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Asymmetric Ni-catalyzed arylation of aromatic aldehydes with arylboroxines

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Abstract—Development of asymmetric Ni-catalyzed 1,2-addition to aromatic aldehydes of arylboroxines is described.

1. Introduction

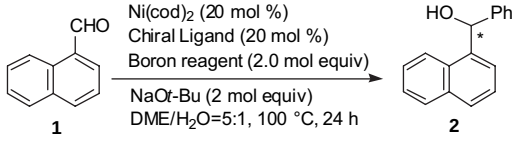
The asymmetric arylation of aromatic aldehydes is one of the most important carbon–carbon bond-forming reactions,[1] because chiral diarylmethanols are important intermediates for the synthesis of biologically active compounds.[2] Among various arylmetal reagents used, arylboron reagents are more desirable due to the recent demand for safe and sustainable organic synthesis, because their reagents are less toxic and air-stable. Miyaura's group found that Rh(I) complexes catalyze 1,2-addition to aldehyde with arylboronic acid in 1998,[3] and later, attention has been focused on the arylation with the combination of the Rh catalyst and arylboronic acid.[4] From the viewpoint of cost and practical convenience, the use of a much more cheaper metal catalyst such as Ni than Rh is desirable.[5,6] Herein, we would like to report a new method for asymmetric Ni-catalyzed arylation of aromatic aldehydes with arylboroxines.

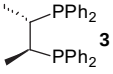
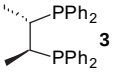
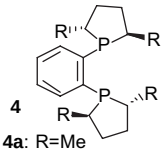
2. Results and discussion

At first, our studies focused on determination of the basic conditions for the asymmetric arylation of 1-naphthaldehyde (**1**). The selected results are summarized in Table 1. The dramatic effect of the boron reagent and ligand was observed. When phenylboronic acid as a boron reagent was used, the results for arylation were not promising at all (entries 1–4). The use of phenylboroxine as a boron reagent was then examined. After intensive screening of ligands as shown in entries 5–10, we found that the result was brought to an acceptable level by using (*R*,*R*)-Et–Duphos (**4b**) (entry 7).

Next, with the promising result using (*R*,*R*)-Et–Duphos (**4b**), further intensive optimization was performed (Table 2). Other bases such as KO*t*-Bu, LiO*t*-Bu and Et_3N gave less satisfactory results. When the reaction time was made longer from 24 to 48 h, an increase in the yield was observed (80% of entry 7, Table 1 vs 97% yield of entry 1, Table 2). As a

Table 1. Initial optimization of phenylation reaction



Entry	Achiral ligand	Boron reagent	Yield[a] (%)	ee[b] (%)
1	(*S*)-DIOP	$PhB(OH)_2$	Trace	—
2	 **3**	$PhB(OH)_2$	7	—
3	(*S*)-BINAP	$PhB(OH)_2$	Trace	—
4	(*S*)-Segphos	$PhB(OH)_2$	Trace	—
5	 **3**	$(PhBO)_3$	65	33 (*R*)
6	 **4** **4a**: R=Me	$(PhBO)_3$	68	67 (*R*)
7	**4b**: R=Et	$(PhBO)_3$	80	69 (*R*)
8	**4c**: R=*i*-Pr	$(PhBO)_3$	Trace	—
9	(*S*)-BINAP	$(PhBO)_3$	Trace	—
10	(*S*)-Segphos	$(PhBO)_3$	Trace	—

[a] Remainder of mass balance was the starting 1-naphthaldehyde **1**.
[b] Determined by HPLC analysis.

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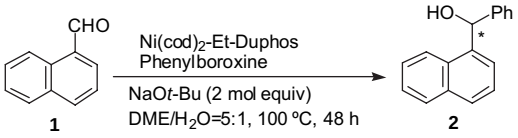
Table 2. Further optimization of the reaction conditions



Entry	$Ni(cod)_2$–**4b** (mol %)	$(PhBO)_3$ (mol equiv)	NaO*t*-Bu (mol equiv)	Yield (%)	ee[a] (%)
1	20	2	1	97	69 (*R*)
2	20	2/3	1	84[b]	69 (*R*)
3	10	2	1	95	69 (*R*)
4	10	2/3	1	64[b]	69 (*R*)
5[c]	10	2/3	1/2	93	68 (*R*)
6	10	2/3	0	90	68 (*R*)

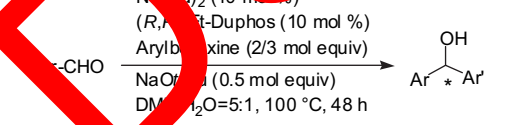
[a] Determined by HPLC analysis.
[b] Remainder of mass balance was the starting **1**.
[c] $Ni(cod)_2$–**4b** of 5 mol % gave same results.

result, the best reaction conditions from the viewpoint of chemical yield and enantioselectivity were determined to be 10 mol % of $Ni(cod)_2$ and (*R*,*R*)-Et–Duphos (**4b**), 2/3 mol equiv of $(PhBO)_3$ and 0.5 mol equiv of NaO*t*-Bu (from the viewpoint of easy handling, NaO*t*-Bu was used in place of NaOH) in DME/H_2O (5:1) at 100 °C for 48 h (entry 5).

Finally, we explored the effects of the aromatic aldehydes and boroxines under the optimal conditions shown in Table 3. 1-Naphthaldehyde and the 2-substituted aromatic aldehydes except for entry 1 exhibited acceptable 65–78% enantioselectivity with good chemical yields. On the other hand, the enantioselectivity of the aromatic aldehydes without a 2-substituted group was low or moderate.

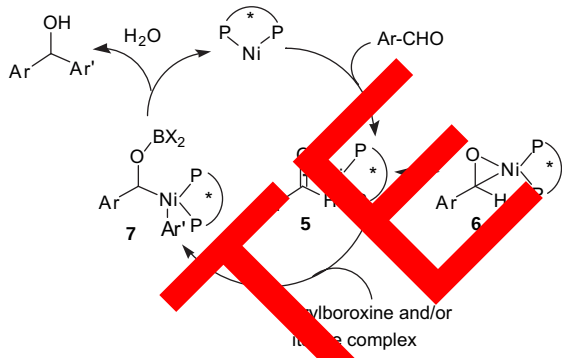
We are tempted to assume the mechanism for this arylation as follows (Scheme 1).[7] A Ni(0) complex initially reacts enantiodiscriminatively with aromatic aldehyde to generate η^2-coordinated complex[8] **5** and/or resonance type **6**. Subsequent trans-metallation with arylboroxine and/or its ate complex by the action of OH affords the intermediate **7**. In this step, enantiodiscrimination of **5** and/or **6** might be kept, although further investigation is needed, and so this asymmetric arylation would give good enantioselectivity. Finally, reductive elimination and protonolysis furnish the diarylmethanol and regenerate the Ni(0) complex. However, the reason that 1-naphthaldehyde and 2-substituted aromatic aldehydes exhibited good enantioselectivity is not clear at the present time.

Table 3. Substituted arylboroxine generality



Entry	Aromatic aldehyde (Ar=)	Arylboroxine (Ar′=)	Yield (%)	ee[a] (%)
1	1-Naphthyl	4-*i*-PrO–C_6H_4	94	49
2	1-Naphthyl	4-F–C_6H_4	83[b]	65
3	1-Naphthyl	4-Cl–C_6H_4	87	66 (*R*)
4	2-Ph–C_6H_4	Ph	83[b]	72
5	2-Me–C_6H_4	Ph	91	78 (*R*)
6	2-Me–4-MeO–C_6H_3	Ph	86[b]	74
7	2-Me–3-F–C_6H_3	Ph	93	75
8	4-Me–C_6H_4	Ph	87[b]	35 (*R*)
9	4-MeO–C_6H_4	Ph	86[b]	32 (*R*)
10	4-F–C_6H_4	Ph	93	55 (*R*)

[a] Determined by HPLC analysis.
[b] Remainder of mass balance was the starting aldehyde.



Scheme 1. Proposed reaction mechanism.

3. Conclusion

In summary, we have found that 1-naphthaldehyde and the 2-substituted aromatic aldehydes as a substrate exhibited up to 78% enantioselectivity with good chemical yields in the asymmetric Ni-catalyzed 1,2-addition to aromatic aldehydes of arylboroxines. In order to catch-up and outrun the successful methods of Shibasaki[9] and Kanai, and Bolm[10]-asymmetric arylation, we have really focused on tuning Duphos.[11]

4. Experimental

4.1. General

IR spectra were measured on a SHIMADZU FTIR-8100 diffraction grating IR spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-EX-270 NMR spectrometer, operating at 270 MHz for ^1H NMR and at 68 MHz for ^{13}C NMR. ^1H and ^{13}C NMR spectra were reported in δ units, parts per million (ppm) downfield from tetramethylsilane (δ=0). EIMS and FABMS spectra were measured on a JEOL JMS-SX-102A instrument.

All aromatic aldehydes, arylboronic acids and reagents were available from commercial sources and used without further purification. In general, all reactions were performed under an argon atmosphere. H_2O was used without purification. DME was distilled from Na/benzophenone ketyl under a nitrogen atmosphere. Silica gel column chromatography was performed on Fuji silysia BW200.

4.2. Representative procedure for the Ni(0)-catalyzed asymmetric arylation of 1-naphthaldehyde (1) with triphenylboroxine (entry 5, Table 2)

To a stirred solution of (*R*,*R*)-Et–Duphos (8.0 mg, 0.022 mmol) in DME/H_2O (5:1, 0.55 mL) were added $Ni(cod)_2$ (6.1 mg, 0.022 mmol), NaO*t*-Bu (10.6 mg, 0.110 mmol), $(PhBO)_3$ (45.9 mg, 0.147 mmol) and 1-naphthaldehyde (**1**) (30 μL, 34.5 mg, 0.221 mmol). The reaction

mixture was stirred for 48 h at 100 °C and allowed to cool. After usual work-up, purification by silica gel column (hexane/EtOAc=20/1 to 4/1) afforded (1*R*)-(1-naphthyl)-phenylmethanol (**2**) (48.1 mg, 93%, 68% ee) as a colourless oil. The spectral data were comparable to those reported.[3] IR (neat): ν=3381 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.42 (s, 1H), 6.48 (s, 1H), 7.21–7.48 (m, 8H), 7.59 (d, *J*=7.1 Hz, 1H), 7.74–7.86 (m, 2H), 7.98–8.02 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=73.50, 123.86, 124.48, 125.17, 125.44, 125.98, 126.90, 127.48, 128.29, 128.35, 128.60, 130.54, 133.75, 138.63, 142.94. EIMS: *m*/*z*=234 (M^+), 217, 157, 129, 128, 105, 77. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.95; H, 5.99. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 mL/min). The absolute configuration was determined by comparison of the reported specific rotation.[3]

4.3. (+)-4-Isopropylphenyl-(1-naphthyl)methanol (entry 1, Table 3)

A colourless oil. $[\alpha]_D^{20}$ +22 (*c* 0.98, EtOH). IR (neat): ν=3408 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.29 (d, *J*=6.1 Hz, 6H), 2.38 (br, 1H), 4.48 (sept, *J*=6.1 Hz, 1H), 6.44 (s, 1H), 6.80 (d, *J*=8.7 Hz, 2H), 7.25 (d, *J*=8.7 Hz, 2H), 7.35–7.52 (m, 3H), 7.67 (d, *J*=7.1 Hz, 1H), 7.74–7.89 (m, 2H), 7.91–7.99 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=22.10, 69.77, 73.16, 115.62, 123.87, 124.00, 125.21, 125.40, 125.91, 128.14, 128.33, 128.59, 130,44, 133.71, 134.97, 138.79, 157.24. EIMS: *m*/*z*=292 (M^+), 121 (bp). HRMS (M^+) calcd for $C_{20}H_{20}O_2$: 292.1463, found: 292.1481. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 mL/min).

4.4. (+)-4-Fluorophenyl-(1-naphthyl)methanol (entry 2, Table 3)

The spectral data were comparable to those reported.[4e] IR (neat): ν=3236 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.25–2.40 (br, 1H), 6.52 (br s, 1H), 6.99 (*J*=8.7 Hz, 1H), 7.02 (d, *J*=8.7 Hz, 1H), 7.29–7.53 (m, 5H), 7.63 (d, *J*=6.8 Hz, 1H), 7.79–7.91 (m, 2H), 7.95–8.02 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=73.03, 115.24 (d, *J*=21.2 Hz), 123.73, 124.42, 125.21, 125.58, 126.11, 128.35, 128.62 (d, *J*=8.4 Hz), 128.72, 130.40, 133.83, 138.44, 142.70 (d, *J*=3.4 Hz), 162.00 (d, *J*=245.4 Hz). FABMS: *m*/*z*=293 (M^++1). Anal. Calcd for $C_{17}H_{13}FO$: C, 80.93; H, 5.19. Found: C, 81.11; H, 5.43. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 mL/min).

4.5. (1*R*)-4-Chlorophenyl-(1-naphthyl)methanol (entry 3, Table 3)

The spectral data were comparable to those reported.[4d] IR (Nujol): ν=3295 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.31–2.42 (br, 1H), 6.49 (br s, 1H), 7.28 (d, *J*=8.6 Hz, 2H), 7.34 (d, *J*=8.6 Hz, 2H), 7.38–7.52 (m, 3H), 7.58 (d, *J*=6.8 Hz, 1H), 7.74–7.92 (m, 2H), 7.94–8.03 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=72.84, 123.66, 124.56, 125.13, 125.58, 126.12, 128.18, 128.41, 128.55, 128.66, 130.32, 133.10, 133.72, 138.10, 141.25. EIMS: *m*/*z*=270 (M^+), 268 (M^+), 253, 251, 129, 128, 77. HRMS (M^+) calcd for $C_{17}H_{13}{}^{35}ClO$: 268.0654, found: 268.0659. Anal. Calcd for $C_{17}H_{13}ClO$: C, 75.98; H, 4.88. Found: C, 76.10; H, 5.23. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH=9:1, flow: 1.0 mL/min).

4.6. (+)-(2-Biphenyl)phenylmethanol (entry 4, Table 3)

A colourless oil. $[\alpha]_D^{22}$ +122 (*c* 1.26, THF). IR (neat): ν=3354 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.12–2.28 (br s, 1H), 5.91 (s, 1H), 7.08–7.41 (m, 13H), 7.49–7.57 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=72.34, 126.49, 127.06, 127.27, 127.76, 128.00, 128.06, 129.23, 129.87, 140.63, 140.88, 141.14, 143.66. EIMS: *m*/*z*=260 (M^+), 242. HRMS (M^+) calcd for $C_{19}H_{16}O$: 260.1201, found: 260.1206. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH=9:1, flow: 1.0 mL/min).

4.7. (1*R*)-Phenyl-2-tolylmethanol (entry 5, Table 3)

The spectral data were comparable to those reported.[12] IR (Nujol): ν=3330 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.14 (br d, *J*=3.3 Hz, 1H), 2.33 (s, 3H), 5.82 (br d, *J*=3.3 Hz, 1H), 7.14 (d, *J*=7.9 Hz, 1H×2), 7.26 (d, *J*=7.9 Hz, 1H×2), 7.28–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=21.16, 76.10, 126.35, 126.42, 127.24, 128.52, 129.06, 137.15, 140.85, 141.24. EIMS: *m*/*z*=198 (M^+), 183, 105, 77. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.69; H, 6.86. The ee was determined by HPLC analysis with Daicel Chiralcel OB-H (eluent: hexane/*i*-PrOH, flow: 1.0 mL/min). The absolute configuration was determined by comparison of the reported specific rotation.[13]

4.8. (+)-(4-Methoxy-2-methylphenyl)phenylmethanol (entry 6, Table 3)

A colourless oil. $[\alpha]_D^{22}$ +16 (*c* 1.33, THF). IR (neat): ν=3383 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=3.14 (s, 3H), 2.26–2.36 (br s, 1H), 3.76 (s, 3H), 5.91 (s, 1H), 6.65–6.77 (m, 2H), 7.18–7.37 (m, 6H). ^{13}C NMR ($CDCl_3$): δ=19.62, 55.15, 72.91, 110.81, 116.07, 126.73, 127.22, 127.69, 128.23, 133.82, 136.91, 143.11, 158.56. EIMS: *m*/*z*=228 (M^+), 151, 123. HRMS (M^+) calcd for $C_{15}H_{16}O_2$: 228.1150, found: 228.1152. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 mL/min).

4.9. (−)-(3-Fluoro-2-methylphenyl)phenylmethanol (entry 7, Table 3)

A colourless oil. $[\alpha]_D^{22}$ –2.4 (*c* 1.64, THF). IR (neat): ν=3331 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.09 (d, *J*=2.0 Hz, 3H), 2.37–2.54 (br s, 1H), 5.91 (s, 1H), 6.90–7.00 (m, 1H), 7.12–7.36 (m, 7H). ^{13}C NMR ($CDCl_3$): δ=10.36 (d, *J*=6.1 Hz), 73.12 (d, *J*=3.4 Hz), 114.05 (d, *J*=23.5 Hz), 121.67 (d, *J*=3.4 Hz), 122.39 (d, *J*=16.2 Hz), 126.63 (d, *J*=8.9 Hz), 126.93, 127.66, 128.43, 142.23, 143.57 (d, *J*=3.4 Hz), 161.03 (d, *J*=243.1 Hz). EIMS: *m*/*z*=216 (M^+), 198, 137, 105. HRMS (M^+) calcd for $C_{14}H_{13}OF$: 216.0951, found: 216.0957. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 mL/min).

4.10. (1*R*)-Phenyl-4-tolylmethanol (entry 8, Table 3)

The spectral data were comparable to those reported.[12] IR (Nujol): ν=3330 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.17 (d,

J=3.3 Hz, 1H), 2.33 (s, 3H), 5.82 (d, J=3.3 Hz, 1H), 7.14 (d, J=7.9 Hz, 1H×2), 7.25 (d, J=7.9 Hz, 1H×2), 7.28–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=21.16, 76.10, 126.35, 126.42, 127.34, 128.32, 129.06, 137.15, 140.85, 143.84. EIMS: m/z=198 (M^+), 183, 105, 77. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.69; H, 6.86. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 mL/min). The absolute configuration was determined by comparison of the reported specific rotation.[13]

4.11. (1*R*)-(4-Methoxylphenyl)phenylmethanol (entry 9, Table 3)

The spectral data were comparable to those reported.[12] IR (Nujol): ν=3404 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.15–2.22 (br, 1H), 3.79 (s, 3H), 5.79–5.87 (br, 1H), 6.87 (br d, J=8.9 Hz, 1H), 7.22–7.43 (m, 8H). ^{13}C NMR ($CDCl_3$): δ=55.22, 75.65, 113.68, 126.23, 127.23, 127.74, 128.25, 135.98, 143.81, 158.72. EIMS: m/z=214 (M^+), 197, 109, 105, 77. The ee was determined by HPLC analysis (Daicel chiralcel AD-H, eluent: hexane/*i*-PrOH). The absolute configuration was determined by comparison of the reported specific rotation.[13]

4.12. (1*R*)-(4-Fluorophenyl)phenylmethanol (entry 10, Table 3)

The spectral data were comparable to those reported.[1] IR (Nujol): ν=3354 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.19 (d, J=3.3 Hz, 1H), 5.83 (d, J=3.3 Hz, 1H), 6.99 (d, J=8.7 Hz, 1H), 7.03 (d, J=8.7 Hz, 1H), 7.22–7.40 (m, 7H). ^{13}C NMR ($CDCl_3$): δ=75.63, 115.06, 115.37, 126.38, 1[illegible]65, 128.08, 128.20, 128.49, 139.44, 139.48, 143.55, 160.[illegible], 163.84. EIMS: m/z=202 (M^+), 183, 105, 77. Anal. Calcd for $C_{13}H_{11}FO$: C, 77.21; H, 5.48. Found: C, [illegible].39; H, [illegible]. The ee was determined by HPLC analysis with Daicel chiralcel OB-H, eluent: hexane/*i*-PrOH). The absolute configuration was determined by comparison of the reported specific rotation.[12]

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