Supporting Information

Palladium-catalyzed Addition of Arylboronic Acids to Aldehydes

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General. All solvents were dried by standard methods and distilled under argon. Commercially available compounds were used without purification. All known products were identified by IR and NMR analyses. Commercially available alcohols, benzhydrol, 4-methylphenyl(phenyl)methanol, and 2-methylphenyl(phenyl)methanol, were identified comparison with those of authentic samples purchased. Nuclear magnetic resonance spectra were measured on a Varian MERCURY plus300-4N spectrometer (1H: 300 MHz, 13C: 75 MHz, 19F: 282 MHz). IR spectra were measured on a Shimadzu IR-408 spectrometer. Exact mass spectrometry were performed on a JEOL JMS-700 (FAB-MS, matrix m-NBA, reference PEG-400). All reactions were carried out under an argon atmosphere by standard Schlenk techniques. All organic and inorganic compounds are commercially available, and are used without purification.

General procedure: Pd complex (0.025 mmol or 0.05 mmol, 5 mol%) and phosphine (0.05 mmol, 5 mol%), arylboronic acid (2.0 mmol), aldehyde (1.0 mmol), and Cs₂CO₃ (1.0 mmol) were dissolved in toluene (2 mL) and chloroform (0.01 mL). After the mixture was stirred at 80 °C for 24 h, then the product was extracted with CH₂Cl₂. The analytically pure alcohol was obtained by chromatography on silica gel.

4-Cyanophenyl(phenyl)methanol (3a)¹⁾

IR (KBr) ν 3409 (-OH), 2233 (-CN), 1599, 1491, 1452, 1406, 1269, 1232, 1115, 1080, 1053, 1024, 982, 918, 870, 851, 804, 770, 700, 648, 629, 532 cm⁻¹; ¹H-NMR (CDCl₃, 300MHz) δ 2.63 (brs, 1H, -OH), 5.82 (s, 1H, -CHOH), 7.24-7.42 (m, 5H, -Ar), 7.49-7.58 (m, 4H, -Ar); ¹³C-NMR (75 MHz) δ 75.9, 111.3, 119.1, 126.9, 127.2, 128.5, 129.1, 132.5, 143.0, 149.1.

Phenyl(4-trifluoromethylphenyl)methanol (3b)²⁾

IR (KBr) ν 3252 (-OH), 1620, 1601, 1494, 1450, 1418, 1335, 1111, 1069, 1016, 924, 866, 849, 818, 731, 702, 534, 457 cm⁻¹; ¹H-NMR (CDCl₃, 300MHz) δ 2.42 (d, J = 2.7, 1H, -OH), 5.84 (d, J = 2.1, 1H, -CHOH), 7.25-7.34 (m, 5H, -Ar), 7.12-7.49 (dd, J = 18.9, 8.1, 4H, -Ar); ¹³C-NMR (75 MHz) δ

75.7, 124.0 (d, $J = 273.0$, $-\underline{\text{C}}\text{F}_3$), 125.2, 125.3, 126.5, 128.0, 128.6, 129.8 (d, $J = 32.0$, $-\underline{\text{C}}-\text{CF}$), 142.9, 147.3; ^{19}F -NMR (282 MHz) δ -63.0.

4-Methoxycarbonylphenyl(phenyl)methanol (3c)³⁾

IR (KBr) ν 3369 (-OH), 2957, 1726, 1609, 1480, 1431, 1406, 1292, 1267, 1180, 1113, 1040, 1016, 959, 872, 826, 748, 700, 623, 544, 509 cm^{-1} ; ^1H -NMR (CDCl_3 , 300MHz) δ 2.86 (brs, 1H, $-\underline{\text{OH}}$), 3.85 (s, 3H, $-\text{OCH}_3$), 5.80 (s, 1H, $-\underline{\text{CHOH}}$), 7.24-7.31 (m, 5H, $-\underline{\text{Ar}}$), 7.41 (d, $J = 8.1$, 2H, $-\underline{\text{Ar}}$), 7.94 (d, $J = 8.1$, 2H, $-\underline{\text{Ar}}$); ^{13}C -NMR (75 MHz) δ 52.1, 75.7, 126.1, 126.5, 127.7, 128.5, 128.9, 129.6, 143.1, 148.6, 166.8.

4-Fluorophenyl(phenyl)methanol (3d)⁴⁾

IR (KBr) ν 3327 (-OH), 1603, 1493, 1232, 1159, 1097, 1022, 922, 851, 816, 791, 727, 696, 648, 563, 532, 469, 409 cm^{-1} ; ^1H -NMR (CDCl_3 , 300MHz) δ 2.70 (brs, 1H, $-\underline{\text{OH}}$), 5.66 (s, 1H, $-\underline{\text{OH}}$), 6.90-6.98 (m, 2H, $-\underline{\text{Ar}}$), 7.18-7.31 (m, 7H, $-\underline{\text{Ar}}$); ^{13}C -NMR (75 MHz) δ 75.8, 115.5 (d, $J = 21.1$, $-\underline{\text{C}}-\text{CF}$), 126.7, 127.9, 128.5 (d, $J = 8.0$, $-\underline{\text{C}}-\text{C}-\text{CF}$), 128.8, 139.8 (d, $J = 3.5$, $-\underline{\text{C}}-\text{C}-\text{C}-\text{CF}$), 143.8, 162.3 (d, $J = 243.8$, $-\underline{\text{CF}}$); ^{19}F -NMR (282 MHz) δ -115.2.

Benzhydrol (3e)

IR (KBr) ν 3283 (-OH), 2683, 1597, 1493, 1447, 1394, 1344, 1250, 1175, 1018, 916, 762, 741, 702, 600, 548, 459 cm^{-1} ; ^1H -NMR (CDCl_3 , 300MHz) δ 2.18 (brs, 1H, $-\underline{\text{OH}}$), 5.83 (s, 1H, $-\underline{\text{CHOH}}$), 7.22-7.39 (m, 10H, $-\underline{\text{Ar}}$); ^{13}C -NMR (75 MHz) δ 76.2, 126.4, 127.5, 128.4, 143.6.

Phenyl(2-naphthyl)methanol (3f)⁵⁾

IR (KBr) ν 3219 (-OH), 3026, 1597, 1508, 1491, 1454, 1358, 1290, 1165, 1119, 1034, 1022, 953, 862, 816, 739, 702, 550, 471 cm^{-1} ; ^1H -NMR (CDCl_3 , 300MHz) δ 2.36 (brs, 1H, $-\underline{\text{OH}}$), 5.98 (s, 1H, $-\underline{\text{OH}}$), 7.23-7.49 (m, 8H, $-\underline{\text{Ar}}$), 7.76-7.88 (m, 4H, $-\underline{\text{Ar}}$); ^{13}C -NMR (75 MHz) δ 76.7, 125.0, 125.2, 126.2, 126.4, 126.9, 127.9, 128.3, 128.5, 128.8, 133.1, 133.4, 141.3, 143.8.

4-Methylphenyl(phenyl)methanol (3g)

IR (KBr) ν 3281 (-OH), 1510, 1456, 1350, 1269, 1171, 1038, 1026, 860, 845, 795, 775, 741, 698, 638, 542, 476 cm^{-1} ; ^1H -NMR (CDCl_3 , 300MHz) δ 2.21 (brs, 1H, $-\underline{\text{OH}}$), 2.32 (s, 3H, $-\underline{\text{CH}}_3$), 5.79 (s, 1H, $-\underline{\text{CHOH}}$), 7.11-7.38 (m, 9H, $-\underline{\text{Ar}}$); ^{13}C -NMR (75 MHz) δ 21.5, 76.4, 126.65, 126.72, 127.6, 128.6, 129.4, 137.5, 141.1, 144.1.

2-Methylphenyl(phenyl)methanol (3h)

IR (KBr) ν 3211 (-OH), 2950, 1602, 1491, 1448, 1348, 1285, 1242, 1173, 1040, 1015, 766, 739, 723, 698, 610 cm^{-1} ; ^1H -NMR (CDCl_3 , 300MHz) δ 2.16 (brs, 1H, $-\underline{\text{OH}}$), 2.24 (s, 3H, $-\underline{\text{CH}}_3$), 5.98 (s, 1H, $-\underline{\text{CHOH}}$), 7.11-7.31 (m, 8H, $-\underline{\text{Ar}}$), 7.48-7.51 (m, 1H, $-\underline{\text{Ar}}$); ^{13}C -NMR (75 MHz) δ 19.8, 73.7,

126.3, 126.5, 127.3, 127.7, 127.8, 128.7, 130.7, 135.6, 141.6, 143.0.

4-Methoxyphenyl(phenyl)methanol (3i)⁶⁾

IR (KBr) ν 3404 (-OH), 3009, 2909, 2835, 1611, 1587, 1516, 1493, 1445, 1304, 1252, 1177, 1111, 1018, 1009, 841, 810, 727, 696, 654, 623 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300MHz) δ 2.34 (brs, 1H, -OH), 3.75 (s, 3H, -OCH₃), 5.74 (s, 1H, -CHOH), 6.83 (d, J = 8.4, 2H, -Ar), 7.20-7.35 (m, 7H, -Ar); $^{13}\text{C-NMR}$ (75 MHz) δ 55.6, 76.1, 114.1, 126.6, 127.6, 128.1, 128.6, 136.4, 144.2, 159.2.

2-Methoxyphenyl(phenyl)methanol (3j)⁷⁾

IR (KBr) ν 3412 (-OH), 2905, 2835, 1587, 1491, 1464, 1437, 1242, 1184, 1112, 1026, 856, 754, 729, 698, 652 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300MHz) δ 3.14 (brs, 1H, -OH), 3.73 (s, 3H, -OCH₃), 6.01 (s, 1H, -CHOH), 6.81-6.92 (m, 2H, -Ar), 7.19-7.36 (m, 7H, -Ar); $^{13}\text{C-NMR}$ (75 MHz) δ 55.3, 71.9, 110.5, 120.6, 126.3, 126.9, 127.6, 127.9, 128.5, 131.8, 143.1, 156.4.

4-Methoxyphenyl(2-naphthyl)methanol (3k)⁸⁾

IR (KBr) ν 3331 (-OH), 1609, 1583, 1510, 1362, 1331, 1248, 1169, 1121, 1032, 951, 889, 866, 818, 781, 745, 600, 552, 475 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300MHz) δ 2.46 (s, 1H, -OH), 3.79 (s, 3H, -OCH₃), 5.94 (s, 1H, -CHOH), 6.86 (d, J = 8.7, 2H, -Ar), 7.25-7.49 (m, 5H, -Ar), 7.77-7.89 (m, 4H, -Ar); $^{13}\text{C-NMR}$ (75 MHz) δ 55.3, 75.8, 113.8, 124.6, 124.6, 125.8, 126.0, 127.5, 127.9, 128.0, 128.1, 132.6, 133.1, 135.8, 141.1, 158.9.

2-Methoxyphenyl(2-naphthyl)methanol (3l)

IR (KBr) ν 3429 (-OH), 1597, 1489, 1456, 1435, 1362, 1290, 1242, 1194, 1159, 1111, 1015, 885, 816, 754, 716, 482 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300MHz) δ 3.14 (brs, 1H, -OH), 3.78 (s, 3H, -CH₃), 6.21 (d, J = 4.2, 1H, -CHOH), 6.86-6.94 (m, 2H, -Ar), 7.21-7.27 (m, 2H, -Ar), 7.39-7.48 (m, 3H, -Ar), 7.75-7.85 (m, 4H, -Ar); $^{13}\text{C-NMR}$ (75 MHz) δ 55.3, 72.1, 110.6, 120.6, 124.7, 124.8, 125.4, 125.7, 127.4, 127.6, 127.80, 127.84, 128.6, 131.6, 132.5, 133.0, 140.4, 156.5; exact mass calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2$ 264.1150; found 264.1157.

4-Methylphenyl(2-naphthyl)methanol (3m)⁹⁾

IR (KBr) ν 3306 (-OH), 1601, 1508, 1412, 1364, 1331, 1244, 1165, 1123, 1016, 953, 903, 891, 866, 822, 762, 745, 544, 478 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300MHz) δ 2.26 (brs, 1H, -OH), 2.32 (s, 3H, -CH₃), 5.95 (s, 1H, -CHOH), 7.13 (d, J = 8.2, 2H, -Ar), 7.23-7.29 (m, 2H, -Ar), 7.29-7.48 (m, 3H, -Ar), 7.75-7.87 (m, 4H, -Ar); $^{13}\text{C-NMR}$ (75 MHz) δ 21.5, 76.5, 125.0, 125.1, 126.1, 126.4, 126.9, 127.9, 128.3, 128.5, 129.5, 133.1, 133.5, 137.6, 141.0, 141.5.

4-Fluorophenyl(2-naphthyl)methanol (3n)¹⁰⁾

IR (KBr) ν 3329 (-OH), 3055, 1601, 1508, 1364, 1225, 1157, 1123, 1097, 1018, 953, 889, 868, 822,

746, 552, 476 cm⁻¹; ¹H-NMR (CDCl₃, 300MHz) δ 2.47 (d, *J* = 3.3, 1H, -OH), 5.92 (d, *J* = 2.1, 1H, -CHOH), 6.96-7.02 (m, 2H, -Ar), 7.31-7.37 (m, 3H, -Ar), 7.42-7.49 (m, 2H, -Ar), 7.75-7.82 (m, 4H, -Ar); ¹³C-NMR (75 MHz) δ 75.7, 115.2 (d, *J* = 21.8, -C-CF), 124.5, 124.9, 126.0, 126.2, 127.6, 127.9, 128.3 (d, *J* = 9.2, -C-C-CF), 128.4, 132.8, 133.1, 139.2 (d, *J* = 2.9, -C-C-C-CF), 140.7, 162.0 (d, *J* = 243.8, -CF); ¹⁹F-NMR (282 MHz) δ -115.0.

4-Cyanophenyl(4-fluorophenyl)methanol (3o)¹¹⁾

IR (KBr) ν 3450 (-OH), 2237 (-CN), 1609, 1506, 1406, 1331, 1223, 1153, 1059, 1013, 874, 822, 781, 748, 586, 571, 536, 511 cm⁻¹; ¹H-NMR (CDCl₃, 300MHz) δ 2.49 (brs, -OH), 5.84 (s, 1H, -CHOH), 7.00-7.05 (m, 2H, -Ar), 7.25-7.32 (m, 2H, -Ar), 7.54 (dd, *J* = 30.9, 8.1, 4H, -Ar); ¹³C-NMR (75 MHz) δ 75.2, 111.5, 116.0 (d, *J* = 21.2, 2C, -C-CF), 118.9, 128.6 (d, *J* = 8.6, 2C, -C-C-CF), 132.5, 138.8, 148.8, 162.6 (d, *J* = 245.5, 1C, -CF); ¹⁹F-NMR (282 MHz) δ -113.9.

4-Cyanophenyl(2-fluorophenyl)methanol (3p)¹²⁾

IR (KBr) ν 3396 (-OH), 2230 (-CN), 1605, 1587, 1487, 1456, 1406, 1342, 1219, 1190, 1173, 1151, 1099, 1042, 1016, 943, 874, 847, 824, 793, 750, 619, 575, 494 cm⁻¹; ¹H-NMR (CDCl₃, 300MHz) δ 2.68 (brs, -OH), 6.16 (s, 1H, -CHOH), 7.00-7.60 (m, 8H, -Ar); ¹³C-NMR (75 MHz) δ 69.5, 111.5, 115.8 (d, *J* = 21.7, 1C, -C-CF), 119.0, 124.9 (d, *J* = 3.4, 1C, -C-C-CF), 127.1, 127.8 (d, *J* = 3.5, 1C, -C-C-CF), 129.9, 130.2 (d, *J* = 16.1, 1C, -C-CF), 132.5, 148.1, 161.6 (d, *J* = 244.9, 1C, -CF); ¹⁹F-NMR (282 MHz) δ -118.6.

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tetsuya041014-04
y4-151-puresamp1
1H

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya041014-04_14Oct2004

Pulse Sequence: s2pul

¹H NMR Spectra of 3a

tetsuya050107-04
y4-165-pure

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya050107-04_07Jan2005

Pulse Sequence: s2pul

^1H NMR Spectra of **3b**

y5-086-HC

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory: tetsuya050106-01_06Jan2005

Pulse Sequence: s2pul

^1H NMR Spectra of **3c**

tetsuya041012-04
y4-148-pure sample
1H

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya041012-04_13Oct2004

Pulse Sequence: s2pul

^1H NMR Spectra of **3d**

Y5-004 (H)

^1H NMR Spectra of **3e**

tetsuya041011-02
y4-150-pure-sample
1H

3m

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya041011-02_11Oct2004

Pulse Sequence: s2pul

¹H NMR Spectra of **3f**

tetsuya041020-01
y4-163-pure sample
1H

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya041020-01_20Oct2004

Pulse Sequence: s2pul

¹H NMR Spectra of **3g**

tetsuya041106-04
y4-195-puresample
1H

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya041106-04_06Nov2004

Pulse Sequence: s2pul

¹H NMR Spectra of **3h**

tetsuya041220-04
y5-015-CH

¹H

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya041220-04_20Dec2004

Pulse Sequence: s2pul

¹H NMR Spectra of **3i**

tetsuya041209-06
y5-001-pure
1H

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya041209-06_09Dec2004

Pulse Sequence: s2pul

¹H NMR Spectra of 3j

4a ¹H 1

¹H NMR Spectra of **3k**

4C (IH)

(11)

¹H NMR Spectra of **3I**

Archive directory: /export/home/vnmr1/vnmrSYS/data
Sample directory: tetsuya041209-09_09Dec2004

Pulse Sequence: s2pul

4c (41,

^{13}C NMR Spectra of **3I**

TETUYA05.IRS: polyallylamine cont b-CD

日付: 2004/12/18
 データ種別: HYPER IR
 横座標: 1/cm
 最小波数: 401.17
 データ点数: 2178
 デイン: auto

時刻: 14:01:36
 ユーザー: 機能有機化学研究室
 縦座標: %T
 最大波数: 4599.91
 データ間隔: 1.92868
 パワー: auto

積算回数: 40
 検出器: Happ
 波数範囲: 1/cm
 分解能: 4.0
 ミラー速度: 2.8(low)

standard

tetsuya041020-09

y4-166-pure sample

¹H

PS

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory: tetsuya041020-09_20Oct2004

Pulse Sequence: s2pul

¹H NMR Spectra of 3m

4g ('H)

y5-088-HFC

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory: tetsuya050107-01_07Jan2005

Pulse Sequence: s2pul

¹H NMR Spectra of **3n**

Y4-164
(14)

^1H NMR Spectra of **30**

15-069
(H)

^1H NMR Spectra of **3p**