

Supporting Information

Electrophile-induced bromocyclization of γ,δ -unsaturated ketimines to intermediate 1-pyrrolinium salts and their selective conversion into novel 5-alkoxymethyl-2-aryl-3-chloropyrroles and 2-arylpyrroles

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3-Chloro-1-isopropyl-5-(methoxymethyl)-2-phenylpyrrole 9a. R_f 0.23 (hexane/EtOAc 9/1). ^1H NMR (270 MHz, CDCl_3): δ 1.34 (6H, d, $J = 6.9$ Hz); 3.35 (3H, s); 4.42 (1H, sept, $J = 6.9$ Hz); 4.43 (2H, s); 6.18 (1H, s); 7.31-7.42 (5H, m). ^{13}C NMR (68 MHz, CDCl_3): δ 22.9, 49.5, 56.9, 66.7, 109.7, 111.3, 128.2, 131.3, 127.6, 131.2, 131.8. IR (NaCl): $\nu = 1439, 1362, 1303, 1204, 1079$ cm^{-1} . MS (70 eV): m/z (%): 263/5 (M^+ , 53); 232/4 (74); 190/2 (100); 189 (15); 154/6 (23); 127 (10); 77 (10); 51 (14); 50 (13). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{ClNO}$: C 68.30, H 6.88, N 5.31. Found: C 68.47, H 7.06, N 5.20.

3-Chloro-1-isopropyl-5-(methoxymethyl)-2-(4-methoxyphenyl)pyrrole 9b. R_f 0.22 (hexane/EtOAc 9/1). ^1H NMR (270 MHz, CDCl_3): δ 1.34 (6H, d, $J = 6.9$ Hz); 3.34 (3H, s); 3.85 (3H, s); 4.42 (1H, sept, $J = 6.9$ Hz); 4.42 (2H, s); 6.16 (1H, s); 6.96 (2H, d, $J = 8.6$ Hz); 7.25 (2H, d, $J = 8.6$ Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 23.0, 49.5, 55.2, 56.9, 66.7, 109.7, 111.1, 113.7, 124.0, 127.3, 130.9, 132.5, 159.5. IR (NaCl): $\nu = 1460, 1362, 1310, 1282, 1245, 1172, 1080, 1030$ cm^{-1} . MS (70 eV): m/z (%): 293/5 (M^+ , 44); 262/4 (67); 235 (15); 221 (34); 220/2 (100); 219 (23); 207 (16); 206 (22); 177 (17); 86 (22); 84 (27); 51 (37); 49 (40). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{ClNO}_2$: C 65.41, H 6.86, N 4.77. Found: C 65.58, H 7.08, N 4.65.

3-Chloro-1-cyclohexyl-5-(methoxymethyl)-2-phenylpyrrole 9c. ^1H NMR (270 MHz, CDCl_3): δ 0.82-1.85 (10H, m); 3.34 (3H, s); 3.88-4.00 (1H, m); 4.44 (2H, s); 6.18 (1H, s); 7.29-7.49 (5H, m). ^{13}C NMR (68 MHz, CDCl_3): δ 25.3, 26.4, 33.4, 57.0, 58.5, 66.8, 109.8, 111.2, 128.1, 131.3, 127.7, 128.0, 132.0. IR (NaCl): $\nu = 2822, 1447, 1351, 1315, 1082, 904$ cm^{-1} . MS (70 eV): m/z (%): 303/5 (M^+ , 40); 272/4 (36); 221 (25); 191 (35); 190/2 (100); 189 (32); 84 (15); 81 (17); 55 (58).

5-(tert-Butoxymethyl)-3-chloro-1-isopropyl-2-phenylpyrrole 9d. R_f 0.12 (hexane/EtOAc 4/1). ^1H NMR (270 MHz, CDCl_3): δ 1.30 (9H, s); 1.35 (6H, d, $J = 6.9$ Hz); 4.41 (2H, s); 4.43 (1H, sept, $J = 6.9$ Hz); 6.15 (1H, s); 7.31-7.42 (5H, m). ^{13}C NMR (68 MHz, CDCl_3): δ 23.1, 27.6, 49.5, 56.9, 73.4, 109.9, 110.0, 128.07, 128.10, 131.4, 129.2, 130.5, 132.2. IR (NaCl): $\nu = 1387, 1362, 1309, 1091, 1054, 1018\text{ cm}^{-1}$. MS (70 eV): m/z (%): 305/7 (M^+ , 46); 232/4 (100); 207 (15); 206 (11); 190/2 (71); 154 (17); 143 (16); 128 (11); 127 (13); 115 (11); 104 (10); 86 (10); 84 (10); 57 (23); 51 (12); 49 (12). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{ClNO}$: C 70.69, H 7.91, N 4.58. Found: C 70.54, H 8.13, N 4.61.

5-(tert-Butoxymethyl)-3-chloro-2-(4-chlorophenyl)-1-isopropylpyrrole 9e. R_f 0.09 (hexane/EtOAc 7/3). ^1H NMR (270 MHz, CDCl_3): δ 1.29 (9H, s); 1.35 (6H, d, $J = 6.9$ Hz); 4.40 (2H, s); 4.41 (1H, sept, $J = 6.9$ Hz); 6.14 (1H, s); 7.26 (2H, d, $J = 8.6$ Hz); 7.40 (2H, d, $J = 8.6$ Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 23.1, 27.6, 49.5, 56.8, 73.5, 110.0, 110.4, 128.4, 132.8, 129.1, 129.7, 130.6, 134.2. IR (NaCl): $\nu = 1310, 1280, 1090, 1014, 835\text{ cm}^{-1}$. MS (70 eV): m/z (%): no M^+ ; 254/6/8 (12); 253/5/7 (52); 212/4/6 (15); 211/3/5 (100); 203 (12); 176/8 (39); 149/51 (21); 141 (14); 140 (13); 114 (10); 113 (13); 73/5/7 (24); 63 (11).

3-Chloro-2-(4-chlorophenyl)-5-(isopropoxymethyl)-1-isopropylpyrrole 9f. R_f 0.27 (hexane/EtOAc 9/1). ^1H NMR (270 MHz, CDCl_3): δ 1.20 (6H, d, $J = 6.3$ Hz); 1.35 (6H, d, $J = 7.3$ Hz); 3.70 (1H, sept, $J = 6.3$ Hz); 4.43 (1H, sept, $J = 7.3$ Hz); 4.47 (2H, s); 6.16 (1H, s); 7.27 (2H, d, $J = 8.6$ Hz); 7.40 (2H, d, $J = 8.6$ Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 22.0, 23.1, 49.6, 62.3, 70.2, 110.2, 110.7, 128.5, 132.7, 129.5, 130.5, 132.5, 134.3. IR (NaCl): $\nu = 1720, 1468, 1262, 1120, 1090, 1040, 740\text{ cm}^{-1}$. MS (70 eV): m/z (%): 325/7/9 (M^+ , 28); 267/69/71 (26); 266/68/70 (47); 225/7/9 (40); 224/6/8 (70); 188/90/92 (24); 84/6/8 (52); 58 (25); 49/51/53 (70). Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{Cl}_2\text{NO}$: C 62.58, H 6.49, N 4.29. Found: C 62.74, H 6.70, N 4.42.

3-Chloro-2-(4-chlorophenyl)-1-isopropyl-5-(methoxymethyl)pyrrole 9g. R_f 0.23 (hexane/EtOAc 9/1). ^1H NMR (270 MHz, CDCl_3): δ 1.34 (6H, d, $J = 6.9$ Hz); 3.34 (3H, s); 4.40 (1H, sept, $J = 6.9$ Hz); 4.42 (2H, s); 6.18 (1H, s); 7.27 (2H, d, $J = 8.3$ Hz); 7.41 (2H, d, $J = 8.3$ Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 23.0, 49.6, 57.0, 66.7, 110.1, 111.3, 128.1, 128.5, 132.6, 129.8, 130.3, 133.0, 134.3. IR (NaCl): $\nu = 1470, 1368, 1310, 1090, 1018\text{ cm}^{-1}$. MS (70 eV): m/z (%): 297/299/301 (M^+ , 44); 267/69/71 (17); 266/68/70 (65); 225/7/9 (34); 224/6/8 (100); 223 (22); 190 (12); 188 (23); 154 (13); 153 (12); 152 (10); 113 (11); 86(14); 77 (11); 76 (11); 75 (10); 63 (12); 51 (26). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{Cl}_2\text{NO}$: C 60.41, H 5.75, N 4.70. Found: C 60.27, H 5.84, N 4.61.

2-(2,2-Dichloro-3-oxo-3-phenylpropyl)-1-isopropylaziridine 13a

^1H NMR (270 MHz, CDCl_3): δ 1.14 (3H, d, $J = 6.3$ Hz); 1.21 (3H, d, $J = 6.3$ Hz); 1.43 (1H, d, $J = 6.3$ Hz); 1.51 (1H, sept, $J = 6.3$ Hz); 1.75 (1H, d, $J = 3.3$ Hz); 1.82-1.92 (1H, m); 2.45 (1H, d \times d, $J = 14.9$, 7.0 Hz); 2.93 (1H, d \times d, $J = 14.9$, 4.6 Hz); 7.18-7.69 (3H, m); 8.30 (2H, d \times d, $J = 8.4$, 1.5 Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 21.9, 22.3, 33.7, 34.9, 47.8, 61.4, 85.6, 128.1, 131.0, 133.6, 187.9. IR (NaCl): $\nu = 1675\text{ cm}^{-1}$. HRMS: m/z calcd for $\text{C}_{14}\text{H}_{17}\text{Cl}_2\text{NO}$: 285.0687; found: 285.0701.

2-[2,2-Dichloro-3-(4-methoxyphenyl)-3-oxopropyl]-1-isopropylaziridine 13b

^1H NMR (270 MHz, CDCl_3): δ 1.13 (3H, d, $J = 6.3$ Hz); 1.20 (3H, d, $J = 6.3$ Hz); 1.43 (1H, d, $J = 6.6$ Hz); 1.53 (1H, sept, $J = 6.3$ Hz); 1.75 (1H, d, $J = 3.6$ Hz); 1.82-1.91 (1H, m); 2.43 (1H, d \times d, $J = 15.0$, 7.1 Hz); 2.93 (1H, d \times d, $J = 15.0$, 3.7 Hz); 3.86 (3H, s); 6.93 (2H, d, $J = 8.9$ Hz); 8.32 (2H, d, $J = 8.9$ Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 21.8, 22.2, 33.7, 35.2, 47.9, 55.5, 61.2, 85.7, 113.4, 123.8, 133.6, 163.8, 186.3. IR (NaCl): $\nu = 2849$, 1678 cm^{-1} .

2-Benzoyl-1-isopropylpyrrole 14a. ^1H NMR (270 MHz, CDCl_3): δ 1.41 (6H, d, $J = 6.6$ Hz); 5.48 (1H, sept, $J = 6.6$ Hz); 6.11 (1H, d \times d, $J = 4.0$, 2.6 Hz); 6.61 (1H, d \times d, $J = 4.0$, 1.7 Hz); 7.13 (1H, d \times d, $J = 2.6$, 1.7 Hz); 7.32-7.47 (3H, m); 7.69-7.74 (2H, m). ^{13}C NMR (68 MHz, CDCl_3): δ 23.9, 48.5, 108.4, 123.6, 125.6, 127.9, 129.2, 131.2, 129.9, 140.5, 186.2. IR (NaCl): $\nu = 1590$ - 1621 cm^{-1} . MS (70 eV): m/z (%): 213 (M^+ , 100); 212 (63); 198 (35); 197 (18); 196 (26); 171 (17); 170 (30); 154 (14); 143 (10); 136 (11); 120 (13); 115 (11); 108 (40); 105 (39); 94 (83); 92 (12); 77 (50); 66 (23); 51 (15). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}$: C 78.84, H 7.09, N 6.57. Found: C 79.06, H 7.24, N 6.44.

2-(4-Methoxybenzoyl)-1-isopropylpyrrole 14b. ^1H NMR (270 MHz, CDCl_3): δ 1.50 (6H, d, $J = 6.9$ Hz); 3.89 (3H, s); 5.52 (1H, sept, $J = 6.9$ Hz); 6.21 (1H, d \times d, $J = 4.0$, 2.6 Hz); 6.70 (1H, d \times d, $J = 4.0$, 1.7 Hz); 6.96 (2H, d, $J = 8.7$ Hz); 7.20 (1H, d \times d, $J = 2.6$, 1.7 Hz); 7.85 (2H, d, $J = 8.7$ Hz). ^{13}C NMR (68 MHz, CDCl_3): δ 24.0, 48.6, 55.4, 108.2, 113.2, 122.4, 125.0, 130.1, 133.0, 131.6, 162.4, 185.2. IR (NaCl): $\nu = 1597\text{ cm}^{-1}$. MS (70 eV): m/z (%): 243 (M^+ , 76); 228 (35); 227 (21); 226 (39); 212 (18); 200 (13); 186 (11); 170 (21); 135 (76); 120 (49); 108 (100); 107 (20); 94 (48); 93 (11); 92 (39); 77 (33); 66 (20); 65 (11); 64 (12). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$: C 74.05, H 7.04, N 5.76. Found: C 74.19, H 7.32, N 5.91.

2-Benzoyl-1-cyclohexylpyrrole 14c. ^1H NMR (270 MHz, CDCl_3): δ 0.80-2.22 (10H, m); 5.03-5.18 (1H, m); 6.16 (1H, d \times d, $J = 4.0, 2.6$ Hz); 6.68 (1H, d \times d, $J = 4.0, 1.7$ Hz); 7.18 (1H, d \times d, $J = 2.6, 1.7$ Hz); 7.38-7.52 (3H, m); 7.77-7.81 (2H, m). ^{13}C NMR (68 MHz, CDCl_3): δ 25.7, 25.9, 34.8, 56.6, 108.3, 123.4, 126.2, 127.9, 129.3, 131.2, 129.9, 140.5, 186.2. IR (NaCl): $\nu = 1605\text{-}1617\text{ cm}^{-1}$. MS (70 eV): m/z (%): 253 (M^+ , 68); 252 (12); 236 (27); 210 (15); 171 (100); 170 (48); 154 (22); 148 (34); 143 (16); 115 (13); 105 (64); 94 (78); 80 (12); 78 (13); 77 (46); 67 (17); 66 (19); 55 (32); 54 (12); 51 (17).