Nickel-Catalyzed C(sp^3)–O Hydrogenolysis via a Remote Concerted Oxidative Addition and its Application to Degradation of a Bisphenol A-Based Epoxy Resin

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KEYWORDS: *Nickel catalyst, C–O transfer hydrogenolysis, epoxy resin degradation.*

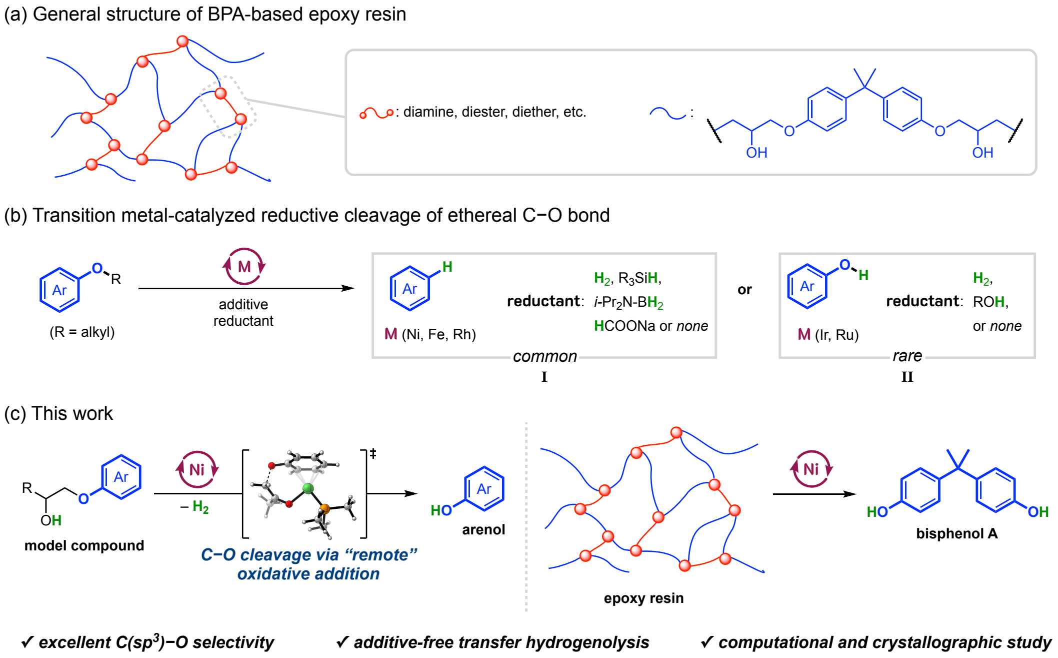
ABSTRACT: In this work, we developed a nickel-catalyzed transfer hydrogenolysis of 1-aryloxy-3-amino-2-propanols, which is a model compound of amine-cured bisphenol A (BPA)-based epoxy resin. Mechanistic investigation revealed that the hydroxy group acts as the hydrogen donor to generate α-aryloxy ketone, which undergoes an unprecedented remote concerted oxidative addition of the C(sp^3)–O bond as suggested by DFT calculation. Successful application of this method was demonstrated by the degradation of a diamine-cured BPA-based epoxy resin, where BPA was directly recovered from the resin.

INTODUCTION

Ethereal C–O bond is a fundamental connection in numerous plastic materials serving as the building block, where the bisphenol A (BPA)-based epoxy resin is also included (Scheme 1a).[1] BPA-based epoxy resins are generally produced via the curing of bisphenol A diglycidyl ether (BADGE) with various ring-opening bridging reagents as the hardener, such as amine, anhydride and phenol oligomer.[2] It is without a doubt that, the selective and reductive cleavage of ethereal C(sp^3)–O bonds to C–H and O–H bonds is attractive since it allows the direct recovery of BPA, to provide an appealing recycling approach for gaining valuable chemical feedstocks from discarded plastic wastes.[3] Over the previous decade, transition metal-catalyzed reductive cleavage of ethereal C–O bonds to form C–H and O–H bonds has been extensively developed using Ni,[4a-4g] Rh,[4h], or Fe[4i] as catalysts and H$_2$, silane, aminoborane or metal formate as reductants or under external reductant-free conditions. However, these previously reported homogeneous catalysis have typically targeted C(sp^2)–O bonds, despite the co-existence of C(sp^3)–O bonds in the substrate in some cases (Scheme 1b, I). Regarding to C(sp^3)–O bonds, silanes and boranes are traditionally used, but a very rare example employing H$_2$ as a cheap reductant is an Ir-catalyzed hydrogenolysis of non-activated aryl methyl ethers by our group in 2015.[5,6] This selective result indicated the potential for degrading BPA-based epoxy resin via disconnection of its C(sp^3)–O bonds to recover BPA, but the high cost and synthetic complexity of the Ir catalyst restrict its industrial implementation. Ru also contributed examples of the reductive cleavage of C(sp^3)–O bonds of lignin model compounds, where Bergman and Ellman further applied Ru catalysis to the depolymerization of a lignin-related polymer without external reductant.[7] Very recently, while our study was ongoing, Ahrens and Skrydstrup reported the pioneering work of disconnecting C(sp^3)–O bonds in BPA-based epoxy resin using homogeneous Ru catalyst employing 2-propanol as a reductant,[8] while up to date, the employment of cheap metal to develop a C(sp^3)–O bond-selective degradation of BPA-based epoxy resin remains highly demanded from economic viewpoint (Scheme 1b, II).

Taking inspiration from the remarkable reactivity of nickel towards ethereal C–O bond activation, along with the fact that nickel represents a cheap and earth-abundant transition metal, in this work, we study the Ni-catalyzed hydrogenolysis of C(sp^3)–O bond using β-hydroxyalkyl aryl ether as the model compound mimicking amine-cured BPA-based epoxy resin, to afford arenols selectively. In the study with model compounds, an unprecedented concerted pathway of C–O cleavage via a remote oxidative addition to Ni(0) is proposed based on our DFT calculations and an experimental support (Scheme 1c, left). Furthermore, we applied this methodology to the degradation of diamine-cured BPA-based epoxy resin and successfully obtained BPA (Scheme 1c, right).

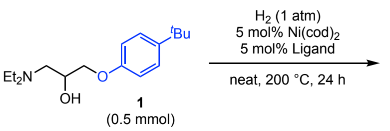
Scheme 1. Concept of This Work



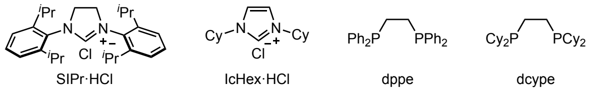
RESULTS & DISCUSSION

Optimization of Conditions. 1-Aryloxy-3-amino-2-propanol (aryloxy = 4-*tert*-butylphenoxy, amino = *N,N*-diethylamino) **1** was synthesized as the model compound mimicking amine-cured epoxy resin. As the initial study, we performed a screening of ligands with Ni(cod)$_2$ as the catalyst precursor (Table 1). In the presence of 1 atm of H_2 gas under 200 °C after 24 h without solvent, NHC ligands SIPr·HCl and IcHex·HCl gave target product with low to moderate yields (11% and 48%, Table 1, entries 1, 2). Monodentate PPh$_3$ and PCy$_3$ ligands gave high or moderate yield of the product (74% and 58%, entries 3, 4). As bidentate ligands, dppe decreased the catalytic reactivity (17%, entry 5), while dcype promoted the reaction more efficiently (70%, entry 6). Under ligand-free conditions, the reaction barely proceeded (17%, entry 7). Notably, the reaction also proceeded even under N_2 atmosphere to give **2** (66%, entry 8), indicating external H_2 is not essential in this reaction. To test the essential stoichiometry of phosphorus atoms to nickel, the reaction with 10 mol% of PPh$_3$ (2 equiv of phosphorus atom to nickel) and 2.5 mol% of dcype (1 equiv of phosphorus atom to nickel) were investigated (entries 9 and 10). The yield was significantly diminished to 25% with 10 mol% of PPh$_3$ (compared to 74% in entry 3), whereas good yield of 62% was obtained with 2.5 mol% of dcype (under N_2 atmosphere, compared to 66% in entry 8). Therefore, 1 equiv of phosphorus atom to nickel is suggested to be essential and dcype is considered to be acting as a monodentate ligand in the reaction conditions.[9] Finally, by employing 10 mol% of isolated Ni(cod)(dcype) complex under N_2 atmosphere, 90% yield of **2** was afforded (entry 11).

Table 1. Screening of Ligands^a



entry	Ligand	recovery of **1**^{b} (%)	yield of **2**^{b} (%)
1	SIPr·HCl/^{t}BuOK	93	11
2	IcHex·HCl/^{t}BuOK	48	48
3	PPh$_3$	15	74
4	PCy$_3$	34	58
5	dppe	84	17
6	dcype	20	70
7	/	84	17
8^c	dcype	26	66
9	PPh$_3$ (10 mol%)	73	25
10^c	dcype (2.5 mol%)	21	62
11^{c,d}	/	0	90

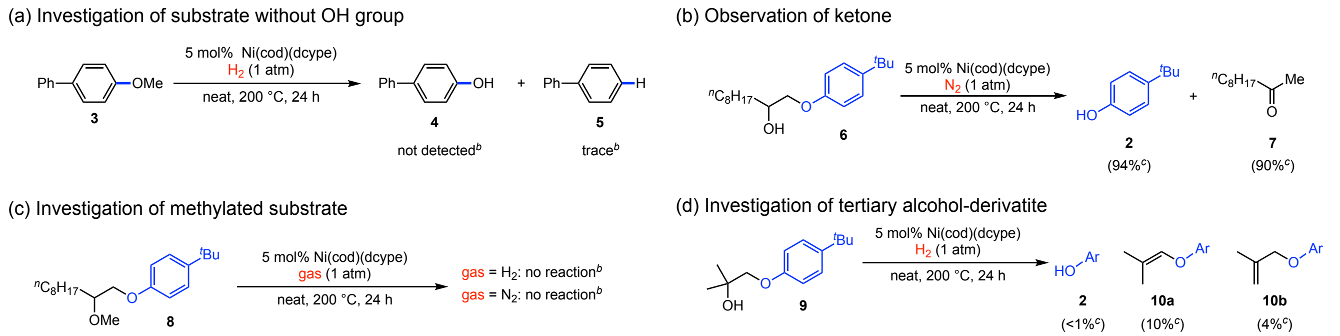


^{a}Reaction conditions: **1** (0.5 mmol), Ni(cod)$_2$ (5 mol%) and ligand (5 mol%) at 200 °C for 24 h under H_2 (1 atm). ^{b}Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard. ^{c}Under N_2 atmosphere. ^{d}Ni(cod)(dcype) (10 mol%) was used.

Mechanistic studies. First, to investigate the importance of β-hydroxyalkyl moiety, 4-phenylanisole (**3**) as an aryl alkyl ether was subjected to the standard conditions, to result in no C(sp^3)–O or C(sp^2)–O cleavage product under H_2 atmosphere (Scheme 2a). This result clearly revealed the substrate specificity of this method to 1-aryloxy-3-amino-2-propanols, where the hydroxy group might play an important role to enable the reaction.

To clarify the role of the –OH group, model compound **6**, which lacks amino group was subjected to the catalytic conditions under N_2 atmosphere (Scheme 2b). Upon work-up, 94% yield of **2** and 90% of 2-decanone **7** were obtained. The cleaved C– and O–sides were found to be both hydrogenated to methyl and hydroxy groups, which strongly indicated the reaction to be a hydrogenolysis pathway rather than a nucleophilic substitution. It should be noted that, the alcohol moiety was oxidized to a ketone after the reaction under N_2 atmosphere. This observation suggests that the hydrogen source for the hydrogenolysis is the secondary alcohol moiety of the substrate, and the reaction is regarded as a transfer hydrogenolysis.[7, 10]

Scheme 2. Control Experiments[a]



[a]Reaction conditions: substrate (0.5 mmol) and Ni(cod)(dcype) (5 mol%) at 200 °C for 24 h under H_2 or N_2 (1 atm). [b]Determined by ^1H NMR and GC-MS. [c]Determined by ^1H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

The requirement for the alcoholic –OH group was further supported by a control experiment using compound **8**, which has an –OMe group instead of –OH, and such compound might have similar electronic state of C–O bond while lacks hydrogen. Treatment of compound **8** with 5 mol% Ni(cod)(dcype) catalyst under H_2 or N_2 atmosphere resulted in no reaction even in the presence of external H_2 reductant (Scheme 2c). Accordingly, the hydroxy group is necessary for the reaction to proceed and the oxidative addition of C(sp^3)–O bond by the chelating effect of the oxygen atom at the *β*-position could be excluded.

The hydrogen atom at α-position to the –OH group was also proven to be essential by the control experiment using compound **9**, which is a tertiary alcohol rather than secondary. The reaction was carried out under H_2 atmosphere, while only the dehydration of the hydroxy group partially occurred to form small amount of olefins **10a** and **10b**, with a trace amount of **2** (Scheme 2d). Based on the above results, we conceive the initial pathway to lead the C–O cleavage is the oxidative addition of Ni(0) to the O–H bond[11] (that was prevented in Scheme 2c), followed by the *β*-H elimination to generate ketone (that did not happen in Scheme 2d). Although epoxide ring-closure from 1-aryloxy-2-propanol would afford arenol **2**, this pathway is less likely because the yield of **2** in the reaction of **9** was negligible.

In order to gain further insights into the reaction mechanism, density functional theory (DFT) calculation was conducted (Figure 1), and Figure 1a represents the key pathway of C(sp^3)–O cleavage. Given the fact that 1.0 equiv of phosphorus atom to nickel is essential for the reaction (Table 1), PMe_3-monocoordination complexes were applied as the model species, and **Int-1**, which is supposed to be generated by the oxidative addition of O–H bond of substrate to zero-valent nickel complex was adopted as the starting complex. First, concerted *β*-H elimination on **Int-1** and subsequent elimination of H_2 and coordination of arene group lead to **Int-4**. The key C–O cleavage occurs via the concerted formation of aryloxide and enolate anions from the aryloxyketone to give intermediate **Int-5a**, whose (C–C–C)η^3-aryloxy ring then turns to (C–C–O)η^3-coordination to form **Int-5b**, and further isomerized to more stable isomer **Int-5c**. At this step, the nickel center is oxidized from Ni(0) to Ni(II). For the successive pathway (Figure 1b), another molecule of substrate (**ROH**) protonates the enolate on **Int-5c** (via **TS-3**) to form an Ni(phenoxy)(alkoxy) species **Int-7**. After substitution of acetone with H_2 to form **Int-9**, undergoes hydrogenolysis (**TS-4**) to generate **Int-10**, which releases PhOH and regenerates **Int-1**.[12] The highest barrier step for the overall reaction would be **TS-4**, and **Int-7** would be the resting state for the reaction pathway.[13] Therefore, the calculated activation energy for the rate-determining steps is 27.0 kcal/mol, which is also consistent with the requirement of a high reaction temperature of 200 °C.

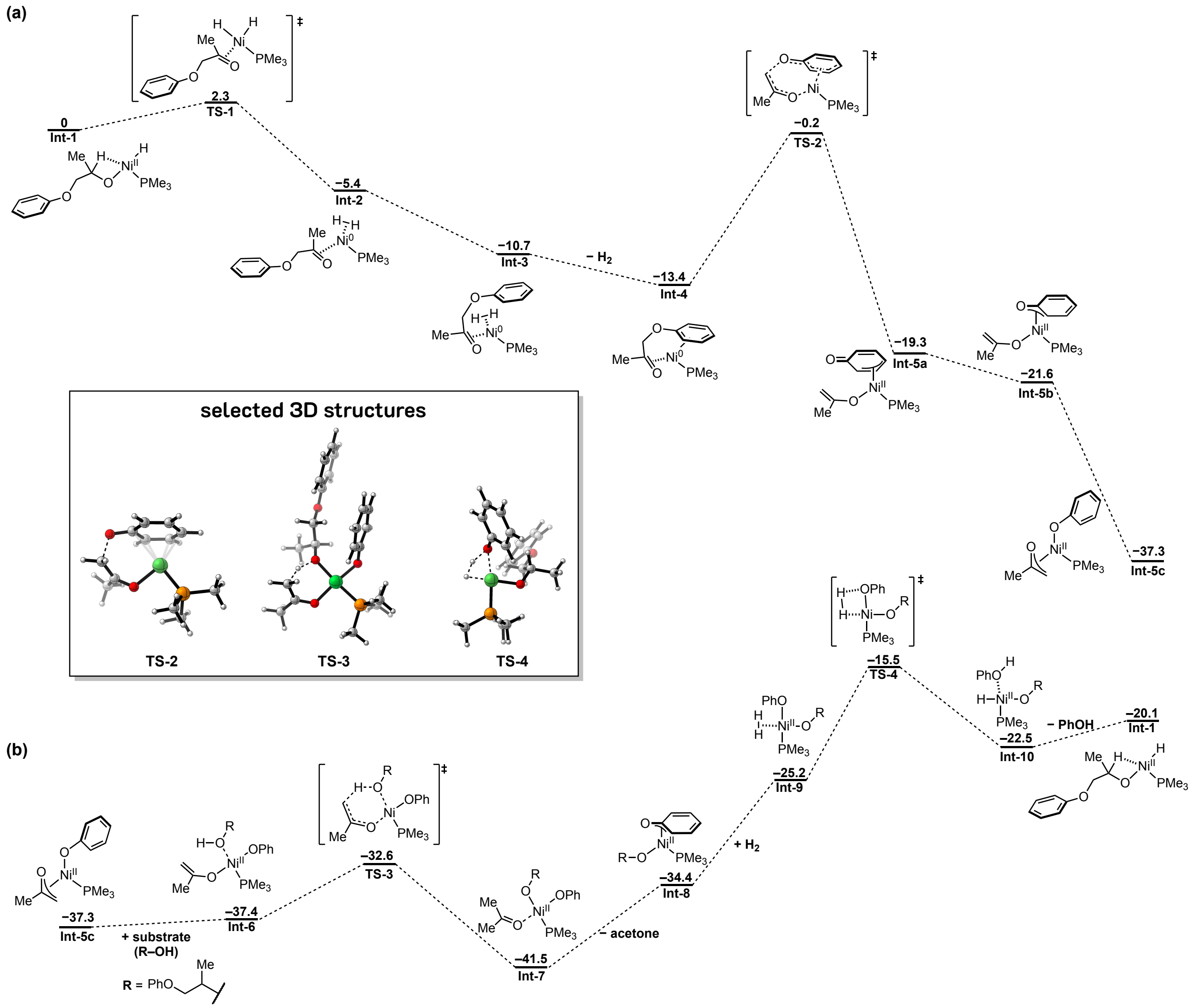
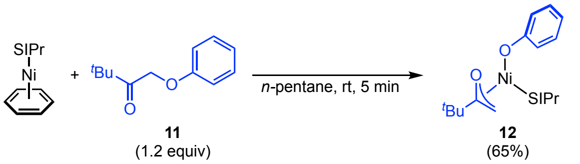


Figure 1. Free energy diagram of reaction pathway at the M06-L/def2svp level of theory in a gas-phase. Simplified structures of phosphine (trimethylphosphine) and substrate (1-phenoxypropan-2-ol) were used. (a) Pathway from **Int-1** to **Int-5b**. (b) Pathways from **Int-5b**. Selected 3D structures of **TS-2**, **TS-3**, and **TS-4** were displayed by the *CYLview* visualization program.[14]

To further support the mechanism, a stoichiometric reaction was carried out using Ni(SIPr)(benzene) complex and 3,3-dimethyl-1-phenoxybutan-2-one (**11**), which is analogous to the suggested intermediate formed by the dehydrogenation in Figure 1a. After mixing Ni(SIPr)(benzene) with 1.2 equiv of **11** in *n*-pentane at room temperature for 5 min, a Ni(η^3-enolate)(phenoxy) complex (**12**) was obtained in 65% yield (Scheme 3), whose structure was unambiguously identified by the single-crystal X-ray diffraction analysis (Figure 2). This experimental result is consistent with the calculation in Figure 1, where the structure of **12** is analogous to **Int-5c**, stabler isomer of phenoxy enolate complex.

Scheme 3. Synthesis of Ni(η^3-enolate)(phenoxy) Complex



11
(1.2 equiv)

12
(65%)

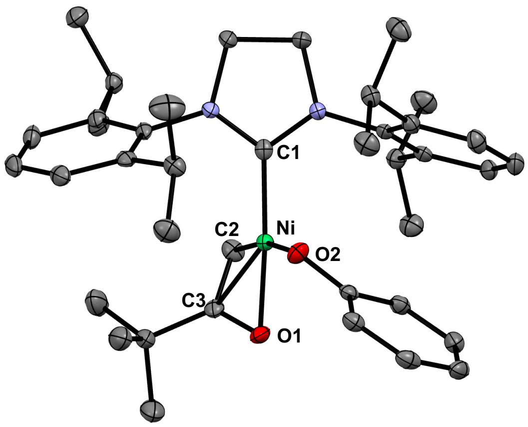
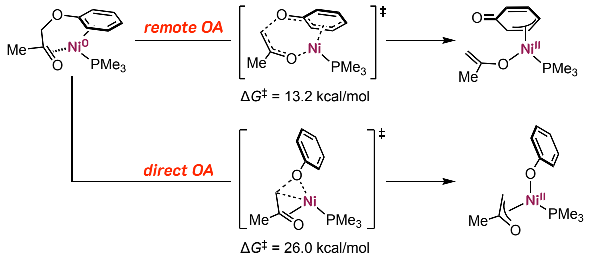


Figure 2. X-ray structure of Ni(SIPr)(η^3-enolate)(phenoxy) complex **12** with ORTEP drawing at the 50% probability level. A solvent molecule (pentane) and H atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): Ni–C1 1.877(2), Ni–C2 1.994(2), Ni–C3 2.078(2), Ni–O1 1.932(1), Ni–O2 1.861(1), O1–Ni–O2 97.19(6), C1–Ni–C2 96.49(7).

The high reactivity of Ni towards C–O bond of **11** which completes within 5 min at r.t. is consistent with the low activation energy estimated by DFT calculation in Figure 1 (**Int-4** to **TS-2**, $\Delta G^‡$ = 13.2 kcal/mol). Notably, the direct oxidative addition where the nickel interacts both C and O atoms of cleaving bond, requires a higher energy ($\Delta G^‡$ = 26.0 kcal/mol, Scheme 4), being inconsistent with the rapid C–O cleavage observed in Scheme 3. Similar difference was also evident in the calculation of exact model using compound **11** as the substrate and SIPr as the ligand instead of PMe_3 (see SI). The oxidative addition of C(sp^3)–O bond here is very unique since the nickel center was oxidized remotely without bonding with the cleaving sites.[15]

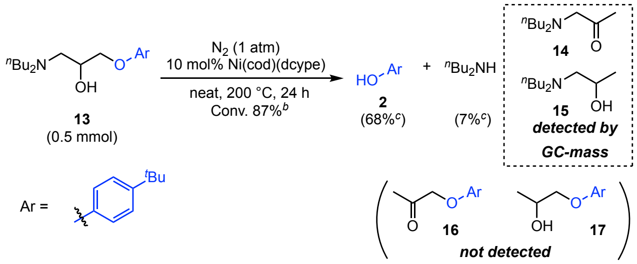
Scheme 4. Remote and Direct Oxidative Additions of C(sp^3)–O Bond[a]



[a]Free energy diagram of reaction pathway at the M06-L/def2svp level of theory in a gas-phase.

Finally, to confirm the fate of the amino group in the model compound **1**, ^{n}Bu$_2$N-substituted model compound **13** was applied to make the amine product less volatile, and treated under catalytic conditions under N_2 (Scheme 5). After the reaction, various ^{n}Bu$_2$N-containing compounds were detected by ^{1}H NMR and GC-mass, which include 1-dibutylaminoacetone (**14**), and 1-dibutylamino-2-propanol (**15**), which are products of desired C–O bond cleavage reaction. Notably, ^{n}Bu$_2$NH, which was supposed to be formed by the hydrogenolysis of C–N bond was also detected with GC-yield of 7%.[16] Neither 1-aryloxyacetone (**16**) nor 1-aryloxy-2-propanol (**17**), which are C–N bond cleavage products maintaining C–O bond were detected. Accordingly, the C–N bond cleavage was supposed to occur after the cleavage of C–O bond. A comparison by DFT calculation also suggested a higher barrier for the C–N bond cleavage relative to the C–O bond (See SI). This is promising since the catalyst not only disconnects C(sp^3)–O bonds, but also enables the recovery of amine curing reagent via C–N bond cleavage. However, the stoichiometry of the hydrogen atoms will not be sufficient if it's only derived from the hydroxy groups. Therefore, dihydrogen should be essential to complete the degradation of amine-cured BPA-based epoxy resin.

Scheme 5. Ni-Catalyzed Hydrogenolysis of ^{n}Bu$_2$NH-Derived Model Compound[a]

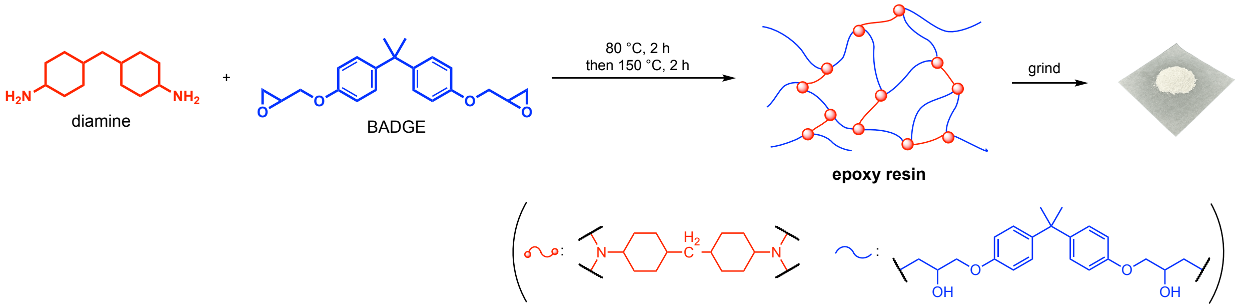


[a]Reaction conditions: **13** (0.5 mmol) and Ni(cod)(dcype) (10 mol%) at 200 °C under N_2 (1 atm) for 24 h. [b]^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard. [c]GC yield using dodecane as the internal standard.

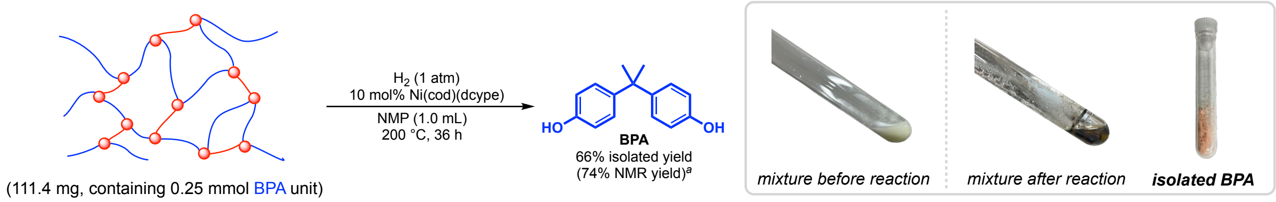
Application on epoxy resin. With the optimized conditions of Ni-catalyzed hydrogenolysis of 1-aryloxy-2-propanols and understanding on the reaction mechanism, we finally employed this method to the degradation of an epoxy resin, a much more challenging material than the model compound. Herein, we synthesized a diamine-cured BPA-based epoxy resin by using bisphenol A diglycidyl ether (BADGE) as the monomer and 4,4'-methylenebis(cyclohexylamine) as the curing reagent by following a reported procedure,[17] and the synthesized epoxy resin was grinded into fine powder for Ni-catalyzed degradation (Scheme 6a). After an extensive optimization of the reaction conditions (see SI), a 66% isolated yield (74% NMR yield before the isolation) of BPA was successfully obtained, by using 10 mol% (relative to C–O bond) of Ni(cod)(dcype) catalyst and heated at 200 °C for 36 h under an atmosphere of 1 atm of H_2 in *N*-methyl-2-pyrrolidone (NMP) as the solvent.[18] To be noted, after the reaction, the initial white suspension transformed into a dark green solution with little precipitation, indicating that the insoluble epoxy resin has significantly been converted into NMP-soluble components (Scheme 6b).

Scheme 6. Study on Diamine-Cured Epoxy Resin

(a) Synthesis of diamine-cured epoxy resin



(b) Ni-catalyzed degradation of epoxy resin



^{a}Determined by ^{1}H NMR before isolation using 1,1,2,2-tetrachloroethane as an internal standard.

CONCLUSIONS

In this paper, we reported a novel Ni-catalyzed hydrogenolysis of C(sp^3)–O bond. As a model compound mimicking amine-cured BPA-based epoxy resin, 1-aryloxy-3-amino-2-propanol was selectively converted to arenols. Subsequent control experiments suggested the conversion of secondary alcohol group of the substrate to ketone is indispensable. DFT calculations suggested that the C–O cleavage proceeds following an unprecedented remote oxidative addition where the nickel center and cleaved C–O atoms are not directly connected. Stoichiometric reaction with aryloxyketone further proved this hypothesis. The method was applied to the degradation of challenging diamine-cured BPA-based epoxy resin with successful recovery of BPA. We believe this approach finds application to chemical recycling especially carbon-fiber reinforced plastic allowing recovery of both carbon fiber and BPA.

ASSOCIATED CONTENT

Supporting Information

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(12) Another pathway without the participation of H_2 was also calculated, where the highest energy barrier is close to H_2-mediated one. See SI for more information.

(13) Although there are numerous possibility for $Ni(OR)_2$ complex (OR = OPh, enolate or Oalkyl), they are supposed to be in rapid equilibrium in a general scheme of $Ni(OR^1)_2 + HOR^2 \rightarrow Ni(OR^1)(OR^2) + HOR^1$ via similar mechanism to **TS-3**.

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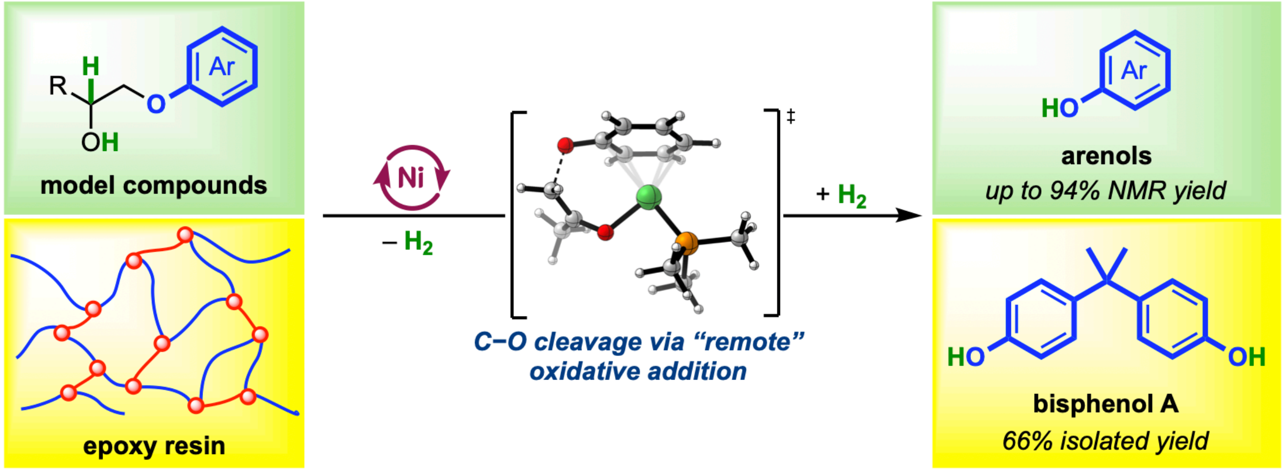
(15) An inverse pathway from this work, which is a remote reductive elimination of C–C bond by Pd was reported, see: Cusumano, A. Q.; Goddard, W. A., III; Stoltz, B. M. The Transition Metal Catalyzed [π2s + π2s + σ2s + σ2s] Pericyclic Reaction: Woodward–Hoffmann Rules, Aromaticity, and Electron Flow. *J. Am. Chem. Soc.* **2020**, *142*, 19033–19039.

(16) Less examples are known for hydrogenolysis of C–N bond with homogeneous catalyst under H_2, see: (a) Laine, R. M.; Thomas, D. W.; Cary, L. W. Modeling Heterogeneous Catalysis with Homogeneous Catalysts. 2. Modeling Catalytic Hydrodenitrogenation. *J. Am. Chem. Soc.* **1982**, *104*, 1763–1765. (b) Gandelman, M.; Milstein, D. Homogeneously catalyzed, chelate assisted hydrogenolysis of an amine C–N bond. *Chem. Commun.* **2000**, 1603–1604.

(17) (a) Deng T.; Liu, Y.; Cui, X.; Yang, Y.; Jia, S.; Wang, Y.; Lu, C.; Li, D.; Cai, R.; Hou, X. Cleavage of C–N bonds in carbon fiber/epoxy resin composites. *Green Chem.* **2015**, *17*, 2141–2145. (b) Wang, Y.; Cui, X.; Ge, H.; Yang, Y.; Wang, Y.; Zhang, C.; Li, J.; Deng, T.; Qin, Z.; Hou, X. Chemical Recycling of Carbon Fiber Reinforced Epoxy Resin Composites via Selective Cleavage of the Carbon–Nitrogen Bond. *ACS Sustainable Chem. Eng.* **2015**, *3*, 3332–3337.

(18) Polymers have better swelling capacity in NMP solvent than others, see: Kuang, X.; Zhou, Y.; Shi, Q.; Wang, T.; Qi, H. J. Recycling of Epoxy Thermoset and Composites via Good Solvent Assisted and Small Molecules Participated Exchange Reactions. *ACS Sustainable Chem. Eng.* **2018**, *6*, 9189–9197.



C−O cleavage via "remote" oxidative addition

✓ ***excellent C(sp^3)−O selectivity*** ✓ ***additive-free*** ✓ ***computational and crystallographic study***