

ELECTRONIC SUPPORTING INFORMATION

Microwave-assisted multicomponent domino cyclization-aromatization: An efficient approach for the synthesis of substituted quinolines

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MATERIALS: All starting chemicals were purchased from Aldrich and used without further purification. CDCl₃ used as a solvent (99.8%) for NMR studies was an Aldrich product. Other solvents used in synthesis with minimum purity of 99.5% were Fisher products.

NMR ANALYSIS: The ¹H, ¹³C and ¹⁹F NMR spectra were obtained on a 300 MHz Varian NMR spectrometer, in CDCl₃ solvent. Tetramethylsilane as internal standards or the residual solvent signal of CDCl₃ were used as reference. The temperature was 25 °C (accuracy ±1 °C) and controlled by the Varian control unit.

GC-MS ANALYSIS: The mass spectrometric identification of the products have been carried out by an Agilent 6850 gas chromatograph-5973 mass spectrometer system (70 eV electron impact ionization) using a 30m long DB-5 type column (J&W Scientific).

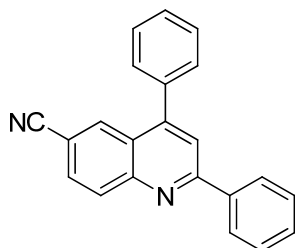
MELTING POINTS: All the melting points are uncorrected and recorded on a MEL-TEMP apparatus.

GENERAL EXPERIMENTAL PROCEDURE: Aniline (109 μL, 1.2 mmol), benzaldehyde (122 μL, 1.2 mmol) and phenylacetylene (110 μL, 1mmol) were dissolved in 3 mL CH₂Cl₂ in a round bottomed flask. 500 mg of K-10 was mixed with the above reaction mixture. After 5 min of stirring the solvent was evaporated under reduced pressure. The dry mixture was then transferred to a reaction vial and irradiated in the microwave reactor for the specified time. After the reaction was complete, CH₂Cl₂ was added to the reaction mixture and filtered. The filtrate was concentrated, and the residue was subjected to column chromatography.

CHARACTERIZATION OF PRODUCTS:

Melting points, ^1H NMR, ^{13}C NMR and Mass spectra of formerly unknown compounds are listed.

2,4-Diphenylquinoline-6-carbonitrile (Table 2 entry 6)



Colorless solid

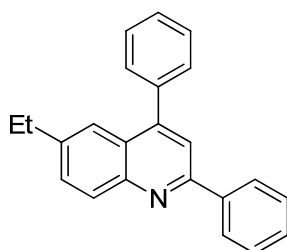
M.P: 189-190 °C

^1H NMR (300.128 MHz, CDCl_3), δ (ppm) 8.29 (m, 2H), 8.22 (m, 2H), 7.94 (s, 1H), 7.86 (dd, $J = 9, 1.5$ Hz, 1H), 7.56 (m, 8H).

^{13}C NMR (75.474 MHz, CDCl_3), δ (ppm) 159.5, 149.8, 138.5, 136.8, 132.3, 131.4, 130.2, 130.1, 129.4, 129.1, 129.0, 127.7, 125.3, 120.5, 118.9, 116.9, 109.6

MS- $\text{C}_{22}\text{H}_{14}\text{N}_2$ (306) m/z (%): 306 (M^+ , 100), 280 (3), 227 (6), 201 (5), 175(1), 77(1).

6-Ethyl-2,4-diphenylquinoline (Table 2, entry 8)



Pale yellow solid

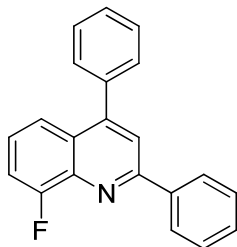
M.P: 88-89 °C

^1H NMR (300.128 MHz, CDCl_3), δ (ppm) 8.16 (d, $J = 6.9$ Hz, 2H), 7.76 (s, 1H), 7.66 (s, 1H), 7.56 (m, 10H), 2.73 (q, $J = 6.9$ Hz, 2H), 1.24 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (75.474 MHz, CDCl_3), δ (ppm) 155.9, 148.4, 147.5, 142.4, 139.6, 138.5, 130.5, 129.9, 129.4, 129.0, 128.7, 128.5, 128.2, 127.4, 125.6, 123.1, 119.3, 29.0, 15.5.

MS- $\text{C}_{23}\text{H}_{19}\text{N}$ (309) m/z (%): 309 (M^+ , 100), 292 (63), 280 (41), 216 (5), 202 (4), 189(6), 77(1).

8-Fluoro-2,4-diphenylquinoline (Table 2, entry 9)



Pale orange solid

M.P: 93-94 °C

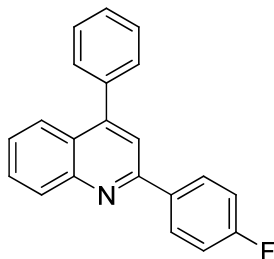
¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.23 (m, 2H), 7.86 (s, 1H), 7.66 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.48 (m, 10H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 160.1, 156.8, 156.7, 149.1, 139.0, 138.0, 129.6, 129.4, 128.8, 128.6, 128.5, 127.6, 127.4, 125.7, 121.4, 121.3, 120.0, 113.6, 113.4

¹⁹F NMR (282.40 MHz, CDCl₃), δ (ppm) -124.36

MS-C₂₁H₁₄FN (299), *m/z* (%): 299 (69), 298 (M⁺, 100), 277 (7), 268 (5), 251 (3), 222 (7), 196 (5), 77 (3).

2-(4-Fluorophenyl)-4-phenylquinoline (Table 3, entry 3)



Colorless solid

M.P: 68-69 °C

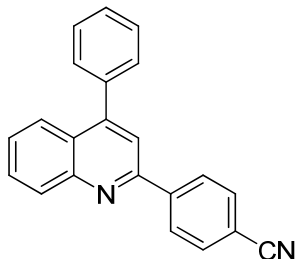
¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.19 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.73 (m, 1H), 7.53 (m, 6H), 7.20 (m, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 165.4, 155.7, 149.3, 148.7, 138.2, 129.9, 129.6, 129.5, 129.4, 129.2, 129.0, 128.9, 128.4, 126.3, 125.6, 118.9, 117.6, 115.8, 115.6, 112.8

¹⁹F NMR (282.40 MHz, CDCl₃), δ (ppm) -112.19

MS-C₂₁H₁₄FN (299), *m/z* (%): 299 (69), 298 (M⁺, 100), 221 (4), 202 (7), 175 (3), 151 (2), 121 (5), 77 (1).

4-(4-Phenylquinolin-2-yl)benzonitrile (Table 3, entry 4)



Yellow solid

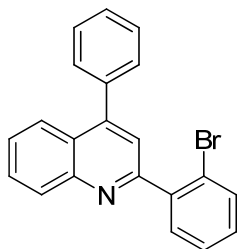
M.P: 154-156 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.33 (d, J = 8.4, 2H), 8.24 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.80 (m, 4H), 7.54 (m, 6H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 132.6, 130.2, 129.9, 129.4, 128.7, 128.0, 127.1, 125.7, 118.9,

MS-C₂₂H₁₄N₂ (306), m/z (%): 306(75), 305(M⁺, 100), 278(3), 202(7), 175(3), 151(2), 77(3).

2-(2-Bromophenyl)-4-phenylquinoline (Table 3, entry 5)



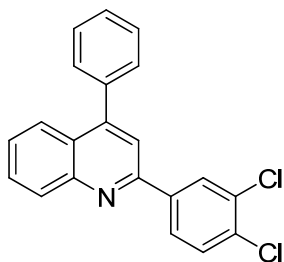
Yellow oil

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.25 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.71 (m, 4H), 7.53 (m, 7H), 7.29 (dt, J = 7.5, 1.5 Hz, 1H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 158.2, 148.4, 147.9, 141.5, 137.9, 133.2, 131.5, 130.0, 129.9, 129.6, 129.5, 128.5, 128.4, 127.6, 126.8, 125.7, 125.6, 122.9, 121.8

MS-C₂₁H₁₄BrN (360), m/z (%): 360 (M⁺, 100), 280 (75), 252 (3), 201 (2), 175 (3), 77(3).

2-(3,4-Dichlorophenyl)-4-phenylquinoline (Table 3, entry 6)



Yellow solid

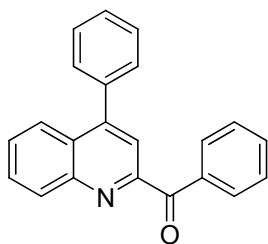
M.P: 87-88 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.27 (d, *J* = 1.8 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.89 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.66 (m, 1H), 7.62 (s, 1H) 7.46 (m, 7H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 153.6, 149.3, 148.4, 139.1, 137.8, 133.3, 132.8, 130.4, 129.9, 129.6, 129.3, 129.1, 128.5, 128.4, 126.6, 126.2, 125.5, 118.2, 117.2, 116.4, 110.4

MS-C₂₁H₁₃Cl₂N (348), *m/z* (%): 348(M⁺, 100), 314(6), 278(10), 202(11), 176(7), 77(3).

Phenyl(4-phenylquinolin-2-yl)methanone (Table 3, entry 8)



Orange solid

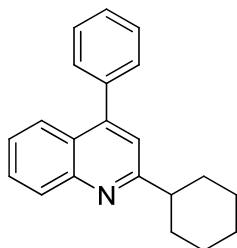
M.P: 111-112 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.26 (d, *J* = 7.8 Hz, 2H), 8.05 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.66 (m, 10H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 193.9, 154.2, 149.6, 147.2, 137.6, 136.1, 133.0, 131.4, 130.9, 129.8, 129.5, 128.6, 128.4, 128.1, 127.4, 125.7, 120.9

MS-C₂₂H₁₅NO (348), *m/z* (%): 309 (M⁺, 46), 280 (100), 232 (9), 203 (11), 176 (4), 105 (8), 77 (10).

2-Cyclohexyl-4-phenylquinoline (Table 3, entry 9)



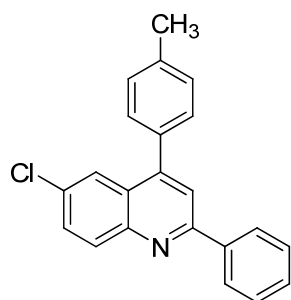
Colorless oil

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.12 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.68 (t, *J* = 8.4 Hz, 1H), 7.46 (m, 6H), 7.27 (s, 1H), 2.95 (tt, *J* = 11.7, 3 Hz, 1H), 1.67 (m, 10H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 166.2, 149.1, 148.4, 138.4, 129.5, 129.2, 129.1, 128.5, 128.4, 125.5, 125.5, 119.8, 114.5, 112.9, 47.6, 38.4, 32.8, 26.5, 26.0, 22.1

MS-C₂₁H₂₁N (287), *m/z* (%): 287 (M⁺, 24), 272 (15), 258 (29), 244 (14), 232 (100), 219 (40), 204 (18), 176(8).

6-Chloro-2-phenyl-4-p-tolylquinoline (Table 4, entry 2)



Pale yellow solid

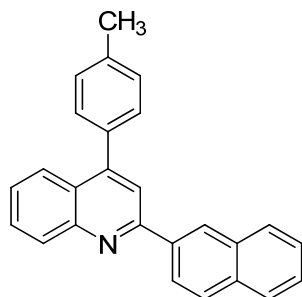
M.P: 87-88 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.15 (m, 3H), 7.89 (d, *J* = 2.1 Hz, 1H), 7.81 (s, 1H), 7.64 (dd, *J* = 9, 2.4 Hz, 1H), 7.47 (m, 7H), 2.48 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 157.0, 148.4, 147.1, 139.2, 138.6, 134.7, 132.0, 131.6, 130.3, 129.5, 129.4, 129.3, 128.8, 127.4, 126.5, 124.5, 119.9, 21.3

MS-C₂₂H₁₆ClN (329), *m/z* (%): 329 (M⁺, 100), 314 (78), 294 (32), 280 (15), 265 (2), 251 (3), 216 (15), 189 (20), 146 (28), 77 (4).

2-(Naphthalen-2-yl)-4-p-tolylquinoline (Table 4, entry 3)



Pale yellow solid

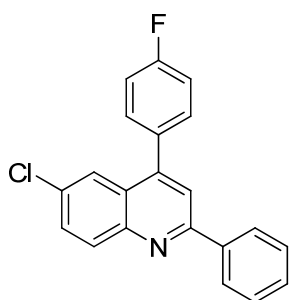
M.P: 108-109 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.63 (s, 1H), 8.40 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.96 (m, 5H), 7.74 (t, *J* = 8.1 Hz, 1H), 7.51 (m, 5H), 7.37 (d, *J* = 7.8 Hz, 2H), 2.48 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 156.8, 149.4, 149.0, 138.5, 137.1, 135.6, 134.0, 133.6, 130.2, 129.6, 129.5, 129.0, 128.7, 127.8, 127.3, 126.8, 126.4, 126.1, 125.9, 125.2, 119.6, 21.5

MS-C₂₆H₁₉N (345), *m/z* (%): 345(M⁺, 100), 330(37), 216(16), 202(5), 176(5), 164(70), 151(15), 77(3).

6-Chloro-4-(4-fluorophenyl)-2-phenylquinoline (Table 4, entry 5)



Colorless solid

M.P: 127-128 °C

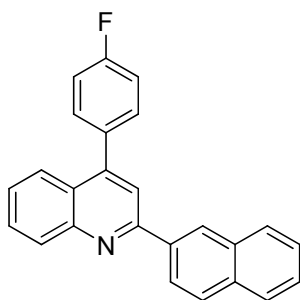
¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.16 (m, 3H), 7.80 (s, 2H), 7.66 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.51 (m, 5H), 7.26 (m, 2H)

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 164.6, 161.3, 157.0, 147.3, 147.0, 139.0, 133.6, 132.3, 131.7, 131.2, 131.0, 130.5, 129.6, 128.9, 127.4, 124.1, 120.0, 116.0, 115.7

¹⁹F NMR (282.40 MHz, CDCl₃), δ (ppm) -112.64

MS-C₂₁H₁₃ClFN (333), *m/z* (%): 333(M⁺, 83), 332(100), 314(5), 298(37), 280(4), 256(8), 219(15), 194(14), 149(28), 75(2).

4-(4-Fluorophenyl)-2-(naphthalen-2-yl)quinoline (Table 4, entry 6)



Pale yellow solid

M.P: 116-118 °C

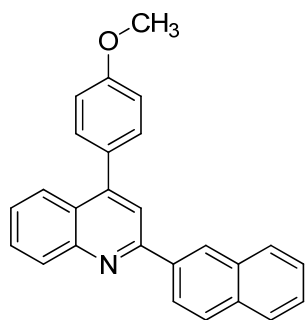
¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.62 (s, 1H), 8.39 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 7.93 (m, 5H), 7.75 (t, *J* = 8.4 Hz, 1H), 7.55 (m, 5H), 7.25 (m, 2H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 164.5, 156.6, 148.8, 148.0, 136.7, 133.8, 133.8, 131.3, 131.2, 130.1, 129.6, 128.7, 128.5, 127.7, 127.1, 126.7, 126.5, 126.3, 125.7, 125.3, 124.9, 119.4, 115.8, 115.5.

¹⁹F NMR (282.40 MHz, CDCl₃), δ (ppm) -113.02

MS-C₂₆H₁₆FN (348), *m/z* (%): 348(M⁺, 100), 253(10), 220(24), 207(15), 194(14), 174(31), 164(20), 126(12), 77(3).

4-(4-Methoxyphenyl)-2-(naphthalen-2-yl)quinoline (Table 4, entry 9)



Pale yellow solid

M.P.: 268-270 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.64 (s, 1H), 8.41 (d, *J* = 9 Hz, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 7.96 (m, 4H), 7.75 (t, *J* = 8.1 Hz, 1H), 7.54 (m, 5H), 7.26 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 164.2, 156.6, 149.8, 147.6, 136.2, 133.4, 131.3, 130.8, 130.0, 129.5, 128.8, 128.5, 127.7, 127.1, 126.6, 125.7, 125.0, 119.4, 114.0, 55.4.

MS-C₂₆H₁₉NO (361), *m/z* (%): 361(M⁺, 100), 331(24), 317(212), 207(21), 164(35), 157(46), 145(36).