Supporting Information – Part 1 of 3

A Highly Efficient Route to *o*-Allylbiaryls via Palladium-Catalyzed Three-Component Coupling of Benzynes, Allylic halides, and Aryl Organometallic reagents

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Experimental Section

General: All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. Acetonitrile was dried with CaH_2 and distilled prior to use. Benzyne precursors[1] **1a-d** were synthesized according to the literature procedures. $Pd(dba)_2$ [2] was prepared by reported procedure. Other reagents were commercially available and used as purchased.

General Procedure for the Synthesis of *o*-Allylbiaryls (4): A 25-mL round-bottom side-arm flask containing $Pd(dba)_2$ (0.0250 mmol), dppb (0.0250 mmol), CsF (2.00 mmol) and arylboronic acid(**3**) (0.50 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added benzyne precursor (**1**) (0.50 mmol), an allyl chloride (**2**) (0.60 mmol), and CH_3CN (3.0 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 8 h. At the end of the reaction, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel. The filtrate was concentrated and the residue was purified through a silica gel column using hexane as eluent to give pure **4**.

Compounds **4a-s**, were prepared by following this procedure. Spectral data of **4a-c**, **4e-h**, **4k-s** are listed below:

References:

1 (a)Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett*. **1983**, 1211. (b) Peña, D.;Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827.

2 Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

2-Allylbiphenyl (4a): colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37 (d, *J* = 15.0 Hz, 2H), 7.33-7.27 (m, 5H), 7.25-7.20 (m, 2H), 5.87-5.82 (m, 1H), 4.99 (dd, *J* = 9.6 Hz, *J* = 1.3 Hz, 1H), 4.90 (dd, *J* = 16.8, *J* = 1.4 Hz, 1H), 3.20 (d, *J* = 6.6 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 141.9, 141.6, 137.7, 137.2, 130.0, 129.7, 129.2, 128.0, 127.4, 126.8, 126.0, 115.7, 37.4; **HRMS** calcd for $C_{15}H_{14}$ 194.1096, found 194.1091. **Registry Numbe**r: [41658-35-9]

2-(2-Methylallyl)biphenyl (4b): colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.25 (m, 7H), 4.80 (d, *J* = 1.8 Hz, 1H), 4.51 (d, *J* = 1.3 Hz, 1H), 3.28 (s, 2H), 1.63 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 145.6, 142.3, 141.7, 136.8, 130.1, 130.0, 129.1, 128.7, 127.9, 126.8, 126.1, 112.1, 41.3, 22.6; **HRMS** calcd for $C_{16}H_{16}$ 208.1252, found 208.1252.

2-[(E)-2-Butenyl]-4,5-dimethylbiphenyl (4c): colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.42 (d, *J* = 12.0 Hz , 2H), 7.36 (m, 3H), 7.10 (s, 1H), 7.05 (s, 1H), 5.52-5.48 (m, 1H), 5.37-5.35 (m, 1H), 3.24 (d, *J* = 6.8, Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 1.65 (d, *J* = 8.8 Hz , 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 141.7, 139.3, 135.6, 135.4, 134.0, 131.3, 130.8, 130.6, 129.3, 127.9, 126.5, 125.8, 35.8, 19.4, 19.2, 17.9; **HRMS** calcd for $C_{18}H_{20}$ 236.1565, found 236.1563.

2-(2-Cyclohexenyl)biphenyl (4e): colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.37-7.30 (m, 5H), 7.26-7.21 (m, 2H), 5.87-5.83 (m, 1H), 5.65 (d, *J* = 10.2 Hz, 1H), 3.59-3.56 (m, 1H), 2.13-2.08 (m, 2H), 1.88 – 1.85 (m, 1H), 1.75-1.70 (m, 1H), 1.54-1.52 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.1, 141.8, 141.6, 131.0, 129.9, 129.3, 128.0, 127.9, 127.8, 127.7, 126.7, 125.6, 37.8, 32.3, 24.8, 21.6; **HRMS** calcd for $C_{18}H_{18}$ 234.1409, found 234.1418.

4'-Fluoro-4,5-dimethyl-2-[(E)-3-phenyl-2-propenyl]biphenyl (4f): colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.29-7.27 (m, 6H), 7.11-7.06 (m, 4H), 7.03 (s, 1H), 6.23 (s, 2H), 3.42 (d, *J* = 4.5 Hz, 2H), 2.30 (s, 3H), 2.28 (s, 3H),; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.7, 138.6, 137.6, 136.0, 134.6, 134.4, 131.4, 131.1, 130.9, 130.8, 129.7, 128.4, 126.9, 126.0, 114.9, 114.7, 36.2, 19.3, 19.2; **HRMS** calcd for $C_{23}H_{21}F$ 316.1627, found 316.1633.

2-Allyl-4,5-dimethylbiphenyl (4g): colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 15 Hz, 2H), 7.35 - 7.33 (m, 3H), 7.09 (s, 1H), 7.06 (s, 1H), 5.93-5.88 (m, 1H), 5.01 (dd, *J* = 10.0, *J* = 1.8 Hz, 1H), 4.95 (dd, *J* = 17.4, *J* = 1.8 Hz, 1H), 3.31 (d, *J* = 6.6 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.9, 139.7, 138.4, 136.0, 134.7, 134.5, 131.6, 131.2, 129.6, 128.2, 126.9, 115.7, 37.3, 19.7, 19.5; **HRMS** calcd for $C_{17}H_{18}$ 222.1409, found 222.1413.

5-Allyl-6-phenylindane (4h): colorless oil; **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.45-7.41 (m, 2H), 7.38-7.35 (m, 3H), 7.23 (s, 1H), 7.17 (s, 1H), 5.98-5.88 (m, 1H), 5.04 (dd, *J* = 8.4Hz, *J* = 1.2 Hz, 1H), 4.98 (dd, *J* = 15.2 Hz, *J* = 3.2 Hz, 1H), 3.36 (d, *J* = 6.8 Hz, 2H), 2.98 (q, *J* = 16.0 Hz, *J* = 7.6 Hz, 4H), 2.19-2.11 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.5, 142.2, 142.0, 139.9, 138.1, 135.0, 129.3, 127.9, 126.6, 125.9, 125.4, 115.3, 37.4, 32.6, 32.5, 25.5; **HRMS** calcd for $C_{18}H_{18}$ 234.1409, found 234.1407.

2-Allyl-3'-methoxybiphenyl (4k): colorless oil; **^{1}H NMR** (600MHz, $CDCl_3$): δ 7.34-7.31 (m, 3H), 7.28-7.27 (m, 2H), 6.93-6.89 (m, 3H), 5.95-5.90 (m, 1H), 5.04 (dd, *J* = 9.6 Hz, *J* = 1.2 Hz, 1H), 4.95 (dd, *J* = 16.8 Hz, *J* = 1.8 Hz, 1H), 3.84 (s, 3H), 3.37 (d, *J* = 9.0 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 159.2, 143.0, 141.8, 137.9, 137.1, 129.9, 129.7, 128.9, 127.5, 126.0, 121.7, 115.7, 114.8, 112.5, 55.2, 37.4; **HRMS** calcd for $C_{16}H_{16}O$ 224.1201, found 224.1207.

2-Allyl-4'-fluorobiphenyl (4l): cololess oil; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.27-7.21 (m, 6H), 7.12-7.07 (m, 2H), 5.93-5.87 (m, 1H), 5.03 (dd, *J* = 9.0 Hz, *J* = 1.5 Hz, 1H), 4.93 (dd, *J* = 15.0 Hz, *J* = 2.0 Hz, 1H), 3.30 (d, *J* = 6.5 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.0, 140.9, 137.6, 137.5, 137.4, 130.7, 130.1, 129.8, 127.6, 126.1, 115.8, 114.9, 37.4; **HRMS** calcd for $C_{15}H_{13}F$ 212.1001, found 212.0996.

2-Allyl-4'-bromobiphenyl (4m): colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 6.0 Hz, 2H), 7.34-7.28 (m, 3H), 7.22-7.20 (m, 3H), 5.91-5.87 (m, 1H), 5.04 (dd, *J* = 10.2, *J* = 3.0 Hz, 1H), 4.92 (dd, *J* = 19.2, *J* = 3.0 Hz, 1H), 3.30 (d, *J* = 5.4 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 140.6, 140.4, 137.5, 137.0, 131.1, 130.9, 129.9, 129.8, 127.7, 126.2, 121.1, 115.9, 37.3; **HRMS** calcd for $C_{15}H_{13}Br$ 272.0201, found 222.0198

2-Allyl-3'-nitrobiphenyl (4n): pale yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.71 (d, *J* = 6.0 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.42-7.35 (m, 4H), 7.29 (d, *J* = 1.2 Hz, 1H), 5.95-5.90 (m, 1H), 5.09 (dd, *J* = 10.2, *J* = 1.8 Hz, 1H), 4.93 (dd, *J* = 17.4, *J* = 1.8 Hz, 1H), 3.36 (d, *J* = 6.0 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 147.9, 143.1, 139.3, 137.0, 136.9, 135.2, 130.1, 129.8, 128.9, 128.4, 126.4, 124.0, 121.9, 116.2, 37.3; **HRMS** calcd for $C_{15}H_{13}NO_2$, 239.0946 found 239.0947.

2-Allyl-4'-formylbiphenyl (4o): colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.65 (s, 1H), 7.90 (d, *J* = 6.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.36-7.21 (m, 4H), 5.89-5.82 (m, 1H), 5.01 (dd, *J* = 10.0, *J* = 1.2 Hz, 1H), 4.87 (dd, *J* = 18.8, *J* = 1.8 Hz, 1H), 3.30 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.0, 148.0, 140.6, 137.3, 136.9, 135.0, 130.0, 129.9, 129.6, 129.5, 129.2, 128.2, 126.3, 116.0, 37.3; **HRMS** calcd for $C_{16}H_{14}O$ 222.1045, found 222.1043.

2-Allyl-4'-vinylbiphenyl (4p): colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.31-7.23 (m, 6H) 6.75 (dd, *J* = 16.4, *J* = 11.2 Hz, 1H), 5.92-5.81 (m, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.8 Hz, 1H), 5.02 (dd, *J* = 10.4, *J* = 1.2 Hz, 1H), 4.92 (dd, *J* = 16.8, *J* = 1.6 Hz, 1H), 3.34 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.0, 139.6, 136.2, 135.6, 135.0, 134.6, 128.4, 128.2, 127.8, 125.9, 124.5, 124.3, 114.7, 112.2, 35.9; **HRMS** calcd for $C_{17}H_{16}$, 220.1252 found 220.1251.

1-(2-Allyl-4,5-dimethylphenyl)naphthalene (4q): colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90-7.84 (m, 2H) 7.52–7.45 (m, 3H), 7.39-7.33 (m, 2H), 7.15 (s, 1H), 7.05 (s, 1H), 5.78-5.71 (m, 1H), 4.87 (dd, *J* = 10.8, *J* = 2.0 Hz, 1H), 4.80 (dd, *J* = 17.0, *J* = 1.6 Hz, 1H), 3.06-3.01 (m, 2H), 2.38 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.3, 137.7, 137.3, 136.0, 135.9, 134.0, 133.5, 132.5, 131.9, 130.4,

128.1, 127.9, 127.1, 126.3, 125.8, 125.6, 125.2, 115.2, 37.2, 19.5, 19.2; **HRM**S calcd for $C_{21}H_{20}$ 272.1565, found 272.1571.

2-(2-Allylphenyl)thiophene (4r): colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.35-7.28 (m, 4H), 7.10-7.07 (m, 2H), 6.01-5.96 (m, 1H), 5.09 (dd, *J* = 11.4, *J* = 1.2 Hz, 1H), 4.99 (dd, *J* = 16.8, *J* = 1.8 Hz, 1H), 3.52 (d, *J* = 6.0 Hz, 2H); **^{13}C NM**R (150 MHz, $CDCl_3$): δ 142.5, 138.1, 137.6, 134.1, 131.0, 130.0, 128.0, 126.9, 126.5, 126.1, 125.2, 115.9, 37.7; **HRMS** calcd for $C_{13}H_{12}S$, 200.0660 found 200.0662.

2-(2-Allylphenyl)benzo[*b*]furan (4s): colorless oil; **^{1}H NM**R (400 MHz, $CDCl_3$): δ 7.78 – 7.76 (m, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.36-7.24 (m, 5H), 6.88 (s, 1H), 6.09-6.02 (m, 1H), 5.09 (dd, *J* = 10.0, *J* = 1.6 Hz, 1H), 5.03 (dd, *J* = 16.8, *J* = 2.0 Hz, 1H), 3.68 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 155.5, 154.6, 137.8, 136.9, 130.5, 129.0, 128.8, 126.5, 124.2, 123.3, 122.8, 121.4, 120.9, 116.2, 111.1, 104.9, 38.3; **HRMS** calcd for $C_{17}H_{14}O$ 234.1045, found 234.1051.