

**Metal-free synthesis of allylic amines by cross-dehydrogenative-coupling of 1,3-diarylpropenes with anilines and amides under mild conditions†**Zhiming Wang,<sup>a,b</sup> Hanjie Mo,<sup>a</sup> Dongping Cheng<sup>a,c</sup> and Weiliang Bao\*<sup>a</sup>

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Dehydrogenative cross-coupling reaction of primary anilines, secondary anilines, carboxamides, and sulfonamides with 1,3-diarylpropenes to form a series of allylic amines promoted by DDQ have been realized. Both monoallylation and diallylation products can be selectively synthesized when primary anilines are used as the starting materials. The method may provide a wide scope of allylamines in scientific research including biologically active compound library construction.

Allylic amines are ubiquitous in various biologically active compounds,<sup>1</sup> such as the antifungal drug Naftifine<sup>2</sup> and the calcium channel blocker Flunarizine,<sup>3</sup> and are highly useful substrates for many types of reactions, such as asymmetric isomerization<sup>4</sup> and ring-closing metathesis.<sup>5</sup> The synthesis of allylic amines usually employs activated allylic compounds, in particular, allylic halides, carboxylates, and carbonates, because of the strong activity of these substrates.<sup>6</sup> But the use of such activated substrates causes the formation of more than stoichiometric amounts of unwanted chemical waste. Then allylic alcohols were used to react with amines to synthesize allylic amines.<sup>7–14</sup> However, most of the reactions required rather severe catalytic reaction conditions and transition metal-based protocols usually have some inherent limitations such as moisture sensitivity, costly metal catalysts and environmental toxicity. Also, because of the higher nucleophilicity of the monoallylation products, the reaction always results both in the formations of monoallylation products and diallylation products.

With the prevalence of “atom economy”<sup>15</sup> and “green chemistry”,<sup>16</sup> the cross-coupling reaction to construct allylic amines directly using allylic sp<sup>3</sup> C–H bond and amines has attracted great interest. Amination reactions of different C–H bonds to form new C–N bonds have been reported by many groups. However, most of the substrates in the amination reactions were amide, sulfonamide or anilines with strong electron withdrawing-groups.<sup>17</sup> Reactions of amines without any electron withdrawing-groups with C–H bonds to form new C–N bonds *via*

cross-dehydrogenative coupling (CDC) has been rarely realized. In 2010, Armstrong and his coworkers reported a copper-catalyzed oxidative amination reaction of azoles on 2-position to form a C–N bond using secondary amines with or without electron withdrawing-groups.<sup>18</sup> In 2010, Wang and his coworkers reported a copper-catalyzed synthesis of polysubstituted oxazoles using benzylamines and 1,3-dicarbonyl derivatives as the substrates. They used iodine as the additive to pre-activate the substrates, and proposed that ethyl 2-iodo-3-oxobutanoate may be a key intermediate.<sup>19</sup> The amination of sp<sup>3</sup> C–H bonds using primary amines without any additives remains a challenge.

In the past few years, our group reported metal-free coupling reactions to form new C–C, C–O and C–S bonds directly using 1,3-diarylpropenes promoted by DDQ.<sup>20</sup> Also, in 2009, we reported a Pd-catalyzed indolation reaction of allylic compounds with DDQ.<sup>21</sup> Herein, we report a metal-free coupling reaction to synthesize both monoallylamines and diallylamines directly using allylic sp<sup>3</sup> C–H bonds and anilines or amides promoted by DDQ under very mild conditions.

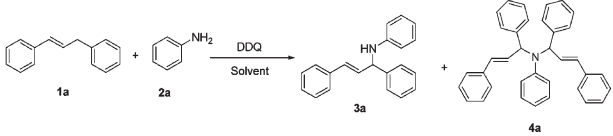
To begin our study, we chose 1,3-diphenylpropene **1a** and aniline **2a** as the standard substrates to search for suitable reaction conditions. Firstly, we mixed two substrates in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C, then a stoichiometric amount of DDQ was added, no desired coupling product was detected. Because aniline possesses strong activity and it's easily oxidized by DDQ, we changed the addition sequence of the substrates. To a solution of 1,3-diarylpropene in 2 mL CH<sub>2</sub>Cl<sub>2</sub>, DDQ was added at 0 °C. After stirring for about 5–10 minutes, aniline was injected into the mixture slowly. The reaction finished in about 10 minutes, and the coupling product *N*-(1,3-diphenylallyl)aniline **3a** was obtained in 51% yield and *N,N*-bis(1,3-diphenylallyl)aniline **4a** in 37% yield (Table 1, entry 1). The conversion rate of 1,3-diphenylpropene (**1a**) was 88%, but the monoallylation or diallylation selectivities were not satisfactory. Then the reaction was carried out under different temperatures (Table 1, entries 2–5). When the temperature was increased to 50 °C, the molar ratio of

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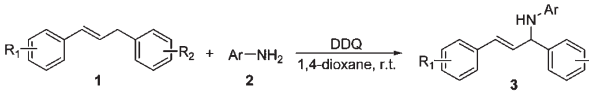
**Table 1** Optimization of the CDC reaction conditions<sup>a</sup>


Entry	Temp (°C)	Solvent	Yield <sup>b</sup> (%)	
			3a	4a
1	0	CH <sub>2</sub> Cl <sub>2</sub>	51	37
2	r.t.	CH <sub>2</sub> Cl <sub>2</sub>	25	50
3	50	CH <sub>2</sub> Cl <sub>2</sub>	3	45
4	-15	CH <sub>2</sub> Cl <sub>2</sub>	55	21
5	-40	CH <sub>2</sub> Cl <sub>2</sub>	52	7
6	0	CHCl <sub>3</sub>	55	30
7	0	DCE	52	33
8	0	Toluene	37	20
9	0	CH <sub>3</sub> CN	46	15
10	0	CH <sub>3</sub> NO <sub>2</sub>	30	11
11	0	DMF	15	Trace
12	0	Cyclohexane	Trace	Trace
13	0	THF	85	3
14	r.t.	1,4-Dioxane	90	<1

<sup>a</sup> 0.5 mmol of **1a**, 0.55 mmol of **2a**, 0.55 mmol of DDQ, 2 mL of solvent, 10 min. <sup>b</sup> Isolated yield.

two products was 1 : 15 (**3a** : **4a**), although the conversion rate of the substrate (**1a**) was only 48% (Table 1, entry 3). When the reaction temperature was lowered to -40 °C, the molar ratio of two products was 7 : 1 (**3a** : **4a**), the yield of **3a** was only 52%, and this result was not satisfactory (Table 1, entry 5). Then a number of solvents were screened. When CHCl<sub>3</sub> and DCE were used as the solvent, the results were similar to the result when CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent (Table 1, entries 6, 7). When toluene, CH<sub>3</sub>CN and CH<sub>3</sub>NO<sub>2</sub> were used as the solvent, the conversion rate of **1a** was moderate and the monoallylation selectivity of aniline was still not satisfactory (Table 1, entries 8, 9, 10). When DMF was used as the solvent, we obtained the monoallylation product **3a** in 15% yield, and product **4a** was not detected (Table 1, entry 11). When cyclohexane was used, no products were obtained because of the poor solubility of DDQ in cyclohexane (Table 1, entry 12). When THF was used as the solvent, the products **3a** and **4a** were obtained in 85% and 3% yield respectively, the molar ratio of two products was 28 : 1 (Table 1, entry 13). Surprisingly, when 1,4-dioxane was used as the solvent and the reaction was carried out at room temperature, the monoallylation product **3a** was obtained in 90% yield and only less than 1% yield of **4a** was gathered (Table 1, entry 14).

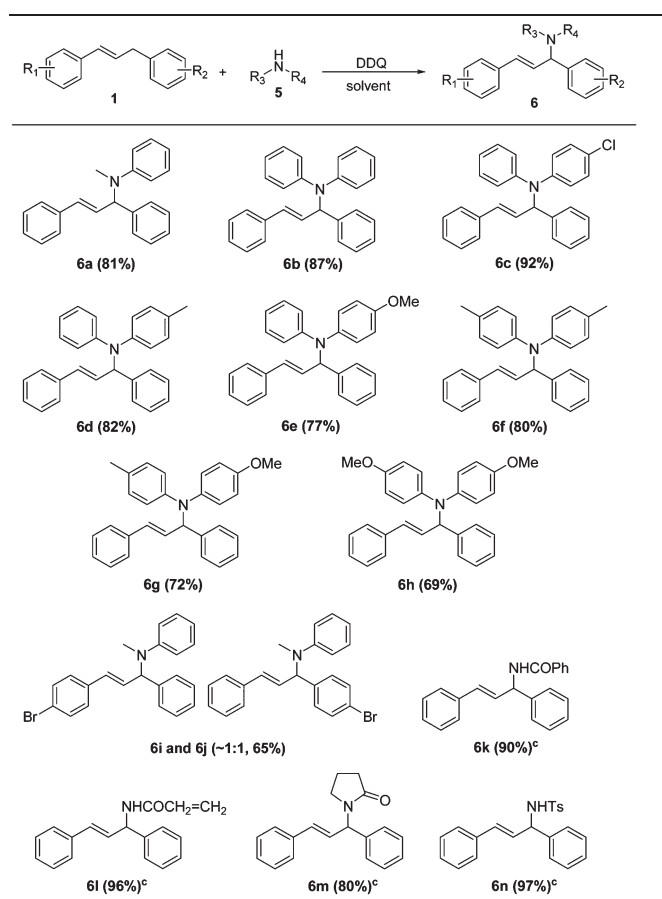
With the optimized reaction conditions established, various substrates were subjected to the CDC reactions and representative results are summarized in Table 2. Anilines with electron withdrawing-groups reacted well with the diarylpropenes under the standard reaction condition (Table 2, **3b–3c**, **3f** and **3h–3k**). When anilines with electron donating-groups were used as the substrates, the yield of desired monoallylation product decreased slightly and was also satisfactory (Table 2, **3l–3o**). Unfortunately, when aliphatic amines were used as the substrates, no desired coupling products were detected. When 1,3-diarylpropene with electron withdrawing-groups on the aromatic ring was used, the

**Table 2** The CDC reaction of 1,3-diarylpropenes with primary anilines<sup>a,b</sup>


<b>3a</b> (90%)	<b>3b</b> (91%)	<b>3c</b> (92%)
<b>3d</b> (85%)	<b>3e</b> (77%)	<b>3f</b> (97%)
<b>3g</b> (81%)	<b>3h</b> (95%)	<b>3i</b> (93%)
<b>3j</b> (82%)	<b>3k</b> (90%)	<b>3l</b> (88%)
<b>3m</b> (85%)	<b>3n</b> (74%)	<b>3o</b> (89%)
<b>3p</b> (81%)	<b>3q and 3r</b> (~1:1, 75%)	
<b>3s and 3t</b> (~1:1.5, 77%)		<b>3u and 3v</b> (~1:1, 69%)
<b>3w and 3x</b> (~1:1, 72%)		

<sup>a</sup> 0.5 mmol of **1**, 0.55 mmol of **2**, 0.55 mmol of DDQ, 2 mL of 1,4-dioxane, r.t., 10 min. <sup>b</sup> Isolated yield.

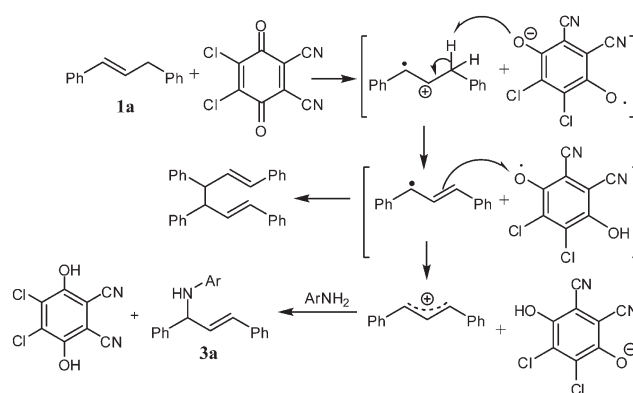
yield of the coupling product was decreased a little but still satisfactory (Table 2, **3p**). To expand the scope of the substrates, we further examined the unsymmetrical 1,3-diarylpropenes and obtained the expected products with poor regioselectivities according to the <sup>1</sup>H NMR and <sup>13</sup>C NMR (Table 2, **3q–3x**). When 1-methyl-1,3-diarylpropene was used, only less than 3%

**Table 3** The CDC reaction of 1,3-diarylpropenes with secondary anilines and amides<sup>ab</sup>

<sup>a</sup> 0.5 mmol of **1**, 0.55 mmol of **5**, 0.55 mmol of DDQ, 2 mL of 1,4-dioxane, r.t. 10 min. <sup>b</sup> Isolated yield. <sup>c</sup> Nitromethane was used as a solvent instead of 1,4-dioxane.

yield of the coupling product was gathered, the steric effect may largely interfere with the reaction.

Then a series of secondary anilines and amides were used as substrates. Under the same reaction condition, a number of coupling products were also obtained in good yield, and representative results are summarized in Table 3. When *N*-methylaniline (**5a**) was used, the coupling product **6a** was obtained in 81% yield. A series of *N,N*-diarylamines were used as substrates to undergo the CDC reaction to form more stable coupling products. When an *N,N*-diarylamine with electron withdrawing-group on the aromatic ring was used, the desired product was obtained in high yield (Table 3, **6c**). When *N,N*-diarylamines with electron donating-groups on the aromatic rings were examined, the yields of the coupling products decreased a little (Table 3, **6d**, **6e**, **6f**, **6g**, **6h**). Then 1-bromo-4-(3-phenylprop-1-enyl)benzene (**1b**) was used as the substrate, isomers **6i** and **6j** were obtained, and the yield of the products was moderate. Interestingly, when benzamide, acrylamide, pyrrolidin-2-one and *p*-toluene sulfonamide were used as the starting materials, the coupling reaction took place smoothly with good to excellent reaction yields (Table 3, **6k–6n**).

**Scheme 1** A possible mechanism.

On the basis of the literature and the experimental observations, a plausible mechanism is proposed in Scheme 1. The CDC reaction may follow two pathways: hydride transferred directly from the allylic position to DDQ and/or proton abstraction after an electron was transferred from the allylic double bond to DDQ.<sup>20,22</sup> In our experiment, when the 1,3-diphenylpropene was treated with aniline, we observed the self-coupling product of 1,3-diphenylpropene. This coupling product may indicate a single-electron transfer in the reaction. Rearranged products **3q–3x** and **6i–6j** were also obtained in the experiments. Therefore, an allylic cation may also be involved in the coupling process. These results may support our proposed mechanism.

In summary, we have developed a new method to synthesize allylic amines *via* CDC reaction between 1,3-diarylpropenes and anilines or amides promoted by DDQ. The methodology is highly facile and efficient, and may provide a wide scope of allylic amines in scientific research and access to more biologically active compounds library.

## Experimental

All <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C MNR (100 MHz) spectra were recorded in CDCl<sub>3</sub> using TMS as an internal standard. The starting materials diarylpropenes<sup>23</sup> and *N,N*-diarylamines<sup>24</sup> were prepared according to the literature procedures.

### General procedure for the preparation of compounds **3a–3x** and **6a–6j**

To a mixture of 1,3-diarylpropene (0.5 mmol) and 2 mL of 1,4-dioxane, DDQ 123 mg (0.55 mmol) was added at room temperature. After stirring for about 5–10 minutes, aniline (0.55 mmol) was dissolved in 1 mL of 1,4-dioxane, and dropped into the mixture slowly. Then the reaction vessel was capped and the mixture stirred for 10 minutes. The resulting mixture was purified by flash column chromatography on silica gel (petroleum ether–ethyl acetate) to give the desired pure product (**3a–3x** or **6a–6j**).

### General procedure for the preparation of compounds 6k–6n

To a 10 mL two-necked round-bottom flask with a mixture of carboxamide or sulfonamide (0.5 mmol) and diarylallylic compound (0.6 mmol) in MeNO<sub>2</sub> (3 mL), DDQ (0.6 mmol) was added under N<sub>2</sub>. The resulting mixture was stirred for 6 h at 50 °C. The resulting mixture was purified by flash column chromatography on silica gel (petroleum ether–ethyl acetate) to give the desired pure product (6k–6n).

**(E)-N-(1,3-Diphenylallyl)aniline (3a)**<sup>25</sup>: light yellow oil; 90% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.47–7.14 (m, 13H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.67–6.62 (m, 3H), 6.41 (dd, *J* = 6.4, 16 Hz, 1H), 5.11 (d, *J* = 6.4 Hz, 1H), 4.14 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 60.6, 113.5, 117.6, 126.4, 127.1, 127.4, 127.6, 128.5, 128.8, 129.1, 130.7, 131.0, 136.6, 142.0, 147.2; IR (neat): 3421, 3026, 2838, 1600, 1491, 1450, 1307, 1251, 1158, 1129, 967, 810, 746, 696 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 285.

**(E)-4-Chloro-N-(1,3-diphenylallyl)aniline (3b)**<sup>26</sup>: light yellow oil; 91% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.45–7.25 (m, 11H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.65–6.55 (m, 3H), 6.40 (dd, *J* = 6.0, 16.0 Hz, 1H), 5.06 (d, *J* = 6.4 Hz, 1H), 4.16 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 60.7, 114.6, 122.3, 126.5, 127.1, 127.7, 127.8, 128.5, 128.8, 128.9, 130.2, 131.3, 136.4, 141.5, 145.7; IR (neat): 3412, 3027, 2852, 1597, 1493, 1450, 1313, 1258, 1177, 1122, 967, 814, 745, 696 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 319.

**(E)-4-Bromo-N-(1,3-diphenylallyl)aniline (3c)**: light yellow oil; 92% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.44–7.22 (m, 13H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 6.8 Hz, 2H), 6.38 (dd, *J* = 6.4, 15.6 Hz, 1H), 5.06 (d, *J* = 6.0 Hz, 1H), 4.17 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 60.5, 109.3, 115.1, 126.4, 127.1, 127.6, 127.7, 128.5, 128.8, 130.0, 131.3, 131.8, 136.4, 141.4, 146.0; IR (neat): 3411, 3026, 2862, 1593, 1492, 1450, 1395, 1314, 1258, 1178, 1123, 968, 812, 746, 697 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 363; HRMS (EI): *m/z* calcd for C<sub>21</sub>H<sub>18</sub>BrN (M<sup>+</sup>): 363.0623, Found 363.0625.

**(E)-N-(1,3-Diphenylallyl)-4-methylaniline (3d)**<sup>26</sup>: light yellow oil; 85% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.49–7.26 (m, 11H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.69–6.59 (m, 3H), 6.44 (dd, *J* = 6.4, 16.0 Hz, 1H), 5.10 (d, *J* = 6.0 Hz, 1H), 4.04 (s, 1H), 2.27 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 20.3, 60.9, 113.7, 126.5, 126.9, 127.2, 127.4, 127.6, 128.5, 128.7, 129.6, 130.8, 130.9, 136.7, 142.2, 145.0; IR (neat): 3406, 2916, 2862, 1615, 1515, 1450, 1402, 1300, 1258, 1182, 1127, 1069, 1028, 967, 807, 744, 696 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 299.

**(E)-N-(1,3-Diphenylallyl)-4-methoxyaniline (3e)**<sup>27</sup>: light yellow oil; 77% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.47–7.24 (m, 11H), 6.78–6.75 (m, 2H), 6.67–6.61 (m, 3H), 6.41 (dd, *J* = 6.4, 16.4 Hz, 1H), 5.03 (d, *J* = 6.4 Hz, 1H), 3.92 (s, 1H), 3.74 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 55.7, 67.0, 114.7, 114.9, 126.4, 127.1, 127.4, 127.5, 128.5, 128.7, 130.8, 131.1, 136.6, 141.4, 142.3, 152.2; IR (neat): 3397, 2949, 2831, 1599, 1509, 1450, 1295, 1236, 1179, 1121, 1035, 968, 914, 819, 745, 697 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 315.

**(E)-N-(1,3-Diphenylallyl)-4-nitroaniline (3f)**: light yellow solid; 97% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.44–7.22 (m, 13H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 9.2 Hz, 2H),

6.38 (dd, *J* = 6.4, 15.6 Hz, 1H), 5.06 (d, *J* = 6.0 Hz, 1H), 4.17 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 67.0, 112.0, 126.1, 126.5, 127.0, 128.0, 128.1, 128.5, 128.6, 129.1, 132.2, 135.9, 138.4, 140.2, 152.0; IR (neat): 3375, 3028, 2916, 1595, 1499, 1470, 1301, 1184, 1109, 1027, 967, 908, 833, 798, 747, 696 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 330; HRMS (EI): *m/z* calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> (M<sup>+</sup>): 330.1368, Found 330.1371.

**(E)-N-(1,3-Diphenylallyl)-3,5-dimethylaniline (3g)**: light yellow oil; 81% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.49–7.26 (m, 11H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.48–6.41 (m, 2H), 6.34 (s, 2H), 5.13 (d, *J* = 6.4 Hz, 1H), 4.05 (s, 1H), 2.26 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.5, 60.5, 111.4, 119.7, 126.5, 127.2, 127.4, 127.5, 128.5, 128.7, 130.8, 130.9, 136.7, 138.8, 142.3, 147.4; IR (neat): 3405, 3025, 2915, 2856, 1599, 1509, 1493, 1449, 1336, 1183, 967, 822, 746, 693 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 313; HRMS (EI): *m/z* calcd for C<sub>23</sub>H<sub>23</sub>N (M<sup>+</sup>): 313.1830, Found 313.1827.

**(E)-N-(1,3-Diphenylallyl)-2-nitroaniline (3h)**: light yellow oil; 95% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.50 (d, *J* = 5.6 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.43–7.23 (m, 11H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.67–6.58 (m, 2H), 6.41 (dd, *J* = 6.4, 15.6 Hz, 1H), 5.31 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 67.0, 115.0, 115.9, 126.6, 126.7, 126.9, 127.9, 128.0, 128.6, 128.9, 129.1, 131.8, 132.4, 136.0, 140.4, 144.1; IR (neat): 3376, 3028, 2855, 1614, 1572, 1500, 1417, 1349, 1259, 1233, 1150, 1038, 966, 872, 740, 693 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 330; HRMS (EI): *m/z* calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> (M<sup>+</sup>): 330.1368, Found 330.1370.

**(E)-N-(1,3-Diphenylallyl)-3-(trifluoromethyl)aniline (3i)**: light yellow oil; 93% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.44–7.19 (m, 11H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J* = 5.6, 16.0 Hz, 1H), 5.11 (d, *J* = 6.0 Hz, 1H), 4.31 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 60.4, 110.1, 114.1, 116.2, 126.5, 127.1, 127.7, 127.8, 128.5, 128.9, 129.6, 129.8, 131.5, 136.4, 141.3, 147.2; IR (neat): 3412, 3027, 2972, 2916, 1614, 1511, 1340, 1163, 1118, 1067, 1028, 911, 865, 783, 744, 695 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 353; HRMS (EI): *m/z* calcd for C<sub>22</sub>H<sub>18</sub>F<sub>3</sub>N (M<sup>+</sup>): 353.1391, Found 353.1392.

**(E)-N-(1,3-Diphenylallyl)-2,4-difluoroaniline (3j)**: light yellow oil; 82% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.46–7.25 (m, 10H), 6.84–6.78 (m, 1H), 6.67–6.57 (m, 3H), 6.41 (dd, *J* = 6.0, 15.6 Hz, 1H), 5.06 (d, *J* = 6.0 Hz, 1H), 4.23 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 60.8, 103.3, 110.5, 113.4, 126.5, 127.0, 127.7, 127.8, 128.5, 128.9, 130.1, 131.3, 132.0, 132.1, 136.3, 141.4, 149.6, 152.0, 153.2; IR (neat): 3425, 3028, 1601, 1515, 1427, 1337, 1267, 1205, 1141, 1093, 962, 848, 796, 747, 697 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 321; HRMS (EI): *m/z* calcd for C<sub>21</sub>H<sub>17</sub>F<sub>2</sub>N (M<sup>+</sup>): 321.1329, Found 321.1327.

**(E)-1-(4-(1,3-Diphenylallylamino)phenyl)ethanone (3k)**: light yellow oil; 90% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.79 (d, *J* = 8.8 Hz, 2H), 7.43–7.24 (m, 11H), 6.63–6.58 (m, 3H), 6.38 (dd, *J* = 6.4, 16.0 Hz, 1H), 5.19 (s, 1H), 4.23 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 25.9, 67.0, 112.3, 126.5, 127.1, 127.8, 127.9, 128.5, 128.9, 129.3, 130.6, 131.7, 136.2, 140.9, 150.9, 196.3; IR (neat): 3344, 3027, 1656, 1593, 1524, 1488, 1356, 1275, 1179, 962, 911, 827, 743, 698 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* = 327; HRMS (EI): *m/z* calcd for C<sub>23</sub>H<sub>21</sub>NO (M<sup>+</sup>): 327.1623, Found 327.1627.

**(E)-N-(1,3-Diphenylallyl)quinolin-6-amine (3l):** light yellow oil; 88% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.62 (d,  $J$  = 4 Hz, 1H), 7.91 (d,  $J$  = 9.2 Hz, 1H), 7.85 (d,  $J$  = 8.4 Hz, 1H), 7.51–7.16 (m, 13H), 6.72–6.66 (m, 2H), 6.46 (dd,  $J$  = 6.0, 16.4 Hz, 1H), 5.24 (t,  $J$  = 4.8 Hz, 1H), 4.52 (d,  $J$  = 4.0 Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 67.0, 104.6, 121.2, 121.5, 126.5, 127.2, 127.7, 127.8, 128.5, 128.9, 129.8, 129.9, 130.2, 131.4, 133.9, 136.4, 141.4, 143.2, 144.9, 146.3; IR (neat): 3409, 3270, 3058, 3026, 1622, 1595, 1514, 1464, 1380, 1238, 1122, 967, 909, 829, 734, 697  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 336; HRMS (EI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2$  ( $\text{M}^+$ ): 336.1626, Found 336.1622.

**(E)-N-(1,3-Diphenylallyl)-4-phenylquinolin-6-amine (3m):** light yellow oil; 85% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.69 (d,  $J$  = 4.8 Hz, 1H), 8.06 (d,  $J$  = 8.8 Hz, 1H), 7.42–7.17 (m, 18H), 6.85 (s, 1H), 6.55 (d,  $J$  = 16.0 Hz, 1H), 6.34 (dd,  $J$  = 6.4, 16.0 Hz, 1H), 5.00 (d,  $J$  = 6.4 Hz, 1H), 4.63 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 67.0, 103.4, 121.4, 121.5, 126.5, 127.1, 127.6, 127.7, 127.9, 128.1, 128.4, 128.5, 128.8, 129.2, 130.0, 130.2, 131.7, 136.4, 138.4, 141.3, 143.1, 144.9, 145.5, 146.3; IR (neat): 3402, 3258, 3029, 1612, 1599, 1508, 1450, 1375, 1248, 1129, 968, 821, 738, 696  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 412; HRMS (EI):  $m/z$  calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_2$  ( $\text{M}^+$ ): 412.1939, Found 412.1941.

**(E)-N-(1,3-Diphenylallyl)pyrimidin-2-amine (3n):** light yellow oil; 74% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.26 (d,  $J$  = 4.0 Hz, 2H), 7.46–7.22 (m, 10H), 6.63 (d,  $J$  = 15.6 Hz, 1H), 6.54–6.42 (m, 2H), 6.09 (d,  $J$  = 8.0 Hz, 1H), 5.98–5.94 (m, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 56.4, 110.9, 126.4, 127.1, 127.4, 127.5, 128.4, 128.6, 129.9, 130.6, 136.6, 141.6, 158.0, 161.5; IR (neat): 3412, 3251, 3021, 1599, 1495, 1465, 1368, 1250, 1122, 969, 817, 735, 697  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 287; HRMS (EI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{17}\text{N}_3$  ( $\text{M}^+$ ): 287.1422, Found 287.1421.

**(E)-2-Chloro-N-(1,3-diphenylallyl)pyridin-4-amine (3o):** light yellow oil; 89% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.92 (d,  $J$  = 6.0 Hz, 1H), 7.41–7.24 (m, 10H), 6.57 (d,  $J$  = 15.6 Hz, 1H), 6.48 (s, 1H), 6.40–6.29 (m, 2H), 5.13 (t,  $J$  = 5.6 Hz, 1H), 4.47 (d,  $J$  = 4.4 Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 67.0, 107.1, 107.8, 126.5, 127.0, 128.0, 128.1, 128.3, 128.6, 129.1, 132.1, 135.9, 140.0, 149.3, 152.1, 154.2; IR (neat): 3417, 3247, 3016, 1601, 1587, 1501, 1447, 1382, 1237, 1121, 967, 820, 736, 696  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 320; HRMS (EI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{17}\text{ClN}_2$  ( $\text{M}^+$ ): 320.1080, Found 320.1081.

**(E)-N-(1,3-bis(4-Dromophenyl)allyl)-4-nitroaniline (3p):** light yellow oil; 81% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.04 (d,  $J$  = 9.2 Hz, 2H), 7.39–7.25 (m, 9H), 6.57–6.49 (m, 3H), 6.32 (dd,  $J$  = 6.4, 16.0 Hz, 1H), 5.18 (t,  $J$  = 6.0 Hz, 1H), 4.91 (d,  $J$  = 4.8 Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 67.0, 112.1, 126.1, 127.7, 128.4, 128.7, 128.8, 129.3, 131.5, 133.9, 134.0, 134.2, 138.5, 138.7, 151.7; IR (neat): 3367, 2973, 1595, 1493, 1303, 1182, 1107, 1010, 968, 906, 828, 729, 696  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 486; HRMS (EI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_2$  ( $\text{M}^+$ ): 485.9579, Found 485.9581.

**(E)-N-(3-(4-Dromophenyl)-1-phenylallyl)aniline (3q) and (E)-N-(1-(4-bromo-phen-yl)-3-phenylallyl)aniline (3r):** light yellow oil; 75% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.47–7.12 (m, 13H), 6.77–6.73 (m, 1H), 6.68–6.59 (m, 3H), 6.40–6.35 (m, 1H), 5.12–5.08 (m, 1H), 4.12 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 60.0, 60.5, 113.5, 113.6, 117.7, 117.9,

126.5, 127.2, 127.6, 127.7, 127.8, 128.4, 128.5, 128.6, 128.8, 128.9, 129.1, 129.2, 129.7, 130.1, 131.3, 131.6, 133.1, 133.2, 135.1, 136.3, 140.5, 141.8, 146.8, 147.1; IR (neat): 3411, 3026, 2926, 1600, 1497, 1450, 1427, 1404, 1314, 1260, 1091, 1012, 968, 908, 823, 748, 695  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 363; HRMS (EI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{18}\text{BrN}$  ( $\text{M}^+$ ): 363.0623, Found 363.0625.

**(E)-N-(3-(2-Chlorophenyl)-1-phenylallyl)benzenamine (3s) and (E)-N-(1-(2-chlorophenyl)-3-phenylallyl)benzenamine (3t):** light yellow oil; 77% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.52–7.11 (m, 29H), 6.71–6.56 (m, 8.5H), 6.38–6.33 (m, 2.5H), 5.53 (br, 1.5H), 5.12 (d,  $J$  = 6.0 Hz, 1H), 4.19–4.13 (br, 2.5H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 56.9, 60.8, 113.5, 113.7, 117.8, 117.9, 126.6, 126.8, 127.0, 127.2, 127.3, 127.5, 127.6, 127.8, 128.2, 128.6, 128.7, 128.9, 129.1, 129.2, 129.7, 129.9, 131.9, 133.2, 133.4, 133.7, 135.0, 136.5, 139.2, 141.8; MS (70 eV, EI)  $m/z$  = 319; HRMS (EI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{18}\text{ClN}$  ( $\text{M}^+$ ): 319.1128, Found 319.1126.

**(E)-N-(1-Phenyl-3-*o*-tolylallyl)benzenamine (3u) and (E)-N-(3-phenyl-1-*o*-tolylallyl)benzenamine (3v):** light yellow oil; 69% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.49–7.31 (m, 11H), 7.26–7.16 (m, 11H), 6.88 (d,  $J$  = 15.6 Hz, 1H), 6.74–6.68 (m, 4H), 6.63–6.60 (m, 3H), 6.44 (dd,  $J$  = 15.6, 5.6 Hz, 1H), 6.28 (dd,  $J$  = 16.0, 6.4 Hz, 1H), 5.27 (d,  $J$  = 5.6 Hz, 1H), 5.14 (d,  $J$  = 6.4 Hz, 1H), 4.13–4.08 (br, 2H), 2.44 (s, 3H), 2.30 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 19.3, 19.7, 56.9, 60.9, 113.2, 113.7, 117.6, 117.7, 125.8, 126.0, 126.4, 126.5, 126.7, 127.2, 127.4, 127.51, 127.56, 127.6, 128.6, 128.8, 129.1, 129.2, 129.3, 129.8, 130.2, 130.8, 131.3, 132.0, 135.6, 135.9, 136.0, 136.7, 139.8, 142.2, 147.2, 147.4; MS (70 eV, EI)  $m/z$  = 299; HRMS (EI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{21}\text{N}$  ( $\text{M}^+$ ): 299.1674, Found 299.1675.

**(E)-N-(3-(4-Chlorophenyl)-1-phenylallyl)benzenamine (3w) and (E)-N-(1-(4-chlorophenyl)-3-phenylallyl)benzenamine (3x):** light yellow oil; 72% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46–7.23 (m, 8H), 7.16–7.12 (m, 2H), 6.96–6.87 (m, 1H), 6.73–6.71 (m, 1H), 6.63–6.55 (m, 3H), 6.39–6.31 (m, 1H), 5.06 (dd,  $J$  = 10.0, 4.8 Hz, 1H), 4.09 (br, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 60.1, 60.6, 113.5, 113.6, 117.8, 118.0, 120.7, 126.5, 127.2, 127.5, 127.6, 127.7, 127.9, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 129.1, 129.2, 129.8, 130.1, 130.7, 131.4, 131.6, 133.2, 133.3, 135.1, 136.4, 140.6, 141.8, 146.9, 147.1; MS (70 eV, EI)  $m/z$  = 319; HRMS (EI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{18}\text{ClN}$  ( $\text{M}^+$ ): 319.1128, Found 319.1129.

***N,N*-bis((E)-1,3-Diphenylallyl)aniline (4a):** light yellow oil; 52% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.45–7.20 (m, 22H), 7.01 (d,  $J$  = 7.2 Hz, 2H), 6.66–6.58 (m, 3H), 6.42–6.29 (m, 2H), 5.06 (d,  $J$  = 6.4 Hz, 1H), 4.77 (d,  $J$  = 7.6 Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 53.3, 60.8, 113.6, 126.1, 126.2, 126.4, 127.0, 127.1, 127.4, 127.6, 128.3, 128.4, 128.5, 128.6, 128.7, 129.2, 130.7, 130.8, 131.0, 132.6, 133.2, 136.6, 137.4, 142.1, 144.0, 145.7; IR (neat): 3409, 3012, 2825, 1599, 1450, 1301, 1250, 1159, 969, 812, 745, 696  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 477; HRMS (EI):  $m/z$  calcd for  $\text{C}_{36}\text{H}_{31}\text{N}$  ( $\text{M}^+$ ): 477.2457, Found 477.2453.

**(E)-N-(1,3-Diphenylallyl)-*N*-methylaniline (6a):** light yellow oil; 81% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.44–7.25 (m, 13H), 6.88 (d,  $J$  = 8.4 Hz, 2H), 6.77 (t,  $J$  = 7.6 Hz, 1H), 6.57 (d,  $J$  = 4.8 Hz, 2H), 5.68 (d,  $J$  = 4.0 Hz, 1H), 2.84

(s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 33.8, 64.6, 113.2, 116.9, 126.5, 127.2, 127.4, 127.6, 127.8, 128.4, 128.5, 129.1, 132.7, 136.7, 140.6, 150.1; IR (neat): 3412, 3011, 2912, 1612, 1479, 1441, 1313, 1249, 1150, 1122, 967, 812, 745, 697  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 299; HRMS (EI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{21}\text{N}$  ( $\text{M}^+$ ): 299.1674, Found, 299.1672.

**(E)-N-(1,3-Diphenylallyl)-N-phenylaniline (6b)**: light yellow oil; 87% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.44 (d,  $J$  = 7.2 Hz, 2H), 7.31–7.16 (m, 14H), 6.94–6.88 (m, 4H), 6.58 (d,  $J$  = 15.6 Hz, 1H), 6.43 (dd,  $J$  = 8.4, 15.6 Hz, 1H), 5.74 (d,  $J$  = 7.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 66.9, 117.7, 122.7, 122.9, 126.4, 127.0, 127.4, 127.5, 128.3, 128.4, 128.9, 129.2, 132.7, 141.2, 147.1; IR (neat): 3030, 2924, 1595, 1497, 1426, 1313, 1026, 969, 911, 748, 696  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 361; HRMS (EI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{23}\text{N}$  ( $\text{M}^+$ ): 361.1830, Found 361.1831.

**(E)-4-Chloro-N-(1,3-diphenylallyl)-N-phenylaniline (6c)**: light yellow oil; 92% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.43–6.96 (m, 18H), 6.78 (d,  $J$  = 8.8 Hz, 2H), 6.58 (d,  $J$  = 15.6 Hz, 1H), 6.42 (dd,  $J$  = 7.6, 16.0 Hz, 1H), 5.71 (d,  $J$  = 7.2 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 67.0, 118.0, 118.7, 122.6, 122.9, 124.3, 125.9, 126.5, 127.2, 127.4, 127.7, 128.5, 128.8, 129.2, 133.0, 136.6, 140.8, 145.9, 146.7; IR (neat): 3029, 2928, 2360, 1591, 1491, 1450, 1309, 1252, 1093, 969, 816, 747, 697  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 395; HRMS (EI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{22}\text{ClN}$  ( $\text{M}^+$ ): 395.1441, Found 395.1444.

**(E)-N-(1,3-Diphenylallyl)-4-methyl-N-phenylaniline (6d)**: light yellow oil; 82% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.47–6.80 (m, 19H), 6.59 (d,  $J$  = 15.6 Hz, 1H), 6.45 (dd,  $J$  = 8.0, 16.0 Hz, 1H), 5.72 (d,  $J$  = 8.4 Hz, 1H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.7, 67.0, 118.5, 119.8, 119.9, 125.6, 126.4, 127.4, 127.5, 128.3, 128.4, 128.5, 128.7, 129.7, 130.0, 132.6, 136.8, 141.4, 144.0, 147.9; IR (neat): 3028, 2922, 1694, 1600, 1508, 1456, 1383, 1313, 1237, 1026, 970, 874, 814, 747, 698  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 375; HRMS (EI):  $m/z$  calcd for  $\text{C}_{28}\text{H}_{25}\text{N}$  ( $\text{M}^+$ ): 375.1987, Found 375.1984.

**(E)-N-(1,3-Diphenylallyl)-4-methoxy-N-phenylaniline (6e)**: light yellow oil; 77% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.48 (d,  $J$  = 8.0 Hz, 1H), 7.36–7.24 (m, 10H), 7.17–7.10 (m, 4H), 6.88 (d,  $J$  = 8.8 Hz, 2H), 6.78–6.70 (m, 3H), 6.63 (d,  $J$  = 15.6 Hz, 1H), 6.45 (dd,  $J$  = 8.4, 16.0 Hz, 1H), 5.74 (d,  $J$  = 8.0 Hz, 1H), 3.82 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.3, 66.9, 114.5, 116.4, 117.9, 126.5, 127.0, 127.5, 128.4, 128.5, 128.6, 128.7, 130.3, 132.4, 136.8, 138.5, 141.4, 148.8, 157.1; IR (neat): 3028, 1694, 1604, 1513, 1465, 1395, 1245, 1179, 1035, 836, 747, 698  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 391; HRMS (EI):  $m/z$  calcd for  $\text{C}_{28}\text{H}_{25}\text{NO}$  ( $\text{M}^+$ ): 391.1936, Found 391.1939.

**(E)-N-(1,3-Diphenylallyl)-4-methyl-N-p-tolylaniline (6f)**: light yellow oil; 80% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.50–7.43 (m, 2H), 7.36–7.23 (m, 9H), 7.02 (d,  $J$  = 8.4 Hz, 4H), 6.86 (d,  $J$  = 8.4 Hz, 4H), 6.61 (d,  $J$  = 16.0 Hz, 1H), 6.49 (dd,  $J$  = 7.6, 15.6 Hz, 1H), 2.27 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.6, 67.1, 122.8, 124.2, 126.5, 126.9, 127.4, 127.5, 128.4, 128.5, 129.5, 130.9, 132.5, 136.9, 141.6, 145.0; IR (neat): 3026, 2919, 1610, 1510, 1450, 1227, 1109, 1028, 968, 807, 749, 697  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 389; HRMS (EI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{27}\text{N}$  ( $\text{M}^+$ ): 389.2143, Found 389.2144.

**(E)-N-(1,3-Diphenylallyl)-4-methoxy-N-p-tolylaniline (6g)**: light yellow oil; 72% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  =

7.45 (d,  $J$  = 7.6 Hz, 2H), 7.33–7.21 (m, 8H), 7.02 (d,  $J$  = 8.8 Hz, 2H), 6.94 (d,  $J$  = 8.4 Hz, 2H), 6.82 (d,  $J$  = 8.4 Hz, 2H), 6.66 (d,  $J$  = 8.0 Hz, 2H), 6.58 (d,  $J$  = 16.0 Hz, 1H), 6.43 (dd,  $J$  = 8.0, 16.0 Hz, 1H), 5.67 (d,  $J$  = 8.0 Hz, 1H), 3.78 (s, 3H), 2.23 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.3, 55.3, 67.1, 114.4, 118.1, 126.4, 126.9, 127.5, 128.1, 128.3, 128.4, 128.7, 129.3, 132.3, 136.9, 139.5, 141.6, 146.3, 156.3; IR (neat): 3027, 2920, 1613, 1507, 1447, 1242, 1180, 1033, 968, 809, 750, 698  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 405; HRMS (EI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{27}\text{NO}$  ( $\text{M}^+$ ): 405.2093, Found 405.2090.

**(E)-N-(1,3-Diphenylallyl)-4-methoxy-N-(4-methoxyphenyl)aniline (6h)**: light yellow oil; 69% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46 (d,  $J$  = 8.0 Hz, 2H), 7.33–7.21 (m, 8H), 6.86 (d,  $J$  = 8.8 Hz, 4H), 6.76 (d,  $J$  = 8.8 Hz, 4H), 6.57 (d,  $J$  = 15.6 Hz, 1H), 6.42 (dd,  $J$  = 7.6, 15.6 Hz, 1H), 5.62 (d,  $J$  = 8.0 Hz, 1H), 3.75 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.4, 67.0, 114.2, 124.1, 126.4, 126.9, 127.5, 127.6, 128.4, 128.5, 128.9, 132.2, 136.9, 141.4, 141.8, 154.5; IR (neat): 3026, 2950, 2833, 1604, 1504, 1454, 1239, 1178, 1036, 969, 822, 751, 698  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 421; HRMS (EI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{27}\text{NO}_2$  ( $\text{M}^+$ ): 421.2042, Found 421.2037.

**(E)-N-(3-(4-Bromophenyl)-1-phenylallyl)-N-methylaniline (6i) and (E)-N-(1-(4-bromophenyl)-3-phenylallyl)-N-methylaniline (6j)**: light yellow oil; 65% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.47–7.21 (m, 12H), 6.92–6.88 (m, 2H), 6.82–6.80 (m, 1H), 6.59–6.53 (m, 2H), 5.70–5.63 (m, 1H), 2.86–2.85 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 33.7, 33.8, 64.3, 64.6, 113.3, 113.4, 117.0, 117.3, 126.5, 126.9, 127.3, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 129.1, 129.2, 131.5, 133.0, 133.2, 135.2, 136.5, 139.2, 140.4, 149.9, 150.0; IR (neat): 3417, 3026, 2927, 1605, 1499, 1447, 1412, 1397, 1313, 1250, 1095, 1015, 969, 912, 821, 749, 695  $\text{cm}^{-1}$ ; MS (70 eV, EI)  $m/z$  = 377; HRMS (EI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{20}\text{BrN}$  ( $\text{M}^+$ ): 377.0779, Found 377.0776.

**(E)-N-(1, 3-Diphenylallyl)benzamide (6k) $^{13c}$** : light yellow solid; m.p. 150–152 °C; 90% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.82 (d,  $J$  = 7.2 Hz, 2H), 7.52–7.21 (m, 13H), 6.43 (dd,  $J$  = 6.0, 16.0 Hz, 1H), 6.02 (t,  $J$  = 6.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.2, 126.5, 127.0, 127.2, 127.7, 127.8, 128.51, 128.54, 128.7, 128.8, 131.57, 131.69, 134.3, 136.3, 140.8, 166.4; MS (70 eV, EI)  $m/z$  = 313.

**(E)-N-(1, 3-Diphenylallyl)acrylamide (6l)**: light yellow solid; m.p.: 121–123 °C; 96% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.37–7.22 (m, 10H), 6.56 (d,  $J$  = 16.4 Hz, 1H), 6.40–6.32 (m, 2H), 6.16 (dd,  $J$  = 6.2, 16.6 Hz, 1H), 6.07 (bs, 1H), 5.90 (t,  $J$  = 7.0 Hz, 1H), 5.68 (d,  $J$  = 10.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 54.8, 126.5, 127.0, 127.1, 127.65, 127.7, 128.5, 128.6, 128.7, 130.6, 131.5, 136.3, 140.6, 164.6; MS (70 eV, EI)  $m/z$  = 263; HRMS (EI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{17}\text{NO}$  ( $\text{M}^+$ ): 263.1310, Found 263.1312.

**(E)-1-N-(1, 3-Diphenylallyl)pyrrolidin-2-one (6m)**: light yellow oil; 80% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.45–7.26 (m, 10H), 6.64 (d,  $J$  = 16.0 Hz, 1H), 6.47 (dd,  $J$  = 6.8, 16.0 Hz, 1H), 6.11 (d,  $J$  = 6.4 Hz, 1H), 3.47–3.41 (m, 1H), 3.17–3.11 (m, 1H), 2.56–2.42 (m, 2H), 2.12–1.94 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 18.1, 31.1, 43.4, 56.2, 125.4, 126.5, 127.66, 127.7, 127.9, 128.60, 128.65, 133.4, 136.4, 138.7, 174.7; MS (70 eV, EI)  $m/z$  = 277; HRMS (EI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{19}\text{NO}$  ( $\text{M}^+$ ): 277.1467, Found 277.1466.

(*E*)-*N*-(1, 3-Diphenylallyl)-4-methylbenzenesulfonamide (**6n**)<sup>13c</sup>: light yellow solid; m.p.: 133–135 °C; 97% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.66–7.64 (m, 2H), 7.27–7.12 (m, 12H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.07 (dd, *J* = 6.6, 15.8 Hz, 1H), 5.15–5.04 (m, 2H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.3, 59.6, 126.4, 126.9, 127.2, 127.7, 127.8, 128.0, 128.3, 128.6, 129.3, 132.0, 135.9, 137.6, 139.5, 143.1; MS (70 eV, EI) *m/z* = 363.

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## References

- For reviews, see: (a) R. B. Cheikh, R. Chaabouni, A. Laurent, P. Mison and A. Nafti, *Synthesis*, 1983, 685; (b) M. Johannsen and K. A. Jørgensen, *Chem. Rev.*, 1998, **98**, 1689; (c) B. M. Trost and M. L. Crawley, *Chem. Rev.*, 2003, **103**, 2921.
- (a) G. Petranyi, N. S. Ryder and A. Stütz, *Science*, 1984, **224**, 1239; (b) H. Kanno and R. J. K. Taylor, *Tetrahedron Lett.*, 2002, **43**, 7337.
- (a) J. J. Olesen, *J. Neurol.*, 1991, **238**, S23; (b) M. T. Marín, M. V. Margarit and G. E. Salcedo, *Farmacologia*, 2002, **57**, 723.
- For reviews, see: (a) S. Akutagawa and K. Tani, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, Wiley-VCH, New York, 2nd edn, 2000; (b) *Asymmetric Catalysis in Organic Synthesis*, ed. R. Noyori, Wiley-VCH, New York, 1994, ch. 3, p. 95.
- For reviews, see: (a) *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, Germany, Vols. 1–3, 2003; (b) K. C. Nicolaou, P. G. Bulger and D. Sarlar, *Angew. Chem., Int. Ed.*, 2005, **44**, 4490.
- (a) H. Kodama, T. Taiji, T. Ohta and I. Furukawa, *Tetrahedron: Asymmetry*, 2000, **11**, 4009; (b) O. Pàmies and M. Diéguez, *Chem.–Eur. J.*, 2008, **14**, 944.
- For review, see: (a) J. Muzart, *Tetrahedron*, 2005, **61**, 4179; (b) J. Muzart, *Eur. J. Org. Chem.*, 2007, 3077; (c) Y. Tamaru, *Eur. J. Org. Chem.*, 2005, 2647.
- (a) F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami and M. Yoshifuji, *J. Am. Chem. Soc.*, 2002, **124**, 10968; (b) F. Ozawa, T. Ishiyama, S. Yamamoto, S. Kawagishi, H. Murakami and M. Yoshifuji, *Organometallics*, 2004, **23**, 1698.
- Y. Kayaki, T. Koda and T. Ikariya, *J. Org. Chem.*, 2004, **69**, 2595.
- H. Kinoshita, H. Shinokubo and K. Oshima, *Org. Lett.*, 2004, **6**, 4085.
- (a) O. Piechaczyk, M. Doux, L. Ricard and P. Le Floch, *Organometallics*, 2005, **24**, 1204; (b) C. Thoumazet, H. Grützmacher, B. Deschamps, L. Ricard and P. Le Floch, *Eur. J. Inorg. Chem.*, 2006, 3911; (c) O. Piechaczyk, C. Thoumazet, Y. Jean and P. Le Floch, *J. Am. Chem. Soc.*, 2006, **128**, 14306; (d) G. Mora, B. Deschamps, S. Van Zutphen, X. F. Le Goff, L. Ricard and P. Le Floch, *Organometallics*, 2007, **26**, 1846.
- I. Usui, S. Schmidt, M. Keller and B. Breit, *Org. Lett.*, 2008, **10**, 1207.
- Lewis acid-catalyzed direct substitution of allylic, propargylic, and benzylic alcohols with electron-deficient nitrogen nucleophiles were reported. For representative examples, see: (a) Y. Nishibayashi, M. D. Milton, Y. Inada, M. Yoshikawa, I. Wakiji, M. Hidai and S. Uemura, *Chem.–Eur. J.*, 2005, **11**, 1433; (b) V. Terrasson, S. Marque, M. Georgy, J.-M. Campagne and D. Prim, *Adv. Synth. Catal.*, 2006, **348**, 2063; (c) H. Qin, N. Yamagiwa, S. Matsunaga and M. Shibasaki, *Angew. Chem., Int. Ed.*, 2007, **46**, 409; (d) S. Guo, F. Song and Y. Liu, *Synlett*, 2007, 964; (e) C. R. Reddy, P. P. Madhavi and A. S. Reddy, *Tetrahedron Lett.*, 2007, **48**, 7169; (f) B. Sreedhar, P. S. Reddy, M. A. Reddy, B. Neelima and R. Arundhathi, *Tetrahedron Lett.*, 2007, **48**, 8174; (g) U. Jana, S. Maiti and S. Biswas, *Tetrahedron Lett.*, 2008, **49**, 858; (h) G.-W. Wang, Y.-B. Shen and X.-L. Wu, *Eur. J. Org. Chem.*, 2008, 4367; (i) W. Huang, Q.-S. Shen, J.-L. Wang and X.-G. Zhou, *Chin. J. Chem.*, 2008, **26**, 729.
- T. Ohshima, Y. Miyamoto, J. Ipposhi, Y. Nakahara, M. Utsunomiya and K. Mashima, *J. Am. Chem. Soc.*, 2009, **131**, 14317.
- (a) B. M. Trost, *Acc. Chem. Res.*, 2002, **35**, 695; (b) B. M. Trost, *Angew. Chem.*, 1995, **107**, 285, (*Angew. Chem., Int. Ed.*, 1995, **34**, 259); (c) B. M. Trost, *Science*, 1991, **254**, 1471.
- N. Winterton, *Green Chem.*, 2001, **3**, G73.
- For recent selected examples of the C–H transformation to C–N, see: (a) C. G. Espino and J. D. Bois, *Angew. Chem., Int. Ed.*, 2001, **40**, 598; (b) C. G. Espino, P. M. Wehn, J. Chow and J. D. Bois, *J. Am. Chem. Soc.*, 2001, **123**, 6935; (c) Y. Cui and C. He, *Angew. Chem., Int. Ed.*, 2004, **43**, 4210; (d) P. Tsang, N. Zheng and S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 14560; (e) G. Pelletier and D. A. Powell, *Org. Lett.*, 2006, **8**, 6031; (f) Y. Zhang, H. Fu, Y. Jiang and Y. Zhao, *Org. Lett.*, 2007, **9**, 3813; (g) K. J. Fraunhoffer and M. C. White, *J. Am. Chem. Soc.*, 2007, **129**, 7274; (h) Z. Wang, Y. Zhang, H. Fu, Y. Jiang and Y. Zhao, *Org. Lett.*, 2008, **10**, 1863; (i) H. Du, B. Zhao and Y. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 8590; (j) S. A. Reed and M. C. White, *J. Am. Chem. Soc.*, 2008, **130**, 3316; (k) G. Liu, G. Yin and L. Wu, *Angew. Chem., Int. Ed.*, 2008, **47**, 4733; (l) T. S. Mei, X. Wang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 10806; (m) L. Wu, S. Qiu and G. Liu, *Org. Lett.*, 2009, **11**, 2707; (n) Y. Shimizu, Y. Obora and Y. Ishii, *Org. Lett.*, 2010, **12**, 1372; (o) H. Zhao, M. Wang, W. Su and M. Hong, *Adv. Synth. Catal.*, 2010, **352**, 1301; (p) Q. Shuai, G. Deng, Z. Chua, D. S. Bohle and C.-J. Li, *Adv. Synth. Catal.*, 2010, **352**, 632; (q) G. Yin, Y. Wu and G. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 11978; (r) G. W. Wang, T. T. Yuan and D. D. Li, *Angew. Chem., Int. Ed.*, 2011, **50**, 1380; (s) M. Miyasaka, K. Hirano, T. Satoh, R. Kowalczyk, C. Bolm and M. Miura, *Org. Lett.*, 2011, **13**, 359; (t) B. J. Stokes and T. G. Driver, *Eur. J. Org. Chem.*, 2011, 4071; (u) S. H. Cho, J. Yoon and S. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 5996; (v) E. J. Yoo, S. Ma, T. S. Mei, K. Chan and J.-Q. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 7652.
- A. Armstrong and J. C. Collins, *Angew. Chem., Int. Ed.*, 2010, **49**, 2282.
- C. Wan, J. Zhang, S. Wang, J. Fan and Z. Wang, *Org. Lett.*, 2010, **12**, 2338.
- (a) D. Cheng and W. L. Bao, *J. Org. Chem.*, 2008, **73**, 6881; (b) D. Cheng and W. L. Bao, *Adv. Synth. Catal.*, 2008, **350**, 1263; (c) Y. Li and W. L. Bao, *Adv. Synth. Catal.*, 2009, **351**, 865; (d) J. Jin, Y. Li, Z. J. Wang, W. X. Qian and W. L. Bao, *Eur. J. Org. Chem.*, 2010, 1235.
- H. J. Mo and W. L. Bao, *Adv. Synth. Catal.*, 2009, **351**, 2845.
- (a) P. P. Fu and R. G. Harvey, *Chem. Rev.*, 1978, **78**, 317; (b) Y. Zhang and C.-J. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4242; (c) B. P. Ying, B. G. Trogden, D. T. Kolhman, S. X. Liang and Y. C. Xu, *Org. Lett.*, 2004, **6**, 1523; (d) P. C. Montecocchi and M. L. Navacchia, *J. Org. Chem.*, 1998, **63**, 8035; (e) B. A. Snider, *Chem. Rev.*, 1996, **96**, 339.
- (a) A. Streitwieser, M. J. Kaufman, D. A. Bors, C. A. MacArthur, J. T. Murphy and F. Guibe, *Arkivoc*, 2005, **6**, 200; (b) J. L. Fabre, M. Julia, B. Mansour and L. Saussine, *J. Organomet. Chem.*, 1979, **177**, 221.
- H. Zhang, Q. Cai and D. Ma, *J. Org. Chem.*, 2005, **70**, 5164.
- T. Ohshima, Y. Miyamoto, J. Ipposhi, Y. Nakahara, M. Utsunomiya and K. Mashima, *J. Am. Chem. Soc.*, 2009, **131**, 14317.
- X. Giner, P. Trillo and C. Nájera, *J. Organomet. Chem.*, 2011, **696**, 357.
- C. Denhez, S. Médégan, F. Hélon, J.-L. Namy, J.-L. Vasse and J. Szymoniak, *Org. Lett.*, 2006, **8**, 2945.