Cross-Coupling Reaction of Allylic Ethers with Aryl Grignard Reagents Catalyzed by a Nickel Pincer Complex

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Abstract: A cross-coupling reaction of allylic aryl ethers with arylmagnesium reagents was investigated using β-aminoketonato- and β-diketiminato-based pincer-type nickel(II) complexes as catalysts. An β-aminoketonato nickel(II) complex bearing a diphenylphosphino group as a third donor effectively catalyzed the reaction to afford the target cross-coupled products, allylbenzene derivatives, in high yield. The regioselective reaction of a variety of substituted cinnamyl ethers proceeded to give the corresponding linear products. In contrast, α- and γ-alkyl substituted allylic ethers afforded a mixture of the linear and branched products. These results indicated that the coupling reaction proceeded via a π-allyl nickel intermediate.

Keywords: pincer-type nickel(II) complex; cross-coupling; allylic ether

1. Introduction

Transition metal-catalyzed cross-coupling reactions are efficient and widely utilized synthetic protocols for constructing carbon–carbon bonds [1]. The reactions of allylic electrophiles with aryl metal reagents provide promising methodologies for the formation of C(sp^3)–C(sp^2) bonds. Allylic electrophiles with efficient leaving groups, such as allylic halides, acetates, and phosphates, are commonly used in these reactions [2–6]. In contrast to these allylic electrophiles, allylic ethers have been considered less-reactive electrophiles in cross-coupling reactions, whereas these electrophiles are easily accessible, cheap, and easy to handle. Therefore, the development of effective metal catalysts for coupling reactions utilizing allylic ethers as electrophiles in a highly regioselective manner has attracted considerable attention. The choice of the metal catalyst is critical for linear and branched selectivity. Although precious metals such as Pd and Ir have been extensively explored in selective allylic substitution reactions [2–4], recent efforts have focused on first-row late transition-metals such as Cu, Co, Fe, and Ni, whose complexes act as highly active catalysts. For example, Feringa reported the asymmetric allylic alkylation of acyclic allylic ethers with organolithium reagents using a Cu/phosphoramidite system [7]. Oshima and Yorimitsu reported a cobalt-catalyzed cross-coupling reaction of allylic ethers with Grignard reagents in a linear manner [8]. Iron catalysts also enable the allylic arylation reaction to be performed [9–12]. Recently, Ni pincer complexes have been reported as effective catalysts for the coupling reaction of allylic ethers with aryl zinc reagents [13].

In recent years, tridentate pincer-type complexes have generated significant interest because the pincer-type ligand stabilizes the metal complex and its properties can be tuned to achieve optimal reactivity [14–25]. We have recently reported the synthesis of a range of pincer-type nickel(II) complexes
(1a–d) utilizing a combination of β-aminoketonato or β-diketiminato frameworks with a third donor such as an amino or phosphino group [26,27]. Our systematic study on these nickel(II) complexes revealed that modifying the ligand framework has a significant influence on the catalytic performance in the cross-coupling reaction of aryl halides with arylmagnesium reagents. In particular, nickel(II) complexes 1b and 1d bearing a diphenylphosphino group as the third donor enable the utilization of aryl fluorides as electrophiles in the reaction [27]. In order to elucidate the reactivity of the nickel(II) complex toward the relatively robust C-O bond in an allylic aryl ether, we herein describe the cross-coupling reaction of allylic ethers with arylmagnesium reagents using nickel(II) complexes (1a–d) (Scheme 1).

Scheme 1. The coupling reaction of allylic ethers with aryl Grignard reagents using Ni(II) pincer complexes (1a–d).

2. Results and Discussion

2.1. Optimization of the Reaction Conditions

2.1.1. Initial Optimization of the Nickel(II) Complexes

To evaluate the catalytic activity of nickel(II) complexes 1a–d, we carried out the reaction between cinnamyl phenyl ether 2a and 3 equivalents of p-tolylmagnesium bromide 3a using nickel(II) complexes 1a–d (2.5 mol%) in THF at room temperature (Table 1), referring to our previously study on the biaryl coupling reaction of aryl chlorides with arylmagnesium reagents [26]. Complex 1a gave the linear product 4a in only 7% yield. Complex 1b showed high catalytic activity to give 4a in 86% yield. Nickel(II) complexes 1c and 1d bearing N,N,N- and N,N,P-type ligands were not shown to exhibit high catalytic activity.

Table 1. The cross-coupling reaction of 2a with 3a using Ni(II) pincer complexes (1).

| Ni cat 1   | Yield of 4a (%) | Recovery of 2a (%) |
|------------|----------------|--------------------|
| 1a (L = NEt₂) | 7             | 43                 |
| 1b (L = PPh₂) | 86            | 0                  |
| 1c (L = NEt₂) | 2             | 83                 |
| 1d (L = PPh₂) | 4             | 90                 |

*The reaction was carried out using 2a (0.5 mmol) and 3a (1.5 mmol) in the presence of 1 (0.0125 mmol, 2.5 mol%) in THF (5 mL) for 24 h at room temperature. The yield of 4a and recovery of 2a were determined by 1H NMR analysis using pyrazine as the internal standard.*
effective in the reaction and afforded the target product in 2% and 4% yield, respectively. In these cases, a large amount of 2a remained unreacted (see 2.3 Reaction mechanism section). In all cases, the branched product 5a was not detected and 4,4′-bitolyl (6a) derived from 3a was formed as a by-product (9–30%). In the absence of complex 1a–d, the reaction did not give any coupled products.

2.1.2. Investigation of the Effect of the Solvent and Nickel(II) Complexes

We next examined the solvent effect using the reaction between 2a and 3 equivalents of 3a with complex 1b. The results are summarized in Table 2. The choice of the solvent used is essential to produce product 4a in satisfactory yield. When cyclopentyl methyl ether (CPME) was employed as solvent, the coupled product 4a was obtained in 89% yield (entry 2). The yield of 4a decreased in 1,4-dioxane (71%, entry 3). t-Butyl methyl ether (MTBE) and toluene were also effective solvents for the reaction and produced 4a in 82% and 83%, respectively (entries 4 and 5). CH2Cl2 and N,N-dimethylformamide (DMF) were not suitable for the reaction (entries 6 and 7). Et2O provided the best result, affording product 4a in 99% yield, from which 4a was isolated in 94% yield (entry 8). The other nickel(II) complexes 1a, 1c, and 1d exhibited relatively low catalytic activity, even in Et2O (entries 9–11). When the amount of Grignard reagent 3a used was reduced to 1.5 equivalents, complex 1b acted as an effective catalyst to give 4a in an isolated yield of 91% (entry 12).

Table 2. Solvent screening using the reaction between 2a and 3a with complex 1. *

| Entry | Ni Cat 1 | Solvent | 4a (%) b | Entry | Ni Cat 1 | Solvent | 4a (%) b |
|-------|----------|---------|----------|-------|----------|---------|----------|
| 1     | 1b       | THF     | 86       | 7     | 1b       | DMF     | 0        |
| 2     | 1b       | CPME    | 89       | 8     | 1b       | Et2O    | 99(94)   |
| 3     | 1b       | 1,4-dioxane | 71 | 9     | 1a       | Et2O    | 22       |
| 4     | 1b       | MTBE    | 82       | 10    | 1c       | Et2O    | 19       |
| 5     | 1b       | toluene | 83       | 11    | 1d       | Et2O    | 30       |
| 6     | 1b       | CH2Cl2  | 24       | 12d   | 1b       | Et2O    | 95(91)   |

* The reaction was carried out using 2a (0.5 mmol) and 3a (1.5 mmol) in the presence of 1 (0.0125 mmol, 2.5 mol%) in solvent (5 mL) for 24 h at room temperature. b The yield of 4a was determined by 1H NMR analysis using pyrazine as the internal standard. c Isolated yield. d 0.75 mmol of 3a was used.

2.1.3. Investigation of the Effect of the Leaving Group on the Allylic Electrophile

In order to investigate the influence of the leaving group (LG) on the allylic substrate, we carried out the reaction between various cinnamyl electrophiles (2a–d, 7, and 8) with 1.5 equivalents of 3a in the presence of 1b (2.5 mol%) in Et2O (Table 3). Cinnamyl phenyl ether 2a was converted into 4a in 91% isolated yield. In the case of cinnamyl p-methoxyphenyl ether 2b, the cross-coupled product 4a was isolated in excellent yield (96%). When the amount of nickel(II) complex 1b used was reduced to 1 mol%, 2a was converted into 4a in 60% yield, whereas in the case of 2b, product 4a was isolated in 95% yield. The reaction of cinnamyl ether 2c bearing a p-trifluoromethylphenyl group in the leaving group afforded 4a in 62% yield. p-Methoxyphenoxide, which has an electron-donating group on the aromatic ring, acted as an effective leaving group. Methyl ether 2d was also applicable in the reaction using 2.5 mol% of 1b to give product 4a in 90% yield. When 1 mol% of 1b was employed, the product was obtained in 73% yield. Cinnamyl alcohol 7 was also able to be used as an electrophile, however, the yield of 4a was low (40%) and 7 was recovered in 54%. In the case of cinnamyl chloride 8, compound 4a was formed in low yield (38%).
2.2. Substrate Scope

With the optimized conditions in hand, we next examined the substrate scope of the reaction using allylic ethers 2 bearing a $\alpha$-methoxyphenoxyl group as the leaving group and a range of arylmagnesium reagents (3) in the presence of 1 mol% of 1b as the catalyst (Table 4). The reaction of cinnamyl ether 2b with phenylmagnesium bromide 3b gave the coupled product 4b in excellent yield (94%) with linear selectivity. In the case of 4-methoxyphenylmagnesium bromide 3c, which has an electron-donating group on the aromatic ring, the coupled product 4c was isolated in 94% yield. The reaction with 4-N,N-dimethylaminophenylmagnesium bromide 3d gave product 4d in 95% yield. We recently reported that complexes 1b and 1d act as an effective catalyst for the cross-coupling reaction of aryl fluorides with arylmagnesium reagents [27]. In the reaction with 4-fluorophenylmagnesium bromide 3e, product 4e was obtained in 96% yield. In the present reaction conditions, the reaction of 4e as an electrophile with Grignard reagent 3e did not occur. In cases of sterically congested arylmagnesium reagents, such as 1-naphthylmagnesium bromide 3f, $\alpha$-tolylmagnesium bromide 3g and 2,4,6-trimethylphenylmagnesium bromide 3h, the corresponding products 4f, 4g, and 4h were obtained in 85%, 79%, and 80%, respectively, in the presence of 2.5 mol% of 1b under refluxing conditions. The reaction of $\pi$-substituted cinnamyl ether 2i, which has an electron-donating group (OMe) on the aromatic ring, with $p$-tolylmagnesium bromide 3a gave product 4i in 78% yield. In the case of electrophile 2j bearing an electron-withdrawing group (F), the coupled product 4j was obtained in 89% yield. In the coupling reaction, alkyl- and benzylmagnesium reagents were not suitable as nucleophiles. In addition, the reaction using a cis/trans mixture of 2b’ (cis:trans = 86:14) with Grignard reagent 3a afforded the trans product (4a) in 88% yield as a sole product (Table 5, entry 1). In contrast to cinnamyl ethers, $\gamma$-alkyl substituted allylic ether 2g afforded a mixture of the linear and branched isomers (4k and 5k) in 96% yield. The ratio of 4k:5k was determined to be 54:46 using $^1$H NMR spectroscopy (entry 2). These results indicate that the reaction proceeds via a $\pi$-allyl nickel intermediate (vide infra). Therefore, we examined the reaction using secondary allylic ethers as electrophiles. The reaction of an allylic ether bearing a phenyl group at the $\alpha$-position (2h) proceeded with linear selectivity to afford product 4a as a single regioisomer in high yield (94%). In this reaction, branched isomer 5a was not detected (entry 3). In contrast, an allylic ether bearing an alkyl group at the $\alpha$-position (2i) was converted into a mixture of regioisomers (4k and 5k) in 93% yield. The ratio of 4k:5k was determined to be 57:43 using $^1$H NMR spectroscopy (entry 4). The reaction of a mixture of 2j and 2k (2j:2k = 67:33) gave the linear product 4l in 90% yield with high regioselectivity. The branched isomer (5l) was not detected (entry 5). The regioselectivity in this reaction probably depends on both maximizing the resonance stabilization energy on the coupling product and minimizing steric hindrance in the coupling of the Grignard reagent with the putative $\pi$-allyl nickel species [13]. In the reaction of the $\gamma$-alkyl substituted allylic ether, the steric influence should operate predominantly for the formation of the product.
The reaction was carried out using 2 (0.5 mmol) and 3 (0.75 mmol) in the presence of 1b (0.005 mmol, 1.0 mol%) in Et₂O (5 mL) for 24 h at room temperature. Isolated yield. b 2.5 mol% of 1b was used. c 2.5 mol% of 1b and 1.5 mmol of 3f were used. The reaction was carried out under reflux conditions for 72 h. d 2.5 mol% of 1b and 1.1 mmol of 3g were used. The reaction was carried out under reflux conditions for 24 h. e 2.5 mol% of 1b and 1.5 mmol of 3h were used. The reaction was carried out under reflux conditions for 72 h. f 2.5 mol% of 1b and 1.5 mmol of 3a were used.

| Entry | 2 | X (mol%) | 4/5 | 4 + 5 (%) |
|-------|---|----------|-----|----------|
| 1     | 2b' (cis:trans = 86:14) | 1.0 | 4a:5a = >99:<1 | 88 |
| 2     | 2g | 2.5 | 4k:5k = 54:46 | 96 |
| 3     | 2h | 2.5 | 4a:5a = >99:<1 | 94 |
| 4     | 2i | 2.5 | 4k:5k = 57:43 | 93 |
| 5     | 2j | 2.5 | 4l:5l = >99:<1 | 90 |

The reaction was carried out using 2 (0.5–1.0 mmol) and 3 (0.75–1.5 mmol) in the presence of 1b (0.005–0.0125 mmol, 1.0–2.5 mol%) in Et₂O (5 mL) for 24 h at room temperature. Isolated yield. (Ar = 4-MeOC₆H₄).
Finally, we investigated the reactivity of the allylic C(sp^3)–O and naphthyl C(sp^3)–O bonds in 2l (Scheme 2). Scission of the allylic C(sp^3)–O bond in 2l selectively occurred and thus, allylated product 4a was obtained in 68% yield.

Scheme 2. Selective cleavage of the allylic C(sp^3)–O bond in cinnamyl naphthyl ether 2l catalyzed by 1b.

2.3. Reaction Mechanism

We examined the stoichiometric reaction to gain insight into the reaction mechanism (Table 6). In the reaction of nickel(II) complex 1b with an equimolar amount of allylic ether 2b, oxidative addition of the C-O bond of 2b to 1b did not occur and 2b was recovered in 96%. In contrast, when 1b was treated with an excess amount of phenylmagnesium reagent 3b, 1b was converted into another nickel species. In the ^31P[^1]H NMR spectrum, the signal derived from 1b (37.5 ppm) disappeared [26] and a new signal was observed at 49.1 ppm, whose resonance was due to the formation of a new nickel species. However, characterization of this nickel complex was not successful. Subsequently, we examined the reaction with various amounts of 3a in the presence of 1b and 2b. The obtained results are summarized in Table 6. In the reaction using a mixture of 1b and 2b with 1 equivalent of 3a, the coupled product 4a was not detected with 2b being recovered in 83%. In the case of the reaction using 2 equivalents of 3a, the coupled product (4a) was formed in 23% yield. Using 3 equivalents of 3a, the reaction proceeded smoothly and 2b was completely consumed to give the coupled product (4a) in 83% yield, along with the formation of 4,4'-bitolyl (6a, 0.19 mmol). The reaction using 4 equivalents of 3a also gave the product (4a) in 83% yield. Therefore, we assumed that two or more equivalents of the arylmagnesium reagent are required to for the reaction to proceed via the generation of an anionic nickel(0) species, which is the active species for the activation of the allylic ether (vide infra).

Table 6. The stoichiometric reaction of allylic ether 2b with aryl Grignard reagent 3a. a

| Entry | X (equiv) | 4a (%) b | 6a (mmol) c | Recovery of 2b (%) b |
|-------|-----------|-----------|-------------|----------------------|
| 1     | 1         | N.D.      | 0.03        | 83                   |
| 2     | 2         | 23        | 0.09        | 40                   |
| 3     | 3         | 83        | 0.19        | 0                    |
| 4     | 4         | 83        | 0.23        | 0                    |

a Reaction conditions: 1b (0.2 mmol), 2b (0.2 mmol), and 3a in Et_2O (5 mL) at room temperature (Ar = 4-MeOC_6H_4).
b The yield of 4a and recovery of 2b were determined by ^1H NMR analysis using pyrazine as the internal standard.
c The amount of 6a was determined by ^1H NMR analysis using pyrazine as the internal standard.
Although the detailed reaction mechanism for the nickel catalyzed allyl-aryl coupling reaction was not clear, a plausible mechanism is proposed in Scheme 3 [13,28]. Initially, nickel(II) complex \(1b\) is converted into anionic nickel(0) species \(I\) through its reaction with at least 2 equivalents of arylmagnesium reagent accompanied by the formation of a biaryl. Then, the low valent nickel(0) species \(I\) reacts with the allylic electrophile at the nickel center to afford \(\pi\)-allyl nickel species \(II\) (as shown in Table 5): For example, \(\gamma\)-alkyl substituted allylic ether \(2g\) was converted into a mixture of linear and branched isomers. We have recently reported that the steric and electronic properties of the nickel(II) complexes \(1\) [26,27]. The DFT calculations of complexes \(1\) reveal that the highest occupied molecular orbital (HOMO) levels of these complexes increase in the order \(1a \approx 1b < 1c \approx 1d\). We expected that complexes \(1c\) and \(1d\) worked as effective catalysts for this coupling reaction. However, the bulky substituent (mesityl group) on the ligand framework inhibits to form \(\pi\)-allyl nickel species derived from \(1c\) and \(1d\). Therefore, complexes \(1c\) and \(1d\) show poor catalytic activities. In contrast, complex \(1b\) acts as an effective catalyst for the coupling reaction, because of constructing an appropriate steric and electronic environment around nickel center by the \(O,N,P\)-pincer ligand.

After the formation of \(\pi\)-allyl nickel species \(II\), its subsequent transmetalation with the arylmagnesium reagent leads to the formation of a \(\sigma\)-allyl nickel species bearing aryl ligand \(III\) and/or \(IV\). We assumed that the formation of intermediate \(III\) is more favorable than \(IV\) due to steric hindrance. Therefore, the selectivity in the reaction was influenced by the substituent on the allylic substrate. Finally, the desired products \(4\) and/or \(5\) are released via reductive elimination from the Ni center to regenerate the nickel(0) species \(I\) and thus, the catalytic cycle is completed. One of the possible reaction pathways involved in an allylic substitution reaction is the attack of the nucleophile on \(\pi\)-allyl nickel species \(I\); this mechanism cannot be excluded.

**Scheme 3.** A plausible catalytic cycle for the cross-coupling reaction of an allylic ether and arylmagnesium reagent.

### 3. Materials and Methods

#### 3.1. General Information

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under a nitrogen atmosphere, which was dried with SICAPENT (Merck Co., Inc., Germany, Darmstadt), using standard Schlenk tube or high vacuum techniques. All solvents were distilled
over appropriate drying agents prior to use. Nickel complexes 1a–c [26] and 1d [27] were prepared according to literature methods. Allylic aryl ethers 2a–c, 2e–g, and 2l were prepared from the reaction of their corresponding allylic halides and 4-substituted phenols using K₂CO₃ in acetone. Allylic methyl ether 2d was prepared via the reduction of the corresponding aldehyde using NaBH₄ followed by methylation using methyl iodide. Allylic methyl ethers 2h and 2i were prepared from addition of the corresponding aldehyde with vinylmagnesium bromide followed by methylation using methyl iodide. A mixture of 2j and 2k was prepared via the reduction of cinnamyl methyl ketone using NaBH₄ followed by a Mitsunobu reaction using 4-methoxyphenol. All other reagents employed in this research were commercially available and used without any further purification.

Proton nuclear magnetic resonance (¹H NMR), carbon nuclear magnetic resonance (¹³C[¹H] NMR), and phosphorus nuclear magnetic resonance (³¹P[¹H] NMR) spectra were recorded on BRUKER DRX-500 and JEOL ECA 500 spectrometers at ambient temperature. ¹H NMR chemical shifts were recorded in ppm using tetramethylsilane (TMS) or the solvent resonance peak as an internal standard (TMS: 0.00 ppm, C₆D₆: 7.16 ppm). ¹³C[¹H] NMR chemical shifts were recorded in ppm using the solvent resonance peak as an internal standard (CDCl₃: 77.0 ppm, C₆D₆: 128.0 ppm). ³¹P[¹H] NMR chemical shifts were recorded in ppm using H₃PO₄ as an external standard (H₃PO₄: 0.0 ppm).

3.2. General Procedure for the Cross-Coupling Reaction of Allylic Ethers with Arylmagnesium Reagents

A 50 mL Schlenk tube was charged with 1b (1.0–2.5 mol%), the respective allylic electrophile (1.0 mmol), Et₂O (2.5–5 mL, 0.2 M based on the electrophile), and the aryl Grignard reagent (1.5–3.0 equiv.) at room temperature. The coupling reaction was carried out at room temperature for 24 h. After quenching with 1 M HCl aq. (5 mL), the aqueous layer was extracted with EtOAc (5 mL) at room temperature for 24 h (194.2 mg, 94% yield). The compound 3b was prepared via the reduction of cinnamyl methyl ketone using NaBH₄ followed by a Mitsunobu reaction using 4-methoxyphenol. All other reagents employed in this research were commercially available and used without any further purification.

Proton nuclear magnetic resonance (¹H NMR), carbon nuclear magnetic resonance (¹³C[¹H] NMR), and phosphorus nuclear magnetic resonance (³¹P[¹H] NMR) spectra were recorded on BRUKER DRX-500 and JEOL ECA 500 spectrometers at ambient temperature. ¹H NMR chemical shifts were recorded in ppm using tetramethylsilane (TMS) or the solvent resonance peak as an internal standard (TMS: 0.00 ppm, C₆D₆: 7.16 ppm). ¹³C[¹H] NMR chemical shifts were recorded in ppm using the solvent resonance peak as an internal standard (CDCl₃: 77.0 ppm, C₆D₆: 128.0 ppm). ³¹P[¹H] NMR chemical shifts were recorded in ppm using H₃PO₄ as an external standard (H₃PO₄: 0.0 ppm).

1-Cinnamyl-4-methylbenzene (4a): The compound 4a was synthesized from 1-methoxy-4-[(2E)-3-phenylprop-2-en-1-yl]oxy]benzene 2b (240.9 mg, 1.00 mmol) with p-tolylmagnesium bromide 3a (1.4 mL, 1.1 M in THF, 1.5 mmol) in the presence of 1b (4.1 mg, 1 mol%) in Et₂O (5 mL) at room temperature for 24 h (198.0 mg, 95% yield, colorless liquid). ¹H and ¹³C[¹H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported ¹H and ¹³C[¹H] NMR data [29].

The compound 4a was synthesized from 2b’ (cis:trans = 86:14, 119.6 mg, 0.50 mmol) with 3a (0.70 mL, 1.1 M in THF, 0.77 mmol) in the presence of 1b (2.0 mg, 1 mol%) in Et₂O (2 mL) at room temperature for 24 h (91.1 mg, 88% yield).

The compound 4a was synthesized from (1-methoxy-2-propen-1-yl)benzene 2h (147.3 mg, 0.99 mmol) with 3a (1.40 mL, 1.1 M in THF, 1.5 mmol) in the presence of 1b (10.1 mg, 2.5 mol%) in Et₂O (5 mL) at room temperature for 24 h (194.2 mg, 94% yield).

The compound 4a was synthesized from 2-[(2E)-3-phenylprop-2-en-1-yl]oxy]naphthalene 2l (260.9 mg, 1.00 mmol) with 3a (1.4 mL, 1.09 M in THF, 1.5 mmol) in the presence of 1b (10.1 mg, 2.5 mol%) in Et₂O (5 mL) at room temperature for 24 h. The yield of 4a was determined by ¹H NMR analysis of the crude product using pyrazine as the internal standard (68% yield).

(E)-Prop-1-ene-1,3-diyl dibenzene (4b). The compound 4b was synthesized from 2b (238.8 mg, 0.99 mmol) with phenylmagnesium bromide 3b (1.4 mL, 1.1 M in THF, 1.5 mmol) in the presence of 1b (4.06 mg, 1 mol%) in Et₂O (5 mL) at room temperature for 24 h (181.2 mg, 94% yield, colorless liquid). ¹H and ¹³C[¹H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported ¹H and ¹³C[¹H] NMR data [30].
1-Cinnamyl-4-methoxybenzene (4e). The compound 4e was synthesized from 2b (238.4 mg, 0.99 mmol) with 4-methoxyphenylmagnesium bromide 3c (3.0 mL, 0.5 M in THF, 1.5 mmol) in the presence of 1b (3.90 mg, 1 mol%) in Et₂O (5 mL) at room temperature for 24 h (209.1 mg, 94% yield, colorless liquid). 1H and 13C[1H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported 1H and 13C[1H] NMR data [29].

1-Cinnamyl-N,N-dimethylaniline (4d). The compound 4d was synthesized from 2b (239.2 mg, 1.00 mmol) with 4-N,N-dimethylanilinophenylmagnesium bromide 3d (2.0 mL, 0.75 M in THF, 1.5 mmol) in the presence of 1b (10.2 mg, 2.5 mol%) in Et₂O (5 mL) at room temperature for 24 h (224.5 mg, 95% yield, yellow liquid). 1H and 13C[1H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported 1H and 13C[1H] NMR data [29].

1-Cinnamyl-4-fluorobenzene (4e). The compound 4e was synthesized from 2b (241.1 mg, 1.00 mmol) with 4-fluorophenylmagnesium bromide 3e (1.5 mL, 1.0 M in THF, 1.5 mmol) in the presence of 1b (9.9 mg, 2.5 mol%) in Et₂O (5 mL) at room temperature for 24 h (230.1 mg, 96% yield, colorless liquid). 1H and 13C[1H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported 1H and 13C[1H] NMR data [29].

1-Cinnamyl-naphthalene (4f). The compound 4f was synthesized from 2b (122.0 mg, 0.51 mmol) with 1-naphthylmagnesium bromide 3f (5.8 mL, 0.26 M in THF, 1.51 mmol) in the presence of 1b (5.1 mg, 2.5 mol%) in Et₂O (5 mL) at reflux conditions for 72 h (105.5 mg, 85% yield, white solid). 1H and 13C[1H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported 1H and 13C[1H] NMR data [31].

1-Cinnamyl-2-methylbenzene (4g). The compound 4g was synthesized from 2b (240.3 mg, 1.00 mmol) with 2,4,6-trimethylphenylmagnesium bromide 3h (3.5 mL, 0.63 M in THF, 2.2 mmol) in the presence of 1b (10.3 mg, 2.5 mol%) in Et₂O (5 mL) at reflux conditions for 24 h (164.7 mg, 79% yield, colorless liquid). 1H and 13C[1H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported 1H and 13C[1H] NMR data [29].

1-Cinnamyl-2,4,6-trimethylbenzene (4h). The compound 4h was synthesized from 2b (241.7 mg, 1.01 mmol) with 2,4,6-trimethylphenylmagnesium bromide 3h (3.5 mL, 0.86 M in THF, 3.0 mmol) in the presence of 1b (10.4 mg, 2.5 mol%) in Et₂O (5 mL) at reflux conditions for 72 h (191.5 mg, 80% yield, colorless liquid). 1H and 13C[1H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported 1H and 13C[1H] NMR data [32].

1-Methoxy-4-[[1(E)-3-(4-methylphenyl)prop-1-ene-1-yl]oxy]benzene (4i). The compound 4i was synthesized from 1-methoxy-4-[[1(E)-3-(4-methylphenyl)prop-1-ene-1-yl]oxy]benzene 2e (134.3 mg, 0.50 mmol) with 3a (0.70 mL, 1.1 M in THF, 0.77 mmol) in the presence of 1b (5.0 mg, 2.5 mol%) in Et₂O (2.5 mL) at room temperature for 24 h (92.9 mg, 78% yield, colorless liquid). 1H and 13C[1H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported 1H and 13C[1H] NMR data [28].

1-Fluoro-4-[[1(E)-3-(4-methylphenyl)prop-1-ene-1-yl]oxy]benzene (4j). The compound 4j was synthesized from 1-fluoro-4-[[1(E)-3-(4-methylphenyl)prop-1-ene-1-yl]oxy]benzene 2f (131.2 mg, 0.51 mmol) with 3a (1.4 mL, 1.1 M in THF, 1.5 mmol) in the presence of 1b (5.3 mg, 2.5 mol%) in Et₂O (2.5 mL) at room temperature for 24 h (102.4 mg, 89% yield, colorless liquid). 1H and 13C[1H] NMR spectra have been attached in the Supplementary Materials. The product was characterized by comparison with the previously reported 1H and 13C[1H] NMR data [33].

Mixture of 1-methyl-4-[[2(E)-5-phenylpent-2-ene-1-yl]oxy]benzene (4k) and 1-methyl-4-[[5-phenylpent-1 -ene-3-yl]oxy]benzene(5k). The compounds 4k and 5k were synthesized from 1-methoxy-4-[[2(E)-5-phenylpent-2-ene-1-yl]oxy]benzene 2g (130.2 mg, 0.49 mmol) with 3a (0.70 mL, 1.1 M in THF, 0.77 mmol)
in the presence of 1b (5.1 mg, 2.5 mol%) in Et₂O (2.5 mL) at room temperature for 24 h (110.1 mg, 96% yield, 4k:5k = 54:46, colorless liquid). ¹H and ¹³C{¹H} NMR spectra of the mixture of 4k and 5k have been attached in the Supplementary Materials. 4k: ¹H NMR (500 MHz, CDCl₃) δ 2.32–2.36 (m, 5H), 2.67–2.71 (m, 2H), 3.22–3.28 (m, 2H), 5.50–5.60 (2H), 7.01–7.03 (m, 2H), 7.07–7.20 (m, 5H), 7.25–7.29 (m, 2H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 21.0, 34.3, 35.9, 38.6, 125.7, 128.2, 128.3, 128.5, 129.0, 129.8, 130.7, 135.3, 137.8, 140.2, 142.0. The product 5k was characterized by comparison with the previously reported ¹H and ¹³C{¹H} NMR data [34].

The compounds 4k and 5k were synthesized from (3-methoxypent-4-en-1-yl)benzene 2i (174.9 mg, 0.99 mmol) with 3a (1.4 mL, 1.1 M in THF, 1.5 mmol) in the presence of 1b (10.1 mg, 2.5 mol%) in Et₂O (5 mL) at room temperature for 24 h (218.2 mg, 93% yield, 4k:5k = 57:43).

1-Methyl-4-[((3E)-4-phenylbut-3-ene-2-yl)oxy]benzene (4l). The compound 4l was synthesized from the mixture of 1-methoxy-4-[((3E)-4-phenylbut-3-en-2-yl)oxy]benzene 2j and 1-methoxy-4-(((2E)-1-phenylbut-2-en-1-yl)oxy]benzene 2k (254.7 mg, 2j:2k = 67:33, 1.00 mmol) with 3a (1.4 mL, 1.1 M in THF, 1.5 mmol) in the presence of 1b (10.1 mg, 2.5 mol%) in Et₂O (5 mL) at room temperature for 24 h (200.2 mg, 90% yield, colorless liquid). ¹H and ¹³C{¹H} NMR spectra of the mixture of 4l and 5l have been attached in the Supplementary Materials. The product 4l was characterized by comparison with the previously reported ¹H and ¹³C{¹H} NMR data [29].

4. Conclusions

We have described the cross-coupling reaction of allylic aryl ethers with arylmagnesium reagents catalyzed by nickel(II) pincer complexes 1. Complex 1b bearing a β-aminoketonato unit tethering a diphenylphosphino group showed excellent catalyst performance. The reactions of a range of cinnamyl ether derivatives proceeded with high regioselectively to afford solely the linear coupled products in high yield. The coupling reactions of α- and γ-alkyl substituted allylic ethers gave a mixture of linear and branched products. These results indicate that the reaction proceeds via a π-allyl nickel intermediate. Based on stoichiometric reactions, we assumed that an anionic Ni(0) species derived from the reduction of nickel(II) complex 1b with an excess amount of a Grignard reagent was the active intermediate in the reaction. Further investigations on mechanistic aspects and the coupling reactions of various organometallic reagents with organic electrophiles are currently underway in our laboratory.

Supplementary Materials: Supplementary materials including ¹H and ¹³C{¹H} NMR spectra are available online.

Author Contributions: T.H. and Y.Y. conceived and designed the experiments; K.F., A.O., and E.A. performed the experiments; T.H. and Y.Y. prepared the manuscript; all authors discussed and commented on the manuscript.

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**Sample Availability:** Samples of the compounds are not available from the authors.