Synthesis of the azepinoindole framework via oxidative Heck (Fujiwara-Moritani) cyclization.

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General Experimental Methods.

$^1$H and $^{13}$C NMR spectra were recorded at 298 K unless otherwise stated. The chemical shifts are reported in parts per million relative to tetramethylsilane using the residual solvent signal as the internal reference. High-resolution EI-mass spectra were recorded with a resolution of 10000. The low-resolution EI- and CI-mass spectra are reported including all peaks with relative intensity ≥10%.

Synthesis of allylamines 7a,c-f,j.

**(E)-N,2-dimethylbut-2-en-1-amine (7a)** prepared according to the reference [1].

$N$-methylbut-2-en-1-amine (7c). Crotyl bromide [2] (97.58 mmol, 13.173 g) was added dropwise at 0 °C to MeNH$_2$ (33 wt.% in EtOH) (5 equiv, 60 mL). The reaction mixture was maintained with stirring at RT overnight, poured into NaOH (1M) and extracted with Et$_2$O. The organic layer was washed with additional amount of NaOH (1M), brine, dried (Na$_2$SO$_4$) and concentrated under reduced pressure. Fractional distillation from CaH$_2$ afforded 7c as solution in EtOH (~ 5:1 ratio by $^1$H NMR). Yield: 4.062 g (~ 90 wt.% solution) – 3.656 g (44%) b.p. 78-86 °C (760 mmHg). (mixture of E/Z isomers ~ 9:1) $^1$H NMR (CDCl$_3$, 300 MHz) : δ 5.42-5.69 (m, 2H), 3.20-3.27 (m, 0.2H), 3.06-3.17 (m, 1.8H), 2.34-2.45 (m, 3H), 1.62-1.72 (m, 3H).

$N$-isopropylbut-2-en-1-amine (7d). Crotyl bromide [2] (97.58 mmol, 13.173 g) was added dropwise at 0 °C to i-PrNH$_2$ (10 equiv, 84 mL). The reaction mixture was maintained with stirring at RT overnight, poured into NaOH (1M) and extracted with Et$_2$O. The organic layer was washed with brine, dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The residue was subjected to fractional distillation from CaH$_2$. Yield: 5.821 g (53%) b.p. 128-130 °C (760 mmHg). (mixture of E/Z isomers ~ 9:1) $^1$H NMR (CDCl$_3$, 400 MHz) : δ 5.47-5.66 (m, 2H), 3.24-3.29 (m, 0.2H), 3.13-3.19 (m, 1.8H), 2.81 (sept, 1H, $J = 6.2$ Hz), 1.61-1.71 (m, 3H), 1.02-1.09 (m, 6H).

1-(cyclohex-1-en-1-yl)-N-methylmethanamine (7e). To a solution of 1-cyclohexene-1-carboxaldehyde (9.29 mmol, 1.024 g) in dry MeOH (10 mL) MeNH$_2$$\cdot$HCl (3 equiv, 1.884 g) was added with stirring at RT followed by Et$_3$N (1.2 equiv, 1.55 mL). After 3h at RT NaBH$_4$ (1.2 equiv, 422 mg) was added at once and stirring was continued for 30min more. The reaction mixture was poured into HCl (3M) (50 mL) and washed with DCM. The aqueous layer was basified with KOH and extracted with Et$_2$O. The organic layer was washed with brine and dried (Na$_2$SO$_4$). Concentration under reduced pressure afforded essentially pure 7e as a solution in Et$_2$O (~ 2:3 ratio by $^1$H NMR). Yield: 1098

mg (~ 53 wt.% solution) – 582 mg (50%). $^1$H NMR (CDCl$_3$, 400 MHz) : δ 5.56 (s, 1H), 3.05 (s, 2H), 2.38 (s, 3H), 1.92-2.05 (m, 4H), 1.52-1.68 (m, 4H).

$N,3$-dimethylbut-2-en-1-amine (7f) prepared according to the reference [3].

$N$-benzyl-2,3-dimethylbut-2-en-1-amine (7g). A solution of $N$-benzyl-2,2,2-trifluoroacetamide (47.12 mmol, 9.373 g) in dry THF (50 mL) was added dropwise to a mixture of NaH (60 wt.% disp.) (1.5 equiv, 2.827 g) and NaI (10 mol%) in THF (50 mL) at RT under argon. Upon completion of addition the mixture was allowed to stir for 1h. Then 2-(bromomethyl)-3-methylbut-2-ene [4] (1.2 equiv, 9.22 g) was added dropwise and the mixture was brought to reflux. After the overnight reflux the reaction was cooled to RT, quenched with H$_2$O and extracted with Et$_2$O. The organic layer was concentrated under reduced pressure. The residue was dissolved in a mixture of MeOH (50 mL), H$_2$O (30 mL) and KOH (4.67 g). The resulting solution was refluxed for 2h, concentrated under reduced pressure down to ~ 30 mL and extracted with Et$_2$O. The organic layer was washed with brine and dried (Na$_2$SO$_4$). Distillation under reduced pressure from CaH$_2$ afforded pure 7f. Yield: 3.893 g (44%) b.p. 193-194 °C (10 mmHg). $^1$H NMR (CDCl$_3$, 400 MHz) : δ 7.31-7.38 (m, 4H), 7.23-7.29 (m, 1H), 3.77 (s, 2H), 3.25 (s, 2H), 1.75 (s, 3H), 1.70 (s, 3H), 1.69 (s, 3H), 1.29 (bs, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) : δ 140.86, 128.30, 128.11, 127.61, 126.77, 126.27, 53.35, 51.72, 20.75, 20.07, 17.45.

$1,2,3,6$-tetrahydropyridine (7h) prepared according to the reference [5].

2-vinylpyrrolidine hydrochloride (7j). HCl (4M) / Dioxane (6 mL) was added to tert-butyl 2-vinylpyrrolidine-1-carboxylate [6] (10.01 mmol, 1.974 g) at RT with stirring. After 1h the reaction mixture was concentrated under reduced pressure. The obtained precipitate was washed with dry Et$_2$O and dried under vacuum (0.02 mbar) at RT for 3h. Yield: 682 mg (51%). $^1$H NMR (CDCl$_3$, 400 MHz) : δ 10.08 (bs, 1H), 9.54 (bs, 1H), 6.02-6.17 (m, 1H), 5.51 (d, 1H, $J$ = 17.2 Hz), 5.39 (d, 1H, $J$ = 9.9 Hz), 3.98-4.14 (m, 1H), 3.25-3.51 (m, 2H), 1.83-2.82 (m, 4H).

General procedure for preparation of the amides 1a-h,j.

3-indoleacetic acid (3 mmol, 526 mg) was suspended in dry DCM (15 mL) at RT. The corresponding free allylamine 7 (1 equiv) (or 7$\cdot$HCl (1 equiv) and the equimolar amount of dry Et$_3$N (0.42 mL)) was added to the suspension followed by EDCI (1 equiv, 575 mg). The reaction mixture was maintained with stirring overnight, diluted with DCM, washed sequentially with HCl (1M), NaHCO$_3$(sat.), brine and dried (MgSO$_4$). After concentration under reduced pressure the residue was subjected to column chromatography on silica gel.

Amides 1a-h,j appear as a mixture of two rotamers. $^{13}$C spectra (example 1a) are not very characteristic in this case due to the overlapping peaks and were not registered. $^1$H NMR spectra of 1a-h,j are described for both rotamers considering the ratio.

2-(1H-indol-3-yl)-N-methyl-N-((E)-2-methylbut-2-enyl)acetamide (1a). Prepared from 7a (297 mg). Eluent - DCM / Et₂O 4:1 (Rf ~ 0.23). Yield: 723 mg (94%). (~ 1:1 mixture of rotamers) ¹H NMR (CDCl₃, 400 MHz): δ 8.29 (bs, 1H), 7.63 (d, 0.5H, J = 7.8 Hz), 7.59 (d, 0.5H, J = 7.8 Hz), 7.31-7.37 (m, 1H), 7.05-7.22 (m, 3H), 5.23-5.36 (m, 1H), 3.96 (s, 1H), 3.85 (s, 1H), 3.78-3.83 (m, 2H), 2.89 (s, 1.5H), 2.87 (s, 1.5H), 1.61 (d, 1.5H, J = 6.9 Hz), 1.57 (d, 1.5H, J = 6.9 Hz), 1.50 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 172.51, 171.98, 136.40, 131.32, 130.50, 127.27, 127.25, 123.13, 123.10, 121.92, 121.80, 121.77, 120.63, 119.26, 118.62, 118.56, 111.52, 108.84, 108.56, 57.29, 54.58, 34.57, 33.70, 31.63, 30.95, 13.76, 13.70, 13.25, 13.15; LRMS (CI) (C₁₆H₂₀N₂O : m/z 256) (m/z, %): 257 ([M+H]+, 100).

N-allyl-2-(1H-indol-3-yl)-N-methylacetamide (1b). Prepared from 7b (213 mg). Eluent - DCM / Et₂O 4:1 (Rf ~ 0.19). Yield: 600 mg (88%). (~ 1:1 mixture of rotamers) ¹H NMR (CDCl₃, 400 MHz): δ 8.16 (bs, 1H), 7.59-7.67 (m, 1H), 7.33-7.38 (m, 1H), 7.09-7.23 (m, 3H), 5.63-5.83 (m, 1H), 5.06-5.22 (m, 2H), 4.01-4.05 (m, 1H), 3.90-3.95 (m, 1H), 3.85 (s, 1H), 3.80 (s, 1H), 2.94-2.98 (m, 3H); LRMS (CI) (C₁₄H₁₆N₂O : m/z 228) (m/z, %): 229 ([M+H]+, 100), 130 (10).

N-(but-2-enyl)-2-(1H-indol-3-yl)-N-methylacetamide (1c). Prepared from 7c (90 wt.% / EtOH) (283 mg). Eluent - DCM / Et₂O 4:1 (Rf ~ 0.19). Yield: 611 mg (84%). (~ 1:1 mixture of rotamers) ¹H NMR (CDCl₃, 400 MHz): δ 8.28 (bs, 1H), 7.62-7.66 (m, 1H), 7.34-7.38 (m, 1H), 7.18-7.24 (m, 1H), 7.08-7.17 (m, 2H), 5.35-5.68 (m, 2H), 4.10-4.14 (m, 0.1H), 3.96-4.01 (m, 0.9H), 3.82-3.89 (m, 3H), 2.93-2.99 (m, 3H), 1.65-1.74 (m, 3H); LRMS (CI) (C₁₅H₁₈N₂O : m/z 242) (m/z, %): 243 ([M+H]+, 100), 130 (14).

N-(but-2-enyl)-2-(1H-indol-3-yl)-N-isopropylacetamide (1d). Prepared from 7d (340 mg). Eluent - DCM / Et₂O 4:1 (Rf ~ 0.26). Yield: 600 mg (74%). (~ 7:3 mixture of rotamers) ¹H NMR (CDCl₃, 400 MHz): δ 8.14 (bs, 1H), 7.61-7.65 (m, 0.3H), 7.56-7.60 (m, 0.7H), 7.32-7.37 (m, 1H), 7.15-7.21 (m, 1H), 7.07-7.14 (m, 2H), 5.35-5.68 (m, 2H),
4.76-4.91 (m, 0.7H), 4.14-4.24 (m, 0.3H), 3.92-3.96 (m, 0.12H), 3.81-3.88 (m, 1.36H),
3.72-3.79 (m, 2.52H), 1.61-1.73 (m, 3H), 1.03-1.15 (m, 6H); \textbf{LRMS (CI)} (C_{17}H_{22}N_{2}O : m/z 270) (m/z, %) : 271 ([M+H]^+, 100), 130 (11).

1e

\textbf{N-(cyclohexenylmethyl)-2-(1H-indol-3-yl)-N-methylacetamide (1e).} Prepared from 7e (53 wt.% / Et\textsubscript{2}O) (709 mg). Eluent - DCM / Et\textsubscript{2}O 4:1 (R\textsubscript{f} ~ 0.22). Yield: 601 mg (71%). (~ 1:1 mixture of rotamers) \textbf{\textsuperscript{1}H NMR} (CDCl\textsubscript{3}, 400 MHz) : \delta 8.13 (bs, 1H), 7.58-7.66 (m, 1H), 7.32-7.37 (m, 1H), 7.15-7.22 (m, 1H), 7.09-7.14 (m, 2H), 5.44-5.51 (m, 1H), 3.93 (s, 1H), 3.85 (s, 1H), 3.80 (s, 1H), 3.77 (s, 1H), 2.91 (s, 1.5H), 2.90 (s, 1.5H), 1.94-2.02 (m, 2H), 1.76-1.86 (m, 2H), 1.50-1.64 (m, 4H); \textbf{LRMS (CI)} (C\textsubscript{18}H\textsubscript{22}N\textsubscript{2}O : m/z 282) (m/z, %) : 283 ([M+H]^+, 100), 130 (11).

1f

\textbf{2-(1H-indol-3-yl)-N-methyl-N-(3-methylbut-2-enyl)acetamide (1f).} Prepared from 7f (298 mg). Eluent - DCM / Et\textsubscript{2}O 4:1 (R\textsubscript{f} ~ 0.21). Yield: 686 mg (89%). (~ 1:1 mixture of rotamers) \textbf{\textsuperscript{1}H NMR} (CDCl\textsubscript{3}, 400 MHz) : \delta 8.11 (bs, 1H), 7.59-7.65 (m, 1H), 7.34 (d, 1H, J = 8.0 Hz), 7.16-7.21 (m, 1H), 7.09-7.14 (m, 2H), 5.11-5.17 (m, 0.5H), 5.02-5.07 (m, 0.5H), 4.02 (d, 1H, J = 6.9 Hz), 3.90 (d, 1H, J = 6.5 Hz), 3.80-3.83 (m, 2H), 2.93 (s, 1.5H), 2.91 (s, 1.5H), 1.69-1.72 (m, 3H), 1.68 (s, 1.5H), 1.62 (s, 1.5H); \textbf{LRMS (CI)} (C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}O : m/z 256) (m/z, %) : 257 ([M+H]^+, 100), 130 (12).

1g

\textbf{N-benzyl-2-(1H-indol-3-yl)-N-(2,3-dimethylbut-2-enyl)acetamide (1g).} Prepared from 7g (568 mg). Eluent - DCM / Et\textsubscript{2}O 4:1 (R\textsubscript{f} ~ 0.44). Yield: 859 mg (83%). (~ 1:1 mixture of rotamers) \textbf{\textsuperscript{1}H NMR} (CDCl\textsubscript{3}, 400 MHz) : \delta 8.12 (bs, 1H), 7.63 (d, 0.5H, J = 7.8 Hz), 7.54 (d, 0.5H, J = 7.8 Hz), 7.30-7.36 (m, 2H), 7.06-7.30 (m, 7H), 4.52 (s, 1H), 4.41 (s, 1H), 4.19 (s, 1H), 3.95 (s, 1H), 3.92 (s, 1H), 3.84 (s, 1H), 1.67 (s, 1.5H), 1.62 (s, 1.5H), 1.53 (s, 3H), 1.47 (s, 1.5H), 1.43 (s, 1.5H); \textbf{LRMS (CI)} (C\textsubscript{23}H\textsubscript{26}N\textsubscript{2}O : m/z 346) (m/z, %) : 347 ([M+H]^+, 100), 255 (11), 130 (10).

1h

\textbf{1-(5,6-dihydropyridin-1(2H)-yl)-2-(1H-indol-3-yl)ethanone (1h).} Prepared from 7h (249 mg). Eluent - DCM / Et\textsubscript{2}O 4:1 (R\textsubscript{f} ~ 0.21). Yield: 641 mg (89%). (~ 1:1 mixture of rotamers) \textbf{\textsuperscript{1}H NMR} (CDCl\textsubscript{3}, 400 MHz) : \delta 8.14 (bs, 1H), 7.60-7.66 (m, 1H), 7.35 (d, 1H, J = 8.0 Hz), 7.17-7.22 (m, 1H), 7.10-7.15 (m, 1H), 7.05-7.09 (m, 1H), 5.82-5.89 (m, 0.5H),
5.66-5.78 (m, 1 H), 5.52-5.58 (m, 0.5 H), 4.08-4.12 (m, 1 H), 3.95-3.99 (m, 1 H), 3.87 (s, 1 H), 3.84 (s, 1 H), 3.72 (t, 1 H, J = 5.7 Hz), 3.52 (t, 1 H, J = 5.6 Hz), 2.13-2.20 (m, 1 H), 1.94-2.01 (m, 1 H); LRMS (El) (C₁₅H₁₆N₂O : m/z 240) (m/z, %) : 240 (M⁺, 45), 130 (100).

Methyl 2-(N-(3-methylbut-2-enyl)acetamido)-3-(1H-indol-3-yl)propanoate (1i). Prepared according to the reference [7].

2-(1H-indol-3-yl)-1-(2-vinylpyrrolidin-1-yl)ethanone (1j). Prepared from 7j•HCl (401 mg). Eluent - DCM / Et₂O 4:1 (Rf ~ 0.17). Yield: 620 mg (81%). (~ 6:4 mixture of rotamers) 1H NMR (CDCl₃, 400 MHz) : δ 8.19 (bs, 1 H), 7.65 (d, 0.4 H, J = 7.8 Hz), 7.58 (d, 0.6 H, J = 7.8 Hz), 7.32-7.36 (m, 1 H), 7.07-7.21 (m, 3 H), 5.72-5.90 (m, 1 H), 5.13-5.23 (m, 1.2 H), 4.97-5.06 (m, 0.8 H), 4.68-4.74 (m, 0.4 H), 4.41-4.47 (m, 0.6 H), 3.66-3.83 (m, 2 H), 3.46-3.65 (m, 2 H), 1.70-2.05 (m, 4 H); LRMS (CI) (C₁₆H₁₈N₂O : m/z 254) (m/z, %) : 255 ([M+H]+, 100), 130 (16).

General procedure for the oxidative Heck cyclization under primary conditions.

Amide 1 (0.2 mmol), PdCl₂(MeCN)₂ (5 mg, 10 mol %), p-benzoquinone (1.5 equiv – either DTBQ (66 mg) or DMBQ (40 mg)) were loaded into a vial with a screw cap equipped with a stirring bar. The vial was evacuated and filled back with argon. Dry THF (4 mL) was added, the vial was sealed under argon and kept with stirring at 110 °C (oil bath temperature). After 16 h the reaction mixture was filtered through a short pad of Celite ® washing with THF. The filtrate was evaporated with silica under reduced pressure. The residue was subjected to column chromatography on silica gel.

3,5-dimethyl-5-vinyl-3,4,5,6-tetrahydroazepino[4,5-b]indol-2(1H)-one (2a). Prepared from 1a (51 mg) with DTBQ. Eluent - Hexane / EtOAc 1:3 (Rf ~ 0.21). Yield: 27 mg (53%). 1H NMR (CDCl₃, 400 MHz) : δ 7.76 (s, 1 H), 7.56 (d, 1 H, J = 7.8 Hz), 7.29 (d, 1 H, J = 7.8 Hz), 7.11-7.20 (m, 2 H), 5.98 (dd, 1 H, J₁ = 10.5 Hz, J₂ = 17.4 Hz), 5.26 (dd, 1 H, J₁ = 0.8 Hz, J₂ = 10.5 Hz), 5.11 (d, 1 H, J = 17.4 Hz), 3.92 (s, 2 H), 3.59-3.77 (bs, 2 H), 3.10 (s, 3 H), 1.49 (s, 3 H); ¹H NMR (DMSO-d₆, 400 MHz, 327 K) : δ 10.55 (s, 1 H), 7.46 (d, 1 H, J = 7.7 Hz), 7.29 (d, 1 H, J = 8.0 Hz), 7.01-7.07 (m, 1 H), 6.95-7.00 (m, 1 H), 6.02 (dd, 1 H, J₁ = 10.6 Hz, J₂ = 17.4 Hz), 5.16 (dd, 1 H, J₁ = 1.2 Hz, J₂ = 10.6 Hz), 4.93 (dd, 1 H, J₁ = 10.6 Hz, J₂ = 17.4 Hz), 4.54, 4.48 (m, 1 H), 3.68-3.80 (m, 2 H), 3.55-3.63 (m, 2 H), 3.10-3.20 (m, 3 H), 2.80-2.90 (m, 2 H), 1.85-1.90 (m, 2 H), 1.35-1.40 (s, 3 H), 1.30-1.40 (s, 3 H), 1.00-1.05 (s, 3 H).
$1H, J_1 = 1.2 \text{ Hz}, J_2 = 17.4 \text{ Hz}), 3.72-3.81 (m, 3H), 3.67 (d, 1H, J = 15.0 \text{ Hz}), 2.95 (s, 3H), 1.45 (s, 3H); ^1\text{C NMR} (\text{CDCl}_3, 100 \text{ MHz}) : \delta 173.47, 141.94, 136.77, 135.27, 127.62, 122.06, 119.53, 118.17, 116.10, 110.47, 104.20, 59.28, 43.44, 37.42, 32.44, 23.84; \text{HRMS (EI) calcd. for C}_{16}H_{18}N_2O : m/z 254.1419, found m/z 254.1428.\]

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\begin{align*}
\text{3,5-dimethyl-3,6-dihydroazepino[4,5-b]indol-2(1H)-one (2b). Prepared from 1b (46 mg) with DMBQ. Eluent - Hexane / EtOAc 1:1 (R_f \sim 0.21). Yield: 16 mg (35%). ^1\text{H NMR} (\text{DMSO}-d_6, 400 MHz) : & \delta 11.15 (s, 1H), 7.61 (d, 1H, J = 7.8 Hz), 7.38 (d, 1H, J = 8.0 Hz), 7.11-7.16 (m, 1H), 7.02-7.07 (m, 1H), 6.32 (d, 1H, J = 1.2 Hz), 3.45 (s, 2H), 3.01 (s, 3H), 2.21 (d, 3H, J = 1.2 Hz); \text{HRMS (EI) calcd. for C}_{14}H_{14}N_2O : m/z 226.1106, found m/z 226.1110.}
\end{align*}
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\begin{align*}
\text{- NOE exo-2c: Mixture of the double bond isomers E/Z \sim 13:1 (based on the integration of vinylic protons in the ^1\text{H NMR spectrum of the crude product after chromatography). E-configuration assigned by NOE.}
\end{align*}
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\begin{align*}
\text{5-ethyl-3-methyl-3,6-dihydroazepino[4,5-b]indol-2(1H)-one (endo-2c). Prepared from 1c (48 mg) with DMBQ. Eluent - Hexane / EtOAc 2:3 (R_f \sim 0.12). Yield: 8 mg (17%). Analytically pure sample obtained after recrystallization from EtOAc. ^1\text{H NMR} (\text{CDCl}_3, 400 MHz) : & \delta 8.10 (s, 1H), 7.52 (d, 1H, J = 7.9 Hz), 7.27 (d, 1H, J = 7.9 Hz), 7.14-7.19 (m, 1H), 7.06-7.11 (m, 1H), 5.95 (q, 1H, J = 7.0 Hz), 4.31 (s, 2H), 3.96 (s, 2H), 3.04 (s, 3H), 1.97 (d, 3H, J = 7.0 Hz); ^1\text{H NMR} (\text{DMSO}-d_6, 400 MHz) : & \delta 11.09 (s, 1H), 7.49 (d, 1H, J = 7.9 Hz), 7.28 (d, 1H, J = 7.9 Hz), 7.05-7.10 (m, 1H), 6.94-6.99 (m, 1H), 6.26 (q, 1H, J = 6.9 Hz), 4.36 (s, 2H), 3.86 (s, 2H), 2.88 (s, 3H), 1.94 (d, 3H, J = 6.9 Hz); ^1\text{C NMR} (\text{DMSO}-d_6, 100 MHz) : & \delta 172.55, 136.16, 134.38, 128.21, 127.28, 122.51, 120.35, 119.27, 118.27, 111.17, 150.47, 47.17, 33.68, 33.06, 13.54; \text{HRMS (EI) calcd. for C}_{15}H_{16}N_2O : m/z 240.1263, found m/z 240.1267.}
\end{align*}
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\begin{align*}
\text{(E)-5-ethylidene-3-methyl-3,4,5,6-tetrahydroazepino[4,5-b]indol-2(1H)-one (exo-2c). Prepared from 1c (48 mg) with DMBQ. Eluent - Hexane / EtOAc 2:3 (R_f \sim 0.12). Yield: 8 mg (17%). Analytically pure sample obtained after recrystallization from EtOAc. ^1\text{H NMR} (\text{CDCl}_3, 400 MHz) : & \delta 8.10 (s, 1H), 7.52 (d, 1H, J = 7.9 Hz), 7.27 (d, 1H, J = 7.9 Hz), 7.14-7.19 (m, 1H), 7.06-7.11 (m, 1H), 5.95 (q, 1H, J = 7.0 Hz), 4.31 (s, 2H), 3.96 (s, 2H), 3.04 (s, 3H), 1.97 (d, 3H, J = 7.0 Hz); ^1\text{H NMR} (\text{DMSO}-d_6, 400 MHz) : & \delta 11.09 (s, 1H), 7.49 (d, 1H, J = 7.9 Hz), 7.28 (d, 1H, J = 7.9 Hz), 7.05-7.10 (m, 1H), 6.94-6.99 (m, 1H), 6.26 (q, 1H, J = 6.9 Hz), 4.36 (s, 2H), 3.86 (s, 2H), 2.88 (s, 3H), 1.94 (d, 3H, J = 6.9 Hz); ^1\text{C NMR} (\text{DMSO}-d_6, 100 MHz) : & \delta 172.55, 136.16, 134.38, 128.21, 127.28, 122.51, 120.35, 119.27, 118.27, 111.17, 150.47, 47.17, 33.68, 33.06, 13.54; \text{HRMS (EI) calcd. for C}_{15}H_{16}N_2O : m/z 240.1263, found m/z 240.1268.}
\end{align*}
\]
5-ethyl-3-isopropyl-3,6-dihydroazepino[4,5-b]indol-2(1H)-one (2d). Prepared from 1d (54 mg) with DMBQ. Eluent Hexane / EtOAc 1:1 (R_f ~ 0.19). Yield: 7 mg (13%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) : δ 7.99 (s, 1H), 7.71 (d, 1H, J = 8.0 Hz), 7.38 (d, 1H, J = 8.0 Hz), 7.21-7.26 (m, 1H), 7.15-7.20 (m, 1H), 6.25 (s, 1H), 4.92 (sept, 1H, J = 6.7 Hz), 3.53 (s, 2H), 2.63 (q, 2H, J = 7.6 Hz), 1.20 (t, 3H, J = 7.6 Hz), 1.18 (d, 6H, J = 6.7 Hz); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) : δ 167.69, 137.59, 132.94, 126.33, 123.91, 122.76, 120.79, 119.90, 118.54, 110.91, 109.59, 46.25, 33.71, 26.47, 20.71, 14.61; HRMS (EI) calcd. for C\(_{17}\)H\(_{20}\)N\(_2\)O : m/z 268.1576, found m/z 268.1573.

2e Mixture of the double bond isomers \(\Delta^{1,2}/\Delta^{2,3} \sim 1:19\) (based on the integration of vinylic protons in the \(^1\)H NMR spectrum of the crude product after chromatography). Partial assignment based on COSY.

3-methyl-3,4-dihydro-1H-spiro[azepino[4,5-b]indole-5,1’-cyclohex[3]en]-2(6H)-one (2e). Prepared from 1e (56 mg) with DTBQ. Eluent - Hexane / EtOAc 1:1 (R_f ~ 0.10). Yield: 22 mg (40%). Analytically pure sample obtained after recrystallization from DMSO. \(^1\)H NMR (CDCl\(_3\), 400 MHz) : δ 8.23 (s, 1H), 7.55 (d, 1H, J = 7.7 Hz), 7.28 (d, 1H, J = 7.8 Hz), 7.09-7.19 (m, 2H), 5.98-6.04 (m, H-C3), 5.90-5.96 (m, H-C2), 3.93 (d, 1H, J = 16.1 Hz), 3.88 (d, 1H, J = 16.1 Hz), 3.85 (d, 1H, J = 14.8 Hz), 3.58 (d, 1H, J = 14.8 Hz), 3.14 (s, 3H), 2.38-2.46 (m, H-C1), 2.29-2.36 (m, 2H-C4), 2.19-2.27 (m, H-C1), 2.01-2.10 (m, H-C5), 1.77-1.85 (m, H-C5); \(^{13}\)C NMR (DMSO-d\(_6\), 100 MHz, 363 K) : δ 173.53, 141.45, 135.88, 127.68, 126.37, 125.14, 121.20, 118.87, 117.67, 111.18, 102.77, 53.48, 38.30, 36.97, 33.74, 32.46, 30.20, 22.58; HRMS (EI) calcd. for C\(_{18}\)H\(_{20}\)N\(_2\)O : m/z 280.1576, found m/z 280.1589.

5-isopropyl-3-methyl-3,6-dihydroazepino[4,5-b]indol-2(1H)-one (2f). Prepared from 1f (51 mg) with DTBQ. Eluent - Hexane / EtOAc 2:1 (R_f ~ 0.16). Yield: 29 mg (57%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) : δ 8.05 (s, 1H), 7.70 (d, 1H, J = 7.8 Hz), 7.32 (d, 1H, J = 8.0 Hz), 7.21-7.26 (m, 1H), 7.15-7.9 (m, 1H), 6.11 (d, 1H, J = 0.8 Hz), 3.55 (s, 2H), 3.13 (s, 3H), 2.93 (sept, 1H, J = 6.7 Hz), 1.27 (d, 6H, J = 6.7 Hz); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) : δ 168.39, 137.67, 132.87, 127.06, 126.16, 125.44, 122.80, 119.89, 118.43, 110.97, 109.57, 36.46, 33.02, 31.08, 22.53; HRMS (EI) calcd. for C\(_{16}\)H\(_{18}\)N\(_2\)O : m/z 254.1419, found m/z 254.1418.

Methyl 3-acetyl-5-isopropyl-1,2,3,6-tetrahydroazepino[4,5-b]indole-2-carboxylate (2i). Prepared from 1i (66 mg) with DMBQ. Eluent - Hexane / EtOAc 2:3 (R_f ~ 0.35). Yield: 11 mg (17%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) : δ 7.98 (s, 1H), 7.56 (d, 1H, J = 7.8 Hz), 7.32 (d, 1H, J = 8.0 Hz), 7.17-7.22 (m, 1H), 7.10-7.15 (m, 1H), 6.52 (s, 1H), 5.66 (t,
1H, J = 5.0 Hz), 3.71 (dd, 1H, J1 = 5.7 Hz, J2 = 16.7 Hz), 3.56 (s, 3H), 3.22 (dd, 1H, J1 = 4.6 Hz, J2 = 16.7 Hz), 2.91 (sept, 1H, J = 6.7 Hz), 2.22 (s, 3H), 1.32 (d, 1H, J = 6.7 Hz); 13C NMR (CDCl3 100 MHz): δ 170.13, 169.72, 135.36, 130.54, 128.59, 127.39, 123.48, 122.91, 119.80, 118.60, 113.03, 110.68, 56.10, 52.11, 30.11, 26.73, 23.24, 22.66, 22.10; HRMS (EI) calcd. for C19H22N2O3: m/z 326.1630, found m/z 326.1637.

During chromatography 26 mg of the starting amide 1i was recovered. Eluent - Hexane / EtOAc 2:3 (R1 ~ 0.14). Recalculated yield of 2i – 28% (brsm).

(Z)-2,3,11,13a-tetrahydro-1H-pyrrolo[1',2':1,8]azocino[5,4-b]indol-5(6H)-one (2j). Prepared from 1j (50 mg) with DMBQ. Eluent - Hexane / EtOAc 1:4 (R1 ~ 0.11). Yield: 10 mg (20%). 1H NMR (CDCl3, 400 MHz): δ 7.96 (s, 1H), 7.65 (d, 1H, J = 7.9 Hz), 7.25 (d, 1H, J = 7.9 Hz), 7.15-7.19 (m, 1H), 7.09-7.14 (m, 1H), 5.59 (dd, 1H, J1 = 4.9 Hz, J2 = 11.9 Hz), 5.00-5.05 (m, 1H), 4.29 (d, 1H, J = 14.5 Hz), 3.77 (d, 1H, J = 14.5 Hz), 3.48-3.62 (m, 2H), 2.08-2.18 (m, 1H), 1.89-2.00 (m, 3H); 13C NMR (DMSO-d6, 100 MHz): δ 169.22, 135.57, 133.46, 131.42, 129.14, 123.99, 122.62, 119.48, 118.74, 111.39, 109.21, 56.69, 45.55, 33.96, 32.78, 23.12; HRMS (EI) calcd. for C16H16N2O: m/z 252.1263, found m/z 252.1276.

General procedure for the oxidative Heck cyclization under secondary conditions.

Amide 1 (0.2 mmol), Pd(MeCN)4(BF4)2 (9 mg, 10 mol %), DTBQ (18 mg, 40 mol %) were loaded into a round-bottom single-neck flask equipped with a stirring bar. Dry DMSO (2 mL) was added and the O2 balloon was attached to the neck via a three-port valve. The flask was evacuated and filled back with O2. After 16h of stirring at elevated temperature (oil bath) under O2 atmosphere the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with water, brine, dried (MgSO4) and concentrated under reduced pressure with silica. The residue was subjected to column chromatography on silica gel.

3-benzyl-5-methyl-5-(prop-1-en-2-yl)-3,4,5,6-tetrahydroazepino[4,5-b]indol-2(1H)-one (2g). Prepared from 1g (69 mg) at 90 °C. Eluent - Hexane / EtOAc 3:1 (R1 ~ 0.16). Yield: 25 mg (36%). 1H NMR (DMSO-d6, 400 MHz, 363 K): δ 10.43 (s, 1H), 7.49 (d, 1H, J = 7.6 Hz), 7.25-7.39 (m, 6H), 6.97-7.08 (m, 2H), 5.01 (m, 1H), 4.65-4.71 (m, 2H), 4.47 (d, 1H, J = 15.3 Hz), 3.93 (d, 1H, J = 15.7 Hz), 3.87 (d, 1H, J = 15.7 Hz), 3.82 (d, 1H, J = 15.2 Hz), 3.57 (d, 1H, J = 15.2 Hz), 1.72 (d, 3H, J = 0.8 Hz), 1.48 (s, 3H); 13C NMR (CDCl3, 75 MHz): δ 173.43, 147.00, 137.92, 137.49, 135.24, 128.75, 128.04, 127.52, 127.48, 121.98, 119.44, 118.09, 115.25, 110.60, 103.92, 54.22, 51.13, 45.68, 32.59, 24.00, 19.99; HRMS (EI) calcd. for C23H24N2O: m/z 344.1889, found m/z 344.1889.
7,8-dihydro-1H-3,7-methanoazonino[5,4-b]indol-2(4H)-one (2h). Prepared from 1h (48 mg) at 80 °C. Eluent - DCM / MeCN 2:1 (Rf ~ 0.26). Yield: 10 mg (20%). \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) : \(\delta\) 11.08 (s, 1H), 7.48 (d, 1H, \(J = 7.8\) Hz), 7.29 (d, 1H, \(J = 7.9\) Hz), 7.04 (m, 1H), 6.98-7.04 (m, 1H), 6.02-6.10 (m, H-C4), 5.72-5.78 (m, H-C5), 4.50 (dd, H-C6, \(J_1 = 4.0\) Hz, \(J_2 = 17.3\) Hz), 4.43 (d, H-C2, \(J = 14.2\) Hz), 4.10 (d, H-C1, \(J = 15.0\) Hz), 3.62 (dd, H-C2, \(J_1 = 3.4\) Hz, \(J_2 = 14.2\) Hz), 3.44-3.55 (m, H-C1, H-C3, H-C6);

\(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) : \(\delta\) 175.48, 136.97, 135.17, 128.89 (C4), 128.03 (C5), 127.97, 121.15, 119.04, 117.82, 110.18, 101.81, 47.06 (C2), 44.30 (C6), 33.56 (C3), 32.13 (C1);

HRMS (EI) calcd. for C\(_{15}\)H\(_{14}\)N\(_2\)O : m/z 238.1106, found m/z 238.1106.

Synthesis of unreactive substrates 3a-f.

\[R = \text{Ac } (3a), \text{ Me } (3b)\]

\[R = \text{H } (3c), \text{ 2-Picolyl } (3d)\]

2-(1-acetyl-1H-indol-3-yl)-N-((E)-but-2-en-2-yl)-N-methylacetamide (3a). To a mixture of amide 1a (3.88 mmol, 994 mg), Bu\(_4\)NHSO\(_4\) (10 mol%, 131 mg) and powdered NaOH (5 equiv, 776 mg) in DCM (20 mL) a solution of freshly distilled AcCl (2.5 equiv, 0.69 mL) in DCM (10 mL) was added dropwise at RT. After 2 h the reaction mixture was diluted with DCM and washed successively with H\(_2\)O and brine, dried (MgSO\(_4\)), concentrated and applied to a column of silica gel as a solution in DCM. Elution with DCM / Et\(_2\)O 4:1 (R\(_f\) ~ 0.23) afforded pure 3a 1058 mg (91%). (mixture of rotamers ~ 1 / 1) \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta\) 8.40-8.46 (m, 1H), 7.54 (d, 0.5H, \(J = 7.8\) Hz), 7.49 (d, 0.5H, \(J = 7.8\) Hz), 7.41-7.46 (m, 1H), 7.33-7.39 (m, 1H), 7.26-7.31 (m, 1H), 5.29-5.39 (m, 1H), 3.99 (s, 1H), 3.83 (s, 1H), 3.79 (d, 1H, \(J = 1.2\) Hz), 3.73 (d, 1H, \(J = 1.2\) Hz), 2.92-2.94 (m, 3H), 2.60-2.62 (m, 3H), 1.59-1.64 (m, 3H), 1.53-1.57 (m, 3H); LRMS (CI) (C\(_{18}\)H\(_{22}\)N\(_2\)O : m/z 298) (m/z, %) : 299 ([M+H\(^+\)], 100), 130 (13).

N-((E)-but-2-en-2-yl)-N-methyl-2-(1-methyl-1H-indol-3-yl)acetamide (3b). Prepared from 1-methyl-3-indoleacetic acid \([8]\) (3 mmol, 568 mg) and amine 7a (1 equiv, 298 mg) according the general procedure for preparation of the starting amides 1a-h,j. Eluent - DCM / Et\(_2\)O 4:1 (R\(_f\) ~ 0.38). Yield: 636 mg (78%). (~ 1:1 mixture of rotamers) \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta\) 7.62 (d, 0.5H, \(J = 7.8\) Hz), 7.41-7.46 (m, 1H), 7.33-7.39 (m, 1H), 7.26-7.31 (m, 1H), 5.29-5.39 (m, 1H), 3.99 (s, 1H), 3.83 (s, 1H), 3.79 (d, 1H, \(J = 1.2\) Hz), 3.73 (d, 1H, \(J = 1.2\) Hz), 2.92-2.94 (m, 3H), 2.60-2.62 (m, 3H), 1.59-1.64 (m, 3H), 1.53-1.57 (m, 3H); LRMS (CI) (C\(_{17}\)H\(_{22}\)N\(_2\)O : m/z 270) (m/z, %) : 271 ([M+H\(^+\)], 100), 144 (17).

**N-(2-(1H-indol-3-yl)ethyl)-2,2,2-trifluoro-N-(3-methylbut-2-enyl)acetamide (3c).** A mixture of tryptamine (10 mmol, 1.602 g), prenal (1 equiv, 0.84 g) and 4Å MS (3 g) in dry DCM (20 mL) was stirred at RT for 3 h. Afterwards the solvent was removed under reduced pressure and the residue was dissolved in MeOH (5 mL) at 0 °C. The reaction mixture was then diluted with DCM, washed with HCl (1 M), NaHCO₃ (sat.), brine, dried (MgSO₄), concentrated and applied to a column of silica gel as a solution in DCM. Elution with DCM (Rf ~ 0.33) afforded pure 3c 1355 mg (42%). (mixture of rotamers ~ 6 / 4) **¹H NMR** (CDCl₃, 400 MHz): δ 7.95-8.13 (m, 1H), 7.63 (d, 0.6H, J = 7.7 Hz), 7.55 (d, 0.4H, J = 7.7 Hz), 7.34-7.41 (m, 1H), 7.09-7.25 (m, 2H), 7.00-7.04 (m, 2H), 5.14-5.22 (m, 0.4H), 5.00-5.08 (m, 0.6H), 4.10 (d, 0.8H, J = 7.0 Hz), 3.83 (d, 1.2H, J = 7.0 Hz), 3.55-3.67 (m, 2H), 3.01-3.11 (m, 2H), 1.75 (s, 1.2H), 1.69-1.72 (m, 3H), 1.51 (s, 1.8H); **LRMS (CI)** (C₁₇H₁₉F₃N₂O : m/z 324) (m/z, %): 325 ([M+H]+, 100), 269 (26), 257 (43), 144 (33), 130 (31).

**2,2,2-trifluoro-N-(3-methylbut-2-enyl)-N-(2-((pyridin-2-yl)methyl)-1H-indol-3-yl)ethyl)acetamide (3d).** To a solution of amide 3c (1 mmol, 324 mg) in dry DMF (3 mL) NaH (60 wt.% disp.) (3 equiv, 120 mg) was added at RT under argon. After 30 min 2-picolyl chloride hydrochloride (1.2 equiv, 197 mg) was added in one portion and the reaction mixture was maintained at RT for 1 h. The reaction was quenched with H₂O and extracted with EtOAc. The organic layer was washed with H₂O, brine, dried (Na₂SO₄), concentrated and applied to a column of silica gel as a solution in DCM. Elution with DCM / Et₂O 4:1 (Rf ~ 0.35) afforded pure 3d 175 mg (42%). (mixture of rotamers ~ 6 / 4) **¹H NMR** (CDCl₃, 400 MHz): δ 8.57-8.61 (m, 1H), 7.64 (d, 0.6H, J = 7.7 Hz), 7.49-7.57 (m, 1.4H), 7.23-7.28 (m, 1H), 7.10-7.22 (m, 3H), 7.02 (s, 1H), 6.69-6.73 (m, 1H), 5.39-5.42 (m, 2H), 5.15-5.21 (m, 0.4H), 5.03-5.09 (m, 0.6H), 4.11 (d, 0.8H, J = 7.0 Hz), 3.86 (d, 1.2H, J = 7.0 Hz), 3.58-3.67 (m, 2H), 3.05-3.11 (m, 2H), 1.75 (s, 1.2H), 1.70 (s, 1.2H), 1.53 (s, 1.8H); **LRMS (CI)** (C₂₃H₂₄F₃N₃O : m/z 415) (m/z, %): 416 ([M+H]+, 100), 221 (48).

**N-(2-(1H-indol-3-yl)ethyl)-N-methylacrylamide (3e).** A solution of acryloyl chloride (1.1 equiv, 0.34 mL) in DCM (10 mL) was added dropwise to a solution of N-methyltryptamine (3.8 mmol, 662 mg) and Et₃N (1.5 equiv, 0.79 mL) in DCM (20 mL) at 0 °C during 30 min. The reaction mixture was quenched with NaHCO₃ (sat.), the organic layer was washed with brine, dried (MgSO₄), concentrated and applied to a column of silica gel as a solution in DCM. Elution with DCM / Et₂O 4:1 (Rf ~ 0.35) afforded pure 3e 700 mg (81%). (mixture of rotamers ~ 6 / 4) **¹H NMR** (CDCl₃, 400 MHz): δ 8.08-8.26 (m, 1H), 7.70 (d, 0.4H, J = 7.8 Hz), 7.59 (d, 0.6H, J = 7.8 Hz), 7.36-7.41 (m, 1H), 7.12-7.26 (m, 2H), 7.07 (d, 0.4H, J = 2.0 Hz), 6.98 (d, 0.6H, J = 2.0 Hz), 6.60 (dd, 0.4H, J₁ = 10.4 Hz, J₂ = 16.8 Hz), 6.33-6.42 (m, 1H), 6.23 (dd, 0.6H, J₁ = 2.1 Hz, J₂ = 16.8 Hz), 5.71 (dd, 0.4H, J₁ = 2.1 Hz, J₂ = 10.4 Hz), 5.50 (dd, 0.6H, J₁ = 2.1 Hz, J₂ = 10.4 Hz), 3.75-3.81 (m, 0.8H), 3.66-3.71 (m, 1.2H), 3.01-3.11 (m, 5H); **LRMS (CI)** (C₁₄H₁₆N₂O : m/z 228) (m/z, %): 229 ([M+H]+, 100), 143 (27).

**N-(2-(1H-indol-3-yl)ethyl)-N,3-dimethylbut-2-en-1-amine (3f).** Et₃N (2 equiv, 0.83 mL) in THF (5 mL) was added dropwise to a solution of N-methyltryptamine (3 mmol, 523 mg) and prenyl bromide (1.5 equiv, 0.53 mL) in THF (12 mL) at 0 °C. Upon completion of the addition the reaction mixture was allowed to warm up to RT during 1 h and was
poured into H$_2$O. The product was extracted with EtOAc, the organic layer was washed with brine, dried (Na$_2$SO$_4$), concentrated and applied to a column of silica gel as a solution in DCM. Elution with DCM / MeOH / NH$_3$ (aq.) 150:15:1 (R$_f$ ~ 0.34) afforded pure 3f 338 mg (46%). \textsuperscript{1}H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.04 (bs, 1H), 7.60 (d, 1H, J = 7.8 Hz), 7.35 (d, 1H, J = 7.8 Hz), 7.15-7.21 (m, 1H), 7.08-7.13 (m, 1H), 7.02 (s, 1H), 5.28-5.35 (m, 1H), 3.12 (d, 2H, J = 6.6 Hz), 2.96-3.03 (m, 2H), 2.73-2.79 (m, 2H), 2.38 (s, 3H), 1.75 (s, 3H), 1.66 (s, 3H); LRMS (CI) (C$_{16}$H$_{22}$N$_2$ : m/z 242) (m/z, %) : 243 ([M+H]$^+$, 100).
$^1$H and $^{13}$C spectra.

$^1$H NMR (CDCl$_3$, 400 MHz)

(~ 1:1 mixture of rotamers)
(~ 1:1 mixture of rotamers)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
\textsuperscript{1}H NMR (DMSO-\textsubscript{d6}, 400 MHz, 327 K)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{1}$H NMR (DMSO-$d_6$, 400 MHz)
$^{13}\text{C NMR}$ (DMSO-$d_6$, 100 MHz)}
endo-2c

$^1$H NMR (CDCl$_3$, 400 MHz)
\textit{endo-2c}

$^{13}\text{C NMR}$ (CDCl$_3$, 100 MHz)
exo-2c

$^1$H NMR (DMSO-$d_6$, 400 MHz)
exo-2c

$^{13}$C NMR (DMSO-$d_6$, 100 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)

2d
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (DMSO-$d_6$, 100 MHz, 363 K)
$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^1$H NMR (DMSO-$d_6$, 400 MHz, 363 K)
$^{13}$C NMR ($\text{CDCl}_3, 75 \text{ MHz}$)
$\text{^13C NMR (DMSO-}d_6, 100 \text{ MHz)}$
$^{1}H$ NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{13}$C NMR (DMSO-$d_6$, 100 MHz)