The Ullmann Coupling Reaction – A new Approach to Tetra-arylstannanes

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SUPPORTING INFORMATION

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**Table S-1. Ullmann Coupling Reaction of 2,4-Dichloriodobenzene:
Results of Initial $^{119}\text{Sn}\{^1\text{H}\}$ NMR analysis^a**

entry	reaction conditions		$^{119}\text{Sn}\{^1\text{H}\}$ NMR	
	ratio of substrate to Cu bronze (w/w)	duration (days)	total no. of signals	chemical shifts (δ ppm) ^b
1 ^{c,d}	3:7	7	3	-89.3 , -127.8, -143.6
2 ^{c,e}	3:7	7	2	-89.3 , -143.6
3 ^{c,f}	3:7	7	2	-143.6 , -175.6
4	3:3	7	1	-143.6
5	3:1	7	2	-143.6 , -175.6
6 ^g	3:7	7	3	-89.3 , -143.6 , -175.6
7 ^h	3:7	7	2	-143.6 , -175.6
8	3:7	2	3	-89.3 , -143.6 , -175.6
9	3:7	4	3	-89.3 , -143.6 , -175.6
10 ⁱ	1:0.5	7	1	-175.6
11	3:7	7	2	-89.3 , -143.6
12 ^j	3:7	7	5	-89.3 , -127.8, -141.1, -143.6 , -175.6
13 ^k	3:7	7	3	-89.3 , -143.6 , -175.6
14 ^l	3:7	7	1	-143.6
15 ^m	3:7	7	3	-89.3 , -143.6 , -175.6

^aUnless otherwise stated, all the reactions were carried out at 230°C using 3 g of **1a** and 7 g of purified Cu bronze (lot **A**). 2,2',4,4'-dichloro-1,1'-biphenyl **2b** was identified by GC/MS. The presence of **3a** in the reaction mixture was verified using its $^{119}\text{Sn}\{^1\text{H}\}$ NMR signal at $\delta = -143.6$. ^bFigures in bold indicates the δ -value of the major component (i.e. **3a**) in the reaction mixture. All signals are singlets. ^cReactions are led to complete conversion. 2,4-dichlorobenzene is formed as the major side product according to GCMS analysis. ^dUsing lot B of Cu bronze from Alfa Aesar. ^eReproduced using lot B of Cu bronze from Alfa Aesar. ^fUsing Cu bronze from Atlantic Equipment Engineers. ^gReaction was performed at 200°C. ^hReaction was performed at 150°C. ⁱUsing Sn-powder. ^jCu bronze was used without purification. ^kAqueous workup. ^lReproduced using starting materials and reagents from the same source (lot **A**). ^mReaction was performed using 1 g of **1a** and 3 g of purified Cu bronze.

Table S-2. $^{119}\text{Sn}\{^1\text{H}\}$ NMR Analysis of Crude Reaction Mixtures of Ullmann Coupling Reactions of Chlorinated Iodobenzenes^a

entry		iodobenzenes (1)	total no. of signals in $^{119}\text{Sn}\{^1\text{H}\}$ NMR	$^{119}\text{Sn}\{^1\text{H}\}$ NMR (δ ppm) ^b
1	1b		1	-122.1
2	1c		2	-100.0 , -149.6
3	1d		2 1	-187.6, -195.5 -187.9^d
4	1e		1 1	-117.0 -115.7^d
5	1f		3	-167.9 , -214.3, -243.8

^a Unless otherwise stated, all the reactions were carried out at 230°C for 7 days using 3 g of **1b-f** and 7 g of purified Cu bronze. ^b Figures in bold indicates the δ -value of the major component in the reaction mixture. All signals are singlets. ^c All reactions are led to complete conversion. Deiodinated chlorobenzenes are formed as the major side products. ^d Reproduced using starting materials and reagents from the same source (lot A).

Table S-3. $^{119}\text{Sn}\{^1\text{H}\}$ NMR Analysis of Crude Reaction Mixtures of Ullmann Coupling Reaction of Functionalized Iodobenzenes^a

entry		iodobenzenes	total no. of signals in $^{119}\text{Sn}\{^1\text{H}\}$ NMR	$^{119}\text{Sn}\{^1\text{H}\}$ NMR (δ ppm) ^b
1	1h		1	-116.8 ^c
2	1i		1 2	-119.4 -115.6, -119.6 ^d
3	1j		2	-91.7, -133.0
4	1k		2	-100.0 , -149.6 ^c
5	1l		0	<i>nd</i> ^c
6	1m		0	<i>nd</i>

^aUnless otherwise stated, all the reactions were carried out at 230°C for 7 days using 3 g of **1h-m** and 7 g of purified Cu bronze. ^bFigures in bold indicates the δ -value of the major component in the reaction mixture. All signals are singlets with exception of entry 2 (found as multiplets due to ^{119}Sn - ^{19}F coupling). ^cAll reactions are led to complete conversion. Deiodinated benzenes are formed as the major side products. ^dReproduced using starting materials and reagents from the same source (lot A). *nd* = not detected by ^{119}Sn NMR.

Procedure for quantitative GC analysis.

Three similar glass vials were tared and was weighed the exact known amount of iodobenzene, authentic product (tetraphenyl stannane **3n**) and standard (diethylene glycol di-*n*-butyl ether) to each vial. The contents were dissolved in HPLC grade CHCl₃ and diluted to 10 mL by using CHCl₃. Each sample was analyzed by GC as follows: a sample (~1 μL) from the vial was injected. The column temperature was programmed from 45 °C to 260 °C (hold 2 min.) at 14 °C/min. The resulting three peaks were integrated. This procedure was repeated three times for each vial (i.e. 3×3 times) and the areas were used to calculate the response ratio of starting material to standard and of the product to standard. The response ratio used to determine yields were an average of the response ratios calculated for the three trials of each sample.

NMR data of biphenyls (2):

2,2',4,4'-tetrachlorobiphenyl or PCB 47 (2a):¹ Crude **2a** was obtained as white solid by column chromatography on silica gel using hexanes as eluent. *R_f* 0.70 (hexanes). ¹H NMR (400 MHz, CDCl₃): δ 7.16 (d, *J* = 8.2 Hz, 2×H-6), 7.29 (dd, *J* = 8.2 Hz & *J* = 2.0 Hz, 2×H-5), 7.48 (d, *J* = 2.0 Hz, 2×H-3). ¹³C NMR (400 MHz, CDCl₃): δ 127 (2×C-5), 129.44 (2×C-6), 131.89 (2×C-3), 134.33 (2×C-2), 134.81 (2×C-4), 135.72 (2×C-1). MS (EI): *m/z* (relative abundance %) 292 (M⁺, 100), 255 (50), 220 (40), 184 (20), 150 (50), 110 (40), 92 (30), 74 (20).

3,3',4,4'-tetrachlorobiphenyl or PCB 77 (2b):¹ White solid (purified by column chromatography by using hexanes). *R_f* 0.58 (hexanes). M.p. = 174-176 °C (Lit.: 173 °C²). ¹H NMR (400 MHz, CDCl₃): δ 7.36 (dd, *J* = 2.2 & *J* = 8.3 Hz, 2×H-6), 7.51 (d, *J* = 8.3 Hz, 2×H-5), 7.61 (d, *J* = 2.2 Hz, 2×H-2). ¹³C NMR (400 MHz, CDCl₃): δ 126.15 (2×C-6), 128.81 (2×C-2), 130.97 (2×C-5), 132.48 (2×C-4), 133.25 (2×C-3), 138.73 (2×C-1). MS (EI): *m/z* (relative

abundance %) 292 (M^+ , 100), 256 ($M^+ - Cl$, 5), 220 ($M^+ - 2Cl$, 40), 184 ($M^+ - 3Cl$, 10), 110 (12), 74 (5).

2,2',4,4',5,5'-hexachlorobiphenyl or PCB 153 (2c):¹ Crude **2c** was obtained as white solid by column chromatography on silica gel using hexanes as eluent. R_f 0.79 (hexanes). 1H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 2×H-3), 7.59 (s, 2×H-6). ^{13}C NMR (400 MHz, $CDCl_3$): δ 130.99 (2×C-6), 131.22 (2×C-2), 132.06 (2×C-3), 132.37 (2×C-5), 133.69 (2×C-4), 135.86 (2×C-1). MS (EI): m/z (relative abundance %) 361 (M^+ , 100), 325 ($M^+ - Cl$, 33), 290 ($M^+ - 2Cl$, 95), 253 ($M^+ - 3Cl$, 18), 218 ($M^+ - 4Cl$, 68), 182 ($M^+ - 5Cl$, 20), 144 ($M^+ - 6Cl$, 48), 109 (40), 73 (20).

2,2',3,3',6,6'-hexachlorobiphenyl or PCB 136 (2d):¹ Crude **2d** was obtained as white solid by column chromatography on silica gel using hexanes as eluent. R_f 0.76 (hexanes). 1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, $J = 8.6$ Hz, 2×H-4), 7.41 (d, $J = 8.6$ Hz, 2×H-5). ^{13}C NMR (400 MHz, $CDCl_3$): δ 128.51 (2×C-3), 131.07 (2×C-4), 132.06 (4×C-2), 132.95 (2×C-5), 136.85 (2×C-1). MS (EI): m/z (relative abundance %) 361 (M^+ , 100), 325 ($M^+ - Cl$, 20), 290 ($M^+ - 2Cl$, 95), 253 ($M^+ - 3Cl$, 10), 218 ($M^+ - 4Cl$, 70), 182 ($M^+ - 5Cl$, 25), 144 ($M^+ - 6Cl$, 52), 109 (40), 73 (20).

2,2',3,3',5,5'-hexachlorobiphenyl or PCB 133 (2e):¹ White solid (purified by column chromatography by using hexanes). R_f 0.56 (hexanes). M.p. = 127-128 °C (Lit.: 128-129 °C³). 1H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, $J = 2.4$ Hz, 2×H-2), 7.54 (d, $J = 2.4$ Hz, 2×H-4). ^{13}C NMR (400 MHz, $CDCl_3$): δ 128.87 (2×C-2), 130.39 (2×C-4), 130.55 (2×C-6), 132.70 (2×C-3), 134.37 (2×C-5), 139.74 (2×C-1). MS (EI): m/z (relative abundance %) 361 (M^+ , 100), 325 ($M^+ - Cl$, 95), 290 ($M^+ - 2Cl$, 97), 253 ($M^+ - 3Cl$, 35), 218 ($M^+ - 4Cl$, 75), 182 ($M^+ - 5Cl$, 25), 144 ($M^+ - 6Cl$, 65), 109 (45), 73 (18).

2,2',4,4',6,6'-hexachlorobiphenyl or PCB 155 (2f):¹ Crude **2f** was obtained as a white solid by column chromatography on silica gel using hexanes as eluent. *R_f* 0.71 (hexanes). ¹H NMR (400 MHz, CDCl₃): δ 7.47 (s, 2×H-3/H-5). ¹³C NMR (400 MHz, CDCl₃): δ 128.17 (2×C-3/C-5), 132.89 (2×C-1), 135.64 (2×C-2/C-6), 135.68 (2×C-4). MS (EI): *m/z* (relative abundance %) 361 (M⁺, 100), 325 (M⁺-Cl, 10), 290 (M⁺-2Cl, 95), 253 (M⁺-3Cl, 20), 218 (M⁺-4Cl, 65), 182 (M⁺-5Cl, 25), 145 (M⁺-6Cl, 50), 109 (40), 73 (20).

4,4'-dimethoxybiphenyl (2h): Crude **2h** was obtained as a white solid by recrystallization from dichloromethane and methanol (1:1, v/v). ¹H NMR (400 MHz, CDCl₃): δ 3.87 (s, 2×-OMe), 6.98 (d, *J* = 8.9 Hz, 2×H-3/H5), 7.51 (d, *J* = 8.9 Hz, 2×H-2/H6). ¹³C NMR (400 MHz, CDCl₃): δ 55.31 (2×OMe), 114.13 (2×C-3/C-5), 127.71 (2×C-2/C-6), 133.44 (2×C-1), 158.66 (2×C-4).

4,4'-difluoro biphenyl (2i): Pale yellow needles (purified by recrystallization from DCM and methanol (1:2, v/v)). M.p. = 89 °C (Lit.: 88-90 °C⁴ to 95 °C⁵). ¹⁹F (300 MHz, CDCl₃): δ -116.19 to -116.24 (m, 2F). ¹H NMR (400 MHz, CDCl₃): δ 7.12 (m, 2×H-3/H5), 7.50 (m, 2×H-2/H6). MS (EI): *m/z* (relative abundance %): 190 (M⁺, 100), 170 (M⁺-F, 65), 144.66 (18), 94.90 (40)

4,4'-dicarbomethoxy biphenyl (2j): White solid (purified by column chromatography using 5-10% ethyl acetate in hexanes). *R_f* 0.41 (45% ethylacetate in hexanes). M.p. = 212-214 °C (Lit.: 212-213 °C⁶ to 218 °C^{7,8}). ¹H NMR (400 MHz, CDCl₃): δ 3.94 (s, 2×-OMe), 7.68 (d, *J* = 8.64 Hz, 2×H-2/H6), 8.12 (d, *J* = 8.16 Hz, 2×H-3/H5).

2,2',4,4'-tetramethyl biphenyl (2k): *R_f* 0.34 (in Hexane). Colorless oil (Lit. m.p.: 38-39 °C⁹ to 40-41 °C¹⁰). ¹H NMR (400 MHz, CDCl₃): δ 2.07 (s, 2×Me_{ortho}), 2.40 (s, 2×Me_{para}), 7.03 (m, 2×H-3), 7.05 (m, 2×H-5), 7.11 (m, 2×H-6). ¹³C NMR (400 MHz, CDCl₃): δ 19.78 (2×Me_{ortho}),

21.10 ($2\times\text{Me}_{para}$), 126.19 (2, $2\times\text{C-6}$), 129.43 ($2\times\text{C-3}$), 130.52 ($2\times\text{C-5}$), 135.76 ($2\times\text{C-1}$), 136.50 ($2\times\text{C-4}$), 138.64 ($2\times\text{C-2}$).

Packing diagrams of 3a, 3b, 3j and 3k.

Figure S-1. A view of the packing of tetrakis(2,4-dichlorophenyl)stannane (**3a**) along the a axis.

All H atoms have been omitted for clarity.

Figure S-2. A view of the packing of tetrakis(2,4-dichlorophenyl)stannane (**3a**) along the b axis.

All H atoms have been omitted for clarity.

Figure S-3. A view of the packing of tetrakis(2,4-dichlorophenyl)stannane (**3a**) along the c axis.

All H atoms have been omitted for clarity.

Figure S-4. A view of the packing of tetrakis(3,4-dichlorophenyl)stannane (**3b**) along the a axis.

All H atoms have been omitted for clarity.

Figure S-5. A view of the packing of tetrakis(3,4-dichlorophenyl)stannane (**3b**) along the b axis.

All H atoms have been omitted for clarity.

Figure S-6. A view of the packing of tetrakis(3,4-dichlorophenyl)stannane (**3b**) along the b axis.

All H atoms have been omitted for clarity.

Figure S-7. A view of the packing of tetrakis(4-carbomethoxyphenyl)stannane (**3j**) along the *a* axis. All H atoms have been omitted for clarity.

Figure S-8. A view of the packing of tetrakis(4-carbomethoxyphenyl)stannane (**3j**) along the b axis. All H atoms have been omitted for clarity.

Figure S-9. A view of the packing of tetrakis(4-carbomethoxyphenyl)stannane (**3j**) along the *c* axis. All H atoms have been omitted for clarity.

Figure S-10. A view of the packing of tetrakis(2,4-dimethylphenyl)stannane (**3k**) along the *a* axis. All H atoms have been omitted for clarity.

Figure S-11. A view of the packing of tetrakis(2,4-dimethylphenyl)stannane (**3k**) along the b axis. All H atoms have been omitted for clarity.

Figure S-12. A view of the packing of tetrakis(2,4-dimethylphenyl)stannane (**3k**) along the c axis. All H atoms have been omitted for clarity.

Table S-4. Summary of published crystal structures of tetraarylstannanes.

compound	formula	space group	$\bar{4}$ symmetry	reference
Tetrakis(4-methylphenyl)stannane	(4-CH ₃ C ₆ H ₄) ₄ Sn	$I\bar{4}$	Yes	11
Tetrakis(4-methoxyphenyl)stannane	(4-CH ₃ OC ₆ H ₄) ₄ Sn	$I\bar{4}$	Yes	12
Tetrakis(4-methylthiophenyl)stannane	(4-CH ₃ SC ₆ H ₄) ₄ Sn	$I\bar{4}$	Yes	12
Tetrakis(4-trifluoromethylphenyl)stannane	(4-CF ₃ SC ₆ H ₄) ₄ Sn	$I\bar{4}$	Yes	13
Tetrakis(pentafluorophenyl)stannane	(C ₆ F ₅) ₄ Sn	IA_1/a	Yes	14
Tetrakis(3-methylphenyl)stannane	(3-(CH ₃)C ₆ H ₄) ₄ Sn	IA_1/a	Yes	15
Tetrakis(3-trifluoromethylphenyl)stannane	(3-CF ₃ SC ₆ H ₄) ₄ Sn	IA_1/a	Yes	16
Tetrakis(phenyl)stannane	(C ₆ H ₅) ₄ Sn	$P\bar{4}2_1/c$	Yes	17,18
Tetrakis(2-methylphenyl)stannane	(2-(CH ₃)C ₆ H ₄) ₄ Sn	$P\bar{4}2_1/c$	Yes	18
Tetrakis(3,5-dimethylphenyl)stannane	(3,5-(CH ₃) ₂ C ₆ H ₃) ₄ Sn	$P\bar{4}2_1/c$	Yes	19
Tetrakis(4-methylsulfinylphenyl)stannane	(4-CH ₃ SOC ₆ H ₄) ₄ Sn	$P4_2/n$	Yes	20
Tetrakis(4-t-butylphenyl)stannane	(4-[(CH ₃) ₃ C]C ₆ H ₄) ₄ Sn	$P4_2/n$	Yes	21
Tetrakis(4-ethoxyphenyl)stannane	(4-CH ₃ CH ₂ OC ₆ H ₄) ₄ Sn	$P2_1/c$	No	22
Tetrakis(3-methoxyphenyl)stannane	(3-CH ₃ OC ₆ H ₄) ₄ Sn	$C2/c$	Yes [#]	23
Tetrakis(4-ethylphenyl)stannane	(4-(CH ₃ CH ₂)C ₆ H ₄) ₄ Sn	$C2/c$	No	21
Tetrakis(4-methylsulfonylphenyl)stannane	(4-CH ₃ SO ₂ C ₆ H ₄) ₄ Sn	$C2/c$	No	20
Tetrakis(3,5-dichlorophenyl)stannane	(3,5-Cl ₂ C ₆ H ₃) ₄ Sn	$C2/c$	No	24
Tetrakis(pentachlorophenyl)stannane	(C ₆ Cl ₅) ₄ Sn	$C2/c$	No	25
Tetrakis(4-chlorophenyl)stannane	(4-ClC ₆ H ₄) ₄ Sn	$P\bar{1}$	No	26
Tetrakis(2-methoxyphenyl)stannane	(2-CH ₃ OC ₆ H ₄) ₄ Sn	$P\bar{1}$	No	23,27

[#] Distorted $\bar{4}$ symmetries with the methoxy groups having all-*exo* conformation.

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