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Two-Step Procedure for the Synthesis of 1,2,3,4-Tetrahydroquinolines

Michael Warsitz and Sven Doye*[a]

Abstract: A new two-step procedure that includes an initial regioselective intermolecular hydroaminoalkylation of *ortho*-chlorostyrenes with *N*-methylanilines and a subsequent intramolecular Buchwald-Hartwig amination gives direct access to 1,2,3,4-tetrahydroquinolines. The hydroaminoalkylation reaction of the *ortho*-chlorostyrenes is catalyzed by a 2,6-bis(phenylamino)pyridinato titanium complex which delivers the linear regioisomers with high selectivities. In addition, the formation of unexpected dihydroaminoalkylation products from styrenes and *N*-methylanilines is reported.

Introduction

1,2,3,4-Tetrahydroquinoline moieties are commonly occurring substructures in a large number of biologically active compounds. For example, the structurally relatively simple 2-substituted 1,2,3,4-tetrahydroquinoline derivatives angustureine (**1**), galipinine (**2**), cuspareine (**3**), and galipeine (**4**) are part of a family of natural products which are known as Hancock alkaloids (Figure 1). These alkaloids were isolated from the trunk bark of the Venezuelan tree *galipea officinalis* Hancock and extracts from the bark were used medically to treat dysentery and fever.[1] Furthermore, the extracts as well as the pure tetrahydroquinoline alkaloids showed cytotoxic and antimalarial activities.[2] Another interesting example is the 1,2-diphenyl-substituted 1,2,3,4-tetrahydroquinoline derivative **5** that acts as a selective estrogen receptor modulator (SERM) and as a consequence, it could serve in the treatment of cancer. The 6-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline unit has a structurally comparable influence as the stilbene unit in traditional SERMs.[3]

Because of the pharmacological relevance of 1,2,3,4-tetrahydroquinolines, the development of new synthetic approaches towards this class of compounds is of high importance for drug research and medicinal chemistry. Catalytic hydroaminoalkylation reactions are a 100% atom efficient way to form new C-C bonds by addition of α-C-H bonds of primary or secondary amines across C-C double bonds (Scheme 1).[4] The corresponding reactions can be achieved in the presence of group 5 metal,[5] ruthenium,[6] iridium,[7] zirconium,[8] and titanium complexes[9]. While group 5 metal catalyzed hydroaminoalkylation reactions selectively deliver the branched products, ruthenium- and iridium-catalyzed hydroaminoalkylation reactions give the linear isomers exclusively but are limited to substrates that contain additional metal-binding directing groups. Although zirconium catalysts have mostly been used for the intramolecular hydroaminoalkylation of aminoalkenes,[8a] very recently, the first examples of zirconium-catalyzed intermolecular hydroaminoalkylation reactions were reported.[8b] In this context, the preferred formation of linear hydroaminoalkylation products from sterically more or less demanding alkyl- or silyl-substituted alkenes with *N*-trimethylsilylbenzylamine was also described. In comparison, the regioselectivity of titanium-catalyzed hydroaminoalkylation reactions can easily be controlled by the structure of the ligands bonded to the titanium center of the catalyst.

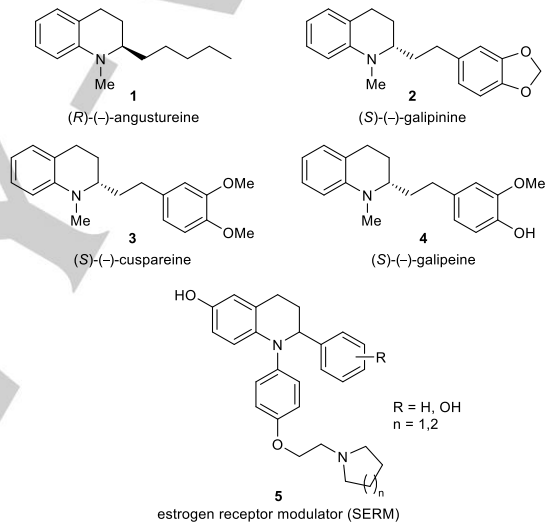
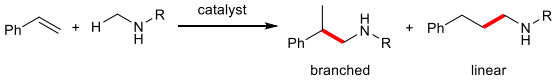


Figure 1. Structures of selected biologically active 1,2,3,4-tetrahydroquinolines.[1,3]



Scheme 1. Intermolecular hydroaminoalkylation of styrene.

In recent years, our group has developed various one-pot procedures which combine regioselective titanium-catalyzed alkene hydroaminoalkylation reactions and palladium-catalyzed Buchwald-Hartwig aminations[10] to obtain biologically relevant compound classes such as 1,5-benzodiazepines,[9o] 1,5-benzoazasilepines,[9p] 1,4-Benzoazasilines,[9q] benzazepines, benzoxazepines and benzothiazepines.[9u] Based on these elegant synthetic pathways, we now present a new two-step procedure that directly gives access to 1,2,3,4-tetrahydroquinolines (Scheme 2).

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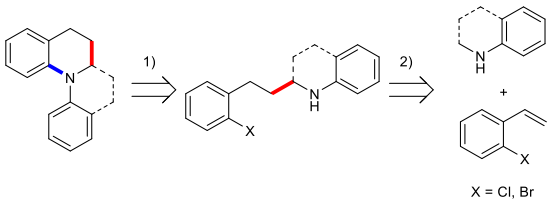
Supporting information for this article is available on the WWW under http://_____.



Scheme 2. Retrosynthetic analysis of 1,2,3,4-tetrahydroquinolines: 1) palladium-catalyzed Buchwald-Hartwig amination; 2) titanium-catalyzed hydroaminoalkylation.

In this new two-step protocol, the initial titanium-catalyzed hydroaminoalkylation step selectively converts *ortho*-halostyrenes with secondary amines into the linear regioisomers which are subsequently cyclized in an intramolecular Buchwald-Hartwig amination reaction to give the desired 1,2,3,4-tetrahydroquinolines. In this context, it must be mentioned that Schafer et al. have already reported a single example of a comparable two-step pathway, where in the presence of a tantalum catalyst the initial hydroaminoalkylation of *ortho*-bromostyrene with *N*-methylaniline delivered the branched regioisomer which gave an indoline derivative in the final amination.[5k] However, in previous studies of our group it was found that titanium complex **I** (Figure 2) represents a suitable catalyst for the conversion of styrenes into the linear hydroaminoalkylation products[9j] and very recently, we reported the analogous complexes **II**-**IV** (Figure 2) to be highly active catalysts in regioselective hydroaminoalkylation reactions of alkyl-substituted alkenes with sterically hindered amines.[9y]

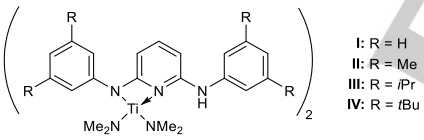
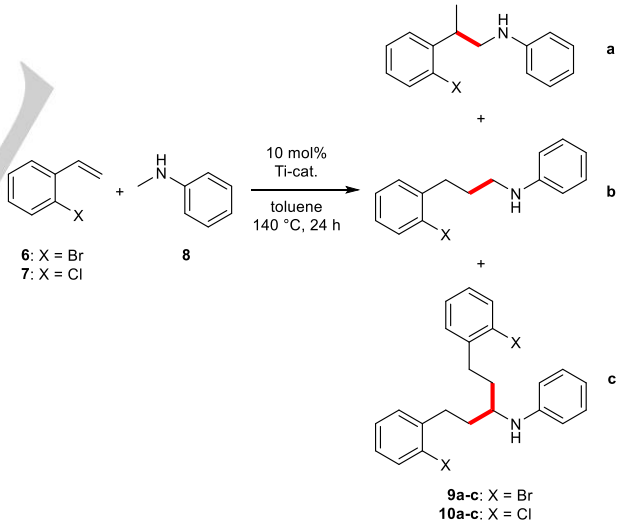


Figure 2. Titanium catalysts for the hydroaminoalkylation of alkenes.

Results and Discussion

We started our investigations by reacting *ortho*-bromostyrene (**6**, 1.2 mmol) with *N*-methylaniline (**8**, 1.0 mmol) in toluene (1 mL) at 140 °C in the presence of 10 mol% of catalyst **I** (Table 1, entry 1). As expected and in good agreement with corresponding reactions of styrenes,[9j] the formation of the desired linear hydroaminoalkylation product **9b** was favored (46 % yield), whereas the branched isomer **9a** could only be isolated in low yield (5 %). Interestingly, we additionally observed the formation of small amounts of an unexpected third product **9c** (3 %), which resulted from a hydroaminoalkylation reaction of *ortho*-bromostyrene (**6**) with the initially formed linear product **9b**. In contrast, an analogous hydroaminoalkylation product formed from the sterically more demanding branched isomer **9a** could not be detected. It is worth mentioning that the unexpected dialkylation of *N*-methylaniline (**8**) represents one of the rare examples in which two hydroaminoalkylation reactions take place subsequently at the same methyl group of the amine substrate.[9c,w,y] An additional reaction performed in the presence of catalyst **II** delivered the linear hydroaminoalkylation product **9b** with a slightly increased yield of 51 % (Table 1, entry 2) while analogous reactions with catalysts **III** or **IV** gave **9b** only in lower yields of 41 % and 39 %, respectively (Table 1, entries 3-4). As can be seen from these four results (Table 1, entries 1-4), a simple relationship between the observed regioselectivities and the size of the *meta*-substituents of the catalysts **I**-**IV** obviously exists: The amount of the undesired branched isomer **9a** seems to increase with increasing size of the *meta*-substituents of the catalyst. This relationship is in sharp contrast to the relationship found for hydroaminoalkylation reactions of alkyl-substituted alkenes with α-substituted *N*-methylanilines. In these cases, increasing size of the *meta*-substituents of the catalyst leads to increased regioselectivities in favor of the linear hydroaminoalkylation products.[9y] Inspired by these promising results and the assumption that the use of a sterically less demanding styrene should lead to improved yields because it facilitates one of the key-steps of the catalytic cycle, namely the insertion of the alkene moiety into the Ti-C bond of the catalytically active titanaaziridine,[9e,n,w] we then performed additional hydroaminoalkylation reactions of sterically less demanding *ortho*-chlorostyrene (**7**) with *N*-methylaniline (**8**) in the presence of the catalysts **I**-**IV** under analogous conditions (Table 1, entries 5-8).

Table 1. Catalyst screening for the hydroaminoalkylation of *ortho*-chlorostyrene and *ortho*-bromostyrene with *N*-methylaniline.[a]



6: X = Br
7: X = Cl

8

9a-c: X = Br
10a-c: X = Cl

Entry	Ti-cat.	Ti-cat. [mol%]	X	Yield %[b]				Ratio **a**:**b**:**c**[c]
				a	**b**	**c**	Σ	
1	**I**	10	Br	5	46	3	54	10:84:6
2	**II**	10	Br	7	51	5	63	11:81:8
3	**III**	10	Br	8	41	5	54	15:77:8
4	**IV**	10	Br	12	39	4	55	22:70:8

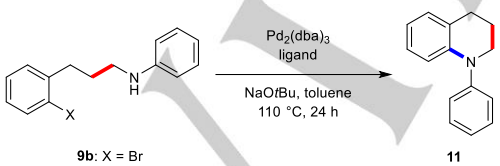
5	**I**	10	Cl	4	47	3	54	7:88:5
6	**II**	10	Cl	7	61	13	81	9:75:16
7	**III**	10	Cl	7	46	5	58	12:80:8
8	**IV**	10	Cl	8	47	4	59	14:79:7
9	**II**	7.5	Cl	7	55	10	72	9:77:14
10	**II**	5	Cl	7	56	7	70	10:81:9

[a] Reaction conditions: *N*-methylaniline (**8**, 1.0 mmol, 107 mg), styrene (1.2 mmol), Ti-catalyst (0.1 mmol, 10 mol% or 0.075 mmol, 7.5 mol%, 0.05 mmol, 5 mol%), toluene (1 mL), 140 °C, 24 h. [b] Isolated yields. [c] Calculated from the obtained isolated yields.

While catalysts **I**, **III**, and **IV** delivered the linear hydroaminoalkylation product **10b** in modest yields of 46-47 % (Table 1, entries 5, 7, and 8), a significantly improved yield of 61 % was obtained in the case of catalyst **II** (Table 1, entry 6). The regioselectivities of these reactions showed the same trend as observed for corresponding reactions of *ortho*-bromostyrene (**6**). The fact that catalyst **II** formed the dihydroaminoalkylation product **10c** in a remarkable yield of 13 %, when compared to the reactions catalyzed by **I**, **III** and, **IV** which gave **10c** only in poor yields of 3-5 %, underlines the high activity of **II** and led to the decision to run all further hydroaminoalkylation reactions with the methyl-substituted catalyst **II**. Additional experiments with reduced catalyst loadings of 7.5 mol% or 5 mol% of **II** gave the linear hydroaminoalkylation product **10b** in slightly decreased yields of 55-56 % (Table 1, entries 9-10). For that reason, all further hydroaminoalkylation reactions were performed with a catalyst loading of 10 mol%.

In a subsequent brief ligand screening for the Buchwald-Hartwig amination, both linear hydroaminoalkylation products **9b** and **10b** were then used as substrates. Initial experiments to achieve the intramolecular cyclization of aryl bromide **9b** were performed in the presence of the phosphine ligands *rac*-BINAP, DPEPhos, or RuPhos (4 mol%) with $Pd_2(dba)_3$ (2 mol%) as the palladium source and sodium *tert*-butoxide as a base and during these experiments, it turned out that **9b** reacts very smoothly to the expected tetrahydroquinoline **11** in excellent yields of 93-97 % (Table 2, entries 1-3).

Table 2. Ligand screening for the Buchwald-Hartwig amination of the linear hydroaminoalkylation products.[a]



9b: X = Br
10b: X = Cl

11

Entry	X	$Pd_2(dba)_3$ [mol%]	Ligand	Ligand [mol%]	Yield [%][b]
1	Br	2	*rac*-BINAP	4	93
2	Br	2	DPEPhos	4	96
3	Br	2	RuPhos	4	97
4	Cl	2	*t*BuXPhos	4	99
5	Cl	2	IPr·HCl	8	99
6	Cl	1	IPr·HCl	4	93

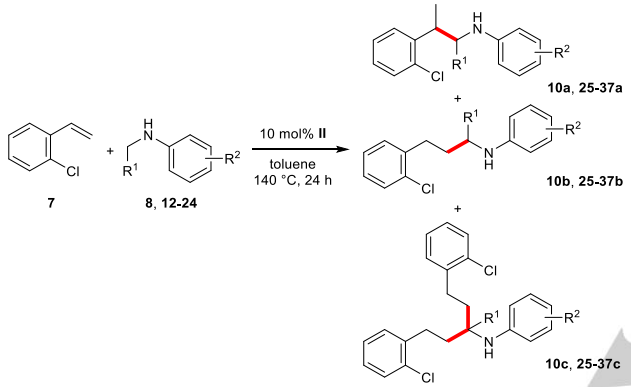
[a] Reaction conditions: amine (1.0 mmol), $Pd_2(dba)_3$ (1 mol% or 2 mol%), ligand (4 mol% or 8 mol%), NaO*t*Bu (1.5 mmol, 144 mg, 1.5 equiv), toluene (3 mL), 110 °C, 24 h. [b] Isolated yield. IPr·HCl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride.

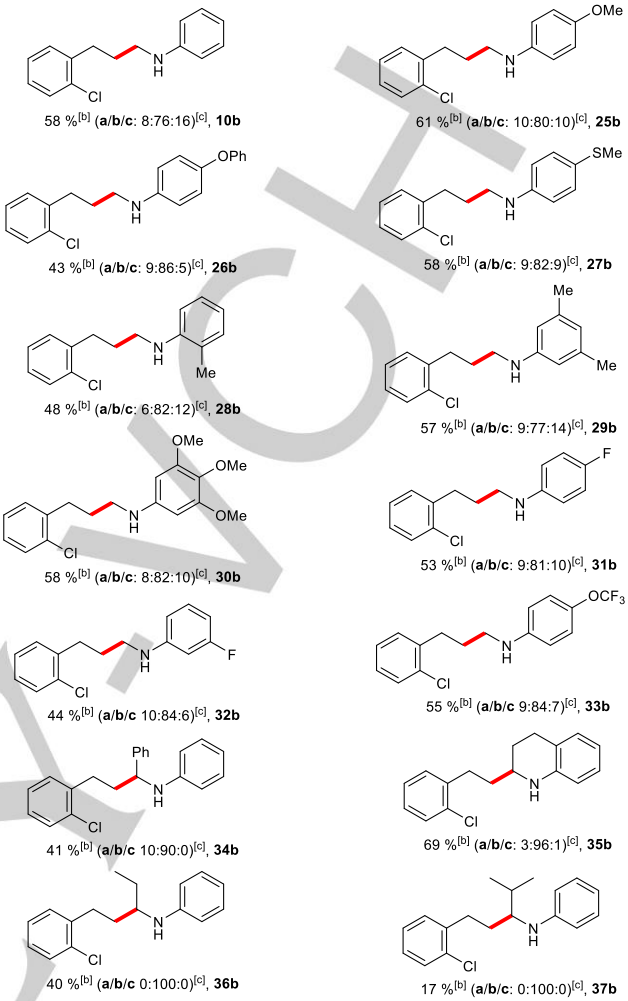
Corresponding reactions of the chloro-substituted substrate **10b** performed in the presence of 2 mol% $Pd_2(dba)_3$ and 4 mol% *t*BuXPhos or 8 mol% 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) then revealed that in these cases, even better results are obtained (Table 2, entries 4-5). Both reactions showed complete conversion of **10b** and gave the cyclization product **11** in quantitative isolated yields. A further experiment to reduce the catalyst loading was carried out with 1 mol% $Pd_2(dba)_3$ and 4 mol% IPr·HCl (Table 1, entry 6). However, in this case, the isolated yield of **11** slightly decreased to 93 %. Delighted by the fact that the chloro-substituted substrates offer advantages in the initial hydroaminoalkylation reaction as well as in the subsequent Buchwald-Hartwig coupling, we used *ortho*-chlorostyrene (**7**) as the starting material for all further studies.

To further investigate the scope of the hydroaminoalkylation of *ortho*-chlorostyrene (**7**) we performed corresponding reactions on a 2 mmol-scale with various functionalized secondary anilines (**12**-**24**) in the presence of 10 mol% of catalyst **II** (Table 3). During this study, it was first found that *para*-methoxy-*N*-methylaniline (**12**) and *para*-thiomethyl-*N*-methylaniline (**14**) deliver the corresponding products **25b** and **27b** in good yields of 61 % and 58 %, respectively. While these yields are comparable to the yield obtained with *N*-methylaniline (**8**, 58 %), the *para*-phenoxy-substituted product **26b** could only be isolated in a lower yield of 43 %. Reactions performed with *meta*-methyl or *meta*-methoxy substituted *N*-methylanilines also led to good yields of the linear products **29b** and **30b** (57 % and 58 %), whereas in the case of a sterically demanding *ortho*-methyl substituent, a slightly decreased yield of the corresponding product **28b** (48 %) was obtained. Further results presented in Table 3 show that the hydroaminoalkylation reaction also tolerates *para*-fluoro and *para*-trifluoromethoxy substitution and as a result, the corresponding products **31b** and **33b** could be isolated in 53 % and 55 % yield, respectively. In contrast, the presence of a *meta*-fluoro substituent resulted in a decreased yield of only 44 % (**32b**). While the selectivities of the hydroaminoalkylation reactions performed with *N*-methylaniline derivatives did not seem to be significantly influenced by the nature of the substituents on the phenyl ring, the use of *N*-alkylanilines with alkyl groups larger than a methyl group revealed that the selectivity is clearly shifted towards the linear products with increasing size of the substituent at the nitrogen atom. In this context, it should be noted that this observation is in good agreement with already reported results for hydroaminoalkylation reactions of styrene.[9j] While *N*-benzylaniline (**21**) and *ortho*-chlorostyrene (**7**) were converted to the linear hydroaminoalkylation product **34b** with a regioselectivity that is still comparable to the regioselectivity obtained with the *N*-methylanilines, the reactions of *N*-

propylaniline (**23**) and *N*-isobutylaniline (**24**) delivered the linear isomers **36b** and **37b** exclusively. Unfortunately, due to the higher steric hindrance of the amine substrates, **34b** and **36b** could only be isolated in moderate yields of 41 % and 40 %, respectively, and in the case of **37b**, the yield further dropped to 17 %. In contrast, the comparable reaction performed with 1,2,3,4-tetrahydroquinoline (**22**) delivered the linear regioisomer **35b** in very good yield of 69 % which can be explained by the cyclic structure of the amine substrate **22** which minimizes its steric hindrance. Unfortunately, the hydroaminoalkylation reaction does not tolerate the presence of carbonyl groups or unprotected alcohols in the substrates.

Table 3. Hydroaminoalkylation of *ortho*-chlorostyrene (**7**) with various *N*-methylanilines and *N*-alkylanilines.[a]





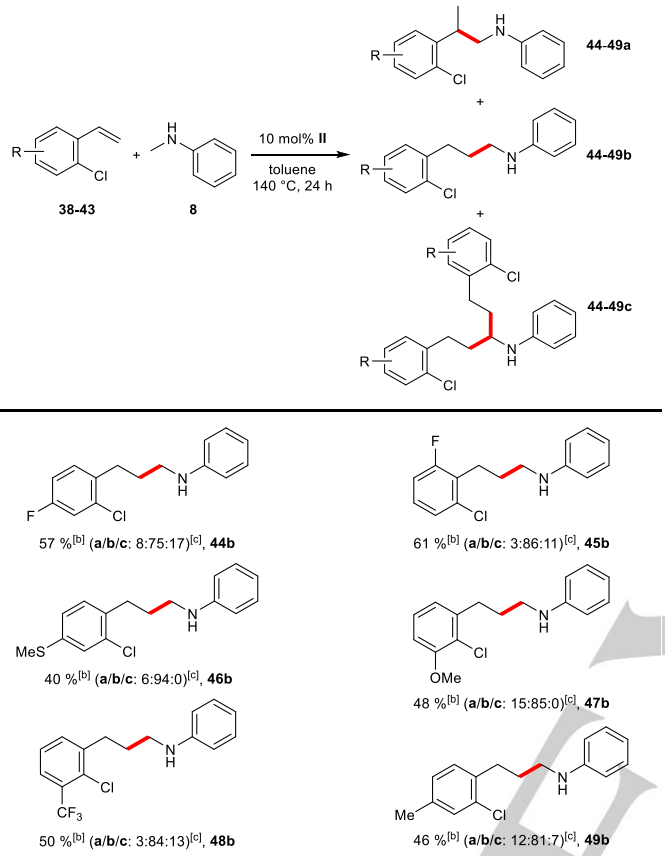
[a] Reaction conditions: amine (2.0 mmol), *ortho*-chlorostyrene (**7**, 2.4 mmol, 333 mg), **II** (0.2 mmol, 154 mg, 10 mol%), toluene (1 mL), 140 °C, 24 h. [b] Isolated yield of the linear product. [c] Calculated from the obtained isolated yields of **a**, **b**, and **c** or determined by ^{1}H NMR analysis of isolated product mixtures.

It is worth mentioning that in comparison to the reactions with *N*-methylanilines, the formation of the dihydroaminoalkylation products **34c**-**37c** is fully suppressed by the steric hindrance of the corresponding amine substrates. Only in the case of 1,2,3,4-tetrahydroquinoline (**22**) as the starting material, a trace amount of **35c** could be detected in the reaction mixture. We also employed *N*-benzylmethylamine as starting material, but in this case, surprisingly, no formation of the corresponding hydroaminoalkylation products could be observed.

In addition, analogous hydroaminoalkylation reactions of various *ortho*-chlorostyrenes were carried out with *N*-methylaniline (**8**) (Table 4). During this study, it was first found that pharmacologically relevant fluoro substituents are well-tolerated at the *para*- or the *ortho*-position of the styrene system as can be seen from the corresponding linear products **44b** and **45b** which were isolated in good yields of 57 % and 61 %, respectively. Furthermore, a strongly electron-withdrawing *meta*-trifluoromethyl substituent as well as electron-donating *meta*-methoxy, *para*-thiomethyl, and *para*-methyl groups are also

tolerated and as a result, the corresponding linear products **46b**-**49b** could be isolated in acceptable yields between 40 % and 50 %.

Table 4. Hydroaminoalkylation of various *ortho*-chlorostyrenes with *N*-methylaniline (**8**).[a]

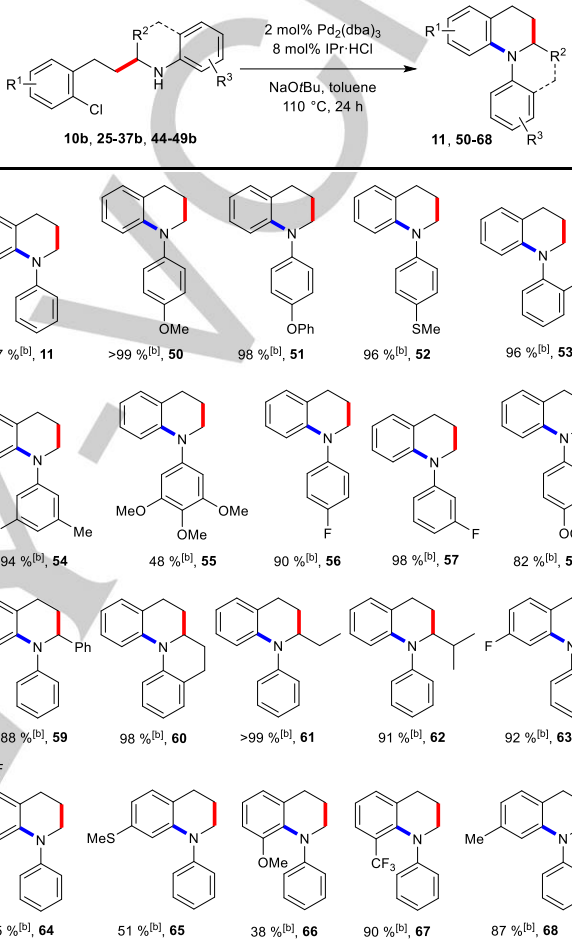


[a] Reaction conditions: *N*-methylaniline (**8**, 2.0 mmol, 214 mg), *ortho*-chlorostyrene (2.4 mmol), **II** (0.2 mmol, 154 mg, 10 mol%), toluene (1 mL), 140 °C, 24 h. [b] Isolated yield of the linear product. [c] Calculated from the obtained isolated yields of **a**, **b**, and **c** or determined by ^{1}H NMR analysis of isolated product mixtures.

Interestingly, no formation of the methoxy- and the thiomethyl-substituted dihydroaminoalkylation products **46c** and **47c** could be observed which suggests a lower reactivity of electron-rich styrenes in the hydroaminoalkylation reaction. This trend in reactivity is further underlined by the observation that the presence of a weaker electron-donating methyl substituent only resulted in the formation of small amounts of the dihydroaminoalkylation product **49c** (7 %) while the corresponding fluoro- and trifluoromethyl-substituted products **44c**, **45c**, and **48c** were formed in increased yields of 11-17 %. Although most of the yields of the hydroaminoalkylation reactions are only moderate it should be mentioned that formation of polystyrene was not observed.

We next turned our attention towards Buchwald-Hartwig aminations of the obtained linear hydroaminoalkylation products to generate the desired 1,2,3,4-tetrahydroquinolines (Table 5). For that purpose, the *ortho*-chlorophenyl-substituted amines were heated to 110 °C for 24 h in the presence of 2 mol% $Pd_2(dba)_3$, 8 mol% 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, and NaO*t*Bu (1.5 equiv) in toluene. The results presented in Table 5 clearly show that under these conditions, the large majority of substrates could be converted to the desired tetrahydroquinolines in excellent isolated yields (≥ 82 %).

Table 5. Buchwald-Hartwig amination of the linear hydroaminoalkylation products.[a]



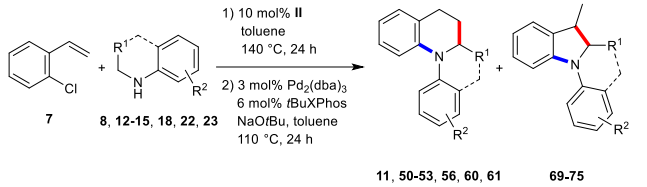
[a] Reaction conditions: amine (0.5 mmol), $Pd_2(dba)_3$ (0.01 mmol, 9 mg, 2 mol%), IPr·HCl (0.04 mmol, 17 mg, 8 mol%), NaO*t*Bu (0.75 mmol, 72 mg, 1.5 equiv), toluene (1.5 mL), 110 °C, 24 h. [b] Isolated yield. IPr·HCl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride.

Although the electron-rich tetrahydroquinolines **55**, **65** and **66** could only be isolated in significantly lower yields (38-51 %) it is worth mentioning that in the case of **55** and **65**, GC analysis of the crude reaction mixtures indicated complete conversion of the substrates **30b** and **46b**. A possible explanation for this observation could be a decomposition of the products during the isolation process. In contrast, in the case of tetrahydroquinoline **66**, GC-analysis revealed that only a small amount of the corresponding sterically more demanding substrate **47b** underwent the cyclization reaction; this easily explains the disappointing yield of only 38 %. If 1,2,3,4-tetrahydroquinoline (**22**) is used as the amine substrate in the initial hydroaminoalkylation step, the presented two-step procedure gives access to quinolizidine **60** which could be regarded as a

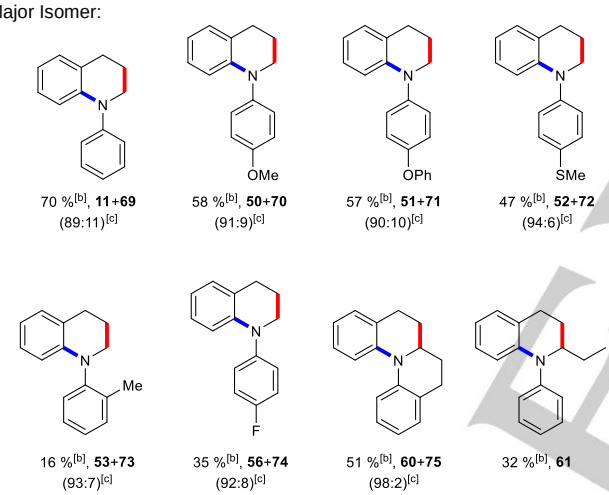
synthetic derivative of naturally occurring quinolizidine alkaloids.[11] As a result of the excellent yield of the intramolecular Buchwald-Hartwig amination (98 %), product **60** could be obtained in 68 % overall yield after both steps.

Finally, the well-established fact that the Buchwald-Hartwig amination usually tolerates the presence of the reagents used in hydroaminoalkylation reactions[9o-q,9u] encouraged us to run the presented two-step procedure for the synthesis of tetrahydroquinolines as a one-pot process. For that purpose, *ortho*-chlorostyrene (**7**) was firstly heated to 140 °C with various amines in the presence of 10 mol% of catalyst **II** for 24 h.

Table 6. One-pot procedure for the synthesis of 1,2,3,4-tetrahydroquinolines.[a]



Major Isomer:



[a] Reaction conditions: 1) amine (1.0 mmol), *ortho*-chlorostyrene (**7**, 1.2 mmol, 166 mg), **II** (0.1 mmol, 77 mg, 10 mol%), toluene (1 mL); 2) $Pd_2(dba)_3$ (0.03 mmol, 27 mg, 3 mol%), *t*BuXPhos (0.06 mmol, 25 mg, 6 mol%), NaO*t*Bu (1.5 mmol, 144 mg, 1.5 equiv), toluene (3 mL), 110 °C, 24 h. [b] Isolated yield. [c] Determined by ^{1}H NMR.

Afterwards, the reagents necessary for the Buchwald-Hartwig amination were added and the mixture was heated to 110 °C for additional 24 h (Table 6). During these experiments, it was surprisingly found that the conversion of the in situ generated linear hydroaminoalkylation products in the Buchwald-Hartwig amination was only poor in the presence of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride. For that reason, we decided to perform the one-pot reactions with *t*BuXPhos as the ligand for the cyclization step. First of all, it can be seen from Table 6 that *ortho*-chlorostyrene (**7**) could successfully be transformed to the corresponding 1,2,3,4-tetrahydroquinolines using the one-pot approach. However, caused by the regioselectivity of the initial hydroaminoalkylation step (*vide supra*), 3-methylindoline derivatives (**69**-**75**) were additionally formed. The latter species result from intramolecular Buchwald-Hartwig amination of the branched hydroaminoalkylation side products. Unfortunately, in most cases, the tetrahydroquinolines and the indolines could not be separated by column chromatography and as a consequence, they were only isolated as mixtures. The only example in which a pure 1,2,3,4-tetrahydroquinoline could be isolated was the conversion of *ortho*-chlorostyrene (**7**) into product **61**, because in this case, the initial hydroaminoalkylation with *N*-propylaniline (**23**) delivers the linear product exclusively.

Conclusions

In summary, we have developed a new two-step procedure for the synthesis of 1,2,3,4-tetrahydroquinolines which combines an initial regioselective hydroaminoalkylation of *ortho*-chlorostyrene with a subsequent intramolecular Buchwald-Hartwig amination. The two-step procedure can in principle be performed as a one-pot process but unfortunately, in this case, most of the 1,2,3,4-tetrahydroquinoline products could not be obtained in pure form. Responsible for this drawback is the formation of small amounts of branched side-products during the hydroaminoalkylation step which deliver indoline derivatives in the Buchwald-Hartwig amination. Because these indolines could not be separated from the desired 1,2,3,4-tetrahydroquinolines by column chromatography, the linear hydroaminoalkylation products needed to be purified prior to the Buchwald-Hartwig amination step to isolate pure 1,2,3,4-tetrahydroquinolines.

Experimental Section

General: Unless otherwise noted, all reactions were performed under an inert atmosphere of nitrogen in oven-dried Schlenk tubes equipped with Teflon® stopcocks and magnetic stirring bars. Toluene was purified by distillation from sodium wire and degassed. THF and diethyl ether were purified by distillation from sodium wire. Petroleum ether (b.p. 40-60 °C, PE) and ethyl acetate used for flash chromatography were distilled prior to use. All substrates were distilled or recrystallized and degassed prior to use. For thin layer chromatography, silica on TLC aluminium foils with fluorescent indicator 254 nm from Fluka were used. For flash chromatography, silica gel from GRACE Davison (particle size 0.037-0.063 mm) was used. The substances were detected with UV light. *N*-methylanilines,[12] *N*-propylaniline,[13] *N*-isobutylaniline[14] and titanium complexes **I**-**IV**[9y] were synthesized according to literature procedures. All other chemicals were purchased from commercial sources and were used without further purification. All products that have already been reported in literature were identified by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy; all analytical data was found to be consistent with the literature. New substances were additionally characterized by infrared spectroscopy (IR), mass spectroscopy (MS), high resolution mass spectrometry (HRMS) and ^{19}F NMR spectroscopy. The ratio of products was calculated from the obtained isolated yields or was determined by ^{1}H NMR analysis of isolated product mixtures. NMR spectra were recorded on a Bruker Avance DRX 500 or a Bruker Avance III, 500 MHz. ^{1}H NMR spectra are referenced to the signal of $CDCl_3$ at δ = 7.26 ppm or the signal of ferrocene at δ = 4.00 ppm. ^{13}C NMR spectra are referenced to the signal of $CDCl_3$ δ = 77.16 ppm or to the signal of d_6-benzene at δ = 128.06 ppm. Infrared spectra were recorded on a Bruker Tensor 27 or Bruker Vector 22 spectrometer. MS analyses were performed on a

Thermo Scientific DFS (EI, 70 eV), Waters Q-TOF Premier (ESI+, TOF) or Shimadzu GSMS-QP2020 (EI, 70 eV). HRMS analyses were performed on a Thermo Scientific DFS (EI, 70 eV) or Waters Q-TOF Premier (ESI+, TOF). GC analyses were performed on a Shimadzu GC-2010 gas chromatograph (column: FS-SE-54-CB-0.25, length = 30 m, inner diameter = 0.32 mm, film thickness = 0.25 µm, (94 %-methyl)-(5 %-phenyl)-(1 %-vinyl)polysiloxane) with a flame ionization detector.

Wittig reaction for the synthesis of styrenes. General procedure A: Under an atmosphere of argon, a dried Schlenk flask was charged with methyltriphenylphosphonium bromide (1.05 equiv) and dry THF. At ambient temperature, *n*-butyllithium (1.05 equiv) was added slowly and after the mixture had been stirred for 15 min 2-chlorobenzaldehyde (1.0 equiv) was added. The reaction mixture was stirred at ambient temperature for 2 h, before it was quenched by addition of saturated ammonium chloride solution and extracted with methylene chloride. The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2).

1-Bromo-2-vinylbenzene (6):[15] A dried Schlenk flask was charged with methyltriphenylphosphonium bromide (42.87 g, 120.0 mmol), evacuated and backfilled with argon three times. Then the solid was suspended in Et_2O (300 mL) and while vigorously stirring KO*t*Bu (13.47 g, 120.0 mmol) was added. After being stirred for 15 min at ambient temperature, the resulting yellow heterogeneous mixture was cooled to 0 °C and 2-bromobenzaldehyde (18.50 g, 100.0 mmol) was added slowly. The reaction was allowed to stir for 15 h at ambient temperature. Afterwards, the reaction mixture was filtered through Celite® and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, PE), to give **6** (15.26 g, 83.37 mmol, 83 %) as a colorless liquid. R_f = 0.57 (SiO_2, PE). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59-7.51 (m, 2 H), 7.31-7.25 (m, 1 H), 7.15-7.02 (m, 2 H), 5.71 (dd, J = 17.4 Hz, J = 2.9 Hz, 1 H), 5.37 (dd, J = 10.9 Hz, J = 2.9 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 137.6 (C), 135.9 (CH), 133.0 (CH), 129.2 (CH), 127.6 (CH), 126.9 (CH), 123.7 (C), 116.8 (CH_2) ppm.

1-Chloro-2-vinylbenzene (7):[16] General procedure A was used to synthesize **7** from 2-chlorobenzaldehyde (12.65 g, 90.0 mmol), methyltriphenylphosphonium bromide (33.76 g, 94.5 mmol), *n*-butyllithium (37.8 mL, 94.5 mmol, c = 2.5 molL^{-1} in *n*-hexane) and THF (750 mL). After purification by flash chromatography (SiO_2, PE), **7** (8.46 g, 61.0 mmol, 68 %) was isolated as a colorless liquid. R_f = 0.37 (SiO_2, PE). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (dd, J = 7.6 Hz, J = 1.5 Hz, 1 H), 7.36 (dd, J = 7.8 Hz, J = 1.3 Hz, 1 H), 7.25-7.18 (m, 2 H), 7.12 (dd, J = 17.5 Hz, J = 11.0 Hz, 1 H), 5.75 (d, J = 17.5 Hz, 1 H), 5.39 (d, J = 11.0 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 135.9 (C), 133.4 (CH), 133.3 (C), 129.8 (CH), 128.9 (CH), 127.0 (CH), 126.7 (CH), 116.7 (CH_2) ppm.

2-Chloro-4-fluoro-1-vinylbenzene (38):[17] Under an atmosphere of argon, a dried Schlenk flask was charged with 2-chloro-4-fluorobenzaldehyde (7.93 g, 50.0 mmol), methyltriphenylphosphonium bromide (21.43 g, 60.0 mmol) and dry THF (250 mL). After the resulting suspension had been cooled to 0 °C, sodium hydride (9.00 g, 225.0 mmol, 60 % dispersion in mineral oil) was added and the reaction mixture was stirred at ambient temperature overnight before it was washed with brine (3 × 100 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, PE/Et_2O, 20:1), to give **38** (4.99 g, 31.8 mmol, 64 %) as a colorless liquid. R_f = 0.77 (SiO_2, PE/Et_2O, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (dd, J = 8.7 Hz, J = 6.1 Hz, 1 H), 7.11 (dd, J = 8.5 Hz, J = 2.6 Hz, 1 H), 7.03 (dd, J = 17.5 Hz, J = 11.0 Hz, 1 H), 6.97 (td, J = 8.3 Hz, J = 2.6 Hz, 1 H), 5.68 (d, J = 17.5 Hz, 1 H), 5.36 (d, J = 11.0 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 162.1 (d, J = 250 Hz, C), 133.8 (d, J = 10 Hz, C), 132.3 (CH), 132.2 (d, J = 3.6 Hz, C), 127.8 (d, J = 8.7 Hz, CH), 116.9 (d, J = 24.6 Hz, CH), 116.5 (d, $J_{C,F}$ = 1.6 Hz, CH_2), 114.5 (d, J = 21.3 Hz, CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −112.60 ppm.

1-Chloro-3-fluoro-2-vinylbenzene (39):[18] General procedure A was used to synthesize **39** from 2-chloro-6-fluorobenzaldehyde (7.93 g, 50.0 mmol), methyltriphenylphosphonium bromide (18.75 g, 52.5 mmol), *n*-butyllithium (21.0 mL, 52.5 mmol, c = 2.5 molL^{-1} in *n*-hexane) and THF (250 mL). After purification by flash chromatography (SiO_2, PE), **39** (3.12 g, 19.9 mmol, 40 %) was isolated as a colorless liquid. R_f = 0.65 (SiO_2, PE). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21-7.17 (m, 1 H), 7.12 (td, J = 8.1 Hz, J = 5.7 Hz, 1 H), 7.02-6.97 (m, 1 H), 6.82 (dd, J = 17.9 Hz, J = 11.9 Hz, 1 H), 5.99 (dt, J = 17.9 Hz, J = 1.4 Hz, 1 H), 5.66 (dt, J = 11.9 Hz, J = 1.8 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 161.5 (d, J = 253 Hz, C), 134.6 (d, J = 5.7 Hz, C), 128.5 (d, J = 10 Hz, CH), 127.7 (CH), 125.6 (d, J = 3 Hz, CH), 124.5 (d, J = 15 Hz, C), 122.4 (d, J = 11 Hz, CH_2), 114.7 (d, J = 24 Hz, CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −112.04 ppm.

2-Chloro-4-(methylthio)benzaldehyde (76): Under an atmosphere of argon, a dried Schlenk flask was charged with 2-chloro-4-fluorobenzaldehyde (9.51 g, 60.0 mmol) and dry DMF (120 mL). To this solution sodium thiomethoxide (4.63 g, 66.0 mmol) was added and the reaction mixture was stirred at 80 °C for 4 h. After cooling down the mixture, it was diluted with water (100 mL) and extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL), dried with $MgSO_4$ and the solvent was removed under reduced pressure. After purification by flash chromatography (SiO_2, PE/EtOAc, 20:1), **76** (3.86 g, 20.7 mmol, 34 %) was isolated as a colorless solid. R_f = 0.37 (SiO_2, PE/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.33 (d, J = 0.6 Hz, 1 H), 7.78 (d, J = 8.3 Hz, 1 H), 7.18 (d, J = 1.8 Hz, 1 H), 7.15 (dd, J = 8.3 Hz, J = 1.1 Hz, 1 H), 2.51 (s, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 188.9 (CH), 149.4 (C), 138.5 (C), 129.3 (CH), 128.8 (C), 125.7 (CH), 123.8 (CH), 14.7 (CH_3) ppm. GC/MS (EI, 70 eV): m/z (%) = 188 (32) [M(^{37}Cl)]$^+$, 187 (45) [$C_8H_6{}^{37}ClOS]^+$, 186 (86) [M(^{35}Cl)]$^+$, 185 (100) [$C_8H_6{}^{35}ClOS]^+$, 170 (4), 157 (5) [$C_7H_6{}^{35}ClS]^+$, 142 (5), 121 (13), 108 (12), 75 (14), 63 (14), 50 (7). HRMS (EI): calcd. (C_8H_7ClOS) 185.9901, found 185.9903 [M]$^+$. IR (ATR, neat): λ^{-1} = 3070, 3017, 2928, 2870, 2753, 1674, 1582, 1540, 1471, 1422, 1379, 1323, 1291, 1263, 1212, 1135, 1097, 1044, 962, 889, 861, 843, 819, 755, 719, 660, 631, 621 cm^{-1}.

(3-Chloro-4-vinylphenyl)(methyl)sulfane (40): General procedure A was used to synthesize **40** from 2-chloro-4-(methylthio)benzaldehyde (**76**, 3.55 g, 19.0 mmol), methyltriphenylphosphonium bromide (7.13 g, 20.0 mmol), *n*-butyllithium (8.0 mL, 20.0 mmol, c = 2.5 molL^{-1} in *n*-hexane) and THF (100 mL). After purification by flash chromatography (SiO_2, PE), **40** (1.67 g, 9.0 mmol, 47 %) was isolated as a colorless liquid. R_f = 0.27 (SiO_2, PE). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.3 Hz, 1 H), 7.21 (d, J = 2.0 Hz, 1 H), 7.10 (dd, J = 8.3 Hz, J = 1.9 Hz, 1 H), 7.05 (dd, J = 17.5 Hz, J = 11.0 Hz, 1 H), 5.71 (d, J = 17.5 Hz, 1 H), 5.34 (d, J = 11.9 Hz, 1 H), 2.48 (s, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 139.8 (C), 133.7 (C), 132.7 (CH), 132.3 (C), 126.6 (CH), 126.6 (CH), 125.0 (CH), 115.8 (CH_2), 15.7 (CH_3) ppm. GC/MS (EI, 70 eV): m/z (%) = 186 (37) [M(^{37}Cl)]$^+$, 184 (100) [M(^{35}Cl)]$^+$, 171 (10) [$C_8H_6{}^{37}ClS]^+$, 169 (27) [$C_8H_6{}^{35}ClS]^+$, 151 (7), 134 (31), 125 (9), 102 (9), 89 (14), 75 (10), 63 (8), 50 (6). HRMS (EI): calcd. (C_9H_9ClS) 184.0108, found 184.0105 [M]$^+$. IR (ATR, neat): λ^{-1} = 3088, 3021, 2986, 2921, 1831, 1623, 1587, 1540, 1472, 1436, 1415, 1374, 1318, 1278, 1261, 1210, 1149, 1108, 1047, 1026, 987, 969, 956, 912, 858, 816, 741, 726, 701, 640, 547 cm^{-1}.

2-Chloro-1-methoxy-3-vinylbenzene (41):[17] General procedure A was used to synthesize **41** from 2-chloro-3-methoxybenzaldehyde (4.61 g, 27.0 mmol), methyltriphenylphosphonium bromide (10.13 g, 28.4 mmol),

n-butyllithium (11.3 mL, 28.4 mmol, *c* = 2.5 molL^{-1} in *n*-hexane) and THF (130 mL). After purification by flash chromatography (SiO_2, PE/Et_2O, 20:1), **41** (3.84 g, 22.8 mmol, 84 %) was isolated as a colorless liquid. R_f = 0.37 (SiO_2, PE/Et_2O, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20-7.18 (m, 2 H), 7.15 (dd, *J* = 17.5 Hz, *J* = 11.0 Hz, 1 H), 6.88-6.83 (m, 1 H), 5.74 (d, *J* = 18.5 Hz, 1 H), 5.39 (d, *J* = 12.0 Hz, 1 H), 3.90 (s, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 155.4 (C), 137.4 (C), 133.5 (CH), 127.0 (CH), 121.8 (C), 118.7 (CH), 117.0 (CH_2), 111.1 (CH), 56.4 (CH_3) ppm.

2-Chloro-1-(trifluoromethyl)-3-vinylbenzene (42):[19] Under an atmosphere of argon, a dried Schlenk flask was charged with methyltriphenylphosphonium bromide (10.22 g, 28.6 mmol) and dry THF (100 mL). The mixture was cooled to 0 °C and KO*t*Bu (3.46 g, 30.8 mmol) was added. After the resulting yellow suspension was stirred for 30 min, 2-chloro-3-(trifluoromethyl)benzaldehyde (4.59 g, 22.0 mmol) was added and stirred for 2 h at 0 °C. The reaction was quenched by addition of water (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. After purification by flash chromatography (SiO_2, PE), **42** (3.43 g, 16.6 mmol, 76 %) was isolated as a colorless liquid. R_f = 0.55 (SiO_2, PE). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 7.9 Hz, *J* = 1.0 Hz, 1 H), 7.62 (dd, *J* = 7.8 Hz, *J* = 1.1 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 7.18 (dd, *J* = 17.5 Hz, *J* = 11.0 Hz, 1 H), 5.76 (dd, *J* = 17.4 Hz, *J* = 0.8 Hz, 1 H), 5.49 (dd, *J* = 11.0 Hz, *J* = 0.8 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 138.5 (C), 132.8 (CH), 131.1 (C), 130.3 (CH), 129.2 (q, *J* = 31 Hz, C), 126.9 (q, *J* = 6 Hz, CH), 126.7 (CH), 123.2 (q, *J* = 273 Hz, C), 118.5 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.51 ppm.

2-Chloro-4-methyl-1-vinylbenzene (43):[20] General procedure A was used to synthesize **43** from 2-chloro-4-methylbenzaldehyde (4.64 g, 30.0 mmol), methyltriphenylphosphonium bromide (11.25 g, 31.5 mmol), *n*-butyllithium (12.6 mL, 31.5 mmol, *c* = 2.5 molL^{-1} in *n*-hexane) and THF (150 mL). After purification by flash chromatography (SiO_2, PE), **43** (3.57 g, 23.4 mmol, 78 %) was isolated as a colorless liquid. R_f = 0.62 (SiO_2, PE). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.0 Hz, 1 H), 7.20 (s, 1 H), 7.10 (dd, *J* = 17.5 Hz, *J* = 11.0 Hz, 1 H), 7.07-7.03 (m, 1 H), 5.72 (dd, *J* = 17.5 Hz, *J* = 1.0 Hz, 1 H), 5.34 (dd, *J* = 11.0 Hz, *J* = 1.0 Hz, 1 H), 2.33 (s, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 139.2 (C), 133.1 (CH), 133.0 (C), 132.9 (C), 130.1 (CH), 127.9 (CH), 126.4 (CH), 115.6 (CH_2), 21.0 (CH_3) ppm.

Hydroaminoalkylation of styrenes with *N*-alkylanilines. General procedure B: An oven-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with the catalyst (0.20 mmol, 10 mol%), amine (2.00 mmol), alkene (2.40 mmol), and toluene (1 mL). The tube was sealed, removed from the glovebox, and placed in an aluminium heating block. The reaction mixture was heated to 140 °C for 24 h. After the reaction mixture had been cooled to room temperature, it was diluted with CH_2Cl_2 (50 mL) and Celite® was added. Then the solvents were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2).

***N*-(2-(2-Bromophenyl)propyl)aniline (9a), *N*-(3-(2-bromophenyl)propyl)aniline (9b) and *N*-(1,5-bis(2-bromophenyl)pentan-3-yl)aniline (9c):** General procedure B was used to synthesize **9b** from *N*-methylaniline (**3**, 2.00 mmol, 214 mg) and *ortho*-bromostyrene (**6**, 2.40 mmol, 439 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 20:1), **9a** (40 mg, 0.14 mmol, 7 %), **9b** (303 mg, 1.04 mmol, 52 %) and **9c** (31 mg, 0.07 mmol, 3 %) were isolated as slightly yellow oils. **9a**: R_f = 0.36 (SiO_2, PE/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1 H), 7.34-7.27 (m, 2 H), 7.21-7.16 (m, 2 H), 7.13-7.09 (m, 1 H), 6.71 (t, *J* = 7.3 Hz, 1 H), 6.63 (d, *J* = 7.7 Hz, 1 H), 3.75 (br. s, 1 H), 3.64 (sext, *J* = 7.0 Hz, 1 H), 3.39 (dd, *J* = 12.3 Hz, *J* = 7.3 Hz, 1 H), 3.28 (dd, *J* = 12.3 Hz, *J* = 7.0 Hz, 1 H), 1.34 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.1 (C), 143.5 (C), 133.2 (CH), 129.3 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 125.2 (C), 117.5 (CH), 113.0 (CH), 50.0 (CH_2), 38.1 (CH), 19.1 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 291 (7) [M(^{81}Br)]$^+$, 289 (7) [M(^{79}Br)]$^+$, 106 (100) [C_7H_8N]$^+$, 91 (3), 77 (42) [C_6H_5]$^+$, 65 (4), 51 (14). HRMS (EI): calcd. ($C_{15}H_{16}BrN$) 289.0461, found 289.0455 [M]$^+$. IR (ATR, neat): λ^{-1} = 3058, 3020, 2965, 2919, 1603, 1507, 1473, 1434, 1381, 1320, 1257, 1181, 1071, 1023, 993, 869, 747, 726 cm^{-1}. **9b**: R_f = 0.30 (SiO_2, PE/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.7 Hz, 1 H), 7.25-7.14 (m, 4 H), 7.10-7.03 (m, 1 H), 6.72 (t, *J* = 7.3 Hz, 1 H), 6.62 (d, *J* = 8.4 Hz, 2 H), 3.65 (br. s, 1 H), 3.19 (t, *J* = 7.0 Hz, 2 H), 2.89-2.82 (m, 2 H), 1.96 (quint, *J* = 7.2 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.4 (C), 141.1 (C), 133.0 (CH), 130.5 (CH), 129.4 (CH), 127.8 (CH), 127.6 (CH), 124.6 (C), 117.4 (CH), 112.9 (CH), 43.5 (CH_2), 33.8 (CH_2), 29.8 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 291 (5) [M(^{37}Br)]$^+$, 289 (5) [M(^{35}Br)]$^+$, 210 (19) [$C_{15}H_{16}N$]$^+$, 106 (100) [C_7H_8N]$^+$, 91 (6), 77 (16) [C_6H_5]$^+$, 65 (5), 50 (5). HRMS (EI): calcd. ($C_{15}H_{16}BrN$) 289.0461, found 289.0453 [M]$^+$. IR (ATR, neat): λ^{-1} = 3050, 3014, 2935, 2862, 1601, 1566, 1505, 1470, 1438, 1320, 1256, 1179, 1154, 1100, 1020, 992, 867, 744 cm^{-1}. **9c**: R_f = 0.39 (SiO_2, PE/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 2 H), 7.23-7.13 (m, 6 H), 7.06 (td, *J* = 7.8 Hz, *J* = 1.9 Hz, 1 H), 6.69 (t, *J* = 7.3 Hz, 1 H), 6.56 (d, *J* = 7.7 Hz, 2 H), 3.61 (br. s, 1 H), 3.48 (quint, *J* = 6.2 Hz, 1 H), 2.91 (ddd, *J* = 13.5 Hz, *J* = 10.3 Hz, *J* = 5.5 Hz, 1 H), 2.81 (ddd, *J* = 13.5 Hz, *J* = 10.4 Hz, *J* = 6.0 Hz, 2 H), 2.00-1.91 (m, 2 H), 1.88-1.79 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.7 (C), 141.4 (C), 133.0 (CH), 130.7 (CH), 129.4 (CH), 127.8 (CH), 127.6 (CH), 124.5 (C), 117.1 (CH), 113.3 (CH), 52.4 (CH), 35.2 (CH_2), 33.0 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 475 (4) [M(^{81}Br^{81}Br)]$^+$, 473 (8) [M(^{79}Br^{81}Br)]$^+$, 471 (4) [M(^{79}Br^{79}Br)]$^+$, 288 (100) [$C_{15}H_{15}{}^{79}$BrN]$^+$, 169 (30) [C_7H_6Br]$^+$, 132 (7), 118 (18), 104 (14), 91 (20), 77 (21) [C_6H_5]$^+$, 65 (6), 50 (4). HRMS (EI): calcd. ($C_{23}H_{23}Br_2N$) 471.0192, found 471.0189 [M]$^+$. IR (ATR, neat): λ^{-1} = 3054, 2948, 2929, 2858, 1600, 1566, 1504, 1470, 1437, 1318, 1261, 1181, 1155, 1129, 1021, 942, 866, 743 cm^{-1}.

***N*-(3-(2-Chlorophenyl)propyl)aniline (10a), *N*-(2-(2-chlorophenyl)propyl)aniline (10b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)aniline (10c):** General procedure B was used to synthesize **10b** from *N*-methylaniline (**3**, 2.00 mmol, 214 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **10a** (25 mg, 0.10 mmol, 5 %), **10b** (287 mg, 1.17 mmol, 58 %) and **10c** (78 mg, 0.20 mmol, 10 %) were isolated as slightly yellow oils. In addition a mixture of **10a** and **10c** (27 mg, **10a**/**10c** = 43:57) was also isolated. **10a**: R_f = 0.35 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.0 Hz, 1 H), 7.33-7.25 (m, 2 H), 7.23-7.15 (m, 3 H), 6.77 (t, *J* = 7.3 Hz, 1 H), 6.72 (d, *J* = 8.0 Hz, 2 H), 3.68 (sext, *J* = 7.0 Hz, 1 H), 3.42 (dd, *J* = 12.4 Hz, *J* = 7.1 Hz, 1 H), 3.30 (dd, *J* = 12.4 Hz, *J* = 7.2 Hz, 1 H), 1.37 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.1 (C), 141.6 (C), 134.2 (C), 129.9 (CH), 129.4 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 118.5 (CH), 113.8 (CH), 50.4 (CH_2), 35.2 (CH), 18.8 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 247 (2) [M(^{37}Cl)]$^+$, 245 (5) [M(^{35}Cl)]$^+$, 139 (1) [$C_8H_8{}^{35}$Cl]$^+$, 106 (100) [C_7H_8N]$^+$, 77 (18) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{15}H_{16}ClN$) 245.0966, found 245.0967 [M]$^+$. IR (ATR, neat): λ^{-1} = 3401, 3055, 2969, 2929, 2873, 1735, 1603, 1507, 1477, 1436, 1321, 1258, 1182, 1037, 749, 693 cm^{-1}. **10b**: R_f = 0.30 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (dd, *J* = 7.7 Hz, *J* = 1.2 Hz, 1 H), 7.25-7.13 (m, 5 H), 6.74 (t, *J* = 7.3 Hz, 1 H), 6.66 (d, *J* = 7.7 Hz, 2 H), 3.20 (t, *J* = 7.0 Hz, 2 H), 2.86 (t, *J* = 7.7 Hz, 2 H), 1.98 (quint, *J* = 7.4 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 147.9 (C), 139.3 (C), 134.1 (C), 130.5 (CH), 129.7 (CH), 129.4 (CH), 127.6 (CH), 127.0 (CH), 118.0 (CH), 113.4 (CH), 44.0 (CH_2), 31.2 (CH_2), 29.5 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 247 (5) [M(^{37}Cl)]$^+$, 245 (14) [M(^{35}Cl)]$^+$, 210 (12) [$C_{15}H_{16}N$]$^+$, 125 (6)

$[C_7H_6{}^{35}Cl]^+$,106 (100) $[C_7H_8N]^+$, 77 (21) $[C_6H_5]^+$. HRMS (ESI, +): calcd. ($C_{15}H_{17}ClN$) 246.1050, found 246.1040 $[M+H]^+$. IR (ATR, neat): λ^{-1} = 3052, 3020, 2932, 2863, 1601, 1505, 1474, 1442, 1431, 1320, 1256, 1179, 1051, 1029, 744, 691 cm^{-1}. **10c**: R_f = 0.38 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.38-7.34 (m, 2 H), 7.24-7.14 (m, 8 H), 6.74 (t, *J* = 7.2 Hz, 1 H), 6.62 (d, *J* = 6.2 Hz, 2 H), 3.48 (quint, *J* = 6.1 Hz, 1 H), 2.96-2.89 (m, 2 H), 2.86-2.79 (m, 2 H), 2.02-1.94 (m, 2 H), 1.93-1.83 (m, 2 H). $^{13}C\{^1H\}$ NMR (125 MHz, DEPT, $CDCl_3$): δ = 147.2 (C), 139.6 (C), 133.9 (C), 130.7 (CH), 129.6 (CH), 129.4 (CH), 127.5 (CH), 126.9 (CH), 117.6 (CH), 113.8 (CH), 52.9 (CH), 34.7 (CH_2), 30.4 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 387 (1) $[M(^{37}Cl^{37}Cl)]^+$, 385 (4) $[M(^{35}Cl^{37}Cl)]^+$, 383 (7) $[M(^{35}Cl^{35}Cl)]^+$, 348 (2) $[C_{23}H_{23}{}^{35}ClN]^+$, 244 (100) $[C_{15}H_{15}{}^{35}ClN]^+$, 125 (41) $[C_7H_6{}^{35}Cl]^+$, 77 (12) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{23}H_{23}Cl_2N$) 383.1202, found 383.1215 $[M]^+$. IR (ATR, neat): λ^{-1} = 3052, 3020, 2932, 2863, 1601, 1505, 1474, 1442, 1431, 1320, 1256, 1179, 1051, 1029, 744, 691 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-4-methoxyaniline (25a), *N*-(3-(2-chlorophenyl)propyl)-4-methoxyaniline (25b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-4-methoxyaniline (25c):** General procedure B was used to synthesize **25b** from 4-methoxy-*N*-methylaniline (**12**, 2.00 mmol, 274 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 10:1), **25a** (22 mg, 0.08 mmol, 4 %), **25b** (276 mg, 1.00 mmol, 50 %) and **25c** (66 mg, 0.16 mmol, 8 %) were isolated as slightly yellow oils. Furthermore, two additional fractions were isolated. The first fraction contained **25a** (20 mg, 0.07 mmol, 4 %) and some amount of the ligand of catalyst **II**. The second fraction contained **25b** (61 mg, 0.22 mmol, 11 %) and some amount of the ligand of catalyst **II**. **25a**: R_f = 0.25 (SiO_2, PE/EtOAc, 10:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.0 Hz, 1 H), 7.31-7.23 (m, 2 H), 7.19-7.14 (m, 1 H), 6.78 (d, *J* = 9.0 Hz, 2 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 3.75 (s, 3 H), 3.64 (sext, *J* = 7.0 Hz, 1 H), 3.36 (dd, *J* = 12.3 Hz, *J* = 7.2 Hz, 1 H), 3.23 (dd, *J* = 12.3 Hz, *J* = 7.0 Hz, 1 H), 1.34 (d, *J* = 7.0 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 152.8 (C), 141.8 (C), 141.4 (C), 134.3 (C), 129.9 (CH), 127.8 (CH), 127.5 (CH), 127.3 (CH), 115.0 (CH), 115.0 (CH), 55.9 (CH_3), 51.3 (CH_2), 35.2 (CH), 18.8 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 277 (2) $[M(^{37}Cl)]^+$, 275 (7) $[M(^{35}Cl)]^+$, 136 (100) $[C_8H_{10}NO]^+$, 121 (6), 108 (5), 93 (4), 77 (8) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{16}H_{18}ClNO$) 275.1077, found 275.1068 $[M]^+$. IR (ATR, neat): λ^{-1} = 2966, 2932, 2841, 1510, 1475, 1439, 1233, 1179, 1034, 819, 752, 676 cm^{-1}. **25b**: R_f = 0.17 (SiO_2, PE/EtOAc, 10:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.8 Hz, 1 H), 7.25-7.13 (m, 3 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 6.61 (d, *J* = 8.9 Hz, 2 H), 3.76 (s, 3 H), 3.44 (br. s, 1 H), 3.15 (t, *J* = 7.0 Hz, 2 H), 2.86 (t, *J* = 7.7 Hz, 2 H), 1.96 (quint, *J* = 7.4 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 152.3 (C), 142.4 (C), 139.4 (C), 134.0 (C), 130.5 (CH), 129.6 (CH), 127.6 (CH), 126.9 (CH), 115.0 (CH), 114.4 (CH), 55.9 (CH_3), 44.7 (CH_2), 31.2 (CH_2), 29.6 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 277 (8) $[M(^{37}Cl)]^+$, 275 (24) $[M(^{35}Cl)]^+$, 260 (2) $[C_{15}H_{15}{}^{35}ClNO]^+$, 240 (2) $[C_{16}H_{18}NO]^+$,136 (100) $[C_8H_{10}NO]^+$, 125 (8) $[C_7H_6{}^{35}Cl]^+$, 108 (6), 77 (5) $[C_6H_5]^+$. HRMS (ESI, +): calcd. ($C_{16}H_{19}ClNO$) 276.1155, found 276.1150 $[M+H]^+$. IR (ATR, neat): λ^{-1} = 2949, 2933, 2830, 1510, 1474, 1441, 1292, 1233, 1178, 1130, 1115, 1036, 817, 750 cm^{-1}. **25c**: R_f = 0.30 (SiO_2, PE/EtOAc, 10:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.33 (m, 2 H), 7.19-7.12 (m, 6 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 6.55 (d, *J* = 7.5 Hz, 2 H), 3.77 (s, 3 H), 3.38 (quint, *J* = 6.1 Hz, 1 H), 2.95-2.87 (m, 2 H), 2.85-2.77 (m, 2 H), 1.99-1.90 (m, 2 H), 1.88-1.80 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 152.1 (C), 141.6 (C), 139.7 (C), 134.0 (C), 130.7 (CH), 129.6 (CH), 127.5 (CH), 126.9 (CH), 115.1 (CH), 115.1 (CH), 55.9 (CH_3), 53.6 (CH), 34.8 (CH_2), 30.4 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 417 (2) $[M(^{37}Cl^{37}Cl)]^+$, 415 (12) $[M(^{35}Cl^{37}Cl)]^+$, 413 (17) $[M(^{35}Cl^{35}Cl)]^+$, 274 (100) $[C_{16}H_{17}{}^{35}ClNO]^+$, 149 (44), 134 (17), 125 (22) $[C_7H_6{}^{35}Cl]^+$, 107 (7) $[C_7H_7O]^+$, 91 (5) $[C_6H_5N]^+$, 77 $[C_6H_5]^+$ (8). HRMS (EI): calcd. ($C_{24}H_{25}Cl_2NO$) 413.1313, found 413.1300 $[M]^+$. IR (ATR, neat): λ^{-1} = 3059, 2952, 2932, 2862, 2832, 1511, 1475, 1443, 1234, 1181, 1134, 1036, 819, 749, 682, 567 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-4-phenoxyaniline (26a), *N*-(3-(2-chlorophenyl)propyl)-4-phenoxyaniline (26b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-4-phenoxyaniline (26c):** General procedure B was used to synthesize **26b** from *N*-methyl-4-phenoxyaniline (**13**, 2.00 mmol, 399 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 20:1), **26a** (30 mg, 0.09 mmol, 4 %), **26b** (291 mg, 0.86 mmol, 43 %) and **26c** (24 mg, 0.05 mmol, 3 %) were isolated as slightly yellow oils. **26a**: R_f = 0.24 (SiO_2, PE/EtOAc, 20:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.9 Hz, 1 H), 7.33-7.24 (m, 4 H), 7.18 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.01 (t, *J* = 7.4 Hz, 1 H), 6.93 (d, *J* = 8.1 Hz, 2 H), 6.90 (d, *J* = 8.7 Hz, 2 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 3.67 (sext, *J* = 7.0 Hz, 1 H), 3.38 (dd, *J* = 12.3 Hz, *J* = 7.3 Hz, 1 H), 3.28 (dd, *J* = 12.3 Hz, *J* = 6.9 Hz, 1 H), 1.36 (d, *J* = 6.9 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 159.1 (C), 148.1 (C), 144.3 (C), 141.7 (C), 134.3 (C), 129.9 (CH), 129.6 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 122.1 (CH), 121.3 (CH), 117.3 (CH), 114.4 (CH), 50.7 (CH_2), 35.3 (CH), 18.9 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 339 (1) $[M(^{37}Cl)]^+$, 337 (6) $[M(^{35}Cl)]^+$, 198 (100) $[C_{13}H_{12}NO]^+$, 139 (4) $[C_8H_8{}^{35}Cl]^+$, 105 (6), 77 (10) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{21}H_{20}ClNO$) 337.1228, found 337.1217 $[M]^+$. IR (ATR, neat): λ^{-1} = 3416, 3390, 3027, 2970, 2926, 2874, 1612, 1588, 1508, 1487, 1441, 1320, 1226, 1162, 1035, 1022, 869, 830, 750, 690, 594 cm^{-1}. **26b**: R_f = 0.20 (SiO_2, PE/EtOAc, 20:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.0 Hz, 1 H), 7.31-7.14 (m, 5 H), 7.02 (t, *J* = 7.4 Hz, 1 H), 6.96-6.89 (m, 4 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 3.18 (t, *J* = 7.0 Hz, 2 H), 2.87 (t, *J* = 7.7 Hz, 2 H), 1.99 (quint, *J* = 7.4 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 159.1 (C), 148.1 (C), 144.5 (C), 139.3 (C), 134.1 (C), 130.5 (CH), 129.7 (CH), 129.6 (CH), 127.7 (CH), 127.0 (CH), 122.1 (CH), 121.3 (CH), 117.3 (CH), 114.4 (CH), 44.4 (CH_2), 31.2 (CH_2), 29.5 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 339 (1) $[M(^{37}Cl)]^+$, 337 (6) $[M(^{35}Cl)]^+$, 198 (100) $[C_{13}H_{12}NO]^+$, 139 (3) $[C_8H_8{}^{35}Cl]^+$, 105 (7), 77 (11) $[C_6H_5]^+$. HRMS (ESI, +): calcd. ($C_{21}H_{21}ClNO$) 338.1312, found 338.1313 $[M+H]^+$. IR (ATR, neat): λ^{-1} = 3065, 3036, 2950, 2935, 2862, 1613, 1588, 1509, 1487, 1474, 1443, 1320, 1288, 1225, 1161, 1113, 1052, 1007, 869, 829, 748, 691, 558 cm^{-1}. **26c**: R_f = 0.29 (SiO_2, PE/EtOAc, 20:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.33 (m, 2 H), 7.29 (t, *J* = Hz, 2 H), 7.18-7.12 (m, 6 H), 7.02 (t, *J* = 7.3 Hz, 1 H), 6.95 (d, *J* = 8.1 Hz, 2 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 6.56 (br. s, 2 H), 3.41 (quint, *J* = 5.7 Hz, 1 H), 2.94-2.87 (m, 2 H), 2.86-2.78 (m, 2 H), 2.01-1.93 (m, 2 H), 1.91-1.82 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 159.3 (C), 147.5 (C), 144.4 (C), 139.7 (C), 134.0 (C), 130.7 (CH), 129.7 (CH), 129.6 (CH), 127.6 (CH), 127.0 (CH), 122.0 (CH), 121.4 (CH), 117.2 (CH), 114.4 (CH), 53.0 (CH), 34.9 (CH_2), 30.4 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 479 (3) $[M(^{37}Cl^{37}Cl)]^+$, 477 (16) $[M(^{35}Cl^{37}Cl)]^+$, 475 (23) $[M(^{35}Cl^{35}Cl)]^+$, 336 (100) $[C_{21}H_{19}{}^{35}ClNO]^+$, 211 (46), 125 (28) $[C_7H_6{}^{35}Cl]^+$, 77 (17) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{29}H_{27}Cl_2NO$) 475.1464, found 475.1465 $[M]^+$. IR (ATR, neat): λ^{-1} = 3066, 2956, 2932, 2862, 1738, 1615, 1590, 1508, 1489, 1476, 1456, 1444, 1319, 1229, 1163, 1135, 1053, 1034, 945, 872, 829, 749, 693, 683, 578, 565 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-4-(methylthio)aniline (27a), *N*-(3-(2-chlorophenyl)propyl)-4-(methylthio)aniline (27b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-4-(methylthio)aniline (27c):** General procedure B was used to synthesize **27b** from *N*-methyl-4-(methylthio)aniline (**14**, 2.00 mmol, 306 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **27b** (339 mg, 1.16 mmol, 58 %) was isolated as a slightly yellow oil. In addition, a second fraction that contained a mixture of **27a** and **27c** (92 mg, **27a**/**27c** = 58:42) was also isolated. **27b**: R_f = 0.25 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.7 Hz, 2 H), 7.24-7.13 (m, 5 H), 6.57 (d, *J* = 7.8 Hz, 2 H), 3.17 (t, *J* = 7.2 Hz, 2 H), 2.85 (t, *J* = 7.7 Hz, 2 H), 2.41 (s, 3 H), 1.96 (quint, *J* = 7.3 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 146.9 (C), 139.2 (C), 134.0 (C), 131.6 (CH), 130.5 (CH), 129.7 (CH), 127.6 (CH), 127.0 (CH), 124.5 (C), 113.7 (CH), 43.7 (CH_2), 31.2 (CH_2), 29.4 (CH_2), 19.3 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z*

(%) = 293 (13) [M(^{37}Cl)]$^+$, 291 (33) [M(^{35}Cl)]$^+$, 276 (3) [$C_{15}H_{15}{}^{35}ClNS]^+$, 256 (2) [$C_{16}H_{18}NS]^+$, 165 (4), 152 (100) [$C_8H_{10}NS]^+$, 137 (12), 125 (10) [$C_7H_6{}^{35}Cl]^+$, 105 (4), 91 (6), 77 (7). HRMS (ESI, +): calcd. ($C_{16}H_{19}NClS$) 292.0927, found 292.0923 [M+H]$^+$. IR (ATR, neat): λ^{-1} = 2951, 2919, 2864, 1598, 1500, 1474, 1440, 1313, 1289, 1250, 1182, 1131, 1051, 1029, 966, 813, 750, 679 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-2-methylaniline (28a), *N*-(3-(2-chlorophenyl)propyl)-2-methylaniline (28b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-2-methylaniline (28c):** General procedure B was used to synthesize **28b** from *N*,2-dimethylaniline (**15**, 2.00 mmol, 242 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 40:1), **28b** (247 mg, 0.95 mmol, 48 %) and **28c** (46 mg, 0.12 mmol, 6 %) were isolated as slightly yellow oils. In addition, a third fraction that contained a mixture of **28a** and **28c** (29 mg, **28a**/**28c** = 68:32) was also isolated. **28b**: R_f = 0.20 (SiO_2, PE/EtOAc, 40:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 (dd, J = 7.7 Hz, J = 1.2 Hz, 1 H), 7.28-7.23 (m, 1 H), 7.20 (td, J = 7.3 Hz, J = 1.3 Hz, 1 H), 7.18-7.12 (m, 2 H), 7.07 (d, J = 7.2 Hz, 1 H), 6.74-6.63 (m, 2 H), 3.25 (t, J = 7.0 Hz, 2 H), 2.90 (t, J = 7.7 Hz, 2 H), 2.16 (s, 3 H), 2.04 (quint, J = 7.3 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 145.8 (C), 139.4 (C), 134.1 (C), 130.5 (CH), 130.3 (CH), 129.7 (CH), 127.6 (CH), 127.3 (CH), 127.0 (CH), 122.4 (C), 117.5 (CH), 110.4 (CH), 43.8 (CH_2), 31.3 (CH_2), 29.6 (CH_2), 17.6 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 261 (7) [M(^{37}Cl)]$^+$, 259 (19) [M(^{35}Cl)]$^+$, 224 (6) [$C_{16}H_{18}N]^+$, 120 (100) [$C_8H_{10}N]^+$, 107 (6), 91 (19) [$C_7H_7]^+$, 77 (14). HRMS (ESI, +): calcd. ($C_{16}H_{19}NCl$) 260.1206, found 260.1201 [M+H]$^+$. IR (ATR, neat): λ^{-1} = 3055, 3016, 2929, 2858, 1606, 1586, 1512, 1473, 1443, 1377, 1316, 1302, 1259, 1176, 1134, 1050, 1029, 985, 743, 715, 679, 603 cm^{-1}. **28c**: R_f = 0.33 (SiO_2, PE/EtOAc, 40:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39-7.32 (m, 2 H), 7.21-7.13 (m, 6 H), 7.11-7.05 (m, 2 H), 6.66 (br. s, 1 H), 6.49 (br. s, 1 H), 3.55 (quint, J = 5.8 Hz, 1 H), 2.98-2.89 (m, 2 H), 2.86-2.76 (m, 2 H), 2.19 (s, 3 H), 2.06-1.83 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 145.5 (C), 139.6 (C), 134.0 (C), 130.7 (CH), 130.5 (CH), 129.6 (CH), 127.6 (CH), 127.2 (CH), 127.0 (CH), 121.8 (C), 116.5 (CH), 110.0 (CH), 52.1 (CH), 35.1 (CH_2), 30.5 (CH_2), 17.8 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 401 (2) [M(^{37}Cl^{37}Cl)]$^+$, 399 (7) [M(^{35}Cl^{37}Cl)]$^+$, 397 (9) [M(^{35}Cl^{35}Cl)]$^+$, 258 (100) [$C_{16}H_{17}{}^{35}ClN]^+$, 125 (31) [$C_7H_6{}^{35}Cl]^+$, 118 (25), 103 (6), 91 (11) [$C_7H_7]^+$, 77 (7). HRMS (ESI, +): calcd. ($C_{24}H_{26}NCl_2$) 398.1442, found 398.1448 [M+H]$^+$. IR (ATR, neat): λ^{-1} = 2956, 2928, 2865, 1605, 1585, 1512, 1474, 1442, 1317, 1261, 1189, 1135, 1050, 1032, 743, 679, 620, 608 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-3,5-dimethylaniline (29a), *N*-(3-(2-chlorophenyl)propyl)-3,5-dimethylaniline (29b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-3,5-dimethylaniline (29c):** General procedure B was used to synthesize **29b** from *N*,3,5-trimethylaniline (**16**, 2.00 mmol, 270 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **29a** (37 mg, 0.14 mmol, 7 %), **29b** (314 mg, 1.15 mmol, 57 %) and **29c** (88 mg, 0.21 mmol, 11 %) were isolated as colorless solids. **29a**: R_f = 0.25 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.0 Hz, 1 H), 7.33-7.23 (m, 2 H), 7.20-7.16 (m, 1 H), 6.40 (s, 1 H), 6.31 (s, 2 H), 3.66 (sext, J = 7.0 Hz, 1 H), 3.39 (dd, J = 12.2 Hz, J = 7.2 Hz, 1 H), 3.25 (dd, J = 12.3 Hz, J = 7.1 Hz, 1 H), 2.25 (s, 6 H), 1.35 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.9 (C), 141.9 (C), 139.0 (C), 134.2 (C), 129.9 (CH), 127.7 (CH), 127.5 (CH), 127.3 (CH), 119.8 (CH), 111.2 (CH), 50.1 (CH_2), 35.3 (CH), 21.6 (CH_3), 18.9 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 275 (3) [M(^{37}Cl)]$^+$, 273 (9) [M(^{35}Cl)]$^+$, 134 (100) [$C_9H_{12}N]^+$, 103 (11), 91 (8), 77 (14). HRMS (EI): calcd. ($C_{17}H_{20}ClN$) 273.1279, found 273.1280 [M]$^+$. IR (ATR, neat): λ^{-1} = 3421, 2965, 2919, 2855, 1600, 1514, 1474, 1441, 1376, 1335, 1303, 1188, 1036, 820, 752, 690 cm^{-1}. **29b**: R_f = 0.22 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.7 Hz, 1 H), 7.25-7.13 (m, 3 H), 6.41 (s, 1 H), 6.30 (s, 2 H), 3.17 (t, J = 7.0 Hz, 2 H), 2.87-2.82 (m, 2 H), 2.25 (s, 6 H), 1.96 (quint, J = 7.4 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.9 (C), 139.4 (C), 139.1 (C), 134.1 (C), 130.5 (CH), 129.7 (CH), 127.6 (CH), 127.0 (CH), 120.0 (CH), 111.4 (CH), 44.0 (CH_2), 31.2 (CH_2), 29.4 (CH_2), 21.6 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 275 (6) [M(^{37}Cl)]$^+$, 273 (18) [M(^{35}Cl)]$^+$, 238 (6) [$C_{17}H_{20}N]^+$, 134 (100) [$C_9H_{12}N]^+$, 105 (6) [$C_8H_9]^+$, 91 (8), 77 (9). HRMS (ESI, +): calcd. ($C_{17}H_{21}ClN$) 274.1363, found 274.1361 [M+H]$^+$. IR (ATR, neat): λ^{-1} = 3411, 3062, 3026, 2946, 2918, 2858, 1600, 1513, 1473, 1443, 1336, 1303, 1189, 1051, 1029, 820, 749, 690 cm^{-1}. **29c**: R_f = 0.32 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41-7.35 (m, 2 H), 7.21-7.14 (m, 6 H), 6.39 (s, 1 H), 6.19 (s, 2 H), 3.44 (quint, ^3J = 6.1 Hz, 1 H), 2.97-2.89 (m, 2 H), 2.86-2.78 (m, 2 H), 2.24 (s, 6 H), 2.00-1.92 (m, 2 H), 1.91-1.82 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.5 (C), 139.7 (C), 139.0 (C), 134.0 (C), 130.7 (CH), 129.6 (CH), 127.5 (CH), 126.9 (CH), 119.3 (CH), 111.3 (CH), 52.1 (CH), 34.9 (CH_2), 30.5 (CH_2), 21.6 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 415 (2) [M(^{37}Cl^{37}Cl)]$^+$, 413 (8) [M(^{35}Cl^{37}Cl)]$^+$, 411 (10) [M(^{35}Cl^{35}Cl)]$^+$, 376 (1) [$C_{25}H_{27}{}^{35}ClN]^+$, 272 (100) [$C_{17}H_{19}{}^{35}ClN]^+$, 147 (14), 132 (10), 125 (21) [$C_7H_6{}^{35}Cl]^+$, 103 (7), 91 (6), 77 (8). HRMS (EI): calcd. ($C_{25}H_{27}Cl_2N$) 411.1515, found 411.1519 [M]$^+$. IR (ATR, neat): λ^{-1} = 3055, 3026, 2927, 2860, 1601, 1516, 1475, 1443, 1339, 1190, 1134, 1053, 1033, 822, 750, 682 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-3,4,5-trimethoxyaniline (30a), *N*-(3-(2-chlorophenyl)propyl)-3,4,5-trimethoxyaniline (30b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-3,4,5-trimethoxyaniline (30c):** General procedure B was used to synthesize **30b** from 3,4,5-trimethoxy-*N*-methylaniline (**17**, 2.00 mmol, 394 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 3:1), **30a** (36 mg, 0.11 mmol, 5 %), **30b** (391 mg, 1.16 mmol, 58 %) and **30c** (70 mg, 0.15 mmol, 7 %) were isolated as slightly yellow oils. **30a**: R_f = 0.27 (SiO_2, PE/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (dd, J = 7.9 Hz, J = 0.9 Hz, 1 H), 7.32-7.26 (m, 2 H), 7.19 (td, J = 7.7 Hz, J = 1.8 Hz, 1 H), 5.87 (s, 2 H), 3.82 (s, 6 H), 3.77 (s, 3 H), 3.67 (sext, J = 6.9 Hz, 1 H), 3.39 (dd, J = 12.3 Hz, J = 7.0 Hz, 1 H), 3.20 (dd, J = 12.3 Hz, J = 7.3 Hz, 1 H), 1.36 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 154.0 (C), 144.7 (C), 141.7 (C), 134.1 (C), 130.2 (C), 129.9 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 90.5 (CH), 61.2 (CH_3), 56.0 (CH_3), 50.4 (CH_2), 35.3 (CH), 18.7 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 337 (6) [M(^{37}Cl)]$^+$, 335 (16) [M(^{35}Cl)]$^+$, 322 (2) [$C_{17}H_{19}{}^{37}ClNO_3]^+$, 320 (5) [$C_{17}H_{19}{}^{35}ClNO_3]^+$, 196 (100) [$C_{10}H_{14}NO_3]^+$, 180 (7). HRMS (EI): calcd. ($C_{18}H_{22}ClNO_3$) 335.1283, found 335.1274 [M]$^+$. IR (ATR, neat): λ^{-1} = 3389, 3066, 2962, 2936, 2825, 1607, 1506, 1463, 1455, 1413, 1379, 1233, 1207, 1185, 1126, 1035, 1007, 922, 801, 754, 730, 687, 677, 635, 552, 526 cm^{-1}. **30b**: R_f = 0.22 (SiO_2, PE/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (dd, J = 7.9 Hz, J = 1.1 Hz, 1 H), 7.25-7.12 (m, 3 H), 5.84 (s, 2 H), 3.80 (s, 6 H), 3.76 (s, 3 H), 3.16 (t, J = 7.0 Hz, 2 H), 2.85 (t, J = 7.7 Hz, 2 H), 1.95 (quint, J = 7.2 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 154.0 (C), 145.0 (C), 139.2 (C), 133.9 (C), 130.5 (CH), 130.1 (C), 129.6 (CH), 127.6 (CH), 126.9 (CH), 90.4 (CH), 61.1 (CH_3), 56.0 (CH_3), 44.0 (CH_2), 31.2 (CH_2), 29.5 (CH_2) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 337 (14) [M(^{37}Cl)]$^+$, 335 (42) [M(^{35}Cl)]$^+$, 322 (34) [$C_{17}H_{19}{}^{37}ClNO_3]^+$, 320 (100) [$C_{17}H_{19}{}^{35}ClNO_3]^+$, 292 (8), 196 (18) [$C_{10}H_{14}NO_3]^+$, 125 (32) [$C_7H_6{}^{35}Cl]^+$. HRMS (EI): calcd. ($C_{18}H_{22}ClNO_3$) 335.1283, found 335.1272 [M]$^+$. IR (ATR, neat): λ^{-1} = 2991, 2940, 2839, 1609, 1508, 1464, 1450, 1411, 1374, 1232, 1206, 1185, 1123, 1051, 1007, 802, 751 cm^{-1}. **30c**: R_f = 0.33 (SiO_2, PE/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 2 H), 7.17-7.12 (m, 6 H), 5.73 (s, 2 H), 3.77 (s, 3 H), 3.75 (s, 6 H), 3.55 (quint, J = 6.2 Hz, 1 H), 2.93-2.87 (m, 2 H), 2.84-2.77 (m, 2 H), 1.99-1.92 (m, 2 H), 1.88-1.80 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 154.0 (C), 144.5 (C), 139.5 (C), 133.9 (C), 130.7 (CH), 129.8 (C), 129.6 (CH), 127.5 (CH), 126.9 (CH), 90.6 (CH), 61.2 (CH_3), 55.9 (CH_3), 52.3 (CH), 34.9 (CH_2), 30.4 (CH_2) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 477 (8) [M(^{37}Cl^{37}Cl)]$^+$, 475 (42) [M(^{35}Cl^{37}Cl)]$^+$, 473 (62) [M(^{35}Cl^{35}Cl)]$^+$, 462 (8) [$C_{25}H_{26}{}^{37}Cl{}^{37}ClNO_3]^+$, 460 (40)

$[C_{25}H_{26}{}^{37}Cl^{35}ClNO_3]^+$, 458 (56) $[C_{25}H_{26}{}^{35}Cl^{35}ClNO_3]^+$, 336 (35) $[C_{18}H_{21}{}^{37}ClNO_3]^+$, 334 (100) $[C_{18}H_{21}{}^{35}ClNO_3]^+$, 209 (39), 194 (62), 168 (32), 140 (14), 127 (24) $[C_7H_6{}^{37}Cl]^+$, 125 (74) $[C_7H_6{}^{35}Cl]^+$. HRMS (EI): calcd. ($C_{26}H_{29}Cl_2NO_3$) 473.1519, found 473.1516 $[M]^+$. IR (ATR, neat): λ^{-1} = 3364, 3060, 2934, 2840, 1607, 1507, 1473, 1451, 1412, 1364, 1258, 1233, 1204, 1186, 1124, 1050, 1034, 1012, 944, 799, 749, 679, 633, 525 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-4-fluoroaniline (31a), *N*-(3-(2-chlorophenyl)propyl)-4-fluoroaniline (31b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-4-fluoroaniline (31c):** General procedure B was used to synthesize **31b** from 4-fluoro-*N*-methylaniline (**18**, 2.00 mmol, 250 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **31a** (33 mg, 0.13 mmol, 6 %), **31b** (280 mg, 1.06 mmol, 53 %) and **31c** (52 mg, 0.13 mmol, 6 %) were isolated as slightly yellow oils. **31a**: R_f = 0.30 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.0 Hz, 1 H), 7.31-7.25 (m, 2 H), 7.21-7.14 (m, 1 H), 6.88 (t, J = 8.7 Hz, 2 H), 6.56 (dd, J = 8.4 Hz, J = 4.1 Hz, 2 H), 3.65 (sext, J = 6.9 Hz, 1 H), 3.40-3.31 (m, 1 H), 3.29-3.20 (m, 1 H), 1.34 (d, J = 7.0 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 156.1 (d, $J_{C,F}$ = 236 Hz, C), 144.2 (C), 141.7 (C), 134.3 (C), 129.9 (CH), 127.8 (CH), 127.4 (CH), 127.4 (CH), 115.7 (d, $J_{C,F}$ = 22 Hz, CH), 114.1 (d, $J_{C,F}$ = 6 Hz, CH), 50.8 (CH_2), 35.3 (CH), 18.8 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −127.45 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 265 (3) $[M(^{37}Cl)]^+$, 263 (8) $[M(^{35}Cl)]^+$, 139 (2) $[C_8H_8{}^{35}Cl]^+$, 124 (100) $[C_7H_7FN]^+$, 95 (13) $[C_6H_4F]^+$. HRMS (EI): calcd. ($C_{15}H_{15}ClFN$) 263.0872, found 263.0881 $[M]^+$. IR (ATR, neat): λ^{-1} = 3411, 3061, 2967, 2930, 2873, 1613, 1508, 1475, 1442, 1405, 1379, 1319, 1255, 1218, 1156, 1142, 1118, 1095, 1052, 1035, 1015, 943, 915, 818, 797, 752, 729, 688, 677, 580, 544, 508 cm^{-1}. **31b**: R_f = 0.20 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.8 Hz, 1 H), 7.25-7.13 (m, 3 H), 6.90 (t, J = 8.6 Hz, 2 H), 6.56 (dd, $J_{H,F}$ = 8.8 Hz, J = 4.4 Hz, 2 H), 3.64 (br. s, 1 H), 3.15 (t, J = 7.0 Hz, 2 H), 2.86 (t, J = 7.7 Hz, 2 H), 1.96 (quint, J = 7.4 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 156.0 (d, $J_{C,F}$ = 235 Hz, C), 144.5 (C), 139.3 (C), 134.0 (C), 130.5 (CH), 129.7 (CH), 127.7 (CH), 127.0 (CH), 115.8 (d, $J_{C,F}$ = 22 Hz, CH), 114.0 (t, $J_{C,F}$ = 7 Hz, CH), 44.4 (CH_2), 31.2 (CH_2), 29.5 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −128.19 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 265 (5) $[M(^{37}Cl)]^+$, 263 (15) $[M(^{35}Cl)]^+$, 228 (9) $[C_{15}H_{15}FN]^+$, 124 (100) $[C_7H_7FN]^+$, 111 (6) $[C_6H_4{}^{35}Cl]^+$, 95 (7) $[C_6H_4F]^+$, 77 (5). HRMS (ESI, +): calcd. ($C_{15}H_{16}ClFN$) 264.0955, found 264.0955 $[M+H]^+$. IR (ATR, neat): λ^{-1} = 3414, 3059, 2933, 2864, 1613, 1509, 1474, 1443, 1404, 1372, 1317, 1255, 1217, 1177, 1156, 1131, 1087, 1051, 1029, 817, 749, 726, 697 cm^{-1}. **31c**: R_f = 0.33 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.33 (m, 2 H), 7.16 (s, 6 H), 6.86 (t, J = 8.5 Hz, 2 H), 6.86 (t, J = 8.5 Hz, 2 H), 3.37 (quint, J = 5.9 Hz, 1 H), 2.93-2.85 (m, 2 H), 2.83-2.76 (m, 2 H), 1.99-1.90 (m, 2 H), 1.87-1.78 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 155.8 (d, $J_{C,F}$ = 233 Hz, C), 143.8 (C), 139.6 (C), 134.0 (C), 130.7 (CH), 129.7 (CH), 127.6 (CH), 127.0 (CH), 115.8 (d, $J_{C,F}$ = 22 Hz, CH), 114.2 (CH), 53.2 (CH), 34.7 (CH_2), 30.4 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −128.49 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 405 (1) $[M(^{37}Cl^{37}Cl)]^+$, 403 (5) $[M(^{35}Cl^{37}Cl)]^+$, 401 (7) $[M(^{35}Cl^{35}Cl)]^+$, 264 (34) $[C_{15}H_{14}{}^{37}ClFN]^+$, 262 (100) $[C_{15}H_{14}{}^{35}ClFN]^+$, 127 (20) $[C_7H_6{}^{37}Cl]^+$, 125 (60) $[C_7H_6{}^{35}Cl]^+$. HRMS (EI): calcd. ($C_{23}H_{22}Cl_2FN$) 401.1108, found 401.1098 $[M]^+$. IR (ATR, neat): λ^{-1} = 3407, 3059, 2932, 2862, 1612, 1572, 1507, 1474, 1454, 1443, 1404, 1316, 1262, 1219, 1155, 1133, 1102, 1051, 1032, 943, 817, 786, 747, 726, 680, 606, 555, 506 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-3-fluoroaniline (32a), *N*-(3-(2-chlorophenyl)propyl)-3-fluoroaniline (32b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-3-fluoroaniline (32c):** General procedure B was used to synthesize **32b** from 3-fluoro-*N*-methylaniline (**19**, 2.00 mmol, 250 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **32b** (230 mg, 0.87 mmol, 44 %) was isolated as slightly yellow oil. In addition, a second fraction that contained a mixture of **32a** and **32c** (52 mg, **32a**/**32c** = 62:38) was also isolated. **32b**: R_f = 0.18 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (dd, J = 7.7 Hz, J = 1.4 Hz, 1 H), 7.25-7.14 (m, 3 H), 7.09 (td, J = 8.1 Hz, J = 6.8 Hz, 1 H), 6.41-6.33 (m, 2 H), 6.28 (dt, J = 11.7 Hz, J = 2.3 Hz, 1 H), 3.81 (br. s, 1 H), 3.16 (t, J = 7.0 Hz, 2 H), 2.89-2.83 (m, 2 H), 2.01-1.92 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 164.3 (d, $J_{C,F}$ = 243 Hz, C), 150.2 (d, $J_{C,F}$ = 11 Hz, C), 139.2 (C), 134.0 (C), 130.4 (CH), 130.3 (d, $J_{C,F}$ = 10 Hz, CH), 129.7 (CH), 127.7 (CH), 127.0 (CH), 108.8 (CH), 103.7 (d, $J_{C,F}$ = 22 Hz, CH), 99.4 (d, $J_{C,F}$ = 25 Hz, CH), 43.4 (CH_2), 31.2 (CH_2), 29.4 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −112.96 (d, $^3J_{H,F}$ = 14.5 Hz) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 265 (5) $[M(^{37}Cl)]^+$, 263 (14) $[M(^{35}Cl)]^+$, 228 (12) $[C_{15}H_{15}FN]^+$, 124 (100) $[C_7H_7FN]^+$, 95 (8) $[C_6H_4F]^+$. HRMS (EI): calcd. ($C_{15}H_{15}ClFN$) 263.0872, found 263.0876 $[M]^+$. IR (ATR, neat): λ^{-1} = 2941, 2862, 1621, 1588, 1510, 1496, 1474, 1442, 1335, 1285, 1257, 1176, 1148, 1051, 1029, 997, 964, 940, 829, 749, 680 cm^{-1}.

***N*-(2-(2-Chlorophenyl)propyl)-4-(trifluoromethoxy)aniline (33a), *N*-(3-(2-chlorophenyl)propyl)-4-(trifluoromethoxy)aniline (33b) and *N*-(1,5-bis(2-chlorophenyl)pentan-3-yl)-4-(trifluoromethoxy)aniline (33c):** General procedure B was used to synthesize **33b** from *N*-methyl-4-(trifluoromethoxy)aniline (**20**, 2.00 mmol, 382 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **33b** (275 mg, 0.83 mmol, 42 %) and **33c** (30 mg, 0.06 mmol, 3 %) were isolated as slightly yellow oils. Furthermore, two additional fractions were isolated. The first fraction contained a mixture of **33a** and **33c** (33 mg, **33a**/**33c** = 68:32). The second fraction contained a mixture of **33a** and **33b** (106 mg, **33a**/**33b** = 17:83). **33b**: R_f = 0.18 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 (dd, J = 7.7 Hz, J = 1.1 Hz, 1 H), 7.25-7.14 (m, 3 H), 7.04 (d, J = 8.6 Hz, 2 H), 6.56 (d, J = 8.9 Hz, 2 H), 3.93 (br. s, 1 H), 3.17 (t, J = 7.0 Hz, 2 H), 2.86 (t, J = 7.7 Hz, 2 H), 1.97 (quint, J = 7.3 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 146.9 (C), 140.7 (C), 139.2 (C), 134.1 (C), 130.5 (CH), 129.8 (CH), 127.7 (CH), 127.0 (CH), 122.5 (CH), 120.9 (q, $J_{C,F}$ = 255 Hz, C), 113.3 (CH), 43.9 (CH_2), 31.2 (CH_2), 29.4 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −58.45 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 331 (5) $[M(^{37}Cl)]^+$, 329 (14) $[M(^{35}Cl)]^+$, 294 (8) $[C_{16}H_{15}F_3NO]^+$, 190 (100) $[C_8H_7F_3NO]^+$, 177 (5), 162 (4), 125 (7) $[C_7H_6{}^{35}Cl]^+$, 77 (8). HRMS (ESI, +): calcd. ($C_{16}H_{16}ClF_3NO$) 330.0873, found 330.0864 $[M+H]^+$. IR (ATR, neat): λ^{-1} = 3424, 3063, 2934, 2866, 1613, 1514, 1475, 1444, 1248, 1220, 1199, 1152, 1117, 1052, 1029, 916, 827, 793, 750, 673 cm^{-1}. **33c**: R_f = 0.23 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38-7.31 (m, 2 H), 7.19-7.10 (m, 6 H), 7.00 (d, J = 8.5 Hz, 2 H), 6.48 (br. s, 2 H), 3.39 (quint, J = 5.8 Hz, 1 H), 2.92-2.84 (m, 2 H), 2.84-2.75 (m, 2 H), 2.01-1.91 (m, 2 H), 1.89-1.77 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 146.1 (C), 140.5 (C), 139.4 (C), 134.0 (C), 130.7 (CH), 129.7 (CH), 127.7 (CH), 127.0 (CH), 122.6 (CH), 120.8 (q, $^1J_{C,F}$ = 255 Hz, C), 113.4 (CH), 52.7 (CH), 34.6 (CH_2), 30.4 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −58.42 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 471 (2) $[M(^{37}Cl^{37}Cl)]^+$, 469 (7) $[M(^{35}Cl^{37}Cl)]^+$, 467 (10) $[M(^{35}Cl^{35}Cl)]^+$, 432 (2) $[C_{24}H_{22}{}^{35}ClF_3NO]^+$, 330 (34) $[C_{16}H_{14}{}^{37}ClF_3NO]^+$, 328 (100) $[C_{16}H_{14}{}^{35}ClF_3NO]^+$, 127 (27) $[C_7H_6{}^{37}Cl]^+$,125 (80) $[C_7H_6{}^{35}Cl]^+$. HRMS (EI): calcd. ($C_{24}H_{22}Cl_2F_3NO$) 467.1025, found 467.1018 $[M]^+$. IR (ATR, neat): λ^{-1} = 3413, 3065, 2930, 2857, 1732, 1611, 1572, 1511, 1474, 1443, 1410, 1324, 1251, 1220, 1199, 1154, 1134, 1112, 1051, 1033, 943, 916, 826, 796, 748, 726, 680, 650, 615, 594, 525 cm^{-1}.

***N*-(2-(2-Chlorophenyl)-1-phenylpropyl)aniline (34a) and *N*-(3-(2-chlorophenyl)-1-phenylpropyl)aniline (34b):** General procedure B was used to synthesize **34b** from *N*-benzylaniline (**21**, 2.00 mmol, 367 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **34a** (26 mg, 0.08 mmol, 4 %) was isolated as a slightly yellow oil. In addition, a second fraction that contained a mixture of **34b**

and *N*-benzylaniline was also isolated. *N*-Benzylaniline was removed by subsequent bulb-to-bulb distillation (140 °C, 1 × 10^{-3} mbar) to obtain **34b** (263 mg, 0.82 mmol, 41 %) as a slightly yellow oil. **34a**: R_f = 0.40 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.33 (m, 3 H), 7.30-7.25 (m, 3 H), 7.24-7.19 (m, 2 H), 7.14 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 1 H), 7.06-7.02 (m, 2 H), 6.61 (t, *J* = 7.3 Hz, 1 H), 6.45 (d, *J* = 7.7 Hz, 2 H), 4.70 (d, *J* = 5.0 Hz, 1 H), 4.23 (br. s, 1 H), 3.85 (qd, *J* = 7.2 Hz, *J* = 5.1 Hz, 1 H), 1.32 (d, *J* = 7.2 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.6 (C), 142.0 (C), 141.0 (C), 134.1 (C), 130.0 (CH), 129.1 (CH), 128.7 (CH), 128.3 (CH), 127.9 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 117.5 (CH), 113.8 (CH), 61.3 (CH), 42.1 (CH), 14.7 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 323 (1) [M(^{37}Cl)]$^+$, 321 (3) [M(^{35}Cl)]$^+$, 182 (100) [$C_{13}H_{12}N$]$^+$, 104 (16), 77 (30) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{21}H_{20}ClN$) 321.1279, found 321.1282 [M]$^+$. IR (ATR, neat): λ^{-1} = 3426, 3404, 3022, 2973, 2925, 2872, 1600, 1503, 1475, 1451, 1433, 1312, 1286, 1180, 1076, 1033, 870, 748, 729, 690 cm^{-1}. **34b**: R_f = 0.35 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43-7.34 (m, 5 H), 7.30-7.25 (m, 1 H), 7.22-7.12 (m, 5 H), 6.70 (t, *J* = 7.3 Hz, 1 H), 6.58 (d, *J* = 7.8 Hz, 2 H), 4.43 (t, *J* = 6.8 Hz, 1 H), 2.99-2.90 (m, 1 H), 2.84-2.76 (m, 1 H), 2.16 (q, *J* = 7.5 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.2 (C), 143.6 (C), 139.2 (C), 133.9 (C), 130.5 (CH), 129.7 (CH), 129.2 (CH), 128.7 (CH), 127.7 (CH), 127.2 (CH), 127.0 (CH), 126.5 (CH), 117.5 (CH), 113.5 (CH), 58.1 (CH), 38.6 (CH_2), 30.9 (CH_2) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 323 (2) [M(^{37}Cl)]$^+$, 321 (5) [M(^{35}Cl)]$^+$, 182 (100) [$C_{13}H_{12}N$]$^+$, 127 (5) [$C_7H_6{}^{37}Cl$]$^+$, 125 (13) [$C_7H_6{}^{35}Cl$]$^+$, 104 (12), 91 (9), 77 (17) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{21}H_{20}ClN$) 321.1279, found 321.1289 [M]$^+$. IR (ATR, neat): λ^{-1} = 3417, 3403, 3053, 3019, 2937, 2863, 1600, 1502, 1473, 1451, 1427, 1316, 1259, 1180, 1051, 1031, 745, 691 cm^{-1}.

2-(1-(2-Chlorophenyl)ethyl)-1,2,3,4-tetrahydroquinoline (35a), 2-(2-chlorophenethyl)-1,2,3,4-tetrahydroquinoline (35b) and 2,2-bis(2-chlorophenethyl)-1,2,3,4-tetrahydroquinoline (35c): General procedure B was used to synthesize **35b** from 1,2,3,4-tetrahydroquinoline (**22**, 2.00 mmol, 266 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **35b** (374 mg, 1.38 mmol, 69 %) was isolated as a slightly yellow oil. In addition, a second fraction that contained a mixture of **35a** and **35c** (20 mg, **35a**/**35c** = 56:44) was also isolated. **35b**: R_f = 0.25 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (dd, *J* = 7.8 Hz, *J* = 1.1 Hz, 1 H), 7.27 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1 H), 7.22 (td, *J* = 7.4 Hz, *J* = 1.2 Hz, 1 H), 7.17 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 1 H), 7.02-6.95 (m, 2 H), 6.64 (t, *J* = 7.4 Hz, 1 H), 6.51 (d, *J* = 7.8 Hz, 1 H), 3.70 (br. s, NH), 3.35 (dtd, *J* = 9.3 Hz, *J* = 6.3 Hz, *J* = 3.0 Hz, 1 H), 2.95-2.74 (m, 4 H), 2.09-2.02 (m, 1 H), 1.86 (q, *J* = 7.9 Hz, 2 H), 1.69-1.78 (m, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 144.5 (C), 139.6 (C), 134.0 (C), 130.4 (CH), 129.7 (CH), 129.4 (CH), 127.6 (CH), 127.0 (CH), 126.9 (CH), 121.5 (C), 117.3 (CH), 114.4 (CH), 51.3 (CH), 36.7 (CH_2), 29.9 (CH_2), 28.0 (CH_2), 26.3 (CH_2) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 273 (4) [M(^{37}Cl)]$^+$, 271 (12) [M(^{35}Cl)]$^+$, 132 (100) [$C_9H_{10}N$]$^+$, 117 (10), 77 (7). HRMS (EI): calcd. ($C_{17}H_{18}ClN$) 271.1122, found 271.1135 [M]$^+$. IR (ATR, neat): λ^{-1} = 3052, 3016, 2926, 2843, 1606, 1585, 1474, 1443, 1354, 1309, 1275, 1251, 1197, 1154, 1123, 1050, 1034, 930, 833, 743, 681 cm^{-1}.

***N*-(1-(2-Chlorophenyl)pentan-3-yl)aniline (36b):** General procedure B was used to synthesize **36b** from *N*-propylaniline (**23**, 2.00 mmol, 270 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **36b** (221 mg, 0.81 mmol, 40 %) was isolated as a slightly yellow oil. R_f = 0.30 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1 H), 7.20-7.11 (m, 5 H), 6.68 (t, *J* = 7.0 Hz, 1 H), 6.61 (d, *J* = 5.5 Hz, 2 H), 3.51 (br. s, 1 H), 3.36 (quint, *J* = 5.9 Hz, 1 H), 2.89 (ddd, *J* = 13.6 Hz, *J* = 10.5 Hz, *J* = 5.3 Hz, 1 H), 2.76 (ddd, *J* = 13.6 Hz, *J* = 10.5 Hz, *J* = 6.0 Hz, 1 H), 1.93-1.84 (m, 1 H), 1.81-1.71 (m, 1 H), 1.70-1.63 (m, 1 H), 1.61-1.51 (m, 1 H), 0.96 (t, *J* = 7.4 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.9 (C), 139.9 (C), 134.0 (C), 130.6 (CH), 129.6 (CH), 129.4 (CH), 127.5 (CH), 126.9 (CH), 117.1 (CH), 113.3 (CH), 54.1 (CH), 34.5 (CH_2), 30.5 (CH_2), 27.4 (CH_2), 10.2 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 275 (5) [M(^{37}Cl)]$^+$, 273 (14) [M(^{35}Cl)]$^+$, 246 (22) [$C_{15}H_{15}{}^{37}ClN$]$^+$, 244 (64) [$C_{15}H_{15}{}^{35}ClN$]$^+$, 134 (100) [$C_9H_{12}N$]$^+$, 127 (10) [$C_7H_6{}^{37}Cl$]$^+$, 125 (31) [$C_7H_6{}^{35}Cl$]$^+$, 77 (14) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{17}H_{20}ClN$) 273.1279, found 273.1286 [M]$^+$. IR (ATR, neat): λ^{-1} = 2963, 2930, 2867, 1600, 1504, 1474, 1429, 1319, 1277, 1249, 1180, 1136, 1051, 1034, 993, 866, 744, 691 cm^{-1}.

***N*-(1-(2-Chlorophenyl)-4-methylpentan-3-yl)aniline (37b):** General procedure B was used to synthesize **37b** from *N*-isobutylaniline (**24**, 2.00 mmol, 298 mg) and *ortho*-chlorostyrene (**7**, 2.40 mmol, 333 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **37b** (100 mg, 0.35 mmol, 17 %) was isolated as a slightly yellow oil. R_f = 0.38 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 7.2 Hz, 1 H), 7.22-7.11 (m, 5 H), 6.69 (t, *J* = 7.1 Hz, 1 H), 6.63 (d, *J* = 7.2 Hz, 2 H), 3.34-3.27 (m, 1 H), 2.98-2.90 (m, 1 H), 2.78-2.69 (m, 1 H), 2.02-1.89 (m, 2 H), 1.68-1.58 (m, 1 H), 0.97 (d, *J* = 7.0 Hz, 3 H), 0.94 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.5 (C), 140.0 (C), 133.9 (C), 130.7 (CH), 129.6 (CH), 129.4 (CH), 127.5 (CH), 126.9 (CH), 116.8 (CH), 113.2 (CH), 58.2 (CH), 31.8 (CH_2), 31.2 (CH), 31.1 (CH_2), 18.5 (CH_3), 18.3 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 289 (3) [M(^{37}Cl)]$^+$, 287 (8) [M(^{35}Cl)]$^+$, 246 (34) [$C_{15}H_{15}{}^{37}ClN$]$^+$, 244 (100) [$C_{15}H_{15}{}^{35}ClN$]$^+$, 148 (19) [$C_{10}H_{14}N$]$^+$, 127 (14) [$C_7H_6{}^{37}Cl$]$^+$, 125 (40) [$C_7H_6{}^{35}Cl$]$^+$, 77 (13) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{18}H_{22}ClN$) 287.1435, found 287.1433 [M]$^+$. IR (ATR, neat): λ^{-1} = 2957, 2932, 2869, 1599, 1504, 1473, 1442, 1430, 1320, 1251, 1180, 1051, 1034, 865, 744 cm^{-1}.

***N*-(2-(2-Chloro-4-fluorophenyl)propyl)aniline (44a), *N*-(3-(2-chloro-4-fluorophenyl)propyl)aniline (44b) and *N*-(1,5-bis(2-chloro-4-fluorophenyl)pentan-3-yl)aniline (44c):** General procedure B was used to synthesize **44b** from *N*-methylaniline (**8**, 2.00 mmol, 214 mg) and 2-chloro-4-fluorostyrene (**38**, 2.40 mmol, 376 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), a mixture of **44b** and *N*-methylaniline was isolated. *N*-Methylaniline was removed by subsequent bulb-to-bulb distillation (90 °C, 1 × 10^{-3} mbar) to obtain **44b** (300 mg, 1.14 mmol, 57 %) as a slightly yellow oil. In addition, a second fraction that contained a mixture of **44a** and **44c** (141 mg, **44a**/**44c** = 32:68) was also isolated. **44b**: R_f = 0.15 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23-7.18 (m, 3 H), 7.13 (dd, *J* = 8.6 Hz, *J* = 2.6 Hz, 1 H), 6.93 (td, *J* = 8.3 Hz, *J* = 2.6 Hz, 1 H), 6.73 (t, *J* = 7.3 Hz, 1 H), 6.64-6.61 (m, 2 H), 3.66 (br. s, 1 H), 3.19 (t, *J* = 7.0 Hz, 2 H), 2.86-2.81 (m, 2 H), 1.98-1.91 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 161.1 (d, $J_{C,F}$ = 248 Hz, C), 148.3 (C), 135.2 (d, $J_{C,F}$ = 4 Hz, C), 134.4 (d, $J_{C,F}$ = 10 Hz, C), 131.2 (d, $J_{C,F}$ = 9 Hz, CH), 129.4 (CH), 117.5 (CH), 116.9 (d, $J_{C,F}$ = 25 Hz, CH), 114.1 (d, $J_{C,F}$ = 21 Hz, CH), 112.9 (CH), 43.4 (CH_2), 30.5 (CH_2), 29.7 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.94 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 265 (5) [M(^{37}Cl)]$^+$, 263 (14) [M(^{35}Cl)]$^+$, 228 (5) [$C_{15}H_{15}FN$]$^+$, 143 (5) [$C_7H_5{}^{35}ClF$]$^+$, 106 (100) [C_7H_8N]$^+$, 93 (6), 77 (14) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{15}H_{15}ClFN$) 263.0872, found 263.0871 [M]$^+$. IR (ATR, neat): λ^{-1} = 2953, 2866, 1601, 1505, 1489, 1430, 1399, 1319, 1261, 1230, 1179, 1040, 992, 903, 857, 818, 747, 690 cm^{-1}.

***N*-(2-(2-Chloro-6-fluorophenyl)propyl)aniline (45a), *N*-(3-(2-chloro-6-fluorophenyl)propyl)aniline (45b) and *N*-(1,5-bis(2-chloro-6-fluorophenyl)pentan-3-yl)aniline (45c):** General procedure B was used to synthesize **45b** from *N*-methylaniline (**8**, 2.00 mmol, 214 mg) and 2-chloro-6-fluorostyrene (**39**, 2.40 mmol, 376 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 50:1), **45b** (321 mg, 1.22 mmol, 61 %) was isolated as a slightly yellow oil. In addition, a second fraction that contained a mixture

of **45a** and **45c** (76 mg, **45a**/**45c** = 22:78) was also isolated. **45b**: R_f = 0.19 (SiO_2, PE/EtOAc, 50:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21-7.08 (m, 4 H), 6.97 (t, J = 8.6 Hz, 1 H), 6.71 (t, J = 7.3 Hz, 1 H), 6.62 (d, J = 7.9 Hz, 2 H), 3.70 (br. s, 1 H), 3.19 (t, J = 7.0 Hz, 2 H), 2.91 (t, J = 7.5 Hz, 2 H), 1.92 (quint, J = 7.0 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 161.6 (d, $J_{C,F}$ = 247 Hz, C), 148.4 (C), 135.2 (d, $J_{C,F}$ = 6 Hz, C), 129.4 (CH), 127.8 (d, $J_{C,F}$ = 10 Hz, CH), 127.7 (d, $J_{C,F}$ = 19 Hz, C), 125.4 (d, $J_{C,F}$ = 3 Hz, CH), 117.4 (CH), 114.0 (d, $J_{C,F}$ = 23 Hz, CH), 112.9 (CH), 43.5 (CH_2), 28.7 (CH_2), 24.1 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.16 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 265 (10) [M(^{37}Cl)]$^+$, 263 (28) [M(^{35}Cl)]$^+$, 228 (4) [$C_{15}H_{15}FN$]$^+$, 143 (7) [$C_7H_5{}^{35}ClF$]$^+$, 106 (100) [C_7H_8N]$^+$, 93 (6), 77 (22) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{15}H_{15}ClFN$) 263.0872, found 263.0873 [M]$^+$. IR (ATR, neat): λ^{-1} = 3416, 2948, 2870, 1602, 1576, 1505, 1450, 1320, 1243, 1181, 1065, 992, 957, 896, 869, 777, 747, 721, 691, 630 cm^{-1}.

***N*-(2-(2-Chloro-4-(methylthio)phenyl)propyl)aniline (46a) and *N*-(3-(2-chloro-4-(methylthio)phenyl)propyl)aniline (46b):** General procedure B was used to synthesize **46b** from *N*-methylaniline (**8**, 2.00 mmol, 214 mg) and 2-chloro-4-(methylthio)styrene (**40**, 2.40 mmol, 443 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 20:1), **46b** (233 mg, 0.80 mmol, 40 %) was isolated as a slightly yellow oil. In addition, a second fraction that contained a mixture of **46a** and *N*-methylaniline (69 mg) was also isolated. **46b**: R_f = 0.19 (SiO_2, PE/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24 (d, J = 1.9 Hz, 1 H), 7.20-7.15 (m, 2 H), 7.13 (d, J = 8.1 Hz, 1 H), 7.08 (dd, J = 8.0 Hz, J = 1.9 Hz, 1 H), 6.70 (t, J = 7.3 Hz, 1 H), 6.60 (d, J = 8.4 Hz, 2 H), 3.74 (br. s, 1 H), 3.17 (t, J = 7.0 Hz, 2 H), 2.83-2.77 (m, 2 H), 2.47 (s, 3 H), 1.93 (quint, J = 7.1 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.3 (C), 137.9 (C), 136.1 (C), 134.5 (C), 130.7 (CH), 129.4 (CH), 127.3 (CH), 125.4 (CH), 117.5 (CH), 113.0 (CH), 43.5 (CH_2), 30.7 (CH_2), 29.6 (CH_2), 16.1 (CH_3) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 293 (5) [M(^{37}Cl)]$^+$, 291 (13) [M(^{35}Cl)]$^+$, 255 (8), 198 (4), 171 (3) [$C_8H_8{}^{35}ClS$]$^+$, 106 (100) [C_7H_8N]$^+$, 77 (14) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{16}H_{18}ClNS$) 291.0843, found 291.0835 [M]$^+$. IR (ATR, neat): λ^{-1} = 3461, 3402, 3371, 3051, 3019, 2926, 2859, 1601, 1505, 1475, 1431, 1379, 1318, 1257, 1179, 1105, 1046, 869, 849, 813, 747, 691 cm^{-1}.

***N*-(2-(2-Chloro-3-methoxyphenyl)propyl)aniline (47a) and *N*-(3-(2-chloro-3-methoxyphenyl)propyl)aniline (47b):** General procedure B was used to synthesize **47b** from *N*-methylaniline (**8**, 2.00 mmol, 214 mg) and 2-chloro-3-methoxystyrene (**41**, 2.40 mmol, 405 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **47a** (45 mg, 0.16 mmol, 8 %) and **47b** containing some impurities were isolated as slightly yellow oils. **47b** (265 mg, 0.96 mmol, 48 %) was purified by subsequent bulb-to-bulb distillation (200 °C, 1 × 10^{-3} mbar). **47a**: R_f = 0.08 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24 (t, J = 8.0 Hz, 1 H), 7.20-7.15 (m, 2 H), 6.93 (dd, J = 7.9 Hz, J = 1.2 Hz, 1 H), 6.84 (dd, J = 8.2 Hz, J = 1.2 Hz, 1 H), 6.70 (t, J = 7.3 Hz, 1 H), 6.62 (d, J = 7.7 Hz, 2 H), 3.92 (s, 3 H), 3.73 (sext, J = 6.9 Hz, 1 H), 3.38 (dd, J = 12.2 Hz, J = 7.4 Hz, 1 H), 3.28 (dd, J = 12.2 Hz, J = 6.9 Hz, 1 H), 1.34 (d, J = 6.9 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 155.3 (C), 148.2 (C), 143.5 (C), 129.3 (CH), 127.5 (CH), 122.6 (C), 119.1 (CH), 117.4 (CH), 113.0 (CH), 110.0 (CH), 56.3 (CH_3), 49.9 (CH_2), 35.5 (CH), 18.9 (CH) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 277 (1) [M(^{37}Cl)]$^+$, 275 (3) [M(^{35}Cl)]$^+$, 240 (2) [$C_{16}H_{18}NO$]$^+$, 106 (100) [C_7H_8N]$^+$, 77 (14) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{16}H_{18}ClNO$) 275.1071, found 275.1072 [M]$^+$. IR (ATR, neat): λ^{-1} = 2958, 2930, 2871, 2838, 1603, 1575, 1507, 1473, 1434, 1380, 1320, 1269, 1182, 1062, 1045, 1022, 871, 782, 749, 724, 694, 643 cm^{-1}. **47b**: R_f = 0.07 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22-7.14 (m, 3 H), 6.87 (d, J = 7.6 Hz, 1 H), 6.82 (d, J = 8.2 Hz, 1 H), 6.71 (t, J = 7.3 Hz, 1 H), 6.62 (d, J = 7.8 Hz, 2 H), 3.91 (s, 3 H), 3.69 (br. s, 1 H), 3.19 (t, J = 7.0 Hz, 2 H), 2.89 (t, J = 7.7 Hz, 2 H), 1.97 (quint, J = 7.3 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 155.3 (C), 148.4 (C), 141.1 (C), 129.3 (CH), 127.1 (CH), 122.3 (CH), 122.3 (C), 117.3 (CH), 112.9 (CH), 109.8 (CH), 56.3 (CH_3), 43.6 (CH_2), 31.4 (CH_2), 29.5 (CH_2) ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 277 (2) [M(^{37}Cl)]$^+$, 275 (7) [M(^{35}Cl)]$^+$, 240 (26) [$C_{16}H_{18}NO$]$^+$, 106 (100) [C_7H_8N]$^+$, 77 (16) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{16}H_{18}ClNO$) 275.1071, found 275.1080 [M]$^+$. IR (ATR, neat): λ^{-1} = 2937, 2836, 1601, 1574, 1505, 1470, 1452, 1433, 1303, 1266, 1179, 1153, 1115, 1081, 1055, 992, 871, 782, 747, 720 cm^{-1}.

***N*-(2-(2-Chloro-3-(trifluoromethyl)phenyl)propyl)aniline (48a), *N*-(3-(2-chloro-3-(trifluoromethyl)phenyl)propyl)aniline (48b) and *N*-(1,5-bis(2-chloro-3-(trifluoromethyl)phenyl)pentan-3-yl)aniline (48c):** General procedure B was used to synthesize **48b** from *N*-methylaniline (**8**, 2.00 mmol, 214 mg) and 2-chloro-3-(trifluoromethyl)styrene (**42**, 2.40 mmol, 496 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 20:1), **48a** (11 mg, 0.04 mmol, 2 %) was isolated as a slightly yellow oil. In addition, a second fraction that contained a mixture of **48b** and **48c** (448 mg) was also isolated. The mixture was subjected to bulb-to-bulb distillation (160 °C, 1 × 10^{-3} mbar) to obtain **48b** (312 mg, 0.99 mmol, 50 %) as a yellow oil. The residue contained **48c** (79 mg, 0.15 mmol, 8 %) as a brown oil. **48a**: R_f = 0.13 (SiO_2, PE/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (dd, J = 7.8 Hz, J = 1.3 Hz, 1 H), 7.49 (dd, J = 7.7 Hz, J = 0.9 Hz, 1 H), 7.36 (t, J = 7.8 Hz, 1 H), 7.19-7.14 (m, 2 H), 6.71 (t, J = 7.3 Hz, 1 H), 6.62 (dd, J = 8.5 Hz, J = 0.9 Hz, 2 H), 3.79 (sext, J = 7.0 Hz, 1 H), 3.42 (dd, J = 12.5 Hz, J = 7.1 Hz, 1 H), 3.29 (dd, J = 12.6 Hz, J = 7.0 Hz, 1 H), 1.36 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.9 (C), 144.5 (C), 132.1 (C), 130.9 (CH), 129.4 (CH), 129.3 (q, $J_{C,F}$ = 31 Hz, C), 127.0 (CH), 126.0 (q, $J_{C,F}$ = 6 Hz, CH), 123.2 (q, $J_{C,F}$ = 273 Hz, C), 117.9 (CH), 113.1 (CH), 49.9 (CH_2), 35.4 (CH), 18.9 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.40 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 315 (1) [M(^{37}Cl)]$^+$, 313 (4) [M(^{35}Cl)]$^+$, 106 (100) [C_7H_8N]$^+$, 77 (14) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{16}H_{15}ClF_3N$) 313.0840, found 313.0837 [M]$^+$. IR (ATR, neat): λ^{-1} = 2967, 2928, 2887, 1604, 1508, 1473, 1433, 1316, 1260, 1167, 1131, 1097, 1045, 871, 804, 751, 736, 694, 636, 610 cm^{-1}. **48b**: R_f = 0.10 (SiO_2, PE/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (dd, J = 7.8 Hz, J = 1.2 Hz, 1 H), 7.44 (d, J = 7.6 Hz, 1 H), 7.30 (t, J = 7.7 Hz, 1 H), 7.22-7.17 (m, 2 H), 6.72 (t, J = 7.3 Hz, 1 H), 6.62 (dd, J = 8.5 Hz, J = 0.9 Hz, 2 H), 3.67 (br. s, 1 H), 3.22 (t, J = 7.0 Hz, 2 H), 2.98-2.92 (m, 2 H), 2.02-1.94 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.3 (C), 142.0 (C), 133.8 (CH), 131.9 (C), 129.4 (CH), 129.2 ($J_{C,F}$ = 31 Hz, C), 126.6 (CH), 125.8 ($J_{C,F}$ = 6 Hz, CH), 123.2 (q, $J_{C,F}$ = 273 Hz, C), 117.6 (CH), 113.0 (CH), 43.6 (CH_2), 31.4 (CH_2), 29.4 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.36 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 315 (4) [M(^{37}Cl)]$^+$, 313 (11) [M(^{35}Cl)]$^+$, 106 (100) [C_7H_8N]$^+$, 77 (13) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{16}H_{15}ClF_3N$) 313.0840, found 313.0838 [M]$^+$. IR (ATR, neat): λ^{-1} = 3423, 3049, 2931, 2870, 1603, 1506, 1433, 1315, 1258, 1163, 1129, 1092, 1041, 800, 748, 733, 692 cm^{-1}. **48c**: R_f = 0.10 (SiO_2, PE/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (dd, J = 7.8 Hz, J = 1.3 Hz, 2 H), 7.36 (d, J = 7.6 Hz, 2 H), 7.25 (t, J = 7.7 Hz, 2 H), 7.21-7.15 (m, 2 H), 6.72 (t, J = 7.3 Hz, 1 H), 6.55 (dd, J = 8.5 Hz, J = 0.9 Hz, 2 H), 3.52 (br. s, 1 H), 3.47 (quint, J = 6.8 Hz, 1 H), 3.00 (ddd, J = 13.7 Hz, J = 10.1 Hz, J = 5.5 Hz, 2 H), 2.90 (ddd, J = 13.6 Hz, J = 10.1 Hz, J = 6.1 Hz, 2 H), 2.03-1.94 (m, 2 H), 1.90-1.81 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.6 (C), 142.1 (C), 134.1 (CH), 131.8 (C), 129.5 (CH), 129.1 (q, $J_{C,F}$ = 31 Hz, C), 126.6 (CH), 125.7 (q, $J_{C,F}$ = 6 Hz, CH), 123.2 (q, $J_{C,F}$ = 273 Hz, C), 117.5 (CH), 113.3 (CH), 52.2 (CH), 34.9 (CH_2), 30.6 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.29 ppm. GC/MS (EI, 70 eV): *m*/*z* (%) = 523 (1) [M(^{37}Cl^{37}Cl)]$^+$, 521 (6) [M(^{35}Cl^{37}Cl)]$^+$, 519 (8) [M(^{35}Cl^{35}Cl)]$^+$, 314 (32) [$C_{16}H_{14}{}^{37}ClF_3N$]$^+$, 312 (100) [$C_{16}H_{14}{}^{35}ClF_3N$]$^+$, 195 (4) [$C_8H_5{}^{37}ClF_3$]$^+$, 193 (12) [$C_8H_5{}^{35}ClF_3$]$^+$, 77 (7) [$C_6H_5$]$^+$. HRMS (EI): calcd. ($C_{25}H_{21}Cl_2F_6N$) 519.0950, found 519.0946 [M]$^+$. IR (ATR, neat): λ^{-1} = 2968, 2932, 1601, 1504, 1433, 1314, 1254, 1163, 1128, 1091, 1045, 799, 748, 733, 693 cm^{-1}.

***N*-(2-(2-Chloro-4-methylphenyl)propyl)aniline (49a), *N*-(3-(2-chloro-4-methylphenyl)propyl)aniline (49b) and *N*-(1,5-bis(2-chloro-4-methylphenyl)pentan-3-yl)aniline (49c):** General procedure B was

used to synthesize **49b** from *N*-methylaniline (**8**, 2.00 mmol, 214 mg) and 2-chloro-4-methylstyrene (**43**, 2.40 mmol, 366 mg) with catalyst **II** (0.20 mmol, 154 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **49a** (35 mg, 0.13 mmol, 7 %), **49b** (238 mg, 0.92 mmol, 46 %) and **49c** (31 mg, 0.08 mmol, 4 %) were isolated as slightly yellow oils. **49a**: R_f = 0.27 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25-7.22 (m, 1 H), 7.21-7.16 (m, 3 H), 7.08 (d, J = 7.0 Hz, 1 H), 6.71 (t, J = 7.3 Hz, 1 H), 6.63 (d, J = 7.7 Hz, 2 H), 3.78 (br. s, 1 H), 3.62 (sext, J = 7.0 Hz, 1 H), 3.37 (dd, J = 12.2 Hz, J = 7.4 Hz, 1 H), 3.26 (dd, J = 12.2 Hz, J = 6.9 Hz, 1 H), 2.33 (s, 3 H), 1.33 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.1 (C), 138.6 (C), 137.8 (C), 133.9 (C), 130.3 (CH), 129.3 (CH), 128.2 (CH), 127.2 (CH), 117.5 (CH), 113.0 (CH), 50.0 (CH_2), 35.0 (CH), 20.8 (CH_3), 19.0 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 261 (2) [M(^{37}Cl)]$^+$, 259 (6) [M(^{35}Cl)]$^+$, 106 (100) [C_7H_8N]$^+$, 77 (13) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{16}H_{18}ClN$) 259.1122, found 259.1120 [M]$^+$. IR (ATR, neat): λ^{-1} = 3413, 3053, 2974, 2965, 1604, 1507, 1496, 1456, 1433, 1398, 1380, 1321, 1257, 1216, 1181, 1155, 1133, 1123, 1070, 1050, 1020, 993, 873, 819, 748, 692 cm^{-1}. **49b**: R_f = 0.18 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20-7.15 (m, 3 H), 7.10 (d, J = 7.7 Hz, 1 H), 6.99 (d, J = 7.6 Hz, 1 H), 6.70 (t, J = 7.3 Hz, 1 H), 6.61 (d, J = 8.0 Hz, 2 H), 3.82 (br. s, 1 H), 3.17 (t, J = 7.0 Hz, 2 H), 2.84-2.77 (m, 2 H), 2.30 (s, 3 H), 1.94 (quint, J = 7.2 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.4 (C), 137.6 (C), 136.1 (C), 133.7 (C), 130.2 (CH), 130.1 (CH), 129.3 (CH), 127.7 (CH), 117.4 (CH), 113.0 (CH), 43.6 (CH_2), 30.8 (CH_2), 29.7 (CH_2), 20.8 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 261 (4) [M(^{37}Cl)]$^+$, 259 (11) [M(^{35}Cl)]$^+$, 224 (14) [$C_{16}H_{18}N$]$^+$, 106 (100) [C_7H_8N]$^+$, 77 (16) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{16}H_{18}ClN$) 259.1122, found 259.1123 [M]$^+$. IR (ATR, neat): λ^{-1} = 3048, 3024, 3953, 2918, 2862, 2845, 1602, 1505, 1494, 1475, 1453, 1430, 1319, 1256, 1214, 1179, 1153, 1114, 1048, 992, 870, 818, 746, 690, 615 cm^{-1}. **49c**: R_f = 0.32 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19-7.13 (m, 4 H), 7.04 (d, J = 7.7 Hz, 2 H), 6.96 (d, J = 7.0 Hz, 2 H), 6.69 (t, J = 7.3 Hz, 1 H), 6.55 (d, J = 7.6 Hz, 2 H), 3.57 (br. s, 1 H), 3.45 (quint, J = 6.2 Hz, 1 H), 2.85 (ddd, J = 13.7 Hz, J = 10.2 Hz, J = 5.6 Hz, 2 H), 2.75 (ddd, J = 13.6 Hz, J = 10.3 Hz, J = 6.0 Hz, 2 H), 2.31 (s, 6 H), 1.96-1.88 (m, 2 H), 1.85-1.77 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 147.8 (C), 137.5 (C), 136.5 (C), 133.6 (C), 130.4 (CH), 130.1 (CH), 129.4 (CH), 127.7 (CH), 117.1 (CH), 113.3 (CH), 52.4 (CH), 35.1 (CH_2), 30.0 (CH_2), 20.8 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 415 (1) [M(^{37}Cl^{37}Cl)]$^+$, 413 (6) [M(^{35}Cl^{37}Cl)]$^+$, 411 (8) [M(^{35}Cl^{35}Cl)]$^+$, 260 (34) [$C_{16}H_{17}{}^{37}ClN$]$^+$, 258 (100) [$C_{16}H_{17}{}^{35}ClN$]$^+$, 141 (20) [$C_8H_8{}^{37}Cl$]$^+$, 139 (61) [$C_8H_8{}^{35}Cl$]$^+$, 77 (11) [C_6H_5]$^+$. HRMS (EI): calcd. ($C_{25}H_{27}Cl_2N$) 411.1515, found 411.1512 [M]$^+$. IR (ATR, neat): λ^{-1} = 3404, 3046, 2921, 2865, 1602, 1496, 1456, 1431, 1396, 1319, 1264, 1216, 1183, 1157, 1100, 1051, 995, 874, 819, 748, 690, 663, 635, 623, 611 cm^{-1}.

Buchwald-Hartwig amination for the synthesis of 1,2,3,4-tetrahydroquinolines. General procedure C: An oven dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with amine (0.50 mmol), $Pd_2(dba)_3$ (0.01 mmol, 9 mg, 2 mol%), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.04 mmol, 17 mg, 8 mol%), NaO*t*Bu (0.75 mmol, 72 mg), and toluene (1.5 mL). The tube was sealed, removed from the glovebox, and placed in an aluminium heating block. The reaction mixture was heated to 110 °C for 24 h. After the reaction mixture had been cooled to room temperature, it was diluted with CH_2Cl_2 (50 mL) and Celite® was added. Then the solvents were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2).

1-Phenyl-1,2,3,4-tetrahydroquinoline (11):[21] General procedure C was used to synthesize **11** from **10b** (0.50 mmol, 123 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **11** (101 mg, 0.48 mmol, 97 %) was isolated as a slightly yellow oil. R_f = 0.55 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (t, J = 7.8 Hz, 2 H), 7.31 (d, J = 7.6 Hz, 2 H), 7.15 (t, J = 7.3 Hz, 1 H), 7.11 (d, J = 7.4 Hz, 1 H), 6.99 (t, J = 7.5 Hz, 1 H), 6.83 (d, J = 8.2 Hz, 1 H), 6.77 (t, J = 7.3 Hz, 1 H), 3.71-3.67 (m, 2 H), 2.92 (t, J = 6.5 Hz, 2 H), 2.11 (quint, J = 6.1 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.5 (C), 144.5 (C), 129.5 (CH), 126.5 (CH), 124.8 (CH), 124.7 (C), 123.7 (CH), 118.4 (CH), 115.9 (CH), 50.9 (CH_2), 27.9 (CH_2), 22.9 (CH_2) ppm.

1-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline (50): General procedure C was used to synthesize **50** from **25b** (0.50 mmol, 138 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **50** (120 mg, 0.50 mmol, >99 %) was isolated as a slightly yellow oil. R_f = 0.47 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23-7.19 (m, 2 H), 7.05 (d, J = 7.3 Hz, 1 H), 6.98-6.90 (m, 3 H), 6.67 (t, J = 7.3 Hz, 1 H), 6.52 (d, J = 8.2 Hz, 1 H), 3.85 (s, 3 H), 3.62-3.58 (m, 2 H), 2.90 (t, J = 6.4 Hz, 2 H), 2.09 (quint, J = 6.0 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 156.9 (C), 145.6 (C), 141.4 (C), 129.4 (CH), 127.7 (CH), 126.6 (CH), 123.1 (C), 117.4 (CH), 114.9 (CH), 114.5 (CH), 55.6 (CH_3), 51.8 (CH_2), 28.0 (CH_2), 22.6 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 239 (100) [M]$^+$, 224 (67) [$C_{15}H_{14}NO$]$^+$. HRMS (ESI, +): calcd. ($C_{16}H_{18}NO$) 240.1388, found 240.1389 [M+H]$^+$. IR (ATR, neat): λ^{-1} = 3036, 2931, 2835, 1600, 1574, 1506, 1454, 1296, 1279, 1238, 1200, 1179, 1095, 1034, 931, 876, 829, 802, 745, 598, 576, 560 cm^{-1}.

1-(4-Phenoxyphenyl)-1,2,3,4-tetrahydroquinoline (51): General procedure C was used to synthesize **51** from **26b** (0.50 mmol, 169 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **51** (148 mg, 0.49 mmol, 98 %) was isolated as a slightly yellow oil. R_f = 0.35 (SiO_2, PE/EtOAc, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (t, J = 7.9 Hz, 2 H), 7.21 (d, J = 8.6 Hz, 2 H), 7.10 (t, J = 7.3 Hz, 1 H), 7.08-6.99 (m, 5 H), 6.94 (t, J = 7.7 Hz, 1 H), 6.71-6.64 (m, 2 H), 3.63-3.58 (m, 2 H), 2.87 (t, J = 6.3 Hz, 2 H), 2.06 (quint, J = 6.2 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 157.6 (C), 153.7 (C), 145.0 (C), 143.9 (C), 129.9 (CH), 129.5 (CH), 127.0 (CH), 126.6 (CH), 123.9 (C), 123.2 (CH), 120.1 (CH), 118.7 (CH), 118.0 (CH), 115.1 (CH), 51.5 (CH_2), 27.9 (CH_2), 22.7 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 301 (100) [M]$^+$, 224 (8) [$C_{15}H_{14}NO$]$^+$. HRMS (ESI, +): calcd. ($C_{21}H_{20}NO$) 302.1545, found 302.1537 [M+H]$^+$. IR (ATR, neat): λ^{-1} = 3064, 3038, 2953, 2934, 2843, 1596, 1574, 1504, 1487, 1453, 1381, 1322, 1292, 1269, 1226, 1205, 1161, 1102, 1075, 1025, 1012, 940, 862, 843, 824, 749, 691, 626, 608, 562 cm^{-1}.

1-(4-(Methylthio)phenyl)-1,2,3,4-tetrahydroquinoline (52): General procedure C was used to synthesize **52** from **27b** (0.50 mmol, 146 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 50:1), **52** (122 mg, 0.48 mmol, 96 %) was isolated as a slightly yellow oil. R_f = 0.33 (SiO_2, PE/EtOAc, 50:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (d, J = 8.5 Hz, 2 H), 7.19 (d, J = 8.6 H, 2 H), 7.06 (d, J = 7.4 Hz, 1 H), 6.95 (t, J = 7.7 Hz, 1 H), 6.79-6.70 (m, 2 H), 3.65-3.58 (m, 2 H), 2.86 (t, J = 6.4 Hz, 2 H), 2.50 (s, 3 H), 2.05 (quint, J = 6.3 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 146.1 (C), 144.2 (C), 132.8 (C), 129.5 (CH), 128.7 (CH), 126.5 (CH), 125.2 (CH), 124.9 (C), 118.8 (CH), 116.1 (CH), 51.1 (CH_2), 27.8 (CH_2), 22.7 (CH_2), 17.0 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 255 (100) [M]$^+$, 240 (54) [$C_{15}H_{14}NS$]$^+$, 180 (16). HRMS (ESI, +): calcd. ($C_{16}H_{17}NSNa$) 278.0979, found 278.0981 [M+Na]$^+$. IR (ATR, neat): λ^{-1} = 3062, 3023, 2921, 2840, 1687, 1589, 1576, 1557, 1489, 1454, 1382, 1307, 1288, 1260, 1238, 1200, 1117, 1086, 1040, 1023, 966, 933, 876, 856, 821, 786, 746, 718, 661 cm^{-1}.

1-(*ortho*-Tolyl)-1,2,3,4-tetrahydroquinoline (53): General procedure C was used to synthesize **53** from **28b** (0.50 mmol, 130 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 50:1), **53** (107 mg, 0.48 mmol, 96 %) was isolated as a slightly yellow oil. R_f = 0.48 (SiO_2, PE/EtOAc, 50:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39-7.18 (m, 4 H), 7.05 (d, J = 7.4 Hz, 1 H), 6.90 (t, J = 7.7 Hz, 1 H), 6.63 (t, J = 7.7 Hz, 1 H), 6.08 (d, J = 8.3 Hz, 1 H), 3.59-3.49 (m, 2 H), 2.94 (t, J = 6.3 Hz, 2 H),

2.23 (s, 3 H), 2.13 (quint, *J* = 6.0 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): *δ* = 146.1 (C), 145.2 (C), 137.1 (C), 131.4 (CH), 129.3 (CH), 128.6 (CH), 127.7 (CH), 126.9 (CH), 126.5 (CH), 121.8 (C), 116.5 (CH), 113.1 (CH), 50.6 (CH_2), 28.1 (CH_2), 22.6 (CH_2), 17.9 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 223 (100) $[M]^+$. HRMS (ESI, +): calcd. ($C_{16}H_{18}N$) 224.1439, found 224.1434 $[M+H]^+$. IR (ATR, neat): λ^{-1} = 3063, 3019, 2926, 2839, 1693, 1605, 1597, 1575, 1491, 1455, 1379, 1341, 1303, 1273, 1241, 1191, 1157, 1118, 1091, 1073, 1040, 1022, 929, 875, 858, 802, 743, 724, 692, 628 cm^{-1}.

1-(3,5-Dimethylphenyl)-1,2,3,4-tetrahydroquinoline (54): General procedure C was used to synthesize **54** from **29b** (0.50 mmol, 137 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **54** (112 mg, 0.47 mmol, 94 %) was isolated as a colorless solid. R_f = 0.58 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.08 (d, *J* = 7.4 Hz, 1 H), 6.97 (t, *J* = 7.6 Hz, 1 H), 6.92 (br. s, 2 H), 6.80 (br. s, 1 H), 6.77 (d, *J* = 8.3 Hz, 1 H), 6.73 (t, *J* = 7.3 Hz, 1 H), 3.67-3.62 (m, 2 H), 2.88 (t, *J* = 6.5 Hz, 2 H), 2.34 (s, 6 H), 2.07 (quint, *J* = 6.1 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DEPT, $CDCl_3$): *δ* = 148.4 (C), 144.7 (C), 139.1 (C), 129.4 (CH), 126.5 (CH), 125.7 (CH), 124.5 (C), 122.6 (CH), 118.2 (CH), 116.1 (CH), 51.1 (CH_2), 27.9 (CH_2), 22.8 (CH_2), 21.5 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 237 (100) $[M]^+$. HRMS (ESI, +): calcd. ($C_{17}H_{20}N$) 238.1596, found 238.1590 $[M+H]^+$. IR (ATR, neat): λ^{-1} = 3053, 3019, 2939, 2839, 1590, 1574, 1493, 1470, 1456, 1375, 1323, 1300, 1270, 1249, 1192, 1175, 1118, 1098, 1038, 1020, 905, 876, 852, 811, 754, 743, 724, 704, 658, 608, 583, 568 cm^{-1}.

1-(3,4,5-Trimethoxyphenyl)-1,2,3,4-tetrahydroquinoline (55): General procedure C was used to synthesize **55** from **30b** (0.50 mmol, 168 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 5:1), **55** (72 mg, 0.24 mmol, 48 %) was isolated as a slightly yellow oil. R_f = 0.37 (SiO_2, PE/EtOAc, 5:1). ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.04 (d, *J* = 8.1 Hz, 1 H), 6.94 (t, *J* = 8.5 Hz, 1 H), 6.68 (t, *J* = 8.6 Hz, 2 H), 6.49 (s, 2 H), 3.88 (s, 3 H), 3.82 (s, 6 H), 3.64-3.58 (m, 2 H), 2.87 (t, *J* = 6.4 Hz, 2 H), 2.11-2.04 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DEPT, $CDCl_3$): *δ* = 153.9 (C), 144.9 (C), 144.4 (C), 135.2 (C), 129.4 (CH), 126.5 (CH), 123.8 (C), 117.9 (CH), 115.4 (CH), 103.2 (CH), 61.0 (CH_3), 56.2 (CH_3), 51.4 (CH_2), 27.8 (CH_2), 22.8 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 299 (54) $[M]^+$, 284 (100) $[C_{17}H_{18}NO_3]^+$. HRMS (EI): calcd. ($C_{18}H_{21}NO_3$) 299.1516, found 299.1515 $[M]^+$. IR (ATR, neat): λ^{-1} = 2935, 2837, 1587, 1574, 1491, 1447, 1413, 1302, 1282, 1227, 1195, 1122, 1042, 1008, 905, 819, 780, 747, 669, 652 cm^{-1}.

1-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinoline (56): General procedure C was used to synthesize **56** from **31b** (0.50 mmol, 132 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **56** (102 mg, 0.45 mmol, 90 %) was isolated as a slightly yellow oil. R_f = 0.48 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.24-7.19 (m, 2 H), 7.09-7.03 (m, 3 H), 6.93 (t, *J* = 7.7 Hz, 1 H), 6.70 (t, *J* = 7.4 Hz, 1 H), 6.58 (d, *J* = 8.2 Hz, 1 H), 3.62-3.57 (m, 2 H), 2.88 (t, *J* = 6.4 Hz, 2 H), 2.07 (quint, *J* = 6.1 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DEPT, $CDCl_3$): *δ* = 159.7 (d, $^1J_{C,F}$ = 244 Hz, C), 145.0 (C), 144.6 (C), 129.6 (CH), 127.4 (d, $^3J_{C,F}$ = 8 Hz, CH), 126.6 (CH), 124.0 (C), 118.3 (CH), 116.4 (d, $^2J_{C,F}$ = 22 Hz, CH), 115.2 (CH), 51.6 (CH_2), 27.9 (CH_2), 22.7 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): *δ* = –118.34 ppm. GC/MS (EI, 70 eV): *m/z* (%) = 227 (100) $[M]^+$. HRMS (EI): calcd. ($C_{15}H_{14}FN$) 227.1105, found 227.1103 $[M]^+$. IR (ATR, neat): λ^{-1} = 3067, 3044, 3020, 2931, 2841, 1601, 1576, 1503, 1492, 1455, 1383, 1342, 1310, 1270, 1216, 1200, 1152, 1118, 1090, 1040, 1023, 945, 931, 877, 861, 832, 813, 746, 718, 683 cm^{-1}.

1-(3-Fluorophenyl)-1,2,3,4-tetrahydroquinoline (57): General procedure C was used to synthesize **57** from **32b** (0.50 mmol, 132 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **57** (111 mg, 0.49 mmol, 98 %) was isolated as a colorless oil. R_f = 0.47 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.28-7.22 (m, 1 H), 7.08 (d, *J* = 7.4 Hz, 1 H), 7.03-6.97 (m, 2 H), 6.95-6.90 (m, 2 H), 6.78 (td, *J* = 7.3 Hz, *J* = 1.2 Hz, 1 H), 6.73 (tdd, *J* = 8.3 Hz, *J* = 2.5 Hz, *J* = 0.8 Hz, 1 H), 3.65-3.60 (m, 2 H), 2.83 (t, *J* = 6.5 Hz, 2 H), 2.07-2.00 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, DEPT, $CDCl_3$): *δ* = 163.7 (d, *J* = 245 Hz, C), 150.3 (d, *J* = 10 Hz, C), 143.5 (C), 130.3 (d, *J* = 10 Hz, CH), 129.5 (CH), 126.5 (CH), 126.4 (C), 119.7 (CH), 118.7 (d, *J* = 3 Hz, CH), 117.3 (CH), 110.2 (d, *J* = 23 Hz, CH), 109.5 (d, *J* = 21 Hz, CH), 50.5 (CH_2), 27.7 (CH_2), 23.1 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): *δ* = –112.17 ppm. GC/MS (EI, 70 eV): *m/z* (%) = 227 (100) $[M]^+$. HRMS (EI): calcd. ($C_{15}H_{14}FN$) 227.1105, found 227.1095 $[M]^+$. IR (ATR, neat): λ^{-1} = 3061, 3024, 2947, 2913, 2846, 1612, 1599, 1574, 1489, 1457, 1444, 1381, 1333, 1300, 1263, 1245, 1209, 1188, 1167, 1148, 1117, 1091, 1069, 1023, 1002, 984, 908, 847, 823, 747, 718, 686, 633, 617 cm^{-1}.

1-(4-(Trifluoromethoxy)phenyl)-1,2,3,4-tetrahydroquinoline (58): General procedure C was used to synthesize **58** from **33b** (0.50 mmol, 165 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **58** (120 mg, 0.41 mmol, 82 %) was isolated as a slightly yellow oil. R_f = 0.47 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 2 H), 7.08 (d, *J* = 7.2 Hz, 1 H), 6.99-6.95 (m, 1 H), 6.80-6.74 (m, 2 H), 3.64-3.60 (m, 2 H), 2.86 (t, *J* = 6.5 Hz, 2 H), 2.05 (quint, *J* = 6.1 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): *δ* = 147.2 (C), 144.7 (C), 144.0 (C), 129.6 (CH), 126.6 (CH), 125.4 (C), 125.2 (CH), 122.2 (CH), 120.7 (q, $J_{C,F}$ = 257 Hz, C), 119.2 (CH), 116.3 (CH), 50.9 (CH_2), 27.8 (CH_2), 22.9 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): *δ* = –58.07 ppm. GC/MS (EI, 70 eV): *m/z* (%) = 293 (100) $[M]^+$, 224 (6) $[C_{15}H_{14}NO]^+$, 208 (6) $[C_{15}H_{14}N]^+$. HRMS (ESI, +): calcd. ($C_{16}H_{15}F_3NO$) 294.1106, found 294.1112 $[M+H]^+$. IR (ATR, neat): λ^{-1} = 3068, 2933, 2845, 1599, 1576, 1504, 1492, 1456, 1385, 1249, 1219, 1195, 1154, 1119, 1016, 920, 877, 859, 840, 807, 748, 672 cm^{-1}.

1,2-Diphenyl-1,2,3,4-tetrahydroquinoline (59): General procedure C was used to synthesize **59** from **34b** (0.50 mmol, 161 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 60:1), **59** (125 mg, 0.44 mmol, 88 %) was isolated as a slightly yellow oil. R_f = 0.25 (SiO_2, PE/EtOAc, 60:1). ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.43-7.28 (m, 9 H), 7.16-7.11 (m, 2 H), 7.09 (d, *J* = 8.4 Hz, 1 H), 7.01 (d, *J* = 8.2 Hz, 1 H), 6.83 (td, *J* = 7.3 Hz, *J* = 1.1 Hz, 1 H), 5.05 (t, *J* = 4.3 Hz, 1 H), 2.80 (dt, *J* = 16.1 Hz, *J* = 4.4 Hz, 1 H), 2.70 (ddd, *J* = 16.3 Hz, *J* = 11.9 Hz, *J* = 5.1 Hz, 1 H), 2.49-2.41 (m, 1 H), 2.25 (dq, *J* = 13.0 Hz, *J* = 4.1 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): *δ* = 148.0 (C), 144.0 (C), 143.9 (C), 129.4 (CH), 129.4 (CH), 128.5 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 125.0 (CH), 124.1 (C), 123.9 (CH), 118.2 (CH), 115.9 (CH), 63.2 (CH), 29.1 (CH_2), 23.8 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 285 (100) $[M]^+$, 208 (86) $[C_{15}H_{14}N]^+$, 194 (58), 180 (74), 77 (23) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{21}H_{19}N$) 285.1512, found 285.1519 $[M]^+$. IR (ATR, neat): λ^{-1} = 3062, 3033, 2928, 2842, 1592, 1574, 1492, 1458, 1448, 1382, 1298, 1272, 1236, 1216, 1172, 1156, 1118, 1102, 1072, 1029, 908, 861, 809, 744, 695, 670, 645, 622, 609 cm^{-1}.

6,6a,7,8-Tetrahydro-5*H*-quinolino[1,2-*a*]quinoline (60): General procedure C was used to synthesize **60** from **35b** (0.50 mmol, 136 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 40:1), **60** (115 mg, 0.49 mmol, 98 %) was isolated as a slightly yellow oil. R_f = 0.52 (SiO_2, PE/EtOAc, 40:1). ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.41 (d, *J* = 8.2 Hz, 2 H), 7.14 (d, *J* = 7.4 Hz, 2 H), 7.07 (t, *J* = 7.7 Hz, 2 H), 6.85 (td, *J* = 7.3 Hz, *J* = 0.8 Hz, 2 H), 3.54 (tt, *J* = 10.9 Hz, *J* = 4.2 Hz, 1 H), 2.89-2.77 (m, 4 H), 2.30-2.22 (m, 2 H), 1.63 (dtd, *J* = 12.9 Hz, *J* = 11.1 Hz, *J* = 6.4 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): *δ* = 142.6 (C), 129.1 (CH), 129.0 (C), 126.1 (CH), 120.0 (CH), 118.4 (CH), 55.9 (CH), 31.1 (CH_2), 27.5 (CH_2) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 235 (100) $[M]^+$. HRMS (EI): calcd. ($C_{17}H_{17}N$) 235.1356, found 235.1359 $[M]^+$. IR (ATR, neat): λ^{-1} = 3018, 2960, 2945, 2930, 2840, 1592, 1569, 1486,

1446, 1385, 1356, 1313, 1266, 1233, 1196, 1151, 1116, 1094, 1063, 1043, 1010, 943, 922, 848, 831, 804, 744, 711, 632 cm^{-1}.

2-Ethyl-1-phenyl-1,2,3,4-tetrahydroquinoline (61): General procedure C was used to synthesize **61** from **36b** (0.50 mmol, 137 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 60:1), **61** (119 mg, 0.50 mmol, >99 %) was isolated as a slightly yellow oil. R_f = 0.24 (SiO_2, PE/EtOAc, 60:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.41-7.36 (m, 2 H), 7.28 (dd, J = 8.5 Hz, J = 1.1 Hz, 2 H), 7.17-7.11 (m, 2 H), 6.99 (t, J = 8.4 Hz, 1 H), 6.80-6.74 (m, 2 H), 3.73 (ddt, J = 8.2 Hz, J = 6.1 Hz, J = 4.0 Hz, 1 H), 2.97-2.88 (m, 1 H), 2.88-2.80 (m, 1 H), 2.10-2.02 (m, 1 H), 2.02-1.95 (m, 1 H), 1.80-1.70 (m, 1 H), 1.61-1.51 (m, 1 H), 1.02 (t, J = 7.4 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.8 (C), 143.6 (C), 129.4 (CH), 129.4 (CH), 126.4 (CH), 125.6 (CH), 124.5 (C), 123.5 (CH), 118.4 (CH), 118.0 (CH), 60.7 (CH), 25.1 (CH_2), 24.1 (CH_2), 23.7 (CH_2), 10.8 (CH_3) ppm. GC/MS (EI, 70 eV): m/z (%) = 237 (46) $[M]^+$, 208 (100) $[C_{15}H_{14}N]^+$, 193 (25), 180 (19), 77 (23) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{17}H_{19}N$) 237.1512, found 237.1522 $[M]^+$. IR (ATR, neat): λ^{-1} = 3033, 2959, 2932, 2871, 1592, 1573, 1489, 1456, 1383, 1336, 1273, 1230, 1206, 1180, 1128, 1106, 1062, 1032, 1002, 937, 896, 872, 843, 745, 722, 695, 656 cm^{-1}.

2-Isopropyl-1-phenyl-1,2,3,4-tetrahydroquinoline (62): General procedure C was used to synthesize **62** from **37b** (0.50 mmol, 144 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 50:1), **62** (114 mg, 0.45 mmol, 91 %) was isolated as a slightly yellow oil. R_f = 0.45 (SiO_2, PE/EtOAc, 50:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.27 (t, J = 7.9 Hz, 2 H), 7.16 (d, J = 7.6 Hz, 2 H), 7.10 (d, J = 7.5 Hz, 1 H), 6.98 (t, J = 7.3 Hz, 2 H), 6.88 (d, J = 8.2 Hz, 1 H), 6.82 (t, J = 7.3 Hz, 1 H), 3.42-3.36 (m, 1 H), 2.87-2.76 (m, 2 H), 2.01-1.89 (m, 2 H), 1.87-1.78 (m, 1 H), 1.13 (d, J = 6.7 Hz, 3 H), 0.97 (d, J = 6.7 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 150.8 (C), 143.2 (C), 129.6 (CH), 129.2 (CH), 127.2 (C), 126.2 (CH), 123.4 (CH), 122.0 (CH), 122.0 (CH), 120.1 (CH), 65.8 (CH), 28.2 (CH), 23.7 (CH_2), 21.7 (CH_2), 21.2 (CH_3), 18.7 (CH_3) ppm. GC/MS (EI, 70 eV): m/z (%) = 251 (10) $[M]^+$, 208 (100) $[C_{15}H_{14}N]^+$, 77 (7) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{18}H_{21}N$) 251.1669, found 251.1676 $[M]^+$. IR (ATR, neat): λ^{-1} = 3060, 3023, 2954, 2867, 1593, 1573, 1490, 1456, 1447, 1375, 1340, 1316, 1263, 1229, 1200, 1111, 1084, 1068, 1035, 995, 942, 864, 819, 749, 722, 694, 660, 619 cm^{-1}.

7-Fluoro-1-phenyl-1,2,3,4-tetrahydroquinoline (63): General procedure C was used to synthesize **63** from **44b** (0.50 mmol, 132 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 50:1), **63** (105 mg, 0.46 mmol, 92 %) was isolated as a slightly yellow oil. R_f = 0.37 (SiO_2, PE/EtOAc, 50:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.39 (t, J = 7.8 Hz, 2 H), 7.26 (d, J = 7.8 Hz, 2 H), 7.18 (t, J = 7.4 Hz, 1 H), 6.96 (t, J = 7.4 Hz, 1 H), 6.41-6.33 (m, 2 H), 3.65-3.60 (m, 2 H), 2.83 (t, J = 6.4 Hz, 2 H), 2.06 (quint, J = 6.0 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 162.0 (d, J = 240 Hz, C), 147.6 (C), 146.0 (d, J = 10 Hz, C), 130.2 (d, J = 10 Hz, CH), 129.8 (CH), 125.6 (CH), 124.8 (CH), 119.2 (d, J = 2 Hz, C), 104.3 (d, J = 22 Hz, CH), 101.6 (d, J = 26 Hz, CH), 50.9 (CH_2), 27.3 (CH_2), 22.7 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −116.08 ppm. GC/MS (EI, 70 eV): m/z (%) = 227 (100) $[M]^+$, 211 (12), 198 (18), 77 (12) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{15}H_{14}FN$) 227.1105, found 227.1108 $[M]^+$. IR (ATR, neat): λ^{-1} = 3031, 2933, 2841, 1614, 1588, 1501, 1427, 1384, 1313, 1273, 1241, 1211, 1161, 1111, 1071, 1027, 938, 834, 785, 761, 696, 610 cm^{-1}.

5-Fluoro-1-phenyl-1,2,3,4-tetrahydroquinoline (64): General procedure C was used to synthesize **64** from **45b** (0.50 mmol, 132 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 50:1), **64** (108 mg, 0.48 mmol, 95 %) was isolated as a slightly yellow oil. R_f = 0.41 (SiO_2, PE/EtOAc, 50:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.43-7.37 (m, 2 H), 7.29-7.25 (m, 2 H), 7.18 (tt, J = 7.4 Hz, J = 1.1 Hz, 1 H), 6.88 (q, J = 8.1 Hz, 1 H), 6.51-6.43 (m, 2 H), 3.67-3.62 (m, 2 H), 2.87 (t, J = 6.6 Hz, 2 H), 2.10-2.04 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 161.5 (d, J = 241 Hz, C), 148.1 (C), 146.4 (d, J = 8 Hz, C), 129.6 (CH), 126.5 (d, J = 11 Hz, CH), 125.6 (CH), 124.5 (CH), 111.3 (d, J = 21 Hz, C), 110.7 (d, J = 2 Hz, CH), 104.2 (d, J = 23 Hz, CH), 50.8 (CH_2), 21.6 (CH_2), 20.4 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −117.94 ppm. GC/MS (EI, 70 eV): m/z (%) = 227 (100) $[M]^+$, 211 (13), 198 (18), 77 (11) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{15}H_{14}FN$) 227.1105, found 227.1098 $[M]^+$. IR (ATR, neat): λ^{-1} = 3053, 2936, 2853, 1621, 1595, 1570, 1496, 1466, 1382, 1349, 1316, 1258, 1239, 1201, 1114, 1075, 1046, 1031, 1007, 995, 913, 761, 698, 655, 617 cm^{-1}.

7-(Methylthio)-1-phenyl-1,2,3,4-tetrahydroquinoline (65): General procedure C was used to synthesize **65** from **46b** (0.50 mmol, 146 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **65** (65 mg, 0.25 mmol, 51 %) was isolated as a slightly yellow oil. R_f = 0.45 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.35 (m, 2 H), 7.27-7.24 (m, 2 H), 7.14 (tt, J = 7.4 Hz, J = 1.1 Hz, 1 H), 6.98 (d, J = 7.8 Hz, 1 H), 6.68 (d, J = 1.8 Hz, 1 H), 6.65 (dd, J = 7.8 Hz, J = 1.9 Hz, 1 H), 3.65-3.61 (m, 2 H), 2.83 (t, J = 6.5 Hz, 2 H), 2.34 (s, 3 H), 2.08-2.02 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.0 (C), 144.9 (C), 135.8 (C), 129.8 (CH), 129.6 (CH), 125.0 (CH), 124.1 (CH), 121.8 (C), 117.0 (CH), 114.1 (CH), 51.0 (CH_2), 27.5 (CH_2), 22.7 (CH_2), 16.4 (CH_3) ppm. GC/MS (EI, 70 eV): m/z (%) = 255 (100) $[M]^+$, 206 (25), 193 (8), 180 (11), 77 (13) $[C_6H_5]^+$. HRMS (EI): calcd. ($C_{16}H_{17}NS$) 255.1076, found 255.1068 $[M]^+$. IR (ATR, neat): λ^{-1} = 2921, 2842, 1589, 1556, 1491, 1436, 1407, 1379, 1308, 1262, 1237, 1203, 1173, 1130, 1092, 1071, 1025, 956, 891, 864, 787, 759, 696, 660, 651 cm^{-1}.

8-Methoxy-1-phenyl-1,2,3,4-tetrahydroquinoline (66): General procedure C was used to synthesize **66** from **47b** (0.50 mmol, 138 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **66** (46 mg, 0.19 mmol, 38 %) was isolated as a slightly yellow oil. R_f = 0.27 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.21 (t, J = 7.9 Hz, 2 H), 7.00 (t, J = 7.9 Hz, 1 H), 6.92-6.86 (m, 3 H), 6.81 (d, J = 7.6 Hz, 1 H), 6.71 (d, J = 8.0 Hz, 1 H), 3.77-3.71 (m, 2 H), 3.61 (s, 3 H), 2.83 (t, J = 6.7 Hz, 2 H), 1.87-1.81 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 152.8 (C), 150.3 (C), 132.6 (C), 132.3 (C), 128.4 (CH), 122.9 (CH), 121.8 (CH), 120.6 (CH), 120.0 (CH), 109.1 (CH), 55.5 (CH_3), 52.0 (CH_2), 27.5 (CH_2), 21.3 (CH_2) ppm. GC/MS (EI, 70 eV): m/z (%) = 239 (100) $[M]^+$, 224 $[C_{15}H_{14}NO]^+$ (57), 208 $[C_{15}H_{14}N]^+$ (10), 196 (24), 180 (15), 167 (19), 130 (9), 117 (8), 104 (6), 91 (12), 77 (21) $[C_6H_5]^+$, 65 (10), 51 (13). HRMS (EI): calcd. ($C_{16}H_{17}NO$) 239.1305, found 239.1311 $[M]^+$. IR (ATR, neat): λ^{-1} = 3003, 2953, 2930, 2893, 2862, 2831, 2343, 1594, 1580, 1490, 1472, 1460, 1433, 1349, 1335, 1301, 1256, 1231, 1215, 1192, 1172, 1102, 1089, 1052, 1026, 963, 915, 889, 842, 768, 756, 745, 700, 673, 644, 625 cm^{-1}.

1-Phenyl-8-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (67): General procedure C was used to synthesize **67** from **48b** (0.50 mmol, 157 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 30:1), **67** (125 mg, 0.45 mmol, 90 %) was isolated as a slightly yellow oil. R_f = 0.39 (SiO_2, PE/EtOAc, 30:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.8 Hz, 1 H), 7.38 (d, J = 7.5 Hz, 1 H), 7.27-7.21 (m, 2 H), 7.17 (t, J = 7.7 Hz, 1 H), 6.97 (t, J = 7.3 Hz, 1 H), 6.85 (d, J = 7.7 Hz, 2 H), 3.74-3.68 (m, 2 H), 2.87 (t, J = 6.9 Hz, 2 H), 1.97-1.90 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, JMOD, $CDCl_3$): δ = 151.8 (C), 143.4 (C), 135.3 (C), 133.1 (CH), 128.7 (CH), 125.9 (q, J = 5 Hz, CH), 125.4 (q, J = 30 Hz, C), 123.9 (q, J = 274 Hz, C), 123.3 (CH), 121.6 (CH), 121.5 (CH), 51.7 (CH_2), 27.1 (CH_2), 20.9 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −60.33 ppm. GC/MS (EI, 70 eV): m/z (%) = 277 (100) $[M]^+$, 262 (7), 256 (8), 242 (8), 228 (14), 208 (36) $[C_{15}H_{14}N]^+$, 193 (6), 180 (72), 166 (7), 115 (5), 104 (6), 91 (8), 77 (22) $[C_6H_5]^+$, 51 (17). HRMS (EI): calcd. ($C_{16}H_{14}F_3N$) 277.1073, found 277.1073 $[M]^+$. IR (ATR, neat): λ^{-1} = 3067, 2942, 2923, 2876, 1592, 1492, 1460, 1336, 1308, 1255, 1236, 1184, 1150, 1116, 1053, 1028, 957, 874, 853, 833, 786, 757, 694, 666, 650, 627, 615 cm^{-1}.

7-Methyl-1-phenyl-1,2,3,4-tetrahydroquinoline (68): General procedure C was used to synthesize **68** from **49b** (0.50 mmol, 130 mg). After purification by flash chromatography (SiO_2, PE/EtOAc, 40:1), **68** (97 mg, 0.43 mmol, 87 %) was isolated as a slightly yellow oil. R_f = 0.35 (SiO_2, PE/EtOAc, 40:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41-7.36 (m, 2 H), 7.30-7.26 (m, 2 H), 7.13 (tt, J = 7.4 Hz, J = 1.2 Hz, 1 H), 6.98 (d, J = 7.6 Hz, 1 H), 6.63 (s, 1 H), 6.58 (d, J = 7.6 Hz, 1 H), 3.67-3.63 (m, 2 H), 2.85 (t, J = 6.5 Hz, 2 H), 2.19 (s, 3 H), 2.03-2.10 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, JMOD, $CDCl_3$): δ = 148.7 (C), 144.4 (C), 136.1 (C), 129.5 (CH), 129.4 (CH), 124.8 (CH), 123.6 (CH), 121.8 (C), 119.4 (CH), 116.4 (CH), 51.1 (CH_2), 27.6 (CH_2), 23.0 (CH_2), 21.4 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 223 (100) $[M]^+$, 208 (12) $[C_{15}H_{14}N]^+$, 194 (12), 180 (6), 165 (3), 144 (3), 130 (4), 115 (6), 104 (5), 97 (12), 91 (10), 77 (13) $[C_6H_5]^+$, 65 (4), 51 (8). HRMS (EI): calcd. ($C_{16}H_{17}N$) 223.1356, found 223.1349 $[M]^+$. IR (ATR, neat): λ^{-1} = 3067, 3031, 2927, 2844, 1614, 1595, 1571, 1505, 1491, 1461, 1417, 1381, 1311, 1272, 1242, 1204, 1163, 1129, 1097, 1071, 1028, 999, 920, 862, 794, 758, 695, 661, 652, 632, 624 cm^{-1}.

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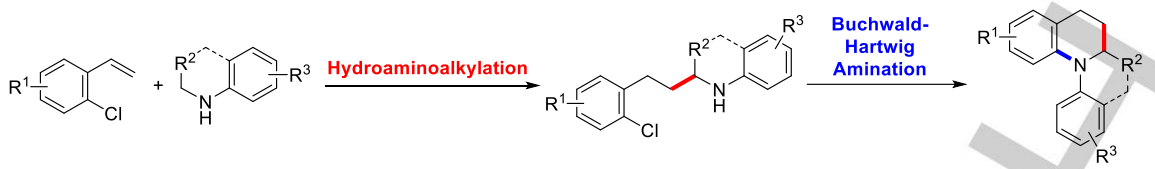

Hydroaminoalkylation reactions of *ortho*-chlorostyrenes with various secondary amines deliver the linear addition products with high regioselectivity. A combination of this reaction with a subsequent intramolecular Buchwald-Hartwig amination creates a new and simple two-step procedure that gives direct access to pharmacologically important 1,2,3,4-tetrahydroquinolines.

Key Topic **Synthetic Methods**