Supporting Information

Electrophilic Aromatic Addition Reaction: Electrophilic Attack at an Aromatic *H* Substituent Position

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Synthesis of Quinaldine Compounds. The corresponding anisidine (10 mL) was added to solution of HCl (50 mL) and AcOH (50 mL). Then crotonaldehyde (10 mL) was added and the reaction was heated at 90 °C until the TLC monitoring showed no anisidine remained (3 h). After cooling, the solution was extracted with CH₂Cl₂ (2 x 200 mL). The dark organic layers were discarded and aqueous layer was made basic by NaOH pellets. The basic solution was extracted with EtOAc (2 x 200 mL) and the combined organic layers were washed by water and brine and dried (Na₂SO₄). The residue was purified by flash column chromatography (15% EtOAc-hexane), yielded the methoxyquinaldine (20-60 %).

8-Methoxyquinaldine (1a). ¹H NMR (200 MHz, CDCl₃) δ 2.78 (s, 3H), 4.03 (s, 3H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.30-7.35 (m, 2H), 7.94 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 25.6, 55.9, 107.5, 119.3, 122.6, 125.6, 127.4, 136.0, 139.6, 154.7, 157.9; MS (EI) 173(M⁺), 172, 144, 143, 142, 128, 115, 102, 89, 77, 63, 51, 39. CAS No. 3033-80-5.

5-Bromo-8-methoxyquinaldine (3a). ^1H NMR (200 MHz, CDCl_3) δ 2.79 (s, 3H), 4.02 (s, 3H), 6.82 (d, $J = 8.4$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 8.4$ Hz, 1H), 8.27 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 25.4, 56.1, 108.1, 111.8, 123.5, 126.3, 128.9, 135.4, 140.2, 154.5, 158.6; MS (CI) 254 ($\text{M}^+ + 1$), 252 ($\text{M}^+ + 1$, 100), 174. Anal. Calcd: C, 52.41; H, 4.00; N, 5.56. Found: C, 52.38; H, 3.85; N, 5.11. CAS No. 103862-55-1.

4-Bromo-1-methoxynaphthalene (3b). ^1H NMR (200 MHz, CDCl_3) δ 3.93 (s, 3H), 6.61 (d, $J = 8.4$ Hz, 1H), 7.45-7.64 (m, 3H), 8.12-8.28 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 56.0, 104.8, 113.5, 122.7, 126.2, 127.1, 127.1, 128.1, 129.8, 132.7, 155.5; MS (CI) 239 ($\text{M}^+ + 1$, 36), 238 (M^+ , 74), 237 ($\text{M}^+ + 1$, 42), 236 (M^+ , 71), 186, 158. CAS No. 5467-58-3.

2,4-Dibromo-1-methoxynaphthalene (4b). ^1H NMR (200 MHz, CDCl_3) δ 4.00 (s, 3H), 7.52-7.58 (m, 2H), 7.87 (s, 3H), 8.08-8.14 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 61.9, 112.3, 118.3, 122.80, 127.8, 127.9, 128.1, 130.0, 132.0, 133.3, 153.4; MS (CI) 319 ($\text{M} + 1^+$), 318 (M^+), 317 ($\text{M} + 1^+$), 316 (M^+), 315 ($\text{M} + 1^+$), 266, 264, 238, 236. CAS No. 28768-94-7.

5-Methoxyquinaldine (1c). ^1H NMR (200 MHz, CDCl_3) δ 2.71 (s, 3H), 3.94 (s, 3H), 6.70 (dd, $J = 7.4$ and 1.2 Hz, 1H), 7.17 (d, $J = 8.8$ Hz, 1H), 7.47-7.62 (m, 2H), 8.39 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 25.4, 55.7, 103.7, 119.0, 120.9, 121.1, 129.5, 131.0, 148.8, 155.3, 159.3; MS (EI) 173 (100, M^+), 158, 143, 130, 115, 103, 89, 77, 63, 51, 39. CAS No. 79205-04-2.

6-Methoxyquinaldine (1d). ^1H NMR (200 MHz, CDCl_3) δ 2.69 (s, 3H), 3.89 (s, 3H), 7.02 (d, $J = 3.0$ Hz, 1H), 7.21 (d, $J = 8.4$ Hz, 1H), 7.33 (dd, $J = 8.4$ and 3.0 Hz, 1H), 7.92 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 25.3, 55.7, 105.5, 122.1, 122.5, 127.6, 130.3, 135.3, 144.1, 156.6, 157.4; MS (CI) 174 ($\text{M}^+ + 1$). CAS No. 1078-28-0

5-Bromo-6-methoxyquinaldine (3d). ^1H NMR (200 MHz, CDCl_3) δ 2.72 (s, 3H), 4.02 (s, 3H) 7.30 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 9.2 Hz, 1H), 7.98 (dd, J = 9.2 and 0.8 Hz, 1H), 8.36 (d, J = 9.0 Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 25.1, 57.3, 107.7, 116.6, 123.6, 127.1, 129.6, 134.8, 144.1, 153.6, 157.5; MS (EI) 253 (M^+), 251 (M^+ , 100), 238, 210, 209, 129, 115, 102, 87, 75. CAS No.475682-39-4.

7-Methoxyisoquinoline (1e). The mixture of m-anisaldehyde (3.66 mL) and aminoacetal (4.36 mL) in dry toluene (90 mL) was refluxed in Dean-Stark trap for 3 h. The residue was evaporated *in vacuo*, then added dropwise into 78% H_2SO_4 solution (10 mL) in ice bath. The reaction was heated at 50 $^\circ\text{C}$ for overnight. After cooling, the solution was poured to water (50 mL) basified by NaOH pellets, then extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layer was dried (Na_2SO_4), and evaporated. Flash column chromatography (50% EtOAc-hexane) gave **1d** (0.66 g, 14%): ^1H NMR (200 MHz, CDCl_3) δ 3.91 (s, 3H), 7.17 (d, J = 2.6 Hz, 1H), 7.31 (dd, J = 9.0 and 2.6 Hz, 1H), 7.54 (d, J = 5.8 Hz, 1H), 7.68 (d, J = 9.2 Hz, 1H), 8.40 (d, J = 6.0 Hz, 1H), 9.13 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 55.6, 104.8, 120.3, 123.7, 128.1, 130.0, 131.5, 141.4, 151.2, 158.5; MS (CI) 160 (M^+ +1). CAS No. 39989-39-4.

8-Bromo-7-methoxyisoquinoline (3e). ^1H NMR (200 MHz, CDCl_3) δ 4.02 (s, 3H), 7.41 (d, J = 9.2 Hz, 1H), 7.52 (dd, J = 5.8 and 0.8 Hz, 1H), 7.75 (d, J = 9.2 Hz, 1H), 8.46 (d, J = 5.8 Hz, 1H), 9.57 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 57.3, 108.3, 118.1, 119.9, 127.9, 128.0, 132.3, 141.8, 151.2, 154.5; MS (CI) 280, 278, 268, 266, 240 (M^+ +1), 238 (M^+ +1), 187. Anal. Calcd: C, 50.45; H, 3.39; N, 5.88. Found: C, 50.41; H, 3.44; N, 5.57. CAS No. 67335-10-8

1-Bromo-2-methoxynaphthalene (3g). ^1H NMR (200 MHz, CDCl_3) δ 4.02 (s, 3H), 7.26 (d, J = 9.2 Hz, 1H), 7.38 (dd, J = 8.0, 1.2 Hz, 1H), 7.56 (dt, J = 7.8, 1.2 Hz, 1H), 7.75-7.83 (m, 2H), 8.22 (d, J = 8.8 Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 57.2, 108.9, 113.8, 124.5, 126.3, 128.0, 128.3, 129.2, 130.0, 133.4, 154.0. MS (CI) 239 (M^+ +1), 238 (M^+), 237 (M^+ +1), 236 (M^+), 186, 158. CAS No. 3401-47-6.

8-Methoxyquinaldine (1a). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

5,7-Dibromo-8,8-dimethoxy-7,8-dihydroquinoline (2a). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

5-Bromo-8-methoxyquinaldine (3a). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

2,4 Dibromo-1,1-dimethoxy-1,2-dihydronaphthalene (2b). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

2,4-Dibromo-1-methoxynaphthalene (4b). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

5-Methoxyquinaldine (1c). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

6,8-Dibromo-5,5-dimethoxy-5,6-dihydroquinoline (2c). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

6-Methoxyquinaldine (1d). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

5-Bromo-6,6-dimethoxyquinaldine (2d). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

5-Bromo-6-methoxyquinaldine (3d). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

7-Methoxyisoquinoline (1e). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

8-Bromo-7,7-dimethoxyisoquinoline (2e). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

8-Bromo-7-methoxyisoquinoline (3e). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

8-(3-Hydroxypropoxy)quinaldine (1f). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

5',7'-Dibromo-7'*H*-spiro[1,3-dioxane-2,8'-quinaldine] (2f) ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

1-Bromo-2-methoxynaphthalene (3g). ^1H NMR (200 MHz, CDCl_3)

^{13}C NMR (50 MHz, CDCl_3)

(*S,R*) and (*R,S*)-5,7-Dibromo-8-ethoxy-8-methoxy-7,8-dihydro-quinaldine (5a). ^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

(*S,S*) and (*R,R*)-5,7-Dibromo-8-ethoxy-8-methoxy-7,8-dihydro-quinaldine (6a). ^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

X-ray data of tetrahedron adduct 2a.

Table 1. Crystal data and structure refinement for k.

Identification code	k
Empirical formula	C ₁₂ H ₁₃ Br ₂ N O ₂
Formula weight	363.05
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2(1)/a (No.14)
Unit cell dimensions	a = 7.1456(14) Å alpha = 90.000(15) deg. b = 12.592(3) Å beta = 98.027(16) deg. c = 14.638(3) Å gamma = 90.000(16) deg.
Volume	1304.2(4) Å ³
Z, Calculated density	4, 1.849 Mg/m ³
Absorption coefficient	6.205 mm ⁻¹
F(000)	712
Crystal size	0.25 x 0.43 x 0.50 mm
Theta range for data collection	1.40 to 25.47 deg.
Limiting indices	0 ≤ h ≤ 8, 0 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected / unique	1700 / 1570 [R(int) = 0.0278]
Completeness to theta = 25.47	64.7 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1570 / 0 / 154
Goodness-of-fit on F ²	1.131
Final R indices [I > 2sigma(I)]	R1 = 0.0598, wR2 = 0.1425
R indices (all data)	R1 = 0.0627, wR2 = 0.1456
Largest diff. peak and hole	1.540 and -0.751 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **k**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	2053(1)	9154(1)	2068(1)	50(1)
Br(2)	7584(2)	9256(1)	156(1)	70(1)
O(1)	7433(7)	8736(4)	3383(3)	40(1)
O(2)	4836(7)	9573(4)	3845(3)	37(1)
N(1)	6296(8)	11251(4)	3180(4)	35(1)
C(1)	5749(10)	9332(5)	3098(5)	34(2)
C(2)	4647(9)	8612(6)	2376(5)	40(2)
C(3)	5518(11)	8546(6)	1526(5)	49(2)
C(4)	6492(11)	9355(6)	1262(5)	44(2)
C(5)	6708(10)	10357(6)	1776(5)	36(2)
C(6)	7222(11)	11317(7)	1412(6)	48(2)
C(7)	7266(11)	12223(6)	1944(6)	51(2)
C(8)	6776(9)	12173(5)	2808(5)	39(2)
C(9)	6246(9)	10377(5)	2662(5)	31(2)
C(10)	6726(12)	13133(6)	3415(6)	55(2)
C(11)	8791(11)	9259(6)	4030(6)	48(2)
C(12)	4319(11)	8671(6)	4372(5)	45(2)

Table 3. Bond lengths [Å] and angles [deg] for **k**.

Br(1)-C(2)	1.967(7)
Br(2)-C(4)	1.897(8)
O(1)-C(11)	1.420(9)
O(1)-C(1)	1.430(8)
O(2)-C(1)	1.383(8)
O(2)-C(12)	1.449(8)
N(1)-C(9)	1.335(9)
N(1)-C(8)	1.347(8)
C(1)-C(2)	1.525(9)
C(1)-C(9)	1.526(9)
C(2)-C(3)	1.469(11)
C(3)-C(4)	1.322(11)
C(4)-C(5)	1.466(10)
C(5)-C(9)	1.382(10)
C(5)-C(6)	1.390(11)
C(6)-C(7)	1.379(11)
C(7)-C(8)	1.360(11)
C(8)-C(10)	1.503(11)

C(11)-O(1)-C(1)	114.8(5)
C(1)-O(2)-C(12)	115.6(5)
C(9)-N(1)-C(8)	117.9(6)
O(2)-C(1)-O(1)	110.8(5)
O(2)-C(1)-C(2)	115.1(6)
O(1)-C(1)-C(2)	102.8(5)
O(2)-C(1)-C(9)	107.8(5)
O(1)-C(1)-C(9)	109.8(6)
C(2)-C(1)-C(9)	110.4(6)
C(3)-C(2)-C(1)	112.5(6)
C(3)-C(2)-Br(1)	108.8(5)
C(1)-C(2)-Br(1)	109.4(5)
C(4)-C(3)-C(2)	120.4(7)
C(3)-C(4)-C(5)	122.4(7)
C(3)-C(4)-Br(2)	119.7(6)
C(5)-C(4)-Br(2)	117.9(6)
C(9)-C(5)-C(6)	117.1(7)
C(9)-C(5)-C(4)	118.4(7)
C(6)-C(5)-C(4)	124.4(7)
C(7)-C(6)-C(5)	119.2(7)
C(8)-C(7)-C(6)	119.9(7)
N(1)-C(8)-C(7)	122.0(7)
N(1)-C(8)-C(10)	115.2(7)
C(7)-C(8)-C(10)	122.9(7)
N(1)-C(9)-C(5)	123.9(7)
N(1)-C(9)-C(1)	117.5(6)
C(5)-C(9)-C(1)	118.6(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for k. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
<hr/>						
Br(1)	38(1)	45(1)	65(1)	-2(1)	-4(1)	-4(1)
Br(2)	61(1)	106(1)	44(1)	-10(1)	11(1)	14(1)
O(1)	36(3)	29(2)	52(3)	0(2)	-6(2)	7(2)
O(2)	44(3)	23(2)	46(3)	2(2)	11(2)	-5(2)
N(1)	26(3)	25(3)	54(4)	2(3)	6(3)	-1(2)
C(1)	37(4)	25(4)	39(4)	1(3)	3(3)	2(3)
C(2)	35(4)	29(4)	55(4)	0(4)	-3(3)	8(3)
C(3)	55(5)	38(4)	49(4)	-7(4)	-9(4)	15(4)

C(4)	38(4)	58(5)	35(4)	-3(4)	7(3)	10(4)
C(5)	30(4)	43(4)	34(4)	5(3)	-2(3)	-2(3)
C(6)	44(4)	54(5)	46(4)	7(4)	3(4)	-9(4)
C(7)	47(5)	44(5)	60(5)	22(4)	-2(4)	-5(4)
C(8)	27(4)	27(4)	60(5)	15(3)	-2(3)	-6(3)
C(9)	22(3)	26(3)	44(4)	2(3)	-2(3)	1(3)
C(10)	52(5)	25(4)	89(6)	-2(4)	12(5)	-7(4)
C(11)	42(4)	42(5)	58(5)	9(4)	-2(4)	-4(4)
C(12)	59(5)	39(4)	38(4)	7(3)	10(4)	-7(4)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for k.

	x	y	z	U(eq)
H(2)	4594	7898	2636	48
H(3)	5383	7930	1172	59
H(6)	7532	11347	816	58
H(7)	7630	12867	1712	61
H(10A)	6346	12924	3992	83
H(10B)	5840	13639	3116	83
H(10C)	7960	13448	3523	83
H(11A)	9872	8808	4182	72
H(11B)	8246	9415	4578	72
H(11C)	9172	9909	3766	72
H(12A)	3682	8916	4868	68
H(12B)	5438	8289	4620	68
H(12C)	3495	8211	3977	68