Efficient Synthesis of 2-(2-Aminophenyl)-2,3-dihydropyridin-4(1*H*)-ones Based on a Cyclization/Ring Cleavage Procedure

by **Vahuni Karapetyan**[a])[b]), **Satenik Mkrtchyan**[a])[b]), **Gnuni Karapetyan**[a]), **Alexander Villinger**[a]), **Ashot Saghiyan**[b])[c]), **Tariel V. Ghochikyan**[b]), and **Peter Langer***[a])[d])

[a]) Institut für Chemie, Universität Rostock, Albert-Einstein-Strasse 3a, D-18059 Rostock
[b]) Faculty of Chemistry, Yerevan State University, Alex Manoogian 1, 0025 Yerevan, Armenia
[c]) CJSC Scientific Research Institute of Biotechnology, Gyurjyan Str. 14, 0056, Yerevan, Armenia
[d]) *Leibniz*-Institut für Katalyse e. V. an der Universität, Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock

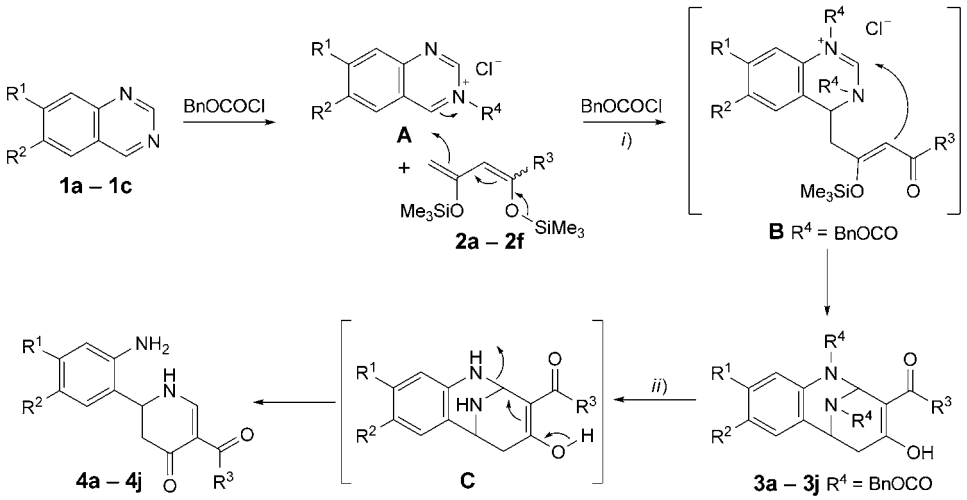
(Benzyloxycarbonyl)-protected 3,4-benzo-7-hydroxy-2,9-diazabicyclo[3.3.1]non-7-enes were prepared by one-pot cyclizations of 1,3-bis(silyl enol ethers) with quinazolines. Subsequent hydrogenation resulted in one-pot deprotection and rearrangement to give 2-(2-aminophenyl)-2,3-dihydropyridin-4(1*H*)-ones.

Functionalized pyridin-4-ones, 2,3-dihydropyridin-4-ones, and tetrahydropyridin-4-ones (piperidin-4-ones) are of great importance in medicinal chemistry [1]. *Christoffers* and co-workers recently developed the first approach to 3-arylpiperidin-4-ones [1]. 2-Aryl-2,3-dihydropyridin-4(1*H*)-ones (which can be regarded as partly unsaturated piperidin-4-ones or as 2,3-dihydropyridin-4(1*H*)-ones) have only scarcely been reported so far. *Barluenga et al.* prepared simple derivatives by cyclization of acrylates with enamines or hydrazones [2]. Iminium salts have been widely used for the synthesis and synthetic transformations of N-heterocycles [3]. In recent years, we have studied the application of iminium salts as building blocks in cyclocondensation reactions with bis(silyl enol ethers). These reactions provide a convenient approach to various N-heterocycles (for a review, see [4]). Recently, we have reported the synthesis of 2,9-bis(methoxycarbonyl)-3,4-benzo-7-hydroxy-2,9-diazabicyclo[3.3.1]non-7-enes, densely functionalized bridged quinazoline derivatives [5], by MeOCOCl-mediated cyclization of 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes [6] with quinazolines. However, our attempts to deprotect the N-atoms by cleavage of the MeOCO group and to isolate the corresponding bicyclic aminals failed, and complex mixtures were obtained [5b]. A possible explanation for that is that electron-rich bicyclic aminals are not stable under reaction conditions and undergo further rearrangements. Recently, we studied the synthesis of 7,8-benzo-9-azabicyclo[3.3.1]nonan-3-ones by cyclocondensation of 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes with isoquinolines [7]. The deprotected products were successfully prepared by employment of the *N*-(benzyloxycarbonyl) protecting group which could be cleaved by hydrogenation under mild conditions. Here, we report new (benzyloxycarbonyl)-protected 3,4-benzo-7-hydroxy-2,9-diazabicyclo[3.3.1]non-7-enes by BnOCOCl-mediated cyclization of 1,3-bis[(trimethylsilyl)-oxy]buta-1,3-dienes with quinazolines. The hydrogenation resulted in deprotection and

subsequent cleavage of a C–N bond to provide functionalized 2-(2-aminophenyl)-2,3-dihydropyridin-4(1*H*)-ones. The highly functionalized products reported here have, to the best of our knowledge, not been previously prepared. They are of pharmacological relevance and can be expected not to be readily available by other methods.

Results and Discussion. – 1,3-Bis[(trimethylsilyl)oxy]buta-1,3-dienes **2b**–**2f** were prepared from the corresponding β-keto esters in two steps [8][9]. Diene **2a** is available from acetylacetone in one step [10]. The cyclization of quinazolines **1a**–**1c** [11] with 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes **2a**–**2f**, in the presence of benzyl chloroformate (4.0 equiv.), afforded the novel (benzyloxycarbonyl) (BnOCO)-protected 3,4-benzo-7-hydroxy-2,9-diazabicyclo[3.3.1]non-7-enes **3a**–**3j** (*Scheme* and *Table*). The use of only 3.0 (rather than 4.0) equiv. of BnOCOCl resulted in a decrease of the yield. Optimal yields were obtained when the reaction was carried out at room temperature, and direct chromatographic purification was performed without aqueous workup. The formation of the products can be explained by the formation of an iminium salt **A** by reaction of **1a** with BnOCOCl and subsequent regioselective attack of the terminal C-atom of the 1,3-bis[(trimethylsilyl)oxy]buta-1,3-diene **2a** onto C(4) of the quinazoline (→ intermediate **A**). The reaction of the second N-atom with BnOCOCl again afforded an iminium ion (intermediate **B**), which is attacked by the central C-atom of the 1,3-dicarbonyl unit to provide product **3a**.

Scheme[a])



i) **1a**–**1c** (1.0 equiv.), **2a**–**2f** (1.4 equiv.), BnOCOCl (4.0 equiv.), CH_2Cl_2, 0°, 2 h, then 20°, 12 h. *ii*) Pd/C (10 mol-%), H_2, MeOH, 20°, 12 h.

[a]) For R^1–R^4 and yields of **3** and **4**, see the *Table*.

The hydrogenation of **3a**–**3j** afforded the 2-(2-aminophenyl)-2,3-dihydropyridin-4(1*H*)-ones **4a**–**4j** (*Scheme* and *Table*). The formation of products **4a**–**4j** can be

Table. *Products and Yields*

1	**2**	**3**, **4**	R^1	R^2	R^3	Yield [%][a]	
						3	**4**
a	**a**	**a**	H	H	Me	40	44
a	**b**	**b**	H	H	MeO	60	90
a	**c**	**c**	H	H	EtO	51	93
a	**d**	**d**	H	H	^{i}PrO	57	83
a	**e**	**e**	H	H	^{i}BuO	53	80
a	**f**	**f**	H	H	$MeO(CH_2)_2O$	49	81
b	**b**	**g**	Me	Me	MeO	43	66
b	**c**	**h**	Me	Me	EtO	42	60
c	**b**	**i**	$-(CH_2)_3-$		MeO	53	65
c	**c**	**j**	$-(CH_2)_3-$		EtO	52	68

[a]) Yields of isolated products.

explained by hydrogenolysis of the BnOCO groups to provide bicyclic aminal **C** and subsequent cleavage of a C–N bond (*retro-Michael* reaction).

All structures were established by spectroscopic methods. The ^{1}H- and ^{13}C-NMR spectra of **3** show a splitting of several signals, due to dynamic processes of the carbamate moiety possessing a significant double-bond character. The structures of **3e** and **4f** were additionally confirmed by X-ray crystal-structure analyses (*Figs. 1* and *2*)[1]).

In conclusion, we have reported the synthesis of BnOCO-protected 3,4-benzo-7-hydroxy-2,9-diazabicyclo[3.3.1]non-7-enes by cyclization of 1,3-bis[(trimethylsilyl)oxy]-buta-1,3-dienes with quinazolines in the presence of BnOCOCl. Their hydrogenation resulted in the formation of functionalized 2-(2-aminophenyl)-2,3-dihydropyridin-4(1*H*)-ones by deprotection and subsequent ring cleavage. The products are of pharmacological relevance and not readily available by other methods.

Experimental Part

General. All solvents were dried by standard methods. CH_2Cl_2 (anh., 99.8%) was purchased from *ACROS* and used without further purification. All reactions were carried out under an inert atmosphere. Anal. TLC: 0.20-mm *60 A* silica-gel plates. Column chromatography (CC): *60 A* silica gel (60–200 mesh; *Merck*). M.p.: Microheating table *HMK 67/1825 Kuestner* (*Büchi* apparatus); uncorrected. IR Spectra: *Nicolet 380* FT-IR spectrometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker Avance 300 III* and *Avance 250 II* in $CDCl_3$ (if not stated otherwise) at 250, 300, and 500 MHz, resp.; chemical shifts in δ [ppm] using the solvent internal standard ($CDCl_3$, δ 7.26 and δ 77.0, resp.), *J* in Hz. MS: *Finnigan MAT 95-XP* instrument; in *m*/*z* (rel.).

General Procedure for the Reaction of 1,3-Bis(silyl enol ethers) with Quinazolines. To a soln. of the quinazoline (4.0 mmol) in CH_2Cl_2 (40 ml), 1,3-bis(silyl enol ether) (5.6 mmol) and BnOCOCl (16.0 mmol) were subsequently added at 0°. The soln. was stirred for 2 h at 0° and for 12 h at 20°. The

1) CCDC-825761 (**4f**) and CCDC-825760 (**3e**) contain all crystallographic details of this publication which are available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: *Cambridge Crystallographic Data Centre*, 12 Union Road, GB-Cambridge CB21EZ; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

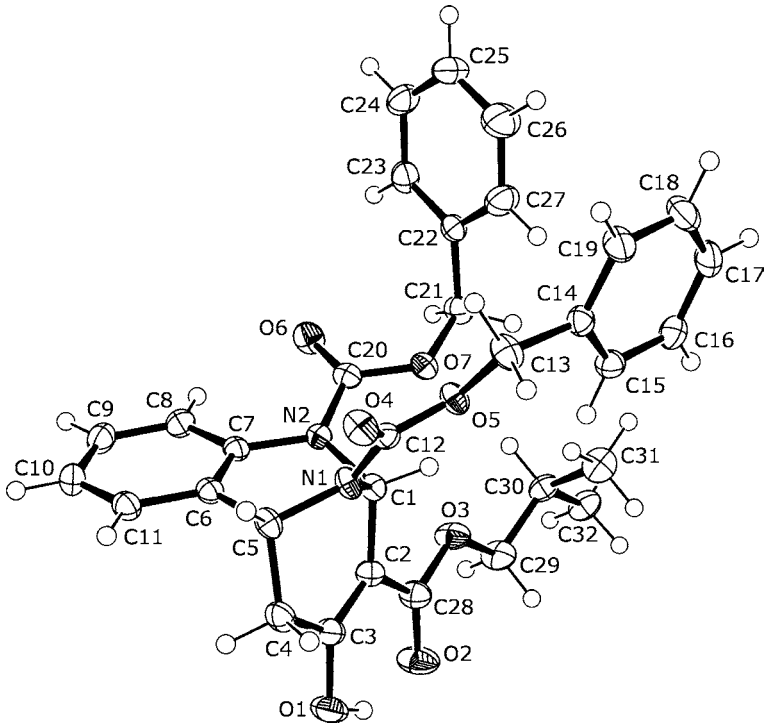


Fig. 1. *ORTEP Plot of* **3e**. The thermal ellipsoids of 50% probability are shown for the non-H-atoms.

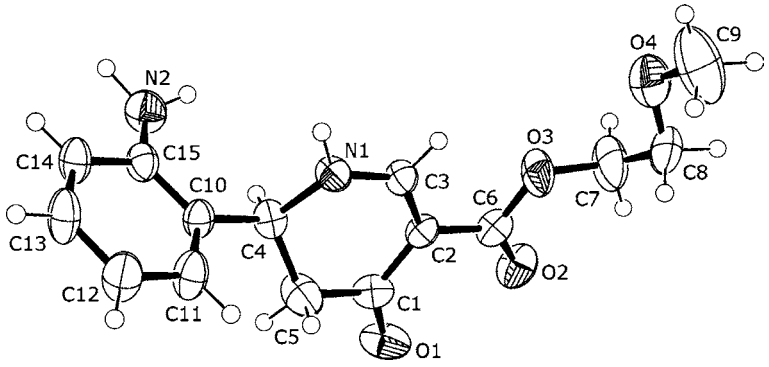


Fig. 2. *ORTEP Plot of* **4f**. The thermal ellipsoids of 50% probability are shown for the non-H-atoms.

solvent was removed *in vacuo*, and the residue was purified by CC (silica gel; AcOEt/ heptane, gradient 0 → 33% AcOEt). Product **3a** was directly transformed into **4a**.

*1,11-Dibenzyl 3-Methyl 5,6-Dihydro-4-hydroxy-2,6-epimino-1-benzazocine-1,3,11(2*H*)-tricarboxylate* (**3b**). Starting from *quinazoline* (**1a**; 0.260 g, 2.0 mmol), *1-methoxy-1,3-bis-[(trimethylsilyl)oxy]-buta-1,3-diene* (**2b**; 0.782 g, 3.0 mmol), and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3b** (0.617 g, 60%) was obtained. Yellow, highly viscous oil. IR (ATR): 3064*w*, 3032*w*, 2952*w*, 1703*s*, 1652*m*, 1490*w*, 1445*m*, 1382*m*, 1258*s*, 1224*s*, 1132*m*, 1102*m*, 1064*m*, 1022*m*, 1000*m*, 909*m*, 763*m*, 728*s*, 695*s*, 648*w*.

^{1}H-NMR (250 MHz): 2.33 (*d*, ^2J = 17.7, 1 H, NCHCH_2); 2.88 (br. *d*, ^2J = 17.7, 1 H, NCHCH_2); 3.38 (*s*, MeO); 4.99 – 5.38 (*m*, 2 CH_2O, NC*H*CH_2); 6.97 – 7.03 (*m*, 2 arom. H); 7.14 – 7.39 (m, 11 arom H, NCHN); 7.76 (*d*, ^3J = 8.3, 1 arom. H); 12.21 (*s*, OH). ^{13}C-NMR (62.9 MHz): 38.1 (NCH*C*H_2); 48.5 (br.), 49.1 (br.) (N*C*HCH_2, rotamers); 51.5 (MeO); 58.8 (br., NCHN); 67.6, 67.8 (CH_2O); 97.8 (NCH*C*CO); 124.2, 126.3, 127.6, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 128.7 (arom. CH); 129.2 (NCHN); 133.2, 134.4 (br.), 135.8, 136.1 (arom. C); 152.8, 153.1 (br.) (NCOO); 170.5 (C); 173.3 (br., C). EI-MS: 514 (M^+, 5), 379 (65), 335 (11), 303 (12), 91 (100), 65 (9). HR-EI-MS: 514.17395 (M^+, $C_{29}H_{26}N_2O_7^+$; calc. 514.17345).

*1,11-Dibenzyl 3-Ethyl 5,6-Dihydro-4-hydroxy-2,6-epimino-1-benzazocine-1,3,11(2*H*)-tricarboxylate* (**3c**). Starting from **1a** (0.260 g, 2.0 mmol), *1-ethoxy-1,3-bis[(trimethylsilyl)oxy]buta-1,3-diene* (**2c**; 0.823 g, 3.0 mmol), and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3c** (0.539 g, 51%) was obtained. Light yellow viscous oil. IR (neat): 3033*m*, 2981*w*, 1709*s*, 1653*s*, 1620*s*, 1491*m*, 1429*s*, 1386*s*, 1327*s*, 1295*s*, 1261*s*, 1228*s*, 1181*m*, 1135*s*, 1065*m*, 1024*m*, 1004*m*, 948*w*, 827*w*, 738*m*. ^{1}H-NMR (300 MHz): 1.06 (*t*, ^3J = 7.1, OCH_2*Me*); 2.41 (*d*, ^3J = 17.6, 1 H, NCHCH_2); 2.93 (*d*, ^3J = 16.1, 1 H, NCHCH_2); 4.04 (*q*, ^3J = 7.1, OCH_2Me); 5.00 – 5.54 (br. *m*, 2 CH_2O, NC*H*CH_2); 7.05 – 7.13 (*m*, 2 arom. H); 7.27 – 7.51 (br. *m*, 11 arom. H, NCHN); 7.82 (*d*, ^3J = 8.2, 1 arom. H); 12.38 (*s*, OH). ^{13}C-NMR (75.5 MHz): 14.0 (OCH_2*Me*); 38.2 (br., NCH*C*H_2); 48.7 (br., N*C*HCH_2); 58.9 (br., NCHN); 60.9 (O*C*H_2Me); 67.7(br., *C*CH_2O); 98.2 (NCH*C*CO); 124.3, 124.5, 126.3, 126.9, 127.7, 128.0, 128.1, 128.3, 128.4, 128.5 (CH of Ar); 134.6, 136.0, 136.1, 152.8, 153.2 (arom. C); 170.2 (C); 173.3 (br., C). EI-MS: 528 (M^+, 11), 456 (2), 393 (88), 349 (25), 303 (30), 258 (11), 212 (10), 91 (100), 65 (14). HR-EI-MS: 528.18879 (M^+, $C_{30}H_{28}N_2O_7^+$; calc. 528.18910).

*1,11-Dibenzyl 3-(1-Methylethyl) 5,6-Dihydro-4-hydroxy-2,6-epimino-1-benzazocine-1,3,11(2*H*)-tricarboxylate* (**3d**). Starting from **1a** (0.260 g, 2.0 mmol), *1-(1-methylethoxy)-1,3-bis[(trimethylsilyl)oxy]buta-1,3-diene* (**2d**; 0.866 g, 3.0 mmol), and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3d** (0.619 g, 57%) was obtained. Yellow, highly viscous oil. IR (ATR): 3064*w*, 3032*w*, 2939*w*, 1704*m*, 1643*m*, 1552*w*, 1490*w*, 1402*m*, 1323*m*, 1257*s*, 1224*s*, 1133*m*, 1100*m*, 1022*m*, 998*m*, 946*w*, 764*w*, 733*s*, 695*s*, 662*w*. ^{1}H-NMR (250 MHz): 1.00, 1.03 (*d*, ^3J = 6.3, OCHMe_2); 2.31 (*d*, ^2J = 17.8, 1 H, NCHCH_2); 2.90 (br. *d*, ^2J = 16.9, 1 H, NCHCH_2); 4.95 (*m*, OC*H*Me_2); 5.00 – 5.38 (br. *m*, 2 CH_2O, NC*H*CH_2); 6.97 – 7.03 (*m*, 2 arom. H); 7.15 – 7.44 (*m*, 11 arom. H, NCHN); 7.71 (*d*, ^3J = 8.4, 1 arom. H); 12.38 (*s*, OH). ^{13}C-NMR (62.9 MHz): 21.5, 21.6 (OCHMe_2); 38.2 (NCH*C*H_2); 48.8 (br., N*C*HCH_2); 58.9 (br., NCHN); 67.6, 67.8 (OCH_2); 68.7 (O*C*HMe_2); 98.4 (NCH*C*CO); 124.3, 124.5, 126.3 (arom. CH); 126.9 (arom. C); 127.6, 127.9, 128.0, 128.2, 128.4 (arom. CH); 128.5 (NCHN); 134.6, 136.0 (arom. C); 152.6, 153.3 (br., NCOO); 169.8 (C); 172.3 (br., C). EI-MS: 542 (M^+, 7), 456 (1), 407 (81), 365 (18), 303 (14), 91 (100), 65 (10). HR-EI-MS: 542.20453 (M^+, $C_{31}H_{30}N_2O_7^+$; calc. 542.20475).

*1,11-Dibenzyl 3-(2-Methylpropyl) 5,6-Dihydro-4-hydroxy-2,6-epimino-1-benzazocine-1,3,11(2*H*)-tricarboxylate* (**3e**). Starting from quinazoline **1a** (0.260 g, 2.0 mmol), *1-(2-methylpropyl)-1,3-bis-[(trimethylsilyl)oxy]buta-1,3-diene* (**2e**; 0.908 g, 3.0 mmol), and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3e** (0.589 g, 53%) was obtained. Colorless solid. M.p. 104 – 105°. IR (ATR): 3071*w*, 2873*w*, 1711*m*, 1688*s*, 1650*m*, 1612*m*, 1454*w*, 1440*m*, 1415*m*, 1379 *m*, 1262*s*, 1220*s* (br.), 1168*m*, 1131*s*, 1062*m*, 1010*s*, 974*m*, 851*s*, 824*m*, 761*m*, 734*s*, 710*m*, 693*s*, 670*m*, 624*m*. ^{1}H-NMR (250 MHz): 0.80 (*d*, ^3J = 6.7, CH_2CHMe_2); 1.76 (CH_2CHMe_2); 2.41 (*d*, ^2J = 17.5, 1 H, NCHCH_2); 2.99 (br. *d*, ^2J = 16.2, 1 H, NCHCH_2); 3.67 – 3.74 (*m*, 1 H, C$H_2$$CHMe_2$); 3.92 – 3.99 (*m*, 1 H, C$H_2$$CHMe_2$); 5.18 – 5.45 (br. *m*, 2 CH_2O, NC*H*CH_2); 7.08 – 7.11 (*m*, 2 arom. H); 7.20 – 7.53 (br. *m*, 11 arom. H, NCHN); 7.73 (*d*, ^3J = 8.2, 1 arom. H); 12.43 (*s*, OH). ^{13}C-NMR (62.9 MHz): 18.6, 18.7 (CH_2CHMe_2); 27.4 (CH_2CHMe_2); 38.1 (NCH*C*H_2); 48.7 (br.) (N*C*HCH_2); 58.9 (br., NCHN); 67.7, 67.9 (CH_2O); 70.9 (C$H_2$$CHMe_2$); 98.1 (NCH*C*CO); 124.4, 124.8, 126.3, 126.9 (arom. CH); 127.0 (arom. C); 127.6, 128.1, 128.4, 128.5 (arom. CH); 134.6 (NCHN); 136.0 (arom. C); 152.7, 153.4 (br., NCOO); 170.3 (C); 173.4 (br., C). EI-MS: 556 (M^+, 8), 421 (68), 377 (13), 347 (14), 321 (22), 303 (38), 241 (14), 213 (21), 108 (26), 91 (100), 79 (23). HR-EI-MS: 556.21991 (M^+, $C_{32}H_{32}N_2O_7^+$; calc. 556.22040).

*1,11-Dibenzyl 3-(2-Methoxyethyl) 5,6-Dihydro-4-hydroxy-2,6-epimino-1-benzazocine-1,3,11(2*H*)-tricarboxylate* (**3f**). Starting from **1a** (0.260 g, 2.0 mmol), *1-(2-methoxyethoxy)-1,3-bis[(trimethylsilyl)-oxy]buta-1,3-diene* (**2f**; 0.914 g, 3.0 mmol), and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3f** (0.551 g, 49%) was obtained. Yellow, highly viscous oil. IR (ATR): 3063*w*, 3032*w*, 2949*w*, 1703*s*, 1651*m*, 1499*w*, 1416*m*, 1384*m*, 1323*m*, 1255*s*, 1222*m*, 1178*w*, 1130*m*, 1063*m*, 1022*m*, 1001*m*, 912*w*, 762*m*, 735*s*, 695*s*, 615*w*. ^{1}H-NMR (250 MHz): 2.41 (*d*, ^2J = 17.5, 1 H, NCHCH_2); 2.98 (br. *d*, ^2J = 16.5, 1 H, NCHCH_2);

3.24 (*s*, CH_2OMe); 3.35 (*m*, CH_2OMe); 4.19 (*m*, OCH_2CH_2O); 5.11–5.45 (br. *m*, 2 CH_2O, $NCHCH_2$); 7.05–7.09 (*m*, 2 arom. H); 7.19–7.54 (br. *m*, 11 arom. H, NCHN); 7.81 (*d*, $^3J = 8.2$, 1 arom. H); 12.25 (*s*, OH). ^{13}C-NMR (62.9 MHz): 38.2 (br., $NCHCH_2$); 48.8 (br., $NCHCH_2$); 58.8 (CH_2OMe) 58.9 (br., NCHN); 63.8 (OCH_2CH_2O); 67.7 (br., CCH_2O); 69.9 (OCH_2CH_2O); 98.0 (NCHCCO); 124.3, 124.5, 126.3 (arom. CH); 126.8 (arom. C); 127.7, 127.9, 128.1, 128.2, 128.5, 128.5 (arom. CH); 134.6, 135.9, 136.1 (arom. C); 152.8, 153.2, 169.9, 173.5 (br., C). EI-MS: 558 (M^+, 9), 423 (87), 379 (17), 347 (11), 303 (32), 241 (14), 108 (59), 91 (100), 79 (48). HR-EI-MS: 558.20031 (M^+, $C_{31}H_{30}N_2O_8^+$; calc. 558.19967).

*1,11-Dibenzyl 3-Methyl 5,6-Dihydro-4-hydroxy-8,9-dimethyl-2,6-epimino-1-benzazocine-1,3,11(2*H*)-tricarboxylate* (**3g**). Starting with *6,7-dimethylquinazoline* (**1b**; 0.316 g, 2.0 mmol), **2b** (0.782 g, 3.0 mmol) and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3g** (0.467 g, 43%) was obtained. Yellow, highly viscous oil. IR (ATR): 3063*w*, 3031*w*, 2923*w*, 1702*m*, 1652*m*, 1615*w*, 1445*m*, 1383*m*, 1326*m*, 1248*s* (br.), 1220*s*, 1170*w*, 1110*m* (br.), 1065*m*, 1011*m*, 951*w*, 783*w*, 730*m*, 695*s*, 597*w*. ^{1}H-NMR (250 MHz): 2.19 (*s*, Me); 2.21 (*s*, Me); 2.40 (*d*, $^2J = 18.0$, 1 H, $NCHCH_2$); 2.94 (br. *d*, $^2J = 13.5$, 1 H, $NCHCH_2$); 3.48, 3.50 (*s*, MeO); 5.07–5.65 (*m*, 2 CH_2O, $NCHCH_2$); 6.80 (br., *s*, 1 arom. H); 7.27–7.60 (*m*, 11 arom. H, NCHN); 12.26, 12.29 (*s*, OH). ^{13}C-NMR (75.5 MHz): 19.1 (Me); 19.8 (Me); 38.2 ($NCHCH_2$); 48.5 (br.) ($NCHCH_2$); 51.5, 51.6 (MeO, rotamers); 58.9 (br., NCHN); 67.5, 67.8 (CH_2O); 98.0 (NCHCCO); 125.1, 127.0, 127.2, 127.6, 128.0, 128.1, 128.2, 128.3, 128.4, 128.6, 128.7, 128.9 (arom. C); 131.9, 132.8, 136.0 (br.); 136.2, 136.3 (arom. C); 152.9, 153.4 (br.); 170.6, 173.5 (C). EI-MS: 542 (M^+, 9), 407 (72), 363 (10), 331 (13), 91 (100), 65 (8). HR-EI-MS: 542.20540 (M^+, $C_{31}H_{30}N_2O_7^+$; calc. 542.20475).

*1,11-Dibenzyl 3-Ethyl 5,6-Dihydro-4-hydroxy-8,9-dimethyl-2,6-epimino-1-benzazocine-1,3,11(2*H*)-tricarboxylate* (**3h**). Starting from **1b** (0.316 g, 2.0 mmol), **2c** (0.822 g, 3.0 mmol), and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3h** (0.467 g, 42%) was obtained. Yellowish, highly viscous oil. IR (ATR): 3032*w*, 2923*w*, 1702*s*, 1650*m*, 1620*w*, 1384*m*, 1368*w*, 1325*m*, 1247*s* (br.), 1219*s*, 1176*m*, 1150*w*, 1110*m* (br.), 1064*m*, 1013*m*, 994*m*, 953*w*, 820*m*, 785*m*, 695*s*, 597*w*. EI-MS: 556 (M^+, 18), 421 (99), 377 (20), 331 (26), 286 (19), 249 (14), 91 (100), 65 (11). HR-EI-MS: 556.22088 (M^+, $C_{32}H_{32}N_2O_7^+$; calc. 556.22040).

*1,12-Dibenzyl 3-Methyl 2,5,6,8,9,10-Hexahydro-4-hydroxy-1*H*-2,6-epiminoindeno[5,6-*b*]azocine-1,3,12-tricarboxylate* (**3i**). Starting with *7,8-dihydro-6*H*-cyclopenta[*g*]quinazoline* (**1c**; 0.340 g, 2.0 mmol), **2b** (0.782 g, 3.0 mmol), and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3i** (0.588 g, 53%) was obtained. Yellow, highly viscous oil. IR (ATR): 3031*w*, 2951*w*, 1699*s*, 1651*m*, 1488*w*, 1427*m*, 1326*m*, 1278*m*, 1238*s*, 1108*m*, 1064*m*, 1008*m*, 943*w*, 823*w*, 695*s*, 585*w*. ^{1}H-NMR (250 MHz): 1.99–2.10 (*m*, $CH_2CH_2CH_2$); 2.41 (*d*, $^3J = 17.6$, 1 H, $NCHCH_2$); 2.81–2.98 (*m*, $CH_2CH_2CH_2$, 1 H of $NCHCH_2$); 3.48 (*s*, MeO); 5.07–5.43 (br. *m*, 2 CH_2O, $NCHCH_2$); 6.91 (*s*, 1 arom. H); 7.26–7.45 (br. *m*, 11 arom. H, NCHN); 7.67 (*s*, 1 arom. H); 12.30 (*s*, OH). ^{13}C-NMR (62.9 MHz): 25.5 ($CH_2CH_2CH_2$); 32.2, 32.8 ($CH_2CH_2CH_2$); 38.4 (br., $NCHCH_2$); 48.7 (br., $NCHCH_2$); 51.5 (MeO); 58.8 (br., NCHN); 67.4, 67.7 (CCH_2O); 97.9 (NCHCCO); 120.2, 121.8 (arom. CH); 124.6 (arom. C); 127.9, 128.0, 128.1, 128.2, 128.4, 128.5 (arom. CH); 132.3, 135.9, 136.3, 140.4, 144.0, 152.9, 153.4, 170 (C); 173.4 (br., COH). EI-MS: 554 (M^+, 5), 446 (3), 419 (33), 343 (8), 108 (17), 91 (100), 79 (16). HR-EI-MS: 554.20427 (M^+, $C_{32}H_{30}N_2O_7^+$; calc. 554.20475).

*1,12-Dibenzyl 3-Ethyl 2,5,6,8,9,10-Hexahydro-4-hydroxy-1*H*-2,6-epiminoindeno[5,6-*b*]azocine-1,3,12-tricarboxylate* (**3j**). Starting from **1c** (0.340 g, 2.0 mmol), **2c** (0.822 g, 3.0 mmol), and BnOCOCl (1.365 g, 8.0 mmol) in CH_2Cl_2 (20 ml), **3j** (0.591 g, 52%) was obtained. Yellow, highly viscous oil. IR (ATR): 3063*w*, 3032*w*, 2842*w*, 1702*s*, 1649*m*, 1616*w*, 1426*m*, 1386*m*, 1325*m*, 1280*s*, 1255*s*, 1238*s*, 1219*s*, 1181*m*, 1108*m*, 1086*m*, 1062*m*, 945*w*, 730*s* (br.), 695*s*, 585*w*. ^{1}H-NMR (300 MHz): 1.06 (*t*, $^3J = 7.1$, OCH_2Me); 2.04 (*m*, $CH_2CH_2CH_2$); 2.39 (*d*, $^3J = 17.7$, 1 H, $NCHCH_2$); 2.77–2.98 (*m*, $CH_2CH_2CH_2$, 1 H of $NCHCH_2$); 4.04 (*q*, $^3J = 7.1$, OCH_2Me); 4.97–5.41 (br. *m*, 2 CH_2O, $NCHCH_2$); 6.90 (*s*, 1 arom. H); 7.31–7.64 (br. *m*, 11 arom. H, NCHN); 12.38 (*s*, OH). ^{13}C-NMR (62.9 MHz): 14.0 (OCH_2Me); 25.6 ($CH_2CH_2CH_2$); 32.3, 32.9 ($CH_2CH_2CH_2$); 38.4 (br., $NCHCH_2$); 49.0 (br., $NCHCH_2$); 58.9 (br., NCHN); 60.9 (OCH_2Me); 67.7 (br., CCH_2O); 98.2 (NCHCCO); 120.3, 121.8 (arom. CH); 124.7 (arom. C); 127.9, 128.0, 128.2, 128.4, 128.5 (arom. CH); 132.5, 136.1, 136.2, 140.5, 144.0, 152.6, 153.6, 170.3, 172.9 (br., C). EI-MS: 568 (M^+, 6), 433 (39), 389 (8), 343 (8), 298 (8), 237 (10), 108 (47), 91 (100), 79 (50). HR-EI-MS: 568.22012 (M^+, $C_{33}H_{32}N_2O_7^+$; calc. 568.22040).

General Procedure for the Synthesis of **4**. The mixture of **3** (1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml) was stirred under H_2 at r.t. (20°) for 12 h. The mixture was filtered through *Celite*, washed

with MeOH (50 ml), and the filtrate was concentrated *in vacuo*. The residue was purified by crystallization from AcOEt.

*5-Acetyl-2-(2-aminophenyl)-2,3-dihydropyridin-4(1*H*)-one* (**4a**). Starting from **3a** (0.498 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4a** (0.102 g, 44%) was obtained. Colorless solid. M.p. 163–165°. IR (ATR): 3413*w*, 3335*w*, 3201*w*, 2834*w*, 1614*m*, 1567*s* (br.), 1497*s*, 1459*m*, 1309*m*, 1241*s*, 1153*m*, 1025*m*, 957*m*, 761*s*, 722*m*, 656*m*. ^{1}H-NMR (250 MHz, (D_6)DMSO): 2.31 (*s*, Me); 2.52–2.57 (*m*, CH_2); 5.06 (*t*, $^3J = 8.2$, C*H*CH_2); 5.16 (*s*, NH_2); 6.57 (*t*, $^3J = 7.4$, $^4J = 1.1$, 1 arom. H); 6.68 (*d*, $^3J = 7.4$, 1 arom. CH); 6.98–7.04 (*m*, 2 arom. H); 8.29 (*d*, $^3J = 7.4$, NHC*H*); 9.44 (*d*, $^3J = 7.4$, N*H*CH). ^{13}C-NMR (75.5 MHz, (D_6)DMSO): 30.0 (Me); 41.1 (CH*C*H_2); 51.0 (*C*HCH$_2$); 108.8 (CO*C*CO); 115.6, 116.2 (arom. CH); 121.4 (arom. C); 126.0, 128.4 (arom. CH); 145.4 (arom. C); 157.3 (CHNH); 188.2, 192.4 (CO). EI-MS: 230 (M^+, 82), 229 (100), 211 (23), 198 (17), 145 (26), 131 (65), 119 (34), 76 (11). HR-EI-MS: 230.10438 (M^+, $C_{13}H_{14}N_2O_2^+$; calc. 230.10498).

Methyl 6-(2-Aminophenyl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate (**4b**). Starting from **3b** (0.514 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4b** (0.221 g, 90%) was obtained. Colorless solid. M.p. 199–200°. IR (ATR): 3404*w*, 3297*w*, 2802*w*, 1699*s*, 1610*m*, 1592*m*, 1571*s*, 1533*m*, 1364*s*, 1318*m*, 1271*s*, 1209*m*, 1194*m*, 1054*s*, 1006*m*, 827*w*, 742*s*. ^{1}H-NMR (250 MHz, (D_6)DMSO): 2.47–2.51 (*m*, CH_2); 3.57 (*s*, MeO); 5.02 (*t*, $^3J = 8.1$, C*H*CH_2); 5.13 (*s*, NH_2); 6.56 (*t*, $^3J = 7.5$, 1 arom. H); 6.67 (*d*, $^3J = 7.7$, 1 arom. H); 6.97–7.05 (*m*, 2 arom. H); 8.25 (*s*, NHC*H*); 9.17 (*s*, N*H*CH). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 41.6 (CH*C*H_2); 50.3 (MeO); 51.0 (*C*HCH$_2$); 98.7 (CO*C*CO); 115.9, 116.4 (arom. CH); 121.9 (arom. C); 126.3, 128.6 (arom. CH); 145.7 (arom. C); 158.0 (CHNH); 165.0 (COO); 186.3 (CO). EI-MS: 246 (M^+, 81), 214 (100), 186 (37), 154 (38), 131 (89), 103 (26), 77 (14). HR-EI-MS: 246.09948 (M^+, $C_{13}H_{14}N_2O_3^+$; calc. 246.09989).

Ethyl 6-(2-Aminophenyl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate (**4c**). Starting with **3c** (0.529 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4c** (0.242 g, 93%) was obtained. Colorless solid. M.p. 165–166°. IR (ATR): 3306*w*, 2890*w*, 1683*m*, 1615*m*, 1398*m*, 1384*m*, 1323*w*, 1276*s*, 1210*m*, 1090*m*, 1049*m*, 950*m*, 838*m*, 748*s*, 622*m*, 590*s*. ^{1}H-NMR (500 MHz, (D_6)DMSO): 1.19 (*t*, $^3J = 7.2$, OCH$_2$*Me*); 2.46 (*dd*, $^2J = 15.8$, $^3J = 6.3$, 1 H, CHC*H*$_2$); 2.52 (*dd*, $^2J = 15.8$, $^3J = 10.1$, 1 H, CHC*H*$_2$); 4.05 (*q*, $^3J = 7.2$, OC*H*$_2$Me); 5.02 (*dd*, $^3J = 10.1$, $^3J = 6.3$, C*H*CH$_2$); 5.13 (*s*, NH_2); 6.57 (*d't'*, $^3J = 7.7$, $^3J = 7.3$, $^4J = 1.3$, 1 arom. H); 6.68 (*dd*, $^3J = 7.9$, $^4J = 1.3$, 1 arom. H); 7.00 (*ddd*, $^3J = 7.9$, $^3J = 7.3$, $^4J = 1.5$, 1 arom. H); 7.05 (*dd*, $^3J = 7.7$, $^4J = 1.5$, 1 arom. H); 8.24 (*s*, C*H*NH); 9.09 (s, NH). ^{13}C-NMR (125.8 MHz, (D_6)DMSO): 14.6 (Me); 41.6 (CH*C*H$_2$); 51.0 (*C*HCH$_2$); 58.4 (O*C*H$_2$Me); 98.9 (CO*C*CO); 115.8, 116.4 (arom. CH); 121.9 (arom. C); 126.3, 128.6 (arom. CH); 145.6 (arom. C); 157.8 (CHNH); 164.3 (COO); 186.3 (CO). EI-MS: 260 (M^+, 33), 214 (74), 186 (19), 168 (17), 145 (28), 131 (100), 103 (37), 76 (17). HR-EI-MS: 260.11536 (M^+, $C_{14}H_{16}N_2O_3^+$; calc. 260.11554).

1-Methylethyl 6-(2-Aminophenyl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate (**4d**). Starting from **3d** (0.543 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4d** (0.227 g, 83%) was obtained. Colorless solid. M.p. 107–108°. IR (ATR): 3203*w*, 2977*w*, 1693*m*, 1574*s*, 1495*m*, 1382*m*, 1372*m*, 1276*s*, 1179*m*, 1158*m*, 1036*s*, 980*w*, 953*w*, 922*w*, 747*s*, 627*m*. ^{1}H-NMR (250 MHz, (D_6)DMSO): 1.18 (*d*, $^3J = 6.3$, CH*Me*$_2$); 2.39–2.51 (*m*, CH_2); 4.91 (*m*, $^3J = 6.3$, C*H*Me$_2$); 5.00 (*dd*, $^3J = 10.1$, $^3J = 6.4$, C*H*CH$_2$); 5.14 (*s*, NH_2); 6.57 (*t*, $^3J = 7.5$, $^4J = 1.1$, 1 arom. H); 6.67 (*d*, $^3J = 8.0$, $^4J = 1.1$, 1 arom. H); 6.97–7.06 (*m*, 2 arom. H); 8.21 (*s*, NHC*H*); 9.08 (br. *s*, N*H*CH). ^{13}C-NMR (62.8 MHz, (D_6)DMSO): 22.2 (CH*Me*$_2$); 41.7 (CH*C*H$_2$); 51.1 (*C*HCH$_2$); 65.3 (O*C*HMe$_2$); 99.2 (CO*C*CO); 115.8, 116.4 (arom. CH); 122.0 (arom. C); 126.4, 128.6 (arom. CH); 145.7 (arom. C); 157.7 (CHNH); 163.6 (COO); 186.5 (CO). EI-MS: 274 (M^+, 12), 215 (35), 187 (24), 155 (100), 128 (21), 91(9), 76 (14). HR-EI-MS: 274.131761 (M^+, $C_{15}H_{18}N_2O_3^+$; calc. 274.13174).

2-Methylpropyl 6-(2-Aminophenyl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate (**4e**). Starting from **3e** (0.556 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4e** (0.231 g, 80%) was obtained. Colorless solid. M.p. 199–200°. IR (ATR): 3396*w*, 2967*w*, 1683*m*, 1564*s*, 1494*m*, 1407*m*, 1386*m*, 1365*m*, 1275*s*, 1235*m*, 1207*m*, 1156*m*, 1045*m*, 987*w*, 826*m*, 747*s*, 666*m*, 590*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 0.91 (*d*, $^3J = 6.7$, CH*Me*$_2$); 1.87 (*m*, $^3J = 6.7$, C*H*Me$_2$); 2.41–2.52 (*m*, CHC*H*$_2$); 3.80 (*d*, $^3J = 6.5$, C*H*$_2$O); 5.00–5.05 (*m*, C*H*CH$_2$); 5.14 (*s*, NH_2); 6.57 (*d't'*, $^3J = 7.4$, $^4J = 1.0$, 1 arom. H); 6.67 (*dd*, $^3J = 8.1$, $^4J = 1.0$, 1 arom. H); 6.98–7.07 (*m*, 2 arom. H); 8.24 (*d*, $^3J = 7.4$, NHC*H*); 9.05 (*d*, $^3J = 7.4$, N*H*CH). ^{13}C-NMR (75.5 MHz, (D_6)DMSO): 19.3 (CH*Me*$_2$); 27.7 (*C*HMe$_2$); 41.7 (CH*C*H$_2$); 51.1 (*C*HCH$_2$); 68.6

(O*C*H$_2$CH); 99.0 (CO*C*CO); 115.8, 116.4 (arom. CH); 121.9 (arom. C); 126.3, 128.6 (arom. CH); 145.7 (arom. C); 157.8 (CHNH); 164.4 (COO); 186.3 (CO). EI-MS: 288 (M^+, 288 (64), 214 (100), 186 (26), 158 (23), 146 (30), 131 (72), 103 (28), 76 (12). HR-EI-MS: 288.14611 (M^+, $C_{16}H_{20}N_2O_3^+$; calc. 288.14684).

2-Methoxyethyl 6-(2-Aminophenyl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate (**4f**). Starting from **3f** (0.558 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4f** (0.235 g, 81%) was obtained. Colorless solid. M.p. 158–159°. IR (ATR): 3388*w*, 3153*m*, 2983*w*, 1681*m*, 1615*m*, 1564*s*, 1495*m*, 1395*m*, 1290*m*, 1274*s*, 1204*m*, 1161*m*, 1089*m*, 1050*m*, 833*m*, 752*s*. ^{1}H-NMR (300 MHz, CD_3OD): 2.62 (*dd*, ^2J = 16.2, ^3J = 6.0, 1 H, CHC*H*$_2$); 2.79 (*dd*, ^2J = 16.2, ^3J = 11.9, 1 H, CHC*H*$_2$); 3.38 (*s*, MeO); 3.63–3.66 (*m*, C*H*$_2$OMe); 4.24–4.27 (*m*, COOC*H*$_2$), 5.08 (*dd*, ^3J = 11.9, ^3J = 6.0, C*H*CH$_2$); 6.69–6.78 (*m*, 2 arom. H); 7.08 (*d't'*, ^3J = 7.5, ^4J = 1.5, 1 arom. H); 7.18 (*dd*, ^3J = 7.6, ^4J = 1.0, 1 arom. H); 8.46 (*s*, NHC*H*). ^{13}C-NMR (62.9 MHz, CD_3OD): 42.4 (CH*C*H$_2$); 53.4 (*C*HCH$_2$); 59.1 (MeO); 63.4 (*C*H$_2$OMe); 71.9 (COO*C*H$_2$); 100.0 (CO*C*CO); 118.0, 119.3 (arom. CH); 123.5 (arom. C); 127.5, 130.2 (arom. CH); 146.3 (arom.); 160.3 (CHNH); 166.0 (COO); 190.8 (CO). EI-MS: 290 (M^+, 17), 214 (81), 145 (45), 131 (100), 103 (79), 76 (54). HR-EI-MS: 290.12601 (M^+, $C_{15}H_{18}N_2O_4^+$; calc. 290.12611).

Methyl 6-(2-Amino-4,5-dimethylphenyl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate (**4g**). Starting from **3g** (0.542 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4g** (0.181 g, 66%) was obtained. Colorless solid. M.p. 167–169°. IR (ATR): 3432*w*, 3171*w*, 2950*w*, 1704*m*, 1688*m*, 1614*m*, 1567*s*, 1439*m*, 1320*m*, 1273*s*, 1274*m*, 1194*m*, 1157*m*, 1095*m*, 809*w*, 773*m*. ^{1}H-NMR (250 MHz, (D_6)DMSO): 2.05 (*s*, Me); 2.07 (*s*, Me); 2.34–2.49 (*m*, CHC*H*$_2$); 3.57 (*s*, MeO); 4.83 (*s*, NH_2); 4.96 (*dd*, ^3J = 10.8, ^3J = 6.6, C*H*CH$_2$); 6.48 (*s*, 1 arom. H); 6.82 (*s*, 1 arom. H); 8.22 (*d*, ^3J = 7.4, NHC*H*); 9.07 (*d*, ^3J = 7.4, N*H*CH). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 18.7, 19.4 (CMe); 42.0 (CH*C*H$_2$); 50.3 (MeO); 50.9 (*C*HCH$_2$); 98.7 (CO*C*CO); 117.4, 119.6 (arom. CH); 123.8, 127.3, 136.2, 143.4 (arom. C); 157.9 (CHNH); 165.0 (COO); 186.4 (CO). EI-MS: 274 (M^+, 37), 242 (56), 213 (21), 197 (13), 186 (15), 173 (31), 158 (100), 143 (25), 130 (19), 104 (21), 77 (15). HR-EI-MS: 274.13059 (M^+, $C_{15}H_{18}N_2O_3^+$; calc. 274.13119).

Ethyl 6-(2-Amino-4,5-dimethylphenyl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate (**4h**). Starting from **3h** (0.556 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4h** (0.172 g, 60%) was obtained. Colorless solid. M.p. 152–154°. IR (ATR): 3369*w*, 3165*w*, 2978*w*, 1694*m*, 1575*m*, 1505*m*, 1404*m*, 1383*m*, 1355*w*, 1319*w*, 1273*s*, 1196*w*, 1164*m*, 1051*m*, 1018*w*. ^{1}H-NMR (250 MHz, CD_3OD): 1.29 (*t*, ^3J = 7.1, CH$_2$*Me*); 2.14 (*s*, Me); 2.15 (*s*, Me); 2.57 (*dd*, ^2J = 16.2, ^3J = 5.8, 1 H, CHC*H*$_2$); 2.79 (*dd*, ^2J = 16.2, ^3J = 12.5, 1 H, CHC*H*$_2$); 4.19 (*q*, ^3J = 7.1, C*H*$_2$Me); 5.03 (*dd*, ^3J = 12.5, ^3J = 5.8, C*H*CH$_2$); 6.61 (*s*, 1 arom. H); 6.94 (*s*, 1 arom. H); 8.40 (*d*, ^3J = 1.1, NHC*H*). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 14.7 (OCH$_2$*Me*); 18.7, 19.4 (C*Me*); 42.0 (CH*C*H$_2$); 50.9 (*C*HCH$_2$); 58.4 (O*C*H$_2$Me); 98.8 (CO*C*CO); 117.4, 119.6 (arom. CH); 123.8, 127.3, 136.2, 143.4 (arom. C); 157.8 (CHNH); 164.3 (COO); 186.5 (CO). EI-MS: 288 (M^+, 60), 242 (79), 213 (32), 186 (21), 173 (37), 159 (100), 143 (22), 130 (23), 104 (20), 69 (27). HR-EI-MS: 288.14621 (M^+, $C_{16}H_{20}N_2O_3^+$; calc. 288.14684).

*Methyl 6-(6-Amino-2,3-dihydro-1*H*-inden-5-yl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate* (**4i**). Starting from **3i** (0.554 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4i** (0.187 g, 65%) was obtained. Colorless solid. M.p. 182–183°. IR (ATR): 3405*w*, 3211*w*, 2943*w*, 1705*s*, 1593*s*, 1432*m*, 1364*s*, 1286*s*, 1187*m*, 1050*s*, 949*w*, 869*w*, 769*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.90–2.02 (*m*, CH$_2$C*H*$_2$CH$_2$); 2.46–2.52 (*m*, CHC*H*$_2$); 2.69–2.77 (*m*, C*H*$_2$CH$_2$C*H*$_2$); 3.62 (*s*, MeO); 4.91 (*s*, NH_2); 5.04 (*t*, ^3J = 7.9, C*H*CH$_2$); 6.61 (*s*, 1 arom. H); 6.94 (*s*, 1 arom. H); 8.28 (*d*, ^3J = 6.6, NHC*H*); 9.27 (*d*, ^3J = 5.6, N*H*CH). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 25.5, 31.8, 32.4 (*C*H$_2$*C*H$_2$*C*H$_2$); 41.8 (CH*C*H$_2$); 50.3 (MeO); 51.1 (*C*HCH$_2$); 98.5 (CO*C*CO); 112.0 (arom. CH); 120.4 (arom. C); 121.6 (arom. CH); 131.7, 144.0, 144.2 (arom. C); 157.9 (CHNH); 165.0 (COO); 186.6 (CO). EI-MS: 286 (M^+, 8), 227 (62), 211 (100), 180 (26), 143 (12), 119 (32), 91 (28), 76 (12). HR-EI-MS: 286.131646 (M^+, $C_{16}H_{18}N_2O_3^+$; calc. 286.131744).

*Ethyl 6-(6-Amino-2,3-dihydro-1*H*-inden-5-yl)-1,4,5,6-tetrahydro-4-oxopyridine-3-carboxylate* (**4j**). Starting from **3j** (0.569 g, 1.0 mmol) and Pd/C (10 mol-%) in MeOH (10 ml), **4j** (0.204 g, 68%) was obtained. Colorless solid. M.p. 163–165°. IR (ATR): 3407*w*, 3307*w*, 2971*w*, 2545*w*, 1699*s*, 1616*m*, 1567*s*, 1490*m*, 1428*m*, 1368*m*, 1321*m*, 1280*s*, 1150*m*, 1062*m*, 1048*m*, 849*m*. ^{1}H-NMR (250 MHz, (D_6)DMSO): 1.18 (*t*, ^3J = 7.1, CH$_2$*Me*); 1.88–1.99 (*m*, CH$_2$C*H*$_2$CH$_2$); 2.40–2.49 (*m*, CHC*H*$_2$); 2.66–2.73 (*m*, C*H*$_2$CH$_2$C*H*$_2$); 4.05 (*q*, ^3J = 7.1, C*H*$_2$Me); 4.88 (*s*, NH_2); 5.03 (*dd*, ^3J = 9.9, ^3J = 6.8, C*H*CH$_2$); 6.57 (*s*, 1 arom. H); 6.92 (*s*, 1 arom. H); 8.22 (*d*, ^3J = 7.4, NHC*H*); 9.06 (*d*, ^3J = 7.4, N*H*CH). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 14.7 (OCH$_2$*Me*); 25.5, 31.8, 32.4 (*C*H$_2$*C*H$_2$*C*H$_2$); 42.0 (CH*C*H$_2$); 51.2 (*C*HCH$_2$); 58.4

(O*C*H$_2$Me); 98.8 (CO*C*CO); 111.9 (arom. C); 120.4 (arom. C); 121.7 (arom. CH); 131.6, 144.1, 144.2 (arom. C); 157.7 (CHNH); 164.3 (COO); 186.5 (CO). EI-MS: 300 (M^+, 5), 255 (15), 211 (100), 186 (16), 116 (23), 76 (12). HR-ESI-MS: 301.15461 ($[M+H]^+$, $C_{17}H_{21}N_2O_3^+$; calc. 301.15467).

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