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HYDROAMINATION OF ALKYNES CATALYZED BY PALLADIUM/BENZOIC ACID

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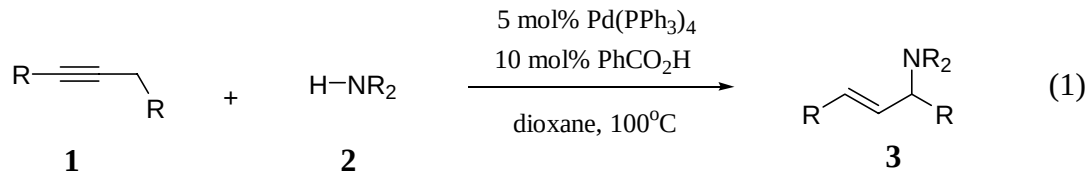
Dedicated to Professor Albert I. Meyers on the occasion of his 70th birthday.

Abstract – The reaction of internal alkynes **(1)** with amines **(2)** in the presence of catalytic amount of $Pd(PPh_3)_4$ and benzoic acid in dioxane at 100ºC gave the allylic amines **(3)** in good to excellent yields. The intramolecular reaction of alkynes with tethered amino groups **(4)** gave 2-vinylpyrrolidines and 2-vinylpiperidines **(5)** in good to excellent yields.

The carbon-nitrogen bond is frequently encountered in fragments of various biologically active natural products. Hence, the development of efficient synthetic approaches leading to nitrogen based compounds is a subject of considerable attraction. The organometallic reactions involving the formal addition of a N-H bond across a carbon-carbon multiple bond appear to offer the most attractive route to such

compounds, because this process does not generate byproducts generally observed in the metal-catalyzed substitution process.[1] The palladium-catalyzed intermolecular hydroaminations of 1,3-dienes,[2] allenes,[3] enynes,[4] and methylenecyclopropanes[5] have been developed to realize the ideal carbon-nitrogen bond formation. On the other hand, we have previously reported that certain alkynes react with carbon pronucleophiles in the presence of palladium/acetic acid catalyst to give the corresponding allylation products.[6] This hydrocarbonation is similar to the hydroacylation process reported by Trost *et al*. for the allylation of acetic acid with alkynes which gives allylic acetates.[7] The utility of this methodology prompted us to extend the formal hydrocarbonation to the formal hydroamination to provide a new atom-economical procedure for the synthesis of amines from alkynes.[8] In fact, the reaction of certain acetylene derivatives **(1)** with amines **(2)** in the presence of 5 mol% $Pd(PPh_3)_4$ and 10 mol% $PhCO_2H$ in dioxane at 100ºC gave the corresponding allylic amines **(3)** in very high to good yields (eq. 1). We describe herein an account of our results, part of which has been reported previously.[9]

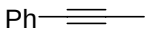
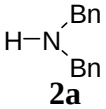
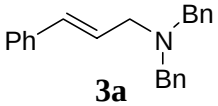
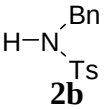
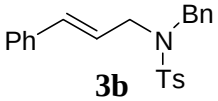
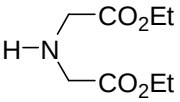
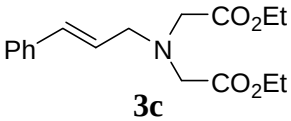
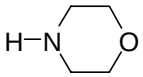
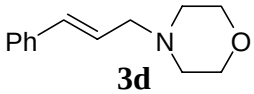
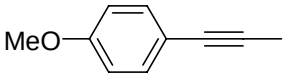
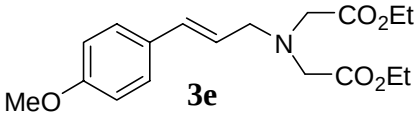
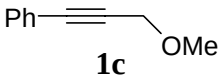
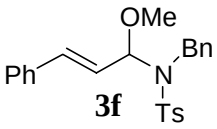
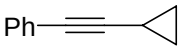
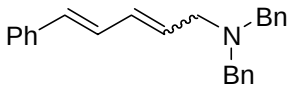


1 **2** **3** (1)

In an initial experiment, 1-phenyl-1-propyne (**1a**) was treated with 1 equiv of dibenzylamine (**2a**), $Pd(PPh_3)_4$ (5 mol%), and benzoic acid (10 mol%) in dioxane at 100ºC to give the allylic amine **(3a)** as a sole product in 98% yield (Table 1, entry 1). Similarly, the reactions of **1a** with secondary amines **(2b-d)** gave the allylic amines **(3b-d)**, respectively, in good to high yields (entries 2-4). In all cases, no regio- or stereoisomers were obtained. The addition of carboxylic acid was essential, as no reaction took place in its absence. Several acids such as acetic, tartaric and benzoic were effective, with the latter giving slightly better yields. Other examples with various alkynes are summarized in Table 1. While *p*-methoxyphenylalkyne **(1b)** also readily reacted, attempts for hydroamination of substrates possessing electron-withdrawing group on the phenyl ring only led to complex mixtures of products. A novel *N*,*O*-acetal **(3f)** was synthesized in good yield from the propargylic ether **(1c)** (entry 6). Treatment of

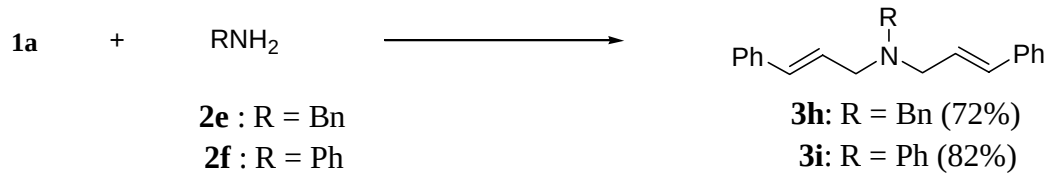
cyclopropylphenylacetylene **(1d)** with **2a** produced an 85 : 15 mixture of the *E* and *Z* linear adducts **(3g)**

Table1. Pd/$PhCO_2H$ Catalyzed Intermolecular Hydroamination of Alkynes[a]

entry	alkyne	amine	product	yield(%)[b]
1	 **1a**	 **2a**	 **3a**	98
2	**1a**	 **2b**	 **3b**	98
3	**1a**	 **2c**	 **3c**	77
4	**1a**	 **2d**	 **3d**	94
5	 **1b**	**2c**	 **3e**	82
6	 **1c**	**2b**	 **3f**	61
7	 **1d**	**2a**	 **3g** (*E* : *Z* = 85 : 15)	72[c]

[a]All reactions were conducted in dioxane using 5 mol% of $Pd(PPh_3)_4$ and 10 mol% of $PhCO_2H$ overnight.
[b]Isolated yield. [c]Inseparable mixture of the stereoisomers. The ratio was determined by ^1H NMR spectral analysis.

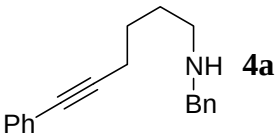
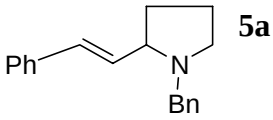
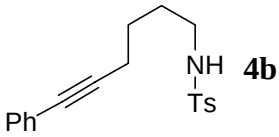
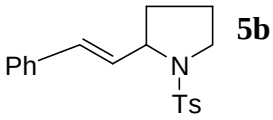
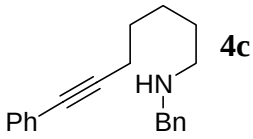
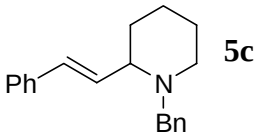
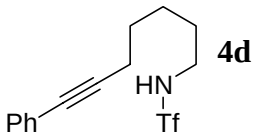
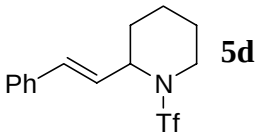
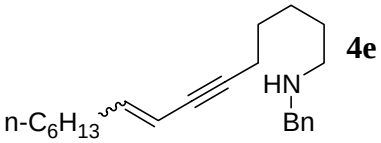
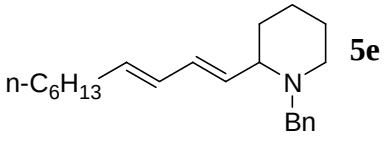
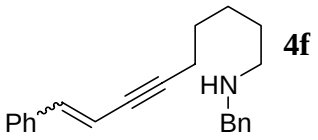
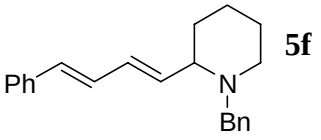
in 72% yield (entry 7). Aliphatic acetylenes such as 3-hexyne and 1-octyne did not react with amines under the conditions mentioned above. The reaction of primary amines **(2e)** and **(2f)** with **1a** afforded the 2 : 1 adducts **(3h)** and **(3i)**, respectively, in good yields (eq. 2).



(2)

The usefulness of this transformation is further demonstrated by the intramolecular version as outlined in Table 2. The reaction of the alkynes **(4a)** and **(4b)** having a monoprotected amino group at the terminus of the carbon chain, under the standard conditions mentioned above gave the pyrrolidines **(5a)** and **(5b)**,

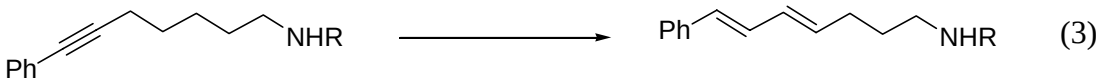
Table 2. Pd/$PhCO_2H$ Catalyzed Intramolecular Hydroamination of Alkynes[a]

entry	substrate	product	yield(%)[b]
1	 **4a**	 **5a**	70
2	 **4b**	 **5b**	82
3	 **4c**	 **5c**	91
4	 **4d**	 **5d**	98
5	 **4e**	 **5e**	52
6	 **4f**	 **5f**	55

[a]All reactions were conducted in dioxane using 5 mol% of $Pd(PPh_3)_4$ and 10 mol% of $PhCO_2H$ overnight. [b]Isolated yield.

respectively, in good yields (entries 1 and 2). Similarly, the benzylamine derivative **(4c)** and the trifluoromethanesufonylamide **(4d)** cyclized to produce piperidines **(5c)** and **(5d)** in 91 and 98% yields,

respectively (entries 3 and 4). When the conjugated enynes **(4e)** and **(4f)** were used as substrates, the cyclic products **(5e)** and **(5f)** were obtained in 52 and 54% unoptimized yields, respectively. Most interestingly, starting with mixtures of *cis* and *trans* isomers, the reaction proceeded in a complete stereoselective manner, affording exclusively the *trans-trans* adducts in both cases (entries 5 and 6). The intramolecular hydroamination of enynes is particularly attracting as it may pave the way to a class of numerous natural products having *trans-trans* conjugated diene moieties. Nevertheless, the expected hydroamination products were not obtained when the tosylamide derivative **(4g)** and the *tert*-butyl carbamate **(4h)** were used as substrates. Instead, the linear dienes **(6a)** and **(6b)** were produced in 80 and 82% yields, respectively (eq. 3). In a previous communication,[9] it was thought that the tosyl group in **4g** would decrease the nucleophilicity of the nitrogen atom, hampering the cyclization. However, this possibility was rouled out as it was later found that the less nucleophilic trifluoromethanesulfonylamide **(4d)** readily cyclized under the same conditions (entry 4). Perhaps the increased steric effects in **4g** and **4h** would render the nucleophilic attack on the π-allylpalladium moiety less effective, leading, as a result, to dienes **(6a)** and **(6b)** *via* β-elimination.

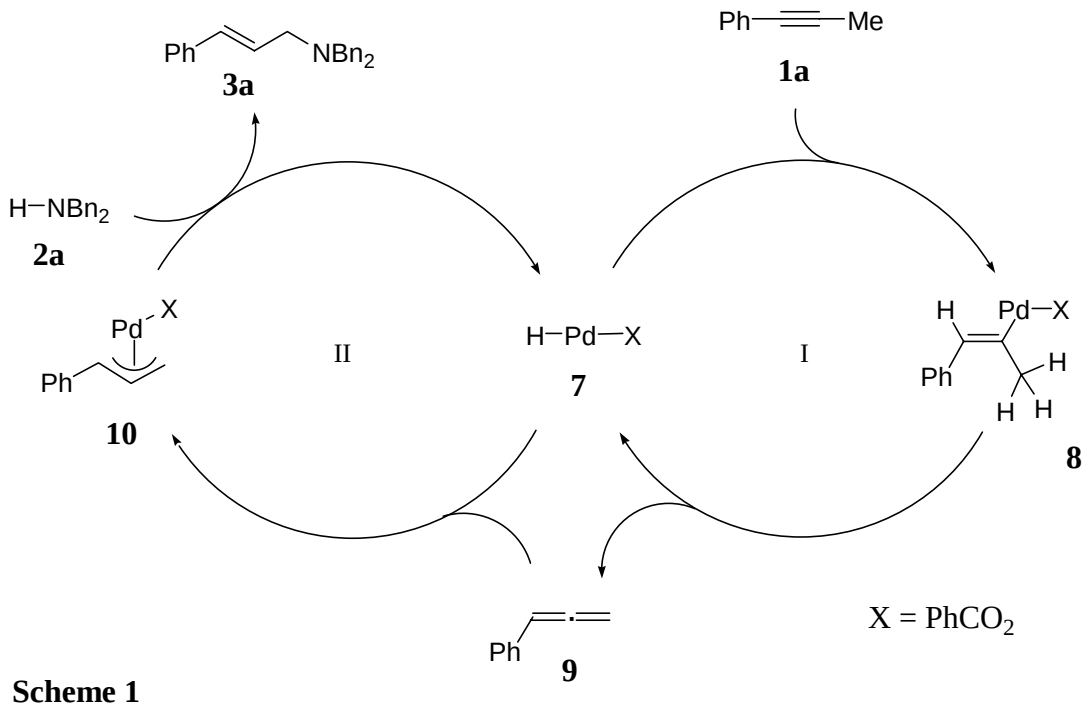


(3)

4g: R = Ts
4h: R = Boc

6a: R = Ts (80%)
6b: R = Boc (82%)

The mechanism of the present hydroamination of alkynes, as exemplified for the transformation of **1a** to **3a** in Scheme 1, is presumably similar to that of the previously reported hydrocarbonation of alkynes.[6] The initial step could be the hydropalladation of **1a** with the hydridopalladium species **(7)** generated from Pd(0) and benzoic acid (catalytic cycle I).[10] The resulting vinylpalladium species **(8)** would produce phenyl allene **(9)** and the active catalyst **(7)** *via* β-elimination.[11] Hydropalladation of **9** with **7** would give the π-allylpalladium species **(10)** which would react with an amine **(2a)** to give the product **(3a)** along with the hydridopalladium **(7)** (cycle II).[12]



Scheme 1

In conclusion, we have developed a simple and efficient method for the synthesis of various acyclic and cyclic allylic amines using palladium/benzoic acid catalyst. The use of readily available starting materials and the cleanness of the process make it an interesting alternative to the existing approaches to these types of compounds.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

The NMR experiments were performed with a JEOL JNM-LA 300 or JEOL GSX-270 spectrometer, and chemical shifts are expressed in ppm (δ) with TMS as an internal reference. IR spectra were measured on a Shimadzu FTIR-8200A or Hitachi M260-10 spectrophotometer. HRMS were recorded on a Hitachi M2500S, JMSDX303 or JMSAX500 spectrometer. All reactions were carried out under an argon atmosphere in a closed vial. The synthesis of unknown alkynylamines **(4)** will be published elsewhere.

General procedure for the intermolecular hydroamination of alkynes:

A mixture of alkyne **(1)** (0.6 mmol), amine **(2)** (0.5 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), and $PhCO_2H$ (6.1 mg, 0.05 mmol) in dry dioxane (2 mL) was stirred overnight at 100ºC. The reaction mixture was then filtered through a short silica gel column using ether as an eluent, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane/AcOEt mixtures) to give **3**.

General procedure for the intramolecular hydroamination of alkynes:

A mixture of alkynylamine **(4)** (0.5 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), and $PhCO_2H$ (6.1 mg, 0.05 mmol) in dry dioxane (2 mL) was stirred overnight at 100ºC. The resulting mixture was treated as above to give **5**.

(*E*)-*N*,*N*-Dibenzyl-3-phenyl-2-propenylamine (3a): IR (neat) 3026, 2922, 1495, 1121, 966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44-7.17 (m, 15 H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.9, 6.4 Hz, 1H), 3.63 (s, 4H), 3.22 (d, *J* = 6.4 Hz, 2H); Anal. Calcd for $C_{23}H_{23}N$: C, 88.13; H, 7.40; N, 4.47. Found: C, 88.18; H, 7.56; N, 4.27.

***N*-Benzyl-*N*-[(*E*)-3-phenyl-2-propenyl]tosylamide (3b):** IR (neat) 3059, 3026, 1337, 1153 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2 H), 7.36-7.21 (m, 10H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.24 (d, *J* = 15.8 Hz, 1H), 5.75 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.38 (s, 2H), 3.90 (d, *J* = 7.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 143.3, 137.5, 136.1, 136.0, 134.2, 133.3, 129.7, 128.55, 128.47, 127.8, 127.7, 127.3, 126.3, 123.3, 50.4, 49.0, 21.5; HRMS (EI) Calcd for $C_{23}H_{23}NO_2S$ (M^+) 377.1448, found 377.1452.

(*E*)-*N*,*N*-Bis(ethoxycarbonylmethyl)-3- phenyl-2-propenylamine (3c): IR (neat) 2982, 2936, 1744, 1512, 1190 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 4H), 3.81 (s, 3H), 3.59 (s, 4H), 3.51 (d, *J* = 6.9 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 6H); Anal. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18. Found: C, 64.34; H, 7.55; N, 4.18.

(*E*)-*N*-(3-Phenyl-2-propenyl)morpholine (3d): IR (neat) 3026, 2959, 2806, 1452, 1119 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.74 (m, 4H), 3.16 (m, 2H), 2.51 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 136.7, 133.3, 128.5, 127.5, 126.3, 126.0, 66.9, 61.4, 53.6; HRMS (EI) Calcd for $C_{13}H_{17}NO$ (M^+) 203.1309, found 203.1313.

(*E*)-*N,N*-Bis(ethoxycarbonylmethyl)-3-(4-methoxyphenyl)-2-propenylamine (3e): IR (neat) 2982, 2936, 1744, 1512, 1190 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 4H), 3.81 (s, 3H), 3.59 (s, 4H), 3.51 (d, *J* = 6.9 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 6H); Anal. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18. Found: C, 64.34; H, 7.55; N, 4.18.

***N*-Benzyl-*N*-[(*E*)-1-methoxy-3-phenyl-2-propenyl]tosylamide (3f):** IR (neat) 3028, 2932, 1339, 1161 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2 H), 7.32-7.08 (m, 12 H), 6.57 (d, *J* = 15.8 Hz, 1 H), 5.75 (dd, *J* = 15.8, 5.0 Hz, 1 H), 5.63 (d, *J* = 5.0 Hz, 1 H), 4.46-4.30 (m, 2 H), 3.22 (s, 3 H), 2.40 (s, 3 H); Anal. Calcd for $C_{24}H_{25}NO_3S$: C, 70.73; H, 6.18; N, 3.44. Found: C, 70.54; H, 6.35; N, 3.40.

(2*E*,4*E* and 2*Z*,4*E*)-*N,N*-Dibenzyl-5-phenyl-2,4-pentadienylamines (3g): IR (neat) 3024, 2795, 1495, 1452, 1366 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) **(2*E*,4*E*)** δ 7.42-7.18 (m, 15H), 6.78 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.35 (dd, *J* = 15.3, 10.5 Hz, 1H), 5.91 (ddd, *J* = 15.3, 6.6, 6.6 Hz, 1H), 3.15 (d, *J* = 6.6 Hz, 2H); **(2*E*,4*Z*)** δ 7.42-7.18 (m, 15H), 6.92 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.31 (dd, *J* = 15.3, 10.5 Hz, 1H), 5.69 (ddd, *J* = 15.3, 6.6, 6.6 Hz, 1H), 3.62 (s, 4H), 3.28 (d, *J* = 7.1 Hz, 2H); Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.10; H, 7.42; N, 3.89.

***N,N*-Bis[(*E*)-3-phenyl-2-propenyl]benzylamine (3h):** IR (neat) 3026, 2795, 1495, 1121, 966 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.18 (m, 15H), 6.55 (d, *J* = 15.7 Hz, 2H), 6.31 (dt, *J* = 15.7, 6.6 Hz, 2H), 3.68 (s, 2H), 3.30 (d, *J* = 6.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 139.3, 137.1, 132.6, 129.0, 128.5, 128.2, 127.6, 127.3, 126.9, 126.3, 58.0, 56.0; HRMS (EI) Calcd for $C_{25}H_{25}N$ (M^+) 339.1986, found 339.1997.

***N*,*N*-Bis[(*E*)-3-phenyl-2-propenyl]aniline (3i):** IR (neat) 3059, 3024, 1599, 1504, 1356 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.18 (m, 12H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 15.7 Hz, 2H), 6.28 (ddd, *J* = 15.7, 5.1, 5.1 Hz, 2H), 4.14 (d, *J* = 5.1 Hz, 4H); Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.90; H, 7.00; N, 4.06.

***N*-Benzyl-2-[(*E*)-2-phenylethenyl]pyrrolidine (5a):** IR (neat) 3026, 2964, 1601, 1495, 1452 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.18 (m, 10H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 8.5 Hz, 1H), 4.06 (d, *J* = 12.8 Hz, 1H), 3.13 (d, *J* = 12.8 Hz, 1H), 3.02-2.92 (m, 2H), 2.22-1.94 (m, 2H), 1.90-1.66 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 139.3, 137.1, 132.5, 131.6, 128.9, 128.5, 128.1, 127.3, 126.7, 126.2, 67.8, 58.3, 53.3, 31.7, 22.1; Anal. Calcd for $C_{19}H_{21}N$: C, 86.55; H, 8.25; N, 5.22. Found: C, 86.64; H, 8.04; N, 5.32.

***N*-Tosyl-2-[(*E*)-2-phenylethenyl]pyrrolidine (5b):** The ^{1}H and ^{13}C NMR spectral data of **5b** were identical with the literature data.[13]

***N*-Benzyl-2-[(*E*)-2-phenylethenyl]piperidine (5c):** IR (neat) 3026, 2932, 1495, 1450 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.18 (m, 10H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 8.4, 15.9 Hz, 1H), 4.09 (d, *J* = 13.6 Hz, 1H), 3.11 (d, *J* = 13.6 Hz, 1H), 2.90-2.78 (m, 2H), 1.93 (ddd, *J* = 11.1, 11.1, 3.3 Hz, 1H), 1.80-1.35 (m, 6H); Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.34; H, 8.19; N, 4.99.

***N*-Triflyl-2-[(*E*)-2-phenylethenyl]piperidine (5d):** IR (neat) 3028, 2949, 1497, 1448 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.19 (m, 5H), 6.54 (dd, *J* = 16.1, 1.7 Hz, 1H), 6.17 (dd, *J* = 16.1, 5.1 Hz, 1H), 4.77 (br s, 1H), 3.78 (br d, *J* = 13.6 Hz, 1H), 3.25 (m, 1H), 1.89 (m, 2H), 1.67-1.52 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 136.0, 133.3, 128.6, 128.1, 126.5, 125.5, 117.8, 56.2, 43.2, 29.6, 25.3, 18.6; HRMS (EI) Calcd for $C_{14}H_{16}NO_2F_3S$ (M^+) 319.0853, found 319.0834.

***N*-Benzyl-2-[(*E*,*E*)-1,3-decadienyl]piperidine (5e):** IR (neat) 3022, 2928, 1495, 1452 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.20 (m, 5H), 6.15 (dd, *J* = 14.8, 10.3 Hz, 1H), 6.04 (dd, *J* = 14.8, 10.4 Hz, 1H), 5.64 (dt, *J* = 14.5, 7.1 Hz, 1H), 5.61 (dd, *J* = 14.8, 8.7 Hz, 1H), 4.05 (d, *J* = 13.5 Hz, 1H), 3.01 (d, *J*

= 13.6 Hz, 1H), 2.79 (m, 1H), 2.6 (m, 1H), 2.06 (m, 2H), 1.90-1.28 (m, 15H), 0.88 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 139.5, 135.1, 134.1, 131.4, 129.9, 129.0, 128.0, 126.5, 65.7, 60.0, 52.2, 33.8, 32.6, 31.7, 29.3, 29.0, 25.8, 24.0, 22.6, 14.1; HRMS (EI) Calcd for $C_{22}H_{33}N$ (M^+) 311.2611, found 311.2572.

***N*-Benzyl-2-[(*E*,*E*)-4-phenyl-1,3-butadienyl]piperidine (5f)**: IR (neat) 3024, 2932, 1495, 1448 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.17 (m, 10H), 6.79 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.35 (dd, *J* = 15.2, 10.5 Hz, 1H), 5.88 (dd, *J* = 15.3, 8.7 Hz, 1H), 4.06 (d, *J* = 13.6 Hz, 1H), 3.03 (d, *J* = 13.5 Hz, 1H), 2.79 (m, 2 H), 1.91 (dt, *J* = 11.1, 3.4 Hz, 1H), 1.76-1.65 (m, 2H), 1.57-1.42 (m, 3H), 1.38-1.23 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 137.3, 131.3, 129.0, 128.9, 128.5, 128.0, 127.3, 126.6, 126.2, 65.7, 60.2, 52.2, 33.7, 25.7, 23.9; HRMS (EI) Calcd for $C_{22}H_{25}N$ (M^+) 303.1986, found 303.2001.

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