AlAr₃(THF): Highly Efficient Reagents for Cross-couplings with Aryl Bromides and Chlorides Catalyzed by the Economic Palladium Complex of PCy₃

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I. General Procedures of Couplings of Aryl Halides with AlAr₃(THF)

To a solution of Pd(OAc)₂ (2.2 mg, 0.010 mmol) and a phosphine ligand (0.020 mmol) in 2 mL solvent at a suitable temperature, AlAr₃(THF) (1.3 mmol) and an aryl halide (1.0 mmol) in 2 mL solvent were added. The mixture was reacted for a reaction time as indicated. The solvent was then removed under reduced pressures. The residue was dissolved in 5 mL CH₂Cl₂ and the resulting solution was passed through a short column of silica gel. The solution was dried and the coupling product was purified by column chromatography with an eluent of EtOAc/hexane. For couplings with the Al(2,4,6-Me₃C₆H₂)₃(THF) reagent, half quantities of substrates, Pd(OAc)₂, PCy₃, and the aluminium reagent were used.

II. Blank Reaction of Al(2,4,6-Me₃C₆H₂)₃(THF) in the Presence of Pd(OAc)₂ and PCy₃

To a solution of Pd(OAc)₂ (0.0561 g, 0.250 mmol) and PCy₃ (0.139 g, 0.500 mmol) in 2 mL toluene, Al(2,4,6-Me₃C₆H₂)₃(THF) (0.286 g, 0.625 mmol) in 2 mL toluene was added under a nitrogen atmosphere at room temperature. The resulting solution was heated at 100 °C for 1 h and then the solvent was removed to give a yellow solid. The solid was dissolved in 5 mL CH₂Cl₂ and the mixture was passed through a short column of silica gel. The solution was dried completely and the resulted white solid was purified by column chromatography with an eluent of AcOEt/hexane (1/50) to afford a white solid of coupling product (0.0561 g, 94.3%). ¹H NMR (400 MHz, CDCl₃): δ 6.93 (s, 4H, Ar), 2.32 (s, 6H, CH₃), 1.86 (s, 12H, CH₃) ppm.

III. ¹H and ¹³C NMR Spectroscopic Data of Coupling Products

1. 4-Methoxybiphenyl¹

White solid (0.167 g, 91.0%). ¹H NMR (400 MHz, CDCl₃): δ 7.54-7.49 (m, 4H, Ar), 7.40-7.36 (m, 2H, Ar), 7.28 (d, 1H, J = 7.6 Hz, Ar), 6.94 (d, 2H, J = 6.8 Hz, Ar), 3.80 (s, 3H, OCH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.1, 140.8, 133.7, 128.6, 128.1, 126.7, 126.1, 114.2, 55.2 ppm

2. 4-phenylthioanisole²

Pale yellow solid (0.186 g, 93.0%). ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.50 (m, 4H, Ar), 7.44-7.40 (m, 2H, Ar), 7.34-7.31 (m, 3H, Ar), 2.51 (s, 3H, SCH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 140.5, 138.0, 137.6, 128.8, 127.5, 127.2, 127.0, 126.8, 15.9 ppm
3. **4-Methybiphenyl**

White solid (0.139 g, 83.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.55 (d, 2H, \(J = 8.0\) Hz, Ar), 7.47 (d, 2H, \(J = 8.0\) Hz, Ar), 7.38 (t, 2H, \(J = 7.6\) Hz, Ar), 7.29 (t, 1H, \(J = 7.6\) Hz, Ar), 7.21 (d, 2H, \(J = 7.6\) Hz, Ar), 2.36 (s, 3H, CH\(_3\)) ppm. \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.1, 138.3, 136.9, 129.4, 128.7, 127.2, 127.1, 126.9, 21.0 ppm.

4. **4-tert-Butylbiphenyl**

White solid (0.199 g, 95%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.57 (d, 2H, \(J = 7.6\) Hz, Ar), 7.52 (d, \(J = 8.4\) Hz, Ar), 7.44 (d, 2H, \(J = 8.4\) Hz, Ar), 7.39 (t, 2H, \(J = 8.0\) Hz, Ar), 7.29 (t, 1H, \(J = 6.8\) Hz, Ar), 1.34 (s, 9H, C(CH\(_3\))\(_3\)) ppm. \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.1, 141.1, 138.3, 128.7, 127.1, 127.0, 126.8, 125.7, 34.5, 31.4 ppm.

5. **4-Fluorobiphenyl**

White solid (0.156 g, 91%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.56-7.52 (m, 4H, Ar), 7.46-7.41 (m, 2H, Ar), 7.36-7.32 (m, 1H, Ar), 7.14-7.05 (m, 2H, Ar) ppm. \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 163.7, 161.2, 140.2, 137.3, 128.8, 128.7, 127.2, 127.1, 127.0, 115.5 (d, \(J = 21.3\) Hz) ppm.

6. **4-Nitrobiphenyl**

Pale yellow solid (0.129 g, 65%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.28 (d, 2H, \(J = 8.0\) Hz, Ar), 7.73 (d, 2H, \(J = 8.0\) Hz, Ar), 7.62 (d, 2H, \(J = 7.6\) Hz, Ar), 7.52-7.42 (m, 3H, Ar) ppm \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 147.6, 147.1, 138.7, 129.1, 128.9, 127.7, 127.3, 124.0 ppm.

7. **3,5-Dimethylbiphenyl**
Colorless liquid (0.172 g, 95%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.53 (d, 2H, \(J = 7.2\) Hz, Ar), 7.36 (t, 2H, \(J = 7.2\) Hz, Ar), 7.32-7.24 (m, 1H, Ar), 7.18 (s, 2H, Ar), 6.94 (s, 1H, Ar), 2.33 (s, 6H, CH\(_3\)) ppm. \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.4, 141.2, 138.1, 128.8, 128.7, 127.1, 127.0, 125.1, 21.3 ppm.

8. 2-Methoxybiphenyl\(^7\)

White solid (0.169 g, 92.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.52 (d, 2H, \(J = 6.8\) Hz, Ar), 7.39 (t, 2H, \(J = 7.6\) Hz, Ar), 7.30 (t, 3H, \(J = 7.6\) Hz, Ar), 7.10 (t, 1H, \(J = 7.6\) Hz, Ar), 6.95 (d, 1H, \(J = 7.6\) Hz, Ar), 3.77 (s, 3H, OCH\(_3\)) ppm. \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 156.4, 138.5, 130.8, 130.7, 129.5, 128.6, 127.9, 126.8, 120.8, 111.3, 55.5 ppm.

9. 2,4-Dimethylbiphenyl

Colorless liquid (0.171 g, 94.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.42-7.25 (m, 5H, Ar), 7.13-7.00 (m, 3H, Ar), 2.33 (s, 3H, CH\(_3\)), 2.22 (s, 3H, CH\(_3\)) ppm. \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.9, 139.1, 136.8, 135.0, 131.0, 129.7, 129.2, 128.7, 128.0, 127.1, 126.5, 20.9, 20.3 ppm.

10. 2,6-Dimethylbiphenyl\(^8\)

Colorless liquid (0.127 g, 70.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.40 (t, 2H, \(J = 7.6\) Hz, Ar), 7.34-7.28 (m, 1H, Ar), 7.15-7.08 (m, 5H, Ar), 2.02 (s, 6H, CH\(_3\)) ppm. \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.9, 141.1, 136.0, 129.0, 128.7, 128.4, 127.2, 126.9, 20.7 ppm.

11. 2-Methylbiphenyl\(^3\)

Colorless liquid (0.158 g, 94.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.64-7.56 (m, 2H, Ar), 7.45-7.38 (m, 3H, Ar), 7.38-7.30 (m, 2H, Ar), 7.27-7.22 (m, 2H, Ar), 2.27 (s, 3H, CH\(_3\)) ppm.
13C{¹H} NMR (100 MHz, CDCl₃): δ 142.0, 141.3, 135.3, 130.3, 129.8, 129.1, 128.8, 127.2, 126.7, 125.7, 20.4 ppm

12. 4-Cyanobiphenyl

White solid (0.166 g, 93.0%). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (dd, 4H, J = 18.0, 8.0 Hz, Ar), 7.63-7.57 (m, 2H, Ar), 7.50-7.40 (m, 3H, Ar) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.7, 139.2, 132.6, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9 ppm.

13. 4-Phenyl-methylbenzoate

White solid (0.197 g, 93.0%). ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, 2H, J = 8.4 Hz, Ar), 7.68-7.48 (m, 4H, Ar), 7.45 (t, 2H, J = 8.4 Hz, Ar), 7.38 (t, 1H, J = 7.6 Hz, Ar), 3.92 (s, 3H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 166.9, 145.6, 140.0, 130.1, 128.9, 128.1, 127.2, 127.0, 52.0 ppm.

14. 4-Methoxy-2’,4’,6’-trimethylbiphenyl

White solid (0.107 g, 95.0 %). ¹H NMR (400 MHz, CDCl₃): δ 7.06-7.03 (m, 2H, Ar), 6.96-6.93 (m, 4H, Ar), 3.85 (s, 3H, OCH₃), 2.32 (s, 3H, CH₃), 2.01 (s, 6H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz): δ 156.7, 136.5, 135.2, 130.9, 129.5, 128.3, 127.9, 120.6, 110.8, 55.4, 21.1, 20.3 ppm.

15. 4-Fluoro-2’,4’,6’-trimethylbiphenyl

White solid (0.101 g, 94.0%). ¹H NMR (400 MHz, CDCl₃): δ 7.10-7.08 (m, 4H, Ar), 6.93 (s, 2H, Ar), 2.32 (s, 3H, CH₃), 1.98 (s, 6H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz): δ 162.9, 160.5, 138.0, 136.9, 136.7, 136.1, 130.8, 130.7, 128.1, 115.4, 115.2, 20.9, 20.6 ppm.
16. **1-Naphthyl-2',4',6'-trimethylbenzene**

White solid (0.124 g, 92.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.86 (dd, 2H, 19.6, 4.0 Hz, Ar), 7.52 (dd, 1H, \(J = 8.4, 7.2\) Hz, Ar), 7.47-7.43 (m, 1H, Ar), 7.36-7.31 (m, 2H, Ar), 7.26-7.23 (m, 1H, Ar), 7.00 (s, 2H, Ar), 2.38 (s, 3H, CH\(_3\)), 1.87 (s, 6H, CH\(_3\)) ppm. \(^{13}\)C\({}^1\)H NMR (100 MHz): \(\delta\) 138.8, 136.9, 136.8, 133.8, 132.0, 128.3, 128.1, 127.0, 126.7, 126.0, 125.7, 125.6, 125.5, 21.1, 20.3 ppm.

17. **1-Methoxy-2',4',6'-trimethylbiphenyl**

White solid (0.108 g, 96.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.34-7.30 (m, 1H, Ar), 7.03-6.93 (m, 5H, Ar), 3.73 (s, 3H, OCH\(_3\)), 2.32 (s, 3H, CH\(_3\)), 1.98 (s, 6H, CH\(_3\)) ppm. \(^{13}\)C\({}^1\)H NMR (100 MHz): \(\delta\) 156.7, 136.6, 136.4, 135.3, 130.9, 129.5, 128.3, 127.9, 120.6, 110.8, 55.3, 21.1, 20.3 ppm.

18. **2,4-Dimethyl-2',4',6'-trimethylbiphenyl**

White solid (0.103 g, 92.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.09 (s, 1H, Ar), 7.04 (d, 1H, \(J = 7.6\) Hz, Ar), 6.92 (s, 2H, Ar), 6.88 (d, 1H, \(J = 7.6\) Hz, Ar), 2.36 (s, 3H, CH\(_3\)), 2.33 (s, 3H, CH\(_3\)), 1.93 (s, 3H, CH\(_3\)), 1.91 (s, 6H, CH\(_3\)) ppm. \(^{13}\)C\({}^1\)H NMR (100 MHz): \(\delta\) 138.2, 137.5, 136.3, 136.2, 135.9, 135.6, 130.6, 129.0, 128.2, 127.9, 126.7, 21.1, 21.0, 20.3, 19.4 ppm.

19. **2-p-Tolynaphthalene**

White solid (0.101 g, 93.0%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.02 (s, 1H, Ar), 7.91-7.84
(m, 3H, Ar), 7.75-7.73 (m, 1H, Ar), 7.64-7.62 (m, 2H, Ar), 7.52-7.44 (m, 2H, Ar), 7.30 (d, 2H, J = 8.4 Hz, Ar), 2.42 (s, 3H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz): δ 138.50, 138.24, 137.14, 133.74, 132.52, 129.57, 128.33, 128.13, 127.62, 127.24, 126.20, 125.74, 125.54, 125.41, 21.10 ppm.

20. 4-trimethylsilyl-4’-methylbiphenyl¹²

   White solid (0.102 g, 85.0%). ¹H NMR (400 MHz, CDCl₃): δ 7.70-7.68 (m, 4H, Ar), 7.60 (d, 2H, J = 8.0 Hz, Ar), 7.34 (d, 2H, J = 8.0 Hz, Ar), 2.49 (s, 3H, CH₃), 0.41 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz): δ 141.55, 138.81, 138.29, 137.05, 133.78, 129.48, 126.99, 126.31, 21.08, -1.08 ppm.

IV. References

V. ¹H and ¹³C NMR Spectra of Coupling Products