SUPPORTING INFORMATION

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"Regioselective Sonogashira Couplings of 2,4-Dibromoquinolines.
A Correction"

- I.** Comparison table of NMR data for **13a** (1 page).
- II.** Characterization data and ^1H and ^{13}C NMR spectra for **8-11**, **13b**, **14a**, and **14b** (21 pages).
- III.** ^{13}C HMBC spectra for **11**, **14a** and **14b** (3 pages).

Total pages of supporting information: (26).

General Experimental Information. All reactions described in the experimental section were performed using oven-dried glassware under an argon or dry nitrogen atmosphere. THF, toluene, and diethyl ether were dried by distillation from sodium/benzophenone.

Table 1. The table below lists NMR and melting point data for **13a** and **5** (R = Ph)¹

	<u>Nolan/Comins (13a)²</u>	<u>Reisch/Gunaherath (5, R = Ph)³</u>
¹ H (δ)	7.39 (m, 3H)	7.35 – 7.44 (m, 3H)
	7.64 (m, 3H)	7.59 – 7.69 (m, 3H)
	7.76 (t, 1H, <i>J</i> = 7.6 Hz)	7.77 (ddd, 1H, <i>J</i> = 1.5, 6.7, and 8.4 Hz)
	7.91 (s, 1H)	7.92 (s, 1H)
	8.11 (d, 1H, <i>J</i> = 8.4 Hz)	8.13 (dd, 1H, <i>J</i> = 1.3 and 8.4 Hz)
	8.15 (d, 1H, <i>J</i> = 8.4 Hz)	8.16 (dd, 1H, <i>J</i> = 1.5 and 8.2 Hz)
m.p.	96 – 97 °C (recrystallized from pentane)	103 °C (recrystallized from light petroleum)

¹ Reisch, J.; Gunaherath, G. M. K. B. *J. Heterocyclic Chem.* **1993**, 30, 1057.

² ¹H NMR spectrum recorded in CDCl₃ using a Varian Mercury 400 MHz spectrometer.

³ ¹H NMR spectrum recorded in CDCl₃ using a Varian Gemini 200 MHz spectrometer.

DATA SHEET

Compound: 2,4-Dibromo-quinoline-3-carbaldehyde

Compound No.: 8

Formula: C₁₀H₅NOBr₂

Notebook Pg(s): JMNIII93Y

Molecular Weight: 314.97

Yield(s): 78%

Other:

Appearance: white solid

Stability: stable

mp/bp: 147 – 149 °C

$[\alpha]^{23}_{\text{D}}$ (c, CHCl₃):

	%C	%H	%N	
Elemental Analysis (Atlantic Microlabs)	Calculated:			Notebook Page:
	Found:			

Exact Mass for C₁₀H₅NOBr₂ (M + 1H) requires *m/z* 313.8816, found *m/z* 313.8819

IR (thin film, neat, NaCl): cm⁻¹: 756.4, 841.9, 1034.2, 1135.7, 1242.5, 1296.0, 1338.7, 1376.1, 1472.2, 1547.0, 1696.6, 2888.9

NMR (CDCl₃):

(¹H, 400 MHz): δ 7.74 (t, 1H, *J* = 7.2 Hz), 7.88 (t, 1H, *J* = 8.4 Hz), 8.05 (d, 1H, *J* = 8.4 Hz), 8.35 (d, 1H, *J* = 8.4 Hz), 10.40 (s, 1H)

(¹³C, 100 MHz): δ 127.3, 128.0, 128.5, 129.3, 129.5, 133.8, 138.1, 139.6, 149.0, 190.5

Literature Reference(s):

DATA SHEET

Compound: (2,4-Dibromo-quinolin-3-yl)-methanol

Compound No.: 9

Formula: C₁₀H₇NOBr₂

Notebook Pg(s): JMNIV07W

Molecular Weight: 316.98

Yield(s): 84%
(recrystallized from toluene)

Other:

Appearance: yellow solid

Stability: stable

mp/bp: 125 – 126 °C

[α]_D²³ (c, CHCl₃):

	%C	%H	%N	
Elemental Analysis (Atlantic Microlabs)	Calculated:			Notebook Page:
	Found:			

Exact Mass for C₁₀H₇NOBr₂ (M + 1H) requires *m/z* 315.8973, found *m/z* 315.8976

IR (thin film, neat, NaCl): cm⁻¹: 758.3, 828.5, 850.4, 896.4, 966.2, 1005.4, 1046.0, 1140.6, 1190.4, 1240.2, 1295.0, 1358.6, 1454.5, 1476.7, 1551.5, 2941.8, 3031.5, 3320.5, 3386.0

NMR (CDCl₃):

(¹H, 400 MHz): δ 2.63 (s, 1H), 5.18 (s, 2H), 7.64 (t, 1H, *J* = 8.0 Hz), 7.73 (t, 1H, *J* = 6.8 Hz), 7.97 (d, 1H, *J* = 8.4 Hz), 8.15 (d, 1H, *J* = 8.4 Hz)

(¹³C, 100 MHz): δ 65.6, 127.5, 128.0, 128.8, 129.0, 131.6, 133.3, 137.7, 143.6, 148.0

Literature Reference(s):

DATA SHEET

Compound: (4-Bromo-2-trimethylsilanylethynyl-quinolin-3-yl)-methanol

Compound No.: **10**

Formula: C₁₅H₁₆NOBrSi

Notebook Pg(s): JMNIV15Y

Molecular Weight: 334.29

Yield(s): 74%

Other:

Appearance: orange solid

Stability: stable (cannot distill)

mp/bp: 97 – 98 °C

[α]_D²³ (c, CHCl₃):

Elemental
Analysis
(Atlantic
Microlabs)

	%C	%H	%N
Calculated:			
Found:			

Notebook
Page:

Exact Mass for C₁₅H₁₆NOBrSi (M + 1H) requires *m/z* 334.0263, found *m/z* 334.0268

IR (thin film, neat, NaCl): cm⁻¹: 697.8, 759.3, 819.2, 826.1, 847.9, 872.6, 925.2, 1027.8, 1103.0, 1163.6, 1217.9, 1250.2, 1321.2, 1358.2, 1385.6, 1452.5, 1478.0, 1547.4, 1566.1, 2897.4, 2957.9, 3382.2

NMR (CDCl₃):

(¹H, 300 MHz): δ 0.33 (s, 9H), 2.54 (t, 1H, *J* = 6.9 Hz), 5.22 (d, 2H, *J* = 6.9 Hz), 7.64 (t, 1H, *J* = 6.9 Hz), 7.75 (t, 1H, *J* = 6.9 Hz), 8.08 (d, 1H, *J* = 8.4 Hz), 8.20 (d, 1H, *J* = 8.4 Hz)

(¹³C, 75 MHz): δ -0.6, 63.7, 100.4, 101.9, 127.5, 127.6, 129.1, 129.9, 131.1, 134.7, 136.4, 143.1, 147.9

Literature Reference(s): Reisch, J.; Kaal, G. M.; Gunaherath, K. B. *J. Heterocyclic Chem.* **1993**, 30, 1057.

DATA SHEET

Compound: [4-Bromo-2-(2-trimethylsilyl-ethyl)-quinolin-3-yl]-methanol

Compound No.: 11

Formula: C₁₅H₂₀NOBrSi

Notebook Pg(s): JMNIV18Y

Molecular Weight: 338.32

Yield(s): 74%

Other:

Appearance: white solid

Stability: stable

mp/bp: 104 – 105.5 °C

[α]_D²³ (c, CHCl₃):

Elemental Analysis (Atlantic Microlabs)		%C	%H	%N	Notebook Page:
	Calculated:			.	
	Found:				

Exact Mass for C₁₅H₂₀NOBrSi (M + 1H) requires *m/z* 338.0584, found *m/z* 338.0584

IR (thin film, neat, NaCl): cm⁻¹: 691.8, 757.5, 806.0, 832.1, 860.2, 932.0, 1031.2, 1092.7, 1172.8, 1247.4, 1322.6, 1391.8, 1481.5, 1555.0, 1577.9, 1613.7, 2894.1, 2950.8, 3355.7

NMR (CDCl₃):

(¹H, 400 MHz): δ 0.08 (s, 9H), 1.04 (m, 2H), 2.27 (t, 1H, *J* = 6.8 Hz), 3.12 (m, 2H), 5.05 (d, 2H, *J* = 6.4 Hz), 7.56 (t, 1H, *J* = 8.0 Hz), 7.70 (t, 1H, *J* = 8.0 Hz), 8.01 (d, 1H, *J* = 8.4 Hz), 8.16 (d, 1H, *J* = 8.4 Hz)

(¹³C, 100 MHz): δ -1.5, 17.5, 31.6, 62.4, 126.9, 127.3, 127.5, 129.2, 130.5, 131.5, 137.5, 148.1, 164.8

HMBC: H-12 & C-2 (²*J*_{CH}), H-13 & C-2 (³*J*_{CH}), H-11 & C-2 (³*J*_{CH}), H-11 & C-4 (³*J*_{CH}), H-5 & C-4 (³*J*_{CH})

NOESY: saturated H-8, NOE response from H-14

Literature Reference(s): Corey, E. J.; Dittami, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 256.

exp1 gHMBc

SAMPLE
date Jul 25 2002
solvent CDCl3
sample jmagain_25-
Jul2002
ACQUISITION
sw 2989.5
at 0.171
np 1024
fb not used
ss 32
d1 1.000
nt 2D ACQUISITION
sw1 15083.0
n1 256
phase 0
TRANSMITTER H1
tn fn
sfreq 299.793
tof -107.5
tpwr 14.500
pw 14.500
DECOUPLER C13
dn -760.6
dof nm
dm nm
dmm wp1
dmf 200
dprf 41
pwxivl 56
pwx 20.000
HMBc 140.0
j1xh 8.0
jnxh

FLAGS
hs
n
n
y
2000
SPECIAL
temp not used
gain 32
spin 0
GRADIENTS
gziv1 2000
gziv11 0.001000
gziv13 1003
g13 0.001000
gstab 0.000500
F2 PROCESSING
sb 0.086
sbs not used
fn 1024
F1 PROCESSING
sb1 0.008
sbs1 not used
fn1 2048
DISPLAY
-161.2
2989.5
-757.0
15083.0
161.2
757.0
0
PLOT
WC 180.0
SC 6.2
WC2 116.2
SC2 0
VS 564
TH 12
at cdc av

DATA SHEET

Compound: 4-Bromo-2-trimethylsilanylethynyl-quinoline

Compound No.: **13b**

Formula: $C_{14}H_{14}NBrSi$

Notebook Pg(s): JMNIV37Y

Molecular Weight: 304.26

Yield(s): 94%

Other:

Appearance: colorless oil

Stability: stable

mp/bp:

$[\alpha]^{23}_D$ (c, $CHCl_3$):

	%C	%H	%N	Notebook Page:
Elemental Analysis (Atlantic Microlabs)	Calculated:			
	Found:			

Exact Mass for $C_{14}H_{14}NBrSi$ ($M + 1H$) requires m/z 304.0157, found m/z 304.0143

IR (thin film, neat, NaCl): cm^{-1} : 759.2, 847.6, 918.5, 1173.1, 1221.2, 1250.4, 1285.3, 1394.9, 1486.4, 1571.9, 2354.7, 2963.7

NMR ($CDCl_3$):

(1H , 400 MHz): δ 0.30 (s, 9H), 7.63 (t, 1H, $J = 7.2$ Hz), 7.75 (t, 1H, $J = 6.8$ Hz), 7.84 (s, 1H), 8.09 (d, 1H, $J = 8.4$ Hz), 8.14 (d, 1H, $J = 8.0$ Hz)

(^{13}C , 100 MHz): δ -0.3, 96.9, 103.0, 126.4, 126.8, 127.9, 128.3, 129.8, 130.8, 133.7, 142.8, 148.3

Literature Reference(s): Reisch, J.; Kaal, G. M.; Gunaherath, K. B. *J. Heterocyclic Chem.* **1993**, 30, 1057.

DATA SHEET

Compound: 4-Bromo-2-phenylethyl-quinoline

Compound No.: **14a**

Formula: C₁₇H₁₄NBr

Notebook Pg(s): JMNIV83W

Molecular Weight: 312.21

Yield(s): 85%

Other:

Appearance: colorless oil

Stability: stable

mp/bp:

[α]_D²³ (c, CHCl₃):

	%C	%H	%N	
Elemental Analysis (Atlantic Microlabs)	Calculated:			Notebook Page:
	Found:			

Exact Mass for C₁₇H₁₄NBr requires *m/z* 311.0310, found *m/z* 311/0301

IR (thin film, neat, NaCl): cm⁻¹: 698.0, 736.5, 757.5, 806.3, 815.5, 846.4, 863.3, 920.0, 1027.7, 1075.8, 1119.2, 1148.1, 1177.6, 1219.5, 1298.6, 1405.1, 1453.0, 1490.1, 1550.5, 1585.8, 2855.1, 2923.8, 3025.3, 3060.0

NMR (CDCl₃):

(¹H, 400 MHz): δ 3.16 (m, 2H), 3.26 (m, 2H), 7.20 – 7.33 (m, 5H), 7.55 (s, 1H), 7.74 (t, 1H, *J* = 7.6 Hz), 8.07 (d, 1H, *J* = 8.4 Hz), 8.14 (d, 1H, *J* = 8.0 Hz)

(¹³C, 100 MHz): δ 35.8, 40.7, 125.6, 126.3, 126.5, 126.8, 127.2, 128.7, 129.5, 130.5, 134.3, 141.3, 148.7, 161.8

HMBC: H-12 & C-2 (³*J*_{CH}), H-11 & C-2 (²*J*_{CH}), H-3 & C-2 (²*J*_{CH}), H-5 & C-4 (³*J*_{CH}), H-3 & C-5 (²*J*_{CH})

Literature Reference(s):

Archive directory: /export/home/comins/vnmr/sys/data
Sample directory: JMN2-ethphen_30dec2002

Pulse Sequence: ghMBC
Solvent: CDCl3
Ambient temperature
File: ghMBC
Mercury-400BB "nsumerc400"

Relax. delay 1.000 sec
Acq. time 0.160 sec
Width 3205.1 Hz
2D Width 20120.7 Hz
8 repetitions
256 increments
OBSERVE H1 400.1351937 MHz
DATA PROCESSING
Sine bell 0.080 sec
F1 DATA PROCESSING
Sine bell 0.006 sec
FT size 1024 x 2048
Total time 45 min, 27 sec

DATA SHEET

Compound: 4-Bromo-2-(2-trimethylsilyl-ethyl)-quinoline

Compound No.: **14b**

Formula: C₁₄H₁₈NBrSi

Notebook Pg(s): JMNIV38W

Molecular Weight: 308.30

Yield(s): 63%

Other:

Appearance: colorless oil

Stability: stable

mp/bp:

[α]_D²³ (c, CHCl₃):

Elemental
Analysis
(Atlantic
Microlabs)

	%C	%H	%N
Calculated:			
Found:			

Exact Mass for C₁₄H₁₈NBrSi (M + 1H) requires *m/z* 308.0470, found *m/z* 308.0488

IR (thin film, neat, NaCl): cm⁻¹: 634.6, 661.9, 691.9, 757.9, 815.2, 833.0, 860.8, 925.4, 1025.4, 1110.0, 1148.0, 1176.6, 1218.8, 1247.7, 1296.1, 1404.1, 1489.9, 1551.5, 1586.3, 1614.0, 2894.7, 2950.8, 3062.3

NMR (CDCl₃):

(¹H, 400 MHz): δ 0.06 (s, 9H), 1.03 (m, 2H), 2.92 (m, 2H), 7.54 (t, 1H, *J* = 7.6 Hz), 7.63 (s, 1H), 7.70 (t, 1H, *J* = 6.8 Hz), 8.01 (d, 1H, *J* = 8.4 Hz), 8.15 (d, 1H, *J* = 8.4 Hz)

(¹³C, 100 MHz): δ -1.5, 17.1, 33.5, 124.9, 126.4, 126.7, 127.0, 129.3, 130.4, 134.3, 148.6, 165.1

HMBC: H-11 & C2 (²*J*_{CH}), H-12 & C-2 (³*J*_{CH}), H-3 & C-2 (²*J*_{CH}), H-3 & C-4 (²*J*_{CH}), H-5 & C-4 (³*J*_{CH})

Literature Reference(s): Pasto, D. J.; Taylor, R. T. In *Organic Reactions*; Paquette, L. A., Ed; John Wiley & Sons Inc.; New York, 1991, Vol. 40, p 91.

Archive directory: /export/home/comins/vnmrsys/data
Sample directory: nolab-30_30Aug2002
File: ghmbc

Pulse Sequence: ghmbc
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nucsmrc400"

Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 4000.0 Hz
2D Width 20120.7 Hz
4 repetitions
200 increments
OBSERVE H1: 400.1352180 MHz
DATA PROCESSING
Sine bell 0.064 sec
F1 DATA PROCESSING
Sine bell 0.005 sec
F1 size 1024 x 2048
Total time 18. min., 18. sec