Electronic Supplementary Information

~ Experimental Procedures and Spectral/Analytical Data ~

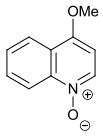
General Comments

Reactions were carried out under an Ar atmosphere using dry solvents. Melting points (mp) were determined with a Yazawa micro melting point apparatus and uncorrected. Infrared (IR) data were recorded on SensIR ATR (Attenuated Total Reflectance) FT-IR and absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). NMR data were recorded on a JEOL AL400 spectrometer. Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in herts (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, m = multiplet. Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC spectrometer respectively.

Materials

Commercially available materials, including *N*-oxides (**1a**, **1d** and **1e**) and aryl acetylenes (**2a**–**d**), were purchased from Tokyo Kasei Co., Aldrich Inc. and other suppliers and were used after appropriate purification (distillation or recrystallization). Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70–230 mesh).

Preparation of 4-Methoxyquinoline *N*-Oxide (1b)



4-Nitroquinoline *N*-oxide (3.8 g, 20 mmol) and NaOMe (2.2 g, 40 mmol) were dissolved in MeOH (30 mL) and the reaction mixture was stirred at 60 ºC for 48 h. The precipitates formed were filtered and the filtrate was concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: hexane/ethyl acetate = 1:1) followed by recrystallization (hexane/ethyl acetate) to give **1b** (2.6 g, 74 %) as yellow needles.

Mp: 58–59 ºC (lit[1] mp: 54–55 ºC).

IR (neat): 3046, 2208, 1565, 1486, 1043, 812, 795 cm^{-1}.

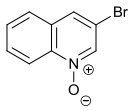
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.75 (d, *J* = 8.3 Hz, 1H), 8.47 (d, *J* = 6.8 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.83–7.79 (m, 1H), 7.67–7.64 (m, 1H), 6.64 (d, *J* = 6.8 Hz, 1H), 4.07 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 56.2, 99.5, 119.9, 122.5, 122.6, 127.9, 130.9, 136.0, 141.2, 154.4.

LRMS (EI) *m/z*: 175 (M^+).

HRMS: Calcd. for $C_{10}H_9NO_2$: 175.0633, found: 175.0616.

Preparation of 3-Bromoquinoline *N*-Oxide (1c)



A mixtrure of 3-bromoquinoline (4.2 g, 20 mmol) and H_2O_2 (35% in H_2O, 20 mL, 20 mmol) in AcOH (30 mL) was stirred at 100 ºC for 24 h. Saturated aqueous Na_2CO_3 (30 mL) was added and the mixture was extracted with $CHCl_3$ (50 mL x 3). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: hexane/ethyl acetate = 1:1) followed by recrystallizeation (ethanol) to give **1c** (2. 8 g, 62 %) as white prisms.

Mp: 109–111 ºC (lit[2] mp: 102–103 ºC).

IR (neat): 3054, 1560, 1491, 1065, 823, 764 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.62 (d, *J* = 8.8 Hz, 1H), 8.57 (s, 1H), 7.85 (s, 1H), 7.77–7.70 (m, 2H), 7.65–7.61 (m, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 114.0, 119.4, 127.0, 127.2, 129.4, 129.8, 130.0, 136.5, 140.1.

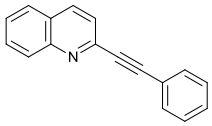
LRMS (EI) *m/z*: 223 (M^+).

HRMS: Calcd. for $C_9H_6{}^{79}BrNO$: 222.9633, found: 222.9615.

Typical Procedure for Reaction of Heteroaromatic *N*-Oxides with *C*-Nucleophiles (Table 1, Entry 5)

A mixture of quinoline *N*-oxide (**1a**, 44 mg, 0.30 mmol), phenylacetylene (**2a**, 46 mg, 0.45 mmol) and *N*,*N*-dimethyltrimethylsilylamine (0.18 g, 1.5 mmol) in DMF (1 mL) was added to TMAF (2.8 mg, 0.030 mmol) at room temperature and the reaction mixture was stirred for 24 h at room temperature. Saturated aqueous NH_4Cl (10 mL) and H_2O (10 mL) were added and the mixture was extracted with AcOEt (20 mL x 3). The combined organic layer was washed with saturated aqueous NaCl (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: hexane/ethyl acetate = 19:1) to give **3aa** as orange oil (67 mg, 97 %).

2-(Phenylethynyl)quinoline (3aa)



IR (neat): 3056, 2219, 1734, 1592, 1499, 1424, 1309, 1240, 1159, 1113, 1045, 827, 752, 689 cm^{-1}.

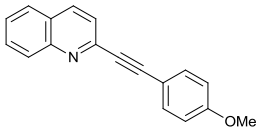
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.14 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.74–7.73 (m, 1H), 7.68–7.65 (m, 2H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.57–7.54 (m, 1H), 7.39–7.38 (m, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 89.4, 89.9, 122.2, 124.4, 127.1, 127.1, 127.5, 128.4, 129.2, 129.3, 130.1, 132.2, 136.1, 143.6, 148.2.

LRMS (EI) *m/z*: 229 (M^+).

HRMS: Calcd. for $C_{17}H_{11}N$: 229.0892, found: 229.0875.

2-(4-Methoxyphenylethynyl)quinoline (3ab)



Recrystallized from ethanol, white needles, mp: 145–147 ºC (lit[3] mp: 145–147 ºC).

IR (neat): 3063, 1499, 1420, 1079, 1009, 830, 822, 788, 751 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.11 (d, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.72–7.70 (m, 1H), 7.61–7.51 (m, 4H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 1H).

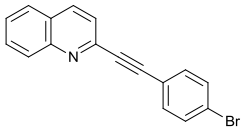
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 55.3, 88.5, 90.4, 114.1, 114.2, 124.3, 126.9, 127.0, 127.5, 129.3, 130.0, 133.8, 136.0, 144.0, 148.3, 160.4.

LRMS (EI) *m/z*: 259 (M^+).

HRMS: Calcd. for $C_{18}H_{13}NO$: 259.0997, found: 259.0997.

Anal. Calcd. for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.14; H, 5.35; N, 5.25.

2-(4-Bromophenylethynyl)quinoline (3ac)



Recrystallized from ethanol, yellow needles, mp: 147–148 ºC.

IR (neat): 3052, 2218, 1592, 1499, 1484, 1067, 1004, 829, 823, 746 cm^{-1}.

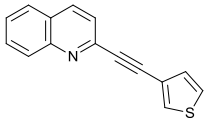
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.17–8.12 (m, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.76–7.73 (m, 1H), 7.61–7.52 (m, 6H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 88.6, 90.3, 121.1, 123.6, 124.2, 127.2, 127.3, 127.5, 129.3, 130.1, 131.7, 133.6, 136.2, 143.2, 148.2.

LRMS (EI) *m/z*: 307 (M^+).

HRMS: Calcd. for $C_{17}H_{10}{}^{79}BrN$: 306.9997, found: 306.9998.

2-(3-Thiophenylethynyl)quinoline (3ad)



Obtained as brown oil.

IR (neat): 3105, 3059, 2206, 1592, 1498, 826, 781, 752 cm^{-1}.

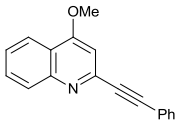
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.14–8.11 (m, 2H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.75–7.70 (m, 2H), 7.60–7.53 (m, 2H), 7.34–7.30 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 85.1, 89.0, 121.2, 124.1, 125.5, 127.0, 127.4, 129.2, 130.0, 130.0, 130.6, 136.1, 143.5, 148.2.

LRMS (EI) *m/z*: 235 (M^+).

HRMS: Calcd. for $C_{15}H_9NS$: 235.0456, found: 235.0457.

2-(Phenylethynyl)-4-methoxyquinoline (3ba)



Obtained as orange oil.

IR (neat): 3058, 2856, 2215, 1582, 1503, 1411, 1363, 1108, 842, 763 cm^{-1}.

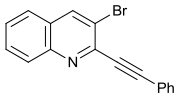
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.16 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.72–7.66 (m, 3H), 7.52–7.48 (m, 1H), 7.39–7.37 (m, 3H), 6.98 (s, 1H), 4.07 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 55.9, 89.1, 89.6, 103.3, 120.6, 121.6, 122.2, 126.2, 128.4, 128.8, 129.1, 130.3, 132.2, 143.4, 149.1, 162.2.

LRMS (EI) *m/z*: 259 (M^+).

HRMS: Calcd. for $C_{18}H_{13}NO$: 259.0997, found: 259.0997.

2-(Phenylethynyl)-3-bromoquinoline (3ca)



Recrystallized from ethanol, yellow needles, mp: 91–92 ºC.

IR (neat): 3057, 2216, 1571, 1490, 1396, 986, 756, 744 cm^{-1}.

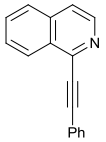
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.42 (s, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.76–7.71 (m, 4H), 7.59–7.57 (m, 1H), 7.53–7.40 (m, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 88.1, 94.2, 119.6, 121.9, 126.6, 128.0, 128.1, 128.4, 129.2, 129.5, 130.3, 132.4, 138.5, 143.4, 146.6.

LRMS (EI) *m/z*: 307 (M^+).

HRMS: Calcd. for $C_{17}H_{10}{}^{79}BrN$: 306.9997, found: 306.9986.

1-(Phenylethynyl)isoquinoline (3da)



Obtained as orange oil.

IR (neat): 3050, 2210, 1734, 1550, 1490, 1394, 1354, 825, 753, 689, 666 cm^{-1}.

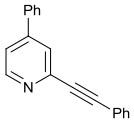
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.55 (d, *J* = 5.7 Hz, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.74–7.68 (m, 4H), 7.63 (d, *J* = 5.7 Hz, 1H), 7.42–7.41 (m, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 87.0, 94.1, 120.8, 122.4, 127.1, 127.1, 128.1, 128.7, 129.4, 129.5, 130.7, 132.4, 136.0, 143.1, 144.5.

LRMS (EI) *m/z*: 229 (M^+).

HRMS: Calcd. for $C_{17}H_{11}N$: 229.0892, found: 229.0879.

2-(Phenylethynyl)-4-phenylpyridine (3ea)



Obtained as brown oil.

IR (neat): 3054, 2206, 1692, 1524, 1468, 1338, 1237, 1055, 829, 740 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.66 (d, *J* = 4.8 Hz, 1H), 7.78 (s, 1H), 7.67–7.62 (m, 4H), 7.52–7.46 (m, 3H), 7.38–7.36 (m, 4H).

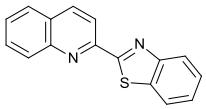
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 88.7, 89.4, 120.8, 122.2, 125.1, 127.0, 128.4, 128.8, 129.0, 129.2, 129.4,

130.9, 132.1, 148.8, 150.4.

LRMS (EI) *m/z*: 255 (M^+).

HRMS: Calcd. for $C_{19}H_{13}N$: 255.1048, found: 255.1050.

2-(2-Benzothiazolyl)quinoline (5aa)



Recrystallized from ethanol, yellow needles, mp: 185–186 ºC (lit[3] mp: 185–186 ºC).

IR (neat): 1595, 1590, 1499, 1452, 1426, 1325, 1308, 1117, 995, 936, 836, 760, 751, 725, 697 cm^{-1}.

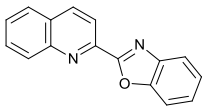
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.49 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.79–7.76 (m, 1H), 7.61–7.58 (m, 1H), 7.53–7.50 (m, 1H), 7.46–7.43 (m, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 118.4, 122.1, 123.9, 125.9, 126.4, 127.7, 127.8, 129.1, 129.9, 130.2, 136.6, 137.1, 148.0, 151.4, 154.5, 170.0.

LRMS (EI) *m/z*: 262 (M^+).

HRMS: Calcd. for $C_{16}H_{10}N_2S$: 262.0565, found: 262.0550.

2-(2-Benzoxazolyl)quinoline (5ab)



Recrystallized from ethanol, orange needles, mp: 177–179 ºC (lit[4] mp: 179–180 ºC).

IR (neat): 3062, 2922, 1780, 1504, 1449, 1076, 837, 766, 734 cm^{-1}.

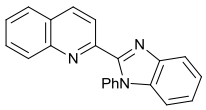
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.49 (d, *J* = 8.8 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 2H), 7.92–7.88 (m, 2H), 7.84–7.80 (m, 1H), 7.76–7.74 (m, 1H), 7.67–7.64 (m, 1H), 7.46–7.42 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 111.5, 120.3, 120.8, 125.0, 126.3, 127.7, 128.1, 128.7, 130.3, 130.4, 137.2, 141.9, 145.9, 148.1, 151.3, 161.7.

LRMS (EI) *m/z*: 246 (M^+).

HRMS: Calcd. for $C_{16}H_{10}N_2O$: 246.0793, found: 246.0792.

***N*-Phenyl-2-(2-quinolyl)benzimidazole (5ac)**



Recrystallized from ethanol, brown needles, mp: 77–79 ºC.

IR (neat): 3060, 2646, 2228, 1724, 1554, 1437, 1342, 1259, 1023, 817, 725 cm^{-1}.

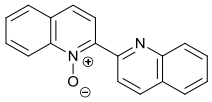
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.34 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.60–7.57 (m, 1H), 7.52–7.49 (m, 6H), 7.42–7.32 (m, 4H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 111.0, 120.3, 121.3, 123.2, 124.2, 127.2, 127.4, 127.6, 127.8, 128.1, 129.1, 129.5, 129.8, 136.2, 138.1, 138.3, 142.8, 147.1, 148.9.

LRMS (EI) *m/z*: 321 (M^+).

HRMS: Calcd. for $C_{22}H_{15}N_3$: 321.1266, found: 321.1275.

2,2'-Biquinoline *N*-Oxide (6)



Recrystallized from ethanol, brown needles, mp: 172–173 ºC (lit[3] mp: 172–173 ºC).

IR (neat): 3108, 3054, 2920, 1559, 1363, 1123, 877, 834, 765, 744, 730 cm^{-1}.

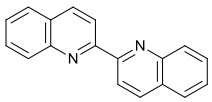
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.94 (d, *J* = 8.8 Hz, 1H), 8.89 (d, *J* = 8.8 Hz, 1H), 8.31 (d, *J* = 2.7 Hz, 1H), 8.29 (d, *J* = 2.7 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.90 (m, 2H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.75 (m, 1H), 7.68 (m, 1H), 7.60 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 120.3, 123.0, 123.8, 125.4, 127.5, 127.7, 128.2, 128.3, 129.0, 129.7, 129.9, 130.4, 130.6, 135.8, 142.4, 143.9, 148.2, 151.6.

LRMS (EI) *m/z*: 272 (M^+).

HRMS: Calcd. for $C_{18}H_{12}N_2O$: 272.0950, found: 272.0943.

2,2'-Biquinoline (7)



Recrystallized from ethanol, brown needles, mp: 198–199 ºC (lit[5] mp: 193–196 ºC).

IR (neat): 3049, 2207, 1758, 1541, 1319, 1275, 825, 734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.85 (d, *J* = 8.5 Hz, 2H), 8.33 (d, *J* = 8.5 Hz, 2H), 8.24 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.78–7.74 (m, 2H), 7.60–7.56 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 119.4, 126.9, 127.6, 128.4, 129.5, 129.9, 136.7, 147.9, 156.2.

LRMS (EI) *m/z*: 256 (M^+).

HRMS: Calcd. for $C_{18}H_{12}N_2$: 256.1000, found: 256.0994.

References

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