

Ruthenium-Catalyzed Coupling of Aldimines with Arylboronates: New Synthetic Method of Diaryl Ketones

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Electronic Supplementary Information (ESI)

General Experiments. Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column chromatography were monitored by analytical thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60 F-254) using UV light as a visualizing agent and *p*-anisaldehyde solution, and heat as developing agent. Infrared spectra were obtained on a Nicolet Impact 400 spectrometer. Gas chromatographic analyses were performed on a Donam DS 6200 instrument with FID detector and a Hewlett Packard HP-5 capillary column. Low-resolution mass spectra were measured on a Hewlett-Packard HP G1800A GCD system equipped with a Hewlett Packard HP-5 capillary column. ¹H NMR and ¹³C NMR were recorded on a Bruker Advance/DPX 250 with chemical shifts reported relative to residual deuterated solvent peaks. ¹H NMR spectra were referenced to tetramethylsilane (δ 0.00 ppm) as an internal standard and are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). ¹³C NMR spectra were referenced to the residual CDCl₃ (δ 77.0 ppm). Elemental Analysis was performed by the Organic Chemistry Research Center, Sogang University (Seoul 121-742, Korea). High-resolution mass spectrometry was performed by the National Center for Inter-University Facilities, Seoul National University (Seoul 151-742, Korea).

Materials. All commercially available reagent grade chemicals (aldehydes, 2-amino-3-picoline, 1-hexene, cyclohexene, methyl vinyl ketone, 1-cyclohexenone, Ru₃(CO)₁₂,

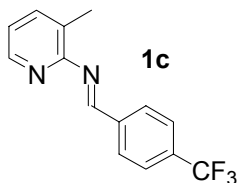
boronic acids) were purchased from Aldrich Chemical Company, TCI, and Junsei Chemical Company and used as received without further purification unless otherwise stated. Anhydrous 1,4-dioxane (Aldrich) and acetone (Merck) were purchased. Reactions requiring anhydrous conditions were performed under argon using a glove box.

Preparation of Picolyl-Imines

The following aldimines are known compounds and gave data consistent with that reported in the literature:

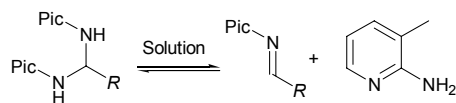
Benzylidene-(3-methyl-pyridin-2-yl)-imine (**1a**)¹ and 4-methoxybenzylidene-(pyridin-2-yl)-imine (**1b**)²

The preparation of **4-trifluoromethylbenzylidene-(3-methyl-pyridin-2-yl)-imine (1c)**:



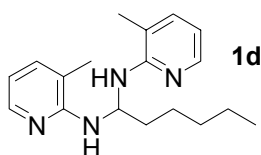
4-Trifluoromethyl-benzaldehyde (2 g, 11.48 mmol) was added to a stirred solution of *p*TSA (5 mol %, 98.8 mg) in benzene (20 mL) at room temperature. 2-Amino-3-picoline (1.24 g, 11.48 mmol) was added and the mixture was refluxed overnight in a Dean-Stark apparatus. When no further evolution of water was observed the reaction mixture was cooled and concentrated *in-vacuo*. The residue was purified by distillation under reduced pressure to give the *imine* (2.15 g, 71%) as a reddish oil. ¹H NMR (250 MHz, CDCl₃): δ 9.1 (s, 1H), 8.3 (d, *J* = 4.7 Hz, 1H), 8.1 (d, *J* = 8 Hz, 2H), 7.7 (d, *J* = 8 Hz, 2H), 7.5 (d, *J* = 7.4 Hz, 1H) 7.1 (dd, *J* = 4.7, 7.4 Hz, 1H), 2.4 (s, 3H); ¹³C NMR (62.9 MHz, CDCl₃): δ 159.8, 158.6, 146.2, 139.4, 139.1, 132.6 (q, *J*_{CF} = 32 Hz, CF₃), 129.5, 126.1, 125.6, 122.5, 121.8, 17.3; MS: *m/z* (%): 263 (M⁺ - H⁺, 40.0) 245 (4.5), 236 (7.4), 222 (0.4), 195 (2.2), 167 (2.0), 145 (2.4), 119 (6.1), 93 (100), 65 (10.5), 51 (1.3), 27 (0.4); IR (neat): 3048, 2928, 1624, 1573, 1452, 1416, 1323, 1260, 1210, 1167, 1127, 1064, 1016, 986, 890, 841, 790, 598 cm⁻¹; Elemental Anal. calcd for C₁₄H₁₁F₃N₂: C ; 63.63, H ; 4.20, N ; 10.60 found C ; 63.65, H ; 4.14, N ; 10.54.

Aminals (1d, 1e)



The following aminals have the above dissociation process also in solution (CDCl_3). For this reason, only major ^1H NMR chemical shifts of aminal are presented.

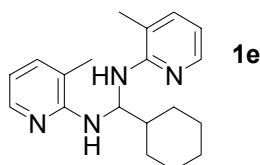
The preparation of *N*-(1-(3-methylpyridin-2-ylamino)hexyl)-3-methylpyridin-2-amine (**1d**):



N-(1-(3-methylpyridin-2-ylamino)hexyl)-3-methylpyridin-2-amine

n-hexanal (1 g, 9.98 mmol) was added to 2-amino-3-picoline (2 equiv.) at room temperature over 4\AA molecular sieve. On standing at room temperature for 2 days, pale yellow solid was formed. It was dissolved in methylene chloride and filtered. The resulting solution was concentrated and then re-crystallized from methylene chloride/hexane mixture at refrigerator. And it was filtered and dried *in-vacuo* to give the *aminal* as a white solid (82%, 2.44 g): ^1H NMR (250 MHz, CDCl_3): δ 7.9 (d, $J = 4.0$ Hz, 2H), 7.1 (d, $J = 6.2$ Hz, 2H), 6.4 (dd, $J = 4.0, 6.2$ Hz, 2H), 5.7 (d, $J = 7.4$ Hz, 2H, NH), 5.6 (dt, $J = 7.5, 7.4$ Hz, 1H), 2.2 (bq, 2H), 1.4-1.3 (m, 6H), 0.9-0.8 (m, 3H); IR (KBr): 3361, 3292, 2960, 2915, 2854, 1600, 1582, 1512, 1469, 1410, 1381, 1331, 1306, 1282, 1249, 1038, 993, 765, 701, 646, 523 cm^{-1} ; HRMS (CI) calcd for $\text{C}_{18}\text{H}_{26}\text{N}_4$ 298.2157; found 299.2232 ($\text{M}+\text{H}^+$).

The preparation of *N*-((3-methylpyridin-2-ylamino)(cyclohexyl)methyl)-3-methylpyridin-2-amine (**1e**):



N-((3-methylpyridin-2-ylamino)(cyclohexyl)methyl)-3-methylpyridin-2-amine

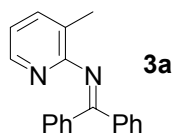
Cyclohexane carboxaldehyde (1 g, 8.91 mmol) was added to 2-amino-3-picoline (2 equiv) at room temperature over 4Å molecular sieve. On standing at room temperature for 2 days, pale yellow solid was formed. It was dissolved in methylene chloride and filtered. The resulting solution was concentrated and then re-crystallized from methylene chloride/hexane mixture at refrigerator. And it was filtered and dried *in-vacuo* to give the *aminal* as a pale yellow solid (67%, 1.85 g): ¹H NMR (250 MHz, CDCl₃): δ 7.9 (d, *J* = 4.3 Hz 2H), 7.1 (d, *J* = 6.3 Hz, 2H), 6.4 (dd, *J* = 4.3, 6.3 Hz, 2H), 5.7 (d, *J* = 7.9 Hz, 2H, NH), 5.3 (bq, 1H), 2.5 (m, 1H), 1.7-0.9 (m, 10H); IR (KBr): 3414, 3003, 2921, 2846, 1608, 1473, 1413, 1383, 1308, 1252, 1181, 1144, 1110, 1062, 1024, 994, 953, 893, 770, 699, 605, 549, 504 cm⁻¹; HRMS (CI) calcd for C₁₉H₂₆N₄ 310.2157; found 311.2231 (M+H⁺). Elemental Anal. calcd for C₁₉H₂₆N₄: C ; 73.51, H ; 8.44, N ; 18.05 found C ; 73.57, H ; 8.46, N ; 18.04.

Coupling Reactions

The following ketones, coupling adducts, are known compounds (commercially available) and were identified by comparison with authentic sample.

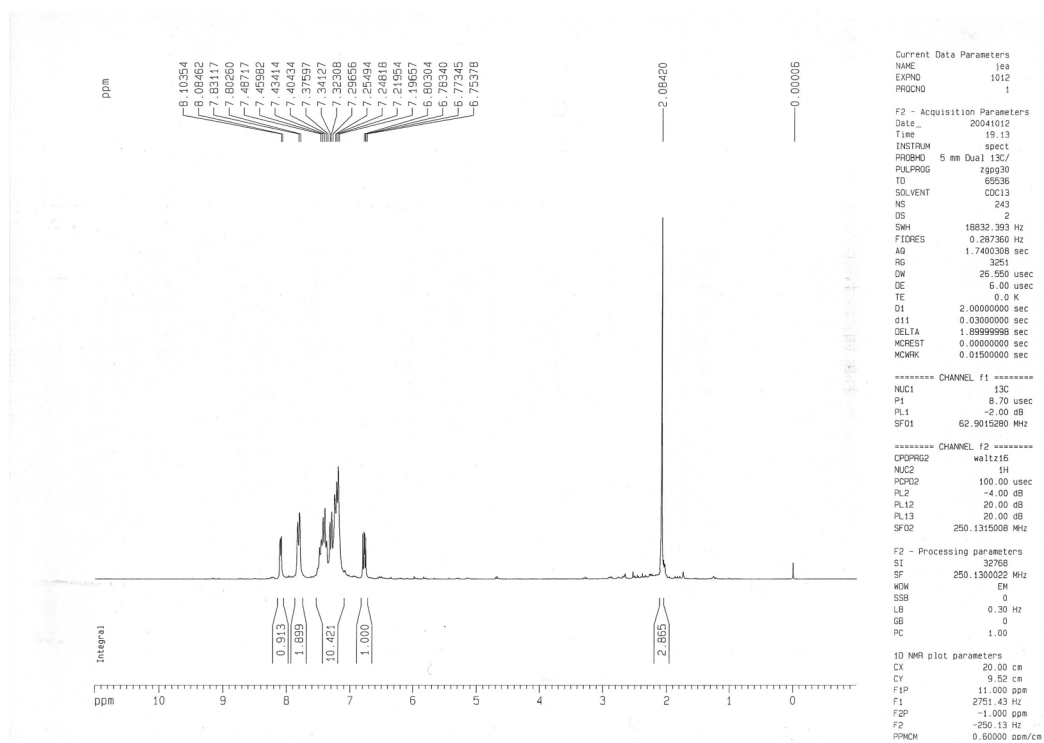
Benzophenone (**4aa**) (registry number: 119-61-9), (4-methoxyphenyl)(phenyl)methanone (**4ab**) (registry number: 611-94-9), (4-methylphenyl)(phenyl)methanone (**4ac**) (registry number: 134-84-9), (2-methylphenyl)(phenyl)methanone (**4ad**) (registry number: 131-58-8), (4-fluorophenyl)(phenyl)methanone (**4ae**) (registry number: 345-83-5), (4-chlorophenyl)(phenyl)methanone (**4af**) (registry number: 134-85-0), (3-chlorophenyl)(phenyl)methanone (**4ag**) (registry number: 1016-78-0), (4-bromophenyl)(phenyl)methanone (**4ah**) (registry number: 90-90-4), bis(4-methoxyphenyl)methanone (**4bb**) (registry number: 90-96-0), (4-(trifluoromethyl)phenyl)(4-methoxyphenyl)methanone (**4cb**) (registry number: 6185-76-8), 1-(4-methoxyphenyl)hexan-1-one (**4db**) (registry number: 6397-82-6), and cyclohexyl(4-fluorophenyl)methanone (**4ee**) (registry number: 85014-02-4) and 1-phenylheptan-1-one (**8**) (registry number: 1671-75-6)

4cb³ (registry number: 6185-76-8), **4de**⁴ (registry number: 1426-70-6), **4eb**⁵ (registry number: 7469-80-9) and **7a**⁶ (registry number: 70720-38-6) are known compounds and gave data consistent with that reported in the literature.



3-methyl-*N*-(diphenylmethylene)pyridin-2-amine

^1H NMR (250 MHz, CDCl_3): δ 8.1 (d, $J = 4.7$ Hz, 1H), 7.8 (d, $J = 7.1$, 2H), 7.4-7.1 (m, 9H), 6.7 (dd, $J = 4.7, 7.2$ Hz, 1H), 2.0 (s, 3H); ^{13}C NMR (62.9 MHz, CDCl_3): δ 145.9, 138.2, 129.8, 129.0, 128.2, 127.9, 123.3, 118.9, 17.6; MS: m/z (%): 272 (M^+ , 33.7), 271 (69.5), 243 (0.4), 228 (0.2), 195 (14.8), 168 (100), 136 (7.3), 135 (13.9), 115 (2.2), 92 (15.9), 51 (3.2), 39 (3.3), 18 (0.3); IR (neat): 2925, 1629, 1583, 1414, 1342, 1113, 954, 793, 697, 582 cm^{-1} .



References

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