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Palladium-Catalyzed Benzylic C–H Benzylation *via* Bis-Benzylpalladium(II) Complexes in Water: An Effective Pathway for the Direct Construction of *N*-(1,2-Diphenylethyl)anilines

Hidemasa Hikawa,[a,*] Kyoko Izumi,[a] Yukari Ino,[a] Shoko Kikkawa,[a] Yuusaku Yokoyama,[a] and Isao Azumaya[a,*]

[a] Faculty of Pharmaceutical Sciences, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan
Fax: (+81)-47-472-1595; phone: (+81)-47-472-1591
isao.azumaya @phar.toho-u.ac.jp; e-mail: hidemasa.hikawa@phar.toho-u.ac.jp

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Abstract: A strategy for the *N*-benzylation/benzylic C–H benzylation cascade of anilines by the π-benzylpalladium system using a water-soluble palladium(0)/sodium diphenylphosphinobenzene-3-sulfonate (TPPMS) catalyst and benzyl alcohol in water has been developed. This tandem process is devised as a novel and efficient synthetic route for *N*-(1,2-diphenylethyl)anilines. Benzylic C–H activation of a mono-*N*-benzylated intermediate with a π-benzylpalladium(II) complex affords a bis-π-benzylated palladium(II) intermediate. The nucleophilic η^1-σ-benzyl anion ligand attacks the electrophilic η^3-π-benzyl ligand to give a dibenzylated product. The intermolecular competition between mono-*N*-benzylaniline and its monodeuterated form (monodeuterated at the benzylic group) with benzyl alcohol gave a KIE = 4.6, suggesting that C–H bond cleavage was involved in the rate-determining step. Hammett studies on the rate constants of benzylation by various substituted anthranilic acids and mono-*N*-benzylanilines show a good correlation between the $\log(k_X/k_H)$ and the σ values of the respective substituents. From the slope, negative ρ values are obtained, suggesting that there is a build-up of positive charge in the transition state. The reaction of anilines with electron-donating and electron-withdrawing groups affords the corresponding *N*-(1,2-diphenylethyl)anilines in moderate to good yields (54–86%). Interestingly, the reaction of anthranilic acids proceeded smoothly to give only the corresponding dibenzylated products in good to excellent yields (70–87%). The carboxyl group of the anthranilic acids acts as a directing group in the benzylic C–H activation process.

Keywords: benzyl alcohol; benzylation; C–H activation; palladium; water

Introduction

Palladium-catalyzed benzylation *via* a π-benzylpalladium intermediate has been successfully developed for the formation of carbon-carbon and carbon-nitrogen bonds.[1] Early studies on the generation of π-benzylpalladium complexes used benzyl halides[2] as electrophilic partners. Hartwig reported the thermal reductive elimination to form a C(sp^3)–N bond in an amine from a benzylpalladium amido complex.[2c] Recently, benzyl esters,[3] carbonates,[4] and phosphates[5] have been developed. Trost reported a palladium-catalyzed asymmetric benzylic alkylation of 3-aryloxindoles with benzylic methyl carbonates.[4a] Kuwano reported a benzylic amination using the DPEphos-palladium catalyst.[4k] In contrast, benzyl alcohols are especially challenging to use because of their low reactivity towards Pd(0) compared with benzyl halides. Therefore, the development of a direct catalytic substitution of benzylic alcohols, which affords the desired products along with water as the sole co-product, is highly essential in synthetic chemistry.[6]

The palladium-catalyzed allylation with allylic alcohols occurs in water (Tsuji–Trost reaction), since water activates the hydroxy group of the allylic alcohol to form the π-allyl palladium(II) complex (Scheme 1).[7] Shinokubo and Oshima performed theoretical calculations to elucidate the importance of hydration of the hydroxy group in allyl alcohol for the smooth generation of the π-allylpalladium intermediate. On the basis of this synthetic strategy, we have developed a selective mono-*N*-allylation for

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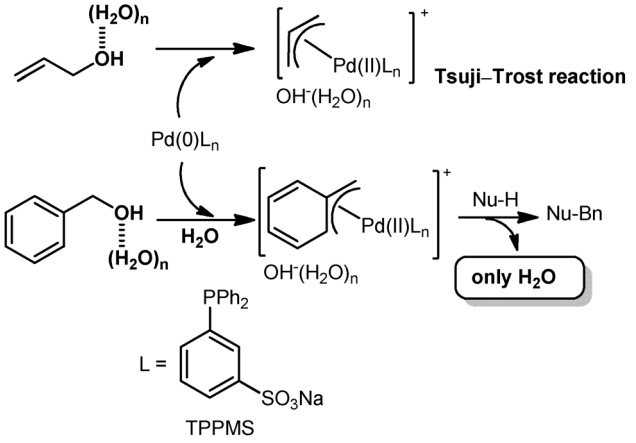
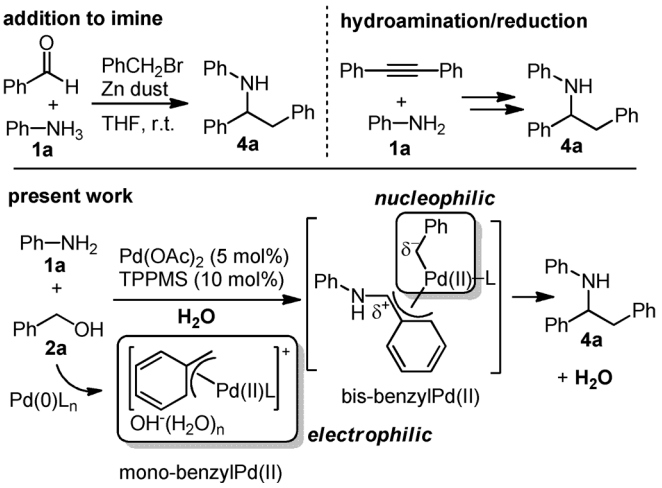


Scheme 1. Our strategy for benzylation using water-soluble Pd catalysts in water.



Scheme 2. Formation of *N*-(1,2-diphenylethyl)anilines.

water-soluble free amino acids and anthranilic acids.[8] Therefore, we expected an analogous reaction for the benzylation of benzyl alcohols due to their structural similarity to allylic alcohols.[9] As proof of the concept, we began our studies of the benzylation with benzyl alcohols **2** in water by choosing water-soluble unprotected anthranilic acids as the substrates, and found that the π-benzylpalladium(II) complexes act as the first water-soluble active catalysts for *benzyl transfer* and *C–H activation*.[9g] However, we could not provide enough support for the benzylation pathway and the scopes of the substrates were limited. In this paper, we describe new insights into the chemistry of the palladium-catalyzed benzylic C–H activation/benzylation pathway *via* bis-benzylpalladium(II) complexes in water and the development of a tandem process as a new synthetic route for *N*-(1,2-diphenylethyl)anilines. Palladium-catalyzed activation of carbon-hydrogen bonds for coupling reactions is a promising strategy in organic synthesis,[10] and therefore the development of a π-benzylpalladium system for C–H activation should be particularly attractive.

It is worth noting that many interesting and important reactions have been reported utilizing the benzylation of imines,[11] hydroamination of alkynes/reduction,[12] and reductive amination of ketones[13] for formation of *N*-(1,2-diphenylethyl)anilines, which are structural constituents of pharmacologically interesting compounds (Scheme 2).[14] However, oxidants are required for preparation of aldehydes from alcohols, and stoichiometric zinc reagents are chemically unstable. In contrast, palladium-catalyzed direct substitution of benzylic alcohols in a one-pot tandem approach in water could achieve reduced waste generation, use safer solvents and reaction conditions, and increase energy efficiency, factors which assess the efficiency of a chemical transformation. Additionally, water has unusual chemical and physical properties such as strongly polar hydrogen bonds, and therefore should play an important role in the development of new and efficient reactions.[15]

Results and Discussion

Effects of Catalysts and Solvents

First, the mixture of aniline (**1a**) and benzyl alcohol (**2a**, 5 equiv.) in the presence of $Pd(OAc)_2$ (5 mol%) and sodium diphenylphosphinobenzene-3-sulfonate (TPPMS, 10 mol%) in water was heated at 120 °C for 16 h in a sealed tube. Dibenzylated product **4a** was obtained in 54% yield along with mono-*N*-benzylated **3a** in 10% yield and imine **5a** in 19% yield (Table 1, entry 1). The use of benzyl chloride (5 equiv.) instead of benzyl alcohol **2a** resulted in no reaction. With regard to the palladium catalyst, the use of $PdCl_2$ resulted in lower yield (entry 2). The use of zero-valent palladium, $Pd_2(dba)_3$, gave the product **4a** in 54% yield (entry 3). Since the benzylation did not proceed in the absence of the palladium catalyst or phosphine ligand (entries 4 and 5) or in the presence of only palladium catalysts (entries 6 and 7), an S_N2-type reaction mechanism was excluded in the formation of the dibenzylated **4a**. Using organic solvents such as EtOH, DMSO, CPME, or toluene instead of H_2O (entries 8–11) or using $Pd(PPh_3)_4$ instead of a water-soluble ligand (entries 12 and 13) resulted in no reaction or lower yield. Therefore, water must play an important role in our catalytic system. When 2 equiv. of benzyl alcohol **2a** were used, the desired **4a** was obtained in only 19% yield (entry 14). The use of 10 equiv. of **2a** was slightly better to give **4a** in 62% yield (entry 15).

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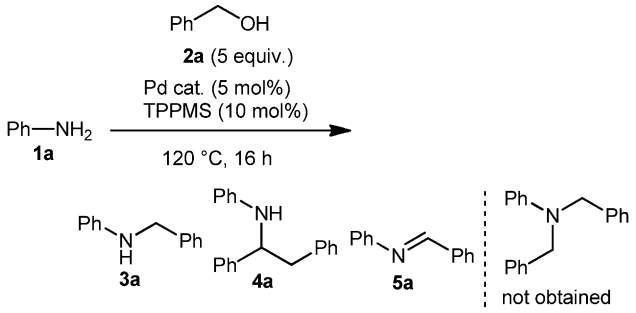
Table 1. Effects of catalysts and solvents.[a]

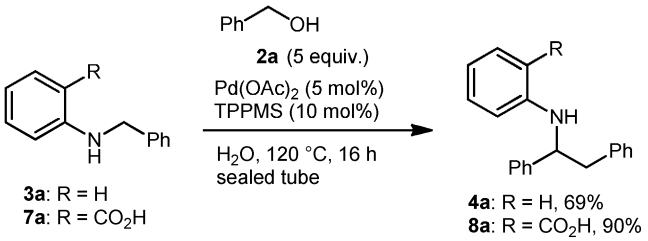


Entry	Pd catalysts	Solvent	Conv. [%][b]		
			3a	4a	5a
1	$Pd(OAc)_2$/TPPMS	H_2O	10	54	19
2	$PdCl_2$/TPPMS	H_2O	15	34	20
3	$Pd_2(dba)_3$/TPPMS	H_2O	5	54	12
4	none	H_2O	0	0	0[e]
5	TPPMS	H_2O	0	0	0[e]
6	$Pd(OAc)_2$	H_2O	0[e]	0	19
7	$Pd_2(dba)_3$	H_2O	10	0	33
8	$Pd(OAc)_2$/TPPMS	EtOH	no reaction		
9	$Pd(OAc)_2$/TPPMS	DMSO	0	23	0
10	$Pd(OAc)_2$/TPPMS	CPME	18	24	46
11	$Pd(OAc)_2$/TPPMS	toluene	0	5	57
12	$Pd(PPh_3)_4$	toluene	17	21	59
13	$Pd(PPh_3)_4$	H_2O	0[e]	0	17
14[c]	$Pd(OAc)_2$/TPPMS	H_2O	14	19	35
15[d]	$Pd(OAc)_2$/TPPMS	H_2O	7	62	6

[a] *Reaction conditions:* aniline **1a** (1 mmol), Pd catalysts (5 mol%), TPPMS (10 mol%), benzyl alcohol **2a** (5 equiv.), solvent (4 mL), 120 °C, 16 h under air in a sealed tube.
[b] The conversion was determined by ^{1}H NMR analysis of the crude product using *para*-nitroanisole as an internal standard.
[c] Benzyl alcohol **2a** (2 equiv.) was used.
[d] Benzyl alcohol **2a** (10 equiv.) was used.
[e] Trace.

Reaction Progress

To gain further understanding of the reaction progress, the reactions of aniline (**1a**) or anthranilic acid (**6a**) with benzyl alcohol (**2a**) were monitored (see Figure S1 in the Supporting Information). After 2 h, the reaction of aniline (**1a**) afforded mono-*N*-benzylated **3a** in 60% yield along with desired **4a** in 18% yield and imine **5a** in 12% yield. Therefore, *N*-benzylation of aniline **1a** with **2a** occurred quickly to form mono **3a**. The resulting *N*-benzylated **3a** then slowly converted to desired **4a** through benzylic C–H benzylation. In contrast, after 2 h, the reaction of anthranilic acid (**6a**) proceeded smoothly to give dibenzylated **8a** in 65% yield along with monobenzylated **7a** in only 15% yield. Furthermore, the reaction proceeded almost completely in 5 h. These results suggested that



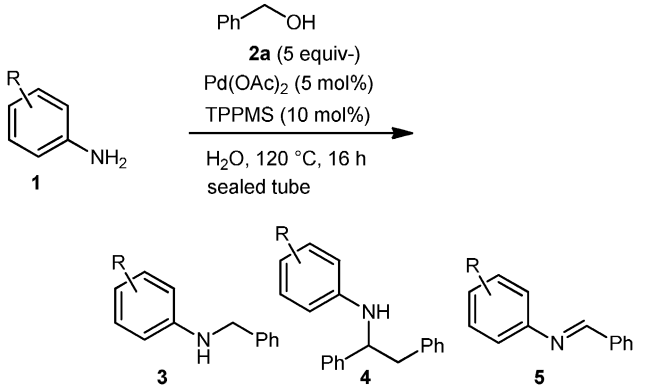
Scheme 3. Pd-catalyzed benzylation of mono-*N*-benzylated **3a** and **7a**.

mono-*N*-benzylated **7a** converted to desired **8a** more smoothly compared with **3a**. To confirm that mono-*N*-benzylated **3a** and **7a** are the intermediates in our catalytic system, we examined the benzylation of **3a** and **7a** instead of aniline **1a** and anthranilic acid **6a** (Scheme 3). As expected, *C*-benzylation proceeded smoothly to give dibenzylated products in good to excellent yields (**4a**, 69%; **8a**, 90%).

Effect of the Carboxyl Group

To determine the effect of the carboxyl group of anthranilic acid (**6a**), palladium-catalyzed benzylations of aniline (**1a**), anthranilic acid (**6a**), and 4-aminobenzoic acid (**6b**) with **2a** were carried out (Table 2). While the reaction of aniline (**1a**) or 4-aminobenzoic acid (**6b**) afforded the desired **4a** or **9** in moderate yields (entry 1, 54%; entry 2, 55%), anthranilic acid (**6a**) resulted in an excellent yield (entry 3, 93%). Fur-

Table 2. Effect of the carboxyl group.[a]



Entry	R	Conversion [%]		
		mono	di	imine
1	H	10 (**3a**)	54 (**4a**)	19 (**5a**)
2	4-CO_2H	16 (**7b**)	55 (**9**)	23 (**10**)
3	2-CO_2H	7 (**7a**)	93 (**8a**)	trace

[a] *Reaction conditions:* **1** or **6** (1 mmol), $Pd(OAc)_2$ (5 mol%), TPPMS (10 mol%), benzyl alcohol **2a** (5 equiv.), H_2O (4 mL), 120 °C, 16 h in sealed tube. The conversion was determined by ^{1}H NMR analysis.

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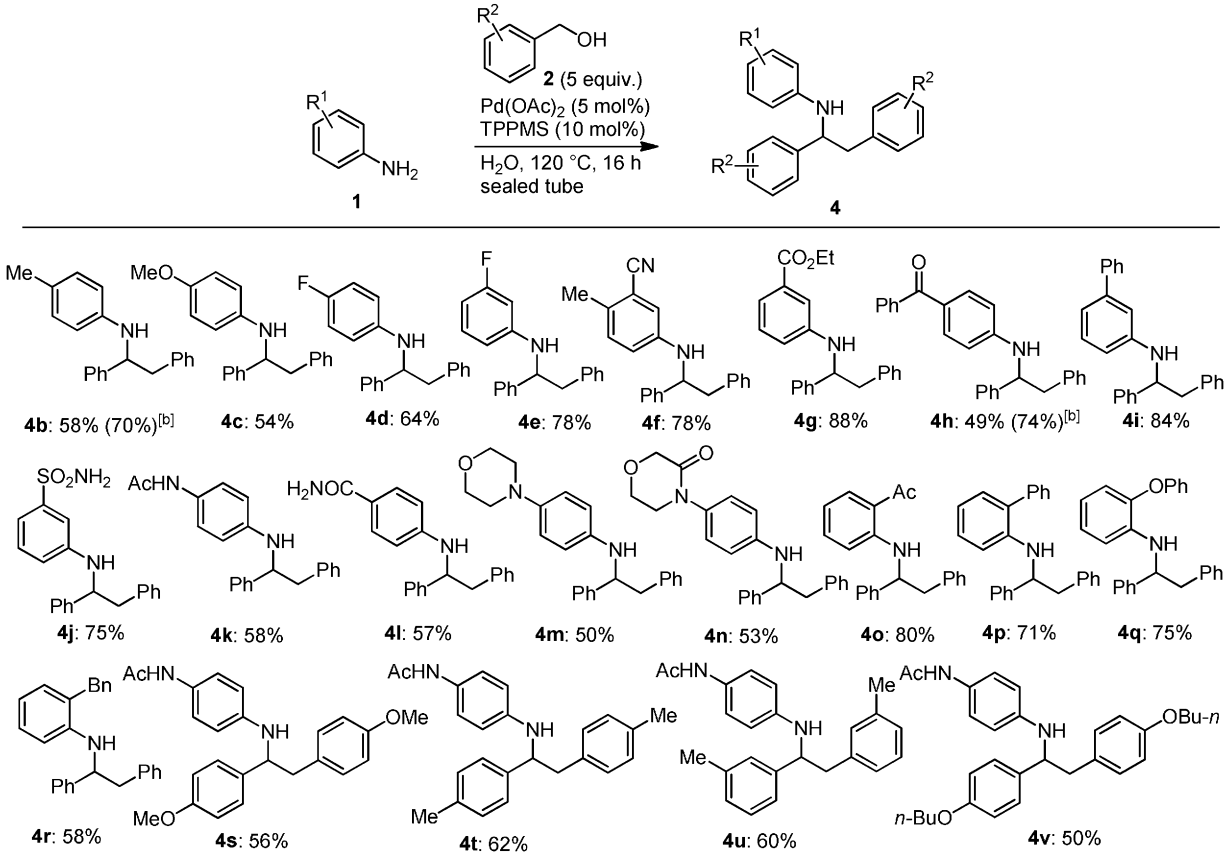
Table 3. Scope of anilines **1** and benzyl alcohols **2**.[a]



[a] *Reaction conditions:* anilines **1** (1 mmol), $Pd(OAc)_2$ (5 mol%), TPPMS (10 mol%), benzyl alcohols **2** (5 equiv.), H_2O (4 mL), 120 °C, 16 h in sealed tube. Yield of isolated product.

[b] Benzyl alcohol **2a** (10 equiv.) was used. NMR yield.

thermore, the reaction of **3a** was not enhanced by the addition of AcOH (1 equiv.), suggesting that the *ortho* substituted carboxyl group of **6a** played an important role for benzylation.

Reaction Scope

Results for the reaction of several anilines **1** with benzyl alcohols **2** using $Pd(OAc)_2$ and TPPMS are summarized in Table 3. The reaction of anilines **1** with electron-donating methyl and methoxy groups proceeded to give dibenzylated **4b** and **4c** in moderate yields (**4b**, 58%; **4c**, 54%). Anilines with electron-withdrawing fluoro, cyano, ester, and benzoyl groups resulted in moderate to good yields (**4d–h**, 49–88%). In contrast, the strong electron-withdrawing nitro group resulted in no reaction. Surprisingly, a hydrophobic aniline gave the dibenzylated product **4i** in 84% yield (3-aminobiphenyl: clogP value of 2.8 *vs.* aniline **1a**: clogP value of 0.9). Furthermore, the reaction of hydrophilic anilines with amide and cyclic amino groups resulted in moderate to good yields (**4j–n**, 50–75%). Sterically demanding acetyl, phenyl, phenoxy, and benzyl groups at the *ortho* position were tolerated in the benzylation (**4o–r**, 58–80%). The reaction of *N*-(4-aminophenyl)acetamide with electron-donating substituted benzyl alcohols **2** proceeded to give dibenzylated **4s–v** in overall yields ranging from 50–62%. In contrast, benzyl alcohol with electron-withdrawing fluoro and nitro groups resulted in no reaction. These results suggested that π-benzylpalladium(II) cations play an important role in the *N*-benzylation step. The reaction of anthranilic acids **6** with benzyl alcohols **2** proceeded smoothly to give dibenzylated products in yields ranging from 66–87% along with no or trace amounts of mono-*N*-benzylated products (see Figure S2 in the Supporting Information).[9g]

Hammett Studies

To demonstrate the electronic effect of benzylation, Hammett studies were conducted for the palladium-catalyzed benzylation of substituted anthranilic acids **6** or mono-*N*-benzylanilines **3** with benzylic alcohol (**2a**). From these studies summarized in Figure 1, the

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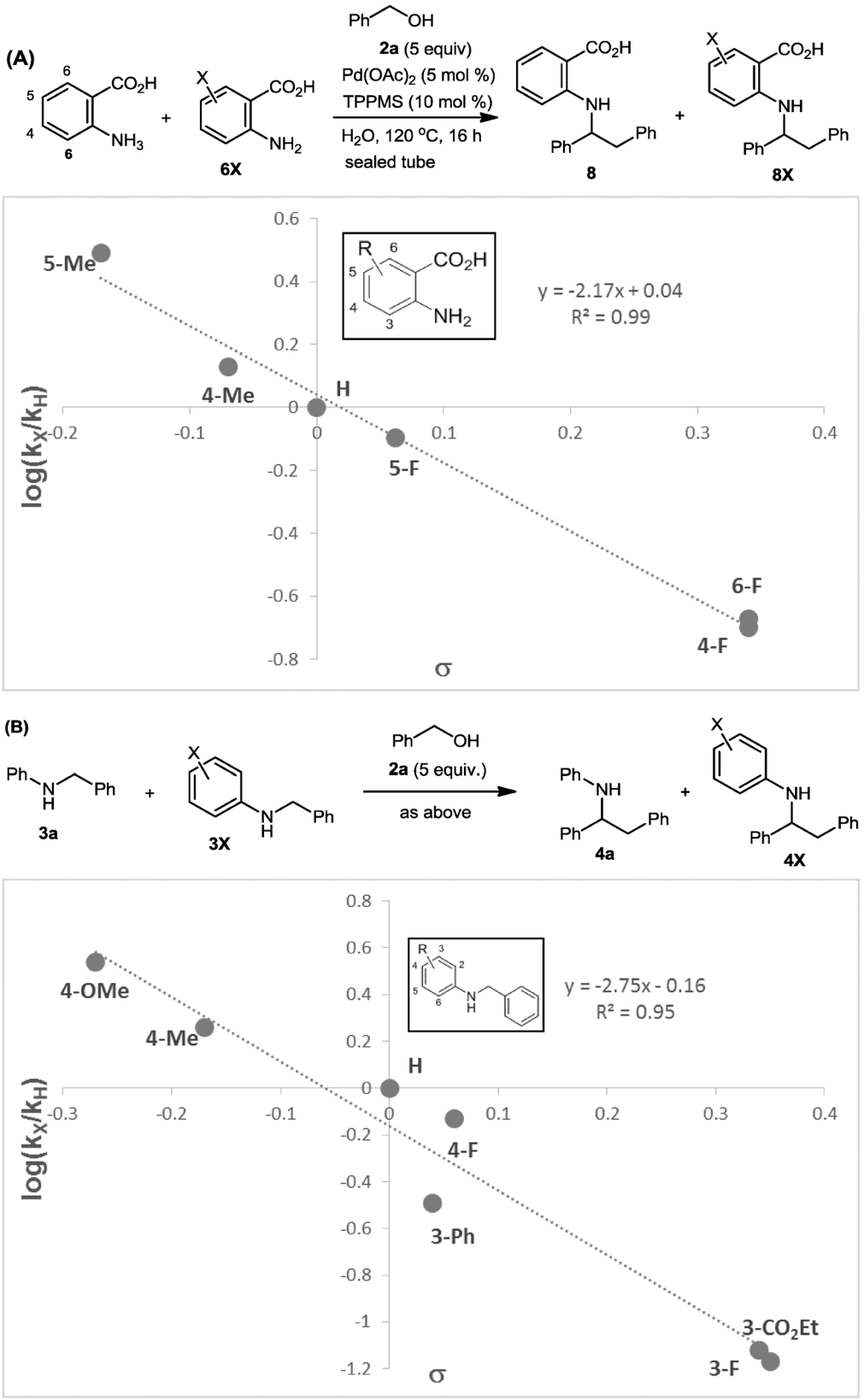

Figure 1. Hammett plots for the rate constants of benzylation by various substituted anthranilic acids **6X** (A) and mono-*N*-benzylanilines **3X** (B).

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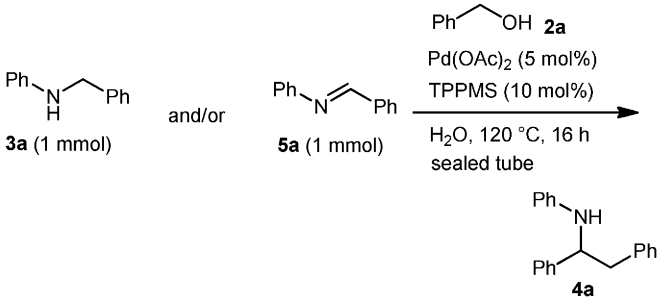
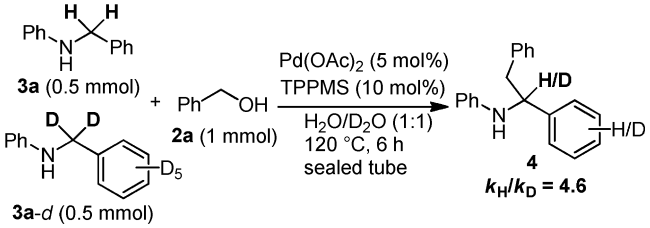
Table 4. Benzylation of mono-*N*-benzylaniline **3a** and imine **5a**.



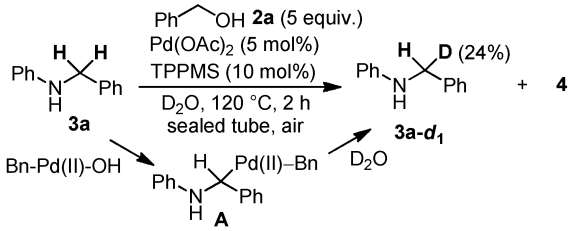
Entry	Substrate (mmol)	**2a** (mmol)	Conversion [%] **4a**	**3a**	**5a**
1	**3a** (1)	1	37	7	27
2	**5a** (1)	1	2	7	52
3[a]	**3a** (1)+**5a** (1)	2	37	10	85
4	**3a** (1)+BHT (1)	1	31	5	30

[a] Conversion yield was calculated from **3a** (1 mmol).

A. Kinetic isotope effects.



B. D incorporation into the benzylic position.



Scheme 4. Mechanistic studies.

ratio of rate constants can be obtained. First, the relative rates of coupling of *meta*- or *para*-substituted anthranilic acids (Me and F groups) with benzyl alcohol (**2a**) were examined. Figure 1 shows a good correlation ($R^2=0.99$) between the $\log(k_X/k_H)$ and the σ values of the respective substituents that resulted in a negative ρ value of 2.17, suggesting that there is a build-up of positive charge in the transition state. Next, the relative rates of coupling of *meta* or *para*-substituted mono-*N*-benzylanilines (OMe, Me, F, Ph, and CO_2Et groups) with benzyl alcohol (**2a**) were examined. Figure 1 shows a good correlation ($R^2=0.95$) between the $\log(k_X/k_H)$ and the σ values of the respective substituents that resulted in a negative ρ value of 2.75. Indeed, the reaction of mono-*N*-benzylanilines **3** with an electron-donating methoxy group proceeded smoothly (entry 1, 70% in Table 4), while the reaction with electron-withdrawing fluoro, cyano, and benzoyl groups proceeded more slowly (entry 2, 67%; entry 3, 51%).

Kinetic Isotope Effects and D Incorporation

A KIE study was performed to gain further mechanistic details of benzylic C–H activation. The intermolecular competition between mono-*N*-benzylated **3a** and **3a**-*d* with benzyl alcohol **2a** gave KIE = 4.6 on the basis of ^{1}H NMR analysis, suggesting that C–H bond cleavage was involved in the rate-determining step (Scheme 4A). In contrast, benzylation of mono-*N*-benzylated **3a** in water and in D_2O afforded dibenzylated **4a** in the same conversion yields, suggesting that the hydrogen bond of water does not enhance the benzylic C–H activation step.[16] Next, we monitored the benzylic C–H activation reaction by ^{1}H NMR spectroscopy (Scheme 4B). Treatment of **3a** with $Pd(OAc)_2$, TPPMS, and benzyl alcohol **2a** in D_2O for 2 h showed 24% deuterium incorporation at the benzylic position of **3a**-d_1. In contrast, in the absence of benzyl alcohol **2a**, $Pd(OAc)_2$, and TPPMS, deuterium was not incorporated.

Mechanistic Considerations

On the basis of these results and our previous report,[6] we favor a catalytic system for the benzylation of anilines **1** with benzyl alcohols **2** in water as illustrated in Scheme 5. The mechanism for *N*-benzylation/benzylic C–H benzylation cascade proceeds as follows: (1) water-activated C–O cleavage of benzyl alcohol **2a** to form mono-π-benzylpalladium(II) complex **11a**, followed by nucleophilic substitution with anilines **1**; (2) the mono-π-benzylpalladium(II)-promoted C–H cleavage to furnish bis-π-benzylpalladium(II) intermediates **I**; (3) benzylic *C*-benzylation of intermediates **II** or **III** with nucleophilic η^1-σ-benzyl ligand and electrophilic η^3-π-benzyl ligand.

Step 1: First, oxidative addition of benzyl alcohol **2a** to water-soluble Pd(0)/TPPMS species affords the cationic mono-π-benzylpalladium(II) complex **11a**. This process should be favored by electron-donating groups on intermediates **11**, since these will stabilize the positive charge on Pd(II). Indeed, the benzylation using 4-fluoro- and 4-nitrobenzyl alcohols **2** did not proceed since the alcohols could not form cationic intermediates (see Table 3). Next, the nucleophilic aniline **1** attacks the electrophilically active π-benzylpalladium(II) intermediate to afford the mono-*N*-benzylated product **3** and regenerate Pd(0).

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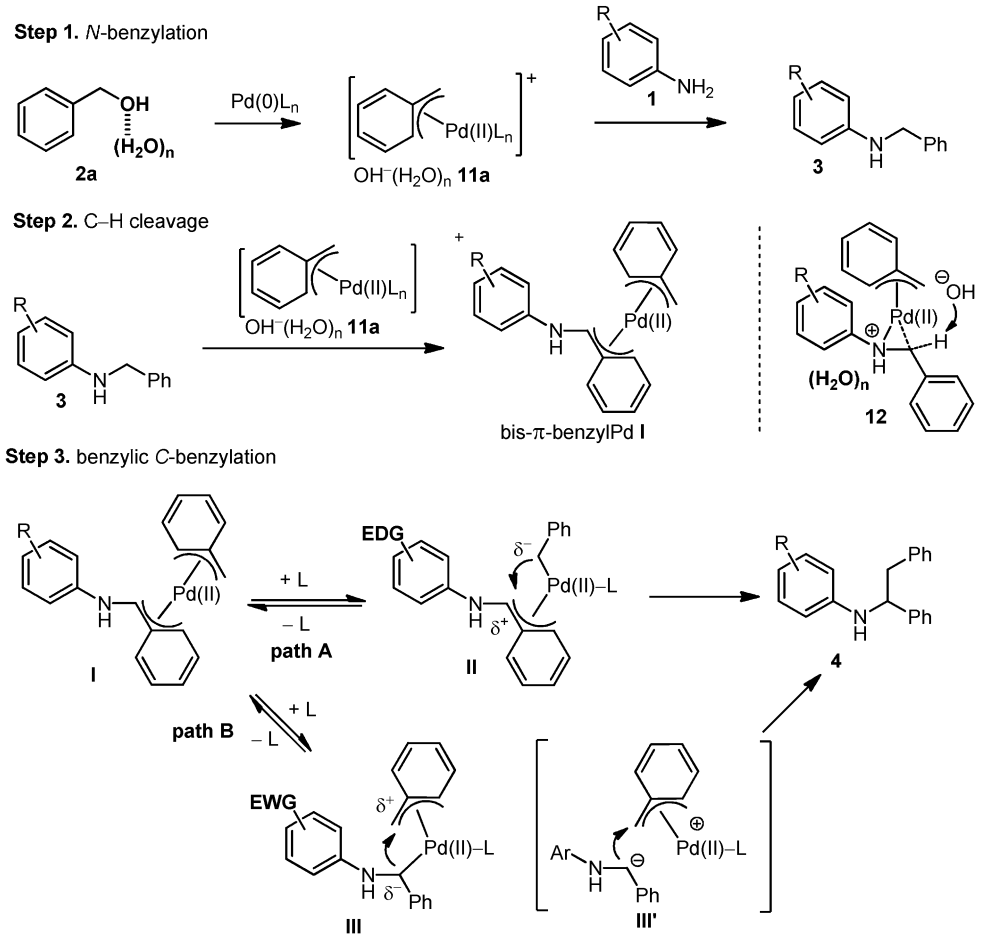
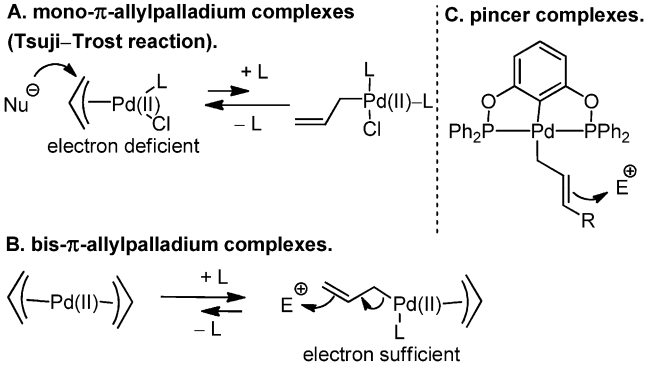


Scheme 5. Proposed mechanism.

Step 2: The mono-*N*-benzylated **3** coordinates with π-benzylpalladium(II) **11a** to form cationic *N*-palladated intermediate **12**, which is favored by electron-donating R groups that stabilize the positive charge. Indeed, Hammett studies show that there is a build-up of positive charge in the transition state. Benzylic C–H cleavage proceeds sequentially, followed by formation of stable bis-π-benzyl palladium(II) intermediate **I** (the KIE of 4.6 indicated that the C–H cleavage might be involved in the turnover-limiting step). A positive charge of *N*-palladated complex **12** would increase the acidity of the benzylic proton. White and co-workers reported electrophilic allylic C–H cleavage of α-olefins using a palladium(II)/sulfoxide catalyst to afford π-allylpalladium(II) intermediates.[17] Additionally, the high reactivity of anthranilic acids **8** compared with anilines **1** would be observed in tandem benzylation, since the carboxyl group plays important roles in the *N*-palladation and benzylic C–H activation (Scheme 7).



Scheme 6. Different reactivity of mono- and bis-π-allylpalladium complexes (**A** and **B**), and pincer complexes (**C**).

Step 3: The bis-benzyl palladium(II) intermediate is in flux between three species; there is one bis-π-benzyl species **I** and two combinations of η^3-π-benzyl-/η^1-σ-benzylpalladium (**II** and **III**). To form the dibenzylated **4**, there are two proposed mechanisms involving the η^3-π-benzyl/η^1-σ-benzyl intermediates **II** or **III** (path A or B). Yamamoto and co-workers reported that bis-π-allylpalladium complexes exhibit nucleophilic reactivity, although it is widely accepted that mono-(π-allyl)PdX-type complexes, where X is an electron-withdrawing group such as Cl or OAc, exhibit electrophilic reactivity (Scheme 6A and B).[18]

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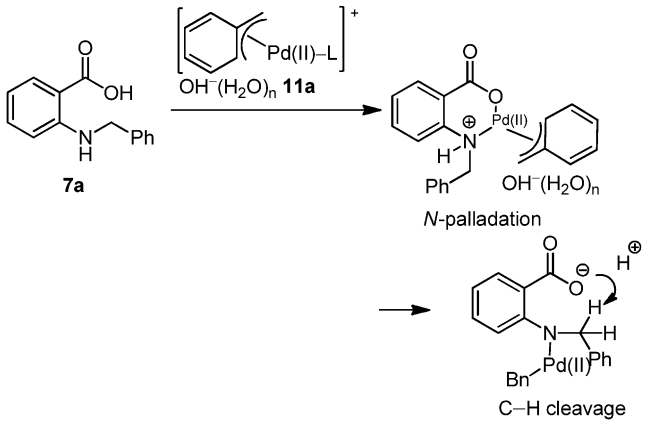
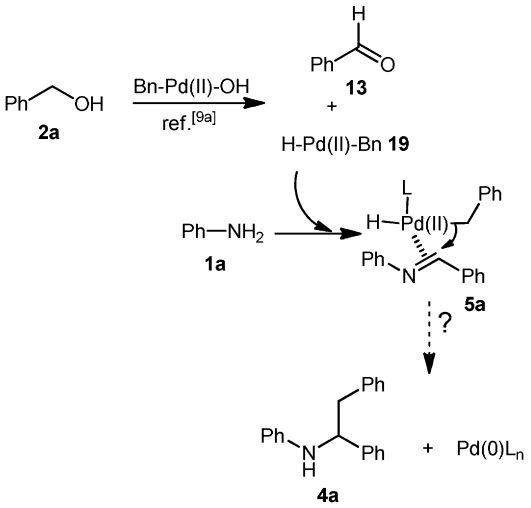


Scheme 7. Role of the carboxy group.



Scheme 8. The possible reaction pathways from imine **5** and hydride palladium species.[21]

Pincer complexes are also employed in catalytic allylations of electrophiles, since the allyl moiety is constrained to an η^1-coordination state required for the nucleophilic reactivity (Scheme 6C).[19] Therefore, we suggest that intermediates **II** and **III** with nucleophilic η^1-σ-benzyl ligand and electrophilic η^3-π-benzyl ligand are involved in the benzylic C–H benzylation. In path A, intermediate **II** with electron-donating groups is generated to stabilize the δ^+ charge in π-benzyl Pd(II), which makes the position more electrophilic for direct intramolecular nucleophilic attack from the σ-benzyl anion ligand to afford dibenzylated **4**. Additionally, this δ^+ charge is stabilized by the nitrogen lone pair, and therefore mono-π-benzyl complex **11a** oxidizes the *N*-benzylated **3** *via* β-hydride elimination to the corresponding imines **5** along with the hydride palladium species. Indeed, the reaction of mono-*N*-benzylaniline with an electron-donating methoxy group gave the imine in 25% yield, while the electron-withdrawing cyano group resulted in trace amounts of imine production (see Table 4). In path B, the nucleophilic σ-benzyl anion ligand attacks the electrophilic η^3-π-benzyl ligand of intermediate **III** or ion pair **III′** to afford dibenzylated **4**. This pathway should be favored by electron-withdrawing groups on intermediate **III**, since these will stabilize the negative charge on the appropriate nucleophilic carbon. Chruma reported the palladium-catalyzed benzylation of benzyl diphenylglycinate imines to the corresponding homobenzylic imines.[20]

With regard to the substituent effect on the benzene ring, the reaction of mono-*N*-benzylanilines **3** with electron-donating groups is favored in our catalytic system (see Hammett studies and Table 4). However, anilines **1** with electron-donating methyl and methoxy groups resulted in moderate yields (see Table 3). These results suggested that anilines **1** with electron-donating groups react with benzaldehyde **13**[21] to give stable imines **5**. In contrast, electron-deficient imines with a cyano group could not be formed, since hydrolysis of unstable imine **5** proceeds quickly in water (see Table 4, entry 3).

Finally, several control experiments were performed to exclude the possibility of some reaction pathways from imine **5** and the hydride palladium species (Scheme 8 and Table 4). The reaction of imine **5a** did not give the desired **4a**, while mono-*N*-benzylaniline (**3a**) with benzyl alcohol (**2a**, 1 equiv.) afforded dibenzylated **4a** in 37% yield (entries 1 and 2). Furthermore, using a 1:1 mixture of mono-*N*-benzylaniline (**3a**) and imine **5a** did not enhance the reaction (entry 3). These results suggested that benzylated **3a** should be the intermediate in the benzylic C–H benzylation process. Additionally, the carbon radical addition to the imine *via* a single electron transfer process did not proceed in our catalytic system, since the reaction of **3a** was not inhibited by the addition of a radical scavenger (BHT) (entry 4).[22] Importantly, our π-benzylpalladium system works on quite a different mechanism from the hydrogen transfer methodology.

Conclusions

In summary, we have demonstrated a *N*-benzylation/benzylic C–H activation strategy by the π-benzylpalladium system for the direct construction of *N*-(1,2-diphenylethyl)anilines. The domino reactions achieved *N*-benzylation and benzylic C–H benzylation in water, which activates the sp^3 C–O bond, then stabilizes the OH^- by hydration for the smooth generation of the activated Pd(II) cation species. Furthermore, the π-benzylpalladium system could be used not only for benzylation, but also for C–H activation. Notably, the bis-benzylpalladium(II) complexes can undergo innovative direct transformation reactions. We are

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currently investigating the scope of various nucleophiles on the benzylation/C–H activation cascade reaction using π-benzylpalladium from benzyl alcohols in aqueous media.

Experimental Section

General Procedure for the Synthesis of *N*-(1,2-Diphenylethyl)anilines 4

A mixture of anilines **1** (1 mmol), palladium(II) acetate (12 mg, 0.05 mmol), sodium diphenylphosphinobenzene-3-sulfonate (TPPMS, 36 mg, 0.1 mmol) and benzyl alcohol **2** (5 mmol) in H_2O (4 mL) was heated for 16 h in sealed tube. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The residue was washed with hexanes, then purified by flash column chromatography (silica gel, hexanes/EtOAc) to give desired product **4**.

***N*-(1,2-Diphenylethyl)aniline (4a):**[12a] Yield: 189 mg (69%); colorless oil; IR (KBr): $\nu = 3470\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.01$ (dd, $J = 13.6$, 8.4 Hz, 1H), 3.13 (dd, $J = 14.5$, 6.0 Hz, 1H), 4.11 (brs, 1H), 4.58 (dd, $J = 8.5$, 6.0 Hz, 1H), 6.46 (dd, $J = 7.6$, 0.8 Hz, 2H), 6.62 (tt, $J = 4.8$, 1.2 Hz, 1H), 7.05 (dd, $J = 7.2$, 7.2 Hz, 2H), 7.12 (dd, $J = 6.8$, 1.6 Hz, 2H), 7.15–7.38 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.3$, 59.3, 113.7, 117.6, 126.5, 126.8, 127.2, 128.7, 129.1, 129.3, 137.8, 143.5, 147.4; MS (EI): *m/z* (%) = 273 (M^+, 17.2), 182 (100).

***N*-(1,2-Diphenylethyl)-4-methylaniline (4b):**[12b] Yield: 167 mg (58%); colorless oil; IR (KBr): $\nu = 3410\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.16$ (s, 3H), 2.99 (dd, $J = 14.4$, 8.4 Hz, 1H), 3.13 (dd, $J = 13.6$, 5.6 Hz, 1H), 4.00 (brs, 1H), 4.55 (dd, $J = 8.4$, 5.6 Hz, 1H), 6.37 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 7.13 (d, $J = 6.4$ Hz, 2H), 7.18–7.39 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.3$, 45.2, 59.4, 113.7, 126.4, 126.6, 126.7, 127.0, 128.5, 129.2, 129.5, 137.8, 143.6, 145.0; MS (EI): *m/z* (%) = 287 (M^+, 6.0), 196 (100).

***N*-(1,2-Diphenylethyl)-4-methoxyaniline (4c):**[12a] Yield: 164 mg (54%); brown oil; IR (KBr): $\nu = 3397\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.99$ (dd, $J = 14.0$, 8.4 Hz 1H), 3.12 (dd, $J = 14.0$, 5.6 Hz 1H), 3.90 (brs, 1H), 3.66 (s, 3H), 4.50 (dd, $J = 8.4$, 5.6 Hz 1H), 6.41 (d, $J = 9.0$ Hz 2H), 6.64 (d, $J = 9.0$ Hz 2H), 7.13 (dd, $J = 8.4$, 1.6 Hz 2H), 7.19–7.35 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.6$, 56.1, 60.4, 115.0, 115.3, 126.9, 127.1, 127.4, 128.9, 129.0, 129.6, 138.2, 141.9, 144.1, 152.4; MS (EI): *m/z* (%) = 303 (M^+, 5.6), 212 (100).

***N*-(1,2-Diphenylethyl)-4-fluoroaniline (4d):**[11c] Yield: 186 mg (64%); colorless oil; IR (KBr): $\nu = 3627\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.99$ (dd, $J = 14.0$, 8.4 Hz, 1H), 3.13 (dd, $J = 14.0$, 5.6 Hz, 1H), 4.00 (brs, 1H), 4.51 (dd, $J = 8.0$, 5.6 Hz, 1H), 6.36 (ddd, $J = 9.2$, 4.4, 2.4 Hz, 2H), 6.74 (ddd, $J = 8.8$, 8.8, 2.4 Hz, 2H), 7.05–7.14 (m, 2H), 7.17–7.34 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.1$, 59.9, 115.4 (d, $J = 22$ Hz), 126.5, 126.8, 127.2, 128.6 (d, $J = 4.7$ Hz), 129.2, 137.6, 143.1, 143.4, 155.9 (d, $J = 234.6$ Hz); MS (EI): *m/z* (%) = 291 (M^+, 4), 200 (100).

***N*-(1,2-Diphenylethyl)-3-fluoroaniline (4e):** Yield: 227 mg (78%); white solid; mp 60–63 °C; IR (KBr): $\nu = 3400\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.00$ (dd, $J = 14.0$, 8.4 Hz, 1H), 3.14 (dd, $J = 14.0$, 5.6 Hz, 1H), 4.23 (d, $J = 3.6$ Hz, 1H), 4.56 (ddd, $J = 8.0$, 5.2, 5.2 Hz), 6.12 (ddd, $J = 11.6$, 2.0 Hz, 1H), 6.23 (ddd, $J = 8.2$, 0.8 Hz, 1H), 6.30 (ddd, $J = 17.2$, 2.0, 1.2 Hz, 1H), 6.96 (ddd, $J = 14.8$, 6.8, 6.8 Hz, 1H), 7.11 (d, $J = 6.4$ Hz, 2H), 7.2–7.37 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.1$, 59.3, 100.5 (d, $J = 25.8$ Hz), 104.0 (d, $J = 21.9$ Hz), 109.5(d, $J = 1.9$ Hz), 126.5, 126.9, 127.4, 128.7, 128.8, 129.3, 130.1 (d, $J = 9.5$ Hz), 137.5, 142.9, 149.1 (d, $J = 10.5$ Hz), 163.9 (d, $J = 241.3$ Hz); anal. calcd. for $C_{20}H_{18}FN \cdot 0.1\,H_2O$: C 81.94, H 6.26, N 4.78; found: C 82.45, H 6.23, N 4.81; MS (EI): *m/z* (%) = 291(M^+, 2), 200 (100).

5-(1,2-Diphenylethylamino)-2-methylbenzonitrile (4f): Yield: 244 mg (78%); white solid; mp 119–121 °C; IR (KBr): $\nu = 3392$, 2222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.31$ (s, 3H), 2.99 (dd, $J = 14.0$, 8.0 Hz, 1H), 3.14 (dd, $J = 14.4$, 5.6 Hz, 1H), 4.19 (d, $J = 3.2$ Hz, 1H), 4.50–4.58 (m, 1H), 6.55 (dd, $J = 8.4$, 2.0 Hz, 1H), 6.59 (d, $J = 2.4$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 7.10 (d, $J = 6.8$ Hz, 2H), 7.20–7.40 (m 8H), 7.17–7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.3$, 45.1, 59.2, 112.8, 116.3, 118.5, 118.7, 126.4, 127.0, 127.5, 128.8, 128.9, 129.2, 130.4, 130.8, 137.3, 142.4, 145.3; MS (EI): *m/z* (%) = 312 (M^+, 3), 221 (100); anal. calcd. for $C_{22}H_{20}N_2$: C 84.58, H 6.45, N 8.97; found: C 84.31, H 6.49, N 8.92.

Ethyl 3-[(1,2-diphenylethyl)amino]benzoate (4g): Yield: 304 mg (88%); white solid; mp 100–103 °C; IR (KBr): $\nu = 3395$, 1695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.33$ (t, $J = 7.2$ Hz, 3H), 3.03 (dd, $J = 14.0$, 8.0 Hz, 1H), 3.15 (dd, $J = 14.0$, 5.6 Hz, 1H), 4.24–4.38 (m, 3H), 4.63 (dd, $J = 8.5$, 6.0 Hz, 1H), 6.59 (ddd, $J = 8.2$, 4.0, 0.8 Hz, 1H), 7.05–7.14 (m, 3H), 7.17–7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.4$, 45.1, 59.2, 60.9, 114.8, 117.6, 118.6, 126.6, 126.9, 127.3, 128.7, 129.1, 129.3, 131.2, 137.5, 142.9, 147.2, 167.0; MS (EI): *m/z* (%) = 345 (M^+, 1), 254 (100); anal. calcd. for $C_{24}H_{26}N_2O \cdot 0.2\,H_2O$: C 79.15, H 6.76, N 4.01; found: C 79.04, H 6.63, N 4.06.

[4-(1,2-Diphenylethylamino)phenyl]phenylmethanone (4h): Yield: 185 mg (49%); white solid; mp 102–105 °C; IR (KBr): $\nu = 3343$, 1692 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 2.98$ (dd, $J = 16.0$, 8.0 Hz, 1H), 3.11 (dd, $J = 12.0$, 8.0 Hz, 1H), 4.76 (dd, $J = 12.0$, 8.0 Hz, 1H), 6.61 (d, $J = 12.0$ Hz, 2H), 7.14–7.36 (m, 9H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.43–7.50 (m, 4H), 7.54 (d, $J = 8.0$ Hz 2H), 7.60 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 47.7$, 111.6, 126.6, 127.5, 127.7, 128.1, 128.9, 129.6, 131.4, 133.1, 138.3, 139.1, 151.9, 195.3; MS (EI): *m/z* (%) = 287 (M^+, 100); HR-MS-EI: *m/z* = 377.1779 (M^+), calcd, for $C_{27}H_{23}NO$: 377.1780

***N*-(1,2-Diphenylethyl)-[1,1′-biphenyl]-3-amine (4i):** Yield: 294 mg (84%); colorless oil; IR (KBr): $\nu = 3414\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.04$ (dd, $J = 13.6$, 8.0 Hz, 1H), 3.16 (dd, $J = 13.6$, 5.2 Hz, 1H), 4.22 (brs, 1H), 4.64 (dd, $J = 8.5$, 6.0 Hz, 1H), 6.42 (dd, $J = 8.0$, 1.6 Hz, 1H), 6.69 (t, $J = 2.0$ Hz, 1H), 6.83–6.88 (m, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 7.14 (dd, $J = 8.4$, 1.6 Hz, 2H), 7.19–7.44 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.1$, 59.3, 112.5, 112.6, 116.6, 137.6, 141.5, 142.0, 143.3, 147.5, 126.4, 126.7, 127.0, 127.1, 128.5, 128.6, 129.2, 129.4; MS (EI): *m/z* (%) = 349 (M^+, 17.5), 258 (100); HR-MS-EI: *m/z* = 349.1832 (M^+), calcd. for $C_{26}H_{23}N$: 349.1830.

3-[(1,2-Diphenylethyl)amino]benzenesulfonamide (4j): Yield: 264 mg (75%); white solid; mp 125–129 °C; IR

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(KBr): $\nu = 3254\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.01$ (dd, $J = 14.0$, 8.4 Hz, 1H), 3.16 (dd, $J = 14.0$, 5.6 Hz, 1H), 4.44 (d, $J = 4.4$ Hz, 1H), 4.59–4.70 (m, 3H), 6.56 (ddd, $J = 7.2$, 2.4, 2.4 Hz, 1H), 7.00 (d, $J = 2.0$ Hz, 1H), 7.08–7.16 (m, 4H), 7.20–7.36 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 45.0, 59.0, 111.1, 114.7, 117.1, 126.5, 127.0, 127.5, 128.8, 129.3, 130.0, 137.3, 142.4, 147.7; MS (EI): *m/z* (%) = 352 (M^+, 1), 261 (100); anal. calcd. for $C_{20}H_{20}N_2O_2S \cdot 0.1\,H_2O$: C 67.81, H 5.75, N 7.91; found: C 67.57, H 5.73, N 7.91.

***N*-[4-(1,2-Diphenylethylamino)phenyl]acetamide (4k):** Yield: 192 mg (58%); white solid; mp 134–138 °C; IR (KBr): $\nu = 3341$, 1632 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 2.08 (s, 3H), 3.00 (dd, $J = 14.0$, 8.4 Hz, 1H), 3.13 (dd, $J =$ 14.0, 5.6 Hz), 4.15 (brs, 1H), 4.55 (dd, $J = 8.4$, 5.6 Hz, 1H), 6.40 (d, $J = 6.8$ Hz, 2H), 6.92 (brs, 1H), 7.08–7.14 (m, 4H), 7.19–7.33 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.3$, 45.2, 59.4, 113.9, 122.3, 126.5, 126.8, 127.2, 128.1, 128.6, 129.2, 137.6, 143.3, 144.6, 168.1; MS (EI): *m/z* (%) = 330 (M^+, 3.9), 239 (100); anal. calcd. for $C_{15}H_{14}N_2$: C 79.97, H 6.71, N 8.48; found: C 80.14, H 6.63, N 8.40.

4-(1,2-Diphenylethylamino)benzamide (4l): Yield: 180 mg (57%); pale yellow solid; mp 62–66 °C; IR (KBr): $\nu = 3329$, 1649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.04$ (dd, $J =$ 14.8 Hz 1H), 3.17 (dd, $J = 14.6$ Hz 1H), 4.51 (brd, $J = 4.8$ Hz 1H), 4.66 (ddd, $J = 8.4$, 5.2, 5.2 Hz 1H), 6.44 (d, $J = 6.8$ Hz 2H), 7.08–7.12 (m, 2H), 7.21–7.35 (m, 8H), 7.53 (d, $J =$ 6.8 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 44.9$, 58.7, 112.7, 126.4, 127.0, 127.4, 128.7, 129.0, 129.1, 137.1, 142.4, 150.2, 169.1; MS (EI): *m/z* (%) = 316 (M^+, 1.4), 225 (100); HR-MS-EI: *m/z* = 316.1575 (M^+), calcd. for $C_{21}H_{20}N_2O$: 316.1576.

***N*-(1,2-Diphenylethyl)-4-morpholinoaniline (4m):** Yield: 179 mg (50%); pale brown solid; mp 90–94 °C; IR (KBr): $\nu = 3362\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.93$ (d, $J =$ 4.8 Hz, 2H), 2.94 (d, $J = 4.8$ Hz, 2H), 2.99 (dd, $J = 14.0$, 8.0 Hz, 1H), 3.12 (dd, $J = 14.0$, 5.6 Hz, 1H), 3.79 (d, $J =$ 4.8 Hz, 2H), 3.80 (d, $J = 4.8$ Hz, 2H), 3.92 (brs, 1H), 4.52 (dd, $J = 8.4$, 5.6 Hz, 1H), 6.42 (d, $J = 8.8$ Hz, 2H), 6.70 (d, $J = 8.8$ Hz, 2H), 7.12 (d, $J = 7.2$ Hz, 2H), 7.18–7.38 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.2$, 51.2, 59.8, 67.0, 114.6, 118.1, 126.5, 126.7, 127.0, 128.5, 129.2, 137.8, 142.0, 143.7; anal. calcd. for $C_{24}H_{26}N_2O$: C 80.41, H 7.31, N 7.81; found: C 80.29, H 7.25, N 7.78; MS (EI): *m/z* (%) = 358 (M^+, 19.4), 267 (100).

4-[4-(1,2-Diphenylethylamino)phenyl]morpholin-3-one (4n): Yield: 197 mg (53%); white solid; mp 143–147 °C; IR (KBr): $\nu = 3390$, 1677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 2.97 (dd, $J = 14.0$, 8.8 Hz, 1H), 3.13 (dd, $J = 14.0$, 5.6 Hz, 1H), 3.58 (dd, $J = 4.4$, 1.2 Hz, 1H), 3.60 (dd, $J = 4.4$, 1.2 Hz, 1H), 3.93 (d, $J = 4.8$ Hz, 1H), 3.94 (d, $J = 4.8$ Hz, 1H), 4.20 (d, $J = 3.2$ Hz, 1H), 4.26 (s, 2H), 4.54 (quin, $J = 4.0$ Hz, 1H), 6.44 (d, $J = 8.8$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 7.12 (dd, $J = 8.4$, 1.6 Hz, 2H), 7.20–7.34 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.3$, 50.2, 59.4, 64.3, 68.6, 114.0, 126.5, 126.6, 126.9, 127.3, 128.7, 128.8, 129.2, 131.2, 137.6, 143.3, 146.5, 166.9; MS (EI): *m/z* (%) = 372 (M^+, 5), 281 (100); anal. calcd. for $C_{24}H_{24}N_2O_2$: C 77.39, H 6.50, N 7.52; found: C 77.40, H 6.52, N 7.44.

1-[2-(1,2-Diphenylethylamino)phenyl]ethan-1-one (4o): Yield: 252 mg (80%); yellow solid; mp 90–94 °C; IR (KBr): $\nu = 3295$, 1700 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta =$ 2.53 (s, 3H), 3.01 (dd, $J = 12.0$, 8.0 Hz, 1H), 3.10 (dd, $J =$ 12.0, 8.0 Hz, 1H), 4.87 (dd, $J = 8.0$, 4.0 Hz, 1H), 6.51 (t, $J =$ 4.0 Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 1H), 7.15–7.40 (m, 10H), 7.77 (d, $J = 8.0$ Hz, 1H), 9.42 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 27.9$, 44.2, 57.5, 112.7, 114.3, 117.3, 126.3, 126.9, 128.1, 128.4, 129.3, 132.9, 134.7, 138.0, 143.1, 149.4, 200.9; MS (EI): *m/z* (%) = 315 (M^+, 1), 224 (100); HR-MS-EI: *m/z* = 315.1625 (M^+), calcd. for $C_{22}H_{21}NO$: 315.1623.

***N*-(1,2-Diphenylethyl)-[1,1′-biphenyl]-2-amine (4p):** Yield: 248 mg (71%); white solid; mp 98–102 °C; IR (KBr): $\nu =$ 3406 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 2.83$ (dd, $J =$ 12.0, 8.0 Hz, 1H), 3.02 (dd, $J = 16.0$, 4.0 Hz, 1H), 4.60–4.70 (m, 2H), 6.33 (d, $J = 8.0$ Hz, 1H), 6.58 (dd, $J = 8.0$, 8.0 Hz, 1H), 6.77–7.00 (m, 2H), 7.07 (dd, $J = 8.0$, 4.0 Hz, 2H), 7.10–7.25 (m, 6H), 7.25–7.50 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.6$, 59.6, 111.7, 126.3, 126.7, 127.1, 127.2, 127.9, 128.5, 128.6, 128.7, 129.0, 129.2, 129.5, 130.0, 137.6, 139.4, 143.7, 144.2; MS (EI): *m/z* (%) = 349 (M^+, 3), 258 (100); anal. calcd. for $C_{26}H_{23}N$: C 89.36, H 6.63, N 4.01; found: C 89.47, H 6.67, N 3.98.

***N*-(1,2-Diphenylethyl)-2-phenoxyaniline (4q):** Yield: 274 mg (75%); white solid; mp 104–106 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.94$ (dd, $J = 13.6$, 8.4 Hz, 1H), 3.05 (dd, $J = 14.0$, 6.0 Hz, 1H), 4.55 (q, $J = 7.2$ Hz, 1H), 4.71 (brs, 1H), 6.41 (d, $J = 7.6$ Hz, 1H), 6.54 (dd, $J = 8.0$, 8.0 Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.82 (dd, $J = 8.0$, 8.0 Hz, 1H), 6.89 (dd, $J = 8.0$, 0.8 Hz, 2H), 6.95–7.20 (m, 2H), 7.06 (dd, $J = 7.2$, 7.2 Hz, 1H), 7.11–7.17 (m, 3H), 7.18–7.35 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 45.4$, 59.3, 112.9, 117.0, 117.3, 119.6, 122.7, 124.9, 126.5, 126.7, 127.2, 128.5, 128.7, 129.3, 129.8, 137.6, 139.7, 143.0, 143.4, 157.8; MS (EI): *m/z* (%) = 365 (M^+, 3), 274 (100); anal. calcd. for $C_{26}H_{23}NO \cdot 0.2\,H_2O$: C 85.61, H 6.39, N 3.80; found: C 84.65, H 6.30, N 3.84.

2-Benzyl-*N*-1,2-diphenylethylaniline (4r): Yield: 211 mg (58%); white solid; mp 68–70 °C; IR (KBr): $\nu = 3415\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.80$ (dd, $J = 14.4$, 8.4 Hz, 1H), 2.98 (dd, $J = 13.6$, 5.6 Hz, 1H), 3.76 (d, $J = 16.0$ Hz, 1H), 3.85 (d, $J = 16.0$ Hz, 1H), 4.02 (brs, 1H), 4.56 (dd, $J =$ 8.0, 6.0 Hz, 1H), 6.34 (d, $J = 7.6$ Hz, 1H), 6.61 (dd, $J = 7.6$, 1.2 Hz, 1H), 6.92–7.03 (m, 6H), 7.10–7.30 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 38.4$, 45.4, 58.8, 112.1, 117.1, 126.4, 126.6, 126.7, 127.0, 127.7, 128.5, 128.6, 128.7, 128.8, 129.3, 130.7, 137.7, 139.4, 143.4, 145.0; MS (EI): *m/z* (%) = 363 (M^+, 3), 272 (100); HR-MS-EI: *m/z* = 363.1988 (M^+), calcd. for $C_{27}H_{25}N$ 363.1978.

***N*-4-[1,2-Bis(4-methoxyphenyl)ethylamino]phenylacetamide (4s):** Yield: 219 mg (56%); white solid; mp 130–133 °C; IR (KBr): $\nu = 3320$, 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.09$ (s, 3H), 2.92 (dd, $J = 14.4$, 8.0 Hz, 1H), 3.03 (dd, $J = 14.4$, 6.0 Hz, 1H), 3.79 (d, $J = 1.6$ Hz, 6H), 4.45 (dd, $J = 8.0$, 6.0 Hz, 1H), 6.40 (d, $J = 8.8$ Hz, 2H), 6.77–6.89 (m, 4H), 6.70 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.8$ Hz, 2H), 7.12 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.3$, 44.3, 55.2, 58.9, 113.8, 113.9, 122.2, 127.5, 128.0, 129.6, 130.2, 135.3, 144.6, 158.3, 158.5, 168.0; MS (EI): *m/z* (%) = 390 (M^+, 1), 269 (100); anal. calcd. for $C_{24}H_{26}N_2O_3$: C 73.82, H 6.71, N 7.17; found: C 73.57, H 6.65, N 7.15.

***N*-4-(1,2-Di-*para*-tolylethyl)aminophenylacetamide (4t):** Yield: 222 mg (62%); white solid; mp 116–120 °C; IR (KBr): $\nu = 3277$, 1615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 2.08 (s, 3H), 2.31 (s, 3H), 2.32 (s, 3H), 2.92 (dd, $J = 14.0$,

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8.4 Hz, 1H), 3.09 (dd, J=14.0, 5.2 Hz, 1H), 4.05 (brs, 1H), 4.49 (dd, J=8.4, 5.6 Hz, 1H), 6.39 (d, J=8.8 Hz, 2H), 6.87 (brs, 1H), 7.01 (d, J=8.0 Hz, 2H), 7.06–7.14 (m, 6H), 7.20 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.1, 24.2, 44.7, 59.1, 113.8, 122.2, 126.3, 127.9, 129.0, 129.2, 129.3, 134.6, 136.2, 136.6, 140.4, 144.7, 168.0; MS (EI): m/z (%)= 358 (M^+, 3), 253 (100); anal. calcd. for $C_{24}H_{26}N_2O$: C 80.41, H 7.31, N 7.81; found: C 80.18, H 7.25, N 7.85.

***N*-[4-(1,2-Di-*meta*-tolylethylamino)phenyl]acetamide (4u):** Yield: 215 mg (60%); white solid; mp 122–124 °C; IR (KBr): ν=3231, 1640 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.08 (s, 3H), 2.31 (s, 3H), 2.33 (s, 3H), 2.88 (dd, J=14.0, 8.8 Hz, 1H), 3.09 (dd, J=14.4, 5.6 Hz, 1H), 4.05 (brs, 1H), 4.48 (dd, J=8.8, 5.2 Hz, 1H), 6.39 (d, J=8.8 Hz, 2H), 6.80–6.98 (m, 3H), 7.02–7.22 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.5, 21.6, 24.3, 45.3, 59.5, 113.9, 122.3, 123.5, 126.2, 127.1, 127.6, 127.8, 127.9, 128.1, 128.5, 130.0, 137.8, 138.3, 143.6, 144.8, 168.2; MS (EI): m/z (%)=358 (M^+, 5), 253 (100); anal. calcd. for $C_{24}H_{26}N_2O$: C 80.41, H 7.31, N 7.81; found: C 80.37, H 7.31, N 7.77.

***N*-4-[1,2-Bis(4-butoxyphenyl)ethylamino]phenylacetamide (4v):** Yield: 201 mg (50%); brown oil; IR (KBr): ν=3306, 1667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.97 (t, J= 7.6 Hz, 6H), 1.48 (sext, J=7.6 Hz, 4H), 1.75 (quin, J= 6.4 Hz, 4H), 2.09 (s, 3H), 2.89 (dd, J=14.4, 8.0 Hz, 1H), 3.02 (dd, J=13.6, 5.6 Hz, 1H), 3.93 (t, J=6.4 Hz, 4H), 4.04 (brs, 1H), 4.43 (dd, J=8.0, 6.0 Hz, 1H), 6.40 (d, J=8.4 Hz, 2H), 6.80 (dd, J=11.2, 8.4 Hz, 4H), 6.89 (brs, 1H), 6.99 (d, J=8.8 Hz, 2H), 7.11 (d, J=9.2 Hz, 2H), 7.18 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0, 19.4, 24.2, 31.5, 44.3, 59.0, 67.8, 113.9, 114.6, 122.3, 127.6, 128.3, 129.6, 130.3, 135.2, 144.7, 158.0, 158.2, 168.5; MS (EI): m/z (%)=474 (M^+, 1), 311 (100); HR-MS-EI: m/z=474.282 (M^+), calcd. for $C_{30}H_{38}N_2O_3$: 474.2883.

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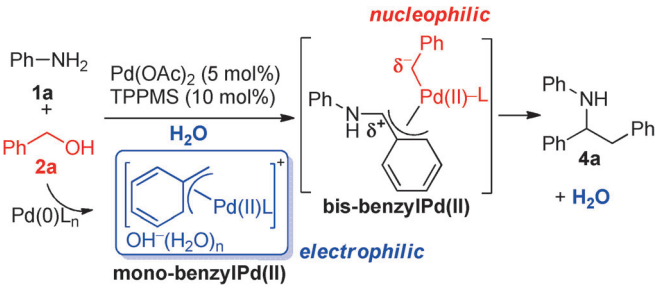

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