**The First General Palladium Catalyst for the Suzuki-Miyaura and Carbonyl
Enolate Coupling of Aryl Arenesulfonates**

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Supporting Information

A. General Considerations

Reagents. Phosphine ligands were commercially available from Strem Chemical Co. or prepared as previously described.¹ Pd(OAc)₂ was purchased from Strem Chemical Co. and used without further purification. K₃PO₄·H₂O was purchased from Alfa Aesar and ground to a fine powder in the ambient atmosphere prior to use. THF was purchased from J. T. Baker in CYCLE-TAINERTM solvent delivery kegs,² which were purged with argon for 2 h and was purified by passing the THF through two packed columns of neutral alumina and copper (II) oxide under argon pressure. *tert*-Butanol was purchased from Aldrich in a Sure/SealTM bottle and used without further purification. Arylboronic acids were purchased from Aldrich, Alfa Aesar or Frontier Scientific and were used without further purification. Aryl tosylates were prepared from the corresponding phenols according to literature procedures.^{3,4} Flash column chromatography was performed with silica gel 60 (0.040-0.063 mm, 230-400 mesh) purchased from EM Science.

Analytical methods. IR spectra were recorded as a neat oil between either sodium chloride or potassium bromide salt plates on a Perkin-Elmer FT-IR 2000 instrument, and were reported in wavenumbers (cm⁻¹). Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. ¹H NMR, ¹³C NMR, ³¹P NMR and ¹⁹F NMR spectra were recorded on a Varian 300 MHz or 500 MHz instrument. For ¹H NMR and ¹³C NMR spectra, chemical shifts were reported relative to residual deuterated solvent peaks or tetramethylsilane internal standard. CF₃COOH was used as external standard for ¹⁹F

NMR analysis. Gas chromatographic analysis was performed on an Agilent 6890 instrument with an FID detector and an Agilent 10 m x 0.10 mm i.d. HP-1 capillary column. Mass spectra (GC/MS) were recorded on a Hewlett Packard model GCD. High-resolution mass spectra (HRMS) were determined on a Bruker Daltonics APEXII 3 Tesla Fourier Transform Mass Spectrometer equipped with a Gilson 215 liquid handler by the Massachusetts Institute of Technology, Department of Chemistry Instrumentation Facility (DCIF). Ionization sources were either electrospray (ESI) or electron impact (EI). Masses were reported in units of mass over charge (m/z) to four decimal places. All yields reported refer to isolated yields (average of two runs) of compounds estimated to be greater than 95% purity as determined by capillary gas chromatography (GC) and ^1H NMR. Compounds described in the literature were characterized by comparison of their melting points, ^1H , and/or ^{13}C NMR spectra to the previously reported data. The procedures in this section are representative, and thus the yields may differ from those reported in tables. All new compounds were further characterized by elemental analysis except for 5-(tosyloxy)-1-tetralone, 3-cyclohex-1-enyl-*N,N*-dimethylbenzamide, 5-(3-pyridyl)-1-tetralone and 3-acetamido-2',6'-dimethylbiphenyl; copies of their ^1H NMR spectra are provided.

B. Experimental Section

1. Preparation of aryl tosylates.

4-*tert*-Butylphenyl tosylate,³ 2-naphthyl tosylate³ and 3,4-methylenedioxyphenyl tosylate⁵ were prepared according to literature procedures.³ Other aryl tosylates such as 2-formylphenyl tosylate,⁶ 4-formyl-2-methoxyphenyl tosylate,⁷ 3-(tosyloxy)pyridine,⁸ 4-chlorophenyl tosylate,⁹ 3-acetamidophenyl tosylate,¹⁰ 6-(tosyloxy)quinoline¹¹ and 2,4-dimethylphenyl tosylate¹² were prepared from their corresponding phenols and TsCl in the presence of triethylamine in CH_2Cl_2 .⁴ Physical characterizations of unknown aryl tosylates which were prepared according to literature procedure are shown below.⁴

2-Methyl-5-(tosyloxy)benzothiazole. Obtained in 98% yield as white crystals: mp 139-140 °C. ^1H NMR (300 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.71-7.66 (m, 3H), 7.40 (d, J

= 2.2 Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.07 (dd, $J = 8.5, 2.2$ Hz, 1H), 2.79 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 and 0.05% v/v TMS) δ 169.6, 153.8, 148.2, 145.7, 134.5, 132.3, 130.0, 128.7, 122.1, 119.9, 116.1, 22.2, 20.7. IR (neat, cm^{-1}): 1597, 1452, 1373, 1193, 1177. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}_2$: C, 56.41; H, 4.10. Found: C, 56.16; H, 4.23.

5-(Tosyloxy)-1-tetralone. Obtained in 92% yield as white crystals: mp 125-126 °C. ^1H NMR (500 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.94 (d, $J = 7.8$ Hz, 1H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 7.24 (t, $J = 7.9$ Hz, 1H), 7.15 (dd, $J = 8.1, 1.2$ Hz, 1H), 2.76 (t, $J = 6.1$ Hz, 2H), 2.58 (t, $J = 6.4$ Hz, 2H), 2.47 (s, 3H), 1.97 (quint, $J = 6.1$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3 and 0.05% v/v TMS) δ 197.8, 147.9, 146.5, 138.9, 135.1, 133.3, 130.7, 129.1, 127.9, 127.7, 126.7, 39.3, 24.3, 23.0, 22.5. IR (neat, cm^{-1}): 2954, 1689, 1600, 1459, 1374, 1278, 1190, 1176, 1090, 933, 815, 754.

3-Methyl-4-(tosyloxy)acetophenone. Obtained in 95% yield as white crystals: mp 84-85 °C. ^1H NMR (500 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.76-7.70 (m, 4H), 7.34 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 8.2 Hz, 1H), 2.56 (s, 3H), 2.45 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3 and 0.05% v/v TMS) δ 197.8, 152.4, 146.5, 136.2, 133.5, 132.8, 132.4, 130.7, 129.0, 128.1, 123.1, 27.4, 22.5, 17.1. IR (neat, cm^{-1}): 1687, 1598, 1493, 1374, 1255, 1192, 1179, 1117, 1091, 838. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{S}$: C, 63.14; H, 5.30. Found: C, 62.95; H, 5.29.

3-Methoxy-4-(tosyloxy)acetophenone. Obtained in 95% yield as white crystals: mp 86-87 °C. ^1H NMR (500 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.72 (d, J = 8.4 Hz, 2H), 7.47 (dd, J = 8.2, 1.8 Hz, 1H), 7.43 (d, J = 1.8 Hz, 1H), 7.29 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 8.2 Hz, 1H), 3.59 (s, 3H), 2.57 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3 and 0.05% v/v TMS) δ 197.5, 152.7, 146.1, 142.7, 137.3, 133.6, 130.2, 129.3, 124.7, 122.4, 112.3, 56.4, 27.3, 22.4. IR (neat, cm^{-1}): 1685, 1598, 1500, 1412, 1374, 1286, 1179, 1165, 1091, 836. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_5\text{S}$: C, 59.99; H, 5.03. Found: C, 59.91; H, 5.06.

2. Procedure for the preparation of vinyl tosylates. Vinyl tosylates such as 1-cyclohexenyl tosylate¹³ and 4-*tert*-butylcyclohex-1-enyl tosylate were prepared using a protocol developed for the synthesis of vinyl nanoflates.¹⁴ TsF was used in place of NsF.

4-*tert*-Butylcyclohex-1-enyl tosylate. Obtained in 43% yield as a colorless oil. ^1H NMR (500 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.81 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.31 (distorted d, J = 5.5 Hz, 1H), 2.46 (s, 3H), 2.13-2.04 (m, 3H), 2.02-1.81 (m, 2H), 1.23-1.19 (m, 2H), 0.84 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3 and 0.05% v/v TMS) δ 148.4, 145.0, 133.9, 129.8, 128.4, 117.3, 43.3, 32.3, 28.9, 27.4, 25.5, 24.3, 21.9. IR (neat, cm^{-1}): 2961, 2868, 1687, 1599, 1369, 1191, 1179, 1081. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{S}$: C, 66.20; H, 7.84. Found: C, 66.42; H, 7.95.

3. General procedure for the Suzuki-Miyaura cross-coupling reaction.

Procedure A: Pd(OAc)₂ (2.3 mg, 0.010 mmol), **1** (11.9 mg, 0.0250 mmol), aryl or vinyl tosylate (0.500 mmol), arylboronic acid (1.00 mmol) and finely ground K₃PO₄•H₂O (345 mg, 1.50 mmol) were added to a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tube was then capped with a rubber septum, evacuated and backfilled with nitrogen and this cycle was repeated two additional times. Under an inert atmosphere, THF (1 mL) was added via syringe. Under a positive pressure of nitrogen, the rubber septum was replaced with a Teflon screw cap and this was sealed. The Schlenk tube was submerged in an oil bath at room temperature and heated to 80 °C for the time indicated. The oil bath reached 80 °C in 12-14 min. When the reaction was completed according to GC, TLC and/or crude ¹H NMR, the reaction tube was allowed to cool to room temperature. Then, the reaction mixture was quenched with water (1 mL) and diluted with EtOAc (5 mL). The organic layer was separated and the aqueous layer was washed with EtOAc (3x5 mL). The combined organic layers were washed with brine and dried over MgSO₄. After filtering off the MgSO₄, the filtrate was concentrated under reduced pressure. Column chromatography on silica gel afforded the product.

Procedure B: Similar as procedure A except that the reaction was performed using a catalyst loading of Pd(OAc)₂ (3.4 mg, 0.015 mmol), **1** (16.7 mg, 0.0350 mmol) and *t*-BuOH (1 mL) as solvent.

2-Methoxy-4'-tert-butylbiphenyl (Table 2, entry 1).¹⁵ Following general procedure A with a reaction time of 3 h, 4-*tert*-butylphenyl tosylate (152 mg, 0.500 mmol) was coupled with 2-methoxyphenylboronic acid (152 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 98:2 hexanes:EtOAc as eluent provided a colorless oil (110 mg, 92% yield). ¹H NMR (300 MHz, CDCl₃ and 0.05% v/v TMS) δ 7.50-7.42 (m, 4H), 7.35-7.28 (m, 2H), 7.05-6.97 (m, 2H), 3.83 (s, 3H), 1.38 (s, 9H).¹⁵

2-Methoxy-4-formylbiphenyl (Table 2, entry 2).¹⁶ Following general procedure A with a reaction time of 3 h, 4-formyl-2-methoxyphenyl tosylate (153 mg, 0.500 mmol) was coupled with phenylboronic acid (122 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 95:5 hexanes:EtOAc as eluent provided a colorless oil (98 mg, 92% yield). ¹H NMR (500 MHz, CDCl₃ and 0.05% v/v TMS) δ 10.03 (s, 1H), 7.57-7.36 (m, 8H), 3.91 (s, 3H).

(2-Methoxy-biphenyl-4-yl)-phenyl-methanol (Table 2) . A byproduct obtained in 3% yield in the cross-coupling reaction of 4-formyl-2-methoxyphenyl tosylate and phenylboronic acid. ¹H NMR (300 MHz, CDCl₃ and 0.05% v/v TMS) δ 7.51-7.24 (m, 11H), 7.05 (distorted d, *J* = 1.4 Hz, 1H), 6.99 (distorted dd, *J* = 7.7, 1.4 Hz, 1H), 5.87 (s, 1H), 3.79 (s, 3H), 2.29 (br s, 1H). ¹³C NMR (75 MHz, CDCl₃ and 0.05% v/v TMS) δ 156.7, 144.6, 143.8, 138.4, 131.0, 130.1, 129.7, 128.8, 128.2, 127.9, 127.1, 126.7, 119.1, 109.5, 76.5, 55.9. IR (neat, cm⁻¹): 3375 (br), 3027, 2935, 1611, 1581, 1485, 1410, 1268, 1041.

2-(3-Nitrophenyl)naphthalene (Table 2, entry 3).¹⁷ Following general procedure A with a reaction time of 3 h, 2-naphthyl tosylate (149 mg, 0.500 mmol) was coupled with 3-nitrophenylboronic acid (167 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 90:10 hexanes:EtOAc provided a white solid (115 mg, 92% yield): mp 126-127 °C (lit.^{17b} mp 130 °C). ¹H NMR (300 MHz, CDCl₃ and 0.05% v/v TMS) δ 8.58 (s, 1H), 8.24 (distorted d, *J* = 8.0 Hz, 1H), 8.09-7.87 (m, 5H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.55-7.53 (m, 2H).

3,4-Methylenedioxy-3'-nitrophenyl (Table 2, entry 4). Following general procedure A with a reaction time of 5 h, 3,4-methylenedioxyphenyl tosylate (146 mg, 0.500 mmol) was coupled with 3-nitrophenylboronic acid (167 mg, 1.00 mmol). Purification of the

crude product by column chromatography on silica gel using 98:2 then 95:5 hexanes:EtOAc as eluent provided a light yellow solid (106 mg, 87% yield): mp = 116-117 °C. ¹H NMR (300 MHz, CDCl₃ and 0.05% v/v TMS) δ 8.37 (t, *J* = 1.9 Hz, 1H), 8.15 (ddd, *J* = 8.1, 2.4, 1.0 Hz, 1H), 7.82 (ddd, *J* = 7.8, 1.8, 1.1 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.12-7.09 (m, 2H), 6.94-6.91 (m, 1H), 6.04 (s, 2H). ¹³C NMR (125 MHz, CDCl₃ and 0.05% v/v TMS) δ 148.9, 148.7, 148.3, 142.8, 133.1, 132.9, 129.9, 121.9, 121.8, 121.2, 109.1, 107.7, 101.7. IR (neat, cm⁻¹): 1607, 1528, 1506, 1473, 1348, 1230, 1038. Anal. Calcd for C₁₃H₉NO₄: C, 64.20; H, 3.73. Found: C, 64.25; H, 3.81.

3-(3-Trifluoromethylphenyl)pyridine (Table 2, entry 5).¹⁸ Following general procedure A with a reaction time of 3 h, 3-(tosyloxy)pyridine (125 mg, 0.500 mmol) was coupled with 3-($\square,\square,\square$ -trifluoromethyl)phenylboronic acid (190 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel 80:20 hexanes:EtOAc as eluent provided a colorless oil (104 mg, 94% yield). ¹H NMR (300 MHz, CDCl₃ and 0.05% v/v TMS) δ 8.84 (d, *J* = 2.5 Hz, 1H), 8.64 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.91-7.75 (m, 3H), 7.68-7.58 (m, 2H), 7.43-7.38 (m, 1H).

6-(3-Trifluoromethylphenyl)quinoline (Table 2, entry 6). Following general procedure A with a reaction time of 3 h, 6-(tosyloxy)quinoline (150 mg, 0.500 mmol) was coupled with 3-($\square,\square,\square$ -trifluoromethyl)phenylboronic acid (190 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 80:20 hexanes:EtOAc as eluent provided a white solid (124 mg, 91% yield): mp 71-72 °C. ¹H NMR (300 MHz, CDCl₃ and 0.05% v/v TMS) δ 8.96 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.26-8.21 (m, 2H), 8.04-7.89 (m, 4H), 7.69-7.60 (m, 2H), 7.45 (dd, *J* = 8.3, 4.1 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃ and 0.05% v/v TMS) δ 151.1, 148.1, 141.3, 138.0, 136.5, 136.6 (q, *J*_{CF} = 32 Hz, chemical shifts for four peaks 131.95, 131.70, 141.44, 131.18), 130.9, 130.5, 129.7, 129.0, 128.6, 126.1, 125.5 (q, *J*_{CF} = 3.5 Hz, chemical shifts for four peaks 124.6, 124.6, 124.5, 124.5), 124.4 (q, *J*_{CF} = 3.5 Hz, chemical shifts for four peaks 124.4, 124.4, 124.3, 124.3), 124.3 (q, *J*_{CF} = 273 Hz, chemical shifts for four peaks 127.6, 125.4, 123.2, 121.0),

121.9. ^{19}F NMR (300 MHz, CDCl_3 and 0.05% v/v TMS; external standard CF_3COOH) $\square$ 15.1. IR (neat, cm^{-1}): 3041, 1595, 1484, 1338, 1318, 1166, 1126. Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}$: C, 70.33; H, 3.69. Found: C, 70.11; H, 3.56.

6-(4-Acetylphenyl)quinoline (Table 2, entry 6). Following general procedure A with a reaction time of 3 h, 6-(tosyloxy)quinoline (150 mg, 0.500 mmol) was coupled with 4-acetylphenylboronic acid (164 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 70:30 hexanes:EtOAc as eluent provided an off-white solid (112 mg, 91% yield): mp 149-150 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3 and 0.05% v/v TMS) $\square$ 8.96 (distorted d, $J = 4.1$ Hz, 1H), 8.25 (d, $J = 8.2$ Hz, 1H), 8.21 (d, $J = 8.7$ Hz, 1H), 8.09 (d, $J = 8.2$ Hz, 2H), 8.07 (s, 1H), 8.02-8.00 (m, 1H), 7.82 (d, $J = 8.2$ Hz, 2H), 7.46 (dd, $J = 8.2, 4.1$ Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3 and 0.05% v/v TMS) $\square$ 197.9, 151.1, 148.2, 145.0, 138.2, 136.6, 136.4, 130.5, 129.3, 129.1, 128.6, 127.8, 126.3, 122.0, 27.0. IR (neat, cm^{-1}): 3038, 1672, 1356, 826. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{NO}$: C, 82.57; H, 5.30. Found: C, 82.30; H, 5.28.

3-Cyclohex-1-enyl-N,N-dimethylbenzamide (Table 2, entry 7). Following general procedure A with a reaction time of 1 h, 1-cyclohexenyl tosylate (141 mg, 0.560 mmol) was coupled with N,N-dimethylbenzamide-3-boronic acid (193 mg, 1.12 mmol). Purification of the crude product by column chromatography on silica gel using 70:30 hexanes:EtOAc as eluent provided a colorless oil (118 mg, 92% yield). ^1H NMR (300 MHz, CDCl_3 and 0.05% v/v TMS) $\square$ 7.42-7.38 (m, 2H), 7.33-7.26 (m, 1H), 7.24-7.21 (m, 1H), 6.16-6.12 (m, 1H), 3.10 (s, 3H), 2.97 (s, 3H), 2.41-2.36 (m, 2H), 2.23-2.16 (m, 2H), 1.81-1.61 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3 and 0.05% v/v TMS) $\square$ 172.6, 143.5, 136.9, 136.7, 128.8, 126.7, 126.3, 125.7, 124.3, 40.3, 36.0, 28.0, 26.6, 23.7, 22.7. IR (neat, cm^{-1}): 2928, 1637, 1502, 1390. HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{20}\text{NO}$ $[\text{M} + \text{H}]^+$: 230.1539; Found: 230.1544.

4-(4-*tert*-Butyl-cyclohex-1-enyl)benzonitrile (Table 2, entry 8). Following general procedure A with a reaction time of 1 h, 4-*tert*-butylcyclohex-1-enyl tosylate (185 mg, 0.600 mmol) was coupled with 4-cyanophenylboronic acid (177 mg, 1.20 mmol). Purification of the crude product by column chromatography on silica gel using hexanes as eluent provided a white solid (133 mg, 93% yield): mp 99-100 °C. ^1H NMR (300 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.56 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 6.26-6.24 (m, 1H), 2.49-2.25 (m, 3H), 2.02-1.93 (m, 2H), 1.40-1.22 (m, 2H), 0.91 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3 and 0.05% v/v TMS) δ 146.6, 135.1, 132.1, 128.7, 125.4, 119.3, 109.8, 43.8, 32.5, 28.7, 27.9, 27.5, 24.4. IR (neat, cm^{-1}): 2943, 2867, 2221, 1642, 1601, 1503, 1364. Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{N}$: C, 85.30; H, 8.84. Found: C, 85.30; H, 8.86.

4-Biphenyl tosylate (Table 2, entry 9).¹⁹ Following general procedure A with a reaction time of 2 h at room temperature, 4-chlorophenyl tosylate (160 mg, 0.500 mmol) was coupled with phenylboronic acid (82 mg, 0.67 mmol). Purification of the crude product

by column chromatography on silica gel using 95:5 then 80:20 hexanes:EtOAc as eluent provided a white solid (144 mg, 89% yield): mp 177-178 °C (lit.¹⁹ mp 178-179 °C). ¹H NMR (500 MHz, CDCl₃ and 0.05% v/v TMS) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.54-7.31 (m, 9H), 7.04 (d, *J* = 8.8 Hz, 2H), 2.47 (s, 3H).

5-(2,6-Dimethoxyphenyl)-2-methylbenzothiazole (Table 3, entry 1). Following the general procedure B with a reaction time of 6 h, 2-methyl-5-(tosyloxy)benzothiazole (160 mg, 0.500 mmol) was coupled with 2,6-dimethoxyphenylboronic acid (182 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 80:20 hexanes:EtOAc as eluent provided a light yellow solid (134 mg, 94%): mp 119-121 °C. ¹H NMR (500 MHz, CDCl₃ and 0.05% v/v TMS) δ 7.99 (d, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.38 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.33 (t, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 2H), 3.76 (s, 6H), 2.86 (s, 3H). ¹³C NMR (125 MHz, CDCl₃ and 0.05% v/v TMS) δ 166.8, 157.8, 153.5, 134.3, 132.1, 129.1, 128.1, 125.0, 125.6, 118.9, 104.3, 56.0, 20.3. IR (neat, cm⁻¹): 3000, 2938, 2835, 1589, 1472, 1246, 1110. Anal. Calcd for C₁₆H₁₅NO₂S: C, 67.34; H, 5.30. Found: C, 67.34; H, 5.30.

4-Formyl-2,2'-dimethoxybiphenyl (Table 3, entry 2). Following general procedure B with a reaction time of 6 h, 4-formyl-2-methoxyphenyl tosylate (153 mg, 0.500 mmol) was coupled with 2-methoxyphenylboronic acid (152 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 90:10 hexanes:EtOAc as eluent provided a colorless oil (103 mg, 85% yield). ¹H NMR (500 MHz, CDCl₃ and 0.05% v/v TMS) δ 10.00 (s, 1H), 7.53-7.41 (m, 2H), 7.39-7.35 (m, 2H), 7.27-7.24 (m, 1H), 7.07-6.99 (m, 2H), 3.86 (s, 3H), 2.80 (s, 3H). ¹³C NMR (125 MHz, CDCl₃ and 0.05% v/v TMS) δ 192.1, 157.8, 156.9, 137.0, 134.9, 132.2, 131.2, 129.6, 126.7, 124.2, 120.6, 111.3, 109.5, 56.2, 56.0. IR (neat, cm⁻¹): 2938, 2835, 2731, 1693, 1264, 1244. Anal. Calcd for C₁₅H₁₄O₃: C, 74.36; H, 5.82. Found: C, 74.21; H, 5.78.

4-Acetyl-2-methoxy-2'-methylbiphenyl (Table 3, entry 3). Following general procedure B with a reaction time of 6 h, 3-methoxy-4-(tosyloxy)acetophenone (160 mg, 0.500 mmol) was coupled with 2-methylphenylboronic acid (136 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 95:5 hexanes:EtOAc as eluent provided a colorless oil (114 mg, 95% yield). ^1H NMR (500 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.62 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.60 (d, $J = 1.5$ Hz, 1H), 7.33-7.26 (m, 4H), 7.18 (d, $J = 6.7$ Hz, 1H), 3.85 (s, 3H), 2.67 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3 and 0.05% v/v TMS) δ 198.1, 157.2, 137.9, 137.8, 136.8, 136.5, 131.3, 130.0, 129.8, 128.1, 125.8, 121.7, 109.6, 55.9, 27.0, 20.1. IR (neat, cm^{-1}): 2937, 1684, 1405, 1276, 1223. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$: C, 79.97; H, 6.71. Found: C, 79.61; H, 6.83.

2-Formyl-2'-methylbiphenyl (Table 3, entry 4).²⁰ Following general procedure B with a reaction time of 6 h, 2-formylphenyl tosylate (138 mg, 0.500 mmol) was coupled with 2-methylphenylboronic acid (136 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using hexanes then 98:2 hexanes:EtOAc as eluent provided a yellow oil (85 mg, 87% yield). ^1H NMR (300 MHz, CDCl_3 and 0.05% v/v TMS) δ 9.74 (s, 1H), 8.01 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.63 (td, $J = 7.4, 1.4$ Hz, 1H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.36-7.24 (m, 4H), 7.18 (d, $J = 6.6$ Hz, 1H), 2.11 (s, 3H).

5-(3-Pyridyl)-1-tetralone (Table 3, entry 5). Following general procedure B with a reaction time of 6 h, 5-(tosyloxy)-1-tetralone (157 mg, 0.500 mmol) was coupled with pyridine-3-boronic acid (123 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 40:60 hexanes:EtOAc as eluent provided a white solid (102 mg, 91% yield): mp 98-99 °C. ^1H NMR (500 MHz, CDCl_3 and 0.05% v/v TMS) δ 8.63 (dd, $J = 4.8, 2.7$ Hz, 1H), 8.60 (dd, $J = 2.3, 1.9$ Hz, 1H), 8.14 (dd, $J =$

6.8, 2.7 Hz, 1H), 7.66 (ddd, $J = 7.8, 2.2, 2.3$ Hz, 1H), 7.45-7.36 (m, 3H), 2.83 (distorted t, $J = 6.0$ Hz, 2H), 2.68 (distorted t, $J = 6.1$ Hz, 2H), 2.10-2.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 and 0.05% v/v TMS) δ 198.4, 150.1, 149.0, 142.2, 138.3, 136.8, 136.4, 135.0, 133.5, 127.7, 126.9, 123.4, 39.1, 28.4, 23.4. IR (neat, cm^{-1}): 2947, 1683. HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}$ $[\text{M} + \text{H}]^+$: 224.1074; Found: 224.1070.

3-Acetamido-2',6'-dimethylbiphenyl (Table 3, entry 6). Following general procedure B with a reaction time of 6 h, 3-acetamidophenyl tosylate (153 mg, 0.500 mmol) was coupled with 2,6-dimethylphenylboronic acid (150 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 70:30 hexanes:EtOAc as eluent provided a white solid (106 mg, 89% yield): mp 195-197 °C. ^1H NMR (300 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.58 (d, $J = 7.7$ Hz, 1H), 7.38-7.07 (m, 6H), 6.87 (d, $J = 7.7$ Hz, 1H), 2.19 (s, 3H), 2.04 (s, 6H). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.97 (s, 1H), 7.52 (d, $J = 7.9$ Hz, 1H), 7.38 (overlapped s, 1H), 7.35 (overlapped t, $J = 7.6$ Hz, 1H),

7.15-7.08 (m, 3H), 6.77 (d, $J = 7.3$ Hz, 1H), 2.03 (s, 3H), 1.96 (s, 6H). ^{13}C NMR (125 MHz, DMSO- d_6) δ 169.1, 142.0, 141.5, 140.3, 135.8, 129.6, 128.0, 127.7, 124.0, 119.8, 118.0, 24.8, 21.1. IR (neat, cm^{-1}): 3302 (br), 2925, 1667, 1610, 1587, 1556. HRMS (ESI): Calcd for $\text{C}_{16}\text{H}_{18}\text{NO}$ $[\text{M} + \text{H}]^+$: 240.1383; Found: 240.1378.

5-(2,6-Dimethylphenyl)-2-methylbenzothiazole (Table 3, entry 7). Following general procedure B with a reaction time of 6 h, 2-methyl-5-(tosyloxy)benzothiazole (160 mg, 0.500 mmol) was coupled with 2,6-dimethylphenylboronic acid (150 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 95:5 hexanes:EtOAc as eluent provided a white solid (120 mg, 95% yield): mp 84-85 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.68 (dd, $J = 8.0, 0.6$ Hz, 1H), 7.65 (distorted t, $J = 0.6$ Hz, 1H), 7.07-7.02 (m, 4H), 2.77 (s, 3H), 1.96 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3 and 0.05% v/v TMS) δ 167.4, 153.8, 141.2, 139.1, 136.3, 134.1, 127.5, 127.3, 126.1, 122.8, 121.5, 21.2, 20.5. IR (neat, cm^{-1}): 2921, 1581, 1526, 1454, 1171, 771. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NS}$: C, 75.85; H, 5.97. Found: C, 75.67; H, 5.91.

2-Methyl-5-(2',4',6'-triisopropylphenyl)benzothiazole (Table 3, entry 8). Following the general procedure B with a reaction time of 6 h, 2-methyl-5-(tosyloxy)benzothiazole (160 mg, 0.500 mmol) was coupled with 2,4,6-triisopropylphenylboronic acid (248 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 98:2 hexanes:EtOAc as eluent provided a white solid (157 mg, 89% yield): mp 166-168 °C. ^1H NMR (300 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.81 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 1.4 Hz, 1H), 7.18 (dd, J = 8.0, 1.4 Hz, 1H), 7.07 (s, 2H), 2.97 (sept, J = 7.0 Hz, 1H), 2.88 (s, 3H), 2.61 (sept, J = 7.0 Hz, 2H), 1.34 (d, J = 6.9 Hz, 6H), 1.10 (overlapped d, J = 6.9 Hz, 6H), 1.08 (overlapped d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3 and 0.05% v/v TMS) δ 167.6, 153.5, 148.2, 146.8, 139.1, 136.5, 134.0, 127.1, 123.5, 120.9, 120.8, 34.7, 30.7, 24.7, 24.5, 24.5, 20.7. IR (neat, cm^{-1}): 2960, 2867, 1608, 1527, 1461, 1170. Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{NS}$: C, 78.58; H, 8.31. Found: C, 78.48; H, 8.36.

5-(4-Acetyl-2-methylphenyl)-N-methylindole (Table 3, entry 9). Following the general procedure B with a reaction time of 9 h, 3-methyl-4-(tosyloxy)acetophenone (152 mg, 0.500 mmol) was coupled with N-methylindole-5-boronic acid (175 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 90:10 hexanes:EtOAc as eluent provided a white solid (109 mg, 92% conversion, 83% yield): mp 113-114 °C. ^1H NMR (300 MHz, CDCl_3 and 0.05% v/v TMS) δ 7.89 (distorted d, J = 1.4 Hz, 1H), 7.82 (dd, J = 8.0, 1.9 Hz, 1H), 7.57 (d, J = 1.7 Hz, 1H), 7.40 (overlapped d, J = 8.0 Hz, 1H), 7.27 (overlapped d, J = 8.3 Hz, 1H), 7.18 (dd, J = 8.3, 1.7 Hz, 1H), 7.12 (d, J = 3.0 Hz, 1H), 6.53 (d, J = 3.0 Hz, 1H), 3.85 (s, 3H), 2.66 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 and 0.05% v/v TMS) δ 198.3, 148.4, 136.3, 136.1, 135.6, 132.2, 130.8, 130.4, 129.8, 128.5, 126.0, 123.0, 121.3, 109.1, 101.4, 33.4, 27.1, 21.3. IR (neat, cm^{-1}): 2919, 1679, 1601. Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}$: C, 82.10; H, 6.51. Found: C, 81.99; H, 6.60.

4-Ethoxy-2',4'-dimethylbiphenyl (Table 3, entry 10). Following the general procedure B at 110 °C with a reaction time of 17 h, 2,4-dimethylphenyl tosylate (138 mg, 0.500 mmol) was coupled with 4-ethoxyphenylboronic acid (166 mg, 1.00 mmol). Purification of the crude product by column chromatography on silica gel using 98:2 hexanes:EtOAc as eluent provided a colorless oil (98 mg, 87% yield). ¹H NMR (300 MHz, CDCl₃ and 0.05% v/v TMS) δ 7.23 (d, *J* = 8.8 Hz, 2H), 7.15-7.04 (m, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.10 (q, *J* = 6.9 Hz, 2H), 2.38 (s, 3H), 2.28 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃ and 0.05% v/v TMS) δ 157.8, 138.8, 136.6, 135.3, 134.2, 131.1, 130.4, 129.9, 126.5, 114.1, 63.6, 21.4, 20.8, 15.3. IR (neat, cm⁻¹): 3033, 2979, 2922, 1609, 1491, 1477, 1244. Anal. Calcd for C₁₆H₁₈O: C, 84.91; H, 8.02. Found: C, 84.75; H, 8.11.

2,4-dimethylbiphenyl (Mentioned in the text).²¹ Following general procedure A at 50 °C with a reaction time of 1 h, 2,4-dimethylchlorobenzene (67 μ L, 0.500 mmol) was coupled with phenylboronic acid (122 mg, 1.00 mmol). GC analysis indicated the reaction proceeded quantitatively.

4. General procedure for the arylation of carbonyl enolates.

An oven-dried resealable Schlenk tube containing a Teflon-coated magnetic stir bar was charged with Pd(OAc)₂ (2.3 mg, 0.010 mmol), **1** (11.9 mg, 0.0250 mmol), the solid reactant(s) and base. The tube was capped with a rubber septum, evacuated and backfilled with argon. The liquid reactant(s) and solvent were added through the septum via syringe. The septum was replaced with a Teflon screw cap under a flow of argon. The Schlenk tube was sealed and put into a pre-heated oil bath at 110 °C. The reaction mixture was stirred for the time specified, then allowed to cool to room temperature, and filtered through Celite with the aid of ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified by chromatography on a silica gel column.

α -(4-*tert*-Butylphenyl)cycloheptanone (Table 4)²² Following the general procedure with a reaction time of 21 h, 4-*t*-butylphenyl benzenesulfonate (145 mg, 0.500 mmol) was coupled with cycloheptanone (90 μ L, 0.75 mmol) using Cs₂CO₃ (408 mg, 1.25

mmol) as the base and toluene / *t*-butanol (1.0 mL / 0.2 mL) as the solvent. Chromatography on silica gel column with 30:1 hexane : ethyl acetate gave 104 mg (85%) of the title compound as a white solid: mp 57-59 °C (lit.²² mp 57-59 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 3.69 (dd, *J* = 11.6, 4.2 Hz, 1H), 2.70 (dt, *J* = 12.1, 3.1 Hz, 1H), 2.6-2.4 (m, 1H), 2.2-1.9 (m, 5H), 1.7-1.4 (m, 3H), 1.30 (s, 9H).

[(2-Methoxyphenyl)pinacolone (Table 4)²³ Following the general procedure with a reaction time of 18 h, 2-methoxyphenyl benzenesulfonate (132 mg, 0.500 mmol) was coupled with pinacolone (95 μ L, 0.75 mmol) using Cs₂CO₃ (408 mg, 1.25 mmol) as the base and toluene / *t*-butanol (1.0 mL / 0.2 mL) as the solvent. Chromatography on silica gel column with 30:1 hexane : ethyl acetate gave 77 mg (75%) of the title compound as a white crystalline solid: mp 34-35 °C (lit.²³ 39.0-40.5 °C). ¹H NMR (300 MHz, CDCl₃) δ 7.20 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.89 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 2H), 3.75 (s, 3H), 1.23 (s, 9H).

***cis*-4-*t*-Butyl-2-(4-methoxyphenyl)-cyclohexanone (Table 4)²⁴** Following the general procedure with a reaction time of 15 h, 4-methoxyphenyl benzenesulfonate (132 mg, 0.500 mmol) was coupled with 4-*t*-butyl-cyclohexanone (116 mg, 0.750 mmol) using Cs₂CO₃ (408 mg, 1.25 mmol) as the base and toluene / *t*-butanol (1.0 mL / 0.2 mL) as the solvent. The ratio of *cis:trans* isomers in crude product according to ¹H NMR was ~5:1. Chromatography on silica gel column with 10 : 1 hexane : ethyl acetate gave 104.2 mg (80% yield) of the title compound as a white crystalline solid: mp 98-99 °C.^{24c} ¹H NMR (300 MHz, CDCl₃) δ 7.06 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.62-3.52 (m, 1H), 2.60-2.41 (m, 2H), 2.30-2.14 (m, 2H), 1.82-1.52 (m, 3H), 0.94 (s, 9H).

Ethyl 1-phenyl-4-(4-*tert*-butylphenyl)acetate (Table 4) Following the general procedure with a reaction time of 20 h, 4-*t*-butylphenyl benzenesulfonate (145 mg, 0.500 mmol) was coupled with ethyl 1-phenylacetate (120 μ L, 0.75 mmol) using Cs_2CO_3 (408 mg, 1.25 mmol) as the base and toluene / *t*-butanol (1.0 mL / 0.2 mL) as the solvent. Chromatography on silica gel column with 4:1 hexane : dichloromethane gave 130 mg (88%) of the title compound as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.20 (m, 9H), 4.96 (s, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 1.29 (s, 9H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.7, 150.0, 139.0, 135.8, 128.7, 128.6, 128.2, 127.2, 125.6, 61.4, 56.9, 34.7, 31.6, 14.5. IR (neat, cm^{-1}) 2962, 1735, 1191, 1148, 1027, 699. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2$: C, 81.04; H, 8.16. Found: C, 80.65; H, 8.20.

Diethyl 4-(4-*t*-butylphenyl)malonate (Table 4)²² Following the general procedure with a reaction time of 18 h, 4-*t*-butylphenyl benzenesulfonate (145 mg, 0.500 mmol) was coupled with diethyl malonate (115 μ L, 0.750 mmol) using Cs_2CO_3 (408 mg, 1.25 mmol) as the base and toluene (1.0 mL) as the solvent. Chromatography on silica gel column with 10:1 hexane : ethyl acetate gave 131 mg (90%) of the title compound as a colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 7.37 (d, $J = 8.7$ Hz, 2H), 7.32 (d, $J = 8.7$ Hz, 2H), 4.59 (s, 1H), 4.21 (m, 4H), 1.31 (s, 9H), 1.27 (t, $J = 7.2$ Hz, 6H).

2-(3-Carboxyphenyl)-1,3-cyclopentanedione methyl ester (Table 4)²² Following the general procedure with a reaction time of 18 h, 3-methoxycarbonylphenyl tosylate (153 mg, 0.500 mmol) was coupled with 1,3-cyclopentanedione (74 mg, 0.75 mmol) using K_2CO_3 (173 mg, 1.25 mmol) as the base and *t*-butanol (2.0 mL) as the solvent. The

reaction mixture was quenched with water and neutralized with 1 M HCl aqueous solution. The mixture was extracted with dichloromethane three times. The organics were combined, dried over Na₂SO₄ and concentrated *in vacuo*. Chromatography on silica gel column with 6:1 dichloromethane : methanol gave 110 mg (95%) of the title compound as a white solid. ¹H NMR (CD₃OD, 300 MHz) δ 8.52 (m, 1H), 8.06 (m, 1H), 7.83 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 3.88 (s, 3H), 2.59 (s, 4H). The methine hydrogen was not observed presumably due to exchange with the deuterated methanol.

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