S_N1-like Reactions of Bicyclic α -Amino Ethers with Sulfur, Nitrogen and Carbon Nucleophiles. Synthesis of 1-Azabicyclo[3.2.2]nonanes Functionalized at Carbon C2 and C6 with Complete Stereocontrol

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Experimental

General. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared spectrometer. ¹H-NMR and ¹³C-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 μ m). Analytical TLC was carried out on aluminum-backed 0.2-mm silica gel 60 F254 plates (E. Merck). Petrol ether (PE) 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. Compounds 1-OMe and 2-OMe were prepared as described previously.⁵

General Procedure A for the substitution at C2 with silylated nucleophiles and BF₃·OEt₂. The α -amino ether (1 equiv.) was dissolved in abs. CH₂Cl₂ (5 ml/mmol) under nitrogen. The reaction mixture was cooled (-40 °C) and TMS-nucleophile (3-5 equiv.) and BF₃·OEt₂ (1.1 - 1.2 equiv.) were added. After stirring was continued for 30 min at -40 °C the reaction was allowed to warm up to room temperature and stirred for additional 3-24 h. Sat. aq. NaHCO₃ was added and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was dried (Na₂SO₄) and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (PE:MTBE 2:1 - MTBE) to furnish the desired substituted product.

6-Vinyl-1-aza-bicyclo[3.2.2]nonane-2-carbonitrile 1-CN

α -Amino ether 1-OMe was allowed to react according general Procedure A with TMS-CN (0.39 ml, 2.32 mmol, 5 equiv.) and $\text{BF}_3 \cdot \text{OEt}_2$ (61 μl , 0.48 mmol, 1.1 equiv.) to afford 1-CN (67 mg, 83 %). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.70 (ddd, $J = 6.90, 10.54, 17.31$ Hz, 1H, H-10); 5.10-4.97 (m, 2H, H-11, H-11); 3.74-3.68 (m, 1H, H-2); 3.42 (dd, $J = 9.41, 14.80$ Hz, 1H, H-7); 3.21-3.12 (m, 1H, H-8); 2.90-2.80 (m, 1H, H-8); 2.69-2.62 (m, 1H, H-7); 2.44-2.36 (m, 1H, H-6); 2.10-2.04 (m, 1H, H-5); 2.04-1.98 (m, 2H, H-3, H-3); 1.86-1.80 (m, 1H, H-9); 1.77-1.63 (m, 3H, H-4, H-4, H-9). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 140.46 (CH, C-10); 120.36 (C, CN); 114.93 (CH_2 , C-11); 59.11 (CH, C-2); 55.41 (CH_2 , C-7); 43.13 (CH, C-6); 41.24 (CH_2 , C-8); 32.37 (CH, C-5); 29.90 (CH_2 , C-3); 27.29 (CH_2 , C-9); 24.89 (CH_2 , C-4). IR (Golden Gate ATR): ν 2931 m, 2864 m, 2233 w, 1723 w, 1637 w, 1451 m, 1358 m, 1277 m, 1136 m, 1115 m, 1073m, 995 m, 917 s, 770 m, 714 m. MS-MAT (r.t.): m/z 177 ($\text{M}^+ + 1$, 12.49); 176 (100); 175 (46.56); 161 (19.53); 150 (20.56); 136 (29.04); 122 (36.32); 109 (33.28); 108 (64.99); 105 (10.69); 95 (31.08); 81 (25.10); 79 (24.45); 70 (25.87); 67 (26.73). HRMS: calcd.: 176.1313; found: 176.1312.

6-Vinyl-1-aza-bicyclo[3.2.2]nonane-2-carbonitrile 2-CN

α -Amino ether 2-OMe (250 mg, 1.38 mmol) was allowed to react according general Procedure A with $\text{BF}_3 \cdot \text{OEt}_2$ (0.19 ml, 1.52 mmol, 1.1 equiv.) and TMS-CN (0.86 ml, 6.91 mmol, 5 equiv.) to afford 2-CN (166 mg, 68 %). $^1\text{H-NMR}$ (400 MHz, CD_3OD): δ 5.96 (ddd, $J = 7.03, 10.41, 17.32$ Hz, 1H, H-10); 5.17-5.08 (m, 2H, H-11, H-11); 4.06 (dd, $J = 5.04, 11.04$ Hz, 1H, H-2); 3.09 (dd, $J = 10.04, 14.68$ Hz, 1H, H-7); 3.02-2.83 (m, 3H, H-8, H-8, H-7); 2.55-2.45 (m, 1H, H-6); 2.18-2.09 (m, 1H, H-5); 2.07-1.95 (m, 4H, H-4, H-9, H-4, H-3); 1.82-1.73 (m, 1H, H-9); 1.65-1.55 (m, 1H, H-3). $^{13}\text{C-NMR}$ (100 MHz, CD_3OD): δ 140.12 (CH, C-10); 121.83 (C, CN); 115.32 (CH_2 , C-11); 56.63 (CH, C-2); 49.13 (CH_2 , C-7); 48.72 (CH_2 , C-8); 42.00 (CH, C-6); 33.95 (CH, C-5); 31.42 (CH_2 , C-4); 30.94 (CH_2 , C-9); 29.67 (CH_2 , C-3). IR (Golden Gate ATR): ν 3337 w, 3077w, 2929 s, 2869 m, 2236 w, 2208 w, 1635 m, 1457 m, 1351 m, 1241 w, 1121 w, 1097 m, 1003 m, 914 s, 757 m, 730 m. MS-MAT (25 $^\circ\text{C}$): m/z 177 ($\text{M}^+ + 1$, 24.58); 176 (100); 162 (7.68); 161 (45.52); 150 (5.73); 148 (34.11); 147 (70.43); 136 (60.92); 122 (57.10); 109 (43.71); 108 (70.80); 96 (14.81); 91 (10.40); 82 (35.24); 70 (27.60). HRMS calcd.: 176.1313; found: 176.1308

2-Azido-6-vinyl-1-aza-bicyclo[3.2.2]nonane 1-N₃

α -Amino ether 1-OMe (59 mg, 0.33 mmol) was allowed to react according general Procedure A with trimethylsilyl azide (0.22 ml, 1.63 mmol, 5 equiv.) and $\text{BF}_3 \cdot \text{OEt}_2$ (48 μl , 0.36 ml, 1.1 equiv.) to afford 1-

N_3 (51 mg, 81%). 1H -NMR (400 MHz, CD_3OD): δ 5.89 (ddd, $J = 7.15, 11.04, 16.71$ Hz, 1H, H-10); 5.16-5.09 (m, 2H, H-11); 4.37-4.33 (m, 1H, H-2); 3.47 (dd, $J = 9.79, 14.30$, 1H, H-7); 3.35-3.26 (m, 1H, H-8); 3.01 (ddd, $J = 2.26, 8.53, 14.18$ Hz, 1H, H-7); 2.97-2.87 (m, 1H, H-8); 2.64-2.55 (m, 1H, H-6); 2.10-2.05 (m, 1H, H-5); 2.02-1.94 (m, 1H, H-9); 1.92-1.85 (m, 1H, H-3); 1.84-1.88 (m, 1H, H-9); 1.77-1.68 (m, 2H, H-4, H-4); 1.65-1.56 (m, 1H, H-3). ^{13}C -NMR (100 MHz, CD_3OD): δ 140.59 (CH, C-10); 116.31 (CH_2 , C-11); 100.24 (CH, C-2); 51.62 (CH_2 , C-7); 41.98 (CH, C-6); 39.76 (CH_2 , C-8); 33.05 (CH, C-5); 29.51 (CH_2 , C-4); 26.40 (CH_2 , C-9); 22.30 (CH_2 , C-3). IR (Golden Gate ATR): ν 3076 w, 2928 s, 2865 s, 2104 m, 2059 w, 1726 m, 1636 m, 1452 m, 1364 m, 1114 m, 1092 s, 1075 s, 989 m, 909 m 896 m. MS-MAT (25 °C): m/z 193 ($M^+ + 1$, 6.48); 192 (M^+ , 32.29); 168 (2.67); 167 (17.85); 166 (90.90); 151 (26.02); 150 (100); 138 (21.75); 136 (12.94); 126 (19.14); 122 (22.69); 112 (10.34); 108 (49.44); 96 (16.20); 87 (30.75); 82 (53.23); 79 (41.85); 67 (42.16); HRMS: calcd.: 192.1374; found: 192.1370.

2-Azido-6-vinyl-1-aza-bicyclo[3.2.2]nonane 2- N_3

α -Amino ether 2-OMe (110 mg, 0.61 mmol) was allowed to react according general Procedure A with trimethylsilyl azide (0.43 ml, 3.04 mmol, 5 equiv.) and $BF_3 \cdot OEt_2$ (92 μ l, 0.73 ml, 1.2 equiv.) to afford 1- N_3 (87.4 mg, 75%).

1H -NMR (400 MHz, CD_3OD): δ 5.91 (ddd, $J = 7.16, 10.42, 17.45$ Hz, 1H, H-10); 5.18-5.07 (m, 2H, H-11, 11); 4.41 (dd, $J = 4.14, 9.16$ Hz, 1H, H-2); 3.22-3.06 (m, 4H, H-7, H-7, H-8, H-8); 2.68-2.50- (m, 1H, H-6); 2.11-1.93 (m, 4H, H-5, H-3, H-9, H-9); 1.86-1.66 (m, 2H, H-4, H-4); 1.57-1.45 (m, 1H, H-3). ^{13}C -NMR (100 MHz, CD_3OD): δ 140.13 (CH, C-10); 116.0 (CH_2 , C-11); 97.79 (CH, C-2); 46.18 (CH_2 , C-7); 46.13 (CH_2 , C-8); 40.32 (CH, C-6); 33.46 (CH, C-5); 29.65 (CH_2 , C-9); 29.17 (CH_2 , C-4); 27.02 (CH_2 , C-3). IR (Golden Gate ATR): ν 2928 m, 2865 m, 2196 w, 2105 m, 2057 w, 1634 w, 1456 m, 1345 m, 1261 m, 1234 w, 1114 m, 1087 s, 1053 m, 1003 m, 908 m. MS-MAT (25 °C): m/z 193 ($M^+ + 1$, 1.94); 192 (M^+ , 6.93); 184 (95.32); 183 (24.01); 169 (10.78); 166 (100); 155 (26.26); 150 (97.93); 138 (20.08); 129 (26.36); 122 (20.20); 108 (46.13); 96 (13.55); 90 (36.59); 81 (44.92); 75 (34.07); 67 (32.40). HRMS: calcd.: 192.1374; found: 192.1371.

2-Ethynyl-6-vinyl-1-aza-bicyclo[3.2.2]nonane 1-ethyne

To a solution of 1-OMe (88 mg, 0.48 mmol) in abs. CH_2Cl_2 (3 ml) were added $BF_3 \cdot OEt_2$ (64.2 μ l, 0.51 mmol, 1.1 equiv.) and Bu_3SnC_2H (0.70 ml, 2.43 mmol, 5 equiv.) at -40 °C. The solution was stirred for 30 min. at -40 °C and was then stirred for another 3h at r.t. The reaction mixture was treated with sat. aq. $NaHCO_3$ and extracted with CH_2Cl_2 . The combined organic layer was dried (Na_2SO_4), evaporated and purified by column chromatography (PE:MTBE 5:1-2:1) to furnish 1-ethyne (33mg, 39%). 1H -NMR (400 MHz, CD_3OD): δ 5.87 (ddd, $J = 7.16, 10.92, 16.82$ Hz, 1H, H-10); 5.11-5.02 (m, 2H, H-11); 3.87-3.80 (m, 1H, H-2); 3.41-3.32 (m, 2H, H-7, H-8); 2.89-2.79 (m, 3H, H-7, H-8, H-12); 2.53-2.44 (m, 1H, H-6); 2.11-2.04 (m, 1H, H-5); 2.03-1.88 (m, 3H, H-4, H-9, H-3); 1.81-1.64 (m, 3H, H-4, H-3, H-9). ^{13}C -NMR (100 MHz, CD_3OD): δ 141.24 (CH, C-10); 115.80 (CH_2 , C-11); 84.47 (CH, C-13); 60.46

(CH, C-2); 55.24 (C, C-12); 43.12 (CH₂, C-7); 41.46 (CH₂, C-8); 40.50 (CH, C-6); 33.60 (CH, C-5); 32.23 (CH₂, C-4); 29.22 (CH₂, C-9); 28.08 (CH₂, C-3). IR (Golden Gate ATR): ν 3159 w, 3073 w, 2924 s, 2867 s, 2361 m, 2110 w, 1709 m, 1600 s, 1563 m, 1449 m, 1368 s, 1262 m, 1116 m, 1070 m, 1000 m, 922 m, 716 s. MS-MAT (25 °C): m/z 176 (M^+ +1, 21.84); 175 (M^+ +1, 82.69); 160 (33.82); 148 (25.81); 146 (100); 136 (19.82); 132 (63.35); 120 (51.21); 108 (28.07); 106 (35.60); 97 (12.70); 94 (20.39); 81 (28.56); 67 (21.12). HRMS: calcd.: 175.1361; found: 175.1359.

2-Ethynyl-6-vinyl-1-aza-bicyclo[3.2.2]nonane 2-ethyne

α -Amino ether 2-OMe (73 mg, 0.40 mmol) was dissolved in abs. CH₂Cl₂ (2 ml). Tributylethynylstannan (0.35 ml, 1.20 mmol, 3 equiv.) and BF₃·OEt₂ (53.28 μ l, 0.42 mmol, 1.1 equiv.) were added at -40 °C and the solution was stirred for 30 min at -40 °C. The reaction mixture was allowed to warm up to r.t. and after 8h the reaction was terminated by addition of sat. aq. KF and sat. aq. NaHCO₃. The aqueous layer was extracted with CH₂Cl₂, the combined organic layer was dried over Na₂SO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography (PE:MTBE 5:1-2:1) to furnish 2-ethyne (49 mg, 70%). ¹H-NMR (400 MHz, CDCl₃): δ 5.95-5.84 (m, 1H, H-10); 5.13-5.06 (m, 2H, H-11); 3.90-3.84 (m, 1H, H-2); 3.22-3.26 (m, 2H, H-7, H-8); 3.10-2.95 (m, 2H, H-7, H-8); 2.52-2.44 (m, 1H, H-6); 2.43 (d, J = 2.39 Hz, 1H, H-13); 2.10-1.95 (m, 3H, H-5, H-4, H-9); 1.90-1.74 (m, 3H, H-4, H-9, H-3); 1.60-1.50 (m, 1H, H-3). ¹³C-NMR (100 MHz, CDCl₃): δ 139.86 (CH, C-10); 114.96 (CH₂, C-11); 84.18 (CH, C-13); 72.40 (C, C-12); 56.04 (CH, C-2); 46.76 (CH₂, C-7); 46.67 (CH₂, C-8); 40.64 (CH, C-6); 32.44 (CH, C-5); 30.24 (CH₂, C-4); 29.20 (CH₂, C-9); 28.49 (CH₂, C-3). IR (Golden Gate ATR): ν 3303 w, 3076 w, 2924 s, 2863 m, 2112 w, 1634 m, 1594 m, 1455m, 1343 m, 1119 w, 1091 m, 991 s, 723 m, 636 s. Ms-MAT (80 °C): m/z 176 (M^+ +1, 4.15); 175 (M^+ , 20.01); 160 (6.23); 150 (2.62); 149 (8.60); 138 (2.35); 122 (100); 108 (4.90); 105 (90.84); 96 (4.02); 81 (11.41); 77 (48.32); 67 (8.25). HRMS: calcd.: 175.1361; found: 175.1361.

2-Allyl-6-vinyl-1-aza-bicyclo[3.2.2]nonane 2-allyl

The solution of α -amino ether 2-OMe in abs. THF (3ml) was cooled (-40 °C) and allyl-magnesium bromide (1.66 ml, 1M, 5 equiv.) and BF₃·OEt₂ (52 μ l, 0.39 mmol, 1.2 eq) were added. The mixture was stirred for 30 min. at -40 °C and was then allowed to warm up to r.t within 1h. After addition of sat. aq. NaHCO₃ and extraction with CH₂Cl₂ the organic layer was dried over Na₂SO₄ and concentrated in vacuo. Column chromatography (MTBE) of the crude product furnished the desired 2-allyl (30.31 mg, 48 %). ¹H-NMR (400 MHz, CD₃OD): δ 5.91 (ddd, J = 7.53, 10.29, 17.44 Hz, 1H, H-10); 5.85-5.73 (m, 1H, H-13); 5.10-4.94 (m, 4H, H-11, H-11, H-14, H-14); 2.95 (m, 5H, H-2, H-7, H-7, H-8, H-8); 2.48-2.38 (m, 1H, H-6); 2.30-2.20 (m, 1H, H-12); 2.13-2.00 (m, 2H, H-12, H-9); 1.98-1.65 (m, 4H, H-9, H-5, H-4, H-3); 1.52-1.39 (m, 2H, H-4, H-3). ¹³C-NMR (100 MHz, CD₃OD): δ 141.63 (CH, C-10); 137.25

(CH, C-13); 116.88 (CH₂, C-14); 114.96 (CH₂, C-11); 64.80 (CH, C-2); 49.33 (CH₂, C-7); 47.91 (CH₂, C-8); 42.37 (CH₂, C-12); 41.86 (CH, C-6); 34.32 (CH, C-5); 33.45 (CH₂, C-9); 31.72 (CH₂, C-4); 31.33 (CH₂, C-3). IR (Golden Gate ATR): ν 3325 w, 3074 w, 2923 m, 2860 m, 1637 m, 1455 m, 1342 w, 1281 w, 1092 m, 1041 w, 990 m, 907 s, 754 w. MS-MAT (70 °C): m/z 192 ($M^+ + 1$, 1.06); 191 (M^+ , 13.07); 190 (11.67); 162 (2.98); 150 (100); 136 (3.51); 122 (4.75); 108 (3.76); 96 (5.13); 81 (3.45); 79 (5.33); 77 (46.12); 67 (5.85). HRMS: calcd.: 191.1674; found: 191.1674.

2-Methyl-2-(6-vinyl-1-aza-bicyclo[3.2.2]non-2-yl)-propionic acid methyl ester 1-ester

A solution of α -amino ether 1-OMe (77 mg, 0.43 mmol) and TTMPP (45.5 mg, 20 mol%) in abs. DCM/MTBE (3ml, 20:1) at r.t. was cooled to -40 °C. The ketene acetal (0.22ml, 1.06 mmol, 2.5 equiv.) and then BF₃·OEt₂ (66 μ l, 0.51 mmol, 1.2 equiv.) were added. The mixture was allowed to warm up to room temperature. After stirring for 3h the reaction mixture was treated with sat. aq. NaHCO₃ and extracted with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄, evaporated and purified by column chromatography (PE:MTBE 1:1) to furnish 1-ester (66 %, 70 mg). ¹H-NMR (400 MHz, CD₃OD): δ 5.97 (ddd, J = 17.19, 9.53, 7.64 Hz, 1H, H-10); 5.05-4.96 (m, 2H, H-11); 3.64 (bs, 3H, OCH₃-); 3.08 (dd, J = 14.43, 9.79 Hz, 1H, H-7_{exo}); 3.04-2.95 (m, 1H, H-8); 2.92 (dd, J = 11.55, 4.49 Hz, 1H, H-2); 2.76-2.69 (m, 1H, H-7_{endo}); 2.69-2.60 (m, 1H, H-8); 2.45-2.36 (m, 1H, H-6); 2.01-1.94 (m, 1H, H-5); 1.84-1.68 (m, 2H, H-9, H-3); 1.67-1.58 (m, 3H, H-9, H-4, H-3); 1.55-1.44 (m, 1H, H-4); 1.13 (bs, 3H, CH₃); 1.05 (bs, 3H, CH₃). ¹³C-NMR (100 MHz, CD₃OD): δ 179.94 (C, C-13); 144.49 (CH, C-10); 114.35 (CH₂, C-11); 72.62 (CH, C-2); 58.26 (CH₂, C-7); 52.01 (CH₃, OCH₃); 45.53 (CH, C-6); 40.55 (CH₂, C-8); 34.83 (CH, C-5); 27.95 (CH₂, C-9); 27.82 (CH₂, C-4); 24.58 (CH₂, C-3); 24.13 (CH₃, C-15); 20.94 (CH₃, C-16). IR (Golden Gate ATR): ν 2973 (m), 2915 (m), 2867 (m), 1726 (s), 1635 (m), 1452 (w), 1278 (m), 1259 (m), 1134 (s), 1076 (m), 993 (m), 908 (m). MS-MAT (25°C): m/z 252 ($M^+ + 1$, 1.16); 251 (M^+ , 6.79); 236 (1.05); 220 (1.86); 192 (10.84); 172 (2.27); 151 (100); 122 (1.76); 108 (1.12); 96 (1.88); 81 (2.35); 79 (3.10). HRMS: calcd.: 251.1885; found: 251.1884.

2-Methyl-2-(6-vinyl-1-aza-bicyclo[3.2.2]non-2-yl)-propionic acid methyl ester 2-ester

A solution of α -amino ether 2-OMe (96 mg, 0.53 mmol) and TTMPP (56.5 mg, 20 mol%) in abs. DCM/MTBE (3ml, 20:1) was cooled to -40 °C and the ketene acetal (0.27ml, 1.32 mmol, 2.5 equiv.) and then BF₃·OEt₂ (83 μ l, 0.64 mmol, 1.2 equiv.) were added. The mixture was allowed to warm up to room temperature. After stirring for 3h the reaction mixture was treated with sat. aq. NaHCO₃ and extracted with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄, evaporated and purified by column chromatography (PE:MTBE 1:1) to furnish 2-ester (93.7 mg, 70 %). ¹H-NMR (400 MHz, CD₃OD): δ 5.88 (ddd, J = 7.78, 10.29, 16.92 Hz, 1H, H-10); 5.02-4.94 (m, 2H, H-11); 3.63 (s, 3H, OMe); 3.04 (dd, J = 4.89, 11.17 Hz, 1H, H-2); 2.90 (dd, J = 9.91, 14.43 Hz, 1H, H-7_{exo}); 2.86-2.78 (m, 1H, H-8_{endo}); 2.77-2.63 (m, 2H, H-8, H-7); 2.36-2.27 (m, 1H, H-6); 2.17-2.08 (m, 1H, H-5); 1.92-1.85

(m, 1H, H-3); 1.84-1.72 (m, 2H, H-9, H-9); 1.64-1.56 (m, 2H, H-4, H-4); 1.48-1.39 (m, 1H, H-3); 1.12 (bs, 3H, CH₃); 1.04 (bs, 3H, CH₃). ¹³C-NMR (100 MHz, CD₃OD): δ 179.90 (C, C-13); 141.98 (CH, C-10); 114.51 (CH₂, C-11); 68.61 (CH, C-2); 52.00 (CH₃, OMe); 51.16 (CH₂, C-7); 50.38 (CH₂, C-8); 50.00 (C, C-12); 42.40 (CH, C-6); 34.81 (CH, C-5); 32.56 (CH₂, C-9); 31.93 (CH₂, C-4); 23.98 (CH₂, C-3), 23.33 (CH₃, C-15), 20.69 (CH₃, C-16). NOE (400 MHz, CD₃OD): H₂ irradi.: H₈_{endo} (4.45 %), H₉ (1.82 %), H₄ (2.22 %), H₃ (1.45 %); H₇_{exo} irradi.: H₈_{endo} (7.30 %), H₆ (8.55 %), H₈_{exo}, H₇ (19.7 %); H₈_{endo} irradi.: H₂ (7.41 %), H₈ (24.85 %), H₇_{exo} (7.79 %); H₇_{endo} irradi.: H₇_{exo} (19.81 %), H₁₀ (3.65). IR (Golden Gate ATR): ν 3075 w, 2927 m, 2871 m, 1725 s, 1635 w, 1461 m, 1434 m, 1271 m, 1256 m, 1192 m, 1129 s, 1111 s, 1092 s, 1054 m, 992 m, 908 m. MS-MAT (25 °C): m/z 252 (M⁺+1, 1.97); 251 (M⁺, 11.45); 236 (1.71); 220 (1.90); 192 (9.88); 164 (2.60); 151 (12.59); 150 (100); 122 (1.82); 108 (1.54); 96 (2.51); 70 (3.48). HRMS: calcd.: 251.1885; found: 251.1879.

2-Phenylsulfanyl-6-vinyl-1-aza-bicyclo[3.2.2]nonane **2-SPh**

α-Amino ether **2-OMe** (84 mg, 0.36 mmol) was allowed to react according general Procedure A with trimethylsilyl thiophenolate (0.44 ml, 2.32 mmol, 5 equiv.) and BF₃·OEt₂ (72 μl, 0.55 mmol, 1.2 equiv.) to afford **2-SPh** (55.1 mg, 59 %). ¹H-NMR (400 MHz, CD₃OD): δ 7.40-7.36 (m, 2H, H-17, H-13); 7.28-7.22 (m, 2H, H-16, H-14); 7.20-7.14 (m, 1H, H-15), 5.92 (ddd, *J* = 7.28, 10.29, 17.32 Hz, 1H, H-10); 5.09-4.99 (m, 2H, H-11, H-11); 4.58 (dd, *J* = 4.02, 12.29 Hz, 1H, H-2); 3.08-3.01 (m, 1H, H-8); 2.93-2.82 (m, 3H, H-8, H-7, H-7); 2.45-2.35 (m, 1H, H-6); 2.11-2.02 (m, 1H, H-3); 1.97-1.89 (m, 2H, H-4, H-5); 1.87-1.68 (m, 3H, H-9, H-9, H-4); 1.54-1.44 (m, 1H, H-3). ¹³C-NMR (100 MHz, CD₃OD): δ 141.72 (CH, C-10); 1137.35 (C, C-12); 132.51 (CH, C-17, C-13); 129.62 (CH, C-16, C-14); 127.47 (CH, C-15); 114.87 (CH₂, C-10); 75.53 (CH, C-2); 49.12 (CH₂, C-7); 46.91 (CH₂, C-8); 42.25 (CH, C-6); 34.28 (CH, C-5); 32.65 (CH₂, C-4); 31.94 (CH₂, C-9); 31.63 (CH₂, C-3). IR (Golden Gate ATR): ν 3057 w, 2926 w, 2860 w, 1797 w, 1637 w, 1574 m, 1473 m, 1437 m, 1298 w, 1154 w, 1072 m, 1022 m, 996 m, 734 s, 686 s. MS-MAT (25 °C): m/z 259 (M⁺, 0.66); 221 (1.09); 220 (11.08); 219 (17.10); 218 (100); 185 (10.89); 155 (12.74); 150 (20.52); 112 (3.15); 109 (58.59); 96 (1.18); 77 (4.77); 69 (5.83); 65 (15.26). HRMS: calcd.: 259.1394; found: 259.1392.

2-Propa-1,2-dienyl-6-vinyl-1-aza-bicyclo[3.2.2]nonane **2-allenyl**

α-Amino ether **2-OMe** (166 mg, 0.92 mmol) was allowed to react according general Procedure A with propargyltrimethylsilane (1.10 ml, 7.34 mmol, 8 equiv.) and BF₃·OEt₂ (0.14 ml, 1.1 mmol, 1.2 equiv.) to afford **2-allenyl** (42 mg, 24 %).

¹H-NMR (400 MHz, CD₃OD): δ 5.91 (ddd, *J* = 7.28, 10.41, 17.44 Hz, 1H, H-10); 5.27-5.20 (m, 1H, H-12); 5.07-4.98 (m, 2H, H-11, H-11), 4.81-4.76 (m, 2H, H-14, H-14); 3.45-3.36 (m, 1H, H-2); 2.98-2.88 (m, 2H, H-7, H-8); 2.87-2.77 (m, 2H, H-7, H-8); 2.48-2.39 (m, 1H, H-6); 2.11-2.03 (m, 1H, H-3); 1.98-1.93 (m, 1H, H-5); 1.92-1.62 (m, 4H, H-4, H-4, H-9, H-9); 1.58-1.47 (m, 1H, H-3). ¹³C-NMR (100 MHz, CD₃OD): δ 208.98 (C, C-13); 141.68 (CH, C-10); 114.86 (CH₂, C-11); 94.80 (CH, C-12); 76.65 (CH₂, C-14); 63.32 (CH, C-2); 48.88 (CH₂, C-7); 47.39 (CH₂, C-8); 42.14 (CH, C-6); 34.10 (CH, C-5); 31.51 (CH₂, C-9); 31.07 (CH₂, C-4); 29.49 (CH₂, C-3). (Golden Gate ATR): ν 3369 m, 3078 m, 2925 s, 2865 m, 2359 w, 2019 w, 1952 w, 1636 m, 1567 m, 1462 m, 1385 m, 1089 s, 999 m, 912 m. MS-MAT (25 °C): *m/z* 190 (*M*⁺+1, 24.30); 189 (*M*⁺, 88.71); 188 (100); 174 (31.26); 166 (18.69); 160 (64.36); 150 (86.94); 148 (22.71); 138 (3.83); 134 (58.98); 122 (18.82); 109 (12.49); 108 (33.02); 96 (18.90); 91 (35.79); 80 (56.78); 67 (43.63). HRMS: calcd.: 189.1517; found: 189.1497.

Roeper RO5N5 33mg CDCl₃/TMS 111-NMR 12.07.01, Retstadt

Roper RO 529 15mg CD3OD/1MS 1H-NMR 21.03.01 Koertje

*** Current Data Parameters ***
 NAME : 10
 EXPNO : 101
 PROCNO : 1

*** Current Data Parameter

NAME :
EXPNO :
PROCNO :

Roper RO 397 40mg CD3OD/TMS 1H-NMR 8.09.2000 Koertje

*** Current Data Parameters
 NAME : 10
 EXPNO : 101
 PROCNO : 1

Roper RO399 55mg CD3OD/TMS 1H-NMR 11.09.00, Rettsstadt

Roper RO 596 75mg CD3OD-TMS 1H-NMR 22.08.01 Koertje

*** Current Data Parameters ***
 NAME :
 EXPNO : 10
 PROCNO : 101
 1

Mayo SO 036 40mg CDCl₃/TMS 1H-NMR 25.04.01 Koertje

*** Current Data Parameters ***
 NAME : 10
 EXPNO : 10
 PROCNO : 1

Roeper RO559 7mg CDCl3/TMS 1H-NMR 08.05.01, Rettstadt

*** Current Data Parameters ***

NAME : 10
EXPNO : 101
PROCNO : 1

*** Current Data Parameters ***

NAME : 10
EXPNO : 101
PROCNO : 1

Roper ROSB6 29mg CDCl3/TMS 1H-NMR 30.05 01, Rettsstadt

*** Current Data Parameters ***
 NAME : 10
 EXPNO : 101
 PROCNO : 1

Roper RO 663 55mg CD3OD/TMS 1H-NMR 3.05.02 Kaerije

Roper RO349 45mg CD3OD/TMS 1H-NMR 04.07.00, Retistadt

*** Current Data Parameters ***

NAME : 10

EXPNO : 101

PROCNO : 1

Roper RO664 35mg CD3OD/TMS 1H-NMR 03.05.02, Retistadt

*** Current Data Parameters ***

NAME : 10
EXPNO : 101
PROCNO : 1