C–O Bond Cleavage

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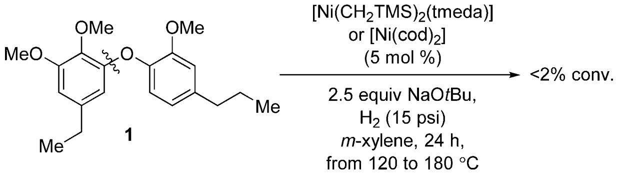
Chemo- and Regioselective Hydrogenolysis of Diaryl Ether C–O Bonds by a Robust Heterogeneous Ni/C Catalyst: Applications to the Cleavage of Complex Lignin-Related Fragments

Fang Gao[+], *Jonathan D. Webb*[+], *and John F. Hartwig**

Abstract: *We report the chemo- and regioselective hydrogenolysis of the C–O bonds in di-ortho-substituted diaryl ethers under the catalysis of a supported nickel catalyst. The catalyst comprises heterogeneous nickel particles supported on activated carbon and furnishes arenes and phenols in high yields without hydrogenation. The high thermal stability of the embedded metal particles allows C–O bond cleavage to occur in highly substituted diaryl ether units akin to those in lignin. Preliminary mechanistic experiments show that this catalyst undergoes sintering less readily than previously reported catalyst particles that form from a solution of [Ni(cod)$_2$].*

The rising concerns about global climate change and the depletion of fossil fuels have stimulated the pursuit of energy and commodity chemicals from renewable sources.[1] Lignin, the most abundant reserve of aromatic compounds besides fossil fuels,[2] has the potential to supplement or replace coal or crude oil as the source of arenes.[3] Although some progress has been made in the transformation of lignin into liquid bio-oils,[4] mixtures of saturated hydrocarbons,[5] emulsifying agents,[6] and well-defined aromatic compounds,[7] further studies are needed to create practical processes. For example, high temperatures (> 220 °C) and a large excess of hydrogen (in the MPa range) are often required for the degradation of lignin to an acceptable extent, and catalysts for the hydrogenolysis of lignin lead to reduction of the arenes.[4–7] This reduction of the arenes consumes hydrogen and prevents the use of lignin as a source of aromatic compounds. Furthermore, few methods have been devised for cleavage of the strong C–O bonds of diaryl ethers;[8] the presence of these entities significantly limits the theoretical yields of monomeric arenes and phenols in the above processes.[7] Therefore, systems are needed that selectively catalyze the hydrogenolysis of diaryl ethers, especially highly substituted biaryl ethers relevant to those found in lignin, under relatively mild conditions.

We previously reported the first examples of the catalytic hydrogenolysis of diaryl ethers under atmospheric hydrogen pressure (15 psi) at low temperatures (80–120 °C) to form arenes and phenols without competing hydrogenation of the aromatic rings;[9] the transformations were catalyzed by a homogeneous NHC–Ni system, inspired by related cross-coupling chemistry involving the activation of aromatic C–O bonds.[10] The added NaO*t*Bu led to chemoselective hydrogenolysis of the C–O bonds over the competitive hydrogenation of aryl groups observed with prior systems.[11] Later, we discovered that heterogeneous nickel particles generated in situ from [Ni(cod)$_2$] without an added ancillary ligand catalyze the cleavage of C–O bonds of biaryl ethers, including those of electron-rich biaryl ethers, with catalyst loadings as low as 0.5 mol % (vs. 20 mol % of the NHC–Ni catalyst).[12] Although this catalyst cleaved the C–O bonds of some biaryl ethers, it did not react with biaryl ethers containing highly electron-rich C–O bonds and multiple substituents that mimic those in lignin. For example, the reaction of biaryl ether **1** led to less than 2 % conversion, even at temperatures up to 180 °C [Eq. (1); cod = 1,5-cyclooctadiene, TMS = trimethylsilyl, tmeda = tetramethylethylenediamine].



(1)

Clearly, a more active and robust set of catalysts are needed to cleave the C–O bonds in biaryl ether units like those in lignin. Herein, we report the cleavage of biaryl C–O bonds by readily available nickel nanoparticles supported on activated carbon. These catalysts are more thermally stable than homogeneous or unsupported nanoparticulate nickel and therefore catalyze the hydrogenolysis of hindered, electron-rich diaryl ethers relevant to those in lignin.[13]

Our efforts to evaluate the reactivity and selectivity of a supported, nanoparticulate nickel catalyst under various conditions for the cleavage of biaryl ethers began with reactions of diphenyl ether (**2a**) itself. These studies showed that the hydrogenolysis of **2a** catalyzed by unsupported Ni precursors was incomplete when conducted at 180 °C, rather than 120 °C (Table 1, entries 1–3), even with prolonged reaction times (data not shown). Faster aggregation of the Ni nanoparticles formed in situ would account for the lower activity of the catalyst generated from [Ni(CH$_2$TMS)$_2$(tmeda)] than that of the supported particles for reactions at 180 °C rather than 120 °C (Table 1, entries 1 and 2).

We hypothesized that the localization of the nanoparticles would inhibit such aggregation at higher temperatures, thus leading to a longer-lived catalyst. Thus, we deposited [Ni-

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[*] Dr. F. Gao,[+] Dr. J. D. Webb,[+] Prof. Dr. J. F. Hartwig
Department of Chemistry, University of California
Berkeley, CA 94720 (USA)
E-mail: jhartwig@berkeley.edu

[+] These authors contributed equally.

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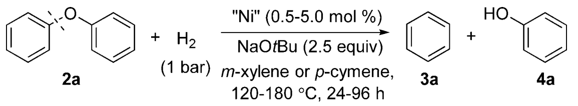
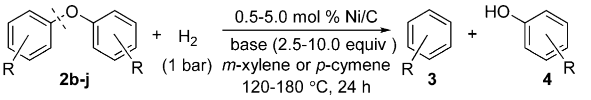
Table 1: Comparison of various nickel catalysts for the hydrogenolysis of diphenyl ether.[a]



Entry	"Ni" (loading [mol %])	*T* [°C]	*t* [h]	Conv. [%]	GC yield [%] **3a**	**4a**
1	[Ni(CH$_2$TMS)$_2$(tmeda)] (2.0)	120	96	>99	99	99
2	[Ni(CH$_2$TMS)$_2$(tmeda)] (2.0)	180	24	85	84	83
3	[Ni(cod)$_2$] (2.0)	180	24	93	93	91
4	Ni/C (0.5)	180	24	>99	99	99
5[b]	Ni/C (2.5)	120	24	>99	99	97
6	Ni/Al$_2$O$_3$/SiO$_2$ (5.0)	180	24	97	96	89
7[c]	Ni–B/C (5.0)	180	24	>99	99	82

[a] Reaction conditions: diaryl ether (1 equiv), H$_2$ (1 bar gauge pressure at 22 °C), "Ni" (0.005–0.05 equiv), NaO*t*Bu (2.5 equiv), *m*-xylene (120 °C) or *p*-cymene (180 °C), 24–96 h. [b] KHMDS (2.5 equiv) was used as the base. [c] Ni–B/C was prepared by the reduction of a Ni^{II} precursor with NaBH$_4$ (see the Supporting Information for details). HMDS = hexamethyldisilazide.

Table 2: Ni/C-catalyzed hydrogenolysis of symmetrical diaryl ethers.[a]



Entry	R	Ni/C loading [mol %]	Base	*T* [°C]	GC Yield [%] **3**	**4**
1	*o*-Me (**2b**)	5.0	KHMDS	180	81	78
2	*p*-Me (**2c**)	2.5	NaO*t*Bu	180	94	91
3	*m*-Me (**2d**)	2.5	NaO*t*Bu	180	94	91
4	*o*-OMe (**2e**)	0.5	NaO*t*Bu	140	95	96
5	*p*-OMe (**2f**)	5.0	KHMDS	120	99	90
6	*m*-OMe (**2g**)	5.0	KHMDS	120	95	82
7	*p*-*tBu* (**2h**)	5.0	KHMDS	120	97	99
8[b]	*o*-OH (**2i**)	5.0	NaO*t*Bu	140	93	83
9[c]	*p*-OH (**2j**)	5.0	NaO*t*Bu	180	84	70

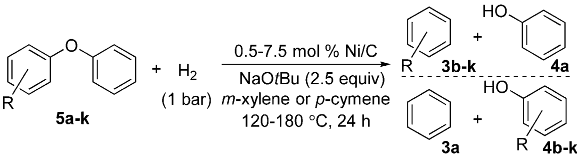
[a] Reaction conditions: diaryl ether (1 equiv), H$_2$ (1 bar gauge pressure at 22 °C), Ni/C (0.005–0.05 equiv), base (2.5–10.0 equiv), *m*-xylene (120–140 °C) or *p*-cymene (180 °C), 24 h. [b] The reaction was carried out with 5.0 equivalents of NaO*t*Bu. [c] The reaction was carried out with 10.0 equivalents of NaO*t*Bu and proceeded to 84 % conversion.

(cod)$_2$] on activated carbon (see the Supporting Information for details); the resulting black powder consists of approximately 3 wt % Ni^0, as determined by elemental analysis. This material is more reactive for C–O bond cleavage of diphenyl ether **2a** at 180 °C; only 0.5 mol % of nickel was required for full conversion within 24 h (Table 1, entry 4).[14] Commercially available Ni/Al$_2$O$_3$/SiO$_2$ and nickel boride prepared from a less expensive Ni^{II} precursor[15] were also effective catalysts, although somewhat higher loadings (5 mol %) were needed for reactions catalyzed by these materials to occur to full conversion (Table 1, entries 6 and 7). As observed in our prior studies, a stoichiometric amount of a base was essential for hydrogenolysis to occur selectively over arene hydrogenation (see Table S1 in the Supporting Information). In addition to the hydrogenolysis with added NaO*t*Bu, the hydrogenolysis of diphenyl ether in the presence of KHMDS proceeded to >99 % conversion within 24 h at 120 °C to deliver benzene and phenol in quantitative yields (Table 1, entry 5).

Having identified conditions for the hydrogenolysis of diphenyl ether with Ni/C, we investigated the scope of the cleavage of biaryl ethers in the presence of Ni/C. In general, we sought to shorten the reaction time required with the previous systems (48–96 h) and to increase the scope of the reaction to encompass diaryl ethers that are less reactive than unsubstituted diphenyl ether. Reactions with symmetrically substituted diaryl ethers are summarized in Table 2. We first examined a set of methyl-substituted biaryl ethers (Table 2, entries 1–3). At 180 °C, Ni/C-catalyzed hydrogenolysis of these substrates proceeded to high conversion within 24 h regardless of the position of the methyl group on the aromatic ring. In comparison, equivalent reactions to those in entries 2 and 3 with unsupported nickel particles generated from 5–10 mol % of a Ni precursor required 96 h at 120 °C to reach similar yields of toluene and phenols.[12a] Reactions of methoxy-containing biaryl ethers that are relevant electronically to biaryl ethers in lignin with Ni/C as the catalyst furnished anisole and hydroxyanisoles in high yields of 90–99 % (Table 2, entries 4–6). In contrast, only 70 % conversion of biaryl ether **2g** had occurred after 48 h when the corresponding hydrogenolysis was conducted with Ni nanoparticles formed in situ from [Ni(CH$_2$TMS)$_2$(tmeda)] (10 mol %) as the catalyst.[12a] The Ni/C material also catalyzed the cleavage of C–O bonds in symmetrical biaryl ethers containing a bulky *p*-*tert*-butyl group (**2h**) or a free hydroxy group (**2i**,**j**) with complete conversion and in high yield within 24 h (Table 2, entries 7–9).

We also investigated the hydrogenolysis of a variety of unsymmetrical diaryl ethers catalyzed by Ni/C (Table 3). In general, the two possible arenes and two possible phenols

Table 3: Hydrogenolysis of unsymmetrical diaryl ethers under the catalysis of nickel particles supported on carbon.[a]



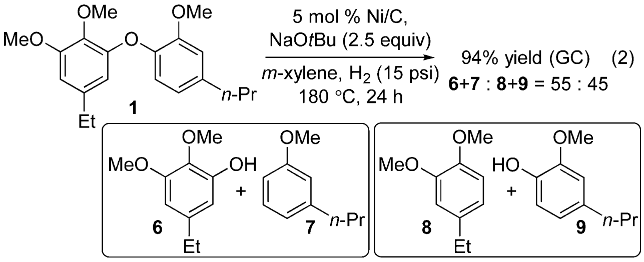
Entry	R	Ni/C loading [mol %]	*T* [°C]	Yield of arenes [%][b] **3b–k**	**3a**	Yield of phenols [%][b] **4a**	**4b–k**
1	*o*-Me (**5a**)	5.0	180	29	73	23	54
2	*m*-Me (**5b**)	2.0	160	18	88	13	71
3	*p*-Me (**5c**)	2.0	160	19	86	15	74
4	*p*-*t*Bu (**5d**)	2.0	160	4	92	2	93
5	3,5-*t*Bu (**5e**)	2.0	160	0	98	0	99
6	*o*-OMe (**5f**)	2.0	160	40	50	43	40
7[c]	*m*-OMe (**5g**)	5.0	180	34	48	21	46
8[c]	*p*-OMe (**5h**)	7.5	180	57	24	53	19
9	*o*-OH (**5i**)	2.0	140	82	14	82	10
10	*m*-OH (**5j**)	2.0	140	90	10	90	8
11	*p*-OH (**5k**)	0.5	120	94	0	94	0

[a] Reaction conditions: diaryl ether (1 equiv), H$_2$ (1 bar gauge pressure at 22 °C), Ni/C (0.005–0.075 equiv), NaO*t*Bu (2.5 equiv), *m*-xylene (120–160 °C) or *p*-cymene (180 °C), 24 h. [b] The yield was determined by GC with dodecane as the internal standard. [c] The reaction was carried out with 2.5 equivalents of KHMDS.

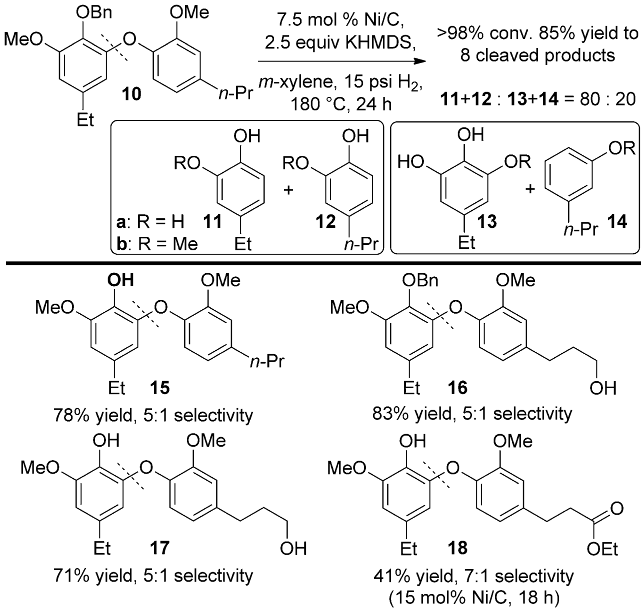
were obtained in high combined yields within 24 h. The steric properties of the aryl rings controlled the site of C–O bond cleavage. As expected, the reactions occurred preferentially at the less hindered C–O bond (Table 3, entries 1–5). However, less straightforward is the high regioselectivity for cleavage of the C–O bond at the less substituted arene in biaryl ethers substituted with *p*-*t*Bu and 3,5-di-*t*Bu groups. The selectivity for cleavage of the C–O bond to the ring lacking the *para* and *meta tert*-butyl groups in substrate **5e** was larger than that for cleavage of the C–O bond to the ring without the *ortho* methyl group in **5a**. Moreover, the same reaction of **5e** conducted with the ligandless Ni catalyst reported previously occurred to only 45 % conversion with 10 mol % nickel and a longer reaction time (48 h, 120 °C).[16] These data suggest that preferential binding of the less substituted aryl unit to the surface of the Ni catalyst determines the identity of the C–O bond that is cleaved, but that the Ni/C catalyst enables the cleavage of aryl ethers containing bulky substituents owing to its greater thermal stability.

The Ni/C-catalyzed hydrogenolysis of biaryl ethers containing an electron-donating OMe group led to aromatic products in excellent combined yields, but unselectively (Table 3, entries 6–8). Similar outcomes were observed for reactions catalyzed by unsupported nanosized nickel species generated in situ, but with considerably lower yields than those observed with Ni/C. For example, C–O bond cleavage of **5h** at 180 °C in the presence of 7.5 mol % Ni/C resulted in an 80 % combined yield of arenes and phenols. In contrast, the same reaction with the unsupported nanoparticulate Ni catalyst (10 mol % [Ni(cod)$_2$], 120 °C) generated phenols and arenes in 20 % combined yield after 48 h. Furthermore, hydrogenolysis catalyzed by Ni/C occurred with high selectivity at the more electron rich C–O bond of biaryl ethers containing free hydroxy substituents (Table 3, entries 9–11), thus implying a possible binding interaction between the metal surface and phenoxy anions formed in situ.

Having established conditions for the cleavage of aryl ethers catalyzed by Ni/C, we tested this system for the cleavage of diaryl ether **1**, which mimics the types of diaryl ethers in lignin. In the presence of 5 mol % of the carbon-supported Ni catalyst, substrate **1** underwent facile hydrogenolysis over 24 h at 180 °C to afford of the four monomeric arenes and phenols from cleavage of either C–O bond in 94 % combined yield and a roughly 1:1 ratio [Eq. (2)]. The same reaction did not proceed at 120 °C (< 2 % conversion of **1**). Thus, this example illustrates the importance of a nickel catalyst that is more stable at high temperatures than unsupported nickel nanoparticles for the hydrogenolysis of the types of C–O bond present in lignin or fragments created from lignin.



Because the 4-*O*-5 linkages in actual lignin samples contain at least one phenoxy group as either a free phenol or an alkyl or aryl ether, we conducted the hydrogenolysis with additional substrates that more closely mimic the fragments in lignin. The benzyl-protected biaryl ether **10** was cleaved effectively in the presence of 7.5 mol % Ni/C and a stoichiometric amount of the base KHMDS[17] to furnish eight aromatic monomers described by structures **11–14** in 85 % combined yield (Scheme 1). Likewise, the model compounds **15–18**, which bear close structural similarities to the diaryl ether units in lignin, reacted in the presence of 7.5–15 mol % Ni/C and KHMDS to form the monomeric products of C–O bond hydrogenolysis at 180 °C within 24 h in yields up to 83 %. In these reactions, the C–O bond adjacent to the free phenol or adjacent to the readily removable Bn group is cleaved preferentially; 4:1 to 7:1 selectivity was observed for reactions of the diaryl ethers in Scheme 1.



Scheme 1. Examples of the nickel-catalyzed hydrogenolysis of compounds that mimic the diaryl ethers in lignin. For reaction details, see the Supporting Information; > 98 % conversion was observed in all cases.

To understand the role of the support and the size of the nanoparticles, we studied the reaction profiles of the hydrogenolysis of **5e** under the catalysis of [Ni(cod)$_2$] and Ni/C at different reaction temperatures. The reaction of diaryl ether **5e** proceeded to 44 % conversion when catalyzed by [Ni(cod)$_2$] (after 48 h) and 57 % conversion with Ni/C (after 48 h) at 120 °C (Figure 1, top graph). The data from the first 6 h of the reactions in which [Ni(cod)$_2$] was the precatalyst reveal an induction period during the reactions. After 2 h, nickel particles with a size of 2–3 nm were observed by TEM. We isolated these nanoparticulate Ni species (see the Supporting

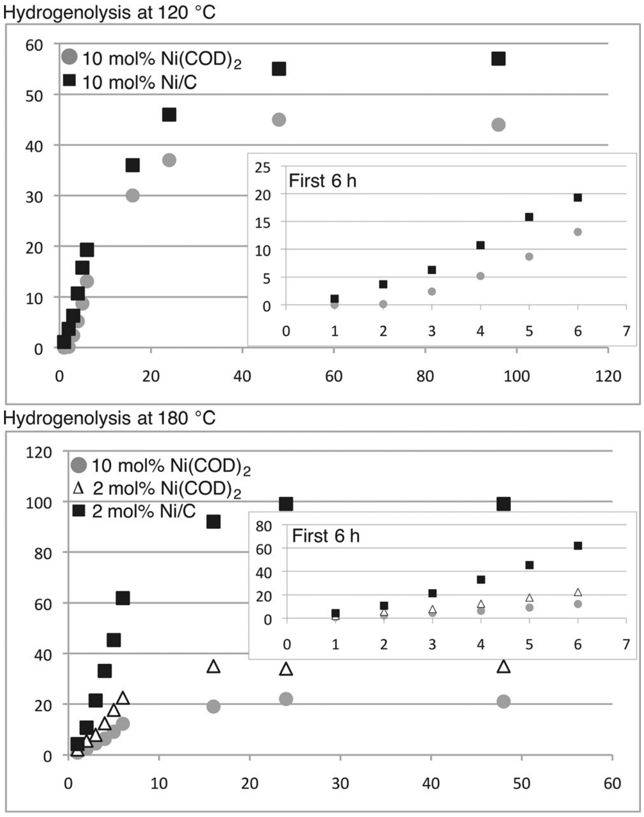


Figure 1. Time profiles for the hydrogenolysis of **5e** by [Ni(cod)$_2$] and Ni/C with hydrogen (15 psi) in *m*-xylene and *p*-cymene in the presence of NaO*t*Bu base at various temperatures. The average of three sets of data is shown for each time point. See the Supporting Information for reaction details.

Information for details) and utilized them instead of [Ni(cod)$_2$] for the hydrogenolysis of **5e** at 120 °C. This reaction occurred to 39 % conversion after 48 h. At later times, the size of the nanoparticulate nickel generated in situ increased. Analysis of the particle size after 24 h showed the presence of particles up to 10 nm in size, as well as the 2–3 nm Ni particles seen at the beginning of the hydrogenolysis (see Figure S6 in the Supporting Information). In contrast, reactions catalyzed by the preformed Ni/C catalyst occurred with a less pronounced induction period, and the size distribution of the embedded nickel particles remained 2–6 nm throughout the course of the hydrogenolysis (see Figure S8).

The data in Figure 1 obtained at 180 °C demonstrate the difference in reactivity of the [Ni(cod)$_2$] and Ni/C catalysts. They show in detail the greater difference in activity of the catalysts at high temperature than at low temperature. This difference is seen by comparing the hydrogenolysis of **5e** by 10 mol % of [Ni(cod)$_2$] and Ni/C. Whereas the reactions with [Ni(cod)$_2$] stalled at 20 % conversion after 24 h, those with Ni/C proceeded to completion after the same time. The data also show the counterintuitive result of lower conversion of the diaryl ether at higher catalyst loadings of [Ni(cod)$_2$] (21 % with 10 mol % of [Ni(cod)$_2$] versus 35 % with 2 mol % of [Ni(cod)$_2$]). Finally, they show that the induction period of reactions catalyzed by [Ni(cod)$_2$] at 180 °C is shorter than that of reactions conducted at 120 °C.

Again, parallel analysis of the catalyst by TEM revealed the origins of these observations. TEM analysis of the hydrogenolysis mixture showed that the nanoparticulate Ni species formed from [Ni(cod)$_2$] had a size of 4–13 nm after 1 h, but after 24 h the particle size had increased significantly to 17–23 nm (see Figure S7). Bulk metal clusters that were larger than 100 nm in size were also observed at this time. A similar analysis of the reactions of **5e** to form 3,5-di-*tert*-butylphenol and benzene under Ni/C catalysis over 24 h showed that these reactions occurred without significant aggregation of the Ni particles on the activated carbon (see Figure S9).

On the basis of the above studies, we propose that sintering of the Ni nanoparticles at 180 °C limits the potential to use elevated temperatures to induce cleavage of the C–O bonds in particularly stable diaryl ethers with the catalyst generated from [Ni(cod)$_2$].[18] However, the supported nickel species is reactive at high temperatures for longer periods because of its slower aggregation, and maintains the high selectivity for hydrogenolysis over hydrogenation in the presence of a base.

In summary, we have developed a hydrogenolysis of diaryl ethers that is catalyzed by nickel nanoparticles supported on activated carbon. The new protocol provides an approach to the cleavage of C–O bonds in more sterically demanding diaryl ethers related to the diaryl ether units of lignin. Preliminary mechanistic studies suggest that the lower propensity of these supported Ni particles towards sintering at higher temperature (up to 180 °C) allows the hydrogenolysis to be conducted with this catalyst at higher temperatures than hydrogenolysis catalyzed by unsupported particles generated from [Ni(cod)$_2$]. Detailed mechanistic investigation of this type of nickel-catalyzed hydrogenolysis, especially the role of the added base in controlling hydrogenolysis versus hydrogenation, is ongoing.

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Keywords: C–O cleavage · diaryl ethers · heterogeneous catalysis · hydrogenolysis · nickel catalysts

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