Palladium-Catalyzed Amination of Aryl Triflates

John P. Wolfe and Stephen L. Buchwald*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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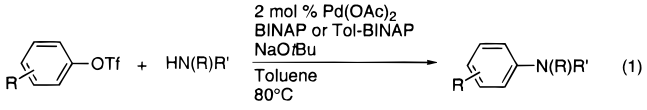
The conversion of aryl triflates to the corresponding aniline derivatives was accomplished in moderate to good yield using a catalyst consisting of the combination of palladium acetate (2 mol %) and either BINAP or Tol-BINAP. In contrast to the corresponding palladium-catalyzed amination of aryl bromides and iodides, electronically neutral aryl triflates gave higher yields of arylamines than did electron deficient aryl triflates, presumably due to the increased rate of base-promoted triflate cleavage in electron deficient substrates.

Several recent reports have detailed the palladium-catalyzed conversion of aryl bromides and iodides to aniline derivatives under mild conditions.[1] In many instances, systems which employed tri-*o*-tolylphosphine as ligand were quite efficient, although the most general catalysts were those which employ chelating bis(phosphines) such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP).[1e,f,h] We felt that the extension of the aryl amination process to the conversion of aryl triflates into aromatic amines would significantly enhance the utility of this methodology due to the wide availability of phenolic intermediates. Herein we report the first palladium-catalyzed method for the conversion of aryl triflates to anilines. Key to the success of this transformation was the use of the chelating bis(phosphine) ligands BINAP or 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl (Tol-BINAP).[2]

Our early attempts to couple aryl triflates with amines which employed catalytic amounts of $Pd_2(dba)_3$/P(*o*-tolyl)$_3$ and a stoichiometric amount of NaO*t*Bu in toluene (the conditions used to couple amines with aryl bromides) were unsuccessful. This protocol gave only phenol products resulting from attack at the electrophilic sulfur center by sodium *tert*-butoxide.[3] Attempts to promote coupling by inclusion of halide additives[4a] such as LiCl or Bu_4NCl and/or by employing coordinating solvents[4b] such as THF or DMF were also unsuccessful. Additionally, procedures which utilized weaker bases such as K_2CO_3 in order to prevent cleavage of the triflate moiety generated no cross-coupled products.

In the related palladium-catalyzed carbonylation,[5a] reduction,[5b] and cyanation[5c] of aryl triflates, chelating phosphines have been shown to promote reactions which failed when monodentate phosphines were employed. Furthermore, Heck arylations using aryl triflates have been shown to proceed in nonpolar solvents such as toluene when chelating phosphines were employed.[6] In light of our and Hartwig's[1h] recent success with chelating phosphines in the amination of aryl bromides, we investigated the use of a combination of $Pd(OAc)_2$ and BINAP or Tol-BINAP to catalyze the coupling of aryl triflates with amines (eqn 1). We found that the reaction of 4-*tert*-butylphenyl triflate with N-methyl piperazine employing a mixture of $Pd(OAc)_2$/BINAP (2 mol % Pd) and NaO*t*Bu (1.4 eq) in toluene at 80 °C for 3 h gave the N-arylpiperazine in 73% yield. The main side product of the reaction was 4-*tert*-butylphenol resulting from nucleophilic cleavage of the triflate, although a small amount of 4-*tert*-butylbenzene resulting from the reduction of the aryl triflate was also detected.



(1)

As is evident (Table 1), the best yields of coupled products were obtained with electronically neutral or electron rich aryl triflates such as 2,4-dimethylphenyl triflate, 4-*tert*-butylphenyl triflate, and 4-methoxyphenyl triflate as substrates. In contrast to results obtained in the amination of aryl bromides, aminations of electron-poor aryl triflates such as 4-cyanophenyl triflate gave significantly lower yields. The moderate yields obtained with electron-poor aryl triflates may be due to the enhanced leaving group ability of the electron-deficient phenoxide which leads to an increased rate of triflate cleavage. Addition of various halides (LiCl, LiBr, Bu_4NBr) failed to increase the yields of these reactions and, in fact, resulted in lower yields of coupled products when electronically neutral triflates were employed. However, employment of $Pd_2(dba)_3$ at high catalyst loading (5 mol % Pd) under high-dilution conditions gave higher yields in some cases. In most cases, use of DPPF as a ligand afforded lower yields of coupled products when $Pd(OAc)_2$ was employed as a precatalyst (2 mol % Pd catalyst loading). However, Hartwig has found that DPPF affords

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(1) (a) Kosugi, M.; Kameyama, M.; Migita, T. *Chem. Lett.* **1983**, 927−928. (b) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348−1350. (c) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133−1135. (d) Wolfe, J. P.; Rennels, R. A.; Buchwald, S. L. *Tetrahedron* **1996**, *52*, 7525−7546. (e) Wolfe, J. P.; Wagaw. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215−7216. (f) Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 7240−1. (g) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609−3612. (h) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217−7218.

(2) Both BINAP and Tol-BINAP are commercially available from Strem Chemicals Inc. The price of 1 g of Tol-BINAP is ∼1/3 the price of 1 g of BINAP. Both enantiomers gave identical results and were used interchangeably.

(3) No traces of sulfonated amines were detected in the crude reaction mixtures. Control experiments which involved the heating of aryl triflates and amines in toluene gave no reaction, suggesting that the amines are not responsible for cleavage of the triflate.

(4) (a) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478−5486. (b) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434−5444.

(5) (a) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1986**, *27*, 3931−3934. (b) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1986**, *27*, 5541−5544. (c) Takagi, K.; Sakakibara, Y. *Chem. Lett.* **1989**, 1957−1958.

(6) Ozawa, F.; Kubo, A.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 1417−1419.

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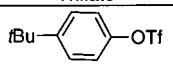
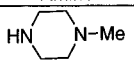
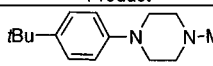
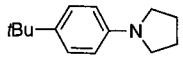
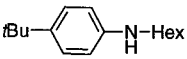
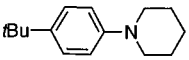
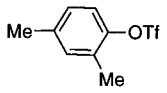
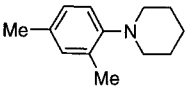
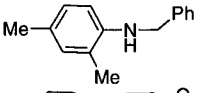
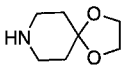
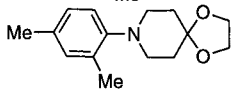
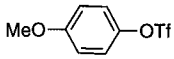
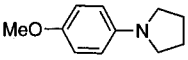
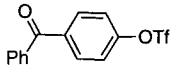
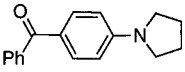
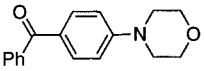
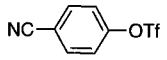
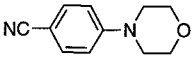
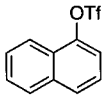
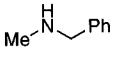
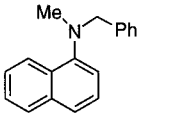
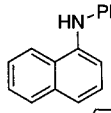
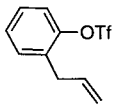
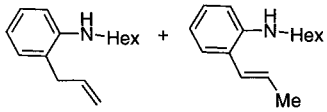
Table 1. Catalytic Amination of Aryl Triflates

Entry	Triflate	Amine	Product	Method[a]	Yield(%)[b]
1				A B	73 75
2				A	67
3		$HexNH_2$		A B C	55 47 65[c]
4				A C	69 35[c]
5				A B	76 73
6		$BnNH_2$		A B	72 73
7				A	77
8				A B	64 61
9				A	49
10				A D	47 53[c]
11				A B C D	28 31[c] 53[c] 60
12				A B C	61 47 56[c]
13		$PhNH_2$		A D	61 68[c]
14		$HexNH_2$		A C	54 (3/1)[d] 48[c] (15/1)[d]

a) Method A: 2 mol% $Pd(OAc)_2$, BINAP/$Pd(OAc)_2$ (1.1/1), 0.25M in aryl halide; Method B: 2 mol% $Pd(OAc)_2$, Tol-BINAP/$Pd(OAc)_2$ (1.1/1), 0.25M in aryl halide; Method C: 2.5 mol% $Pd_2(dba)_3$ (5 mol% Pd), BINAP/$Pd_2(dba)_3$ (2.2/1), 0.02M in aryl halide. Method D: Same as method A, but triflate added over 30 min. See experimental section for further details b) All yields represent isolated yields (average of two runs) unless otherwise noted. c) Isolated yield obtained from a single experiment. d) Ratio (GC, ^1H NMR) of 2-propenyl/1-propenyl.

the coupled products in good yields when a higher catalyst loading (5 mol %) of $Pd(dba)_2$ was employed at 100 °C under more dilute conditions.[7] Additionally, Hartwig has shown that yields for some coupling reactions may be improved by slow addition of the triflate to the reaction mixture.[7] We have found that in some cases this works well, and yields are significantly improved (Table 1, entry 11); however, for others there is only slight improvement (Table 1, entry 10). Procedures employing other chelating ligands such as DPPE, DPPP, and DPPBenzene or 1,10-phenanthroline derivatives resulted in little or no product formation.[8] In some cases, $Pd_2(dba)_3$ gave lower yields than $Pd(OAc)_2$, presumably due to inhibition of the catalytic reaction by the dba ligand.[9] Solvents such as DMF, THF, and dioxane also afforded lower yields of aminated products, presumably due to increased solvation of Na^+ resulting in enhanced nucleophilicity of the alkoxide base. Bases weaker than NaO*t*-Bu such as K_2CO_3, Na_2CO_3, DABCO, DBU, Proton Sponge, Et_3N, Na_3PO_4, and NaOH failed to promote coupling.

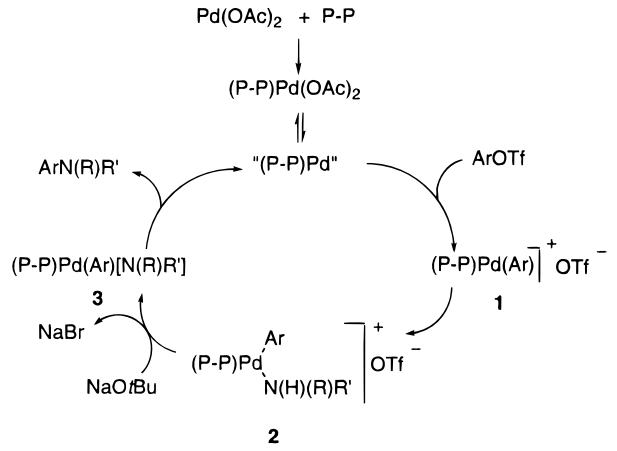
A plausible catalytic cycle for amination of aryl triflates is shown in Scheme 1. The mixture of $Pd(OAc)_2$ and bis(phosphine) (P-P) reacts to form (P-P)$Pd(OAc)_2$[10a] which

(7) Louie, J.; Driver, M. S.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 1268−1273.

(8) DPPF = 1,1′-Bis(diphenylphosphino)ferrocene; DPPE = 1,2-bis(diphenylphosphino)ethane; DPPP = 1,3-bis(diphenylphosphino)propane; DPPBenzene = 1,2-bis(diphenylphosphino)benzene.

(9) (a) Amatore has shown that the oxidative addition of iodobenzene to mixtures of $Pd(dba)_2$/2 PPh_3 proceeds 10 times more slowly than oxidative addition of iodobenzene to $Pd(PPh_3)_4$. Amatore, C.; Jutand, A.; Khalil, F.; M'Barki, M. A.; Mottier, L. *Organometallics* **1993**, *12*, 3168−3178. (b) In the catalytic amination of aryl bromides, added dba (dibenzylideneacetone) slows the coupling reaction. Wolfe, J. P.; Buchwald, S. L. Unpublished results.

Scheme 1



is then reduced under the reaction conditions to a zerovalent Pd species ["(P-P)Pd"].[10b] Oxidative addition of aryl triflate to this species forms the palladium aryl cation **1** which likely exists as a tight ion pair in toluene.[11] Amine coordination follows to give **2** which is deprotonated by NaO*t*Bu to afford palladium amido complex **3**. Reductive elimination from **3** yields the arylamine and regenerates the Pd(0) catalyst.

In conclusion, we have demonstrated the first palladium-catalyzed amination of aryl triflates. This protocol further expands the scope of catalytic amination methodology and allows for the conversion of phenols to anilines.

Experimental Section

General. All reactions were carried out under an argon atmosphere in oven-dried glassware. Elemental analyses were performed by E & R Microanalytical Laboratory Inc., Corona, N.Y. Toluene was continuously refluxed and freshly distilled under nitrogen from molten sodium. Triflic anhydride, 1-naphthyl triflate, and 1,1′-bis(diphenylphosphino)ferrocene were purchased from Aldrich Chemical Co. and were used without further purification. Morpholine, pyrrolidine, piperidine, hexylamine, aniline, 1-methylpiperazine, *N*-benzylmethylamine, and 1,4-dioxa-8-azaspiro[4.5]decane were purchased from Aldrich Chemical Co. and were passed through alumina before use. Sodium *tert*-butoxide was purchased from Aldrich Chemical Co. and stored in a Vacuum Atmospheres glovebox under nitrogen. Pyridine was distilled from calcium hydride and stored over molecular sieves. Palladium acetate was purchased from Alfa Chemical Co. and used without further purification. BINAP and Tol-BINAP were purchased from Strem Chemical Co. and used without further purification. Aryl triflates were prepared according to the procedure of Stille.[14] 4-*tert*-Butylphenyl triflate,[12] 4-cyanophenyl triflate,[13] 4-methoxyphenyl triflate,[14] and 2-(2-propenyl)phenyl triflate have been previously reported and adequately characterized in the literature. Preparative flash chromatography was performed on ICN Biomedicals Silitech 32-63d silica gel. Yields in Table 1 refer to isolated yields (average of two runs) of compounds estimated to be ≥95% pure as determined by ^{1}H NMR and either capillary GC (known compounds) or combustion analysis (new compounds). The procedures described in the Experimental Section are representative, thus the yields may differ from those given in Table 1.

2,4-Dimethylphenyl Triflate.[15] The procedure of Stille[14] gave 3.34 g (88%) of a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 6H), 7.00−7.15 (m, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 16.2, 20.7, 118.7 (q, J = 318 Hz), 120.9, 128.1, 130.4, 132.7, 138.2, 146.5; IR (neat, cm^{-1}) 2930, 1493, 1421, 1248, 1143, 1089, 876. Anal. Calcd for $C_9H_9SO_3F_3$: C, 42.52; H, 3.57. Found: C, 42.48; H, 3.62.

4-Benzoylphenyl Triflate.[16] The procedure of Stille[14] gave 4.24 g (86%) of a colorless oil which solidified upon standing to give a white solid, mp 41−42 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) 7.41 (d, 2H, J = 8.7 Hz), 7.52 (t, 2H, J = 7.3 Hz), 7.64 (t, 1H, J = 7.5 Hz), 7.80 (d, 2H, J = 7.1 Hz), 7.91 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 118.7 (q, J = 319 Hz), 121.3, 128.5, 129.9, 132.1, 133.0, 136.7, 137.5, 151.9, 194.7; IR (KBr, cm^{-1}) 3068, 1665, 1597, 1497, 1427, 1278, 1251, 1218, 1141, 888. Anal. Calcd for $C_{14}H_9SO_4F_3$: C, 50.91; H, 2.75. Found: C, 50.86; H, 2.91.

General Procedures for the Catalytic Amination of Aryl Triflates. Methods A and B: A Schlenk tube was charged with palladium acetate (0.01 mmol, 2 mol % Pd), BINAP (0.011 mmol, 2.2 mol %) (method A) or Tol-BINAP (0.011 mmol, 2.2 mol %) (method B), and sodium *tert*-butoxide (0.7 mmol). To this mixture was added a solution of aryl triflate (0.5 mmol) and amine (0.6 mmol) in toluene (2 mL, 0.25 M in aryl halide) via syringe. The mixture was heated to 80 °C with stirring until the triflate had been consumed as judged by GC analysis. The mixture was cooled to room temperature, taken up in ether, filtered, and concentrated. The crude material was purified by flash chromatography on silica gel.

Method C: A Schlenk tube was charged with tris(dibenzylideneacetone)dipalladium(0) (0.0125 mmol, 5 mol % Pd), BINAP (0.0275 mmol, 5.5 mol %), sodium *tert*-butoxide (0.7 mmol), and toluene (20 mL). To this mixture was added a solution of aryl triflate (0.5 mmol) and amine (0.6 mmol) in toluene (5 mL, 0.02 M in aryl halide after addition) via syringe. The mixture was heated to 80 °C with stirring until the triflate had been consumed as judged by GC analysis (2−8 h). The mixture was cooled to room temperature, taken up in ether, filtered, and concentrated. The crude material was purified by flash chromatography on silica gel.

Method D: A Schlenk tube was charged with palladium acetate (0.01 mmol, 2 mol % Pd), BINAP (0.011 mmol, 2.2 mol %), sodium *tert*-butoxide (0.7 mmol), toluene (1.5 mL), and amine (0.6 mmol). The mixture was heated to 80 °C with stirring, and a solution of the triflate (0.5 mmol) in toluene (0.5 mL) was added dropwise to the reaction mixture over 30 min via syringe. After the addition was complete, the mixture was heated at 80 °C with stirring until the triflate had been consumed as judged by GC analysis. The mixture was cooled to room temperature, taken up in ether, filtered, and concentrated. The crude material was purified by flash chromatography on silica gel.

***N*-(*p*-Cyanophenyl)morpholine.**[16] General procedure A gave 31 mg (33%) of a yellow solid, mp 65−66 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.23 (t, 4H, J = 4.9 Hz), 3.82 (t, 4H, J = 4.8 Hz), 6.81 (d, 2H, J = 9.6 Hz), 7.47 (d, 2H, J = 9.5 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 47.2, 66.4, 100.8, 114.0, 119.8, 133.5, 153.5; IR (KBr, cm^{-1}) 2981, 2218, 1606, 1518, 1246, 1182, 1116. Anal. Calcd for $C_{11}H_{12}NO$: C, 70.19; H, 6.43. Found: C, 69.97; H, 6.50.

***N*-(*p*-*tert*-Butylphenyl)piperidine.** General procedure A gave 70 mg (64%) of a white solid, mp 37−38 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29 (s, 9H), 1.50−1.60 (m, 2H), 1.67−1.75 (m, 4H), 3.11 (t, 4H, J = 5.5 Hz), 6.89 (d, 2H, J = 9.7 Hz), 7.26 (d, 2H, J = 9.8 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ

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24.3, 26.0, 31.4, 33.9, 50.9, 116.2, 125.7, 141.9, 150.0; IR (KBr, cm^{-1}) 2930, 1609, 1518, 1237, 820. Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67. Found: C, 82.78; H, 10.91.

***N*-(*p*-*tert*-Butylphenyl)-*N'*-methylpiperazine.** General procedure A gave 86 mg (74%) of a tan solid, mp 82−83 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29 (s, 9H), 2.35 (s, 3H), 2.57 (t, 4H, J = 5.0 Hz), 3.19 (t, 4H, J = 4.8 Hz), 6.88 (d, 2H, J = 8.9 Hz), 7.29 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 31.4, 33.9, 46.1, 49.2, 55.2, 115.7, 125.8, 142.3, 148.9; IR (KBr, cm^{-1}) 2961, 1521, 1458, 1295, 1244, 1150, 820. Anal. Calcd for $C_{15}H_{24}N_2$: C, 77.53; H, 10.41. Found: C, 77.69; H, 10.29.

***N*-(*p*-*tert*-Butylphenyl)pyrrolidine.** General procedure A gave 68 mg (67%) of a white solid, mp 38−39 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29 (s, 9H), 1.95−2.01 (m, 4H), 3.22−3.30 (m, 4H), 6.53 (d, 2H, J = 8.7 Hz), 7.27 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 25.4, 31.6, 33.7, 47.6, 111.3, 125.9, 137.9, 145.9; IR (KBr, cm^{-1}) 2962, 1522, 1364, 811. Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41. Found: C, 82.95; H, 10.60.

N-*p*-Anisidylpyrrolidine.[17] General procedure A gave 56 mg (63%) of a white solid, mp 40−41 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.90−2.02 (m, 4H), 3.20−3.28 (m, 4H), 3.76 (s, 3H), 6.53 (d, 2H, J = 9.0 Hz), 6.84 (d, 2H, J = 9.1 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 25.3, 48.2, 55.9, 112.5, 115.0, 143.2, 150.7; IR (KBr, cm^{-1}); IR (KBr, cm^{-1}) 2962, 1516, 1371, 1283, 1238, 1044, 814.

***N*-(2,4-Dimethylphenyl)benzylamine.** General procedure A gave 79 mg (75%) of a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.15 (s, 3H), 2.23 (s, 3H), 3.73 (s, br, 1H), 4.35 (s, 2H), 6.52 (d, 1H, J = 7.2 Hz), 6.89−6.91 (m, 2H), 7.26−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 17.5, 20.3, 48.5, 110.2, 122.0, 126.3, 127.1, 127.3, 127.5, 128.6, 130.9, 139.7, 143.8; IR (neat, cm^{-1}) 3438, 2916, 1515. Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11. Found: C, 85.34; H, 8.25.

***N*-(*p*-*tert*-Butylphenyl)hexylamine.** General procedure A gave 62 mg (53%) of a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, 3H, J = 6.8 Hz), 1.27 (s, 9H), 1.28−1.45 (m, 6H), 1.55−1.66 (m, 2H), 3.08 (t, 2H, J = 6.6 Hz), 3.51 (s, br, 1H), 6.56 (d, 2H, J = 8.9 Hz), 7.20 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 14.0, 22.6, 26.9, 29.6, 31.5, 31.6, 33.8, 44.2, 112.4, 125.9, 139.8, 146.2; IR (neat, cm^{-1}) 3412, 1616, 1520. Anal. Calcd for $C_{15}H_{23}N$: C, 82.34; H, 11.66. Found: C, 82.30, H, 11.66.

***N*-(2,4-Dimethylphenyl)piperidine.**[18] General procedure A gave 71 mg (75%) of a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49−1.60 (m, 2H), 1.62−1.75 (m, 4H), 2.26 (s, 6H), 2.80 (t, 4H, J = 5.1 Hz), 6.88−7.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 17.6, 20.7, 24.4, 26.7, 53.5, 118.9, 126.8, 131.6, 131.9, 132.6, 150.5; IR (neat, cm^{-1}) 2933, 1503, 1226.

***N*-(2,4-Dimethylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane.** General procedure A gave 93 mg (75%) of a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.87 (t, 4H, J = 6.1 Hz), 2.266 (s, 3H), 2.274 (s, 3H), 2.95 (t, 4H, J = 6.0 Hz), 4.00 (s, 4H), 6.95 (d, 2H, J = 1.7 Hz), 7.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 17.5, 20.6, 35.6, 50.3, 64.2, 107.2, 119.1, 126.9, 131.6, 132.4, 132.5, 149.4; IR (neat, cm^{-1}) 2954, 1499, 1103, 1038. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56. Found: C, 72.61; H, 8.48.

***N*-(*p*-Benzoylphenyl)pyrrolidine.** General procedure A gave 62 mg (49%) of a yellow solid, mp 138 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.01−2.09 (m, 4H), 3.35−3.42 (m, 4H), 6.54 (d, 2H, J = 9.6 Hz), 7.40−7.55 (m, 3H), 7.71 (d, 2H, J = 8.1 Hz), 7.80 (d, 2H, J = 9.5 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 25.4, 47.5, 110.5, 124.1, 127.9, 129.3, 130.9, 132.9, 139.4, 150.8, 195.0; IR (KBr, cm^{-1}) 2852, 1654, 1601, 1574, 1540, 1400, 1320, 1285, 1150. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82. Found: C, 81.39; H, 6.92.

***N*-(*p*-Benzoylphenyl)morpholine.**[16,19] General procedure A gave 67 mg (50%) of a yellow solid, mp 137−138 °C (lit. mp 140 °C).[16] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.29 (t, 4H, J = 4.7 Hz), 3.83 (t, 4H, J = 4.9 Hz), 6.85 (d, 2H, J = 9.6 Hz), 7.38−7.55 (m, 3H), 7.68−7.71 (m, 2H), 7.76 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 47.5, 66.5, 113.1, 127.7, 128.0, 129.5, 131.5, 132.4, 138.6, 154.0, 195.2; IR (KBr, cm^{-1}) 2966, 1639, 1597, 1236, 924.

***N*-Benzyl-*N*-methyl-1-naphthylamine.**[20] General procedure A gave 76 mg (61%) of a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.78 (s, 3H), 4.28 (s, 2H), 7.10 (d, 1H, J = 7.3 Hz), 7.25−7.50 (m, 8H), 7.55 (d, 1H, J = 8.4 Hz), 7.80−7.88 (m, 1H), 8.32−8.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 41.7, 61.5, 115.6, 123.2, 123.8, 125.3, 125.7, 127.0, 128.26, 128.35, 134.9, 138.8, 150.2; IR (neat, cm^{-1}) 3048, 1575, 1396, 724.

***N*-Phenyl-1-naphthylamine.**[21] General procedure A gave 68 mg (62%) of a yellow solid, mp 56−57 °C (lit. mp 62 °C).[21] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.90 (s, br, 1H), 6.80−7.00 (m, 3H), 7.02−7.20 (m, 2H), 7.22−7.60 (m, 5H), 7.80-8.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 115.9, 117.3, 120.4, 121.8, 122.9, 125.6, 126.0, 126.1, 127.7, 128.5, 129.3, 134.7, 138.7, 144.7; IR (KBr, cm^{-1}) 3408, 3051, 1576, 1307, 742.

***N*-[2-(2-Propenyl)phenyl]hexylamine.** General procedure A gave 60 mg (55%) of a colorless oil which was a 3/1 mixture (determined by GC, NMR) of the title compound and its olefin regioisomer *trans*-N-[2-(1-propenyl)phenyl]hexylamine (olefin stereochemistry assigned based on the coupling constant of olefinic protons). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88−0.92 (m, 4H), 1.25−1.47 (m, 4H), 1.55−1.70 (m, 11H), 1.90 (dd, 1H, J = 1.3, 6.1 Hz), 3.05−3.15 (m, 3H), 3.28 (d, 2H, J = 6.5 Hz), 3.68 (s, br, 1H), 5.05−5.15 (m, 2H), 5.85−6.10 (m, 2 H), 6.38 (d, 1H, J = 15.6 Hz), 6.55−6.70 (m, 3H), 7.00−7.20 (m, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 14.0, 18.9, 22.6, 26.9, 29.4, 29.5, 31.6, 36.6, 43.8, 44.1, 110.3, 116.1, 116.8, 116.9, 123.3, 126.7, 127.4, 127.7, 128.1, 128.2, 129.7, 136.3, 145.2, 146.7; IR (neat, cm^{-1}) 3421, 1604, 1512, 745. Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67. Found: C, 83.15; H, 10.53.

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