# Synthesis of Functionalized Pyrrole and Indole Derivatives through Carbometallation of Lithiated Double Bonds

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**Abstract:** Bis(2-lithioallyl)amines derived from bis(2-bromoallyl)amines undergo intramolecular carbometallation of a lithiated double bond, giving dilithiated dihydropyrroles. The cyclizations are promoted by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). Reaction of these intermediates with electrophiles allows the preparation of some new fused and nonfused five-membered functionalized heterocycles. Although 2-lithioallylamines do not suffer intermolecular carbometallation, dimerization products are obtained with their copper or zirconium derivatives. Finally, the application of this new reaction to 2-lithio-*N*-(2-lithioallyl)anilines leads to 3-lithiomethylindole derivatives, which are transformed to functionalized indole derivatives by reaction with electrophiles.

**Keywords:** carbanions · carbolithiation · heterocycles · indoles · pyrroles

## Introduction

Ring-forming reactions are very important processes in the field of synthetic methodology. Whereas a large number of routes have been developed for cationic,[1] radical,[2] and stabilized anionic[3] cyclizations, the use of highly reactive carbanions in these reactions presents the potential disadvantage that the electrophilic site must tolerate the anion-forming conditions. Their classical utilization has been restricted to the synthesis of polymers or of rather simple hydrocarbons. Moreover, with carbanions generated from weak acids, ion pairs or clusters are the reactive intermediates, and their reactivity is increased by using donor solvents, polydentate ligands, and crown ethers, an effect attributed to the lowering of the degree of aggregation rather than to the separation of cation from anion.[4] Although simple alkenes and alkynes are not usually thought of as sites of nucleophilic attack, the addition of alkyl-[5] and vinyllithium[6] reagents to inactivated carbon–carbon multiple bonds has been used in recent years as a tool for the construction of carbocycles. However, the carbolithiation of alkynes is of limited preparative value because terminal alkynes are always deprotonated by organolithium reagents and disubstituted ones are not readily carbolithiated if other reaction pathways, such as deprotonations at propargylic positions, occur more readily. In the case of isolated carbon–carbon double bonds, only terminal olefins and 1,2-disubstituted alkenes in which the initially formed alkyllithium product is substituted with a leaving group in a $\beta$-position[7] or is stabilized by a moderately strong activating group[8] are useful substrates for the carbolithiation reaction. Despite these limitations, organolithium cyclizations can be a powerful synthetic tool, although it has not been developed extensively, especially in the case of reactions that involve the formation of heterocycles instead of carbocycles.[9] Interestingly, with this methodology it could be possible to functionalize the cyclized product by reaction with electrophiles; this represents an important advantage over the corresponding radical cyclizations. Moreover, cyclizations of vinyllithium reagents, rather than alkyllithium reagents, would also incorporate an alkene into the product with control of its stereochemistry; this could allow further functionalization. On the other hand, the use of vinylmetals as electrophiles is not usual and only the allylzincation of vinylorganometallics is a general reaction. Nevertheless, this process is believed to proceed through the formation of an allylvinylzinc derivative, which then undergoes a 3,3-sigmatropic rearrangement (metallo-Claisen reaction) to give the corresponding 1,1-diorganometallic compound.[10]

The development of new strategies directed toward the preparation of heterocyclic systems continues to be an important synthetic goal. In this context, the synthesis of

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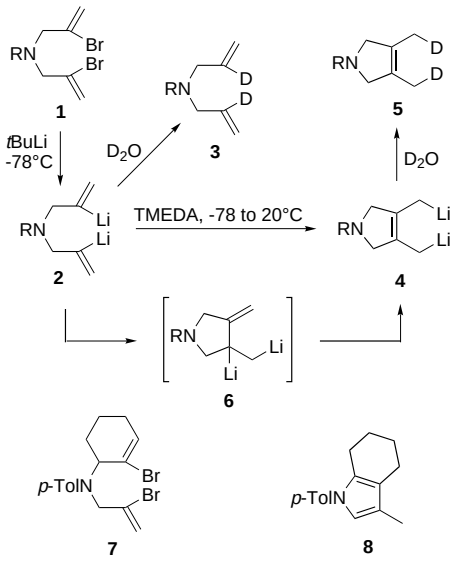
pyrrole and indole derivatives has been an active field due to the wide range of these derivatives that occur in nature and to the biological activity found among these compounds of both natural and synthetic origin.[11] In connection with our interest in the preparation of *N*-heterocycles through carbometallation reactions, we have recently reported the easy intramolecular carbolithiation of *N*-allyl-*N*-(2-lithioallyl)amines that proceeds by 5-*exo* or 6-*endo* modes depending on the electron density on the nitrogen atom.[12] In this paper, we describe the first intramolecular carbometallation of lithiated double bonds and its application to the synthesis of functionalized pyrrole and indole derivatives.[13]

## Results and Discussion

**Intramolecular carbometallation of *N*,*N*-bis(2-lithioallyl)-amines**: Treatment of *N*,*N*-bis(2-bromoallyl)amines **1** with four equivalents of *tert*-butyllithium[14] in diethyl ether at $-78\,^{\circ}C$ gave the dianions **2**, which were characterized by deuteriolysis to give dideuterated amines **3** (Scheme 1). These dianions




Scheme 1. Intramolecular carbolithiation of *N*,*N*-bis(2-lithioallyl)-amines **2**.

**Abstract in Spanish:** *Las bis(2-litioalil)aminas derivadas de bis(2-bromoalil)aminas experimentan una reacción de carbometalación intramolecular del doble enlace litiado generando dihidropirroles dilitiados. Las ciclaciones son aceleradas y, en ocasiones promovidas, por TMEDA. La reacción de estos intermedios con electrófilos permite la preparación de nuevos heterociclos funcionalizados de cinco eslabones. Aunque las 2-litioalilaminas no experimentan esta carbometalación de forma intermolecular, es posible obtener productos de dimerización con sus derivados de cobre o de zirconio. Finalmente, la aplicación de esta nueva reacción a 2-litio-N-(2-litioalil)-anilinas conduce a derivados de 3-litiometilindoles, los cuales son transformados en derivados de indoles funcionalizados por reacción con electrófilos.*

were stable in solution at $-78\,^{\circ}C$, but the addition of four equivalents of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) at low temperature afforded 3,4-bis(lithiomethyl)dihydropyrrole derivatives **4**. In the case of aromatic amine derivatives **1b** and **1c** the cyclizated products **4b** and **4c**, respectively, were generated at temperatures ranging between $-78$ and $-50\,^{\circ}C$ in 1 h, whereas non-aromatic derivatives **1a** and **1d** undergo complete cyclization in 1 h at room temperature to afford dilithiated compounds **4a** and **4d**, respectively. This transformation involving the cycloisomerization of vinyllithium to allyllithium moieties with formation of a new carbon–carbon double bond allows the preparation of dihydropyrrole derivatives from bis(2-bromoallyl)amines. These dilithiated intermediates **4** were characterized by their treatment with deuterium oxide giving rise to 3,4-bis(deuteromethyl)dihydropyrrole derivatives **5** in excellent yield (Scheme 1 and Table 1). The fact that the reaction works for

Table 1. Preparation of dihydropyrrole and pyrrole derivatives **5**, **9**–**12**, **15**, and **16** from 2-bromoallylamines **1**.

| Starting amine | R | $E^+$ | Product | E/M | Yield [%][a] |
|---|---|---|---|---|---|
| **1a** | $PhCH_2$ | $D_2O$ | **5a** | D | 85 |
| **1b** | Ph | $D_2O$ | **5b** | D | 91 |
| **1c** | 4-$MeC_6H_4$ | $D_2O$ | **5c** | D | 90 |
| **1a** | $PhCH_2$ | $Me_3SiCl$ | **9a** | $SiMe_3$ | 82 |
| **1a** | $PhCH_2$ | $Bu_3SnCl$ | **9b** | $SnBu_3$ | 79 |
| **1b** | Ph | $Me_3SiCl$ | **9c** | $SiMe_3$ | 87 |
| **1b** | Ph | $Bu_3SnCl$ | **9d** | $SnBu_3$ | 85 |
| **1d** | *c*-$C_6H_{11}$ | $Me_3SiCl$ | **9e** | $SiMe_3$ | 77 |
| **1d** | *c*-$C_6H_{11}$ | $Bu_3SnCl$ | **9f** | $SnBu_3$ | 75 |
| **1c** | 4-$MeC_6H_4$ | PhCH=NPh | **9g** | PhCHNHPh | 73 |
| **1c** | 4-$MeC_6H_4$ | $Me_2CO$ | **9h** | $Me_2CHOH$ | 75 |
| **1b** | Ph | $D_2O$ | **10a** | D | 84 |
| **1b** | Ph | $CO_2$/EtOH | **10b** | $CO_2Et$ | 79 |
| **1c** | 4-$MeC_6H_4$ | PhCH=NPh | **10c** | PhCHNHPh | 72 |
| **1c** | 4-$MeC_6H_4$ | $Me_2CO$ | **10d** | $Me_2CHOH$ | 75 |
| **1a** | $PhCH_2$ | $Ph_2SiCl_2$ | **11a** | $SiPh_2$ | 77 |
| **1a** | $PhCH_2$ | $Et_2GeCl_2$ | **11b** | $GeEt_2$ | 82 |
| **1b** | Ph | $Ph_2SiCl_2$ | **11c** | $SiPh_2$ | 86 |
| **1b** | Ph | $Et_2GeCl_2$ | **11d** | $GeEt_2$ | 90 |
| **1b** | Ph | $Me_2SnCl_2$ | **11e** | $SnMe_2$ | 84 |
| **1b** | Ph | $Ph_2SiCl_2$ | **12a** | $SiPh_2$ | 78 |
| **1b** | Ph | $Et_2GeCl_2$ | **12b** | $GeEt_2$ | 81 |
| **1b** | Ph | $D_2O$ | **15a** | D | 55 |
| **1b** | Ph | $Me_3SiCl$ | **15b** | $SiMe_3$ | 60 |
| **1b** | Ph | $Bu_3SnCl$ | **15c** | $SnBu_3$ | 56 |
| **1b** | Ph | $Ph_2S_2$ | **15d** | SPh | 58 |
| **1b** | Ph | $D_2O$ | **16a** | D | 58 |

[a] Isolated yield based on the starting amine **1**.

aromatic and nonaromatic amines but that the reaction conditions and reaction times are different indicates a strong influence of the electron density on the nitrogen atom in the outcome of the process. It is also interesting to note that the cyclization also works in the absence of TMEDA,[15] but it needs about 45–60 minutes at room temperature for aromatic amines **1b** and **1c** and about 3–4 hours for nonaromatic amines **1a** and **1d**. These results indicate an strong accelerating effect of the lithium-coordinating diamine and the role of TMEDA is really important in the case of amine **7**, which

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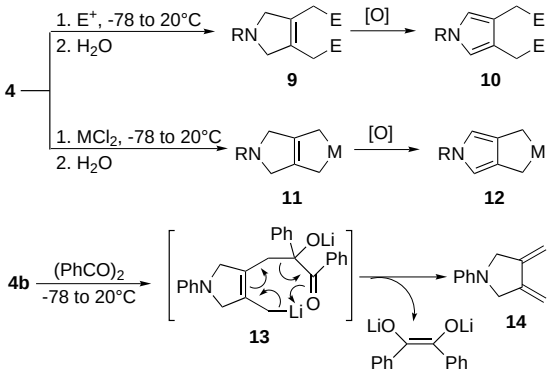
under treatment with four equivalents of *t*BuLi and further addition of four equivalents of TMEDA afforded the bicyclic amine **8** in 73% yield after 30 min at 20°C, hydrolysis, and further oxidation with oxygen. However, if TMEDA is not added only 40% of **8** is formed, and decomposition products were obtained along with the expected compound if the reaction time is longer.

The formation of dilithiated dihydropyrrole derivatives **4** by treatment of dianions **2** with TMEDA could be explained by assuming first an intramolecular carbolithiation of one vinyllithium moiety by the other one, affording methylenepyrrolidine derivatives **6**. These intermediates could undergo an allylic rearrangement to give dilithiated compounds **4** (Scheme 1). Other pathways involving single electronic transfer process could be feasible as in the case of the radical cyclization of *N*,*N*-bis(2-bromo-2-propenyl)benzenesulfonamide to the corresponding 3,4-dimethyl-3-pyrroline derivative.[16]

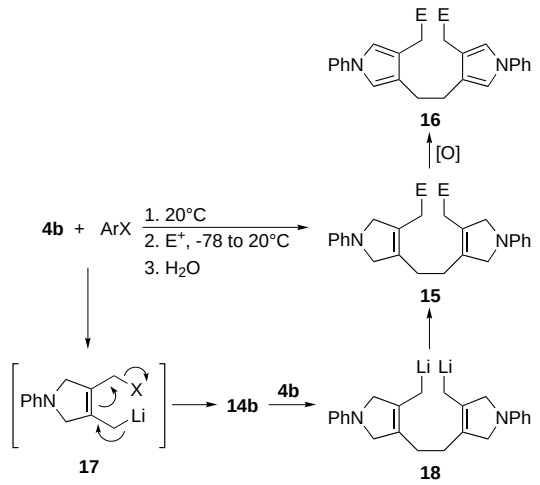
To extend the synthetic scope of this new reaction we carried out the functionalization of the new dilithiated dihydropyrrole derivatives **4** with different electrophiles. In this way, treatment of dianions **4** with imines, carbonyl compounds, carbon dioxide, and silicon or tin chlorides gave rise to functionalized dihydropyrrole derivatives **9** in good yields (Scheme 2 and Table 1). These 3,4-bis(functionalized-




Scheme 2. Reaction of dianions **4** with electrophiles. Preparation of pyrrole derivatives **9**–**12**.

methyl)-3-pyrrolines are interesting heterocycles, not previously reported.[17] In the case of aromatic amine-derived dihydropyrroles, their subsequent oxidation with oxygen or with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) allowed the synthesis of the corresponding 3,4-difunctionalized pyrrole derivatives **10**. Moreover, the reaction of **4** with some silicon, tin, and germanium dichlorides produces new hexahydrometallacyclopenta[3,4-*c*]pyrrole derivatives **11** in good yields (Scheme 2 and Table 1). Again, compounds **11** derived from aromatic amines were easily oxidized with DDQ to the tetrahydrometallacyclopenta[3,4-*c*]pyrrole derivatives **12**. It is interesting to note that compounds **11** and **12** represent a new class of five-membered fused heterocycles. It is also noteworthy that the 3,4-disubstituted pyrrole system is probably the most difficult to be prepared, since most electrophilic aromatic substitution and lithiation reactions occur at the $\alpha$-positions.[18] Disappointingly, when we tried the formation of a six-membered cycle by reaction of dianion **4b** with 1,2-diphenylethanedione or iodoacetonitrile, an undesired reaction took place that resulted in the formation of the exocyclic diene **14** and the corresponding reduction product derived from the electrophile. A proposal for the unexpected reaction of **4b** with 1,2-diphenylethanedione is presented in Scheme 2 in which we assume a stepwise mechanism that involves the initial attack of one extreme of the dianion **4b** to the electrophile which gives rise to the unstable intermediate **13**. After an elimination process, homologated by the double bond, diene **14** and benzoin were isolated after hydrolysis.[19] In the same way, the reaction between **4b** and diphenyl disulfide also afforded diene **14** and thiophenol. These results indicate that when an electrophile which contains an adequately positioned good leaving group is added to dianion **4**, the formation of diene **14** is preferred over the double reaction with the electrophile. In this context, Maruoka et al. have recently reported the cleavage of $\alpha,\beta$ carbon–carbon bond of $\gamma$-lithiocarbonyl substrates by the use of a Lewis acid,[20] a reaction that takes place in a similar way to what we postulate here.

Interestingly, treatment of dianion **4b** with an equimolecular amount of an aryl halide, such as bromobenzene or 1,2-dichlorobenzene, gave rise to an unexpected result. After quenching the reaction with different electrophiles (deuterium oxide, chlorotrimethylsilane, tributyltin chloride, and diphenyl disulfide) the dihydropyrrole dimers **15** were isolated, which could be easily oxidized to the aromatic pyrrole derivatives **16** (Scheme 3 and Table 1). The outcome of the




Scheme 3. Intermolecular coupling of dianion **4b**.

reaction could be explained by assuming an halogen–lithium exchange that produces monoanion **17**, which upon $\delta$-elimination affords the exocyclic diene **14b**. Further carbolithiation of **14b** by the dianion **4b**, probably favored by TMEDA, would produce the dilithiated dimers **18**, which by reaction with electrophiles lead to **15**. In order to support this mechanistic proposal, we carried out the reaction by adding 0.5 equivalents of the aryl halide, and the result was the same. This fact is in agreement with the role we have assigned to the halide. An alternative mechanism for the formation of



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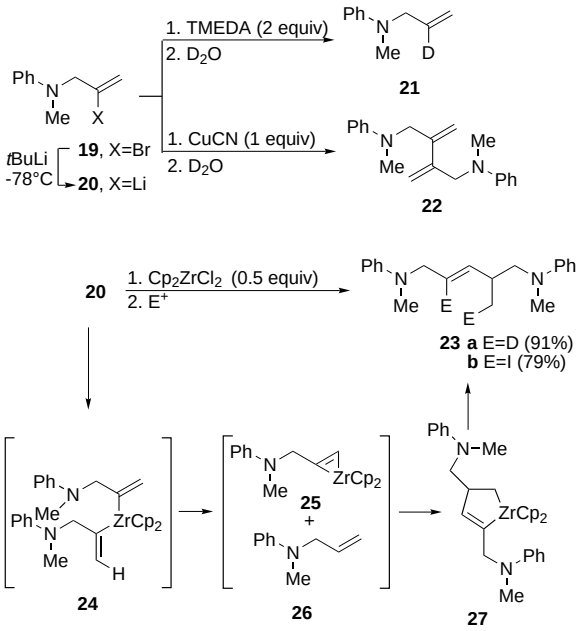
dilithiated dimer **18** could involve an electron-transfer process to the aryl halide and further coupling of the resulting radicals. It is interesting to note that, as far as we know, these derivatives of 3,3′-(1,2-ethanediyl)-bis(2,5-dihydro-1*H*-pyrrole) **15** and their aromatic counterparts **16** have not been previously described.

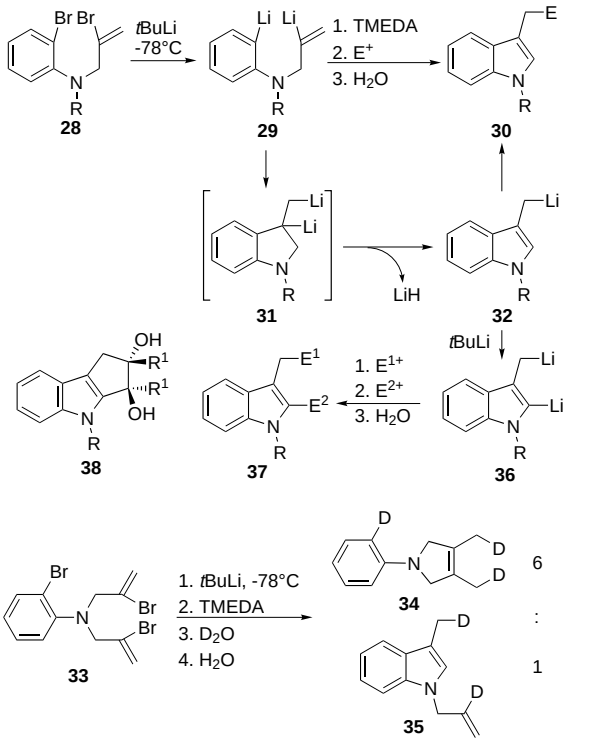
**Intermolecular carbometallation of *N*-(2-lithioallyl)amines**: The successful results of the intramolecular carbometallation of metallated double bonds prompted us to consider the possibility of carrying out this process in an intermolecular way, by using 2-lithioallylamines. Accordingly, two equivalents of TMEDA were added to *N*-(2-lithioallyl)-*N*-methylaniline **20**, generated from 2-bromoallylamine **19** by treatment with two equivalents of *tert*-butyllithium (Scheme 4).




Scheme 4. Zirconium- and copper-mediated intermolecular coupling of 2-lithioallylamine **20**.

However, after deuteriolysis the deuterated amine **21** was isolated along with the $\beta$-elimination product *N*-methylaniline. In an attempt to force the carbometallation reaction one equivalent of CuCN was added to anion **20**; in this case compound **22** was isolated in 81 % yield. The formation of **22** could be explained considering a thermal dimerization of the lower order cuprate generated from **20** and one equivalent of CuCN (Scheme 4). It is well known that the thermal decomposition of alkenylcopper(I) yields copper(0) and butadiene derivatives with retention of configuration at the olefinic double bonds.[21] In connection with our interest in the applications of the chemistry of organozirconium complexes in organic synthesis,[22] we turned our attention to the corresponding organozirconocene compounds derived from 2-lithioallylamines. Thus, reaction of organolithium reagent **20** and zirconocene dichloride (0.5 equiv) in diethyl ether/THF, followed by treatment with electrophiles (deuterium oxide and iodine) furnished the diamines **23** in good yields. A proposal to account for the formation of **23** involves a lithium–zirconium transmetallation that leads to the divinylzirconium derivative **24**, which is thermally unstable and undergoes a $\beta$-hydrogen abstraction reaction that gives rise to the $\eta^2$-propargylamino complex **25** and *N*-allyl-*N*-methylaniline **26**. Regioselective insertion of the alkene moiety of **26** into the zirconium–carbon bond of **25** affords zirconacyclopentene derivative **27**.[23] Further deuteriolysis or iodonolysis of **27** produces the diamines **23** (Scheme 4). It is interesting to note that complex **24** undergoes a C–H activation process through a favorable agostic interaction between the C–H σ bond and an empty MO of the metal. Moreover, for this multicentered pathway in cyclometalation reactions, only alkyl, benzyl, or phenyl groups are usually used as the fragments that accept the leaving hydrogen. In our case an alkene is generated in the $\beta$-hydrogen abstraction.[24] These reactions allow the dimerization or the reductive dimerization and functionalization of 2-lithioallylamines by using copper- or zirconium-mediated processes.

**Intramolecular carbometallation of 2-lithio-*N*-(2-lithioallyl)-anilines**: In order to extend the scope of this new carbometallation reaction of lithiated double bonds, we carried out the reaction with 2-bromo-*N*-(2-bromoallyl)anilines **28** as starting materials. With tertiary amines **28a** and **28b** bromine–lithium exchange at low temperature afforded the dianions **29**, which under the addition of TMEDA and further treatment with different electrophiles led to the isolation of functionalized indoles **30** (Scheme 5 and Table 2). The formation of the indole nucleus could be explained assuming an initial carbometallation of the vinyllithium moiety by the aryllithium in the dianions **29** to afford dilithiated indoline derivatives **31**.




Scheme 5. Intramolecular carbolithiation of *N*-(2-lithioallyl)-2-lithioanilines **29**. Preparation of indole derivatives **30**, **37**, and **38**.

Table 2. Preparation of indole derivatives **30**, **37**, and **38** from *N*-(2-bromoallyl)-2-bromoanilines **28**.

| Starting amine | R | $E^+$ | Product | E | Yield (%)[a] |
|---|---|---|---|---|---|
| **28a** | $PhCH_2$ | $D_2O$ | **30a** | D | 72 |
| **28a** | $PhCH_2$ | $Me_3SiCl$ | **30b** | $SiMe_3$ | 65 |
| **28a** | $PhCH_2$ | $(PhCH_2S)_2$ | **30c** | $SCH_2Ph$ | 63 |
| **28b** | Me | $D_2O$ | **30d** | D | 79 |
| **28b** | Me | $Me_3SiCl$ | **30e** | $SiMe_3$ | 68 |
| **28b** | Me | 4-$ClC_6H_4CHO$ | **30f** | 4-$ClC_6H_4CHOH$ | 71 |
| **28b** | Me | PhCH=NCHMePh | **30g** | PhCHNHCHMePh | 61[b] |
| **28b** | Me | 4-$MeC_6H_4CN$ | **30h** | 4-$MeC_6H_4CO$ | 75 |
| **28b** | Me | PhNCO | **30i** | PhNHCO | 67 |
| **28b** | Me | $(PhS)_2$ | **30j** | SPh | 70 |
| **28b** | Me | MeCOCOMe | **30k** | MeC(OH)COMe | 68 |
| **28c** | H | $D_2O$ | **30l** | D | 51 |
| **28c** | H | $Et_2CO$ | **30m** | $Et_2COH$ | 55 |
| **28c** | H | $Ph_2CO$ | **30n** | $Ph_2COH$ | 57 |
| **28c** | H | PhCH=NPh | **30o** | PhCHNHPh | 59 |
| **28b** | Me | $E^{1+}=E^{2+}=D_2O$ | **37a** | $E^1=E^2=D$ | 70 |
| **28b** | Me | $E^{1+}=Me_3SiCl$, $E^{2+}=D_2O$ | **37b** | $E^1=SiMe_3$, $E^2=D$ | 61 |
| **28b** | Me | $E^{1+}$–$E^{2+}$ = PhCOCOPh | **38a** | $R^1$ = Ph | 47[c] |
| **28b** | Me | $E^{1+}$–$E^{2+}$ = MeCOCOMe | **38b** | $R^1$ = Me | 42[c] |

[a] Isolated yield based on the starting amine **28**. [b] A 6:1 mixture of diastereoisomers was obtained. [c] Only one diastereoisomer was obtained.

In this case, since an allylic rearrangement would involve the loss of aromaticity in the aromatic ring, elimination of lithium hydride takes place affording 3-lithiomethylindole derivatives **32**. Reaction of intermediates **32** with electrophiles leads to the 3-substituted indole derivatives **30**. It is interesting to note that in this case the reaction is slower than with aromatic amines **1b** and **1c**, and, after the addition of TMEDA, three hours at 20 °C were necessary in order to get an almost complete conversion. Moreover, without the addition of TMEDA the cyclization is still slower, with several hours needed for the subsequent partial hydrolysis of the starting dianion **29**. To check the different rates of reactivity between **28** and **1**, we synthesized the 2-bromo-*N*,*N*-bis(2-bromoallyl)-aniline **33**. Its sequential treatment with six equivalents of *t*BuLi and TMEDA at −78 °C, followed by warming to room temperature and further deuteriolysis, led to a 6:1 mixture of the dihydropyrrole derivative **34** and the indole derivative **35** in over 90% combined yield (Scheme 5). This result shows that intramolecular carbometallation of a lithiated double bond by a vinyllithium is faster than by an aryllithium.

The preparation of *N*-unsubstituted indoles by this new process would be of great interest. Thus, the reaction of secondary amine **28c** (R = H) with five equivalents of *t*BuLi afforded the corresponding trianion **29** (R = Li). Further addition of TMEDA causes the evolution to the indole derivative **32** (R = Li). However, the process is slower at 20 °C and decomposition of 3-lithiomethylindole is in competition with the cyclization. After eight hours at room temperature and subsequent deuteriolysis, an equimolecular mixture of **30** (E = D, R = H) and the dideuteriated amine corresponding to the intermediate **29** was obtained. For longer reaction times (16 h), 3-methylindole **30** (R = E = H) was obtained in 60% yield. To our delight, when the suspension of trianion **29** (R = Li) in diethyl ether/TMEDA was heated under reflux for 3 h, the cyclization product **32** (R = Li) was obtained in nearly 65% yield without significant decomposition of the carbanion. In this way, 3-functionalized indoles **30** (R = H) were prepared by addition of different electrophiles after heating the mixture under reflux (Scheme 5 and Table 2).

It is well known that 1-protected indoles can be lithiated at C2 with strong bases like *tert*-butyllithium.[25] Therefore, the treatment of **28b** with five equivalents of *t*BuLi afforded, in the presence of TMEDA, the dilithiated indole derivative **36**. Its further reaction with two different electrophiles led to 2,3-difunctionalized indole derivatives **37**. Moreover, the treatment of **36** with 1,2-diketones gave rise to cyclopent-[*b*]indole derivatives **38** as a single diastereoisomer[26] (Scheme 5 and Table 2). This new synthesis of indoles, with formation of the C3–C3a bond, has the advantage over the Pd-catalyzed cyclizations of *o*-halo-*N*-allyl or *N*-vinylanilines[27] that a further functionalization could be carried out in the same reaction step.

## Conclusion

In summary, we have described the first TMEDA-promoted intramolecular carbometallation of lithiated double bonds in bis(2-lithioallyl)amines to afford 3,4-bis(lithiomethyl)dihydropyrrole derivatives. It is noteworthy that this transformation represents a cycloisomerization of vinyllithium to allyllithium moieties with formation of a new carbon–carbon double bond. The resulting allylic organodilithium reagents react with a range of electrophiles to give new and interesting fused and nonfused heterocyclic compounds. Although the intermolecular process does not proceed in the same way, an interesting reductive dimerization of 2-bromoallylamines mediated by zirconocene complexes has been achieved. Moreover, a simple and straightforward synthesis of indoles has also been developed. Further studies on the applications of this novel reaction to organic syntheses are actively underway.

## Experimental Section

**General**: All reactions were carried out under nitrogen atmosphere in oven-dried glassware. Temperatures are reported as bath temperatures. Benzene, diethyl ether, and tetrahydrofuran were continuously heated under reflux and freshly distilled from sodium or sodium/benzophenone under nitrogen. Tetramethylethylendiamine (TMEDA) was distilled under vacuum from potasium/benzophenone under nitrogen. Solvents used in extraction and purification were distilled prior to use. Compounds were visualized on analytical thin-layer chromatograms (TLC) by UV light (254 nm) or iodine. Silica gel (230–400 mesh) was used for flash



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chromatography. NMR spectra were recorded at 400, 300, 200, and 80 MHz for proton frequency and 75.5, 50.5, and 20.2 MHz for carbon frequency with the DEPT pulse sequence. IR spectra were recorded as neat samples. Elemental analyses were performed by the Microanalytical Laboratory, Universidad de Oviedo. Mass spectra were usually carried out by electron impact at 70 eV. Only the most significant IR absorptions and the molecular ions and/or base peaks in MS are given. Melting points are uncorrected. Amines, 2,3-dibromopropene, electrophiles (carbonyls, nitriles, disulfides, isocyanates, metalloid chlorides and dichlorides), copper cyanide, zirconocene dichloride, iodine, and deuterium oxide were purchased from Aldrich or Acros Organics and were used without further purification. *t*BuLi was used as 1.5 M solutions in pentane. BuLi was used as 1.6 or 2.5 M solutions in hexane. *N*-Benzylideneamines were prepared by heating under reflux a mixture of benzaldehyde and the corresponding amine in presence of a catalytic amount of *p*-toluenesulfonic acid in toluene in a system equipped with a Dean–Stark trap. Amine **19** was prepared by treatment of *N*-methylaniline with BuLi and 2,3-dibromopropene according with a published procedure.[28]

**Preparation of *N,N*-bis(2-bromoallyl)amines 1 and 33. General procedure**: A mixture of the primary amine (benzylamine, aniline, *p*-toluidine, or 2-bromoaniline; 50 mmol), 2 equiv of $K_2CO_3$ (13.82 g, 100 mmol) and 2 equiv of 2,3-dibromopropene (10.34 mL, 100 mmol) in 100 mL of acetonitrile was stirred for 24–48 hours under reflux. The mixture was extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were washed with saturated $Na_2CO_3$ aqueous solution and dried over anhydrous $Na_2SO_4$. The solvents were removed under vacuum, and the residue was purified by flash column chomatography or crystallization to afford amines **1** and **33**.

***N,N*-Bis(2-bromoallyl)benzylamine (1a)**: Reaction of benzylamine (5.46 mL, 50 mmol), $K_2CO_3$ (13.82 g, 100 mmol), and 2,3-dibromopropene (10.34 mL, 100 mmol) in acetonitrile (100 mL). Work-up as above yielded **1a** (13.11 g, 76%) as a colorless oil. $R_f = 0.28$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.55-7.3$ (m, 5H), 6.0 and 5.7 (2s, 4H), 3.8 (s, 2H), 3.45 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 137.9$, 130.9, 128.4, 128.1, 127.0, 118.5, 60.9, 56.7; LRMS (70 eV, EI): *m*/*z* (%): 349 (10) $[M+4]^+$, 347 (21) $[M+2]^+$, 345 (10) $[M]^+$, 84 (100); elemental analysis calcd (%) for $C_{13}H_{15}NBr_2$ (345.1): C 45.25, H 4.38, N 4.06; found C 45.17, H 4.35, N 3.99.

***N,N*-Bis(2-bromoallyl)aniline (1b)**: Reaction of aniline (4.56 mL, 50 mmol), $K_2CO_3$ (13.82 g, 100 mmol), and 2,3-dibromopropene (10.34 mL, 100 mmol) in acetonitrile (100 mL). Work-up as above yielded **1b** (13.16 g, 80%) as a white solid. M.p. 44–46 °C (hexane), (lit.[29] 47.0–47.8 °C); $R_f = 0.39$ (hexane/ethyl acetate 40:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-6.7$ (m, 5H), 5.75 and 5.65 (2s, 4H), 4.2 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 146.4$, 129.2, 128.5, 118.1, 116.1, 112.1, 58.4; LRMS (70 eV, EI): *m*/*z* (%): 333 (18) $[M+4]^+$, 331 (37) $[M+2]^+$, 329 (18) $[M]^+$, 130 (100); HRMS (70 eV, EI) calcd for $C_{12}H_{13}Br_2N$ ($[M]^+$): 328.9415, found 328.9410; elemental analysis calcd (%) for $C_{12}H_{13}Br_2N$ (331.0): C 43.54, H 3.96, N 4.23; found C 43.43, H 3.91, N 4.15.

***N,N*-Bis(2-bromoallyl)-4-methylaniline (1c)**: Reaction of *p*-toluidine (5.46 mL, 50 mmol), $K_2CO_3$ (13.82 g, 100 mmol), and 2,3-dibromopropene (10.34 mL, 100 mmol) in acetonitrile (100 mL). Work-up as above yielded **1c** (13.21 g, 77%) as a white solid. M.p. 63–65 °C (hexane), (lit.[29] 65.8–66.7 °C); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.2$ (d, $J = 9.6$ Hz, 2H), 6.6 (d, $J = 9.6$ Hz, 2H), 5.8–5.5 (m, 4H), 4.15 (s, 4H), 2.3 (s, 3H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 144.4$, 129.7, 129.1, 127.3, 116.2, 112.4, 58.7, 20.1; LRMS (70 eV, EI): *m*/*z* (%): 347 (26) $[M+4]^+$, 345 (53) $[M+2]^+$, 343 (26) $[M]^+$, 144 (100); elemental analysis calcd (%) for $C_{13}H_{15}Br_2N$ (345.1): C 45.25, H 4.38, N 4.06; found C 45.31, H 4.41, N 3.98.

**2-Bromo-*N,N*-bis(2-bromoallyl)aniline (33)**: Reaction of 2-bromoaniline (8.6 g, 50 mmol), $K_2CO_3$ (13.82 g, 100 mmol), and 2,3-dibromopropene (10.34 mL, 100 mmol) in acetonitrile (100 mL). Work-up as above yielded **33** (15.19 g, 75%) as a colorless oil. $R_f = 0.28$ (hexane); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.6-6.8$ (m, 4H), 6.0–5.9 (m, 2H), 5.6–5.5 (m, 2H), 4.1 (s, 4H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 147.0$, 134.0, 129.7, 127.7, 125.3, 125.2, 120.3, 118.8, 60.2; LRMS (70 eV, EI): *m*/*z* (%): 411 (16) $[M+4]^+$, 409 (33) $[M+2]^+$, 407 (16) $[M]^+$, 304 (100); elemental analysis calcd (%) for $C_{12}H_{12}Br_3N$ (409.9): C 35.16, H 2.95, N 3.42; found C 35.12, H 2.91, N 3.37.

**Preparation of *N*-(2-bromoallyl)-*N*-(2-bromo-2-cyclohexenyl)-4-methylaniline (7)**: A mixture of 4-methylaniline (5.35 g, 50 mmol), $K_2CO_3$ (3.46 g, 25 mmol), and 2,3-dibromopropene (2.56 mL, 25 mmol) in acetonitrile (50 mL) was stirred for 48 h under reflux. The mixture was extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were washed with saturated $Na_2CO_3$ aqueous solution and dried over anhydrous $Na_2SO_4$. The solvents were removed under vacuum and the residue was purified by column chomatography (hexane/ethyl acetate 20:1) to afford *N*-(2-bromoallyl)-4-methylaniline (4.5 g, 80%). A mixture of *N*-(2-bromoallyl)-4-methylaniline (4.5 g, 20 mmol), $K_2CO_3$ (2.77 g, 20 mmol), and 1,6-dibromocyclohexene[30] (4.8 g, 20 mmol) in acetonitrile (50 mL) was stirred for 48 h under reflux. Work-up as above yielded **7** (6.54 g, 85%) as a colorless oil. $R_f = 0.43$ (hexane/ethyl acetate 20:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.0$ (d, $J = 8.6$ Hz, 2H), 6.7 (d, $J = 8.6$ Hz, 2H), 6.4–6.3 (m, 1H), 5.85–5.75 (m, 1H), 5.55–5.5 (m, 1H), 4.6–4.5 (m, 1H), 4.2–3.8 (m, 2H), 2.25 (s, 3H), 2.2–1.6 (m, 6H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta =$ 145.0, 134.6, 130.5, 129.5, 126.8, 124.7, 116.5, 113.5, 60.6, 55.0, 30.0, 27.4, 20.6, 20.2; LRMS (70 eV, EI): *m*/*z* (%): 387 (10) $[M+4]^+$, 385 (21) $[M+2]^+$, 383 (10) $[M]^+$, 120 (100); elemental analysis calcd (%) for $C_{16}H_{19}Br_2N$ (385.1): C 49.90; H 4.97; N 3.64; found C 50.11; H 4.86; N 3.55.

**Preparation of *N*-(2-bromoallyl)anilines 28a and 28b. General procedure**: A solution of 2-bromoaniline (8.6 g, 50 mmol) in THF (60 mL) was treated with BuLi (10 mL of a 2.5 M solution in hexanes, 25 mmol) at −40 °C. The reaction was stirred for 15 min at this temperature, then it was allowed to reach 20 °C and stirring was continued for 45 min. The reaction was cooled to −60 °C and benzyl chloride (3.16 g, 25 mmol) or methyl iodide (3.55 g, 25 mmol) was added. After 15 min at this temperature, the reaction was allowed to warming up and stirring was continued for 5 h. The mixture was hydrolyzed with water, extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were washed with saturated $Na_2CO_3$ aqueous solution and dried over anhydrous $Na_2SO_4$. The solvents were removed under vacuum, and the residue was purified by silica gel column chomatography (hexane/ethyl acetate 30:1) to afford *N*-alkyl-2-bromoaniline. A mixture of *N*-alkyl-2-bromoaniline (15 mmol), $K_2CO_3$ (2.07 g, 15 mmol), and 2,3-dibromopropene (1.55 mL, 15 mmol) in acetonitrile (50 mL) was stirred for 24–48 h under reflux. Work-up as for **7** afforded amines **28a** and **28b**.

***N*-Benzyl-2-bromo-*N*-(2-bromoallyl)aniline (28a)**: Isolated in 71% yield. $R_f = 0.22$ (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.6$ (dd, $J = 7.5$, 1.5 Hz, 1H), 7.4–6.9 (m, 8H), 5.9–5.85 (m, 1H), 5.6–5.55 (m, 1H), 4.3 (s, 2H), 3.9 (s, 2H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 148.0$, 137.4, 133.9, 129.8, 128.5, 128.2, 127.6, 127.2, 124.9, 124.6, 120.8, 118.7, 59.4, 56.8; LRMS (70 eV, EI): *m*/*z* (%): 383 (7) $[M+4]^+$, 381 (15) $[M+2]^+$, 379 (7) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{16}H_{15}Br_2N$ (381.1): C 50.42; H 3.97; N 3.68; found C 50.59; H 3.93; N 3.55.

**2-Bromo-*N*-(2-bromoallyl)-*N*-methylaniline (28b)**: Isolated in 76% yield. $R_f = 0.32$ (hexane); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.5$ (dd, $J = 7.5$, 1.6 Hz, 1H), 7.3–6.7 (m, 3H), 6.0 (q, $J = 1.6$ Hz, 1H), 5.6 (dd, $J = 2.7$ and 1.1 Hz, 1H), 3.9 (2, 2H), 2.8 (s, 3H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 151.2$, 135.2, 131.4, 129.2, 125.7, 123.6, 120.7, 119.2, 64.8, 42.0; LRMS (70 eV, EI): *m*/*z* (%): 307 (16) $[M+4]^+$, 305 (33) $[M+2]^+$, 303 (16) $[M]^+$, 198 (100); elemental analysis calcd (%) for $C_{10}H_{11}Br_2N$ (305.0): C 39.38; H 3.64; N 4.59; found C 39.29; H 3.63; N 4.45.

**Preparation of 2-bromo-*N*-(2-bromoallyl)aniline 28c**: A mixture of 2-bromoaniline (8.6 g, 50 mmol), $K_2CO_3$ (3.46 g, 25 mmol), and 2,3-dibromopropene (2.59 mL, 25 mmol) in acetonitrile (50 mL) was stirred for 48 hours under reflux. The mixture was extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were washed with saturated $Na_2CO_3$ aqueous solution and dried over anhydrous $Na_2SO_4$. The solvents were removed under vacuum, and the residue was purified by silica gel column chomatography to afford **28c** (5.51 g, 79%) as a colorless oil. $R_f =$ 0.45 (hexane/ethyl acetate 20:1); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.5-6.5$ (m, 4H), 5.9–5.8 (m, 1H), 5.65–5.55 (m, 1H), 4.9 (br s, 1H), 4.05 (d, $J =$ 6.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 143.5$, 132.4, 130.1, 128.4, 118.7, 116.6, 111.7, 109.7, 51.8; LRMS (70 eV, EI): *m*/*z* (%): 293 (23) $[M+4]^+$, 291 (45) $[M+2]^+$, 289 (23) $[M]^+$, 130 (100); elemental analysis calcd (%) for $C_9H_9Br_2N$ (291.0): C 37.15; H 3.12; N 4.81; found C 37.21; H 3.07; N 4.69.

**General Procedure for the preparation of deuterated amines 3 by deuteriolysis of *N,N*-bis(2-lithioallyl)amines 2**: A solution of the starting amine **1** (2 mmol) in diethyl ether (15 mL) was treated with 4 equiv of *t*BuLi (8 mmol) at −78 °C. The reaction was stirred for 30 min at this temperature, and then an excess of deuterium oxide was added to the

solution. The cooling bath was removed allowing the reaction to achieve room temperature. The mixture was hydrolyzed with water and extracted with ethyl acetate ($3 \times 10$ mL).The combined organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography (hexane/ethyl acetate) to afford products **3**.

***N,N*-Bis(2-deuterioallyl)benzylamine (3a)**: Reaction of **1a** (0.69 g, 2 mmol) and *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) was followed by addition of deuterium oxide (excess). Work-up as above yielded **3a** (0.34g, 91%) as a colorless oil. $R_f = 0.23$ (hexane/ethyl acetate 10:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-7.2$ (m, 5H), 5.3–5.15 (m, 4H), 3.65 (s, 2H), 3.15 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 139.3$, 135.4 (t, $J$(C,D) = 23.6 Hz), 128.8, 128.1, 126.7, 117.2, 57.4, 56.2; LRMS (70 eV, EI): $m/z$ (%): 189 (18) $[M]^+$, 91 (100); HRMS (70 eV, EI) calcd for $C_{13}H_{15}D_2N$ ($[M]^+$): 189.1486, found 189.1483.

***N,N*-Bis(2-deuterioallyl)aniline (3b)**: Amine **1c** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) was followed by addition of deuterium oxide (excess). Work-up as above yielded **3b** (0.32g, 92%) as a colorless oil. $R_f = 0.43$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-6.8$ (m, 5H), 5.3 (s, 4H), 4.1 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 148.5$, 133.6 (t, $J$(C,D) = 22.6 Hz), 128.9, 116.2, 115.7, 112.2, 52.5; LRMS (70 eV, EI): $m/z$ (%): 175 (61) $[M]^+$, 77 (100).

***N,N*-Bis(2-deuterioallyl)-4-methylaniline (3c)**: Reaction of **1c** (0.66 g, 2 mmol) and *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) was followed by addition of deuterium oxide (excess). Work-up as above yielded **3c** (0.34g, 91%) as a colorless oil. $R_f = 0.43$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.0$ (d, $J = 8.2$ Hz, 2H), 6.6 (d, $J = 8.2$ Hz, 2H), 5.2–5.1 (m, 4H), 3.85 (s, 4H), 2.2 (s, 3H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 146.5$, 133.8 (t, $J$(C,D) = 23.5 Hz), 129.4, 125.3, 115.6, 112.6, 52.7, 20.1; LRMS (70 eV, EI): $m/z$ (%): 189 (1) $[M]^+$, 187 (100); elemental analysis calcd (%) for $C_{13}H_{15}D_2N$ (189.3): C 82.49, H/D 10.12, N 7.40; found C 82.25, H/D 10.01, N 7.29.

**Intramolecular carbolithiation of *N,N*-bis(2-lithioallyl)amines 2. General procedure for the preparation of dihydropyrrole derivatives 5, 9, and 11**: TMEDA (1.2 mL, 8 mmol) at $-78$ °C was added to a solution of dianion **2** (2 mmol), which was formed by reaction of the corresponding amine **1** (2 mmol) with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) at $-78$ °C as described above. The resulting mixture was stirred at temperatures ranging between $-78$ and $-50$ °C for 1 h in the case of aromatic amines **1b** and **1c** and at room temperature for 1 h when nonaromatic amines **1a** and **1d** were used (in the absence of TMEDA 1 h at room temperature for aromatic amines **1b** and **1c** and 4 h at the same temperature for aliphatic amines **1a** and **1d** were needed). In both cases, the ethereal solution of the corresponding dianion **4** was cooled to $-78$ °C and 2.1 equiv (4.2 mmol) of electrophiles (deuterium oxide, water, chlorotrimethylsilane, tributyltin chloride, carbon dioxide, acetone, *N*-benzylideneaniline) or 1.0 equiv (2 mmol) for the metallodichlorides (dichlorodiphenylsilane, dichlorodiethylgermane, dimethyltin dichloride) were added. Then, the mixture was allowed to reach room temperature, and the reaction was stirred for 3 h. The mixture was hydrolyzed with water and extracted with ethyl acetate ($3 \times 20$ mL).The combined organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum and the resulting residue was crystallized or purified by flash column chromatography yielding the functionalized dihydropyrroles **5**, **9**, and **11**.

**1-Benzyl-3,4-bis(deuteriomethyl)-1,5-dihydro-2*H*-pyrrole (5a)**: Amine **1a** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of deuterium oxide (excess) and work-up as above yielded **5a** (0.32 g) as a colorless oil. $R_f = 0.1$ (ethyl acetate); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-7.2$ (m, 5H), 3.8 (s, 2H), 3.4 (s, 4H), 1.6 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 139.4$, 128.6, 128.2, 126.8, 64.4, 60.4, 11.2 (t, $J$(C,D) = 19.6 Hz); IR (neat): $\tilde{\nu} = 1680$ cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 189 (10) $[M]^+$, 91 (100); HRMS (70 eV, EI) calcd for $C_{13}H_{15}D_2N$ ($[M]^+$): 189.1487, found 189.1484; elemental analysis calcd (%) for $C_{13}H_{15}D_2N$ (189.3): C 82.48, H/D 10.12, N 7.40; found C 82.41, H/D 9.98, N 7.42.

**3,4-Bis(deuteriomethyl)-1,5-dihydro-1-phenyl-2*H*-pyrrole (5b)**: Amine **1b** (0.66 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of deuterium oxide (excess) and work-up as above yielded **5b** (0.32 g) as a white solid. M.p. 111–113 °C (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-6.6$ (m, 5H), 4.1 (s, 4H), 1.7 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 147.0$, 129.1, 126.8, 115.0, 110.7, 58.9, 11.0 (t, $J$(C,D) = 19.6 Hz); IR (KBr): $\tilde{\nu} = 1615$ cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 175 (91) $[M]^+$, 77 (100); HRMS (70 eV, EI) calcd for $C_{12}H_{13}D_2N$ ($[M]^+$): 175.1330, found 175.1326; elemental analysis calcd (%) for $C_{12}H_{13}D_2N$ (175.3): C 82.23, H/D 9.78, N 7.99; found C 82.28, H/D 9.59, N 7.89.

**3,4-Bis(deuteriomethyl)-1,5-dihydro-1-(4-methylphenyl)-2*H*-pyrrole (5c)**: Amine **1c** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of deuterium oxide (excess) and work-up as above yielded **5c** (0.34 g) as a white solid. M.p. 120–122 °C (hexane); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.1$ (d, $J = 8.5$ Hz, 2H), 6.45 (d, $J = 8.5$ Hz, 2H), 4.0 (s, 4H), 2.3 (s, 3H), 1.75 (s, 4H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 145.2$, 129.7, 127.0, 124.1, 110.9, 59.3, 20.2, 11.0 (t, $J$(C,D) = 18.4 Hz); LRMS (70 eV, EI): $m/z$ (%): 189 (71) $[M]^+$, 188 (100); elemental analysis calcd (%) for $C_{13}H_{15}D_2N$ (189.3): C 82.49, H/D 10.12, N 7.40; found C 82.29, H/D 9.99, N 7.70.

**1-Benzyl-1,5-dihydro-3,4-bis(trimethylsilylmethyl)-2*H*-pyrrole (9a)**: Amine **1a** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of chlorotrimethylsilane (0.46 g, 4.2 mmol) and work-up as above yielded **9a** (0.54 g) as a yellow oil. $R_f = 0.36$ (hexane/ethyl acetate 3:1); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.4-7.2$ (m, 5H), 3.8 (s, 2H), 3.4 (s, 4H), 1.45 (s, 4H), 0.0 (s, 18H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 139.6$, 128.5, 128.1, 126.9, 126.7, 64.5, 60.8, 17.1, $-0.8$; IR (neat): $\tilde{\nu} = 1660$ cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 331 (17) $[M]^+$, 244 (100); HRMS (70 eV, EI) calcd for $C_{19}H_{33}NSi_2$ ($[M]^+$) 331.2152, found 331.2129; elemental analysis calcd (%) for $C_{19}H_{33}NSi_2$ (331.6): C 68.81, H 10.03, N 4.22; found C 68.71, H 10.07, N 4.17.

**1-Benzyl-1,5-dihydro-3,4-bis(tributyltinmethyl)-2*H*-pyrrole (9b)**: Amine **1a** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of tributyltin chloride (1.37 g, 4.2 mmol) and work-up as above yielded **9b** (1.21 g) as a colorless oil. $R_f = 0.39$ (hexane/ethyl acetate 5:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-7.25$ (m, 5H), 3.8 (s, 2H), 3.35 (s, 4H), 1.65 (s, 4H), 1.6–0.8 (m, 54H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 140.0$, 128.4, 128.1, 126.6, 126.5, 64.9, 60.9, 29.1, 27.4, 13.7, 9.9, 8.1; LRMS (70 eV, EI): $m/z$ (%): 765 (1) $[M-2]^+$, 184 (100); HRMS (70 eV, EI) calcd for $C_{37}H_{67}NSn_2$ ($[M-2]^+$): 765.3333, found 765.3346.

**1,5-Dihydro-1-phenyl-3,4-bis(trimethylsilylmethyl)-2*H*-pyrrole (9c)**: Amine **1b** (0.66 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of chlorotrimethylsilane (0.46 g, 4.2 mmol) and work-up as above yielded **9c** (0.55 g) as a white solid. M.p. 74–76 °C (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.35-6.5$ (m, 5H), 4.0 (s, 4H), 1.6 (s, 4H), 0.1 (s, 18H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 147.0$, 129.2, 125.7, 115.0, 110.7, 58.6, 16.9, $-0.7$; LRMS (70 eV, EI): $m/z$ (%): 317 (70) $[M]^+$, 230 (100); HRMS (70 eV, EI) calcd for $C_{18}H_{31}NSi_2$ ($[M]^+$): 317.1995, found 317.1992; elemental analysis calcd (%) for $C_{18}H_{31}NSi_2$ (317.6): C 68.07, H 9.84, N 4.41; found C 68.19, H 9.81, N 4.31.

**1,5-Dihydro-1-phenyl-3,4-bis(tributyltinmethyl)-2*H*-pyrrole (9d)**: Amine **1b** (0.66 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of tributyltin chloride (1.37 g, 4.2 mmol) and work-up as above yielded **9d** (1.28 g) as a colorless oil. $R_f = 0.41$ (hexane/ethyl acetate 25:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.3-6.5$ (m, 5H), 3.95 (s, 4H), 1.7 (s, 4H), 1.6–0.8 (m, 54H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta =$ 147.1, 129.2, 125.3, 114.8, 110.6, 58.7, 29.1, 27.4, 13.7, 9.9, 8.0; LRMS (70 eV, EI): $m/z$ (%): 753 (1) $[M]^+$, 170 (100); HRMS (70 eV, EI) calcd for $C_{36}H_{67}NSn_2$ ($[M]^+$): 753.3333, found 753.3309; elemental analysis calcd (%) for $C_{36}H_{67}NSn_2$ (751.3): C 57.55, H 8.99, N 1.86; found C 57.39, H 9.05, N 1.87.

**1-Cyclohexyl-1,5-dihydro-3,4-bis(trimethylsilylmethyl)-2*H*-pyrrole (9e)**: Amine **1d** (0.67 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of chlorotrimethylsilane (0.46 g, 4.2 mmol) and work-up as above yielded **9e** (0.50 g) as a colorless oil. $R_f = 0.24$ (ethyl acetate); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 3.35$ (s, 4H), 2.2–2.15 (m, 1H), 1.9–1.6 (m, 5H), 1.4 (s, 4H), 1.25–0.85 (m, 5H), 0.0 (s, 18H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 126.5$, 63.1, 62.0, 31.5, 25.8, 24.8, 17.0, $-0.9$; LRMS (70 eV, EI): $m/z$ (%): 323 (30) $[M]^+$, 236 (100); HRMS (70 eV, EI) calcd for $C_{18}H_{37}NSi_2$ ($[M]^+$): 323.2465,



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found 323.2472; elemental analysis calcd (%) for $C_{18}H_{37}NSi_2$ (323,7): C 66.80, H 11.52, N 4.32; found C 66.69, H 11.55, N 4.34.

**1-Cyclohexyl-1,5-dihydro-3,4-bis(tributyltinmethyl)-2*H*-pyrrole (9f)**: Amine **1d** (0.67 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of tributyltin chloride (1.37 g, 4.2 mmol) and work-up as above yielded **9f** (1.13 g) as a colorless oil. $R_f = 0.37$ (hexane/ethyl acetate 5:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 3.3$ (s, 4H), 2.1–0.8 (m, 69H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 126.3$, 62.9, 62.5, 31.6, 29.1, 27.4, 26.1, 24.8, 13.7, 9.8, 8.1; LRMS (70 eV, EI): *m*/*z* (%): 757 (2) $[M-2]^+$, 176 (100); HRMS (70 eV, EI) calcd for $C_{36}H_{71}NSn_2$ ($[M-2]^+$): 757.3646, found 757.3649.

**1,5-Dihydro-1-(4-methylphenyl)-3,4-bis(2-phenyl-2-phenylaminoethyl)-2*H*-pyrrole (9g)**: Amine **1c** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of *N*-benzylideneaniline (0.76 g, 4.2 mmol) and work-up as above yielded **9g** (0.80 g) as a white solid. M.p. 88–90 °C (hexane/chloroform); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-7.0$ (m, 16H), 6.7–6.3 (m, 8H), 4.55–4.45 (m, 2H), 4.2 (br s, 2H), 4.1 (s, 4H), 2.7 (dd, $J = 14.0$, 8.8 Hz, 2H), 2.5 (dd, $J = 14.0$, 5.2 Hz, 2H), 2.3 (s, 3H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 146.8$, 144.7, 143.3, 131.8, 129.7, 129.0, 128.6, 127.2, 125.9, 124.7, 117.8, 113.8, 111.0, 57.3, 56.7, 36.1, 20.1; elemental analysis calcd (%) for $C_{39}H_{39}N_3$ (549.8): C 85.21, H 7.15, N 7.64; found C 85.11, H 7.08, N 7.53.

**1,5-Dihydro-3,4-bis(2-hydroxy-2-methylpropyl)-1-(4-methylphenyl)-2*H*-pyrrole (9h)**: Amine **1c** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of acetone (0.24 g, 4.2 mmol) and work-up as above yielded **9h** (0.45 g) as a white solid. M.p. 123–125 °C (chloroform); $^1$H NMR (DMSO-$d_6$, 200 MHz): $\delta = 7.0$ (d, $J = 8.4$ Hz, 2H), 6.35 (d, $J = 8.4$ Hz, 2H), 4.4 (s, 2H), 4.1 (s, 4H), 2.3 (s, 4H), 2.2 (s, 3H), 1.1 (s, 12H); $^{13}$C NMR ([$D_6$]DMSO, 50.5 MHz): $\delta = 145.0$, 131.3, 129.4, 122.8, 110.5, 69.6, 58.1, 40.3, 29.7, 19.9; LRMS (70 eV, EI): *m*/*z* (%): 303 (9) $[M]^+$, 222 (100); elemental analysis calcd (%) for $C_{19}H_{29}NO_2$ (303.4): C 75.21, H 9.63, N 4.62; found C 75.30, H 9.41, N 4.58.

**2-Benzyl-1,2,3,4,5,6-hexahydro-5,5-diphenylsilol[3,4-*c*]pyrrole (11a)**: Amine **1a** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of dichlorodiphenylsilane (0.51 g, 2 mmol) and work-up as above yielded **11a** (0.56 g) as a colorless oil. $R_f = 0.23$ (hexane/ethyl acetate 2:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.7-7.3$ (m, 15H), 4.0 (s, 2H), 3.6 (s, 4H), 1.9 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 139.4$, 139.2, 135.7, 134.4, 129.4, 128.6, 128.1, 127.8, 126.7, 61.0, 60.8, 13.9; IR (neat): $\tilde{\nu} = 1425$ cm$^{-1}$; elemental analysis calcd (%) for $C_{25}H_{25}NSi$ (367.6): C 81.69, H 6.86, N 3.81; found C 81.58, H 6.78, N 3.79.

**2-Benzyl-5,5-diethyl-1,2,3,4,5,6-hexahydrogermol[3,4-*c*]pyrrole (11b)**: Amine **1a** (0.69 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of dichlorodiethylgermane (0.4 g, 2 mmol) and work-up as above yielded **11b** (0.52 g) as a colorless oil. $R_f = 0.30$ (hexane/ethyl acetate 3:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-7.2$ (m, 5H), 3.85 (s, 2H), 3.4 (s, 4H), 1.35 (s, 4H), 1.15–0.85 (m, 10H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 139.7$, 139.4, 128.7, 128.1, 126.8, 61.1, 60.8, 12.1, 8.9, 6.5; IR (neat): $\tilde{\nu} = 1455$ cm$^{-1}$; LRMS (70 eV, EI): *m*/*z* (%): 315 (27) $[M-2]^+$, 91 (100); HRMS (70 eV, EI) calcd for $C_{17}H_{23}GeN$ ($[M-2]^+$): 315.1045, found 315.1041; elemental analysis calcd (%) for $C_{17}H_{25}GeN$ (316.0): C 64.62, H 7.97, N 4.43; found C 64.43, H 7.79, N 4.51.

**1,2,3,4,5,6-Hexahydro-2,5,5-triphenylsilol[3,4-*c*]pyrrole (11c)**: Amine **1b** (0.66 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of dichlorodiphenylsilane (0.51 g, 2 mmol) and work-up as above yielded **11c** (0.60 g) as a white solid. M.p. 170–172 °C (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.7-6.5$ (m, 15H), 4.1 (s, 4H), 1.9 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 147.5$, 137.9, 135.4, 134.5, 129.5, 129.2, 128.0, 115.2, 110.7, 55.7, 13.9; IR (KBr): $\tilde{\nu} = 1595$ cm$^{-1}$; elemental analysis calcd (%) for $C_{24}H_{23}NSi$ (353.5): C 81.54, H 6.56, N 3.96; found C 81.49, H 6.71, N 3.81.

**5,5-Diethyl-1,2,3,4,5,6-hexahydro-2-phenylgermol[3,4-*c*]pyrrole (11d)**: Amine **1b** (0.66 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of dichlorodiethylgermane (0.4 g, 2 mmol) and work-up as above yielded **11d** (0.54 g) as a white solid. M.p. 116–118 °C (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.3-6.5$ (m, 5H), 4.0 (s, 4H), 1.5 (s, 4H), 1.2–0.9 (m, 10H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 147.6$, 138.4, 129.1, 114.9, 110.6, 55.8, 11.9, 8.9, 6.6; IR (KBr): $\tilde{\nu} =$ 1455 cm$^{-1}$; LRMS (70 eV, EI): *m*/*z* (%): 303 (17) $[M]^+$, 170 (100); HRMS (70 eV, EI) calcd for $C_{16}H_{23}GeN$ ($[M]^+$): 303.1045, found 303.1044; elemental analysis calcd (%) for $C_{16}H_{23}GeN$ (302.0): C 63.64, H 7.68, N 4.64; found C 63.49, H 7.72, N 4.49.

**1,2,3,4,5,6-Hexahydro-5,5-dimethyl-2-phenylstannol[3,4-*c*]pyrrole (11e)**: Amine **1b** (0.66 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol). Addition of dimethyltin dichloride (0.44 g, 2 mmol) and work-up as above yielded **11e** (0.54 g) as a white solid. M.p. 121–123 °C (hexane); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.3-6.5$ (m, 5H), 4.0 (s, 4H), 1.55 (s, 4H), 0.45 (s, 6H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta =$ 147.6, 138.6, 129.1, 114.9, 110.6, 57.3, 10.7, −1.4; IR (KBr): $\tilde{\nu} = 1615$ cm$^{-1}$; LRMS (70 eV, EI): *m*/*z* (%): 321 (5) $[M]^+$, 170 (100); HRMS (70 eV, EI) calcd for $C_{14}H_{19}NSn$ ($[M]^+$): 321.0541, found 321.0536; elemental analysis calcd (%) for $C_{14}H_{19}NSn$ (320.0): C 52.55, H 5.98, N 4.38; found C 52.31, H 6.05, N 4.51.

**General procedure for the preparation of pyrrole derivatives 8, 10, and 12**: Reaction of amines **1b**, **1c**, and **7** (2 mmol) with *t*BuLi (5.3 mL, 8 mmol) and the corresponding electrophile, as described above, was followed by stirring overnight under an atmospheric pressure of $O_2$ (alternatively, an equimolar amount of dichlorodicyanobenzoquinone (DDQ) was added to a solution of the corresponding dihydropyrrole derivatives **9** and **11** in dioxane). The resulting mixture was stirred for 6 h. Water was added and the organic product was extracted with ethyl acetate ($3 \times 20$ mL) The combined organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum and the resulting residue was crystallized or purified by flash column chromatography (silica gel, hexane/ethyl acetate) giving rise to compounds **8**, **10**, and **12**.

**4,5,6,7-Tetrahydro-3-methyl-1-(4-methylphenyl)-1*H*-indol (8)**: Amine **7** (0.77 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of water (excess) followed by stirring under an atmospheric pressure of oxygen and work-up as above yielded **8** (0.33 g, 73%) as a colorless oil. $R_f = 0.26$ (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.2-7.0$ (m, 4H), 6.5 (s, 1H), 2.5–2.35 (m, 4H), 2.3 (s, 3H), 2.0 (s, 3H), 1.8–1.6 (m, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 137.8$, 135.3, 129.5, 127.9, 124.1, 118.5, 117.3, 23.5, 23.4, 23.2, 21.5, 20.8, 9.7; LRMS (70 eV, EI): *m*/*z* (%): 225 (100) $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{19}N$ (225.3): C 85.28, H 8.50, N 6.22; found C 85.41, H 8.41, N 6.05.

**3,4-Bis(deuteriomethyl)-1-phenyl-1*H*-pyrrole (10a)**: Reaction of amine **1b** (0.66 g, 2 mmol) with *t*BuLi (5.3 mL, 8 mmol) and deuterium oxide (excess), was followed by stirring under an atmospheric pressure of oxygen. Work-up as above yielded **10a** (0.29 g) as a reddish solid. M.p. 68–70 (methanol); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.6-6.25$ (m, 5H), 7.0 (s, 2H), 2.3–2.2 (m, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 140.6$, 129.3, 124.4, 120.6, 119.2, 116.6, 9.8 (t, $J$(C,D) = 19.6 Hz); LRMS (70 eV, EI): *m*/*z* (%): 173 (83) $[M]^+$, 172 (100); HRMS (70 eV, EI) calcd for $C_{12}H_{11}D_2N$ ($[M]^+$): 173.1173, found 173.1166.

**3,4-Bis(ethoxycarbonylmethyl)-1-phenyl-1*H*-pyrrole (10b)**: Amine **1b** (0.66 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol); after the addition of $CO_2$ (excess) at −78 °C and the extractive work-up, the resulting crude product was dissolved in EtOH (20 mL), and chlorotrimethylsilane (0.98 g, 9 mmol) was added. The mixture was stirred at 20 °C overnight followed by stirring under an atmospheric pressure of oxygen. Work-up as above yielded **10b** (0.50 g) as a colorless oil. $R_f = 0.23$ (hexane/ethyl acetate 6:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.45-7.15$ (m, 5H), 7.05 (s, 2H), 4.2 (q, $J = 7.0$ Hz, 4H), 3.6 (s, 4H), 1.3 (t, $J = 7.0$ Hz, 6H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 171.9$, 140.2, 129.3, 125.2, 119.8, 118.4, 117.1, 60.6, 31.4, 14.1; LRMS (70 eV, EI): *m*/*z* (%): 315 (43) $[M]^+$, 170 (100); HRMS (70 eV, EI) calcd for $C_{18}H_{21}NO_4$ ($[M]^+$): 315.1471, found 315.1470; elemental analysis calcd (%) for $C_{18}H_{21}NO_4$ (315.4): C 68.55, H 6.71, N 4.44, found C 68.39, H 6.61, N 4.33.

**1-(4-Methylphenyl)-3,4-bis(2-phenyl-2-diphenylaminoethyl)-1*H*-pyrrole (10c)**: Reaction of amine **1c** (0.69 g, 2 mmol) with *t*BuLi (5.3 mL, 8 mmol) and *N*-benzylideneaniline (0.76 g, 4.2 mmol) was followed by treatment with DDQ (0.46 g, 2 mmol) in dioxane (20 mL) at 20 °C. Work-up as above yielded **10c** (0.79 g) as a reddish solid. M.p. 74–76 °C (methanol); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.4-6.4$ (m, 26H), 4.5–4.4 (m, 2H), 4.2 (br s, 2H), 2.9–2.7 (m, 4H), 2.3 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 147.2$, 143.8, 137.8, 135.0, 129.9, 128.9, 128.4, 126.9, 126.3, 120.5, 119.7, 117.9, 117.3,

113.7, 58.0, 34.8, 20.7; elemental analysis calcd (%) for $C_{39}H_{37}N_3$ (547.7): C 85.52, H 6.81, N 7.67, found C 85.41, H 6.75, N 7.52.

**3,4-Bis(2-hydroxy-2-methylpropyl)-1-(4-methylphenyl)pyrrole (10d)**: Reaction of amine **1c** (0.69 g, 2 mmol) with *t*BuLi (5.3 mL, 8 mmol) and acetone (0.24 g, 4.2 mmol) was followed by treatment with DDQ (0.46 g, 2 mmol). Work-up as above yielded **10d** (0.45 g) as a red oil. $R_f = 0.27$ (hexane/ethyl acetate 1:1); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.15$ (d, $J =$ 2.9 Hz, 2H), 7.1 (d, $J = 2.9$ Hz, 2H), 6.8 (s, 2H), 2.6 (s, 4H), 2.3 (s, 3H), 1.2 (s, 12H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 137.9$, 134.7, 129.9, 121.0, 119.4, 118.1, 70.4, 38.6, 29.1, 20.6; LRMS (70 eV, EI): $m/z$ (%): 283 (25) $[M-18]^+$, 222 (100); elemental analysis calcd (%) for $C_{19}H_{27}NO_2$ (301.4): C 75.71, H 9.03, N 4.65; found C 75.80, H 9.02, N 4.55.

**2,4,5,6-Tetrahydro-2,5,5-triphenylsilol[3,4-*c*]pyrrole (12a)**: Product **11c** (0.35 g, 1 mmol), prepared as described above, was treated with DDQ (0.23 g, 1 mmol) in dioxane (20 mL) at 20 °C. Work-up as above yielded **12a** (0.55 g) as a white solid. M.p. 112–114 °C (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.8-7.3$ (m, 15H), 7.0 (s, 2H), 2.5 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 141.1$, 135.8, 134.6, 129.5, 129.3, 127.9, 127.4, 124.7, 119.7, 114.3, 10.2. IR (KBr): $\tilde{\nu} = 1595$ cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 351 (83) $[M]^+$, 44 (100); HRMS (70 eV, EI) calcd for $C_{24}H_{21}NSi$ ($[M]^+$): 351.1443, found 351.1442; elemental analysis calcd (%) for $C_{24}H_{21}NSi$ (351.5): C 82.00, H 6.02, N 3.99; found C 81.86, H 5.91, N 3.89.

**5,5-Diethyl-2,4,5,6-tetrahydro-2-phenylgermol[3,4-*c*]pyrrole (12b)**: Product **11d** (0.3 g, 1 mmol) was treated with DDQ (0.23 g, 1 mmol) in dioxane (20 mL) at 20 °C. Work-up as above yielded **12b** (0.49 g) as a white solid. M.p. 65–67 °C (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.5-7.1$ (m, 5H), 6.9 (s, 2H), 2.0 (s, 4H), 1.25–1.0 (m, 10H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 141.2$, 129.8, 129.3, 124.5, 119.8, 114.1, 9.1, 8.1, 6.6; IR (KBr): $\tilde{\nu} = 1600$ cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 301 (100) $[M]^+$; HRMS (70 eV, EI) calcd for $C_{16}H_{21}GeN$ ($[M]^+$): 301.0889, found 301.0878; elemental analysis calcd (%) for $C_{16}H_{21}GeN$ (299.9): C 64.07, H 7.06, N 4.67; found C 64.00, H 7.15, N 4.81.

**Treatment of dianion 4b with benzil and diphenyldisulfide. Preparation of 3,4-dimethylene-*N*-phenylpyrrolidine (14b)**: To a yellow suspension of **4b**, obtained by reaction of amine **1b** (0.66 g, 2 mmol) with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) at −78 °C followed by warming up to 20 °C, was added benzil (0.42 g, 2 mmol) or diphenyldisulfide (0.91 g, 4.2 mmol) at −78 °C. The mixture was stirred, while the temperature raised room temperature, and then hydrolyzed with water. After the usual work-up described above a residue was obtained of benzoine or phenylthiol and diene **14b**. Purification by flash column chromatography yielded **14b** (0.24 g, 71%) as a colorless oil. $R_f = 0.28$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-6.7$ (m, 5H), 5.6 (s, 2H), 5.2 (s, 2H), 4.2 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 147.2$, 143.0, 129.1, 116.6, 112.0, 104.4, 53.5; LRMS (70 eV, EI): $m/z$ (%): 171 (75) $[M]^+$, 170 (100); HRMS (70 eV, EI) calcd for $C_{12}H_{13}N$ ($[M]^+$): 171.1048, found 171.1044.

**Reaction of dianion 4b with aromatic halides and electrophiles. Preparation of compounds 15 and 16**: At room temperature 1,2-dichlorobenzene (0.15 g, 1 mmol) or bromobenzene (0.16 g, 1 mmol) was added to a yellow suspension of **4b**, obtained by reaction of amine **1b** (0.66 g, 2 mmol) with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) as described above, and the mixture was stirred for 1 h. To the resulting reddish solution of the resulting dianion **18**, the corresponding electrophile (deuterium oxide, chlorotrimethylsilane, tributyltin chloride and diphenyl disulfide) was added at −78 °C and stirred while the temperature raised room temperature. The mixture was subjected to the usual work-up. The organic residue was purified by recrystallization or column chromatography.

**3,3′-(1,2-Ethanediyl)bis(4-deuteriomethyl-1-phenyl-2,5-dihydro-1*H*-pyrrole) (15a)**: The reddish solution of **18** indicated above was treated with deuterium oxide (excess). Work-up as above yielded **15a** (0.38 g) as a colorless oil. $R_f = 0.1$ (hexane/ethyl acetate 1:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.3-6.5$ (m, 10H), 4.15–3.95 (m, 8H), 2.35 (s, 4H), 1.7 (s, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 147.0$, 130.5, 129.2, 128.0, 115.2, 110.8, 59.0, 56.9, 25.1, 11.2 (t, $J$(C,D) = 19.9 Hz); LRMS (70 eV, EI): $m/z$ (%): 346 (9) $[M]^+$, 173 (100); HRMS (70 eV, EI) calcd for $C_{24}H_{26}D_2N_2$ ($[M]^+$): 346.2378, found 346.2378.

**3,3′-(1,2-Ethanediyl)bis(2,5-dihydro-1-phenyl-4-trimethylsilyl-1*H*-pyrrole) (15b)**: The reddish solution of **18** indicated above was treated with chlorotrimethylsilane (0.24 g, 2.2 mmol). Work-up as above yielded **15b** (0.59 g) as a colorless oil. $R_f = 0.33$ (hexane/ethyl acetate 25:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-6.6$ (m, 10H), 4.2 and 4.1 (2s, 8H), 2.4 (s, 4H), 1.75 (s, 4H), 0.2 (s, 18H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 147.0$, 129.4, 129.2, 127.5, 115.3, 110.8, 59.0, 56.6, 25.6, 17.0, −0.9; IR (neat): $\tilde{\nu} =$ 1600 cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 488 (17) $[M]^+$, 244 (100); HRMS (70 eV, EI) calcd for $C_{30}H_{44}N_2Si_2$ ($[M]^+$): 488.3043, found 488.3026, elemental analysis calcd (%) for $C_{30}H_{44}N_2Si_2$ (488.9): C 73.71, H 9.07, N 5.73; found C 73.79, H 9.21, N 5.58.

**3,3′-(1,2-Ethanediyl)bis(2,5-dihydro-1-phenyl-4-tributyltin-1*H*-pyrrole) (15c)**: The reddish solution of **18** indicated above was treated with tributyltin chloride (0.72 g, 2.2 mmol). Work-up as above yielded **15c** (0.97 g) as a colorless oil. $R_f = 0.40$ (hexane/ethyl acetate 25:1); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.3-6.5$ (m, 10H), 4.1 and 4.0 (2s, 8H), 2.3 (s, 4H), 1.8 (s, 4H), 1.6–0.8 (m, 54H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 147.0$, 131.8, 129.1, 124.8, 115.1, 110.7, 59.0, 56.6, 29.0, 27.3, 25.4, 13.6, 9.8, 7.9; IR (neat): $\tilde{\nu} = 1600$ cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 867 (1) $[M-57]^+$, 170 (100); HRMS (70 eV, EI) calcd for $C_{44}H_{71}N_2Sn_2$ ($[M-57]^+$): 867.3679, found 867.3622.

**3,3′-(1,2-Ethanediyl)bis(2,5-dihydro-1-phenyl-4-phenyltiomethyl-1*H*-pyrrole) (15d)**: The reddish solution of **18** indicated above was treated with diphenyl disulfide (0.48 g, 2.2 mmol). Work-up as above yielded **15d** (0.65 g) as a colorless oil. $R_f = 0.25$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.4-6.5$ (m, 20H), 4.2 and 4.0 (2s, 8H), 3.6 (s, 4H), 2.0 (s, 4H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 146.7$, 135.4, 134.9, 131.3, 129.2, 128.1, 127.0, 115.7, 110.9, 57.0, 56.6, 31.2, 25.0; LRMS (70 eV, EI): $m/z$ (%): 558 (5) $[M-2]^+$, 170 (100); HRMS (70 eV, EI) calcd for $C_{36}H_{34}N_2S_2$ ($[M-2]^+$): 558.2163, found 558.2180.

**3,3′-(1,2-Ethanediyl)bis(4-deuteriomethyl-1-phenyl-1*H*-pyrrole) (16a)**: The reddish solution of **18** indicated above was treated with deuterium oxide (excess) followed by stirring overnight under an atmospheric pressure of $O_2$. Work-up as above yielded **16a** (0.40 g) as a white solid. M.p. 148–150 °C (hexane/chloroform); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta =$ 7.45–7.2 (m, 10H), 6.95 and 6.9 (2d, $J = 2.6$ Hz, 4H), 2.8 (s, 4H), 2.2 (m, 4H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 140.7$, 129.4, 125.8, 124.6, 120.2, 119.4, 116.8, 116.1, 26.4, 9.9 (t, $J$(C,D) = 19.6 Hz); LRMS (70 eV, EI): $m/z$ (%): (19) $[M]^+$, 171 (100); HRMS (70 eV, EI) calcd for $C_{24}H_{22}D_2N_2$ ($[M]^+$): 342.2065, found 342.2062, elemental analysis calcd (%) for $C_{24}H_{22}D_2N_2$ (342.5): C 84.17, H/D 7.65, N 8.18; found C 84.19, H/D 7.45, N 8.21.

**Coupling reaction of 20. Isolation of *N*,*N*′-dimethyl-2,3-dimethylene-*N*,*N*′-diphenyl-1,4-butanediamine (22)**: Amine **19** (0.45 g, 2 mmol) was treated with *t*BuLi (2.7 mL, 4 mmol) at −78 °C in diethyl ether (15 mL). Then, CuCN (0.18 g, 2 mmol) was added to a solution of the resulting anion **20** at −78 °C. The mixture was warmed to room temperature and stirred for 8 h. The reaction was quenched with saturated ammonium chloride and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over anhydrous $Na_2SO_4$.The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to afford **22** (0.47 g, 81%) as a colorless oil. $R_f = 0.31$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-6.7$ (m, 10H), 5.3 (s, 2H), 5.15 (s, 2H), 4.2 (s, 4H), 3.1 (s, 6H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 149.1$, 140.1, 128.9, 116.0, 111.5, 111.1, 55.5, 38.2; LRMS (70 eV, EI): $m/z$ (%): 292 (38) $[M]^+$, 120 (100); HRMS (70 eV, EI) calcd for $C_{20}H_{24}N_2$ ($[M]^+$): 292.1939, found 292.1944; elemental analysis calcd (%) for $C_{20}H_{24}N_2$ (292.4): C 82.15, H 8.27, N 9.58; found C 81.97, H 8.16, N 9.46.

**Reaction of anion 20 with zirconocene dichloride**: **isolation of compounds 23**: A solution of anion **20** (2 mmol) in diethyl ether (15 mL) was added to a solution of zirconocene dichloride (0.29 g, 1 mmol) in THF (15 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, then warmed to room temperature and stirred for 4 h. An excess of deuterium oxide or, alternatively, 2.5 equiv of iodine (1.27 g, 5 mmol) was added at 20 °C. The reaction was quenched with aqueous $Na_2S_2O_3$ and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with aqueous $NaHCO_3$ (3 × 20 mL), dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography (hexane/ethyl acetate) to afford products **23**.

**(*E*)-2-Deuterio-4-deuteriomethyl-*N*,*N*′-dimethyl-2-penten-1,5-diamine (23a)**: Amine **19** (0.45 g, 2 mmol) was treated with *t*BuLi (2.7 mL, 4 mmol) and $Cp_2ZrCl_2$ (0.29 g, 1 mmol). Work-up as above yielded **23a** (0.54 g, 91%) as a colorless oil. $R_f = 0.34$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4-6.7$ (m, 10H), 5.7–5.6 (m, 1H), 3.9 (s, 2H), 3.3



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(d, $J = 7.0$ Hz, 2H), 3.0 (s, 3H), 2.95 (s, 3H), 2.8–2.6 (m, 1H), 1.1 (d, $J = 7.0$ Hz, 2H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 149.4$, 149.2, 135.6, 129.0, 124.7 (t, $J$(C,D) = 24.4 Hz), 116.2, 115.6, 112.4, 111.7, 59.1, 39.2, 37.6, 35.3, 17.5 (t, $J = 19.8$ Hz); IR (neat): $\tilde{\nu} = 1620$ cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 296 (29) $[M]^+$, 120 (100); HRMS (70 eV, EI) calcd for $C_{20}H_{24}D_2N_2$ ($[M]^+$): 296.2222, found 296.2223; elemental analysis calcd (%) for $C_{20}H_{24}D_2N_2$ (296.5): C 81.03, H/D 9.52, N 9.45; found C 80.89, H/D 9.41, N 9.33.

**(*Z*)-2,5-Diiodo-*N*,*N*′-dimethyl-*N*,*N*′-diphenyl-2-penten-1,5-diamine (23b)**: Amine **19** (0.45 g, 2 mmol) was treated with *t*BuLi (2.7 mL, 4 mmol) and $Cp_2ZrCl_2$ (0.29 g, 1 mmol) followed by addition of iodine (1.07 g, 4.2 mmol). Work-up as above yielded **23b** (0.86 g, 79%) as a colorless oil. $R_f = 0.33$ (hexane/ethyl acetate 10:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta =$ 7.35–6.7 (m, 10H), 5.65–5.6 (m, 1H), 4.2 (s, 2H), 3.4–3.1 (m, 5H), 3.0 (s, 6H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 148.7$, 148.1, 134.3, 129.0, 116.9, 116.4, 112.2, 111.9, 108.4, 64.8, 55.8, 46.1, 39.3, 38.1, 9.0; IR (neat): $\tilde{\nu} =$ 1600 cm$^{-1}$; LRMS (70 eV, EI): $m/z$ (%): 546 (15) $[M]^+$, 120 (100); HRMS (70 eV, EI) calcd for $C_{20}H_{24}I_2N_2$ ($[M]^+$): 546.0029, found 546.0036, elemental analysis calcd (%) for $C_{20}H_{24}I_2N_2$ (546.2): C 43.98, H 4.43, N 5.13; found C 43.79, H 4.39, N 5.17.

**General procedure for the preparation of indole derivatives 30**: A solution of amine **28** (2 mmol) in diethyl ether (20 mL) precooled at $-78\,^\circ$C was treated with 4 equiv of *t*BuLi (8 mmol) when amines **28a** and **28b** were used, or 5 equiv *t*BuLi (10 mmol) in the case of **28c**. The solution was stirred at $-78\,^\circ$C for 1 h and then 4 equiv of TMEDA (1.2 mL, 8 mmol) were added. The resulting mixture was stirred at this temperature for 30 min. Then, the reaction was allowed to reach room temperature. The stirring was continued for 3 h. In the case of secondary amine **28c** 5 equiv of TMEDA (1.5 mL, 10 mmol) were added, and the resulting solution was heated under reflux in diethyl ether for 3 h [until the starting trianion **29** (R = Li) had been consumed as much as possible whereas the expected dianion **32** (R = Li) is not hydrolized, as judged by GC-MS analysis]. In all the cases, the solution of the corresponding anions **32** in diethyl ether was cooled to $-78\,^\circ$C and excess (2–3 equiv) of electrophiles (deuterium oxide, chlorotrimethylsilane, dibenzyl disulfide, diphenyl disulfide, *N*-benzylidene-$\alpha$-methylbenzylamine, 4-chlorobenzaldehyde, *N*-benzylideneaniline, 3-pentanone, 2,3-butanedione, phenylisocyanate, 4-methylbenzonitrile) were added. Then, the mixture was allowed to reach room temperature, and the reaction was stirred for 3 h. The mixture was hydrolyzed with water and extracted with ethyl acetate ($3 \times 20$ mL). The combined organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate) yielding the functionalized indoles **30**.

**1-Benzyl-3-deuteriomethyl-1*H*-indole (30a)**: Amine **28a** (0.76 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of deuterium oxide (excess) and work-up as above yielded **30a** (0.32 g) as a colorless oil. $R_f = 0.26$ (hexane); $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.70$–$7.20$ (m, 9H), 7.00 (s, 1H), 5.30 (s, 2H), 2.45–2.40 (m, 2H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 137.8$, 136.5, 128.6, 127.4, 126.7, 125.7, 121.5, 118.9, 118.7, 110.7, 109.4, 49.6, 9.3 (t, $J$(C,D) = 19.6 Hz); HRMS (70 eV, EI) calcd for $C_{16}H_{14}DN$ ($[M]^+$): 222.1267, found 222.1270, elemental analysis calcd (%) for $C_{16}H_{14}DN$ (222.3): C 86.45, H/D 7.25, N 6.30; found C 86.31, H/D 7.27, N 6.19.

**1-Benzyl-3-trimethylsilylmethyl-1*H*-indole (30b)**: Amine **28a** (0.76 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of chlorotrimethylsilane (0.43 g, 4 mmol) and work-up as above yielded **30b** (0.38 g) as a colorless oil. $R_f = 0.36$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta =$ 7.60–7.10 (m, 9H), 6.80 (s, 1H), 5.30 (s, 2H), 2.20 (s, 2H), 0.1 (s, 9H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 138.0$, 136.4, 129.1, 128.6, 127.3, 126.5, 124.3, 121.2, 119.4, 118.3, 112.7, 109.2, 49.6, 13.8, $-1.5$; HRMS (70 eV, EI) calcd for $C_{19}H_{23}NSi$ ($[M]^+$): 293.1600, found 293.1590.

**1-Benzyl-3-benzyltiomethyl-1*H*-indole (30c)**: Amine **28a** (0.76 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of dibenzyl disulfide (0.98 g, 4 mmol) and work-up as above yielded **30c** (0.43 g) as a colorless oil. $R_f = 0.36$ (hexane/ethyl acetate 15:1); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.80$–$7.20$ (m, 14H), 7.05 (s, 1H), 5.35 (s, 2H), 3.90 and 3.75 (2s, 4H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 138.4$, 137.3, 136.8, 128.9, 128.6, 128.3, 127.5, 127.4, 127.0, 126.7, 121.9, 119.4, 119.2, 111.0, 109.6, 49.7, 35.7, 26.1; elemental analysis calcd (%) for $C_{23}H_{21}NS$ (343.5): C 80.43, H 6.16, N 4.08; found C 80.69, H 6.17, N 4.09.

**3-Deuteriomethyl-1-methyl-1*H*-indole (30d)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of deuterium oxide (excess) and work-up as above. yielded **30d** (0.23 g) as a colorless oil. $R_f = 0.24$ (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.80$–$7.25$ (m, 4H), 6.90 (s, 1H), 3.80 (s, 3H), 2.50–2.45 (m, 2H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 136.8$, 128.5, 126.4, 121.3, 118.8, 118.4, 109.9, 108.9, 32.3, 9.2 (t, $J$(C,D) = 19.5 Hz); HRMS (70 eV, EI) calcd for $C_{10}H_{10}DN$ ($[M]^+$): 146.0954, found 146.0959.

**1-Methyl-3-trimethylsilylmethyl-1*H*-indole (30e)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of chlorotrimethylsilane (0.43 g, 4 mmol) and work-up as above yielded **30e** (0.30 g) as a colorless oil. $R_f = 0.46$ (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.65$–$7.10$ (m, 4H), 6.80 (s, 1H), 3.80 (s, 3H), 2.25 (s, 2H), 0.15 (s, 9H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 136.7$, 128.4, 124.9, 121.0, 119.2, 118.0, 111.8, 108.7, 32.3, 13.7, $-1.5$; HRMS (70 eV, EI) calcd for $C_{13}H_{19}NSi$ ($[M]^+$): 217.1287, found 217.1279; elemental analysis calcd (%) for $C_{13}H_{19}NSi$ (217.4): C 71.83, H 8.81, N 6.44; found C 71.69, H 8.87, N 6.59.

**3-[2-Hydroxy-2-(4-chlorophenyl)ethyl]-1-methyl-1*H*-indole (30f)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of 4-chlorobenzaldehyde (0.56 g, 4 mmol) and work-up as above yielded **30f** (0.40 g) as a colorless oil. $R_f = 0.32$ (hexane/ethyl acetate 9:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.65$–$7.20$ (m, 8H), 6.90 (s, 1H), 4.95 (dd, $J = 8.6$, 4.3 Hz, 1H), 3.80 (s, 3H), 3.20 (dd, $J = 14.6$, 4.3 Hz, 1H), 3.05 (dd, $J = 14.6$, 8.6 Hz, 1H), 2.50–2.20 (br s, 1H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 142.4$, 136.8, 132.7, 127.9, 127.7, 127.6, 121.6, 118.8, 118.7, 109.6, 109.2, 73.0, 35.6, 32.4; elemental analysis calcd (%) for $C_{17}H_{16}ClNO$ (285.8): C 71.45, H 5.64, N 4.90; found C 71.61, H 5.52, N 4.79.

**1-Methyl-3-[2-phenyl-2-(1-phenylethylamino)ethyl]-1*H*-indole (30g)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of *N*-benzylidene-$\alpha$-methylbenzylamine (0.84 g, 4 mmol) and work-up as above yielded **30g** (0.43 g) as a colorless oil and a 6:1 mixture of diastereoisomers. $R_f = 0.45$ (hexane: ethyl acetate 5:1); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta = 7.55$–$6.80$ (m, 14H), 6.70 (s, 1H; =CHN, major diastereoisomer), 6.67 (s, 1H; =CHN, minor diastereoisomer), 4.15 (t, $J = 6.7$ Hz, 1H; C*H*CH$_2$, minor diastereoisomer), 3.80 (t, $J = 6.5$ Hz, 1H; C*H*NCH$_2$, major diastereoisomer), 3.80–3.75 (m, 1H; C*H*Me, minor diastereoisomer), 3.75 (s, 3H; Me, major diastereoisomer), 3.70 (s, 3H; Me, minor diastereoisomer), 3.53 (q, $J = 6.7$ Hz, 1H; C*H*Me, major diastereoisomer), 3.20 (dd, $J = 14.4$, 6.7 Hz, 1H; C*H*H, minor diastereoisomer), 3.13 (dd, $J =$ 14.4, 6.7 Hz, 1H; CH*H*, minor diastereoisomer), 3.03 (d, $J = 6.5$ Hz, 2H; CH$_2$, major diastereoisomer), 2.1–1.9 (br s, 2H; NH, major and minor diastereoisomers), 1.28 (d, $J = 6.3$ Hz, 3H; CH$_3$, minor diastereoisomer), 1.24 (d, $J = 6.7$ Hz, 3H; CH$_3$, major diastereoisomer); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 145.0$, 144.5, 136.8, 128.1, 128.0, 127.2, 126.7, 126.6, 126.4, 126.3, 126.2, 121.4, 119.1, 118.6, 111.1, 108.8, 59.5, 54.9, 34.8, 32.3, 24.5 (major diastereoisomer).

**3-[2-(4-methylphenyl)-2-oxoethyl)]-1-methyl-1*H*-indole (30h)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of 4-methylbenzonitrile (0.47 g, 4 mmol) and work-up as above yielded **30h** (0.39 g) as a white solid. M.p. 110–112 °C (hexane/chloroform); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 8.0$–$7.0$ (m, 8H), 6.90 (s, 1H), 4.3 (s, 2H), 3.55 (s, 3H), 3.20 (s, 3H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 197.1$, 143.3, 136.7, 134.1, 129.0, 128.4, 127.6, 121.5, 118.9, 118.7, 109.0, 107.3, 35.1, 32.2, 21.3; LRMS (70 eV, EI): $m/z$ (%): 263 (13) $[M]^+$, 144 (100); elemental analysis calcd (%) for $C_{18}H_{17}NO$ (263.3): C 82.10, H 6.51, N 5.32; found C 82.21, H 6.45, N 5.21.

**1-Methyl-3-(*N*-phenylcarbamoylmethyl)-1*H*-indole (30i)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of phenylisocyanate (0.48 g, 4 mmol) and work-up as above yielded **30i** (0.35 g) as a white solid. M.p. 99–101 °C (hexane/chloroform); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.7$–$7.1$ (m, 10H), 7.0 (s, 1H), 3.85 (s, 2H), 3.75 (s, 3H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 169.8$, 137.8, 137.1, 128.6, 128.3, 127.3, 124.0, 122.0, 119.9, 119.5, 118.6, 109.4, 107.0, 34.1, 32.4; LRMS (70 eV, EI):

*m*/*z* (%): 264 (20) $[M]^+$, 144 (100); elemental analysis calcd (%) for $C_{17}H_{16}N_2O$ (264.3): C 77.25, H 6.10, N 10.60; found C 77.31, H 6.03, N 10.45.

**1-Methyl-3-(phenyltiomethyl)-1*H*-indole (30j)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of diphenyl disulfide (0.87 g, 4 mmol) and work-up as above yielded **30j** (0.35 g) as a white solid. M.p. 92–94 (hexane/chloroform); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.85-7.1$ (m, 9H), 7.0 (s, 1H), 4.45 (s, 2H), 3.75 (s, 3H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 137.4$, 136.9, 129.0, 128.5, 127.6, 127.2, 125.6, 121.6, 118.9, 109.8, 109.1, 32.1, 29.5; LRMS (70 eV, EI): *m*/*z* (%): 253 (7) $[M]^+$, 14 (100); elemental analysis calcd (%) for $C_{16}H_{15}NS$ (253.4): C 75.85, H 5.97, N 5.53; found C 75.74, H 5.92, N 5.41.

**3-(2-Hydroxy-2-methyl-3-oxobutyl)-1-methyl-1*H*-indole (30k)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (5.3 mL of a 1.5 M solution in pentane, 8 mmol) and TMEDA (1.2 mL, 8 mmol). Addition of butanedione (0.34 g, 4 mmol) and work-up as above yielded **30k** (0.31 g) as a colorless oil. $R_f = 0.43$ (hexane/ethyl acetate 1:1); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.7-7.0$ (m, 4H), 6.95 (s, 1H), 3.7 (s, 3H), 3.55 (br s, 1H), 3.25 (d, $J = 13.9$ Hz, 1H), 3.1 (d, $J = 13.9$ Hz, 1H), 2.2 (s, 3H), 1.45 (s, 3H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 212.3$, 136.6, 128.3, 128.0, 121.3, 118.9, 108.9, 108.1, 79.4, 34.7, 32.2, 24.9, 24.2; LRMS (70 eV, EI): *m*/*z* (%): 231 (6) $[M]^+$, 144 (100); elemental analysis calcd (%) for $C_{14}H_{17}NO_2$ (231.3): C 72.70, H 7.41, N 6.06; found C 72.83, H 7.36, N 5.94.

**3-Deuteriomethyl-1*H*-indole (30l)**: Amine **28c** (0.58 g, 2 mmol) was treated with *t*BuLi (6.7 mL of a 1.5 M solution in pentane, 10 mmol) and TMEDA (1,5 mL, 10 mmol); after heating the mixture under reflux, the addition of deuterium oxide (excess) and work-up as above yielded **30l** (0.13 g) as a white solid. M.p. 96–97 °C (methanol); $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 8.00-7.10$ (m, 5H), 6.95 (s, 1H), 2.40 (s, 2H); $^{13}$C NMR (50.5 MHz, $CDCl_3$): $\delta = 136.1$, 128.1, 121.7, 121.5, 119.0, 118.7, 111.5, 110.8, 9.3 (t, $J$(C,D) = 19.5 Hz); HRMS (70 eV, EI) calcd for $C_9H_8DN$ ($[M]^+$): 132.0798, found 132.0793; elemental analysis calcd (%) for $C_9H_8DN$ (132.2): C 81.78, H/D 7.62, N 10.60; found C 81.88, H/D 7.47, N 10.59.

**3-(2,2-Diethyl-2-hydroxyethyl)-1*H*-indole (30m)**: Amine **28c** (0.58 g, 2 mmol) was treated with *t*BuLi (6.7 mL of a 1.5 M solution in pentane, 10 mmol) and TMEDA (1,5 mL, 10 mmol); after heating the mixture under reflux, the addition of 3-pentanone (0.51 g, 6 mmol) and work-up as above yielded **30m** (0.24 g) as a brown solid. M.p. 155–157 °C (diethyl ether); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 8.1$ (br s, 1H), 7.6 (d, $J = 6.9$ Hz, 1H), 7.4–6.9 (m, 5H), 2.85 (s, 2H), 1.45 (q, $J = 7.4$ Hz, 4H), 0.9 (t, $J = 7.4$ Hz, 6H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 136.3$, 129.1, 128.7, 123.5, 122.0, 119.5, 111.5, 111.0, 74.7, 34.5, 30.5, 8.1; LRMS (70 eV, EI): *m*/*z* (%): 217 (14) $[M]^+$, 130 (100); elemental analysis calcd (%) for $C_{14}H_{19}NO$ (217.3): C 77.38, H 8.81, N 6.45; found C 77.47, H 8.75, N 6.34.

**3-(2,2-Diphenyl-2-hydroxyethyl)-1*H*-indole (30n)**: Amine **28c** (0.58 g, 2 mmol) was treated with *t*BuLi (6.7 mL of a 1.5 M solution in pentane, 10 mmol) and TMEDA (1.5 mL, 10 mmol); after heating the mixture under reflux, the addition of benzophenone (1.1 g, 6 mmol) and work-up as above yielded of **30n** (0.36 g) as a colorless oil. $R_f = 0.26$ (hexane/ethyl acetate 3:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.75$ (s br, 1H), 7.4–6.8 (m, 14H), 6.25 (d, $J = 2.3$ Hz, 1H), 3.6 (s, 2H), 2.6 (s br, 1H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 146.9$, 135.5, 128.0, 126.6, 126.1, 125.8, 124.0, 121.9, 119.4, 118.9, 111.0, 109.0, 78.1, 37.8; LRMS (70 eV, EI): *m*/*z* (%): 313 (1) $[M]^+$, 131 (100); elemental analysis calcd (%) for $C_{22}H_{19}NO$ (313.4): C 84.32, H 6.11, N 4.47; found C 84.29, H 6.07, N 4.29.

**3-(2-Phenyl-2-phenylaminoethyl)-1*H*-indole (30o)**: Amine **28c** (0.58 g, 2 mmol) was treated with *t*BuLi (6.7 mL of a 1.5 M solution in pentane, 10 mmol) and TMEDA (1.5 mL, 10 mmol); after heating the mixture under reflux, the addition of *N*-benzylideneaniline (1.09 g, 6 mmol) and work-up as above yielded **30o** (0.37 g) as a colorless oil. $R_f = 0.37$ (hexane/ethyl acetate 3:1); $^1$H NMR ($CDCl_3$, 80 MHz): $\delta = 7.8$ (s br, 1H), 7.7–6.5 (m, 15H), 4.8 (dd, $J = 7.5$ and 5.9 Hz, 1H), 4.15 (s br, 1H), 3.45–3.25 (m, 2H); $^{13}$C NMR ($CDCl_3$, 20.2 MHz): $\delta = 147.4$, 144.0, 136.0, 129.1, 128.9, 128.3, 127.5, 126.7, 126.3, 122.5, 121.8, 119.3, 118.4, 117.2, 114.9, 113.5, 111.5, 111.1, 58.1, 34.6; LRMS (70 eV, EI): *m*/*z* (%): 312 (1) $[M]^+$, 182 (100); elemental analysis calcd (%) for $C_{22}H_{20}N_2$ (312.4): C 84.58, H 6.45, N 8.97; found C 84.69, H 6.37, N 8.89.

**Preparation of 34 and 35**: A solution of the amine **33** (0.82 g, 2 mmol) in diethyl ether (15 mL) was treated with 6 equiv of *t*BuLi (8 mL of a 1.5 M solution in pentane, 12 mmol) at −78 °C. The reaction was stirred for 30 min at this temperature, and then 6 equiv of TMEDA (1.8 mL, 12 mmol) were added. The cooling bath was removed allowing the reaction to reach room temperature. An excess of deuterium oxide was used to quench the reaction mixture. The mixture was hydrolyzed with water and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under vaccum affording a 6:1 mixture of **34** and **35** in almost quantitative yield (94%). This mixture could not be separated by column chromatography. The spectroscopic data of **34** are the same than **5b** except an extra deuterium atom is present in the aromatic ring. The spectroscopic data of the mixture are the following: $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.5-7.0$ (m, 6H; ArH, **34** + **35**), 6.8 (s, 1H; N=CH, **35**), 6.7–6.4 (m, 2H; ArH, **34**), 5.15–4.95 (m, 2H; =$CH_2$, **35**), 4.6 (s, 2H; $NCH_2$, **35**), 4.0 (s, 2H; $NCH_2$, **34**), 2.2–2.15 (m, 2H; $CH_2D$, **35**), 1.75–1.65 (m, 2H; $CH_2D$, **34**); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 146.9$, 129.1, 129.0, 126.8, 124.4, 121.3, 119.2, 118.9, 118.5, 116.7, 116.6, 115.0, 110.7, 109.2, 58.9, 11.0 (t, $J$(C,D) = 19.5 Hz), 9.5 (t, $J$(C,D) = 19 Hz); LRMS (70 eV, EI): *m*/*z* (%): (**34**): 176 (95) $[M]^+$, 160 (100). LRMS (70 eV, EI): *m*/*z* (%): (**35**): 173 (100) $[M]^+$.

**General procedure for the preparation of indole derivatives 37 and 38**: The procedure is the same as described for the preparation of **30**, but excess *t*BuLi (7.3 mL of a 1.5 M solution in pentane, 11 mmol) and TMEDA (1.65 mL, 11 mmol) were added successively to the amine **28b** (0.61 g, 2 mmol). The same or different electrophiles were added at −78 °C and then stirred at room temperature for 4 h. The mixture was hydrolyzed with water and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under vaccum, and the resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) giving rise to compounds **37** and **38**.

**2-Deuterio-3-deuteriomethyl-1-methyl-1*H*-indole (37a)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (7.3 mL of a 1.5 M solution in pentane, 11 mmol) and TMEDA (1.65 mL, 11 mmol). Addition of deuterium oxide (excess) and work-up as above yielded **37a** (0.21 g) as a colorless oil. $R_f = 0.24$ (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.70-7.15$ (m, 4H), 3.80 (s, 3H), 2.40 (t, $J = 2.2$ Hz, 2H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 136.8$, 128.5, 126.4 (t, $J$(C,D) = 13.5 Hz), 121.2, 118.8, 118.3, 109.6, 108.8, 32.2, 9.1 (t, $J$(C,D) = 19.5 Hz); HRMS (70 eV, EI) calcd for $C_{10}H_9D_2N$ ($[M]^+$): 147.1017, found 147.1014; elemental analysis calcd (%) for $C_{10}H_9D_2N$ (147.2): C 81.59, H/D 8.90, N 9.51; found C 81.63, H/D 8.79, N 9.31.

**2-Deuterio-1-methyl-3-trimethylsilylmethyl-1*H*-indole (37b)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (7.3 mL of a 1.5 M solution in pentane, 11 mmol) and TMEDA (1.65 mL, 11 mmol). Sequential addition of chlorotrimethylsilane (0.21 g, 2 mmol) and deuterium oxide (excess) and work-up as above yielded **37b** (0.26 g) as a colorless oil. $R_f = 0.46$ (hexane); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.65-7.10$ (m, 4H), 3.80 (s, 3H), 2.25 (s, 2H), 0.15 (s, 9H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 136.7$, 128.4, 124.9 (t, $J$(C,D) = 13.5 Hz), 121.0, 119.2, 118.0, 111.8, 108.7, 32.3, 13.7, −1.5; elemental analysis calcd (%) for $C_{13}H_{18}DNSi$ (218.4): C 71.50, H/D 9.23, N 6.41; found C 71.28, H/D 9.16, N 4.02.

**1,2,3,4-Tetrahydro-2,3-dihydroxy-4-methyl-2,3-diphenylcyclopent[*b*]indole (38a)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (7.3 mL of a 1.5 M solution in pentane, 11 mmol) and TMEDA (1.65 mL, 11 mmol). Addition of benzil (0.42 g, 2 mmol) and work-up as above yielded **38a** (0.33 g) as a colorless oil. $R_f = 0.45$ (hexane/ethyl acetate 5:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.70-6.60$ (m, 14H), 3.75 (d, $J = 15.2$ Hz, 1H), 3.60 (s, 3H), 3.20 (d, $J = 15.2$ Hz, 1H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta = 144.2$, 141.5, 139.8, 127.5, 127.2, 127.1, 126.2, 126.0, 123.8, 121.7, 119.5, 115.1, 110.1, 91.9, 85.5, 37.4, 30.2; elemental analysis calcd (%) for $C_{24}H_{21}NO_2$ (355.4): C 81.10, H 5.96, N 3.94; found C 81.23, H 5.79, N 4.11.

**1,2,3,4-Tetrahydro-2,3-dihydroxy-2,3,4-trimethylcyclopent[*b*]indole (38b)**: Amine **28b** (0.61 g, 2 mmol) was treated with *t*BuLi (7.3 mL of a 1.5 M solution in pentane, 11 mmol) and TMEDA (1.65 mL, 11 mmol). Addition of 2,3-butanedione (0.17 g, 2 mmol) and work-up as above yielded **38b** (0.18 g) as a colorless oil. $R_f = 0.25$ (hexane/ethyl acetate 5:1); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 7.50-7.10$ (m, 4H), 3.80 (s, 3H), 2.90 (s, 2H), 1.60–1.25 (br s, 2H), 1.46 and 1.44 (2s, 6H); $^{13}$C NMR ($CDCl_3$, 50.5 MHz): $\delta =$ 146.0, 141.1, 123.9, 121.2, 119.2, 119.1, 112.5, 109.5, 86.6, 78.5, 38.2, 29.7, 22.4, 20.9; LRMS (70 eV, EI): *m*/*z* (%): 231 (82) $[M]^+$, 170 (100); elemental analysis calcd (%) for $C_{14}H_{17}NO_2$ (231.3): C 72.70, H 7.41, N 6.06; found C 72.90, H 7.22, N 5.93.



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