Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information for

Sn atom-economical approach to aryl stannanes: Ni-catalysed stannylation of arylhalides with Bu_3SnOMe

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1 **General Information.** All reactions were performed using oven- or flame-dried glassware under argon. Flash column chromatography was performed with silica gel 60 (KANTO Chemical Co. Inc., 40-50 nm). Preparative recycling gel permeation chromatography (GPC) was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and H-2002L column (chloroform as an eluent). TLC monitoring was carried out with silica gel aluminum sheets (Merck, type 60 F_{254}). Gas chromatography (GC) monitoring was performed on a Shimadzu GC-2014 with an autosampler. Nuclear magnetic resonance (NMR) spectra were measured on Varian-400 (^{1}H NMR: 400 MHz; ^{13}C NMR: 101 MHz) spectrometer or Varian-500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 126 MHz) spectrometers, calibrated from residual deuterated chloroform as an internal standard at 7.26 ppm for ^{1}H NMR spectra and at 77.0 ppm for ^{13}C NMR spectra, respectively. Low-resolution mass spectrum (LRMS) was recorded on Shimadzu GCMS-QP5050 (EI, 70 eV). High-resolution mass spectrum (HRMS) was performed by the Natural Science Center for Basic Research and Development (N-BARD) of Hiroshima University using LTQ Orbitrap XL from Thermo Fisher Scientific.

2 **Materials.** *N*,*N*-Dimethylformamide (DMF) was dried over activated molecular sieves 4Å, distilled, and stored with activated MS 4Å under argon. $NiBr_2$, Mn powder (99.9 %), and all ligands were purchased and used as received. $NiBr_2$(bpy) was prepared by reported method. [1] Substrates (*E*)-**1t**, [2] (*Z*)-**1t**, [3] 2-trifluoromethanesulfonylnaphthalene, [4] **1v**, [5] and **1w** [6] were

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[1] M. Chemli, A. H. Said, J.-L. Fave, C. Barthou, M. Majdoub, *J. Appl. Polym. Sci.* 2012, **125**, 3913.

[2] J. McNulty, P. Das, *Eur. J. Org. Chem.* 2009, 4031.

[3] T. Suzuki, M. N. A. Khan, H. Sawada, E. Imai, Y. Itoh, K. Yamatsuta, N. Tokuda, J. Takeuchi, T. Seko, H. Nakagawa, N. Miyata, *J. Med. Chem.* 2012, **55**, 5760.

[4] C. K. De, F. Pesciaioli, B. List, *Angew. Chem. Int. Ed.,* 2013, **52**, 9293.

[5] Y. Zou, L. Qin, X. Ren, Y. Lu, Y. Li, J. Zhou, *Chem. Eur. J.* 2013, **19**, 3504.

prepared by reported methods. Unless otherwise noted, commercially available reagents were used as received without further purification.

3 Experimental procedure of Ni-catalyzed stannylation of aryl halides

3.1 General procedure for stannylation of arylhalides (Table 1, entry 13).

In Schlenk tube, Mn powder (0.5 mmol, 2.0 equiv.) and $NiBr_2$ (10 mol%) were added and heated at 400 ºC for 5 – 10 min under vacuum. The Schlenk tube was charged with PPh_3 (30 mol%) and Et_4NI (20 mol%). After that, DMF (1.0 mL) and TMSCl (20 mol%) were added, followed by stirring for 10 min at the same temperature. 4-trifluoromethylbromobenzene (**1b**, 0.25 mmol) and Bu_3SnOMe (3.0 mmol) were successively added, and the resulting mixture was stirred at 25 ºC for appropriate reaction times. The reaction mixture was quenched with water and then diluted with Et_2O. The aqueous phase was extracted with Et_2O. The combined ethereal solution was dried over Na_2SO_4. After filtration and removal of solvent, the residue was purified by silica gel flash chromatography. If the stannylated product was unstable to contact with silica gel, the purification was carried out by GPC with chloroform as an eluent.

3.2 General procedure for stoichiometric reaction (Scheme 2).

In Schlenk tube, Mn powder (0.9 – 2.3 equiv.) and $NiBr_2$(bpy) (1.0 equiv.) were added and heated at 400 ºC for 5 – 10 min under vacuum. The Schlenk tube was charged with DMF and TMSCl (20 mol%) were added, followed by stirring for 10 min at 25 ºC for 30 min. **1a** and Bu_3SnOMe (1.2 euiqv.) were successively added, and the resulting mixture was stirred at 50 ºC for 4 h. The reaction mixture was quenched with water and then diluted with Et_2O. Yields were determined by GC using dimethylterephthalate as an internal standard.

3.3 General procedure for stoichiometric reaction (eqn (3)).

$Ni(COD)_2$ (1.0 equiv.) and bpy (1.0 equiv.) were added to an Schlenk tube in argon-filled grove-box. The tube was removed from the grove-box, poured DMF. The mixture was stirred for 10 min at 25 ºC. **1a** (1.0 equiv.) and Bu_3SnOMe (1.2 equiv.) were successively added, and the resulting mixture was stirred at 50 ºC for 4 h. The reaction mixture was quenched with water and then diluted with Et_2O. Yields were determined by GC using dimethylterephthalate as an internal standard.

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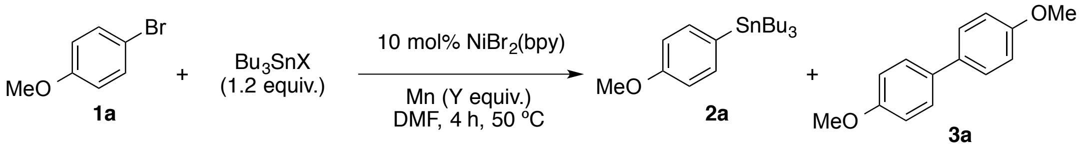
[6] J. Uenishi, R. Kawahama, O. Yonemitsu, *J. Org. Chem.* 1998, **63**, 8965.

4 Ligand effect on the nickel-catalyzed stannylation

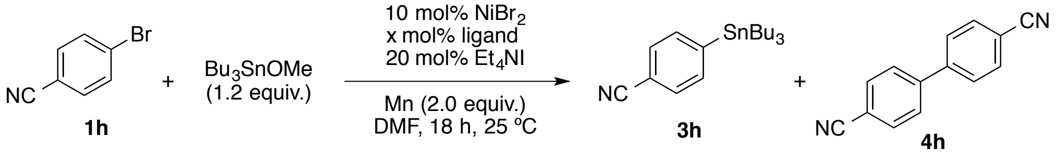
Table S1. Leaving group effect of stannyl electrophiles in the Ni-catalyzed stannylation of 4-methoxy bromobenzene (**1a**).



entry	X	Y	product and yield (%)[a]	
			2a	**3a**
1	OMe	1.5	41	54
2	OMe	2.0	91	9
3	OMe	2.5	74	27
4	Cl	2.0	74	28
5	OC(O)Me	2.0	54	35
6	O*t*Bu	2.0	69	22

[a] Determined by GC with dimethyl terephthalate as an internal standard.

Table S2. Ligand screening on the stannylation of 4-cyano bromobenzene (**1h**)

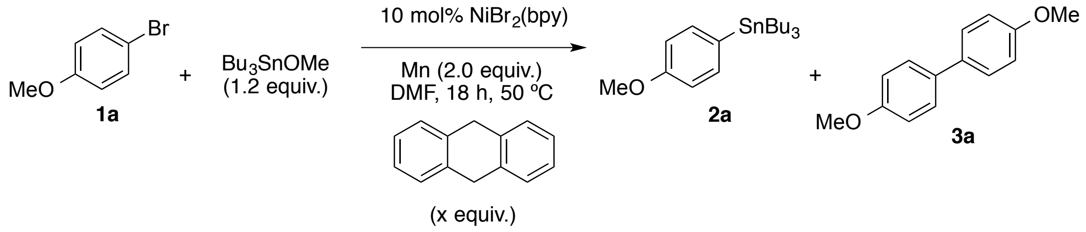


entry	ligand (x mol%)	product and yield (%)[a]	
		3h	**4h**
1	PCy_3 (30)[b]	0	0
2	P(*n*-Bu)$_3$ (30)	0	0
3	$PMePh_2$ (30)	0	0
4	P(4-tolyl)$_3$ (30)	0	0
5	P(4-anisyl)$_3$ (30)	19	11
6	P[2,6-(MeO)$_2$C$_6$H$_3$]$_3$ (30)	0	0
7	P[2,4,6-Me$_2$C$_6$H$_2$]$_3$ (30)	0	0
8	P(C$_6$F$_5$)$_3$ (30)	0	0

9	$P(4\text{-}CF_3C_6H_4)_3$ (30)	0	0
10	$P(4\text{-}FC_6H_4)_3$ (30)	47	43
11	$P(OPh)_3$	0	0
12	dppe (20)[c]	0	0
13	dppb (20)[d]	3	0
14	dppf (20)[e]	60	22
15	xantphos (20)[f]	52	7
16	xantphos (20)[f,g]	77	6

[a] Determined by GC with dimethylterephthalate as an internal standard. [b] Cy = cyclohexyl. [c] dppe = 1,2-diphenylphosphinoethane. [d] dppb = 1,3-diphenylphosphinobutane. [e] dppf = 1,1'-diphenylhposphinoferrocene. [f] 4,5-bis(diphenylphosphino)-9,9-dimethyl xanthene. [g] Reaction temperature: 40 °C.

Table S3. Ni-catalyzed stannylation of 4-methoxy bromobenzene (**1a**) in the presence of 9,10-dihydroanthracene.



entry	9,10-dihydroanthracene (x equiv.)	product and yield (%)[a]	
		2a	**3a**
1	none	91	9
2	1.0	62	16
3	2.0	45	31
4	3.0	52	23

[a] Determined by GC with dimethylterephthalate as an internal standard.

Spectra date for all stannylated products

4-Methoxy-1-tributylstannylbenzene (2a) [7]

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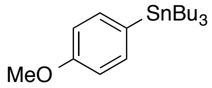
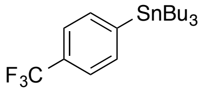
[7] P. Tangm T. Furuya, T. Ritter, *J. Am. Chem. Soc.* 2010, **132**, 12150.



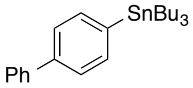
Isolated as colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 1.72 – 1.44 (m, 6H), 1.42 – 1.28 (m, 6H), 1.15 – 0.96 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.64, 137.46 (J = 34.7 Hz), 131.94, 113.87 (J = 44.1 Hz), 54.90, 29.10 (J = 20.0 Hz), 27.38 (J = 56.5 Hz), 13.68, 9.56 (J = 341.2, 326.2 Hz); LRMS *m/z*: 341 (M^+–Bu, 100), 339 (72), 285 (62), 229 (83), 227 (91).

4-Trifluoromethyl-1-tributylstannylbenzene (2b)



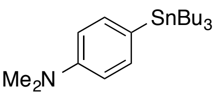
Isolated as colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.9 Hz, 2H), 1.66 – 1.47 (m, 6H), 1.42 – 1.30 (m, 6H), 1.20 – 1.04 (m, 6H), 0.92 (t, J = 7.3 Hz, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.65, 136.60 ($J_{\text{C-Sn}}$ = 30.5 Hz), 130.04 (q, $J_{\text{C-F}}$ = 32.2 Hz), 124.41 (q, $J_{\text{C-F}}$ = 272.3 Hz), 124.14 ($J_{\text{C-F}}$ =3.8 Hz, $J_{\text{C-Sn}}$ = 39.0 Hz), 29.04 ($J_{\text{C-Sn}}$ = 21.0 Hz), 27.37 ($J_{\text{C-Sn}}$ = 56.5 Hz), 13.65, 9.65 ($J_{\text{C-Sn}}$ = 343.3, 328.6 Hz); LRMS *m/z*: 379 (M^+–Bu, 71), 323 (84), 267 (98), 265 (100), 263 (70); HRMS *m/z*: calcd for $C_{19}H_{31}F_3Sn$: 436.1400, found: 436.1411.

4-Phenyl-1-tributylstannylbenzene (2c) [7]



Isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 – 7.51 (m, 6H), 7.50 – 7.41 (m, 2H), 7.41 – 7.31 (m, 1H), 1.73 – 1.47 (m, 6H), 1.46 – 1.28 (m, 6H), 1.23 – 1.00 (m, 6H), 0.93 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 141.28, 140.83, 140.70, 136.87 (J = 30.7 Hz), 128.69, 127.14, 127.08, 126.59 (J = 41.0 Hz), 29.12 (J = 20.1 Hz), 27.38 (J = 100.0, 56.9 Hz), 13.70, 9.60 (J = 340.6, 325.4 Hz); LRMS *m/z*: 387 (M^+–Bu, 92), 385 (77), 275 (92), 273 (100), 271 (66).

4-(*N,N*-Dimethyl)-1-tributylstannylbenzene (2d) [8]



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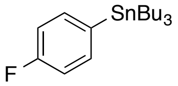
[8] V. Farina, B. Krishnan, D. R. Marshall, G. P. Roth, *J. Org. Chem.* 1993, **58**, 5434.

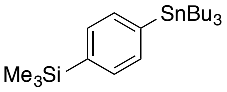
Isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, J = 7.6 Hz, 2H), 6.79 (d, J = 7.6 Hz, 2H), 2.98 (s, 6H), 1.70 – 1.47 (m, 6H), 1.45 – 1.30 (m, 6H), 1.14 – 0.97 (m, 6H), 0.93 (t, J = 7.3, 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 150.40, 137.20 (d, J = 35.2 Hz), 126.37, 112.61 (d, J = 43.1 Hz), 40.31, 29.14 (d, J = 20.2 Hz), 27.43 (d, J = 56.2 Hz), 13.71, 9.49 (dd, J = 339.3, 324.0 Hz); LRMS *m/z*: 354 (M^+–Bu, 48), 352 (38), 298 (35), 240 (48), 120 (100).

4-Fluoro-1-tributylstannylbenzene (2e) [7]



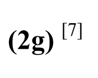
Isolated as colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 (dd, J = 8.6, 6.5 Hz, 2H), 7.05 (dd, J = 9.7, 8.5 Hz, 2H), 1.67 – 1.43 (m, 6H), 1.42 – 1.25 (m, 6H), 0.91 (t, J = 7.2 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.19 (d, J = 246.1 Hz), 137.80 (d, $J_{\text{C-F}}$ = 6.0 Hz, $J_{\text{C-Sn}}$ = 41.6, 28.3 Hz,), 136.66 (d, J = 3.7 Hz), 115.09 (d, J = 19.4 Hz), 29.05 (d, J = 19.6 Hz), 27.36 (d, J = 57.2 Hz), 13.67, 9.64 (dd, J = 341.7, 327.3 Hz); LRMS (eV) *m/z*: 329 (M^+–Bu,100), 327 (74), 273 (78), 217 (85), 215 (95).

4-Methoxy-1-tributylstannylbenzene (2f) [9]



Isolated as colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 – 7.43 (m, 4H), 1.69 – 1.48 (m, 6H), 1.45 – 1.31 (m, 6H), 1.20 – 0.98 (m, 6H), 0.93 (t, J = 7.3 Hz, 9H), 0.30 (d, J = 1.2 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.83, 139.73, 135.91 (d, J = 28.9 Hz), 132.73 (d, J = 39.0 Hz), 29.11 (d, J = 19.9 Hz), 27.43 (d, J = 55.7 Hz), 13.70, 9.51 (dd, J = 339.1, 324.0 Hz), -1.15; LRMS *m/z*: 383 (M^+–Bu, 98), 381 (74), 271 (92), 269 (92), 135 (100).

4-Methylthio-1-tributylstannylbenzene (2g) [7]



Isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H), 1.64 – 1.42 (m, 6H), 1.39 – 1.26 (m, 6H), 1.15 – 0.94 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.17 (d, J = 10.5 Hz), 137.81, 136.75 (d, J = 31.2 Hz),

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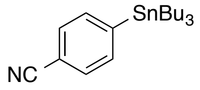
[9] A. Nagaki, Y. Tomida, H. Usutani, H. Kim, N. Takabayashi, T. Nokami, H. Okamoto, J-I. Yoshida, *Chem. Asian. J.* 2007, **2**, 1513.

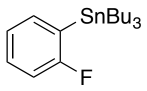
126.01 (d, J = 41.4 Hz), 29.05 (d, J = 20.2 Hz), 27.36 (d, J = 55.9 Hz), 15.52, 13.67, 9.54 (dd, J = 340.1, 324.8 Hz); LRMS *m/z*: 357 (M$^+$–Bu, 100), 355 (84), 301 (72), 245 (94), 243 (90).

4-Methylthio-1-tributylstannylbenzene (2h) [7]



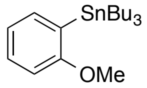
Isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 – 7.51 (m, 4H), 1.67 – 1.42 (m, 6H), 1.41 – 1.25 (m, 6H), 1.21 – 1.01 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 150.30, 136.83 (J = 29.1 Hz), 130.66 (J = 37.2 Hz), 119.20, 111.48, 28.93 (J = 20.9 Hz), 27.26 (J = 56.9 Hz), 13.60, 9.68; LRMS *m/z*: 336 (M$^+$–Bu, 80), 279 (95), 278 (73), 223 (97), 222 (100).

2-Fluoro-1-tributylstannylbenzene (2i)[10]



Isolated as colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (ddd, J = 7.2, 3.9, 1.9 Hz, 1H), 7.37 – 7.25 (m, 1H), 7.14 (tt, J = 7.2, 7.2, 1.4 Hz, 1H), 7.07 – 6.95 (m, 1H), 1.68 – 1.44 (m, 6H), 1.43 – 1.28 (m, 6H), 1.26 – 1.02 (m, 7H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.30 (d, J = 234.1 Hz), 137.24 (d, $J_{\text{C-F}}$ = 16.1 Hz, $J_{\text{C-Sn}}$ = 15.5 Hz), 130.20 (d, $J_{\text{C-F}}$ = 7.5 Hz), 126.84 (d, $J_{\text{C-F}}$ = 46.4 Hz), 124.04 (d, $J_{\text{C-F}}$ = 3.1, $J_{\text{C-Sn}}$ = 32.8, Hz), 114.15 (d, $J_{\text{C-F}}$ = 28.3, $J_{\text{C-Sn}}$ = 17.4 Hz), 29.00 (J = 20.0 Hz), 27.29 (J = 60.5 Hz), 13.66, 9.85 (J = 353.8, 336.4 Hz); LRMS *m/z*: 329 (M$^+$–Bu, 100), 273 (94), 271 (76), 217 (77), 215 (85).

2-Methoxy-1-tributylstannylbenzene (2j)[11]



Isolated as yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 (dd, J = 7.0, 1.7 Hz, 1H), 7.30 (ddd, J = 8.1, 7.3, 1.8 Hz, 1H), 6.96 (td, J = 7.2, 0.9 Hz, 1H), 6.81 (dd, J = 8.2, 0.9 Hz, 1H), 3.77 (s, 3H), 1.59 – 1.44 (m, 6H), 1.38 – 1.26 (m, 6H), 1.11 – 0.96 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 163.75, 136.94 (J = 22.2 Hz), 130.32, 129.63 (J = 7.3 Hz), 120.85 (J = 39.0 Hz), 108.89 (J = 20.8 Hz), 55.01, 29.15 (J = 19.5 Hz), 27.36 (J = 59.2 Hz), 13.72, 9.74; LRMS *m/z*: 341 (M$^+$–Bu, 100), 339 (81), 337 (49), 227 (64), 225 (46).

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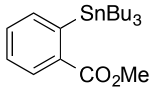
[10] H. Yoshida, R. Yoshida, K. Takaki, *Angew. Chem. Int. Ed.* 2013, **52**, 8629.

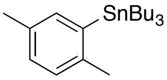
[11] J.-H. Chun, S. Lu, Y.-S. Lee, V. W. Pike, *J. Org. Chem.* 2010, **75**, 3332.

2-Methoxycarbonyl-1-tributylstannylbenzene (2k)[12]



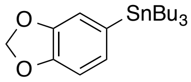
Isolated as colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.08 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.63 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.47 (td, *J* = 7.2, 1.4 Hz, 1H), 7.36 (td, *J* = 7.6, 1.4 Hz, 1H), 3.89 (s, 3H), 1.61 – 1.37 (m, 6H), 1.35 – 1.23 (m, 6H), 1.14 – 0.93 (m, 6H), 0.85 (t, *J* = 7.3, 7.3 Hz, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 168.95, 146.93, 137.00 (*J* = 28.3 Hz), 135.47 (*J* = 16.4 Hz), 131.71 (*J* = 38.7 Hz), 129.77 (*J* = 27.1 Hz), 127.91 (*J* = 28.6 Hz), 52.24, 29.17 (*J* = 19.3 Hz), 27.43 (*J* = 61.2 Hz), 13.71, 11.02 (*J* = 362.6, 345.5 Hz); LRMS *m/z*: 369 (M$^+$–Bu, 100), 368 (36), 367 (70), 365 (36), 255 (37)

2,5-Dimethyl-1-tributylstannylbenzene (2l)



Isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 (s, 1H), 7.17 – 7.00 (m, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 1.67 – 1.43 (m, 6H), 1.43 – 1.29 (m, 6H), 1.20 – 0.98 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 141.70, 141.35, 137.16 (*J* = 30.8 Hz), 133.85, 128.97 (*J* = 9.7 Hz), 128.61 (*J* = 37.7 Hz), 29.13 (*J* = 19.6 Hz), 27.38 (*J* = 57.7 Hz), 24.40 (*J* = 23.2 Hz), 20.98, 13.63, 9.91 (*J* = 337.4, 321.5 Hz); LRMS *m/z*: 339 (M$^+$–Bu, 92), 283 (77), 227 (100), 225 (99), 105 (89); HRMS *m/z*: calcd for $C_{20}H_{36}Sn$: 396.1840, found: 396.1844.

3,4-Methylenedioxy-1-tributylstannylbenzene (2m)[13]



Isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.00 – 6.82 (m, 3H), 5.92 (s, 2H), 1.66 – 1.41 (m, 6H), 1.40 – 1.25 (m, 6H), 1.14 – 0.93 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.41 (*J* = 17.2 Hz), 133.84, 129.51 (*J* = 32.5 Hz), 115.46 (*J* = 38.8 Hz), 108.79 (*J* = 49.2 Hz), 100.12, 29.00 (*J* = 20.5 Hz), 27.33 (*J* = 58.2 Hz), 13.65, 9.67 (*J* = 341.3, 326.4 Hz); LRMS *m/z*: 355 (M$^+$–Bu, 99), 353 (70), 299 (77), 243 (91), 241 (100).

1-Tributylstannylnaphthalene (2n)

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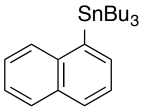
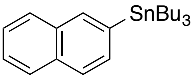
[12] A. Kalivretenos, J. K. Stille, L. S. Hegedus, *J. Org. Chem*. 1991, **56**, 2883.

[13] H. Suginome, K. Orito, K. Yorita, M. Ishikawa, N. Shimoyama, T. Sasaki, *J. Org. Chem.* 1995, **60**, 3052.



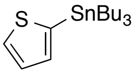
Isolated as colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.76 (m, 3H), 7.77 – 7.58 (m, 1H), 7.59 – 7.41 (m, 3H), 1.74 – 1.49 (m, 6H), 1.48 – 1.31 (m, 6H), 1.36 – 1.14 (m, 6H), 0.92 (t, J = 7.2 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.89, 138.97, 135.08 (J = 27.4 Hz), 133.62, 130.14 (J = 26.6 Hz), 128.87, 128.37 (J = 4.5 Hz), 125.60, 125.30 (J = 45.9 Hz), 29.19 (J = 19.5 Hz), 27.38 (J = 58.6 Hz), 13.66, 10.37 (J = 339.6, 324.4 Hz); LRMS *m/z*: 361 (M^+–Bu, 55), 305 (48), 249 (60), 247 (100), 245 (69); HRMS *m/z* calcd for $C_{26}H_{38}Sn$: 418.1744, found: 418.1749.

2-Tributylstannylnaphthalene (2o)[14]



Isolated as colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J_{\text{Sn-H}}$ = 44.4 Hz, 1H), 7.88 – 7.79 (m, 3H), 7.67 – 7.54 (m, 1H), 7.55 – 7.43 (m, 2H), 1.73 – 1.51 (m, 6H), 1.47 – 1.33 (m, 6H), 1.28 – 1.06 (m, 6H), 0.94 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 139.59, 136.51 (J = 29.1 Hz), 133.28, 133.23, 133.13, 127.74, 127.55, 126.74 (J = 38.8 Hz), 125.68, 125.65, 29.14 (J = 20.6 Hz), 27.40 (J = 57.1 Hz), 13.70, 9.64 (J = 339.3, 324.7 Hz); LRMS *m/z*: 361 (M^+–Bu, 87), 359 (65), 249 (80), 247 (100), 245 (68).

2-Tributylstannylthiophene (2p)[15]



Isolated as colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 (d, J = 4.9 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.25 – 7.17 (m, 1H), 1.69 – 1.46 (m, 6H), 1.44 – 1.28 (m, 6H), 1.23 – 1.05 (m, 6H), 0.92 (t, J = 7.3 Hz, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.16, 135.15 (J = 25.2 Hz), 130.56 (J = 12.4 Hz), 127.81 (J = 38.6 Hz), 28.96 (J = 21.2 Hz), 27.27 (J = 58.9 Hz), 13.67, 10.80 (J = 357.1, 341.3 Hz); LRMS *m/z*: 317 (M^+–Bu, 100), 315 (80), 261 (77), 259 (60), 203 (73).

3-Tributylstannylthiophene (2q)[16]

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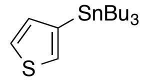
[14] Y. Chen, M. Chem, Y. Liu, *Angew. Chem. Int. Ed.* 2012, **51**, 6181.

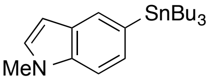
[15] T. Pinault, F. Chérioux, B. Therrien, G. Sűss-Fink, *Heteroatom Chem.* 2004, **15**, 121.

[16] A. Leliège, C-H. L. Régent, M. Allain, P. Blanchard, J. Roncali, *Chem. Commun.* 2012, **48**, 8907.



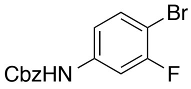
Isolated as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 4.7, 2.5 Hz, 1H), 7.35 (dd, J = 2.4, 0.7 Hz, $J_{Sn\text{-}H}$ = 23.9 Hz, 1H), 7.18 (dd, J = 4.7, 0.8 Hz, $J_{Sn\text{-}H}$ = 16.6 Hz, 1H), 1.70 – 1.45 (m, 6H), 1.43 – 1.25 (m, 6H), 1.19 – 0.96 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.69, 133.08 (J = 46.0 Hz), 131.23 (J = 42.6 Hz), 124.84 (J = 45.5 Hz), 29.08 (J = 20.5 Hz), 27.31 (J = 56.6 Hz), 13.68, 10.07 (J = 341.7, 334.2 Hz); LRMS *m/z*: 317 (M^+–Bu, 100), 315 (73), 261 (75), 205 (62), 203 (68).

5-Tributylstannyl-*N*-methylindole (2r)



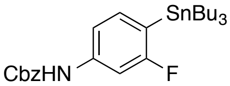
Isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, $J_{Sn\text{-}H}$ = 43.3 Hz, 1H), 7.40 – 7.29 (m, 2H), 7.04 (d, J = 2.3 Hz, 2H), 6.49 (brs, 1H), 3.80 (s, 3H), 1.72 – 1.48 (m, 6H), 1.46 – 1.31 (m, 6H), 1.10 (m, $J_{Sn\text{-}H}$ = 50.3 Hz, 7H), 0.92 (t, J = 7.3 Hz, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.75, 129.69, 129.06 ($J_{Sn\text{-}C}$ = 34.6 Hz), 128.91 ($J_{Sn\text{-}C}$ = 38.5 Hz), 128.86, 128.27, 109.00 ($J_{Sn\text{-}C}$ = 47.6 Hz), 100.43, 32.64, 29.18 ($J_{Sn\text{-}C}$ = 19.4 Hz), 27.45 ($J_{Sn\text{-}C}$ = 56.1 Hz), 13.72, 9.64 ($J_{Sn\text{-}C}$ = 337.5, 322.1 Hz); LRMS *m/z*: 364 (M^+–Bu, 100), 362 (73), 308 (65), 252 (81), 250 (89); HRMS *m/z*: calcd for $C_{21}H_{36}NSn[M+H]^+$: 422.1864, found: 422.1864.

1-Bromo-2-fluoro-4-benzyloxycarbonylaminobenzene (1s)



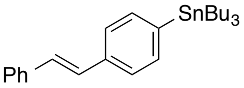
A solution of 4-bromo-3-fluoroaniline (500 mg, 2.63 mmol) in THF (10 mL) was added $NaHCO_3$ (251.9 mg, 3.0 mmol) and benzyl chloroformate (0.43 mL, 3.00 mmol). After 15 min, the mixture was warmed to rt, and then quenched with H_2O. The aqueous phase was extracted with Et_2O. The combined ethereal layer was dried over $MgSO_4$, filtered, and concentrated to afford the crude product. Analytically pure **1s** was obtained by recrystallization of the crude product in 76% yield (650.0 mg). Isolated as a white solid (Mp.: 103.5 – 104.4 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.29 (m, 7H), 6.94 (dd, J = 8.8, 2.4 Hz, 1H), 6.86 (brs, 1H), 5.19 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.19 (d, J = 246.1 Hz), 152.94, 138.64 (d, J = 10.5 Hz), 135.56, 133.35 (d, J = 1.4 Hz), 128.69, 128.57, 128.39, 115.08, 107.08 (d, J = 26.9 Hz), 102.26 (d, J = 20.9 Hz), 67.42; HRMS *m/z* calcd for $C_{14}H_{11}BrFNNaO_2$ $[M+Na]^+$: 345.9849, found: 345.9850.

2-Fluoro-4-benzyloxycarbonylamino-1-tributylstannylbenzene (2s)



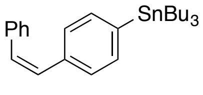
Isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 5H), 7.27 (tt, *J* = 10.2, 10.2, 5.7, 5.7 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 10.8 Hz, 1H), 5.21 (s, 2H), 1.65 – 1.41 (m, 6H), 1.41 – 1.24 (m, 6H), 1.21 – 0.98 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.65 (d, $J_{C\text{-}F}$ = 233.4 Hz), 153.03, 139.78 (d, $J_{C\text{-}F}$ = 10.5 Hz), 137.37 (d, $J_{C\text{-}F}$ = 18.0, $J_{C\text{-}Sn}$ = 18.0 Hz), 135.82, 128.59, 128.38, 128.30, 120.63 (d, $J_{C\text{-}F}$ = 46.4 Hz), 114.19, 104.90 (d, $J_{C\text{-}F}$ = 35.2 Hz), 67.11, 28.95 (d, $J_{C\text{-}Sn}$ = 20.2 Hz), 27.24 ($J_{C\text{-}Sn}$ = 59.2 Hz), 13.64, 9.81 ($J_{C\text{-}Sn}$ = 352.8, 337.0 Hz); HRMS *m/z*: calcd for $C_{26}H_{38}FNO_2Sn[M+H]^+$: 536.1981, found: 536.1981.

4-[(*E*)-stylyl]-1-tributylstannylbenzene (*E*-2t)



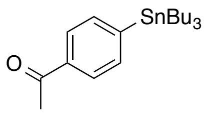
Isolated as brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 4H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.23 (m, 1H), 7.16 (d, *J* = 16.3 Hz, 1H), 7.k11 (d, *J* = 16.3 Hz, 1H), 1.70 – 1.47 (m, 6H), 1.44 – 1.29 (m, 6H), 1.20 – 0.98 (m, 6H), 0.92 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.82, 137.34, 136.80 (*J* = 10.5 Hz), 136.72 (*J* = 30.7 Hz), 128.83, 128.56, 128.33, 127.44, 126.40, 125.84 (*J* = 41.4 Hz), 29.02 (*J* = 20.0 Hz), 27.31 (*J* = 56.1 Hz), 13.62, 9.52 (*J* = 339.9, 325.1 Hz). LRMS *m/z*: 413 (M^+–Bu, 100), 411 (75), 301 (66), 299 (94), 178 (61); HRMS *m/z* calcd for $C_{26}H_{38}Sn$: 470.1996, found: 470.2005

4-[(*Z*)-stylyl]-1-tributylstannylbenzene (*Z*-2t)



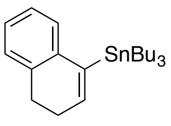
Isolated as yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.31 – 7.21 (m, 5H), 6.62 (s, 2H), 1.62 – 1.56 (m, 6H), 1.34 – 1.43 (m, 6H), 1.19 – 1.01 (m, 6H), 0.94 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.13, 137.45, 136.73 (*J* = 10.2 Hz), 136.29 (*J* = 31.7 Hz), 130.42 (*J* = 5.3 Hz), 130.06, 128.84, 128.24 (*J* = 40.9 Hz), 128.16, 127.00, 29.09 (*J* = 20.0 Hz), 27.35 (*J* = 55.8 Hz), 13.68 (*J* = 3.1 Hz), 9.58 (*J* = 340.2, 324.5 Hz); LRMS *m/z*: 413 (M^+–Bu, 100), 411 (81), 357 (61), 301 (91), 299 (92); HRMS *m/z* calcd for $C_{26}H_{38}Sn$: 470.1996, found: 470.2008.

4-Acetyl-1-tributylstannylbenzene (2u)[17]



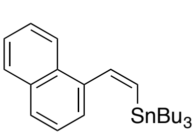
Isolated as colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, J = 8.0 Hz, $J_{\text{Sn-H}}$ = 7.9 Hz, 2H), 7.58 (d, J = 8.1 Hz, $J_{\text{Sn-H}}$ = 36.0 Hz, 2H), 2.60 (s, 3H), 1.65 – 1.41 (m, 6H), 1.40 – 1.26 (m, 6H), 1.20 – 0.98 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.64, 150.25, 136.60 (J = 30.1 Hz), 136.51, 127.06 (J = 39.0 Hz), 29.01 (J = 20.3 Hz), 27.32 (J = 56.6 Hz), 26.55, 13.66, 9.63 (J = 342.8, 326.8 Hz); LRMS *m/z*: 353 (M$^+$–Bu, 77), 351 (63) 297 (63), 241 (100), 239 (93).

1-Tributylstannyl-3,4-dihydronaphthalene (2v)[18]



Isolated as brown oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.20 – 7.13 (m, 1H), 7.13 – 7.07 (m, 2H), 6.96 (d, J = 7.3 Hz, 1H), 6.25 (d, J = 4.6 Hz, $J_{\text{Sn-H}}$ = 59.7 Hz, 1H), 2.74 (td, J = 8.1 Hz, 3H), 2.29 (td, J = 8.1, 4.6 Hz, 3H), 1.61 – 1.44 (m, 6H), 1.40 – 1.29 (m, 6H), 1.10 – 0.95 (m, 6H), 0.89 (t, J = 7.1 Hz, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 140.76, 140.15 (J = 20.3 Hz), 138.99, 136.28, 127.93, 127.89 (d, J = 19.1 Hz), 126.62, 126.43, 28.85 (J = 19.1 Hz), 27.82, 27.05 (J = 57.5 Hz), 24.43 (J = 46.3 Hz), 13.32, 9.60 (J = 339.6, 324.3 Hz); LRMS *m/z*: 363 (M$^+$–Bu, 75), 361 (69), 251 (74), 249 (100), 247 (67).

1-[(*Z*)-2-Tributylstannylethenyl]naphthalene (2w)[19]



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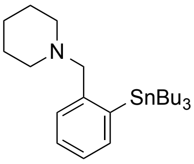
[17] R. N. Hanson, C. J. Friel, R. Dilis, A. Hughes, E. R. DeSombre, *J. Med. Chem.* 2005, **48**, 4300.

[18] A. Darwish, J. M. Chong, *J. Org. Chem.* 2007, **72**, 1507.

[19] The stereochemistry was determined based on the following literatures: (*a*) A. J. Leusink, H. A. Budding, J. W. Marsman, *J. Organomet. Chem.* 1967, **9**, 285; (*b*) J. C. Cochran, H. K. Phillips, S. Tom, A. R. Hurd, B. S. Bronk, *Organometallics*, 1994, **13**, 947; (*c*) P. M. Mirzayans, R. H. Pouwer, C. M. Williams, P. V. Bernhardt, *Tetrahedron*, 2009, **39**, 8297; (*d*) B. Ghosh, M. D. R. I. Amado-Sierra, D. Holmes , R. E. Maleczka, Jr. *Org. Lett.*, 2014, **16**, 2318.

Isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, *J* = 13.5 Hz, $J_{\text{Sn–H}}$ = 134.1, 128.4 Hz, 1H), 8.09 – 8.02 (m, 1H), 7.91 – 7.81 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.44 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.34 (dd, *J* = 7.0, 1.2 Hz, 1H), 6.49 (d, *J* = 13.5 Hz, $J_{\text{Sn–H}}$ = 64.8, 63.4 Hz, 1H), 1.46 – 1.16 (m, 6H), 1.19 – 1.05 (m, 6H), 0.76 (t, *J* = 7.2 Hz, 9H), 0.76 – 0.53 (m, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 145.99, 139.87, 135.51 (dd, *J* = 364.6, 348.2 Hz), 133.26, 131.75, 128.24, 127.79, 125.82, 125.80, 125.36, 124.94, 124.70 (d, *J* = 6.0 Hz), 29.01 (d, *J* = 20.2 Hz), 27.24 (d, *J* = 58.4 Hz), 13.60, 10.66 (dd, *J* = 344.3, 328.7 Hz); LRMS *m/z*: 387 (M^+–Bu, 100), 386 (38), 385 (72), 383 (44). 153 (52); HRMS *m/z*: calcd for $C_{20}H_{27}Sn[M-C_4H_9]^+$: 387.1129, found: 387.1130.

1-Piperidylmethyl-2-tributylstannylbenzene (2x)



Isolated as brown oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, *J* = 13.5 Hz, $J_{\text{Sn–H}}$ = 134.1, 128.4 Hz, 1H), 8.09 – 8.02 (m, 1H), 7.91 – 7.81 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.44 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.34 (dd, *J* = 7.0, 1.2 Hz, 1H), 6.49 (d, *J* = 13.5 Hz, $J_{\text{Sn–H}}$ = 64.8, 63.4 Hz, 1H), 1.46 – 1.16 (m, 6H), 1.19 – 1.05 (m, 6H), 0.76 (t, *J* = 7.2 Hz, 9H), 0.76 – 0.53 (m, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 145.73 (*J* = 26.4 Hz), 142.67 (*J* = 408.8, 391.3 Hz), 136.99 (*J* = 31.5 Hz), 129.37 (*J* = 36.4 Hz), 127.75 (*J* = 9.9 Hz), 126.17 (*J* = 43.2 Hz), 66.73 (*J* = 19.2 Hz), 54.85, 29.24 (*J* = 19.2 Hz), 27.53 (*J* = 61.7, 59.6 Hz), 25.66, 24.55, 13.71, 10.53 (*J* = 342.8, 328.1 Hz): LRMS *m/z*: 408 (M^+–Bu, 100), 407 (43), 406 (82), 405 (31), 404 (49); HRMS *m/z* calcd for $C_{20}H_{34}NSn[M-C_4H_9]^+$: 408.1708, found: 408.1706.