Supporting Information

Efficient synthesis of quinolines via a Knoevenagel/Staudinger/aza-Wittig sequence

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General preparation of quinolines (2a-2p). To a solution of 2-azidobenzaldehyde **1** (0.44 g, 3 mmol) and catalytic amount of piperidine (2 drops) in dry tetrahydrofuran at room temperature (15 mL), carbonyl compound (3 mmol) in dry tetrahydrofuran (5 mL) was added under nitrogen. The Knoevenagel reaction was carried out smoothly and the condensation was completed within 2 hours. And then triphenylphosphine (0.79 g, 3 mmol) was added to the mixture at the reflux temperature without the isolation of the Knoevenagel product, and with the end of the nitrogen evolution of the Staudinger reaction, the solution was heated at reflux for a reasonable time to complete the intramolecular aza-Wittig reaction to afford quinoline derivatives. After the completion of the reaction (monitoring by TLC), the solvent was evaporated, and the residue was purified by recrystallization from dichloromethane/ether.

11H-indeno[1,2-b]quinoline (2a) White crystals, mp 168-169 °C (lit.¹ mp: 166 °C); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.33-8.20 (m, 3H, Ar-H), 7.84-7.49 (m, 6H, Ar-H), 4.06 (s, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 161.6, 148.0, 145.0, 140.3, 134.5, 131.1, 129.9, 129.0, 128.7, 127.7, 127.4, 127.3, 125.6, 125.4, 122.0, 33.9. MS (m/z, %): 217 (M⁺, 100), 203 (80), 127 (67). Anal. Calcd for C₁₆H₁₁N: C, 88.45; H, 5.10; N, 6.45; Found: C, 88.38; H, 5.21; N, 6.41.

2-phenylquinoline (2b) White crystals, mp 84-85 °C (lit.² mp: 82-83 °C); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.19-8.13 (m, 4H, Ar-H), 7.82-7.69 (m, 3H, Ar-H), 7.52-7.44 (m, 4H, Ar-H). MS (m/z, %): 205 (M⁺, 100), 128 (46), 76 (89). Anal. Calcd for C₁₅H₁₁N: C, 87.77; H, 5.40; N, 6.83; Found: C, 87.85; H, 5.51; N, 6.64.

2-(4-chlorophenyl)quinoline (2c) White crystals, mp 113-114 °C (lit.² mp: 111-113 °C); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.22-8.11 (m, 4H, Ar-H), 7.84-7.71 (m, 3H, Ar-H), 7.55-7.48 (m, 3H, Ar-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.9, 148.2, 138.0, 136.9, 135.5, 129.8, 129.6, 129.0, 128.8, 127.5, 127.2, 126.5, 118.5. MS (m/z, %): 239 (M⁺, 100), 127 (47), 113 (86), 76 (84). Anal. Calcd for C₁₅H₁₀ClN: C, 75.16; H, 4.21; N, 5.84; Found: C, 75.10; H, 4.30; N, 5.77.

2,3-dihydro-1H-cyclopenta[b]quinoline (2d) White crystals, mp 61-62 °C (lit.³ mp: 58-59 °C); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.02 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.87 (s, 1H, Ar-H), 7.72 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.61 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.45 (d, *J* = 7.6 Hz, 1H, Ar-H), 3.16 (t, *J* = 7.6 Hz, 2H, CH₂), 3.08 (t, *J* = 7.6 Hz, 2H, CH₂), 2.24-2.17 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 167.6, 147.3, 135.3, 130.0, 128.3, 128.1, 127.2, 127.1, 125.2, 34.4, 30.3, 23.4. MS (m/z, %): 169 (M⁺, 100), 156 (32), 142 (29), 126 (52). Anal. Calcd for C₁₂H₁₁N: C, 85.17; H, 6.55; N, 8.28; Found: C, 85.11; H, 6.60; N, 8.29.

1,2,3,4-tetrahydroacridine (2e) White crystals, mp 58-59 °C (lit.³ mp: 55-56 °C); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.96 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.78 (s, 1H, Ar-H), 7.68 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.61-7.57 (m, 1H, Ar-H), 7.42 (d, *J* = 7.6 Hz, 1H, Ar-H), 3.12 (t, *J* = 6.4 Hz, 2H, CH₂), 2.96 (t, *J* = 6.4 Hz, 2H, CH₂), 2.02-1.96 (m, 2H, CH₂), 1.91-1.85 (m, 2H, CH₂). MS (m/z, %): 183 (M⁺, 100), 170 (42), 156 (56), 142 (19), 126 (87). Anal. Calcd for C₁₃H₁₃N: C, 85.21; H, 7.15; N, 7.64; Found: C, 85.26; H, 7.24; N, 7.50.

2-(4-fluorophenyl)quinoline (2f) White crystals, mp 95-96 °C (lit.⁴ mp: 92-93 °C); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.22-8.14 (m, 4H, Ar-H), 7.82 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.75-7.71 (m, 1H, Ar-H), 7.55-7.51 (m, 1H, Ar-H), 7.21 (t, *J* = 8.4 Hz, 2H, Ar-H). MS (m/z, %): 223 (M⁺, 100), 204 (81), 127 (32), 94 (50), 76 (97). Anal. Calcd for C₁₅H₁₀FN: C, 80.70; H, 4.52; N, 6.27; Found: C, 80.63; H, 4.64; N, 6.12.

2-(4-bromophenyl)quinoline (2g) White crystals, mp 124-125 °C (lit.² mp: 121-122 °C); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.23-8.04 (s, 4H, Ar-H), 7.84-7.52 (m, 6H, Ar-H). MS (m/z, %): 283 (M⁺, 100), 204 (75), 156 (62), 94 (35), 76 (77). Anal. Calcd for C₁₅H₁₀BrN: C, 63.40; H, 3.55; N, 4.93; Found: C, 63.35; H, 3.67; N, 4.85.

2-(3-nitrophenyl)quinoline (2h) Yellow crystals, mp 122-123 °C (lit.² mp: 121-124 °C); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 9.04-9.02 (m, 1H, Ar-H), 8.53 (s, 1H, Ar-H), 8.31-8.17 (m, 3H, Ar-H), 7.94-7.58 (m, 5H, Ar-H). MS (m/z, %): 250 (M⁺, 100), 204 (65), 127 (68), 76 (89). Anal. Calcd for C₁₅H₁₀N₂O₂: C, 71.99; H, 4.03; N, 11.19; Found: C, 72.08; H, 4.16; N, 11.11.

2-(4-chlorophenyl)-3-(1H-1,2,4-triazol-1-yl)quinoline (2i) White solid, mp: 157-158 °C; IR (KBr, cm⁻¹): 2921 (w), 1619 (s), 1588 (s), 1538 (m), 1506 (s), 1317 (m), 1092 (s), 989 (m), 755 (m), 673 (m); ¹H NMR (CDCl₃, 600 MHz) δ (ppm): 8.36 (s, 1H, C-H), 8.20 (d, *J* = 3.0 Hz, 1H, Ar-H), 8.12 (s, 1H, C-H), 7.93 (s, 1H, Ar-H), 7.90 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.84-7.82 (m, 1H, Ar-H), 7.66-7.63 (m, 1H, Ar-H), 7.34-7.30 (m, 4H, Ar-H); ¹³C NMR (CDCl₃, 150 MHz) δ (ppm): 153.0, 152.7, 147.9, 144.5, 135.7, 135.5, 134.1, 131.4, 129.8, 129.7, 129.3, 129.1, 128.1, 127.8, 126.8; LC/MS: m/z 306.3 [M]⁺; Anal. Calcd for C₁₇H₁₁ClN₄: C, 66.56; H, 3.61; N, 18.26; Found: C, 66.59; H, 3.65; N, 18.30.

2-(tert-butyl)-3-(1H-1,2,4-triazol-1-yl)quinolone (2j) White solid, mp: 127-128 °C; IR (KBr, cm^{-1}): 3127 (w), 2956 (w), 1619 (s), 1598 (s), 1552 (s), 1503 (m), 1307 (s), 1019 (m), 949 (m), 762 (s); ^1H NMR (CDCl_3 , 600 MHz) δ (ppm): 8.30 (s, 1H, C-H), 8.18 (s, 1H, C-H), 8.14 (d, J = 8.4 Hz, 1H, Ar-H), 7.94 (s, 1H, Ar-H), 7.81-7.79 (m, 2H, Ar-H), 7.58 (t, J = 7.2 Hz, 1H, Ar-H), 1.29 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 150 MHz) δ (ppm): 163.7, 151.7, 147.1, 145.7, 136.8, 130.8, 129.6, 129.4, 127.1, 126.9, 125.6, 39.6, 29.9; MS (EI, 70 eV) m/z (%): 251 (M^+ , 60), 237 (100), 224 (32), 210 (53), 183 (69), 169 (33), 142 (30), 115 (30), 91 (20); Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_4$: C, 71.40; H, 6.39; N, 22.21; Found: C, 71.45; H, 6.43; N, 22.28.

1-(2-methylquinolin-3-yl)ethan-1-one (2k) White crystals, mp 75-76 °C (lit.⁵ mp: 73-74 °C); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 8.49 (s, 1H, Ar-H), 8.05-7.77 (m, 3H, Ar-H), 7.58-7.54 (m, 1H, Ar-H), 2.92 (s, 3H, CH_3), 2.73 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 199.8, 157.5, 148.2, 138.1, 131.6, 131.1, 128.5, 128.3, 126.6, 125.5, 29.2, 25.6. MS (m/z , %): 185 (M^+ , 100), 142 (45), 127 (79). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}$: C, 77.81; H, 5.99; N, 7.56; Found: C, 77.86; H, 6.07; N, 7.62.

3,4-dihydroacridin-1(2H)-one (2l) White crystals, mp 110-111 °C (lit.⁵ mp: 110-111 °C); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 8.86 (s, 1H, Ar-H), 8.06 (d, J = 8.4 Hz, 1H, Ar-H), 7.94 (d, J = 8.4 Hz, 1H, Ar-H), 7.84-7.80 (m, 1H, Ar-H), 7.56 (t, J = 7.6 Hz, 1H, Ar-H), 3.33 (t, J = 6.4 Hz, 2H, CH_2), 2.81 (t, J = 6.4 Hz, 2H, CH_2), 2.32-2.26 (m, 2H, CH_2). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 197.8, 161.9, 149.6, 137.0, 132.3, 129.7, 128.5, 126.7, 126.6, 126.2, 39.0, 33.4, 21.7. MS (m/z , %): 197 (M^+ , 100), 184 (61), 156 (54), 127 (64), 91 (79). Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}$: C, 79.16; H, 5.62; N, 7.10; Found: C, 79.09; H, 5.71; N, 7.07.

3,3-dimethyl-3,4-dihydroacridin-1(2H)-one (2m) White crystals, mp 113-114 °C (lit.³ mp: 112-113 °C); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 8.83 (s, 1H, Ar-H), 8.06 (d, J = 8.4 Hz, 1H, Ar-H), 7.95-7.93 (m, 1H, Ar-H), 7.83-7.79 (m, 1H, Ar-H), 7.58-7.54 (m, 1H, Ar-H), 3.21 (s, 2H, CH_2), 2.66 (s, 2H, CH_2), 1.16 (s, 6H, 2 CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 197.9, 160.7, 149.9, 136.5, 132.2, 129.7, 128.5, 126.7, 126.6, 125.2, 52.4, 47.1, 32.7, 28.3. MS (m/z , %): 225 (M^+ , 100), 197 (85), 184 (32), 156 (70), 91 (56). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$: C, 79.97; H, 6.71; N, 6.22; Found: C, 79.86; H, 6.78; N, 6.11.

Ethyl 2-methylquinoline-3-carboxylate (2n) White crystals, mp 71-72 °C (lit.³ mp: 69-70 °C); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 8.74 (d, J = 6.0 Hz, 1H, Ar-H), 8.04 (d, J = 8.8 Hz, 1H, Ar-H), 7.87-7.76 (m, 2H, Ar-H), 7.56-7.52 (m, 1H, Ar-H), 4.45 (q, J = 7.2 Hz, 2H, CH_2), 2.99 (s, 3H, CH_3), 1.46 (t, J = 7.2 Hz, 3H, CH_3). MS (m/z , %): 215 (M^+ , 100), 186 (68), 170 (37), 128 (71), 91 (44). Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2$: C, 72.54; H, 6.09; N, 6.51; Found: C, 72.55; H, 6.12; N, 6.66.

1-(3-methylquinolin-2-yl)ethanone (2o) White crystals, mp 63-64 °C (lit.⁶ mp: 61-63 °C); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 8.06 (d, J = 8.4 Hz, 1H, Ar-H), 7.84 (s, 1H, Ar-H), 7.68-7.51 (m, 3H, Ar-H), 2.82 (s, 3H, CH_3), 2.64 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 202.4, 152.7, 145.3, 137.8, 129.9, 129.7, 128.9, 128.8, 128.1, 126.4, 27.9, 20.2. MS (m/z , %): 185 (M^+ , 100), 170 (77), 128 (46), 91 (90). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}$: C, 77.81; H, 5.99; N, 7.56; Found: C, 77.75; H, 6.10; N, 7.41.

1-(3-ethylquinolin-2-yl)ethanone (2p) White crystals, mp 31-32 °C; IR (KBr, cm^{-1}): 2991 (w), 1706 (C=O) (s), 1684 (C=N) (s), 1602 (s), 1482 (m). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 8.08 (d, J = 8.8 Hz, 1H, Ar-H), 7.84 (s, 1H, Ar-H), 7.74-7.64 (m, 2H, Ar-H), 7.54 (t, J = 7.2 Hz, 1H, Ar-H), 3.07 (q, J = 7.6 Hz, 2H, CH_2), 2.83 (s, 3H, CH_3), 1.29 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 202.5, 153.2, 145.2, 136.2, 135.8, 129.6, 129.0, 128.9, 128.0, 126.7, 28.3, 25.7, 15.1. MS (m/z , %): 199 (M^+ , 100), 184 (80), 170 (77), 156 (39), 128 (46), 91 (90). Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}$: C, 78.36; H, 6.58; N, 7.03; Found: C, 78.24; H, 6.61; N, 7.09.

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Copies of NMR spectra