Synthesis of Cyclopenta[*b*]indol-1-ones and Carbazol-4-ones from *N*-(2-Halophenyl)-Substituted Enaminones by Intramolecular *Heck* Reaction

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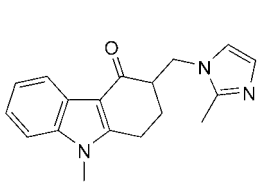
An efficient synthetic route towards *N*-methylated or nonmethylated 3,4-dihydrocyclopent[*b*]indol-1(2*H*)-ones (**3**) and 1,2,3,9-tetrahydrocarbazol-4(4*H*)-one (**10**) was elaborated, based on Pd-catalyzed intramolecular *Heck* reaction. The chemoselectivity of the cyclization was studied in the case of the bi- and trifunctional substrates **12** and **17**, respectively. In the latter case, depending on the catalyst, either the brominated indole **18** or the tetracyclic compound **19** were obtained by single and double *Heck* reaction, respectively.

Introduction. – A group of serotonin (5-HT_3) receptor antagonists are structurally based on the tricyclic carbazolone ring system. Examples of this class of neuroactive compounds are ondansetron (**1**) and alosetron (**2**) [1], developed as an antiemetic and a treatment of the so-called *irritable bowel syndrome* (IBS), respectively.



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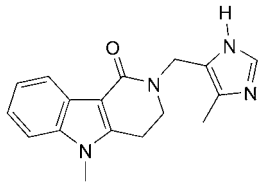

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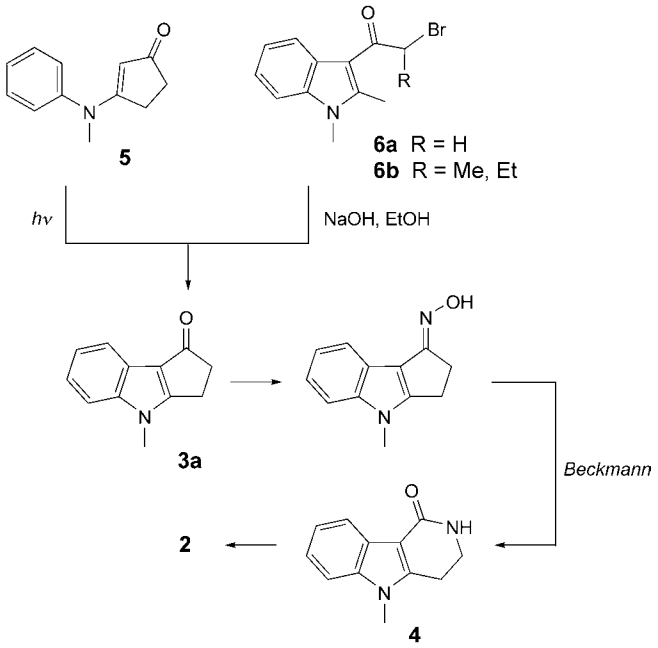
Ondansetron (**1**) contains a hex-2-enone ring, but the key intermediate in a synthesis of **2** is the cyclopenta[*b*]indol-1(2*H*)-one (**3a**), which, by *Beckmann* rearrangement, can be converted into the 'lactam' **4**, which, in several steps, can be further modified to give **2** (*Scheme 1*) [1c].

We were particularly interested in the preparation of 3,4-dihydro-4-methylcyclopental[*b*]indol-1(2*H*)-one (**3a**). Previously described syntheses of **3a** gave only low yields, and were mostly based on photochemical activation [1c][2] or the *Fischer* indole synthesis [1c]. Thus, cyclization of **5** under UV light for 4 d gave **3a** in 40% yield (*Scheme 1*) [2]. Base-promoted intramolecular alkylation of indole **6a** has also been reported to give **3a**, but only in 4% isolated yield, in contrast to the sterically hindered **6b**, which gave much higher yields of **3a** (*Scheme 1*) [3]. Furthermore, carbazolones and carbolines (azacarbazoles) have been prepared from *N*-(2-haloaryl)-substituted enaminones by palladium catalyzed cyclization [4] and by a coupling entirely promoted by equivalent or excess amounts of CuI [5].

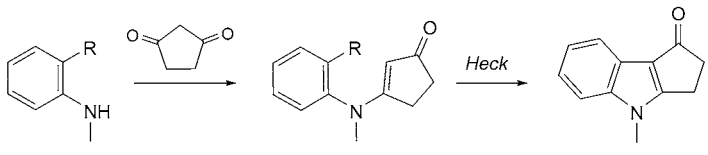
Scheme 1



Due to the limited success reported for the preparation of **3a**, we were looking for a more-efficient synthesis.

Results and Discussion. – Our strategy was to use an intramolecular *Heck* reaction, starting with substrates of type **7**, in which a bond is formed between the *ortho*-halogenated C-atom and the enone ring (*Scheme 2*).

Scheme 2



From *N*-methyl-2-iodoaniline (**8a**) [6] and commercially available cyclopentane-1,3-edione, the condensation product **7a** was synthesized by heating overnight without any solvent. The key synthetic step was the Pd-catalyzed cyclization of **7a** to **3a** in the presence of $Pd(OAc)_2$ (5 mol%) and tri(*o*-tolyl)phosphine ($(2\text{-}MeC_6H_4)_3P$) in DMF under microwave heating [7] (100°, 5 min) to afford, after column chromatography and recrystallization, 99% of **3a** (*Table*, *Entry 1*). Thus, a short and efficient synthesis of this key building block of alosetron (**2**) was obtained. However, further improvements

could be made if it was possible to replace the 2-iodoaniline **8a** with the much cheaper bromoaniline **8b** as the precursor of **7b** (*Scheme 2*). Unfortunately, the latter turned out to be less reactive in the above cyclization reaction (30% conversion to **3a** after 30 min; *Table*, *Entry 5*). However, upon conventional heating at 120° overnight, **3a** was isolated in 95% yield (*Entry 7*). In the case of the nonmethylated substrate **7c**, the reactivity was lower, leading to only 3% conversion after 30 min at 100° (*Entry 2*). However, upon increasing the amount of Pd catalyst as well as both the reaction time and temperature, **3b** could be isolated in 80% yield (*Entry 3*). For the corresponding bromo-substituted substrate **7d**, these conditions and a prolonged reaction time of 16 h were not sufficient to drive the reaction to completion (37% conversion; *Entry 8*). However, replacing $(2\text{-MeC}_6H_4)_3P$ with $(t\text{-Bu})_3P$ improved the yield to 85%, with only small amounts of remaining unreacted starting material (*Entry 9*). And in the presence of 1,3-bis(diphenylphosphino)propane (dppp), complete conversion and 92% isolated yield of **3b** were achieved (*Entry 10*).

Table. *Experimental Details for the Synthesis of* **3a**,**b** *by Pd-catalyzed*[a]) Heck *Reaction of* **7a**–**d**

7a–**d** **3a** R = Me **3b** R = H

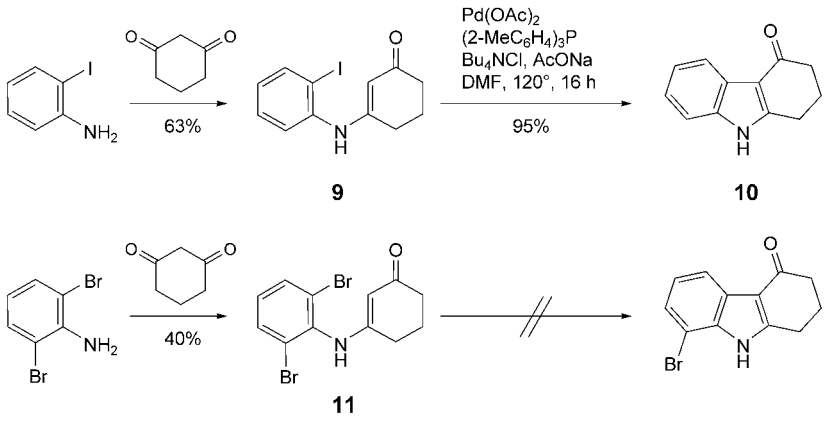
Entry	Substrate	R′	R	Reaction time	Temp. [°]	Heating	P-Ligand	Product	Yield [%]
1	**7a**	I	Me	30 min	100	Microwave	$(2\text{-MeC}_6H_4)_3P$	**3a**	99
2	**7c**	I	H	30 min	100	Microwave	$(2\text{-MeC}_6H_4)_3P$	**3b**	3[b])
3	**7c**	I	H	16 h	120	Oil bath	$(2\text{-MeC}_6H_4)_3P$	**3b**	80
4	**7c**	I	H	30 min	100	Microwave	dppp	**3b**	25[b])
5	**7b**	Br	Me	30 min	100	Microwave	$(2\text{-MeC}_6H_4)_3P$	**3a**	30[b])
6	**7b**	Br	Me	30 min	100	Microwave	dppp	**3a**	35[b])
7	**7b**	Br	Me	16 h	120	Oil bath	$(2\text{-MeC}_6H_4)_3P$	**3a**	95
8	**7d**	Br	H	16 h	120	Oil bath	$(2\text{-MeC}_6H_4)_3P$	**3b**	37[c])
9	**7d**	Br	H	16 h	120	Oil bath	$(t\text{-Bu})_3P$	**3b**	85
10	**7d**	Br	H	16 h	120	Oil bath	dppp	**3b**	92

[a]) For microwave and oil-bath experiments, 5 and 10 mol-% of catalyst were used, resp. [b]) Conversion into product (%) determined by ^{1}H-NMR of crude product. [c]) Separated from starting material by recrystallization (AcOEt).

After these successful results, we carried out experiments to extend the above procedure to the synthesis of carbazoles (*Scheme 3*). The cyclohex-2-enone **9**, formed by condensation of 2-iodoaniline and cyclohexane-1,3-dione, underwent cyclization cleanly to afford the carbazolone **10** in 95% yield. In contrast, compound **11** did, surprisingly, not give the desired product. Different methods were tested, but only starting material or side products could be isolated.

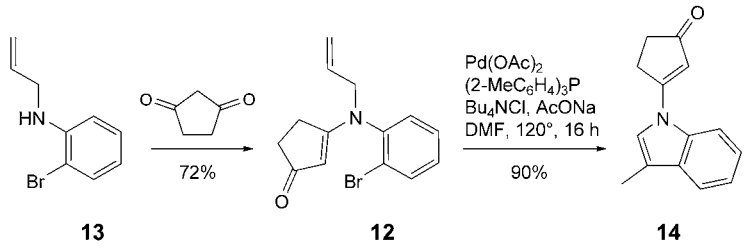
We were further interested in determining the selectivity of the *Heck* coupling with respect to different unsaturated systems. Thus compound **12**, containing the enone

Scheme 3



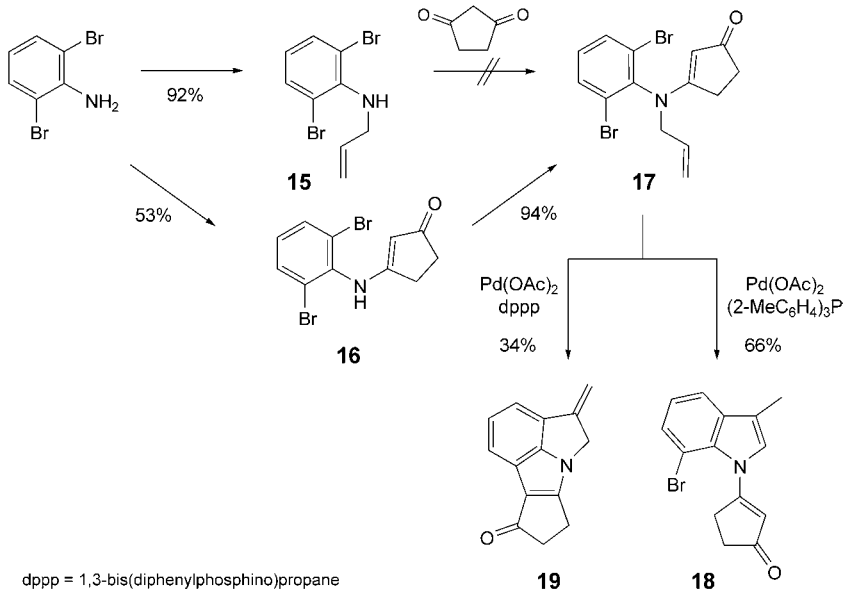
function as well as an *N*-allyl group, was synthesized from **13** and subjected to intramolecular *Heck* coupling (*Scheme 4*). Interestingly, **12** exclusively underwent intramolecular *endo*-cyclization with the allyl function to give indole **14** in excellent yield. Eventually, the higher electron density of the allyl group compared to the more-delocalized enone moiety could explain this interesting and highly chemoselective transformation.

Scheme 4



Extending the above observations to a 2,6-dibromo substituted analog, it should, in principle, be possible to achieve a multiple cyclization to the corresponding indole and the indol-1-one. Starting from 2,6-dibromoaniline, we first prepared **15**, which, however, gave only a black residue upon reaction with cyclopentane-1,3-dione (*Scheme 5*). However, when performing first the condensation with 2,6-dibromoaniline to give **16**, followed by *N*-alkylation with allylbromide, the desired substrate **17** could be prepared in 50% overall yield. Pd-catalyzed cyclization gave, after 16 h at 120°, compound **18** as the only major product, *i.e.*, only cyclization to the 3-methylindole had taken place, the second Br-atom being left unreacted in the presence of $(2\text{-MeC}_6\text{H}_4)_3\text{P}$. However, when dppp was used as phosphine ligand, a more-complex reaction was observed, and, apart from small amounts of **18**, the only product isolated was the tetracyclic compound **19**, the latter lacked the expected 3-methylindole moiety of **18**, and the presence of an exocyclic methylidene group was apparent. The structural

Scheme 5



assignment of **19** was supported by NOE, DEPT, ^{1}H-COSY, and C/H-correlation spectroscopy. We speculate that, in this case, the 3-methylindolyl moiety was initially formed and that the second cyclization then gave rise to a migration of the double bond to **19**.

The authors thank Mr. *Regis Denay* for the structural characterisation of **19**.

Experimental Part

General. Reagents and solvents were purchased from commercial sources and used without further purification, unless stated otherwise. Melting points (m.p.) were determined in open capillaries, uncorrected. Microwave irradiation was performed with a *MLS-Ethos-1600* instrument (*Milestone*). Column chromatography (CC) was performed on silica gel *60* (0.040–0.063 mm; *Merck*) or with prepacked *Flashpack* silica-gel columns (50 or 70 g; *Jones Chromatography Ltd.*, UK). Compounds were visualized by thin-layer chromatography (TLC; silica-gel *60* F_{254} plates; *Merck*) using UV light and $KMnO_4$ spraying reagent. ^{1}H- and ^{13}C-NMR spectra[1]): *Bruker*, at 400 or 100 MHz, resp. HR-MS: performed by the Analytics Department at *Novartis Pharma AG* (Basel) on an *Agilent Series 1100 LC/MSD* instrument; in *m/z*. Elemental analyses were performed by *Solvias AG*, Basel.

General Procedure 1 (*GP1*) *for the* N-*Alkylation of Anilines.* See the synthesis of **13** (below).

2-Bromo-N-*(prop-2-enyl)aniline* (**13**). *GP1:* 2-Bromoaniline (7.00 g, 40.7 mmol), dissolved in anh. THF (100 ml), was cooled to −78° under Ar. To the stirred mixture was slowly added a 1.6M soln. of MeLi in Et_2O (28.0 ml, 44.8 mmol), followed, after stirring for 30 min, by dropwise addition of allyl bromide (5.42 g, 44.8 mmol). The mixture was stirrred for 10 min at −78°, then 2 h at r.t. Then, aq. $NaHCO_3$ soln. was added, and the mixture was extracted with AcOEt (3×). The combined org. layer was dried ($MgSO_4$), filtered, and

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[1]) [1]) Note that the various (phenylamino)cyclopent-2-enone and (phenylamino)cyclohex-2-enone moieties gave rise to tautomerism (typically 1:9), and that the chemical shifts δ (in ppm rel. to $SiMe_4$) and the coupling constants *J* (in Hz) are stated for the most-abundant forms only.

concentrated *in vacuo*. The residue was purified by CC (0–5% AcOEt in hexane) to give **13** (7.13 g, 83%). Oil. ^{1}H-NMR ($CDCl_3$): 3.76–3.82 (*m*, 2 H); 4.45 (br. *s*, 1 H); 5.15–5.18 (*m*, 1 H); 5.23–5.29 (*m*, 1 H); 5.86–5.98 (*m*, 1 H); 6.50–6.61 (*m*, 2 H); 7.10–7.16 (*m*, 1 H); 7.37–7.42 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$) [8]: 46.1; 109.7; 111.5; 116.3; 117.8; 128.4; 132.3; 134.6; 144.7. ESI-MS: 314 (100, $[M+1]^+$).

N-*Methyl-2-bromoaniline* (**8b**). *GP1:* 5.43 g (84%). Oil. ^{1}H-NMR ($CDCl_3$): 5.40 (*s*, 3 H); 6.85 (br. *s*, 1 H); 9.06–9.18 (*m*, 2 H); 9.70–9.76 (*m*, 1 H); 9.92–10.0 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 33.5; 112.5; 113.6; 120.5; 131.5; 135.2; 148.9. ESI-MS: 187 (20, $[M+1]^+$).

2,6-Dibromo-N-*(prop-2-enyl)aniline* (**15**). *GP1:* 6.41 g (92%). Oil. ^{1}H-NMR ($CDCl_3$): 3.86–3.91 (*m*, 2 H); 3.98 (br. *s*, 1 H); 5.11–5.15 (*m*, 1 H); 5.23–5.30 (*m*, 1 H); 5.92–6.02 (*m*, 1 H); 6.67 (*t*, $J=8.0$, 1 H); 7.45 (*d*, $J=8.0$, 2 H). ^{13}C-NMR ($CDCl_3$): 50.8; 116.7; 117.3; 123.8; 132.7; 135.6; 144.7. ESI-MS: 292 (100, $[M+1]^+$).

3-[(2,6-Dibromophenyl)(prop-2-enyl)amino]cyclopent-2-en-1-one (**17**). Compound **16** (1.00 g, 3.02 mmol), dissolved in anh. DMF (10 ml), was cooled on ice under Ar. To the stirred soln. was added NaH (181 mg, 4.53 mmol; 60% dispersion in mineral oil), followed, after stirring for 45 min, by dropwise addition of allyl bromide (365 mg, 3.02 mmol). The mixture was allowed to warm to r.t. and was stirrred for 4 h. Then, aq. $NaHCO_3$ soln. was added, and the mixture was extracted with AcOEt (3×). The combined org. layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by CC (SiO_2; AcOEt) to give **17** (1.05 g, 94%). Oil. ^{1}H-NMR ($CDCl_3$): 2.18–2.22 (*m*, 2 H); 2.34–2.38 (*m*, 2 H); 4.15 (*d*, $J=6.9$, 2 H); 5.14–5.30 (*m*, 2 H); 5.36 (*s*, 1 H); 5.93–6.05 (*m*, 1 H); 7.16 (*t*, $J=8.1$, 1 H); 7.65 (*d*, $J=8.1$, 2 H). ^{13}C-NMR ($CDCl_3$): 28.1; 34.0; 56.1; 102.8; 120.3; 125.8; 130.9; 131.0; 132.8; 140.6; 176.0; 204.8. ESI-MS: 372 (100, $[M+1]^+$). HR-MS: 369.9444 ($C_{14}H_{14}Br_2NO^+$; calc. 369.9442).

General Procedure 2 (*GP2*) *for the Condensation of Anilines and Cyclic 1,3-Diones.* See the synthesis of **9** (below).

3-[(2-Iodophenyl)amino]cyclohex-2-en-1-one (**9**). *GP2:* 2-Iodoaniline (8.50 g, 38.8 mmol) and cyclohexa-1,3-dione (4.35 g, 38.8 mmol) were stirred overnight at 120°. The mixture was cooled to r.t., dissolved in a small amount of CH_2Cl_2, and purified by CC (CH_2Cl_2/AcOEt/Et_3N 10:88:2) to give **9** (7.67 g, 63%). Solid. M.p. 156.5–157.5° (lit. 155–156° [4b]). ^{1}H-NMR ($CDCl_3$): 2.02–2.10 (*m*, 2 H); 2.37 (*t*, $J=6.6$, 2 H); 2.54 (*t*, $J=6.1$, 2 H); 5.34 (*s*, 1 H); 6.18 (br. *s*, 1 H); 6.89–6.95 (*m*, 1 H); 7.31–7.35 (*m*, 2 H); 7.82–7.86 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 21.8; 29.6; 36.5; 95.9; 100.7; 126.2; 127.7; 129.2; 139.3; 139.6; 161.5; 198.3. ESI-MS: 314 (100, $[M+1]^+$).

3-[(2-Iodophenyl)(methyl)amino]cyclopent-2-en-1-one (**7a**). *GP2:* 6.83 g (63%). Yellowish gum. ^{1}H-NMR ($CDCl_3$): 2.13–2.21 (*m*, 2 H); 2.32–2.40 (*m*, 2 H); 3.22 (*s*, 3 H); 5.21 (*s*, 1 H); 7.02–7.46 (*m*, 3 H); 7.88–7.92 (*m*, 1 H). ESI-MS: 314 (100, $[M+1]^+$).

3-[(2-Bromophenyl)(methyl)amino]cyclopent-2-en-1-one (**7b**). *GP2:* 2.17 g (76%). Oil. ^{1}H-NMR ($CDCl_3$): 2.18–2.45 (*m*, 4 H); 3.25 (*s*, 3 H); 5.22 (*s*, 1 H); 7.22–7.45 (*m*, 3 H); 7.65–7.72 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 28.1; 34.4; 40.7; 101.7; 123.1; 128.9; 129.6; 130.1; 133.9; 143.0; 177.0; 204.5. ESI-MS: 266 (100, M^+).

3-[(2-Iodophenyl)amino]cyclopent-2-en-1-one (**7c**). *GP2:* 3.80 g (46%). Solid. M.p. 178.5–179.5°. ^{1}H-NMR ($CDCl_3$): 2.45–2.51 (*m*, 2 H); 2.80–2.85 (*m*, 2 H); 5.42 (*s*, 1 H); 6.85–6.99 (*m*, 2 H); 7.32–7.39 (*m*, 2 H); 7.82–7.86 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 28.91; 33.59; 93.12; 103.42; 123.14; 127.00; 129.39; 139.57; 140.29; 172.37; 205.75. ESI-MS: 299 (100, M^+). Anal. calc. for $C_{11}H_{10}INO \cdot 0.05\ Et_3N$: C 44.62, H 3.56, N 4.84; found: C 44.22, H 3.33, N 5.19.

3-[(2-Bromophenyl)amino]cyclopent-2-en-1-one (**7d**). *GP2:* 4.86 g (70%). Solid. M.p. 166.5–168.0°. ^{1}H-NMR ($CDCl_3$): 2.45–2.52 (*m*, 2 H); 2.79–2.84 (*m*, 2 H); 5.60 (*s*, 1 H); 6.81 (br. *s*, 1 H); 7.00–7.05 (*m*, 1 H); 7.32–7.42 (*m*, 2 H); 7.57–7.62 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 29.2; 33.4; 104.0; 115.7; 122.2; 125.9; 128.5; 133.2; 137.5; 171.2; 205.9. ESI-MS: 252 (100, M^+). Anal. calc. for $C_{11}H_{10}BrNO \cdot 0.05\ Et_3N$: C 52.78, H 4.21, N 5.72; found: C 52.47, H 4.03, N 6.09.

3-[(2,6-Dibromophenyl)amino]cyclohex-2-en-1-one (**11**). *GP2:* 1.65 g (40%). Solid. M.p. 255–257°. ^{1}H-NMR ($CDCl_3$): 2.03–2.12 (*m*, 2 H); 2.36 (*t*, $J=6.5$, 2 H); 2.52 (*t*, $J=6.2$, 2 H); 4.82 (*s*, 1 H); 5.92 (br. *s*, 1 H); 7.06 (*t*, $J=8.1$, 1 H); 7.60 (*d*, $J=8.1$, 2 H). ^{13}C-NMR ($CDCl_3$): 21.8; 28.7; 36.4; 101.6; 124.5; 130.0; 132.7; 135.5; 161.6; 198.2. ESI-MS: 346 (100, $[M+1]^+$). Anal. calc. for $C_{12}H_{11}Br_2NO$: C 41.77, H 3.21, N 4.06; found: C 41.65, H 3.24, N 3.99.

3-[(2-Bromophenyl)(prop-2-enyl)amino]cyclopent-2-en-1-one (**12**). *GP2:* 2.98 g (72%). Oil. ^{1}H-NMR ($CDCl_3$): 2.17–2.23 (*m*, 2 H); 2.30–2.35 (*m*, 2 H); 3.97 (*dd*, $J=6.5$, 15.6, 2 H); 4.28 (*dd*, $J=5.7$, 15.6, 2 H); 5.15–5.33 (*m*, 3 H); 5.82–5.95 (*m*, 1 H); 7.20–7.42 (*m*, 3 H); 7.65–7.71 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 28.5; 34.1; 56.5; 102.1; 119.3; 123.5; 128.6; 130.1; 130.7; 130.8; 133.8; 141.7; 176.4; 204.6. ESI-MS: 292 (100, M^+).

3-[(2,6-Dibromophenyl)amino]cyclopent-2-en-1-one (**16**). *GP2:* 2.77 g (53%). Solid. An anal. sample was recrystallized from AOEt/MeOH. M.p. 210.1–211.0°. ^{1}H-NMR ((D_6)DMSO): 2.20–2.30 (*m*, 2 H); 2.65–2.75 (*m*, 2 H); 3.30–3.34 (*m*, 1 H); 4.28 (br. *s*, 1 H); 7.24 (*t*, $J=8.1$, 1 H); 7.79 (*d*, $J=8.1$, 2 H). ^{13}C-NMR

((D$_6$)DMSO): 27.4; 34.2; 100.9; 123.9; 131.0; 133.2; 137.4; 175.1; 203.0. ESI-MS: 332 (100, $[M+1]^+$). Anal. calc. for $C_{11}H_9Br_2NO$: C 39.92, H 2.74, N 4.23; found: C 39.91, H 2.67, N 4.44.

General Procedure 3 (*GP3*) *for the Preparation of Cyclopenta[*b*]indol-1-ones.* See the synthesis of **3a** (below).

*3,4-Dihydro-4-methylcyclopenta[*b*]indol-1(2*H*)-one* (**3a**). *GP3:* A stirred soln. of **7a** (6.00 g, 19.2 mmol), AcONa (6.29 g, 76.6 mmol), Bu_4NCl (5.33 g, 19.2 mmol), tri(*o*-tolyl)phosphine (583 mg, 1.92 mmol), and $Pd(OAc)_2$ (0.96 mmol, 215 mg) in anh. DMF (300 ml) under Ar was heated in a microwave oven at 100° for 30 min. The mixture was cooled to r.t., added to aq. $NaHCO_3$ soln., and extracted with AcOEt (3 ×). The org. layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*, and the remaining solid was purified by CC (CH_2Cl_2/AcOEt 1:1, then AcOEt/Et_3N 98:2) and recrystallization (AcOEt/MeOH) to give **3a** (3.52 g; 99%). Solid. M.p. 214.3–216.0° (lit. 209–210° [3]). ^{1}H-NMR ($CDCl_3$): 2.80 (*s*, 4 H); 3.58 (*s*, 3 H); 7.16–7.26 (*m*, 3 H); 7.84–7.90 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 20.4; 30.4; 40.7; 110.0; 119.1; 120.7; 121.3; 122.2; 123.3; 143.0; 168.2; 195.1. ESI-MS: 185 (100, M^+). Anal. calc. for $C_{12}H_{11}NO$: C 77.81, H 5.99, N 7.56; found: C 77.61, H 5.91, N 7.62.

*3,4-Dihydrocyclopenta[*b*]indol-1(2*H*)-one* (**3b**). *GP3:* 228 mg (80%). Solid. M.p. 259.5–260.5° (lit. 257–259° [9]). ^{1}H-NMR ((D$_6$)DMSO): 3.00–3.03 (*m*, 2 H); 3.25–3.29 (*m*, 2 H); 7.30–7.40 (*m*, 2 H); 7.60–7.65 (*m*, 1 H); 7.82–7.87 (*m*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 21.4; 41.0; 113.0; 119.6; 119.8; 121.3; 121.9; 123.3; 142.6; 168.2; 195.1. ESI-MS: 172 (100, $[M+1]^+$).

*1,2,3,9-Tetrahydrocarbazol-4(4*H*)-one* (**10**). *GP3:* 169 mg (95%). Solid. M.p. 223–225° (dec.). ^{1}H-NMR ((D$_6$)DMSO): 2.06–2.16 (*m*, 2 H); 2.43 (*t*, *J* = 6.3, 2 H); 2.96 (*t*, *J* = 6.1, 2 H); 7.10–7.19 (*m*, 2 H); 7.36–7.42 (*m*, 1 H); 7.91–7.98 (*m*, 1 H); 11.8 (br. *s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 23.1; 23.8; 38.2; 111.9; 112.1; 120.5; 121.9; 122.8; 124.9; 136.1; 152.6; 193.2. ESI-MS: 186 (100, $[M+1]^+$).

*3-(3-Methyl-1*H*-indol-1-yl)]cyclopent-2-en-1-one* (**14**). *GP3:* 310 mg (90%). Solid. M.p. 162.5–163.5°. ^{1}H-NMR ($CDCl_3$): 2.32 (*s*, 3 H); 2.58–2.62 (*m*, 2 H); 3.21–3.25 (*m*, 2 H); 6.26 (*s*, 1 H); 7.13 (*s*, 1 H); 7.26–7.38 (*m*, 2 H); 7.54–7.58 (*m*, 1 H); 7.65–7.69 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 9.6; 29.4; 33.5; 111.6; 113.5; 118.3; 119.8; 122.2; 122.8; 124.6; 132.3; 136.2; 167.5; 206.9. ESI-MS: 212 (100, $[M+1]^+$). Anal. calc. for $C_{14}H_{13}NO$: C 79.59, H 6.20, N 6.63; found: C 79.45, H 6.37, N 6.60.

*3-(7-Bromo-3-methyl-1*H*-indol-1-yl)cyclopent-2-en-1-one* (**18**). *GP3:* 155 mg (66%). Solid. M.p. 125.3–127.3°. ^{1}H-NMR ($CDCl_3$): 2.31 (*s*, 3 H); 2.64–2.69 (*m*, 2 H); 3.12–3.17 (*m*, 2 H); 5.97 (*s*, 1 H); 7.11–7.17 (*m*, 2 H); 7.48–7.54 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 9.5; 30.0; 34.7; 106.3; 116.5; 118.7; 123.6; 123.7; 125.1; 129.7; 134.6; 135.0; 166.5; 205.8. ESI-MS: 291 (100, $[M+1]^+$). Anal. calc. for $C_{14}H_{12}BrNO$: C 57.95, H 4.17, N 4.83; found: C 58.03, H 4.30, N 4.74.

*4,5,7,8-Tetrahydro-4-methylidene-9*H*-cyclopenta[*b*]pyrrolo[3,2,1-*hi*]indol-9-one* (**19**). According to *GP3*, but with 1,3-bis(diphenylphosphino)propane (dppp) as phosphine ligand:125 mg (34%). Solid. M.p. 192–193°. IR (KBr): 1663, 1650. Raman (powder): 3092, 3097, 2984, 2960, 2931, 1656, 1645, 1581, 1491, 1475, 1439, 1419, 1409, 1532, 1176, 676, 698, 366. ^{1}H-NMR ($CDCl_3$): 2.89–2.99 (*m*, 4 H); 4.95 (*s*, 2 H); 5.29 (*s*, 1 H); 5.67 (*s*, 1 H); 7.15–7.25 (*m*, 2 H); 7.60–7.62 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 21.0; 40.8; 53.5; 106.7; 114.5; 115.5; 120.5; 123.4; 123.6; 124.5; 144.7; 155.0; 164.1; 195.4. ESI-MS: 210 (100, $[M+1]^+$). HR-MS: 210.0917 ($[M+H]^+$, $C_{14}H_{12}NO^+$; calc. 210.0919). Anal. calc. for $C_{14}H_{11}NO \cdot 0.5\ H_2O$: C 77.05, H 5.54, N 6.42, O 11.00; found: C 77.25, H 5.23, N 6.50, O 11.02.

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