Supporting Information

General. Spectroscopic measurement were carried out with the following instruments: Bruker DPX-400 and DRX-500 (^{1}H-NMR), JEOL FT/IR-350 (FT-IR). Alkynes were purchased from Aldrich or TCI and used without further purification. Allyl tosylates were prepared by reaction of a corresponding allylic alcohol with excess tosyl chloride and potassium hydroxide. 1,2-Dichloroethane was distilled from CaH_2 under nitrogen atmosphere and degassed prior to use.

General procedure of the benzannulation from alkynes and allyl tosylates. To a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (26 mg, 0.025 mmol) and PPh_3 (13 mg, 0.05 mmol) in 1,2-dichloroethane (3 ml) was added an alkyne (2 mmol) and an allyl tosylate (0.5 mmol) under nitrogen atmosphere in a pressure bial. After heating at 80°C for 12 h, the mixture was filtered through a short column using ether as an eluent. Solvents and excess alkyne were removed under reduced pressure, and the benzene derivative was purified by silica gel column chromatography.

1-Methyl-2,3,4,5-tetrapropylbenzene (3a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97-1.06 (m, 12H), 1.48-1.52 (m, 8H), 2.25 (s, 3H), 2.48-2.56 (m, 8H), 6.81(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.6, 15.0, 15,1, 15.1, 19.9, 23.7, 24.8, 24.9, 25.0, 31.6, 32.0, 32.2, 35.3, 129.2, 133.4, 136.5, 137.0, 138.1, 138.9; IR (neat) 2955, 2870, 1466, 1376, 1088, 865, 738 cm^{-1}; Anal. Calcd for $C_{19}H_{32}$: C, 87.62; H, 12.38. Found: C, 87.40; H, 12.69.

Pentamethylbenzene (3b): The spectroscopic data of **3b** were consistent with a commercially available authentic sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 6H), 2.21 (s, 3H), 2.24 (s, 6H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 16.3, 20,5, 129.0, 132.3, 133.3, 134.9; IR (KBr) 2968, 2920, 2865, 1473,1439, 1012, 863 cm^{-1}.

1,2,3,4-Tetraethyl-5-methylbenzene (3c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12-1.23 (m, 12H), 2.28 (s, 3H), 2.60-2.68 (m, 8H), 6.86 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.6, 15.6, 15,7, 16.0, 19.8, 21.8, 22.0, 22.5, 25.6, 128.6, 133.6, 137.5, 138.1, 139.4, 139.7; IR (neat) 2964, 2870, 1464, 1375, 1059, 873 cm^{-1}; Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.10; H, 11.70.

1,2,3,4-Tetrabutyl-5-methylbenzene (3d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93-1.00 (m, 12H), 1.40-1.55 (m, 16H), 2.25 (s, 3H), 2.50-2.56(m, 8H), 6.81 (d, 1H, J = 0.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.1, 19,9, 23.2, 23.5, 23.6, 23.7, 28.9, 29.2, 29.5, 32.6, 32.8, 33.8, 34.0, 34.1, 129.2, 133.4, 136.5, 137.0, 138.2, 138.8; IR (neat) 2955, 2871, 1464, 1377, 1103, 867, 730 cm^{-1}; Anal. Calcd for $C_{23}H_{40}$: C, 87.26; H, 12.74. Found: C, 87.23; H, 12.91.

1-Methyl-2,3,4,5-tetraphenylbenzene (3e). Analytical pure **3e** was obtained by recrystalization from ethanol after preparative MPLC (hexane/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 1.40 (s, 9H), 6.76-6.89 (m, 10H), 7.03-7.16 (m, 10H), 7.40 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.1, 124.2, 124.4, 125.0, 125.1, 125.5, 125.8, 126.5, 126.6, 128.9, 129.1, 130.2, 130.6, 134.4, 136.7, 139.0, 139.4, 139.5, 139.6, 139.8, 140.4, 140.9; IR (neat) 3056, 3022, 1600, 1440, 1071, 1027, 762, 735, 699 cm^{-1}; Anal. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found: C, 93.70; H, 6.10.

1,2,3,4-Tetrakis(methoxymethyl)-5-methylbenzene (3f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.37 (s, 6H), 3.40 (s, 3H), 3.43 (s, 3H), 4.53-4.55 (m, 6H), 4.59 (s, 2H), 7.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 58.1, 58.2, 58.5, 67.6, 67.9, 68.3, 72.4, 131.1, 133.4, 135.4, 137.1, 137.7, 138.5; IR (neat) 2924, 2816, 1459, 1374, 1190, 1098, 946 cm^{-1}; Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.14; H, 8.99.

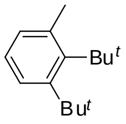
1,2,3,4-Tetrakis(carbomethoxy)-5-methylbenzene (3g). The spectroscopic data of **3g** were consistent with an authentic sample reported previously (Munz, C.; Stephan, C.; tom Dieck, H. *J. Organomet. Chem.* **1991**, *407*, 413). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.86 (s, 3H), 3.91-3.93 (m, 9H), 7.94 (d, 1H, *J* = 0.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 52.8, 52.9, 53.1, 129.7, 130.0, 133.0, 134.6, 137.1, 138.1, 165.1, 165.8, 167.5, 167.6; IR (KBr) 2959, 1736, 1439, 1257-1161 cm^{-1}

1-Ethyl-2,3,4,5-tetrapropylbenzene (6a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99-1.06 (m, 12H), 1.21 (t, 3H, *J* = 7.5 Hz), 1.48-1.61 (m, 8H), 2.50-2.55 (m, 8H), 2.59 (q, 2H, *J* = 7.5 Hz), 6.85(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.6, 15.0, 15,1, 15.1, 19.9, 23.7, 24.8, 24.9, 25.0, 31.6, 32.0, 32.2, 35.3, 129.2, 133.4, 136.5, 137.0, 138.1, 138.9; IR (neat) 2955, 2870, 1466, 1376, 1088, 865, 738 cm^{-1}; Anal. Calcd for $C_{20}H_{34}$: C, 87.51; H, 12.49. Found: C, 87.64; H, 12.49.

1-Butyl-2,3,4,5-tetrapropylbenzene (6b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, 3H, *J* = 7.2 Hz), 0.98-1.06 (m, 12H), 1.41 (q, 2H, *J* = 7.2 Hz), 1.47-1.64 (m, 10H), 2.45-2.55 (m, 10H), 6.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.6, 15,0, 15.1, 15.3, 23.1, 24.7, 24.8, 24.9, 25.0, 31.6, 32.1, 32.3, 32.8, 33.9, 35.3, 127.9, 136.3, 136.8, 138.0, 138.1, 138.9; IR (neat) 2955, 2870, 1466, 1376, 1088, 865, 738 cm^{-1}; Anal. Calcd for $C_{22}H_{38}$: C, 87.34; H, 12.66. Found: C, 87.50; H, 12.86.

1,3-di-*tert*-Butyl-6-methylbenzene (7a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.42 (s, 9H), 2.51 (s, 3H), 7.05 (d, 1H, *J* = 7.9 HZ), 7.12 (dd, 1H, *J* = 7.9, 2.1 Hz), 7.42 (d, 1H, *J* = 2.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 30.5, 31.5, 34.5, 36.1, 122.6, 123.1, 132.4, 133.1, 147.3, 148.2; IR (neat) 2961, 2874, 1609, 1465, 1397, 1362, 1245, 817cm^{-1}; Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.12; H, 11.52; mp. 179.5 °C.

The structure of **7a** was determined as follows. The 1,2,3-substituted benzenes **A**, **B** and the 1,3,5-substituted benzene **C** were excluded by analyses of the IR spectrum and the coupling constants of ^{1}H-NMR. The structure **D** was also excluded by a comparison with an authentic sample reported previously (Hambley, T. W.; Sternhell, S.; Tansey, C. W. *Aust. J. Chem.* **1990**, *43*, 807). Finally, the structure of **7a** was determined by NOE experiments. Irradiation of the methyl protons showed a 9.4% increment on the doublet peak at 7.05 ppm, whereas no increment was observed on the other aromatic protons, indicating that the structure of **7a** was **F**.



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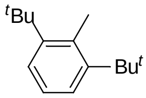

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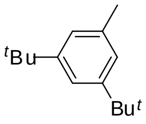

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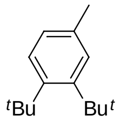

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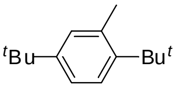

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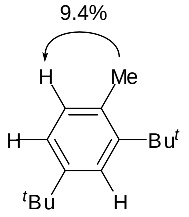

F

1,3-Phenyl-6-methylbenzene (7b): The spectroscopic data of **7b** were consistent with an authentic sample reported previously (Dauben, W. G.; Spitzer, W. A.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3674) ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 3H), 7.21-7.44 (m, 9H), 7.48-7.51 (m. 2H), 7.61 (d, 2H, J = 1.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 125.9, 127.0, 127.1, 127.2, 128.2, 128.7, 128.8, 129.3, 130.9, 134.6, 138.8, 141.0, 142.0, 142.4; IR (neat) 3060, 3025, 2958, 2921, 1600, 1479, 1441, 760, 698 cm^{-1}.

NMR experiment of the benzannulation from 2a and allyl tosylate. To a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (0.05 mmol), triphenylphosphine (0.1 mmol) and **2a** (0.2mmol) in $CDCl_3$ (3 mL) was added allyl tosylate (0.1 mmol) at room temperature. In the ^{1}H-NMR spectrum of the reaction mixture, **8** was observed with noncoordinating dibenzylideneacetone (dba). The alkyne **2a** coodinating to palladium and any palladacycle were not observed. Consecutively, the reaction mixture was heated at 80 °C after adding more **2a** (0.8 mmol). The reaction gave **3a** in 28% yield.

η^3-allyl(*p*-toluenesulfonato)(triphenylphosphine)palladium(II) (8).

Analytical pure **8** was synthesized by the reaction of η^3-allylchloro(triphenylphosphine)palladium with AgOTs. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.35 (m, 17H), 7.01 (d, 2H, J = 8.1 Hz), 5.74-5.66 (m, 1H), 5.40 (t, 1H, J = 7.0 Hz), 4.16 (dd, 1H, J = 14.1, 9.0), 3.07 (br, 1H), 2.74 (br, 1H), 2.30 (s, 3H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 140.6, 134.5 (d, $J = 13$ Hz), 132.0, 131.7, 131.4 (d, $J = 2$ Hz), 129.5 (d, $J = 10$ Hz), 129.1, 126.9, 118.9 (d, $J = 4$ Hz), 85.1 (d, $J = 27$ Hz), 55.0, 22.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.2; IR (KBr) ν 3042, 1434, 1191, 1129, 691; mp. 82 °C (decomp.)