A Novel Approach to 2-Substituted Quinolines:
Electrocyclization of Alkynyl Imines *via* Vinylidene Complexes
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Supporting Information

General: All the materials were purified by distillation or recrystallization. THF and diethyl ether were distilled from sodium benzophenone just before use. Dichloromethane and toluene were distilled and stored over molecular sieves 4A. Preparative thin layer chromatography (preparative TLC) was conducted on silica gel (Wakogel B-5F, Wako Pure Chemical Industries). All the reactions were carried out under nitrogen atmosphere. Irradiation was performed with a 450W high-pressure mercury lamp (USHIO INC.).

NMR spectra were recorded on a Unity Inova-400 instrument (Varian Japan Ltd., 400 MHz for ^1H , 100 MHz for ^{13}C) or a JNM-AL300 (JEOL, 300 MHz for ^1H , 75 MHz for ^{13}C) using CDCl_3 as a solvent. Chemical shifts (δ) for ^1H were referenced to tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. Chemical Shifts (δ) for ^{13}C were referenced to a solvent signal (CDCl_3 , $\delta = 77.00$ ppm). IR spectra were recorded on FTIR-8600PC instrument (Shimadzu Co.) using CHCl_3 as a solvent. Elemental analysis (EA) was carried out on EA1110 instrument (Amco Inc.).

Preparation of alkynyl imine 1a-1l:

Procedure for preparation of **1a** will be described below.

N-phenyl-benzimidoyl chloride **12a**

Imidoyl chloride **12a** was prepared according to the literature.¹

N-Phenyl-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-imine **13a**²

A mixture of imidoyl chloride **12a** (2.16 g, 10.0 mmol), triphenylphosphine (37 mg, 0.1 mmol), palladium(II) acetate (24 mg, 0.1 mmol), and trimethylsilylacetylene (1.42 mL, 10.0 mmol) in degassed triethylamine (25 mL) was slowly heated to 80 °C and kept the temperature for 2 h. After cooling, the solution was diluted with diethyl ether (25 mL) and filtered through Celite[®]. The filtrate was concentrated and passed through a short column of silica gel (CH₂Cl₂ : hexane = 1 : 5). The eluate was concentrated under reduced pressure, and the resulting residue was purified by bulb-to-bulb distillation to give **13a** (0.1 mmHg/130–150 °C, 2.52 g, 91%).

N-Phenyl-1-phenylprop-2-yn-1-imine **1a**²

To a solution of *N*-phenyl-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-imine **13a** (2.32 g, 8.4 mmol) in methanol (15 mL) was added anhydrous potassium carbonate (150 mg). Immediately **1a** was precipitated as a pale yellow crystalline. The mixture was filtered and the solid was washed with cold methanol. The crude product was recrystallized from methanol to give alkynyl imine **1a** (1.38 g, 80%).

Typical procedure for electrocyclization of alkynyl imines **1**:

A slurry of tungsten hexacarbonyl (70 mg, 0.20 mmol) in dry THF (2 mL) was irradiated for 2 h using high pressure mercury lamp (450W). To the resulting yellow solution was added a solution of **1a** (41 mg, 0.20 mmol) in THF and the solution was heated at 80°C for 2 h. After confirmation that alkynyl imine **1a** was consumed completely by TLC analysis, the solvent was removed *in vacuo*, a solution of NMO (70 mg, 0.60 mmol) in dichloromethane was added and stirred at rt for 1 h. The reaction mixture was filtered through a small pad of silica gel using ethyl acetate as an eluent. The filtrate was concentrated and purified by preparative TLC (silica gel, 10:1 hexane/ethyl acetate) to afford the quinoline derivatives **2a** as a yellow solid (28.6 mg, 70%).

2-Phenylquinoline 2a

^1H NMR δ 7.46 (t, 1H, $J = 7.8$ Hz), 7.50-7.58 (m, 3H), 7.73 (t, 1H, $J = 7.8$ Hz), 7.83 (d, 1H, $J = 8.1$ Hz), 7.88 (d, 1H, $J = 8.6$ Hz), 8.13-8.26 (m, 4H); ^{13}C NMR δ 118.90, 126.15, 127.05, 127.33, 127.44, 128.70, 129.18, 129.51, 129.62, 136.61, 139.55, 148.13, 157.17; IR $\bar{\nu}$ 3040, 1620, 1599, 1556, 1508 cm^{-1} ; EA Found: C, 87.95%; H, 5.68%; N, 6.56%. Calcd for $\text{C}_{15}\text{H}_{11}\text{N}$: C, 87.77%; H, 5.40%; N, 6.82%. Yellow solid.

6-Methoxy-2-phenylquinoline 2b

^1H NMR δ 3.94 (s, 3H), 7.08 (d, 1H, $J = 2.7$ Hz), 7.38 (dd, 1H, $J = 2.7, 9.2$ Hz), 7.44 (t, 1H, $J = 7.5$ Hz), 7.51 (t, 2H, $J = 7.5$ Hz), 7.83 (d, 1H, $J = 8.6$ Hz), 8.04-8.16 (m, 4H); ^{13}C NMR δ 55.54, 104.90, 119.09, 122.18, 127.13, 127.98, 128.65, 128.79, 131.03, 135.32, 139.62, 144.19, 154.84, 157.46; IR $\bar{\nu}$ 3015, 1624, 1601, 1495 cm^{-1} ; EA Found: C, 81.50%; H, 5.34%; N, 5.94%. Calcd for $\text{C}_{16}\text{H}_{13}\text{ON}$: C, 81.68%; H, 5.57%; N, 5.95%. Yellow solid.

6-Methyl-2-phenylquinoline 2c

^1H NMR δ 2.53 (s, 3H), 7.40-7.62 (m, 5H), 7.82 (d, 1H, $J = 8.8$ Hz), 8.03-8.18 (m, 4H); ^{13}C NMR δ 21.56, 118.95, 126.29, 127.16, 127.43, 128.77, 129.08, 129.36, 131.90, 136.05, 136.10, 139.77, 146.82, 156.48; IR $\bar{\nu}$ 3036, 1599, 1560, 1493, 1207 cm^{-1} ; EA Found: C, 87.66%; H, 6.04%; N, 6.43%. Calcd for $\text{C}_{16}\text{H}_{13}\text{N}$: C, 87.64%; H, 5.98%; N, 6.39%. Yellow solid.

6-Chloro-2-phenylquinoline 2d

^1H NMR δ 7.43-7.57 (m, 3H), 7.65 (dd, 1H, $J = 2.4, 8.8$ Hz), 7.80 (d, 1H, $J = 2.4$ Hz), 7.89 (d, 1H, $J = 8.6$ Hz), 8.04-8.18 (m, 4H); ^{13}C NMR δ 119.65, 125.99, 127.37, 127.57, 128.76, 129.43, 130.41, 131.18, 131.74, 135.66, 139.04, 146.48, 157.34; IR $\bar{\nu}$ 3026, 1599, 1551, 1487, 1076 cm^{-1} ; EA Found: C, 75.29%; H, 4.22%; N, 6.02%. Calcd for $\text{C}_{15}\text{H}_{10}\text{NCl}$: C, 75.16%; H, 4.21%; N, 5.84%. Yellow solid.

6-Fluoro-2-phenylquinoline 2e

^1H NMR δ 7.40-7.60 (m, 5H), 7.88 (d, 1H, $J = 8.6$ Hz), 8.10-8.26 (m, 4H); ^{13}C NMR δ 110.45 (d, $^2J_{\text{C-F}} = 21.3$ Hz), 119.71, 119.84 (d, $^2J_{\text{C-F}} = 25.2$ Hz), 127.43, 127.69 (d, $^3J_{\text{C-F}}$

= 10.0 Hz), 128.88, 129.38, 132.17 (d, $^3J_{\text{C-F}} = 9.1$ Hz), 136.12 (d, $^4J_{\text{C-F}} = 5.3$ Hz), 139.36, 145.36, 157.92 (d, $^1J_{\text{C-F}} = 234.9$ Hz), 161.56; IR $\bar{\nu}$ 3067, 2982, 1622, 1607, 1556, 1495, 1236 cm^{-1} ; EA Found: C, 80.81%; H, 4.32%; N, 6.14%. Calcd for $\text{C}_{15}\text{H}_{10}\text{NF}$: C, 80.70%; H, 4.51%; N, 6.27%. Yellow solid.

8-Methyl-2-phenylquinoline **2f**

^1H NMR δ 2.90 (s, 3H), 7.38 (t, 1H, $J = 7.2$ Hz), 7.44 (tt, 1H, $J = 1.4, 7.4$ Hz), 7.51 (t, 2H, $J = 7.4$ Hz), 7.55 (d, 1H, $J = 7.2$ Hz), 7.63 (d, 1H, $J = 7.2$ Hz), 7.86 (d, 1H, $J = 8.6$ Hz), 8.14 (d, 1H, $J = 8.6$ Hz), 8.22-8.28 (m, 2H); ^{13}C NMR δ 17.88, 118.16, 125.35, 125.99, 127.05, 127.43, 128.74, 129.19, 129.64, 136.90, 137.64, 139.82, 147.14, 155.49; IR $\bar{\nu}$ 3026, 1599, 1560, 1489 cm^{-1} ; EA Found: C, 87.51%; H, 5.86%; N, 6.49%. Calcd for $\text{C}_{16}\text{H}_{13}\text{N}$: C, 87.64%; H, 5.98%; N, 6.39%. Yellow oil.

7-Methyl-2-phenylquinoline **2g**

^1H NMR δ 2.57 (s, 3H), 7.34 (dd, 1H, $J = 1.3, 8.2$ Hz), 7.44 (t, 1H, $J = 7.3$ Hz), 7.51 (t, 2H, $J = 7.3$ Hz), 7.70 (d, 1H, $J = 8.2$ Hz), 7.79 (d, 1H, $J = 8.6$ Hz), 7.96 (s, 1H), 8.11-8.18 (m, 3H); ^{13}C NMR δ 21.85, 118.13, 125.17, 127.03, 127.47, 128.48, 128.69, 128.74, 129.14, 136.37, 139.77, 139.85, 148.44, 157.24; IR $\bar{\nu}$ 3057, 1626, 1601, 1512 cm^{-1} ; EA Found: C, 87.81%; H, 5.80%; N, 6.33%. Calcd for $\text{C}_{16}\text{H}_{13}\text{N}$: C, 87.64%; H, 5.98%; N, 6.39%. Yellow solid.

This product was obtained as a 97/3 regioisomeric mixture. The ratio was determined by integration of distinguishable peaks which are assigned for the minor isomer ($\delta = 2.57$ ppm, singlet for **2g** vs. $\delta = 2.70$ ppm, singlet for regioisomer).

2-Phenylbenzo[h]quinoline **2h**

^1H NMR δ 7.46 (t, 1H, $J = 7.4$ Hz), 7.54 (t, 2H, $J = 7.4$ Hz), 7.61-7.77 (m, 4H), 7.88 (d, 1H, $J = 8.2$ Hz), 7.95 (d, 1H, $J = 8.2$ Hz), 8.15 (d, 1H, $J = 8.2$ Hz), 8.32 (d, 2H, $J = 7.4$ Hz), 9.49 (d, 1H, $J = 8.2$ Hz); ^{13}C NMR δ 118.69, 124.61, 124.93, 124.99, 126.73, 127.29, 127.62, 127.99, 128.67, 129.05, 131.67, 133.71, 136.32, 139.57, 146.04, 155.26; IR $\bar{\nu}$ 3015, 1595, 1560, 1514 cm^{-1} ; EA Found: C, 89.17%; H, 4.92%; N, 5.69%. Calcd for $\text{C}_{19}\text{H}_{13}\text{N}$: C, 89.38%; H, 5.13%; N, 5.49%. Yellow solid.

2-(4-Methoxyphenyl)quinoline **2i**

^1H NMR δ 3.88 (s, 3H), 7.04 (d, 2H, J = 8.8 Hz), 7.49 (t, 1H, J = 7.4 Hz), 7.66-7.73 (m, 1H), 7.79 (d, 1H, J = 8.6 Hz), 7.82 (d, 1H, J = 8.2 Hz), 8.10-8.18 (m, 4H); ^{13}C NMR δ 55.34, 114.19, 118.52, 125.88, 126.87, 127.40, 128.86, 129.48, 129.54, 132.22, 136.60, 148.26, 156.88, 160.77; IR $\bar{\nu}$ 2978, 1601, 1501, 1250 cm^{-1} ; EA Found: C, 81.76%; H, 5.49%; N, 5.74%. Calcd for $\text{C}_{16}\text{H}_{13}\text{ON}$: C, 81.68%; H, 5.57%; N, 5.95%. Yellow solid.

2-(4-Methylphenyl)quinoline **2j**

^1H NMR δ 2.42 (s, 3H), 7.32 (d, 2H, J = 8.4 Hz), 7.49 (t, 1H, J = 7.9 Hz), 7.70 (t, 1H, J = 7.9 Hz), 7.79 (d, 1H, J = 7.9 Hz), 7.84 (d, 1H, J = 8.6 Hz), 8.06 (d, 2H, J = 8.4 Hz), 8.16 (d, 1H, J = 7.9 Hz), 8.17 (d, 1H, J = 8.6 Hz); ^{13}C NMR δ 21.30, 118.81, 126.03, 127.05, 127.40, 129.53, 129.61, 136.61, 136.83, 139.35, 148.25, 157.28; IR $\bar{\nu}$ 3044, 1599, 1555, 1499, 1209 cm^{-1} ; EA Found: C, 87.86%; H, 6.24%; N, 6.41%. Calcd for $\text{C}_{16}\text{H}_{13}\text{N}$: C, 87.64%; H, 5.98%; N, 6.39%. Yellow solid.

2-(3-Methylphenyl)quinoline **2k**

^1H NMR δ 2.48 (s, 3H), 7.28 (d, 1H, J = 7.6 Hz), 7.41 (dt, 1H, J = 2.6, 7.6 Hz), 7.48-7.54 (m, 1H), 7.68-7.75 (m, 1H), 7.81 (d, 1H, J = 8.1 Hz), 7.85 (dd, 1H, J = 2.7, 8.6 Hz), 7.92 (d, 1H, J = 7.6 Hz), 8.01 (s, 1H), 8.15-8.22 (m, 2H); ^{13}C NMR δ 21.67, 119.01, 124.56, 126.06, 127.02, 127.30, 128.11, 128.57, 129.45, 129.55, 129.95, 136.51, 138.33, 139.48, 148.08, 157.36; IR $\bar{\nu}$ 3011, 1620, 1599, 1558, 1506 cm^{-1} ; EA Found: C, 87.44%; H, 6.28%; N, 6.12%. Calcd for $\text{C}_{16}\text{H}_{13}\text{N}$: C, 87.64%; H, 5.98%; N, 6.39%. Yellow solid.

2-(4-Chlorophenyl)quinoline **2l**

^1H NMR δ 7.48 (d, 2H, J = 8.4 Hz), 7.52 (t, 1H, J = 7.5 Hz), 7.72 (t, 1H, J = 7.5 Hz), 7.81 (d, 2H, J = 8.6 Hz), 8.11 (d, 2H, J = 8.4 Hz), 8.15 (d, 1H, J = 8.6 Hz), 8.19 (d, 1H, J = 8.6 Hz); ^{13}C NMR δ 118.50, 126.46, 127.18, 127.45, 128.77, 128.97, 129.67, 129.80, 135.50, 136.91, 138.01, 148.20, 155.95; IR $\bar{\nu}$ 3013, 1620, 1599, 1556, 1094 cm^{-1} ; EA Found: C, 75.42%; H, 4.16%; N, 5.97%. Calcd for $\text{C}_{15}\text{H}_{10}\text{NCl}$: C, 75.16%; H, 4.21%; N, 5.84%. Yellow solid.

References

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