Efficient Stille Cross-Coupling Reaction Catalyzed by Pd(OAc)₂/Dabco Catalytic System

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Supporting Information

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(A) Typical experimental procedure

(1) Typical experimental procedure for the palladium-catalyzed Stille cross-coupling reaction. A mixture of aryl halide **1** (0.5 mmol), organotin **2** (0.55 mmol), Pd(OAc)₂ (3 mol%), Dabco (6 mol%), the indicated base (3 equiv), and dioxane (5 mL) was added to a sealed tube. Then the mixture was stirred at 100 °C for desired time until complete consumption of starting material as judged by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography (hexane or hexane/ethyl acetate) to afford **3—13**.

(2) Typical experimental procedure for 0.0001 mol% of Pd and 0.0002 mol% of Dabco-catalyzed Stille cross-coupling reaction of 1-bromo-4-nitrobenzene (1e) and furan-2-yltributyltin (2b) (entry 3 in Table 3). First, Pd(OAc)₂ (4.5 mg, 0.02 mmol) was dissolved in 200 mL of dioxane, and Dabco (4.5 mg, 0.04 mmol) was also dissolved in another 200 mL of dioxane. Then 5 µL of Pd(OAc)₂ dioxane solution and 5 µL of Dabco dioxane solution were added to a mixture of 1-bromo-4-nitrobenzene (**1e**) (0.5 mmol), furan-2-yltributyltin (**2b**) (0.55 mmol), Bu₄NF (3 equiv), and dioxane (5 mL) in a sealed tube, respectively (by syringe). The mixture was stirred at 100 °C for 40 h determined by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography (hexane) to afford 98% yield of **8** (70.5 mg, TONs: 980 000)

(B) Analytical data for 3—13

4-Methoxy-biphenyl (3)¹

White solid; ^1H NMR (300 MHz, CDCl_3): δ 7.54 (t, $J = 8.4$ Hz, 4H), 7.41 (t, $J = 7.2$ Hz, 2H), 7.31 (t, $J = 7.2$, 1H), 6.98 (d, $J = 6.7$, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

4-Nitro-biphenyl (4)¹

Pale yellow solid; ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 6.9$ Hz, 2H), 7.52–7.44 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 147.6, 147.2, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1.

1-Biphenyl-4-yl-ethanone (5)¹

White solid; ^1H NMR (300 MHz, CDCl_3): δ 8.04 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 7.6$ Hz, 2H), 7.50–7.40 (m, 3H), 2.64 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 197.8, 145.8, 139.9, 135.8, 128.9, 128.9, 128.2, 127.3, 127.2, 26.7.

Biphenyl (6)¹

White solid; ^1H NMR (300 MHz, CDCl_3) δ : 7.59 (d, $J = 8.4$ Hz, 4H), 7.43 (t, $J = 7.2$ Hz, 4H), 7.36 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ : 141.6, 129.1, 127.6, 127.5.

3,5-Dimethyl-biphenyl (7)²

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.59 (d, $J = 8.4$ Hz, 2H), 7.44–7.40 (m, 2H), 7.31–7.28 (m, 1H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 9.2$ Hz, 1H), 2.35 (d, $J =$

8.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 141.5, 138.1, 128.9, 128.7, 127.9, 127.2, 127.1, 125.1, 21.4.

2-(4-nitrophenyl)furan (8)³

Yellow solid; ^1H NMR (400 MHz, CDCl_3) δ : 8.24 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 1.2 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.55 (t, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 151.7, 146.4, 144.1, 136.4, 124.3, 123.3, 112.4, 108.6.

2-(4-nitrophenyl)thiophene (9)³

Yellow solid; ^1H NMR (400 MHz, CDCl_3) δ : 8.23 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 9.6 Hz, 2H), 7.48 (d, J = 4.0 Hz, 1H), 7.44 (d, J = 5.2 Hz, 1H), 7.15 (t, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 146.6, 141.6, 140.6, 128.7, 127.7, 126.0, 125.7, 124.4.

4-nitrostyrene (10)⁴

Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 8.19 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.79 (dd, J = 10.8, 11.2 Hz, 1H), 5.93 (d, J = 17.2 Hz, 1H), 5.50 (d, J = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 147.2, 143.8, 135.0, 126.8, 123.9, 118.6.

1-(2-(4-nitrophenyl)ethynyl)benzene (11)⁵

Pale yellow solid; ^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.

2-phenylfuran (12)⁶

White solid; ^1H NMR (300 MHz, CDCl_3) δ : 7.67 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 8.8 Hz, 2H), 7.46–7.34 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ : 142.0, 128.7, 128.6, 127.3, 127.2, 127.1, 123.7, 111.6.

1,2-diphenylethyne (13)⁷

White solid; ^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.

(c) References

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(E) Spectra

4-Methoxy-biphenyl (3)

¹³C NMR spectrum (CDCl₃) of compound 1. The x-axis represents chemical shift in ppm, ranging from 0 to 160. The spectrum shows several sharp peaks. Key peaks are labeled with their chemical shift values: 158.081, 149.758, 133.760, 128.791, 128.133, 126.715, 126.637, 116.146, 55.329, and a cluster of peaks near 0 ppm labeled 27.038, 26.600, and 26.571.

4-Nitro-biphenyl (4)

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1- Biphenyl-4-yl-ethanone (5)

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Biphenyl (6)

Biphenyl (6)

3,5-Dimethyl-biphenyl (7)

3,5-Dimethyl-biphenyl (7)

2-(4-nitrophenyl)furan (8)

L-9.14/C13
 exp2 52pul

SAMPLE		SPECIAL	
date	temp	not	used
Sep 16 2004	36		
solvent	CDC13	gain	0
file	exp	spin	0
ACQUISITION	exp	0.000	
sv	23081.7	pw90	9.300
at	1.091	flfa	20.000
np	50198	flags	
td	13069	l1	n
td	13069	l2	n
dl	1.000	dp	y
nt	10000	hs	mm
ct	854	lb	PROCESSING 2.00
tn	TRANSMITTER C13	fn	not used
sfreq	100.584	fn	DISPLAY
tof	766.0	sp	1531.7
tpur	4.650	rf1	885.0
pw	4.650	rf2	7744.2
dn	H1	rf3	-188.8
dof	-345.0	lp	133.4
dms	377.0	mc	250
dpr	41	sc	70
daf	13120	vs	70
	nm	ph	

151.709
 144.136
 140.391
 136.417
 124.293
 123.910
 112.421
 108.959
 77.914
 77.000
 76.679

ppm

2-(4-nitrophenyl)thiophene (9)

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4-nitrostyrene (10)

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1-[2-(4-nitrophenyl)ethynyl]benzene (11)

1-[2-(4-nitrophenyl)ethynyl]benzene (11)

2-phenylfuran (12)

2-phenylfuran (12)

1,2-diphenylethyne (13)

1,2-diphenylethyne (13)