Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron Letters
Tetrahedron Letters 47 (2006) 6439–6443

Allylindation of 1*H*-indole-3-carboxaldehyde in the presence of azoles—revisited

Giancarlo Cravotto,[a] Giovanni B. Giovenzana,[b] Angelo Maspero,[c] Tullio Pilati,[d] Andrea Penoni[c] and Giovanni Palmisano[c,*]

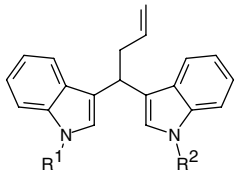
[a]*Dipartimento di Scienza e Tecnologia del Farmaco, via Giuria 9, 10125 Torino, Italy*
[b]*DISCAFF and DFB Center, via Bovio 6, 28100 Novara, Italy*
[c]*Dipartimento di Scienze Chimiche ed Ambientali, via Valleggio 11, 22100 Como, Italy*
[d]*CNR—Istituto di Scienze e Tecnologie Molecolari, via Golgi 19, 20133 Milano, Italy*

Received 4 May 2006; revised 20 June 2006; accepted 23 June 2006

Abstract—The allylindation of 1*H*-indole-3-carboxaldehyde in the presence of azoles (e.g., pyrazoles and imidazole) under aqueous Barbier-like conditions was reinvestigated and improved. Some of the results were at variance with a previous report (*Tetrahedron Lett.* **2003**, *44*, 2101).

Since its introduction in the late eighties for Barbier-type reactions,[1] indium has rapidly gained wide popularity. Several features of this metal recommend its application to organic synthesis: (i) stability to air and water at room temperature, (ii) high reactivity towards SET reactions, (iii) the low heterophilicity that makes indium organometallics tolerant to many functionalities and (iv) the absence, up to date, of toxic effects. Indium organometallics have been usually employed to form many different types of C–C bonds, for example, them in allylation and propargylation reactions, Pd-catalyzed couplings and Reformatsky-type reactions. Indium-mediated allylation (hereafter named allylindation) of carbonyl compounds is copiously described in the literature: efficiency, mildness and selectivity are the key features of this method for the synthesis of homoallylic alcohols.[2]

The synthetic potential of allylindation was recently shown to extend beyond this target. Concomitant with the outset of the present study, Kumar et al.[3] reported that 1*H*-indole-3-carboxaldehyde **1a** (as well as its 1-benzyl derivative **1b**) reacted with indium and allyl bromide in the presence of *N*-heterocycles (e.g., indoles, pyrazoles and imidazole) to give the corresponding 3-[1-(1*H*-hetar-4-yl)-but-3-enyl]-1*H*-indoles **2a**–**f** in isolated yields of just under 95% (Scheme 1). Except for the adduct **2b** (from **1b** and 1-methyl-1*H*-indole), substantial spectroscopic evidence for these structures and, in particular, verification of structures **2c**–**f** was lacking. We verified the correctness of structures **2a**–**b** for compounds formed in the above reactions when they were carried out in the presence of indole and its 1-methyl derivative, respectively.



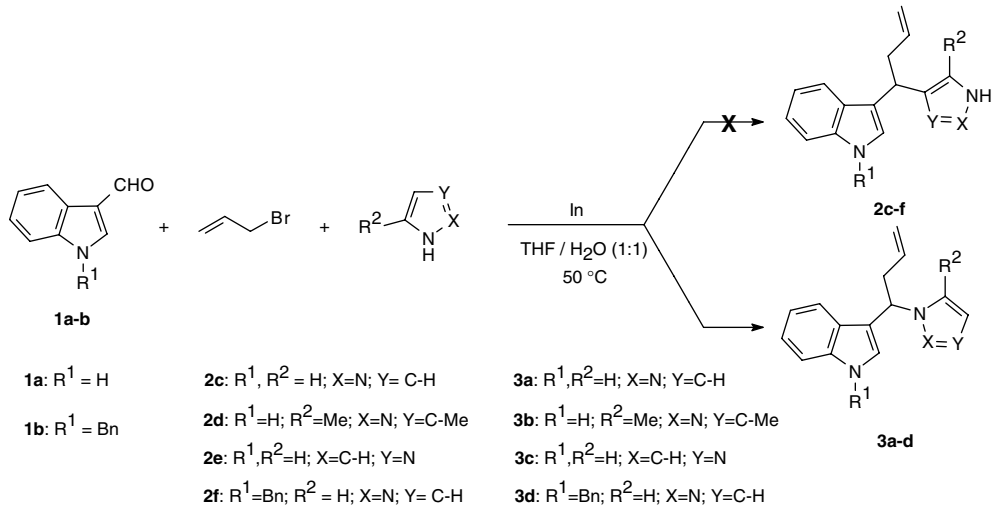
2a: R^1, R^2 = H

2b: R^1 = Bn; R^2 = Me

However, the evidence presented by the authors led us to cast in doubt some of the proposed structures **2c**–**f** for the adducts with azoles. As we also noted some discrepancies between our results and the previously published ones, we suspected that the products of ternary reactions between 1*H*-indole-3-carboxaldehyde, allyl bromide and azoles were the *N*-derivatives **3a**–**d**, rather than the postulated **2c**–**f** (Scheme 1).

* Corresponding author. Tel.: +39 031 2386234; fax: +39 031 2386449; e-mail: giovanni.palmisano@uninsubria.it

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.06.124



Scheme 1.

Our interest in indole chemistry prompted us to reexamine this reaction.[4] On attempting to repeat some of the cited reactions, we immediately noted some differences. Although the suggested solvent combination (i.e., THF–H_2O, 1:1) was by far the most advantageous, in our hands conversions were generally slower, requiring higher temperatures and longer times (typically 6–10 vs 2–3 h). A 100% excess of allyl bromide (2 equiv) and indium (1.4 vs 0.7 equiv) was also needed for the reaction to go to completion (checked by TLC or GCMS). The time required for the disappearance of In was highly variable, ranging from 2 days to 1.5 h.[5] Under our optimized conditions, the allylindation of **1a** in the presence of pyrazole (1 equiv) gave in 5 h a 65% isolated yield of a 1:1:1 adduct [HR-EIMS: $M^{+\cdot}$ at m/z 237.1260 (calculated for $C_{15}H_{15}N_3$ 237.1265, $\Delta = 0.5$ ppm)]. We also carried out this reaction under high-intensity ultrasound (HIU) (20 kHz, 40 W) that dramatically reduced the reaction time (1.5 h) without significantly affecting the yield (62%).

The chemical behaviour and a careful analysis of the adduct raised questions about the proposed structure **2c**. By a combination of 1D and 2D NMR experiments [i.e., gCOSY, ^1H–^{13}C (gHSQC, gHMBC) and ^1H–^{15}N (gHSQC, gHMBC)] we were able to unambiguously assign all ^1H, ^{13}C and ^{15}N resonances of the adduct in DMSO-d_6. The ^1H and ^{13}C NMR (APT) spectra revealed a total of 14 protons attached to carbons (viz. $2CH_2$, 10CH), 3 additional quaternary carbons and the presence of one exchangeable proton at 11.05 ppm. In the 2D NMR, spectra the pyrazole moiety was revealed by signals at δ_H 6.19 (δ_C 104.49), 7.44 (137.73) and 7.70 (128.26). ^1H and ^{15}N HMBC correlations (optimized for $^nJ_{NH} = 3$ Hz) observed from both N-1″ (δ_N 131.0) and N-2″(δ_N 305.0) to H-3″ (δ_H7.70) indicated the connection between N-1″ (of the pyrazole unit) and C-4 [of the (but-3-enyl)-1*H*-indole unit]. 1D and 2D NMR data for the rest of the molecule were consistent with structure **3a**.[6] Likewise, 1-benzyl-1*H*-indole-3-carboxaldehyde **1b**[7] reacting in the presence of pyrazole gave over a similar reaction time, the corresponding derivative **3d**[6] (rather than **2b**) in 72% yield. 3,5-Dimethylpyrazole took a little longer (7 h) to fully react, still delivering a satisfactory 60% yield of adduct **3b**[6] (rather than **2d**). Finally, we confirmed the structure of **3b** by X-ray crystallography (Fig. 1).[8]

Taken together, the foregoing observations leave little doubt that 1-(1*H*-indol-3-yl)but-3-en-1-ol **4** is involved in this reaction. Indoles of this type are thought to react with a nucleophile (e.g., pyrazoles) to give adducts **3a**,**b**,**d** through the intermediacy of highly reactive 3-alkylideneindolenine **5** (viz. a vinylogous imine),[9] in a three-component one-pot domino dehydrative allylindation–alkylation process.[10] Because of its electrophilic character, the exocyclic alkylidene carbon of **5** could be considered as a likely candidate for intermolecular nucleophilic attack. Furthermore, the fact that pyrazoles are regioselectively alkylated at N(1″) rather than at C(3″) is consistent with the well-known chemistry of azoles. Accordingly, in free (NH)azoles, where (neutral) pyrrole-like and (basic/nucleophilic) pyridine-like nitrogen atoms occur in the same molecule, an electrophile will *always* react with the pyridine-like nitrogen.[11] All attempts to obtain the corresponding three-component

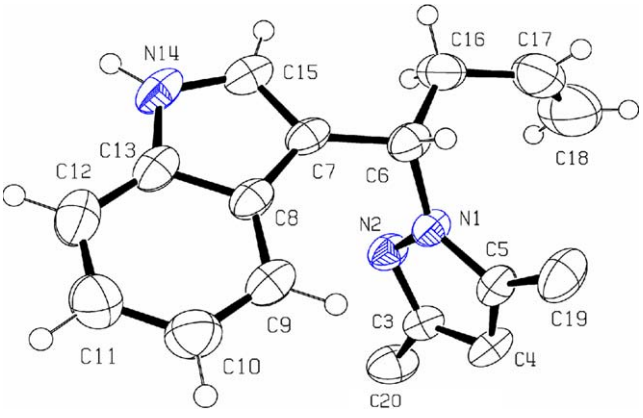
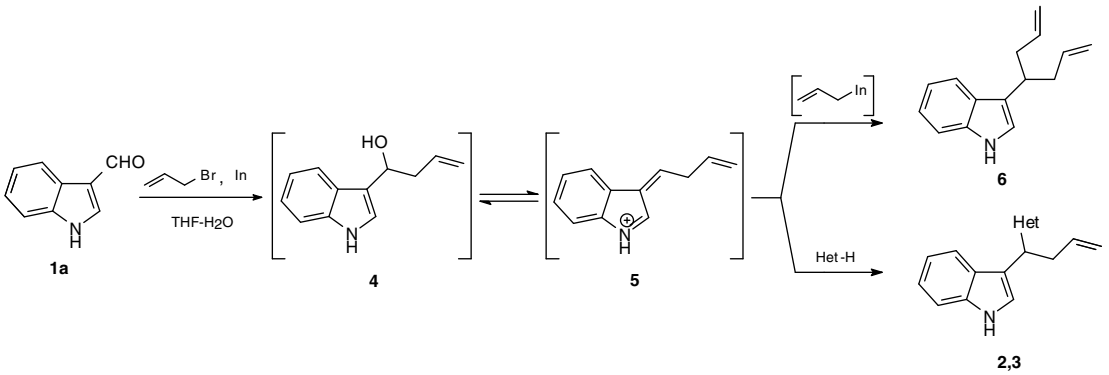


Figure 1. ORTEP diagram for compound **3b**.



Scheme 2.

adducts by allylindation of 1-EWG-substituted 1*H*-indole-3-carboxaldehydes in the presence of pyrazole were unsuccessful, which points to the involvement of the 3-alkylideneindolenine species in the reaction sequence. Interestingly, when allylindation was carried out under our optimized conditions in the presence of imidazole, not even trace amounts of a three-component adduct could be detected (TLC). A substantial amount of indium metal was present as a silvery nugget even after 24 h, while 1-allylimidazole and 1,3-diallylimidazolium bromide were the sole identifiable products. There are no substantial differences between our conditions and those previously reported;[3] however, even when we exactly adopted the conditions of the cited work,[3] we could not observe any Barbier-type reaction: **1a** and indium remained mostly unchanged and **2e** could not be detected. We do not dispute the findings of Kumar, although at this time we can offer no explanation for this discrepancy. It is reasonable to assume that when the reaction is carried out in the presence of imidazole, its alkylation and subsequent quaternization take precedence over the oxidative insertion to allylindium(I) intermediate[12] because imidazole is a stronger nucleophile than pyrazole.[13] For this multicomponent reaction to succeed, imidazole must not be included at the beginning of the reaction but added after 1-(1*H*-indol-3-yl)-but-3-en-1-ol **4** has already formed. In the event, **3c**[6] would be formed through a one-pot three-component consecutive allylindation–alkylation reaction.[10] Optimal conditions (giving 51% yield) were found to be the following: sequential treatment of **1a** with allyl bromide and indium in THF–H_2O (1:1) at 50 °C for 2 h (monitored by TLC), followed by addition of imidazole and heating for a further 3 h. Alternatively, **3c** was obtained (69% yield) by reacting **4** (prepared by the method of Sheu et al.)[14] and imidazole (1.1 equiv) through the agency of $InBr_3$ (10 mol %)[15] in chlorobenzene at 110 °C for 3 h. The homoallylic alcohol **4** was unstable when stored at room temperature for several days. Its lability so affected chromatography on silica gel that its purification was impossible (vide supra). Interestingly, under our conditions and in the absence of competing nucleophiles, attempts to prepare **4** were thwarted by its proclivity to undergo subsequent addition of allylindium(I) (via **5**) leading to 4(1*H*-indol-3-yl)-hepta-1,4-diene **6**[6,16] (42% yield) along with several by-products (Scheme 2).[17]

Preliminary data in the present report indicate that Barbier allylindation on **1a**, dehydration and nucleophilic addition can be combined in a convergent one-pot approach to the synthesis of a variety of indole derivatives. Investigations are underway involving other carbonyls, allylic and propargylic halides, *N*- and *C*-nucleophiles. In particular, when generated under our conditions, indolenine **5** was efficiently trapped by a range of carbon nucleophiles (e.g., electron-rich aromatics, π-excessive heterocycles and some stabilized enols) leading to a two-fold C–C bond formation, and this will be reported in due time. This multicomponent procedure could be useful for the production of a wide library with intriguing complexity.

Acknowledgements

We thank Dr. K. N. Nicholas (University of Oklahoma) for stimulating discussion and helpful suggestions, Dr. S. Milanesi (Sanofi-Aventis, Milano) for 1D- and 2D ^{15}N NMR spectra, Dr. E. De Franco and Dr. F. Colombo (Università dell'Insubria) for experimental assistance.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.06.124.

References and notes

1. Araki, S.; Ito, H.; Batsugan, Y. *J. Org. Chem.* **1988**, *53*, 1831.
2. For reviews on indium-mediated reactions: (a) Cintas, P. *Synlett* **1995**, 1089; (b) Podlech, J.; Maier, T. C. *Synthesis* **2003**, 633; (c) Li, C. J. *Tetrahedron* **1996**, *52*, 5643; (d) Marshall, J. A. *Chemtracts, Org. Chem.* **1977**, *10*, 481–496; (e) Li, C. J. In *Green Chemistry, Frontiers in Benign Chemical Syntheses and Processes*; Anastas, P., Williamson, T. C., Eds.; Oxford University Press: New York, 1998, Chapter 14; (f) Paquette, L. A. In *Green Chemistry, Frontiers in Benign Chemical Syntheses and Processes*; Anastas, P., Williamson, T. C., Eds.; Oxford University Press: New York, 1998, Chapter 15; (g) Li, C. J.; Chan, T. K. *Tetrahedron* **1999**, *55*, 11149; (h) Araki, S.; Hirashita,

T. Indium in Organic Synthesis. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, 2004; pp 323–386; (i) Nair, V.; Ros, S.; Jayan, C. N.; Pillai, B. S. *Tetrahedron* **2004**, *60*, 1959.

3. Kumar, S.; Kumar, V.; Chimni, S. S. *Tetrahedron Lett.* **2003**, *44*, 2101.
4. Some of the results described herein were presented at the 13th IUPAC International Symposium on Organometallic Chemistry directed towards Organic Synthesis (Geneva, Switzerland, July 17–21, 2005) (Poster #P510).
5. General procedure. Indium powder (100 mesh, 99.99%) (320 mg, 2.8 mmol) was added to a vigorously stirred suspension in H_2O–THF (12 mL, 1:1, v/v) of 1*H*-indole-3-carboxaldehyde **1a** (291 mg, 2.0 mmol), allyl bromide (345 μL, 4.0 mmol) and azole (2.0 mmol). The mixture was stirred at 50 °C (oil bath) and monitored by TLC. Upon completion of the reaction, water (25 mL) and EtOAc (20 mL) were added. The organic layer was collected and the aqueous layer was further extracted with EtOAc (2 × 10 mL). The combined organic extracts were dried and concentrated. Products **3a**,**b**,**d** were purified by flash column chromatography (Silica gel). Two-step Preparation of compound **3c**. Homoallylic alcohol (57 mg, 0.30 mmol) **4** (prepared in 90% yield from 1a and allylMgBr according to Sheu et al.[14]) was dissolved in chlorobenzene (4 mL) in the presence of imidazole (45 mg, 0.67 mmol) and indium(III) bromide (11 mg, 0.03 mmol) and the mixture was heated at 110 °C under nitrogen for 3 h. Evaporation of the solvent and purification by flash column chromatography (CH_2Cl_2–EtOAc 1:1) afforded compound **3c** (49 mg, 69% yield) as a colourless solid.
6. Analytical data: Compound **3a**: Mp 102.8–103.5 °C (CH_2Cl_2–hexanes); R_f 0.67 (CH_2Cl_2–AcOEt, 3:2; violet spot/Ehrlich), ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.0–3.2 (2H, m, diastereotopic H-3), 4.96 (1H, d, $J = 10.3$, H-1$_{cis}$), 5.09 (1H, dd; $J = 17.2$, 1.8; H-1$_{trans}$), 5.69 (1H, ddt; $J = 17.2$, 10.3, 2.5; H-2), 5.75 (1H, dd, $J = 8.3$, 6.2; H-4), 6.19 (1H, t, $J = 2.0$, H-4″), 6.94 (1H, t, $J = 7.1$, H-5), 7.07 (1H, t, $J = 7,1$, H-6′), 7.36 (1H, d, $J = 7.1$, H-4′), 7.41 (1H, d, $J = 7.1$, H-7′), 7.44 (1H, d, $J = 2.0$, H-5″), 7.45 (1H, s, H-2′), 7.70 (1H, d, $J = 2.0$, H-3″), 11.05 (1H, s, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 36.7 (CH_2), 57.9 (CH), 104.5 (CH), 111.4 (CH), 114.0 (C), 117.0 (CH_2), 118.5 (CH), 118.6 (CH), 121.1 (CH), 123.3 (CH), 125.8 (C), 128.3 (CH), 134.8 (CH), 136.1 (C), 137.7 (CH). ^{15}N NMR (40.5 MHz, DMSO-d_6; referenced to liquid NH_3) δ 131.0 (N-1′), 224.0 (N-1″), 305.1 (N-2″). Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.80; H, 6.54; N, 17.43. HR-EIMS: $M^{+\cdot}$ at *m*/*z* 237.1260 (calculated for $C_{15}H_{15}N_3$ 237.1265, $\Delta = 0.5$ ppm). Compound **3b**: Mp 161.8–162.5 °C (CH_2Cl_2–hexanes), R_f 0.31 (CH_2Cl_2–AcOEt, 6:4; violet spot/Ehrlich), ^{1}H NMR ($CDCl_3$) δ 2.26 (3H, s, Me), 2.31 (3H, s, Me), 3.03 (1H, m, H-3a), 3.24 (1H, m, H-3b), 5.04 (1H, d, $J = 10.1$, H-1$_{cis}$), 5.14 (1H, d, $J = 17.1$; H-1$_{trans}$), 5.55 (1H, dd, $J = 9.5$, 5.6; H-4), 7.08 (1H, s, H-2′), 7.08 (1H, t., $J = 7.6$, H-5′), 7.17 (1H, t, $J = 7.3$, H-6′), 7.34 (1H, d, $J = 8.1$, H-7′), 7.40 (1H, t, $J = 7.6$, H-4′), 8.54 (1H, br s, NH). ^{13}C NMR ($CDCl_3$) δ 11.9 (Me), 14.1 (Me), 39.8 (CH_2), 105.2 (CH), 111.7 (CH), 116.3 (C), 117.8 (CH_2), 119.0 (CH), 120.0 (CH), 122.4 (CH), 123.0 (CH), 126.5 (C), 135.4 (CH), 136.7 (C), 139.4 (C), 147.6 (C). Anal. Calcd for $C_{17}H_{19}N_3$: C, 76.95; H, 7.22; N, 15.84. Found: C, 76.74; H, 7.09; N, 15.66. MS (CI): *m*/*z* 266 $(M+H)^+$. Compound **3c**: Mp 154.0–154.7 °C (CH_2Cl_2–hexanes), R_f 0.15 (CH_2Cl_2–AcOEt, 1:1; pink spot/Ehrlich),^{1}H NMR ($CDCl_3$)δ 2.99 (1H, m, H-3a), 3.13 (1H, m, H-3b), 5.11 (1H, d, $J = 10.3$, H-1$_{cis}$), 5.12 (1H, dd, $J = 17.1$, 1.5; H-1$_{trans}$), 5.54 (1H, dd, $J = 8.6$, 6.2; H-4), 5.74 (1H, m, H-2), 6.99 (1H, s, H-5″), 7.07 (1H, s, H-4″), 7.08 (1H, t, $J = 7.7$, H-5′), 7.23 (1H, t, $J = 7.7$, H-6′), 7.31 (1H, d, $J = 8.2$, H-7′), 7.41 (1H, d, $J = 8.1$, H-1′), 7.65 (1H, s, H-2″), 8.57 (1H, br s, NH).^{13}C NMR ($CDCl_3$) δ 40.8 (CH_2), 55.1 (CH), 111.9 (CH), 115.3 (C), 118.3 (CH), 119.0 (C), 119.1 (CH), 120.7 (C), 122.6 (CH), 123.2 (CH), 125.4 (CH), 126.2 (C), 129.4 (CH), 133.9 (CH), 135.6 (C). Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.72; H, 6.58; N, 17.61. MS (CI): *m*/*z* 238 $(M+H)^+$. Compound **3d**. R_f 0.27 (CH_2Cl_2; reddish violet spot/Ehrlich), ^{1}H NMR δ 3.10 (1H, m, H-3a), 3.20 (1H, m, H-3b), 5.06 (1H, d, $J = 10.2$, H-1$_{cis}$), 5.14 (1H, d, $J = 17.1$, H-1$_{trans}$), 5.33 (2H, s, NCH_2), 5.79 (1H, t, $J = 7.5$), 5.80 (1H, m, H-2), 6.22 (1H, s), 7.10 (1H, t, $J = 7.5$), 7.15 (2H, d, $J = 7.0$), 7.20 (1H, t, $J = 7.2$), 7.26 (1H, s, H-2′), 7.29 (1H, d, $J = 8.5$), 7.30–7.35 (3H, m), 7.41 (1H, d, $J = 2.1$, H-5″), 7.45 (1H, d, $J = 7.9$, H-7′), 7.57 (1H, s).^{13}C NMR δ 40.0 (CH_2), 50.8 (CH_2), 59.3 (CH), 105.5 (CH), 110.4 (CH), 114.6 (C), 118.1 (CH_2), 119.7 (CH), 120.3 (CH), 127.1 (CH), 127.2 (C), 127.3 (CH), 128.1 (CH), 128.5 (CH), 129.2 (CH), 134.7 (CH), 137.2 (C), 137.6 (C), 139.2 (CH). Anal. Calcd for $C_{22}H_{21}N_3$: C, 80.70; H, 6.46; N, 12.83. Found: C, 80.33; H, 6.61; N, 12.95. MS (CI): *m*/*z* 328 $(M+H)^+$. Compound **6**. R_f 0.58 (CH_2Cl_2–hexanes, 7:3; pink spot/Ehrlich),^{1}H NMR δ 2.58 (4H, t, $J = 7.0$, H-3/H-5), 3.17 (1H, quint, $J = 7.0$, H-4), 5.03 (2H, d, $J = 10.1$; H-1$_{cis}$/H-7$_{cis}$), 5.08 (2H, d, $J = 17.0$; H-1$_{trans}$/H-7$_{trans}$), 5.84 (2H, ddt; $J = 17.0$, 10.1, 7.0; H-2/H-6), 6.98 (1H, m d, $J = 2.2$, H-2′), 7.17 (1H, t, $J = 7.2$), 7.25 (1H, t, $J = 7.2$), 7.39 (1H, d, $J = 7.2$), 7.71 (1H, d, $J = 8.1$), 7.92 (1H, br s, NH). ^{13}C NMR δ 36.8 (CH), 39.7 (CH_2), 111.5 (CH), 116.2 (CH_2), 119.5 (CH), 119.8 (CH), 119.9 (C), 121.4 (CH), 122.3 (CH), 127.4 (C), 136.8 (C), 137.7 (CH). Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.49; H, 8.12; N, 6.35. MS (CI): *m*/*z* 212$(M+H)^+$.
7. Reimann, E.; Erdle, W. *Pharmazie* **2000**, *55*, 907.
8. Crystal data for $C_{17}H_{19}N_3$: $M = 265.35$, monoclinic, $P2_1/n$, $a = 8.913(2)$, $b = 8.649(2)$, $c = 18.808(3)$ Å, $\beta = 90.48(2)°$, $V = 1449.8(5)$ Å^3, $Z = 4$, $D_c = 1.216$ g cm^{-3}, μ(Mo-Kα) = 0.073 cm^{-1}, $F(000) = 568$; $T = 293(2)$ K; colourless needle, $0.42 \times 0.12 \times 0.08$ mm, Bruker APEX diffractometer with CCD area detector. The structure was solved by direct methods, and refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.0421$, $wR_2 = 0.1103$ for 3352 independent observed reflections [$|F_0| > 4\sigma(|F_0|)$, $2\theta \leqslant 55°$] and 216 parameters (CCDC 298821).
9. For some example, see: (a) Barcock, R. A.; Moorcroft, N. A.; Storr, R. C.; Young, J. H.; Fuller, L. S. *Tetrahedron Lett.* **1993**, *34*, 1187; (b) Bergman, J.; Bergman, S.; Lindstrom, J.-O. *Tetrahedron Lett.* **1989**, *30*, 5337; (c) Magnus, P.; Sear, N. L.; Kim, C. S.; Vicker, N. *J. Org. Chem.* **1992**, *57*, 70; (d) Yu, J.; Wearing, X. Z.; Cook, J. H. *J. Org. Chem.* **2005**, *70*, 3963, and references cited therein; (e) Nicolaou, K. C.; Lee, S. H.; Estrada, A. A.; Kak, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3736; (f) Myers, A. G.; Herzon, J. B. *J. Am. Chem. Soc.* **2003**, *125*, 12080.
10. We use this term in the conventional sense defined by Tietze and Beifuss (Tietze, L. F.; Beifuss, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 131); See also: Tietze, L. F.; Rackelmann, N. *Pure Appl. Chem.* **2004**, *76*, 1967.
11. Katritzky, A. R.; Rees, C. W. In *Comprehensive Heterocyclic Chemistry (The Structure, Reactions, Synthesis and Uses of Heterocyclic Compounds)*; Potts, K. T., Ed.; Pergamon Press, 1984; Vol. 5.
12. It is stated that allylindium (I) is formed by reaction of allyl halides and indium in aqueous media (Chan, T. H.;

Yang, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3228, and references cited therein).
13. Zoltewicz, J. A.; Deady, L. W. *Adv. Heterocycl. Chem.* **1978**, *22*, 71.
14. Sheu, J. H.; Chen, Y. K.; Chung, H. F.; Sung, P. Y.; Lin, S. F. *Heterocycles* **1996**, *43*, 1751.
15. The catalytic activation of allylic and benzylic alcohols with indole in the presence of In(III) salts has been recently reported, see: Yasuda, M.; Somyo, T.; Baba, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 793.
16. Kumar, S.; Kumar, V.; Chimni, S. S. *Tetrahedron Lett.* **2002**, *43*, 8029.
17. For examples of allylindation of imines or iminium compounds, see: (a) Beuchet, P.; Le Marrec, N.; Mosset, P. *Tetrahedron Lett.* **1992**, *33*, 5959; (b) Choudhury, P. K.; Foubelo, F.; Yus, M. *J. Org. Chem.* **1999**, *64*, 3376.