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Allylic Amination of Internal Alkynes with Aromatic and Aliphatic Amines Using Polymer-Supported Triphenylphosphane–Palladium Complex as a Heterogeneous and Recyclable Catalyst

Yogesh S. Wagh,[a] Pawan J. Tambade,[a] Dinesh N. Sawant,[a] and Bhalchandra M. Bhanage*[a]

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A facile and novel protocol for the allylic amination of internal alkynes with amines by using a polymer-supported triphenylphosphane–palladium complex [PS–TPP–Pd] as a highly active heterogeneous reusable catalyst was developed. The catalyst exhibited remarkable activity and is reusable over five consecutive cycles. The protocol was applicable for a variety of hindered and functionalized aromatic/aliphatic amines and afforded the desired allylic products in good to excellent yield.

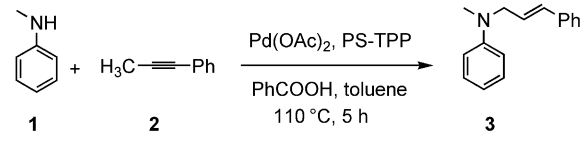
Introduction

The synthesis of allylamines is important due to their wide applications as intermediates in organic synthesis,[1] biological properties,[2] and their existence in several natural products.[3] One of the trustworthy routes for the synthesis of this class of compounds involves allylic substitution of allylic alcohol derivatives such as acetates, carbonates, and halides in the presence of Pd^0 catalysts.[4,5] Yamamoto and co-workers[6] have reported a new methodology for the synthesis of allylamines through hydroamination of internal alkynes by using a homogeneous Pd^0/carboxylic acid catalytic system. As products of this reaction were obtained through formal addition of pronucleophiles to alkynes, no waste was produced after completion of the reaction; moreover, the reaction proceeds without addition of any base. However, the use of a homogeneous palladium complex for allylic amination produces palladium-based waste products in the reaction and lacks catalyst recyclability. The loss of palladium catalyst, even at the ppm level, is not desirable due to its high cost and environmental effects. The most probable way to develop an atom economic process that can minimize the loss of expensive palladium is to employ a heterogeneous catalyst for this transformation. Therefore, the search for a heterogeneous and reusable catalyst that could efficiently catalyze the hydroamination of internal alkynes is the subject of the present work.

Considering drawbacks of previously reported methods, we employed polymer-supported triphenylphosphane–palladium complex [PS–TPP–Pd] as a heterogeneous and recyclable catalyst for the allylic amination of internal alkynes. The polymer-supported Pd catalyst has been used earlier for various chemical reactions.[7a–7g] However, to the best of our knowledge, such a type of catalyst has not yet been explored for the allylic amination reaction. The excellent yields of desired allylic amines were obtained by using 10 mol-% of catalyst under optimized reaction conditions.

Results and Discussion

To develop a suitable protocol for the allylic amination reactions, initially the reaction of 1-phenyl-1-propyne (**2**) with *N*-methylaniline (**1**) in the presence of PS–TPP–Pd was chosen as a model reaction (Scheme 1), and the influence of various reaction parameters such as catalyst concentration, temperature, and time were studied (Table 1, Entries 1–10).



Scheme 1. Palladium-catalyzed allylation of *N*-methylaniline with 1-phenyl-1-propyne.

In the case of transition-metal-catalyzed reactions, the amount of catalyst employed proves to be an important feature, and considering such, efforts were made to determine the optimum concentration of the catalyst (Table 1, Entries 1–3). Various catalyst loadings were used ranging from

[a] Department of Chemistry, Institute of Chemical Technology (Autonomous),
N. Parekh Marg, Matunga, Mumbai 400019, India
Fax: +91-2224145614
E-mail: bhalchandra_bhanage@yahoo.com

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Table 1. Effect of reaction parameters on the allylic amination of 1-phenyl-1-propyne with *N*-methylaniline.[a]

Entry	Catalyst conc. [mol-%]	Temp. [°C]	Time [h]	Yield [%][b]
	Effect of catalyst concentration			
1	0.05	110	5	85
2	0.10	110	5	94
3	0.15	110	5	94
	Effect of temperature			
4	0.10	90	5	82
5	0.10	100	5	90
6	0.10	110	5	94
7	0.10	120	5	94
	Effect of time			
8	0.10	110	4	84
9	0.10	110	5	94
10	0.10	110	6	94
11[c]	0.10	110	5	61

[a] Reaction conditions: PS–TPP [4 equiv. to $Pd(OAc)_2$], 1-phenyl-1-propyne (1 mmol), *N*-methylaniline (1 mmol), PhCOOH (10 mol-%), toluene (4 mL). [b] GC yield. [c] Without benzoic acid.

5 to 15 mol-%. Initially, the reaction was carried out by using 5 mol-% of the catalyst, which provided desired product **3** in 85% yield. An increase in the catalyst concentration to 10 mol-% resulted in an increase in the yield of **3** up to 94% (Table 1, Entry 2). Further increase in the amount of catalyst had no profound effect on the yield of the desired product (Table 1, Entry 3).

Also, the reaction was carried out at different temperatures ranging from 90 to 120 °C (Table 1, Entries 4–7). It was observed that at 90 °C, the yield of the product was very low, and with an increase in the temperature to 110 °C, the yield of **3** increased to 94%. However, a further increase in temperature did not show any significant enhancement in the yield (Table 1, Entry 7). The influence of time on the reaction outcome was also studied (Table 1, Entries 8–10), reflecting 5 h to be sufficient under the present reaction conditions (Table 1, Entry 9). We also checked the role of benzoic acid in our catalytic system. In the presence of benzoic acid, the yield of the desired product was optimum, that is, 94%; however, in the absence of benzoic acid, the yield obtained was low (Table 1, Entry 11). We think that the presence of benzoic acid plays the role of cocatalyst, which is to be in agreement with the observation made by Yamamoto and co-workers.[6d]

The effect of various polar and nonpolar solvents on allylic amination was studied to find out the optimum solvent for the reaction (Table 2, Entries 1–7). Polar solvents such as acetonitrile and DMF provided lower yields of the products (Table 2, Entries 1 and 3). However, 1,4-dioxane offered a moderate yield of the product (Table 2, Entry 2). Nonpolar solvents like toluene, xylene, cyclohexane, and hexane were screened, and it was observed that the reaction did not proceed in the case of low-boiling solvents such as cyclohexane. In the case of *n*-hexane, the reaction gave only 10% yield of the desired product. High-boiling nonpolar solvents such as toluene and xylene produced good to excellent yields of the products. Among all the solvents screened, toluene was found to provide an excellent yield of the product (94%; Table 2, Entry 6).

Table 2. Effect of solvent on the allylic amination of 1-phenyl-1-propyne with *N*-methylaniline.[a]

Entry	Solvent	Temp. [°C]	Yield [%][b]
1	acetonitrile	82	06
2	1,4-dioxane	100	52
3	DMF	140	05
4	cyclohexane	80	–
5	hexane	70	10
6	toluene	110	94
7	xylene	140	70

[a] Reaction conditions: $Pd(OAc)_2$ (10 mol-%), PS–TPP (40 mol-%), 1-phenyl-1-propyne (1 mmol), *N*-methylaniline (1 mmol), PhCOOH (10 mol-%), 5 h. [b] GC yield.

During optimization of the reaction parameters, we observed that if the ratio palladium/PS–TPP (Pd/P) employed is 1:1, a 52% yield of the product was observed, but the complex turns black after completion of the reaction, which reveals that Pd is reduced to Pd^0. The conversion of Pd to metallic Pd^0 may be due to an unstable palladium complex formed due to the unavailability of a ligand. We tested the same catalyst for its reuse but it was completely ineffective, providing no yield of the desired product. We then carried out allylic amination of 1-phenyl-1-propyne with *N*-methylaniline by using Pd/C (which is also Pd^0) as a catalyst, but nor product was formed. From these results we conclude that phosphane is essential for this reaction, as Pd^0 in the metallic state is completely ineffective.

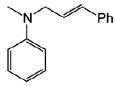
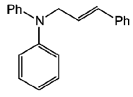
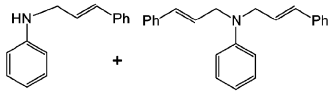
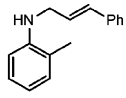
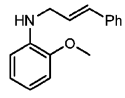
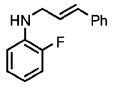
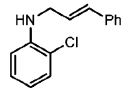
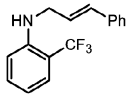
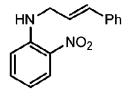
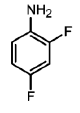
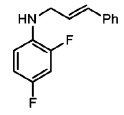
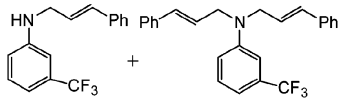
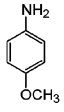
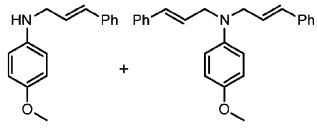
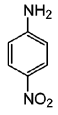
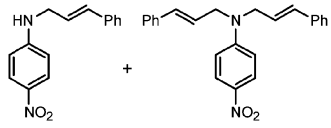
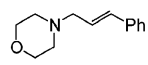
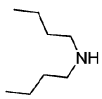
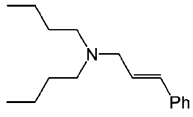
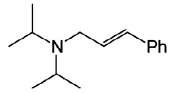
The catalytic activity at different Pd/P ratios was studied for the allylic amination of 1-phenyl-1-propyne with *N*-methylaniline by using the optimized reaction conditions. Pd/P ratios of 1:1, 1:2, 1:3, 1:4, and 1:5 were evaluated, and it was observed that the yield of the product increases with a smaller Pd/P ratio. During the reaction with Pd/P ratios of 1:1, 1:2, and 1:3, the yield of the product was found to be 52–75%; however, the color of the catalyst was found to change from yellow to black (Table 3, Entries 1–3). The complete conversion of the starting material was observed for a Pd/P ratio of 1:4, providing 94% yield of the desired product; the catalyst was isolated quantitatively after the reaction as a yellowish solid. With a further decrease in the ratio of Pd/P to 1:5, almost similar results were obtained. A Pd/P ratio of 1:4 was used as the optimum henceforth.

Table 3. Effect of Pd/PS–TPP (Pd/P) ratio on the allylic amination of 1-phenyl-1-propyne with *N*-methylaniline.[a]

Entry	Pd/P ratio	$Pd(OAc)_2$ [mol-%]	PS–TPP [mol-%]	Color of catalyst	Yield [%][b]
1	1:1	10	10	black	52
2	1:2	10	20	black	70
3	1:3	10	30	brown-black	75
4	1:4	10	40	yellow	94
5	1:5	10	50	yellow	94

[a] Reaction conditions: 1-phenyl-1-propyne (1 mmol), *N*-methylaniline (1 mmol), PhCOOH (10 mol-%), toluene (4 mL). [b] GC yield.

Table 4. Allylic amination of 1-phenylpropyne with various amines.[a]

Entry	Amine **1**	Product **3**	Time [h]	Yield [%][b]	Ref.
1			5	94	[6c]
2			10	75	[6c]
3			5	95 (90:10)	[6c]
4			5	94	[8]
5			5	90	–
6			5	97	–
7			5	90	[9]
8			5	98	–
9			8	88	[6c]
10			5	98	–
11			8	83 (90:10)	–
12			8	85 (85:15)	[6c]
13			10	82 (80:20)	[6c]
14			5	90	[6c]
15			8	75	[10]
16			8	60	–

[a] Amine (1) (1 mmol), 1-phenyl-1-propyne (2) (1 mmol), $Pd(OAc)_2$ (10 mol-%), PS–TPP (40 mol-%), PhCOOH (10 mol-%), toluene (4 mL) at 110 °C. [b] Isolated yields.

Thus, the optimized reaction conditions are: $Pd(OAc)_2$ (10 mol-%), PS–TPP (40 mol-%), toluene (4 mL) at 110 °C for 5 h.

The optimized reaction conditions were used in the allylic amination of 1-phenylpropyne (**2**) with different aromatic and aliphatic amines, and the desired products were obtained in moderate to excellent yields (Table 4, Entries 1–16). The reaction of **2** with *N*-phenylaniline provided a moderate yield of the desired product (Table 4, Entry 2). The reaction of aniline with **2** gave an excellent yield of the product with 90:10 ratio (mono-/diallylated; Table 4, Entry 3). The effect of various activating groups such as Me, OMe, F, and Cl at the *ortho* position of aniline were well tolerated to give selectively the monoallylic product in excellent yields (Table 4, Entries 4–7). The reaction of **2** with *o*-trifluoromethylaniline and *o*-nitroaniline furnished the monoallylated products in excellent yields (Table 4, Entries 8 and 9). The reaction of **2** with disubstituted 2,4-difluoroaniline provided the desired monoallylated product in excellent yield (Table 4, Entry 10). Compound **2** reacted smoothly with *m*-trifluoromethylaniline, providing a mixture of mono- and diallylated product in a ratio of 90:10 (Table 4, Entry 11). *p*-Anisidine also reacted efficiently with **2**, providing a mixture of mono- and diallylated product in a ratio of 85:15 (Table 4, Entry 12). The reaction of *p*-nitroaniline with **2** proceeded smoothly, providing 82% of product with a 80:20 ratio of mono-/diallylated products (Table 4, Entry 13).

To explore the generality and applicability of the protocol, we turned our attention towards the allylation of alicyclic amines such as morpholine as well as secondary aliphatic amines such as dibutylamine and diisopropylamine with **2** (Table 4, Entries 14–16). The reaction with morpholine gave 90% yield of 4-(3-phenylallyl)morpholine under the optimized reaction conditions, whereas dibutylamine and diisopropylamine were found to be less reactive, providing the product in moderate to good yields (Table 4, Entries 15 and 16). Thus, the developed protocol proved to be general for the allylic amination of 1-phenyl-1-propyne (**2**) with various structurally and electronically different aromatic and aliphatic amines, providing good to excellent yields of the desired product.

To check whether the catalyst was active to catalyze the reaction in more catalytic cycles and to make the protocol economically viable we attempted to recycle the catalyst. Recyclability experiments at different Pd/P ratios were studied for the allylic amination of 1-phenyl-1-propyne with *N*-methylaniline by using standard reaction conditions. A Pd/P ratio of 1:1 did not give any product during the recycling experiment, and the starting material was recovered quantitatively. Pd/P ratios of 1:2 and 1:3 showed lower yields of the products during the first recycling run. However, Pd/P ratios of 1:4 and 1:5 both gave excellent yields of the desired products during the first recycling run, and hence we checked the recyclability in both cases for further consecutive cycles. It was observed that in case of a Pd/P ratio of 1:4 there was no significant decrease in the yield of the product in the second recycling, whereas the yield declined to 85% at the end of the fifth consecutive cycle and the color of the catalyst turned black-brown after completion of the fifth cycle, which was yellow up this cycle (Table 5).

Table 5. Reusability of the catalyst.[a]

Entry	Pd/P ratio	PS–TPP [mol-%]	Recycle no. (% yield[b]) 1	2	3	4	5
1	1:1	10	–	–	–	–	–
2	1:2	20	36	–	–	–	–
3	1:3	30	38	–	–	–	–
4	1:4	40	90	88	85	85	85
5	1:5	50	92	88	88	85	85

[a] Reaction conditions: $Pd(OAc)_2$ (10 mol-%), 1-phenyl-1-propyne (1 mmol), *N*-methylaniline (1 mmol), PhCOOH (10 mol-%), toluene (4 mL), 110 °C, 5 h. [b] GC yield.

Maintaining the color of the catalyst after reaction indirectly indicates that palladium is complexed to phosphane. In the case of a Pd/P ratio of 1:5 similar results were obtained. To check whether the palladium leached during the reaction, we carried out ICP-AES analysis of the reaction mixture after completion of the reaction. The result of ICP-AES analysis revealed that there was no leaching of palladium.

Conclusions

In conclusion, we have developed an efficient protocol for the allylation of aromatic and aliphatic amines by using a [PS–TPP–Pd] complex as a heterogeneous and recyclable catalyst. The reaction was optimized with respect to various reaction parameters and enabled allylation reactions of various electron-rich, electron-deficient, and sterically hindered aromatic and aliphatic amines, affording excellent yields of the desired products, thus illustrating the broad applicability of the methodology. Further, the [PS–TPP–Pd] complex was recycled for five consecutive cycles without any significant loss in catalytic activity.

Experimental Section

Materials and Methods: Palladium acetate, polymer-supported triphenylphosphane (loading ca. 3 mmol/g), 1-phenyl-1-propyne, amines, and benzoic acid were purchased from Sigma–Aldrich Ltd. in their highest purity available and were used as is. Optimized yields were based on GC (Chemito 1000) and GC–MS (Shimadzu QP 2010) analysis. All the products are known, and representative products were characterized by ^1H NMR (Varian 300 MHz or Varian 400 MHz) and ^{13}C NMR (Varian 75 MHz) spectroscopy and GC–MS (Shimadzu QP 2010) analysis. Purity of all the compounds were determined by GC–MS analysis.

General Procedure for the Allylation of Amines: In a typical experiment, a 25-mL round-bottomed flask was charged with $Pd(OAc)_2$ (22.4 mg, 10 mol-%), polymer-supported triphenylphosphane (PS–TPP; 133 mg, 40 mol-%), and toluene (4 mL), and the mixture was stirred for 20 min at 110 °C.[7c] The reaction mixture was cooled to room temperature followed by the addition of 1-phenyl-1-propyne (116 mg, 1 mmol), amine (1 mmol), and benzoic acid (12 mg,

10 mol-%). The resulting mixture was stirred for 5 h at 110 °C and then cooled to room temperature. The catalyst was separated by filtration, washed with an excess amount of toluene and dried under vacuum. The filtrate obtained was removed under reduced pressure, and the product was purified by column chromatography (silica gel, 60–120 mesh; petroleum ether/ethyl acetate, 95:05) to afford the desired products. All the prepared compounds were confirmed by GC–MS and ^{1}H and ^{13}C NMR spectroscopy.

***N*-Cinnamyl-*N*-methylaniline:** Liquid. Yield: 209 mg, 94% (Table 4, Entry 1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.16–7.34 (m, 7 H, 7 C*H*, Ar), 6.76 (d, J = 7.69 Hz, 2 H, 2 C*H*, Ar), 6.71 (t, J = 7.33 Hz, 1 H, C*H*, Ar), 6.49 (d, J = 16.13 Hz, 1 H, CH=C*H*Ar), 6.21 (td, J = 16.13, 5.49 Hz, 1 H, CH_2CH=CH), 4.03 (dd, J = 5.49, 1.46 Hz, 2 H, NCH_2CH), 2.94 (s, 3 H, NCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 149.75 (N-*C*q, Ar), 137.08 (*C*q, Ar), 131.44 (CH_2CH=CH), 129.37 (2 *C*H, Ar), 128.70 (2 *C*H, Ar), 127.57 (*C*H, Ar), 126.50 (2 *C*H, Ar), 125.93 (CH=*C*HAr), 116.78 (*C*H, Ar), 112.81 (2 *C*H, Ar), 55.05 (NCH_2CH), 38.17 (NCH_3) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 223 (40) [M]$^+$, 118 (12), 117 (100), 115 (45), 91 (25), 51 (8.9), 44 (15.2).

***N*-Cinnamyl-*N*-phenylaniline:** Solid. Yield: 213 mg, 75% (Table 4, Entry 2). GC–MS (EI, 70 eV): *m*/*z* (%) = 285 (20) [M]$^+$, 167 (12.7), 118 (10), 117 (100), 115 (30), 91 (16.5), 77 (12), 44 (15.7).

***N*-Cinnamylaniline:** Liquid. Yield: 170 mg, 82% (Table 4, Entry 3). GC–MS (EI, 70 eV): *m*/*z* (%) = 209(39) [M$^+$], 117 (100), 115 (45), 91 (24), 77 (20), 44 (21).

***N*,*N*-Dicinnamylaniline:** Liquid. Yield: 35 mg, 11% (Table 4, Entry 3). MS–MS (ESI+): *m*/*z* = 326.07 [M + 1]$^+$.

***N*-Cinnamyl-2-methylaniline:** Liquid. Yield: 209 mg, 94% (Table 4, Entry 4). GC–MS (EI, 70 eV): *m*/*z* (%) = 223 (33.7) [M]$^+$, 117 (100), 115 (38), 91 (29), 77 (9), 44 (14).

***N*-Cinnamyl-2-methoxyaniline:** Liquid. Yield: 215 mg, 90% (Table 4, Entry 5). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.22–7.39 (m, 5 H, 5 C*H*, Ar), 6.6–6.89 [m, 5 H, (4 C*H*, Ar, CH=C*H*Ar)], 6.35 (td, J = 15.76, 5.86 Hz, 1 H, CH_2CH=CH), 4.42 (br. s, 1 H, N*H*), 3.95 (dd, J = 5.5, 1.46 Hz, 2 H, $HNCH_2CH$), 3.85 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 146.92 (*C*q, Ar), 138.02 (N-*C*q, Ar), 136.99 (*C*q, Ar), 131.35 (CH_2CH=CH), 128.56 (2 *C*H, Ar), 127.46 (*C*H, Ar), 127.27 (CH=*C*HAr), 126.36 (2 *C*H, Ar), 121.34 (*C*H, Ar), 116.71 (*C*H, Ar), 110.24 (*C*H, Ar), 109.45 (*C*H, Ar), 55.41 (OCH_3), 45.94 ($HNCH_2CH$) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 239 (43) [M]$^+$, 117 (100), 115 (41), 91 (31), 77 (10), 45 (46), 44 (38).

***N*-Cinnamyl-2-fluoroaniline:** Liquid. Yield: 220 mg, 97% (Table 4, Entry 6). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.18–7.36 (m, 5 H, 5 C*H*, Ar), 6.94–7.0 (m, 2 H, 2 C*H*, Ar), 6.73 (t, J = 8.8 Hz, 1 H, C*H*, Ar), 6.63 (m, 1 H, C*H*, Ar), 6.6 (d, J = 15.76 Hz, 1 H, CH=C*H*Ar), 6.28 (td, J = 15.76, 5.5 Hz, 1 H, CH_2CH=CH), 4.1 (br. s, 1 H, N*H*), 3.93 (d, J = 5.5 Hz, 2 H, $HNCH_2CH$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 151.93 (F-*C*q, Ar), 136.77 (*C*q, Ar), 136.6 (N-*C*q, Ar), 131.70 (CH_2CH=CH), 128.61 (2 *C*H, Ar), 127.64 (*C*H, Ar), 126.56 (CH=*C*HAr), 126.40 (2 *C*H, Ar), 124.64 (*C*H, Ar), 116.84 (*C*H, Ar), 114.45 (*C*H, Ar), 112.44 (*C*H, Ar), 45.74 ($HNCH_2CH$) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 227 (33.7) [M]$^+$, 117 (100), 115 (44), 91 (20), 77 (10).

***N*-Cinnamyl-2-chloroaniline:** Liquid. Yield: 218 mg, 90% (Table 4, Entry 7). GC–MS (EI, 70 eV): *m*/*z* (%) = 245 (7.2), 243 (21.7) [M]$^+$, 117 (100), 115 (40), 91 (19), 45 (39), 44 (32).

***N*-Cinnamyl-2-(trifluoromethyl)aniline:** Liquid. Yield: 218 mg, 98% (Table 4, Entry 8). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.23–7.45 (m, 7 H, 7 C*H*, Ar), 6.61–6.79 (m, 2 H, 2 C*H*, Ar), 6.63 (d, J = 16 Hz, 1 H, CH=C*H*Ar), 6.31 (td, J = 16, 5.6 Hz, 1 H, CH_2CH=CH), 4.59 (br. s, 1 H, N*H*), 4.02 (d, J = 4.8 Hz, 2 H, $HNCH_2CH$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 145.74 (N-*C*q, Ar), 136.67 (*C*q, Ar), 133.17 (*C*H, Ar), 131.94 (CH_2CH=CH), 128.65 (2 *C*H, Ar), 127.75 (*C*H, Ar), 127.15 (*C*H, Ar), 126.67 (CF_3), 126.46 (2 *C*H, Ar), 125.94 (CH=*C*HAr), 116.21 (*C*H, Ar), 113.56 (*C*q, Ar), 112.24 (*C*H, Ar), 45.63 (NCH_2CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 277 (29) [M]$^+$, 117 (100), 115 (38), 91 (19), 77 (5.5).

***N*-Cinnamyl-2-nitroaniline:** Solid. Yield: 223 mg, 88% (Table 4, Entry 9). MS–MS (ESI–): *m*/*z* = 253.13 [M – 1]$^-$.

***N*-Cinnamyl-2,4-difluoroaniline:** Solid. Yield: 244 mg, 98% (Table 4, Entry 10). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.22–7.38 (m, 7 H, 7 CH, Ar), 6.66–6.83 (m, 2 H, 2 CH, Ar), 6.63 (d, J = 16 Hz, 1 H, CH=C*H*Ar), 6.26 (d, J = 16 Hz, 1 H, CH_2CH=CH), 3.95 (d, J = 3.7 Hz, 2 H, $HNCH_2CH$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.51 (F-*C*q, Ar), 150.58 (F-*C*q, Ar), 136.77 (*C*q, Ar), 133.07 (N-*C*q, Ar), 131.92 (CH_2CH=CH), 128.73 (2 *C*H, Ar), 127.80 (*C*H, Ar), 126.49 (3 *C*H, CH=*C*HAr, Ar), 112.42 (*C*H, Ar), 110.74 (*C*H, Ar), 103.53 (*C*H, Ar), 46.27 (NCH_2CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 245(24) [M]$^+$, 117 (100), 115 (43), 91 (19).

***N*-Cinnamyl-3-(trifluoromethyl)aniline:** Liquid. Yield: 206 mg, 74% (Table 4, Entry 11). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.2–7.38 (m, 6 H, 6 C*H*, Ar), 6.94 (d, J = 7.3 Hz, 1 H, 1 C*H*, Ar), 6.84 (s, 1 H, Ar), 6.76 (d, J = 8 Hz, 1 H, CH, Ar), 6.62 (d, J = 15.76 Hz, 1 H, CH=C*H*Ar), 6.27 (td, J = 15.76, 5.5 Hz, 1 H, CH_2CH=CH), 4.01 (br. s, 1 H, N*H*), 3.39 (d, J = 4.8 Hz, 2 H, $HNCH_2CH$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 148.21 (N-*C*q, Ar), 136.7 (*C*q, Ar), 132.1 (2 C, CH_2CH=CH, *C*q-CF_3), 129.72 (*C*H, Ar), 128.69 (2 *C*H, Ar), 127.77 (*C*H, Ar), 126.43 (2 *C*H, Ar), 126.11 (CH=*C*HAr), 115.96 (*C*H, Ar), 114.0 (*C*H, Ar), 109.25 (*C*H, Ar), 45.97 (NCH_2CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 277 (29) [M]$^+$, 117 (100), 115 (38), 91 (19), 77 (6).

***N*,*N*-Dicinnamyl-3-(trifluoromethyl)aniline:** Liquid. Yield: 32 mg, 8.3% (Table 4, Entry 11). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.21–7.55 (m, 11 H, 11 CH, Ar), 7.00 (s, 1 H, CH, Ar), 6.92–6.98 (m, 2 H, Ar), 6.54 (d, J = 16.12 Hz, 2 H, CH=C*H*Ar), 6.24 (td, J = 16.12, 5.5 Hz, 2 H, CH_2CH=CH), 4.17 (d, J = 4.40 Hz, 4 H, $HNCH_2CH$) ppm. ^{13}C NMR (75 MHz, CDCl3, 25 °C): δ = 148.02 (N-*C*q, Ar), 136.73 (2 *C*q, Ar), 131.81 (2 CH_2CH=CH), 129.74 (*C*q-CF_3), 128.67 (4 *C*H, Ar), 127.70 (2 *C*H, Ar), 126.45 (4 *C*H, Ar), 124.93 (*C*H, Ar), 115.53 (*C*H, Ar), 113.07 (*C*H, Ar), 108.80 (*C*H, Ar), 52.31 ($HNCH_2CH$) ppm. MS–MS (ESI+): *m*/*z* = 394.33 [M + 1]$^+$.

***N*-Cinnamyl-4-methoxyaniline:** Solid. Yield: 172 mg, 72% (Table 4, Entry 12). MS–MS (ESI+): *m*/*z* = 240.139 [M + 1]$^+$.

***N*,*N*-Dicinnamyl-4-methoxyaniline:** Solid. Yield: 42 mg, 12% (Table 4, Entry 12). MS–MS (ESI+): *m*/*z* = 356.05 [M + 1]$^+$.

***N*-Cinnamyl-4-nitroaniline:** Solid, Yield: 166 mg, 65% (Table 4, Entry 13). MS–MS (ESI–): *m*/*z* = 253.20 [M + 1]$^-$.

***N*,*N*-Dicinnamyl-4-nitroaniline:** Solid, Yield: 60 mg, 16% (Table 4, Entry 13). MS–MS (ESI–): *m*/*z* = 369.27 [M + 1]$^-$.

4-Cinnamylmorpholine: Liquid. Yield: 182 mg, 90% (Table 4, Entry 14). MS (EI, 70 eV): *m*/*z* (%) = 203(32) [M]$^+$, 144 (15), 117 (71), 115 (50), 112 (100), 91 (28), 56 (34).

***N*-Butyl-*N*-cinnamylbutan-1-amine:** Liquid. Yield: 183 mg, 75% (Table 4, Entry 14). MS (EI, 70 eV): *m*/*z* (%) = 245 (3.5) [M]$^+$, 202 (20.9), 117 (100), 115 (16).

***N*,*N*-Diisopropyl-3-phenylprop-2-en-1-amine:** Liquid. Yield: 130 mg, 60% (Table 4, Entry 15). MS (EI, 70 eV): *m*/*z* (%) = 217 (7) $[M]^+$, 202 (19), 117 (100), 115 (19), 91 (11), 44.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra of the prepared compounds.

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