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Reusable Co-catalysts for general and selective α-alkylation of nitriles with alcohols†

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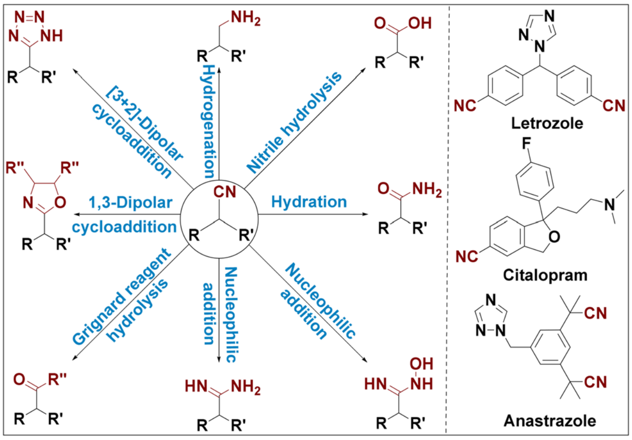
A general cobalt-catalyzed α-alkylation of nitriles with alcohols is reported. Utilizing this straightforward borrowing hydrogen methodology, a series of substituted and functionalized nitriles can be easily coupled with benzylic, heterocyclic, and aliphatic alcohols to prepare diverse functionalized nitriles in good to excellent yields (>70 examples). Key for this synthesis is the use of specific cobalt-nanoparticles supported on N-doped carbon, which were conveniently prepared by pyrolysis of a templated material generated *in situ* by mixing cobalt chloride, zinc chloride, D-glucosamine hydrochloride, and colloidal silica, and subsequent removal of the silica.

Introduction

The construction of carbon–carbon bonds is of central importance in organic synthesis. Among the many known methods, base- or metal-catalyzed alkylations of carbonyl compounds continue to be of major interest. In this respect, nitriles also represent valuable starting materials, which can be readily transformed into a plethora of amines, carboxylic acids, amides, acetamidines, ketones, N-heterocycles, and so on (Scheme 1).[1–3] In addition, nitrile moieties constitute integral parts of several drugs and biomolecules.[4–7] Because of their importance, synthetic methods for their preparation are continuously improved. Traditionally, stoichiometric nucleophilic substitution reactions with (over)stoichiometric amounts of metal hydrides prevailed in this area.[8,9] However, these processes have environmental drawbacks due to the inevitable generation of large amounts of waste.

Clearly, α-alkylation of nitriles with alcohols *via* the so-called borrowing hydrogen (BH) or hydrogen auto-transfer methodologies offers more sustainable approaches. Notably, the utilization of alcohols as starting materials allows the application of bio-based feedstocks and there is no need for any external/additional hydrogen as the alcohol substrate serves as the hydrogen donor. The general mechanism for the alkylation of nitriles with alcohols is shown in Scheme 2 (bottom). First the alcohol undergoes catalytic dehydrogenation to give the corresponding aldehyde, which is then condensed with the nitrile to form the respective α,β-unsaturated nitrile as an intermediate. Finally, this intermediate is reduced in the presence of the catalyst to produce the desired alkylated nitrile. Consequently, this method features high step- and atom-economy as water is the only by-product.

Until now, a variety of molecularly-defined catalysts have been successfully developed for catalytic α-alkylation of nitriles with alcohols.[10–27] Pioneering work was reported by Grigg and co-workers utilizing ruthenium catalysts for α-alkylation of acetonitrile in 1981.[10] Afterwards, Ir,[11–14] Rh,[15–17] Ru,[13,18–21] and Os[22] based catalytic protocols were developed for this transformation. Mainly in the past decade, homogeneous non-



Scheme 1 Various synthetic applications of nitriles and selected nitrile-containing drugs.

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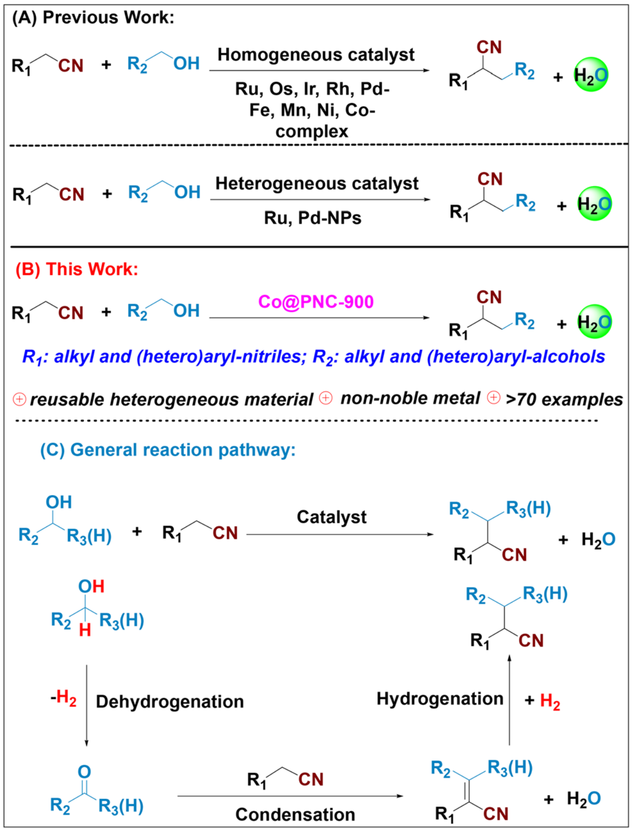


Scheme 2 State-of-the-art transition-metal-catalysed α-alkylation of nitriles with alcohols. (A) Previous works, (B) this work, and (C) general reaction pathway.

noble metal complexes based on Fe,[23] Mn,[3,24] Ni[25] and Co[26,27] were also reported to be effective in the α-alkylation of nitriles.

An ideal catalyst system for nitrile alkylation should be environmentally benign, inexpensive, generally applicable, stable, and easily recyclable. In this respect, especially the development of heterogeneous catalysts is desirable, although surprisingly few materials are known. In 2004, Kaneda and coworkers developed the first heterogeneous ruthenium supported hydrotalcite catalyst, which required prolonged heating at high temperature (180 °C, 20–30 h) and a large excess of alcohols as alkylating reagents.[28] Since then, only two other materials based on palladium and ruthenium have been introduced for such transformations.[29,30] Indeed, to the best of our knowledge, no heterogeneous non-noble metal catalyst is known so far to promote nitrile alkylation *via* hydrogen borrowing methodologies (Scheme 2).

In recent years, many research groups including ours have explored metal complexes with nitrogen-containing ligands and metal–organic frameworks (MOFs) with different linkers as suitable precursors for the preparation of supported metal nanoparticles.[31–45] Utilizing controlled pyrolysis conditions, well-dispersed metal–nitrogen–carbon catalysts are formed. The resulting materials were successfully applied for many reactions such as oxidations,[41,45] reductive aminations,[39,46] and hydrogenation and related transformations.[31,38,43,44] Notably, the synthesis of such doped-carbonaceous materials is also possible from sustainable resources. Following this approach, abundantly available cellulose, chitin, and glucose constitute ideal candidates for the development of new catalysts.[47–50]

Herein, we report the synthesis, characterization, and application of novel supported cobalt-nanoparticles for the preparation of functionalized nitriles. The optimal catalyst was prepared by pyrolysis of a templated material obtained *in situ* from a reaction mixture of cobalt and zinc salts, glucosamine, and commercially available colloidal silica (LUDOX® HS-40; 40 wt% suspension in H_2O) and subsequent removal of the silica content.

Results and discussion

Preparation and catalytic evaluation of Co-nanoparticles

At the start of this project, we synthesized different Co–N–C materials by mixing $CoCl_2{\cdot}6H_2O$ with D-glucosamine hydrochloride and colloidal silica. To obtain hierarchically porous materials, $ZnCl_2$ was also added which is known to create porous nanostructures.[50,51] After pyrolysis of the catalyst precursors under argon at 800–1000 °C, the formed silica was removed with 5 M NH_4HF_2 solution (Fig. 1). The details of the synthetic procedure are described in the ESI.† The resulting cobalt materials are represented as Co@PNC-*T*, where PNC and *T* denote porous N-doped carbon and the pyrolysis temperature, respectively.

The activities and selectivities of these Co-materials (Co@NC-*T*) were initially evaluated for the *N*-alkylation of phenylacetonitrile **1** with benzyl alcohol **2** to prepare 2,3-diphenylpropanenitrile **3** in the presence of 1 equivalent of K_3PO_4 at 140 °C for 24 h in toluene solvent (Table 1).

Among all the prepared materials, Co@PNC-900 was found to be the best one and a quantitative yield of the desired product **3** was obtained (Table 1; entry 1). The material prepared using the cobalt salt and D-glucosamine hydrochloride, without the zinc salt as a precursor, showed lower activity and produced 71% of the desired product **3** (Table 1; entry 2), which indicates the beneficial effect of the porous material. Next, we tested the effect of different pyrolysis temperatures on the yield of product **3**. Here, a pyrolysis temperature of 900 °C was the best one (Table 1; entries 1, 3 and 4). Notably, no zinc was detected by ICP-OES in these three samples. In addition,

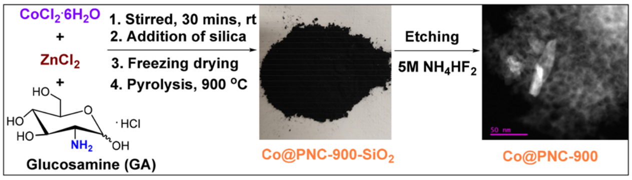
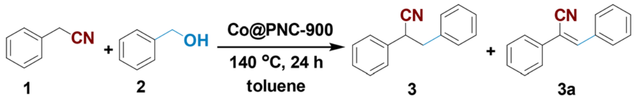


Fig. 1 Preparation of cobalt nanoparticles supported on porous N-doped carbon.

Table 1 α-Alkylation of phenylacetonitrile with benzyl alcohol: testing of cobalt catalysts



Entry	Catalyst	Conv.1 (%)	Yield 3 (%)	Yield 3a (%)
1	Co@PNC-900	99	95	2
2	Co@NC-900 (without zinc)	88	71	10
3	Co@PNC-800	87	74	9
4	Co@PNC-1000	82	72	7
5	Porous N-doped carbon (without cobalt)	<5	<5	—
6	Co-particles-900 (without a ligand)	61	43	15
7	Co@NC-900-SiO_2 (remaining SiO_2)	57	42	11
8	CoZn-L-SiO_2 (unpyrolyzed)	<5	<5	—
9	$Co(NO_3)_2·6H_2O$	<5	<5	—
10	$Zn(NO_3)_2·6H_2O$	<5	<5	—
11	$Co(NO_3)_2$-L	<5	<5	—
12[a]	Co@NC-900-1 (without a base)	68	57	10
13[b]	0.5 mmol K_3PO_4 (without a catalyst)	<5	<5	—

Reaction conditions: 0.5 mmol phenylacetonitrile, 1 mmol benzyl alcohol, 50 mg catalyst (2.04 mol% Co), 0.5 mmol K_3PO_4 (1 equiv.), 2 mL toluene, 140 °C, 24 h. Conversions and yields are based on phenylacetonitrile and determined by GC using *n*-hexadecane as a standard. In homogeneous catalytic reactions, 10 mol% of cobalt nitrate and 30 mol% of ligand were used. [a] Without a base. [b] Without a catalyst and in the presence of 0.5 mmol K_3PO_4 (1 equiv.).

we also synthesised a porous carbon material without using the cobalt salt and tested its activity. As expected, only trace amounts of **3** were formed (Table 1; entry 5). Furthermore, the material prepared without D-glucosamine hydrochloride or the one with remaining silica was found to be less active and produced 43% and 30% of **3**, respectively (Table 1; entries 6 and 7). Using related homogeneous catalysts and non-pyrolyzed materials also gave only traces of **3** (Table 1; entries 8–11). Interestingly, by applying Co@PNC-900, the model reaction was also promoted in the absence of a base and gave 57% of 2,3-diphenylpropanenitrile **3** (Table 1; entry 12). Finally, different solvents, bases, and other reaction parameters such as the temperature, amount of catalyst and reaction time were evaluated for the model reaction (Tables S2–S4; ESI†).

Characterization of Co-based materials

To further understand the structure of the catalytic active material, we performed X-ray powder diffraction (XRD), scanning transmission electron microscopy (STEM), and X-ray photoelectron spectroscopy (XPS) characterization studies. The X-ray diffraction pattern of Co@NC-900-SiO_2 does not exhibit diffraction peaks which can be assigned to crystalline metallic or oxidic cobalt species. Instead, only amorphous silica is indicated by a broad peak around 22° 2theta (Fig. S1†). Even after the removal of SiO_2 or recycling of the catalysts, no additional peaks can be found, indicating a high dispersion of metal species. However, distorted carbon might be the origin of wide peaks in the regions of 20–30° and 40–45° 2theta which can be interpreted as the partly graphitic-like structure (Fig. S2 and 3†). Next, STEM analysis of Co@PNC-900 showed the presence of highly porous carbon with sizes similar to those of mostly dissolved SiO_2 particles (Fig. 2). In the carbon phase, small amounts of N, O, Si and Co could also be detected (Fig. S4†) without accompanying particles, indicating a highly distributed phase. Additionally, few rather large Co oxide particles and SiO_2 particles could be identified as minority phases. Zn traces were not found, indicating that zinc was completely removed at 900 °C.

XPS analysis was used to further determine the surface elemental compositions and chemical state. XPS analysis revealed the composition of the surface, as shown in Table S1.† Besides carbon, nitrogen, and cobalt, there are also oxygen and traces of silica, probably originating from the support and/or the preparation process. In the C 1s spectra, five peaks are observed at ∼284.7, 289.1, 287.7, 288.9 and 291.1 eV, which are assigned to C–C, C–O, C=O, and C=O–C as well as satellite peaks, respectively (Fig. 3a).[31] The O 1s spectra (Fig. 3b) showed three peaks at 531.7, 533.4, and 536.2 eV, which correspond to the C=O, C–O, and COO– bonds.[31] The N 1s spectra (Fig. 3c) displayed five peaks with binding energies at 398.3, 399.8, 401.0, and 402.8 eV as well as 405.8 eV, which can be ascribed to pyridinic, pyrrolic, graphitic, and oxidized pyridinic *N*, respectively.[52,53] The fifth peak at 405.8 eV only appears for the samples treated with NH_4HF_2 to remove the Si and might be originating from the nitrite groups ($-NO_2$) remaining at the surface.[54] In the cobalt region, the Co $2p_{3/2}$ peak is located at 780.4 eV and can be attributed to the Co^{2+} species[55] with a pronounced satellite feature at 786.4 eV (Fig. 3d). For the recycled catalyst, Co@PNC-900-R,

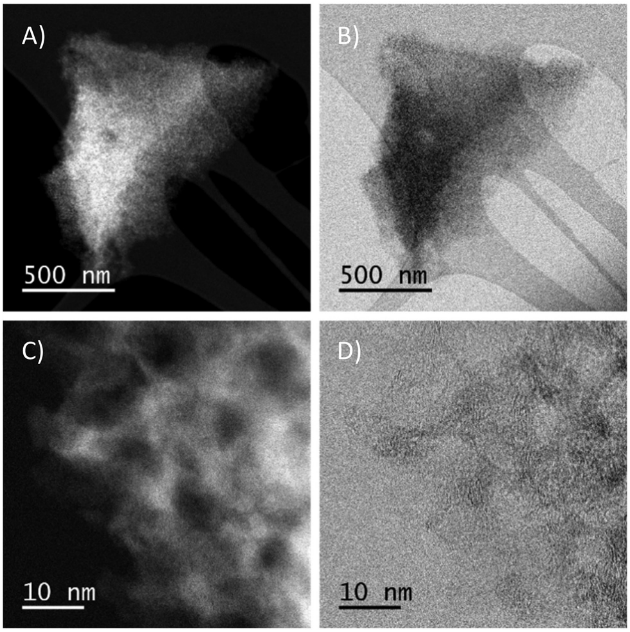


Fig. 2 STEM-HAADF (A and C) and STEM-ABF (B and D) images of the Co@PNC-900 catalyst showing an overview (A and B) and high-resolution details (C and D) of the highly porous carbon framework containing Co.

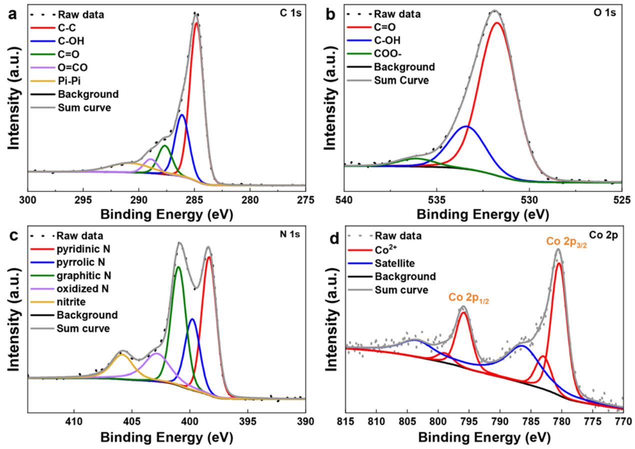


Fig. 3 X-ray photoelectron spectra for Co@PNC-900. (a) C 1s, (b) O 1s, (c) N 1s and (d) Co 2p regions.

identical cobalt and nitrogen species could be observed with similar binding energies and oxidation states like in the case of the fresh catalyst, thus confirming the high stability of the catalyst (see Fig. S6† for comparison).

Stability, recycling, and reusability of the Co@PNC-900 catalyst

For any given heterogeneous catalyst, its stability and reusability are important aspects. To prove these features, we performed recycling experiments for the model reaction under two different reaction conditions (24 h, complete conversion and 5 h, around 50% conversion). As shown in Fig. 4, Co@PNC-900 exhibited high stability and was recycled and reused up to 7 times without significant deactivation.

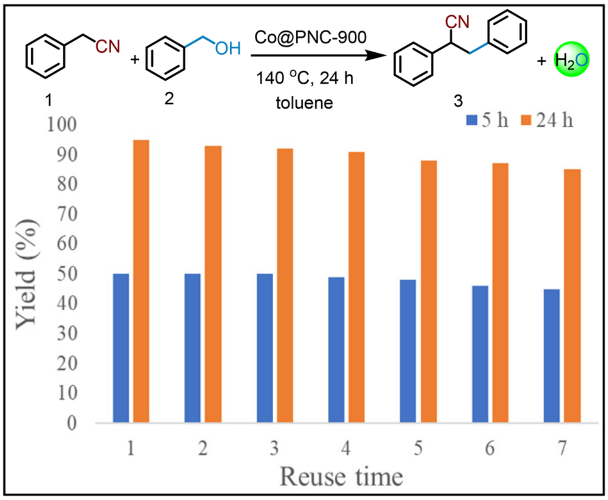
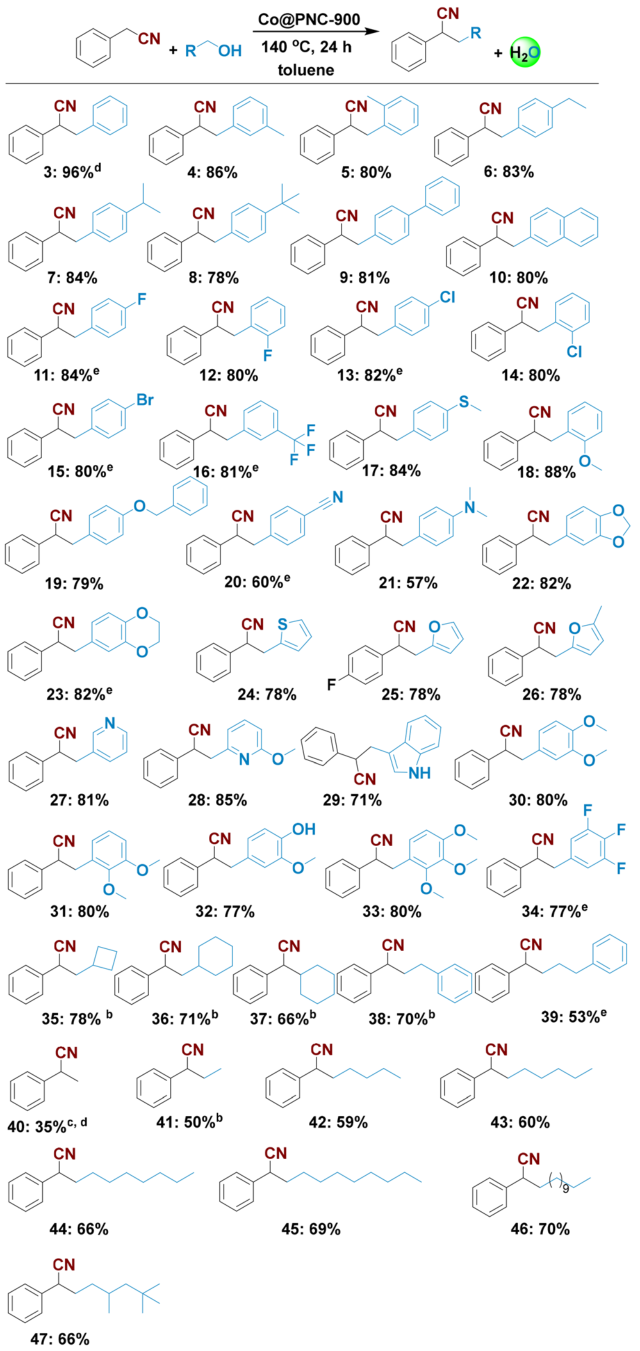


Fig. 4 Stability and recycling of the Co@PNC-900 catalyst for the synthesis of 2,3-diphenylpropanenitrile. Reaction conditions: 1.5 mmol phenylacetonitrile, 3 mmol benzyl alcohol, 160 mg catalyst (2.17 mol% Co), 1.5 mmol K_3PO_4, 4 mL toluene, 140 °C, 5 h and 24 h. Conversions and yields are based on phenylacetonitrile and determined by GC using *n*-hexadecane as a standard.

α-Alkylation of phenylacetonitrile 2 with different alcohols

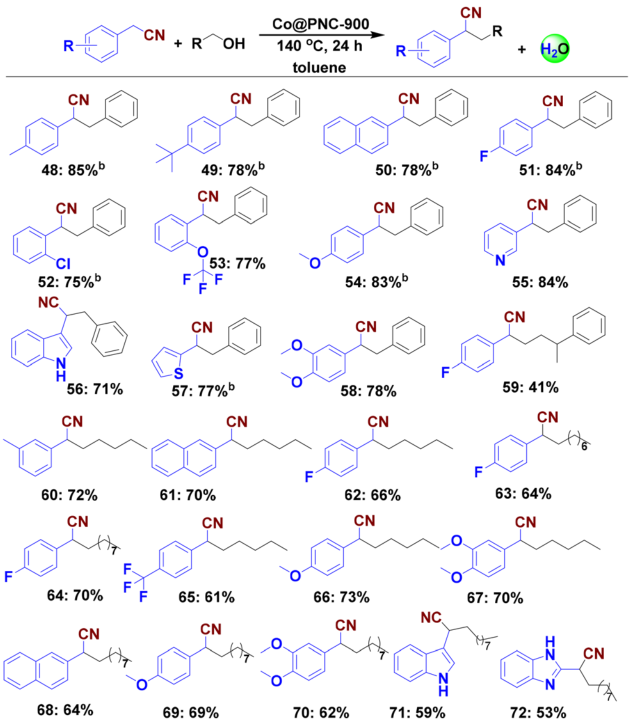
With the optimal catalyst (Co@PNC-900) and the optimal reaction conditions in hand, we explored its general applicability for the synthesis of functionalized nitrile products. First, we investigated the α-alkylation of 2 using various alcohols. As



Scheme 3 Co-nanoparticle-catalyzed α-alkylation of phenylacetonitrile with different alcohols.[a] [a] Reaction conditions: 0.5 mmol nitrile, 1 mmol alcohol, 50 mg catalyst (2.04 mol% Co), 0.5 mmol K_3PO_4 (1 equiv.), 2 mL toluene, 140 °C, 24 h, isolated yields. [b] The same as "a" with 80 mg catalyst (3.27 mol% Co) at 150 °C. [c] The same as "b" with 1 mmol KoMe. [d] GC yields obtained using *n*-hexadecane as a standard. [e] ^1H NMR yields obtained using *n*-hexadecane as a standard.

shown in Scheme 3, various benzylic, heterocyclic, and aliphatic primary alcohols reacted well with phenylacetonitrile and gave the corresponding α-alkylated nitriles in up to 86% yield (Scheme 3; products **4–10**). Halide substituents (F-, Cl-, Br-) at the *meta*- or *para*-position of the phenyl ring were well tolerated (Scheme 3, products **11–15**). Similarly, trifluoromethyl-, thioether-, ether-, nitrile-, and *N*,*N*-dimethyl group containing substrates gave the desired products in up to 88% yield (Scheme 3; products **16–21**). Next, different heterocyclic alcohols containing O, S and N atoms, such as piperonyl alcohol, 1,4-benzodioxin-6-methanol, 2-thiophenemethanol, and furane-, pyridine-, and indole-based alcohols were coupled with **2** to provide the corresponding heterocyclic compounds in up to 85% yield (Scheme 3; products **22–29**). In addition, multi-substituted alcohols smoothly reacted and produced the corresponding alkylated nitriles (Scheme 3, products **28** and **30–34**).

Compared to benzylic alcohols, aliphatic alcohols are less reactive, and thus more difficult to activate.[31] Nevertheless, our catalyst allowed for alkylation of such alcohols, albeit at higher temperature in the presence of 3.27 mol% catalyst (Scheme 3; products **35–47**). Under these conditions, linear and cyclic aliphatic alcohols gave up to 78% of α-alkylated nitriles. Furthermore, we prepared the corresponding methylated products by simply utilizing methanol. Compared to traditional methylation reagents such as methyl iodide and dimethyl sulfate, methanol constitutes a more benign C1 source; however, it is particularly difficult to dehydrogenate.[56] Nonetheless, starting from phenylacetonitrile **2** and methanol, selective monomethylation occurred to give nitrile **40** in 35% yield.



Scheme 4 Co-nanoparticle-catalyzed α-alkylation of various nitriles with alcohols. Reaction conditions: 0.5 mmol nitrile, 1 mmol alcohol, 50 mg catalyst (2.04 mol% Co), 0.5 mmol K_3PO_4 (1 equiv.), 2 mL toluene, 140 °C, 24 h, isolated yields. [a] ^1H NMR yields obtained using *n*-hexadecane as a standard.

α-Alkylation of different nitriles with benzylic alcohols: scope of nitriles

Next, we explored the reactivity of different nitriles to prepare substituted and functionalized nitriles under standard conditions. Exemplarily, F-, Cl- and CF_3-substituted as well as methoxy- and heterocyclic-containing substrates provided the corresponding products in good isolated yields up to 85% (Scheme 4; products **51–58**). However, on performing the alkylation of five aliphatic nitriles as coupling partners, only small amounts of the desired products or no desired products were obtained (Scheme S1†).

In contrast, benzylic, araliphatic and aliphatic primary alcohols reacted well with different nitriles to give the desired α-alkylated products in up to 73% yield (Scheme 4, products **59–72**). Finally, using glucose as an alkylating agent under the optimal conditions provided a complex reaction mixture.

Conclusions

In summary, we present the Co containing N-doped carbon matrix Co@PNC-900 as a novel heterogeneous catalyst, which allows for the general and selective synthesis of alkylated nitriles from alcohols by an atom-efficient borrowing hydrogen methodology. The optimal material is easily generated by mixing cobalt and zinc salts, D-glucosamine hydrochloride, and colloidal silica, followed by pyrolysis of the templated material, and subsequent removal of the silica. Functionalized and structurally diverse nitriles can be conveniently prepared starting from inexpensive and easily available alcohols and nitriles in the presence of Co@PNC-900.

Data availability

Data for this article, including compound characterization, calculations, and experimental data, are available as the ESI† at **https://doi.org/10.1039/d3gc04436j**.

Conflicts of interest

There are no conflicts to declare.

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