Synthesis of Fused-polycyclic Indoles by Brønsted Acid-catalyzed Intramolecular Alkylation of Indoles with Alcohols

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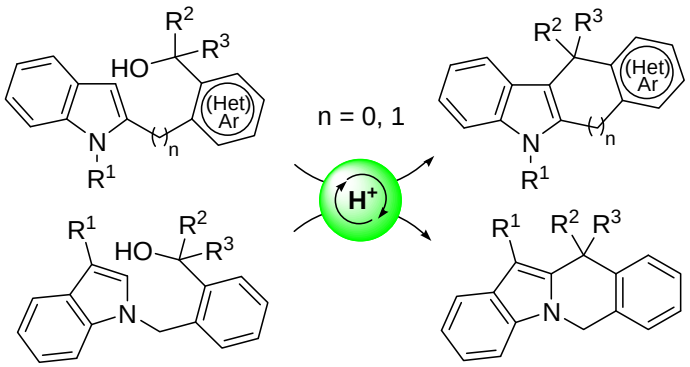
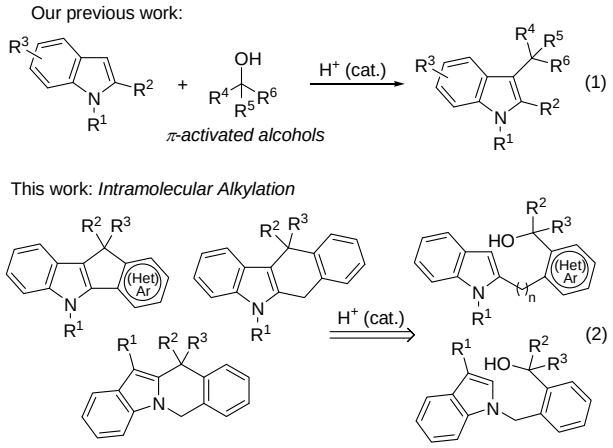


Abstract. An efficient methodology for the synthesis of a series of new fused polyclyclic indoles has been developed by Brønsted acid-catalyzed intramolecular Friedel–Crafts reactions of properly designed indolyl alcohols.

Polycyclic fused indoles are considered "privileged structures" for drug discovery since they are present in numerous natural or synthetic bioactive compounds.[1] So, the research community has devoted considerable efforts to develop sustainable and chemically efficient methodologies to prepare or functionalize such indole-based scaffolds.[2] In this sense, dihydroindenoindoles[3] have gained attention as crucial intermediates in the synthesis of BARAC reagents,[4] as potential anticancer and antioxidant agents[5] and as ligands for polymerization catalysts.[6] Despite these significant applications, no general synthetic methods are available to build libraries of some derivatives such as 10-substituted 5,10-dihydroindeno-[l,2-*b*]indoles.[7,8] Thus, most of the reported protocols only permit monosubstitution at that carbon with limited groups.[9] Likewise, methodologies to obtain other relevant fused tetracyclic indoles such as dihydrobenzo[*b*]carbazoles and indolo[1,2-*b*]isoquinolines having varied substitution at equivalent 11 position, are scarce.[10]

On the other hand, alkylation of indoles by direct nucleophilic substitution reactions with alcohols has important advantages due to the wide availability of alcohols as well as the fact that water is the only byproduct of the process.[11] Thus, different catalytic strategies have been reported over the last years mainly using Lewis acids,[12] Brønsted acids,[13] or transition metal complexes[14] as catalysts. In this field, we pioneered the use of a simple Brønsted acid (PTSA) as a robust methodology for the intermolecular alkylaton of indoles with π-activated alcohols (Scheme 1, eq 1).[15] However, intramolecular Friedel–Crafts alkylation reactions with alcohols are not so common although they represent an easy and efficient way for accessing (poly)cyclic structures.[16] To the best of our knowledge, no examples of catalytic metal-free intramolecular dehydrative alkylation of indoles with alcohols have been previously described.[17]

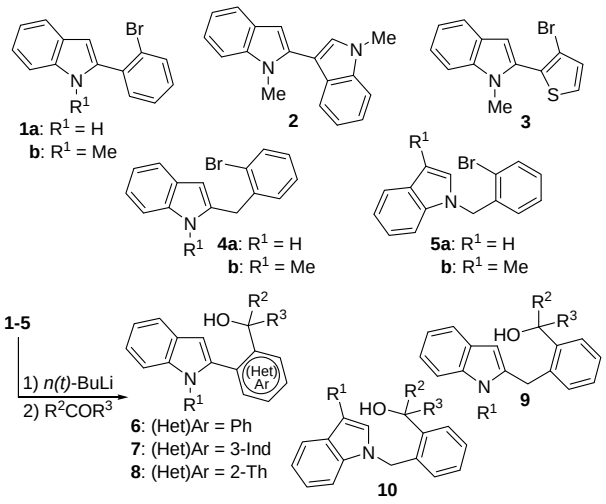
Scheme 1. Reported Direct Acid-catalyzed Alkylation of Indoles with Alcohols and Retrosynthetic Approach to Polycyclic Fused Indoles



In this scenario, we envisioned that indole derivatives bearing an activated alcohol in their structure could be feasible building blocks to access diverse polycyclic frameworks by Brønsted acid-catalyzed intramolecular Friedel–Crafts alkylation reactions, with the remarkable advantage of the formation of water as the only stoichiometric byproduct (Scheme 1, eq 2). Herein we report our results in the application of this hypothesis to achieve a general and concise synthesis of C- and N-fused tetracyclic indoles with elusive substitution patterns, including thieno or indole fused cyclopenta[1,2-*b*]indoles that have been synthesized for the first time.

To enact the proposed approach we selected alcohol derivatives **6**-**10** (Scheme 2) as suitable precursors to polycyclic fused indoles. The preparation of these substrates was performed by lithiation and subsequent carbonyl addition of indoles **1**-**5**, which were easily obtained in gram scale by standard methodologies from commercially available starting materials.

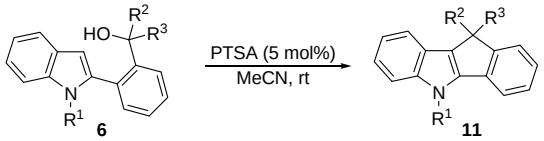
Scheme 2. Preparation of starting alcohol derivatives 6-10



We first investigated the Brønsted acid-catalyzed intramolecular alkylation of 2-arylindoles **6** possessing diverse substitution patterns at the hydroxylic carbon, which would allow the preparation of 5,10-dihydroindeno-[l,2-*b*]indoles **11**. Pleasantly, using the reaction conditions developed in our group for the related intermolecular process (MeCN, 5 mol% PTSA, rt, open vessel),[15] substrates **6a-h** having a tertiary alcohol efficiently reacted to furnish the tetracyclic adducts **11a-h** with varied substitution at carbon 10 (Table 1, entries 1 - 8). Some of the starting alcohols **6** were directly used after flash column chromatography, although not characterized due to non-removable impurities that didn´t significantly affect the yield of the cyclization step. It is worth pointing out that these tertiary alcohols react efficiently without any significant elimination process, even with alcohol **6c** that is really prone to elimination, allowing the construction of fully substituted carbon centres.[18] This acid-catalyzed protocol also succeeded with indoles **6i-o** bearing a secondary alcohol (R^3 = H), provided that the additional substituent R^2 was an activating group. Thus, dihydroindenoindoles **11i-o** bearing an (hetero)aromatic or an olefin group at 10 position, were efficiently synthesized (entries 9 - 15). All these acid-catalyzed reactions occurred in good to excellent yields to give the corresponding 5,10-dihydroindeno-[l,2-*b*]indoles **11** mono- or disubstitued at carbon 10. Notably, and in contrast to previous synthesis of this tetracyclic skeleton,[7,9] this substitution is quite general and includes alkyl, cycloalkyl, both electron donating and electron withdrawing aryl, heteroaryl, alkenyl and alkynyl groups. In addition, the reaction

tolerates the presence of free *N*-H indole moiety as it was demonstrated for substrates **6e,j,l,n** (entries 5, 10, 12 and 14). Indole derivatives holding secondary alcohols having a branched or linear alkyl R^2 group did not react under these reaction conditions, even heating under reflux. However, the less activated substrate **6p** could be transformed into the corresponding indenoindoles **11p** by heating it at 50 ºC in 1,2-dichloroethane for 24 h in the presence of substoichometric amounts of $FeCl_3$ (15 mol%) and $AgSbF_6$ (45 mol%) (entry 16).[19]

Table 1. Synthesis of indeno[1,2-*b*]indoles **11**

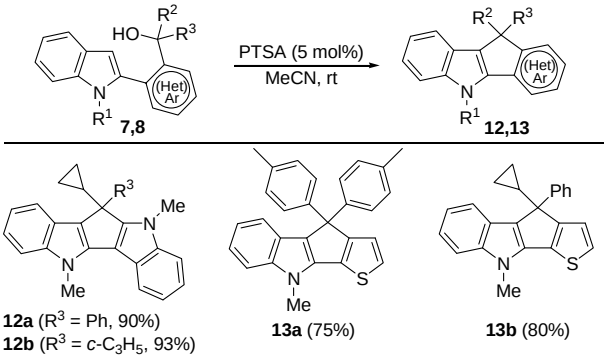


entry	**6**	R^1	R^2	R^3	product	yield (%)[a]
1	**6a**	Me	Me	Ph	**11a**	90
2[b]	**6b**	Me	*c*-C_3H_5	Ph	**11b**	85
3[b]	**6c**	Me	Et	2-Th	**11c**	80
4[b]	**6d**	Me	Me	*c*-C_3H_5	**11d**	63
5[b]	**6e**	H	Me	*c*-C_3H_5	**11e**	73
6	**6f**	Me	Me	(*E*)-PhCH=CH–	**11f**	80
7	**6g**	Me	Me	3-ThC≡C–	**11g**	80
8[b]	**6h**	Me	*c*-C_3H_5	PhC≡C–	**11h**	88
9[b]	**6i**	Me	4-$MeOC_6H_4$	H	**11i**	97
10	**6j**	H	4-$MeOC_6H_4$	H	**11j**	80
11[b]	**6k**	Me	4-ClC_6H_4	H	**11k**	82
12[b]	**6l**	H	4-ClC_6H_4	H	**11l**	65
13[b]	**6m**	Me	5-Me-2-Fur	H	**11m**	55
14	**6n**	H	2-Th	H	**11n**	80
15	**6o**	Me	(*E*)-PhCH=CH–	H	**11o**	79
16[c]	**6p**	Me	*n*-Pr	H	**11p**	69

[a]Yields of isolated products **11** based on the starting indole **6**. [b]The corresponding alcohol was used directly after flash column chromatography. [c]Reaction conducted at 50 ºC in DCE in the presence of $FeCl_3$ (15 mol%) and $AgSbF_6$ (45 mol%). *c*-C_3H_5 = cyclopropyl. 5-Me-2-Fur = 5-methylfur-2-yl. Th = thienyl.

To extend the versatility of the intramolecular acid-catalyzed alkylation we intended the construction of unknown polycyclic skeletons. Thus, substrates **7** and **8**, where the aromatic ring linked to carbon 2 of the starting indole is an heterocycle, reacted analogously to related alcohol derivatives **6** to produce indole or thieno fused dihydrocyclopenta[1,2-*b*]indoles **12** and **13** in high yields (Scheme 3).[20] Remarkably, to the best of our knowledge, these are the first examples of synthesis of such densely functionalized penta- or tetracyclic skeletons and further demonstrate the potential usefulness of the Brønsted acid-catalyzed intramolecular alkylation to synthesize novel polyheterocyclic compounds.

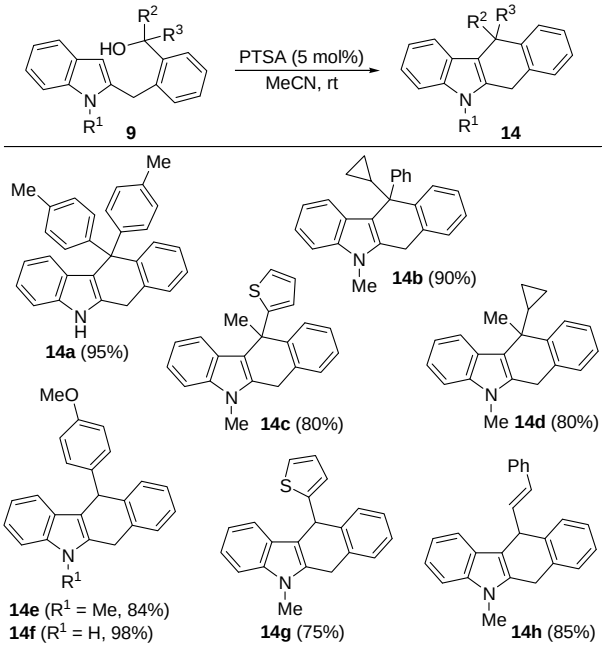
Scheme 3. Synthesis of fused heterocyclic dihydrocyclopenta[1,2-*b*]indoles **12** and **13**



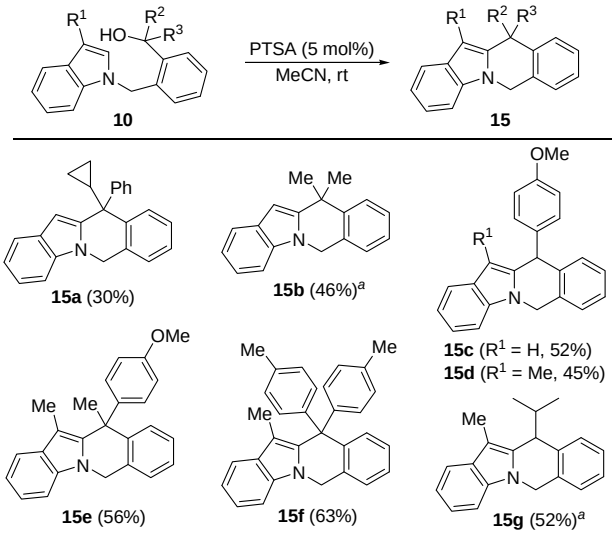
Having verified the viability of the developed protocol to obtain polycyclic fused indoles **11**-**13** through the creation of a five-membered ring, we further tested the synthetic value of our methodology to get other tetracyclic fused indoles by exploring the possibility of assembling six-membered rings. For that goal, we selected as targets the barely reported 6,11-dihydro-5*H*-benzo[*b*]carbazole **14** and indolo[1,2-*b*]isoquinoline frameworks **15** and, so, C2- and *N*-benzyl indoles **9** and **10** were used as starting materials. Reactions of representative benzylindole derivatives possessing a tertiary or an activated secondary alcohol at the appropriate position under the standard Brønsted acid-catalysis, afforded the desired C- and *N*-fused indole tetracycles **14** and **15** with elusive substitution at carbon 11 (Schemes 4 and 5). Thus, diaryl, (hetero)aryl-(cyclo)alkyl, dialkyl as well as (hetero)aryl substituted polycycles **14**,**15** were synthesized in yields that were good to excellent for C-fused tetracycles and moderate for *N*-fused ones. Moreover, as in the case of indeno[1,2-*b*]indoles **11,** *N*-H

dihydrobenzo[*b*]carbazoles **14a,f** could be obtained under the same metal-free conditions (Scheme 4). In addition, reactions of C-3 substituted *N*-benzyl indoles **10d-g** also occurred affording *N*-fused indole tetracycles **15d-g** substituted at carbon 12 (Scheme 5). Not surprisingly (see reaction of **5p**; Table 1, entry 16), *N*-benzyl indoles **10b,g** did not react in the presence of PTSA. Therefore, the formation of the corresponding 11-alkyl mono- or di-substituted indolo[1,2-*b*]isoquinoline **15b,g** was carried out under metal-catalyzed conditions (Scheme 5).

Scheme 4. Synthesis of dihydrobenzo[*b*]carbazoles **14**



Scheme 5. Synthesis of indolo[1,2-*b*]isoquinolines **15**[a]



[a]All the products were obtained using PTSA as catalyst with the expception of **15b** and **15g** that were synthesized in DCE at 50 ºC in the presence of $FeCl_3$ (15 mol%) and $AgSbF_6$ (45 mol%)

In conclusion, we have outlined efficient Brønsted acid-catalyzed intramolecular dehydrative alkylation reactions of selected hydroxyl-functionalized indoles. The present metal-free procedure easily leads to the synthesis of a wide range of regioselectively substituted fused tetracyclic indole derivatives in high yields. The obtained scaffolds present high interest due to their potential biological and pharmaceutical activity and our strategy provides a practical way to construct them.

Experimental Section

General Methods. All common reagents, catalysts and solvents were obtained from commercial suppliers and used without any further purification. Solvents were dried by standard methods. Hexane and ethyl acetate were purchased as extra pure grade reagents and used as received. TLC was performed on aluminum-backed plates coated with silica gel 60 with F254 indicator; the chromatograms were visualized under ultraviolet light and/or by staining with a Ce/Mo reagent and subsequent heating. R_f values are reported on silica gel. Flash column chromatography was carried out on silica gel 60, 230-240 mesh. Unless noted ^{1}H NMR spectra were recorded at 300 or 400 MHz in $CDCl_3$. Chemical shifts are reported in ppm using residual solvent peak as reference ($CHCl_3$: δ 7.16). Data are reported as

follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, dd: doublet of doublets, dt: doublet of triplets, tt: triplet of triplets, dq: doublet of quartets, td: triplet of doublets, ddd: doublet of doublet of doublets, bs: broad singlet, at: apparent triplet), coupling constant (*J* in Hz) and integration. ^{13}C NMR spectra were recorded at 75.4 MHz or 100.6 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference ($CDCl_3$: δ 77.16). Carbon multiplicities were assigned by DEPT techniques. High resolution mass spectra (HRMS) were recorded on an instrument equipped with a magnetic sector ion analyzer using EI at 70eV. Melting points were measured on a microscopic apparatus using open capillary tubes and are uncorrected. GC-MS and low resolution mass spectra (LRMS) measurements were recorded on an instrument equipped with a HP-5MS column.

Synthesis of Indole Derivatives 1-5. Indoles **1** and **3** were prepared by Fisher indolization[21] followed by *N*-methylation[22] when necessary. 2-Bromobenzylindoles **4-5** were prepared by *N*-benzylation,[22] followed by benzyl migration[23] for **4** (and a subsequent *N*-methylation for **4b**). 1,1´-Dimethyl-1*H*,1´*H*-2,3´-biindole **2** was prepared by oxidative homocoupling of *N*-methylindole.[24]

2-(3-Bromothiophen-2-yl)-1-methyl-1H-indole ***(3):*** yellow foam; yield = 55% (1.60 g); R_f = 0.23 (hexane/EtOAc, 30/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 3H), 6.77 (s, 1H), 7.16 - 7.26 (m, 2H), 7.33 - 7.45 (m, 3H), 7.73 (dd, *J* = 7.9, 0.9 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 31.1 (CH_3), 105.2 (CH), 109.8 (CH), 112.4 (C), 120.1 (CH), 121.0 (CH), 122.5 (CH), 127.5 (CH), 129.4 (C), 130.8 (C), 130.9 (CH), 138.1 (C); LRMS (70 eV, EI) *m/z* (%) 293 [$(M+2)^+$, 98], 291 (M^+, 100); HRMS (EI^+) calcd for $C_{13}H_{10}BrNS$ 290.9717, found 290.9719.

2-(2-Bromobenzyl)-1-methyl-1H-indole ***(4b):*** brown solid; yield = 60% (1.80 g); mp 110–112 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.61 (s, 3H), 4.27 (s, 2H), 6.29 (s, 1H), 7.01 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.12 - 7.17 (m, 2H), 7.20 - 7.26 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.3 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.8 (CH_3), 33.6 (CH_2), 101.7 (CH), 109.1 (CH), 119.5 (CH), 120.2 (CH), 121.1 (CH), 124.5 (C), 127.8 (CH), 127.9 (C), 128.3 (CH), 130.4 (CH), 132.8 (CH),

137.7 (C), 137.9 (C), 138.1 (C); LRMS (70 eV, EI) *m/z* (%) 301 [$(M+2)^+$, 99], 299 (M^+, 100); HRMS (EI^+) calcd for $C_{16}H_{14}BrN$ 299.0310, found 299.0309.

*1-(2-Bromobenzyl)-3-methyl-1H-indole (**5b**):* white solid; yield = 80% (2.4 g); mp 56–58 ºC; ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 5.34 (s, 2H), 6.56 (dd, J = 5.6, 3.8 Hz, 1H), 6.91 (s, 1H), 7.11 - 7.22 (m, 5H), 7.59 - 7.65 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.8 (CH_3), 50.0 (CH_2), 109.6 (CH), 111.4 (C), 119.1 (CH), 119.2 (CH), 122.0 (CH), 122.2 (C), 126.0 (CH), 127.9 (CH), 128.2 (CH), 129.02 (C), 129.04 (CH), 132.8 (CH), 136.7 (C), 137.1 (C); HRMS (EI^+) calcd for $C_{16}H_{14}BrN$ 299.0310, found 299.0312.

General Procedure for the Synthesis of Alcohol Derivatives 6-10. To a solution of the corresponding starting bromoindole **1-5** (1 mmol) in THF (2 mL) at −78ºC, was added *n*-BuLi [for **1b**, **3, 4b, and 5a,b**: (1.1 mmol, 1.6M in hexanes, 0.68 mL); for **1a** and **4a**: (2.2 mmol 1.6M in hexanes, 1.36 mL); for starting indole **2**, *t*-BuLi (1.1 mmol, 1.7M in pentane, 0.65 mL) was used as lithiation reagent from −78 to 0 ºC for 15 min)]. The solution was stirred at −78 ºC for 15 min and subsequently the appropriate aldehyde or ketone was added. The resulting mixture was warmed to room temperature and stirred until the corresponding bromoindole was consumed as determined by TLC or GC-MS. The reaction was quenched with a saturated NH_4Cl aqueous solution and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The residue was purified by flash silica gel column chromatography using mixtures of hexane and EtOAc as eluents to obtain the corresponding alcohols **6-10**. In some cases, the synthesized alcohols were not characterized due to the presence of impurities after the column chromatography. So, in these cases the products obtained after the column chromatography were directly used in the cyclization step. No further attempts were made to identify these impurities as they do not have a significant influence in the cyclization (a selection of NMR spectra of these non-characterized alcohols used for the subsequent reactions is also provided in the Supporting Information).

Spectroscopic and Characterization Data for Alcohols 6-10. *1-(2-(1-Methyl-1H-indol-2-yl)phenyl)-1-phenylethanol (**6a**):* white foam; yield = 64% (209 mg); ^1H and ^{13}C NMR were consistent

with the formation of rotamers in a ~2:1 ratio, designed as M (major rotamer) and m (minor rotamer); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1,89 (s, 3H, M), 1.95 (s, 3H, m), 2.54 (s, 3H, M), 2.65 (s, 1H, m), 3.32 (s, 3H, m), 4.11 (s, 1H, M), 5.63 (s, 1H, m), 6.49 (s, 1H, M), 6.87 - 6.93 (m, 3H), 7.07 - 7.31 (m, 14H), 7.35 - 7.58 (m, 6H), 7.66 (d, *J* = 7.7 Hz, 1H, M), 7.84 - 7.87 (m, 2H, M + m); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.4 (CH_3, M), 30.5 (CH_3, m), 31.2 (CH_3, M), 31.9 (CH_3, m), 77.1 (C, M), 77.3 (C, m), 101.7 (CH, M), 103.0 (CH, m), 109.6 (2 × CH, M + m), 119.7 (CH, m), 120.0 (CH, M), 120.5 (CH, M), 120.6 (CH, m), 121.7 (CH, m), 121.9 (CH, M), 124.9 (2 × CH, M), 125.4 (2 × CH, m), 126.27 (CH, M), 126.32 (CH, M), 126.82 (CH, m), 126.84 (CH, m), 127.0 (CH, M), 127.2 (2 × C, M + m), 127.4 (CH, m), 127.9 (2 × CH, M), 128.0 (2 × CH, m), 128.5 (CH, m), 129.0 (CH, M), 130.7 (C, m), 131.3 (C, M), 133.4 (2 × C, M + m), 136.6 (C, M), 136.9 (C, m), 139.4 (C, m), 139.6 (C, M), 147.5 (C, m), 147.7 (C, M), 148.5 (C. M), 149.8 (C, m); LRMS (70 eV, EI) *m/z* (%) 327 (M^+, 100); HRMS (EI^+) calcd for $C_{23}H_{21}NO$ 327.1623, found 327.1626.

(E)-2-(2-(1-Methyl-1H-indol-2-yl)phenyl)-4-phenylbut-3-en-2-ol ***(6f):*** yellow foam; yield = 62% (219 mg); R_f = 0.20 (hexane/EtOAc, 7/1); ^{1}H and ^{13}C NMR were consistent with the formation of rotamers in a ~1:1 ratio; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 3H), 1.81 (s, 3H), 2.43 (s, 1H), 3.27 (s, 3H), 3.35 (s, 1H), 3.38 (s, 3H), 6.03 - 6.11 (m, 1H), 6.27–6.37 (m, 3H), 6.48–6.58 (m, 2H), 6.75–6.81 (m, 1H), 7.03 - 7.14 (m, 4H), 7.18 - 7.29 (m, 11H), 7.35 - 7.60 (m, 6H), 7.66 - 7.71 (m, 2H), 7.76 - 7.79 (m, 1H), 7.88 - 7.90 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 28.9 (CH_3), 30.6 (2 × CH_3), 31.3 (CH_3), 75.4 (C), 75.6 (C), 101.7 (CH), 102.4 (CH), 109.7 (CH), 109.8 (CH), 119.8 (CH), 120.1 (CH), 120.4 (CH), 120.5 (CH), 121.75 (CH), 121.82 (CH), 126.2 (CH), 126.47 (4 × CH), 126.51 (CH), 126.6 (CH), 126.9 (CH), 127.41 (CH), 127.46 (C), 127.50 (CH), 127.56 (C), 127.7 (CH), 128.35 (CH), 128.45 (2 × CH), 128.52 (2 × CH), 129.1 (CH), 129.2 (CH), 130.2 (C), 131.0 (C), 132.9 (CH), 133.2 (CH), 136.2 (CH), 136.6 (2 × C), 136.9 (CH), 137.0 (C), 137.1 (C), 140.3 (C), 140.5 (C), 146.6 (C), 147.3 (C); LRMS (70 eV, EI) *m/z* (%) 353 (M^+, 34), 218 (100); HRMS (EI^+) calcd for $C_{25}H_{23}NO$ 353.1780, found 353.1781.

2-(2-(1-Methyl-1H-indol-2-yl)phenyl)-4-(thiophen-3-yl)but-3-yn-2-ol ***(6g):*** white foam; yield = 59% (211 mg); ^{1}H and ^{13}C NMR were consistent with the formation of rotamers in a ~1:1 ratio; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.00 (s, 3H), 2.83 (s, 1H), 3.38 (s, 1H), 3.45 (s, 3H), 3.46 (s, 3H), 6.58 (d, *J* = 5.0 Hz, 1H), 6.62 - 6.65 (m, 2H), 6.74 (d, *J* = 2.9 Hz, 1H), 6.80 (d, *J* = 5.0 Hz, 1H), 7.02–7.13 (m, 2H), 7.14–7.35 (m, 9H), 7.36–7.47 (m, 2H), 7.48 - 7.58 (m, 2H), 7.68 - 7.72 (m, 2H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.7 (CH_3), 30.8 (CH_3), 31.0 (CH_3), 34.0 (CH_3), 69.4 (C), 69.8 (C), 79.4 (C), 80.0 (C), 91.4 (C), 92.2 (C), 102.2 (CH), 103.1 (CH), 109.6 (CH), 109.7 (CH), 119.7 (CH), 120.0 (CH), 120.5 (CH), 120.6 (CH), 121.3 (C), 121.5 (C), 121.7 (CH), 121.9 (CH), 124.9 (CH), 125.2 (CH), 125.7 (CH), 125.8 (CH), 127.1 (CH), 127.4 (CH), 127.7 (2 × C), 128.7 (CH), 128.9 (CH), 129.1 (CH), 129.2 (CH), 129.7 (CH), 129.8 (CH), 130.1 (C), 131.2 (C), 132.8 (CH), 133.2 (CH), 137.2 (2 × C), 139.4 (C), 140.0 (C), 144.4 (C), 145.5 (C); LRMS (70 eV, EI) *m/z* (%) 357 (M^+, 11), 339 (100); HRMS (EI^+) calcd for $C_{23}H_{19}NOS$ 357.1187, found 357.1188.

(2-(1H-Indol-2-yl)phenyl)-(4-methoxyphenyl)methanol ***(6j):*** yellow foam; yield = 49% (161 mg); R_f = 0.25 (hexane/EtOAc, 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.69 (d, *J* = 5.1 Hz, 1H), 3.80 (s, 3H), 6.05 (d, *J* = 5.0 Hz, 1H), 6.62 - 6.65 (m, 1H), 6.84 - 6.91 (m, 2H), 7.11 - 7.25 (m, 4H), 7.28 - 7.42 (m, 4H), 7.61 (dd, *J* = 6.5, 1.0 Hz, 1H), 7.64 - 7.70 (m, 1H), 9.30 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 55.4 (CH_3), 73.3 (CH), 102.7 (CH), 111.2 (CH), 114.0 (2 × CH), 120.1 (CH), 120.6 (CH), 122.1 (CH), 128.0 (2 × CH), 128.29 (CH), 128.32 (CH), 128.5 (CH), 128.6 (C), 130.6 (CH), 133.3 (C), 134.8 (C), 136.5 (C), 137.4 (C), 140.4 (C), 159.1 (C); LRMS (70 eV, EI) *m/z* (%) 329 (M^+, 15), 311 (100); HRMS (EI^+) calcd for $C_{22}H_{19}NO_2$ 329.1416, found 329.1413.

(2-(1H-Indol-2-yl)phenyl)(thiophen-2-yl)methanol ***(6n):*** yellow foam; yield = 51% (155 mg); R_f = 0.25 (hexane/EtOAc, 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.90 (s, 1H), 6.27 (s, 1H), 6.54 - 6.64 (m, 1H), 6.76 - 6.87 (m, 1H), 6.93 - 7.01 (m, 1H), 7.12 - 7.44 (m, 6H), 7.53 - 7.62 (m, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 8.87 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 70.1 (CH), 103.1 (CH), 111.2 (CH), 120.2 (CH), 120.7 (CH), 122.3 (CH), 125.4 (CH), 125.7 (CH), 127.0 (CH), 127.9 (CH), 128.56 (CH), 128.60 (CH +

C), 130.4 (CH), 132.5 (C), 136.5 (C), 136.7 (C), 140.2 (C), 147.4 (C); LRMS (70 eV, EI) *m/z* (%) 305 (M^+, 4), 287 (100); HRMS (EI^+) calcd for $C_{19}H_{15}NOS$ 305.0877, found 305.0876.

(E)-1-(2-(1-Methyl-1H-indol-2-yl)phenyl)-3-phenylprop-2-en-1-ol ***(6o):*** white foam; yield = 55% (186 mg); R_f = 0.25 (hexane/EtOAc, 4/1); ^{1}H NMR (400 MHz, $CDCl_3$, 50 ºC) δ 2.00 (bs, 1H), 3.45 (s, 3H), 5.44 (bs, 1H), 6.25 (m, 2H), 6.52 (s, 1H), 7.16 - 7.32 (m, 9H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.7 (CH_3), 72.1 (CH), 102.0 (CH), 109.7 (CH), 119.9 (CH), 120.6 (CH), 121.7 (CH), 126.6 (2 × CH), 127.4 (CH), 127.8 (CH), 127.9 (C), 128.6 (2 × CH), 129.5 (CH), 130.5 (CH), 131.2 (C), 131.4 (CH), 136.5 (C), 137.3 (C), 138.7 (C), 142.8 (C), two aromatic CH peaks were not observed; LRMS (70 eV, EI) *m/z* (%) 339 (M^+, 19), 248 (100); HRMS (EI^+) calcd for $C_{24}H_{21}NO$ 339.1623, found 339.1624.

1-(2-(1-Methyl-1H-indol-2-yl)phenyl)butan-1-ol ***(6p):*** white foam; yield = 45% (125 mg); R_f = 0.25 (hexane/EtOAc, 6/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.3 Hz, 3H), 1.10–1.42 (m, 3H), 1.52–1.77 (m, 3H), 1.85 (bs, 1H), 3.54 (s, 3H), 4.71 (bs, 1H), 6.47 (s, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.24–7.32 (m, 2H), 7.33–7.43 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.63–7.71 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.0 (CH_3), 19.1 (CH_2), 30.7 (CH_3), 70.9 (CH), 102.6 (CH), 109.6 (CH), 119.9 (CH), 120.5 (CH), 121.6 (CH), 126.1 (CH), 127.1 (CH), 128.0 (C), 129.4 (CH), 131.0 (C), 131.4 (CH), 137.4 (C), 139.0 (C), 144.8 (C), two aliphatic CH_2 peaks were not observed; LRMS (70 eV, EI) *m/z* (%) 279 (M^+, 100), 218 (61); HRMS (EI^+) calcd for $C_{19}H_{21}NO$ 279.1623, found 279.1623.

Dicyclopropyl-(1,1'-dimethyl-1H,1'H-[2,3'-biindol]-2'-yl)methanol ***(7b):*** yellow foam; yield = 42% (156 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.25–0.68 (m, 7H), 0.76–0.85 (m, 1H), 1.35–1.49 (m, 1H), 1.50–1.64 (m, 1H), 2.09 (s, 1H), 3.59 (s, 3H), 4.19 (s, 3H), 6.61 (s, 1H), 7.10–7.19 (m, 2H), 7.19–7.23 (m, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.41–7.49 (m, 2H), 7.71 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 1.1 (CH_2), 1.8 (CH_2), 1.9 (CH_2), 3.3 (CH_2), 19.9 (CH), 21.1 (CH), 30.4 (CH_3), 33.3 (CH_3), 73.7 (C), 103.3 (CH), 104.4 (C), 109.2 (CH), 109.5 (CH), 119.4 (2 × CH), 120.2 (CH), 120.3 (CH), 121.2 (CH), 122.3 (CH), 128.1 (C), 129.2 (C), 135.6 (C), 137.3 (C), 137.4 (C),

143.6 (C); LRMS (70 eV, EI) *m/z* (%) 352 (M^+, 100), 323 (27); HRMS (EI^+) calcd for $C_{25}H_{24}N_2$ 352.1939, found 352.1940.

*(2-(1-Methyl-1H-indol-2-yl)thiophen-3-yl)di-p-tolylmethanol (**8a**):* yellow foam; yield = 50% (212 mg); R_f = 0.25 (hexane/EtOAc, 15/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 6H), 3.23 (s, 1H), 3.52 (s, 3H), 6.29 (d, *J* = 2.5 Hz, 1H), 6.66 (dd, *J* = 5.3, 3.0 Hz, 1H), 7.05–7.18 (m, 8H), 7.22–7.36 (m, 3H), 7.53 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.2 (2 × CH_3), 30.8 (CH_3), 81.0 (C), 104.9 (CH), 109.7 (CH), 120.0 (CH), 120.8 (CH), 122.4 (CH), 125.4 (CH), 126.0 (CH), 127.4 (C), 127.6 (2 × CH), 128.0 (C), 128.6 (2 × CH), 128.9 (CH), 130.5 (CH), 132.0 (C), 137.1 (2 × C), 137.7 (C), 144.5 (2 × C), 148.6 (C); LRMS (70 eV, EI) *m/z* (%) 423 (M^+, 100); HRMS (EI^+) calcd for $C_{28}H_{25}NOS$ 423.1657, found 423.1655.

*(2-((1H-Indol-2-yl)methyl)phenyl)di-p-tolylmethanol (**9a**):* yellow foam; yield = 52% (217 mg); R_f = 0.30 (hexane/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 6H), 3.26 (s, 1H), 4.04 (s, 2H), 6.24–6.30 (m, 1H), 6.73 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.99–7.10 (m, 3H), 7.12–7.23 (m, 10H), 7.32 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.48–7.55 (m, 1H), 8.01 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.2 (2 × CH_3), 32.8 (CH_2), 83.5 (C), 100.2 (CH), 110.5 (CH), 119.3 (CH), 119.9 (CH), 120.9 (CH), 125.5 (CH), 127.9 (4 × CH), 128.2 (CH), 128.6 (C), 129.0 (4 × CH), 129.9 (CH), 132.7 (CH), 136.3 (C), 137.4 (2 × C), 139.3 (C), 139.8 (C), 144.1 (C), 144.3 (2 ×C); LRMS (70 eV, EI) *m/z* (%) 399 [$(M–H_2O)^+$, 45), 308 (100); HRMS (EI^+) calcd for $C_{30}H_{25}N$ $(M–H_2O)^+$ 399.1887, found 399.1885.

*Cyclopropyl-(2-((1-methyl-1H-indol-2-yl)methyl)phenyl)(phenyl)methanol (**9b**):* yellow foam; yield = 48% (176 mg); R_f = 0.30 (hexane/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.33–0.44 (m, 1H), 0.52–0.72 (m, 3H), 1.66 (ddd, *J* = 16.3, 8.0, 5.7 Hz, 1H), 2.08 (s, 1H), 3.13 (s, 3H), 3.61 (d, *J* = 17.2 Hz, 1H), 4.13 (d, *J* = 17.2 Hz, 1H), 6.03 (d, *J* = 0.7 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.02–7.09 (m, 1H), 7.13 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.16–7.20 (m, 1H), 7.21–7.34 (m, 6H), 7.38 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.46–7-52 (m, 1H), 8.15 (dd, *J* = 7.8, 1.4 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 2.0 (CH_2),

2.4 (CH_2), 23.5 (CH), 29.4 (CH_3), 31.4 (CH_2), 78.0 (C), 101.2 (CH), 108.9 (CH), 119.3 (CH), 119.9 (CH), 120.7 (CH), 126.1 (CH), 126.3 (2 × CH), 126.8 (CH), 127.7 (CH), 127.9 (2 × CH), 128.1 (CH), 131.3 (CH), 137.6 (C), 138.0 (C), 140.4 (C), 144.5 (C), 145.6 (C); one aromatic carbon peak was misssing due to overlapping; LRMS (70 eV, EI) *m/z* (%) 349 [$(M–H_2O)^+$, 57), 308 (100); HRMS (EI^+) calcd for $C_{26}H_{23}N$ $(M–H_2O)^+$ 349.1830, found 349.1832.

*1-(2-((1-Methyl-1H-indol-2-yl)methyl)phenyl)-1-(thiophen-2-yl)ethanol (**9c**):* yellow foam; yield = 60% (208 mg); R_f = 0.25 (hexane/EtOAc, 6/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.50 (bs, 1H), 3.35 (s, 3H), 3.95 (d, *J* = 17.0 Hz, 1H), 4.23 (d, *J* = 17.1 Hz, 1H), 6.05 (d, *J* = 0.7 Hz, 1H), 6.76 (dd, *J* = 3.5, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.00–7.05 (m, 1H), 7.08 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.12–7.20 (m, 1H), 7.21–7.35 (m, 4H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.72 (dd, *J* = 7.7, 1.2 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.5 (CH_3), 31.6 (CH_2), 33.3 (CH_3), 75.6 (C), 101.3 (CH), 108.9 (CH), 119.3 (CH), 120.0 (CH), 120.8 (CH), 123.8 (CH), 124.5 (CH), 126.2 (CH), 126.4 (CH), 126.7 (CH), 127.8 (C), 128.3 (CH), 131.5 (CH), 137.3 (C), 137.7 (C), 140.4 (C), 143.9 (C), 153.5 (C); LRMS (70 eV, EI) *m/z* (%) 347 (M^+, 77), 110 (100); HRMS (EI^+) calcd for $C_{22}H_{21}NOS$ 347.1344, found 347.1345.

*1-Cyclopropyl-1-(2-((1-methyl-1H-indol-2-yl)methyl)phenyl)ethanol (**9d**):* yellow oil; yield = 62% (189 mg); R_f = 0.23 (hexane/EtOAc, 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.46–0.54 (m, 1H), 0.58–0.74 (m, 3H), 1.48–1.58 (m, 1H), 1.56 (s, 3H), 1.85 (s, 1H), 3.73 (s, 3H), 4.55–4.70 (m, 2H), 6.02 (s, 1H), 7.14–7.40 (m, 6H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.74–7.81 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 1.7 (CH_2), 3.3 (CH_2), 23.0 (CH), 27.9 (CH_3), 29.7 (CH_3), 32.5 (CH_2), 75.0 (C), 100.8 (CH), 108.8 (CH), 119.3 (CH), 119.9 (CH), 120.7 (CH), 126.5 (CH), 126.9 (CH), 127.2 (CH), 127.9 (C), 132.2 (CH), 136.4 (C), 137.6 (C), 142.1 (C), 145.5 (C); LRMS (70 eV, EI) *m/z* (%) 305 (M^+, 30), 110 (100); HRMS (EI^+)calcd for $C_{21}H_{23}NO$ 305.1780, found 305.1779.

*(4-Methoxyphenyl)-(2-((1-methyl-1H-indol-2-yl)methyl)phenyl)methanol (**9e**):* yellow foam; yield = 56% (200 mg); R_f = 0.19 (hexane/EtOAc, 5/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.29–2.48 (m, 1H), 3.40 (s, 3H), 3.79 (s, 3H), 3.98 (d, *J* = 16.9 Hz, 1H), 4.08 (d, *J* = 16.9 Hz, 1H), 6.01 (s, 1H), 6.13 (d, *J* = 3.9

Hz, 1H), 6.84–6.90 (m, 2H), 6.99 (d, J = 7.6 Hz, 1H), 7.07–7.15 (m, 1H), 7.18–7.31 (m, 5H), 7.35 (t, J = 7.5 Hz, 1H), 7.51–7.58 (m, 1H), 7.64 (d, J = 7.7 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.5 (CH_3), 30.2 (CH_2), 55.3 (CH_3), 73.0 (CH), 101.4 (CH), 108.9 (CH), 113.9 (2 × CH), 119.4 (CH), 120.1 (CH), 120.9 (CH), 126.9 (CH), 127.0 (CH), 127.8 (C), 127.9 (CH), 128.5 (2 × CH), 129.7 (CH), 135.0 (C), 135.7 (C), 137.7 (C), 138.9 (C), 141.4 (C), 159.2 (C); LRMS (70 eV, EI) *m/z* (%) 357 (M^+, 100), 355 (5); HRMS (EI^+) calcd for $C_{24}H_{23}NO_2$ 357.1729, found 357.1728.

(2-((1H-Indol-2-yl)methyl)phenyl)-(4-methoxyphenyl)methanol ***(9f):*** yellow foam; yield = 40% (137 mg); R_f = 0.25 (hexane/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.56 (bs, 1H), 3.79 (s, 3H), 3.98 (d, J = 15.9 Hz, 1H), 4.09 (d, J = 15.9 Hz, 1H), 6.00 (d, J = 3.3 Hz, 1H), 6.27 (d, J = 1.9 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.03–7.12 (m, 3H), 7.19–7.30 (m, 5H), 7.45–7.55 (m, 2H), 7.88 (bs, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.5 (CH_2), 55.4 (CH_3), 73.0 (CH), 100.6 (CH), 110.6 (CH), 114.0 (2 × CH), 119.6 (CH), 119.9 (CH), 121.2 (CH), 127.1 (CH), 127.5 (CH), 128.1 (CH), 128.4 (2 × CH), 128.6 (C), 130.8 (CH), 135.1 (C), 136.3 (C), 136.5 (C), 137.9 (C), 141.3 (C), 159.2 (C); LRMS (70 eV, EI) *m/z* (%) 325 [$(M–H_2O)^+$, 62], 217 (100); HRMS (EI^+) calcd for $C_{23}H_{19}NO$ $(M–H_2O)^+$ 325.1467, found 325.1466.

(E)-1-(2-((1-Methyl-1H-indol-2-yl)methyl)phenyl)-3-phenylprop-2-en-1-ol ***(9h):*** yellow foam; yield = 64% (226 mg); R_f = 0.10 (hexane/EtOAc, 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16 (bs, 1H), 3.60 (s, 3H), 4.25–4.30 (m, 2H), 5.64 (d, J = 5.9 Hz, 1H), 6.11 (d, J = 0.6 Hz, 1H), 6.40 (dd, J = 15.9, 5.9 Hz, 1H), 6.64 (dd, J = 15.9, 1.2 Hz, 1H), 7.08 (dd, J = 7.6, 1.1 Hz, 1H), 7.12 (dd, J = 7.8, 1.0 Hz, 1H), 7.20 (dd, J = 8.2, 1.2 Hz, 1H), 7.23–7.34 (m, 7H), 7.37 (dd, J = 7.4, 1.4 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.63 (dd, J = 7.6, 1.4 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.8 (CH_3), 30.5 (CH_2), 71.9 (CH), 101.4 (CH), 109.0 (CH), 119.5 (CH), 120.1 (CH), 121.1 (CH), 126.7 (2 × CH), 127.0 (CH), 127.4 (CH), 127.86 (C), 127.92 (CH), 128.3 (CH), 128.7 (2 × CH), 130.2 (CH), 130.7 (CH), 130.9 (CH), 135.8 (C), 136.5 (C), 137.8 (C), 139.3 (C), 140.6 (C); LRMS (70 eV, EI) *m/z* (%) 353 (M^+, 100); HRMS (EI^+) calcd for $C_{25}H_{23}NO$ 353.1780, found 353.1780.

*(2-((1H-Indol-1-yl)methyl)phenyl)(cyclopropyl)(phenyl)methanol (**10a**):* yellow oil; yield = 71% (250 mg); R_f = 0.26 (hexane/EtOAc, 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.32–0.45 (m, 1H), 0.52–0.62 (m, 1H), 0.64–0.7 (m, 2H), 1.75 (tt, *J* = 8.2, 5.5 Hz, 1H), 2.26 (s, 1H), 4.85 (d, *J* = 17.5 Hz, 1H), 5.44 (d, *J* = 17.5 Hz, 1H), 6.44–6.53 (m, 2H), 6.57–6.63 (m, 1H), 6.85 (d, *J* = 3.1 Hz, 1H), 6.99–6.05 (m, 1H), 7.06–7.11 (m, 1H), 7.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29–7.45 (m, 6H), 7.59–7.65 (m, 1H), 8.12 (dd, *J* = 7.8, 1.2 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 1.5 (CH_2), 2.9 (CH_2), 23.4 (CH), 47.9 (CH_2), 78.7 (C), 101.3 (CH), 109.9 (CH), 119.3 (CH), 120.7 (CH), 121.4 (CH), 126.6 (CH), 126.7 (2 × CH), 127.1 (CH), 127.3 (CH), 127.5 (CH), 128.0 (2 × CH), 128.4 (CH), 128.5 (C), 128.9 (CH), 136.3 (C), 138.0 (C), 143.5 (C), 144.1 (C); LRMS (70 eV, EI) *m/z* (%) 353 (M^+, 100); HRMS (EI^+) calcd for $C_{25}H_{23}NO$ 353.1780, found 353.1777.

*2-(2-((1H-Indol-1-yl)methyl)phenyl)propan-2-ol (**10b**):* yellow oil; yield = 40% (106 mg); R_f = 0.17 (hexane/EtOAc, 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 6H), 5.84 (s, 2H), 6.63–6.74 (m, 2H), 7.07–7.30 (m, 6H), 7.32–7.42 (m, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.69–7.81 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ31.9 (2 × CH_3), 48.8 (CH_2), 74.2 (C), 101.5 (CH), 110.0 (CH), 119.5 (CH), 121.0 (CH), 121.7 (CH), 125.7 (CH), 127.2 (CH), 127.7 (CH), 128.5 (CH), 128.70 (C), 128.73 (CH), 136.1 (C), 136.6 (C), 144.6 (C); LRMS (70 eV, EI) *m/z* (%) 265 (M^+, 80), 232 (100); HRMS (EI^+) calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1467.

*(2-((1H-Indol-1-yl)methyl)phenyl)-(4-methoxyphenyl)methanol (**10c**):* white foam; yield = 50% (171 mg); R_f = 0.13 (hexane/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (bs, 1H), 3.83 (s, 3H), 5.16 (d, *J* = 16.4 Hz, 1H), 5.27 (d, *J* = 16.4 Hz, 1H), 5.94 (s, 1H), 6.56 (d, *J* = 3.1 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.88–6.94 (m, 2H), 6.97 (d, *J* = 3.1 Hz, 1H), 6.98–7.04 (m, 1H), 7.12–7.20 (m, 3H), 7.22–7.29 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.66–7.70 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 47.2 (CH_2), 55.4 (CH_3), 73.1 (CH), 101.7 (CH), 109.7 (CH), 114.1 (2 × CH), 119.6 (CH), 121.0 (CH), 121.7 (CH), 127.0 (CH), 127.4 (CH), 127.7 (CH), 128.2 (CH), 128.4 (CH),

128.5 (2 × CH), 128.6 (C), 134.5 (C), 134.9 (C), 136.3 (C), 140.5 (C), 159.3 (C); LRMS (70 eV, EI) *m/z* (%) 343 (M^+, 100); HRMS (EI^+) calcd for $C_{23}H_{21}NO_2$ 343.1572, found 343.1574.

1-(4-Methoxyphenyl)-1-(2-((3-methyl-1H-indol-1-yl)methyl)phenyl)ethanol ***(10d):*** yellow oil; yield = 73% (271 mg); R_f = 0.21 (hexane/EtOAc, 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.35 (s, 3H), 2.40 (bs, 1H), 3.85 (s, 3H), 4.92 (d, *J* = 17.4 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 6.65 (s, 1H), 6.71 (dd, *J* = 6.3, 2.1 Hz, 1H), 6.87–6.99 (m, 2H), 7.01–7.19 (m, 3H), 7.23–7.41 (m, 3H), 7.59 (dd, *J* = 6.2, 2.4 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.7 (CH_3), 33.7 (CH_3), 47.7 (CH_2), 55.4 (CH_3), 76.7 (C), 109.8 (CH), 110.5 (CH), 113.8 (2 × CH), 118.6 (CH), 118.8 (CH), 121.4 (CH), 126.0 (CH), 126.5 (CH), 126.57 (2 × CH), 126.64 (CH), 127.8 (CH), 128.3 (C), 128.7 (C), 136.7 (C), 138.0 (C), 139.8 (C), 143.4 (C), 158.7 (C); LRMS (70 eV, EI) *m/z* (%) 371 (M^+, 100), 338 (72); HRMS (EI^+) calcd for $C_{25}H_{25}NO_2$ 371.1885, found 371.1884.

(4-Methoxyphenyl)-(2-((3-methyl-1H-indol-1-yl)methyl)phenyl)methanol ***(10e):*** yellow oil; yield = 49% (175 mg); R_f = 0.20 (hexane/EtOAc, 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22 (d, *J* = 3.6 Hz, 1H), 2.30 (s, 3H), 3.82 (s, 3H), 5.09 (d, *J* = 16.3 Hz, 1H), 5.21 (d, *J* = 16.3 Hz, 1H), 5.97 (d, *J* = 3.6 Hz, 1H), 6.66–6.73 (m, 2H), 6.89 (dd, *J* = 9.1, 2.7 Hz, 2H), 6.93–7.02 (m, 1H), 7.08–7.13 (m, 2H), 7.13–7.20 (m, 1H), 7.21–7.27 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.54–7.64 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.7 (CH_3), 46.9 (CH_2), 55.4 (CH_3), 73.0 (CH), 109.5 (CH), 110.9 (CH), 114.1 (2 × CH), 118.9 (CH), 119.0 (CH), 121.6 (CH), 125.9 (CH), 126.9 (CH), 127.60 (CH), 127.63 (CH), 128.1 (C), 128.5 (2 × CH), 128.9 (C), 134.6 (C), 135.1 (C), 136.7 (C), 140.6 (C), 159.3 (C); LRMS (70 eV, EI) *m/z* (%) 357 (M^+, 16), 132 (100); HRMS (EI^+) calcd for $C_{24}H_{23}NO_2$ 357.1729, found 357.1728.

(2-((3-Methyl-1H-indol-1-yl)methyl)phenyl)di-p-tolylmethanol ***(10f):*** yellow oil; yield = 67% (289 mg); R_f = 0.21 (hexane/EtOAc, 10/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (d, *J* = 1.0 Hz, 3H), 2.47 (s, 6H), 3.10 (s, 1H), 5.37 (s, 2H), 6.55–6.62 (m, 1H), 6.69–6.83 (m, 3H), 7.02–7.13 (m, 4H), 7.18–7.29 (m, 8H), 7.56–7.63 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.8 (CH_3), 21.2 (2 × CH_3), 48.3 (CH_2), 83.3 (C), 109.8 (CH), 110.4 (CH), 118.5 (CH), 118.8 (CH), 121.3 (CH), 125.9 (CH), 126.6 (CH), 127.5

(CH), 127.8 (4 × CH), 128.2 (CH), 128.7 (C), 129.0 (4 × CH), 129.6 (C), 136.8 (C), 137.4 (2 × C), 138.8 (C), 143.5 (C), 143.6 (2 × C); LRMS (70 eV, EI) *m/z* (%) 431 (58), 322 (100); HRMS (EI^+) calcd for $C_{31}H_{29}NO$ 431.2249, found 431.2248.

2-Methyl-1-(2-((3-methyl-1H-indol-1-yl)methyl)phenyl)propan-1-ol ***(10g):*** yellow oil; yield = 51% (149 mg); R_f = 0.20 (hexane/EtOAc, 8/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (d, J = 6.7 Hz, 3H), 1.11 (d, J = 6.5 Hz, 3H), 1.96 (bs, 1H), 1.99–2.10 (m, 1H), 2.38 (s, 3H), 4.64 (dd, J = 7.1, 2.7 Hz, 1H), 5.32 (d, J = 16.0 Hz, 1H), 5.41 (d, J = 16.0 Hz, 1H), 6.72–6.90 (m, 2H), 7.10–7.31 (m, 4H), 7.34 (t, J = 7.4 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.66 (d, J = 7.4 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.8 (CH_3), 18.3 (CH_3), 19.6 (CH_3), 34.8 (CH), 47.1 (CH_2), 76.0 (CH), 109.4 (CH), 111.1 (C), 119.0 (CH), 119.2 (CH), 121.8 (CH), 125.7 (CH), 127.0 (CH), 127.8 (CH), 127.9 (2 × CH), 129.0 (C), 134.8 (C), 136.8 (C), 141.4 (C); LRMS (70 eV, EI) *m/z* (%) 293 (M^+, 100); HRMS (EI^+) calcd for $C_{20}H_{23}NO$ 293.1780, found 293.1778.

General Procedure for the Synthesis of Polycyclic Adducts 11-15. *Acid-catalyzed procedure***:** PTSA (5 mol%, 5 mg) was added to a solution of the corresponding alcohol derivative **6-10** (0.5 mmol) in MeCN (1 mL) and the resulting reaction mixture was stirred at rt until the alcohol was consumed as determined by TLC (0.5-24 h). The crude mixture was quenched with aqueous NaOH (0.5M) and extracted with EtOAc (3 × 10 mL), and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The residue was purified by flash chromatography using mixtures of hexane and EtOAc as eluents to obtain the corresponding cycloadducts **11-15** in the yields reported in Table 1 or Schemes 3-5. In some cases the final product precipitates from the reaction mixture and could be isolated by simple filtration in pure form.

Fe-catalyzed procedure (for the preparation of ***11p****, and* ***15b,g*****):**[19] To an oven dried vial containing $FeCl_3$ (0.075 mmol, 12 mg) was added a solution of the alcohol **6p,** or **10b,g** (0.5 mmol) in DCE (3 mL), and allowed to stir until $FeCl_3$ was completely dissolved (10–15min). Then $AgSbF_6$ (0.225 mmol, 77 mg) was added and the resulting reaction mixture was stirred at 50 ºC for 24 h. The reaction was

quenched with aqueous HCl (1M), extracted with DCM (3 × 10 mL), and the water layer was basified with aqueous NaOH (1M), and extracted with DCM (2 × 5 mL). The organic extracts combined and dried, filtered and concentrated to give the residue. The residue was purified by silica flash chromatography using mixtures of hexane and EtOAc as eluents to obtain the corresponding cycloadducts **11p,** and **15b,g** in the yields reported in Table 1 and Scheme 5.

Spectroscopic and Characterization Data for Cycloadducts 11-15. *5,10-Dimethyl-10-phenyl-5,10-dihydroindeno[1,2-b]indole (**11a**):* white solid; yield = 90% (140 mg); mp 178–180 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.06 (s, 3H), 4.13 (s, 3H), 7.12–7.20 (m, 1H), 7.22–7.40 (m, 6H), 7.42–7.52 (m, 5H), 7.70 (dd, *J*= 7.5, 0.6 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 24.8 (CH_3), 31.3 (CH_3), 50.3 (C), 110.0 (CH), 118.0 (CH), 119.0 (CH), 119.8 (CH), 121.4 (CH), 123.0 (C), 124.4 (CH), 125.7 (CH), 126.41 (2 × CH), 126.43 (CH), 126.9 (CH), 128.4 (2 × CH), 130.0 (C), 133.7 (C), 142.1 (C), 142.4 (C), 144.5 (C), 159.0 (C); LRMS (70 eV, EI) *m/z* (%) 309 (M^+, 80), 294 (100); HRMS (EI^+) calcd for $C_{23}H_{19}N$ 309.1517, found 309.1518.

*10-Cyclopropyl-5-methyl-10-phenyl-5,10-dihydroindeno[1,2-b]indole (**11b**):* white solid; yield= 85% (168 mg); mp 174–176 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00–0.05 (m, 1H), 0.39–0.46 (m, 1H), 0.63–0.82 (m, 2H), 2.00–2.12 (m, 1H), 4.09 (s, 3H), 7.08–7.15 (m, 1H), 7.20–7.49 (m, 9H), 7.56–7.63 (m, 2H), 7.69 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 1.6 (CH_2), 4.1 (CH_2), 18.4 (CH), 31.2 (CH_3), 56.0 (C), 109.9 (CH), 117.9 (CH), 119.4 (CH), 119.9 (CH), 121.2 (CH), 124.0 (C), 124.9 (CH), 125.6 (CH), 125.9 (C), 126.4 (CH), 126.9 (CH), 127.4 (2 × CH), 128.3 (2 × CH), 134.3 (C), 141.9 (C), 143.7 (C), 144.8 (C), 157.6 (C); LRMS (70 eV, EI) *m/z* (%) 335 (M^+, 43), 307 (100); HRMS (EI^+) calcd for $C_{25}H_{21}N$ 335.1674, found 335.1677.

*10-Ethyl-5-methyl-10-(thiophen-2-yl)-5,10-dihydroindeno[1,2-b]indole (**11c**):* white solid; yield = 80% (132 mg); mp 136–138 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.70 (t, *J* = 7.3 Hz, 3H), 2.38 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.71 (dq, *J* = 14.5, 7.3 Hz, 1H), 4.09 (s, 3H), 6.90 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.97 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.09–7.38 (m, 5H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.53–7.70 (m, 3H); ^{13}C NMR

($CDCl_3$, 75.4 MHz) δ 9.9 (CH_3), 31.3 (CH_3), 33.8 (CH_2), 53.6 (C), 110.0 (CH), 118.1 (CH), 119.88 (CH), 119.93 (CH), 121.4 (CH), 123.3 (CH), 123.7 (CH), 123.8 (C), 124.4 (CH), 125.7 (CH), 126.1 (C), 126.6 (CH), 127.2 (CH), 133.8 (C), 142.1 (C), 143.5 (C), 149.3 (C), 155.8 (C); LRMS (70 eV, EI) *m/z* (%) 330 [$(M+1)^+$, 6], 329 (M^+, 24), 300 (100); HRMS (EI^+) calcd for $C_{22}H_{19}NS$ 329.1238, found 329.1237.

10-Cyclopropyl-5,10-dimethyl-5,10-dihydroindeno[1,2-b]indole ***(11d):*** white solid; yield= 63% (87 mg); mp 135–137 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.10 (bs, 1H), 0.33 (bs, 1H), 0.54–0.64 (m, 1H), 0.67–0.77 (m, 1H), 1.32–1.45 (m, 1H), 1.66 (s, 3H), 4.07 (s, 3H), 7.19–7.47 (m, 5H), 7.56 (d, J = 6.2 Hz, 1H), 7.65 (d, J = 7.3 Hz, 1H), 7.72–7.76 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 1.1 (CH_2), 2.7 (CH_2), 19.7 (CH_3), 22.8 (CH), 31.2 (CH_3), 47.4 (C), 110.0 (CH), 117.9 (CH), 119.4 (CH), 119.7 (CH), 121.1 (CH), 123.3 (CH), 124.0 (C), 125.3 (CH), 126.7 (CH), 127.1 (C), 133.8 (C), 142.0 (C), 142.9 (C), 158.6 (C); LRMS (70 eV, EI) *m/z* (%) 273 (M^+, 100), 258 (53); HRMS (EI^+) calcd for $C_{20}H_{19}N$ 273.1517, found 273.1515.

10-Cyclopropyl-10-methyl-5,10-dihydroindeno[1,2-b]indole ***(11e):*** brown solid; yield = 73% (95 mg); mp 110–112 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02–0.04 (m, 1H), 0.22–0.26 (m, 1H), 0.45–0.54 (m, 1H), 0.57–0.63 (m, 1H), 1.24–1.36 (m, 1H), 1.58 (s, 3H), 7.12–7.19 (m, 2H), 7.20–7.32 (m, 2H), 7.37–7.43 (m, 2H), 7.47 (dd, J = 7.3, 0.6 Hz, 1H), 7.61–7.68 (m, 1H), 8.24 (bs, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 1.1 (CH_2), 2.2 (CH_2), 19.6 (CH_3), 22.5 (CH), 47.9 (C), 112.3 (CH), 117.6 (CH), 119.4 (CH), 120.4 (CH), 121.7 (CH), 123.2 (CH), 124.7 (C), 125.5 (CH), 126.8 (CH), 128.8 (C), 133.4 (C), 140.8 (C), 141.5 (C), 158.2 (C); LRMS (70 eV, EI) *m/z* (%) 259 (M^+, 76), 231 (100); HRMS (EI^+) calcd for $C_{19}H_{17}N$ 259.1361, found 259.1363.

(E)-5,10-Dimethyl-10-styryl-5,10-dihydroindeno[1,2-b]indole ***(11f):*** white solid; yield = 80% (134 mg); mp 150–152 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88 (s, 3H), 4.13 (s, 3H), 6.57 (d, J = 15.9 Hz, 1H), 6.77 (d, J = 15.9 Hz, 1H), 7.21–7.45 (m, 9H), 7.49 (d, J = 8.2 Hz, 1H), 7.54–7.60 (m, 1H), 7.67–7.77 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 23.8 (CH_3), 31.2 (CH_3), 49.0 (C), 110.0 (CH),

118.1 (CH), 119.0 (CH), 119.9 (CH), 121.4 (CH), 123.6 (C), 124.0 (CH), 125.6 (CH), 126.4 (2 × CH), 127.11 (CH), 127.14 (CH), 127.39 (CH), 127.49 (C), 128.5 (2 × CH), 133.6 (C), 134.3 (CH), 137.6 (C), 142.1 (C), 142.4 (C), 156.7 (C); LRMS (70 eV, EI) *m/z* (%) 335 (M^+, 92), 320 (17); HRMS (EI^+) calcd for $C_{25}H_{21}N$ 335.1674, found 335.1673.

5,10-Dimethyl-10-(thiophen-3-ylethynyl)-5,10-dihydroindeno[1,2-b]indole ***(11g):*** brown solid; yield = 80%; mp 156–158 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (CH_3), 4.05 (CH_3), 7.05–7.09 (m, 1H), 7.17–7.44 (m, 7H), 7.62 (d, J = 7.2 Hz, 1H), 7.68–7.75 (m, 1H), 7.79–7.86 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 27.5 (CH_3), 31.2 (CH_3), 40.3 (C), 74.5 (C), 91.4 (C), 110.1 (CH), 118.1 (CH), 118.8 (CH), 120.1 (CH), 121.7 (CH), 122.7 (C), 124.2 (CH), 124.9 (CH), 126.1 (CH), 126.3 (C), 127.7 (CH), 128.2 (CH), 130.3 (CH), 133.3 (C), 142.0 (2 × C), 155.3 (C); one aromatic C peak was missing due to overlapping; LRMS (70 eV, EI) *m/z* (%) 339 (M^+, 100); HRMS (EI^+) calcd for $C_{23}H_{17}NS$ 339.1082, found 339.1083.

10-Cyclopropyl-5-methyl-10-(phenylethynyl)-5,10-dihydroindeno[1,2-b]indole ***(11h):*** white solid; yield= 88% (158 mg); mp 163–165 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60–0.78 (m, 2H), 0.99–1.15 (m, 2H), 1.18–1.27 (m, 1H), 4.05 (s, 3H), 7.24–7.47 (m, 10H), 7.64 (d, J = 7.1 Hz, 1H), 7.79–7.89 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 1.7 (CH_2), 2.4 (CH_2), 19.3 (CH), 31.2 (CH_3), 46.4 (C), 81.0 (C), 87.9 (C), 110.1 (CH), 118.1 (CH), 119.6 (CH), 120.2 (CH), 121.6 (CH), 123.3 (C), 123.6 (C), 124.9 (CH), 125.5 (C), 126.1 (CH), 127.76 (CH), 127.83 (CH), 128.2 (2 × CH), 131.9 (2 × CH), 133.4 (C), 142.0 (C), 142.6 (C), 155.0 (C); LRMS (70 eV, EI) *m/z* (%) 359 (M^+, 100); HRMS (EI^+) calcd for $C_{27}H_{21}N$ 359.1676, found 359.1679.

10-(4-Methoxyphenyl)-5-methyl-5,10-dihydroindeno[1,2-b]indole ***(11i):*** white solid; yield = 97% (158 mg); mp 180–182 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.10 (s, 3H), 4.92 (s, 1H), 6.83 (d, J = 8.4 Hz, 2H), 7.08 (t, J = 7.5 Hz, 1H), 7.13–7.28 (m, 4H), 7.29–7.46 (m, 4H), 7.66 (d, J = 7.4 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 31.3 (CH_3), 47.8 (CH), 55.3 (CH_3), 109.9 (CH), 114.2 (2 × CH), 117.8 (CH), 119.1 (CH), 119.8 (CH), 121.4 (CH), 123.9 (C), 124.6 (C), 125.4 (CH), 125.6 (CH), 127.0

(CH), 129.0 (2 × CH), 132.9 (C), 134.7 (C), 142.1 (C), 144.2 (C), 153.5 (C), 158.6 (C); LRMS (70 eV, EI) *m/z* (%) 325 (M^+, 40), 324 (100); HRMS (EI^+) calcd for $C_{23}H_{19}NO$ 325.1467, found 325.14678.

10-(4-Methoxyphenyl)-5,10-dihydroindeno[1,2-b]indole ***(11j):*** white solid; yield = 80% (124 mg); mp 180–182 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.94 (s, 1H), 6.79–6.83 (m, 2H), 7.03–7.08 (m, 1H), 7.11–7.19 (m, 4H), 7.28 (d, J = 7.4 Hz, 1H), 7.31–7.38 (m, 2H), 7.44 (t, J = 7.5 Hz, 2H), 8.40 (bs, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 48.1 (CH), 55.4 (CH_3), 109.9 (CH), 114.2 (2 × CH), 117.5 (CH), 119.1 (CH), 120.5 (CH), 122.0 (CH), 124.5 (C), 125.5 (CH), 125.6 (CH), 126.1 (C), 127.0 (CH), 129.0 (2 × CH), 132.6 (C), 134.3 (C), 140.9 (C), 142.9 (C), 153.2 (C), 158.6 (C); LRMS (70 eV, EI) *m/z* (%) 311 (100); HRMS (EI^+) calcd for $C_{22}H_{17}NO$ 311.1310, found 311.1307.

10-(4-Chlorophenyl)-5-methyl-5,10-dihydroindeno[1,2-b]indole ***(11k):*** white solid; yield = 82% (135 mg); mp 139–141 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 4.06 (s, 3H), 4.85 (s, 1H), 7.12–7.22 (m, 3H), 7.24–7.28 (m, 1H), 7.29–7.36 (m, 3H), 7.37–7.47 (m, 4H), 7.69 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 31.2 (CH_3), 47.6 (CH), 110.0 (CH), 117.9 (CH), 118.9 (CH), 119.9 (CH), 1121.6 (CH), 123.6 (C), 123.8 (C), 125.48 (CH), 125.54 (CH), 127.2 (CH), 128.9 (2 × CH), 129.4 (2 × CH), 132.4 (C), 134.6 (C), 139.6 (C), 142.0 (C), 144.2 (C), 152.7 (C); LRMS (70 eV, EI) *m/z* (%) 331 [$(M+2)^+$, 34], 329 (M^+, 100), 218 (29); HRMS (EI^+) calcd for $C_{22}H_{16}ClN$ 329.0971, found 329.0972.

10-(4-Chlorophenyl)-5,10-dihydroindeno[1,2-b]indole ***(11l):*** yellow solid; yield = 65% (102 mg); mp 180–182 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 4.94 (s, 1H), 7.07–7.30 (m, 7H), 7.31–7.41 (m, 3H), 7.42–7.53 (m, 2H), 8.37 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 48.0 (CH), 112.3 (CH), 117.7 (CH), 118.9 (CH), 120.6 (CH), 122.1 (CH), 124.2 (C), 125.36 (C), 125.42 (CH), 125.7 (CH), 127.3 (CH), 128.9 (2 × CH), 129.4 (2 × CH), 132.5 (C), 134.2 (C), 139.3 (C), 140.8 (C), 143.0 (C), 152.4 (C); LRMS (70 eV, EI) *m/z* (%) 317 [$(M+2)^+$, 34], 315 (M^+, 100), 313 (35); HRMS (EI^+) calcd for $C_{21}H_{14}ClN$ 315.0815, found 315.0813.

5-Methyl-10-(5-methylfuran-2-yl)-5,10-dihydroindeno[1,2-b]indole ***(11m):*** white solid; yield = 55% (82 mg); mp 146–148 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.07 (s, 3H), 5.07 (s, 1H), 5.86-

5.92 (m, 2H), 7.16-7.30 (m, 3H), 7.31-7.43 (m, 2H), 7.64-7.78 (m, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9 (CH_3), 31.2 (CH_3), 41.8 (CH), 106.06 (CH), 106.14 (CH), 109.9 (CH), 118.0 (CH), 119.6 (CH), 119.9 (CH), 120.9 (C), 121.4 (CH), 124.0 (C), 125.4 (CH), 126.1 (CH), 127.4 (CH), 134.6 (C), 142.0 (C), 144.2 (C), 149.5 (C), 151.6 (C), 151.9 (C); LRMS (70 eV, EI) *m/z* (%) 299 (M^+, 100), 298 (61); HRMS (EI^+) calcd for $C_{21}H_{17}NO$ 299.1310, found 299.1310.

10-(Thiophen-2-yl)-5,10-dihydroindeno[1,2-b]indole ***(11n):*** white solid; yield = 80% (115 mg); mp 137–139 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (s, 1H), 6.95 (dd, *J* = 4.8, 3.8 Hz, 1H), 7.04 (dd, *J*= 3.3, 1.0 Hz, 1H), 7.09–7.15 (m, 2H), 7.17–7.24 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.42–7.47 (m, 2H), 7.49–7.55 (m, 2H), 8.35 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 43.5 (CH), 112.3 (CH), 117.7 (CH), 119.3 (CH), 120.7 (CH), 122.1 (CH), 123.9 (CH), 124.4 (C), 124.9 (CH), 125.0 (C), 125.6 (CH), 125.8 (CH), 126.9 (CH), 127.5 (CH), 133.8 (C), 140.8 (C), 142.8 (C), 143.6 (C), 151.6 (C); LRMS (70 eV, EI) *m/z* (%) 287 (M^+, 100); HRMS (EI^+) calcd for $C_{19}H_{13}NS$ 287.0769, found 287.0768.

(E)-5-Methyl-10-styryl-5,10-dihydroindeno[1,2-b]indole ***(11o):*** white solid; yield = 79% (127 mg); mp 125–127 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.10 (s, 3H), 4.63 (d, *J* = 8.4 Hz, 1H), 6.26 (dd, *J*= 15.6, 8.4 Hz, 1H), 7.00 (d, *J*= 15.6 Hz, 1H), 7.16–7.50 (m, 10H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.67–7.75 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 31.2 (CH_3), 46.4 (CH), 110.0 (CH), 117.8 (CH), 119.1 (CH), 119.9 (CH), 121.5 (CH), 122.9 (C), 124.3 (C), 125.3 (CH), 125.8 (CH), 126.4 (2 × CH), 127.3 (2 × CH), 128.6 (2 × CH), 129.5 (CH), 131.7 (CH), 134.8 (C), 137.5 (C), 142.0 (C), 144.1 (C), 151.3 (C); LRMS (70 eV, EI) *m/z* (%) 321 (M^+, 100), 320 (26); HRMS (EI^+) calcd for $C_{24}H_{19}N$ 321.1517, found 321.1520.

5-Methyl-10-propyl-5,10-dihydroindeno[1,2-b]indole ***(11p):*** white solid; yield = 69%; mp 130–132 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.3 Hz, 3H), 1.48–1.58 (m, 2H), 1.17–1.86 (m, 1H), 2.12–2.23 (m, 1H), 3.88–3.99 (m, 1H), 4.06 (s, 3H), 7.17–7.22 (m, 1H), 7.23–7.29 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.54 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.71 (dd, *J* = 7.8, 0.6 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.6 (CH_3), 20.4 (CH_2), 31.2 (CH_3), 35.7 (CH_2),

42.9 (CH), 109.9 (CH), 117.7 (CH), 119.6 (CH), 119.7 (CH), 121.2 (CH), 124.4 (C), 124.7 (CH), 124.9 (CH), 126.7 (CH), 135.0 (C), 142.0 (C), 144.1 (C), 153.1 (2 × C); LRMS (70 eV, EI) *m/z* (%) 261 (M^+, 21), 218 (100); HRMS (EI^+) calcd for $C_{19}H_{19}N$ 261.1517, found 261.1519.

11-Cyclopropyl-5,10-dimethyl-11-phenyl-10,11-dihydro-5H-cyclopenta[1,2-b:3,4-b']diindole ***(12a):*** yellow solid; yield = 90% (175 mg); mp 299–301 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.19–0.11 (m, 1H), 0.24–0.33 (m, 1H), 0.91–1.00 (m, 1H), 1.05–1.13 (m, 1H), 1.96–2.04 (m, 1H), 3.70, (s, 3H), 4.20 (s, 3H), 6.96–7.08 (m, 2H), 7.17–7.39 (m, 7H), 7.40–7.47 (m, 1H), 7.51–7.62 (m, 2H), 7.85–7.98 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 0.3 (CH_2), 5.9 (CH_2), 15.4 (CH), 31.2 (CH_3), 32.6 (CH_3), 54.7 (C), 109.6 (CH), 110.5 (CH), 111.1 (C), 116.6 (CH), 118.1 (CH), 118.4 (C), 119.5 (CH), 119.6 (C), 119.9 (CH), 120.5 (CH), 120.7 (CH), 125.6 (C), 126.8 (CH), 126.9 (2 × CH), 128.7 (2 × CH), 139.1 (C), 140.3 (C), 142.8 (C), 143.9 (C), 160.4 (C); LRMS (70 eV, EI) *m/z* (%) 388 (M^+, 100), 360 (76); HRMS (EI^+) calcd for $C_{28}H_{24}N_2$ 388.1939, found 388.1938.

11,11-Dicyclopropyl-5,10-dimethyl-10,11-dihydro-5H-cyclopenta[1,2-b:3,4-b']diindole ***(12b):*** yellow solid; yield = 93% (164 mg); mp 291–293 ºC; ^{1}H NMR (400 MHz, C_6D_6) δ 0.13–0.22 (m, 2H), 0.27–0.32 (m, 2H), 0.34–0,41 (m, 2H), 0.87–0.93 (m, 2H), 1.01–1.08 (m, 2H), 3.38 (s, 3H), 3.41 (s, 3H), 7.05 (d, J = 8.1 Hz, 1H), 7.08–7.09 (m, 1H), 7.13 (dd, J = 8.1, 1.1 Hz, 1H), 7.19–7.23 (m, 1H), 7.23–7.29 (m, 2H), 7.69–7.74 (m, 2H); ^{13}C NMR (100.6 MHz, C_6D_6) δ 0.8 (2 × CH_2), 4.1 (2 × CH_2), 14.8 (2 × CH), 31.2 (CH_3), 31.9 (CH_3), 52.1 (C), 110.2 (CH), 110.7 (CH), 110.8 (C), 117.0 (C), 118.3 (CH), 118.6 (CH), 119.9 (CH), 120.3 (C), 120.6 (CH), 120.7 (CH), 120.8 (CH), 127.0 (C), 140.0 (C), 141.0 (C), 144.4 (C), 160.4 (C); LRMS (70 eV, EI) *m/z* (%) 352 (M^+, 100), 323 (38); HRMS (EI^+) calcd for $C_{25}H_{24}N_2$ 352.1939, found 352.1937.

9-Methyl-4,4-di-p-tolyl-4,9-dihydrothieno[3',2':4,5]cyclopenta[1,2-b]indole ***(13a):*** white solid; yield = 75% (152 mg); mp 213–215 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 6H), 3.92 (s, 3H), 7.02 (dd, J = 7.9, 0.6 Hz, 4H), 7.06–7.09 (m, 1H), 7.10–7.15 (m, 1H), 7.16–7.19 (m, 1H), 7.20–7.24 (m, 5H), 7.31–7.35 (m, 1H), 7.45–7.47 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.1 (2 × CH_3), 31.6 (CH_3),

60.3 (C), 110.2 (CH), 118.6 (CH), 120.4 (CH), 120.5 (CH), 124.0 (CH), 124.6 (C), 125.3 (CH), 128.0 (4 × CH), 128.6 (C), 129.1 (4 × CH), 132.2 (C), 136.2 (2 × C), 140.0 (C), 140.7 (C), 141.6 (2 × C), 160.5 (C); LRMS (70 eV, EI) *m/z* (%) 405 (M^+, 100), 314 (73); HRMS (EI^+) calcd for $C_{28}H_{23}NS$ 405.1551, found 405.1551.

4-Cyclopropyl-9-methyl-4-phenyl-4,9-dihydrothieno[3',2':4,5]cyclopenta[1,2-b]indole ***(13b):*** white solid; yield = 80% (136 mg); mp 152–154 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14–0.24 (m, 1H), 0.38–0.62, (m, 3H), 1.86–1.96 (m, 1H), 3.95 (s, 3H), 7.09 (d, J = 4.9 Hz, 1H), 7.11–7.34 (m, 6H), 7.36 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.9 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 2.4 (CH_2), 3.1 (CH_2), 18.3 (CH), 31.6 (CH_3), 56.1 (C), 110.2 (CH), 118.7 (CH), 120.2 (CH), 120.3 (CH), 123.1 (CH), 124.9 (CH), 126.6 (CH), 127.1 (C), 127.2 (2 × CH), 128.5 (2 × CH), 132.1 (C), 140.4 (C), 141.2 (C), 143.9 (C), 160.0 (C); one aromatic C peak was missing due to overlapping; LRMS (70 eV, EI) *m/z* (%) 341 (M^+, 88), 313 (100); HRMS (EI^+) calcd for $C_{23}H_{19}NS$ 341.1238, found 341.1238.

5-Methyl-11,11-di-p-tolyl-6,11-dihydro-5H-benzo[b]carbazole ***(14a):*** white solid; yield = 95% (196 mg); mp 267–269 ºC; ^{1}H NMR (400 MHz, acetone-d_6) δ 2.26 (s, 6H), 4.01 (s, 2H), 6.50 (d, J = 8.1 Hz, 1H), 6.73 (ddd, J = 8.1, 7.2, 1.0 Hz, 1H), 6.94 –7.02 (m, 10H), 7.12–7.17 (m, 1H), 7.20 (dd, J = 7.4, 1.5 Hz, 1H), 7.33–7.40 (m, 2H), 10.21 (bs, 1H); ^{13}C NMR (100.6 MHz, acetone-d_6) δ 20.8 (2 × CH_3), 55.8 (C), 111.6 (CH), 117.7 (C), 119.4 (CH), 120.5 (CH), 121.0 (CH), 126.3 (CH), 126.5 (CH), 127.9 (C), 128.9 (4 × CH), 129.2 (CH), 130.3 (4 × CH), 131.1 (CH), 134.9 (C), 135.7 (C), 135.9 (2 × C), 137.6 (C), 145.2 (2 × C), 146.1 (C); the peak corresponding to the aliphatic CH_2 was overlapped by the peak of the deuterated solvent; LRMS (70 eV, EI) *m/z* (%) 399 (M^+, 33), 308 (100); HRMS (EI^+) calcd for $C_{30}H_{25}N$ 399.1987, found 399.1989.

11-Cyclopropyl-5-methyl-11-phenyl-6,11-dihydro-5H-benzo[b]carbazole ***(14b):*** white solid; yield = 90% (157 mg); mp 239–241 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.6–0.11 (m, 2H), 0.34–0.50 (m, 2H), 1.82 (tt, J = 8.2, 5.6 Hz, 1H), 3.79 (s, 3H), 4.24 (s, 2H), 6.62 (d, J = 8.0 Hz, 1H), 6.80 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.94 (dd, J = 7.8, 1.4 Hz, 1H), 7.09 (ddd, J = 8.2, 5.3, 1.2 Hz, 1H), 7.14 (dd, J = 7.5, 1.2

Hz, 1H), 7.18–7.38 (m, 6H), 7.63 (d, J = 6.9 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 2.3 (CH_2), 2.9 (CH_2), 23.4 (CH), 27.8 (CH_2), 29.5 (CH_3), 50.0 (C), 108.7 (CH), 112.5 (C), 118.8 (CH), 120.1 (CH), 120.6 (CH), 125.7 (CH), 126.0 (CH), 126.2 (CH), 126.6 (C), 127.9 (2 × CH), 128.6 (CH), 129.6 (2 × CH), 130.4 (CH), 132.5 (C), 134.2 (C), 137.5 (C), 144.2 (C), 149.6 (C); LRMS (70 eV, EI) *m/z* (%) 349 (M^+, 30), 260 (100); HRMS (EI^+) calcd for $C_{26}H_{23}N$ 349.1830, found 349.183.

5,11-Dimethyl-11-(thiophen-2-yl)-6,11-dihydro-5H-benzo[b]carbazole ***(14c):*** white solid; yield = 80% (131 mg); mp 179–181 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (s, 3H), 3.77 (s, 3H), 4.22 (d, J = 20.6 Hz, 1H), 4.31 (d, J = 20.6 Hz, 1H), 6.96–7.04 (m, 2H), 7.15–7.29 (m, 6H), 7.31–7.44 (m, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 27.2 (CH_2), 29.4 (CH_3), 31.9 (CH_3), 42.9 (C), 108.8 (CH), 115.4 (C), 119.0 (CH), 119.5 (CH), 121.0 (CH), 124.1 (CH), 124.9 (CH), 125.5 (C), 125.9 (CH), 126.1 (CH), 127.0 (CH), 128.8 (CH), 129.2 (CH), 130.3 (C), 131.7 (C), 137.8 (C), 144.7 (C), 156.3 (C); LRMS (70 eV, EI) *m/z* (%) 329 (M^+, 30), 314 (100); HRMS (EI^+) calcd for $C_{22}H_{19}NS$ 329.1238, found 329.1241.

11-Cyclopropyl-5,11-dimethyl-6,11-dihydro-5H-benzo[b]carbazole ***(14d):*** white solid; yield = 80% (115 mg); mp 135–137 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01–0.09 (m, 1H), 0.21–0.36 (m, 3H), 1.34–1.42 (m, 1H), 1.99 (s, 3H), 3.72 (s, 3H), 4.06–4.16 (m, 2H), 7.08–7.13 (m, 1H), 7.18 (d, J = 7.3 Hz, 1H), 7.22 (d, J = 8.3 Hz, 1H), 7.26–7.36 (m, 3H), 7.67 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 2.9 (CH_2), 3.8 (CH_2), 25.9 (CH_3), 27.3 (CH), 27.6 (CH_2), 29.3 (CH_3), 40.8 (C), 109.0 (CH), 112.8 (C), 118.7 (CH), 120.6 (CH), 121.1 (CH), 125.8 (CH), 126.5 (CH), 127.5 (CH), 129.0 (CH), 131.6 (C), 133.2 (C), 137.7 (C), 144.7 (C), one aromatic carbon peak was missing due to overlapping; LRMS (70 eV, EI) *m/z* (%) 287 (M^+, 28), 246 (100); HRMS (EI^+) calcd for $C_{21}H_{21}N$ 287.1674, found 287.1671.

11-(4-Methoxyphenyl)-5-methyl-6,11-dihydro-5H-benzo[b]carbazole ***(14e):*** white solid; yield = 84% (142 mg); mp 239–241 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.77 (s, 3H), 4.16 (dd, J = 20.5, 4.0 Hz, 1H), 4.34 (dd, J = 20.5, 4.0 Hz, 1H), 5.42 (t, J = 4.0 Hz, 1H), 6.81 (d, J = 8.5 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 7.15–7.29 (m, 7H), 7.33 (d, J = 8.2 Hz, 1H), 7.36–7.43 (m, 1H); ^{13}C NMR (75.4 MHz,

$CDCl_3$) δ 27.2 (CH_2), 29.4 (CH_3), 44.1 (CH), 55.2 (CH_3), 108.6 (CH), 111.0 (C), 113.9 (2 × CH), 118.9 (CH), 119.1 (CH), 121.0 (CH), 126.0 (CH), 126.3 (C), 126.7 (CH), 129.3 (CH), 129.6 (2 × CH), 130.5 (CH), 131.7 (C), 132.8 (C), 137.7 (C), 139.2 (C), 139.7 (C), 157.9 (C); LRMS (70 eV, EI) *m/z* (%) 339 (M^+, 25), 337 (100); HRMS (EI^+) calcd for $C_{24}H_{21}NO$ 339.1623, found 339.1622.

*11-(4-Methoxyphenyl)-6,11-dihydro-5H-benzo[b]carbazole (**14f**):* white solid; yield = 98% (159 mg); mp 180–182 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 4.14 (dd, J = 20.4, 4.0 Hz, 1H), 4.32 (dd, J = 20.4, 3.8 Hz, 1H), 5.39 (at, J = 3.8 Hz, 1H), 6.73–6.82 (m, 2H), 6.94–6.99 (m, 1H), 7.08–7.13 (m, 1H), 7.15–7.32 (m, 8H), 7.85 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 28.1 (CH_2), 44.0 (CH), 55.3 (CH_3), 110.6 (CH), 112.3 (C), 114.0 (2 × CH), 119.1 (CH), 119.5 (CH), 121.6 (CH), 126.1 (CH), 126.7 (CH), 126.9 (C), 129.1 (CH), 129.6 (2 × CH), 130.6 (CH), 131.3 (C), 131.9 (C), 136.6 (C), 138.9 (C), 139.6 (C), 158.0 (C); LRMS (70 eV, EI) *m/z* (%) 325 (M^+, 94), 218 (100); HRMS (EI^+) calcd for $C_{23}H_{19}NO$ 325.1467, found 325.1468.

*5-Methyl-11-(thiophen-2-yl)-6,11-dihydro-5H-benzo[b]carbazole (**14g**):* yellow solid; yield = 75% (118 mg); mp 163–165 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.15 (dd, J = 20.3, 3.7 Hz, 1H), 4.28 (dd, J = 20.3, 3.7 Hz, 1H), 5.61 (t, J = 3.7 Hz, 1H), 6.73 (dd, J = 4.9, 1.1 Hz, 1H), 7.03 (t, J = 7.5 Hz, 2H), 7.11 (dd, J = 4.9, 2.9 Hz, 1H), 7.16–7.44 (m, 8H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 27.3 (CH_2), 29.5 (CH_3), 40.0 (CH), 108.8 (CH), 110.3 (C), 118.8 (CH), 119.1 (CH), 120.8 (CH), 121.1 (CH), 125.8 (CH), 126.2 (CH), 126.4 (C), 126.7 (CH), 127.9 (CH), 129.4 (CH), 130.2 (CH), 132.0 (C), 132.9 (C), 137.7 (C), 138.6 (C), 147.2 (C); LRMS (70 eV, EI) *m/z* (%) 315 (M^+, 100), 232 (97); HRMS (EI^+) calcd for $C_{21}H_{17}NS$ 315.1082, found 315.1083.

*(E)-5-Methyl-11-styryl-6,11-dihydro-5H-benzo[b]carbazole (**14h**):* yellow solid; yield = 85% (142 mg); mp 159–161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 4.13 (dd, J = 20.4, 3.8 Hz, 1H), 4.22 (dd, J = 20.3, 3.7 Hz, 1H), 5.04–5.10 (m, 1H), 6.24 (dd, J = 15.6, 9.0 Hz, 1H), 6.79 (d, J = 15.6 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.16–7.24 (m, 2H), 7.24–7.31 (m, 4H), 7.32–7.41 (m, 4H), 7.50–7.57 (m, 1H), 7.69 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.2 (CH_2), 29.5 (CH_3), 42.9 (CH),

108.4 (C), 108.8 (CH), 119.17 (CH), 119.19 (CH), 121.2 (CH), 126.5 (3 × CH), 126.7 (CH), 126.8 (C), 127.2 (CH), 128.6 (2 × CH), 129.3 (CH), 129.5 (CH), 130.4 (CH), 132.1 (C), 132.9 (C), 134.4 (CH), 137.3 (C), 137.6 (C), 137.7 (C); LRMS (70 eV, EI) *m/z* (%) 335 (M^+, 63), 333 (100); HRMS (EI^+) calcd for $C_{25}H_{21}N$ 335.1674, found 335.1674.

11-Cyclopropyl-11-phenyl-6,11-dihydroindolo[1,2-b]isoquinoline ***(15a):*** yellow solid; yield = 30% (50 mg); mp 163–165 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.08–0.16 (m, 1H), 0.28–0.36 (m, 1H), 0.67–0.77 (m, 2H), 1.70–1.79 (m, 1H), 4.86 (d, J = 15.2 Hz, 1H), 5.26 (d, J = 15.2 Hz, 1H), 6.49 (s, 1H), 7.14–7.42 (m, 10H), 7.47 (d, J = 8.1 Hz, 1H), 7.61–7.74 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 1.0 (CH_2), 1.9 (CH_2), 20.3 (CH), 45.1 (C), 50.1 (CH_2), 99.9 (CH), 108.8 (CH), 119.7 (CH), 120.6 (CH), 120.9 (CH), 126.4 (CH), 126.6 (CH), 126.7 (CH), 127.4 (CH), 127.5 (2 × CH), 128.2 (CH), 128.3 (C), 130.0 (2 × CH), 133.3 (C), 135.6 (C), 142.2 (C), 142.6 (C), one aromatic carbon peak was missing due to overlapping; LRMS (70 eV, EI) *m/z* (%) 335 (M^+, 84), 294 (100); HRMS (EI^+) calcd for $C_{25}H_{21}N$ 335.1674, found 335.1677.

11,11-Dimethyl-6,11-dihydroindolo[1,2-b]isoquinoline ***(15b):*** yellow oil; yield = 46% (57 mg); R_f = 0.23 (hexane/EtOAc, 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 (s, 6H), 5.30 (s, 2H), 6.47 (s, 1H), 7.12–7.20 (m, 1H), 7.21–7.26 (m, 1H), 7.26–7.32 (m, 1H), 7.35 (d, J = 6.8 Hz, 1H), 7.38 (d, J = 7.1 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.64 (dd, J = 7.8, 0.7 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 30.3 (2 × CH_3), 36.5 (C), 44.8 (CH_2), 95.1 (CH), 108.7 (CH), 119.8 (CH), 120.4 (CH), 120.7 (CH), 124.7 (CH), 126.4 (CH), 126.6 (CH), 128.0 (CH), 128.7 (C), 131.2 (C), 135.8 (C), 142.5 (C), 145.3 (C); LRMS (70 eV, EI) *m/z* (%) 247 (M^+, 19), 232 (100); HRMS (EI^+) calcd for $C_{18}H_{17}N$ 247.1361, found 247.1360.

11-(4-Methoxyphenyl)-6,11-dihydroindolo[1,2-b]isoquinoline ***(15c):*** yellow solid; yield = 52% (85 mg); mp 138–140 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 5.31 (s, 2H), 5.46 (s, 1H), 6.28 (d, J = 0.8 Hz, 1H), 6.86 (d, J = 8.3 Hz, 2H), 7.10–7.21 (m, 3H), 7.22–7.36 (m, 4H), 7.37–7.44 (m, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.61 (dd, J = 7.8, 0.6 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 44.5 (CH_2),

44.9 (CH), 55.4 (CH_3), 98.4 (CH), 108.9 (CH), 114.1 (2 × CH), 119.9 (CH), 120.4 (CH), 120.8 (CH), 126.5 (CH), 126.8 (CH), 127.7 (CH), 128.8 (C), 129.0 (CH), 129.7 (2 × CH), 131.8 (C), 135.2 (C), 135.7 (C), 136.9 (C), 139.3 (C), 158.5 (C); LRMS (70 eV, EI) *m/z* (%) 325 (M^+, 100), 217 (30); HRMS (EI^+) calcd for $C_{23}H_{19}NO$ 325.1467, found 325.1466.

11-(4-Methoxyphenyl)-11,12-dimethyl-6,11-dihydroindolo[1,2-b]isoquinoline ***(15d):*** yellow solid; yield = 56% (99 mg); mp 124–126 ºC; ^1H NMR (400 MHz, $CDCl_3$,) δ 1.79 (s, 3H), 1.95 (s, 3H), 3.80 (s, 3H), 5.26 (d, J = 15.7 Hz, 1H), 5.39 (d, J = 15.7 Hz, 1H), 6.79–6.84 (m, 2H), 7.01 (dd, J = 7.7, 1.5 Hz, 1H), 7.12–7.16 (m, 1H), 7.18 (dd, J = 7.3, 1.5 Hz, 1H), 7.20–7.27 (m, 4H), 7.32–7.35 (m, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.50–7.54 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.2 (CH_3), 29.3 (CH_3), 44.5 (CH_2), 55.2 (CH_3), 105.6 (C), 108.7 (CH), 113.4 (2 × CH), 118.2 (CH), 119.3 (CH), 120.9 (CH), 126.1 (CH), 126.2 (CH), 127.6 (CH), 128.3 (CH), 129.4 (2 × CH), 129.7 (C), 129.9 (C), 134.6 (C), 138.7 (C), 139.7 (C), 143.3 (C), 157.9 (C); LRMS (70 eV, EI) *m/z* (%) 353 (M^+, 55), 338 (100); HRMS (EI^+) calcd for $C_{25}H_{23}NO$ 353.1780, found 353.1782.

11-(4-Methoxyphenyl)-11-methyl-6,11-dihydroindolo[1,2-b]isoquinoline ***(15e):*** yellow oil; yield = 65% (110 mg); R_f = 0.20 (hexane/EtOAc, 5/1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 3H), 3.76 (s, 3H), 4.83 (d, J = 15.2 Hz, 1H), 5.25 (d, J = 15.2 Hz, 1H), 6.47 (s, 1H), 6.72–6.76 (m, 2H), 6.97–7.00 (m, 2H), 7.14–7.19 (m, 1H), 7.23–7.45 (m, 5H), 7.55 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 7.7 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 28.1 (CH_3), 44.97 (CH_2), 45.03 (C), 55.3 (CH_3), 97.6 (CH), 108.7 (CH), 113.4 (2 × CH), 119.7 (CH), 120.6 (CH), 120.9 (CH), 126.2 (CH), 126.6 (2 × CH), 127.7 (CH), 128.5 (2 × CH), 133.3 (C), 135.8 (C), 138.6 (C), 142.4 (C), 144.2 (C), 158.0 (C); LRMS (70 eV, EI) *m/z* (%) 339 (M^+, 100), 324 (28); HRMS (EI^+) calcd for $C_{24}H_{21}NO$ 339.1623, found 339.1623.

12-Methyl-11,11-di-p-tolyl-6,11-dihydroindolo[1,2-b]isoquinoline ***(15f):*** yellow solid; yield = 63% (130 mg); mp 129–131 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 1.58 (s, 3H), 2.34 (s, 6H), 4.93 (s, 2H), 6.83–6.89 (m, 4H), 7.01–7.08 (m, 4H), 7.13 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H), 7.19–7.28 (m, 3H), 7.29–7.35 (m, 1H), 7.37–7.42 (m, 1H), 7.56–7.60 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.5 (CH_3), 21.1 (2 × CH_3),

44.7 (CH_2), 56.6 (C), 107.9 (C), 108.4 (CH), 118.7 (CH), 118.9 (CH), 121.1 (CH), 126.2 (CH), 126.5 (CH), 126.9 (CH), 128.8 (4 × CH), 129.7 (CH), 129.8 (C), 130.2 (4 × CH), 133.9 (C), 134.4 (C), 136.3 (2 × C), 137.6 (C), 141.1 (2 × C), 143.8 (C); LRMS (70 eV, EI) *m/z* (%) 413 (100); HRMS (EI^+) calcd for $C_{31}H_{27}N$ 413.2143, found, 413.2142.

*11-Isopropyl-12-methyl-6,11-dihydroindolo[1,2-b]isoquinoline (**15g**):* yellow solid; yield= 60% (83 mg); mp 120–122 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89–1.00 (m, 6H), 2.07–2.17 (m, 1H), 2.41 (s, 3H), 4.07 (dd, J = 6.2, 3.5 Hz, 1H), 5.18 (dd, J = 15.5, 2.3 Hz, 1H), 5.31 (dd, J = 15.5, 2.5 Hz, 1H), 7.12–7.46 (m, 7H), 7.59–7.65 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.4 (CH_3), 20.4 (CH_3), 20.8 (CH_3), 37.0 (CH_2), 45.5 (CH), 45.7 (CH), 105.3 (C), 108.4 (CH), 118.5 (CH), 118.9 (CH), 120.6 (CH), 126.4 (CH), 126.5 (CH), 126.9 (CH), 129.3 (C), 129.8 (CH), 133.3 (C), 134.7 (C), 135.4 (C), 136.9 (C); LRMS (70 eV, EI) *m/z* (%) 275 (M^+, 14), 232 (100); HRMS (EI^+) calcd for $C_{20}H_{21}N$ 275.1674, found, 275.1675.

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Supporting Information Available. Copies of ^1H and ^{13}C NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For recent reviews, see: (a) Ishikura, M.; Yamada, K. *Nat. Prod. Rep.* **2009**, *26*, 803–852. (b) Kochanowska-Karamyan, A. J.; Hamann, M. T. *Chem. Rev.* **2010**, *110*, 4489–4497. (c) Zhang, M.-Z.; Chen, Q.; Yang, G.-F. *Eur. J. Med. Chem.* **2015**, *89*, 421–441.

(2) For selected revisions on indole synthesis or functionalization see: (a) Barluenga, J.; Rodríguez, F.; Fañanás, F. J. *Chem. Asian J.* **2009**, *4*, 1036–1048. (b) Bandini, M.; Eichholzer, A. *Angew. Chem.*

Int. Ed. **2009**, *48*, 9608–9644. (c) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2011**, *111*, PR215–PR283. (d) Shiri, M. *Chem. Rev.* **2012**, *112*, 3508–3549. (e) Inman, M.; Moody, C. J. *Chem. Sci.* **2013**, *4*, 29–41.

(3) For a revision on synthesis and applications of indenoindoles see: Rongved, P.; Kirsch, G.; Bouaziz, Z.; Jose, J.; Le Borgne, M. *Eur. J. Med. Chem.*, **2013**, *69*, 465–479.

(4) Jewett, J. C.; Sletten, E. M.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2010**, *132*, 3688–3690.

(5) (a) Talaz, O.; Gülçin, I.; Göksu, S.; Saracoglu, N. *Bioorg. Med. Chem.* **2009**, *17*, 6583–6589. (b) Kashyap, M.; Das, D.; Preet, R.; Mohapatra, P.; Satapathy, S. R.; Siddharth, S.; Kundu, C. N.; Guchhait, S. K. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 2474–2479.

(6) Grandini, C.; Camurati, I.; Guidotti, S.; Mascellani, N.; Resconi, L. *Organometallics* **2004**, *23*, 344–360.

(7) (a) Xu, H.-Y.; Xu, X.-P.; Wang, S.-Y.; Ji, S.-J. *Eur. J. Org. Chem.* **2012**, 5440–5445. (b) Das, D.; Pratihar, S.; Roy, S. *Org. Lett.* **2012**, *14*, 4870–4873. (c) Oh, C. H.; Park, H. S.; Park, N.; Kim, S. Y.; Piao, L. *Synlett* **2014**, *25*, 579–585. (d) Chu, X.-Q.; Zi, Y.; Lu, X.-M.; Wang, S.-Y.; Ji, S.-J.; *Tetrahedron* **2014**, *70*, 232–238. (e) Kotha, S.; Ali, R.; Srinivas, V.; Krishna, N. G. *Tetrahedron* **2015**, *71*, 129–138.

(8) For the synthesis of related indenoindolones see: (a) Chernyak, N.; Tilly, D.; Li, Z.; Gevorgyan, V. *Chem. Commun.* **2010**, *46*, 150–152. (b) Jiang, B.; Li, Q.-Y.; Tu, S.-J.; Li, G. *Org. Lett.* **2012**, *14*, 5210–5213.

(9) Very recently the synthesis of 10-aryl-5,10-dihydroindeno[l,2-*b*]indoles was described including few compounds possessing a quaternary 10^{th} carbon bearing a methyl and an aryl group: Reddy, A. G. K.; Satyanarayana, G. *Synthesis* **2015**, *47*, 1269–1279.

(10) (a) Sanz, R.; Ignacio, J. M.; Castroviejo, M. P.; Fañanás, F. J. *ARKIVOC* **2007**, *(iv)*, 84–91. (b) Takaya, J.; Udagawa, S.; Kusama, H.; Iwasawa, N. *Angew. Chem. Int. Ed.* **2008**, *47*, 4906–4909. (c) Zhou, J.-L.; Ye, M.-C.; Sun, X.-L.; Tang, Y. *Tetrahedron* **2009**, *65*, 6877–6881. (d) Suarez, L. L.; Greany, M. F. *Chem. Commun.* **2011**, *47*, 7992–7994. (e) Swami, A.; Ramana, C. *Synlett* **2015**, *26*, 604–608.

(11) For a review on the direct nucleophilic S_N1-type reactions of alcohols, see: Emer, E.; Sinisi, R.; Capdevila, M. G.; Petruzziello, D.; De Vincentiis, F.; Cozzi, P. G. *Eur. J. Org. Chem.* **2011**, 647–666.

(12) For recent examples, see: (a) Zhang, L.; Zhu, Y.; Yin, G.; Lu, P.; Wang, Y. *J. Org. Chem.* **2012**, *77*, 9510–9520. (b) Gohain, M.; Marais, C.; Bezuidenhoudt, B. C. B. *Tetrahedron Lett.* **2012**, *53*, 4704–4707. (c) Hikawa, H.; Suzuki, H.; Azumaya, I. *J. Org. Chem.* **2013**, *78*, 12128–12135.

(13) See, for instance: (a) Shirakawa, S.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 311–314. (b) Motokura, K.; Nakagiri. N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2007**, *72*, 6006–6015. (c) Liu, Y.-L.; Liu, L.; Wang, Y.-L.; Han, Y.-C.; Wang, D.; Chen, Y.-J. *Green Chem.* **2008**, *10*, 635–640.

(14) For recent examples, see: (a) Putra, A. E.; Takigawa, K.; Tanaka, H.; Ito, Y.; Oe, Y.; Ohta, T. *Eur. J. Org. Chem.* **2013**, 6344–6354. (b) Hakim Siddiki, S. M. A.; Kon, K.; Shimizu, K.-i. *Chem. Eur. J.* **2013**, *19*, 14416–14419. (c) Chen, S.-j.; Lu, G.-p.; Cai, C. *Synthesis* **2014**, *46*, 1717–1724.

(15) (a) Sanz, R.; Martínez, A.; Miguel, D.; Álvarez-Gutiérrez, J. M.; Rodríguez, F. *Adv. Synth. Catal.* **2006**, *348*, 1841–1845. (b) Sanz, R.; Miguel, D.; Álvarez-Gutiérrez, J. M.; Rodríguez, F. *Synlett* **2008**, 975–978. (c) Sanz, R.; Miguel, D.; Martínez, A.; Gohain, M.; García-García, P.; Fernández-Rodríguez, M. A.; Álvarez, E.; Rodríguez, F. *Eur. J. Org. Chem.* **2010**, 7027–7039.

(16) See, for instance: (a) Huang, W.; Zheng, P.; Zhang, Z.; Liu, R.; Chen, Z.; Zhou, X. *J. Org. Chem.* **2008**, *73*, 6845–6848. (b) Bandini, M.; Tragni, M.; Umani-Ronchi, A. *Adv. Synth. Catal.* **2009**, *351*, 2521–2524. (c) Kumar Das, S.; Singh, R.; Panda, G. *Eur. J. Org. Chem.* **2009**, 4757–4761. (d) Panteleev, J.; Huang, R. Y.; Lui, E. K. J.; Lautens, M. *Org. Lett.* **2011**, *13*, 5314–5317. (e) Sarkar, S.; Maiti, S.; Bera, K.; Jalal, S.; Jana, U. *Tetrahedron Lett.* **2012**, *53*, 5544–5547. (f) Zheng, H.; Ghanbari, S.; Nakamura, S.; Hall, D. G. *Angew. Chem. Int. Ed.* **2012**, *51*, 6187–6190. (g) Nammalwar, B.; Bunce, R. A. *Tetrahedron Lett.* **2013**, *54*, 4330–4332.

(17) For metal-catalyzed examples, see: (a) Namba, K.; Yamamoto, H.; Sasaki, I.; Mori, K.; Imagawa, H.; Nishizawa, M. *Org. Lett.* **2008**, *10*, 1767–1770. (b) Bandini, M.; Eichholzer, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 9533–9537. (c) Bandini, M.; Bottoni, A.; Chiarucci, M.; Cera, G.; Miscione, G. P. *J. Am.*

Chem. Soc. **2012**, *134*, 20690−20700. (d) Wong, C. M.; Vuong, K. Q.; Gatus, M. R. D.; Hua, C.; Bhadbhade, M. *Organometallics* **2012**, *31*, 7500−7510.

(18) Chen, L.; Yin, X.-P.; Wang, C.-H.; Zhou, J. *Org. Biomol. Chem.* **2014**, *12*, 6033−6048.

(19) Jefferies, L. R.; Cook, S. P. *Org. Lett.* **2014**, *16*, 2026−2029.

(20) Notably, the cyclopenta[1,2-*b*]indole is a key structural motif of wide range of biological active products. See for instance: (a) Zhang, W.; Liu, Z.; Li, S.; Yang, T.; Zhang, Q.; Ma, L.; Tian, X.; Zhang, H.; Huang, C.; Zhang, S.; Ju, J.; Shen, Y.; Zhang, C. *Org. Lett.* **2012**, *14*, 3364−3367. (b) Harms, H.; Rempel, V.; Kehraus, S.; Kaiser, M.; Hufendiek, P.; Müller, C. E.; König, G. M. *J. Nat. Prod.* **2014**, *77*, 673−677.

(21) So, C. M.; Lau, C. P.; Kwong, F. Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 8059−8063.

(22) Heany, H.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1973**, 499−500.

(23) Wiedenou, P.; Blechert, S. *Synth. Commun.* **1997**, *27*, 2033−2039.

(24) Liang, Z.; Zhao, J.; Zhang, Y. *J. Org. Chem.* **2010**, *75*, 170−177.