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An Air/Water-Stable Tridentate N-Heterocyclic Carbene-Palladium(II) Complex: Catalytic C–H Activation of Hydrocarbons *via* Hydrogen/Deuterium Exchange Process in Deuterium Oxide

Joo Ho Lee,[a] Kyung Soo Yoo,[a] Chan Pil Park,[a] Janet M. Olsen,[a]
Satoshi Sakaguchi,[b] G. K. Surya Prakash,[a] Thomas Mathew,[a]
and Kyung Woon Jung[a,]*

[a] Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089, USA
Fax: (+1)-213-821-4096; e-mail: kwjung@usc.edu
[b] Department of Applied Chemistry, Kansai University, Osaka 564-8680, Japan

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Abstract: While developing novel catalysts for carbon-carbon or carbon-heteroatom coupling (nitrogen, oxygen, or fluorine), we were able to introduce tridentate N-heterocyclic carbene (NHC)-amidate-alkoxide palladium(II) complexes. In aqueous solution, these NHC-Pd(II) complexes showed high ability for C–H activation of various hydrocarbons (cyclohexane, cyclopentane, dimethyl ether, tetrahydrofuran, acetone, and toluene) under mild conditions.

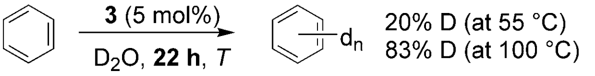
Keywords: C–H activation; H/D exchange; intermolecular reactions; N-heterocyclic carbene (NHC) ligands; palladium complexes

Carbon-carbon or carbon-heteroatom cross-coupling reactions catalyzed by transition metal catalysts have been widely investigated and established because of their significance in organic synthesis. In particular, homogeneous Pd catalysis has been well studied in the most powerful and versatile synthetic processes such as Heck,[1] Suzuki,[2] Stille,[3] Sonogashira,[4] Negishi,[5] and Buchwald–Hartwig reactions.[6] However, these reactions have required alkenyl/aryl halide substrates. Alternatively, the more desirable direct functionalization of hydrocarbons *via* C–H bond activation has still remained a challenge in cross-coupling reactions.

In recent years, a substantial number of metal complexes that are able to selectively activate C–H bonds under mild conditions have been discovered.[7] In spite of these advances, practical catalysts for the C–H bond functionalization remain elusive, due to the requirement of high energy to break C–H bond and subsequent vulnerability of the metal-carbon bond. Additionally, the C–H bond activation is often inhibited by water or by the product eliminated from the metal complex during the reaction.[8]

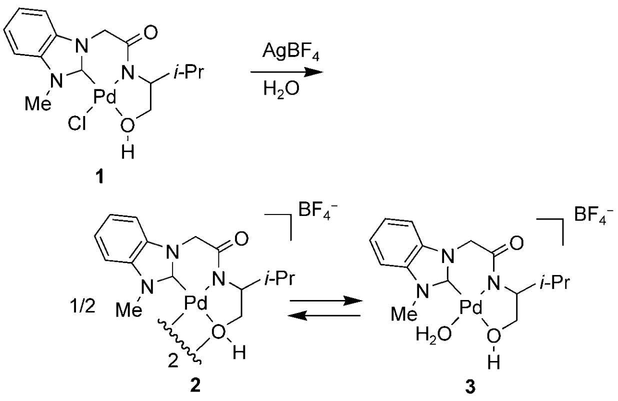
N-Heterocyclic carbene (NHC) ligands, which are known to enhance σ-donor coordination, have shown improved behaviour toward C–H bond activation during the past several years.[9] A number of organometallic species at various oxidation states (Pd, Pt, Ru, and Ir) are stabilized by the use of NHC ligands, increasing the capability to obtain efficient catalysts for C–H activation.[10] However, most examples refer to intramolecular processes, while intermolecular or catalytic examples remain rare. With these challenges in mind, we report herein the efficient C–H bond activation of hydrocarbons in aqueous solution containing catalytic amounts of tridentate NHC ligand-Pd complex *via* H/D exchange as a probe for direct C–H functionalization. Such reactions have been studied in heterogeneous Pd catalytic systems but are rarely observed in homogeneous Pd systems.[11]

Recently, we have succeeded in preparing the air-stable tridentate NHC-amidate-alkoxide ligand/palladium complex **1** from an amino alcohol.[12] We found that H/D exchange on benzene using D_2O as both the solvent and deuterium source, occurred *via* C–H bond activation in the presence of Pd complex **1** and silver tetrafluoroborate. As shown in Eq. (1), the H/D exchange reaction was demonstrated with benzene



(1)

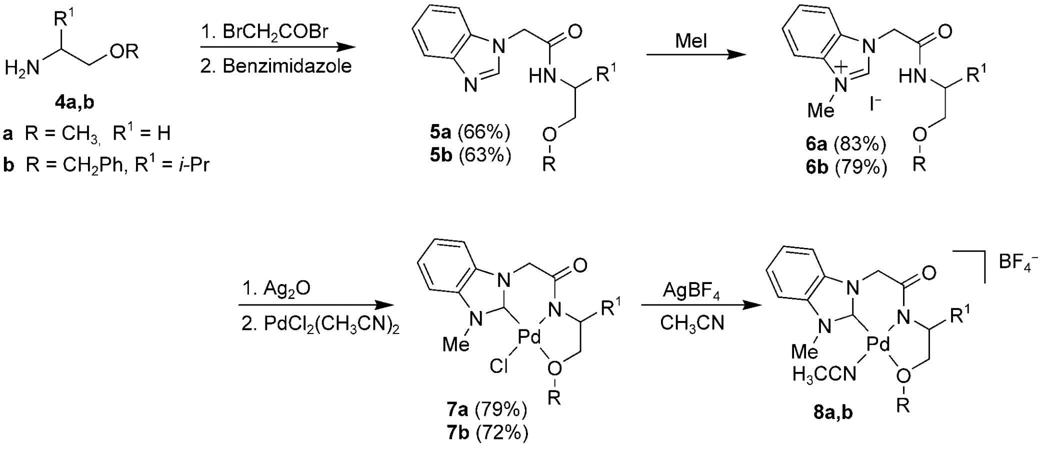
(20 µL), palladium complex **1** (5 mol%) and $AgBF_4$ in deuterium oxide (700 µL) for 22 h at 55 °C and 100 °C. The efficiency of the H/D exchange giving deuterated isotopomers showed significant enhancement when the temperature was increased from 55 °C to 100 °C. While evaluating H/D exchange with palladium complex **1** and $AgBF_4$, we found that a dimeric structure **2** was present in the solution as indicated by ^{1}H NMR spectroscopy.[13] At an elevated temperature, however, the concentration of monomeric species **3** was observed to be higher than complex **2**. Consequently, we confirmed that the H/D displacement *via* C–H bond activation worked well only in the presence of the monomeric species **3**. As shown in Eq. (2), the NHC ligand/palladium complex **1** was converted to the palladium complex **2** by treating with aqueous $AgBF_4$ for the C–H bond activation, and subsequently the monomer/dimer equilibrium process (**2**$\rightleftarrows$**3**) took place depending on the temperature of the aqueous solution.[14] The higher efficiency of the H/D exchange process at 100 °C compared to 55 °C is attributable to the conversion of the catalyst into active mode **3** from complex **2** at the elevated temperature.



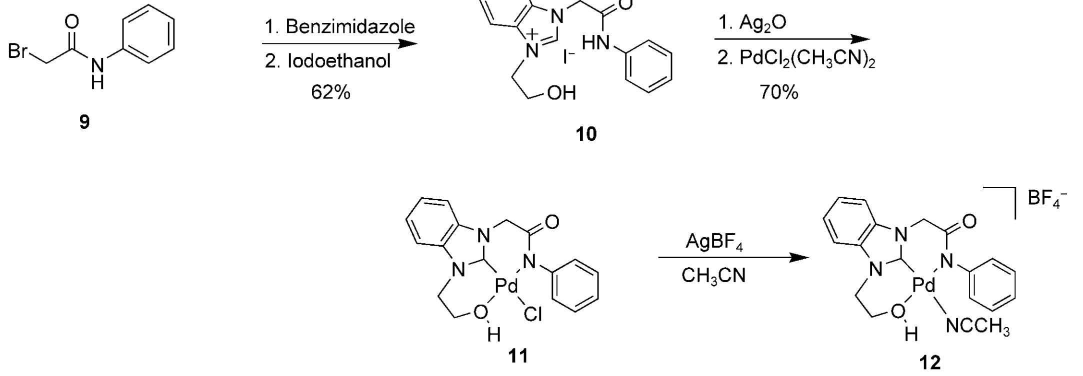
(2)

To further investigate the C–H activation of this class of Pd complexes, we extended the structural motifs of palladium to various tridentate ligands. To circumvent the dimerization of monomeric species in aqueous solution at low temperatures, we employed a methyl ether (**7a**) or benzyl ether (**7b**) group instead of the previously employed hydroxy moiety as oxygen-site of the ligands (Scheme 1). Compounds **4a** and **4b** were prepared from ethanolamine and valinol, respectively.[15] Bromoacetylation of the amino ethers was followed by amide formation and *N*-alkylation with benzimidazole to yield **5a** and **5b**. The benzimidazole salts **6a** and **6b** were obtained by allowing **5a** and **5b** to react with CH_3I in THF. For the coordination of the NHCs to palladium, metal exchange was carried out through a silver NHC complex.[16] *N*-Methyl iodide salts **6a** and **6b** were reacted with Ag_2O to give silver NHC complexes, and subsequent treatment of the silver compounds with $PdCl_2(CH_3CN)_2$ in CH_3CN provided the desired complexes **7a** and **7b** in 79% and 72% yields, respectively. The structures of Pd/ligand complexes **7a** and **7b** were further confirmed by the molecular ion peaks (ESI-MS) at $m/z = 388.0029$ [M$^+$] (calcd.: 388.0044) and $m/z = 506.0813$ [M$^+$] (calcd.: 506.0827).

In addition, we designed an O–C–N tridentate ligand system, an example of which is the alkoxy-NHC-amidate ligand/palladium complex **11** (Scheme 2). Amide compound **9** was easily derived from aniline and bromoacetyl bromide. By means of *N*-alkylation with benzimidazole and compound **9**, the benzimidazole-amide adduct was obtained in DMF solution, which after second *N*-alkylation with iodoethanol gave the iodine salt **10** in 62% yield for two



Scheme 1.

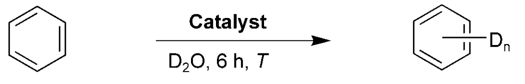


Scheme 2.

steps. Subsequently, construction of alkoxy-NHC-amidate ligand/palladium complex **11** was successfully accomplished by treatment with half an equivalent of Ag_2O and one equivalent of $PdCl_2(CH_3CN)_2$ sequentially in CH_3CN solution at room temperature.

First, to optimize the H/D exchange reaction conditions, various reaction temperatures and catalyst loadings were screened with Pd complexes **8a**, **8b** and **12** for benzene in D_2O. The H/D exchange can be conveniently monitored by ^{1}H NMR spectroscopy through observation of the decreasing proton signals of benzene in the aqueous phase relative to the poly(dimethylsiloxane) as an external reference standard. Before H/D exchange, $AgBF_4$ was added into a MeCN solution of Pd complexes **7a**, **7b** and **11** to remove Cl anion, so that Pd complexs **8a**, **8b**, and **12** could be ready for the C–H activation. In addition, unreacted $AgBF_4$ and AgCl were removed by a celite column. In D_2O solution, the MeCN ^{1}H-signal shifted from 2.06 ppm (free MeCN in D_2O) to 2.16 ppm with a broadening of the signal indicating that there was weak interaction between MeCN and Pd metal.

Table 1. H/D exchange of benzene in D_2O by **8a**, **8b**, and **12**.[a]

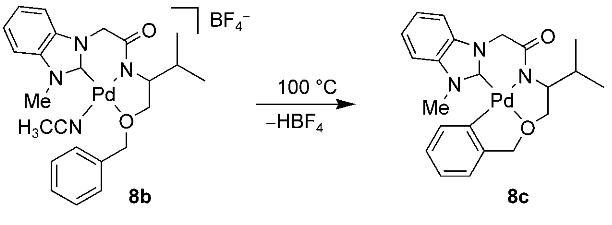


Entry	Catalyst (mol%)	H/D conversions [%][b]			
		55 °C (6 h)	100 °C (6 h)	55 °C (22 h)	100 °C (22 h)
1	**8a** (0.4)	48	–	–	–
2	**8a** (0.9)	81	–	–	–
3	**8a** (1.7)	90	89	95	96
4	**8a** (6.9)	89	89	–	–
5	**8b** (1.7)	69	8	–	–
6	**12** (1.7)	23	86	–	–

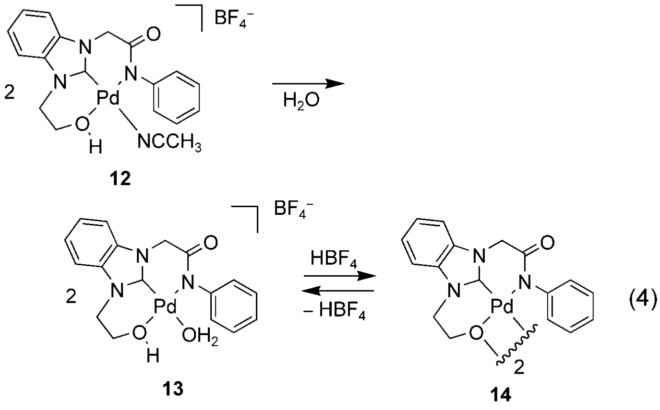
[a] All reactions were carried out with 20 μL of benzene in 0.7 mL of D_2O.

[b] The H/D conversions were determined by ^{1}H NMR.

As shown in Table 1, we found that the reaction temperature could be lowered to 55 °C without causing a significant decrease in the extent of deuterium incorporation relative to that observed in reactions run at 100 °C (entry 3). Interestingly, we discovered that at 55 °C increasing the catalyst loading beyond 1.7 mol% (entry 4) did not lead to a detectable increase in deuterium incorporation. While use of less catalyst (entries 1 and 2) led to a decrease in the extent of H/D exchange, 1.7 mol% is apparently enough to saturate the system and achieve optimum conversion. In addition, longer reaction times may not affect the catalytic cycle dramatically (entry 3). When the ligand **8b** possessing a benzyl ether group was utilized, deuterium incorporation slowed down somewhat at 55 °C (entry 5), however deuterium incorporation was barely seen at an elevated temperature (100 °C) due to deactivation of **8b** by coordination between palladium and benzyl aromatic C–H intramolecular activation to generate **8c** [Eq. (3)].[17] Moreover, alkoxy-NHC-amidate ligand/palladium complex **12** gave the lowest level of deuterium incorporation into benzene at 55 °C because of the steric hindrance of the phenyl group as well as the existence of a dimer/monomer equilibrium in aqueous solution [Eq. (4)].[14] This result wherein the efficiency of the H/D exchange showed significant enhancement at a higher temperature is in accordance with behaviour of the active catalyst derived from **1** [Eq. (1)].



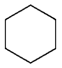
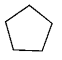
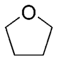
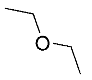
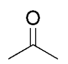
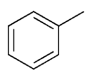
(3)



Additionally, in an experiment designed to study the time dependence of the deuterium displacement, a solution of benzene with catalyst **8a** in D_2O was heated to 55 °C and monitored by ^{1}H NMR spectroscopy. As shown in Figure 1(**A**), over a period of 22 h, the resonances for the benzene ($\delta = 6.71$ at 55 °C) disappeared without any significant change in the signal intensities of the other resonances. Furthermore, to unequivocally establish C–H activation with Pd complex, we also probed deuterium-proton displacement between C_6D_6 and H_2O at 55 °C and H/D incorporation was monitored by ^{2}H NMR spectroscopy. As shown in Figure 1(**B**), the signal for benzene-d_6 decreased in intensity over a period of 16 h. Overall conversion of C_6D_6 to C_6H_6 by 3.6 μmol of **8a** was 75%, which is lower than the percent of conversion of C_6H_6 to C_6D_6 (89.5% in 6 h, entry 2 in Table 1) as expected.

On the basis of these results, various organic substrates were investigated to explore the feasibility of the H/D exchange reaction with palladium NHC-ligand complex **8a**. In general, effective multiple deuterium incorporation into the alkyl C–H bond was observed with D_2O as both the solvent and deuterium source. Table 2 lists the organic substrates examined and their corresponding extents of deuterium incorpo-

Table 2. H/D exchange of various organic substrates in D_2O by Pd catalyst **8a**.[a]

Entry	**8a**	Substrate[b]	T [°C]	D conversion [%][c]/TON[d]	
				6 h	22 h
1	3.86		55	81/464	93/536
2	3.86		100	96/552	93/536
3	3.86		55	72/399	76/422
4	3.86		100	96/533	97/541
5	3.86		55	2/10	2/10
6	3.86		100	44/222	52/267
7	3.86		55	0.5/2	1/4
8	3.86		100	5/25	9/43
9	15.4		100	27/27	46/46
10	3.86		55	12/52	15/65
11	3.86		100	26/110	52/218
12	15.4		100	55/58	63/66
13	3.86		55	83/323	87/340
14	3.86		100	95/369	97/379

[a] All reactions were performed with Pd complex **8a** (μmol) in sealed glass tubes containing D_2O and substrate at 55 and 100 °C.

[b] 20 μL.

[c] For % D, ^{1}H NMR spectroscopy was used for analysis.

[d] [D conversion × mole of substrate]/[mole of Pd × 100].

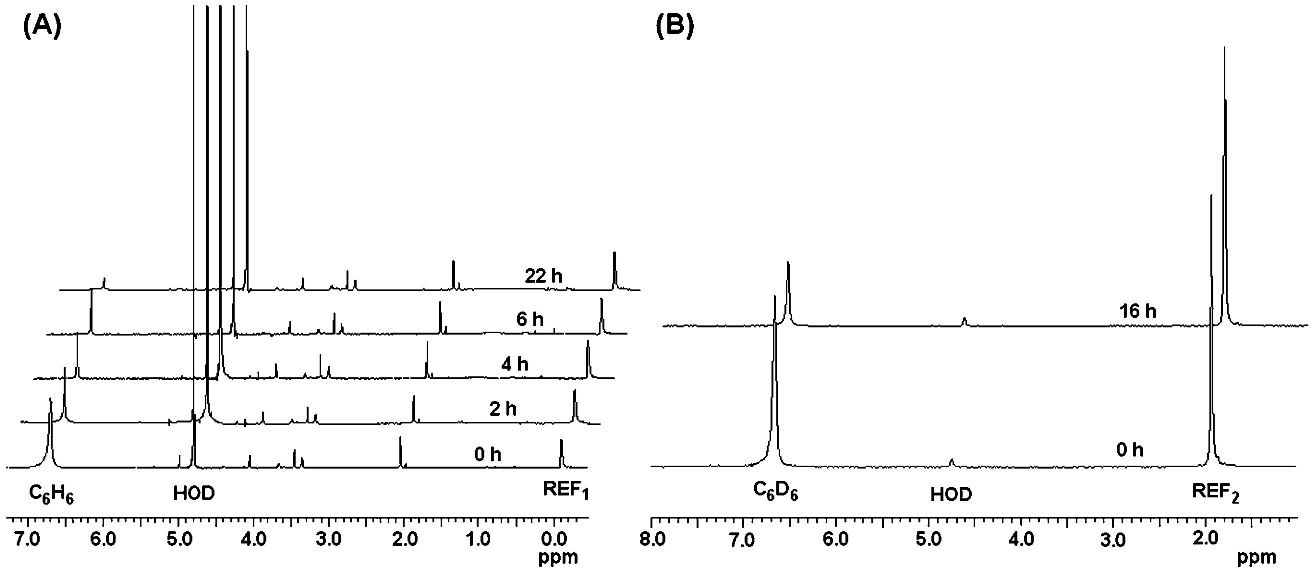
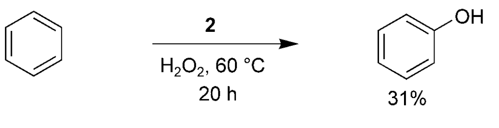


Figure 1. (**A**) ^{1}H NMR spectra of a solution of **8a** and C_6H_6 in D_2O at 55 °C recorded over a period of 22 h. REF$_1$ (internal standard): poly(dimethylsiloxane). (**B**) ^{2}H NMR spectra of solution of **8a** and C_6D_6 in H_2O at 55 °C recorded after 16 h REF$_2$ (internal standard): CD_3CN.

ration. Catalyst **8a** showed deuteration ability for a wide range of molecules including saturated hydrocarbons, ethers, and ketones. Remarkably, the catalyst was also capable of C–H activation of saturated hydrocarbons such as cyclohexane and cyclopentane, and excellent total deuterium incorporation (96–97%) was observed (entries 1–4). Recently, there have been a few examples for the H/D exchange of cyclohexane and cyclopentane, in which efficient thermal catalysis was carried out by Ir or Pt species using deuterated organic solvents or D_2 as the deuterium source.[18] These C–H activations were developed with modest conversions, and they had additional drawbacks such as air/water sensitivity of the metal catalysts and high reaction temperature requirement. On the contrary, our palladium complex **8a** appeared to be superior for C–H activation of saturated hydrocarbons with significant air/water stability.

Ether compounds such as THF and diethyl ether showed lower levels of D-incorporation compared to aromatic and saturated hydrocarbons, however we observed that it was also a facile process with catalyst **8a** under conditions of higher temperatures and longer reaction times (entries 6 and 8) with increased catalyst loading (entry 9). To the best of our knowledge, there are only few examples for the H/D exchange of THF, which were effected by Ir catalysis at lower levels of D-incorporation at longer reaction times and higher temperatures.[19] Although the selective C–H activation for the α- and β-positions of THF and diethyl ether was not examined under these conditions, we demonstrated H/D exchange for these ether compounds with palladium complexes. These findings were quite similar to the case of H/D exchange with ketone as the substrate. While deuterium was incorporated into acetone at higher initial conversion values than the ethers, an increase in the three aforementioned reaction variables led to a significant improvement of percent D-incorporation for this substrate (entries 10–12). Also, we examined the deuterium incorporation of toluene in D_2O to elucidate the possibility of selective C–H activation for aryl and alkyl groups. Similarly to other examined substrates, toluene showed high H/D conversions (95–97%) at 100 °C (entry 14), however we were not able to observe selective C–H activation for CH_3 (95% after 6 h) or C_6H_5 C–H bonds (95% after 6 h).

Based on these studies, which tested the possibility of direct oxidation of an *sp*^{2} C–H bond, C_6H_6, was added to a reaction mixture of **2** (10 mol%) in 30% H_2O_2 solution [Eq. (5)]. We detected the oxidation product of benzene *via* C–H activation to afford phenol as a product.



(5)

In summary, we have demonstrated efficient and strong C–H activation with water soluble NHC-Pd(II) complexes that showed efficient H/D exchange of various organic substrates in D_2O under mild conditions (55 °C or 100 °C). Importantly, the catalytic reaction was not inhibited by coordination of water to Pd. Strongly electron-donating groups such as NHC, amide N, and O would increase the electron density of Pd, allowing a weak interaction between electrophilic Pd and water. In addition, we were able to obtain a preliminary result for the direct functionalization in aqueous media. This independent character of the developed catalysts from water and polar solvents can open up a new avenue in Pd(II) catalysis. Accordingly, utilization of this system for the incorporation of deuterium and other useful functional groups into the C–H bonds of numerous classes of organic compounds will be extensively pursued and reported in due course.

Experimental Section

Catalytic H/D Exchange Reaction

Pd cationic compounds were prepared when required. Catalyst (**7a**, **7b**, or **11**) and 1.5 equiv. of $AgBF_4$ were stirred in 2 mL of MeCN solvent for 30 min. After passing through a celite column, the filtrate was dried in a rotary evaporator. The dried compound was dissolved in 0.7 mL of D_2O and placed in a J-Young NMR tube with an external standard capillary consisting of C_6F_6 solution with the poly(dimethylsiloxane). Then the hydrocarbon substrate (20 μL) was added in D_2O solution. The resulting mixture was heated at 55 °C/100 °C. Deuteration levels were monitored by ^{1}H NMR using an external capillary standard consisting of a solution of the poly(dimethylsiloxane).

Oxidation of Benzene [Eq. (5)]

The Pd cationic compound **2** was prepared when required. The catalyst **1** (2 mg, 0.5 mol%) and $AgBF_4$ (1.5 equiv.) were stirred in 2 mL of MeCN solvent for 30 min. Then the filtrate was dried in a rotary evaporator after passage through celite column. The dried compound was dissolved in 0.2 mL of H_2O. Then 0.2 mL of H_2O_2 and 0.1 mL of C_6H_6 were added to the aqua solution. The resulting mixture was heated at 60 °C for 20 h. After the catalytic reaction, 2 μL of pyridine for the internal reference and 0.2 mL of D_2O were added. The production of 16 equivalents of phenol was detected by the WET1D NMR technique.

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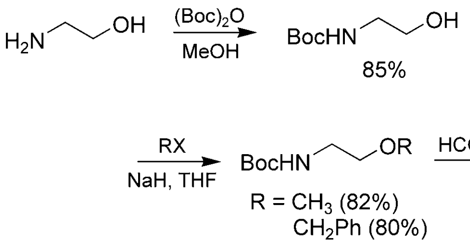

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