Primary 1-Arylcyclopropylamines from Aryl Cyanides with Diethylzinc and Titanium Alkoxides

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Supporting Information

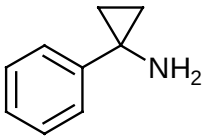
General Remarks: All chemicals used are commercially available. All reactions were performed in anhydrous solvents under an atmosphere of N_2. Solvents were dried under N_2 with sodium. Reactions were monitored by thin-layer chromatography on silica gel plates (Macherey-Nagel SIL G/UV_{254}). The chromatograms were visualized by UV light or ninhydrine. Silica gel 60 (0.063–0.200 mm, 230–400 mesh) obtained from E. Merck, Darmstadt (VWR Intl) were used for column chromatography. Eluents were distilled before use. NMR spectra were recorded on a Bruker AM 250 instrument at 250 MHz (^{1}H) and at 62.9 MHz (^{13}C) in $CDCl_3$. Chemical shifts are reported in ppm relative to C*H*Cl_3 (^{1}H, 7.26 ppm) and *C*DCl_3 (^{13}C, 77.0 ppm) as internal standards. ^{13}C NMR spectral assignments are supported by DEPT analysis; *designates interchangeable assignments. Infrared spectra were recorded on a Bruker IFS 66 (FT-IR) instrument. Mass spectra were recorded using Varian MAT CH 7, MAT 731 and Varian MAT 311 A (for HRMS) instruments. Microanalyses were carried out by the Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Universität Göttingen. Melting points were measured using a Büchi 510 capillary melting point apparatous and are uncorrected.

Optimized Procedure for the Reductive Cyclopropanation of *N*,*N*-Dibenzylformamide with Diethylzinc to Yield *N*,*N*-Dibenzylaminocyclopropane (2)

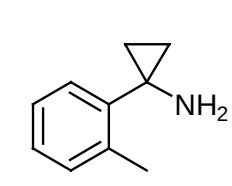
To a solution of 1.13 g (5 mmol) of *N*,*N*-dibenzylformamide, 1.44 g (6 mmol) of $MeTi(OiPr)_3$ and 820 mg (10 mmol) of NaOiPr in 10 mL of THF was added 1 mL (10 mmol) of diethylzinc. The resulting dark mixture was stirred at room temperature overnight. The reaction was quenched by careful addition of 2 mL of H_2O, and the mixture was filtered. The residue was washed with diethyl ether (3 10 mL), and the two layers were separated. The aqueous phase was extracted with diethyl ether (2 10 mL), the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography eluting with pentane/diethyl ether 1 : 10 (R_f = 0.65) to afford 1.05 g (89%) of **2** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.30–0.37 (m, 2 H, *c*Pr-H), 0.40–0.47 (m, 2 H, cPr-H), 1.80–1.87 (m, 1 H, 1-H), 3.69 (s, 4 H, NCH_2), 7.26–7.36 (m, 10 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 7.6 (–, 2 C, *c*Pr-C), 36.2 (+, 1 C, C-1), 58.2 (–, 2 C, NCH_2), 126.7 (+, 2 C, Ph-C), 127.9 (+, 4 C, Ph-C), 129.4 (+, 4 C, Ph-C), 138.6 (C_{quat}, 2 C, Ph-C).

General Procedure for the Reductive Cyclopropanation of Aromatic Nitriles (GP): To a solution of LiOiPr (660 mg, 10 mmol) in 10 mL of THF was added LiI (1.34 g, 10 mmol), then carefully $MeTi(OiPr)_3$ (1.2 g, 5 mmol) and 4 mmol of the respective nitrile. Subsequently a solution of Et_2Zn (0.5 mL, 5 mmol) in 10 mL of THF was added dropwise within 60 min. The mixture was stirred at 20 °C for an additional 8 h. Then the reaction was quenched by addition of 2 mL of H_2O. The resulting slurry was stirred until the color had turned yellow. The precipitate was filtered off and washed with diethyl ether (3 10 mL). The combined filtrates were washed with H_2O (3 10 mL) to remove the inorganic salts. The combined aqueous solutions were extracted with ether (3 10 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed, and the residue subjected to column chromatography.

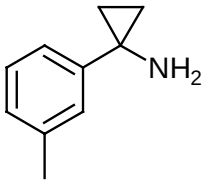
1-Phenylcyclopropylamine (4a): According to GP, benzonitrile (412 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.24) 330 mg (62%) of **4a** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.96–1.01 (m, 2 H, *c*Pr-H), 1.06–1.10 (m, 2 H, *c*Pr-H), 2.03 (bs, 2 H, NH_2), 7.16–7.43 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 17.8 (–, 2 C, *c*Pr-C), 36.7 (C_{quat}, 1 C, C-1), 125.4 (+, 2 C, C-2', C-6'), 125.9 (+, 1 C, C-4'), 128.4 (+, 2 C, C-3', C-5'), 146.9 (C_{quat}, 1 C, C-1').[14]



1-(2'-Methylphenyl)cyclopropylamine (4b): According to GP 2-methylbenzonitrile (468 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.20) 319 mg (54%) of **4b** as a colorless oil. – IR (film): = 3275 cm^{-1}, 3060, 3018, 2967, 2927, 2875, 1684, 1653, 1457, 1380, 1287, 1267, 1030. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.85–0.89 (m, 2 H, *c*Pr-H), 1.00–1.04 (m, 2 H, *c*Pr-H), 2.24 (bs, 2 H, NH_2), 2.51 (s, 3 H, CH_3), 7.06–7.20 (m, 3 H, Ph-H), 7.31–7.34 (m, 1 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 14.9 (–, 2 C, *c*Pr-C), 19.1 (+, 1 C, CH_3), 37.0 (C_{quat}, 1 C, C-1), 126.0 (+, 1 C, Ph-C), 127.0 (+, 1 C, Ph-C), 128.6 (+, 1 C, Ph-C), 130.6 (+, 1 C, Ph-C), 137.1 (C_{quat}, 1 C, C-2'), 143.6 (C_{quat}, 1 C, C-1'). – MS (70 eV), *m*/*z* (%): 146 (100) [M^+ – H], 132 (83), 118 (75), 105 (4), 91 (25), 77 (4).



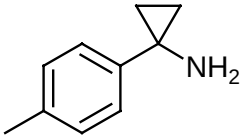
1-(3'-Methylphenyl)cyclopropylamine (4c): According to GP, 3-methylbenzonitrile (468 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.19) 310 mg (53%) of **4c** as a colorless solid, m. p. 95 °C. – IR (KBr): = 3376 cm^{-1}, 3017, 2922, 2860, 1700, 1684, 1653, 1559, 1506, 1457, 1387, 1091. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.96–1.01 (m, 2 H, *c*Pr-H), 1.06–1.10 (m, 2 H, *c*Pr-H), 1.93 (bs, 2 H, NH_2), 2.38 (s, 3 H, CH_3), 7.00–7.24 (m, 4 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 17.7 (–, 2 C, *c*Pr-C), 21.5



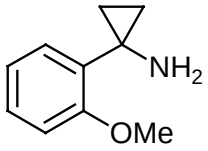
[14] For a classical preparation of **7a** see: Bonnekessel J., Rüchardt C. *Chem. Ber.* **1973**, *106*, 2890–2903.

(+, 1 C, CH_3), 36.0 (C_{quat}, 1 C, C-1), 122.4 (+, 1 C, C-2'*), 126.2 (+, 1 C, C-4'*), 126.7 (+, 1 C, C-5'*), 131.9 (+, 1 C, C-6'*), 138.0 (C_{quat}, 1 C, C-3'), 147.0 (C_{quat}, 1 C, C-1'). – MS (70 eV), *m*/*z* (%): 146 (100) [M^+ – H], 132 (100), 118 (62), 105 (8), 91 (16), 77 (4).

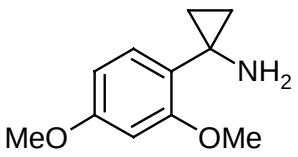
1-(4'-Methylphenyl)cyclopropylamine (4d): According to GP, 4-methylbenzonitrile (468 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.20) 330 mg (56%) of **4d** as a colorless solid, m. p. 79 °C. –IR (KBr): = 3365 cm^{-1}, 3088, 3007, 2921, 2866, 1901, 1616, 1515, 1456, 1317, 1301, 1268, 1128, 1116, 1092, 1014, 875. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.91–0.98 (m, 2 H, *c*Pr-H), 1.00–1.06 (m, 2 H, *c*Pr-H), 1.86 (bs, 2 H, NH_2), 2.32 (s, 3 H, CH_3), 7.12 (d, ^3J = 8.2 Hz, 2 H, 3'-H, 5'-H), 7.20 (d, ^3J = 8.2 Hz, 2 H, 2'-H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 17.5 (–, 2 C, *c*Pr-C), 20.9 (+, 1 C, CH_3), 36.5 (C_{quat}, 1 C, C-1), 125.4 (+, 2 C, C-3', C-5'), 129.1 (+, 2 C, C-2', C-6'), 135.5 (C_{quat}, 1 C, C-4'), 144.0 (C_{quat}, 1 C, C-1'). – MS (70 eV), *m*/*z* (%): 146 (100) [M^+ – H], 132 (83), 118 (75), 105 (4), 91 (25), 77 (4).



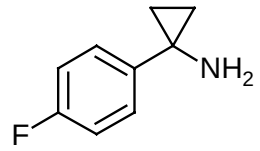
1-(2'-Methoxyphenyl)cyclopropylamine (4e): According to GP 2-methoxybenzonitrile (532 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.05) 310 mg (46%) of **4e** as a colorless solid, m. p. 46 °C. – IR (KBr): = 3371 cm^{-1}, 3051, 3009, 2963, 2837, 1653, 1490, 1457, 1288, 1265, 1235, 1181, 1091, 1046, 1029, 880, 852, 788. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.79–0.86 (m, 2 H, *c*Pr-H), 0.89–0.96 (m, 2 H, *c*Pr-H), 2.17 (bs, 2 H, NH_2), 3.91 (s, 3 H, OCH_3), 6.84–6.90 (m, 2 H, Ph-H), 7.19–7.26 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 14.0 (–, 2 C, *c*Pr-C), 34.9 (C_{quat}, 1 C, 1-C), 55.2 (+, 1 C, OCH_3), 110.0 (+, 1 C, C-3'), 120.2 (+, 1 C, C-5'), 127.9 (+, 1 C, C-4'*), 128.0 (+, 1 C, C-6'*), 134.0 (C_{quat}, 1 C, C-1'), 158.5 (C_{quat}, 1 C, C-2'). – MS (70 eV), *m*/*z* (%): 162 (100) [M^+ – H], 148 (37), 134 (23), 119 (8), 104 (14), 91 (11), 77 (9). – Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.34; H, 7.80; N, 8.36.



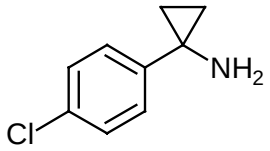
1-(2',4'-Dimethoxyphenyl)cyclopropylamine (4f): According to GP, 2,4-dimethoxybenzonitrile (652 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.07) 310 mg (40%) of **4f** as colorless needles, m. p. 65 °C. – IR (KBr): = 3370 cm^{-1}, 3053, 3009, 2986, 2837, 1490, 1466, 1266, 1235, 1091, 1045, 1020, 895. – ^1H NMR (250 MHz, $CDCl_3$): = 0.71–0.78 (m, 2 H, *c*Pr-H), 0.81–0.92 (m, 2 H, *c*Pr-H), 1.94 (bs, 2 H, NH_2), 3.79 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 6.37 (dd, ^4J = 2.4, ^3J = 8.3 Hz, 1 H, 5'-H), 6.46 (d, ^4J = 2.4 Hz, 1 H, 3'-H), 7.12 (d, ^3J = 8.3 Hz, 1 H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 14.1 (–, 2 C, *c*Pr-C), 34.4 (C_{quat}, 1 C, C-1), 55.3 (+, 1 C, OCH_3), 55.4 (+, 1 C, OCH_3), 98.8 (+, 1 C, C-3'), 103.1 (+, 1 C, C-5'), 128.4 (+, 1 C, C-6'), 131.9 (C_{quat}, 1 C, C-1'), 159.5 (C_{quat}, 1 C, C-2'*), 159.8 (C_{quat}, 1 C, C-4'*). – MS (70 eV), *m*/*z* (%): 192 (100) [M^+ – H], 178 (24), 164 (18), 149 (9), 134 (11), 121 (8), 77 (5).



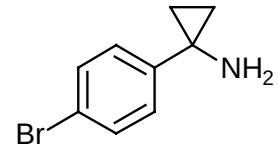
1-(4'-Fluorophenyl)cyclopropylamine (4g): According to GP, 4-fluorobenzonitrile (484 mg, 4 mmol) gave after column chromatography (diethylether, R_f = 0.17) 393 mg (65%) of **4g** as a colorless oil. – IR (film): = 3370 cm^{-1}, 3087, 3008, 2968, 2937, 2889, 1653, 1602, 1511, 1457, 1310, 1225, 1163, 1093, 1014, 875. – ^1H NMR (250 MHz, $CDCl_3$): = 0.90–0.96 (m, 2 H, *c*Pr-H), 1.00–1.06 (m, 2 H, *c*Pr-H), 1.82 (bs, 2 H, NH_2), 6.93–7.02 (m, 2 H, Ph-H), 7.22–7.32 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 17.5 (–, 2 C, *c*Pr-C), 36.4 (C_{quat}, 1 C, C-1), 115.1 (+, d, ^2J(CF) = 21.2 Hz, 2 C, C-3', C-5'), 127.3 (+, d, ^3J(CF) = 7.9 Hz, 2 C, C-2', C-6'), 142.6 (C_{quat}, d, ^4J(CF) = 3.1 Hz, 1 C, C-1'), 161.2 (C_{quat}, d, ^1J(CF) = 243.5 Hz, 1 C, C-4'). – MS (70 eV), *m*/*z* (%): 152 (80) [M^+ + H], 151 (100) [M^+], 133 (8), 122 (43), 109 (8), 95 (10), 75 (5).



1-(4'-Chlorophenyl)cyclopropylamine (4h): According to GP 4-chlorobenzonitrile (550 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.18) 503 mg (75%) of **4h** as a colorless solid, m. p. 27 °C. –IR (KBr): = 3366 cm^{-1}, 3087, 3008, 1896, 1596, 1496, 1456, 1399, 1310, 1101, 1012, 873, 814. – ^1H NMR (250 MHz, $CDCl_3$): = 0.91–0.98 (m, 2 H, *c*Pr-H), 1.02–1.09 (m, 2 H, *c*Pr-H), 1.85 (bs, 2 H, NH_2), 7.18–7.31 (m, 4 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 18.1 (–, 2 C, *c*Pr-C), 36.3 (C_{quat}, 1 C, C-1), 126.9 (+, 2 C, C-2', C-6'), 128.4 (+, 2 C, C-3', C-5'), 131.6 (C_{quat}, 1 C, C-4'), 145.6 (C_{quat}, 1 C, C-1'). – MS (70 eV), *m*/*z* (%): 168/166 (39/100) [M^+ – H], 140/138 (15/41), 132 (26), 111 (7), 75 (9).[15]

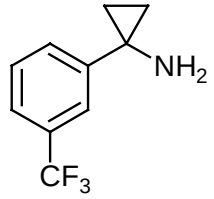


1-(4'-Bromophenyl)cyclopropylamine (4i): According to GP 4-bromobenzonitrile (728 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.15) 610 mg (72%) of **4i** as a colorless solid, m. p. 80 °C. – IR (KBr): = 3378 cm^{-1}, 3088, 3049, 3009, 2980, 1900, 1684, 1589, 1492, 1452, 1395, 1265, 1095, 1008, 895. – ^1H NMR (250 MHz, $CDCl_3$): = 0.92–0.99 (m, 2 H, *c*Pr-H), 1.02–1.09 (m, 2 H, *c*Pr-H), 1.91 (bs, 2 H, NH_2), 7.16 (dd, ^5J = 2.0, ^3J = 7.7 Hz, 2 H, 3'-H, 5'-H), 7.41 (dd, ^5J = 2.0, ^3J = 7.7 Hz, 2 H, 2'-H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 18.1 (–, 2 C, *c*Pr-C), 36.3 (C_{quat}, 1 C, C-1), 119.6 (C_{quat}, 1 C, C-4'), 127.2 (+, 2 C, C-2', C-6'), 131.3 (+, 2 C, C-3', C-5'), 146.0 (C_{quat}, 1 C, C-1'). – MS (70 eV), *m*/*z* (%): 211/209 (95/100), 184/182 (37/35), 115 (13), 103 (18), 76 (19), 49 (27). – Anal. Calcd for $C_9H_{10}NBr$: C, 50.97; H, 4.75. Found C, 50.79; H, 4.86.

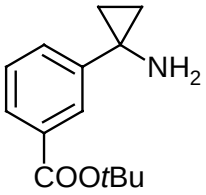


[15] For spectroscopic data see: Harnisch J., Szeimis G. *Chem. Ber*. **1979**, *112*, 3914–3933.

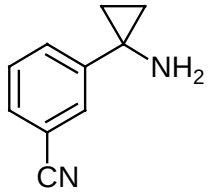
1-(3'-(Trifluoromethyl)phenyl)cyclopropylamine (4j): According to GP, 3-trifluoromethylbenzonitrile (684 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.29) 590 mg (73%) of **4j** as a colorless solid, m. p. 69 °C. – IR (KBr): = 3377 cm^{-1}, 3088, 3012, 2972, 1890, 1616, 1595, 1491, 1456, 1436, 1338, 1283, 1165, 1124, 1073, 1018, 892. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.99–1.06 (m, 2 H, *c*Pr-H), 1.10–1.17 (m, 2 H, cPr-H), 1.96 (bs, 2 H, NH_2), 7.41–7.48 (m, 3 H, Ph-H), 7.58 (bs, 1 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 18.5 (–, 2 C, *c*Pr-C), 36.4 (C_{quat}, 1 C, C-1), 122.1 (q, ^3J(CF) = 3.8 Hz, 1 C, C-4'), 122.7 (q, ^3J(CF) = 3.8 Hz, 1 C, C-2'), 124.2 (q, ^1J(CF) = 204.3 Hz, 1 C, CF_3), 128.5 (+, 1 C, Ph-C), 128.5 (+, 1 C, Ph-C), 130.6 (q, ^2J(CF) = 24.0 Hz, 1 C, C-3'), 148.1 (C_{quat}, 1 C, C-1'). – MS (70 eV), *m*/*z* (%): 200 (46) [M^+ – H], 172 (52), 145 (24), 132 (100), 115 (11), 95 (13), 54 (43).



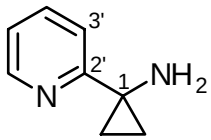
1-(3'-*tert*-Butoxycarbonylphenyl)cyclopropylamine (4k): According to GP, *tert*-butyl 3-cyanobenzoic acid (812 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.13) 680 mg (73%) of **4k** as a colorless oil. – IR (film): = 3375 cm^{-1}, 3077, 3005, 2977, 2933, 1717, 1605, 1584, 1477, 1457, 1368, 1281, 1164, 1127, 1083, 1017, 909, 849. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.99–1.02 (m, 2 H, *c*Pr-H), 1.07–1.11 (m, 2 H, *c*Pr-H), 1.59 [s, 9 H, $C(CH_3)_3$], 1.88 (bs, 2 H, NH_2), 7.33 (dd, ^3J = 7.6, ^3J = 7.7 Hz, 1 H, 5'-H), 7.44 (ddd, ^4J = 1.3, ^4J = 2.0, ^3J = 7.7 Hz, 1 H, 6'-H), 7.80 (ddd, ^4J = 1.3, ^4J = 1.6, ^3J = 7.6 Hz, 1 H, 4'-H), 7.93 (dd, ^4J = 1.6, ^4J = 2.0 Hz, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 18.0 (–, 2 C, *c*Pr-C), 28.2 [+, 3 C, $C(CH_3)_3$], 36.6 (C_{quat}, 1 C, C-1), 81.0 [C_{quat}, 1 C, $C(CH_3)_3$], 126.3 (+, 1 C, Ph-C), 127.0 (+, 1 C, Ph-C), 128.2 (+, 1 C, Ph-C), 129.4 (+, 1 C, Ph-C), 132.0 (C_{quat}, 1 C, C-3'), 147.2 (C_{quat}, 1 C, C-1'), 165.8 (C_{quat}, 1 C, COO). – MS (70 eV), *m*/*z* (%): 234 (14) [M^+ + H], 176 (87), 148 (20), 132 (100), 91 (2), 77 (4). – Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21. Found: C, 72.32; H, 8.21.



1-(3'-Cyanophenyl)cyclopropylamine (4l): According to GP, 1,3-dicyanobenzene (512 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.10) 475 mg (75%) of **4l** as a colorless solid, m. p. 61 °C. – IR (KBr): = 3447 cm^{-1}, 3055, 2987, 2230, 1700, 1653, 1457, 1419, 1265, 1093, 896. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.98–1.09 (m, 2 H, *c*Pr-H), 1.12–1.17 (m, 2 H, *c*Pr-H), 1.94 (bs, 2 H, NH_2), 7.39 (dd, ^3J = 7.6, ^3J = 7.6 Hz, 1 H, 5'-H), 7.45 (ddd, ^4J = 1.5, ^4J = 1.6, ^3J = 7.6 Hz, 1 H, 4'-H), 7.47 (ddd, ^4J = 1.6, ^4J = 1.7, ^3J = 7.6 Hz, 1 H, 6'-H), 7.60 (dd, ^4J = 1.5, ^4J = 1.7 Hz, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 18.9 (–, 2 C, *c*Pr-C), 36.2 (C_{quat}, 1 C, C-1), 112.3 (C_{quat}, 1 C, C N), 119.0 (C_{quat}, 1 C, C-3'), 128.9 (+, 1 C, Ph-C), 129.1 (+, 1 C, Ph-C), 129.4 (+, 1 C, Ph-C), 129.6 (+, 1 C, Ph-C), 148.6 (C_{quat}, 1 C, C-1'). – MS (70 eV), *m*/*z* (%): 157 (100) [M^+ – H], 129 (35), 116 (4), 102 (13), 76 (4), 54 (4). – Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; Found: C 75.73; H 6.65.



1-(2'-Pyridyl)cyclopropylamine (4m): According to GP, picolinic nitrile (416 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.05) 430 mg (80%) of **4m** as a yellowish solid, m. p. 62 °C. – IR (KBr): = 3421 cm^{-1}, 3060, 3018, 1653, 1591, 1418, 1194, 1113, 1025, 805, 712. – ^{1}H NMR (250 MHz, $CDCl_3$): = 1.09–1.14 (m, 2 H, *c*Pr-H), 1.23–1.28 (m, 2 H, *c*Pr-H), 2.14 (bs, 2 H, NH_2), 7.04 (ddd, ^4J = 0.6, ^3J = 4.9, ^3J = 7.4 Hz, 1 H, 5'-H), 7.27 (dd, ^4J = 0.6, ^3J = 7.4 Hz, 1 H, 3'-H), 7.57 (ddd, ^4J = 0.6, ^3J = 7.4, ^3J = 7.4 Hz, 1 H, 4'-H), 8.46 (dd, ^4J = 0.6, ^3J = 4.9 Hz, 1 H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 19.7 (–, 2 C, *c*Pr-C), 37.7 (C_{quat}, 1 C, C-1), 118.0 (+, 1 C, C-3'), 120.3 (+, 1 C, C-5'), 136.1 (+, 1 C, C-4'), 148.7 (+, 1 C, C-6'), 159.0 (C_{quat}, 1 C, C-2'). – MS (70 eV), *m*/*z* (%): 133 (100) [M^+ – H], 117 (22), 106 (27), 93 (9), 79 (96), 52 (19).



1-(3'-Pyridyl)cyclopropylamine (4n): According to GP, nicotinic nitrile (416 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.05) 440 mg (82%) of **4n** as a yellowish oil. – IR (film): = 3421 cm^{-1}, 3060, 3018, 1653, 1576, 1480, 1456, 1418, 1194, 1113, 1025, 805, 712. – ^{1}H NMR (250 MHz, $CDCl_3$): = 0.93–1.00 (m, 2 H, *c*Pr-H), 1.04–1.10 (m, 2 H, *c*Pr-H), 2.08 (bs, 2 H, NH_2), 7.18 (ddd, ^5J = 0.8, ^3J = 4.7, ^3J = 7.9 Hz, 1 H, 5'-H), 7.54 (ddd, ^4J = 1.6, ^4J = 2.4, ^3J = 7.9 Hz, 1 H, 4'-H), 8.38 (dd, ^4J = 1.6, ^3J = 4.7 Hz, 1 H, 6'-H), 8.53 (dd, ^5J = 0.8, ^4J = 2.4 Hz, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 17.9 (–, 2 C, *c*Pr-C), 34.9 (C_{quat}, 1 C, C-1), 123.1 (+, 1 C, C-5'), 133.0 (+, 1 C, C-4'), 142.1 (C_{quat}, 1 C, C-3'), 147.2 (+, 1 C, C-6'*), 147.3 (+, 1 C, C-2'*). – MS (70 eV), *m*/*z* (%): 133 (100) [M^+ – H], 105 (41), 93 (7), 78 (13), 51 (12).

1-(1'-Naphthyl)cyclopropylamine (4o): According to GP, 1-naphthonitrile (612 mg, 4 mmol) gave after column chromatography (diethyl ether, R_f = 0.26) 520 mg (71%) of **4o** as a colorless solid, m. p. 85 °C. – IR (KBr): = 3349 cm^{-1}, 3049, 3009, 2984, 1942, 1684, 1653, 1507, 1265, 1197, 1026, 895, 805. – ^{1}H NMR (250 MHz, $CDCl_3$): = 1.02–1.06 (m, 2 H, *c*Pr-H), 1.19–1.25 (m, 2 H, *c*Pr-H), 2.17 (bs, 2 H, NH_2), 7.41 (dd, ^3J = 7.2, ^3J = 7.6 Hz, 1 H, 3'-H), 7.51 (ddd, ^4J = 0.9, ^3J = 7.2, ^3J = 7.2 Hz, 1 H, 7'-H), 7.52 (dd, ^4J = 0.9, ^3J = 6.9 Hz, 1 H, 5'-H), 7.59 (ddd, ^4J = 1.3, ^3J = 6.9, ^3J = 7.2 Hz, 1 H, 6'-H), 7.80 (d, ^3J = 7.2 Hz, 1 H, 4'-H), 7.90 (dd, ^4J = 1.3, ^3J = 7.2 Hz, 1 H, 8'-H), 8.45 (d, ^3J = 7.6 Hz, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): = 14.8 (–, 2 C, *c*Pr-C), 36.4 (C_{quat}, 1 C, C-1), 124.3 (+, 1 C, Ph-C), 125.3 (+, 1 C, Ph-C), 125.6 (+, 1 C, Ph-C), 125.7 (+, 1 C, Ph-C), 126.1 (+, 1 C, Ph-C), 127.6 (+, 1 C, Ph-C), 129.0 (+, 1 C, Ph-C), 131.6 (C_{quat}, 1 C, Ph-C), 134.2 (C_{quat}, 1 C, Ph-C), 142.0 (C_{quat}, 1 C, Ph-C). – MS (70 eV), *m*/*z* (%): 182 (100) [M^+ – H], 165 (19), 154 (24), 141 (8), 127 (16), 90 (5), 77 (4). – Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7. 15. Found C, 84.99; H, 7.18.