Synthesis of Indolo[2,1-*a*][2]benzazepine and Indolo[2,1-*a*][2]-benzazocine

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Abstract: The synthesis of functionalised 6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepine and 5,6,7,8-tetrahydroindolo[2,1-*a*][2]benzazocine from methyl 2-bromo-3-cyclohexyl-1*H*-indole-6-carboxylate, involving RCM as the key step to generate the tetracyclic indolo[2,1-*a*][2]benzazepine and indolo[2,1-*a*][2]benzazocine core structure, is outlined.

Key words: hepatitis C, HCV NS5B polymerase inhibitor, 5,6,7,8-tetrahydroindolo[2,1-*a*][2]benzazocine, 6,7-dihydro-5*H*-indolo[2,1-*a*]benzazepine, ring-closing metathesis

Recent research identified substituted 5,6,7,8-tetrahydroindolo[2,1-*a*][2,5]benzodiazocines (**1**) and 6,7-dihydro-5*H*-indolo[1,2-*d*][1,4]benzodiazepines (**2**) as novel RNA-dependent RNA polymerase inhibitors of hepatitis C virus (HCV)[1] (Figure 1).

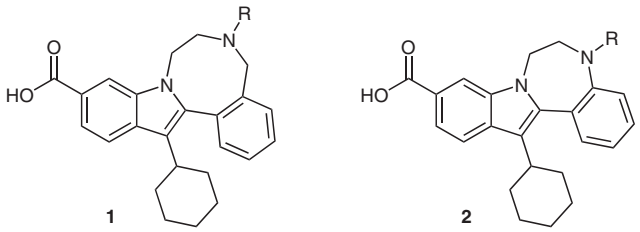

Figure 1 5,6,7,8-Tetrahydroindolo[2,1-*a*][2,5]benzodiazocines (**1**) and 6,7-dihydro-5*H*-indolo[1,2-*d*][1,4]benzodiazepines (**2**)

In the process of carrying out structure–activity relationship studies we became interested in the preparation of functionalized 6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepines and 5,6,7,8-tetrahydroindolo[2,1-*a*][2]benzazocines (**3**–**6**, Figure 2).

Earlier research had addressed the tethering via alkylation processes and cyclisation via aromatic cross-coupling or via Buchwald–Hartwig coupling to construct the indole[2–7] (Scheme 1). However, all of these methods leave an unfunctionalised alkyl chain as tethering group.

Therefore, we chose to construct the tether between the indole nitrogen and the aryl group via a ring-closure metathesis leaving a double bond. This approach allowed for the functionalisation of the positions of interest and gave access to the tetracyclic indolobenzazocines **3**–**6a** and indolobenzazepines **3b**–**d**, **4b**,**c**, **5b**–**d**, **6b**,**c**).

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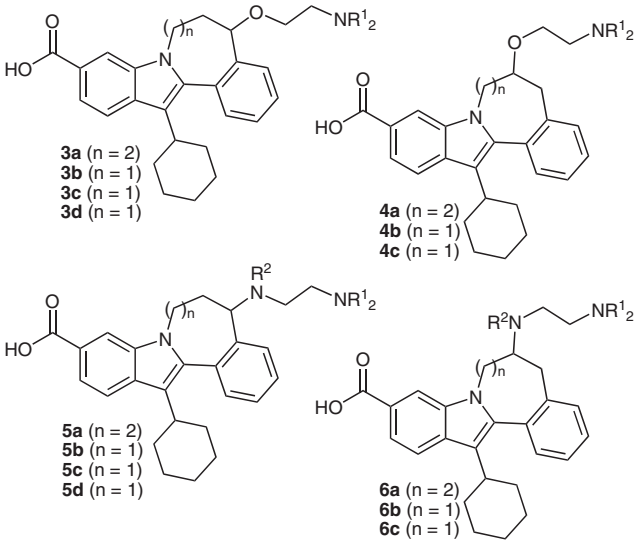
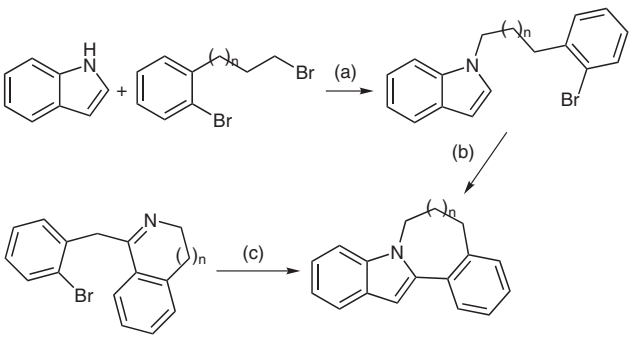
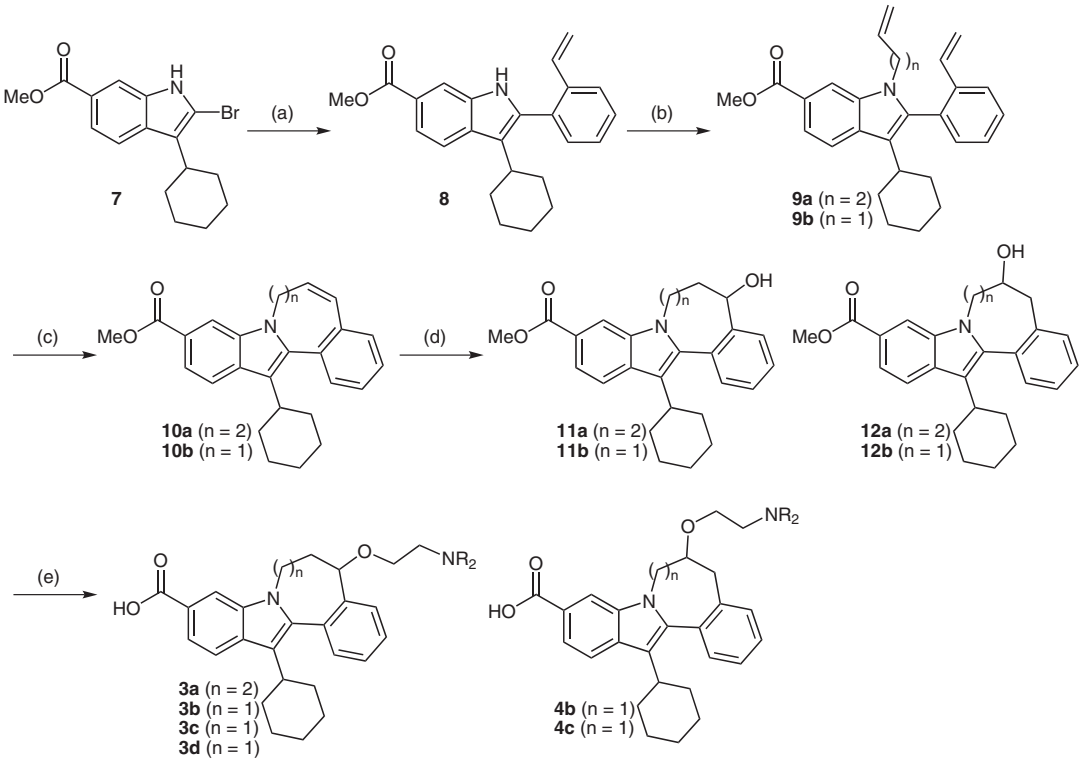


Figure 2 6,7-Dihydro-5*H*-indolo[2,1-*a*][2]benzazepines and 5,6,7,8-tetrahydroindolo[2,1-*a*][2]benzazocines



Scheme 1 *Reagents and conditions*: (a) KOH, DMSO; (b) $Pd(PPh_3)_4$, KOAc, DMA, reflux; (c) $Pd_2(dba)_3$, SIPr, NaO*t*-Bu, toluene.

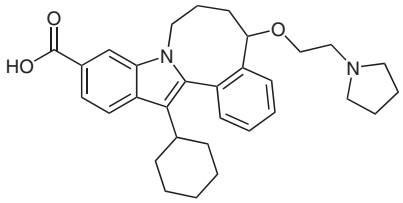
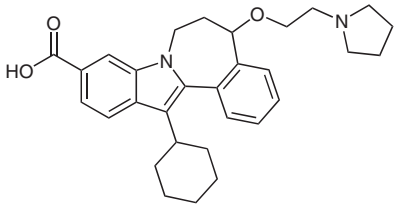
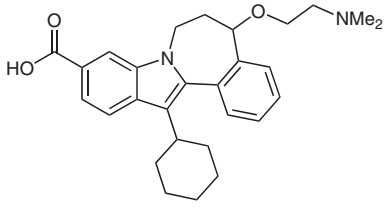
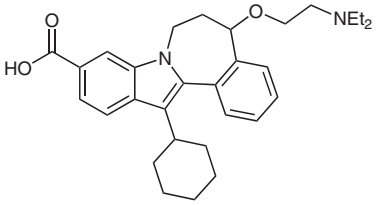
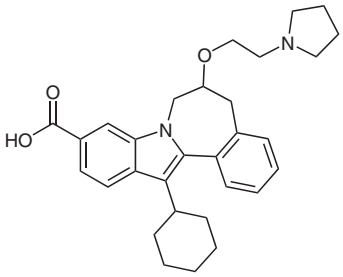
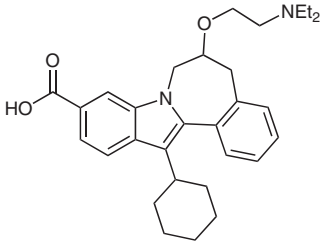
To this end methyl 3-cyclohexyl-2-(2-vinylphenyl)-1*H*-indole-6-carboxylate (**8**) was prepared from methyl 2-bromo-3-cyclohexyl-1*H*-indole-6-carboxylate (**7**) by Suzuki[8] reaction with 2-vinylbenzene boronic acid. This was followed by N-alkylation with 4-bromo-1-butene or allylbromide to furnish the intermediates **9a** and **9b** in excellent yield (Scheme 2). Treatment of **9a**,**b** with Zhannan catalyst I[9] in dichloromethane resulted in a clean cyclisation to **10a**,**b**. In the benzazepine series hydroboration followed by oxidative workup yielded a 4:1 mixture of **11b** and the isomeric homobenzylic alcohol **12b**, while in the benzazocine series only benzylic alcohol **11a** was formed. Products of type **3** and **4** were readily obtained by direct



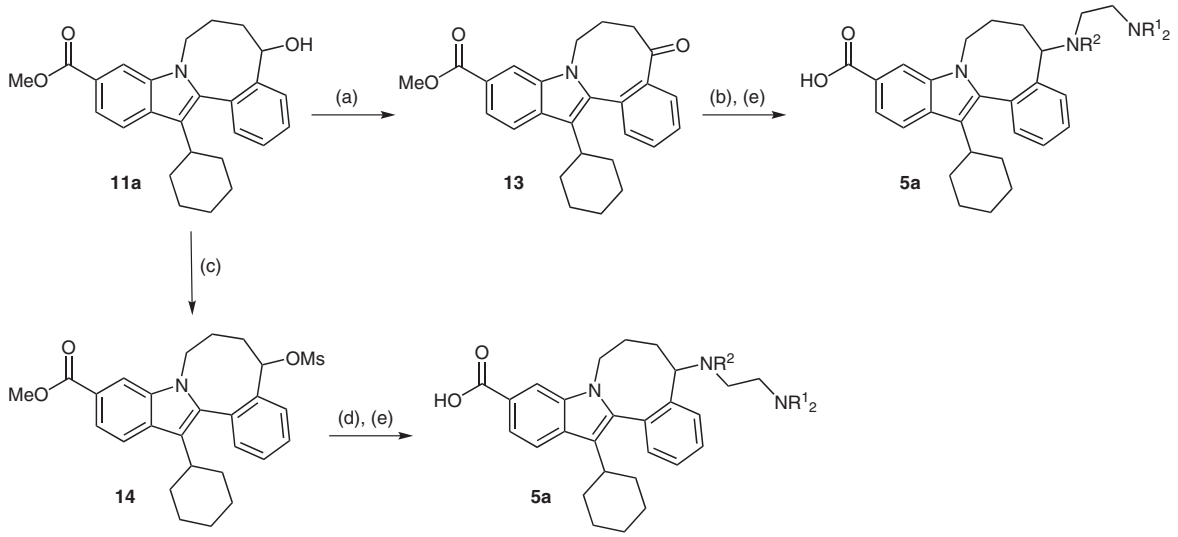
Scheme 2 *Reagents and conditions*: (a) 2-vinylbenzene boronic acid, $PdCl_2(PPh_3)_2$, 2 M Na_2CO_3, dioxane, 110 °C, 91%; (b) NaH, 4-bromo-1-butene, DMF, 40 °C, 60% or NaH, allylbromide, DMF, r.t., 98%; (c) Zhannan catalyst I, CH_2Cl_2, 35 °C, 68–84%; (d) BH_3·DMS, THF, then (3 N) NaOH, H_2O_2, 0 °C; (e) NaOH (40%), TBAB, toluene, *N*,*N*-dialkylamino ethyl chloride, 70 °C.

alkylation of the benzylic and homobenzylic alcohols **11** and **12** (Scheme 2). The yields obtained for the last two steps are reported in Table 1.

Table 1 Synthesis of Compounds **3** and **4**[13]

Compd	Structure[a]	Yield (%)[b]
3a (n = 2)		63
3b (n = 1)		29
3c (n = 1)		18
3d (n = 1)		49
4b (n = 1)		42
4c (n = 1)		18

[a] All compounds were obtained as a racemic mixture.
[b] Yield for steps d,e for compounds obtained as TFA salts after HPLC purification.



Scheme 3 *Reagents and conditions*: (a) DMP, CH_2Cl_2, quant.; (b) amine, $NaBH(OAC)_3$, DCE, r.t. to 50 °C or $TiCl_4$, $NaCNBH_3$, MeOH; (c) MsCl, Et_3N, CH_2Cl_2, quantit. as crude; (d) amine, CH_2Cl_2; (e) 1 M KOH, dioxane, 70 °C.

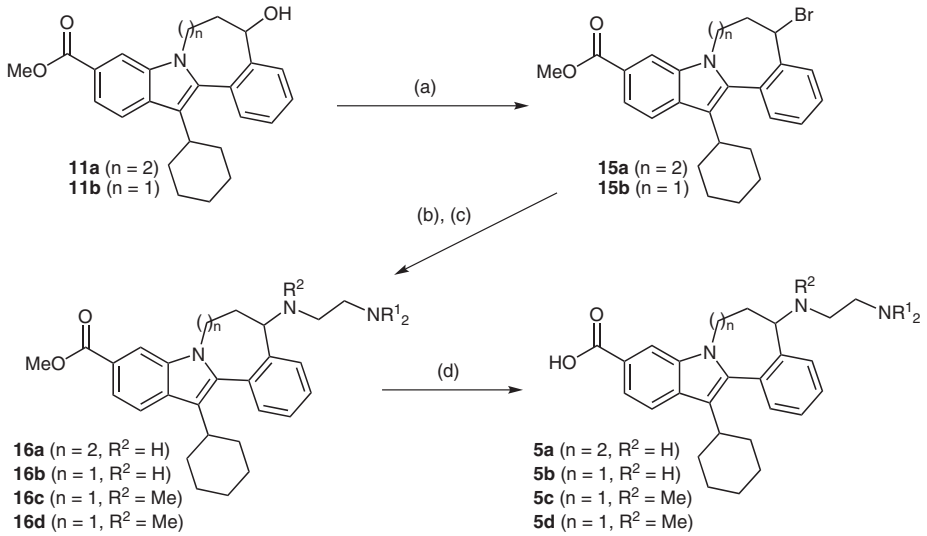
To access the benzylic amine analogues **5** the benzylic alcohol **11a** was oxidised with DMP in dichloromethane yielding the corresponding ketone **13** (Scheme 3).

Surprisingly, this ketone did not react with selected amines under any reductive amination conditions attempted (Scheme 3). Also the approach via the treatment of the alcohol **11a** with mesyl chloride and triethylamine in dichloromethane followed by nucleophilic displacement with the selected amine was not successful. This was due to the instability of the mesylate **14** which underwent facile elimination to **10a**.

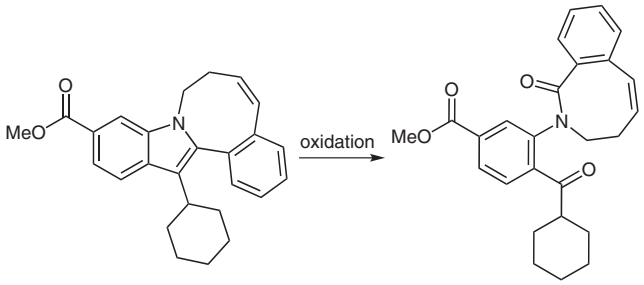
To resolve this issue the benzylic alcohols **11a**,**b** were brominated with phosphorus tribromide and the resulting bromides **15a**,**b** were reacted with different amines (Scheme 4). A subsequent reductive amination with formaldehyde gave products **16a–d** (Scheme 4). Hydrolysis of the methyl ester was achieved by heating at 70 °C in 1 M KOH. The results obtained are reported in Table 2.

To gain reasonable access to the homobenzylic alcohols, both in the benzazepine and the benzazocine series, an alternative approach needed to be developed.

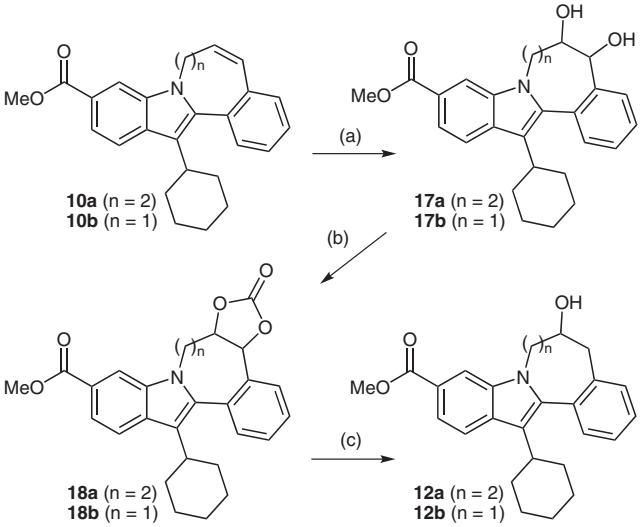
First attempts to access the homobenzylic alcohols **12a**,**b**, either via the bromohydrin[10] or by inducing regioselectivity in the hydroboration step[11] using a bulky borane were unsuccessful. Also the approach to form the epoxide using MCPBA in chloroform failed, giving rise to opening of the indole ring (Scheme 5). We observed this same side reaction under various oxidative conditions [e.g., CrO_3(pyridine)$_3$; SeO_2, *t*-BuOOH; $CuCl_2{\cdot}2H_2O$, *t*-BuOOH, O_2; $Pd(OH)_2$/C, K_2CO_3, *t*-BuOOH; CrO_3, 3,5-DMP, *t*-BuOOH]. To circumvent this problem we decided to proceed via the treatment of alkene (**10a**,**b**) with osmium tetroxide in THF–acetone–water to access diols **17a** and **17b**. These intermediates opened the route to the cyclic carbonates **18a** and **18b** obtained by reaction with triphosgene and triethylamine in dichloromethane.[12] The



Scheme 4 *Reagents and conditions*: (a) PBr_3, CH_2Cl_2, 0 °C to r.t.; (b) *N*,*N*-dialkyl ethylenediamine, MeCN, 55 °C; (c) HCHO, AcOH, $NaCNBH_3$, CH_2Cl_2; (d) 1 M KOH, dioxane, 70 °C.



Scheme 5 Oxidative ring opening



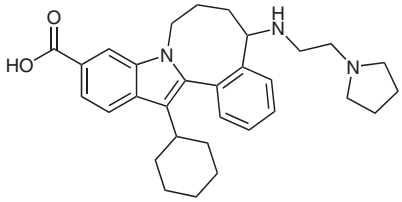
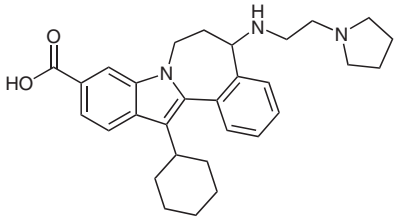
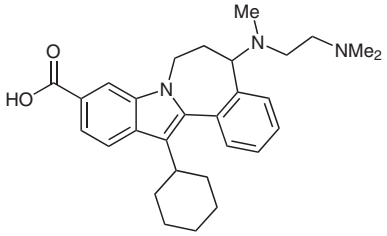
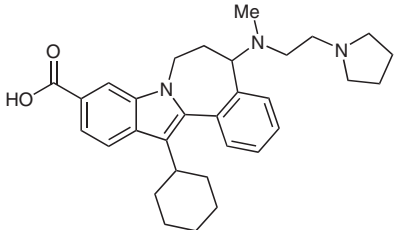
Scheme 6 *Reagents and conditions*: (a) NMO, OsO_4 (4% wt in H_2O), acetone–THF–H_2O; (b) Et_3N, $CO(OCCl_3)_2$, CH_2Cl_2, –50 °C to r.t.; (c) H_2, Raney/Ni, acetone–MeOH, quant. as crude for steps a–c.

Raney nickel mediated reduction of the cyclic carbonate gave access to the homobenzylic alcohols **12a**,**b** in a very clean fashion (Scheme 6). Products of type **4a**[16] were readily obtained by direct alkylation of the homobenzylic alcohol **12a** (Scheme 7).

To gain access to the amine analogues of the type **6b**,[15] which could not be obtained by nucleophilic displacement of the corresponding bromide as was possible in the case of benzylic analogues, the homobenzylic alcohol **12b** was oxidised with DMP in dichloromethane (Scheme 8).

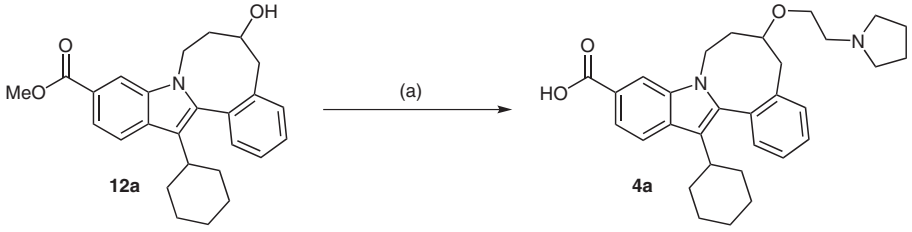
The ketone **19** was treated with the selected amine in reductive amination conditions. After base-mediated (1 M KOH) hydrolysis the desired acid **6b** was efficiently obtained (Scheme 8).

Table 2 Synthesis of Compounds **5**[14]

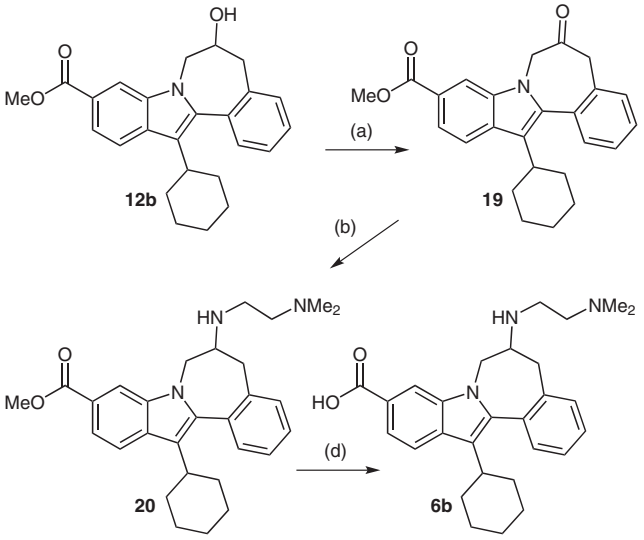
Compd	Structure[a]	Yield (%)[b]
5a (n = 2)		53
5b (n = 1)		24
5c (n = 1)		49
5d (n = 1)		29

[a] All compounds were obtained as a racemic mixture.
[b] Yield for steps a–d for compounds obtained as TFA salts after HPLC purification.

In summary, we have reported a novel synthesis of two scaffolds, 6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepines and 5,6,7,8-tetrahydroindolo[2,1-*a*][2]benzazocines applying a highly efficient ring-closure metathesis reaction. As shown, this new approach allowed the wide and facile functionalisation both in the benzylic and the homobenzylic positions. In order to do so, two main synthetic strategies were successfully employed. The versatility of the double bond installed via RCM creates a synthetic advantage and makes our synthesis a favourable and interesting alternative to other ways.



Scheme 7 *Reagents and conditions*: (a) NaOH (40%), TBAB, toluene, 1-(2-chloroethyl)pyrrolidine, 70 °C.



Scheme 8 *Reagents and conditions*: (a) DMP, CH_2Cl_2, 0 °C to r.t.; (b) *N*,*N*-dimethyl ethylenediamine, AcOH, $NaCNBH_3$, DCE; (c) 1 M KOH, dioxane, 70 °C, 31% for steps a–c.

References and Notes

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(13) **Typical Procedure for Compounds 3a–d, 4b,c**
Methyl 2-bromo-3-cyclohexyl-1*H*-indole-6-carboxylate (**7**) and (2-vinylphenyl)boronic acid (1.5 equiv) were dissolved in dioxane (0.07 M) and 2 M aq Na_2CO_3 (6 equiv) was added. The soln was degassed by bubbling argon, $Pd(PPh_3)_2Cl_2$ (0.2 equiv) was added, and the reaction mixture was refluxed for 1 h; after cooling, EtOAc was added, and the solution washed with H_2O and brine, dried over Na_2SO_4 and concentrated in vacuo. Methyl 3-cyclohexyl-2-(2-vinylphenyl)-1*H*-indole-6-carboxylate (**8**) was isolated by chromatography (PE–EtOAc); yield 91%. To a 0.3 M soln of methyl 3-cyclohexyl-2-(2-vinylphenyl)-1*H*-indole-6-carboxylate (**8**) in dry DMF, 60% NaH (1.5 equiv) in mineral oil was added at 0 °C, after 1 h allyl bromide (1.5 equiv) or 4-bromo-1-butene (2 equiv) were added, and the suspension was stirred at r.t. for 2 h or at 40 °C for 5 h. The mixture was diluted with EtOAc, washed with 1 N HCl, H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo to give methyl 1-allyl-3-cyclohexyl-2-(2-vinylphenyl)-1*H*-indole-6-carboxylate (**9b**, 98%) or methyl 1-buten-3-en-1-yl-3-cyclohexyl-2-(2-vinylphenyl)-1*H*-indole-6-carboxylate (**9a**, 60%). Methyl 1-allyl-3-cyclohexyl-2-(2-vinylphenyl)-1*H*-indole-6-carboxylate (**9b**) or methyl 1-buten-3-en-1-yl-3-cyclohexyl-2-(2-vinylphenyl)-1*H*-indole-6-carboxylate (**9a**) were dissolved in CH_2Cl_2 (0.02 M) and treated with Zhannan catalyst I (0.3 equiv) at 35 °C for 1 h. After removal of solvent the residue was purified by chromatography (PE–EtOAc) to afford methyl 13-cyclohexyl-7*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**10b**) or methyl 14-cyclohexyl-7,8-dihydroindolo[2,1-*a*][2]benzazocine-11-carboxylate (**10a**) in 84% and 80% yield. $BH_3{\cdot}SMe_2$ (1.6 equiv, 2 M soln in THF) was added to a 0.2 M solution of methyl 13-cyclohexyl-7*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**10b**) in THF or methyl 14-cyclohexyl-7,8-dihydroindolo[2,1-*a*][2]benzazocine-11-carboxylate (**10a**), and the mixture was stirred for 2 h at r.t.; 3 M aq NaOH (3 equiv) and 35% H_2O_2 (3 equiv) were added at 0 °C, and stirring was continued overnight at r.t. After dilution with sat. $NaHCO_3$ the aqueous phase was extracted with EtOAc, the organic phase was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo to give a 4:1 mixture of methyl 13-cyclohexyl-5-hydroxy-6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**11b**) and methyl 13-cyclohexyl-6-hydroxy-6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**12b**) or methyl 14-cyclohexyl-5-hydroxy-5,6,7,8-tetrahydroindolo[2,1-*a*][2]benzazocine-11-carboxylate (**11a**). The foregoing crude was dissolved in toluene (20 mL/mmol), 40% aq NaOH (15 equiv) and TBAB (0.25 equiv) were added, and the mixture was stirred for 30 min. Selected dialkylaminoethyl chloride (3 equiv) was then added and the resulting mixture heated at 70 °C for 1 d; evaporation to dryness gave a residue which was purified by RP-HPLC to give products **3a–d**, **4b,c**.

Selected Data for 3a

^{1}H NMR (TFA salt, 400 MHz, DMSO-d_6, 300 K): δ = 1.16–2.30 (20 H, m), 2.61–2.72 (1 H, m), 2.93–3.05 (2 H, m), 3.15–3.30 (3 H, m), 3.41–3.52 (2 H, m), 3.78 (1 H, d, *J* = 9.0 Hz), 4.40–4.45 (1 H, m), 7.38 (1 H, d, *J* = 7.4 Hz), 7.47–7.50 (1 H, m), 7.62–7.71 (3 H, m), 7.85 (1 H, d, *J* = 8.3 Hz), 8.07 (1 H, s), 9.31 (1 H, br s), 12.59 (1 H, br s). MS (ES$^+$): *m/z* = 487 [M + H]$^+$.

Selected Data for 3d

^{1}H NMR (TFA salt, 400 MHz, DMSO-d_6, 300 K): δ = 0.58–0.67 (1 H, m), 0.79–0.82 (1 H, m), 1.16–1.23 (6 H, m), 1.38–1.49 (2 H, m), 1.58–2.06 (8 H, m), 2.62–2.90 (3 H, m), 3.05–3.80 (7 H, m), 4.23–4.28 (1 H, m), 4.58–4.71 (1 H, m), 7.43–7.64 (5 H, m), 7.83–7.87 (1 H, d, *J* = 8.4 Hz), 8.13 (1 H, s). MS (ES$^+$): *m/z* = 475 [M + H]$^+$.

(14) **Typical Procedure for Compounds 5a–d**
Phosphorus tribromide (0.5 equiv) was added at 0 °C to a 0.2 M soln of methyl 13-cyclohexyl-5-hydroxy-6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**11b**) or methyl 14-cyclohexyl-5-hydroxy-5,6,7,8-tetrahydroindolo-[2,1-*a*][2]benzazocine-11-carboxylate (**11a**) in CH_2Cl_2, and the mixture was stirred at r.t. for 2 h. The reaction mixture

was diluted with EtOAc, washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo to give methyl 5-bromo-13-cyclohexyl-6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**15b**) or methyl 5-bromo-14-cyclohexyl-5,6,7,8-tetrahydroindolo[2,1-*a*][2]benzazocine-11-carboxylate (**15a**) that were dissolved in MeCN and treated with the selected *N*,*N*-dialkylethylenediamine (8 equiv) at 55 °C for 3 h; evaporation in vacuo to dryness gave crude products **16a**,**b**, an amount of which was dissolved in CH_2Cl_2 and pH adjusted to 6 with AcOH; 37% aq HCHO and $NaCNBH_3$ (3 equiv, after 30 min) were added, and the mixture was stirred at r.t. overnight. The reaction mixture was diluted with EtOAc and washed with 1 N NaOH and brine, dried, and evaporated affording compounds **16c**,**d**. Hydrolysis of the foregoing methyl esters was done with 1 M aq KOH (6 equiv) in dioxane (0.1 M) at 60 °C; the reaction was complete in 2 h, and the title compounds **5a**–**d** were obtained after RP-HPLC purification.

Selected Data for 5b

^{1}H NMR (TFA salt, 400 MHz, DMSO-d_6, 300 K): δ = 1.15–1.77 (7 H, m), 1.90–2.17 (10 H, m), 2.78–2.91 (2 H, m), 3.40–3.59 (7 H, m), 4.11–4.16 (1 H, m), 4.75–4.81 (1 H, m), 7.51–7.66 (5 H, m), 7.92 (1 H, d, *J* = 8.5 Hz), 8.20 (1 H, s). MS (ES$^+$): *m/z* = 472 [M + H]$^+$.

Selected Data for 5d

^{1}H NMR (TFA salt, 400 MHz, DMSO-d_6, 300 K): δ = 1.16–1.77 (8 H, m), 1.80–2.11 (8 H, m), 2.19–2.31 (2 H, m), 2.61–2.87 (5 H, m), 2.98–3.41 (7 H, m), 4.54–4.66 (1 H, m), 7.42 (1 H, d, *J* = 8.1 Hz), 7.47–7.54 (2 H, m), 7.63 (1 H, d, *J* = 8.3 Hz), 7.69–7.75 (1 H, m), 7.86 (1 H, d, *J* = 8.3 Hz), 8.12 (1 H, s). MS (ES$^+$): *m/z* = 486 [M + H]$^+$.

(15) **Typical Procedure for Compounds 6b**

A soln (0.11 M) of methyl 13-cyclohexyl-7*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**10b**) in acetone–THF–H_2O (1:1:1) was treated with *N*-methylmorpholine-*N*-oxide (1.2 equiv), followed by OsO_4 (4% wt in H_2O; 0.1 equiv) and left stirring at r.t. overnight. The clear soln was then treated with 10% wt Na_2SO_3 and left stirring for 30 min, then diluted with H_2O, and extracted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4, and evaporated in vacuo to give methyl 13-cyclohexyl-5,6-dihydroxy-6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**17b**). A soln (0.05 M) of methyl 13-cyclohexyl-5,6-dihydroxy-6,7-dihydro-5*H*-indole[2,1-*a*][2]benzazepine-10-carboxylate (**17b**) in CH_2Cl_2 was treated with Et_3N (4 equiv), and cooled to –50 °C. Triphosgene (0.4 equiv) was added, and the soln was allowed to warm to r.t. over 30 min. After 2 h at r.t., sat. $NaHCO_3$ was added and the solution extracted with EtOAc. The organic phase was washed with H_2O, brine, dried over Na_2SO_4, and evaporated in vacuo to leave methyl 10-cyclohexyl-2-oxo-3a,14b-dihydro-4*H*-[1,3]dioxolo[4,5-*d*]indolo[2,1-*a*][2]benzazepine-7-carboxylate (**18b**). A solution (0.02 M) of methyl 10-cyclohexyl-2-oxo-3a,14b-dihydro-4*H*-[1,3]dioxolo[4,5-*d*]indolo[2,1-*a*][2] benzazepine-7-carboxylate (**18b**) in acetone–MeOH (3:1) was treated with Raney-Ni (slurry in H_2O), and the vigorously stirred reaction mixture was hydrogenated at 1 atm H_2. After 48 h the solid was filtered and the filtrates evaporated in vacuo to leave the clean methyl 13-cyclohexyl-6-hydroxy-6,7-dihydro-5*H*-indolo[2,1-*a*] [2]benzazepine-10-carboxylate (**12b**). A solution (0.05 M) of methyl 13-cyclohexyl-6-hydroxy-6,7-dihydro-5*H*-indolo[2,1-*a*][2] benzazepine-10-carboxylate (**12b**) in CH_2Cl_2 was treated with DMP (1.3 equiv) at 0 °C and left warming to r.t. and then stirred for 2 h under nitrogen. The solution was then diluted with EtOAc and washed with sat. $NaHCO_3$, H_2O, brine, dried over Na_2SO_4, and evaporated in vacuo to afford methyl 13-cyclohexyl-6-oxo-6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**19**). The crude material was dissolved in DCE (0.05 M), 2-dimethylaminoethylamine was added, the pH adjusted to 6 with AcOH, and the soln left stirring for 30 min. $NaBH(OAc)_3$ was added, and the soln was left stirring at r.t. overnight. After diluting with EtOAc, the organic phase was washed with NaOH (1 N), H_2O, brine, dried over Na_2SO_4, and evaporated in vacuo to afford methyl 13-cyclohexyl-6-{[2-(dimethylamino)ethyl]amino}-6,7-dihydro-5*H*-indolo[2,1-*a*][2]benzazepine-10-carboxylate (**20**). Hydrolysis of the foregoing methyl ester was done with 1 M aq KOH (6 equiv) in dioxane (0.1 M) at 60 °C; the reaction was complete in 2 h, and the title compound was obtained after RP-HPLC purification.

Selected Data for 6b

^{1}H NMR (TFA salt, 400 MHz, DMSO-d_6, 300 K): δ = 1.16–1.59 (4 H, m), 1.61–2.12 (6 H, m), 2.74–2.98 (8 H, m), 3.12–3.43 (7 H, m), 4.69–4.73 (1 H, m), 7.49–7.58 (4 H, m), 7.67–7.73 (1 H, m), 7.90–7.93 (1 H, m), 8.24 (1 H, br s). MS (ES$^+$): *m/z* = 446.4 [M + H]$^+$.

(16) **Typical Procedure for Compounds 4a**

Methyl 14-cyclohexyl-6-hydroxy-5,6,7,8-tetrahydroindolo[2,1-*a*][2]benzazocine-11-carboxylate (**12a**), prepared as its seven-membered ring analogue as reported above, was dissolved in toluene (20 mL/mmol), 40% aq NaOH (15 equiv), and TBAB (0.25 equiv) were added, and the mixture was stirred for 30 min. 1-(2-chloroethyl)-pyrrolidine (3 equiv) was then added and the resulting mixture heated at 70 °C for 1 d; evaporation to dryness gave a residue which was purified by RP-HPLC to give product **4a**; yield 23% from the alkene **10a**.

Selected Data for 4a

^{1}H NMR (TFA salt, 400 MHz, DMSO-d_6, 300 K): δ = 1.16–1.39 (3 H, m), 1.43–1.58 (2 H, m), 1.64–1.75 (2 H, m), 1.82–2.18 (9 H, m), 2.18–2.34 (1 H, m), 2.57–2.68 (1 H, m), 2.99–3.11 (3 H, m), 3.12–3.29 (2 H, m), 3.50–3.65 (4 H, m), 3.73–3.94 (2 H, m), 4.26–4.45 (1 H, m), 7.31–7.56 (4 H, m), 7.66–7.68 (1 H, d, *J* = 8.4 Hz), 7.86–7.88 (1 H, d, *J* = 8.4 Hz), 8.08 (1 H, s). MS (ES$^+$): *m/z* = 487 [M + H]$^+$.