

Synthesis of 2,3-Dihydroindoles, Indoles, and Anilines by Transition Metal-Free Amination of Aryl Chlorides

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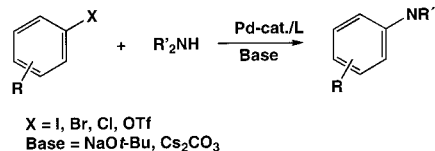
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Aliphatic and aromatic amines react with 2- and 3-chlorostyrene in the presence of potassium *tert*-butoxide to give *N*-substituted 2,3-dihydroindoles in good yields. The combination of this domino-amination protocol with a suitable dehydrogenation reaction gives access to pharmacologically interesting indoles in a one-pot procedure. Overall product yields of *N*-substituted indoles >50% are obtained by this method starting from commercially available substrates. In addition to the intramolecular base-promoted amination of aromatic C–Cl bonds, metal-free intermolecular aminations of aryl chlorides with primary and secondary amines are described. The use of potassium *tert*-butoxide as base allows the synthesis of various anilines in good to excellent yields. Due to the formation of aryne intermediates, either *N*-substituted anilines or *meta*-substituted anilines are produced with excellent selectivities.

Introduction

Amines and their derivatives are of fundamental importance as natural products, pharmacological agents, fine chemicals, dyes, and polymers.¹ There is thus considerable interest in developing efficient synthetic protocols for the construction of carbon–nitrogen bonds. While the hydroamination of olefins² constitutes the most elegant approach to aliphatic amines, aromatic amines are generally synthesized by nitration and reduction or nucleophilic substitution reactions. Based on the important developments by Buchwald et al.³ and Hartwig et

Scheme 1. Palladium-Catalyzed Amination of Aryl Halides (Buchwald–Hartwig Reaction)



al.,⁴ the palladium-catalyzed C–N-coupling reaction of aryl halides has recently become the most important laboratory scale synthesis of substituted arylamines (Scheme 1).⁵

It is desirable to use aryl chlorides as substrates in amination reactions of aryl halides since they are both inexpensive and generally available. Despite significant improvements in the amination of chloroaromatics, comparably large amounts of the palladium catalyst (in general ca. 1 mol %) and the sensitive and expensive phosphine ligands (1–4 mol %) still have to be used for successful amination. In a preliminary communication⁷ we have shown that the intramolecular amination of

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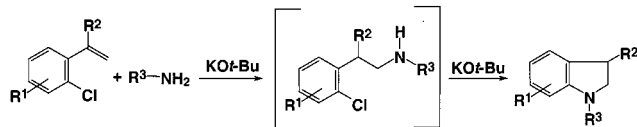
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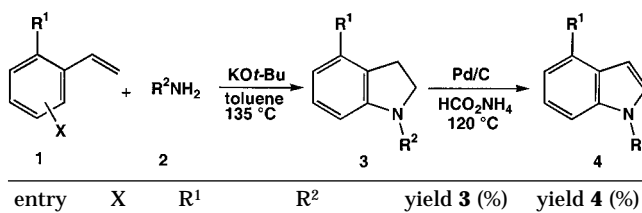
Scheme 2. Synthesis of *N*-Aryl-2,3-dihydroindoles ($R^2 = \text{H, CH}_3$; $R^3 = \text{Aryl}$)


o-halostyrenes proceeds selectively without needing a palladium catalyst. As shown in Scheme 2, *N*-aryl-2,3-dihydroindoles were synthesized by a *KOt*-Bu-mediated domino reaction of 2-chlorostyrene with anilines.

The crucial point for the success of the intramolecular amination reactions was the use of *KOt*-Bu as the base, which both catalyzes the hydroamination of styrenes and leads to the formation of aryne intermediates. Subsequent intramolecular attack of the amino group or the corresponding potassium amide on the aryne gave the desired product. To the best of our knowledge the amination of aryl chlorides via aryne intermediates has been reported in the literature to occur only in the presence of more expensive and sensitive lithium alkyls or lithium amides.⁸ Hence, we were interested in the general application of our aryne generation protocol to synthesize substituted anilines. Herein, we describe a full account of our efforts toward this goal. In addition, an extension of the domino-hydroamination–intramolecular-aryne-amination procedure to give new *N*-alkyl- and *N*-aryl-2,3-dihydroindolines and substituted indoles is described.⁹

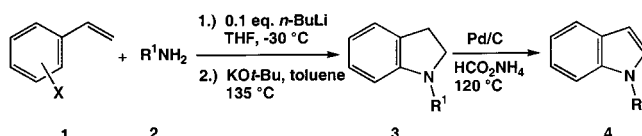
Results and Discussion

Synthesis of *N*-Aryl-2,3-dihydroindoles and *N*-Arylindoles. Starting from commercially available halo-styrenes (2-chlorostyrene, 3-chlorostyrene, 2,6-dichlorostyrene) various 2,3-dihydroindoles were obtained in the presence of *KOt*-Bu in toluene at 135 °C (Table 1). Since *KOt*-Bu is a precatalyst for the hydroamination reaction and a mediator for the aryne-amination reaction, stoichiometric amounts of base have to be used in order to obtain full conversion. In general 3 equiv of *KOt*-Bu were applied in these reactions; however, the amount of base could be reduced to 1.5 equiv (relative to the aryl chloride) without significantly decreasing the yield (Table 1, entries 7–9). Electron-withdrawing (F, CF₃, Ph) as well as electron-donating (OCH₃) substituents on the aniline ring gave similar yields in the 2,3-dihydroindole synthesis compared to aniline (Table 1, entries 1–5). Despite possible side reactions to give alternative aryne intermediates, 3-chlorostyrene reacts with 4-fluoroaniline to yield the substituted 2,3-dihydroindole in a similar yield (50 vs 54%; Table 1, entries 3 and 4) to 2-chlorostyrene.

Table 1. *N*-Arylindolines Synthesized by a Domino Hydroamination–Aryne-Cyclization Reaction


entry	X	R ¹	R ²	yield 3 (%)	yield 4 (%)
1	2-Cl	H	C ₆ H ₅	53 (3a)	58 (4a)
2	2-Cl	H	2-MeO-C ₆ H ₄	58 (3b)	—
3	2-Cl	H	4-F-C ₆ H ₄	54 (3c)	—
4	3-Cl	H	4-F-C ₆ H ₄	50 (3c)	—
5	3-Cl	H	3-CF ₃ -C ₆ H ₄	44 (3d)	48 (4d)
6	3-Cl	H	4-biphenyl	47 (3e)	56 (4e)
7 ^a	2-Cl	6-Cl	4-F-C ₆ H ₄	50 (3f)	—
8 ^b	2-Cl	6-Cl	2-F-C ₆ H ₄	42 (3g)	51 (4g)
9 ^a	2-Cl	6-Cl	1-anthracenyl	37 (3h)	—

^a 1.5 equiv of *KOt*-Bu, 1.2 equiv of amine. ^b 1.5 equiv of *KOt*-Bu, 1.1 equiv of amine.

Table 2. *N*-Substituted Indolines from the Base-Catalyzed and Base-Promoted Domino Reaction of Aliphatic Amines and Chlorostyrenes^a


entry	X	R ¹	yield 3 (%)	yield 4 (%)
1	2-Cl	<i>n</i> -Bu	45 (3i)	50 (4i)
2	3-Cl	<i>n</i> -Bu	43 (3i)	50 (4i)
3	3-Cl	<i>t</i> -Bu	40 (3j)	—
4	3-Cl	C ₆ H ₅ -(CH ₂) ₂	43 (3k)	—
5	2-Cl	C ₂ H ₅ -O-(CH ₂) ₃	41 (3l)	—

^a (1) 1.5 equiv of amine; 0.1 equiv of *n*-BuLi in THF, 3 h, –30 °C. (2) 3 equiv of *KOt*-Bu in toluene, 20 h, 135 °C.

2,6-Dichlorostyrene (Table 1, entries 7–9) is an interesting starting material for the domino-hydroamination–aryne-amination process, because the resulting chloro-substituted *N*-aryl-indolines represent valuable starting materials for further functionalization. Due to the increased tendency toward side reactions of the second chloro-substituent slightly lower product yields (37–50%) were observed. Attempts to react α - or β -methyl-2-chlorostyrene with aniline in the presence of stoichiometric amounts of *KOt*-Bu do not result in the corresponding 2- and 3-substituted 2,3-dihydroindoles. In this case aryne generation as a first reaction step is favored compared to olefin hydroamination. The resulting 3-substituted anilines (see Table 3) are unable to undergo intramolecular cyclization via hydroamination.

Next, we were interested in a direct synthesis of *N*-arylindoles.^{3h,10,11} In general the corresponding *N*-arylindoles were obtained in yields of up to 10% as side-products of the domino reaction sequence. To circumvent the isolation of the corresponding 2,3-dihydroindole, we attempted to dehydrogenate the crude reaction mixture

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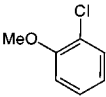
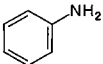
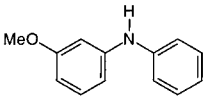
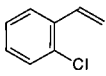
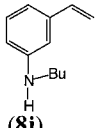
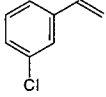

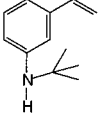
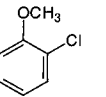
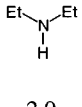
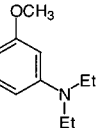
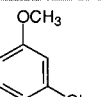
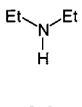
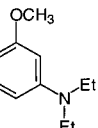
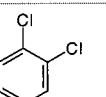
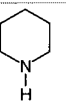
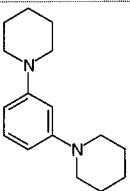
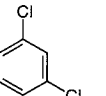
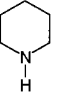
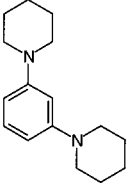
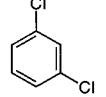
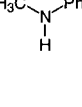
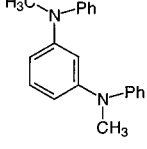
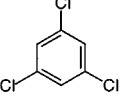
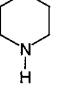
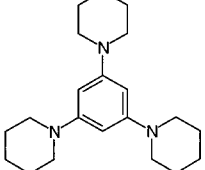
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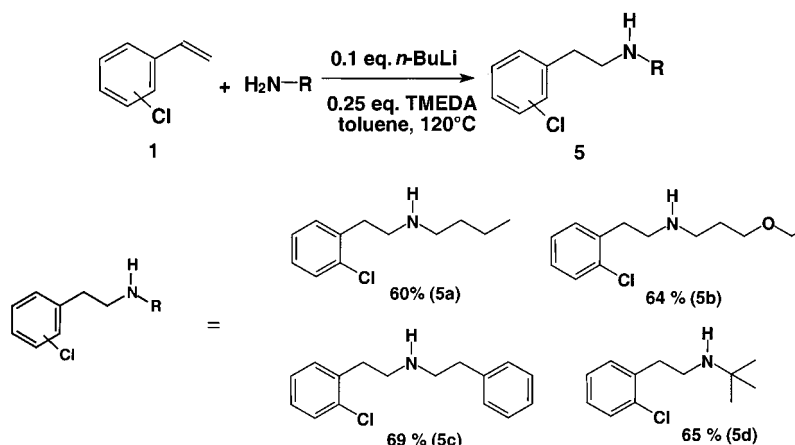
Table 3. Base Mediated Amination of Aryl Chlorides

Entry	Aryl Chloride [eq]	Amine [eq]	<i>KOt-Bu</i> [eq]	Product	Yield [%]
1	 2.0	 1.0	3	 (8a)	92 ^a (85) ^b
2	 2.0	 1.0	3	 (8b)	78 ^a (72) ^b
3	 2.0	 1.0	3	 (8c)	84 ^a (76) ^b
4	 2.0	 1.0	3	 (8d)	65 ^a (59) ^b
5	 1.0	 2.5	3	 (8e)	73 (68)
6	 1.0	 H	4	 (8f)	87 ^a (78) ^b
7	 1.0	4.0			
8	 2.0	 1.0	3	 (8g)	87 ^a (81) ^b
9	 3.0	 1.0	3	 (8h)	89 ^a (78) ^b
10	 2.0	 1.0	3	 (8i)	82 ^a (77) ^b

Table 3 (Continued)

Entry	Aryl Chloride [eq]	Amine [eq]	<i>KOt-Bu</i> [eq]	Product	Yield [%]
11	 2.0	 1.0	3	 (8i)	79 ^a (70) ^b
12	 1.0	H ₂ N-Bu 1.5	3	 (8j)	61 ^a (52) ^b
13	 1.0	 1.5	3	 (8k)	36 ^a (26) ^b
14	 1.0	 2.0	3	 (8l)	81 ^b
15	 1.0	 2.0	3	 (8l)	93 ^b
16	 1.0	 3.0	4	 (8m)	82 ^a
17	 1.0	 3.0	4	 (8m)	86 ^b
18	 1.0	 3.0	4	 (8n)	85 ^b
19	 1.0	 5.0	6	 (8o)	66 ^b

^a GC-yield. ^b Isolated yield.

Scheme 3. β -Arylethylamines Synthesis from Chlorostyrenes and Primary Aliphatic Amines

in situ. Among different dehydrogenation protocols tested, the combination of 10 mol % Pd/C and stoichiometric amounts of cyclohexene or ammonium formate gave the best results at 120 °C (5 h). As shown in Table 1, *N*-aryloindoles are obtained by a “one-pot” protocol in 48–58% total yield. This direct procedure is about three times more effective than similar multistep syntheses described previously in the literature (<20% overall yield).¹²

Synthesis of *N*-Alkyl-2,3-dihydroindoles and *N*-Alkylindoles. Due to the importance of *N*-alkyl-substituted indole and indoline subunits as common structural elements in pharmacologically active compounds, we focused our attention on the extension of the chemistry described above to aliphatic amines. Since KO*t*-Bu is *not* a precatalyst for the hydroamination of aromatic olefins with aliphatic amines, the first step of the domino sequence does not occur. Hence, only amination of the aromatic nucleus is observed (see Table 3). Given the success of the hydroamination of aromatic olefins with aliphatic amines in the presence of catalytic amounts of *n*-butyllithium,¹³ we attempted the synthesis of *N*-alkyl-substituted indolines with stoichiometric amounts of *n*-butyllithium (toluene; 90 °C). The formation of 2,3-dihydroindoles was not observed; instead a mixture of different amines (mainly hydroamination of the double bond) was obtained. Even better yields of pharmaceutically interesting *N*-(2-arylethyl)alkylamines were obtained in the presence of catalytic amounts of *n*-butyllithium (0.1 equiv) and tetramethylethylenediamine (0.25 equiv).

As shown in Scheme 3, *N*-butyl-*N*-(2-*o*-chlorophenylethyl)amine **5a**, *N*-(3-ethoxypropyl)-*N*-(2-*o*-chlorophenylethyl)amine **5b**, *N*-(2-*o*-chlorophenylethyl)-*N*-(2-phenylethyl)amine **5c**, and *N*-*tert*-butyl-*N*-(2-*o*-chlorophenylethyl)amine **5d** were obtained in 60–69% yield. Due to the high reactivity of the intermediate lithium amides, hydroamination of 2-chlorostyrene occurs even at –30 °C in THF. By combining this low-temperature hydroamination with a subsequent aryne cyclization, it is possible to obtain *N*-alkyl-2,3-dihydroindoles in substantial yields. The best yields were observed by reacting 2- or 3-chlorostyrene with an aliphatic amine at –30 °C (THF; 3 h) in the presence of 10 mol % *n*-butyllithium, removal of

the solvent, addition of toluene, and 3 equiv of KO*t*-Bu, and stirring the mixture for 20 h at 135 °C. As illustrated in Table 2, *N*-alkyl-2,3-dihydroindoles were obtained in 40–45% overall yield. Apart from *n*- and *tert*-butylamine, 2-phenylethylamine, 3-ethoxypropylamine, and benzylamine were cyclized with 2- and 3-chlorostyrene under these conditions. Again the major byproduct is the corresponding *N*-alkyl-substituted indole, which was isolated and characterized in up to 12% yield. We believe that 2- or 3-chlorostyrene acts as a hydrogen acceptor for this dehydrogenation reaction because we were able to identify 1-chloro-2- and 1-chloro-3-ethylbenzene by GC/MS.

Similar to the preparation of *N*-aryl-2,3-dihydroindoles the crude reaction mixture of *N*-alkylindolines can easily be transformed to *N*-alkylindoles. The direct oxidation of *N*-benzyl-2,3-dihydroindole to indole **4m** (55% overall yield) is noteworthy and demonstrates the possibility of obtaining *N*-unsubstituted indoles. Ammonium formate in the presence of catalytic amounts of Pd/C in methanol operates as an efficient debenzyl/dehydrogenation system.

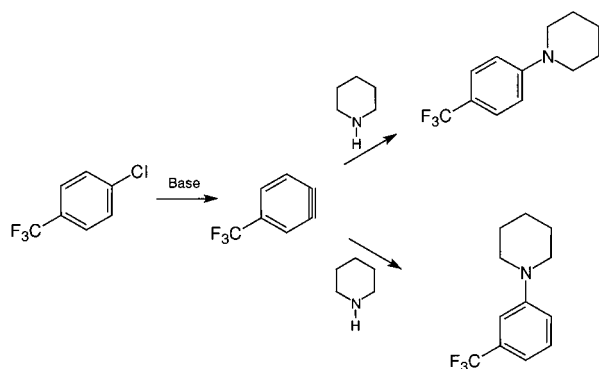
Synthesis of Substituted Anilines. Substituted anilines are common structural units in dyes, organic materials, and agricultural and pharmaceutical chemistry. Recently, the palladium-catalyzed amination of aryl halides and aryl triflates (Buchwald–Hartwig reaction)^{3,4} has become a powerful tool for the synthesis of this class of compounds. For successful coupling reactions, the presence of a palladium salt and phosphine ligands as well as overstoichiometric amounts of a strong base, e.g., sodium *tert*-butoxide or cesium carbonate, are necessary. While studying the palladium-catalyzed amination of 4-trifluoromethyl-1-chlorobenzene, we observed that the use of potassium *tert*-butoxide instead of sodium *tert*-butoxide, but under otherwise similar reaction conditions, leads to a mixture 4-trifluoromethylaniline and 3-trifluoromethylaniline.¹⁴ The product mixture obtained was explained by the formation of in situ aryne intermediates (Scheme 4).

On the basis of this observation as well as the possibility of performing intramolecular aminations of 2- and 3-chlorostyrenes in a regioselective manner, we were interested in the amination of simple aryl chlorides in the presence of KO*t*-Bu. To the best of our knowledge no

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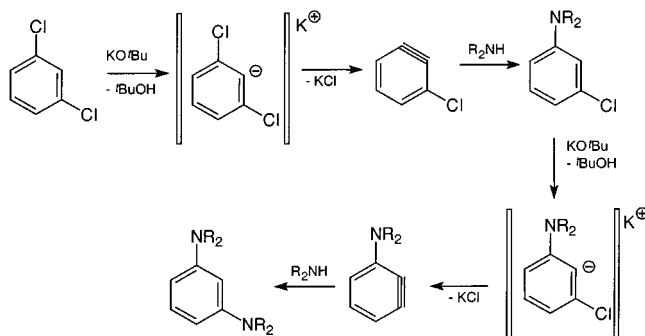
Scheme 4. Amination of 4-Trifluoromethyl-chlorobenzene with and without a Pd Catalyst



transition metal-free aminations of aryl chlorides in the presence of $\text{KO}t\text{-Bu}$ have been described.¹⁵ An initial screening of reaction conditions for the coupling of piperidine with chlorobenzene revealed that excellent yields (>90%) of *N*-phenylpiperidine were obtained in xylene, toluene, dioxane, and THF at 135 °C. Lower yields were obtained in dimethoxyethane and dimethyl sulfoxide. A critical parameter is the temperature of the reaction: increasing the temperature from 100 to 120 to 135 °C under otherwise similar conditions increased the yield of *N*-phenylpiperidine from 5 to 38 to 82%, respectively. Although the stoichiometry of the starting materials and the amount of base were of minor importance, in general 2 equiv of aryl chloride and 3 equiv of $\text{KO}t\text{-Bu}$ were reacted at 135 °C in toluene. The observed results are summarized in Table 3. The reaction of chlorobenzene with piperidine, di-*n*-butylamine, dibenzylamine, and aniline proceeds to give the secondary and tertiary amines in good to excellent yields (78–92%; Table 3, entries 1–3, 8, 9). It is noteworthy that aryne formation and subsequent amination proceed under similar conditions compared to the Buchwald–Hartwig amination. The use of $\text{KO}t\text{-Bu}$ instead of $\text{NaO}t\text{-Bu}$ has the considerable advantage that it allows the omission of the palladium catalyst.

Aryl chlorides which form symmetric aryne intermediates such as 2,5-dimethyl-1-chlorobenzene yielded the corresponding anilines regioselectively (65%; Table 3, entry 4). Recently, the palladium-catalyzed amination of aryl halides has been used for the synthesis of di- and triaminobenzenes.^{3d,16} Again the use of $\text{KO}t\text{-Bu}$ as the base allows similar multiple aminations of aryl halides *without* palladium catalysis. Depending on the amount of amine used (2.5 or 4.0 equiv), the amination of dichloro- and trichlorobenzenes gave either chloroanilines or diaminobenzenes in good yield (73–87%; Table 3, entries 5–7). Both the reaction of 1,2-dichlorobenzene and 1,3-dichlorobenzene with morpholine (or piperidine) gave the same product bis-1,3-(*N,N*-morpholino)benzene (or bis-1,3-(*N,N*-piperidinyl)benzene) in 79 and 87% yield (or 82 vs 86% yield) (Table 3, entries 6 and 7, and 16 and 17), respectively (Scheme 5). Similarly 2- and 3-chloroanisole react with aniline to give *N*-(3-methoxyphenyl)-*N'*-phenylamine in 79 and 82% (Table 3, entries 10 and 11), respectively. The regioselective formation of these

Scheme 5. Double Amination of 1,3-Dichlorobenzene



meta-substituted anilines is explained by the higher acidity of the hydrogen in position 2 of the aromatic ring and the polarization of the aryne intermediate.¹⁷

The synthetic utility of the aryne generation protocol was further demonstrated in the preparation of tris-1,3,5-(piperidinyl)benzene in 66% yield (Table 3, entry 19).

Conclusions

We have shown that the domino reaction of 2- or 3-chlorostyrenes and primary amines in the presence of base represents an elegant route to *N*-substituted 2,3-dihydroindoles and indoles. *N*-Substituted 2,3-dihydroindoles are obtained in good yields of up to 58% by combining a base-catalyzed hydroamination with a base-promoted aryne ring closure. Aromatic amines react in the presence of $\text{KO}t\text{-Bu}$ (3 equiv relative to olefin) in toluene, whereas chlorostyrenes undergo hydroamination with aliphatic amines in the presence of catalytic amounts of *n*-butyllithium (10 mol %) in THF. Further ring closure proceeds in the presence of an excess of $\text{KO}t\text{-Bu}$ in toluene. Apart from intramolecular aminations, intermolecular amination of aryl chlorides also proceed efficiently in the presence of an excess of $\text{KO}t\text{-Bu}$.

From the results presented it is clear that the amination of aryl halides via aryne intermediates allows an efficient synthesis of *N*-substituted anilines. The regioselective synthesis of *ortho*- and *para*-substituted anilines is difficult; however, *meta*-substituted anilines and polysubstituted anilines can be synthesized *without* a Pd catalyst with high selectivities. These *meta*-substituted anilines might be synthesized advantageously from cheaper *para*- or *ortho*-substituted halobenzenes or even mixtures of aryl halides. Hence, aminations of aryl chlorides with palladium catalysts or via arynes are complementary to each other and will both be of value for the synthesis of anilines.

Experimental Section

General Methods. All reactions were carried out in Ace pressure tubes under argon and heated in an oil bath. Anhydrous grade toluene and THF were purchased from Fluka and stored under argon. Potassium *tert*-butoxide, *n*-butyllithium (1.6 M in hexane), amines, and olefins were purchased from Aldrich. All amines were refluxed in the presence of

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calcium hydride and distilled prior to use. All reactions were monitored by GC and GC-MS.

General Procedure for the Reaction of Aromatic Amines with 2- or 3-Chlorostyrene. In an Ace pressure tube 2- or 3-chlorostyrene (2.0 mmol) and the aromatic amine (3.0 mmol) were dissolved in 10 mL of toluene under argon. After addition of 0.67 g of KO t -Bu (6.0 mmol), the sealed reaction vessel was stirred and heated to 135 °C. After 36 h, the reaction mixture was allowed to cool to room temperature and was quenched with 20 mL of water. The aqueous phase was extracted three times with dichloromethane. The combined organic phases were dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography with hexane/ethyl acetate as solvent.

***N*-Phenyl-2,3-dihydroindole (3a).** 2-Chlorostyrene (0.28 g, 2.0 mmol) and aniline (0.28 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography, **3a** was isolated as a light yellow oil in 53% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.32 (dd, J = 8.0 Hz, J = 7.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.1 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.05 (dd, J = 8.0 Hz, J = 7.5 Hz, 1H), 6.94 (t, J = 7.1 Hz, 1H), 6.73 (dd, J = 7.5 Hz, J = 7.1 Hz, 1H), 3.92 (t, J = 8.4 Hz, 2H), 3.10 (t, J = 8.4 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 147.1, 144.2, 131.2, 129.1, 127.1, 125.0, 120.9, 118.8, 117.7, 108.2, 52.1, 28.2; MS (70 eV): m/z = 195 (M^+), 165, 116, 91, 77.

***N*-(2-Methoxyphenyl)-2,3-dihydroindole (3b).** 2-Chlorostyrene (0.28 g, 2.0 mmol) and 2-methoxyaniline (0.37 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:50), **3b** was isolated as a light yellow oil in 58% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.35 (d, J = 7.5 Hz, 1H), 7.15–7.11 (m, 2H), 7.10–9.90 (m, 3H), 6.68 (dd, J = 8.0 Hz, J = 7.5 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 3.88 (t, J = 8.4 Hz, 2H), 3.84 (s, 3H), 3.14 (t, J = 8.4 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 154.5, 149.6, 134.0, 130.2, 126.9, 125.3, 124.6, 123.3, 121.0, 118.0, 112.3, 109.0, 55.5, 53.5, 28.8; MS (70 eV): m/z = 225 (M^+), 210 ($\text{M}^+ - \text{CH}_3$), 194, 180, 165, 152.

***N*-(4-Fluorophenyl)-2,3-dihydroindole (3c).** 2-Chlorostyrene (0.28 g, 2.0 mmol) and 4-fluoroaniline (0.33 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (hexane), **3c** was isolated as a light yellow oil in 54% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.19–6.95 (m, 7H), 6.73 (dd, J = 7.5 Hz, J = 7.1 Hz, 1H), 3.85 (t, J = 8.4 Hz, 2H), 3.08 (t, J = 8.4 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 157.7 (d, J = 241 Hz), 147.6, 140.5, 130.9, 127.1, 125.0, 119.8 (d, J = 8 Hz), 118.8, 115.7 (d, J = 21 Hz), 107.6, 52.7, 28.2; MS (70 eV): m/z = 213 (M^+), 183, 165, 116, 105, 91.

***N*-(3-Trifluoromethylphenyl)-2,3-dihydroindole (3d).** 3-Chlorostyrene (0.28 g, 2.0 mmol) and 3-trifluoromethylaniline (0.38 mL, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:3), **3d** was isolated as a yellow oil in 44% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.85–7.44 (m, 5H), 7.37 (d, J = 7.2 Hz, 1H), 7.26–6.96 (m, 2H), 3.83 (t, J = 7.0 Hz, 2H), 3.31 (t, J = 7.0 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 148.4, 141.4, 134.6 (q, J = 22 Hz), 130.3, 129.7, 128.8, 128.7, 127.0, 122.2, 119.9, 115.3, 113.5 (q, J = 176 Hz), 114.9 (q, J = 8 Hz), 52.4, 30.1; MS (70 eV): m/z = 263 (M^+), 242, 193 ($\text{M}^+ - \text{CF}_3 - \text{H}$), 165, 118, 91 (benzyl $^+$), 65.

***N*-(4-Biphenyl)-2,3-dihydroindole (3e).** 3-Chlorostyrene (0.28 g, 2.0 mmol) and 4-phenylaniline (0.51 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:10), **3e** was isolated as a light brown oil in 47% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.30–6.67 (m, 13H), 3.84 (t, J = 7.9 Hz, 2H), 3.12 (t, J = 8.0 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 143.9, 142.6, 137.6, 129.8, 129.6, 127.7, 127.4, 127.0, 126.7, 121.1, 120.1, 120.0, 118.3, 117.7, 52.8, 28.1; MS (70 eV): m/z = 271 (M^+), 254, 165, 135, 91 (benzyl $^+$), 77.

4-Chloro-*N*-(4-fluorophenyl)-2,3-dihydroindole (3f). 2,6-Dichlorostyrene (0.35 g, 2.0 mmol), 4-fluoroaniline (0.28 g, 2.5 mmol), and 0.34 g KO t -Bu (3.0 mmol) were reacted according

to the general procedure. After column chromatography (hexane), **3f** was isolated as a yellow oil in 50% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.12–6.64 (m, 7H), 3.88 (t, J = 8.4 Hz, 2H), 3.10 (t, J = 8.4 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 157.8 (d, J = 241 Hz), 149.1, 140.0, 131.0, 128.9, 128.7, 120.4 (d, J = 7 Hz), 118.7, 115.9 (d, J = 22 Hz), 105.7, 52.5, 27.5; MS (70 eV): m/z = 247 (M^+), 211 ($\text{M}^+ - \text{HCl}$), 183, 105, 89.

4-Chloro-*N*-(2-fluorophenyl)-2,3-dihydroindole (3g). 2,6-Dichlorostyrene (0.41 mL, 3.0 mmol), 2-fluoroaniline (0.32 mL, 3.3 mmol), and 0.50 g KO t -Bu (4.5 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:20), **3g** was isolated as a yellow oil in 42% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.76 (m, 1H), 7.63–7.44 (m, 3H), 7.39 (t, J = 8.1 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 6.87 (dd, J = 7.9 Hz, J = 2.7 Hz, 1H), 3.95 (t, J = 7.9 Hz, 2H), 3.21 (t, J = 7.9 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 157.7 (d, J = 245 Hz), 150.1, 131.2, 129.0, 128.8, 125.7, 125.6, 124.9, 123.7, 119.1, 117.4 (d, J = 22 Hz), 107.1, 53.4, 28.4; MS (70 eV): m/z = 247 (M^+), 211 ($\text{M}^+ - \text{HCl}$), 183, 95, 63.

***N*-(1-Anthracenyl)-4-chloro-2,3-dihydroindole (3h).** 2,6-Dichlorostyrene (0.27 mL, 2.0 mmol), 1-aminoanthracene (0.48 g, 2.5 mmol), and 0.34 g KO t -Bu (3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:10), **3h** was isolated in 37% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 8.21 (s, 1H), 7.90 (t, J = 6.2 Hz, 2H), 7.51–6.84 (m, 8H), 6.62 (d, J = 6.2 Hz, 1H), 3.89 (t, J = 8.2 Hz, 2H), 3.18 (t, J = 8.2 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 141.8, 132.5, 131.6, 130.9, 128.4, 128.1, 128.1, 127.6, 127.5, 126.6, 125.8, 125.5, 125.1, 123.8, 132.3, 119.6, 119.2, 118.6, 117.3, 107.5, 60.4, 21.0; MS (70 eV): m/z = 329 (M^+), 293 ($\text{M}^+ - \text{HCl}$), 178, 146, 28.

General Procedure for the Reaction of Aliphatic Amines with 2- or 3-Chlorostyrene. The aliphatic amine (3.0 mmol) was dissolved in 10 mL of THF in an Ace pressure tube under argon. The solution was cooled to –30 °C, and *n*-butyllithium (10 mol % relative to olefin) was added. After addition of 2- or 3-chlorostyrene (2.0 mmol), the mixture was stirred at –30 °C for 3 h. After removal of the solvent in vacuo, the crude product was dissolved in 10 mL of toluene, 0.67 g KO t -Bu (6 mmol) was added and the pressure tube was heated to 135 °C for 20 h. All products were isolated by column chromatography.

***N*-*n*-Butyl-2,3-dihydroindole (3i).** 2-Chlorostyrene (0.28 g, 2.0 mmol) and *n*-butylamine (0.30 mL, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:5), **3i** was isolated in 45% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 6.93 (m, 2H), 6.52 (t, J = 7.5 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 3.23 (t, J = 7.5 Hz, 2H), 2.96 (t, J = 7.5 Hz, 2H), 2.84 (t, J = 7.5 Hz, 2H), 1.62 (quint, 2H), 1.48 (sext, J = 7.5 Hz, 2H), 0.87 (t, J = 7.5 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 152.1, 129.3, 126.6, 123.6, 116.5, 106.2, 52.4, 48.3, 29.1, 28.8, 27.9, 13.3; MS (70 eV): m/z = 175 (M^+), 132 ($\text{M}^+ - \text{C}_3\text{H}_7$), 117, 91, 77.

***N*-(*tert*-Butyl)-2,3-dihydroindole (3j).** 3-Chlorostyrene (0.28 g, 2.0 mmol) and *tert*-butylamine (0.22 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:5), **3j** was isolated as a light yellow oil in 40% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.32–6.81 (m, 4H), 3.23 (m, 2H), 2.81 (m, 2H), 1.79 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 145.1, 129.7, 127.2, 124.9, 118.8, 114.1, 57.2, 44.2, 29.5, 29.3; MS (70 eV): m/z = 176 (M^+), 161 ($\text{M}^+ - \text{CH}_3$), 120 ($\text{M}^+ - (\text{CH}_3)_2\text{C}=\text{CH}_2$), 105, 91, 77.

***N*-(2-Phenylethyl)-2,3-dihydroindole (3k).** 3-Chlorostyrene (0.28 g, 2.0 mmol) and 2-phenylethylamine (0.36 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:5), **3k** was isolated as a light yellow oil in 43% yield. ^1H NMR (360 MHz, 25 °C, CDCl $_3$) δ = 7.38–6.98 (m, 9H), 3.35 (m, 4H), 2.91 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl $_3$) δ = 152.1, 140.0, 130.1, 128.7, 128.5, 127.3, 126.2, 124.4, 117.7, 107.0, 53.1, 51.0,

33.6, 28.7; MS (70 eV): $m/z = 223$ (M^+), 132 ($M^+ - \text{CH}_2\text{Ph}$), 117, 103, 77.

***N*-(3-Ethoxypropyl)-2,3-dihydroindole (3l).** 2-Chlorostyrene (0.28 g, 2.0 mmol) and 3-ethoxypropylamine (0.31 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:5), **3l** was isolated as a light yellow oil in 41% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 7.22$ (m, 2H), 6.81 (m, 1H), 6.66 (t, $J = 7.1$ Hz, 1H), 3.69 (m, 4H), 3.48 (dd, $J = 7.1$ Hz, 2H), 3.34 (dd, $J = 7.1$ Hz, 2H), 3.13 (dd, $J = 7.1$ Hz, 2H), 2.05 (quint, $J = 7.1$ Hz, 2H), 1.38 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 152.6$, 129.9, 127.3, 124.3, 117.3, 106.9, 68.2, 66.2, 53.1, 46.3, 28.5, 27.8, 15.2; MS (70 eV): $m/z = 205$ (M^+), 132 ($M^+ - \text{CH}_2\text{-CH}_2\text{OEt}$), 117, 103, 91, 77.

General Procedure for the Synthesis of *N*-Substituted Indoles. *N*-Substituted 2,3-dihydroindoles were synthesized as described above. Pd/C (10 mol %, 0.2 mmol) and 5.0 equiv (10.0 mmol) of ammonium formate were added to the crude product mixture. The sealed pressure tube was stirred and heated to 120 °C for 5 h. After the mixture was cooled to room temperature, the product was isolated by column chromatography.

***N*-Phenylindole (4a).** 2-Chlorostyrene (0.28 g, 2.0 mmol) and aniline (0.28 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:10), **4a** was isolated as a yellow oil in 58% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 7.71$ –7.03 (m, 10H), 6.41 (d, $J = 4.7$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 144.5$, 133.4, 129.3, 127.5, 125.7, 122.3, 120.0, 118.9, 118.3, 117.5, 116.1, 103.2; MS (70 eV): $m/z = 193$ (M^+), 165, 139, 96, 89.

***N*-(3-Trifluoromethylphenyl)indole (4d).** 3-Chlorostyrene (0.28 g, 2.0 mmol) and 3-trifluoromethylaniline (0.38 mL, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:15), **4d** was isolated as a light brown oil in 48% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 8.22$ –7.93 (m, 4H), 7.75 (d, $J = 6.5$ Hz, 1H), 7.71–7.18 (m, 4H), 7.16 (d, $J = 6.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 145.2$, 137.9, 133.2 (q, $J = 22$ Hz), 132.1, 129.9, 127.6, 122.1, 121.1, 120.8, 119.8, 118.3 (q, $J = 176$ Hz), 114.6, 114.3, 111.9, 104.5; MS (70 eV): $m/z = 261$ (M^+), 240, 191 ($M^+ - \text{CF}_3 - \text{H}$), 165, 89, 63.

***N*-(4-Biphenyl)indole (4e).** 3-Chlorostyrene (0.28 g, 2.0 mmol) and 4-phenylaniline (0.51 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (hexane), **4e** was isolated in 56% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 7.63$ –7.26 (m, 5H), 7.10 (m, 1H), 7.01 (m, 8H), 6.45 (d, $J = 4.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 143.1$, 137.4, 137.2, 129.8, 129.6, 127.5, 127.4, 127.3, 126.3, 125.0, 122.3, 120.5, 120.0, 118.2, 110.7, 104.1; MS (70 eV): $m/z = 269$ (M^+), 192 ($M^+ - \text{phenyl}$), 134, 119, 89.

4-Chloro-*N*-(2-fluorophenyl)indole (4g). 2,6-Dichlorostyrene (0.41 mL, 3.0 mmol) and 2-fluoroaniline (0.32 mL, 3.3 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:20), **4g** was isolated as a yellow oil in 51% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 7.64$ –7.12 (m, 9H), 6.43 (d, $J = 4.7$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 152.6$ (d, $J = 241$ Hz), 135.5, 131.9, 131.7, 126.1, 125.8, 125.5, 123.0, 121.5, 120.1, 119.7 (d, $J = 8$ Hz), 115.8 (d, $J = 21$ Hz), 110.2, 103.5; MS (70 eV): $m/z = 245$ (M^+), 209 ($M^+ - \text{HCl}$), 149, 124, 94, 77.

***N*-*n*-Butylindole (4i).** 3-Chlorostyrene (0.28 g, 2.0 mmol) and *n*-butylamine (0.22 g, 3.0 mmol) were reacted according to the general procedure. After column chromatography (ethyl acetate/hexane = 1:5), **4i** was isolated as a yellow oil in 50% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 7.55$ (d, $J = 7.3$ Hz, 1H), 7.43 (d, $J = 7.3$ Hz, 1H), 7.28 (d, $J = 5.2$ Hz, 1H), 7.12–7.05 (m, 2H), 6.39 (d, $J = 5.2$ Hz, 1H), 2.74 (t, $J = 7.3$ Hz, 2H), 1.66 (quint, $J = 7.1$ Hz, 2H), 1.41 (sext, $J = 7.1$ Hz, 2H), 0.75 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 136.6$, 128.8, 128.1, 127.5, 120.3, 119.3, 112.7, 104.7, 51.2, 29.9, 19.9, 12.4; MS (70 eV): $m/z = 173$ (M^+), 158 ($M^+ - \text{CH}_3$), 144 ($M^+ - \text{C}_2\text{H}_5$), 130 ($M^+ - \text{C}_3\text{H}_7$), 89.

Procedure for Synthesis of Indole (4m). Benzylamine (0.32 g, 3.0 mmol) was dissolved in 6 mL of THF in an Ace pressure tube under argon. The solution was cooled to -78 °C, and *n*-butyllithium (10 mol % relative to olefin) was added. After addition of 2-chlorostyrene (0.27 g, 2.0 mmol), the mixture was stirred at -30 °C for 3 h. After removal of the solvent in vacuo, the crude product was dissolved in 10 mL of toluene, 0.67 g of $\text{KO}t\text{-Bu}$ (6 mmol) was added, and the pressure tube was heated to 135 °C for 20 h. *N*-Benzyl-2,3-dihydroindole was not isolated. After 20 h, the reaction mixture was allowed to cool to room temperature. Then 0.2 g of Pd/C (0.2 mmol, 10 mol %) and 1.26 g of ammonium formate (20.0 mmol) in methanol were added to the reaction mixture. The sealed pressure tube was stirred and heated to 70 °C for 5 h. After the mixture was cooled to room temperature the product was isolated by column chromatography (ethyl acetate/hexane = 1:20). **4m** was isolated as a colorless solid in 55% yield. ^1H NMR (250 MHz, 25 °C, d_6 -DMSO) $\delta = 7.62$ (d, $J = 7.5$ Hz, 1H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.35 (d, $J = 4.5$ Hz, 1H), 7.12–7.01 (m, 2H), 6.48 (d, $J = 4.5$ Hz, 1H), 3.54 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (63 MHz, 25 °C, d_6 -DMSO) $\delta = 135.8$, 127.6, 125.1, 120.8, 120.0, 118.7, 111.3, 100.9; MS (70 eV): $m/z = 116$ (M^+), 72, 37.

General Procedure for the Base-Catalyzed Hydroamination of Aliphatic Amines with 2- or 3-Chlorostyrene. In an Ace pressure tube, amine (2.0 mmol) was dissolved in 10 mL of toluene, and 0.25 equiv of TMEDA (0.5 mmol) was added. After cooling to -78 °C, 0.1 equiv of *n*-butyllithium (0.2 mmol, 1.6 M in hexane) was added. The sealed vessel was stirred, and the mixture was allowed to warm to room temperature. Then olefin (2.0 mmol) was added, and the reaction mixture was heated to 120 °C for 20 h. After being cooled to room temperature, the mixture was quenched with 10 mL of water, and the aqueous phase was extracted three times with dichloromethane. The combined organic phases were dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography.

***N*-Butyl-*N*-(2-*o*-chlorophenylethyl)amine (5a).** 2-Chlorostyrene (0.28 g, 2.0 mmol) and *n*-butylamine (0.20 mL, 2.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 5:1), **5a** was isolated as a light yellow liquid in 60% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 7.79$ –7.12 (m, 4H), 2.91 (m, 4H), 2.68 (m, 2H), 1.94 (br, 1H, NH), 1.62–1.27 (m, 4H), 0.98 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 142.1$, 134.1, 129.6, 128.7, 126.8, 126.3, 51.8, 50.8, 35.9, 32.0, 20.4, 13.9; MS (70 eV): $m/z = 211$ (M^+), 209, 168 ($M^+ - \text{C}_3\text{H}_7$), 139 ($M^+ - \text{NH} - \text{Bu}$), 103, 86, 44.

***N*-(2-*o*-Chlorophenylethyl)-*N*-(3-ethoxypropyl)amine (5b).** 2-Chlorostyrene (0.56 g, 4.0 mmol) and 3-ethoxypropylamine (0.72 mL, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 5:1), **5b** was isolated as a light yellow liquid in 64% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 7.43$ –7.02 (m, 4H), 4.21 (t, $J = 7.1$ Hz, 2H), 4.19 (t, $J = 7.1$ Hz, 2H), 3.91–3.79 (m, 6H), 2.54 (quint, $J = 7.1$ Hz, 2H), 1.94 (br, 1H, NH), 1.84 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 140.8$, 132.3, 129.0, 128.7, 126.5, 126.0, 65.1, 60.2, 53.9, 42.6, 31.3, 29.7, 14.4; MS (70 eV): $m/z = 242$ ($M^+ + 1$), 168, 139, 116, 103, 72, 44.

***N*-(2-*o*-Chlorophenylethyl)-*N*-(2-phenylethyl)amine (5c).** 2-Chlorostyrene (0.56 g, 4.0 mmol) and 2-phenylethylamine (0.51 mL, 4.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 5:1), **5c** was isolated as a light yellow liquid in 69% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) $\delta = 7.18$ –6.89 (m, 9H), 3.58–3.33 (m, 4H), 3.13–2.84 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) $\delta = 139.8$, 138.6, 131.2, 128.9, 128.5, 128.4, 128.1, 127.4, 127.3, 126.7, 50.1, 49.7, 36.8, 30.1; MS (70 eV): $m/z = 261$ ($M^+ + 2$), 168, 139, 134, 105, 91, 77.

***N*-*tert*-Butyl-*N*-(2-*o*-chlorophenylethyl)amine (5d).** 2-Chlorostyrene (0.56 g, 4.0 mmol) and *tert*-butylamine (0.42 mL, 4.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 10:1),

5d was isolated as a light yellow liquid in 65% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.51–7.22 (m, 4H), 3.12–2.86 (m, 4H), 1.82 (br, 1H, NH), 1.66 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 139.4, 132.1, 128.9, 129.0, 126.6, 124.6, 45.8, 44.6, 32.1, 29.7; MS (70 eV): m/z = 211 (M^+), 196, 153, 139, 125, 103, 86, 57.

General Procedure for the Amination of Chlorobenzenes. In a pressure tube the aryl chloride (4.0 mmol) and amine (2.0 mmol) were dissolved in 10 mL of toluene. After addition of 3 equiv of $\text{KO}t\text{-Bu}$ (6.0 mmol), the pressure tube was sealed and heated to 135 °C. After 36 h, the reaction mixture was allowed to cool to room temperature and was quenched with 10 mL of water. The aqueous phase was extracted three times with 10 mL of dichloromethane. The combined organic phases were dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography.

***N*-Phenylpiperidine (8a).** Chlorobenzene (0.46 g, 4.0 mmol), piperidine (0.20 mL, 2.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 2:1), **8a** was isolated as a liquid in 85% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.20 (t, J = 7.5 Hz, 2H), 6.88 (d, J = 7.5 Hz, 2H), 6.78 (t, J = 7.5 Hz, 1H), 3.13 (t, J = 6.2 Hz, 4H), 1.69 (m, 4H), 1.53 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 152.0, 129.0, 121.1, 116.7, 51.0, 25.7, 24.2; MS (70 eV): m/z = 161 (M^+), 132, 120, 105, 77, 51.

***N,N*-Di-*n*-butylaniline (8b).** Chlorobenzene (0.46 g, 4.0 mmol), di-*n*-butylamine (0.34 mL, 2.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 1:1), **8b** was isolated as a liquid in 72% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.22 (t, J = 7.7 Hz, 2H), 6.79 (d, J = 7.7 Hz, 2H), 6.68 (t, J = 7.7 Hz, 1H), 3.15 (t, J = 7.9 Hz, 4H), 1.63 (m, 4H), 1.41 (m, 4H), 0.98 (t, J = 7.8 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 147.2, 130.4, 119.2, 113.9, 49.5, 33.1, 20.8, 14.3; MS (70 eV): m/z = 205 (M^+), 162 (M^+ - propyl), 120, 105, 77.

***N,N*-Dibenzylaniline (8c).** Chlorobenzene (0.46 g, 4.0 mmol), dibenzylamine (0.39 mL, 2.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 20:1), **8c** was isolated as a liquid in 76% yield. ^1H NMR (400 MHz, 25 °C, CDCl_3) δ = 7.19 (m, 15H), 4.61 (s, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 25 °C, CDCl_3) δ = 143.3, 138.6, 129.3, 128.7, 127.0, 126.8, 116.9, 112.6, 54.3; MS (70 eV): m/z = 273 (M^+), 196, 182, 91, 77, 65.

***N*-(1-Cyclohexylethyl)-2,4-dimethylaniline (8d).** 2-Chloro-*p*-xylol (0.54 mL, 4.0 mmol), 1-cyclohexylethylamine (0.30 mL, 2.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 20:1), **8d** was isolated as a liquid in 59% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.37–7.18 (m, 2H), 6.78 (s, 1H), 3.72 (s, 1H, NH), 2.71–2.44 (m, 7H), 2.41 (s, 3H), 2.08 (m, 3H), 1.66–1.38 (m, 8H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 145.5, 136.6, 130.5, 119.2, 117.9, 113.6, 43.0, 28.6, 28.5, 27.8, 26.5, 26.4, 21.6, 17.2; MS (70 eV): m/z = 231 (M^+), 148, 132, 105, 41.

***N*-(3-Chlorophenyl)morpholine (8e).** 1,3-Dichlorobenzene (0.23 mL, 2.0 mmol), morpholine (0.45 mL, 5.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 1:1), **8e** was isolated as a light yellow liquid in 68% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.14 (t, J = 8.0 Hz, 1H), 6.87 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 3.82 (t, J = 4.9 Hz, 4H), 3.11 (t, J = 4.9 Hz, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 152.2, 135.0, 130.4, 119.7, 115.5, 113.6, 66.6, 28.9; MS (70 eV): m/z = 197 (M^+), 139, 111, 75.

1,3-Bismorpholinobenzene (8f). 1,3-Dichlorobenzene (0.23 mL, 2.0 mmol), morpholine (0.72 mL, 8.0 mmol), and $\text{KO}t\text{-Bu}$ (0.90 g, 8.0 mmol) were reacted according to the general procedure. After column chromatography with (hexane/ethyl acetate = 2:1), **8f** was isolated as a liquid in 78% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.14 (t, J = 8.4 Hz, 1H),

6.43 (d, J = 8.4 Hz, 2H), 6.42 (s, 1H), 3.79 (t, J = 4.8 Hz, 8H), 3.10 (t, J = 4.8 Hz, 8H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 152.3, 129.7, 108.1, 103.9, 66.9, 49.6; MS (70 eV): m/z = 248 (M^+), 233, 190, 132, 104, 77, 28.

***N,N*-Diphenylamine (8g).** Chlorobenzene (0.46 g, 4.0 mmol), aniline (0.18 mL, 2.0 mmol), and $\text{KO}t\text{-Bu}$ (0.45 g, 4.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 10:1), **8g** was isolated as a liquid in 81% yield. ^1H NMR (250 MHz, 25 °C, CDCl_3) δ = 7.76–7.64 (m, 4H), 7.53 (d, J = 8.4 Hz, 4H), 7.38 (t, J = 8.4 Hz, 2H), 6.16 (br, 1H, NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (63 MHz, 25 °C, CDCl_3) δ = 143.5, 129.8, 121.5, 118.4; MS (70 eV): m/z = 169 (M^+), 154, 139, 115.

Triphenylamine (8h). Chlorobenzene (0.69 g, 6.0 mmol), aniline (0.18 mL, 2.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 20:1), **8h** was isolated as a liquid in 78% yield. ^1H NMR (250 MHz, 25 °C, CDCl_3) δ = 7.67 (t, J = 7.5 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (63 MHz, 25 °C, CDCl_3) δ = 148.3, 129.6, 124.6, 123.1; MS (70 eV): m/z = 245 (M^+), 167, 141, 115, 77, 51.

***N*-(3-Methoxyphenyl)aniline (8i).** 3-Chloroanisole (0.50 mL, 4.0 mmol), aniline (0.18 mL, 2.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 5:1), **8i** was isolated as a yellow liquid in 77% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.56 (t, J = 7.5 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.32–6.11 (m, 3H), 3.65 (s, 3H), 2.76 (s, 1H, NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 161.1, 142.5, 139.4, 129.9, 129.5, 128.2, 117.8, 116.9, 110.3, 103.4, 55.2; MS (70 eV): m/z = 199 (M^+), 184, 170, 154, 129, 92, 51.

***N*-*n*-Butyl-(3-vinylphenyl)amine (8j).** 2-Chlorostyrene (0.25 mL, 2.0 mmol), *n*-butylamine (0.30 mL, 3.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 20:1), **8j** was isolated as a yellow liquid in 52% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.14 (dd, J = 7.9 Hz, J = 7.5 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 6.67 (dd, J = 10.9 Hz, J = 17.6 Hz, 1H), 6.65 (dd, J = 2.0 Hz, J = 2.0 Hz, 1H), 6.53 (ddd, J = 0.8 Hz, J = 2.4 Hz, J = 8.1 Hz, 1H), 5.72 (dd, J = 17.6 Hz, J = 1.2 Hz, 1H), 5.21 (dd, J = 10.9 Hz, J = 1.0 Hz, 1H), 3.61 (s, 1H), 3.13 (t, J = 7.1 Hz, 2H), 1.62 (m, 2H), 1.45 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 148.7, 138.5, 137.4, 129.3, 115.4, 113.3, 112.4, 110.3, 43.6, 31.6, 20.3, 13.9; MS (70 eV): m/z = 175 (M^+), 132 (M^+ - C_3H_7), 77.

***N*-*tert*-Butyl-(3-vinylphenyl)amine (8k).** 3-Chlorostyrene (0.25 mL, 2.0 mmol), *tert*-butylamine (0.32 mL, 3.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 10:1), **8k** was isolated as a light yellow liquid in 26% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.13 (dd, J = 7.7 Hz, J = 7.9 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 6.79 (dd, J = 2.0 Hz, J = 1.8 Hz, 1H), 6.70–6.62 (m, 2H), 5.70 (dd, J = 17.6 Hz, J = 1.2 Hz, 1H), 5.21 (dd, J = 10.9 Hz, J = 1.0 Hz, 1H), 3.41 (s, 1H), 1.36 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 147.0, 138.2, 137.3, 129.0, 117.0, 116.4, 115.3, 113.2, 51.5, 30.1; MS (70 eV): m/z = 175 (M^+), 160, 119, 77, 41.

***N,N*-Dimethyl-3-methoxyaniline (8l).** 3-Chloroanisole (0.50 mL, 4.0 mmol), diethylamine (0.29 g, 4.0 mmol), and $\text{KO}t\text{-Bu}$ (0.67 g, 6.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 5:1), **8l** was isolated as a yellow liquid in 93% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.10 (dd, J = 7.5 Hz, J = 8.4 Hz, 1H), 6.30–6.19 (m, 3H), 3.76 (s, 3H), 3.30 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 161.0, 149.2, 129.9, 105.2, 100.1, 98.5, 55.0, 44.4, 12.6; MS (70 eV): m/z = 179 (M^+), 164, 150, 136, 108, 77.

Bis-1,3-piperidinobenzene (8m). 1,3-Dichlorobenzene (0.23 mL, 2.0 mmol), piperidine (0.51 g, 6.0 mmol), and $\text{KO}t\text{-Bu}$ (0.90 g, 8.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 2:1), **8m**

was isolated as a liquid in 86% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.10 (t, J = 8.0 Hz, 1H), 6.53 (s, 1H), 6.43 (d, J = 8.0 Hz, 2H), 3.11 (m, 8H), 1.66 (m, 8H), 1.55 (m, 4H); ^{13}C - $\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3): δ = 153.4, 129.3, 108.6, 106.0, 51.1, 26.1, 24.5; MS (70 eV): m/z = 244 (M^+), 229, 215, 202, 187, 173, 160, 147, 132.

Bis-1,3-(*N*-methyl-*N*-phenylamino)benzene (8n). 1,3-Dichlorobenzene (0.23 mL, 2.0 mmol), *N*-methylaniline (0.64 g, 6.0 mmol), and $\text{KO}t\text{-Bu}$ (0.90 g, 8.0 mmol) were reacted according to the general procedure. After column chromatography (hexane/ethyl acetate = 2:1), **8n** was isolated as a liquid in 85% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 7.23 (dd, J = 7.0 Hz, J = 8.0 Hz, 4H), 7.13 (t, J = 7.9 Hz, 1H), 7.01 (d, J = 8.0 Hz, 4H), 6.90 (t, J = 7.0 Hz, 2H), 6.70 (t, J = 2.2 Hz, 1H), 7.23 (dd, J = 7.9 Hz, J = 2.2 Hz, 2H), 3.25 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 149.9, 148.9, 129.7, 129.0, 121.1, 120.3, 113.7, 112.7, 40.2; MS (70 eV): m/z = 288 (M^+), 196, 181, 167.

Tris-1,3,5-piperidinobenzene (8o). 1,3,5-Trichlorobenzene (0.36 g, 2.0 mmol), piperidine (0.85 g, 10.0 mmol), and $\text{KO}t\text{-Bu}$ (0.90 g, 12.0 mmol) were reacted according to the

general procedure. After column chromatography (hexane/ethyl acetate = 2:1), **8o** was isolated as a liquid in 66% yield. ^1H NMR (360 MHz, 25 °C, CDCl_3) δ = 6.11 (s, 3H), 3.10 (m, 12H), 1.70 (m, 12H), 1.52 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, 25 °C, CDCl_3) δ = 154.0, 99.2, 51.5, 26.2, 24.5; MS (70 eV): m/z = 327 (M^+), 312, 298, 284, 271, 258, 245, 230, 164.

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