Supporting information.

Efficient Synthesis of the 3-Benzazepine Framework via Intramolecular Heck Reductive Cyclization

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General Experimental Methods.

^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 or Bruker 400 instruments. The ^1H and ^{13}C chemical shifts are reported in parts per million relative to tetramethylsilane using the residual solvent signal as the internal reference. Mass spectra were recorded on Kratos MS50TC and Kratos Mach III system. The ion source temperature was 150-250°C, as required. High-resolution EI-mass spectra were recorded with a resolution of 10 000. The low-resolution spectra were obtained with HP5989A MS instrument. For thin-layer chromatography, analytical TLC plates (Alugram SIL G/UV254 and 70-230 mesh silica gel (E. M. Merck) were used.

Microwave Irradiation Experiments.

A multimode Milestone MicroSYNTH microwave reactor (Laboratory Microwave Systems) was used in the standard configuration as delivered, including proprietary software. All experiments were carried out in sealed microwave process vials (15 mL). After completion of the reaction, the vial was cooled down to 25 °C via air jet cooling before opening.

Synthesis of the starting amines:

[2-(2-Bromo-4,5-dimethoxyphenyl)ethyl]-(4-methoxybenzyl)amine (2a), [2-(2-Bromo-4,5-dimethoxyphenyl)ethyl]-(4-methoxybenzyl)methylamine (2b), 2-(2-Bromo-4,5-dimethoxyphenyl)ethylamine (2c) were synthesized according to the references 1, 2 and 3 respectively.

[2-(2-Bromophenyl)ethyl]methylamine (2d) was synthesized following the known procedure². 2-(2-Bromophenyl)ethylamine 2 g (10 mmol) and benzaldehyde 1.061 g (10 mmol) in toluene (50 mL) were refluxed with azeotropic water removal during 4h. After cooling to 90°C Me_2SO_4 0.95 mL (10 mmol) was added and heating was continued for 12h. Upon cooling to ambient temperature aqueous 10% HCl (30 mL) was added and the mixture was stirred for 1h. Further aqueous layer was washed with DCM, basified with NaOH pellets to pH~10 and extracted again with DCM. Drying with Na_2SO_4 and concentration under reduced pressure gave the pure methylated amine 1.930g (84%) as a colourless oil. (DCM / MeOH / $\text{NH}_3(\text{aq})$ 150 / 15 / 0.5) (R_f 0.26); ^1H NMR (CDCl_3 , 300 MHz) : δ 7.53 (d, 1H, J = 7.9 Hz), 7.23 (m, 2H), 7.02-7.10 (m, 1H), 2.80-3.00 (m, 4H), 2.47 (s, 3H), 1.26 (bs, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) : δ 139.61, 133.30, 131.17, 128.28, 127.85, 124.98, 51.97, 36.86, 36.76; **LRMS (CI)** (m/z , relative intensity) : 214 / 216 ($[\text{M}+\text{H}]^+$, 100), 183 / 185 (44), 134 (19).

[2-(2-Bromophenyl)ethyl]isopropylamine (2e). 2-(2-Bromophenyl)ethylamine 1g (5 mmol) and anhydrous acetone 348 mg (1.2 equiv) in DCE (5 mL) were stirred at ambient temperature for 2h. Then freshly prepared $\text{NaBH}(\text{OAc})_3$ 318 mg (1.5 equiv) was added and stirring was continued. Another portion of $\text{NaBH}(\text{OAc})_3$ 318 mg (1.5 equiv) was added after 8h and the reaction was left with stirring overnight. Afterwards the reaction mixture was diluted with DCM and washed with 1M NaOH. The organic layer was dried (Na_2SO_4), concentrated and applied to a silica gel column. Elution with DCM / MeOH / $\text{NH}_3(\text{aq})$ (150 / 15 / 1) (R_f 0.40) afforded pure isopropylated amine 847 mg (70%) as colourless oil. ^1H NMR (CDCl_3 , 300 MHz) : δ 7.54 (d, 1H, J = 7.7 Hz), 7.26 (m, 1H), 7.00-7.14 (m, 1H), 2.80-3.00 (m, 5H), 1.40-2.00 (bs, 1H), 1.09 (d, 6H, J = 5.5 Hz); ^{13}C NMR (CDCl_3 , 75 MHz): 139.82, 133.30, 131.11, 128.30, 127.87, 124.98, 48.88, 47.43, 37.34, 23.29; **LRMS (CI)** (m/z , relative intensity) : 242 / 246 ($[\text{M}+\text{H}]^+$, 100), 226 / 228 (26), 183 / 185 (12), 162 (19), 72 (60), 59 (38).

1) **3-(2-Bromo-4,5-dimethoxyphenyl)-N-(4-methoxybenzyl)acrylamide.** 2-Bromo-4,5-dimethoxycinnamic acid 2.01g (7 mmol) and p-methoxybenzylamine 947mg (6.9 mmol), DMAP 86 mg (10 mol%) were all mixed up in dry DCM (50 mL). DCC 1.465 mg (7.1 mmol) was added and the reaction mixture was stirred at ambient temperature overnight. Afterwards the precipitate of dicyclohexylurea was filtered off and washed well with EtOAc. Silica was added to the filtrate and the solvent was removed under reduced pressure. The resulting powder was applied to a silica gel column. Elution with DCM / Et₂O (4 / 1) (*R_f* 0.43) afforded the required amide 2.749 g (98%) slightly contaminated with dicyclohexylurea. ¹H NMR (DMSO-*d*₆, 300 MHz) : δ 8.50 (bs, 1H), 7.64 (d, 1H, *J* = 14.9 Hz), 7.10-7.25 (m, 4H), 6.89 (d, 2H, *J* = 7.9 Hz), 6.63 (d, 1H, *J* = 14.9 Hz), 4.31 (s, 2H), 3.81 (s, 6H), 3.73 (s, 3H); ¹³C NMR (DMSO-*d*₆, 75 MHz) : δ 164.60, 158.27, 150.62, 148.52, 136.60, 131.25, 128.79, 126.22, 123.12, 115.59, 113.72, 109.41, 56.01, 55.58, 55.06, 41.87.

2) **3-(2-Bromo-4,5-dimethoxyphenyl)-N-(4-methoxybenzyl)propionamide.** 3-(2-Bromo-4,5-dimethoxyphenyl)-N-(4-methoxybenzyl)acrylamide 2.719 g (6.69 mmol) and TsNHNH₂ 12.5 g (10 equiv) were dissolved in DME (120 mL) and the solution was brought to reflux. Solution of AcONa 9.6 g (17.5 equiv) in water (70 mL) was added dropwise to the boiling reaction mixture during 2h. After cooling to ambient temperature the solvent was removed under reduced pressure. The residue was dissolved in DCM and washed successively with 1M NaOH, 1M HCl and water. The organic layer was dried (MgSO₄), concentrated. The product was isolated by column chromatography on silica gel eluting with DCM / Et₂O (4 / 1) (*R_f* 0.43). Yield: 2.420 g (89%). ¹H NMR (DMSO-*d*₆, 300 MHz) : δ 8.28 (bs, 1H), 7.04-7.12 (m, 3H), 6.90 (s, 1H), 8.83 (d, 2H, *J* = 8.4 Hz), 4.18 (d, 2H, *J* = 5.3 Hz), 3.74 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 2.87 (t, 2H, *J* = 7.7 Hz), 2.41 (t, 2H, *J* = 7.7 Hz); ¹³C NMR (DMSO-*d*₆, 75 MHz) : δ 170.79, 158.15, 148.19, 147.89, 132.08, 131.47, 128.48, 115.50, 113.59, 113.13, 55.86, 55.56, 55.03, 35.52, 31.03.

3) **[3-(2-Bromo-4,5-dimethoxyphenyl)propyl]-(4-methoxybenzyl)amine.** 3-(2-Bromo-4,5-dimethoxyphenyl)-N-(4-methoxybenzyl)propionamide 2.420 g (5.93 mmol) was dissolved in dry THF (20 mL) under argon atmosphere and the solution was cooled to 0°C. 1M solution of BH₃·THF complex 11.86 mL (2 equiv) was added via cannula and after 30min of stirring at ambient temperature the reaction mixture was refluxed overnight. Afterwards 3M HCl (8 mL) was added dropwise and the solution was boiled for 30min. THF was evaporated under reduced pressure, the resulting mixture was basified with NaOH pellets till pH~10, extracted with DCM. The organic layer was dried (Na₂SO₄) and concentrated. The required amine was isolated by column chromatography on silica gel eluting with DCM / MeOH / NH₃(aq) (150 / 15 / 0.5) (*R_f* 0.38). Yield: 2.016 g (86%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.23 (d, 2H, *J* = 8.7 Hz), 6.98 (s, 1H), 6.85 (d, 2H, *J* = 8.7 Hz), 6.71 (s, 1H), 3.63 (s, 3H), 3.62 (s, 3H), 3.79 (s, 3H), 3.73 (s, 2H), 2.66-2.73 (m, 4H), 1.80 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) : δ 159.01, 148.72, 148.16, 133.88, 133.03, 129.70, 129.43, 128.64, 115.91, 114.35, 114.17, 113.32, 56.54, 56.41, 55.65, 53.85, 49.13, 33.95, 30.98; LRMS (CI) (*m/z*, relative intensity) : 394 / 396 ([M+H]⁺, 24), 314 (34), 286 / 288 (12), 225 (9), 149 (10), 121 (100).

Synthesis of the propynoic acid amides (3a-o,10a,b). (¹H and ¹³C NMR spectra are described for both rotamers on the amide bond (E / Z ratio in most cases 1 / 1, unless specified):

3-Phenylpropynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]-(4-methoxybenzyl)amide (3a). Amine **2a** 3.8 g (10 mmol) dry Et₃N 1.67 mL (1.2 equiv), DMAP 366 mg (10 mol%) were mixed up in dry DCM (50 mL) under argon atmosphere and the mixture was cooled to 0°C. Phenylpropionic acid chloride 1.810 g (1.1 equiv) dissolved in DCM (15 mL) was added dropwise during 1h. After completion of the addition the mixture was stirred at ambient temperature for 40min more. Then DCM was added and the organic layer was washed successively with 1M HCl, NaHCO₃ saturated solution and water. After drying (MgSO₄) and concentration the residue was applied to a silica gel column. Elution with DCM / MeOH (80 / 1) (*R_f* 0.32) afforded the product 4.762 g (94%) as a transparent viscous oil, which further solidified on standing. ¹H NMR (CDCl₃, 400 MHz) : δ 7.49-7.55 (m, 4H), 7.31-7.43 (m, 6H), 7.26 (d, 2H, *J* = 8.3 Hz), 7.23 (d, 2H, *J* = 8.3 Hz), 6.98 (s, 1H), 6.91 (s, 1H), 6.87 (d, 4H, *J* = 8.3 Hz), 6.76 (s, 1H), 6.54 (s, 1H), 4.62 (s, 2H), 4.60 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.79 (s, 6H), 3.77 (s, 3H), 3.70-3.75 (m, 2H), 3.64 (s, 3H), 3.50-3.56 (m, 2H), 2.92-3.00 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) : δ 159.77, 159.62, 155.1, 154.96, 148.94, 148.87, 148.71, 132.84, 132.69, 130.53, 130.43, 130.35, 129.86, 129.55, 129.22, 128.93, 128.73, 121.00, 120.78, 116.01, 115.78, 114.57, 114.44, 113.99, 113.78, 90.53, 90.16, 82.37, 82.12, 56.53, 56.27, 55.67, 53.34, 48.53, 47.88, 44.72, 35.61, 33.60.

General procedure⁴ for the synthesis of propynoic acid amides:

3-substituted 2-propynoic acid (1.1 equiv) and N-hydroxysuccinimide 127 mg (1.1 equiv) were dissolved in dry dioxane (10 mL). DCC 217 mg (1.05 equiv) was added and the reaction was stirred at ambient temperature for 4-5h. Amine (1 mmol, 1 equiv) dissolved in dioxane (5 mL) was added in one portion and the reaction was left with stirring overnight. The precipitate was filtered off and washed well with Et₂O. The organic layer was washed with brine, dried (MgSO₄) and concentrated. Pure amides were isolated by column chromatography on silica gel.

2-Butynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]-(4-methoxybenzyl)amide (3b). Synthesized from 2-butynoic acid 92 mg and amine **2a** 380 mg. Yield: 361 mg (81%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.12-7.24 (m, 4H), 6.97 (d, 2H, J = 5.7 Hz), 6.81-6.90 (m, 4H), 6.73 (s, 1H), 6.54 (s, 1H), 4.52 (s, 4H), 3.77-3.88 (m, 18H), 3.65 (t, 2H, J = 7.1 Hz), 3.44 (t, 2H, J = 7.1 Hz), 2.90 (t, 4H, J = 7.1 Hz), 2.00 (s, 3H), 1.98 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) : δ 159.68, 159.52, 155.26, 155.11, 148.89, 148.62, 130.47, 130.24, 130.00, 129.46, 129.28, 128.85, 115.93, 115.71, 114.78, 114.69, 114.47, 114.38, 113.95, 89.37, 89.08, 74.05, 73.78, 56.59, 56.51, 55.68, 53.12, 48.16, 47.67, 44.37, 35.45, 33.50, 4.60, 4.50.

3-Trimethylsilylpropynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]-(4-methoxybenzyl)amide (3c). Synthesized from trimethylsilylpropynoic acid 156 mg and amine **2a** 380 mg. Yield: 504 mg (100%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.15-7.25 (m, 4H), 6.98 (d, 2H, J = 7.7 Hz), 6.81-6.90 (m, 4H), 6.72 (s, 1H), 6.56 (s, 1H), 4.52 (s, 4H), 3.75-3.88 (m, 18H), 3.67 (t, 2H, J = 7.3 Hz), 3.45 (t, 2H, J = 7.3 Hz), 2.83-2.97 (m, 4H), 0.24 (s, 9H), 0.22 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) : δ 159.77, 159.56, 154.51, 154.28, 148.98, 148.89, 148.68, 130.40, 130.29, 129.82, 129.66, 129.09, 128.71, 116.05, 115.75, 114.71, 114.47, 114.38, 113.98, 113.90, 97.75, 96.90, 56.59, 56.53, 55.67, 53.31, 48.18, 47.49, 44.48, 35.27, 33.45, 31.98, -0.14, -0.28.

3-(4-Methoxyphenyl)propynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]-(4-methoxybenzyl)amide (3d). Synthesized from (4-methoxyphenyl)propynoic acid 194 mg and amine **2a** 380 mg. Yield: 538 mg (100%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.47 (m, 4H), 7.25 (m, 2H), 6.81-7.00 (m, 10H), 6.76 (s, 1H), 6.56 (s, 1H), 4.60 (s, 4H), 3.63-3.93 (m, 26H), 3.52 (t, 2H, J = 8.0 Hz), 2.91-3.02 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) : δ 161.74, 161.38, 159.73, 159.56, 155.44, 155.29, 148.94, 148.87, 148.68, 134.65, 134.52, 130.52, 130.31, 129.98, 129.55, 129.34, 129.91, 116.02, 115.76, 114.62, 114.55, 114.41, 114.01, 113.82, 112.89, 112.67, 91.14, 90.77, 81.66, 81.37, 56.53, 56.35, 55.78, 55.68, 53.34, 48.43, 47.81, 44.65, 36.46, 35.64, 33.63.

3-(4-Methoxyphenyl)propynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]-methanamide (3e). Synthesized from (4-methoxyphenyl)propynoic acid 194 mg and amine **2b** 274 mg. Yield: 432 mg (100%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.44-7.50 (m, 4H), 7.00 (s, 1H), 6.94 (s, 1H), 6.84-6.88 (m, 4H), 6.80 (s, 1H), 6.64 (s, 1H), 3.84-3.87 (m, 6H), 3.82 (s, 6H), 3.78 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H), 3.65 (t, 2H, J = 7.6 Hz), 3.15 (s, 3H), 2.94-3.04 (m, 7H); ¹³C NMR (CDCl₃, 75 MHz) : δ 161.39, 161.32, 155.24, 148.98, 148.92, 148.70, 134.52, 130.31, 129.74, 116.09, 115.82, 114.60, 114.51, 114.38, 113.95, 113.86, 112.89, 112.75, 90.35, 81.45, 81.15, 56.53, 56.41, 55.77, 51.58, 47.40, 37.67, 35.58, 35.40, 33.50, 33.20.

3-Phenylpropynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]methanamide (3f). Synthesized from phenylpropynoic acid 161 mg and amine **2b** 274 mg. Yield: 402 mg (100%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.48-7.57 (m, 4H), 7.31-7.44 (m, 6H), 7.00 (s, 1H), 6.92 (s, 1H), 6.80 (s, 1H), 6.62 (s, 1H), 3.82-3.91 (m, 8H), 3.77 (s, 3H), 3.6-3.74 (m, 5H), 3.16 (s, 3H), 2.94-3.08 (m, 7H); ¹³C NMR (CDCl₃, 75 MHz) : δ 154.93, 148.96, 148.74, 132.87, 132.73, 130.44, 130.34, 130.22, 129.64, 128.92, 128.85, 121.02, 120.90, 116.09, 15.84, 114.68, 114.41, 113.93, 113.80, 90.72, 89.79, 82.15, 81.90, 56.52, 56.35, 53.85, 51.63, 47.76, 37.67, 35.40, 33.48, 33.26.

2-Butynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]methanamide (3g). Synthesized from 2-butynoic acid 92 mg and amine **2b** 274 mg. Yield: 332 mg (98%). ¹H NMR (CDCl₃, 300 MHz) : δ 6.98-7.02 (m, 2H), 6.76 (s, 1H), 6.64 (s, 1H), 3.85 (s, 12H), 3.77 (t, 2H, J = 7.1 Hz), 3.59 (t, 2H, J = 7.3 Hz), 3.06 (s, 3H), 2.88-2.99 (m, 7H), 2.00 (s, 3H), 1.96 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) : δ 155.04, 148.96, 148.90, 148.65, 130.26, 130.16, 129.74, 116.02, 115.78, 114.75, 114.36, 113.95, 113.83, 89.46, 88.61, 73.96, 73.56, 56.59, 56.53, 51.30, 49.29, 47.18, 37.53, 35.27, 34.33, 33.39, 33.04, 26.04, 25.34.

3-Trimethylsilylpropynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]methyl amide (3h). Synthesized from trimethylsilylpropynoic acid 156 mg and amine **2b** 274 mg. Yield: 386 mg (97%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.01 (s, 1H), 6.99 (s, 1H), 6.75 (s, 1H), 6.62 (s, 1H), 3.75-3.90 (m, 14H), 3.59 (t, 2H, J = 7.8 Hz), 3.08 (s, 3H), 2.89-3.00 (m, 7H), 0.2-0.25 (m, 18H); ¹³C NMR (CDCl₃, 75 MHz) : δ 154.30, 149.01, 148.93, 148.72, 130.18, 129.58, 116.09, 115.81, 114.71, 114.35, 113.89, 96.84, 96.23, 56.54, 51.42, 47.27, 37.64, 35.15, 33.32, 33.02, -0.17, -0.24.

3-Phenylpropynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]amide (3i). (one rotamer almost exclusively) Synthesized from phenylpropynoic acid 161 mg and amine **2c** 260 mg. Yield: 369 mg (95%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.51 (d, 2H, J = 7.6 Hz), 7.32-7.43 (m, 3H), 7.02 (s, 1H), 6.76 (s, 1H), 6.01 (bs, 1H), 3.86 (s, 6H), 3.55-3.64 (m, 2H), 2.96 (t, 2H, J = 7.1 Hz); ¹³C NMR (CDCl₃, 75 MHz) : δ 153.95, 148.90, 148.77, 132.88, 130.50, 130.10, 128.94, 120.51, 115.99, 114.56, 113.63, 85.17, 83.37, 56.56, 56.51, 40.21, 35.54.

2-Butynoic acid [2-(2-bromo-4,5-dimethoxyphenyl)ethyl]amide (3j). (one rotamer almost exclusively) Synthesized from 2-butynoic acid 92 mg and amine **2c** 260 mg. Yield: 268 mg (82%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.00 (s, 1H), 6.73 (s, 1H), 5.90 (bs, 1H), 3.85 (s, 6H), 3.46-3.58 (m, 2H), 2.91 (t, 2H, J = 6.9 Hz), 1.92 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) : δ 153.98, 148.86, 148.74, 130.14, 115.97, 114.53, 113.83, 83.71, 75.24, 56.56, 56.51, 39.99, 35.48, 4.02.

2-Octynoic acid [2-(2-bromophenyl)ethyl]methylamide (3k). Synthesized from 2-octynoic acid 154 mg and amine **2d** 214 mg. Yield: 327 mg (97%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.50-7.59 (m, 2H), 7.06-7.30 (m, 6H), 3.80 (t, 2H, J = 7.5 Hz), 3.52-3.67 (m, 2H), 2.94-3.12 (m, 10H), 2.24-2.42 (m, 4H), 1.48-1.65 (m, 4H), 1.24-1.47 (m, 8H), 0.83-0.97 (m, 6H); ¹³C NMR (CDCl₃, 75 MHz) : δ 155.15, 138.52, 137.90, 133.33, 133.21, 131.62, 131.47, 128.94, 128.70, 128.15, 128.09, 124.92, 124.80, 93.68, 92.99, 74.66, 74.11, 51.20, 47.19, 37.44, 35.61, 33.95, 32.99, 31.52, 31.41, 27.85, 26.01, 22.53, 19.37, 19.28, 14.29.

3-(4-Methoxyphenyl)propynoic acid [2-(2-bromo-phenyl)ethyl]methylamide (3l). (mixture of rotamers 2 / 3) Synthesized from 3-(4-methoxyphenyl)propynoic acid 194 mg and amine **2d** 214 mg. Yield: 361 mg (96%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.43-7.59 (m, 6H), 7.05-7.16 (m, 4H), 7.04-7.14 (m, 2H), 6.87 (d, 4H, J = 8.5 Hz), 3.79-3.92 (m, 8H), 3.60-3.71 (m, 2H), 3.17 (s, 2H), 3.00-3.13 (m, 8H); ¹³C NMR (CDCl₃, 75 MHz) : δ 161.38, 161.33, 155.26, 137.87, 134.67, 134.59, 133.39, 133.24, 131.65, 131.53, 129.00, 128.74, 128.21, 128.15, 124.92, 124.83, 114.59, 114.54, 112.68, 91.23, 90.50, 81.48, 81.09, 55.77, 51.36, 47.33, 37.53, 36.03, 35.71, 34.03, 33.14.

2-Butynoic acid [2-(2-bromophenyl)ethyl]methylamide (3m). (mixture of rotamers 1 / 2) Synthesized from 2-butynoic acid 92 mg and amine **2d** 214 mg. Yield: 236 mg (84%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.49-7.57 (m, 1H), 7.20-7.29 (m, 1H), 7.05-7.18 (m, 2H), 3.74-3.86 (m, 1H), 3.51-3.66 (m, 1H), 2.91-3.11 (m, 5H), 2.00 (s, 1H), 1.94 (s, 2H); ¹³C NMR (CDCl₃, 75 MHz) : δ 155.11, 155.05, 138.46, 137.81, 133.36, 133.26, 133.22, 131.60, 131.38, 128.97, 128.73, 128.18, 128.12, 124.98, 124.80, 89.50, 88.77, 73.93, 73.40, 51.08, 37.47, 35.57, 33.93, 32.95, 4.53, 4.52.

3-(4-Methoxyphenyl)propynoic acid [2-(2-bromophenyl)ethyl]isopropylamide (3n). Synthesized from 3-(4-methoxyphenyl)propynoic acid 194 mg and amine **2e** 242 mg. Yield: 360 mg (90%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.46-7.59 (m, 6H), 7.19-7.43 (m, 4H), 7.04-7.17 (m, 2H), 6.91 (d, 4H, J = 8.7 Hz), 4.76 (m, 2H), 3.72-3.96 (m, 8H), 3.48 (t, 2H, J = 8.0 Hz), 3.04-3.24 (m, 4H), 1.17-1.41 (m, 12H); ¹³C NMR (CDCl₃, 75 MHz) : δ 161.32, 155.38, 155.14, 139.22, 138.60, 134.54, 133.36, 133.05, 131.94, 131.45, 128.88, 128.60, 128.21, 128.13, 124.80, 124.74, 114.60, 112.93, 90.65, 90.13, 82.40, 81.59, 55.77, 51.05, 46.11, 45.13, 41.34, 38.59, 35.39, 21.59, 20.87.

3-(3,4,5-Trimethoxyphenyl)propynoic acid [2-(2-bromophenyl)ethyl]isopropylamide (3o). Synthesized from 3-(3,4,5-trimethoxyphenyl)propynoic acid 260 mg and amine **2e** 242 mg. Yield: 331 mg (72%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.56 (d, 2H, J = 8.3 Hz), 7.18-7.43 (m, 4H), 7.06-7.17 (m, 2H), 6.81 (s, 4H), 4.75 (m, 2H), 3.72-3.97 (m, 20H), 3.44-3.55 (m, 2H), 3.07-3.25 (m, 4H), 1.22-1.36 (m, 12H); ¹³C NMR (CDCl₃, 75 MHz) : δ 155.08, 154.80, 153.50, 140.55, 139.10, 138.54, 133.39, 133.03, 131.90, 131.29, 128.92, 128.61, 128.11, 124.77, 115.87, 115.82, 110.08, 110.03, 90.47, 89.80, 82.27, 81.48, 61.34, 56.57, 51.113, 46.20, 45.09, 41.36, 38.55, 35.30, 21.61, 20.85.

2-Butynoic acid [3-(2-bromo-4,5-dimethoxyphenyl)propyl]-(4-methoxybenzyl)amide (10a). Synthesized from 2-butynoic acid 92 mg and [3-(2-Bromo-4,5-dimethoxyphenyl)propyl]-(4-methoxybenzyl)amine 408 mg. Yield: 440 mg (96%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.17 (d, 4H, J = 8.7 Hz), 6.99 (d, 2H, J = 7.7 Hz), 6.81-6.92 (m, 4H), 6.72 (s, 1H), 6.61 (s, 1H), 4.72 (s, 2H), 4.57 (s, 2H), 3.78-3.9 (m, 18H), 3.51 (t, 2H, J = 7.1 Hz), 3.52 (t, 2H, J = 7.1 Hz), 2.55-2.72 (m, 4H), 2.02 (s, 3H), 1.97 (s, 3H), 1.72-1.92 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) : δ 159.68, 159.44, 155.32, 155.14, 148.78, 148.41, 148.23, 133.09, 132.81, 130.01, 129.34, 128.85, 116.03, 115.91, 114.53, 114.38, 114.23, 113.31, 89.56, 89.49, 74.08, 73.87, 56.56, 56.49, 55.67, 52.37, 47.82, 47.10, 43.49, 33.42, 29.15, 27.43, 4.51, 4.37.

3-Phenylpropynoic acid [3-(2-bromo-4,5-dimethoxyphenyl)propyl]-(4-methoxy-benzyl)amide (10b). Synthesized from phenylpropynoic acid 161 mg and [3-(2-Bromo-4,5-dimethoxyphenyl)propyl]-(4-methoxybenzyl)amine 408 mg. Yield: 514 mg (98%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.47-7.57 (m, 4H), 7.31-7.46 (m, 6H), 7.18-7.30 (m, 4H), 6.83-7.02 (m, 6H), 6.75 (s, 1H), 6.59 (s, 1H), 4.82 (s, 2H), 4.65 (s, 2H), 3.73-3.93 (m, 18H), 3.64 (t, 2H, J = 7.2 Hz), 3.43 (t, 2H, J = 7.2 Hz), 2.60-2.74 (m, 4H), 1.75-1.98 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) : δ 159.72, 159.49, 155.14, 154.96, 148.75, 148.37, 148.22, 132.96, 132.78, 132.72, 132.62, 130.48, 130.09, 129.43, 129.22, 128.92, 128.71, 120.83,

115.87, 114.59, 114.41, 114.32, 114.26, 113.26, 113.19, 90.63, 82.40, 82.15, 56.45, 56.38, 55.64, 52.61, 48.22, 47.40, 43.63, 33.54, 33.44, 29.36, 27.53.

General procedure for the Heck reductive cyclization:

$\text{Pd(PPh}_3)_4$ 14 mg (3 mol%) and HCOONa 41 mg (1.5 equiv) were loaded into the microwave instrument vial. The vial was evacuated and flushed with argon. Propynoic acid amide (**3** or **10**) (0.4 mmol) dissolved in DMF (4.5 mL) was added, followed by distilled water (1.5 mL). The vial was sealed and irradiated with stirring at a ceiling temperature of 110 °C at 150 W maximum power level for 15min. Upon completion of the reaction time the vial was cooled with a stream of air. After dilution with DCM the organic phase was washed several times with brine, dried (MgSO_4) and concentrated under reduced pressure. Products were isolated by column chromatography on silica gel.

In $^1\text{H NMR}$ spectra of benzazepinones **6**, recorded at 25°C, signals of protons at C^3 and C^{16} (on the example of **6a**) are often broadened, even merging with the baseline due to the 7-membered ring flipping⁵. Assignment for the **6a** was performed on the bases of COSY, HMBC and HMQC spectra. Configuration of the double bond was established with NOE effect (interaction between protons at C^{11} and C^7).

1-Benzylidene-7,8-dimethoxy-3-(4-methoxybenzyl)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6a). Synthesized from amide **3a** 203 mg. Eluent DCM / Et_2O (4 / 1) (R_f 0.46). Yield: 139 mg (81%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz) : δ 7.53 (d, 2H- C^{13} , $J = 7.2$ Hz), 7.31 (m, 2H- C^{14}), 7.20-7.27 (m, H- C^{15} , 2H- C^{18}), 6.94 (s, H- C^7), 6.85 (d, 2H- C^{19} , $J = 8.6$ Hz), 6.63 (s, H- C^{11}), 6.53 (s, H- C^{10}), 3.91 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 2.90 (bs, 2H- C^4); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) : δ 170.67 (C^2), 159.21 (C^{20}), 149.12 (C^9), 147.81 (C^8), 138.70 (C^1), 135.68 (C^{12}), 131.28 (C^{11}), 129.75 (C^{18}), 129.42 (C^{17}), 128.62 (C^{13}), 128.46 (C^{14}), 128.21 (C^5), 127.97 (C^{15}), 127.64 (C^6), 114.09 (C^{19}), 112.85 (C^{10}), 112.50 (C^7), 56.10 (OCH_3), 56.00 (OCH_3), 55.29 (OCH_3), 47.55 (C^{16}), 44.60 (C^3), 31.80 (C^4); **HRMS** calcd. For $\text{C}_{27}\text{H}_{27}\text{NO}_4$: m/z 429.1940, found m/z 429.1937

1-Ethylidene-7,8-dimethoxy-3-(4-methoxybenzyl)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6b). Synthesized from amide **3b** 179 mg. Eluent DCM / Et_2O (4 / 1) (R_f 0.34). Yield: 96 mg (65%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz) : δ 7.23 (d, 2H, $J = 8.6$ Hz), 6.86 (d, 2H, $J = 8.6$ Hz), 6.77 (s, 1H), 6.49 (s, 1H), 5.93 (q, 1H, $J = 7.0$ Hz), 4.63 (bs, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 3.79 (s, 3H), 3.58 (bs, 2H), 2.84 (t, 2H, $J = 5.4$ Hz), 1.97 (d, 3H, $J = 7.0$ Hz); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) : δ 171.10, 159.43, 148.89, 147.80, 139.91, 130.01, 129.84, 127.91, 127.42, 144.44, 112.98, 112.78, 56.30, 55.68, 48.10, 44.97, 32.53, 16.02; **HRMS** calcd. For $\text{C}_{22}\text{H}_{25}\text{NO}_4$: m/z 367.1784, found m/z 367.1793

7,8-Dimethoxy-3-(4-methoxy-benzyl)-1-trimethylsilylmethylene-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6c). Synthesized from amide **3c** 202 mg and HCOONa 82 mg (3 equiv). Solvent – mixture of DME (4.8 mL) and H_2O (1.2 mL). Reaction temperature 120°C. Eluent DCM / Et_2O (20 / 1) (R_f 0.36). Yield: 61 mg (36%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz) : δ 7.23 (d, 2H, $J = 8.8$ Hz), 6.83 (d, 2H, $J = 8.8$ Hz), 6.79 (s, 1H), 6.42 (s, 1H), 6.02 (s, 1H), 4.59 (s, 2H), 3.88 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.61 (m, 2H), 2.75 (m, 2H), 0.18 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) : δ 171.65, 159.13, 154.33, 149.00, 147.62, 135.95, 130.00, 129.88, 129.48, 126.90, 114.01, 112.83, 112.23, 56.05, 55.89, 55.25, 48.26, 44.68, 32.33, -0.59; **HRMS** calcd. For $\text{C}_{24}\text{H}_{31}\text{NO}_4\text{Si}$: m/z 425.2022, found m/z 425.2019

7,8-Dimethoxy-3-(4-methoxybenzyl)-1-(4-methoxybenzylidene)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6d). Synthesized from amide **3d** 215 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.47). Yield: 142 mg (77%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.49 (d, 2H, *J* = 8.7 Hz), 7.25 (d, 2H, *J* = 8.5 Hz), 6.93 (s, 1H), 6.84-6.87 (m, 4H), 6.57 (s, 1H), 6.52 (s, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 2.89 (bs, 2H); ¹³C NMR (CDCl₃, 75 MHz) : δ 171.44, 159.83, 159.53, 149.20, 148.02, 136.63, 131.38, 130.49, 130.13, 129.80, 128.76, 127.79, 114.44, 114.32, 112.98, 112.70, 56.44, 56.35, 55.69, 47.91, 44.99, 32.16; **HRMS** calcd. For C₂₈H₂₉NO₅: *m/z* 459.2046, found *m/z* 459.2040

7,8-Dimethoxy-1-(4-methoxybenzylidene)-3-methyl-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6e). Synthesized from amide **3e** 173 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.32). Yield: 100 mg (71%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.48 (d, 2H, *J* = 8.6 Hz), 6.94 (s, 1H), 6.86 (d, 2H, *J* = 8.6 Hz), 6.58 (s, 1H), 6.55 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.14 (s, 3H), 3.04 (bs, 2H); ¹³C NMR (CDCl₃, 75 MHz) : δ 171.65, 159.82, 149.18, 148.04, 136.41, 131.10, 130.43, 128.81, 128.64, 127.73, 114.60, 114.40, 113.01, 112.74, 56.44, 56.36, 55.66, 48.06, 32.96, 31.53; **HRMS** calcd. For C₂₁H₂₃NO₄: *m/z* 353.1627, found *m/z* 353.1631

1-Benzylidene-7,8-dimethoxy-3-methyl-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6f). Synthesized from amide **3f** 161 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.43). Yield: 88 mg (68%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.52 (d, 2H, *J* = 7.4 Hz), 7.22-7.35 (m, 3H), 6.92 (s, 1H), 6.61 (s, 1H), 6.59 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.13 (s, 3H), 3.04 (bs, 2H); ¹³C NMR (CDCl₃, 75 MHz) : δ 171.35, 149.38, 148.07, 138.75, 135.89, 131.39, 128.96, 128.52, 128.40, 127.94, 113.07, 112.74, 56.44, 56.38, 48.02, 32.93, 31.50; **HRMS** calcd. For C₂₀H₂₁NO₃: *m/z* 323.1521, found *m/z* 323.1515

1-Ethylidene-7,8-dimethoxy-3-methyl-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6g). Synthesized from amide **3g** 136 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.33). Yield: 64 mg (61%). ¹H NMR (CDCl₃, 300 MHz) : δ 6.75 (s, 1H), 6.65 (s, 1H), 5.91 (q, 1H, *J* = 6.7 Hz), 3.86 (s, 3H), 3.84 (s, 3H), 3.68 (bs, 2H), 3.09 (s, 3H), 3.00 (m, 2H), 1.92 (d, 3H, *J* = 6.7 Hz); ¹³C NMR (CDCl₃, 75 MHz) : δ 171.20, 148.89, 147.80, 139.84, 129.63, 127.97, 127.33, 112.98, 112.83, 56.29, 48.03, 33.11, 31.87, 15.90; **HRMS** calcd. For C₁₅H₁₉NO₃: *m/z* 261.1365, found *m/z* 261.1371

7,8-Dimethoxy-3-methyl-1-trimethylsilylmethylene-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6h). Synthesized from amide **3h** 159 mg and HCOONa 82 mg (3 equiv). Solvent – mixture of DME (4.8 mL) and H₂O (1.2 mL). Reaction temperature 120°C. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.47). Yield: 41 mg (32%). ¹H NMR (CDCl₃, 400 MHz) : δ 6.77 (s, 1H), 6.50 (s, 1H), 5.99 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.65 (m, 2H), 3.03 (s, 3H), 2.99 (m, 2H), 0.15 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) : δ 172.2, 154.75, 149.26, 147.95, 135.83, 130.10, 127.12, 112.82, 112.56, 56.38, 56.30, 48.06, 33.36, 32.23, -0.39; **LRMS** (*m/z*, relative intensity) : 319 (M⁺, 5), 304 (100), 288 (20), 164 (6); **HRMS** calcd. For C₁₇H₂₅NO₃Si: *m/z* 319.1604, found *m/z* 319.1604

1-Benzylidene-7,8-dimethoxy-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6i). Synthesized from amide **3i** 155 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.24). Yield: 48 mg (39%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.58 (d, 2H, *J* = 7.5 Hz), 7.26-7.37 (m, 3H), 6.92 (s, 1H), 6.69 (s, 1H), 6.59 (s, 1H), 6.47 (m, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 3.67 (m, 2H), 3.05 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) : δ 174.30, 149.42, 148.13, 137.78, 135.80, 132.41, 128.94, 128.49, 128.43, 128.00, 113.24, 112.69, 56.46, 56.38, 39.81, 34.69; **HRMS** calcd. For C₁₉H₁₉NO₃: *m/z* 309.1365, found *m/z* 309.1362

1-Ethylidene-7,8-dimethoxy-1,3,4,5-tetrahydro-benzo[d]azepin-2-one (6j). Synthesized from amide **3j** 130 mg. Eluent DCM / Et₂O (20 / 1) (*R_f* 0.29). Yield: 52 mg (53%). ¹H NMR (CDCl₃, 300 MHz) : δ 6.95 (bs, 1H), 6.73 (s, 1H), 6.54 (s, 1H), 5.97 (q, 1H, *J* = 6.9 Hz), 3.86 (s, 3H), 3.84 (s, 3H), 3.54 (m, 2H), 2.99 (m, 2H), 1.96 (d, 3H, *J* = 6.9 Hz); ¹³C NMR (CDCl₃, 75 MHz) : δ 174.03, 148.96, 147.90, 138.78, 132.42, 131.15, 128.98, 128.82, 127.76, 113.01, 56.32, 39.96, 34.79, 15.93; **HRMS** calcd. For C₁₄H₁₇NO₃: *m/z* 247.1208, found *m/z* 247.1213

1-Hexylidene-3-methyl-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6k). Synthesized from amide **3k** 135 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.50). Yield: 83 mg (81%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.23-7.27 (m, 1H), 7.15-7.20 (m, 2H), 7.05-7.09 (m, 1H), 5.86 (t, 1H, *J* = 7.5 Hz), 3.70 (bs, 2H), 3.05-3.10 (m, 5H), 2.32 (q, 2H, *J* = 7.5 Hz), 1.45-1.53 (m, 2H), 1.29-1.37 (m, 4H), 0.89 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (CDCl₃, 75 MHz) : δ 171.13, 139.24, 136.77, 135.86, 135.24, 130.31, 130.23, 127.94, 127.00, 47.99, 33.23, 32.26, 31.89, 30.20, 29.39, 22.88, 14.44; **HRMS** calcd. For C₁₇H₂₃NO: *m/z* 257.1780, found *m/z* 257.1785

1-(4-Methoxybenzylidene)-3-methyl-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6l). Synthesized from amide **3l** 149 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.41). Yield: 94 mg (80%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.48 (d, 2H, *J* = 8.7 Hz), 7.40-7.43 (m, 1H), 7.21-7.24 (m, 2H), 7.09-7.13 (m, 1H), 6.87 (d, 2H, *J* = 8.7 Hz), 6.59 (s, 1H), 3.81 (s, 3H), 3.10-3.17 (m, 5H); ¹³C NMR (CDCl₃, 75 MHz) : δ 171.56, 159.93, 136.71, 136.56, 135.65, 132.01, 130.65, 130.55, 129.91, 128.67, 128.27, 127.21, 114.44, 55.68, 47.92, 33.02, 31.87; **HRMS** calcd. For C₁₉H₁₉NO₂: *m/z* 293.1416, found *m/z* 293.1419

1-Ethylidene-3-methyl-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6m). Synthesized from amide **3m** 112 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.32). Yield: 49 mg (61%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.06-7.31 (m, 4H), 5.97 (q, 1H, *J* = 6.9 Hz), 3.72 (bs, 2H), 3.02-3.18 (m, 5H), 1.95 (d, 3H, *J* = 6.9 Hz); ¹³C NMR (CDCl₃, 75 MHz) : δ 171.04, 140.15, 135.76, 135.25, 130.82, 130.34, 130.12, 127.97, 126.99, 47.98, 33.23, 32.23, 16.08; **HRMS** calcd. For C₁₃H₁₅NO: *m/z* 201.1154, found *m/z* 201.1145

3-Isopropyl-1-(4-methoxybenzylidene)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6n). Synthesized from amide **3n** 160 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.48). Yield: 112 mg (87%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.39-7.50 (m, 3H), 7.21-7.29 (m, 2H), 7.07-7.14 (s, 1H), 6.87 (d, 2H, *J* = 8.6 Hz), 6.56 (s, 1H), 4.96-5.05 (m, 1H), 3.72-3.92 (m, 5H), 3.13 (bs, 2H), 1.27 (d, 6H, *J* = 6.5 Hz); ¹³C NMR (CDCl₃, 75 MHz) : δ 171.13, 159.86, 137.41, 136.92, 135.52, 132.05, 130.46, 129.76, 128.76, 128.18, 127.11, 114.36, 55.68, 44.03, 39.64, 34.90, 20.99; HRMS calcd. For C₂₁H₂₃NO₂: *m/z* 321.1729, found *m/z* 321.1736

3-Isopropyl-1-(3,4,5-trimethoxybenzylidene)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6o). Synthesized from amide **3o** 184 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.44). Yield: 137 mg (90%). ¹H NMR (CDCl₃, 300 MHz) : δ 7.39-7.45 (m, 1H), 7.20-7.32 (m, 2H), 7.09-7.17 (m, 1H), 6.87 (s, 2H), 6.53 (s, 1H), 4.92-5.03 (m, 1H), 3.87 (s, 9H), 3.14 (bs, 2H), 1.26 (d, 6H, *J* = 6.7 Hz); ¹³C NMR (CDCl₃, 75 MHz) : δ 170.74, 153.43, 138.81, 138.53, 136.83, 135.52, 132.36, 131.51, 130.43, 129.86, 128.38, 127.11, 106.49, 61.25, 56.48, 44.22, 39.74, 34.76, 21.09; HRMS calcd. For C₂₃H₂₇NO₄: *m/z* 381.1940, found *m/z* 381.1942

1-Ethylidene-8,9-dimethoxy-3-(4-methoxybenzyl)-3,4,5,6-tetrahydro-1H-benzo[d]azocin-2-one (11a). Synthesized from amide **10a** 184 mg. Eluent DCM / Et₂O (4 / 1) (*R_f* 0.30). Yield: 84 mg (55%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.26 (d, 2H, *J* = 8.6 Hz), 7.01 (s, 1H), 6.87 (d, 2H, *J* = 8.6 Hz), 6.56 (s, 1H), 5.92 (q, 1H, *J* = 6.9 Hz), 4.59 (s, 2H), 3.67 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.43 (t, 2H, *J* = 6.2 Hz), 2.62-2.66 (m, 2H), 1.80-1.89 (m, 5H); ¹³C NMR (CDCl₃, 75 MHz) : δ 172.71, 159.44, 148.74, 147.99, 140.00, 130.95, 130.25, 129.95, 129.46, 124.71, 114.65, 114.23, 114.46, 56.31, 55.65, 46.73, 45.20, 31.82, 29.21, 15.42; HRMS calcd. For C₂₃H₂₇NO₄: *m/z* 381.1940, found *m/z* 381.1952

1-Benzylidene-8,9-dimethoxy-3-(4-methoxybenzyl)-3,4,5,6-tetrahydro-1H-benzo[d]azocin-2-one (11b). Synthesized from amide **10b** 209 mg. Eluent DCM / Et₂O (20 / 1) (*R_f* 0.24). Yield: 62 mg (35%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.49-7.52 (m, 2H), 7.30-7.34 (m, 3H), 7.13 (s, 1H), 6.99 (d, 2H, *J* = 8.5 Hz), 6.77 (d, 2H, *J* = 8.5 Hz), 6.69 (s, 1H), 6.64 (s, 1H), 4.56 (s, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 3.80 (s, 3H), 3.39 (m, 2H), 2.74-2.78 (m, 2H), 1.85-1.91 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) : δ 171.97, 159.01, 148.81, 147.84, 138.86, 135.82, 131.65, 130.67, 129.70, 128.59, 128.52, 128.43, 128.32, 127.85, 114.35, 113.90, 112.36, 56.10, 56.02, 55.25, 46.89, 45.85, 32.43, 28.99; HRMS calcd. For C₂₈H₂₉NO₄: *m/z* 443.2097, found *m/z* 443.2105

Hydrogenation.

Compounds **6a,g,m,o** were hydrogenated under atmospheric pressure of H₂ over (10%) Pd/C (5 mol%) using THF / MeOH (1 / 1) mixture as the solvent to give the compounds **9a-d** respectively. After completion of the reaction indicated by MS analysis the catalyst was filtered off, the filtrate was concentrated and applied to a silica gel column. Elution with DCM / Et₂O (4 / 1) mixture afforded compounds **9a-d**.

1-Benzyl-7,8-dimethoxy-3-(4-methoxybenzyl)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (9a). Eluent DCM / Et₂O (4 / 1) (*R_f* 0.46). Yield: 90%. ¹H NMR (CDCl₃, 400 MHz) : δ 7.24-7.28 (m, 4H), 7.17-7.21 (m, 1H), 6.95 (d, 2H, *J* = 8.4 Hz), 6.74 (d, 2H, *J* = 8.4 Hz), 6.61 (s, 1H), 6.47 (s, 1H), 4.60 (d, 1H, *J* = 14.6 Hz), 4.46 (t, 1H, *J* = 7.0 Hz), 3.81-3.87 (m, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.59-3.64 (dd, 1H, *J*₁ = 8.3 Hz, *J*₂ = 13.6 Hz), 3.41-3.48 (dt, 1H, *J*₁ = 6.0 Hz, *J*₂ = 15.2 Hz), 3.19-3.24 (dd, 1H, *J*₁ = 6.3 Hz, *J*₂ = 13.6 Hz), 2.99-3.06 (dt, 1H, *J*₁ = 5.6 Hz, *J*₂ = 16.9 Hz), 2.75-2.84 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) : δ 173.01, 159.06, 147.83, 147.40, 140.16, 129.91, 129.34, 128.43, 128.30, 128.27, 126.28, 114.01, 113.62, 111.17, 56.07, 56.01, 55.34, 50.21, 49.57, 45.69, 36.41, 32.43; HRMS calcd. For C₂₇H₂₉NO₄: *m/z* 431.2097, found *m/z* 431.2095

1-Benzyl-7,8-dimethoxy-3-methyl-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (9b). Eluent DCM / Et₂O (4 / 1) (*R_f* 0.43). Yield: 96%. ¹H NMR (CDCl₃, 400 MHz) : δ 7.24-7.28 (m, 4H), 7.16-7.22 (m, 1H), 6.61 (s, 1H), 6.57 (s, 1H), 4.41 (t, 1H, *J* = 7.3 Hz), 3.90-3.98 (m, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 3.56-3.62 (dd, 1H, *J*₁ = 7.8 Hz, *J*₂ = 13.6 Hz), 3.48-3.54 (m, 1H), 3.18-3.24 (m, 2H), 3.04-3.12 (m, 1H), 2.97 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) : δ 173.13, 147.92, 147.49, 140.49, 129.64, 128.73, 128.61, 126.53, 113.46, 111.30, 56.29, 56.23, 49.55, 49.23, 36.61, 35.88, 32.15; HRMS calcd. For C₂₀H₂₃NO₃: *m/z* 325.1678, found *m/z* 325.1679

1-Ethyl-3-methyl-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (9c). Eluent DCM / Et₂O (4 / 1) (*R_f* 0.32). Yield: 96%. ¹H NMR (CDCl₃, 400 MHz) : δ 7.13-7.19 (m, 3H), 7.08-7.12 (m, 2H), 3.87-3.99 (m, 2H), 3.46-3.53 (m, 1H), 3.21-3.28 (m, 1H), 3.07-3.14 (m, 1H), 2.96 (s, 3H), 2.20-2.31 (m, 1H), 1.87-1.97 (m, 1H), 1.03 (t, 3H, *J* = 7.3 Hz); ¹³C NMR (CDCl₃, 100 MHz) : δ 173.08, 137.36, 136.60, 129.85, 127.27, 126.83, 126.81, 50.54, 49.31, 35.81, 32.33, 23.55, 13.02; HRMS calcd. For C₂₀H₂₃NO₃: *m/z* 203.1310, found *m/z* 203.1315

3-Isopropyl-1-(3,4,5-trimethoxybenzyl)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (9d). Eluent DCM / Et₂O (4 / 1) (*R_f* 0.44). Yield: 95%. ¹H NMR (CDCl₃, 400 MHz) : δ 7.11-7.18 (m, 3H), 7.03-7.08 (m, 1H), 6.48 (s, 2H), 4.74-4.84 (s, 1H, *J* = 6.7 Hz), 4.40-4.45 (m, 1H), 3.77-3.87 (m, 10H), 3.50-3.63 (m, 2H), 3.19-3.27 (m, 1H), 3.03-3.13 (s, 1H); 1.08 (d, 3H, *J* = 6.7 Hz), 1.02 (d, 3H, *J* = 6.7 Hz); ¹³C NMR (CDCl₃, 100 MHz) : δ 172.47, 152.97, 136.54, 136.47, 136.22,

135.70, 130.37, 126.85, 126.80, 126.42, 106.29, 60.77, 56.08, 49.89, 44.60, 38.95, 35.92, 34.08, 20.21; **HRMS** calcd. For $C_{13}H_{17}NO$: m/z 203.1310, found m/z 203.1312

MW-assisted PMB-deprotection under acidic conditions.

1-Benzylidene-7,8-dimethoxy-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (6i). 1-Benzylidene-7,8-dimethoxy-3-(4-methoxybenzyl)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (**6a**) 710 mg (1.65 mmol) was dissolved in the mixture of DCM (12 mL), TFA (4 mL) containing the catalytic amount of TfOH (100 μ L). The reaction mixture was loaded into the microwave instrument vial and irradiated with stirring at 110°C with the maximum power level of 300W during 45min. The volatiles were removed under reduced pressure, the residue was taken up in DCM, washed with 1M NaOH and brine. After drying ($MgSO_4$) and concentration the crude product was purified by column chromatography on silica gel as described earlier. Yield: 426 mg (84%).

1-Ethylidene-7,8-dimethoxy-1,3,4,5-tetrahydro-benzo[d]azepin-2-one (6j). was synthesized similarly as described for (**6i**) from 1-Ethylidene-7,8-dimethoxy-3-(4-methoxybenzyl)-1,3,4,5-tetrahydrobenzo[d]azepin-2-one (**6b**) 606 mg (1.65 mmol). Yield: 326 mg (80%).

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6f

6g

6j

6k

61

6m

11a

11b