An Efficient Approach to N-Protected
1,2,3,3a-Tetrahydrocyclopenta[b]quinolin-1-ones

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In the course of our investigations into the synthesis of benzoanalogues of streptazolin we also studied the construction of 1,2,3,3a-tetrahydrocyclopenta[b]quinolin-1-ones which could be successfully solved by an intramolecular acylation using a bromo-lithium exchange, starting from 3-bromoquinoline.

The antibiotic streptazolin (**1**) has stimulated several total syntheses [1-4] with regard to its exceptional structure and its properties [5,6]. The diene systeme represents a structural feature essential for antibiotic (and antifungal) activity but gives rise to the tendency of streptazolin to polymerize. This propensity and its limited antibiotic activity motivated us to produce mimicries, which contain the units of streptazolin, required for biological activity, and which reach better stability and (possibly) enhanced activity [7]. Our interest in further exploration of this subject focussed on the synthesis of benzoannulated streptazolin derivatives. During a synthetic approach to these analogues we investigated the construction of the cyclopenta[b]quinolin-1-one skeleton (**2**).
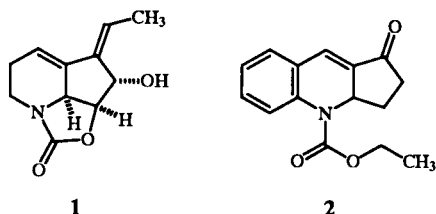

The planned synthetic sequence directed toward the preparation of **2** is outlined in Scheme 1. Yamaguchi and co-workers have demonstrated the regioselective 2-allylation of pyridines and quinolines applying allylic tin reagents [8]. Following their report, quinoline (**3**) was reacted with allyl-tri-*n*-butyltin in the presence of ethyl chloroformate yielding the 2-allyl compound **4** in excellent yield without formation of the 4-allylated regioisomer. On the other hand, a two step procedure, performing the 2-alkylation by allyl Grignard reagents, followed by 1-acylation with chloroformates, provided the 2-allyl compound only in low amounts [9]. Hydroboration with 9-borabicyclo[3.3.1]nonane led to the alcohol **5**. The following oxidation step to **6** was successfully accomplished either applying Swern conditions (dimethylsulfoxid/oxalyl chloride) or using pyridinium chlorochromate, supported on aluminum oxide [10]. Formation of the oxime **7** furnished the starting compound for the crucial step, the INOC-

cyclization to **8**. The further sequence should consist in a hydrogenolytic cleavage to the β-hydroxy ketone **9** and a dehydration yielding the target tricyclic ketone **2**.
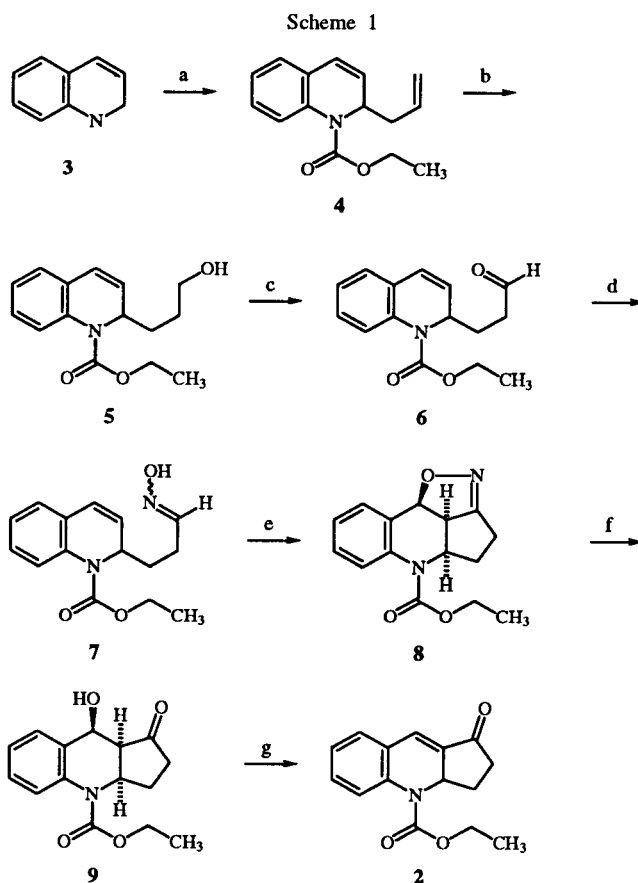
Scheme 1

a) allyltri-*n*-butyltin, ClCOOEt, CH$_2$Cl$_2$, -10°; b) 9-borabicyclo-[3.3.1]nonane (9-BBN), tetrahydrofuran; NaOH, H$_2$O$_2$ c) (PCC), CH$_2$Cl$_2$ or (COCl)$_2$/dimethyl sulfoxide, CH$_2$Cl$_2$; d) NH$_2$OH•HCl, pyridine; e) NaOCl, CH$_2$Cl$_2$; f) Raney-Ni, CH$_3$OH, H$_2$O; g) CH$_3$SO$_2$Cl, triethylamine

Though, the 2+3 cycloaddition, carried out according to the protocol published by Kozikowski [2] — in situ generation of the nitrile oxide by means of sodium hypochlorite
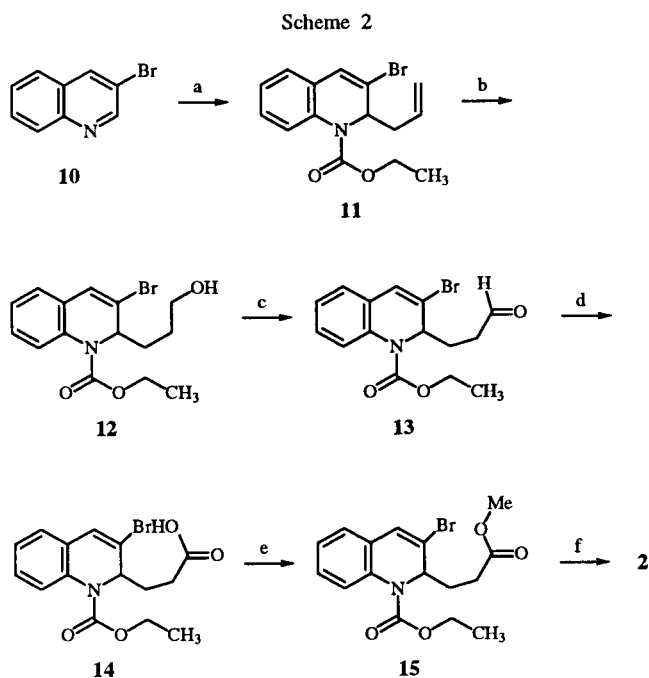
Scheme 2

a) allyltri-*n*-butyltin, ClCOOEt, CH$_2$Cl$_2$, -10°; b) 9-borabicyclo-
[3.3.1]nonane (9-BBN), tetrahydrofuran; NaOH, H$_2$O$_2$ c) (PCC),
CH$_2$Cl$_2$ or (COCl)$_2$/dimethyl sulfoxide, CH$_2$Cl$_2$; d) Ag$_2$O, tetrahydrofu-
ran; e) MeOH/SOCl$_2$; f) *sec*-butyllithium, tetrahydrofuran, -78°

in a two-solvent system of water and dichloromethane [11]
— did not yield the desired isoxazoline **8**. Numerous vari-
ations of these reaction conditions (separate oxidation to
the nitrile oxide by means of sodium hyprobromite, *N*-bro-
mosuccinimide, and comparable oxidation reactions
[12,13]) did give evidence for the formation of the
attempted *N,O*-heterocycle **8**. Apparently, the enhance-
ment of rigidity, caused by the annulated aromatic ring,
prevented the fruitful orientation for the intramolecular
1,3-dipolar cycloaddition.

Therefore, we initiated an alternative approach (Scheme
2). We repeated the described sequence, but we started
with 3-bromoquinoline (**10**). By using tin reagents for
2-allylation, the high chemoselectivity gives the opportu-
nity to tolerate the bromo substituent. The 2-regioselec-
tivity was found to be as excellent as in the former case,
although **10** is carrying a substituent at the 3-position. The
occupied 3-position facilitated the estimation of regio-
selectivity by ^{1}H nmr spectroscopy. In this case, a singlet is
produced (for 4-H of the 2-allylated product **11**, or for 2-H
of the 4-allylated compound) at typical field.

In the following, the primary alcohol **12** was obtained by
hydroboration of **11**. The oxidation to the aldehyde (→**13**)
could be performed using the same reaction conditions, as
described before. A second oxidation step by treating of **13**
with silver oxide yielded the carboxylic acid **14**. The direct
oxidation of the alkylboronic acid, produced by reaction of

11 with dibromoborane dimethyl sulfid complex and oxida-
tion with chromium trioxide, as described by Brown, was
proved to be ineffective [14]. Esterification (methanol/
thionyl chloride) furnished the methyl ester **15**. The
intramolecular 3-C—3'-C formation could be solved by an
intermediary bromo-lithium-exchange, initiated by slow
addition of *sec*-butyllithium to the bromoester **15** in a
tetrahydrofuran solution at -78°. The desired ketone **2** was
furnished in pretty good yield, providing a further of few
examples of successful intramolecular acylations, described
in the literature, in which an alkyl ester reacts with an
organolithium intermediate [3,15].

EXPERIMENTAL

Solvents and common reagents were obtained commercially
and used as received. Solvents were dried as follows:
dichloromethane was distilled under argon from phosphorus pen-
toxide, methanol was refluxed under argon over magnesium, and
tetrahydrofuran was refluxed under argon over sodium ben-
zophenone ketyl and distilled. Ir spectra were recorded as liquid
films between potassium bromide salt disks using a Perkin Elmer
model 298 spectrophotometer. Nmr spectra were determined on
Bruker AC 80 and Varian Unity-plus 300 spectrometers. All sub-
stances were measured in deuteriochloroform as a solvent. The
[1]H nmr spectra were recorded with tetramethylsilan as the inter-
nal reference, the chemical shifts of the ^{13}C nmr spectra are given
in ppm related to the resonance of deuteriochloroform (77.0
ppm). Mass spectra were recorded on Shimadzu QP 5000,
Finnigan 8230 and Finnigan MAT 900S instruments. Column
chromatography was conducted on Merck silica gel 60.

General Procedure for the Reactions of Quinolines **3** and **10** with
Allyltri-*n*-butyltin and Ethyl Chloroformate.

A solution of 88 mmoles of quinoline (**3** or **10**, respectively)
and 26.6 g (80 mmoles) of allyltri-*n*-butyltin, dissolved in 150 ml
of dry dichloromethane, was cooled to -10°. Then, 10 ml (105
mmoles) of ethyl chloroformate was slowly added. The reaction
mixture was stirred over night and evaporated *in vacuo* to give a
colorless oil. The residue was separated by column chromatogra-
phy, elution with light petroleum afforded tri-*n*-butyl chloride,
solvent change to dichloromethane gave the 2-allyl-1,2-dihydro-
quinoline **4** or **11**, respectively.

2-Allyl-1,2-dihydroquinoline-1-carboxylic Acid Ethyl Ester (**4**).

Performing the reaction, starting from 10.4 ml (88 mmoles) of
3, gave 20.9 g (98%) of **4** as a colorless oil; ir: ν 1705 cm^{-1}
(NCOO); ^{1}H nmr: (80 MHz) δ 1.22 (t, 3H, OCH$_2$CH_3, J = 7.0
Hz), 2.20 (t, 2H, 1'-H, J = 7.5 Hz), 4.18 (q, 2H, OCH_2CH$_3$, J =
7.0 Hz), 4.80-5.25 (m, 3H, 2-H, 3'-H), 5.55-5.90 (m, 1H, 2'-H),
6.04 (dd, 1H, 3-H, J = 6.0, 9.5 Hz), 6.48 (d, 1H, 4-H, J = 9.5 Hz),
7.00-7.35 (m, 3H, 5-H, 6-H, 7-H), 7.52 ppm (d, 1H, 8-H, J = 7.5
Hz); ^{13}C nmr: (20.12 MHz) δ 14.1 (OCH$_2$CH_3), 37.2 (1'-C), 52.3
(2-C), 62.4 (OCH_2CH$_3$), 117.1 (3'-C), 123.7, 124.2, 124.5, 125.7,
127.0, 128.7, 133.1 (arom CH, 3-C, 4-C, 2'-C), 126.6 (4a-C),
134.0 (8a-C), 154.2 ppm (NCOO); ms: m/z 202 (M$^+$-41).

Anal. Calcd. for C$_{15}$H$_{17}$NO$_2$: C, 74.05; H, 7.04; N, 5.76.
Found: C, 73.82; H, 6.93; N, 5.74.

2-Allyl-3-bromo-1,2-dihydroquinoline-1-carboxylic Acid Ethyl Ester (11).

Performing the reaction, starting from 18.3 g (88 mmoles) of 10, gave 27.2 g (92%) of 11 as a yellowish oil; ir: ν 1705 cm^{-1} (NCOO); ^{1}H nmr: (80 MHz) δ 1.25 (t, 3H, OCH$_2$CH_3, J = 7.0 Hz), 1.80-2.50 (m, 2H, 1'-H), 4.20 (q, 2H, OCH_2CH$_3$, J = 7.0 Hz), 4.70-5.30 (m, 3H, 2-H, 3'-H), 5.40-5.90 (m, 1H, 2'-H), 6.70 (s, 1H, 4-H), 6.85-7.30 (m, 3H, 5-H, 6-H, 7-H), 7.52 ppm (d, 1H, 8-H, J = 7.5 Hz); ^{13}C nmr: (20.12 MHz) δ 14.2 (OCH$_2$CH$_3$), 34.6 (1'-C), 52.3 (2-C), 62.8 (OCH$_2$CH$_3$), 117.8 (3'-C), 124.2, 124.6, 125.2, 126.6, 127.4, 132.5 (arom CH, 4-C, 2'-C), 121.1, 126.8, 132.5 (3-C, 4a-C, 8a-C), 153.9 ppm (NCOO); ms: m/z 280/282 (M$^+$–41).

Anal. Calcd. for C$_{15}$H$_{16}$NO$_2$Br: C, 55.92; H, 5.01; N, 4.35. Found: C, 55.74; H, 4.78; N, 4.31.

General Procedure for the Reactions of 2-Allyl-1,2-dihydroquinolines 4 and 11 with 9-Borabicyclo[3.3.1]nonane.

To a solution of 43 mmoles of the selected 2-allyl-1,2-dihydroquinoline (4 or 11, respectively), dissolved in 50 ml of dry tetrahydrofuran, 120 ml of a 0.5 *M* solution of 9-borabicyclo[3.3.1]nonane were slowly added at 0°. The reaction mixture was stirred for 2 hours. After cooling to 0° the solution was hydrolized by simultaneous addition of 15 ml of a 30% solution of hydrogen peroxide and 15 ml of an aqueous 3 *N* solution of sodium hydroxide. Then, the solution was heated to 50° for 4 hours. The reaction mixture was extracted with diethyl ether (4 x 50 ml), the combined ether layers were dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was purified by column chromatography (ethyl acetate) yielding the alcohols 5 or 12, respectively.

2-(3-Hydroxypropyl)-1,2-dihydroquinoline-1-carboxylic Acid Ethyl Ester (5).

Performing the reaction, starting from 10.5 g (43 mmoles) of 4, gave 10.2 g (90%) of 5 as a yellowish oil; ir: ν 1705 (NCOO), 3450 cm^{-1} (OH); ^{1}H nmr: (80 MHz) δ 1.22 (t, 3H, OCH$_2$CH_3, J = 7.0 Hz), 1.35-1.65 (m, 4H, 1'-H, 2'-H), 3.45-3.70 (m, 2H, 3'-H), 4.20 (q, 2H, OCH_2CH$_3$, J = 7.0 Hz), 5.00 (m, 1H, 2-H), 6.03 (dd, 1H, 3-H, J = 6.0, 9.5 Hz), 6.47 (d, 1H, 4-H, J = 9.5 Hz), 6.95-7.30 (m, 3H, 5-H, 6-H, 7-H), 7.48 ppm (d, 1H, 8-H, J = 7.0 Hz); ^{13}C nmr: (20.12 MHz) δ 13.9 (OCH$_2$CH$_3$), 27.8, 28.9 (1'-C, 2'-C), 52.2 (2-C), 61.6 (3'-C), 62.3 (OCH$_2$CH$_3$), 124.0, 124.3, 124.4, 125.8, 127.0, 129.5 (arom. CH, 3-C, 4-C), 127.6 (4a-C), 133.8 (8a-C), 154.7 ppm (NCOO); ms: m/z 261 (M$^+$).

Anal. Calcd. for C$_{15}$H$_{19}$NO$_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.92; H, 7.12; N, 5.36.

3-Bromo-2-(3-hydroxypropyl)-1,2-dihydroquinoline-1-carboxylic Acid Ethyl Ester (12).

Performing the reaction, starting from 13.8 g (43 mmoles) of 11, gave 12.8 g (88%) of 12 as a yellowish oil; ir: ν 1705 (NCOO), 3450 cm^{-1} (OH); ^{1}H nmr: (80 MHz) δ 1.30 (t, 3H, OCH$_2$CH_3, J = 7.0 Hz), 1.40-2.05 (m, 4H, 1'-H, 2'-H), 3.56 (m, 2H, 3'-H), 4.25 (q, 2H, OCH_2CH$_3$, J = 7.0 Hz), 5.22 (m, 1H, 2-H), 6.78 (s, 1H, 4-H), 7.00-7.35 (m, 3H, 5-H, 6-H, 7-H), 7.58 ppm (d, 1H, 8-H, J = 7.0 Hz); ^{13}C nmr: (75.45 MHz) δ 14.3 (OCH$_2$CH$_3$), 35.0 (1'-C), 59.1 (2-C), 62.2 (OCH$_2$CH$_3$), 118.0 (3'-C), 124.4, 125.0, 125.5, 127.0, 127.7, 133.0 (arom CH, 4-C, 2'-C), 121.5, 127.2, 132.9 (arom C, 3-C), 153.8 ppm (NCOO); ms: m/z 339/341 (M$^+$).

Anal. Calcd. for C$_{15}$H$_{18}$NO$_3$Br: C, 52.96; H, 5.33; N, 4.12. Found: C, 52.92; H, 5.24; N, 4.08.

General Procedure for the Oxidation of Alcohols 5 and 12 to the Aldehydes 6 and 13.

Method A.

To a solution of 38.3 mmoles of primary alcohol (5 or 12, respectively) in 200 ml of dichloromethane were added 40 g of pyridinium chlorochromate, supported on aluminum oxide (1 g of this reagent is able to oxidize 1 mmole of an alcohol) [10]. The reaction mixture was stirred over night, filtrated through Celite and evaporated *in vacuo*. Purification by column chromatography (ethyl acetate) yielded 6 or 13, respectively.

Method B.

A solution of 5.0 ml (57.4 mmoles) of oxalyl chloride in 50 ml of dry dichloromethane was cooled to –78° and treated with 5.45 ml (76.6 mmoles) of dimethylsulfoxide. After 5 minutes at –78° 38.3 mmoles of primary alcohol (5 or 12, respectively), dissolved in 50 ml dichloromethane, were added. Then, the solution was stirred for 30 minutes After slow addition of 27.5 ml (197.5 mmoles) of triethylamine the cooling bath was removed, the reaction was stirred for 1 hour and then quenched with water. The aqueous layer was extracted twice with dichloromethane. The combined organic layers was washed with brine, dried over anhydrous sodium sulfate and evaporated *in vacuo*. Purification by column chromatography (ethyl acetate) yielded 6 or 13, respectively.

2-(3-Oxopropyl)-1,2-dihydroquinoline-1-carboxylic Acid Ethyl Ester (6).

Performing the reaction, starting from 10.0 g (38.3 mmoles) of 5, gave 6.75 g (68%, method A) and 9.1 g (92%, method B) of 6, respectively; ir: ν 1700 cm^{-1} (NCOO, CHO); ^{1}H nmr: (80 MHz) δ 1.28 (t, 3H, OCH$_2$CH_3, J = 7.5 Hz), 1.45-2.00 (m, 2H, 1'-H), 2.30-2.55 (m, 2H, 2'-H), 4.19 (q, 2H, OCH_2CH$_3$, J = 7.5 Hz), 4.85-5.15 (m, 1H, 2-H), 6.02 (dd, 1H, 3-H, J = 6.0, 9.5 Hz), 6.50 (d, 1H, 4-H, J = 9.5 Hz), 7.00-7.35 (m, 3H, 5-H, 6-H, 7-H), 7.55 (d, 1H, 8-H, J = 7.0 Hz), 9.70 ppm (s, 1H, CHO); ^{13}C nmr: (75.45 MHz) δ 14.6 (OCH$_2$CH$_3$), 23.1 (1'-C), 39.5 (2'-C), 59.1 (2-C), 62.4 (OCH$_2$CH$_3$), 124.3, 124.6, 125.1, 126.1, 127.4, 128.7 (arom CH, 3-C, 4-C), 126.8 (4a-C), 132.7 (8a-C), 154.2 (NCOO), 200.6 ppm (C=O); ms: m/z 259 (M$^+$).

Anal. Calcd. for C$_{15}$H$_{17}$NO$_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.28; H, 6.53; N, 5.38.

3-Bromo-2-(3-oxopropyl)-1,2-dihydroquinoline-1-carboxylic Acid Ethyl Ester (13).

Performing the reaction, starting from 11.7 g (38.3 mmoles) of 12, gave 7.6 g (65%, method A) and 9.9 g (85%, method B) of 13, respectively; ir: ν 1700 cm^{-1} (NCOO, CHO); ^{1}H nmr: (300 MHz) δ (ppm) 1.23 (t, 3H, OCH$_2$CH_3, J = 7.0 Hz), 1.55-1.72, 1.96-2.08 (each m, each 1H, 1'-H), 2.39 (m, 2H, 2'-H), 4.18 (m, 2H, OCH_2CH$_3$), 5.11 (dd, 1H, 2-H, J = 4.0, 10.0 Hz), 6.72 (s, 1H, 4-H), 6.94-7.05 (m, 2H, arom H), 7.16 (t, 1H, arom H, J = 8.0 Hz), 7.42 (d, 1H, 8-H, J = 8.0 Hz), 9.62 ppm (1H, CHO); ^{13}C nmr: (75.45 MHz) δ 14.3 (OCH$_2$CH$_3$), 23.1 (1'-C), 39.4 (2'-C), 59.1 (2-C), 62.6 (OCH$_2$CH$_3$), 124.9, 126.1, 125.7, 127.2, 127.9 (arom CH, 4-C), 123.3, 127.1, 132.6 (arom C, 3-C), 154.1 (NCOO), 200.5 ppm (CHO); ms: m/z 337/339 (M$^+$).

Anal. Calcd. for C$_{15}$H$_{16}$NO$_3$Br: C, 53.27; H, 4.77; N, 4.14. Found: C, 52.95; H, 4.58; N, 4.08.

2-(3-Hydroximino)-1,2-dihydroquinoline-1-carboxylic Acid Ethyl Ester (7).

To a solution of 405 mg (1.5 mmoles) of 6 in 5 ml of dry pyridine 420 mg (6 mmoles) of hydroxylammonium chloride were added. The solution was stirred over night, partitioned between water and diethyl ether and, in the following, extracted twice with diethylether. The combined organic layers were washed with aqueous 1 N hydrochloric acid and brine, dried over anhydrous sodium sulfate and evaporated in vacuo providing 290 mg (67%) of 7 as a colorless oil; ir: ν 1700 cm^{-1} (NCOO, HC=N-OH); ^{1}H nmr: (80 MHz) δ 1.28 (t, 3H, OCH$_2$CH_3, J = 7.5 Hz), 1.40-1.80 (m, 2H, 1'-H), 2.10-2.55 (m, 2H, 2'-H), 5.07 (m, 1H, 2-H), 6.06 [dd, 0.5H, 3-H (oxime-I), J = 6.0, 9.5 Hz], 6.02 [dd, 0.5H, 3-H (oxime-II), J = 6.0, 9.5 Hz], 6.48 (d, 1H, 4-H, J = 9.5 Hz), 6.68 [t, 0.5H, HC=N-OH (oxime-1), J = 5.5 Hz], 7.00-7.40 [m, 4.5H, arom H, HC=N-OH (oxime-2)], 7.54 ppm (d, 1H, 8-H, J = 7.0 Hz); ms: m/z 288 (M$^+$).

Anal. Calcd. for C$_{15}$H$_{18}$N$_2$O$_3$: C, 65.68; H, 6.61; N, 10.21. Found: C, 65.52; H, 6.43; N, 10.18.

3-(3-Bromo-1-ethoxycarbonyl-1,2-dihydroquinolin-2-yl)-propionic Acid (14).

A solution of 1.0 g (6 mmoles) of silver nitrate in 5 ml of water was added under stirring to a solution of 0.48 g (12 mmoles) of sodium hydroxide in 5 ml of water. The resulting silver oxide suspension was combined with a solution which was prepared by dissolution of 1.35 g (4 mmoles) of 13 in 50 ml of tetrahydrofuran. The reaction mixture was stirred over night, filtrated through Celite, and the filtrate was evaporated in vacuo. The residue was partitioned between water and ethyl acetate, then, the ethyl acetate layer was extracted twice with water. The combined water layers were acidified with aqueous 2 N hydrochloric acid and extracted with ethyl acetate. The organic phases were dried over anhydrous sodium sulfate and evaporated in vacuo giving 1.50 g (74%) of 14 as colorless oil; ir: ν 1710 cm^{-1} (COOH, NCOO); ^{1}H nmr: (80 MHz) δ 1.25 (t, 3H, J = 7.5 Hz, OCH$_2$CH_3), 1.45-1.90 (m, 2H, 1'-H), 2.40 (t, 2H, J = 7.5 Hz, 2'-H), 4.20 (q, 2H, J = 7.5 Hz, OCH$_2$CH$_3$), 4.95-5.20 (m, 1H, 2-H), 6.70 (s, 1H, 4-H), 6.90-7.30 (m, 3H, arom. H), 7.48 ppm (1H, J = 8.0 Hz, 8-H); ^{13}C nmr: (75.45 MHz) δ 14.3 (OCH$_2$CH_3), 25.4 (1'-C), 29.6 (2'-C), 59.0 (2-C), 62.6 (OCH$_2$CH$_3$), 124.9, 125.1, 125.7, 127.1, 127.9 (arom. CH, 4-C), 121.3, 127.2, 132.6 (arom C, 3-C), 154.2 (NCOO), 177.8 ppm (COOH); ms: m/z 353/355 (M$^+$).

Anal. Calcd. for C$_{15}$H$_{16}$NO$_4$Br: C, 50.87; H, 4.55; N, 3.95. Found: C, 50.66; H, 4.42; N, 3.88.

3-(3-Bromo-1-ethoxycarbonyl-1,2-dihydroquinolin-2-yl)-propionic Acid Methyl Ester (15).

A solution of 1.06 g (3 mmoles) of 14 in 10 ml of dry methanol was cooled to 0°, then 0.5 ml of thionyl chloride was slowly added. The reaction mixture was stirred over night, evaporated in vacuo and partitioned between saturated aqueous sodium bicarbonate and dichloromethane. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with saturated aqueous sodium bicarbonate and brine. After drying with anhydrous sodium sulfate the solution was evaporated in vacuo giving 1.02 g (93%) of 15 as colorless oil; ir: ν 1715 cm^{-1} (COOH, NCOO); ^{1}H nmr: (300 MHz) δ 1.19 (t, 3H, OCH$_2$CH_3, J = 8.0 Hz), 1.58-1.62, 1.93-2.02 (each m, each 1H, 1'-H), 2.26 (m, 2H, 2'-H), 3.52 (s, 3H, OCH$_3$), 4.10-4.19 (m, 2H, OCH$_2$CH$_3$), 5.10 (dd, 1H, 2-H, J = 3.5, 10.0 Hz), 6.68 (s, 1H,

4-H), 6.90-6.99 (m, 2H, arom H), 7.12 (t, 1H, arom H, J = 9.0 Hz), 7.42 ppm (1H, 8-H, J = 8.0 Hz); ^{13}C nmr: (75.45 MHz) δ 14.3 (OCH$_2$CH$_3$), 25.7 (1'-C), 29.8 (2'-C), 51.5 (OCH$_3$), 59.1 (2-C), 62.5 (OCH$_2$CH$_3$), 124.8, 125.2, 125.7, 127.1, 127.9 (arom CH, 4-C), 121.4, 127.2, 132.7 (arom C, 3-C), 154.1 (NCOO), 172.9 ppm (COOCH$_3$); ms: m/z 367/369 (M$^+$).

Anal. Calcd. for C$_{16}$H$_{18}$NO$_4$Br: C, 52.19; H, 4.93; N, 3.80. Found: C, 51.95; H, 4.75; N, 3.78.

1-Oxo-1,2,3,3a-tetrahydrocyclopenta[b]quinoline-4-carboxylic Acid Ethyl Ester (2).

A solution of 1.85 g (5 mmoles) of 15 in dry tetrahydrofuran was cooled to –78°. At this temperature 4.3 ml of a 1.4 M solution of sec-butyl lithium was added very slowly. Stirring was continued for 2 hours, then the reaction mixture was quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether, the combined organic phases were washed with brine, dried over anhydrous sodium sulfate and evaporated in vacuo. The residue was purified by column chromatography (light petroleum-diethyl ether = 1+1) affording 880 mg (68%) of 2 as yellow oil which shows intensive yellow fluorescence (356 nm); ir ν 1655 (NCOO), 1715 cm^{-1} (C=O); ^{1}H nmr: (300 MHz) δ 1.33 (t, 3H, OCH$_2$CH_3, J = 7.5 Hz), 1.96-2.12, 2.18-2.31 (each m, each 1H, 3-H), 2.47 (dd, 1H, 2α-H, J = 8.0, 18.0 Hz), 3.05-3.14 (m, 1H, 2β-H), 4.21-4.33 (m, 2H, OCH$_2$CH$_3$), 4.77-4.83 (m, 1H, 3a-H), 6.97 (t, 1H, arom H, J = 7.5 Hz), 7.13-7.25 (m, 3H, arom H, 9-H), 7.58 ppm (d, 1H, 5-H, J = 8.5 Hz); ^{13}C nmr: (75.45 MHz) δ 14.3 (OCH$_2$CH$_3$), 30.2 (3-C), 37.2 (2-C), 56.7 (3a-C), 62.3 (OCH$_2$CH$_3$), 121.2, 123.7, 127.9, 130.2, 131.0 (arom CH, 9-C), 124.7, 135.5, 138.6 (4a-C, 8a-C, 9a-C), 202.3 ppm (1-C); ms: m/z 257 (M$^+$).

Anal. Calcd. for C$_{15}$H$_{15}$NO$_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.85; H, 5.62; N, 5.28.

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