CuI-Catalyzed Suzuki-Miyaura and Sonogashira Cross-Coupling Reactions Using DABCO as Ligand

Jin-Heng Li,* Ji-Lan Li, De-Ping Wang, Shao-Feng Pi, Ye-Xiang Xie, Man-Bo Zhang
and Xi-Chao Hu

Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research

(Ministry of Education), College of Chemistry and Chemical Engineering, Hunan

Normal University, Changsha 410081, China

jhli@hunnu.edu.cn

Supporting Information

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(A) Typical Experimental Procedure

Typical Experimental Procedure for the CuI/DABCO-catalyzed Suzuki-Type Cross-Coupling Reactions

A mixture of vinyl or aryl halide **1** (the indicated amount), boronic acid **2** (the indicated amount), CuI (10 mol %), DABCO (20 mol %), Cs₂CO₃ (2.0 equiv), TBAB (1 equiv) and DMF (3 mL) in a Schlenk tube was stirred under N₂ at 125-130 °C (oil bar temperature) for desired time (indicated in Table 1, Scheme 2 and Scheme 4) until complete consumption of starting material as monitored by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography (hexane or hexane/ethyl acetate) to afford the corresponding coupled products.

Typical Experimental Procedure for the CuI/DABCO-catalyzed Sonogashira-Type Cross-Coupling Reactions

A mixture of aryl halide **1** (the indicated amount), alkyne **4** (the indicated amount), CuI (10 mol %), DABCO (20 mol %), Cs₂CO₃ (2.0 equiv) and DMF (3 mL) in a Schlenk tube was stirred under N₂ at 135-140 °C (oil bar temperature) for desired time (indicated in Table 2, Table 3 and Scheme 3) until complete consumption of starting material as monitored by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography (hexane or hexane /ethyl acetate) to afford the corresponding coupled products.

(B) Analytical data for 3 and 5

(*E*)-1,2-Diphenylethene (3aa):¹ ¹H NMR (300 MHz, CDCl₃) δ: 7.51 (d, *J* = 8.4 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 4H), 7.27 (t, *J* = 6.3 Hz, 2H), 7.11 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ: 137.3, 128.7 (2C), 127.6, 126.5.

(*E*)- 1-Chloro-4-styrylbenzene (3ba):¹ ¹H NMR (400 MHz, CDCl₃) δ: 7.50 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.38–7.26 (m, 5H), 7.07 (dd, *J* = 16.4 Hz, 16.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 136.9, 135.8, 133.1, 129.3, 128.8, 128.7, 127.9, 127.6, 127.3, 126.5.

(*E*)-1-(4-Methoxystyryl)benzene (3ca):¹ ¹H NMR (400 MHz, CDCl₃) δ: 7.49–7.44 (m, 4H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.24–7.23 (m, 1H), 7.02 (dd, *J* = 16.8 Hz, 16.4 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: 160.0, 137.7, 130.2, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 114.1, 55.3.

1,1-Diphenylethene (3ea):¹ ¹H NMR (400 MHz, CDCl₃) δ: 7.35–7.30 (m, 10H), 5.45 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 150.0, 141.5, 128.2, 128.1, 127.7, 114.3.

1-Methoxy-4-(1-phenylvinyl)benzene (3eb):¹ ¹H NMR (400 MHz, CDCl₃) δ: 7.33–7.31 (m, 5H), 7.27 (d, *J* = 9.2 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 1H), 5.35 (s, 1H), 3.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 159.3, 149.5, 141.8, 134.0, 129.4, 128.3, 128.1, 127.6, 113.5, 112.9, 55.3.

1-Fluoro-4-(1-phenylvinyl)benzene (3ed):¹ ¹H NMR (400 MHz, CDCl₃) δ: 7.32–7.27 (m, 7H), 7.00 (t, *J* = 8.1 Hz, 2H), 5.42 (s, 1H), 5.40 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ: 163.7, 161.3, 149.0, 141.3, 137.5, 129.9, 128.2, 128.8, 115.0 (d, *J* = 20.6 Hz, 1C), 114.2.

1,3-Piphenylbenzene (3ga):² ¹H NMR (500 MHz, CDCl₃) δ: 7.91 (s, 1H), 7.90–7.73 (m, 4H), 7.66 (t, *J* = 8.0 Hz, 2H), 7.60–7.53 (m, 5H), 7.45 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: 141.9, 141.3, 129.2, 128.8, 127.4, 173.3, 126.2 (2C).

1,4-Diphenylbenzene (3ha):² ¹H NMR (500 MHz, CDCl₃) δ: 7.72–7.68 (m, 8H), 7.50 (t, *J* = 7.2 Hz, 4H), 7.40 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: 140.8, 140.2, 128.8, 127.5, 127.3, 127.0.

1,3,5-Triphenylbenzene (3ia):² ¹H NMR (500 MHz, CDCl₃) δ: 7.84 (s, 3H), 7.75 (d, *J* = 8.0 Hz, 6H), 7.53 (t, *J* = 7.5 Hz, 6H), 7.44 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 142.4, 141.2, 128.8, 127.5, 127.4, 127.3, 125.2.

(*E*)-1,4-Diphenylbut-1-en-3-yne (5aa):^{3j} ¹H NMR (400 MHz, CDCl₃) δ: 7.47 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.33–7.26 (m, 6H), 7.03 (d, *J* = 16.4 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 141.2, 136.3, 131.5, 128.7, 128.6, 128.3, 128.2, 126.3, 123.4, 108.1, 91.8, 88.9.

(*E*)-1-Chloro-4-(4-phenylbut-1-en-3-ynyl)benzene (5ba):^{1, 3} ¹H NMR (400 MHz, CDCl₃) δ: 7.48–7.45 (m, 2H), 7.33–7.30 (m, 7H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 139.8, 134.8, 134.2, 131.5, 128.9, 128.4, 128.3 (2C), 127.4, 108.8, 92.3, 88.6.

(*E*)-1-(Non-1-en-3-ynyl)benzene (5da):¹ ¹H NMR (400 MHz, CDCl₃) δ: 7.35 (t, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.16 (d, *J* = 16.0 Hz, 1H), 2.36 (t, *J* = 6.8 Hz, 2H), 1.59–1.56 (m, 2H), 1.41–1.34 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 139.9, 136.5, 128.5, 128.1, 125.9, 108.8, 93.0, 80.0, 31.0, 28.4, 22.2, 19.5, 13.9.

1-Methoxy-4-(2-phenylethynyl)benzene (5ja):³ ¹H NMR (400 MHz, CDCl₃) δ: 7.52–7.51 (m, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.34–7.32 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3.

1-(Dec-1-ynyl)-4-methoxybenzene (5jb):³ ¹H NMR (400 MHz, CDCl₃) δ: 7.33 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.38 (t, *J* = 7.6 Hz, 2H), 1.61–1.57 (m, 2H), 1.45–1.40 (m, 2H), 1.31–1.24 (m, 8H), 0.88 (t, *J* = 6.4 Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ : 158.9, 132.8, 116.1, 113.7, 88.8, 80.1, 55.2, 31.8, 29.2, 29.1, 28.9, 28.8, 22.7, 19.4, 14.1.

2-(3-(4-Methoxyphenyl)prop-2-ynoxy)-tetrahydro-2H-pyran (5jc):³ ^1H NMR (400 MHz, CDCl_3) δ : 7.39 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 4.90 (t, $J = 3.2$ Hz, 1H), 4.53–4.22 (m, 2H), 3.89 (t, $J = 7.2$ Hz, 1H), 3.80 (s, 3H), 3.58–3.54 (m, 1H), 1.76–1.54 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 159.6, 133.3, 114.8, 113.8, 96.8, 85.7, 83.6, 62.0, 55.2, 54.8, 30.3, 25.4, 19.1.

1-(2-(4-Nitrophenyl)ethynyl)benzene (5ka):³ ^1H NMR (300 MHz, CDCl_3) δ : 8.21 (d, $J = 8.8$ Hz, 2H), 7.65 (d, $J = 8.8$ Hz, 2H), 7.58–7.54 (m, 2H), 7.40–7.38 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 141.3, 132.6, 132.2, 130.6, 129.6, 128.8, 124.0, 122.5, 95.0, 87.9. Elem. Anal.: calcd. C, 75.33; H, 4.06; N, 6.27, found C, 75.29; H, 4.09; N, 6.25.

1-(Dec-1-ynyl)-4-nitrobenzene (5kb):³ ^1H NMR (400 MHz, CDCl_3) δ : 8.15 (d, $J = 8.8$ Hz, 2H), 7.51 (d, $J = 8.8$ Hz, 2H), 2.44 (t, $J = 7.2$ Hz, 2H), 1.74–1.59 (m, 2H), 1.47–1.43 (m, 2H), 1.31–1.26 (m, 8H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 132.6, 131.6, 123.8, 118.5, 97.2, 79.6, 32.2, 29.5, 29.4, 29.3, 28.7, 23.0, 19.9, 14.4.

1-(2-(2-Nitrophenyl)ethynyl)benzene (5la):³ ¹H NMR (300 MHz, CDCl₃) δ: 8.10 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.64–7.60 (m, 3H), 7.48 (t, *J* = 8.4 Hz, 1H), 7.40–7.38 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: 149.5, 132.9, 132.0, 129.2, 128.5, 128.4, 124.7, 122.3, 118.7, 97.1, 84.8.

1,2-Diphenylethyne (5ma):³ ¹H NMR (300 MHz, CDCl₃) δ: 7.60–7.51 (m, 4H), 7.39–7.26 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ: 132.0, 128.7, 128.6, 123.7, 89.7.

1-(2-*p*-Tolylethynyl)benzene (5na):³ ¹H NMR (300 MHz, CDCl₃) δ: 7.54–7.50 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.35–7.31 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 138.7, 132.9, 131.9, 129.6, 129.5, 128.8, 128.7, 128.4, 89.1, 83.4, 21.9.

1-(Dec-1-ynyl)-4-methylbenzene (5nb):³ ¹H NMR (400 MHz, CDCl₃) δ: 7.28 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.61–1.55 (m, 2H), 1.46–1.42 (m, 2H), 1.31–1.29 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 137.4, 131.4, 128.9, 121.0, 89.6, 80.6, 31.9, 29.2, 29.1, 28.9, 28.8, 23.7, 21.4, 18.4, 14.1.

1-(2-*o*-Tolylethynyl)benzene (5oa):² ¹H NMR (400 MHz, CDCl₃) δ: 7.53–7.52 (m, 3H), 7.35–7.33 (m, 4H), 7.23–7.22 (m, 2H), 2.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃)

δ : 140.2, 132.6, 131.9, 131.6, 129.5, 129.2, 128.4, 128.3, 128.2, 125.6, 88.4, 81.7, 20.7.

1-(2-(4-Methoxyphenyl)ethynyl)-4-nitrobenzene (5pd):³ ¹H NMR (400 MHz, CDCl₃) δ : 8.20 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.4, 146.7, 134.0, 133.4, 132.0, 123.6, 114.2, 114.1, 95.1, 86.6, 55.3.

1-Fluoro-4-(2-(4-nitrophenyl)ethynyl)benzene (5pe):³ ¹H NMR (400 MHz, CDCl₃) δ : 8.23 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.57–7.54 (m, 2H), 7.10 (t, J = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 164.3, 161.8, 146.9, 133.8, 132.2, 130.0, 123.7, 116.0 (d, J = 22 Hz, 1C), 93.6, 87.3.

2-Phenylbenzofuran (5va):³ ¹H NMR (400 MHz) δ : 7.87 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.03 (s, 1H); ¹³C NMR (100 MHz) δ : 155.9, 154.9, 130.4, 129.2, 128.8, 128.5, 124.9, 124.2, 122.9, 120.9, 111.2, 101.3.

2-Octylbenzofuran (5vb): ¹H NMR (400 MHz, CDCl₃) δ : 7.48 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.22–7.15 (m, 2H), 6.37 (s, 1H), 2.76 (t, J = 7.6 Hz, 2H), 1.77–1.70 (m, 2H), 1.41–1.27 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); ¹³C NMR (100

MHz, CDCl₃) δ : 159.8, 154.6, 129.0, 123.0, 122.3, 120.1, 110.7, 101.7, 31.8, 29.3, 29.2, 28.4, 27.7, 22.7, 14.1; LRMS (EI, 70 eV) m/z (%): 230 (M^+ , 64), 187 (11), 173 (8), 145 (13), 131 (100); HRMS (EI) for C₁₆H₂₂O (M^+): calcd. 230.1680, found 230.1678.

2-Phenylethynylaniline (5wa):⁴ ¹H NMR (400 MHz, CDCl₃) δ : 7.53 (d, J = 9.6 Hz, 2H), 7.38–7.33 (m, 4H), 7.14 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 8.0 Hz, 2H), 4.28 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 147.6, 132.1, 131.5, 129.7, 128.4, 128.2, 123.3, 118.1, 114.4, 108.0, 94.7, 85.8.

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(D) Spectra

Figure 1. TEM picture of CuI (CuI was obtained under thermal conditions in the presence of *n*-Bu₄NBr, and it was not nano-scale based on the picture)

(E)-1,2-diphenylethene (3aa)

(E)-1,2-diphenylethene (3aa)

(E)- 1-chloro-4-styrylbenzene (3ba)

(E)- 1-chloro-4-styrylbenzene (3ba)

(*E*)-1-(4-methoxystyryl)benzene (3ca)

(E)-1-(4-methoxystyryl)benzene (3ca)

1,1-diphenylethene (3ea)

1,1-diphenylethene (3ea)

1-Methoxy-4-(1-phenylvinyl)benzene (3eb)

1-Methoxy-4-(1-phenylvinyl)benzene (3eb)

1-Fluoro-4-(1-phenylvinyl)benzene (3ed)

1-Fluoro-4-(1-phenylvinyl)benzene (3ed)

1,3-diphenylbenzene (3ga)

1,3-diphenylbenzene (3ga)

1,4-Diphenylbenzene (3ha)

1,4-diphenylbenzene (3ha)

1,3,5-triphenylbenzene (3ia)

1,3,5-triphenylbenzene (3ia)

(*E*)-1,4-Diphenylbut-1-en-3-yne (5aa)

(*E*)-1,4-Diphenylbut-1-en-3-yne (5aa)

(*E*)-1-Chloro-4-(4-phenylbut-1-en-3-ynyl)benzene (5ba)

(*E*)-1-Chloro-4-(4-phenylbut-1-en-3-ynyl)benzene (5ba)

(E)-1-(Non-1-en-3-ynyl)benzene (5db)

(E)-1-(Non-1-en-3-ynyl)benzene (5db)

1-Methoxy-4-(2-phenylethynyl)benzene (5ja)

1-methoxy-4-(2-phenylethynyl)benzene (5ja)

1-(dec-1-ynyl)-4-methoxybenzene (5jb)

1-(dec-1-ynyl)-4-methoxybenzene (5jb)

2-(3-(4-Methoxyphenyl)prop-2-ynyloxy)-tetrahydro-2H-pyran (5jc)

2-(3-(4-Methoxyphenyl)prop-2-ynoxy)-tetrahydro-2H-pyran (5jc)

1-(2-(4-nitrophenyl)ethynyl)benzene (5ka)

1-(2-(4-nitrophenyl)ethynyl)benzene (5ka)

1-(dec-1-ynyl)-4-nitrobenzene (5kb)

1-(dec-1-ynyl)-4-nitrobenzene (5kb)

[illegible]

L-05-1-13/C13

exp2 \$20u1

SAMPLE SPECIAL

date Jan 26 2005 temp not used

solvent CCl3 gain 56

TI 11.111 Hz

ACQUISITION exp hst 0.008

sw 24002.4 pw30 9.300

at 1.031 atfa 20.000

pp 32300 1) FLAGS

pp 32300 1) n

pp 32300 1) n

bs 8 in n

dl 1.000 dp y

nt 4000 hs PROCESSING nm

ct TRANSMITTER 608 1b not used

ln 100.583 f1 DISPLAY 1.00

sfra 100.583 sp 1496.7

lof 100.0 wp1 1579.2

tpwr 4.530 rfp 2410.0

DECOUPLER H1 TP 39.8

dn -349.0 1p -236.8

dof PLOT 250

dm yy wc 74

dm 41 sc 0

dpr 13120 th 3

nm ph

149.475

134.566

132.862

131.995

129.235

128.536

128.441

124.734

122.301

116.711

97.080

84.757

77.350

77.029

76.709

ppm

1,2-diphenylethyn (5ma)

1,2-diphenylethyn (5ma)

1-(2-*p*-tolylethynyl)benzene (5na)

1-(2-*p*-tolylethynyl)benzene (5na)

1-(dec-1-ynyl)-4-methylbenzene (5nb)

1-(dec-1-ynyl)-4-methylbenzene (5nb)

1-(2-*o*-tolylethynyl)benzene (5oa)

1-(2-*o*-tolylethynyl)benzene (50a)

1-(2-(4-Methoxyphenyl)ethynyl)-4-nitrobenzene (5pd)

1-(2-(4-Methoxyphenyl)ethynyl)-4-nitrobenzene (5pd)

1-fluoro-4-(2-(4-nitrophenyl)ethynyl)benzene (5pe)

1-fluoro-4-(2-(4-nitrophenyl)ethynyl)benzene (5pe)

2-Phenylbenzofuran (5va)

2-Phenylbenzofuran (5va)

2-Octylbenzofuran (5vb)

2-Octylbenzofuran (5vb)

2-Phenylethynylaniline (5wa)

2-Phenylethynylaniline (5wa)