

## Supplementary Materials

*For*

### Zr-promoted Linear Coupling of Alkynes to Bis(allene)

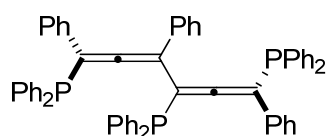
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#### **Experimental Sections**

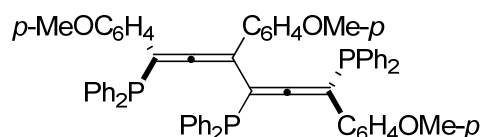
**General.** All manipulations were conducted in Schlenk tube and under nitrogen with a slightly positive pressure. The reaction progress was monitored by  $^{31}\text{P}$  NMR. The  $^{31}\text{P}$  NMR yields were obtained in proportion to the integral area of all the  $^{31}\text{P}$  signals determined by integration. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran (THF) was refluxed and freshly distilled from dark purple solutions of sodium and benzophenone under nitrogen atmosphere.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on JOEL 300 NMR spectrometer with TMS as internal standard.  $^{31}\text{P}$  NMR spectra were recorded on Bruker AC 200 NMR spectrometer at 81 MHz under  $^1\text{H}$  decoupled conditions using 85%  $\text{H}_3\text{PO}_4$  ( $\delta_{\text{P}} = 0$  ppm) as an external standard. Elemental analyses were performed on a Flash EA 1112 instrument. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in positive ion mode. Flash column chromatography was performed using silica gel (200-300 mesh).

**Representative procedure for coupling of alkynes to bis(allene).** To a solution of phenylacetylene (3 mmol) in THF (5 mL) was added *n*-BuLi (3.2 mmol, 2 mL, 1.6 M solution in hexane) at  $-78^{\circ}\text{C}$  and the mixture was warmed up to room temperature and kept for 1 h. To the reaction system,  $\text{Cp}_2\text{ZrCl}_2$  (1 mmol, 292 mg) was added at  $-78^{\circ}\text{C}$ . This mixture was kept at room temperature for 12 h to afford a dark red solution. Then  $\text{PPh}_2\text{Cl}$  (3.0 mmol, 552 mL) was added to the solution and was stirred for another 3 h at room temperature. The reaction mixture was monitored by  $^{31}\text{P}$  NMR and three signals appeared in -6.7, -7.6, -9.3 ppm.  $^{31}\text{P}$  NMR yield 97%. The reaction mixture was quenched by 3N HCl solution extracted with  $\text{CH}_2\text{Cl}_2$ . The organic extract was dried over  $\text{MgSO}_4$ . Removing the solvent and subsequent purification by column chromatography on silica gel (petroleum ether : ethyl acetate = 25 : 1) afforded 1,4,6-triphenyl-1,3,6-tris(diphenylphosphino)hexa-1,2,4,5-tetraene (**1a**) (454 mg, 53%) as yellow solid.



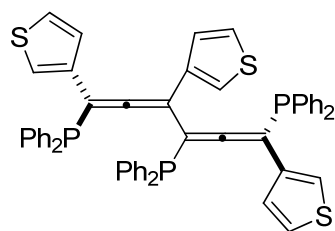
$^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  6.70-7.65 (m, 45H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  103.3 (d,  $^1J_{\text{PC}} = 18.6$  Hz, 1C), 105.5 (d,  $^1J_{\text{PC}} = 15.8$  Hz, 1C), 107.2 (d,  $^2J_{\text{PC}} = 20.8$  Hz,  $^3J_{\text{PC}} = 2.9$  Hz, 1C), 108.6 (d,  $^1J_{\text{PC}} = 33.0$  Hz, 1C), 126.9-136.9 (m, aromatic), 209.0 (d,  $^2J_{\text{PC}} = 5.0$  Hz, 1C), 209.9 (d,  $^2J_{\text{PC}} = 2.9$  Hz, 1C);  $^{31}\text{P}$  NMR (81MHz,  $\text{CDCl}_3$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  -6.9, -7.9, -9.8; Positive ion ESI-MS: 881.2 ( $\text{M}+\text{Na}^+$ ). Anal. calcd for  $\text{C}_{60}\text{H}_{45}\text{P}_3 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ : C, 76.17; H, 5.13. Found: C, 75.92; H, 5.23.

1,4,6-tri(4-methoxyphenyl)-1,3,6-tris(diphenylphosphino)hexa-1,2,4,5-tetraene **1b**



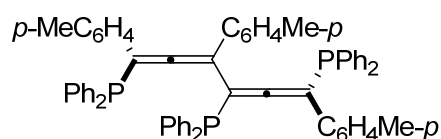
$^{31}\text{P}$  NMR yield 72%. Isolated yield 29%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  3.71 (s, 3H), 3.81 (s, 6H), 6.47-7.64 (m, 42H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  55.2, 55.3, 55.4, 103.7 (d,  $^1J_{\text{PC}} = 17.2$  Hz, 1C), 104.5 (d,  $^1J_{\text{PC}} = 15.1$  Hz, 1C), 106.1 (d,  $^2J_{\text{PC}} = 19.4$  Hz,  $^3J_{\text{PC}} = 2.2$  Hz, 1C), 108.2 (d,  $^1J_{\text{PC}} = 33.0$  Hz, 1C), 113.1, 113.4, 113.5, 128.0-136.1 (m, aromatic), 158.5, 158.6, 159.0, 209.0 (d,  $^2J_{\text{PC}} = 3.6$  Hz, 1C), 209.0 (d,  $^2J_{\text{PC}} = 3.6$  Hz, 1C), 209.7 (d,  $^2J_{\text{PC}} = 2.1$  Hz, 1C);  $^{31}\text{P}$  NMR (81MHz,  $\text{CDCl}_3$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  -7.3, -8.5, -10.3; Positive ion ESI-MS: 971.2 ( $\text{M}+\text{Na}^+$ ).

1,4,6-tri(thiophen-3-yl)-1,3,6-tris(diphenylphosphino)hexa-1,2,4,5-tetraene **1c**



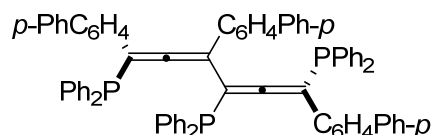
$^{31}\text{P}$  NMR yield 77%. Isolated yield 36%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  6.78-7.69 (m, aromatic, 39H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  101.3 (d,  $^1J_{\text{PC}} = 16.5$  Hz, 1C), 102.6 (d,  $^1J_{\text{PC}} = 16.5$  Hz, 1C), 102.7 (d,  $^2J_{\text{PC}} = 20.8$  Hz,  $^3J_{\text{PC}} = 2.9$  Hz, 1C), 103.6 (d,  $^1J_{\text{PC}} = 32.3$  Hz, 1C), 121.4-136.5 (m, aromatic), 209.4 (d,  $^2J_{\text{PC}} = 3.6$  Hz, 1C), 210.4 (d,  $^2J_{\text{PC}} = 2.9$  Hz, 1C);  $^{31}\text{P}$  NMR (81MHz,  $\text{CDCl}_3$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  -5.7, -8.2, -9.4; Positive ion ESI-MS: 899.2 ( $\text{M}+\text{Na}^+$ ).

1,4,6-tri(*p*-tolyl)-1,3,6-tris(diphenylphosphino)hexa-1,2,4,5-tetraene **1d**



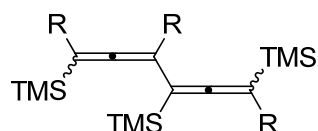
$^{31}\text{P}$  NMR yield 91%. Isolated yield 49%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  2.27 (s, 3H), 2.40 (s, 3H) 2.42 (s, 3H), 6.79-7.69 (m, 42H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  21.2, 21.3, 21.4, 103.5 (d,  $^1J_{\text{PC}} = 18.6$  Hz, 1C), 105.0 (d,  $^1J_{\text{PC}} = 14.3$  Hz, 1C), 106.8 (d,  $^2J_{\text{PC}} = 19.9$  Hz,  $^3J_{\text{PC}} = 2.7$  Hz, 1C), 108.6 (d,  $^1J_{\text{PC}} = 33.8$  Hz, 1C), 127.0-137.0 (m, aromatic), 209.1 (d,  $^2J_{\text{PC}} = 4.3$  Hz, 1C), 209.9 (d,  $^2J_{\text{PC}} = 3.6$  Hz, 1C);  $^{31}\text{P}$  NMR (81MHz,  $\text{CDCl}_3$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  -7.3, -8.2, -10.4; Positive ion ESI-MS: 923.5 ( $\text{M}+\text{Na}^+$ ).  
Anal. calcd for  $\text{C}_{63}\text{H}_{51}\text{P}_3 \cdot 2\text{H}_2\text{O}$ : C, 80.75; H, 5.92. Found: C, 81.03; H, 5.90.

1,4,6-tri(biphenyl-4-yl)-1,3,6-tris(diphenylphosphino)hexa-1,2,4,5-tetraene **1e**



$^{31}\text{P}$  NMR yield 84%. Isolated yield 37%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  6.77-7.70 (m, 57H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  103.3 (d,  $^1J_{\text{PC}} = 19.4$  Hz, 1C), 105.3 (d,  $^1J_{\text{PC}} = 16.5$  Hz, 1C), 107.2 (d,  $^2J_{\text{PC}} = 20.1$  Hz,  $^3J_{\text{PC}} = 2.2$  Hz, 1C), 108.4 (d,  $^1J_{\text{PC}} = 33.0$  Hz, 1C), 126.4-140.9 (m, aromatic), 209.3 (d,  $^2J_{\text{PC}} = 5.0$  Hz, 1C), 210.4 (d,  $^2J_{\text{PC}} = 2.9$  Hz, 1C);  $^{31}\text{P}$  NMR (81MHz,  $\text{CDCl}_3$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  -7.0, -7.2, -9.5; Positive ion ESI-MS: 1109.3 ( $\text{M}+\text{Na}^+$ ). Anal. calcd for  $\text{C}_{78}\text{H}_{57}\text{P}_3 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{Et}_3\text{N}$ : C, 80.18; H, 5.86; N, 1.10. Found: C, 79.68; H, 5.95; N, 0.94.

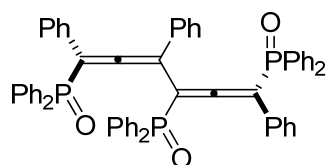
1,4,6-triphenyl-1,3,6-tris(trimethylsilyl)hexa-1,2,4,5-tetraene **1f**



To the solution of  $\text{Cp}_2\text{Zr}(\text{CCPh})_3$  (1 mmol) in THF, 4 mmol TMSOTf was added and kept at room temperature for 10 hours. 57% isolated yield (1:1 de isomer).  $^1\text{H}$  NMR

(300MHz, CDCl<sub>3</sub>)  $\delta$  0.07, 0.08, 0.11, 0.16, 0.21, 0.29, 7.10-7.38; <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>)  $\delta$  -0.2, -0.2, -0.1, 0, 0, 0.1, 89.8, 90.3, 94.3, 94.6, 101.6, 101.7, 102.6, 103.0, 125.8, 126.5, 126.6, 126.6, 127.5, 127.6, 127., 127.7, 128.0, 128.1, 128.2, 128.2, 128.5, 128.6, 128.6, 137.2, 137.2, 137.6, 137.6, 137.7, 137.7, 208.9, 209.6, 209.8, 209.9. GC-MS: 522.

1,4,6-triphenyl-1,3,6-tris(diphenylphosphino)hexa-1,2,4,5-tetraene oxide **2a**



<sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta$  6.61(d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), 6.86-7.50 (m, 39H), 7.92(dd, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>4</sup>J<sub>PH</sub> = 12 Hz, 2H), 8.20-8.25(m, 2H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta$  102.3 (ddd, <sup>1</sup>J<sub>PC</sub> = 91.8 Hz, <sup>3</sup>J<sub>PC</sub> = 11.5 Hz, <sup>4</sup>J<sub>PC</sub> = 7.2 Hz, 1C), 104.0 (ddd, <sup>2</sup>J<sub>PC</sub> = 5.7 Hz, <sup>3</sup>J<sub>PC</sub> = 12.9 Hz, <sup>4</sup>J<sub>PC</sub> = 5.7 Hz, 1C), 105.1 (d, <sup>1</sup>J<sub>PC</sub> = 94.6 Hz, 1C), 105.4 (d, <sup>1</sup>J<sub>PC</sub> = 93.2 Hz, <sup>3</sup>J<sub>PC</sub> = 10.0 Hz, 1C), 127.1-135.7 (m, aromatic), 211.6 (dd, <sup>2</sup>J<sub>PC</sub> = 2.9 Hz, <sup>2</sup>J<sub>PC</sub> = 2.2 Hz, 1C), 213.0 (dd, <sup>2</sup>J<sub>PC</sub> = 5.0 Hz, <sup>3</sup>J<sub>PC</sub> = 8.6 Hz, 1C); <sup>31</sup>P NMR (81MHz, CDCl<sub>3</sub>, 85%<sup>3</sup>H<sub>3</sub>PO<sub>4</sub>)  $\delta$  25.5, 29.1, 30.0; Positive ion ESI-MS: 929.3 (M+Na<sup>+</sup>). Anal. calcd for C<sub>60</sub>H<sub>45</sub>P<sub>3</sub>O<sub>3</sub>: C, 79.46 H, 5.00. Found: C, 79.56; H, 5.10.