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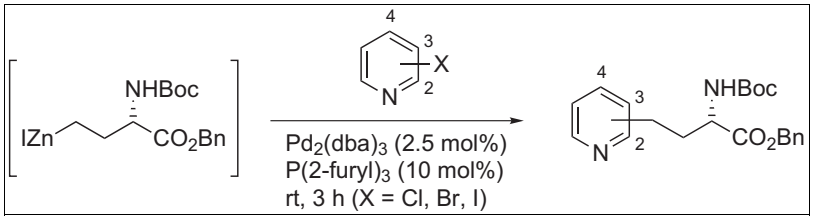

The Negishi cross-coupling reaction of an organozinc derivative prepared from protected L-aspartic acid with monohalopyridines was improved by employing a combination catalyst of $Pd_2(dba)_3$ and $P(2\text{-furyl})_3$ and removing an extra Zn from the organozinc reagent via centrifugation. The reactivity of halogenated pyridines (Cl, Br, I) with substituents at the C2, C3, and C4 positions of the pyridine ring was investigated, and it was found that the use of 4-iodopyridine as a substrate gave the best yield (90%) for the cross-coupling reaction.

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INTRODUCTION

The Negishi cross-coupling reaction [1–3] of organozinc reagents derived from amino acids with aryl halides using a catalytic amount of palladium has been investigated for the production of enantiomerically pure non-natural amino acid derivatives [4] that can be used for the preparation of numerous organic molecules, including biologically active compounds. For example, the cross-coupling reaction between organozinc reagents derived from serine and aryl halides was reported by Jackson and co-workers to afford the corresponding phenylalanine derivatives in moderate yields [5–8]. Moreover, the palladium-catalyzed Negishi cross-coupling reaction of serine derived organozinc reagents with halopyridines was shown to afford azatyrosine derivatives [9,10]. Studies of the cross-coupling of aspartic acid derived organozinc reagents with halopyridines has, however, not been clearly investigated to date.

Improvement of the cross-coupling reaction to achieve C–C bond formation between L-aspartic acids and pyridines would lead to a practical preparation method for naturally occurring pyridinium amino acids such as the osteoporosis biomarkers pyridinoline (**1**) and deoxypyridinoline (**2**) [11,12] and the chronic obstructive pulmonary disease (COPD) biomarkers desmosine (**3**) and isodesmosine (**4**) [13–16], as illustrated in Scheme 1. Herein, we report the palladium-catalyzed Negishi cross-coupling reaction of an organozinc reagent derived from protected L-aspartic acid with monohalopyridines and optimization of the reaction conditions via separation of the extra insoluble Zn species via centrifugation. The effect of halogen substituents (Cl, Br, I) at different positions (C2, C3, C4) of the pyridine ring on the Negishi cross-coupling reaction was also investigated.

RESULTS AND DISCUSSION

For the study of the Negishi cross-coupling reaction, benzyl 2-(*S*)-(*tert*-butoxycarbonylamino)-4-iodobutanoate (**5**) [17] and 3-iodopyridine were chosen as the substrates. The protected amino acid **5** was prepared from commercially available 4-benzoxyl-(*S*)-3-(*tert*-butoxycarbonylamino)-4-oxobutanoic acid in two steps. A combination of 2.5 mol% $Pd_2(dba)_3$ [tris(dibenzylideneacetone)dipalladium(0)] and 10 mol% $P(o\text{-tol})_3$ [tri(*o*-tolyl)phosphine] (final concentration of 1 M) in *N*,*N*-dimethylformamide (DMF) at room temperature [18] was used for the reaction between **5** and 3-iodopyridine. Zn dust was activated with 1,2-dibromoethane and trimethylsilyl chloride (TMSCl) in DMF. To the solution of activated Zn was then added a DMF solution of 1.3 equimolar amounts of iodo amino acid **5**. After monitoring the generation of the organozinc reagent from **5** by TLC, a DMF solution of $Pd_2(dba)_3$, $P(o\text{-tol})_3$, and one equimolar amount of 3-iodopyridine was added to the solution of the freshly prepared organozinc reagent. The reaction proceeded for 2 h to afford the corresponding coupling product **7** in 48% yields (entry 1, Table 1). When the reaction was carried out with the bidentate ligand DPEphos (bis[2-(diphenylphosphino)phenyl]ether) for 15 h, only a trace amount of **7** was obtained (entry 2, Table 1). Use of triphenylarsine ($AsPh_3$) and tri(2-furyl)phosphine

Scheme 1. Pyridinolines (**1** and **2**) and desmosines (**3** and **4**).

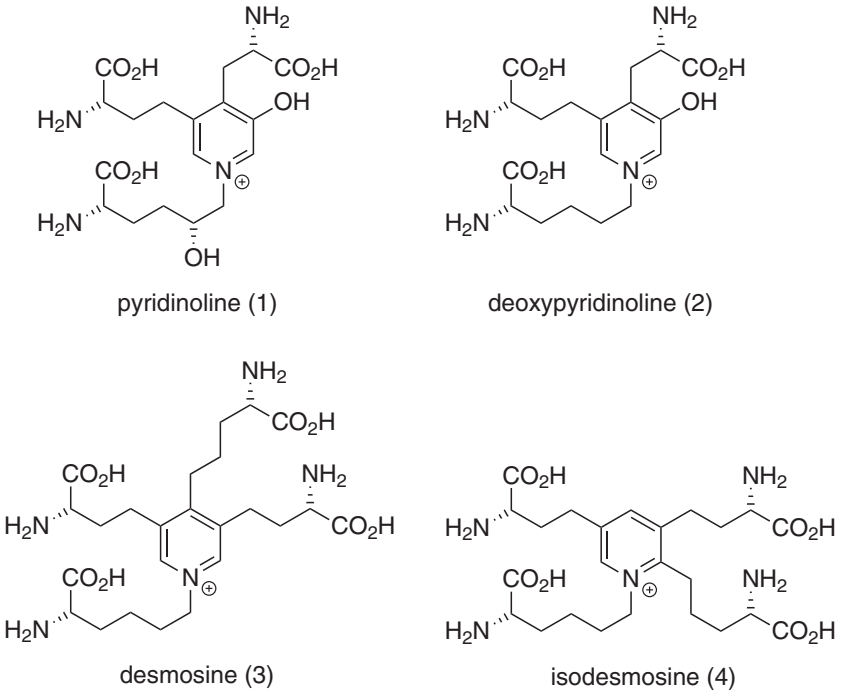
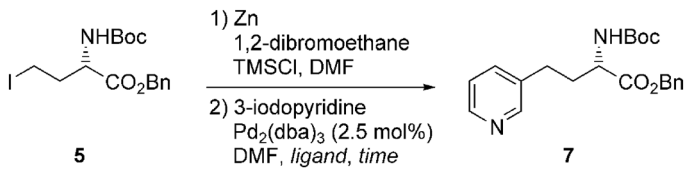


Table 1

Effect of ligands on the Negishi cross-coupling reaction with **5**.



5 **7**

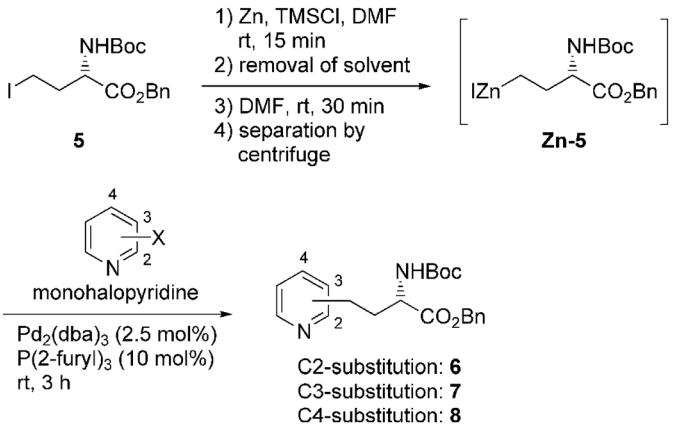
Entry	Ligand	Time (h)	Yield (%)
1	P(*o*-tol)$_3$, 10 mol%	2	48
2	DPEphos, 5 mol%	15	Trace
3	AsPh$_3$, 10 mol%	24	32
4	P(2-furyl)$_3$, 10 mol%	3	67

(P(2-furyl)$_3$), which are known as useful ligands in the Stille reaction [19], gave the desired coupling product **7** in 32 and 67% yield, respectively (entries 3 and 4, Table 1). It has been proposed that AsPh$_3$ and P(2-furyl)$_3$ enhance the rate of the transmetalation step in the Stille reaction, which is the rate-determining step in the catalytic cycle [19,20]. Thus, a combination of 2.5 mol% $Pd_2(dba)_3$ and 10 mol% P(2-furyl)$_3$ in the Negishi cross-coupling reaction was found to be an outstanding catalytic system for affording **7**, which was isolated as a non-racemic product as confirmed by optical rotation analysis.

In order to improve the yield of the cross-coupling reaction, the experimental procedure was modified with respect to the activation of Zn. Because the coupling conditions described earlier were not reproducible, particularly for small scale experiments, it was considered that 1,2-dibromoethane and TMSCl residue from the activation of Zn might affect the activity of the catalytic systems for the cross-coupling. A filtration technique was considered to be unsuitable for removal of any extra insoluble Zn and other activating species from the organozinc reagent reaction mixture because of high viscosity (concentration) of the reactant at small scale. Therefore, separation by centrifugation using a microtube seemed to be a promising method for overcoming this issue. The advantages of separation by centrifuge are as follows: (1) TMSCl can be easily removed from the activated

Table 2

Negishi cross-coupling reaction of **5** and monohalopyridines.



Entry	Position	X	Yield (%)[a]
1	2	Cl	NR
2	3	Cl	NR
3	4	Cl	NR
4	2	Br	44
5	3	Br	Trace (33[b])
6	4	Br	23
7	2	I	72
8	3	I	78
9	4	I	90

[a]Isolated yields.
[b]Reaction time was 15 h.

Zn; (2) the high concentration can be maintained, even for small scale reactions; (3) the coupling reaction can be monitored more clearly by TLC because removal of Zn leads to a clear solution; and (4) side reactions caused by the extra Zn and TMSCl residue can be prevented. A reproducible method for the activation of Zn was achieved as follows: (1) DMF and TMSCl are added to a 1.5 mL microtube (Eppendorf type) containing Zn dust; (2) after the mixture is stirred vigorously for 30 min at room temperature, the solution, including TMSCl, is removed by syringe; (3) iodo amino acid **5** in DMF is added to the activated Zn to form the organozinc amino acid reagent **Zn-5**; (4) the **Zn-5** solution is centrifuged in order to enable isolation of the organozinc amino acid reagent **Zn-5** for the cross-coupling reaction. Utilizing this method, the Negishi cross-coupling reaction between 3-iodopyridine and **5** gave the desired product **6** in much better yield (78%, entry 8, Table 2).

Utilizing the optimized conditions, the reactivity of different halogenated pyridines with Cl, Br, and I substituents at the C2, C3, and C4 positions of the pyridine ring was investigated (Table 2). The cross-coupling reactions with monochloropyridines did not proceed to afford the corresponding coupling products (entries 1–3), even if the reaction time was prolonged. Reactions with 2- and 4-bromopyridine gave the products **6** and **8** in 44 and 23% yields, respectively (entries 4 and 6), whereas the reaction with 3-bromopyridine for 3 h gave only a trace amount of the coupling product **7** and for 15 h gave **7** in a 33% yield. These results indicate that the reactivity of 2- and 4-bromopyridines is much better than that of 3-bromopyridine in the Negishi reaction [8]. Finally, reactions with 2-, 3-, and 4-iodopyridine gave the desired products **6**, **7**, and **8** in 72, 78, and 90% yield, respectively (entries 7–9). These results indicate that the reactivity of halogen substituents on the pyridine ring is in the order $I > Br >> Cl$, but no clear trends can be assumed regarding the substituent position.

CONCLUSION

The combination of $Pd_2(dba)_3$ and P(2-furyl)$_3$ was found to be an excellent catalyst system for the Negishi cross-coupling reaction of an organozinc reagent derived from protected L-aspartic acid with monohalopyridines. The reaction was improved by removing both the undesired Zn (II) species and an extra Zn metal from the activated organozinc reagent via centrifugation. On the basis of the studies of the reactivity of different halogenated (Cl, Br,

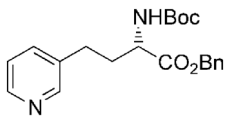
I) pyridines at different substitution positions (C2, C3, C4) on the pyridine ring, it was determined that 4-iodopyridine gives the best yield (90%) in the cross-coupling. The optimized Negishi reaction can be useful for the preparation of important biomarkers **1–4**, as well as biologically-related molecules and several building blocks [21].

EXPERIMENTAL

General experimental procedures. All reactions were conducted under an atmosphere of nitrogen with magnetic stirring in DMF, which was dried by distillation from magnesium sulfate and stored over molecular sieves. All reagents were obtained from commercial suppliers unless otherwise stated. Analytical TLC was performed on Silica gel 60 F_{254} plates produced by Merck (Whitehouse Station, NJ). Visualization was accomplished with UV light and phosphomolybdic acid followed by heating. Column chromatography was performed with acidic or neutral Silica gel 60 (spherical, 40–50 μm) produced by Kanto Chemical Co. Ltd (Tokyo, Japan). Centrifugation was performed by LMS Mini Centrifuge MCF-2360 (6,600 rpm). Benzyl 2-(*S*)-(*tert*-butoxycarbonylamino)-4-iodobutanoate **5** was prepared following the literature procedure [7] and was recrystallized from pentane before use. Zinc dust was purchased from Wako Pure Chemical Industries (Osaka, Japan). 4-Bromopyridine hydrochloride and 4-chloropyridine hydrochloride were converted to the corresponding free pyridines by mixing in an ice-cold 1 M potassium hydroxide solution followed by extraction with cold ether. The extracts were dried over magnesium sulfate in the refrigerator and evaporated under reduced pressure to give the free pyridines, which were used immediately [22].

Optical rotations were measured on a JASCO (Tokyo, Japan) P-2200 digital polarimeter at the sodium lamp (λ = 589 nm) D line and are reported as follows: $[\alpha]_D^T$ (*c* g/100 mL, solvent). Infrared (IR) spectra were recorded on a JASCO FT-IR 4100 spectrometer and are reported in wavenumbers (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EXC 300 spectrometer (300 MHz) and a JEOL (Tokyo, Japan) JNM-ECA 500 spectrometer (500 MHz) in deuterated solvents. ^1H NMR data are reported as follows: chemical shift (δ, ppm), integration, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, or unresolved), coupling constants (*J*) in Hz, assignments. ^{13}C NMR data are reported in terms of chemical shift (δ, ppm). ESI–HRMS spectra were recorded on a JEOL JMS-T100LC instrument or on a Thermo (MA, USA) Exactive spectrometer.

Benzyl 2-(S)-(tert-butoxycarbonylamino)-4-(3-pyridyl) butanoate (7).



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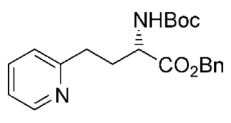
Initial method. Zinc dust (200 mg, 3.0 mmol) was placed in a nitrogen-purged flask. Dry DMF (150 μL) and 1,2-dibromoethane (13 μL, 0.15 mmol) were added to a flask, and the solution was heated at 60°C for 30 min in an oil bath. The mixture was allowed to cool to room temperature, and then trimethylsilyl chloride (4.0 μL, 0.03 mmol) was added. After the resulting mixture was stirred vigorously for 30 min, a solution of benzyl 2-(*S*)-(*tert*-butoxycarbonylamino)-4-iodobutanoate **5** (210 mg, 0.5 mmol) in dry DMF (100 μL × 2) was added to the solution of activated zinc. The reaction mixture was heated to 35°C and followed by TLC. When insertion of zinc was confirmed by TLC, the solution was cooled to room temperature. The time for the insertion ranges from approximately 30 min to 3 h. $Pd_2(dba)_3$ (10.4 mg, 0.01 mmol), ligand (0.04 mmol), and 3-iodopyridine (76.9 mg, 0.38 mmol) were then added to the solution of the organozinc reagent. After stirring for 3 h at room temperature, the reaction mixture was diluted with ethyl acetate (50 mL), washed with brine (30 mL × 3), dried over sodium sulfate and concentrated under reduced pressure to give the crude product as oil. Purification by silica gel column chromatography (hexane/ethyl acetate = 1:2) afforded the pure benzyl 2-(*S*)-(*tert*-butoxycarbonylamino)-4-(3-pyridyl)butanoate **7** as a yellow oil (91.8 mg, 0.25 mmol, 67%); R_f = 0.56 (hexane/ethyl acetate = 1:2); $[\alpha]_D^{21}$ −16.5 (*c*1.0, MeOH); IR (neat, cm^{-1}) 3351, 3227, 3032, 2976, 2933, 1710, 1499, 1455, 1366, 1249, 1165, 1026, 866, 752, 699,607, 496; ^1H NMR (300 MHz, $CDCl_3$) δ 8.44 (1H, d, *J* = 4.5 Hz, Py-H6), 8.37 (1H, s, Py-H2), 7.43 (1H, d, *J* = 7.8 Hz, Py-H4), 7.36 (5H, s, Bn), 7.19 (1H, dd, *J* = 7.8, 4.8 Hz, Py-H5), 5.21 (1H, d, *J* = 12.3 Hz, Bn), 5.12 (1H, d, *J* = 12.0 Hz, Bn), 4.40 (1H, d, *J* = 5.1 Hz, CH), 2.70–2.52 (2H, m, CH_2), 2.20–2.09 (1H, m, CH), 1.99–1.87 (1H, m, CH), 1.47 (9H, s, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.17, 149.22, 147.12, 140.11, 137.43, 135.30, 128.83, 128.76, 128.62, 124.06, 80.30, 67.41, 53.17, 34.12, 31.06, 28.78, 28.42; ESI–HRMS (*m/z*) calcd for $C_{21}H_{26}O_4N_2Na$ $[M + Na]^+$ 393.1790, found 393.1785.

Improved method. Zinc dust (200 mg, 3.0 mmol) was placed in a nitrogen-purged 1.5 mL Eppendorf microtube. Dry DMF (150 μL) and trimethylsilyl chloride (60.0 μL, 0.47 mmol) were added to the microtube, and the resulting mixture was stirred vigorously for 30 min at room temperature. After stirring, the solution was removed by microsyringe. The remaining solid was dried using a hot air gun at reduced pressure. The activated zinc was then cooled to room temperature. A solution of benzyl 2-(*S*)-(*tert*-butoxycarbonylamino)-4-iodobutanoate **5** (210 mg, 0.5 mmol) in dry DMF (100 μL × 2) was then added to the activated zinc. The reaction mixture was then stirred at room temperature. The insertion of zinc was monitored by TLC, with the insertion time ranging from approximately 10 min to 1 h. After completion of the insertion, the zinc solution was allowed to settle using a centrifuge for 1 min at room temperature. The organozinc solution was removed via a microsyringe and added to a 10 mL flask containing $Pd_2(dba)_3$ (12.2 mg, 0.01 mmol), P(2-furyl)$_3$ (9.29 mg, 0.04 mmol), and 3-iodopyridine (76.9 mg, 0.38 mmol), rinse with DMF (150 μL). After stirring for 3 h at room temperature, the reaction mixture was diluted with ethyl acetate (50 mL), washed with brine (30 mL × 3), dried over sodium sulfate, and concentrated under reduced pressure to give the crude product as oil. Purification by silica gel column chromatography (hexane/ethyl acetate = 1:2) afforded the pure benzyl 2-(*S*)-(*tert*-butoxycarbonylamino)-4-(3-pyridyl)butanoate **7** as a yellow oil (107 mg, 0.29 mmol, 78%).

Benzyl 2-(S)-(tert-butoxycarbonylamino)-4-(2-pyridyl) butanoate (6).



6

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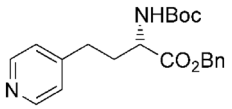
Benzyl 2-(S)-(tert-butoxycarbonylamino)-4-(4-pyridyl) butanoate (8).



8

Zinc dust (200 mg, 3.0 mmol) was placed in a nitrogen-purged 1.5 mL Eppendorf microtube. Dry DMF (150 μL) and trimethylsilyl chloride (60.0 μL, 0.47 mmol) were added to the microtube, and the resulting mixture was stirred vigorously for 30 min at room temperature. After stirring, the solution was removed by microsyringe. The remaining solid was dried using a hot air gun at reduced pressure. The activated zinc was cooled to room temperature. A solution of benzyl 2-(*S*)-(*tert*-butoxycarbonylamino)-4-iodobutanoate **5** (210 mg, 0.5 mmol) in dry DMF (100 μL × 2) was then added to the activated zinc. The reaction mixture was stirred at room temperature. The insertion of zinc was monitored by TLC, with insertion time ranging from approximately 10 min to 1 h. After stirring, the zinc solution was allowed to settle by using a centrifuge for 1 min at room temperature. The organozinc solution was removed via microsyringe and added to a 10 mL flask, containing $Pd_2(dba)_3$ (12.2 mg, 0.01 mmol), P(2-furyl)$_3$ (9.29 mg, 0.04 mmol), and 4-iodopyridine (76.9 mg, 0.38 mmol), rinse with DMF (150 μL). After stirring for 3 h at room temperature, the reaction mixture was diluted with ethyl acetate (50 mL), washed with brine (30 mL × 3), dried over sodium sulfate, and concentrated under reduced pressure to give the crude product as oil. Purification by silica gel column chromatography (hexane/ethyl acetate = 1:1) afforded the pure benzyl 2-(*S*)-(*tert*-butoxycarbonylamino)-4-(4-pyridyl)butanoate **8** as a yellow oil (124.2 mg, 0.34 mmol, 90%); R_f = 0.47 (hexane/ethyl acetate = 1:2); $[\alpha]_D^{21}$ −20.0 (*c* 0.1, MeOH); IR (neat, cm^{-1}) 3356, 2978, 1710, 1619, 1514, 1454, 1367, 1168, 1027, 914, 737, 699, 578, 499, 472, 419; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (2H, d, J = 5.7 Hz, Py-H2,H6), 7.35 (5H, s, Bn), 7.20 (2H, d, J = 5.7 Hz, Py-H3,H4), 5.24–5.09 (2H, dd, J = 12.3, 12.0 Hz, Bn), 5.16 (1H, s, NH), 4.36 (1H, s, CH), 2.75–2.55 (2H, m, CH_2), 2.20–2.08 (1H, m, CH), 1.99–1.87 (1H, m, CH), 1.43 (9H, s, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.96, 152.62, 148.67, 134.75, 128.36, 128.34, 128.23, 128.15, 124.45, 79.88, 66.98, 51.62, 32.64, 30.58, 27.93; ESI–HRMS (*m/z*) calcd for $C_{21}H_{26}N_2NaO_4$ $[M + Na]^+$ 393.1790, found 393.1776.

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