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A Direct Synthesis of 1-Aryl- and 1-Alkenylcyclopropylamines from Aryl and Alkenyl Nitriles

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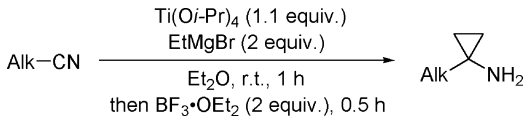
Abstract: The reaction of various aromatic nitriles with 1.1 equiv of Ti(O*i*-Pr)$_4$ and 2.2 equiv of EtMgBr followed by addition of a Lewis acid gave 1-aryl cyclopropylamines in 43−76% yields. Under similar conditions, conjugated alkenenitriles afford 1-alkenylcyclopropylamines (42−65%).

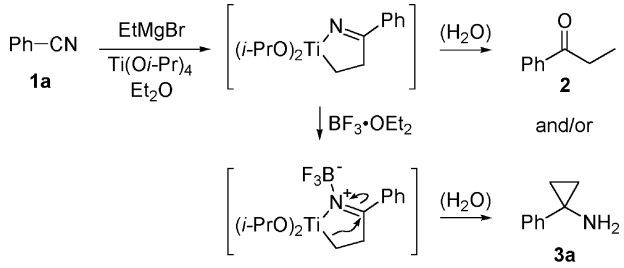
Aminocyclopropane moiety is frequently found in numerous biologically active substances such as natural amino acids[1] and synthetic drugs.[2] Recently, we proposed a method of preparing primary cyclopropylamines from aliphatic nitriles,[3] by the use of titanium isopropoxide and a Grignard reagent, and subsequent addition of a Lewis acid (Scheme 1). This reaction can be considered as an extension of the zirconium-mediated synthesis of cyclopropanes from carbonyl compounds.[4] It is related to the Kulinkovich[5] and de Meijere[6] conversions of esters and tertiary amides to cyclopropanols and tertiary cyclopropylamines, respectively.[7]

However, primary 1-arylcyclopropylamines were not accessible in good yield from aryl cyanides or amides by the above procedures.[3a,8] To overcome this problem, de Meijere et al. proposed very recently a new method for preparing 1-arylcyclopropylamines from aromatic nitriles, by using diethylzinc and MeTi(O*i*-Pr)$_3$ in the presence of lithium salts (*i*-PrOLi and LiI).[8] The yields obtained by this method are fair to good, depending on the substitution on the aromatic ring. These results led us to propose here our own solution of this problem through organomagnesium-based chemistry.

SCHEME 1



SCHEME 2



First, the optimization of the reaction was performed with benzonitrile (Scheme 2). When ethylmagnesium bromide was added to a solution of the nitrile and titanium isopropoxide in ether, only a small quantity of cyclopropylamine product **3a** was formed (15% yield) after 1 h, the main product being propiophenone (**2**, 31%). Letting the reaction continue longer (20 h) did not favor the formation of **3a**. However, the addition of a Lewis acid (BF$_3$•OEt$_2$) to the reaction mixture before hydrolysis increases significantly the yield of cyclopropylamine (47%). As for aliphatic nitriles, the role of the Lewis acid is important in the cyclization step leading to cyclopropane.

The yield of cyclopropylamine was further increased when modifying the experimental procedure. Most importantly, ethylmagnesium bromide (2.2 equiv) was added at lower temperature (−70 °C) before the reaction mixture was warmed to room temperature.[9] 1-Phenylcyclopropylamine (**3a**) was thus obtained in good yield (65%), similar to that obtained by the de Meijere procedure (62%).[8] Modification of these optimized conditions by the use of substoichiometric quantities of titanium alkoxide (0.2 equiv) or an excess of Grignard reagent (3 equiv) led to the total disappearance of the cyclopropylamine.

This procedure for the conversion of substituted aromatic nitriles[10] to 1-arylcyclopropylamines appears to be

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(3) (a) Bertus, P.; Szymoniak, J. *Chem. Commun.* **2001**, 1792−1793. (b) Bertus, P.; Szymoniak, J. *J. Org. Chem.* **2002**, *67*, 3965−3968. (c) Bertus, P.; Szymoniak, J. *Synlett* **2003**, 265−267. (d) Laroche, C.; Bertus, P.; Szymoniak, J. *Tetrahedron Lett.* **2003**, *44*, 2485−2487.

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(5) (a) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevsky, D. A.; Prityckaja, T. S. *Zh. Org. Khim.* **1989**, *25*, 2244−2245. (b) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevsky, D. A. *Synthesis* **1991**, 234. (c) See also: Lee, J.; Kim, H.; Cha, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 4198−4199.

(6) (a) Chaplinski, V.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 413−414. (b) Chaplinski, V.; Winsel, H.; Kordes, M.; de Meijere, A. *Synlett* **1997**, 111−114. (c) Kordes, M.; Winsel, H.; de Meijere, A. *Eur. J. Org. Chem.* **2000**, 3235−3245. (d) See also: Lee, J.; Cha, J. K. *J. Org. Chem.* **1997**, *62*, 1584−1585.

(7) Reviews: (a) de Meijere, A.; Kulinkovich, O. G. *Chem. Rev.* **2000**, *100*, 2789−2834. (b) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835−2886. (c) de Meijere, A.; Koshushkov, S. I.; Savchenko, A. I. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; pp 390−434.

(8) Wiedemann, S.; Frank, D.; Winsel, H.; de Meijere, A. *Org. Lett.* **2003**, *5*, 753−755.

(9) Similarly, the Kulinkovich conversion of aromatic esters to aryl cyclopropanols is best performed when the reagents are mixed at low temperature, and warmed afterwards to 0 °C. See: Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A.; Savchenko, A. I.; Prityts kaya, T. S. *Zh. Org. Khim.* **1991**, *27*, 294−298; *J. Org. Chem. USSR* **1991**, *27*, 250−253.

(10) Nitriles **1b**−**f**, **1h**, **1k**, and **6a**−**e** were conveniently prepared in good yields from the corresponding aldehydes by action of I$_2$/NH$_4$-OH. See: Talukdar, S.; Hsu, J.-L.; Chou, T.-C.; Fang, J.-M. *Tetrahedron Lett.* **2001**, *42*, 1103−1105.

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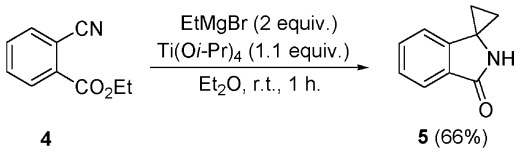
TABLE 1. Preparation of 1-Arylcyclopropylamines

Entry	Nitrile	Product	Yield[a] (%)
1	**1b** R = OMe	**3b**	43
2	**1c** R = Me	**3c**	73
3	**1d** R = F	**3d**	64
4	**1e** R = OMe	**3e**	73
5	**1f** R = Cl	**3f**	72
6	**1g** R = Br	**3g**	76
7	**1h** R = OMe	**3h**	58
8	**1i** R = Br	**3i**	71
9	**1j**	**3j**	57
10	**1k**	**3k**	57

[a] Isolated yields.

SCHEME 3



4 **5** (66%)

general, as shown in Table 1. The cyclopropanation occurred smoothly with the acceptor as well as the alkyl-substituted nitriles (entries 2, 3, 5, 6, and 8). Starting from the donor-substituted nitriles, however, the yield depends on the substitution pattern, *o*- and *p*-methoxy substituted benzonitriles giving lower yields than the *m*-methoxy substituted benzonitrile (entries 1 and 7 vs 4). Isomeric 1-naphthyl cyclopropylamines **3j**,**k** were obtained in comparable yields (entres 9−10). A sterically crowded cyanide, i.e., 2,4,6-trimethylbenzonitrile, could also be used, but the yield was low (15%).

Starting from ethyl *o*-cyanobenzoate (**4**),[11] the spirocyclic lactam **5** was directly obtained, via a cyclopropanation−lactamization sequence (Scheme 3). This reaction was best performed at room temperature. As observed for aliphatic β-cyanoesters, the addition of a Lewis acid is not required.[3c] Several natural and synthetic isoindolin-1-one moieties are biologically active products.[12] The presented method thus provides easy access to the analogues bearing a cyclopropane ring.

When higher Grignard reagents were used, 1,2-substituted cyclopropylamines were formed albeit in low yield. For example, a 25% yield of 2-ethyl-1-phenylcyclopropylamine was obtained from benzonitrile and either *n*-BuMgBr or *s*-BuMgBr.

(11) Nitrile **4** was prepared from phthalic anhydride according to: Carpino, L. A. *J. Am. Chem. Soc.* **1962**, *84*, 2196−2201.

(12) Kundu, N. G.; Wahab Khan, M. *Tetrahedron* **2000**, *56*, 4777−4792 and references therein.

TABLE 2. Preparation of 1-Alkenylcyclopropylamines

Entry	Nitrile		Product		Yield[a] (%)
1	Ph, CN	**6a**	Ph, NH_2	**7a**	65
2	*n*-C_7H_{15}, CN	**6b**	*n*-C_7H_{15}, NH_2	**7b**	50
3	O, CN	**6c**	O, NH_2	**7c**	42
4	Ph, CN, Me	**6d**	Ph, NH_2, Me	**7d**	46
5	CN	**6e**	NH_2	**7e**	62

[a] Isolated yields.

1-Alkenylcyclopropylamines contain both vinylcyclopropane and cyclopropylamine moieties. Despite their great synthetic potential, only a few syntheses of vinylcyclopropylamines have been reported.[13,14] These compounds were mostly used as intermediates for the synthesis of 2,3-methanoamino acids.[13]

With the conditions we used for aryl nitriles, the α,β-unsaturated nitriles can be converted to the corresponding cyclopropylamines. Representative examples are shown in Table 2. The reaction employing (*E*)-cinnamonitrile and (*E*)-2-decenenitrile proceeded smoothly to afford the cyclopropylamines **7a** and **7b** in satisfactory yields and without isomerization of the double bond (entries 1 and 2). Starting from 3-(2-furyl)acrylonitrile (**6c**), however, the yield was lower, possibly due to the instability of the product (entry 3). 2,3-Substituted alkenenitriles **6d** and **6e** reacted in a similar way (entries 4 and 5).

In summary, we have presented an easy preparation of primary 1-arylcyclopropylamines from readily available and cheap starting materials and reagents. Moreover, this method provides rapid access to 1-alkenylcyclopropylamines. The synthetic potential of these compounds is currently studied in our laboratory.

Experimental Section[15]

General Procedure for the Synthesis of Cyclopropylamines 3a−k and 7a−e. Ethylmagnesium bromide (2.2 mmol, 1 to 2 M in ether) was added at −70 °C to a solution of a nitrile (1 mmol) and Ti(O*i*-Pr)$_4$ (0.33 mL, 1.1 mmol) in Et_2O (5 mL). The yellow solution was stirred for 10 min. After the solution was warmed to rt (1 h), $BF_3{\cdot}OEt_2$ (0.25 mL, 2 mmol) was added. After the mixture was stirred for 1 h, 1 N HCl (ca. 3 mL) and ether (ca. 15 mL) were added. NaOH (10% aq, ca. 10 mL) was added to the resulting two clear phases and the mixture was

(13) (a) Aufranc, P.; Ollivier, J.; Stolle, A.; Bremer, C.; Es-Sayed, M.; de Meijere, A.; Salaün, J. *Tetrahedron Lett.* **1993**, *34*, 4193−4196. (b) Atlan, V.; Racouchot, S.; Rubin, M.; Bremer, C.; Ollivier, J.; de Meijere, A.; Salaün, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1131−1135. (c) Racouchot, S.; Ollivier, J.; Salaün, J. *Synlett* **2000**, 1729−1732. (d) Racouchot, S.; Sylvestre, I.; Ollivier, J.; Kozyrkov, Y. Y.; Pukin, A.; Kulinkovich, O. G.; Salaün, J. *Eur. J. Org. Chem.* **2002**, 2160−2176.

(14) The Ti(II)-mediated conversion of amides into tertiary cyclopropylamines has never been applied to synthesize vinylcyclopropylamines, see ref 7. Similarly, unsaturated esters did not convert efficiently to vinylcyclopropanols, see ref 13d.

(15) For general experimental methods, see ref 3b.

extracted with ether. The combined ether layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Et_2O).

1-Phenylcyclopropylamine (3a).[8,16] Colorless oil; 65% yield (87 mg); IR (neat) 3365, 1601, 1496, 1454 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.94−1.10 (m, 4 H), 1.96 (br s, 2 H), 7.14−7.35 (m, 5 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.8, 36.7, 125.3, 125.9, 128.3, 146.9; MS *m/z* (%) 133 ($M^{+\bullet}$, 16), 162 (78), 134 (100). Anal. Calcd for $C_9H_{11}N\cdot HCl$: C, 63.72; H, 7.13; N, 8.26. Found: C, 63.57; H, 7.16; N, 7.90.

1-(4-Methoxyphenyl)cyclopropylamine (3b).[17] Pale yellow oil; 43% yield (70 mg); IR (neat) 3366, 1513 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.85−1.00 (m, 4 H), 1.86 (br s, 2 H), 3.75 (s, 3 H), 6.84 (d, J = 8.9 Hz, 2 H), 7.23 (d, J = 8.9 Hz, 2 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 16.9, 36.4, 55.2, 113.6, 126.8, 139.0, 157.8; MS *m/z* (%) 163 ($M^{+\bullet}$, 16), 162 (78), 134 (100). Anal. Calcd for $C_{10}H_{13}NO\cdot HCl$: C, 60.15; H, 7.07; N, 7.01. Found: C, 59.87; H, 7.20; N, 6.82.

1-(4-Methylphenyl)cyclopropylamine (3c).[8] White solid; 73% yield (107 mg); mp 92−94 °C; IR (neat) 3364, 1515, 1451 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.91−1.04 (m, 4 H), 1.88 (br s, 2 H), 2.33 (s, 3 H), 7.12 (d, J = 8.1 Hz, 2 H), 7.24 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.3, 20.8, 36.4, 125.3, 128.9, 135.4, 143.8; MS *m/z* (%) 147 ($M^{+\bullet}$, 15), 146 (89), 132 (100), 118 (94). Anal. Calcd for $C_{10}H_{13}N\cdot HCl$: C, 65.39; H, 7.68; N, 7.63. Found: C, 65.35; H, 7.87; N, 7.44.

1-(4-Fluorophenyl)cyclopropylamine (3d).[8] Pale yellow oil; 64% yield (94 mg); IR (neat) 3363, 1601, 1511, 1223 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.89−1.06 (m, 4 H), 1.86 (br s, 2 H), 6.96 (t, J = 8.7 Hz, 2 H), 7.25 (dd, J = 8.7, 5.4 Hz, 2 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.3, 36.9, 114,7 (d, J_{C-F} = 21.0 Hz), 127.1 (d, J_{C-F} = 7.5 Hz), 142.5, 161.1 (d, J_{C-F} = 243.9 Hz); ^{19}F NMR (235 MHz, $CDCl_3$) δ −117.7 (tt, J = 8.5, 5.4 Hz); MS *m/z* (%) 151 ($M^{+\bullet}$, 32), 150 (100), 122 (87). Anal. Calcd for $C_9H_{10}FN\cdot HCl$: C, 57.61; H, 5.91; N, 7.46. Found: C, 57.56; H, 5.69; N, 7.33.

1-(3-Methoxyphenyl)cyclopropylamine (3e). Colorless oil; 73% yield (119 mg); IR (neat) 3365, 1603, 1581 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.95−1.10 (m, 4 H), 1.90 (br s, 2 H), 3.79 (s, 3 H), 6.72 (dd, J = 8.2, 2.2 Hz, 1 H), 6.82−6.88 (m, 2 H), 7.22 (t, J = 8.2 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.9, 36.5, 55.0, 110.8, 111.4, 117.5, 129.2, 148.7, 159.5; MS *m/z* (%) 163 ($M^{+\bullet}$, 18), 162 (76), 134 (68), 132 (100). Anal. Calcd for $C_{10}H_{13}NO\cdot HCl$: C, 60.15; H, 7.07; N, 7.01. Found: C, 60.36; H, 7.25; N, 6.98.

1-(3-Chlorophenyl)cyclopropylamine (3f). Colorless oil; 72% yield (122 mg); IR (neat) 3371, 1597, 1569 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.91−1.10 (m, 4 H), 1.91 (br s, 2 H), 7.09−7.30 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.3, 36.3, 123.2, 125.5, 125.8, 129.5, 134.1, 149.1; MS *m/z* (%) 168 (M − H, 19), 166 (M − H, 56), 140 (28), 138 (78), 132 (95), 75 (100). Anal. Calcd for $C_9H_{10}ClN\cdot HCl$: C, 52.96; H, 5.43; N, 6.86. Found: C, 53.10; H, 5.42; N, 6.83.

1-(3-Bromophenyl)cyclopropylamine (3g). Colorless oil; 76% yield (161 mg); IR (neat) 3373, 1594, 1564 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.92−1.12 (m, 4 H), 1.82 (br s, 2 H), 7.10−7.18 (m, 2 H), 7.25−7.33 (m, 1 H), 7.42−7.45 (m, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.2, 36.2, 122.4, 123.6, 128.4, 128.7, 129.7, 149.4; MS *m/z* (%) 212 (M − H, 23), 210 (M − H, 26), 184 (48), 182 (47), 132 (100). Anal. Calcd for $C_9H_{10}BrN\cdot HCl$: C, 43.49; H, 4.46; N, 5.64. Found: C, 43.34; H, 4.47; N, 5.40.

1-(2-Methoxyphenyl)cyclopropylamine (3h).[8] White solid; 58% yield (95 mg); mp 47−48 °C; IR (KBr) 3338, 1599, 1582, 1490, 1232 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.79−0.93 (m, 4 H), 2.12 (br s, 2 H), 3.89 (s, 3 H), 6.84−6.89 (m, 2 H), 7.18−7.23 (m, 2 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.9, 34.8, 55.1, 110.3, 120.1, 127.8, 127.9, 133.9, 158.4; MS *m/z* (%) 163 ($M^{+\bullet}$, 14), 162 (100), 148 (50). Anal. Calcd for $C_{10}H_{13}NO\cdot HCl$: C, 60.15; H, 7.07; N, 7.01. Found: C, 59.95; H, 7.45; N, 6.84.

1-(2-Bromophenyl)cyclopropylamine (3i). Colorless oil; 71% yield (151 mg); IR (neat) 3370, 1588, 1564, 1468 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.88−0.93 (m, 2 H), 1.05−1.11 (m, 2 H), 2.09 (br s, 2 H), 7.10 (td, J = 7.8, 1.8 Hz, 1 H), 7.24 (td, J = 7.6, 1.1 Hz, 1 H), 7. 35 (dd, J = 7.6, 1.8 Hz, 1 H), 7.56 (dd, J = 7.8, 1.1 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 15.3, 38.6, 125.3, 127.4, 128.3, 130.1, 133.0, 144.4; MS *m/z* (%) 213 ($M^{+\bullet}$, 12), 212 (98), 211 ($M^{+\bullet}$, 26), 210 (100). Anal. Calcd for $C_9H_{10}BrN\cdot HCl$: C, 43.49; H, 4.46; N, 5.64. Found: C, 43.84; H, 4.23; N, 5.62.

1-(1-Naphthyl)cyclopropylamine (3j).[8] Pale yellow oil; 57% yield (104 mg); IR (neat) 3363, 1594, 1508 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.00−1.07 (m, 2 H), 1.16−1.23 (m, 2 H), 1.95 (br s, 2 H), 7.37−7.63 (m, 4 H), 7.76 (d, J = 8.1 Hz, 1 H), 7.90 (d, J = 8.0 Hz, 1 H), 8.45 (d, J = 8.3 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.7, 36.3, 124.1, 125.2, 125.5, 125.6, 126.0, 127.5, 128.8, 131.5, 134.1, 141.9; MS *m/z* (%) 183 ($M^{+\bullet}$, 34), 182 (100), 154 (50). Anal. Calcd for $C_{13}H_{13}N\cdot HCl$: C, 71.07; H, 6.42; N, 6.38. Found: C, 70.93; H, 6.40; N, 6.28.

1-(2-Naphthyl)cyclopropylamine (3k). Pale yellow oil; 57% yield (104 mg); IR (neat) 3377, 1631, 1598 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.01−1.11 (m, 4 H), 1.92 (br s, 2 H), 7.24 (d, J = 8.6 Hz, 1 H), 7.33−7.48 (m, 2 H), 7.70−7.78 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.7, 36.7, 123.4, 123.9, 125.2, 126.0, 127.3, 127.5, 128.0, 131.7, 133.1, 144.1; MS *m/z* (%) 183 ($M^{+\bullet}$, 50), 182 (100), 154 (92). Anal. Calcd for $C_{13}H_{13}N\cdot HCl$: C, 71.07; H, 6.42; N, 6.38. Found: C, 70.83; H, 6.31; N, 6.31.

Spiro[cyclopropane-1,3′-(2′,3′-dihydro-1′-isoindolone)] (5). Ethylmagnesium bromide (2.0 mmol, 1 to 2 M in ether) was added at rt to a solution of **4** (1 mmol) and Ti(O*i*-Pr)$_4$ (0.33 mL, 1.1 mmol) in Et_2O (5 mL). After the mixture was stirred for 1 h, 1 N HCl (ca. 3 mL) and CH_2Cl_2 (ca. 15 mL) were added. The mixture was then extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH_2Cl_2−acetone 8:2) giving **5** as a white solid; 73% yield (116 mg); mp 164−166 °C; IR (KBr) 3188, 1707, 1650 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.42−1.68 (m, 4 H), 7.08 (d, J = 7.6 Hz, 1 H), 7.44 (t, J = 7.5 Hz, 1 H), 7.88 (t, J = 7.3 Hz, 1 H), 7.88 (d, J = 7.3 Hz, 1 H), 8.38 (br s, 1 H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 13.6, 41.8, 117.8, 123.5, 127.0, 131.6, 131.8, 148.7, 171.2. Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.11; H, 5.76; N, 8.69.

1-(2-Phenylvinyl)cyclopropylamine (7a).[13a] Colorless oil; 65% yield (103 mg); IR (neat) 3367, 1645, 1600, 1493, 1448 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.74−0.81 (m, 2 H), 0.94−1.01 (m, 2 H), 1.76 (br s, 2 H), 5.94 (d, J = 15.9 Hz, 1 H), 6.46 (d, J = 15.9 Hz, 1 H), 7.11−7.32 (m, 5 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.3, 35.5, 125.2, 125.7, 126.6, 128.4, 137.2, 138.1; MS *m/z* (%) 159 ($M^{+\bullet}$, 25), 158 (100), 130 (51). Anal. Calcd for $C_{11}H_{13}N\cdot HCl$: C, 67.51; H, 7.21; N, 7.16. Found: C, 67.12; H, 7.18; N, 7.11.

1-(1-Nonenyl)cyclopropylamine (7b). Colorless oil; 50% yield (91 mg); IR (neat) 3370, 1466 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.55−0.61 (m, 2 H), 0.79−0.90 (m, 5 H), 1.18−1.35 (m, 10 H), 1.71 (br s, 2 H), 2.02 (q, J = 6.7 Hz, 2 H), 5.20 (d, J = 15.4 Hz, 1 H), 5.51 (dt, J = 15.4, 6.7 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.0, 16.3, 22.6, 29.1, 29.1, 29.7, 31.8, 32.1, 34.7, 125.9, 137.2; MS *m/z* (%) 181 ($M^{+\bullet}$, 6), 152 (20), 110 (67), 82 (100), 130 (51). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79. Found: C, 79.55; H, 13.17.

1-[2-(2-Furanyl)vinyl]cyclopropylamine (7c). Orange oil; 42% yield (63 mg); IR (neat) 3358, 1656, 1601, 1491, 1150 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.75−0.81 (m, 2 H), 0.94−1.00 (m, 2 H), 1.75 (br s, 2 H), 5.94 (dd, J = 15.8, 1.0 Hz, 1 H), 6.14 (d, J = 2.8 Hz, 1 H), 6.30−6.36 (m, 2 H), 7.29 (s, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.5, 35.4, 105.9, 111.2, 114.2, 137.2, 141.1, 153.0; MS *m/z* (%) 149 ($M^{+\bullet}$, 37), 148 (37), 121 (38), 120 (100). Anal. Calcd for $C_9H_{11}NO\cdot HCl$: C, 58.23; H, 6.52; N, 7.54. Found: C, 58.28; H, 6.41; N, 7.26.

1-(1-Methyl-2-phenylvinyl)cyclopropylamine (7d). Pale yellow oil; 46% yield (80 mg); IR (neat) 3369, 1632, 1600, 1492, 1444 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.80−0.86 (m, 4 H), 1.82 (br s, 2 H), 1.86 (s, 3 H), 6.52 (s, 1 H), 7.18−7.34 (m, 5 H);

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^{13}C NMR (63 MHz, $CDCl_3$) δ 14.6, 15.2, 40.3, 123.9, 126.0, 128.0, 128.8, 138.2, 141.5; MS *m*/*z* (%) 173 ($M^{+\bullet}$, 19), 172 (74), 158 (100), 115 (98). Anal. Calcd for $C_{12}H_{15}N\cdot HCl$: C, 68.73; H, 7.69; N, 6.68. Found: C, 68.80; H, 7.82; N, 6.72.

1-(6,6-Dimethylbicyclo[3.1.1]hept-2-enyl)cyclopropylamine (7e). Colorless oil; 62% yield (110 mg); IR (neat) 3365, 1637 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.62−0.67 (m, 4 H), 0.79 (s, 3 H), 1.12 (d, J = 8.6 Hz, 1 H), 1.28 (s, 3 H), 1.71 (br s, 2 H), 1.94 (br t, J = 5.6 Hz, 1 H), 2.05−2.14 (m, 1 H), 2.22−2.42 (m, 3 H), 5.36−5.41 (m, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 12.7, 21.1, 26.2, 31.0, 31.5, 36.6, 37.6, 40.7, 42.9, 114.1, 151.3; MS *m*/*z* (%) 177 ($M^{+\bullet}$, 3), 176 (4), 162 (12), 136 (60), 108 (100). Anal. Calcd for $C_{12}H_{19}N\cdot HCl$: C, 67.43; H, 9.43; N, 6.55. Found: C, 67.29; H, 9.47; N, 6.49.

Supporting Information Available: ^{1}H spectra for compounds **7a**−**e** and ^{13}C spectra for compounds **3e**−**g**, **3i**, **3k**, **5**, and **7a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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