Efficient Palladium-Catalyzed Homocoupling Reaction and Sonogashira Cross-Coupling Reaction of Terminal Alkynes under Aerobic Conditions

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Supporting Information

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(A) Typical experimental procedure

(1) Typical Experimental Procedure for the Palladium-Catalyzed Homocoupling of Alkynes. A mixture of alkyne **1** (1 mmol), Pd(OAc)₂ (2.0 mol%), CuI (2.0 mol%), DABCO (3 equiv), and MeCN (5 mL) was stirred at room temperature for desired time until complete consumption of starting material as judged by TLC and GC analysis. After usual workup, the residue was purified by flash column chromatography to give **2** (hexane or hexane/ethyl acetate).

(2) Typical Experimental Procedure for Pd(OAc)₂-Catalyzed Sonogashira Cross-Coupling Reactions. Firstly, Pd(OAc)₂ (4.5 mg, 2.0 mol%) was dissolved in MeCN (200 mL). Then the indicated amount of Pd(OAc)₂ acetonitrile solution was added to a mixture of alkyne **1** (the indicated amount in Table 4), ArX **3** (1 mmol), DABCO (3 equiv), and MeCN (5 mL). Then the mixture was stirred at the indicated reaction temperature for desired time until complete consumption of starting material as judged by TLC and GC analysis. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography (hexane or hexane/ethyl acetate) to afford the desired coupled products **4–10**.

(B) Analytical data for **2¹⁻⁴ and **4–10**⁵⁻¹³:**

1,4-Diphenyl buta-1,3-diyne (2a)

¹H NMR (400 MHz, CDCl₃) δ: 7.54 (d, *J* = 7.4 Hz, 4H), 7.38–7.34 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 132.8, 129.6, 128.8, 122.1, 81.9, 74.2. LRMS (EI, 20 eV) *m/z* (%): 202 (M⁺, 100).

1,4-Bis(*p*-methylphenyl) buta-1,3-diyne (2b)

^1H NMR (400 MHz, CDCl_3) δ : 7.41 (d, $J = 8.0$ Hz, 4H), 7.14 (d, $J = 8.0$ Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 139.5, 132.4, 129.2, 118.8, 81.5, 73.4, 21.6. LRMS (EI, 20 eV) m/z (%): 230 (M^+ , 100).

1,4-Bis(*p*-methoxyphenyl) buta-1,3-diyne (2c)

^1H NMR (400 MHz, CDCl_3) δ : 7.46 (d, $J = 8.8$ Hz, 4H), 6.85 (d, $J = 8.8$ Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 160.2, 134.0, 114.1, 113.9, 81.2, 72.9, 55.3. LRMS (EI, 20 eV) m/z (%): 262 (M^+ , 100).

1,4-Bis(trifluoromethylphenyl) buta-1,3-diyne (2d)

^1H NMR (400 MHz, CDCl_3) δ : 7.65 (d, $J = 8.4$ Hz, 4H), 7.62 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ : 132.8, 131.2, 130.9, 125.5, 125.4, 125.2, 125.0, 122.3, 81.0, 75.6. MS m/z (%): 182 (M^+ , 100), 164 (53), 92 (40), 75 (13). LRMS (EI, 20 eV) m/z (%): 338 (M^+ , 100).

1,4-Bis(2-pyridine)buta-1,3-diyne (2e)

^1H NMR (400 MHz, CDCl_3) δ : 8.63 (d, $J = 4.4$ Hz, 2H), 7.71 (t, $J = 7.6$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.31 (t, $J = 4.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 150.3, 141.8, 134.3, 128.4, 123.8, 80.8, 73.2; LRMS (EI, 20 eV) m/z (%): 204 (M^+ , 100).

Tetradeca-6,8-diyne (2f)

^1H NMR (400 MHz, CDCl_3) δ : 2.25 (t, $J = 7.2$ Hz, 4H), 1.54–1.46 (m, 4H), 1.39–1.28 (m, 8H), 0.89 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 77.5, 65.2, 31.0, 28.0, 22.2, 19.2, 13.9. LRMS (EI, 20 eV) m/z (%): 190 (M^+ , 1), 105 (57), 91 (100), 79 (49), 67 (31), 41 (27).

Icosa-9,11-diyne (2g)

^1H NMR (400 MHz, CDCl_3) δ : 2.27 (t, $J = 7.2$ Hz, 4H), 1.57–1.50 (m, 4H), 1.43–1.38 (m, 4H), 1.34–1.20 (m, 16H), 0.90 (t, $J = 6.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 77.5, 65.2, 31.8, 29.1, 29.0, 28.8, 28.3, 22.6, 19.2, 14.1. LRMS (EI, 20 eV) m/z (%): 182 (M^+ , 100), 164 (53), 92 (40), 75 (13).

2,2,7,7-Tetramethyl octa-3,5-diyne (2h)

^1H NMR (400 MHz, CDCl_3) δ : 1.23 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ : 86.3, 63.6, 30.6, 28.0. LRMS (EI, 20 eV) m/z (%): 162 (M^+ , 8), 161 (25), 133 (37), 119 (55), 91 (100), 79 (59), 67 (57), 41 (50).

1,4-Bis(cyclohex-1-enyl) buta-1,3-diyne (2i)

^1H NMR (400 MHz, CDCl_3) δ : 6.25 (t, $J = 4.0$ Hz, 2H), 2.12–2.10 (m, 8H), 1.66–1.57 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ : 138.0, 119.9, 82.7, 71.5, 28.6, 25.8, 22.1, 21.3. LRMS (EI, 20 eV) m/z (%): 210 (M^+ , 3), 111 (20), 85 (71), 71 (95), 57 (100), 41 (69).

1,4-Bis(1-hydroxycyclohexyl) buta-1,3-diyne (2j)

^1H NMR (400 MHz, CDCl_3) δ : 1.95–1.91 (m, 4H), 1.82 (s, 2H), 1.71 (t, $J = 8.0$ Hz, 4H), 1.63–1.53 (m, 8H), 1.26–1.20 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ : 83.0, 69.2, 68.3, 39.7, 25.0, 23.1. LRMS (EI, 20 eV) m/z (%): 246 (M^+ , 1), 210 (100), 167 (32), 141 (19), 77 (10).

2,4,9,11-Tetramethyl dodeca-5,7-diyne-4,9-diol (2k)

^1H NMR (400 MHz, CDCl_3) δ : 4.82 (s, 2H), 1.95–1.56 (m, 2H), 1.61 (d, $J = 6.4$ Hz, 4H), 1.51 (s, 6H), 1.02 (d, $J = 5.2$ Hz, 6H), 1.00 (d, $J = 5.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 83.4, 68.6, 67.7, 51.5, 34.6, 25.1, 24.2, 24.0. LRMS (EI, 20 eV) m/z (%): 250 (M^+ , 1), 232 (1), 85 (51), 71 (100), 57 (96), 41 (60).

Acetic acid 6-acetoxy hexa-2,4-diynyl ester (2l)

^1H NMR (400 MHz, CDCl_3) δ : 4.73 (s, 4H), 2.10 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.4, 73.6, 70.3, 52.8, 20.6. LRMS (EI, 20 eV) m/z (%): 194 (M^+ , 5), 135 (3), 76 (100).

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

^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.

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

^1H NMR (400 MHz) 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) 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 (6)

^1H NMR (300 MHz, CDCl_3) 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); ^{13}C NMR (75 MHz, CDCl_3) 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 (7)

^1H NMR (300 MHz, CDCl_3) δ : 7.60–7.51 (m, 4H), 7.39–7.26 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : 132.0, 128.7, 128.6, 123.7, 89.7.

1-(2-*p*-tolylethynyl)benzene (8)

^1H NMR (300 MHz) 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); ^{13}C NMR (100 MHz) δ : 138.7, 132.9, 131.9, 129.6, 129.5, 128.8, 128.7, 128.4, 89.1, 83.4, 21.9.

1-(2-*o*-tolylethynyl)benzene (9)

¹H NMR (400 MHz) 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) 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-methoxy-4-(2-phenylethynyl)benzene (10)

¹H NMR (400 MHz) 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) δ : 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3.

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(D) NMR spectra

1,4-Diphenyl buta-1,3-diyne (2a)

○—237—230—○

C#CC1=CC=CC=C1C2=CC=CC=C2C#CC3=CC=CC=C3C

[illegible]

1,4-Bis(*p*-methoxyphenyl) buta-1,3-diyne (2c)

[illegible]

$$\text{---}[\text{C}_6\text{H}_4\text{---C}(\text{O})\text{---C}(\text{O})\text{---C}_6\text{H}_4\text{---}]_n\text{---}$$

1,4-Bis(trifluoromethylphenyl) buta-1,3-diyne (2d)

c1ccccc1C#CC#CC#CC#Cc2ccccc2

c1ccccc1C#CC#Cc2ccccc2

Tetradeca-6,8-diyne (2f)

$$n\text{-C}_5\text{H}_{11}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-n\text{-C}_5\text{H}_{11}$$

Icosa-9,11-diyne (2g)

Icosa-9,11-diyne (2g)

2,2,7,7-Tetramethyl octa-3,5-diyne (2h)

2,2,7,7-Tetramethyl octa-3,5-diyne (2h)

c1ccccc1C#CC#CC#CC#Cc2ccccc2

C1=CC=C(C(=C1)C#N)C#NC2=CC=CC=C2

[illegible]

1,4-Bis(1-hydroxycyclohexyl) buta-1,3-diyne (2j)

2,4,9,11-Tetramethyl dodeca-5,7-diyne-4,9-diol (2k)

2,4,9,11-Tetramethyl dodeca-5,7-diyne-4,9-diol (2k)

Acetic acid 6-acetoxy hexa-2,4-diynyl ester (2l)

Acetic acid 6-acetoxy hexa-2,4-diynyl ester (2l)

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

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

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

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

[illegible]

L-05-1-19/c13

exp2 \$20v1

SAMPLE SPECIAL
date Jan 26 2005 temp not used
solvent CCl₃ gain 56
f1 100.628 mhz
F2 ACQUISITION exp hst 0.008
sw 24002.4 pw30 9.300
at 1.031 atfa 20.000
pp 32300 flags
pr 12000 i) n
ps 12000 s tn n
dl 1.000 dp y
nt 4000 hs PROCESSING nm
ct TRANSMITTER 608 lb not used
ln 100.583 fh DISPLAY 1.00
sfra 100.583 sp 1496.7
lof 100.0 wp1 1579.2
tpw 54 wpt 2410.0
pw 4.650 rfp 39.8
DECOUPLER H1 tp -236.8
dn -349.0 PLOT 250
dm yy wc 0
am yy sc 74
dpmr 41 vs 3
dmf 13120 th nm

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128.441

124.734

122.301

118.711

97.080

84.757

77.350
77.029
76.709

180 160 140 120 100 80 60 40 ppm

1,2-diphenylethyne (7)

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1-(2-*p*-tolylethynyl)benzene (8)

1-(2-*p*-tolylethynyl)benzene (8)

1-(2-*o*-tolylethynyl)benzene (9)

1-(2-*o*-tolylethynyl)benzene (9)

1-methoxy-4-(2-phenylethynyl)benzene (10)

S46