Synthesis of Enantiopure 1-Azabicyclo[3.2.2]nonanes *via* Stereoselective Capture of Chiral Carbocations

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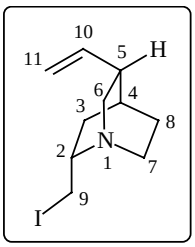
Supplementary Material

Experimental

General. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVS 400 and Bruker AVM 500 spectrometer in deuterated chloroform unless otherwise stated, with tetramethylsilane as internal standard. Mass spectra were recorded on a Finnigan MAT 312 (70 eV) or a VG Autospec spectrometer. Microanalyses were performed in the Department of Organic Chemistry of the University of Hannover. Preparative column chromatography was performed on J. T. Baker silica gel (particle size 30 - 60 μm). Analytical TLC was carried out on aluminum-backed 0.2-mm silica gel 60 F_{254} plates (E. Merck). Ethyl acetate (EA) and methyl *t*-butyl ether (MTBE) were distilled before use. Methanol was dried over calcium hydride and citric acid and distilled over magnesium before use. Silver triflate was purchased from Aldrich, whereas silver benzoate was freshly prepared before use. Compounds **2** and **5** were prepared as described previously.[11]

General Procedure I for the preparation of C9-iodinated quincorine and quincoridine derivatives. The unprotected quincorine or quincoridine (1 equiv.) was dissolved in abs. CH_2Cl_2 (5 ml/mmol) at r.t. under argon. After stirring for 10 min abs. Et_3N (2.0 equiv) was added, the reaction mixture was cooled (0 °C) and stirring was continued for 15 min at 0 °C. The colourless reaction mixture was treated without delay with MsCl (1.3 equiv) and stirred for 14 h at r.t. Sat. aq. $NaHCO_3$ was added and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (EtOAc/MeOH 20:1) and dissolved in abs. dioxane (2 ml/mmol), followed by addition of finely powdered lithium iodide (3 equiv.). Then, the heterogeneous reaction mixture was refluxed at 100 °C for 6 h. After cooling to r.t., sat. aq. $NaHCO_3$ and sat. aq. NaCl were added and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography of the crude product (EtOAc/MeOH 20:1) afforded the desired C9-iodide.

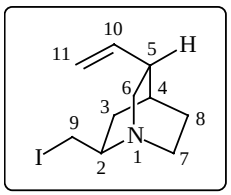
(1S,2S,4S,5R)-2-Iodomethyl-5-vinyl-1-azabicyclo[2.2.2]octane ***2***



O-Mesylated quincorine **1-OMs** (900 mg, 3.67 mmol, 1 equiv) was allowed to react

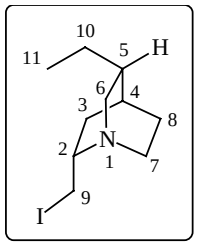
iodide **2** (84 %, 855 mg, 3.08 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): ɔ 5.86 (ddd, 1 H, *J* 7.5, 10.4 and 16.9 Hz, H-10), 5.07-5.01 (m, 2 H, H-11), 3.26-3.16 (m, 3 H, H-9, H-9, H-6), 3.03-2.85 (m, 2 H, H-7, H-2), 2.74-2.63 (m, 2 H, H-7, H-6), 2.29-2.21 (m, 1 H, H-5), 2.06-1.98 (m, 1 H, H-3), 1.83-1.77 (m, 1 H, H-4), 1.54-1.47 (m, 2 H, H-8, H-8) and 1.05-0.97 (m, 1 H, H-3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.5 (CH, C-10), 114.4 (CH_2, C-11), 57.7 (CH, C-2), 57.7 (CH_2, C-7), 40.2 (CH_2, C-6), 39.0 (CH, C-5), 29.1 (CH_2, C-3), 28.7 (CH, C-4), 27.5 (CH_2, C-8), 10.09 (CH_2, C-9); IR ($CHCl_3$): ν 3080 cm^{-1} w, 2948 vs, 2866 w, 1637 w, 1453 m, 1180 m, 992 w, 917 m; MS-MAT (r.t.): m/z 277 (M^+, 36.82), 236 (17.90), 182 (32.38), 150 (100), 136 (95.04), 108 (10.78), 82 (15.35), 79 (16.76), 67 (12.95); HRMS: calcd.: 277.0327; found: 277.0326.

*(1S,2R,4S,5R)-2-Iodomethyl-5-vinyl-1-azabicyclo[2.2.2]octane **5***



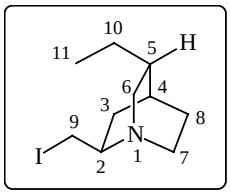
O-mesylated quincoridine **4-OMs** (750 mg, 3.06 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (1.23 g, 9.18 mmol, 3 equiv) to afford C9-iodide **5** (77 %, 653 mg, 2.35 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.84 (ddd, *J* 6.9, 10.3 and 17.1 Hz, H-10), 5.03 (m, 2 H, H-11), 3.23 (dd, 1 H, *J* 9.8 and 7.7 Hz, H-9), 3.16 (dd, 1 H, *J* 7.9 and 9.8 Hz, H-9), 2.92 (m, 4 H, H-7, H-7, H-2, H-6), 2.66 (m, 1 H, H-6), 2.26 (m, 1 H, H-5), 1.79 (m, 1 H, H-4), 1.73 (m, 1 H, H-3), 1.53 (m, 2 H, H-8) and 1.31 (m, 1 H, H-3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.2 (CH, C-10), 114.8 (CH_2, C-11), 57.8 (CH, C-2), 49.3 (CH_2, C-6), 46.9 (CH_2, C-7), 39.7 (CH, C-5), 28.7 (CH, C-4), 28.5 (CH_2, C-3), 26.2 (CH_2, C-8), 9.4 (CH_2, C-9); IR ($CHCl_3$): ν 3080 cm^{-1} w, 2941 vs, 2868 w, 1602 m, 1455 m, 1265 s, 1177 m, 1095 m, 991 m, 917 m, 866 w; MS-MAT (r.t.): *m/z* 277 (M^+, 41.81), 236 (13.31), 183 (27.42), 150 (100.00), 136 (22.51), 80 (12.62), 70 (17.94), 67 (10.17); HRMS: calcd.: 277.0327; found: 277.0326

*(1S,2S,4S,5R)-2-Iodomethyl-5-ethyl-1-azabicyclo[2.2.2]octane **7***



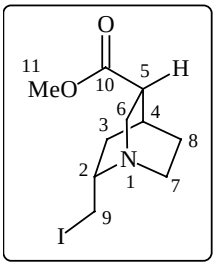
O-Mesylated dihydroquincorine (550 mg, 2.23 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (821 mg, 6.68 mmol, 3 equiv) to afford C9-iodide **7** (82 %, 509 mg, 1.83 mmol). ^{1}H-NMR (400 MHz, CD_3OD): δ 3.76-3.67 (m, 1 H, H-9), 3.60-3.40 (m, 3 H, H-9, H-7, H-2), 3.48-3.40 (m, 1 H, H-6), 3.16-3.09 (m, 1 H, H-7), 2.93-2.87 (ddd, 1 H, *J* 12.9, 6.1 and 2.8 Hz, H-6), 2.36-2.28 (m, 1 H, H-4), 2.10-2.05 (m, 1 H, H-3), 2.01-1.94 (m, 2 H, H-8, H-8), 1.90-1.81 (m, 1 H, H-5), 1.54-1.44 (m, 3 H, H-10, H-10, H-3) and 0.94 (t, 3 H, *J* 7.4 Hz, H-11); ^{13}C-NMR (100 MHz, CD_3OD): δ 60.3 (CH, C-2), 56.5 (CH_2, C-6), 41.7 (CH_2, C-7), 36.1 (CH, C-5), 28.3 (CH_2, C-8), 27.3 (CH_2, C-10), 26.6 (CH, C-4), 25.48 (CH, C-3),11.9 (CH_3, C-11), 2.90 (CH_2, C-9); IR ($CHCl_3$): ν 2936 cm^{-1} s, 2872 m, 1456 m, 1176 m, 1052 w, 963 w, 863 w; MS-MAT (r.t.): *m/z* 279 (M^+, 19.57), 210 (2.98), 182 (15.65), 153 (12.51), 152 (100.00), 138 (6.29), 119 (11.18), 95 (6.19), 82 (9.11), 70 (8.43); HRMS: calcd.: 279.0484, found: 279.0483.

*(1S,2R,4S,5R)-2-Iodomethyl-5-ethyl-1-azabicyclo[2.2.2]octane **9***



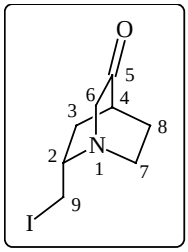
O-Mesylated dihydroquincoridine (550 mg, 2.23 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (892 mg, 6.68 mmol, 3 equiv) to afford C9-iodide **9** (78 %, 485 mg, 1.74 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.24 (dd, *J* 9.7 and 7.5 Hz, 1 H, H-9), 3.14 (dd, 1 H, *J* 9.7 and 8 Hz, H-9), 2.98-2.81 (m, 4 H, H-7, H-7, H-6, H-2), 2.36 (ddd, 1 H, *J* 14.0, 7.7 and 2.2 Hz, H-6), 1.71-1.65 (m, 2 H, H-4, H-3), 1.57 (dddd, 1 H, *J* 12.5, 10.0, 7.8 and 1.9 Hz, H-8), 1.50-1.39 (m, 2 H, H-8, H-5), 1.33 (q, 2 H, *J* 7.3 Hz, H-10), 1.30-1.23 (m, 1 H, H-3) and 0.68 (t, 3 H, *J* 7.3 Hz, H-11); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 57.81 (CH, C-2), 49.35 (CH_2, C-6), 48.74 (CH_2, C-7), 37.45 (CH, C-5), 28.35 (CH_2, C-8), 27.03 (CH, C-4), 26.96 (CH_2, C-10), 25.60 (CH_2, C-3), 12.02 (CH_3, C-11), 9.70 (CH_2, C-9); IR ($CHCl_3$): ν 2922 cm^{-1} s, 2852 m, 1678 w, 1598 w, 1548 m, 1451 m, 1375 s, 1313 w, 1260 m, 1069 s, 1024 m, 799 w, 719 s; MS-MAT (60 °C): m/z 279 (M^+, 20.10), 193 (10.97), 191 (14.29), 182 (18.70), 179 (14.73), 167 (13.40), 154 (10.75), 152 (100.00), 149 (26.66), 139 (20.84), 138 (21.65), 136 (29.82), 124 (20.54), 123 (29.97), 111 (48.83), 105 (24.89), 96 (24.82), 83 (68.78), 79 (18.19), 71 (63.99), 69 (76.73); HRMS: calcd.: 279.0484, found: 279.0843.

(1S,2S,4S,5R)-2-Iodomethyl-1-azabicyclo[2.2.2]octane-5-carboxylic acid methyl ester ***11***



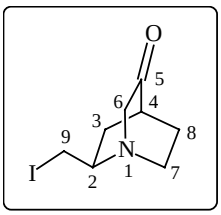
O-Mesylated quincorine-C5-methyl ester (300 mg, 1.08 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (436 mg, 3.25 mmol, 3 equiv) to furnish C9-iodide **11** (81 %, 271 mg, 0.88 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 3 H, H_3CO_2CR), 3.36-3.31 (dd, 1 H, *J* 9.9 and 7.9 Hz, H-9), 3.29-3.22 (m, 2 H, H-6, H-9), 3.01-2.83 (m, 4 H, H-2, H-6, H-7, H-7), 2.53-2.48 (m, 1 H, H-5), 2.24-2.21 (m, 1 H, H-4), 1.76-1.69 (m, 1 H, H-3), 1.59-1.54 (m, 2 H, H-8, H-8) and 1.28-1.22 (m, 1 H, H-3); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 174.94 (C, C-10), 57.61 (CH, C-2), 51.87 (CH_3, C-11), 49.22 (CH_2, C-6), 43.30 (CH_2, C-7), 41.34 (CH, C-5), 29.29 (CH_2, C-3), 26.68 (CH, C-4), 25.38 (CH_2, C-8), 9.38 (CH_2, C-9); IR ($CHCl_3$): ν 2999 cm^{-1} w, 2951 s, 2871 m, 1725 s, 1456 m, 1436 m, 1368 m, 1324 m, 1249 m, 1198 s, 1175 s, 1141 w, 1100 m, 1047 m, 1031 m, 1008 w, 863 m; MS-MAT (r.t.): *m/z* 309 (M^+, 24.24), 278 (7.70), 268 (8.57), 250 (1.28), 182 (100.00), 168 (4.19), 140 (1.09), 122 (4.15), 96 (3.44), 82 (4.81); HRMS (M^+ = $C_{10}H_{16}N_1O_2I$): calcd.: 309.0226, found: 309.0225.

(1S,2S,4S)-2-Iodomethyl-1-azabicyclo[2.2.2]octan-5-one ***13***



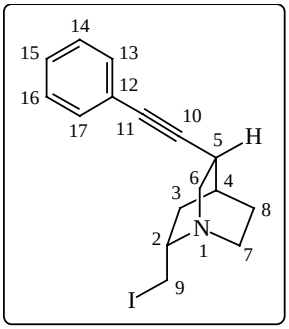
O-Mesylated quincorine C5-ketone (448 mg, 1.92 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (773 mg, 5.77 mmol, 3 equiv) to afford C9-iodo ketone **13** (71 %, 367 mg, 1.38 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.43-3.38 (d, 1 H, *J* 18.7 Hz, H-6), 3.32-3.29 (m, 3 H, H-9, H-9, H-6), 3.16-3.06 (m, 2 H, H-2, H-7), 2.83-2.75 (m, 1 H, H-7), 2.46-2.43 (m, 1 H, H-4), 2.33-2.26 (m, 1 H, H-3), 1.96-1.91 (m, 2 H, H-8, H-8) and 1.64-1.58 (ddd, 1 H, *J* 13.8, 7.5 and 2.3 Hz, H-3); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 218.50 (C, C-5), 64.16 (CH_2, C-6), 57.99 (CH, C-2), 40.82 (CH, C-4), 39.76 (CH_2, C-7), 32.74 (CH_2, C-3), 25.37 (CH_2, C-8), 8.13 (CH_2, C-9); IR ($CHCl_3$): ν 2962 cm^{-1} s, 2873 m, 1732 s, 1472 m, 1457 m, 1407 m, 1308 m, 1281 m, 1230 s, 1183 s, 1083 s, 1071 m, 1028 m, 985 m; MS-MAT (RT): *m/z* 265 (M^+, 9.02), 237 (56.12), 182 (1.07), 111 (100.00), 82 (11.47); HRMS ($M^+ = C_8H_{12}N_1O_1I$): calcd.: 264.9964, found: 264.9965.

(1S,2R,4S)-2-Iodomethyl-1-azabicyclo[2.2.2]octan-5-one ***15***



O-Mesylated quincoridine C5-ketone (483 mg, 2.08 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (834 mg, 6.23 mmol, 3 equiv) to afford C9-iodo ketone **13** (74 %, 407 mg, 1.53 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.38-3.32 (dd, 1 H, *J* 19.2 and 1.6 Hz, H-6), 3.20-3.13 (m, 2 H, H-9, H-9), 3.12-2.92 (m, 4 H, H-2, H-6, H-7, H-7), 2.50-2.46 (m, 1 H, H-4), 2.34-2.27 (m, 1 H, H-3), 2.02-1.90 (m, 2 H, H-8, H-8) and 1.60-1.53 (m, 1 H, H-3); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 218.41 (C, C-5), 56.85 (CH, C-2), 56.39 (CH_2, C-6), 41.18 (CH_2, C-7), 40.97 (CH, C-4), 32.34 (CH_2, C-3), 24.53 (CH_2, C-8), 7.88 (CH_2, C-9); IR ($CHCl_3$): ν 2961 cm^{-1} s, 2874 m, 1732 s, 1454 m, 1454 w, 1407 m, 1308 w, 1231 s, 1186 s, 1170 w, 1073 s, 1038 m, 863 m; MS-MAT (RT): *m/z* 265 (M^+, 8.73), 237 (71.28), 182 (1.58), 111 (100.00), 82 (11.12); HRMS ($M^+ = C_8H_{12}N_1O_1I$): calcd.: 264.9964, found: 264.9964.

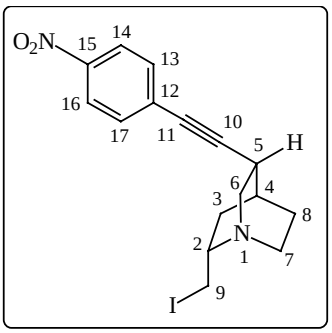
(1S,2S,4S,5S)-2-Iodomethyl-5-phenylethynyl-1-azabicyclo[2.2.2]octane ***17a***



O-Mesylated phenyl-substituted didehydroquincorine (349 mg, 1.09 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (440 mg, 3.28 mmol, 3 equiv) to furnish C9-iodide **17a** (79 %, 303 mg, 0.86 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.38 (m, 2 H, Ph-H), 7.31-7.26 (m, 3 H, Ph-H), 3.42-3.36 (dd, 1 H, *J* 13.5 and 10.0 Hz, H-6), 3.25-3.20 (m, 3 H, H-9, H-9, H-2), 3.05-2.99 (m, 1 H, H-6), 2.94-2.85 (m, 1 H, H-7), 2.72-2.62 (m, 2 H, H-7, H-5), 2.40-2.33 (m, 1 H, H-3), 2.09-2.05 (m, 1 H, H-4), 1.59-1.44 (m, 2 H, H-8, H-8) and 1.11-1.05 (m, 1 H, H-3); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$) δ 131.59 (CH, C-13, C-17), 128.24 (CH, C-14, C-16), 127.73 (CH, C-15), 123.63 (C, C-12), 93.10 (C, C-10), 81.18 (C, C-11), 57.43 (CH, C-2), 57.34 (CH_2, C-6), 39.84 (CH_2, C-7), 29.67 (CH_2, C-8), 28.27 (CH, C-5), 27.80 (CH, C-4), 26.11 (CH_2, C-3), 9.57 (CH_2, C-9); IR ($CHCl_3$): ν 3062 cm^{-1} w, 2999 m, 2950 s, 2885 m,2868 m, 2225 w, 1598 m, 1491 m, 1444 m, 1421 w, 1345 m, 1264 m, 1180 m, 1081 w, 1070 w, 1031 w, 997 w; MS-MAT (70 °C): *m/z* 351 (M^+,

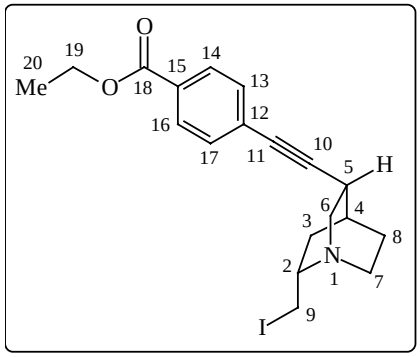
11.43), 224 (100.00), 182 (7.99), 153 (3.83), 128 (28.14); HRMS (M^+ = $C_{16}H_{18}N_1I$): calcd.: 351.0484, found: 351.0486.

(1S,2S,4S,5S)-2-Iodomethyl-5-(15-nitrophenyl-ethynyl)-1-azabicyclo[2.2.2]octane ***17b***



O-Mesylated *p*-nitrophenyl-substituted didehydroquincorine (675 mg, 1.85 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (745 mg, 5.56 mmol, 3 equiv) to afford C9-iodide **17b** (82 %, 581 mg, 1.52 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.19-8.15 (d, 2 H, *J* 8.9 Hz, H-14, H-16), 7.55-7.52 (d, 2 H, *J* 8.9 Hz, H-13, H-17), 3.45-3.39 (dd, 1 H, *J* 13.7 and 10.0 Hz, H-6), 3.26-3.16 (m, 3 H, H-9, H-9, H-2), 3.06-3.00 (m, 1 H, H-6), 2.96-2.87 (m, 1 H, H-7), 2.78-2.64 (m, 2 H, H-7, H-5), 2.36-2.29 (m, 1 H, H-3), 2.13-2.09 (m, 1 H, H-4), 1.62-1.46 (m, 2 H, H-8, H-8) and 1.15-1.08 (m, 1 H, H-3); ^{13}C NMR-DEPT (100 MHz, $CDCl_3$) δ 146.71 (C, C-15), 132.34 (CH, C-13, C-17), 130.71 (C, C-12), 123.53 (CH, C-14, C-16), 99.24 (C, C-10), 79.81 (C, C-11), 57.42 (CH, C-2), 57.07 (CH_2, C-6), 39.79 (CH_2, C-7), 29.66 (CH_2, C-8), 28.16 (CH, C-5), 27.99 (CH, C-4), 25.98 (CH_2, C-3), 9.42 (CH_2, C-9); IR ($CHCl_3$): ν 3081 cm^{-1} w, 2999 m, 2944 s, 2886 m, 2869 m, 2224 m, 1595 s, 1519 s, 1491 m, 1452 m, 1421 w, 1378 m, 1344 s, 1308 m, 1284 m, 1265 m, 1179 m, 1108 m, 855 s; MS-MAT (80 °C): *m/z* 396 (M^+, 8.86), 351 (11.56), 269 (53.60), 224 (100.00), 182 (14.02), 165 (8.87), 129 (34.86), 109 (7.76), 91 (6.72); HRMS (M^+ = $C_{16}H_{17}N_2O_2I$): calcd.: 396.0335, found: 396.0334.

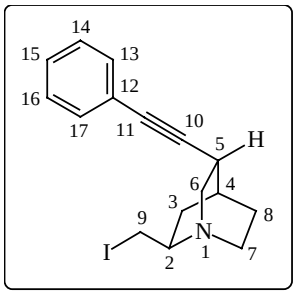
(1S,2S,4S,5S)-2-Iodomethyl-5-(15-ethanoyl-phenylethynyl)-1-azabicyclo[2.2.2]octane ***17c***



O-Mesylated *p*-ethanoylphenyl-substituted didehydroquincorine (629 mg, 1.61 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (647 mg, 4.83 mmol, 3 equiv) to provide C9-iodide **17c** (75 %, 510 mg, 1.21 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.99-7.96 (d, 2 H, *J* 8.5 Hz, H-14, H-16), 7.47-7.45 (d, 2 H, *J* 8.5 Hz, H-13, H-17), 4.41-4.35 (q, 2 H, *J* 7.2 Hz, H-19), 3.44-3.38 (dd, 1 H, *J* 13.6 and 9.9 Hz, H-6), 3.26-3.18 (m, 3 H, H-9, H-9, H-2), 3.06-2.99 (m, 1 H, H-6), 2.96-2.87 (m, 1 H, H-7), 2.74-2.63 (m, 2 H, H-7, H-5), 2.40-2.32 (m, 1 H, H-3), 2.11-2.07 (m, 1 H, H-4), 1.61-1.48 (m, 2 H, H-8, H-8), 1.42-1.38 (t, 3 H, *J* 7.2 Hz, H-20) and 1.13-1.07 (m, 1 H, H-3); ^{13}C NMR-DEPT (100 MHz, $CDCl_3$) δ 168.86 (C, C-18), 134.23 (CH, C-13, C-17), 134.04 (C, C-12), 132.14 (CH, C-14, C-16), 131.05 (C, C-15), 99.15 (C, C-10), 83.46 (C, C-11), 63.83 (CH_2, C-19), 60.11 (CH, C-2), 59.99 (CH_2, C-6), 42.56 (CH_2, C-7), 32.42 (CH_2, C-8), 30.97 (CH, C-5), 30.67 (CH, C-4), 28.80 (CH_2, C-3), 17.06 (CH_3, C-20), 12.25 (CH_2, C-9); IR ($CHCl_3$): ν 2944 cm^{-1} s, 2869

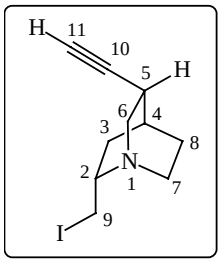
s, 1176 s, 1108 s, 1020 m, 858 m; MS-MAT (100 °C): *m/z* 423 (M^+, 14.19), 378 (7.64), 296 (100.00), 282 (10.35), 268 (5.05), 236 (7.57), 200 (13.48), 182 (6.47), 155 (8.74), 126 (6.64); HRMS ($M^+ = C_{19}H_{22}N_1O_2I$): calcd.: 423.0695, found: 423.0694.

(1S,2R,4S,5S)-2-Iodomethyl-5-phenylethynyl-1-azabicyclo[2.2.2]octane ***19***



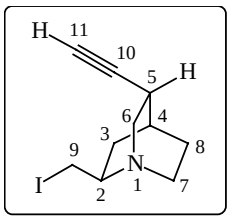
O-Mesylated phenyl-substituted didehydroquincoridine (300 mg, 0.94 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (378 mg, 2.82 mmol, 3 equiv) to furnish C9-iodide **19** (76 %, 251 mg, 0.71 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43-7.39 (m, 2 H, Ph-H), 7.33-7.29 (m, 3 H, Ph-H), 3.42-3.37 (dd, 1 H, *J* 10.0 and 8.2 Hz, H-9), 3.35-3.31 (dd, 1 H, *J* 10.0 and 7.5 Hz, H-9), 3.17-3.10 (dd, 1 H, *J* 14.2 and 10.1 Hz, H-6), 3.09-3.00 (m, 1 H, H-2), 2.99-2.92 (m, 3 H, H-6, H-7, H-7), 2.75-2.70 (m, 1 H, H-5), 2.10-2.06 (m, 1 H, H-4), 1.84-1.71 (m, 2 H, H-3, H-8), 1.66-1.58 (m, 1 H, H-8) and 1.57-1.47 (m, 1 H, H-3); ^{13}C NMR-DEPT (100 MHz, $CDCl_3$) δ 131.59 (CH, C-15), 128.26 (CH, C-13, C-17), 127.79 (CH, C-14, C-16), 123.51 (C, C-12), 92.61 (C, C-10), 81.81 (C, C-11), 57.70 (CH, C-2), 48.86 (CH_2, C-6), 48.41 (CH_2, C-7), 28.91 (CH_2, C-8), 28.89 (CH, C-5), 28.77 (CH, C-4), 24.79 (CH_2, C-3), 9.31 (CH_2, C-9); IR ($CHCl_3$): ν 3063 cm^{-1} w, 2999 w, 2946 s, 2876 m, 2225 w, 1599 m, 1490 m, 1455 m, 1443 w, 1322 m, 1261 w, 1176 m, 1138 w, 1092 m, 1075 w, 1045 m, 1031 w, 934 w; MS-MAT (90 °C): *m/z* 351 (M^+, 14.26), 275 (6.52), 224 (100.00), 182 (12.82), 165 (4.83), 148 (42.07), 128 (39.54), 109 (4.52), 91 (9.22), 77 (7.49); HRMS ($M^+ = C_{16}H_{18}N_1I$): calcd.: 351.0484, found: 351.0484.

(1S,2S,4S,5S)-2-Iodomethyl-5-ethynyl-1-azabicyclo[2.2.2]octane ***21***



O-Mesylated 10,11-didehydroquincorine (600 mg, 2.47 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (993 mg, 7.41 mmol, 3 equiv) to afford C9-iodide **21** (77 %, 523 mg, 1.90 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.34-3.16 (m, 4 H, H-9, H-9, H-6, H-2), 2.96-2.84 (m, 2 H, H-6, H-7), 2.67-2.59 (m, 1 H, H-7), 2.54-2.48 (m, 1 H, H-5), 2.35-2.28 (m, 1 H, H-3), 2.11 (d, 1 H, *J* 2.5 Hz, H-11), 2.02-1.98 (m, 1 H, H-4), 1.58-1.49 (m, 1 H, H-8), 1.49-1.41 (m, 1 H, H-8) and 1.10-1.04 (m, 1 H, H-3); ^{13}C NMR-DEPT (100 MHz, $CDCl_3$) δ 87.21 (C, C-10), 69.35 (CH, C-11), 57.31 (CH, C-2), 56.73 (CH_2, C-6), 39.79 (CH_2, C-7), 29.34 (CH_2, C-8), 27.79 (CH, C-5), 26.76 (CH, C-4), 25.75 (CH_2, C-3), 8.84 (CH_2, C-9); IR ($CHCl_3$): ν 3305 cm^{-1} s, 2999 w, 2952 s, 2868 m, 2111 w, 1471 w, 1454 m, 1421 w, 1345 w, 1322 m, 1263 m, 1197 w, 1180 m, 1109 w, 1047 m, 834 w; MS-MAT (RT): *m/z* 275 (M^+, 13.43), 236 (4.63), 182 (23.62), 148 (100.00), 91 (9.34); HRMS ($M^+ = C_{10}H_{14}N_1I$): calcd.: 275.0171, found: 275.0165.

(1S,2R,4S,5S)-2-Iodomethyl-5-ethynyl-1-azabicyclo[2.2.2]octane ***23***



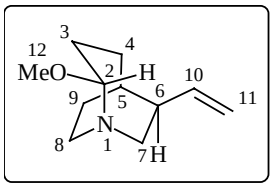
O-Mesylated 10,11-didehydroquincoridine (200 mg, 0.82 mmol, 1 equiv) was allowed to react according to general procedure I with LiI (331 mg, 2.47 mmol, 3 equiv) to afford C9-iodide **23** (73 %, 165 mg, 0.60 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.42-3.37 (dd, 1 H, *J* 9.9 and 7.8 Hz, H-9), 3.30-3.25 (dd, 1 H, *J* 9.9 and 7.8 Hz, H-9), 3.13-3.04 (m, 2 H, H-6, H-2), 2.98-2.86 (m, 3 H, H-6, H-7, H-7), 2.57-2.52 (m, 1 H, H-5), 2.13-2.12 (d, 1 H, *J* 2.5 Hz, H-11), 2.03-2.00 (m, 1 H, H-4), 1.84-1.76 (m, 1 H, H-3), 1.71-1.57 (m, 2 H, H-8, H-8) and 1.55-1.48 (m, 1 H, H-3); ^{13}C NMR-DEPT (100 MHz, $CDCl_3$) δ 86.79 (C, C-10), 69.69 (CH, C-11), 57.76 (CH, C-2), 48.73 (CH_2, C-6), 47.95 (CH_2, C-7), 28.58 (CH, C-5), 28.46 (CH_2, C-8), 27.85 (CH, C-4), 24.51 (CH_2, C-3), 8.55 (CH_2, C-9); IR ($CHCl_3$): ν 3305 cm^{-1} s, 2999 w, 2947 s, 2870 w, 2110 w, 1456 m, 1421 w, 1321 w, 1261 m, 1230 m, 1176 m, 1141 w, 1096 m, 1046 m, 1004 w, 862 w; MS-MAT (RT): *m/z* 275 (M^+, 19.78), 236 (5.80), 182 (22.58), 148 (100.00), 91 (10.17); HRMS (M^+ = $C_{10}H_{14}N_1I$): calcd.: 275.0171, found: 275.0171.

General Procedure II for the AgOTf-mediated ring expansion of C9-iodinated quincorine and quincoridine derivatives. Quincorine and Quincoridine iodides **2**, **5**, **13** and **15** were dissolved in abs. MeOH (4 ml/mmol alkaloid) and stirred for 5 min at r.t. under argon, followed by addition of finely powdered dry AgOTf (1.05 equiv). The resulting yellowish reaction mixture was stirred at r.t. (1-20 h), filtered and the precipitate was washed with MeOH. The solvent was removed under reduced pressure and CH_2Cl_2, sat. aq. $NaHCO_3$ and sat. aq. NaCl were added with subsequent extraction of the aqueous layer (CH_2Cl_2). The collected organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. Column chromatography (MTBE) of the crude product furnished the desired substituted 1-azabicyclo[3.2.2]nonane.

General Procedure III for the AgOBz-mediated ring expansion of C9-iodinated quincorine and quincoridine derivatives in MeOH. Freshly prepared dry silver benzoate (1.1 equiv) was added to a solution of the corresponding quincorine or quincoridine C9-iodide in abs. MeOH (5 ml/mmol alkaloid) at r.t. under argon. The reaction mixture was stirred at 50 °C for 20 h (unless otherwise stated), filtered and the precipitate was washed with MeOH. After the solvent was removed under reduced pressure, CH_2Cl_2, sat. aq. $NaHCO_3$ and sat. aq. NaCl were added. The aqueous layer was extracted with CH_2Cl_2, the organic layer dried ($MgSO_4$), filtered and concentrated under reduced pressure. Column chromatography (MTBE) of the resulting crude product afforded the desired rearranged 1-azabicyclo[3.2.2]nonane.

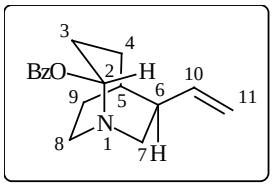
General Procedure IV for thr AgOBz-mediated ring expansion of C-9 iodinated quincorine and quincoridine in acetone. Freshly prepared anhydrous silver benzoate (1.1 equiv) was added to a solution of the corresponding quincorine or quincoridine C9 iodide in abs. Me_2CO (7 ml/mmol) at r.t. under nitrogen in the dark. The reaction mixture was stirred for 20 h, filtered and the precipate was washed with Me_2CO. After the solvent was removed under reduced pressure, CH_2Cl_2, sat. aq. $NaHCO_3$ and sat. aq. NaCl were added. The aqueous layer was extracted with CH_2Cl_2, the organic layer dried (Na_2SO_4), filtered and concentrated under reduced pressure. Column chromatography (MTBE/PE 1:1) of the resulting crude product afforded the desired rearranged 1-azabicyclo[3.2.2]nonane.

(1S,2R,5R,6R)-2-Methoxy-5-vinyl-1-azabicyclo[3.2.2]nonane ***3-OMe***



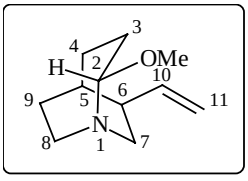
C9-iodinated quincorine **2** (500 mg, 1.81 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz (455 mg, 1.98 mmol, 1.1 equiv) to afford rearranged 1-azabicyclo[3.2.2]nonane **3-OMe** (86 %, 282 mg, 1.56 mmol). ^{1}H-NMR (400 MHz, CD_3OD): δ 5.87 (ddd, *J* 7.4, 10.8 and 17.1, 1 H, H-10), 5.04-4.98 (m, 2 H, H-11), 3.87-3.82 (m, 1 H, H-2), 3.34-3.26 (m, 1 H, H-7_{exo}), 3.24 (s, 3 H, H-12), 3.08-2.99 (m, 1 H, H-8), 2.74-2.66 (m, 1 H, H-7_{endo}), 2.65-2.56 (m, 1 H, H-8), 2.44-2.35 (m, 1 H, H-6), 1.97-1.90 (m, 1 H, H-5), 1.89- 1.81 (m, 1 H, H-3), 1.72-1.56 (m, 4 H, H-3, H-9, H-9, H-4) and 1.54-1.43 (m, 1 H, H-4); ^{13}C-NMR (100 MHz,CD_3OD): δ 143.3 (CH, C-10), 115.3 (CH_2, C-11), 100.9 (CH, C-2), 55.2 (CH_3, C-12), 53.2 (CH_2, C-7), 45.8 (CH, C-6), 39.6 (CH_2, C-8), 34.5 (CH, C-5), 31.7 (CH_2, C-3), 28.9 (CH_2, C-9), 23.4 (CH_2, C-4); IR ($CHCl_3$): ν 3079 cm^{-1} w, 2934 s, 2868 m, 1635 w, 1453 m, 1363 w, 1264 w, 1142 w, 1074 vs, 999 m; MS-MAT (r.t.): *m/z* 181 (M^+, 47.24), 166 (100.00), 150 (64.68), 136 (11.22), 108 (9.64), 81 (4.32); HRMS: calcd.:181.1466, found: 181.1467.

(1S,2R,5R,6R)-2-Benzoyloxy-5-vinyl-1-azabicyclo[3.2.2]nonane ***3-OBz***



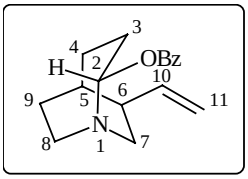
C9-iodinated quincorine **2** (525 mg, 1.89 mmol, 1 equiv) was allowed to react according to general procedure IV with AgOBz to afford rearranged 1-azabicyclo[3.2.2]nonane **3-OBz** (68 %, 234.8 mg, 1.30 mmol). ^{1}H-NMR (400 MHz, CD_3OD): δ 8.03-7.99 (m, 2 H, Ar-H), 7.62-7.57 (m, 1 H, Ar-H), 7.50-7.44 (m, 2 H, Ar-H), 5.95 (ddd, 1 H, *J* 17.82, 10.17, 7.65 and 2.76 Hz, H-10), 5.11-5.02 (m, 2 H, H-11), 3.61 (dd, 1 H, *J* 11.3 and 7.9 Hz, H-2), 3.19- 3.11 (m, 1 H, H-8), 3.06-2.98 (m, 2 H, H-7, H-7), 2.94-2.86 (m, 1 H, H-8), 2.43- 2.33 (m, 1 H, H-6), 1.95-1.84 (m, 1 H, H-5), 1.76-1.72 (m, 1 H, H-3), 1.63-1.56 (m, 3 H, H-9, H-9, H-4), 1.20-1.12 (m, 1 H, H-4) and 1.09-1.03 (m, 1 H, H-3); ^{13}C-NMR (100 MHz, CD_3OD): δ 168.12 (C, C-12), 142.64 (CH, C-10), 133.92 (CH, C-16), 131.41 (C, C-13), 13.51 (CH, C-14, C-18), 129.62 (CH, C-15, C-17), 114.83 (CH_2, C-11), 99.85 (CH, C-2), 54.77 (CH_2, C-7), 39.15 (CH_2, C-8), 45.46 (CH, C-6), 34.09 (CH, C-5), 28.21 (CH_2, C-9), 25.77 (CH_2, C-4), 22.05 (CH_2, C-3); IR ($CHCl_3$): ν 3069 cm^{-1} w, 2932 w, 2864 w, 1717 s, 1637 w, 1582 w, 1450 m, 1315 m, 1270 s, 1114 m, 1070 w, 912 m, 712 m; MS-MAT (r.t.): *m/z* 272 (M^++1, 2.19), 271 (9.05), 230 (3.90), 182 (2.17), 166 (7.53), 151 (2.72), 150 (17.94), 149 (8.16), 137 (10.19), 136 (100), 122 (25.53), 108 (5.93), 105 (57.95), 94 (4.02) 82 (10.65), 79 (8.28), 77 (27.31); HRMS: calcd.: 271.1572, found: 271.1572.

(1S,2S,5R,6R)-2-Methoxy-6-vinyl-1-azabicyclo[3.2.2]nonane ***6-OMe***



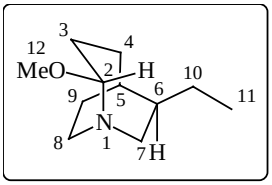
C9-iodinated Quincoridine **5** (650 mg, 2.35 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz to afford 1-azabicyclo[3.2.2]nonane **6** (74 %, 314 mg, 1.74 mmol). ^{1}H-NMR (400 MHz, CD_3OD): δ 5.90 (ddd, 1 H, *J* 7.4, 10.3 and 17.1 Hz, H-10), 5.07-5.02 (m, 2 H, H-11), 3.96 (dd, 1 H, *J* 10.4 and 4.2 Hz, H-2), 3.24 (s, 3 H, H-12), 2.97-2.91 (m, 2 H, H-8, H-8), 2.90-2.84 (m, 2 H, H-7, H-7), 2.44-2.34 (m, 1 H, H-6), 2.00-1.91 (m, 1 H, H-4), 1.91-178 (m, 3 H, H-5, H-9, H-3), 1.69-1.57 (m, 2 H, H-9, H-3) and 1.45-1.35 (m, 1 H, H-4); ^{13}C-NMR (100 MHz, CD_3OD): δ 141.6 (CH, C-10), 114.8 (CH_2, C-11), 97.4 (CH, C-2), 54.5 (CH_3, C-12), 46.9 (CH_2, C-7), 45.9 (CH_2, C-8), 42.2 (CH, C-6), 34.2 (CH, C-5), 33.0 (CH_2, C-3), 30.3 (CH_2, C-9), 28.7 (CH_2, C-4); IR ($CHCl_3$): ν 3074 cm^{-1} w, 2930 s, 2866 m, 1624 m, 1591 m, 1456 m, 1345 m, 1316 m, 1316 s, 1278 m, 1104 w, 1079 vs, 1027 w, 911 m; MS-MAT (r.t.): *m/z* 181 (M^+, 46.36), 166 (100), 150 (75.67), 136 (8.21), 108 (28.63), 81 (29.42); HRMS: calcd.: 181.1466, found: 181.1467.

(1S,2S,5R,6R)-2-Benzoyloxy-6-vinyl-1-azabicyclo[3.2.2]nonane ***6-OBz***



C9-iodinated Quincoridine **5** (280 mg, 1.01 mmol, 1 equiv) was allowed to react according to general procedure IV with AgOBz to afford 1-azabicyclo[3.2.2]nonane **6-OBz** (66 %, 0.67 mmol, 180 mg). ^{1}H-NMR (400 MHZ, $CDCl_3$): δ 8.07-8.04 (m, 2 H, H-Ar), 7.57-7.52 (m, 1 H, H-Ar), 7.44-7.40 (m, 2 H, H-Ar), 5.90 (ddd, *J* 7.2, 10.0 and 17.6 Hz, 1 H, H-10), 5.08-5.02 (m, 2 H, H-11), 4.30 (m, 1 H, H-2), 3.25-3,15 (m, 1 H, H-7), 3.00-2.87 (m, 2 H, H-8), 2.84-2.76 (m, 1 H, H-7), 2.32-2.24 (m, 1 H, H-6), 2.06-2.00 (m, 1 H, H-5), 1.81-1.78 (m, 1 H, H-3), 1.70-1.56 (m, 4 H, H-9, H-4, H-4, H-3) and 1.47-1.39 (m, 1 H, H-9); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.02 (C, C-12), 140.15 (CH, C-10), 133.24 (CH, C-16), 130.37 (CH, C-13), 129.77 (CH, C-14, C-18), 128.53 (CH, C-15, C-17), 114.55 (CH_2, C-11), 104.43 (CH, C-2), 54.43 (CH_2, C-7), 46.58 (CH_2, C-8), 39.05 (CH, C-6), 30.34 (CH, C-5), 28.23 (CH_2, C-9), 25.52 (CH_2, C-4), 23.21 (CH_2, C-3); IR ($CHCl_3$): ν 3080 cm^{-1} w, 2944 vs, 1716 m, 1601 m, 1561 m, 1382 m, 1337 w, 1280 s, 1158 w, 1019 m, 918 m, 823 w; MS-MAT (r.t.): *m/z* 271 (M^+, 1.02), 212 (1.56), 185 (1.68), 168 (5.64), 167 (39.31), 166 (9.99), 151 (2.79), 150 (15.63), 149 (4.34), 137 (11.02), 136 (100.00), 127 (2.13), 126 (16.58), 105 (48.37), 95 (6.43), 94 (6.23), 82 (20.18), 81 (14.59), 79 (13.06), 77 (25.12), 73 (21.65); HRMS: calcd.: 271.1571, found: 271.1572.

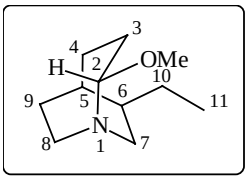
(1S,2R,5R,6R)-2-Methoxy-5-ethyl-1-azabicyclo[3.2.2]nonane ***8***



C-9 iodinated dihydroquincorine **7** (340 mg, 1.22 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz to afford 1-azabicyclo[3.2.2]nonane **8** (66 %, 148 mg, 0.81 mmol); ^{1}H-NMR (400 MHZ, $CDCl_3$): δ 3.84-3.74 (m, 1 H, H-2), 3.36 (m, 1 H, H-7), 3.27 (s, 3 H, H-12), 3.11-3.02 (m, 1 H, H-8), 2.69-2.56 (m, 2 H, H-7, H-8), 2.43-2.34 (m, 1 H, H-6), 1.98-1.92 (m, 1 H, H-5), 1.90-1.82 (m, 1 H, H-3), 1.76-1.67 (m, 1 H, H-9), 1.65-1.61 (m, 2 H, H-3, H-9), 1.60-.148 (m, 3 H, H-4, H-10, H-10), 1.34-1.24 (m, 1 H, H-4) and 0.89 (m, 3 H, H-11); ^{13}C-NMR (100 MHZ, $CDCl_3$): δ 98.32 (CH, C-2), 54.28 (CH_3, C-12), 52.27 (CH_2, C-7), 44.08 (CH, C-6), 38.70 (CH_2, C-3), 31.88 (CH, C-5), 29.65 (CH_2, C-9), 28.89 (CH_2, C-4), 23.71 (CH_2, C-10), 22.94 (CH_3, C-11); IR ($CHCl_3$): ν cm^{-1} 2928 s, 2864 s, 1636 w, 1470 w, 1451 m, 1363 m, 1263 w, 1204 w, 1181 m, 1143 m, 1113 m, 1076

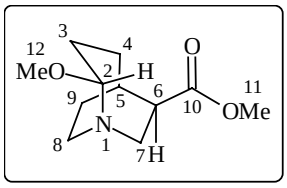
s, 989 m, 939 w, 911 m; MS-MAT (r.t.): *m/z* 183 (M^+, 2.85), 181 (3.36), 167 (1.08), 166 (7.03), 160 (11.67), 159 (100), 151 (1.23), 150 (6.44), 144 (6.84), 138 (1.46), 129 (10.96), 128 (3.53), 120 (21.63), 117 (4.96), 116 (49.95), 108 (2.68), 102 (3.09), 96 (1.28), 89 (11.27), 87 (3.33), 81 (3.22), 77 (3.46); HRMS: calcd.:183.1623, found: 183.1624.

(1S,2S,5R,6R)-2-Methoxy-5-ethyl-1-azabicyclo[3.2.2]nonane ***10***



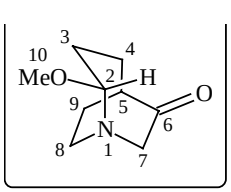
C9-iodinated dihydroquincoridine **9** (280 mg, 1.00 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz to afford 1-azabicyclo[3.2.2]nonane **10** (62 %, 114 mg, 0.62 mmol); ^{1}H-NMR (400 MHz, CD_3OD): δ 3.96 (m, 1 H, H-2), 3.31 (m, 1 H, H-7_{exo}), 3.24 (s, 3 H, H-12), 3.01 (m, 1 H, H-8), 2.57 (m, 1 H, H-8), 2.38 (ddd, 1 H, *J* 15.7, 7.0 and 2.6 Hz, H-7_{endo}), 1.90 (m, 1 H, H-6), 1.83 (m, 1 H, H-5), 1.75 (m, 1 H, H-3), 1.64 (m, 2 H, H-9, H-4), 1.52 (m, 4 H, H-10, H-4, H-3, H-9), 1.35 (m, 2 H, H-3, H-10) and 0.87 (t, 3 H, *J* 7.4 Hz, H-11); ^{13}C-NMR (100 MHz, CD_3OD): δ 97.92 (CH, C-2), 53.63 (CH_2, C-7), 53.08 (CH_3, C-12), 40.67 (CH, C-6), 37.62 (CH_2, C-3), 29.61 (CH, C-5), 29.37 (CH_2, C-9), 27.11 (CH_2, C-4), 26.27 (CH_2, C-10), 20.36 (CH_3, C-11); IR ($CHCl_3$): ν 2922 cm^{-1} s, 2852 m, 1677 w, 1598 w, 1550 m, 1457 m, 1375 s, 1261 m, 1171 w, 1069 m, 1024 w, 833 w, 719 m; MS-MAT (r.t.): *m/z* 183 (M^+, 45.63), 168 (100.00), 154 (35.96), 152 (92.92), 140 (21.36), 126 (35.26), 112 (12.96), 98 (9.94), 87 (10.01), 72 (22.75); HRMS: calcd.: 183.1623, found: 183.1623.

(1S,2R,5R,6R)-2-Methoxy-1-azabicyclo[3.2.2]nonane-6-carboxylic acid methyl ester ***12***



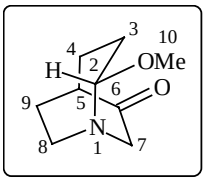
C9-iodinated quincorine C5-methyl ester **11** (190 mg, 0.62 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz (155 mg, 0.68 mmol, 1.1 equiv) to afford rearranged ester **12** (75 %, 98 mg, 0.46 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.86-3.82 (dd, 1 H, *J* 10.5 und 4.1 Hz, H-2), 3.69 (s, 3 H, H-11), 3.54-3.48 (ddd, 1 H, *J* 14.8, 7.0 and 2.4 Hz, H-7_{exo}), 3.25 (s, 3 H, OMe), 3.03-2.88 (m, 3 H, H-8, H-8, H-7_{endo}), 2.62-2.56 (m, 1 H, H-6), 2.40-2.34 (m, 1 H, H-5), 2.04-1.97 (m, 1 H, H-3), 1.88-1.78 (m, 2 H, H-4, H-4), 1.70-1.56 (m, 2 H, H-9, H-9) and 1.41-1.32 (m, 1 H, H-3); NOE (400 MHz, $CDCl_3$): H-2 irrad. (3.84): H-12 (4.4 %), H-7_{endo} (7.4 %), H-4 (3.2 %), H-3 (1.3 %); H-7_{exo} irrad. (3.51): H-7_{endo} (21.5 %), H-8 (5.9 %); H-6 irrad. (2.59): H-7_{exo} (6.1 %), H-5 (3.8 %), H-9 (2.4 %); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 173.63 (C, C-10), 95.48 (CH, C-2), 52.92 (CH_3, C-12), 50.61 (CH_3, C-11), 45.03 (CH_2, C-7), 41.06 (CH, C-6), 40.96 (CH_2, C-8), 31.17 (CH_2, C-4), 29.01 (CH, C-5), 27.93 (CH_2, C-9), 27.32 (CH_2, C-3); IR ($CHCl_3$): ν 2999 cm^{-1} m, 2939 s, 2871 s, 2825 w, 1726 s, 1459 m, 1435 m, 1368 m, 1347 m, 1267 m, 1195 s, 1175 s, 1159 s, 1139 m, 1098 s, 1072 s, 1002 m, 968 m, 928 w; MS-MAT (60 °C): *m/z* 213 (M^+, 65.22), 198 (41.91), 182 (100.00), 170 (14.97), 154 (36.62), 138 (5.89), 126 (36.27), 112 (2.58), 82 (3.05); HRMS ($M^+ = C_{11}H_{19}N_1O_3$): calcd.: 213.1365, found: 213.1364.

(1S,2R,5R)-2-Methoxy-1-azabicyclo[3.2.2]nonan-6-one ***14***



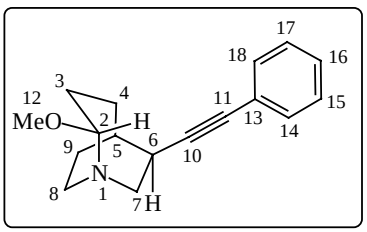
C9-iodinated quinbiscorinone **13** (250 mg, 0.94 mmol, 1 equiv) was allowed to react according to general procedure II with AgOTf (255 mg, 0.99 mmol, 1.05 equiv) to afford a 80:20 mixture of rearranged ketones **14** and **16** (47 %, 75 mg, 0.44 mmol). AgOBz-mediated ring expansion furnished diastereomerically pure **14** in 76 % yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.82-3.77 (dd, 1 H, *J* 10.4 and 4.2 Hz, H-2), 3.26-3.22 (d, 1 H, *J* 14.7 Hz, H-7$_{exo}$), 3.19 (s, 3 H, OMe), 3.07-2.99 (m, 1 H, H-8), 2.96-2.92 (dd, 1 H, *J* 14.9 and 2.4 Hz, H-7$_{endo}$), 2.64-2.56 (m, 1 H, H-8), 2.18-2.08 (m, 1 H, H-5), 2.00-1.90 (m, 1 H, H-3), 1.90-1.83 (m, 1 H, H-4), 1.81-1.61 (m, 3 H, H-9, H-4, H-3) and 1.61-1.50 (m, 1 H, H-9); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 216.00 (C, C-6), 96.51 (CH, C-2), 58.44 (CH_2, C-7), 54.13 (CH_3, C-10), 38.19 (CH_2, C-8), 33.76 (CH, C-5), 30.42 (CH_2, C-4), 22.70 (CH_2, C-9), 22.39 (CH_2, C-3); IR ($CHCl_3$): ν 2999 cm^{-1} m, 2942 s, 2872 m, 1730 s, 1470 m, 1451 m, 1385 w, 1357 m, 1334 w, 1265 s, 1230 m, 1146 m, 1112 s, 1090 m, 1060 s, 1039 m, 1002 m, 957 m; MS-MAT (70 °C): *m/z* 171 (M^+ + 2, 44.08), 169 (11.97), 154 (17.21), 126 (17.03), 110 (45.82), 100 (100.00), 84 (16.08), 71 (57.26); HRMS (M^+ = $C_9H_{15}N_1O_2$): calcd.: 169.1103, found: 169.1099.

(1S,2S,5R)-2-Methoxy-1-azabicyclo[3.2.2]nonan-6-one ***16***



C9-iodinated quinbiscorinone **15** (307 mg, 1.16 mmol, 1 equiv) was allowed to react according to general procedure II with AgOTf (312 mg, 1.22 mmol, 1.05 equiv) to afford a 32:68 mixture of rearranged ketones **14** and **16** (41 %, 80 mg, 0.47 mmol). AgOBz-mediated ring expansion furnished diastereomerically pure **16** in 72 % yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.85-3.81 (dd, 1 H, *J* 10.6 and 4.2 Hz, H-2), 3.49-3.43 (dd, 1 H, *J* 19.2 and 2.4 Hz, H-7$_{exo}$), 3.26 (s, 3 H, OMe), 3.14-3.09 (dd, 1 H, *J* 19.2, H-7$_{endo}$), 3.04-2.96 (m, 1 H, H-8), 2.88-2.80 (m, 1 H, H-8), 2.29-2.25 (m, 1 H, H-5), 2.12-1.97 (m, 2 H, H-3, H-4), 1.95-1.85 (m, 2 H, H-9, H-4), 1.78-1.68 (m, 1 H, H-3) and 1.53-1.46 (m, 1 H, H-9); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 215.41 (C, C-6), 94.82 (CH, C-2), 53.55 (CH_3, C-10), 52.94 (CH_2, C-7), 44.09 (CH_2, C-8), 31.92 (CH, C-5), 29.07 (CH_2, C-4), 28.02 (CH_2, C-9), 26.19 (CH_2, C-3); IR ($CHCl_3$): ν 2999 cm^{-1} m, 2936 s, 2873 m, 1720 s, 1458 m, 1405 w, 1349 w, 1260 m, 1230 m, 1179 w, 1142 m, 1107 s, 1074 m, 1047 s, 1008 m, 956 w; MS-MAT (RT): *m/z* 169 (M^+, 24.01), 168 (43.52), 152 (34.59), 138 (20.20), 126 (29.10), 112 (17.92), 71 (100.00); HRMS (M^+ = $C_9H_{15}N_1O_2$): calcd.: 169.1103, found: 169.1098.

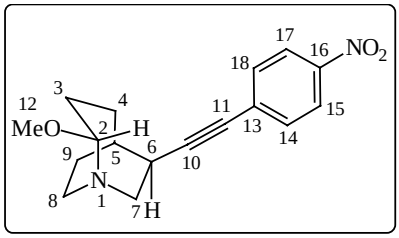
(1S,2R,5R,6S)-2-Methoxy-6-phenylethynyl-1-azabicyclo[3.2.2]nonane ***18a***



C9-iodinated phenyl-didehydroquincorine **17a** (256 mg, 0.73 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz (184 mg, 0.80 mmol, 1.1 equiv) to

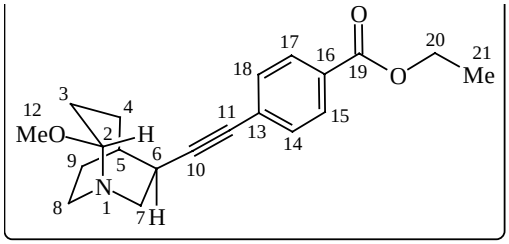
furnish 1-azabicyclo[3.2.2]nonane **18a** (82 %, 153 mg, 0.59 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2 H, Ph-H), 7.30-7.25 (m, 3 H, Ph-H), 3.92-3.89 (dd, 1 H, *J* 10.1 and 4.5 Hz, H-2), 3.58-3.52 (dd, 1 H, *J* 14.2 and 9.4 Hz, H-7$_{exo}$), 3.24 (s, 3 H, OMe), 3.11-3.03 (m, 1 H, H-8), 2.98-2.92 (ddd, 1 H, *J* 14.2, 6.1 and 2.5 Hz, H-7$_{endo}$), 2.89-2.84 (m, 1 H, H-6), 2.61-2.53 (m, 1 H, H-8), 2.17-2.07 (m, 2 H, H-5, H-3), 1.98-1.92 (m, 1 H, H-4), 1.76-1.60 (m, 3 H, H-9, H-4, H-3) and 1.55-1.47 (m, 1 H, H-9); NOE (400 MHz, $CDCl_3$): H-2 irrad. (3.89): H-12 (6.9 %), H-7$_{endo}$ (8.2 %), H-3 (1.1 %), H-4 (3.6 %); H-7$_{exo}$ irrad. (3.58): H-7$_{endo}$ (24.4 %), H-6 (10.7 %), H-8 (4.6 %); H-8$_{endo}$ irrad. (3.11): H-2 (1.0 %), H-8$_{exo}$ (23.2 %), H-9 (8.0 %); H-7$_{endo}$ irrad. (2.98): H-2 (13.7 %), H-7$_{exo}$ (27.1 %), H-4 (2.1 %); H-8$_{exo}$ irrad. (2.61): H-7$_{exo}$ (4.3 %), H-8$_{endo}$ (24.5 %), H-6 (1.6 %), H-9 (5.2 %); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 131.53 (CH, C-14, C-18), 128.21 (CH, C-15, C-17), 127.59 (CH, C-16), 123.92 (C, C-13), 97.55 (CH, C-2), 93.69 (C, C-10), 83.05 (C, C-11), 54.17 (CH_3, C-12), 54.16 (CH_2, C-7), 37.90 (CH_2, C-8), 33.60 (CH, C-6), 31.91 (CH, C-5), 30.48 (CH_2, C-4), 25.90 (CH_2, C-9), 23.75 (CH_2, C-3); IR ($CHCl_3$): ν 3060 cm^{-1} w, 2999 m, 2935 s, 2870 s, 2826 w, 2219 w, 1598 m, 1490 m, 1452 m, 1359 m, 1271 m, 1230 m, 1179 w, 1140 s, 1114 s, 1075 s, 995 m, 966 m, 915 m; MS-MAT (70 °C): *m/z* 255 (M^+, 65.39), 240 (18.77), 224 (67.49), 196 (100.00), 182 (92.04), 167 (23.07), 155 (12.20), 141 (19.08), 128 (23.65), 115 (30.52), 102 (5.37), 91 (14.42); HRMS (M^+ = $C_{17}H_{21}N_1O_1$): calcd.: 255.1623, found: 255.1624.

(1S,2R,5R,6S)-2-Methoxy-6-(16-nitro-phenylethynyl)-1-azabicyclo[3.2.2]nonane ***18b***



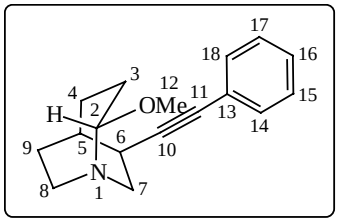
C9-iodinated *p*-NO_2-phenyl-didehydroquincorine **17b** (500 mg, 1.26 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz (318 mg, 1.39 mmol, 1.1 equiv) to furnish 1-azabicyclo[3.2.2]nonane **18b** (77 %, 292 mg, 0.97 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.16-8.14 (d, 2 H, *J* 8.8 Hz, H-15, H-17), 7.54-7.51 (d, 2 H, *J* 8.8 Hz, H-14, H-18), 3.93-3.89 (dd, 1 H, *J* 10.2 and 5.4 Hz, H-2), 3.63-3.57 (dd, 1 H, *J* 13.3 and 8.6 Hz, H-7$_{exo}$), 3.25 (s, 3 H, OMe), 3.15-3.06 (m, 1 H, H-8), 3.01-2.91 (m, 2 H, H-7$_{endo}$, H-6), 2.64-2.56 (m, 1 H, H-8), 2.21-2.15 (m, 1 H, H-5), 2.10-1.94 (m, 2 H, H-3, H-4), 1.80-1.62 (m, 3 H, H-9, H-4, H-3) and 1.58-1.51 (m, 1 H, H-9); NOE (400 MHz, $CDCl_3$): H-2 irrad. (3.91): H-12 (9.7 %), H-7$_{endo}$ (9.9 %), H-3 (4.4 %), H-4 (4.0 %); H-7$_{exo}$ irrad. (3.59): H-7$_{endo}$ (28.1 %), H-6 (10.0 %), H-8 (4.9 %); H-8$_{endo}$ irrad. (3.10): H-2 (1.5 %), H-8$_{exo}$ (24.6 %), H-9 (8.4 %); H-7$_{endo}$ irrad. (2.96): H-2 (6.5 %), H-7$_{exo}$ (15.6 %), H-5 (2.9 %), H-4 (2.5 %); H-8$_{exo}$ irrad. (2.60): H-7$_{exo}$ (5.8 %), H-8$_{endo}$ (26.9 %), H-6 (1.6 %), H-9 (4.7 %); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 146.66 (C, C-16), 132.23 (CH, C-15, C-17), 130.95 (C, C-13), 123.48 (CH, C-14, C-18), 99.91 (C, C-10), 97.51 (CH, C-2), 81.71 (C, C-11), 54.16 (CH_3, C-12), 53.73 (CH_2, C-7), 37.79 (CH_2, C-8), 33.81 (CH, C-6), 31.78 (CH, C-5), 30.42 (CH_2, C-4), 25.72 (CH_2, C-9), 23.87 (CH_2, C-3); IR ($CHCl_3$): ν 3081 cm^{-1} w, 2999 m, 2936 s, 2870 s, 2827 w, 2219 m, 1594 s, 1519 s, 1492 m, 1451 m, 1344 s, 1311 m, 1284 m, 1271 m, 1176 m, 1151 m, 1140 m, 1112 s, 1075 s, 855 s; MS-MAT (120 °C): *m/z* 300 (M^+, 58.88), 285 (34.93), 269 (69.20), 257 (10.16), 241 (100.00), 223 (6.33), 194 (6.34), 183 (17.32), 165 (12.86), 153 (21.66), 138 (11.49); HRMS (M^+ = $C_{17}H_{20}N_2O_3$): calcd.: 300.1474, found: 300.1474.

(1S,2R,5R,6S)-2-Methoxy-6-(16-ethanoyl-phenylethynyl)-1-azabicyclo[3.2.2]nonane ***18c***



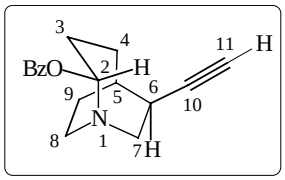
C9-iodinated *p*-EtO_2C-phenyl-didehydroquincorine **17c** (462 mg, 1.09 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz (275 mg, 1.20 mmol, 1.1 equiv) to furnish 1-azabicyclo[3.2.2]nonane **18c** (74 %, 264 mg, 0.81 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (d, 2 H, *J* 8.7 Hz, H-15, H-17), 7.46-7.44 (d, 2 H, *J* 8.6 Hz, H-14, H-18), 4.39-4.33 (q, 2 H, *J* 7.0 Hz, H-20), 3.93-3.89 (dd, 1 H, *J* 10.0 and 4.3 Hz, H-2), 3.60-3.54 (dd, 1 H, *J* 14.0 and 9.3 Hz, H-7_{exo}), 3.25 (s, 3 H, OMe), 3.12-3.05 (m, 1 H, H-8), 2.99-2.88 (m, 2 H, H-7_{endo}, H-6), 2.62-2.54 (m, 1 H, H-8), 2.18-2.03 (m, 2 H, H-5, H-3), 1.99-1.93 (m, 1 H, H-4), 1.77-1.60 (m, 3 H, H-9, H-4, H-3), 1.56-1.48 (m, 1 H, H-9) and 1.40-1.36 (t, 3 H, *J* 7.2 Hz, H-21); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 166.16 (C, C-19), 131.49 (CH, C-15, C-17), 129.47 (C, C-16), 129.44 (CH, C-14, C-18), 128.67 (C, C-13), 97.63 (C, C-10), 97.11 (CH, C-2), 82.69 (C, C-11), 61.11 (CH_2, C-20), 54.25 (CH_3, C-12), 54.04 (CH_2, C-7), 37.93 (CH_2, C-8), 33.83 (CH, C-6), 31.94 (CH, C-5), 30.55 (CH_2, C-4), 25.92 (CH_2, C-9), 23.90 (CH_2, C-3), 14.41 (CH_3, C-21); IR ($CHCl_3$): ν 2985 cm^{-1} m, 2936 s, 2870 s, 2827 w, 2219 m, 1711 s, 1606 s, 1507 w, 1471 m, 1451 m, 1406 m, 1368 s, 1307 s, 1275 s, 1239 m, 1176 s, 1151 m, 1140 m, 1109 s, 1075 s; MS-MAT (90 °C): *m/z* 327 (M^+, 57.81), 312 (11.06), 297 (47.05), 283 (20.59), 266 (87.24), 240 (5.75), 211 (9.43), 182 (13.68), 167 (10.57), 153 (11.33), 136 (10.98), 105 (100.00); HRMS (M^+ = $C_{20}H_{25}N_1O_3$): calcd.: 327.1834, found: 327.1833.

(1S,2S,5R,6S)-2-Methoxy-6-phenylethynyl-1-azabicyclo[3.2.2]nonane ***20***



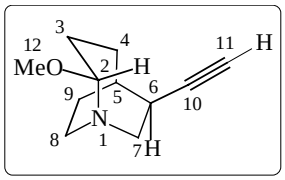
C9-iodinated phenyl-didehydroquincoridine **19** (351 mg, 1.00 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz (252 mg, 1.10 mmol, 1.1 equiv) to furnish 1-azabicyclo[3.2.2]nonane **20** (70 %, 179 mg, 0.70 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39-7.36 (m, 2 H, Ph-H), 7.29-7.25 (m, 3 H, Ph-H), 3.94-3.90 (dd, 1 H, *J* 10.0 and 4.5 Hz, H-2), 3.28 (s, 3 H, OMe), 3.24-3.18 (ddd, 1 H, *J* 14.4, 6.8 and 2.2 Hz, H-7_{endo}), 3.17-3.10 (dd, 1 H, *J* 14.4 and 9.9 Hz, H-7_{exo}), 3.06-2.98 (m, 1 H, H-8), 2.97-2.89 (m, 1 H, H-8), 2.85-2.79 (m, 1 H, H-6), 2.26-2.15 (m, 2 H, H-5, H-3), 2.06-1.95 (m, 2 H, H-9, H-9), 1.81-1.73 (m, 1 H, H-4), 1.71-1.62 (m, 1 H, H-4) and 1.46-1.38 (m, 1 H, H-3); NOE (400 MHz, $CDCl_3$): H-2 irrad. (3.90): H-12 (8.0 %), H-8 (6.4 %), H-9 (5.5 %), H-4 (1.2 %), H-3 (1.2 %); H-7_{endo} irrad. (3.24): H-2 (0.8 %), H-7_{exo} (27.1 %), H-6 (2.3 %), H-3 (5.9 %); H-7_{exo} irrad. (3.15): H-7_{endo} (24.4 %), H-6 (11.1 %), H-8_{exo} (4.4 %); ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 131.55 (CH, C-14, C-18), 128.30 (CH, C-15, C-17), 127.54 (CH, C-16), 123.94 (C, C-13), 96.50 (CH, C-2), 92.12 (C, C-10), 82.21 (C, C-11), 54.15 (CH_3, C-12), 47.08 (CH_2, C-7), 45.54 (CH_2, C-8), 32.08 (CH, C-6), 30.83 (CH_2, C-4), 29.52 (CH_2, C-9), 29.25 (CH, C-5), 28.27 (CH_2, C-3); IR ($CHCl_3$): ν 3062 cm^{-1} w, 2999 m, 2934 s, 2872 s, 2825 w, 2223 w, 1598 m, 1491 m, 1456 m, 1443 m, 1346 m, 1315 m, 1269 m, 1176 m, 1158 m, 1103 s, 1093 s, 1071 s, 995 m; MS-MAT (RT): *m/z* 255 (M^+, 27.57), 240 (8.46), 224 (29.37), 196 (42.98), 182 (8.52), 167 (11.22), 155 (6.52), 141 (8.23), 122 (84.01), 105 (100.00), 90 (10.28), 77 (54.98); HRMS (M^+ = $C_{17}H_{21}N_1O_1$): calcd.: 255.1623, found: 255.1622.

(1S,2R,5R,6S)-2-Benzoyloxy-6-ethynyl-1-azabicyclo[3.2.2]nonane ***22-OBz***



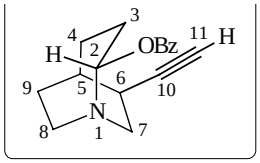
C-9 iodinated didehydroquincorine **21** (370 mg, 1.35 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz to afford 1-azabicyclo[3.2.2]nonane **22-OBz** (48 %, 173.65 mg, 0.65 mmol); ^{1}H-NMR (400 MHz, CD_3OD): δ 8.03-7.98 (m, 2 H, H-Ar), 7.64-7.58 (m, 1 H, H-Ar), 7.52-7.44 (m, 2 H, H-Ar), 3.88 (m, 1 H, H-2), 3.47 (dd, 1 H, *J* 9.7 and 14.3, H-7), 3.32-3.29 (m, 1 H, H-8), 3.06-2.96 (m, 1 H, H-8), 2.85 (ddd, 1 H, *J* 14.3, 6.1 and 2.6 Hz, H-7), 2.73-2.61 (m, 1 H, H-6), 2.59-2.48 (m, 1 H, H-11), 2.05-1.98 (m, 1 H, H-5), 1.94-1.84 (m, 1 H, H-3), 1.83-1.64 (m, 2 H, H-4, H-9) and 1.63-1.43 (m, 2 H, H-4, H-3); ^{13}C-NMR (100 MHz, CD_3OD): δ 168.55 (C, C-12), 134.23 (CH, C-16), 132.56 (C, C-13), 130.51 (CH, C-14, C-18), 129.59 (CH, C-15, C-17), 98.08 (CH, C-2), 88.67 (C, C-10), 72.01 (CH, C-11), 54.98 (CH_2, C-7), 38.90 (CH_2, C-8), 33.71 (CH, C-6), 32.98 (CH, C-5), 31.29 (CH_2, C-4), 26.68 (CH_2, C-9), 24.45 (CH_2, C-3); IR ($CHCl_3$): ν 3306 cm^{-1} s, 3065 w, 2947 s, 2492 w, 2110 w, 1716 s, 1603 w, 1584 w, 1472 w, 1452 m, 1315 m, 1274 vs, 1178 m, 1119 m, 1070 w, 1026 m, 979 w, 818 w; MS-MAT (r.t.): *m/z* 269 (M^+, 11.48), 240 (1.00), 230 (4.49), 228 (1.11), 182 (1.10), 165 (1.23), 164 (8.96), 149 (3.04), 148 (26.52), 146 (7.22), 135 (9.89), 134 (100), 122 (2.69), 108 (2.20), 106 (18.47), 105 (67.80), 91 (4.16), 82 (4.86), 79 (4.72), 77 (25.66); HRMS: calcd.: 269.1415; found: 269.1413.

(1S,2R,5R,6S)-2-Methoxy-6-ethynyl-1-azabicyclo[3.2.2]nonane ***22-OMe***



C-9 iodinated didehydroquincorine **21** (230 mg, 0.84 mmol, 1 equiv) was allowed to react according to general procedure III with $AgNO_3$ instead of AgOBz to afford 1-azabicyclo[3.2.2]nonane **22-OMe** (61 %, 91.3 mg, 0.51 mmol); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.88 (dd, 1 H, *J* 10.1 and 4.2 Hz, H-2), 3.51 (dd, 1 H, *J* 14.4 and 9.8 Hz, H-7), 3.24 (s, 3 H, OMe), 3.16-3.01 (m, 1 H, H-8), 2.85 (ddd, 1 H, *J* 14.4, 6.3 and 2.6 Hz, H-7), 2.72-2.65 (m, 1 H, H-8), 2.60-2.51 (m, 1 H, H-6), 2.19 (d, 1 H, *J* 2.5 Hz, H-11), 2.09-2.04 (m, 1 H, H-5), 1.97-1.91 (m, 1 H, H-3), 1.75-1.69 (m, 1 H, H-4), 1.68-1.59 (m, 4 H, H-3, H-4, H-9) and 1.52-1.42 (m, 1 H, H-9); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 97.45 (CH, C-2), 87.15 (C, C-10), 70.48 (CH, C-11), 54.13 (CH_3, C-12), 53.79 (CH_2, C-7), 37.75 (CH_2, C-8), 32.61(CH, C-6), 31.42 (CH, C-5), 30.82 (CH_2, C-4), 25. 68(CH_2, C-9), 23.32 (CH_2, C-3); IR ($CHCl_3$): ν 3431 cm^{-1} w, 3288 m, 3214 w, 2108 w, 1451 s, 1342 m, 1320 m, 1320 m, 1301 m, 1266 m, 1179 s, 1150 w, 1107 w, 1084 m, 980 w, 931 m, 848 w; MS-MAT (r.t.): *m/z* 183 (M^+, 45.63), 171 (2.04), 168 (100), 169 (12.01), 168 (100), 154 (35.96), 152 (92.92), 150 (2.04), 140 (21.36), 126 (35.62), 124 (7.22), 122 (6.48), 116 (4.35), 112 (12.96), 108 (3.45), 98 (9.94), 96 (6.97), 87 (10.01), 72 (22.75); HRMS: calcd.:183.1623, found: 183.1623.

(1S,2S,5R,6S)-2-Methoxy-6-ethynyl-1-azabicyclo[3.2.2]nonane ***24-OBz***



C-9 iodinated didehydroquincoridine **23** (300 mg, 1.09 mmol, 1 equiv) was allowed to react according to general procedure III with AgOBz to afford 1-azabicyclo[3.2.2]nonane **24-OBz** (43 %, 127.36 mg, 0.47 mmol); ^{1}H-NMR (CD_3OD): δ 8.08-7.99 (m, 2 H, H-Ar), 7.63-7.56 (m, 1 H, H-Ar), 7.50-7.45 (m, 2 H, H-Ar), 3.66 (dd, 1 H, *J* 11.3 and 8.1 Hz, H-2), 3.48 (dd, 1 H, *J* 11.4 and 6.2 Hz, H-7), 3.06-2.95 (m, 1 H, H-8), 2.85-2.79 (m, 1 H, H-8), 2.69-2.53 (m, 2 H, H-7, H-6), 2.47-2.42 (m, 1 H, H-11), 2.19-2.10 (m, 1 H, H-5), 1.70-1.60 (m, 2 H, H-3, H-9), 1.60-1.48 (m, 2 H, H-4, H-9), 1.36-1.28 (m, 1 H, H-4), 1.24-1.17 (m, 1 H, H-3); ^{13}C-NMR (100 MHz, CD_3OD): δ 167.06 ($C_{,}$ C-12), 133.34 (CH, C-16), 133.20 (CH, C-13), 129.40 (CH, C-14, C-18), 128.50 (CH, C-15, C-17), 98.79 (CH, C-2), 87.21 (C , C-10), 72.60 (CH, C-11), 54.70 (CH_2, C-7), 40.35 (CH_2, C-8), 28.05 (CH, C-6), 27.44 (CH_2, C-4), 26.60 (CH, C-5), 25.67 (CH_2, C-4), 25.03 (CH_2, C-3); IR ($CHCl_3$): ν 3306 cm^{-1} s, 3094 w, 2944 vs,2873 w, 2110 w, 1715 w, 1660 m, 1602 w, 1453 m, 1322 m, 1260 m, 1176 w,1096 m, 1038 m, 924 m, 888 m; MS-MAT (r.t.): m/z 269 (M^+, 1.59), 256 (1.67), 202 (1.01), 167 (1.27), 165 (4.15), 164 (4.57), 149 (3.05), 148 (5.40), 147 (4.89), 146 (9.11), 136 (1.39), 134 (25.46), 123 (9.41), 122 (100), 109 (1.43), 106 (8.54), 105 (82.57), 94 (2.94), 92 (2.40), 82 (3.67), 81 (2.07), 78 (5.04), 77 (42.22); HRMS: calcd.: 269.1415, found: 269.1414.

Pharmacological investigations

Substituted 1-azabicyclo[3.2.2]nonanes **3-OMe**, **12**, **17a** and **17b** were selected for *in vitro* tests with cell-lines from gastric adenocarcinoma (HMO2), colon carcinoma (KATO III) and human heptocellular carcinoma (HEP G2). **3-OMe** and **17a** show weak cytostatic activity in the HMO2 cell line, the other rearranged alkaloids were inactive in all cell lines.

Alkyne	**GI_{50}**[a])			**TGI**[b])			**LC_{50}**[c])		
	HMO2	KATO III	HEP G2	HMO2	KATO III	HEP G2	HMO2	KATO III	HEP G2
3-OMe	**7.1**	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10
12	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10
17a	**6.2**	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10
17b	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10

[a]) Drug concentration causing 50% growth inhibition.

[b]) Drug concentration causing 100% growth inhibition.

[c]) Drug concentration causing 50% reduction of the cells present at time point zero, i.e. at 24 h.