Supporting Information

A Ruthenium-catalyzed Reaction of Aromatic Ketones with Arylboronates: A New Method for the Arylation of Aromatic Compounds

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General Information. ^1H NMR and ^{13}C NMR were recorded on a JEOL JNM-EX270 spectrometer operating at 270 and 67.5 MHz, respectively. ^{11}B NMR was recorded on a JEOL ECP-400 spectrometer operating at 128 MHz. The chemical shift of ^1H NMR and ^{13}C NMR signals are quoted relative to internal CHCl_3 ($\delta = 7.26$ and 77.0) or tetramethylsilane. The ^{11}B NMR signals are quoted relative to BF_3 . ^1H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), relative intensity, and interpretation. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ). IR spectra were measured on a Hitachi 270-50 infrared spectrometer. The GCMS analysis were measured on a Shimadzu GCMS QP-5000 gas chromatography mass spectrometer.

GC Analysis. The conditions used for the GC analysis were as follows: Shimadzu GC-14A (equipped with CBP-20 25 m x 0.2 mm); initial temperature, $70\text{ }^\circ\text{C}$ (0 min); final temperature, $230\text{ }^\circ\text{C}$ (30 min); rate, $10\text{ }^\circ\text{C} / \text{min}$; injection temperature, $270\text{ }^\circ\text{C}$; detector temperature, $270\text{ }^\circ\text{C}$

Solvents and Materials. Toluene was distilled under nitrogen from CaH_2 . $\text{Ru}(\text{H})_2(\text{CO})(\text{PPh}_3)_3$ was prepared by literature method.

General Procedure. The apparatus consisted of 10-mL two-necked flask equipped with a reflux condenser connected to a nitrogen line, a rubber septum, and a magnetic stirring bar was flame dried under a flow of nitrogen. In the flask were placed the ruthenium complex (0.02 mmol), 1 mL of toluene, aromatic ketone (2 mmol), and arylboronic acid ester (1 mmol). The resulting mixture was refluxed under nitrogen atmosphere. The progress of the reaction was monitored by a GC analysis. The product was isolated by a silica gel column chromatography.

1-(3-Methyl-biphenyl-2-yl)-ethanone (4).

^1H NMR (CDCl_3) 1.94 (s, 3 H, $\text{CH}_3\text{C}(\text{O})$), 2.34 (s, 3 H, CH_3), 7.2-7.4 (m, 8 H, ArH); ^{13}C NMR (CDCl_3) 19.63, 32.12, 127.20, 127.58, 128.46, 128.71, 128.86, 129.45, 133.55, 138.42, 140.29, 141.24, 207.42; IR (neat) 3062 w, 3030 w, 2962 w, 2928 w, 1697 s, 1590 w, 1499 w, 1462 m, 1447 w, 1423 m, 1385 w, 1350 m, 1252 s, 1232 m, 1073 w, 1051 w, 1030 w, 962 w, 795 m, 760 s, 702 s cm^{-1} ; MS m/z (% relative intensity) 210 (41, M^+), 195 (100), 168 (21), 165 (50), 152 (35), 83 (19), 76 (11), 63 (13), 51 (14). Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}$: C, 85.68; H, 6.71%. Found: C, 85.46; H, 6.47%.

1-[1,1';3',1'']Terphenyl-2'-yl-ethanone.

^1H NMR (CDCl_3) 1.88 (s, 3 H, CH_3), 7.3-7.5 (m, 13 H, ArH); ^{13}C NMR (CDCl_3) 33.00, 127.49, 128.27, 128.55, 128.97, 129.11, 138.89, 140.20, 141.14, 206.04; IR (KBr) 3064 w, 1693 s, 1569 w, 1495 w, 1455 m, 1442 m, 1344 m, 1242 s, 1179 w, 1101 w, 1071 w, 1044 w, 1027 w, 804 w, 771 s, 759 s, 705 s, 669 m, 595 w, 508 w cm^{-1} ; MS m/z (% relative intensity) 272 (M^+ , 28), 258 (22), 257 (100), 229 (22), 228 (30), 227 (14), 226 (18), 202 (10), 128 (11), 126 (16), 114 (12), 113 (19), 101 (15). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}$: C, 88.20; H, 5.92%. Found: C, 88.01; H, 5.80%.

1-Biphenyl-2-yl-2-methyl-propan-1-one.

¹H NMR (CDCl₃) 0.87 (d, *J* = 7.0 Hz, 6 H, CH₃), 2.42 (q, *J* = 7.0 Hz, 1H, CH), 7.3-7.5 (m, 9H); ¹³C NMR (CDCl₃) 18.72, 40.27, 127.24, 127.67, 127.89, 128.57, 128.73, 129.88, 130.03, 139.54, 140.49, 140.61, 212.48, 216.48; MS *m/z* (% relative intensity) 224 (M⁺, 4.7), 182 (15), 181 (100), 153 (23), 152 (34). HRMS Calcd for C₁₆H₁₆O: 224.1201. Found: 224.1193.

2-Methyl-1-[1,1';3',1'']terphenyl-2'-yl-propan-1-one.

¹H NMR (CDCl₃) 0.49 (d, *J* = 7.0 Hz, 6 H, CH₃), 2.07 (q, *J* = 7.0 Hz, 1 H, CH), 7.3-7.5 (m, 13 H, ArH); ¹³C NMR (CDCl₃) 17.66, 42.19, 127.38, 127.93, 128.29, 129.02, 129.89, 139.06, 140.25, 140.40, 211.54; IR (neat) 3058 w, 3026 w, 2972 m, 2930 w, 2872 w, 1704 s, 1600 w, 1586 w, 1571 w, 1497 m, 1468 m, 1456 m, 1418 w, 1381 w, 1361 w, 1363 w, 1338 w, 1283 w, 1206 m, 1178 w, 1071 w, 1027 w, 973 s, 920 w, 815 m, 775 s, 759 s, 702 s, 669 w, 655 w cm⁻¹; MS *m/z* (% relative intensity) 258 [(M-42)⁺, 21], 257[(M-43)⁺, 100], 229 (14), 228 (24), 227 (11), 226 (12). Anal. Calcd for C₂₂H₂₀O: C, 87.96; H, 6.71%. Found: C, 87.68; H, 6.62%.

1-Biphenyl-2-yl-2,2-dimethyl-propan-1-one.

¹H NMR (CDCl₃) 0.87 (s, 9 H, CH₃), 7.14 (d, *J* = 3.8 Hz, 1 H, ArH), 7.3-7.5 (m, 8 H, ArH); ¹³C NMR (CDCl₃) 27.29, 45.00, 125.59, 126.65, 127.48, 128.33, 128.60, 129.48, 129.63, 137.92, 140.82, 140.95, 216.38; IR (neat) 3060 w, 2976 m, 2934 w, 2870 w, 1683 s, 1479 s, 1463 w, 1450 w, 1433 w, 1395 w, 1365 w, 1287 w, 1276 w, 1186 m, 967 m, 952 m, 918 m, 784 w, 773 m, 744 s, 703 s, 674 m, 612 w, 596 w, 572 w, 552 w, 518 m cm⁻¹; MS *m/z* (% relative intensity) 238 (M⁺, 1.3), 182 (15), 181 (100), 153 (20), 152 (34). Anal. Calcd for C₁₇H₁₈O: C, 85.67; H, 7.61%. Found: C, 85.37; H, 7.62%.

1-(5'-Methoxy-[1,1';3',1'']terphenyl-2'-yl)-ethanone.

¹H NMR (CDCl₃) 1.85 (s, 3 H, CH₃), 3.88 (s, 3 H, OCH₃), 6.89 (s, 2H, ArH), 7.3-7.4 (m, 10 H, ArH); ¹³C NMR (CDCl₃) 33.14, 55.49, 114, 127.56, 128.28, 128.76, 134.31, 140.39, 141.08, 158.94, 205.61; IR (neat) 3056 m, 2968 m, 2936 m, 2844 m, 1696 s, 1598 s, 1576 s, 1498 s, 1464 s, 1448 s, 1430 s, 1348 s, 1248 s, 1206 s, 1178 s, 1154 m, 1076 m, 1030 m, 876 m, 860 m, 782 m, 762 m, 702 m, 664 w, 632 w, 616 w, 578 w, 548 w cm⁻¹; MS *m/z* (% relative intensity) 302 (M⁺, 24), 288 (19), 287 (100), 272 (13), 226 (12), 215 (31), 113 (11). Anal. Calcd for C₂₁H₁₈O₂: C, 83.42; H, 6.00%. Found: C, 83.16; H, 6.02%.

1-(5'-Fluoro-[1,1';3',1'']terphenyl-2'-yl)-ethanone.

¹H NMR (CDCl₃) 1.85 (s, 3 H), 7.07 (d, *J*_{H-F} = 8.9 Hz, 2 H, ArH), 7.3-7.5 (m, 10 H, ArH); ¹³C NMR (CDCl₃) 33.00, 115.88 (d, *J*_{C-F} = 21.2 Hz), 127.95, 128.41, 128.75, 137.51, 139.17 (d, *J*_{C-F} = 2.2 Hz), 141.54 (d, *J*_{C-F} = 8.3 Hz), 163.41, 205.10; IR (neat) 3366 w, 3066 m, 2912 w, 1759 w, 1693 s, 1593 s, 1574 s, 1498 m, 1446 w, 1411 m, 1360 s, 1330 m, 1274 w, 1256 w, 1231 s, 1168 s, 1155 m, 1075 m, 1044 w, 1029 m, 1002 w, 963 m, 919 w, 880 s, 859 w, 851 w, 782 s, 769 s, 748 m, 701 s, 655 m, 606 m, 569 m, 545 m, 503 m, 431 w, 362 w cm⁻¹; MS *m/z* (% relative intensity) 290 (M⁺, 21), 276 (21), 275 (100), 246 (17), 244 (15), 227 (12), 226 (23), 136 (16), 123 (10), 122 (16), 113 (11), 110 (12), 51 (11). Anal. Calcd for C₂₀H₁₅FO: C, 82.74; H, 5.21%. Found: C, 82.49; H, 5.21%.

1-(3-Trifluoromethyl-biphenyl-2-yl)-ethanone.

¹H NMR (CDCl₃) 2.00 (s, 3 H, CH₃), 7.28-7.35 (m, 2 H, ArH), 7.38-7.44 (m, 3 H, ArH), 7.52-7.58 (m, 2 H, ArH), 7.67-7.74 (m, 1 H, ArH); ¹³C NMR (CDCl₃) 31.760 (d, *J* = 1.7 Hz, CH₃), 123.65 (q, *J* = 274.0 Hz, CF₃), 125.25 (q, 5.0 Hz), 126.68 (q, 31.9 Hz), 128.36, 128.72, 128.91, 129.19, 133.61 (broad), 138.56, 139.41, 139.966, 204.110; IR (KBr) 3064 w, 1705 s, 1582 w, 1498 w, 1455 m, 1439 m, 1417 w, 1354 m, 1329 s, 1287 m, 1266 m, 1242 s, 1194 m, 1171 s, 1118 s, 1075 m, 1044 m, 1023 w, 996 w, 965 w, 932 w, 923 w, 854 w, 817 m, 767 s, 759 m, 709 s, 703 s, 669 w, 654 w, 634 w, 596 w cm⁻¹; MS *m/z* (% relative intensity) 264 (M⁺, 34), 250 (16), 249 (100), 229 (36), 201 (59), 152 (28), 151 (14), 101 (13), 98 (14), 76 (10), 75 (15), 63 (11), 51 (18), 50 (12). HRMS Calcd for C₁₅H₁₁F₃O: 264.0762. Found: 264.0759.

1-(2-Phenyl-naphthalen-1-yl)-ethanone.

¹H NMR (CDCl₃) 2.12 (s, 3 H, CH₃), 7.40-7.60 (m, 8 H, ArH), 7.89-7.96 (m, 3 HArH); ¹³C NMR (CDCl₃) 32.60, 124.55, 126.06, 127.18, 127.75, 128.02, 128.49, 128.60, 129.10, 129.19, 132.31, 135.72, 138.05, 140.04, 206.98; IR (neat) 3056 w, 1693 s, 1595 m, 1495 m, 1448 m, 1423 m, 1375 w, 1350 m, 1280 w, 1214 s, 1127 w, 1084 w, 1070 w, 1028 w, 954 w, 865 w, 823 m, 763 s, 746 w, 701 s, 601 w cm⁻¹; MS *m/z* (% relative intensity) 246 (M⁺, 36), 232 (17), 231 (100), 203 (29), 202 (60), 201 (15), 200 (13), 100 (42), 88 (13). Anal. Calcd for C₁₈H₁₄O: C, 87.78; H, 5.73%. Found: C, 87.49; H, 5.74.

8-Phenyl-3,4-dihydro-2H-naphthalen-1-one.

¹H NMR (CDCl₃) 2.13 (tt, *J* = 6.5, 5.9 Hz, 2 H, CH₂), 2.61 (t, *J* = 6.5 Hz, 2 H, C(O)CH₂), 3.00 (t, *J* = 5.9 Hz, 2 H, ArCH₂), 7.08-7.46 (m, 8 H, ArH); ¹³C NMR (CDCl₃) 23.09, 30.74, 40.46, 126.43, 127.62, 127.98, 130.09, 131.03, 131.64, 142.71, 143.75, 145.40, 198.193; IR (neat) 3056 w, 3030 w, 2938 m, 2866 w, 1683 s, 1587 m, 1576 w, 1497 w, 1460 m, 1440 w, 1402 w, 1346 w, 1319 w, 1289 w, 1248 m, 1205 m, 1180 w, 1075 w, 1015 w, 934 w, 829 w, 804 w, 760 s, 697 s, 669 w, 655 m, 525 w, 508 w cm⁻¹; MS *m/z* (% relative intensity) 222 (M⁺, 49), 221 (100), 194 (38), 166 (20), 165 (87), 164 (14), 110 (13), 97 (11), 95 (13), 89 (13), 82 (73), 76 (13), 70 (16), 63 (16), 51 (14). HRMS Calcd for C₁₆H₁₄O: 222.1044. Found: 222.1052.

4-Phenyl-6,7,8,9-tetrahydro-benzocyclohepten-5-one.

¹H NMR (CDCl₃) 1.80-1.95 (m, 4 H, CH₂CH₂); 2.65 (t, *J* = 5.8 Hz, 2 H, C(O)CH₂), 2.78 (t, *J* = 6.1 Hz, 2 H, ArCH₂), 7.11 (d, *J* = 7.6 Hz, 1 H, ArH), 7.18-7.38 (m, 7 H, ArH); ¹³C NMR (CDCl₃) 22.86, 25.60, 32.49, 42.86, 126.93, 127.57, 128.08, 128.45, 128.63, 129.62, 137.37, 139.97, 140.25, 140.67, 209.93; IR (KBr) 3058 w, 3022 w, 2932 m, 2858 m, 1684 s, 1587 m, 1574 m, 1498 w, 1457 m, 1405 w, 1343 w, 1328 w, 1312 w, 1277 w, 1239 s, 1214 m, 1176 w, 1165 w, 1076 w, 1031 w, 1022 w, 968 w, 953 w, 916 w, 898 w, 876 w, 832 w, 809 m, 774 m, 756 s, 699 s, 630 w, 586 w cm⁻¹; MS *m/z* (% relative intensity) 237 ((M+1)⁺, 17), 236 (M⁺, 100), 235 (94), 208 (31), 207 (96), 194 (12), 193 (13), 181 (12), 180 (31), 179 (39), 178 (54), 167 (20), 166 (16), 165 (70), 164 (13), 159 (12), 152 (37), 151 (15), 115 (14), 102 (10), 94 (19), 89 (32), 88 (16), 82 (55), 77 (17), 76 (34), 75 (13), 70 (12), 63 (25), 51 (27), 50 (11). HRMS Calcd for C₁₇H₁₆O: 236.1202. Found: 236.1199.

1-(4'-Dimethylamino-biphenyl-2-yl)-2,2-dimethyl-propan-1-one.

¹H NMR (CDCl₃) 0.89 (s, 9 H, C(CH₃)₃), 2.96 (s, 6 H, N(CH₃)₂), 6.72 (ddd, *J* = 9.3, 2.7, 2.4 Hz, 2 H, ArH), 7.08 (ddd, *J* = 7.6, 1.3, 0.66 Hz, 1 H, ArH), 7.2-7.3 (m, 3 H), 7.3-7.4 (m, 2H); ¹³C NMR (CDCl₃) 27.31, 40.45, 44.98, 112.18, 125.59, 128.47, 128.87, 129.26, 130.09, 138.09, 140.66, 149.72, 217.14; IR (neat) 2974 m, 2866 m, 1681 s, 1611 s, 1596 m, 1533 s, 1480 s, 1462 m, 1443 s, 1392 w, 1365 s, 1306 w, 1275 w, 1226 m, 1200 m, 1187 m, 1059 w, 964 m, 947 m, 873 w, 825 m, 778 w, 762 s, 749 m, 720 m, 707 w, 573 w, 560 w cm⁻¹; MS *m/z* (% relative intensity) 281 (M⁺, 30), 225 (17), 224 (100), 209 (13), 181 (13), 180 (11), 153 (21), 152 (25), 57 (13). Calcd for C₁₉H₂₃NO: C, 81.10; H, 8.24; N, 4.98. Found: C, 80.96; H, 8.22; N, 4.97.

1-(4'-Methoxy-biphenyl-2-yl)-2,2-dimethyl-propan-1-one.

¹H NMR (CDCl₃) 0.88 (s, 9 H, CH₃), 3.82 (s, 3 H, OCH₃), 6.91 (ddd, *J* = 4.9 Hz, 1.5 Hz, 0.9 Hz, 2 H, ArH), 7.11 (ddd, *J* = 7.6 Hz, 1.4 Hz, 0.5 Hz, 1 H, ArH), 7.2-7.4 (m, 5 H, ArH); ¹³C NMR (CDCl₃) 27.18, 44.90, 55.22, 113.84, 125.62, 126.27, 128.61, 129.61, 130.66, 133.41, 137.65, 140.95, 159.20, 216.79; IR (neat) 3060 w, 2970 s, 2908 m, 2872 w, 2840 w, 1690 s, 1613 s, 1580 w, 1521 s, 1480 s, 1466 s, 1443 s, 1394 m, 1365 m, 1294 m, 1277 m, 1249 s, 1178 s, 1114 w, 1105 w, 1053 w, 1036 s, 1016 w, 1000 w, 964 s, 948 m, 874 w, 836 s, 818 w, 805 w, 762 s, 717 m, 667 w, 634 w, 596 w, 575 m, 554 w, 527 w cm⁻¹; MS *m/z* (% relative intensity) 268 (M⁺, 4), 212 (16), 211 (100), 168 (20), 140 (12), 139 (17). Anal. Calcd for C₁₈H₂₀O: C, 80.56; H, 7.51%. Found: C, 80.33; H, 7.46%.

1-(4'-Fluoro-biphenyl-2-yl)-2,2-dimethyl-propan-1-one.

^1H NMR (CDCl_3) 0.89 (s, 9 H, CH_3), 7.0-7.2 (m, 3 H, ArH), 7.3-7.5 (m, 5 H, ArH); ^{13}C NMR (CDCl_3) 27.25, 45.00, 125.28(d, $J_{\text{C-F}} = 21.1\text{ Hz}$), 125.54, 126.74, 128.61, 129.65, 131.16 (d, $J_{\text{C-F}} = 7.8\text{ Hz}$), 136.84 (d, $J_{\text{C-F}} = 3.3\text{ Hz}$), 140.88, 162.29 (d, $J_{\text{C-F}} = 246.6\text{ Hz}$), 216.01; IR (neat) 3062 w, 2972 m, 2938 w, 2908 w, 2872 w, 1685 s, 1601 m, 1517 s, 1479 m, 1442 w, 1397 w, 1368 w, 1357 w, 1274 w, 1219 s, 1191 m, 1164 s, 1097 w, 1006 w, 967 m, 954 m, 942 w, 885 w, 844 s, 819 m, 778 m, 766 s, 722 m, 669 m, 655 m, 594 w, 574 w, 562 m, 552 w, 522 m, 403 w cm^{-1} ; MS m/z (% relative intensity) 256 (M^+ , 3), 200 (26), 199 (100), 171 (34), 170 (55). HRMS Calcd for $\text{C}_{17}\text{H}_{17}\text{OF}$: 256.1263. Found: 256.1272.

2,2-Dimethyl-1-(2'-methyl-biphenyl-2-yl)-propan-1-one.

^1H NMR (CDCl_3) 0.92 (s, 9 H, CH_3), 2.22 (s, 3 H, ArCH_3), 7.1-7.4 (m, 8 H, ArH); ^{13}C NMR (CDCl_3) 20.47, 27.43, 44.53, 125.08, 125.21, 126.42, 127.67, 127.91, 130.14, 130.44, 130.61, 136.16, 137.33, 139.65, 141.59, 215.04; IR (neat) 3060 w, 3020 w, 2970 m, 2932 m, 2870 m, 1690 s, 1595 w, 1479 s, 1462 m, 1393 m, 1365 m, 1275 m, 1226 w, 1188 s, 1159 w, 1120 w, 1051 w, 1005 m, 965 s, 946 w, 750 s, 726 m, 672 m, 622 w, 595 w, 567 w, 521 w, 461 w, 365 w cm^{-1} ; MS m/z (% relative intensity) 252 (M^+ , 0), 196 (17), 195 (100), 194 (11), 167 (16), 165 (29), 152 (19). HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{O}$: 253.1592. Found: 253.1600.

2,2-Dimethyl-1-(2-naphthalen-1-yl-phenyl)-propan-1-one.

^1H NMR (CDCl_3) 0.79 (s, 9 H, CH_3), 7.2-7.5 (m, 8 H, ArH), 7.7-7.9 (m, 3 H, ArH); ^{13}C NMR (CDCl_3) 27.47, 44.67, 124.83, 125.64, 125.69, 126.02, 126.12, 126.82, 127.85, 128.10, 128.17, 128.76, 131.54, 131.85, 133.60, 135.96, 137.52, 142.34, 215.06; MS m/z (% relative intensity) 288 (M^+ , 10), 232 (19), 231 (100), 203 (10), 202 (37). HRMS Calcd for $\text{C}_{21}\text{H}_{20}\text{O}$: 288.1514. Found: 288.1516.

Reaction of 2,2-dimethylpropiophenone (5) with the phenylboronate 2 in an NMR tube.

In an NMR tube were placed $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, the phenylboronate **2**, 0.7 mL of toluene- d_8 , and the ketone **5**, then the resulting solution was heated at 115 $^\circ\text{C}$ in an oil bath for 1 h. After 1 h, the reaction mixture was cooled at room temperature. The ^1H and ^{11}B NMR spectra of the reaction mixture were measured, and the reaction mixture was analyzed by GC and GCMS.