SUPPORTING INFORMATION

Experimental

General informations. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Avance 250MHz spectrometer. $^1$H NMR spectra are reported as follows: chemical shifts in ppm (δ) down field from TMS as an internal standard, multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet and br= broadened), integration and coupling constants spectra (Hz). $^{13}$C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77 ppm. IR spectra were recorded on a Perkin-Elmer FT PARAGON 1000PC spectrometer, absorption are reported in cm⁻¹. Mass spectra (IS) were acquired on a Perkin-Elmer Scieix PI 300 spectrometer. Melting points uncorrected values were performed on a Büchi 510. GC analyses were carried out on a Varian 3400 gas chromatograph equipped with a C₁₈ Restek RTX 5 column (L=5, ID= 0.32, DF= 0.5). Column chromatography was carried out using Silica gel 60N (spherical, neutral, 63~200µm, Merck). Analytical thin-layer chromatography (TLC) was performed on 0.2mm precoated Kieselgel 60 F₂₅₄ (Merck) plates.

Materials. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled over sodium and benzophenone before use. 3-Methylthio-1,2,4-triazine was prepared according to the literature. Tributyltin derivatives (2c, 2e, and 2f) were prepared respectively according to the literature and compound 2g was synthesized according to the following procedure. All other compounds used were commercially available.

3-[(E)-2-phenylethynyl]-ltributyltin (2g). CuCN (268 mg, 3 mmol) was placed in a 50-mL Schlenk tube under argon and was activated by heating under reduced pressure. After cooling at room temperature THF (10mL) was added. This solution was cooled at -78°C and degassed with argon. n-BuLi (1.4M hexane solution, 4.3mL, 6 mmol) was then added. The suspension was warmed until it was homogenous (-60°C max). The homogenous solution was cooled at -78°C and Bu₃SnH (1.75 mL, 6 mmol) was added. The mixture was stirred at -78°C for 30 minutes. Phenylacetylene (0.3 mL, 2.73 mmol) was then added and the reaction mixture was stirred at -78°C for 15 minutes. The reaction mixture was quenched with a saturated aqueous NH₄Cl solution (10 mL) and then extracted with ethyl acetate (10 mL × 2). The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residual colorless oil was purified by chromatography on silica gel (Et₂N/petroleum ether : 01/99), the desired product 2g (1.05g, 98%, isomer E >98%) was obtained as a colorless oil.

3-[(E)-2-phenylethynyl]-ltributyltin (2g): colorless oil; $^1$H NMR (250MHz, CDCl₃) δ 7.40 (d, 2H, J=8.5) ; 7.31 (t, 2H, J=8.5) ; 7.20 (m, 1H) ; 6.87 (8 br, 2H-C₆H) ; 1.61-1.48 (m, 6H) ; 1.41-1.27 (m, 8H) ; 0.99-0.87 (m, 17H) ; $^{13}$C NMR (62.5MHz, CDCl₃) δ 146.2, 138.9, 129.7 (C), 128.6 (2C), 127.6 (C), 126.1 (2C), 29.3 (3C, $^2J_{Sn-C}$=20), 27.5 (3C, $^3J_{Sn-C}$=55), 13.8 (3C), 9.7 (3C, $^1J_{Sn-C}$=327/343).

Typical procedure for the palladium-catalysed cross-coupling reaction.

2-tributylstannylfuran 2a (550µL, 1.73mmol), CuBr·Me₂S (356mg, 1.73mmol), and 3-methylthio-1,2,4-triazine (100mg, 0.787mmol) were placed in a 25mL round-bottom flask under argon with THF (6mL). After 10 minutes under argon, Pd(PPh₃)₄ (46mg, 5%mol) was added. The reaction mixture was stirred for 24h under reflux. After purification by column chromatography on silica gel (Et₂N/petroleum ether/ethyl acetate : 01/94/05), the desired product 3a (105mg, 90%) was obtained as a yellow powder.
Analytical Data

3-(2-furyl)-1,2,4-triazine (3a) (lit.): tan solid; mp 75°C; (M+1)⁺ (IS) 148; ¹H NMR (250 MHz, CDCl₃) δ 9.09 (d, 1H, J= 2.5); 8.62 (d, 1H, J= 2.5); 7.72 (dd, 1H, J= 0.9, 1.6); 7.54 (dd, 1H, J= 0.9, 3.5); 6.65 (dd, 1H, J= 1.6, 3.5); ¹³C NMR (62.5 MHz, CDCl₃) δ 158.1, 149.5, 148.8, 147.2, 146.6, 115.7, 112.3; IR (KBr) 1587, 1488, 1422, 1345, 756. Anal. Calc. for C₇H₅N₃O (147): C, 57.14; H, 3.42; N, 28.55. Found: C, 57.43; H, 3.56; N, 28.32.

3-(2-thienyl)-1,2,4-triazine (3b) (lit.): yellow solid; mp 72°C; (M+1)⁺ (IS) 164; ¹H NMR (250 MHz, CDCl₃) δ 9.05 (d, 1H, J= 2.4); 8.57 (d, 1H, J= 2.4); 8.17 (dd, 1H, J= 1.2, 5.2); 7.61 (dd, 1H, J= 1.2, 5.2); 7.21 (t, 1H, J= 5.2); ¹³C NMR (62.5 MHz, CDCl₃) δ 161.7, 148.8, 147.1, 139.4, 131.7, 130.7, 128.7; IR (KBr) 1531, 1521, 1436, 858, 847, 731. Anal. Calc. for C₇H₅N₃S (163): C, 51.51; H, 3.09; N, 25.74. Found: C, 51.77; H, 3.18; N, 25.53.

3-(3-nitrophenyl)-1,2,4-triazine (3c): yellow solid; mp: 95 °C (lit.¹ 106-107°C); (M+1)⁺ (IS) 203; ¹H NMR (250 MHz, CDCl₃) δ 9.40 (t, 1H, J= 2.4); 9.3 (d, 1H, J= 2.1); 8.9 (dt, 1H, J= 1.5, 8.0); 8.79 (d, 1H, J= 2.4); 8.41 (ddd, 1H, J= 1.5, 2.1, 8.0); 7.76 (t, 1H, J= 8.0); ¹³C NMR (62.5 MHz, CDCl₃) δ 162.5, 149.2, 149.1, 148.6, 136.6, 133.9, 130.1, 126.4, 123.4; IR (KBr) 1538, 1405, 1348, 1070, 734.

3-phenyl-1,2,4-triazine (3d): yellow solid; mp: 51°C (lit.² 52-55°C); (M+1)⁺ (IS) 158; ¹H NMR (250 MHz, CDCl₃) δ 9.16 (d, 1H, J= 2.4); 8.67 (d, 1H, J= 2.4); 8.53-8.57 (m, 2H); 7.54-7.56 (m, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 164.3, 148.8, 147.8, 134.8, 131.9, 129.0 (2C); 128.4 (2C); IR (KBr) 1521, 1403, 1354, 752, 694.

3-(4-methoxyphenyl)-1,2,4-triazine (3e): yellow solid; mp: 91 °C (lit.¹ 99-103°C); (M+1)⁺ (IS) 188; ¹H NMR (250 MHz, CDCl₃) δ 9.06 (d, 1H, J= 2.1); 8.61 (d, 1H, J= 2.1); 8.51 (d, 2H, J= 7.0); 7.03 (d, 2H, J= 7.0); 3.90 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 164.3, 149.0, 147.4, 130.0, 127.6, 114.7, 55.8; IR (KBr) 1607, 1523, 1398, 1254, 1173, 1023, 839, 803.

3-(4-pyridinyl)-1,2,4-triazine (3f) (lit.): yellow solid; mp: 130°C; (M+1)⁺ (IS) = 149; ¹H NMR (250 MHz, CDCl₃) δ 9.29 (d, 1H, J= 2.4); 8.86 (br s, 2H); 8.77 (d, 1H, J= 2.4); 8.38-8.40 (m, 2H); ¹³C NMR (62.5 MHz, CDCl₃) δ = 162.7, 150.9, 149.1 (2C), 148.9, 142.1, 121.8 (2C); IR (KBr) 1602, 1524, 1410, 1374, 1045, 990, 840, 790.

3-[(E)-2-phenylethenyl]-1,2,4-triazine (3g): tan solid; mp: 85°C; (M+1)⁺ (IS) 172; ¹H NMR (250 MHz, CDCl₃) δ 9.09 (br s, 1H); 8.58 (br s, 1H); 8.10 (d, 1H, J= 16); 7.64-7.67 (m, 2H); 7.39-7.45 (m, 4H); ¹³C NMR (62.5 MHz, CDCl₃) δ 164.8, 148.6, 147.1, 140.4, 135.5, 129.8, 129.0 (2C), 127.9 (2C), 124.1; IR (KBr) 1633, 1522, 1410, 1365, 1049, 979, 692. Anal. Calc. for C₁₁H₉N₃ (171): C, 72.11; H, 4.95; N, 22.93. Found: C, 71.42; H, 5.03; N, 22.68.

2-(2-furyl)pyrimidine (3h) (lit.): yellow solid; mp 64°C; (M+1)⁺ (IS) 147; ¹H NMR (250 MHz, CDCl₃) δ 8.73 (d, 2H, J= 4.7); 7.63 (dd, 1H, J= 0.6, 1.9); 7.34 (dd, 1H, J= 0.6, 3.4); 7.11 (t, 1H, J= 4.7); 6.75 (dd, 1H, J= 1.9, 3.4); ¹³C NMR (62.5 MHz, CDCl₃) δ 157.6, 157.2 (2C), 151.9, 145.0, 118.6, 113.4, 112.2; IR (KBr) 1978, 1594, 1224, 1168, 1096, 1012, 996, 912, 883, 798.
2-(3-nitrophenyl)pyrimidine (3i) (lit.\textsuperscript{11}): white solid; mp: 145 °C; (M+1) \(^+\) (IS) 202; \(^1^H\) NMR (250MHz, CDCl\textsubscript{3}) \(\delta\) 9.30 (t, 1H, \(J=2.0\)); 8.86 (d, 2H, \(J=5.0\)); 8.78 (dt, 1H, \(J=2.0, 8.0\)); 8.32 (ddd, 1H, \(J=1.3, 2.0, 8.0\)); 7.66 (t, 1H, \(J=8.0\)); 7.30 (t, 1H, \(J=5.0\)); \(^1^3^C\) NMR (62.5MHz, CDCl\textsubscript{3}) \(\delta\) 162.5, 157.6 (2C), 148.8, 139.4, 133.9, 129.6, 125.3, 123.3, 120.2; IR (KBr) 1567, 1522, 1351, 803, 734, 673.

2-(2-furyl)-1,3-benzothiazole (3j) (lit.\textsuperscript{12}): white solid; mp: 98°C; (M+1) \(^+\) (IS) 202; \(^1^H\) NMR (250MHz, CDCl\textsubscript{3}) \(\delta\) 8.05 (d, 1H, \(J=8.0\)); 7.87 (d, 1H, \(J=8.0\)); 7.59 (br s, 1H); 7.48 (t, 1H, \(J=7.3\)); 7.36 (t, 1H, \(J=7.3\)); 7.19 (d, 1H, \(J=3.4\)); 6.58 (br s, 1H); \(^1^3^C\) NMR (62.5MHz, CDCl\textsubscript{3}) \(\delta\) 157.6, 153.8, 148.8, 144.7, 134.3, 126.5, 125.3, 123.2, 121.6, 112.6, 111.5; IR (KBr) 1503, 1244, 1018, 896, 746.

2-[(E)-2-phenylethenyl]-benzothiazole (3k) (lit.\textsuperscript{13}): yellow solid; mp: 104°C (crystallization CHCl\textsubscript{3}/Petroleum ether); (M+1) \(^+\) (IS) 238; \(^1^H\) NMR (250MHz, CDCl\textsubscript{3}) \(\delta\) 8.02 (d, 1H, \(J=8.0\)); 7.83 (d, 1H, \(J=8.0\)); 7.58-7.25 (m, 9H); \(^1^3^C\) NMR (62.5MHz, CDCl\textsubscript{3}) \(\delta\) 165.0, 153.4, 145.0, 138.2, 135.3, 129.7, 129.0 (2C), 127.5 (2C), 126.6, 125.6, 122.8, 121.8, 121.6; IR (KBr) 1630, 1445, 1432, 966, 841, 755, 726, 691.

2-vinyl-1,3-benzothiazole (3l): unstable brown solid; \(^1^H\) NMR (250MHz, CDCl\textsubscript{3}) \(\delta\) 8.16 (d, 1H, \(J=8.5\)); 7.87 (d, 1H, \(J=8.5\)); 7.60-7.35 (m, 2H); 7.12 (dd, 1H, \(J=11.0, 17.6\)); 6.21 (d, 1H, \(J=17.6\)); 5.75 (d, 1H, \(J=11.0\)).

REFERENCES
