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PALLADIUM-CATALYZED INTER- AND INTRAMOLECULAR HYDROAMINATION OF METHYLENECYCLOPROPANES WITH AMINES*

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The inter- and intramolecular addition of nitrogen pronucleophiles to methylenecyclopropanes proceeds smoothly in the presence of palladium catalyst, giving the corresponding hydroamination products in good to excellent yields. The reaction proceeds mainly through cleavage of a distal bond of methylenecyclopropanes.

Keywords: azepane derivative, methylenecyclopropane, nitrogen pronucleophile, hydroamination, palladium catalyst.

Catalytic addition of nitrogen pronucleophiles to carbon-carbon multiple bonds, that is, hydroamination, is a desirable methodology to construct carbon-nitrogen bonds because this process is not only highly effective but also atom-economic and ecological [1-3]. The *intermolecular* hydroamination reactions catalyzed by titanium [4], zirconium [5], iridium [6, 7], rhodium [8], lanthanide [9], or actinide complexes [10] were reported by several groups. The catalytic cycle of these reactions involves the insertion process of a carbon-carbon double bond into the N–M bond (Fig. 1, type I). On the other hand, the palladium catalyzed *intermolecular* hydroamination of 1,3-dienes [11], allenes [12-14], enynes [15], propargylic compounds [16], and styrenes [17] proceeds through the insertion of the double bond to the H–M bond (type II). We were interested in assessing the reactivity of alkenes, other than those mentioned above, in the palladium-catalyzed hydroamination reactions.

Type I, M = Ti, Zr, Ir, Rh, lanthanide, actinide

Type II, M = Pd(0)

Fig. 1. Transition metal-catalyzed hydroamination.

* Dedicated to Prof. E. Lukevics on the occasion of his 65th birthday.

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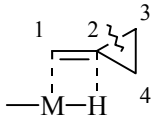
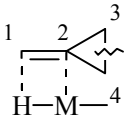
Meanwhile, methylenecyclopropanes are of current interest as a component of transition metal-catalyzed reactions. Characteristically, the reaction of methylenecyclopropanes usually proceeds through cleavage of the cyclopropane ring at the two different positions. The palladium-catalyzed hydrostannation [18] and rhodium-catalyzed hydrosilylation [19] of methylenecyclopropanes proceed through the anti-Markovnikov type addition **1** followed by the cleavage of the proximal bond C(2)–C(3) of the cyclopropane ring, whereas the palladium-catalyzed hydrocarbonation [20, 21] and hydroalkoxylation [22, 23] proceed mainly through the Markovnikov type addition **2** followed by the cleavage of the distal bond C(3)–C(4).

Accordingly, we investigated the palladium-catalyzed hydroamination of methylenecyclopropanes **1** and revealed that it mainly proceeds through a π-allylpalladium intermediate formed by distal bond cleavage [24]. Now, we report the detailed study of the *intermolecular* hydroamination together with the palladium-catalyzed *intramolecular* hydroamination of methylenecyclopropanes.



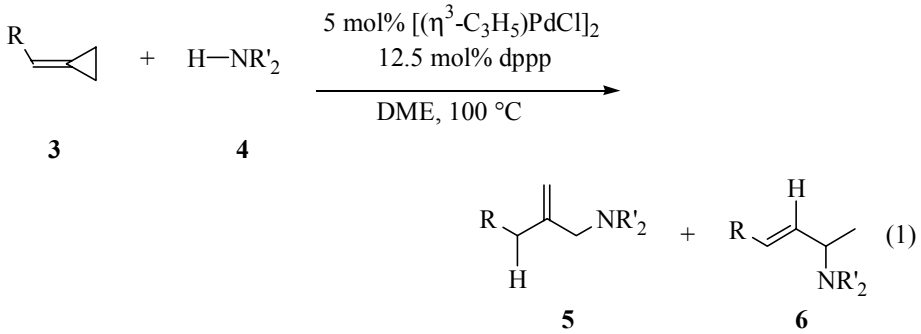
1



2

Intermolecular Hydroamination

The methylenecyclopropanes **3** underwent palladium-catalyzed intermolecular addition of the nitrogen pronucleophiles **4** to give the corresponding hydroamination products **5** in good to high yields (Eq. 1).

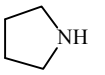
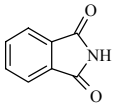


3 **5** **6**

3 **a** R = $PhCH_2CH_2CH_2$; **b** R = $PhCH_2CH_2$; **c** R = cyclohexyl; **d** R = Ph

The results are summarized in Table 1. The reaction of 4-phenylbutylidenecyclopropane **3a** with dibenzylamine **4a** in the presence of catalytic amounts of allylpalladium chloride dimer (5 mol%) and 1,3-bis(diphenylphosphino)propane (dppp, 12.5 mol%) gave the corresponding hydroamination product **5a** in 91% yield (entry 1). The use of $Pd_2(dba)_3{\cdot}CHCl_3$, $Pd(PPh_3)_4$, or $PdCl_2(PPh_3)_2$ as a catalyst gave **5a** in lower yields, and $Pd(OAc)_2$ did not promote the reaction at all. Although the reaction of **3a** with diethylamine **4b** gave **5b** in low yield (entry 2), the reaction with pyrrolidine **4c** afforded the hydroamination product **5c** in good yield (entry 3). The carbamate **4d** reacted with **3a** very smoothly (entry 4). The reaction of 3-phenylpropylidene-cyclopropane **3b** with **4a** gave **5e** in 82% yield (entry 5), and the reaction of cyclohexylmethylenecyclopropane **3c** with **4a** afforded **5f** in 72% yield (entry 6). In the above reactions, no trace amounts of the regioisomeric products **6** were detected. On the other hand, the reactions of benzylidenecyclopropane **3d** lead exclusively to the regioisomeric hydroamination products **6**; **6a** was obtained from **4a** in 19% yield (entry 7) and **6b** in 84% yield from **4e** (entry 8).

TABLE 1. Palladium Catalyzed Addition of **4** to Methylenecyclopropane **3***

Entry	**3**	**4**	Yield of **5**, %*[2]	Yield of **6**, %*[2]
1	**3a**	Bn_2NH **4a**	**5a** (91)	—
2	**3a**	Et_2NH **4b**	**5b** (31)	—
3	**3a**	 **4c**	**5c** (64)*[3]	—
4	**3a**	$(Boc)_2NH$ **4d**	**5d** (68)	—
5	**3b**	Bn_2NH **4a**	**5e** (82)	—
6	**3c**	**4a**	**5f** (72)	—
7	**3d**	**4a**	—	**6a** (19)*[4]
8	**3d**	 **4e**	—	**6b** (84)*[4]

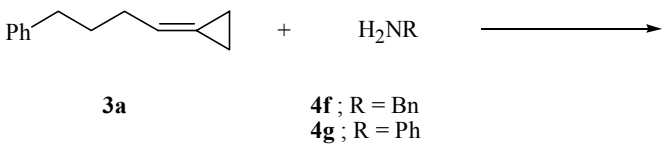
* The reaction of **3** (1.0 mmol) with **4** (0.5 mmol) was carried out in the presence of 5 mol% of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and 12.5 mol% of dppp in DME at 100°C for 3 days.

*[2] Isolated yield.

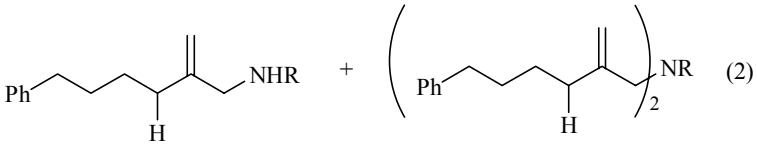
*[3] 10 mol% of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and 25 mol% of dppp were used.

*[4] The *trans* configuration of the double bond of **6a** was confirmed by the coupling constant of the olefinic protons (16.2 Hz).

The use of primary amines as nitrogen pronucleophiles also gave the corresponding alkylated products. In the reaction of benzylamine **4f** with **3a**, the dialkylated compound **7a** was produced as a major product along with a small amount of the monoalkylated **5g**. However, the reaction of aniline **4g** led to only the monoalkylated product **5h** (Eq. 2). The reaction of the tetrasubstituted alkene **3e** with **4a** proceeded smoothly to give **5i** in 79% yield (Eq. 3). The methylenecyclopropane **3f** having a substituent on the ring reacted with **4a** to give **5j** (Eq. 4).



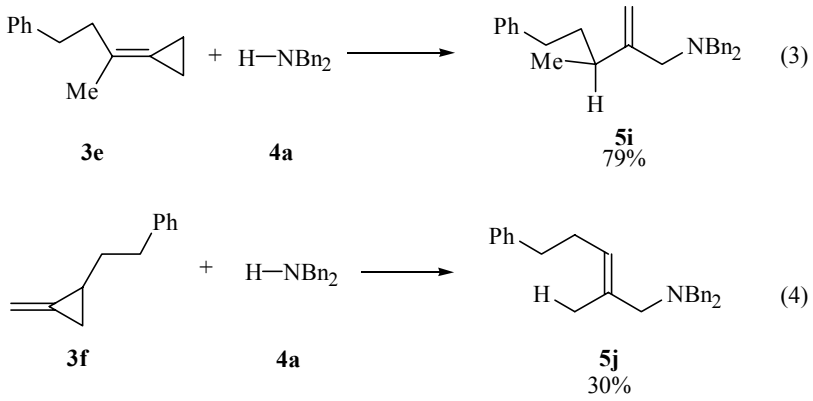
3a **4f** ; R = Bn
4g ; R = Ph



(2)

5g ; R = Bn 12%
5h ; R = Ph 50%

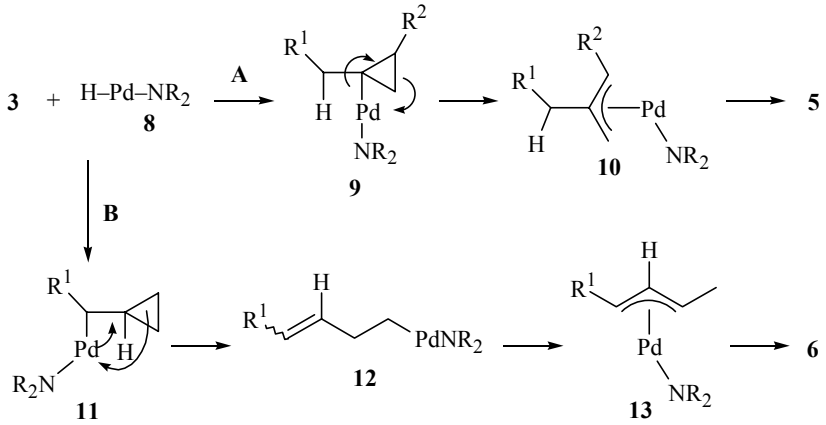
7a ; R = Bn 43%



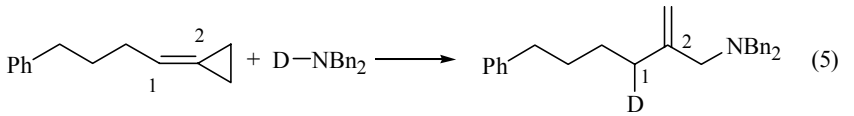
Mechanism

We propose the mechanism shown in Scheme 1 to explain the formation of **5** and **6**. Oxidative addition of zero-valent palladium into the nitrogen-hydrogen bond of amines would produce the hydridopalladium species **8** [25, 26], which would react with methylenecyclopropanes **3** *via* two different orientations; the Markovnikov hydropalladation (**A**) would produce **9**, whereas the anti-Markovnikov hydropalladation (**B**) would give **11** [27]. The distal bond cleavage of **9** would afford the π-allylpalladium intermediate **10**, leading to **5** and Pd(0) upon reductive coupling. The proximal bond cleavage of **11** would give homoallylpalladium **12** [28-30], which would undergo migration to π-allylpalladium **13**, and subsequent reductive coupling would produce **6** and Pd(0).

Scheme 1

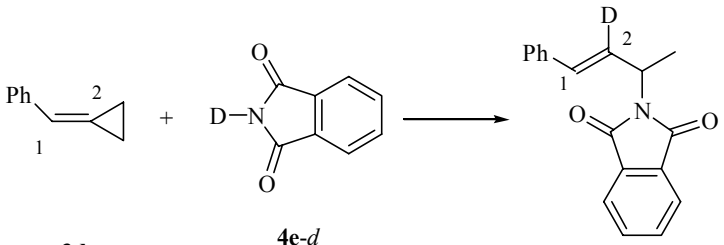


To confirm the hydroamination mechanism, the reactions of deuterated amines **4a**-*d* (D-content 86%) and **4e**-*d* (D-content 95%) were carried out. The reaction of **3a** with **4a**-*d* under the same conditions as above gave **5a**-*d* in 78% yield in which the deuterium content at the C(1) position was 63% (Eq. 5). Deuterium incorporation did not occur at the other carbons of **5a**. The result supports the Markovnikov hydropalladation mechanism. The reaction of **3d** with **4e**-*d* afforded **6b**-*d* in 75% yield in which the deuterium content at the C(2) position was 20%, and the other protons were not deuterated at all (Eq. 6). The loss of deuteriums most probably occurred on the way from **12** to **13**, which required a sequential process of β-hydride elimination-addition. In the reaction of **3d** with **4a**, 1-phenyl-1,3-butadiene **17** was obtained in 19% yield as a byproduct. This result clearly indicates that **17** was produced *via* the β-elimination of **12** (R^1 = Ph, R^2 = Bn).



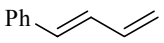
(5)

3a **4a**-*d* 86% D **5a**-*d* 78% yield 63% D



(6)

3d **4e**-*d* 95% D **6b**-*d* 75% yield 20% D



17

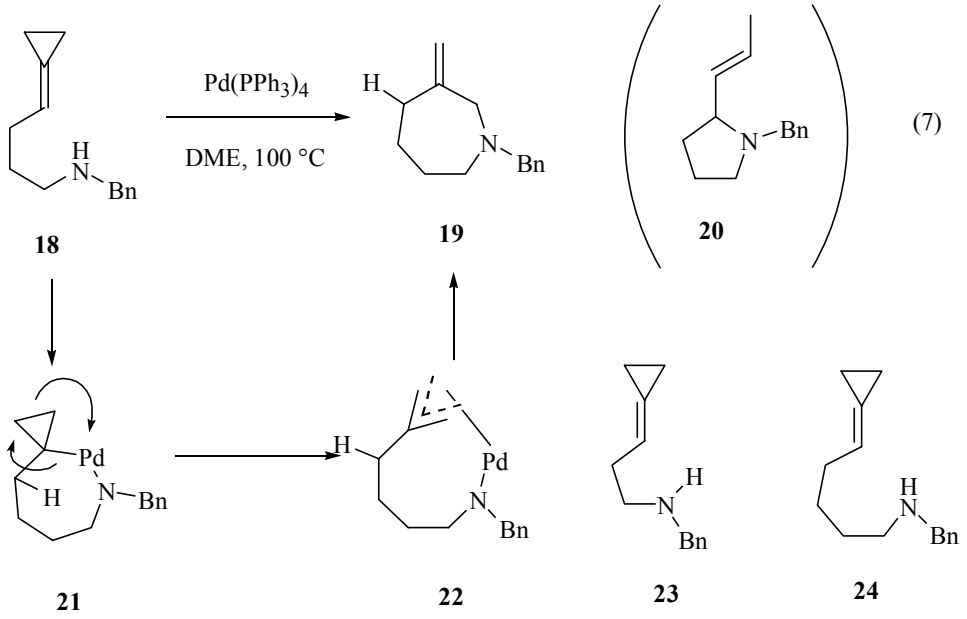
The regioselectivity of the hydropalladation and the ring-opening mode clearly depended on the substituent at the double bond of methylenecyclopropanes. Alkyl-substituents at the double bond tend to decrease the electron density on the C(1) atom of **3** and the hydropalladation proceeds *via* the Markovnikov type **2**. On the contrary, in the reaction of the phenyl-substituted methylenecyclopropane **3e**, the phenyl group increases the electron density on the C(1) atom and the hydropalladation proceeds through the anti-Markovnikov orientation **1**. AM1 calculations predicted higher negative charges on the C(1) atom of **3e**, compared to the C(1) atoms of **3a-c**.

Intramolecular Hydroamination

We extended the catalytic hydroamination of methylenecyclopropanes to the intramolecular version. In the presence of 5 mol% of $Pd(PPh_3)_4$, the reaction of **18** gave the corresponding azepane derivative **19** in 48% yield (Eq. 7). In this reaction other cyclized products such as **20** were not obtained. This reaction can be explained by the hydropalladation mechanism as shown in Scheme 1. The hydropalladation of **18** would give the cyclopropylpalladium species **21**, which would undergo a rearrangement to **22**. Subsequent reductive elimination of Pd(0) would produce **19**. The hydroamination reaction of **23** and **24** was attempted, but the desired cyclic amines were not afforded under the reaction conditions mentioned above.

Conclusion

The intermolecular hydroamination of methylenecyclopropanes with amines proceeds smoothly in the presence of palladium catalyst, giving the allylamines **5** (or **6**) in good to high yields. The intramolecular hydroamination gives cyclic allylamines in a moderate yield, although the structural variation of the intramolecular reaction is very limited. This reaction seems to be potentially useful for the synthesis of various types of allylamine derivatives, and further seems to be desirable from the eco-chemical point of view since the most previous syntheses of substituted amines need a substitution process and liberate a leaving group.



EXPERIMENTAL

General. Spectroscopic measurements were carried out with the following instruments: JEOL GSX-270 and JEOL LA-300 (^{1}H NMR), Shimadzu FTIR-8200A (FT-IR), Hitachi M-2500S (HRMS). Dehydrated tetrahydrofuran was purchased from Kanto Chemical Co. Methylenecyclopropanes were prepared by the reported procedure [31]. Palladium complex $[(\eta^3\text{-}C_3H_5)PdCl]_2$, dppp, amines, and all other dehydrated solvents were purchased from Wako Pure Chemical Inc.

General Procedure of the Addition of Nitrogen Pronucleophile 4 to Methylenecyclopropanes 3. To a mixture of methylenecyclopropanes **3** (1.0 mmol), $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (9.1 mg, 0.025 mmol), and dppp (25.8 mg, 0.0625 mmol) were added DME (1 ml) and nitrogen pronucleophiles **4** (0.5 mmol) under Ar atmosphere in a pressure vial. After heating at 100°C for 3 days, the mixture was filtered through a short florisil column using ethyl acetate as an eluent. Separation by passing though a florisil column (hexane–ethyl acetate as an eluent) and purification by middle-pressure liquid column chromatography (RP-18) using methanol as an eluent afforded adducts **5** or **6**.

N,N-Dibenzyl-2-methylene-6-phenylhexylamine (5a). IR (neat), ν, cm^{-1}: 3084-2711, 1645, 1602, 1494, 1452, 1367, 1244, 1120, 1028, 902, 746, 698. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.17 (m, 2H); 1.60 (m, 2H); 2.13 (t, *J* = 7.6, 2H); 2.53 (t, *J* = 7.8, 2H); 2.91 (s, 2H); 3.84 (s, 4H); 4.84 (s, 1H); 4.99 (s, 1H); 7.12-7.60 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 27.13, 31.29, 33.85, 35.84, 58.02, 59.14, 112.19, 125.56, 126.76, 128.13, 128.22, 128.35, 128.76, 139.81, 142.78, 147.61. HRMS (EI). Found: *m/z* 369.2444. $C_{27}H_{31}N$. Calculated: *m/z* 369.2455.

N,N-Diethyl-2-methylene-6-phenylhexylamine (5b). IR (neat), ν, cm^{-1}: 3064-2721, 1647, 1496, 1454, 1382, 1194, 1168, 1060, 896, 746, 698. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 0.98 (t, *J* = 7.2, 6H); 1.50 (m, 2H); 1.63 (m, 2H); 2.09 (t, *J* = 7.5, 2H); 2.44 (q, *J* = 7.1, 4H); 2.62 (t, *J* = 7.4, 2H); 2.90 (s, 2H); 4.81 (s, 1H); 4.90 (s, 1H); 7.14-7.29 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 11.62, 27.21, 31.16, 33.81, 35.85, 46.71, 58.86, 11.25, 125.35, 128.19, 128.39, 142.76, 148.09. HRMS (EI). Found: *m/z* 245.2144. $C_{17}H_{27}N$. Calculated: *m/z* 245.2142.

N-(2-Methylene-6-phenylhexyl)pyrrolidine (5c). IR (neat), ν, cm^{-1}: 3059, 2872, 1590, 1495, 1448, 1427, 1325, 1091, 1066, 966, 814, 750, 694, 667. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.53 (m, 2H); 1.66 (m, 2H); 1.76 (m, 4H); 2.11 (t, *J* = 7.5, 2H); 2.43 (m, 4H); 2.62 (t, *J* = 7.6, 2H); 2.97 (s, 2H); 4.79 (s, 1H); 4.91 (s, 1H); 7.13-7.41 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 23.49, 27.29, 31.12, 34.06, 35.84, 54.26, 62.05, 110.81, 125.55, 128.19, 128.40, 142.74, 147.67. HRMS (EI). Found: *m/z* 243.1989. $C_{17}H_{25}N$. Calculated: *m/z* 243.1987.

Di-*t*-butyl N-(2-methylene-6-phenylhexyl)iminodicarboxylate (5d). IR (neat), ν, cm^{-1}: 3084-2860, 1789, 1747, 1701, 1654, 1604, 1454, 1425, 1367, 1228, 1147, 1110, 891, 858, 748, 700. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.54 (s, 18H); 1.57 (m, 2H); 1.74 (m, 2H); 2.11 (t, *J* = 7.5, 2H); 2.68 (t, *J* = 7.6, 2H); 4.19 (s, 2H); 5.32 (s, 1H); 5.34 (s, 1H); 7.19-7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 27.14, 27.82, 31.02, 33.67, 35.60, 49.97, 81.98, 108.27, 125.48, 128.09, 128.20, 142.32, 144.91, 152.32. HRMS (EI). Found: *m/z* 389.2567. $C_{23}H_{35}NO_4$. Calculated: *m/z* 389.2566. Found, %: C 70.52; H 8.82; N 3.64. Calculated, %: C 70.92; H 9.06; N 3.60.

N,N-Dibenzyl-2-methylene-5-phenylpentylamine (5e). IR (neat), ν, cm^{-1}: 3084-2711, 1645, 1602, 1494, 1452, 1367, 1244, 1120, 1072, 1028, 974, 900, 746, 698. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm: 1.58 (m, 2H); 2.16 (m, 2H); 2.55 (m, 2H); 2.90 (s, 2H); 3.44 (s, 4H); 4.86 (s, 1H); 5.11 (s, 1H); 6.97-7.54 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 29.16, 33.61, 35.67, 58.04, 59.20, 112.86, 125.58, 126.74, 128.13, 128.46, 128.72, 139.72, 142.44, 147.41. HRMS (EI). Found: *m/z* 355.2292. $C_{26}H_{29}N$. Calculated: *m/z* 355.2298. Found, %: C 87.94; H 8.52; N 3.98. Calculated, %: C 87.84; H 8.22; N 3.94.

2-(Cyclohexylmethyl)-N,N-dibenzyl-2-propenylamine (5f). IR (neat), ν, cm^{-1}: 3064-2711, 1645, 1602, 1494, 1448, 1365, 1244, 1116, 1070, 1028, 972, 898, 746, 698. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 0.75 (m, 2H); 1.04 (m, 4H); 1.58 (m, 5H); 1.99 (d, *J* = 7.0, 2H); 2.94 (s, 2H); 3.47 (s, 4H); 4.80 (s, 1H); 5.00 (s, 1H); 7.18-7.60 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 26.28, 26.63, 33.30, 34.80, 42.27, 58.10, 58.79, 113.41, 126.74, 128.12, 128.83, 139.89, 146.14. HRMS (EI). Found: *m/z* 333.2457. $C_{24}H_{31}N$. Calculated: *m/z* 333.2455. Found, %: C 86.46; H 9.37; N 4.29. Calculated, %: C 86.43; H 9.37; N 4.20.

N-Benzyl-2-methylene-6-phenylhexylamine (5g). IR (neat), ν, cm^{-1}: 3084-2856, 1647, 1602, 1494, 1452, 1107, 1076, 1028, 970, 899, 804, 744, 698. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.46 (m, 2H); 1.61 (m, 2H); 2.12 (t, *J* = 7.5, 2H); 2.61 (t, *J* = 7.5, 2H); 3.19 (s, 2H); 3.72 (s, 2H); 4.85 (s, 1H); 4.94 (s, 1H); 7.14-7.41 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 27.35, 31.15, 34.17, 35.79, 53.10, 53.61, 110.05, 125.60, 126.88, 128.13, 128.23, 128.34, 128.36, 140.35, 142.61, 147.60. HRMS (EI). Found: *m/z* 279.1992. $C_{20}H_{25}N$. Calculated: *m/z* 279.1986.

N-(2-Methylene-6-phenylhexyl)aniline (5h). IR (neat), ν, cm^{-1}: 3084-2711, 1645, 1603, 1494, 1452, 1367, 1244, 1120, 1072, 1028, 985, 904, 746, 698. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.50 (m, 2H); 1.71 (m, 2H); 2.12 (t, *J* = 7.5, 2H); 2.63 (t, *J* = 7.5, 2H); 3.67 (s, 2H); 3.79 (s, 1H); 4.87 (s, 1H); 5.00 (s, 1H); 6.55-6.71 (m, 5H); 7.10-7.30 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 27.32, 31.14, 33.98, 35.76, 48.72, 110.21, 112.80, 117.29, 125.67, 128.27, 128.39, 129.15, 142.54, 146.57, 148.28. HRMS (EI). Found: *m/z* 265.1820. $C_{19}H_{23}N$. Calculated: *m/z* 265.1829.

N,N-Dibenzyl-3-methyl-2-methylene-5-phenylpentylamine (5i). IR (neat), ν, cm^{-1}: 3084-2711, 1643, 1602, 1494, 1452, 1371, 1244, 1122, 1072, 1028, 985, 902, 746, 698. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.01 (d, *J* = 6.8, 3H); 1.51 (m, 1H); 1.66 (m, 1H); 2.39 (m, 1H); 2.45 (t, *J* = 8.3, 2H); 2.96 (m, 2H); 3.50 (m, 4H); 4.92 (s, 1H); 5.16 (s, 1H); 7.03-7.37 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 19.58, 33.58, 36.22, 37.32, 58.24, 58.68, 110.90, 125.51, 126.76, 128.18, 128.19, 128.34, 128.69, 139.79, 142.77, 151.94. HRMS(EI). Found: *m/z* 369.2459. $C_{27}H_{31}N$. Calculated: *m/z* 369.2456.

N,N-Dibenzyl-2-methyl-5-phenyl-2-pentenylamine (5j). IR (neat), δ, cm^{-1}: 3084-2792, 1602, 1494, 1454, 1363, 1126, 1070, 1028, 744, 698, 665. ^{1}H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.60 (s, 3H); 2.33 (q, *J* = 7.5, 2H); 2.63 (t, *J* = 7.7, 2H); 2.85 (s, 2H); 3.43 (s, 4H); 5.40 (t, *J* = 7.1, 1H); 7.08-7.35 (m, 15H). ^{13}C NMR

($CDCl_3$, 75 MHz), δ, ppm: 14.84, 29.68, 35.85, 57.80, 62.60, 125.68, 126.64, 126.92, 128.09, 128.20, 128.41, 128.70, 134.20, 140.04, 142.07. HRMS (EI). Found: *m/z* 355.2271. $C_{26}H_{29}N$. Calculated: *m/z* 355.2298.

N,N-Dibenzyl-1-methyl-3-phenyl-2-propenylamine (6a). IR (neat), ν, cm^{-1}: 3084-2800, 1601, 1494, 1452, 1375, 1363, 1143, 1072, 1028, 970, 746, 696. ^1H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.28 (d, *J* = 6.6, 3H); 3.47 (m, 1H); 3.62 (m, 4H); 6.30 (dd, *J* = 16.2, 6.4, 1H); 6.43 (d, *J* = 16.2, 1H); 7.16-7.42 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 15.82, 53.66, 54.85, 126.25, 126.69, 127.26, 128.19, 128.52, 130.95, 131.62, 137.30, 140.56. HRMS (EI). Found: *m/z* 327.1989. $C_{24}H_{25}N$. Calculated: *m/z* 327.1986.

N-(1-Methyl-3-phenyl-2-propenyl)phthalimide (6b). IR (KBr), ν, cm^{-1}: 3055-2906, 1776, 1699, 1612, 1465, 1446, 1390, 1355, 1332, 1112, 1072, 1018, 974, 881, 750, 715, 692. ^1H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.67 (d, *J* = 7.0, 3H); 5.09 (m, 1H); 6.64 (m, 2H); 7.20-7.39 (m, 5H); 7.67-7.86 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 18.95, 48.92, 123.10, 126.51, 127.77, 128.05, 128.48, 131.94, 132.01, 133.84, 136.32, 167.93. HRMS (EI). Found: *m/z* 277.1103. $C_{18}H_{15}NO_2$. Calculated: *m/z* 277.1103.

N-Benzylbis(2-methylene-6-phenylhexyl)amine (7a). IR (neat), ν, cm^{-1}: 3084-2792, 1645, 1602, 1494, 1452, 1367, 1118, 1029, 898, 744, 698, 665. ^1H NMR ($CDCl_3$, 300 MHz), δ, ppm, *J* (Hz): 1.36 (m, 4H); 1.55 (m, 4H); 2.10 (t, *J* = 7.6, 4H); 2.56 (t, *J* = 7.7, 4H); 2.90 (s, 4H); 3.41 (s, 2H); 4.82 (s, 1H); 4.96 (s, 1H); 7.13-7.33 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 27.22, 31.34, 33.85, 35.88, 58.13, 59.26, 112.00, 125.57, 126.68, 128.07, 128.23, 128.36, 128.81, 140.02, 142.74, 147.70. HRMS (EI). Found: *m/z* 451.3236. $C_{33}H_{41}N$. Calculated: *m/z* 451.3239.

1-Benzyl-3-methyleneazepane (19). IR (neat), ν, cm^{-1}: 3064-2800, 1639, 1494, 1452, 1361, 1338, 1315, 1271, 1249, 1205, 1145, 1116, 1074, 1058, 1028, 983, 887, 736, 698. ^1H NMR ($CDCl_3$, 300 MHz), δ, ppm: 1.61 (m, 4H); 2.39 (m, 2H); 2.63 (m, 2H); 3.31 (s, 2H); 3.65 (s, 2H); 4.71 (m, 1H); 4.80 (m, 1H); 7.20-7.37 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ, ppm: 28.37, 29.35, 34.87, 55.49, 60.80, 61.31. HRMS (EI). Found: *m/z* 201.1522. $C_{14}H_{19}N$. Calculated: *m/z* 201.1517.

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