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Supporting Information

Remote Enantioselective Epoxidation Reactions Catalyzed by Chiral Iron Porphyrin Complexes with a Hydrogen Bonding Site

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1. General information

All air- or moisture-sensitive reactions were performed under argon atmosphere (argon 5.0, *Westfalen AG*). Reaction vessels were flame-dried with a heat air blower at around 650 °C under reduced pressure. Moisture sensitive reactions were performed with anhydrous solvents and standard *Schlenk* techniques were applied.

Solvents and reagents were used without further purification, unless otherwise mentioned. Anhydrous tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were obtained from an *MBraun* MB-SPS 800 solvent purification system. Following columns were used in order to remove water:

Dichloromethane (CH_2Cl_2): 2 × MB-KOL-M Typ 2 (Al_2O_3);

Tetrahydrofuran (THF): 2 × MB-KOL-A (Molecular sieve 3 Å);

Diethylether (Et_2O): 1 × MB-KOL-A Typ 2 (Al_2O_3)
1 × MB-KOL-A Typ 2 (Molecular sieve 3 Å);

Other anhydrous solvents were obtained from *Sigma Aldrich, Merck* and *Acros* in the highest purity available and used without further purification. Other technical solvents used for aqueous workup and for column chromatography were used without further purification. Unless otherwise stated, reagents were available commercially (*Sigma-Aldrich, Acros Organics*, *TCI Europe*, *Alfa-Aesar*) and used without further purification. Iodosobenzene (PhIO) was prepared according to a literature procedure and stored under argon at 20 °C.[1] Iron tetrakis(pentafluorophenyl)porphyrin chloride [Fe(TPFPP)Cl] **9** was prepared according to a literature procedure and similarly stored under argon at 20 °C.[2]

Ice/water (0 °C) or dry ice/acetone (78 °C) were used as cooling baths. Reactions at elevated temperatures were performed in silicone oil baths and the temperature was regulated by a contact thermometer. Microwave reactions were performed at the indicated temparatures in an *Anton Paar* 30G 30 mL glass vial with an *Anton Paar* Monowave 450.

2. Analytical Methods

Thin layer chromatography (TLC) was performed on silica coated glass plates (Silica 60 F254) with detection by UV (λ= 254 and 366 nm) and/or by staining with a potassium permanganate solution ($KMnO_4$) followed by heat treatment. Column chromatography was performed using silica (230–400 mesh, ASTM) with particle size 40–63 µm (SI 60) by *Merck*. The amounts of silica and the column diameter were calculated according to the mass of the crude product and the separation difficulty.

Automated column chromatography was performed by two chromatography instruments: *Büchi* C-815 Flash and *Biotage* Select. In all cases, *Biotage® Sfär* Silica columns (5, 10, 25, 50, 100 or 200 g) were used in combination with different methods using mixtures of EtOAc/Hexanes, CH_2Cl_2/MeOH or EtOAc/Hexanes/NEt_3 as eluent and UV detection.

Melting points were measured on a *Büchi* M-565 instrument and are not corrected.

IR spectra were recorded on a *Perkin Elmer* Frontier FT/IR (ATR). The signal intensity is assigned using the following abbreviations: vs (very strong), s (strong), m (medium), w (weak).

^{1}H and ^{13}C NMR spectra were recorded at 298 K either on a *Bruker* AVHD400, AVHD500 or an AVHD500cryo spectrometer. NMR spectra were calibrated to the respective residual solvent signals of $CDCl_3$ [δ (^{1}H) = 7.26 ppm, δ (^{13}C) = 77.16 ppm], CD_2Cl_2 [δ (^{1}H) = 5.32 ppm, δ (^{13}C) = 53.84 ppm], DMSO-d_6 [δ (^{1}H) = 2.50 ppm, δ (^{13}C) = 39.52 ppm] and MeOD [δ (^{1}H) = 3.31 ppm, δ (^{13}C) = 49.00 ppm]. ^{19}F NMR spectra were not referenced. The multiplicities within the 1H-NMR-spectra were assigned as follows: b (broad signal), s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet). Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (*virt.*). The multiplicity of the ^{13}C NMR signals were determined by two-dimensional NMR spectra (COSY, HSQC, HMBC).

High resolution mass spectroscopy (HR-MS) was performed using electrospray ionization (ESI) on a *Thermo Scientific* LTQ-FT Ultra (ESI) or a SYNAPT XS High Resolution Mass Spectrometer (ESI) from *Waters*.

Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was performed using a LIFDI ionisation cell from *Linden CMS GmbH*. The spectra were recorded on an Exactive^{TM} Plus Orbitrap from *Thermo Scientific*.

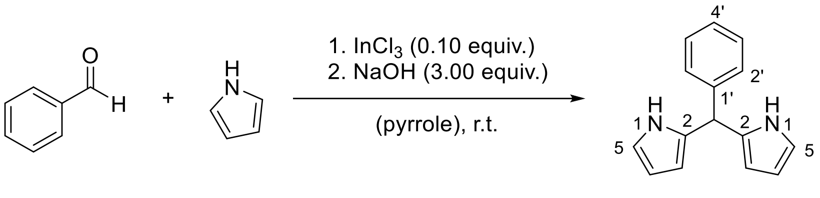
High performance liquid chromatography (HPLC) was performed (*Thermo Fisher, Dionex* Ultimate 3000 pump, *Dionex* Ultimate 3000 Autosampler, *Dionex* Ultimate 3000 photodiode array detector) using different chiral stationary phases (Daicel ChiralCel, *Chemical Industries*) and UV detection (λ = 215 and 254 nm) at 20 °C. Preparative HPLC was conducted on an apparatus consisting of a HPG 3200BX pump (*Thermo Fisher*) and a MWD 3000-RS UV-detector (*Dionex*). For normal-phase HPLC a Daicel ChiralPak AD-H was used as stationary phase and a mixture of *n*-heptane/*i*-propanol (*i*PrOH) was used as mobile phase.

Elemental Analysis (EA) was performed on a *Vario EL* (elementar).

UV-Vis Spectroscopy was performed on an *Agilent* Cary 60 UV-Vis spectrometer. Spectra were recorded using a *Hellma* precision cell made of quartz SUPRASIL® with a pathway of 1 mm. Solvents and concentrations are given for each spectrum.

3. Substrate and Catalyst Synthesis

2,2'-(Phenylmethylene)bis(1*H*-pyrrole) (S1)



S1

Benzaldehyde (4.58 g, 4.40 mL, 43.1 mmol, 1.00 equiv.) was dissolved in freshly distilled pyrrole (300 mL, 4.31 mmol, 100 equiv.). The solution was degassed with an argon stream for 15 min, $InCl_3$ (953 mg, 4.31 mmol, 0.10 equiv.) was added and the orange solution was stirred at room temperature for 2.5 hours under argon atmosphere. Powdered NaOH (8.62 g, 216 mmol, 5.00 equiv.) was added and the reaction mixture was stirred at room temperature for one hour. The solution was filtered through a fritted glass funnel, washed with distilled pyrrole (2 × 20 mL) and the filtrate was concentrated under reduced pressure. The crude material was washed with hexanes (150 mL) in the sonicator and the suspension was filtered to obtain the title compound S**1** as a pale grey solid (4.77 g, 21.5 mmol, 50%).

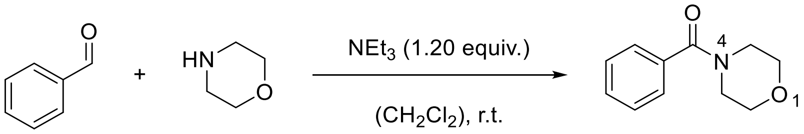
TLC: R_f **=** 0.20 (CH_2Cl_2/Hexanes = 6/4), [UV].

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 10.54 (s, 2H, NH), 7.32 – 7.23 (m, 2H, H-3’), 7.22 – 7.14 (m, 3H, H-1’, H-4’), 6.66 – 6.54 (m, 2H, H-5), 5.90 (m, 2H, H-4), 5.73 – 5.62 (m, 2H, H-3), 5.35 (s, 1H, H-benzylic).

^{13}C-NMR (101 MHz, DMSO-d_6, 298 K) δ [ppm] = 143.9 (s, C-1’), 133.1 (s, C-2), 128.1 (d, C-2’), 128.0 (d, C-3’), 126.1 (d, C-4’), 116.8 (d, C-5), 106.9 (d, C-4), 106.1 (d, C-3), 43.5 (d, C-benzylic).

The analytical data are in accordance with the literature values.[3]

4-Benzoylmorpholine (S2)



S2

Morpholine (6.75 mL, 78.3 mmol, 1.10 equiv.) and Et_3N (12.4 mL, 88.9 mmol, 1.20 equiv.) were dissolved in anhydrous CH_2Cl_2 (150 mL) under inert atmosphere. Benzoyl chloride (8.20 mL, 71.1 mmol, 1.00 equiv.) was added to the solution and the reaction solution was stirred at room temperature for 1.5 hours. The reaction was quenchedquenched by addition of CH_2Cl_2 (210 mL) and aq. HCl (1M ,350 mL). The organic phase was separated, filtered through a pad of silica, and washed with a mixture of ethyl acetate and hexanes (1:1, 600 mL). After removal of all volatiles under reduced pressure the title compound S**2** was obtained as a white solid (13.3 g, 69.7 mmol, 98%).

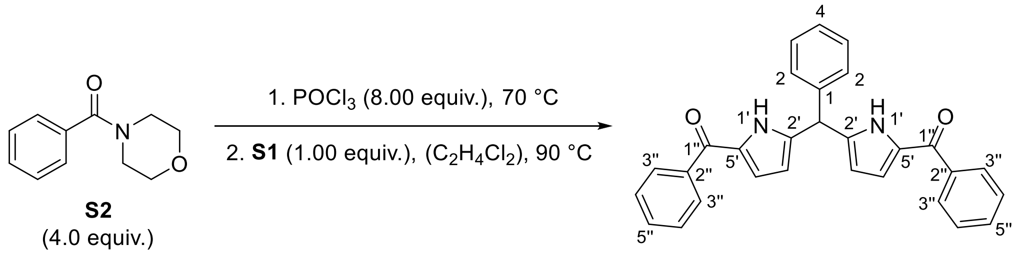
TLC: R_f **=** 0.14 (EtOAc/CH_2Cl_2 = 5/95), [UV].

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm] = 7.34 – 7.46 (m, 5H, H-aryl), 3.14 – 4.04 (m, 8H, H-alkyl).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm] = 170.5 (s, C=O), 135.5 (s, C-aryl), 130.0 (d, C-aryl), 128.7 (d, C-aryl), 127.2 (d, C-aryl), 67.0 (t, C-alkyl), 48.4 (t, C-alkyl), 47.7 (t, C-alkyl).

The analytical data are in accordance with the literature values.[4]

[(Phenylmethylene)bis(1*H*-pyrrole-5,2-diyl)]bis(phenylmethanone) (S3)



S2
(4.0 equiv.)

S3

$POCl_3$ (1.87 mL, 3.06 g, 20.0 mmol, 8.00 equiv.) and **S2** (1.91 g, 9.99 mmol, 4.00 equiv.) were combined and the reaction mixture was stirred at 70 °C for three hours. Subsequently the mixture was cooled to room temperature. Dipyrrole **S1** (555 mg, 2.50 mmol, 1.00 equiv.) and dichloroethane (15 mL) were added and the resulting brown solution was stirred at 90 °C for two hours under argon atmosphere. The mixture was cooled to room temperature and the reaction was quenched by addition of sat. aq. NaOAc (15 mL). The mixture was heated to 80 °C and stirred for 50 minutes at that temperature. Subsequently the reaction mixture was cooled to room temperature again, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined and washed with water (2 × 40 mL) and sat. aq. NaCl (50 mL). The organic phase was dried over Na_2SO_4 and after removal of all volatiles under reduced pressure, the crude material was purified by column chromatography (silica, EtOAc/CH_2Cl_2 0/100 → 2/98 → 3/97 → 5/95) to obtain the title compound **S3** as a brown solid (530 mg, 1.25 mmol, 50%).

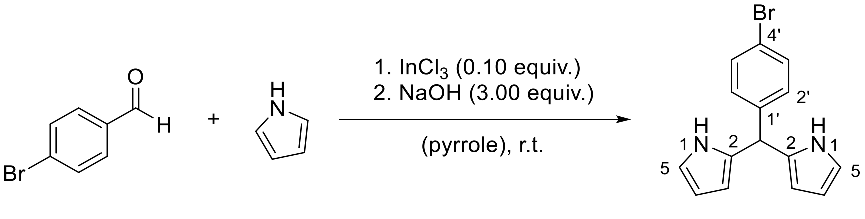
TLC: R_f **=** 0.31 (EtOAc/CH_2Cl_2 = 5/95), [VIS, brown].

^{1}H-NMR (400 MHz, DMSO-*d*$_6$, 298 K) δ [ppm] = 12.14 (s, 2H, NH), 7.80 – 7.75 (m, 4H, H-3’’), 7.63 – 7.56 (m, 2H, H-5’’), 7.56 – 7.48 (m, 4H, H-4’’), 7.35 (dd, ^3J = 8.5 Hz, ^3J = 6.4 Hz, 2H, H-3), 7.29 – 7.22 (m, 3H, H-2, H-4), 6.71 (dd, ^3J = 3.8 Hz, ^4J = 2.3 Hz, 2H, H-4’), 6.04 (dd, ^3J = 3.8 Hz, ^4J = 2.3 Hz, 2H, H-3’), 5.77 (s, 1H, H-benzylic).

^{13}C-NMR (126 MHz, DMSO-*d*$_6$, 298 K) δ [ppm] = 183.4 (s, C-1’’), 141.4 (s, C-2’), 138.6 (s, C-2’’), 131.6 (d, C-5’’), 130.2 (s, C-1), 128.5 (d, C-phenyl), 128.4 (d, C-phenyl), 128.3 (d, C-2, C-4), 126.8 (C-5’), 119.9 (d, C-4’), 109.9 (d, C-3’), 42.9 (d, C-benzylic).

The analytical data are in accordance with the literature values.[5]

2,2'-(4-Bromophenylmethylene)bis(1*H*-pyrrole) (S4)



S4

4-Bromobenzaldehyde (4.58 g, 10.8 mmol, 1.00 equiv.) was dissolved in freshly distilled pyrrole (75.0 mL, 1.08 mol, 100 equiv.). The solution was degassed with an argon stream for 15 minutes, $InCl_3$ (239 mg, 1.08 mmol, 0.10 equiv.) was added and the orange solution was stirred at room temperature for 1.5 hours under argon atmosphere. Powdered NaOH (1.30 g, 32.6 mmol, 3.01 equiv.) was added and the reaction mixture was stirred at room temperature for one hour. The solution was filtered through a fritted glass funnel, washed with distilled pyrrole (2 × 20 mL) and the filtrate was concentrated under reduced pressure. The obtained crude material was co-evaporated thrice with toluene. After final removal of all volatiles under reduced pressure the crude material was purified by column chromatography (silica, $CH_2Cl_2/Et_2O/n$-pentane 1/1/10 → 2/2/10) to obtain the title compound **S4** as a yellow solid (2.02 g, 7.37 mmol, 68%).

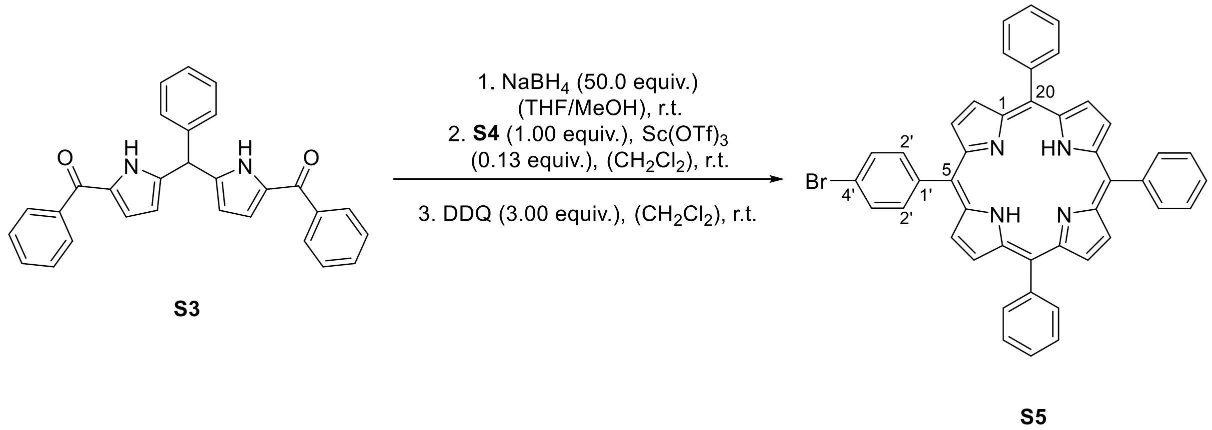
TLC: R_f **=** 0.24 ($CH_2Cl_2/Et_2O/n$-pentane = 2/2/10), [UV].

^{1}H-NMR (500 MHz, DMSO-d_6, 298 K) δ [ppm] = 10.58 (s, 2H, NH), 7.49 – 7.45 (m, 2H, H-3’), 7.14 – 7.07 (m, 2H, H-2’), 6.62 (d, $^3J = 2.7$, $^4J = 1.6$ Hz, 2H,), 5.91 (*virt*. q, $^3J \approx {}^3J \approx {}^4J = 2.7$ Hz, 2H, H-4), 5.70 – 5.63 (m, 2H, H-3), 5.35 (s, 1H, H-benzylic).

^{13}C-NMR (101 MHz, DMSO-d_6, 298 K) δ [ppm] = 143.3 (s, C-1’), 132.6 (s, C-2), 130.9 (d, C-3’), 130.4 (d, C-2’), 119.2 (s, C-4’), 117.1 (d, C-5), 107.0 (d, C-4), 106.2 (d, C-3), 42.9 (d, C-benzylic).

Literature spectra were recorded in deuterated chloroform.[6]

5-(4-Bromophenyl)-10,15,20-triphenylporphyrin (S5)



$NaBH_4$ (879 mg, 23.2 mmol, 50.0 equiv.) was added to a solution of **S3** (200 mg, 465 µmol, 1.00 equiv.) in anhydrous THF (11 mL) and anhydrous MeOH (4 mL) over ten minutes. The solution was stirred at room temperature for 45 minutes and then quenched by addition of CH_2Cl_2 (80 mL) and sat. aq. NH_4Cl (80 mL). The organic layer was separated, washed with water (80 mL) and brine (80 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the residue was dried for 20 min under high vacuum. After re-dissolving the residue in anhydrous CH_2Cl_2 (185 mL), **S4** (140 mg, 465 µmol, 1.00 equiv.) and $Sc(OTf)_3$ (32.0 mg, 65.0 µmol, 0.14 equiv.) were added and the reaction mixture was stirred at room temperature for 20 min under argon atmosphere. DDQ (316 mg, 1.39 mmol, 3.00 equiv.) was added and the reaction mixture was stirred for one additional hour at room temperature. Et_3N (401 µL, 2.88 mmol, 6.20 equiv.) was added and the black reaction solution was stirred for another ten minutes. The reaction mixture was filtered through a pad of silica (5 cm), which was rinsed with CH_2Cl_2 (500 mL) until the solvent showed no coloration. After removal of all volatiles under reduced pressure the crude material was purified by column chromatography (silica, CH_2Cl_2/Hexanes 25/75 → 5/5) to obtain the title porphyrin **S5** as a purple shimmering solid (55.0 mg, 79.3 µmol, 17%).

TLC: R_f **=** 0.37 (CH_2Cl_2/Hexanes = 30/70), [VIS, purple].

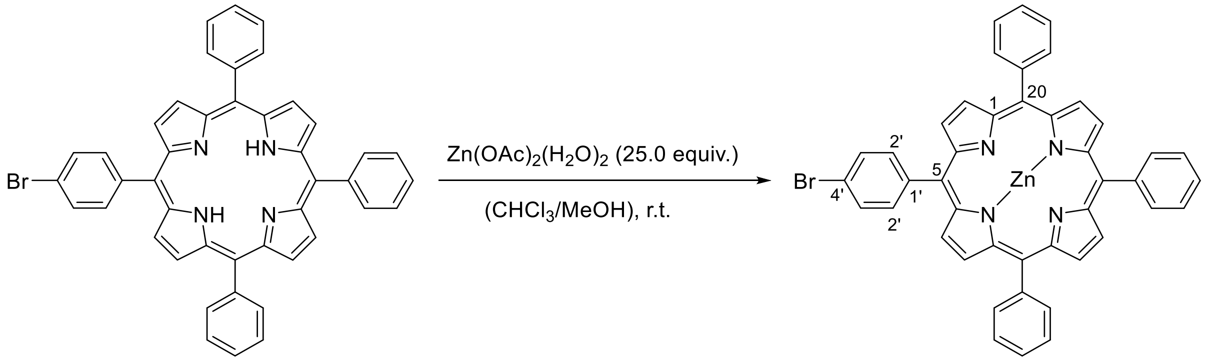
^{1}H-NMR (400 MHz, CD2Cl$_2$, 298 K) δ [ppm] = 8.92 – 8.81 (m, 8H, H-porphyrin), 8.26 – 8.19 (m, 6H, H-phenyl), 8.15 – 8.07 (m, 2H, H-2’), 7.96 – 7.88 (m, 2H, H-3’), 7.85 – 7.73 (m, 9H, H-phenyl), −2.84 (s, 2H, NH).

^{13}C-NMR (126 MHz, CD_2Cl_2, 298 K) δ [ppm] = 142.0 (s, C-phenyl), 141.9 (s, C-phenyl), 141.1 (s, C-1’), 135.9 (d, C-3’), 134.5 (d, C-phenyl), 129.9 (d, C-2’), 127.8 (d, C-phenyl), 126.8 (d, C-phenyl), 122.3 (s, C-4’), 120.5 (s, C-porphyrin), 120.4 (s, C-porphyrin), 118.4 (s, C-porphyrin).

HRMS (ESI): calc. for $C_{44}H_{27}BrN_4Zn$ $[M+H]^+$: 693.1643; found: 693.1634.

Literature spectra were recorded in deuterated chloroform.[7]

Zn(II)-5-(4-bromophenyl)-10,15,20-triphenylporphyrin (S6)



S5 **S6**

Porphyrin **S5** (115 mg, 166 µmol, 1.00 equiv.) and $Zn(OAc)_2(H_2O)_2$ (910 mg, 4.14 mmol, 25.0 equiv.) were dissolved in a mixture of anhydrous MeOH (4 mL) and anhydrous $CHCl_3$ (11 mL). The solution was stirred at room temperature for 20 h. After removal of all volatiles under reduced pressure the crude material was purified by column chromatography (silica, CH_2Cl_2/Hexanes 2/8 → 3/7 → 5/5) to obtain the title porphyrin **S6** as a purplepurple shimmering solid (80 mg, 106 µmol, 64%).

TLC: R_f **=** 0.29 (CH_2Cl_2/Hexanes = 40/60), [VIS, purple].

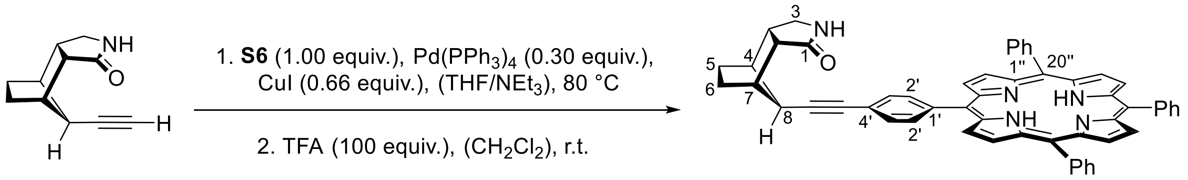
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3049 (w), 1596 (w), 1519 (m), 1482 (m), 1440 (m), 1337 (m), 1204 (m), 1070 (m), 994 (s), 794 (s), 699 (s).

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ [ppm] = 9.00 – 8.90 (m, 8H, H-porphyrin), 8.27 – 8.16 (m, 6H, H-phenyl), 8.15 – 8.07 (m, 2H, H-3’), 7.95 – 7.87 (m, 2H, H-2’), 7.85 – 7.71 (m, 9H, H-phenyl).

^{13}C NMR (126 MHz, CD_2Cl_2, 298 K) δ (ppm) = 150.7 (s, C-porphyrin), 150.6 (s, C-porphyrin), 150.6 (s, C-porphyrin), 150.2 (s, C-porphyrin), 143.0 (s, C-phenyl), 142.2 (s, C-phenyl), 136.2, 134.8, 132.5, 132.4, 132.4, 131.9, 130.1, 127.9, 127.0, 122.4, 121.8, 121.7, 119.8.

HRMS (LIFDI): calc. for $C_{44}H_{27}BrN_4Zn$ $[M-e^-]^+$: 754.0705; found: 754.0698.

(3a*S*,4*R*,7*S*,7a*R*,8*R*)-8-{[4-(10,15,20-Triphenylporphyrin-5-yl)phenyl]ethynyl}octahydro-1*H*-4,7-methanoisoindol-1-one (S7)



4
(1.86 equiv.)

S7

Porphyrin **S6** (80 mg, 106 µmol, 1.00 equiv.) and (3a*S*,4*R*,7*S*,7a*R*,8*R*)-8-ethynyloctahydro-1*H*-4,7-methanoisoindol-1-one[8] **4** (22.2 mg, 127 µmol, 1.20 equiv.) were dissolved in anhydrous Et_3N (5.4 mL) and anhydrous THF (5.4 mL) and the solution was degassed by three freeze-thaw cycles. CuI (6.04 mg, 31.7 µmol, 30.0 mol%) and $Pd(PPh_3)_4$ (18.3 mg, 15.9 µmol, 15.0 mol%) were added and the solution was stirred for 18 hours at 50 °C and inert atmosphere. Additional equivalents of **4** (12.3 mg, 70.2 µmol, 0.66 equiv.), CuI (7.20 mg, 37.8 µmol, 36.0 mol%), and $Pd(PPh_3)_4$ (18.3 mg, 15.9 µmol, 15.0 mol%) were added and the solution was heated to 75 °C for additional two hours. The reaction mixture was cooled to room temperature and all volatiles were removed under reduced pressure. The crude product was filtered through a pad of silica (4 cm) and the silica pad was washed with MeOH/CH_2Cl_2 (0/100 → 2/98, 100 mL). The obtained filtrate was concentrated under reduced pressure and the crude material was re-dissolved in distilled CH_2Cl_2 (60 mL). TFA (737 µL, 9.63 mmol, 90.0 equiv.) was added over one minute and the solution was stirred at room temperature for 1.5 h. The reaction was quenched by addition of sat. aq. $NaHCO_3$ (40 mL). The organic layer was separated, washed with sat. aq. NaCl (2 × 35 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure the crude material was purified by column chromatography (silica, MeOH/CH_2Cl_2 0/100 → 1/99 → 3/97) to obtain the title porphyrin **S7** as a purple solid (62.7 mg, 68.7 µmol, 65%).

TLC: R_f = 0.15 (MeOH/CH_2Cl_2 = 1/99), [VIS, brown].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3316 (w, NH-Porphyrin), 3028 (w), 2949 (m), 1696 (s, C=O), 1654 (s), 1474 (m), 1442 (m), 965 (s), 799 (s), 725 (s), 700 (s).

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K) δ [ppm] = 8.87 (d, ^3J = 3.6 Hz, 8H, H-porphyrin), 8.28 – 8.19 (m, 6H, H-phenyl), 8.18 – 8.12 (m, 2H, H-3'), 7.84 – 7.72 (m, 11H, H-phenyl, H-2'), 5.51 (s, 1H, NH), 3.80 (dd, ^3J = 9.7 Hz, ^3J = 4.4 Hz, 1H, H-3), 3.72 (*virt*. t, $^2J \approx {}^3J$ = 9.7 Hz, 1H, H-3), 2.95 (d, ^3J = 4.0 Hz, 1H, H-4), 2.78 (s, 1H, H-8), 2.66 (td, ^3J = 9.7 Hz, ^3J = 4.4 Hz, 1H, H-

3a), 2.62 (d, ^3J = 4.0 Hz, 1H, H-7), 2.57 (d, ^3J = 9.4 Hz, 1H, H-7a), 1.86 – 1.67 (m, 2H, H-5/6-equatorial), 1.40 – 1.26 (m, 2H, H-5/6-axial), −2.84 (s, 2H, NH-porphyrin).

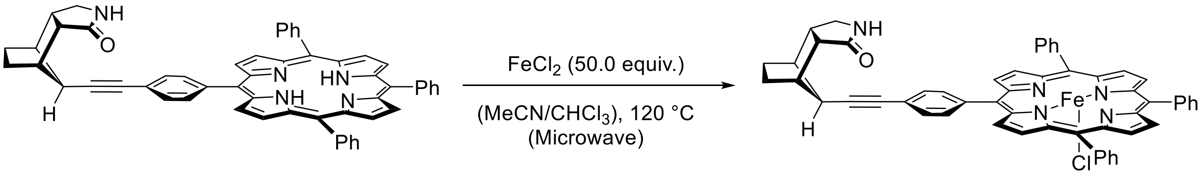
^{13}C NMR (126 MHz, CD_2Cl_2, 298 K) δ [ppm] = 179.2 (s, C=O), 142.4, 142.0, 135.0 (d, C-phenyl), 134.9 (d, C-3'), 129.9 (d, C-phenyl), 128.1 (d, C-2'), 127.1 (d, C-phenyl), 123.6, 120.7, 120.7, 119.8, 90.7 (s, C-6'), 82.4 (s, C-5'), 50.6 (d, C-7a), 47.3 (d, C-7), 46.8 (t, C-3), 45.1 (d, C-4) , 42.3 (d, C-3a), 39.5 (d, C-8), 29.1 (t, *C-5), 28.9 (t, *C-6).

*The assignments are interconvertible.

UV-Vis (33.3 µM, CH_2Cl_2): λ (nm): 418 (ε = 364 521 M^{-1} cm^{-1}), 516 (ε =°23 310 M^1cm^{-1}), 570 (ε = 15 943 M^{-1} cm^{-1}).

HRMS (ESI): calc. for $C_{55}H_{41}N_5O$ $[M+H]^+$: 788.3384; found: 788.3386.

Fe(III)-5-[(3a*R*,4*S*,7*R*,7a*S*,8*S*)-8-phenylethynyloctahydro-1*H*-4,7-methanoisoindol-1-oneyl]-10,15,20-triphenylporphyrin (6)



S7 **6**

Porphyrin **S7** (20.0 mg, 25.4 µmol, 1.00 equiv.) and $FeCl_2$ (96.5 mg, 761 µmol, 30.0 equiv.) were dissolved in a mixture of anhydrous CH_3CN (2 mL) and anhydrous $CHCl_3$ (2.5 mL). The solution was stirred at room temperature for one hour and heated to 120 °C in the microwave for 45 minutes. $FeCl_2$ (64.4 mg, 507 µmol, 20.0 equiv.) was added and the reaction mixture was again stirred at room temperature for one hour and heated to 120 °C in the microwave for 45 minutes. All volatiles were removed under reduced pressure and the residue was re-dissolved in CH_2Cl_2 (30 mL). The solution was washed with deionized water (7 × 40 mL) until the aqueous phase became clear and showed no orange-red coloration. The organic layer was dried over Na_2SO_4 and all volatiles were removed under reduced pressure. The obtained dark green/black crude material was dissolved in distilled CH_2Cl_2 and precipitated by addition of distilled hexanes. The suspension was filtered through a sintered glass funnel and the title iron porphyrin **6** was obtained as a black solid (16.6 mg, 18.9 µmol, 75%).

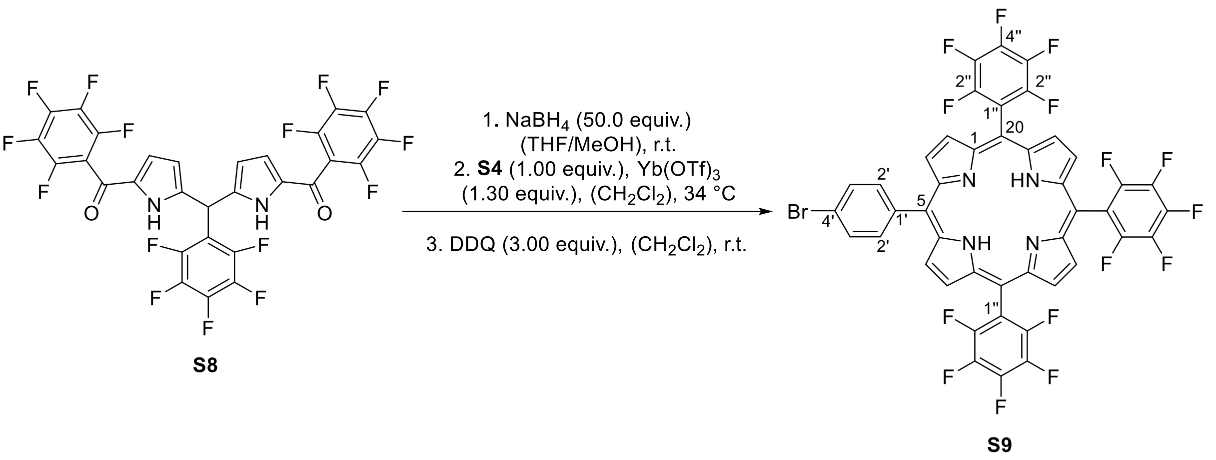
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3355 (bw), 2960 (w), 2923 (w), 2852 (w), 1686 (bm, C=O), 1259 (s), 1071 (bs), 995 (s), 798 (s), 702 (m).

UV-Vis (0.10 mM, CH_2Cl_2): λ (nm): 251 (ε = 38 227 M^{-1} cm^{-1}), 318 (ε = 33 526 M^{-1} cm^{-1}), 409 (ε = 102 374 M^{-1} cm^{-1}), 570 (ε = 11 135 M^{-1} cm^{-1}).

HRMS (ESI): calc. for $C_{55}H_{39}ClFeN_5O$ $[M-Cl]^+$: 841.2504; found: 841.2512.

EA (CHN): calc. for $C_{55}H_{39}ClFeN_5O$ (%): C 75.30, H 4.48, N 7.98; found (%): C 74.65, H 4.54, N 7.49.

5-(4-Bromophenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (S9)



$NaBH_4$ (540 mg, 14.3 mmol, 50.0 equiv.) was added to a solution of {[(pentafluorophenyl) methylene]bis(1H-pyrrole-5,2-diyl)}bis[(pentafluorophenyl)methanone][9] **S8** (200 mg, 286 µmol, 1.00 equiv.) in a mixture of anhydrous THF (11 mL) and anhydrous MeOH (4 mL) over ten minutes. The solution was stirred at room temperature for 25 minutes and then quenched by addition of CH_2Cl_2 (60 mL) and sat. aq. NH_4Cl (60 mL). The organic layer was separated, washed with water (60 mL) and brine (60 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure the obtained residue was dried for one hour under high vacuum. After re-dissolving the residue in anhydrous CH_2Cl_2 (110 mL), **S4** (86.0 mg, 286 µmol, 1.00 equiv.) and $Yb(OTf)_3$ (230 mg, 371 µmol, 1.30 equiv.) were added and the reaction mixture was stirred at 34 °C for 90 min under argon atmosphere. DDQ (194 mg, 857 µmol, 3.00 equiv.) was added and the reaction mixture was stirred for further 30 minutes at room temperature. Et_3N (260 µL, 1.87 mmol, 6.50 equiv.) was added and the black reaction solution was stirred for another ten minutes. The reaction mixture was filtered through a pad of silica (5 cm), which was rinsed with CH_2Cl_2 (500 mL) until the coloration of the solvent disappeared. After removal of all volatiles under reduced pressure the crude material was purified by column chromatography (silica, CH_2Cl_2/Hexanes 15/85) to obtain the title porphyrin **S9** as a purple shimmering solid (70.0 mg, 72.7 µmol, 25%).

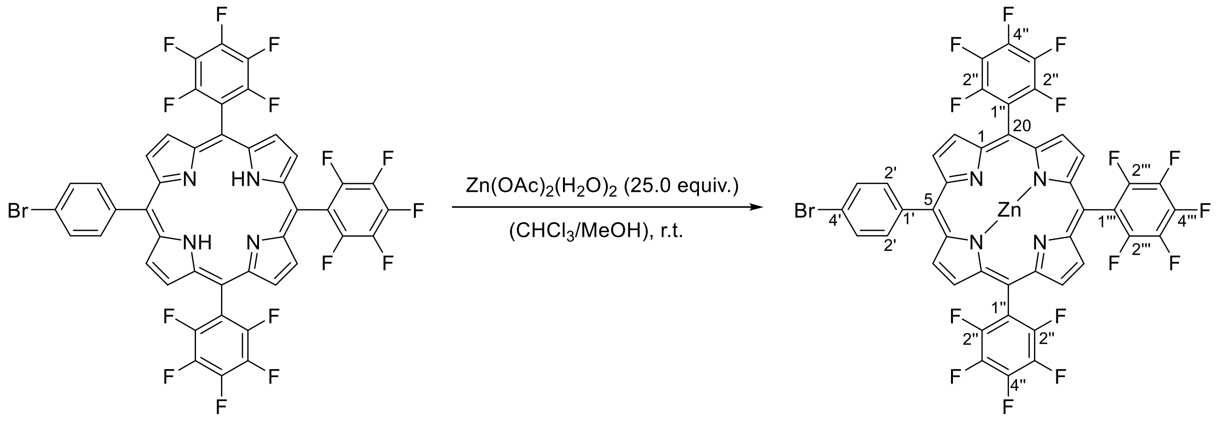
TLC: R_f **=** 0.45 (CH_2Cl_2/Hexanes = 2/8), [VIS, purple].

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K) δ [ppm] = 9.00 (d, ^3J = 4.9 Hz, 2H, H-porphyrin), 8.98 – 8.92 (m, 4H, H-porphyrin), 8.89 (d, ^3J = 4.9 Hz, 2H, H-porphyrin), 8.17 – 8.08 (m, 2H, H-3’), 8.01 – 7.91 (m, 2H, H-2’) 2.91 (s, 2H, NH-porphyrin) .

^{19}F-NMR (376 MHz, CD_2Cl_2, 298 K) δ [ppm] = −137.6 (d, 1F, *J* = 8.2 Hz), −137.6 – −137.67 (m, 3F), −137.7 (d, 2F, *J* = 8.2 Hz), −152.7 – −153.0 (m, 3F), −162.4 – −162.6 (m, 6F).

Literature spectra were recorded in deuterated chloroform.[10]

Zn(II)-5-(4-bromophenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (S10)



S9 S10

Porphyrin **S9** (115 mg, 119 µmol, 1.00 equiv.) and Zn(OAc)$_2$(H$_2$O)$_2$ (655 mg, 2.98 mmol, 25.0 equiv.) were dissolved in a mixture of anhydrous MeOH (3 mL) and anhydrous CHCl$_3$ (9 mL). The solution was stirred at room temperature for 24 h. After removal of all volatiles under reduced pressure the crude material was purified by column chromatography (ssilica, CH$_2$Cl$_2$/*n*-pentane 15/85 → 3/7 → 5/5) to obtain the title porphyrin **S10** as a purple shimmering solid (98 mg, 106 µmol, 80%).

TLC: R_f = 0.50 (CH$_2$Cl$_2$/Hexanes = 4/6), [VIS, purple].

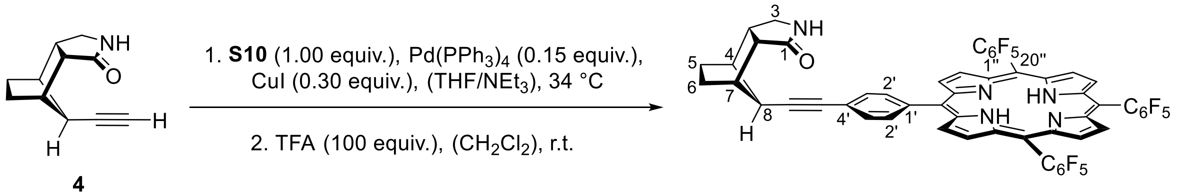
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3360 (w), 2951 (s), 2890 (w), 1650 (w), 1519 (s), 1489 (s), 1339 (w), 1074 (m), 989 (s), 940 (s), 760 (w).

^{1}H-NMR (400 MHz, CD$_2$Cl$_2$, 298 K) δ [ppm] = 9.09 (d, ^3J = 4.8 Hz, 2H, H-porphyrin), 9.04 (dd, ^3J = 4.8 Hz, ^3J = 4.8 Hz, 4H, H-porphyrin), 8.97 (d, ^3J = 4.8 Hz, 2H, H-porphyrin), 8.17 – 8.08 (m, 2H, H-3'), 8.01 – 7.91 (m, 2H, H-2').

^{19}F-NMR (376 MHz, CD$_2$Cl$_2$, 298 K) δ [ppm] = −137.8 (d, 1F, J = 8.3 Hz), −137.9 – −138.0 (m, 3F), −138.0 (d, 2F, J = 8.3 Hz), −153.4 – −153.7 (m, 3F), −162.7 – −163.3 (m, 6F).

HRMS (ESI): calc. for C$_{44}$H$_{12}$N$_4$Zn [M+Cl]$^-$: 1068.9279; found: 1068.9288.

(3a*S*,4*R*,7*S*,7a*R*,8*R*)-8-{[4-(10,15,20-Tris(pentafluorophenyl)porphyrin-5-yl]phenyl}ethynyl)octahydro-1*H*-4,7-methanoisoindol-1-one (S11)



4
(1.20 equiv.)

S11

Porphyrin **10** (85 mg, 83 µmol, 1.00 equiv.) and (3a*S*,4*R*,7*S*,7a*R*,8*R*)-8-ethynyloctahydro-1*H*-4,7-methanoisoindol-1-one **4** (17.4 mg, 99.3 µmol, 1.20 equiv.) were dissolved in a mixture of anhydrous Et_3N (4.2 mL) and anhydrous THF (4.2 mL) and the solution was degassed by three freeze-thaw cycles. CuI (4.73 mg, 24.8 µmol, 30.0 mol%) and $Pd(PPh_3)_4$ (14.4 mg, 12.4 µmol, 15.0 mol%) were added and the solution was stirred for 22 hours at 50 °C. The reaction mixture was cooled to room temperature and all volatiles were removed under reduced pressure. Ethyl acetate (20 mL) and water (20 mL) were added to the obtained purple crude product, the organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with sat. aq. NaCl and dried over Na_2SO_4. After removal of all volatiles the crude material was purified by column chromatography ($MeOH/CH_2Cl_2$ 0/100 → 1/99 → 3/97) to obtain the zinc inserted coupling product with aliphatic impurities as a purple solid. The obtained material was immediately re-dissolved in distilled CH_2Cl_2 (60 mL) and. TFA (368 µL, 539 mg, 4.73 mmol, 57.0 equiv.) was added over one minute. The solution was stirred at room temperature for one hour. The reaction was quenched by addition of sat. aq. $NaHCO_3$ (15 mL). The organic layer was separated, washed with sat. aq. NaCl (25 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure the crude material was purified by column chromatography (silica, $MeOH/CH_2Cl_2$ 0/100 → 1/99) to obtain the title porphyrin **S11** as a purple solid (43.0 mg, 40.7 µmol, 43%).

TLC: R_f = 0.18 ($MeOH/CH_2Cl_2$ = 1/99), [VIS, purple].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3359 (w), 3319 (w, NH-Porphyrin), 2981 (s), 2929 (m), 1687 (m), 1518 (s), 1498 (s), 1381 (w), 1026 (m), 988 (s), 919 (s), 764 (s), 756 (s).

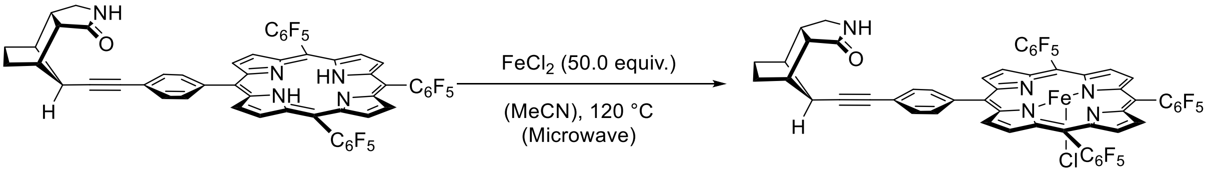
^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K) δ [ppm] = 9.06 (d, ^3J = 4.9 Hz, 2H, H-porphyrin), 9.02 – 8.94 (m, 4H, H-porphyrin), 8.91 (d, ^3J = 4.9 Hz, 2H, H-porphyrin), 8.24 – 8.17 (m, 2H, H-3’), 7.85 – 7.81 (m, 2H, H-2’), 5.46 (s, 1H, NH), 3.84 (dd, ^3J = 9.6 Hz, ^3J = 4.4 Hz, 1H, H-3), 3.77 (*virt* t, $^2J \approx {}^3J$ = 9.6 Hz, 1H, H-3), 3.00 (d, ^3J = 3.9 Hz, 1H, H-4), 2.82 (s, 1H, H-8), 2.70 (dd, ^3J

= 9.6 Hz, ^3J = 4.4 Hz, 1H, H-3a), 2.67 (d, ^3J = 3.9 Hz, 1H, H-7), 2.62 (d, ^3J = 9.4 Hz, 1H, H-7a), 1.90 – 1.72 (m, 2H, H-5/6-equatorial), 1.42 – 1.24 (m, 2H, H-5/6-axial), −2.86 (s, 2H, NH-porphyrin).

^{19}F-NMR (376 MHz, CD_2Cl_2, 298 K) δ [ppm] = 137.6 (1F, d, *J* = 8.2 Hz), 137.6 (3F, t, *J* = 8.5 Hz), 137.7 (2F, d, *J* = 8.2 Hz), 152.9 (3F, q, *J* = 21.5 Hz), 162.4 – 162.8 (m, 6F).

HRMS (ESI): calc. for $C_{55}H_{26}F_{15}N_5O$ $[M+H]^+$: 1058.1971; found: 1058.1991.

Fe(III)-5-[(3a*R*,4*S*,7*R*,7a*S*,8*S*)-8-phenylethynyloctahydro-1*H*-4,7-methanoisoindol-1-oneyl]-10,15,20-triphenylporphyrin (5)



S11 **5**

Porphyrin **S11** (28.0 mg, 26.5 µmol, 1.00 equiv.) and $FeCl_2$ (101 mg, 792 µmol, 30.0 equiv.) were dissolved in anhydrous CH_3CN (5 mL). The solution was stirred at room temperature for one hour and heated to 120 °C in the microwave for 45 minutes. $FeCl_2$ (67.1 mg, 528 µmol, 20.0 equiv.) was added and the reaction mixture was again stirred at room temperature for one hour and heated to 120 °C in the microwave for 45 minutes. After removal of all volatiles under reduced pressure the residue was re-dissolved in CH_2Cl_2 (30 mL). The solution was washed with deionized water (10 × 40 mL) until the aqueous phase became clear and showed no orange-red coloration. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained dark green/black crude material was dissolved in distilled CH_2Cl_2 and precipitated by addition of distilled hexanes. The suspension was filtered through a sintered glass funnel and the title iron porphyrin **5** was obtained as a black solid (16.1 mg, 14.0 µmol, 53%).

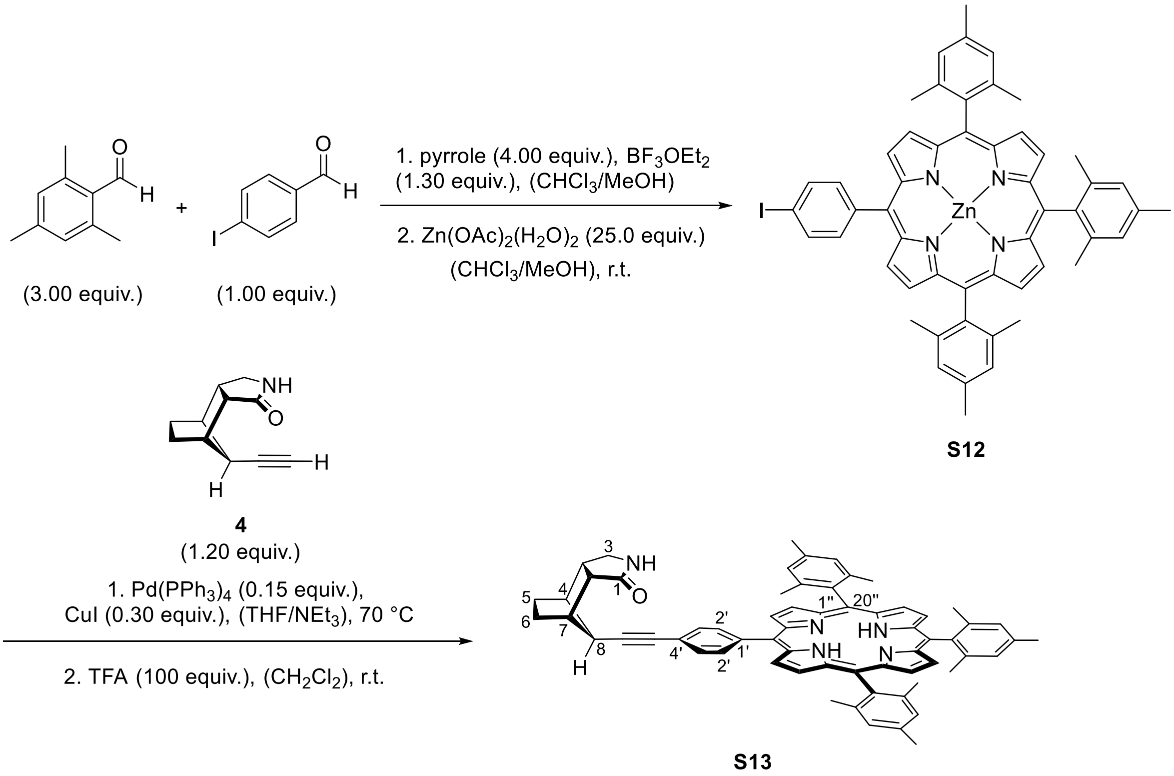
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960 (w), 2921 (m), 2852 (w), 2852 (w), 1683 (bm, C=O), 1259 (s), 1072 (bs), 1012 (s), 874 (m), 799 (s), 702 (m).

UV-Vis (CH_2Cl_2): λ (nm): 266 (ε = 11 326 M^{-1} cm^{-1}), 423 (ε = 105 227 M^{-1} cm^{-1}), 576 (ε = 11 326 M^{-1} cm^{-1}).

HRMS (EI): calc. for $C_{55}H_{24}ClF_{15}FeN_5O$ [M-Cl]$^+$: 1111.1091; found: 1111.1093.

EA (CHN): calc. for $C_{55}H_{24}ClF_{15}FeN_5O$ (%): C 57.59, H 2.11, N 6.11; found (%): C 58.28, H 2.15, N 5.82.

5-[(3a*R*,4*S*,7*R*,7a*S*,8*S*)-8-Phenylethynyloctahydro-1*H*-4,7-methanoisoindol-1-oneyl]-10,15,20-trimesitylporphyrin (S13)



According to a literature procedure,[11] 4-Iodobenzaldehyde (1.30 g, 5.60 mmol, 1.00 equiv.), mesityl aldehyde (2.49 g, 16.8 mmol, 3.00 equiv.), and pyrrole (1.55 ml, 22.4 mmol, 4.00 equiv.) were dissolved in a mixture of anhydrous CHCl$_3$ (2 L) and anhydrous ethanol (24 mL). Subsequently the solution was degassed with a stream of argon for 10 minutes, BF$_3$·Et$_2$O (1.38 ml, 10.9 mmol, 1.30 equiv.) was added and the solution was stirred for 1 hour at room temperature. DDQ (3.82 g, 16.8 mmol, 3.00 equiv.) was added and the reaction mixture was stirred at room temperature for one hour. The dark reaction solution was filtered through a pad of silica, which was rinsed with CHCl$_3$ until the coloration of the solvent disappeared. The obtained filtrate was concentrated under reduced pressure. Purification by three separate column chromatography steps (Al$_2$O$_3$, All three columns: CH$_2$Cl$_2$/*n*-hexane 8/92 → 1/9) only furnished a mixture of different porphyrins as a purple lustrous solid. The porphyrin mixture and Zn(OAc)$_2$(H$_2$O)$_2$ (1.43 g, 6.50 mmol, 1.16 equiv.) were dissolved in a mixture of anhydrous MeOH (7 mL) and anhydrous CHCl$_3$ (18 mL). The solution was stirred at room temperature overnight. Similarly, after removal of all volatiles under reduced pressure the crude material was purified by three consecutive column chromatography steps [sSilica, CH$_2$Cl$_2$/Hexanes 2/8 (1st column); 1/9 → 15/85 → 25/75 (2nd column); 1/9 → 15/85 → 25/75

(3^{rd} column)] to obtain a mixture of Zn-inserted tetramesitylporphyrin and porphyrin **S12** as a pink shimmering solid. The porphyrin mixture was used without further purification.

The porphyrin mixture (90 mg, 102 µmol, 1.00 equiv.) and alkyne **4** (21.4 mg, 123 µmol, 1.20 equiv.) were dissolved in a mixture of anhydrous Et_3N (5 mL) and anhydrous THF (5 mL) and the solution was degassed by three freeze-thaw cycles. CuI (5.82 mg, 30.6 µmol, 30.0 mol%) and $Pd(PPh_3)_4$ (17.7 mg, 15.3 µmol, 15.0 mol%) were added and the solution was stirred for 18 hours at 70 °C inert atmosphere. The reaction mixture was cooled to room temperature and all volatiles were removed under reduced pressure. The crude product was filtered through a pad of silica (4 cm) and the silica pad was washed with $MeOH/CH_2Cl_2$ (2/98, 150 mL) until the coloration disappeared. The obtained filtrate was concentrated under reduced pressure and the crude material was re-dissolved in distilled CH_2Cl_2 (50 mL). TFA (779 µL, 1.16 g, 10.2 mmol, 100 equiv.) was added over one minute and the solution was stirred at room temperature for 1.5 hours. The reaction was quenched by addition of sat. aq. $NaHCO_3$ (40 mL). The organic layer was separated, washed with sat. aq. NaCl (2 × 35 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure the crude material was purified by column chromatography (silica, $MeOH/CH_2Cl_2$ 0/100 → 1/99 → 2/98 → 4/96) to obtain the title porphyrin **S13** as a purple solid (72.0 mg, 78.8 µmol, 77%, 1% over all reaction steps).

TLC: R_f **=** 0.17 ($MeOH/CH_2Cl_2$ = 1/99), [VIS, purple].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3319 (w, NH-Porphyrin), 2951 (s), 2918 (m), 1604 (s, C=O), 1470 (m), 1346 (m), 967 (s), 802 (s), 739 (m).

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K) δ [ppm] = 8.79 (d, ^3J = 4.8 Hz, 2H, H-porphyrin), 8.66 (d, ^3J = 4.8 Hz, 2H, H-porphyrin), 8.62 (s, 4H, H-porphyrin), 8.18 – 8.12 (m, 2H, H-3'), 7.77 – 7.71 (m, 2H, H-2'), 7.29 (s, 6H, H-mesityl), 5.42 (bs, 1H, NH), 3.79 (dd, ^3J = 9.6 Hz, ^3J = 4.4 Hz, 1H, H-3), 3.71 (*virt* t, $^2J \approx {}^3J$ = 9.6 Hz, 1H, H-3), 2.94 (d, ^3J = 3.9 Hz, 1H, H-4), 2.77 (s, 1H, H-8), 2.66 (td, ^3J = 9.8 Hz, ^3J = 4.4 Hz, 1H, H-3a), 2.63 – 2.59 (m, 10H, H-7, *para*-CH_3-mesityl), 2.57 (d, ^3J = 9.4 Hz, 1H, H-7a), 1.86 (s, 6H, CH_3-mesityl), 1.84 (s, 12H, CH_3-mesityl), 1.81 – 1.69 (m, 1H, H-5/6-equatorial), 1.40 – 1.23 (m, 2H, H-5/6-axial), −2.62 (s, 2H, NH-porphyrin).

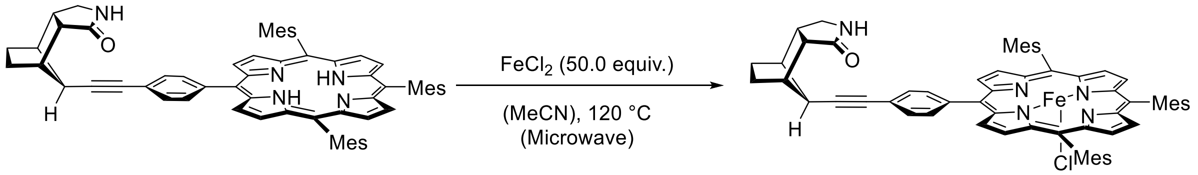
^{13}C-NMR (126 MHz, CD_2Cl_2, 298 K) δ [ppm] = 179.1 (s, C=O), 142.0, 139.6, 139.5 (s, C-mesityl), 138.6, 138.4, 138.2 (s, C-mesityl), 134.9 (d, C-3'), 129.9 (d, C-2'), 128.1 (d, C-mesityl), 123.4, 118.9, 118.3, 118.2, 90.6 (s, C-6'), 82.4 (s, C-5'), 50.6 (d, C-7a), 47.3 (d, C-7), 46.8 (t, C-3), 45.1 (d, C-4), 42.3 (d, C-3a), 39.5 (d, C-8), 29.1 (t, *C-5), 28.9 (t, *C-6), 21.8 (q, *para*-CH_3-mesityl), 21.7 (q, CH_3-mesityl) 21.5 (q, CH_3-mesityl).

*The assignments are interconvertible.

UV-Vis (33.3 μM, CH_2Cl_2): λ (nm): 418 (ε = 324 846 M^{-1} cm^{-1}), 516 (ε = 23 039 M^{-1} cm^{-1}), 570 (ε = 15 088 M^{-1} cm^{-1}).

HRMS (ESI): calc. for $C_{64}H_{59}N_5O$ $[M+H]^+$: 914.4793; found: 914.4829.

Fe(III)-5-[(3aR,4S,7R,7aS,8S)-8-phenylethynyloctahydro-1H-4,7-methanoisoindol-1-oneyl]-10,15,20-trimesitylporphyrin (7)



S13 **7**

Porphyrin **S13** (19.0 mg, 20.8 µmol, 1.00 equiv.) and $FeCl_2$ (79.0 mg, 623 µmol, 30.0 equiv.) were dissolved in a mixture of anhydrous CH_3CN (4 mL) and anhydrous $CHCl_3$ (2 mL). The solution was stirred at room temperature for one hour and heated to 120 °C in the microwave for 45 minutes. $FeCl_2$ (52.7 mg, 416 µmol, 20.0 equiv.) was added and the reaction mixture was again stirred at room temperature for one hour and heated to 120 °C in the microwave for 45 minutes. After removal of all volatiles under reduced pressure the residue was re-dissolved in CH_2Cl_2 (30 mL). The solution was washed with deionized water (10 × 40 mL) until the aqueous phase became clear and showed no orange-red coloration. The organic phase was dried over Na_2SO_4 and all volatiles were removed under reduced pressure. The obtained dark green/black crude material was dissolved in distilled CH_2Cl_2 and precipitated by addition of distilled hexanes. The suspension was filtered through a sintered glass funnel and the title porphyrin **7** was obtained as a black solid (11.5 mg, 11.5 µmol, 55%).

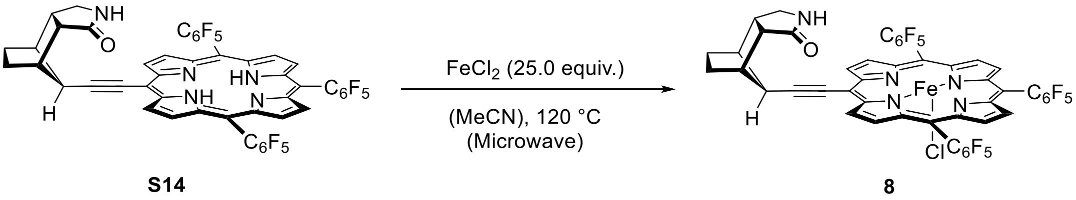
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3326 (bs), 2952 (m), 2821 (w), 2852 (w), 1687 (bm, C=O), 1250 (s), 1087 (bs), 1015 (s), 996 (s), 800 (s).

UV-Vis (0.1 mM, CH_2Cl_2): λ (nm): 377 (ε = 558 05 M^{-1} cm^{-1}), 418 (ε = 103 453 M^{-1} cm^{-1}), 509 (ε = 16 603 M^{-1} cm^{-1}).

HRMS (ESI): calc. for $C_{64}H_{47}ClFeN_5O$ [M-Cl]$^+$: 967.3913; found: 967.3907.

EA (CHN): calc. for $C_{64}H_{47}ClFeN_5O$ (%): C 76.60, H 5.73, N 6.98; found (%): C 74.23, H 5.58, N 6.45.

Fe(III)-5-[(3a*R*,4*S*,7*R*,7a*S*,8*S*)-8-ethynyloctahydro-1*H*-4,7-methanoisoin-dol-1-one-yl]-10,15,20-tri(pentafluorophenyl)porphyrin-chloride (8)



Porphyrin **S14**[12] (30.0 mg, 30.6 µmol, 1.00 equiv.) and $FeCl_2$ (116 mg, 917 µmol, 30.0 equiv.) were dissolved in anhydrous CH_3CN (6 mL). The solution was stirred at room temperature for 1.5 h and heated to 120 °C in the microwave for 30 minutes. $FeCl_2$ (96.8 mg, 764 µmol, 25.0 equiv.) was added and the reaction mixture was again stirred at room temperature for 1 h and heated to 120 °C in the microwave for 30 minutes. After removal of all volatiles under reduced pressure and the residue was re-dissolved in $CHCl_3$ (30 mL). The solution was washed with deionized water (7 × 30 mL) until the aqueous phase became clear and showed no orange-red coloration. The organic phase was dried over Na_2SO_4 and all volatiles were removed under reduced pressure. The obtained dark green/black crude material was dissolved in distilled CH_2Cl_2 and precipitated by addition of distilled hexanes. The suspension was filtered through a sintered glass funnel and the title porphyrin **17** was obtained as a black solid (24.0 mg, 22.4 µmol, 73%).

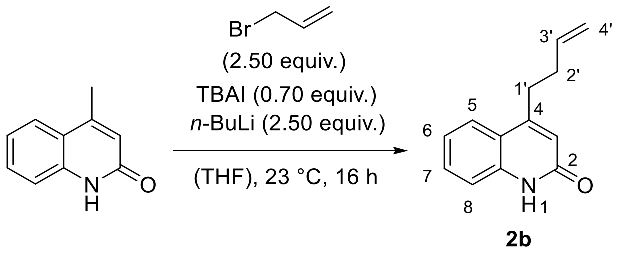
IR (film) $\tilde{\nu}_{max}/cm^{-1}$ = 2929 (m), 1704 (s, C=O), 1529(v), 1494 (v), 1374 (w), 1339 (w), 1281 (w), 1161 (w), 1051 (w), 988 (s), 940 (m), 761 (w).

UV-Vis (0.1 mM, CH_2Cl_2): λ (nm): 318 (ε = 40 822 M^{-1} cm^{-1}), 418 (ε = 122 290 M^{-1} cm^{-1}), 571 (ε = 13 039 M^{-1} cm^{-1}).

HRMS (ESI): calc. for $C_{49}H_{20}ClF_{15}FeN_5O$ $[M-Cl]^+$: 1035.0778; found: 1035.0775.

EA (CHN): calc. for $C_{49}H_{20}ClF_{15}FeN_5O$ (%): C 54.95, H 1.88, N 6.54; found (%): C 54.64, H 2.12, N 6.19.

4-(But-4-en-1-yl)quinolin-2(1*H*)-one (2b)



n-Butyllithium (2.5 M in *n*-hexane, 9.42 mL, 23.6 mmol, 2.50 equiv.) was added dropwise to a solution of 4-methyl quinolone (1.50 g, 9.42 mmol, 1.00 equiv.) in anhydrous THF (40 mL) at 0 °C. The reaction mixture was stirred for 30 minutes at 0 °C. The cooling bath was removed and the reaction mixture was stirred for further 2 hours at room temperature under argon atmosphere. The resulting dark red/green reaction solution was cooled to −78 °C. Tetra-*n*-butyl ammonium iodide (2.44 g, 6.60 mmol, 0.70 equiv.) and allyl bromide (2.15 mL, 23.6 mmol, 2.50 equiv.) were added at −78 °C. The reaction mixture was stirred for 20 hours, while the reaction mixture was allowed to warm to room temperature. The reaction was quenched by addition of aq. HCl (1 M, 40 mL) and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl (60 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the crude product was purified by automated column chromatography (silica, EtOAc/Hexanes 2/8 → 6/4 → 1/0). Subsequent precipitation from ethyl acetate/hexanes gave the title quinolone **2b** as an off-white crystalline solid (420 mg, 9.42 mmol, 22%).

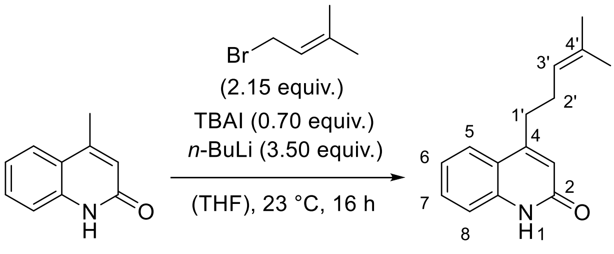
TLC: R_f = 0.25 (EtOAc/Hexanes = 3/7), [UV].

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm] = 12.62 (s, 1H), 7.71 (d, ^3J = 8.1 Hz, 1H, H-5), 7.55 – 7.44 (m, 2H, H-7, H-8), 7.26 – 7.21 (m, 1H, H-6), 6.60 (s, 1H, H-3), 6.00 – 5.83 (m, 1H, H-3'), 5.16 – 5.00 (m, 2H, H-4'), 2.97 (t, ^3J = 7.8 Hz, 2H, H-1'), 2.56 – 2.42 (m, 2H, H-2').

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm] = 164.6 (s, C=O), 152.4 (s, C-4), 138.8 (s, C-8a), 137.1 (d, C-3'), 130.5 (d, C-7), 124.2 (d, C-5), 122.6 (d, C-6), 119.9 (s, C-4a), 119.8 (d, C-3), 117.1 (d, C-8), 116.0 (d, C-4'), 32.8 (t, C-2'), 31.7 (t, C-1').

The analytical data are in accordance with the literature values.[13]

4-(4-Methylpent-3-en-1-yl)quinolin-2(1*H*)-one (12b)



12b

n-Butyllithium (2.5 M in *n*-hexane, 17.5 mL, 44.0 mmol, 3.50 equiv.) was added dropwise to a solution of 4-methyl quinolone (2.00 g, 12.6 mmol, 1.00 equiv.) in anhydrous THF (40 mL) at 0 °C. The reaction mixture was stirred for 30 minutes at 0 °C. The cooling bath was removed and the reaction mixture was stirred for further 3 hours at room temperature under argon atmosphere. The resulting dark red/green reaction solution was cooled to −78 °C. Tetra-*n*-butyl ammonium iodide (2.44 g, 6.60 mmol, 0.70 equiv.) and dimethylallyl bromide (2.30 mL, 3.30 g, 27.0 mmol, 2.15 equiv.) were added at −78 °C. The reaction mixture was stirred for 16 h, while the reaction mixture was allowed to warm to room temperature. The reaction was quenched by addition of aq. HCl (1 M, 80 mL). The reaction mixture was concentrated under reduced pressure and the residue was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl (60 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the crude product was purified by column chromatography (silica, EtOAc/Hexanes 5/5 → 2/1). Subsequent precipitation from ethyl acetate/hexanes gave the title quinolone **12b** as an off-white solid (1.22 g, 5.70 mmol, 46%).

M.p. = 120 °C

TLC: R_f **=** 0.31 (EtOAc/Hexanes = 4/6), [UV].

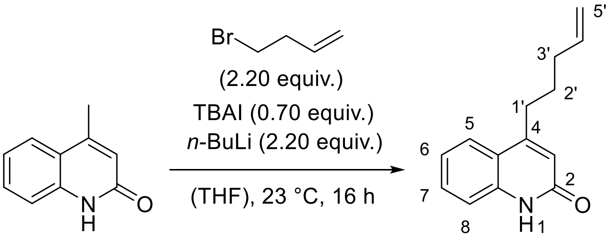
IR (film) $\tilde{\nu}_{max}/cm^{-1}$ = 2964 (m), 2851 (m), 1648 (s, C=O), 1509 (m), 1433 (m), 867 (m), 769 (w), 750 (m).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) δ [ppm] = 12.65 (s, 1H, NH), 7.74 (dd, ^3J = 8.2 Hz, ^4J =1.2 Hz, 1H, H-5), 7.55 – 7.44 (m, 2H, H-7, H-8), 7.24 (ddd, ^3J = 8.2 Hz, ^3J = 6.6 Hz, ^4J = 1.7 Hz, 1H, H-6), 6.61 (s, 1H, H-3), 5.26 – 5.17 (m, 1H, H-4’), 2.92 – 2.85 (m, 2H, H-1’), 2.42 (q, ^3J = 7.8 Hz, 2H, H-2’), 1.71 (s, 3H, CH_3), 1.59 (s, 3H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm] = 164.7 (s, C=O), 153.0 (s, C-4), 138.6 (s, C-8a), 133.4 (s, C-4’), 130.5 (d, C-7), 124.2 (d, C-5), 122.8 (d, C-6), 122.6 (d, C-3’), 120.0 (s, C-4a), 119.6 (d, C-3), 117.0 (d, C-8), 32.5 (t, C-2’), 27.4 (t, C-1’), 25.9 (q, CH_3), 17.9 (q, CH_3).

HRMS (ESI): calc. for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1383; found: 228.1381.

4-(Pent-5-en-1-yl)quinolin-2(1*H*)-one (2c)



2c

n-Butyllithium (2.5 M in *n*-hexane, 11.1 mL, 27.6 mmol, 2.20 equiv.) was added dropwise to a solution of 4-methyl quinolone (2.00 g, 12.6 mmol, 1.00 equiv.) in anhydrous THF (40 mL) at 0 °C. The reaction mixture was stirred for 30 minutes at 0 °C. The cooling bath was removed and the reaction mixture was stirred for further 2 hours at room temperature under argon atmosphere. The resulting dark red/green reaction solution was cooled to -78 °C. Tetra-*n*-butyl ammonium iodide (2.44 g, 6.60 mmol, 0.70 equiv.) and 4-bromo-1-butene (3.73 g, 2.81 mL, 27.6 mmol, 2.20 equiv.) were added -78 °C. The reaction mixture was stirred for 20 hours, while the reaction mixture was allowed to warm to room temperature. The reaction was quenched by addition of aq. HCl (1 M, 40 mL) and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl (50 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the crude product was purified by automated column chromatography (silica, EtOAc/Hexanes 2/8 → 6/4 → 1/0). Subsequent precipitation from ethyl acetate/hexanes gave the title compound **2c** as a white powder (1.40 mg, 6.56 mmol, 52%).

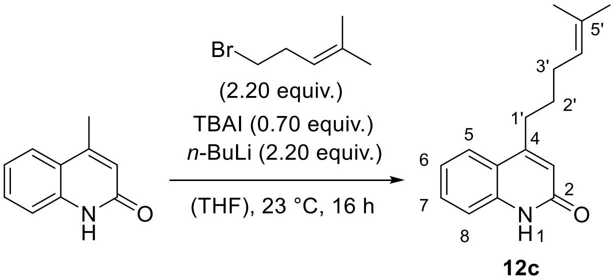
TLC: R_f = 0.20 (EtOAc/Hexanes = 4/6), [UV].

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm] = 12.71 (s, 1H, NH), 7.70 (d, ^3J = 8.2 Hz, 1H, H-5), 7.54 – 7.44 (m, 2H, H-7, H-8), 7.23 (ddd, ^3J = 8.2 Hz, ^3J = 5.5 Hz, ^4J = 2.8 Hz, 1H, H-6), 6.61 (s, 1H, H-3), 5.92 – 5.77 (m, 1H, H-4'), 5.13 – 4.99 (m, 2H, H-5'), 2.87 (t, ^3J = 7.6 Hz, 2H, H-1'), 2.31 – 2.11 (m, 2H, H-3'), 1.84 (*virt* p, $^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 7.6 Hz, 2H, H-2').

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm] = 164.8 (s, C=O), 153.2 (s, C-4), 138.7 (s, C-8a), 137.9 (d, C-4'), 130.5 (d, C-7), 124.2 (d, C-5), 122.6 (d, C-6), 119.9 (s, C-4a), 119.6 (d, C-3), 117.1 (d, C-8), 115.7 (t, C-5'), 33.5 (t, C-3'), 31.6 (t, C-1'), 28.0 (t, C-2').

The analytical data are in accordance with the literature values.[14]

4-(5-Methyl-hex-4-en-1-yl)quinolin-2(1*H*)-one (12c)



12c

n-Butyllithium (2.5M in *n*-hexane, 11.1 mL, 27.6 mmol, 2.20 equiv.) was added dropwise to a solution of 4-methyl quinolone (2.00 g, 12.6 mmol, 1.00 equiv.) in anhydrous THF (40 mL) at 0 °C. The reaction mixture was stirred for 30 minutes at 0 °C. The cooling bath was removed and the reaction mixture was stirred for further 2 hours at room temperature under argon atmosphere. The resulting dark red/green reaction solution was cooled to −78 °C. Tetra-*n*-butyl ammonium iodide (2.44 g, 6.60 mmol, 0.70 equiv.) and 5-bromo-2-methylpent-1-ene (4.51 g, 3.70 mL, 27.6 mmol, 2.20 equiv.) were added at −78 °C. The reaction mixture was stirred for 20 hours, while the reaction mixture was allowed to warm to room temperature. The reaction was quenched by addition of aq. HCl (1 M, 40 mL) and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl (50 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the crude product was purified by automated column chromatography (silica, EtOAc/Hexanes 20% → 60% → 100%). Subsequent precipitation from ethyl acetate/hexanes gave the title compound **12c** as a white solid (1.66 g, 6.88 mmol, 55%).

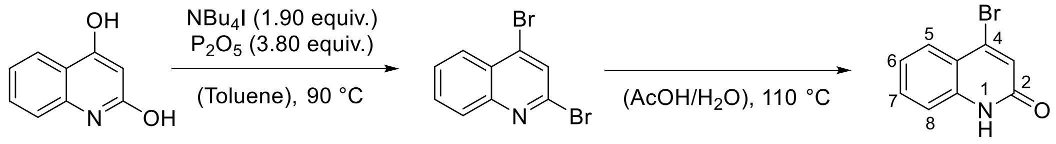
TLC: R_f = 0.25 (EtOAc/Hexanes = 4/6), [UV].

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) δ [ppm] = 12.79 (s, 1H, NH), 7.70 (d, ^3J = 8.1 Hz, 1H, H-5), 7.54 – 7.44 (m, 2H, H-7, H-8), 7.25 – 7.19 (m, 1H, H-6), 6.61 (s, 1H, H-3), 5.21 – 5.12 (m, 1H, H-4’), 2.85 (t, ^3J = 7.5 Hz, 2H, H-1’), 2.13 (q, ^3J = 7.5 Hz, 2H, H-3’), 1.77 (*virt.* p, $^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 7.5 Hz, 2H, H-2’) 1.72 (s, 3H, CH_3), 1.62 (s, 3H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm] = 164.8 (s, C=O), 153.5 (s, C-4), 138.7 (s, C-8a), 132.8 (s, C-5’), 130.5 (d, C-7), 124.3 (d, C-5), 123.7 (d, C-4’), 122.5 (d, C-6), 120.0 (s, C-4a), 119.4 (d, C-3), 117.1 (d, C-8), 31.8 (t, C-3’), 29.1 (t, C-2’), 27.8 (t, C-1’), 25.9 (q, CH_3), 18.0 (q, CH_3).

The analytical data are in accordance with the literature values.[14]

4-Bromquinolin-2(1*H*)-one (S16)



S15 **S16**

Dihydroxyquinoline (5.15 g, 31.9 mmol, 1.00 equiv.) and tetrabutylammonium bromide (19.6 g, 60.7 mmol, 1.90 equiv.) were dissolved in toluene (350 mL) and phosphorus pentoxide (17.2 g, 121 mmol, 3.80 equiv.) was added stepwise to the reaction solution over a period of 25 minutes. The reaction mixture was then stirred for 19 hours at 90 °C. The reaction mixture was cooled to room temperature and diluted by addition of toluene (100 mL) and water (150 mL). The solution was adjusted to a pH of 8-9 using solid sodium hydrogen carbonate (50 g) and the organic phase was separated. The aqueous phase was extracted with toluene (2×50 mL), the combined organic phases were dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the dibromoquinoline **S15** was obtained as a white solid (8.10 g, 28.2 mmol, 88%) and used without further purification.

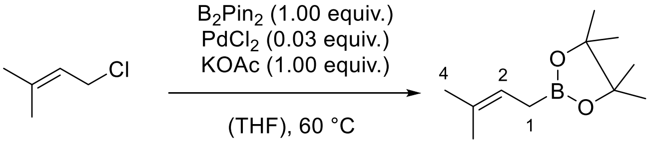
2,4-dibromoquinoline (8.03 g, 28.0 mmol, 1.00 equiv.) was dissolved in a solvent mixture of glacial acetic acid/deionized water (90 mL/45 mL) and stirred for 19 hoursat 110 °C. The reaction mixture was cooled to 0 °C, while an off-white solid was precipitating. The suspension was filtered through a sintered glass funnel and the collected solids were washed with deionized water (20 mL). The solid was collected and dried at 80 °C under reduced pressure and the title product **S16** was obtained as an off-white solid (4.94 g, 22.0 mmol, 79%).

^{1}H-NMR (500 MHz, DMSO-d_6, 298 K) δ [ppm] = 12.05 (s, 1H, NH), 7.82 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H, H-8), 7.61 (ddd, ^3J = 8.4 Hz, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1H, H-6), 7.35 (dd, ^3J = 8.4 Hz, ^4J = 1.1 Hz, 1H, H-7), 7.30 (ddd, ^3J = 8.2 Hz, ^3J = 7.2 Hz, ^4J = 1.1 Hz, 1H, H-5).

^{13}C-NMR (126 MHz, DMSO-d_6, 298 K) δ [ppm] = 160.3 (s, C=O), 138.2 (s, C-8a), 136.0 (s, C-7), 131.9 (d, C-7), 127.2 (s, C-4a), 125.3 (d, C-5), 122.8 (d, C-6), 118.3 (d, C-8), 115.8 (d, C-3).

The analytical data are in accordance with the literature values.[15]

3-Methyl-2-butenylboronsäurepinakolester (S17)



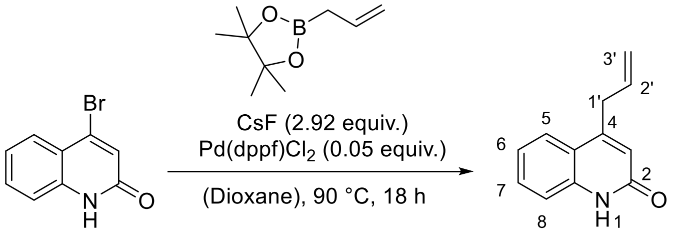
Palladium dichloride (52.5 mg, 296 µmol, 3.00 mol%), bis-(pinacolato)-diborane (2.53 g, 9.86 mmol, 1.00 equiv.), and potassium acetate (968 mg, 9.86 mmol, 1.00 equiv.) were added to a flame-dried *Schlenk* tube. The solids were evacuated and purged with argon three times and subsequently tetrahydrofuran (5 mL) was added. 1-chloro-3-methylbut-2-ene (1.09 mL, 1.01 g, 9.67 mmol, 1.00 equiv.) was added to the reaction solution and the mixture was stirred at 60 °C overnight. After removal of all volatiles under reduced pressure the crude grey suspension was filtered through a silica pad (5 cm) and the silica pad was washed with EtOAc/Hexanes (1.5:98.5, 200 mL). All volatiles were again removed under reduced pressure to obtain the title compound **S17** as a colorless oil (807 mg, 4.09 mmol, 42%).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) δ [ppm] = 5.29 – 5.15 (m, 1H, H-2), 1.71 – 1.66 (m, 3H, CH_3), 1.63 – 1.55 (m, 5H, H-1, CH_3), 1.24 (s, 12H, CH_3-Pinakol).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm] = 131.6 (C-3), 118.7 (s, C-2), 83.2 (s, O*C*(CH_3)$_2$) 25.8 (q, CH_3), 24.9 (q, CH_3-Pinakol), 17.8 (q, CH_3).

The NMR spectra should be recorded immediately, the compound decomposes over time in $CDCl_3$. The analytical data are in accordance with the literature values.[16]

4-Prop-2-enyl-quinolin-2(1*H*)-one (2a)



12c

Cesium fluoride (795 mg, 5.25 mmol, 2.92 equiv.), [1,1‘-Bis- (diphenylphosphino)-ferrocen]-dichloropalladium(II) (64.0 mg, 87.5 µmol, 5.00 mol%), 4-Bromquinolin-2(1H)-on **S16** (402 mg, 1.79 mmol, 1.00 Äq) and the allylic boronic ester (0.79 mL, 708 mg, 4.21 mmol, 2.35 Äq) were dissolved in dioxane (13 mL). The solution was degassed by two freeze-thaw cycles. The reaction mixture was stirred for 18 h at 90 °C. The reaction mixture was cooled to room temperature- Subsequently ethyl acetate (70 mL) and water (50mL) were added to the reaction mixture. The organic layer was separated and the aqueous layers was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over sodium sulfate. After removal of all volatiles under reduced pressure the crude material was purified by column chromatography (silica, EtOAc/Hexanes 4/6) to obtain the title quinolone **2a** as an off-white solid (273 mg, 1.48 mmol, 82%).

M.p. = 200 °C

TLC: R_f **=** 0.29 (EtOAc/Hexanes = 4/6), [UV].

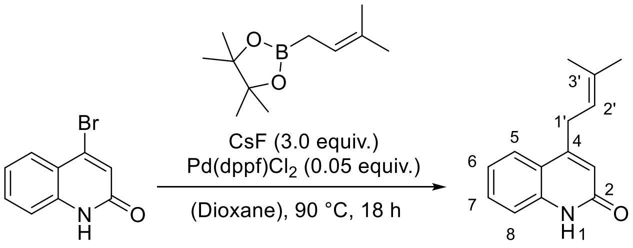
IR (film) $\tilde{\nu}_{max}$/cm^{-1} = 2832 (bm), 1647 (s, C=O), 1610 (s), 1553 (m), 1396 (m), 910 (s), 753 (s), 517 (s).

^{1}H-NMR (400 MHz, CDCl$_3$, 298 K) δ [ppm] = 12.71 (s, 1H, NH), 7.72 (d, ^3J = 8.1 Hz, 1H, H-5), 7.57 – 7.44 (m, 2H, H-7, H-8), 7.22 (ddd, ^3J = 8.1 Hz ^3J = 6.1 Hz, ^4J = 2.2 Hz, 1H, H-6), 6.63 (d, J = 1.1 Hz, 1H, H-3), 6.03 (m, 2H, H-3’), 5.28 – 5.16 (m, 2H, H-2’), 3.62 (dd, J = 6.5 Hz, 1.0 Hz, 2H, H-1’).

^{13}C-NMR (126 MHz, CDCl$_3$, 298 K) δ [ppm] = 164.7 (s, C=O), 151.1 (s, C-4), 138.7 (s, C-8a), 134.0 (d, C-2’), 130.6 (s, C-7), 124.4 (s, C-5), 122.6 (s, C-6), 120.2 (s, C-4a), 119.8 (s, C-3), 118.5 (s, C-3’), 117.0 (s, C-8), 36.5 (t, C-1’).

HRMS (ESI): calc. for $C_{12}H_{11}NO$ [M+H]$^+$: 186.0913; found: 186.0912.

4-(3-Methylbut-2-en-1-yl)quinolin-2(1*H*)-one (12a)



12a

Cesium fluoride (1.38 g, 9.11 mmol, 2.89 equiv.), [1,1'-Bis- (diphenylphosphino)-ferrocen]-dichloropalladium(II) (165.0 mg, 226 µmol, 7.00 mol%),4-Bromquinolin-2(1H)-on **S16** (707 mg, 3.15 mmol, 1.00 equiv.) and Boronic ester **S17** (1.32 mL, 6.73 mmol, 2.13 equiv.) were dissolved in dioxane (23 mL). The solution was degassed by two freeze-thaw cycles. The reaction mixture was stirred for 18 h at 90 °C. The reaction mixture was cooled to room temperature- Subsequently ethyl acetate (70 mL) and water (50mL) were added to the reaction mixture. The organic layer was separated and the aqueous layers was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over sodium sulfate. After removal of all volatiles under reduced pressure the crude material was purified three times by automated column chromatography [Silica, EtOAc/Hexanes 5/95 → 75/25 (1st column); EtOAc/Hexanes 5/95 → 50/50 (2nd column); EtOAc/CH_2Cl_2 0/100 → 25/75 (3rd column)]. Subsequently the material was recrystallized from EtOAc/Hexanes to obtain the title quinolone **12a** as an off-white solid (68.0 mg, 319 µmol, 10%).

M.p. = 174 °C

TLC: R_f **=** 0.35 (EtOAc/Hexanes = 4/6), [UV].

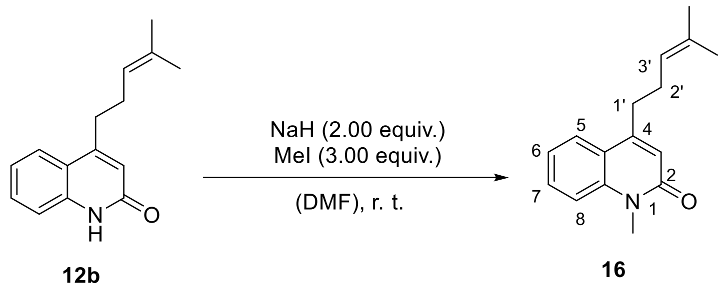
IR (film) $\tilde{\nu}_{max}$/cm^{-1} = 2968 (m), 2845 (m), 1646 (s, C=O), 1510 (m), 1423 (m), 867 (m), 769 (w), 749 (m).

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm] = 12.02 (s, 1H, NH), 7.73 (dd, ^3J = 8.3 Hz, ^3J = 1.3 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H, H-7), 7.42 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 1H, H-8), 7.25 – 7.20 (m, 1H, H-6), 6.62 (s, 1H, H-3), 5.41 – 5.27 (m, 1H, H2'), 3.56 (d, ^3J = 7.1 Hz, 2H), 1.80 (d, 3H, CH_3), 1.73 (s, 3H, CH_3).

^{13}C-NMR (126 MHz, $CDCl_3$, 298 K) δ [ppm] = 164.5 (s, C=O), 152.3 (s, C-4), 138.5 (s, C8a), 135.8 (s, C-3'), 130.5 (d, C-7), 124.3 (d, C-5), 122.6 (d, C-6), 120.2 (s, C-4a), 119.5 (d, C-3), 119.4 (d, C-2'), 116.7 (d, C-8), 31.0 (t, C-1'), 26.0 (q, CH_3), 18.1 (q, CH_3).

HRMS (ESI): calc. for $C_{12}H_{11}NO$ $[M+H]^+$: 214.1226; found: 214.1225.

1-Methyl-4-(4-methylpent-3-en-1-yl)quinolin-2(1*H*)-one (16)



Quinolone **12b** (300 mg, 1.32 mmol, 1.00 equiv.) was dissolved in DMF (20 mL) and sodium hydride (60 weight%, 106 mg, 2.64 mmol, 2.00 equiv.) was added to the solution at 0 °C. The resulting mixture was stirred for 30 minutes at 0 °C. Then MeI (246 µL, 562 mg, 3.96 mmol, 3.00 equiv.) was added dropwise to the reaction mixture The cooling bath was removed and the reaction mixture was stirred for further 4 h at room temperature under argon atmosphere. The reaction was quenched by addition of H_2O (10 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with sat. aq. NaCl (60 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the crude product was purified by automated column chromatography (Silica, EtOAc/Hexanes 0/100 → 3/7) to obtain the title quinolone **16** as an off-white solid (271 mg, 1.19 mmol, 85%).

M.p. = 53 °C

TLC: R_f = 0.45 (EtOAc/Hexanes = 2/8), [UV].

IR (film) $\tilde{\nu}_{max}/cm^{-1}$ = 3085 (w), 2888 (bm), 1644 (s, C=O), 1588 (s), 1453 (s), 1323 (w), 752 (s), 742 (s).

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm] = 7.76 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-5), 7.56 (ddd, ^3J = 8.5 Hz, ^3J = 7.1 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.38 (dd, ^3J = 8.5 Hz, ^4J = 1.1 Hz, 1H, H-8), 7.28 – 7.22 (m, 1H, H-6), 6.61 (s, 1H, H-3), 5.25– 5.16 (m, 1H, H-3'), 3.71 (s, 3H, NCH_3), 2.88 – 2.79 (m, 2H, H-1'), 2.44 – 2.34 (m, 2H, H-2'), 1.70 (s, 3H, CH_3), 1.59 (s, 3H, CH_3).

^{13}C-NMR (126 MHz, $CDCl_3$, 298 K) δ [ppm] = 162.4 (s, C=O), 150.0 (s, C-4), 140.1 (s, C-8a), 133.3 (s, C-4'), 130.4 (d, C-7), 125.0 (d, C-5), 122.9 (d, C-3'), 122.0 (d, C-6), 120.8 (s, C-4a), 120.2 (d, C-3), 114.7 (d, C-8), 32.3 (t, C-1'), 29.4 (q, NCH_3), 27.4 (t, C-2'), 25.8 (q, CH_3), 17.9 (q, CH_3).

HRMS (ESI): calc. for $C_{16}H_{19}NO$ $[M+H]^+$: 242.1539; found: 242.1539.

4. Reaction condition screening

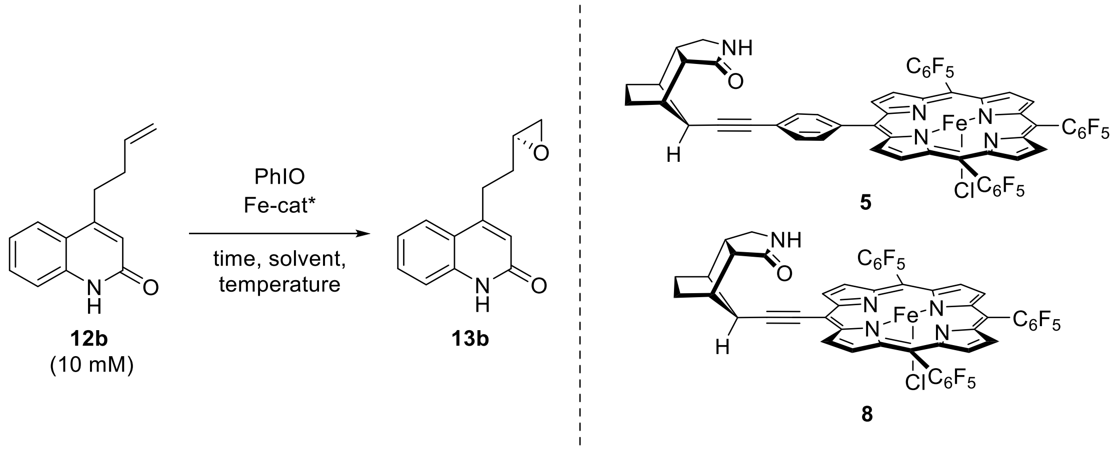


Table 1: Screening of the reaction conditions for the selective oxidation with iron porphyrin catalysts.

entry	PhIO [equiv.]	cat.	cat. loading [mol%]	solvent	temp [°C]	time [h]	isolated yield	*ee*	conv.[a]
1	1.5	**5**	0.2	CH_2Cl_2	r.t.	24	37%	37%	57%
2	1.5	**5**	0.2	CH_2Cl_2	0	24	42%	38%	50%
3	1.5	**5**	0.2	CH_2Cl_2	0	4	42%	39%	44%
4	1	**5**	0.2	CH_2Cl_2	0	4	31%	44%	39%
5[b]	2 x 0.75	**5**	0.2	CH_2Cl_2	0	4	21%	41%	31%
6	1	**8**	0.2	CH_2Cl_2	0	4	22%	18%	27%
7	1	**5**	0.1	CH_2Cl_2	0	4	7%	35%	31%
8	1	**5**	0.5	CH_2Cl_2	0	4	46%	47%	54%
9	1	**5**	1	CH_2Cl_2	0	4	66%	49%	34%
10	1	**5**	3	CH_2Cl_2	0	4	95%	49%	95%
11	1	**5**	0.2	PhH	0	4	29%	29%	31%
12	1	**5**	0.2	$PhCF_3$	0	4	25%	33%	30%
13	1	**5**	0.2	DCE	0	4	25%	33%	30%
14	1	**5**	0.2	CH_2Cl_2	-20	4	25%	46%	32%

[a] Conversion was calculated based on recovered starting material. [b] Iodosobenzene was added in two portions at the start and after two hours.

5. Catalytic epoxidation experiments

General Procedure 1 (GP1, Epoxidation of substrates with iron porphyrin catalysts)

The iron porphyrin catalyst (0.20 mol%) was dissolved in anhydrous CH_2Cl_2 (5 mL per 50.0 µmol substrate) and added to the substrate (1.00 equiv.) in a flame-dried *Schlenk* tube. The solution was stirred for 10 min at 0 °C. PhIO (1.00 equiv.) was added to the reaction solution in one portion and the resulting reaction suspension was stirred for 4 h at 0 °C. The reaction was quenched by removing all volatiles under high vacuum and the crude material was purified by automated column chromatography (silica, MeOH/CH_2Cl_2 0/100 → 3/97 or EtOAc/Hexanes 5/95 → 75/25).

General procedure 2 (GP3, Epoxidation of substrate 12c with iron porphyrin catalysts and opening of the epoxide with $NaBH_3CN$)

The iron porphyrin catalyst was dissolved in anhydrous CH_2Cl_2 (10 mL) and added to alkene **12c** (24.1 mg, 100 µmol, 1.00 equiv.) in a flame-dried *Schlenk* tube. The solution was stirred for 10 min at 0 °C. PhIO (22.0 mg, 100 µmol, 1.00 equiv.) was added to the reaction solution in one portion and the resulting reaction suspension was stirred for 4 h at 0 °C. The reaction was quenched by removing all volatiles under high vacuum and the crude material was purified by automated column chromatography (EtOAc/Hexanes 5/95 → 75/25) to yield epoxide **13c**.

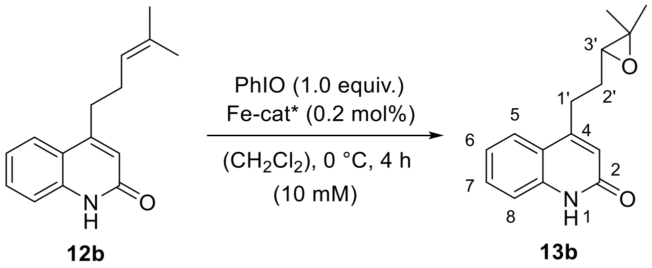
In a flame-dried *Schlenk* tube bromocresol green (5.00 mol%) and epoxide **13c** (1.00 equiv.) were dissolved in anhydrous THF (2.5 mL per 40.0 µmol substrate). $NaBH_3CN$ (4.00 equiv.) and $BF_3 \cdot OEt_2$ (3.00 equiv.) were added to the reaction solution in succession ultimately resulting in a yellow solution. The reaction mixture was stirred at room temperature until reaction control by TLC indicated full conversion (usually 16 h). The reaction was quenched by addition of HCl (1 M, 0.5 mL per 40 µmol substrate) and the reaction mixture was stirred for additional 20 minutes at room temperature. Subsequently aq. NaOH (10%) was added until the reaction solution turned blue. The phases were separated and the aqueous phase was extracted with ethyl acetate (3×). The combined organic phases were dried over Na_2SO_4 and after removal of all volatiles under reduced pressure the crude material was purified by automated column chromatography (silica, EtOAc/Hexanes/Et_3N 80/20/1 → 100/0/1) to obtain alcohol **14**.

General procedure 3 [GP2, Epoxidation of substrate 2c with iron porphyrin catalysts and opening of the epoxide with lithium aluminum hydride (LAH)]

The iron porphyrin catalyst was dissolved in anhydrous CH_2Cl_2 (10 mL) and added to alkene **2c** (21.3 mg, 100 µmol, 1.00 equiv.) in a flame-dried *Schlenk* tube. The solution was stirred for 10 min at 0 °C. PhIO (22.0 mg, 100 µmol, 1.00 equiv.) was added to the reaction solution in one portion and the resulting reaction suspension was stirred for 4 h at 0 °C. The reaction was quenched by removing all volatiles under high vacuum and the crude material was purified by automated column chromatography (silica, MeOH/CH_2Cl_2 0/100 → 3/97) to obtain epoxide **10c**.

LAH (2.50 equiv.) was added to a flame-dried *Schlenk* tube, suspended in anhydrous THF (1 mL per 20.0 µmol substrate) and the suspension was cooled to 0 °C. Epoxide **10c** (1.00 equiv.) was dissolved in anhydrous THF (2 mL per 20.0 µmol substrate) and added to the flame-dried *Schlenk* tube at 0 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature until reaction control by TLC indicated full conversion (usually 1.5 h). The reaction was quenched by addition of sat. aq. Na_2SO_4, the mixture was filtered over ®Celite and the filter cake was washed with EtOAc. All volatiles of the obtained filtrate were removed under reduced pressure and the crude material was purified by automated column chromatography (silica, MeOH/CH_2Cl_2 0/100 → 5/95) to obtain alcohol **11**.

4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]quinolin-2(1*H*)-one (13b)



<u>A) Racemic Reaction with Fe(TPFPP)Cl 9</u>: Following **GP1**, alkene **12b** (11.4 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **9** (106 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 1/3) the title epoxide **13b** was obtained as an off-white solid (9.00 mg, 37.0 µmol, 74%), [Recovered Alkene: (3.00 mg, 13.2 µmol, 26%)].

<u>B) Reaction with chiral iron porphyrin catalyst 5</u>: Following **GP1**, alkene **12b** (11.4 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **5** (114 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **13b** was obtained as an off-white solid (11.0 mg, 45.2 µmol, 90%, 27% *ee*), [Recovered Alkene: (1.00 mg, 4.40 µmol, 9%)].

<u>C) Reaction with chiral iron porphyrin catalyst 6</u>: Following **GP1**, alkene **12b** (11.4 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **6** (87.7 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **13b** was obtained as an off-white solid (4.90 mg, 20.1 µmol, 40%, 38% *ee*), [Recovered Alkene: (5.70 mg, 25.0 µmol, 50%)].

<u>D) Reaction with chiral iron porphyrin catalyst 7</u>: Following **GP1**, alkene **12b** (11.4 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **7** (100 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **13b** was obtained as an off-white solid (6.40 mg, 26.3 µmol, 53%, 35% *ee*), [Recovered Alkene: (3.80 mg, 16.7 µmol, 33%)].

<u>E) Reaction with chiral iron porphyrin catalyst 8</u>: Following **GP1**, alkene **12b** (11.4 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **8** (107 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **13b** was obtained as an off-white solid (5.50 mg, 22.6 µmol, 45%, 3% *ee*), [Recovered Alkene: (4.30 mg, 18.6 µmol, 38%)].

F) Reaction with chiral iron porphyrin catalyst 7 and additional lactam binder -4-pentyl quinolin-2(1H)-one: : Modifying **GP1**, alkene **12b** (22.8 mg, 100 µmol, 1.00 equiv.) and 4-pentyl quinolin-2(1H)-one[17] was reacted with catalyst **8** (214 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **13b** was obtained as an off-white solid (15.3 mg, 62.9 µmol, 63%, 29% *ee*), [Recovered Alkene: (7.50 mg, 33.1 µmol, 33%)].

M$_p$: 151 °C.

TLC: R_f **=** 0.24 (MeOH/CH_2Cl_2 = 4/96), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2969 (m), 2820 (bm), 1652 (s, C=O), 1614 (m), 1557 (m), 1438 (m), 1123 (m), 931 (m), 879 (s), 855 (m), 769 (m), 747 (s).

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 11.62 (s, 1H, NH), 7.77 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.49 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.3 Hz, 1H, H-7), 7.32 (dd, ^3J = 8.3 Hz, ^4J =1.2 Hz, 1H, H-8), 7.19 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, H-6), 6.41 (s, 1H, H-3), 3.04 – 2.85 (m, 2H, H-1'), 2.81 (t, ^3J = 6.3 Hz, 1H, H-3'), 1.93 – 1.73 (m, 2H, H-2'), 1.18 (s, 3H, CH_3), 1.06 (s, 3H, CH_3).

^{13}C-NMR (101 MHz, DMSO-d_6, 298 K) δ [ppm] = 161.6 (s, C=O), 150.8 (s, C-4), 138.9 (s, C-8a), 130.2 (d, C-7), 124.3 (d, C-5), 121.7 (d, C-6), 120.3 (d, C-3), 118.6 (d, C-7a), 115.7 (d, C-8), 62.5 (d, C-3'), 57.8 (s, C-4'), 28.2 (d, C-3'), 28.0 (d, C-2'), 24.5 (q, CH_3), 18.5 (q, CH_3).

HRMS (ESI): calc. for $C_{15}H_{17}NO_2$ [M+H]$^+$ 244.1332; found: 244.1330.

B) Chiral HPLC: 27% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.8 min (major), t_R = 12.5min (minor)].

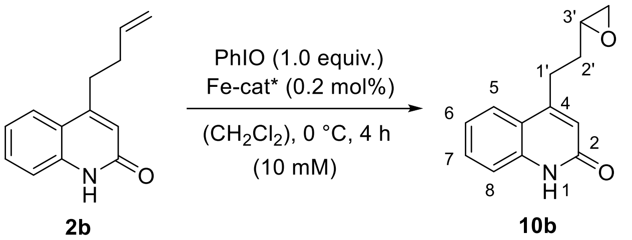
C) Chiral HPLC: 38% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.8 min (major), t_R = 12.5 min (minor)].

D) Chiral HPLC: 35% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.8 min (major), t_R = 12.5 min (minor)].

E) Chiral HPLC: 3% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 8.7 min (major), t_R = 12.4 min (minor)].

F) Chiral HPLC: 29% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 9.0 min (major), t_R = 12.7 min (minor)].

4-[2-(Oxiran-2-yl)ethyl]quinolin-2(1*H*)-one (10b)



A) Racemic Reaction with Fe(TPFPP)Cl 9: Following **GP1**, alkene **2b** (9.96 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **9** (106 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10b** was obtained as an off-white solid (2.90 mg, 13.5 µmol, 27%), [Recovered Alkene: (6.30 mg, 31.6 µmol, 63%)].

B) Reaction with chiral iron porphyrin catalyst 5: Following **GP1**, alkene **2b** (9.96 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **5** (114 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10b** was obtained as an off-white solid (3.30 mg, 15.3 µmol, 31%, 44% *ee*), [Recovered Alkene: (6.00 mg, 30.1 µmol, 60%)].

C) Reaction with chiral iron porphyrin catalyst 6: Following **GP1**, alkene **2b** (9.96 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **6** (87.7 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10b** could not be obtained (no conversion), [Recovered Alkene: (9.00 mg, 45.2 µmol, 90%)].

D) Reaction with chiral iron porphyrin catalyst 7: Following **GP1**, alkene **2b** (9.96 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **7** (100 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10b** was obtained as an off-white solid (1.30 mg, 6.04 µmol, 12%, 22% *ee*), [Recovered Alkene: (8.20 mg, 41.2 µmol, 82%)].

E) Reaction with chiral iron porphyrin catalyst 8: Following **GP1**, alkene **2b** (9.96 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **8** (107 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10b** was obtained as an off-white solid (2.40 mg, 11.2 µmol, 22%, 18% *ee*), [Recovered Alkene: (7.00 mg, 35.1 µmol, 70%)].

M.p. = 157 °C

TLC: R_f **=** 0.30 (MeOH/CH_2Cl_2 = 4/96), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2853 (bm), 1646 (s, C=O), 1612 (s), 1556 (s), 1519 (s), 1437 (s), 1405 (m), 1263 (w), 858 (s), 772 (s), 750 (s).

^{1}H-NMR (500 MHz, DMSO-*d*$_6$, 298 K) δ [ppm] = 11.65 (s, 1H, NH), 7.77 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, H-5), 7.49 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, H-7), 7.31 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, H-8), 7.20 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, H-6), 6.39 (s, 1H, H-3), 3.07 – 3.00 (m, 1H, H-3'), 2.99 – 2.86 (m, 2H, H-1'), 2.71 (dd, ^3J = 5.1 Hz, ^3J = 4.0 Hz, 1H, H-4'), 2.53 – 2.51 (m, 1H, H-4'), 1.94 – 1.83 (m, 1H, H-2'), 1.82 – 1.71 (m, 1H, H-2').

^{13}C-NMR (126 MHz, DMSO-*d*$_6$, 298 K) δ [ppm] = 161.6 (s, C=O), 150.8 (s, C-4), 139.0 (s, C-8a), 130.3 (d, C-7), 124.4 (d, C-5), 121.8 (d, C-6), 120.1 (d, C-3), 118.6 (s, C-7a), 115.7 (d, C-8), 51.2 (d, C-3'), 46.2 (t, C-4'), 31.4 (t. C-2'), 27.8 (t, C-1').

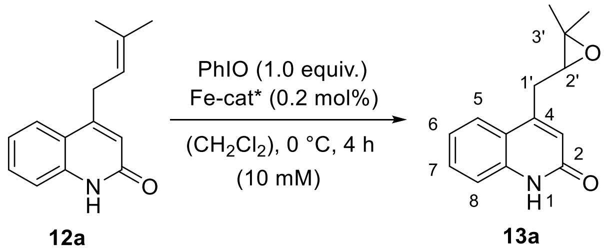
HRMS (ESI): calc. for $C_{14}H_{13}NO_2$ $[M+H]^+$ 216.1019; found: 216.1018.

B) Chiral HPLC: 44% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 90% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 26.1 min (major), t_R = 27.7 min (minor)].

D) Chiral HPLC: 22% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 90% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 25.6 min (major), t_R = 27.1 min (minor)].

E) Chiral HPLC: −18% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 90% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 25.5 min (minor), t_R = 27.0 min (major)].

4-[(3,3-Dimethyloxiran-2-yl)methyl]quinolin-2(1H)-one (13a)



Racemic Reaction with Fe(TPFPP)Cl 9: Following **GP1**, alkene **12a** (10.7 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **9** (106 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 72/25) the title epoxide **13a** was obtained as an off-white solid (4.00 mg, 17.5 µmol, 35%), [Recovered Alkene: (6.60 mg, 31.0 µmol, 62%)].

B) Reaction with chiral iron porphyrin catalyst 5: Following **GP1**, alkene **12a** (10.7 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **5** (228 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 72/25) the title epoxide **13a** was obtained as an off-white solid (7.20 mg, 31.4 µmol, 63%, 15% *ee*), [Recovered Alkene: (3.40 mg, 15.9 µmol, 32%)].

C) Reaction with chiral iron porphyrin catalyst 6: Following **GP1**, alkene **12a** (10.7 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **6** (87.7 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 72/25) the title epoxide **13a** was obtained as an off-white solid (1.30 mg, 5.67 µmol, 11%, 19% *ee*), [Recovered Alkene: (7.00 mg, 32.9 µmol, 66%)].

B) Reaction with chiral iron porphyrin catalyst 7: Following **GP1**, alkene **12a** (10.7 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **7** (100 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 72/25) the title epoxide **13a** was obtained as an off-white solid (1.60 mg, 6.98 µmol, 14%, 43% *ee*), [Recovered Alkene: (9.20 mg, 43.1 µmol, 84%)].

B) Reaction with chiral iron porphyrin catalyst 8: Following **GP1**, alkene **12a** (10.7 mg, 50.0 µmol, 1.00 equiv.) was reacted with catalyst **8** (107 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 72/25) the title epoxide **13a** was obtained as an off-white solid (5.70 mg, 24.9 µmol, 50%, 3% *ee*), [Recovered Alkene: (3.80 mg, 17.8 µmol, 36%)].

M.p. = 176 °C

TLC: R_f **=** 0.20 ($MeOH/CH_2Cl_2$ = 4/96), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2953 (bw), 2925 (w), 1655 (s, C=O), 1557 (w), 1431 (m), 1398 (w), 853 (w), 760 (m).

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 11.67 (s, 1H, NH), 7.81 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.51 (ddd, ^3J = 8.4 Hz, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.32 (dd, ^3J = 8.4 Hz, ^4J =1.2 Hz, 1H, H-8), 7.20 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, H-6), 6.42 (s, 1H, H-3), 3.17 – 3.05 (m, 1H, H-2'), 3.05 – 2.96 (m, 2H, H-1'), 1.35 (s, 3H, CH_3), 1.29 (s, 3H, CH_3).

^{13}C-NMR (126 MHz, DMSO-d_6, 298 K) δ [ppm] = 162.0 (s, C=O), 149.1 (s, C-4), 139.3 (s, C-8a), 130.9 (d, C-7), 125.4 (d, C-5), 122.2 (d, C-6), 121.0 (d, C-3), 119.4 (d, C-7a), 116.0 (d, C-8), 62.0 (s, C-2'), 58.7 (s, C-3'), 31.5 (t, C-1'), 24.9 (q, CH_3), 19.2 (q, CH_3).

HRMS (ESI): calc. for $C_{14}H_{15}NO_2$ $[M+H]^+$ 230.1176; found: 230.1174.

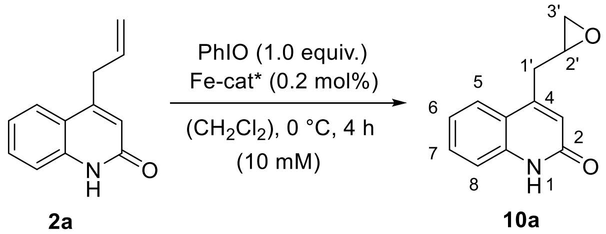
B) Chiral HPLC: 15% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.5 min (major), t_R = 9.7 min (minor)].

C) Chiral HPLC: 19% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.5 min (major), t_R = 9.7 min (minor)].

D) Chiral HPLC: 43% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.4 min (major), t_R = 9.6 min (minor)].

E) Chiral HPLC: 3% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.5 min (major), t_R = 9.7 min (minor)].

4-(Oxiran-2-ylmethyl)quinolin-2(1H)-one (10a)



A) Racemic Reaction with Fe(TPFPP)Cl 9: Following **GP1**, alkene **2a** (18.5 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **9** (213 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10a** was obtained as an off-white solid (2.80 mg, 13.9 µmol, 14%), [Recovered Alkene: (15.0 mg, 81.0 µmol, 81%)].

B) Reaction with chiral iron porphyrin catalyst 5: Following **GP1**, alkene **2a** (18.5 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **5** (228 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10a** was obtained as an off-white solid (7.00 µg, 34.8 µmol, 35%, 12% ee), [Recovered Alkene: (11.1 mg, 59.9 µmol, 60%)].

C) Reaction with chiral iron porphyrin catalyst 6: Following **GP1**, alkene **2a** (18.5 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **6** (175 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide could not be obtained (no conversion), [Recovered Alkene: (15.6 mg, 84.0 µmol, 84%)].

D) Reaction with chiral iron porphyrin catalyst 7: Following **GP1**, alkene **2a** (18.5 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **7** (200 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10a** was obtained as an off-white solid (900 µg, 13.9 µmol, 14%, 4% ee), [Recovered Alkene: (15.0 mg, 81.0 µmol, 81%)].

E) Reaction with chiral iron porphyrin catalyst 8: Following **GP1**, alkene **2a** (18.5 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **8** (214 µg, 0.10 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) the title epoxide **10a** was obtained as an off-white solid (4.30 mg, 21.4 µmol, 21%, 22% ee), [Recovered Alkene: (12.5 mg, 67.5 µmol, 67%)].

M.p. = 179 °C

TLC: R_f **=** 0.23 (MeOH/CH_2Cl_2 = 4/96), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2923 (w), 2851 (s), 1650 (s, C=O), 1610 (s), 1552 (s), 1509 (m), 1436 (s), 1266 (w), 968 (m), 912 (m), 884 (s), 834 (s), 772 (s), 753 (s), 679 (w).

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 11.67 (s, 1H, NH), 7.79 (dd, ^3J = 8.2 Hz, ^3J = 1.4 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^3J = 1.3 Hz, 1H, H-7), 7.32 (dd, ^3J = 8.3 Hz, ^3J =1.2 Hz, 1H, H-8), 7.19 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^3J = 1.2 Hz, 1H, H-6), 6.48 (s, 1H, H-3), 3.29 – 3.22 (m, 1H, H-2’), 3.10 (ddd, ^3J = 15.3 Hz, ^3J = 4.6 Hz, ^4J = 1.0 Hz, 1H, H-23’), 3.04 – 2.96 (dd, ^3J = 15.3 Hz, ^3J = 4.6 Hz, 1H, H-23’), 2.79 (dd, ^3J = 5.2 Hz, ^3J = 3.9 Hz, 1H, H-1’), 2.62 (dd, ^3J = 5.2 Hz, ^3J = 2.6 Hz, 1H, H-1’).

^{13}C-NMR (126 MHz, DMSO-d_6, 298 K) δ [ppm] = 161.5 (s, C=O), 148.0 (s, C-4), 138.9 (s, C-8a), 130.4 (d, C-7), 124.9 (d, C-5), 121.8 (d, C-6), 121.1 (d, C-3), 119.0 (d, C-7a), 115.6 (d, C-8), 50.4 (d, C-2’), 46.3 (t, C-1’), 34.1 (t, C-3’).

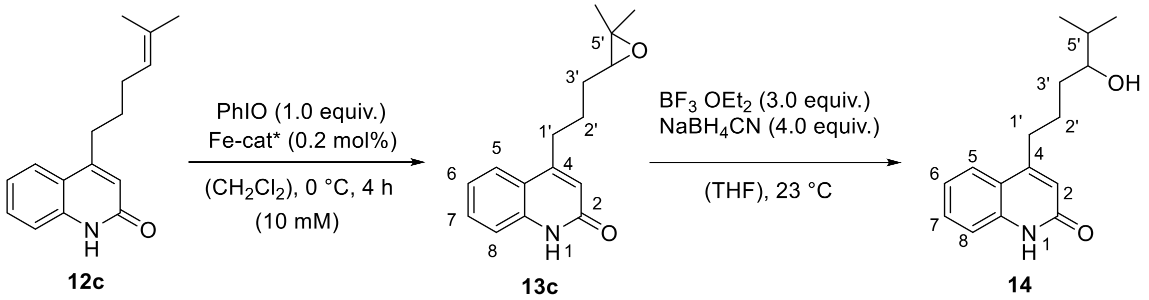
HRMS (ESI): calc. for $C_{12}H_{11}NO_2$ $[M+H]^+$ 202.0863; found: 202.0861.

B) Chiral HPLC: 12% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 20 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 6.9 min (major), t_R = 9.2 min (minor)].

D) Chiral HPLC: −4% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 20 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 7.1 min (minor), t_R = 9.3 min (major)].

E) Chiral HPLC: 22% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 20 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 7.1 min (major), t_R = 9.3 min (minor)].

4-(4-Hydroxy-5-methylhexyl)-2-oxo-1,2-dihydroquinolin-1-ium (14)



Racemic Reaction with Fe(TPFPP)Cl 9: Following **GP1**, alkene **12c** (24.1 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **9** (213 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 75/25) epoxide **13c** was obtained as an off-white solid (18.4 mg, 71.5 µmol, 72%), [Recovered Alkene: (6.1 mg, 25.3 µmol, 25%)].

B) Reaction with chiral iron porphyrin catalyst 5: Following **GP2**, alkene **12c** (24.1 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **5** (228 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 75/25) epoxide **13c** was obtained as an off-white solid (20.1 mg, 78.1 µmol, 78%), [Recovered Alkene: (5.80 mg, 15.7 µmol, 16%)]. Epoxide **13c** (20.1 mg, 78.1 µmol, 1.00 equiv.) was further reacted with $NaBH_3CN$ (19.5 mg, 311 µmol, 4.0 equiv.), $BF_3·OEt_2$ (33.1 mg, 28.8 µL 233 µmol, 3.0 equiv.) and bromocresol green (2.71 mg, 3.89 µmol, 5.00 mol%). After purification by automated column chromatography (silica, EtOAc/Hexanes/Et_3N 80/20/1 → 100/0/1) title alcohol **14** was obtained as an off-white solid (9.50 mg, 36.6 µmol, 47%, 7% *ee*).

C) Reaction with chiral iron porphyrin catalyst 6: Following **GP2**, alkene **12c** (24.1 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **6** (175 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 75/25) epoxide **13c** was obtained as an off-white solid (9.10 mg, 35.4 µmol, 35%), [Recovered Alkene: (13.4 mg, 55.5 µmol, 56%)]. The epoxide (9.10 mg, 35.4 µmol, 1.00 equiv.) was further reacted with $NaBH_3CN$ (9.28 mg, 148 µmol, 4.0 equiv.), $BF_3·OEt_2$ (15.7 mg, 13.7 µL 111 µmol, 3.0 equiv.) and bromocresol green (1.29 mg, 1.85 µmol, 5.00 mol%). After purification by automated column chromatography (silica, EtOAc/Hexanes/Et_3N 80/20/1 → 100/0/1) title alcohol **14** was obtained as an off-white solid (8.60 mg, 33.1 µmol, 90%, 16% *ee*).

D) Reaction with chiral iron porphyrin catalyst 7: Following **GP2**, alkene **12c** (24.1 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **7** (200 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 75/25) epoxide **13c** was obtained as an off-white solid (12.1 mg, 47.0 µmol, 47%), [Recovered Alkene: (8.10 mg, 33.5 µmol, 33%)]. The epoxide (12.1 mg, 47.0 µmol, 1.00 equiv.) was further reacted with $NaBH_3CN$ (11.8 mg, 188 µmol, 4.0 equiv.), $BF_3{\cdot}OEt_2$ (20.0 mg, 17.4 µL 141 µmol, 3.0 equiv.) and bromocresol green (1.64 mg, 2.35 µmol, 5.00 mol%). After purification by automated column chromatography (silica, EtOAc/Hexanes/Et_3N 80/20/1 → 100/0/1) title alcohol **14** was obtained as an off-white solid (10.5 mg, 40.5 µmol, 86%, 22% *ee*).

<u>E) Reaction with chiral iron porphyrin catalyst 8</u>: Following **GP2**, alkene **12c** (24.1 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **8** (214 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 75/25) epoxide **13c** was obtained as an off-white solid (15.9 mg, 61.8 µmol, 62%), [Recovered Alkene: (6.00 mg, 24.9 µmol, 25%)]. The epoxide (15.9 mg, 61.8 µmol, 1.00 equiv.) was further reacted with $NaBH_3CN$ (15.5 mg, 247 µmol, 4.0 equiv.), $BF_3{\cdot}OEt_2$ (26.3 mg, 22.9 µL 185 µmol, 3.0 equiv.) and bromocresol green (2.16 mg, 3.09 µmol, 5.00 mol%). After purification by automated column chromatography (silica, EtOAc/Hexanes/Et_3N 80/20/1 → 100/0/1) title alcohol **14** was obtained as an off-white solid (7.40 mg, 28.5 µmol, 46%, 18% *ee*).

<u>Epoxide 13c</u>:

M.p. = 110 °C

TLC: R_f **=** 0.17 (MeOH/CH_2Cl_2 = 4/96), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2929 (w), 2861 (s), 1659 (s, C=O), 1611 (m), 1557 (m), 1509 (m), 1440 (s), 1265 (w), 1122 (m), 982 (m), 928 (m), 881 (s), 838 (m), 751 (s), 675 (m).

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 11.60 (s, 1H, NH), 7.76 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.49 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.31 (dd, ^3J = 8.3 Hz, ^4J =1.2 Hz, 1H, H-8), 7.19 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, H-6), 6.38 (s, 1H, H-3), 2.93 – 2.79 (m, 2H, H-1’), 2.75 (dd, ^3J = 6.7 Hz, ^3J = 5.6 Hz, 1H, H-4’), 1.83 – 1.65 (m, 2H, H-3’), 1.65 – 1.49 (m, 2H, H-2’), 1.23 (s, 3H, CH_3), 1.19 (s, 3H, CH_3).

^{13}C-NMR (126 MHz, DMSO-d_6, 298 K) δ [ppm] = 161.7 (s, C=O), 151.4 (s, C-4), 139.0 (s, C-8a), 130.2 (d, C-7), 124.4 (d, C-5), 121.7 (d, C-6), 120.1 (d, C-3), 118.7 (s, C-7a), 115.7 (d, C-8), 62.8 (d, C-4’), 57.6 (s, C-5’), 31.0 (t, C-3’), 28.1 (t, C-1’), 25.7 (t, C-2’), 24.7 (q, CH_3), 18.6 (q, CH_3).

HRMS (ESI): calc. for $C_{16}H_{19}NO_2$ $[M+H]^+$ 258.1489; found: 258.1487.

<u>Alcohol 14</u>:

M.p. = 127 °C

TLC: R_f **=** 0.09 (MeOH/CH_2Cl_2 = 4/96), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3303 (bm, O-H), 2958 (m), 2967 (m), 1645 (s, C=O), 1615 (s), 1551 (s), 1429 (s), 1405 (m), 978 (m), 910 (m), 888 (m), 872 (s), 770 (m), 757 (s), 701 (m), 679 (s).

^{1}H-NMR (400 MHz, MeOD, 298 K) δ [ppm] = 7.90 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.57 (ddd, ^3J = 8.4 Hz, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.43 – 7.37 (m, 1H, H-8), 7.32 (ddd, ^3J = 8.2 Hz, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H, H-6), 6.54 (s, 1H, H-3), 3.41 – 3.35 (m, 1H, H-4’), 2.96 (m, 2H, H-1’), 2.05 – 1.87 (m, 1H, H-5’), 1.87 – 1.59 (m, 3H, H-3’, H-2’), 1.53 (m, 1H, H-2’), 0.94 (*virt.* d, $^3J \approx$ 6.7 Hz, 6H).

^{13}C-NMR (126 MHz, MeOD, 298 K) δ [ppm] = 165.1 (s, C=O), 155.7 (s, C-4), 139.8 (s, C-8a), 131.8 (d, C-7), 125.8 (d, C-5), 124.0 (d, C-6), 121.0 (d, C-3), 119.9 (s, C-7a), 117.3 (d, C-8), 77.0 (d, C-4’), 35.1 (d, C-5’), 34.8 (t, C-3’), 33.2 (t, C-1’), 27.11 (t, C-2’), 19.3 (q, CH_3), 18.0 (q, CH_3).

HRMS (ESI): calc. for $C_{16}H_{21}NO_2$ $[M+H]^+$ 260.1645; found: 260.1646.

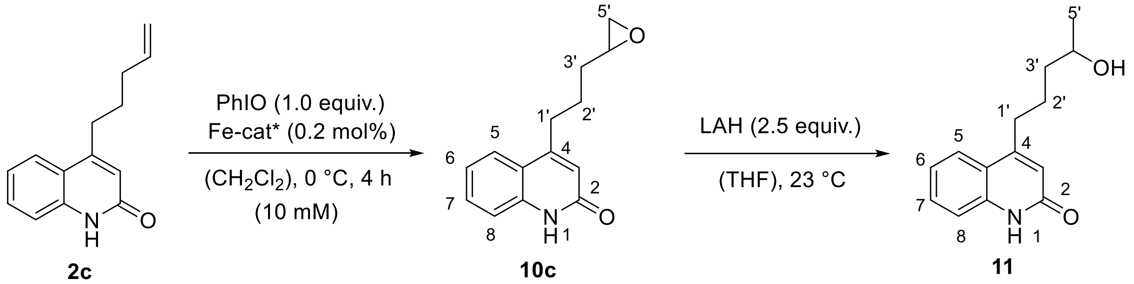
B) Chiral HPLC: 7% *ee* [©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.4 min (major), t_R = 12.4 min (minor)].

C) Chiral HPLC: 16% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.6 min (major), t_R = 12.5 min (minor)].

D) Chiral HPLC: 22% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.5 min (major), t_R = 12.5 min (minor)].

E) Chiral HPLC: 18% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 7.4 min (major), t_R = 12.4 min (minor)].

4-(4-Hydroxypentyl)quinolin-2(1H)-one (11)



Racemic Reaction with Fe(TPFPP)Cl 9: Following **GP1**, alkene **2c** (21.3 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **9** (213 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) epoxide **10c** was obtained as an off-white solid (5.80 mg, 25.3 µmol, 25%), [Recovered Alkene: (14.6 mg, 68.4 µmol, 68%)].

B) Reaction with chiral iron porphyrin catalyst 5: Following **GP3**, alkene **2c** (21.3 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **5** (228 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) epoxide **10c** was obtained as an off-white solid (5.10 mg, 22.2 µmol, 1.00 equiv.), [Recovered Alkene: (14.6 mg, 68.4 µmol, 68%)]. The epoxide (5.10 mg, 22.2 µmol, 22%) was further reacted with lithium aluminum hydride (2.11 mg, 55.6 µmol, 2.5 equiv.) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 5/95) title alcohol **11** was obtained as an off-white solid (5.10 mg, 22.0 µmol, 99%).

C) Reaction with chiral iron porphyrin catalyst 6: Following **GP3**, alkene **2c** (21.3 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **6** (175 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) and epoxide **10c** could not be obtained (no conversion), [Recovered Alkene: (21.1 mg, 98.9 µmol, 99%)].

D) Reaction with chiral iron porphyrin catalyst 7: Following **GP3**, alkene **2c** (21.3 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **7** (200 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) epoxide **10c** was obtained as an off-white solid (0.80 mg, 3.49 µmol, 3%), [Recovered Alkene: (17.1 mg, 80.0 µmol, 80%)]. The epoxide (0.80 mg, 3.49 µmol, 1.00 equiv.) was further reacted with lithium aluminum hydride (331 µg, 8.72 µmol, 2.5 equiv.) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 5/95) title alcohol **11** was obtained as an off-white solid (0.65 mg, 2.80 µmol, 80%, 7% *ee*).

E) Reaction with chiral iron porphyrin catalyst 8: Following **GP3**, alkene **2c** (21.3 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **8** (214 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 3/97) epoxide **10c** was obtained as an off-white solid (5.00 mg, 21.8 µmol, 22%), [Recovered Alkene: (14.6 mg, 68.4 µmol, 68%)]. The epoxide (5.00 mg, 21.8 µmol, 1.00 equiv.) was further reacted with lithium aluminum hydride (2.11 mg, 55.6 µmol, 2.5 equiv.) and after purification by automated column chromatography (silica, MeOH/CH_2Cl_2 0/1 → 5/95) title alcohol **11** was obtained as an off-white solid (5.80 mg, 25.3 µmol, 25%).

Epoxide 10c:

M.p. = 168 °C

TLC: R_f **=** 0.23 (MeOH/CH_2Cl_2 = 4/96), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3059 (w), 2963 (w), 2845 (bm), 1655 (s), 1612 (s), 1553 (s), 1509 (m), 1432 (s), 1364 (m), 1258 (m), 1139 (w), 980 (m), 921 (m), 874 (s), 830 (s), 769 (s), 756 (s).

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 11.61 (s, 1H), 7.76 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.48 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.31 (dd, ^3J = 8.3 Hz, ^4J =1.2 Hz, 1H, H-8), 7.19 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, H-6), 6.37 (s, 1H, H-3), 3.00 – 2.91 (m, 1H, H-4'), 2.84 (t, ^3J = 7.6 Hz, 2H, H-1'), 2.68 (dd, ^3J = 5.1 Hz, ^3J = 4.0 Hz, 1H, H-5'), 2.46 (dd, ^3J = 5.1 Hz, ^3J = 2.7 Hz, 1H, H-5'), 1.81 – 1.59 (m, 3H, H-3', H-4'), 1.58 – 1.45 (m, 1H, H-3').

^{13}C-NMR (126 MHz, DMSO-d_6, 298 K) δ [ppm] = 161.7 (s, C=O), 151.4 (s, C-4), 139.0 (s, C-8a), 130.2 (d, C-7), 124.5 (d, C-5), 121.7 (d, C-6), 120.1 (d, C-3), 118.7 (s, C-7a), 115.7 (d, C-8), 51.3 (s, C-4'), 46.1 (t, C-5'), 31.6 (t, C-3'), 31.0 (q, C-1'), 25.2 (q, C-2').

HRMS (ESI): calc. for $C_{15}H_{17}NO_2$ $[M+H]^+$ 230.1176; found: 230.1174.

Alcohol 11:

M.p. = 168 °C

TLC: R_f **=** 0.12 (MeOH/CH_2Cl_2 = 4/96), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3303 (bw, O-H), 2924 (m), 2854 (w), 1651 (s, C=O), 1508 (m), 1428 (s), 1399 (m), 1040 (m), 942 (s).

^{1}H NMR (400 MHz, MeOD, 298 K) δ [ppm] = 7.87 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.55 (ddd, ^3J = 8.4 Hz, ^3J = 7.2 Hz, ^4J = 1.3 Hz, 1H, H-7), 7.37 (dd, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 1H, H-6), 7.30 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, H-8), 6.52 (s, 1H, H-3), 3.79 (*virt.* h, $^3J \approx {}^3J \approx {}^3J \approx {}^3J \approx {}^3J$ = 6.2 Hz, 1H, H-4'), 3.02 – 2.84 (m, 2H, H-1'), 1.94 – 1.69 (m, 2H, H-3'), 1.64 – 1.51 (m, 2H, H-2'), 1.17 (d, ^3J = 6.2 Hz, 3H, CH_3).

^{1}H NMR (126 MHz, MeOD, 298 K) δ [ppm] = 165.1 (s, C=O), 155.6 (s, C-4), 139.8 (s, C-8a), 131.8 (d, C-7), 125.8 (d, C-5), 124.0 (d, C-6), 121.0 (d, C-3), 119.9 (s, C-7a), 117.3 (d, C-8), 68.2 (d, C-4'), 39.8 (t, C-2'), 33.2 (s, C-1'), 26.7 (s, C-3'), 23.6 (s, C-5').

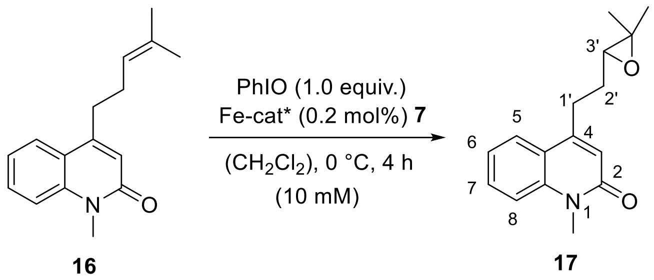
HRMS (ESI): calc. for $C_{14}H_{17}NO_2$ $[M+H]^+$ 232.1332; found: 232.1331.

B) Chiral HPLC: 3% *ee* [©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.9 min (major), t_R = 12.1 min (minor)].

D) Chiral HPLC: 7% *ee* ©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.1 min (major), t_R = 12.4 min (minor)].

E) Chiral HPLC: 13% *ee* [©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, 210 nm, t_R = 7.9 min (major), t_R = 12.2 min (minor)].

4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]-1-methylquinolin-2(1H)-one (17)



Reaction with chiral iron porphyrin catalyst 7: Following **GP1**, alkene **16** (22.7 mg, 100 µmol, 1.00 equiv.) was reacted with catalyst **7** (200 µg, 0.20 µmol, 0.20 mol%) and after purification by automated column chromatography (silica, EtOAc/Hexanes 5/95 → 3/7) epoxide **17** was obtained as an off-white solid (5.6 mg, 21.8 µmol, 22%, 5% *ee*), [Recovered Alkene: (2.9 mg, 12.1 µmol, 12%)].

M.p. = 67 °C

TLC: R_f **=** 0.32 (EtOAc/Hexanes = 2/8), [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3428 (bw), 2963 (w), 2927 (w), 1655 (s, C=O), 1644 (s), 1587 (s), 1455 (m), 1322 (w), 1081 (w), 753 (m).

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 7.87 (dd, ^3J = 8.1 Hz, ^4J =1.5 Hz, 1H, H-5), 7.66 – 7.61 (m, 1H, H-7), 7.55 (dd, ^3J =8.6 Hz, ^4J =1.2 Hz, 1H, H-6), 7.30 (ddd, ^3J = 8.1 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, H-8), 6.55 (s, 1H, H-3), 3.61 (s, 3H, NH_3), 3.05 – 2.88 (m, 2H, H-1'), 2.82 (t, ^3J = 6.3 Hz, 1H, H-3'), 1.93 – 1.76 (m, 2H, H-2'), 1.18 (s, 3H, CH_3), 1.07 (s, 3H, CH_3).

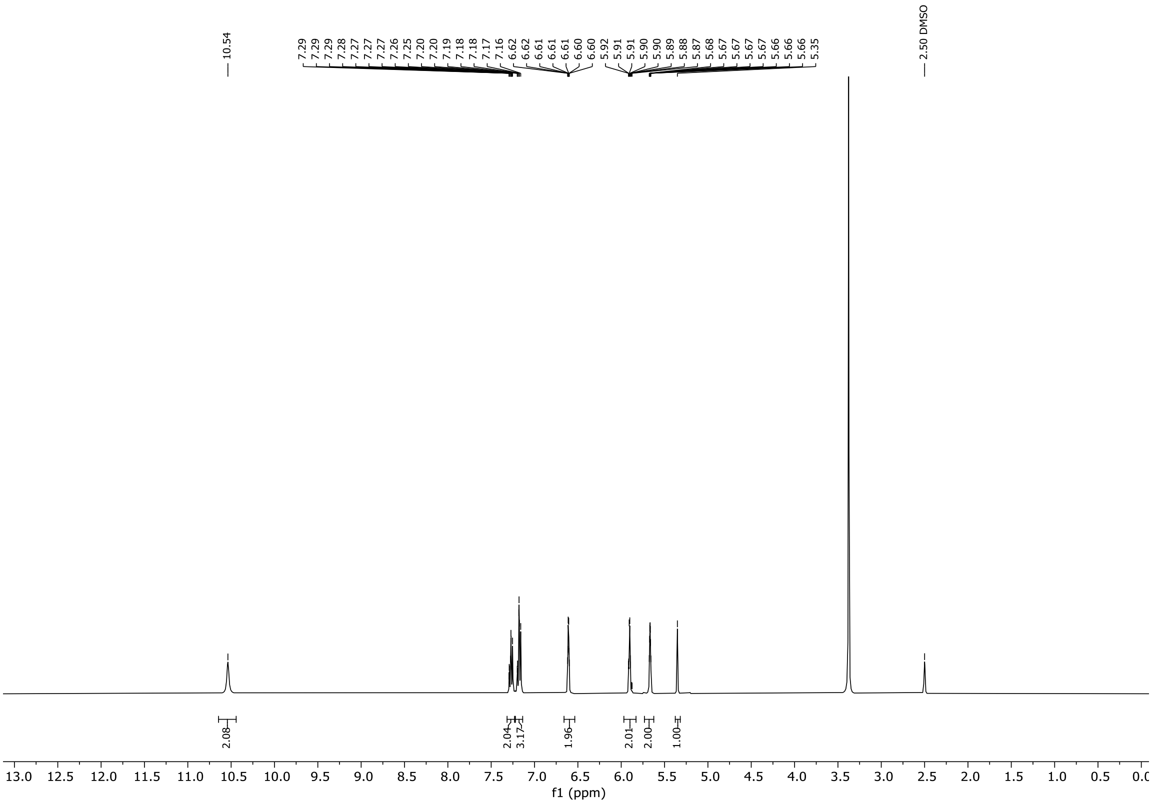
^{13}C-NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 160.8 (s, C=O), 149.4 (s, C-4), 139.8 (s, C-8a), 130.8 (d, C-7), 125.0 (d, C-5), 122.0 (d, C-6), 119.7 (s, C-4a), 119.7 (d, C-3), 115.2 (s, C-8), 62.5 (d, C-3'), 57.9 (s, C-4'), 28.9 (q, NCH_3), 28.1 (t, C-1'), 28.0 (t, C-2'), 24.61 (q, CH_3), 18.5 (q, CH_3) .

HRMS (ESI): calc. for $C_{16}H_{19}NO_2$ $[M+H]^+$ 258.1489; found: 258.1487.

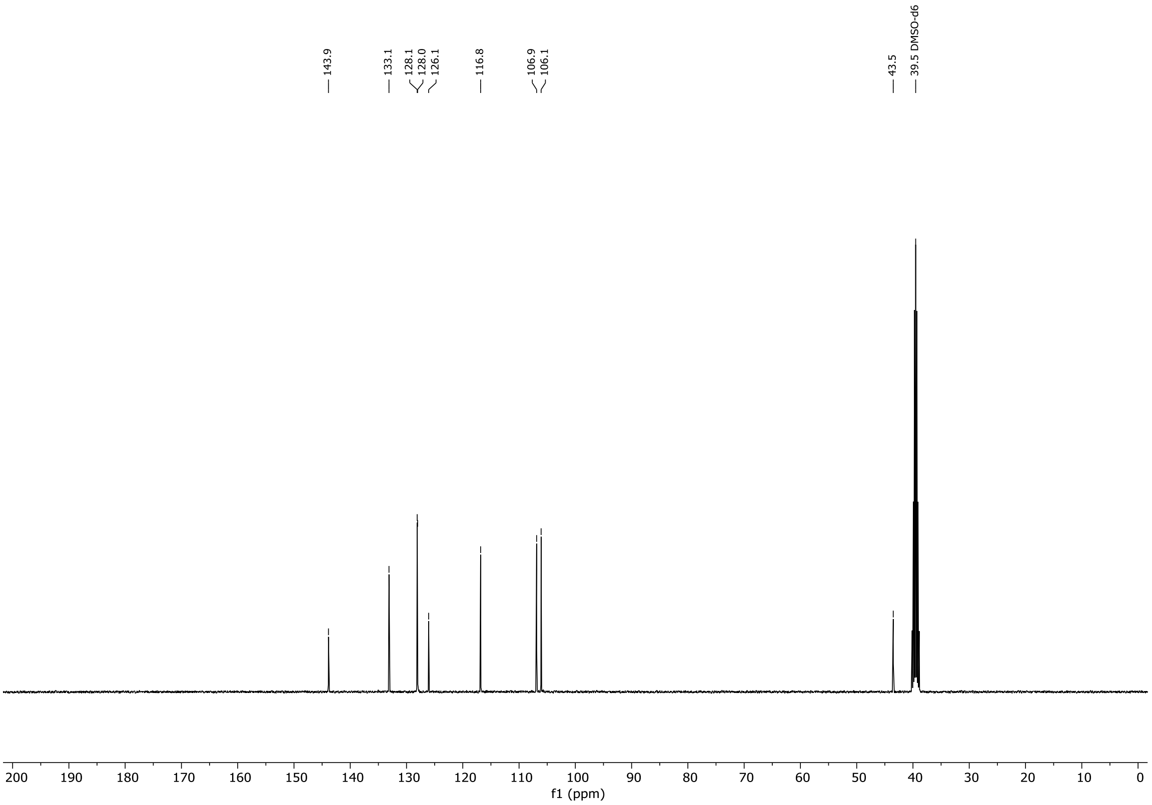
Chiral HPLC: 3% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 90% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 16.4 min (minor), t_R = 18.8 min (major)].

6. NMR spectra for prepared compounds

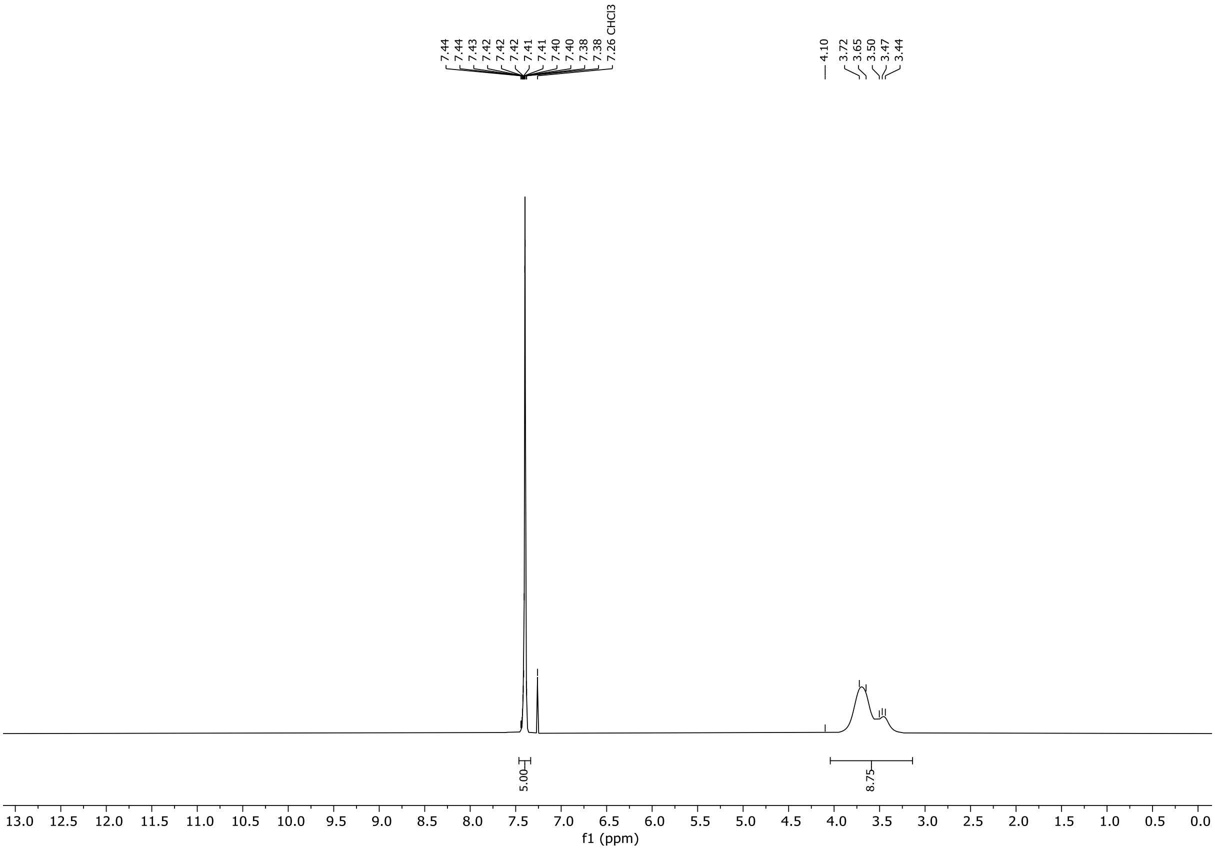
Compound S1: ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K)



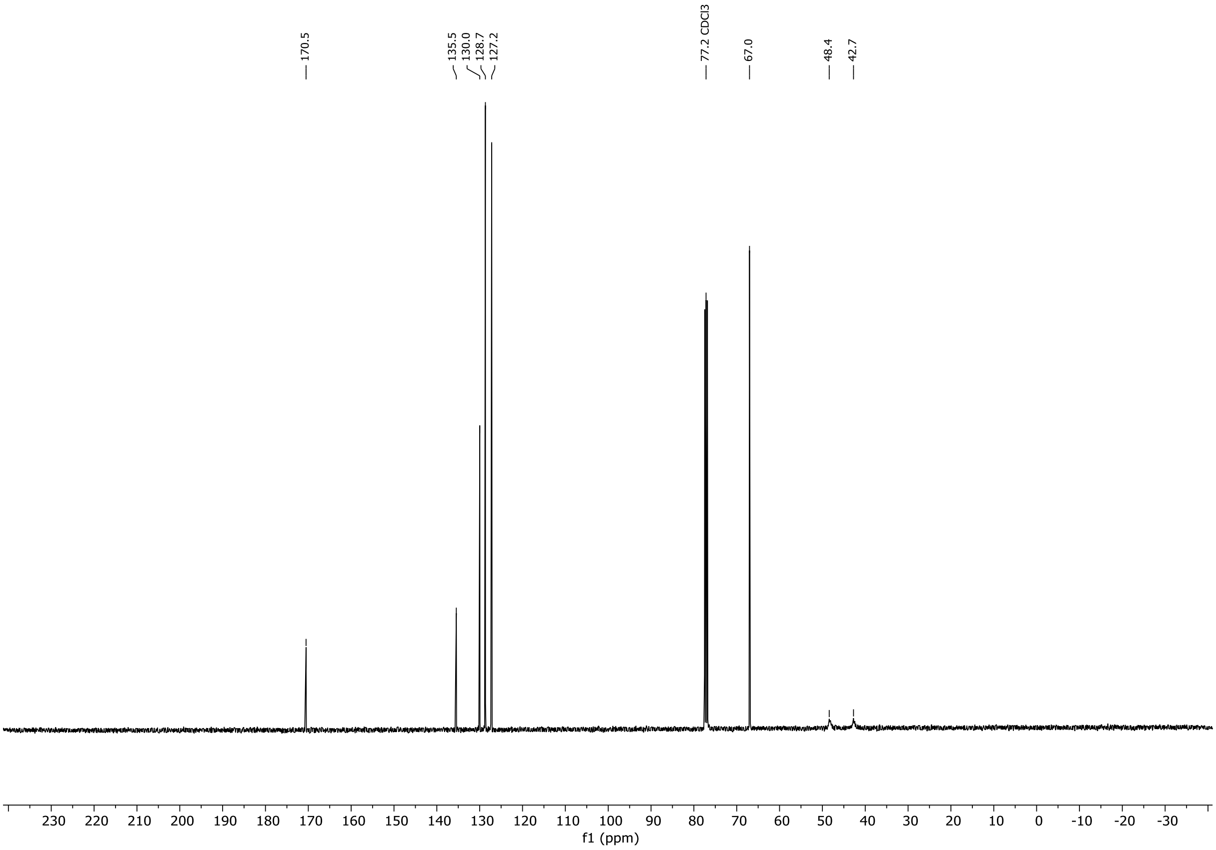
Compound S1: ^{13}C-NMR (101 MHz, DMSO-d_6, 298 K)



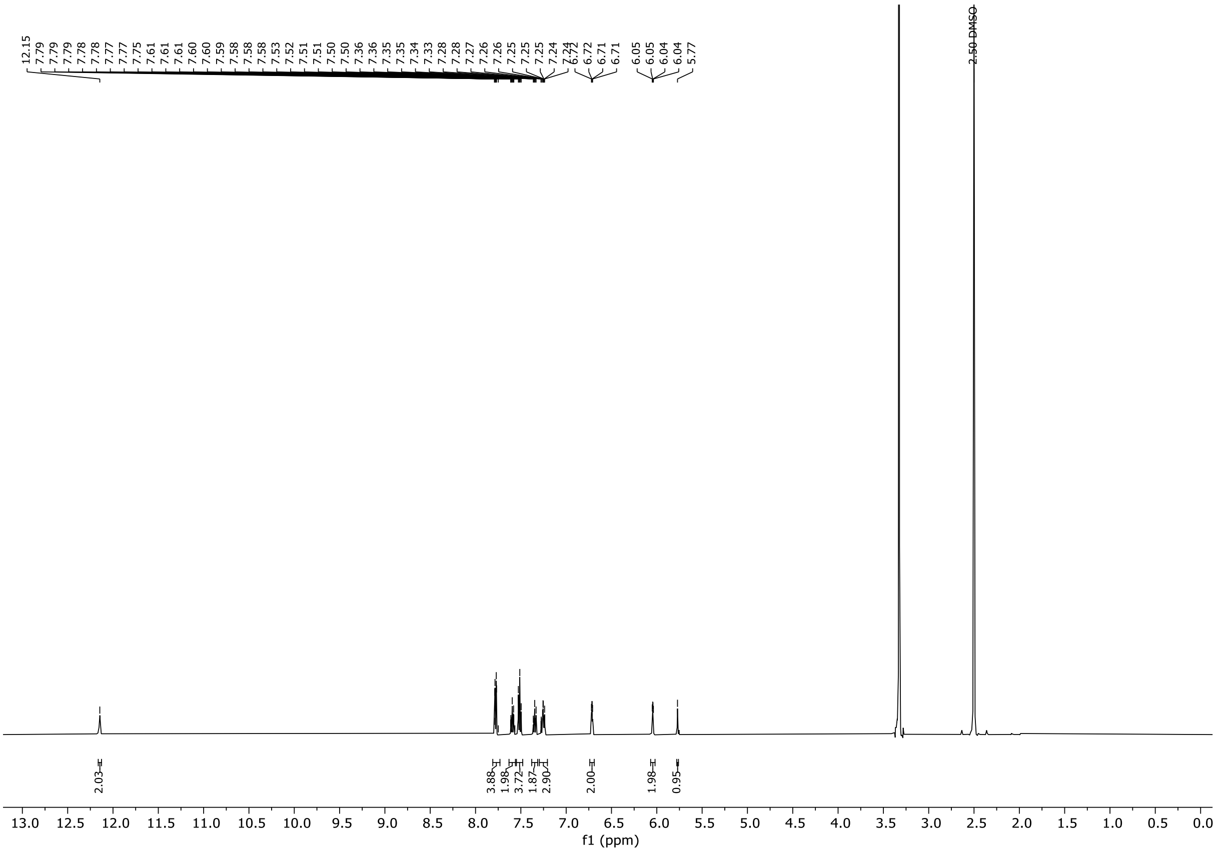
Compound S2: ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K)



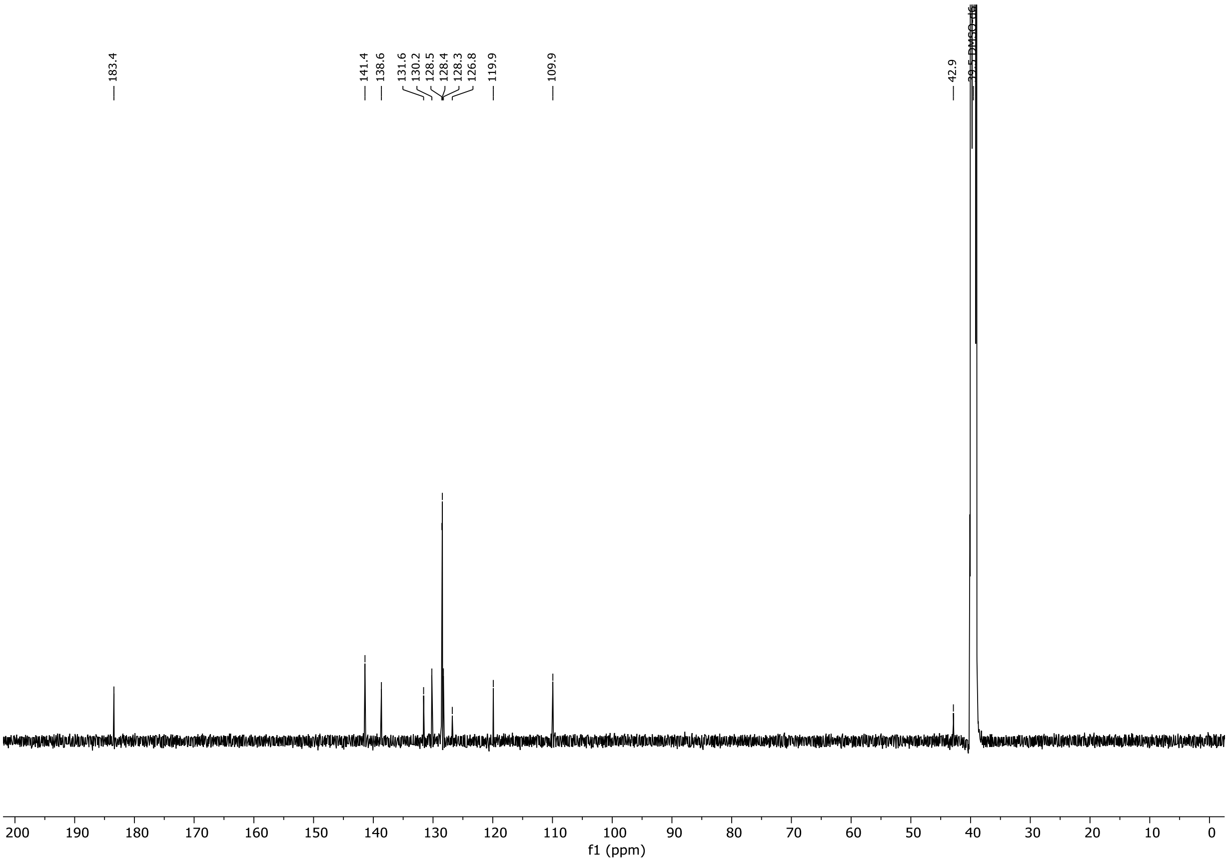
Compound S2: ^{13}C-NMR (101 MHz, CDCl$_3$, 298 K)



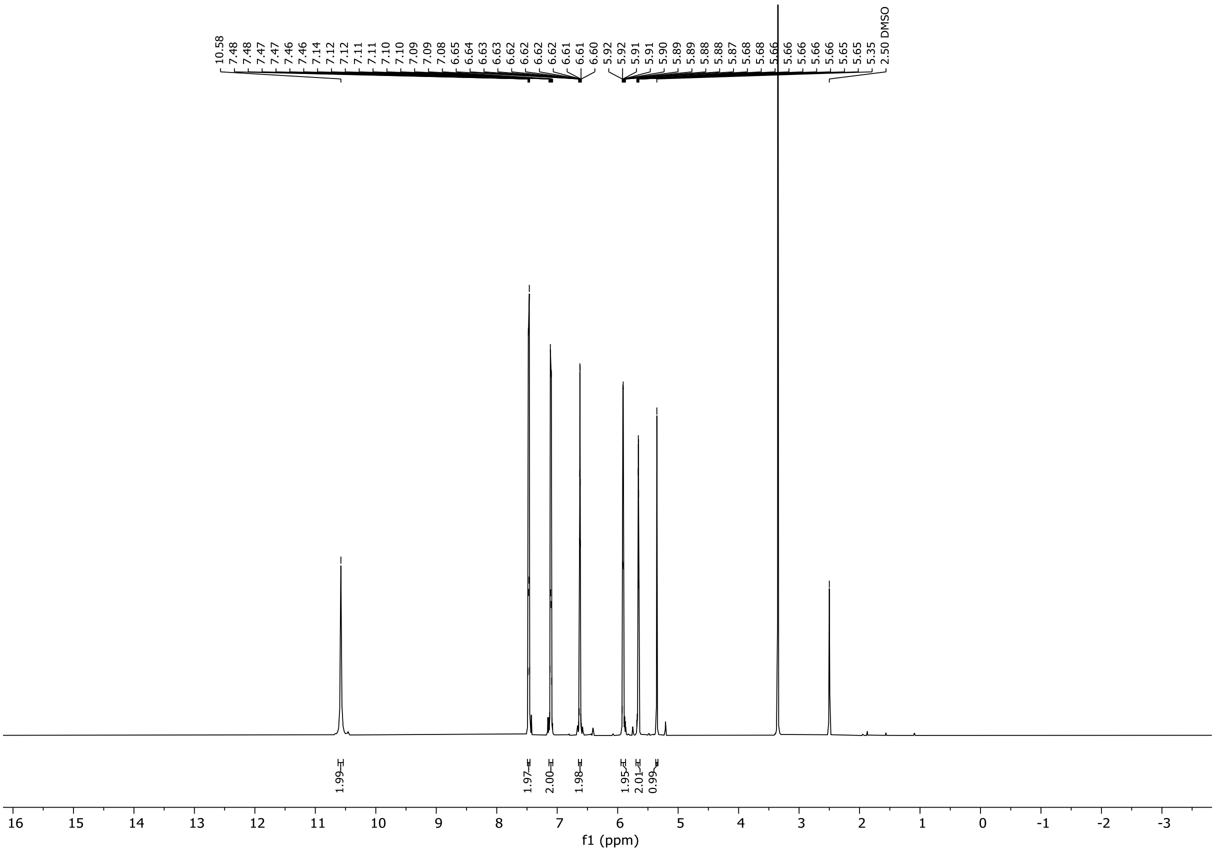
Compound S3: ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K)



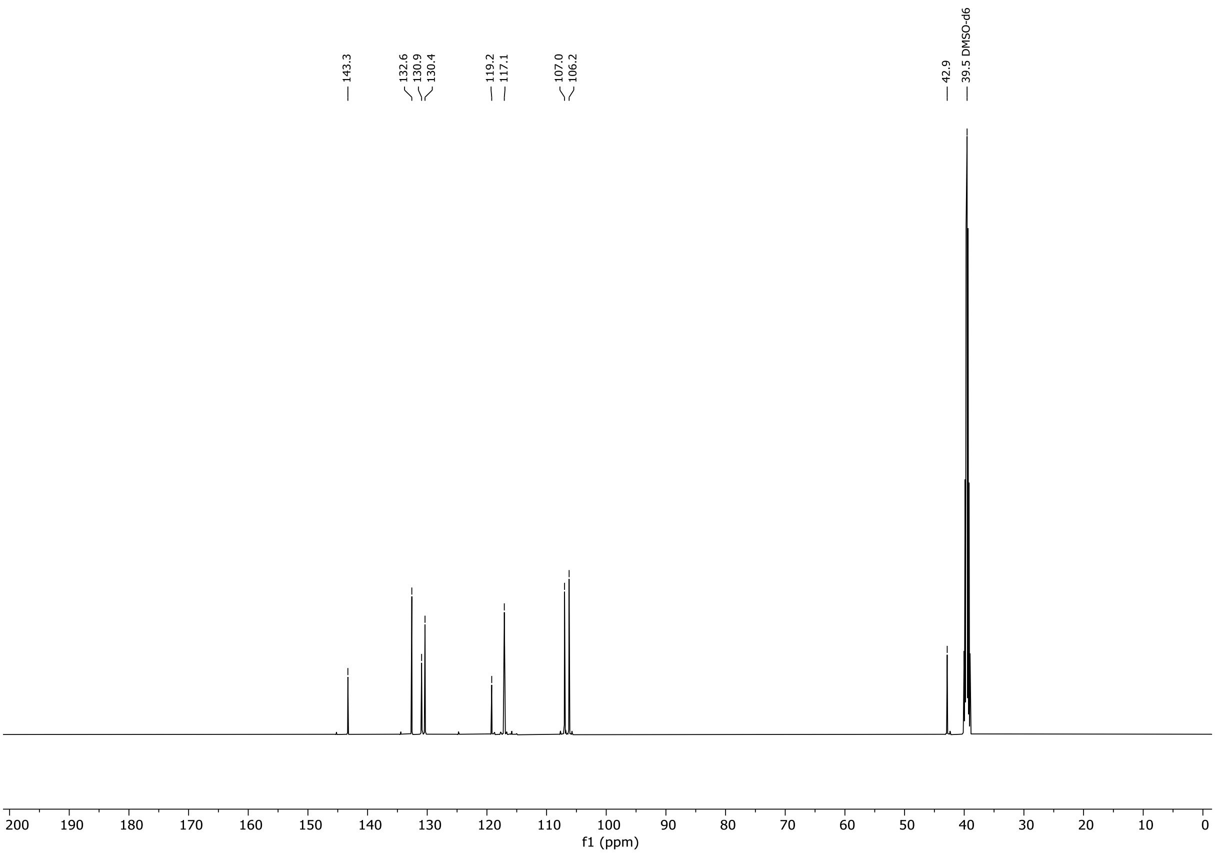
Compound S3: ^{13}C-NMR (126 MHz, DMSO-d_6, 298 K)



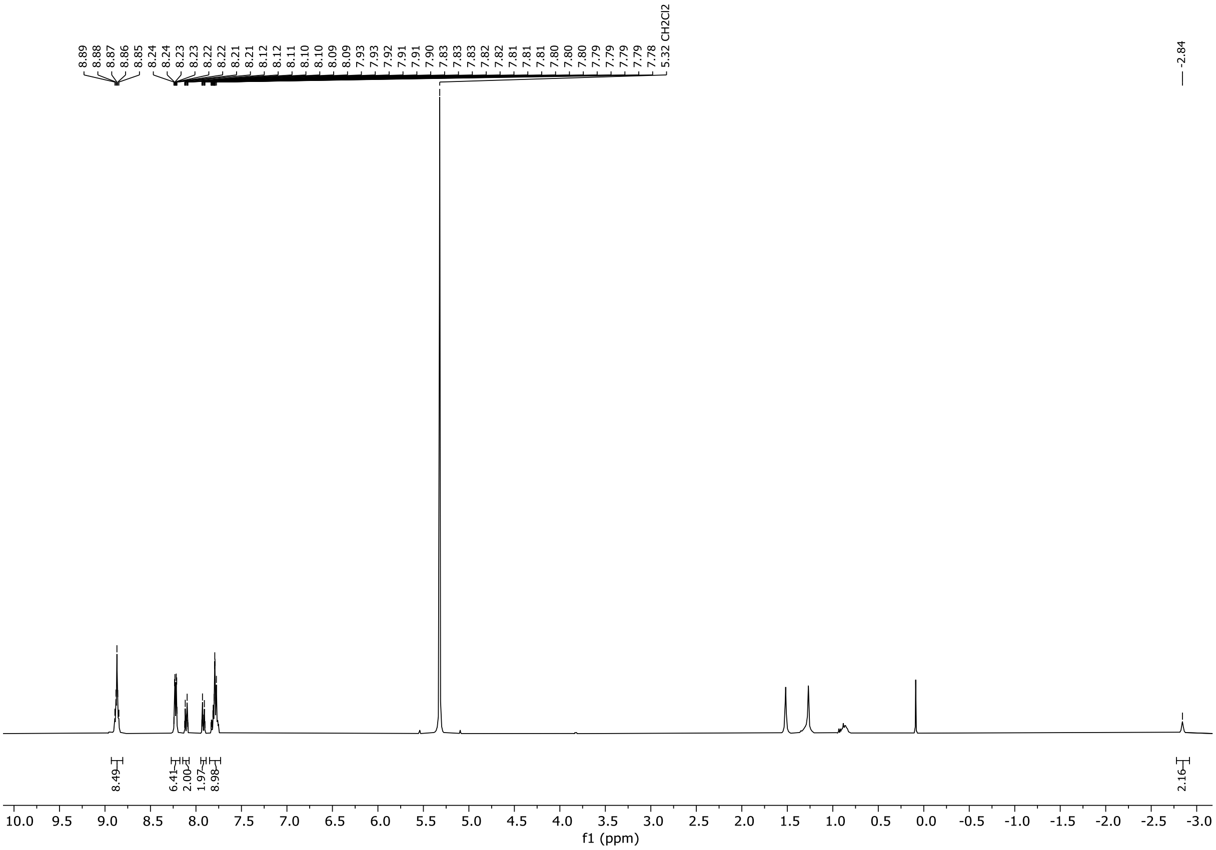
Compound S4: ^{1}H-NMR (500 MHz, DMSO-d_{6}, 298 K)



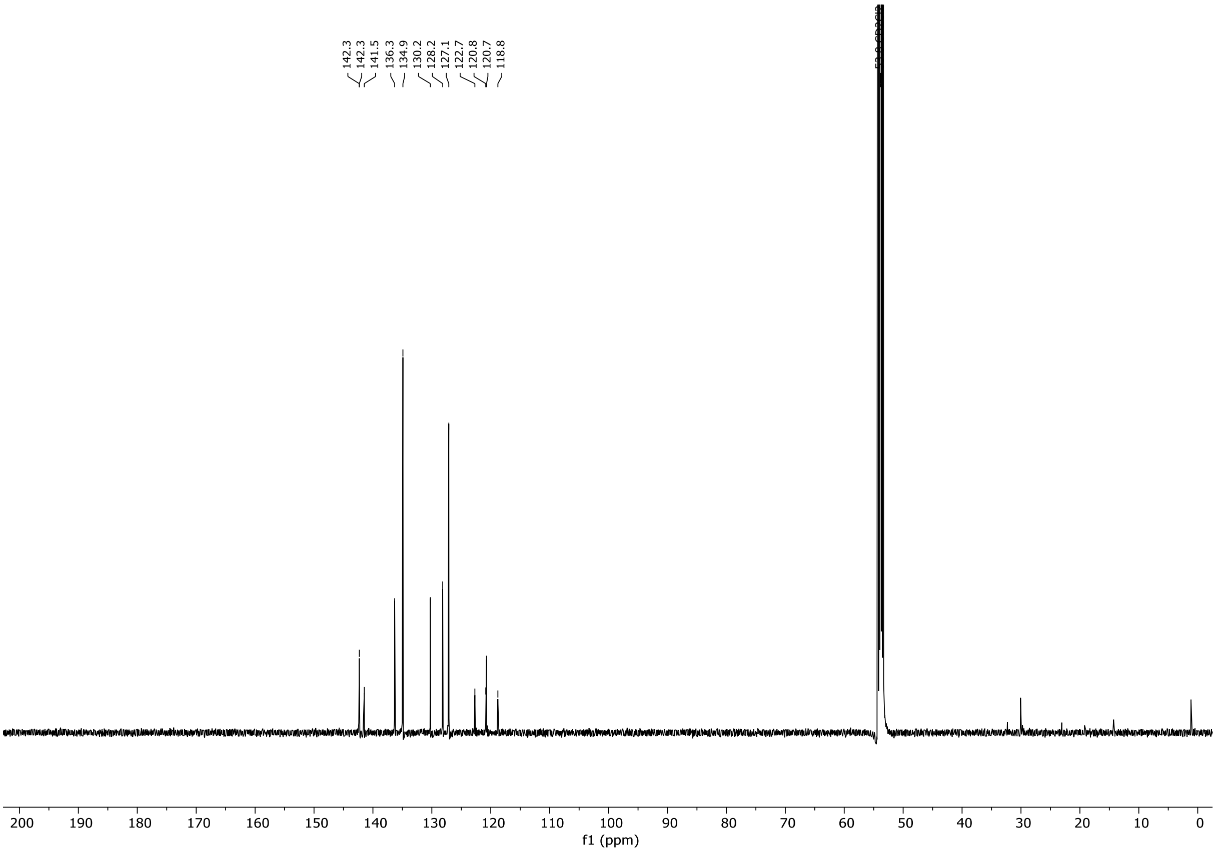
Compound S4: ^{13}C-NMR (126 MHz, DMSO-d_{6}, 298 K)



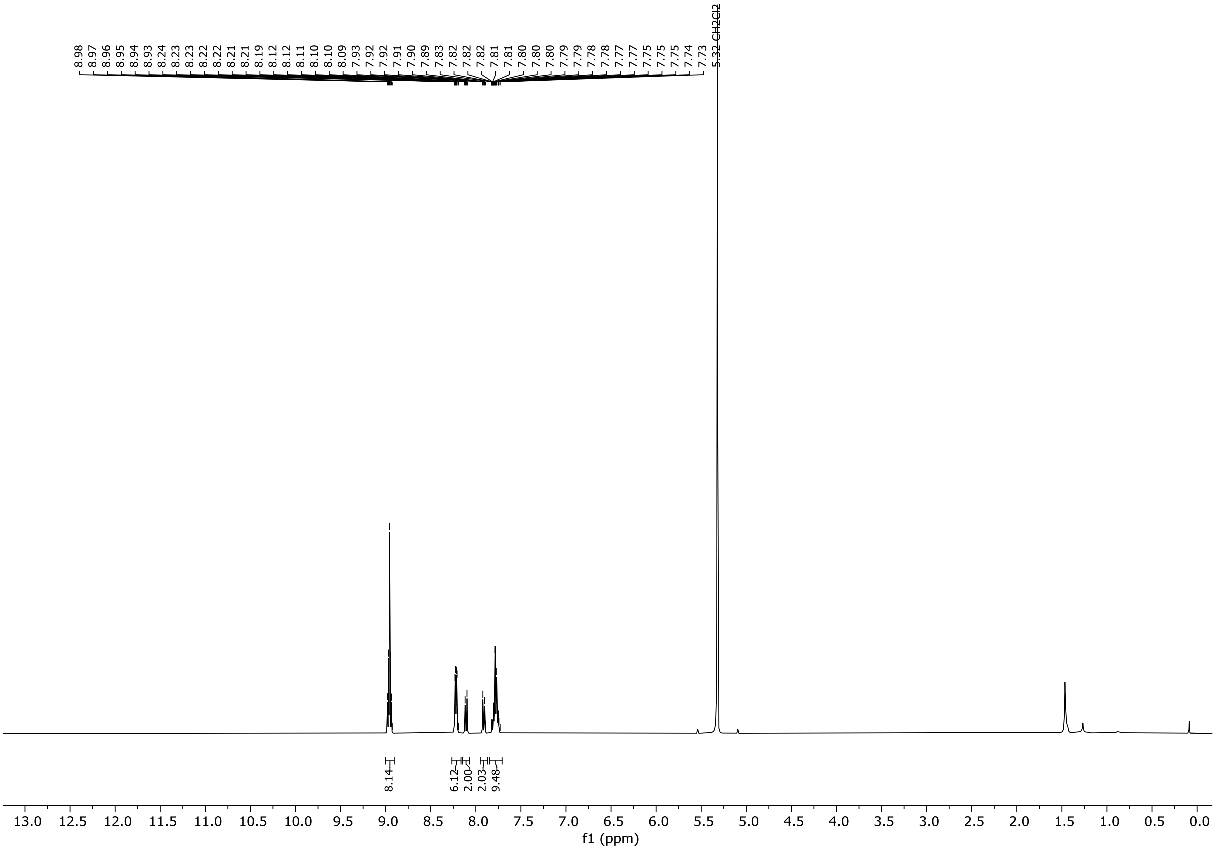
Compound S5: ^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K)



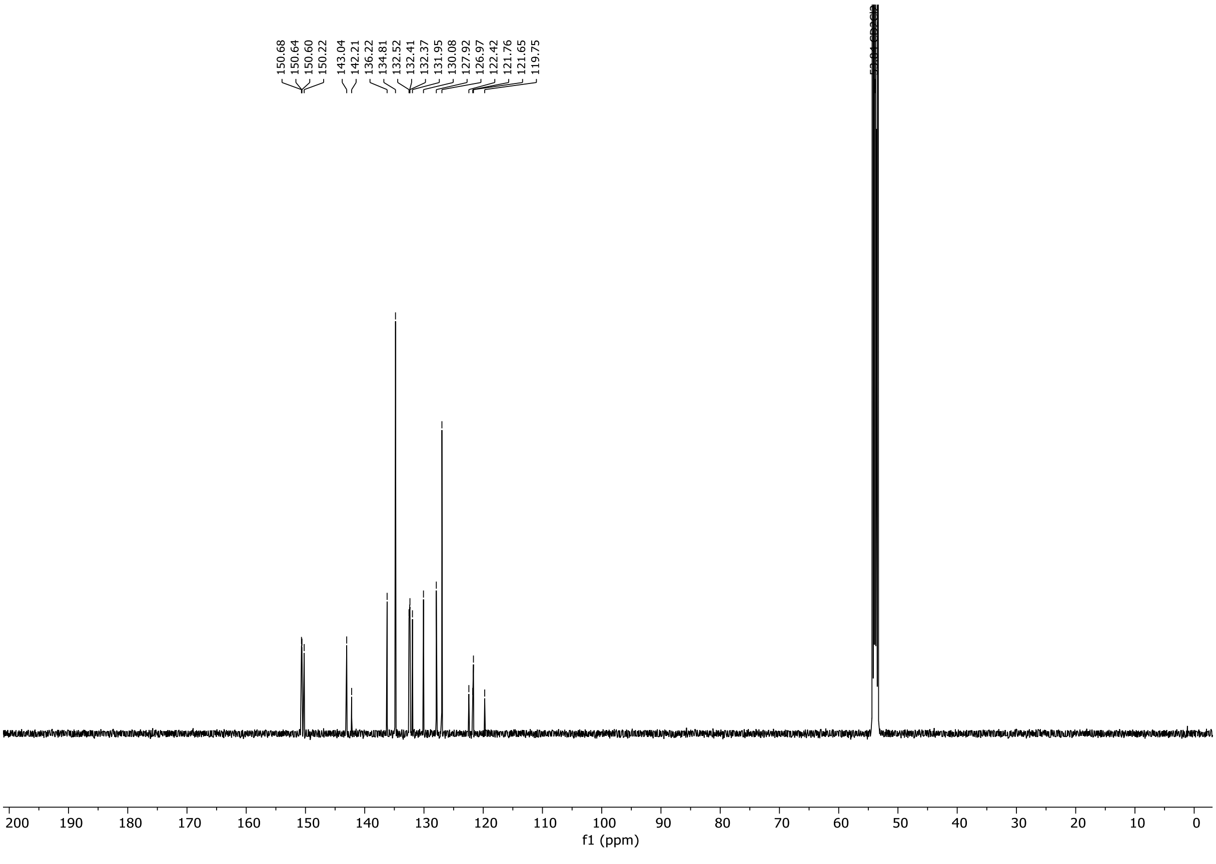
Compound S5: ^{13}C-NMR (126 MHz, CD_2Cl_2, 298 K)



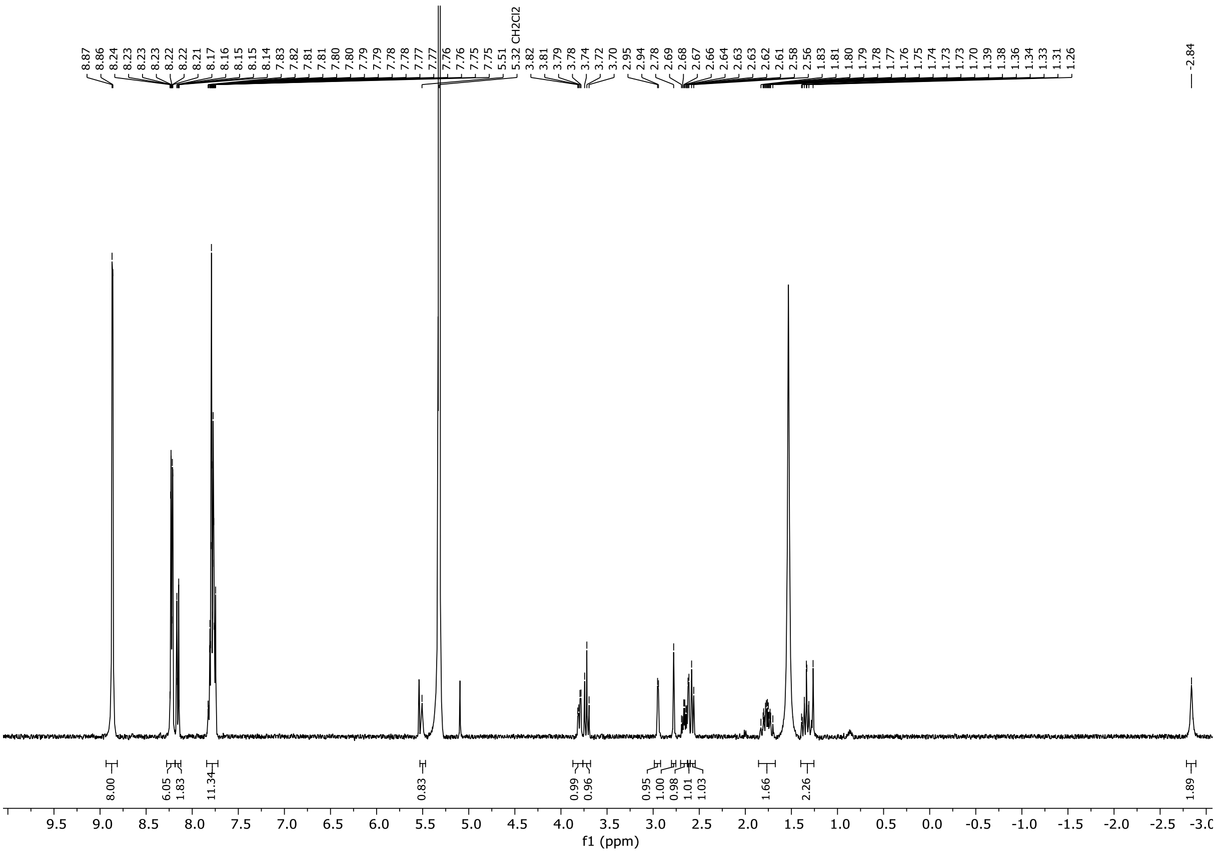
Compound S6: ^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K)



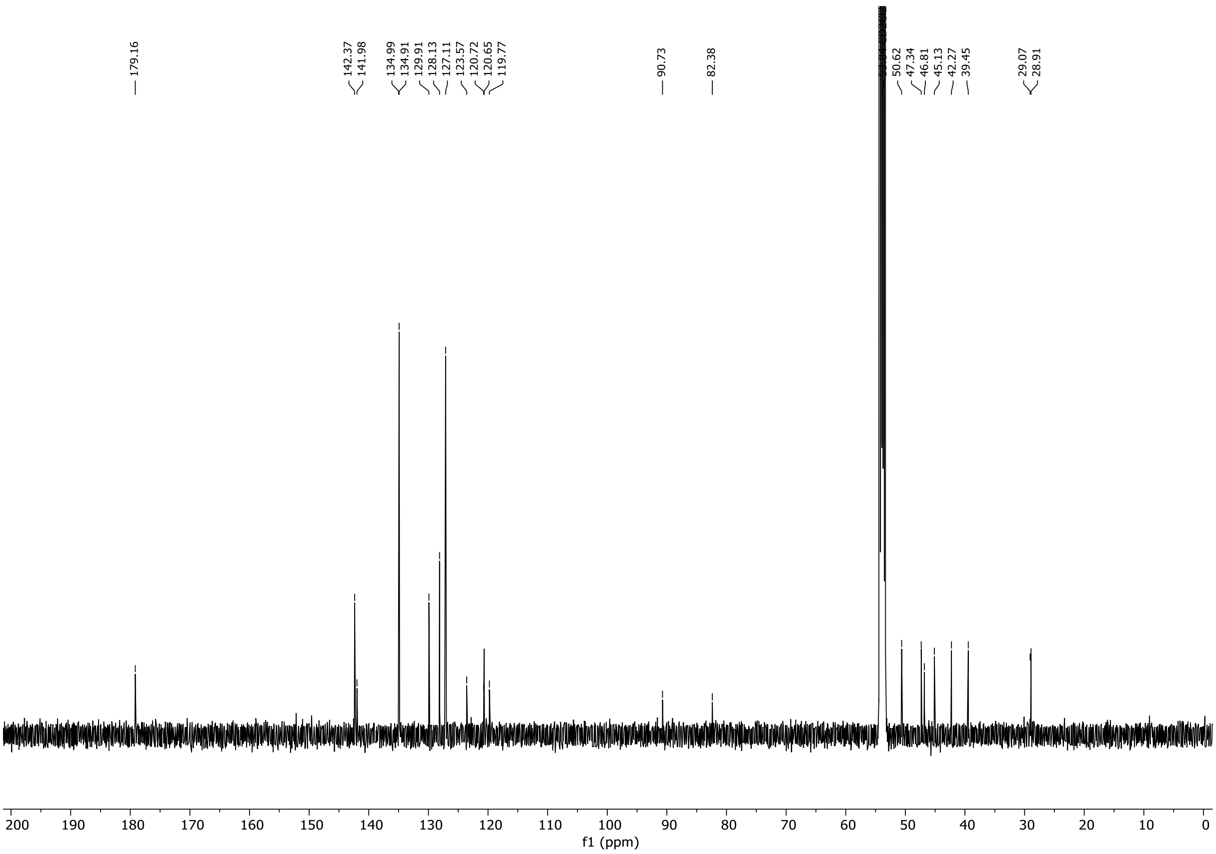
Compound S6: ^{13}C-NMR (126 MHz, CD_2Cl_2, 298 K)



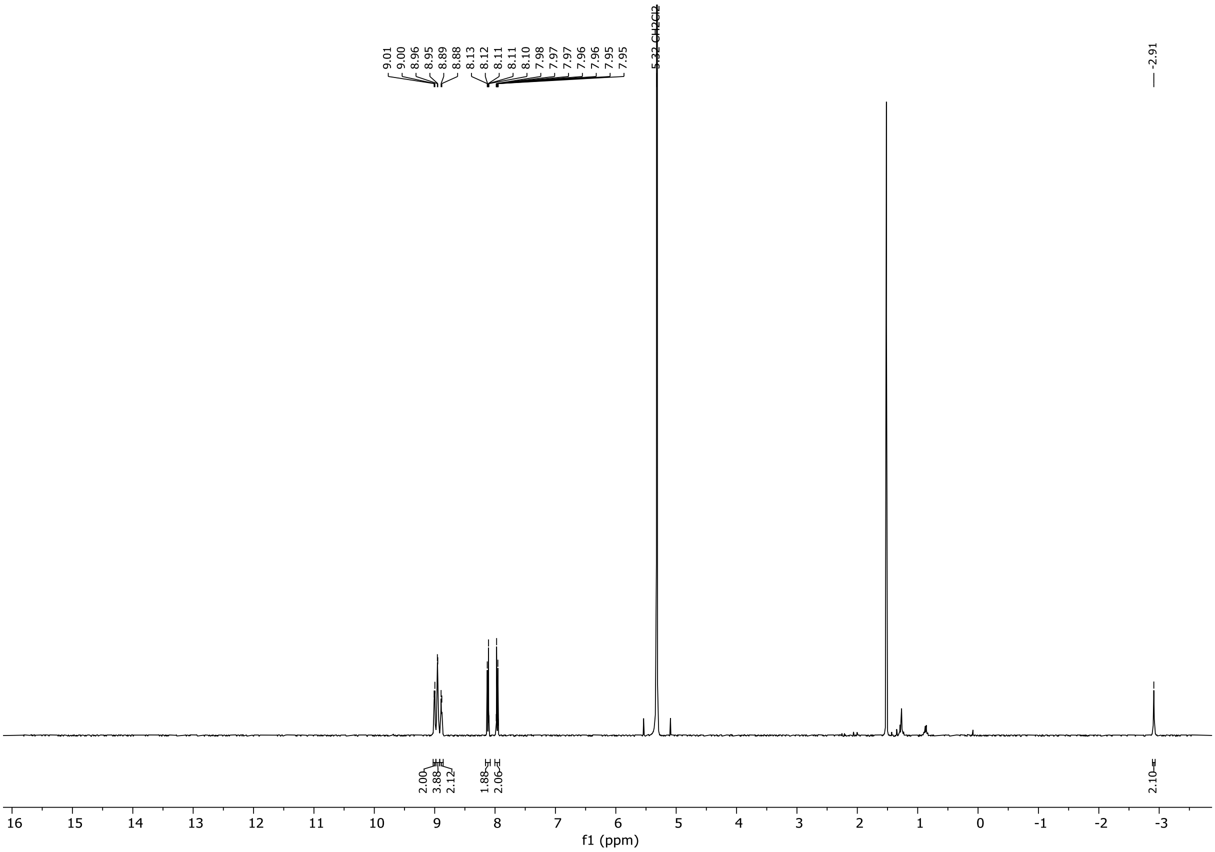
Compound S7: ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$, 298 K)



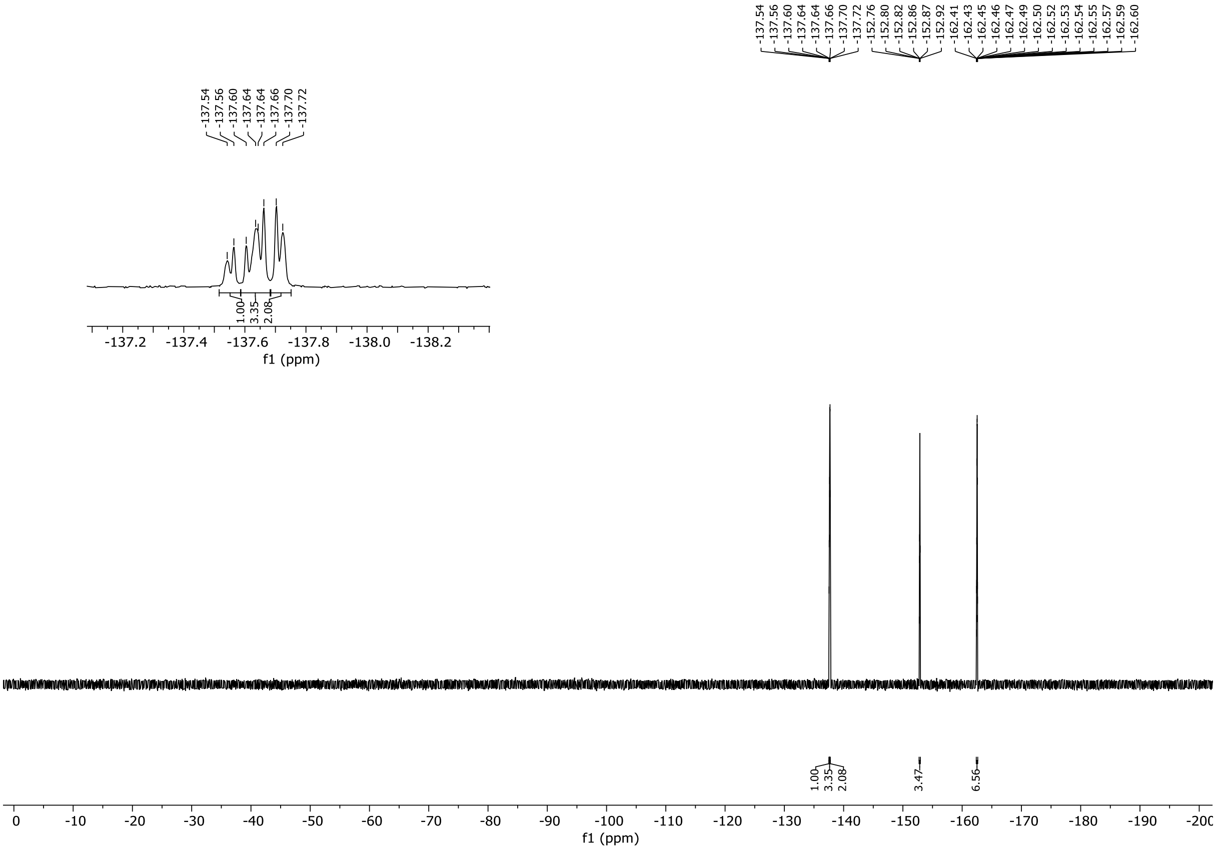
Compound S7: ^{13}C-NMR (500 MHz, CD$_2$Cl$_2$, 298 K)



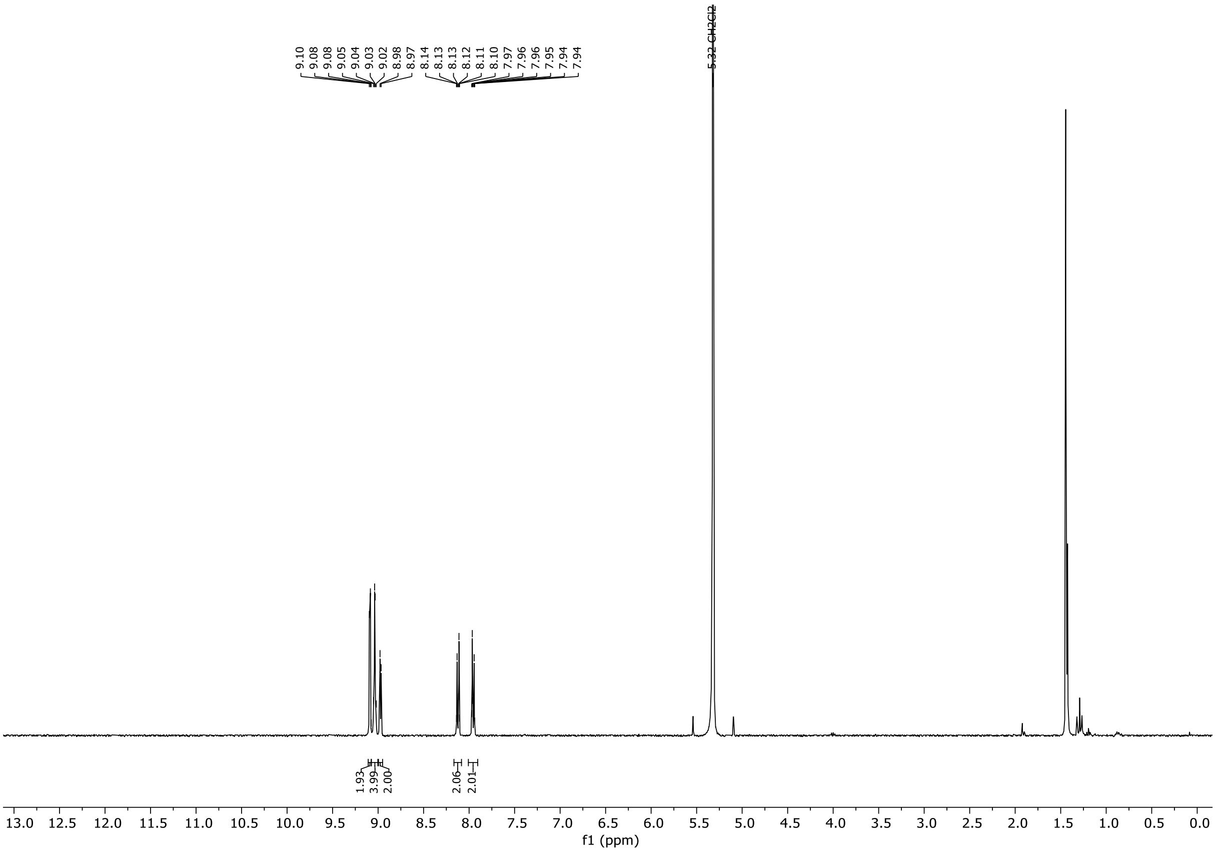
Compound S9: ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$, 298 K)



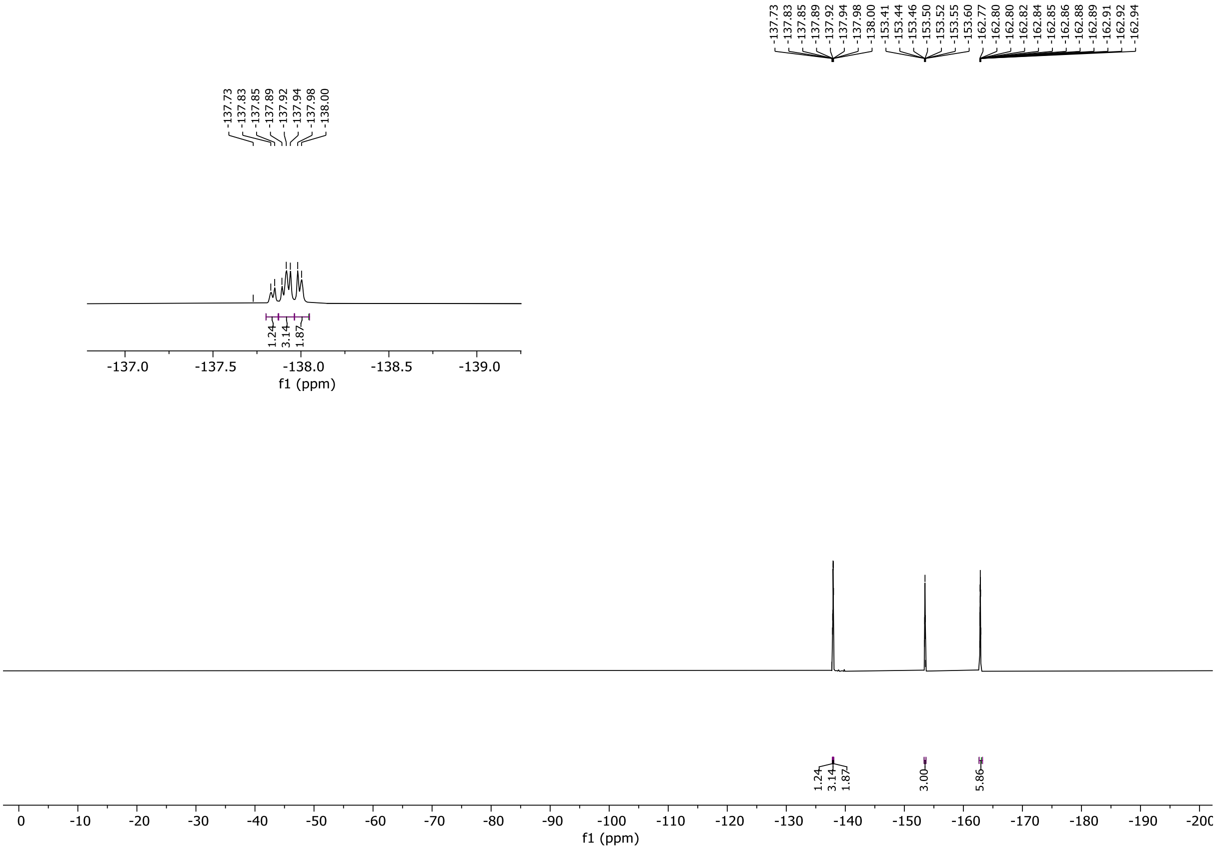
Compound S9: ^{19}F-NMR (376 MHz, CD$_2$Cl$_2$, 298 K)



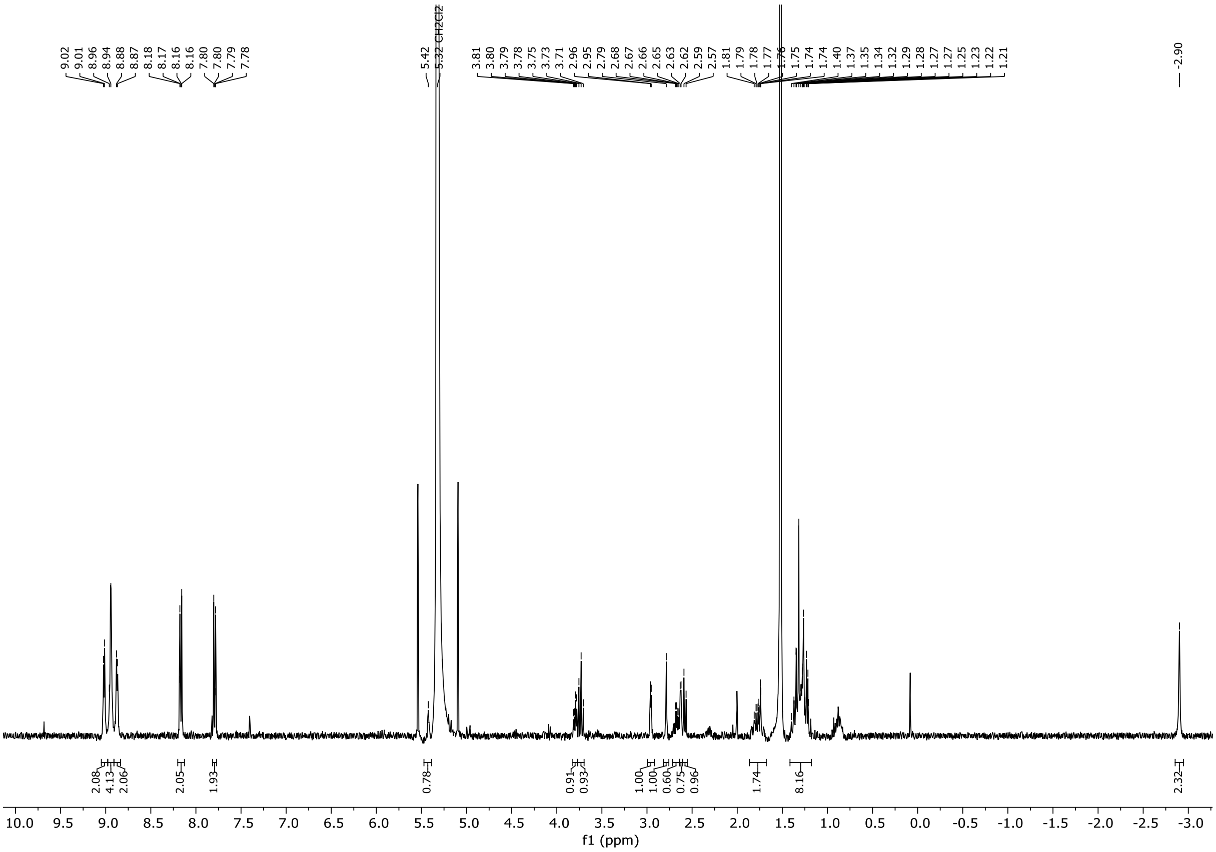
Compound S10: ^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K)



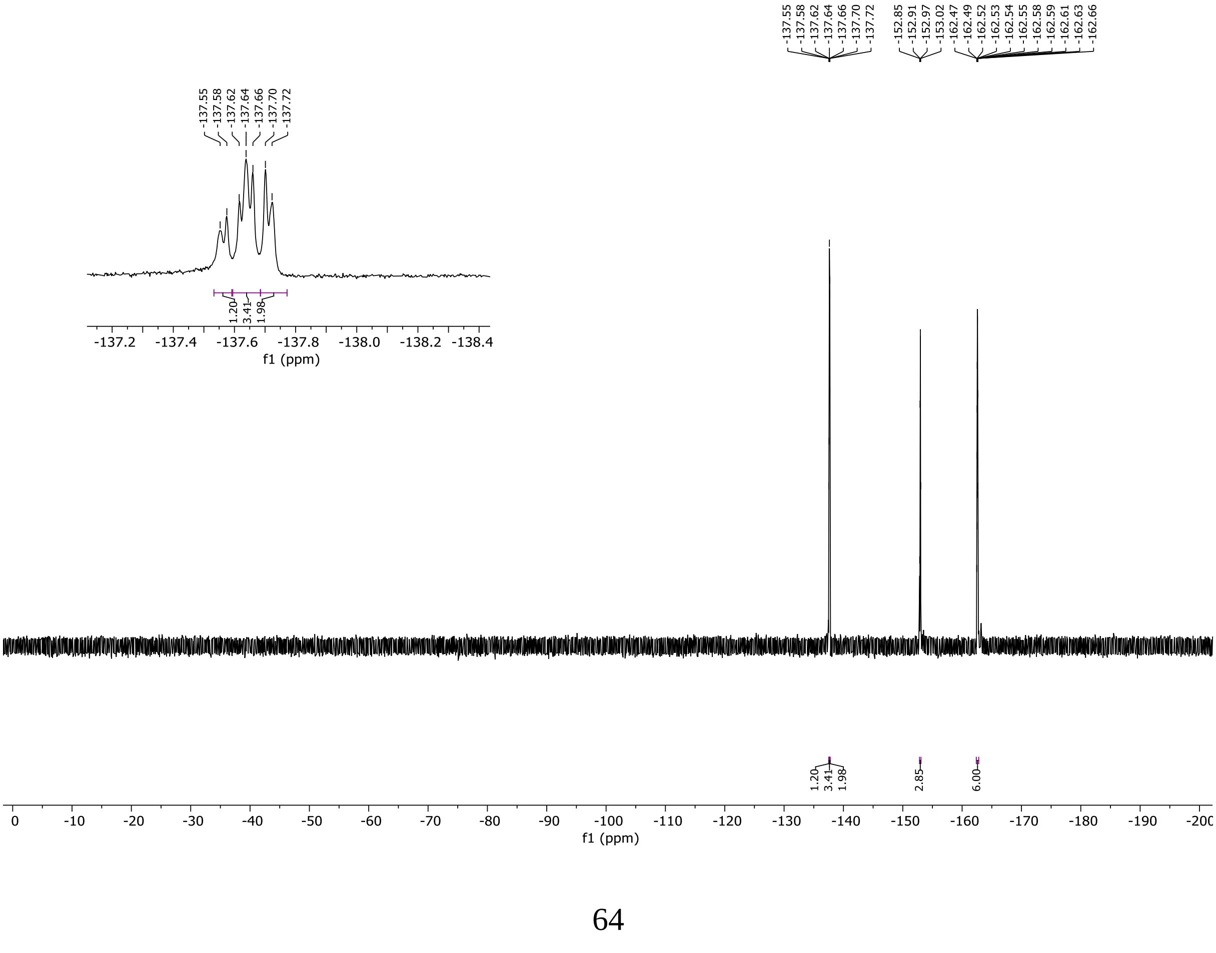
Compound S10: ^{19}F-NMR (376 MHz, CD_2Cl_2, 298 K)



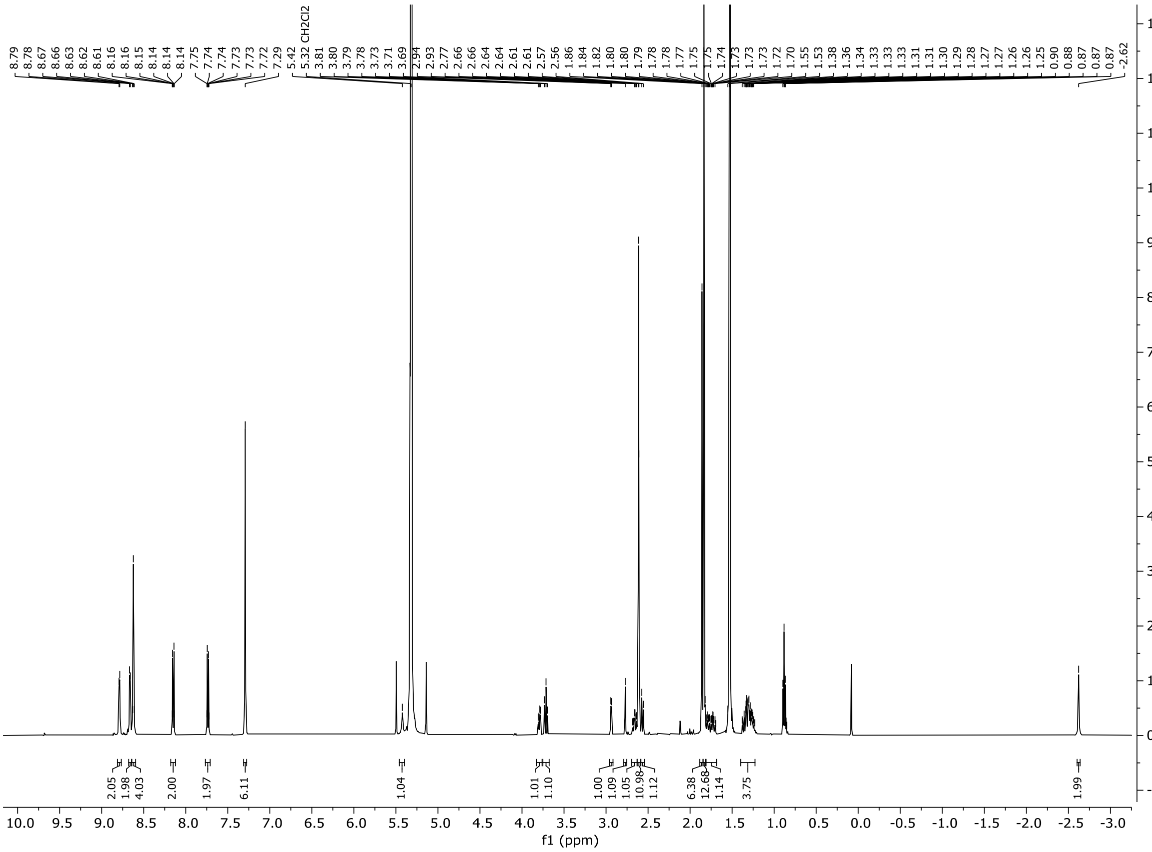
Compound S11: ^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K)



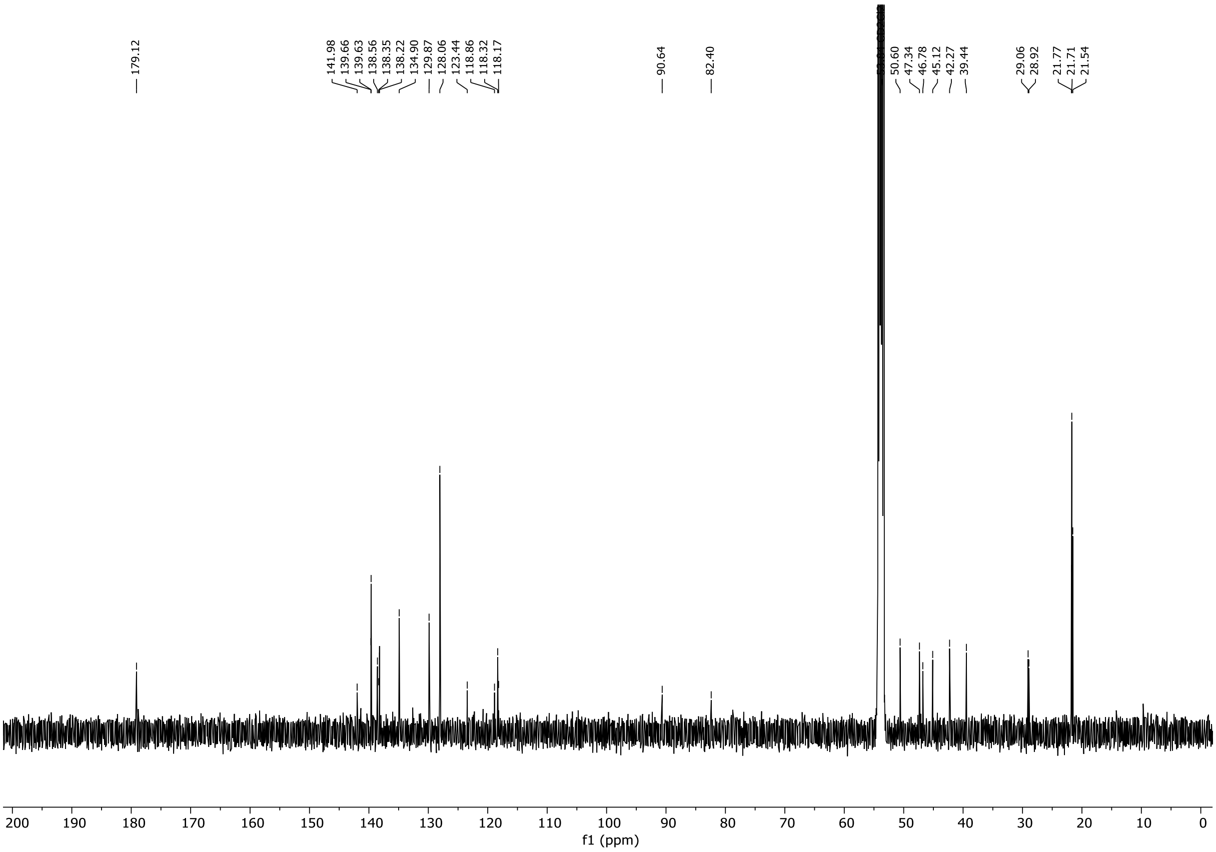
Compound S11: ^{19}F-NMR (376 MHz, CD_2Cl_2, 298 K)



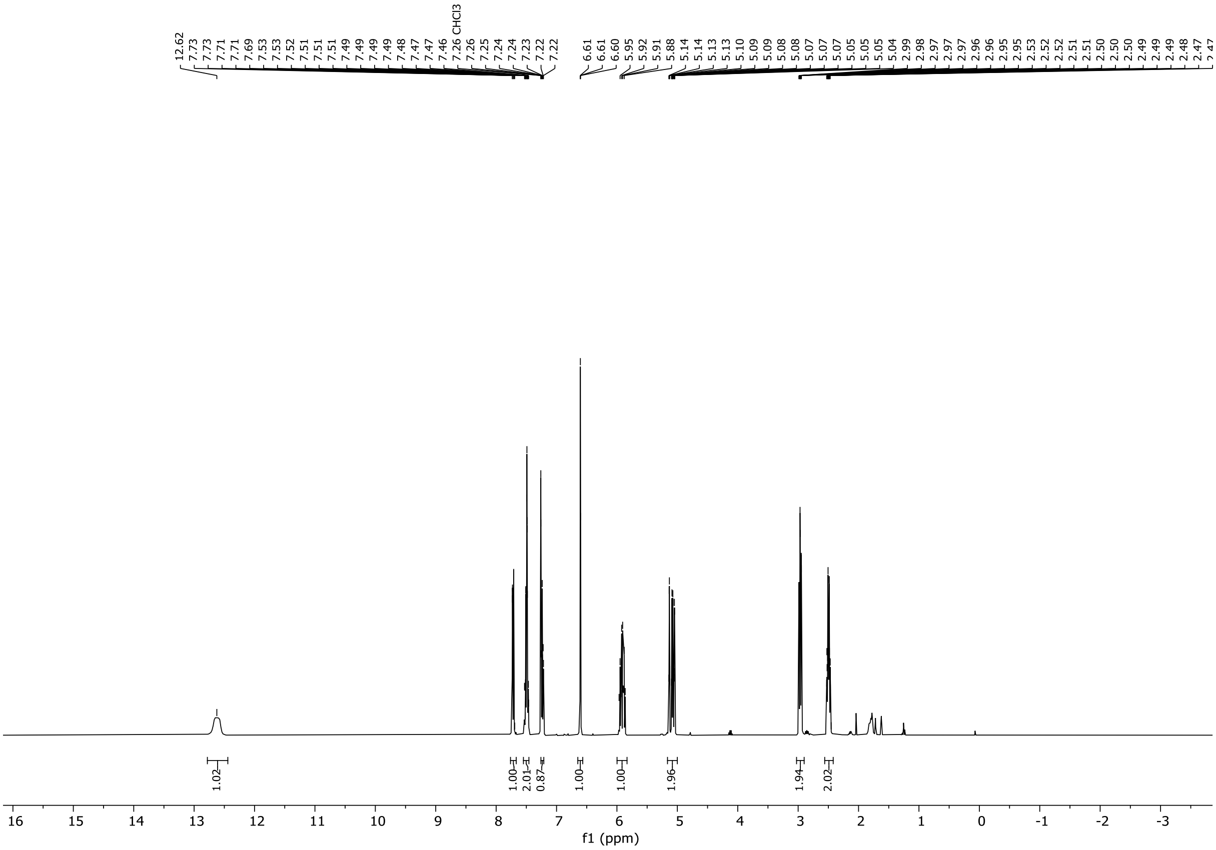
Compound S13: ^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K)



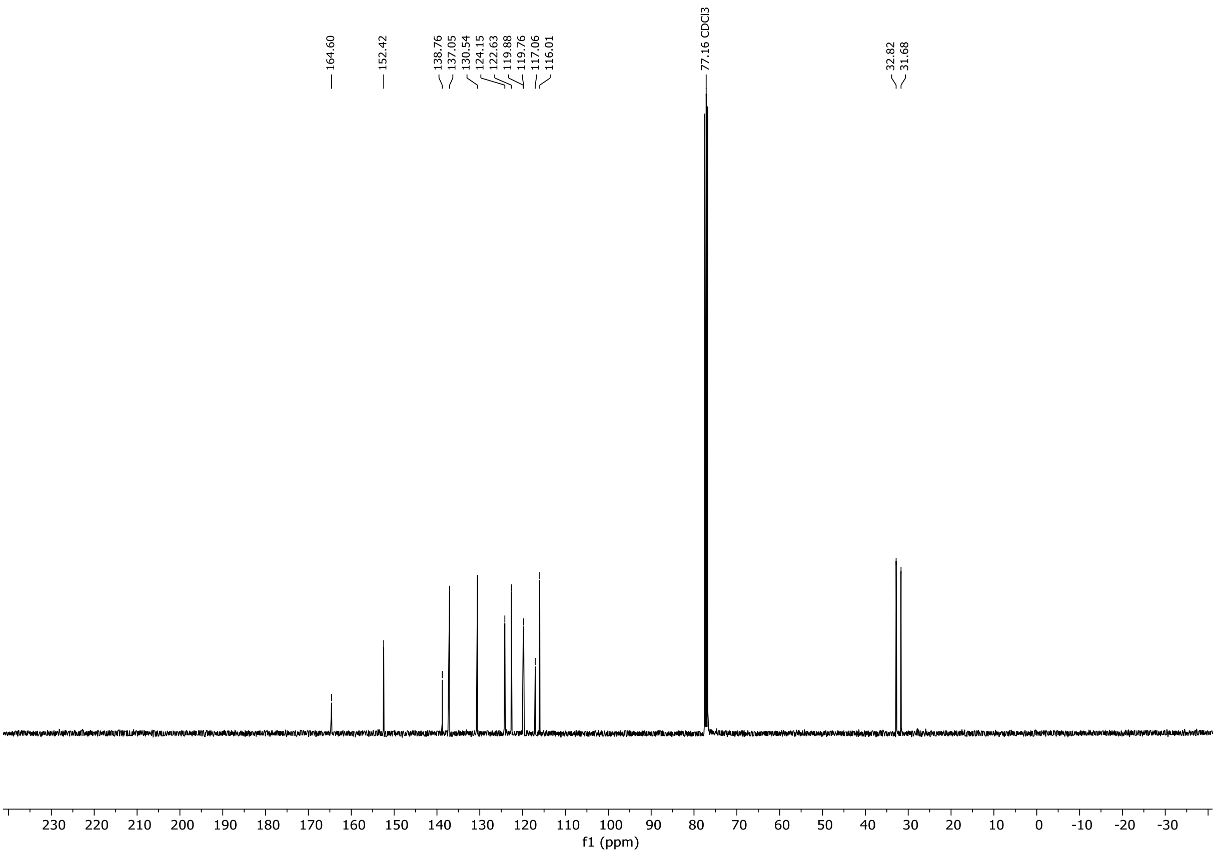
Compound S13: ^{13}C-NMR (126 MHz, CD_2Cl_2, 298 K)



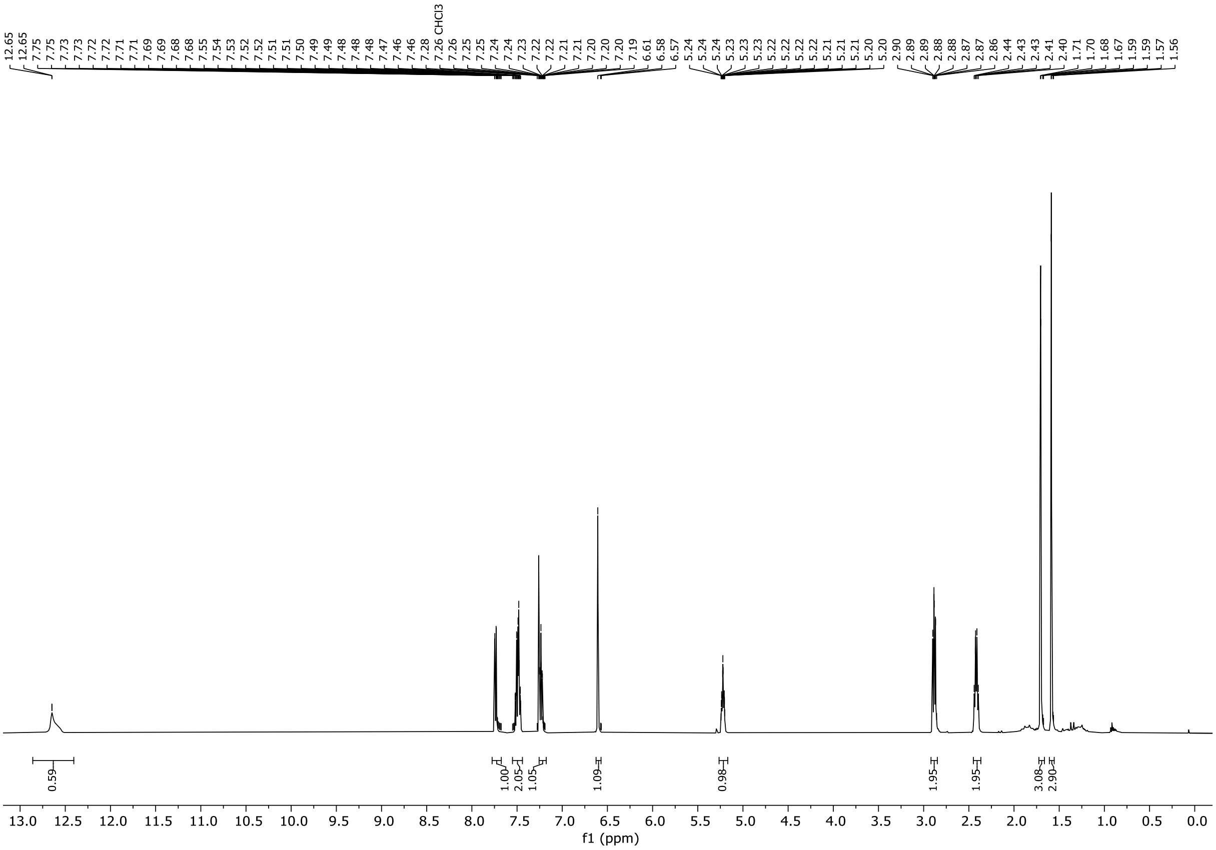
Compound 2b: ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K)



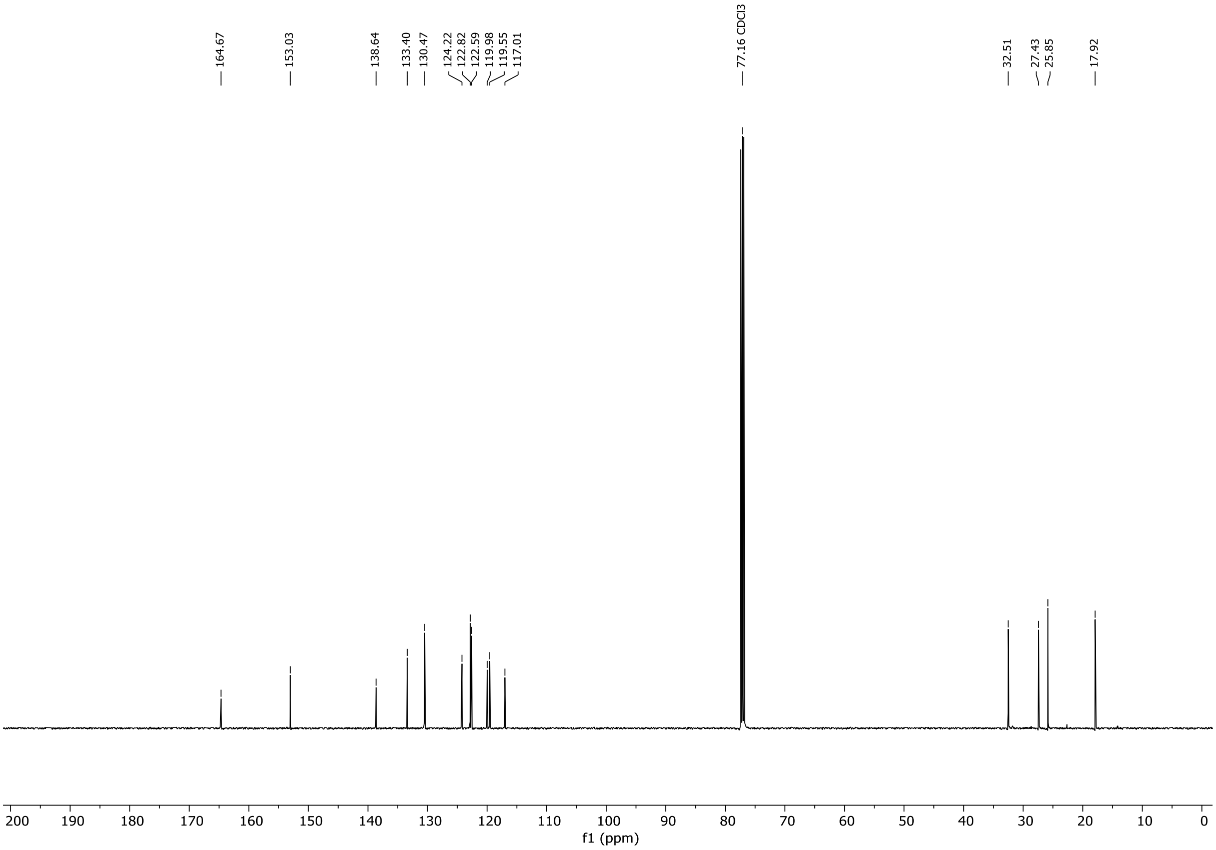
Compound 2b: ^{13}C-NMR (101 MHz, CDCl$_3$, 298 K)



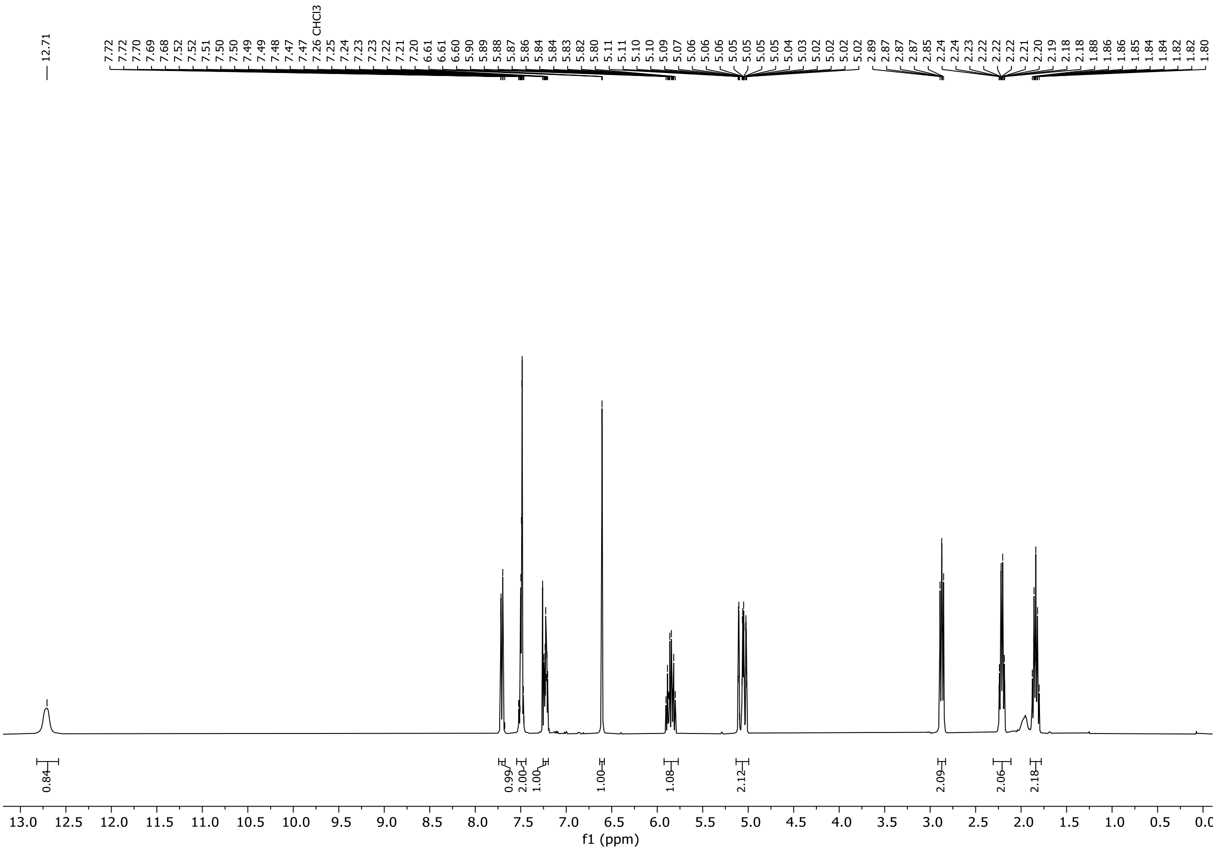
Compound 12b: ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K)



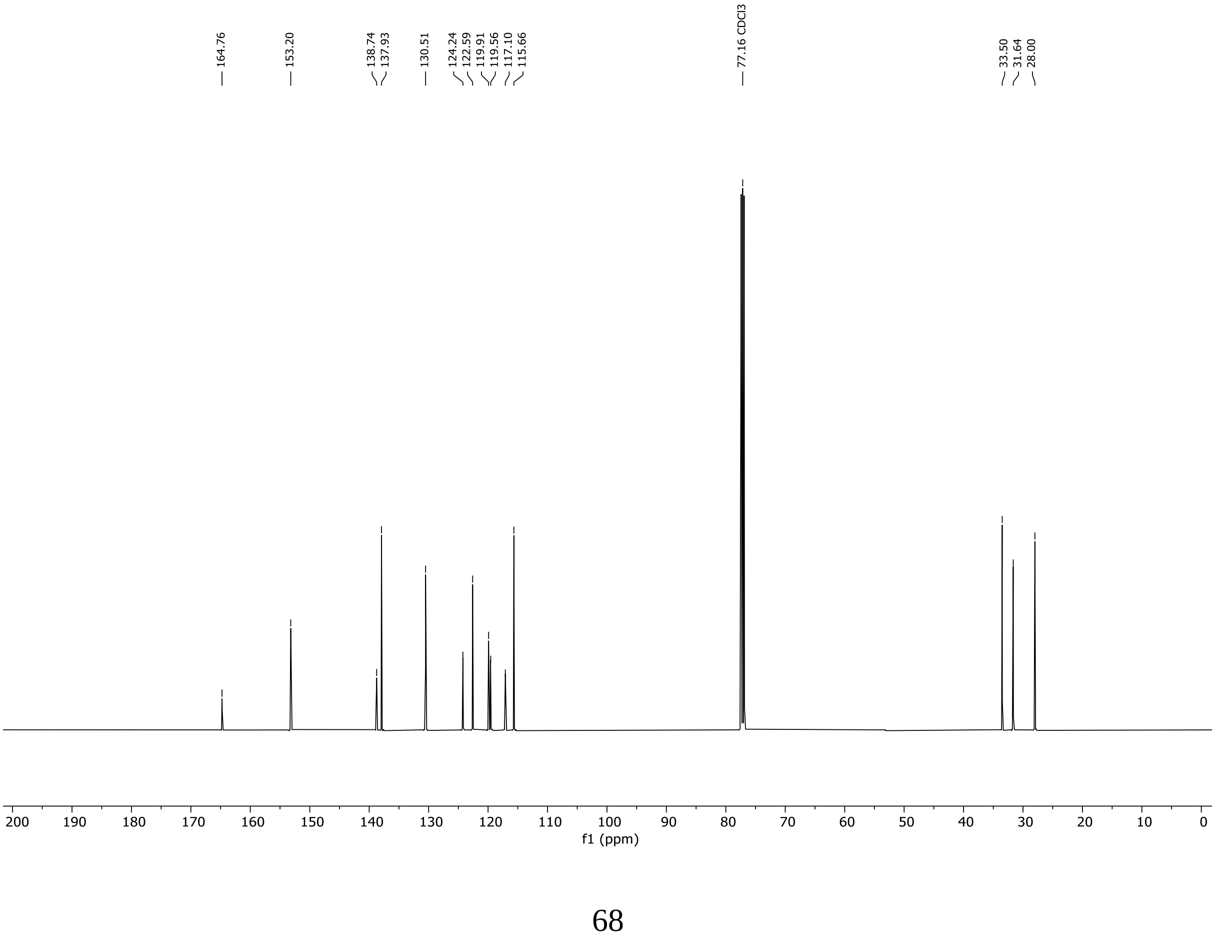
Compound 12b: ^{13}C-NMR (101 MHz, CDCl$_3$, 298 K)



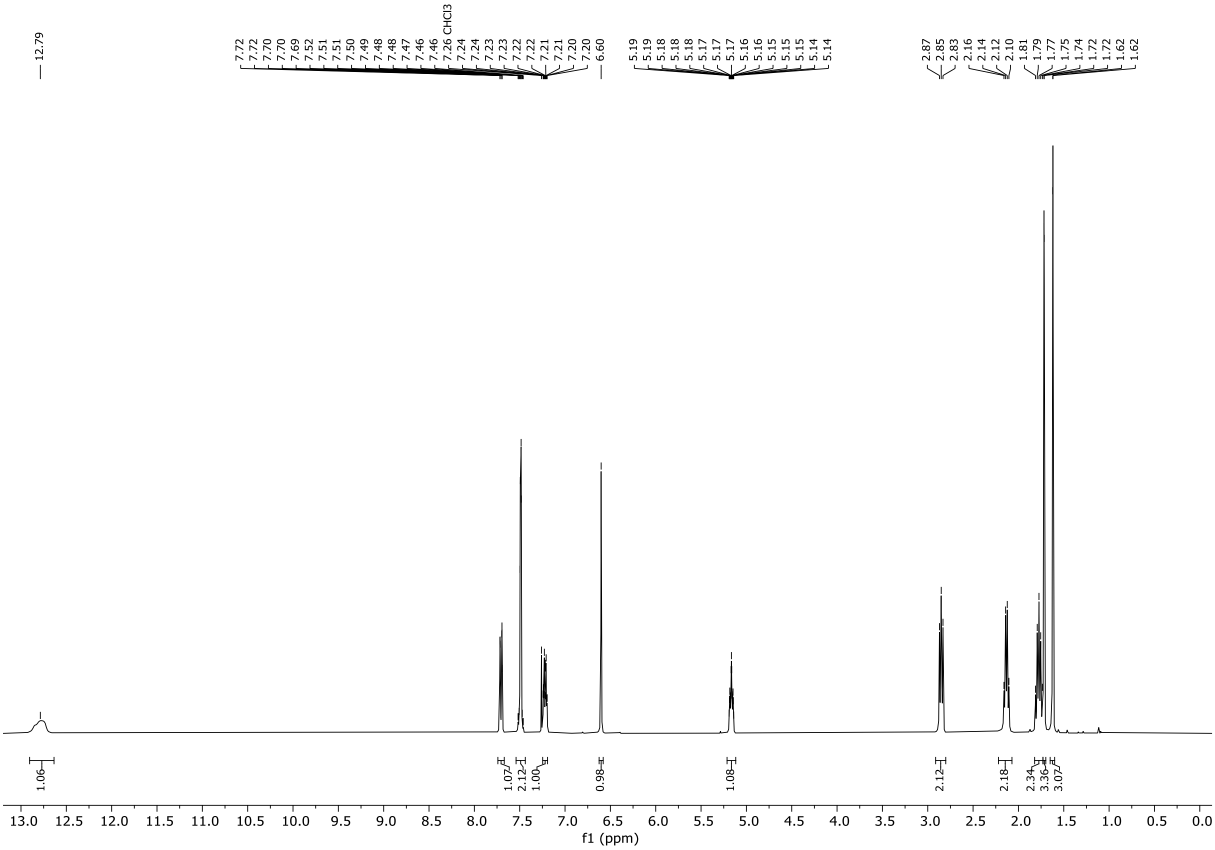
Compound 2c: ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K)



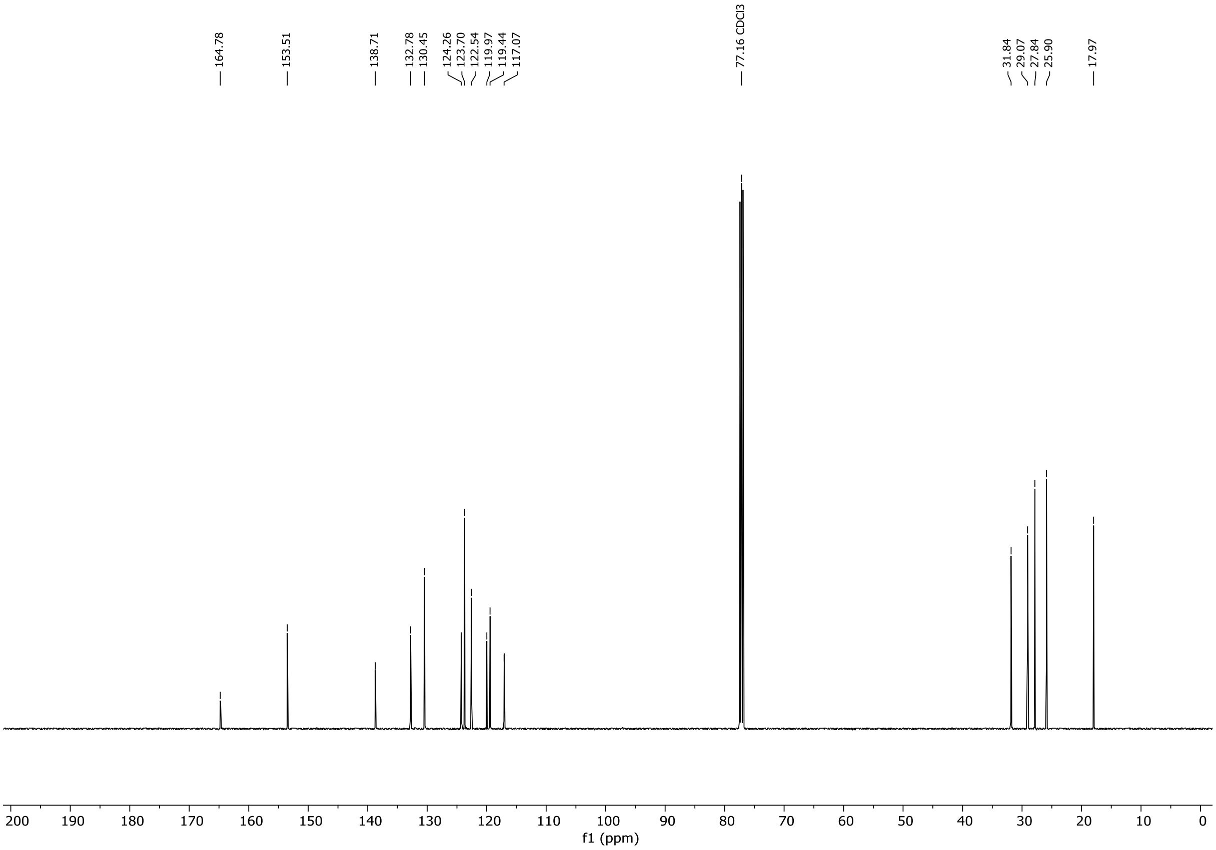
Compound 2c: ^{13}C-NMR (126 MHz, CDCl$_3$, 298 K)



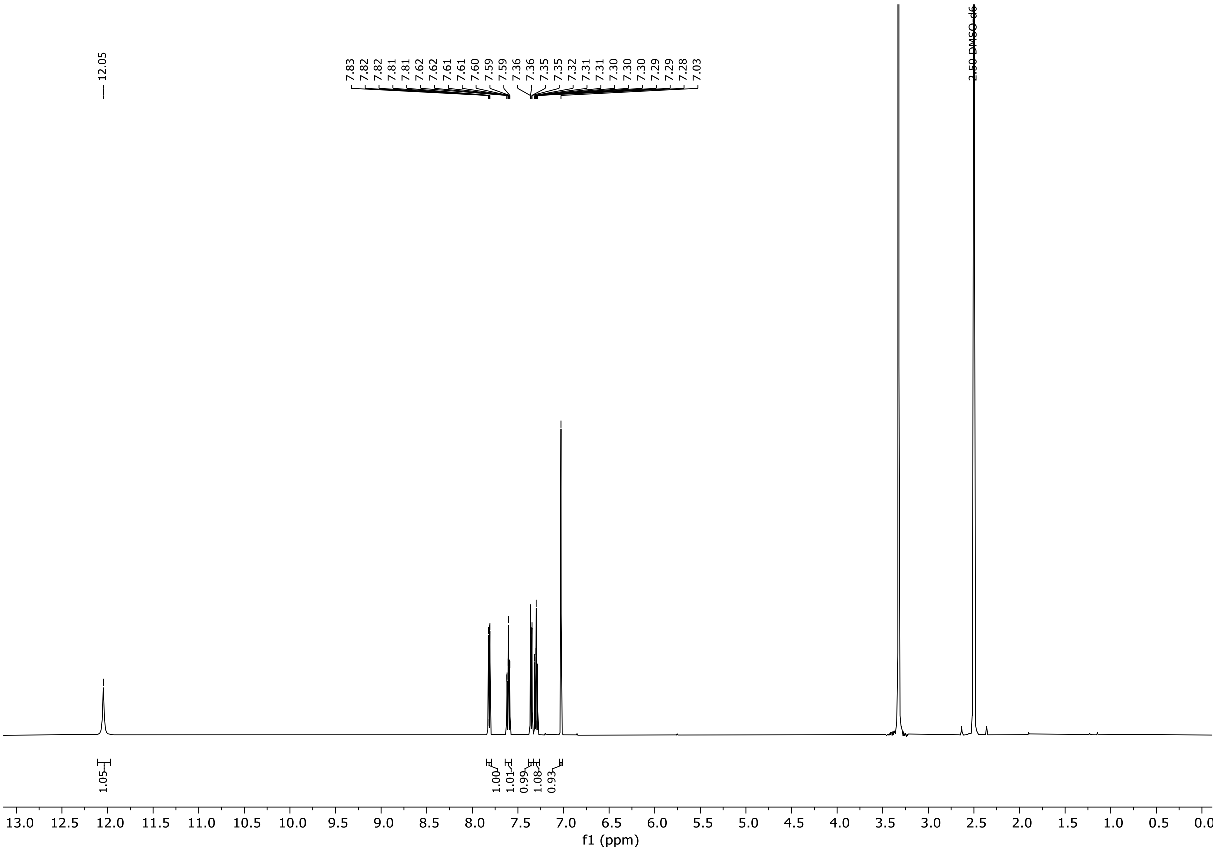
Compound 12c: ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K)



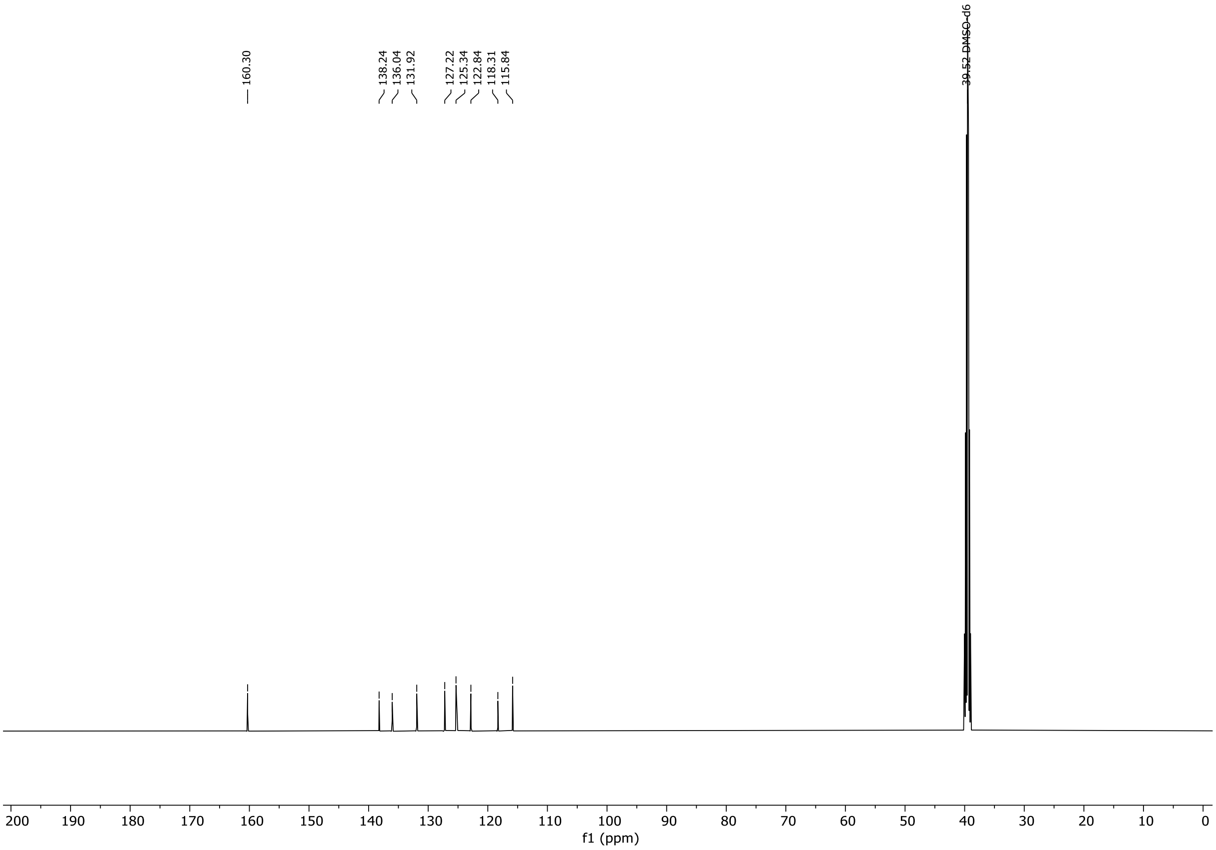
Compound 12c: ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K)



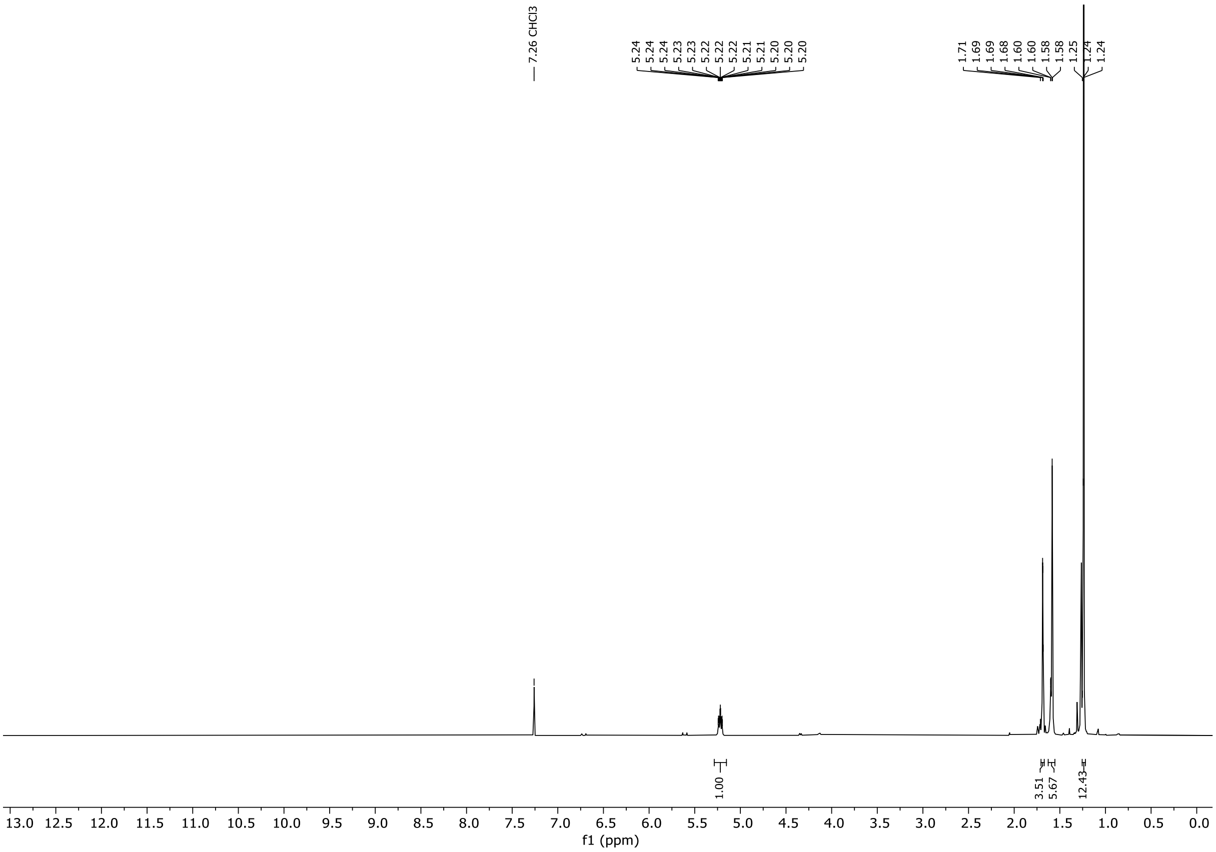
Compound S16: ^{1}H-NMR (500 MHz, DMSO-*d*$_{6,}$ 298 K)



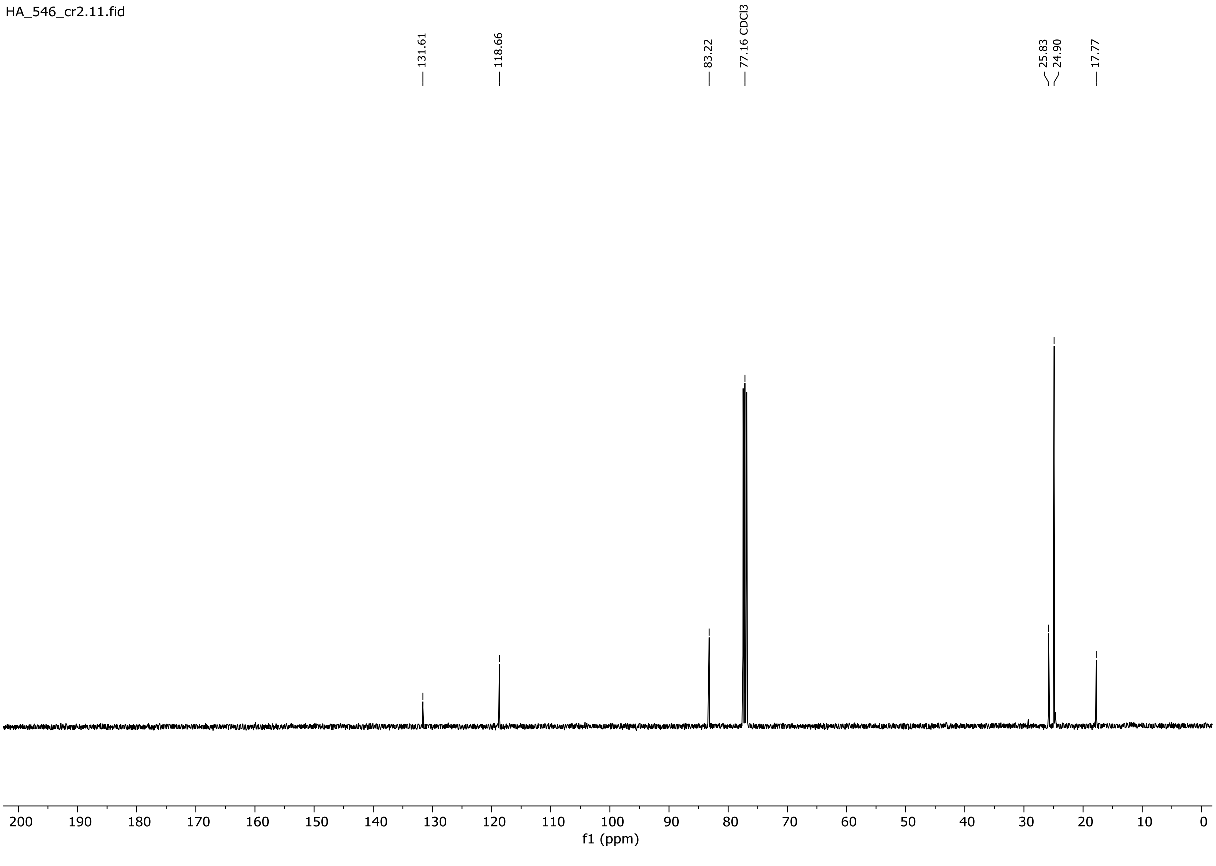
Compound S16: ^{13}C-NMR (126 MHz, DMSO-*d*$_{6,}$ 298 K)



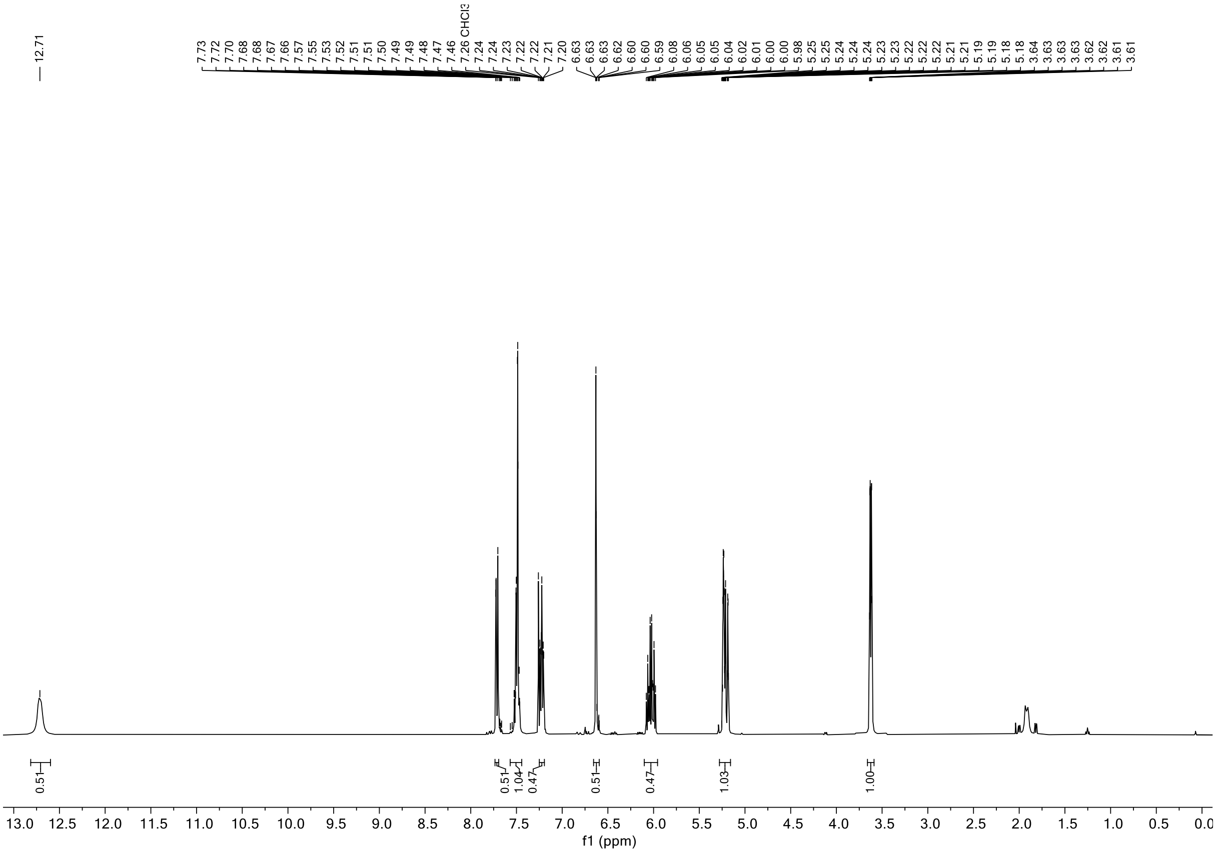
Compound S17: ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K)



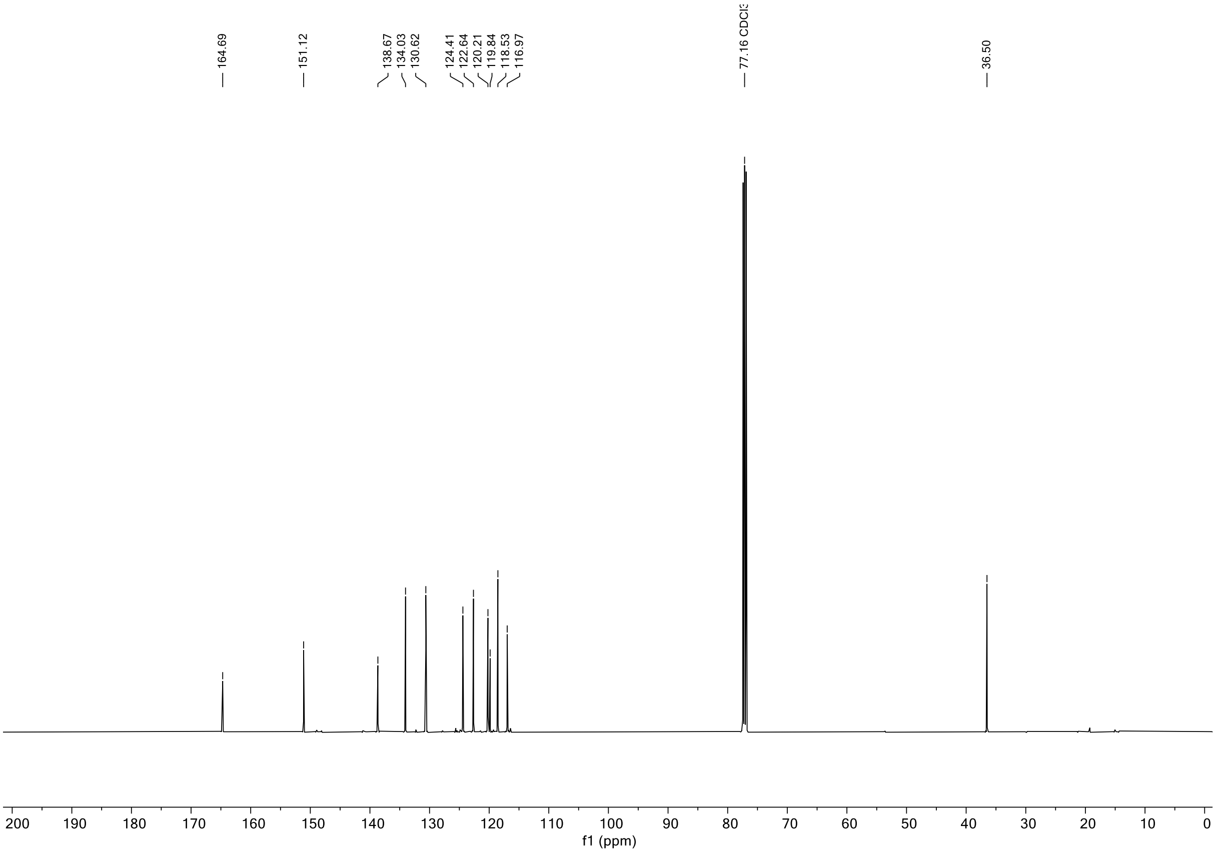
Compound S17: ^{13}C-NMR (101 MHz, $CDCl_3$, 298 K)



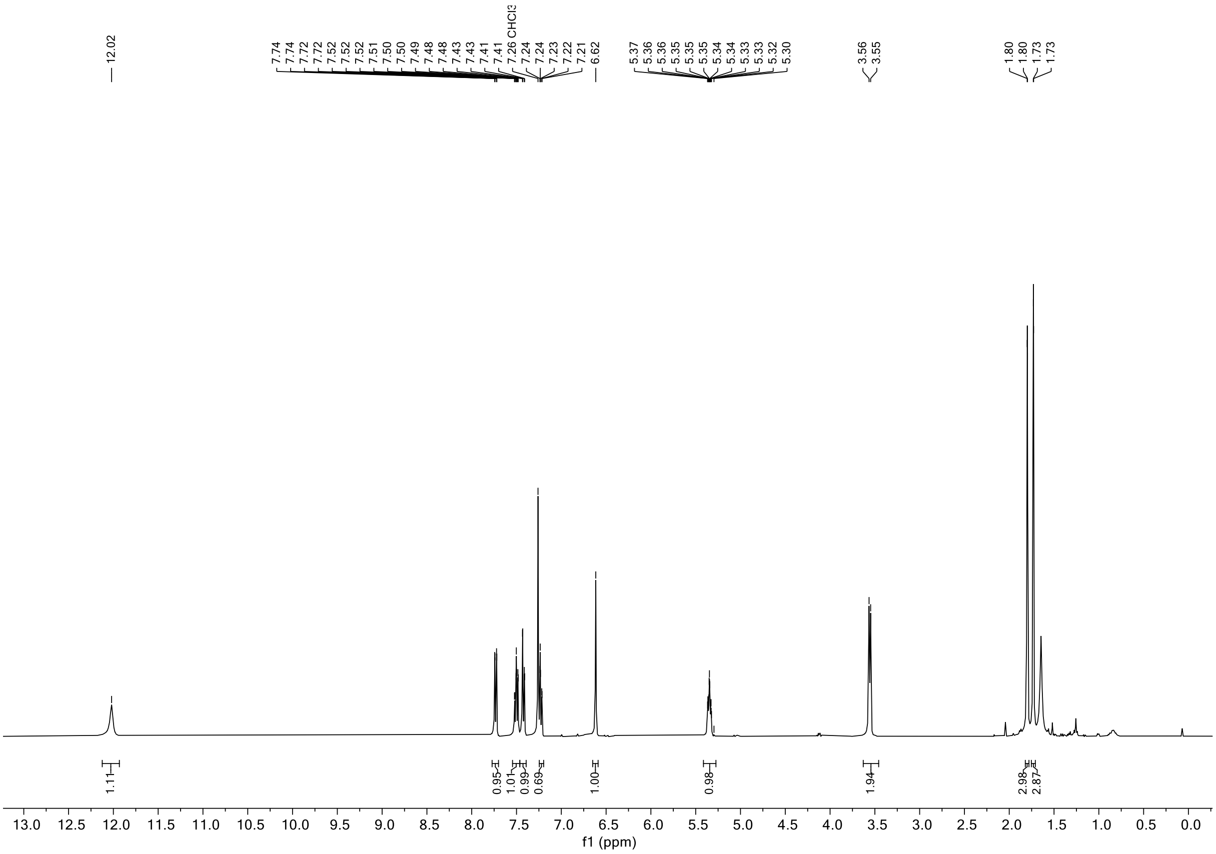
Compound 2a: ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K)



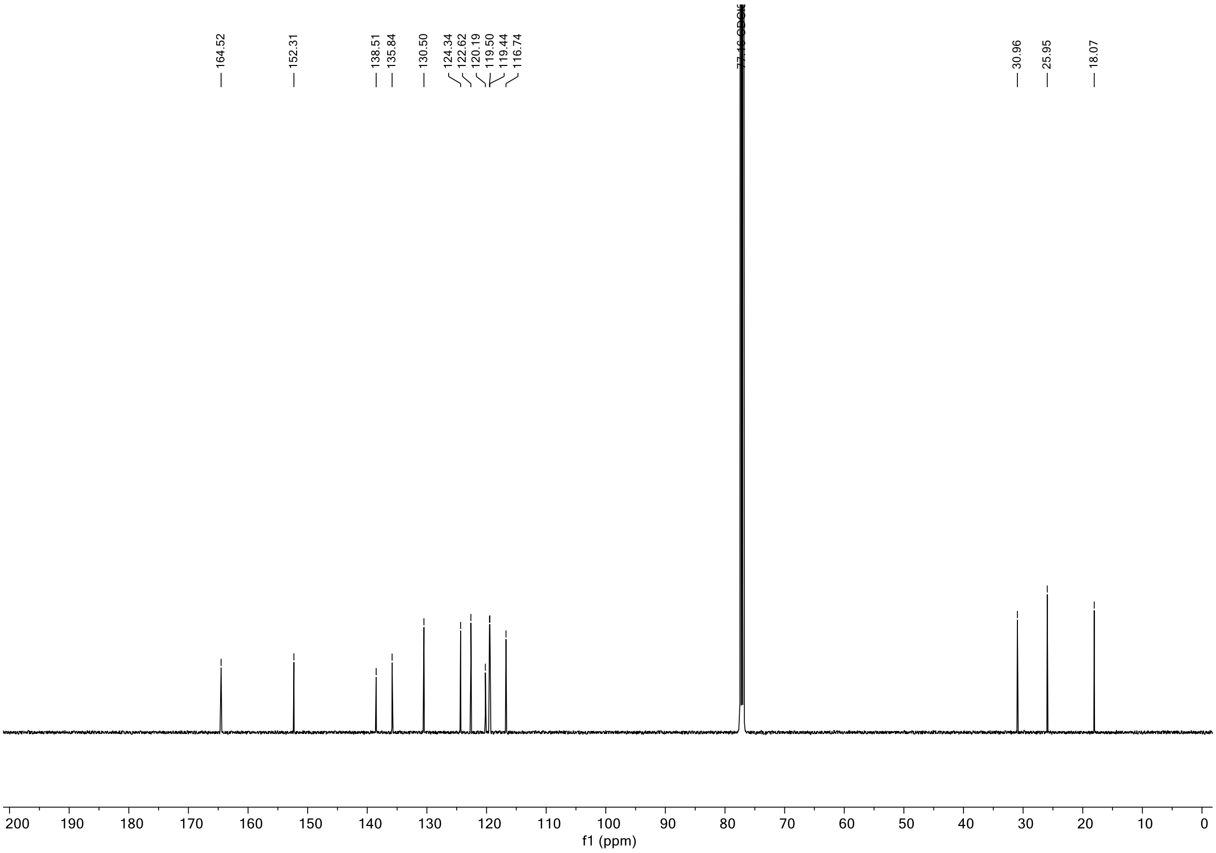
Compound 2a: ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K)



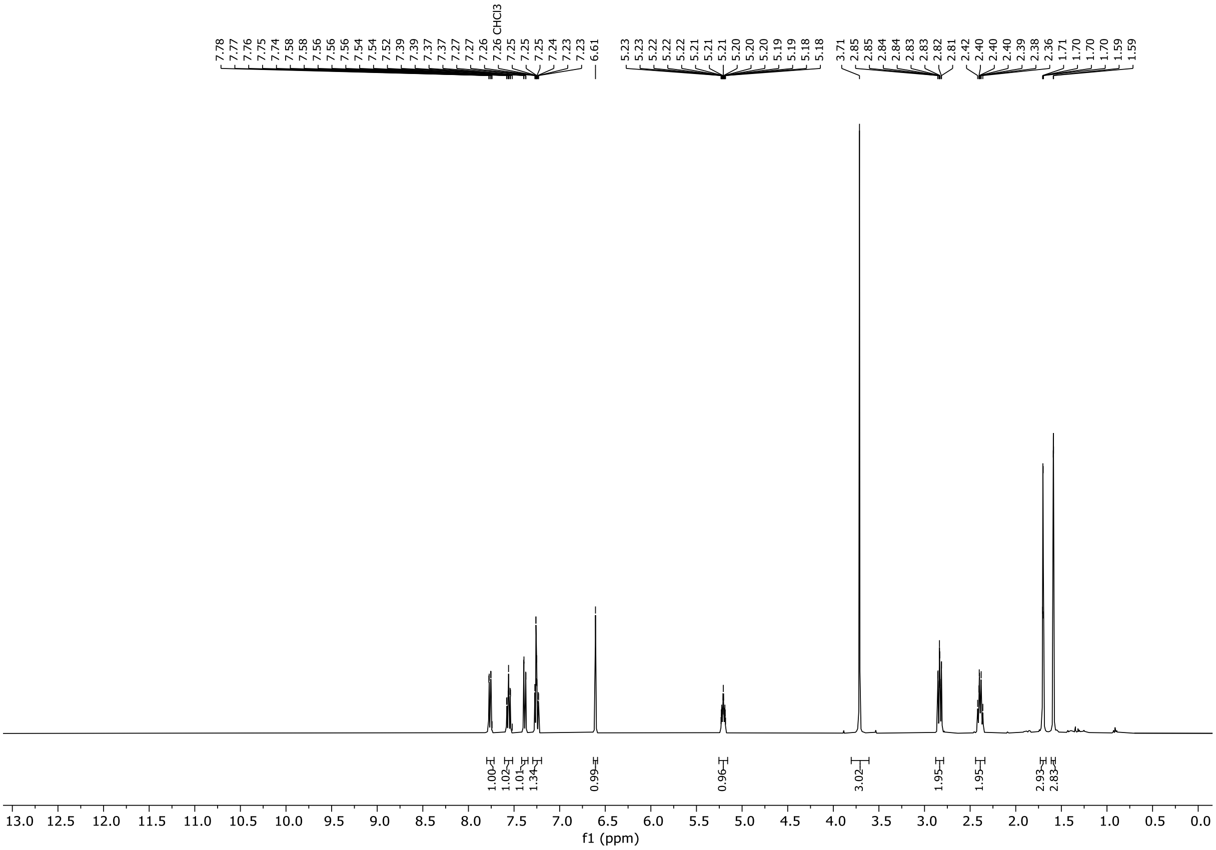
Compound 12a: ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K)



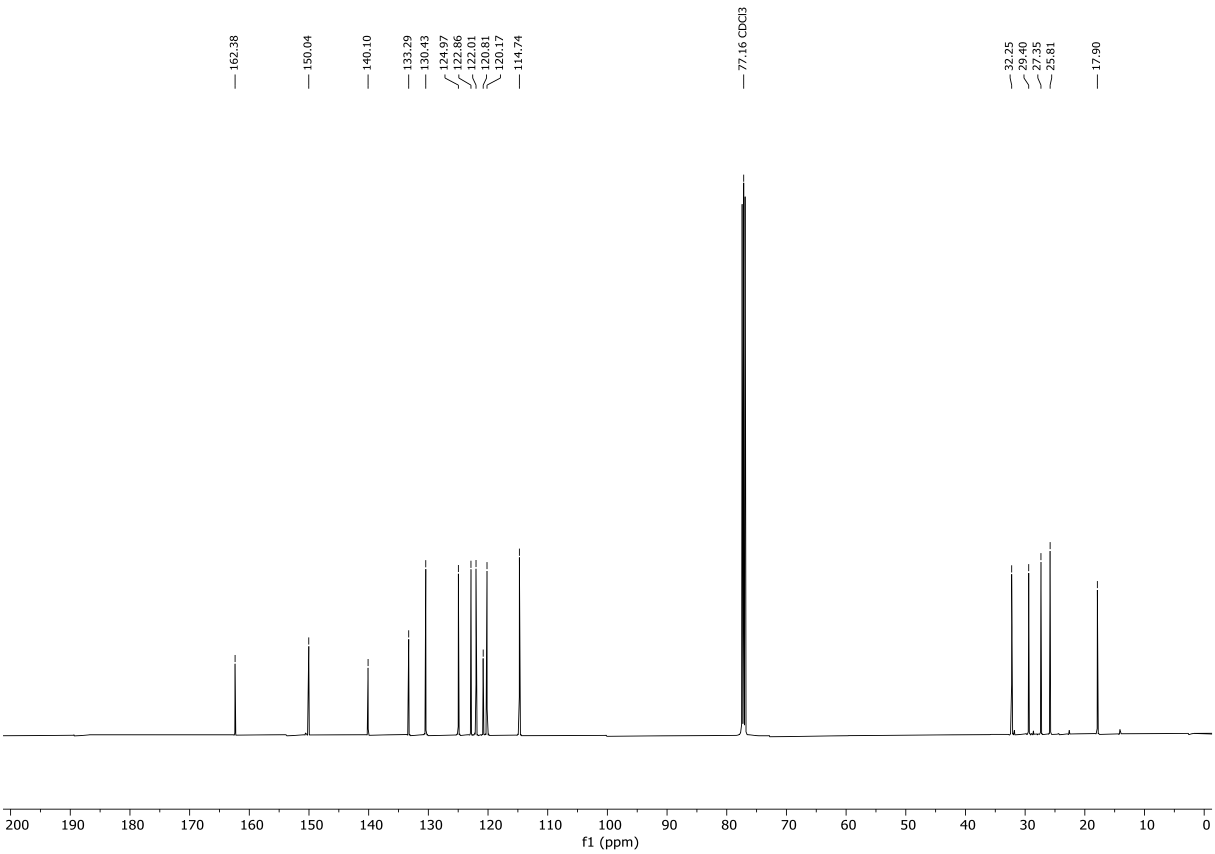
Compound 12a: ^{13}C-NMR (126 MHz, CDCl$_3$, 298 K)



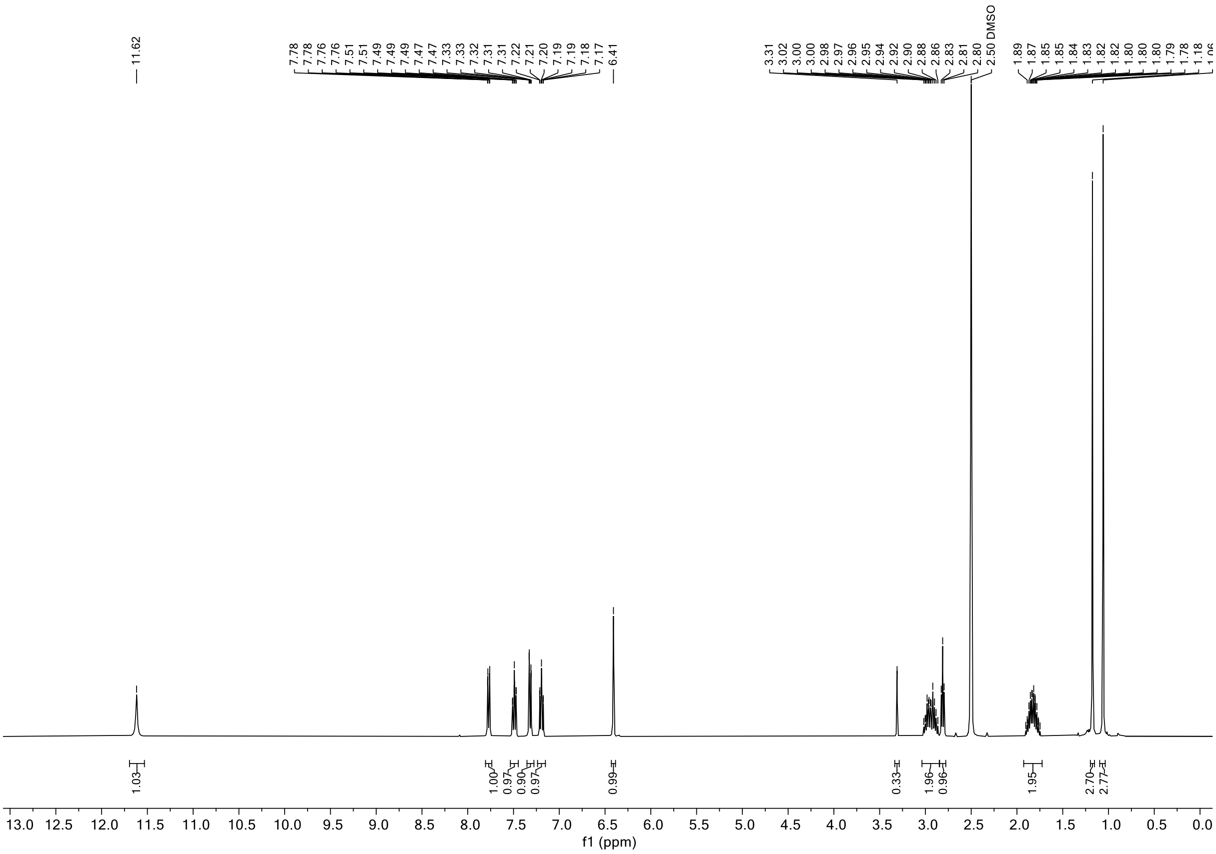
Compound 16: ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K)



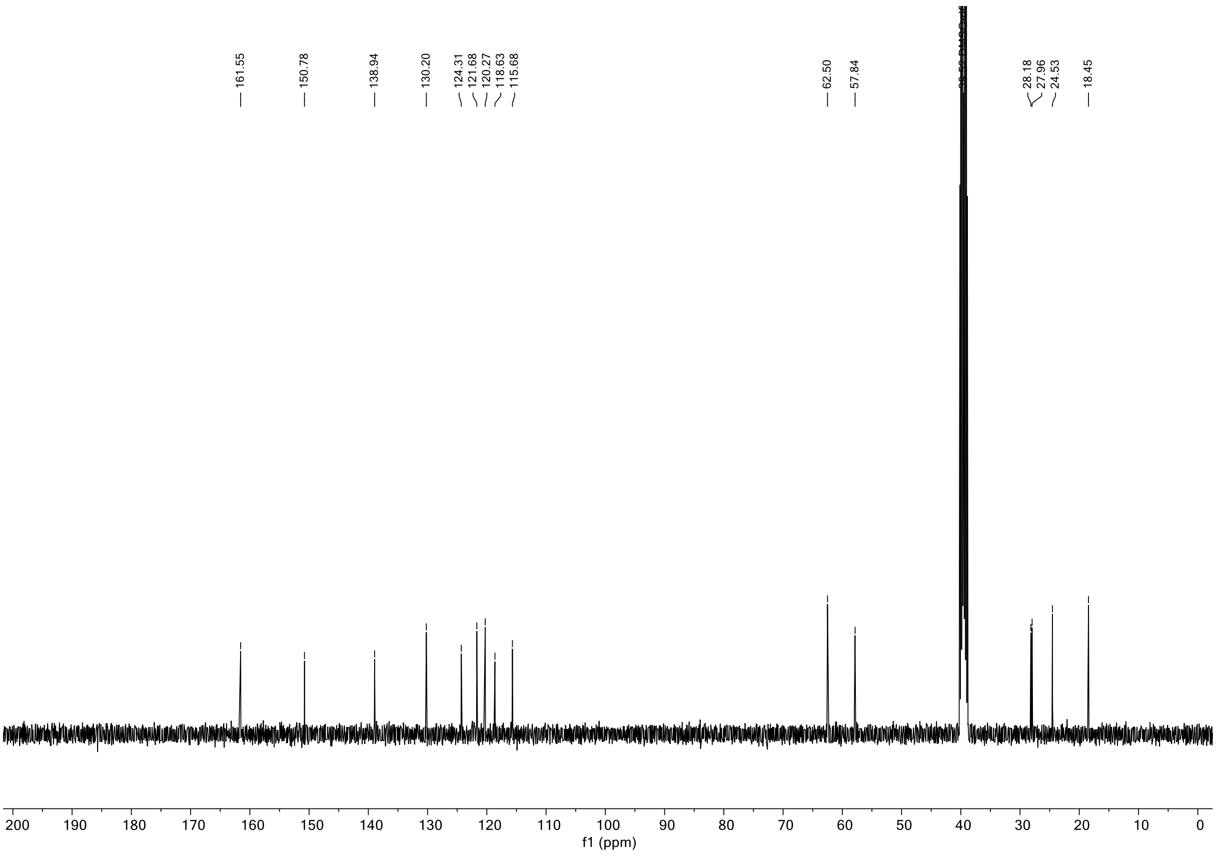
Compound 16: ^{13}C-NMR (126 MHz, CDCl$_3$, 298 K)



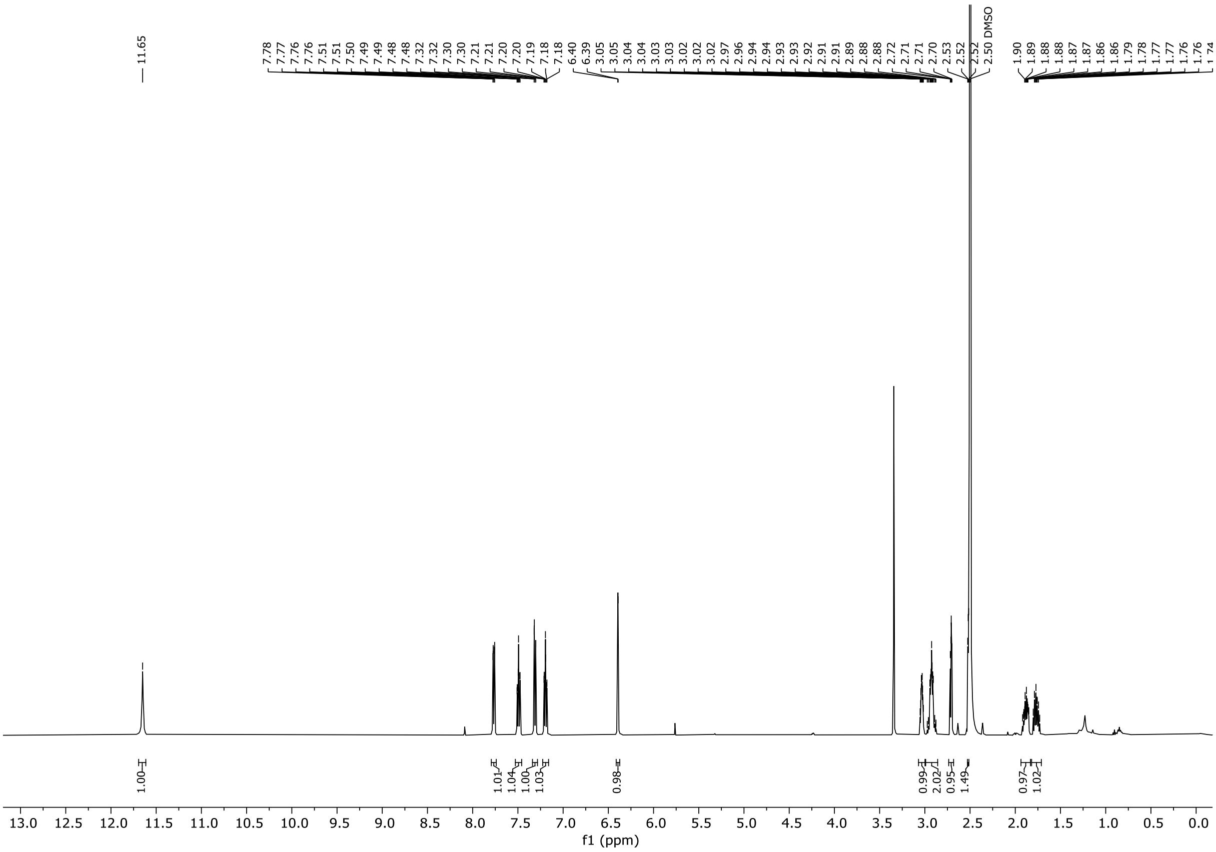
Compound 13b: ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K)



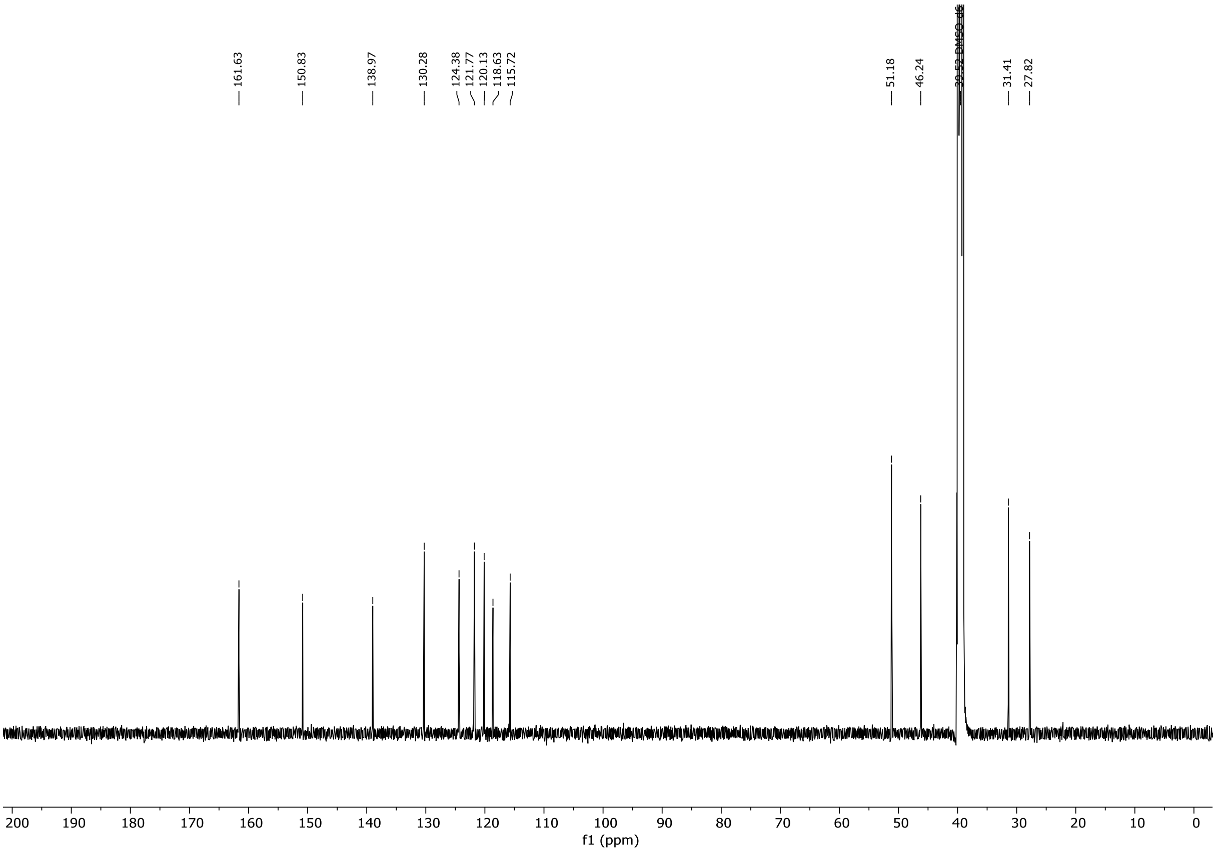
Compound 13b: ^{13}C-NMR (101 MHz, DMSO-d_6, 298 K)



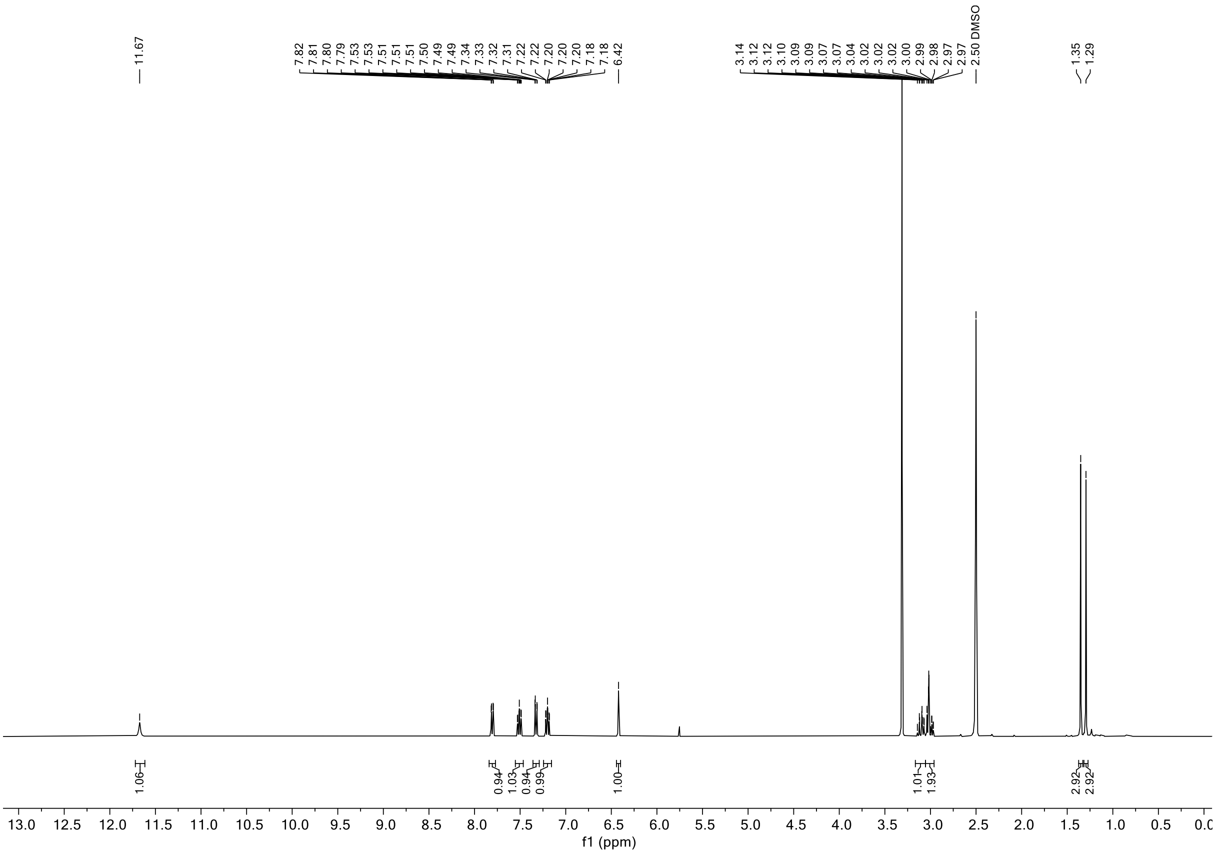
Compound 3b: ^{1}H-NMR (400 MHz, DMSO-$d_{6,}$ 298 K)



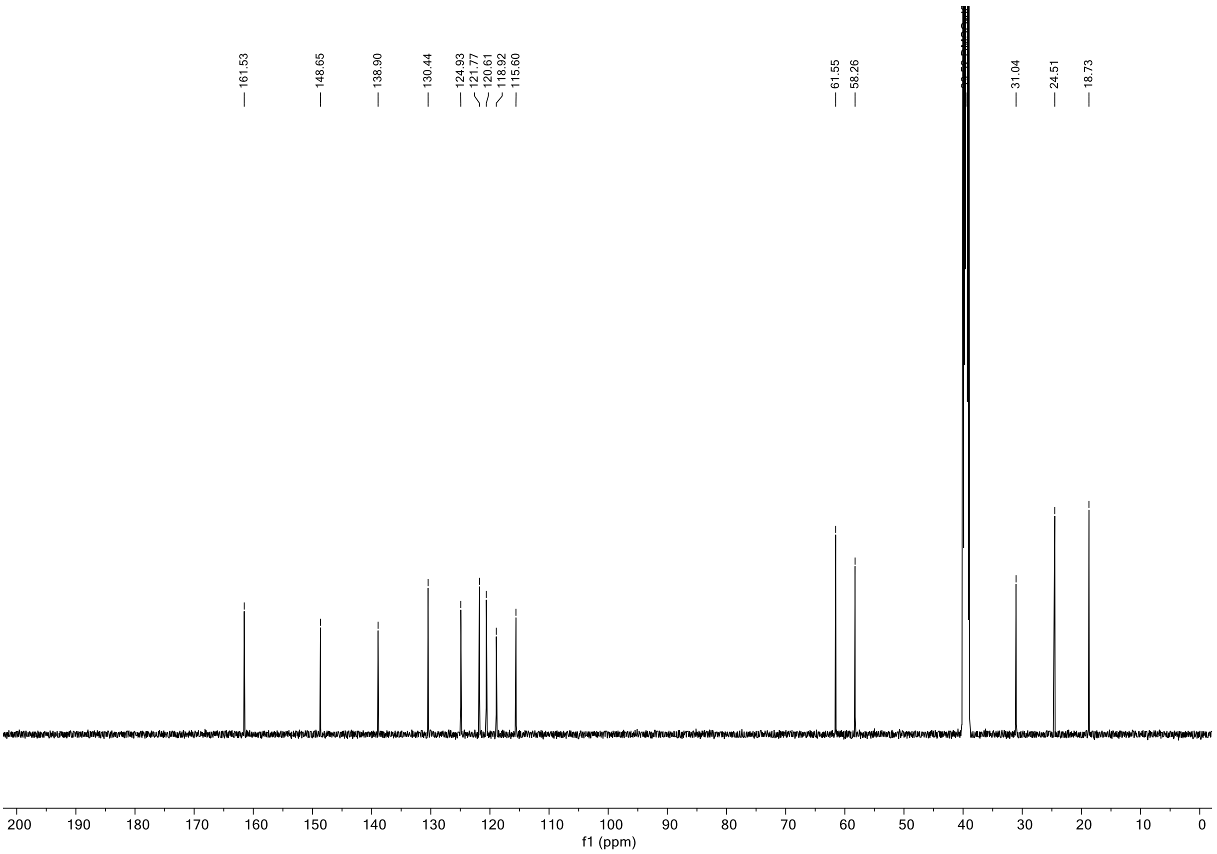
Compound 3b: ^{13}C-NMR (126 MHz, DMSO-$d_{6,}$ 298 K)



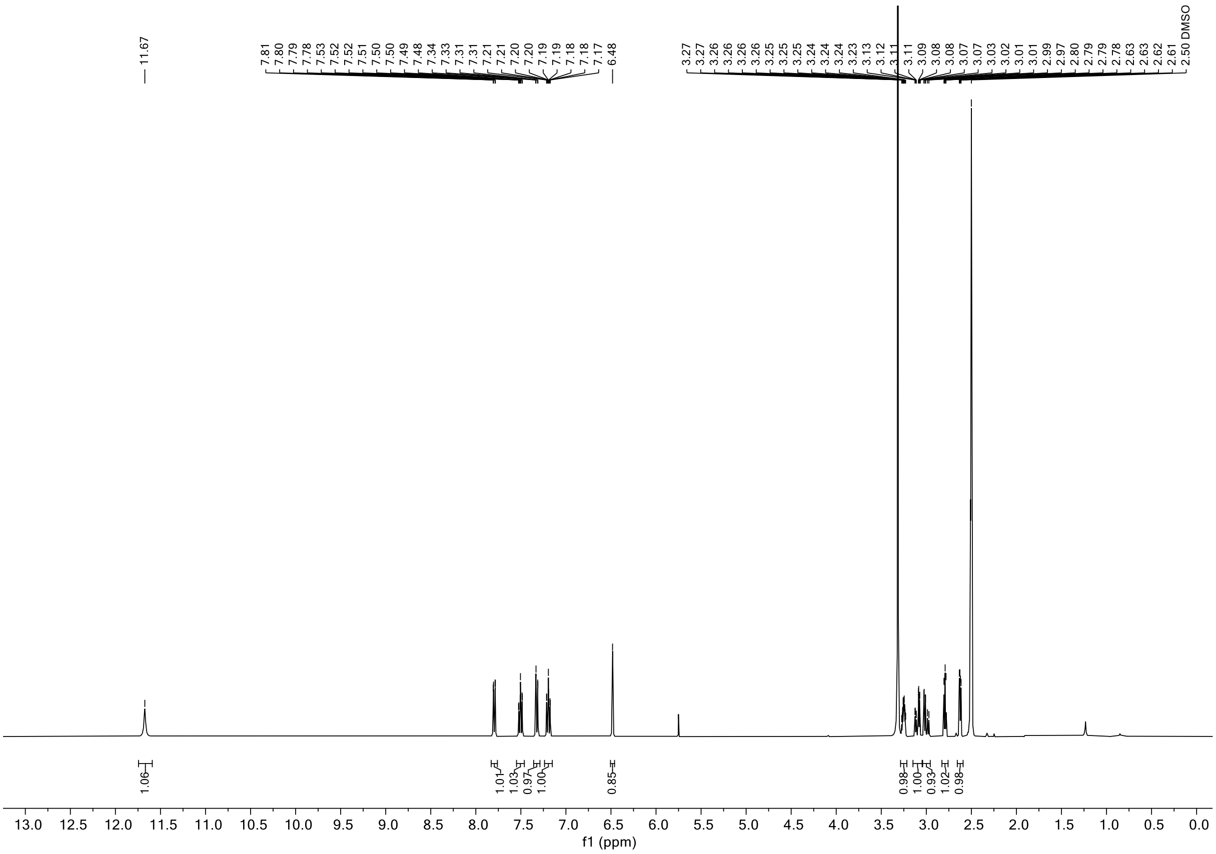
Compound 13a: ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K)



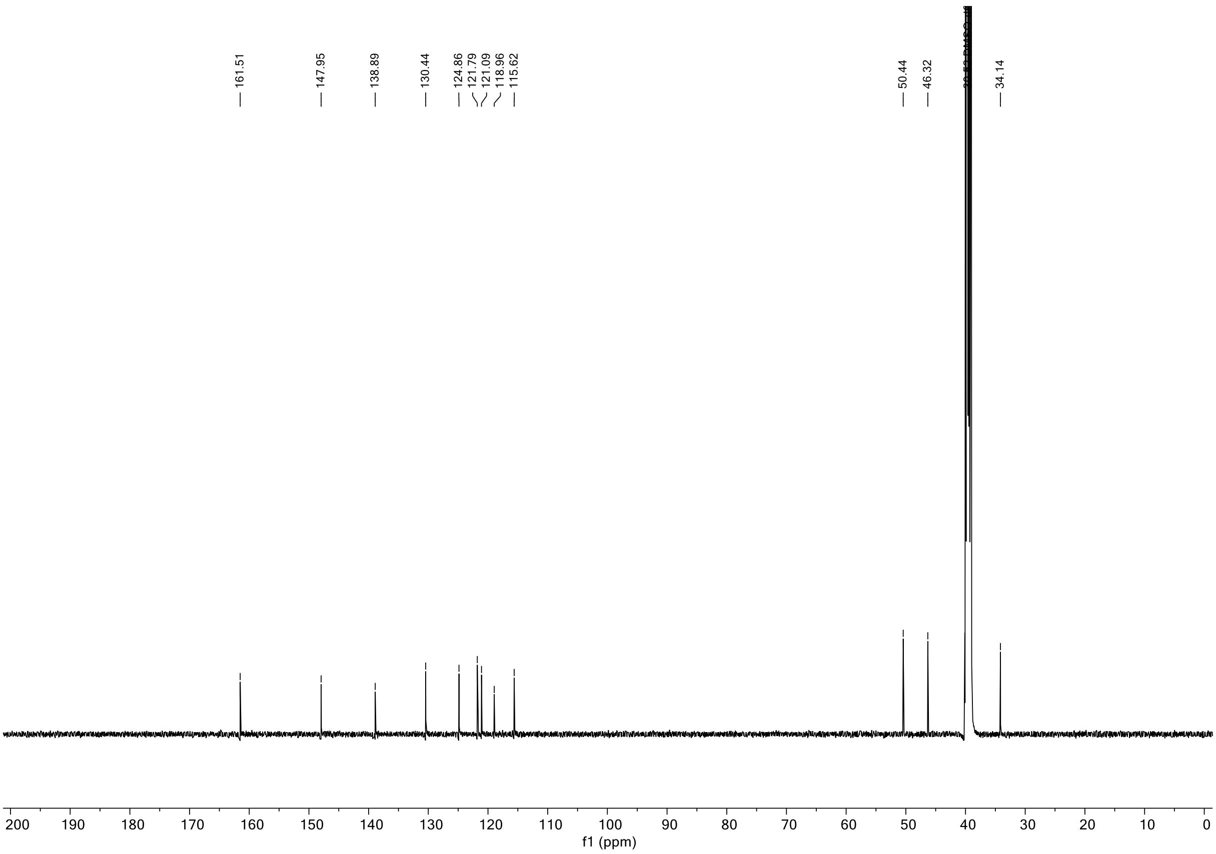
Compound 13a: ^{13}C-NMR (126 MHz, DMSO-d_6, 298 K)



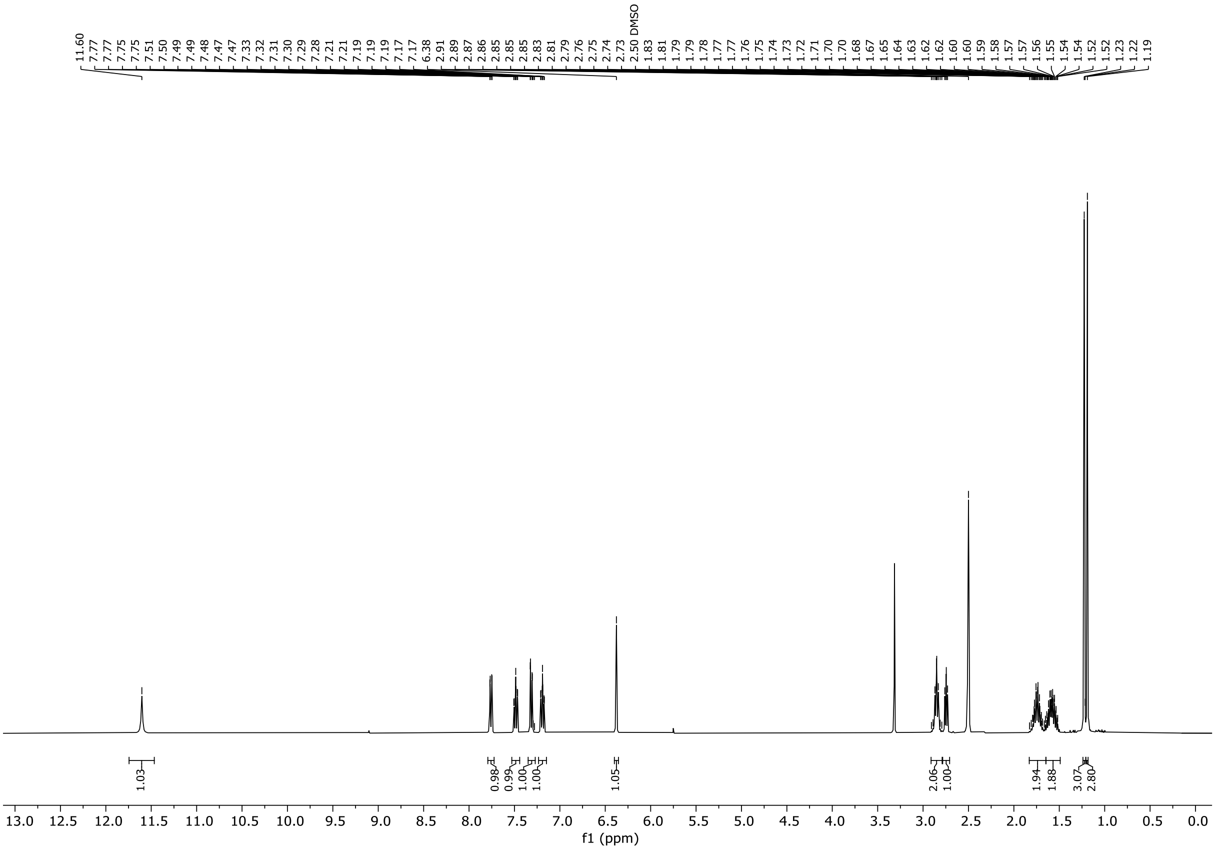
Compound 10a: ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K)



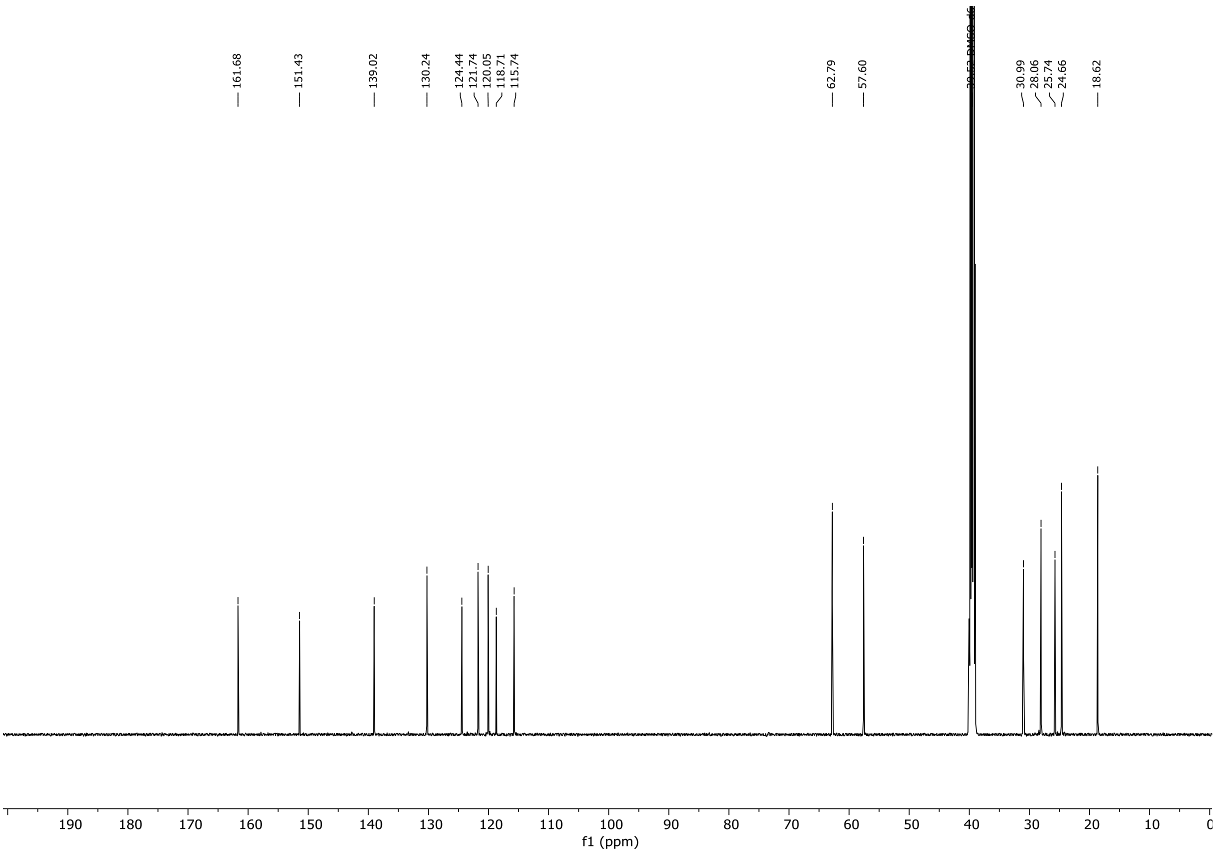
Compound 10a: ^{13}C-NMR (126 MHz, DMSO-d_6, 298 K)



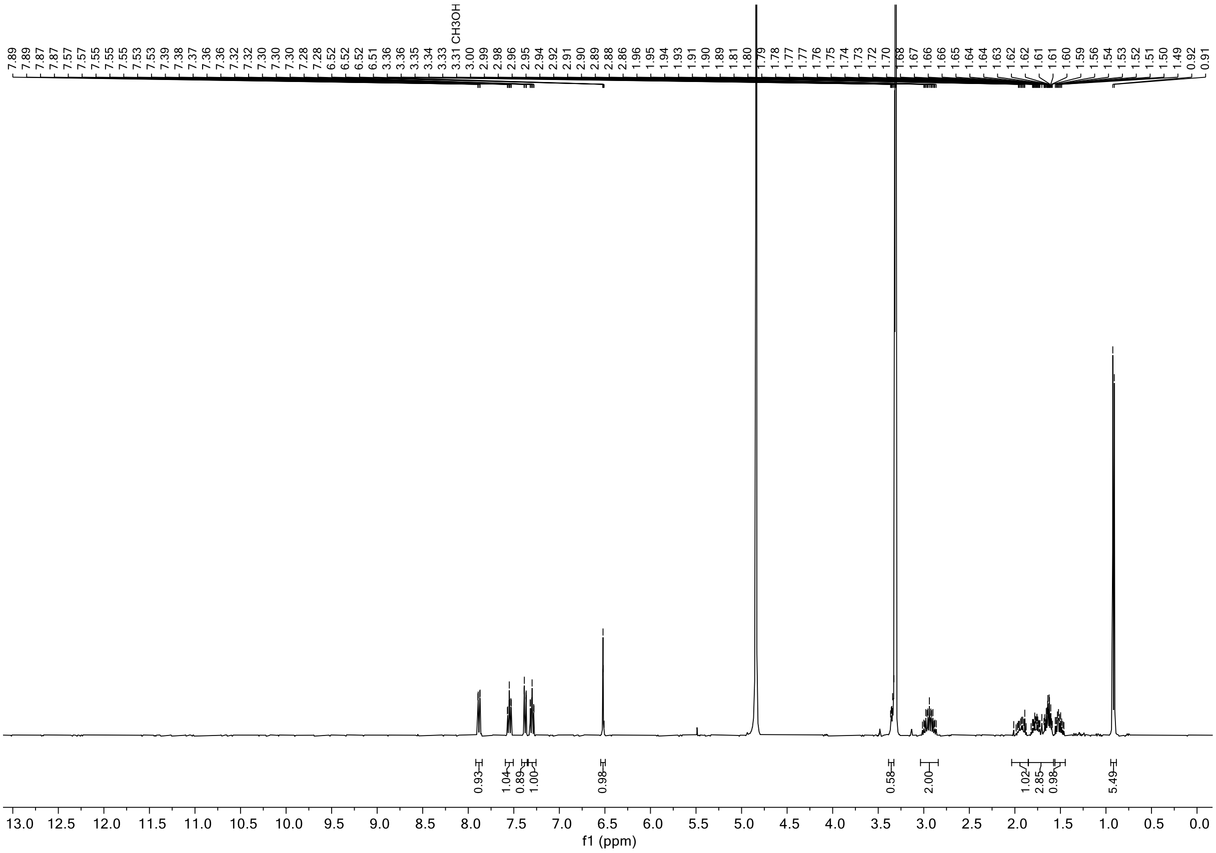
Compound 13c: ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K)



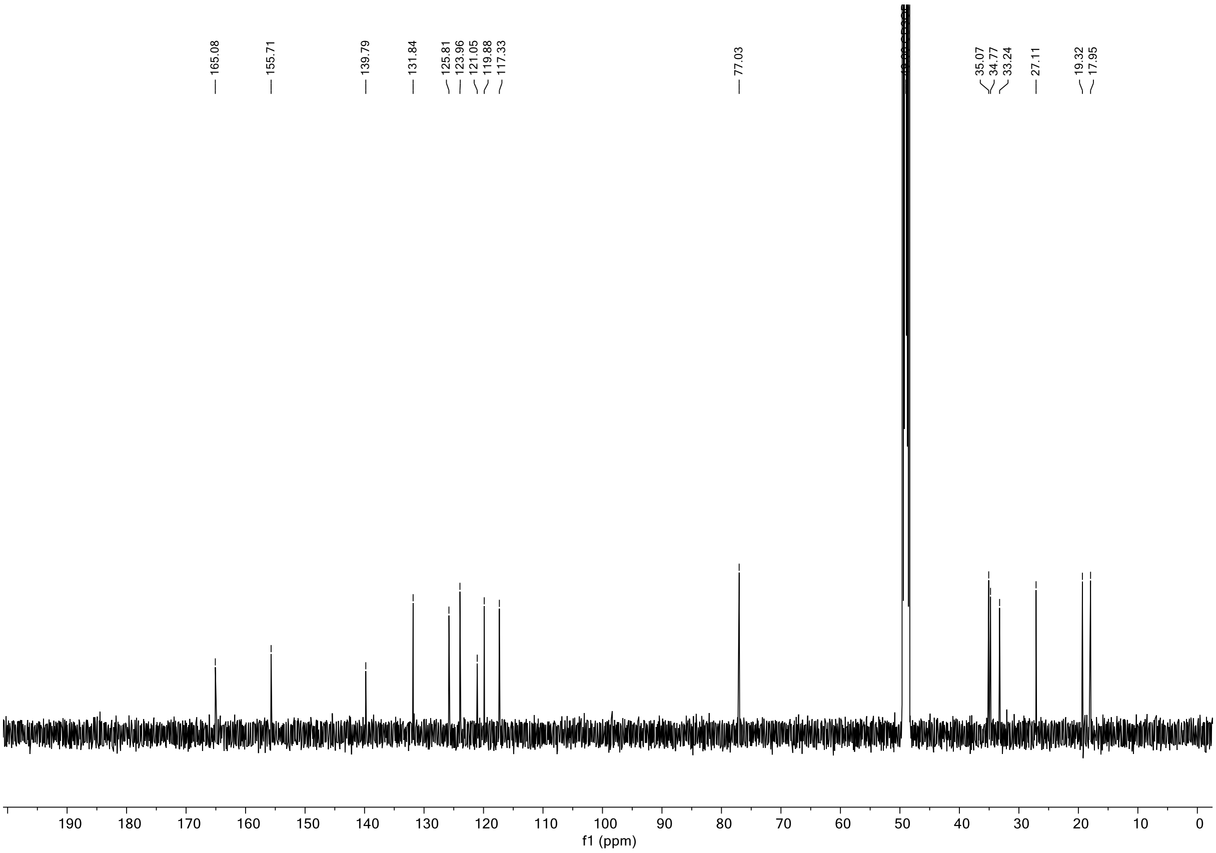
Compound 13c: ^{13}C-NMR (126 MHz, DMSO-d_6, 298 K)



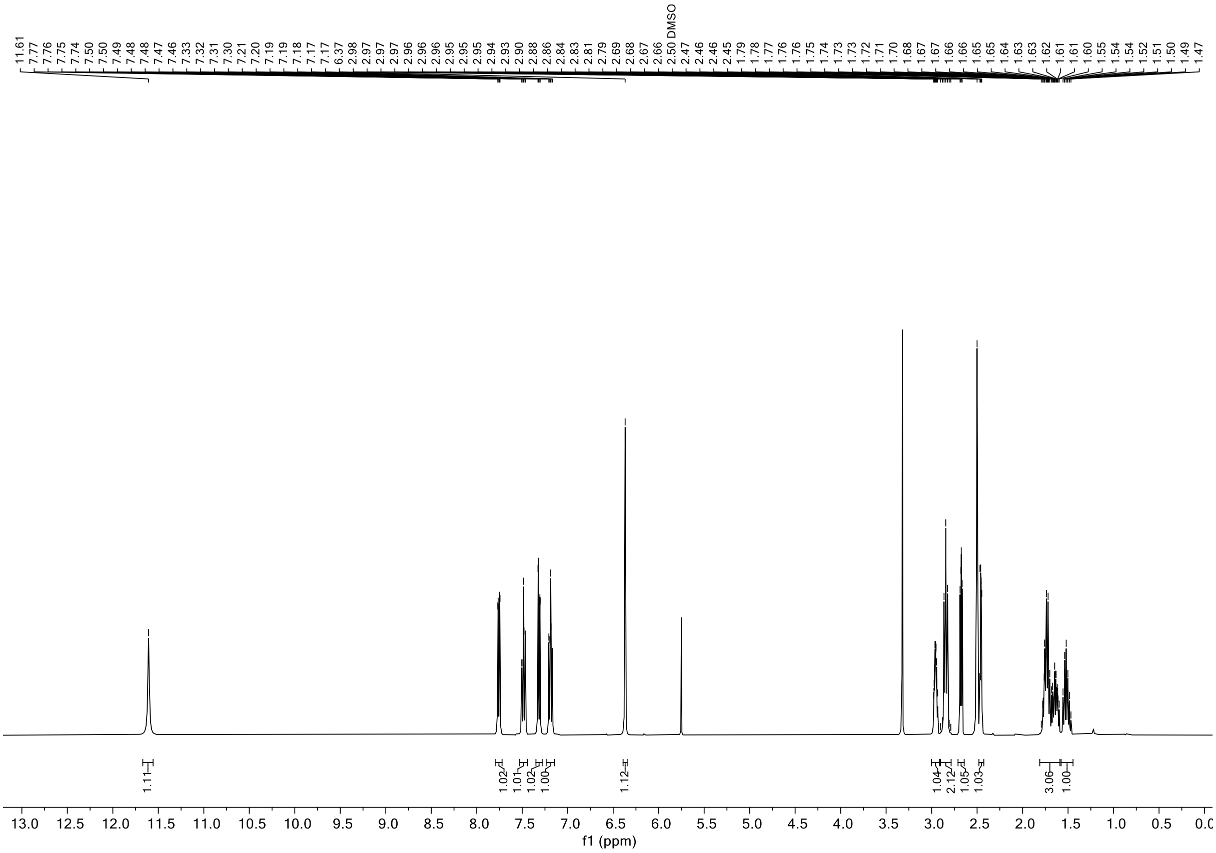
Compound 14: ^{1}H-NMR (400 MHz, CD_3OD, 298 K)



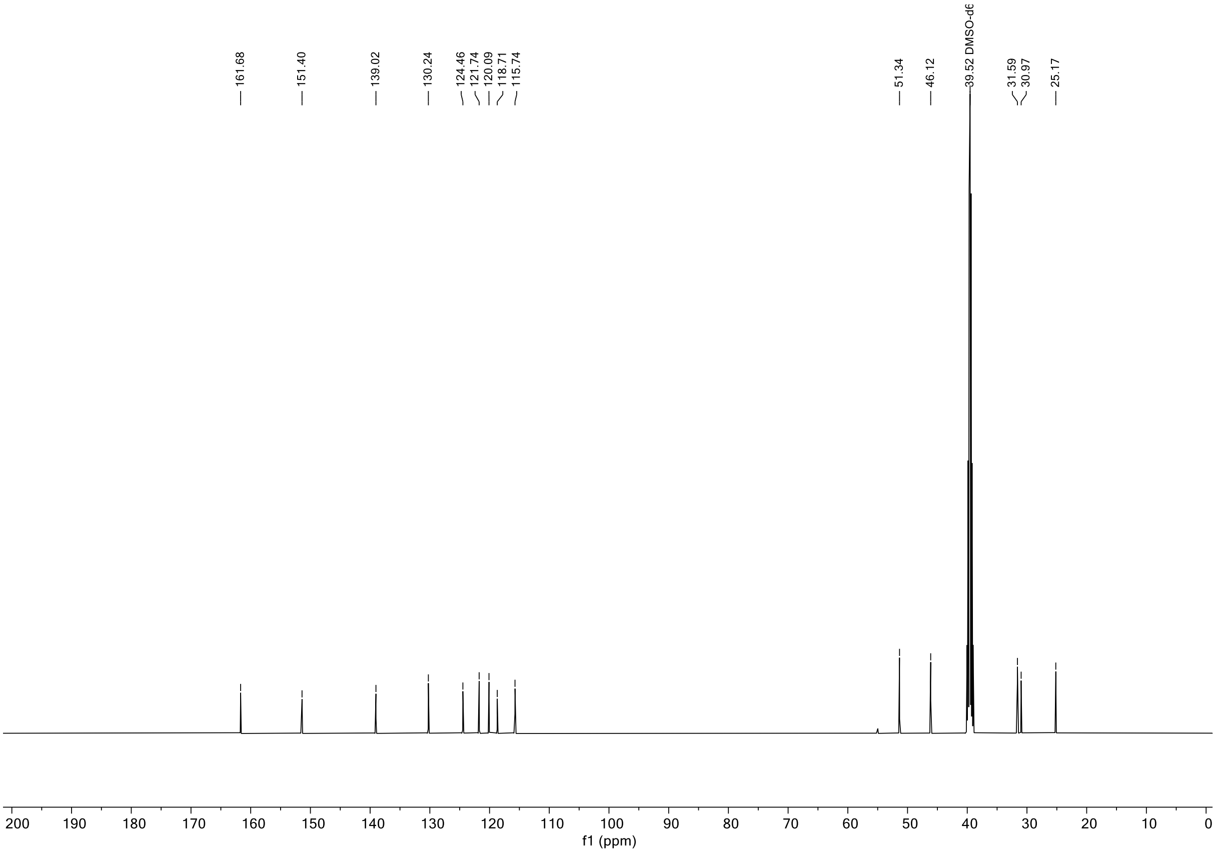
Compound 14: ^{13}C-NMR (126 MHz, CD_3OD, 298 K)



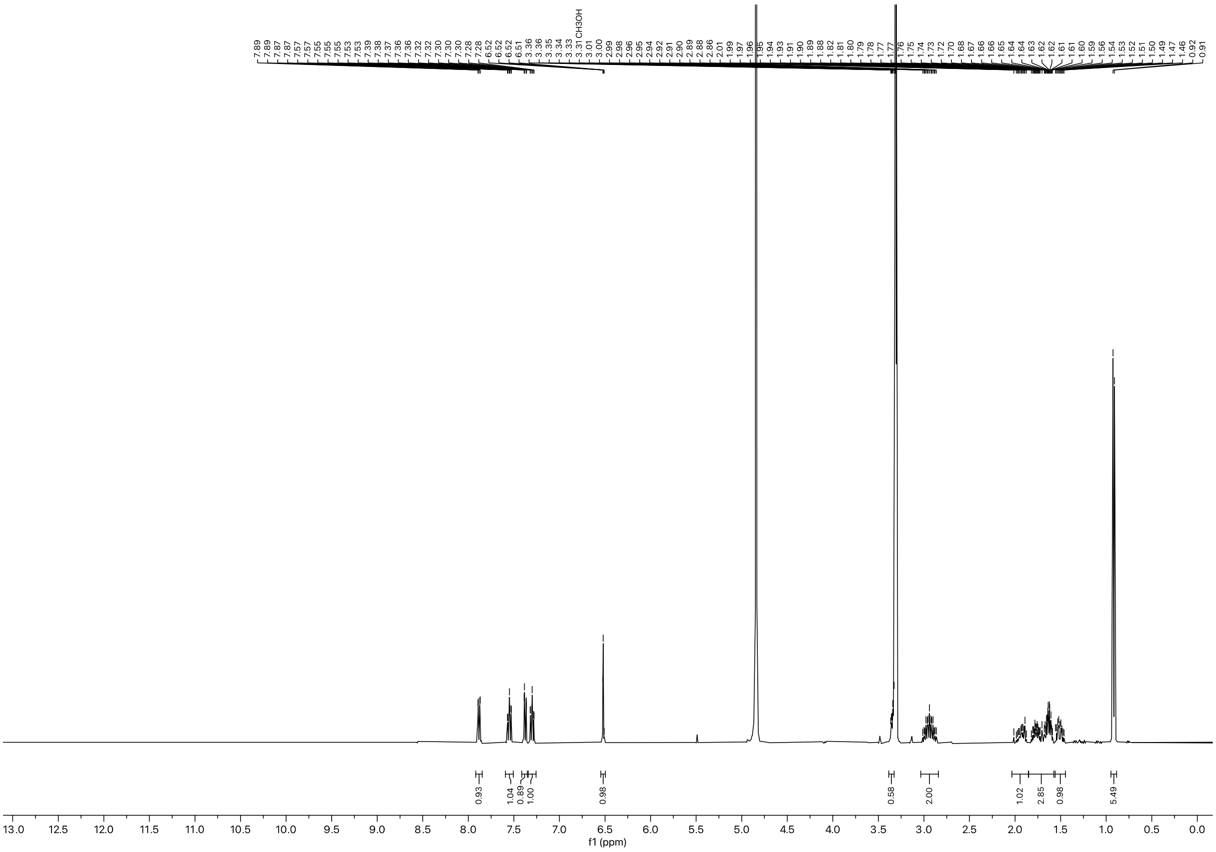
Compound 10c: ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K)



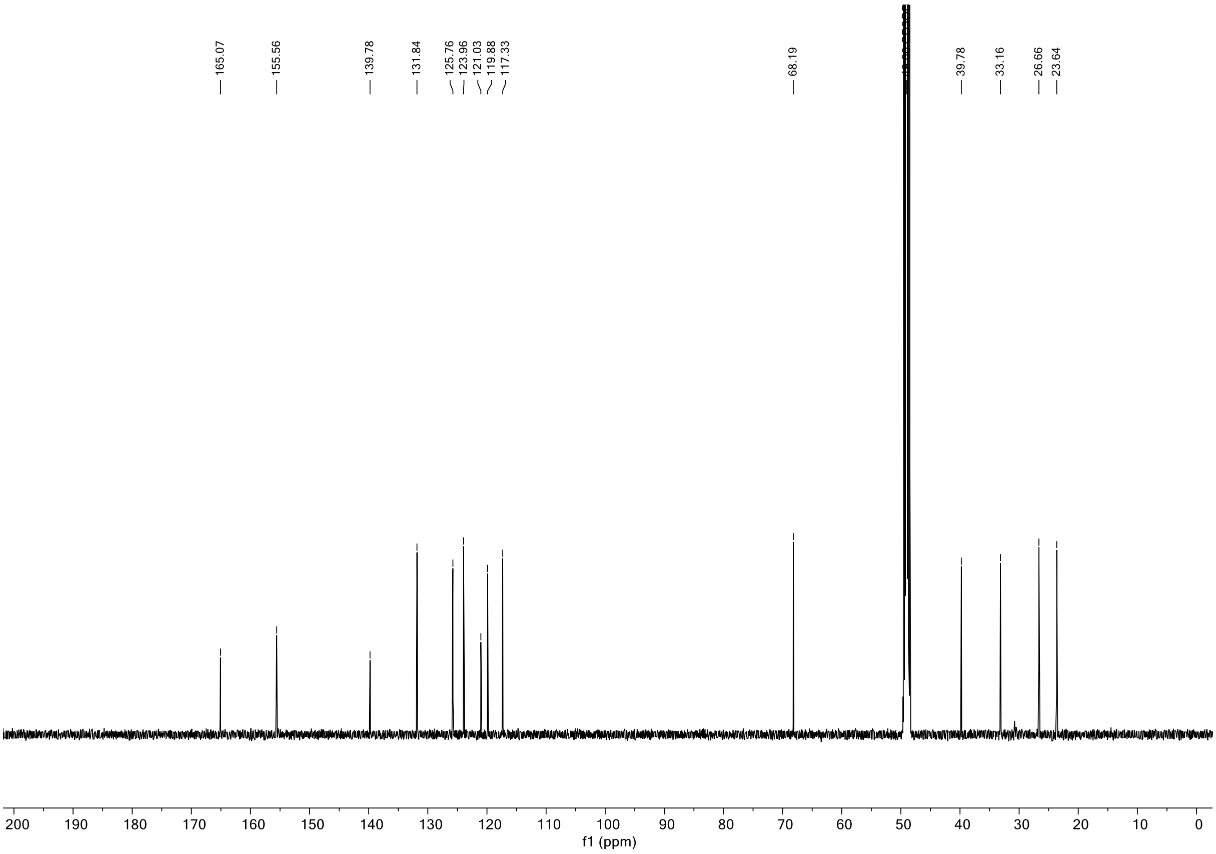
Compound 10c: ^{13}C-NMR (126 MHz, DMSO-d_6, 298 K)



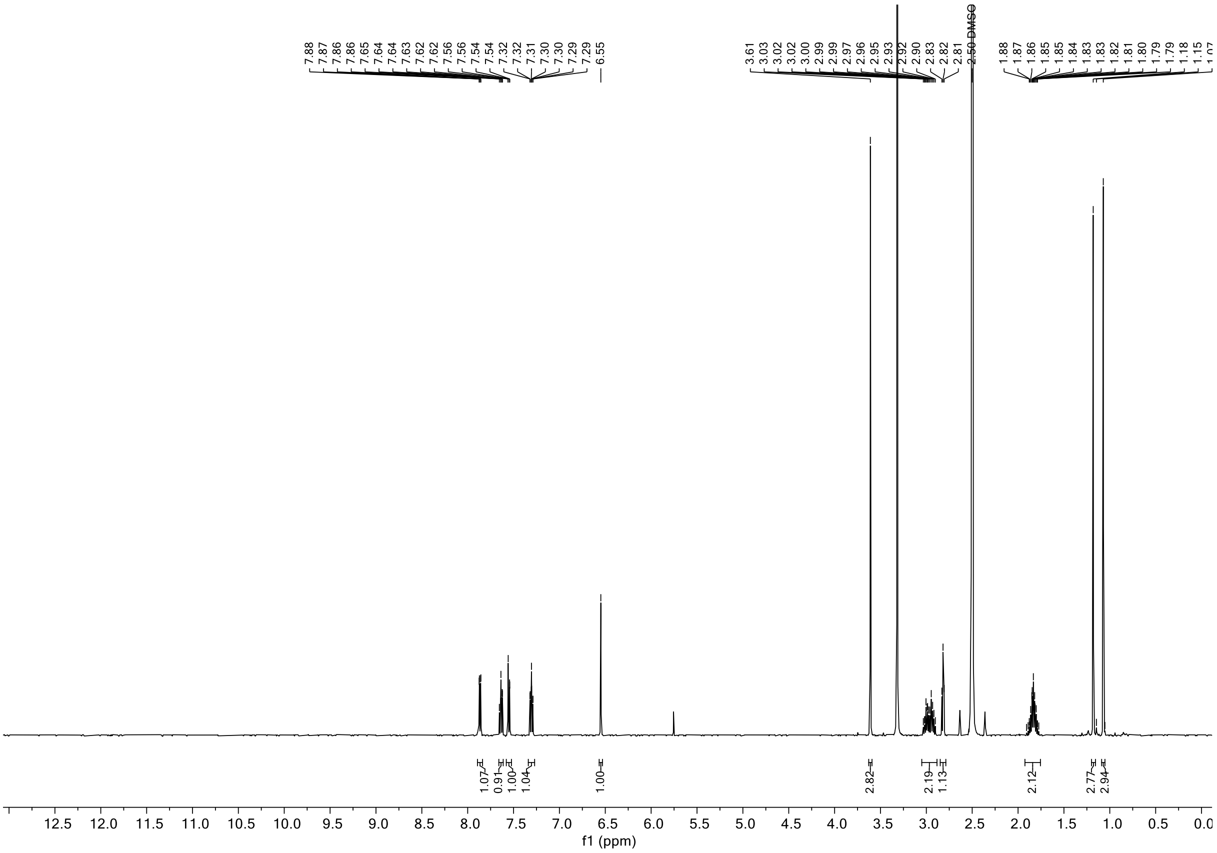
Compound 14: ^{1}H-NMR (400 MHz, CD$_3$OD, 298 K)



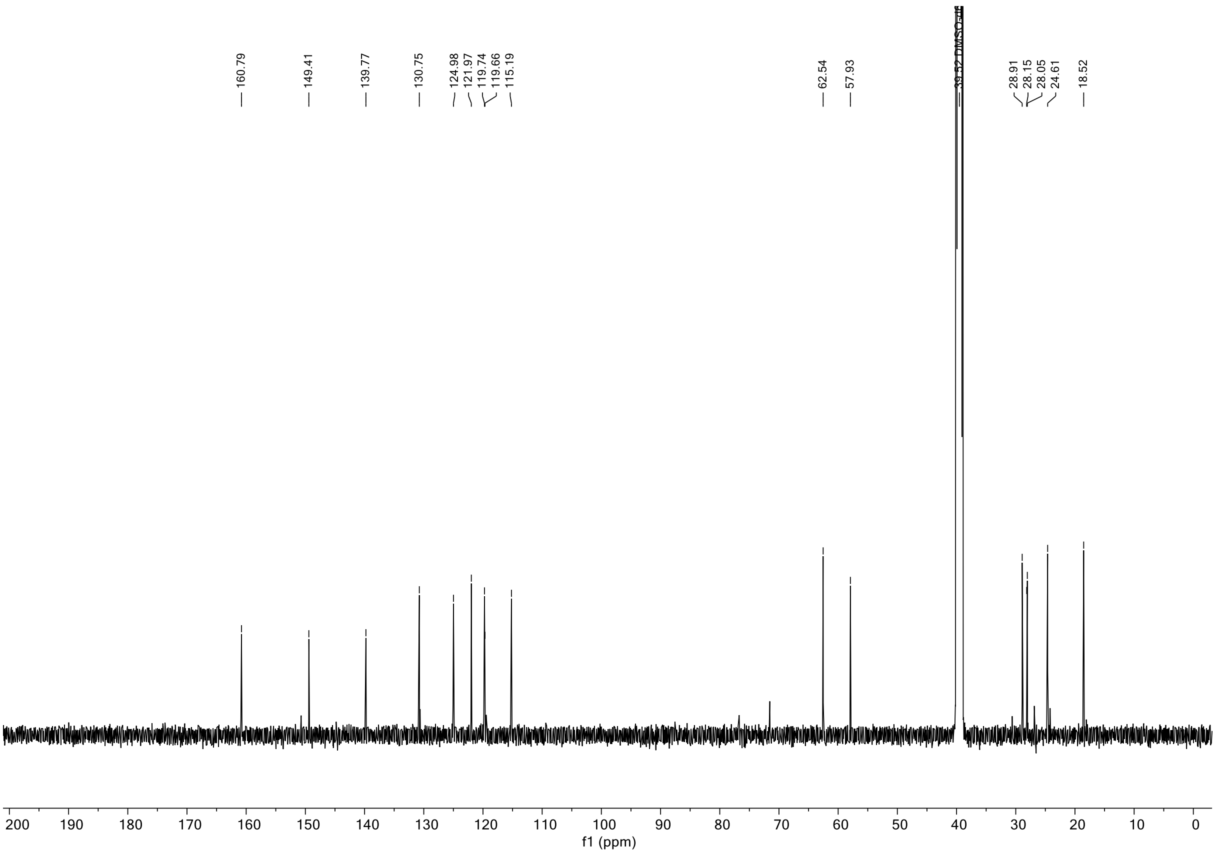
Compound 14: ^{13}C-NMR (126 MHz, CD$_3$OD, 298 K)



Compound 17: ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K)



Compound 17: ^{13}C-NMR (126 MHz, DMSO-d_6, 298 K)



7. Crystallographic Details

Single Crystal Structure Determination via 3D Electron Diffraction

(General remarks) Electrons feature very strong interactions with the electrostatic potential of atoms. Subsequently, electron diffraction allows for performing experiments with crystallites in the nanometer range. However, it needs to be considered that the absorption of the samples is much stronger and the data are affected by dynamical diffraction as well as ionic scattering factors compared to X-ray diffraction. This can lead to seemingly bad R-values for the refinement in the simplistic kinematic approximation.

Electron diffraction measurements for **13b** were collected using the Rigaku XtaLAB Synergy-ED, equipped with a Rigaku HyPix-ED detector optimized for operation in the continuous rotation 3D-ED experimental setup.[18] Data acquisition was performed at ambient temperature under high vacuum with an electron wavelength of 0.0251 Å (200 kV). The instrument was operated and the diffraction data were processed in the program CrysAlis^{Pro}.[19] A multi-scan absorption correction was performed using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm in CrysAlis^{Pro}. The structure was solved using ShelXT,[20] and subsequently, refined with kinematical approximation using ShelXL[21] in the crystallographic program suite Olex2.[22,23] Since we wanted to conduct dynamical refinement to determine the absolute configuration of **13b**, a single dataset with as much completeness as possible was collected and thus used for refinement; instead of collecting several datasets followed by data merging for full data completeness. For initial kinematical refinement, non-hydrogen atoms were assigned isotropic displacement parameters. The hydrogen atoms bonded to nitrogen atoms were located from Fourier difference maps. Other hydrogen atoms were placed in idealized positions and included as riding. Isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with $U_{iso}(H) = 1.2\ U_{eq}$(parent atom). The experimental and refinement details are given below. CCDC 2296673 contains the supplementary crystallographic data for this publication. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Microcrystalline powder of **13b** was spread on a standard continuous-carbon-coated copper TEM grid. A colourless plate-like crystallite with a few 100 nm thickness was selected for 3D-ED/microED measurement.

Table 2: Data collection parameter overview.

Compound	Scan range [°]	Scan width [°]	Number of frames	Exposure time/frame [s]	Total exposure time [s]	Dose rate [e$^-$/(Å^2·s)]	Dose [e$^-$/(Å^2)]
13b	-70 to +75	0.25	580	0.25	145	1.14E-03	0.17

Crystal data for **13b**: CCDC 2296673, colourless plate, $C_{15}H_{17}NO_2$, M_r = 243.30 gmol^{-1}, monoclinic, space group $P2_1$ (No. 4), a = 10.15(18) Å, b = 9.0(2) Å, c = 14.3(2) Å, α = 90°, β = 97.0(4)°, γ = 90°, V = 1297(41) Å^3, Z = 4, Z' = 2, T = 293 K, *m*(transmission electron microscope) = 0.000, 8174 total reflections, 1273 with $I_0 > 2\sigma(I_0)$, resolution = 0.80 Å, completeness = 95.1%, redundancy = 3.0, R_{int} = 0.168, R_{pim} = 0.122, *CC1/2* = 0.999, 5042 data, 126 parameters, 12 restraints, GOF = 1.060, R_1 = 0.1800 and wR_2 = 0.4057 [$I_0 > 2\sigma(I_0)$], R_1 = 0.3576 and wR_2 = 0.4926 (all reflections), $0.153 < d\Delta\rho < -0.129$.

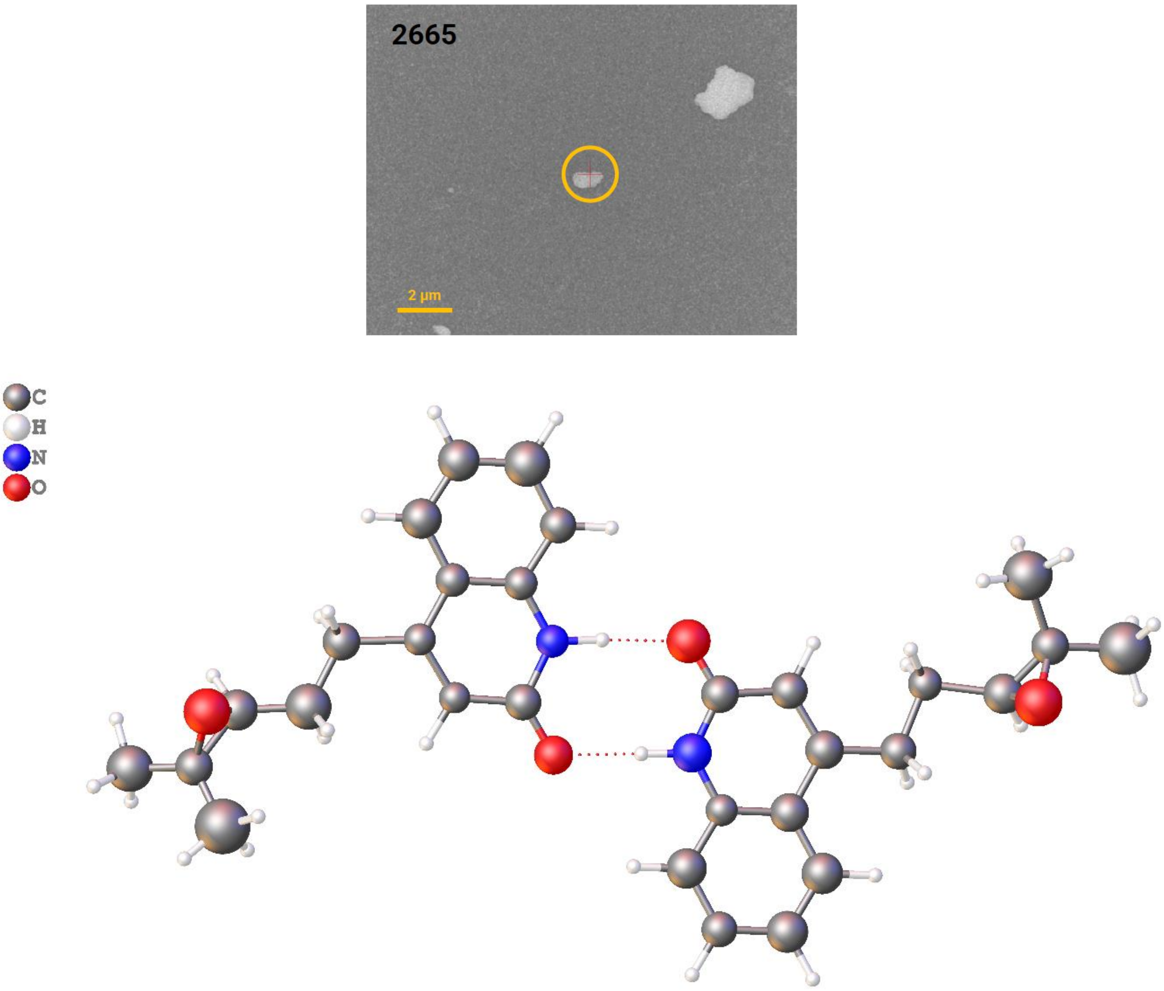


Figure 1: (Top) Transmission electron microscope image, and (bottom) the asymmetric unit of **13b** showing two molecules forming dimeric pairs. Red dotted lines represent N–H…O hydrogen bonding.

Table 3: Comparison of both enantiomers. The absolute configuration of 13b was determined by dynamical refinement[24] using the program suite Jana2020.[25] A background noise-adjusted z-score of 4.56 was computed in favor for the S-enantiomer.[26]

Enantiomer	Refinement	R_{obs}	wR_{obs}	R_{all}	wR_{all}	$\mathrm{GOF}_{\mathrm{obs}}$	$\mathrm{GOF}_{\mathrm{all}}$
***R*-form**	dynamical	12.92	35.52	28.57	48.04	1.99	1.02
***S*-form**	dynamical	11.61	33.78	27.30	46.99	1.88	1.00

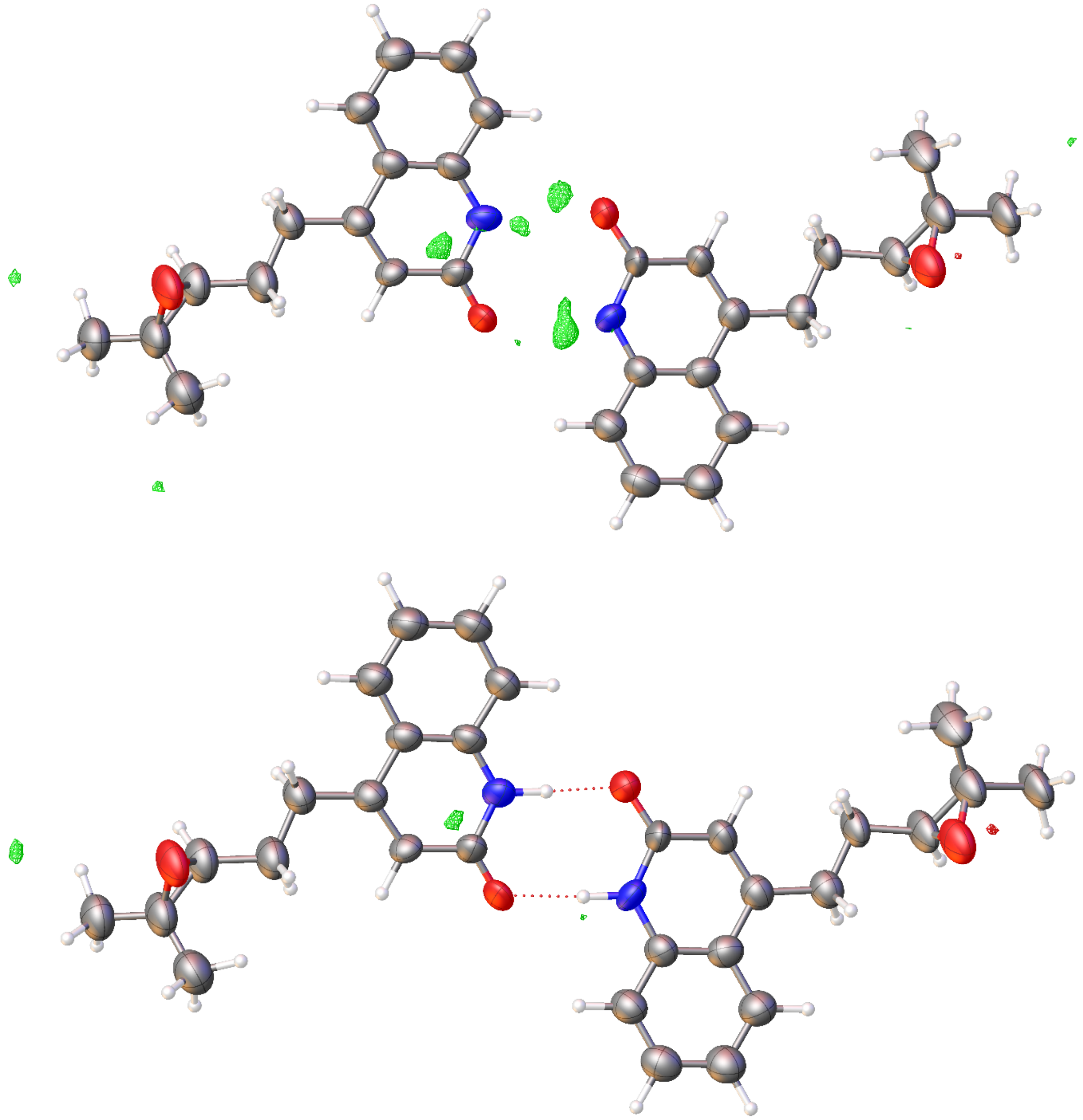


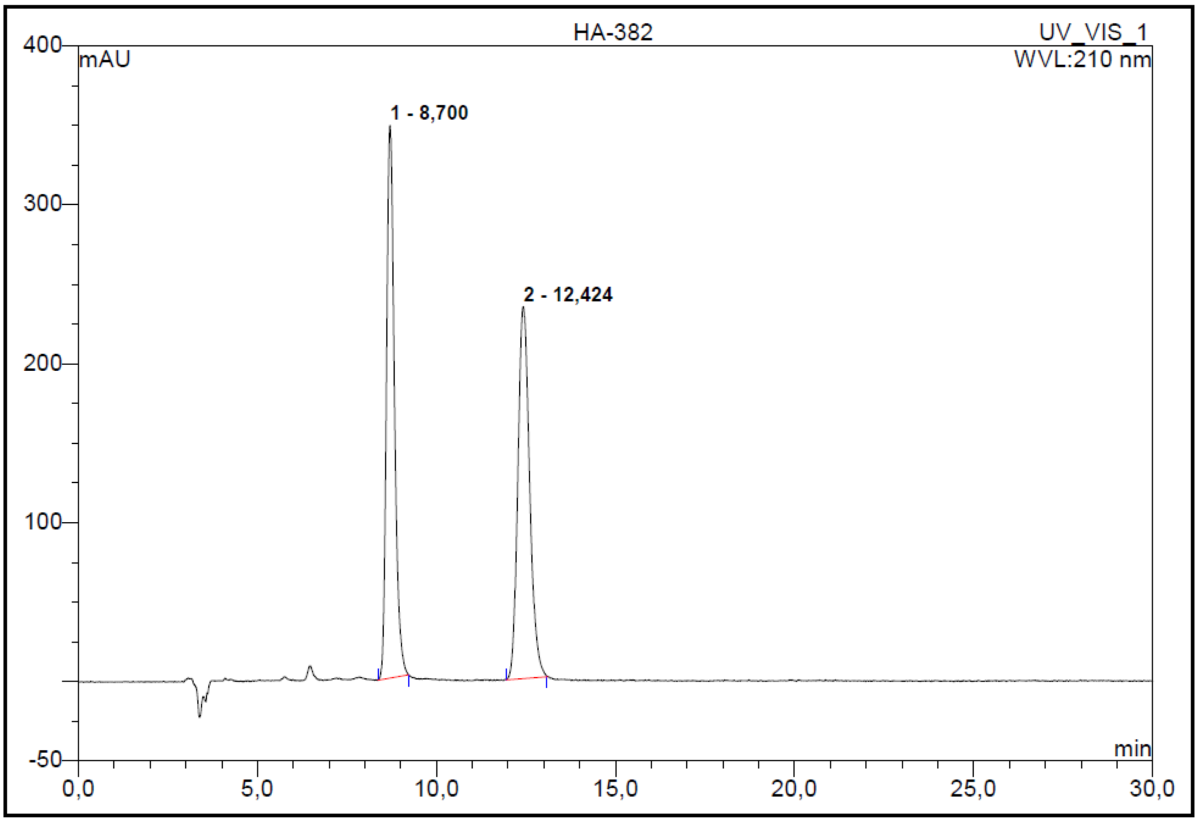
Figure 2: Difference Fourier Map of 13b based on ED data (after dynamical refinement): (top) excluding, and (bottom) including the hydrogen atoms bonded to the nitrogens. Level = 0.25 e-/(Å3).

8. Chiral HPLC traces

Trace of the racemic compound:

Chiral HPLC: Racemic [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.7 min, t_R = 12.4 min].

4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**13b**)

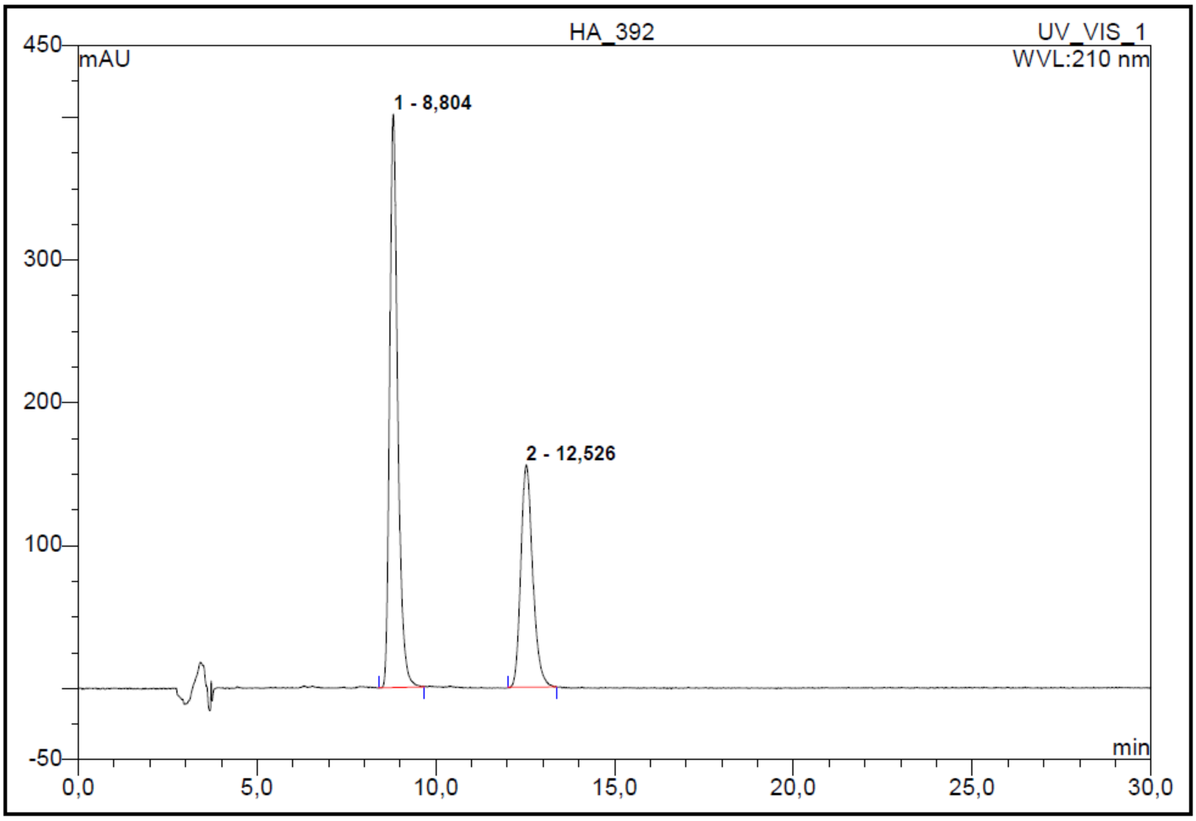


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,70	n.a.	347,523	89,037	50,09	n.a.	BMB
2	12,42	n.a.	233,961	88,703	49,91	n.a.	BMB
Total:			581,484	177,740	100,00	0,000	

Traces of the enantioenriched compound:

Chiral HPLC: 27% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.8 min (major), t_R = 12.5min (minor)].

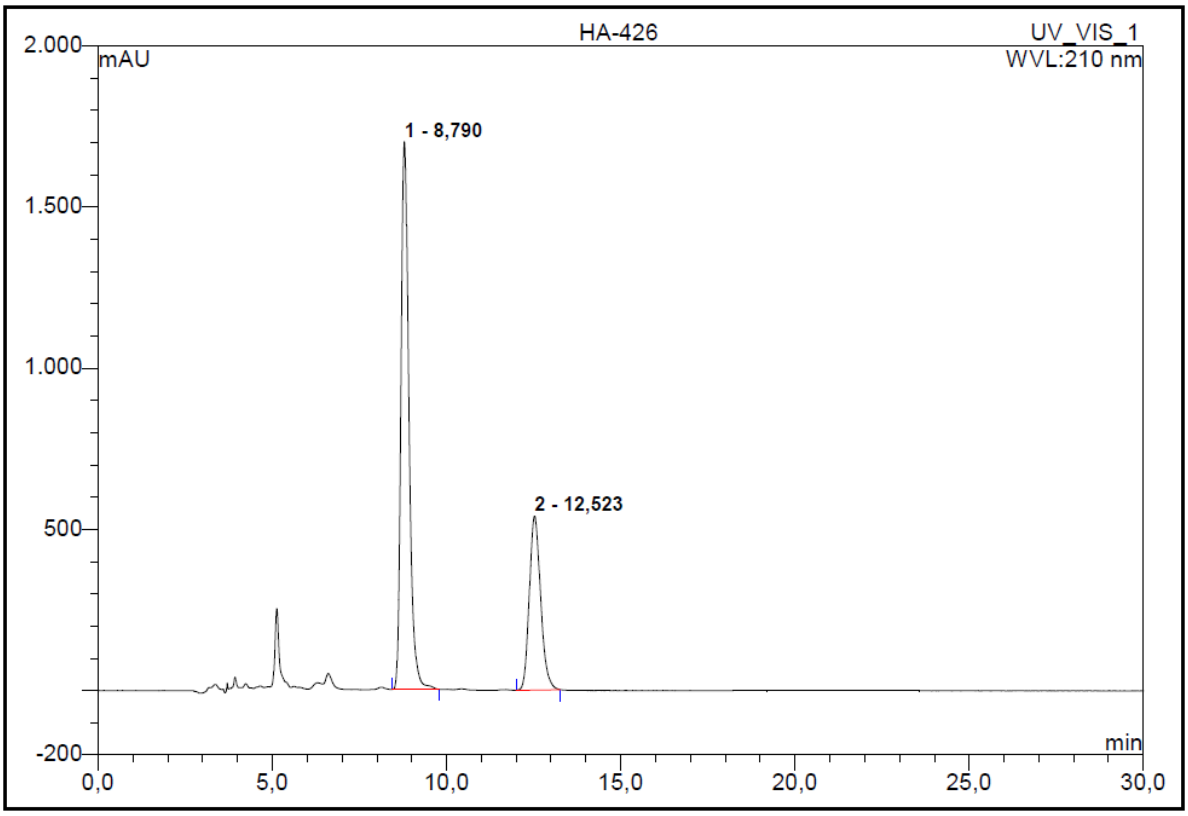
4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**13b**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,80	n.a.	401,330	105,888	63,82	n.a.	BMB*
2	12,53	n.a.	155,537	60,041	36,18	n.a.	BMB*
Total:			556,867	165,929	100,00	0,000	

Chiral HPLC: 38% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.8 min (major), t_R = 12.5 min (minor)].

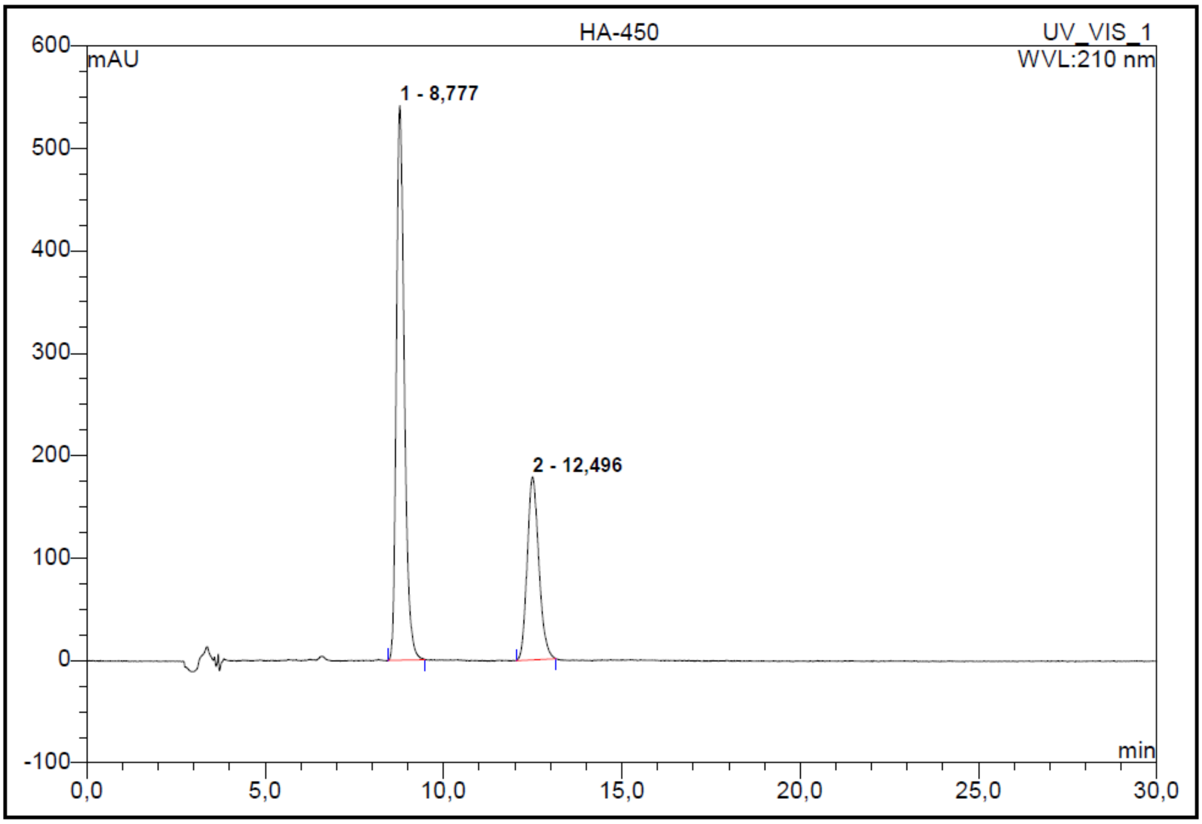
4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**13b**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,79	n.a.	1698,818	454,970	69,12	n.a.	BMB
2	12,52	n.a.	539,584	203,280	30,88	n.a.	BMB
Total:			2238,402	658,250	100,00	0,000	

Chiral HPLC: 35% *ee* [$^{\copyright}$CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.8 min (major), t_R = 12.5 min (minor)].

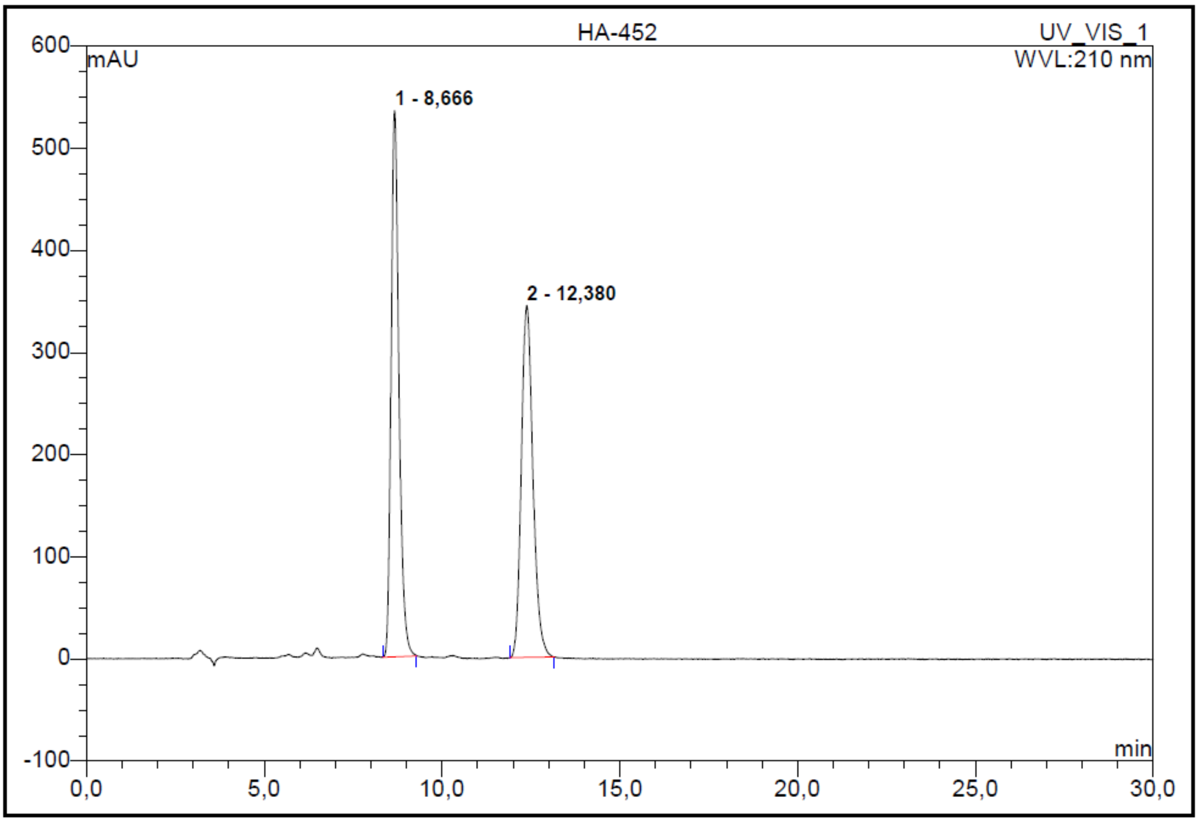
4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**13b**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,78	n.a.	541,113	139,605	67,38	n.a.	BMB
2	12,50	n.a.	178,456	67,595	32,62	n.a.	BMB
Total:			719,569	207,201	100,00	0,000	

Chiral HPLC: 3% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 8.7 min (major), t_R = 12.4 min (minor)].

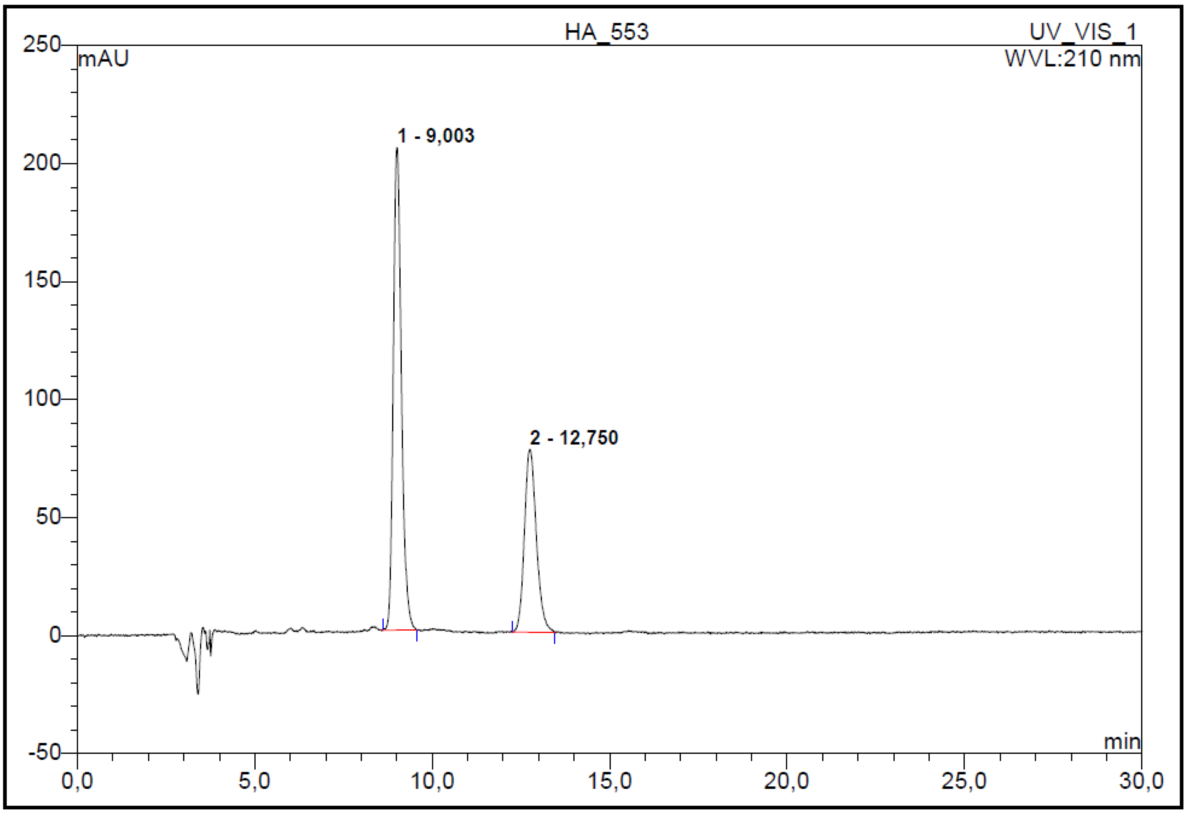
4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**13b**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,67	n.a.	534,448	137,314	51,34	n.a.	BMB
2	12,38	n.a.	344,276	130,142	48,66	n.a.	BMB
Total:			878,724	267,456	100,00	0,000	

Chiral HPLC: 29% *ee* [$^{\copyright}$CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 9.0 min (major), t_R = 12.7 min (minor)].

4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**13b**)

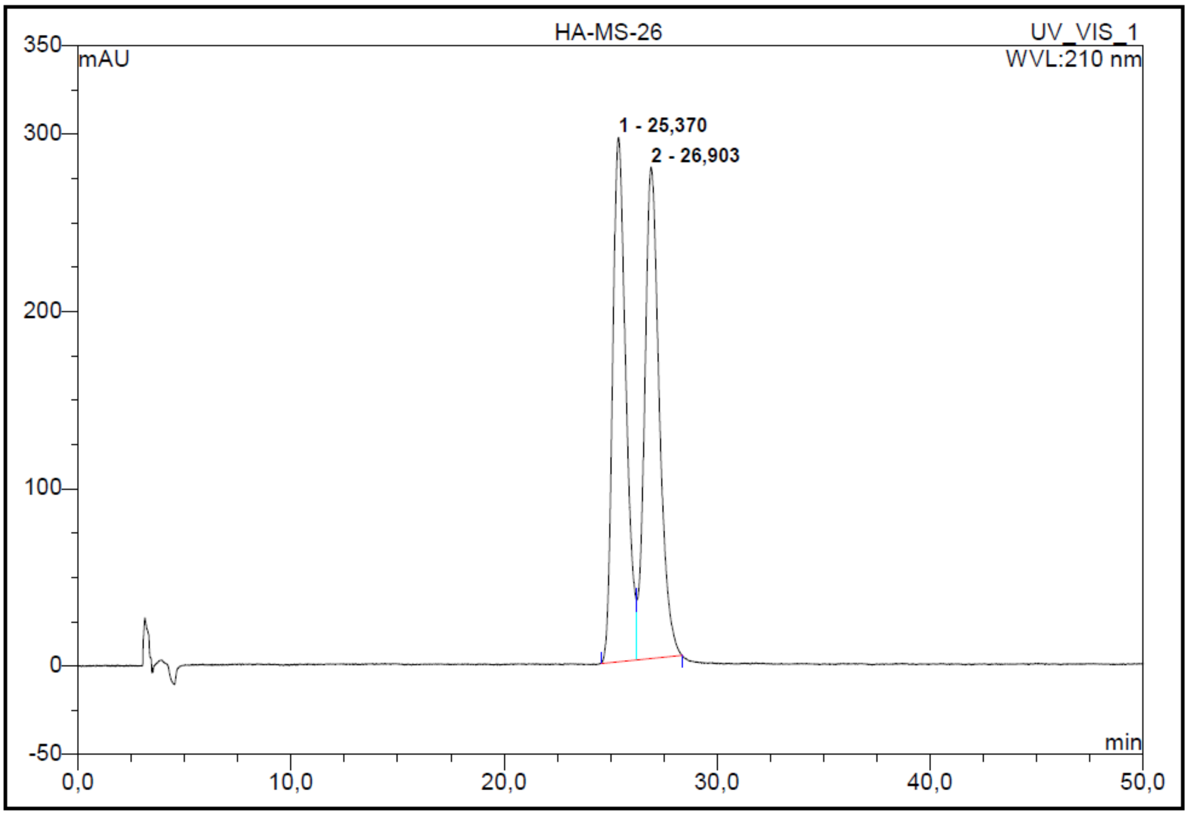


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,00	n.a.	204,405	53,863	64,08	n.a.	BMB*
2	12,75	n.a.	77,549	30,197	35,92	n.a.	BMB*
Total:			281,954	84,060	100,00	0,000	

Trace of the racemic compound:

Chiral HPLC: Racemate [$^{\copyright}$CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 90% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 25.6 min, t_R = 27.1 min].

4-[2-(Oxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**10b**)

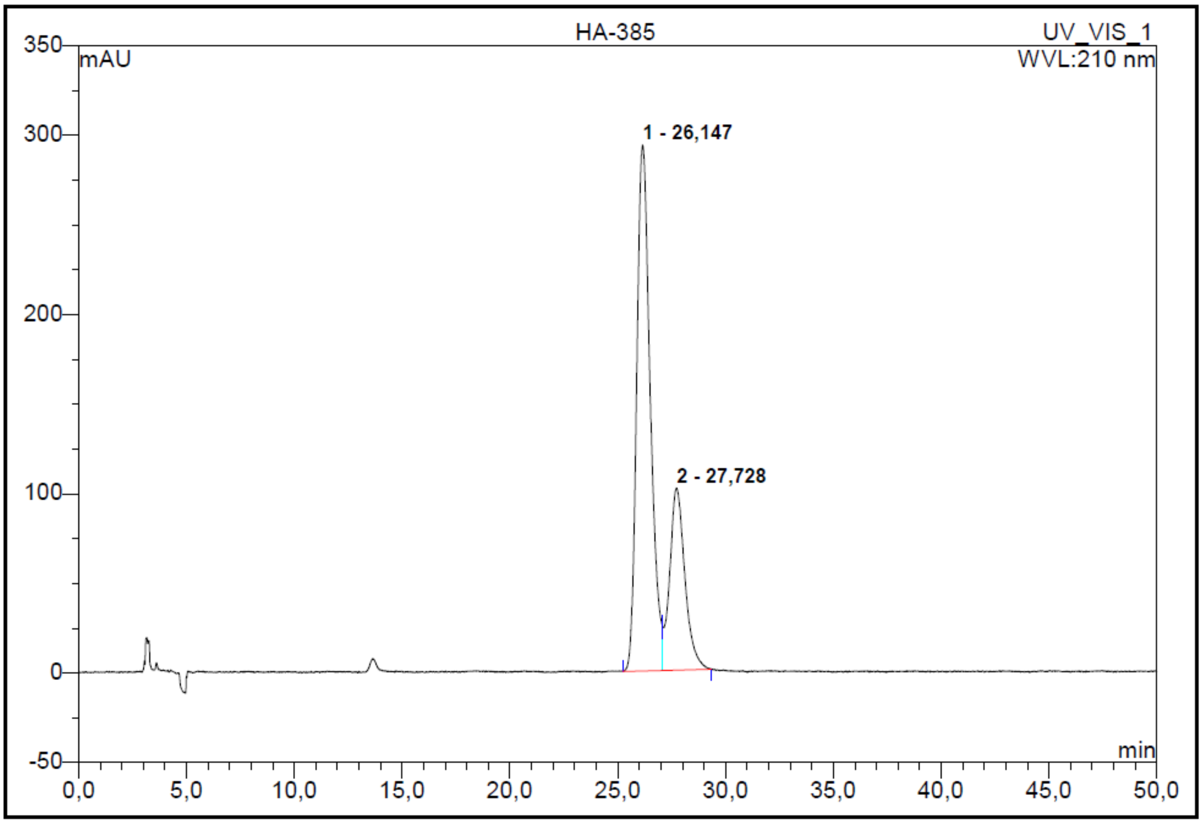


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	25,37	n.a.	295,919	215,201	49,24	n.a.	BM
2	26,90	n.a.	277,250	221,879	50,76	n.a.	MB
Total:			573,169	437,080	100,00	0,000	

<u>Traces of the enantioenriched compound</u>:

Chiral HPLC: 44% *ee* [$^{©}$CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 90% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 26.1 min (major), t_R = 27.7 min (minor)].

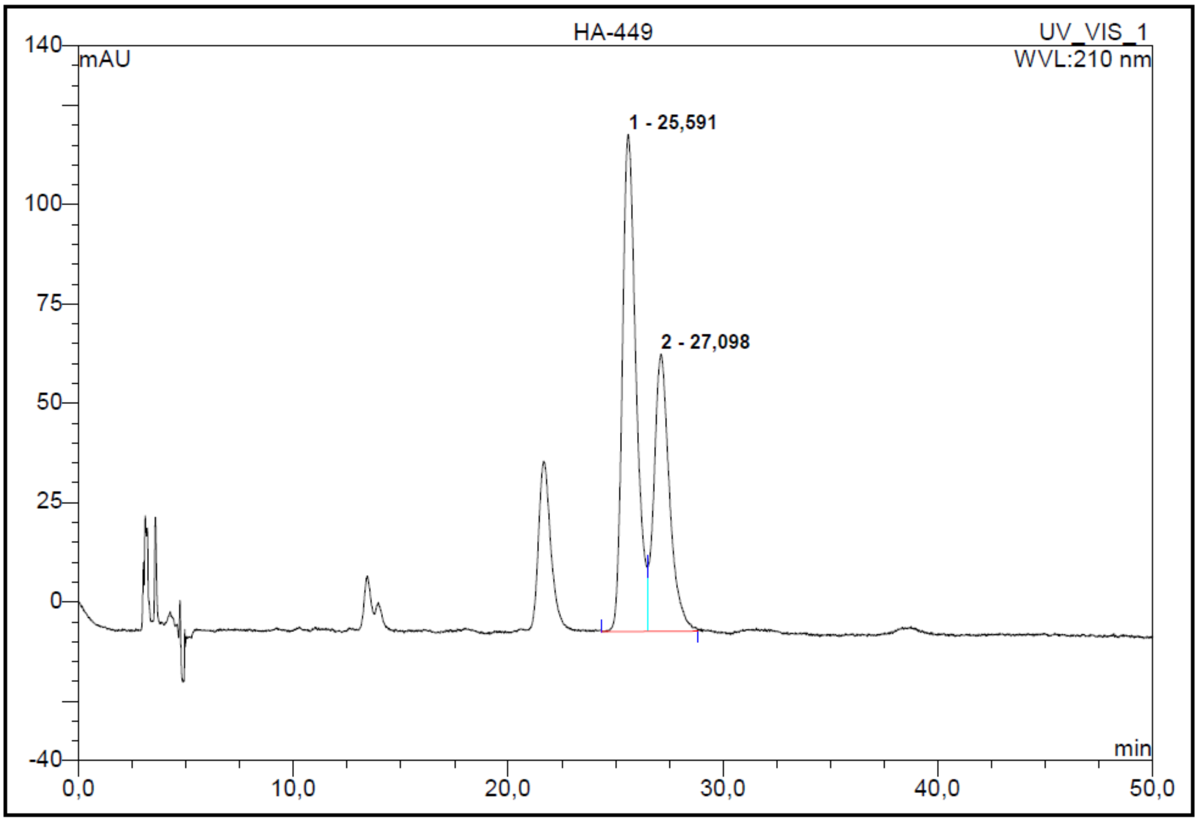
4-[2-(Oxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**10b**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26,15	n.a.	293,529	214,230	71,96	n.a.	BM *
2	27,73	n.a.	101,625	83,476	28,04	n.a.	MB*
Total:			395,154	297,706	100,00	0,000	

Chiral HPLC: 22% *ee* [$^{©}$CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 90% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 25.6 min (major), t_R = 27.1 min (minor)].

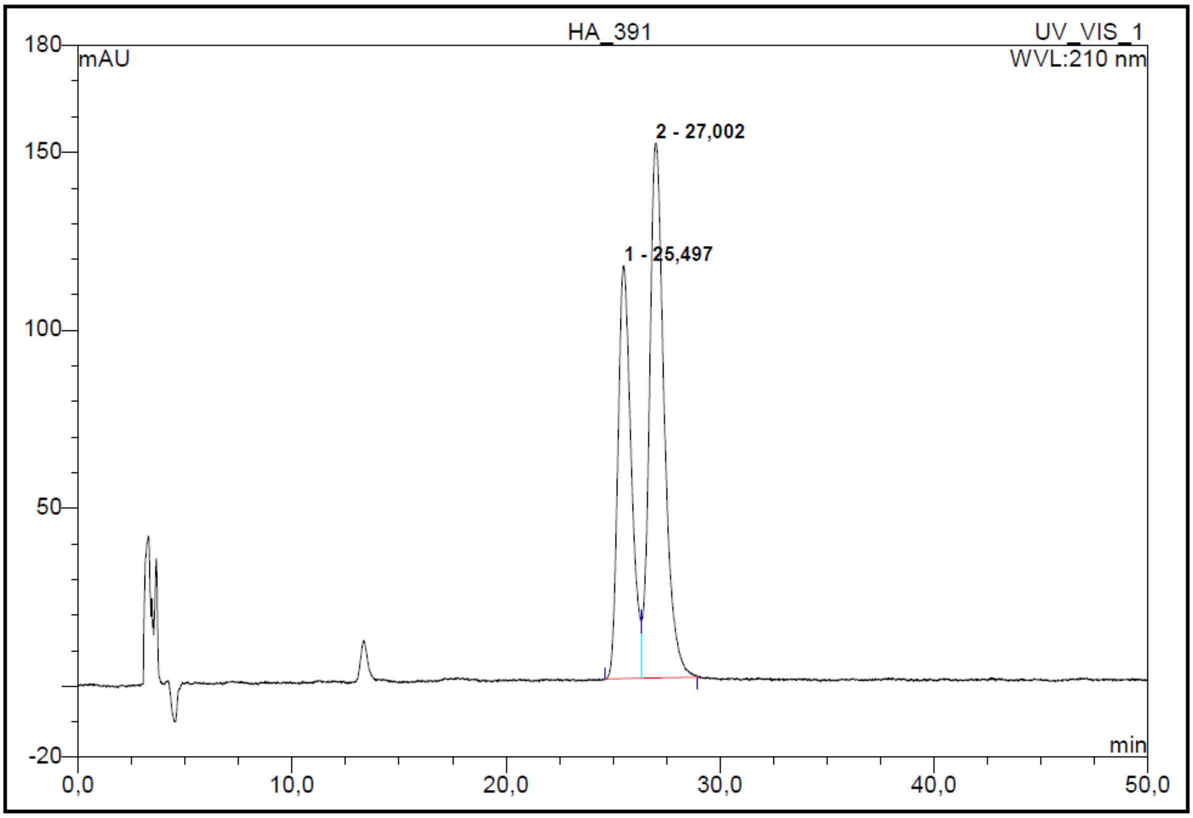
4-[2-(Oxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**10b**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	25,59	n.a.	125,109	92,583	61,23	n.a.	BM *
2	27,10	n.a.	69,795	58,618	38,77	n.a.	MB*
Total:			194,905	151,201	100,00	0,000	

Chiral HPLC: -18% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 90% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 25.5 min (major), t_R = 27.0 min (minor)].

4-[2-(Oxiran-2-yl)ethyl]quinolin-2(1*H*)-one (**10b**)

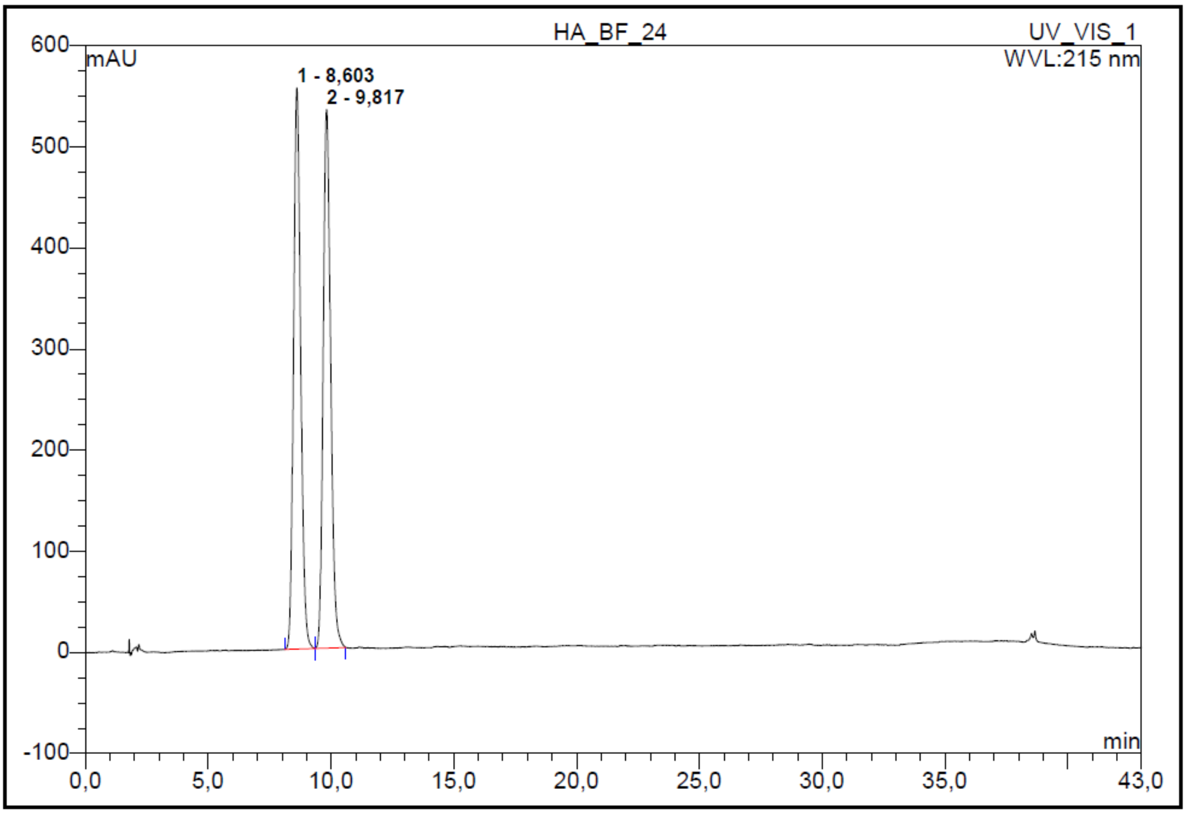


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	25,50	n.a.	115,996	83,226	40,76	n.a.	BM *
2	27,00	n.a.	150,214	120,940	59,24	n.a.	MB*
Total:			266,210	204,166	100,00	0,000	

Trace of the racemic compound:

Chiral HPLC: Racemate [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.6 min, t_R = 9.8 min].

4-[(3,3-Dimethyloxiran-2-yl)methyl]quinolin-2(1*H*)-one (**13a**)

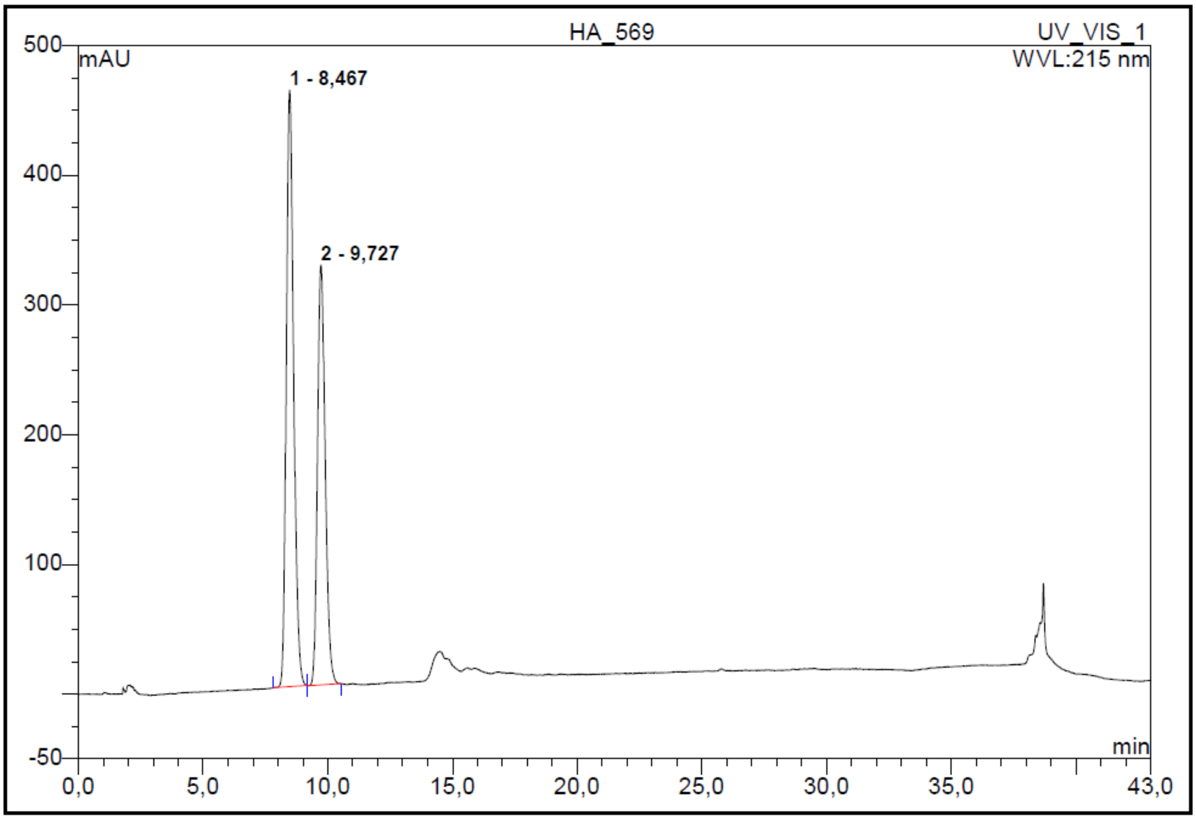


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,60	n.a.	554,844	188,092	49,86	n.a.	BM
2	9,82	n.a.	532,642	189,135	50,14	n.a.	MB
Total:			1087,486	377,227	100,00	0,000	

Traces of the enantioenriched compound:

Chiral HPLC: 15% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.5 min (major), t_R = 9.7 min (minor)].

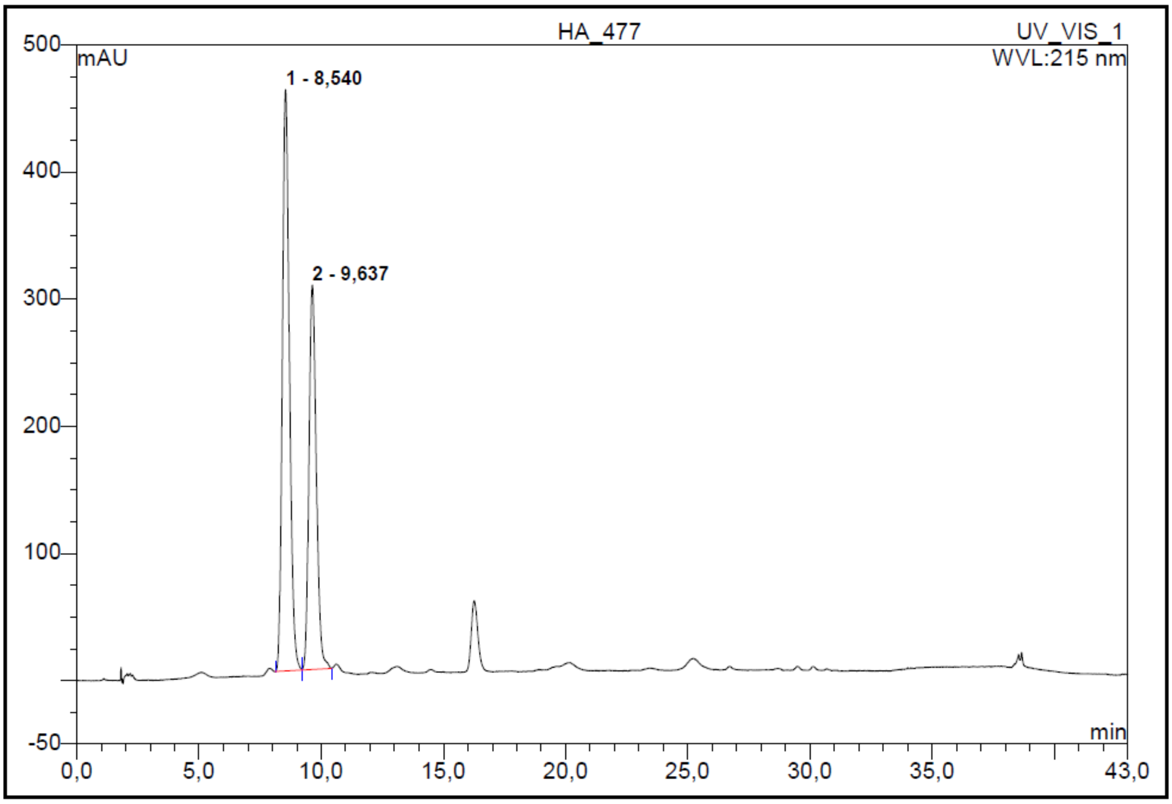
4-[(3,3-Dimethyloxiran-2-yl)methyl]quinolin-2(1*H*)-one (**13a**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,47	n.a.	459,681	156,792	57,52	n.a.	BMB*
2	9,73	n.a.	323,737	115,811	42,48	n.a.	BMB*
Total:			783,418	272,604	100,00	0,000	

Chiral HPLC: 19% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.5 min (major), t_R = 9.7 min (minor)].

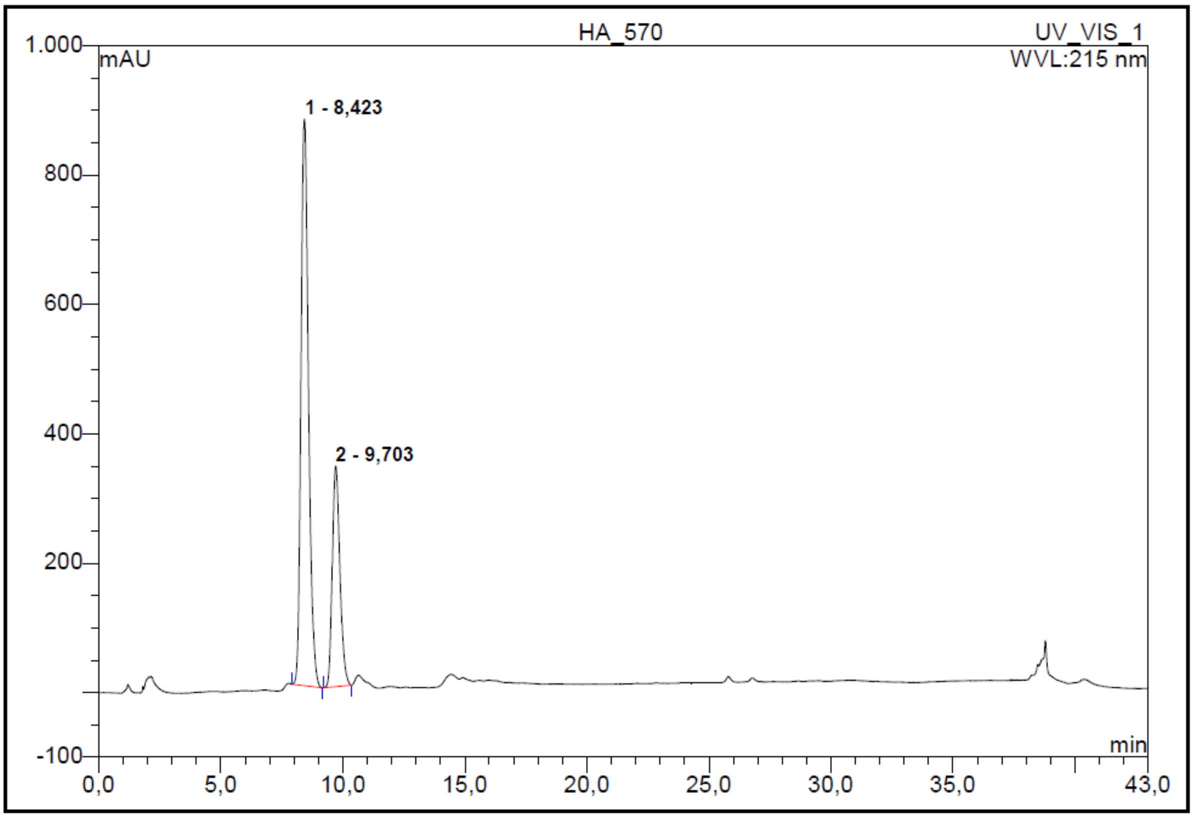
4-[(3,3-Dimethyloxiran-2-yl)methyl]quinolin-2(1*H*)-one (**13a**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,54	n.a.	457,366	152,734	59,16	n.a.	BM
2	9,64	n.a.	302,424	105,444	40,84	n.a.	MB
Total:			759,790	258,178	100,00	0,000	

Chiral HPLC: 43% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.4 min (major), t_R = 9.6 min (minor)].

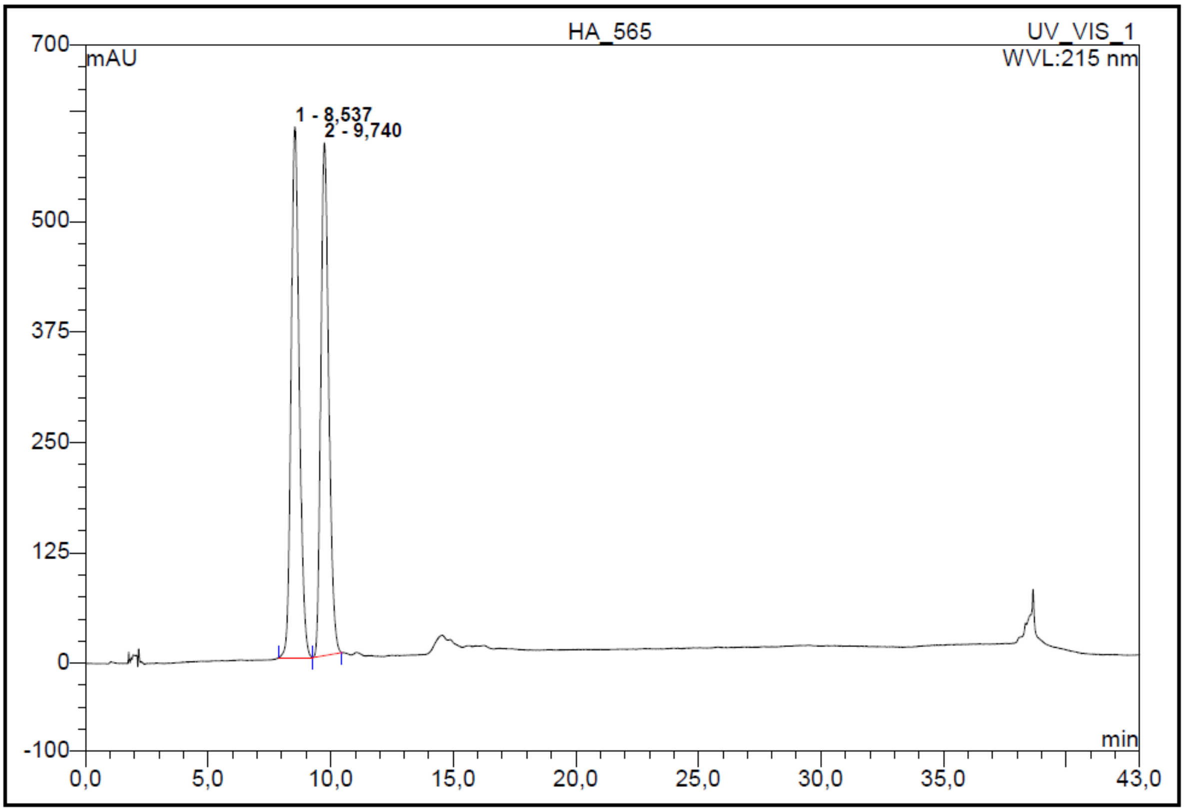
4-[(3,3-Dimethyloxiran-2-yl)methyl]quinolin-2(1*H*)-one (**13a**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,42	n.a.	876,311	310,230	71,56	n.a.	BMB
2	9,70	n.a.	340,856	123,270	28,44	n.a.	BMB
Total:			1217,167	433,500	100,00	0,000	

Chiral HPLC: 3% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 5 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 8.5 min (major), t_R = 9.7 min (minor)].

4-[(3,3-Dimethyloxiran-2-yl)methyl]quinolin-2(1*H*)-one (**13a**)

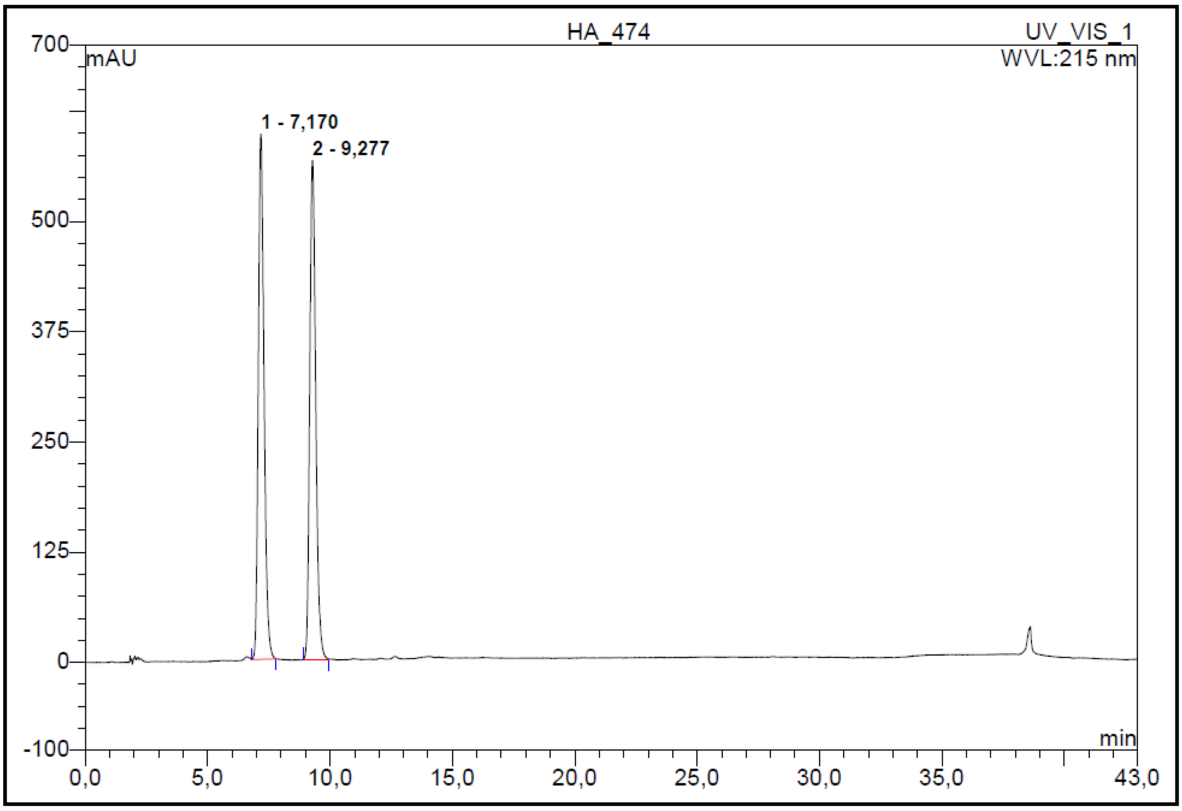


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,54	n.a.	600,740	231,875	51,46	n.a.	BMB
2	9,74	n.a.	580,492	218,758	48,54	n.a.	BMB
Total:			1181,232	450,633	100,00	0,000	

Trace of the racemic compound:

Chiral HPLC: Racemate [$^{\copyright}$CHIRALPAK AS-RH 150 × 4.6 mm, 20 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 7.2 min, t_R = 9.3 min].

4-(Oxiran-2-ylmethyl)quinolin-2(1*H*)-one (**10a**)

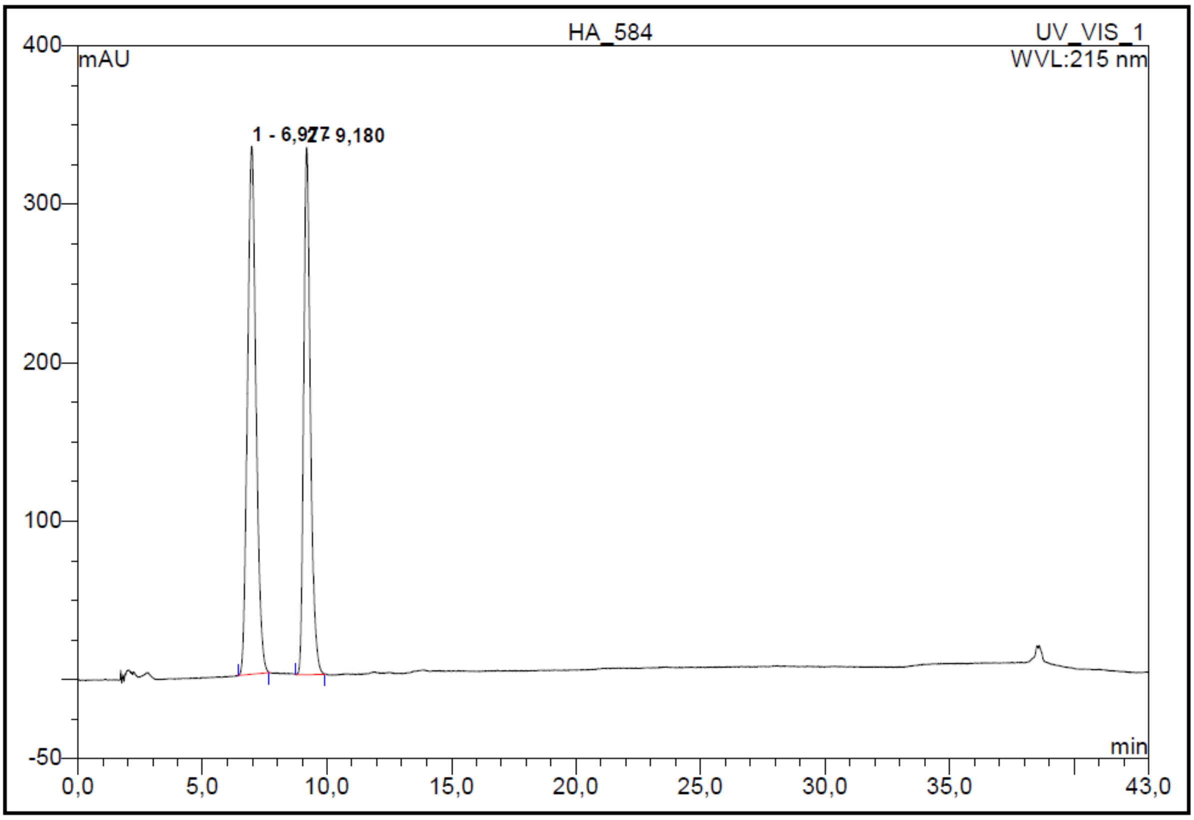


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,17	n.a.	595,616	161,175	49,97	n.a.	BMB
2	9,28	n.a.	565,796	161,339	50,03	n.a.	BMB
Total:			1161,412	322,514	100,00	0,000	

<u>Traces of the enantioenriched compound</u>:

Chiral HPLC: 12% *ee* [$^{\copyright}$CHIRALPAK AS-RH 150 × 4.6 mm, 20 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 6.9 min (major), t_R = 9.2 min (minor)].

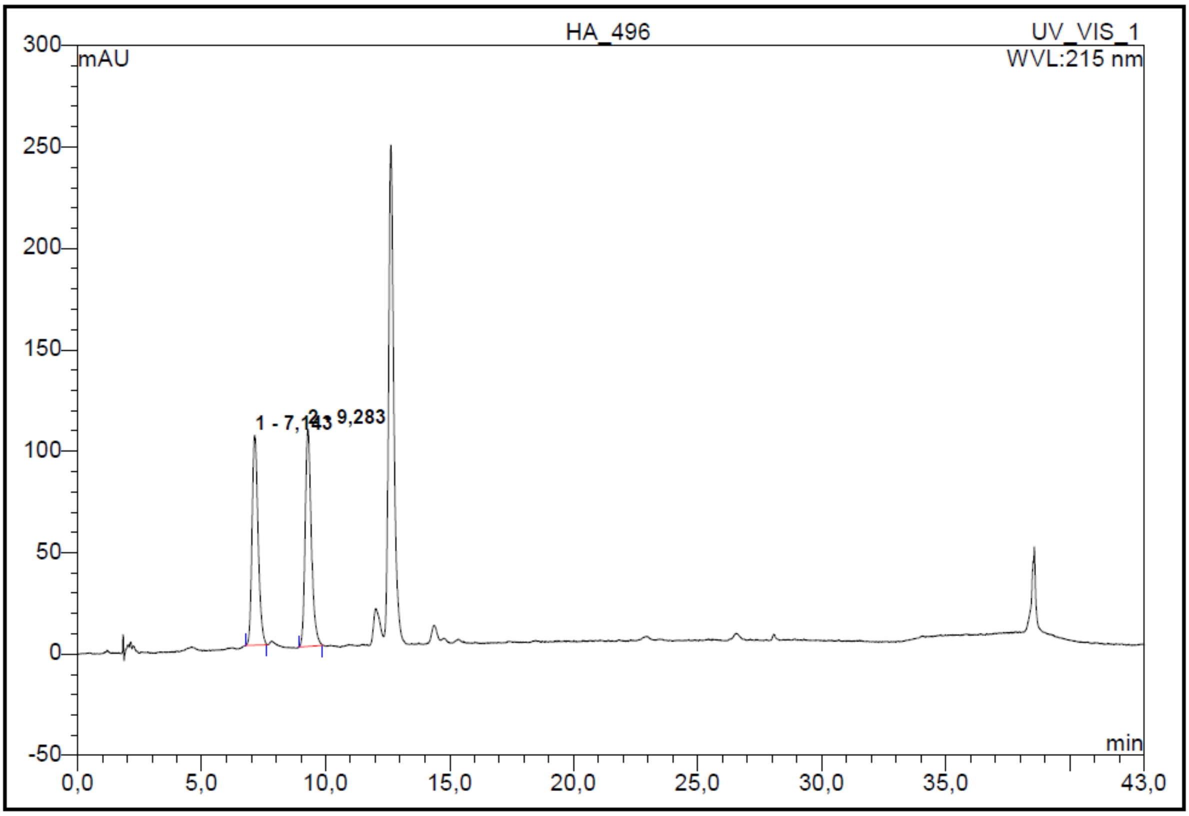
4-(Oxiran-2-ylmethyl)quinolin-2(1*H*)-one (**10a**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,98	n.a.	333,144	132,535	55,97	n.a.	BMB
2	9,18	n.a.	332,649	104,282	44,03	n.a.	BMB
Total:			665,793	236,817	100,00	0,000	

Chiral HPLC: 4% *ee* [$^{©}$CHIRALPAK AS-RH 150 × 4.6 mm, 20 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 7.1 min (minor), t_R = 9.3 min (major)].

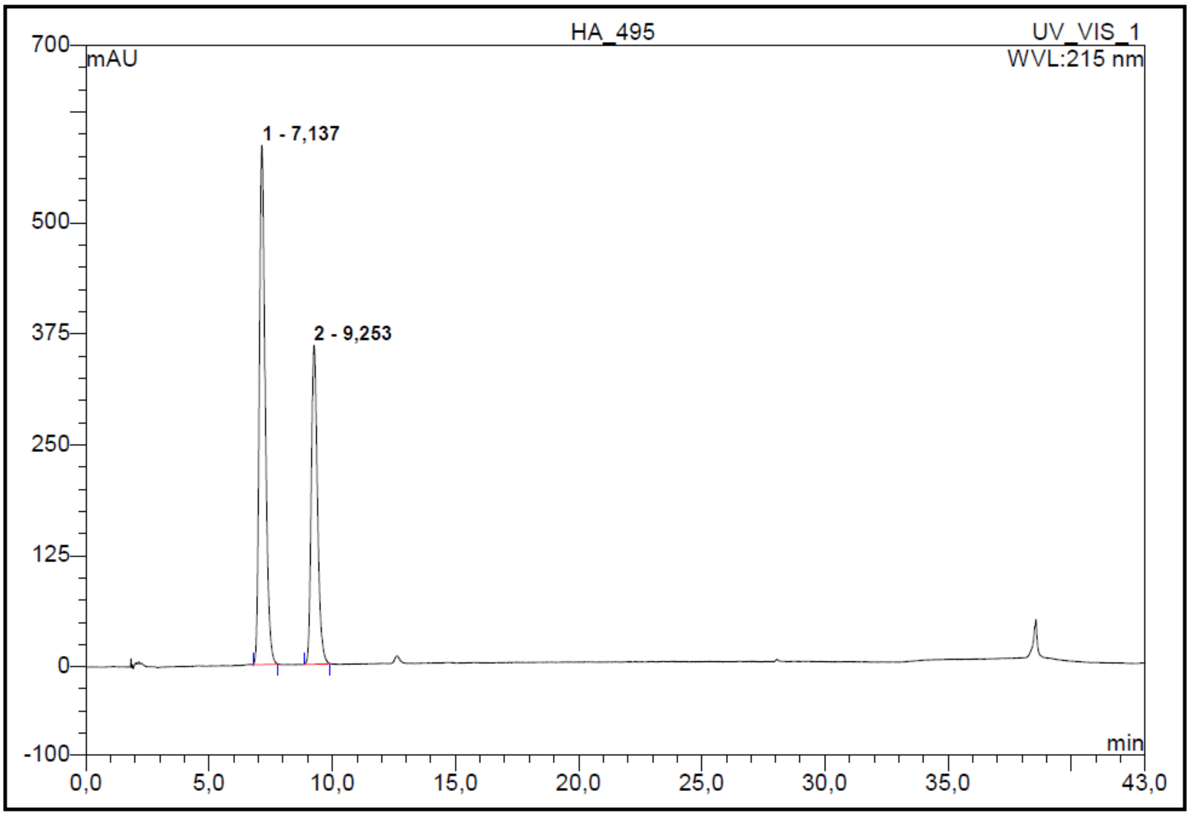
4-(Oxiran-2-ylmethyl)quinolin-2(1*H*)-one (**10a**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,14	n.a.	103,399	28,960	48,18	n.a.	BMB
2	9,28	n.a.	107,066	31,148	51,82	n.a.	BMB
Total:			210,465	60,108	100,00	0,000	

Chiral HPLC: 22% *ee* [©CHIRALPAK AS-RH 150 × 4.6 mm, 20 °C, 80% → 0% → 70% H_2O/MeCN, 1 mL/min, 210 nm, t_R = 7.1 min (major), t_R = 9.3 min (minor)].

4-(Oxiran-2-ylmethyl)quinolin-2(1*H*)-one (**10a**)

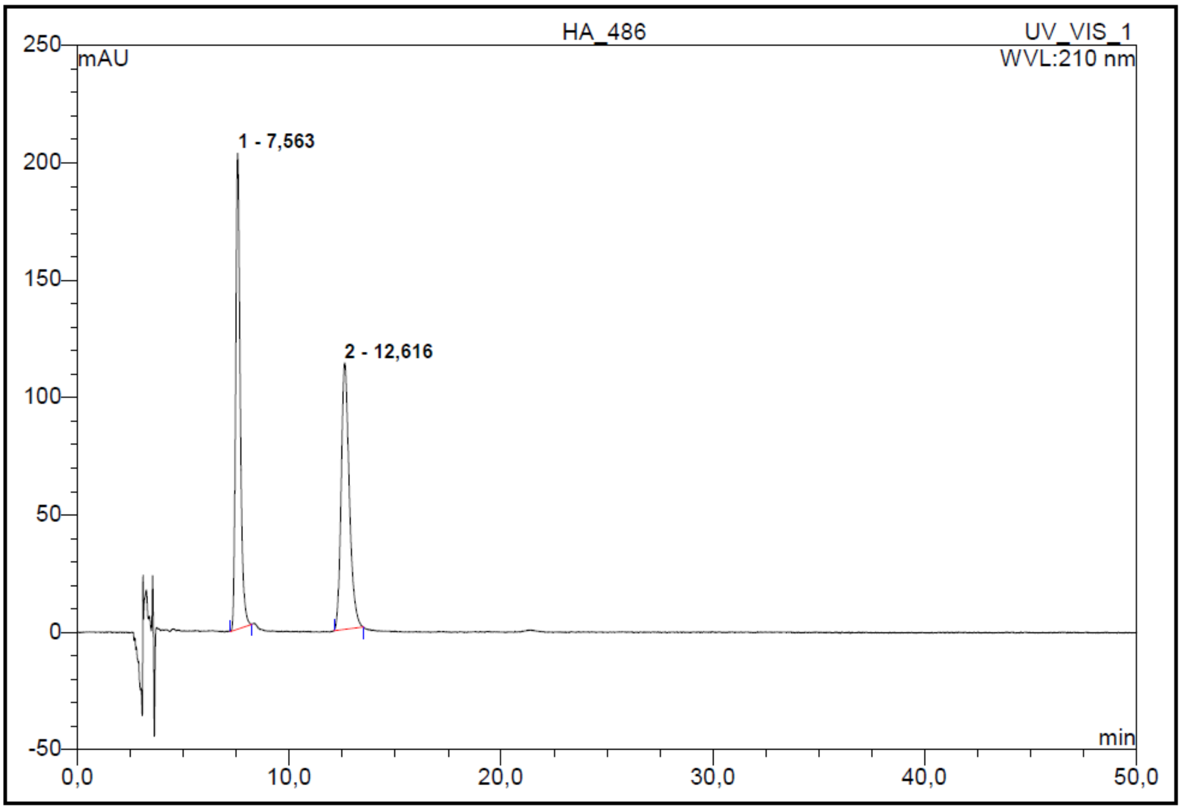


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,14	n.a.	584,687	164,151	60,92	n.a.	BMB
2	9,25	n.a.	359,432	105,319	39,08	n.a.	BMB
Total:			944,119	269,469	100,00	0,000	

Trace of the racemic compound:

Chiral HPLC: Racemate [©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.6 min (major), t_R = 12.6 min (minor)].

4-(4-Hydroxy-5-methylhexyl)quinolin-2(1*H*)-one (**14**)

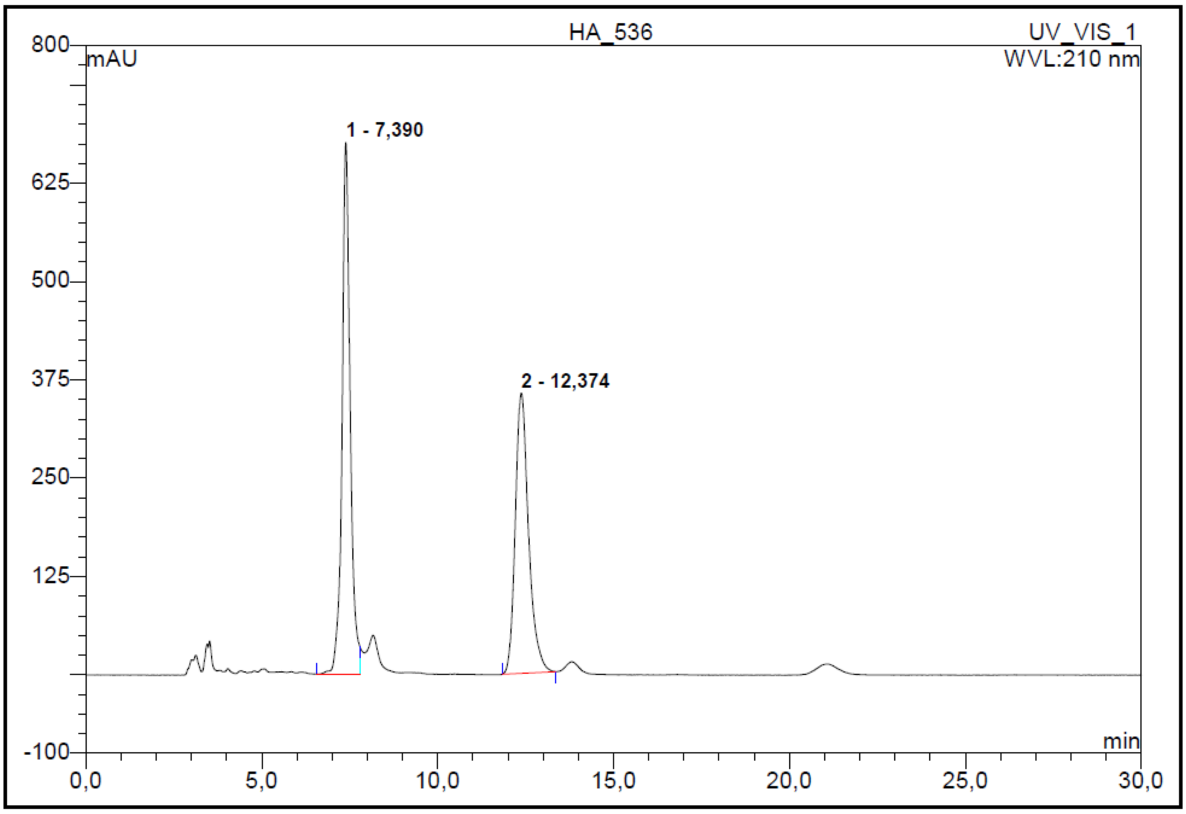


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,56	n.a.	202,650	51,239	50,26	n.a.	BMB
2	12,62	n.a.	113,510	50,699	49,74	n.a.	BMB
Total:			316,160	101,938	100,00	0,000	

Traces of the enantioenriched compound:

Chiral HPLC: 7% *ee* [$^{©}$CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.4 min (major), t_R = 12.4 min (minor)].

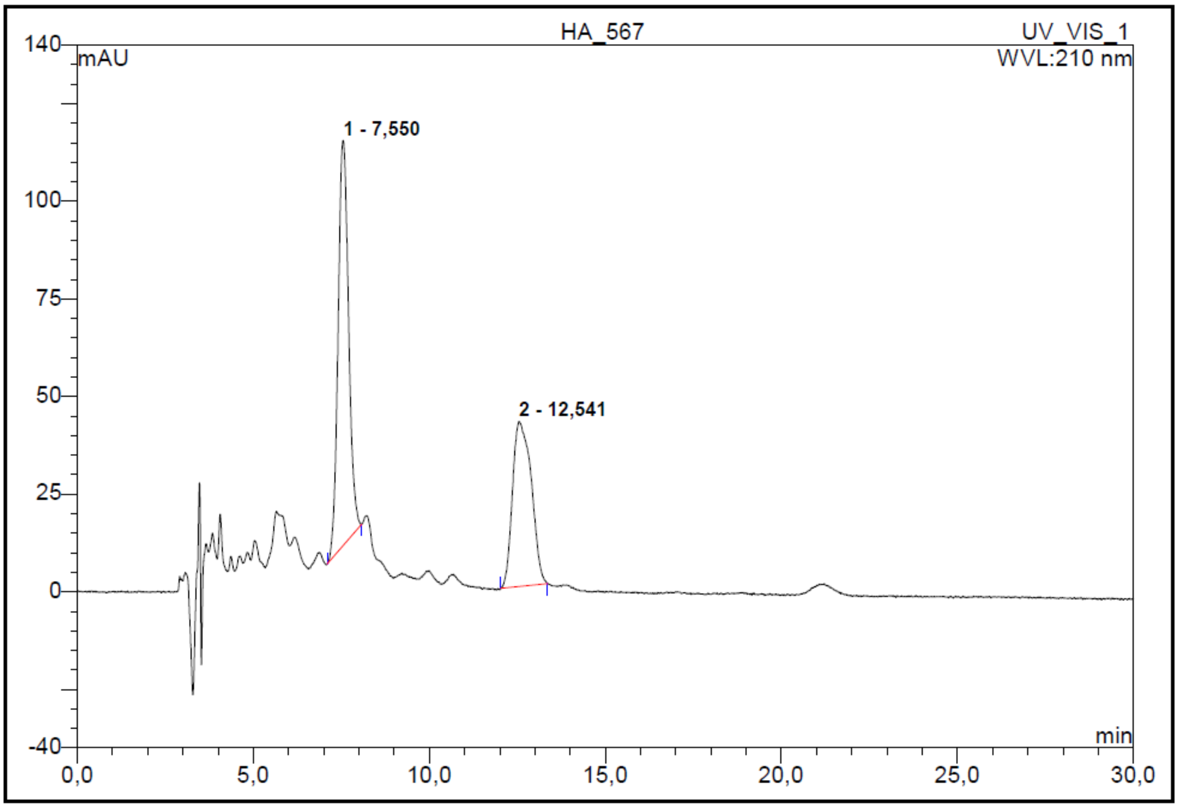
4-(4-Hydroxy-5-methylhexyl)quinolin-2(1*H*)-one (**14**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,39	n.a.	675,802	181,364	53,76	n.a.	BM *
2	12,37	n.a.	356,401	156,010	46,24	n.a.	BMB
Total:			1032,203	337,374	100,00	0,000	

Chiral HPLC: 16% *ee* [©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.6 min (major), t_R = 12.5 min (minor)].

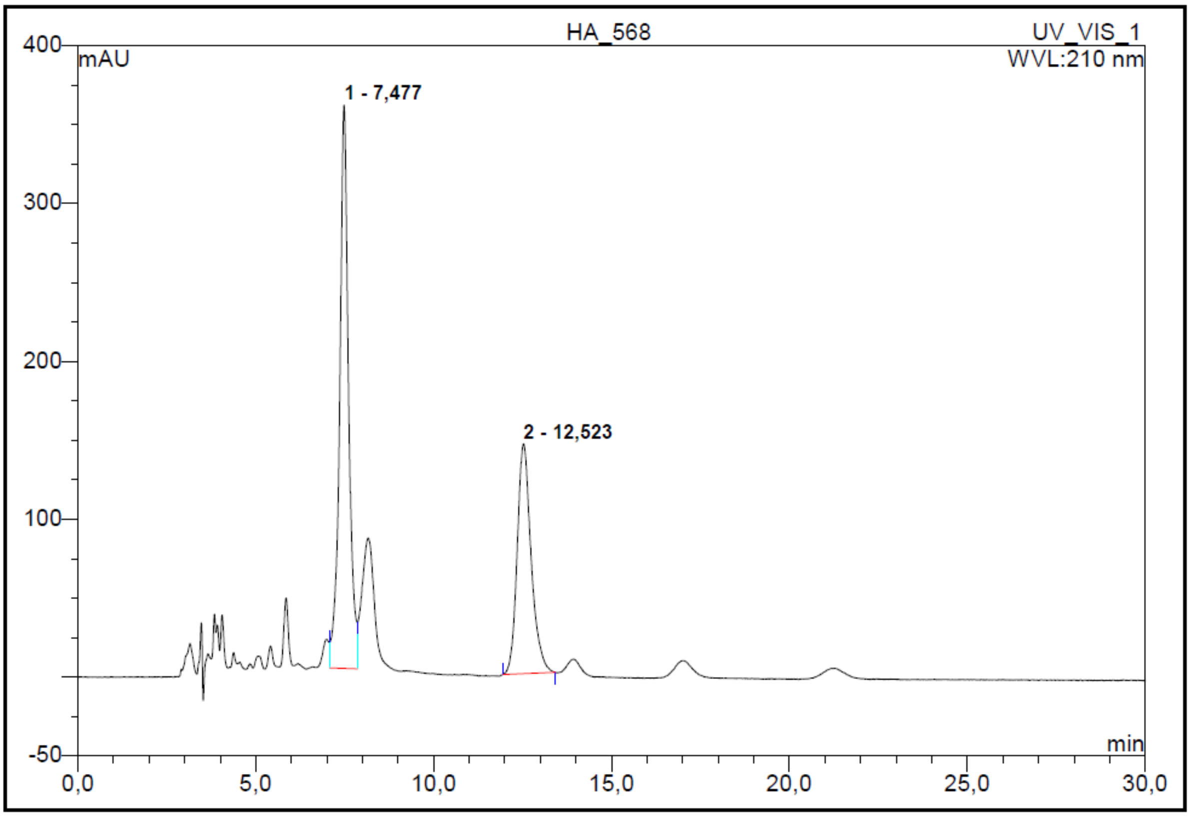
4-(4-Hydroxy-5-methylhexyl)quinolin-2(1*H*)-one (**14**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,55	n.a.	103,791	35,866	57,90	n.a.	BMB
2	12,54	n.a.	42,287	26,076	42,10	n.a.	BMB
Total:			146,078	61,942	100,00	0,000	

Chiral HPLC: 22% *ee* [$^{\copyright}$CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.5 min (major), t_R = 12.5 min (minor)].

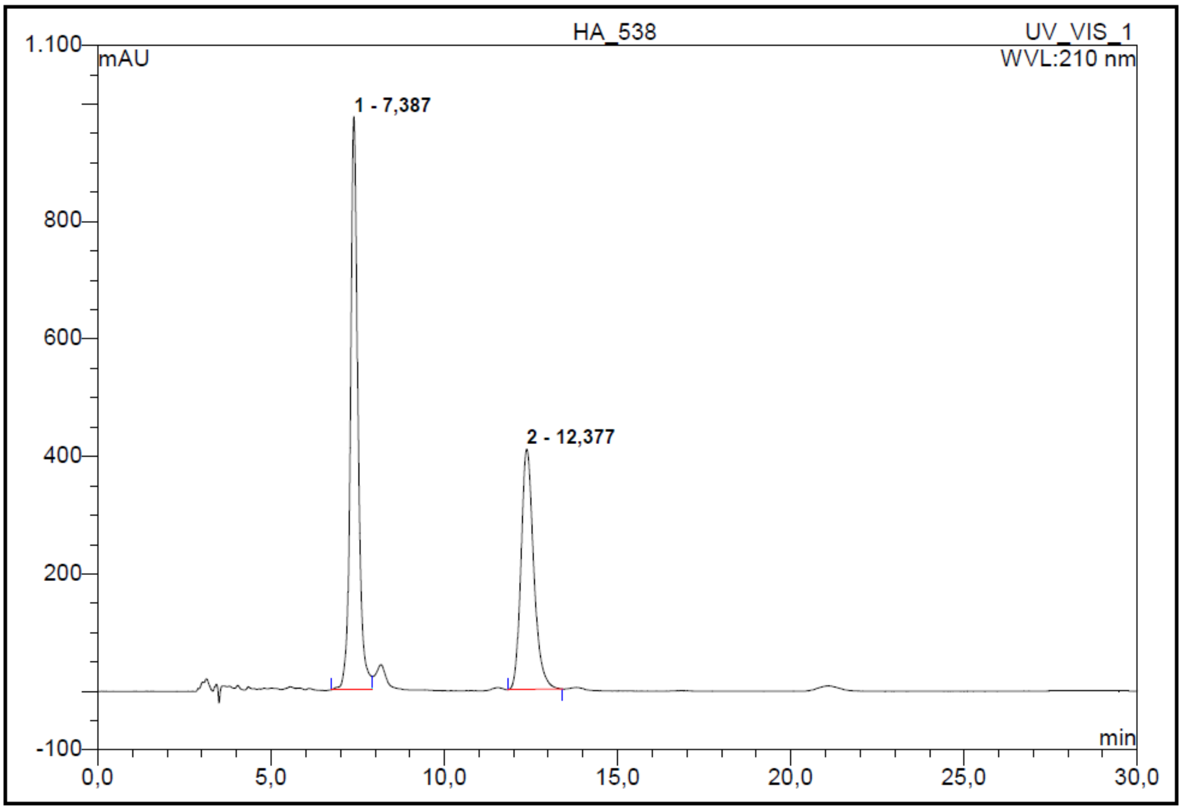
4-(4-Hydroxy-5-methylhexyl)quinolin-2(1*H*)-one (**14**)

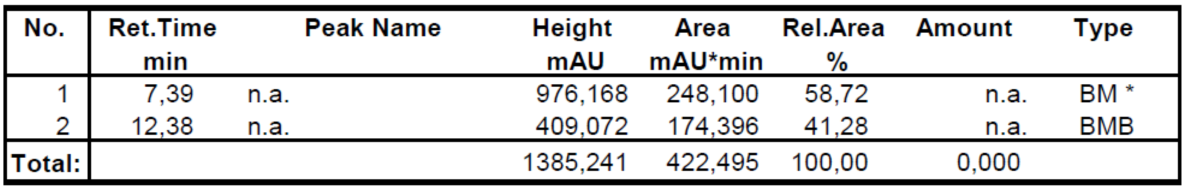


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,48	n.a.	356,796	104,329	61,20	n.a.	M *
2	12,52	n.a.	145,594	66,145	38,80	n.a.	BMB
Total:			502,390	170,474	100,00	0,000	

Chiral HPLC: 18% *ee* [$^{\copyright}$CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH,, 1 mL/min, 210 nm, t_R = 7.4 min (major), t_R = 12.4 min (minor)].

4-(4-Hydroxy-5-methylhexyl)quinolin-2(1*H*)-one (**14**)



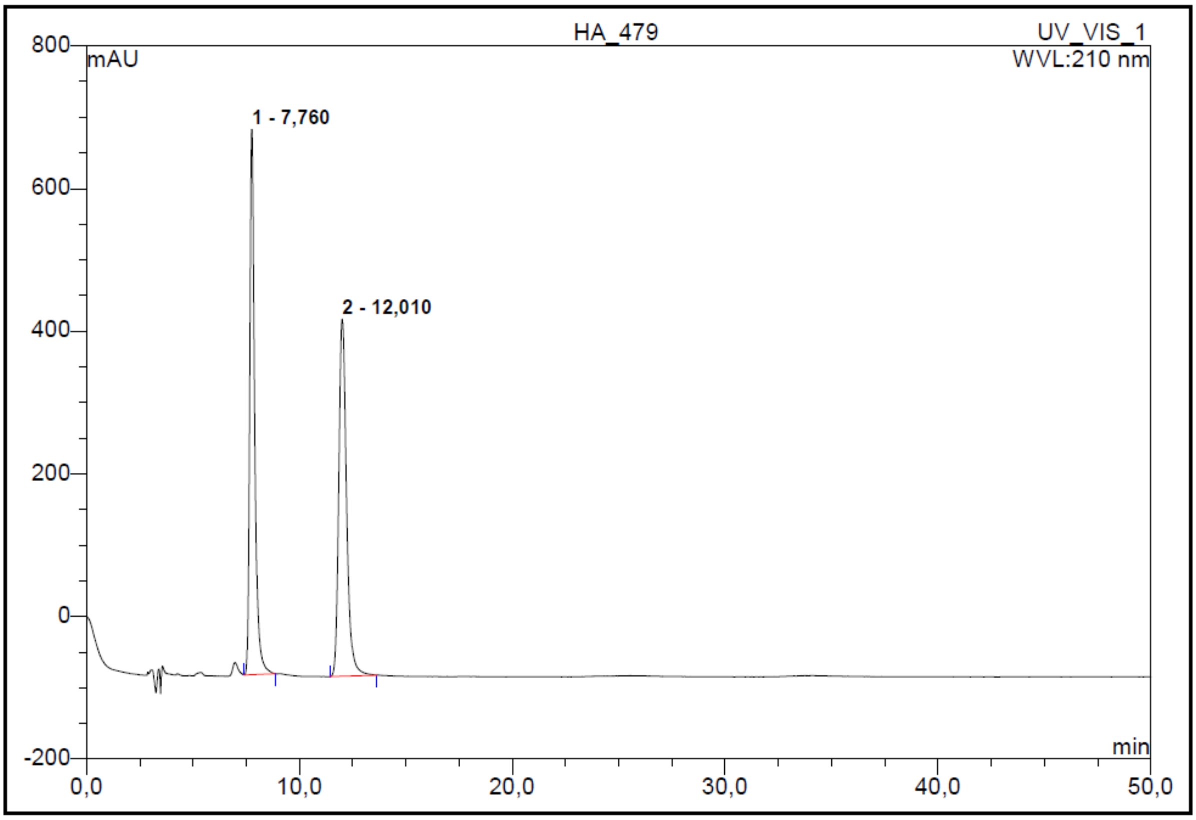


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,39	n.a.	976,168	248,100	58,72	n.a.	BM *
2	12,38	n.a.	409,072	174,396	41,28	n.a.	BMB
Total:			1385,241	422,495	100,00	0,000	

Trace of the racemic compound:

Chiral HPLC: Racemate [©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.8 min (major), t_R = 12.0 min (minor)].

4-(4-Hydroxypentyl)quinolin-2(1*H*)-one (**11**)

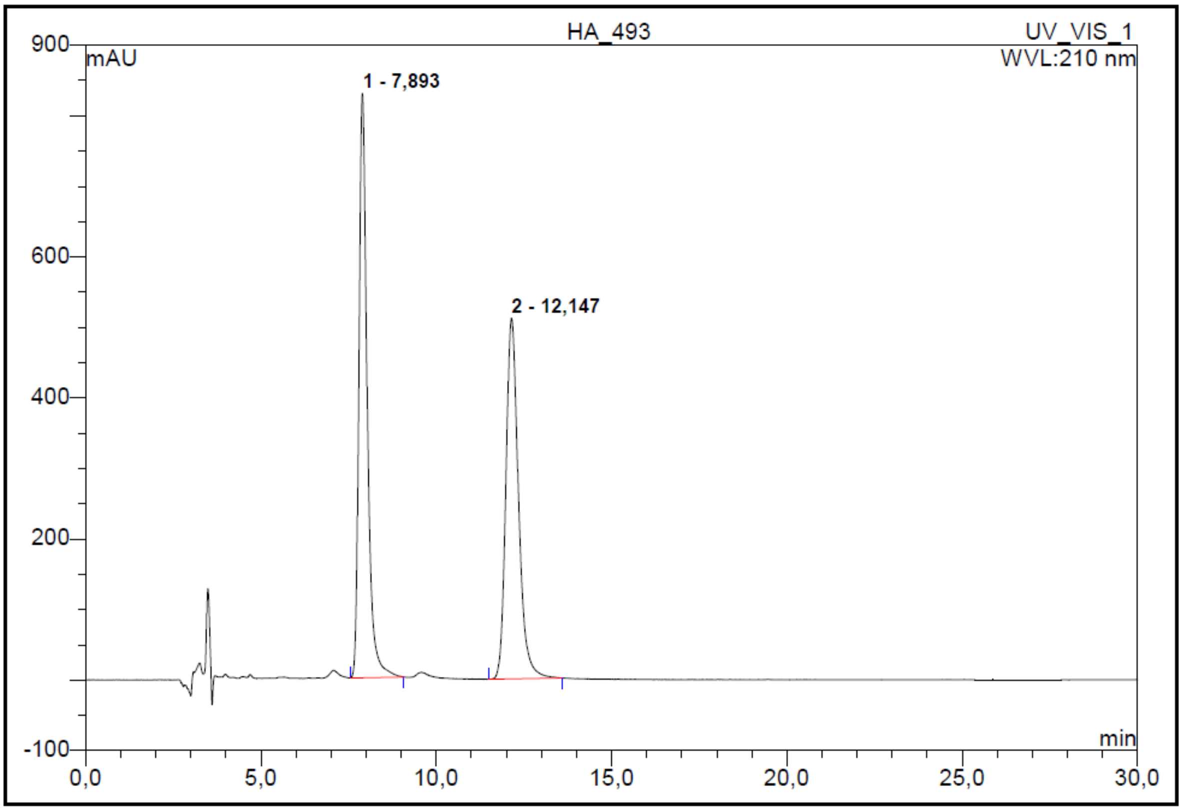


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,76	n.a.	764,142	211,366	50,03	n.a.	BMB
2	12,01	n.a.	500,592	211,154	49,97	n.a.	BMB
Total:			1264,734	422,519	100,00	0,000	

Traces of the enantioenriched compound:

Chiral HPLC: 3% *ee* [$^{©}$CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 7.9 min (major), t_R = 12.1 min (minor)].

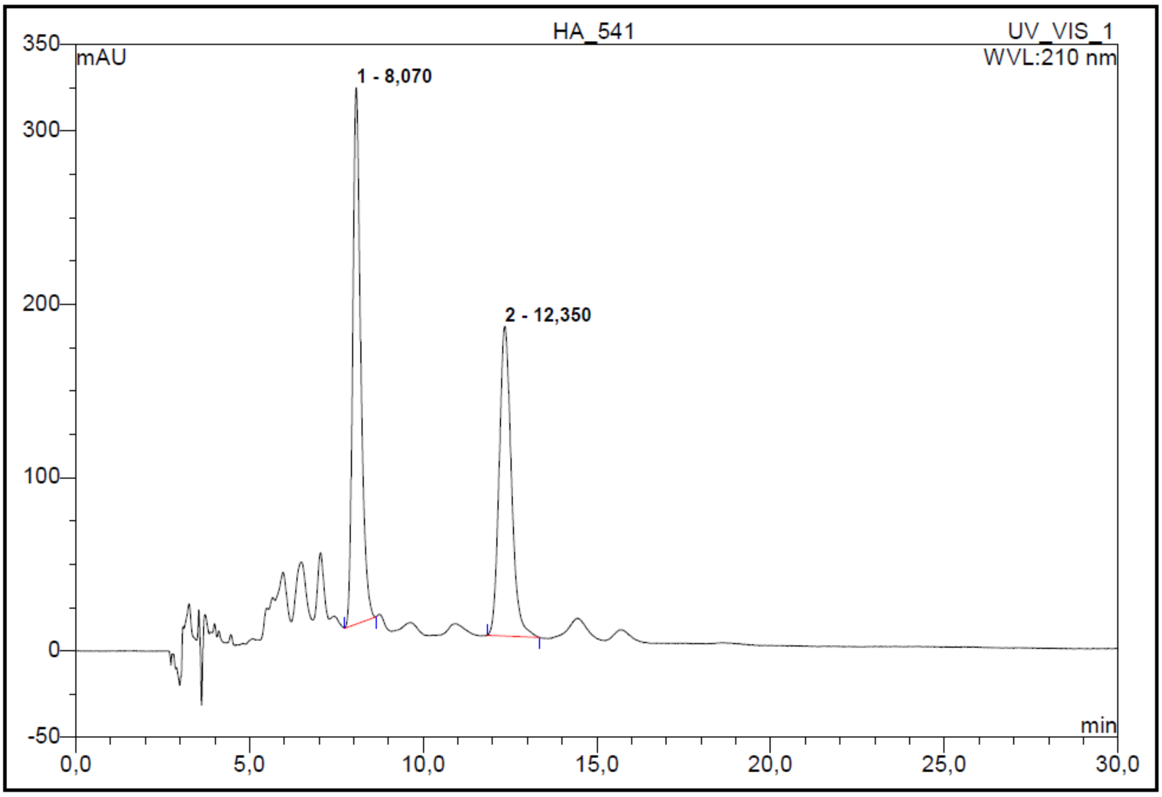
4-(4-Hydroxypentyl)quinolin-2(1*H*)-one (**11**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,89	n.a.	827,963	226,826	51,59	n.a.	BMB
2	12,15	n.a.	511,167	212,878	48,41	n.a.	BMB*
Total:			1339,130	439,704	100,00	0,000	

Chiral HPLC: 7% *ee* ©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.1 min (major), t_R = 12.4 min (minor)].

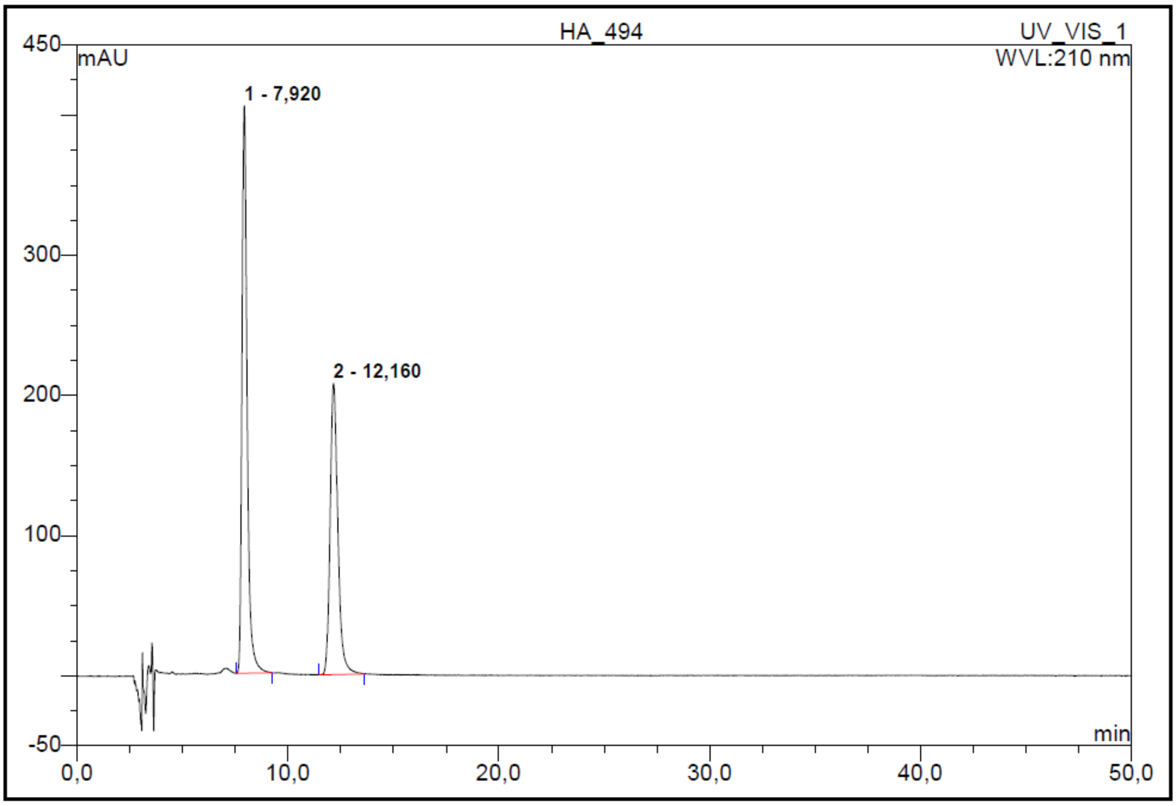
4-(4-Hydroxypentyl)quinolin-2(1*H*)-one (**11**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,07	n.a.	309,520	82,972	53,25	n.a.	BMB
2	12,35	n.a.	178,680	72,858	46,75	n.a.	BMB
Total:			488,199	155,830	100,00	0,000	

Chiral HPLC: 13% *ee* [©CHIRALPAK IA 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, 210 nm, t_R = 7.9 min (major), t_R = 12.2 min (minor)].

4-(4-Hydroxypentyl)quinolin-2(1*H*)-one (**11**)

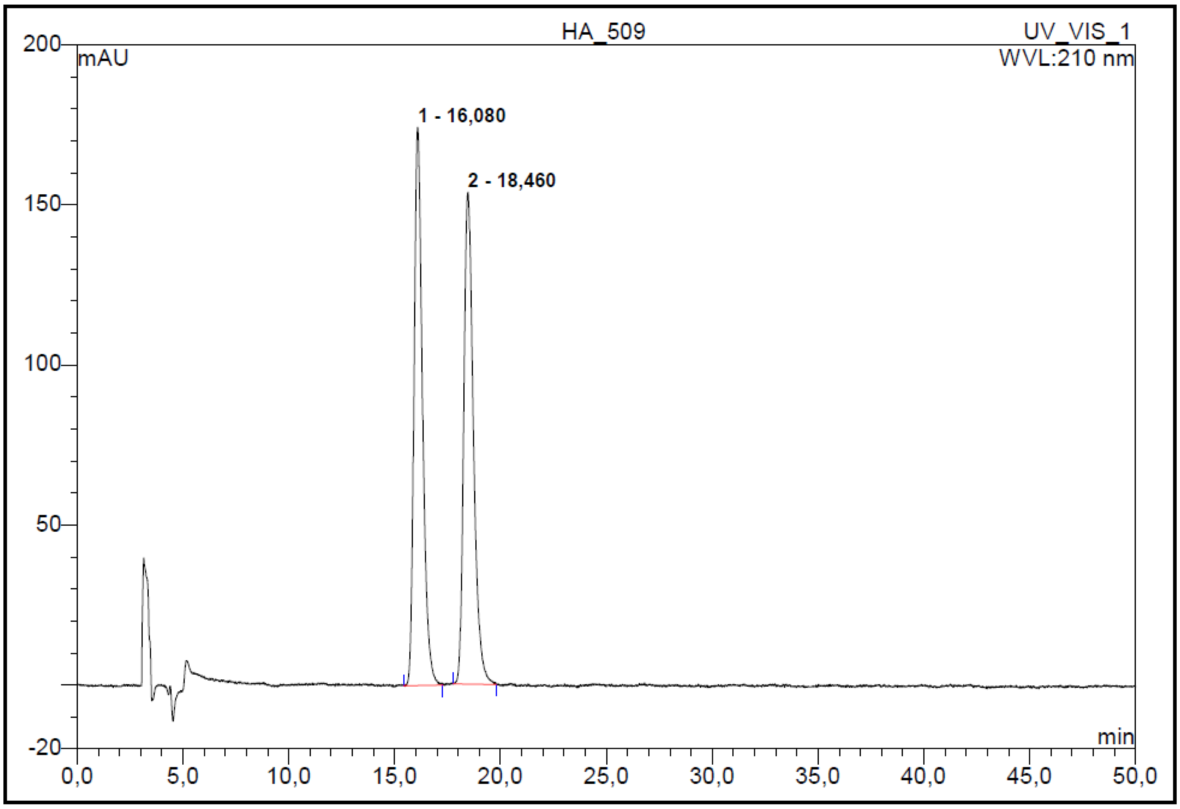


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,92	n.a.	404,939	113,564	56,29	n.a.	BMB*
2	12,16	n.a.	207,601	88,197	43,71	n.a.	BMB*
Total:			612,540	201,761	100,00	0,000	

Trace of the racemic compound:

Chiral HPLC: Racemic [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.7 min, t_R = 12.4 min].

4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]-1-methylquinolin-2(1H)-one (**17**)

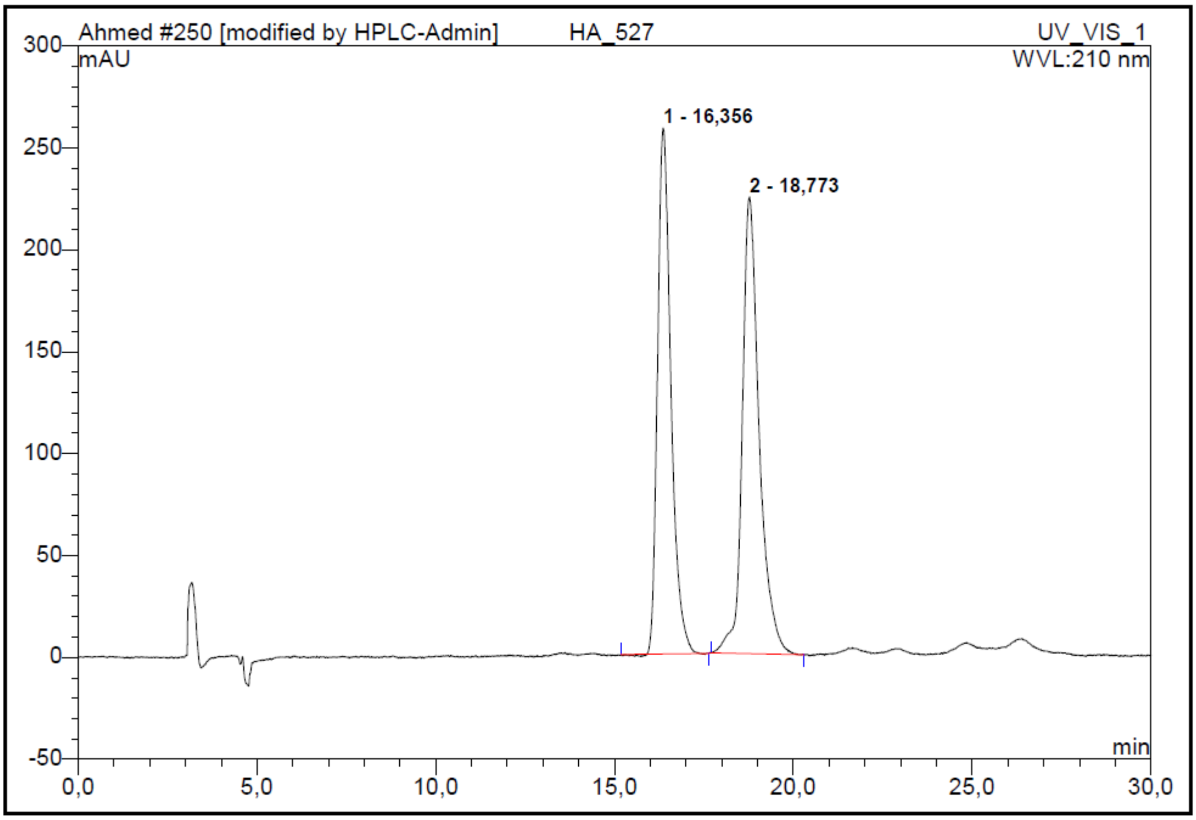


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,08	n.a.	174,429	81,342	50,03	n.a.	BMB*
2	18,46	n.a.	153,683	81,238	49,97	n.a.	BMB*
Total:			328,112	162,580	100,00	0,000	

<u>Trace of the enantioenriched compound</u>:

Chiral HPLC: 5% *ee* [©CHIRALPAK AD-H 250 × 4.6 mm, 20 °C, 70% *n*-heptane/*i*PrOH, 1 mL/min, 210 nm, t_R = 8.7 min, t_R = 12.4 min].

4-[2-(3,3-Dimethyloxiran-2-yl)ethyl]-1-methylquinolin-2(1H)-one (**17**)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,36	n.a.	257,903	111,773	47,55	n.a.	BMB*
2	18,77	n.a.	223,929	123,302	52,45	n.a.	BMB*
Total:			481,832	235,075	100,00	0,000	

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