ChemPubSoc Europe

DOI: 10.1002/chem.201304215

CHEMISTRY
A European Journal
Full Paper

Synthetic Methods

Palladium-Catalyzed One-Pot Three- or Four-Component Coupling of Aryl Iodides, Alkynes, and Amines through C–N Bond Cleavage: Efficient Synthesis of Indole Derivatives

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Dedicated to Professor Max Malacria on the occasion of his 65th birthday

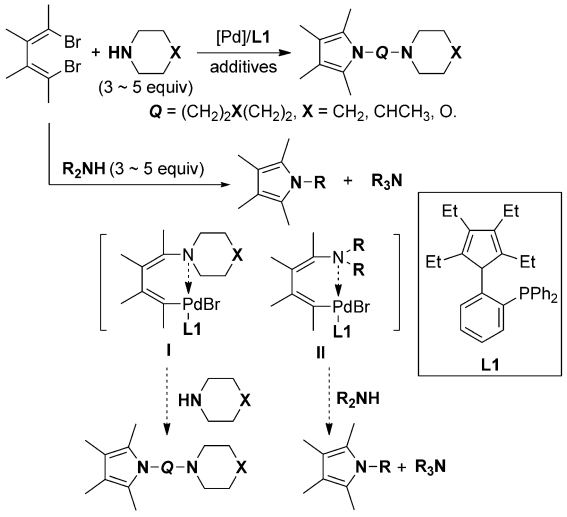
Abstract: An efficient synthesis of N-substituted indole derivatives was realized by combining the Pd-catalyzed one-pot multicomponent coupling approach with cleavage of the C(sp^3)–N bonds. Three or four components of aryl iodides, alkynes, and amines were involved in this coupling process. The cyclopentadiene–phosphine ligand showed high efficiency. A variety of aryl iodides, including cyclic and acyclic tertiary amino aryl iodides, and substituted 1-bromo-2-iodobenzene derivatives could be used. Both symmetric and unsymmetric alkynes substituted with alkyl, aryl, or trimethylsilyl groups could be applied. Cyclic secondary amines such as piperidine, morpholine, 4-methylpiperidine, 1-methylpiperazine, 2-methylpiperidine, and acyclic amines including secondary and primary amines all showed good reactivity. Further application of the resulting indole derivatives was demonstrated by the synthesis of benzosilolo[2,3-*b*]indole.

Introduction

The synthesis of indole derivatives has been a major subject both in academia and industry, since the substituted indole nucleus appears in a vast number of natural products and pharmacologically active compounds.[1–3] Among the many approaches to indole derivatives,[4] transition-metal-catalyzed multicomponent coupling reactions have attracted much attention.[5]

In addition, transition-metal-catalyzed cleavage of C(sp^3)–N bonds is of significant synthetic interest, because such bonds are common in organic chemistry and usually unreactive.[6,7] In this article, we report an efficient synthesis of N-substituted indole derivatives by combining the palladium-catalyzed multicomponent coupling process with cleavage of the C(sp^3)–N bonds.

Scheme 1 outlines our previous report on the synthesis of pyrrole derivatives from secondary amines and butadienyl dibromides. Formation of intermediates **I** and **II** was proposed. These intermediates would undergo C(sp^3)–N bond cleavage and a second amination reaction, thus leading to the final pyrrole derivatives. The cyclopentadiene–phosphine ligand **L1** showed high efficiency.[8]



Scheme 1. Our previous work: palladium-catalyzed synthesis of pyrrole derivatives through C–N bond cleavage.

Enlightened by our previous findings (Scheme 1), we envisioned that 1-(2-iodophenyl)piperidine would form intermediate **III** by means of Pd-catalyzed alkyne insertion into the C–I bond (Scheme 2). Intermediate **III** would undergo C(sp^3)–N bond cleavage and an amination reaction to lead to N-substituted indole derivatives. Similarly, 1-bromo-2-iodobenzene would form intermediate **IV** by means of Pd-catalyzed selective

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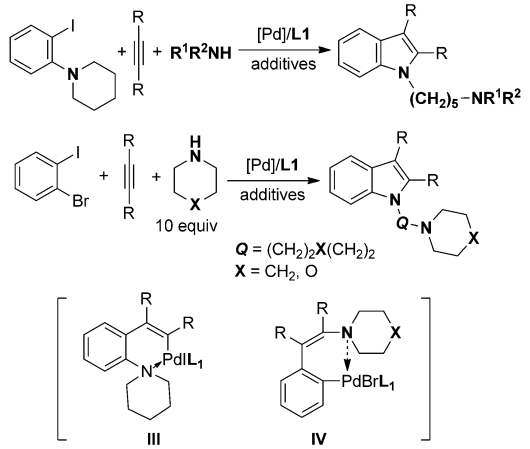
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304215.

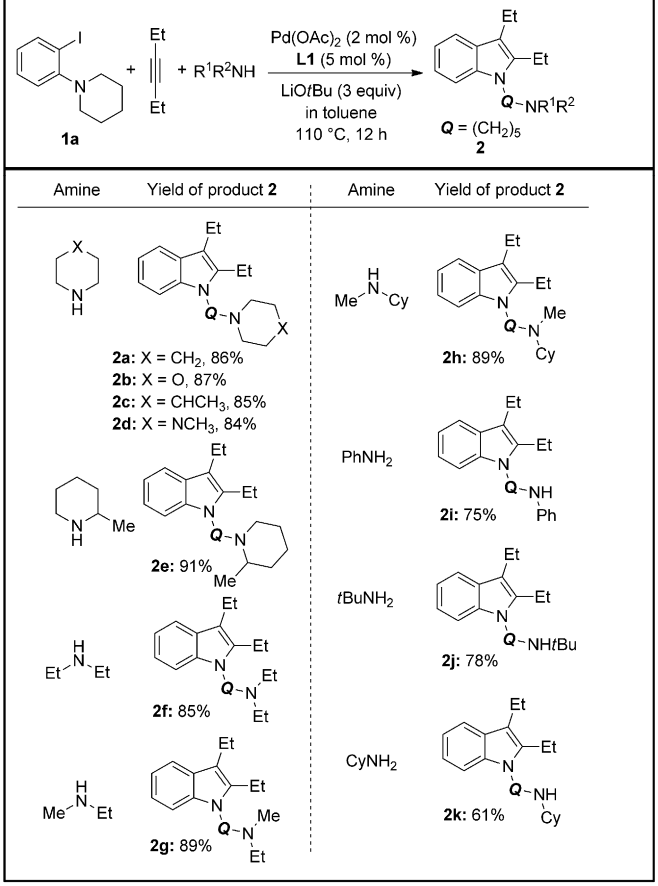


Scheme 2. This work: synthesis of N-substituted indole derivatives by combining the palladium-catalyzed multicomponent coupling process with cleavage of the C(sp^3)–N bonds.

insertion of alkyne into the C–I bond followed by amination. Thus, synthesis of indole derivatives would be realized by means of a Pd-catalyzed three- or four-component coupling process.

Scheme 2 shows the new synthetic methods developed in this work for the synthesis of N-substituted indole derivatives by means of the palladium-catalyzed multicomponent coupling of aryl iodides, alkynes, and amines. The cleavage of C(sp^3)–N bonds takes place as a key step in this catalytic process. The cyclopentadiene–phosphine ligand **L1** again shows high efficiency.

Table 1. Substrate scope: different amines.



Results and Discussion

Synthesis of N-substituted indole derivatives by means of three-component coupling

We initially investigated the reaction of 1-(2-iodophenyl)piperidine (**1a**) with 3-hexyne and piperidine to optimize the reaction conditions. The optimal reaction conditions were realized as follows: $Pd(OAc)_2$ (2 mol%), **L1** (5 mol%), Li*O*t*Bu* (3 equiv), 110 °C, 12 h. With these optimized conditions, indole derivative **2a** was obtained in 86% isolated yield (Table 1).

The substrate scope of this multicomponent cross-coupling process for the synthesis of N-substituted indole derivatives was then investigated. Results are summarized in Table 1 and Figure 1. Given in Table 1 are results obtained from **1a**, 3-hexyne, and various amines. A significant variation of amines could be applied to afford their corresponding indole derivatives in good to excellent isolated yields. In addition to cyclic secondary amines such as piperidine, morpholine, 4-methylpiperidine, 1-methylpiperazine, and 2-methylpiperidine (**2a**–**e**), acyclic amines could also be used (**2f**–**h**). Notably, besides secondary amines, primary amines such as aniline, *t*$BuNH_2$, and $CyNH_2$ also showed good reactivity (**2i**–**k**).

Figure 1 shows results obtained from the reaction of piperidine with various 2-amino iodobenzene derivatives **1** (**1a**–**d**) and different alkynes by following the reaction conditions

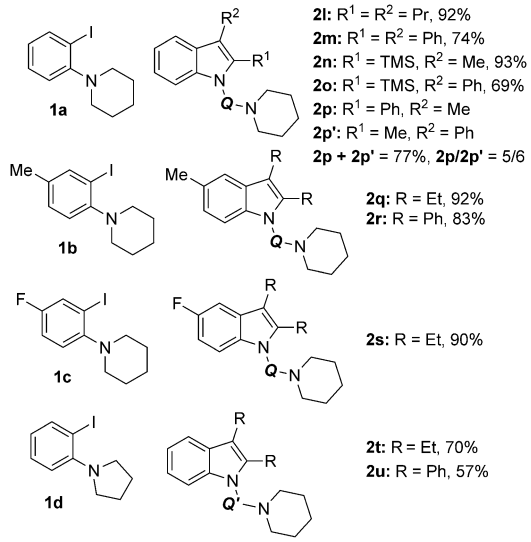


Figure 1. Substrate scope: Various 2-amino iodobenzenes and alkynes. $Q = (CH_2)_5$, $Q' = (CH_2)_4$

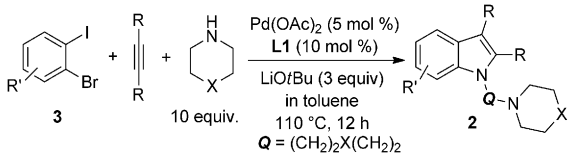
given in Table 1. Both alkyl and aryl alkynes could be used. Trimethylsilyl (TMS)-substituted unsymmetrical alkynes afforded their corresponding products regioselectively with the TMS group at the 2-position of the indole derivatives (**2n**,**o**). On the

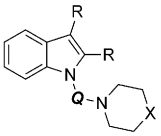
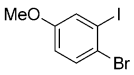
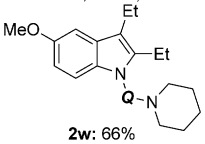
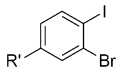
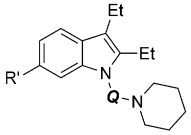
contrary, 1-phenyl-1-propyne gave a mixture of regioisomers (**2p**,**p**′). It should be noted that when terminal alkynes were used, formation of Sonogashira coupling products was observed.[9] Compounds **1b**,**c** with both electron-donating and electron-withdrawing substituents showed good reactivity (**2q**–**s**). Compound **1d** with a five-membered azacycle could be also used, thereby affording its corresponding indole derivatives (**2t**,**u**) with a shorter bridge.

Synthesis of N-substituted indole derivatives through four-component coupling

When the reaction of 1-bromo-2-iodobenzene (**3a**) with 3-hexyne and 2 molecules of piperidine was carried out under the above reaction conditions, the indole derivative **2a** was obtained in 72% isolated yield (Table 2). It should be noted that when 1,2-dibromobenzene was used, no reaction took place. As shown in Table 2, a one-pot four-component coupling process was realized for the synthesis of N-substituted indole derivatives. Compounds **3b**,**c** with both electron-donating and electron-withdrawing substituents showed good reactivity (**2w**–**z**). Highly selective formation of the products can be rationalized by the higher reactivity of the C–I bond than the C–Br bond, and the faster alkyne insertion reaction than the amination reaction.

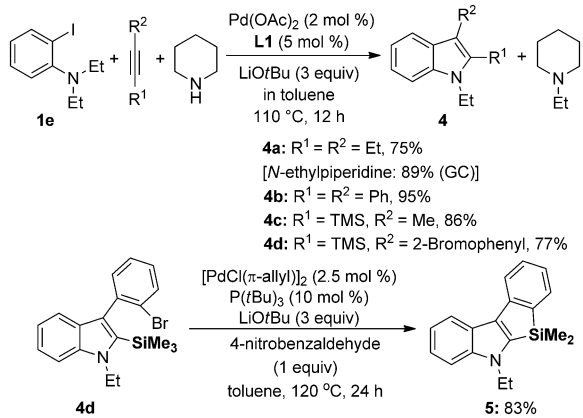
Table 2. One-pot four-component coupling for the synthesis of indole derivatives.



Compound **3**	Yield of product **2**
 **3a**	 **2a:** R = Et, **X** = CH_2, 72% **2l:** R = Pr, **X** = CH_2, 65% **2v:** R = Et, **X** = O, 82%
 **3b**	 **2w:** 66%
 **3c**	 **2x:** R' = Me, 74% **2y:** R' = F, 58% **2z:** R' = Cl, 62%

Application of *N*-ethyl indole derivatives for the synthesis of benzosilolo[2,3-*b*]indole

The C–N bond of cyclic amines in compounds **1** could be effectively cleaved and utilized for the synthesis of indole derivatives **2**. This reaction encouraged us to test acyclic amine-substituted iodobenzene derivatives such as 2-iodo-*N*,*N*-diethylaniline (**1e**). Thus, as shown in Scheme 3, when the reaction of **1e**, alkyne, and piperidine was carried out under the above reaction conditions, the *N*-ethyl indole derivative **4a** was obtained in 75% isolated yield. Different alkynes including alkyl, aryl, and $SiMe_3$-substituted ones could be used. Formation of *N*-ethylpiperidine was observed by using GC analysis. It should be noted that, in the absence of piperdine, only trace amounts of **4** could be detected.

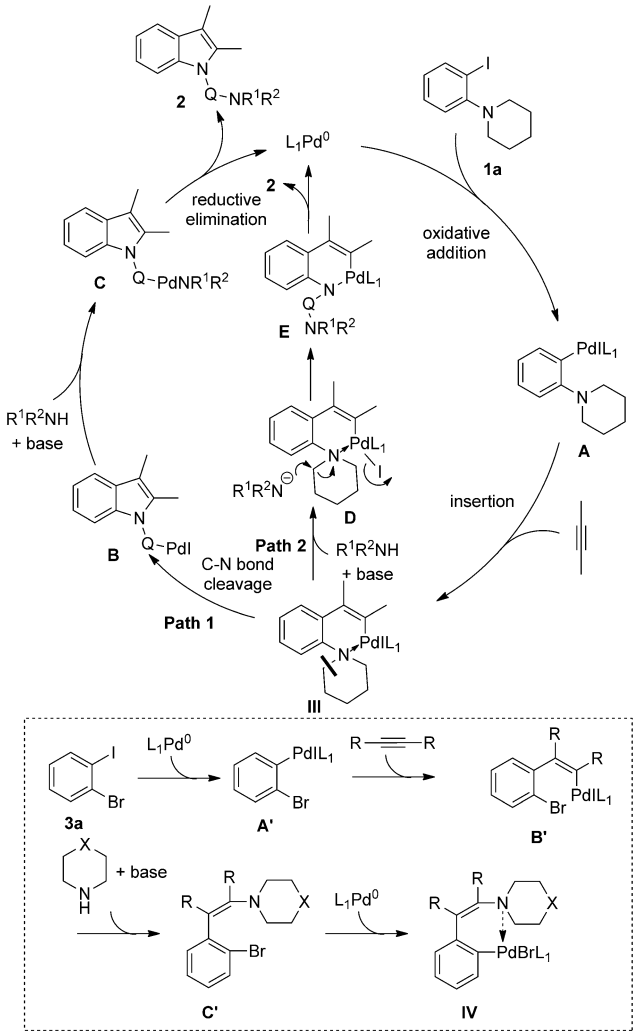


Scheme 3. Synthesis of *N*-alkyl indole derivatives and further application.

When (2-bromophenylethynyl)trimethylsilane was used as the alkyne, its corresponding indole derivative **4d** was isolated in 77% yield. As a demonstration of the further application of the products, product **4d** was subjected to our previous reaction conditions,[10c] and the benzosilolo[2,3-*b*]indole **5** was obtained in 83% isolated yield.[10] Siloles are very important for materials science.[11] The type of silole derivative **5** is not readily available by other means.[10,12] This multicomponent coupling process provides a good method for the synthesis of their precursors.

Mechanistic aspects

On the basis of the above observations and related literature,[8,13] possible reaction mechanisms are proposed and given in Scheme 4. Thus, intermediate **III** would be formed from 1-(2-iodophenyl)piperidine (**1a**) and alkyne by means of oxidative addition followed by alkyne insertion,[13] whereas intermediate **IV** would be formed through an oxidative addition/alkyne insertion/amination/oxidative addition process with 1-bromo-2-iodobenzene (**3a**), alkyne, and piperidine.[13] For cleavage of the C(sp^3)–N bond in intermediates **III** and **IV**, two possible pathways are proposed with **III** as the example. Along path 1,



Scheme 4. Proposed reaction mechanisms.

a direct cleavage of the C(sp^3)–N bond to lead to intermediate **B** would take place due to the coordination of the N atom to the Pd^{II} center. In addition, formation of the aromatic indole species **B** is also considered to be a driving force. However, path 2, which involves intermediates **D** and **E**, could not be excluded. Detailed investigation into the reaction mechanism will be carried out and will be reported in due course.

Conclusion

In summary, we have developed an efficient synthetic method for the synthesis of N-substituted indole derivatives by combining a palladium-catalyzed multicomponent coupling process with cleavage of C(sp^3)–N bonds. Three or four components of aryl iodides, alkynes, and amines were involved in this coupling process. The cyclopentadiene–phosphine ligand showed high efficiency. A variety of aryl iodides, including cyclic and acyclic tertiary amino aryl iodides, and substituted 1-bromo-2-iodobenzene derivatives could be used. Cyclic secondary amines and acyclic amines including secondary and primary amines all showed good reactivity. Further application of the resulting indole derivative was demonstrated by the synthesis of benzosilolo[2,3-*b*]indole.

Experimental Section

General methods

Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified using an Mbraun SPS-800 Solvent Purification System. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere under slight positive pressure by using Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker ARX400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) unless otherwise noted. High-resolution mass spectra were recorded using a Bruker Apex IV FTMS mass spectrometer using electrospray ionization (ESI). GC analyses were recorded using a SHIMADZU GC-2010 spectrometer using a flame-ionization detector (FID).

Typical procedure for the preparation of 2 or 4

Under an atmosphere of nitrogen, $Pd(OAc)_2$ (2 mol%), **L1** (5 mol%), and Li*O*tBu (1.5 mmol) were added to toluene (2 mL). After this reaction mixture was stirred at room temperature for 5 min, compound **1** or **3** (0.5 mmol), alkyne (0.6 mmol), and amine (2.5 mmol) were added, and this reaction mixture was stirred at 110 °C for 12 h. The reaction mixture was quenched with water and extracted with Et_2O. The extraction was washed with brine and dried over $MgSO_4$. The solvent was then evaporated under vacuum, and the residue was purified by using a silica gel column with petroleum ether and ethyl acetate as eluent to afford the final products.

Compound 2a: Yellow oil, isolated in a yield of 86% (140 mg). NMR spectroscopic data are consistent with the reported data.[8]

Compound 2b: Yellow oil, isolated yield of 87% (143 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 1.18–1.25 (m, 6H; CH_3), 1.34–1.42 (m, 2H; CH_2), 1.47–1.55 (m, 2H; CH_2), 1.72–1.80 (m, 2H; CH_2), 2.29 (t, J = 7.5 Hz, 2H; CH_2), 2.39 (br s, 4H; CH_2), 2.70–2.77 (m, 4H; CH_2), 3.69 (t, J = 4.3 Hz, 4H; CH_2), 4.03 (t, J = 7.6 Hz, 2H; CH_2), 7.05 (t, J = 7.3 Hz, 1H; CH), 7.12 (t, J = 7.4 Hz, 1H; CH), 7.23 (d, J = 8.0 Hz, 1H; CH), 7.53 ppm (d, J = 7.7 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 15.3 (CH_3), 16.1 (CH_3), 17.7 (2CH_2), 25.0 (CH_2), 26.3 (CH_2), 30.3 (CH_2), 43.2 (CH_2), 53.8 (2CH_2), 58.8 (CH_2), 67.0 (2CH_2), 108.9 (CH), 112.8 (quat. C), 118.2 (CH), 118.4 (CH), 120.3 (CH), 127.7 (quat. C), 135.8 (quat. C), 137.4 ppm (quat. C); HRMS: *m/z* calcd for $C_{21}H_{33}N_2O$ $[M+H]^+$: 329.2587; found: 329.2592.

Compound 2c: Yellow oil, isolated yield of 85% (144 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.91 (d, J = 6.2 Hz, 3H; CH_3), 1.18–1.41 (m, 11H; 2CH_3 + 2CH_2 + CH), 1.50–1.62 (m, 4H; CH_2), 1.72–1.80 (m, 2H; CH_2), 1.83–1.89 (m, 2H; CH_2), 2.27 (t, J = 7.8 Hz, 2H; CH_2), 2.70–2.77 (m, 4H; CH_2), 2.86 (d, J = 11.6 Hz, 2H; CH_2), 4.03 (t, J = 7.7 Hz, 2H; CH_2), 7.03–7.07 (m, 1H; CH), 7.12 (td, J = 7.5 Hz, 1.1 Hz, 1H; CH), 7.24 (d, J = 8.5 Hz, 1H; CH), 7.53 ppm (d, J = 7.7 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 15.3 (CH_3), 16.1 (CH_3), 17.7 (2CH_2), 21.9 (CH_2), 25.3 (CH_3), 26.9 (CH_2), 30.4 (CH_2), 30.8 (CH_2), 34.4 (2CH_2), 43.2 (CH_2), 54.2 (2CH_2), 59.0 (CH_2), 109.0 (CH), 112.7 (quat. C), 118.2 (CH), 118.4 (CH), 120.3 (CH), 127.7 (quat. C), 135.8 (quat. C), 137.5 ppm (quat. C); HRMS: *m/z* calcd for $C_{23}H_{37}N_2$ $[M+H]^+$: 341.2951; found: 341.2956.

Compound 2d: Yellow oil, isolated yield of 84% (143 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 1.18–1.25 (m, 6H; CH_3), 1.33–1.41 (m, 2H; CH_2), 1.49–1.56 (m, 2H; CH_2), 1.72–1.80 (m, 2H; CH_2), 2.30 (s,

3H; CH_3), 2.34 (t, J=7.7 Hz, 2H; CH_2), 2.50 (br s, 8H; CH_2), 2.70–2.77 (m, 4H; CH_2), 4.03 (t, J=7.6 Hz, 2H; CH_2), 7.04 (t, J=7.1 Hz, 1H; CH), 7.12 (td, J=7.5 Hz, 1.0 Hz, 1H; CH), 7.23 (d, J=8.0 Hz, 1H; CH), 7.53 ppm (d, J=7.7 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=15.3 (CH_3), 16.1 (CH_3), 17.7 (2CH_2), 25.1 (CH_2), 26.4 (CH_2), 30.3 (CH_2), 43.1 (CH_2), 45.8 (CH_3), 52.8 (2CH_2), 54.8 (2CH_2), 58.2 (CH_2), 109.0 (CH), 112.8 (quat. C), 118.2 (CH), 118.4 (CH), 120.3 (CH), 127.7 (quat. C), 135.8 (quat. C), 137.4 ppm (quat. C); HRMS: m/z calcd for $C_{22}H_{36}N_3$ $[M+H]^+$: 342.2904; found: 342.2902.

Compound 2e: Yellow oil, isolated yield of 91% (155 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.04 (d, J=6.2 Hz, 3H; CH_3), 1.18–1.25 (m, 6H; CH_3), 1.28–1.37 (m, 4H; CH_2), 1.49–1.66 (m, 6H; CH_2), 1.72–1.78 (m, 2H; CH_2), 2.10 (td, J=11.1 Hz, 3.2 Hz, 1H; CH), 2.21–2.32 (m, 2H; CH_2), 2.61–2.78 (m, 6H; CH_2), 4.03 (t, J=7.7 Hz, 2H; CH_2), 7.05 (td, J=7.4 Hz, 1.0 Hz, 1H; CH), 7.12 (td, J=7.5 Hz, 1.2 Hz, 1H; CH), 7.24 (d, J=8.0 Hz, 1H; CH), 7.53 ppm (d, J=7.7 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=15.3 (CH_3), 16.1 (CH_3), 17.7 (2CH_2), 19.2 (CH_3), 24.1 (CH_2), 25.3 (CH_2), 25.4 (CH_2), 26.2 (CH_2), 30.4 (CH_2), 34.7 (CH_2), 43.2 (CH_2), 52.3 (CH_2), 54.0 (CH_2), 55.9 (CH), 109.0 (CH), 112.8 (quat. C), 118.2 (CH), 118.4 (CH), 120.3 (CH), 127.7 (quat. C), 135.8 (quat. C), 137.5 ppm (quat. C); HRMS: m/z calcd for $C_{23}H_{37}N_2$ $[M+H]^+$: 341.2951; found: 341.2953.

Compound 2f: Yellow oil, isolated yield of 85% (133 mg). NMR spectroscopic data are consistent with the reported data.[8]

Compound 2g: Yellow oil, isolated yield of 89% (133 mg). ^{1}H NMR (400 MHz, C_6D_6): δ=0.97 (t, J=7.1 Hz, 3H; CH_3), 1.05 (t, J=7.5 Hz, 3H; CH_3), 1.12–1.17 (m, 2H; CH_2), 1.25–1.29 (m, 5H; CH_2+CH_3), 1.46–1.53 (m, 2H; CH_2), 2.05 (s, 3H; CH_3), 2.10 (t, J=7.0 Hz, 2H; CH_2), 2.24 (q, J=7.1 Hz, 2H; CH_2), 2.52 (q, J=7.5 Hz, 2H; CH_2), 2.74 (q, J=7.5 Hz, 2H; CH_2), 3.67 (t, J=7.5 Hz, 2H; CH_2), 7.18–7.29 (m, 3H; CH), 7.68 ppm (d, J=7.6 Hz, 1H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ=12.8 (CH_3), 15.5 (CH_3), 16.5 (CH_3), 17.9 (CH_2), 18.1 (CH_2), 25.1 (CH_2), 27.5 (CH_2), 30.5 (CH_2), 41.6 (CH_3), 43.2 (CH_2), 51.9 (CH_2), 57.3 (CH_2), 109.4 (CH), 113.1 (quat. C), 118.8 (CH), 119.1 (CH), 120.9 (CH), 128.6 (quat. C), 136.7 (quat. C), 137.1 ppm (quat. C); HRMS: m/z calcd for $C_{20}H_{33}N_2$ $[M+H]^+$: 301.2638; found: 301.2630.

Compound 2h: Yellow oil, isolated yield of 89% (158 mg). ^{1}H NMR (400 MHz, C_6D_6): δ=1.04–1.33 (m, 17H; $2CH_3+5CH_2+CH$), 1.50–1.56 (m, 2H; CH_2), 1.70–1.74 (m, 4H; CH_2), 2.12 (s, 3H; CH_3), 2.23 (t, J=6.9 Hz, 2H; CH_2), 2.54 (q, J=7.5 Hz, 2H; CH_2), 2.74 (q, J=7.5 Hz, 2H; CH_2), 3.70 (t, J=7.6 Hz, 2H; CH_2), 7.19–7.28 (m, 3H; CH), 7.65–7.67 ppm (m, 1H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ=15.5 (CH_3), 16.5 (CH_3), 17.9 (CH_2), 18.2 (CH_2), 25.0 (CH_2), 26.4 (2CH_2), 26.8 (CH_2), 28.2 (CH_2), 28.9 (2CH_2), 30.6 (CH_2), 37.5 (CH_3), 43.3 (CH_2), 53.4 (CH_2), 63.3 (CH), 109.5 (CH), 113.1 (quat. C), 118.8 (CH), 119.1 (CH), 120.9 (CH), 128.6 (quat. C), 136.7 (quat. C), 137.1 ppm (quat. C); HRMS: m/z calcd for $C_{24}H_{39}N_2$ $[M+H]^+$: 355.3108; found: 355.3107.

Compound 2i: Yellow oil, isolated yield of 75% (125 mg). ^{1}H NMR (400 MHz, C_6D_6): δ=0.90–0.96 (m, 2H; CH_2), 1.00–1.05 (m, 5H; CH_3+CH_2), 1.25 (t, J=7.5 Hz, 3H; CH_3), 1.32–1.39 (m, 2H; CH_2), 2.48 (q, J=7.5 Hz, 2H; CH_2), 2.60 (t, J=6.6 Hz, 2H; CH_2), 2.71 (q, J=7.5 Hz, 2H; CH_2), 2.91 (br s, 1H; NH), 3.58 (t, J=7.4 Hz, 2H; CH_2), 6.40 (d, J=7.8 Hz, 2H; CH), 6.72 (t, J=7.3 Hz, 1H; CH), 7.12 (d, J=5.8 Hz, 2H; CH), 7.17–7.27 (m, 3H; CH), 7.64 ppm (d, J=7.3 Hz, 1H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ=15.5 (CH_3), 16.5 (CH_3), 17.9 (CH_2), 18.1 (CH_2), 24.6 (CH_2), 29.4 (CH_2), 30.4 (CH_2), 43.0 (CH_2), 43.6 (CH_2), 109.4 (CH), 112.9 (2CH), 113.2 (quat. C), 117.4 (CH), 118.9 (CH), 119.2 (CH), 120.9 (CH), 128.6 (quat. C), 129.5 (2CH), 136.7 (quat. C), 137.1 (quat. C), 148.8 ppm (quat. C); HRMS: m/z calcd for $C_{23}H_{31}N_2$ $[M+H]^+$: 335.2482; found: 335.2486.

Compound 2j: Yellow oil, isolated yield of 78% (122 mg). ^{1}H NMR (400 MHz, C_6D_6): δ=1.03–1.15 (m, 14H; $4CH_3+CH_2$), 1.27 (t, J=7.5 Hz, 3H; CH_3), 1.38–1.45 (m, 2H; CH_2), 1.49–1.52 (m, 2H; CH_2), 2.10 (br s, 1H; NH), 2.32 (t, J=7.2 Hz, 2H; CH_2), 2.54 (q, J=7.5 Hz, 2H; CH_2), 2.74 (q, J=7.51 Hz, 2H; CH_2), 3.69 (t, J=7.5 Hz, 2H; CH_2), 7.22–7.30 (m, 3H; CH), 7.66–7.68 ppm (m, 1H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ=15.5 (CH_3), 16.5 (CH_3), 17.9 (CH_2), 18.1 (CH_2), 24.9 (CH_2), 28.2 (3 CH_3), 29.9 (CH_2), 30.5 (CH_2), 42.0 (CH_2), 43.1 (CH_2), 51.7 (quat. C), 109.5 (CH), 113.2 (quat. C), 118.8 (CH), 119.1 (CH), 120.9 (CH), 128.6 (quat. C), 136.7 (quat. C), 137.2 ppm (quat. C); HRMS: m/z calcd for $C_{21}H_{35}N_2$ $[M+H]^+$: 315.2795; found: 315.2794.

Compound 2k: Yellow oil, isolated yield of 61% (104 mg). ^{1}H NMR (400 MHz, C_6D_6): δ=1.04–1.30 (m, 16H; $2CH_3+5CH_2$), 1.46–1.54 (m, 3H; CH_2+NH), 1.65–1.68 (m, 2H; CH_2), 1.76–1.79 (m, 2H; CH_2), 2.25–2.32 (m, 1H; CH), 2.40 (t, J=6.8 Hz, 2H; CH_2), 2.53 (q, J=7.5 Hz, 2H; CH_2), 2.74 (q, J=7.5 Hz, 2H; CH_2), 3.68 (t, J=7.6 Hz, 2H; CH_2), 7.19–7.30 (m, 3H; CH), 7.68 ppm (d, J=7.1 Hz, 1H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ=15.5 (CH_3), 16.5 (CH_3), 17.9 (CH_2), 18.1 (CH_2), 25.1 (CH_2), 25.2 (2CH_2), 26.7 (CH_2), 30.6 (CH_2), 30.7 (CH_2), 34.0 (2CH_2), 43.2 (CH_2), 46.9 (CH_2), 57.0 (CH), 109.4 (CH), 113.1 (quat. C), 118.8 (CH), 119.1 (CH), 120.9 (CH), 128.6 (quat. C), 136.7 (quat. C), 137.1 ppm (quat. C); HRMS: m/z calcd for $C_{23}H_{37}N_2$ $[M+H]^+$: 341.2951; found: 341.2954.

Compound 2l: Yellow oil, isolated yield of 92% (163 mg). NMR spectroscopic data are consistent with the reported data.[8]

Compound 2m: Yellow oil, isolated yield of 74% (156 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.11–1.18 (m, 2H; CH_2), 1.31–1.40 (m, 4H; CH_2), 1.50–1.56 (m, 4H; CH_2), 1.63–1.71 (m, 2H; CH_2), 2.13 (t, J=7.7 Hz, 2H; CH_2), 2.26 (br s, 4H; CH_2), 4.05 (t, J=7.6 Hz, 2H; CH_2), 7.10–7.41 (m, 13H; CH), 7.80 ppm (d, J=7.9 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=24.4 (CH_2), 24.9 (CH_2), 25.9 (2CH_2), 26.4 (CH_2), 29.8 (CH_2), 43.7 (CH_2), 54.6 (2CH_2), 59.1 (CH_2), 109.9 (CH), 115.2 (quat. C), 119.7 (CH), 120.0 (CH), 122.0 (CH), 125.3 (CH), 127.1 (quat. C), 128.0 (CH), 128.0 (2CH), 128.4 (2CH), 129.8 (2CH), 131.1 (2CH), 132.2 (quat. C), 135.2 (quat. C), 136.4 (quat. C), 137.4 ppm (quat. C); HRMS: m/z calcd for $C_{30}H_{35}N_2$ $[M+H]^+$: 423.2795; found: 423.2801.

Compound 2n: Yellow oil, isolated yield of 93% (166 mg). NMR spectroscopic data are consistent with the reported data.[8]

Compound 2o: Yellow oil, isolated yield of 69% (144 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=0.15 (s, 9H; $Si(CH_3)_3$), 1.40–1.46 (m, 4H; CH_2), 1.55–1.63 (m, 6H; CH_2), 1.85–1.93 (m, 2H; CH_2), 2.29–2.37 (m, 6H; CH_2), 4.25 (t, J=8.2 Hz, 2H; CH_2), 7.03 (t, J=7.4 Hz, 1H; CH), 7.20–7.24 (m, 1H; CH), 7.33–7.38 ppm (m, 7H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=1.3 (3CH_3), 24.5 (CH_2), 25.3 (CH_2), 26.0 (2CH_2), 26.8 (CH_2), 30.7 (CH_2), 46.7 (CH_2), 54.7 (2CH_2), 59.3 (CH_2), 109.3 (CH), 119.2 (CH), 119.8 (CH), 122.4 (CH), 126.6 (CH), 127.7 (2CH), 128.2 (quat. C), 129.3 (quat. C), 131.3 (2CH), 135.7 (quat. C), 137.1 (quat. C), 138.3 ppm (quat. C); HRMS: m/z calcd for $C_{27}H_{39}N_2Si$ $[M+H]^+$: 419.2877; found: 419.2883.

Compound 2p/2p′: Yellow oil, combined isolated yield of 77% (5:6) (139 mg) (the values in parentheses refer to the ratio of regioisomers determined by GC). For **2p**: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.03–1.14 (m, 2H; CH_2), 1.25–1.41 (m, 4H; CH_2), 1.52–1.64 (m, 6H; CH_2), 2.13 (t, J=7.8 Hz, 2H; CH_2), 2.23 (s, 3H; CH_3), 2.28 (br s, 4H; CH_2), 4.01 (t, J=7.6 Hz, 2H; CH_2), 7.13 (t, J=7.4 Hz, 1H; CH), 7.22 (t, J=7.5 Hz, 1H; CH), 7.33–7.49 (m, 6H; CH), 7.59 ppm (d, J=7.8 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=9.2 (CH_3), 24.4 (CH_2), 24.9 (CH_2), 25.9 (2CH_2), 26.4 (CH_2), 29.9 (CH_2), 43.8 (CH_2), 54.6 (2CH_2), 59.2 (CH_2), 108.7 (quat. C), 109.6 (CH), 118.9 (CH), 119.0 (CH), 121.5 (CH), 127.8 (CH), 128.4 (2CH), 128.6 (quat. C), 130.6 (2CH), 132.5 (quat. C), 136.3 (quat. C), 137.4 ppm (quat. C). For **2p′**: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.37–1.44 (m, 4H; CH_2), 1.52–1.61 (m, 6H; CH_2), 1.77–1.85 (m, 2H; CH_2), 2.28

(t, J=7.8 Hz, 2H; CH_2), 2.36 (br s, 4H; CH_2), 2.47 (s, 3H; CH_3), 4.11 (t, J=7.5 Hz, 2H; CH_2), 7.09 (t, J=7.5 Hz, 1H; CH), 7.16–7.20 (m, 1H; CH_2), 7.27–7.32 (m, 2H; CH), 7.43–7.50 (m, 4H; CH), 7.65 ppm (d, J=7.8 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=11.1 (CH_3), 24.4 (CH_2), 25.3 (CH_2), 26.0 (2CH_2), 26.7 (CH_2), 30.1 (CH_2), 43.4 (CH_2), 54.7 (2CH_2), 59.4 (CH_2), 109.0 (CH), 114.1 (quat. C), 118.8 (CH), 119.5 (CH), 121.0 (CH), 125.6 (CH), 127.1 (quat. C), 128.4 (2CH), 129.8 (2CH_2), 132.8 (quat. C), 135.8 (quat. C), 135.9 ppm (quat. C); HRMS: m/z calcd for $C_{25}H_{33}N_2$ $[M+H]^+$: 361.2638; found: 361.2643.

Compound 2q: Yellow oil, isolated yield of 92% (156 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.17–1.24 (m, 6H; CH_3), 1.33–1.44 (m, 4H; CH_2), 1.50–1.60 (m, 6H; CH_2), 1.70–1.78 (m, 2H; CH_2), 2.25 (t, J=7.8 Hz, 2H; CH_2), 2.34 (br s, 4H; CH_2), 2.44 (s, 3H; CH_3), 2.67–2.75 (m, 4H; CH_2), 3.99 (t, J=7.7 Hz, 2H; CH_2), 6.94 (dd, J=7.0 Hz, 1.3 Hz, 1H; CH), 7.12 (d, J=8.3 Hz, 1H; CH), 7.31 ppm (s, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=15.3 (CH_3), 16.1 (CH_3), 17.7 (CH_2), 17.7 (CH_2), 21.5 (CH_3), 24.5 (CH_2), 25.3 (CH_2), 26.0 (2CH_2), 26.7 (CH_2), 30.4 (CH_2), 43.2 (CH_2), 54.7 (2CH_2), 59.4 (CH_2), 108.7 (CH), 112.2 (quat. C), 118.0 (CH), 121.8 (CH), 127.5 (quat. C), 127.9 (quat. C), 134.3 (quat. C), 137.6 ppm (quat. C); HRMS: m/z calcd for $C_{23}H_{37}N_2$ $[M+H]^+$: 341.2951; found: 341.2953.

Compound 2r: Yellow oil, isolated yield of 83% (182 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.11–1.18 (m, 2H; CH_2), 1.31–1.41 (m, 4H; CH_2), 1.52–1.58 (m, 4H; CH_2), 1.62–1.70 (m, 2H; CH_2), 2.14 (t, J=7.8 Hz, 2H; CH_2), 2.28 (br s, 4H; CH_2), 2.46 (s, 3H; CH_3), 4.05 (t, J=7.6 Hz, 2H; CH_2), 7.09–7.16 (m, 2H; CH), 7.22–7.37 (m, 10H; CH), 7.57 ppm (s, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=21.5 (CH_3), 24.4 (CH_2), 25.0 (CH_2), 25.9 (2CH_2), 26.4 (CH_2), 29.9 (CH_2), 43.8 (CH_2), 54.6 (2CH_2), 59.2 (CH_2), 109.6 (CH), 114.9 (quat. C), 119.3 (CH), 123.5 (CH), 125.3 (CH), 127.4 (quat. C), 128.0 (CH), 128.1 (2CH), 128.4 (2CH), 129.4 (quat. C), 129.9 (2CH), 131.1 (2CH), 132.4 (quat. C), 134.8 (quat. C), 135.4 (quat. C), 137.6 ppm (quat. C); HRMS: m/z calcd for $C_{31}H_{37}N_2$ $[M+H]^+$: 437.2951; found: 437.2959.

Compound 2s: Yellow oil, isolated yield of 90% (155 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.20 (td, J=7.6 Hz, 2.6 Hz, 6H; CH_3), 1.31–1.43 (m, 4H; CH_2), 1.48–1.60 (m, 6H; CH_2), 1.70–1.77 (m, 2H; CH_2), 2.25 (t, J=7.8 Hz, 2H; CH_2), 2.33 (br s, 4H; CH_2), 2.64–2.76 (m, 4H; CH_2), 4.00 (t, J=7.7 Hz, 2H; CH_2), 6.84 (td, J=9.1 Hz, 2.5 Hz, 1H; CH), 7.10–7.17 ppm (m, 2H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=15.2 (CH_3), 15.9 (CH_3), 17.6 (CH_2), 17.8 (CH_2), 24.5 (CH_2), 25.3 (CH_2), 26.0 (2CH_2), 26.7 (CH_2), 30.4 (CH_2), 43.4 (CH_2), 54.7 (2CH_2), 59.3 (CH_2), 103.1 (d, J=22.8 Hz, CH), 108.3 (d, J=26.0 Hz, CH), 109.4 (d, J=9.6 Hz, CH), 112.8 (d, J=4.5 Hz, quat. C), 127.9 (d, J=9.3 Hz, quat. C), 132.4 (quat. C), 139.3 (quat. C), 157.5 ppm (d, J=231.7 Hz, quat. C); HRMS: m/z calcd for $C_{22}H_{34}FN_2$ $[M+H]^+$: 345.2701; found: 345.2700.

Compound 2t: Yellow oil, isolated yield of 70% (109 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.19–1.25 (m, 6H; CH_3), 1.36–1.43 (m, 2H; CH_2), 1.54–1.60 (m, 6H; CH_2), 1.71–1.79 (m, 2H; CH_2), 2.28–2.35 (m, 6H; CH_2), 2.70–2.78 (m, 4H; CH_2), 4.05 (t, J=7.7 Hz, 2H; CH_2), 7.04 (t, J=7.3 Hz, 1H; CH), 7.12 (t, J=7.3 Hz, 1H; CH), 7.26 (d, J=8.1 Hz, 1H; CH), 7.53 ppm (d, J=7.8 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=15.3 (CH_3), 16.1 (CH_3), 17.7 (2CH_2), 24.5 (CH_2), 24.5 (CH_2), 26.0 (2CH_2), 28.5 (CH_2), 43.1 (CH_2), 54.6 (2CH_2), 58.8 (CH_2), 109.0 (CH), 112.8 (quat. C), 118.2 (CH), 118.4 (CH), 120.3 (CH), 127.7 (quat. C), 135.9 (quat. C), 137.5 ppm (quat. C); HRMS: m/z calcd for $C_{21}H_{33}N_2$ $[M+H]^+$: 313.2638; found: 313.2643.

Compound 2u: Yellow oil, isolated yield of 57% (116 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.34–1.39 (m, 4H; CH_2), 1.50–1.56 (m, 4H; CH_2), 1.64–1.72 (m, 2H; CH_2), 2.12–2.25 (m, 6H; CH_2), 4.09 (t, J=7.7 Hz, 2H; CH_2), 7.12–7.16 (m, 2H; CH), 7.27–7.37 (m, 10H; CH), 7.44 (d, J=8.2 Hz, 1H; CH), 7.79 ppm (d, J=7.9 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=24.2 (CH_2), 24.4 (CH_2), 25.9 (2CH_2), 28.1 (CH_2), 43.7 (CH_2), 54.5 (2CH_2), 58.5 (CH_2), 110.0 (CH), 115.3 (quat. C), 119.7 (CH), 120.1 (CH), 122.0 (CH), 125.4 (CH), 127.2 (quat. C), 128.1 (3 CH), 128.4 (2CH), 129.8 (2CH), 131.1 (2CH), 132.3 (quat. C), 135.2 (quat. C), 136.4 (quat. C), 137.4 ppm (quat. C); HRMS: m/z calcd for $C_{29}H_{33}N_2$ $[M+H]^+$: 409.2638; found: 409.2641.

Compound 2v: Yellow oil, isolated yield of 82% (135 mg). NMR spectroscopic data are consistent with the reported data.[8]

Compound 2w: Yellow oil, isolated yield of 66% (117 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.18–1.24 (m, 6H; CH_3), 1.35–1.60 (m, 10H; CH_2), 1.70–1.78 (m, 2H; CH_2), 2.26 (t, J=7.8 Hz, 2H; CH_2), 2.35 (br s, 4H; CH_2), 2.67–2.75 (m, 4H; CH_2), 3.86 (s, 3H; CH_3), 3.99 (t, J=7.7 Hz, 2H; CH_2), 6.79 (dd, J=8.7 Hz, 2.5 Hz, 1H; CH), 7.00 (d, J=2.4 Hz, 1H; CH), 7.13 ppm (d, J=8.8 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=15.3 (CH_3), 16.0 (CH_3), 17.7 (CH_2), 17.8 (CH_2), 24.5 (CH_2), 25.3 (CH_2), 26.0 (2CH_2), 26.7 (CH_2), 30.5 (CH_2), 43.3 (CH_2), 54.7 (2CH_2), 56.1 (CH_3), 59.4 (CH_2), 100.7 (CH), 109.6 (CH), 110.0 (CH), 112.4 (quat. C), 127.9 (quat. C), 131.2 (quat. C), 138.3 (quat. C), 153.5 ppm (quat. C); HRMS: m/z calcd for $C_{23}H_{37}N_2O$ $[M+H]^+$: 357.2900; found: 357.2903.

Compound 2x: Yellow oil, isolated yield of 74% (126 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.17–1.24 (m, 6H; CH_3), 1.33–1.44 (m, 4H; CH_2), 1.51–1.61 (m, 6H; CH_2), 1.71–1.79 (m, 2H; CH_2), 2.27 (t, J=7.8 Hz, 2H; CH_2), 2.35 (br s, 4H; CH_2), 2.47 (s, 3H; CH_3), 2.67–2.75 (m, 4H; CH_2), 3.99 (t, J=7.8 Hz, 2H; CH_2), 6.88 (d, J=7.9 Hz, 1H; CH), 7.02 (s, 1H; CH), 7.41 ppm (d, J=8.0 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ=15.3 (CH_3), 16.1 (CH_3), 17.6 (CH_2), 17.7 (CH_2), 21.8 (CH_3), 24.5 (CH_2), 25.3 (CH_2), 26.0 (2CH_2), 26.7 (CH_2), 30.3 (CH_2), 43.1 (CH_2), 54.7 (2CH_2), 59.4 (CH_2), 109.0 (CH), 112.5 (quat. C), 117.9 (CH), 120.0 (CH), 125.6 (quat. C), 130.0 (quat. C), 136.2 (quat. C), 136.7 ppm (quat. C); HRMS: m/z calcd for $C_{23}H_{37}N_2$ $[M+H]^+$: 341.2951; found: 341.2960.

Compound 2y: Yellow oil, isolated yield of 58% (100 mg). ^{1}H NMR (400 MHz, C_6D_6): δ=1.00 (t, J=7.6 Hz, 3H; CH_3), 1.21 (t, J=7.4 Hz, 3H; CH_3), 1.33–1.42 (m, 8H; CH_2), 1.49–1.55 (m, 4H; CH_2), 2.07 (t, J=7.2 Hz, 2H; CH_2), 2.22 (br s, 4H; CH_2), 2.44 (q, J=7.5 Hz, 2H; CH_2), 2.63 (q, J=7.6 Hz, 2H; CH_2), 3.51 (t, J=7.6 Hz, 2H; CH_2), 6.95–7.00 (m, 2H; CH), 7.33–7.37 ppm (m, 1H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ=15.4 (CH_3), 16.4 (CH_3), 17.9 (CH_2), 18.0 (CH_2), 25.0 (CH_2), 25.0 (CH_2), 26.5 (2CH_2), 26.9 (CH_2), 30.2 (CH_2), 43.3 (CH_2), 55.0 (2CH_2), 59.1 (CH_2), 96.1 (d, J=25.7 Hz, CH), 107.3 (d, J=24.0 Hz, CH), 113.2 (quat. C), 119.4 (d, J=10.1 Hz, CH), 125.0 (quat. C), 136.6 (d, J=11.6 Hz, quat. C), 137.6 (d, J=3.7 Hz, quat. C), 160.1 ppm (d, J=233.7 Hz, quat. C); HRMS: m/z calcd for $C_{22}H_{34}FN_2$ $[M+H]^+$: 345.2701; found: 345.2708.

Compound 2z: Yellow oil, isolated yield of 62% (112 mg). ^{1}H NMR (400 MHz, C_6D_6): δ=0.98 (t, J=7.4 Hz, 3H; CH_3), 1.18 (t, J=7.6 Hz, 3H; CH_3), 1.26–1.39 (m, 8H; CH_2), 1.49–1.55 (m, 4H; CH_2), 2.06 (t, J=7.2 Hz, 2H; CH_2), 2.22 (br s, 4H; CH_2), 2.42 (q, J=7.6 Hz, 2H; CH_2), 2.60 (q, J=7.5 Hz, 2H; CH_2), 3.49 (t, J=7.6 Hz, 2H; CH_2), 7.19–7.21 (m, 1H; CH), 7.31–7.34 ppm (m, 2H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ=15.2 (CH_3), 16.3 (CH_3), 17.8 (CH_2), 17.9 (CH_2), 25.0 (CH_2), 26.5 (2CH_2), 26.9 (CH_2), 30.2 (CH_2), 30.3 (CH_2), 43.3 (CH_2), 55.0 (2CH_2), 59.1 (CH_2), 109.6 (CH), 113.3 (quat. C), 119.6 (CH), 119.6 (CH), 127.0 (quat. C), 127.0 (quat. C), 137.0 (quat. C), 138.1 ppm (quat. C); HRMS: m/z calcd for $C_{22}H_{34}ClN_2$ $[M+H]^+$: 361.2405; found: 361.2412.

Compound 4a: Yellow oil, isolated yield of 75% (75 mg). NMR spectroscopic data are consistent with the reported data.[8]

Compound 4b: Yellow oil, isolated yield of 95% (141 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ=1.26 (t, J=7.2 Hz, 3H; CH_3), 4.11 (q, J=7.2 Hz, 2H; CH_2), 7.12–7.36 (m, 12H; CH), 7.42 (d, J=8.2 Hz, 1H; CH), 7.81 ppm (d, J=8.0 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$,

Me_4Si): $\delta = 15.4$ (CH_3), 38.6 (CH_2), 109.8 (CH), 115.3 (quat. C), 119.8 (CH), 120.1 (CH), 122.0 (CH), 125.4 (CH), 127.3 (quat. C), 128.1 (CH), 128.1 (2CH), 128.4 (2CH), 129.8 (2CH), 131.1 (2CH), 132.3 (quat. C), 135.2 (quat. C), 136.1 (quat. C), 137.3 ppm (quat. C); HRMS: *m/z* calcd for $C_{22}H_{20}N$ $[M+H]^+$: 298.1590; found: 298.1595.

Compound 4c: Yellow oil, isolated yield of 86% (99 mg). NMR spectroscopic data are consistent with the reported data.[8]

Compound 4d: Yellow oil, isolated yield of 77% (143 mg). ^1H NMR (400 MHz, C_6D_6): $\delta = 0.15$ (s, 9H; CH_3), 1.08 (t, $J = 7.1$ Hz, 3H; CH_3), 3.91 (q, $J = 7.1$ Hz, 2H; CH_2), 6.80 (td, $J = 7.7$ Hz, 1.7 Hz, 1H; CH), 6.92–6.96 (m, 1H; CH), 7.08–7.13 (m, 2H; CH), 7.21–7.25 (m, 2H; CH), 7.36 (d, $J = 8.0$ Hz, 1H; CH), 7.52 ppm (dd, $J = 8.0$ Hz, 0.8 Hz, 1H; CH); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 0.5$ (3 CH_3), 15.6 (CH_3), 41.1 (CH_2), 109.7 (CH), 119.9 (CH), 120.5 (CH), 122.8 (CH), 126.8 (CH), 128.9 (CH), 129.8 (quat. C), 132.6 (CH), 133.0 (quat. C), 133.0 (CH), 133.8 (quat. C), 135.5 (quat. C), 138.6 (quat. C), 139.1 ppm (quat. C); HRMS: *m/z* calcd for $C_{19}H_{23}BrNSi$ $[M+H]^+$: 372.0778; found: 372.0788.

Typical procedure for the preparation of benzosilolo[2,3-*b*]indole (5)

Under a nitrogen atmosphere, [PdCl(π-allyl)] (2.5 mol%) and P(tBu)$_3$ (10 mol%) were added to toluene (2 mL). After this reaction mixture was stirred at room temperature for 15 min, compound **4d** (0.3 mmol), LiO*t*Bu (0.9 mmol), and 4-nitrobenzaldehyde (0.3 mmol) were added and this reaction mixture was stirred at 120 °C for 24 h.[9d] The reaction mixture was quenched with water and extracted with Et_2O. The extraction was washed with brine and dried over $MgSO_4$. The solvent was then evaporated under vacuum, and the residue was purified by using a silica gel column with petroleum ether and ethyl acetate as eluent to afford the final product **5**.

Benzosilolo[2,3-*b*]indole (5): Colorless oil, isolated yield of 83% (69 mg). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 0.51$ (s, 6H; CH_3), 1.47 (t, $J = 7.3$ Hz, 3H; CH_3), 4.21 (q, $J = 7.27$, 2H; CH_2), 7.06–7.10 (m, 1H; CH), 7.15–7.25 (m, 2H; CH), 7.34–7.40 (m, 2H; CH), 7.46 (d, $J = 7.0$ Hz, 1H; CH), 7.74 (d, $J = 7.6$ Hz, 1H; CH), 7.98 ppm (d, $J = 7.7$ Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta = -3.34$ (2CH_3), 16.06 (CH_3), 42.34 (CH_2), 109.99 (CH), 119.83 (CH), 120.16 (CH), 120.19 (CH), 122.11 (CH), 124.10 (CH), 124.33 (quat. C), 130.27 (CH), 131.52 (quat. C), 132.39 (CH), 138.06 (quat. C), 141.73 (quat. C), 143.90 (quat. C), 145.64 ppm (quat. C); HRMS: *m/z* calcd for $C_{18}H_{20}NSi$ $[M+1]^+$: 278.1360; found: 278.1354.

Acknowledgements

This work was supported by the 973 Program (2012CB821600) and the Natural Science Foundation of China (NSFC).

Keywords: cleavage reactions · indoles · multicomponent reactions · palladium · synthetic methods

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Received: October 29, 2013
Published online on January 21, 2014

