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A General Route to β-Substituted Pyrroles by Transition-Metal Catalysis

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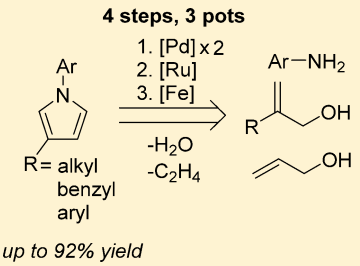
Supporting Information

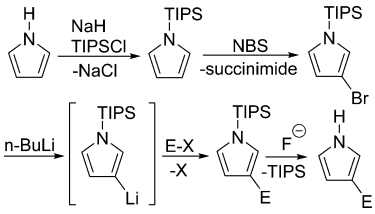
ABSTRACT: An atom-efficient route to pyrroles substituted in the β-position has been achieved in four high yielding steps by a combination of Pd, Ru, and Fe catalysis with only water and ethene as side-products. The reaction is general and gives pyrroles substituted in the β-position with linear and branched alkyl, benzyl, or aryl groups in overall good yields. The synthetic route includes a Pd-catalyzed monoallylation step of amines with substituted allylic alcohols that proceeds to yield the monoallylated products in moderate to excellent yields. In a second step, unsymmetrical diallylated aromatic amines are generated from the reaction of a second allylic alcohol with high selectivity in moderate to good yields by control of the reaction temperature. Ru-catalyzed ring-closing metathesis performed on the diallylated aromatic amines yields the pyrrolines substituted in the β-position in excellent yields. By addition of ferric chloride to the reaction mixture, a selective aromatization to yield the corresponding pyrroles substituted in the β-position was achieved. A reaction mechanism involving a palladium hydride, generated from insertion of palladium to O−H of an allyl alcohol, that is responsible for the C−O bond cleavage to generate the π-allyl intermediate is proposed.



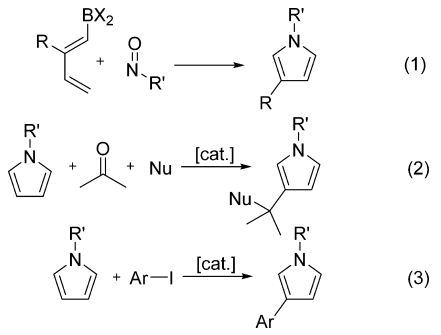
INTRODUCTION

Pyrroles, substituted in the β-position are structural motifs in biologically active compounds[1] and functional materials.[2] Traditionally, β-substituted pyrroles are synthesized in a five-step procedure in which a bulky silyl group is introduced on the nitrogen to direct the substitution to the β-position of the pyrrole ring (Scheme 1).[3] These directing groups are rather efficient, however, not perfect, leading to product mixtures that are tedious to purify. In addition, the procedure requires two stoichiometric derivatization steps that lower the atom economy.[4] Other procedures to generate β-substituted pyrroles include using phenylsulfonyl pyrroles,[5] a pyrrole with an electron-withdrawing group in the α-position,[6] or similar strategies.[7] These methodologies are not desired from synthetic or environmental perspectives, and therefore, advances in synthesis of β-substituted pyrroles are desired.

Scheme 1. Traditional Route to β-Substituted *N*-Aryl Pyrroles



Recently, a series of greener methodologies to β-substituted *N*-aryl pyrroles have emerged. Carboni and Whiting reported an efficient route to β-alkyl *N*-aryl pyrroles by a [4 + 2]-cycloaddition/ring contraction cascade reaction starting from arylnitroso and 1-boronodienes (eq 1).[8] Tsuchiomoto has, in several reports, demonstrated both Lewis and Brønsted acid catalyzed β-alkylations of pyrroles to yield pyrroles with branched alkyls using alkynes or ketones as substrates by highly efficient one-step procedures (eq 2).[9] Donohoe reported a cross-metathesis and Heck arylation approach to generate β-aryl pyrroles.[10] Very recently, C−H activation of pyrroles has been used to promote arylation in the β-position either through initial borylation or directly (eq 3).[11] These reports encouraged us to develop a general and atom-efficient methodology to generate *N*-aryl pyrroles substituted in the β-position with linear and branched alkyls, benzyl, and aryl groups.



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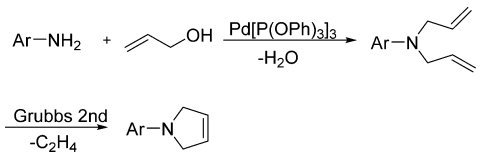
We have previously reported a two-step procedure to symmetrical pyrrolines using palladium and ruthenium catalysis (Scheme 2).[12] The $Pd[P(OPh)_3]_3$ complex[13] promoted the

Scheme 2. Previous Report Generated Nonsubstituted Pyrrolines by Pd and Ru Catalysis



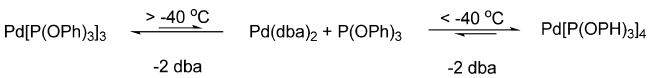
diallylation of aromatic amines using nonderivatized allylic alcohols as substrates to yield symmetrical diallylated products in the first step. Thereby, only water was generated as a side-product. The phosphite-based catalyst is easily accessible and reactive with nonderivatized allylic alcohols.[14] In a second step, ring-closing metathesis yielded the symmetrical pyrrolines. Attempts to synthesize usymmetrical pyrrolines were not successful. One challenge was to selectively perform mono-allylation of an aromatic amine while minimizing undesired diallylated product. Another challenge was to control a second diallylation step with a different allyl alcohol to obtain the unsymmetrical diallylated products where the reversible reaction lead to complex mixtures of undesired symmetrical allylated aromatic amines.

In this study, we report a method to efficiently generate unsymmetrical diallylated aromatic amines by $Pd[P(OPh)_3]_3$ catalysis with only water as a side-product. These products were reacted to give pyrrolines by ring-closing metathesis using Grubbs second-generation catalyst.[15] The pyrrolines were aromatized using Fe(III)-chloride as catalyst to generate the corresponding β-substituted pyrroles in overall good yields.

RESULTS AND DISCUSSION

Catalyst Preparation and Characterization. The palladium phosphite catalyst precursor used in this study was first reported by Ikariya's group to promote the Tsuji−Trost reaction[16] of nonderivatized allylic alcohols.[9,17] The catalyst can be prepared either by reacting $PdCl_2$ with $P(OPh)_3$ in the presence of NEt_3 or by mixing $Pd(dba)_2$ and $P(OPh)_3$. By X-ray crystallography, it was found that the precatalyst has three ligands coordinated ($Pd[P(OPh)_3]_3$) at room temperature (Scheme 3).[18] This is different from the related $Pd[PPh_3]_4$ in

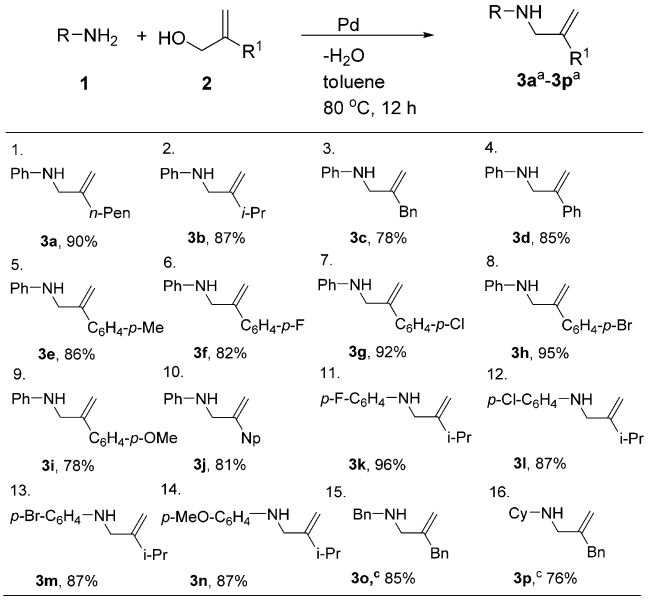
Scheme 3. Coordination Number Is Dependent on the Temperature for $Pd[P(OPh)_3]_x$



which tetracoordination dominates.[19] When a solution of $Pd(dba)_2$ and $P(OPh)_3$ was cooled below −40 °C, the tetracoordinated $Pd[P(OPh)_3]_4$ was observed. At temperatures below −60 °C, tetracoordinated complex $Pd[P(OPh)_3]_4$ was favored over the tricoordinated complex $Pd[P(OPh)_3]_3$. During reaction conditions, i.e., 50−80 °C, only the tricoordinated complex is present as the resting state of the catalyst, which, upon dissociation of a ligand, generates the reactive $Pd[P(OPh)_3]_2$ complex.

Monoallylation between Aromatic Amines and Allyl Alcohols. The catalyst precursor ($Pd[P(OPh)_3]_3$), was conveniently generated *in situ* from $Pd(dba)_2$ and $P(OPh)_3$ prior to the reactions. By employing a slight excess of the aniline, an efficient and highly selective monoallylation of the aromatic amine occurred within 12 h (Table 1). The

Table 1. Scope of the Monoallylations of Aromatic Amines 1 and Allyl Alcohols 2[b]



[a]Isolated yields. [b]Reaction conditions using flame-dried Schlenk tube: **1** (1.5 mmol), **2** (1.0 mmol), toluene (1.5 mL), and $Pd[P(OPh)_3]_3$ (2 mol %) were stirred at 80 °C for 12 h. [c]Reaction conditions using flame-dried Schlenk tube: **1** (2.0 mmol), **2** (1.0 mmol), and 5 mol % of $Pd(OAc)_2$, 20 mol % of P^nBu_3, and 25 mol % of BEt_3, in 2 mL of THF at 66 °C for 12 h.

monoallylated products were easily separated from the aniline by a short silica plug. Linear and branched allyl alcohols were investigated. The aliphatic allyl alcohols were monoallylated by aniline to afford products **3a**−**3b** in good yields (Table 1, entries 1−2). A benzylic group on the allyl alcohol gave the corresponding allylated aniline in a moderate yield (Table 1, entry 3). Allylic alcohols branched with an aryl group was investigated (Table 1, entries 4−10). The electronic property of the aryl of the allyl alcohol was varied, and it was found that the reaction was tolerant to both electron-donating and electron-withdrawing groups. The corresponding products were generated in yields up to 95% (Table 1, entries 4−10). The electronic property of aromatic amines was investigated by introducing electron-withdrawing and electron-donating groups in the *para*-position. The sterically demanding isopropyl allyl alcohol was selected as substrate to explore the effect of the aniline derivatives. The monoallylation of aromatic amines was achieved to give products **3k**−**3n** in good to excellent yields (Table 1, entries 11−14). This is in accordance to earlier reports where a zero-order dependence of aniline was observed.[20] Hence, the monoallylation of aromatic amines has a wide scope in respect to both the allyl alcohol and the aromatic amine. Benzyl and aliphatic amines were also allylated to generate products **3o** and **3p** in moderate yield (Table 1, entries 15−16). However, for these substrates, different reaction conditions using $Pd(OAc)_2$, electron-rich PBu_3 and BEt_3 as Lewis acid were required.

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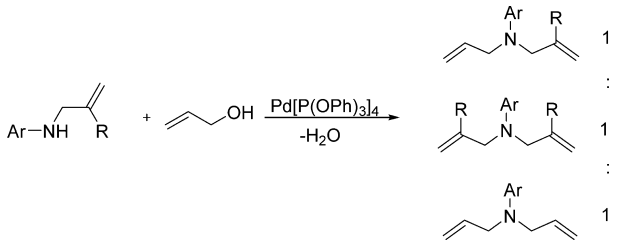
Diallylation between Monoallylated Aromatic Amines and Allyl Alcohol. The monoallylated aromatic amines were diallylated with allyl alcohol to generate unsymmetrical diallylated aromatic amines. By using the optimized reaction conditions for the monoallylation, *vide supra*, the reaction was sluggish, and an equilibrium between the three possible diallylated products was observed (Scheme 4). This was also observed in our previous report.[12]

Scheme 4. Performing the Diallylation Step at 80 °C Gave an Equilibrium Reaction

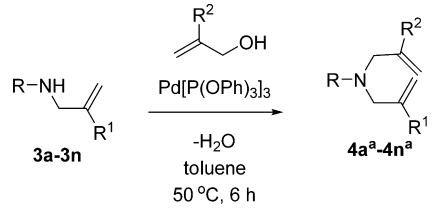


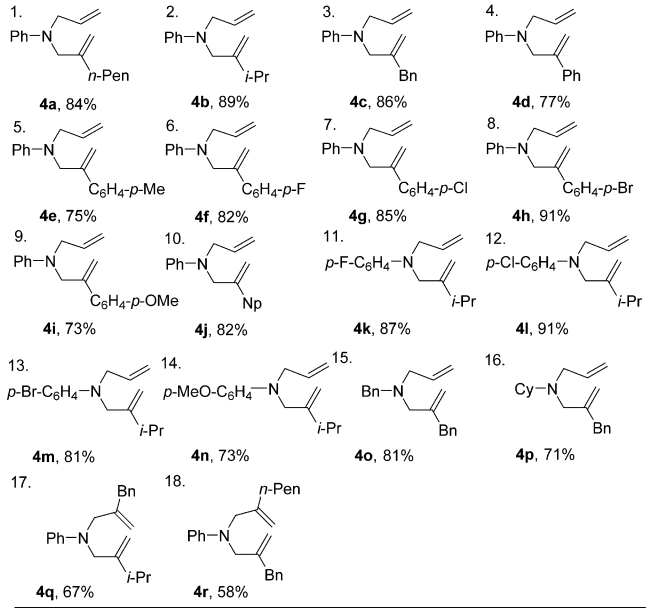
By increasing the amount of allyl alcohol (4.0 equiv) and lowering the reaction temperature to 50 °C, this problem was circumvented and a selective reaction to generate the unsymmetrical diallylated aromatic amines in good yields was achieved. The excess allyl alcohol can easily be recycled together with toluene by distillation.[12] When monoallylated amine **3a** was employed as a model substrate for diallylation, the reaction was finished within 6 h. The diallylation was successfully performed with full conversion to diallylated amine **4a** that was isolated in 84% yield (Table 2, entry 1). With the optimized reaction conditions in hand, we further investigated the scope of diallylation with monoallylated anilines **3**. The reaction has a wide substrate scope in which steric influence in the vinylic position had a negligible effect in the transformation where products **4a**–**4n** were isolated in good yields (Table 2, entries 1–14). Gratifyingly, the $Pd[P(OPh)_3]_3$ complex was reactive for both monoallylated benzyl and alkyl amines and gave products **4o** and **4p** in moderate yield (Table 2, entries 15–16). The scope of the second allyl alcohol was successfully increased to substituted allyl alcohols to generate products **4q** and **4r** (Table 2, entries 17–18). It should be noted that all reactions gave full conversion of unsymmetrical diallylated aromatic amines; however, purification by column chromatography lowered the isolated yields.

Ring-Closing Metathesis of Diallylated Amines. Ring-closing metathesis (RCM) was performed on the unsymmetrical diallylated amines. The reactions were run in dichloromethane using 5 mol % of $(H_2IMes)(PCy_3)Cl_2RuCHPh$ that generally performs better than $(PCy_3)_2Cl_2RuCHPh$ in RCM reactions to generate trisubstituted olefins.[21] The reactions of substrates **4a**–**4d** proceeded smoothly to produce the trisubstituted olefinic pyrrolines **5a**–**5d** in good to excellent yields (Table 3, entries 1–4). The naphthyl substituted substrate **4j** required 10 mol % catalyst loading to get to full conversion of **5j** (Table 3, entry 5). Once the reaction was completed, the RCM products were purified by column chromatography using deactivated silica. The unsymmetrical pyrrolines could be important substrates for asymmetric hydrogenation or other reactions.[22]

Generation of Pyrroles in One Pot from Disubstituted Aromatic Amines. To expand the methodology, a two-step, one-pot procedure to generate the pyrroles substituted in the β-position was envisaged.[23] The advantage of this methodology is that it is both atom economical and general in respect to the R-group in the β-position. Previous reports on atom-efficient routes to β-substituted pyrroles are efficient for either alkyl groups or aryl groups.[8,9,11] Preliminary results showed that SiO_2 efficiently aromatized, e.g., substrates **5c** and **5d** to pyrroles **6c** and **6d**. However, other substrates such as **5a** and **5b** only partially aromatized even after extended reaction times. To achieve a more general methodology, a short screening of the aromatization of **5a** to **6a** was performed. It was found that ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was efficient in the aromatization of the pyrrolines to pyrroles. In order to reduce the purification steps and thereby improve the environmental

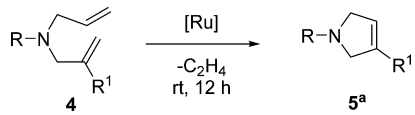
Table 2. Scope of the Diallylations of Amines 3 and Allyl Alcohol[b]

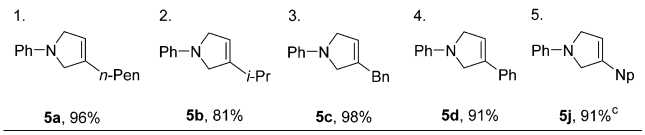




[a]Isolated yields. [b]Reaction conditions using flame-dried Schlenk tube: **3** (1.0 mmol), allyl alcohol (4.0 mmol), toluene (1.5 mL), and $Pd[P(OPh)_3]_3$ (2 mol %) were stirred at 50 °C for 6 h.

Table 3. Ring-Closing Metathesis of Diallylated Amines 4[b]





[a]Isolated yields. [b]Required 10 mol % of $(H_2IMes)(PCy_3)Cl_2RuCHPh$. [c]Reaction conditions: **4** (0.5 mmol), CH_2Cl_2 (5 mL), and catalyst (5 mol %) were stirred at rt for 12 h.

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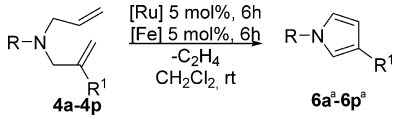
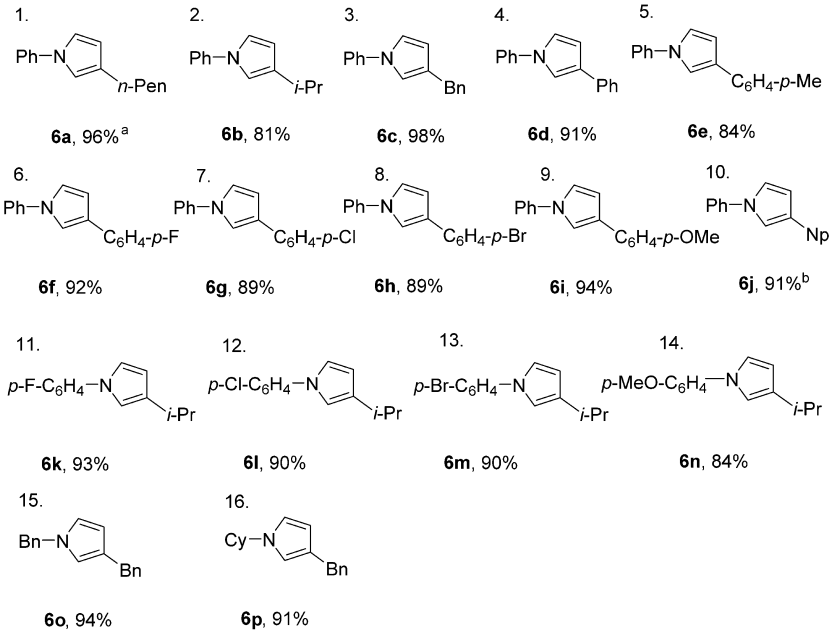
Table 4. Ru-Catalyzed Ring-Closing Metathesis and Fe-Catalyzed Aromatization To Yield Substituted Pyrroles





[a]Isolated yields. [b]Reaction conditions: **4** (0.5 mmol), CH_2Cl_2 (5 mL), and catalyst (5 mol %) were stirred at rt for 12 h.

factor,[24] the aromatization of the ring-closed pyrrolines was performed in the same pot as the RCM reaction. After full conversion to the pyrrolines was achieved, $FeCl_3{\cdot}6H_2O$ was added to the reaction mixture and the aromatization was run overnight. With this procedure, the pyrroles were efficiently generated directly from the diallylated aromatic amines in one pot. All pyrroles with alkyl, benzyl, or aryl groups in the β-position were isolated in good to excellent yields (Table 4). Attempts to ring-close substrates **4q** and **4r** to generate the corresponding tetrasubstituted olefins were unsuccessful even using the (H_2ITol) derivative of Grubbs–Hoveyda catalyst.[25] To our knowledge, this is the first time a general methodology to produce pyrroles substituted in the β-position with either alkyl, benzyl, or aryl groups has been reported. Noteworthy, these β-substituted pyrroles have been synthesized from simple starting materials with only water and ethane as side-products.

Mechanistic Considerations of the Pd-Catalyzed C–O Bond Cleavage of Allylic Alcohols. We have performed a mechanistic study of the $Pd[P(OPh)_3]_3$-catalyzed substitution of the OH group of an allylic alcohol.[20] Rate-order determination showed a second-order dependence of the allylic alcohol, a first-order dependence in $Pd[P(OPh)_3]_3$, and a zero-order dependence in aromatic amine (eq 4). Furthermore, the reaction rate was not dependent on the water concentration in the reaction mixture.

$$\text{rate} = k[Pd[P(OPh)_3]_3][\text{allyl alcohol}]^2 \quad (4)$$

Kinetic isotope effects of the allylic alcohol in which the allylic alcohol was labeled in the O–H/D and C–H/D were performed. The use of $CH_2{=}CHCH_2OD$ for the substitution of the OD/H group of the allylic alcohol by aniline with $Pd[P(OPh)_3]_3$ showed a primary deuterium KIE (k_{OH}/k_{OD} = 2.05 ± 0.02), suggesting that the cleavage of the O–H bond occurs in the rate-determining step (Table 5, entry 2). The use of $CH_2{=}CHCD_2OH$ gave a large secondary deuterium KIE (k_{CH}/k_{CD} = 1.34 ± 0.01) (Table 5, entry 1). Interestingly, the reaction of $CH_2{=}CHCD_2OD$ gave a combined deuterium KIE of (k_{CHOH}/k_{CDOD} = 2.06 ± 0.08) (Table 5, entry 3), and thereby, doubly labeled allyl alcohol $CH_2{=}CHCD_2OD$ displayed a similar KIE (2.06) to the monolabeled $CH_2{=}CHCH_2OD$ (2.05).[26] This is indicative of a reaction mechanism in which the cleavage of the O–H and C–O bonds takes place in two discriminate steps and not concertedly.[27]

Table 5. Kinetic Isotope Effects of the Allylation Step by $Pd[P(OPh)_3]_3$

1	k_{CH}/k_{CD}	1.34 ± 0.01
2	k_{OH}/k_{OD}	2.05 ± 0.02
3	k_{CHOH}/k_{CDOD}	2.06 ± 0.08

Previously proposed reaction mechanisms have invoked protonation of the leaving hydroxyl group of the allyl alcohol by a protonated amine (Scheme 5, route a).[28] With this reaction mechanism, a first-order rate dependence in aniline would be expected. However, a zero-order dependence in aniline was observed, which is not consistent with this reaction mechanism. An alternative reaction mechanism is that the allyl alcohol operates as the proton donor to promote the cleavage of the C–O bond in the allylic alcohol (Scheme 5, route b). The second-order rate dependence is consistent with this proposal. However, this requires that the O–H and C–O bonds are cleaved simultaneously and this would give a product isotope

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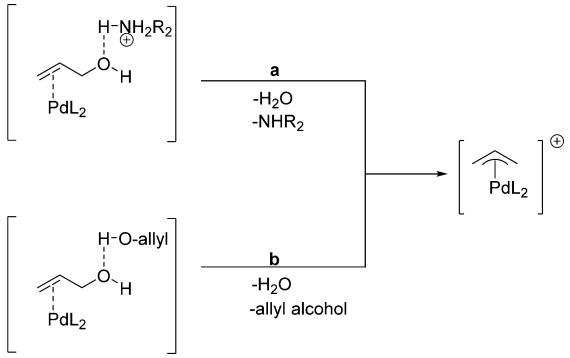
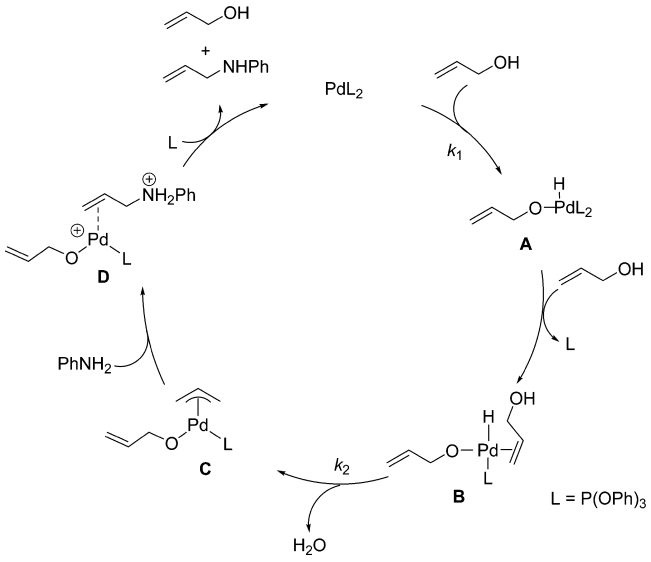
Scheme 5. Previously Proposed Reaction Mechanisms for the Cleavage of the C−O Bond Promoted by Protonation



effect (k_{CHOH}/k_{CDOD} = 2.75), which was not observed (Table 5, (k_{CHOH}/k_{CDOD} = 2.06)). Thereby, previously proposed reaction mechanisms that have invoked protonation of the leaving hydroxyl group of the allyl alcohol by either a protonated aromatic amine or allyl alcohol would not explain the rate equation and the KIE of the present study using $Pd[P(OPh)_3]_3$ as catalyst. Instead, a reaction mechanism that includes the cleavage of the O−H and C−O bonds in two discriminate high energy barrier steps is expected.

We propose the following reaction mechanism (Scheme 6). The palladium catalyst performs an insertion of the O−H bond

Scheme 6. Proposed Reaction Mechanism



of the allylic alcohol, resulting in palladium hydride intermediate **A**. The primary KIE for the cleavage of the O−H bond ($k_{OH/OD}$ = 2.05) indicates that this step has an activation barrier which is either equal to or insignificantly lower than the rate-determining step ($k_2 \geq k_1$). By ESI-MS and MS/MS CID, a corresponding palladium hydride complex was detected.[20] In the next step of the reaction mechanism, intermediate **A** coordinates to the double bond of another allylic alcohol to yield intermediate **B**. From this key intermediate, the C−O bond cleavage of the allylic alcohol occurs to form the π-allylpalladium intermediate **C**. An observed large secondary KIE ($k_{CH/CD}$ = 1.34) visualizes this energy barrier using the deuterated compound $CH_2{=}CHCD_2OH$. However, this effect is hidden when $CH_2{=}CHCD_2OD$ ($k_{CHOH/CDOD}$ = 2.06) is used as substrate. This is in line with that the cleavage of the C−O bond takes place after the cleavage of the O−H bond. The amine attacks the π-allyl at either terminal carbon via an outer-sphere mechanism, followed by proton transfer from the amine, to produce the allylamine and regenerate the $Pd[P(OPh)_3]_2$. In the absence of amine, the allyl alcohol operates as the nucleophile and corresponding symmetrical ethers are generated as products. Ozawa and Yoshifuji have proposed a similar reaction mechanism in which a hydridopalladium complex with a diphosphinidenecyclobutene ligand was responsible for the cleavage of the C−O bond in an allylic alcohol.[14d,29] Our mechanistic study supports this proposal also for the $Pd[P(OPh)_3]_3$ complex.

CONCLUSIONS

A general and efficient route to β-substituted pyrroles from amines and allylic alcohols using Pd, Ru, and Fe catalysis was achieved. A variety of pyrroles substituted in the β-position with aryl, benzyl, or alkyl groups were obtained in overall good yields. The monoallylation step of aromatic amines by differently substituted allylic alcohols was carried out using $Pd[P(OPh)_3]_3$ as catalyst. By increasing the amount of allyl alcohol and lowering the reaction temperature, a selective diallylation step of the monoallylated amines was achieved to afford the unsymmetrical diallylated aromatic amines using the same palladium catalyst. The RCM of diallylated amines was performed with $(H_2IMes)(PCy_3)Cl_2RuCHPh$. $FeCl_3{\cdot}6H_2O$ was added to the same batch, to aromatize the pyrrolines to the corresponding pyrroles. Thereby, the overall reaction only generated water and ethene as side-products. A reaction mechanism involving a palladium hydride generated from insertion of palladium to O−H of an allyl alcohol is proposed.

EXPERIMENTAL SECTION

General Information. ^1H NMR spectra was recorded with 300 and 400 MHz spectrometers as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.26 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals include s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, and bs = broad singlet. ^{13}C NMR spectra were recorded with 75 and 100 MHz spectrometers as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. IR spectra were recorded by a PerkinElmer FT-IR spectrometer. High-resolution mass spectra (HRMS) were performed with a micrOTOF spectrometer. The molecular fragments are quoted as the relation between mass and charge (m/z). The routine monitoring of reactions was performed by crude ^1H NMR and/or with a silica gel precoated Al plate, which was analyzed with iodine and/or UV light. All reactions were executed with oven-dried glassware under an argon atmosphere. Dichloromethane and toluene were dried by passage through activated alumina columns. Alkyl, benzyl,[30] and aryl[31] substituted allylic alcohols were synthesized according to literature procedures.

Monoallylation of Aniline and 2-Methyleneheptan-1-ol. A flame-dried Schlenk tube was charged with $Pd(dba)_2$ (8.6 mg, 0.10 mmol, 0.02 equiv) and dissolved in dry CH_2Cl_2 (0.5 mL), and $P(OPh_3)$ (15.6 μL, 0.41 mmol, 0.08 equiv) was added. The slurry was degassed by three freeze−pump−thaw cycles and stirred under argon at room temperature for 30 min. The solvent was removed *in vacuo*. Dry toluene (1.5 mL) and aniline (102.6 μL, 2.69 mmol, 1.5 equiv) were added. Then, 2-methyleneheptan-1-ol (230 mg, 1.79 mmol, 1.0 equiv) was added. The mixture was degassed by three freeze−pump−thaw cycles. The resulting mixture was stirred at 80 °C for 12 h. After

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completion monitored by TLC, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (basidify SiO_2 with Et_3N, pentane/CH_2Cl_2) to obtain *N*-(2-methyleneheptyl)aniline (**3a**) as a yellow solid (328 mg, 1.61 mmol, 90% yield).

Diallylation of *N*-(2-methyleneheptyl)aniline (3a) and Allyl Alcohol. A flame-dried Schlenk tube was charged with $Pd(dba)_2$ (8.6 mg, 0.0151 mmol, 0.02 equiv) and dissolved in dry CH_2Cl_2 (0.5 mL), and $P(OPh_3)$ (10.1 μL, 0.038 mmol, 0.08 equiv) was added. The slurry was degassed by three freeze−pump−thaw cycles and stirred under argon at room temperature for 30 min. The solvent was removed *in vacuo*. Dry toluene (1.5 mL) and *N*-(2-methyleneheptyl)-aniline (**3a**) (153 mg, 0.754 mmol, 1.0 equiv) were added. Then, allyl alcohol (200 μL, 3.00 mmol, 4.0 equiv) was added. The mixture was degassed by three freeze−pump−thaw cycles. The resulting mixture was stirred at 50 °C for 6 h. After completion monitored by TLC, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (basidify SiO_2 with Et_3N, pentane/CH_2Cl_2) to obtain *N*-allyl-*N*-(2-methylene-heptyl)aniline (**4a**) as a yellow oil (154 mg, 0.633 mmol, 84% yield).

Ring-Closing Metathesis of *N*-Allyl-*N*-(2-methyleneheptyl)-aniline (4a). *N*-Allyl-*N*-(2-methyleneheptyl)aniline (**4a**) (248 mg, 1.02 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2. Grubbs second-generation catalyst (43 mg, 0.051 mmol, 0.05 equiv) was added to the mixture, and the mixture was stirred at room temperature for 12 h. After completion monitored by TLC, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (basidify SiO_2 with Et_3N, pentane/CH_2Cl_2) to obtain 3-pentyl-1-phenyl-2,5-dihydro-1*H*-pyrrole (**5a**) as a yellow solid (211 mg, 0.978 mmol, 96% yield).

Ring-Closing Metathesis and Aromatization of *N*-Allyl-*N*-(2-methyleneheptyl)aniline (4a). *N*-Allyl-*N*-(2-methyleneheptyl)-aniline (**4a**) (50 mg, 0.205 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2. Grubbs second-generation catalyst (8.7 mg, 0.010 mmol, 0.05 equiv) was added to the mixture, and the mixture was stirred at room temperature for 6 h. After completion monitored by TLC, $FeCl_3 \cdot 6H_2O$ (0.010 mmol) was added to the reaction mixture, and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (pentane/CH_2Cl_2) to obtain 3-pentyl-1-phenyl-1*H*-pyrrole (**6a**) as a yellow solid (42 mg, 0.197 mmol, 96% yield).

*N-(2-Methyleneheptyl)aniline (**3a**).*[32] Colorless oil. Yield: 328 mg (90%). IR (neat): 3421, 3053, 3021, 2956, 2928, 2858, 1651, 1602, 1505, 1466, 1314, 1266, 1253, 1197, 1180, 894, 865, 746, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.17 (t, J = 7.6 Hz, 2H), 6.71 (t, J = 7.2 Hz, 2H), 6.62 (d, J = 8.0 Hz, 2H), 5.02 (s, 1H), 4.90 (s, 1H), 3.88 (bs, 1H), 3.71 (s, 2H), 2.10 (t, J = 7.6 Hz, 2H), 1.55−1.46 (m, 2H), 1.39−1.27 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.6, 146.9, 129.3, 117.4, 113.0, 110.0, 48.9, 34.3, 31.8, 27.6, 22.7, 14.2 ppm. HRMS (ESI): m/z calcd. for $C_{14}H_{22}N$ [M + H] 204.1747, found 204.1746.

*N-(3-Methyl-2-methylenebutyl)aniline (**3b**).* Colorless oil. Yield: 283 mg (87%). IR (neat): 3421, 3079, 3051, 3020, 2961, 2871, 1647, 1602, 1505, 1464, 1315, 1268, 1179, 1097, 896, 867, 746, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.21 (t, J = 7.3 Hz, 2H), 6.74 (t, J = 7.1 Hz, 1H) 6.65 (d, J = 8.6 Hz, 2H), 5.03 (s, 1H), 4.96 (s, 1H), 3.86 (bs, 1H), 3.78 (s, 2H), 2.40 (m, 1H), 1.16 (d, J = 6.6 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.8, 148.5, 129.3, 117.4, 112.9, 107.9, 47.7, 32.2, 21.9 ppm. HRMS (ESI): m/z calcd. for $C_{12}H_{18}N$ [M + H] 176.1434, found 176.1436.

*N-(2-Benzylallyl)aniline (**3c**).* Yellow solid; mp 66−69 °C. Yield: 352 mg (78%). IR (neat): 3421, 3082, 3054, 3024, 2910, 1652, 1601, 1506, 1494 c, 1453, 1432, 1313, 1259, 906, 869, 731, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35−7.14 (m, 7H), 6.71 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.7 Hz, 2H), 5.14 (s, 1H), 4.98 (s, 1H), 3.85 (bs, 1H), 3.69 (s, 2H), 3.45 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 146.2, 139.3, 129.1, 128.6, 126.5, 117.5, 113.0, 112.6, 48.3, 41.3 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{18}N$ [M + H] 224.1434, found 224.1427.

*N-(2-Phenylallyl)aniline (**3d**).*[33] White solid; mp 78−82 °C. Yield: 265 mg (85%). IR (neat): 3062, 3036, 2924, 2854, 1628, 1592, 1595, 1571, 1595, 1399, 1342, 1237, 1190, 1028, 987, 908, 858, 780, 747, 711, 689 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dd, J = 3.6, 1.6 Hz, 2H), 7.37−7.16 (m, 3H), 7.18 (t, J = 7.6 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 6.62 (d, J = 7.6 Hz, 2H), 5.48 (s, 1H), 5.33 (s, 1H), 4.16 (s, 2H), 3.88 (bs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.5, 142.0, 139.6, 129.1, 128.5, 127.9, 126.1, 116.5, 112.2, 112.0, 54.2 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{16}N$ [M + H] 210.1277, found 210.1277.

*N-(2-(p-Tolyl)allyl)aniline (**3e**).*[34] White soild; mp 82−85 °C. Yield: 257 mg (86%). IR (neat): 3423, 3022, 2919, 2854, 1603, 1508, 1439, 1321, 1330,1309,1275, 1261, 1180, 1119, 1065, 1015, 901, 826, 744, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.1 Hz, 2H), 7.26−7.21 (m, 4H), 6.77 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 7.5 Hz, 2H), 5.51 (s, 1H), 5.35 (s, 1H), 4.19 (s, 2H), 3.91 (bs, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2, 144.6, 137.8, 136.4, 129.3, 126.1, 117.6, 113.0, 112.9, 48.2, 21.3 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{18}N$ [M + H] 224.1434, found 224.1430.

*N-(2-(4-Fluorophenyl)allyl)aniline (**3f**).*[34] Yellow solid; mp 80−83 °C. Yield: 272 mg (82%). IR (neat): 3438, 3054, 2915, 2880, 1373, 2321, 1685, 1599, 1505, 1443, 1330, 1281, 1225, 1177, 1124, 1067, 1011, 992, 900, 837, 750, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47−7.42 (m, 2H), 7.23−7.20 (m, 2H), 7.17−7.02 (m, 2H), 6.74 (t, J = 7.8 Hz, 1H), 6.64 (d, J = 7.5 Hz, 2H), 5.44 (s, 1H), 5.34 (s, 1H), 4.14 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, J_{CF} = 240 Hz), 147.8, 143.8, 135.2 (d, J_{CF} = 3 Hz), 129.2, 127.7 (d, J_{CF} = 10 Hz), 117.6, 115.3 (d, J_{CF} = 20 Hz), 113.7, 112.9, 48.2 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{15}NF$ [M + H] 228.1183, found 228.1191.

*N-(2-(4-Chlorophenyl)allyl)aniline (**3g**).*[34] Yellow solid; mp 78−80 °C. Yield: 133 mg (92%). IR (neat): 3413, 3051, 2911, 1602, 1514, 1492, 1335, 1278, 1181, 1097, 1009, 906, 833, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44−7.41 (m, 2H), 7.40−7.32 (m, 2H), 7.26−7.20 (m, 2H), 6.79 (t, J = 1.2 Hz, 1H), 6.65 (d, J = 5.1 Hz, 2H), 5.50 (s, 1H), 5.39 (s, 1H), 4.15 (s, 2H), 3.88 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 143,7, 137.7, 133.7, 129.3, 128.7, 127.5, 117.7, 114.3, 112.9, 48.0 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{15}NCl$ [M + H] 244.0887, found 244.0882.

*N-(2-(4-Bromophenyl)allyl)aniline (**3h**).*[35] White solid; mp 89−91 °C. Yield: 274 mg (95%). IR (neat): 3413, 3049, 2919, 2852, 1899, 1820, 1683, 1599, 1513, 1488, 1334, 1237, 1179, 1086, 1075, 1004, 906, 828, 749, 738, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 2H), 6.75 (t, J = 8.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 5.49 (s, 1H), 5.37 (s, 1H), 4.13 (s, 2H), 3.85 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 143.8, 138.2, 131.6, 129.3, 127.8, 121.9, 117.8, 114.4, 112.9, 48.0 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{15}NBr$ [M + H] 288.0382, found 288.0373.

*N-(2-(4-Methoxyphenyl)allyl)aniline (**3i**).*[35] White solid; mp 84−86 °C. Yield: 240 mg (78%). IR (neat): 3415, 3044, 2960, 2929, 2837, 1602, 1506, 1298, 1246, 1179, 1031, 906, 833, 730, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ = 747−7.45 (m, 2H), 7.23 (t, J = 7.8 Hz), 6.95−6.93 (m, 2H), 6.76 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 8.1 Hz, 2H), 5.46 (s, 1H), 5.30 (s, 1H), 4.17 (2, 2H), 3.86 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 148.2, 144.1, 131.7, 129.3, 127.3, 117.6, 114.0, 113.0, 112.2, 55.4, 48.2 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{18}NO$ [M + H] 240.1383, found 240.1377.

*N-(2-(Naphthalen-2-yl)allyl)aniline (**3j**).* White solid; mp 88−90 °C. Yield: 256 mg (81%). IR (neat): 3417, 3052, 3020, 2921, 2850, 1601, 1504, 1430, 1326, 1270, 1253, 1180, 895, 858, 818, 746, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.93−7.84 (m, 4H), 7.66−7.61 (m, 1H), 7.52−7.44 (m, 2H), 7.26−7.19 (m, 2H), 6.78−6.66 (m, 3H), 5.66 (s, 1H), 5.48 (s, 1H), 3.31 (s, 2H), 4.02 (bs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.9, 144.5, 136.4, 133.3, 129.2, 128.2, 128.1, 127.6, 126.3, 124.8, 124.4, 117.6, 114.3, 113.0, 48.2 ppm. HRMS (ESI): m/z calcd. for $C_{19}H_{18}N$ [M + H] 260.1434, found 260.1422.

*4-Fluoro-N-(3-methyl-2-methylenebutyl)aniline (**3k**).* Yellow oil. Yield: 199 mg (96%). IR (neat): 3423, 2960, 2925, 2871, 1677, 1650, 1621, 1508, 1464, 1363, 1315, 1221, 1155, 1104, 897, 817, 743 cm^{-1}.

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (t, J = 8.4 Hz, 2H), 6.58−6.54 (m, 2H), 5.02 (s, 1H), 4.96 (s, 1H), 3.73 (bs, 1H), 2.41−2.34 (m, 1H), 1.15 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5 (d, J_{CF} = 230 Hz), 152.5, 144.6 (d, J_{CF} = 2 Hz), 115.4 (d, J_{CF} = 20 Hz), 113.4 (d, J_{CF} = 10 Hz), 113.5, 107.8, 48.2, 32.1, 31.9, 21.8 ppm. HRMS (ESI): m/z calcd. for $C_{12}H_{17}NF$ [M + H] 194.1339, found 194.1339.

4-Chloro-N-(3-methyl-2-methylenebutyl)aniline (**3l**). Yellow oil. Yield:155 mg (87%). IR (neat) 3426, 2962, 2928, 2872, 1846, 1649, 1612, 1505, 1465, 1315, 1267, 1220, 1155, 1104, 1076, 897, 816, 741 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.91−6.85 (m, 2H), 6.56−6.52 (m, 2H), 4.98 (s, 1H), 4.92 (s, 1H), 3.71 (s, 2H), 2.37−2.30 (m, 1H), 1.11 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2, 152.6, 115.7, 115.4, 113.6, 113.5, 107.8, 48.2, 32.1, 21.8 ppm. HRMS (ESI): m/z calcd. for $C_{12}H_{17}NCl$ [M + H] 210.1044, found 210.1040.

4-Bromo-N-(3-methyl-2-methylenebutyl)aniline (**3m**). Yellow oil. Yield: 189 mg (86%). IR (neat): 3428, 3085, 2961, 2927, 2870, 1860, 1648, 1594, 1495, 1464, 1396, 1363, 1315, 1239, 1267, 1177, 1069, 999, 896, 809 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30−7.25 (m, 2H), 6.52−6.48 (m, 2H), 4.98 (s, 1H), 4.96 (s, 1H), 3.91 (bs, 1H), 3.74 (s, 2H), 2.42−2.32 (m, 1H), 1.16 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.1, 147.4, 131.9, 114.4, 108.7, 107.9, 47.5, 32.1, 21.9 ppm. HRMS (ESI): m/z calcd. for $C_{12}H_{17}NBr$ [M + H] 254.0539, found 254.0537.

4-Methoxy-N-(3-methyl-2-methylenebutyl)aniline (**3n**). Colorless oil. Yield: 282 mg (87%). IR (neat): 3413, 2959, 2871, 2831, 1648, 1618, 1510, 1463, 1441, 1298, 1231, 1179, 1118, 1036, 962, 895, 816, 734 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.80−6.76 (m, 2H), 6.61−6.56 (m, 2H), 4.99 (s, 1H), 4.91 (s, 1H), 3.74 (s, 3H), 3.71 (s, 2H), 2.38−2.32 (m, 1H), 1.11 (d, J = 6.3 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 151.9, 142.7, 114.8, 114.0, 107.6, 55.8, 48.5, 32.1, 21.8 ppm. HRMS (ESI): m/z calcd. for $C_{13}H_{20}NO$ [M + H] 206.1539, found 206.1534.

N,2-Dibenzylprop-2-en-1-amine (**3o**). Colorless oil. Yield: 113.2 mg (85%). IR (neat): 3339,3083,3027, 2914, 2830,1946, 1873, 1648, 1602, 1494, 1453, 1360, 1155, 1075, 1029, 901, 823, 736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44−7.32 (m, 10H), 5.20−5.19 (m, 1H), 5.03−5.02 (m,1H), 3.85 (s, 2H), 3.55 (s, 2H), 3.31 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 140.4, 139.4, 128.9, 128.2, 127.9, 126.7, 125.9, 112.0, 53.1, 52.9, 41.1 ppm. HRMS (ESI): m/z calcd. for $C_{17}H_{20}N$ [M + H] 238.1590, found 238.1590.

N-(2-Benzylallyl)cyclohexanamine (**3p**). Colorless oil. Yield: 143.1 mg (76%). IR (neat): 3083, 3062, 3027, 2927, 2853, 1650, 1602, 1494, 1452, 1371, 1348, 1259, 1122, 1050, 1030, 966, 898, 825, 788, 740 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33−7.28 (m, 2H), 7.24−7.20 (m, 3H), 5.04−5.02 (m, 1H), 4.88−4.86 (m, 1H), 3.41 (s, 2H), 3.19 (s, 2H), 2.43−2.36 (m, 1H), 1.86−1.80 (m, 2H), 1.76−1.71 (m, 2H), 1.64−1.59 (m, 1H), 1.30−1.01 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 139.6, 128.9, 128.3, 126.1, 111.6, 55.9, 50.8, 41.5, 33.6, 26.2, 25.3 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{24}N$ [M + H] 230.1903, found 230.1908.

N-Allyl-N-(2-methyleneheptyl)aniline (**4a**). Yellow oil. Yield: 154 mg (84%). IR (neat): 3083, 3063, 2957, 2928, 1644, 1598, 1574, 1505, 1458, 1388, 1361, 1232, 1189, 989, 915, 896, 744, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (t, J = 7.3 Hz, 2H), 6.71−6.68 (m, 3H), 5.89 (m, 1H), 5.22−5.13 (m, 2H), 4.88 (s, 2H), 3.95 (d, J = 3.1 Hz, 2H), 3.84 (s, 2H), 2.06 (t, J = 7.6 Hz, 2H), 1.58−1.50 (m, 2H), 1.44−1.26 (m, 4H), 0.95 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 144.9, 134.0, 129.1, 116.2, 116.1, 112.2, 109.3, 55.3, 52.7, 33.9, 31.9, 27.7, 22.7, 14.2 ppm. RMS (ESI): m/z calcd. for $C_{17}H_{26}N$ [M + H] 244.2059, found 244.2053.

N-Allyl-N-(3-methyl-2-methylenebutyl)aniline (**4b**). Yellow oil. Yield: 803 mg (89%). IR (neat): 3091, 3063, 2960, 2927, 2871, 1644, 1598, 1574, 1504, 1462, 1389, 1362, 1234, 1188, 989, 958, 916, 898, 860, 744, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23−7.17 (m, 2H), 6.71−6.63 (m, 3H), 5.89 (m, 1H), 5.22−5.16 (m, 1H), 4.89 (s, 1H), 4.82−4.78 (m, 1H), 3.94 (d, J = 4.6 Hz, 2H), 3.89 (s, 2H), 2.30 (m, 1H), 1.16 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 149.1, 134.0, 129.1, 116.2, 116.1, 112.1, 106.9, 54.0, 52.9, 31.9, 22.0 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{22}N$ [M + H] 216.1747, found 216.1736.

N-Allyl-N-(2-benzylallyl)aniline (**4c**). Yellow oil. Yield: 305 mg (86%). IR (neat): 3062, 3026, 2980, 2905, 1643, 1597, 1574, 1504, 1452, 1432, 1387, 1361, 1344, 1231, 1187, 1074, 1029, 988, 960, 902, 860, 743, 689 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36−7.15 (m, 7H), 6.68 (t, J = 7.s Hz, 1H), 6.62 (d, J = 8.2 Hz, 2H), 5.84 (m, 1H), 5.16−5.09 (m, 2H), 5.00 (s, 1H), 4.94 (s, 1H), 3.89 (d, J = 3.9 Hz, 2H), 3.40 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 144.3, 139.2, 133.9, 129.1, 128.6, 126.5, 116.3, 116.2, 116.1, 112.5, 112.3, 54.7, 52.9, 41.0 ppm. HRMS (ESI): m/z calcd. for $C_{19}H_{22}N$ [M + H] 264.1747, found 264.1734.

N-Allyl-N-(2-phenylallyl)aniline (**4d**). Yellow oil. Yield: 142 mg (77%). IR (neat): 3060, 3026, 2979, 2910, 2859, 1641, 1596, 1574, 1504, 1387, 1355, 1232, 1181, 988, 954, 914, 744, 689 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 5.2 Hz, 1H), 7.45−7.38 (m, 1H), 7.30−7.25 (m, 3H), 6.80−6.74 (m, 5H), 6.00−5.89 (m, 2H), 5.52 (s, 1H), 5.29−5.22 (m, 2H), 4.36 (s, 1H), 4.07 (d, J = 4.8 Hz, 1H), 3.99 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 142.4, 139.7, 134.1, 133.8, 129.1, 128.5, 127.9, 126.1, 116.4, 116.3, 116.2, 116.0, 112.4, 112.3, 112.2, 54.1, 52.8 ppm. HRMS (ESI): m/z calcd. for $C_{18}H_{20}N$ [M + H] 250.1590, found 250.1578.

N-Allyl-N-(2-(p-tolyl)allyl)aniline (**4e**).[36] Yellow oil. Yield: 126 mg (75%). IR (neat): 3060, 3026, 2979, 2919, 2859, 1641, 1597, 1574, 1503, 1378, 1354, 1232, 1181, 988, 954, 915, 823, 749, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 10.8 Hz, 1H), 7.45−7.39 (m, 4H), 6.99−6.92 (m, 4H), 6.18−6.04 (m, 2H), 5.68 (s, 1H), 5.48−5.35 (m, 2H), 4.52 (s, 1H), 4.23 (d, J = 6.0 Hz, 1H), 4.15 (d, J = 6.0 Hz, 2H), 2.60 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 142.0, 137.4, 136.5, 133.9, 133.6, 129.0, 128.9, 125.7, 116.2, 115.9, 115.8, 112.2, 112.0, 111.2, 53.8, 52.6, 21.0 ppm. HRMS (ESI): m/z calcd. for $C_{19}H_{22}N$ [M + H] 264.1746, found 264.1735.

N-Allyl-N-(2-(4-fluorophenyl)allyl)aniline (**4f**). White solid; mp 77−81 °C. Yield: 139 mg (82%). IR (neat): 3089, 3052, 2980, 2923, 1930, 1883, 1594, 1571, 1505, 1428, 1395, 1360, 1351, 1236, 1212, 1185, 1159, 1068, 987, 923, 906, 832, 819, 748, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49−7.45 (m, 2H), 7.29−7.22 (m, 2H), 7.13−7.05 (m, 2H), 6.78−6.71 (m, 3H), 6.00−5.87 (m, 1H), 5.44 (s, 1H), 5.31−5.19 (m, 1H), 4.28 (s, 1H), 4.04 (d, J = 4.8 Hz, 2H), 3.97 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, J_{CF} = 247.5 Hz), 148.6, 141.6, 135.7, 134.1, 133.7, 129.1, 127.7, 127.6, 116.4 (d, J_{CF} = 22.5 Hz), 116.1 (d, J_{CF} = 15 Hz), 225.5, 115.2, 112.4, 112.2 54.1, 52.8 ppm. HRMS (ESI): m/z calcd. for $C_{18}H_{19}NF$ [M + H] 268.1496, found 268.1485.

N-Allyl-N-(2-(4-chlorophenyl)allyl)aniline (**4g**). Yellow solid; ; mp 80−83 °C. Yield: 123 mg (85%). IR (neat): 3089, 3052, 2979, 2992, 2866, 1926, 1892, 1818, 1594, 1570, 1505, 1491, 1431, 1392, 1359, 1348, 1235, 1182, 1097, 1009, 986, 955, 923, 907, 828, 747, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42−7.33 (m, 4H), 7.26−7.23 (m, 2H), 6.76−6.72 (m, 3H), 5.97−5.85 (m, 1H), 5.45 (d, J = 3.0 Hz, 1H), 5.25−5.18 (m, 3H), 4.26 (d, J = 3.6 Hz, 2H), 4.01 (dd, J = 3.0, 1.8 Hz, 2H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 148.6, 141.5, 138.0, 133.7, 133.6, 129.1, 128.6, 127.3, 116.6, 116.3, 112.9, 112.2, 53.9, 52.8 ppm. HRMS (ESI): m/z calcd. for $C_{18}H_{19}NCl$ [M + H] 284.1200, found 284.1186.

N-Allyl-N-(2-(4-bromophenyl)allyl)aniline (**4h**). Yellow solid; mp 79−81 °C. Yield: 228 mg (90%). IR (neat): 3048, 2924, 2854, 1595, 1505, 1489, 1391, 1345, 1236, 1182, 1092, 1006, 986, 910, 830, 747, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.22−7.18 (m, 2H), 6.72−6.68 (m, 3H), 5.92−5.83 (m, 1H), 5.44 (s, 1H), 5.21−5.14 (m, 3H), 4.23 (s, 2H), 3.98 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.6, 141.6, 138.5, 133.6, 131.5, 129.1, 127.7, 121.8, 116.6, 116.3, 113.0, 53.9, 52.8 ppm. HRMS (ESI): m/z calcd. for $C_{18}H_{19}NBr$ [M + H] 328.0695, found 328.0680.

N-Allyl-N-(2-(4-methoxyphenyl)allyl)aniline (**4i**). White soild; mp 77−80 °C. Yield: 85.3 mg (73%). IR (neat): 3061, 3039, 3004, 2937, 2908, 2836, 1597, 1504, 1245, 1234, 1178, 1032, 833, 745, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44−7.41 (m, 2H), 7.24−7.20 (m, 3H), 6.96−6.93 (m, 2H), 6.78−6.73 (m, 3H), 5.95−5.94 (m, 1H),

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5.43 (q, J = 1.3 Hz), 5.28−5.21 (m, 2H), 5.12 (q, J = 1.3 Hz, 1H), 4.31 (s, 2H), 4.06 (d, J = 4.8 Hz, 2H), 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 148.9, 141.7, 133.9, 129.8, 129.2, 127.2, 116.5, 116.3, 114.0, 112.3, 110., 54.4, 54.2, 52.9 ppm. HRMS (ESI): m/z calcd. for $C_{19}H_{22}NO$ [M + H] 280.1696, found 280.1697.

*N-Allyl-N-(2-(naphthalen-2-yl)allyl)aniline (**4j**).* Colorless oil. Yield: 167 mg (82%). IR (neat): 3058, 2913, 2857, 1597, 1505, 1391, 1345, 1234, 1184, 989, 958, 903, 857, 818, 747, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91−7.85 (m, 4H), 7.70−7.68 (m, 1H), 7.56−7.50 (m, 2H), 7.29−7.24 (m, 2H), 6.81−6.74 (m, 3H), 5.98 (m, 1H), 5.64 (s, 1H), 5.30−5.18 (m, 3H), 4.45 (s, 2H), 4.09 (d, J = 4.7, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 142.4, 137.0, 133.9, 133.5, 133.1, 129.3, 128.3, 128.2, 127.8, 126.4, 126.2, 124.7, 124.6, 116.6, 112.9, 112.4, 54.2, 53.1 ppm. HRMS (ESI): m/z calcd. for $C_{22}H_{22}N$ [M + H] 300.1747, found 300.1744.

*N-Allyl-4-fluoro-N-(3-methyl-2-methylenebutyl)aniline (**4k**).* Yellow oil. Yield: 108 mg (87%). IR (neat): 3083, 2962, 2929, 2871, 1840, 1644, 1611, 1509, 1391, 1362, 1225, 1183, 1143, 991, 960, 899, 810, 716 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97−6.90 (m, 2H), 6.66−6.60 (m, 2H), 5.97−5.85 (m, 1H), 4.94 (s, 1H), 4.85 (s, 1H), 3.95−3.93 (m, 2H), 3.89 (s, 2H), 2.36−2.27 (m, 1H), 1.18 (d, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2 (d, J_{CF} = 240 Hz), 148.0 (d, J_{CF} = 2.0 Hz), 133.9, 116.1, 115.3 (d, J_{CF} = 20 Hz), 113.0 (d, J_{CF} = 10 Hz), 107.0, 54.6, 53.4, 31.7, 21.9 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{21}NF$ [M + H] 234.1653, found 234.1658.

*N-Allyl-4-chloro-N-(3-methyl-2-methylenebutyl)aniline (**4l**).* Yellow oil. Yield: 124 mg (91%). IR (neat): 3085, 2961, 2928, 2871, 1855, 1644, 1596, 1497, 1463, 1439, 1390, 1361, 1234, 1184, 1096, 958, 917, 898, 805, 770 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 9.2 Hz, 2H), 5.89−5.79 (m, 1H), 5.18−5.15 (m, 1H), 5.12 (s, 1H), 3.89−3.88 (m, 2H), 3.83 (s, 2H), 2.27−2.17 (m, 1H), 1.11 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 147.4, 133.3, 128.7, 120.7, 116.1, 113.0, 106.9, 54.1, 52.9, 31.7, 21.8 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{21}NCl$ [M + H] 250.1357, found 250.1353.

*N-Allyl-4-bromo-N-(3-methyl-2-methylenebutyl)aniline (**4m**).* Yellow oil. Yield: 93.7 mg (81%). IR (neat): 3085, 2960, 1926, 2870, 1854, 1644, 1590, 1495, 1463, 1390, 1361, 1234, 1183, 1082, 993, 958, 917, 898, 803, 764 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27−7.22 (m, 2H), 6.54−6.46 (m, 2H), 5.90−5.78 (m, 1H), 5.19−4.74 (m, 2H), 4.58 (s, 1H), 4.74 (s, 1H), 3.88 (d, J = 4.8 Hz, 2H), 3.72 (s, 2H), 2.30−2.21 (m, 1H), 1.30 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 147.8, 133.2, 131.6, 116.1, 113.6, 107.8, 106.9, 54.0, 52.9, 31.7, 21.8 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{21}NBr$ [M + H] 294.0852, found 294.0853.

*N-Allyl-4-methoxy-N-(3-methyl-2-methylenebutyl)aniline (**4n**).* Yellow oil. Yield: 178 mg (73%). IR (neat): 3080, 2960, 2930, 2871, 2831, 1643, 1510, 1463, 1441, 1362, 1261, 1230, 1180, 1943, 992, 959, 897, 809, 788, 708 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (d, J = 9.2 Hz, 2H), 6.60 (d, J = 8.0 Hz, 2H), 5.90−5.82 (m, 1H), 5.18 (d, J = 8.4 Hz, 1H), 3.88 (s, 2H), 3.78 (s, 2H), 3.75 (s, 3H), 2.31−2.18 (m, 1H), 1,12 (d, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 150.9, 143.7, 134.4, 115.9, 114.6, 113.5, 107.0, 55.8, 54.7, 53.4, 31.6, 21.9 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{24}NO$ [M + H] 246.1852, found 246.1850.

*N-Allyl-N,2-dibenzylprop-2-en-1-amine (**4o**).* Colorless oil. Yield: 90.7 mg (71%). IR (neat): 3063, 3027, 2921, 2771, 1945, 1806, 1743, 1645, 1602, 1499, 1453, 1368, 1255, 1153, 1120, 1073, 1029, 994, 905, 739 cm^{-1}. ^{1}H NMR (400 MHz, CDCl3): δ = 7.44−7.22 (m, 10H), 5.98−5.88 (m, 1H), 5.27−5.20 (m, 1H), 5.18 (s, 2H), 4.95 (s, 1H), 3.62 (s, 2H), 3.51 (s, 2H), 3.12−3.09 (m, 2H), 3.03 (s, 2H) ppm. ^{13}C NMR (100 MHz, CDCl3): δ = 147.2, 139.7, 139.7, 135.8, 129.1, 128.8, 128.1, 126.7, 125.9, 117.2, 113.9, 58.6, 57.7, 56.2, 40.6 ppm. HRMS (ESI): m/z calcd. for $C_{20}H_{24}N$ [M + H] 278.1903, found 278.1917.

*N-Allyl-N-(2-benzylallyl)cyclohexanamine (**4p**).* Yellow oil. Yield: 102.0 mg (81%). IR (neat): 3076, 3027, 2927, 2853, 2811, 1738, 1644, 1602, 1494, 1451, 1346, 1261, 1161, 1121, 1098, 993, 913, 900, 739 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32−7.19 (m, 5H), 5.84−5.74 (m, 1H), 5.14 (dq, J = 16 Hz, J = 4 Hz, 1H), 5.06−5.04 (m, 1H), 5.03 (dq, J = 8 Hz, J = 4 Hz, 1H), 4.81 (m, 1H), 3.41 (s, 2H), 3.08 (dt, J = 4 Hz, J = 2 Hz, 2H), 2.67 (s, 2H), 2.55−2.47 (m, 1H), 1.78−1.72 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 140.1, 138.1, 129.2, 128.1, 125.8, 115.5, 113.2, 58.4, 54.5, 52.7, 40.4, 28.7, 26.5, 26.2 ppm. HRMS (ESI): m/z calcd. for $C_{19}H_{28}N$ [M + H] 270.2216, found 270.2207.

*N-(2-Benzylallyl)-N-(3-methyl-2-methylenebutyl)aniline (**4q**).* Colorless oil. Yield: 76.9 mg (61%). IR (neat): 3062, 3027, 2960, 2924, 2870, 2854, 1649, 1597, 1506, 1494, 1453, 1432, 1391, 1363, 1234, 1190, 1162, 1054, 989,966, 899, 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36−7.23 (m, 8H), 7.18−7.14 (m, 2H), 6.66 (t, J = 8 Hz, 1H), 6.55 (d, J = 8 Hz, 2H), 3.83 (s, 2H), 3.79 (s, 2H), 3.39 (s, 2H), 2.24−2.19 (m, 1H), 1.09 (d, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 148.8, 143.8, 139.0, 128.8, 128.4, 126.3, 115.8, 111.7, 111.6, 106.6, 54.5, 40.8, 31.8, 21.8 ppm. HRMS (ESI): m/z calcd. for $C_{22}H_{28}N$ [M + H] 306.2216, found 306.2236.

*N-(2-Benzylallyl)-N-(2-methyleneheptyl)aniline (**4r**).* Colorless oil. Yield: 81.3 mg (58%). IR (neat): 3084, 3062, 3027, 2955, 2927, 2857, 1651, 1599, 1506, 1453, 1390, 1364, 1262, 1233, 1190, 1075, 1030, 989, 967, 898, 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37−7.33 (m, 2H), 7.28−7.25 (m, 3H), 7.18−7.14 (m, 2H), 6.66 (t, J = 8 Hz, 2H), 3.80 (d, J = 8 Hz, 2H), 3.40 (s, 2H), 2.00 (t, J = 8 Hz, 2H), 1.48 (quin, J = 4 Hz, 2H), 1.39−1.28 (m, 4H), 0.93 (t, J = 8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 144.3, 143.7, 139.0, 128.9 128.8, 128.4, 126.3, 115.9, 111.8, 111.6, 108.9, 55.1, 54.6, 40.8, 33.8, 31.7, 27.5, 22.5, 14.6 ppm. HRMS (ESI): m/z calcd. for $C_{24}H_{32}N$ [M + H] 334.2529, found 334.2498.

*3-Pentyl-1-phenyl-2,5-dihydro-1H-pyrrole (**5a**).* Yellow solid; mp 81−83 °C. Yield: 211 mg (96%). IR (neat): 3046, 2955, 2925, 2855, 1714, 1600, 1506, 1459, 1374, 1358, 1323, 1209, 1071, 1051, 935, 752, 688 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, J = 8.0 Hz, 2H), 6.68 (t, J = 8.1 Hz, 1H), 6.53 (d, J = 8.2 Hz, 2H), 5.55 (s, 1H), 4.09−3.99 (m, 4H), 2.18 (t, J = 7.5 Hz, 2H), 1.58−1.44 (m, 2H), 1.40−1.25 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.2, 140.5, 129.4, 129.0, 118.8, 115.3, 111.1, 110.8, 56.5, 54.7, 31.6, 29.1, 27.2, 22.5, 14.0 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{22}N$ [M + H] 216.1746, found 216.1755.

*3-Isopropyl-1-phenyl-2,5-dihydro-1H-pyrrole (**5b**).* Colorless oil. Yield: 35 mg (81%). IR (neat): 3043, 2958, 2925, 2869, 1656, 1600, 1507, 1473, 1373, 1306, 1215, 1183, 1155, 1070, 986, 802, 744, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16−7.09 (m, 2H), 6.57 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 8.4 Hz, 2H), 5.42 (d, J = 1.2 Hz, 1H), 3.96 (d, J = 3.2 Hz, 4H), 2.54 (m, 1H), 1.03 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.3, 146.4, 129.2, 117.0, 115.4, 111.0, 55.1, 54.7, 28.3, 21.3 ppm. HRMS (ESI): m/z calcd. for $C_{13}H_{18}N$ [M + H] 188.1434, found 188.1435.

*3-Benzyl-1-phenyl-2,5-dihydro-1H-pyrrole (**5c**).* Yellow oil. Yield: 120 mg (89%). IR (neat): 3056, 3026, 2903, 2818, 1662, 1600, 1507, 1495, 1452, 1375, 1207, 1182, 1154, 1127, 1074, 1029, 988, 748, 703, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40−7.25 (m, 7H), 6.72 (t, J = 7.5 Hz, 1H), 6.53 (d, J = 10.4 Hz, 2H), 5.62 (t, J = 1.8 Hz, 1H), 4.16−4.12 (m, 2H), 4.02 (d, J = 3.9 Hz, 2H), 3.56 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 139.4, 138.5, 129.2, 128.7, 128.5, 126.4, 121.0, 115.4, 110.9, 56.2, 54.7, 35.9 ppm. HRMS (ESI): m/z calcd. for $C_{17}H_{18}N$ [M + H] 236.1434, found 236.1428.

*1,3-Diphenyl-2,5-dihydro-1H-pyrrole (**5d**).* Yellow solid; mp 85−88 °C. Yield: 156 mg (91%). IR (neat): 3662, 2923, 1724, 1598, 1505, 1448, 1364, 1264, 1182, 1066, 1037, 742, 689, 667 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 6.9 Hz, 2H), 7.50−7.19 (m, 5H), 6.74 (t, J = 7.2 Hz, 1H), 6.68−6.63 (m, 3H), 4.52−4.40 (m, 2H), 4.32−4.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.6, 129.4, 128.7, 128.6, 128.0, 125.9, 125.8, 125.4, 125.2, 120.4, 120.3, 115.8, 111.1, 108.7, 55.4, 54.8 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{16}N$ [M + H] 222.1277, found 222.1273.

*3-(Naphthalen-2-yl)-1-phenyl-2,5-dihydro-1H-pyrrole (**5j**).* White solid; mp 88−90 °C. Yield: 55.1 mg (91%). IR (neat): 3043, 2806, 1600, 1504, 1417, 1364, 1325, 1267, 1231, 1176, 1131, 995, 863, 800, 750, 740, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.77 (m, 3H), 7.73−7.70 (m, 2H), 7.52−7.48 (m, 2H), 7.33 (t, J = 8.0 Hz, 2H), 6.77 (t, J = 8.0 Hz, 1H), 6.70 (d, J = 8.0 Hz, 2H), 6.46 (s, 1H), 4.63

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(dd, J = 4.0, 4.0 Hz, 2H), 4.36 (dd, J = 4.0, 4.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 138.1, 133.4, 132.9, 131.0, 129.4, 128.2, 128.1, 127.6, 126.4, 126.1, 124.3, 123.4, 121.0, 115.8, 111.1, 55.4, 54.8 ppm. HRMS (ESI): m/z calcd. for $C_{20}H_{18}N$ [M + H] 272.1434, found 272.1422.

3-Pentyl-1-phenyl-1H-pyrrole (**6a**). Yellow solid; mp 82−84 °C. Yield: 42 mg (96%). IR (neat): 2955, 2854, 2924, 1713, 1600, 1506, 1459, 1361, 1323, 1208, 1070, 1051, 981, 935, 896, 755, 689 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40−7.33 (m, 4H), 7.18 (t, J = 8.0 Hz, 1H), 6.99 (t, J = 4.0 Hz, 1H), 6.86 (s, 1H), 6.18 (dd, J = 2.4, 2.0 Hz,1H), 2.49 (t, J = 8.0 Hz, 2H), 1.62−1.56 (m, 2H), 1.37−1.33 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 129.4, 127.0, 125.0, 119.9, 118.8, 116.3, 110.9, 31.7, 30.7, 27.0, 22.6, 14.1 ppm. HRMS (ESI): m/z calcd. for $C_{15}H_{20}N$ [M + H] 214.1596, found 214.1596.

3-Isopropyl-1-phenyl-1H-pyrrole (**6b**).[37] White solid; mp 80−83 °C. Yield: 35 mg (81%). IR (neat): 3047, 2957, 2926, 2868, 1712, 1600, 1504, 1459, 1357, 1305, 1232, 1211, 1071, 1051, 965, 935, 897, 753, 688 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40−7.34 (m, 2H), 7.18 (dt, J = 6.4, 2.0 Hz, 1H), 7.01 (d, J = 8.4 Hz, 2H), 5.42 (d, J = 1.2 Hz, 1H), 3.96 (d, J = 3.2 Hz, 4H), 2.54 (m, 1H), 1.03 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 129.4, 127.0, 125.0, 119.9, 118.8, 116.3, 110.8, 31.7, 30.7, 27.0, 22.6, 14.1 ppm. HRMS (ESI): m/z calcd. for $C_{13}H_{16}N$ [M + H] 186.1277, found 186.1276.

3-Benzyl-1-phenyl-1H-pyrrole (**6c**). Yellow solid; mp 81−83 °C. Yield: 120 mg (98%). IR (neat): 3027, 2921, 2851, 1714, 1599, 1056, 1453, 1359, 1331, 1300, 1231, 1071, 1050, 1029, 979, 935, 897, 753, 708 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38−7.31 (m, 4H), 7.30−7.27 (m, 4H), 7.21−7.16 (m, 2H), 7.01 (t, J = 7.01 Hz, 1H), 6.83 (dd, J = 4.0, 2.0 Hz, 1H), 6.17 (dd, J = 4.0, 2.0 Hz, 1H), 3.87 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 140.6, 129.4, 128.6, 128.3, 125.8, 125.5, 125.2, 119.9, 119.2, 117.2, 111.2, 33.5 ppm. HRMS (ESI): m/z calcd. for $C_{17}H_{16}N$ [M + H] 234.1277, found 234.1283.

1,3-Diphenyl-1H-pyrrole (**6d**).[37] Yellow solid; mp 83−85 °C. Yield: 156 mg (91%). IR (neat): 3137, 3049, 2922, 2853, 1597, 1559, 1507, 1449, 1363, 1306, 1265, 1237, 1185, 1156, 1111, 1079, 1064, 1036, 934, 918, 781, 751, 688 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, J = 8.4, 1.2 Hz, 2H), 7.43 (dd, J = 4.8, 4.8 Hz, 4H), 7.37−7.33 (m, 3H), 7.27−7.24 (m, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.11 (dd, J = 2.8, 2.4 Hz, 1H), 6.65 (dd, J = 2.8, 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 135.3, 129.6, 128.7, 126.8, 125.8, 125.7, 125.2, 120.4, 120.3, 115.8, 108.7 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{14}N$ [M + H] 220.1121, found 220.1151

1-Phenyl-3-(p-tolyl)-1H-pyrrole (**6e**). Yellow solid; mp 89−91 °C. Yield: 41.3 mg (84%). IR (neat): 3028, 2920, 2854, 1710, 1597, 1557, 1503, 1360, 1263, 1235, 1112, 1069, 1037, 918, 821, 767, 747, 687 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47−7.42 (m, 6H), 7.34 (s, 1H), 7.25 (s, 1H), 7.18 (s, 1H), 7.16 (s, 1H), 7.10 (t, J = 2.4 Hz, 1H), 6.63 (s, 1H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 135.4, 132.4, 129.6, 129.4, 128.6, 125.7, 125.1, 120.3, 120.1, 115.4, 108.7, 21.1 ppm. HRMS (ESI): m/z calcd. for $C_{17}H_{16}N$ [M + H] 234.1277, found 234.1274.

3-(4-Fluorophenyl)-1-phenyl-1H-pyrrole (**6f**). Yellow solid; mp 100−103 °C. Yield: 28.8 mg (92%). IR (neat): 3047, 2924, 1891, 1711, 1598, 1560, 1506, 1459, 1360, 1267, 1236, 1158, 1112, 1067, 1036, 895, 837, 768, 753, 713, 688 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54−7.52 (m, 2H), 7.42−7.46 (m, 3H), 7.29 (s, 1H), 7.26−7.28 (m,1H), 7.13 (s, 1H), 7.08 (t, J = 8.0 Hz, 2H), 6.61 (d, J = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6, 160.2 (d, J_{CF} = 240 Hz), 140.5, 131.5, 129.6, 126.6 (d, J_{CF} = 10 Hz), 126.0 125.9, 120.4, 120.3, 115.4 (d, J_{CF} = 20 Hz), 108.6 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{12}NF$ [M + H] 237.0954, found 237.0953.

3-(4-Chlorophenyl)-1-phenyl-1H-pyrrole (**6g**). Yellow solid; mp 105−110 °C. Yield: 48.1 mg (89%). IR (neat): 3136, 3050, 2924, 2854, 1710, 1661, 1597, 1552, 1508, 1495, 1360, 1265, 1080, 1066, 1011, 918, 834, 767, 753, 712, 687 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51−7.42 (m, 6H), 7.37−7.29 (m, 4H), 7.13 (dd, J = 5.2, 2.8 HZ, 1H), 6.63 (dd, J = 2.8, 1.6, Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 133.9, 131.3, 129.6, 128.8, 126.4, 126.0, 125.7, 120.6, 120.4, 115.9, 108.6 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{13}NCl$ [M + H] 254.0731, found 254.0730.

(4-Bromophenyl)-1-phenyl-1H-pyrrole (**6h**). Yellow solid; mp 114−117 °C. Yield: 48.1 mg (89%). IR (neat): 3044, 2926, 2818, 1723, 1599, 1548, 1505, 1489, 1355, 1325, 1262, 1183, 1074, 1035, 1005, 918, 827, 795, 769, 745, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47−7.41 (m, 7H), 7.35 (s, 1H), 7.28−7.24 (m, 2H), 7.10 (t, J = 2.8 Hz, 1H), 6.60 (t, J = 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 134.3, 131.7, 129.6, 126.7, 126.0, 125.7, 120.6, 120.4, 119.3, 115.9, 108.6 ppm. HRMS (ESI): m/z calcd. for $C_{16}H_{13}NBr$ [M + H] 298.0226, found 298.0226.

3-(4-Methoxyphenyl)-1-phenyl-1H-pyrrole (**6i**). White solid; mp 115−118 °C. Yield: 42.3 mg (94%). IR (neat): 3044, 3007, 2960, 2937, 2812, 1603, 1508, 1476, 1373, 1264, 1179, 1033, 838, 797, 751, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (dd, J = 6.4, 2.0 Hz, 2H), 7.43 (d, J = 5.2 Hz, 4H), 7.30 (t, J = 2.0 Hz, 1H), 7.25 (s, 1H), 7.10 (t, J = 2.4 Hz, 1H), 6.91 (dd, J = 6.4, 2.4 Hz, 2H), 6.59 (dd, J = 3.2, 2.0, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 140.6, 129.6, 128.1, 126.6, 126.3, 125.6, 120.2, 120.1, 115.0, 114.1, 108.6, 55.3 ppm. HRMS (ESI): m/z calcd. for $C_{17}H_{16}NO$ [M + H] 250.1226, found 250.1221.

3-(Naphthalen-2-yl)-1-phenyl-1H-pyrrole (**6j**).[11] White solid; mp 118−120 °C. Yield: 55.1 mg (91%). IR (neat): 3051, 2923, 1625, 1599, 1590, 1550, 1514, 1506, 1459, 1373, 1348, 1281, 1268, 1226, 1187, 1159, 1132, 1109, 1033, 1015, 923, 899, 860, 820, 773, 748, 685 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.83 (t, J = 8.8 Hz, 3H), 7.50 (d, J = 8.8 Hz, 1H), 7.52 (s, 1H), 7.49−7.40 (m, 6H), 7.30−7.27 (m, 1H) 7.17 (dd, J = 4.8, 2.4 Hz, 1H), 6.80 (dd, J = 4.4, 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 133.9, 132.8, 132.1, 129.6, 128.2, 127.7, 127.7, 126.8, 126.1, 125.8, 125.0, 124.5, 122.8, 120.6, 120.4, 116.2, 108.9 ppm. HRMS (ESI): m/z calcd. for $C_{20}H_{15}N$ [M + H] 270.1283, found 270.1282.

1-(4-Fluorophenyl)-3-isopropyl-1H-pyrrole (**6k**). Yellow solid; mp 109−111 °C. Yield: 36.8 mg (93%). IR (neat): 2959, 2870, 1715, 1512, 1463, 1382, 1360, 1305, 1226, 1156, 1098, 1072, 1048, 965, 936, 829, 815, 768, 690, 666 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32−7.27 (m, 2H), 7.08 (t, J = 6.8 Hz, 2H), 6.92 (dd, J = 4.8, 2.4 Hz, 1H), 6.78 (s, 1H), 6.22 (dd, J = 4.8, 2.8 Hz, 1H), 2.86 (sext, J = 7.2 Hz, 1H), 1.24 (d, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3 (d, J_{CF} = 250 Hz), 134.1, 121.7 (d, J_{CF} = 10 Hz), 119.1, 116.1 (d, J_{CF} = 20 Hz), 115.2, 109.3, 26.4, 23.8 ppm. HRMS (APCI): m/z calcd. for $C_{13}H_{15}FN$ [M + H] 204.1183, found 204.1187.

1-(4-Chlorophenyl)-3-isopropyl-1H-pyrrole (**6l**). Yellow solid; mp 110−113 °C. Yield: 47.9 mg (90%). IR (neat): 2958, 2924, 2868, 1706, 1596, 1503, 1461, 1417, 1328, 1354, 1307, 1245, 1217, 1121, 1097, 1052, 1007, 931, 820, 763, 735, 688, 654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (dd, J = 7.2, 2.4 Hz, 2H), 7.27 (dd, J = 6.4, 2.8, 2H), 6.96 (dd, J = 4.8, 2.8 Hz, 1H), 6.82 (d, J = 2.4 Hz, 1H), 6.24 (dd, J = 2.4, 2.0 Hz, 1H), 2.87 (sext, J = 6.8 Hz, 1H), 1.24 (d, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 134.4, 130.4, 129.5, 121.0, 118.8, 114.8, 109.9, 26.5, 23.8 ppm. HRMS (APCI): m/z calcd. for $C_{13}H_{15}ClN$ [M + H] 220.0888, found 220.0900.

1-(4-Bromophenyl)-3-isopropyl-1H-pyrrole (**6m**). Yellow solid; mp 112−115 °C. Yield: 47.9 mg (90%). IR (neat): 2957, 2925, 2866, 1589, 1501, 1461, 1382, 1353, 1310, 1264, 1245, 1217, 1120, 1076, 1051, 1003, 929, 870, 817, 762, 687, 653 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (dd, J = 11.6, 2.8 Hz, 2H), 7.22 (dd, J = 6.8, 2.0 Hz, 2H), 6.96 (t, J = 2.8 Hz, 1H), 6.82 (s, 1H), 6.24 (dd, J = 2.0, 1.6 Hz, 1H), 2.86 (sext, J = 7.2 Hz, 1H), 1.24 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8, 134.5, 132.4, 121.3, 118.8, 118.0, 114.7, 109.8, 26.5, 23.8 ppm. HRMS (APCI): m/z calcd. for $C_{13}H_{15}BrN$ [M + H] 264.0382, found 264.0380.

3-Isopropyl-1-(4-methoxyphenyl)-1H-pyrrole (**6n**). White solid; mp 110−113 °C. Yield: 59.5 mg (84%). IR (neat): 3137, 2957, 2868, 1515, 1464, 1400, 1358, 1309, 1258, 1243, 1182, 1057, 1039, 1027, 967, 935, 897, 826, 813, 769, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (dd, J = 8.0, 2.4 Hz, 2H), 6.64−6.92 (m, 3H), 6.80 (s, 1H), 6.21 (t, J = 2.0 Hz, 1H), 3.82 (s, 3H), 2.88 (sext, J = 8.0 Hz, 1H), 1.25 (d, J = 8.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3,

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134.7, 133.5, 121.7, 119.2, 115.4, 114.6, 108.7, 55.5, 31.8, 26.5, 24.0, 21. ppm. HRMS (ESI): m/z calcd. for $C_{14}H_{18}NO$ [M + H] 216.1383, found 216.1381.

*1,3-Dibenzyl-1H-pyrrole (**6o**).*[38] Colorless oil. Yield: 80.7 mg (94%). IR (neat): 3084, 3062, 3027, 2925, 2872, 2801, 1947, 1806, 1724, 1647, 1603, 1495, 1453, 1355, 1155, 1071, 999, 904, 721 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37−7.13 (m, 10H), 6.63 (t, J = 4 Hz, 1H), 6.46 (t, J = 4 Hz, 1H), 6.04 (t, J = 4 Hz, 1H), 5.01 (s, 2H), 3.84 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.3, 138.3, 128.7, 128.6, 128.2, 127.5, 126.9, 125.6, 123.5, 121.2, 119.3, 109.0, 53.3., 33.5 ppm. HRMS (ESI): m/z calcd. for C18H17NNa [M + Na] 270.1523, found 270.1521.

*3-Benzyl-1-cyclohexyl-1H-pyrrole (**6p**).* Colorless oil. Yield: 95.4 mg (91%). IR (neat): 3083, 3061, 3026, 2929, 2854, 1942, 1738, 1707, 1603, 1493, 1452, 1355, 1318, 1284, 1264, 1157, 1071, 1029, 977, 892, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32−7.25 (m, 5H), 7.22−7.18 (m, 1H), 6.66 (t, J = 4 Hz, 1H), 6.47 (s, 1H), 5.98 (t, J = 4 Hz, 1H), 3.84 (s, 2H), 3.73 (tt, J = 12 Hz, J = 4 Hz, 1H), 2.09 (d, J = 12 Hz, 2H), 1.88 (d, J = 12 Hz, 2H), 1.60 (dq, J = 12 Hz, J = 4 Hz, 2H), 1.44−1.16 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = ppm. HRMS (ESI): m/z calcd. for $C_{17}H_{22}N$ [M + H] 240.1747, found 240.1742.

Procedure for the Kinetic Study. $Pd(dba)_2$ (30 mg, 0.0525 mmol) was added to a flame-dried Schlenk flask containing a stirring bar. The flask was capped with a rubber septum and degassed with argon. CH_2Cl_2 (0.8 mL) and $P(OPh)_3$ (108 μL, 0.42 mmol) were added via syringe. The resulting slurry was degassed and then stirred for 30 min at room temperature. The progress of forming the $Pd[P(OPh)_3]_3$ complex was monitored by ^{31}P NMR spectroscopy. Solvents were distilled off. An NMR tube was charged with 0.4 mL of aniline solution (0.435 M in C_6D_6) and 0.2 mL of $Pd[P(OPh)_3]_4$ (2.9 mM in C_6D_6), and then degassed allylic alcohol (47 μL, 0.696 mmol), under argon atmosphere, and the NMR tube was shaken and inserted into a preheated spectrometer (65 °C). Rate dependence on reactant concentrations was determined using the initial rate method. Initial rates were determined from the concentration of the product (below 15% conversion) vs time. The allylation kinetics were measured by ^1H NMR spectroscopy. The reaction was monitored by ^1H NMR spectroscopy measuring the integrals for *N*-allylaniline at δ = 3.35 ppm, as well as *N*,*N*-diallylaniline at δ = 3.60 ppm using the ferrocene as the internal standard (δ = 4.00 ppm). Aniline could not be integrated directly because of overlapping peaks. Therefore, the aniline concentration was determined by the following method. After every kinetic run, the reaction was let to go to completion to determine the total conversion to diallylated product, and thereby, also the initial concentration of aniline could be decided. At a given data point, the aniline concentration was resolved by subtracting the concentration of allylation products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02581.

^{13}C and ^1H NMR spectra for all monoallylated, diallylated intermediates and products (PDF)

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Notes

The authors declare no competing financial interest.

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