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Nickel-Catalyzed Denitrogenative Annulation Reactions of 1,2,3-Benzotriazin-4(3*H*)-ones with 1,3-Dienes and Alkenes

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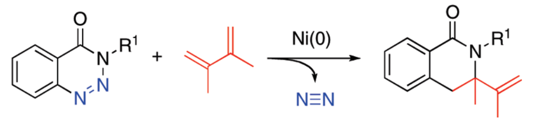
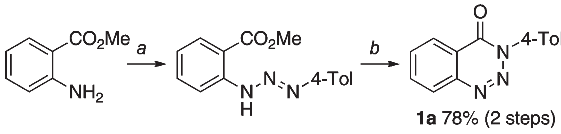


1,2,3-Benzotriazin-4(3*H*)-ones react with 1,3-dienes in the presence of a nickel(0)/phosphine complex to give a variety of 3,4-dihydroisoquinolin-1(2*H*)-ones. Oxidative insertion of nickel(0) into the triazinone moiety prompts extrusion of dinitrogen to give a five-membered ring azanickelacyclic intermediate. Subsequent insertion of 1,3-dienes into the nickel−carbon bond followed by allylic amidation affords 3,4-dihydroisoquinolin-1(2*H*)-ones. Alkenes also undergo insertion into the five-membered ring azanickelacyclic intermediate, and subsequent reductive elimination gives 3-substituted 3,4-dihydroisoquinolin-1(2*H*)-ones.

Transition-metal-catalyzed annulation reactions provide an efficient synthetic route to heterocyclic compounds.[1] Heterometalacyclic complexes are often involved as the key intermediates, which can induce the incorporation of unsaturated molecules into the heterocyclic skeleton. It has been demonstrated that relatively stable heterocyclic compounds act as precursors of heterometalacyclic complexes. Oxidative addition to a low-valent transition metal and extrusion of gaseous molecules such as N_2, CO, and CO_2 lead to the formation of new heterocyclic systems. For example, pyridotriazoles[2] reacted with alkynes in the presence of a rhodium catalyst to give indolizine derivatives with extrusion of N_2.[3] Phthalimide,[4a] phthalic anhydride,[4b] and isatoic anhydride[4c] were also utilized in the nickel-catalyzed annulation reaction with alkynes to form isoquinolin-1(2*H*)-ones, isochromen-1-ones, and quinolin-4(1*H*)-ones, respectively, with extrusion of CO or CO_2.[5] We have recently shown that nickel-catalyzed denitrogenative annulation reactions of 1,2,3-benzotriazin-4(3*H*)-ones with alkynes[6a] and allenes[6b] provide new synthetic approaches to isoquinolin-1(2*H*)-ones and 4-methylene-3,4-dihydroisoquinolin-1(2*H*)-ones. Thus, 1,2,3-benzotriazin-4(3*H*)-ones can be exploited as a precursory platform for the synthesis of isoquinolin-1(2*H*)-one derivatives,[7] which are found in a wide variety of plant alkaloids and bioactive compounds. We next examined the possibility of their reactions with other unsaturated molecules to expand the reaction scope. In this paper are described the results of the nickel-catalyzed annulation reactions of 1,2,3-benzotriazin-4(3*H*)-ones with 1,3-dienes and alkenes.

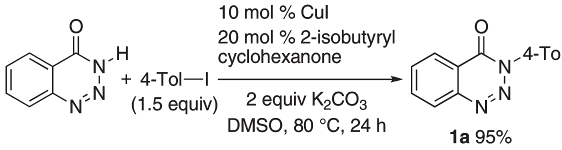
The model substrate, *N*-tolyl-1,2,3-benzotriazin-4(3*H*)-one (**1a**), was readily prepared from methyl anthranilate in two steps (eq 1);[8] methyl anthranilate was diazotized by $NaNO_2$ and then coupled with 4-toluidine to give methyl 2-[3-(4-tolyl)triaz-2-enyl]benzoate. Subsequent heating in refluxing ethanol prompted six-membered ring closure to afford **1a** as a white solid (78% yield over two steps).



(1)

^{a}NaNO$_2$, 2M HCl, H$_2$O, 0 °C, 30 min, then NaOAc, 4-toluidine, 0 °C, 3 h; ^{b}ethanol, reflux, 3 h.

In addition, we developed an alternative simple route to **1a** from commercially available *N*H-1,2,3-benzotriazin-4(3*H*)-one through direct *N*-arylation catalyzed by copper (eq 2).[9] When *N*H-1,2,3-benzotriazin-4(3*H*)-one was treated with 4-iodotoluene (1.5 equiv) in the presence of CuI (10 mol %) and 2-isobutyrylcyclohexanone (20 mol %) in DMSO at 80 °C, an *N*-arylation reaction took place and **1a** was obtained in 95% yield. The isolated **1a** was stable at room temperature and could be kept for months without any decomposition.[10]



(2)

We initiated our study by conducting a reaction of **1a** with 2,3-dimethylbuta-1,3-diene (**2a**, 2 equiv) in THF at 60 °C in

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[1] For reviews, see: (a) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127. (b) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285. (c) D'Souza, D. M.; Müller, T. J. J. *Chem. Soc. Rev.* **2007**, *36*, 1095.

[2] (a) Chuprakov, S.; Hwang, F. W.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2007**, *46*, 4757. (b) Chuprakov, S.; Gevorgyan, V. *Org. Lett.* **2007**, *9*, 4463.

[3] For related examples, see: (a) Horneff, T.; Chuprakov, S.; Chernyak, N.; Gevorgyan, V.; Fokin, V. V. *J. Am. Chem. Soc.* **2008**, *130*, 14972. (b) Miura, T.; Yamauchi, M.; Murakami, M. *Chem. Commun.* **2009**, 1470. (c) Nakamura, I.; Nemoto, T.; Shiraiwa, N.; Terada, M. *Org. Lett.* **2009**, *11*, 1055. (d) Chuprakov, S.; Kwok, S. W.; Zhang, L.; Lercher, L.; Fokin, V. V. *J. Am. Chem. Soc.* **2009**, *131*, 18034. (e) Grimster, N.; Zhang, L.; Fokin, V. V. *J. Am. Chem. Soc.* **2010**, *132*, 2510.

[4] (a) Kajita, Y.; Matsubara, S.; Kurahashi, T. *J. Am. Chem. Soc.* **2008**, *130*, 6058. (b) Kajita, Y.; Kurahashi, T.; Matsubara, S. *J. Am. Chem. Soc.* **2008**, *130*, 17226. (c) Yoshino, Y.; Kurahashi, T.; Matsubara, S. *J. Am. Chem. Soc.* **2009**, *131*, 7494.

[5] For related examples, see: (a) O'Brien, E. M.; Bercot, E. A.; Rovis, T. *J. Am. Chem. Soc.* **2003**, *125*, 10498. (b) Wang, C.; Tunge, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 8118.

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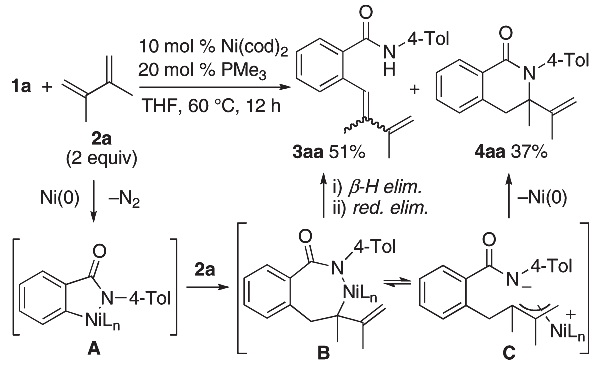
SCHEME 1. Ni(0)-Catalyzed Reaction of 1a with 2a Using PMe_3 as the Ligand



the presence of a nickel(0) catalyst generated *in situ* from $Ni(cod)_2$ (10 mol %) and PMe_3 (20 mol %) (Scheme 1). The substrate **1a** was consumed in 12 h, and after chromatographic isolation, the noncyclized product **3aa** and the denitrogenative annulation product **4aa** were obtained in 51% and 37% yields, respectively. We assume the following reaction mechanism, which is analogous to what we previously reported for the annulation reaction with allenes.[6b] Oxidative addition of a C(O)N–N bond to nickel(0) prompts extrusion of N_2 to generate five-membered ring azanickelacyclic intermediate **A**. Subsequent insertion of a carbon–carbon double bond of **2a** into the nickel–carbon bond gives seven-membered ring azanickelacyclic intermediate **B**, which is in equilibrium with zwitterionic π-allylnickel species **C**. The intermediate **B** undergoes β-hydride elimination and reductive elimination to afford **3aa** along with nickel(0). On the other hand, the intermediate **C** undergoes intramolecular recombination to afford **4aa** along with nickel(0).

Next, several phosphine ligands were examined using **1a** and **2a** as the substrates (Table 1). Although the use of PMe_2Ph increased the yield of **4aa** to 52% (entry 1), other monophosphine ligands such as $PMePh_2$, PPh_3, P(n-Bu)$_3$, and P(t-Bu)$_3$ gave considerably inferior results in terms of reactivity (entries 2–5). The yield and product-selectivity were both improved when bisphosphine ligands such as Dppb and Dppf were employed (entries 6 and 7). In particular, the use of Dppf gave **4aa** in 87% isolated yield along with a trace amount of **3aa**.

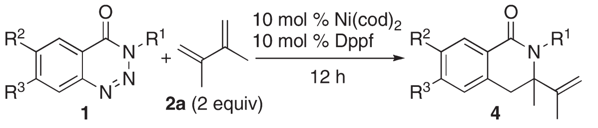
As we previously reported,[6b] the five-membered ring azanickelacycle **A·Dppbenz** was easily isolated by the treatment of **1a** with equimolar amounts of $Ni(cod)_2$ and 1,2-bis(diphenylphosphino)benzene (Dppbenz). Although a reaction of **A·Dppbenz** with **2a** (3 equiv) was attempted in toluene at 110 °C, only a trace amount of **4aa** was obtained (eq 3). When Dppf was added to a mixture of **A** and **2a** (3 equiv) as an additional ligand and the reaction mixture was heated in toluene at 110 °C, the annulation reaction proceeded to give **4aa** in 40% yield. These contrasting results demonstrated the effect of the Dppf ligand accelerating incorporation of **2a**.

TABLE 1. Ni(0)-Catalyzed Reaction of 1a with 2a: Screening of Phosphine Ligands[a]

entry	ligand (mol %)	yield of **3aa** (%)	yield of **4aa** (%)
1	PMe_2Ph (20)	21	52
2	$PMePh_2$ (20)	< 5	9
3	PPh_3 (20)	0	< 5
4	P(n-Bu)$_3$ (20)	< 5	< 5
5	P(t-Bu)$_3$ (20)	0	0
6	Dppb (10)	12	54
7	Dppf (10)	< 5	87

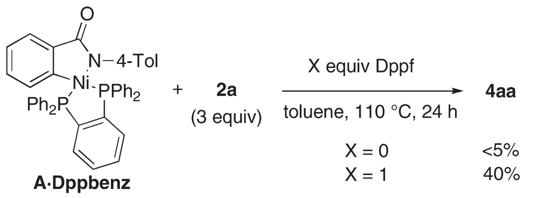
[a] Conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(cod)_2$ (20 μmol, 10 mol %), ligand (10 or 20 mol %) in THF (1 mL) at 60 °C for 12 h. Dppb = 1,4-Bis(diphenylphosphino)butane. Dppf = 1,1′- Bis(diphenylphosphino)ferrocene.

TABLE 2. Ni(0)-Catalyzed Reaction of 1,2,3-Benzotriazin-4(3*H*)-ones 1b–g with 2,3-Dimethylbuta-1,3-diene (2a)[a]



entry	1	R^1	R^2	R^3	solvent	T (°C)	4	yield (%)
1	**1b**	Ph	H	H	THF	60	**4ba**	87
2	**1c**	4-MeOC$_6$H$_4$	H	H	toluene	80	**4ca**	85
3	**1d**	4-CF$_3$C$_6$H$_4$	H	H	THF	60	**4da**	88
4	**1e**	Bn	H	H	toluene	110	**4ea**	24
5	**1f**	Ph	H	CO$_2$Me	THF	60	**4fa**	74
6	**1g**	Ph	MeO	MeO	toluene	80	**4ga**	86

[a] Conditions: **1** (0.2 mmol), **2** (0.4 mmol), $Ni(cod)_2$ (20 μmol, 10 mol %), Dppf (20 μmol, 10 mol %) in solvent (1 mL).



(3)

Under the optimized reaction conditions using Dppf as the ligand, various benzotriazinones **1b–g** were subjected to the catalytic reaction with **2a** (Table 2). Substrates **1b–d** possessing an aryl group on the nitrogen atom reacted smoothly to afford the corresponding products **4ba–da** in high yield (entries 1–3). However, the reaction of benzyl-substituted substrate **1e** was slower even at the higher temperature (110 °C) and the product **4ea** was obtained in only 24% yield (entry 4). Benzotriazinones **1f** and **1g** having electron-withdrawing and -donating substituents on the benzene ring were both competent substrates for the annulation reaction (entries 5 and 6).

Next, various 1,3-dienes **2b–f** were subjected to the annulation reaction of **1a** (Table 3). Symmetrical 1,3-dienes such as buta-1,3-diene (**2b**) and 1,2-dimethylenecyclohexane (**2c**) reacted well to give the corresponding products **4ab** and **4ac** in 81% and 92% yields, respectively (entries 1 and 2). Unsymmetrical 1,3-dienes were also used, and the regioselectivity of the annulation reaction was examined. The reaction with isoprene (**2d**) gave a mixture of regioisomers **4ad** and **5ad** in a 86:14 ratio. The two regioisomers could be

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(6) (a) Miura, T.; Yamauchi, M.; Murakami, M. *Org. Lett.* **2008**, *10*, 3085. (b) Yamauchi, M.; Morimoto, M.; Miura, T.; Murakami, M. *J. Am. Chem. Soc.* **2010**, *132*, 54.

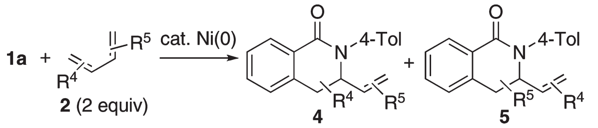
(7) For a review of 1(2*H*)-isoquinolone synthesis, see: Glushkov, V. A.; Shklyaev, Y. V. *Chem. Heterocycl. Compd.* **2001**, *37*, 663.

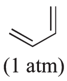
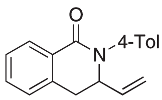
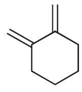
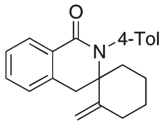
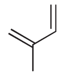
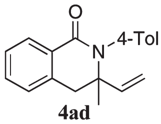
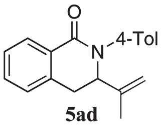
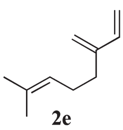
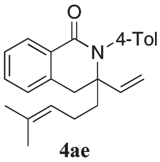
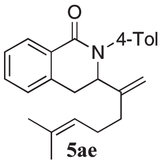
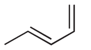
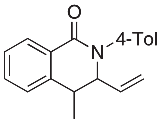
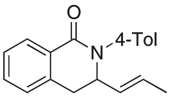
(8) Clark, A. S.; Deans, B.; Stevens, M. F. G.; Tisdale, M. J.; Wheelhouse, R. T.; Denny, B. J.; Hartley, J. A. *J. Med. Chem.* **1995**, *38*, 1493.

(9) (a) Sugahara, M.; Ukita, T. *Chem. Pharm. Bull.* **1997**, *45*, 719. (b) Shafir, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 8742.

(10) Barker, A. J.; Paterson, T. M.; Smalley, R. K.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2203.

TABLE 3. **Ni(0)-Catalyzed Reaction of *N*-Tolyl-1,2,3-benzotriazin-4(3*H*)-one (1a) with 1,3-Dienes 2b−f**[a]



entry	2	4	5	yield of **4** (%)[b]
1	 (1 atm) **2b**	 **4ab**	—	81
2	 **2c**	 **4ac**	—	92[c]
3	 **2d**	 **4ad**	 **5ad**	66 (86:14)
4	 **2e**	 **4ae**	 **5ae**	53 (83:17)
5	 **2f**[d]	 **4af**[e]	 **5af**	85 (90:10)[f,g]

[a] Conditions: **1** (0.2 mmol), **2** (0.4 mmol), Ni(cod)$_2$ (20 μmol, 10 mol %), Dppf (20 μmol, 10 mol %) in THF (2 mL) at 60 °C for 6−12 h unless otherwise noted. [b] The **4**/**5** ratios given in parentheses. [c] Using toluene (2 mL) at 80 °C. [d] *E*/*Z* = >95:5. [e] *cis*/*trans* = 12:88. [f] Combined yield of isomers. [g] Using Ni(cod)$_2$ (40 μmol, 20 mol %) and Dppf (40 μmol, 20 mol %).

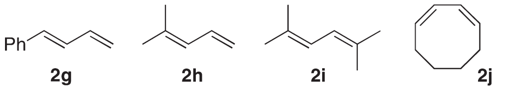
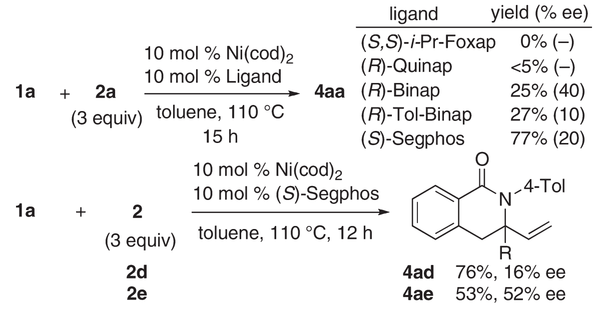
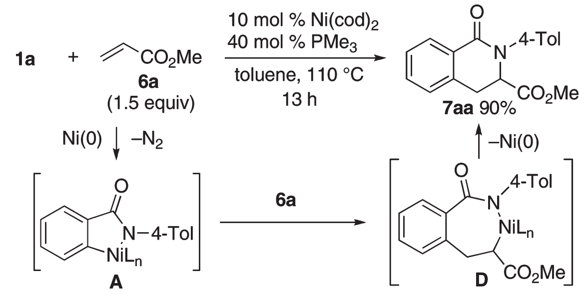


FIGURE 1. Other 1,3-dienes **2g**−**j**.

SCHEME 2. **Ni(0)-Catalyzed Asymmetric Reaction of 1a with 1,3-Dienes**



SCHEME 3. **Ni(0)-Catalyzed Reaction of 1a with 6a Using PMe$_3$ as the Ligand**



separated by silica gel chromatography, and the major isomer **4ad** was obtained in 66% yield (entry 3). Myrcene (**2e**) exhibited a similar regioselectivity (**4ae**/**5ae** = 83:17), and after chromatographic isolation, the major isomer **4ae** was obtained in 53% yield (entry 4). When (*E*)-penta-1,3-diene (**2f**) was employed, the product **4af** was formed with good regioselectivity (**4af**/**5af** = 90:10, entry 5).[11] Thus, insertion of unsymmetrical 1,3-dienes occurs preferentially at the more substituted carbon−carbon double bond.[12]

Other 1,3-dienes **2g**−**j** shown in Figure 1 were less reactive and failed to undergo the annulation reaction of **1a**.

The asymmetric version was attempted using **1a** and **2a** as the substrates (Scheme 2). Among various chiral ligands examined,[13] only (*S*)-Segphos gave the product **4aa** in an acceptable yield (77%), albeit with low enantioelectivity (20% ee). Although the use of (*S*)-Segphos was also examined in the reaction of **1a** with **2d** and **2e**, the enantioselectivities were 16% ee for **4ad** and 52% ee for **4ae**. These results inferred that the reaction step of 1,3-diene insertion that determines the enantioselectivity is different from that for allene insertion.[6b]

We next turned our attention to the use of alkenes as coupling partners instead of 1,3-dienes. When oct-1-ene was subjected to the annulation reaction of **1a** using PMe$_3$ as the ligand (110 °C in toluene), no reaction was observed. On the other hand, the reaction with methyl acrylate (**6a**) proceeded cleanly to give 3,4-dihydroisoquinolin-1(2*H*)-one **7aa** in 90% yield as a single regioisomer. The methoxycarbonyl group was bound to the C(3) position next to the nitrogen atom. This regiochemistry resulted from the electronic demand expected for the insertion process of the electron-deficient carbon−carbon double bond of methyl acrylate (**6a**) into the nucleophilic nickel−carbon bond. Therefore, we assume the mechanism of the annulation reaction as shown in Scheme 3. Insertion of **6a** into the five-membered ring azanickelacycle **A** gives seven-membered ring azanickelacycle **D**, and the following reductive elimination releases **7aa** and nickel(0).

Other phosphine ligands were screened in the reaction of **1a** with **6a**, and P(n-Bu)$_3$ gave the best result (Table 4, entries 1−4). Furthermore, the amount of P(n-Bu)$_3$ could be reduced to 20 mol % (entry 5).

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[11] The product **4af** was obtained as a mixture of two diastereomers (*cis*/*trans* = 12:88). This result infers a mechanism involving a π−σ−π isomerization of π-allylnickel intermediate.

[12] (a) Ogoshi, S.; Tonomori, K.; Oka, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 7077. (b) Kimura, M.; Ezoe, A.; Mori, M.; Iwata, K.; Tamaru, Y. *J. Am. Chem. Soc.* **2006**, *128*, 8559.

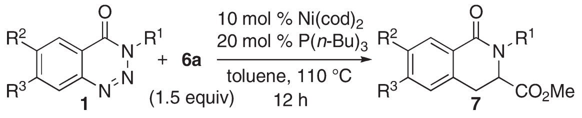
[13] Abbreviations: (*S*,*S*)-*i*-Pr-Foxap = (*S*,*S*)-[2-(4′-isopropyloxazolin-2′-yl)ferrocenyl]diphenylphosphine. (*R*)-Quinap = (*R*)-1-(2-diphenylphosphino-1-naphtyl)isoquinoline. (*R*)-Binap = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl. (*R*)-Tol-Binap = 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl. (*S*)-Segphos = 5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole.

TABLE 4. Ni(0)-Catalyzed Reaction of 1a with 6a: Screening of Phosphine Ligands[a]

entry	ligand (mol %)	yield of **7aa** (%)
1	PPh_3 (40)	96
2	P(*n*-Bu)$_3$ (40)	99
3	P(*t*-Bu)$_3$ (40)	< 5
4	Dppf (20)	88
5	P(*n*-Bu)$_3$ (20)	91

[a] Conditions: **1a** (0.1 mmol), **6a** (0.15 mmol), Ni(cod)$_2$ (10 μmol, 10 mol %), ligand (20 or 40 mol %) in toluene (1 mL) at 110 °C for 13−14 h.

TABLE 5. Ni(0)-Catalyzed Reaction of 1,2,3-Benzotriazin-4(3*H*)-ones 1b−j with Methyl Acrylate (6a)[a]



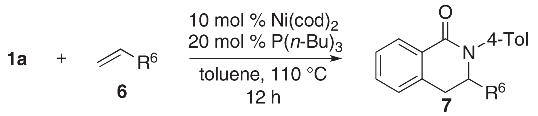
entry	**1**	R^1	R^2	R^3	**7**	yield (%)
1	**1b**	Ph	H	H	**7ba**	99
2	**1c**	4-MeOC$_6$H$_4$	H	H	**7ca**	96
3	**1d**	4-CF$_3$C$_6$H$_4$	H	H	**7da**	98
4	**1h**	4-ClC$_6$H$_4$	H	H	**7ha**	81
5	**1i**	2-MeOC$_6$H$_4$	H	H	**7ia**	77
6	**1e**	Bn	H	H	**7ea**	99
7	**1j**	Me	H	H	**7ja**	97
8	**1f**	Ph	H	CO$_2$Me	**7fa**	96
9	**1g**	Ph	MeO	MeO	**7ga**	98

[a] Conditions: **1** (0.2 mmol), **6a** (0.3 mmol), Ni(cod)$_2$ (20 μmol, 10 mol %), P(*n*-Bu)$_3$ (40 μmol, 20 mol %) in toluene (2 mL) at 110 °C for 12 h.

Other examples of the reaction of benzotriazinones **1b−j** with methyl acrylate (**6a**) under the optimized reaction conditions using P(*n*-Bu)$_3$ as the ligand are listed in Table 5. The reaction of aryl-substituted substrates **1b−d** and **1h−i** with **6a** afforded the corresponding products **7ba−da** and **7ha−ia** in yields ranging from 77% to 99% (entries 1−5). Interestingly, unlike the results obtained with 1,3-diene **2a**, benzyl- and methyl-substituted substrates **1e** and **1j** could readily participate in the reaction with **6a** (entries 6 and 7). Electronically perturbed benzotriazinones **1f** and **1g** were also converted to the corresponding products **7fa** and **7ga** in 96% and 98% yields, respectively (entries 8 and 9).[14]

The results of the nickel-catalyzed annulation reaction of **1a** with various electron-deficient alkenes **6b−g** are summarized in Table 6. Acrylonitrile (**6b**) and *N*,*N*-dimethylacrylamide (**6c**) were incorporated well to give the corresponding products **7ab** and **7ac** in good yield (entries 1 and 2), whereas ethyl vinyl ketone (**6d**) gave the product **7ad** in only 39% yield (entry 3). In addition to **6a−c**, vinylpyridines **6e** and **6f** successfully participated in the annulation reaction (entries 4 and 5). However, the reaction of the styrene derivative **6g** having a trifluoromethyl group was sluggish even under more forcing conditions (entry 6).

TABLE 6. Ni(0)-Catalyzed Reaction of *N*-Tolyl-1,2,3-benzotriazin-4(3*H*)-one (1a) with Alkene 6b−g[a]



entry	**6** (equiv)	R^6	**7**	yield (%)
1	**6b** (1.5)	CN	**7ab**	92
2	**6c** (3.0)	CONMe$_2$	**7ac**	83
3	**6d** (1.5)	COEt	**7ad**	39[b,c]
4	**6e** (3.0)	2-pyridyl	**7ae**	83[c]
5	**6f** (1.5)	4-pyridyl	**7af**	73[d]
6	**6g** (1.5)	4-CF$_3$C$_6$H$_4$	**7ag**	11[b]

[a] The reaction conditions are the same as those in Table 5 unless otherwise noted. [b] Using mesitylene (2 mL) at 160 °C. [c] Using PMe$_3$ (80 μmol, 40 mol %). [d] Using toluene (4 mL).

In summary, we have demonstrated that a five-membered ring azanickelacycle generated from 1,2,3-benzotriazin-4(3*H*)-ones with extrusion of N_2 successfully incorporates 1,3-dienes and alkenes, disclosing the potential as a versatile synthetic intermediate. This catalytic system provides a convenient and regioseletive method for the synthesis of substituted 3,4-dihydroisoquinolin-1(2*H*)-ones from readily available precursors. Noteworthy is that dinitrogen is the only byproduct of the present annulation reaction.

Experimental Section

Representative Procedure for the Nickel-Catalyzed Annulation Reaction of 1,2,3-Benzotriazin-4(3*H*)-ones with 1,3-Dienes (Table 1, entry 7). To an oven-dried flask was added **1a** (44.6 mg, 0.2 mmol), Ni(cod)$_2$ (5.6 mg, 20 μmol), Dppf (11.0 mg, 20 μmol), THF (1 mL), and **2a** (45 μL, 0.4 mmol). After being heated at 60 °C for 12 h, the reaction mixture was cooled to room temperature and stirred for 30 min in open air. The resulting mixture was passed through a pad of Florisil and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (hexane/ethyl acetate 5:1) to give **4aa** (48.2 mg, 0.174 mmol, 87% yield). IR (KBr): 2980, 1644, 1512, 1374 cm^{-1}. ^{1}H NMR: δ = 1.31 (s, 3H), 1.71 (s, 3H), 2.37 (s, 3H), 3.18 (d, J = 15.9 Hz, 1H), 3.28 (d, J = 15.6 Hz, 1H), 4.93 (s, 1H), 5.05 (s, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.16−7.20 (m, 4H), 7.29−7.37 (m, 1H), 7.39−7.46 (m, 1H), 8.05−8.10 (m, 1H). ^{13}C NMR: δ = 19.8, 21.1, 26.5, 41.2, 64.6, 114.8, 126.7, 126.9, 128.2, 128.8, 129.2, 129.6, 131.8, 136.1, 136.8, 137.1, 146.0, 165.5. HRMS (EI$^+$): calcd for $C_{20}H_{21}NO$, M$^+$ 291.1623, found *m*/*z* 291.1626.

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Supporting Information Available: Experimental details, structural data for all new compounds, and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) We also attempted the asymmetric version using **1a** and **6a** as the substrates. Although various chiral ligands were examined, both the yield and the enantioselectivity of **7aa** were low.