I. General experimental procedure

All experiments were performed in flame-dried glassware under an argon atmosphere and under anhydrous conditions using Schlenk techniques.

Solvents and reagents: Dry dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were obtained from an *MBraun* MB-SPS 800 solvent purification system. Dry benzene (PhH), dimethylformamide (DMF), methanol (MeOH) and pyridine (py) were obtained from either *Sigma-Aldrich* or *Acros* in the highest available purity (>99%, extra dry over molecular sieves) and used without further purification. Technical solvents used for aqueous workup and purification by either crystallization or column chromatography [acetone, dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), ethyl acetate (EtOAc), hexane, methanol (MeOH), pentane] were distilled prior to use. Iodosobenzene[1] (PhIO) and manganese(III)-5,10,15,20-tetrakis(pentafluorophenyl)-porphyrin chloride[2] (Mn[TPFPP]Cl) were synthesized according to procedures previously described in literature and. PhIO was stored at –20 °C under argon.

Chromatography: Thin layer chromatography (TLC) was performed on pre-coated glass-backed Merck Kieselgel 60 F_{254} plates with visualization effected with ultra-violet irradiation (λ = 254, 366 nm) and/or staining using potassium permanganate ($KMnO_4$) solution prepared from potassium permanganate (3.00 g), potassium carbonate (20.0 g) and 5% aqueous sodium hydroxide solution (5.00 mL) in water (300 mL). Flash column chromatography was performed on silica 60 (*Merck*, 230–400 mesh) with the indicated eluent mixtures. Automated flash column chromatography was performed on a *Büchi C-815 Flash* chromatography instrument for clean separation of all products of the enantioselective oxygenation reaction. In all cases, *Büchi FlashPure* silica flash cartridges (12 g, manufacturer number 11067704) were used in combination with either method A (acetone/CH_2Cl_2 solvent mixture, flow rate 30 mL/min, 4% [1 min], 4% → 8% [11 min], 8% [7 min], 8% → 12% [8 min], 12% [6 min], ELSD detection) or method B (MeOH/CH_2Cl_2 solvent mixture, flow rate 30 mL/min, 1% [1 min], 1% → 3% [5 min], 3% [10 min], 3% → 5% [5 min], 5% → 10% [5 min], 10% [3 min], UV detection).

Melting points: Determined using a *Kofler* heating bar designed by *L. Kofler* (*Reichert*) without correction or using a *Büchi* M-510 melting point apparatus, with range quoted to the nearest whole number.

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

NMR spectroscopy: ^{1}H NMR spectra were recorded on *Bruker* AVHD-300, AVHD-400 or AVHD-500 spectrometers at 303 K operating at 300 MHz, 400 MHz and 500 MHz, respectively. Data is reported in the following manner: chemical shift [in parts per million (ppm) relative to residual $CHCl_3$ (δ_H = 7.26 ppm), MeOD-d_3 (δ_H = 3.31 ppm) or DMSO-d_5 (δ_H = 2.50 ppm)], number of protons, multiplicity and coupling constant *J* (measured in Hz to the nearest 0.1 Hz). The multiplicity of a signal is indicated as: s-singlet, bs-broad singlet, d-doublet, t-triplet, q-quartet, hept-heptet, m-multiplet, or combinations of these. Apparent multiplets which occur as a result of coupling constant equality between magnetically non-equivalent protons are marked as virtual (*virt*). ^{13}C NMR spectra were recorded on the same AVHD-400 or AVHD-500 spectrometers at 303 K operating at 101 MHz and

126 MHz respectively with proton decoupling. The chemical shift [in parts per million (ppm)] is reported relative to residual $CHCl_3$ (δ_C = 77.16 ppm), MeOD-d_3 (δ_C = 49.00 ppm) or DMSO-d_5 (δ_C = 39.52 ppm). ^{19}F NMR spectra were recorded on a *Bruker* AVHD-500 (471 MHz) spectrometer and used without reference. Spectra are reported based on appearance, not on theoretical multiplicities derived from structural information.

Mass Spectroscopy (ESI): High-resolution mass spectra (HRMS) were recorded on a *Thermo Finnigan* LTQ FT (HRMS-ESI) with each value obtained within 5 ppm of the calculated mass.

Specific rotations: Optical rotations were determined using a *Bellingham+Stanley* ADP440+ polarimeter with a 0.5 cm cuvette at λ = 589 nm (Na-D-line) at 303 K. Specific rotation is reported as followed: $[\alpha]_D^T$ in 10^{-1} grad cm^2 g^{-1} (c was defined as g per 100 mL solvent).

GLC-FID: GC analysis for kinetic studies was performed on an *Agilent Technologies* 7890B with a DB-5ht column (15 m, 0.32 mm, 0.10 µM). Standard method used for separation of all the compounds **2a**, **3a** and **4a**: 60 °C [1 min], 15 °C/min → 300 °C, 300 °C [5 min].

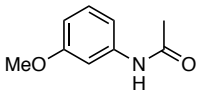
Chiral HPLC: Analytical HPLC (*Thermo Fisher, Dionex* Ultimate 3000 pump, *Dionex* Ultimate 3000, LPG 3400SD Pump, WPS3000SL Autosampler, DAD 3000 photodiode array detector) was performed using different chiral stationary phases (*Daicel ChiralCel*, *Chemical Industries*, flow rate, type and eluent is given for the corresponding compounds) and UV detection (λ = 210 or 254 nm) at 303 K.

II. Chemical syntheses

1 General procedures for the synthesis of quinolones

1.1 Synthesis of non-commercially available acetanilides S1

*1.1.1 m-Acetanisidide (**S1j**)*



Py (1.96 mL, 1.93 g, 24.4 mmol, 0.6 equiv) and Ac_2O (4.22 mL, 4.56 g, 44.7 mmol, 1.1 equiv) were added sequentially to a solution of *m*-anisidine (4.56 mL, 5.00 g, 40.6 mmol, 1.0 equiv) in CH_2Cl_2 (60 mL, 0.67 M) at 0 °C and the reaction mixture was stirred for 20 h at ambient temperature. The reaction was quenched by addition of H_2O (80 mL) and the organic layer was separated. The aqueous layer was extracted twice with CH_2Cl_2 (2 × 160 mL) and the combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (80 mL) and brine (80 mL). After removal of all volatiles *in vacuo* *m*-acetanisidide (**S1j**) was obtained as an off-white solid in high purity (6.55 g, 39.7 mmol, 98%) and was used without further purification for the next step.

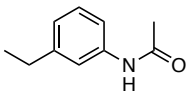
^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.27 (t, ^4J = 2.4 Hz, 1H, H-2), 7.21 (t, ^3J = 8.1 Hz, 1H, H-5), 7.14 (br s, 1H, NH), 6.95 (d, ^3J = 8.0 Hz, 1H, H-4), 6.66 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H, H-6), 3.80 (s, 3H, OCH_3), 2.17 (s, 3H $COCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] =168.4 (CO), 160.3 (C-3), 139.2 (C-1), 129.8 (C-5), 112.0 (C-4), 110.2 (C-6), 105.7 (C-2), 55.5 (OCH_3), 24.9 (CH_3).

HRMS (+ESI): calc. for $C_9H_{12}O_2N$ $[M+H]^+$: 166.0863; found: 166.0863.

Spectral data matches those reported in the literature.[3]

*1.1.2 3'-Ethylacetanilide (**S1n**)*



NEt_3 (5.02 mL, 36.0 mmol, 1.2 equiv) was added to a solution of 3-ethylaniline (3.73 mL, 30.0 mmol, 1.0 equiv) in CH_2Cl_2 (48 mL, 0.6 M) and the solution was cooled to 0 °C. AcCl (2.35 mL, 33.0 mmol, 1.1 equiv) was added dropwise and the reaction mixture was allowed to stir at 23 °C for 4 h. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (80 mL) and H_2O (10 mL) and the organic layer was separated. The aqueous layer was extracted twice with CH_2Cl_2 (2 × 160 mL) and the combined organic layers were washed with brine (150 mL) and dried over Na_2SO_4. After removal of all volatiles *in vacuo* the crude 3'-ethylacetanilide (**S1n**) was obtained as a pale brown solid in high purity and was used without further purification for the next step (4.81 g, 29.5 mmol, 98%).

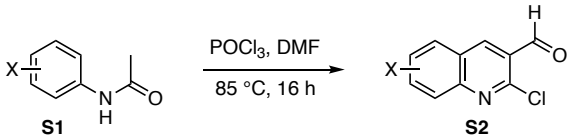
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.64 (br s, 1H, NH), 7.36 (d, ^4J = 2.1 Hz, 1H, H-4), 7.32 (dd, ^3J = 8.1 Hz, ^4J = 2.0 Hz, 1H, H-6), 7.21 (t, ^3J = 7.8 Hz, 1H, H-5), 6.94 (d, ^3J = 7.6 Hz, 1H, H-4), 2.61 (q, ^3J = 7.6 Hz, 2H, CH_2), 2.16 (s, 3H, $COCH_3$) 1.21 (t, ^3J = 7.6 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 168.7 (CO), 145.4 (C-3), 138.0 (C-1), 129.0 (C-5), 124.0 (C-4), 119.6 (C-2), 117.4 (C-6), 29.0 (CH_2), 24.7 ($CO\underline{C}H_3$), 15.6 (CH_3).

HRMS (+ESI): calc. for $C_{10}H_{14}ON$ $[M+H]^+$: 164.1070; found: 164.1070.

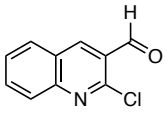
Spectral data matches those reported in the literature.[4]

1.2 General procedure 1 (GP1): Synthesis of 2-chloroquinoline-3-carbaldehydes S2



$POCl_3$ (9.6 equiv) was added dropwise to neat DMF (3.4 equiv) at 0 °C and upon complete addition the solution was allowed to warm to ambient temperature. Acetanilide **S1** (1.0 equiv) was added in one portion and the reaction mixture was heated to 85 °C for 16 h. The reaction was cooled to ambient temperature and was poured into ice water whereupon a yellow or orange solid precipitated. The resulting suspension was stirred at 0 °C for 30 min before it was filtered over a sintered glass funnel. The remaining solids were washed with H_2O, dried under high vacuum and eventually recrystallized to yield the entitled 2-chloroquinoline-3-carbaldehyde **S2**.

*1.2.1 2-Chloroquinoline-3-carbaldehyde (**S2a**)*



Following GP1 the entitled 2-chloroquinoline-3-carbaldehyde (**S2a**) was obtained from acetanilide (5.41 g, 40.0 mmol, 1.0 equiv) as bronze needles *via* recrystallization from EtOAc (3.29 g, 17.2 mmol, 50%).

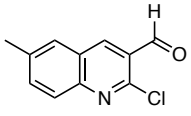
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.6 (s, 1H, CHO), 8.77 (s, 1H, H-4), 8.08 (dd, ^3J = 8.5 Hz, ^4J = 1.1 Hz, 1H, H-7), 7.99 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1H, H-6), 7.89 (ddd, ^3J = 8.5, 6.9 Hz, ^4J = 1.4 Hz, 1H, H-8), 7.66 (ddd, ^3J = 8.0, 6.9 Hz, ^4J = 1.1 Hz, 1H, H-5).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.3 (CHO), 150.3 (C-2), 149.7 (C-8a), 140.5 (C-4), 133.8 (C-8), 129.9 (C-6), 128.8 (C-7), 128.3 (C-5), 126.7 (C-4a), 126.5 (C-3).

HRMS (+ESI): calc. for $C_{10}H_7OClN$ $[M+H]^+$: 192.0211; found: 192.0211.

Spectral data matches those reported in the literature.[5]

*1.2.2 2-Chloro-6-methylquinoline-3-carbaldehyde (**S2f**)*



Following GP1 the entitled 2-chloro-6-methylquinoline-3-carbaldehyde (**S2f**) was obtained as a yellow crystalline solid from 4'-methylacetanilide (2.61 g, 1.75 mmol, 1.0 equiv) *via* recrystallization from EtOAc (1.28 g, 6.22 mmol, 36%).

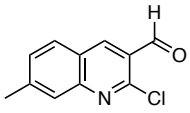
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.6 (s, 1H, CHO), 8.68 (s, 1H, H-4), 7.98 (d, ^3J = 8.6 Hz, 1H, H-8), 7.74 (d, ^4J = 1.7 Hz, 1H, H-5), 7.72 (dd, ^3J = 8.6 Hz, ^4J = 2.0 Hz, 1H, H-7), 2.57 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.4 (CHO), 149.3 (C-2), 148.3 (C-8a), 139.6 (C-4), 138.5 (C-6), 136.0 (C-7), 128.4 (C-5), 128.2 (C-8), 126.6 (C-4a), 126.3 (C-3), 21.6 (CH_3).

HRMS (+ESI): calc. for $C_{11}H_9OClN$ $[M+H]^+$: 206.0367; found: 206.0367.

Spectral data matches those reported in the literature.[5]

*1.2.3 2-Chloro-7-methylquinoline-3-carbaldehyde (**S2g**)*



Following GP1 the entitled 2-chloro-7-methylquinoline-3-carbaldehyde (**S2g**) was obtained as pale yellow needles from 3'-methylacetanilide (2.61 g, 1.75 mmol, 1.0 equiv) *via* recrystallization from EtOAc (2.14 g, 10.4 mmol, 59%).

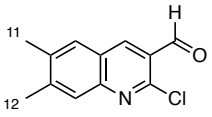
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.54 (s, 1H, CHO), 8.72 (d, ^5J = 0.8 Hz, 1H, H-4), 7.87 (d, ^3J = 8.4 Hz, 1H, H-5), 7.85 (dd, ^4J = 1.7, ^5J = 0.9 Hz, 1H, H-8), 7.48 (dd, ^3J = 8.3 Hz, ^4J = 1.7 Hz, 1H, H-6), 2.61 (d, ^4J = 0.9 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.3 (CHO), 150.3 (C-2), 149.9 (C-8a), 145.1 (C-7), 139.9 (C-4), 130.5 (C-6), 129.4 (C-5), 127.7 (C-8), 125.7 (C-3), 124.6 (C-4a), 22.4 (CH_3).

HRMS (+ESI): calc. for $C_{11}H_9OClN$ $[M+H]^+$: 206.0367; found: 206.0367.

Spectral data matches those reported in the literature.[5]

*1.2.4 2-Chloro-6,7-dimethylquinoline-3-carbaldehyde (**S2h**)*



Following GP1 the entitled 2-chloro-6,7-dimethylquinoline-3-carbaldehyde (**S2h**) was obtained as a yellow crystalline solid from 3',4'-dimethylacetanilide (2.45 g, 15.0 mmol, 1.0 equiv) *via* recrystallization from EtOAc (2.00 g, 9.10 mmol, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.5 (br s, 1H, NH), 8.63 (s, 1H, H-4), 7.82 (s, 1H, H-8), 7.69 (s, 1H, H-5), 2.50 (s, 3H), 2.46 (s, 3H).

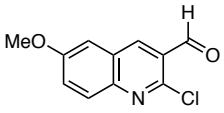
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.6 (CHO), 149.6 (C-2), 148.9 (C-8a), 145.2 (C-7), 139.3 (C-4), 138.6 (C-6), 128.8 (C-5), 128.1 (C-8), 125.8 (C-3), 125.3 (C-4a), 21.1 (C-11), 20.2 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{11}OClN$ $[M+H]^+$: 220.0524; found: 220.0523.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2966 (w, sp^3 C-H), 2855 (w, C-HO), 1657 (vs, C=O), 1555 (vs, C=C), 1484 (m, C=C), 1411 (m), 1050 (m, sp^2 C-Cl), 891 (s, sp^2 C-H), 828 (m, sp^2 C-H), 772 (s, sp^2 C-H), 660 (m).

m.p. = 169 °C.

*1.2.5 2-Chloro-6-methoxyquinoline-3-carbaldehyde (**S2i**)*



Following GP1 the entitled 2-chloro-6-methoxyquinoline-3-carbaldehyde (**S2i**) was obtained as an orange crystalline solid from *p*-acetanisidide (6.00 g, 36.3 mmol, 1.0 equiv) *via* recrystallization from EtOAc (2.98 g, 13.5 mmol, 37%).

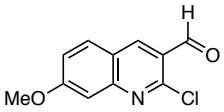
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.6 (s, 1H, CHO), 8.64 (s, 1H, H-4), 7.97 (d, ^3J = 9.2 Hz, 1H, H-8), 7.52 (dd, ^3J = 9.3 Hz, ^4J = 2.8 Hz, 1H, H-7), 7.20 (d, ^4J = 2.8 Hz, 1H, H-5), 3.96 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.5 (CHO), 158.8 (C-6), 147.7 (C-2), 145.8 (C-8a), 138.7 (C-4), 129.9 (C-8), 127.8 (C-3), 126.6 (C-7), 126.4 (C-4a), 106.4 (C-5), 55.8 (OCH_3).

HRMS (+ESI): calc. for $C_{11}H_9O_2ClN$ $[M+H]^+$: 222.0316; found: 222.0317.

Spectral data matches those reported in the literature.[5]

*1.2.6 2-Chloro-7-methoxyquinoline-3-carbaldehyde (**S2j**)*



Following GP1 the entitled 2-chloro-7-methoxyquinoline-3-carbaldehyde (**S2j**) was obtained as a light brown solid from *m*-acetanisidide (**S1j**) (6.55 g, 39.7 mmol, 1.0 equiv) *via* recrystallization from EtOAc (5.18 g, 27.7 mmol, 70%).

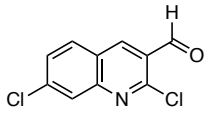
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 10.5 (s, 1H, CHO), 8.67 (s, 1H, H-4), 7.85 (d, ^3J = 9.0 Hz, 1H, H-5), 7.38 (d, ^2J = 2.4 Hz, 1H, H-8), 7.29-7.26 (m, 1H, H-6), 3.98 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.2 (CHO), 164.2 (C-7), 152.0 (C-4a), 151.1 (C-8a), 139.5 (C-4), 130.9 (C-5), 124.4 (C-2), 121.8 (C-3), 121.6 (C-6), 106.8 (C-8), 55.9 (OCH_3).

HRMS (+ESI): calc. for $C_{11}H_9O_2ClN$ $[M+H]^+$: 222.0316; found: 222.0317.

Spectral data matches those reported in the literature.[5]

*1.2.7 2,7-Dichloroquinoline-3-carbaldehyde (**S2k**)*



Following GP1 the entitled 2,7-dichloroquinoline-3-carbaldehyde (**S2k**) was obtained as colorless needles from 3'-chloroacetanilide (2.97 g, 1.75 mmol, 1.0 equiv) *via* recrystallization from MeCN (1.05 g, 4.64 mmol, 27%).

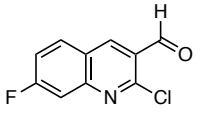
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.4 (s, 1H, CHO), 9.02 (s, 1H, H-4), 8.33 (d, ^3J = 8.8 Hz, 1H, H-5), 8.14 (d, ^4J = 2.0 Hz, 1H, H-8), 7.81 (dd, ^3J = 8.8 Hz, ^4J = 2.1 Hz, 1H, H-7).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.6 (CHO), 150.9 (C-2), 149.2 (C-7), 141.7 (C-4), 139.0 (C-8a), 132.5 (C-5), 129.5 (C-6), 127.2 (C-8), 127.1 (C-3), 125.6 (C-4a).

HRMS (+ESI): calc. for $C_{10}H_6OCl_2N$ $[M+H]^+$: 225.9821; found: 225.9821.

Spectral data matches those reported in the literature.[5]

*1.2.8 2-Chloro-7-fluoroquinoline-3-carbaldehyde (**S2l**)*



Following GP1 the entitled 2-chloro-7-fluoroquinoline-3-carbaldehyde (**S2l**) was obtained as colorless needles from 3'-chloroacetanilide (2.68 g, 1.75 mmol, 1.0 equiv) *via* recrystallization from EtOAc (2.08 g, 9.92 mmol, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 10.6 (s, 1H, CHO), 8.76 (s, 1H, H-4), 8.01 (dd, ^3J = 9.0 Hz, $^4J_{HF}$ = 5.9 Hz, 1H, H-5), 7.72 (dd, $^3J_{HF}$ = 9.6 Hz, ^4J = 2.5 Hz, 1H, H-8), 7.45 (ddd, $^3J_{HF}$ = 9.0 Hz, ^3J = 8.1 Hz, ^4J = 2.5 Hz, 1H, H-6).

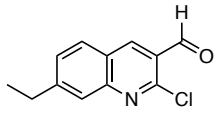
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.0 (CHO), 165.7 (d, $^1J_{CF}$ = 257.5 Hz, C-7), 151.7 (C-2), 151.1 (d, $^3J_{CF}$ = 13.7 Hz, C-8a), 140.1 (C-4), 132.2 (d, $^3J_{CF}$ = 10.6 Hz, C-5), 126.0 (d, $^4J_{CF}$ = 2.6 Hz, C-4a), 123.8 (C-3), 119.1 (d, $^2J_{CF}$ = 25.6 Hz, C-6), 113.1 (d, $^2J_{CF}$ = 21.6 Hz, H-8).

^{19}F NMR (376 MHz, $CDCl_3$) δ [ppm] = –101.3 (td, $^3J_{HF}$ = 9.1 Hz, $^4J_{HF}$ = 6.0 Hz, 1F)

HRMS (+ESI): calc. for $C_{10}H_6OClFN$ $[M+H]^+$: 210.0116; found: 210.0116.

Spectral data matches those reported in the literature.[6]

*1.2.9 2-Chloro-7-ethylquinoline-3-carbaldehyde (**S2m**)*



Following GP1 the entitled 2-chloro-7-ethylquinoline-3-carbaldehyde (**S2m**) was obtained as a bronze crystalline solid from 3'-ethylacetanilide (**S1n**) (3.26 g, 20.0 mmol, 1.0 equiv). Excess toluene was removed *via* azeotropic distillation from toluene and the desired product **S2m** was used without further purification (4.05 g, 18.4 mmol, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.6 (s, 1H, CHO), 8.74 (s, 1H, H-4), 7.89 (d, ^3J = 8.4 Hz, H-5), 7.87 (d, ^4J = 1.7 Hz, 1H, H-8), 7.54 (dd, ^3J = 8.4 Hz, ^4J = 1.7 Hz, 1H, H-6), 2.93 (q, ^3J = 7.5 Hz, 2H, CH_2), 1.39 (t, ^3J = 7.6 Hz, 3H, CH_3).

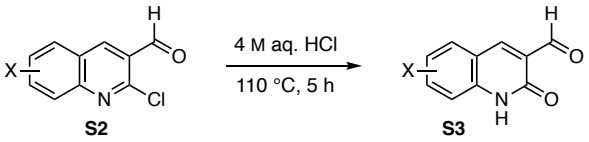
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 189.4 (CHO), 151.3 (C-7), 150.4 (C-2), 150.2 (C-8a), 140.0 (C-4), 129.7 (C-6), 129.6 (C-5), 126.5 (C-8), 125.8 (C-3), 125.0 (C-4a), 29.5 (CH_2), 14.9 (CH_3).

HRMS (+ESI): calc. for $C_{12}H_{11}OClN$ $[M+H]^+$: 220.0524; found: 220.0524.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2876 (w, C-HO), 1687 (vs, C=O), 1580 (vs, C=C), 1483 (m, C=C), 1134 (m, sp^2 C-Cl), 984 (s, sp^2 C-H), 821 (m, sp^2 C-H), 755 (m, sp^2 C-H).

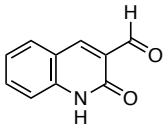
m.p. = 101 °C.

1.3 General procedure 2 (GP2): Synthesis of 2-quinolone-3-carbaldehydes S3



A 4 M aqueous HCl solution (0.14 M) was added to the corresponding 2-chloroquinoline-3-carbaldehyde **S2** (1.0 equiv) and the suspension was heated to 110 °C for 5 h. The reaction was cooled to ambient temperature and the suspension was filtered over a sintered glass funnel. The remaining solids were washed with water and dried under high vacuum to yield the entitled 2-quinolone-3-carbaldehyde **S3** in high purity, which was used without further purification for the next step.

*1.3.1 2-Quinolone-3-carbaldehyde (**S3a**)*



Following *GP2* the entitled 2-quinolone-3-carbaldehyde **S3a** was obtained from 2-chloroquinoline-3-carbaldehyde (3.82 g, 19.9 mmol, 1.0 equiv) as a pale yellow powder (3.31 g, 19.1 mmol, 96%).

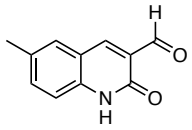
^{1}H NMR (300 MHz, DMSO-d_6) δ [ppm] = 12.2 (s, 1H, NH), 10.2 (s, 1H, CHO), 8.51 (s, 1H H-4), 7.92 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.66 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.36 (dq, ^3J = 8.4 Hz, ^4J = 0.8 Hz, 1H, H-8), 7.25 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6).

^{13}C NMR (101 MHz, DMSO-d_6) δ [ppm] = 189.7 (CHO), 161.4 (C-2), 142.4 (C-4), 141.1 (C-8a), 133.7 (C-7), 130.9 (C-5), 125.6 (C-3), 122.6 (C-6), 118.1 (C-4a), 115.4 (C-8).

HRMS (+ESI): calc. for $C_{10}H_8O_2N$ $[M+H]^+$: 174.0550; found: 174.0550.

Spectral data matches those reported in the literature.[5]

*1.3.2 6-Methyl-2-quinolone-3-carbaldehyde (**S3f**)*



Following *GP2* the entitled 6-methyl-2-quinolone-3-carbaldehyde (**S3f**) was obtained from 6-methyl-2-chloroquinoline-3-carbaldehyde (**S2f**) (949 mg, 4.61 mmol, 1.0 equiv) as a yellow powder (700 mg, 3.74 mmol, 81%).

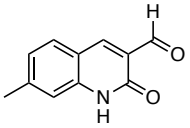
^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.2 (s, 1H, NH), 10.2 (s, 1H, CHO), 8.43 (s, 1H, H-4), 7.71 (d, ^4J = 2.54 Hz, 1H, H-5), 7.50 (dd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, 1H, H-7), 7.27 (d, ^3J = 8.4 Hz, 1H, H-8), 2.34 (s, 3H, CH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 189.9 (CHO), 161.4 (C-2), 142.1 (C-4), 139.3 (C-8a), 135.2 (C-7), 131.8 (C-6), 130.1 (C-5), 125.5 (C-3), 118.1 (C-4a), 115.4 (C-8), 20.3 (CH_3).

HRMS (+ESI): calc. for $C_{11}H_{10}O_2N$ $[M+H]^+$: 188.0706; found: 188.0706.

Spectral data matches those reported in the literature.[7]

*1.3.3 7-Methyl-2-quinolone-3-carbaldehyde (**S3g**)*



Following *GP2* the entitled 7-methyl-2-quinolone-3-carbaldehyde (**S3g**) was obtained from 7-methyl-2-chloroquinoline-3-carbaldehyde (**S2f**) (1.33 g, 6.47 mmol, 1.0 equiv) as a yellow powder (1.09 g, 5.85 mmol, 90%).

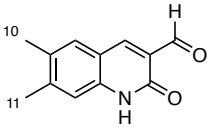
^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.2 (s, 1H, NH), 10.2 (s, 1H, CHO), 8.43 (s, 1H, H-4), 7.71 (d, ^4J = 2.54 Hz, 1H, H-5), 7.50 (dd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, 1H, H-6), 7.27 (d, ^3J = 8.4 Hz, 1H, H-8), 2.34 (s, 3H, CH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 189.9 (CHO), 161.4 (C-2), 142.1 (C-4), 139.3 (C-8a), 135.2 (C-7), 131.8 (C-6), 130.1 (C-5), 125.5 (C-3), 118.1 (C-4a), 115.4 (C-8), 20.3 (CH_3).

HRMS (+ESI): calc. for $C_{11}H_{10}O_2N$ $[M+H]^+$: 188.0706; found: 188.0706.

Spectral data matches those reported in the literature.[8]

*1.3.4 6,7-Dimethyl-2-quinolone-3-carbaldehyde (**S3h**)*



Following *GP2* the entitled 6,7-dimethyl-2-quinolone-3-carbaldehyde (**S3h**) was obtained from 6,7-methyl-2-chloroquinoline-3-carbaldehyde (**S2h**) (879 mg, 4.00 mmol, 1.0 equiv) as a yellow powder (804 mg, 4.00 mmol, *quant*).

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.1 (br s, 1H, NH), 10.2 (s, 1H, CHO), 8.36 (s, 1H, H-4), 7.63 (s, 1H, H-5), 7.11 (s, 1H, C-8), 2.31 (s, 3H, H-11), 2.25 (s, 3H, H-10).

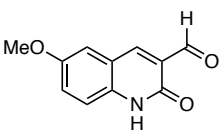
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 189.7 (CHO), 161.6 (C-2), 144.3 (C-7), 141.9 (C-4), 139.8 (C-8a), 131.5 (C-6), 130.3 (C-5), 124.6 (C-3), 116.4 (C-4a), 115.6 (C-8), 20.4 (C-11), 18.8 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{12}O_2N$ $[M+H]^+$: 202.0863; found: 202.0862.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2909 (w, sp^3 C-H), 2849 (w, C-HO), 1650 (vs, C=O), 1553 (s, C=C), 1478 (s, C=C), 1230 (m), 942 (w, sp^2 C-H) 880 (s, sp^2 C-H), 829 (m, sp^2 C-H).

m.p. = 303 °C.

*1.3.5 6-Methoxy-2-quinolone-3-carbaldehyde (**S3i**)*



Following *GP2* the entitled 2-quinolone-3-carbaldehyde **S3i** was obtained from 6-methoxy-2-chloroquinoline-3-carbaldehyde (856 mg, 3.86 mmol, 1.0 equiv) as a yellow powder (671 mg, 3.30 mmol, 86%).

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.2 (s, 1H, NH), 10.2 (s, 1H, CHO), 8.44 (s, 1H, H-4), 7.46 (d, ^4J = 2.5 Hz, 1H, H-5), 7.32 (dd, ^3J = 9.0 Hz, ^4J = 2.6 Hz, 1H, H-7), 7.29 (d, ^3J = 9.1 Hz, 1H, H-8), 3.79 (s, 3H, OCH_3).

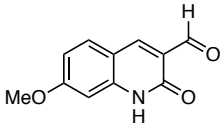
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 189.9 (CHO), 161.1 (C-2), 154.5 (C-6), 141.8 (C-4a), 136.0 (C-8a), 125.7 (C-3), 123.7 (C-7), 118.7 (C-4a), 116.8 (C-8), 111.1 (C-5), 55.6 (OCH_3).

HRMS (+ESI): calc. for $C_{11}H_{10}O_3N$ $[M+H]^+$: 204.0655; found: 204.0655.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2843 (w, C-HO), 1663 (vs, C=O), 1556 (s, C=C), 1500 (s, C=C), 1378 (s), 1231 (s, C-O), 1177 (s), 1111 (s), 1034 (s, C-O), 914 (s, sp^2 C-H), 820 (vs, sp^2 C-H), 676 (s).

m.p. = 285 °C.

*1.3.6 7-Methoxy-2-quinolone-3-carbaldehyde (**S3j**)*



Following *GP2* the entitled 2-quinolone-3-carbaldehyde **S3j** was obtained from 6-methoxy-2-chloroquinoline-3-carbaldehyde (1.50 g, 6.77 mmol, 1.0 equiv) as a brown powder (1.25 g, 6.15 mmol, 91%).

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.1 (bs, 1H. NH), 10.2 (s, 1H, CHO), 8.42 (s, 1H, H-4), 7.83 (d, ^3J = 8.8 Hz, 1H, H-5), 6.88 (dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, 1H, H-6), 6.81 (d, ^4J = 2.4 Hz, 1H, H-8), 3.85 (s, 3H, OCH_3).

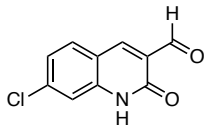
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 189.4 (CHO), 163.9 (C-7), 161.9 (C-2), 143.6 (C-8a), 142.3 (C-4), 132.7 (C-5), 122.5 (C-3), 112.6 (2C, C-4a, C-6), 97.6 (C-8), 55.7 (OCH_3).

HRMS (+ESI): calc. for $C_{11}H_{10}O_3N$ $[M+H]^+$: 204.0655; found: 204.0655.

m.p. = 275 °C.

Spectral data matches those reported in the literature.[9]

*1.3.7 7-Chloro-2-quinolone-3-carbaldehyde (**S3k**)*



Following *GP2* the entitled 7-chloro-2-quinolone-3-carbaldehyde (**S3k**) was obtained from 2,7-dichloroquinoline-3-carbaldehyde (**S2k**) (721 mg, 3.19 mmol, 1.0 equiv) as a white powder (620 mg, 2.99 mmol, 94%).

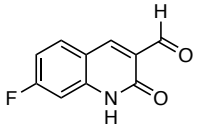
^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.3 (s, 1H, NH), 10.2 (s, 1H, CHO), 8.53 (d, ^5J = 0.6 Hz, 1H, H-4), 7.97 (d, ^3J = 8.5 Hz, 1H, H-5), 7.37 (d, ^4J = 2.0 Hz, 1H, H-8), 7.32 (dd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, 1H, H-6).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 189.6 (CHO), 161.3 (C-2), 141.9 (2C, C-4, C-7), 138.2 (C-8a), 132.8 (C-5), 125.7 (C-3), 123.0 (C-6), 117.0 (C-4a), 114.7 (C-8).

HRMS (+ESI): calc. for $C_{10}H_7O_2ClN$ $[M+H]^+$: 208.0160; found: 208.0159.

Spectral data matches those reported in the literature.[5]

*1.3.8 7-Fluoro-2-quinolone-3-carbaldehyde (**S3l**)*



Following *GP2* the entitled 7-fluoro-2-quinolone-3-carbaldehyde (**S3l**) was obtained from 7-fluoro-2-chloroquinoline-3-carbaldehyde (**S2l**) (1.04 g, 4.60 mmol, 1.0 equiv) as a white powder (866 mg, 4.17 mmol, 91%).

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.3 (s, 1H, NH), 10.2 (s, 1H, CHO), 8.53 (s, 1H, H-4), 8.03 (dd, ^3J = 8.8 Hz, $^4J_{HF}$ = 6.2 Hz, 1H, H-5), 7.16 (*virt* td, $^3J \approx {}^3J_{HF}$ = 8.8 Hz, ^4J = 2.5 Hz, 1H, H-6), 7.08 (dd, $^3J_{HF}$ = 10.2 Hz, ^4J = 2.5 Hz, 1H, H-8).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 189.6 (CHO), 165.0 (d, $^1J_{CF}$ = 251.9 Hz, (C-7), 161.5 (C-2), 143.0 (d, $^3J_{CF}$ = 13.2 Hz, C-8a), 142.1 (C-4), 134.0 (d, $^3J_{CF}$ = 11.1 Hz, H-5), 124.7 (d, $^4J_{CF}$ = 2.7 Hz, C-4a), 115.4 (C-3), 111.4 (d, $^2J_{CF}$ = 23.7 Hz, C-6), 101.3 (d, $^2J_{CF}$ = 25.9 Hz, C-8).

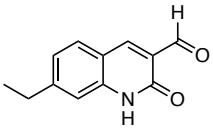
^{19}F NMR (471 MHz, DMSO-d_6) δ [ppm] = –103.5 (*virt* q, $^3J \approx {}^4J_{HF}$ = 8.9 Hz, 1F).

HRMS (+ESI): calc. for $C_{10}H_7O_2FN$ $[M+H]^+$: 192.0455; found: 192.0455.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2861 (w, sp^2 C-H), 2802 (w, C-HO), 1680 (vs, C=O), 1623 (s, C=C), 1560 (s, C=C), 1507 (s, C=C), 1414 (m), 1228 (s, sp^2 C-F), 1125 (s), 900 (s, sp^2 C-H), 826 (s, sp^2 C-H), 769 (s, sp^2 C-H), 671 (m).

m.p. = >300 °C (decomposition).

*1.3.9 7-Ethyl-2-quinolone-3-carbaldehyde (**S3m**)*



Following *GP2* the entitled 6,7-dimethyl-2-quinolone-3-carbaldehyde (**S3m**) was obtained from 7-ethyl-2-chloroquinoline-3-carbaldehyde (**S2m**) (3.52 g, 16.0 mmol, 1.0 equiv) as a yellow powder (2.46 mg, 12.2 mmol, 76%).

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.2 (br s, 1H, NH), 10.2 (s, 1H, CHO), 8.46 (s, 1H, H-4), 7.82 (d, ^3J = 8.1 Hz, 1H, H-5), 7.16 (d, ^4J = 1.9 Hz, 1H, H-8), 7.13 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 1H, H-6), 2.69 (q, ^3J = 7.6 Hz, 2H, CH_2), 1.20 (t, ^3J = 7.6 Hz, 3H, CH_3).

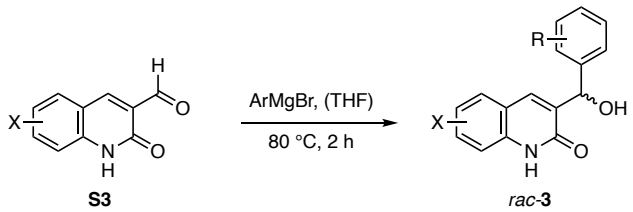
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 189.7 (CHO), 161.7 (C-2), 150.7 (C-7), 142.3 (C-4), 141.5 (C-8a), 130.9 (C-5), 124.7 (C-3), 123.3 (C-6), 116.3 (C-4a), 113.9 (C-8), 28.7 (CH_2), 15.0 (CH_3).

HRMS (+ESI): calc. for $C_{12}H_{12}O_2N$ $[M+H]^+$: 202.0863; found: 202.0863.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2877 (w, C-HO), 1686 (vs, C=O), 1624 (s), 1580 (s, C=C), 1483 (m, C=C), 1365 (m), 1134 (m, sp^2 C-Cl), 984 (s, sp^2 C-H), 821 (m, sp^2 C-H), 755 (m, sp^2 C-H).

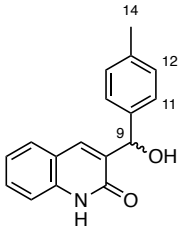
m.p. = 273 °C.

1.4 General procedure 3 (GP3): Synthesis of 3-(hydroxy(aryl)methyl)-2-quinolones *rac*-3



One third of the required aryl bromide (total amount: 2.5 equiv) was added to a vigorously stirring mixture of Mg turnings (2.5 equiv) in approximately one third of the required amount of THF (1.0 M). Once heat evolution was observed the rest of the aryl bromide and THF were added and the reaction mixture was heated to 80 °C for 1 h affording a 1.0 M *Grignard* solution. Once cooled the freshly prepared arylmagnesium bromide solution was added to a suspension of the corresponding 2-quinolone-3-carbaldehyde **S3** in THF (0.4 M) and the reaction mixture was heated to 80 °C until TLC indicated complete consumption of the starting material (typically 2 h). The reaction was cooled to ambient temperature and quenched by addition of saturated aqueous $NaHCO_3$ solution and EtOAc. The organic layer was separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine solution and dried over Na_2SO_4. After removal of all volatiles *in vacuo* the crude material was purified by FCC on silica gel (1% → 4% MeOH/CH_2Cl_2 + 0.1% Et_3N) to yield the entitled racemic benzylic alcohol.

*1.4.1 3-(Hydroxy(p-tolyl)methyl)-2-quinolone (rac-**3a**)*



A 1.0 M solution of *p*-tolylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 4-bromotoluene (369 µL, 3.00 mmol, 2.5 equiv) in THF (2.6 mL) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3 mL) according to *GP3*. After purification by FCC the entitled benzylic alcohol *rac*-**3a** was obtained as a white solid (278 mg, 1.05 mmol, 87%).

***R*f** (5% MeOH/CH_2Cl_2): 0.31.

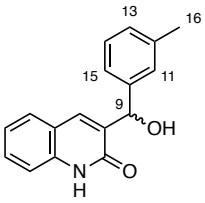
^{1}H NMR (300 MHz, MeOD-d_4) δ [ppm] 8.06 (d, ^4J = 1.0 Hz, 1H, H-4), 7.67 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.32 (m, 3H, H-8, H-11), 7.24 (ddd, ^3J = 7.9, 7.2 Hz, ^4J = 1.2 Hz, 1H, H-6), 7.13 (d, ^3J = 7.9 Hz, 2H, H-12), 5.92 (s, 1H, H-9), 2.30 (s, 3H, H-14).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-2), 141.0 (C-10), 139.0 (C-8a), 138.3 (C-13), 137.0 (2C, C-4, C-3), 131.3 (C-7), 129.9 (C-12), 129.2 (C-5), 128.1 (C-11), 123.9 (C-6), 121.4 (C-4a), 116.2 (C-8), 71.4 (C-9), 21.2 (C-14).

HRMS (+ESI): calc. for $C_{17}H_{16}O_2N$ $[M+H]^+$: 266.1176; found: 266.1176.

Spectral data matches those reported in the literature,[10] however decomposition in $CDCl_3$ after a time period of >16 h was observed. Accordingly, an additional data set in MeOD-d_4 is provided.

*1.4.2 3-(Hydroxy(m-tolyl)methyl)-2-quinolone (rac-**3b**)*



A 1.0 M solution of *m*-tolylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 3-bromotoluene (364 µL, 3.00 mmol, 2.5 equiv) in THF (2.7 mL) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL) according to *GP3.* After purification by FCC the entitled benzylic alcohol *rac*-**3b** was obtained as a white solid (289 mg, 1.09 mmol, 91%).

***R*f** (5% MeOH/CH_2Cl_2): 0.34.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.07 (s, 1H, H-4), 7.68 (dd, ^3J = 8.0 Hz, ^4J =1.3 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.33 (d, ^3J = 8.2 Hz, 1H, H-8), 7.25 (d, ^4J = 2.0 Hz, 1H, H-11), 7.29-7.22 (m, 2H, H-6, H-13), 7.19 (t, ^3J = 7.5 Hz, 1H, H-14), 7.06 (d, ^3J = 7.3 Hz, 1H, H-15), 5.92 (s, 1H, H-9), 2.31 (s, 3H, H-16).

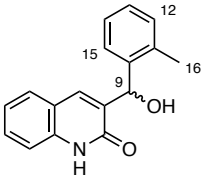
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-2), 143.9 (C-10), 139.0 (2C, C-8a, C-12), 137.1 (C-4), 137.0 (C-3), 131.3 (C-7), 129.2 (3C, C-5, C-14, C-15), 128.8 (C-11), 125.3 (C-15), 123.9 (C-6), 121.4 (C-4a), 116.2 (C-8), 71.5 (C-9), 21.5 (C-16).

HRMS (+ESI): calc. for $C_{17}H_{16}O_2N$ $[M+H]^+$: 266.1776; found: 266.1777.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3392 (bs, O-H), 2971 (w, sp^3 C-H), 2919 (w, sp^3 C-H), 1651 (vs, C=O), 1585 (m, C=C), 1569 (m, C=C), 1428 (w), 1215 (w), 1036 (w), 789 (w, sp^2 C-H), 754 (m, sp^2 C-H).

m.p. = 184 °C.

*1.4.3 3-(Hydroxy(o-tolyl)methyl)-2-quinolone (rac-**3c**)*



A 1.0 M solution of *o*-toluylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 2-bromotoluene (361 µL, 3.00 mmol, 2.5 equiv) in THF (2.6 mL) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL) according to *GP3.* After purification by FCC the entitled benzylic alcohol *rac*-**3c** was obtained as a white solid (315 mg, 1.19 mmol, 99%).

***R*f** (5% MeOH/CH_2Cl_2): 0.37.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.91 (t, ^4J = 0.9 Hz, 1H, H-4), 7.64 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.51 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.34 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.30 (dd, ^3J = 6.2 Hz, ^4J = 2.5 Hz, 1H, H-15), 7.25 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 7.20-7.12 (m, 3H, H-12, H-13, H-14), 6.21 (d, ^4J = 1.1 Hz, 1H, H-9), 2.44 (s, 3H, H-16).

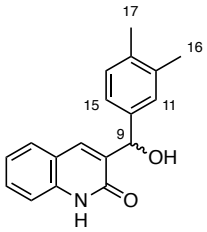
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.8 (C-2), 141.5 (C-10), 139.1 (C-8a), 137.9 (C-4), 137.5 (C-11), 136.5 (C-3), 131.5 (C-12), 131.4 (C-7), 129.2 (C-5), 128.6 (C-13), 127.5 (C-15), 126.9 (C-14), 123.9 (C-6), 121.3 (C-4a), 116.2 (C-8), 68.1 (C-9), 19.4 (C-16).

HRMS (+ESI): calc. for $C_{17}H_{16}O_2N$ $[M+H]^+$: 266.1776; found: 266.1776.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3301 (bs, w, O-H), 2925 (w, sp^3 C-H), 2855 (w, sp^3 C-H), 1649 (vs, C=O), 1586 (m, C=C), 1570 (m, C=C), 1428 (w), 1215 (w), 1024 (w), 751 (m, sp^2 C-H).

m.p. = 208 °C.

*1.4.4 3-((3,4-Dimethylphenyl)(hydroxy)methyl)-2-quinolone (rac-**3d**)*



A 1.0 M solution of 3,4-dimethylphenylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 4-bromo-*o*-xylene (406 µL, 3.00 mmol, 2.5 equiv) in THF (2.6 mL) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL) according to *GP3.* After purification by FCC the entitled benzylic alcohol *rac*-**3d** was obtained as a white solid (318 mg, 1.14 mmol, 95%).

***R*$_f$** (5% MeOH/CH_2Cl_2): 0.37.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.06 (t, ^4J = 0.8 Hz, 1H, H-4), 7.68 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.32 (dd, ^3J = 8.3 Hz, ^4J = 0.9 Hz, 1H, H-8), 7.24 (ddd, ^3J = 8.2, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 7.20 (d, ^4J = 1.9 Hz, 1H, H-11), 7.14 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 1H, H-15), 7.06 (d, ^3J = 7.8 Hz, 1H, H-14), 5.89 (d, ^4J = 1.0 Hz, 1H, H-9), 2.23 (s, 3H, H-16), 2.22 (s, 3H, H-17).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-2), 141.3 (C-10), 138.9 (C-8a), 137.3 (C-12), 137.0 (C-3), 137.0 (C-4), 136.8 (C-13), 131.3 (C-7), 130.4 (C-14), 129.4 (C-11), 129.2 (C-5), 125.6 (C-15), 123.9 (C-6), 121.4 (C-4a), 116.2 (C-8), 71.4 (C-9), 19.9 (C-16*), 19.5 (C-17*).

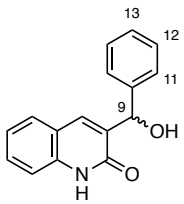
HRMS (+ESI): calc. for $C_{18}H_{18}O_2N$ $[M+H]^+$: 280.1332; found: 280.1334.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3367 (bs, w, O-H), 2970 (w, sp^3 C-H), 2919 (w, sp^3 C-H), 1651 (vs, C=O), 1586 (m, C=C), 1570 (m, C=C), 1501 (w), 1428 (w), 1214 (w), 1025 (w), 824 (w, sp^2 C-H), 802 (w, sp^2 C-H), 755 (m, sp^2 C-H).

m.p. = 190 °C.

*assignment is interconvertible

*1.4.5 3-(Hydroxy(phenyl)methyl)-2-quinolone (rac-**3e**)*



A commercially available solution of phenylmagnesium bromide (1.0 M in THF, 3.00 mL, 3.00 mmol, 2.5 equiv) was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL). After purification by FCC the entitled benzylic alcohol *rac*-**3e** was obtained as a white solid (278 mg, 1.05 mmol, 87%).

***R*$_f$** (5% MeOH/CH_2Cl_2): 0.33.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.08 (t, ^4J = 0.9 Hz, 1H, H-4), 7.68 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.47-7.43 (m, 2H, H-11), 7.35-7.28 (m, 3H, H-8, H-12), 7.27-7.21 (m, 2H, H-6, H-13), 5.96 (s, 1H, H-9).

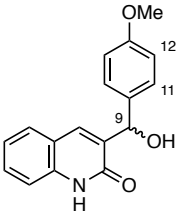
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-2), 144.1 (C-10), 139.0 (C-8a), 137.1 (C-3), 136.9 (C-4), 131.4 (C-7), 129.3 (C-12), 129.2 (C-5), 128.5 (C-13), 128.2 (C-11), 123.9 (C-6), 121.3 (H-4a), 116.2 (C-8), 71.5 (C-9).

HRMS (+ESI): calc. for $C_{16}H_{14}O_2N$ $[M+H]^+$: 252.1019; found: 252.1020.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3368 (bs, m, O-H), 3061 (w), 3030 (w), 1649 (vs, C=O), 1569 (m, C=C), 1427 (w), 1215 (w), 1021 (w), 740 (s, sp^2 C-H), 700 (s, sp^2 C-H).

m.p. = 200 °C.

*1.4.6 3-(Hydroxy(4-methoxyphenyl)methyl)-2-quinolone (rac-**3f**)*



A 1.0 M solution of *p*-anisylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (91.1 mg, 3.75 mmol, 2.5 equiv) and 4-bromoanisole (471 µL, 3.75 mmol, 2.5 equiv) in THF (3.3 mL) and was added to a solution of aldehyde **S3a** (260 mg, 1.50 mmol, 1.0 equiv) in THF (3.8 mL) according to *GP3*. After purification by FCC the entitled benzylic alcohol *rac*-**3f** was obtained as a white solid (389 mg, 1.38 mmol, 92%).

***R*$_f$** (5% MeOH/CH_2Cl_2): 0.27.

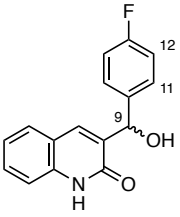
^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.09 (s, 1H, H-4), 7.70 (d, ^3J = 7.9 Hz, 1H, H-5), 7.51 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.3 Hz, 1H, H-7), 7.43-7.30 (m, 3H, H-8, H-11), 7.26 (td, ^3J = 7.6, 7.1 Hz, ^4J = 1.0 Hz, 1H, H-6), 6.87 (d, ^3J = 8.7 Hz, 2H, H-12), 5.90 (s, 1H, H-9), 3.76 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-2), 160.6 (C-13), 139.0 (C-8a), 137.1 (C-3), 136.8 (C-4), 136.0 (C-10), 131.3 (C-7), 129.5 (C-11), 129.2 (C-5), 123.9 (C-6), 121.4 (C-4a), 116.2 (C-8), 114.6 (C-12), 71.2 (C-9), 55.7 (OCH_3).

HRMS (+ESI): calc. for $C_{17}H_{16}O_3N$ $[M+H]^+$: 282.1125; found: 282.1125.

Spectral data matches those reported in the literature,[10] however decomposition in $CDCl_3$ after a time period of >16 h was observed. Accordingly, an additional data set in MeOD-d_4 is provided.

*1.4.7 3-((4-Fluorophenyl)(hydroxy)methyl)-2-quinolone (rac-**3g**)*



A 1.0 M solution of *p*-fluorophenylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 1-bromo-4-fluorobenzene (330 µL, 3.00 mmol, 2.5 equiv) in THF (2.8 mL) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL) according to *GP3*. After purification by FCC the entitled benzylic alcohol *rac*-**3g** was obtained as a white solid (278 mg, 1.05 mmol, 87%).

***R*$_f$** (5% MeOH/CH_2Cl_2): 0.35.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.12 (d, ^4J = 1.0 Hz, 1H, H-4), 7.69 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.47 (dd, ^3J = 8.6 Hz, $^4J_{HF}$ = 5.5 Hz, 2H, H-11), 7.32 (d, ^3J = 8.3 Hz, 1H, H-8), 7.25 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 7.03 (*virt* t, $^3J \approx {}^3J_{HF}$ = 8.9 Hz, 2H, H-12), 5.94 (s, 1H, H-9).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (d, $^{1}J_{CF}$ = 244.0 Hz, C-13), 163.4 (C-2), 140.2 (d, $^{4}J_{CF}$ = 3.2 Hz, C-10), 139.0 (C-8a), 137.0 (d, $^{4}J_{CF}$ = 4.8 Hz, C-3), 136.8 (C-4), 131.4 (C-7), 130.0 (d, $^{3}J_{CF}$ = 8.1 Hz, C-11), 129.2 (C-5), 123.9 (C-6), 121.3 (C-4a), 116.2 (C-8), 115.8 (d, $^{2}J_{CF}$ = 21.6 Hz, C-12), 70.8 (C-9).

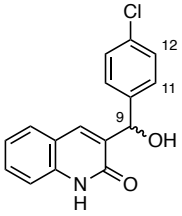
^{19}F NMR (471 MHz, MeOD-d_4) δ [ppm] = –113.5 (tt, $^{3}J_{HF}$ = 9.2 Hz, $^{4}J_{HF}$ = 5.4 Hz, 1F).

HRMS (+ESI): calc. for $C_{16}H_{13}O_2FN$ $[M+H]^+$: 270.0925; found: 270.0924.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3177 (w, O-H), 2891 (w, sp^3 C-H), 1651 (vs, C=O), 1606 (m, C=C), 1571 (m, C=C), 1509 (m, C=C), 1428 (w), 1222 (m, C-F), 1156 (w), 837 (m, sp^2 C-H), 755 (m, sp^2 C-H).

m.p. = 194 °C.

*1.4.8 3-((4-Chlorophenyl)(hydroxy)methyl)-2-quinolone (rac-**3h**)*



A 1.0 M solution of *p*-chlorophenylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 1-chloro-4-fluorobenzene (574 mg, 3.00 mmol, 2.5 equiv) in THF (3.0 mL) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL) according to *GP3*. After purification by FCC the entitled benzylic alcohol *rac*-**3h** was obtained as an off-white solid (277 mg, 0.97 µmol, 81%).

***R*$_f$** (4% MeOH/CH_2Cl_2): 0.16.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.10 (t, ^{4}J = 0.8 Hz, 1H, H-4), 7.68 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.3 Hz, 1H, H-5), 7.50 (ddd, ^{3}J = 8.5, 7.2 Hz, ^{4}J = 1.4 Hz, 1H, H-7), 7.44 (d, ^{3}J = 8.4 Hz, 2H, H-11), 7.34-7.27 (m, 1H, H-8), 7.31 (d, ^{3}J = 8.5 Hz, 2H, H-12), 7.24 (ddd, ^{3}J = 8.1, 7.2 Hz, ^{4}J = 1.1 Hz, 1H, H-6), 5.93 (d, ^{4}J = 1.0 Hz, 1H, H-9).

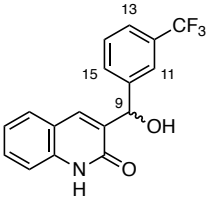
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.4 (C-2), 143.1 (C-10), 139.0 (C-8a), 137.1 (C-4), 136.6 (C-3), 134.2 (C-13), 131.4 (C-7), 129.8 (C-11), 129.3 (C-12), 129.3 (C-5), 123.9 (C-6), 121.3 (C-4a), 116.2 (C-8), 70.8 (C-9).

HRMS (+ESI): calc. for $C_{16}H_{13}O_2ClN$ $[M+H]^+$: 286.0629; found: 286.0629.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3160 (w, O-H), 2860 (w, sp^3 C-H), 1661 (vs, C=O), 1572 (m, C=C), 1490 (m), 1433 (m), 1091 (w), 1012 (m, C-Cl), 947 (w), 859 (w), 809 (m, sp^2 C-H), 752 (s, sp^2 C-H).

m.p. = 188 °C.

*1.4.9 3-(Hydroxy(3-(trifluoromethyl)phenyl)methyl)-2-quinolone(rac-**3i**)*



A 1.0 M solution of 3-(trifluoromethyl)-phenylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 3-bromobenzotrifluoride (413 µL, 3.00 mmol, 2.5 equiv) in THF (2.6 mL) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL) according to *GP3.* After purification by FCC the entitled benzylic alcohol *rac*-**3i** was obtained as a white solid (299 mg, 936 µmol, 78%).

***R*f** (5% MeOH/CH_2Cl_2): 0.40.

^{1}H NMR (500 MHz, MeOD-*d*$_4$) δ [ppm] = 8.15 (t, ^4J = 0.8 Hz, 1H, H-4), 7.80 (dq, ^4J = 1.9 Hz, $^4J_{HF}$ = 1.0 Hz, 1H, H-11), 7.76-7.63 (m, 2H, H-5, H-15), 7.58-7.46 (m, 3H, H-7, H-13, H-14), 7.32 (dt, ^3J = 8.3 Hz, ^4J = 0.9 Hz, 1H, H-8), 7.25 (ddd, ^3J = 8.1 Hz, ^4J = 7.2, 1.1 Hz, 1H, H-6), 6.01 (d, ^4J = 1.0 Hz, 1H. H-9).

^{13}C NMR (126 MHz, MeOD-*d*$_4$) δ [ppm] = 163.4 (C-2), 145.9 (C-10), 139.1 (C-8a), 137.2 (C-4), 136.4 (C-3), 131.8 (d, ^5J = 1.5 Hz, C-15), 131.5 (C-7), 131.5 (q, $^2J_{CF}$ = 31.9 Hz, C-12), 130.0 (C-14), 129.3 (C-5), 125.6 (q, $^1J_{CF}$ = 271.4 Hz, CF_3), 125.2 (q, $^3J_{CF}$ = 3.8 Hz, C-13), 124.7 (q, $^3J_{CF}$ = 3.8 Hz, C-11), 123.9 (C-6), 121.3 (C-4a), 116.3 (C-8), 70.8 (C-9).

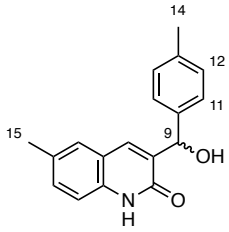
^{19}F NMR (376 MHz, MeOD-*d*$_4$) δ [ppm] = –64.0 (s, 1F).

HRMS (+ESI): calc. for $C_{17}H_{13}O_2F_3N$ $[M+H]^+$: 320.0893; found: 320.0894.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3363 (bs, w, O-H), 1649 (vs, C=O), 1585 (m, C=C), 1569 (m, C=C), 1327 (vs, C-F), 1164 (m), 1121 (vs), 1072 (m), 754 (m, sp^2 C-H), 702 (m sp^2 C-H).

m.p. = 168 °C.

*1.4.10 3-(Hydroxy(p-tolyl)methyl)-6-methyl-2-quinolinone (rac-**3j**)*



A 1.0 M solution of *p*-tolylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 4-bromotoluene (369 µL, 3.00 mmol, 2.5 equiv) in THF (2.6 mL) and was then added to a solution of aldehyde **S3f** (225 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL). After purification by FCC the entitled benzylic alcohol *rac*-**3j** was obtained as a white solid (308 mg, 1.10 mmol, 92%).

***R*f** (5% MeOH/CH_2Cl_2): 0.35.

^{1}H NMR (500 MHz, MeOD-*d*$_4$) δ [ppm] = 8.01 (s, 1H, H-4), 7.47 (s, 1H, H-5), 7.35 (dd, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 1H, H-7), 7.31 (d, ^3J = 8.2 Hz, 2H, H-11), 7.23 (d, ^3J = 8.3 Hz, 1H, H-8), 7.13 (d, ^3J = 7.8 Hz, 2H, H-12), 5.91 (s, 1H, H-9), 2.41 (s, 3H, H-15), 2.30 (s, 3H, H-14).

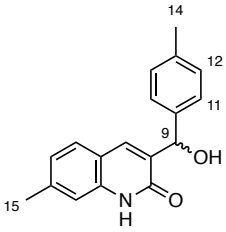
^{13}C NMR (126 MHz, MeOD-*d*$_4$) δ [ppm] = 163.5 (C-2), 141.0 (C-10), 138.3 (C-13), 136.9 (2C, C-3, C-4), 136.8 (C-8a), 133.7 (C-6), 132.7 (C-7), 129.9 (C-12), 128.7 (C-5), 128.1 (C-11), 121.4 (C-4a), 116.1 (C-8), 71.4 (C-9), 21.2 (C-14), 20.9 (C-15).

HRMS (+ESI): calc. for $C_{18}H_{18}O_2N$ $[M+H]^+$: 280.1332; found: 280.1331.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3392 (bs, w, O-H), 2920 (w, sp^3 C-H), 1651 (vs, C=O), 1583 (m, C=C), 1502 (w), 1446 (w), 1224 (w), 1036 (w), 816 (w, sp^2 C-H), 758 (m, sp^2 C-H).

m.p. = 205 °C.

*1.4.11 3-(Hydroxy(p-tolyl)methyl)-7-methyl-2-quinolinone (rac-**3k**)*



A 1.0 M solution of *p*-tolylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 4-bromotoluene (369 µL, 3.00 mmol, 2.5 equiv) in THF (2.6 mL) and was then added to a solution of aldehyde **S3g** (225 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL). After purification by FCC the entitled benzylic alcohol *rac*-**3k** was obtained as a white solid (263 mg, 942 µmol, 79%).

***R*f** (3% MeOH/CH_2Cl_2): 0.21.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.00 (s, 1H, H-4), 7.56 (d, ^3J = 8.0 Hz, 1H, H-5), 7.31 (d, ^3J = 8.2 Hz, 2H, H-11), 7.15-7.11 (m, 3H, H-8, H-12), 7.10 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-6), 5.91 (s, 1H, H-9), 2.44 (s, 3H, H-15), 2.30 (s, 3H, H-14).

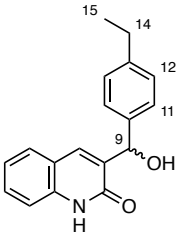
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.7 (C-2), 142.3 (C-7), 141.1 (C-3), 139.1 (C-8a), 138.3 (C-13), 137.0 (C-4), 135.8 (C-10), 129.9 (C-12), 129.0 (C-5), 128.1 (C-11), 125.4 (C-6), 119.2 (C-4a), 116.1 (C-8), 71.4 (C-9), 21.8 (C-15), 21.2 (C-14).

HRMS (+ESI): calc. for $C_{18}H_{18}O_2N$ $[M+H]^+$: 280.1332; found: 280.1333.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3300 (bs, w, O-H), 2920 (w, sp^3 C-H), 2855 (w, sp^3 C-H), 1656 (vs, C=O), 1614 (m, C=C), 1512 (m, C=C), 1484 (w), 1228 (w), 1149 (w), 1026 (w), 802 (m, sp^2 C-H), 791 (m, sp^2 C-H).

m.p. = 196 ° C.

*1.4.12 3-(Hydroxy(4-ethylphenyl)methyl)-2-quinolone (rac-**3l**)*



A 1.0 M solution of *p*-ethylphenylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 1-bromo-4-ethylbenzene (414 µL, 3.00 mmol, 2.5 equiv) in THF (2.6 mL) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF (3.0 mL) according to *GP3*. After purification by FCC the entitled benzylic alcohol *rac*-**3l** was obtained as a white solid (314 mg, 1.12 mmol, 94%).

***R*f** (5% MeOH/CH_2Cl_2): 0.34.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.08 (s, 1H, H-4), 7.68 (dd, ^3J = 7.9, ^4J = 1.3 Hz 1H, H-5), 7.50 (ddt, ^3J = 8.4, 7.2 Hz, ^4J = 1.3 Hz, 1H, H-7), 7.38-7.28 (m, 3H, H-8, H-11), 7.25 (tt, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 7.16 (d, ^3J = 7.9 Hz, 2H, H-12), 5.93 (d, ^4J = 1.0 Hz, 1H, H-9), 2.61 (q, ^3J = 7.6 Hz, 2H, H-14), 1.19 (t, ^3J = 7.6 Hz, 3H, H-15).

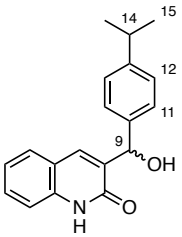
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-2), 144.9 (C-13), 141.2 (C-10), 139.0 (C-8a), 137.0 (2C, C-3, C-4), 131.3 (C-7), 129.2 (C-5), 128.7 (C-12), 128.2 (C-11), 123.9 (C-6), 121.4 (C-4a), 116.2 (C-8), 71.4 (C-9), 29.6 (C-14), 16.3 (C-15).

HRMS (+ESI): calc. for $C_{18}H_{18}O_2N$ $[M+H]^+$: 280.1332; found: 280.1334.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3391 (bs, w, O-H), 2952 (w, sp^3 C-H), 2930 (w, sp^3 C-H), 1651 (vs, C=O), 1586 (m, C=C), 1570 (m, C=C), 1462 (w), 1428 (w), 1216 (w), 1030 (w), 831 (w, sp^2 C-H), 755 (m, sp^2 C-H).

m.p. = 157 °C.

*1.4.13 3-(Hydroxy(4-isopropylphenyl)methyl)-2-quinolone (rac-**3m**)*



A 1.0 M solution of *p*-cumylmagnesium bromide (3.00 mL, 3.00 mmol, 2.5 equiv) was prepared from Mg turnings (72.9 mg, 3.00 mmol, 2.5 equiv) and 1-bromo-4-fluorobenzene (464 µL, 3.00 mmol, 2.5 equiv) and was added to a solution of aldehyde **S3a** (208 mg, 1.20 mmol, 1.0 equiv) in THF and the experiment was conducted as described in *GP3*. After purification by FCC the entitled benzylic alcohol *rac*-**3m** was obtained as a white solid (319 mg, 1.09 mmol, 91%).

R_f (5% MeOH/CH_2Cl_2): 0.35.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.09 (t, ^4J = 0.9 Hz, 1H, H-4), 7.67 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.49 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.35 (d, ^3J = 8.2 Hz, 2H, H-11), 7.32 (d, ^3J = 8.6 Hz, 1H, H-8), 7.22 (ddd, ^3J = 8.2, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 7.18 (d, ^3J = 8.29 Hz, 2H, H-12), 5.93 (d, ^4J = 1.1 Hz, 1H, H-9), 2.87 (hept, ^3J = 7.0 Hz, 1H, H-14), 1.21 (d, ^3J = 6.9 Hz, 6H, H-15).

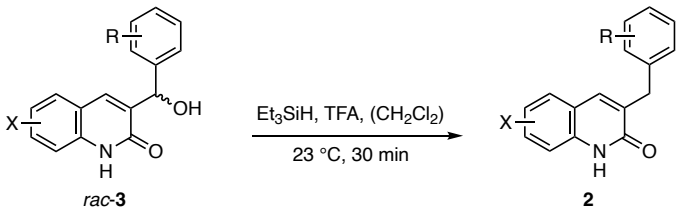
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-2), 149.4 (C-13), 141.4 (C-10), 139.0 (C-8a), 137.0 (2C, C-3, C-4), 131.3 (C-7), 129.2 (C-5), 128.2 (C-11), 127.3 (C-12), 123.9 (C-6), 121.4 (C-4a), 116.2 (C-8), 71.4 (C-9), 35.2 (C-14), 24.5 (C-15), 24.4 (C-15‘).

HRMS (+ESI): calc. for $C_{19}H_{20}O_2N$ $[M+H]^+$: 294.1489; found: 294.1491.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3390 (bs, w, O-H), 2959 (w, sp^3 C-H), 2870 (w, sp^3 C-H), 1649 (vs, C=O), 1568 (m, C=C), 1462 (w), 1427 (w), 1213 (w), 1017 (w), 830 (w, sp^2 C-H), 754 (m, sp^2 C-H).

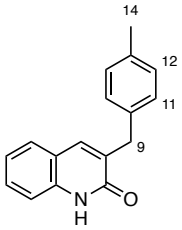
m.p. = 180 ° C.

1.5 General procedure 4 (GP4): Synthesis of 3-benzyl-2-quinolones 2



Et_3SiH (2.5 equiv) and TFA (32 equiv) were added sequentially to a suspension of alcohol *rac*-**3** (1.0 equiv) in CH_2Cl_2 (0.2 M) affording a clear solution. The reaction mixture was stirred at 23 °C for 30 min before the reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude material was subjected to FCC (5% → 20% acetone/*n*-pentane) to yield the entitled quinolone.

*1.5.1 3-(4-Methylbenzyl)-2-quinolone (**2a**)*



Following *GP4* the entitled quinolone **2a** was obtained from benzylic alcohol *rac*-**3a** (540 mg, 2.04 mmol, 1.0 equiv) as an off-white solid (462 mg, 1.85 mmol, 91%).

***R*f** (5% MeOH/CH_2Cl_2): 0.33.

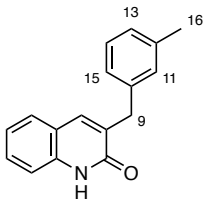
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 9.95 (br s, 1H, NH), 7.43 (m, 2H, H-5, H-7), 7.39 (s, 1H, H-4), 7.21 (d, ^3J = 7.9 Hz, 2H, H-11), 7.17 (m, 4H, H-6, H-8, H-12), 3.95 (s, 2H, H-9), 2.35 (s, 3H, H-14).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.3 (C-2), 137.6 (C-8a), 137.5 (C-4), 136.1 (C-10), 136.0 (C-13), 133.8 (C-3), 129.6 (C-7), 129.5 (C-11), 129.4 (C-12), 127.4 (C-5), 122.5 (C-6), 120.3 (C-4a), 115.8 (C-8), 35.9 (C-9), 21.2 (C-14).

HRMS (+ESI): calc. for $C_{17}H_{16}ON$ $[M+H]^+$: 250.1226; found: 250.1227.

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

*1.5.2 3-(3-Methylbenzyl)-2-quinolone (**2b**)*



Following *GP4* the entitled quinolone **2b** was obtained from benzylic alcohol *rac*-**3b** (220 mg, 829 µmol, 1.0 equiv) as a white solid (188 mg, 754 µmol, 91%).

***R*f** (20% acetone/CH_2Cl_2): 0.76.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.79 (br s, 1H, NH), 7.65 (s, 1H, H-4), 7.57 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.43 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.28 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz,

1H, H-8), 7.17 (t, ^3J = 7.5 Hz, 1H, H-14), 7.13 (ddd, ^3J = 8.0, 7.3 Hz, ^4J = 1.1 Hz, 1H, H-6), 7.11-7.05 (m, 2H, H-11, H-15), 7.03-6.97 (m, 1H, H-13), 3.78 (s, 2H, H-9), 2.26 (s, 3H, H-16).

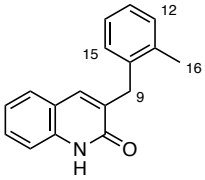
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.8 (C-2), 139.6 (C-12), 137.9 (C-8a), 137.3 (C-3), 136.7 (C-4), 133.3 (C-10), 129.5 (C-7, C-13), 128.2 (C-14), 127.3 (C-5), 126.7 (C-11), 126.0 (C-15), 121.7 (C-6), 119.3 (C-4a), 114.8 (C-8), 35.4 (C-9), 21.1 (C-16).

HRMS (+ESI): calc. for $C_{17}H_{16}ON$ $[M+H]^+$: 250.1226; found: 250.1228.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2819 (w, sp^3 C-H), 1657 (vs, C=O), 1574 (m, C=C), 1435 (w), 1218 (w), 928 (m), 746 (vs, sp^2 C-H), 691 (s, sp^2 C-H).

m.p. = 151 °C.

*1.5.3 3-(2-Methylbenzyl)-quinolone (**2c**)*



Following GP4 the entitled quinolone **2c** was obtained from benzylic alcohol *rac*-**3c** (282 mg, 1.06 mmol, 1.0 equiv) as a white solid (241 mg, 967 µmol, 91%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.61.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.51 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.43 (ddd, ^3J = 8.4, 7.1 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.34-7.28 (m, 2H, H-4, H-8), 7.23-7.18 (m, 1H, H-12), 7.18-7.13 (m, 3H, H-13, H-14, H-15), 7.10 (ddd, ^3J = 8.1, 7.1 Hz, ^4J = 1.1 Hz, 1H, H-6), 3.81 (d, ^4J = 1.3 Hz, 2H, H-9), 2.24 (s, 3H, H-16).

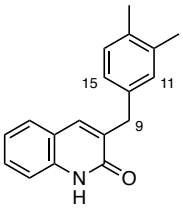
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.9 (C-2), 137.8 (C-8a), 137.4 (C-11), 136.3 (C-10), 136.0 (C-4), 132.6 (C-3), 130.1 (C-12), 129.6 (C-15), 129.4 (C-7), 127.3 (C-5), 126.5 (C-13), 126.0 (C-14), 121.7 (C-6), 119.2 (C-4a), 114.8 (C-8), 32.9 (C-9), 19.1 (C-16).

HRMS (+ESI): calc. for $C_{17}H_{16}ON$ $[M+H]^+$: 250.1226; found: 250.1228.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2819 (w, sp^3 C-H), 1657 (vs, C=O), 1574 (m, C=C), 1437 (w), 1267 (w), 948 (m), 910 (m), 746 (s, sp^2 C-H), 729, (s, sp^2 C-H), 698 (s, sp^2 C-H).

m.p. = 195 °C.

*1.5.4 3-(3,4-Dimethylbenzyl)-2-quinolone (**2d**)*



Following *GP4* the entitled quinolone **2d** was obtained from benzylic alcohol *rac*-**3d** (280 mg, 1.00 mmol, 1.0 equiv) as a white solid (235 mg, 0.89 mmol, 89%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.73.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.60 (s, 1H, H-4), 7.56 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.42 (ddd, ^3J = 8.3, 7.3 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.28 (d, ^3J = 8.2 Hz, 1H, H-8), 7.12

(ddd, ^3J = 8.3, 7.3 Hz, ^4J = 1.4 Hz, 1H, H-6), 7.07-7.01 (m, 2H, H-11, H-14), 6.99 (dd, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, H-15), 3.74 (s, 2H, H-9), 2.17 (s, 3H, H-16*), 2.17 (s, 3H, H-17*).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.9 (C-2), 137.9 (C-8a), 136.9 (C-12), 136.5 (C-4), 135.9 (C-3), 133.7 (C-13), 133.6 (C-10), 130.0 (C-11), 129.4 (C-7, C-14), 127.3 (C-5), 126.3 (C-15), 121.7 (C-6), 119.3 (C-4a), 114.7 (C-8), 35.1 (C-9), 19.4 (C-16*), 19.0 (C-17*).

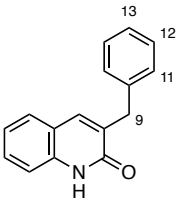
HRMS (+ESI): calc. for $C_{18}H_{18}ON$ $[M+H]^+$: 264.1383; found: 264.1384.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2851 (w, sp^3 C-H), 1656 (vs, C=O), 1572 (m, C=C), 1501 (w), 1433 (w), 1230 (w), 916 (m), 794 (m, sp^2 C-H), 747 (vs, sp^2 C-H).

m.p. = 183 °C.

*assignment is interconvertible

*1.5.5 3-Benzyl-2-quinolone (**2e**)*



Following *GP4* the entitled quinolone **2e** was obtained from benzylic alcohol *rac*-**3e** (282 mg, 1.12 mmol, 1.0 equiv) as an off-white solid (219 mg, 0.93 µmol, 83%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.55.

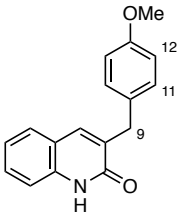
^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.65 (s, 1H, H-4), 7.55 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.43 (ddd, ^3J = 8.3, 7.1 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.32-7.25 (m, 5H, H-8, H-11, H-12), 7.19 (m, 1H, H-13), 7.12 (dt, ^3J = 7.4 Hz, ^4J = 1.4 Hz, 1H, H-6), 3.83 (s, 2H, H-9).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.8 (C-2), 139.7 (C-10), 137.9 (C-8a), 136.7 (C-4), 133.3 (C-3), 129.5 (C-7), 128.9 (C-12), 128.3 (C-11), 127.3 (C-5), 126.1 (C-13), 121.7 (C-6), 119.3 (C-4a), 114.8 (C-8), 35.5 (C-9).

HRMS (+ESI): calc. for $C_{16}H_{14}O_2N$ $[M+H]^+$: 236.1070; found: 236.1070.

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

*1.5.6 3-(4-Methoxybenzyl)-2-quinolone (**2f**)*



Following *GP4* the entitled quinolone **2f** was obtained from benzylic alcohol *rac*-**3f** (326 mg, 1.16 mmol, 1.0 equiv) as an off-white solid (287 mg, 1.08 mmol, 94%).

***R*$_f$** (10% MeOH/CH_2Cl_2): 0.65.

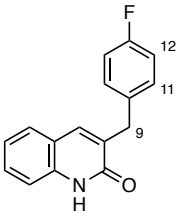
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.1 (br s, 1H, NH), 7.44 (m, 2H, H-5, H-7), 7.40 (s, 1H, H-4), 7.24 (d, ^3J = 8.6 Hz, 2H, H-11), 7.21-7.14 (m, 2H, H-6, H-8), 6.88 (d, ^3J = 8.6 Hz, 2H, H-12), 3.93 (s, 2H, H-9), 3.81 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 163.8 (C-2), 158.3 (C-13), 137.4 (2C, C-4, C-8a), 134.1 (C-3), 131.1 (C-10), 130.6 (C-11), 129.7 (C-7), 127.5 (C-5), 122.6 (C-6), 120.3 (C-4a), 115.5 (C-8), 114.1 (C-12), 55.4 (OCH_3), 35.4 (C-9).

HRMS (+ESI): calc. for $C_{17}H_{16}O_2N$ $[M+H]^+$: 266.1176; found: 266.1175.

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

*1.5.7 3-(4-Fluorobenzyl)-2-quinolone (**2g**)*



Following *GP4* the entitled quinolone **2g** was obtained from benzylic alcohol *rac*-**3g** (185 mg, 687 µmol, 1.0 equiv) as an off-white solid (165 mg, 651 µmol, 95%).

R_f (20% acetone/CH_2Cl_2): 0.57.

^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.67 (s, 1H, H-4), 7.57 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.43 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.33 (dd, ^3J = 8.6 Hz, $^4J_{HF}$ = 5.7 Hz, 1H, H-11), 7.29 (dd, ^3J = 8.1 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.12 (ddd, ^3J = 8.2, 7.2 Hz, ^4J = 1.2 Hz, 1H, H-6), 7.11 (*virt* t, $^3J \approx {}^3J_{HF}$ = 8.9 Hz, 1H, H-12), 3.81 (s, 1H, H-9).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.8 (C-2), 160.8 (d, $^1J_{CF}$ = 241.6 Hz, C-13), 138.0 (C-8a), 136.8 (C-4), 135.8 (d, $^4J_{CF}$ = 2.7 Hz, C-10), 133.2 (C-3), 130.6 (d, $^3J_{CF}$ = 7.8 Hz, C-11), 129.5 (C-7), 127.4 (C-5), 121.8 (C-6), 119.3 (C-4a), 115.1 (d, $^2J_{CF}$ = 21.1 Hz, C-12), 114.9 (C-8), 34.7 (C-9).

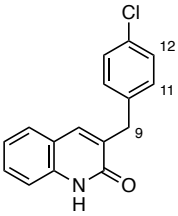
^{19}F NMR (376 MHz, DMSO-d_6) δ [ppm] = –117.2 (td, $^3J_{HF}$ = 9.1 Hz, $^4J_{HF}$ = 5.5 Hz, 1F)

HRMS (+ESI): calc. for $C_{16}H_{13}O_2FN$ $[M+H]^+$: 254.0976; found: 254.0975.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2824 (w, sp^3 C-H), 1650 (vs, C=O), 1570 (s, C=C), 1502 (vs, C=C), 1434 (m), 1212 (s, C-F), 1159 (m), 947 (w), 859 (w), 797 (m, sp^2 C-H), 751 (s, sp^2 C-H).

m.p. = 186 °C.

*1.5.8 3-(4-Chlorobenzyl)-2-quinolone (**2h**)*



Following *GP4* the entitled quinolone **2h** was obtained from benzylic alcohol *rac*-**3h** (157 mg, 549 µmol, 1.0 equiv) as an off-white solid (130 mg, 515 µmol, 94%).

R_f (20% acetone/CH_2Cl_2): 0.66.

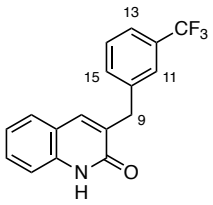
^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.70 (s, 1H, H-4), 7.58 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.44 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.35 (d, ^3J = 8.7 Hz, 2H, H-12), 7.32 (d, ^3J = 8.6 Hz, 2H, H-11), 7.28 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.14 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 3.82 (s, 2H, H-9).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.7 (C-2), 138.8 (C-10), 138.0 (C-8a), 137.0 (C-4), 132.8 (C-3), 130.7 (2C, C-11, C-13), 129.6 (C-7), 128.3 (C-12), 127.4 (C-5), 121.8 (C-6), 119.3 (C-4a), 114.8 (C-8), 34.9 (C-9).

HRMS (+ESI): calc. for $C_{16}H_{13}O_2ClN$ $[M+H]^+$: 286.0629; found: 286.0629.

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

*1.5.9 3-(3-(Trifluoromethyl)benzyl)-2-quinolone (**2i**)*



Following *GP4* the entitled quinolone **2i** was obtained from benzylic alcohol *rac*-**3i** (233 mg, 730 µmol, 1.0 equiv) as a white solid (185 mg, 610 µmol, 84%).

R_f (20% acetone/CH_2Cl_2): 0.71.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.81 (s, 1H, H-4), 7.68 (s, 1H, H-11), 7.65-7.49 (m, 4H, H-5, H-13, H-14, H-15), 7.44 (td, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, H-7), 7.29 (d, ^3J = 8.2 Hz, 1H, H-8), 7.15 (t, ^3J = 7.5 Hz, 1H, H-6), 3.94 (s, 2H, H-9).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.8 (C-2), 141.3 (C-10), 138.1 (C-8a), 137.3 (C-4), 133.0 (C-15), 132.4 (C-3), 129.7 (C-7), 129.3 (C-14), 129.9 (q, ^2J = 31.3 Hz, C-12), 127.5 (C-5), 125.2 (q, ^3J = 3.9 Hz, C-11), 124.3 (q, ^1J = 272.2 Hz, CF_3), 122.9 (q, ^3J = 3.9 Hz, C-13), 121.8 (C-6), 119.3 (C-4a), 114.8 (C-8), 35.4 (C-9).

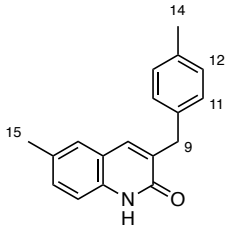
^{19}F NMR (376 MHz, DMSO-d_6) δ [ppm] =-60.95 (s, 1F)

HRMS (+ESI): calc. for $C_{17}H_{13}OF_3N$ $[M+H]^+$: 304.0944; found: 304.0944.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2849 (w, sp^3 C-H), 1661 (vs, C=O), 1573 (m, C=C), 1437 (m), 1331 (m, C-F), 1149 (m), 1113 (vs), 753 (s, sp^2 C-H), 700 (s sp^2 C-H).

m.p. = 171 °C.

*1.5.10 6-Methyl-3-(4-methylbenzyl)-2-quinolone (**2j**)*



Following GP4 the entitled quinolone **2j** was obtained from benzylic alcohol *rac*-**3j** (249 mg, 892 µmol, 1.0 equiv) as a white solid (211 mg, 800 µmol, 90%).

R_f (20% acetone/CH_2Cl_2): 0.70.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.7 (br s, 1H, NH), 7.54 (s, 1H, H-4), 7.35 (d, ^3J = 1.9 Hz, 1H, H-5), 7.26 (dd, ^3J = 8.4 Hz, ^4J = 1.9 Hz, 1H, H-7), 7.20-7.14 (m, 3H, H-8, H-11), 7.10 (d, ^3J = 7.8 Hz, 2H, H-12), 3.77 (s, 2H, H-9), 2.31 (s, 3H, H-15), 2.26 (s, 3H, H-14).

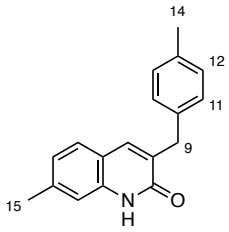
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.7 (C-2), 136.6 (C-10), 136.3 (2C, C-4, C-6), 135.9 (C-8a), 135.0 (C-13), 133.4 (C-3), 130.6 (C-7), 128.9 (C-12), 128.8 (C-11), 126.8 (C-5), 119.3 (C-4a), 114.6 (C-8), 35.1 (C-9), 20.7 (C-14), 20.4 (C-15).

HRMS (+ESI): calc. for $C_{18}H_{18}ON$ $[M+H]^+$: 264.1383; found: 264.1382.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2922 (w, sp^3 C-H), 2852 (w, sp^3 C-H), 1658 (vs, C=O), 1578 (m, C=C), 1479 (m), 897 (m, sp^2 C-H), 810 (vs, sp^2 C-H), 749 (m, sp^2 C-H).

m.p. = 200 °C.

*1.5.11 7-Methyl-3-(4-methylbenzyl)-2-quinolone (**2k**)*



Following *GP4* the entitled quinolone **2k** was obtained from benzylic alcohol *rac*-**3k** (231 mg, 827 µmol, 1.0 equiv) as a white solid (187 mg, 710 µmol, 86%).

R_f (20% acetone/CH_2Cl_2): 0.46.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.7 (br s, 1H, NH), 7.55 (s, 1H, H-4), 7.43 (d, ^3J = 8.0 Hz, 1H, H-5), 7.16 (d, ^3J = 8.0 Hz, 2H, H-11), 7.09 (d, ^3J = 7.8 Hz, 2H, H-12), 7.07 (d, ^4J = 1.5 Hz, 1H, H-8), 6.95 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-6), 3.75 (s, 2H, H-9), 2.34 (s, 3H, H-15), 2.25 (s, 3H, H-14).

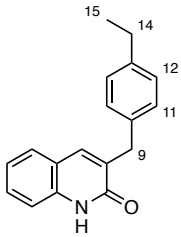
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 162.4 (C-2), 139.8 (C-7), 138.5 (C-8a), 137.1 (C-10), 136.8 (C-4), 135.4 (C-13), 132.8 (C-3), 129.4 (C-12), 129.2 (C-11), 127.6 (C-5), 123.6 (C-6), 117.6 (C-4a), 114.9 (C-8), 35.5 (C-9), 21.8 (C-15), 21.1 (C-14).

HRMS (+ESI): calc. for $C_{18}H_{18}ON$ $[M+H]^+$: 264.1383; found: 264.1382.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2915 (w, sp^3 C-H), 2843 (w, sp^3 C-H), 1650 (vs, C=O), 1570 (m, C=C), 1513 (m, C=C), 1220 (m), 902 (m), 811 (m, sp^2 C-H), 773 (m, sp^2 C-H).

m.p. = 223 °C.

*1.5.12 3-(4-Ethylbenzyl)-2-quinolone (**2l**)*



Following *GP4* the entitled quinolone **2l** was obtained from benzylic alcohol *rac*-**3l** (243 mg, 860 µmol, 1.0 equiv) as a white solid (213 mg, 809 µmol, 93%).

R_f (20% acetone/CH_2Cl_2): 0.75.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.65 (s, 1H, H-4), 7.56 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.43 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.28 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 1H, H-8), 7.19 (d, ^3J = 8.1 Hz, 2H, H-11), 7.16-7.09 (m, 3H, H-6, H-12), 3.78 (s, 2H, H-9), 2.55 (q, ^3J = 7.6 Hz, 2H, H-14), 1.15 (t, ^3J = 7.6 Hz, 3H, H-15).

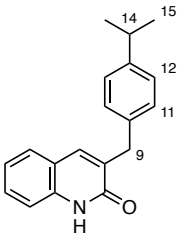
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.9 (C-2), 141.4 (C-13), 137.9 (C-8a), 136.9 (C-10), 136.6 (C-4), 133.5 (C-3), 129.4 (C-7), 128.8 (C-11), 127.7 (C-12), 127.3 (C-5), 121.7 (C-6), 119.3 (C-4a), 114.7 (C-8), 35.1 (C-9), 27.8 (C-14), 15.7 (C-15).

HRMS (+ESI): calc. for $C_{18}H_{18}ON$ $[M+H]^+$: 264.1383; found: 264.1385.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2961 (w, sp^3 C-H), 2854 (w, sp^3 C-H), 1650 (vs, C=O), 1571 (m, C=C), 1511 (w, C=C), 1433 (m), 1218 (w), 895 (m), 756 (vs, sp^2 C-H).

m.p. = 172 °C.

*1.5.13 3-(4-Isopropylbenzyl)-2-quinolone (**2m**)*



Following *GP4* the entitled quinolone **2m** was obtained from benzylic alcohol *rac*-**3m** (232 mg, 791 µmol, 1.0 equiv) as a white solid (211 mg, 761 µmol, 96%).

***R*f** (20% acetone/CH_2Cl_2): 0.79.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.68 (s, 1H, H-4), 7.57 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.43 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.28 (dd, ^3J = 8.1 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.20 (d, ^3J = 8.2 Hz, 2H, H-11), 7.15 (d, ^3J = 8.1 Hz, 2H, H-12), 7.13 (ddd, ^3J = 8.1, 7.3 Hz, ^4J = 1.2 Hz, 1H, H-6), 3.78 (s, 2H, H-9), 2.83 (hept, ^3J = 7.0 Hz, 1H, H-14), 1.17 (d, ^3J = 6.9 Hz, 6H, H-15).

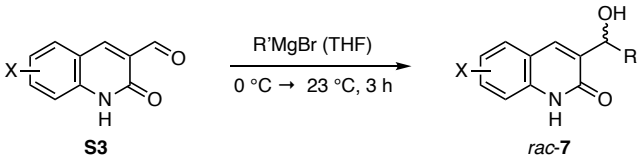
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.9 (C-2), 146.0 (C-13), 137.9 (C-8a), 137.1 (C-10), 136.6 (C-4), 133.4 (C-3), 129.4 (C-7), 128.7 (C-11), 127.3 (C-5), 126.2 (C-12), 121.7 (C-6), 119.3 (C-4a), 114.7 (C-8), 35.1 (C-9), 33.1 (C-14), 24.0 (C-15).

HRMS (+ESI): calc. for $C_{19}H_{20}ON$ $[M+H]^+$: 278.1539; found: 278.1542.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2960 (w, sp^3 C-H), 2860 (w, sp^3 C-H), 1652 (vs, C=O), 1573 (m, C=C), 1434 (m), 1425 (m), 1217 (w), 895 (m), 751 (vs, sp^2 C-H).

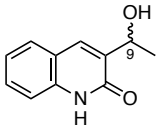
m.p. = 168 °C.

1.6 General procedure 5 (GP5): Synthesis of 3-(1-hydroxyalkyl)-2-quinolones *rac*-7



The required commercially available *Grignard* solution (3.0 equiv) was added to a suspension of the corresponding 2-quinolone-3-carbaldehyde **S3** (1.0 equiv) in THF at 0 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred at 23 °C until TLC indicated complete consumption of the starting material (typically <3 h). The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine solution and dried over Na_2SO_4 and after removal of all volatiles *in vacuo* the crude material was purified by FCC on silica gel (1% → 5% MeOH/CH_2Cl_2 + 0.1% Et_3N) to yield the entitled alcohol *rac*-7.

*1.6.1 3-(1-Hydroxyethyl)-2-quinolinone (rac-**7a**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 3.00 mL, 9.00 mmol, 3.0 equiv) was added to a solution of aldehyde **S3a** (520 mg, 3.00 mmol, 1.0 equiv) in THF (15 mL). After purification by FCC the entitled alcohol *rac*-**7a** was obtained as a white solid (260 mg, 2.67 mmol, 89%).

***R*$_f$** (3% MeOH/CH_2Cl_2): 0.14.

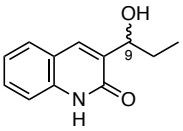
^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.8 (br s, 1H, NH), 7.89 (t, ^4J = 0.9 Hz, 1H, H-4), 7.68 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.44 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.29 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1H, H-8), 7.16 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.2 Hz, 1H, H-6), 5.18 (d, ^3J = 4.4 Hz, 1H, OH), 4.84-4.74 (m, 1H, H-9), 1.31 (d, ^3J = 6.3 Hz, 3H, H-10).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.1 (C-2), 138.7 (C-3), 137.7 (C-8a), 133.0 (C-4), 129.4 (C-7), 127.7 (C-5), 121.8 (C-6), 119.3 (C-4a), 114.7 (C-8), 63.5 (C-9), 23.4 (C-10).

HRMS (+ESI): calc. for $C_{11}H_{12}O_2N$ $[M+H]^+$: 190.0863; found: 190.0862.

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

*1.6.2 3-(1-Hydroxypropyl)-2-quinolinone (rac-**7b**)*



Following GP5 a commercially available solution of EtMgBr (2.0 M in Et_2O, 1.80 mL, 3.60 mmol, 3.0 equiv) was added to a solution of aldehyde **S3a** (208 mg, 1.20 µmol, 1.0 equiv) in THF (4.5 mL). After purification by FCC the entitled alcohol *rac*-**7b** was obtained as a white solid (210 mg, 1.03 mmol, 86%).

R_f (5% MeOH/CH_2Cl_2): 0.40.

^{1}H NMR (300 MHz, MeOD-d_4) δ [ppm] = 7.97 (d, ^4J = 0.9 Hz, 1H, H-4), 7.66 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.34 (dd, ^3J = 8.3 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.24 (ddd, ^3J = 8.2, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 4.82 (ddd, ^3J = 7.7, 4.1 Hz, ^4J = 1.1 Hz, 1H, H-9), 1.91 (dqd, ^2J = 13.7 Hz, ^3J = 7.5, 4.1 Hz, 1H, H-10), 1.72-1.52 (m, 1H, H-10'), 1.00 (t, ^3J = 7.4 Hz, 3H, H-11).

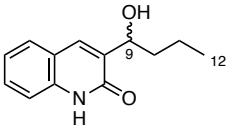
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.8 (C-2), 138.8 (C-8a), 137.4 (C-3), 136.7 (C-4), 131.2 (C-7), 129.0 (C-5), 123.8 (C-6), 121.4 (C-4a), 116.2 (C-8), 70.7 (C-9), 30.6 (C-10), 10.3 (C-11).

HRMS (+ESI): calc. for $C_{12}H_{14}O_2N$ $[M+H]^+$: 204.1019; found: 204.1019.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3436 (w, O-H), 2962 (w, sp^3 C-H), 2874 (w, sp^3 C-H), 2850 (w, sp^3 C-H), 1657 (vs, C=O), 1564 (s, C=C), 1427 (m), 1214 (w), 1046 (w), 900 (m), 749 (s, sp^2 C-H), 704 (m).

m.p. = 168 °C.

*1.6.3 3-(1-Hydroxybutyl)-2-quinolinone (rac-**7c**)*



Following GP5 a commercially available solution of ^{n}PrMgBr (3.0 M in Et_2O, 1.20 mL, 3.60 mmol, 3.0 equiv) was added to a solution of aldehyde **S3a** (208 mg, 1.20 µmol, 1.0 equiv) in THF (5.0 mL). After purification by FCC the entitled alcohol *rac*-**7c** was obtained as a white solid (135 mg, 0.62 mmol, 52%).

R_f (5% MeOH/CH_2Cl_2): 0.41.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.97 (s, 1H, H-4), 7.67 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.34 (d, ^3J = 8.2 Hz, 1H, H-8), 7.25 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 4.90-4.87 (m, 1H, H-9), 1.83 (dddd, ^2J = 13.6 Hz, ^3J = 9.9, 6.1, 4.0 Hz, 1H, H-10), 1.69-1.38 (m, 3H, H-10', H-11, H-11'), 0.97 (t, ^3J = 7.4 Hz, 3H, H-12).

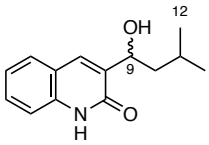
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.8 (C-2), 138.8 (C-8a), 137.8 (C-3), 136.5 (C-4), 131.1 (C-7), 129.0 (C-5), 123.8 (C-6), 121.5 (C-4a), 116.2 (C-8), 69.3 (C-9), 40.1 (C-10), 20.1 (C-11), 14.4 (C-12).

HRMS (+ESI): calc. for $C_{13}H_{16}O_2N$ $[M+H]^+$: 218.1176; found: 218.1175.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3422 (w, O-H), 2955 (w, sp^3 C-H), 2926 (w, sp^3 C-H), 2869 (w, sp^3 C-H), 1644 (vs, C=O), 1565 (s, C=C), 1424 (m), 1212 (m), 1061 (m), 900 (s), 762 (vs, sp^2 C-H), 705 (m).

m.p. = 185 °C.

*1.6.4 3-(1-Hydroxy-3-methylbutyl)-2-quinolone (rac-**7d**)*



Following GP5 a commercially available solution of ^{i}BuMgBr (2.0 M in Et_2O, 1.80 mL, 3.60 mmol, 3.0 equiv) was added to a solution of aldehyde **S3a** (208 mg, 1.20 µmol, 1.0 equiv) in THF (4.4 mL). After purification by FCC the entitled alcohol *rac*-**7d** was obtained as a yellowish solid (207 mg, 0.90 mmol, 75%).

***R*$_f$** (5% MeOH/CH_2Cl_2): 0.38.

^{1}H NMR (300 MHz, MeOD-d_4) δ [ppm] = 7.97 (s, 1H, H-4), 7.66 (dd, ^3J = 7.9, 1.3 Hz, 1H, H-5), 7.49 (ddd, ^3J = 8.3, 7.2 Hz, ^4J = 1.3 Hz, 1H, H-7), 7.34 (dd, ^3J = 8.3 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.24 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 4.96 (ddd, ^3J = 9.3 Hz, ^4J = 3.6, 1.1 Hz, 1H, H-9), 1.92 (dpd, ^3J = 9.0, 6.7, 4.7 Hz, 1H, H-11), 1.63 (ddd, ^4J = 13.7 Hz, ^3J = 9.1, 3.6 Hz, 1H, H-10), 1.51 (ddd, ^4J = 13.9 Hz, ^3J = 9.3, 4.7 Hz, 1H, H-10'), 1.03 (d, ^3J = 6.6 Hz, 3H, H-12), 0.97 (d, ^3J = 6.7 Hz, 3H, H-12').

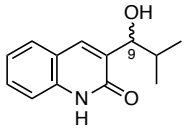
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.8 (C-2), 138.8 (C-8a), 138.3 (C-3), 136.3 (C-4), 131.1 (C-7), 128.9 (C-5), 123.8 (C-7), 121.5 (C-4a), 116.2 (C-8), 67.8 (C-9), 47.3 (C-11), 26.1 (C-10), 24.1 (C-12), 22.0 (C-12').

HRMS (+ESI): calc. for $C_{14}H_{18}O_2N$ $[M+H]^+$: 232.1332; found: 232.1332.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3313 (w, O-H), 2952 (w, sp^3 C-H), 2868 (w, sp^3 C-H), 1658 (vs, C=O), 1572 (s, C=C), 1424 (m), 1217 (m), 946 (s), 748 (vs, sp^2 C-H), 736 (m), 708 (m).

m.p. = 174 °C.

*1.6.5 3-(1-Hydroxy-2-methylpropyl)-2-quinolone (rac-**7e**)*



Following GP5 a commercially available solution of ^{i}PrMgBr (0.75 M in THF, 4.00 mL, 3.00 mmol, 3.0 equiv) was added to a suspension of aldehyde **S3a** (173 mg, 1.00 mmol, 1.0 equiv) in THF (2 mL). After purification by FCC the entitled alcohol *rac*-**7e** was obtained as a white solid (93.0 mg, 0.43 mmol, 43%).

***R*$_f$** (5% MeOH/CH_2Cl_2): 0.39.

^{1}H NMR (300 MHz, MeOD-d_4) δ [ppm] = 7.94 (s, 1H, H-4), 7.67 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.42-7.31 (m, 1H, H-8), 7.25 (ddd, ^3J = 8.2, 7.2 Hz, ^4J = 1.2 Hz, 1H, H-6), 4.70 (dd, ^3J = 5.0 Hz, ^4J = 1.0 Hz, 1H, H-9), 2.11 (pd, ^3J = 6.9, 5.1 Hz, 1H, H-10), 1.01 (d, ^3J = 6.9 Hz, 3H, H-11), 0.90 (d, ^3J = 6.8 Hz, 3H, H-11').

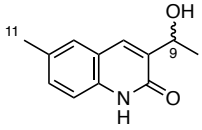
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 164.0 (C-2), 138.8 (C-8a), 137.7 (C-4), 136.6 (C-3), 131.2 (C-7), 129.0 (C-5), 123.8 (C-6), 121.4 (C-4a), 116.2 (C-8), 74.1 (C-9), 33.9 (C-10), 20.0 (C-11), 16.9 (C-11').

HRMS (+ESI): calc. for $C_{13}H_{16}O_2N$ $[M+H]^+$: 218.1176; found: 218.1175.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3409 (w, O-H), 2960 (w, sp^3 C-H), 2867 (w, sp^3 C-H), 1651 (vs, C=O), 1560 (m, C=C), 1416 (w), 1214 (w), 1008 (w), 916 (w), 747 (vs, sp^2 C-H).

m.p. = 185 °C.

*1.6.6 3-(1-Hydroxyethyl)-6-methyl-2-quinolone (rac-**7f**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 1.20 mL, 3.60 mmol, 3.0 equiv) was added to a solution of aldehyde **S3f** (224 mg, 1.20 mmol, 1.0 equiv) in THF (6.0 mL). After purification by FCC the entitled alcohol *rac*-**7f** was obtained as a white solid (236 mg, 1.16 mmol, 97%).

R_f (5% MeOH/CH_2Cl_2): 0.32.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.94 (s, 1H, H-4), 7.47 (d, ^4J = 2.0 Hz, 1H, H-5), 7.35 (dd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, 1H, H-7), 7.24 (d, ^3J = 8.4 Hz, 1H, H-8), 5.00 (qd, ^3J = 6.4 Hz, ^4J = 1.2 Hz, 1H, H-9), 2.41 (s, 3H, H-11), 1.45 (d, ^3J = 6.4 Hz, 3H, H-10).

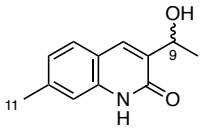
^{13}C NMR (101 MHz, MeOD-d_4) δ [ppm] = 163.7 (C-2), 138.4 (C-3), 136.8 (C-8a), 135.7 (C-4), 133.7 (C-6), 132.5 (C-7), 128.5 (C-5), 121.5 (C-4a), 116.1 (C-8), 65.8 (C-9), 23.3 (C-10), 20.9 (C-11).

HRMS (+ESI): calc. for $C_{12}H_{14}O_2N$ $[M+H]^+$: 204.1019; found: 204.1020.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3312 (w, O-H), 2972 (w, sp^3 C-H), 2924 (w, sp^3 C-H), 2853 (w, sp^3 C-H), 1622 (vs, C=O), 1576 (m, C=C), 1423 (m), 1068 (w), 814 (m, sp^2 C-H).

m.p. = 215 °C.

*1.6.7 3-(1-Hydroxyethyl)-7-methyl-2-quinolone (rac-**7g**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 1.50 mL, 4.50 mmol, 3.0 equiv) was added to a solution of aldehyde **S3g** (281 mg, 1.50 mmol, 1.0 equiv) in THF (7.5 mL). After purification by FCC the entitled alcohol *rac*-**7g** was obtained as a white solid (260 mg, 1.28 mmol, 85%).

R_f (5% MeOH/CH_2Cl_2): 0.38.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.95 (s, 1H, H-4), 7.55 (d, ^3J = 8.0 Hz, 1H, H-5), 7.15 (s, 1H, H-8), 7.09 (dd, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 1H, H-6), 4.99 (qd, ^3J = 6.3 Hz, ^4J = 1.1 Hz, 1H, H-9), 2.44 (s, 3H, H-11) 1.45 (d, ^3J = 6.4 Hz, 3H, H-10).

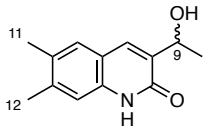
^{13}C NMR (101 MHz, MeOD-d_4) δ [ppm] = 163.9 (C-2), 142.1 (C-7), 139.0 (C-8a), 137.3 (C-3), 135.8 (C-4), 128.8 (C-5), 125.4 (C-6), 119.4 (C-4a), 116.0 (C-8), 65.8 (C-9), 23.3 (C-10), 21.9 (C-11).

HRMS (+ESI): calc. for $C_{12}H_{14}O_2N$ $[M+H]^+$: 204.1019; found: 204.1020.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3301 (w, O-H), 2971 (w, sp^3 C-H), 2927 (w, sp^3 C-H), 2857 (w, sp^3 C-H), 1648 (vs, C=O), 1568 (m, C=C), 1448 (m), 1280 (w) 1075 (w), 807 (m, sp^2 C-H).

m.p. = 238 °C.

*1.6.8 3-(1-Hydroxyethyl)-6,7-dimethyl-2-quinolone (rac-**7h**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 1.50 mL, 4.50 mmol, 3.0 equiv) was added to a solution of aldehyde **S3h** (302 mg, 1.50 mmol, 1.0 equiv) in THF (7.5 mL). After purification by FCC the entitled alcohol *rac*-**7h** was obtained as a white solid (313 mg, 1.44 mmol, 96%).

R_f (5% MeOH/CH_2Cl_2): 0.39.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.92 (s, 1H, H-4), 7.42 (s, 1H, H-5), 7.14 (s, 1H, H-8), 4.99 (q, ^3J = 6.4 Hz, 1H, H-9), 2.37 (s, 3H, H-12), 2.33 (s, 3H, H-11), 1.45 (d, ^3J = 6.4 Hz, 3H, H-10).

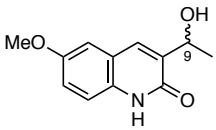
^{13}C NMR (101 MHz, MeOD-d_4) δ [ppm] = 163.7 (C-2), 141.4 (C-7), 137.3 (C-3), 137.2 (C-8a), 135.6 (C-4), 133.0 (C-6), 128.9 (C-5), 119.8 (C-4a), 116.6 (C-8), 65.8 (C-9), 23.4 (C-10), 20.3 (C-12), 19.4 (C-11).

HRMS (+ESI): calc. for $C_{13}H_{16}O_2N$ $[M+H]^+$: 218.1176; found: 218.1176.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3308 (w, O-H), 2973 (w, sp^3 C-H), 2920 (w, sp^3 C-H), 2846 (w, sp^3 C-H), 1659 (vs, C=O), 1566 (m, C=C), 1440 (w), 1070 (w), 870 (m, sp^2 C-H).

m.p. = 238 °C.

*1.6.9 3-(1-Hydroxyethyl)-6-methoxy-2-quinolone (rac-**7i**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 1.50 mL, 4.50 mmol, 3.0 equiv) was added to a solution of aldehyde **S3i** (305 mg, 1.50 mmol, 1.0 equiv) in THF (7.5 mL). After purification by FCC the entitled alcohol *rac*-**7i** was obtained as a white solid (316 mg, 1.44 mmol, 96%).

R_f (5% MeOH/CH_2Cl_2): 0.39.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.98 (s, 1H, H-4), 7.28 (d, ^3J = 8.9 Hz, 1H, H-8), 7.18 (d, ^4J = 2.7 Hz, 1H, H-5), 7.15 (dd, ^3J = 9.0 Hz, ^4J = 2.7 Hz, 1H, H-7), 5.01 (qd, ^3J = 6.4 Hz, ^4J = 1.1 Hz, 1H, H-9), 3.85 (s, 3H, OCH_3), 1.46 (d, ^3J = 6.4 Hz, 3H, H-10).

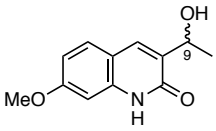
^{13}C NMR (101 MHz, MeOD-d_4) δ [ppm] = 163.3 (C-2), 156.9 (C-6), 138.8 (C-3), 135.6 (C-4), 133.2 (C-8a), 122.2 (C-4a), 120.8 (C-7), 117.5 (C-8), 109.9 (C-5), 65.8 (C-9), 56.1 (OCH_3), 23.4 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{14}O_3N$ $[M+H]^+$: 220.0968; found: 220.0969.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3304 (w, O-H), 2971 (w, sp^3 C-H), 2930 (w, sp^3 C-H), 2839 (w, sp^3 C-H), 1655 (vs, C=O), 1622 (m, C=C), 1504 (m, C=C), 1421 (m), 1236 (m, C-O) 1075 (w), 821 (m, sp^2 C-H).

m.p. = 208 °C.

*1.6.10 3-(1-Hydroxyethyl)-7-methoxy-2-quinolone (rac-**7j**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 1.50 mL, 4.50 mmol, 3.0 equiv) was added to a solution of aldehyde **S3j** (305 mg, 1.50 mmol, 1.0 equiv) in THF (7.5 mL). After purification by FCC the entitled alcohol *rac*-**7j** was obtained as a white solid (298 mg, 1.36 mmol, 91%).

***R*f** (5% MeOH/CH_2Cl_2): 0.41.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.92 (d, ^4J = 1.0 Hz, 1H, H-8), 7.56 (d, ^3J = 8.6 Hz, 1H, H-5), 6.86 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1H, H-6), 6.83 (d, ^4J = 2.4 Hz, 1H, H-8), 4.98 (qd, ^3J = 6.4 Hz, ^4J = 1.1 Hz, 1H, H-9), 3.87 (s, 3H, OCH_3), 1.44 (d, ^3J = 6.4 Hz, 3H, H-10).

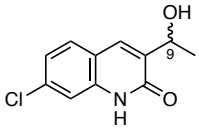
^{13}C NMR (101 MHz, MeOD-d_4) δ [ppm] = 164.1 (C-2), 163.1 (C-7), 140.5 (C-8a), 135.9 (C-4), 135.0 (C-3), 130.4 (C-5), 115.7 (C-4a), 113.2 (C-6), 98.7 (C-8), 65.7 (C-9), 56.0 (OCH_3), 23.3 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{14}O_3N$ $[M+H]^+$: 220.0968; found: 220.0969.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3294 (w, O-H), 2970 (w, sp^3 C-H), 2933 (w, sp^3 C-H), 2849 (w, sp^3 C-H), 1647 (vs, C=O), 1568 (m, C=C), 1511 (m, C=C), 1407 (w), 1229 (m, C-O) 1075 (w), 825 (w, sp^2 C-H).

m.p. = 225 °C.

*1.6.11 7-Chloro-3-(1-hydroxyethyl)-2-quinolone (rac-**7k**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 636 µL, 1.91 mmol, 3.0 equiv) was added to a solution of aldehyde **S3k** (132 mg, 637 µmol, 1.0 equiv) in THF (3.2 mL). After purification by FCC the entitled alcohol *rac*-**7k** was obtained as a white solid (116 mg, 519 µmol, 82%) including 12% of an unknown isomer that was inseparable by FCC.

***R*f** (5% MeOH/CH_2Cl_2): 0.43.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.98 (s, 1H, H-4), 7.65 (d, ^3J = 8.5 Hz, 1H, H-5), 7.36 (d, ^4J = 2.0 Hz, 1H, H-8), 7.23 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H, H-6), 4.98 (qd, ^3J = 6.4 Hz, ^4J = 1.1 Hz, 1H, H-9), 1.45 (d, ^3J = 6.5 Hz, 3H, H-10).

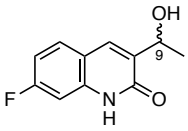
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-2), 139.7 (C-8a), 139.1 (C-3), 136.8 (C-7), 135.1 (C-4), 130.5 (C-5), 124.1 (C-6), 120.1 (C-4a), 115.7 (C-8), 65.6 (C-9), 23.2 (C-10).

HRMS (+ESI): calc. for $C_{11}H_{11}O_2ClN$ $[M+H]^+$: 224.0473; found: 224.0473.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3233 (w, O-H), 2969 (w, sp^3 C-H), 2929 (w, sp^3 C-H), 2841 (w, sp^3 C-H), 1638 (vs, C=O), 1565 (m, C=C), 1374 (m), 1297 (w), 1212 (w), 1080 (vs, C-Cl) 943 (m), 787 (s, sp^2 C-H), 731 (m, sp^2 C-H).

m.p. = 253 °C.

*1.6.12 7-Fluoro-3-(1-hydroxyethyl)-2-quinolone (rac-**7l**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 1.50 mL, 4.50 mmol, 3.0 equiv) was added to a solution of aldehyde **S3l** (287 mg, 1.50 mmol, 1.0 equiv) in THF (7.5 mL). After purification by FCC the entitled alcohol *rac*-**7l** was obtained as a white solid (309 mg, 1.49 mmol, 99%).

***R*f** (5% MeOH/CH_2Cl_2): 0.50.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.98 (d, ^4J = 1.1 Hz, 1H, H-4), 7.70 (dd, ^3J = 8.7 Hz, $^4J_{HF}$ = 5.9 Hz, 1H, H-5), 7.05 (dd, $^3J_{HF}$ = 9.9 Hz, ^4J = 2.5 Hz, 1H, H-6), 7.01 (*virt* td, $^3J_{HF}$ = 8.7 Hz, ^4J = 2.5 Hz, 1H, H-8), 4.98 (qd, ^3J = 6.4 Hz, ^4J = 1.1 Hz, 1H, H-9), 1.45 (d, ^3J = 6.4 Hz, 3H, H-10).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 165.0 (d, $^1J_{CF}$ = 248.0 Hz, C-7), 163.8 (C-2), 140.3 (d, $^3J_{CF}$ = 12.1 Hz, C-8a), 137.7 (s, C-3), 135.4 (C-4), 131.4 (d, $^3J_{CF}$ = 10.4 Hz, C-5), 118.3 (d, $^4J_{CF}$ = 2.0 Hz, C-4a), 112.0 (d, $^2J_{CF}$ = 23.9 Hz, C-8), 102.2 (d, $^2J_{CF}$ = 26.0 Hz, C-6), 65.6 (C-9), 23.3 (C-10).

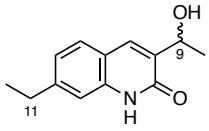
^{19}F NMR (376 MHz, MeOD-d_4) δ [ppm] = –111.2 (td, $^3J_{HF}$ = 9.3 Hz, $^4J_{HF}$ = 5.9 Hz, 1F).

HRMS (+ESI): calc. for $C_{11}H_{11}O_2FN$ $[M+H]^+$: 208.0768; found: 208.0769.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3305 (w, O-H), 2976 (w, sp^3 C-H), 2928 (w, sp^3 C-H), 2858 (w, sp^3 C-H), 1652 (vs, C=O), 1580 (m, C=C), 1513 (m, C=C), 1227 (m, C-F), 1147 (w), 930 (w), 850 (m, sp^2 C-H), 822 (m, sp^2 C-H).

m.p. = 226 °C.

*1.6.13 3-(1-Hydroxyethyl)-7-ethyl-2-quinolone (rac-**7m**)*



Following GP5 a commercially available solution of MeMgBr (3.0 M in Et_2O, 1.5 mL, 4.5 mmol, 3.0 equiv) was added to a solution of aldehyde **S3m** (302 mg, 1.50 mmol, 1.0 equiv) in THF (7.5 mL). After purification by FCC the entitled alcohol *rac*-**7m** was obtained as a white solid (260 mg, 1.20 mmol, 80%).

***R*f** (5% MeOH/CH_2Cl_2): 0.41.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.96 (s, 1H, H-4), 7.58 (d, ^3J = 8.0 Hz, 1H, H-5), 7.18 (d, ^4J = 1.4 Hz, 1H, H-8), 7.12 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-6), 5.00 (qd, ^3J = 6.4 Hz, ^4J = 1.1 Hz, 1H, H-9), 2.75 (q, ^3J = 7.6 Hz, 2H, H-11), 1.45 (d, ^3J = 6.3 Hz, 3H, H-10), 1.28 (t, ^3J = 7.6 Hz, 3H, H-12).

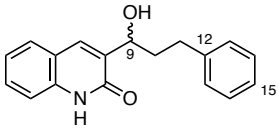
^{13}C NMR (101 MHz, MeOD-d_4) δ [ppm] = 163.9 (C-2), 148.5 (C-7), 139.0 (C-3), 137.4 (C-8a), 135.8 (C-4), 129.0 (C-5), 124.3 (C-6), 119.6 (C-4a), 114.8 (C-8), 65.7 (C-9), 30.0 (C-11), 23.3 (C-10), 15.9 (C-12).

HRMS (+ESI): calc. for $C_{13}H_{16}O_2N$ $[M+H]^+$: 218.1176; found: 218.1177.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3432 (w, O-H), 2967 (w, sp^3 C-H), 2931 (w, sp^3 C-H), 2871 (w, sp^3 C-H), 1652 (vs, C=O), 1563 (m, C=C), 1409 (m), 1281 (w) 1067 (w), 898 (m, sp^2 C-H), 823 (m, sp^2 C-H).

m.p. = 206 °C.

*1.6.14 3-(1-Hydroxy-3-phenylpropyl)-2-quinolone (rac-**7o**)*



Following GP5 a commercially available solution of phenethylmagnesium bromide (1.0 M in Et_2O, 3.60 mL, 3.60 mmol, 3.0 equiv) was added to a solution of aldehyde **S3a** (208 mg, 1.20 µmol, 1.0 equiv) in THF (2.6 mL). After purification by FCC the entitled alcohol *rac*-**7o** was obtained as a white solid (242 mg, 0.87 mmol, 72%).

R_f (5% MeOH/CH_2Cl_2): 0.39.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.01 (s, 1H, H-4), 7.67 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.50 (ddd, ^3J = 8.5, 7.1 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.34 (d, ^3J = 8.2 Hz, 1H, H-8), 7.25 (ddd, ^3J = 8.2, 7.2 Hz, ^4J = 1.2 Hz, 1H, H-6), 7.23-7.20 (m, 4H, H-13, H-14), 7.13-7.09 (m, 1H, H-15), 4.91 (ddd, ^3J = 8.2, 3.7, ^4J = 1.1 Hz, 1H, H-9), 2.84 (ddd, ^2J = 13.7 Hz, ^3J = 10.7 Hz, ^4J = 5.1 Hz, 1H, H-10), 2.76 (ddd, ^2J = 13.7 Hz, ^3J = 10.4 Hz, ^4J = 6.3 Hz, 1H, H-10'), 2.23-2.14 (m, 1H, H-11), 1.89 (dddd, ^2J = 13.5 Hz, ^3J = 10.4, 8.2 Hz, ^4J = 5.1 Hz, 1H, H-11').

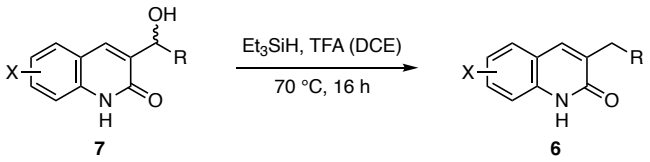
^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.8 (C-2), 143.5 (C-12), 138.9 (C-8a), 137.4 (C-3), 136.7 (C-4), 131.2 (C-7), 129.5 (C-14), 129.3 (C-13), 129.0 (C-5), 126.7 (C-15), 123.9 (C-6), 121.5 (C-4a), 116.2 (C-8), 69.2 (C-9), 39.7 (C-10), 33.2 (C-11).

HRMS (+ESI): calc. for $C_{18}H_{18}O_2N$ $[M+H]^+$: 280.1332; found: 280.1332.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3435 (w, O-H), 2943 (w, sp^3 C-H), 2910 (w, sp^3 C-H), 1652 (vs, C=O), 1568 (s, C=C), 1428 (m), 1215 (w), 1067 (m), 882 (w), 750 (s, sp^2 C-H), 730 (s, sp^2 C-H), 701 (s, sp^2 C-H).

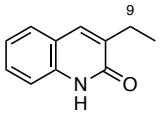
m.p. = 190 °C.

1.7 General procedure 6 (GP6): Synthesis of 3-alkyl-2-quinolones 6



Et_3SiH (10 equiv) and TFA (32 equiv) were added sequentially to a suspension of the corresponding alcohol (1.0 equiv) in DCE (0.2 M) affording a clear solution. The reaction mixture was stirred at 70 °C for 16 h before the reaction was carefully quenched by addition of saturated aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude material was subjected to FCC (5% → 20% acetone/CH_2Cl_2) to yield the entitled quinolone **6**.

*1.7.1 3-Ethyl-2-quinoilone (**6a**)*



Following GP6 the entitled quinolone **6a** was obtained from alcohol **7a** (284 mg, 1.50 mmol, 1.0 equiv) as a white solid (242 mg, 1.40 mmol, 93%).

***R*f** (20% acetone/CH_2Cl_2): 0.41.

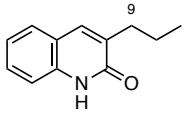
^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.70 (br s, 1H, NH), 7.71 (d, ^4J = 1.4 Hz, 1H, H-4), 7.60 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.42 (ddd, ^3J = 8.4, 7.1, ^4J = 1.4 Hz, 1H, H-7), 7.28 (dd, ^3J = 8.2, ^4J = 1.1 Hz, 1H, H-8), 7.14 (ddd, ^3J = 8.2, 7.3, ^4J = 1.1 Hz, 1H, H-6), 2.50 (dq, ^3J = 7.4, ^4J = 1.7 Hz, 2H, H-9), 1.16 (t, ^3J = 7.4 Hz, 3H, H-10).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 162.0 (C-2), 137.7 (C-8a), 135.3 (C-3), 134.7 (C-4), 129.1 (C-7), 127.2 (C-5), 121.6 (C-6), 119.5 (C-4a), 114.7 (C-8), 22.9 (C-9), 12.7 (C-10).

HRMS (+ESI): calc. for $C_{11}H_{12}ON$ $[M+H]^+$: 174.0913; found: 174.0914.

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

*1.7.2 3-Propyl-2-quinolone (**6b**)*



Following GP6 the entitled quinolone **6b** was obtained from alcohol **7b** (142 mg, 700 µmol, 1.0 equiv) as a white solid (80.0 mg, 427 µmol, 61%).

***R*f** (20% acetone/CH_2Cl_2): 0.62.

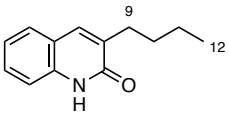
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.0 (s, 1H, NH), 7.63 (d, ^4J = 1.0 Hz, 1H, H-4), 7.54 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.46 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.31 (d, ^3J = 8.2 Hz, 1H, H-8), 7.21 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 2.66 (ddd, ^3J = 7.7, 6.9 Hz, ^4J = 1.1 Hz, 2H, H-9), 1.73 (h, ^3J = 7.4 Hz, 2H, H-10), 1.03 (t, ^3J = 7.4 Hz, 3H, H-11).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 163.8 (C-2), 137.2 (C-8a), 137.1 (C-4), 134.1 (C-3), 129.6 (C-7), 127.3 (C-5), 122.8 (C-6), 120.6 (C-4a), 115.6 (C-8), 32.4 (C-9), 21.7 (C-10), 14.1 (C-11).

HRMS (+ESI): calc. for $C_{12}H_{14}ON$ $[M+H]^+$: 188.1070; found: 188.1070.

Spectral data matches those reported in the literature.[14]

*1.7.3 3-Butyl-2-quinolone (**6c**)*



Following GP6 the entitled quinolone **6c** was obtained from alcohol **7c** (119 mg, 547 µmol, 1.0 equiv) as a white solid (94.0 mg, 467 µmol, 85%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.71.

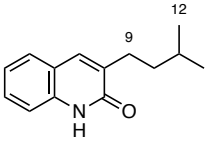
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 12.0 (s, 1H, NH), 7.62 (s, 1H, H-4), 7.52 (dd, ^3J = 7.8 Hz, ^4J =1.3 Hz, 1H, H-5), 7.45 (ddd, ^3J = 8.4, 7.1 Hz, ^4J =1.4 Hz, 1H, H-7), 7.39 (d, ^3J = 8.1 Hz, 1H, H-8), 7.19 (ddd, ^3J = 8.0, 7.1 Hz, ^4J =1.2 Hz, 1H, H-6), 2.81-2.61 (m, 2H, H-9), 1.77-1.61 (m, 2H, H-10), 1.46 (h, ^3J = 7.4 Hz, 2H, H-11), 0.99 (t, ^3J = 7.4 Hz, 3H, H-12).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.5 (C-2), 137.5 (C-8a), 136.7 (C-4), 134.5 (C-3), 129.4 (C-7), 127.1 (C-5), 122.5 (C-6), 120.5 (C-4a), 115.7 (C-8), 30.7 (C-10), 30.1 (C-9), 22.7 (C-11), 14.2 (C-12).

HRMS (+ESI): calc. for $C_{13}H_{16}ON$ $[M+H]^+$: 202.1226; found: 202.1227.

Spectral data matches those reported in the literature.[15]

*1.7.4 3-Isopentyl-2-quinolone (**6d**)*



Following GP6 the entitled quinolone **6d** was obtained from alcohol **7d** (173 mg, 173 µmol, 1.0 equiv) as a white solid (152 mg, 706 µmol, 94%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.74.

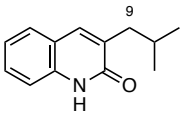
^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.7 (br s, 1H, NH), 7.72 (d, ^4J = 0.9 Hz, 1H, H-4), 7.59 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.41 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.27 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 7.13 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.2 Hz, 1H, H-8), 2.49-2.45 (m, 2H, H-9), 1.57 (dp, ^3J = 13.2, 6.6 Hz, 1H, H-11), 1.50-1.41 (m, 2H, H-10), 0.92 (d, ^3J = 6.6 Hz, 6H, H-12).

^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 162.1 (C-2), 137.7 (C-8a), 135.5 (C-4), 134.2 (C-3), 129.1 (C-7), 127.1 (C-5), 121.6 (C-8), 119.5 (C-4a), 114.7 (C-6), 37.2 (C-10), 27.7 (C-9), 27.5 (C-11), 22.5 (C-12).

HRMS (+ESI): calc. for $C_{14}H_{18}ON$ $[M+H]^+$: 216.1383; found: 216.1384.

Spectral data matches those reported in the literature.[16]

*1.7.5 3-Isobutyl-2-quinolone (**6e**)*



Following GP6 the entitled quinolone **6e** was obtained from alcohol **7e** (93.0 mg, 428 µmol, 1.0 equiv) as a white solid (83.0 mg, 412 µmol, 96%).

R_f (20% acetone/CH_2Cl_2): 0.65.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 11.8 (s, 1H, NH), 7.58 (s, 1H, H-4), 7.52 (dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.45 (ddd, ^3J = 8.4, 7.0 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.36 (d, ^3J = 8.1 Hz, 1H, H-8), 7.19 (ddd, ^3J = 8.0, 7.1 Hz, ^4J = 1.2 Hz, 1H, H-6), 2.56 (dd, ^3J = 7.1 Hz, ^4J = 0.9 Hz, 2H, H-9), 2.14 (dp, ^3J = 13.5, 6.7 Hz, 1H, H-10), 0.99 (d, ^3J = 6.6 Hz, 6H, H-11).

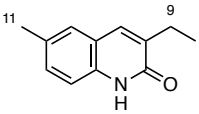
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.6 (C-2), 137.8 (C-4), 137.7 (C-8a), 133.3 (C-3), 129.5 (C-7), 127.2 (C-5), 122.5 (C-6), 120.4 (C-4a), 115.7 (C-8), 39.8 (C-9), 27.6 (C-10), 22.7 (C-11).

HRMS (+ESI): calc. for $C_{13}H_{16}ON$ $[M+H]^+$: 202.1226; found: found: 202.1227.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2951 (w, sp^3 C-H), 2900 (w, sp^3 C-H), 2864 (w, sp^3 C-H), 1655 (vs, C=O), 1575 (m, C=C), 1435 (m), 1214 (w), 1089 (w), 917 (w), 756 (m, sp^2 C-H).

m.p. = 188 °C.

*1.7.6 3-Ethyl-6-methyl-2-quinolone (**6f**)*



Following GP6 the entitled quinolone **6f** was obtained from alcohol **7f** (152 mg, 750 µmol, 1.0 equiv) as a white solid (126 mg, 673 µmol, 90%).

R_f (20% acetone/CH_2Cl_2): 0.49.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 11.6 (br s, 1H, NH), 7.62 (d, ^4J = 1.4 Hz, 1H, H-4), 7.44-7.34 (m, 1H, H-5), 7.24 (dd, ^3J = 8.4 Hz, ^4J = 1.9 Hz, 1H, H-7), 7.18 (d, ^3J = 8.3 Hz, 1H, H-8), 2.47 (qd, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 2H, H-9), 2.32 (s, 3H, H-11), 1.15 (t, ^3J = 7.5 Hz, 3H, H-10).

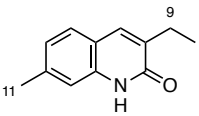
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 161.9 (C-2), 135.7 (C-8a), 135.2 (C-3), 134.5 (C-4), 130.5 (C-6), 130.3 (C-7), 126.7 (C-5), 119.4 (C-4a), 114.6 (C-8), 23.0 (C-9), 20.5 (C-11), 12.8 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{14}O_1N$ $[M+H]^+$: 180.1070; found: 180.1071.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2957 (w, sp^3 C-H), 2920 (w, sp^3 C-H), 2850 (w, sp^3 C-H), 1652 (vs, C=O), 1578 (s, C=C), 1410 (m), 1257 (w) 911 (m), 814 (m, sp^2 C-H), 675 (m).

m.p. = 177 °C.

*1.7.7 3-Ethyl-7-methyl-2-quinolone (**6g**)*



Following GP6 the entitled quinolone **6g** was obtained from alcohol **7g** (152 mg, 750 µmol, 1.0 equiv) as a white solid (123 mg, 657 µmol, 88%).

***R*f** (20% acetone/CH_2Cl_2): 0.57.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.7 (br s, 1H, NH), 7.58 (s, 1H, H-4), 7.41 (d, ^3J = 7.9 Hz, 1H, H-5), 7.17 (d, ^4J = 1.4 Hz, 1H, H-8), 7.01 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, H-6), 2.72 (q, ^3J = 7.5 Hz, 2H, H-9), 2.45 (s, 3H, H-11), 1.30 (t, ^3J = 7.4 Hz, 3H, H-10).

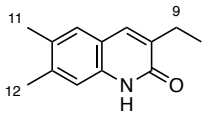
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.5 (C-2), 140.0 (C-7), 137.5 (C-8a), 135.6 (C-4), 134.4 (C-3), 127.0 (C-5), 124.1 (C-6), 118.3 (C-4a), 115.6 (C-8), 23.3 (C-9), 21.8 (C-11), 12.9 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{14}O_1N$ $[M+H]^+$: 180.1070; found: 180.1071.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2957 (w, sp^3 C-H), 2923 (w, sp^3 C-H), 2852 (w, sp^3 C-H), 1650 (vs, C=O), 1568 (s, C=C), 1451 (w), 1225 (m) 914 (m), 801 (m, sp^2 C-H).

m.p. = 172 °C.

*1.7.8 3-Ethyl-6,7-dimethyl-2-quinolone (**6h**)*



Following GP6 the entitled quinolone **6h** was obtained from alcohol **7h** (199 mg, 916 µmol, 1.0 equiv) as a white solid (167 mg, 830 µmol, 90%).

***R*f** (20% acetone/CH_2Cl_2): 0.46.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.4 (br s, 1H, NH), 7.53 (s, 1H, H-4), 7.26 (s, 1H, H-5) , 7.12 (s, 1H, H-8), 2.70 (q, ^3J = 7.4 Hz, 2H, H-9), 2.35 (s, 3H, H-12), 2.30 (s, 3H, H-11), 1.29 (t, ^3J = 7.4 Hz, 3H, H-10).

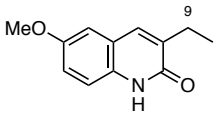
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.2 (C-2), 139.2 (C-7), 135.8 (C-8a), 135.4 (C-4), 134.4 (C-3), 131.3 (C-6), 127.3 (C-5), 118.7 (C-4a), 116.0 (C-8), 23.4 (C-9), 20.3 (C-12), 19.5 (C-11), 12.9 (C-10).

HRMS (+ESI): calc. for $C_{13}H_{16}O_1N$ $[M+H]^+$: 202.1226; found: 202.1228.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2960 (w, sp^3 C-H), 2920 (w, sp^3 C-H), 2851 (w, sp^3 C-H), 1649 (vs, C=O), 1571 (m, C=C), 1448 (w), 1237 (m), 916 (m) 894 (m, sp^2 C-H).

m.p. = 195 °C.

*1.7.9 3-Ethyl-6-methoxy-2-quinolone (**6i**)*



Following GP6 the entitled quinolone **6i** was obtained from alcohol **7i** (164 mg, 750 µmol, 1.0 equiv) as a white solid (140 mg, 689 µmol, 92%).

***R*f** (20% acetone/CH_2Cl_2): 0.36.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.8 (br s, 1H, NH), 7.56 (s, 1H, H-4), 7.31 (d, ^3J = 8.9 Hz, 1H, H-8), 7.09 (dd, ^3J = 8.9 Hz, ^4J = 2.7 Hz, 1H, H-7), 6.96 (d, ^4J = 2.7 Hz, 1H, H-5), 3.85 (s, 3H, OCH_3), 2.72 (q, ^3J = 7.5 Hz, 2H, H-9), 1.30 (t, ^3J = 7.4 Hz, 3H, H-10).

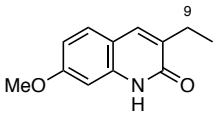
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 163.8 (C-2), 155.2 (C-6), 136.2 (C-3), 135.3 (C-4), 132.1 (C-8a), 121.1 (C-4a), 118.8 (C-7), 116.9 (C-8), 108.6 (C-5), 55.8 (OCH_3), 23.5 (C-9), 12.9 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{14}O_1N$ $[M+H]^+$: 204.1019; found: 204.1020.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2924 (w, sp^3 C-H), 2851 (w, sp^3 C-H), 1653 (vs, C=O), 1626 (s, C=C), 15042 (m, C=C), 1464 (m), 1240 (m, C-O) 1043 (m), 901 (m), 831 (m, sp^2 C-H).

m.p. = 185 °C.

*1.7.10 3-Ethyl-7-methoxy-2-quinolone (**6j**)*



Following *GP6* the entitled quinolone **6j** was obtained from alcohol **7j** (164 mg, 750 µmol, 1.0 equiv) as a white solid (132 mg, 649 µmol, 87%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.41.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.8 (br s, 1H, NH), 7.54 (s, 1H, H-4), 7.41 (d, ^3J = 8.6 Hz, 1H, H-5), 6.82 (d, ^4J = 2.4 Hz, 1H, H-8), 6.79 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1H, H-6), 3.89 (s, 3H, OCH_3), 2.68 (qd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 2H, H-9), 1.29 (t, ^3J = 7.5 Hz, 3H, H-10).

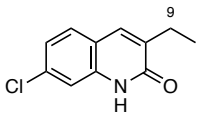
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.7 (C-2), 160.9 (C-7), 139.1 (C-8a), 135.8 (C-4), 132.3 (C-3), 128.5 (C-5), 114.7 (C-4a), 112.0 (C-6), 98.1 (C-8), 55.7 (OCH_3), 23.3 (C-9), 13.0 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{14}O_1N$ $[M+H]^+$: 204.1019; found: 204.1020.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2964 (w, sp^3 C-H), 2921 (w, sp^3 C-H), 2852 (w, sp^3 C-H), 1654 (vs, C=O), 1573 (s, C=C), 1510 (m, C=C), 1229 (m, C-O) 1032 (m), 913 (m), 812 (w, sp^2 C-H).

m.p. = 190 °C.

*1.7.11 3-Ethyl-7-chloro-2-quinolone (**6k**)*



Following GP6 the entitled quinolone **6k** was obtained from alcohol **7k** (166 mg, 742 µmol, 1.0 equiv) as a white solid (119 mg, 573 µmol, 77%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.72.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 12.0 (br s, 1H, NH), 7.58 (s, 1H, H-4), 7.45 (d, ^3J = 8.4 Hz, 1H, H-5), 7.39 (d, ^4J = 2.0 Hz, 1H, H-8), 7.16 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H, H-6), 2.72 (qd, ^3J = 7.5, 1.3 Hz, 2H, H-9), 1.31 (t, ^3J = 7.4 Hz, 3H, H-10).

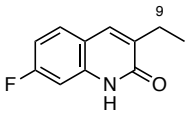
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.3 (C-2), 138.1 (C-8a), 135.9 (C-3) 135.4 (C-4), 135.3 (C-7), 128.4 (C-5), 123.2 (C-6), 119.0 (C-4a), 115.4 (C-8), 23.4 (C-9), 12.7 (C-10).

HRMS (+ESI): calc. for $C_{11}H_{11}O_1ClN$ $[M+H]^+$: 208.0524; found: 208.0525.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2970 (w, sp^3 C-H), 2937 (w, sp^3 C-H), 2846 (w, sp^3 C-H), 1739 (m) 1659 (vs, C=O), 1571 (m, C=C), 1376 (m), 1217 (m), 1083 (m, C-Cl) 908 (m), 800 (w, sp^2 C-H), 751 (w, sp^2 C-H).

m.p. = 205 °C.

*1.7.12 3-Ethyl-7-fluoro-2-quinolone (**6l**)*



Following GP6 the entitled quinolone **6l** was obtained from alcohol **7l** (155 mg, 750 µmol, 1.0 equiv) as a white solid (128 mg, 672 µmol, 90%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.59.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 12.09 (br s, 1H, NH), 7.59 (d, ^4J = 1.3 Hz, 1H, H-4), 7.50 (dd, ^3J = 8.7 Hz, $^4J_{HF}$ = 5.8 Hz, 1H, H-5), 7.10 (dd, $^3J_{HF}$ = 9.5 Hz, ^4J = 2.5 Hz, 1H, H-8), 6.93 (*virt* td, $^3J \approx {}^3J_{HF}$ = 8.6 Hz, ^4J = 2.4 Hz, 1H, H-6), 2.70 (qd, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 2H, H-9), 1.30 (t, ^3J = 7.4 Hz, 3H, H-10).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.8 (C-2), 163.3 (d, $^1J_{CF}$ = 248.9 Hz, C-7), 138.8 (d, $^3J_{CF}$ = 12.0 Hz, C-8a), 135.4 (C-4), 134.6 (C-3), 129.1 (d, $^3J_{CF}$ = 10.1 Hz, C-5), 117.2 (d, $^4J_{CF}$ = 2.0 Hz, C-4a), 111.0 (d, $^2J_{CF}$ = 23.3 Hz, C-6), 102.0 (d, $^2J_{CF}$ = 25.2 Hz, C-8), 23.3 (C-9), 12.8 (C-10).

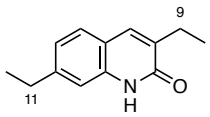
^{19}F NMR (376 MHz, $CDCl_3$) δ [ppm] = –109.8 (td, $^3J_{HF}$ = 9.1 Hz, $^4J_{HF}$ = 5.8 Hz, 1F).

HRMS (+ESI): calc. for $C_{11}H_{11}OFN$ $[M+H]^+$: 192.0819; found: 192.0820.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2927 (w, sp^3 C-H), 2855 (w, sp^3 C-H), 1673 (vs, C=O), 1582 (s, C=C), 1514 (s, C=C), 1226 (s, C-F), 1165 (w), 905 (w), 853 (m, sp^2 C-H), 822 (m, sp^2 C-H), 747 (w, sp^2 C-H).

m.p. = 199 °C.

*1.7.13 3-Ethyl-7-ethyl-2-quinolone (**6m**)*



Following GP6 the entitled quinolone **6m** was obtained from alcohol **7m** (163 mg, 750 µmol, 1.0 equiv) as a white solid (131 mg, 651 µmol, 87%).

***R*$_f$** (20% acetone/CH_2Cl_2): 0.68.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.3 (br s, 1H, NH), 7.58 (s, 1H, H-4), 7.43 (d, ^3J = 8.0 Hz, 1H, H-5), 7.14 (d, ^4J = 1.5 Hz, 1H, H-8), 7.04 (dd, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 1H, H-6), 2.81-2.64 (m, 4H, H-9, H-11), 1.38-1.22 (m, 6H, H-10, H-12).

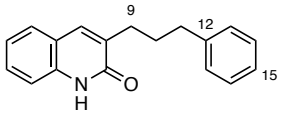
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 164.6 (C-2), 146.3 (C-7), 137.7 (C-8a), 135.7 (C-4), 134.5 (C-3), 127.0 (C-5), 122.9 (C-6), 118.6 (C-4a), 114.5 (C-8), 29.2 (C-11), 23.4 (C-9), 15.6 (C-12), 12.9 (C-10).

HRMS (+ESI): calc. for $C_{13}H_{16}O_1N$ $[M+H]^+$: 202.1226; found: 202.1228.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2965 (m, sp^3 C-H), 2932 (w, sp^3 C-H), 2870 (w, sp^3 C-H), 1650 (vs, C=O), 1568 (s, C=C), 1410 (m), 1222 (w), 1060 (w), 911 (s), 817 (m, sp^2 C-H), 739 (m, sp^2 C-H).

m.p. = 153 °C.

*1.7.14 3-(3-Phenylpropyl)-2-quinolone (**6o**)*



Following GP6 the entitled quinolone **6o** was obtained from alcohol **7o** (210 mg, 750 µmol, 1.0 equiv) as a white solid (167 mg, 634 µmol, 85%).

***R*f** (20% acetone/CH_2Cl_2): 0.69.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.3 (br s, 1H, NH), 7.62 (s, 1H, H-4), 7.52 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.46 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.33 (d, ^3J = 8.2 Hz, 1H, H-8), 7.33-7.26 (m, 2H, H-14), 7.27-7.16 (m, 4H, H-6, H-13, H-15), 2.80-2.70 (m, 4H, H-9, H-11), 2.10-2.00 (m, 2H, H-10).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 163.9 (C-2), 142.3 (C-12), 137.3 (C-8a), 137.1 (C-4), 133.8 (C-3), 129.7 (C-7), 128.6 (C-13), 128.5 (C-14), 127.3 (C-5), 125.9 (C-15), 122.8 (C-6), 120.5 (C-4a), 115.6 (C-8), 35.8 (C-11), 30.2 (C-9), 30.1 (C-10).

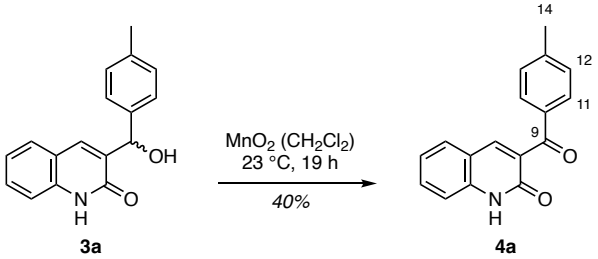
HRMS (+ESI): calc. for $C_{18}H_{18}ON$ $[M+H]^+$: 264.1383; found: 264.1384.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2931 (w, sp^3 C-H), 2890 (w, sp^3 C-H), 2850 (w, sp^3 C-H), 1659 (vs, C=O), 1574 (m, C=C), 1424 (m), 1217 (w), 1027 (m), 898 (m), 749 (s, sp^2 C-H), 737 (m, sp^2 C-H), 693 (m, sp^2 C-H).

m.p. = 149 °C.

1.8 Single procedures

*1.8.1 3-(4-Methylbenzoyl)-2-quinolone (**4a**)*



3a **4a**

MnO_2 (1.27 g, 14.6 mmol, 15 equiv) was added in one portion to a solution of **3a** (258 mg, 972 µmol, 1.0 equiv) and the resulting black suspension was stirred for 19 h at 23 °C. Excess MnO_2 was removed *via* filtration over celite and the filtrate was concentrated under reduced pressure. The residual crude material was purified by FCC (2% → 5% MeOH/CH_2Cl_2) to yield the entitled ketone **4a** as an off-white fluffy solid (102 mg, 387 µmol, 40%).

R_f (5% MeOH/CH_2Cl_2): 0.43.

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] = 12.1 (br s, 1H, NH), 8.17 (s, 1H, H-4), 7.78 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, H-5), 7.73 (d, ^3J = 8.0 Hz, 2H, H-11), 7.60 (ddd, ^3J = 8.5, 7.1 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.37 (d, ^3J = 8.3 Hz, 1H, H-8), 7.33 (d, ^3J = 8.0 Hz, 2H, H-12), 7.24 (dt, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 1H, H-6), 2.39 (s, 3H, H-14).

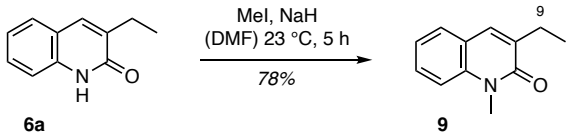
^{13}C NMR (126 MHz, DMSO-d_6) δ [ppm] = 193.6 (C-9), 159.9 (C-2), 144.1 (C-13), 140.3 (C-4), 139.6 (C-8a), 134.2 (C-10), 132.2 (C-3), 131.8 (C-7), 129.5 (C-11), 129.2 (C-12), 129.0 (C-5), 122.3 (C-6), 118.4 (C-4a), 115.3 (C-8), 21.3 (C-14).

HRMS (+ESI): calc. for $C_{17}H_{14}O_2N$ $[M+H]^+$: 264.1019; found: 264.1020.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2949 (w, sp^3 C-H), 1662 (vs, C=O), 1607 (m, C=C), 1562 (m, C=C), 1432 (w), 1254 (w), 1102 (w), 921 (m), 838 (w, sp^2 C-H), 755 (vs, sp^2 C-H).

m.p. = 304 °C.

*1.8.2 3-Ethyl-N-methyl-2-quinolone (**9**)*



6a **9**

NaH (60% on mineral oil, 15.6 mg, 390 µmol, 1.3 equiv) and MeI (2.80 µL, 450 µmol, 1.5 equiv) were added sequentially to a solution of **6a** (52.0 mg, 300 µmol, 1.0 equiv) in DMF (1.2 mL) and the resulting grey suspension was stirred for 5 h at 23 °C. The reaction was quenched by addition of saturated aqueous NH_4Cl and the aqueous layer was extracted with EtOAc (3x). The combined organic layers were washed with saturated aqueous NH_4Cl (2x), brine (2x), dried over Na_2SO_4 and after removal of all solvents *in vacuo* the crude product was subjected to FCC (1% → 3% MeOH/CH_2Cl_2) to yield the entitled quinolone **9** as a white solid (44.0 mg, 235 µmol, 78%).

***R*$_f$** (5% MeOH/CH_2Cl_2): 0.50.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.57-7.47 (m, 3H, H-4, H-5, H-7), 7.34 (dd, ^3J = 8.5 Hz, ^4J = 0.9 Hz, 1H, H-8), 7.22 (td, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 1H, H-6), 3.75 (s, 3H, NCH_3), 2.68 (qd, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 2H, H-9), 1.27 (t, ^3J = 7.4 Hz, 3H, H-10).

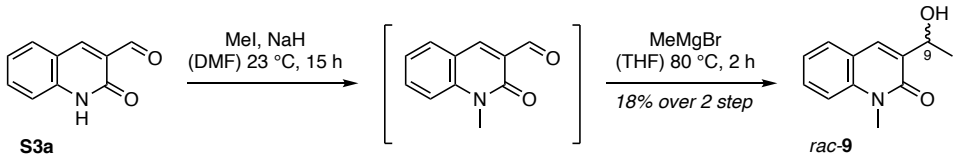
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 162.7 (C-2), 139.0 (C-8a), 135.6 (C-3), 134.0 (C-4), 129.4 (C-7), 128.1 (C-5), 122.1 (C-6), 120.9 (C-4a), 114.0 (C-8), 29.8 (NCH_3), 24.2 (C-9), 12.7 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{14}ON$ $[M+H]^+$: 188.1070; found: 188.1070.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2966 (w, sp^3 C-H), 2914 (w, sp^3 C-H), 2877 (w, sp^3 C-H), 1642 (vs, C=O), 1622 (s), 1593 (s), 1456 (m), 1224 (m), 1092 (w), 908 (m), 750 (vs, sp^2 C-H), 717 (s, sp^2 C-H).

m.p. = 55 °C.

*1.8.3 3-(1-Hydroxyethyl)-N-methyl-2-quinolinone (rac-**9***



MeI (93.0 µmol, 1.50 mmol, 1.5 equiv) was added to a grey suspension of aldehyde **S3a** (173 mg, 1.00 mmol, 1.0 equiv) and NaH (60% on mineral oil, 52.0 mg, 1.30 mmol, 1.3 equiv) in DMF (4.0 mL) and the reaction mixture was stirred at 23 °C for 15 h. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (15 mL) and EtOAc (20 mL) and the organic layer was separated. The aqueous layer was extracted twice with EtOAc (2× 20 mL) and the combined organic layers were washed with saturated aqueous NH_4Cl solution (2× 50 mL), brine (2× 50 mL) and eventually dried over Na_2SO_4. After removal of all volatiles *in vacuo* the crude *N*-methylated aldehyde was used without further purification for the next step (209 mg).

MeMgBr (3.0 M in Et_2O, 500 µL, 1.5 mmol) was added to a suspension of the crude aldehyde (112 mg) in THF (3.0 mL) and the resulting orange solution was heated to 80 °C for 2 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (10 mL) and the aqueous layer was extracted with EtOAc (3× 10 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. After removal of all volatiles *in vacuo* the crude material was subjected to FCC to yield the entitled *N*-methylated alcohol *rac*-**9** as a light brown gum (19.1 mg, 94.0 µmol, 18% over 2 steps).

R_f (5% MeOH/CH_2Cl_2): 0.75.

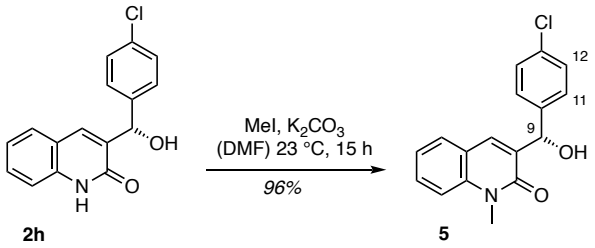
^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.97 (br s, 1H, H-4), 7.71 (dd, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 1H, H-5), 7.63 (ddd, ^3J = 8.6, 7.1 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.57 (dd, ^3J = 8.5 Hz, ^4J = 1.6 Hz, 1H, H-8), 7.31 (ddd, ^3J = 8.0, 7.0 Hz, ^4J = 1.1 Hz, 1H, H-6), 5.01 (qd, ^3J = 6.4 Hz, ^4J = 1.2 Hz, 1H, H-9), 3.76 (s, 3H, NCH_3), 1.45 (d, ^3J = 6.4 Hz, 3H, H-10).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 162.9 (C-2), 140.1 (C-8a), 138.0 (C-3), 134.8 (C-4), 131.5 (C-7), 129.9 (C-5), 123.8 (C-6), 122.0 (C-4a) 115.5 (C-8), 66.2 (C-9), 30.0 (NCH_3), 23.2 (C-10).

HRMS (+ESI): calc. for $C_{12}H_{14}O_2N$ $[M+H]^+$: 204.1019; found: 204.1019.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3408 (w, O-H) 2972 (w, sp^3 C-H), 2929 (w, sp^3 C-H), 1641 (vs, C=O), 1589 (s), 1572 (s), 1453 (m), 1219 (m), 1080 (w), 908 (m), 787 (m, sp^2 C-H) 752 (vs, sp^2 C-H), 740 (s, sp^2 C-H).

*1.8.4 (S)-3-((4-Chlorophenyl)(hydroxy)methyl)-N-methyl-2-quinolone (**5**)*



MeI (16.3 µmol, 262 µmol, 5.0 equiv) was added to a suspension of **2h** (15.0 mg, 52.5 µmol, 1.0 equiv) and K_2CO_3 (10.9 mg, 1.5 equiv) in DMF (500 µL) and the reaction mixture was stirred for 15 h at 23 °C. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (3 mL) and H_2O (5 mL) the aqueous layer was extracted with EtOAc (3× 15 mL). The combined organic layers were washed with saturated aqueous NH_4Cl solution (2× 20 mL) and brine (3× 20 mL), dried over Na_2SO_4 and after removal of all volatiles *in vacuo* the crude material was subjected to FCC (1% → 5% MeOH/CH_2Cl_2) to yield the entitled *N*-methylalcohol **5** as white foam (15.1 mg, 50.4 µmol, 96%). Colorless crystals with suitable quality for x-ray crystallography were obtained by slow evaporation from CH_2Cl_2 (2.0 mL).

R_f (5% MeOH/CH_2Cl_2): 0.77.

^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.10 (t, ^4J = 0.8 Hz, 1H, H-4), 7.73 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, H-5), 7.62 (ddd, ^3J = 8.6, 7.1 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.54 (dd, ^3J = 8.5 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.43 (d, ^3J = 8.4 Hz, 2H, H-11), 7.31 (ddd, ^3J = 8.6, 7.1 Hz, ^4J = 1.5 Hz, 1H, H-6), 7.30 (d, ^3J = 8.6 Hz, 2H, H-12), 5.93 (d, ^4J = 1.1 Hz, 1H, H-9), 3.71 (s, 3H, NCH_3).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 162.7 (C-2), 143.1 (C-10), 140.3 (C-8a), 136.0 (C-4), 134.2 (C-3), 131.8 (C-7), 130.2 (C-5), 129.9 (C-11), 129.3 (C-12), 123.9 (C-6), 121.9 (C-4a), 115.6 (C-8), 71.4 (C-9), 30.1 (NCH_3).

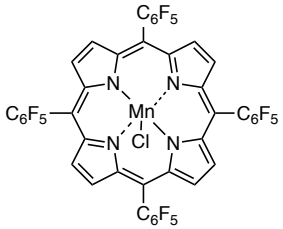
HRMS (+ESI): calc. for $C_{17}H_{15}O_2ClN$ $[M+H]^+$: 300.0786; found: 300.0786.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3379 (w, O-H), 2926 (w, sp^3 C-H), 1644 (vs, C=O), 1489 (s, C=C), 1489 (m), 1461 (m), 1089 (w), 1014 (w, C-Cl), 949 (w), 840 (w), 753 (s, sp^2 C-H).

m.p. = 172 °C.

2 Oxygenation of quinolones

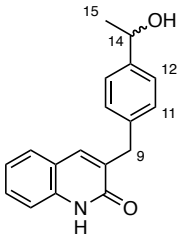
2.1 General procedure 7 (GP7): Racemic oxygenation of 3-substituted quinolones



Mn(TPFPP)Cl

A solution of Mn(TPFPP)Cl[2] (6.0 mM in CH_2Cl_2, 200 µL, 0.90 µmol, 2.0 mol%) was added to a suspension of the corresponding quinolone (180 µmol, 3.0 equiv) and PhIO (60.0 µmol, 1.0 equiv) in CH_2Cl_2 (2.8 mL) affording a deep brown suspension, which was stirred at ambient temperature for 24 h. The solvent was removed *in vacuo* and the crude material purified by automated flash column chromatography (method B).

*2.1.1 3-(4-(1-Hydroxyethyl)benzyl)-2-quinolone (**2n**)*



Following GP7 the entitled alcohol **2n** was obtained as a white solid (4.60 mg, 16.4 µmol, 27%) and quinolone **2l** was recovered as a white solid (41.5 mg, 158 µmol, 2.6 equiv).

R_f (5% MeOH/CH_2Cl_2): 0.27.

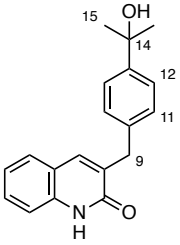
^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.60 (s, 1H, H-4), 7.52 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.47 (ddd, ^3J = 8.4, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.34-7.29 (m, 3H, H-8, H-12), 7.27 (d, ^3J = 8.2 Hz, 2H, H-11), 7.19 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 4.81 (q, ^3J = 6.5 Hz, 1H, H-14), 3.90 (d, ^4J = 1.0 Hz, 2H, H-9), 1.43 (d, ^3J = 6.5 Hz, 3H, H-15).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 164.7 (C-2), 145.6 (C-13), 139.4 (C-10), 139.2 (C-4), 138.8 (C-8a), 134.5 (C-3), 130.9 (C-7), 130.1 (C-11), 128.6 (C-5), 126.8 (C-12), 123.7 (C-6), 121.6 (C-4a), 116.2 (C-8), 70.7 (C-14), 36.6 (C-9), 25.5 (C-15).

HRMS (+ESI): calc. for $C_{18}H_{18}O_2N$ $[M+H]^+$: 280.1332; found: 280.1332.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3300 (bs, w, O-H), 2968 (w, sp^3 C-H), 2926 (w, sp^3 C-H), 2856 (w, sp^3 C-H), 1649 (vs, C=O), 1573 (m, C=C), 1427 (w), 1219 (w), 1087 (w), 815 (w, sp^2 C-H), 754 (m, sp^2 C-H).

*2.1.2 3-(4-(2-Hydroxypropan-2-yl)benzyl)-2-quinolone (**2o**)*



Following GP7 the entitled alcohol **2o** was obtained as a white solid (3.60 mg, 12.3 µmol, 20%) and quinolone **2m** was recovered as a white solid (42.3 mg, 152 µmol, 2.5 equiv).

R_f (5% MeOH/CH_2Cl_2): 0.29.

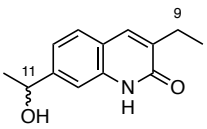
^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.60 (q, ^4J = 1.0 Hz, 1H, H-4), 7.52 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.46 (ddd, ^3J = 8.6, 7.2 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.43 (d, ^3J = 8.3 Hz, 2H, H-12), 7.32 (dd, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.25 (d, ^3J = 8.3 Hz, 2H, H-11), 7.19 (ddd, ^3J = 8.1, 7.2 Hz, ^4J = 1.1 Hz, 1H, H-6), 3.90 (d, ^4J = 1.0 Hz, 2H, H-9), 1.52 (s, 6H, H-15).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 164.7 (C-2), 148.9 (C-13), 139.2 (C-4), 138.8 (C-8a), 138.5 (C-10), 134.5 (C-3), 130.9 (C-7), 129.8 (C-11), 128.6 (C-5), 125.8 (C-12), 123.7 (C-6), 121.6 (C-4a), 116.2 (C-8), 72.9 (C-14), 36.5 (C-9), 31.9 (C-15).

HRMS (+ESI): calc. for $C_{19}H_{21}O_2N$ $[M+H]^+$: 294.1489; found: 294.1489.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3386 (bs, w, O-H), 2973 (w, sp^3 C-H), 2926 (w, sp^3 C-H), 2856 (w, sp^3 C-H), 1649 (vs, C=O), 1573 (m, C=C), 1464 (w), 1427 (w), 1220 (w), 1020 (w), 810 (w, sp^2 C-H), 755 (m, sp^2 C-H).

*2.1.3 3-Ethyl-7-(1-hydroxyethyl)-2-quinolone (rac-**6n**)*



Following GP7 the entitled alcohol *rac*-**6n** was obtained as a white solid (2.60 mg, 12.0 µmol, 20%) and quinolone **6m** was recovered as a white solid (31.4 mg, 156 µmol, 2.6 equiv).

R_f (5% MeOH/CH_2Cl_2): 0.25.

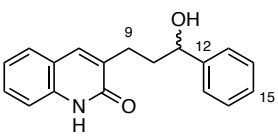
^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.76 (q, ^4J = 1.1 Hz, 1H, H-4), 7.59 (d, ^3J = 8.2 Hz, 1H, H-5), 7.36 (d, ^4J = 1.4 Hz, 1H, H-8), 7.24 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 1H, H-6), 4.90 (q, ^3J = 6.5 Hz, 1H, H-11), 2.62 (qd, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 2H, H-9), 1.47 (d, ^3J = 6.5 Hz, 3H, H-12), 1.26 (t, ^3J = 7.5 Hz, 3H, H-10).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 165.1 (C-2), 150.0 (C-7), 138.7 (C-8a), 137.3 (C-4), 135.8 (C-3), 128.5 (C-5), 121.4 (C-6), 120.9 (C-4a), 112.7 (C-12), 70.5 (C-11), 25.6 (C-12), 24.3 (C-9), 13.2 (C-10).

HRMS (+ESI): calc. for $C_{13}H_{16}O_2N$ $[M+H]^+$: 218.1176; found: 218.1176.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3299 (w, O-H), 2969 (w, sp^3 C-H), 2928 (w, sp^3 C-H), 2874 (w, sp^3 C-H), 1647 (vs, C=O), 1567 (m, C=C), 1408 (m), 1285 (w), 1073 (w), 895 (m, sp^2 C-H), 819 (m, sp^2 C-H).

*2.1.4 3-(3-hydroxy-3-phenylpropyl)-2-quinolone (rac-**6p**)*



Following GP7 the entitled alcohol *rac*-**6p** was obtained as a white solid (3.50 mg, 12.5 µmol, 21%) and quinolone **6o** was recovered as a white solid (40.8 mg, 155 µmol, 2.6 equiv).

***R*f** (4% MeOH/CH_2Cl_2): 0.32.

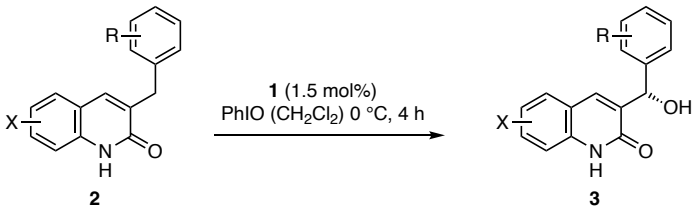
^{1}H NMR (500 MHz, MeOD-d_4) δ [ppm] = 7.75 (s, 1H, H-4), 7.59 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, H-5), 7.46 (ddd, ^3J = 8.5, 7.2 Hz, ^4J = 1.4 Hz, 1H, H-7), 7.39-7.36 (m, 2H, H-13), 7.36-7.29 (m, 3H, H-8, H-14), 7.26-7.17 (m, 2H, H-6, H-15), 4.68 (t, ^3J = 6.7 Hz, 1H, H-11), 2.80-2.70 (m, 1H, H-9), 2.69-2.56 (m, 1H, H-9'), 2.06 (td, ^3J = 8.0, 6.7 Hz, 2H, H-10).

^{13}C NMR (126 MHz, MeOD-d_4) δ [ppm] = 164.9 (C-2), 146.3 (C-12), 138.8 (C-8a), 138.7 (C-4), 134.4 (C-3), 130.8 (C-7), 129.3 (C-14), 128.5 (C-15), 128.3 (C-5), 127.1 (C-13), 123.7 (C-6), 121.7 (C-4a), 116.1 (C-8) , 74.6 (C-11), 38.9 (C-10), 28.1 (C-9).

HRMS (+ESI): calc. for $C_{18}H_{18}O_2N$ $[M+H]^+$: 280.1332; found: 280.1332.

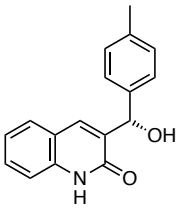
IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3312 (w, O-H), 2920 (m, sp^3 C-H), 2852 (w, sp^3 C-H), 1649 (vs, C=O), 1572 (s, C=C), 1494 (w), 1428 (m), 1059 (w), 754 (s, sp^2 C-H), 701 (s, sp^2 C-H).

2.2 General procedure 8 (GP8): Enantioselective oxygenation of 3-benzylquinolones 2



A solution of the chiral manganese porphyrin catalyst **1** (4.5 mM in CH_2Cl_2, 200 µL, 0.90 µmol 1.5 mol%) was added to a solution of the corresponding benzylquinolone **2** (180 µmol, 3.0 equiv) in CH_2Cl_2 (5.8 mL) affording a deep green solution, which was cooled to 0 °C. PhIO was added in three portion (first 6.60 mg, 0.5 equiv, then 3.30 mg, 0.25 equiv after 60 and 90 min respectively) and the reaction mixture was stirred for 4 h (*i.e.* 2.5 h after addition of the last portion of PhIO) at 0 °C. After removal of all volatiles *in vacuo* the crude material was purified by automated flash column chromatography (method A).

*2.2.1 (S)-3-(Hydroxy(p-tolyl)methyl)-2-quinolone (**3a**)*



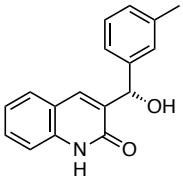
Following GP8 the entitled benzylic alcohol **3a** was obtained as a white solid (9.50 mg, 35.8 µmol, 60%) and quinolone **2a** was recovered as a white solid (33.7 mg, 135 µmol, 2.26 equiv, 75% recovery yield).

Specific rotation: $[a]_D^{25}$ = +4.0 (c = 1.0, MeOH, 96% *ee*).

Chiral HPLC: 96% *ee* [©CHIRALPAK AS-H, 20 °C, 50% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 7.61 min (minor), 10.7 min (major)].

The entitled compound **3a** was synthesized in a preliminary experiment (Scheme 1) using the following conditions: A solution of the chiral manganese porphyrin catalyst **1** (6.0 mM in CH_2Cl_2, 200 µL, 1.20 µmol 2.0 mol%) was added to a stirring suspension of quinolone **2a** (15.0 mg, 60.0 µmol, 1.0 equiv) and PhIO (26.4 mg, 120 µmol, 2.0 equiv) in CH_2Cl_2 (5.8 mL) at 0 °C and the reaction mixture was stirred for 16 h affording a green solution. The reaction mixture was filtered over celite and the solvent was removed *in vacuo*. The crude material was subjected to FCC (5% → 25% acetone/CH_2Cl_2 + 0.1% Et_3N) to yield the alcohol **3a** as white solid (4.80 mg, 18.1 µmol, 30%, 95% *ee*).

*2.2.2 (S)-3-(Hydroxy(m-tolyl)methyl)-2-quinolone (**3b**)*

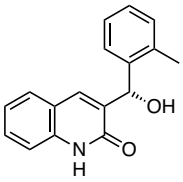


Following GP8 the entitled benzylic alcohol **3b** was obtained as a white solid (9.30 mg, 35.1 µmol, 58%) and quinolone **2b** was recovered as a white solid (34.2 mg, 137 µmol, 2.28 equiv, 76% recovery yield).

Specific rotation: $[a]_D^{25}$ = +6.4 (c = 2.5, MeOH, 99% *ee*).

Chiral HPLC: 99% ee [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 10.6 min (major), 12.7 min (minor)].

*2.2.3 (S)-3-(Hydroxy(o-tolyl)methyl)-2-quinolone (**3c**)*

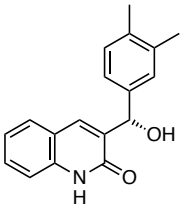


Following GP8 the entitled benzylic alcohol **3c** was obtained as a white solid (10.2 mg, 38.5 µmol, 64%) and quinolone **2c** was recovered as a white solid (34.4 mg, 138 µmol, 2.29 equiv, 76% recovery yield).

Specific rotation: $[a]_D^{25}$ = +20.8 (c = 2.5, MeOH, 97% *ee*).

Chiral HPLC: 97% ee [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 10.9 min (major), 16.0 min (minor)].

*2.2.4 (S)-3-((3,4-Dimethylphenyl)(hydroxy)methyl)-2-quinolone (**3d**)*

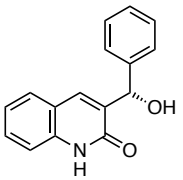


Following GP8 the entitled benzylic alcohol **3d** was obtained as a white solid (9.90 mg, 35.4 µmol, 59%) and quinolone **2d** was recovered as a white solid (33.8 mg, 128 µmol, 2.14 equiv, 71% recovery yield).

Specific rotation: $[a]_D^{25}$ = +2.0 (c = 2.0, MeOH, 92% *ee*).

Chiral HPLC: 92% ee [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 9.96 min (minor), 15.9 min (major)].

*2.2.5 (S)-3-(Hydroxy(phenyl)methyl)-2-quinolone (**3e**)*

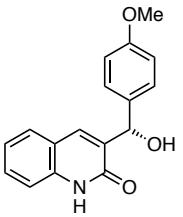


Following GP8 the entitled benzylic alcohol **3e** was obtained as a white solid (9.20 mg, 38.6 µmol, 61%) and quinolone **2e** was recovered as a white solid (31.6 mg, 134 µmol, 2.23 equiv, 74% recovery yield).

Specific rotation: $[a]_D^{25}$ = +3.2 (c = 2.5, MeOH, 95% *ee*).

Chiral HPLC: 95% *ee* [©CHIRALPAK AS-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 11.7 min (minor), 23.1 min (major)].

*2.2.6 (S)-3-(Hydroxy(4-methoxyphenyl)methyl)-2-quinolone (**3f**)*

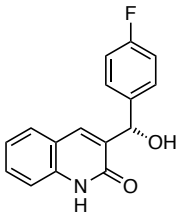


Following GP8 the entitled benzylic alcohol **3f** was obtained as a white solid (9.00 mg, 32.0 µmol, 53%) and quinolone **2f** was recovered as a white solid (36.4 mg, 137 µmol, 2.28 equiv, 76% recovery yield).

Specific rotation: $[a]_D^{25}$ = +24.0 (c = 1.0, MeOH, 93% *ee*).

Chiral HPLC: 93% *ee* [©CHIRALPAK AS-H, 20 °C, 50% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 11.0 min (minor), 13.7 min (major)].

*2.2.7 (S)-3-((4-Fluorophenyl)(hydroxy)methyl)-2-quinolone (**3g**)*

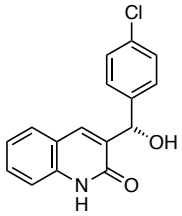


Following GP8 the entitled benzylic alcohol **3g** was obtained as a white solid (8.50 mg, 31.6 µmol, 53%) and quinolone **2g** was recovered as a white solid (32.1 mg, 127 µmol, 2.11 equiv, 70% recovery yield).

Specific rotation: $[a]_D^{25}$ = +12.0 (c = 2.0, MeOH, 91% *ee*).

Chiral HPLC: 91% *ee* [©CHIRALPAK AS-H, 20 °C, 50% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 7.33 min (minor), 10.4 min (major)].

*2.2.8 (S)-3-((4-Chlorophenyl)(hydroxy)methyl)-2-quinolone (**3h**)*

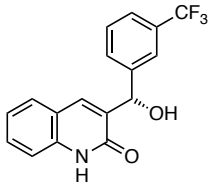


Following GP8 the entitled benzylic alcohol **3h** was obtained as a white solid (3.00 mg, 10.5 µmol, 18%) and quinolone **2h** was recovered as a white solid (44.0 mg, 163 µmol, 2.72 equiv, 91% recovery yield).

Specific rotation: $[a]_D^{25}$ = +2.7 (c = 1.5, MeOH, 98% *ee*).

Chiral HPLC: 98% *ee* [©CHIRALPAK AS-H, 20 °C, 20% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 16.0 min (minor), 14.2 min (major)].

*2.2.9 (S)-3-(Hydroxy(3-(trifluoromethyl)phenyl)methyl)-2-quinolone (**3i**)*

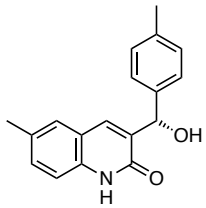


Following GP8 the entitled benzylic alcohol **3i** was obtained as a white solid (5.00 mg, 15.7 µmol, 26%) and quinolone **2i** was recovered as a white solid (45.9 mg, 151 µmol, 2.52 equiv, 84% recovery yield).

Specific rotation: $[a]_D^{25}$ = +3.0 (c = 2.0, MeOH, 92% *ee*).

Chiral HPLC: 92% ee [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 6.85 min (major), 8.77 min (minor)]

*2.2.10 (S)-3-(Hydroxy(p-tolyl)methyl)-6-methyl-2-quinolone (**3j**)*

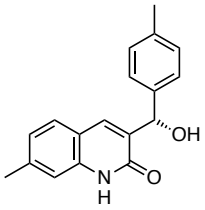


Following GP8 the entitled benzylic alcohol **3j** was obtained as a white solid (10.0 mg, 35.8 µmol, 60%) and quinolone **2j** was recovered as a white solid (34.0 mg, 129 µmol, 2.15 equiv, 72% recovery yield).

Specific rotation: $[a]_D^{25}$ = +34.0 (c = 1.0, MeOH, 98% *ee*).

Chiral HPLC: 98% ee [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 11.2 min (minor), 14.3 min (major)]

*2.2.11 (S)-3-(Hydroxy(p-tolyl)methyl)-7-methyl-2-quinolone (**3k**)*

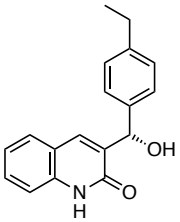


Following GP8 the entitled benzylic alcohol **3k** was obtained as a white solid (8.80. mg, 31.5 µmol, 53%) and quinolone **2k** was recovered as a white solid (34.4 mg, 131 µmol, 2.18 equiv, 73% recovery yield).

Specific rotation: $[a]_D^{25}$ = +4.0 (c = 1.0, MeOH, 96% *ee*)

Chiral HPLC: 96% ee [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 12.8 min (minor), 15.0 min (major)].

*2.2.12 (S)-3-((4-Ethylphenyl)(hydroxy)methyl)-2-quinolone (**3l**)*

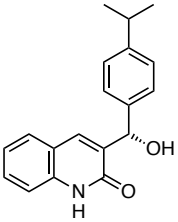


Following GP8 the entitled benzylic alcohol **3l** was obtained as a white solid (9.60 mg, 34.4 µmol, 57%) and quinolone **2l** was recovered as a white solid (34.9 mg, 133 µmol, 2.21 equiv, 74% recovery yield).

Specific rotation: $[a]_D^{25}$ = +10.7 (c = 1.5, MeOH, 93% *ee*).

Chiral HPLC: 93% *ee* [©CHIRALPAK AS-H, 20 °C, 50% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 7.17 min (minor), 10.2 min (major)].

*2.2.13 (S)-3-(Hydroxy(4-isopropylphenyl)methyl)-2-quinolone (**3m**)*

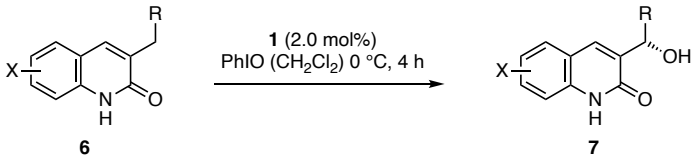


Following GP8 the entitled benzylic alcohol **3m** was obtained as a white solid (8.80 mg, 30.0 µmol, 50%) and quinolone **2m** was recovered as a white solid (40.6 mg, 146 µmol, 2.44 equiv, 81% recovery yield).

Specific rotation: $[a]_D^{25}$ = +7.0 (c = 2.0, MeOH, 91% *ee*).

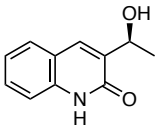
Chiral HPLC: 91% *ee* [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 7.54 min (minor), 8.89 min (major)].

2.3 General procedure 9 (GP9): Enantioselective oxygenation of 3-alkylquinolones 6



A solution of the chiral manganese porphyrin catalyst **1** (6.0 mM in CH_2Cl_2, 200 µL, 0.90 µmol 2.0 mol%) was added to a solution of the corresponding quinolone **6** (180 µmol, 3.0 equiv) in CH_2Cl_2 (5.8 mL) affording a deep green solution, which was cooled to 0 °C. PhIO was added in three portion (6.60 mg, 0.5 equiv and 3.30 mg, 0.25 equiv after 60 and 90 min respectively) and the reaction mixture was stirred for further 2.5 h at 0 °C after the last PhIO addition. The solvent was removed *in vacuo* and the crude material was purified by automated flash column chromatography (method B).

*2.3.1 (S)-3-(1-Hydroxyethyl)-2-quinolone (**7a**)*

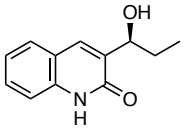


Following GP9 the entitled alcohol **7a** was obtained as a white solid (6.30 mg, 33.5 µmol, 56%) and quinolone **6a** was recovered as a white solid (24.8 mg, 143 µmol, 2.38 equiv, 79% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –51.5 (c = 0.66, THF, 95% *ee*).

Chiral HPLC: 95% ee [©CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 18.3 min (major), 21.6 min (minor)].

*2.3.2 (S)-3-(1-Hydroxypropyl)-2-quinolone (**7b**)*

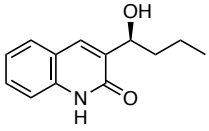


Following GP9 the entitled alcohol **7b** was obtained as a white solid (6.50 mg, 32.0 µmol, 53%) and quinolone **6b** was recovered as a white solid (26.7 mg, 142 µmol, 2.37 equiv, 79% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –56 (c = 1.0, MeOH, 88% *ee*).

Chiral HPLC: 88% ee [©CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 20.6 min (major), 23.9 min (minor)].

*2.3.3 (S)-3-(1-Hydroxybutyl)-2-quinolone (**7c**)*

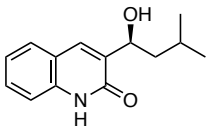


Following GP9 the entitled alcohol **7c** was obtained as a white solid (6.50 mg, 29.9 µmol, 50%) and quinolone **6c** was recovered as a white solid (27.3 mg, 136 µmol, 2.27 equiv, 76% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –60 (c = 1.0, MeOH, 86% *ee*).

Chiral HPLC: 86% ee [©CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 20.5 min (major) 24.5 min (minor)].

*2.3.4 (S)-3-(1-Hydroxy-3-methylbutyl)-2-quinolone (**7d**)*

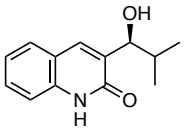


Following GP9 the entitled alcohol **7d** was obtained as a white solid (6.70 mg, 29.0 µmol, 48%) and quinolone **6d** was recovered as a white solid (32.3 mg, 150 µmol, 2.50 equiv, 83% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –66 (c = 1.0, MeOH, 88% *ee*).

Chiral HPLC: 88% ee [©CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 18.9 min (major), 27.2 min (minor)].

*2.3.5 (S)-3-(1-Hydroxy-2-methylpropyl)-2-quinolone (**7e**)*

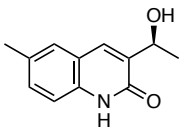


Following GP9 the entitled alcohol **7e** was obtained as a white solid (6.20 mg, 28.5 µmol, 48%) and quinolone **6e** was recovered as a white solid (29.8 mg, 148 µmol, 2.47 equiv, 82% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –66 (c = 1.0, MeOH, 80% *ee*).

Chiral HPLC: 80% ee [©CHIRALPAK AS-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 8.02 min (major), 14.9 min (minor)].

*2.3.6 (S)-3-(1-Hydroxyethyl)-6-methyl-2-quinolone (**7f**)*

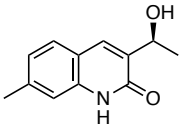


Following GP9 the entitled alcohol **7f** was obtained as a white solid (6.20 mg, 30.5 µmol, 51%) and quinolone **6f** was recovered as a white solid (27.6 mg, 147 µmol, 2.45 equiv, 82% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –52.0 (c = 1.0, MeOH, 94% *ee*).

Chiral HPLC: 94% ee [©CHIRALPAK AS-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 8.40 min (minor), 14.6 min (major)].

*2.3.7 (S)-3-(1-Hydroxyethyl)-7-methyl-2-quinolone (**7g**)*

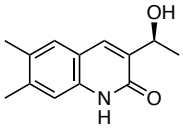


Following GP9 the entitled alcohol **7g** was obtained as a white solid (7.10 mg, 34.9 µmol, 58%) and quinolone **6g** was recovered as a white solid (26.7 mg, 143 µmol, 2.38 equiv, 79% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –54.0 (c = 1.0, MeOH, 96% *ee*).

Chiral HPLC: 96% ee [©CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 20.1 min (major), 28.5 min (minor)].

*2.3.8 (S)-3-(1-Hydroxyethyl)-6,7-dimethyl-2-quinolone (**7h**)*

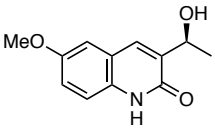


Following GP9 the entitled alcohol **7h** was obtained as a white solid (6.60 mg, 30.4 µmol, 51%) and quinolone **6h** was recovered as a white solid (29.8 mg, 148 µmol, 2.46 equiv, 82% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –44.0 (c = 1.0, MeOH, 95% *ee*).

Chiral HPLC: 95% ee [©CHIRALPAK AD-H, 5 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 16.1 min (major), 18.4 min (minor)].

*2.3.9 (S)-3-(1-Hydroxyethyl)-6-methoxy-2-quinolone (**7i**)*

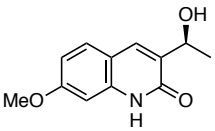


Following GP9 the entitled alcohol **7i** was obtained as a white solid (2.80 mg, 12.6 µmol, 21%) and quinolone **6i** was recovered as a white solid (29.9 mg, 147 µmol, 2.47 equiv, 82% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –20.0 (c = 1.0, MeOH, 96% *ee*).

Chiral HPLC: 96% ee [©CHIRALPAK AS-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 10.0 min (minor), 25.5 min (major)].

*2.3.10 (S)-3-(1-Hydroxyethyl)-7-methoxy-2-quinolone (**7j**)*

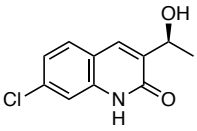


Following GP9 the entitled alcohol **7j** was obtained as a white solid (8.10 mg, 37.0 µmol, 62%) and quinolone **6j** was recovered as a white solid (26.2 mg, 129 µmol, 2.15 equiv, 72% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –64.0 (c = 1.0, MeOH, 95% *ee*).

Chiral HPLC: 95% ee [©CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 24.8 min (major), 35.8 min (minor)].

*2.3.11 (S)-7-Chloro-3-(1-hydroxyethyl)-2-quinolone (**7k**)*

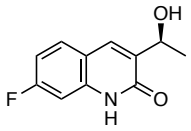


Following GP9 the entitled alcohol **7k** was obtained as a white solid (4.60 mg, 20.6 µmol, 34%) and quinolone **6k** was recovered as a white solid (32.9 mg, 159 µmol, 2.64 equiv, 88% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –54.0 (c = 1.0, MeOH, 95% *ee*).

Chiral HPLC: 95% ee [©CHIRALPAK AS-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 5.88 min (major), 8.31 min (minor)].

*2.3.12 (S)-7-Fluoro-3-(1-hydroxyethyl)-2-quinolone (**7l**)*

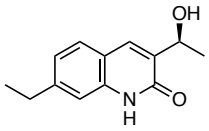


Following GP9 the entitled alcohol **7l** was obtained as a white solid (5.20 mg, 25.1 µmol, 42%) and quinolone **6l** was recovered as a white solid (28.7 mg, 150 µmol, 2.50 equiv, 83% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –48.0 (c = 1.0, MeOH, 96% *ee*).

Chiral HPLC: 96% ee [©CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 15.6 min (major), 21.0 min (minor)].

*2.3.13 (S)-3-(1-Hydroxyethyl)-7-ethyl-2-quinolone (**7m**)*

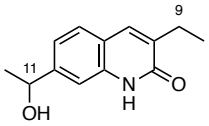


Following GP9 the entitled alcohol **7m** was obtained as a white solid (7.80 mg, 35.9 µmol, 60%), the entitled isomer **6n** was obtained as a colorless solid (1.10 mg, 5.06 µmol, 8%), and quinolone **6m** was recovered as a white solid (27.6 mg, 137 µmol, 2.29 equiv, 76% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –56.0 (c = 1.0, MeOH, 98% *ee*).

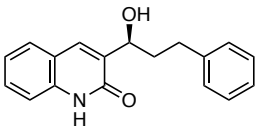
Chiral HPLC: 98% ee [©CHIRALPAK AS-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 8.51 min (major), 11.0 min (minor)].

*2.3.14 (S)-3-Ethyl-7-(1-hydroxyethyl)-2-quinolone (**6n**)*



Chiral HPLC: 10% ee [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 11.9 min (major), 14.5 min (minor)].

*2.3.15 (S)-3-(1-Hydroxy-3-phenylpropyl)-2-quinolone (**7o**)*

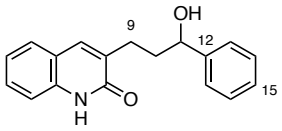


Following GP9 the entitled alcohol **7o** was obtained as a white solid (7.60 mg, 27.2 µmol, 45%) the entitled isomer **6p** was obtained as a colorless solid (4.10 mg, 14.6 µmol, 24%), and quinolone **6o** was recovered as a white solid (36.3 mg, 138 µmol, 2.30 equiv, 77% recovery yield).

Specific rotation: $[\alpha]_D^{25}$ = –30.0 (c = 1.0, MeOH, 84% *ee*).

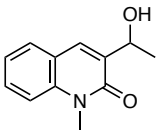
Chiral HPLC: 84% ee [©CHIRALPAK AD-H, 20 °C, 10% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 18.9 min (minor), 27.2 min (major)].

*2.3.16 3-(3-Hydroxy-3-phenylpropyl)-2-quinolone (**6p**)*



Chiral HPLC: 16% ee [©CHIRALPAK AD-H, 20 °C, 30% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 12.4 min (major), 14.6 min (minor)].

*2.3.17 3-(1-Hydroxyethyl)-N-methyl-2-quinolone (**10**)*



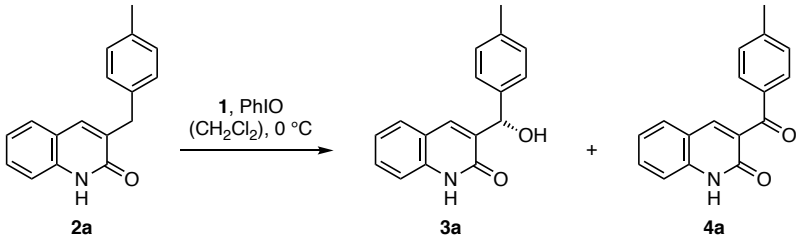
Following GP9 the entitled alcohol **10** was obtained as a white solid (2.70 mg, 13.3 µmol, 22%) and quinolone **9** was recovered as a white solid (27.8 mg, 148 µmol, 2.47 equiv, 82% recovery yield).

Chiral HPLC: *racemic* [©CHIRALPAK AS-H, 20 °C, 50% ^{i}PrOH/^{n}heptane, 1 mL/min, 210 nm, t_R = 4.84 min, 7.07 min].

3 Kinetic experiments

Individual stock solutions (5.000 mM) of the three components **2a**, **3a** and **4a** were prepared and diluted to the following concentrations 1.500 mM (100%), 0.900 mM (60%), 0.450 mM (30%), 0.150 mM (10%) and 0.075 mM (5%) each containing ^{n}dodecane as the internal standard (1.50 mM). The samples were submitted to GLC analysis and the method for quantification of the compounds was calibrated according to the corresponding instrument response factors from the initial measurements. A correlation of $R^2 \geq 0.999$ was obtained for each compound.

3.1 General procedure 10 (GP10): Rate profiling of the enantioselective oxygenation



A solution of the chiral manganese porphyrin catalyst **1** (3.0 mM in CH_2Cl_2) was added to a suspension of **2a**, ^{n}dodecane (13.6 µL, 60.0 µmol, 1.0 equiv) and PhIO in CH_2Cl_2 (final concentration of internal standard c = 10 mM) at 0 °C whereupon the reaction was initiated. At the indicated times, aliquots of 100 µL were transferred to a GLC vial containing CH_2Cl_2 (700 µL) and a 10% aqueous $Na_2S_2O_3$ solution (500 µL) affording a biphasic mixture. After vigorous mixing for approximately 30 sec the organic layer was separated *via* syringe filtration and submitted to GLC analysis.

3.1.1 *Conditions: **1** (2 mol%), **2a** (1.0 equiv), PhIO (2.0 equiv)*

t [min]		0	15	30	45	60	90	120	180	240
2a	[%]	87	61	58	57	57	56	56	54	53
	[mM]	8.65	6.08	5.82	5.74	5.70	5.61	5.59	5.44	5.33
3a	[%]	6	24	25	25	26	26	27	27	27
	[mM]	0.60	2.40	2.54	2.55	2.59	2.63	2.71	2.68	2.74
4a	[%]	1	7	8	8	9	9	10	11	12
	[mM]	0.11	0.67	0.80	0.83	0.86	0.94	0.98	1.06	1.16
balance [%]		95	94	91	92	91	91	92	93	92

3.1.2 *Conditions: **1** (2 mol%), **2a** (1.0 equiv), PhIO (2.0 equiv)*

t [h]		0	1	2	4	8	24	28	32	48
2a	[%]	87	56	55	51	47	30	29	29	28
	[mM]	8.66	5.55	5.45	5.13	4.72	2.96	2.94	2.87	2.80
3a	[%]	6	25	26	27	28	22	19	16	11
	[mM]	0.59	2.49	2.60	2.69	2.81	2.16	1.86	1.61	1.07
4a	[%]	1	8	9	11	15	36	39	42	48
	[mM]	0.09	0.79	0.92	1.13	1.47	3.60	3.93	4.23	4.83
balance [%]		95	93	88	90	89	90	87	87	87

3.1.3 *Conditions: **1** (1 mol%), **2a** (1.0 equiv), PhIO (2.0 equiv) (Figure 3, dashed lines)*

t [min]		0	5	10	15	30	60	120	180	240
2a	[%]	96	85	80	78	78	77	76	75	74
	[mM]	9.56	8.50	7.96	7.77	7.76	7.65	7.57	7.53	7.41
3a	[%]	2	10	14	14	15	15	16	16	17
	[mM]	0.22	1.01	1.40	1.42	1.47	1.53	1.60	1.61	1.67
4a	[%]	0	2	3	3	3	3	4	4	4
	[mM]	0.04	0.15	0.28	0.30	0.32	0.34	0.35	0.39	0.42
balance [%]		98	97	97	96	95	95	95	95	95

3.1.4 *Conditions: **1** (3 mol%), **2a** (1.0 equiv), PhIO (2.0 equiv)*

t [min]		0	5	10	15	30	60	120	180	240
2a	[%]	90	75	65	58	47	45	42	41	39
	[mM]	8.98	7.54	6.53	5.76	4.69	4.50	4.23	4.07	3.87
3a	[%]	5	17	23	26	31	31	31	32	32
	[mM]	0.46	1.67	2.33	2.63	3.09	3.07	3.14	3.17	3.16
4a	[%]	3	5	7	10	17	18	20	21	22
	[mM]	0.30	0.48	0.70	0.98	1.69	1.80	1.96	2.11	2.21
balance [%]		97	97	96	94	95	94	93	94	92

3.1.5 *Conditions: **1** (5 mol%), **2a** (1.0 equiv), PhIO (2.0 equiv)*

t [min]		0	5	10	15	30	60	120	180	240
2a	[%]	90	76	66	54	38	23	18	19	18
	[mM]	8.97	7.57	6.55	5.45	3.78	2.26	1.84	1.86	1.81
3a	[%]	4	14	21	28	32	30	27	27	26
	[mM]	0.42	1.45	2.12	2.76	3.24	2.97	2.67	2.69	2.64
4a	[%]	2	5	7	12	23	38	46	46	47
	[mM]	0.18	0.46	0.67	1.16	2.26	3.82	4.56	4.63	4.69
balance [%]		98	97	97	96	95	95	95	95	95

3.1.6 *Conditions: **1** (1 mol%), **2a** (3.0 equiv), PhIO (1.0 equiv) (Figure 3, solid lines)*

t [min]		0	5	10	15	30	60	120	180	240
2a	[%]	298	292	282	276	261	244	233	238	235
	[mM]	29.8	29.2	28.2	27.6	26.1	24.4	23.3	23.8	23.5
3a	[%]	3	7	14	19	32	45	49	48	48
	[mM]	0.27	0.72	1.40	1.94	3.24	4.49	4.92	4.78	4.83
4a	[%]	1	1	2	2	5	8	10	10	10
	[mM]	0.07	0.09	0.16	0.22	0.48	0.77	1.01	0.96	0.96
balance [%]		302	302	300	298	298	298	297	292	295

3.1.7 *Conditions: **1** (1 mol%), **2a** (2.0 equiv), PhIO (1.0 equiv)*

t [min]		0	5	10	15	30	60	120	180	240
2a	[%]	201	198	193	190	176	158	144	143	143
	[mM]	20.09	19.80	19.34	19.03	17.57	15.77	14.37	14.27	14.25
3a	[%]	2	5	8	11	22	33	41	41	42
	[mM]	0.19	0.46	0.75	1.09	2.16	3.30	4.08	4.14	4.22
4a	[%]	0	0	1	1	3	6	11	12	12
	[mM]	0.00	0.00	0.09	0.15	0.32	0.65	1.07	1.16	1.17
balance [%]		203	203	202	203	200	197	195	196	196

3.1.8 *Conditions: **1** (1 mol%), **2a** (3.0 equiv), PhIO (0.5 equiv + 2× 0.25 equiv after t = 60, 120 min)*

t [min]		0	5	10	15	30	60	120	180	240
2a	[%]	286	283	283	282	274	266	242	231	227
	[mM]	28.6	28.3	28.3	28.2	27.4	26.6	24.2	23.1	22.7
3a	[%]	0	2	3	5	9	16	32	41	43
	[mM]	0.00	0.15	0.33	0.53	0.95	1.63	3.25	4.07	4.29
4a	[%]	0	0	0	0	2	3	7	11	13
	[mM]	0.00	0.00	0.00	0.00	0.16	0.25	0.70	1.12	1.27
balance [%]		286	284	287	287	285	285	282	283	282

3.1.9 *Conditions: **1** (0.5 mol%), **2a** (3.0 equiv), PhIO (0.5 equiv + 2× 0.25 equiv after t = 45, 90 min)*

t [min]		5	10	15	30	45	60	120	180	240
2a	[%]	311	312	303	297	291	285	267	264	263
	[mM]	31.1	31.2	30.3	29.7	29.1	28.5	26.7	26.4	26.3
3a	[%]	2	4	5	12	16	0	35	36	37
	[mM]	0.15	0.35	0.54	1.20	1.64	0.04	3.49	3.65	3.69
4a	[%]	0	0	1	3	3	4	8	8	9
	[mM]	0.00	0.00	0.11	0.25	0.30	0.41	0.76	0.84	0.87
balance [%]		312	316	309	312	310	289	310	309	308

3.1.10 *Conditions: **1** (1.5 mol%), **2a** (3.0 equiv), PhIO (0.5 equiv + 2× 0.25 equiv after t = 60, 90 min)*

t [min]		5	10	15	30	45	60	120	180	240
2a	[%]	306	302	300	286	279	276	242	226	224
	[mM]	30.6	30.2	30.0	28.6	27.9	27.6	24.2	22.6	22.4
3a	[%]	2	5	7	14	20	23	47	57	56
	[mM]	0.22	0.47	0.70	1.41	1.99	2.30	4.75	5.66	5.62
4a	[%]	2	2	2	3	4	5	13	17	17
	[mM]	0.21	0.19	0.20	0.29	0.39	0.47	1.29	1.70	1.71
balance [%]		310	309	309	303	303	304	302	299	297

3.2 Kinetic profiling using the "same excess" protocol

A: **1** (1 mol%), **2a** (1.0 equiv), PhIO (2.0 equiv) (Figure 5, solid line)

t [min]		3	6	9	12	15	30	45	60	63	66	69	72	75	90	105	120
2a	[%]	93	91	88	85	82	72	71	70	70	70	70	70	70	70	69	68
	[mM]	9.29	9.12	8.83	8.52	8.23	7.16	7.12	7.03	7.04	7.03	7.05	7.04	6.97	6.97	6.95	6.82
3a	[%]	1	3	5	7	9	16	16	17	17	17	17	18	18	18	18	18
	[mM]	0.13	0.29	0.50	0.70	0.92	1.57	1.61	1.67	1.72	1.68	1.71	1.75	1.76	1.79	1.79	1.81
4a	[%]	0	0	1	2	2	5	5	5	6	6	6	6	6	6	6	6
	[mM]	0.00	0.00	0.10	0.16	0.22	0.45	0.52	0.55	0.55	0.57	0.59	0.58	0.61	0.59	0.63	0.63
balance [%]		94	94	94	94	94	92	92	93	93	93	93	94	93	94	94	93

B: **1** (1 mol%), **2a** (0.70 equiv), **3a** (0.17 equiv), **4a** (0.07 equiv), PhIO (1.69 equiv)* (Figure 5, dashed line)

t [min]		0	3	6	9	12	15	30	45	60
2a	[%]	71	70	69	67	66	64	57	57	56
	[mM]	7.10	7.00	6.89	6.72	6.58	6.36	5.72	5.67	5.64
3a	[%]	15	16	17	19	20	21	24	25	25
	[mM]	1.51	1.61	1.70	1.85	1.96	2.12	2.43	2.46	2.51
4a	[%]	6	8	9	10	10	11	13	13	13
	[mM]	0.63	0.80	0.86	0.96	0.97	1.07	1.27	1.32	1.34
balance [%]		92	94	94	95	95	95	94	94	95

*In this specific case, the reaction was initiated by addition of the oxidant (PhIO) to a pre-cooled reaction mixture of all reactants **2a**, **3a**, **4a** and the catalyst **1**

C: **1** (1 mol%), **2a** (1.0 equiv), PhIO (2× 2.0 equiv after *t* = 0, 60 min)

t [min]		3	6	9	12	15	30	45	60	63	66	69	72	75	90	105	120
2a	[%]	96	93	90	86	84	79	79	78	78	78	78	78	78	77	78	77
	[mM]	9.56	9.25	9.00	8.64	8.38	7.86	7.88	7.84	7.84	7.83	7.79	7.77	7.82	7.75	7.75	7.70
3a	[%]	3	4	7	9	11	14	14	15	16	15	15	15	16	16	16	16
	[mM]	0.25	0.44	0.69	0.93	1.13	1.39	1.44	1.50	1.56	1.52	1.54	1.53	1.58	1.57	1.62	1.64
4a	[%]	0	1	2	2	3	4	4	5	5	5	5	5	5	5	5	5
	[mM]	0.00	0.10	0.16	0.22	0.30	0.40	0.44	0.46	0.47	0.49	0.49	0.51	0.50	0.50	0.53	0.53
balance [%]		98	98	98	98	98	97	98	98	99	98	98	98	99	98	99	99

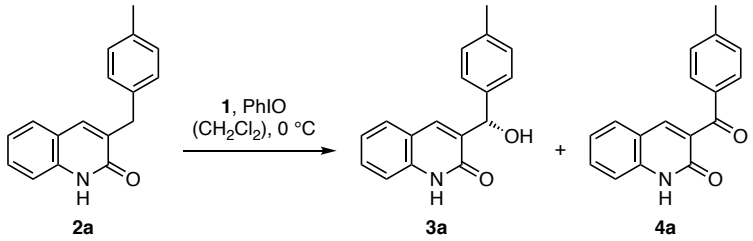
D: **1** (2× 1 mol% after *t* = 0, 60 min), **2a** (1.0 equiv), PhIO (2.0 equiv)

t [min]		3	6	9	12	15	30	45	60	63	66	69	72	75	90	105	120
2a	[%]	90	89	86	83	80	76	75	75	69	64	60	59	58	58	57	56
	[mM]	8.95	8.91	8.62	8.28	8.01	7.64	7.47	7.46	6.90	6.36	6.03	5.89	5.83	5.78	5.71	5.59
3a	[%]	2	3	6	8	10	13	13	13	17	21	22	23	23	23	24	24
	[mM]	0.16	0.31	0.59	0.80	1.00	1.28	1.26	1.32	1.70	2.05	2.21	2.27	2.29	2.31	2.41	2.43
4a	[%]	0	0	1	2	3	3	4	4	6	8	9	10	10	10	12	12
	[mM]	0.00	0.00	0.07	0.16	0.25	0.34	0.39	0.40	0.60	0.76	0.90	0.96	1.02	1.05	1.18	1.15
balance [%]		91	92	93	92	93	93	91	92	92	92	91	91	91	91	93	92

E: **1** (1 mol%), **2a** (1.0 equiv), PhIO (2× 1.0 equiv after *t* = 0, 60 min)

t [min]		3	6	9	12	15	30	45	60	63	66	69	72	75	90	105	120
2a	[%]	99	99	98	97	96	86	79	74	74	73	74	74	73	72	72	71
	[mM]	9.92	9.94	9.84	9.68	9.57	8.61	7.94	7.42	7.38	7.32	7.36	7.39	7.27	7.23	7.22	7.14
3a	[%]	0	1	2	3	4	10	15	18	18	19	18	18	19	19	19	20
	[mM]	0.00	0.10	0.17	0.30	0.37	0.96	1.46	1.79	1.82	1.85	1.84	1.82	1.87	1.89	1.94	1.99
4a	[%]	0	0	0	0	0	2	4	6	6	6	7	7	7	7	7	7
	[mM]	0.00	0.00	0.00	0.00	0.00	0.20	0.39	0.55	0.61	0.61	0.66	0.72	0.65	0.69	0.72	0.74
balance [%]		99	100	100	100	99	98	98	98	98	98	99	99	98	98	99	99

3.3 Kinetic resolution of 3-(hydroxy(*p*-tolyl)methyl)-2-quinolone (*rac*-3a)



A solution of the chiral manganese porphyrin catalyst **1** (3.0 mM in CH_2Cl_2, 200 µL, 0.60 µmol, 1.0 mol%) was added to a suspension of *rac*-**3a** (15.9 mg, 60 µmol, 1.0 equiv), ^{n}dodecane (13.6 µL, 60.0 µmol, 1.0 equiv) and PhIO (13.2 mg, 60.0 µmol, 1.0 equiv) in CH_2Cl_2 (5.8 mL) whereupon the reaction was initiated. At the indicated times, aliquots of 100 µL were transferred to a GLC vial containing CH_2Cl_2 (700 µL) and a 10% aqueous $Na_2S_2O_3$ solution (500 µL) affording a biphasic mixture. After vigorous mixing for approximately 30 sec the organic layer was separated *via* syringe filtration and submitted to GLC and HPLC analysis.

3.3.1 Numerical data (Figure 4)

t [min]		0	5	10	15	20	25	30	35	40	45
3a	[%]	44	43	43	41	39	37	35	33	32	32
	[mM]	4.38	4.31	4.30	4.12	3.92	3.66	3.50	3.31	3.22	3.18
	% ee	3	6	11	20	28	41	51	64	66	71
ent-***3a***	[%]	41	38	35	28	22	16	11	7	7	6
	[mM]	4.09	3.81	3.47	2.77	2.21	1.55	1.12	0.73	0.65	0.55
4a	[%]	8	12	18	26	34	43	50	56	58	59
	[mM]	0.75	1.23	1.79	2.60	3.44	4.33	4.96	5.57	5.77	5.89

3.3.2 Determination of the selectivity (s factor)

The selectivity factor *s* is defined by the ratio of the rate constant of the favoured (*ent*-**3a** = (*R*)-**3a**) over the unfavoured enantiomer (**3a** = (*S*)-**3a**):

(1) $$s = \frac{k_R}{k_S}$$

For a reaction that follows first order kinetics the following kinetic equations can be derived

(2) $$\frac{d[(R)\text{-}\mathbf{3a}]}{dt} = -k_R \times [(R)\text{-}\mathbf{3a}] \times f(x) \quad \text{and} \quad \frac{d[(S)\text{-}\mathbf{3a}]}{dt} = -k_S \times [(S)\text{-}\mathbf{3a}] \times f(x)$$

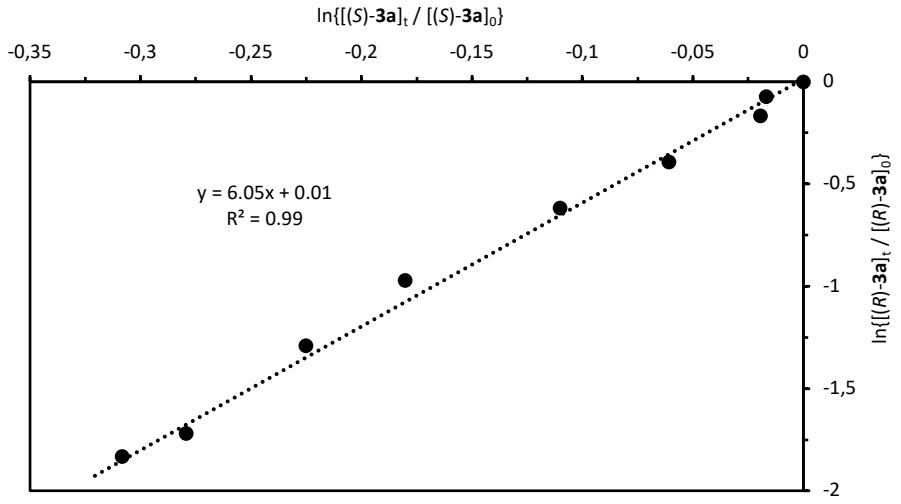
whereas *f*(x) is the function of all other concentrations independent of (*R*)-**3a** and (*S*)- **3a**. Resolving equation (2) into k_R and k_S respectively and inserting the term of k_R and k_S into equation (1) results in the following expression:

(3) $$S = \frac{\frac{d[(R)\text{-}\mathbf{3a}]}{[(R)\text{-}\mathbf{3a}]} \times \frac{1}{dt \times f(X)}}{\frac{d[(S)\text{-}\mathbf{3a}]}{[(S)\text{-}\mathbf{3a}]} \times \frac{1}{dt \times f(X)}} = \frac{\frac{d[(R)\text{-}\mathbf{3a}]}{[(R)\text{-}\mathbf{3a}]}}{\frac{d[(S)\text{-}\mathbf{3a}]}{[(S)\text{-}\mathbf{3a}]}}$$

After reducing and integration equation (4) is obtained

(4) $$ln\left(\frac{[(R)\text{-}\mathbf{3a}]_t}{[(R)\text{-}\mathbf{3a}]_0}\right) = S \times ln\left(\frac{[(S)\text{-}\mathbf{3a}]_t}{[(S)\text{-}\mathbf{3a}]_0}\right)$$

Plotting $ln\frac{[(R)\text{-}\mathbf{3a}]_t}{[(R)\text{-}\mathbf{3a}]_0}$ against $ln\frac{[(S)\text{-}\mathbf{3a}]_t}{[(S)\text{-}\mathbf{3a}]_0}$ gives a linear function where the value of the *s* factor is equal to the slope of the line of best fit.



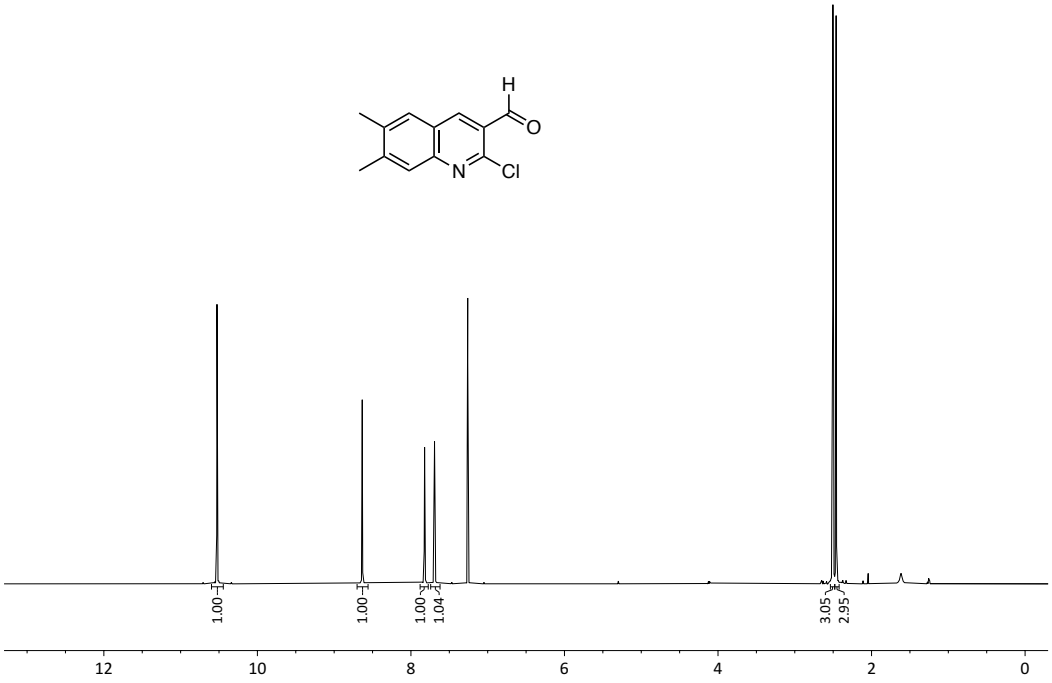
III. Analytical Data

1 ^{1}H and ^{13}C spectra of new compounds

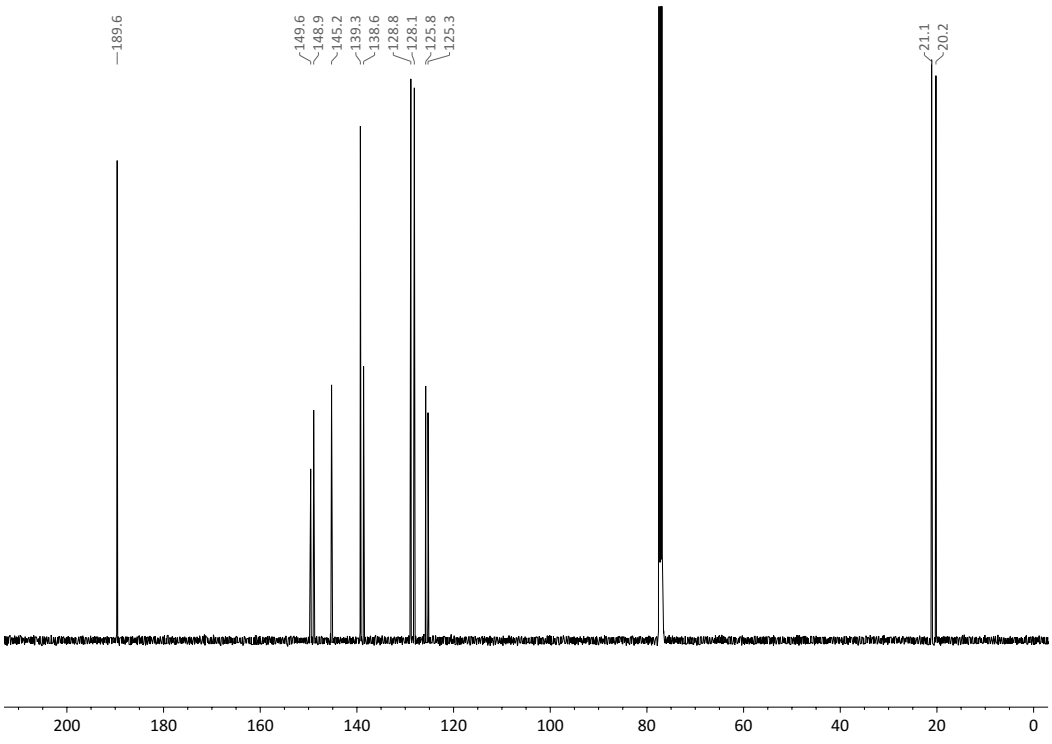
1.1 2-Chloroquinoline-3-carbaldehydes S2

*1.1.1 2-Chloro-6,7-dimethylquinoline-3-carbaldehyde (**S2h**)*

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

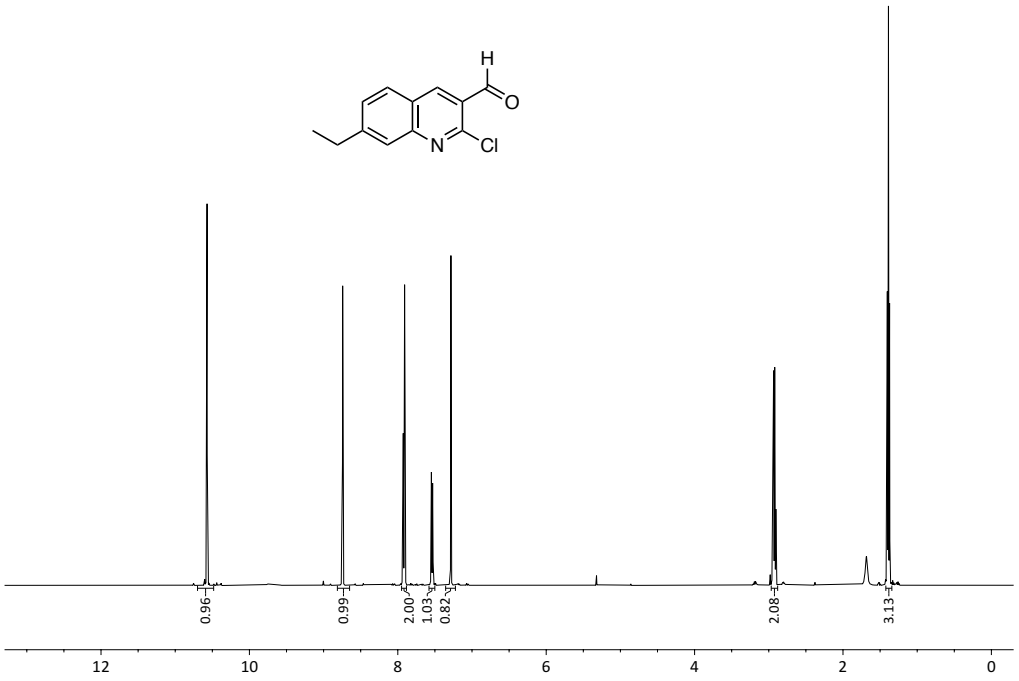


^{13}C NMR (126 MHz, $CDCl_3$)

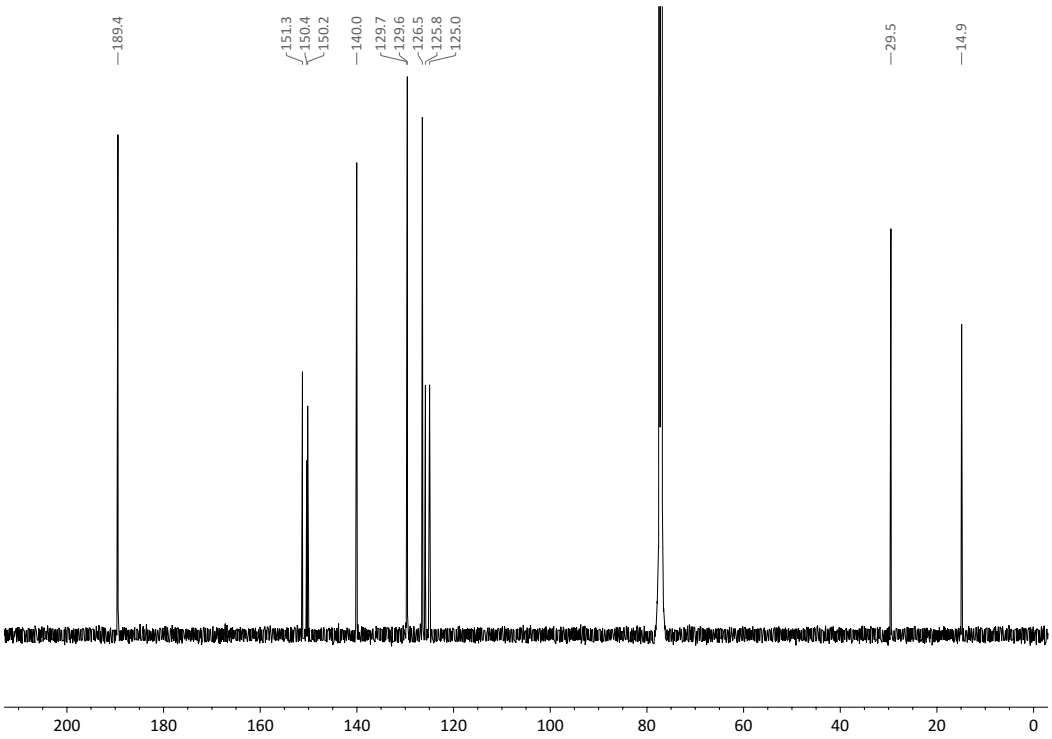


*1.1.2 2-Chloro-7-ethylquinoline-3-carbaldehyde (**S2m**)*

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



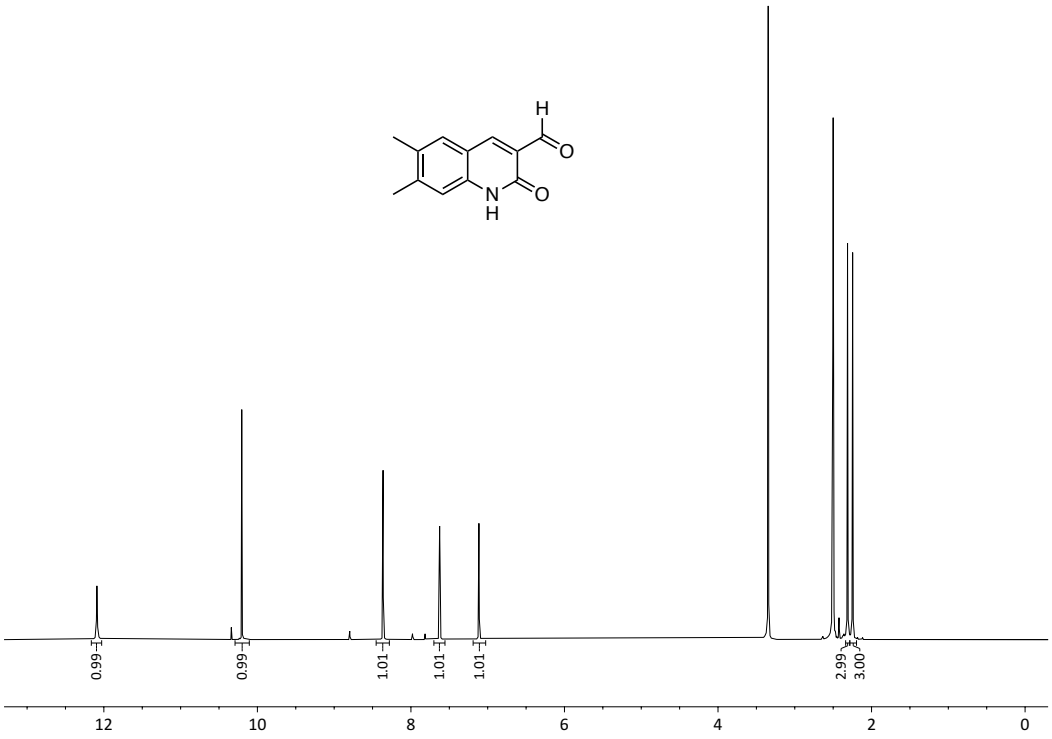
^{13}C NMR (126 MHz, $CDCl_3$)



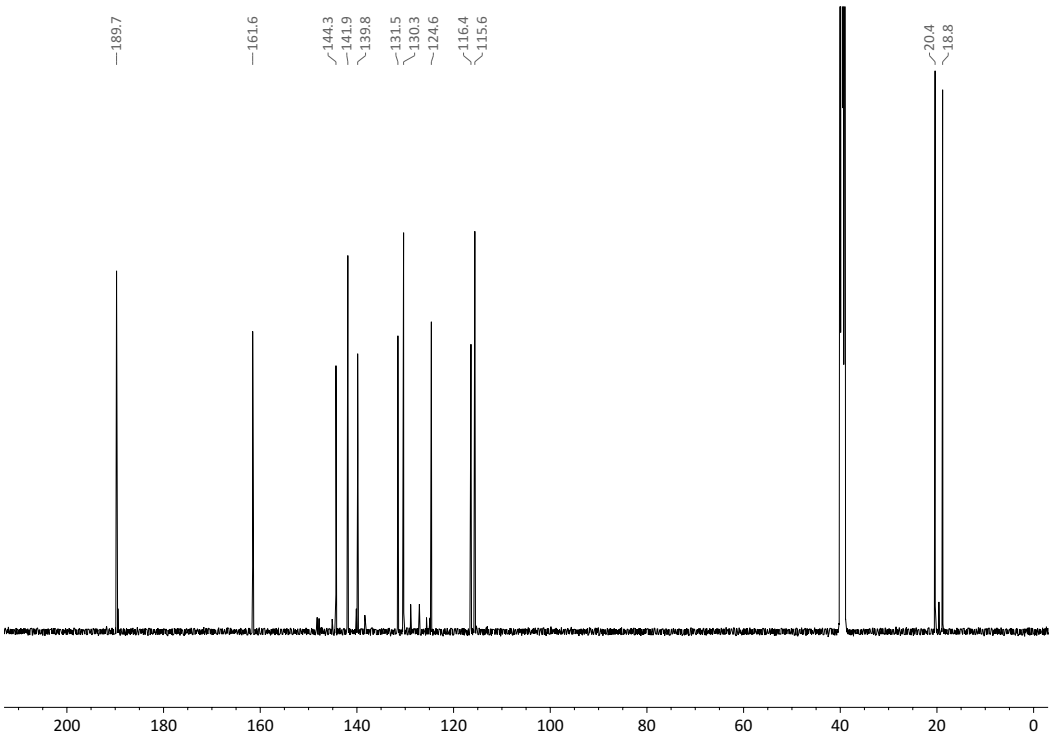
1.2 2-Quinolone-3-carbaldehydes S3

*1.2.1 6,7-Dimethyl-2-quinolone-3-carbaldehyde (**S3h**)*

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

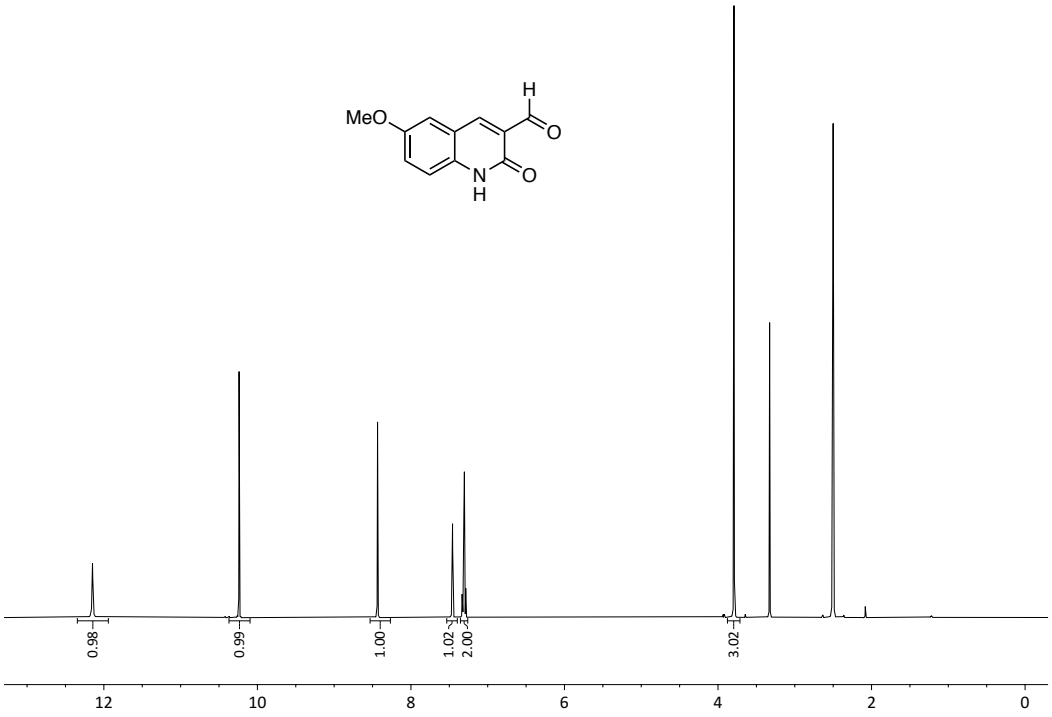


^{13}C NMR (126 MHz, DMSO-d_6)

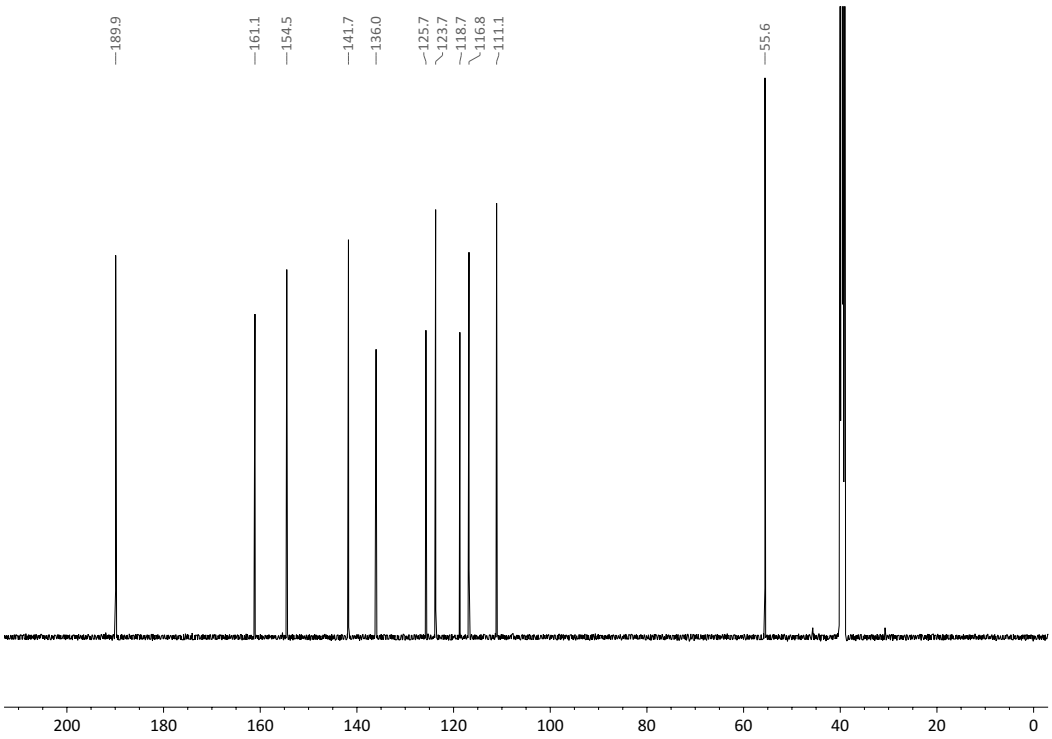


*1.2.2 6-Methoxy-2-quinolone-3-carbaldehyde (**S3i**)*

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

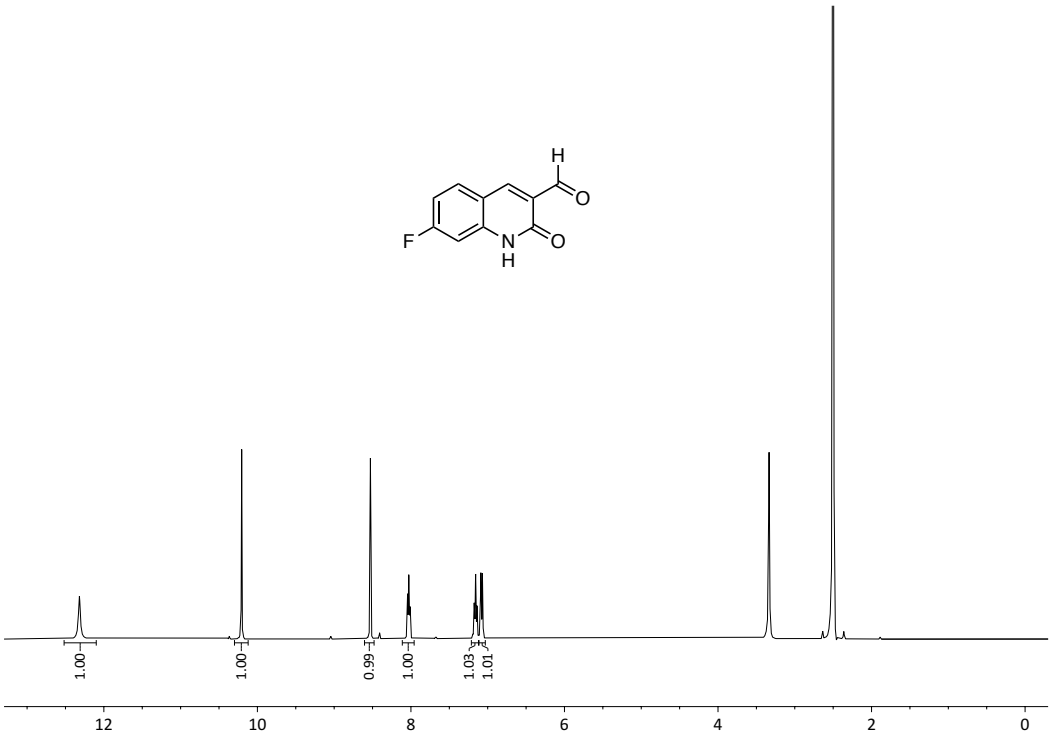


^{13}C NMR (126 MHz, DMSO-d_6)

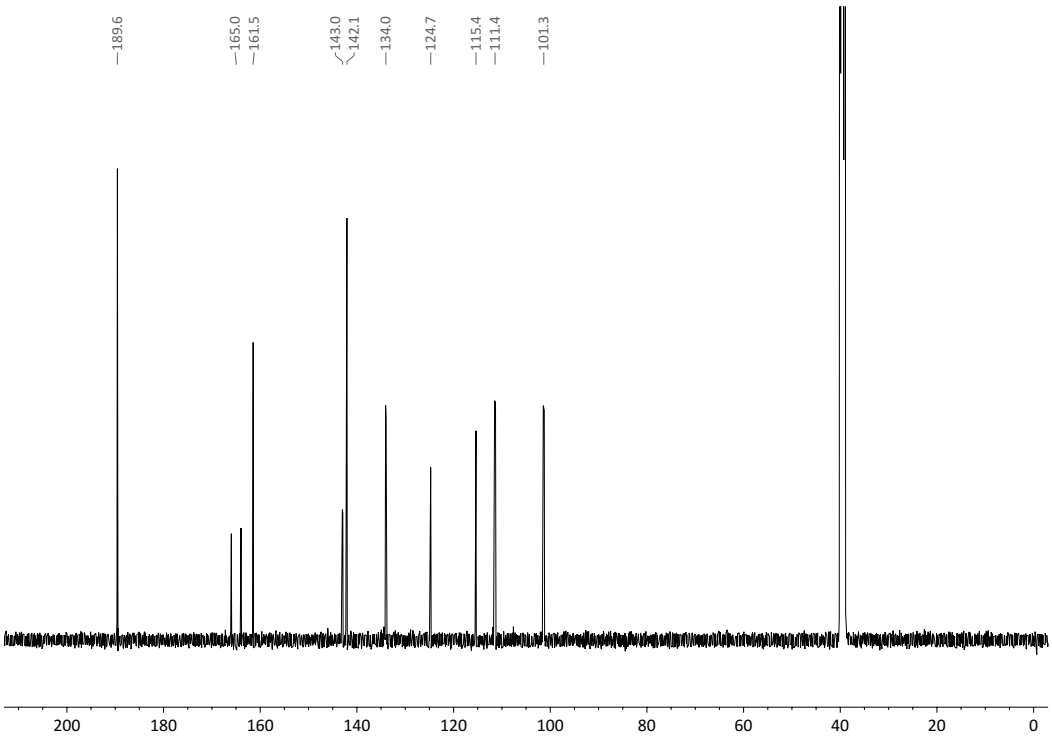


*1.2.3 7-Fluoro-2-quinolone-3-carbaldehyde (**S3l**)*

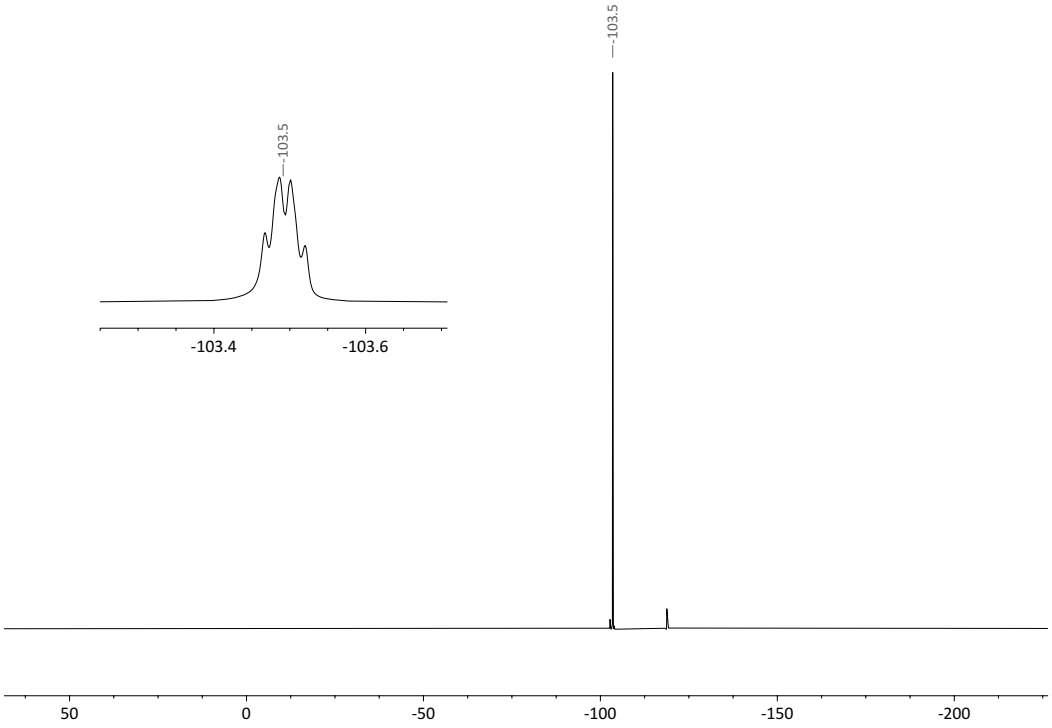
^{1}H NMR (500 MHz, DMSO-d_6)



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

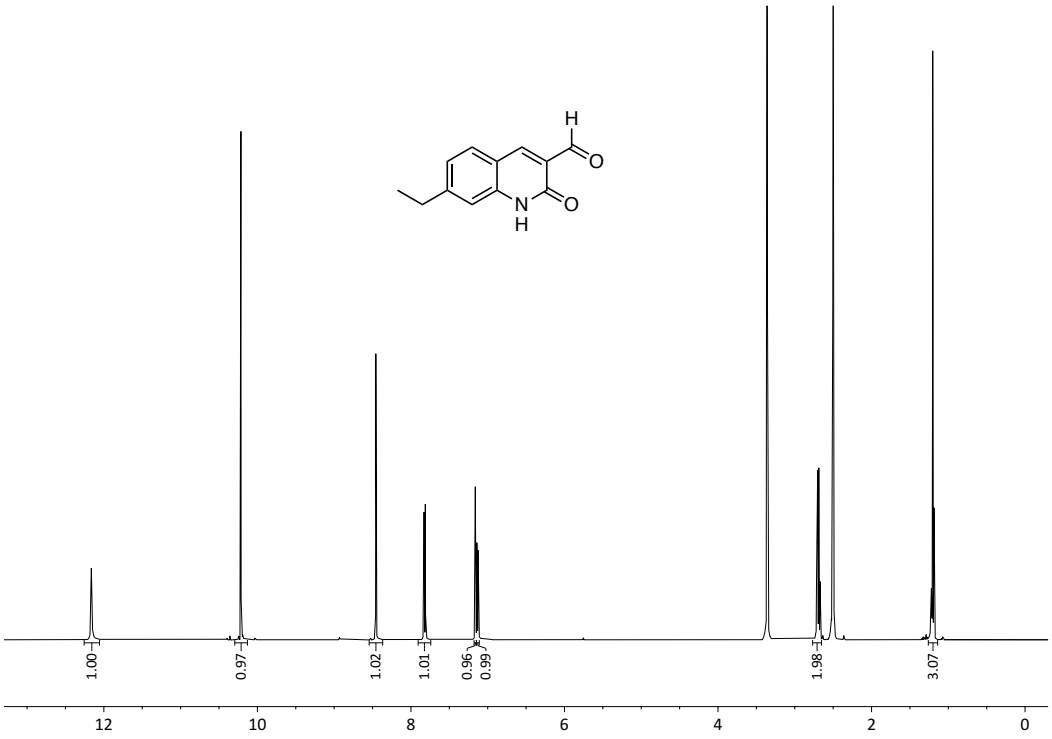


^{19}F NMR (471 MHz, DMSO-d_6)

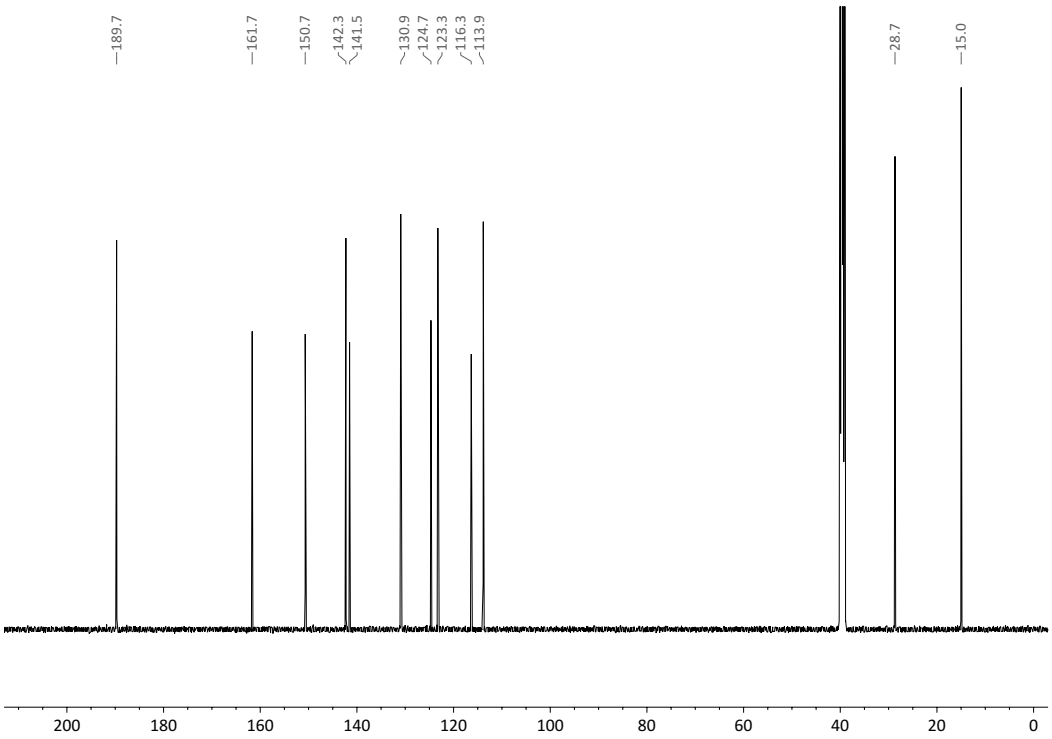


*1.2.4 7-Ethyl-2-quinolone-3-carbaldehyde (**S3m**)*

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



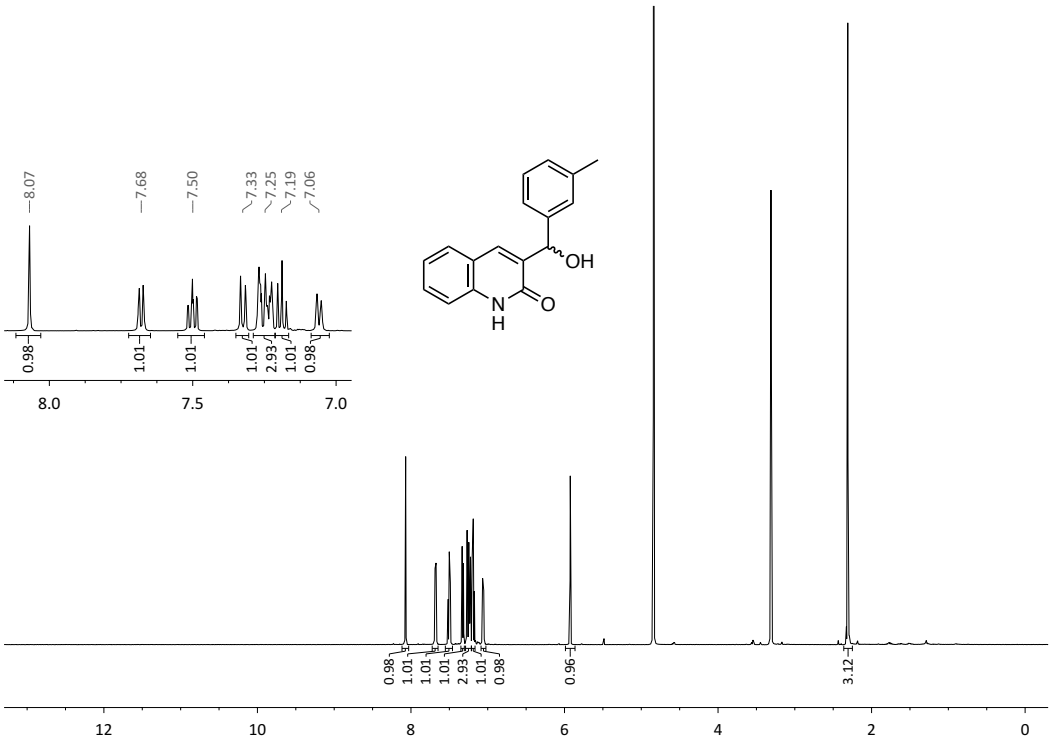
^{13}C NMR (126 MHz, DMSO-d_6)



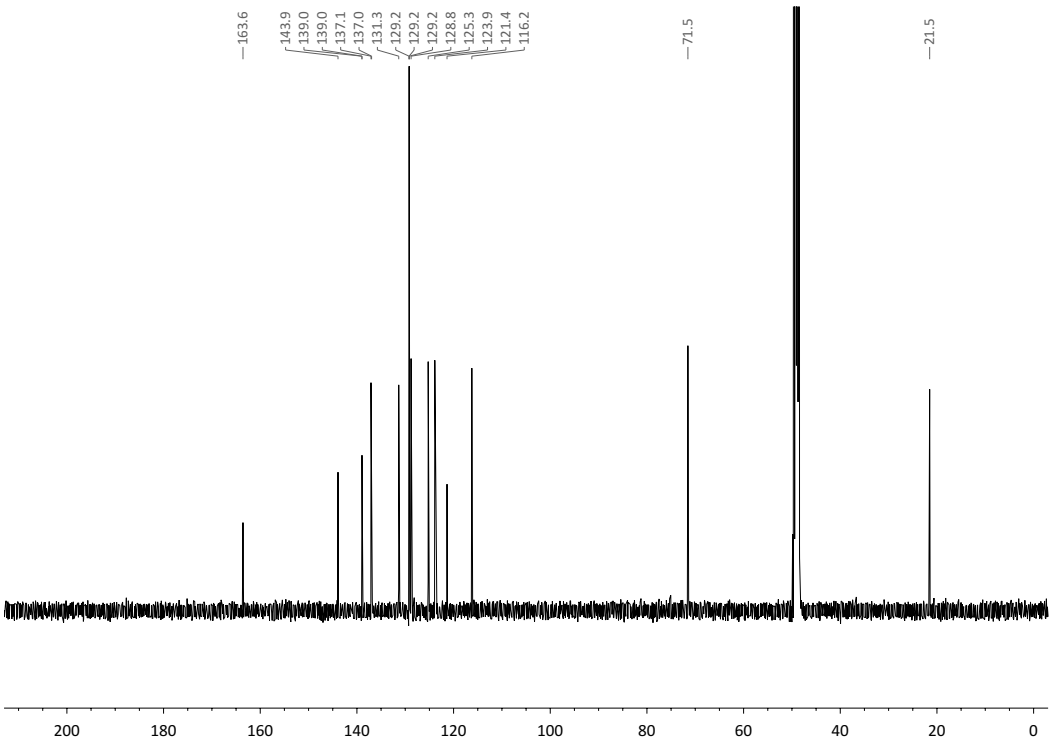
1.3 3-(Hydroxy(aryl)methyl)-2-quinolones 3

*1.3.1 3-(Hydroxy(m-tolyl)methyl)-2-quinolone (**3b**)*

^{1}H NMR (500 MHz, MeOD-d_4)

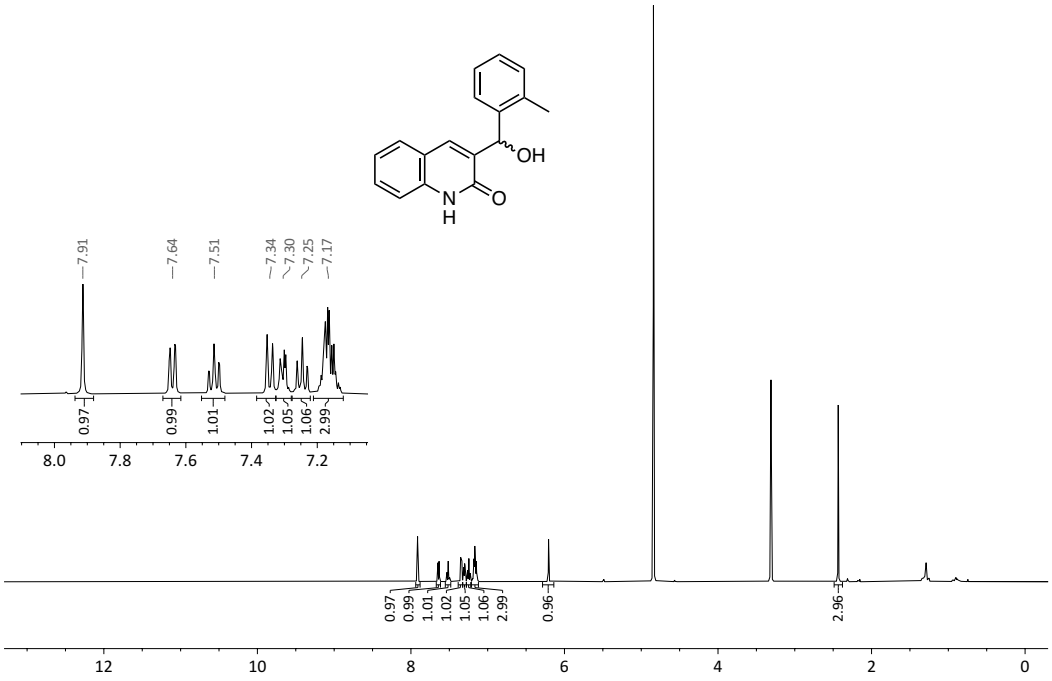


^{13}*C NMR (126 MHz, MeOD-d_4)*

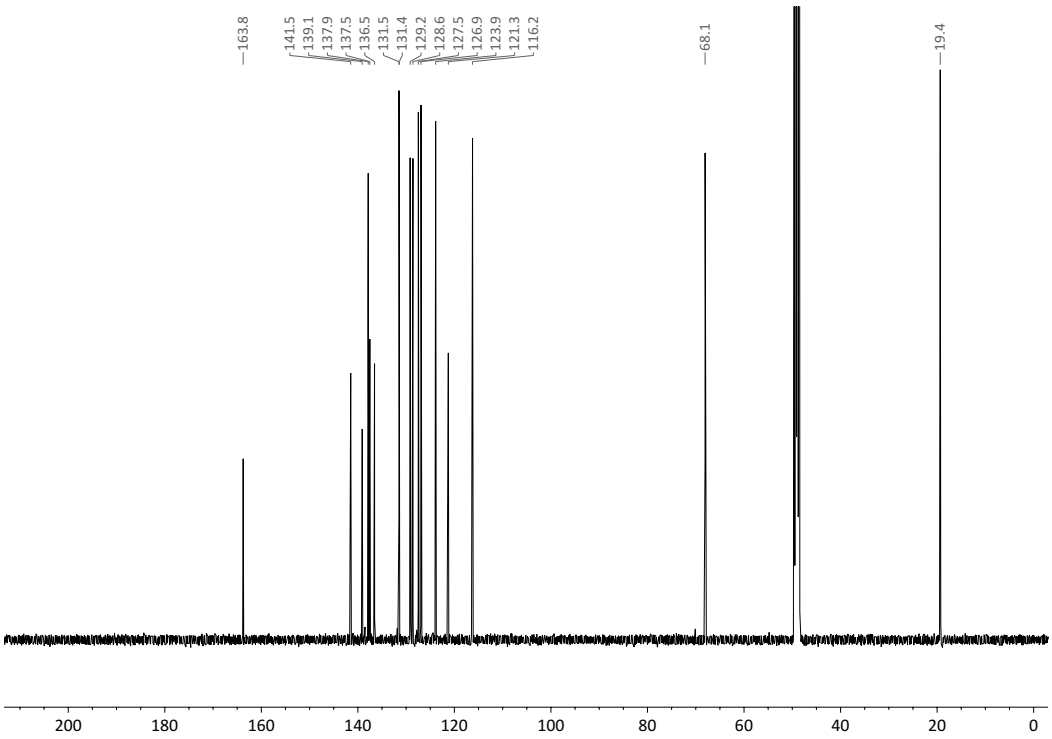


*1.3.2 3-(Hydroxy(o-tolyl)methyl)-2-quinolone (**3c**)*

^{1}H NMR (500 MHz, MeOD-d_4)

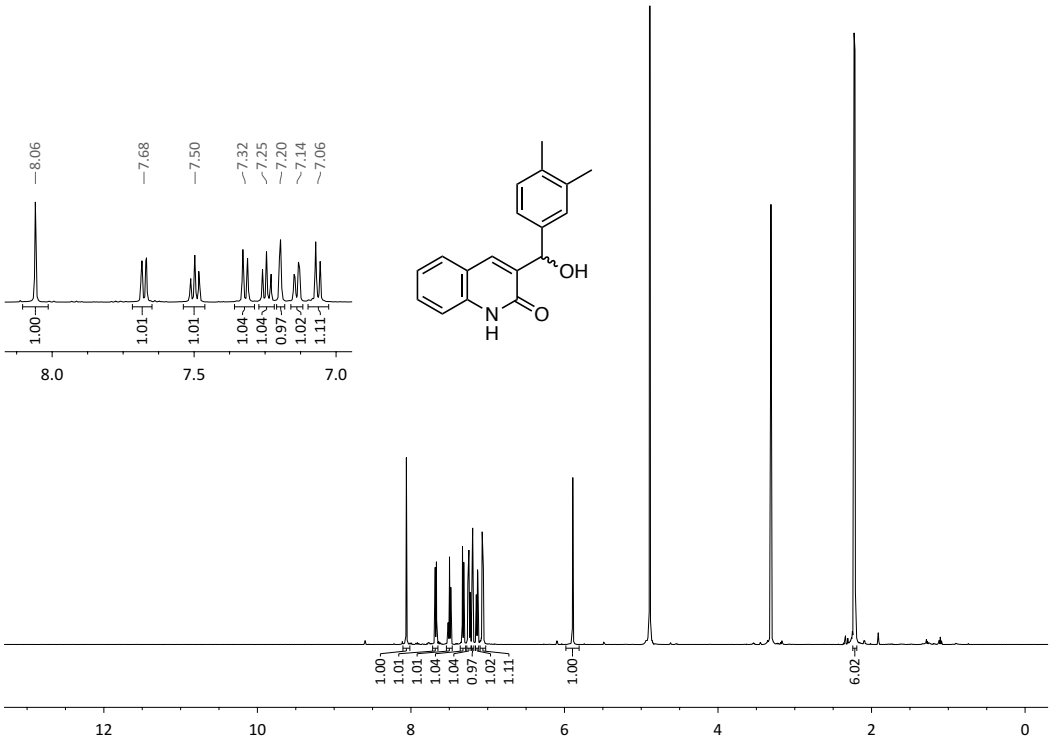


^{13}C NMR (126 MHz, MeOD-d_4)

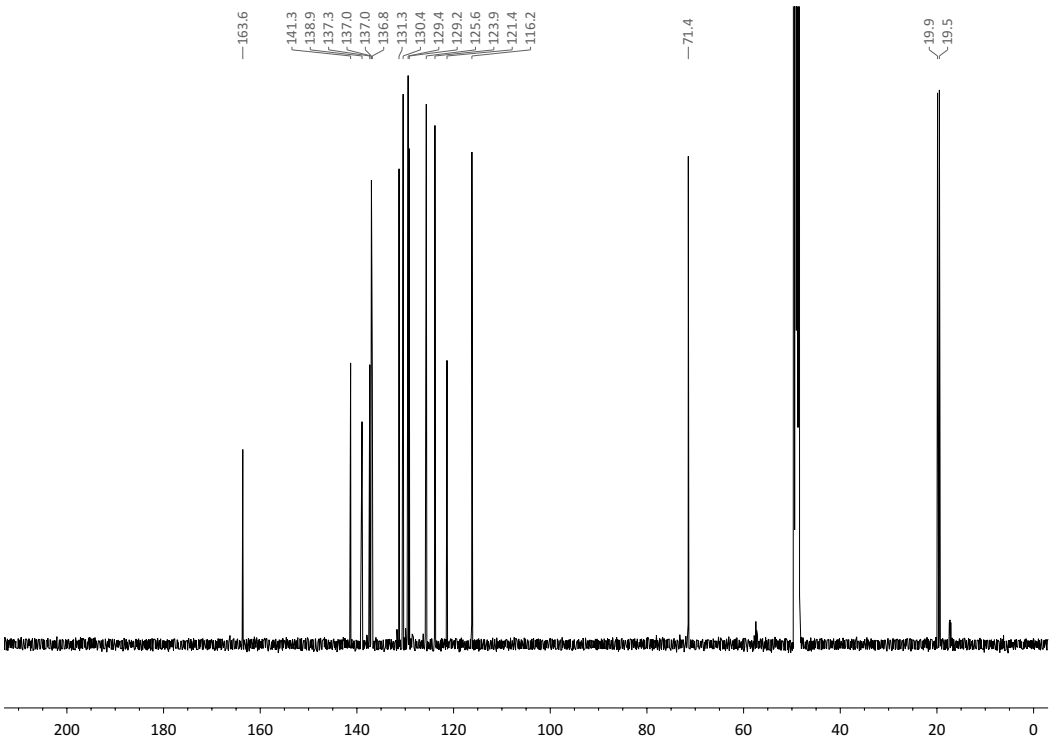


*1.3.3 3-((3,4-Dimethylphenyl)(hydroxy)methyl)-2-quinolone (**3d**)*

^{1}H NMR (500 MHz, MeOD-d_4)

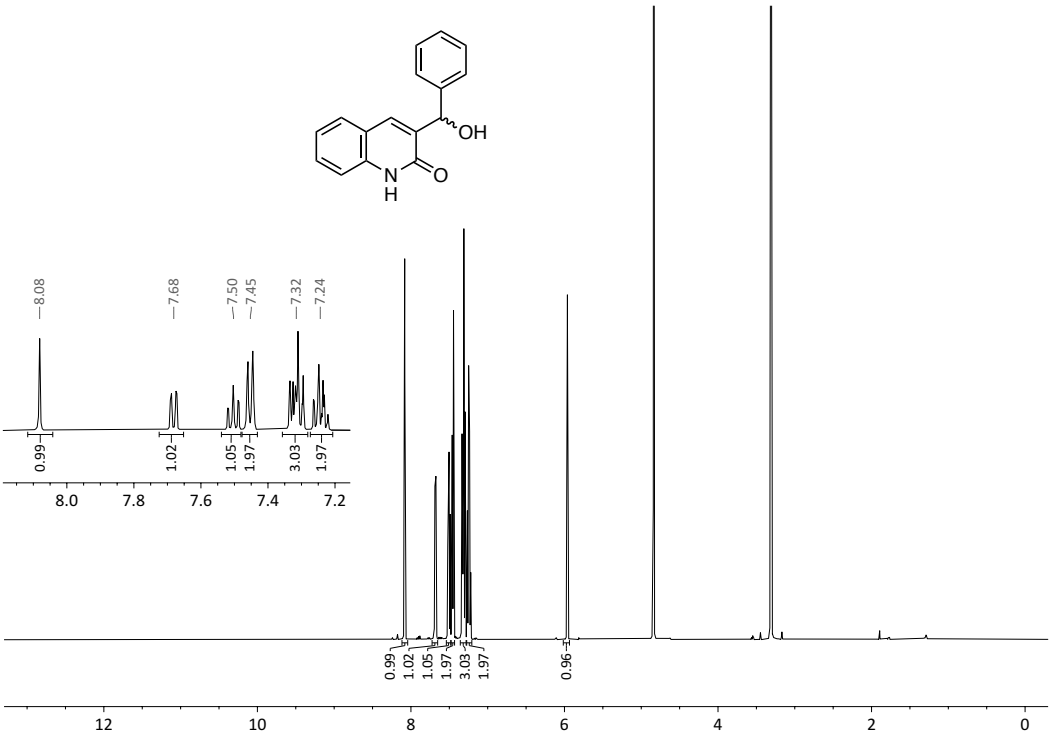


^{13}C NMR (126 MHz, MeOD-d_4)

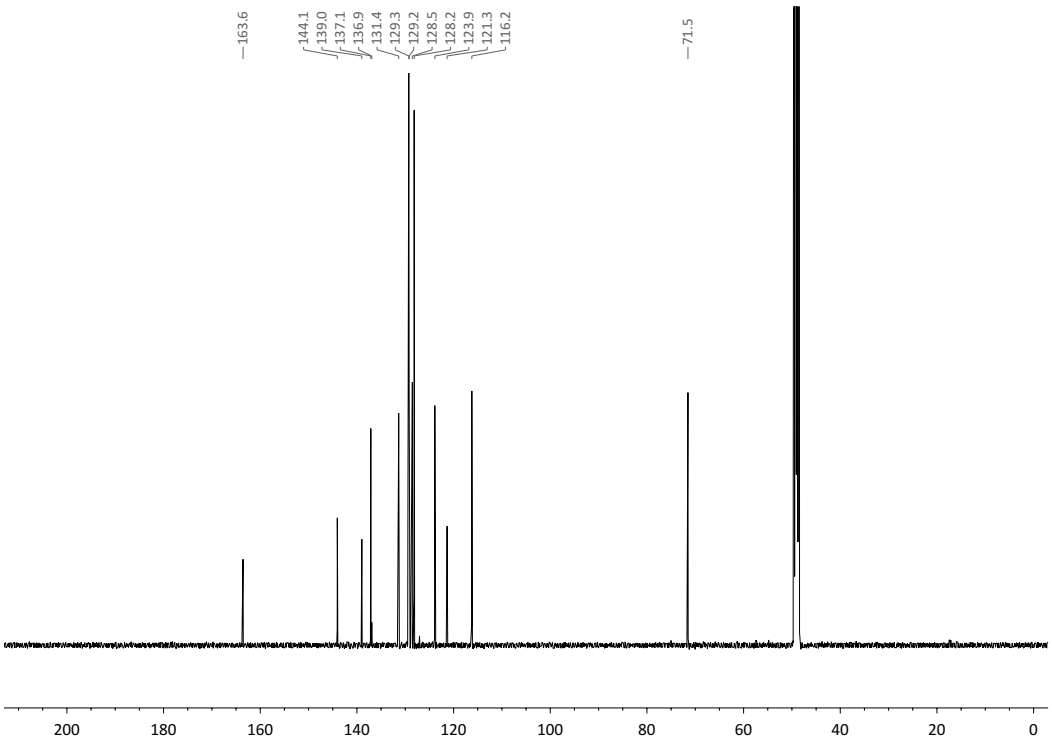


*1.3.4 3-(Hydroxy(phenyl)methyl)-2-quinolone (**3e**)*

^{1}H NMR (500 MHz, MeOD-d_4)

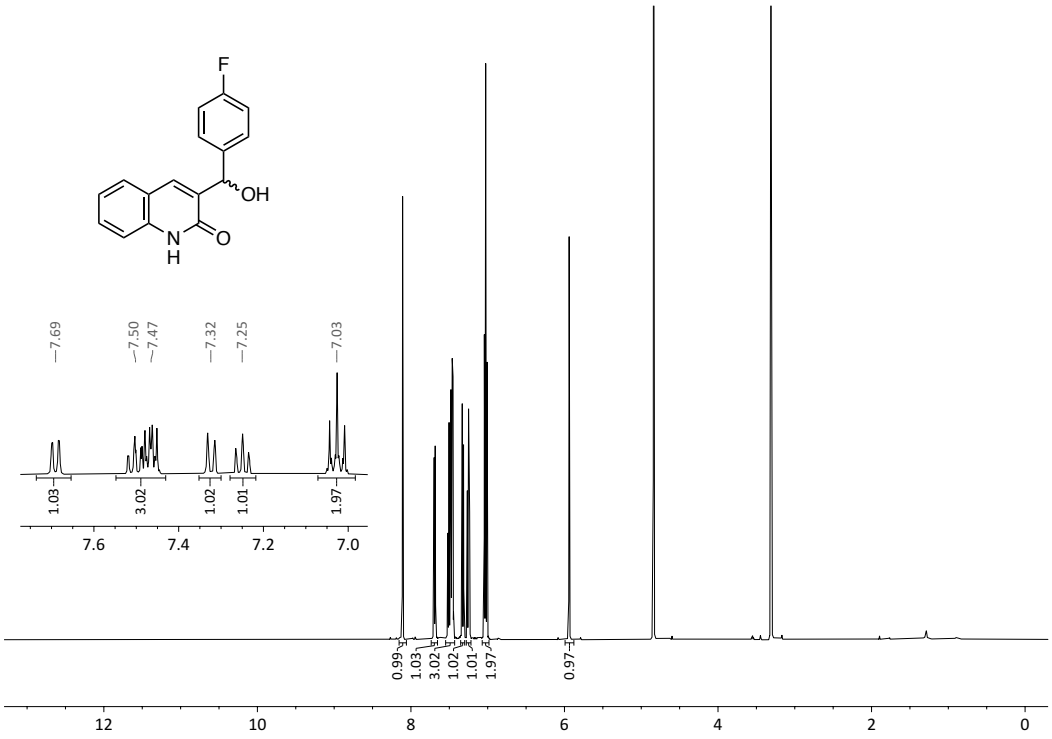


^{13}C NMR (126 MHz, MeOD-d_4)

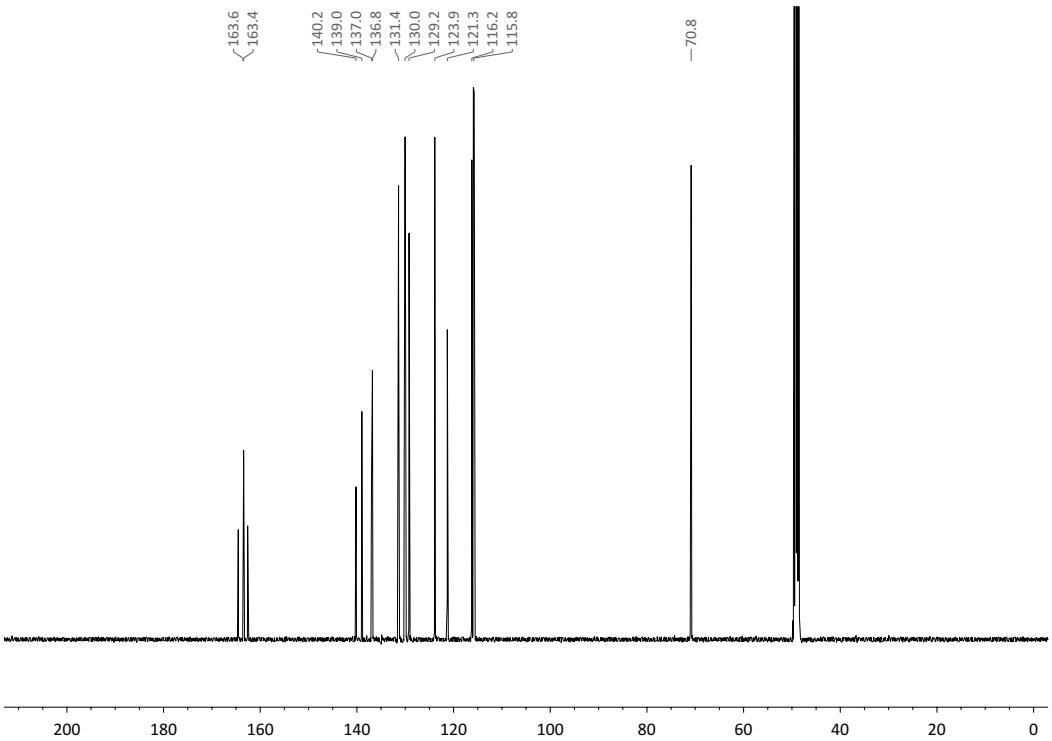


*1.3.5 3-((4-Fluorophenyl)(hydroxy)methyl)-2-quinolone (**3g**)*

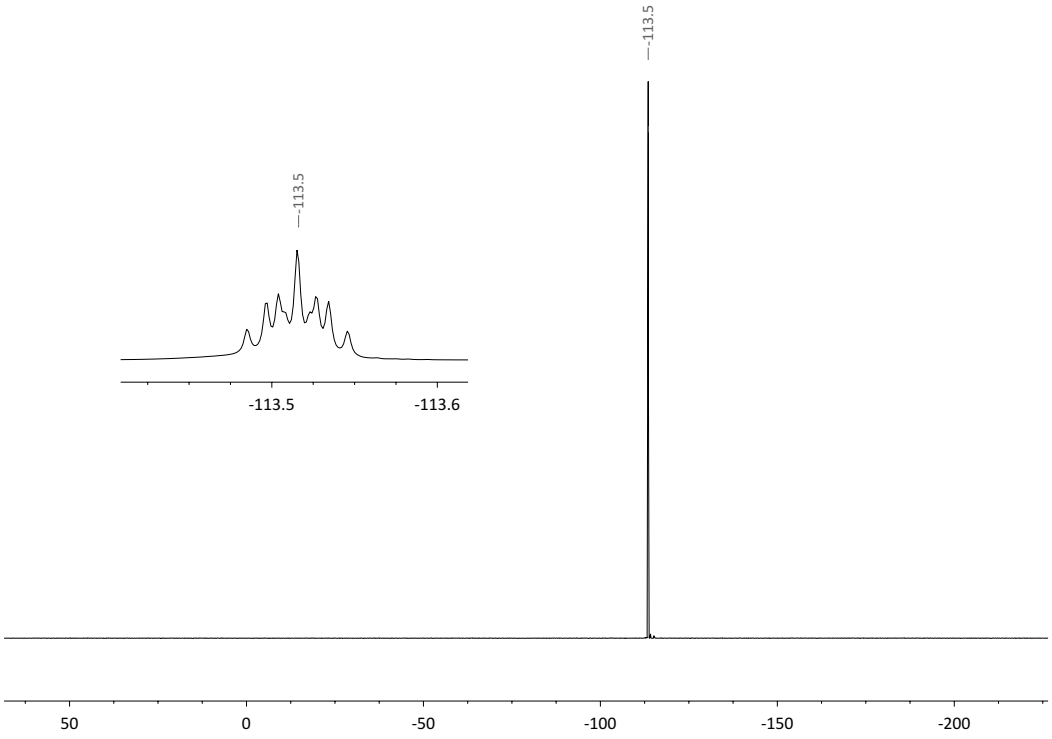
^{1}H NMR (500 MHz, MeOD-d_4)



^{13}C NMR (126 MHz, MeOD-d_4)

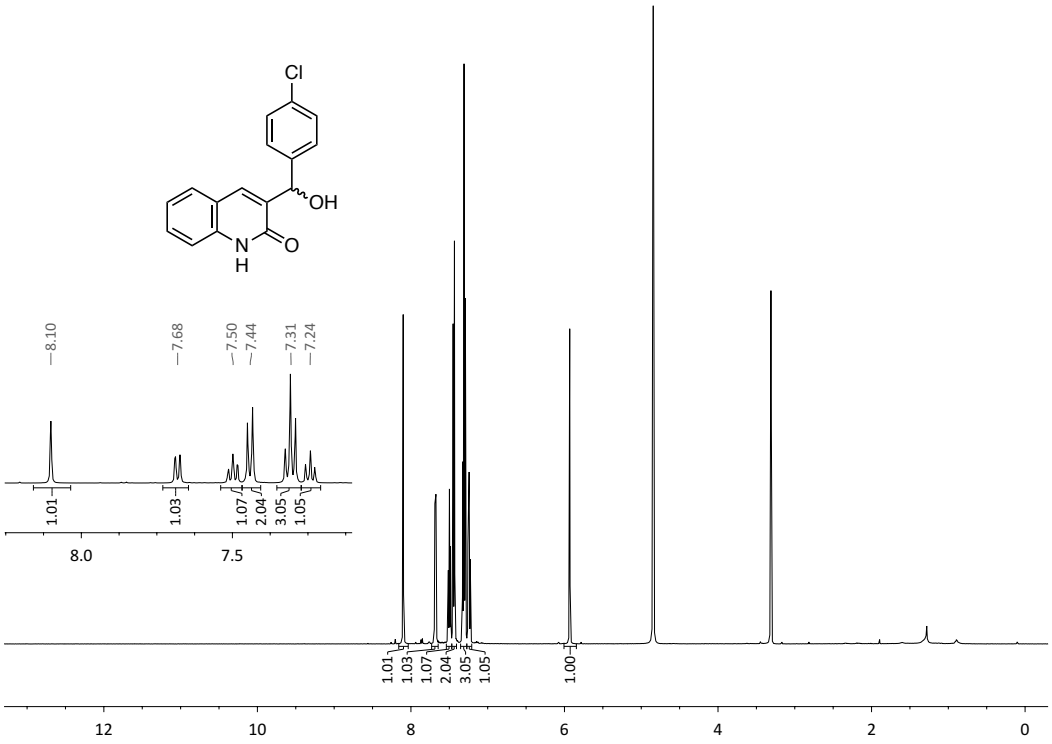


^{19}F NMR (471 MHz, MeOD-d_4)

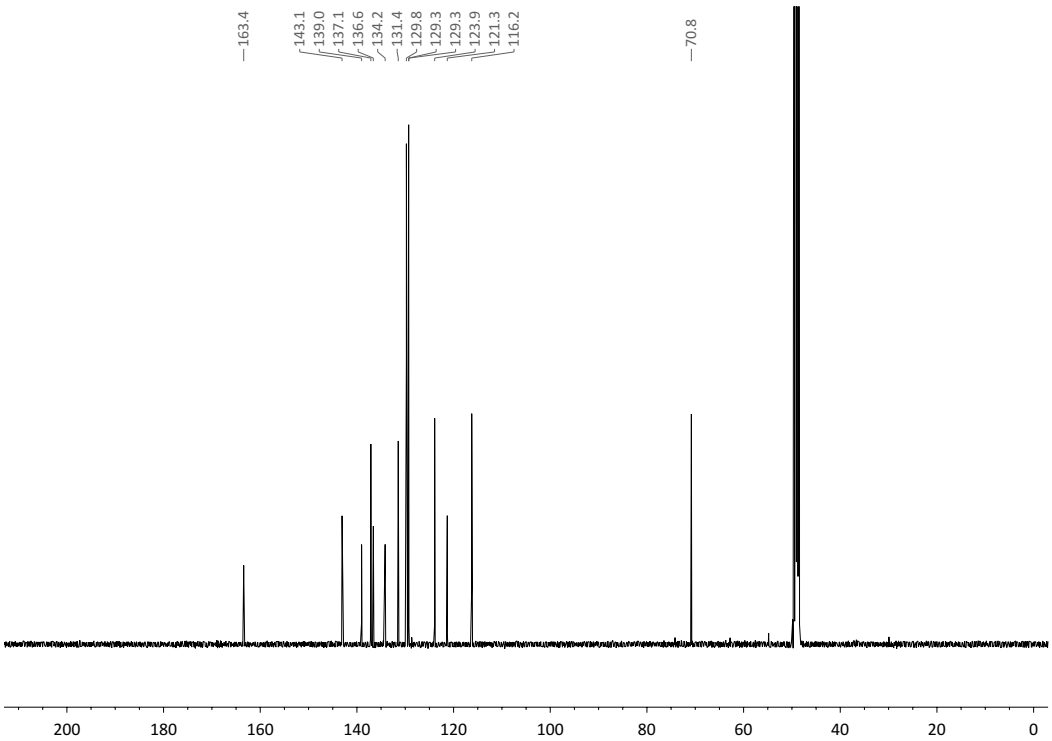


*1.3.6 3-((4-Chlorophenyl)(hydroxy)methyl)-2-quinolone (**3h**)*

^{1}H NMR (500 MHz, MeOD-d_4)

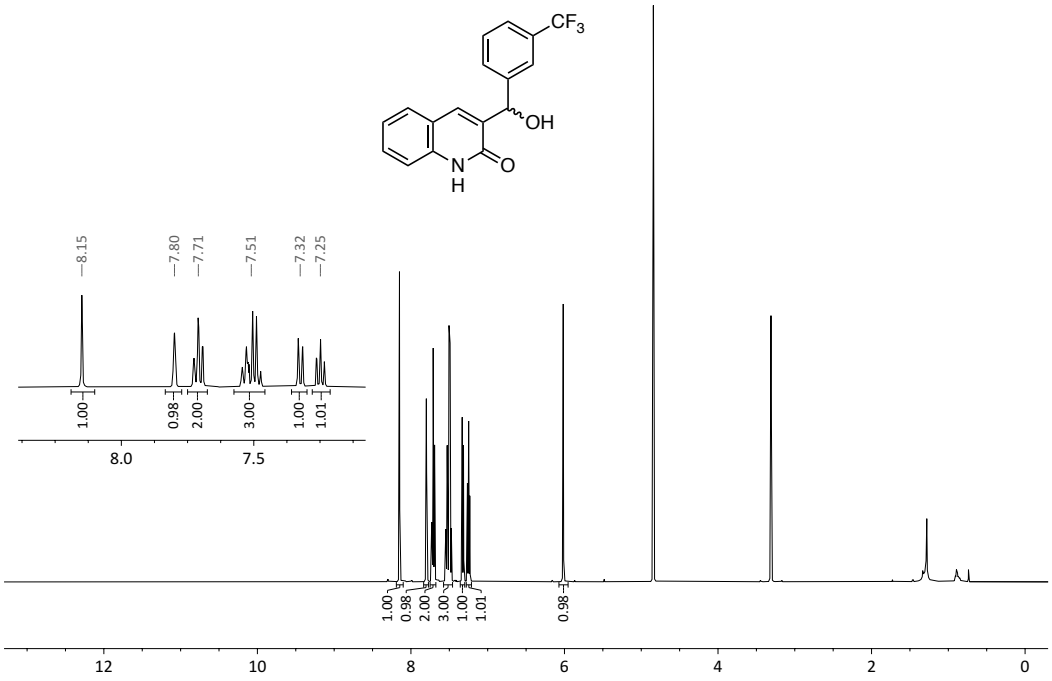


^{13}C NMR (126 MHz, MeOD-d_4)

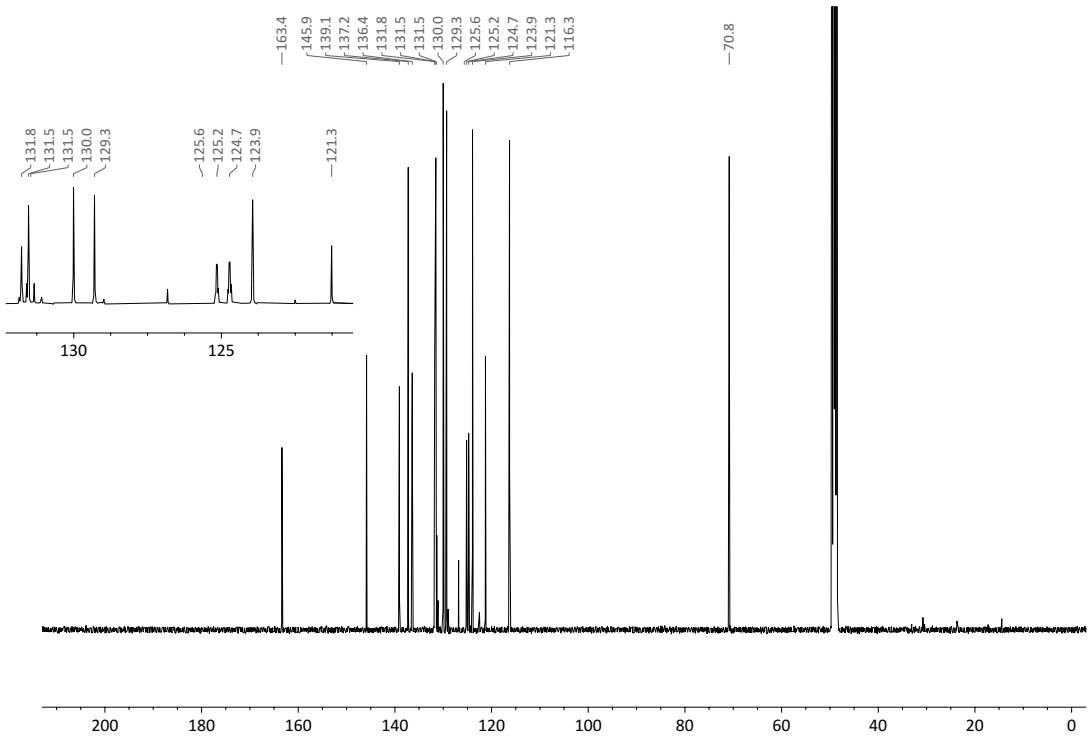


*1.3.7 3-(Hydroxy(3-(trifluoromethyl)phenyl)methyl)-2-quinolone (**3i**)*

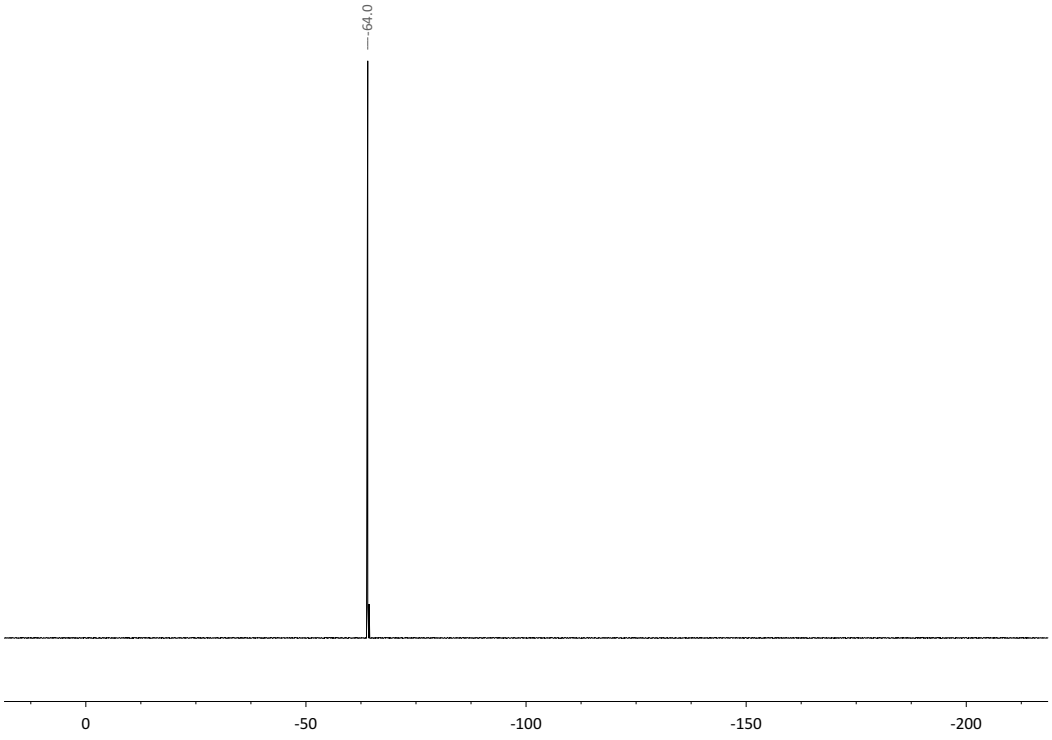
^{1}H NMR (500 MHz, MeOD-d_4)



^{13}C NMR (126 MHz, MeOD-d_4)

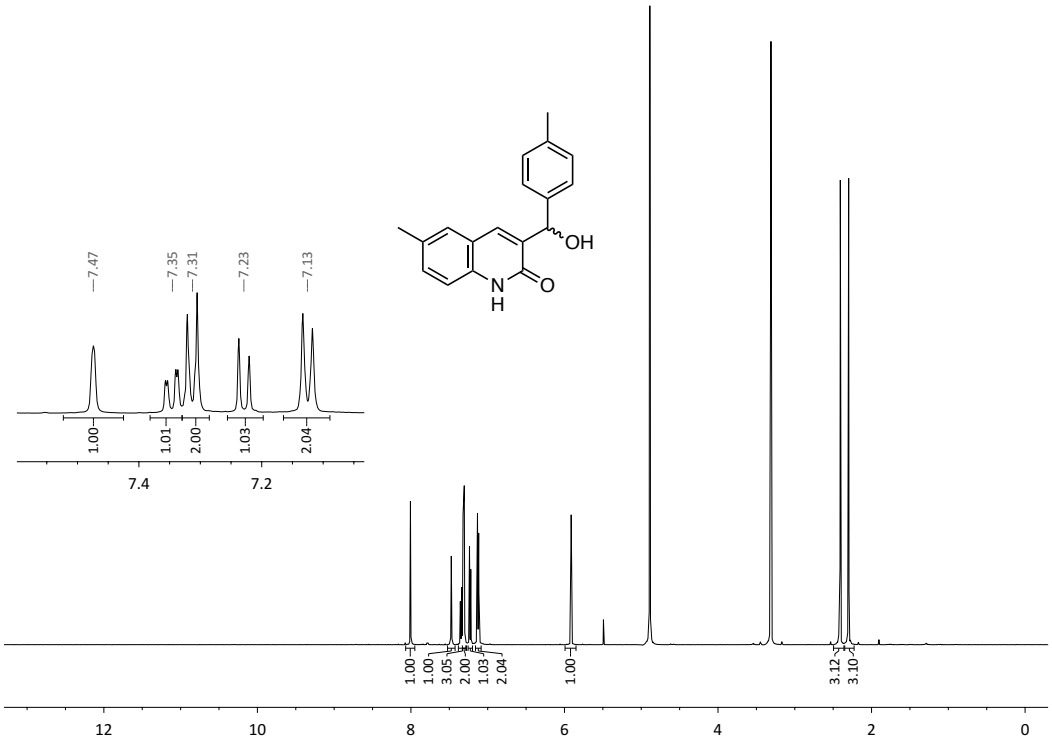


^{19}F NMR (376 MHz, MeOD-d_4)

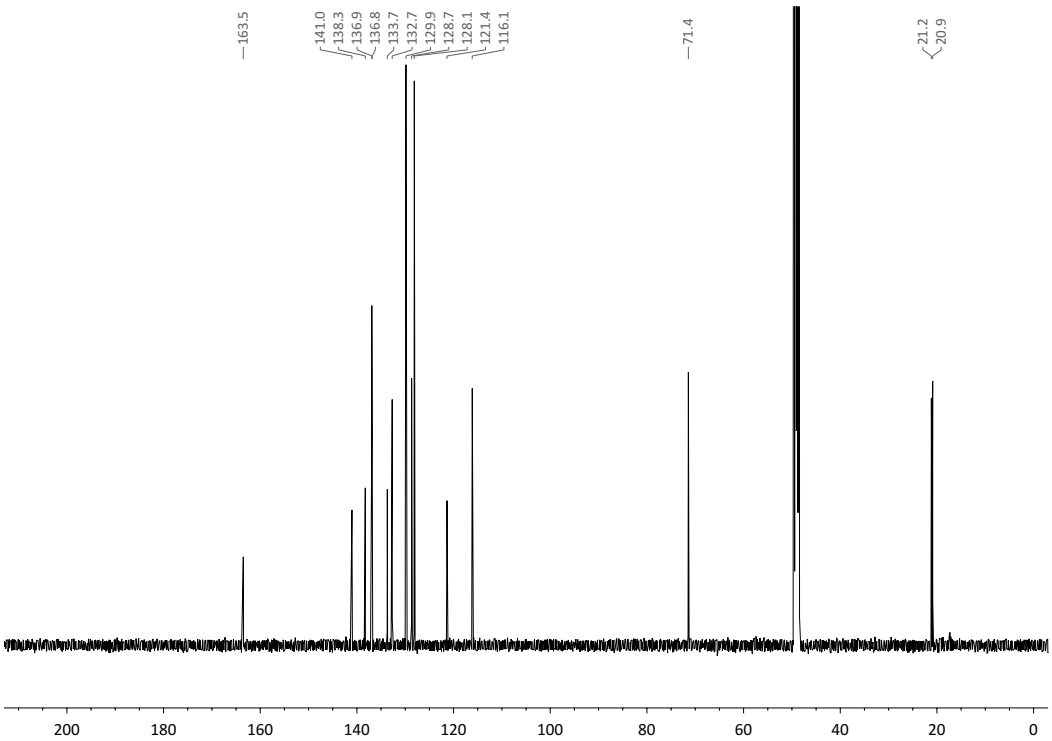


*1.3.8 3-(Hydroxy(p-tolyl)methyl)-6-methyl-2-quinolinone (**3j**)*

^{1}H NMR (500 MHz, MeOD-d_4)

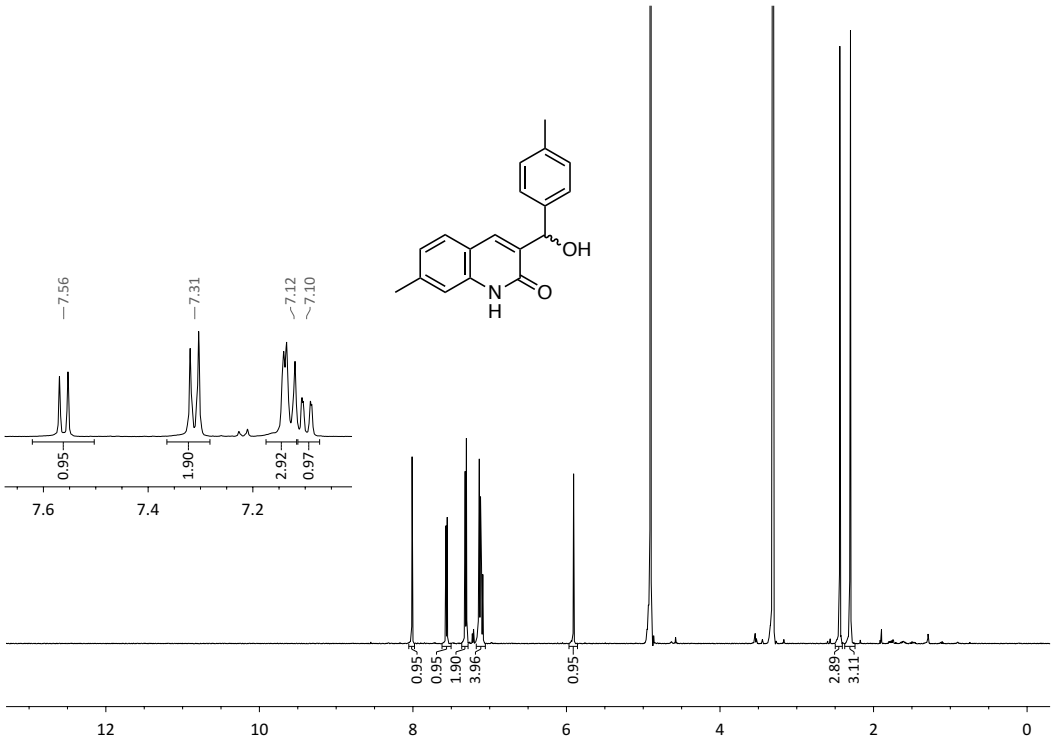


^{13}C NMR (126 MHz, MeOD-d_4)

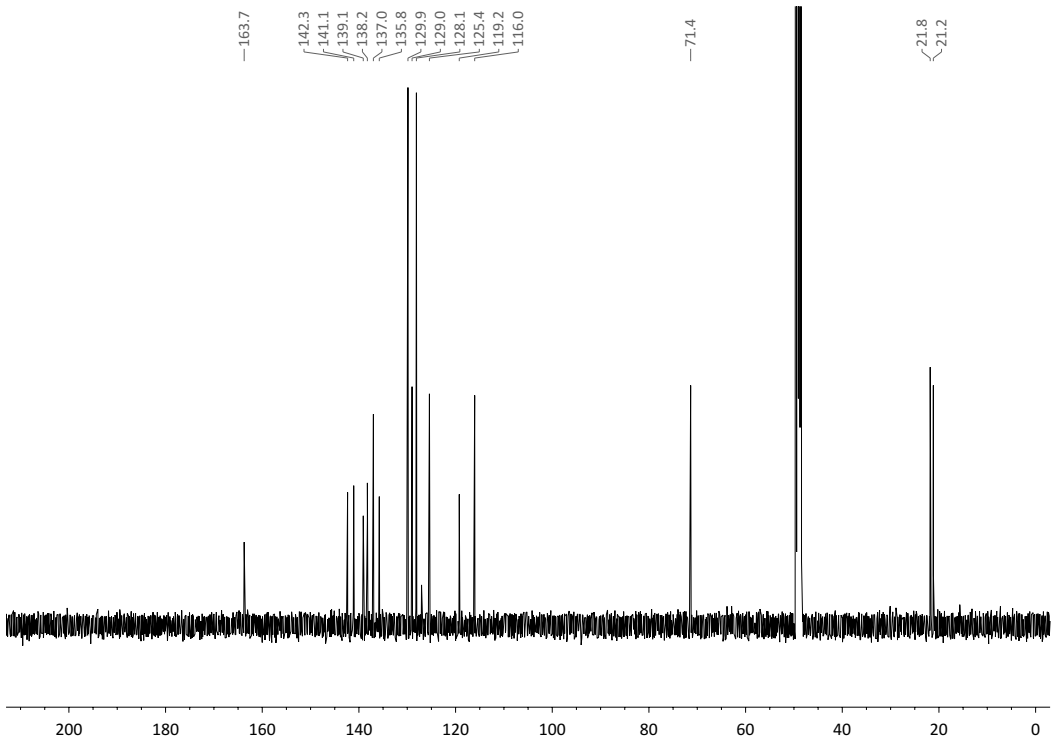


*1.3.9 3-(Hydroxy(p-tolyl)methyl)-7-methyl-2-quinolinone (**3k**)*

^{1}H NMR (500 MHz, MeOD-d_4)

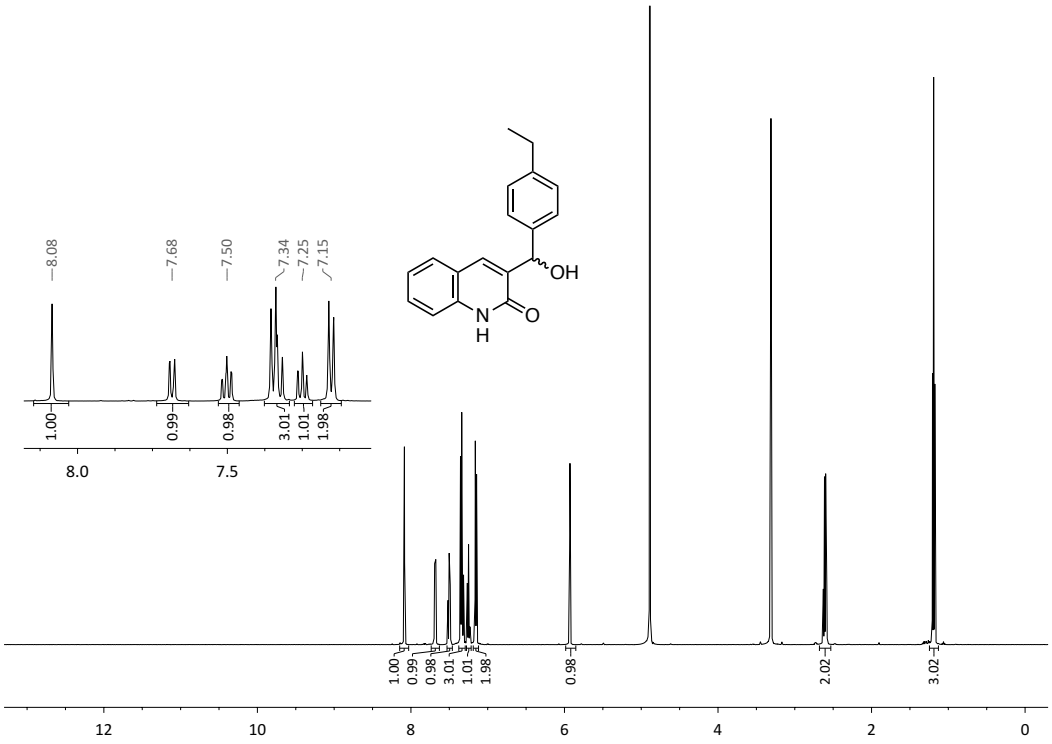


^{13}C NMR (126 MHz, MeOD-d_4)

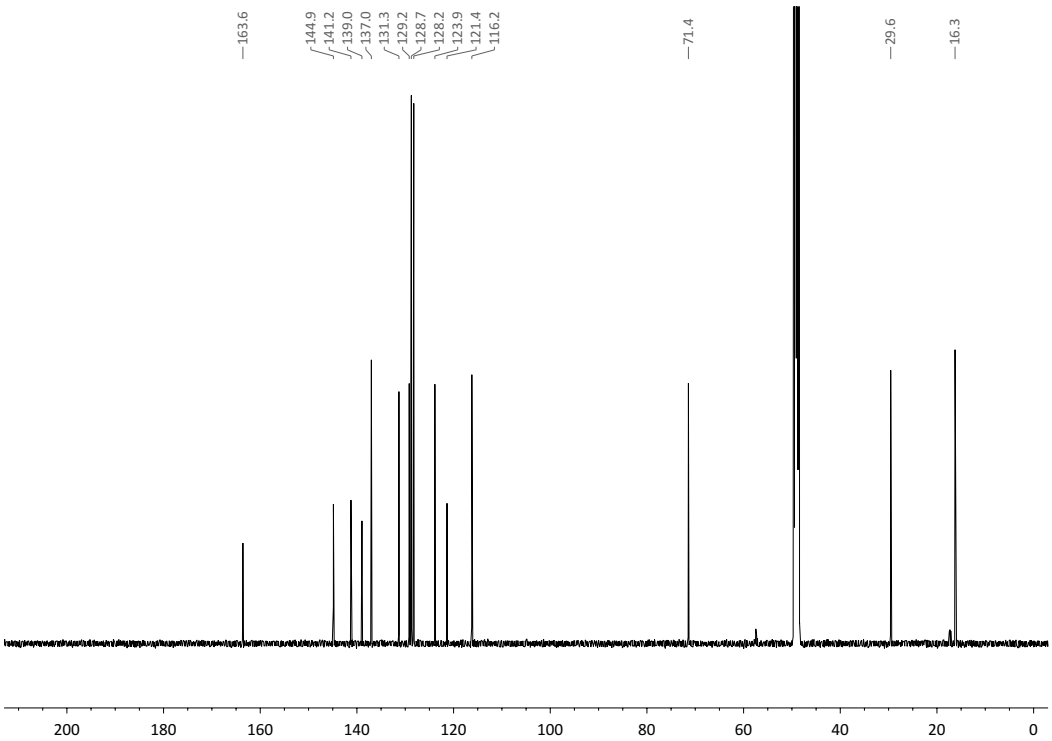


*1.3.10 3-(Hydroxy(4-ethylphenyl)methyl)-2-quinolone (**3l**)*

^{1}H NMR (500 MHz, MeOD-d_4)

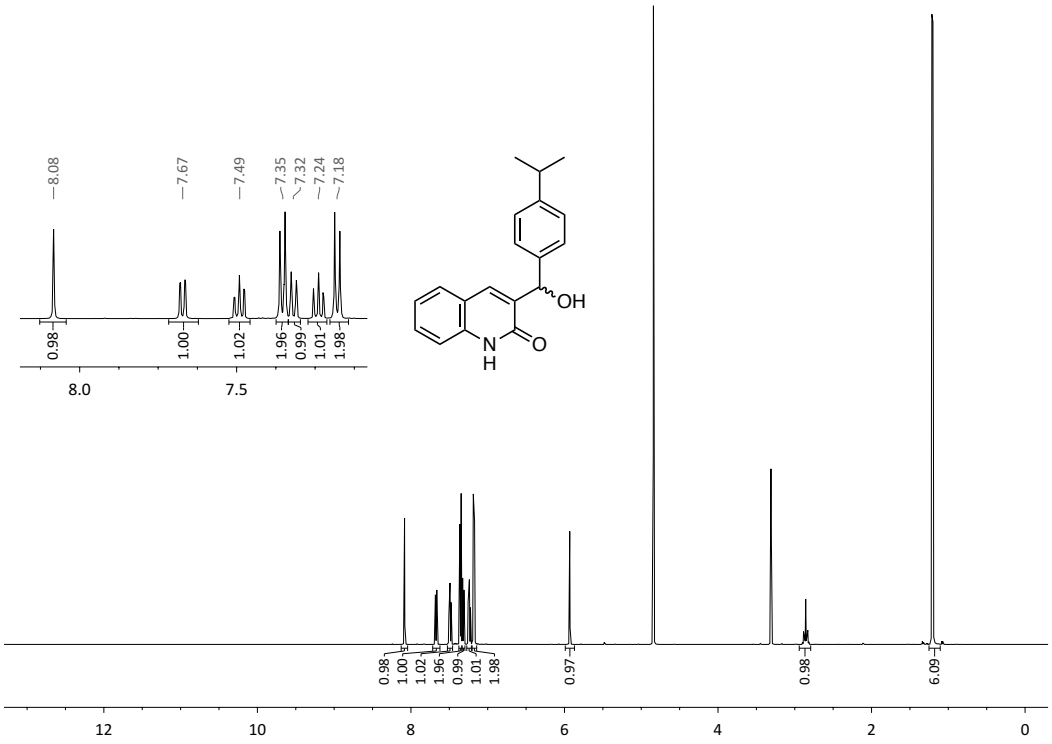


^{13}C NMR (126 MHz, MeOD-d_4)

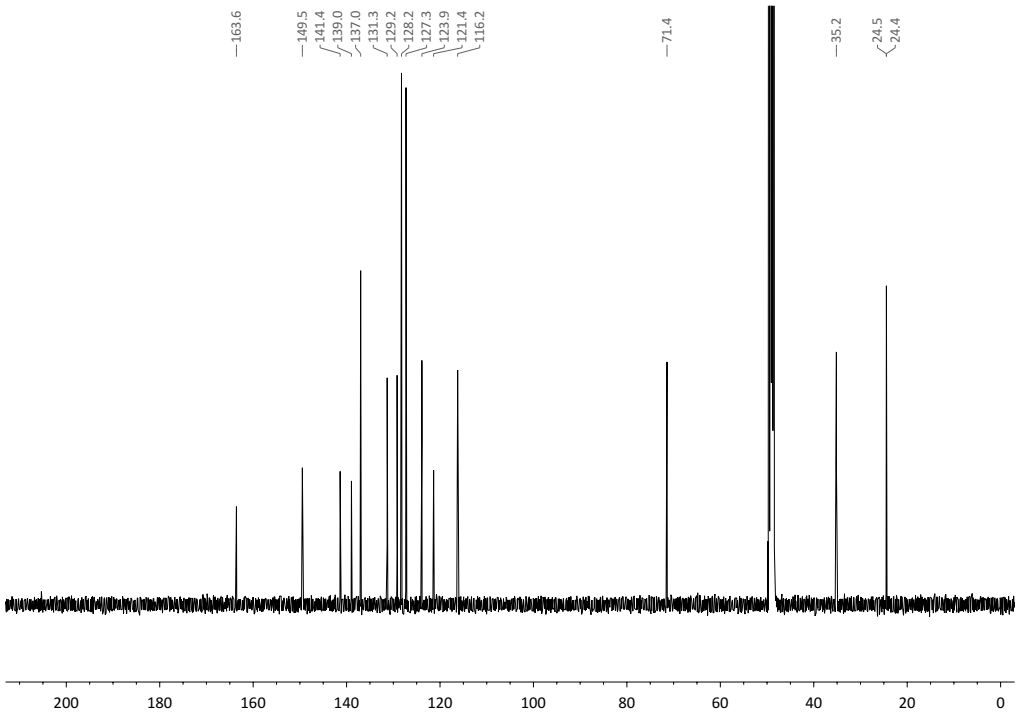


*1.3.11 3-(Hydroxy(4-isopropylphenyl)methyl)-2-quinolone (**3m**)*

^{1}H NMR (500 MHz, MeOD-d_4)



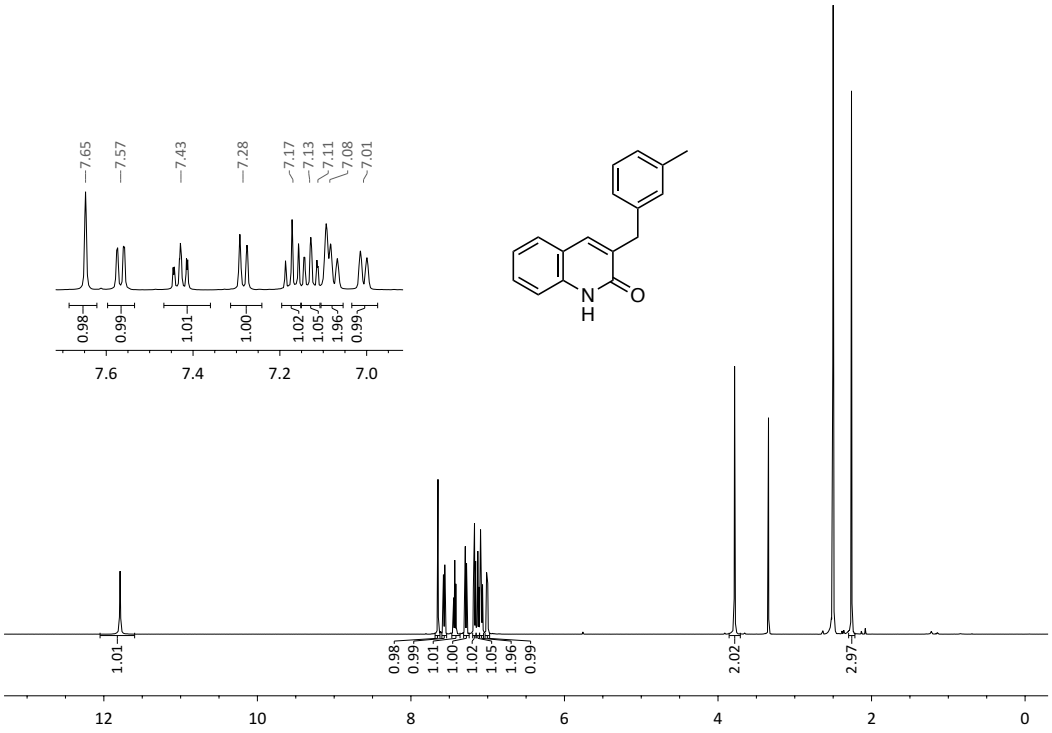
^{13}C NMR (126 MHz, MeOD-d_4)



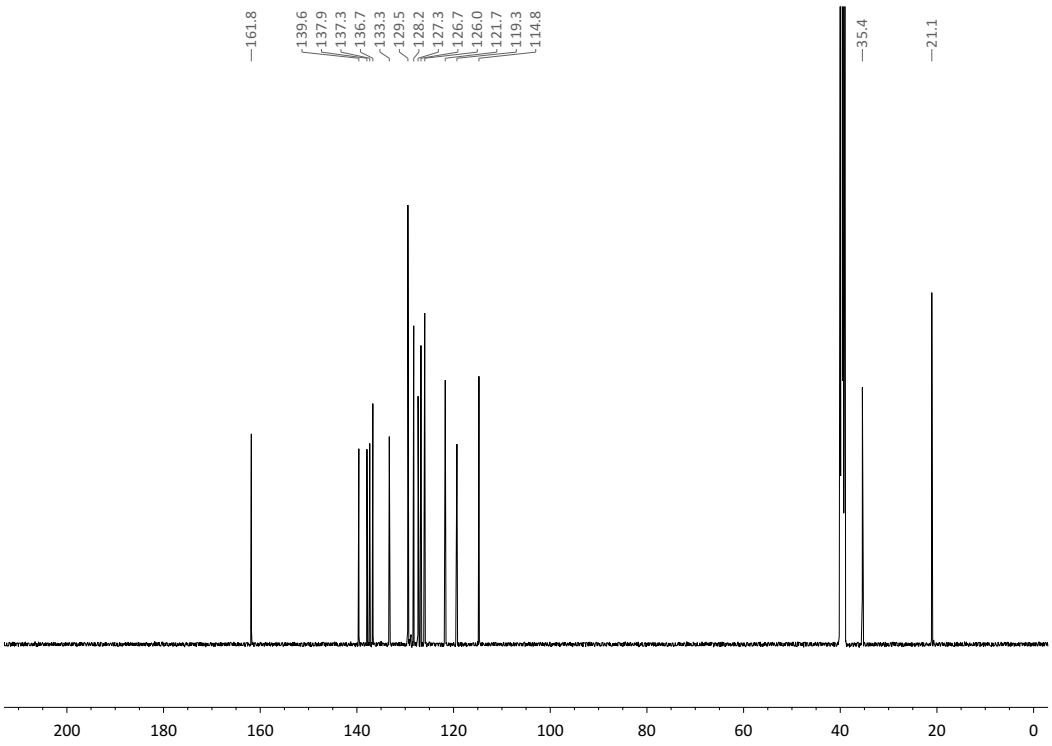
1.4 3-Benzyl-2-quinolones 2

*1.4.1 3-(3-Methylbenzyl)-2-quinolone (**2b**)*

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

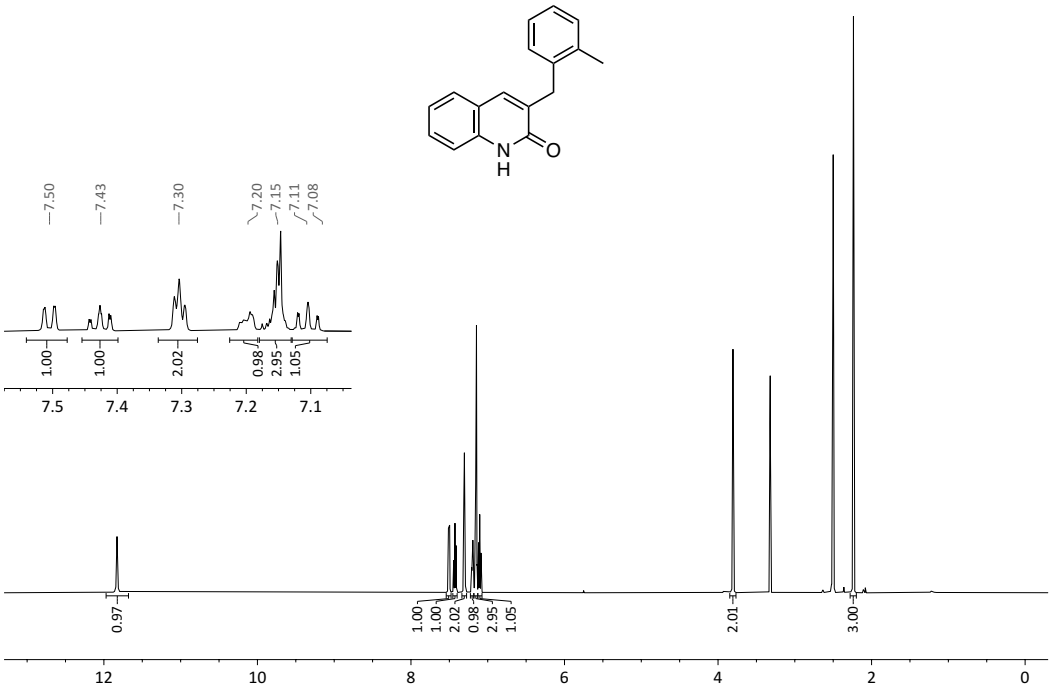


^{13}C NMR (126 MHz, DMSO-d_6)

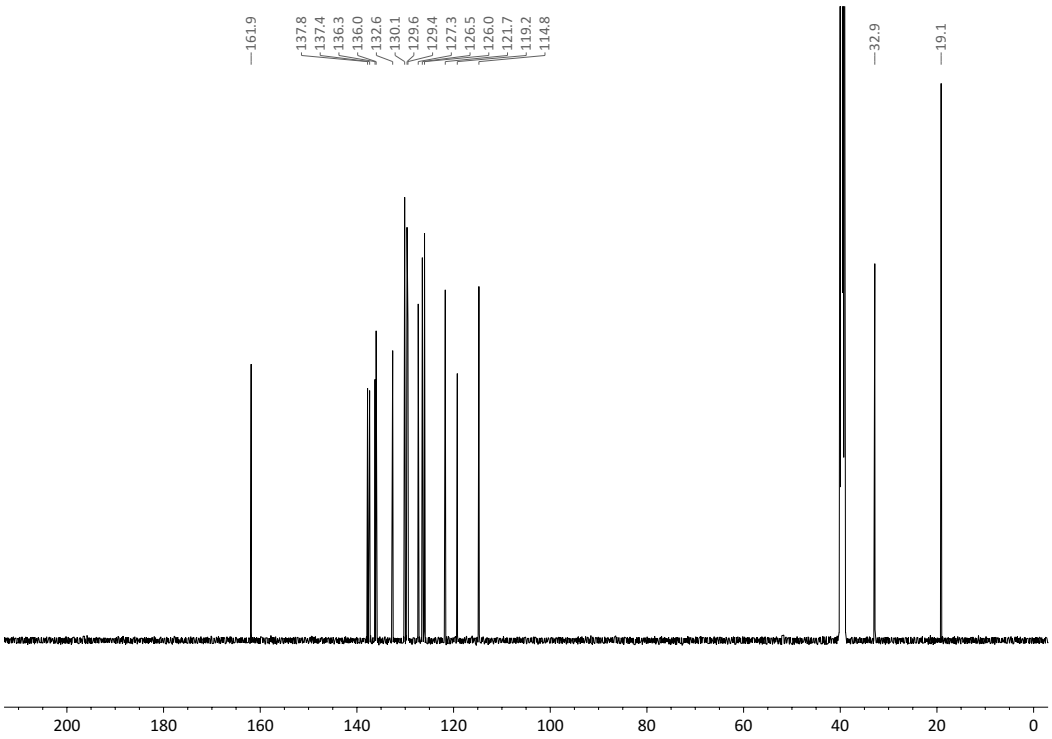


*1.4.2 3-(2-Methylbenzyl)-quinolone (**2c**)*

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

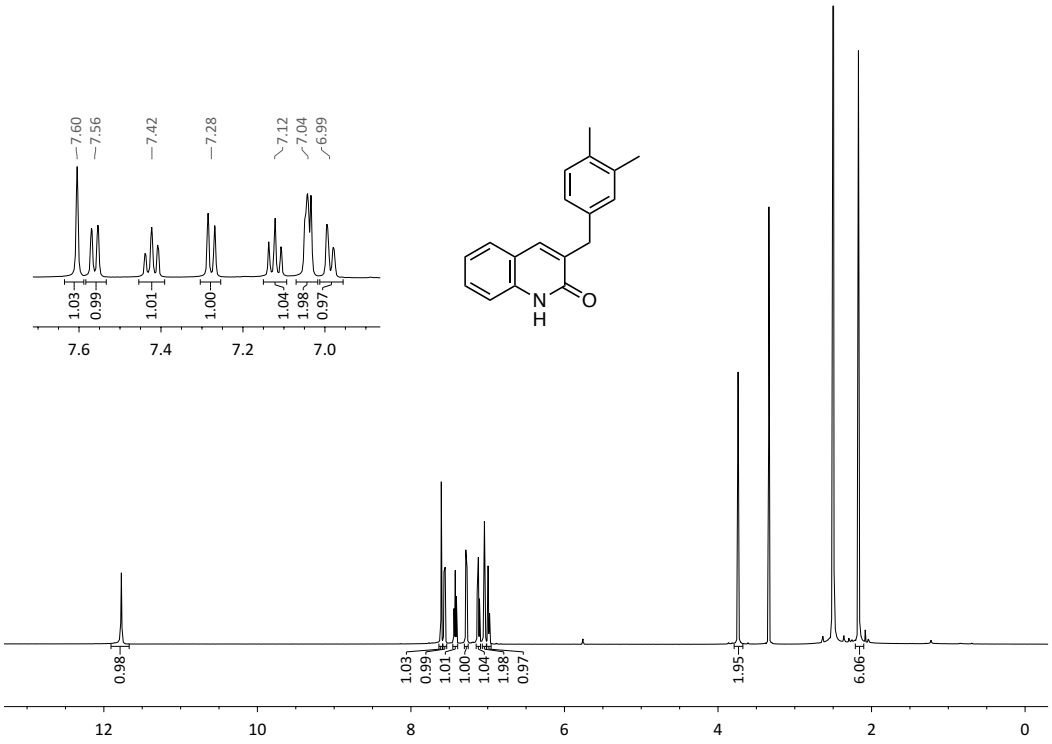


^{13}C NMR (126 MHz, DMSO-d_6)

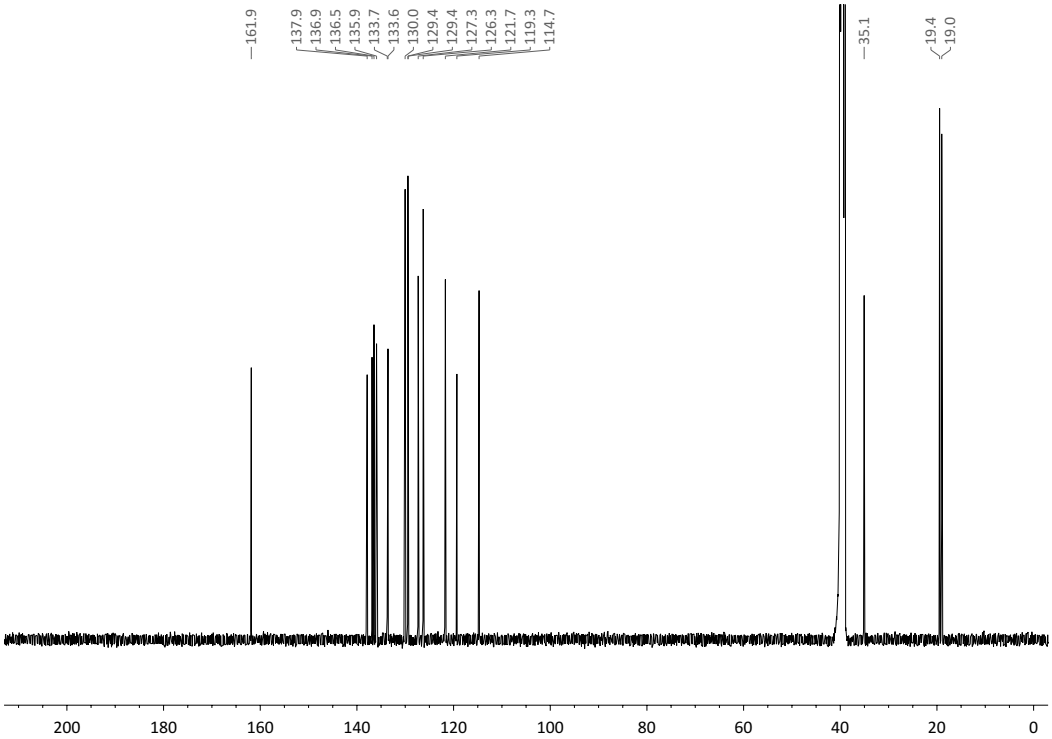


*1.4.3 3-(3,4-Dimethylbenzyl)-2-quinolone (**2d**)*

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

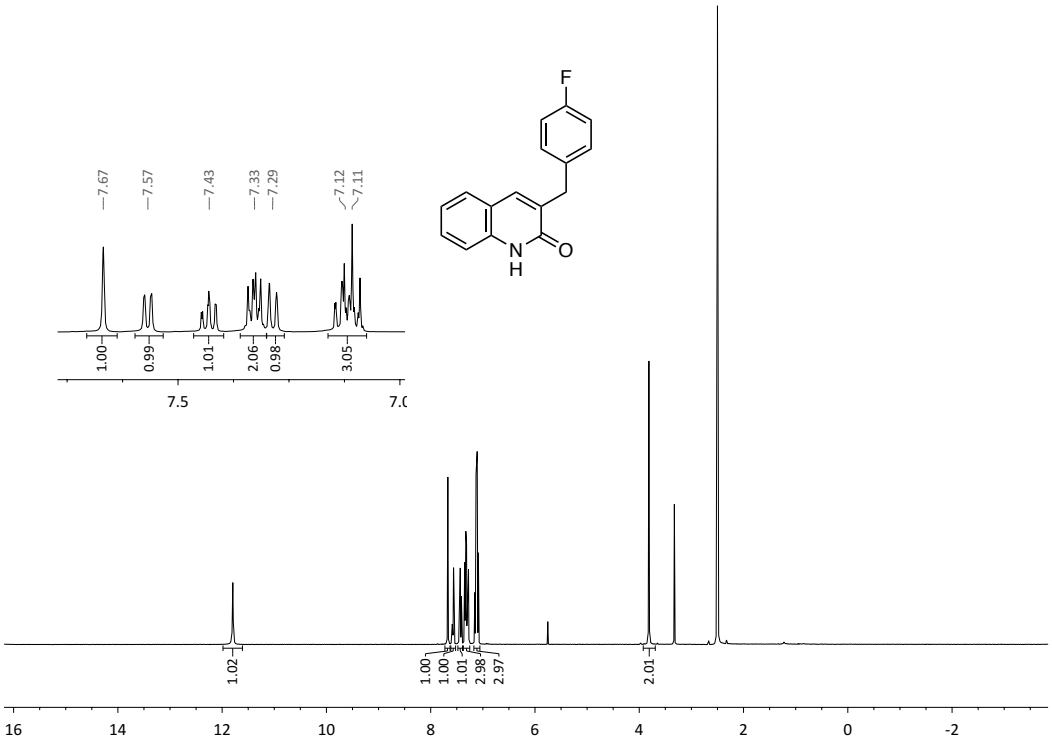


^{13}C NMR (126 MHz, DMSO-d_6)

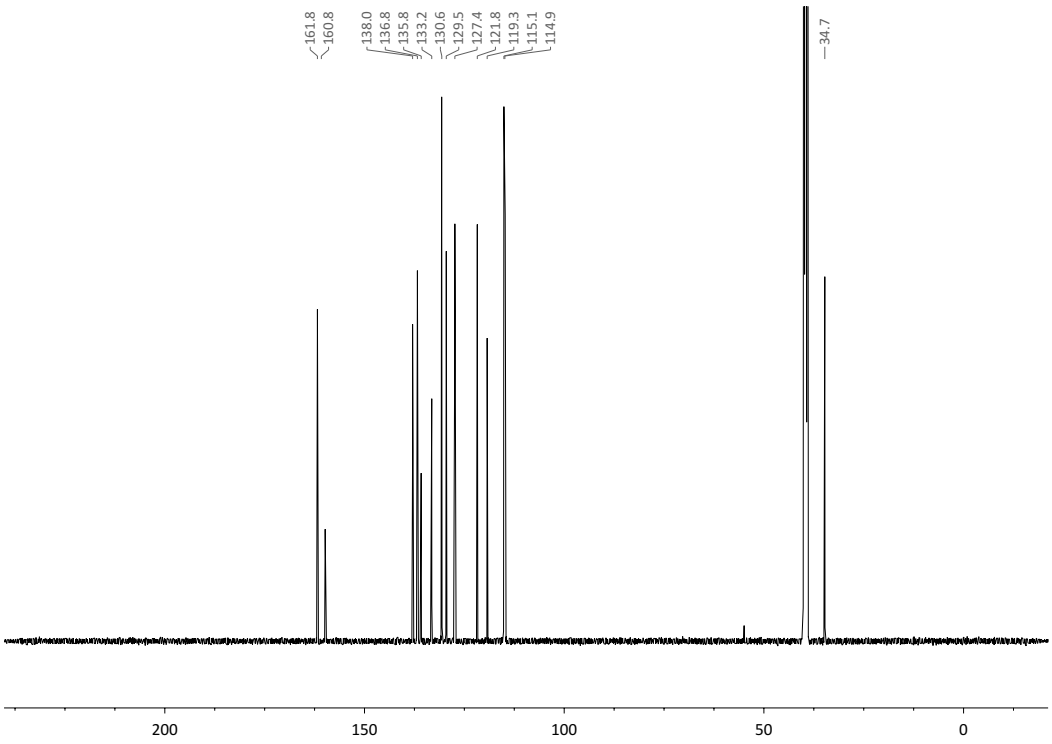


*1.4.4 3-(4-Fluorobenzyl)-2-quinolone (**2g**)*

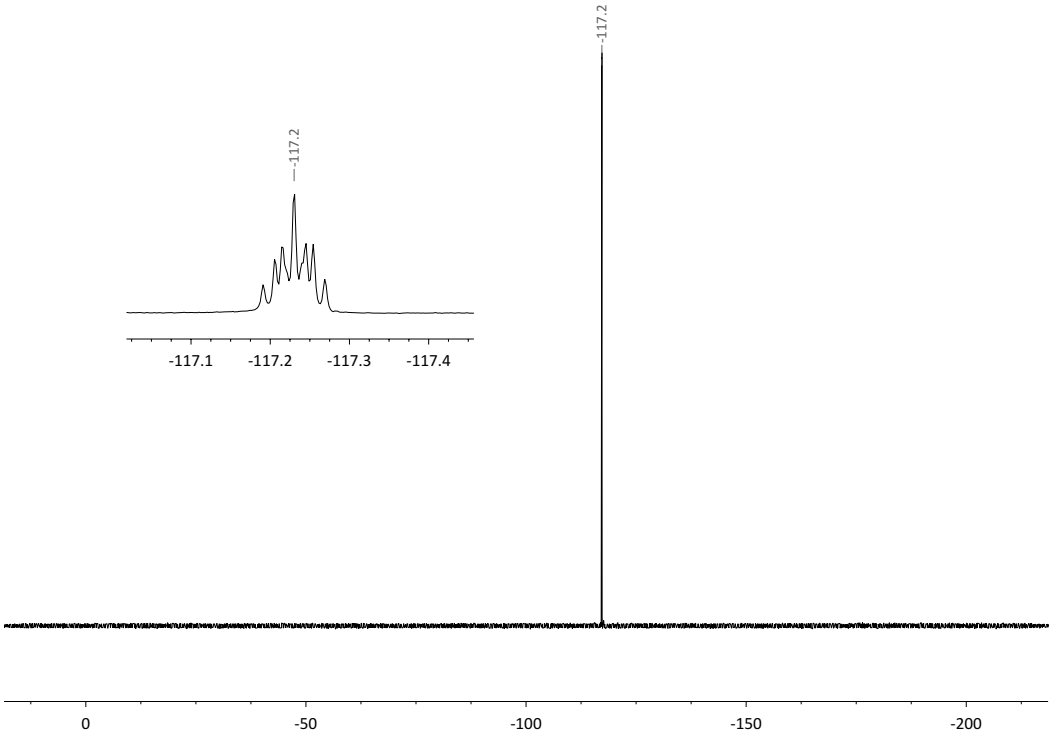
^{1}H NMR (500 MHz, DMSO-d_6)



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

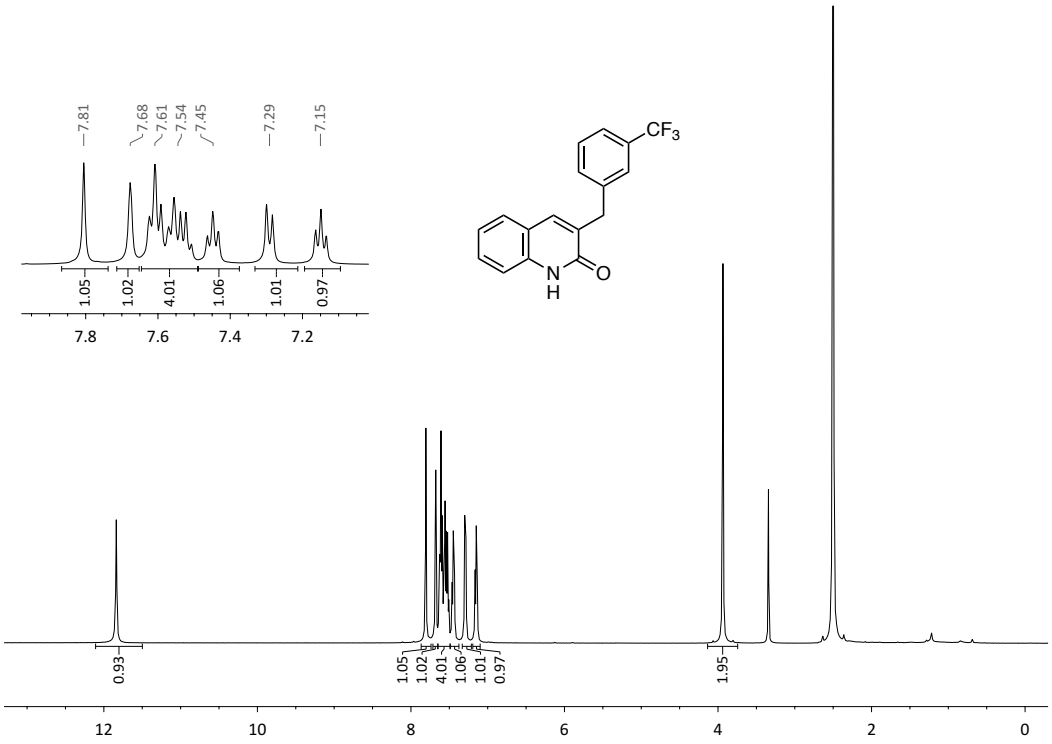


^{19}F NMR (471 MHz, DMSO-d_6)

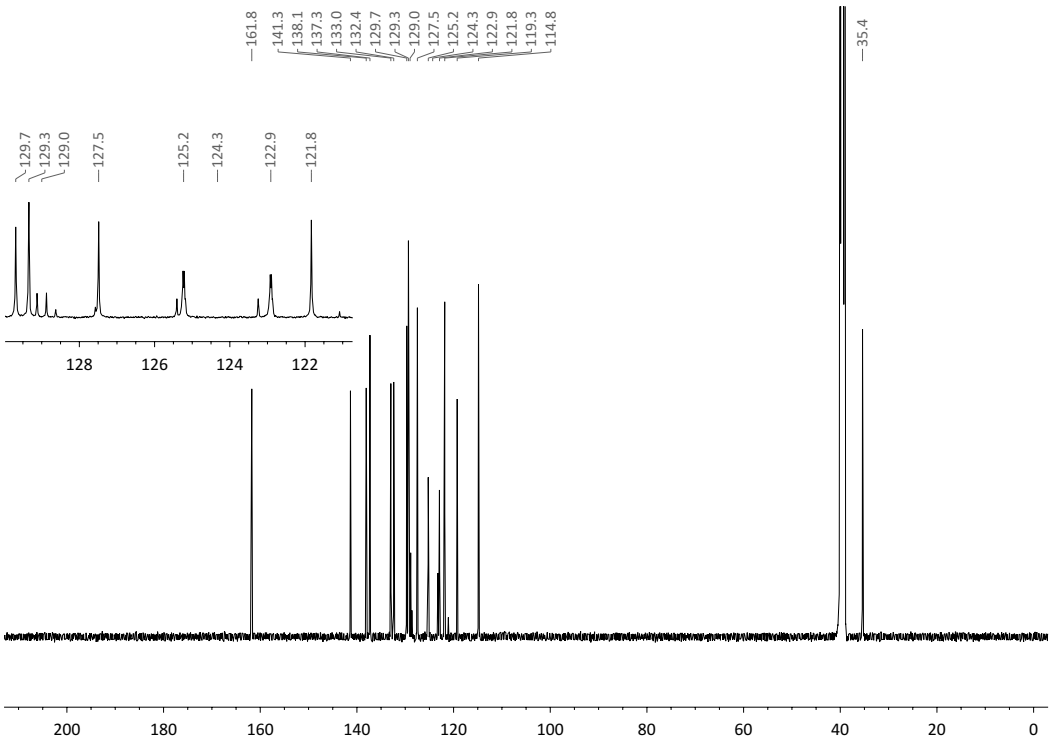


*1.4.5 3-(3-(Trifluoromethyl)benzyl)-2-quinolone (**2i**)*

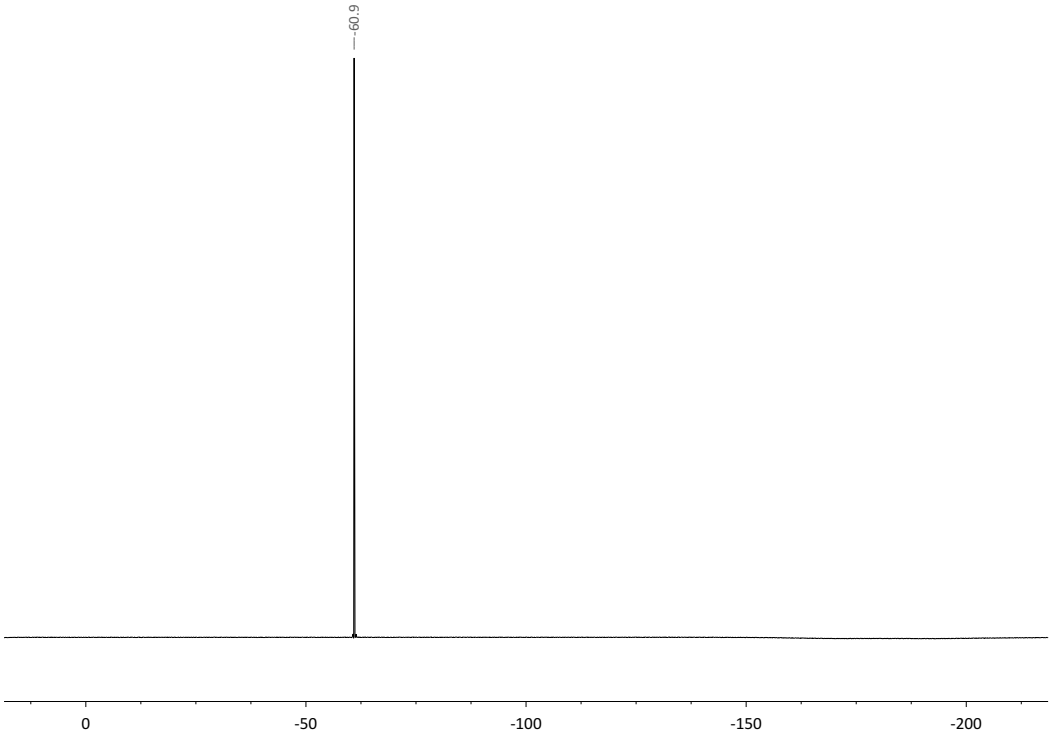
^{1}H NMR (500 MHz, DMSO-d_6)



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

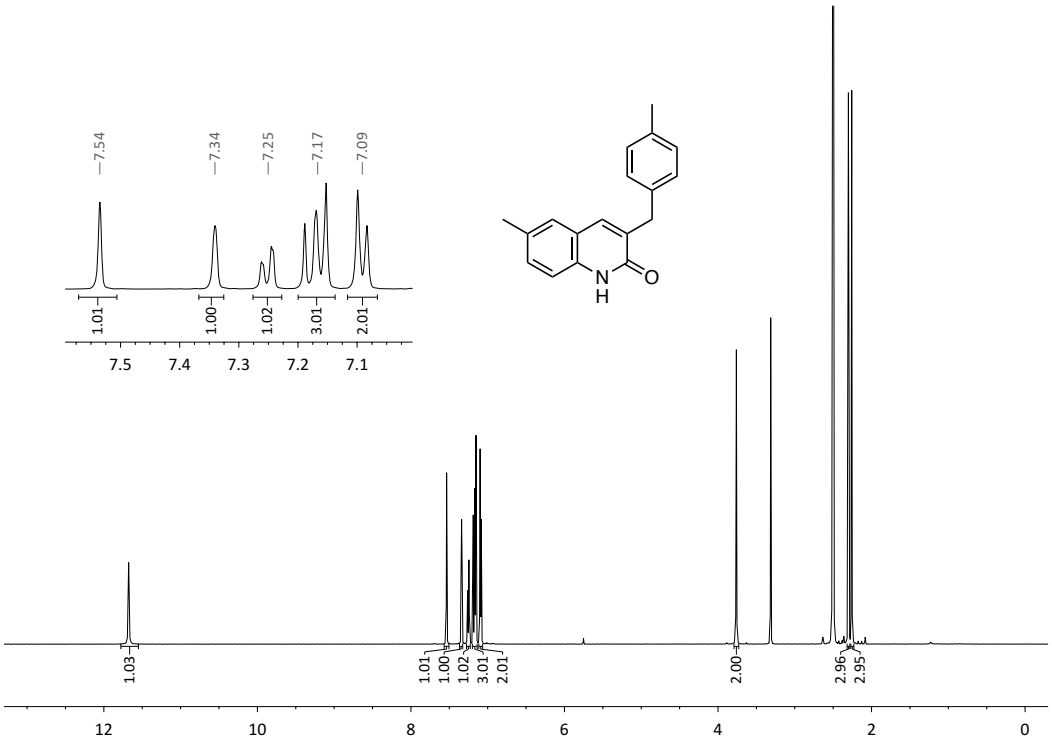


^{19}F NMR (376 MHz, DMSO-d_6)

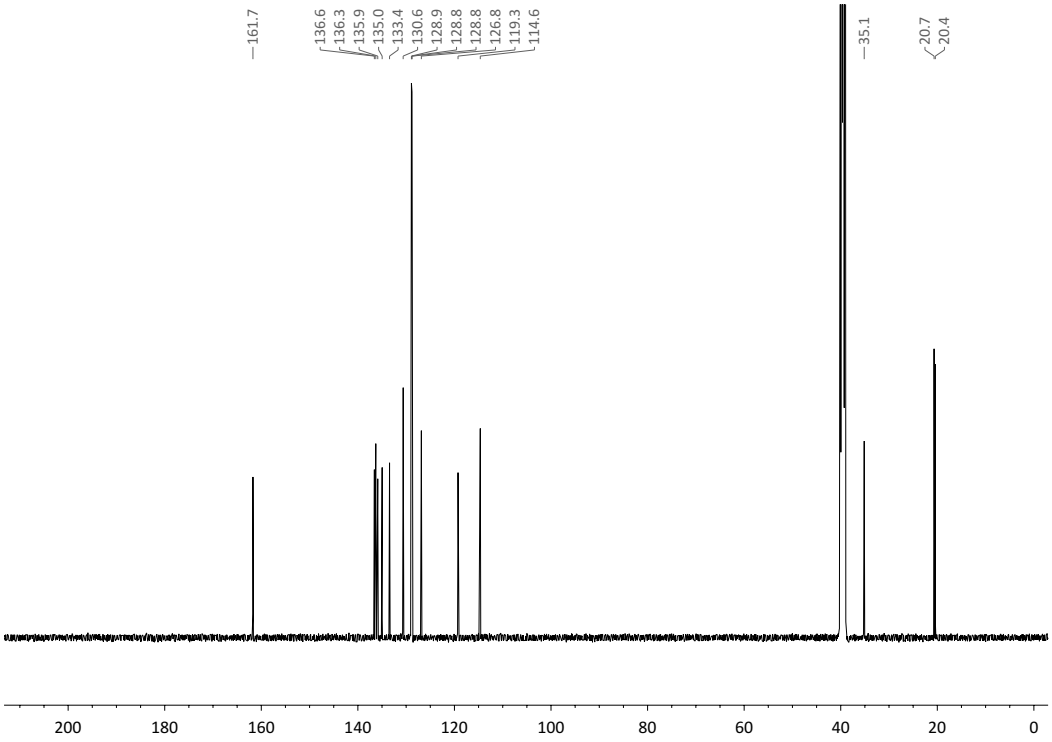


*1.4.6 6-Methyl-3-(4-methylbenzyl)-2-quinolone (**2j**)*

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

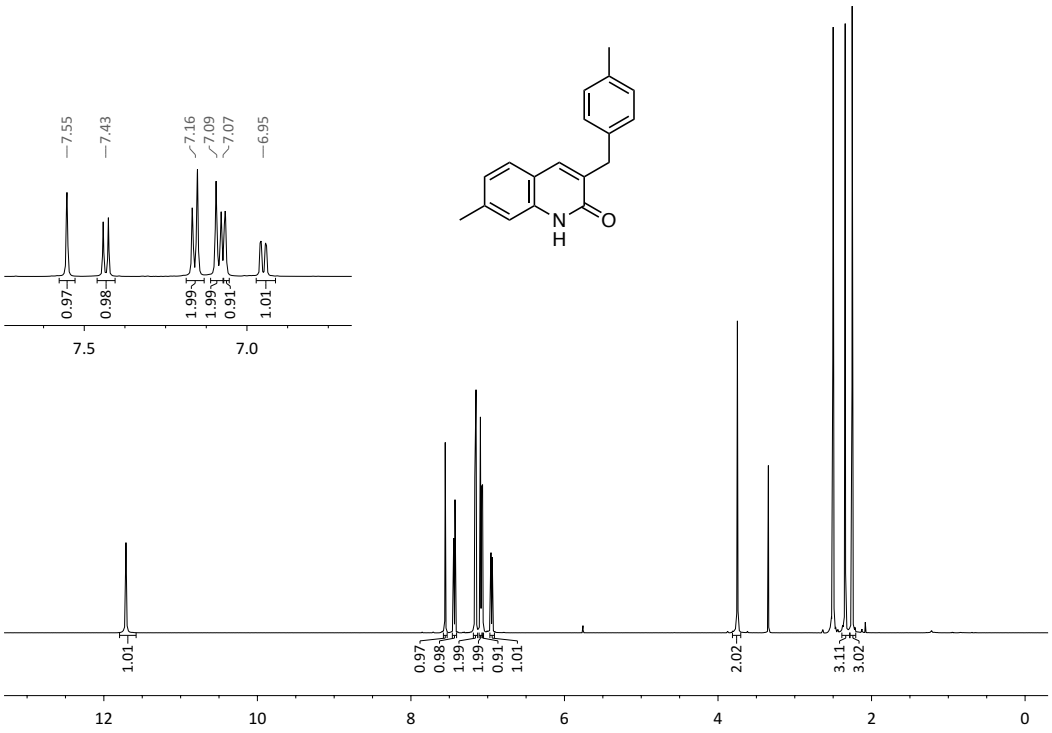


^{13}C NMR (126 MHz, DMSO-d_6)

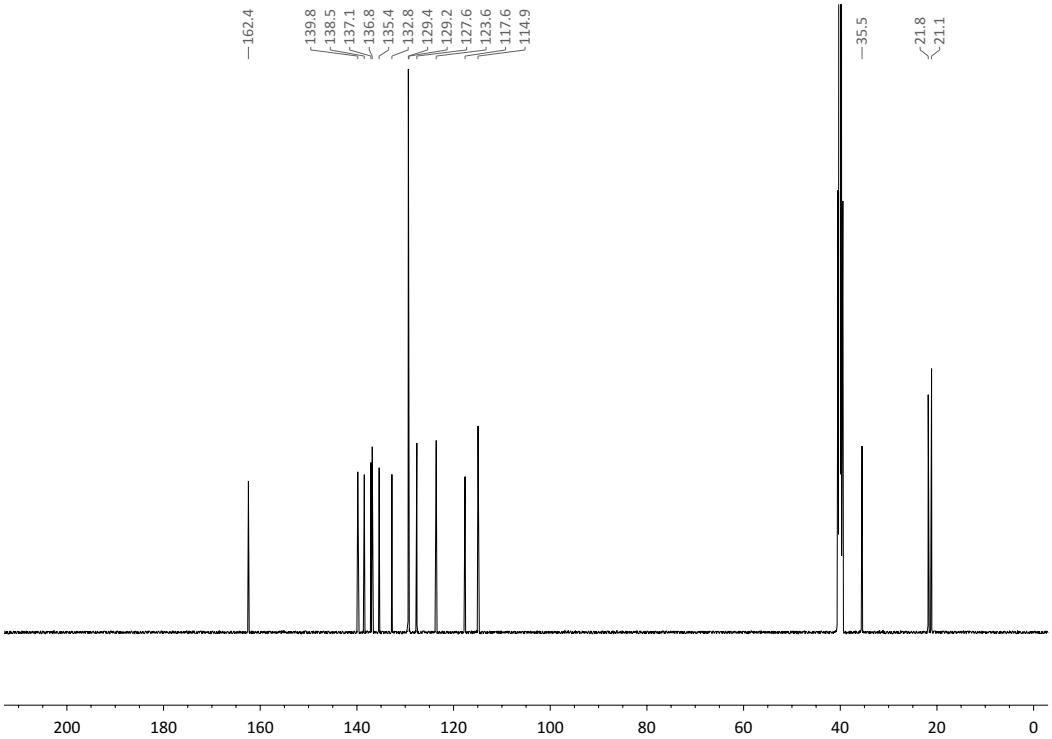


*1.4.7 7-Methyl-3-(4-methylbenzyl)-2-quinolone (**2k**)*

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

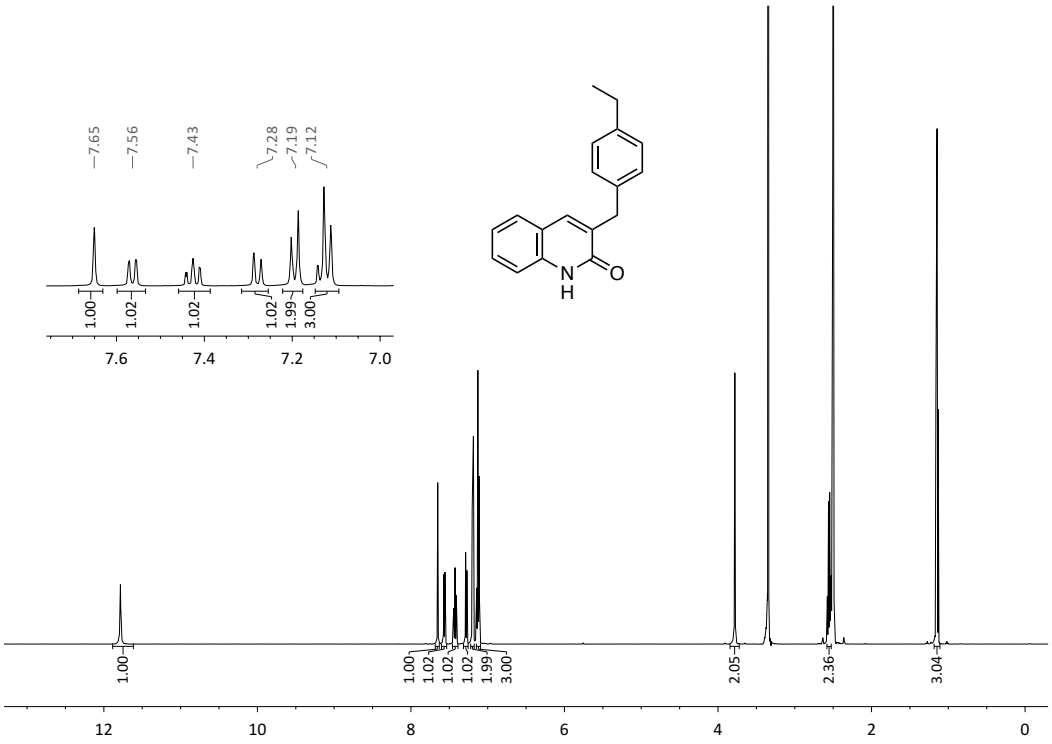


^{13}C NMR (126 MHz, DMSO-d_6)

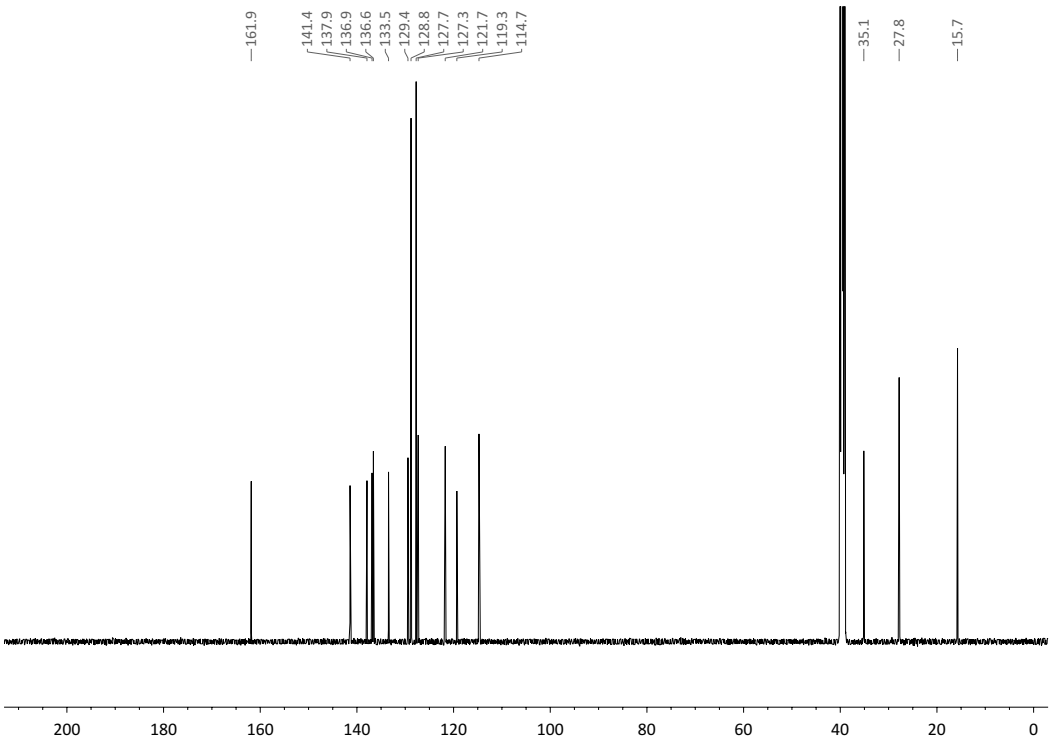


*1.4.8 3-(4-Ethylbenzyl)-2-quinolone (**2l**)*

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

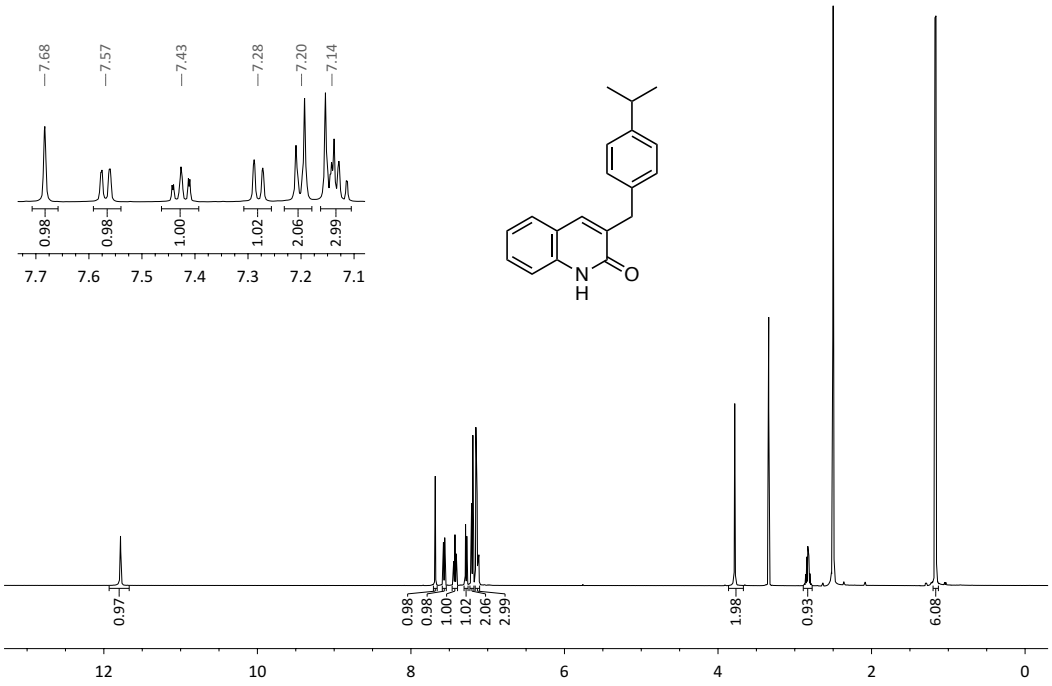


^{13}C NMR (126 MHz, DMSO-d_6)

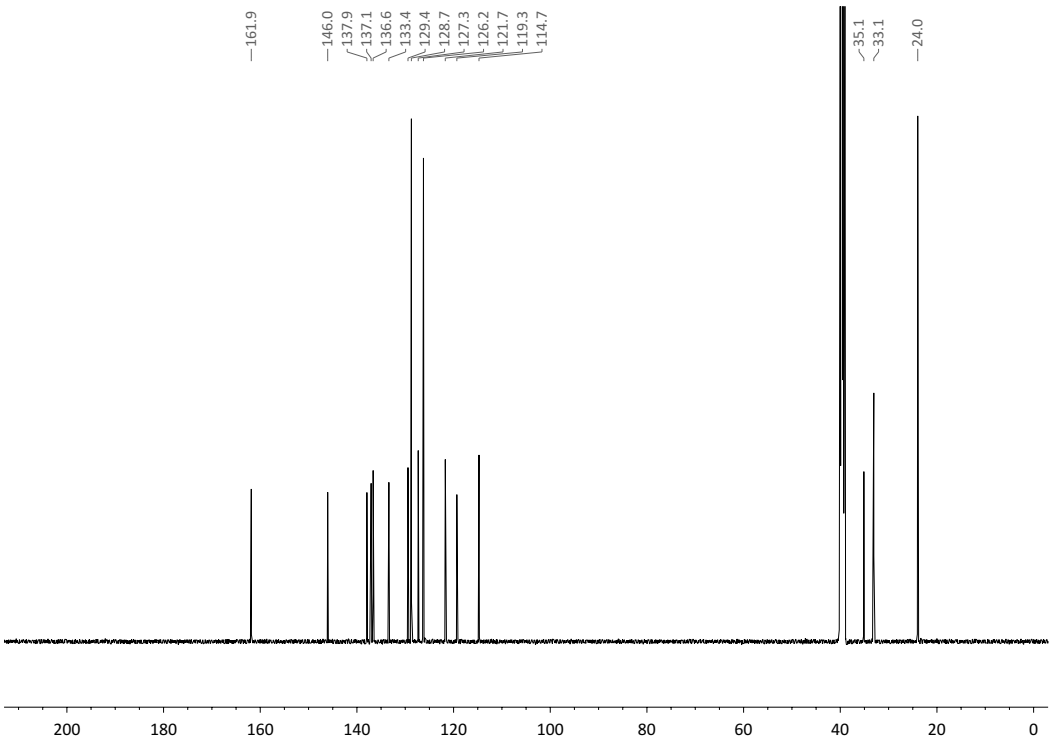


*1.4.9 3-(4-Isopropylbenzyl)-2-quinolone (**2m**)*

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

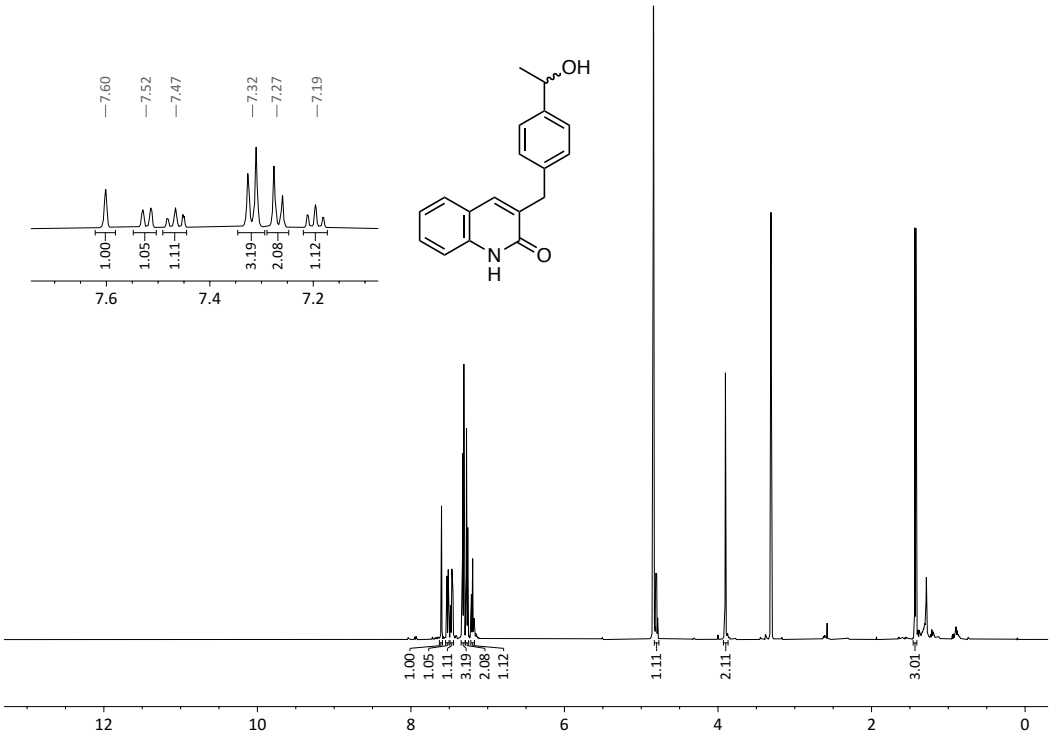


^{13}C NMR (126 MHz, DMSO-d_6)

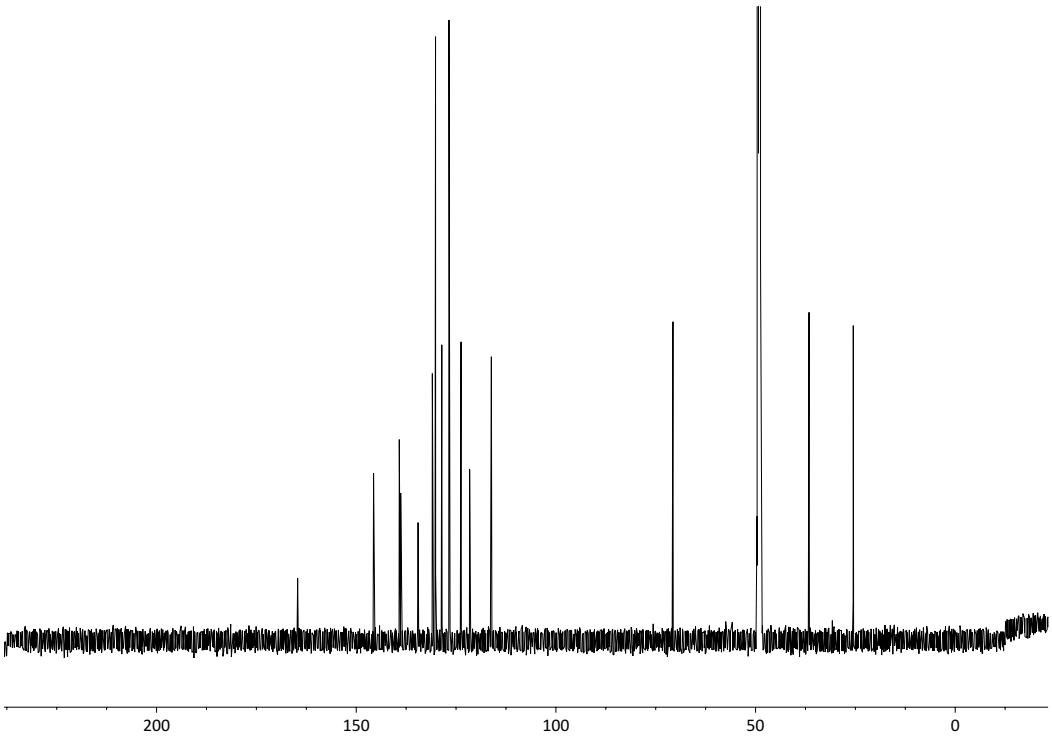


*1.4.10 3-(4-(1-Hydroxyethyl)benzyl)-2-quinolone (**2n**)*

^{1}H NMR (500 MHz, MeOD-d_4)

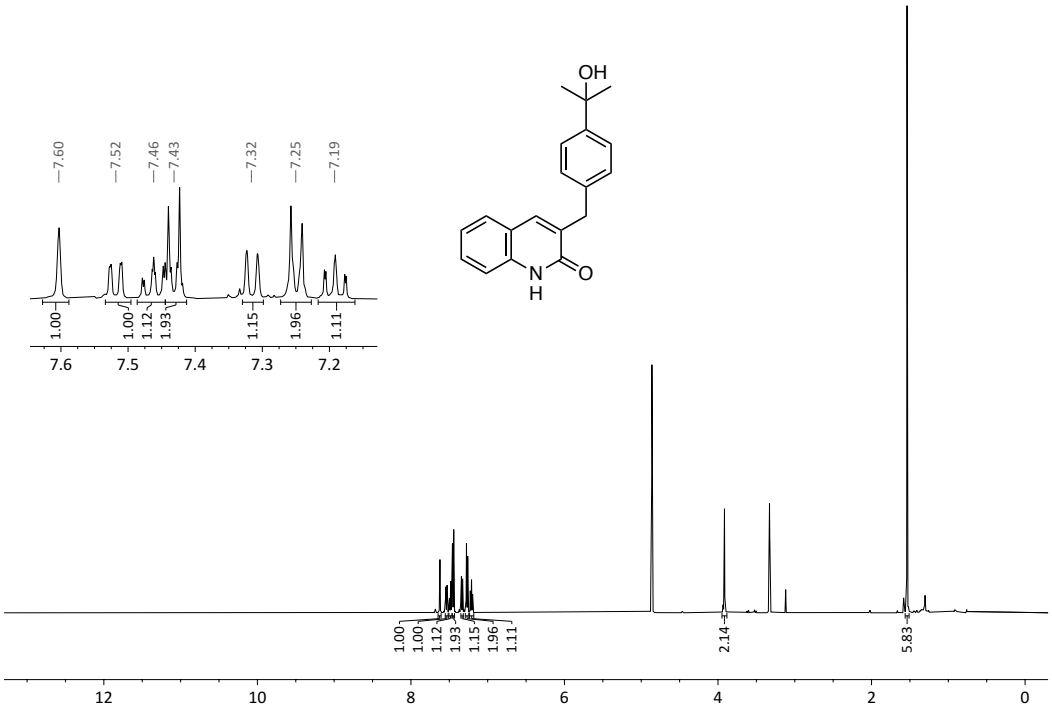


^{13}C NMR (126 MHz, MeOD-d_4)

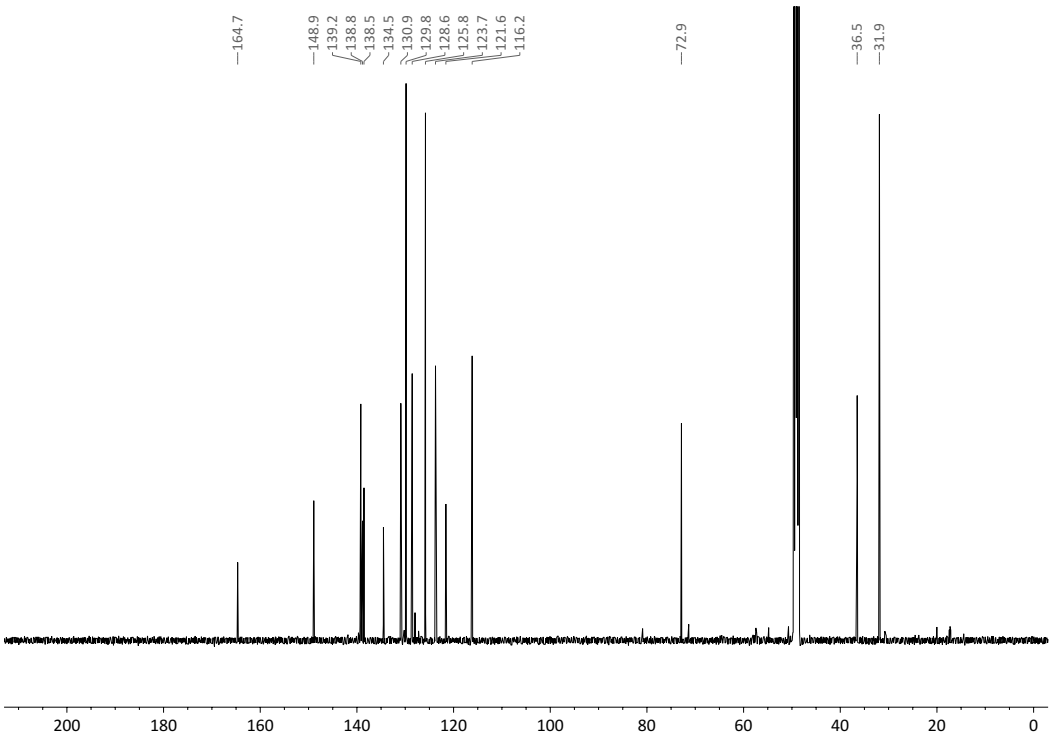


*1.4.11 3-(4-(2-Hydroxypropan-2-yl)benzyl)-2-quinolone (**2o**)*

^{1}H NMR (500 MHz, MeOD-d_4)



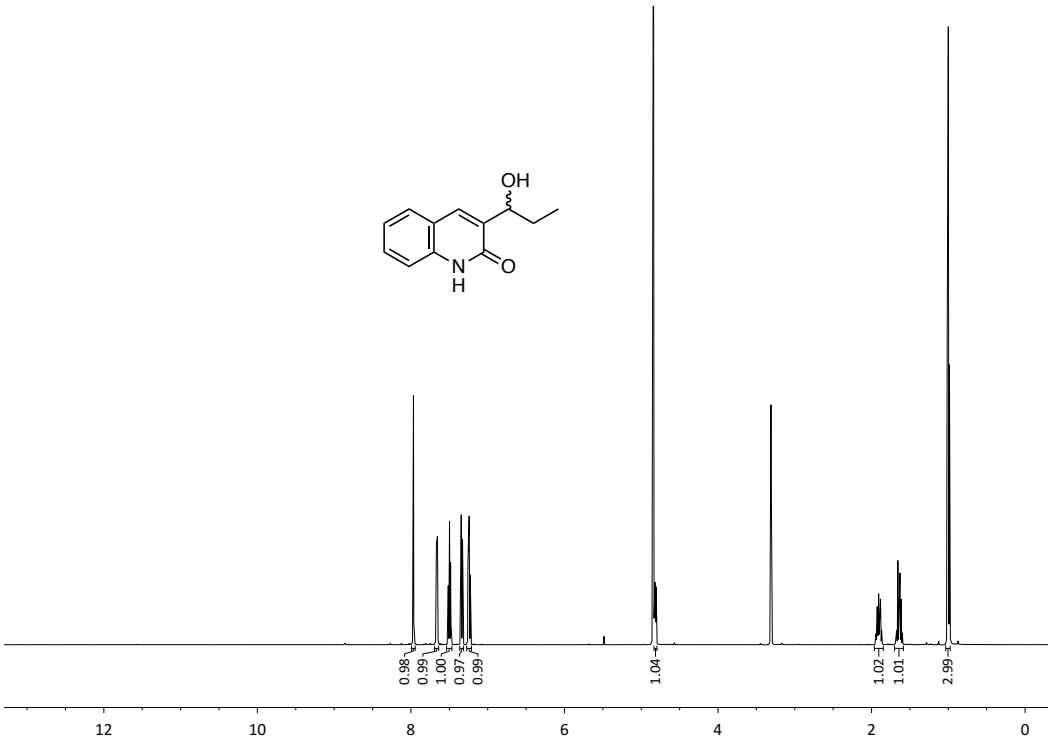
^{13}C NMR (126 MHz, MeOD-d_4)



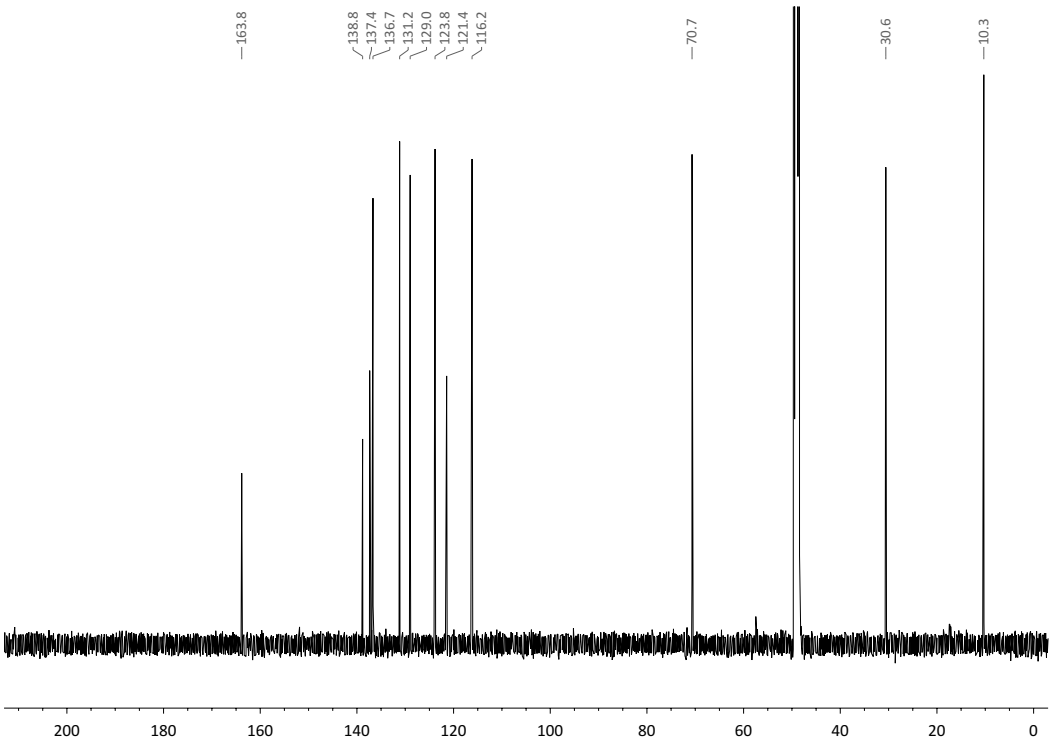
1.5 3-(1-Hydroxyalkyl)-2-quinolones 7

*1.5.1 3-(1-hydroxypropyl)-2-quinolinone (**7b**)*

^{1}H NMR (500 MHz, MeOD-d_4)

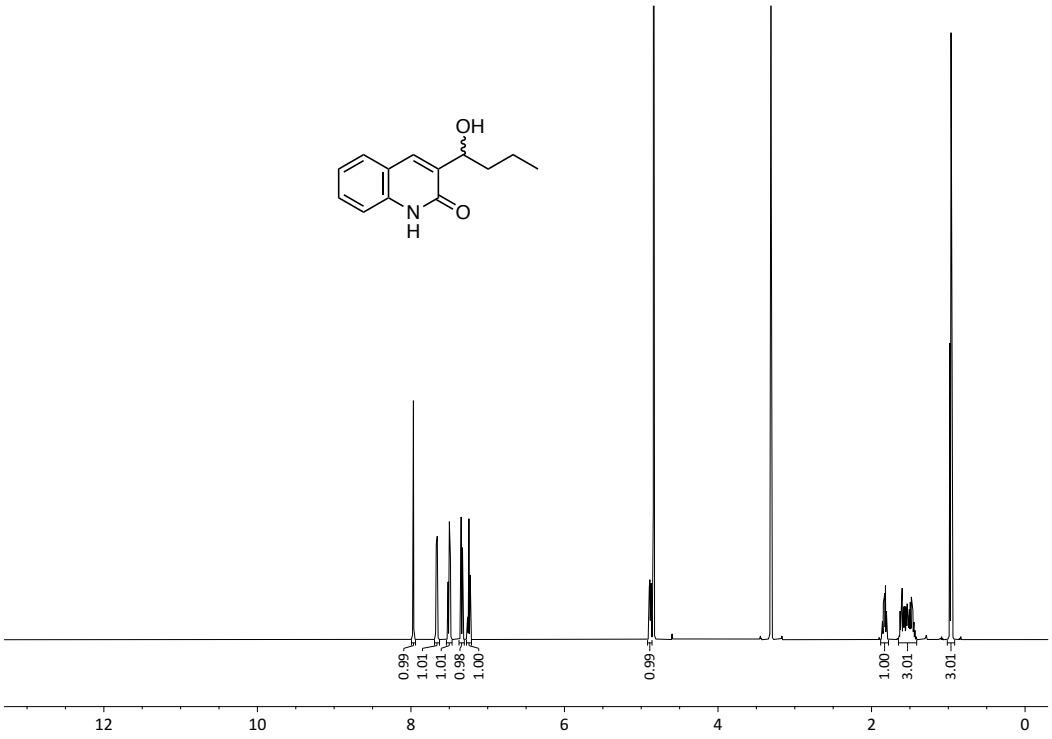


^{13}C NMR (126 MHz, MeOD-d_4)

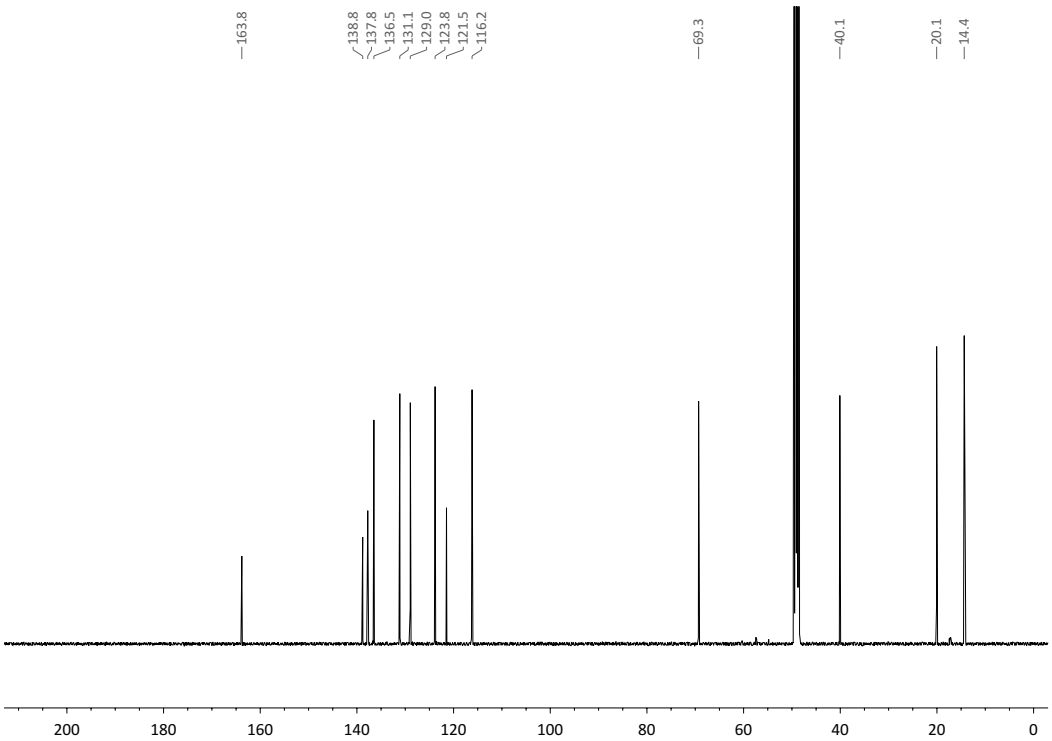


*1.5.2 3-(1-Hydroxybutyl)-2-quinolinone (**7c**)*

^{1}H NMR (500 MHz, MeOD-d_4)

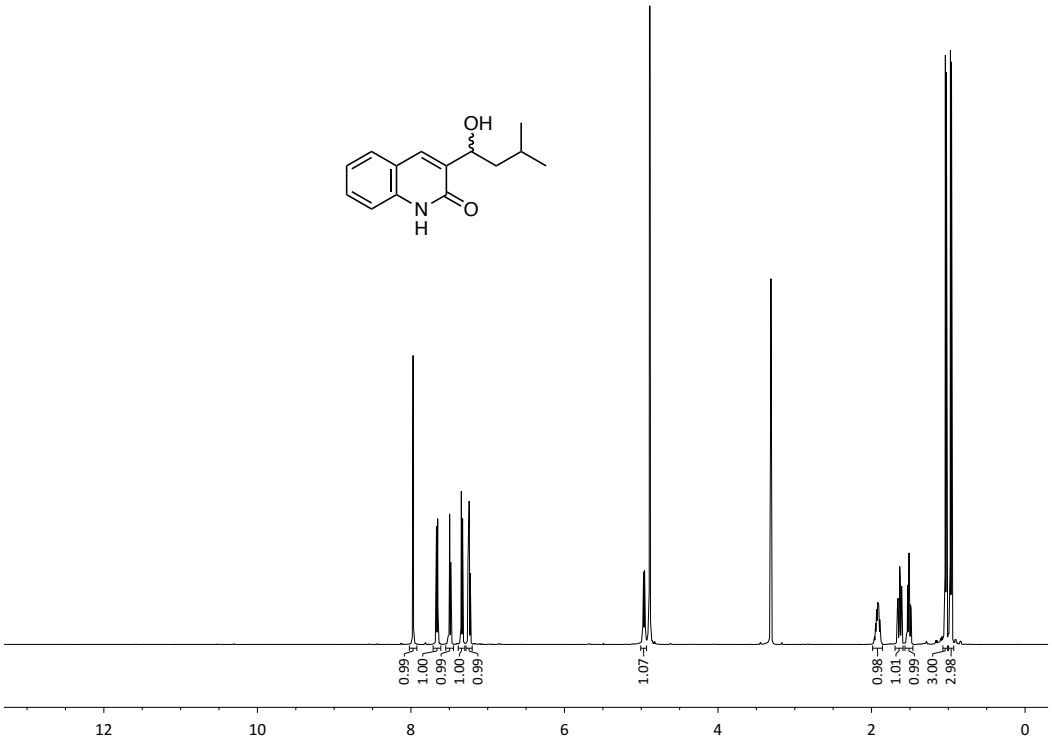


^{13}C NMR (126 MHz, MeOD-d_4)

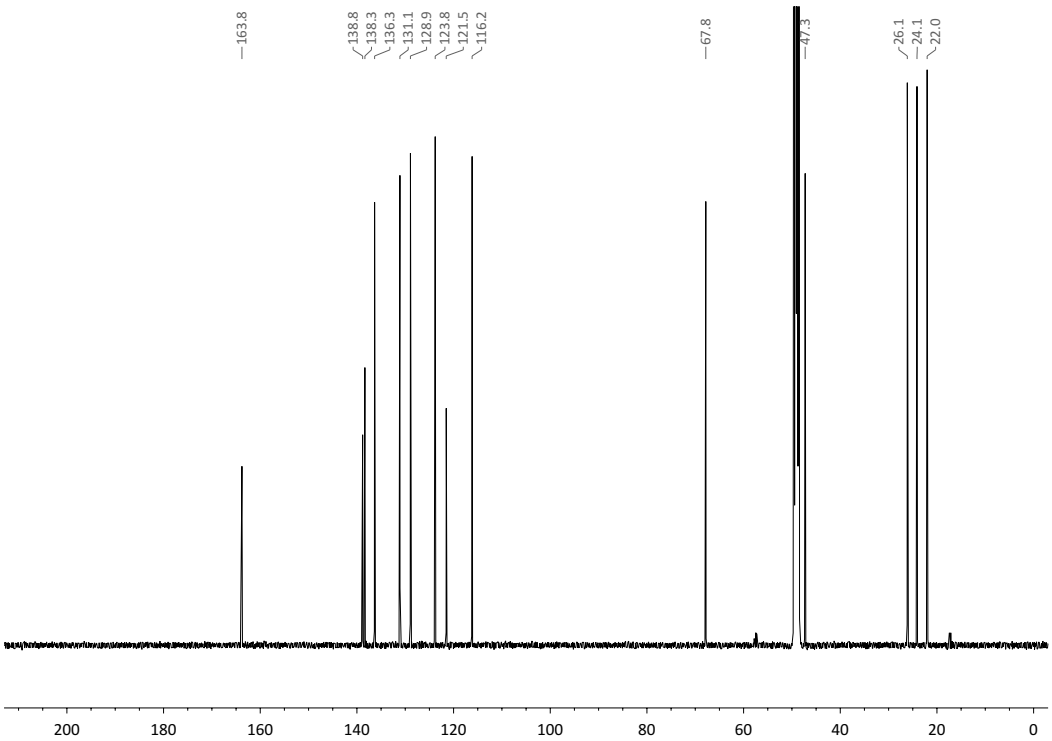


*1.5.3 3-(1-Hydroxy-3-methylbutyl)-2-quinolone (**7d**)*

^{1}H NMR (500 MHz, MeOD-d_4)

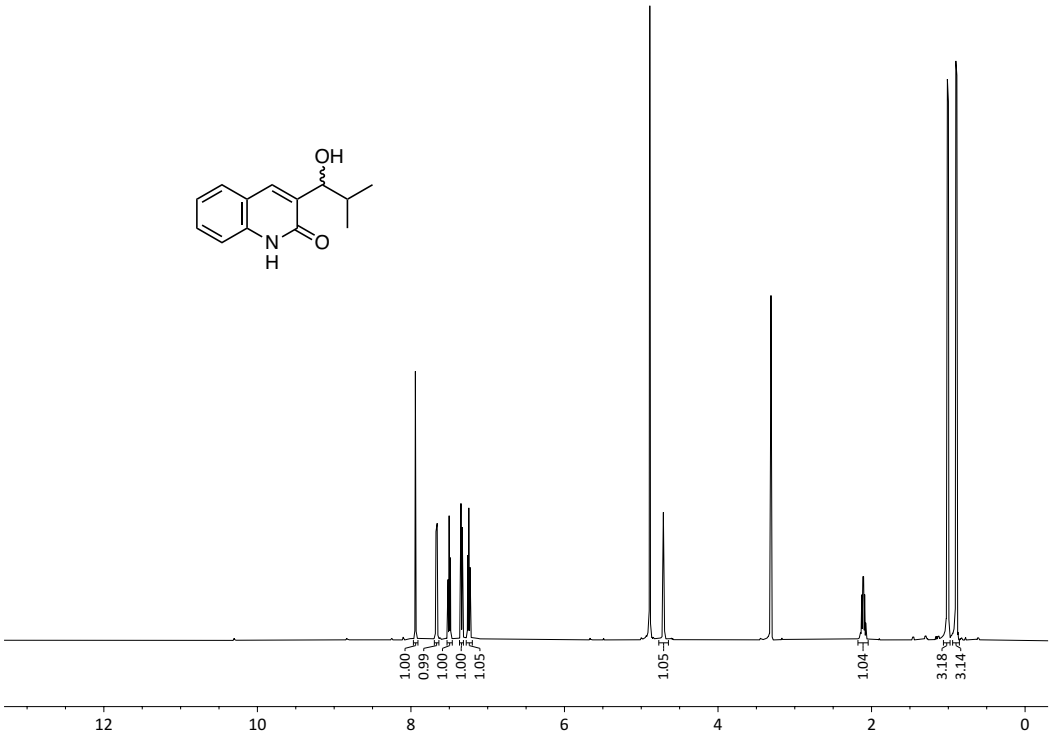


^{13}C NMR (126 MHz, MeOD-d_4)

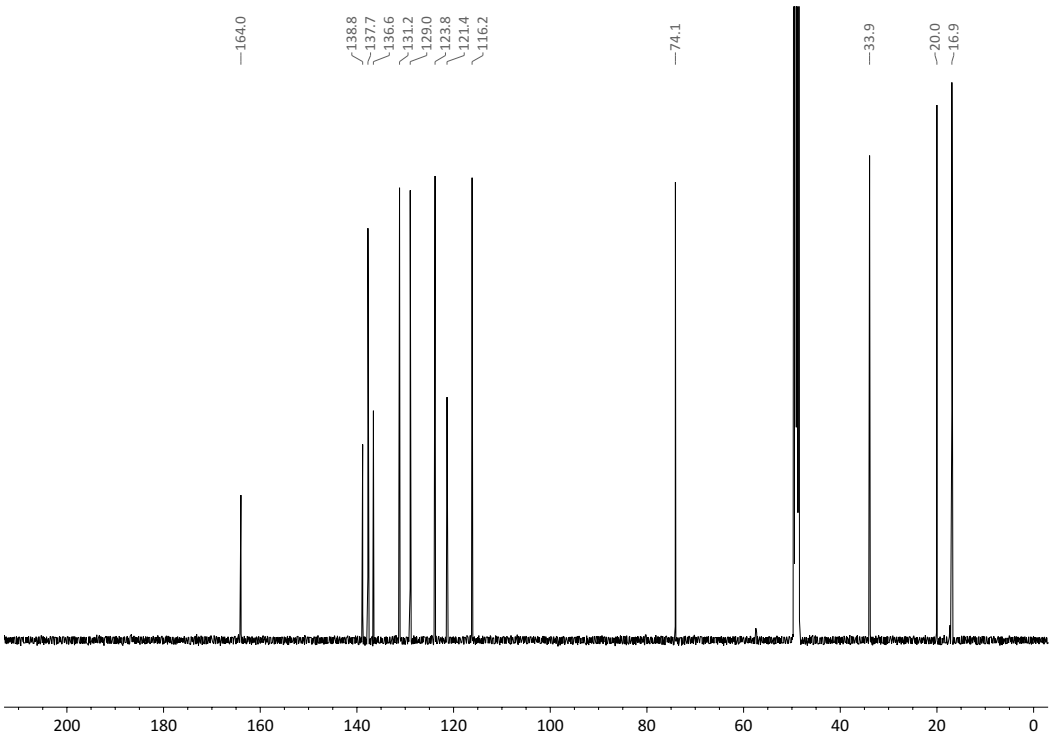


*1.5.4 3-(1-Hydroxy-2-methylpropyl)-2-quinolone (**7e**)*

^{1}H NMR (500 MHz, MeOD-d_4)

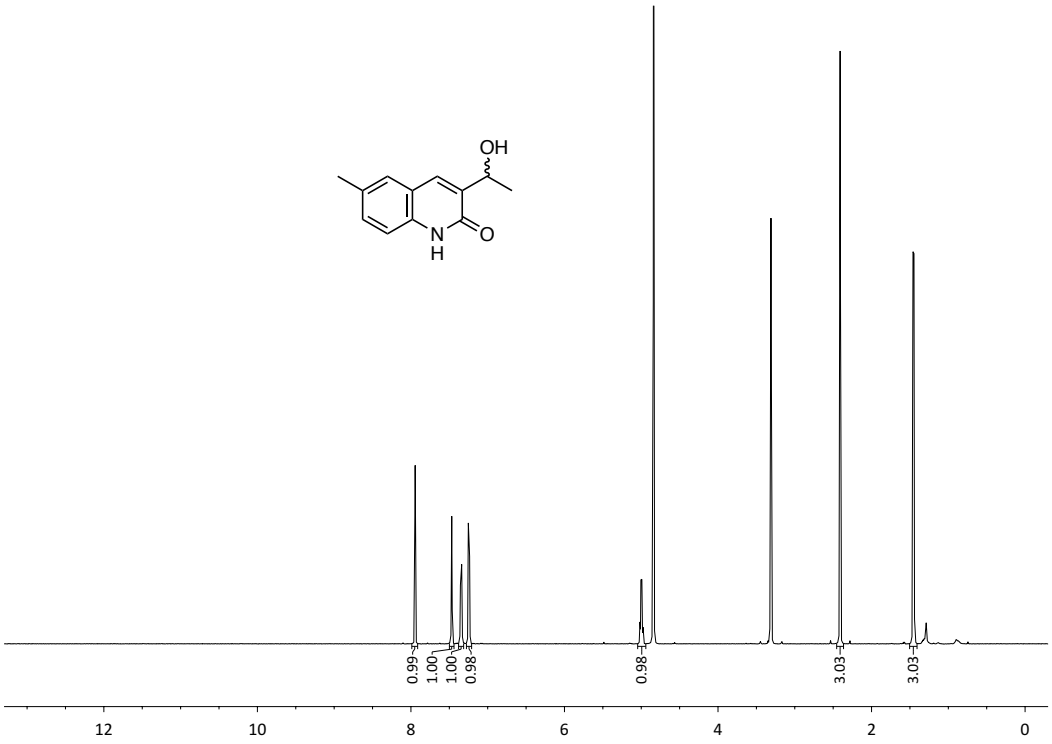


^{13}C NMR (126 MHz, MeOD-d_4)

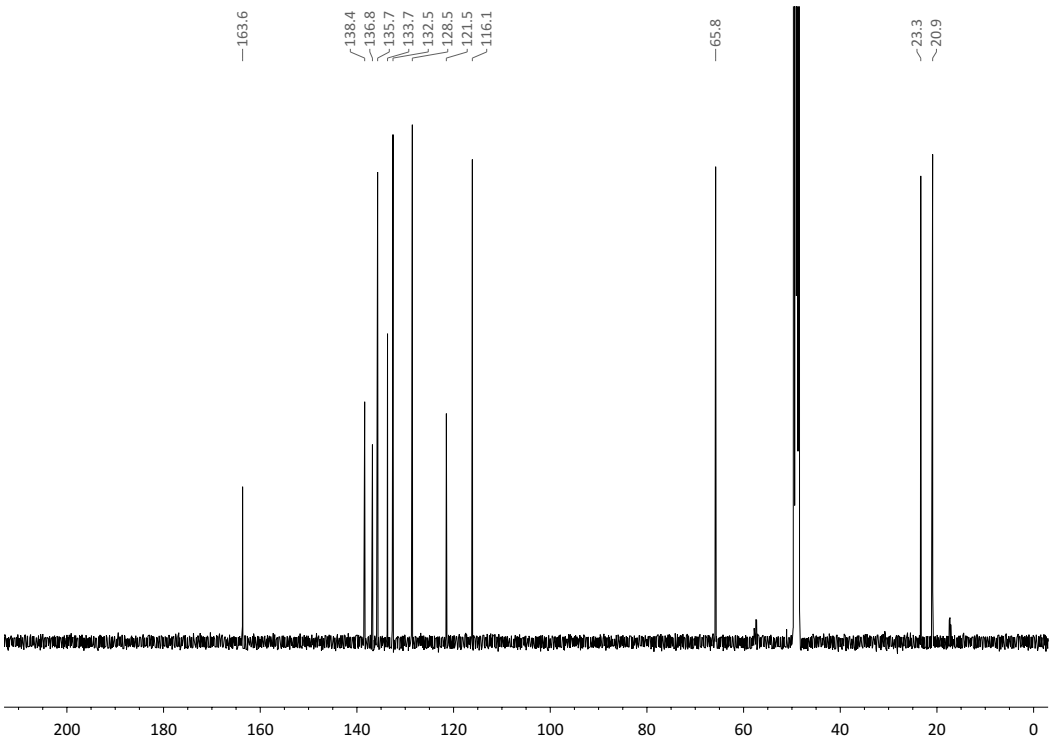


*1.5.5 3-(1-Hydroxyethyl)-6-methyl-2-quinolone (**7f**)*

^{1}H NMR (500 MHz, MeOD-d_4)

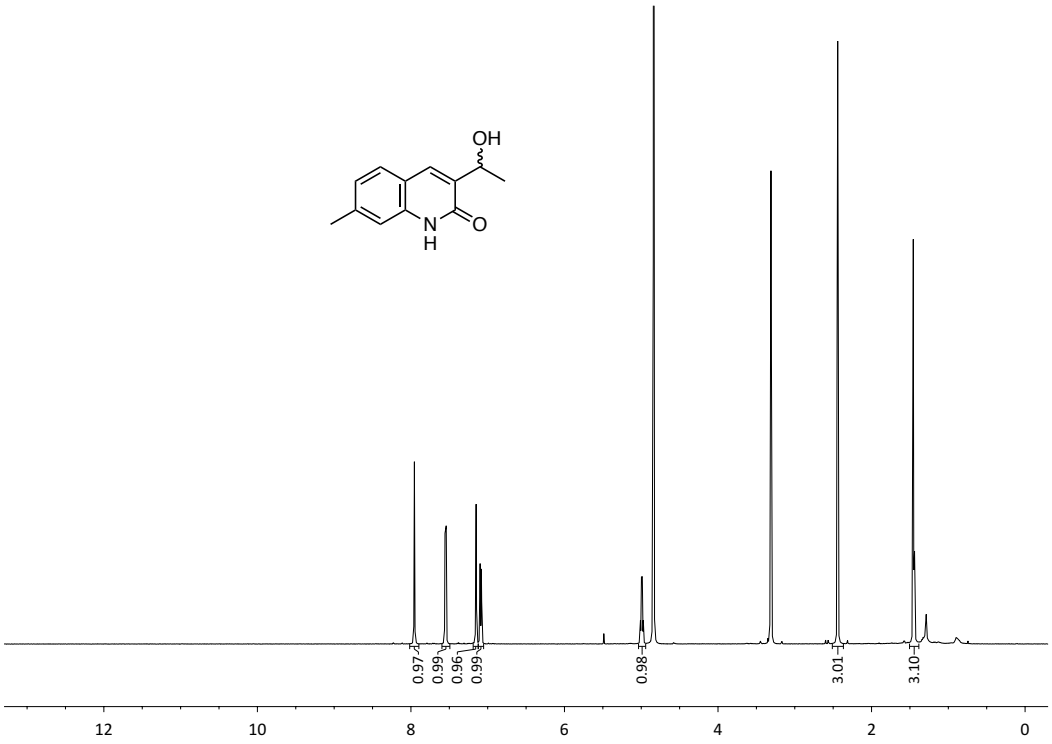


^{13}C NMR (126 MHz, MeOD-d_4)

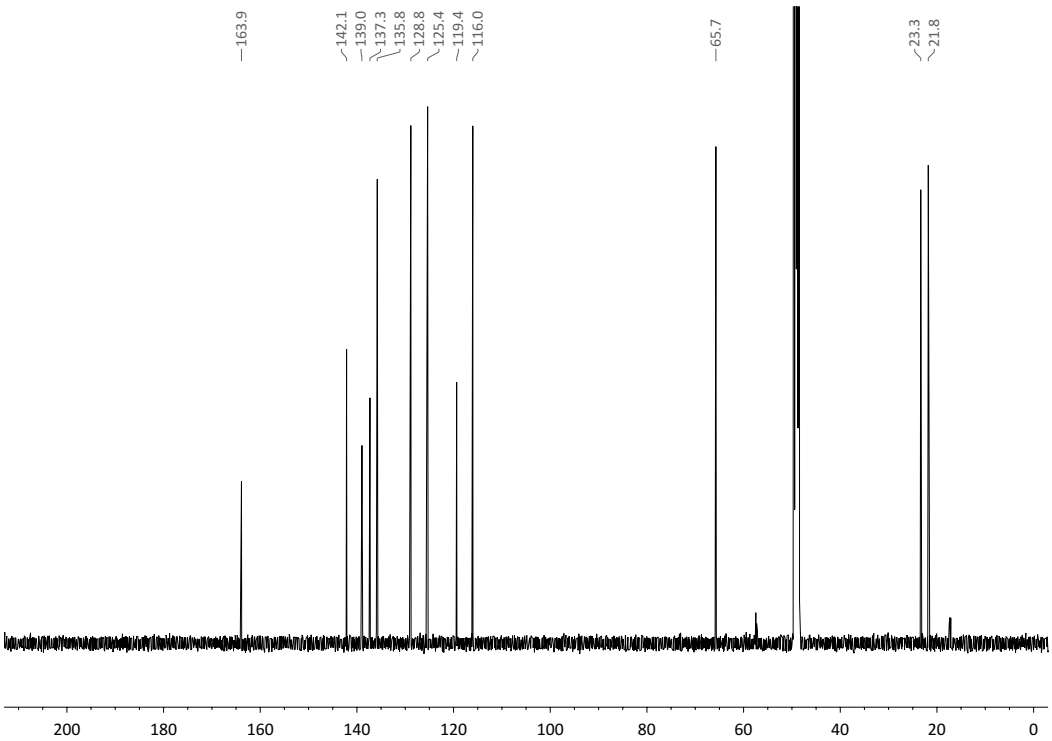


*1.5.6 3-(1-Hydroxyethyl)-7-methyl-2-quinolone (**7g**)*

^{1}H NMR (500 MHz, MeOD-d_4)

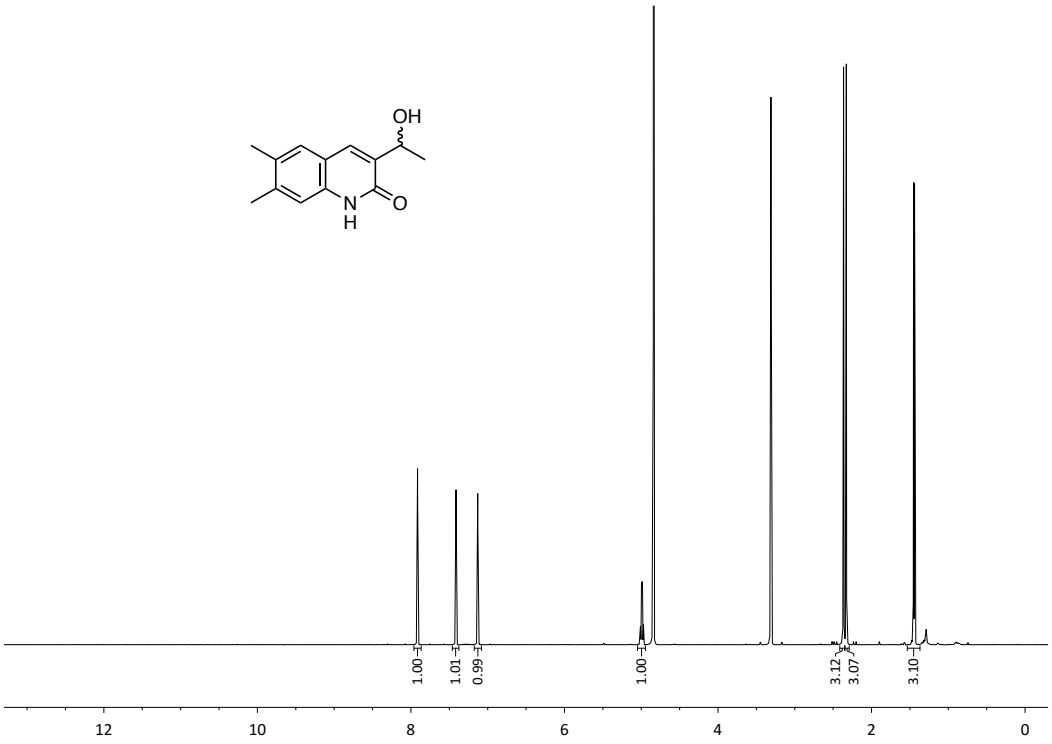


^{13}C NMR (126 MHz, MeOD-d_4)

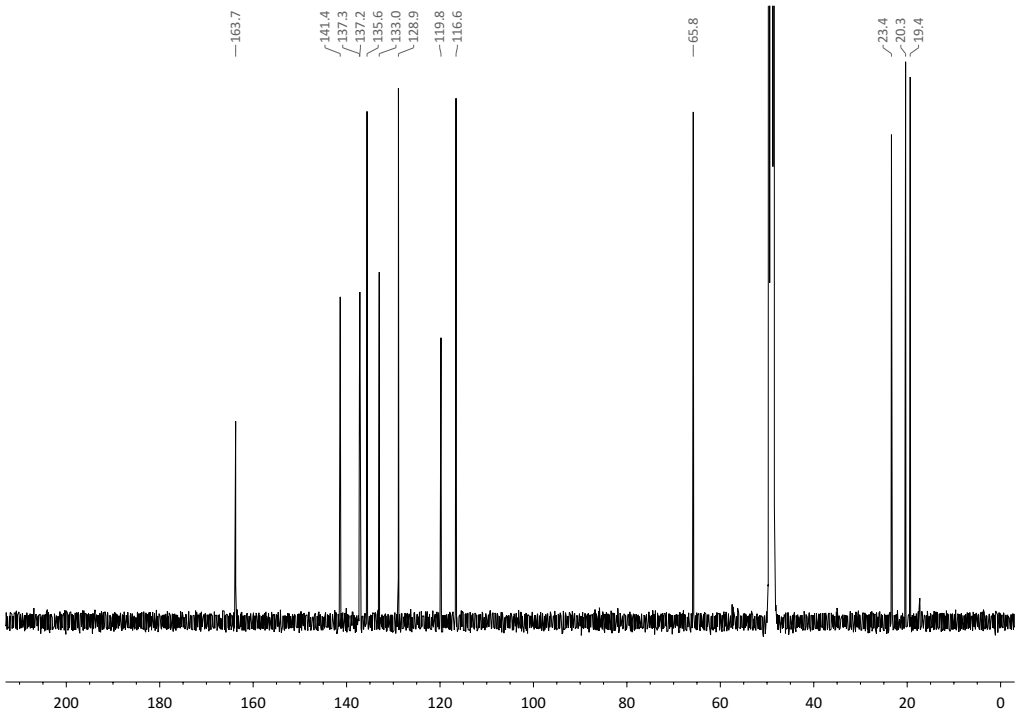


*1.5.7 3-(1-Hydroxyethyl)-6,7-dimethyl-2-quinolone (**7h**)*

^{1}H NMR (500 MHz, MeOD-d_4)

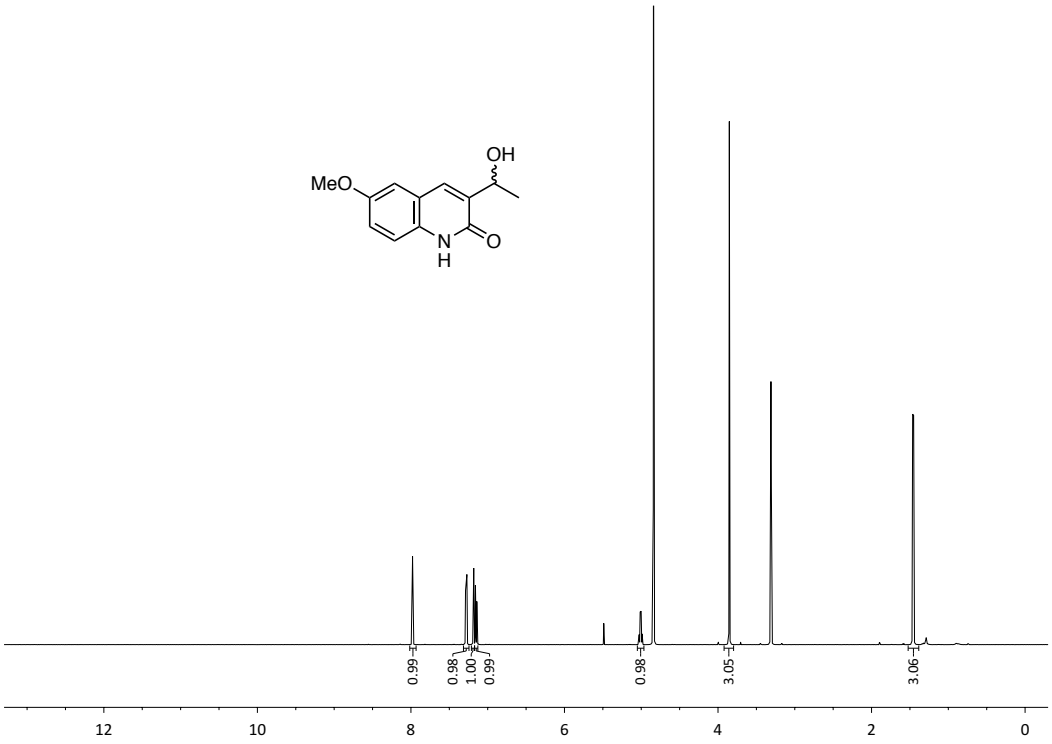


^{13}C NMR (126 MHz, MeOD-d_4)

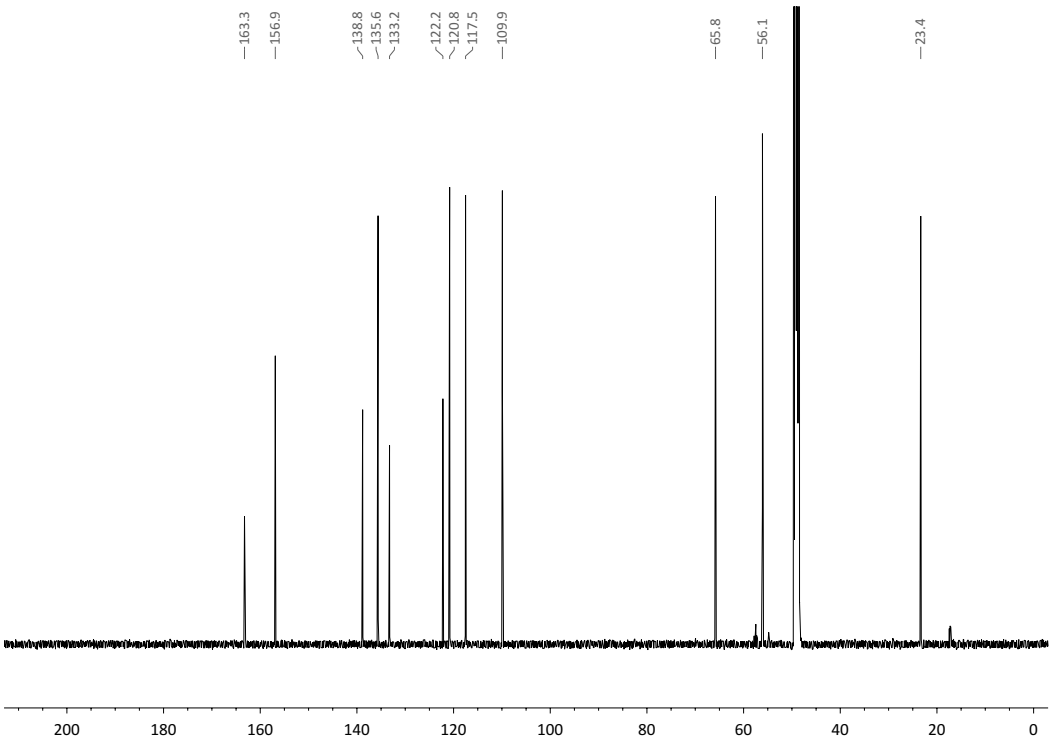


*1.5.8 3-(1-Hydroxyethyl)-6-methoxy-2-quinolone (**7i**)*

^{1}H NMR (500 MHz, MeOD-d_4)

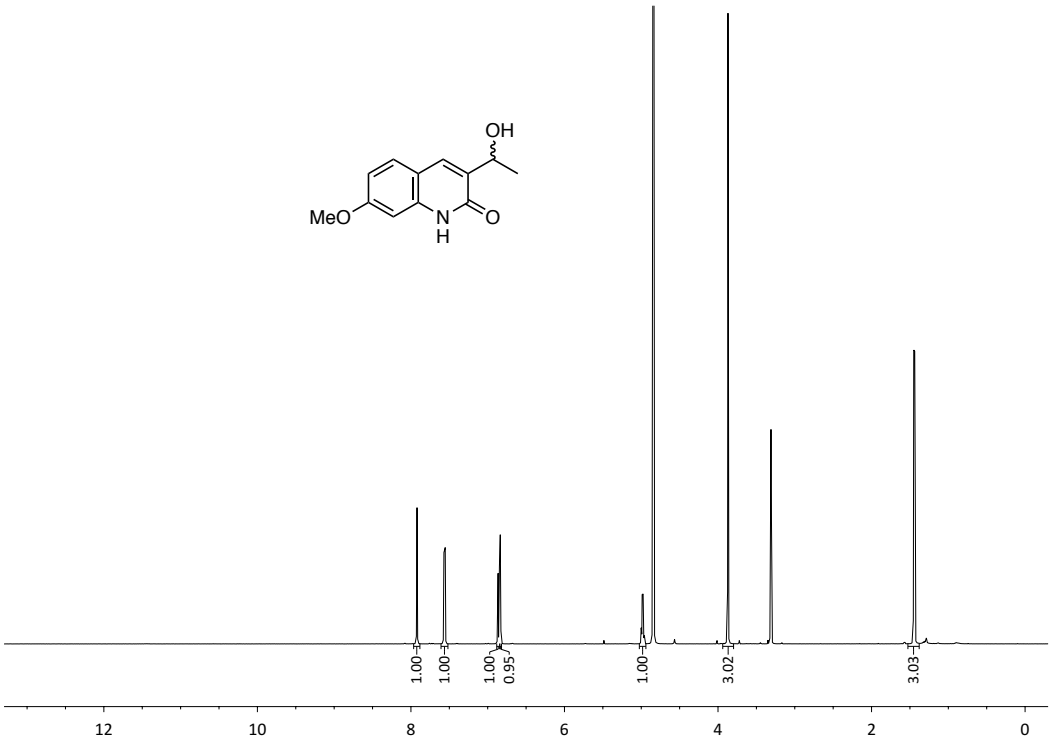


^{13}C NMR (126 MHz, MeOD-d_4)

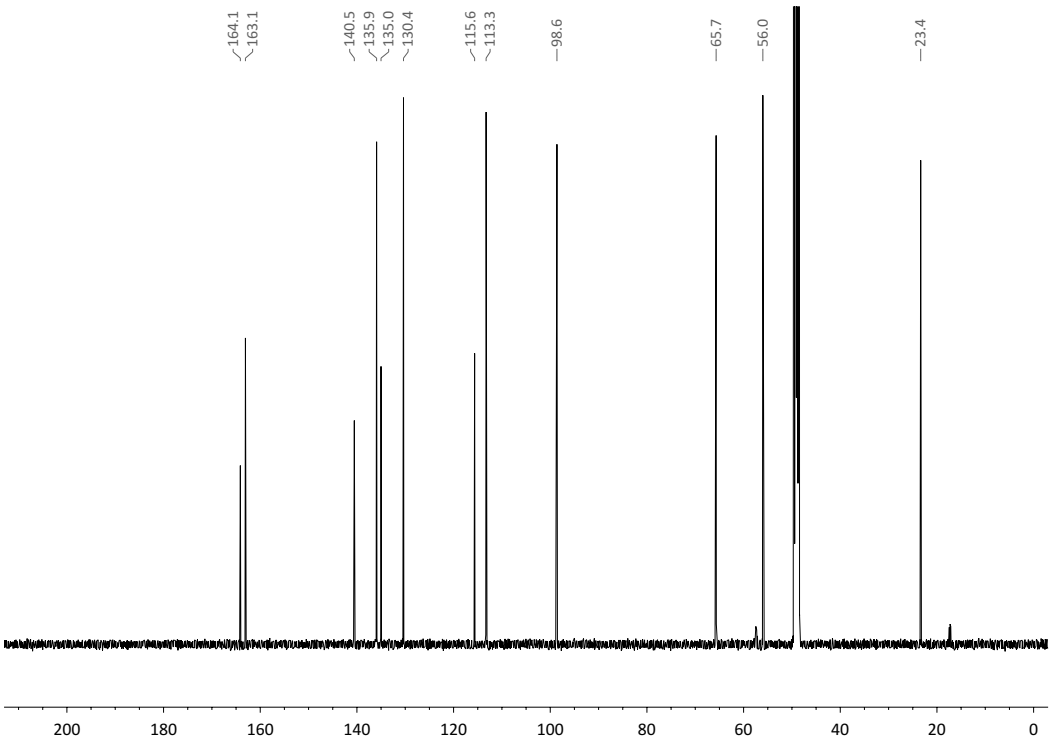


*1.5.9 3-(1-Hydroxyethyl)-7-methoxy-2-quinolone (**7j**)*

^{1}H NMR (500 MHz, MeOD-d_4)

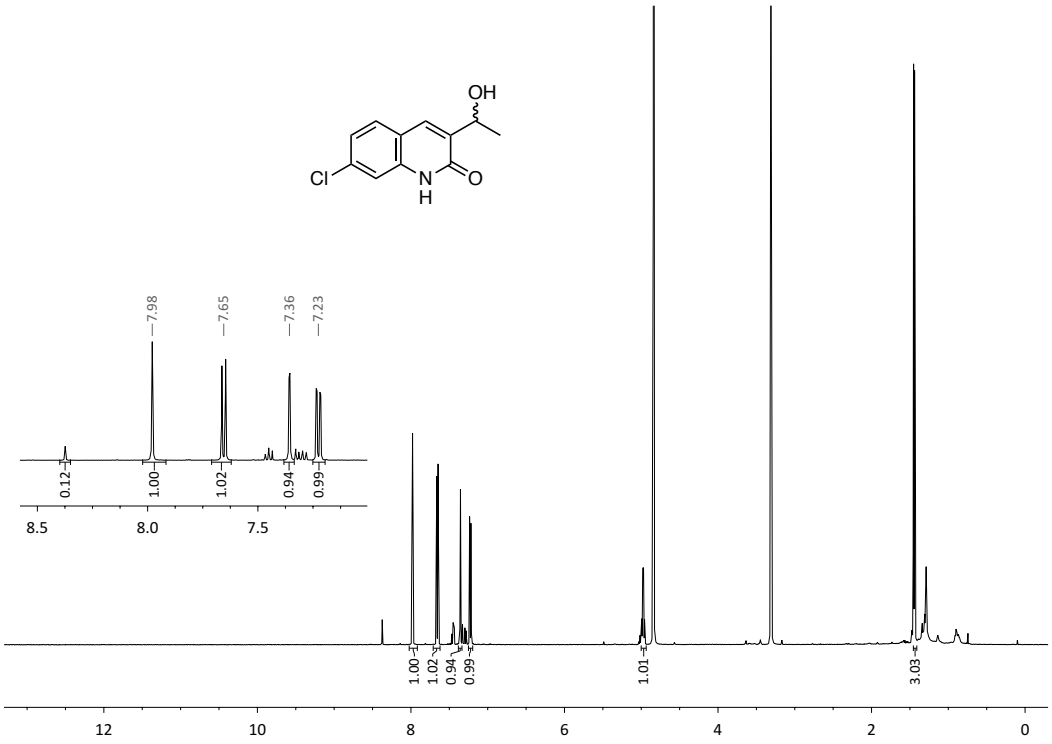


^{13}C NMR (126 MHz, MeOD-d_4)

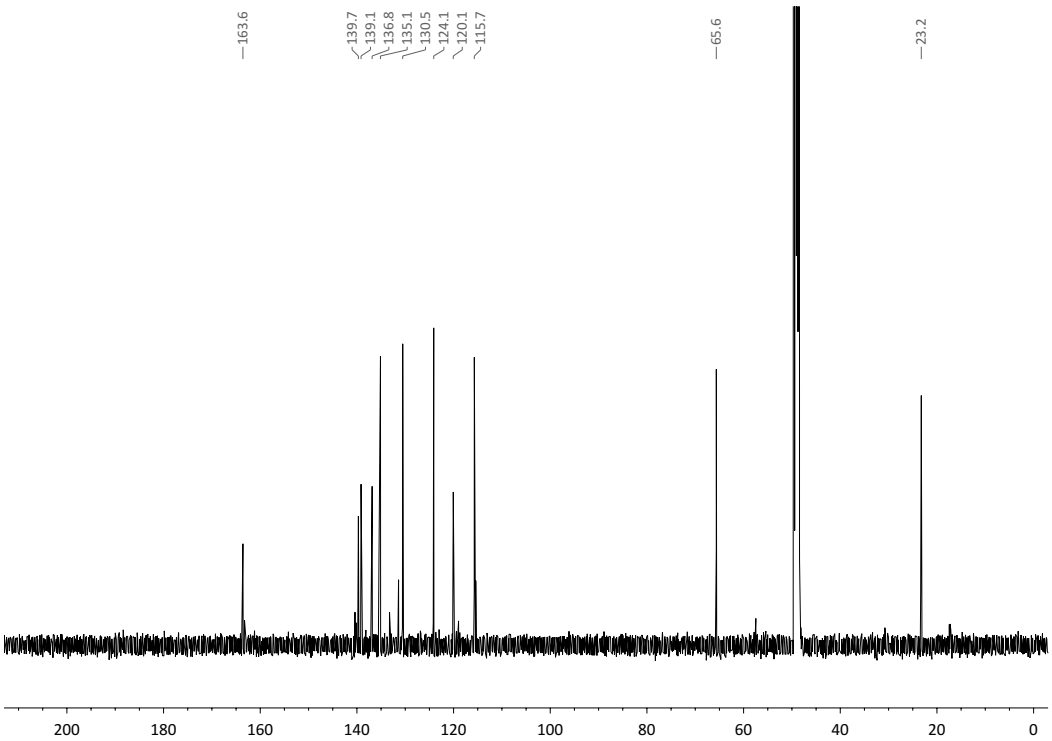


*1.5.10 7-Chloro-3-(1-hydroxyethyl)-2-quinolone (**7k**)*

^{1}H NMR (500 MHz, MeOD-d_4)

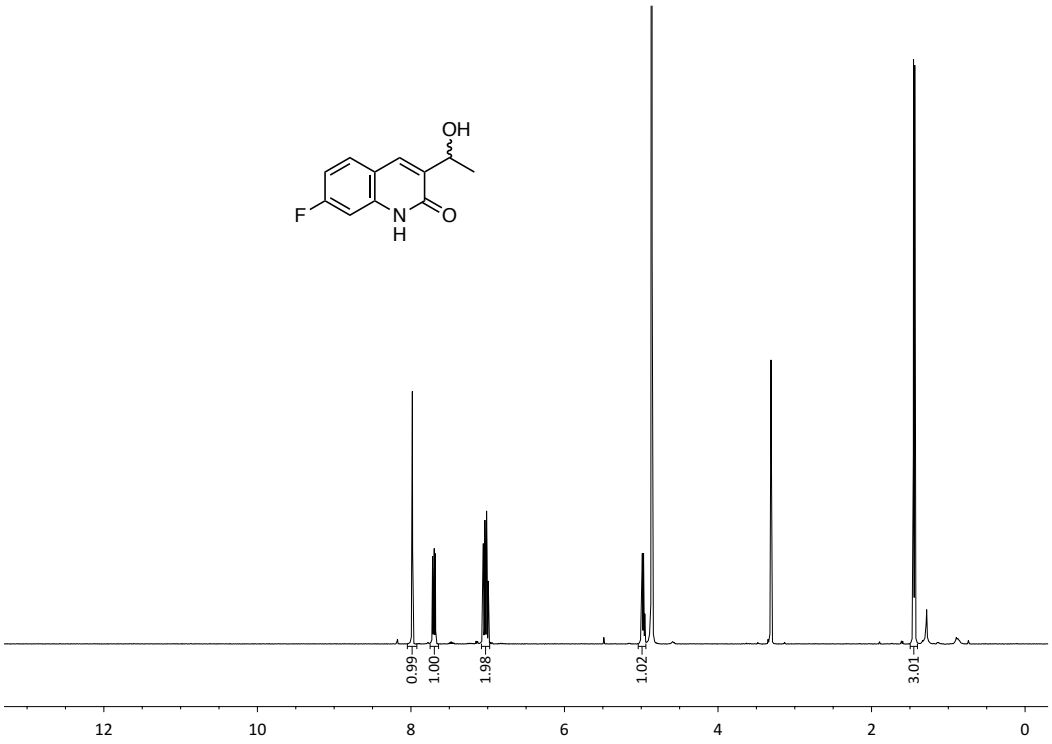


^{13}C NMR (126 MHz, MeOD-d_4)

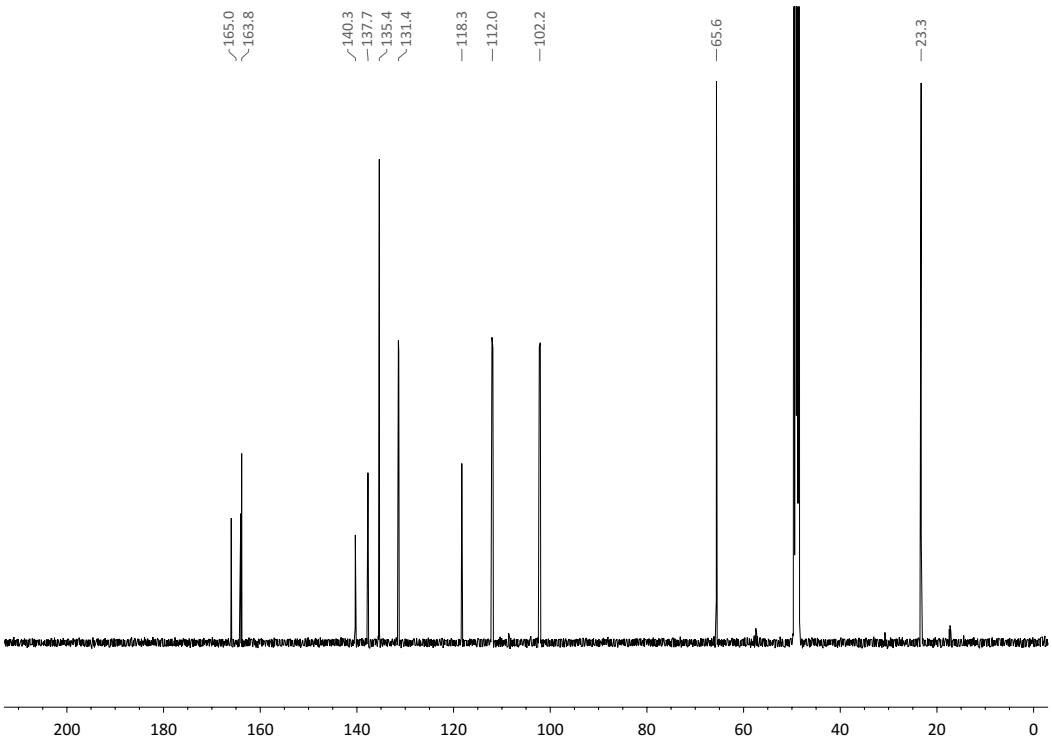


*1.5.11 7-Fluoro-3-(1-hydroxyethyl)-2-quinolone (**7l**)*

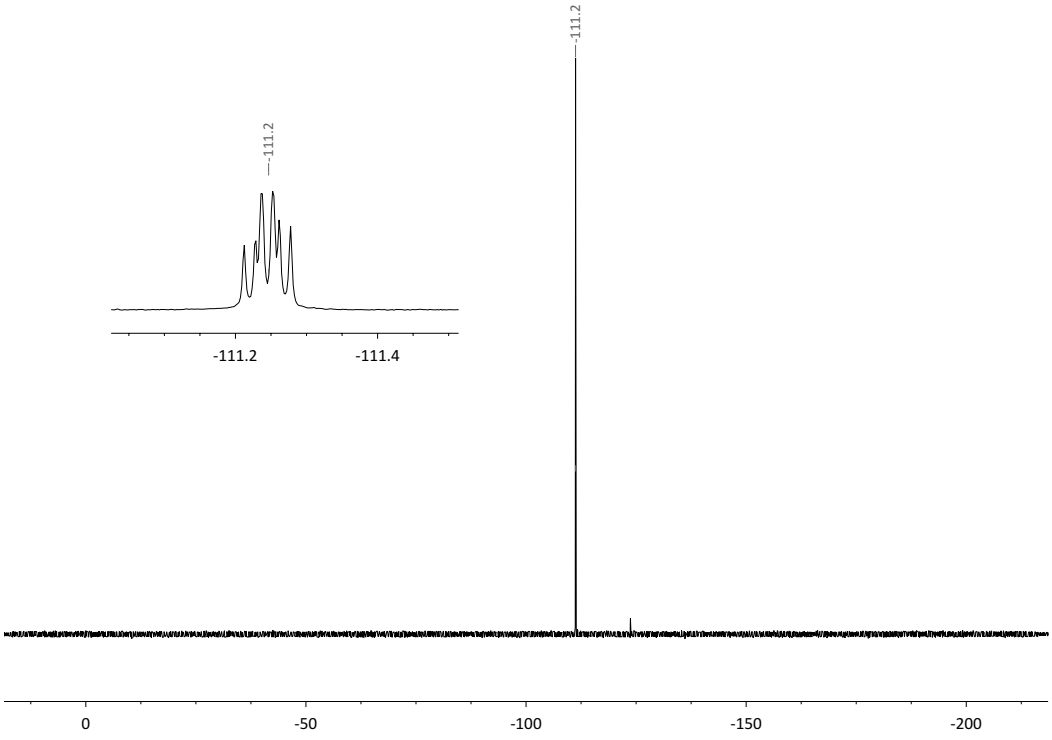
^{1}H NMR (500 MHz, MeOD-d_4)



^{13}C NMR (126 MHz, MeOD-d_4)

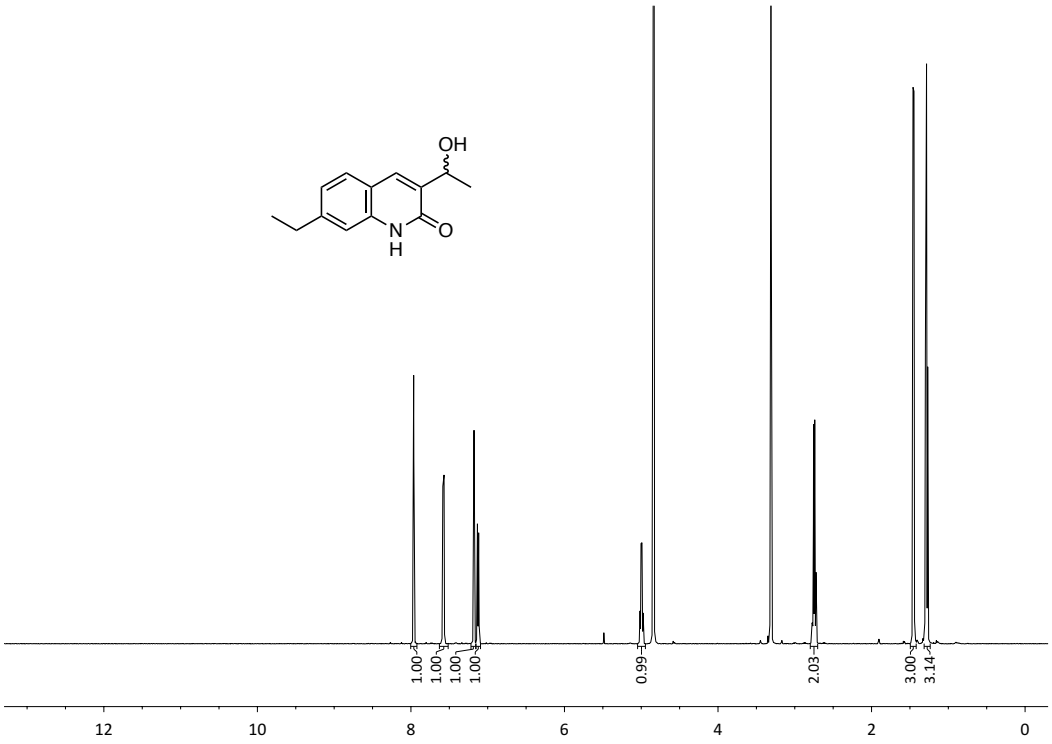


^{19}F NMR (376 MHz, MeOD-d_4)

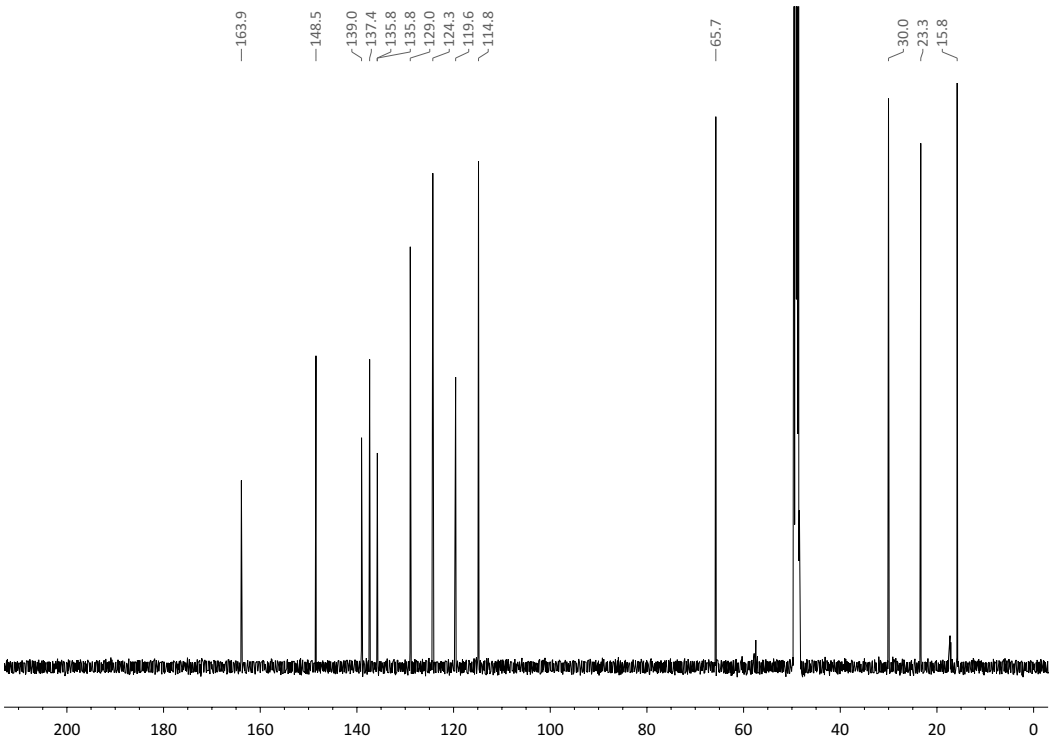


*1.5.12 3-(1-Hydroxyethyl)-7-ethyl-2-quinolone (**7m**)*

^{1}H NMR (500 MHz, MeOD-d_4)

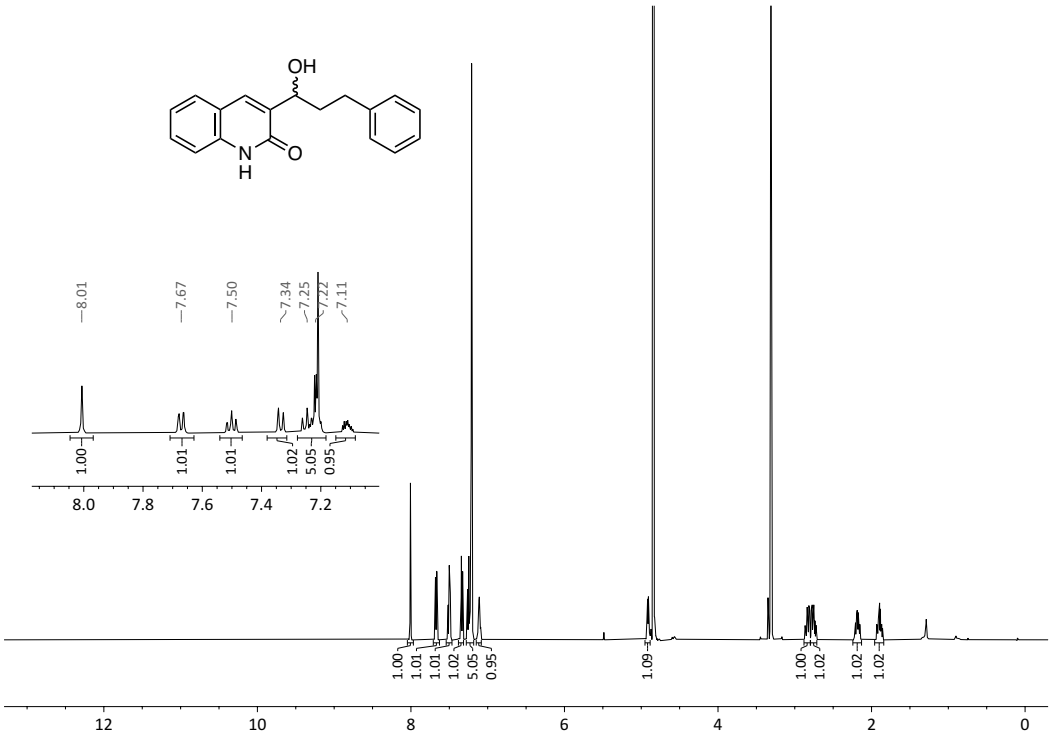


^{13}C NMR (126 MHz, MeOD-d_4)

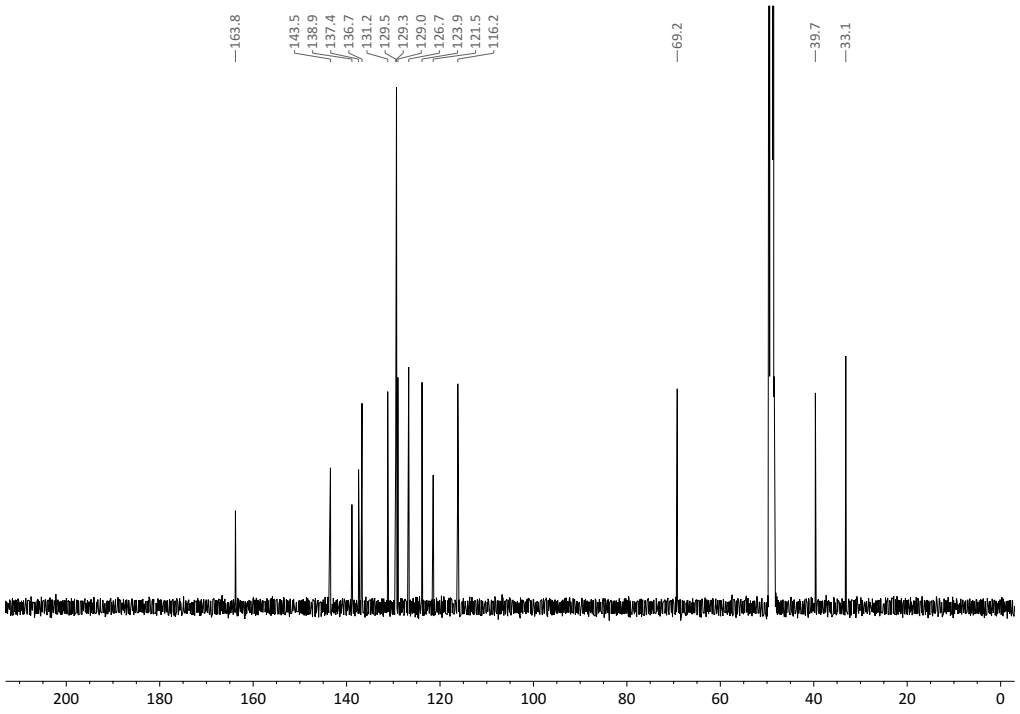


*1.5.13 3-(1-Hydroxy-3-phenylpropyl)-2-quinolone (**7o**)*

^{1}H NMR (500 MHz, MeOD-d_4)



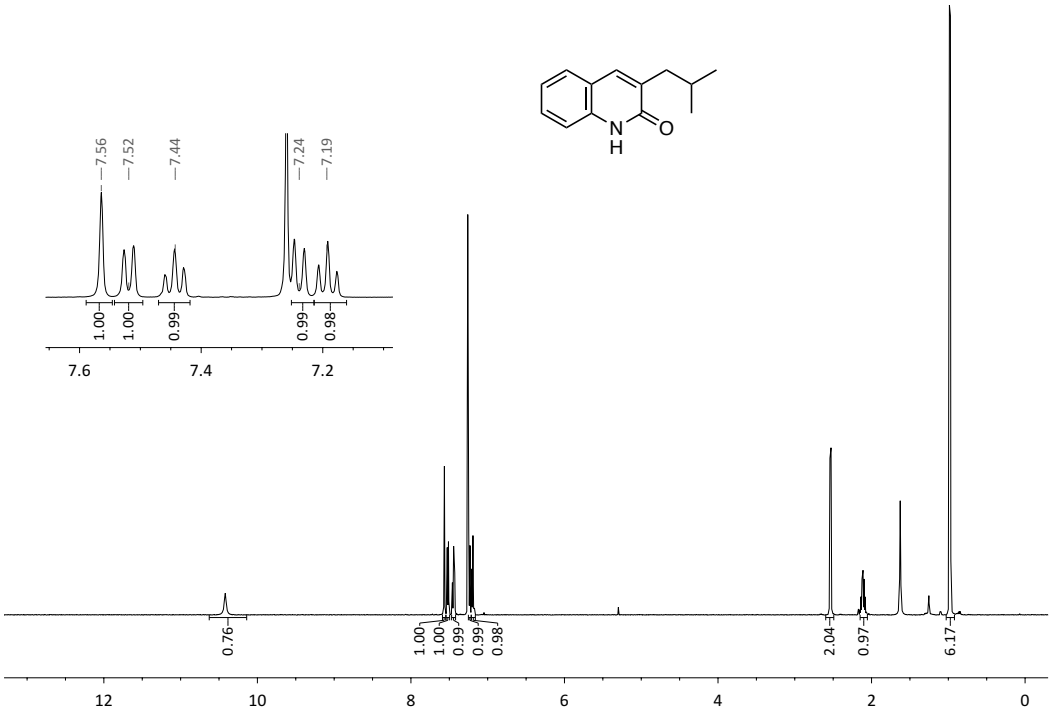
^{13}C NMR (126 MHz, MeOD-d_4)



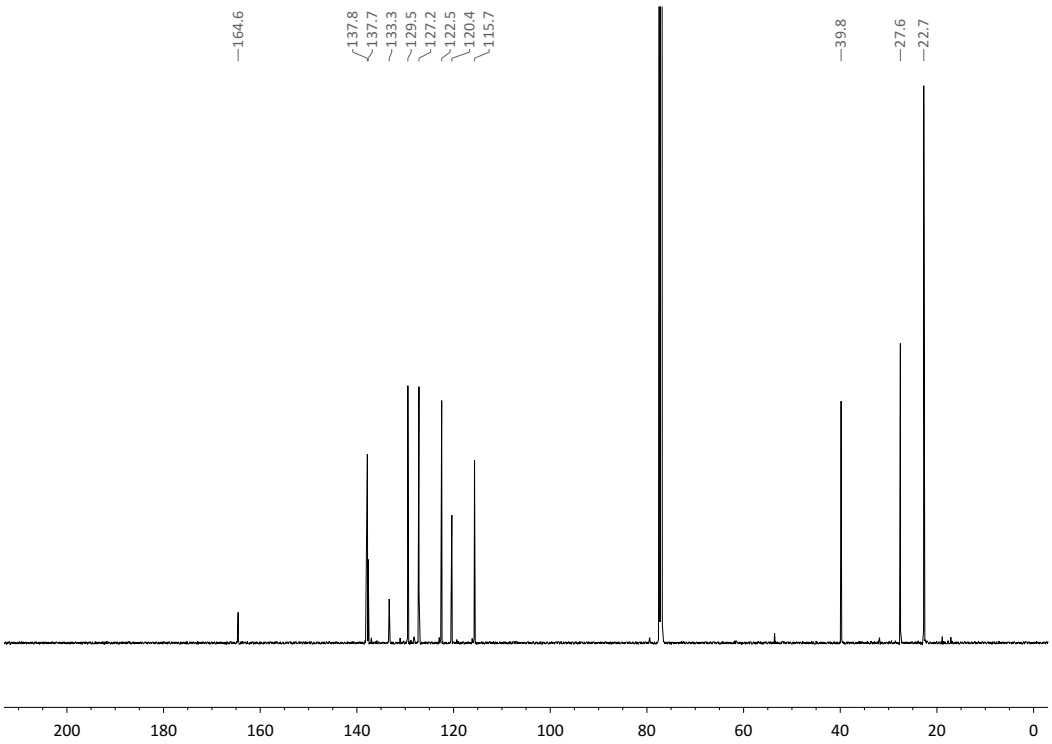
1.6 3-Alkyl-2-quinolones 6

*1.6.1 3-Isobutyl-2-quinolone (**6e**)*

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

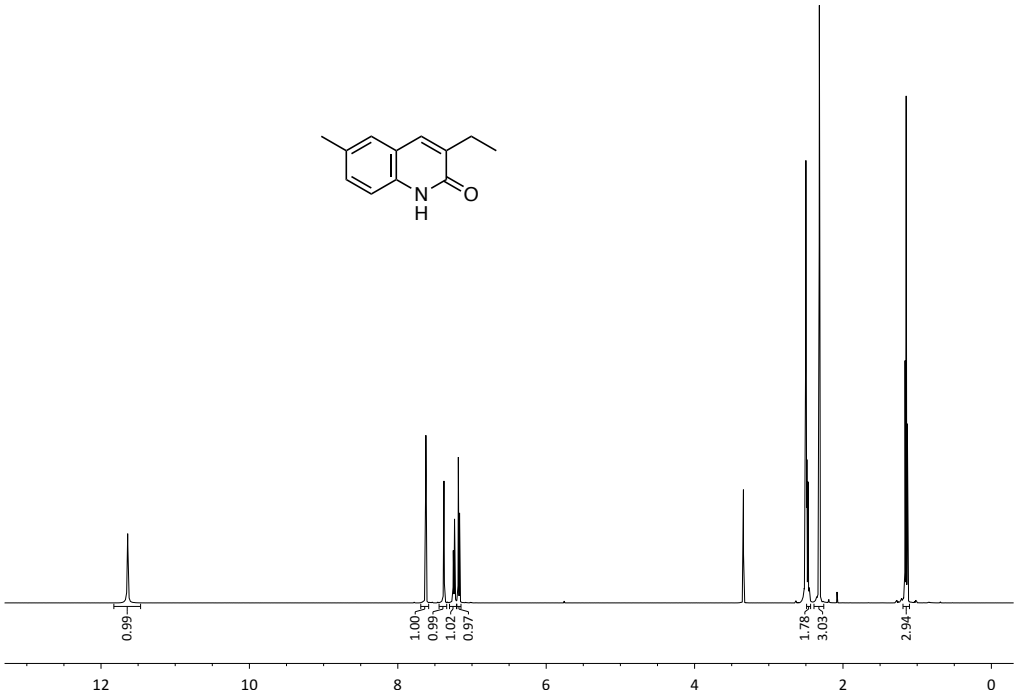


^{13}C NMR (126 MHz, $CDCl_3$)

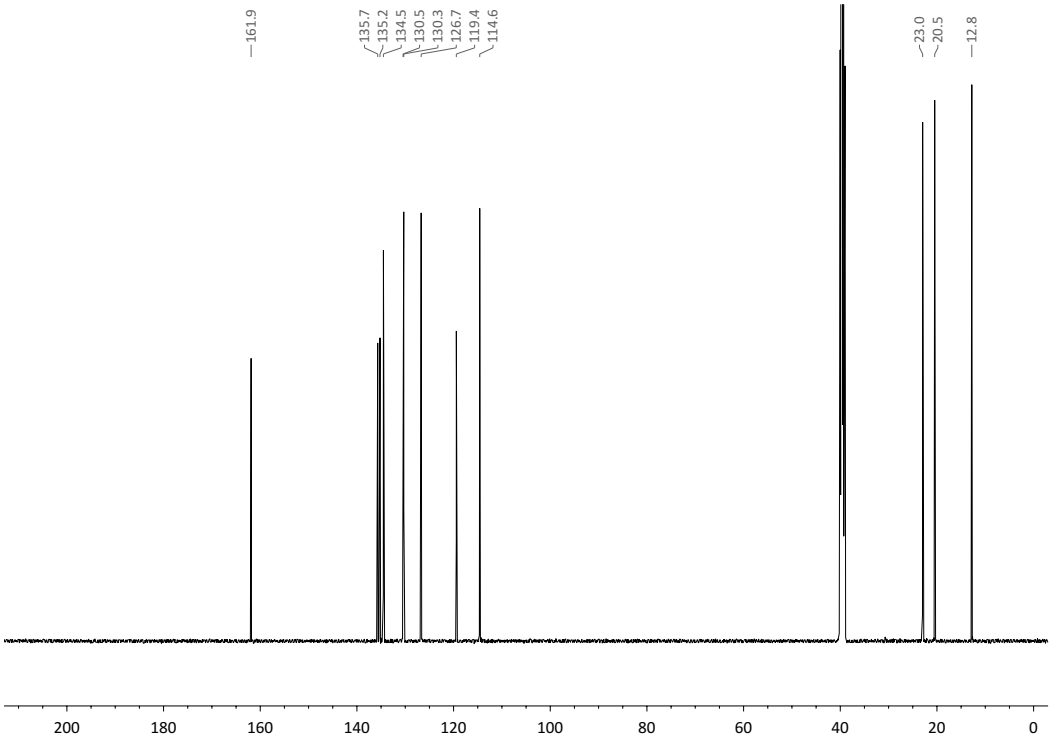


*1.6.2 3-Ethyl-6-methyl-2-quinolone (**6f**)*

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

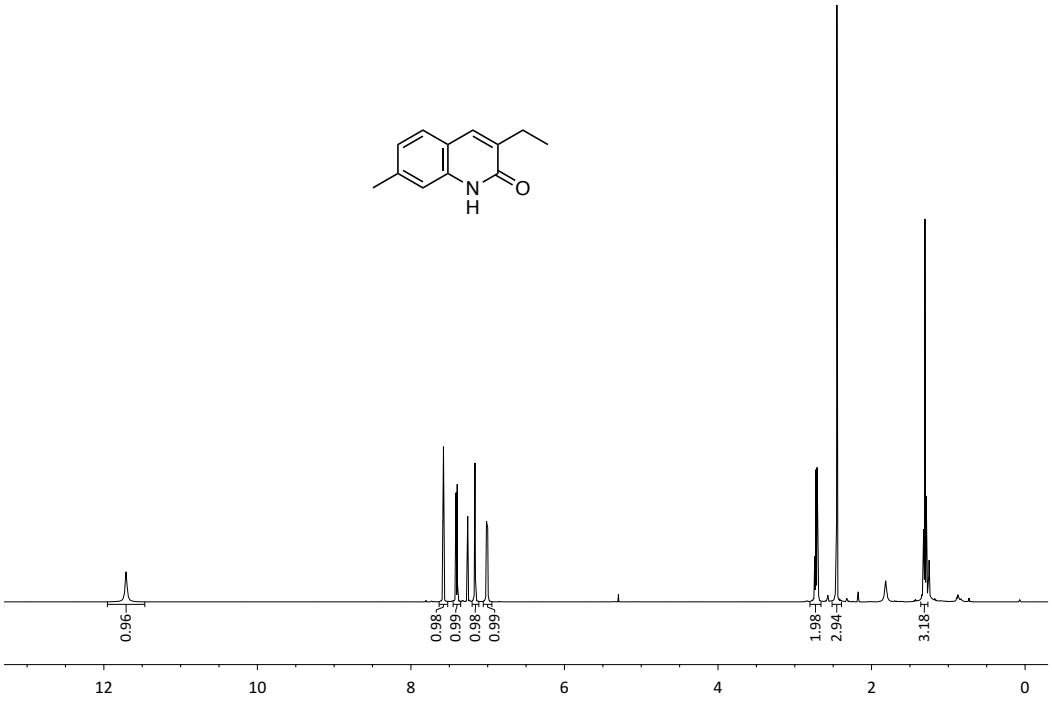


^{13}C NMR (126 MHz, DMSO-d_6)

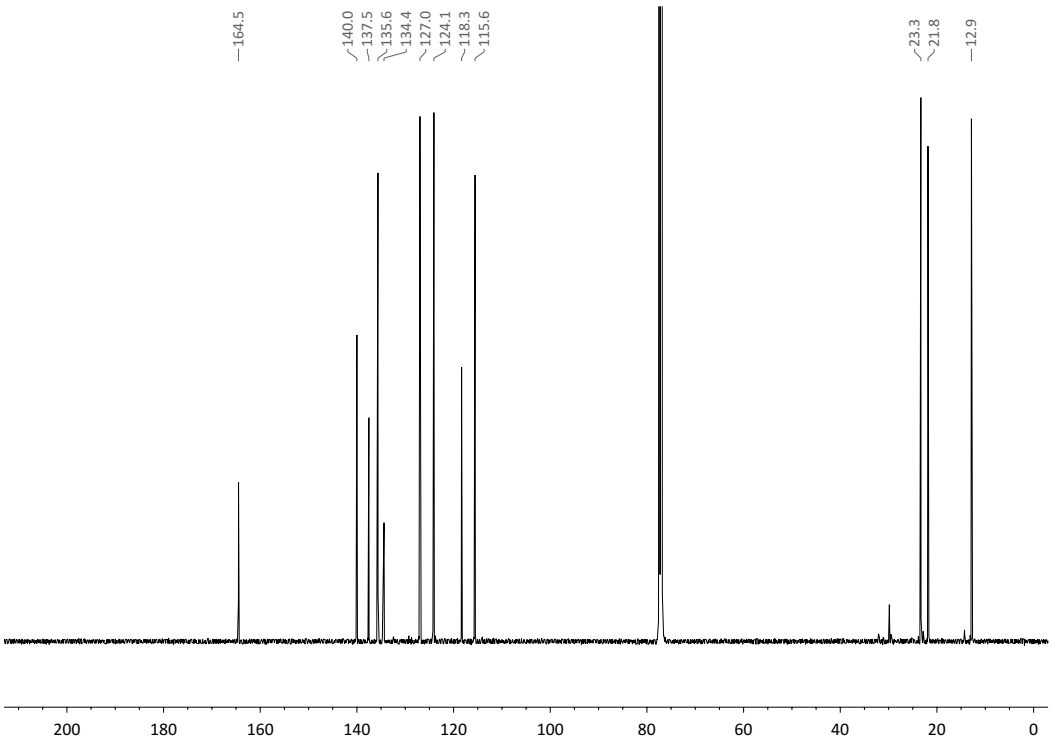


*1.6.3 3-Ethyl-7-methyl-2-quinolone (**6g**)*

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

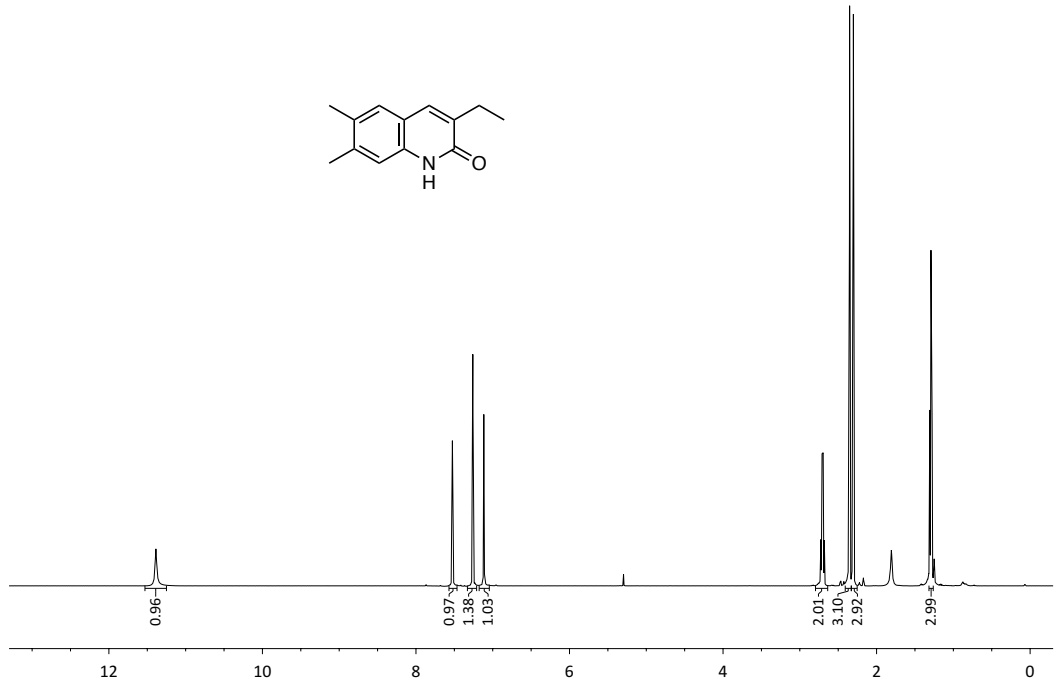


^{13}C NMR (126 MHz, $CDCl_3$)

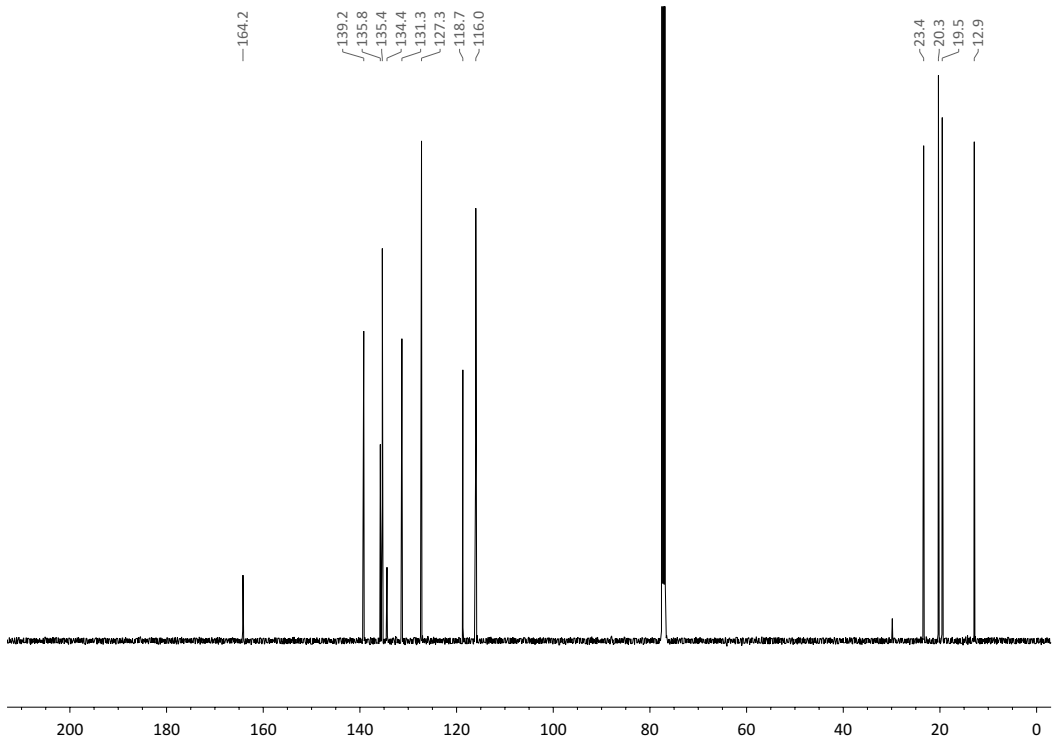


*1.6.4 3-Ethyl-6,7-dimethyl-2-quinolone (**6h**)*

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

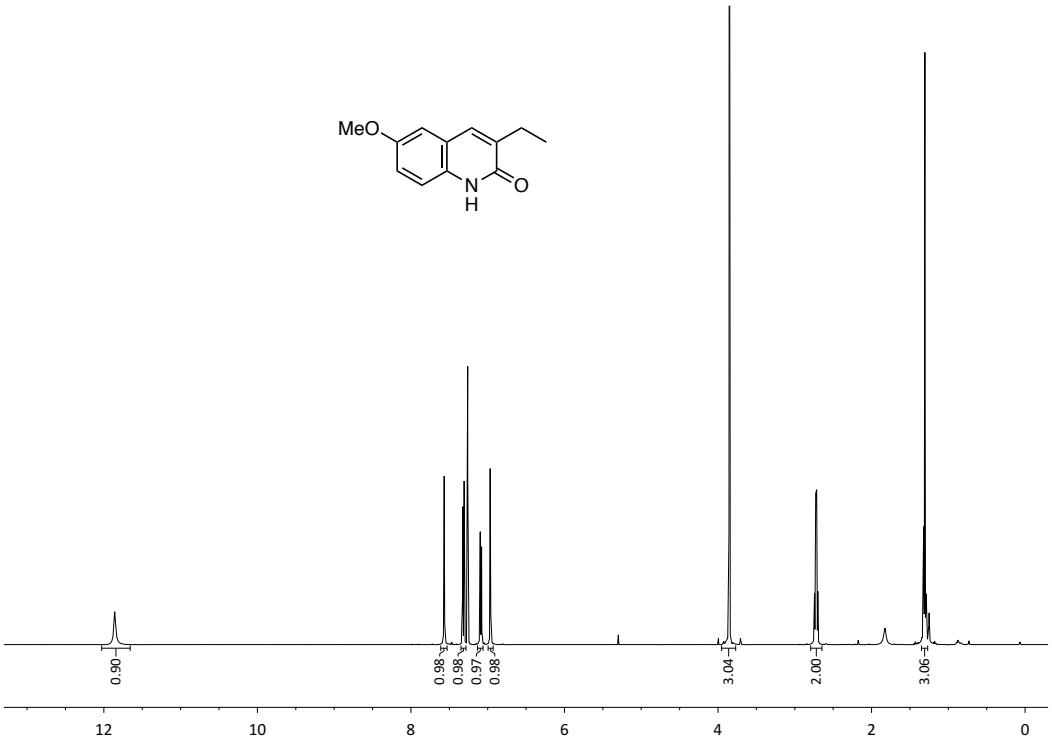


^{13}C NMR (126 MHz, $CDCl_3$)

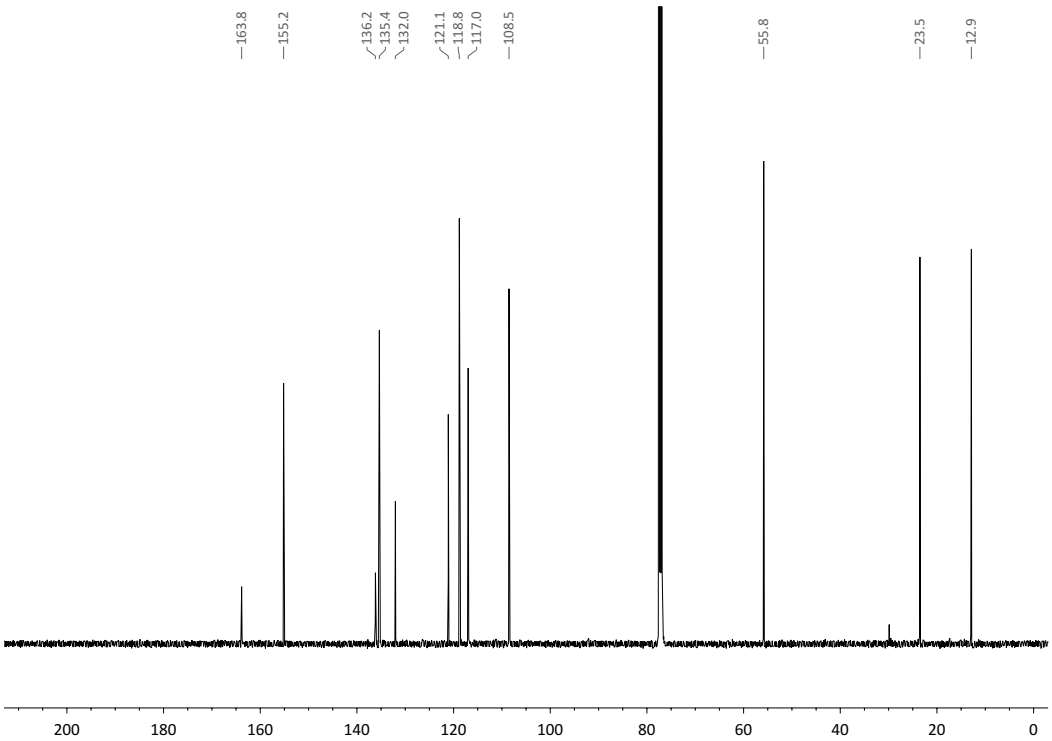


*1.6.5 3-Ethyl-6-methoxy-2-quinolone (**6i**)*

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

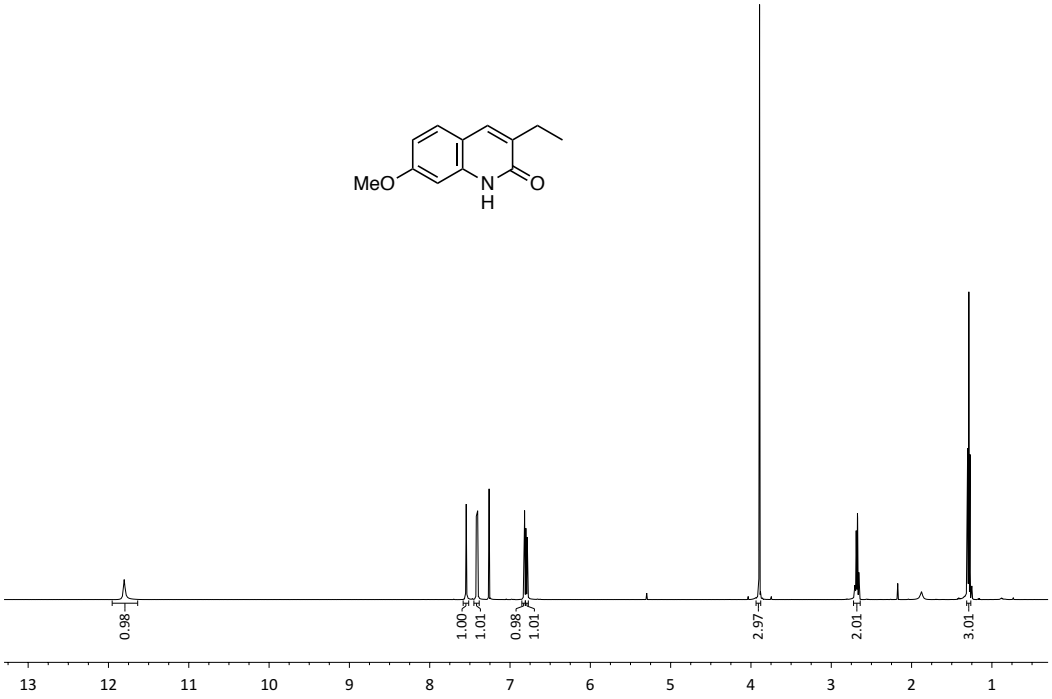


^{13}C NMR (126 MHz, $CDCl_3$)

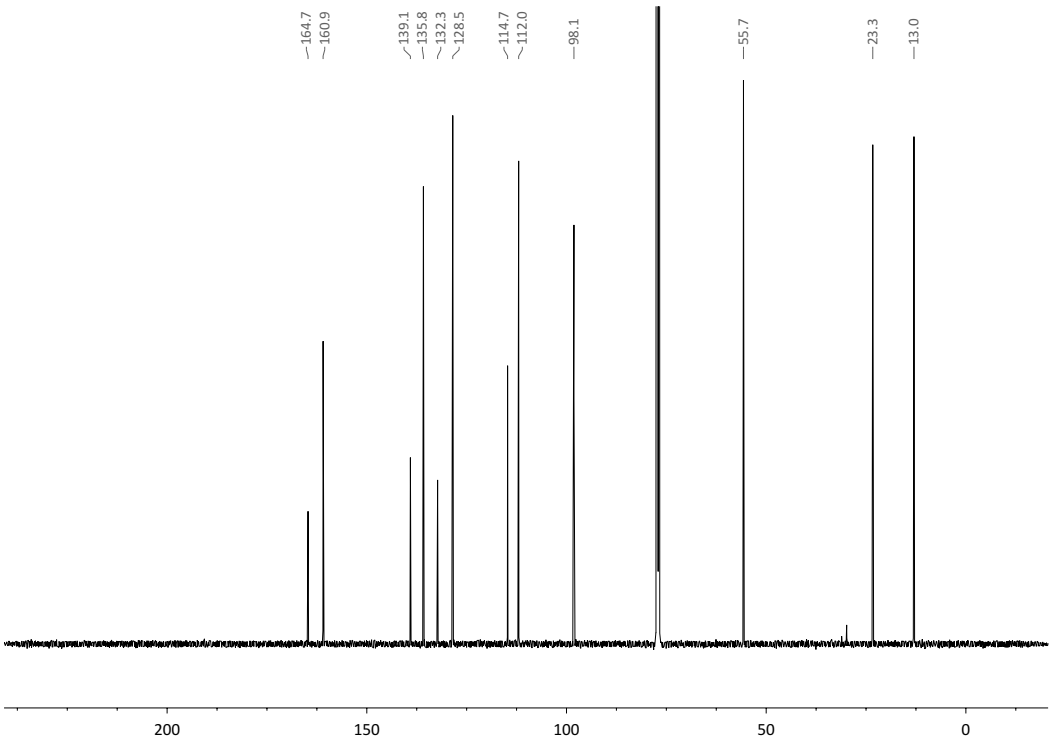


*1.6.6 3-Ethyl-7-methoxy-2-quinolone (**6j**)*

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

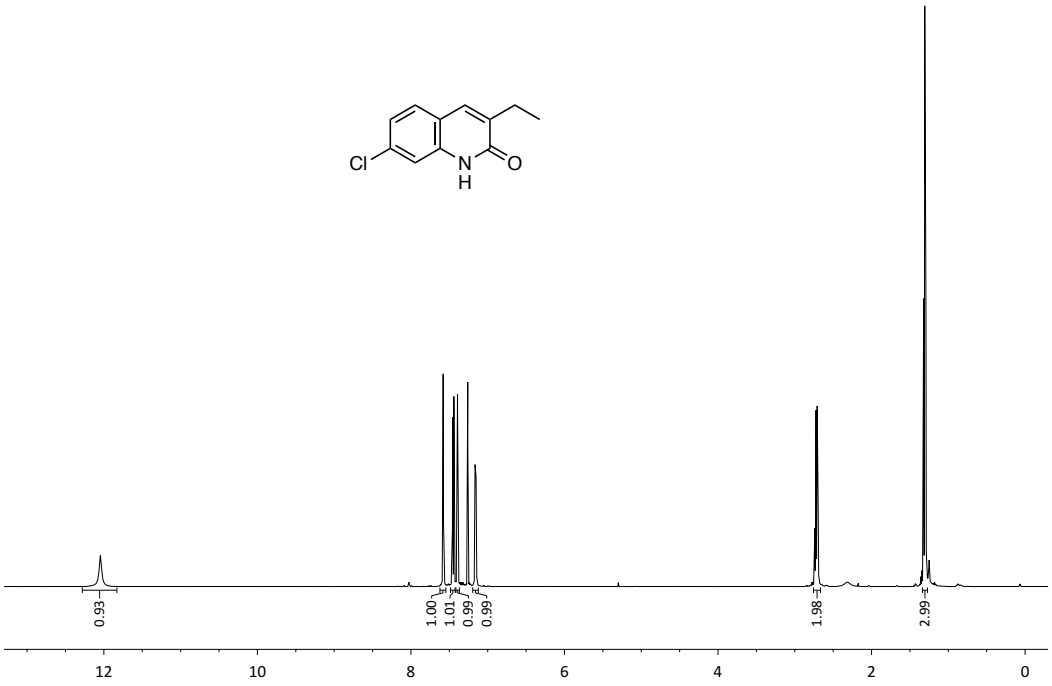


^{13}C NMR (126 MHz, $CDCl_3$)

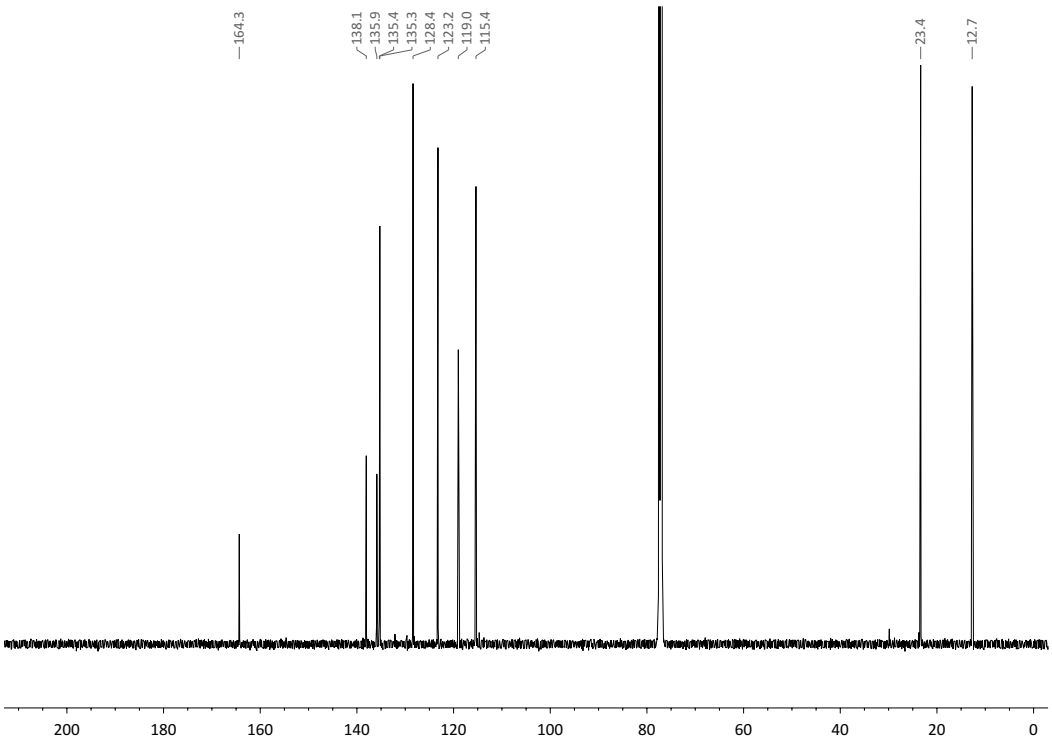


*1.6.7 3-Ethyl-7-chloro-2-quinolone (**6k**)*

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

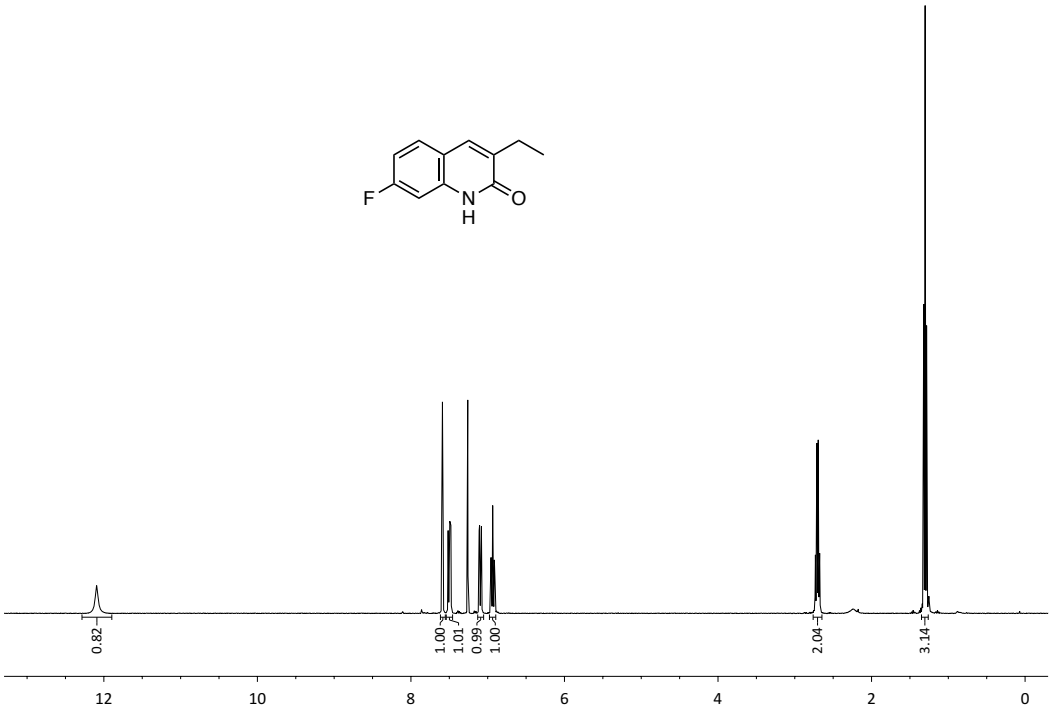


^{13}C NMR (126 MHz, $CDCl_3$)

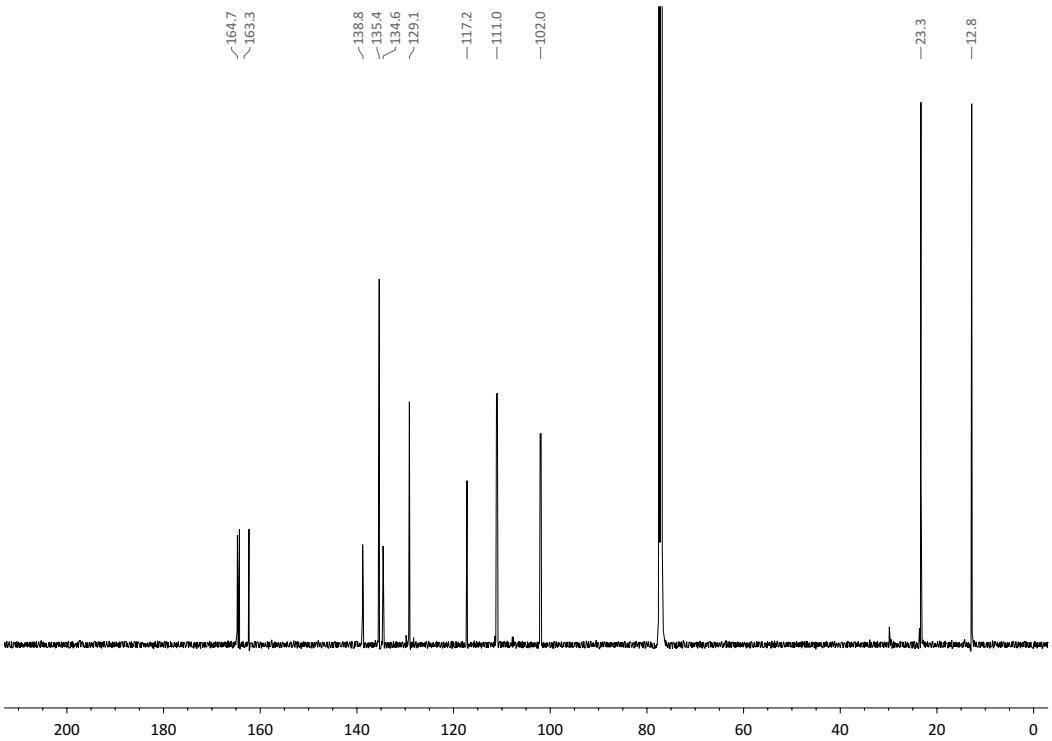


*1.6.8 3-Ethyl-7-fluoro-2-quinolone (**6l**)*

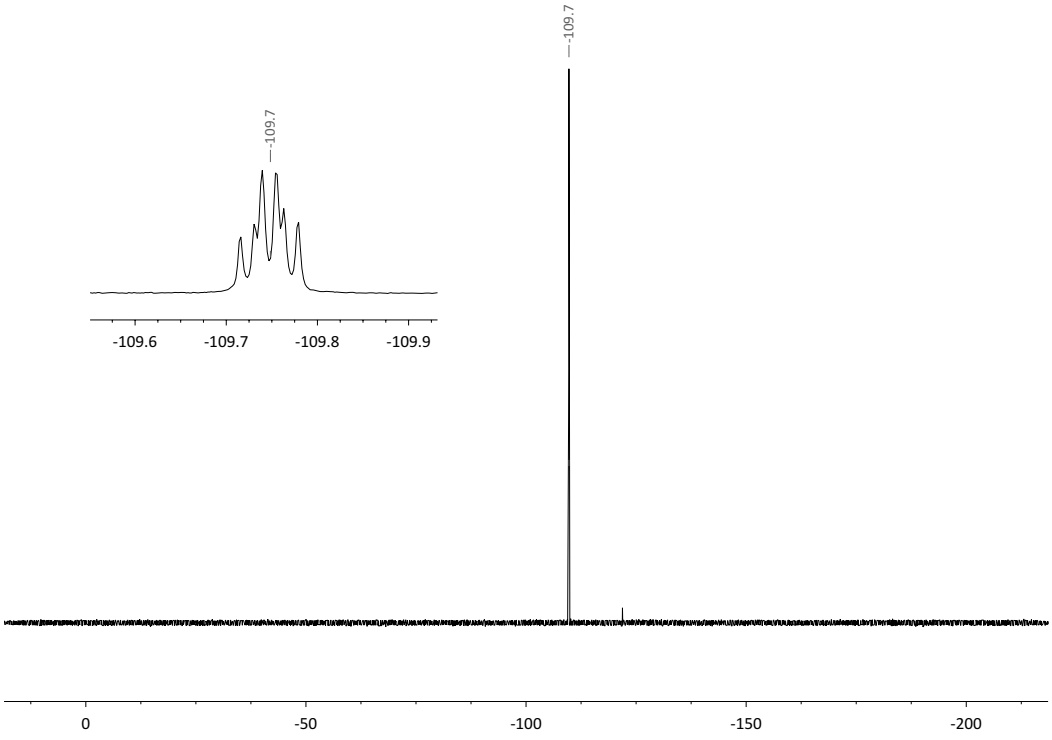
^{1}H NMR (500 MHz, $CDCl_3$)



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

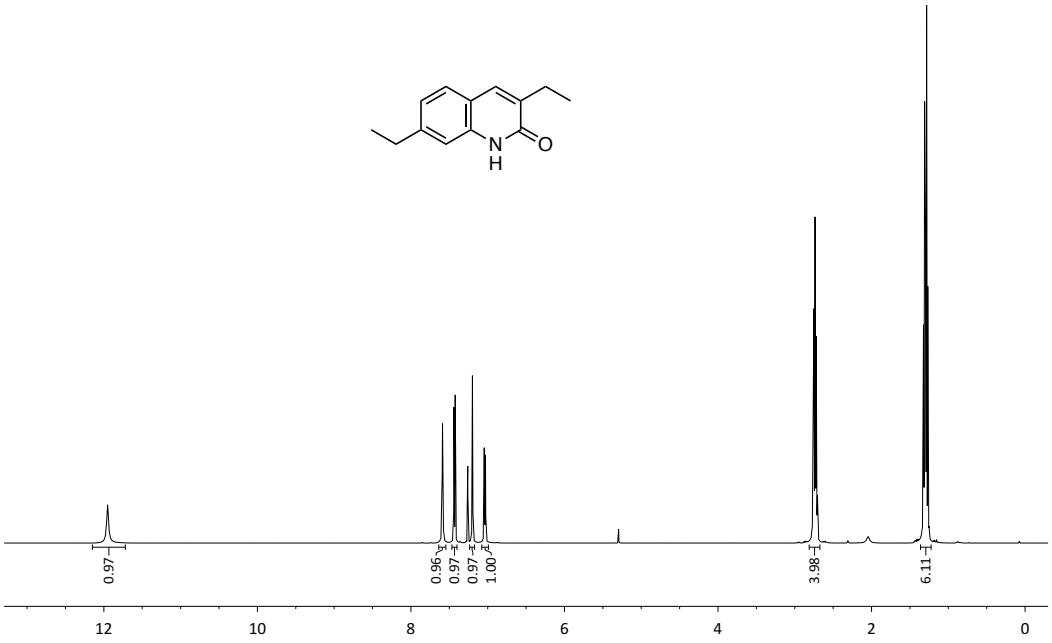


^{19}F NMR (376 MHz, $CDCl_3$)

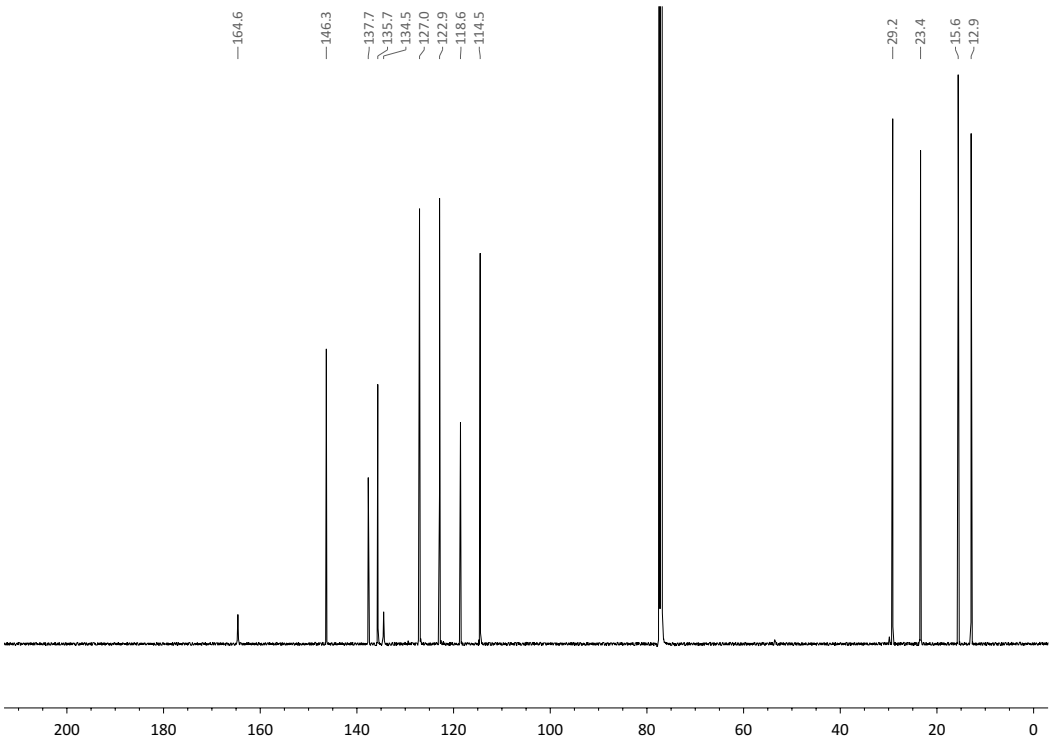


*1.6.9 3-Ethyl-7-ethyl-2-quinolone (**6m**)*

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

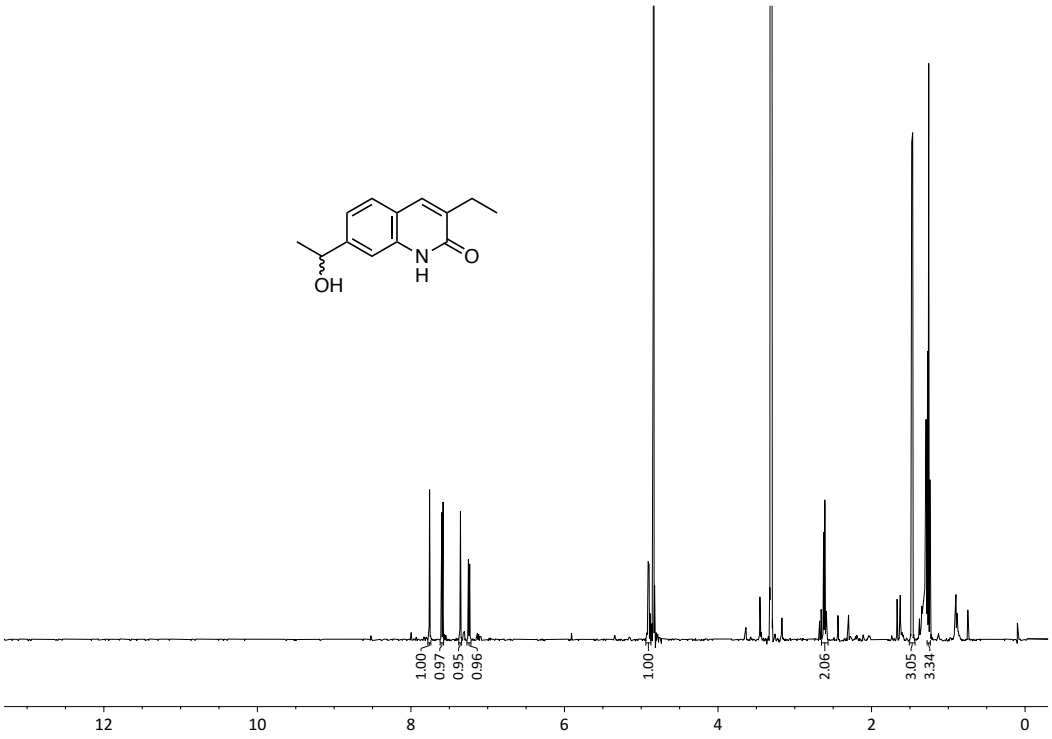


^{13}C NMR (126 MHz, $CDCl_3$)

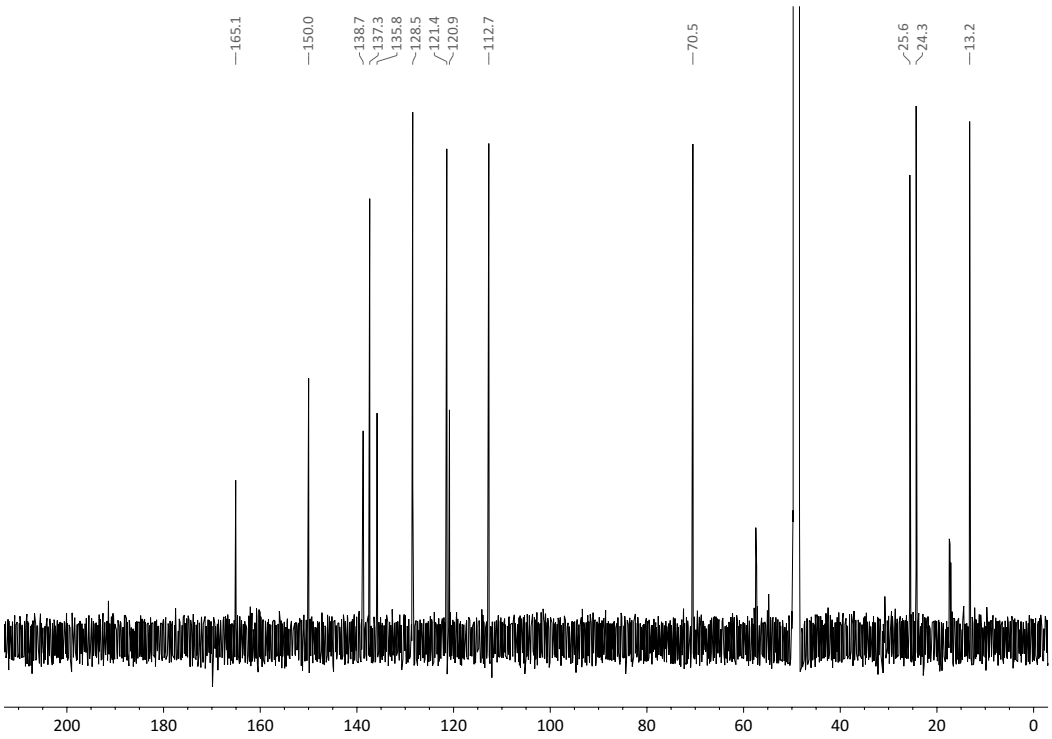


*1.6.10 3-Ethyl-7-(1-hydroxyethyl)-2-quinolone (**6n**)*

^{1}H NMR (500 MHz, MeOD-d_4)

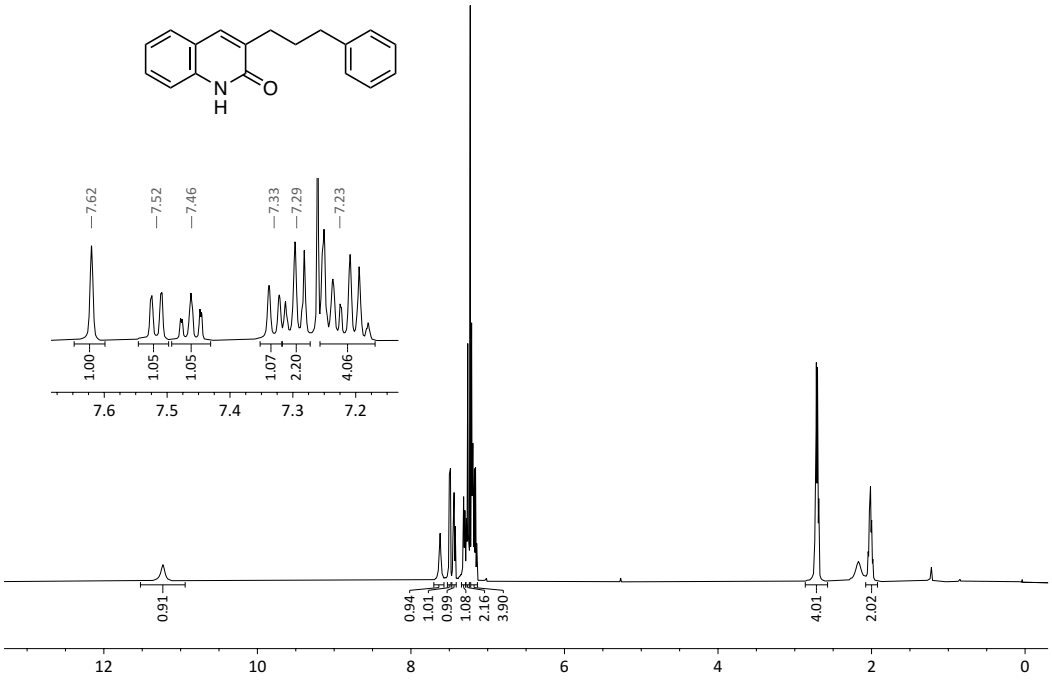


^{13}C NMR (126 MHz, MeOD-d_4)

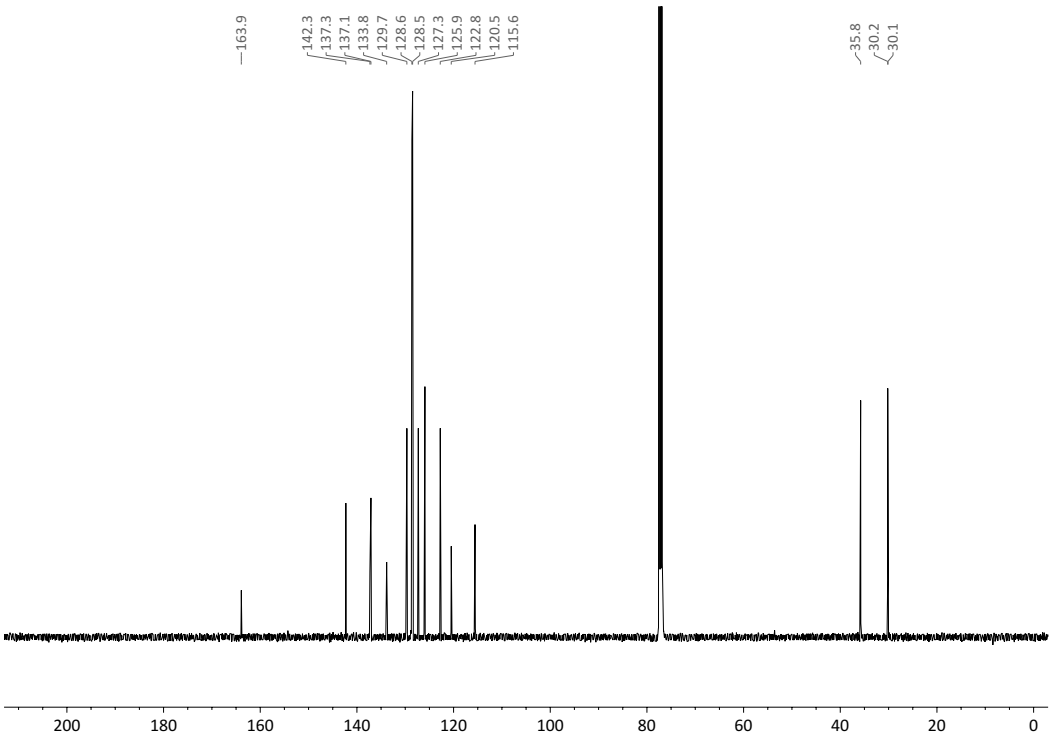


*1.6.11 3-(3-Phenylpropyl)-2-quinolone (**6o**)*

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

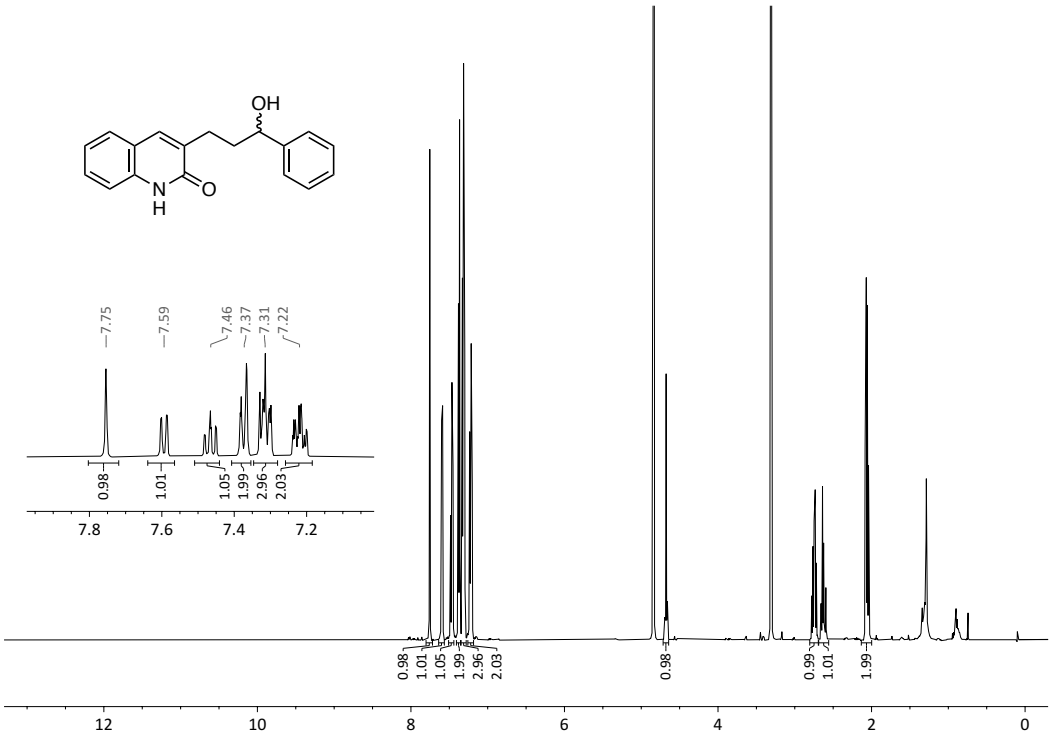


^{13}C NMR (126 MHz, $CDCl_3$)

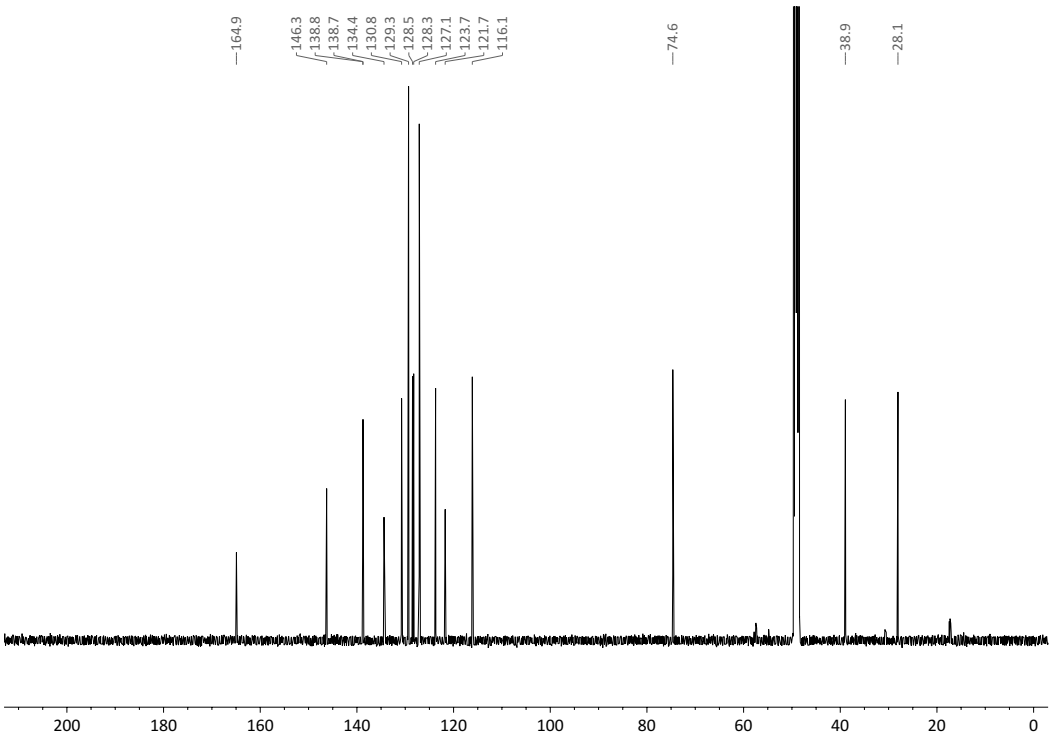


*1.6.12 3-(3-Hydroxy-3-phenylpropyl)-2-quinolone (**6p**)*

^{1}H NMR (500 MHz, MeOD-d_4)



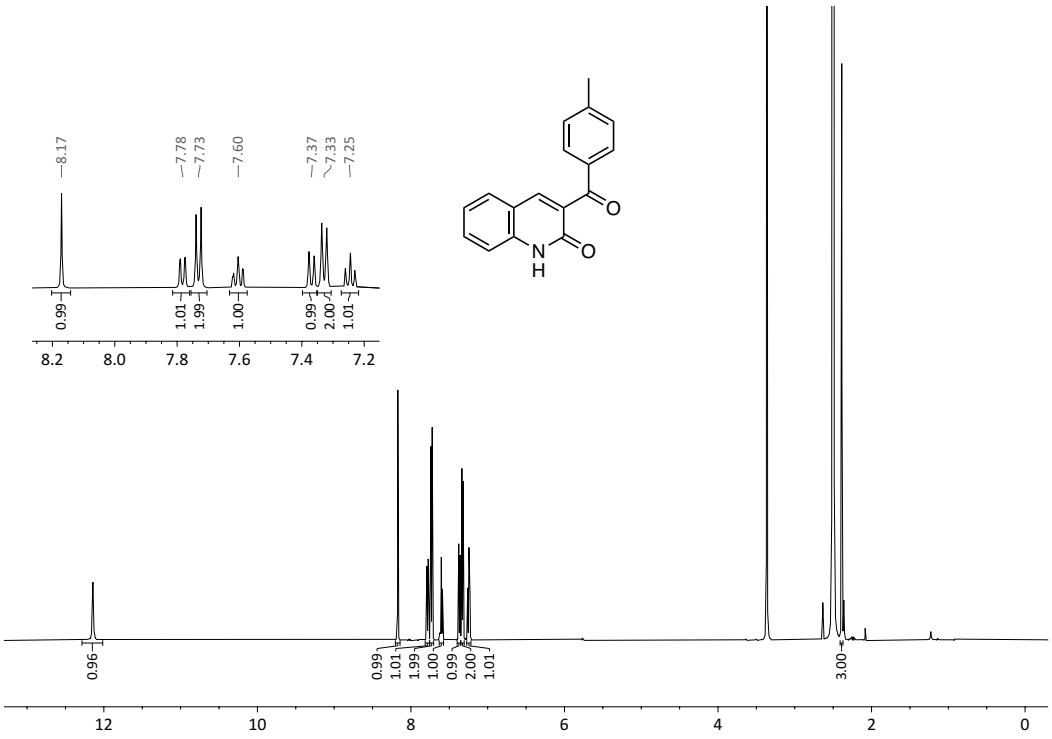
^{13}C NMR (126 MHz, MeOD-d_4)



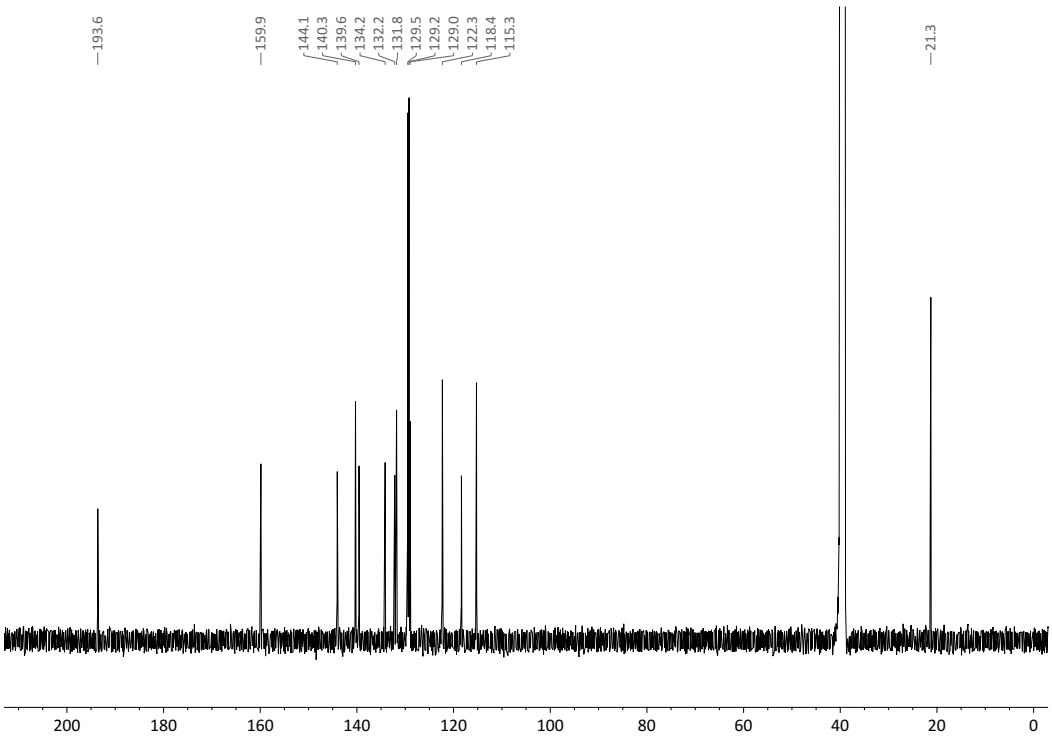
1.7 Other compounds

*1.7.1 3-(4-Methylbenzoyl)-2-quinolone (**4a**)*

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

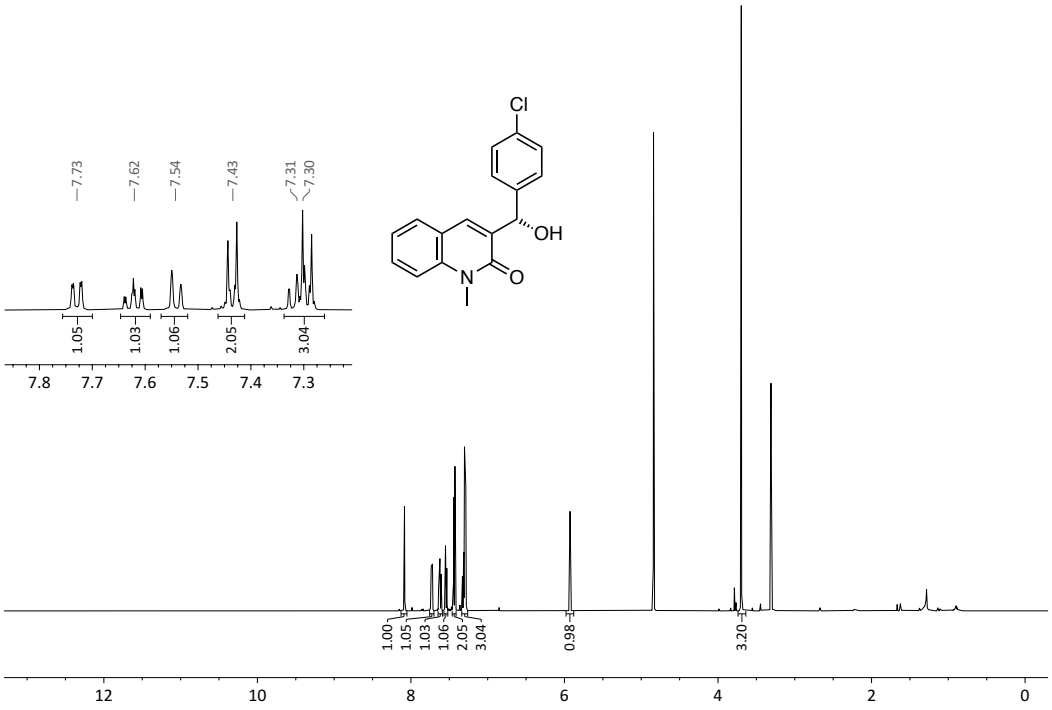


^{13}C NMR (126 MHz, DMSO-d_6)

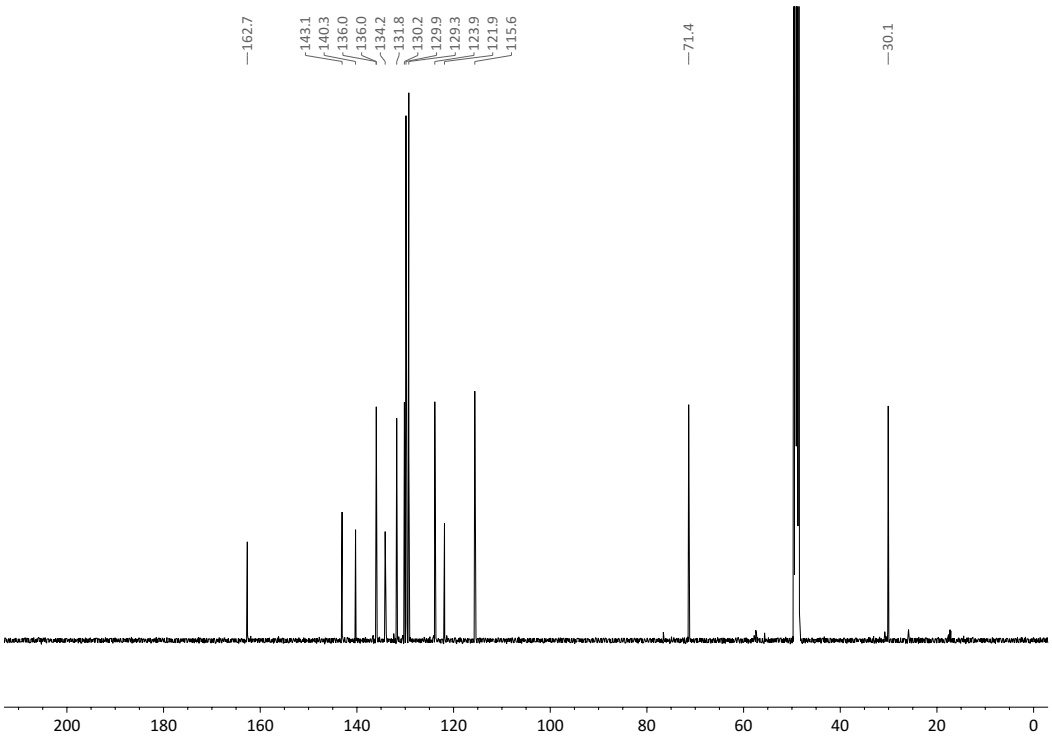


*1.7.2 (S)-3-((4-Chlorophenyl)(hydroxy)methyl)-N-methyl-2-quinolone (**5**)*

^{1}H NMR (500 MHz, MeOD-d_4)

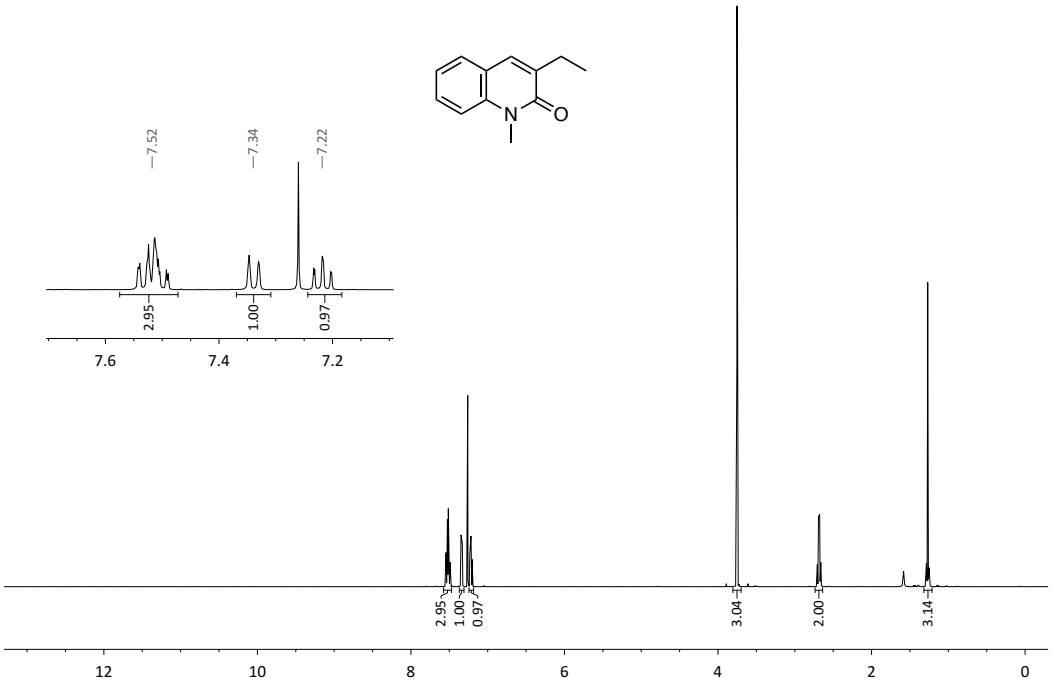


^{13}C NMR (126 MHz, MeOD-d_4)

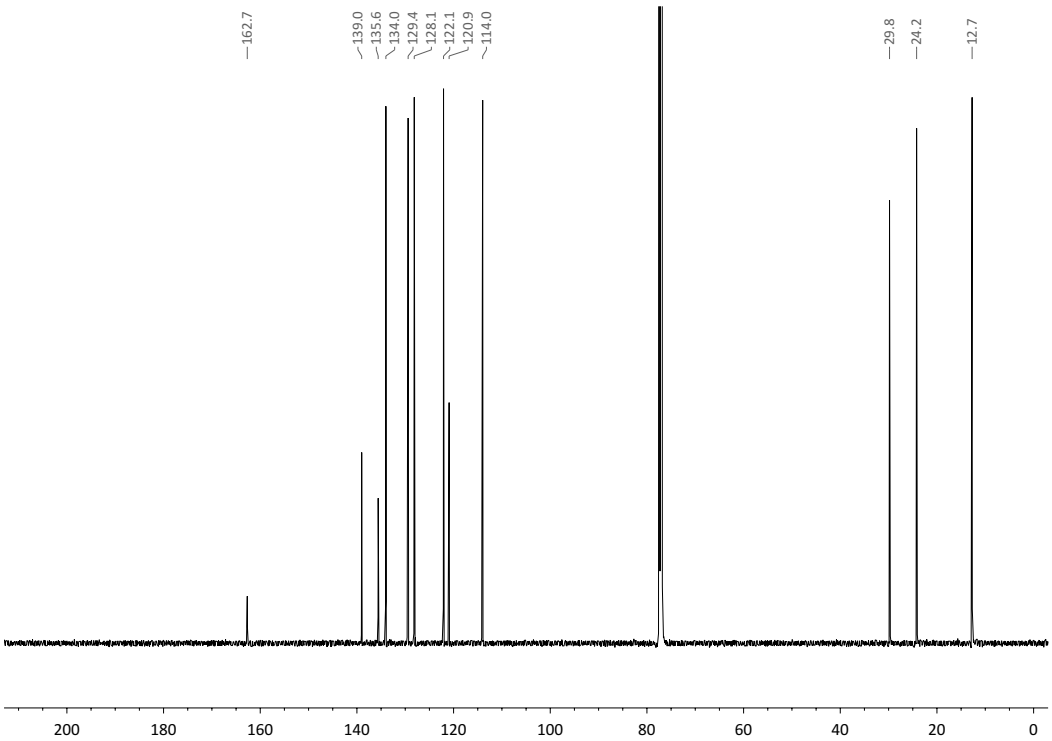


*1.7.3 3-Ethyl-N-methy-2-lquinolone (**9**)*

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

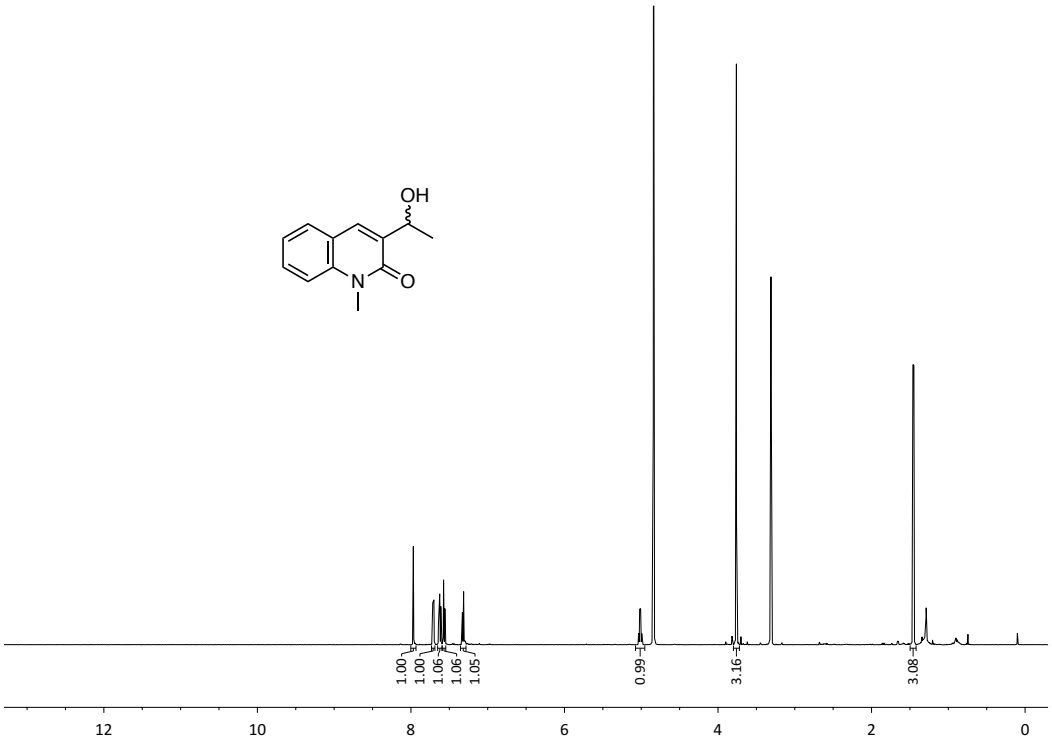


^{13}C NMR (126 MHz, $CDCl_3$)

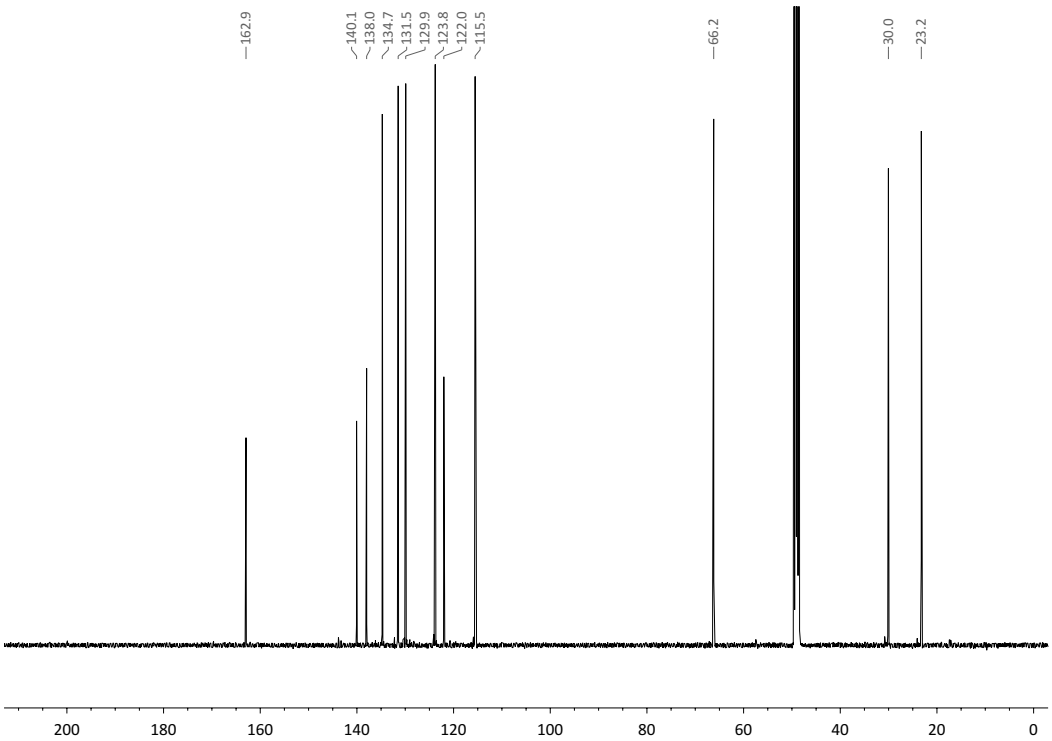


*1.7.4 3-(1-Hydroxyethyl)-N-methyl-2-quinolone (**10**)*

^{1}H NMR (500 MHz, MeOD-d_4)



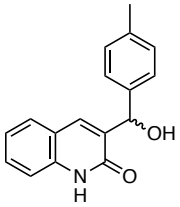
^{13}C NMR (126 MHz, MeOD-d_4)

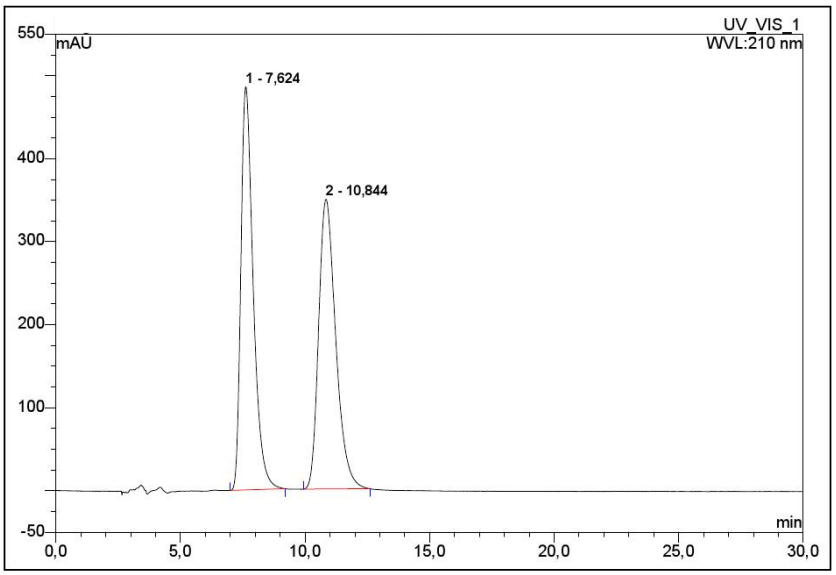


2 HPLC Traces

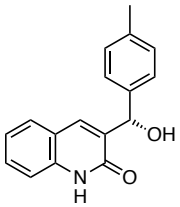
2.1 3-(Hydroxy(aryl)methyl)-2-quinolones 3

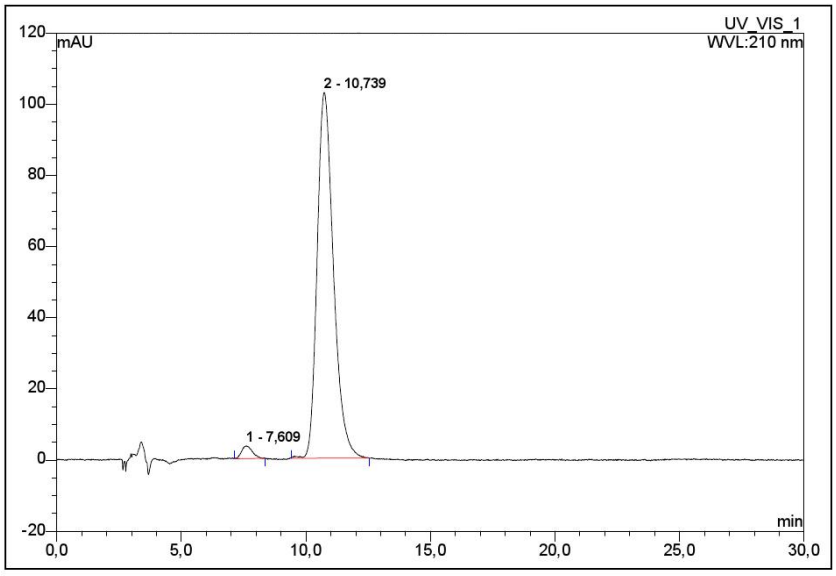
*2.1.1 (S)-3-(Hydroxy(p-tolyl)methyl)-2-quinolinone (**3a**)*





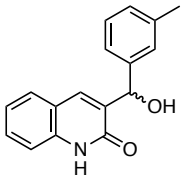
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,62	n.a.	485,722	277,893	50,09	n.a.	BMB
2	10,84	n.a.	348,901	276,935	49,91	n.a.	BMB
Total:			834,623	554,828	100,00	0,000	

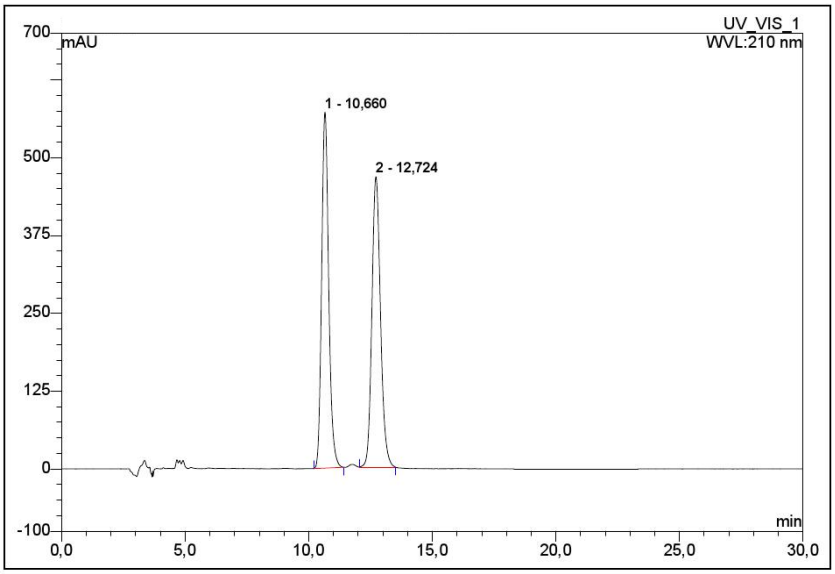




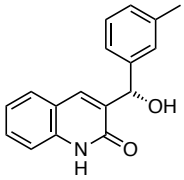
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,61	n.a.	3,535	1,726	2,17	n.a.	BMB*
2	10,74	n.a.	102,811	77,953	97,83	n.a.	BMB*
Total:			106,346	79,679	100,00	0,000	

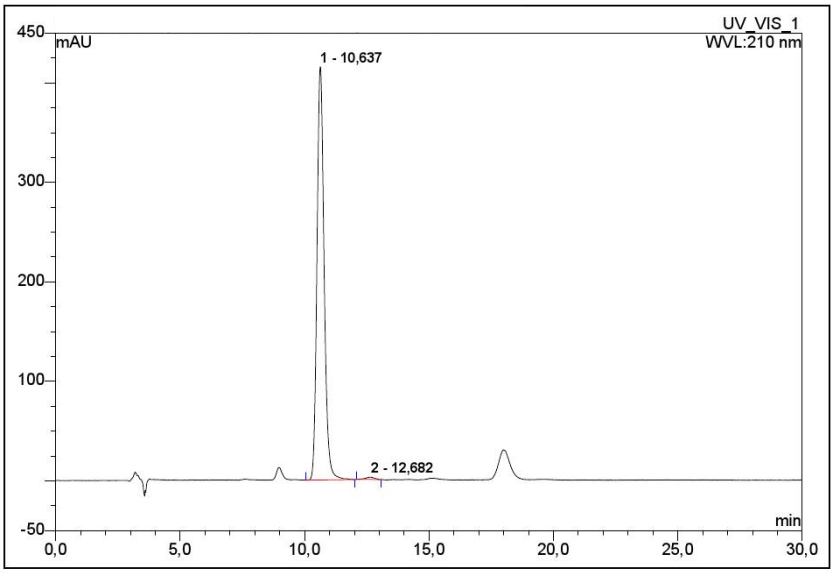
*2.1.2 (S)-3-(Hydroxy(m-tolyl)methyl)-2-quinolone (**3b**)*





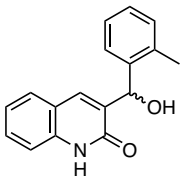
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,66	n.a.	571,678	188,561	50,06	n.a.	BMB
2	12,72	n.a.	466,483	188,112	49,94	n.a.	BMB
Total:			1038,162	376,674	100,00	0,000	

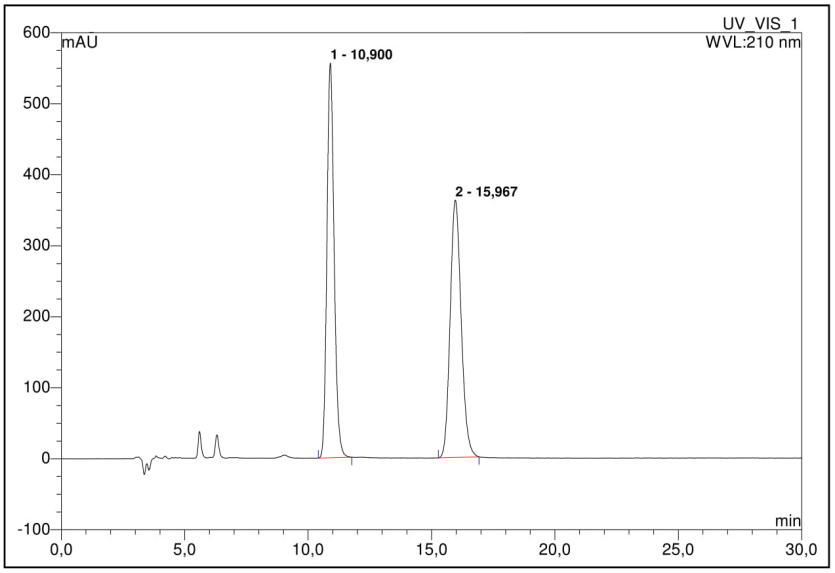




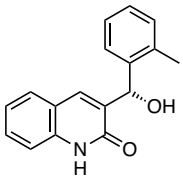
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,64	n.a.	415,410	137,053	99,26	n.a.	BMB*
2	12,68	n.a.	2,460	1,015	0,74	n.a.	BMB*
Total:			417,870	138,068	100,00	0,000	

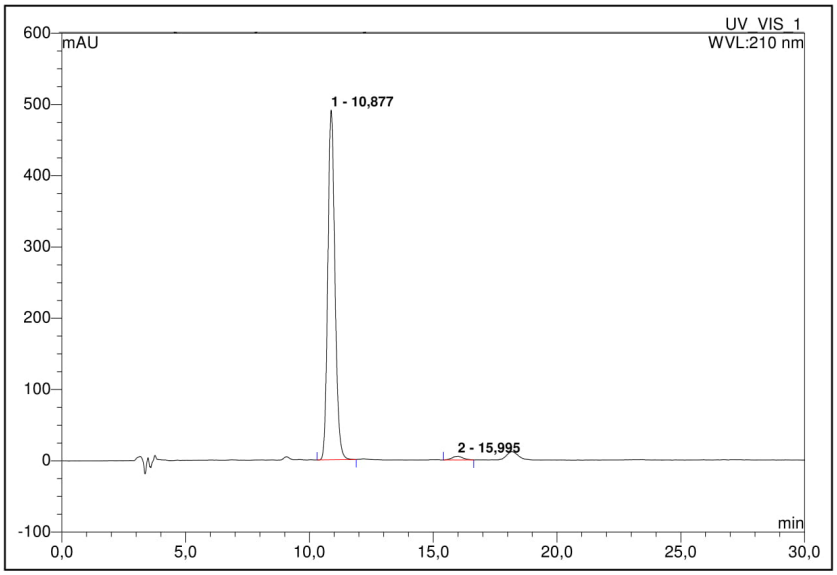
*2.1.3 (S)-3-(Hydroxy(o-tolyl)methyl)-2-quinolone (**3c**)*





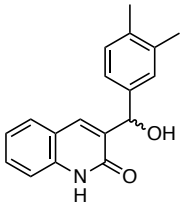
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,90	n.a.	556,140	187,918	50,07	n.a.	BMB
2	15,97	n.a.	362,528	187,380	49,93	n.a.	BMB
Total:			918,668	375,299	100,00	0,000	

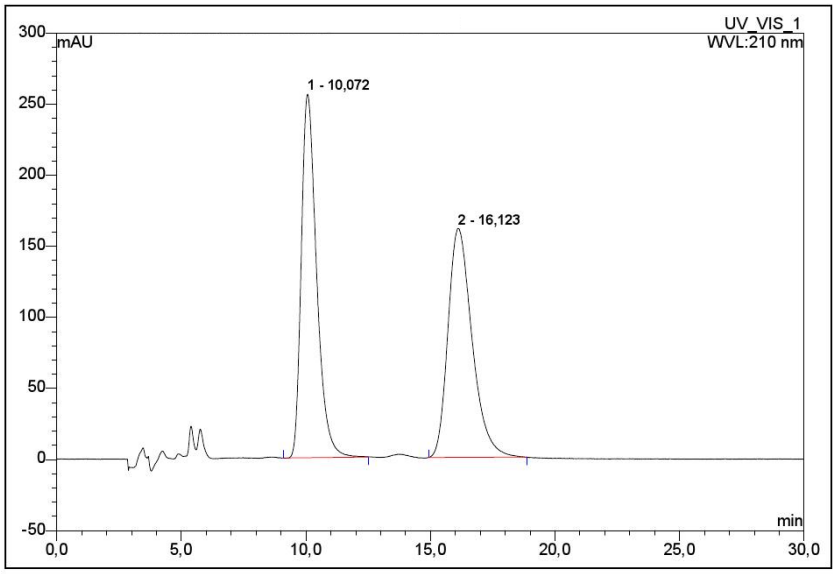




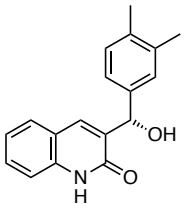
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,88	n.a.	490,946	163,762	98,44	n.a.	BMB*
2	16,00	n.a.	5,088	2,589	1,56	n.a.	BMB*
Total:			496,033	166,351	100,00	0,000	

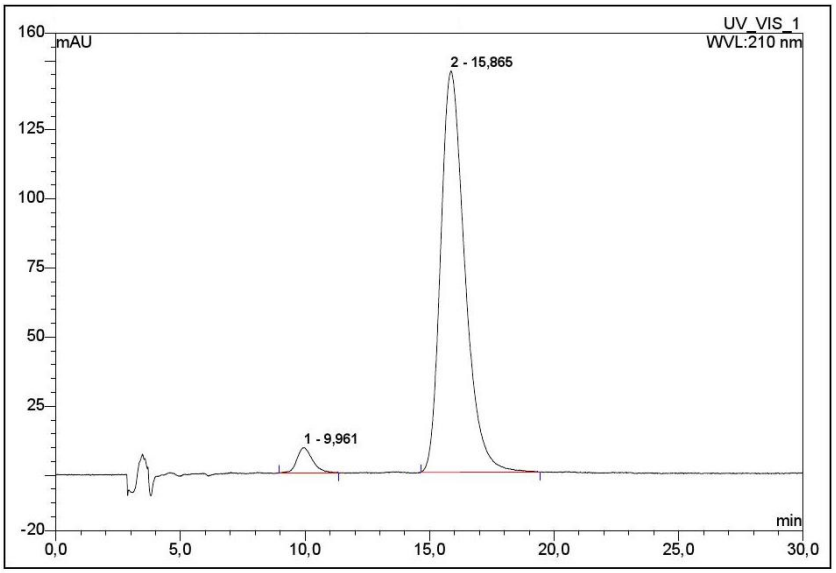
*2.1.4 (S)-3-((3,4-Dimethylphenyl)(hydroxy)methyl)-2-quinolone (**3d**)*





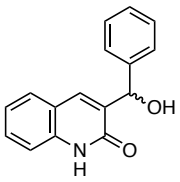
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,07	n.a.	255,734	181,944	50,16	n.a.	BMB*
2	16,12	n.a.	161,104	180,804	49,84	n.a.	BMB*
Total:			416,838	362,748	100,00	0,000	

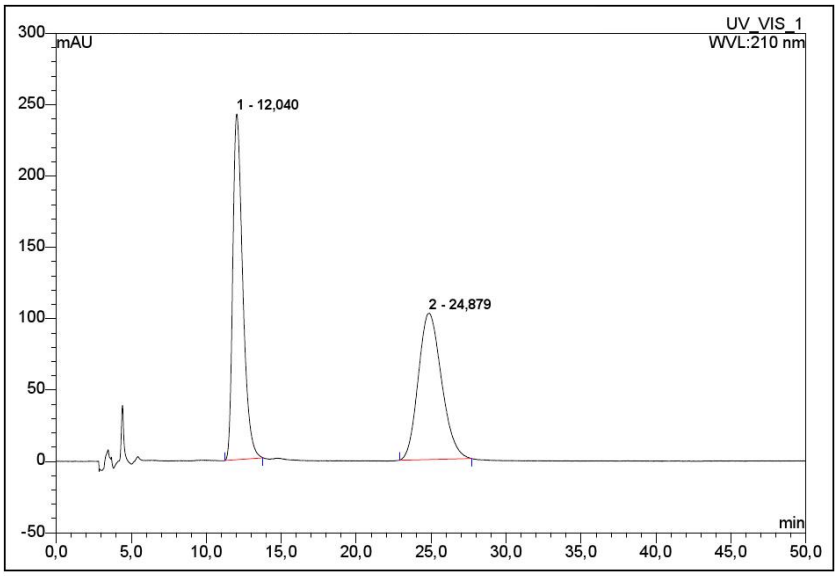




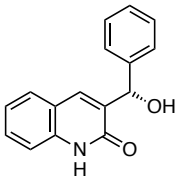
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,96	n.a.	9,199	6,753	3,97	n.a.	BMB*
2	15,87	n.a.	145,311	163,149	96,03	n.a.	BMB*
Total:			154,510	169,902	100,00	0,000	

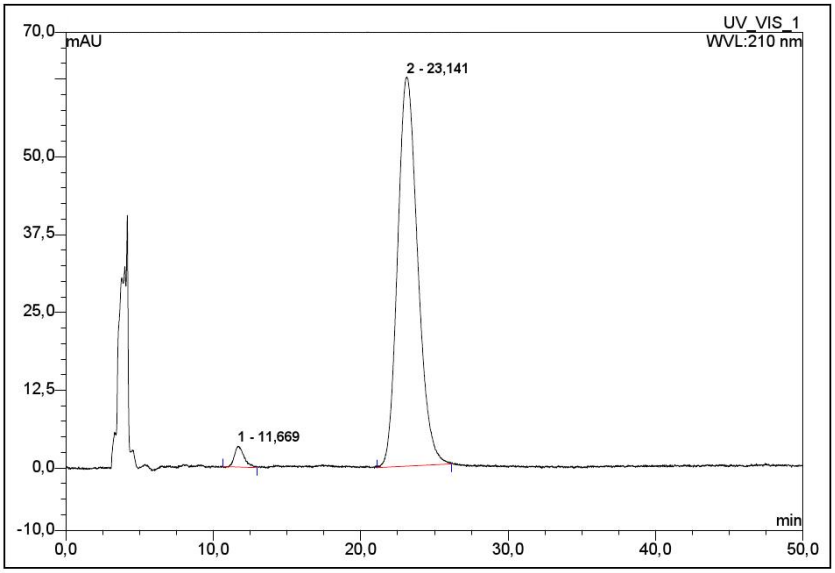
*2.1.5 (S)-3-Hydroxy(phenyl)methyl)-2-quinolone (**3e**)*





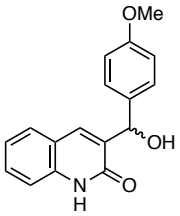
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,04	n.a.	242,225	186,081	50,26	n.a.	BMB
2	24,88	n.a.	102,508	184,159	49,74	n.a.	BMB
Total:			344,733	370,240	100,00	0,000	

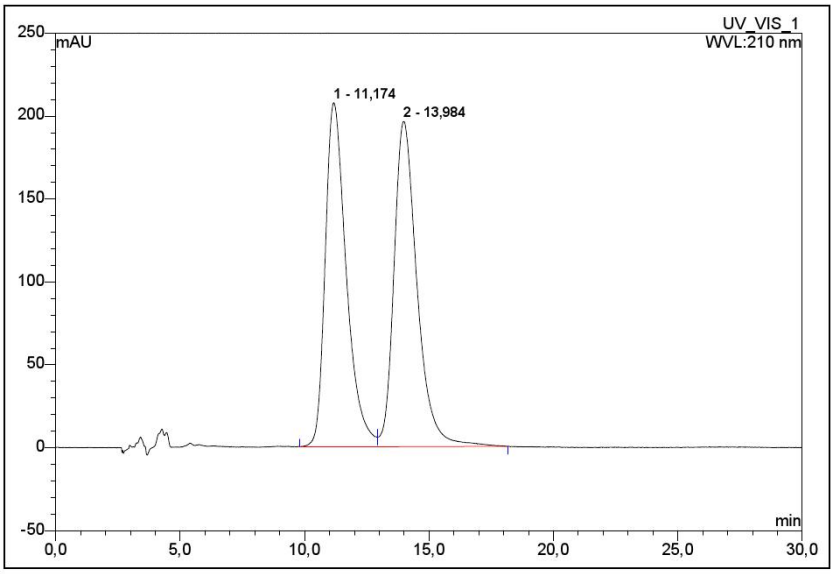




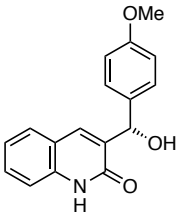
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,67	n.a.	3,345	2,503	2,47	n.a.	BMB*
2	23,14	n.a.	62,536	98,798	97,53	n.a.	BMB*
Total:			65,881	101,301	100,00	0,000	

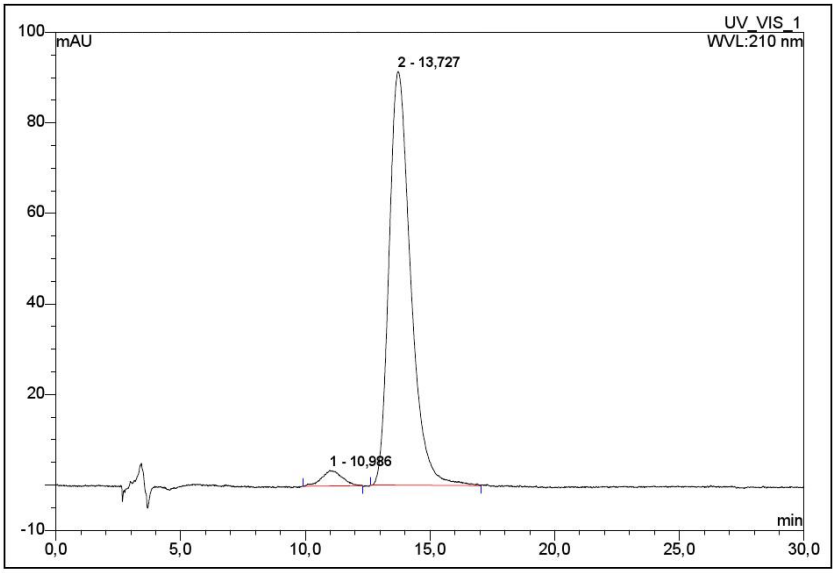
*2.1.6 (S)-3-(Hydroxy(4-methoxyphenyl)methyl)-2-quinolone (**3f**)*





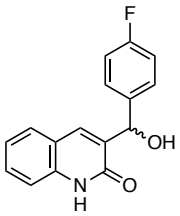
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,17	n.a.	207,543	203,642	49,06	n.a.	BM *
2	13,98	n.a.	196,114	211,449	50,94	n.a.	MB*
Total:			403,657	415,091	100,00	0,000	

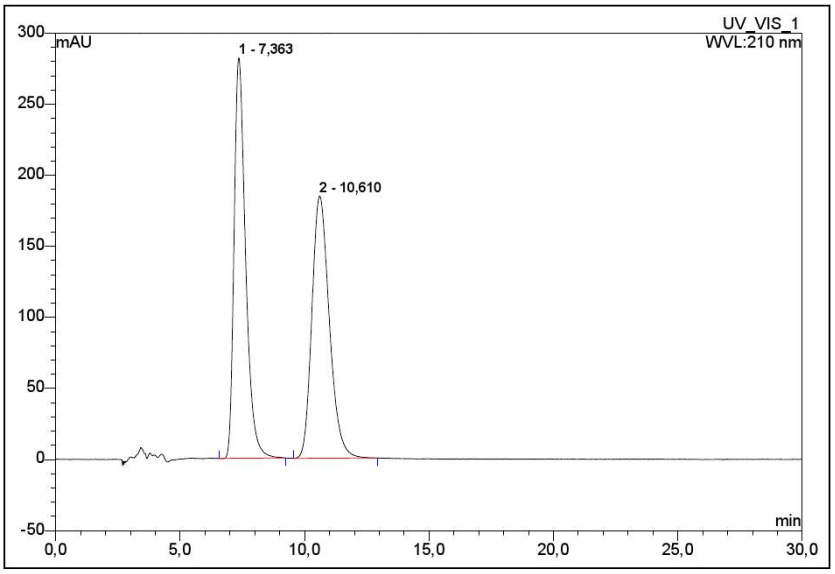




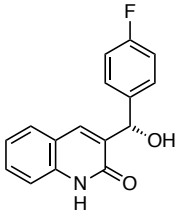
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,99	n.a.	3,456	3,237	3,41	n.a.	BMB*
2	13,73	n.a.	91,379	91,555	96,59	n.a.	BMB*
Total:			94,835	94,792	100,00	0,000	

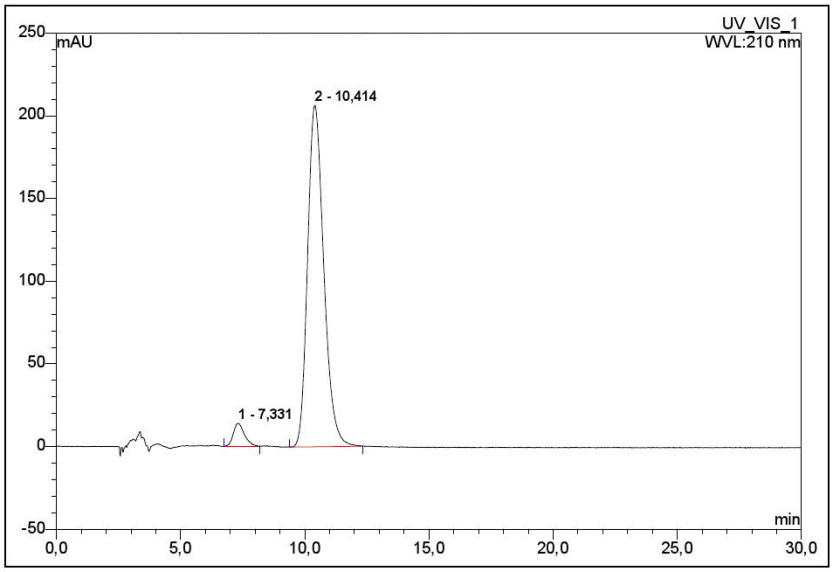
*2.1.7 (S)-3-((4-Fluorophenyl)(hydroxy)methyl)-2-quinolone (**3g**)*





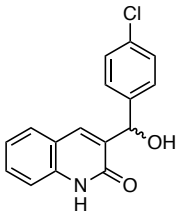
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,36	n.a.	281,795	150,704	50,17	n.a.	BMB*
2	10,61	n.a.	184,463	149,698	49,83	n.a.	BMB*
Total:			466,258	300,402	100,00	0,000	

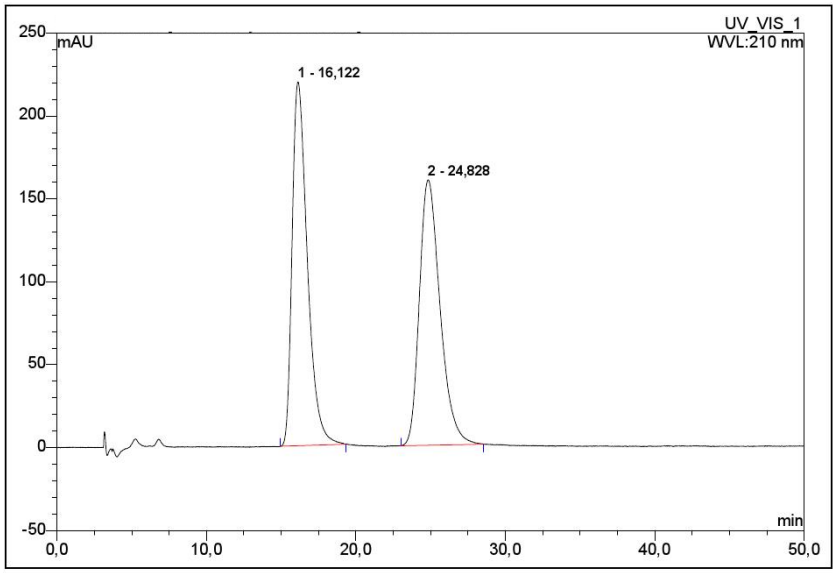




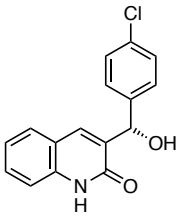
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,33	n.a.	13,944	7,213	4,43	n.a.	BMB*
2	10,41	n.a.	206,538	155,733	95,57	n.a.	BMB*
Total:			220,482	162,946	100,00	0,000	

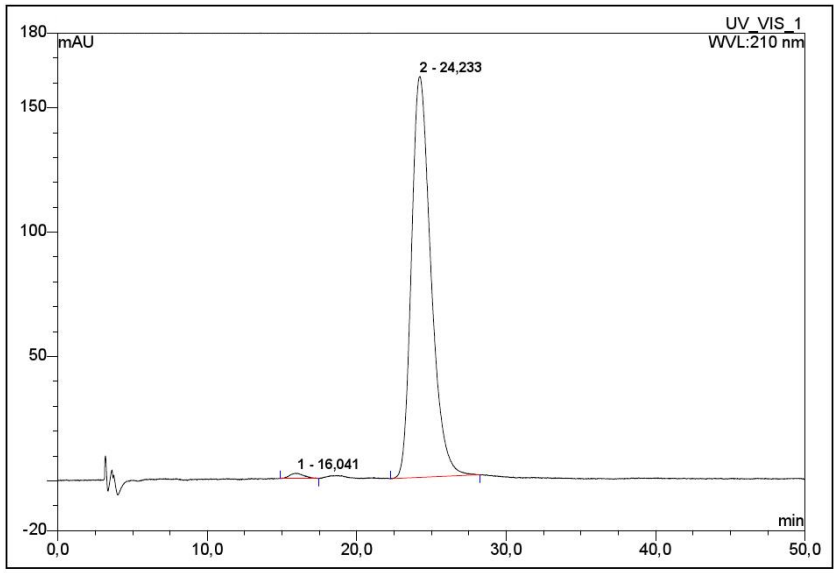
*2.1.8 (S)-3-((4-Chlorophenyl)(hydroxy)methyl)-2-quinolone (**3h**)*





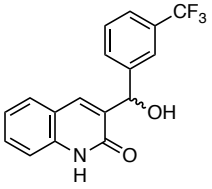
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,12	n.a.	219,415	258,494	50,16	n.a.	BMB*
2	24,83	n.a.	160,137	256,823	49,84	n.a.	BMB*
Total:			379,552	515,317	100,00	0,000	

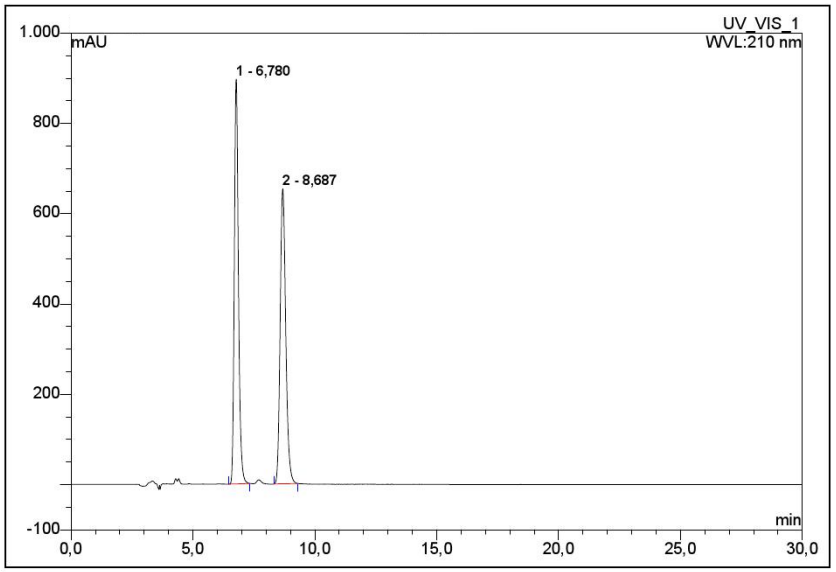




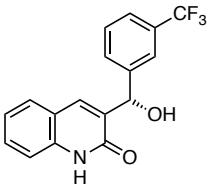
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,04	n.a.	2,092	2,315	0,94	n.a.	BMB*
2	24,23	n.a.	161,244	242,921	99,06	n.a.	BMB*
Total:			163,336	245,235	100,00	0,000	

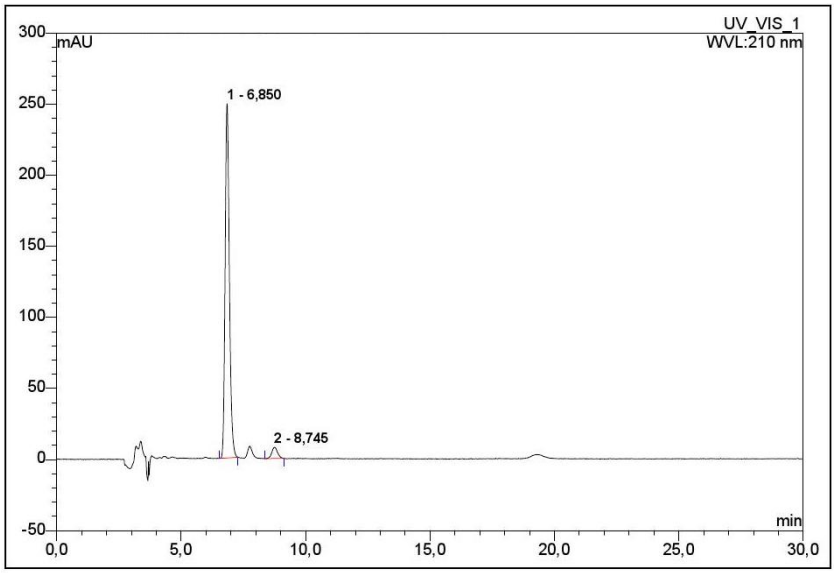
*2.1.9 (S)-3-Hydroxy(3-(trifluoromethyl)phenyl)methyl)-2-quinolone (**3i**)*





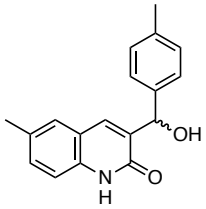
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,78	n.a.	896,011	174,787	50,14	n.a.	BMB
2	8,69	n.a.	653,165	173,812	49,86	n.a.	BMB
Total:			1549,176	348,599	100,00	0,000	

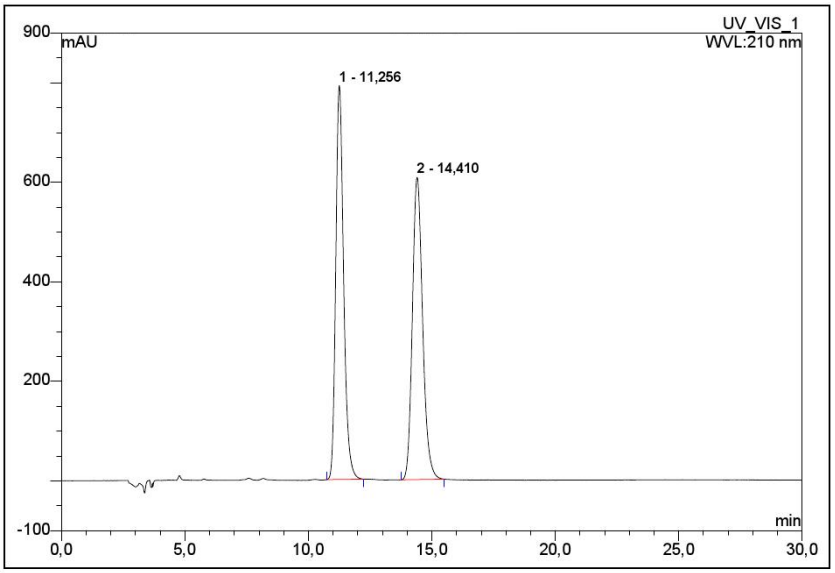




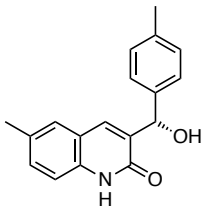
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,85	n.a.	249,315	49,074	95,85	n.a.	BMB
2	8,75	n.a.	7,947	2,122	4,15	n.a.	BMB*
Total:			257,262	51,196	100,00	0,000	

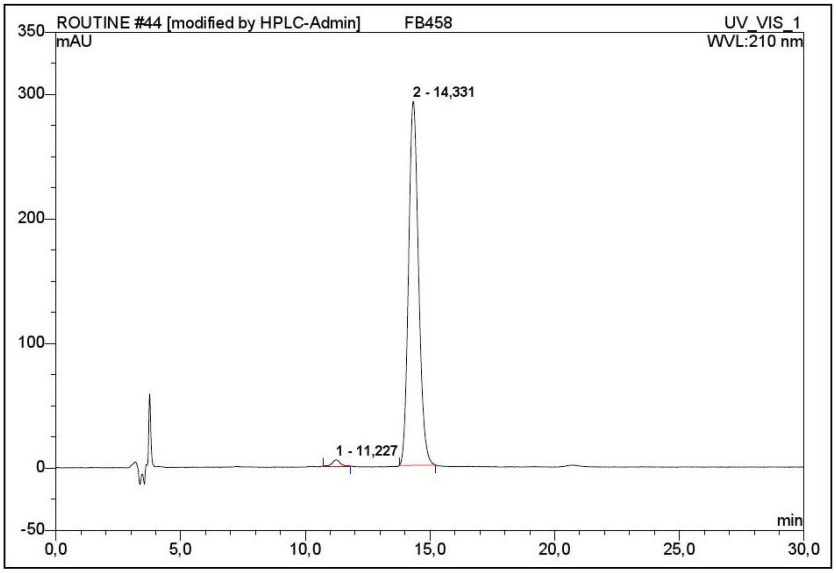
*2.1.10 (S)-3-(Hydroxy(p-tolyl)methyl)-6-methyl-2-quinolone (**3j**)*





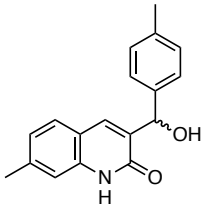
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,26	n.a.	791,721	291,724	50,02	n.a.	BMB
2	14,41	n.a.	607,443	291,444	49,98	n.a.	BMB
Total:			1399,165	583,168	100,00	0,000	

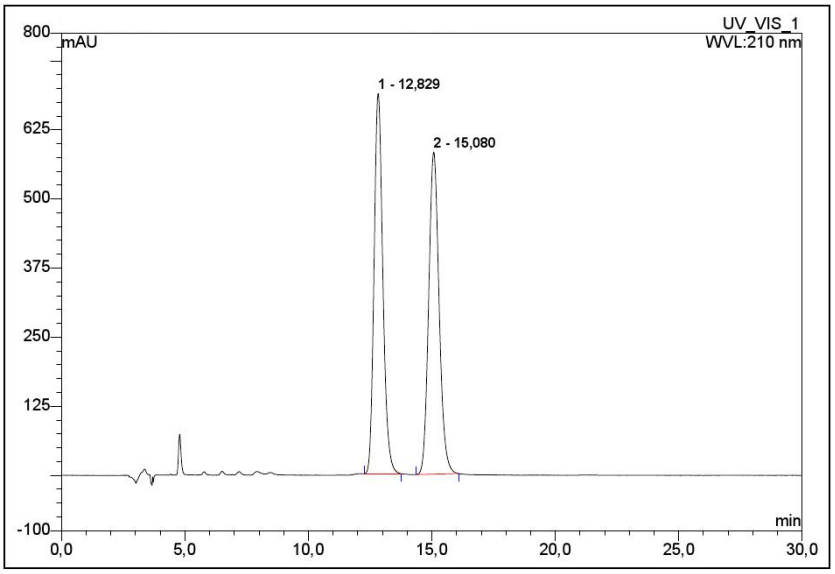




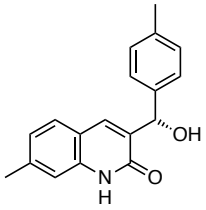
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,23	n.a.	4,946	1,683	1,22	n.a.	BMB*
2	14,33	n.a.	292,398	135,729	98,78	n.a.	BMB
Total:			297,344	137,412	100,00	0,000	

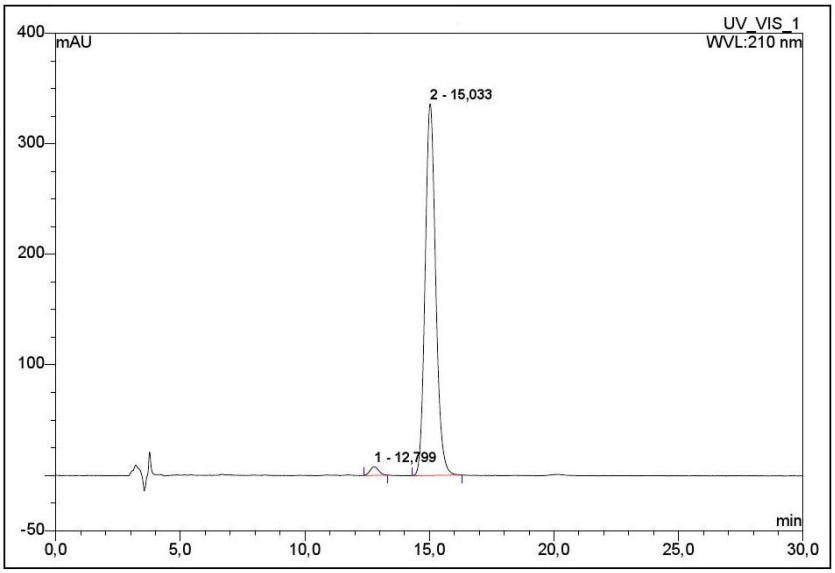
*2.1.11 (S)-3-(Hydroxy(p-tolyl)methyl)-7-methyl-2-quinolone (**3k**)*





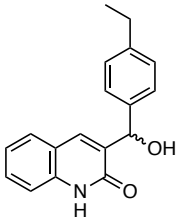
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,83	n.a.	688,174	283,353	49,91	n.a.	BMB
2	15,08	n.a.	582,601	284,385	50,09	n.a.	BMB
Total:			1270,775	567,738	100,00	0,000	

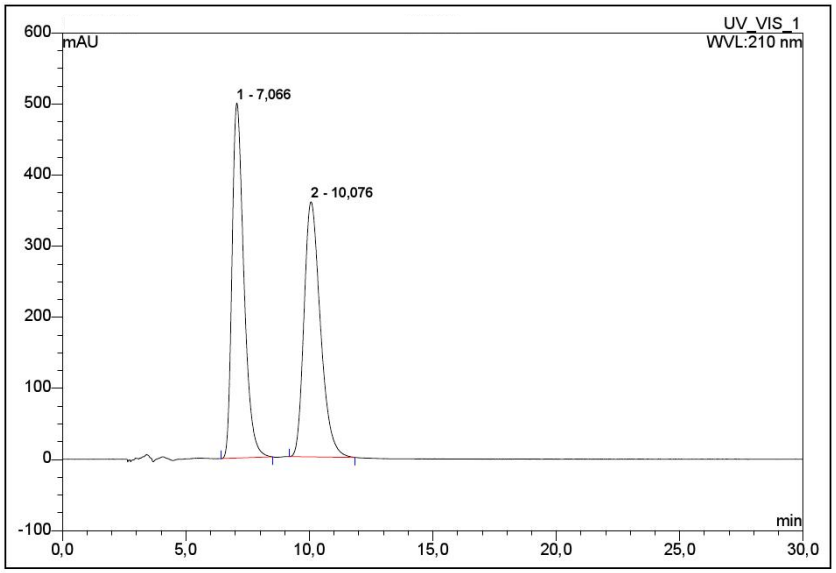




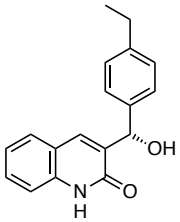
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,80	n.a.	7,930	3,168	1,88	n.a.	BMB*
2	15,03	n.a.	336,195	164,941	98,12	n.a.	BMB*
Total:			344,125	168,109	100,00	0,000	

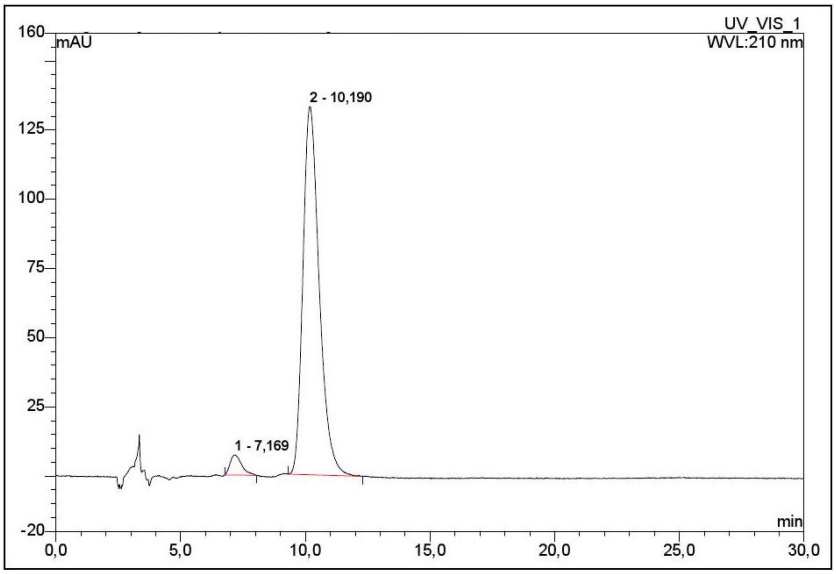
*2.1.12 (S)-3-((4-Ethylphenyl)(hydroxy)methyl)-2-quinolone (**3l**)*





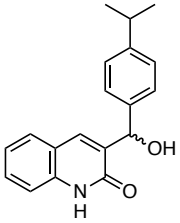
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,07	n.a.	499,376	277,383	50,16	n.a.	BMB
2	10,08	n.a.	358,732	275,664	49,84	n.a.	BMB
Total:			858,108	553,047	100,00	0,000	

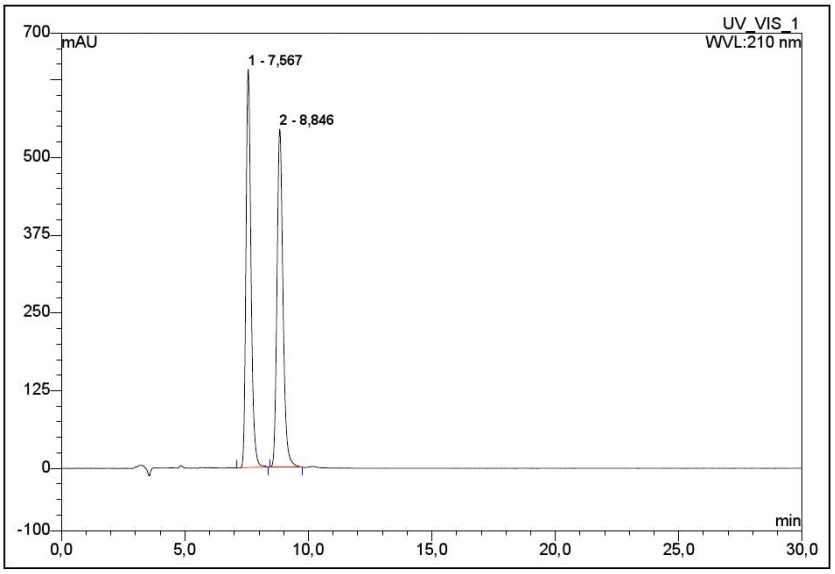




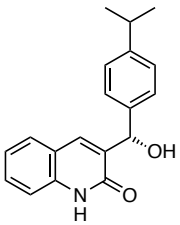
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,17	n.a.	7,315	3,891	3,71	n.a.	BMB*
2	10,19	n.a.	133,069	100,837	96,29	n.a.	BMB*
Total:			140,384	104,727	100,00	0,000	

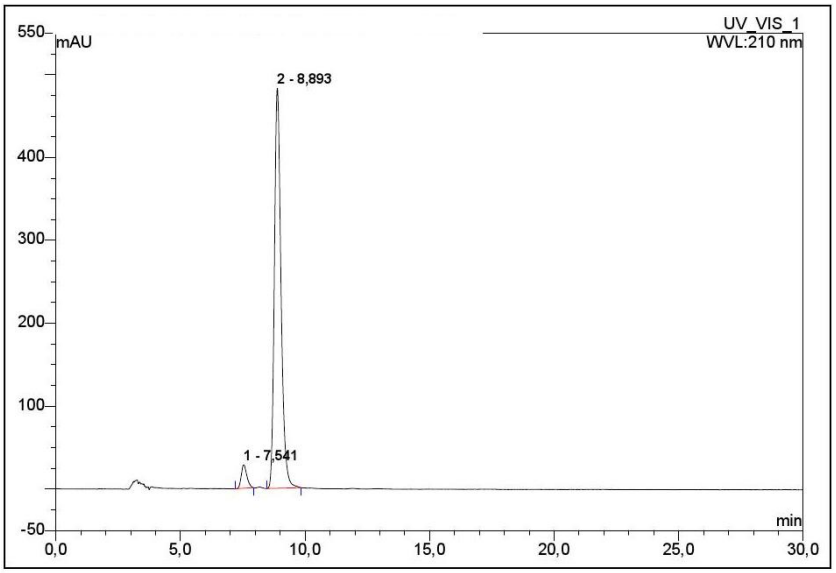
*2.1.13 (S)-3-(Hydroxy(4-isopropylphenyl)methyl)-2-quinolone (**3m**)*





No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,57	n.a.	640,313	151,030	49,77	n.a.	BMB*
2	8,85	n.a.	543,656	152,442	50,23	n.a.	BMB
Total:			1183,969	303,471	100,00	0,000	

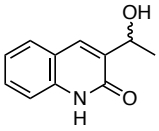


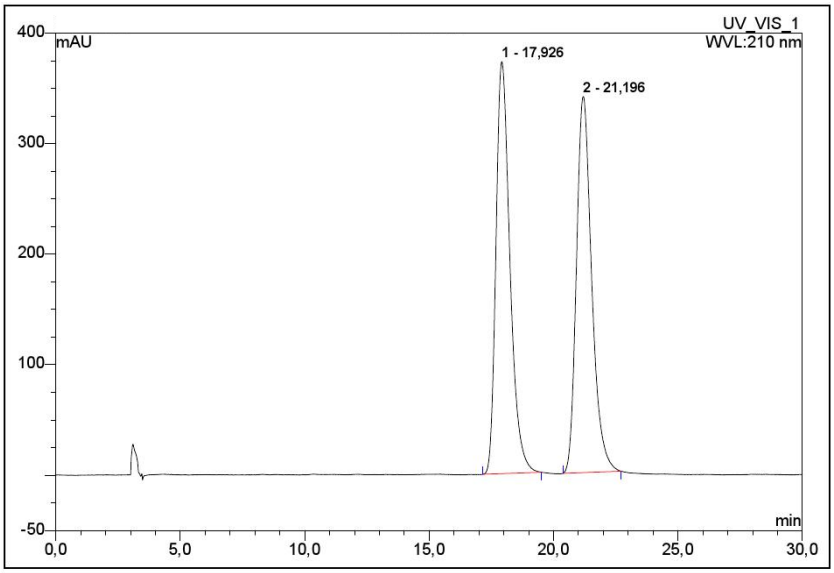


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,54	n.a.	28,286	7,275	4,66	n.a.	BMB*
2	8,89	n.a.	482,670	148,834	95,34	n.a.	BMB
Total:			510,955	156,109	100,00	0,000	

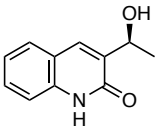
2.2 3-(1-Hydroxyalkyl)-2-quinolones 7

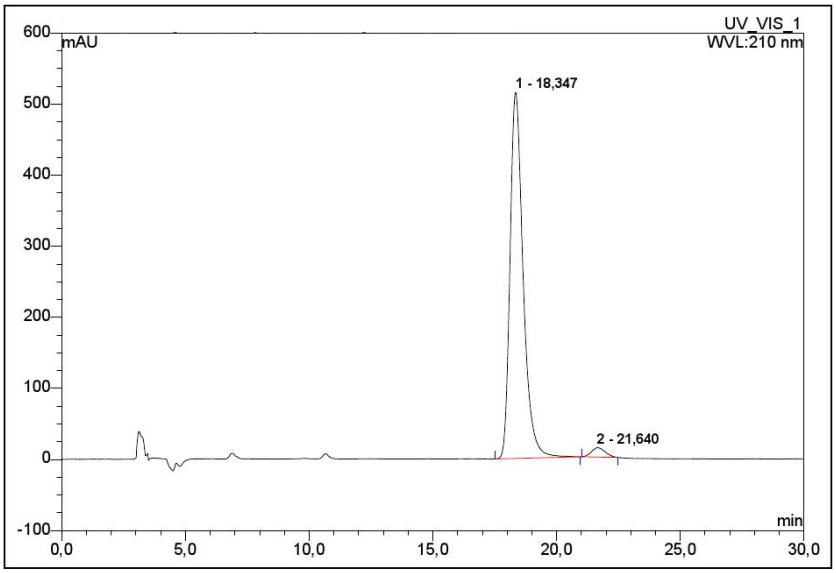
*2.2.1 (S)-3-(1-Hydroxyethyl)-2-quinolone (**7a**)*





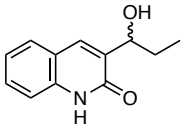
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17,93	n.a.	372,715	242,437	50,05	n.a.	BMB
2	21,20	n.a.	340,259	241,980	49,95	n.a.	BMB
Total:			712,973	484,417	100,00	0,000	

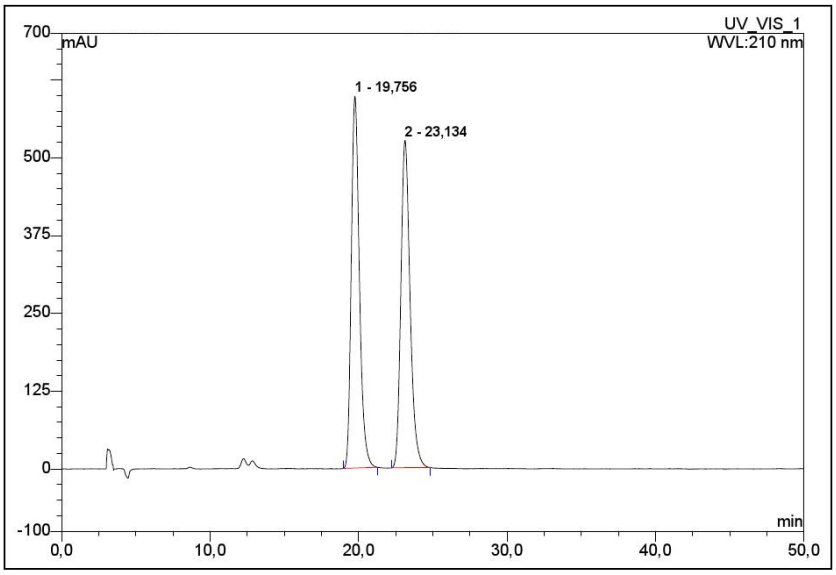




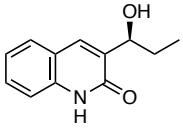
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18,35	n.a.	515,158	315,793	97,40	n.a.	BMB*
2	21,64	n.a.	13,153	8,432	2,60	n.a.	BMB*
Total:			528,311	324,225	100,00	0,000	

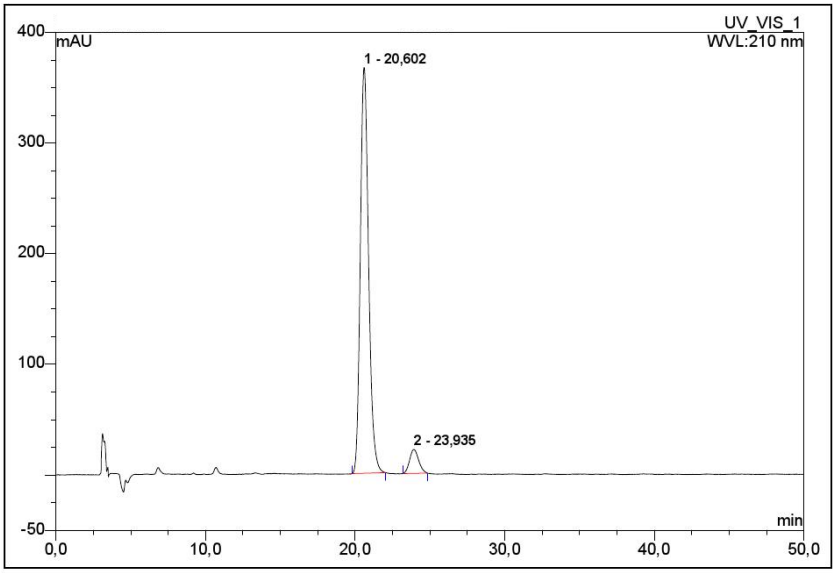
*2.2.2 (S)-3-(1-Hydroxypropyl)-2-quinolone (**7b**)*





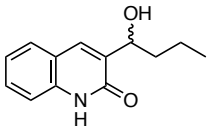
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19,76	n.a.	597,167	377,030	49,92	n.a.	BMB
2	23,13	n.a.	525,919	378,278	50,08	n.a.	BMB
Total:			1123,086	755,309	100,00	0,000	

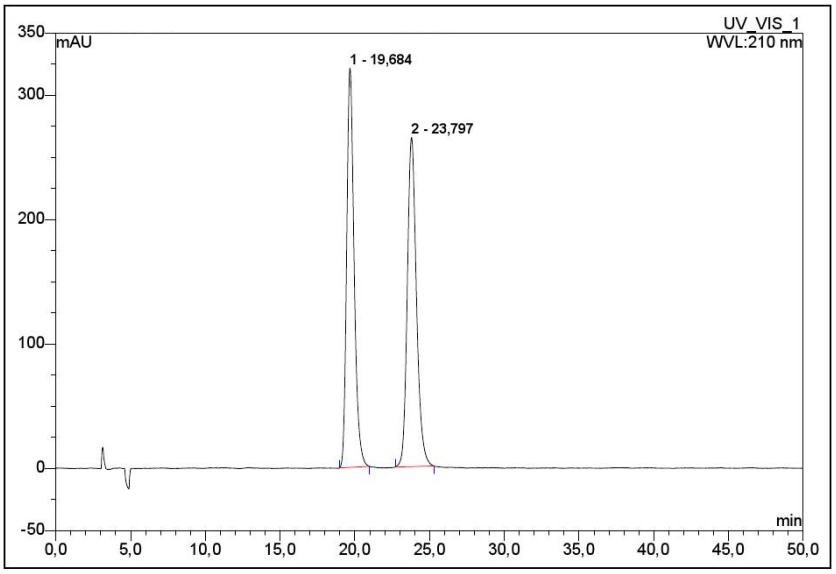




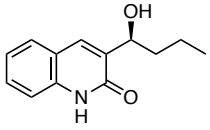
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20,60	n.a.	366,734	234,148	93,99	n.a.	BMB
2	23,94	n.a.	21,508	14,973	6,01	n.a.	BMB
Total:			388,242	249,121	100,00	0,000	

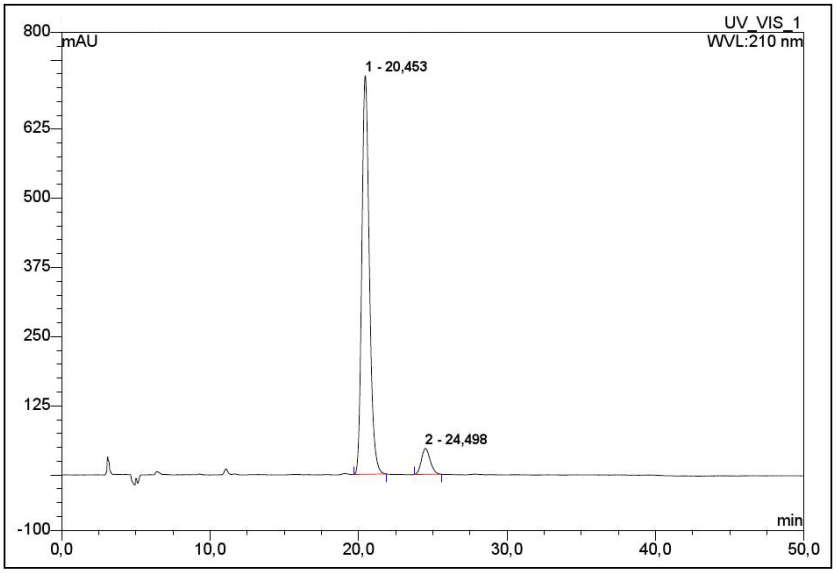
*2.2.3 (S)-3-(1-Hydroxybutyl)-2-quinolone (**7c**)*





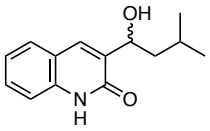
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19,68	n.a.	321,066	184,427	49,55	n.a.	BMB
2	23,80	n.a.	264,624	187,814	50,45	n.a.	BMB
Total:			585,690	372,241	100,00	0,000	

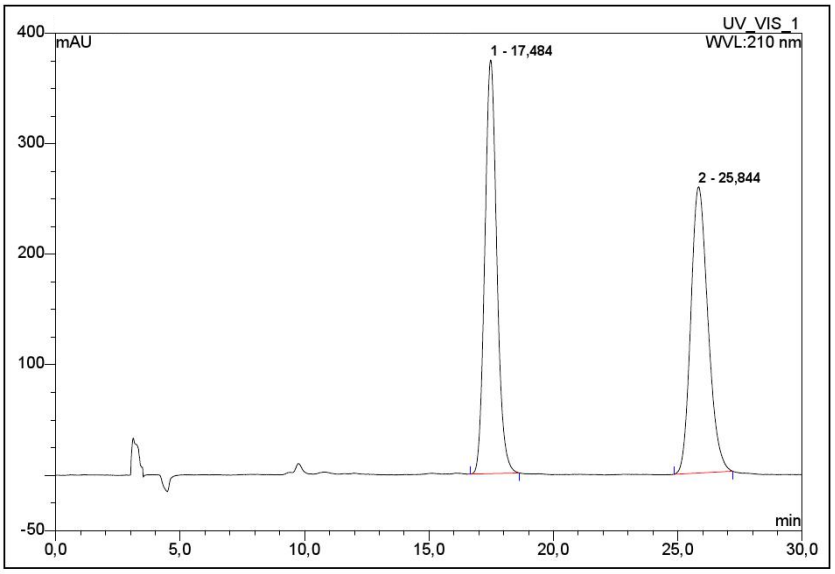




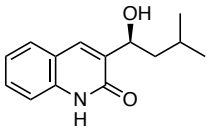
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20,45	n.a.	720,344	423,776	92,95	n.a.	BMB
2	24,50	n.a.	46,896	32,155	7,05	n.a.	BMB
Total:			767,240	455,931	100,00	0,000	

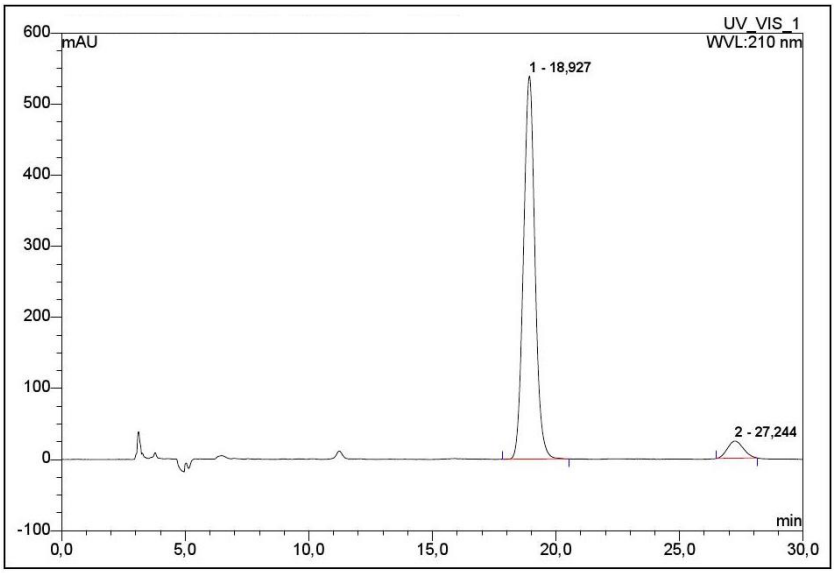
*2.2.4 (S)-3-(1-Hydroxy-3-methylbutyl)-2-quinolone (**7d**)*





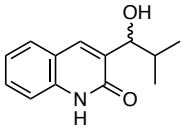
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17,48	n.a.	374,296	208,843	50,27	n.a.	BMB
2	25,84	n.a.	259,106	206,638	49,73	n.a.	BMB
Total:			633,402	415,481	100,00	0,000	

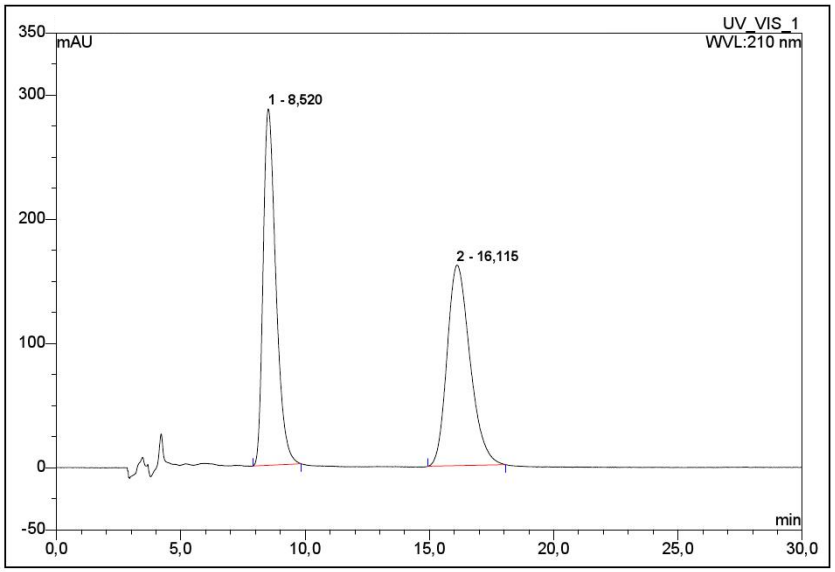




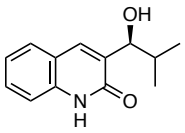
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18,93	n.a.	539,017	290,047	94,14	n.a.	BMB*
2	27,24	n.a.	24,211	18,044	5,86	n.a.	BMB
Total:			563,228	308,090	100,00	0,000	

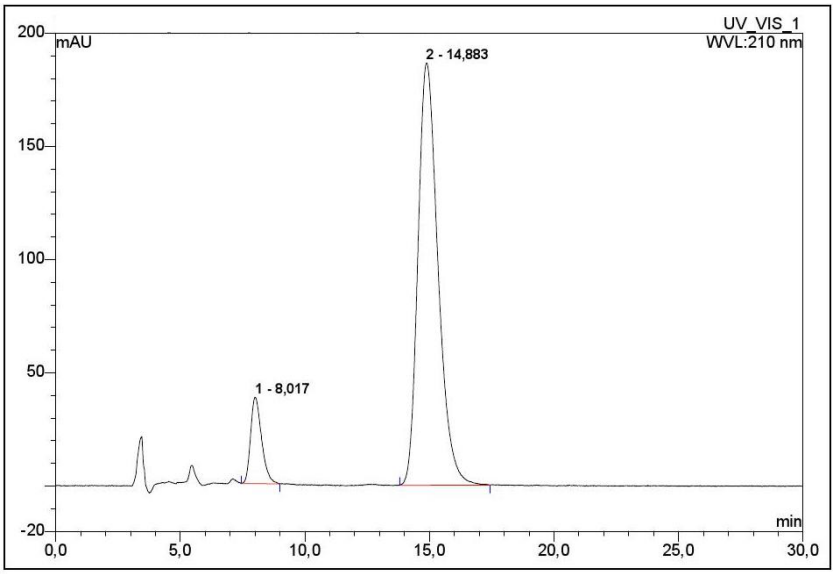
*2.2.5 (S)-3-(1-Hydroxy-2-methylpropyl)-2-quinolone (**7e**)*





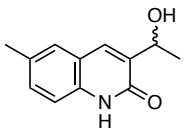
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,52	n.a.	287,056	170,860	49,71	n.a.	BMB
2	16,11	n.a.	161,534	172,823	50,29	n.a.	BMB
Total:			448,590	343,682	100,00	0,000	

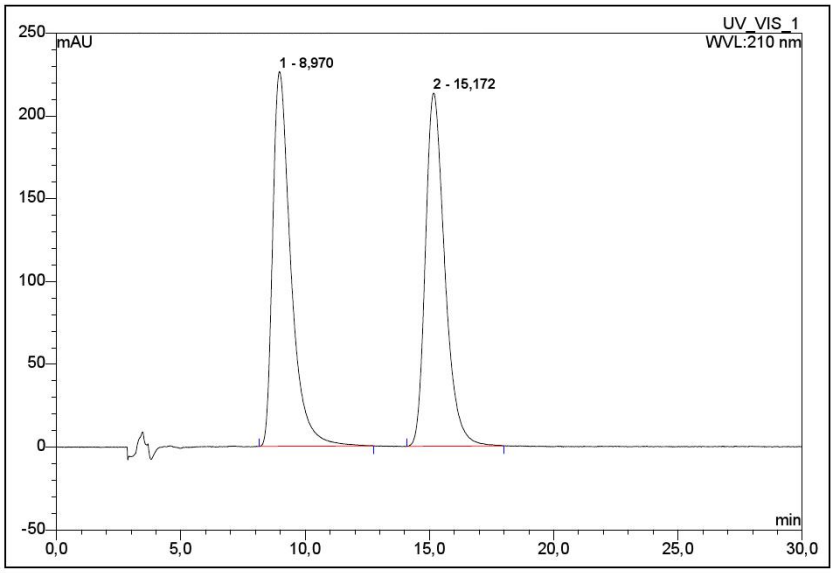




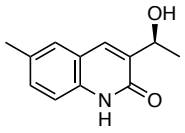
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,02	n.a.	38,197	19,614	10,13	n.a.	BMB*
2	14,88	n.a.	186,434	173,963	89,87	n.a.	BMB*
Total:			224,632	193,577	100,00	0,000	

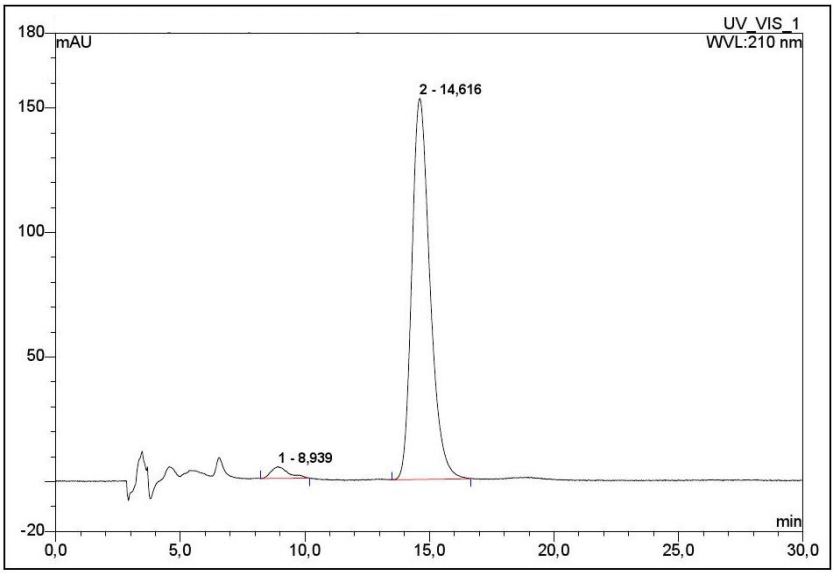
2.2.6 (S)-3-(1-Hydroxyethyl)-6-methyl-2-quinolone (7f)





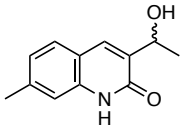
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,97	n.a.	226,367	191,973	49,91	n.a.	BMB*
2	15,17	n.a.	213,332	192,649	50,09	n.a.	BMB*
Total:			439,699	384,622	100,00	0,000	

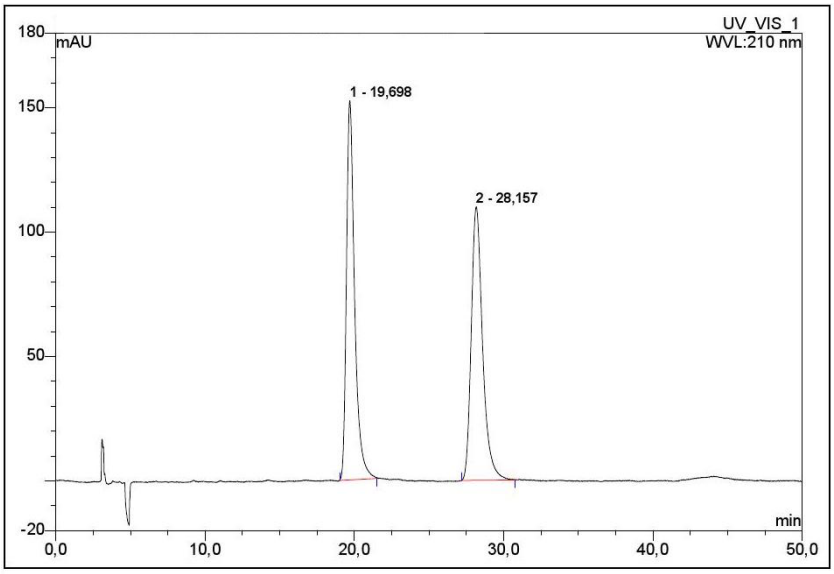




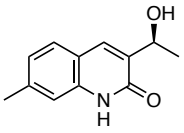
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,94	n.a.	4,666	3,782	2,84	n.a.	BMB*
2	14,62	n.a.	152,950	129,290	97,16	n.a.	BMB*
Total:			157,617	133,071	100,00	0,000	

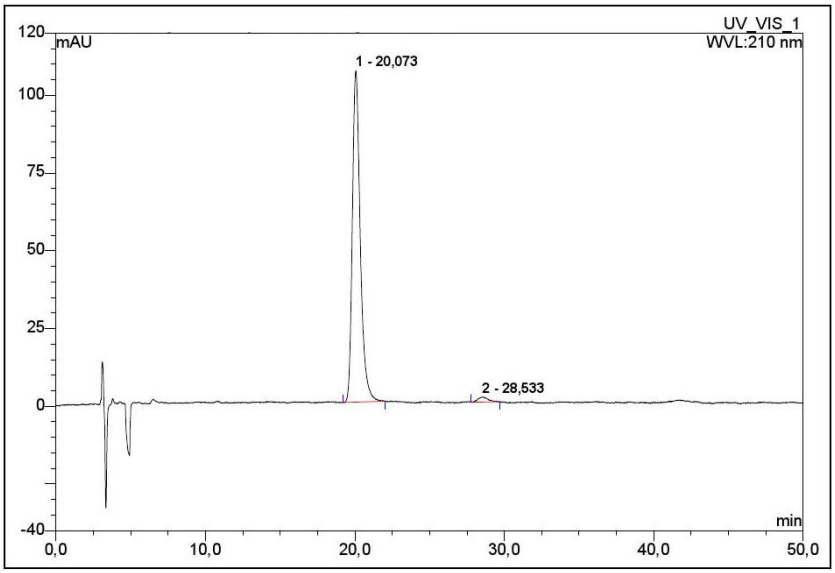
*2.2.7 (S)-3-(1-Hydroxyethyl)-7-methyl-2-quinolone (**7g**)*





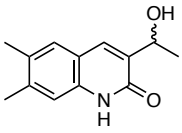
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19,70	n.a.	152,513	96,464	49,93	n.a.	BMB*
2	28,16	n.a.	109,978	96,716	50,07	n.a.	BMB*
Total:			262,491	193,180	100,00	0,000	

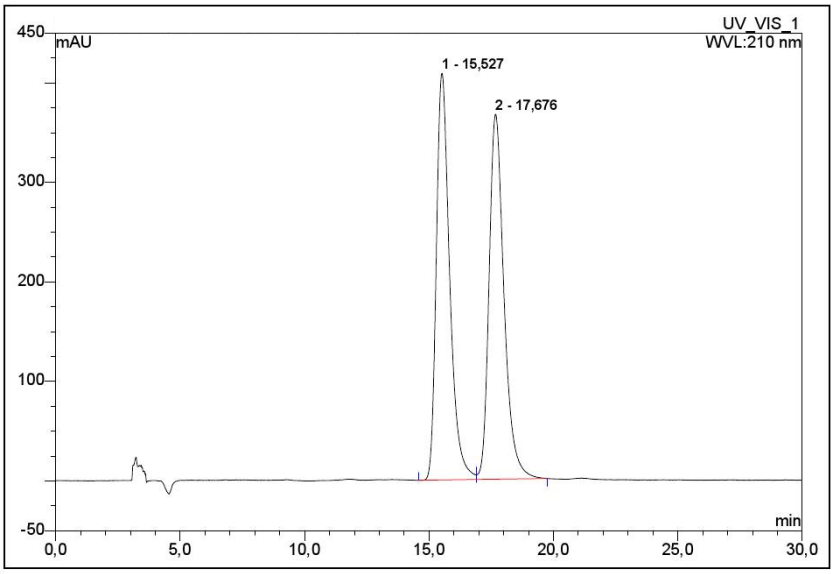




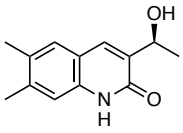
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20,07	n.a.	106,686	65,154	98,19	n.a.	BMB*
2	28,53	n.a.	1,591	1,204	1,81	n.a.	BMB*
Total:			108,277	66,358	100,00	0,000	

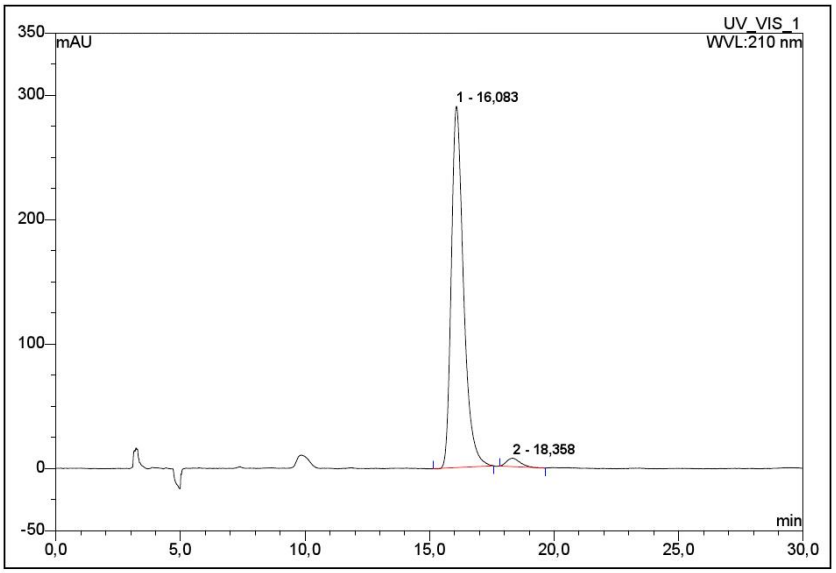
*2.2.8 (S)-3-(1-Hydroxyethyl)-6,7-dimethyl-2-quinolone (**7h**)*





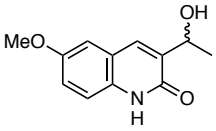
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15,53	n.a.	408,723	253,897	49,86	n.a.	BM *
2	17,68	n.a.	366,888	255,320	50,14	n.a.	MB*
Total:			775,611	509,217	100,00	0,000	

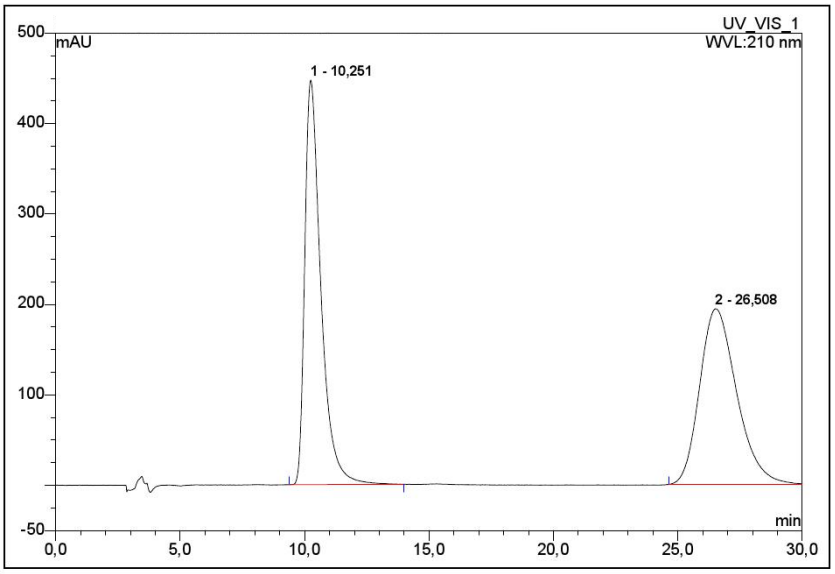




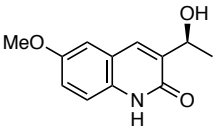
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,08	n.a.	290,604	164,940	97,48	n.a.	BMB*
2	18,36	n.a.	6,874	4,271	2,52	n.a.	BMB*
Total:			297,478	169,210	100,00	0,000	

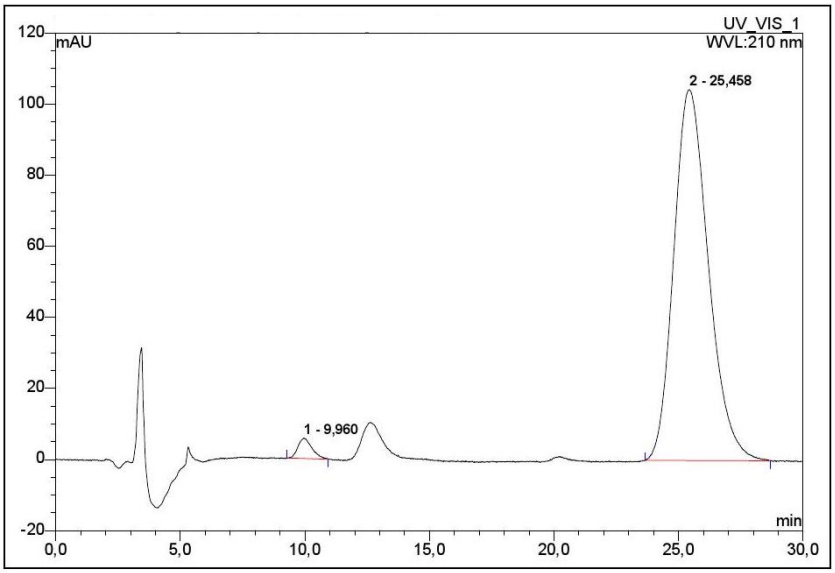
*2.2.9 (S)-3-(1-Hydroxyethyl)-6-methoxy-2-quinolone (**7i**)*





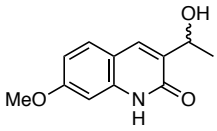
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,25	n.a.	447,278	335,739	49,98	n.a.	BMB*
2	26,51	n.a.	194,292	336,046	50,02	n.a.	BMB*
Total:			641,569	671,785	100,00	0,000	

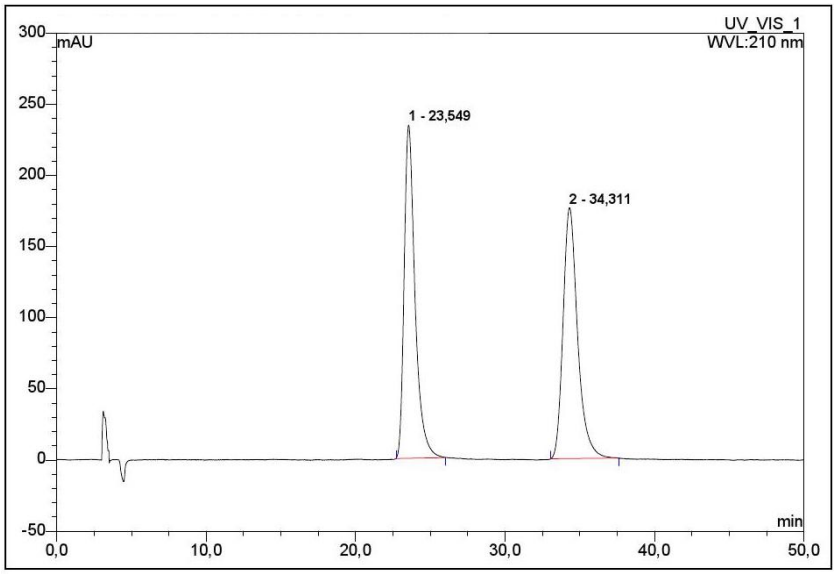




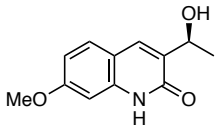
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,96	n.a.	5,786	3,695	2,15	n.a.	BMB*
2	25,46	n.a.	104,405	168,071	97,85	n.a.	BMB*
Total:			110,191	171,766	100,00	0,000	

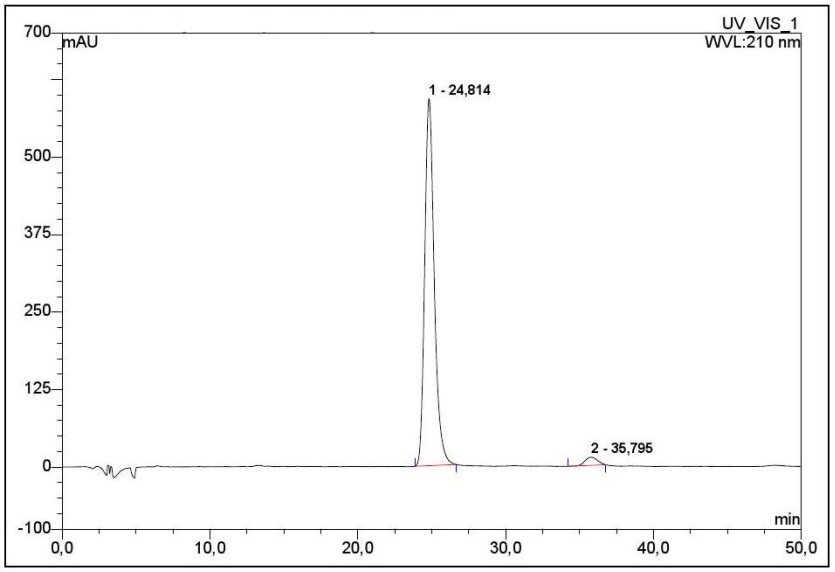
*2.2.10 (S)-3-(1-Hydroxyethyl)-7-methoxy-2-quinolone (**7j**)*





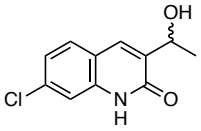
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23,55	n.a.	234,023	196,772	49,82	n.a.	BMB*
2	34,31	n.a.	176,278	198,198	50,18	n.a.	BMB*
Total:			410,300	394,969	100,00	0,000	

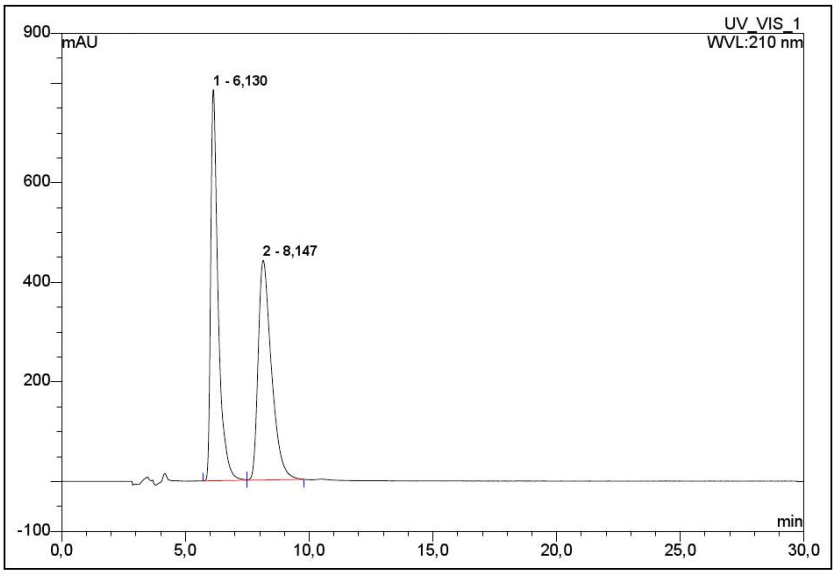




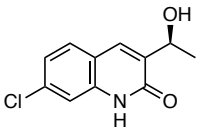
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24,81	n.a.	591,881	442,437	97,26	n.a.	BMB
2	35,80	n.a.	13,107	12,474	2,74	n.a.	BMB*
Total:			604,988	454,911	100,00	0,000	

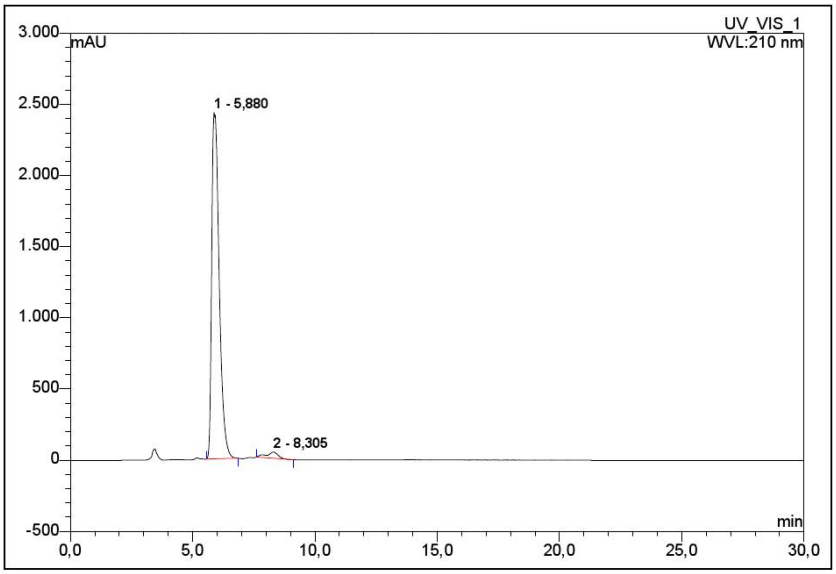
*2.2.11 (S)-7-Chloro-3-(1-hydroxyethyl)-2-quinolone (**7k**)*





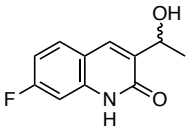
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,13	n.a.	785,833	274,225	50,04	n.a.	BM
2	8,15	n.a.	441,303	273,782	49,96	n.a.	MB
Total:			1227,136	548,007	100,00	0,000	

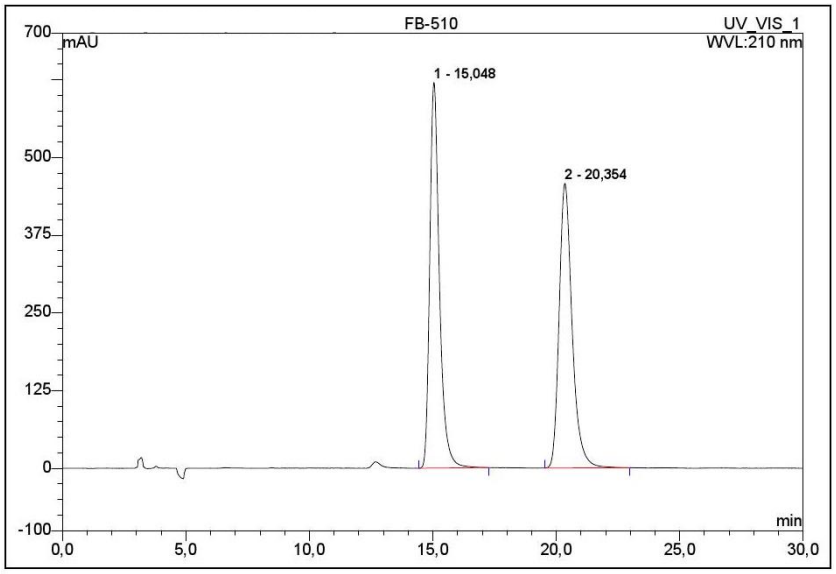




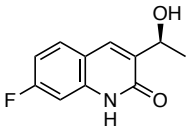
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5,88	n.a.	2434,867	862,050	97,31	n.a.	BMB*
2	8,30	n.a.	44,005	23,854	2,69	n.a.	BMB*
Total:			2478,872	885,903	100,00	0,000	

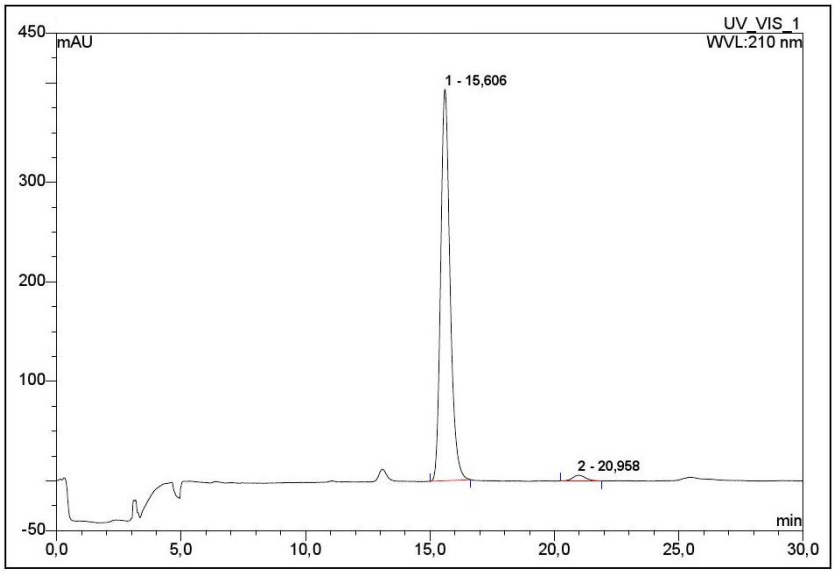
*2.2.12 (S)-7-Fluoro-3-(1-hydroxyethyl)-2-quinolone (**7l**)*





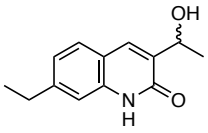
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15,05	n.a.	620,168	280,853	50,24	n.a.	BMB*
2	20,35	n.a.	457,563	278,214	49,76	n.a.	BMB*
Total:			1077,731	559,067	100,00	0,000	

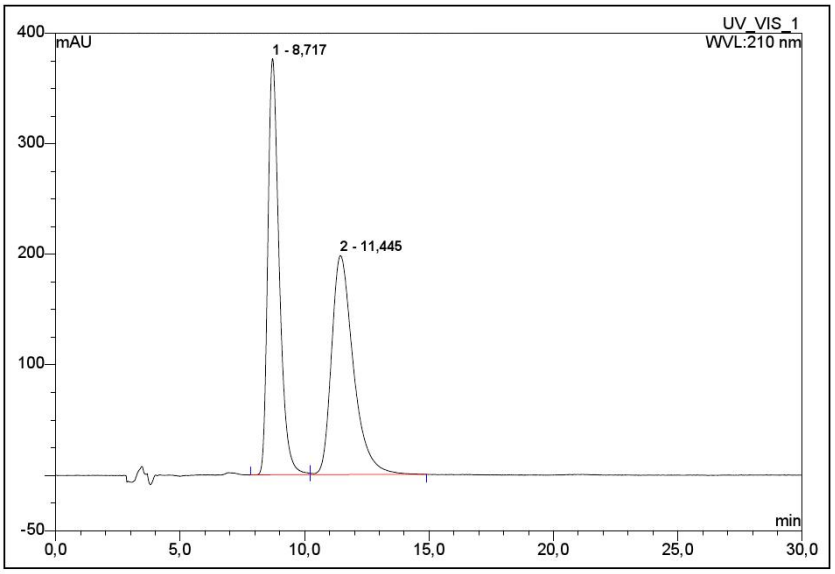




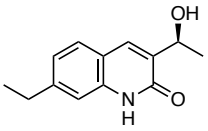
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15,61	n.a.	393,482	171,642	98,08	n.a.	BMB
2	20,96	n.a.	5,675	3,361	1,92	n.a.	BMB*
Total:			399,156	175,003	100,00	0,000	

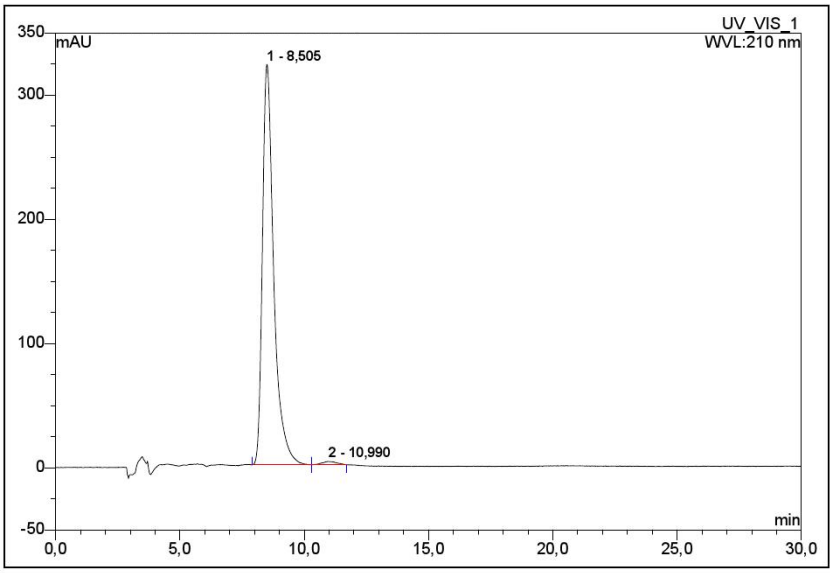
*2.2.13 (S)--3-(1-Hydroxyethyl)-7-ethyl-2-quinolone (**7m**)*





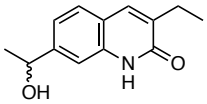
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,72	n.a.	376,520	199,371	49,70	n.a.	BM *
2	11,44	n.a.	198,154	201,807	50,30	n.a.	MB*
Total:			574,673	401,178	100,00	0,000	

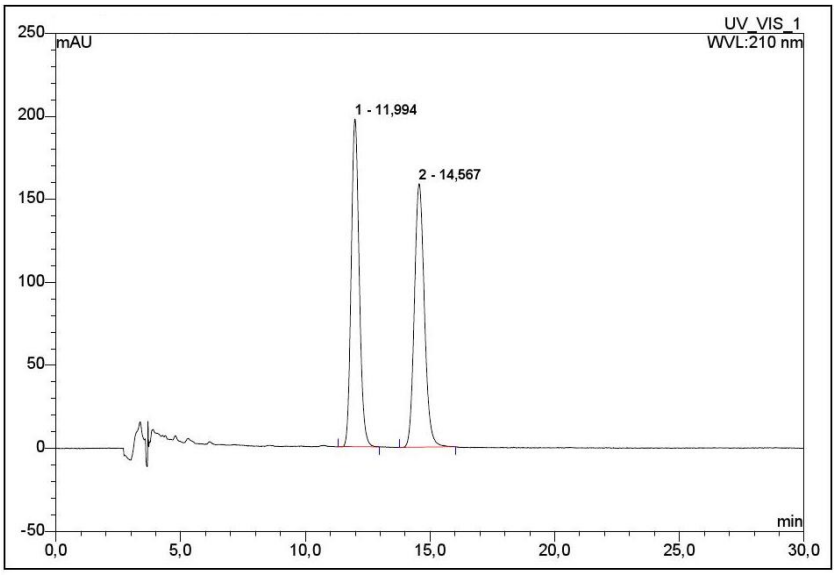




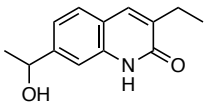
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,51	n.a.	322,323	169,779	98,90	n.a.	BMb*
2	10,99	n.a.	2,723	1,886	1,10	n.a.	bMB*
Total:			325,046	171,665	100,00	0,000	

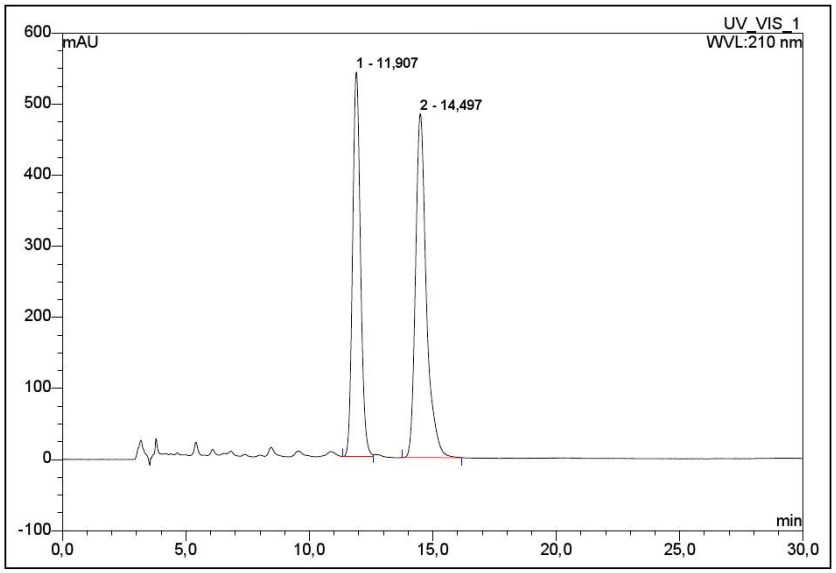
*2.2.14 (S)-3-Ethyl-7-(1-hydroxyethyl)-2-quinolone (**6n**)*





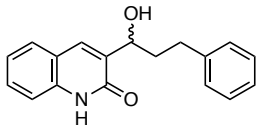
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,99	n.a.	197,426	73,266	49,81	n.a.	BMB*
2	14,57	n.a.	158,600	73,829	50,19	n.a.	BMB*
Total:			356,026	147,095	100,00	0,000	

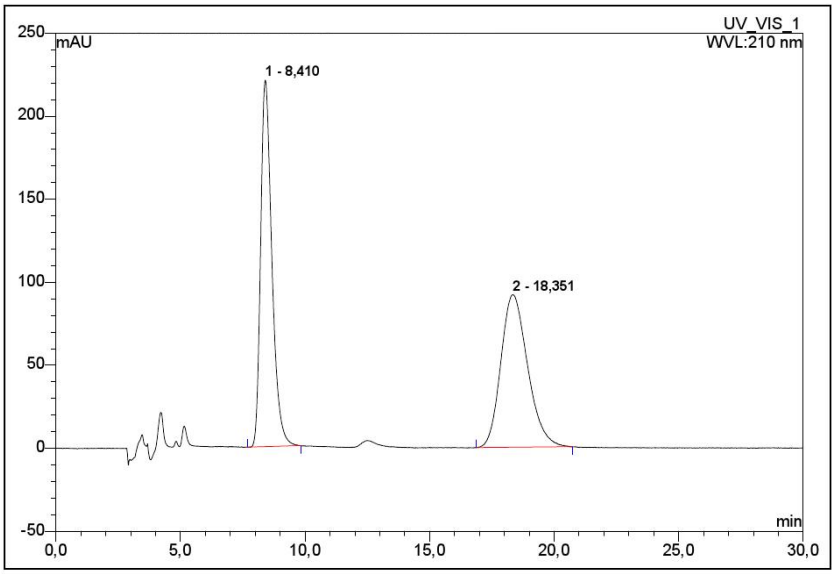




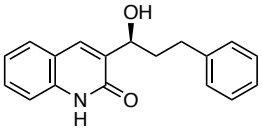
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,91	n.a.	541,070	200,013	44,91	n.a.	BM *
2	14,50	n.a.	483,753	245,352	55,09	n.a.	BMB*
Total:			1024,823	445,365	100,00	0,000	

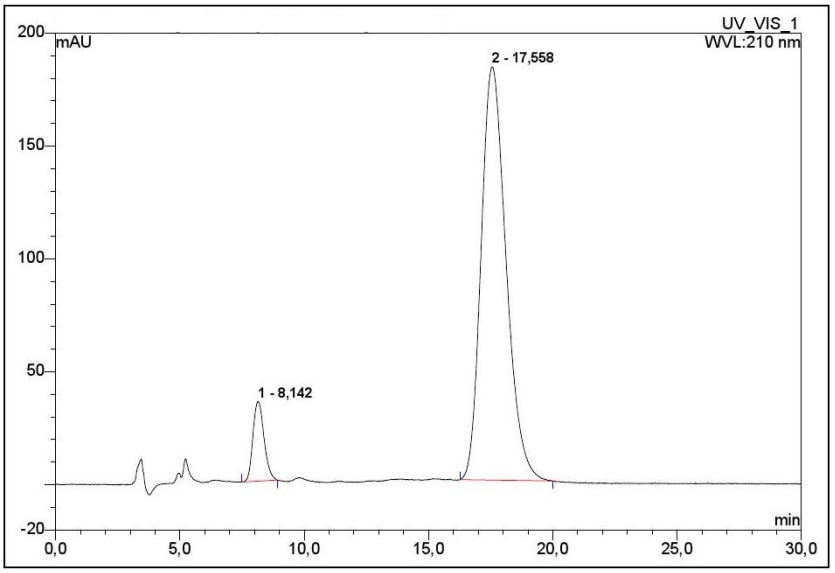
*2.2.15 (S)-3-(1-Hydroxy-3-phenylpropyl)-2-quinolone (**7o**)*





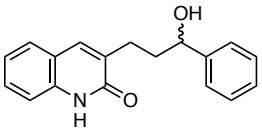
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,41	n.a.	220,730	115,085	50,10	n.a.	BMB*
2	18,35	n.a.	91,911	114,609	49,90	n.a.	BMB*
Total:			312,641	229,694	100,00	0,000	

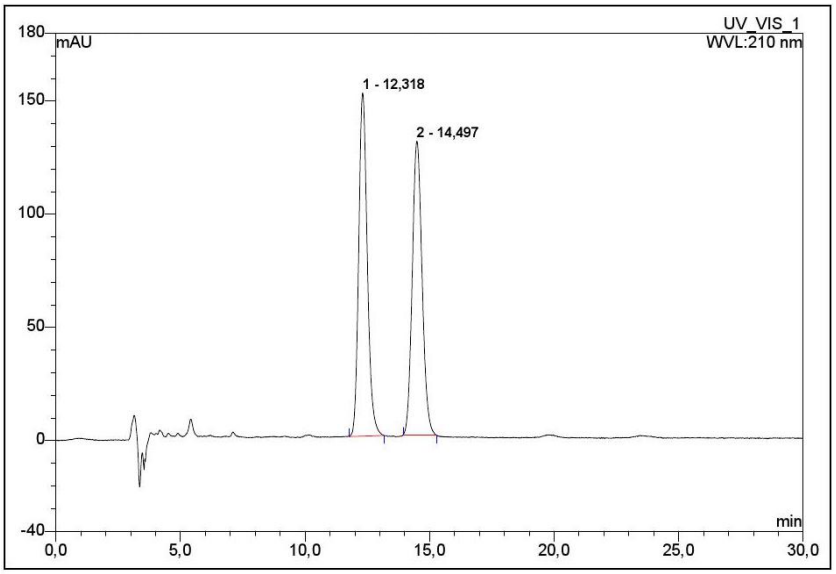




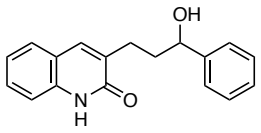
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,14	n.a.	35,300	18,228	7,90	n.a.	BMB*
2	17,56	n.a.	183,012	212,586	92,10	n.a.	BMB*
Total:			218,312	230,814	100,00	0,000	

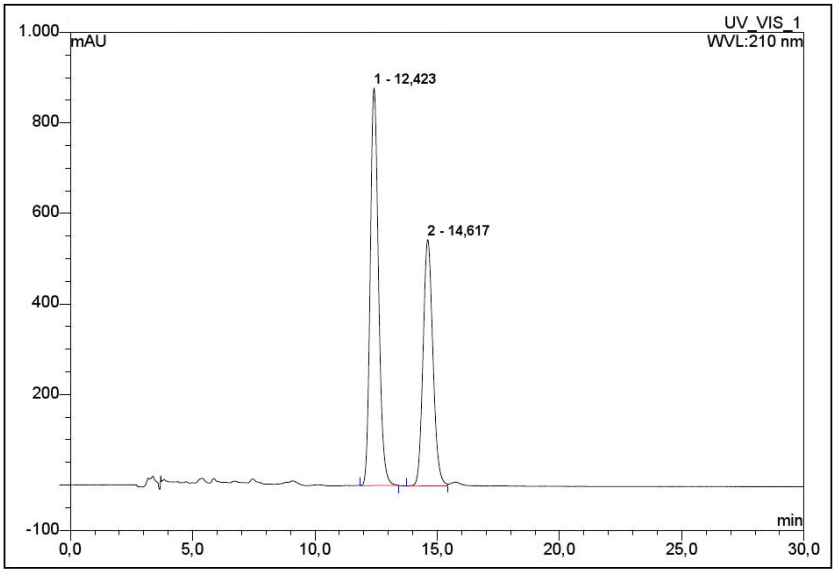
*2.2.16 3-(3-Hydroxy-3-phenylpropyl)-2-quinolone (**6p**)*





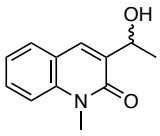
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,32	n.a.	151,616	60,391	50,38	n.a.	BMB
2	14,50	n.a.	129,877	59,479	49,62	n.a.	BMB
Total:			281,492	119,870	100,00	0,000	

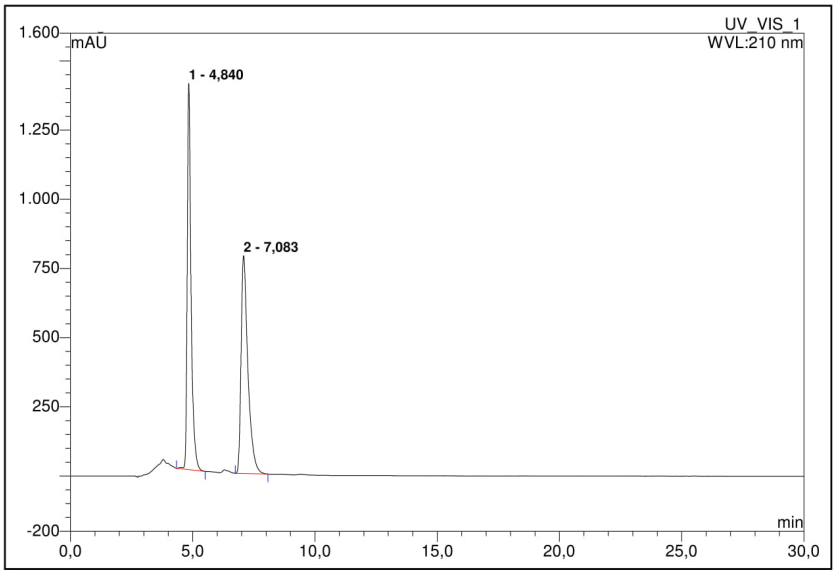




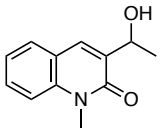
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,42	n.a.	878,257	344,286	57,64	n.a.	BMB
2	14,62	n.a.	543,961	253,059	42,36	n.a.	BM *
Total:			1422,218	597,345	100,00	0,000	

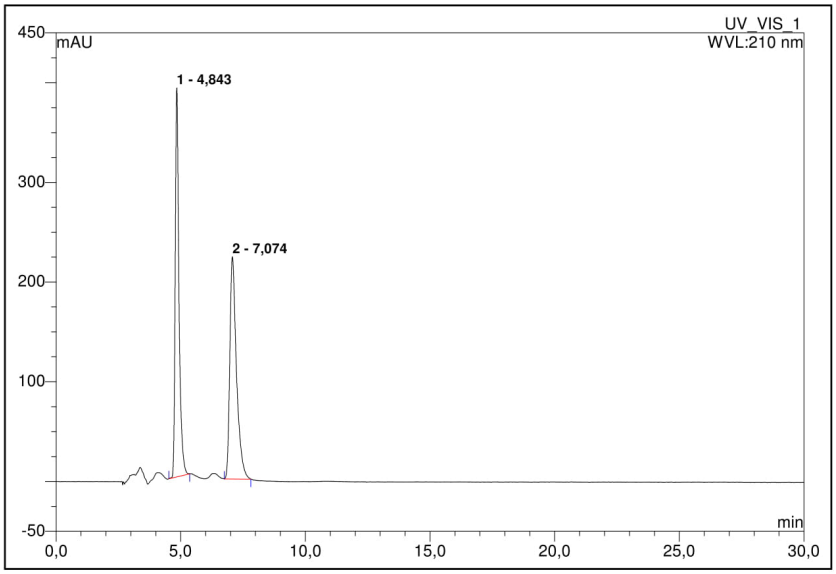
*2.2.17 3-(1-Hydroxyethyl)-N-methyl-2-quinolone (**10**)*





No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4,84	n.a.	1396,924	255,388	50,06	n.a.	BMB
2	7,08	n.a.	787,522	254,787	49,94	n.a.	BMB
Total:			2184,445	510,175	100,00	0,000	





No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4,84	n.a.	390,327	68,160	49,60	n.a.	BMB
2	7,07	n.a.	223,080	69,261	50,40	n.a.	BMB
Total:			613,407	137,421	100,00	0,000	

3 X-ray crystallographic data

3.1 Crystal structure report for compound 5 (CCDC 1967795)

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (*Bruker* APEX III, κ-CMOS), a TXS rotating anode with MoK_α radiation (λ = 0.71073 Å) and a *Helios* optic using the APEX3 software package.[17] Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[18] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[18]Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL in conjunction with SHELXLE.[19-21] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)}$ = 1.5·$U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å, all with $U_{iso(H)}$ = 1.2·$U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL weighting scheme.[19] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[22] Images of the crystal structures were generated with PLATON.[23] CCDC 1967795 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

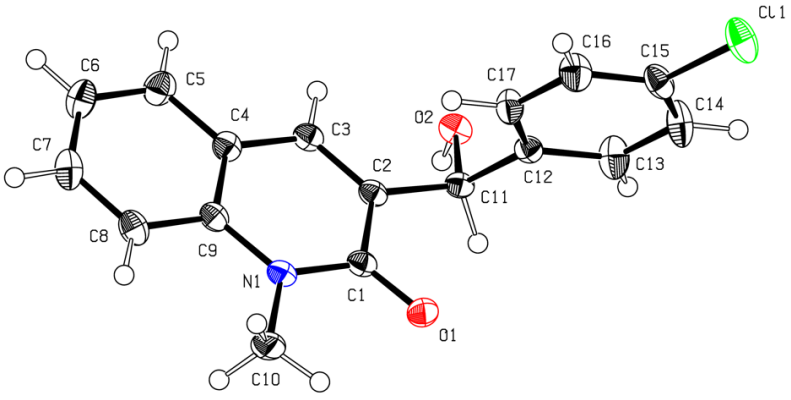


Figure S1 ORTEP style representation of compound **5** (CCDC 1967795) showing the atom numbering scheme with ellipsoids at the 50% probability level.

Diffractometer operator C. Jandl
scanspeed 1-10 s per frame
dx 50 mm
2350 frames measured in 10 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{17}H_{14}ClNO_2$

M_r = 299.74	D_x = 1.428 mg m^{-3}
Orthorhombic, $P2_12_12_1$	Melting point: ? K
Hall symbol: P 2ac 2ab	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 5.3182 (4) Å	Cell parameters from 9204 reflections
b = 10.9400 (7) Å	θ = 2.6–26.9°
c = 23.9705 (16) Å	μ = 0.28 mm^{-1}
V = 1394.63 (17) Å^3	T = 123 K
Z = 4	Fragment, colourless
F(000) = 624	0.44 × 0.25 × 0.11 mm

Data collection

Bruker Photon CMOS diffractometer	2851 independent reflections
Radiation source: TXS rotating anode	2821 reflections with $I > 2\sigma(I)$
Helios optic monochromator	R_{int} = 0.019
Detector resolution: 16 pixels mm^{-1}	θ_{max} = 26.4°, θ_{min} = 2.5°
phi– and ω–rotation scans	h = −6 6
Absorption correction: multi-scan *SADABS* 2016/2, Bruker	k = −13 13
T_{min} = 0.720, T_{max} = 0.745	l = −29 29
37764 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.027	$W = 1/[\Sigma^2(FO^2) + (0.0421P)^2 + 0.4183P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$wR(F^2)$ = 0.074	$(\Delta/\sigma)_{max}$ = 0.001

S = 1.08

2851 reflections

195 parameters

0 restraints

0 constraints

Primary atom site location: iterative

Secondary atom site location: difference Fourier map

$\Delta\rho_{max}$ = 0.19 e Å^{-3}

$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Extinction correction: none

Extinction coefficient: -

Absolute structure: Flack (1983), Parsons (2013)[24, 25]

Absolute structure parameter: 0.022 (6)

IV. Abbreviations

°	degree
Ac	acetyl
aqueous	aqueous
br	broad
Bu	butyl
C	Celsius
calc.	calculated
δ	chemical shift
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
ee	enantiomeric excess
EI	Electron Ionization
ESI	Electrospray Ionization
et. al.	et alii (and others)
Et	ethyl
equiv	equivalents
FCC	flash column chromatography
FTIR	fourier transformed infrared spectroscopy
g	gram
h	hour(s)
HPLC	high performance liquid chromatography
HR	high resolution
Hz	hertz
i	*iso*
IR	infrared
J	coupling constant
L	liter
µ	micro
m	milli, meter, multiplet
m	*meta*
M	molar
Me	methyl
min	minute(s)
MS	mass spectrometry
NMR	Nuclear Magnetic Resonance
o	*ortho*
p	*para*
Ph	phenyl
ppm	parts per million
Pr	propyl
py	pyridine
q	quartet
quant.	quantitative
R_f	retardation factor
s	singlet
saturated	saturated
t	triplet
t	*tert*

TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
virt	virtual
UV	ultra-violet

V. References

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