Supporting Information

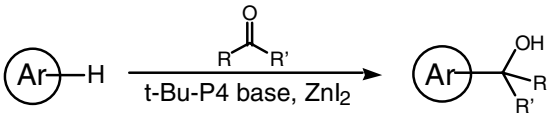
For

A New Strategy for Deprotonative Functionalization of Aromatics: Transformation with Excellent Chemoselectivity and Unique Regioselectivities Using t-Bu-P4 base

General Comments.

^{1}H-NMR spectra were recorded on a Varian Gemini 2000 using tetramethylsilane as a internal standard. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in herts (Hz). The following abbreviations are used : s= singlet, d= doublet, m= multiplet, brs= broad singlet and dd= double-doublet. Mass spectra were recorded on JEOL JMS-DX303 or JEOL JMS-AX500 spectrometer. IR spectra were measured with SensIR ATR FT-IR.

Genaral procedure for deprotonative functionalization of aromatics with t-Bu-P4 base and ZnI_2



A mixture of a substrate (**3**, **5**, **7**, **9**) (0.3 mmol), an electrophile (0.5 mmol) and dry THF (1 mL) or dry toluene (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under Argon atmosphere. ZnI_2 (100mg, 0.31 mmol) was added to the mixture and the suspension was stirred for 10 minutes at ambient temperature. t-Bu-P4 base (0.3-0.9 mmol) was added to the suspension at –78 ˚C and the reaction was allowed to warm to the ambient temperature gradually and the mixture was stirred overnight. After the reaction, saturated aq. NH_4Cl and H_2O were added to the mixture. The mixture was extracted with $CHCl_3$ (30 mL x 3) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography.

(2-Benzothiazolyl)diphenylmethanol (2)

Colorless needles (recrystallized from ether-hexane)

mp 147-148 °C (lit.[a] mp 149.5-150 °C)

^{1}H-NMR (300MHz, $CDCl_3$): δ 4.36 (s, 1H), 7.33-7.42 (m, 7H), 7.45-7.52 (m, 5H), 7.84 (d, 1H, *J*=7.4 Hz), 8.04(d, 1H, *J*=8.8 Hz)

IR (crystal) 3323, 1490, 1447, 1436, 1335, 1316, 1216, 1138, 1042 cm^{-1}

MS (EI) *m/z* 317(M^+)

HRMS: Calcd.$C_{20}H_{15}NOS$: 317.0874, Found: 317.0862

3-Bromo-α, α-diphenyl-4-pyridinemethanol (4a)

Colorless needles (recrystallized from ether)

mp 182-183 °C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 4.34 (s, 1H), 6.70 (d, 1H, *J*=4.9 Hz), 7.21-7.27 (m, 4H), 7.31-7.40 (m, 6H), 8.38 (d, 1H, *J*=4.9 Hz), 8.72(s, 1H)

IR (crystal) 3159, 3054, 3031, 1578, 1490, 1445, 1399, 1196, 1028 cm^{-1}

MS (EI) *m/z* 339, 341(M^+)

HRMS: Calcd.$C_{18}H_{14}NO^{79}Br$: 339.0259, Found: 339.0259

3-Bromo-α-phenyl-4-pyridinemethanol (4b)

Colorless needles (recrystallized from petroleum ether- ether)

mp 133-134 °C (lit.[b] mp 130-132 °C)

^{1}H-NMR (300MHz, $CDCCl_3$): δ 2.80 (brs, 1H), 6.07 (s, 1H), 7.31-7.41 (m, 5H), 7.68 (d, 1H, *J*=5.2 Hz), 8.53 (d, 1H, *J*=5.2 Hz), 8.61(s, 1H)

IR (crystal) 3114, 3083, 1586, 1457, 1403, 1310, 1055, 1023 cm^{-1}

MS (EI) *m/z* 263, 265(M^+)

HRMS: Calcd.$C_{12}H_{10}NO^{79}Br$: 262.9946, Found: 262.9976

3-Bromo-α-(t-butyl)-4-pyridinemethanol (4c)

Colorless plates (recrystallized from petroleum ether- ether)

mp 107-109 °C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 1.00 (s, 9H), 2.59 (brs, 1H), 4.91 (s, 1H), 7.47 (d, 1H, *J*=5.2 Hz), 8.45 (d, 1H, *J*=5.2 Hz), 8.63(s, 1H)

IR (crystal) 3159, 3097, 2962, 2896, 2867, 1588, 1468, 1397, 1362, 1210, 1071, 1015 cm^{-1}

MS (EI) *m/z* 243, 245(M^+)

Diphenyl(4-pyridazinyl)methanol (6a)

Colorless needles (recrystallized from $CHCl_3$-petroleum ether)

mp 229-230 °C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 2.98 (s, 1H), 7.20-7.26 (m, 4H), 7.33-7.39 (m, 6H), 7.49 (dd, 1H, *J*=5.4 Hz, *J*=2.4 Hz), 9.13 (dd, 1H, *J*=5.4 Hz, *J*=1.2 Hz), 9.20 (dd, 1H, *J*=2.4 Hz, *J*=1.2 Hz)

IR (crystal) 3105, 3054, 1590, 1486, 1447, 1422, 1351, 1210, 1183, 1167, 1046, 1027 cm^{-1}

MS (EI) *m/z* 262 (M^+)

HRMS: Calcd.$C_{17}H_{14}N_2O$: 262.1105, Found: 262.1058

4-Benzoylpyridazine (6b´)

Colorless plates (recrystallized from petroleum ether- ether)

mp 105.5-107 °C (lit.[c] mp 106-108 °C)

^{1}H-NMR (300MHz, $CDCCl_3$): δ 7.54-7.60 (m, 2H), 7.69-7.77 (m, 2H), 7.81-7.85 (m, 2H), 9.45-9.49 (m, 2H)

IR (crystal) 3056, 2925, 2852, 1654, 1592, 1578, 1451, 1353, 1318, 1289, 1275, 1175, 1158, 1050 cm^{-1}

MS (EI) *m/z* 184 (M^+)

HRMS: Calcd.$C_{11}H_8N_2O$: 184.0636, Found: 084.0632

2,2-dimethyl-1-(4-pyridazinyl)propanol (6c)

Colorless needles (recrystallized from petroleum ether- ether)

mp 155-156.5 °C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 0.94 (s, 9H), 2.72 (brs, 1H), 4.44 (s, 1H), 7.47 (dd, 1H, *J*=5.2 Hz, *J*=2.2 Hz), 9.10-9.12 (m, 2H)

IR (crystal) 3195, 2962, 2865, 2715, 1592, 1476, 1383, 1061 cm^{-1}

MS (EI) *m/z* 166 (M^+)

HRMS: Calcd.$C_9H_{14}N_2O$: 166.1105, Found: 166.1090

Diphenyl(5-pyrimidinyl)methanol (8a)

Colorless prisms (recrystallized from ether-hexane)

mp 171-172 °C (lit.[d] mp 171-173 °C)

^{1}H-NMR (300MHz, $CDCCl_3$): δ 3.13 (s, 1H), 7.20-7.26 (m, 4H), 7.30-7.39 (m, 6H), 8.70(s, 2H), 9.10 (s, 1H)

IR (crystal) 3251, 1559, 1436, 1407, 1229, 1165, 1040, 1025 cm^{-1}

MS (EI) *m/z* 262 (M^+)

HRMS: Calcd.$C_{17}H_{14}N_2O$: 262.1105, Found: 262.1096

Phenyl(5-pyrimidinyl)methanol (8b)

Viscous oil

^{1}H-NMR (300MHz, $CDCCl_3$): δ 3.20 (brs, 1H), 5.88 (s, 1H), 7.31-7.43 (m, 5H), 8.71 (s, 2H), 9.05 (s, 1H)

IR (crystal) 3242, 1565, 1407, 1289, 1177, 1038, 1025 cm^{-1}

MS (EI) *m/z* 186 (M^+)

HRMS: Calcd.$C_{11}H_{10}N_2O$: 186.0793, Found: 186.0759

2,2-Dimethyl-1-(5-pyrimidinyl)propanol (8c)

Colorless plates (recrystallized from petroleum ether- ether)

mp 95-97.5 °C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 0.95 (s, 9H), 2.30 (brs, 1H), 8.69 (s, 2H), 9.12 (s, 1H)

IR (crystal) 3299, 2960, 2869, 2856, 1567, 1409, 1364, 1192, 1167, 1065, 1044, 1013 cm^{-1}

MS (EI) *m/z* 166 (M^+)

HRMS: Calcd.$C_9H_{14}N_2O$: 166.1105, Found: 166.1067

(2-Bromo-5-cyanophenyl)diphenylmethanol (10a)

Colorless needles (recrystallized from ether-petroleum ether)

mp 157.5-158.5 °C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 4.31 (s, 1H), 7.05 (d, 1H, *J*=2.2 Hz), 7.20-7.24 (m, 4H), 7.26-7.40 (m, 6H), 7.45 (dd, 1H, *J*=8.2 Hz, *J*=2.2 Hz), 7.74 (d, 1H, *J*=8.2 Hz)

IR (crystal) 3529, 2231, 1584, 1447, 1383, 1335, 1310, 1273, 1158, 1032, 1015 cm^{-1}

MS (EI) *m/z* 363, 365 (M^+)

HRMS: Calcd.$C_{20}H_{14}NO^{79}Br$: 363.0259, Found: 363.0226

(2-Bromo-5-cyanophenyl)phenylmethanol (10b)

Colorless prisms (recrystallized from ether-hexane)

mp 103-105 °C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 2.59 (brs, 1H), 6.15 (s, 1H), 7.32-7.38 (m, 5H), 7.43 (dd, 1H, *J*=8.2 Hz, *J*=2.2 Hz), 7.65 (d, 1H, *J*=8.2 Hz), 8.01 (d, 1H, *J*=2.2 Hz)

IR (crystal) 3423, 3089, 3054, 2240, 1590, 1453, 1391, 1312, 1239, 1216, 1185, 1136, 1052, 1017 cm^{-1}

MS (EI) *m/z* 287, 289 (M^+)

HRMS: Calcd.$C_{14}H_{10}NO^{79}Br$: 286.9946, Found: 286.9973

1-(2-Bromo-5-cyanophenyl)-2,2-dimethylpropanol (10c)

Colorless needles (recrystallized from hexane)

mp 100-102 °C

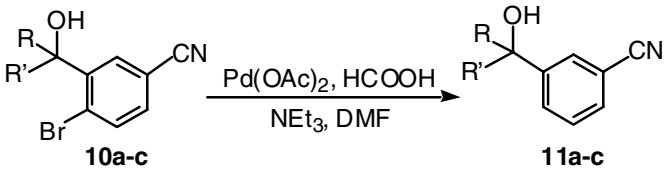
^{1}H-NMR (300MHz, $CDCCl_3$): δ 0.99 (s, 9H), 2.04 (s, 1H), 4.99 (s, 1H), 7.39 (dd, 1H, *J*=8.52 Hz, *J*=2.20 Hz), 7.65 (d, 1H, *J*=8.52 Hz), 7.85 (d, 1H, *J*=2.20 Hz)

IR (crystal) 3467, 2956, 2238, 1588, 1461, 1065, 1021, 1009 cm^{-1}

MS (EI) *m/z* 267, 269 (M^+)

HRMS: Calcd.$C_{12}H_{14}NO^{79}Br$: 267.0259, Found: 267.0267

Ref.15: Determination of the regiochemistry of the reaction with 4-bromobenzonitrile



10a-c **11a-c**

A mixture of the generated 1,2-adducts (**10a-c**), $Pd(OAc)_2$, hormicacid, NEt_3 and DMF(1 ml) was placed in sealed tube under Argon atmosphere. The reaction was carried out at 50°C overnight. After the reaction, saturated aq. NH_4Cl and H_2O were added to the mixture. The mixture was extracted with $CHCl_3$ (30 mL x 3) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography.

(3-Cyanophenyl)diphenylmethanol (11a)

Colorless prisms (recrystallized from $CHCl_3$-petroleum ether)

mp 96.5-97 °C (lit.[e] mp 96.5-98.5 °C)

^{1}H-NMR (300MHz, $CDCCl_3$): δ 2.83 (s, 1H), 7.21-7.45 (m, 11H), 7.56-7.62 (m, 2H), 7.66 (d, 1H, *J*=1.65 Hz)

IR (crystal) 3504, 2223, 1598, 1578, 1447, 1434, 1164, 1025 cm^{-1}

MS (EI) *m/z* 285 (M^+)

HRMS: Calcd.$C_{20}H_{15}NO$: 285.1153, Found: 285.1154

(3-Cyanophenyl)phenylmethanol (11b)

Colorless prisms (recrystallized from ether-hexane)

mp 109-111°C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 2.38 (brs, 1H), 5.85 (s, 1H), 7.28-7.39 (m, 5H), 7.43 (t, 1H, *J*=7.69 Hz), 7.53-7.56 (m, 1H), 7.62 (d, 1H, *J*=7.69 Hz), 7.71 (s, 1H)

IR (crystal) 3425, 2229, 1582, 1493, 1480, 1453, 1225, 1191, 1140, 1038, 1023 cm^{-1}

MS (EI) *m/z* 209 (M^+)

HRMS: Calcd.$C_{14}H_{11}NO$: 209.0840, Found: 209.0867

1-(3-cyanophenyl)-2,2-dimethylpropanol (11c)

Pale yellow viscous oil

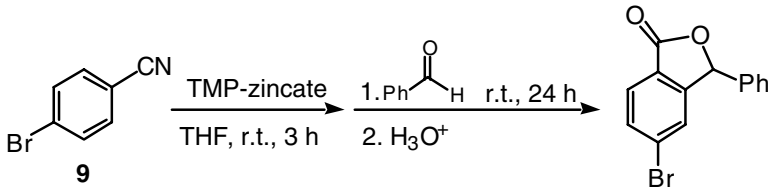
^{1}H-NMR (300MHz, $CDCCl_3$): δ 0.92 (s, 9H), 2.03 (brs, 1H), 4.43 (s, 1H), 7.42 (m, 1H), 7.54-7.58 (m, 2H), 7.62 (d, 1H, *J*=1.65 Hz)

IR (neat) 3491, 2231, 1480, 1364, 1237, 1144, 1054, 1011cm^{-1}

MS (EI) *m/z* 189 (M^+)

HRMS: Calcd.$C_{12}H_{15}NO$: 189.1153, Found: 189.1142

Ref.16: The reaction of 4-bromobenzonitrile with TMP-zincate [f]



5-Bromo-3-phenylphthalide

Colorless needles (recrystallized from ether-petroleum ether)

mp 187-190°C

^{1}H-NMR (300MHz, $CDCCl_3$): δ 6.37 (s, 1H), 7.26-7.29 (m, 2H), 7.40-7.43 (m, 3H), 7.50 (s, 1H), 7.70 (d, 1H, *J*=8.2 Hz), 7.83 (d, 1H, *J*=8.2 Hz)

IR (crystal) 1742, 1603, 1590, 1465, 1416, 1324, 1291, 1202, 1177, 1123, 1071cm^{-1}

MS (EI) *m/z* 288, 290 (M^+)

HRMS: Calcd.$C_{14}H_9O_2{}^{79}Br$: 287.9786, Found: 287.9773

References of supporting information

a) Chikashita, H.; Ishibaba, M.; Ori, K.; Ito, K. *Bull, Chem, Soc, Jpn.* **1988**, *61*, 3637.

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d) Kress, T. J.; Moore, L. L. *J. Het. Chem.* **1972**, *9*, 1161.

e) Parham, W. E.; Jones, L. D. *J. Org. Chem.* **1976**, *41*, 1187.

f) General procedure for the reaction with TMP-zincate, see; (1) Kondo, Y.; Shilai, M.; Uchiyama, M.; Sakamoto, T. *J. Am. Chem. Soc.* **1999**, *121*, 3539-3540. (2) Imahori, T.; Uchiyama, M.; Sakamoto, T.; Kondo, Y. *Chem. Commun.* **2001**, 2450-2451. (3) Uchiyama, M.; Miyoshi, T.; Kajihara, Y.; Sakamoto, T.; Otani, Y.; Ohwada, T.; Kondo, Y. *J. Am. Chem. Soc.* **2002**, *124*, 8514-8515.