Supporting Information

Synthesis of 1-arylmethyl-2-(cyanomethyl)aziridines and their ring transformation into methyl *N*-(2-cyanocyclopropyl)benzimidates

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General Information

¹H NMR spectra were recorded at 270 MHz or at 300 MHz with CDCl₃ as solvent and tetramethylsilane as internal standard. ¹³C NMR spectra were recorded at 68 MHz or at 75 MHz with CDCl₃ as solvent. Dichloromethane was distilled over calcium hydride and ether over sodium benzophenon ketyl, while other solvents were used as received from the supplier.

1-Benzyl-2-(cyanomethyl)aziridine 2a. Yield 82%, colorless oil. Filtration on silica gel (Hexane/EtOAc 3/2). ¹H NMR (270 MHz, CDCl₃): δ 1.55 (1H, d, J=5.3 Hz); 1.80-1.83 (2H, m); 2.47-2.50 (2H, m); 3.46-3.48 (2H, m); 7.27-7.35 (5H, m). ¹³C NMR (68 MHz, CDCl₃): δ 21.5, 33.1, 34.1, 63.9, 117.3, 127.3, 128.0, 128.5 and 138.3. IR (NaCl, cm⁻¹): ν_{CN} = 2251. MS (70 eV): m/z (%): 202 (M⁺; 14); 165 (4); 138 (6); 121 (100); 91 (14); 77 (11); 65 (6). Anal. Calcd for C₁₁H₁₂N₂: C 76.71, H 7.02, N 16.27. Found: C 76.98, H 7.19, N 16.06.

1-(4-Bromobenzyl)-2-(cyanomethyl)aziridine 2b. Yield 88%, colorless oil. Filtration on silica gel (Hexane/EtOAc 3/2). ^1H NMR (270 MHz, CDCl_3): δ 1.55 (1H, d, $J=5.9$ Hz); 1.79 (1H, m); 1.83 (1H, d, $J=2.6$ Hz); 2.50-2.52 (2H, m); 3.40 and 3.47 (2H, 2 $\times$ d, $J=13.5$ Hz); 7.22 and 7.47 (4H, 2 $\times$ d, $J=8.3$ Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 21.4, 33.1, 34.1, 63.0, 117.3, 121.0, 129.6, 131.4 and 137.4. IR (NaCl, cm^{-1}): $\nu_{\text{CN}} = 2253$. MS (70 eV): m/z (%): 250/2 (M^+ ; 11); 171 (97); 169 (100); 90 (22); 89 (17); 81 (40); 54 (26). Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{BrN}_2$: C 52.61, H 4.42, N 11.16. Found: C 52.91, H 4.63, N 11.02.

2-(Cyanomethyl)-1-(4-methylbenzyl)aziridine 2c. Yield 70%, colorless oil. Filtration on silica gel (Hexane/EtOAc 3/2). ^1H NMR (270 MHz, CDCl_3): δ 1.55 (1H, d, $J=5.9$ Hz); 1.79-1.81 (2H, m); 2.35 (3H, s); 2.44 and 2.55 (2H, 2 $\times$ d $\times$ d, $J=17.0, 5.3$ Hz); 3.44-3.46 (2H, m); 7.16 and 7.22 (4H, 2 $\times$ d, $J=7.9$ Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 21.1, 21.6, 33.1, 34.1, 63.7, 117.4, 128.0, 129.2, 135.2, 137.0. IR (NaCl, cm^{-1}): $\nu_{\text{CN}} = 2250$. MS (70 eV): m/z (%): 186 (M^+ ; 56); 122 (62); 105 (100); 91 (68); 77 (72). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2$: C 77.38, H 7.58, N 15.04. Found: C 77.52, H 7.77, N 14.87.

4-Chloro-3-(N-chloro-N-(dichloro(4-bromophenyl)methyl)amino)butanenitrile 5b. Yield 81%, yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 2.85 and 2.90 (2H, 2 $\times$ d $\times$ d, $J=16.8, 5.8, 5.2$ Hz); 3.69-3.79 (2H, m); 4.39-4.55 (1H, m); 7.51-7.58 and 7.88-7.92 (4H, 2 $\times$ m). ^{13}C NMR (75 MHz, CDCl_3): δ 21.3, 44.9, 60.2, 95.9, 116.4, 127.1, 130.6, 131.5, 145.4. IR (NaCl, cm^{-1}): $\nu_{\text{CN}} = 2252$. Due to the lability of this compound, neither acceptable elemental analysis nor mass spectral data could be obtained.

4-Chloro-3-(N-chloro-N-(dichloro(4-methylphenyl)methyl)amino)butanenitrile 5c. Yield 82%, yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 2.41 (3H, s); 2.86 and 2.90 (2H, 2 $\times$ d $\times$ d, $J=16.7, 5.6, 5.2$ Hz); 3.70-3.81 (2H, m); 4.43-4.51 (1H, m); 7.22-7.24 and 7.92-7.95 (4H, 2 $\times$ m). ^{13}C NMR (75 MHz, CDCl_3): δ 21.5, 21.6, 44.7, 60.2, n.d., 116.6, 129.2, 129.4, 132.0, 143.1. IR (NaCl, cm^{-1}): $\nu_{\text{CN}} = 2253$. Due to the lability of this compound, neither acceptable elemental analysis nor mass spectral data could be obtained.

4-Chloro-3-(*N*-chloro-*N*-(dichloro(2-chlorophenyl)methyl)amino)butanenitrile 5d. Yield 80%, yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 2.87-2.95 (2H, m); 3.73-3.84 (2H, m); 4.46-4.54 (1H, m); 7.23-7.60 (4H, m). ^{13}C NMR (75 MHz, CDCl_3): δ 21.4, 44.6, 60.8, 96.0, 116.3, 126.9, 129.9, 130.3, 130.6, 144.2. IR (NaCl, cm^{-1}): $\nu_{\text{CN}} = 2254$. Due to the lability of this compound, neither acceptable elemental analysis nor mass spectral data could be obtained.

Methyl *N*-(2-chloro-1-(cyanomethyl)ethyl)benzimidate 6a. Yield 30%, yellow oil. Flash chromatography on silica gel: Hexane/EtOAc 4/1, $R_f=0.27$. ^1H NMR (300 MHz, CDCl_3): δ 2.54 and 2.67 (2H, 2 $\times$ m); 3.48 and 3.54 (2H, 2 $\times$ d $\times$ d, $J=11.0, 6.9, 6.3$ Hz); 3.79-3.86 (1H, m); 3.85 (3H, s); 7.32-7.38 and 7.42-7.48 (5H, 2 $\times$ m). ^{13}C NMR (75 MHz, CDCl_3): δ 23.2, 46.6, 53.4, 56.1, 117.3, 127.1, 128.0, 128.3, 129.6, 165.2. IR (NaCl, cm^{-1}): $\nu_{\text{C}\equiv\text{N}} = 2252$, $\nu_{\text{C}=\text{N}} = 1655$. MS (70 eV): m/z (%): 236/8 (M^+ ; 14); 235/7 (88); 201 (53); 196/8 (82); 187 (100); 160 (21); 147 (32); 146 (47); 132 (20); 105 (46); 104 (85); 103 (73); 91 (14); 77 (83); 66 (17); 51 (27). Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{ClN}_2\text{O}$: C 60.89, H 5.54, N 11.84. Found: C 61.07, H 5.74, N 11.70.

Methyl *N*-(2-chloro-1-(cyanomethyl)ethyl)-4-bromobenzimidate 6b. Yield 16%, yellow oil. Flash chromatography on silica gel: Hexane/EtOAc 4/1, $R_f=0.30$. ^1H NMR (300 MHz, CDCl_3): δ 2.59 and 2.62 (2H, 2 $\times$ d $\times$ d, $J=16.4, 6.9, 5.0$ Hz); 3.46 and 3.53 (2H, 2 $\times$ d $\times$ d, $J=11.0, 6.6, 6.5$ Hz); 3.76-3.81 (1H, m); 3.83 (3H, s); 7.23-7.27 and 7.57-7.63 (4H, 2 $\times$ m). ^{13}C NMR (75 MHz, CDCl_3): δ 23.7, 47.1, 54.0, 56.6, 117.3, 124.4, 129.4, 130.3, 132.0, 164.2. IR (NaCl, cm^{-1}): $\nu_{\text{C}\equiv\text{N}} = 2252$, $\nu_{\text{C}=\text{N}} = 1662$. MS (70 eV): m/z (%): 314/6/8 (M^+ ; 17); 313/5/7 (85); 279/81 (61); 274/6/8 (78); 265/7 (100); 225/7 (28); 224/6 (25); 183/5 (42); 182/4 (45); 155/7 (38); 102 (28); 76 (28). Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{BrClN}_2\text{O}$: C 45.67, H 3.83, N 8.88. Found: C 45.89, H 4.01, N 8.70.

Methyl *N*-(2-chloro-1-(cyanomethyl)ethyl)-2-chlorobenzimidate 6d. Yield 13%, yellow oil. Flash chromatography on silica gel: Hexane/EtOAc 5/1, $R_f=0.47$. ^1H NMR (300 MHz, CDCl_3): δ 2.69 (2H, m); 3.44-3.55 (2H, m); 3.86-3.90 (1H, m); 3.89 (3H, s); 7.34-7.47 (4H, m). ^{13}C NMR (75 MHz, CDCl_3): δ 23.1, 46.6, 54.2, 57.0, 117.3, 127.2, 129.5, 129.7, 131.1, 131.2, 131.6, 162.4. IR (NaCl, cm^{-1}): $\nu_{\text{C}\equiv\text{N}} = 2252$, $\nu_{\text{C}=\text{N}} = 1666$. MS (70 eV): m/z (%): 270/2/4 (M^+ ; 17); 269/71/73 (94); 235/7 (43); 230 (75); 221/3 (100); 180/2 (33); 138/40 (60);

111/3 (37); 102 (32); 75/7 (26). Anal. Calcd for C₁₂H₁₂Cl₂N₂O: C 53.16, H 4.46, N 10.33. Found: C 53.30, H 4.67, N 10.19.

Methyl N-(2-cyanocyclopropyl)-4-bromobenzimidate 10b. Spectral data derived from the mixture of *cis*- and *trans*-**10b** (*cis*-**10b**/*trans*-**10b** 45/55). Yellow oil. Filtration on silica gel (Hexane/EtOAc 9/1). ¹H NMR (300 MHz, CDCl₃): δ 1.32-1.45 (2×2H, 2×m); 1.59-1.67 (2×1H, 2×m); 3.16-3.22 and 3.29-3.34 (2×1H, 2×m); 3.71 and 3.83 (2×3H, 2×s); 7.34-7.38 and 7.60-7.64 (2×4H, 2×m). ¹³C NMR (75 MHz, CDCl₃): δ 7.0, 16.2, 16.6, 36.8, 39.9, 53.6, 54.0, 119.4, 120.5, 124.5, 124.8, 129.6, 129.8, 130.1, 131.8, 131.9, 162.9, 163.2. IR (NaCl, cm⁻¹): ν_{C≡N} = 2239, ν_{C=N} = 1668. MS_{*trans*-10b} (70 eV): m/z (%): 278/80 (M⁺; 21); 277/9 (12); 183/5 (100); 172 (12); 155/7 (29); 146 (9); 76 (16). MS_{*cis*-10b} (70 eV): m/z (%): 278/80 (M⁺; 19); 277/9 (10); 183/5 (100); 172 (12); 155/7 (27); 146 (9); 76 (16). Anal. Calcd for C₁₂H₁₁BrN₂O: C 51.63, H 3.97, N 10.04. Found: C 51.79, H 4.19, N 9.88.

Methyl N-(2-cyanocyclopropyl)-4-methylbenzimidate 10c. Spectral data derived from the mixture of *cis*- and *trans*-**10c** (*cis*-**10c**/*trans*-**10c** 40/60). Yellow oil. Filtration on silica gel (Hexane/EtOAc 9/1). ¹H NMR (300 MHz, CDCl₃): δ 1.30-1.43 (2×2H, 2×m); 1.58-1.65 (2×1H, 2×m); 2.39 and 2.40 (2×3H, 2×s); 3.26 (1H, d×d×d, J=6.6, 6.6, 5.0 Hz); 3.39 (1H, d×d×d, J=6.2, 6.2, 3.2 Hz); 3.71 and 3.83 (2×3H, 2×s); 7.23-7.29 and 7.36-7.39 (2×4H, 2×m). ¹³C NMR (75 MHz, CDCl₃): δ 6.8, 16.2, 16.6, 21.4, 37.1, 40.2, 53.4, 53.8, 119.6, 120.8, 128.1, 128.5, 129.1, 129.3, 140.3, 140.5, 164.1, 164.8. IR (NaCl, cm⁻¹): ν_{C≡N} = 2238, ν_{C=N} = 1658. MS_{*trans*-10c} (70 eV): m/z (%): 214 (M⁺; 33); 199 (5); 182 (15); 172 (16); 146 (9); 119 (100); 91 (26); 65 (9). MS_{*cis*-10c} (70 eV): m/z (%): 214 (M⁺; 34); 199 (4); 182 (15); 172 (17); 146 (10); 119 (100); 91 (25); 65 (9). Anal. Calcd for C₁₃H₁₄N₂O: C 72.87, H 6.59, N 13.07. Found: C 73.05, H 6.75, N 12.91.

Methyl N-(2-cyanocyclopropyl)-2-chlorobenzimidate 10d. Spectral data derived from the mixture of *cis*- and *trans*-**10d** (*cis*-**10d**/*trans*-**10d** 40/60). Yellow oil. Filtration on silica gel (Hexane/EtOAc 9/1). ¹H NMR (300 MHz, CDCl₃): δ 1.18-1.43 (2×2H, m); 1.53-1.65 (2×1H, m); 2.85 (1H, d×d×d, J=6.6, 6.6, 4.8 Hz); 2.96-3.01 (1H, m); 3.76 and 3.87 (2×3H, 2×s); 7.27-7.50 (2×4H, m). ¹³C NMR (75 MHz, CDCl₃): δ 6.2, 15.7, 16.0, 36.5, 39.5, 53.8, 54.2, 119.5, 127.1, 127.2, 129.1, 129.3, 129.7, 129.9, 130.9, 131.1, 131.8, 131.9, 132.2, 162.3, 162.6. IR

(NaCl, cm^{-1}): $\nu_{\text{C}\equiv\text{N}} = 2237$, $\nu_{\text{C}=\text{N}} = 1660$. $\text{MS}_{\text{trans-10d}}$ (70 eV): m/z (%): 234/6 (M^+ ; 16); 219/21 (5); 199 (20); 139/41 (100); 111/3 (25); 75 (13). $\text{MS}_{\text{cis-10d}}$ (70 eV): m/z (%): 234/6 (M^+ ; 15); 219/21 (4); 199 (20); 139/41 (100); 111/3 (25); 75 (12). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{ClN}_2\text{O}$: C 61.41, H 4.72, N 11.94. Found: C 61.54, H 4.90, N 11.77.