), 2933 (s, C_{sp3}–H), 2865 (m), 1673 (s, C=O), 1425 (m), 1283 (w), 1173 (w), 1062 (m), 989 (w), 669 (w).

*3.1.16. (*3a*SR,*5*RS,*7a*SR)-5-Trifluoromethyloctahydroindol-2-one* (**3q**)



Following GP2 the entitled compound **3q** was obtained as an off-white solid (95.8 mg, 462 μmol, 93%).

dr = 95:5.

***R*$_f$** (EtOAc): 0.10.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.81 (s, 1H, NH), 3.83 (*virt.* td, $^{3}J \approx {}^{3}J$ = 4.5 Hz, ^{3}J = 2.5 Hz, 1H, H-7a), 2.57 (dd, ^{2}J = 16.4 Hz, ^{3}J = 6.8 Hz, 1H, *H*H-3), 2.36 (*virt.* dp, ^{3}J = 11.9 Hz, $^{3}J \approx {}^{3}J \approx {}^{3}J \approx {}^{3}J$ = 5.9 Hz, 1H, H-3a), 2.09 – 1.94 (m, 3H, H*H*-3, H-5, *H*H-7), 1.92 – 1.83 (m, 1H, *H*H-6), 1.82 – 1.73 (m, 1H, H*H*-6), 1.68 – 1.59 (m, 1H, *H*H-4), 1.56 – 1.43 (m, 1H, H*H*-7), 1.34 (*virt.* q, $^{2}J \approx {}^{3}J \approx {}^{3}J$ = 12.8 Hz, 1H, H*H*-4).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.1 (CO), 127.4 (q, $^{1}J_{CF}$ = 278.3 Hz, CF_3), 52.2 (C-7a), 40.2 (q, $^{2}J_{CF}$ = 27.2 Hz, C-5), 40.0 (C-3), 33.9 (C-3a), 26.6 (C-7), 26.3 (q, $^{3}J_{CF}$ = 2.6 Hz, C-4), 18.8 (q, $^{3}J_{CF}$ = 2.6 Hz, C-6).

^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = −73.9.

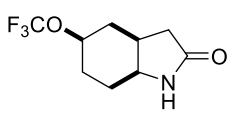
HRMS (EI) m/z: $[M]^+$ calcd for $C_9H_{12}NOF_3$ 207.0866; Found 207.0860.

MS (EI^+, 70 eV): m/z (%) = 207 (30) $[M]^+$, 163 (3), 149 (3), 135 (3), 96 (100) $[M\text{-}C_2HNOF_3]^+$.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3236 (m, N–H), 2949 (s, C_{sp3}–H), 2874 (m), 1696 (s, C=O), 1447 (m), 1341 (m), 1258 (s, C–F), 1159 (s), 1146 (s), 1119 (m), 1087 (m), 821 (w), 728 (w).

m.p. = 134-136 °C.

*3.1.17. (*3a*SR,*5*RS,*7a*SR)-5-(Trifluoromethoxy)octahydroindol-2-one* (**3r**)



Following GP2 the entitled compound **3r** was obtained as a colorless oil (73.9 mg, 331 μmol, 66%).

dr = 86:14.

***R*f** (EtOAc): 0.15.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.81 (s, 1H, NH), 3.68 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 5.1 Hz, 1H, H-7a), 2.40 – 2.31 (m, 1H, *H*H-3), 2.18 – 1.96 (m, 2H, H*H*-3, H-3a), 1.80 – 1.58 (m, 3H, H-4, H-5), 1.56 – 1.23 (m, 4H, H-6, H-7).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.9 (CO), 121.6 (q, $^1J_{CF}$ = 254.6, CF_3), 53.4 (C-7a), 37.9 (C-5), 34.4 (C-3), 28.7 (C-3a), 27.3 (C-7), 22.7 (C-4), 20.6 (C-6).

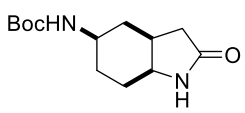
^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = −57.9.

HRMS (EI) m/z: $[M]^+$ calcd for $C_9H_{12}NO_2F_3$ 223.0815; Found 223.0814.

MS (EI^+, 70 eV): m/z (%) = 223 (10) $[M]^+$, 139 (25) $[M\text{-}CF_3O]^+$, 96 (100) $[M\text{-}C_2HNO_2F_3]^+$.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3224 (m, N–H), 2929 (s, C_{sp3}–H), 2856 (m), 1684 (s, C=O), 1447 (m), 1379 (w), 1279 (s, C_{sp3}–F), 1132 (s), 1018 (w), 862 (w), 704 (w).

*3.1.18. (*3a*SR,*5*RS,*7a*SR)-5-tert-Butyl(octahydroindole-2-one)carbamate* (**3s**)



Following GP2 the entitled compound **3s** was obtained as a colorless solid (89.5 mg, 352 μmol, 70%).

dr = 86:14.

***R*f** (EtOAc): 0.13.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.50 (s, 1H, NH), 4.38 (s, 1H, NHBoc), 3.76 (*virt.* td, $^3J \approx {}^3J$ = 4.4 Hz, ^3J = 2.2 Hz, 1H, H-7a), 3.41 (br s, 1H, H-5), 2.54 (dd, ^2J = 16.3 Hz, ^3J = 6.7 Hz, 1H, *H*H-3), 2.42 (*virt.* dp, ^3J = 11.8 Hz, $^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 5.9 Hz, 1H, H-3a), 2.00 – 1.86 (m, 3H, H*H*-3, *H*H-4, *H*H-7), 1.82 – 1.65 (m, 2H, *H*H-6, H*H*-7), 1.44 [s, 9H, $(CH_3)_3$], 1.35 – 1.22 (m, 1H, H*H*-6), 1.12 (*virt.* q, $^2J \approx {}^3J \approx {}^3J$ = 12.2 Hz, 1H, H*H*-4).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.8 (CO), 155.3 (*C*O*O*tBu), 79.6 (Me_3C), 52.4 (C-7a), 47.8 (C-5), 40.1 (C-3), 34.9 (C-3a), 34.8 (C-4), 28.5 [C(CH_3)$_3$], 26.8 (C-7), 26.8 (C-6).

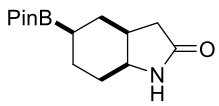
HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_{22}N_2O_3$ 254.1625; Found 254.1624.

MS (EI^+, 70 eV): m/z (%) = 254 (5) $[M]^+$, 198 (100) $[M\text{-}C_4H_9]^+$, 181 (40), 137 (75) $[M\text{-}C_5H_{10}NO_2]^+$, 96 (20), 83 (13).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3292 (m, N–H), 2975 (s, C_{sp3}–H), 2934 (s, C_{sp3}–H), 2866 (m), 1688 (s, C=O), 1525 (s, C=O), 1446 (m), 1390 (m), 1247 (w), 1170 (s), 1045 (m), 1022 (m), 921 (w), 731 (w).

m.p. = 149-151 °C.

*3.1.19. (*3a*SR,*5*RS,*7a*SR)-5-*(4,4,5,5-Tetramethyl-1,2,3-oxadiborolan-2-yl)Ioctahydroindol-2one (**3t**)



Following GP2 the entitled compound **3t** was obtained as a colorless solid (125.2 mg, 472 μmol, 94%).

dr = 95:5.

***R*f** (EtOAc): 0.23.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.31 (s, 1H, NH), 3.79 (*virt.* td, $^{3}J \approx {}^{3}J$ = 3.7 Hz, ^{3}J = 2.3 Hz, 1H, H-7a), 2.46 (dd, ^{2}J = 16.2 Hz, ^{3}J = 6.8 Hz, 1H, *H*H-3), 2.28 – 2.18 (m, 1H, H-3a), 1.99 – 1.91 (m, 1H, H*H*-3), 1.89 – 1.81 (m, 1H, *H*H-7), 1.76 – 1.66 (m, 1H, *H*H-6), 1.61 – 1.52 (m, 2H, H*H*-6, H*H*-7), 1.46 – 1.26 (m, 2H, H-4), 1.22 [s, 12H, $(CH_3)_2$], 0.85 (*virt.* tt, $^{3}J \approx {}^{3}J$ = 12.7 Hz, $^{3}J \approx {}^{3}J$ = 2.8 Hz, 1H, H-5).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.8 (CO), 83.2 (quart. C_{BPin}), 53.2 (C-7a), 40.1 (C-3), 35.0 (C-3a), 29.0 (C-7), 28.6 (C-6), 24.9 [C(CH_3)$_{2\ BPin}$], 21.2 (C-4), 19.5 (C-5).

^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = 34.0.

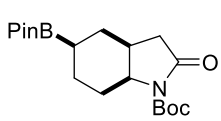
HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{24}BNO_3$ 265.1844; Found 265.1841.

MS (EI^+, 70 eV): m/z (%) = 265 (5) $[M]^+$, 207 (30), 182 (35), 165 (95) $[M\text{-}C_6H_{12}O]^+$, 96 (100) $[M\text{-}C_7H_{13}BNO_3]^+$, 83 (13).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3222 (m, N–H), 2977 (s, C_{sp3}–H), 2928 (s, C_{sp3}–H), 2857 (m), 1695 (s, C=O), 1381 (s), 1320 (s), 1145 (s), 1022 (m), 1006 (m), 853 (s), 661 (w).

m.p. = 170-172 °C.

*3.1.20. (*3a*SR,*5*RS,*7a*SR)-tert-Butyl-2-oxo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydroindole-1-carboxylate (***3u***)*



Following GP2 the entitled compound **3u** was obtained as a colorless oil (109 mg, 459 μmol, 92%).

dr = 95:5.

***R*f** (EtOAc): 0.53.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.97 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 6.4 Hz, ^{3}J = 4.8 Hz, 1H, H-7a), 2.45 – 2.38 (m, 2H, H-3), 2.40 – 2.28 (m, 1H, H-3a), 1.96 – 1.85 (m, 1H, *H*H-7), 1.83 – 1.70 (m, 2H, H*H*-7, *H*H-4), 1.70 – 1.57 (m, 2H, H*H*-4, *H*H-6), 1.52 [s, 9H, $C(CH_3)_3$], 1.47 – 1.39 (m, 1H, H*H*-6), 1.23 [s, 12H, $(CH_3)_2$], 1.15 – 1.07 (m, 1H, H-5).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 174.9 (CO), 150.3 (*C*OO*t*Bu), 83.4 (quart. C_{BPin}), 82.6 (Me_3C), 57.9 (C-7a), 38.1 (C-3), 31.4 (C-3a), 28.1 [C(CH_3)$_3$], 27.4 (C-7), 26.8 (C-6), 24.9 [C(CH_3)$_{2\ BPin}$], 24.8 (C-4), 22.5 (C-5).

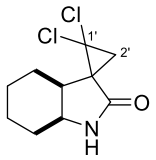
^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = 34.5.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{32}BNO_5$ 365.2351; Found 265.2368.

MS (EI^+, 70 eV): m/z (%) = 365 (5) $[M]^+$, 265 (30), 182 (35), 193 (45), 166 (100) $[M\text{-}C_{10}H_{16}BNO_3]^+$, 96 (45).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2978 (s, C_{sp3}–H), 2932 (s, C_{sp3}–H), 2860 (m), 1783 (s, C=O), 1750 (s, C=O), 1714 (s, C=O), 1307 (s), 1144 (s), 1022 (m), 853 (s), 661 (w).

*3.1.21. (1RS,3a'SR,7a'SR)-2,2-Dichlorohexahydrospiro[cyclopropane-1,3'-indol]-2'(1'H)-one (rac-**7**)*



Following GP2 the entitled compound *rac*-**7** was obtained as a colorless solid (94.8 mg, 437 µmol, 87%).

dr > 99:1.

***R*$_f$** (EtOAc): 0.45.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.47 (s, 1H, NH), 3.84 (*virt.* td, $^3J \approx {}^3J$ = 4.1 Hz, ^3J = 2.4 Hz, 1H, H-7a), 2.36 (*virt.* ddt, ^2J = 14.0 Hz, ^3J = 6.6 Hz, $^3J \approx {}^3J$ = 2.4 Hz, 1H, *H*H-4), 2.08 (*virt.* dt, ^3J = 10.3 Hz, $^3J \approx {}^3J$ = 4.9 Hz, 1H, H-3a), 1.93 (*virt.* dt, ^2J = 14.0 Hz, $^3J \approx {}^3J$ = 2.6 Hz, 1H, H*H*-4), 1.85 (d, ^2J = 6.5 Hz, 1H, *H*H-2'), 1.79 (d, ^2J = 6.5 Hz, 1H, H*H*-2'), 1.77 – 1.71 (m, 1H, *H*H-7), 1.66 – 1.62 (m, 1H, H*H*-7), 1.58 – 1.52 (m, 2H, H-6), 1.51 – 1.39 (m, 1H, *H*H-5), 1.21-1.16 (m, 1H, H*H*-5).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 174.1 (CO), 61.1 (C-1'), 49.9 (C-7a), 43.0 (C-3a), 41.3 (C-3), 32.0 (C-2'), 27.7 (C-7), 24.3 (C-4), 23.8 (C-5), 19.7 (C-6).

HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{13}NO^{35}Cl_2$ 233.0366; Found 233.0369;

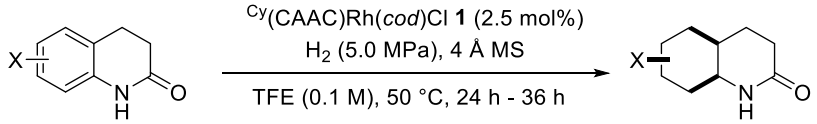
MS (EI^+, 70 eV): m/z (%) = 233 (55) $[M]^+$, 198 (100) $[M\text{-}Cl]^+$, 137 (40) $[M\text{-}C_2H_2Cl_2]^+$, 109 (80), 91 (15), 81 (22).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3269 (m, N–H), 2934 (s, C_{sp3}–H), 2859 (m), 1695 (s, C=O), 1708 (s), 1447 (w), 1381 (w), 1243 (w), 1047 (w), 933 (w), 870 (w), 763 (w).

m.p. = 167-169 °C.

Chiral HPLC = [CHIRALPAK AS-RH, 40 °C, 20% MeCN/H_2O (0 min) → 100% MeCN (30 min), 1 mL/min, 215 nm], t_{R1} = 12.9 min, t_{R2} = 14.7 min.

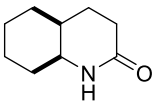
3.2. General Procedure 3 (GP3): Hydrogenation of 3,4-dihydroquinolone derivatives



4 **5**

Rhodium catalyst **1** (7.31 mg, 12.5 μmol, 2.5 mol%), the respective 3,4-dihydroquinolone derivative **4** (500 μmol, 1.0 equiv.) and powdered 4 Å MS (50 mg) were filled in an oven-dried 10 mL screw-cap vial equipped with a stirring bar. 2,2,2-Trifluoroethanol (5.0 mL) was added under argon atmosphere. The glass vial was placed in a 60 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the hydrogen pressure was set to 5.0 MPa. The reaction mixture was stirred at 50 °C for 24 h to 36 h. Afterwards, the autoclave was carefully depressurized. The crude mixture was filtered over *Celite* (eluent: ethyl acetate). After removal of all volatiles *in vacuo* the *dr* was determined by NMR analysis of the crude product. Subsequently, the crude material was purified by flash column chromatography (SiO_2, pentane/ethyl acetate = 4:1→ 1:1 → 0:1) yielding the entitled hydrogenated heterocycle **5**.

*3.2.1. (4aSR,8aSR)-Octahydroquinolin-2-one (**5a**)*



Following GP3 the entitled compound **5a** was obtained as a colorless solid (73.9 mg, 482 μmol, 96%).

dr > 99:1.

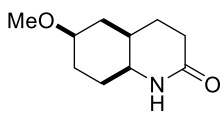
***R*f** (25% EtOAc/Pentane): 0.18.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.57 (s, 1H, NH), 3.52 (*virt*. td, $^3J \approx {}^3J$ = 5.9 Hz, ^3J = 4.0 Hz, 1H, H-8a), 2.51 – 2.27 (m, 2H, H-3), 2.01 – 1.79 (m, 2H, H-4), 1.78 – 1.16 (m, 9H, H-4a, H-5, H-6, H-7, H-8).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 172.5 (CO), 52.4 (C-8a), 33.0 (C-3), 31.7(C-4), 28.9 (C-4a), 26.5 (C-8), 24.5 (C-5), 23.5 (C-7), 21.5 (C-6).

Spectral data matche those reported in the literature.[13]

*3.2.2. (4aRS,6RS,8aSR)-6-Methoxyoctahydroquinolin-2-one (**5b**)*



Following GP3 the entitled compound **5b** was obtained as a colorless solid (85.9 mg, 469 μmol, 94%).

dr = 85:15

***R*f** (EtOAc): 0.12.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.37 (s, 1H, NH), 3.57 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 4.5 Hz, 1H, H-8a), 3.34 (s, 3H, OCH_3), 3.24 (*virt.* tt, $^3J \approx {}^3J$ = 9.6 Hz, $^3J \approx {}^3J$ = 3.6 Hz, 1H, H-6), 2.45 – 2.31 (m, 2H, H-3), 1.96 (*virt.* dp, ^3J = 12.1 Hz, $^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 4.2 Hz, 1H, H-4a), 1.93 – 1.83 (m, 2H, H-4), 1.84 – 1.71 (m, 3H, *H*H-5, *H*H-7, *H*H-8), 1.68 – 1.58 (m, 1H, H*H*-5), 1.56 – 1.39 (m, 2H, H*H*-7, H*H*-8).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 173.1 (CO), 77.7 (C-6), 55.9 (OCH_3), 51.3 (C-8a), 31.9 (C-4a), 30.5 (C-8), 28.9 (C-5), 27.5 (C-3), 25.5 (C-7), 25.3 (C-4).

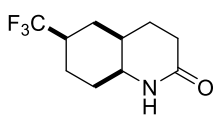
HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{17}NO_2$ 183.1259; Found 183.1253.

MS (EI^+, 70 eV): m/z (%) = 183 (20) $[M]^+$, 151 (100) $[M\text{-}CH_4O]^+$, 110 (30), 97 (20), 82 (10).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3180 (m, NH), 3051 (m), 2933 (s, C_{sp3}–H), 1653 (s, C=O), 1442 (w), 1353 (m), 1320 (s), 1120 (m), 1093 (s), 1006 (m), 917 (m), 735 (w).

m.p. = 170-173 °C.

*3.2.3. (4aRS,6RS,8aSR)-6-Trifluoromethyloctahydroquinolin-2-one (**5c**)*



Following GP3 the entitled compound **5c** was obtained as an off-white solid (97.1 mg, 439 μmol, 87%).

dr = 80:20.

***R*$_f$** (EtOAc): 0.14.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.07 (s, 1H, NH), 3.67 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 3.2 Hz, 1H, H-8a), 2.40 – 2.32 (m, 2H, H-3), 2.10 (dddd, ^3J = 15.6 Hz, ^3J = 11.8 Hz, ^3J = 7.8 Hz, ^3J = 3.7 Hz, 1H, H-6), 2.02 – 1.89 (m, 2H, *H*H-4, H-4a,), 1.87 – 1.71 (m, 3H, H*H*-4, *H*H-7, *H*H-8), 1.71 – 1.60 (m, 2H, *H*H-5, H*H*-8), 1.60 – 1.48 (m, 2H, H*H*-5, H*H*-7).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 172.8 (CO), 127.4 (q, ^1J = 278.6 Hz, CF_3), 50.5 (C-8a), 41.5 (q, ^2J = 27.1 Hz, C-6), 32.0 (C-4a), 30.1 (C-8), 26.8 (C-3), 25.9 (C-4), 22.8 (q, ^3J = 2.8 Hz, C-5), 18.3 (q, ^3J = 2.8 Hz, C-7).

^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = −73.8.

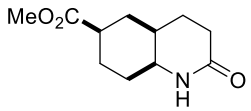
HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{14}NOF_3$ 221.1022; Found 221.1021.

MS (EI^+, 70 eV): m/z (%) = 221 (30) $[M]^+$, 110 (100) $[M\text{-}C_3H_3OF_3]^+$, 96 (5), 82 (7).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3208 (m, NH), 2946 (s, C_{sp3}–H), 1659 (s, C=O), 1409 (w), 1353 (m), 1335 (s), 1269 (s), 1160 (s), 1093 (s), 1060 (m), 835 (m), 738 (w).

m.p. = 126-128 °C.

*3.2.4. (4aRS,6RS,8aSR)-Methyl-2-oxodecahydroquinolin-6-carboxylate (***5d***)*



Following GP3 the entitled compound **5d** was obtained as an off-white solid (97.1 mg, 462 μmol, 91%).

dr = 90:10.

***R*f** (EtOAc): 0.10.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.60 (s, 1H, NH), 3.68 (s, 3H, COO*C*H$_3$), 3.64 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 3.2 Hz, 1H, H-8a), 2.44 – 2.31 (m, 3H, H-3, H-6), 1.99 – 1.87 (m, 2H, H-4a, *H*H-5), 1.84 – 1.73 (m, 3H, H*H*-5, *H*H-7, *H*H-8), 1.73 – 1.54 (m, 4H, H-4, H*H*-7, H*H*-8).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 175.5 (CO), 172.7 (*C*OOCH$_3$), 51.9 (COO*C*H$_3$), 50.9 (C-8a), 42.4 (C-6), 32.5 (C-4a), 30.9 (C-8), 27.1 (C-3), 26.7 (C-4), 26.0 (C-5), 22.1 (C-7).

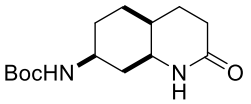
HRMS (EI) m/z: $[M]^+$ calcd for $C_{11}H_{17}NO_3$ 211.1203; Found 211.1189.

MS (EI^+, 70 eV): m/z (%) = 211 (25) $[M]^+$, 180 (15) $[M\text{-}CH_3O]^+$, 110 (100) $[M\text{-}C_4H_6O_3]^+$, 97 (15), 82 (5).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3192 (m, NH), 2942 (s, C_{sp3}–H), 1727 (s, C=O), 1656 (s, C=O), 1441 (w), 1337 (w), 1242 (w), 1176 (w), 1082 (w), 1033 (w), 837 (m), 738 (w).

m.p. = 162-164 °C.

*3.2.5. (4aSR,7SR,8aSR)-tert-Butyl-(2-oxodecahydroquinolin-7-yl)carbamate (***5e***)*



Following GP3 the entitled compound **5e** was obtained as a colorless solid (128 mg, 478 μmol, 94%).

dr = 73:27.

***R*f** (10% MeOH in DCM): 0.23.

^{1}H NMR (500 MHz, benzene-d_6): δ [ppm] = 6.42 (s, 1H, NH), 4.21 (s, 1H, NHBoc), 3.29 (*virt.* dt, ^3J = 11.2 Hz, $^3J \approx {}^3J$ = 3.8 Hz, 1H, H-8a), 2.62 (*virt.* t, $^3J \approx {}^3J$ = 10.5 Hz, 1H, H-7), 2.43 – 2.17 (m, 1H, H-4a), 2.15 – 1.99 (m, 2H, H-3), 1.49 [s, 9H, $(CH_3)_3$], 1.41 – 0.95 (m, 4H, H-6, H-8), 0.95 – 0.88 (m, 4H, H-4, H-5).

^{13}C NMR (126 MHz, benzene-d_6): δ [ppm] = 171.2 (CO), 155.0 (*C*O*t*Bu), 78.7 (Me_3C), 51.6 (C-8a), 47.8 (C-7), 37.3 (C-8), 32.4 (C-4a), 31.7 (C-3), 28.6 [C(CH_3)$_3$], 27.7 (C-6), 25.3 (C-5), 23.2 (C-4).

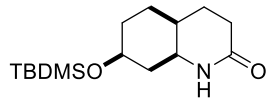
HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{24}N_2O_3$ 268.1781; Found 268.1787.

MS (EI^+, 70 eV): m/z (%) = 268 (20) $[M]^+$, 212 (100) $[M\text{-}C_4H_9]^+$, 182 (95), 151 (80) $[M\text{-}C_5H_{10}NO_2]^+$, 110 (90), 97 (55).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3289 (m, NH), 2932 (s, C_{sp3}–H), 1690 (s, C=O), 1655 (s, C=O), 1525 (m), 1365 (w), 1300 (m), 1170 (s), 1045 (m), 1021 (m), 778 (w), 710 (w).

m.p. = 194-196 °C.

*3.2.6. (4aSR,7SR,8aSR)-7-((tert-Butyldimethylsilyl)oxy)octahydroquinolin-2-one (**5f**)*



Following GP3 the entitled compound **5f** was obtained as a colorless solid (116 mg, 487 μmol, 87%).

dr = 98:2.

***R*f** (EtOAc): 0.10.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.92 (s, 1H, NH), 3.56 (*virt.* tt, $^{3}J \approx {}^{3}J$ = 8.9 Hz, $^{3}J \approx {}^{3}J$ = 4.0 Hz, 1H, H-7), 3.38 (*virt.* dt, ^{3}J = 8.0 Hz, $^{3}J \approx {}^{3}J$ = 4.1 Hz, 1H, H-8a), 2.48 – 2.19 (m, 2H, H-3), 2.03 – 1.88 (m, 2H, *H*H-4, H-4a), 1.84 (*virt.* dt, ^{2}J = 13.2 Hz, $^{3}J \approx {}^{3}J$ = 4.3 Hz, 1H, *H*H-8), 1.71– 1.35 (m, 6H, H*H*-4, H-5, H-6, H*H*-8), 0.83 [s, 9H, $C(CH_3)_3$], 0.02 [s, 3H, $Si(CH_3)$], 0.00 [s, 3H, $Si(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 171.7 (CO), 69.1 (C-7), 51.8 (C-8a), 40.4 (C-3), 32.2 (C-4a), 30.8 (C-8), 30.8 (C-6), 26.0 [C-5, $C(CH_3)_3$], 22.2 (C-4), 18.2 [$C(CH_3)_3$], −4.5 [$Si(CH_3)$], −4.6 [$Si(CH_3)$].

^{29}Si NMR (99 MHz, $CDCl_3$): δ [ppm] = 17.5.

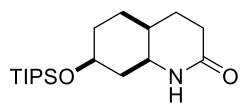
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{29}NO_2Si$ 283.1917; Found 283.1918.

MS (EI^+, 70 eV): m/z (%) = 283 (10) $[M]^+$, 226 (100) $[M\text{-}C_4H_9]^+$, 208 (50) $[M\text{-}C_5H_{12}]^+$, 110 (5), 93 (7).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3498 (m), 3179 (m, NH), 3037 (w), 2930 (s, C_{sp3}–H), 2858 (m), 1646 (s, C=O), 1413 (m), 1353 (w), 1257 (w), 1099 (m), 1097 (m), 1081 (m), 856 (m), 776 (w).

m.p. = 116-118 °C.

*3.2.7. (4aSR,7SR,8aSR)-7-((Triisopropylsilyl)oxy)octahydroquinolin-2-one (**5g**)*



Following GP3 the entitled compound **5g** was obtained as a colorless oil (148 mg, 453 μmol, 91%).

dr = 90:10.

***R*f** (EtOAc): 0.18.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.85 (s, 1H, NH), 3.70 (*virt.* tt, $^{3}J \approx {}^{3}J$ = 9.3 Hz, $^{3}J \approx {}^{3}J$ = 4.0 Hz, 1H, H-7), 3.42 (*virt.* dt, ^{3}J = 10.7 Hz, $^{3}J \approx {}^{3}J$ = 4.0 Hz, 1H, H-8a), 2.48 – 2.27 (m, 2H, H-3), 2.06 – 1.90 (m, 3H, H-4a, *H*H-4, *H*H-8), 1.85 – 1.40 {m, 9H, *H*H-4, H-5, H-6, *H*H-8, $Si[CH(CH_3)_2]_3$}, 1.06 – 1.03 {m, 18H, $Si[CH(CH_3)_2]_3$}.

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 172.2 (CO), 69.0 (C-7), 52.0 (C-8a), 40.5 (C-3), 32.0 (C-4a), 30.9 (C-8), 30.6 (C-6), 26.1 (C-5), 22.0 (C-4), 18.2 {s, $Si[CH(CH_3)_2]_3$}, 12.4 {s, $Si[CH(CH_3)_2]_3$}.

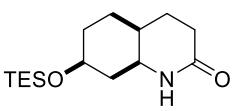
^{29}Si NMR (99 MHz, $CDCl_3$): δ [ppm] = 12.2.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{35}NO_2Si$ 325.2432; Found 325.2436.

MS (EI^+, 70 eV): m/z (%) = 325 (4) $[M]^+$, 282 (55) $[M\text{-}C_3H_7]^+$, 182 (100), 110 (10), 91 (4).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3210 (m, NH), 2939 (s, C_{sp3}–H), 2891 (w), 2865 (m), 1664 (s, C=O), 1464 (m), 1374 (m), 1299 (w), 1119 (s), 1096 (m), 1067 (m), 881 (m), 788 (w).

*3.2.8. (4aSR,7SR,8aSR)-7-((Triethylsilyl)oxy)octahydroquinolin-2-one (**5h**)*



Following GP3 the entitled compound **5h** was obtained as a colorless oil (126 mg, 444 μmol, 89%).

dr = 89:11.

***R*$_f$** (EtOAc): 0.21.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.04 (s, 1H, NH), 3.58 (tt, $^3J \approx {}^3J$ = 9.8 Hz, $^3J \approx {}^3J$ = 4.1 Hz, ^3J = 4.1 Hz, 1H, H-7), 3.41 (*virt.* dt, ^3J = 11.3 Hz, $^3J \approx {}^3J$ = 4.0 Hz, 1H, H-8a), 2.64 – 2.21 (m, 2H, H-3), 2.06 – 1.85 (m, 3H, *H*H-4, H-4a, *H*H-8), 1.83 – 1.38 (m, 6H, H*H*-4, H-5, H-6, H*H*-8), 0.94 (t, ^3J = 8.0 Hz, 9H, CH_2CH_3), 0.57 (q, ^3J = 8.0 Hz, 6H, CH_2CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 171.9 (CO), 69.0 (C-7), 51.9 (C-8a), 40.5 (C-3), 32.0 (C-4a), 31.0 (C-8), 30.7 (C-6), 26.4 (C-5), 21.9 (C-4), 7.0 (CH_2CH_3), 4.9 (CH_2CH_3).

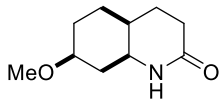
^{29}Si NMR (99 MHz, $CDCl_3$): δ [ppm] = 18.1.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{29}NO_2Si$ 283.1962; Found 283.1957.

MS (EI^+, 70 eV): m/z (%) = 283 (5) $[M]^+$, 254 (100) $[M\text{-}C_2H_5]^+$, 236 (50) $[M\text{-}C_3H_{12}]^+$, 103 (50), 93 (5).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3206 (m, NH), 2935(s, C_{sp3}–H), 2875 (w), 1661 (s, C=O), 1458 (m), 1376 (m), 1231 (w), 1160 (w), 1092 (s), 1075 (s), 845 (s), 741 (s).

*3.2.9. (4aSR,7SR,8aSR)-7-Methoxyoctahydroquinolin-2-one (**5i**)*



Following GP3 the entitled compound **5i** was obtained as a colorless solid (83.7 mg, 457 μmol, 92%).

dr = 90:10.

***R*$_f$** (EtOAc): 0.07.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.25 (s, 1H, NH), 3.48 – 3.39 (m, 1H, H-8a), 3.33 (s, 3H, CH_3), 3.15 (*virt.* tt, $^3J \approx {}^3J$ = 9.8 Hz, $^3J \approx {}^3J$ = 3.6 Hz, 1H, H-7), 2.52 – 2.28 (m, 2H, H-3), 2.10 – 2.01 (m, 2H, *H*H-8, H-4a), 2.01 – 1.91 (m, 1H, H*H*-8), 1.81 – 1.74 (m, 2H, H-6), 1.63 – 1.34 (m, 4H, H-4, H-5).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 171.9 (CO), 55.9 (C-7), 51.6 (C-8a), 36.3 (C-8), 32.2 (C-4a), 30.7 (C-3), 26.4 (OCH_3), 25.9 (C-5, C-6), 21.9 (C-4).

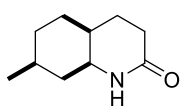
HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{17}NO_2$ 183.1254; Found 183.1257.

MS (EI^+, 70 eV): m/z (%) = 183 (10) $[M]^+$, 168 (45), 153 (100) $[M\text{-}CH_3O]^+$, 136 (20), 110 (50) $[M\text{-}C_3H_5NO]^+$, 97 (60).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3202 (m, NH), 2934 (s, C_{sp3}–H), 2867 (m), 1656 (s, C=O), 1471 (w), 1372 (w), 1297 (w), 1164 (w), 1096 (m), 1020 (w), 773 (w).

m.p. = 131-133 °C.

*3.2.10. (4aSR,7SR,8aSR)-7-Methyloctahydroquinolin-2-one (**5j**)*



Following GP3 the entitled compound **5j** was obtained as a colorless solid (78.3 mg, 468 μmol, 94%).

dr = 70:30.

***R*$_f$** (EtOAc): 0.24.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.18 (s, 1H, NH), 3.39 – 3.31 (m, 1H, H-8a), 2.43 – 2.27 (m, 2H, H-3), 2.11 – 2.03 (m, 1H, H-4a), 1.99-1.91 (m, 1H, *H*H-4), 1.89 – 1.69 (m, 2H, *H*H-5, *H*H-8), 1.67 – 1.34 (m, 3H, H*H*-4, H*H*-5, *H*H-6), 1.32 – 1.10 (m, 2H, H-7, H*H*-8), 1.07 – 0.95 (m, 1H, H*H*-6), 0.92 (d, ^3J = 6.4 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 172.0 (CO), 53.2 (C-8a), 39.8 (C-8), 32.2 (C-4a), 31.6 (C-3), 31.5 (C-7), 29.9 (C-5), 29.1 (C-6), 22.2 (CH_3), 21.39 (C-4).

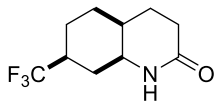
HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{17}NO$ 167.1310; Found 167.1319.

MS (EI^+, 70 eV): m/z (%) = 167 (25) $[M]^+$, 110 (100) $[M\text{-}C_3H_6O]^+$, 96 (3), 82 (5).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3204 (m, NH), 2923 (s, C_{sp3}–H), 2868 (m), 1659 (s, C=O), 1456 (w), 1329 (w), 1215 (w), 1116 (w), 980 (w), 773 (w), 705 (w).

m.p. = 128-130 °C.

*3.2.11. (4aSR,7SR,8aSR)-7-Trifluormethyloctahydroquinolin-2-one (**5k**)*



Following GP3 the entitled compound **5k** was obtained as a colorless solid (96.9 mg, 438 μmol, 88%).

dr = 64:36.

***R*$_f$** (EtOAc): 0.14.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 6.14 (s, 1H, NH), 3.43 (m, 1H, H-8a), 2.67 – 2.36 (m, 2H, H-3), 2.32 – 2.25 (m, 1H, H-7), 2.22 – 2.14 (m, 1H, H-4a), 2.10 – 1.95 (m, 2H, *H*H-8, *H*H-4), 1.95 – 1.85 (m, 1H, *H*H-6), 1.85 – 1.50 (m, 4H, H*H*-4, H-5, H*H*-6), 1.45 – 1.35 (m, 1H, H*H*-8).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 171.9 (CO), 127.0 (q, $^1J_{CF}$ = 278.3 Hz, CF_3), 51.8 (C-8a), 40.8 (q, $^2J_{CF}$ = 27.3 Hz, C-7), 31.7 (C-4a), 31.2 (C-3), 28.5 (C-4), 24.0 (q, $^3J_{CF}$ = 3.0 Hz, C-8), 20.8 (C-5), 19.2 (q, $^3J_{CF}$ = 2.8 Hz, C-6).

^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = −73.6.

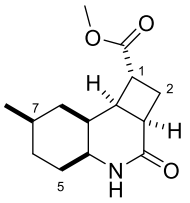
HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{14}NOF_3$ 221.1022; Found 221.1023.

MS (EI^+, 70 eV): m/z (%) = 221 (45) $[M]^+$, 110 (100) $[M\text{-}C_3H_3OF_3]^+$, 96 (5), 82 (8).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3211 (m, NH), 2942 (s, C_{sp3}–H), 1656 (s, C=O), 1409 (w), 1353 (m), 1335 (s), 1273 (s), 1149 (s), 1121 (s), 1095 (m), 861 (m), 702 (m).

m.p. = 142-144 °C.

*3.2.12. Methyl-(1RS,2aRS,4aSR,7RS,8aSR,8bRS)-7-methyl-3-oxododecahydrocyclobuta[c]quinoline-1-carboxylate (rac-**9**)*



Following GP3 the entitled compound *rac*-**9** was obtained as a colorless solid (117 mg, 464 μmol, 93%).

dr > 99:1.

***R*$_f$** (EtOAc): 0.43.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.43 (s, 1H, NH), 3.70 (s, 3H, OCH_3), 3.52 (*virt.* q, $^3J \approx {}^3J \approx {}^3J$ = 2.8 Hz, 1H, H-4a), 3.24 (ddd, ^3J = 10.6 Hz, ^3J = 9.1 Hz, ^3J = 7.1 Hz, 1H, H-2a), 3.08 (*virt.* dtd, ^3J = 9.8 Hz, $^3J \approx {}^3J$ = 7.1 Hz, ^4J = 1.4 Hz, 1H, H-1), 2.94 (dd, ^3J = 10.6 Hz, ^3J = 5.7 Hz, 1H, H-8b), 2.58 – 2.42 (m, 2H, H-2), 2.05 (*virt.* ddt, ^3J = 12.9 Hz, ^3J = 9.2 Hz, $^3J \approx {}^3J$ = 3.5 Hz, 1H, H-8a), 1.80 – 1.64 (m, 2H, H-5), 1.57 – 1.42 (m, 3H, H-6, H-7), 1.21 – 1.10 (m, 2H, H-8), 0.95 (d, ^3J = 6.4 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 175.5 (CO), 175.1 (COOMe), 52.1 (OCH_3), 50.3 (C-4a), 40.1 (C-2a), 37.0 (C-1), 36.5 (C-8a), 33.2 (C-8b), 32.2 (C-7), 31.4 (C-8), 30.0 (C-5), 28.0 (C-6), 25.6 (C-2), 22.6 (CH_3).

HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{21}NO_3$ 251.1516; Found 251.1516.

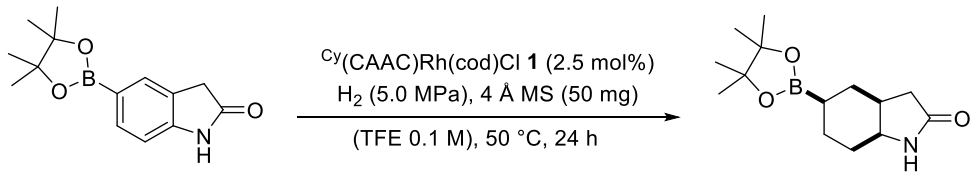
MS (EI^+, 70 eV): m/z (%) = 251 (30) $[M]^+$, 192 (30) $[M\text{-}C_2H_3O_2]^+$, 165 (90), 108 (100) $[M\text{-}C_7H_{12}O_3]^+$, 110 (90), 91 (5).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3203 (m, NH), 2949 (w), 2925 (s, C_{sp3}–H), 2870 (w), 1733 (s, C=O), 1633 (s, C=O), 1437 (m), 1372 (w), 1259 (m), 1173 (m), 1034 (m), 941 (m), 816 (w).

m.p. = 142-144 °C.

Chiral HPLC = [CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm], t_{R1} = 12.9 min, t_{R1} = 14.7 min.

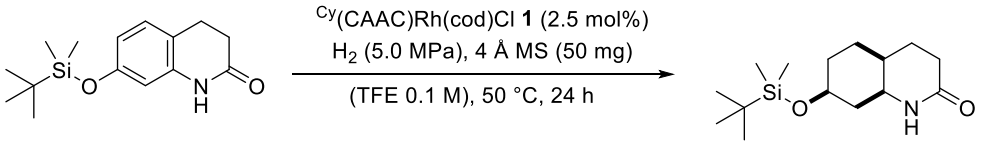
4. Gramm scale experiments



2t
(5.00 mmol)

3t
1.31 g
93%, dr = 95:5

The rhodium catalyst **1** (75.3 mg, 125 μmol, 2.5 mol%), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-2-one **2t** (1.30 g, 5.00 mmol, 1.0 equiv.) and powdered 4 Å MS (500 mg) were filled in a oven-dried 100 mL screw-cap vial. 2,2,2-trifluoroethanol (50.0 mL) was added under argon atmosphere. The glass vial was placed in a 250 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the hydrogen pressure was set to 5.0 MPa. The reaction mixture was stirred at 50 °C for 24 h. Afterwards, the autoclave was carefully depressurized. The crude mixture was filtered over *Celite*® (eluent: ethyl acetate). After removal of all volatiles *in vacuo* the diastereomeric ratio was determined *via* NMR analysis of the crude product as well as the overall yield was determined (1.31 g, 4.81 mmol, 98%, *dr* = 95:5). Following, the crude material was purified by flash column chromatography (SiO_2, pentane/ethyl acetate = 4:1→ 1:1 → 0:1) yielding the major diastereoisomer **3t** as colorless powder (1.24 g, 4.68 mmol, 93%).



4f
(5.00 mmol)

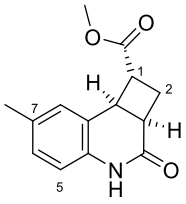
5f
1.40 g
98%, dr = 98:2

The rhodium catalyst **1** (75.3 mg, 125 μmol, 2.5 mol%), 7-((tert-butyldimethylsilyl)oxy)-3,4-dihydroquinolin-2(1H)-one **4f** (1.39 g, 5.00 mmol, 1.0 equiv.) and powdered 4 Å MS (500 mg) were filled in a oven-dried 100 mL screw-cap vial. TFE (50.0 mL) was added under argon atmosphere. The glass vial was placed in a 250 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the hydrogen pressure was set to 5.0 MPa. The reaction mixture was stirred at 50 °C for 24 h. Afterwards, the autoclave was carefully depressurized. The crude mixture was filtered over *Celite*® (eluent: ethyl acetate). After removal of all volatiles *in vacuo* the diastereomeric ratio was determined *via* NMR analysis of the crude product as well as the overall yield was determined (1.40 g, 4.89 mmol, 98%, *dr* = 98:2). Following, the crude material was purified by flash column chromatography (SiO_2, pentane/ethyl acetate = 4:1→ 1:1 → 0:1) yielding the major diastereoisomer **5f** as colorless powder (1.35 g, 4.79 mmol, 96%).

5. Enantioselective intermolecular [2 + 2] photocycloaddition

*5.1.1. Methyl (1R,2aR,8bR)-7-methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-1-carboxylate (**8**)*

The synthesis was conducted according to a modified literature procedure.[14]



Racemic [2+2] photocycloaddition: 6-Methyl-2(1H)-quinolone (20 mg, 140 μmol, 1.0 equiv.) and thioxanthen-9-one (15 mg, 0.07 mmol, 0.5 equiv.) were dissolved in acetonitrile (10 mL). After degassing the solution, methyl acrylate (125 μl, 1.40 mmol, 10.0 equiv.) 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 (SiO_2, pentane:EtOAc 1:1). The title compound was obtained as a colorless solid (22.4 mg, 0.10 mmol, 69%).

Enantioselective [2+2] photocycloaddition: 6-Methyl-2(1H)-quinolone (22.0 mg, 150 μmol, 1.0 equiv.) and chiral thioxanthen-9-one (6.6 mg, 15.0 μmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (60 mL). After degassing the solution, methyl acrylate (113 μl, 750 μmol, 50.0 equiv.) 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 was obtained as a colorless solid (30.3 mg, 124 μmol, 82%, 70% *ee*).

dr > 99:1.

***R*f** (EtOAc): 0.65.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.20 (s, 1H, NH), 6.97 (dd, ^3J = 8.2 Hz, ^3J = 2.3 Hz, 1H, H-6), 6.92 (s, 1H, H-8), 6.64 (d, ^3J = 8.2 Hz, 1H, H-5), 3.98 (*virt.* t, $^3J \approx {}^3J$ = 8.8 Hz, 1H, H-8b), 3.74 (s, 3H, OCH_3), 3.36 – 3.26 (m, 2H, H-1, H-2a), 2.84 (*virt.* dt, ^2J = 12.4 Hz, $^3J \approx {}^3J$ = 9.7 Hz, 1H, *H*H-2), 2.63 (*virt.* dt, ^2J = 12.4 Hz, $^3J \approx {}^3J$ = 8.3 Hz, 1H, H*H*-2), 2.27 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 174.0 (CO), 172.4 (*C*$OOCH_3$), 134.3 (C-4a), 133.4 (C-7), 129.0 (C-6), 128.5 (C-8), 122.4 (C-8a), 115.8 (C-5), 52.2 (OCH_3), 45.1 (C-2a) , 40.1 (C-8b), 34.9 (C-1), 29.4 (C-2), 20.9 (CH_3).

HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{15}NO_3$ 245.1046; Found 245.1042.

MS (EI^+, 70 eV): m/z (%) = 245 (30) $[M]^+$, 186 (100) $[M\text{-}C_2H_3O_2]^+$, 159 (90) $[M\text{-}C_4H_6O_2]^+$, 110 (90), 91 (5).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3203 (m, NH), 3060 (w), 2952 (s, C_{sp3}–H), 1731 (s, C=O), 1668 (s, C=O), 1508 (s), 1376 (m), 1241 (m), 1172 (m), 1034 (m), 962 (w), 819 (m).

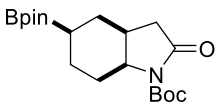
m.p. = 151-154 °C.

Chiral HPLC = [CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm], t_{R1} = 14.7 min, t_{R2} = 17.1 min.

6. Application

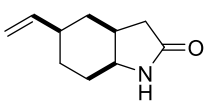
6.1. Functionalization of the borylated indolin-2-ones

*6.1.1. (*3a*SR,*5*RS,*7a*SR)-tert-Butyl-2-oxo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-1H-indole-1-carboxylate (**3u**)*



Octahydroindolin-2-one **3t** (500 mg, 1.89 mmol, 1.0 equiv.) was dissolved in THF (10 mL). 4-(Dimethylamino)pyridine (46.1 mg, 377 mmol, 0.2 equiv.), and di-*tert*-butyl dicarbonate (1.23 g, 5.66 mmol, 3.0 equiv.) in THF (19 mL) were added and the mixture was stirred at 60 °C for 3 h. After removal of all volatiles *in vacuo* the crude product was purified by flash column chromatography (SiO_2, hexane/EtOAc 80:20) to yield the protected heterocycle **3u** as a colorless oil (634 mg, 1.81 mmol, 96%). The analytical data are in accordance with the previous obtained product **3u**.

*6.1.2. (3aSR,5RS,7aSR)-5-vinyloctahydro-2H-indol-2-one (**3v**)*



The synthesis was conducted according to a modified literature procedure.[15] Vinyl magnesium bromide (1.00 mL, 1.0 M in THF, 1.00 mmol, 5.0 equiv.) was added dropwise to a solution of pinacol ester **3t** (53.0 mg, 200 μmol, 1.0 equiv.) in THF (2.00 mL) at –78 °C and reaction mixture was stirred for 1h at –78 °C. Following, a solution of I_2 (253 mg, 1.00 mmol, 5.0 equiv.) dissolved in MeOH (2.00 mL) was added at –78 °C and the reaction was stirred for an additional hour at – 78 °C. The mixture was warmed to 0 °C and afterwards the reaction was quenched by addition of a saturated aqueous solution of NaS_2O_3 (3 mL). Subsequently, water (10 mL) and ethyl acetate (20 mL) were added, the organic layer was separated, and the aqueous phase was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (30 mL), dried over $NaSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane/ethyl acetate = 4:1→ 1:1 → 0:1) yielding **3v** as a colorless solid (26.1 mg, 158 μmol, 79%).

dr = 95:5.

R_f (EtOAc): 0.25.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 5.73 (ddd, ^3J = 17.2 Hz, ^3J = 10.4 Hz, ^3J = 6.5 Hz, 1H, C*H*=CH_2), 5.42 (s, 1H, NH), 4.98 (*virt.* dt, ^3J = 17.2 Hz, $^2J \approx {}^4J$ = 1.4 Hz, 1H, CH=CH_2), 4.93 (*virt.* dt, ^3J = 10.4 Hz, $^2J \approx {}^4J$ = 1.4 Hz, 1H, CH=CH_2), 3.80 (*virt.* td, $^3J \approx {}^3J$ = 4.5 Hz, ^3J = 2.3 Hz, 1H, H-7a), 2.53 (dd, ^2J = 16.2 Hz, ^3J = 6.7 Hz, 1H, *H*H-3), 2.32 (*virt.* dp, ^3J = 11.9 Hz, $^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 5.9 Hz, 1H, H-3a), 2.01 – 1.88 (m, 3H, H*H*-3, *H*H-4, H-5), 1.72 – 1.66 (m, 1H, *H*H-7), 1.62 – 1.53 (m, 1H, H*H*-7), 1.34 – 1.21 (m, 2H, H-6), 1.14 (*virt.* dt, ^2J = 13.4 Hz, $^3J \approx {}^3J$ = 12.1 Hz, 1H, H*H*-4).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.7 (CO), 143.2 (*C*H=CH_2), 112.8 (CH=*C*H_2), 52.8 (C-7a), 40.4 (C-3), 39.4 (C-5), 34.8 (C-3a), 33.8 (C-4), 27.5 (C-7), 25.7 (C-6).

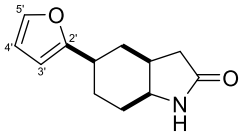
HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{15}NO$ 165.1148; Found 165.1148.

MS (EI$^+$, 70 eV): m/z (%) = 165 (25) [M]$^+$, 139 (5), 106 (5), 96 (100) [M-C_3H_4NO]$^+$.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3224 (m, NH), 3081 (w, C_{sp3}–H), 2927 (s, C_{sp3}–H), 1690 (s, C=O), 1425 (w), 1525 (w), 1382 (w), 1306 (w), 1181 (w), 1107 (m), 997 (m), 910 (m), 720 (w).

m.p. = 146-148 °C.

*6.1.3. (3aSR,5RS,7aSR)-5-(furan-2-yl)octahydro-2H-indol-2-one (**3w**)*



The synthesis was conducted according to a modified literature procedure.[16] A solution of furane (31.1 μL, 440 μmol, 2.2 equiv.) in THF (1.0 mL) was cooled to –78 °C, *n*-BuLi (176 μL, 2.5 M in THF, 1.00 mmol, 2.2 equiv.) was added dropwise, and the reaction mixture was stirred for 1h at rt. Following, a solution of the boronic ester **3t** (53.3 mg, 200 μmol, 1.0 equiv.) dissolved in THF (1.5 mL) was added at –78 °C and the reaction was stirred for 3h at –78 °C. Afterwards, a solution of *N*-bromosuccinimide (78.3 mg, 440 μmol, 2.2 equiv.) in THF (1.0 mL) was added dropwise and the reaction was stirred for 3h at –78 °C. The mixture was warmed to 0 °C and afterwards the reaction was quenched by addition of a saturated aqueous solution of NaS_2O_3 (5 mL). Subsequently, water (10 mL) and ethyl acetate (20 mL) were added, the organic layer was separated, and the aqueous phase was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (30 ml), dried over $NaSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, pentane/ethyl acetate = 4:1→ 1:1 → 0:1) yielding **3w** as a colorless solid (29.6 mg, 144 μmol, 72%).

dr = 95:5.

***R*$_f$** (EtOAc): 0.26.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.29 (dd, ^3J = 1.9 Hz, ^4J = 0.8 Hz, 1H, H-5'), 6.28 (dd, ^3J = 3.3 Hz, ^3J = 1.9 Hz, 1H, H-4'), 5.96 (*virt.* dt, ^3J = 3.3 Hz, $^4J \approx {}^4J$ = 0.9 Hz, 1H, HH-3'), 5.40 (s, 1H, NH), 3.86 (*virt.* td, $^3J \approx {}^3J$ = 4.5 Hz, ^3J = 2.4 Hz, 1H, H-7a), 2.66 – 2.52 (m, 2H, *H*H-3, H-3a), 2.42 (*virt.* tt, $^3J \approx {}^3J$ = 11.8 Hz, $^3J \approx {}^3J$ = 6.0 Hz, 1H, H-5), 2.05 – 1.96 (m, 3H, H*H*-3, *H*H-4, *H*H-7), 1.93 – 1.82 (m, 1H, *H*H-6), 1.76 (virt. ddt, ^2J = 14.9 Hz, ^3J = 13.3 Hz, $^3J \approx {}^3J$ = 4.2 Hz, 1H, *H*H-7), 1.54 (*virt.* tdd, $^3J \approx {}^3J$ = 13.2 Hz, ^2J = 11.8 Hz, ^3J = 3.6 Hz, 1H, H*H*-6), 1.44 (*virt.* dt, ^2J = 13.4 Hz, $^3J \approx {}^3J$ = 12.1 Hz, 1H, H*H*-4).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 178.4 (CO), 159.2 (C-2'), 140.8 (C-5'), 110.0 (C-4'), 103.1 (C-3'), 52.5 (C-7a), 40.1 (C-3), 34.9 (C-5), 34.6 (C-3a), 32.6 (C-4), 27.4 (C-7), 24.8 (C-6).

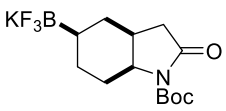
HRMS (EI) m/z: [M]$^+$ calcd for $C_{12}H_{15}NO_2$ 205.1097; Found 205.1097.

MS (EI$^+$, 70 eV): m/z (%) = 205 (100) [M]$^+$, 136 (30) [M-C_3H_5O]$^+$, 109 (50), 151 (80) [M-$C_5H_{10}NO_2$]$^+$, 96 (80).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3222 (m, NH), 2931 (s, C_{sp3}–H), 2859 (w), 1736 (m), 1691 (s, C=O), 1507 (m), 1444 (m), 1325 (m), 1008 (s), 930 (w), 885 (w), 734 (w).

m.p. = 155-157 °C.

*6.1.4. (3aSR,5RS,7aSR)-Potassium 1-(tert-butoxycarbonyl)-2-oxooctahydro-1H-indol-5-yl)trifluoroborate (**10**)*



The synthesis was conducted according to a modified literature procedure.[17] Protected pinacol ester **3u** (150 mg, 417 μmol, 1.0 equiv.) was dissolved in methanol (1.27 mL) and an aqueous solution of KHF_2 (0.93 mL, 4.18 mmol, 10.0 equiv., 4.5 M) was added. The resulting mixture was stirred for 17 h at room temperature then concentrated *in vacuo*. The residue was washed with hot acetone and the combined filtrate were concentrated. The crude residue was washed with pentane and diethyl ether. Subsequently, the product was dried to afford the corresponding trifluoroborate potassium salt **10** as a colorless solid (111 mg, 321 μmol, 83%).

dr = 95:5.

^{1}H NMR (500 MHz, acetone-d_6): δ [ppm] = 3.94 (*virt.* td, ^3J = 5.4 Hz, ^3J = 4.2 Hz, 1H, H-7a), 2.46 – 2.36 (m, 1H, *H*H-3), 2.25 (*virt.* dt, ^2J = 14.1 Hz, $^3J \approx {}^3J$ = 5.7 Hz, 1H, *H*H-4), 2.16 – 2.06 (m, 2H, H*H*-3, H-3a), 1.67 – 1.57 (m, 2H, H-7), 1.48 [s, 9H, C(CH_3)$_3$], 1.43 – 1.34 (m, 1H, *H*H-6), 1.24 – 1.18 (m, 2H, H*H*-5, H*H*-6), 1.10 (ddd, ^2J = 14.1 Hz, ^3J = 11.5 Hz, ^3J = 10.2 Hz, 1H, H*H*-4).

^{13}C NMR (126 MHz, acetone-d_6): δ [ppm] = 175.9 (CO), 151.7 (*C*O*t*Bu), 81.9 (Me_3C), 59.2 (C-7a), 40.9 (C-3), 33.3 (C-3a), 31.1 (C-7), 28.3 [C(*C*H_3)$_3$], 28.2 (C-4), 25.2 (C-5), 23.0 (C-6).

^{11}B NMR (128 MHz, acetone-d_6): δ [ppm] = 5.2.

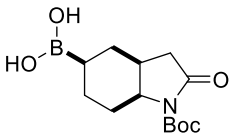
^{19}F NMR (376 MHz, acetone-d_6): δ [ppm] = −144.2.

HRMS (ESI) m/z: $[M\text{-}K]^-$ calcd. for $C_{13}H_{20}NO_3BF_3$ 306.1494; Found 306.1497.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3533 (w), 2978 (m), 2928 (s, C_{sp3}–H), 2855 (w), 1771 (s, C=O), 1717 (s, C=O), 1456 (w), 1348 (w), 1290 (s), 1157 (s), 1012 (m), 961 (m), 850 (w), 787 (w).

m.p. > 220 °C.

*6.1.5. (3aSR,5RS,7aSR)-(tert-Butoxycarbonyl)-2-oxooctahydro-1H-indol-5-yl) boronic acid (**11**)*



The synthesis was conducted according to a modified literature procedure.[18] Protected pinacol ester **3u** (150 mg, 417 μmol, 1.0 equiv.) was dissolved in acetone/H_2O (2 mL, 1:1, v/v), $NaIO_4$ (178 mg, 834 μmol, 2.0 equiv.) and NH_4OAc (300 mg, 834 μmol, 2.0 equiv.) were added. The reaction mixture was stirred at room temperature for 48 h. After addition of water and ethyl acetate the organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over $NaSO_4$, filtered and concentrated *in vacuo*. The crude alkyl boronic acid was washed with pentane and Et_2O to give the corresponding alkyl boronic acid **11** as a colorless solid (97.9 mg, 346 μmol, 77%).

dr = 95:5.

^{1}H NMR (500 MHz, DMSO-d_6): δ [ppm] = 4.79-3.81 (s, 2H, OH), 3.82 – 3.57 (m, 1H, H-7a), 2.78 – 2.54 (m, 1H, H-5), 2.44 – 2.17 (m, 2H, H-3), 1.96 – 1.57 (m, 3H, H-3a, *H*H-4, *H*H-7), 1.44 [m, 12H, H-6, H*H*-7, C(CH_3)$_3$], 1.32 – 1.01 (m, 1H, H*H*-4).

^{13}C NMR (126 MHz, DMSO-d_6): δ [ppm] = 174.2 (CO), 150.1 (*C*OO*t*Bu), 81.9 (Me$_3$*C*), 64.7 (C-5), 57.1 (C-7a), 38.9 (C-3), 33.5 (C-3a), 30.3 (C-7), 29.5 (C-4), 28.1 [C(*C*H$_3$)$_3$], 22.5 (C-6).

^{11}B NMR (128 MHz, DMSO-d_6): δ [ppm] = 1.6.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_{22}BNO_5$ 283.1519; Found 283.1524.

MS (EI^+, 70 eV): m/z (%) = 283 (20) $[M]^+$, 238 (100) $[M\text{-}BH_2O_2]^+$, 226 (85) $[M\text{-}C_4H_9]^+$, 182 (95), 137 (80), 97 (55).

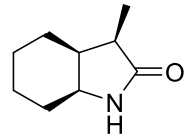
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3468 (m, OH), 2932 (s, C_{sp3}–H), 1775 (s, C=O), 1715 (s, C=O), 1458 (m), 1369 (s), 1288 (s), 1153 (s), 1051 (m), 981 (m), 851 (w), 778 (w).

m.p. = 115 - 117 °C.

7. Hydrogenation of enantioenriched starting materials

7.1. Indol-2-one derivatives

*7.1.1. (3R,3aS,7aS)-3-Methyloctahydro-2H-indol-2-one (ent-**3f**)*

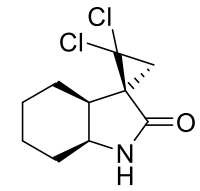


94%, dr = 90:10
*(*95% *ee)*

Following GP2 employing the enantiopure starting material *ent*-**2f** (95% *ee*) the entitled enantiopure compound *ent*-**3f** was obtained as a colorless solid (72.1 mg, 471 μmol, 94%, *dr* = 90:10, 95% *ee*). The analytical data are in accordance with the racemic product **3f**. Enantiomeric excess was determined by chiral GC.

Chiral GC = 95% *ee*; [CycloSil-B, 60 °C (0 min), 150 °C (10 °C/min), 150 °C (50 min), 250 °C (10 °C/min), 250 °C (3 min)], t_{R1} = 44.1 min (minor), t_{R2} = 44.6 min (minor); t_{R1} = 48.1 min (major), t_{R2} = 49.1 min (major).

*7.1.2. (1R,3a'S,7a'S)-2,2-Dichlorohexahydrospiro[cyclopropane-1,3'-indol]-2'(1'H)-one (**7**)*



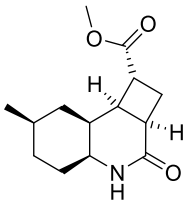
87%, dr > 99:1
(>99% ee)

Following GP2 employing the enantiopure starting material **6** (>99% *ee*) the entitled enantiopure compound **7** was obtained as a colorless solid solid (94.3 mg, 437 μmol, 87%, dr > 99:1, >99% *ee*). The analytical data are in accordance with the racemic product *rac*-**7**. Enantiomeric excess was determined by chiral HPLC.

Chiral HPLC = >99% *ee*; [CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm], t_{R1} = 12.9 min, t_{R2} = 14.7 min.

7.2. Quinoline-2-one derivatives

*7.2.1. Methyl (1R,2aR,4aS,7R,8aS,8bR)-7-methyl-3-oxododecahydrocyclobuta[c]quinoline-1-carboxylate (**9**)*



93%, dr > 99:1
(70% ee)

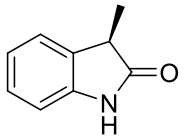
Following GP3 employing the enantioenriched starting material **8** (70% *ee*) the entitled enantioenriched compound **9** was obtained as a colorless solid (117 mg, 464 μmol, 93%, dr > 99:1, 70% *ee*). The analytical data are in accordance with the racemic product *rac*-**9**. Enantiomeric excess was determined by chiral HPLC.

Chiral HPLC = 70% *ee*; [CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm], t_{R1} = 12.9 min, t_{R2} = 14.7 min.

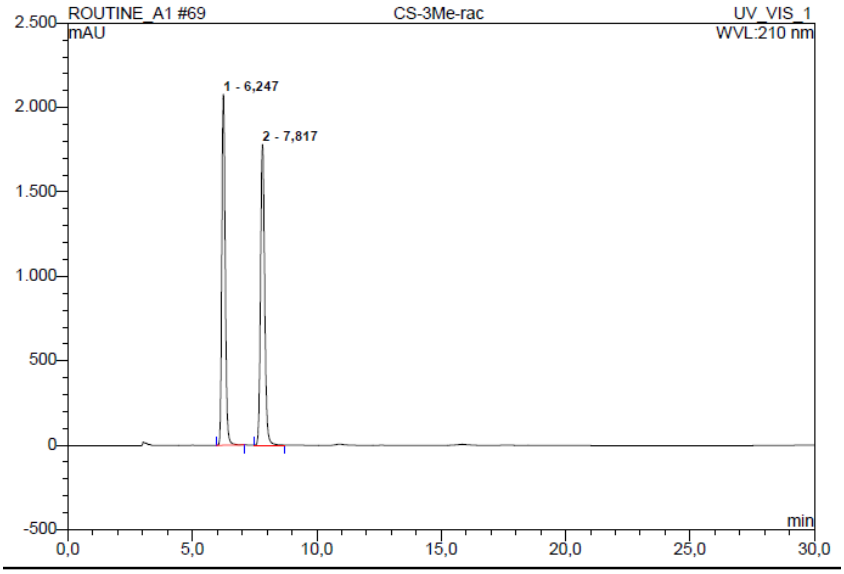
8. Chiral GC and chiral HPLC traces

8.1. Indol-2-one derivatives

*8.1.1. (R)-3-Methylindolin-2-one (**2f**)*

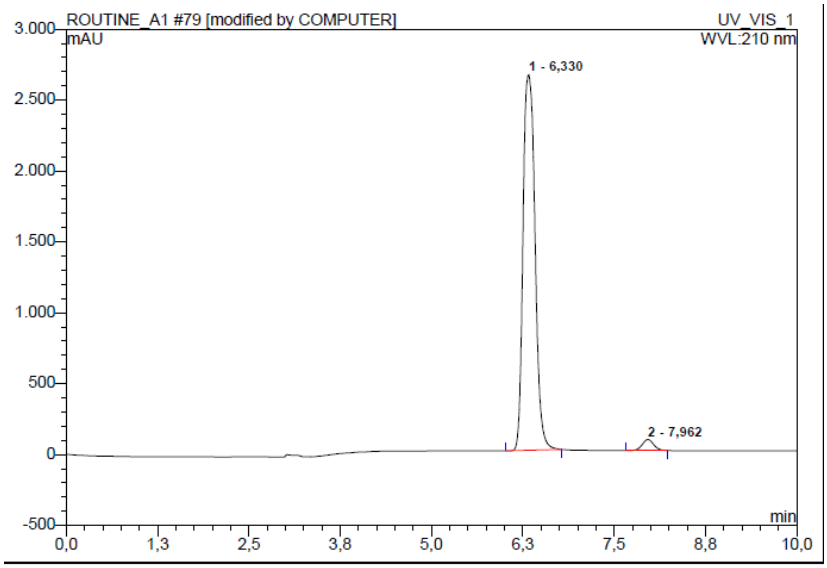


racemic product



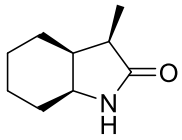
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,25	n.a.	2077,211	333,513	49,15	n.a.	BMB
2	7,82	n.a.	1778,805	344,999	50,85	n.a.	BMB
Total:			3856,016	678,512	100,00	0,000	

enantioenriched product (*95% ee*)

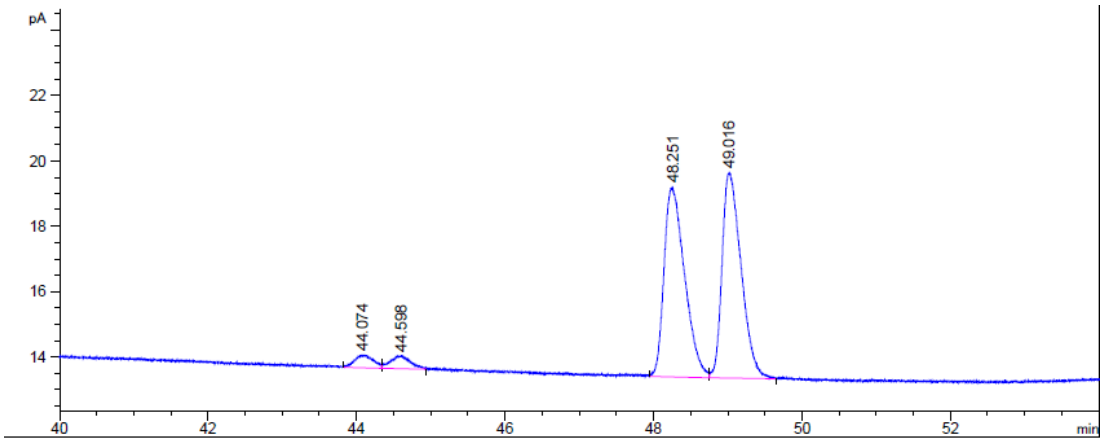


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,33	n.a.	2649,307	503,490	97,22	n.a.	BMB*
2	7,96	n.a.	78,404	14,403	2,78	n.a.	BMB*
Total:			2727,711	517,893	100,00	0,000	

*8.1.2. (3R,3aS,7aS)-3-Methyloctahydro-2H-indol-2-one (**3f**)*

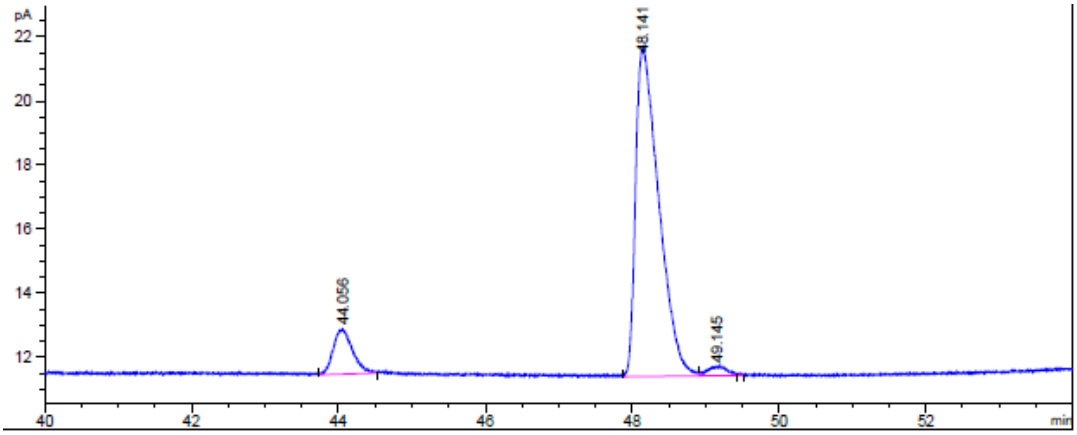


racemic product



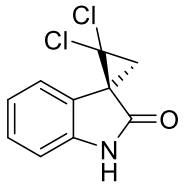
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.074	BV	0.2106	7.06227	4.01898e-1	2.96548
2	44.598	VB	0.2259	7.46398	3.88223e-1	3.13416
3	48.251	BV	0.2281	111.60492	5.81133	46.86337
4	49.016	VB	0.2136	112.01842	6.28295	47.03700

enantioenriched product (*95% ee*)

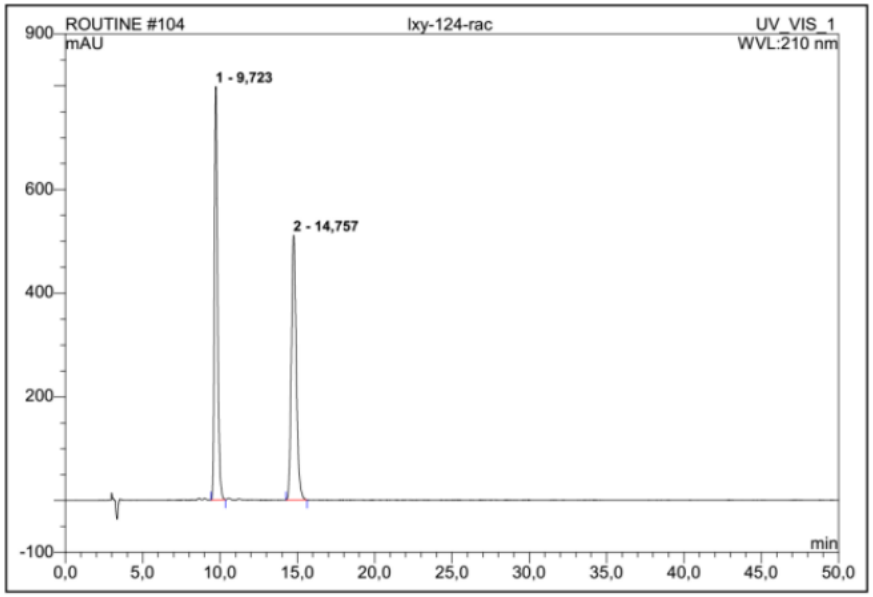


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.056	BB	0.2182	25.59575	1.39402	9.98961
2	48.141	BV R	0.2655	225.07367	10.26320	87.84264
3	49.145	VV E	0.2353	5.55430	2.77282e-1	2.16776

*8.1.3. (S)-2,2-Dichlorospiro[cyclopropane-1,3'-indolin]-2'-one (**6**)*

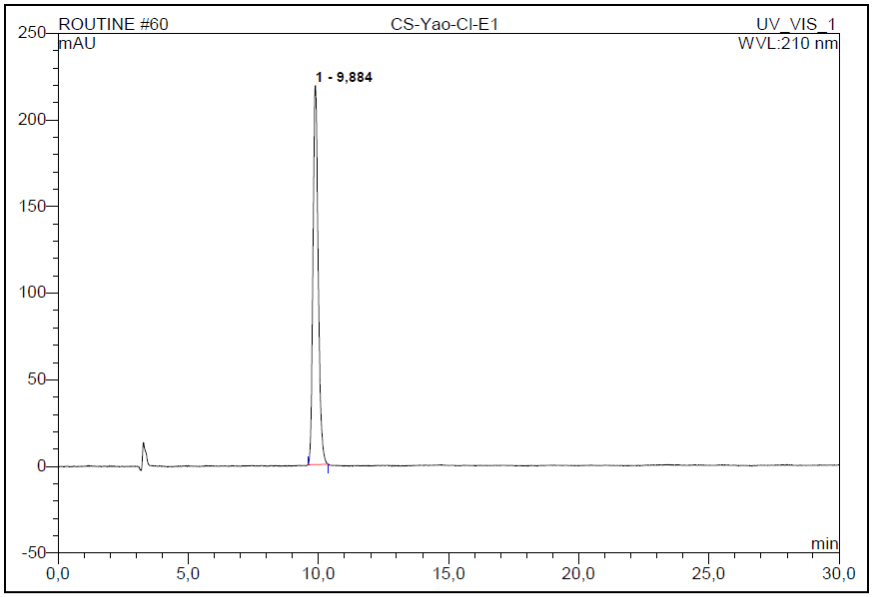


racemic product



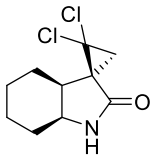
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,72	n.a.	797,103	187,676	49,87	n.a.	BMB
2	14,76	n.a.	510,560	188,654	50,13	n.a.	BMB
Total:			1307,663	376,330	100,00	0,000	

enantioenriched product (*> 99% ee*)

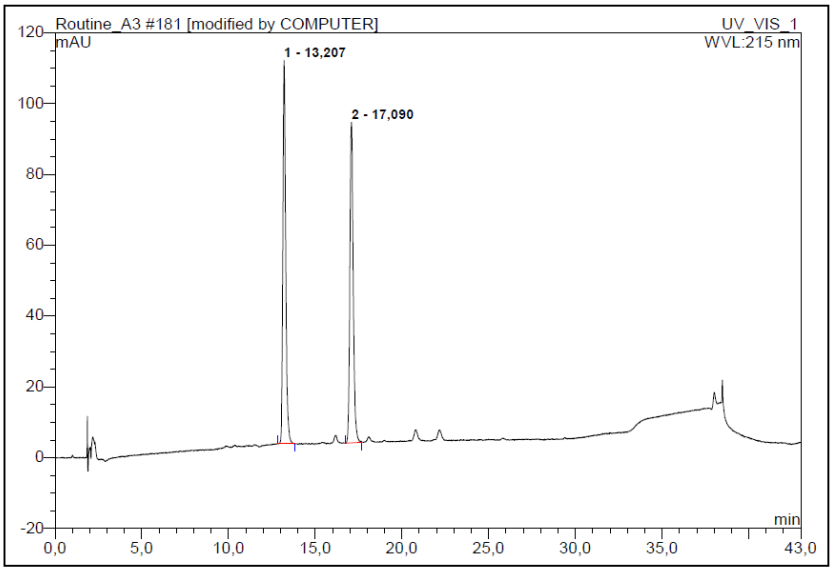


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,88	n.a.	218,881	51,052	100,00	n.a.	BMB
Total:			218,881	51,052	100,00	0,000	

*8.1.4. (1R,3a'S,7a'S)-2,2-Dichlorohexahydrospiro[cyclopropane-1,3'-indol]-2'(1'H)-one (**7**)*

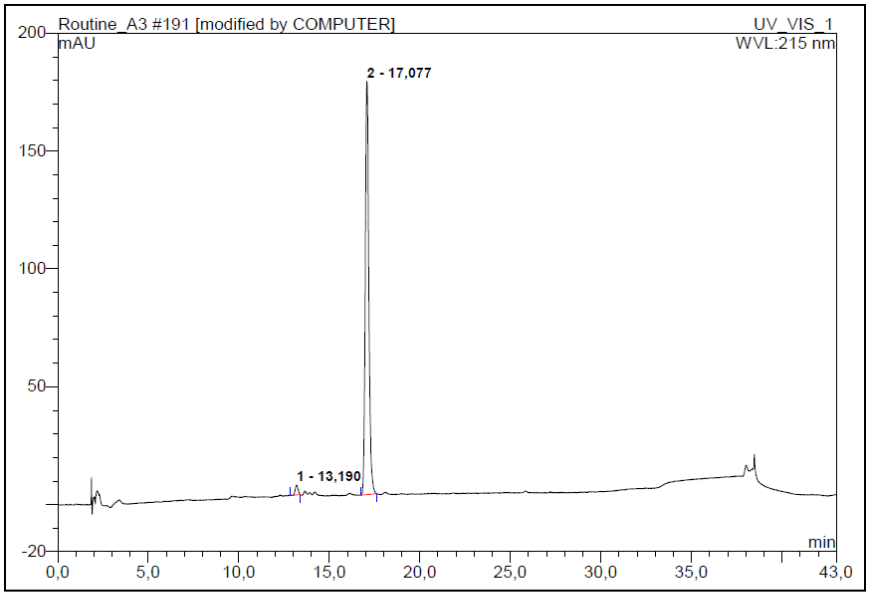


racemic product



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,21	n.a.	108,180	20,870	50,80	n.a.	BMB*
2	17,09	n.a.	90,557	20,211	49,20	n.a.	BMB*
Total:			198,737	41,081	100,00	0,000	

enantioenriched product (*>99% ee*)

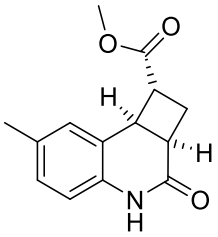


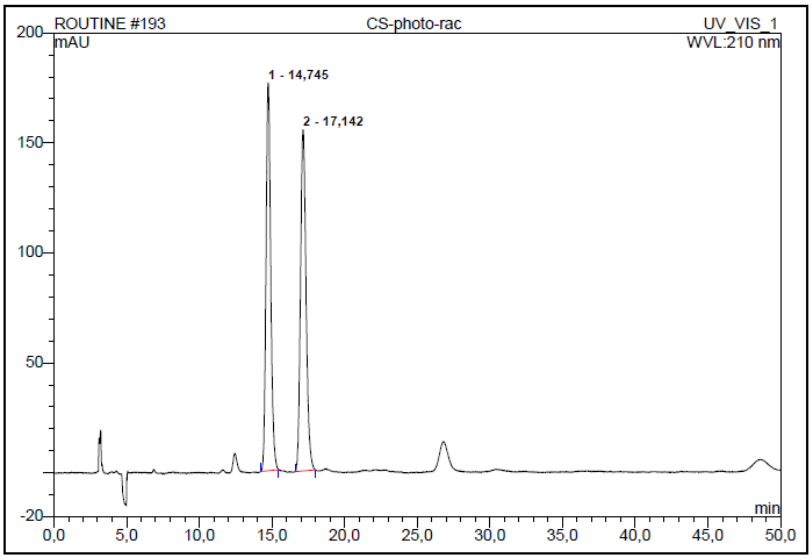
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,19	n.a.	4,203	0,750	1,85	n.a.	BMB*
2	17,08	n.a.	175,399	39,701	98,15	n.a.	BMB
Total:			179,602	40,451	100,00	0,000	

8.2. Quinoline-2-one derivatives

*8.2.1. Methyl (1R,2aR,8bR)-7-methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-1-carboxylate (**8**)*

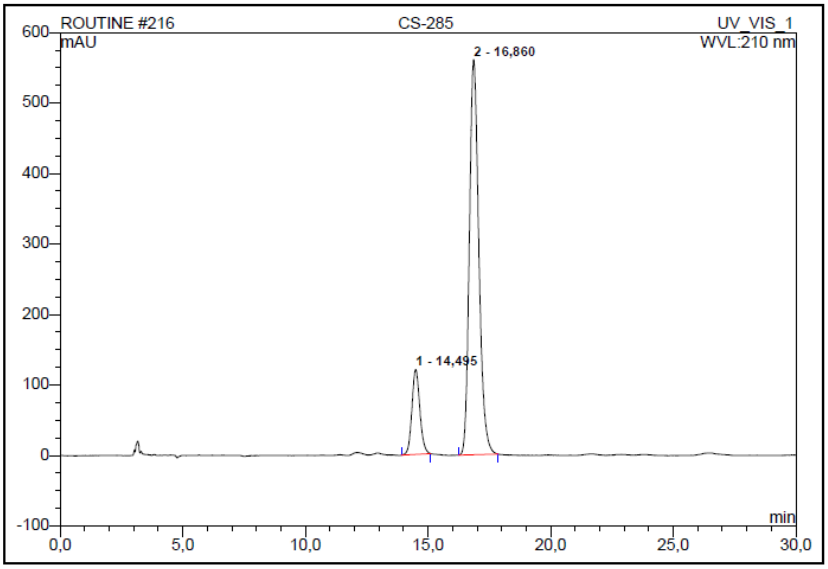
racemic product





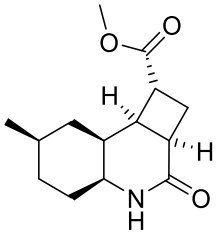
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14,75	n.a.	176,313	66,229	49,13	n.a.	BMB
2	17,14	n.a.	155,217	68,583	50,87	n.a.	BMB
Total:			331,530	134,812	100,00	0,000	

enantioenriched product (*70% ee*)

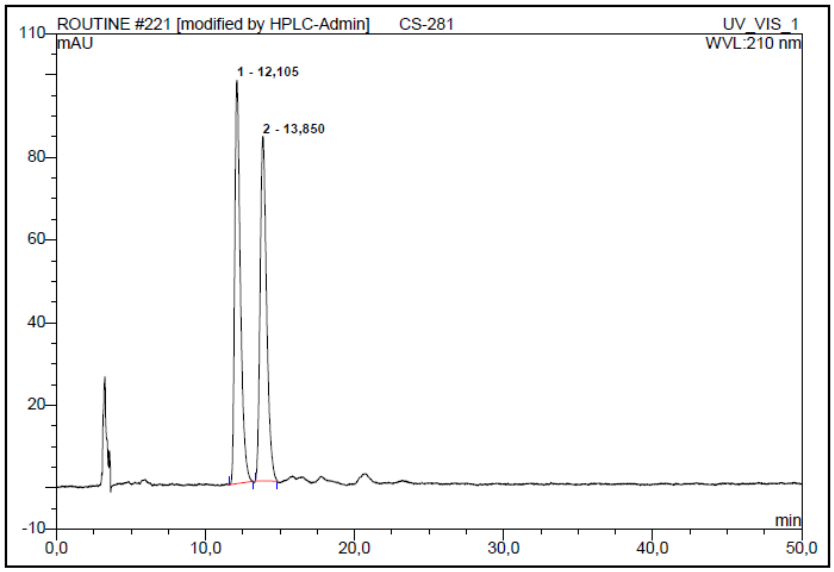


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14,49	n.a.	120,651	45,230	15,27	n.a.	BMB
2	16,86	n.a.	560,501	250,966	84,73	n.a.	BMB
Total:			681,152	296,196	100,00	0,000	

*8.2.2. Methyl (1R,2aR,4aS,7R,8aS,8bR)-7-methyl-3-oxododecahydrocyclobuta[c]quinoline-1-carboxylate (**9**)*

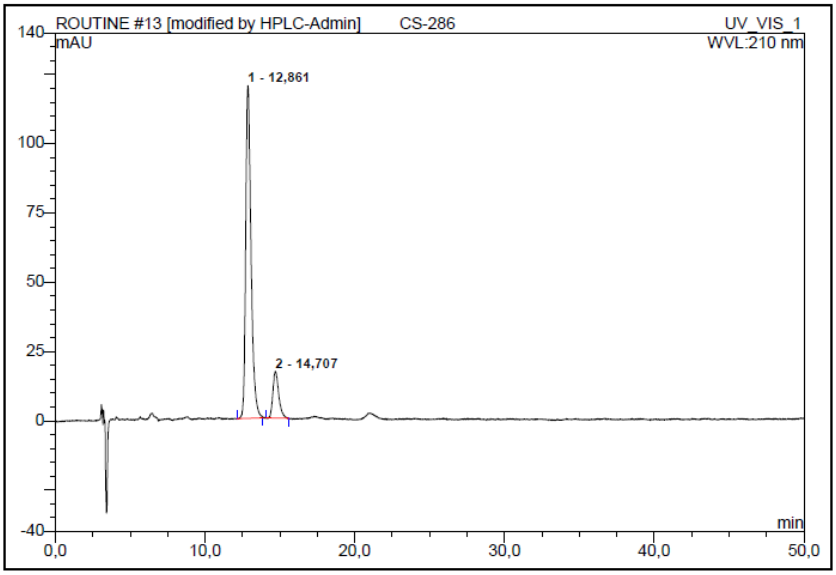


racemic product



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,11	n.a.	97,626	43,360	50,64	n.a.	BMB*
2	13,85	n.a.	83,424	42,269	49,36	n.a.	BMB
Total:			181,051	85,629	100,00	0,000	

enantioenriched product (*70% ee*)



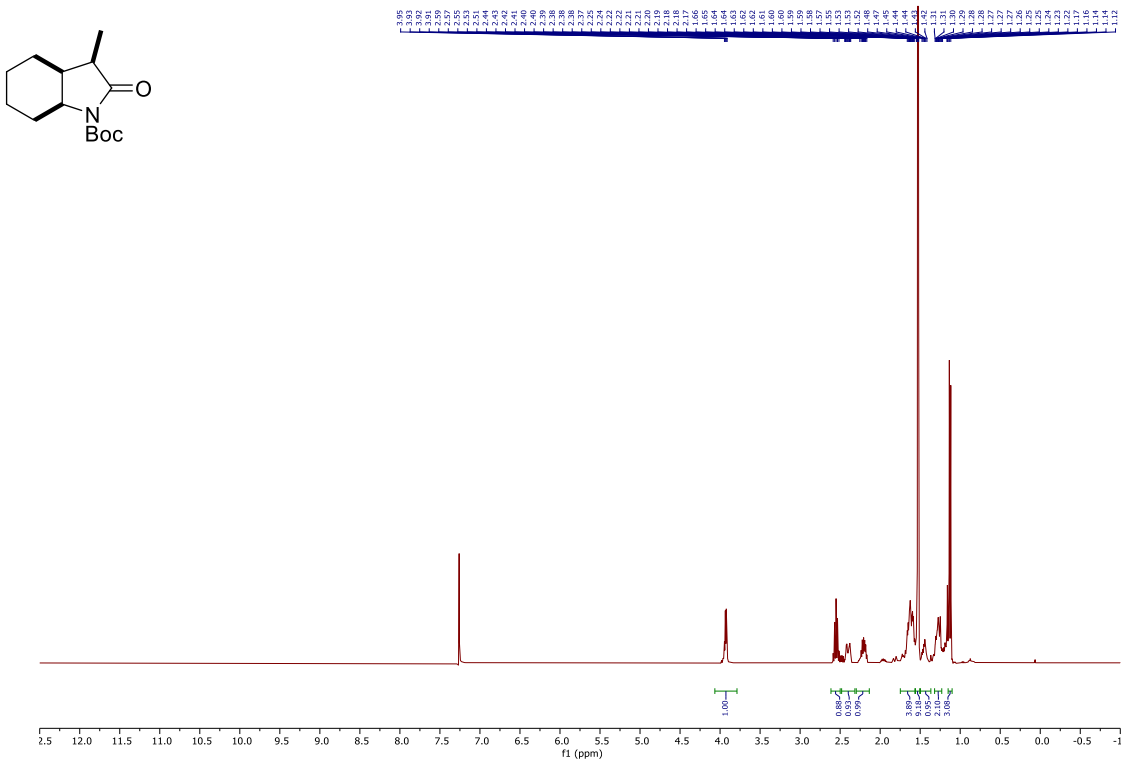
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,86	n.a.	120,092	49,371	86,59	n.a.	BMB*
2	14,71	n.a.	16,939	7,648	13,41	n.a.	BMB*
Total:			137,030	57,019	100,00	0,000	

9. NMR Spectra of new compounds

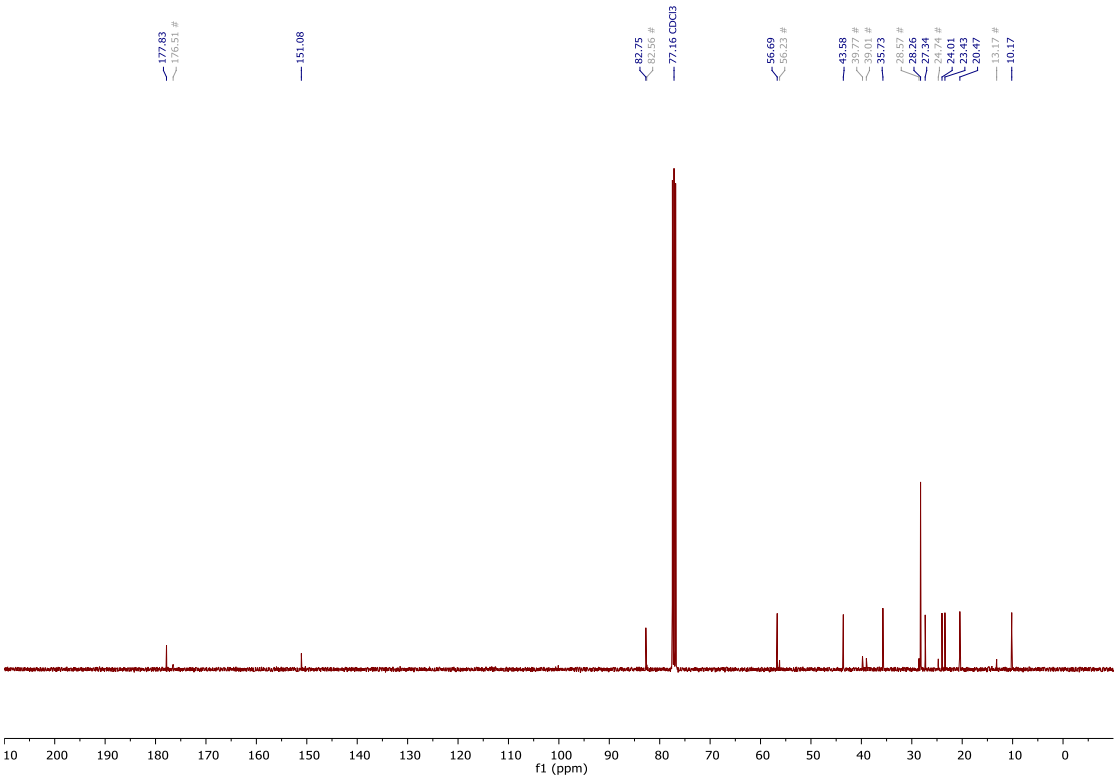
9.1. Indol-2-one derivatives

*9.1.1. (3RS,*3a*SR,*7a*SR)-tert-Butyl-3-methyl-2-oxooctahydroindole-1-carboxylate (***3e**)

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

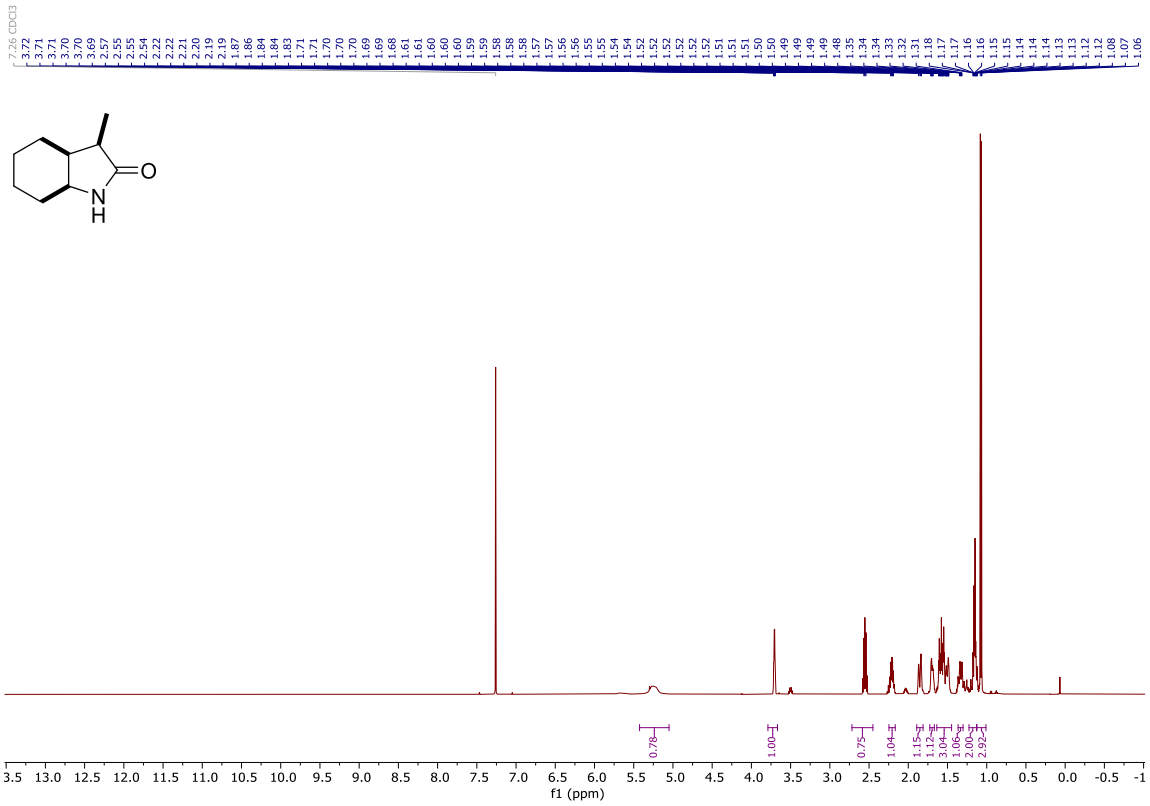


^{13}C NMR (126 MHz, $CDCl_3$):

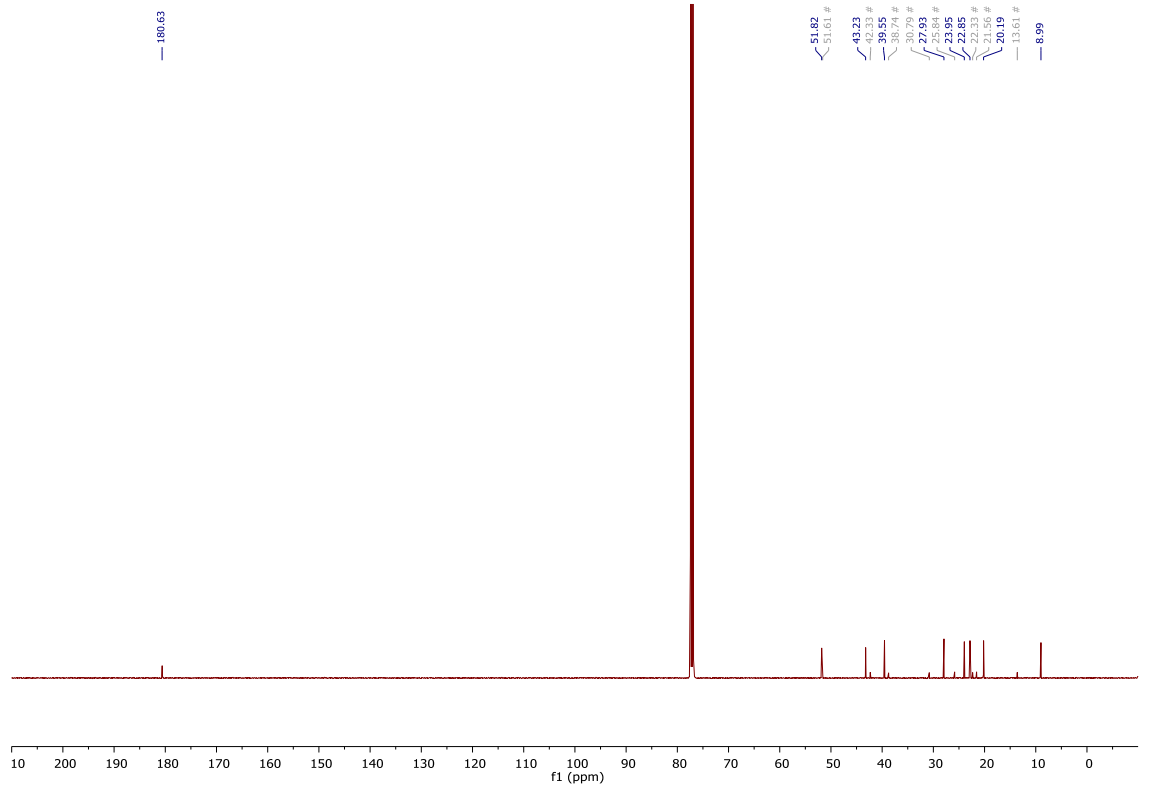


*9.1.2. (3RS,*3a*SR,*7a*SR)-3-Methyloctahydroindol-2-one (***3f**)*

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

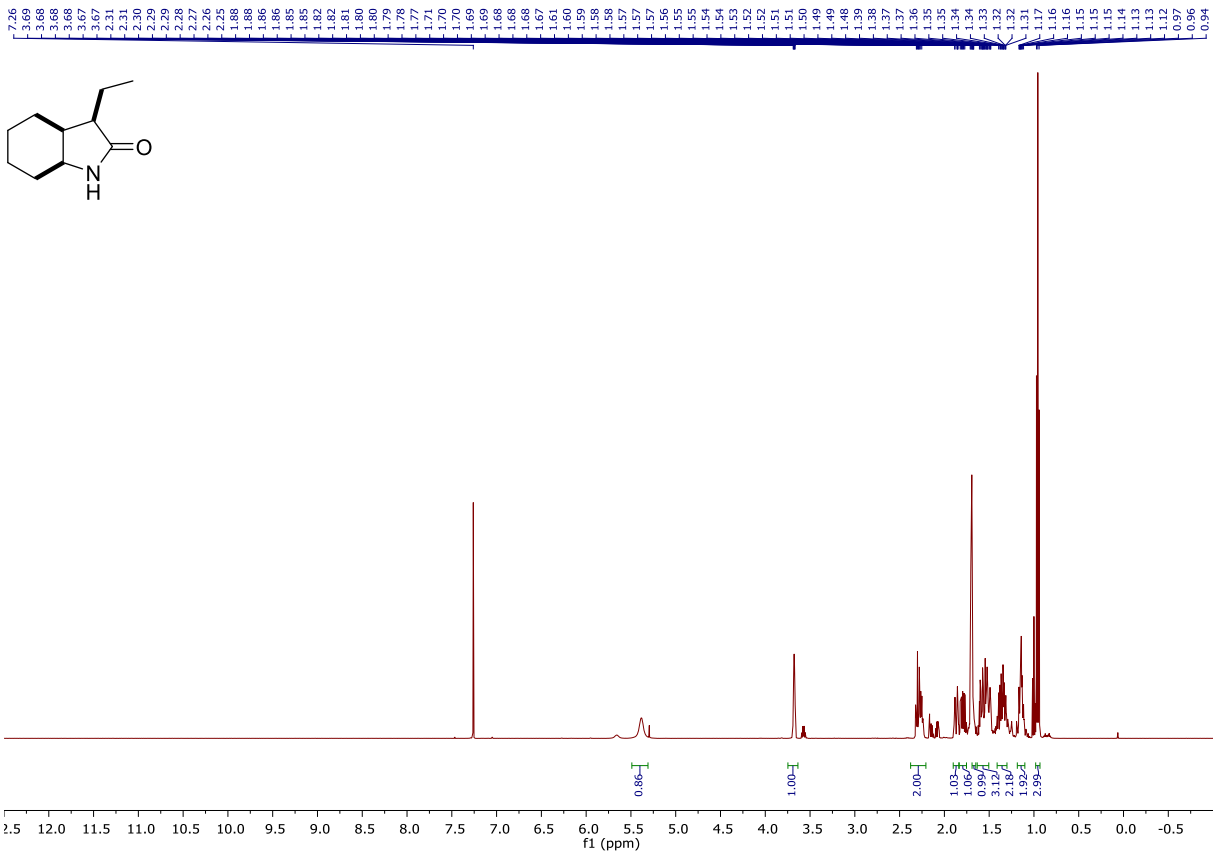


^{13}C NMR (126 MHz, $CDCl_3$):

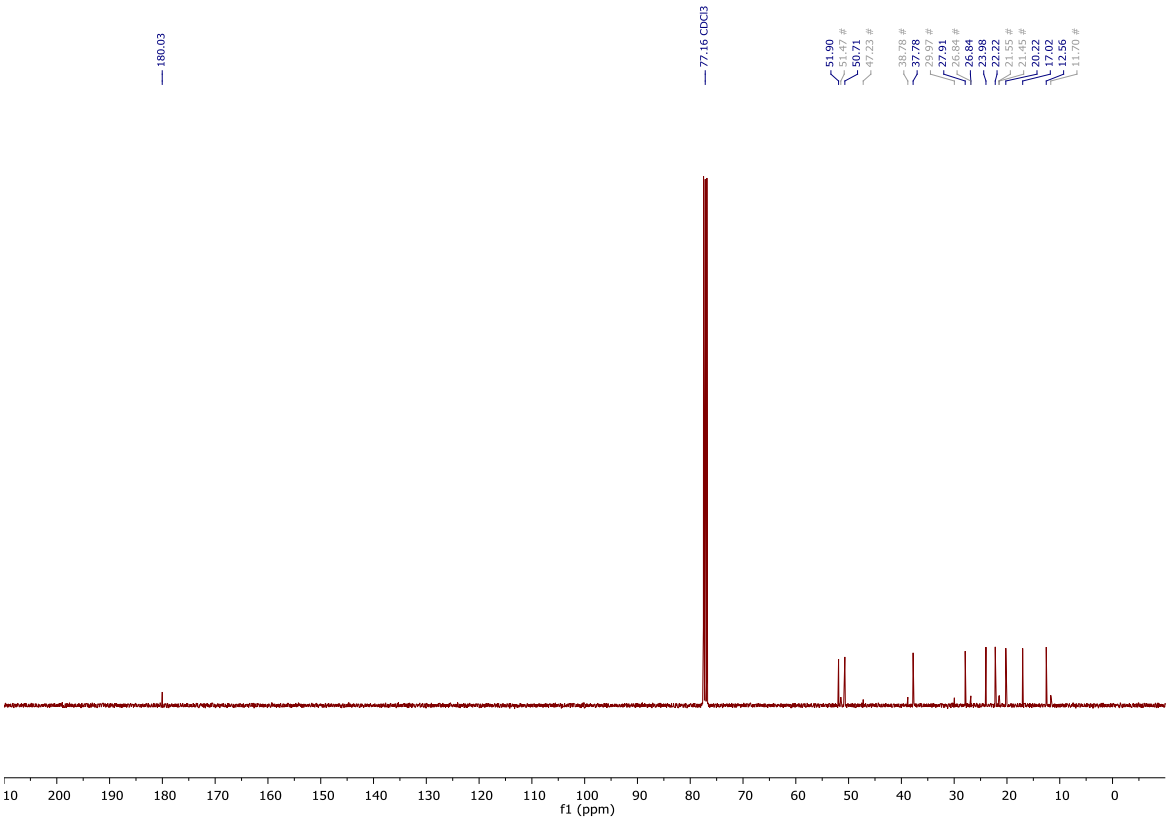


*9.1.3. (3RS,*3a*SR,*7a*SR)-3-Ethyloctahydroindol-2-one* (**3g**)

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

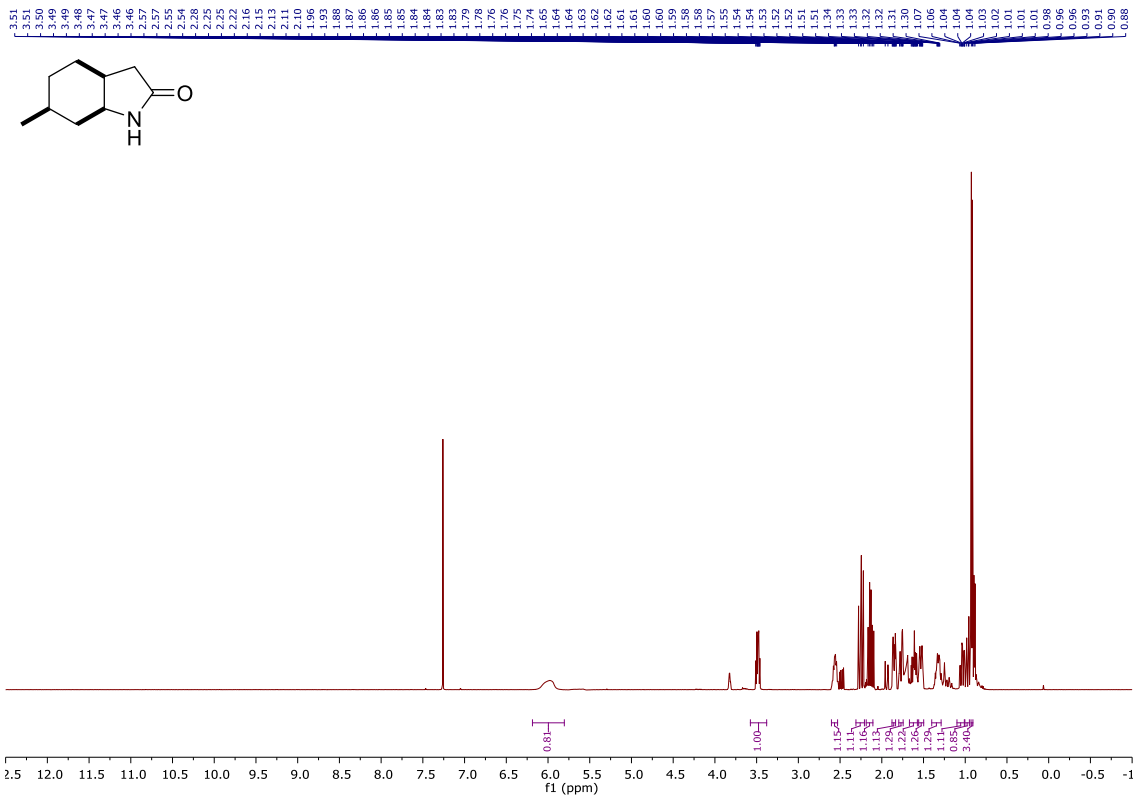


^{13}C NMR (126 MHz, $CDCl_3$):

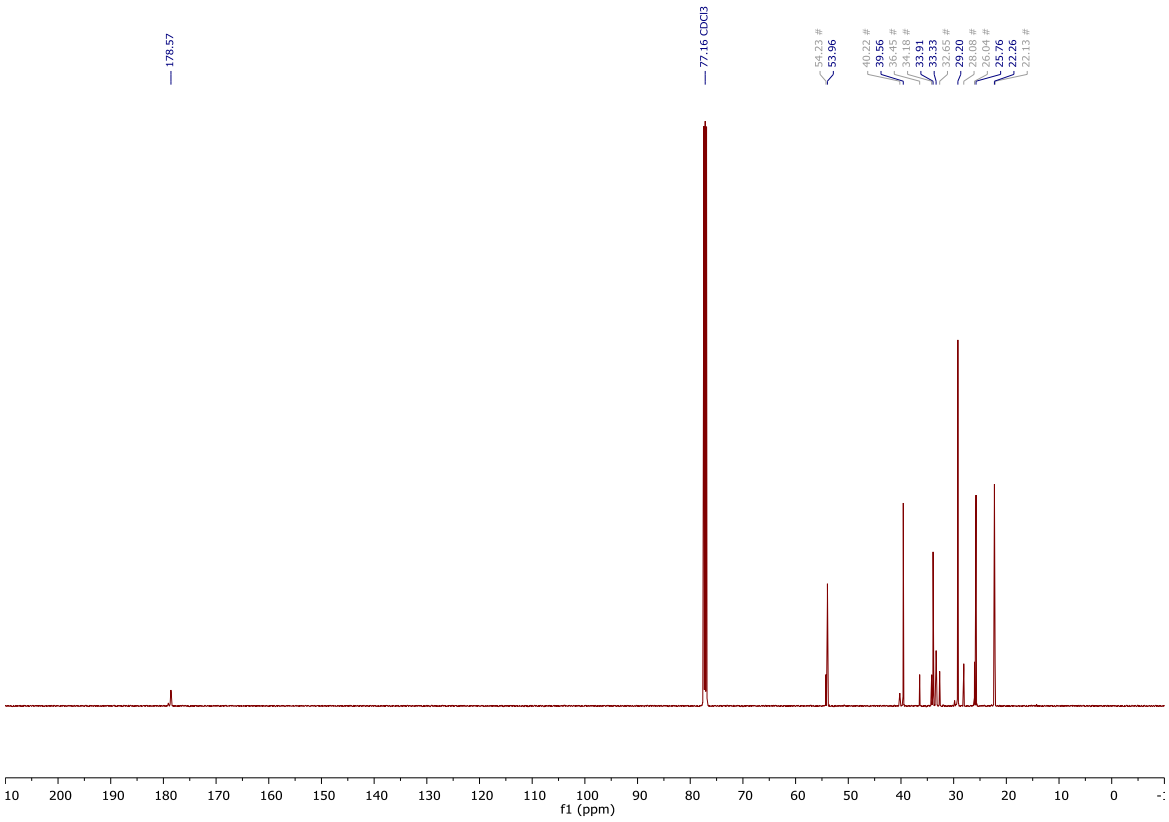


*9.1.4. (3a*SR,6*SR,7a*SR)-6-Methyloctahydroindol-2-one (***3h**)

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

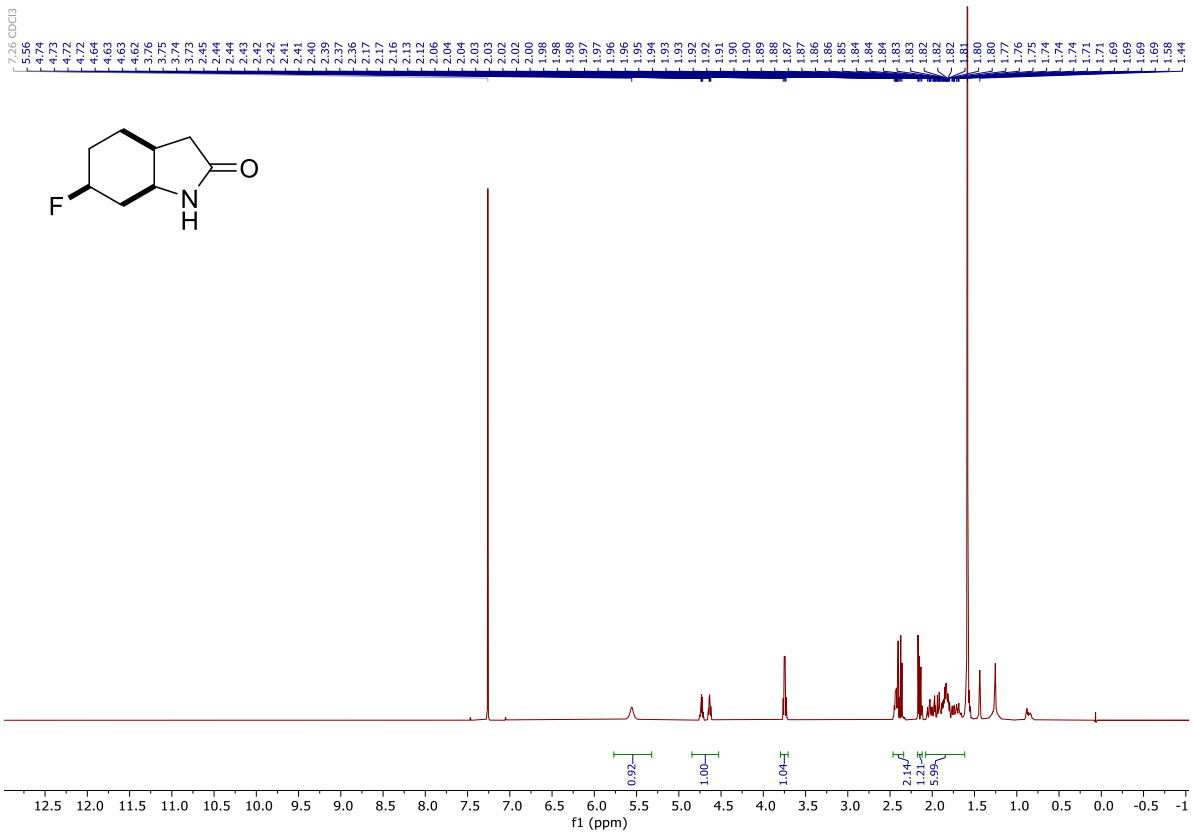


^{13}C NMR (126 MHz, $CDCl_3$):

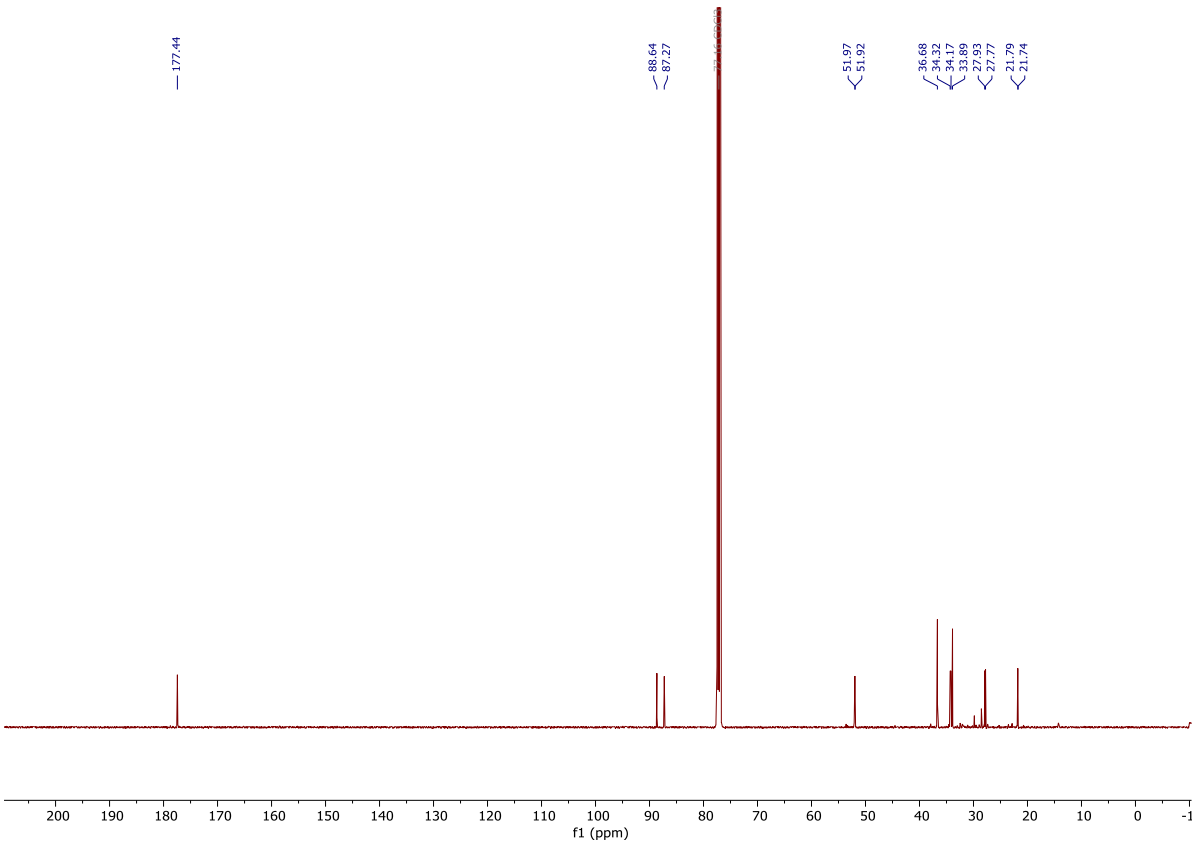


*9.1.5. (3a*SR,6*SR,7a*SR)-6-Fluorooctahydroindol-2-one (***3i**)*

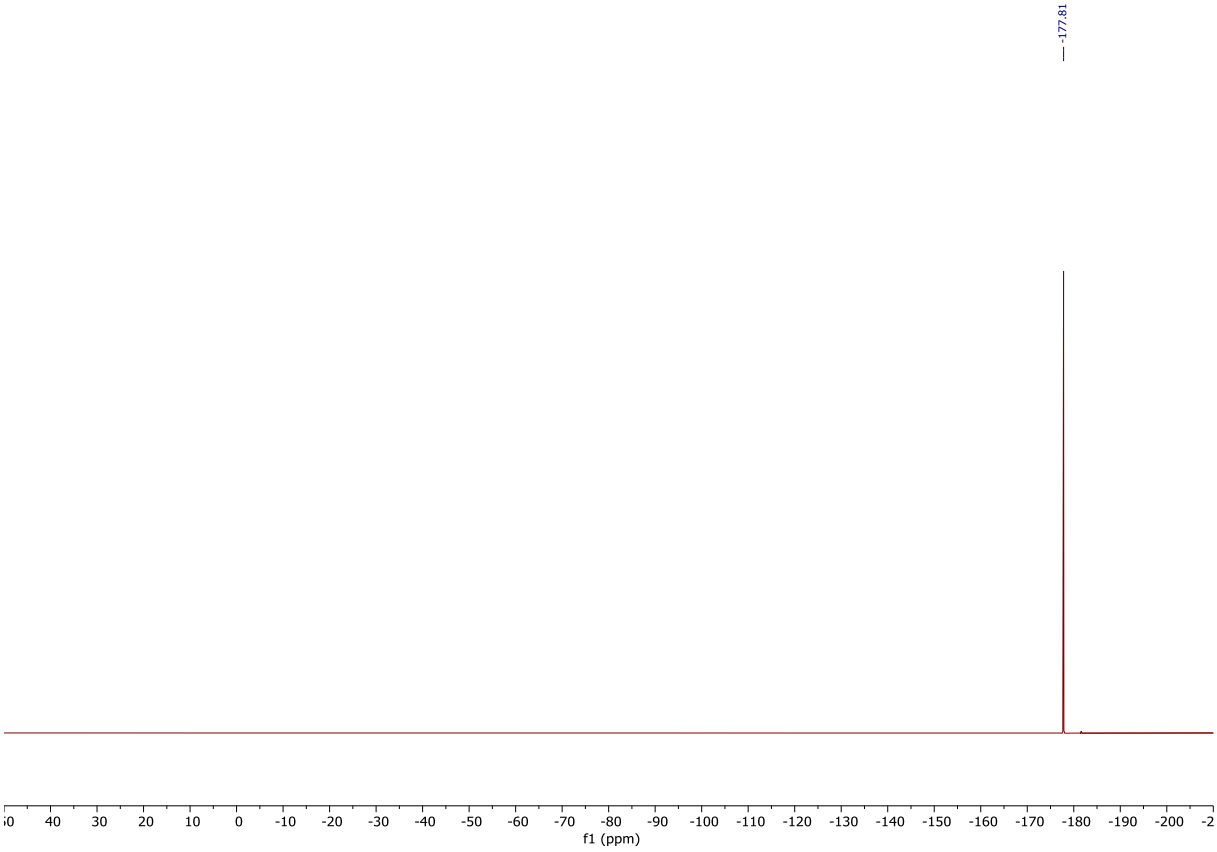
^{1}H NMR (500 MHz, $CDCl_3$):



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

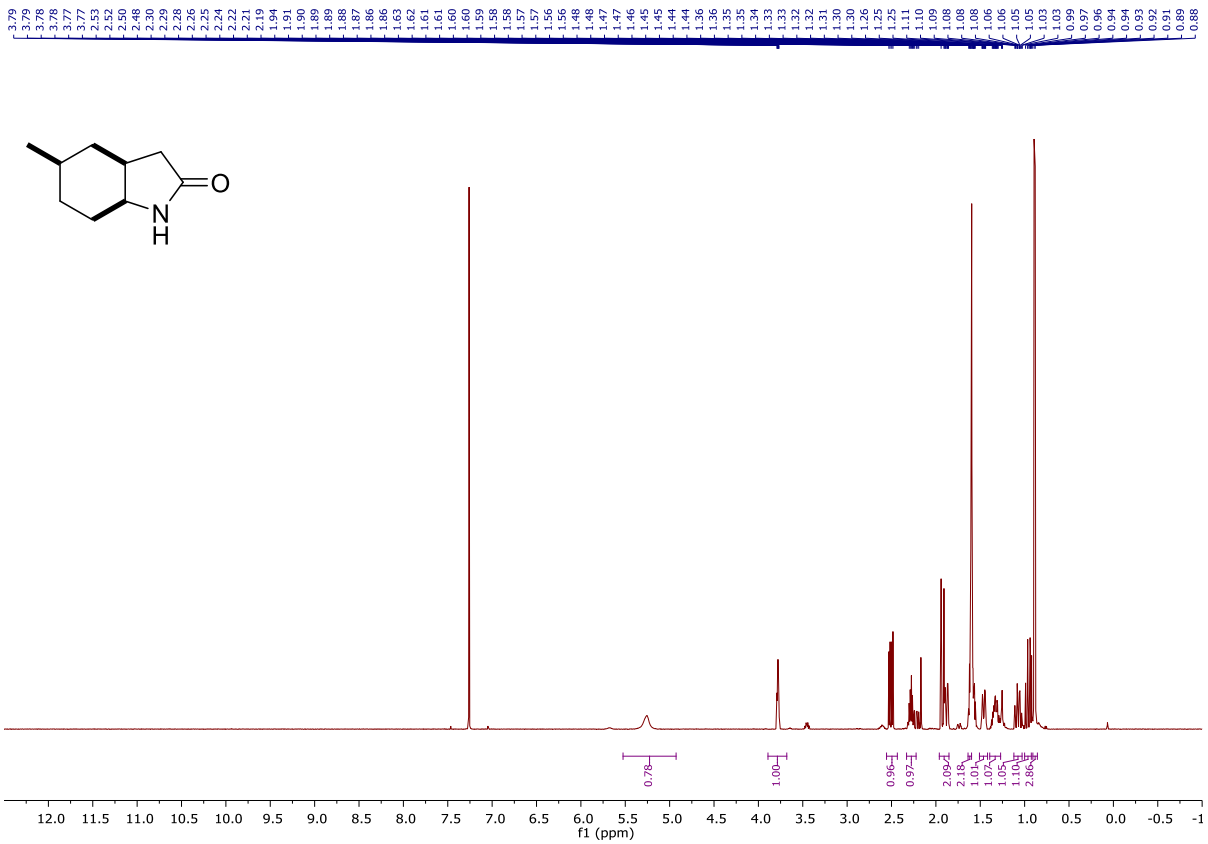


^{19}F NMR (471 MHz, $CDCl_3$):

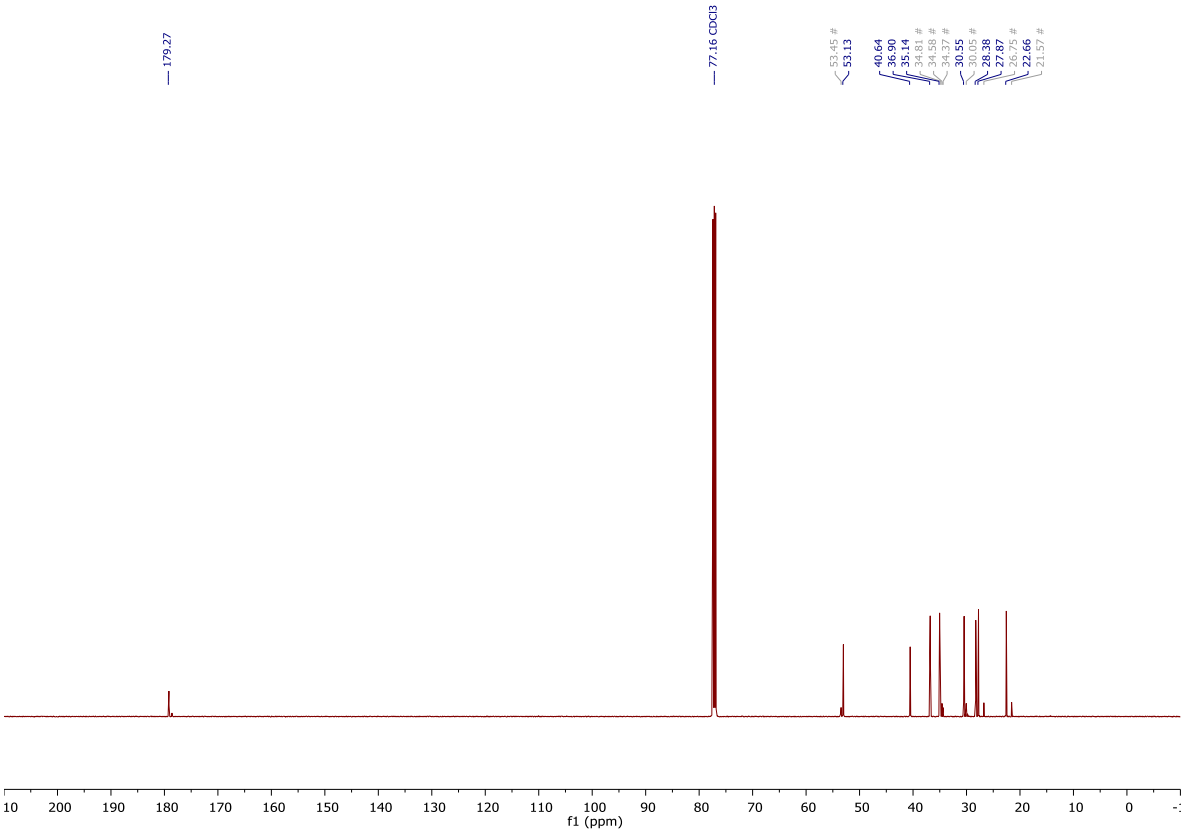


*9.1.6. (3a*SR,5*RS,7a*SR)-5-Methyloctahydroindol-2-one (***3k**)*

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

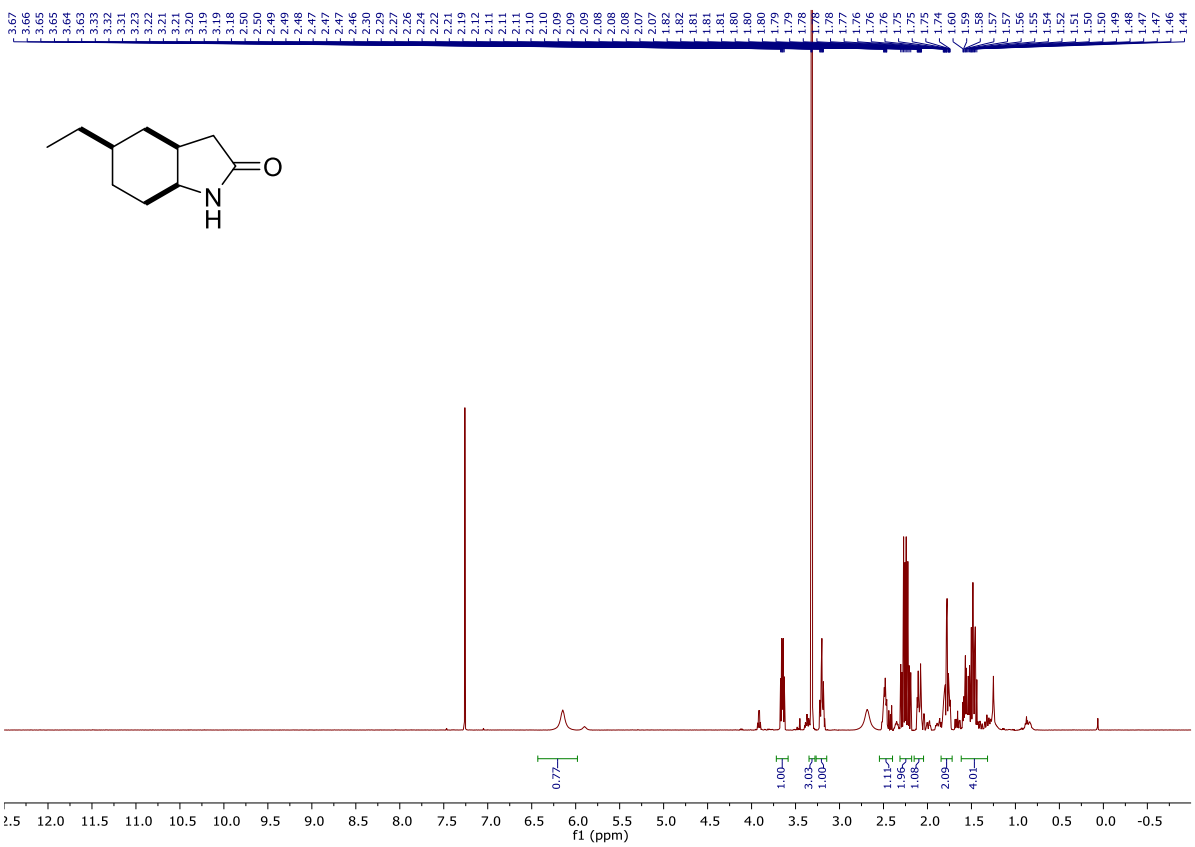


^{13}C NMR (126 MHz, $CDCl_3$):

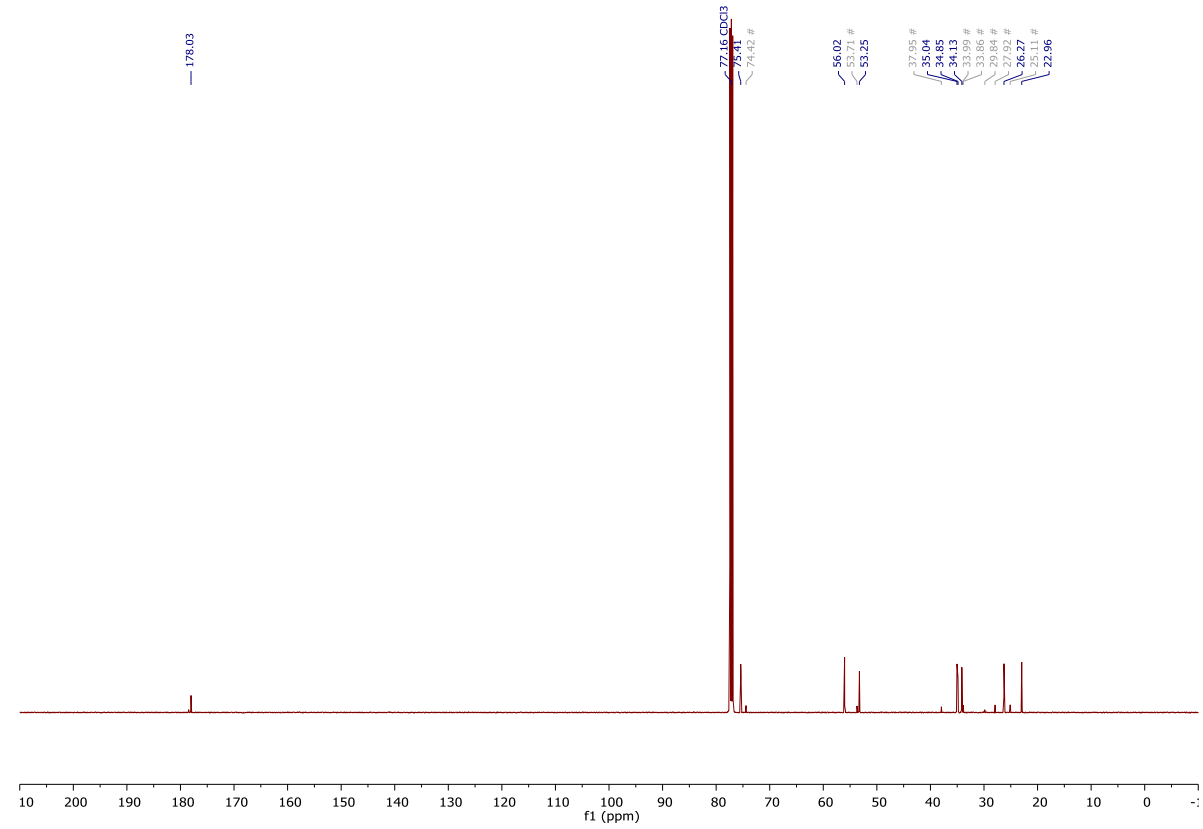


*9.1.7. (3a*SR,5*RS,7a*SR)-5-Ethyloctahydroindol-2-one (***3l***)*

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

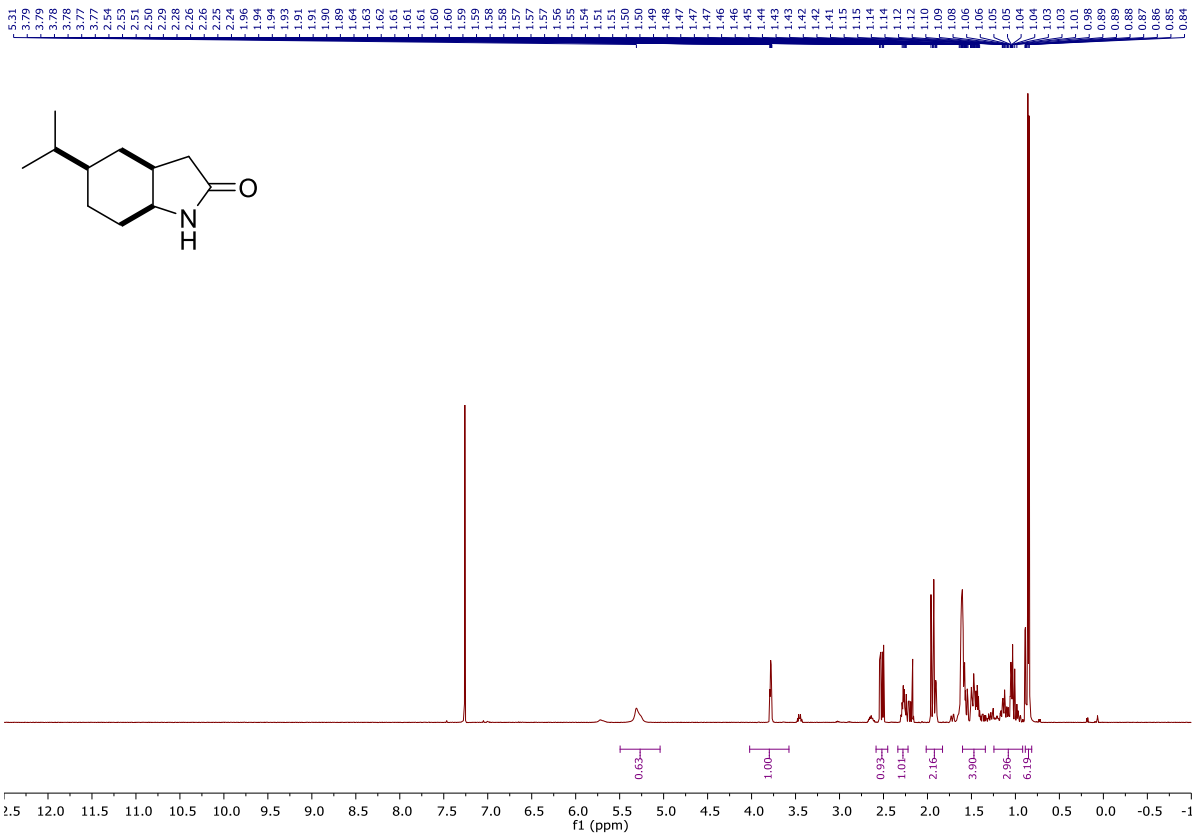


^{13}C NMR (126 MHz, $CDCl_3$):

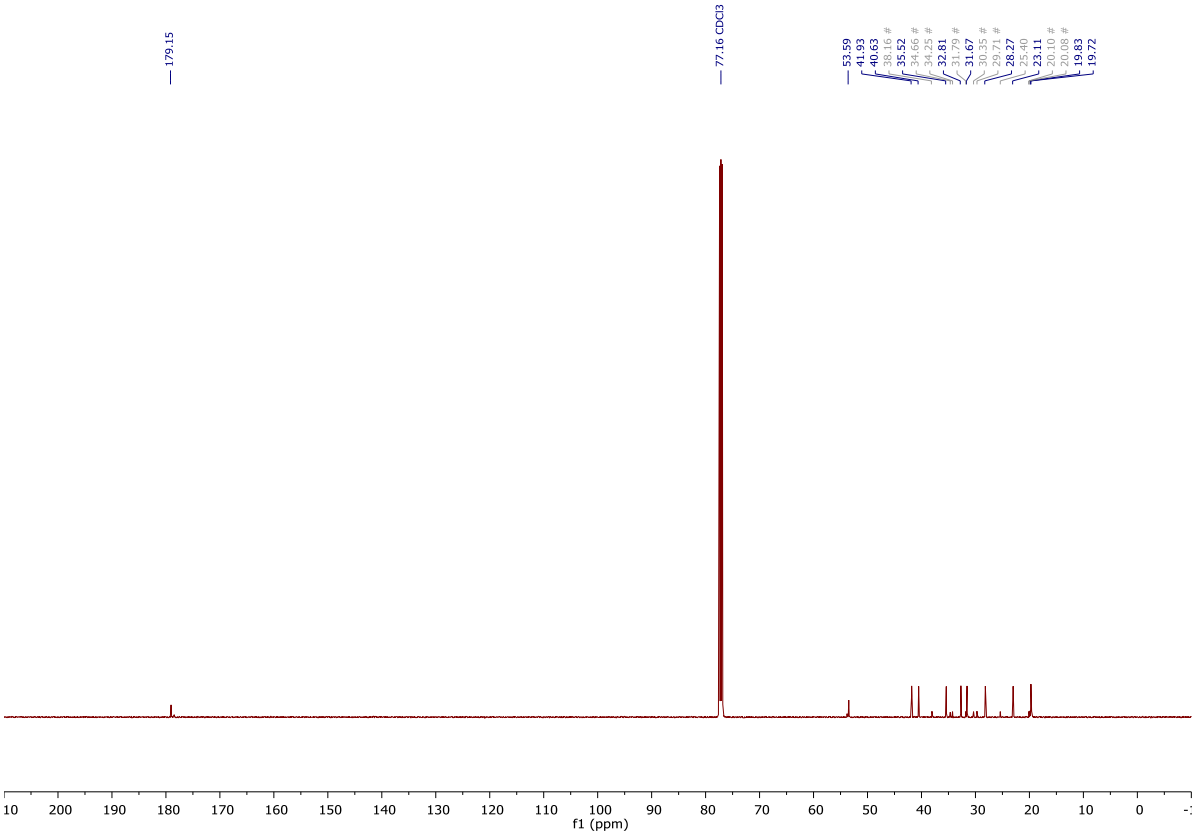


9.1.8. *(3aSR,5RS,7aSR)-5-Isopropyloctahydroindol-2-one* (**3m**)

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

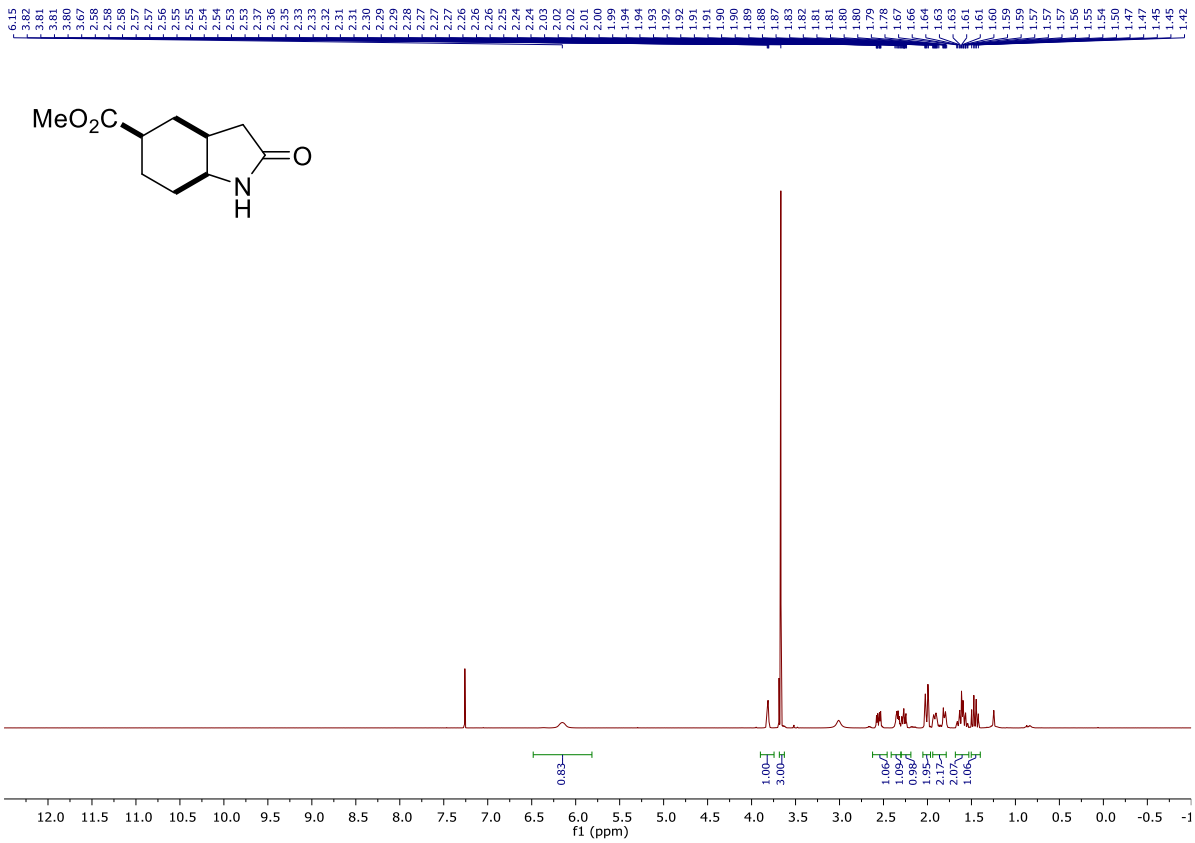


^{13}C NMR (126 MHz, $CDCl_3$):

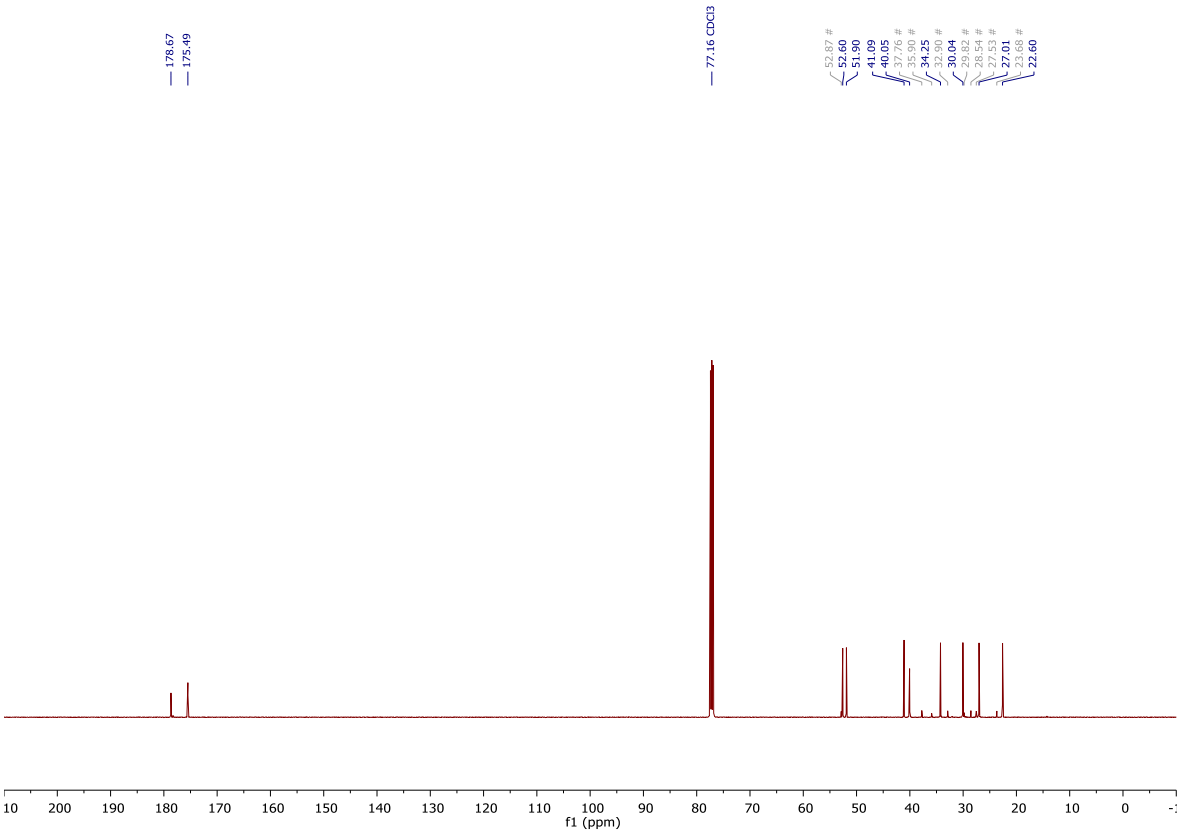


*9.1.9. (3a*SR,5*RS,7a*SR)-5-Methylcarboxy-octahydroindol-2-one* (**3n**)

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

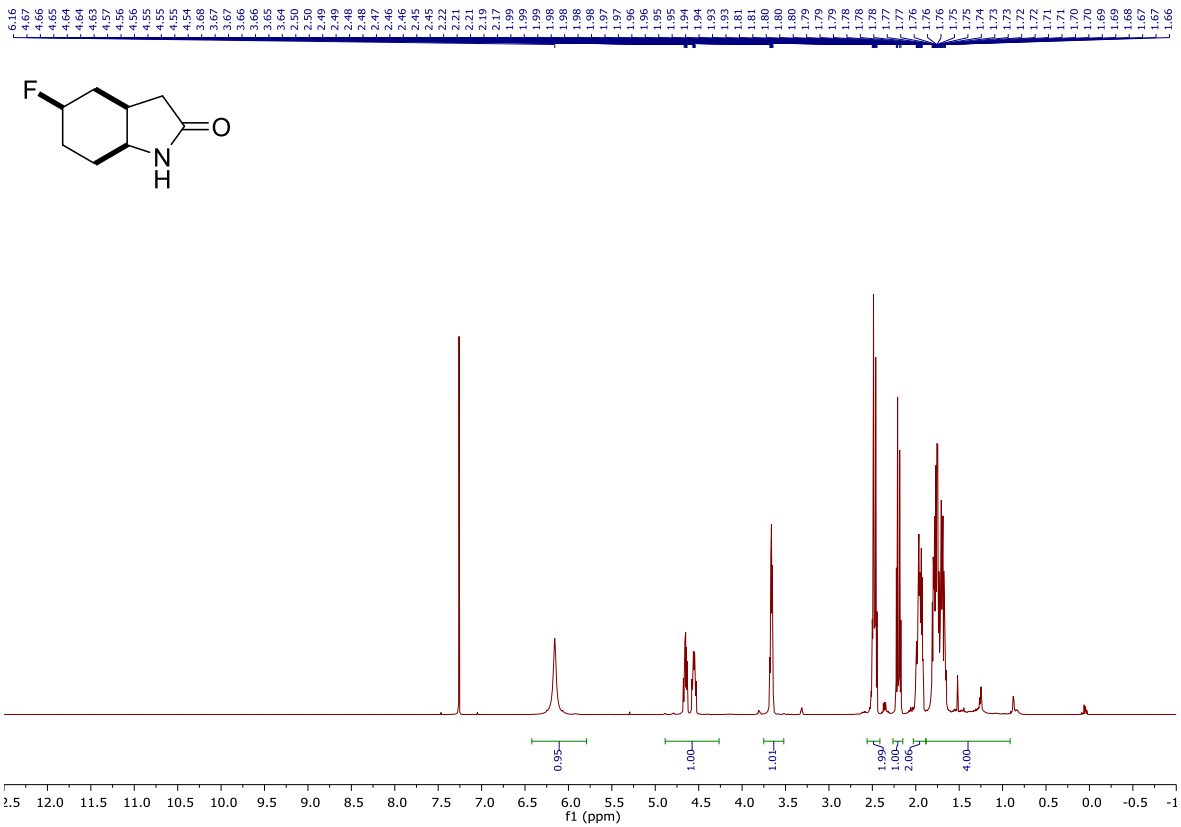


^{13}C NMR (126 MHz, $CDCl_3$):

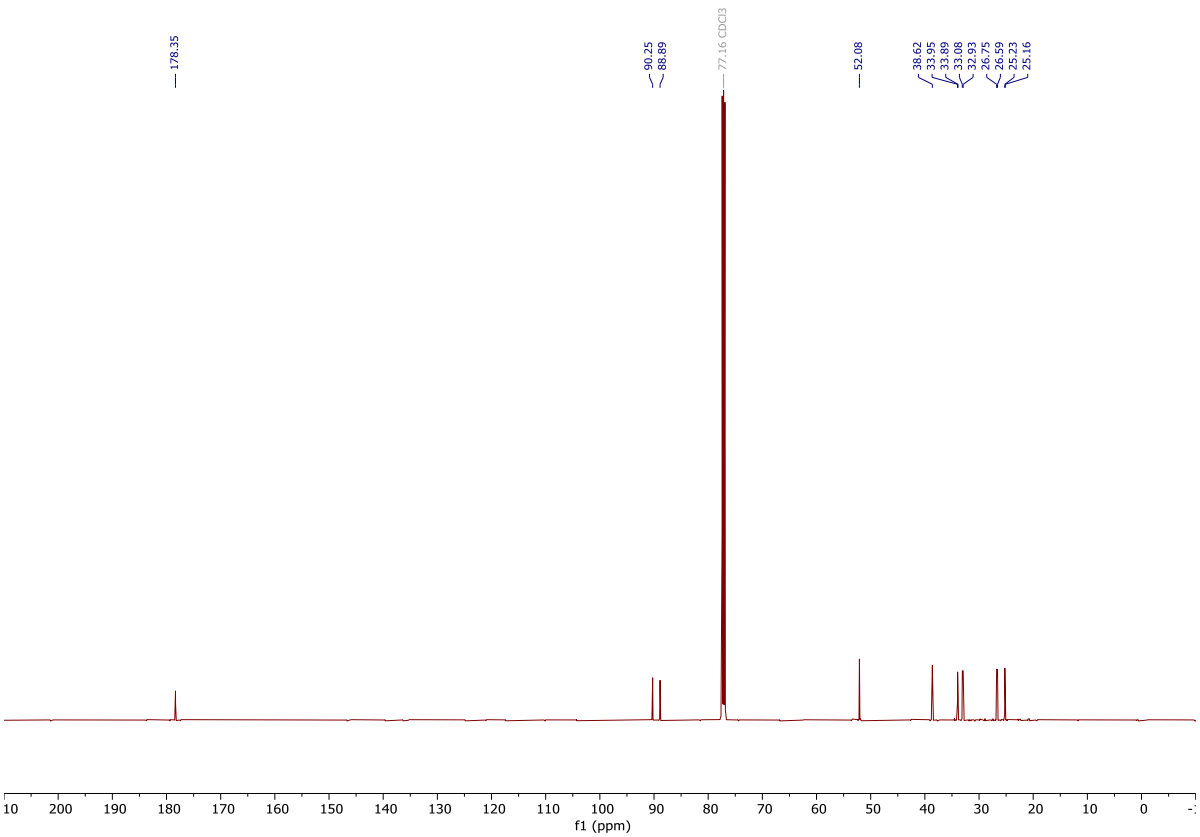


9.1.10. *(3a*RS,5*RS,7a*SR)-5-Fluoroctahydroindol-2-one* (**3o**)

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



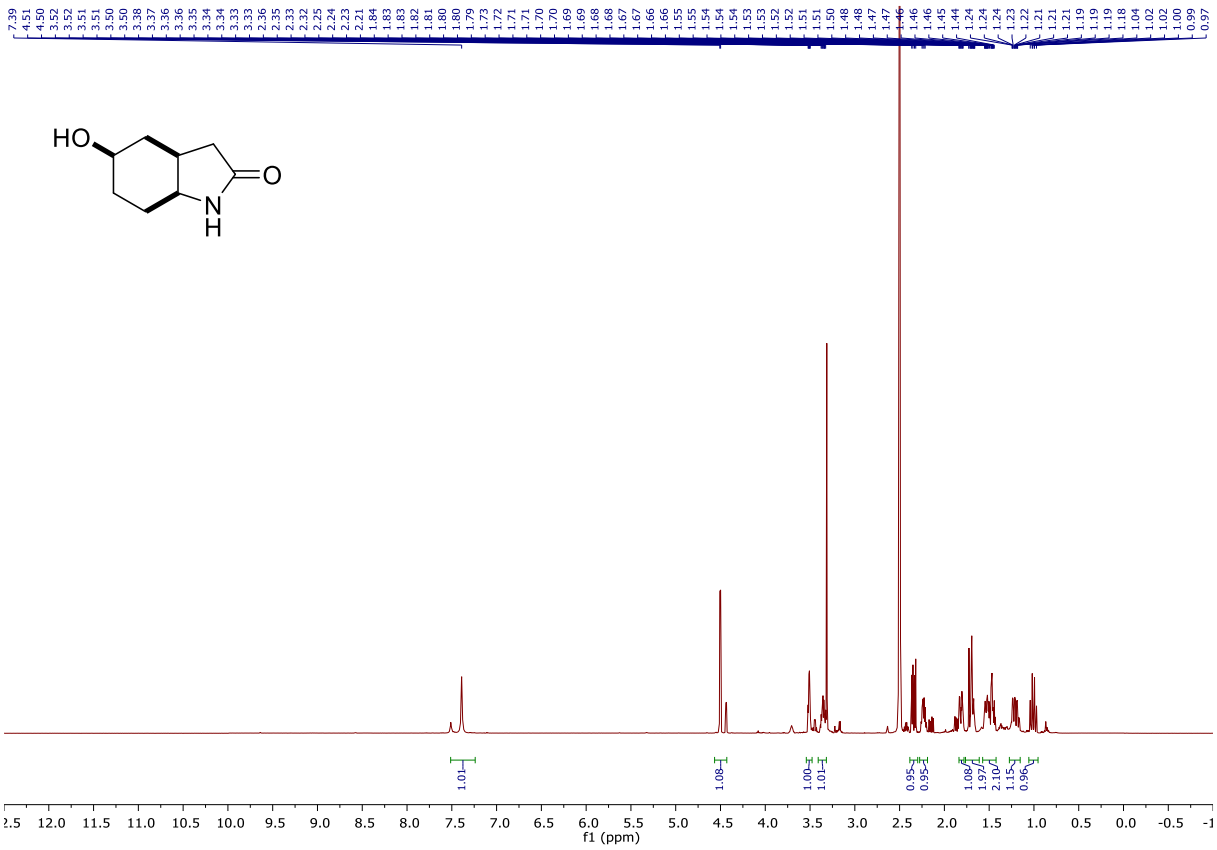
^{13}C NMR (126 MHz, $CDCl_3$):



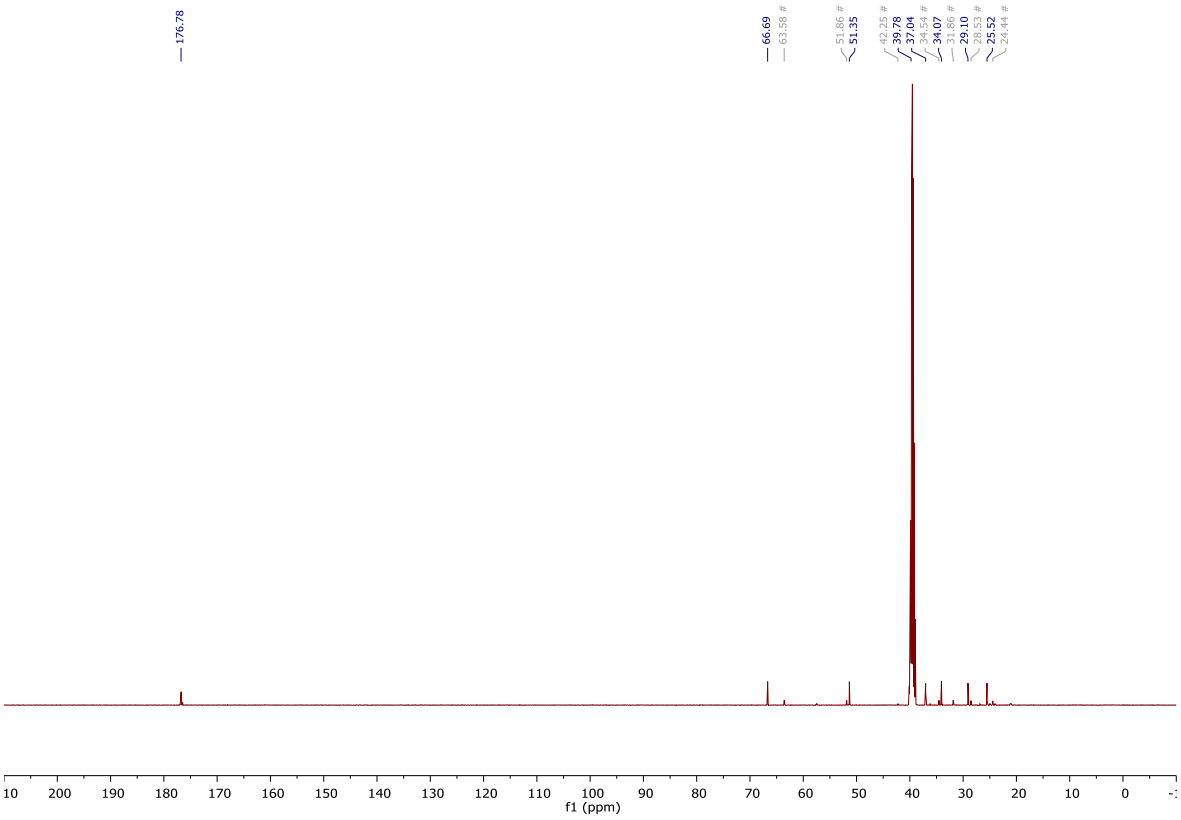
^{19}F NMR (471 MHz, $CDCl_3$):

*9.1.11. (3a*SR,5*RS,7a*SR)-5-Hydroxyoctahydroindol-2-one (***3p**)

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

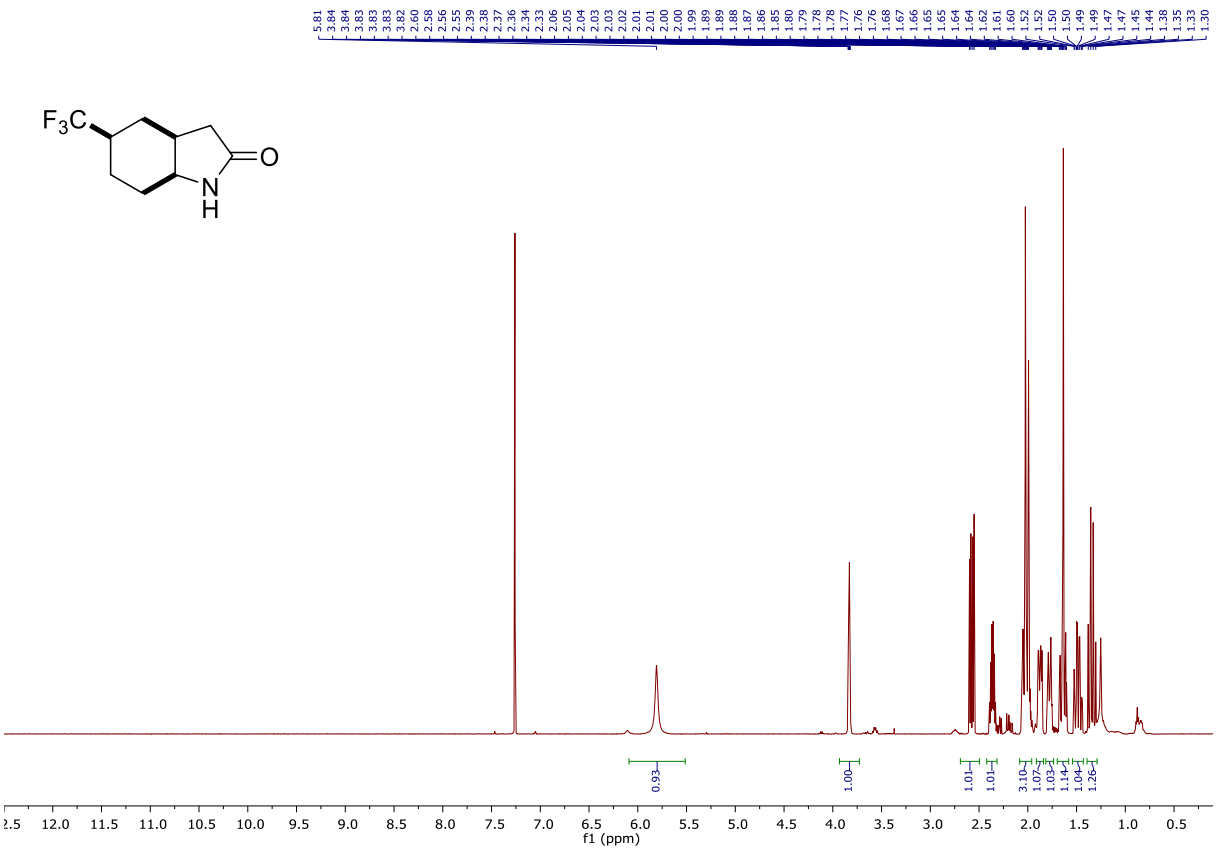


^{13}C NMR (126 MHz, DMSO-d_6):

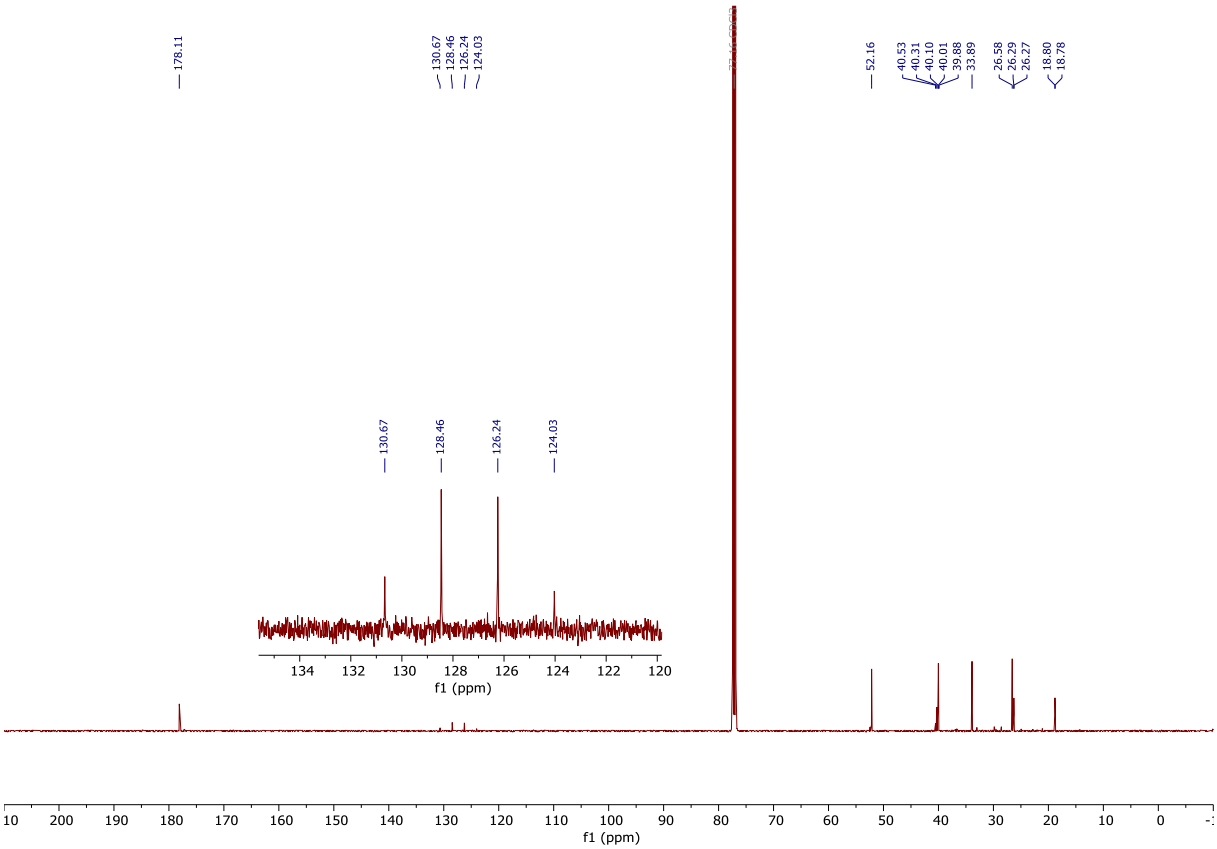


*9.1.12. (3a*SR,5*RS,7a*SR)-5-Trifluoromethyloctahydroindol-2-one* (**3q**)

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

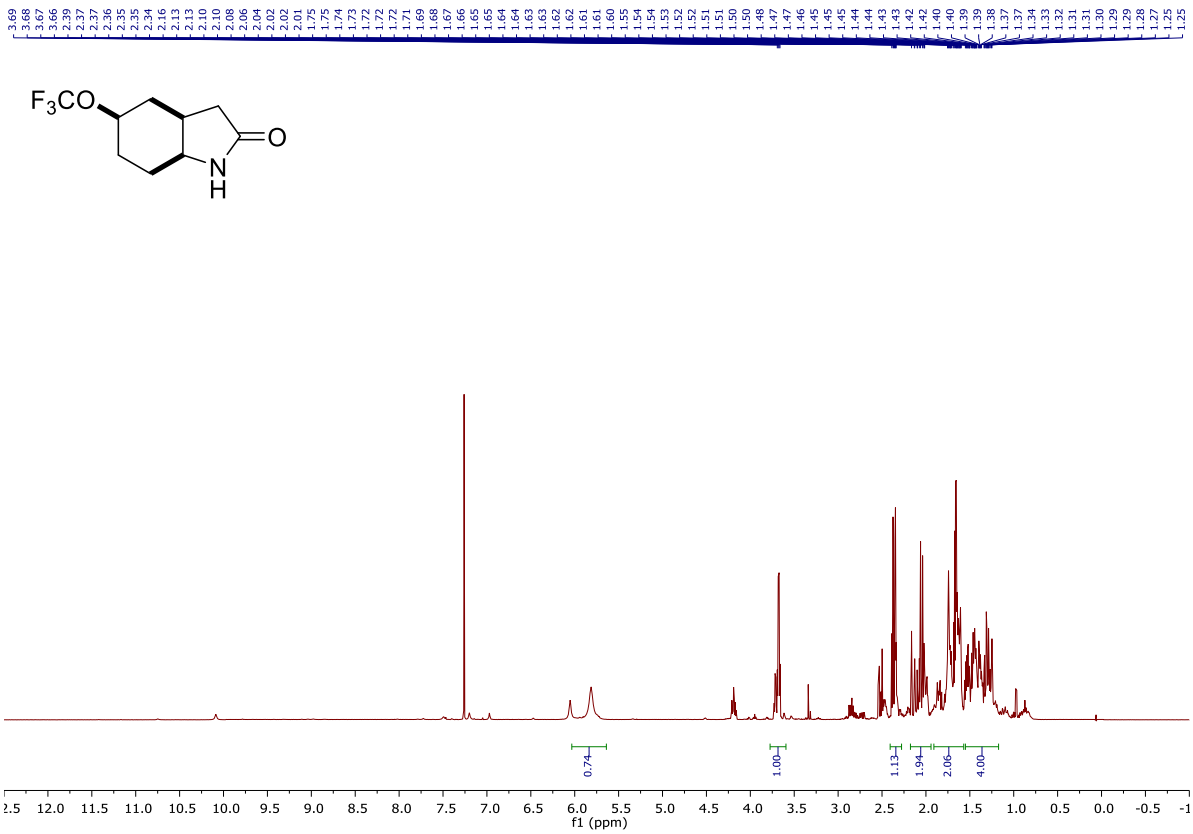


^{13}C NMR (126 MHz, $CDCl_3$):

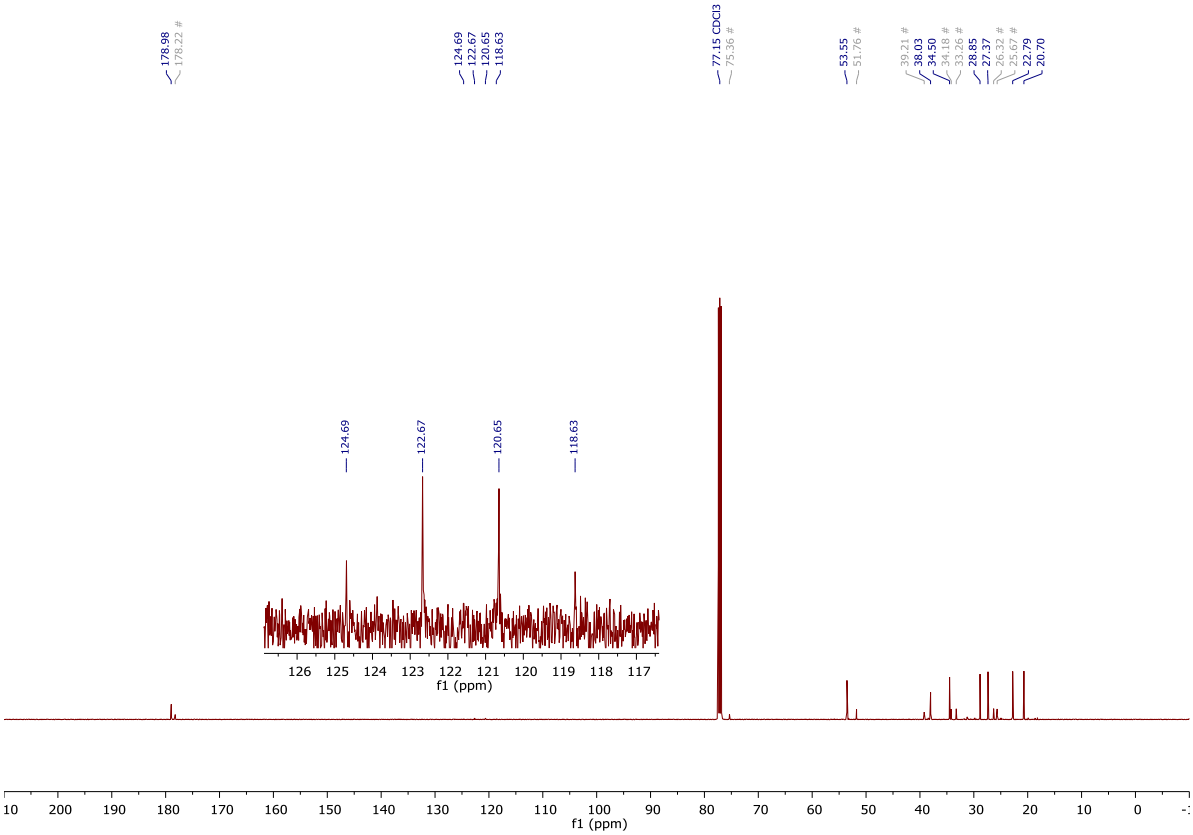


9.1.13. *(3a*SR,5*RS,7a*SR)-5-(Trifluoromethoxy)octahydroindol-2-one* (**3r**)

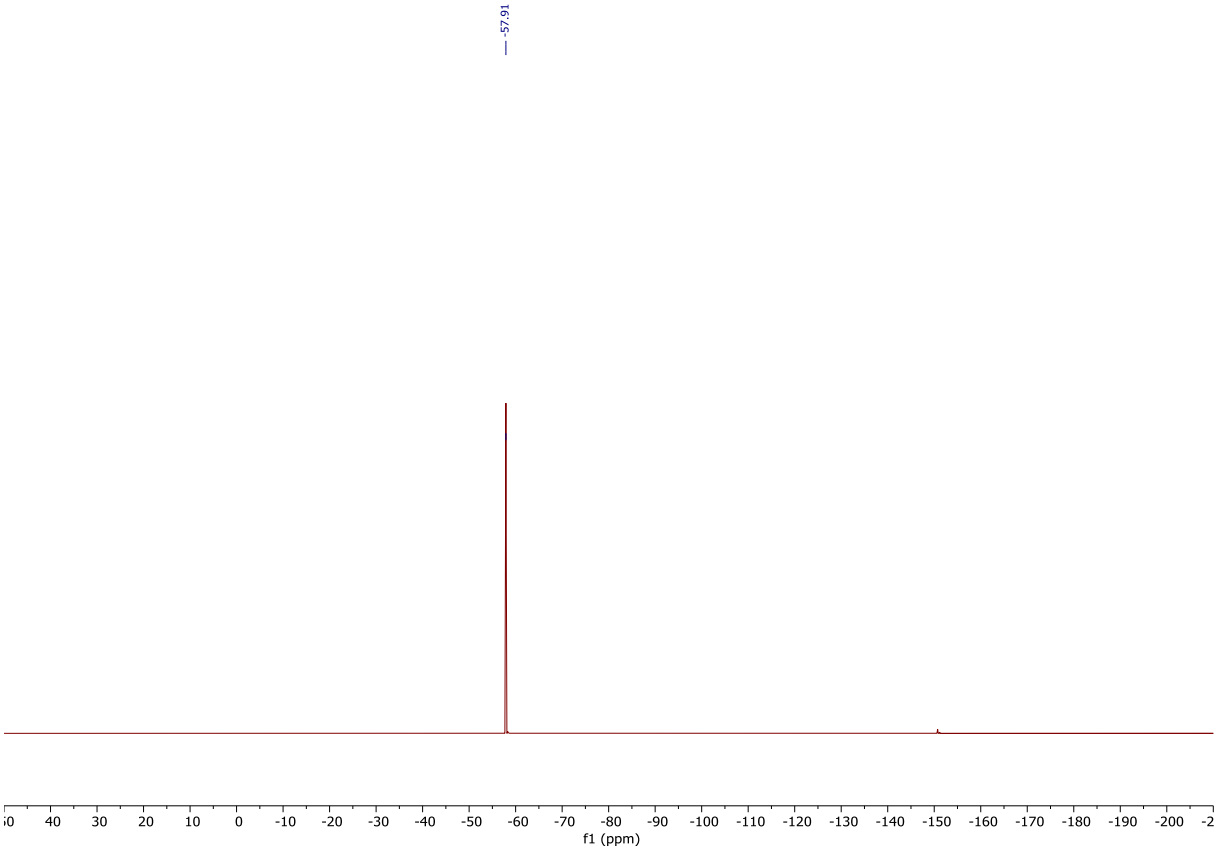
^{1}H NMR (500 MHz, $CDCl_3$):



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

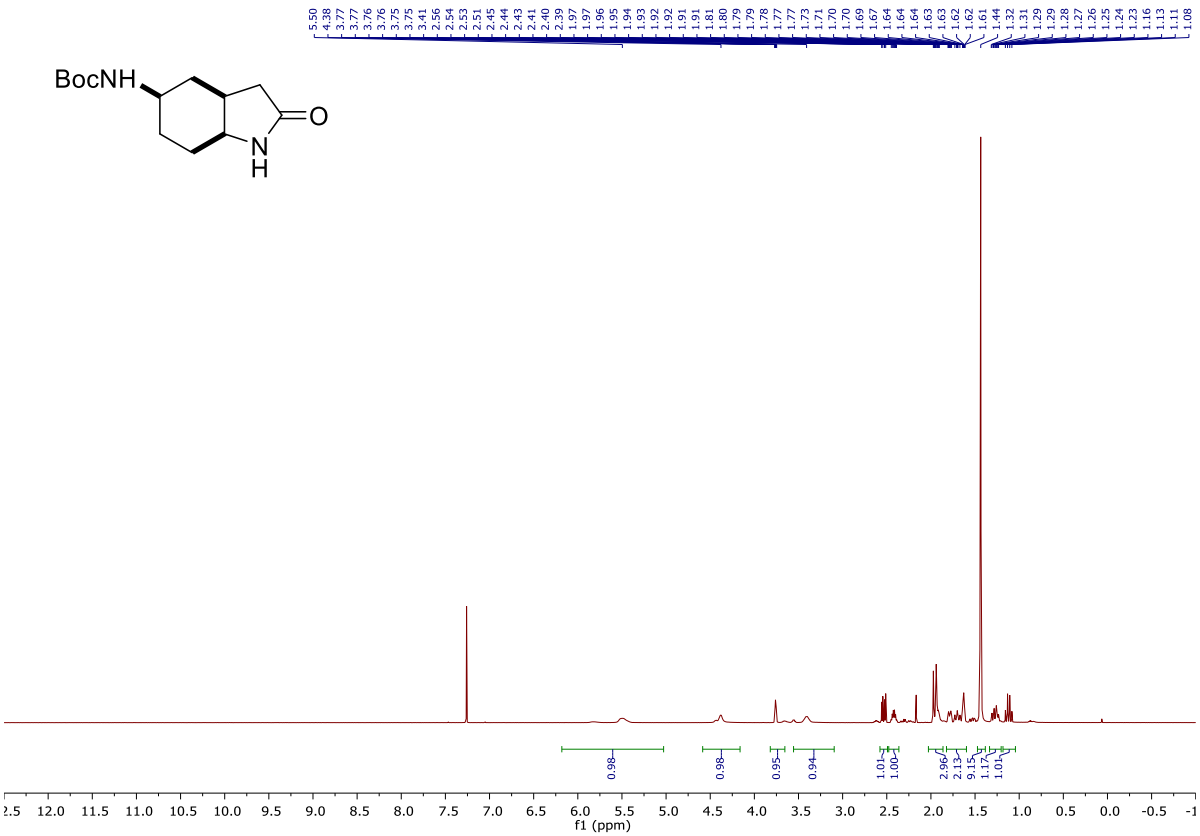


^{19}F NMR (471 MHz, $CDCl_3$):

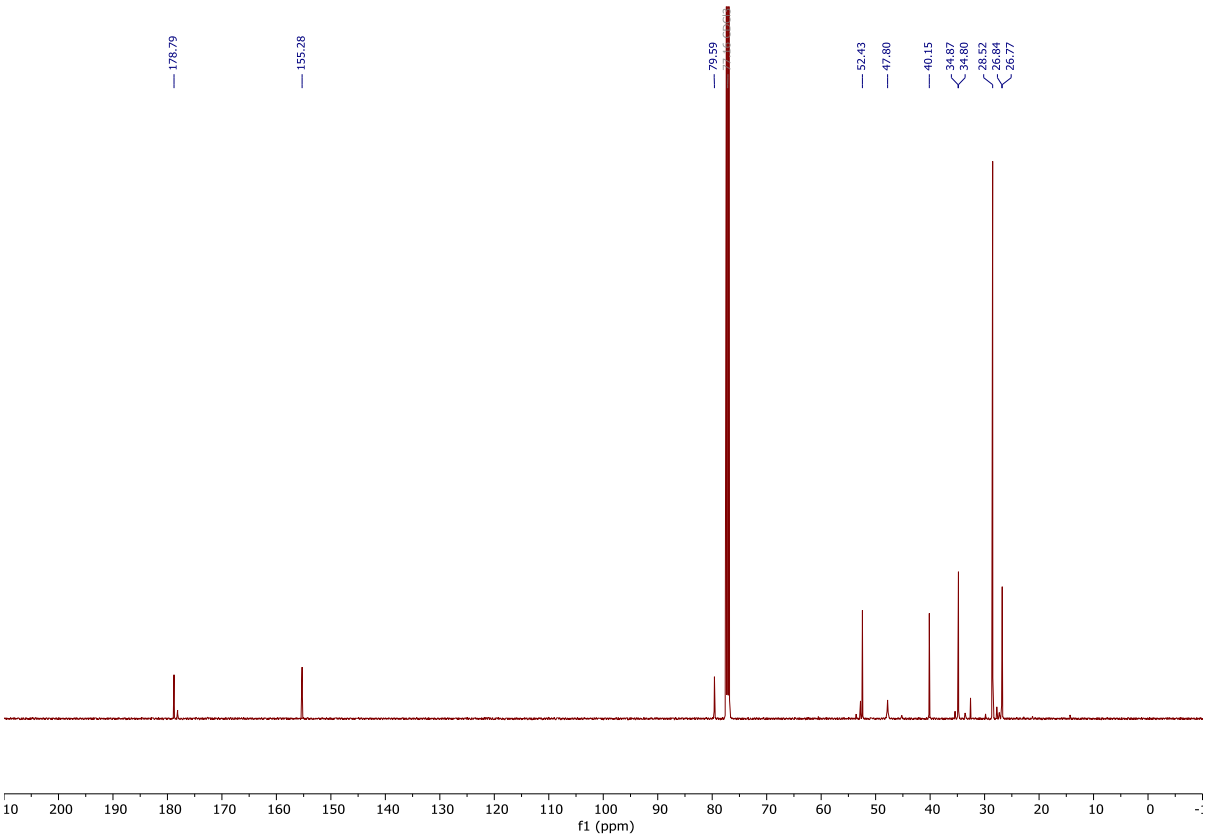


*9.1.14. (3a*SR,5*RS,7a*SR)-5-tert-Butyl(octahydroindole-2-one)carbamate* (**3s**)

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

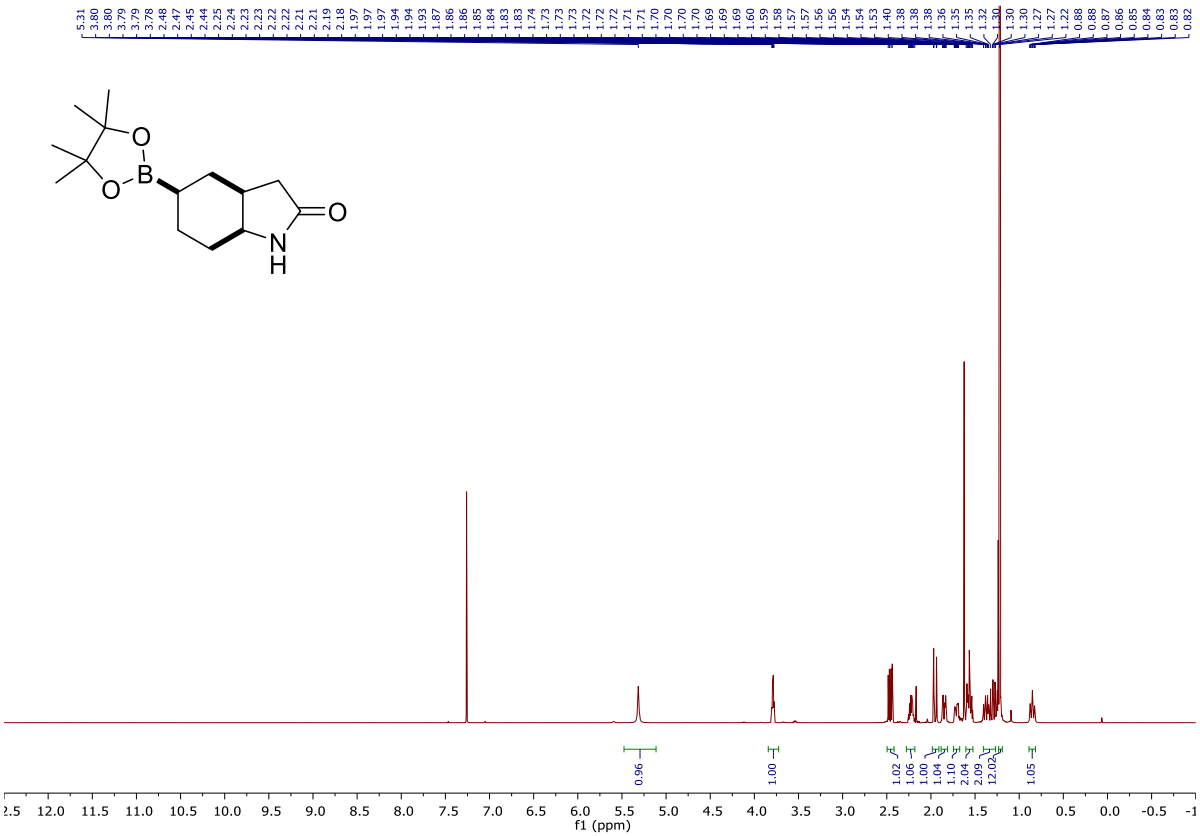


^{13}C NMR (126 MHz, $CDCl_3$):

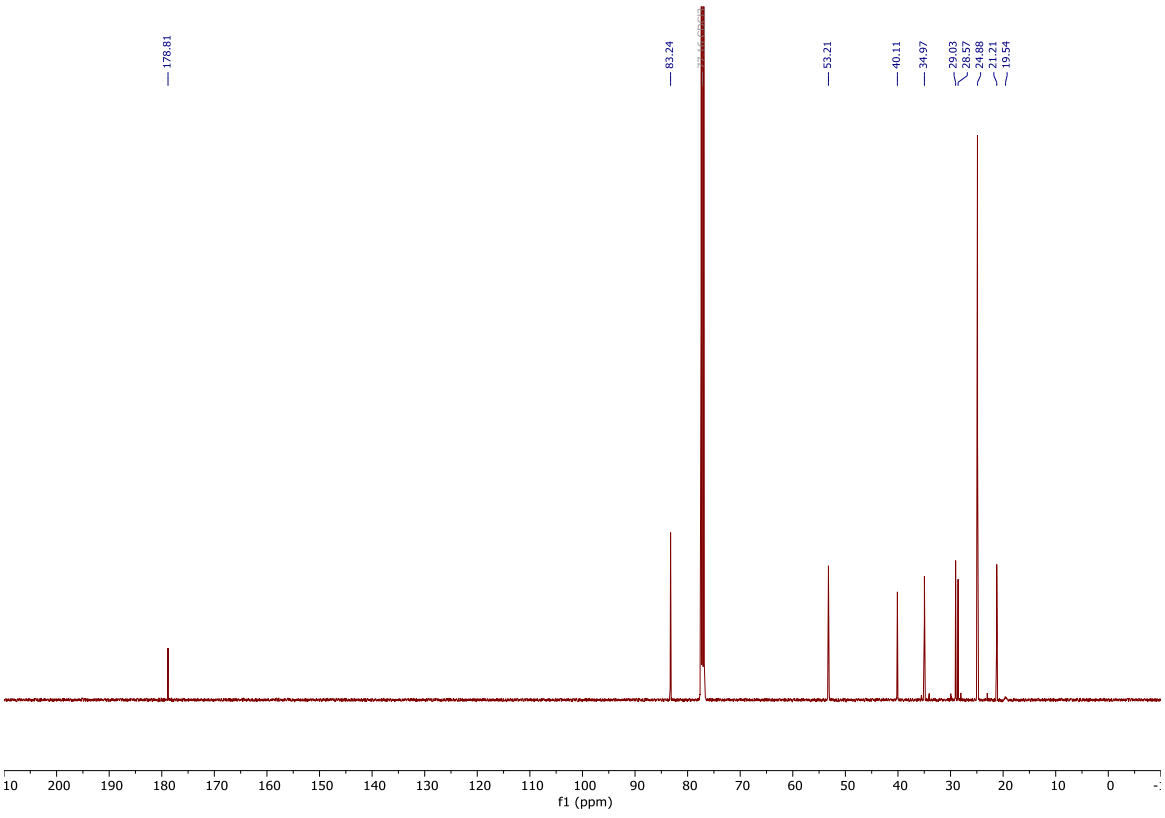


9.1.15. *(*3a*SR,*5*RS,*7a*SR)-5-*(4,4,5,5-Tetramethyl-1,2,3-oxadiborolan-2-yl)Ioctahydroindol-2one (**3t**)

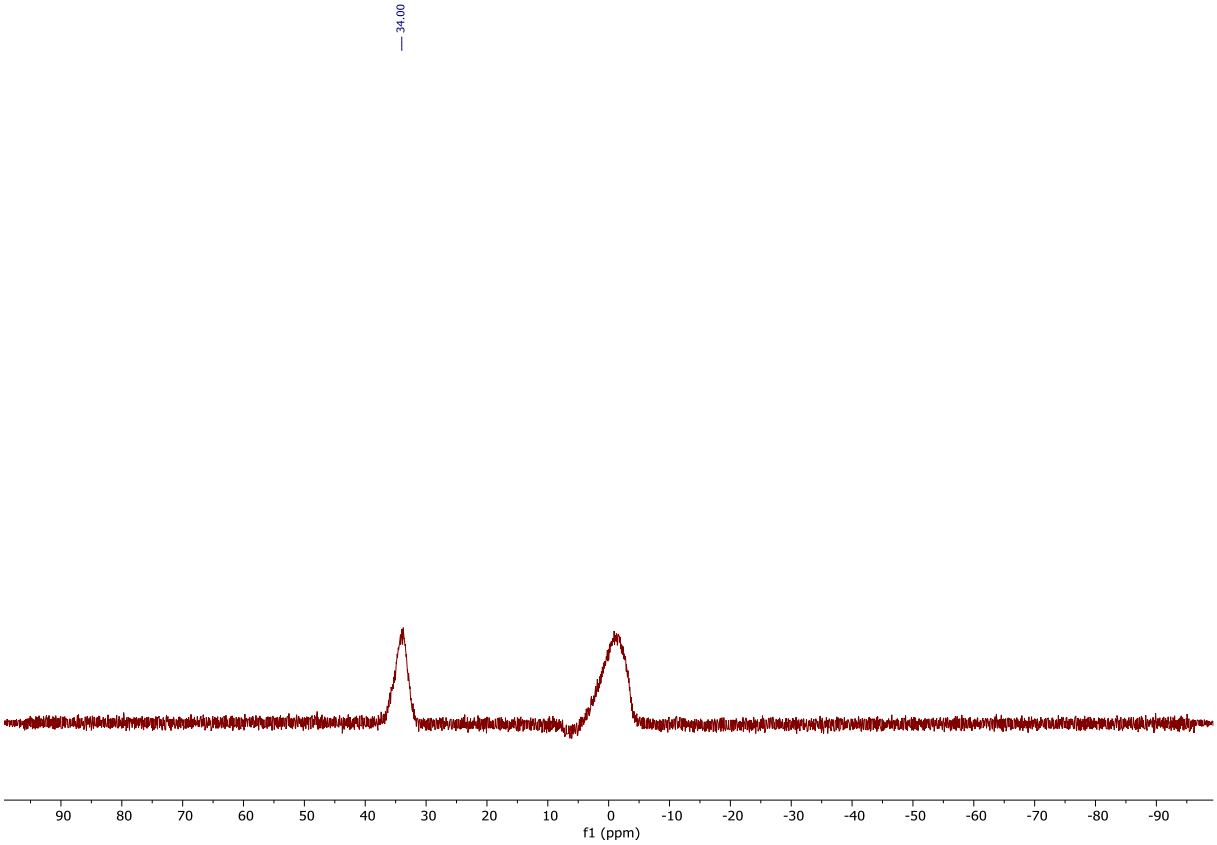
^{1}H NMR (500 MHz, $CDCl_3$):



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

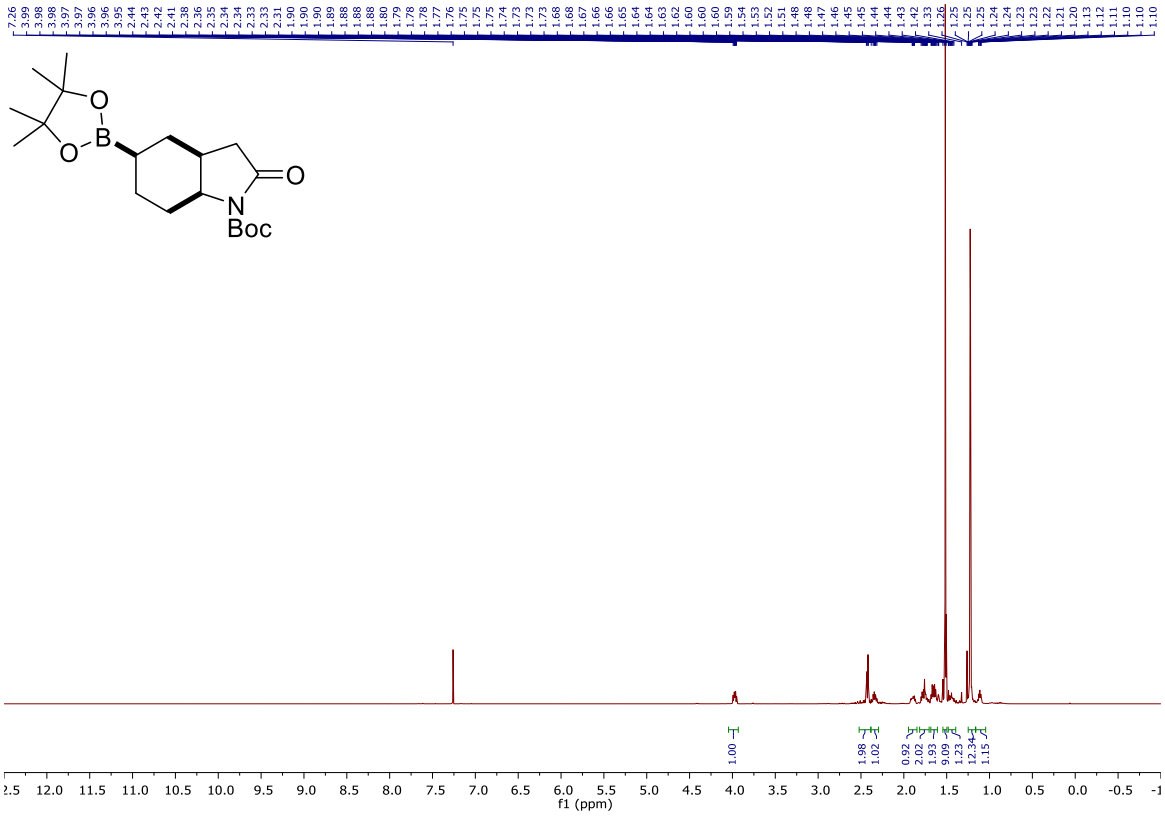


^{11}B NMR (128 MHz, $CDCl_3$):

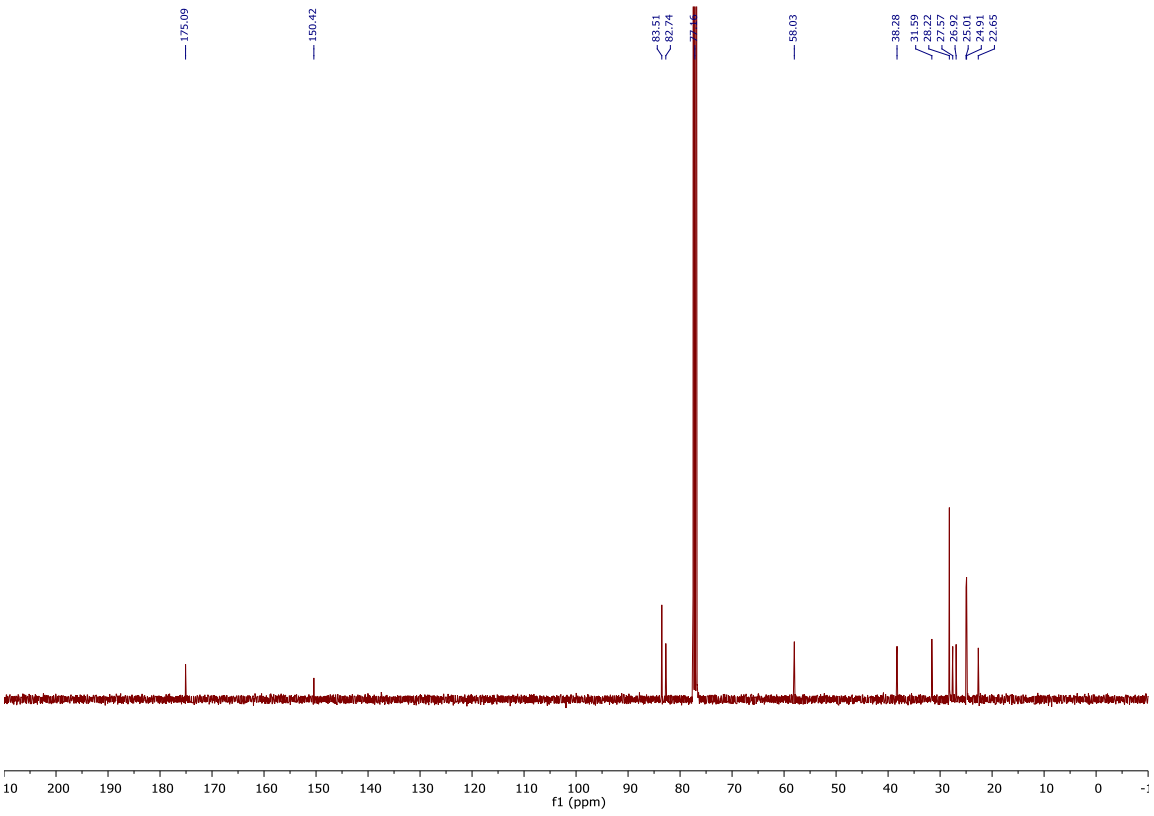


*9.1.16. (3a*SR,5*RS,7a*SR)-tert-Butyl-2-oxo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydroindole-1-carboxylate (**3u**)*

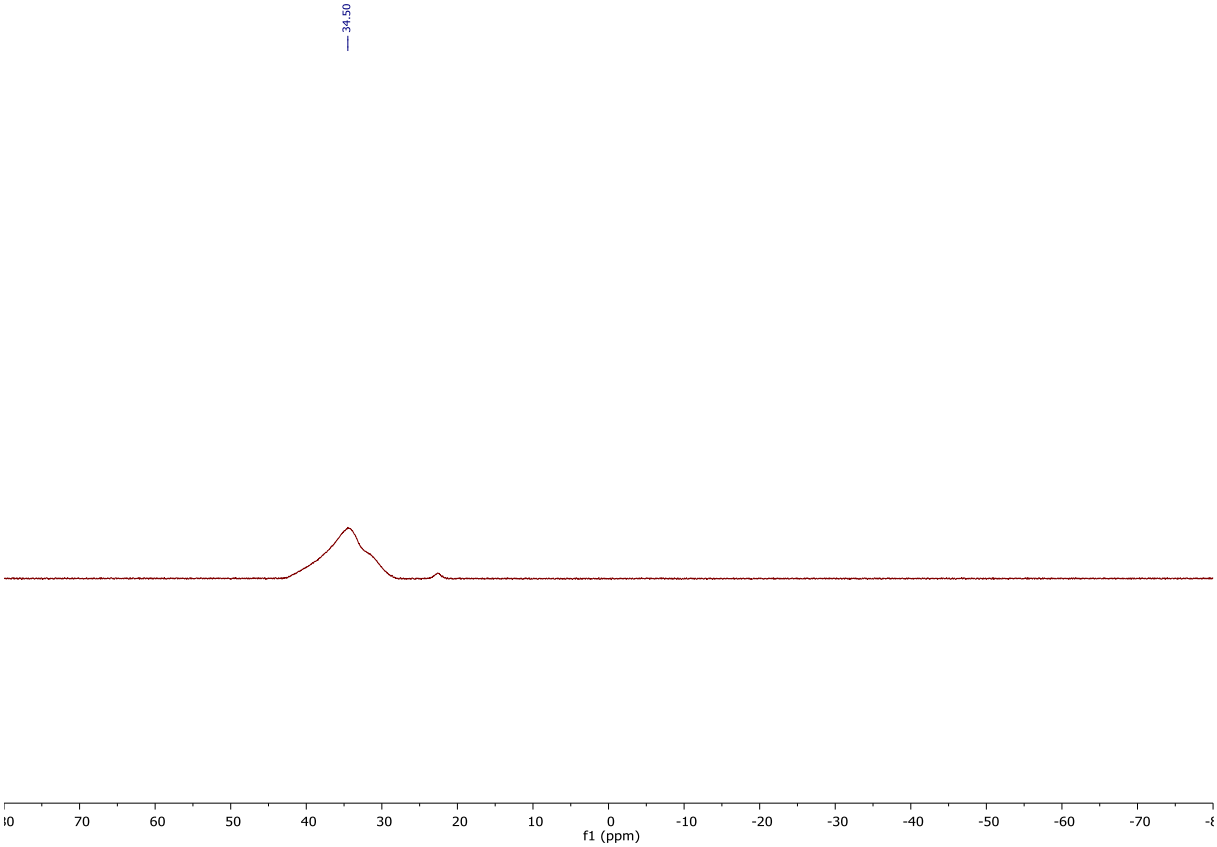
^{1}H NMR (500 MHz, $CDCl_3$):



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

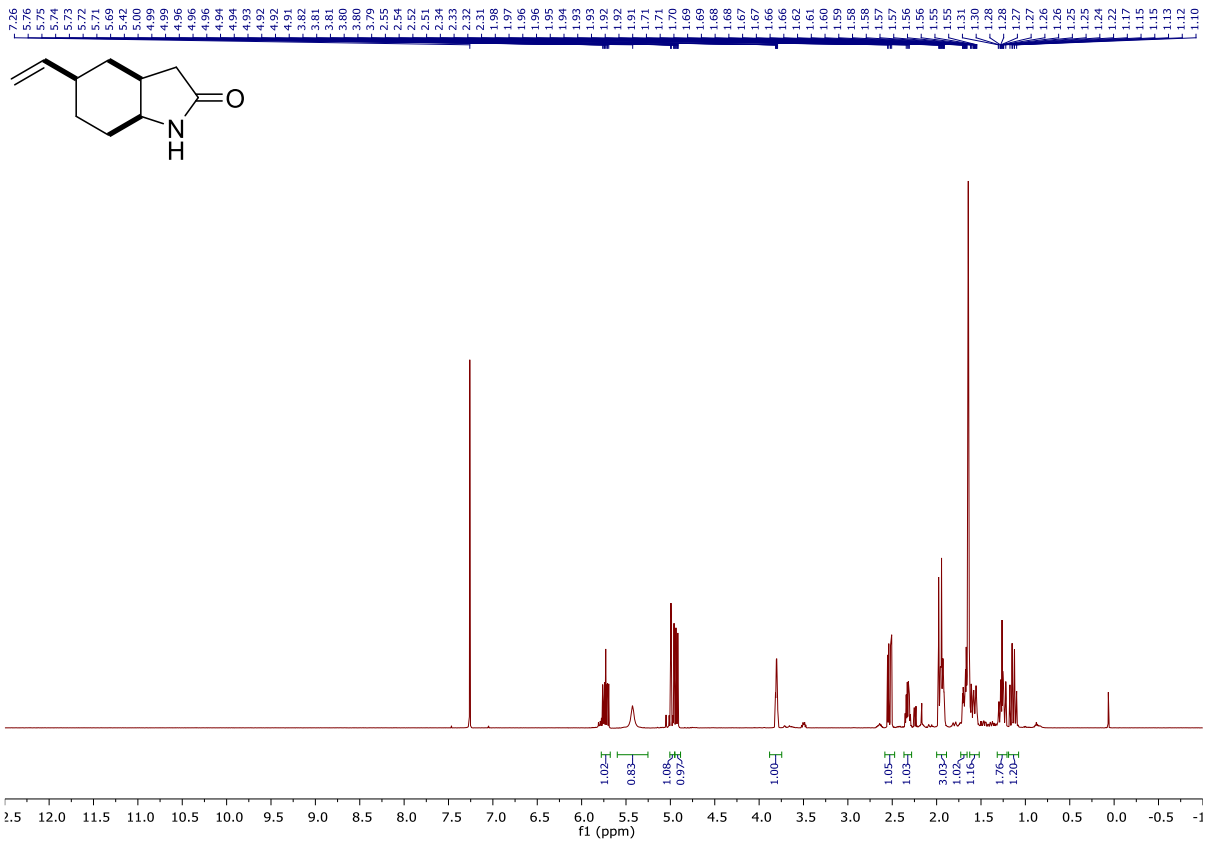


^{11}B NMR (128 MHz, $CDCl_3$):

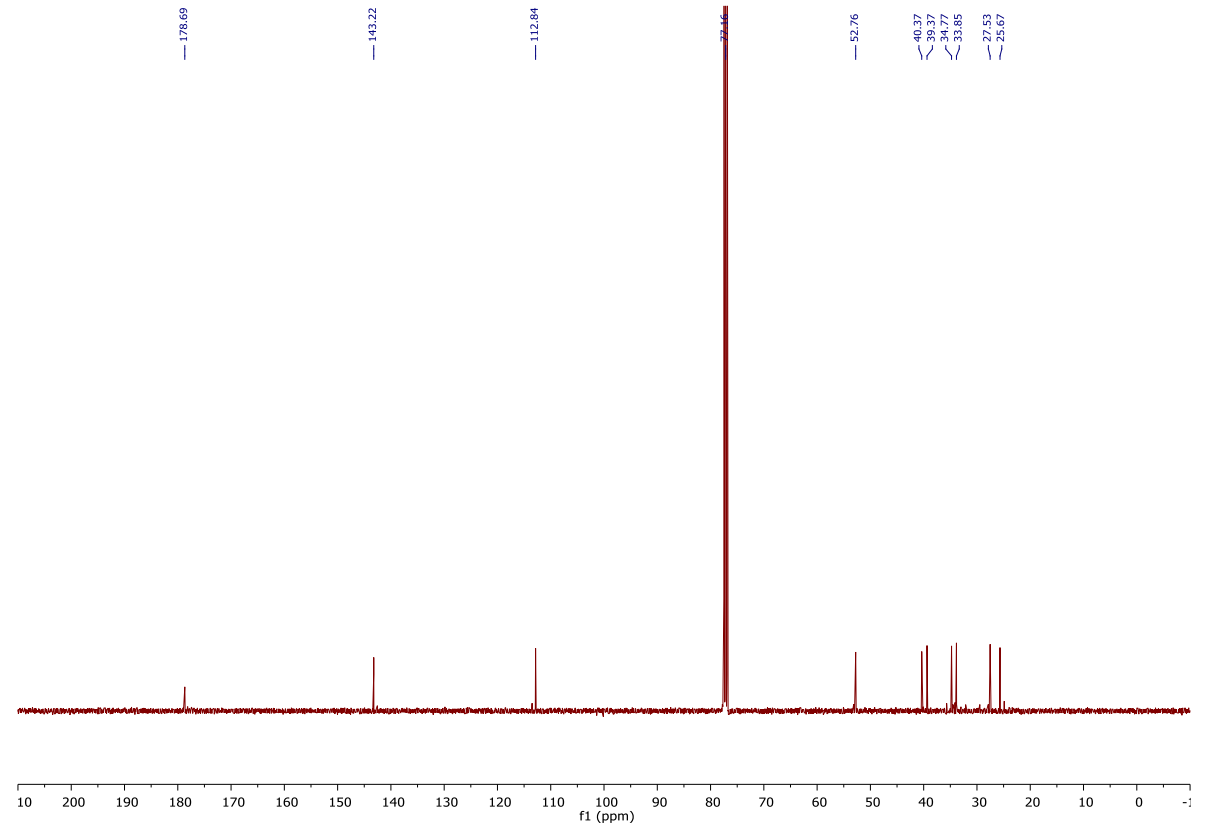


*9.1.17. (3a*SR,5RS,7a*SR)-2-Oxo-5-vinyloctahydro-1H-indole-1-carboxylate (**3v**)*

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

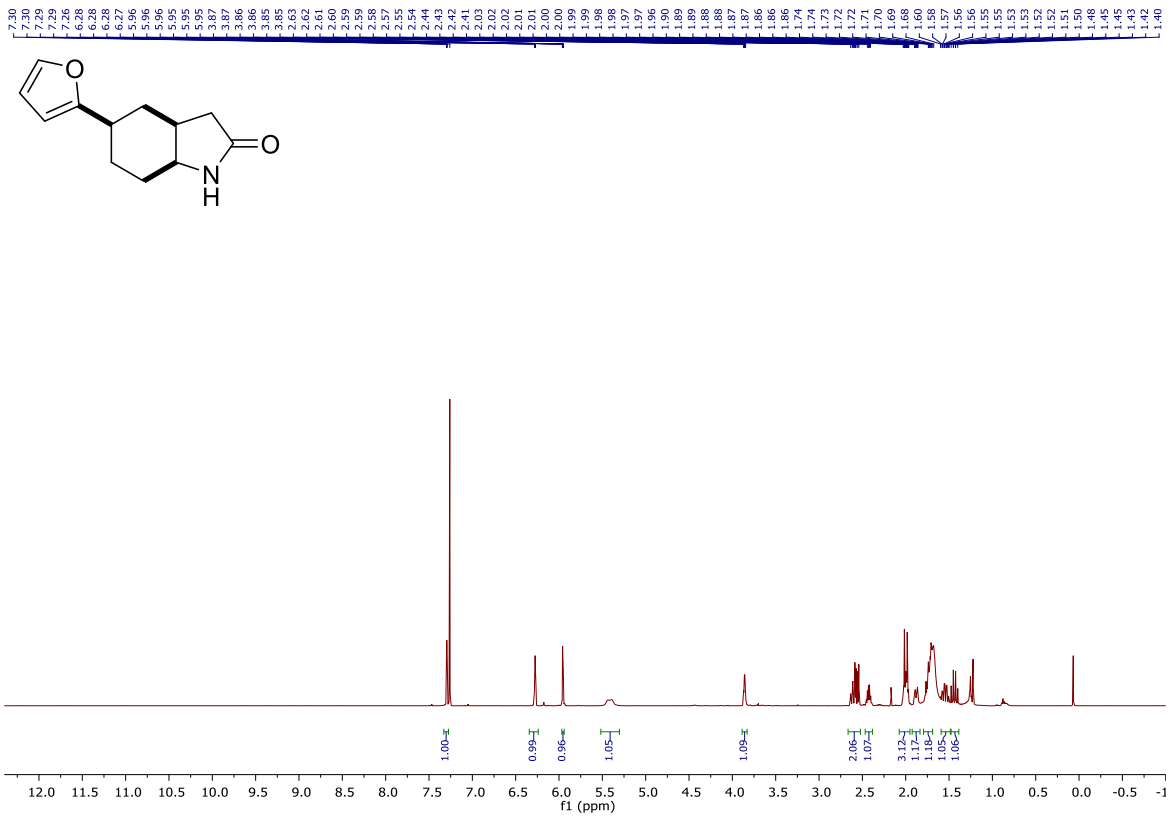


^{13}C NMR (126 MHz, $CDCl_3$):

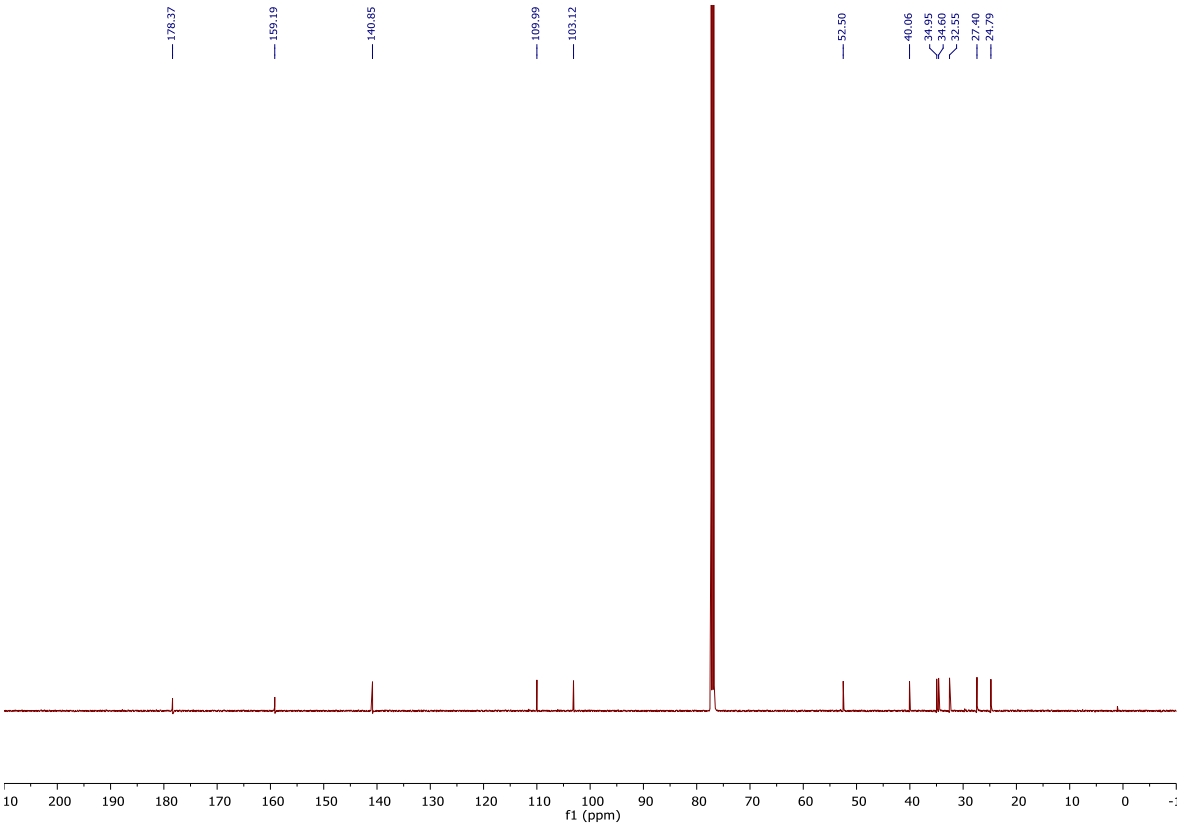


*9.1.18. (3a*SR*,5*RS*,7a*SR*)-5-(Furan-2-yl)octahydro-2H-indol-2-one (**3w**)*

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

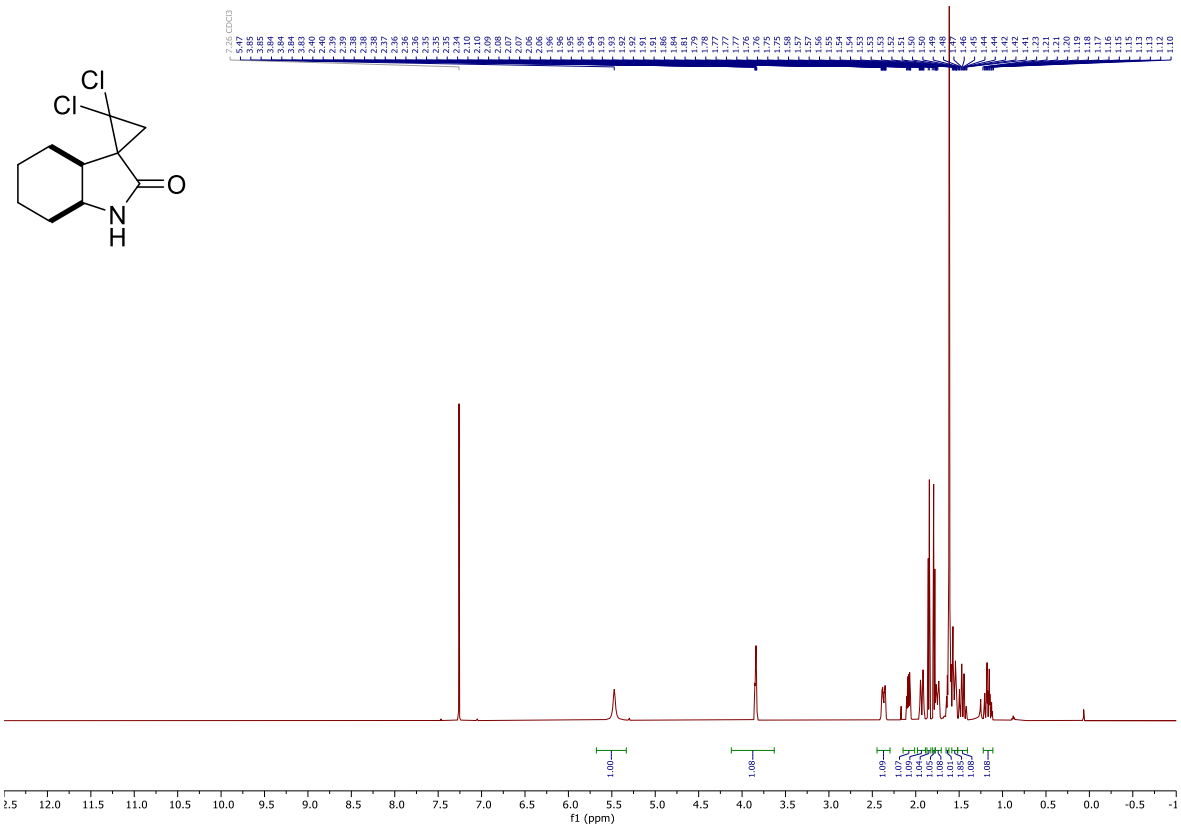


^{13}C NMR (126 MHz, $CDCl_3$):

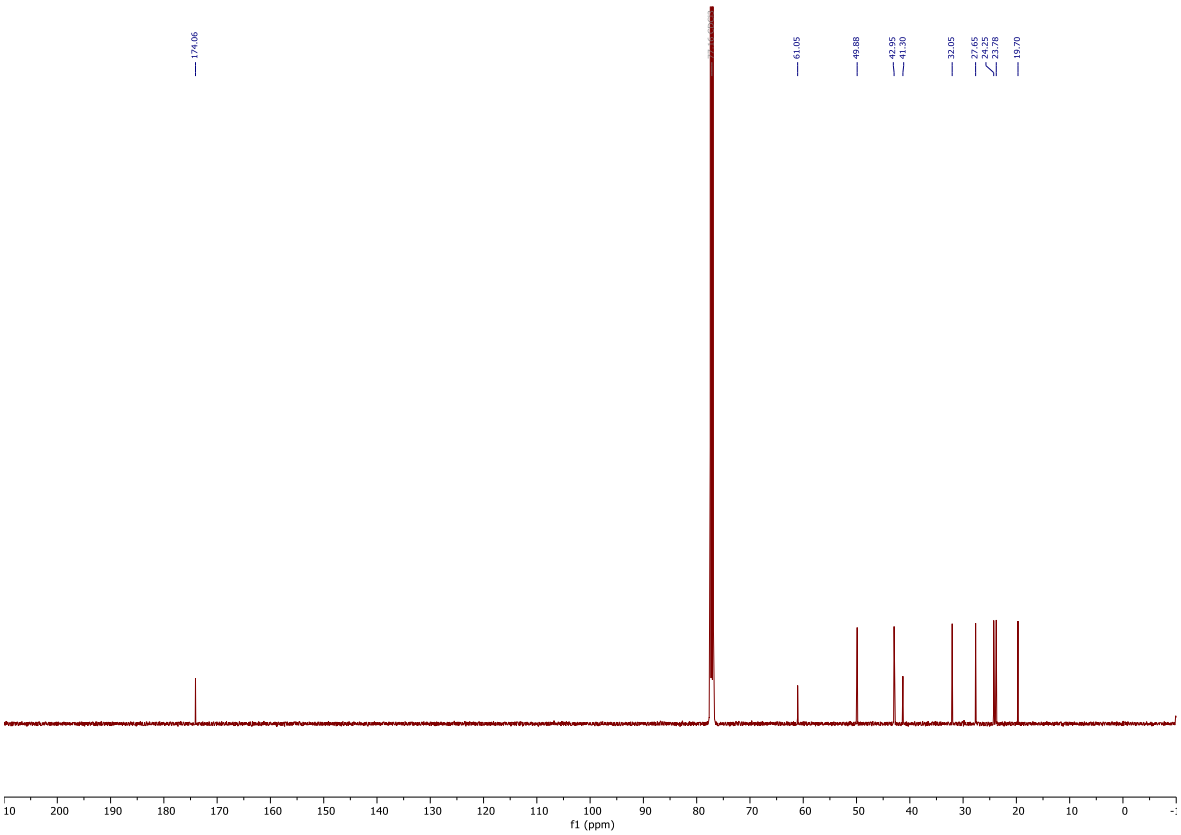


*9.1.19. (1RS,3a'SR,7a'SR)-2,2-Dichlorohexahydrospiro[cyclopropane-1,3'-indol]-2'(1'H)-one (rac-**7**)*

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

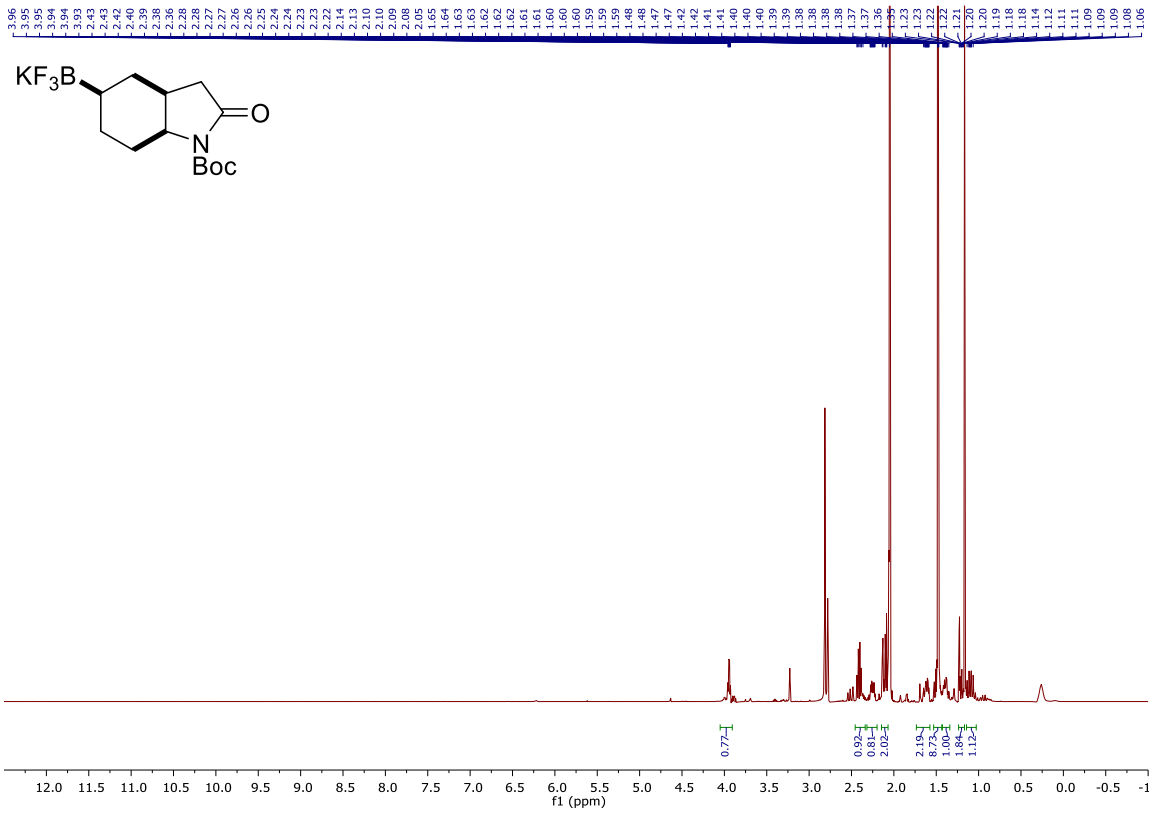


^{13}C NMR (126 MHz, $CDCl_3$):

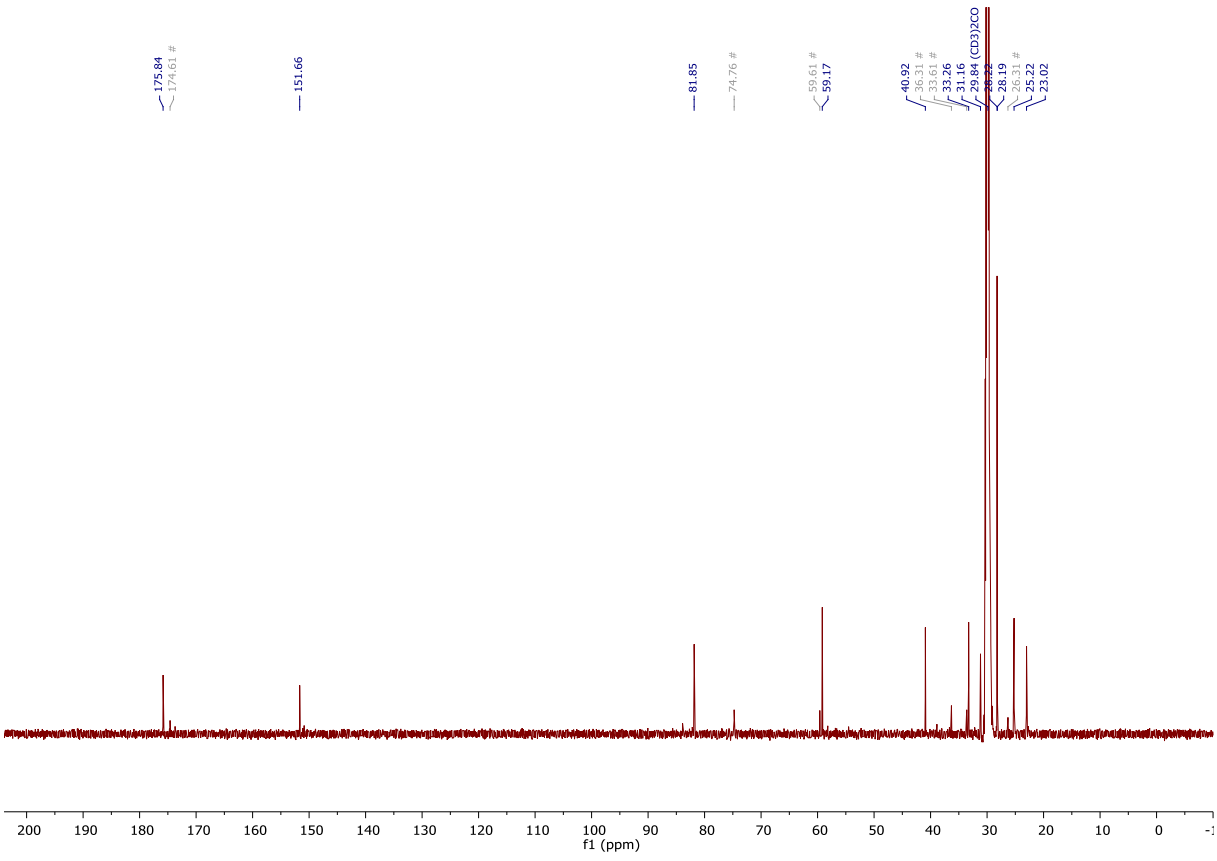


*9.1.20. (3aSR,5RS,7aSR)-Potassium 1-(tert-butoxycarbonyl)-2-oxooctahydro-1H-indol-5-yl)trifluoroborate (**10**)*

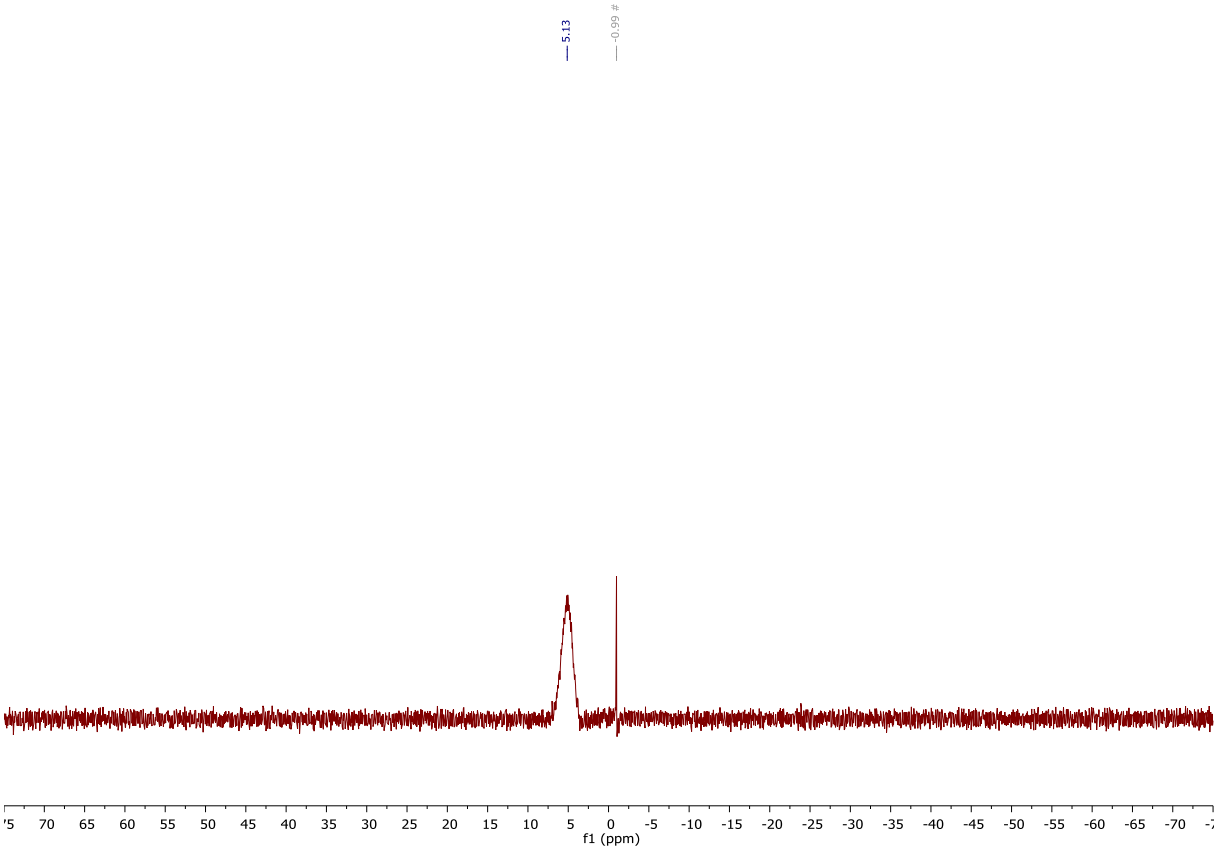
^{1}H NMR (500 MHz, acetone-d_6):



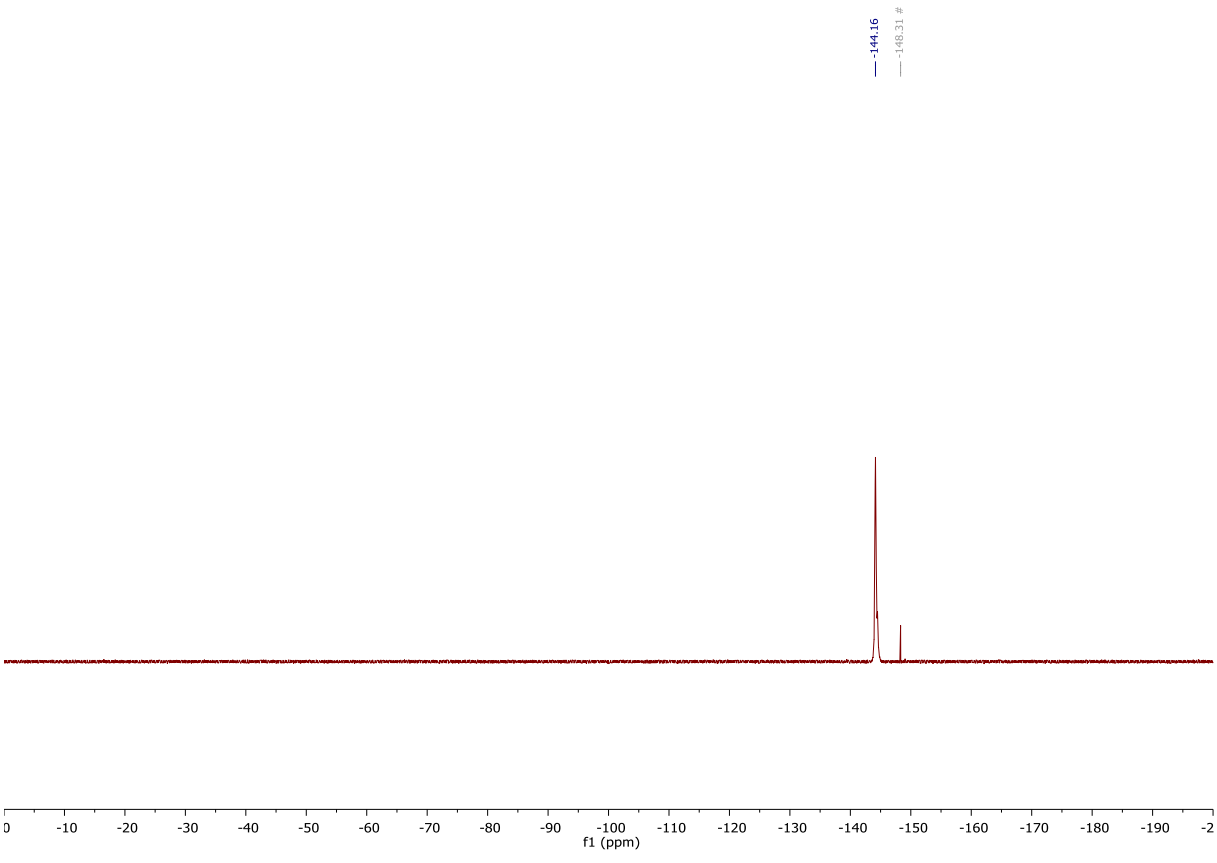
^{13}C NMR (126 MHz, acetone-d_6):



^{11}B NMR (128 MHz, acetone-d_6):

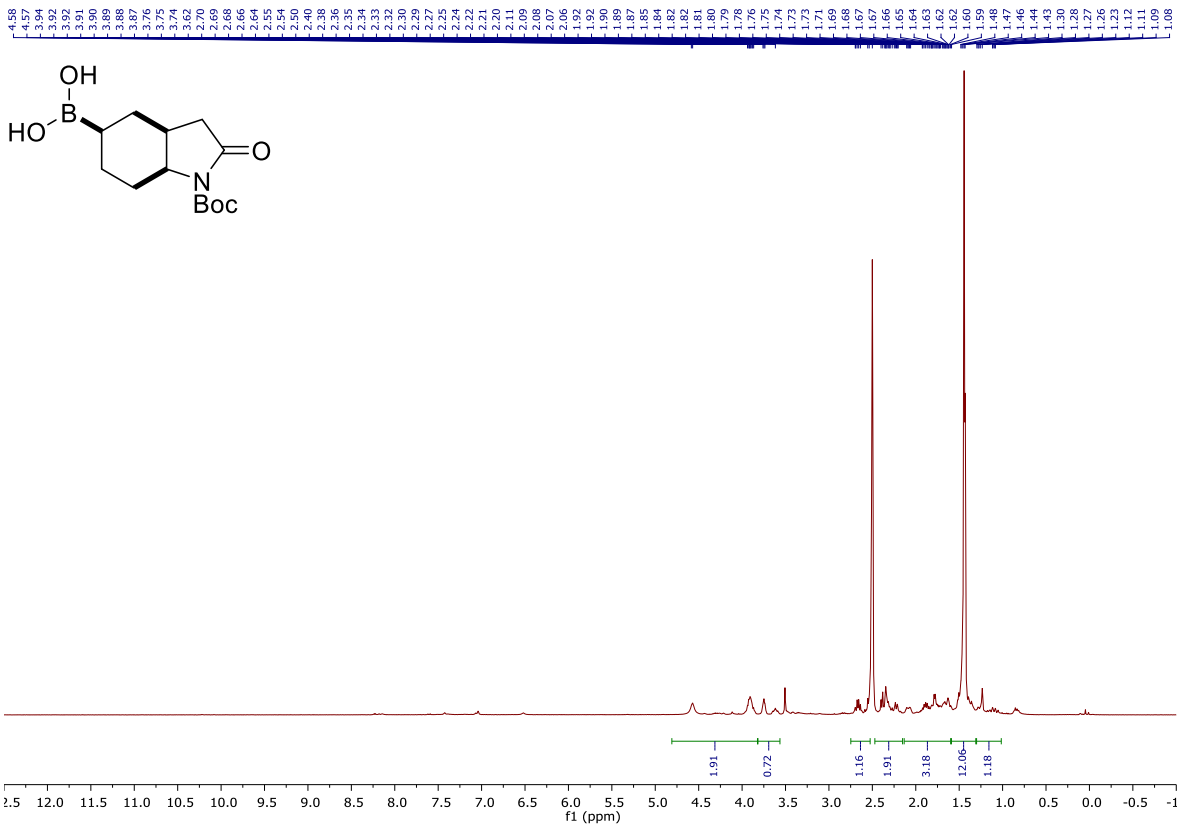


^{19}F NMR (471 MHz, acetone-d_6):

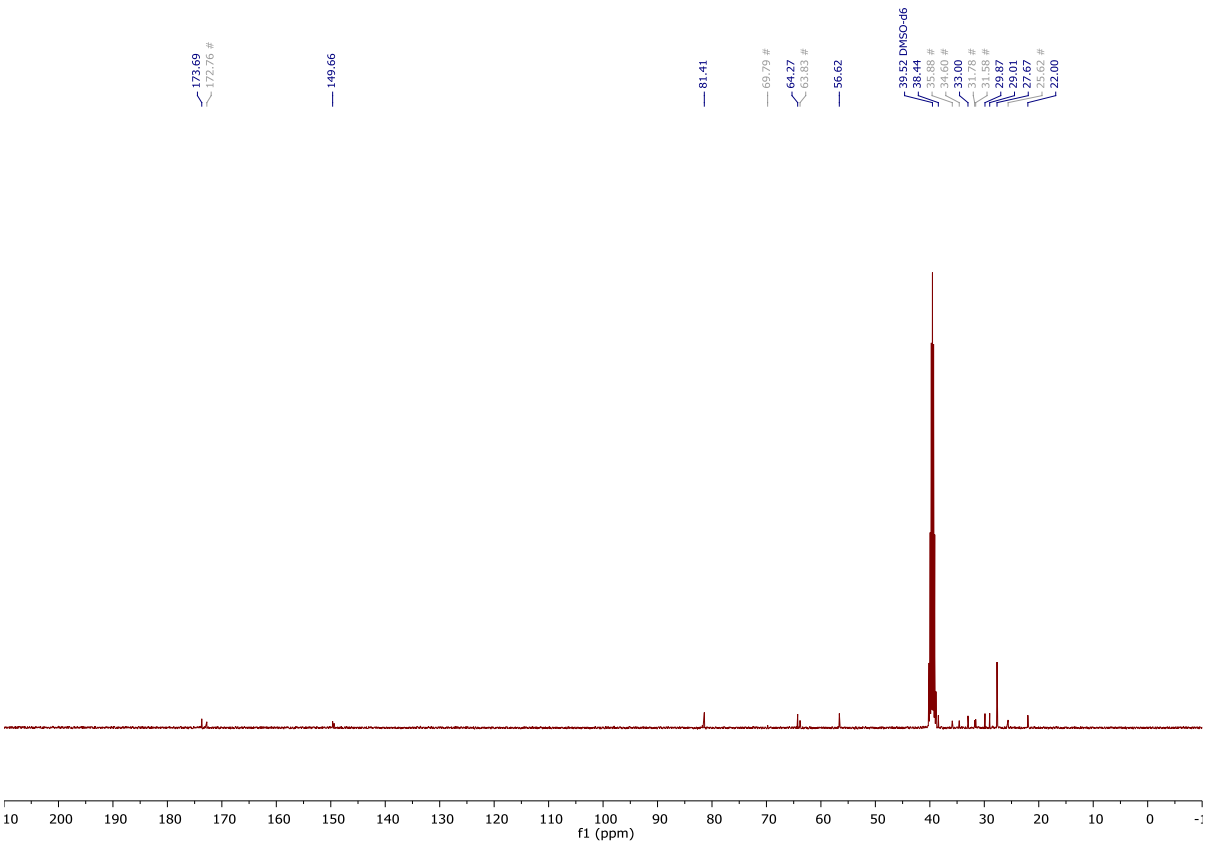


*9.1.21. (3aSR,5RS,7aSR)-(tert-Butoxycarbonyl)-2-oxooctahydro-1H-indol-5-yl) boronic acid (**11**)*

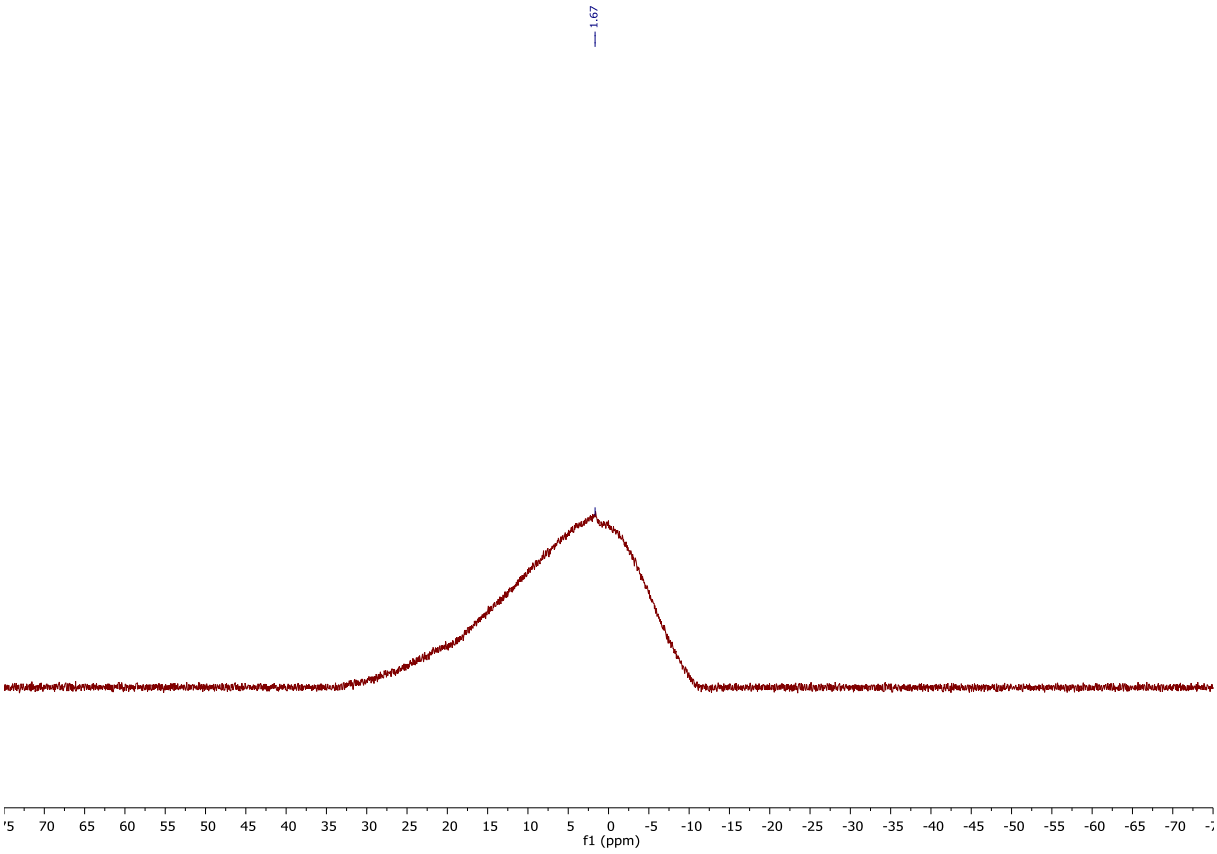
^{1}H NMR (500 MHz, DMSO-d_6):



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



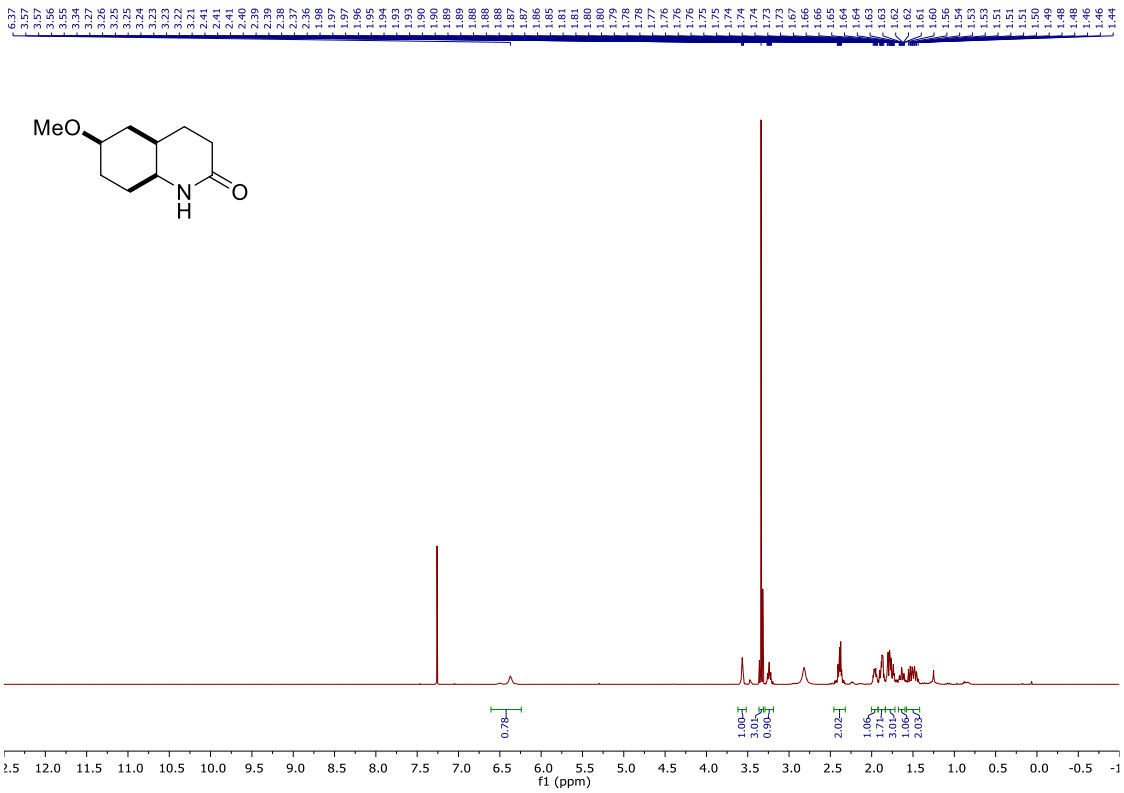
^{11}B NMR (128 MHz, DMSO-d_6):



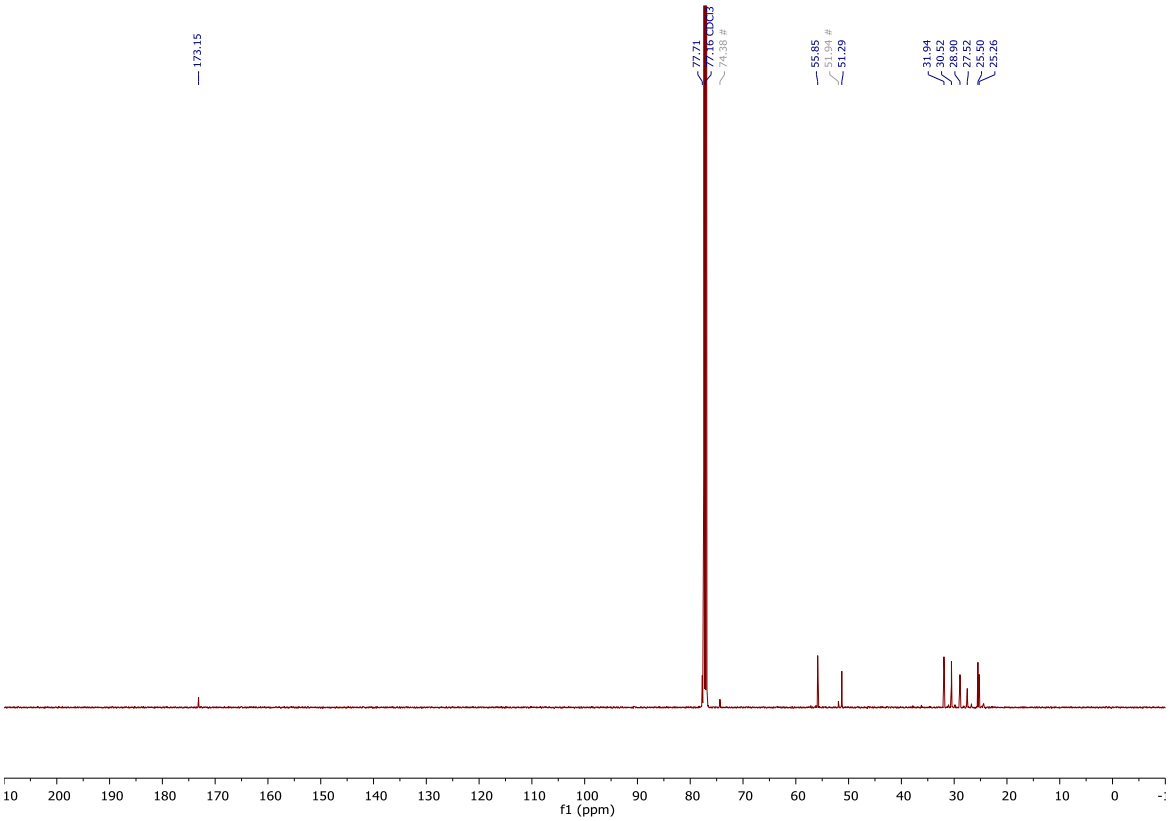
9.2. Quinoline-2-one derivatives

*9.2.1. (4aRS,6RS,8aSR)-6-Methoxyoctahydroquinolin-2-one (**5b**)*

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

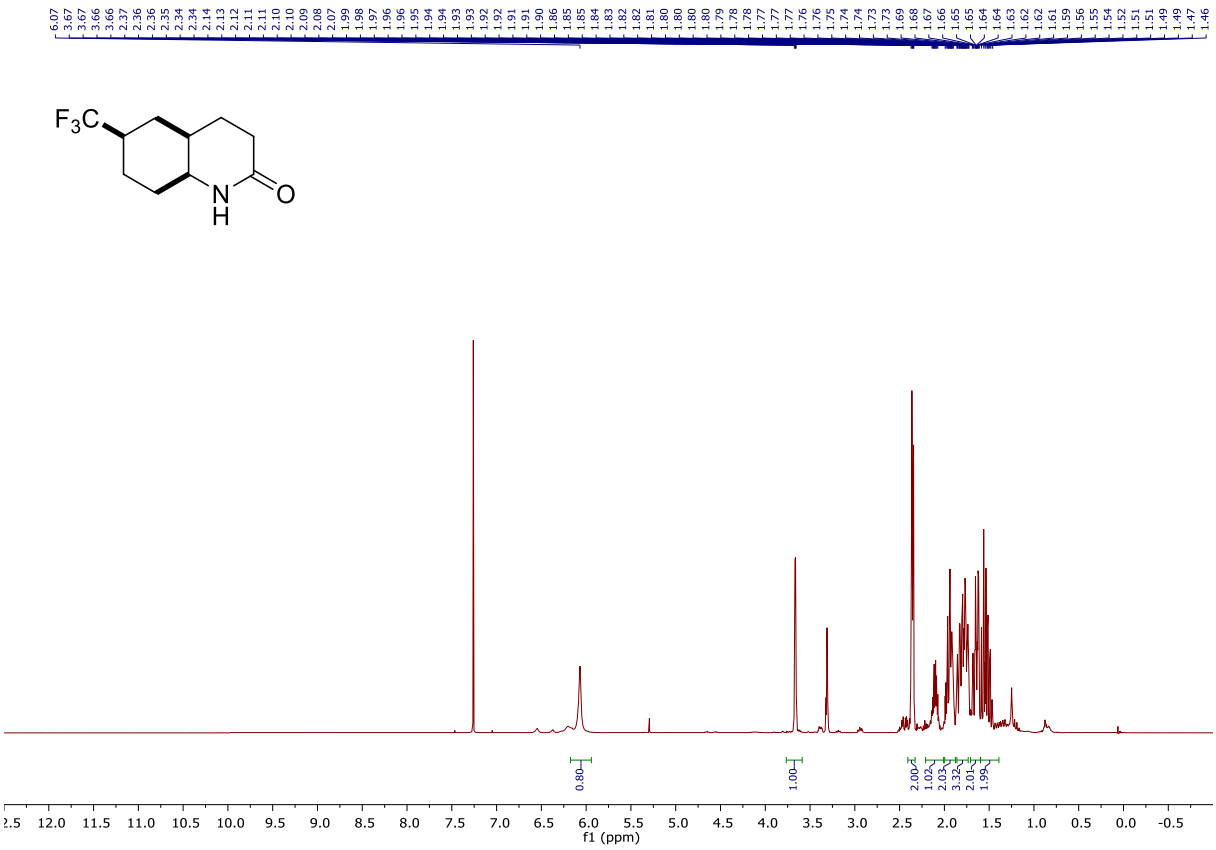


^{13}C NMR (126 MHz, $CDCl_3$):

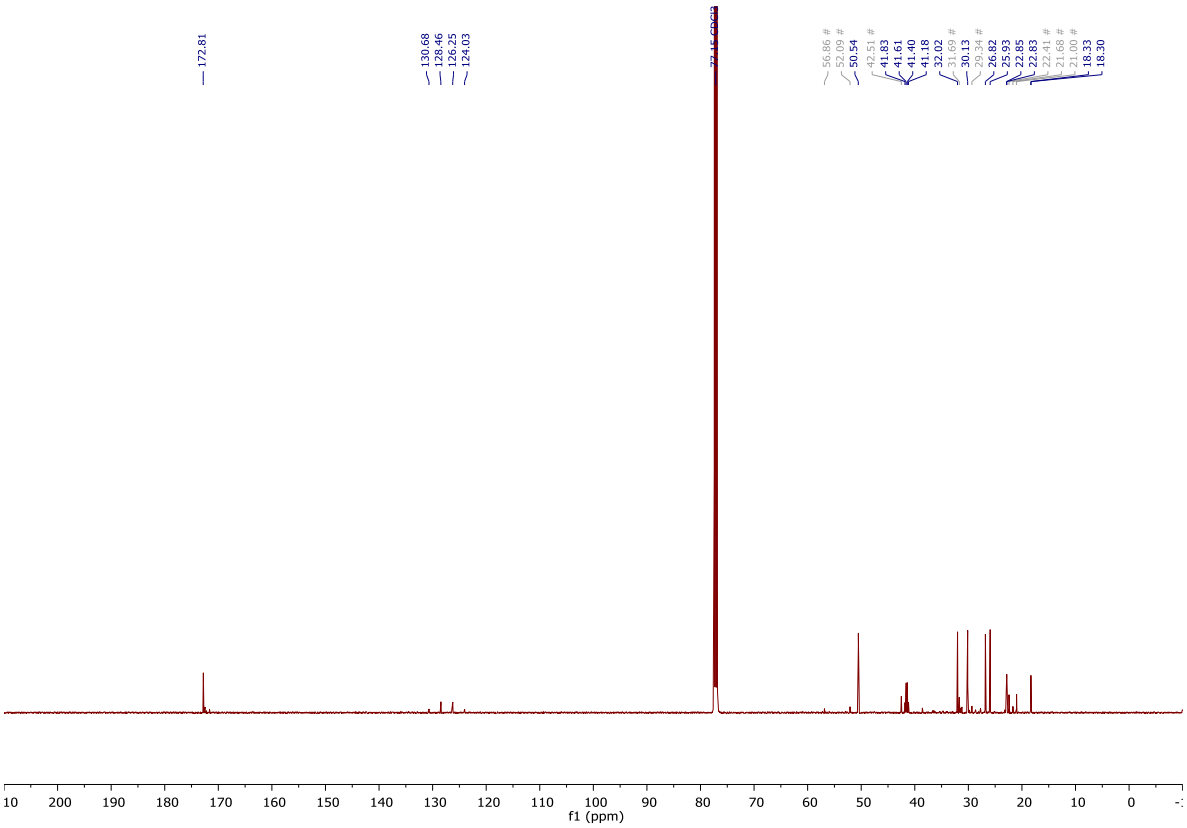


*9.2.2. (4aRS,6RS,8aSR)-6-Trifluoromethyloctahydroquinolin-2-one (**5c**)*

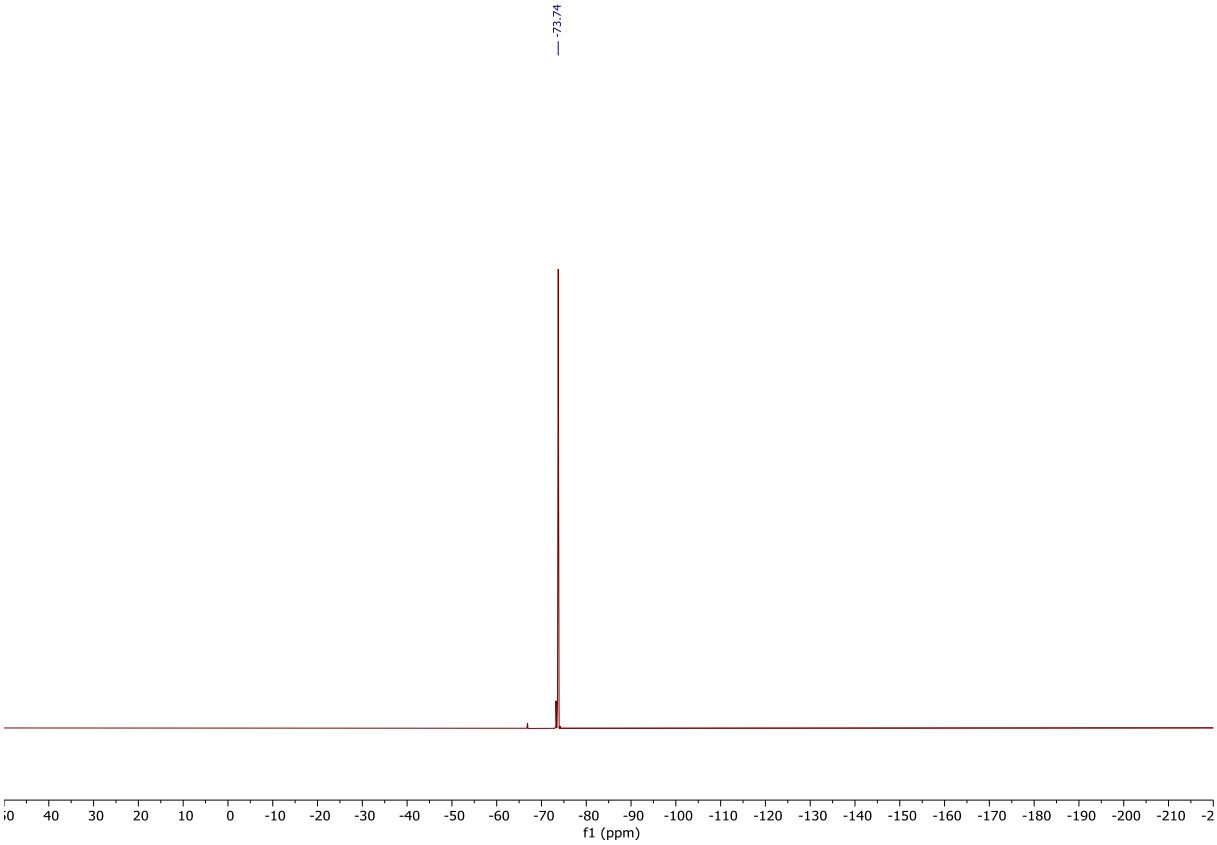
^{1}H NMR (500 MHz, $CDCl_3$):



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

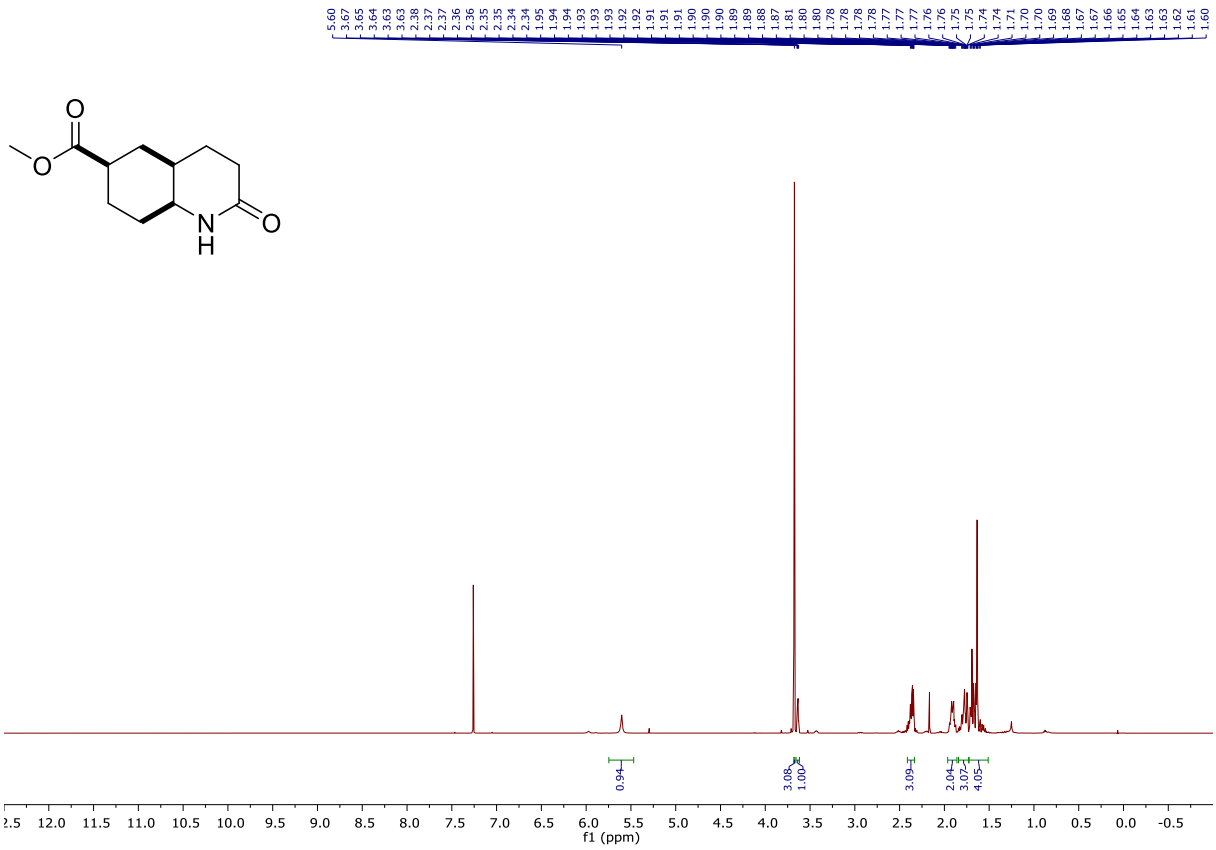


^{19}F NMR (471 MHz, $CDCl_3$):

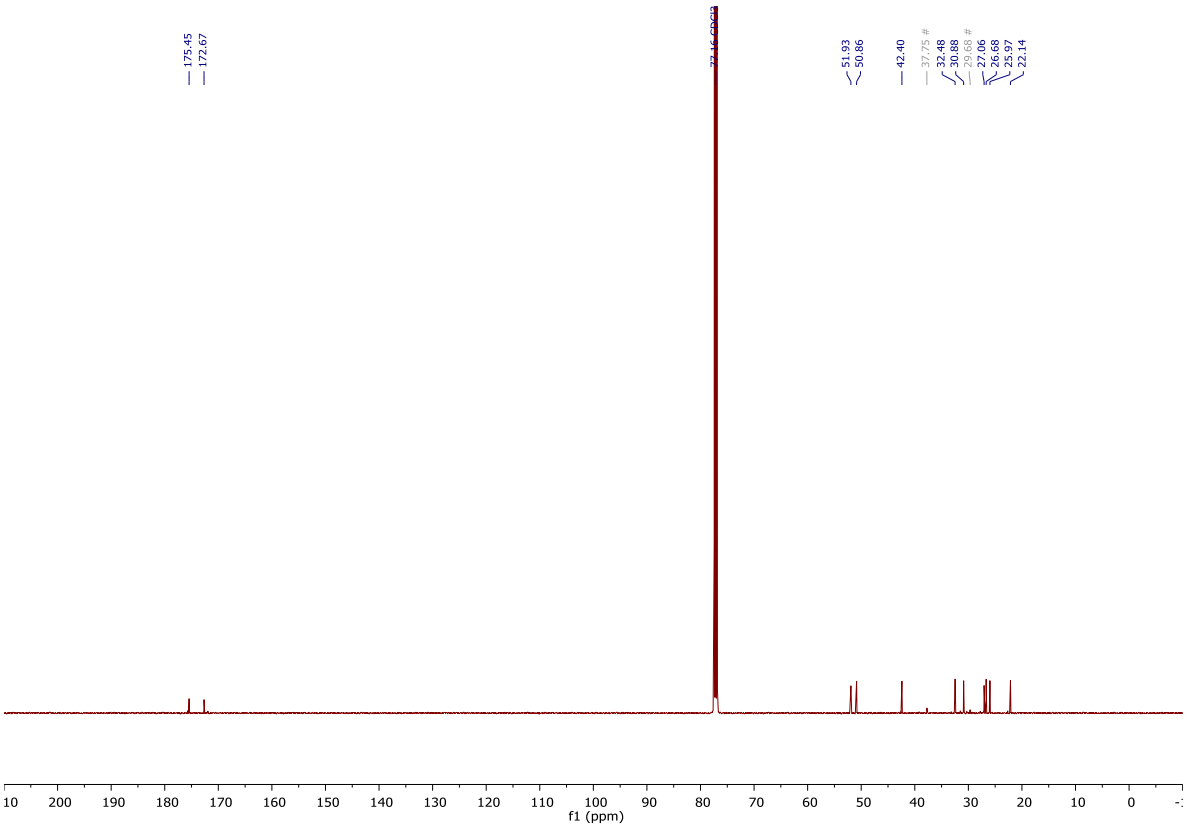


*9.2.3. (4aRS,6RS,8aSR)-Methyl-2-oxodecahydroquinolin-6-carboxylate (***5d***)*

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

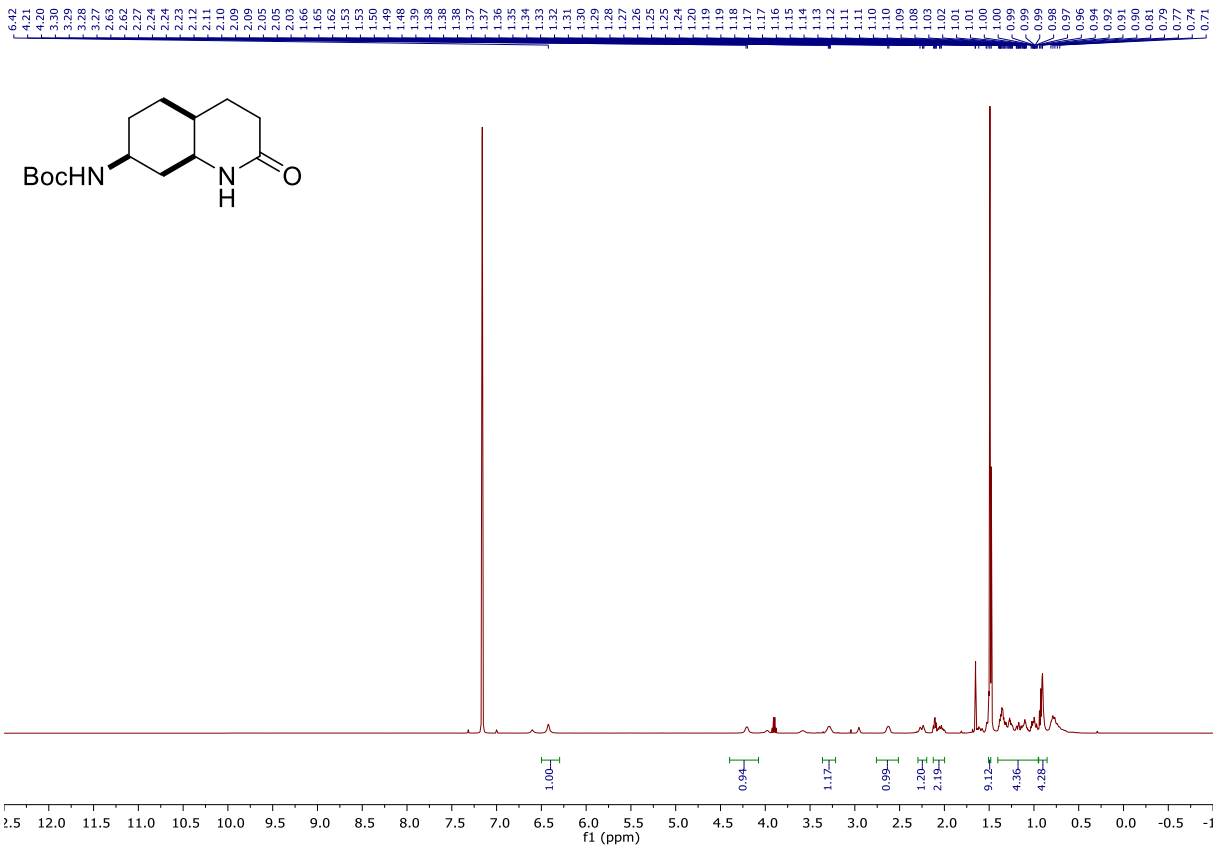


^{13}C NMR (126 MHz, $CDCl_3$):

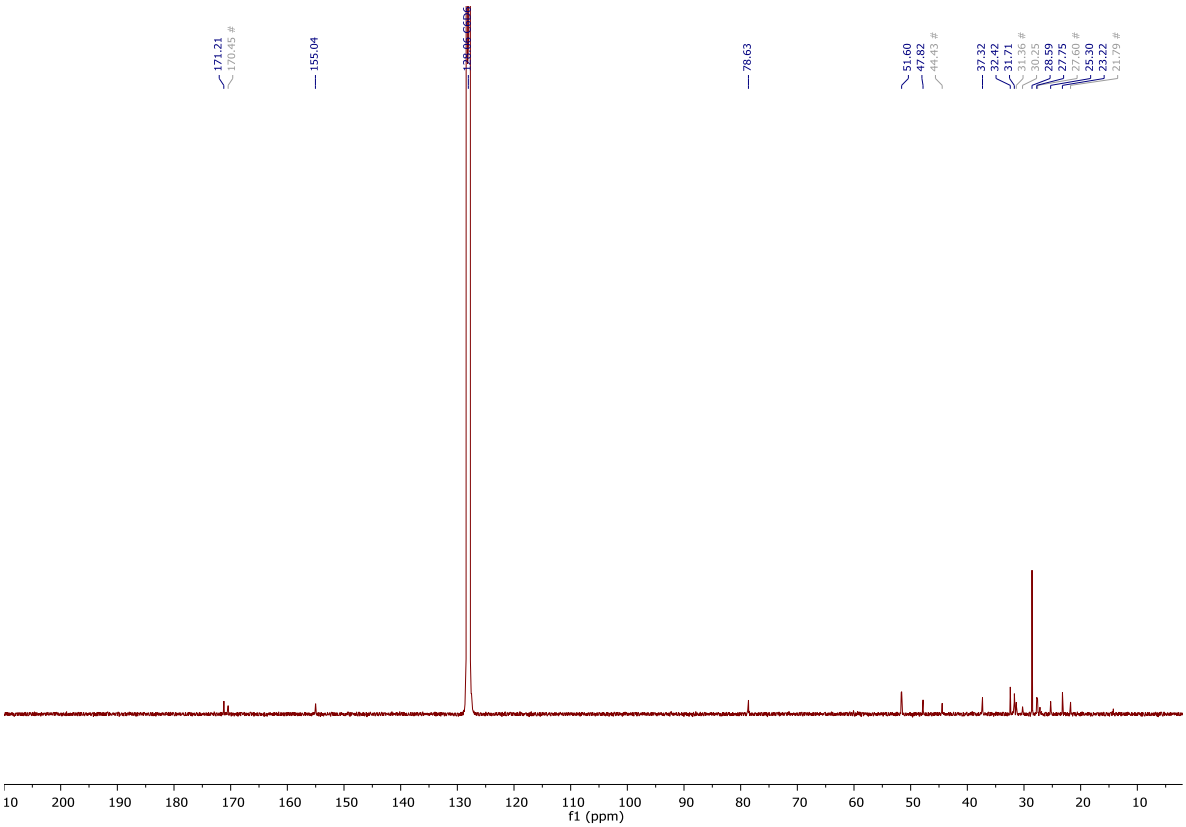


*9.2.4. (4aSR,7SR,8aSR)-tert-Butyl-(2-oxodecahydroquinolin-7-yl)carbamate (**5e**)*

^{1}H NMR (500 MHz, benzene – d_6):

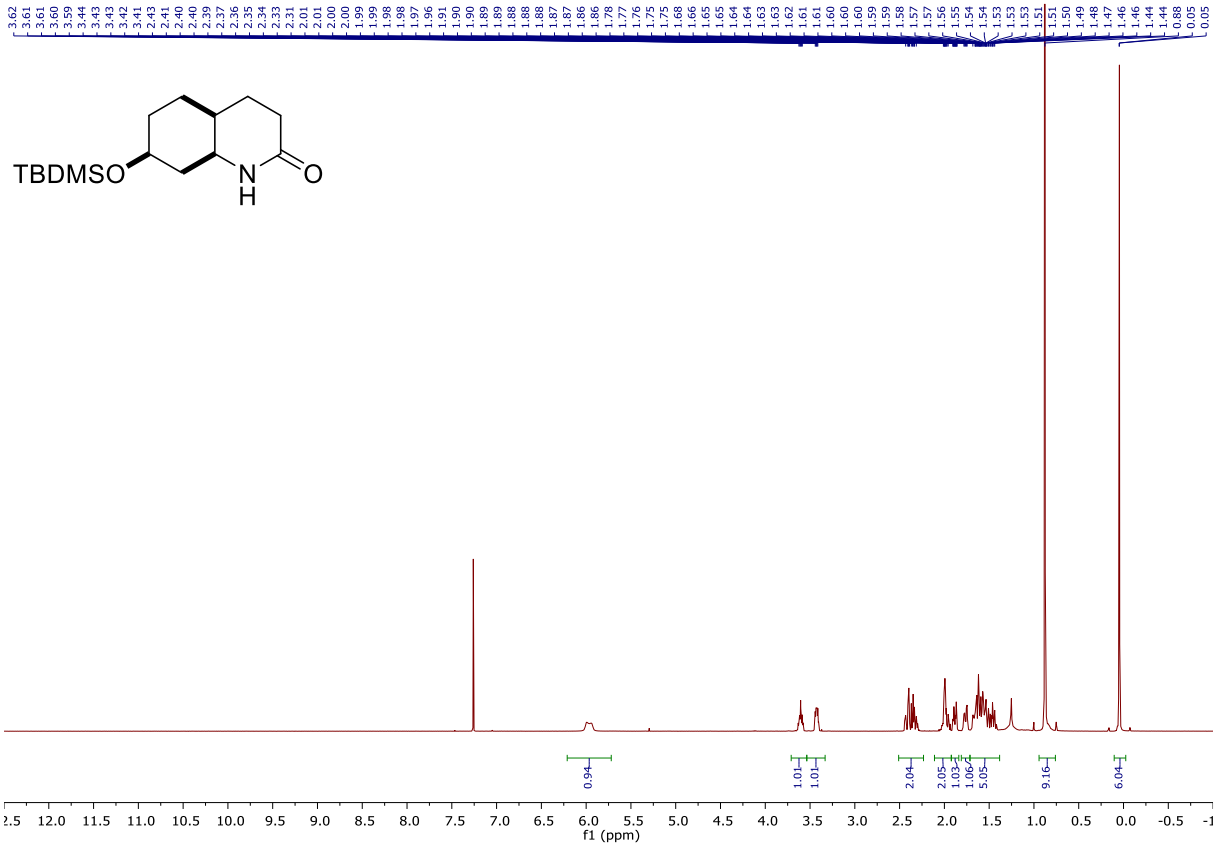


^{13}C NMR (126 MHz, benzene – d_6):

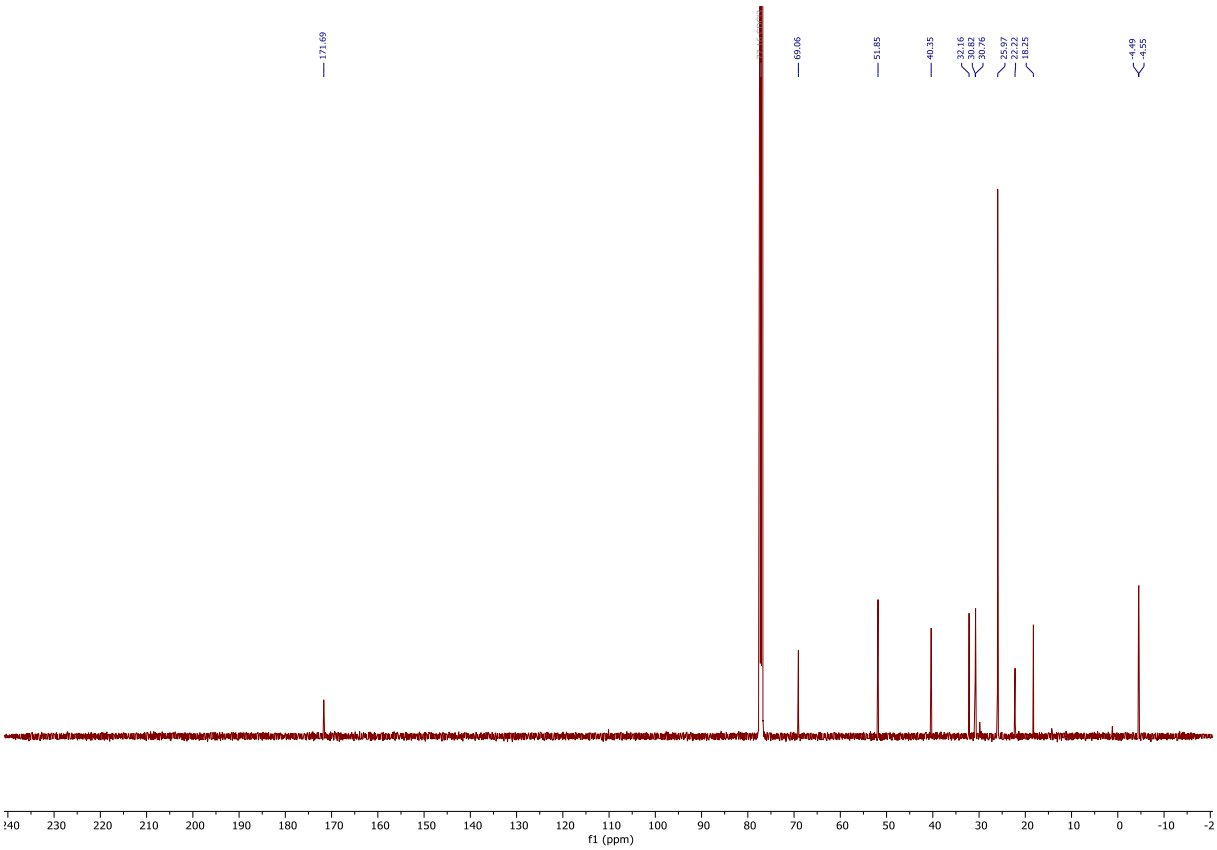


*9.2.5. (4aSR,7SR,8aSR)-7-((tert-Butyldimethylsilyl)oxy)octahydroquinolin-2-one (**5f**)*

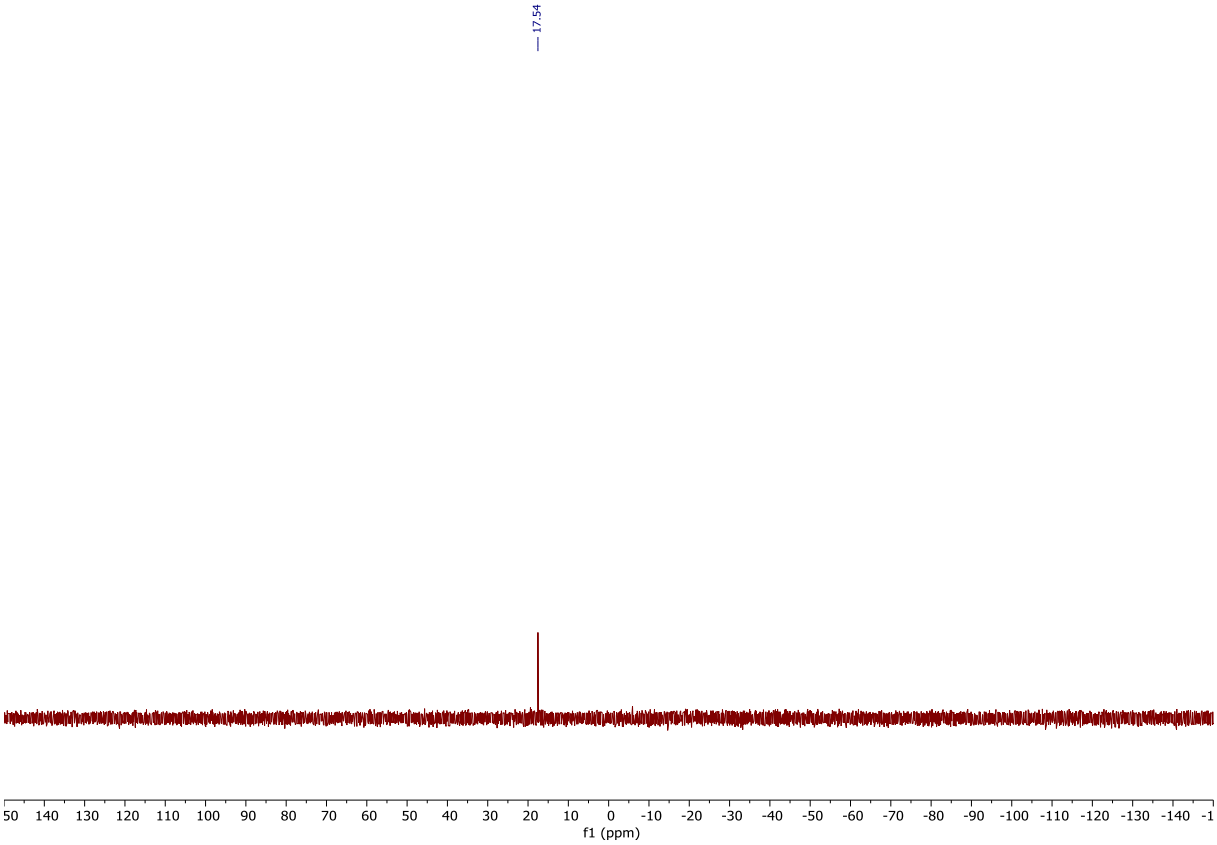
^{1}H NMR (500 MHz, $CDCl_3$):



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

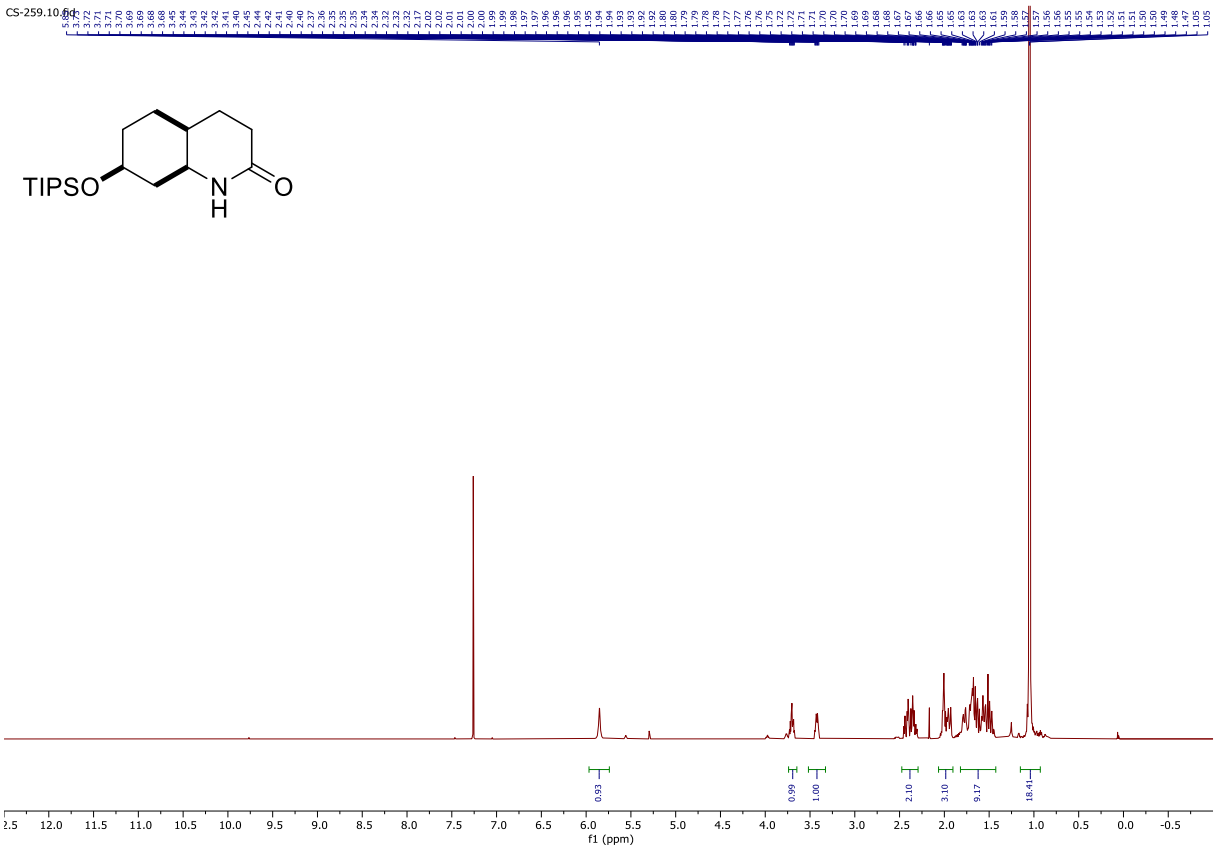


^{29}Si NMR (99 MHz, $CDCl_3$):

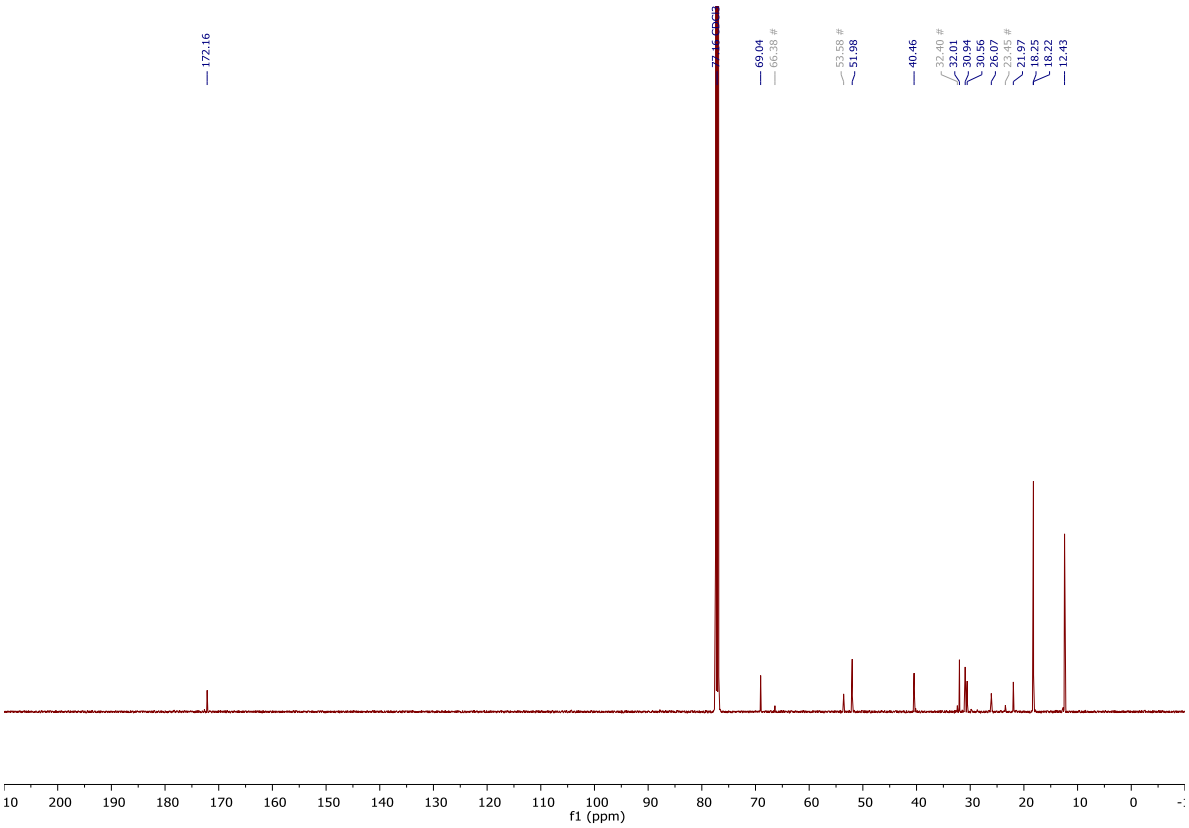


*9.2.6. (4aSR,7SR,8aSR)-7-(Triisopropylsilyl)oxy)octahydroquinolin-2-one (**5g**)*

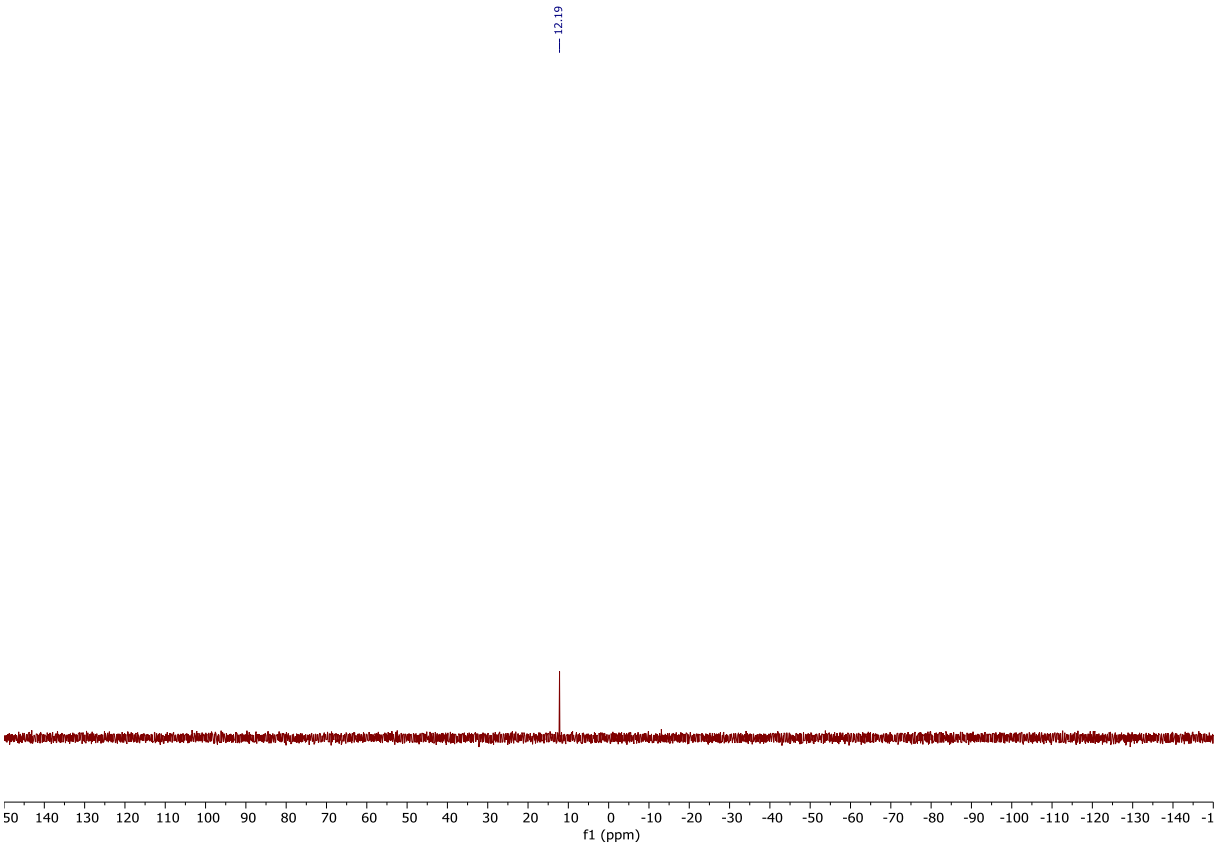
^{1}H NMR (500 MHz, $CDCl_3$):



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

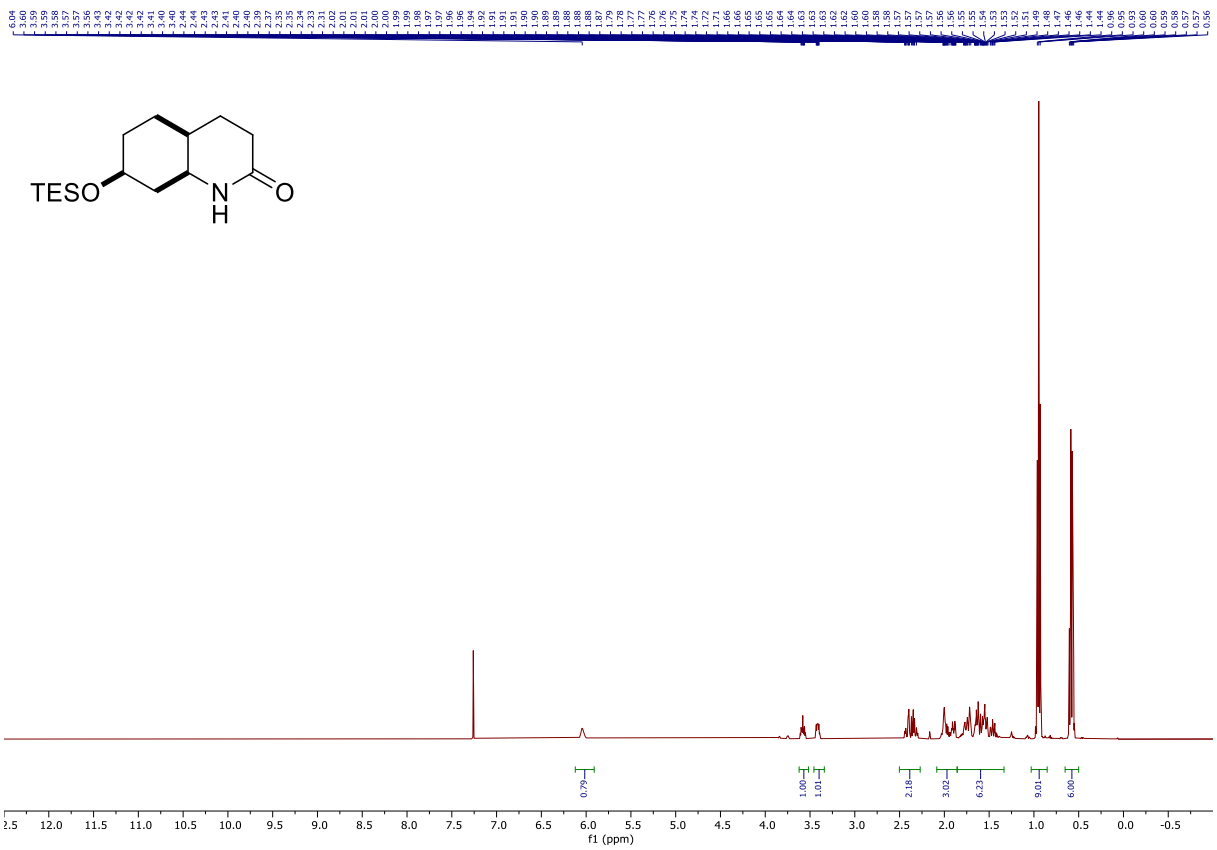


^{29}Si NMR (99 MHz, $CDCl_3$):

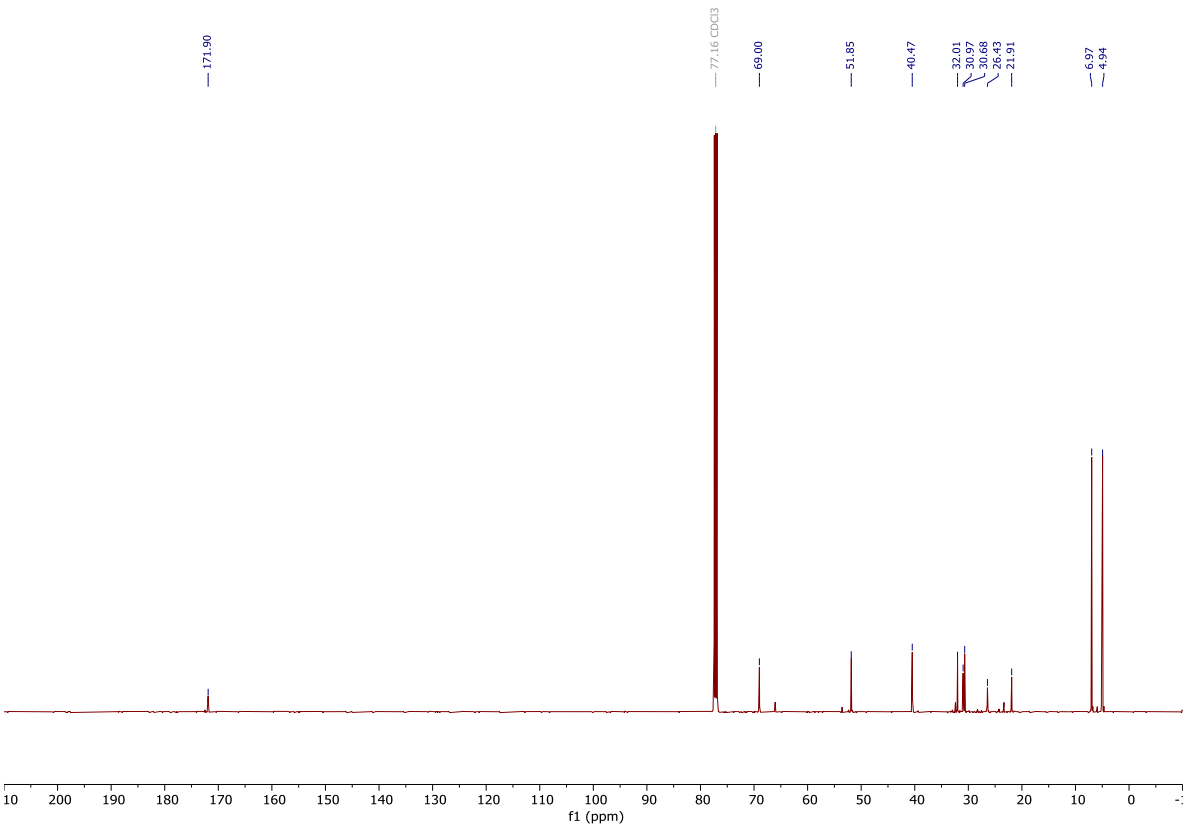


*9.2.7. (4aSR,7SR,8aSR)-7-((Triethylsilyl)oxy)octahydroquinolin-2-one (**5h**)*

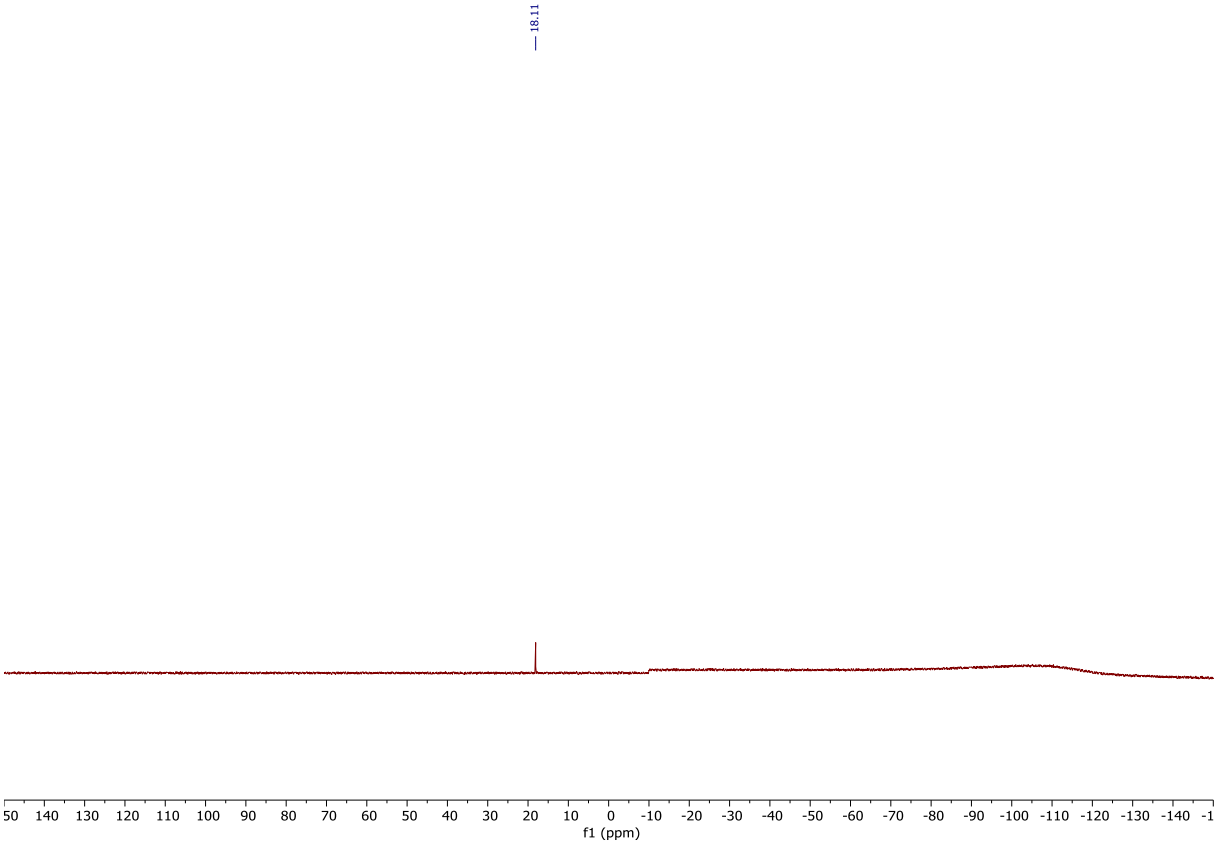
^{1}H NMR (500 MHz, $CDCl_3$):



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

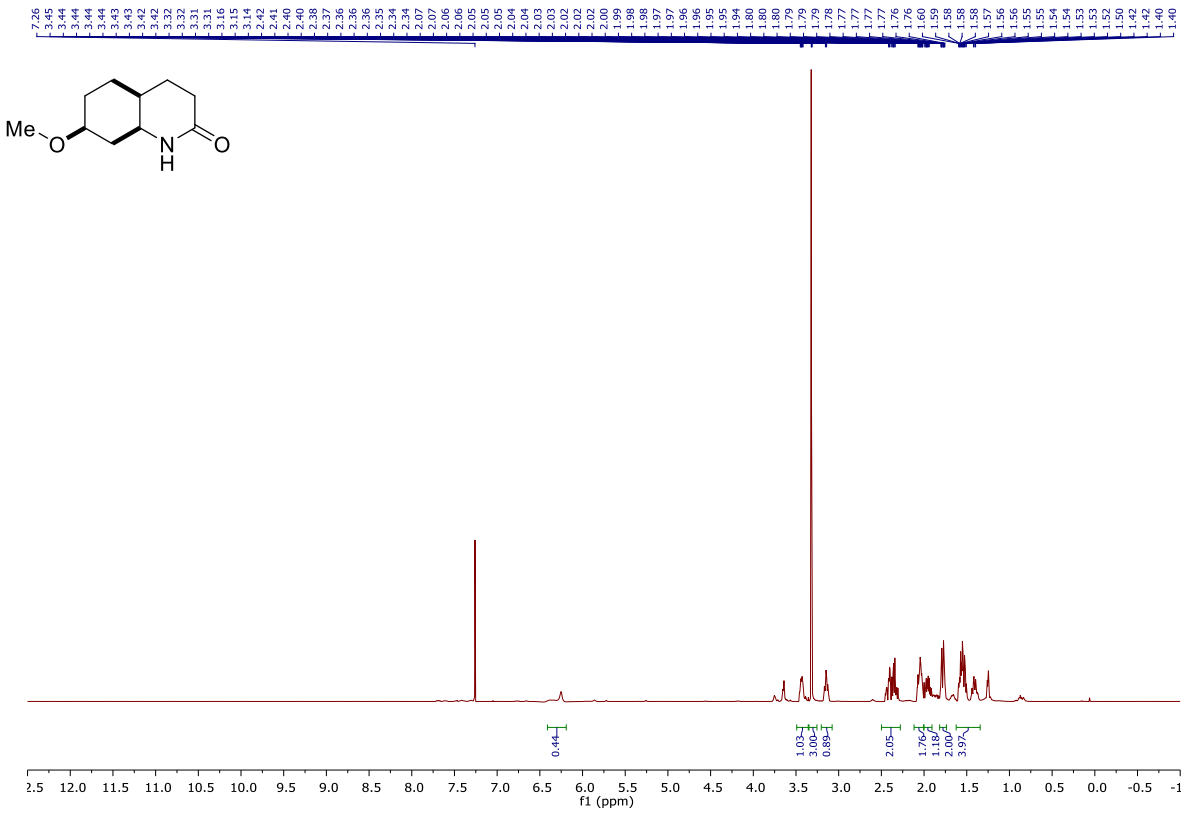


^{29}Si NMR (99 MHz, $CDCl_3$):

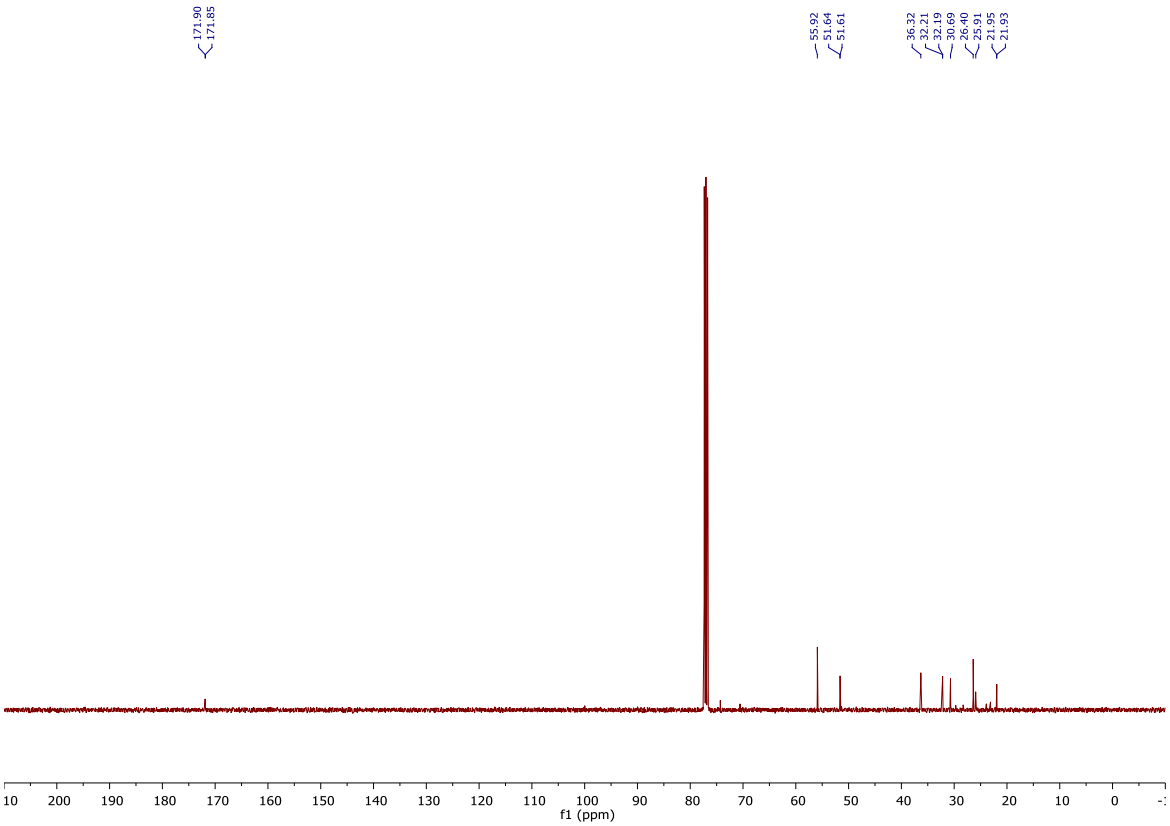


*9.2.8. (4aSR,7SR,8aSR)-7-Methoxyoctahydroquinolin-2-one (**5i**)*

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

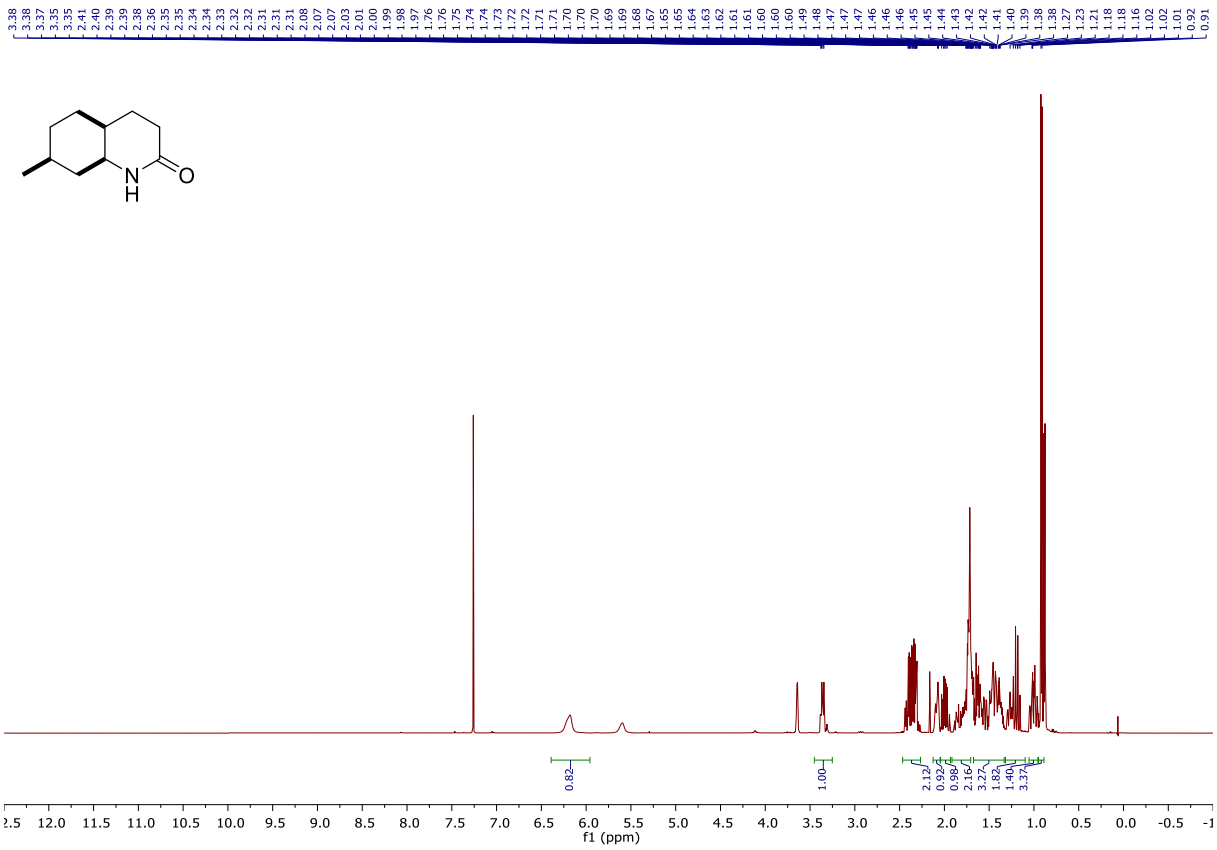


^{13}C NMR (126 MHz, $CDCl_3$):

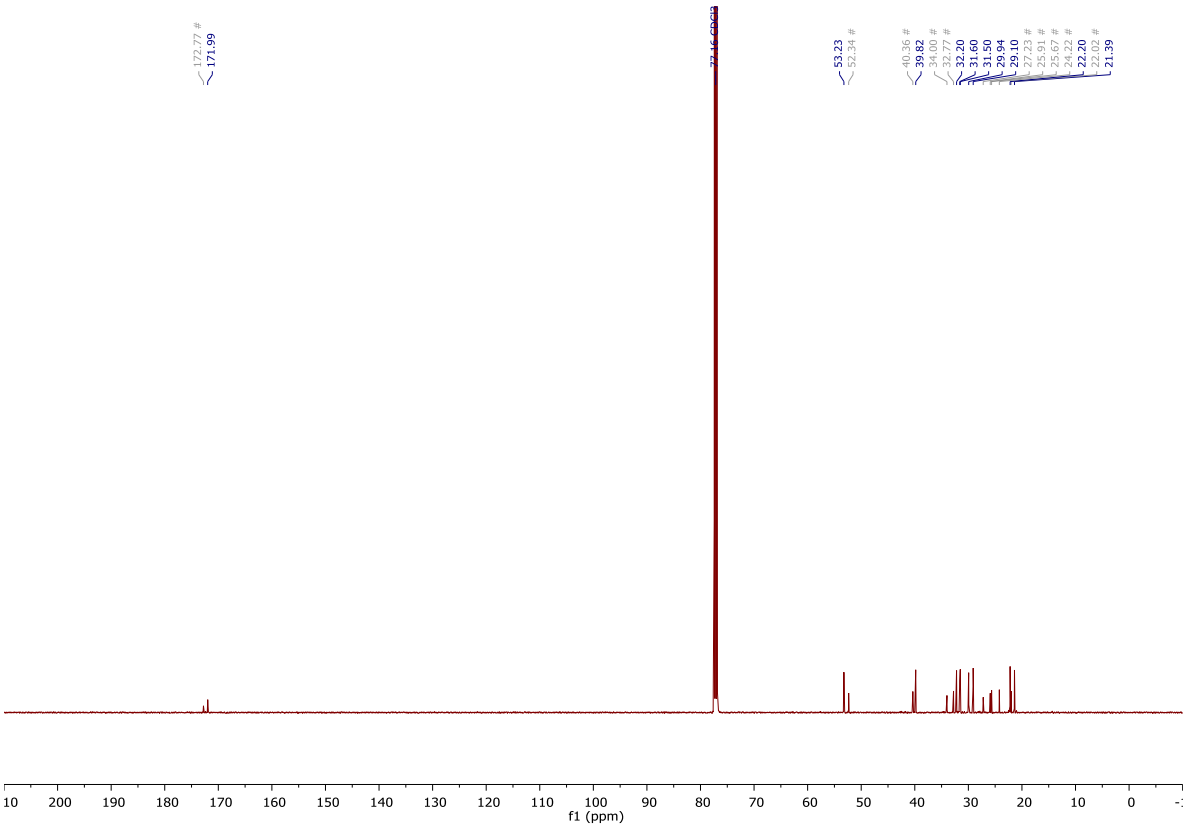


*9.2.9. (4aSR,7SR,8aSR)-7-Methyloctahydroquinolin-2-one (***5j***)*

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

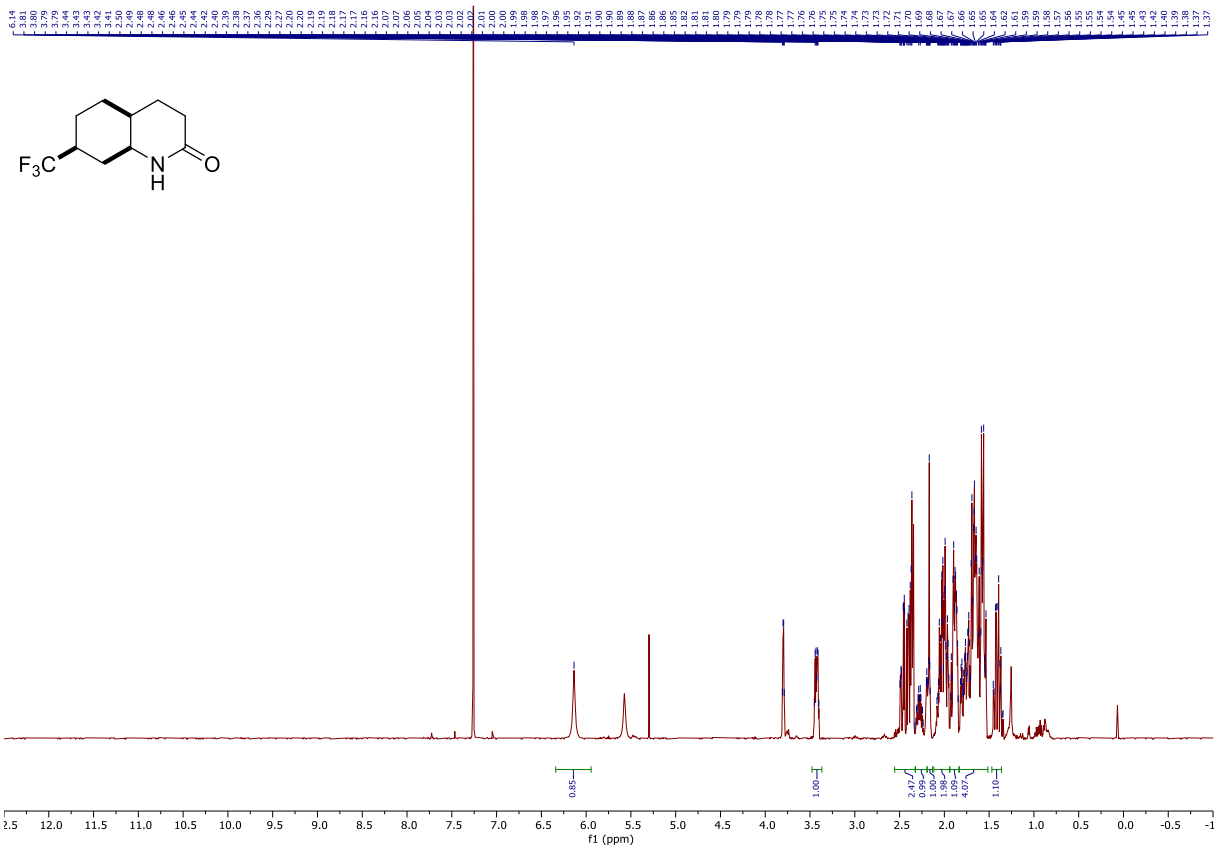


^{13}C NMR (126 MHz, $CDCl_3$):

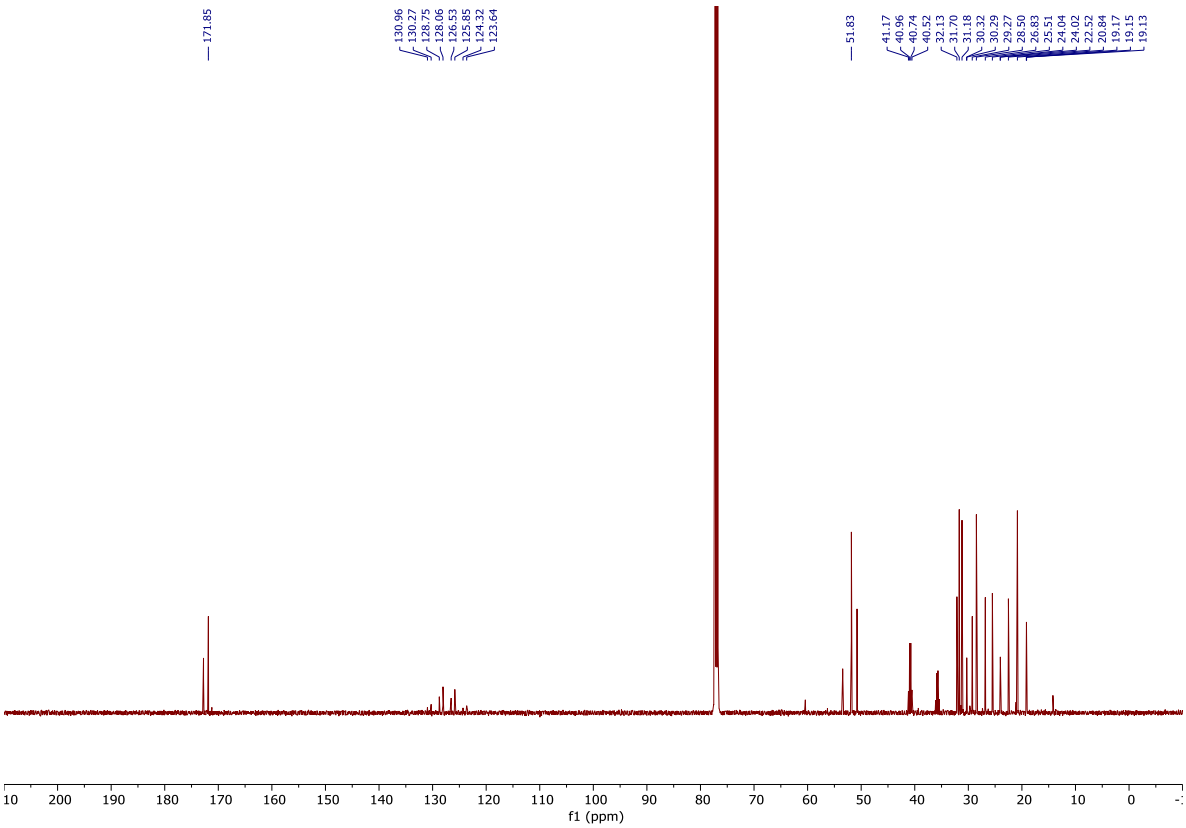


*9.2.10. (4aSR,7SR,8aSR)-7-Trifluormethyloctahydroquinolin-2-one (**5k**)*

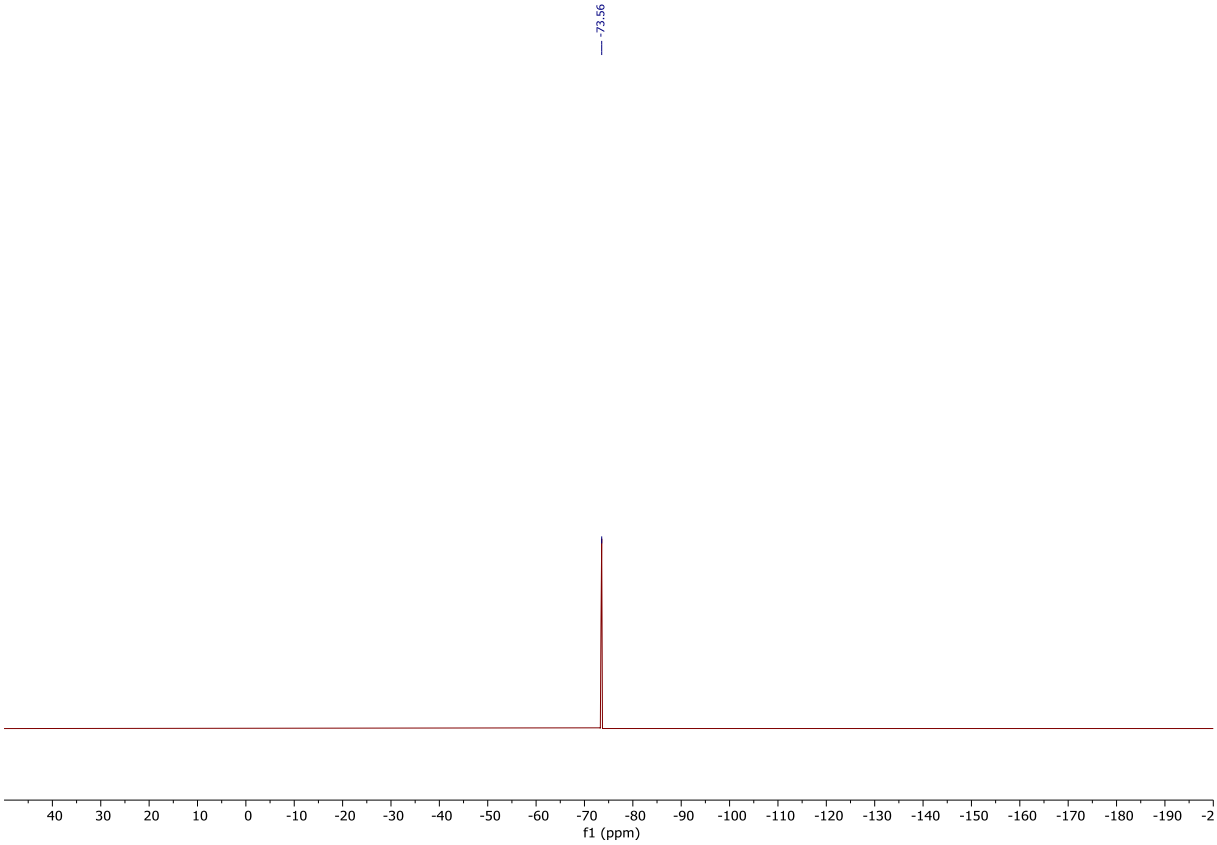
^{1}H NMR (500 MHz, $CDCl_3$):



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

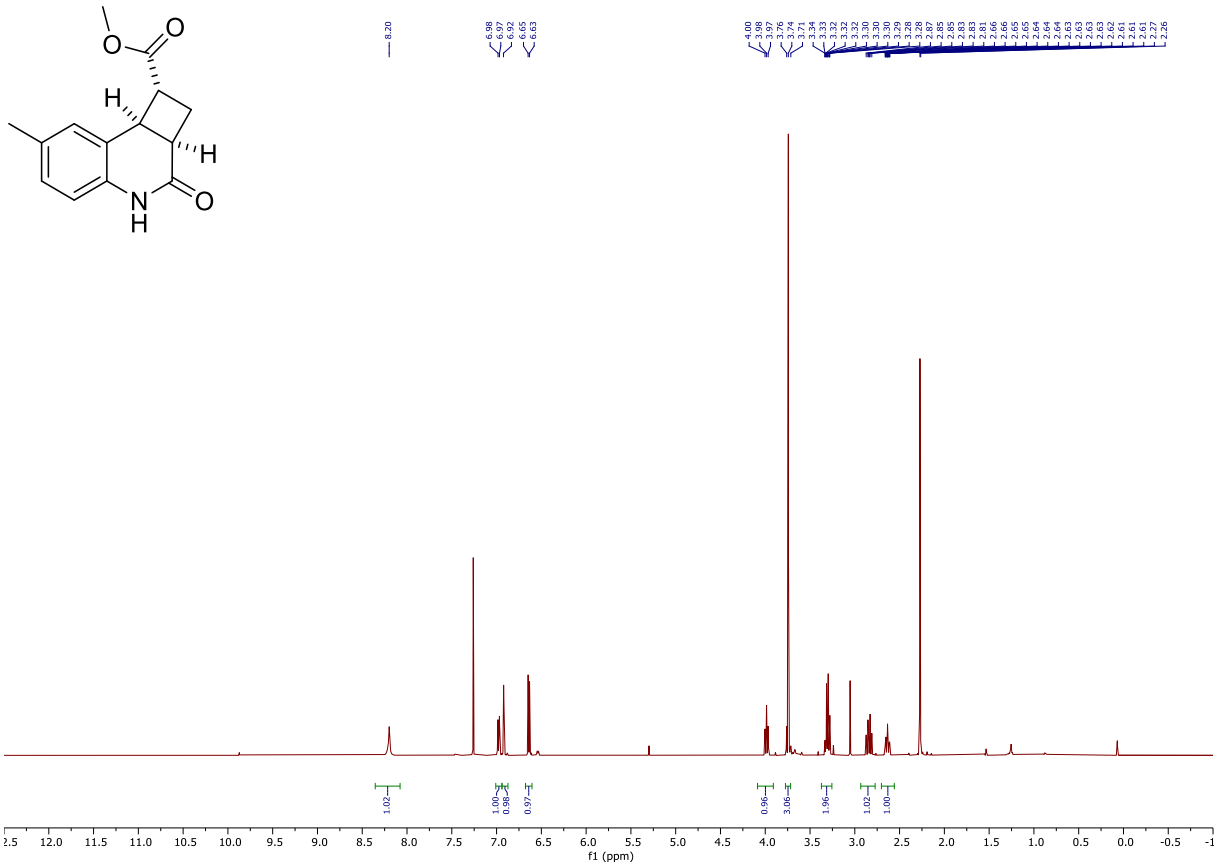


^{19}F NMR (471 MHz, $CDCl_3$):

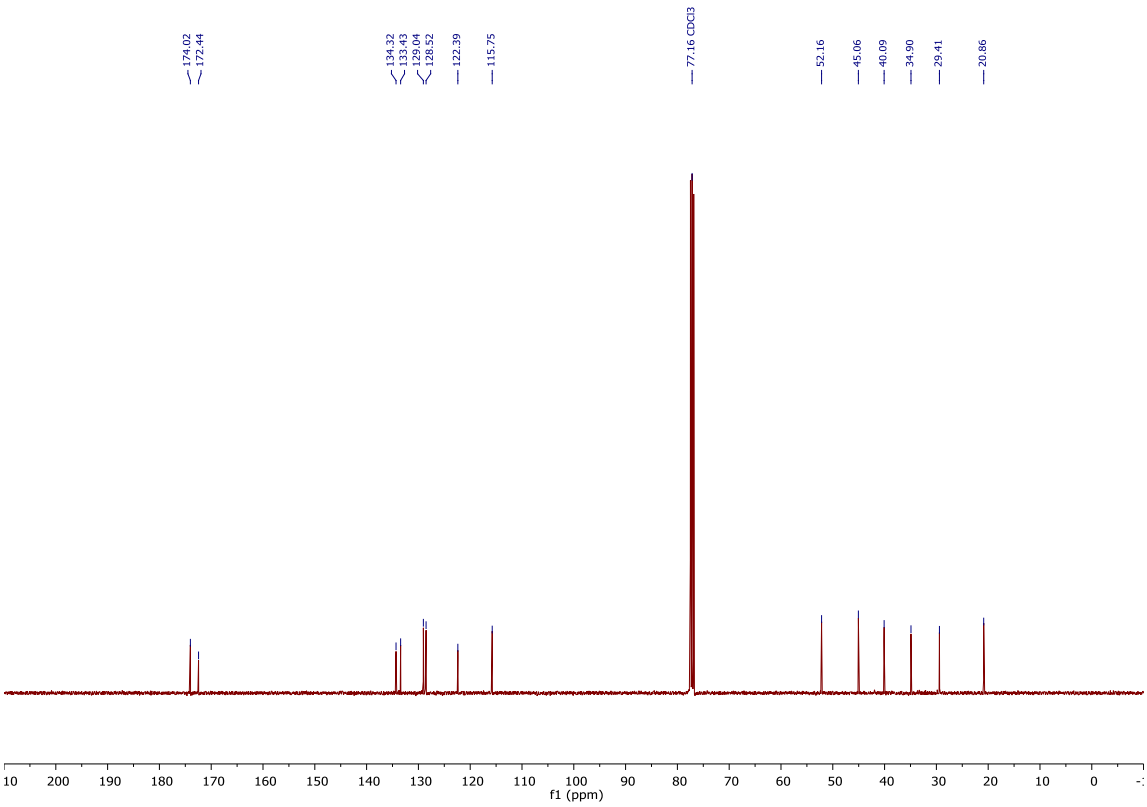


*9.2.11. Methyl-7-methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-1-carboxylate (**8**)*

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

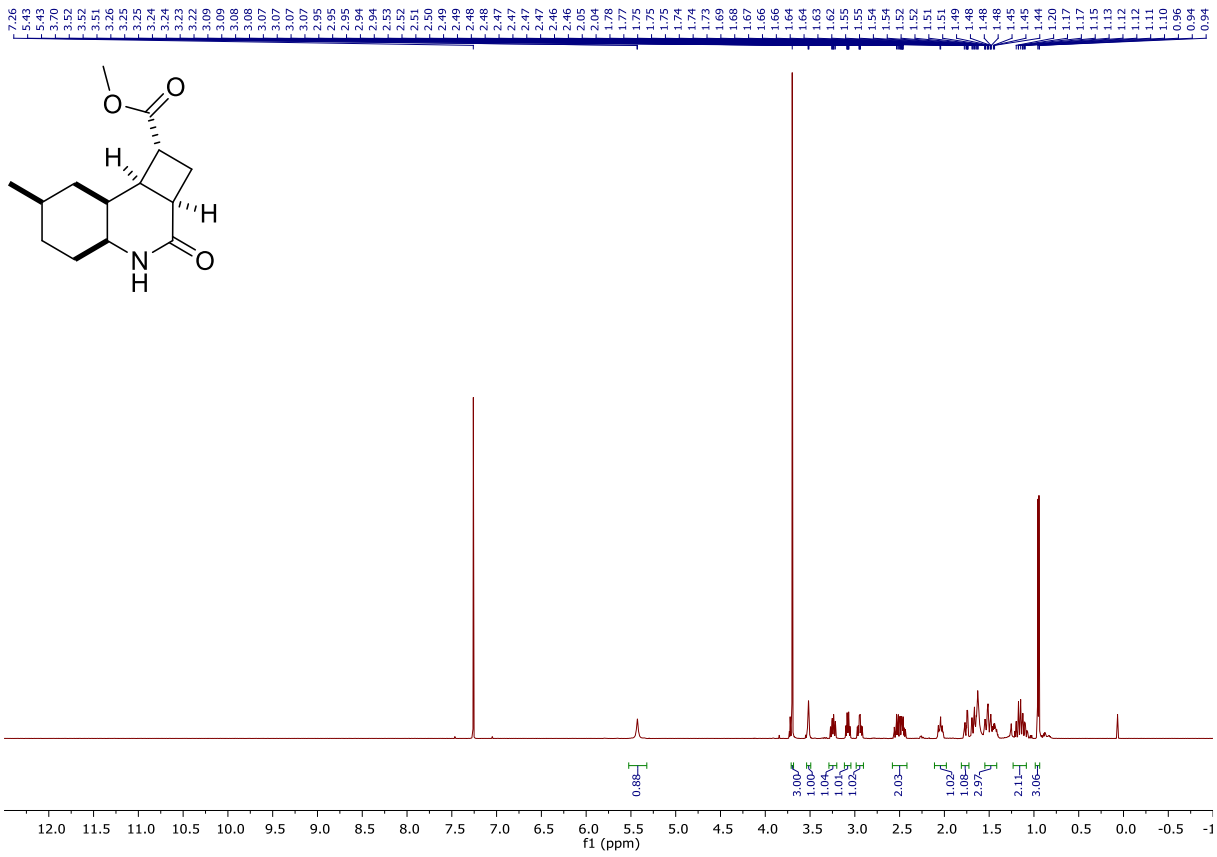


^{13}C NMR (126 MHz, $CDCl_3$):

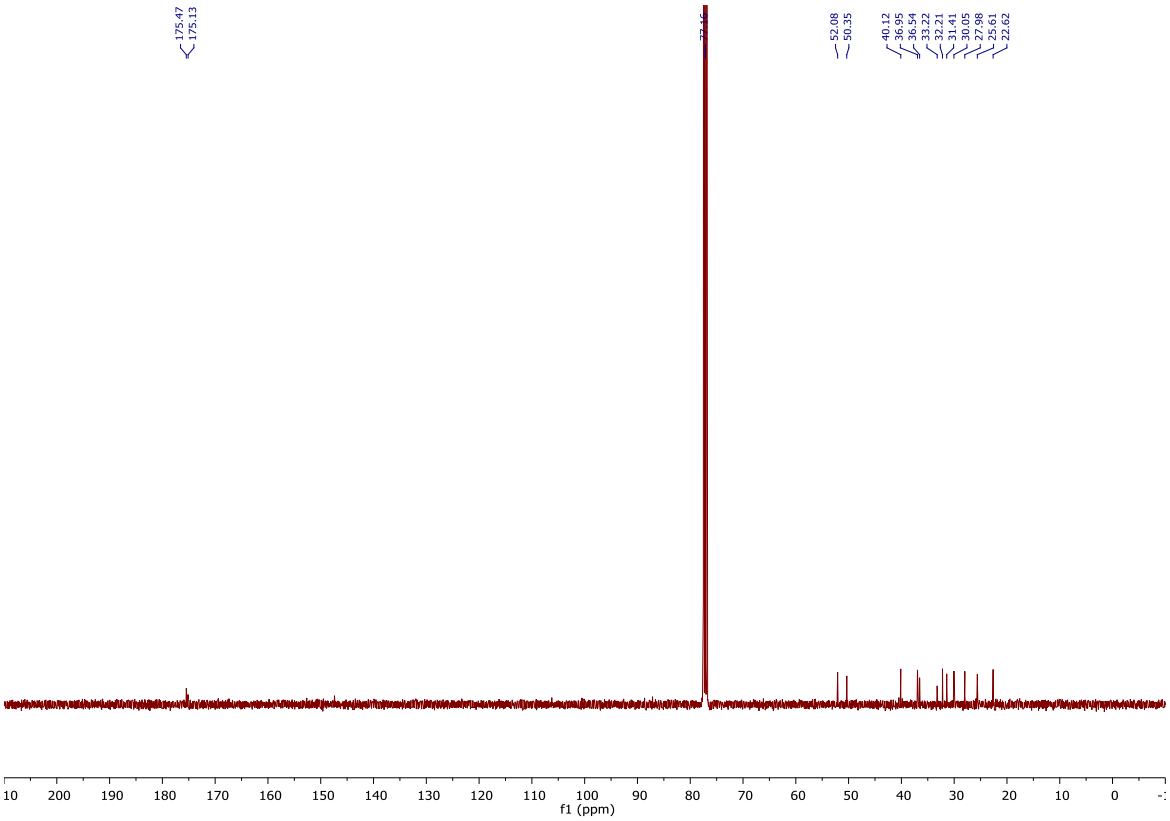


*9.2.12. Methyl 7-methyl-3-oxododecahydrocyclobuta[c]quinoline-1-carboxylate (rac-**9**)*

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



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



10. X-ray crystallographic details

Data were collected on a Bruker D8 Venture single crystal x-ray diffractometer equipped with a CPAD detector (Bruker Photon II), an IMS micro source with MoK_α radiation (λ = 0.71073 Å) and a Helios optic (**3q**, **3s**, **5d**, **5f**) or a CMOS detector (Bruker Photon-100), a TXS rotating anode with MoK_α radiation (λ = 0.71073 Å) and a Helios optic (**3n**) using the APEX3 software package.[19] Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[20] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[20] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL in conjunction with SHELXLE.[21] Hydrogen atoms (except on heteroatoms) were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å, all with $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)$[21b] with the SHELXL weighting scheme.[21c] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[22] The structure of **3q** features a whole molcule disorder, for which a split layer refinement was used employing similarity restraints on distances and anisotropic displacement parameters. The unit cell of compound **5f** contains four disordered molecules of water which were treated as a diffuse contribution to the overall scattering without specific atom positions using the PLATON/SQUEEZE procedure.[23] Images of the crystal structures were generated with PLATON.[24] CCDC 2036220-2036224 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

10.1. Indol-2-one derivatives

*10.1.1. Report for compound **3n** (CCDC 2036221)*

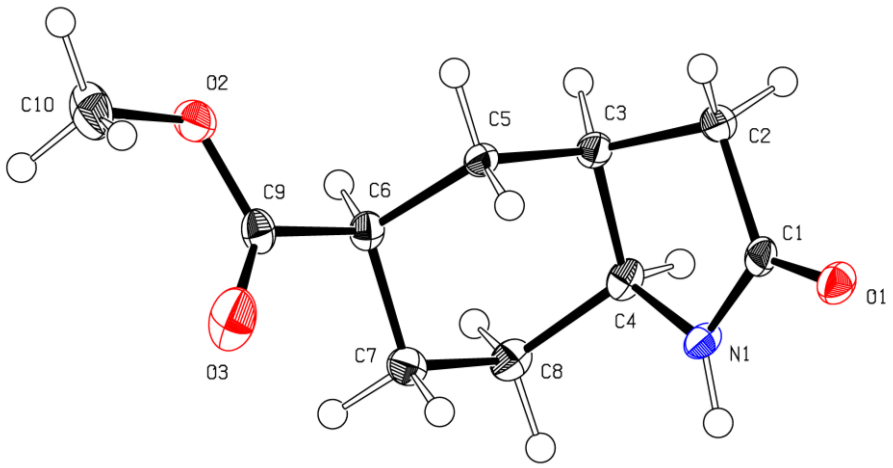


Figure S2. Crystal structure of compound **3n**. Thermal ellipsoids are shown at 50% probability.

Diffractometer operator C. Jandl
scanspeed 1-10 s per frame
dx 40 mm
1729 frames measured in 9 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{10}H_{15}NO_3$

M_r = 197.23	D_x = 1.304 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: ? K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 5.2226 (10) Å	Cell parameters from 9914 reflections
b = 9.5920 (18) Å	θ = 2.4–26.3°
c = 20.060 (4) Å	μ = 0.10 mm^{-1}
β = 90.915 (6)°	T = 100 K
V = 1004.8 (3) Å^3	Rod, colourless
Z = 4	0.34 × 0.09 × 0.07 mm
F(000) = 424	

Data collection

Bruker D8 Venture diffractometer	1994 independent reflections
Radiation source: TXS rotating anode	1801 reflections with $I > 2\sigma(I)$

Helios optic monochromator

Detector resolution: 16 pixels mm^{-1}

phi– and ω–rotation scans

Absorption correction: multi-scan *SADABS* 2016/2, Bruker

T_{min} = 0.723, T_{max} = 0.745

24575 measured reflections

R_{int} = 0.039

θ_{max} = 26.0°, θ_{min} = 2.4°

h = −6 6

k = −11 11

l = −24 24

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.038

$wR(F^2)$ = 0.103

S = 1.05

1994 reflections

132 parameters

0 restraints

0 constraints

Primary atom site location: iterative

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$W = 1/[\Sigma^2(FO^2) + (0.0539P)^2 + 0.4695P]$ WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{max}$ < 0.001

$\Delta\rho_{max}$ = 0.29 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.24 e $Å^{-3}$

Extinction correction: none

Extinction coefficient: -

*10.1.2. Report for Compound **3q** (CCDC 2036223)*

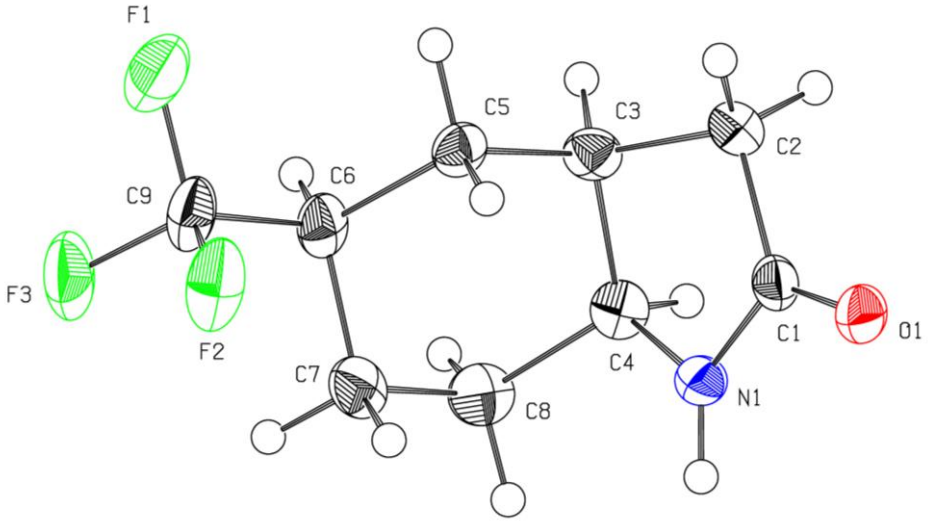


Figure S3. Crystal structure of compound **3q**. Thermal ellipsoids are shown at 50% probability.

Diffractometer operator C. Jandl
scanspeed 1-10 s per frame
dx 80 mm
4318 frames measured in 16 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_9H_{12}F_3NO$

M_r = 207.20	D_x = 1.439 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: ? K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 12.0613 (15) Å	Cell parameters from 9735 reflections
b = 8.1757 (11) Å	θ = 2.5–26.4°
c = 9.8397 (13) Å	μ = 0.13 mm^{-1}
β = 99.826 (3)°	T = 100 K
V = 956.1 (2) Å^3	Fragment, colourless
Z = 4	0.32 × 0.30 × 0.22 mm
F(000) = 432	

Data collection

Bruker D8 Venture diffractometer	1873 independent reflections
Radiation source: IMS microsource	1809 reflections with $I > 2\sigma(I)$

Helios optic monochromator

Detector resolution: 7.5 pixels mm^{-1}

phi– and ω–rotation scans

Absorption correction: multi-scan *SADABS* 2016/2, Bruker

T_{min} = 0.720, T_{max} = 0.745

31470 measured reflections

R_{int} = 0.023

θ_{max} = 26.0°, θ_{min} = 3.0°

h = −14 14

k = −10 10

l = −12 12

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.038

$wR(F^2)$ = 0.091

S = 1.19

1873 reflections

254 parameters

546 restraints

0 constraints

Primary atom site location: iterative

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$W = 1/[\Sigma^2(FO^2) + (0.0277P)^2 + 0.5004P]$ WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{max}$ < 0.001

$\Delta\rho_{max}$ = 0.24 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.22 e $Å^{-3}$

Extinction correction: none

Extinction coefficient: -

*10.1.3. Report for compound **3s** (CCDC 2036222)*

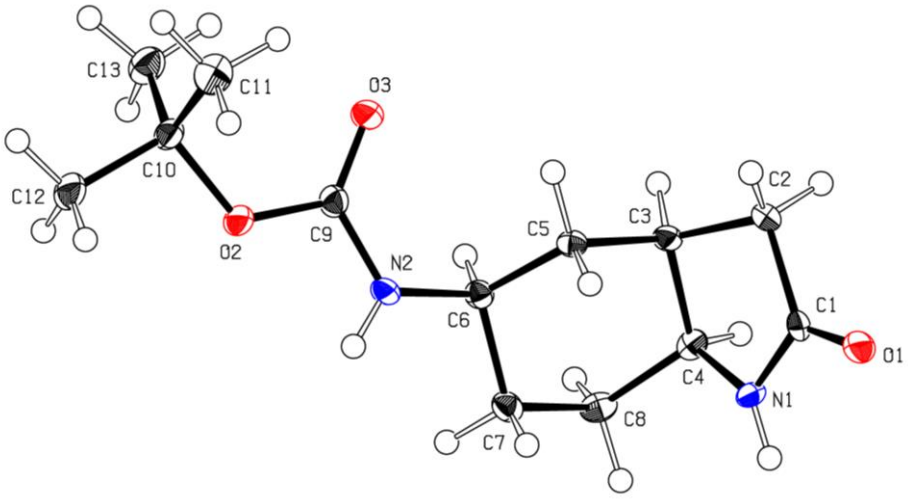


Figure S4. Crystal structure of compound **3s**. Thermal ellipsoids are shown at 50% probability.

Diffractometer operator C. Jandl
scanspeed 2-20 s per frame
dx 90 mm
4326 frames measured in 14 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{13}H_{22}N_2O_3$

M_r = 254.33	D_x = 1.225 Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point: ? K
Hall symbol: -C 2yc	Mo *K*α radiation, λ = 0.71073 Å
a = 45.393 (10) Å	Cell parameters from 9987 reflections
b = 6.4608 (14) Å	θ = 2.7–26.1°
c = 9.4244 (19) Å	μ = 0.09 mm^{-1}
β = 94.114 (5)°	*T* = 100 K
V = 2756.8 (10) Å^3	Fragment, colourless
Z = 8	0.20 × 0.16 × 0.05 mm
F(000) = 1104	

Data collection

Bruker D8 Venture diffractometer	2603 independent reflections
Radiation source: IMS microsource	2530 reflections with $I > 2\sigma(I)$

Helios optic monochromator

Detector resolution: 7.5 pixels mm^{-1}

phi– and ω–rotation scans

Absorption correction: multi-scan *SADABS* 2016/2, Bruker

T_{min} = 0.671, T_{max} = 0.745

41085 measured reflections

R_{int} = 0.046

θ_{max} = 25.7°, θ_{min} = 2.7°

h = −54 54

k = −7 7

l = −11 11

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.064

$wR(F^2)$ = 0.114

S = 1.28

2603 reflections

174 parameters

0 restraints

0 constraints

Primary atom site location: iterative

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

W = $1/[\Sigma^2(FO^2) + (0.012P)^2 + 7.7805P]$ WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{max}$ < 0.001

$\Delta\rho_{max}$ = 0.29 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.25 e $Å^{-3}$

Extinction correction: none

Extinction coefficient: -

10.2. Quinoline-2-one derivatives

*10.2.1. Report for compound **5d** (CCDC 2036220)*

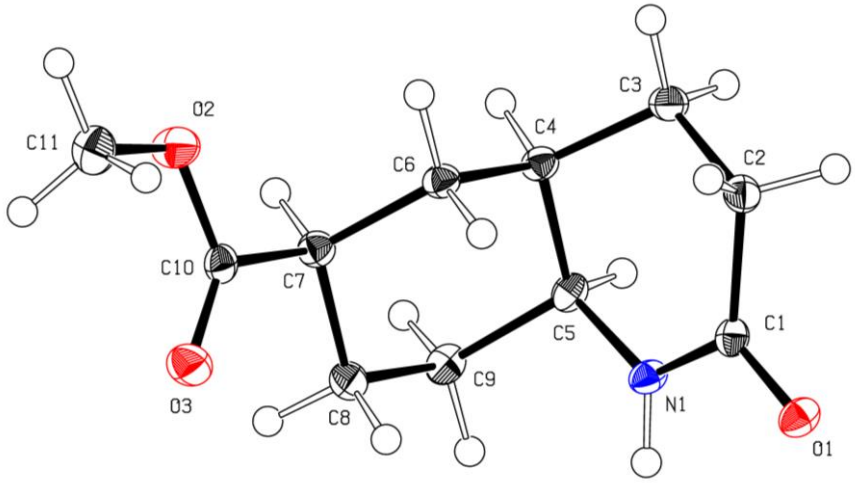


Figure S5. Crystal structure of compound **5d**. Thermal ellipsoids are shown at 50% probability.

Diffractometer operator C. Jandl
scanspeed 2-20 s per frame
dx 37 mm
1285 frames measured in 7 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{11}H_{17}NO_3$

M_r = 211.26	D_x = 1.329 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: ? K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 15.211 (3) Å	Cell parameters from 7070 reflections
b = 6.9069 (15) Å	θ = 2.8–25.8°
c = 10.651 (2) Å	μ = 0.10 mm^{-1}
β = 109.394 (8)°	T = 100 K
V = 1055.5 (4) Å^3	Fragment, colourless
Z = 4	0.24 × 0.16 × 0.04 mm
F(000) = 456	

Data collection

Bruker D8 Venture diffractometer	2009 independent reflections
Radiation source: IMS microsource	1799 reflections with $I > 2\sigma(I)$
Helios optic monochromator	R_{int} = 0.034
Detector resolution: 7.5 pixels mm^{-1}	θ_{max} = 25.7°, θ_{min} = 2.8°
phi– and ω–rotation scans	h = −18 18
Absorption correction: multi-scan *SADABS* 2016/2, Bruker	k = −8 8
T_{min} = 0.707, T_{max} = 0.745	l = −12 12
12010 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.035	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.083	W = 1/[$\Sigma^2(FO^2)$ + (0.0322P)^2 + 0.4844P] WHERE P = (FO^2 + 2FC^2)/3
S = 1.07	$(\Delta/\sigma)_{max}$ < 0.001
2009 reflections	$\Delta\rho_{max}$ = 0.24 e Å^{-3}
141 parameters	$\Delta\rho_{min}$ = −0.20 e Å^{-3}
0 restraints	Extinction correction: none
0 constraints	Extinction coefficient: -
Primary atom site location: iterative	

*10.2.2. Report for compound **5f** (CCDC 2036224)*

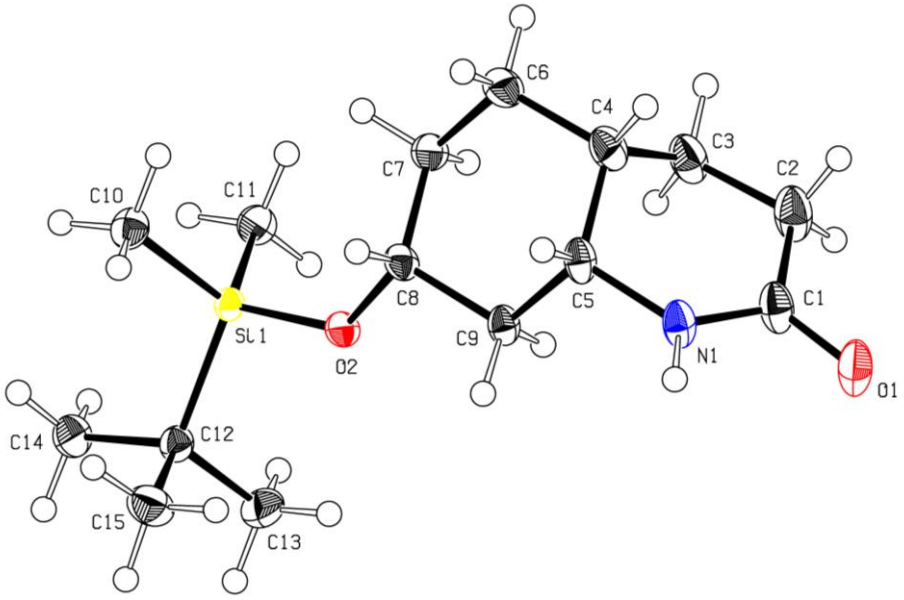


Figure S6. Crystal structure of compound **5f**. Thermal ellipsoids are shown at 50% probability.

Diffractometer operator C. Jandl
scanspeed 2-20 s per frame
dx 60 mm
2277 frames measured in 7 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{15}H_{29}NO_2Si$

M_r = 283.48	D_x = 1.083 Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point: ? K
Hall symbol: -C 2yc	Mo *K*α radiation, λ = 0.71073 Å
a = 39.228 (3) Å	Cell parameters from 9986 reflections
b = 8.1290 (6) Å	θ = 2.6–25.8°
c = 10.9166 (8) Å	μ = 0.14 mm^{-1}
β = 92.495 (2)°	*T* = 100 K
V = 3477.8 (4) Å^3	Fragment, colourless
Z = 8	0.54 × 0.25 × 0.13 mm
F(000) = 1248	

Data collection

Bruker D8 Venture diffractometer	3176 independent reflections
Radiation source: IMS microsource	2840 reflections with $I > 2\sigma(I)$
Helios optic monochromator	R_{int} = 0.056
Detector resolution: 7.5 pixels mm^{-1}	θ_{max} = 25.3°, θ_{min} = 2.1°
phi– and ω–rotation scans	h = −46 46
Absorption correction: multi-scan *SADABS* 2016/2, Bruker	k = −8 9
T_{min} = 0.459, T_{max} = 0.745	l = −11 13
26919 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.047	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.113	W = 1/[$\Sigma^2(FO^2)$ + (0.0329P)^2 + 6.2087P] WHERE P = (FO^2 + 2FC^2)/3
S = 1.14	$(\Delta/\sigma)_{max}$ < 0.001
3176 reflections	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
181 parameters	$\Delta\rho_{min}$ = −0.33 e Å^{-3}
0 restraints	Extinction correction: none
0 constraints	Extinction coefficient: -
Primary atom site location: iterative	

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