Supporting Information for

Pt-Catalyzed Reaction of Alkynes with ArI (Ar = aryl and thienyl) and Ar'SM (M = Na, K and Sn(Bu-*n*)₃): Three-Component vs. Two-Component Cross-coupling Reaction

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The Preparation of Authentic 1a and 1b: To a toluene (10 mL) solution of Pt(PPh₃)₄ (622.1 mg, 0.5 mmol) was added 4-iodotoluene (327.0 mg, 1.5 mmol) at room temperature under nitrogen atmosphere. Then the yellow mixture was heated at 110 °C for 30 h, solvent was evaporated in vacuo, and the white precipitate was washed with hexane (50 mL × 5) to give Pt(C₆H₄Me-*p*)(I)(PPh₃)₂ (468.9 mg, 100%). Then the resultant Pt(C₆H₄Me-*p*)(I)(PPh₃)₂ was reacted with *p*-MeOC₆H₄SNa (486.6 mg, 3.0 mmol) in THF (50 mL) under N₂ atmosphere at room temperature for 50 h. Then the solvent was evaporated in vacuo, the crude yellow precipitate was dissolved in CH₂Cl₂ (ca. 10 mL), the solution was filtered, and pentane (100 mL) was added. A resultant yellow precipitate was collected by filtration to give platinum complexes (**1a**) (199.4 mg, 42%). The complex was reprecipitated from CH₂Cl₂ solution with pentane at room temperature.

Pt(C₆H₄CF₃-*p*)(SC₆H₂OMe-*p*)(PPh₃)₂ (**1b**) was also prepared similarly (63% isolated yield).

The reaction of Pt(PPh₃)₄ with *p*-CF₃C₆H₄I and the reaction of Pt(C₆H₄CF₃-*p*)(I)(PPh₃)₂ with *p*-MeOC₆H₄SNa were run for 24 h and 30 h, respectively.

1a; yellow solid; ¹H NMR (benzene-*d*₆, 400 MHz) δ 7.76-7.71 (m, 12H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.00-6.94 (m, 18H), 6.39 (d, *J* = 8.8 Hz, 2H), 6.30 (d, *J* = 8.8 Hz), 3.33 (s, 3H), 2.00 (s, 3H); ³¹P NMR (benzene-*d*₆, 160 MHz) δ 21.8 (s, *J*_{Pt-P} = 3084 Hz); IR (KBr) 3048, 3004, 2914, 2831, 1588, 1571, 1483, 1434, 1272, 1236, 1181, 1096, 1036, 1000, 821, 790, 752, 742, 691, 640, 624, 523, 511, 498, 459, 427 cm⁻¹; Anal. Calcd for C₅₀H₄₄O₁P₂Pt₁S₁: C, 63.22; H, 4.67. Found: C, 63.19; H, 4.67.

1b; yellow solid; ¹H NMR (benzene-*d*₆, 400 MHz) δ 7.70-7.65 (m, 12H), 7.17-7.15 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.93-6.92 (m, 18H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.38-6.36 (m, 2H), 3.32 (s, 3H); ³¹P NMR (benzene-*d*₆, 160 MHz) δ 21.6 (s, *J*_{Pt-P} = 3020 Hz); IR (KBr) 3054, 2935, 2831, 1591, 1483, 1435, 1389, 1325, 1273, 1233, 1180, 1152, 1098, 1075, 1030, 1012, 817, 770, 743, 692, 639, 624, 598, 514, 497, 459, 422 cm⁻¹; Anal. Calcd for C₅₀H₄₁F₃O₁P₂Pt₁S₁: C, 59.82; H, 4.12. Found: C, 59.76; H, 4.12.

The Preparation of Sodium Thiolate (7a) (General Procedure): In a dry two-necked flask with stirring bar were added a suspension of NaH (0.92 g, 50-72%) and anhydrous THF (50 mL). PhSH (3.3 g, 30 mmol) was dropwised to the NaH/THF solution at 0 °C, the reaction mixture was stirred overnight, and the precipitate was collected by filtration and washed with hexane (50 mL × 5) and chloroform (50 mL × 5). The white solid was dried in vacuo

overnight to give PhSNa (3.6 g). Other Sodium thiolates were prepared similarly and potassium thiolate was prepared using KH instead of NaH.

The Preparation of Lithium Thiolate Salt (7c): In a dry two-necked flask with stirring bar were added PhSH (1.1 g, 10 mmol) and dehydrated THF (1.0 mol/l solution was prepared) and then 0.9 equiv of lithium wire was added under N₂ atmosphere. The mixture was stirred at room temperature until the lithium wire disappeared (ca. 12 h). Then THF was evaporated and the precipitated white solid was washed with dehydrated hexane (30 mL × 5). The resultant white solid was dried in vacuo overnight to give PhSLi (1.0 g, 90% based on Li).

RN of (Z)-5a (run 3, Table 1): 347887-07-4

RN of (Z)-5b (run 8, Table 1): 347887-13-2

5c (entry 9, Table 1): colorless oil; ¹H NMR (CDCl₃, 400 MHz) δ 7.63 (d, *J* = 6.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H) 7.22-7.35 (m, 5H), 6.75 (s, 1H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.50-1.58 (m, 2H), 1.17-1.28 (m, 6H), 0.84 (t, *J* = 6.8 Hz, 3H); NOE experiment: Irradiation of the vinyl singlet at δ 6.75 resulted in a 11.2% enhancement of the signal at δ 2.27 (C-3 methylene triplet); ¹³C NMR (CDCl₃, 100 MHz) δ 140.1, 139.2, 133.3, 131.3, 129.6, 129.2, 128.8, 127.0, 124.8, 124.7, 38.3, 31.7, 28.9, 28.6, 22.7, 14.2, IR (neat) 3010, 2930, 2857, 1615, 1477, 1324, 1166, 1125, 1068, 745; mass spectrum (EI) *m/e* 364 (M⁺, 100); Anal. Calcd for C₂₁H₂₃F₃S₁: C, 69.20; H, 6.36; S, 8.80. Found: C, 69.30; H, 6.11; S, 8.96.

RN of (Z)-5d (run 10, Table 1): 347887-08-5

5e (entry 11, Table 1): pale yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (d, $J = 7.2$ Hz, 2H), 7.33 (m, $J = 7.6$ Hz, 3H), 7.20-7.27 (m, 2H), 6.83 (d, $J = 7.2$ Hz, 2H), 6.63 (s, 1H), 3.79 (s, 3H), 2.18 (t, $J = 7.2$ Hz, 2H), 1.53 (m, 2H), 1.24 (m, 6H), 0.85 (t, $J = 7.2$ Hz, 3H); NOE experiment: Irradiation of the vinyl singlet at δ 6.83 resulted in a 7.0% enhancement of the signal at δ 2.18 (C-3 methylene triplet); ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.1, 137.8, 136.8, 134.2, 129.1, 128.8, 127.8, 126.6, 123.9, 114.3, 55.4, 37.8, 31.7, 29.0, 28.6, 22.7, 14.2; IR (neat) 3021, 2999, 2929, 2855, 1529, 1571, 1492, 1462, 1442, 1286, 1245, 1180, 1033, 827, 750, 694 cm^{-1} ; mass spectrum (EI) m/e 326 (M^+ , 100); Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_1\text{S}_1$: C, 77.25; H, 8.03; S, 9.82. Found: C, 77.08; H, 8.01; S, 9.80.

5f (entry 12, Table 1): colorless oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.48-7.52 (m, 4H), 7.22-7.38 (m, 5H), 6.96 (s, 1H), 2.32 (t, $J = 7.6$ Hz, 2H), 1.51-1.59 (m, 2H), 1.25-1.30 (m, 6H), 0.86 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.3, 136.1, 135.3, 133.5, 128.9, 128.8, 127.9, 127.5, 125.6, 122.7, 38.9, 31.7, 28.9, 28.6, 22.7, 14.2; IR (neat) 3023, 2929, 2856, 1606, 1494, 1466, 1445, 1325, 1165, 1126, 1091, 1062, 830, 751, 694 cm^{-1} ; mass spectrum (EI) m/e 364 (M^+ , 100);. Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{S}_1$: C, 69.20; H, 6.36; S, 8.80. Found: C, 69.16; H, 6.56; S, 9.03.

5g (entry 13, Table 1): colorless oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.45 (d, $J = 8.0$ Hz, 2H), 7.33-7.30 (m, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.83-6.80 (m, 2H), 6.61 (s, 1H), 3.79 (s, 3H), 2.34 (s, 3H), 2.16 (t, $J = 7.6$ Hz, 2H), 1.53-1.48 (m, 2H), 1.27-1.19 (m, 6H), 0.85 (t, $J = 7.0$ Hz, 3H); NOE experiment: Irradiation of the vinyl singlet at δ 6.61 resulted in a 10.0%

enhancement of the signal at δ 2.16 (C-3 methylene triplet); ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 136.7, 136.4, 134.1, 133.9, 129.0, 128.9, 128.5, 124.1, 114.3, 55.4, 37.8, 31.7, 29.0, 28.6, 22.7, 21.4, 14.3; IR (neat) 2998, 2954, 2928, 2855, 2277, 1896, 1592, 1571, 1509, 1493, 1462, 1440, 1406, 1377, 1353, 1286, 1246, 1100, 1172, 1125, 1104, 1034, 1008, 943, 861, 827, 806, 724, 712, 640 cm^{-1} ; mass spectrum (EI) m/e 340 (M^+ , 100); Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_1\text{S}_1$: C, 77.60; H, 8.29; S, 9.42. Found: C, 77.35; H, 8.21; S, 9.34.

5h (entry 14, Table 1): pale yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.53 (d, J = 8.0 Hz, 2H), 7.15-7.34 (m, 8H), 6.77 (s, 1H), 2.26 (t, J = 7.6 Hz, 2H), 1.42-1.48 (m, 3H), 0.78 (d, J = 6.0 Hz, 6H); NOE experiment: Irradiation of the vinyl singlet at δ 6.77 resulted in a 6.8% enhancement of the signal at δ 2.26 (C-3 methylene triplet); ^{13}C NMR (CDCl_3 , 100 MHz) δ 136.6, 136.2, 134.0, 131.5, 131.0, 129.0, 128.6, 127.8, 127.0, 126.6, 38.4, 36.3, 27.5, 22.6; IR (neat) 3058, 3021, 2953, 2867, 1582, 1492, 1475, 1466, 1439, 1366, 1082, 1024, 914, 742 cm^{-1} ; mass spectrum (EI) m/e 282 (M^+ , 100), 226 (45), 135 (38), 116 (61); Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{S}$: C, 80.80; H, 7.85; S, 11.35. Found: C, 80.54; H, 7.77; S, 11.15.

5i (entry 15, Table 1): pale yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ :light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.18 (m, 7H), 7.06 (s, 1H), 7.01-6.98 (m, 1H), 2.42 (t, J = 7.0 Hz, 2H), 2.24 (t, J = 7.0 Hz, 2H), 1.88-1.81 (m, 2H); NOE experiment: Irradiation of the vinyl singlet at δ 7.06 resulted in a 6.4% enhancement of the signal at δ 2.42 (C-3 methylene triplet); ^{13}C NMR (100 MHz, CDCl_3) δ 138.91, 132.89, 130.02, 129.13, 129.10, 128.91,

126.83, 126.81, 125.91, 119.11, 36.34, 24.09, 15.93; IR (neat) 3504, 3071, 3002, 2936, 2652, 2245, 1802, 1613, 1582, 1476, 1439, 1424, 1363, 1316, 1217, 1080, 1050, 1024, 1000, 855, 745, 703 cm⁻¹; mass spectrum (EI) m/e 285 (M⁺, 100); Anal. Calcd for C₁₆H₁₅N₁S₂: C, 67.33; H, 5.30; N, 4.91; S, 22.47. Found: C, 67.20; H, 5.26; N, 5.02; S, 22.25.

5j (entry 16, Table 1): pale yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ light yellow oil; ¹H NMR (400 MHz, CDCl₃) 7.35-7.15 (m, 7H), 7.02 (s, 1H), 7.00-6.98 (m, 1H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.64-1.47 (m, 4H), 1.37 (br s, 1H); NOE experiment: Irradiation of the vinyl singlet at δ 7.02 resulted in a 7.1% enhancement of the signal at δ 2.33 (C-3 methylene triplet); ¹³C NMR (100 MHz, CDCl₃) δ 139.63, 133.81, 131.92, 130.01, 129.32, 128.82, 127.76, 126.53, 126.39, 125.88, 62.66, 37.95, 31.93, 25.03; IR (neat) 3334, 3071, 2937, 2861, 1582, 1476, 1439, 1361, 1216, 1068, 1024, 854, 742, 700 cm⁻¹; mass spectrum (EI) m/e 290 (M⁺, 100); Anal. Calcd for C₁₆H₁₈O₁S₂: C, 66.16; H, 6.25; S, 22.08. Found: C, 65.93; H, 6.23; S, 21.31.

5k (entry 17, Table 1): pale yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.37-6.98 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 136.5, 135.48, 135.47, 135.0, 129.3, 128.9, 128.5, 127.99, 129.97, 127.8, 127.7, 127.6, 125.6; IR (neat) 3057, 3020, 1947, 1876, 1801, 1597, 1581, 1488, 1478, 1445, 1311, 1234, 1182, 1156, 1076, 1024, 1000, 965, 939, 912, 871, 842, 762, 739, 691, 612 cm⁻¹; mass spectrum

(EI) m/e 288 (M^+ , 48), 178 (100); Anal. Calcd for $C_{20}H_{16}S_1$: C, 83.29; H, 5.59; S, 11.12.

Found: C, 83.12; H, 5.46; S, 10.95.

5l (entry 18, Table 1): yellow oil; 1H NMR ($CDCl_3$, 400 MHz) δ 7.69-7.67 (m, 2H), 7.38 (s, 1H), 7.34-7.10 (m, 8H), 0.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 136.8, 136.6, 129.3, 129.2, 128.8, 128.5, 128.0, 127.8, 125.5, -0.49; IR (neat) 3058, 3022, 2955, 2896, 2360, 2341, 1943, 1872, 1583, 1491, 1477, 1439, 1406, 1248, 1184, 1156, 1078, 1024, 1000, 940, 913, 837, 758, 739, 691, 630 cm^{-1} ; mass spectrum (EI) m/e 284 (M^+ , 60), 73 (100); exact mass (M^+) calcd for $C_{17}H_{20}S_1Si_1$ 284.1055, found 284.1074.

5n (run 21, Table 1): light yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.39 (m, 2H), 7.38-7.12 (m, 5H), 6.99 (s, 1H), 6.96-6.89 (m, 1H), 2.29 (t, $J = 7.6$ Hz, 2H), 1.58-1.50 (m, 2H), 1.28-1.17 (m, 6H), 0.85 (t, $J = 6.8$ Hz, 3H); NOE experiment: Irradiation of the aryl triplet at δ 2.29 resulted in a 7.8% enhancement of the signal at δ 6.99 (C-1 vinyl singlet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.77, 134.00, 132.49, 129.95, 129.10, 128.72, 127.37, 126.36, 126.19, 125.79, 38.30, 31.64, 28.86, 28.59, 22.62, 14.19; IR (NaCl) 3071, 2954, 2928, 2855, 1582, 1476, 1439, 1377, 1361, 1315, 1216, 1068, 1050, 1024, 1000, 854, 818, 741, 699 cm^{-1} ; mass spectrum (EI) m/e 302 (M^+ , 100); Anal. Calcd for $C_{18}H_{22}S_2$: C, 71.47; H, 7.33; S, 21.20. Found: C, 71.38; H, 7.33; S, 20.96.

(Z)-5o (run 27, Table 1): light yellow oil; ^1H NMR (400 MHz, CDCl_3) yellow solid: ^1H NMR (400 MHz, CDCl_3) δ 7.66-7.63 (m, 4H), 7.43 (s, 2H), 7.28-7.17 (m, 12H), 7.10-7.00 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 140.1, 134.8, 131.0, 130.3, 129.5, 128.41, 128.35, 127.9, 127.4, 127.2, 125.5; mass spectrum (EI) m/e 504 (M^+ , 100); exact mass (M^+) calcd for $\text{C}_{34}\text{H}_{26}\text{S}_2$ 504.1040, found 504.1042.

RN of (Z)-5p (run 28, Table 1): 791120-31-5

5q (run 29, Table 1): light yellow solid, mp: 94–95 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.67-7.65 (m, 2H), 7.54 (s, 1H), 7.33-7.02 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.18, 140.15, 134.80, 131.36, 130.11, 129.95, 128.65, 128.27, 128.15, 127.87, 127.62, 127.37, 126.09, 125.74; IR (KBr) 3107, 3056, 3000, 1577, 1478, 1444, 1437, 1424, 1312, 1238, 1212, 1194, 1155, 1076, 1054, 1023, 916, 876, 850, 816, 767, 748, 704, 691, 576, 562, 506, 478, 458, 418 cm^{-1} ; mass spectrum (EI) m/e 294 (M^+ , 99), 173 (100); Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{S}_2$: C, 73.43; H, 4.79; S, 21.78. Found: C, 73.18; H, 4.82; S, 21.77.

RN of (Z)-5r (run 30, Table 1): 79112-28-0

(Z)-5s (run 31, Table 1): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.18 (m, 7H), 7.06 (s, 1H), 7.01-6.98 (m, 1H), 2.42 (t, J = 7.0 Hz, 2H), 2.24 (t, J = 7.0 Hz, 2H), 1.88-1.81 (m, 2H); NOE experiment: Irradiation of the vinyl singlet at δ 7.06 resulted in a 6.4%

enhancement of the signal at δ 2.42 (C-3 methylene triplet); ^{13}C NMR (100 MHz, CDCl_3) δ 138.91, 132.89, 130.02, 129.13, 129.10, 128.91, 126.83, 126.81, 125.91, 119.11, 36.34, 24.09, 15.93; IR (NaCl) 3504, 3071, 3002, 2936, 2652, 2245, 1802, 1613, 1582, 1476, 1439, 1424, 1363, 1316, 1217, 1080, 1050, 1024, 1000, 855, 745, 703 cm^{-1} ; mass spectrum (EI) m/e 285 (M^+ , 100); Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{N}_1\text{S}_2$: C, 67.33; H, 5.30; N, 4.91; S, 22.47. Found: C, 67.20; H, 5.26; N, 5.02; S, 22.25.

(Z)-5t (run 32, Table 1): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.15 (m, 7H), 7.02 (s, 1H), 7.00-6.98 (m, 1H), 3.58 (t, J = 6.2 Hz, 2H), 2.33 (t, J = 7.2 Hz, 2H), 1.64-1.47 (m, 4H), 1.37 (br s, 1H); NOE experiment: Irradiation of the vinyl singlet at δ 7.02 resulted in a 7.1% enhancement of the signal at δ 2.33 (C-3 methylene triplet); ^{13}C NMR (100 MHz, CDCl_3) δ 139.63, 133.81, 131.92, 130.01, 129.32, 128.82, 127.76, 126.53, 126.39, 125.88, 62.66, 37.95, 31.93, 25.03; IR (NaCl) 3334, 3071, 2937, 2861, 1582, 1476, 1439, 1361, 1216, 1068, 1024, 854, 742, 700 cm^{-1} ; mass spectrum (EI) m/e 290 (M^+ , 100); Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_1\text{S}_2$: C, 66.16; H, 6.25; S, 22.08. Found: C, 65.93; H, 6.23; S, 21.31.

(Z)-5u (run 33, Table 1): pail yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.17 (m, 7H), 7.12 (s, 1H), 7.01-6.99 (m, 1H), 4.54 (t, J = 3.4 Hz, 1H), 3.93-3.78 (m, 2H), 3.62-3.56 (m, 1H), 3.48-3.44 (m, 1H), 2.60 (t, J = 6.6 Hz, 2H), 1.79-1.47 (m, 6H); NOE experiment: Irradiation of the vinyl singlet at δ 7.12 resulted in a 2.9% enhancement of the signal at δ 2.60 (C-3 methylene triplet); ^{13}C NMR (100 MHz, CDCl_3) δ 139.6, 133.9, 129.8, 129.5,

128.9, 128.4, 126.6, 126.5, 125.9, 98.7, 65.9, 62.2, 38.7, 30.7, 25.6, 19.6; IR (neat) 3070, 2940, 2869, 2737, 2556, 1946, 1880, 1614, 1582, 1476, 1439, 1426, 1384, 1352, 1322, 1283, 1260, 1216, 1200, 1182, 1156, 1136, 1120, 1078, 1032, 988, 969, 906, 870, 814, 742, 700 cm^{-1} ; mass spectrum (EI) m/e 346 (M^+ , 100); Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{S}_2$: C, 65.86; H, 6.40; O, 9.23; S, 18.51. Found: C, 65.64; H, 6.22; S, 18.47.

The Pd-Catalyzed Reaction of 5d with PhMgBr: Into two necked flask equipped with reflux condenser were added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (19 mg, 0.025 mmol), **5d** (155 mg, 0.5 mmol), PhMgBr (1.0 mmol, 1 N in THF), and $\text{PBU}_3 \cdot n$ (22 mg, 0.1 mmol). After the solution was refluxed for 8 h, the resultant reaction mixture was separated by PTLC to give 91 mg (69%) of (Z)(n- C_6H_{13})(Ph) $\text{C}=\text{C}(\text{H})(\text{Ph})$ (**13**). RN of 13: 254731-20-9