이학석사 학위논문

Cobalt/Rhodium Heterobimetallic Nanoparticle-Catalyzed Aerobic Oxidative Carbonylation of β-Amino Alcohols to Oxazolidinones

코발트/로듐 이핵 나노입자를 촉매를 이용한

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공 명 진

Cobalt/Rhodium Heterobimetallic Nanoparticle-Catalyzed Aerobic Oxidative Carbonylation of β-Amino Alcohols to Oxazolidinones

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2012 년 6 월

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위 원 _____ **(인)**

Abstract

The cobalt-rhodium heterobimetallic nanoparticle (Co_2Rh_2 NP) on charcoal-catalyzed synthesis of oxazolidinones from β-amino alcohols, carbon monoxide, and oxygen under relatively mild reaction conditions is described. In addition, the catalyst is also effective for the oxidative carbonylative cyclization reactions of 1-phenylethane-1,2-diol, o-phenylenediamine, and 2-aminobenzenethiol.

Keywords: β-amino alcohols; oxazolidinones; nano catalyst; oxidative; cyclocarbonylation; cyclic carbonate; dithiocarbonate; benzimidazolone; 2(3*H*)-benzothiazolone

Contents

Introduction

Oxazolidinones are heterocyclic organic compounds containing both nitrogen and oxygen in a 5-membered ring that are useful as intermediates in organic synthesis[1] and biologically active compounds as synthetic antimicrobial agents.[2] Thus, many synthetic methods of oxazolidinones have been studied using various starting materials, catalysts, and reaction conditions.[3] Among them, an oxidative carbonylation is one of the most commonly practiced methods to produce oxazolidinones from β-amino alcohols, CO, and oxygen in the presence of Pd- and Co-based catalytic systems with high efficiency.[4] For example, Gabriele group reported[4a] a method for the synthesis of 2-oxazolidinones by direct palladium-catalyzed oxidative carbonylation of *β*-amino alcohols (Scheme 1). The reaction was carried out in MeOH at 100 °C using a 1/6/5 CO/O_2/air mixture (60 atm total pressure at 25 °C) and was characterized by high to excellent yields (86-100%) and unprecedented catalytic efficiencies. The catalytic system consisted of PdI_2 in conjunction with an excess of KI. Reoxidation of Pd(0) ensuing from the cyclocarbonylation process occurred through oxidation of HI (also ensuing from substrate carbonylation) to iodine by oxygen, followed by oxidative addition of I_2 to Pd(0). They have now found that by just changing the reaction solvent from MeOH to 1,2-dimethoxyethane (DME), the oxidative carbonylation of **1** to **2** can be carried out under much milder conditions than those reported above with even higher catalytic efficiencies.[4b] In fact, by working in DME the reaction could be effectively

performed using only 10 equiv of KI with respect to PdI_2 and under 20 atm of a 4:1 mixture of CO/air. However, in some cases, the usefulness of these catalytic systems is debased because of the requirement of high pressure (20-60 atm total pressure at 25°C) of carbon monoxide[4] or specially designed ligands.[4c-e] It would be desirable to develop new oxidative carbonylation catalysts that can be carried out under mild reaction conditions.

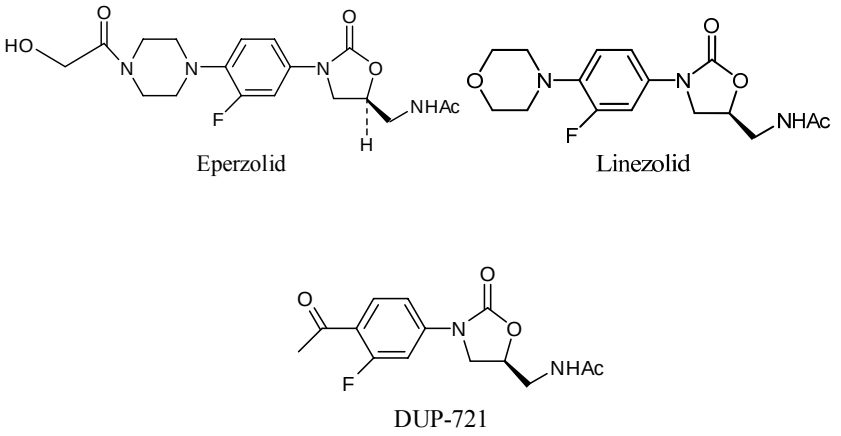
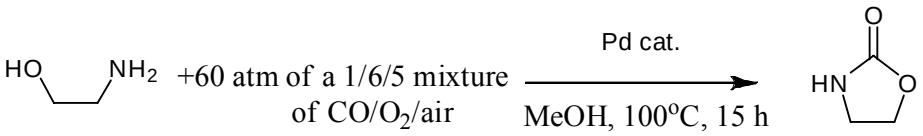
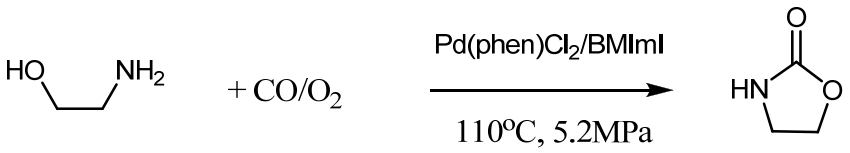


Figure 1. Chemical structures of eperezolid, linezolid, and DUP-721.[2]

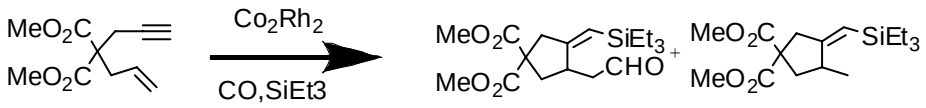


Scheme 1. PdI_2/KI-catalyzed oxidative carbonylation of the amino-alkohol.[4a]

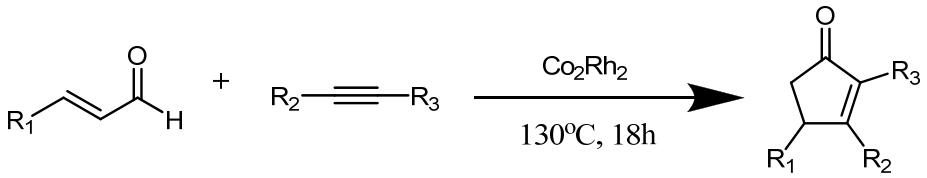


Scheme 2. Pd(phen)Cl_2/ 1-butyl-3-methyl-imidazolium iodide salts (BMImI)-catalyzed oxidative carbonylation of the aminoalkohol. [4-c]

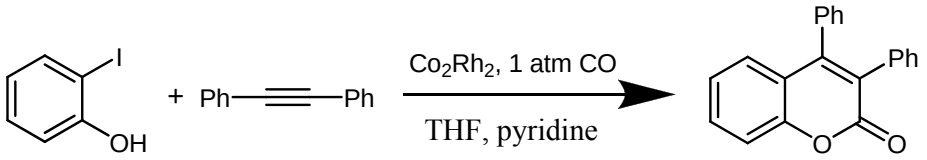
Recently, transition metal nanoparticles have been used widely as catalysts for organic synthesis due to their high catalytic activity and recyclability.[5] We recently found[6] that cobalt/rhodium nanoparticles (Co_2Rh_2 NPs) derived from $Co_2Rh_2(CO)_{12}$ were quite useful catalysts in carbonylation related reactions. In the context of our studies on the use of transition metal nanoparticles in organic reactions, we recently found that Co_2Rh_2 NPs were also effective for the oxidation reaction.[7] While we were studying the use of Co_2Rh_2 NP as a catalyst in oxidation and carbonylation reactions, we recently found that Co_2Rh_2 NP can act as a catalyst in the transformation of β-amino alcohols to oxazolidinones. We herein report the Co_2Rh_2 NP on chrcoal-catalyzed cyclization of β-amino alcohols in the presence of carbon monoxide to give oxazolidinones. There are some reports[7b,8] on the use of transition metal nanoparticles as catalysts in oxidative carbonylations. However, this is the first use of transition metal nanoparticles as catalysts in the synthesis of oxazolidinones. The catalytic system does not require any additives or promoters and can be recycled several times without any significant loss of its catalytic activity. For the catalytic synthesis of oxazolidinones, the catalytic reaction can be carried out under relatively low CO pressure (6.5 atm).



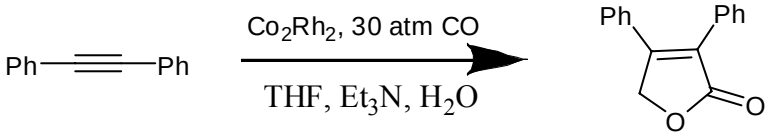
Scheme 3. Reaction of 1,6-enynes with a hydrosilane in the presence of immobilized cobalt/rhodium bimetallic nanoparticles gives 2-methyl-1-silylmethylidene-2-cyclopentanes under 1 atm of carbon monoxide**.** [6a]



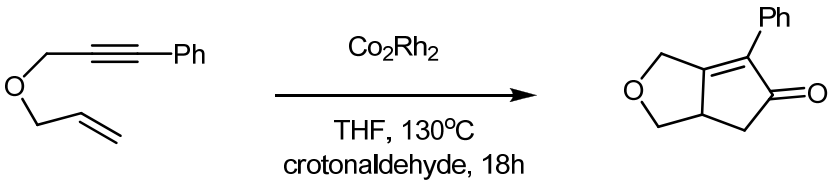
Scheme 4. Co_2Rh_2 NP/C react with alkynes and α,β-unsaturated aldehydes release products resulting from [2 + 2 + 1]cycloaddition of alkyne, carbon monoxide, and alkene. [6b]



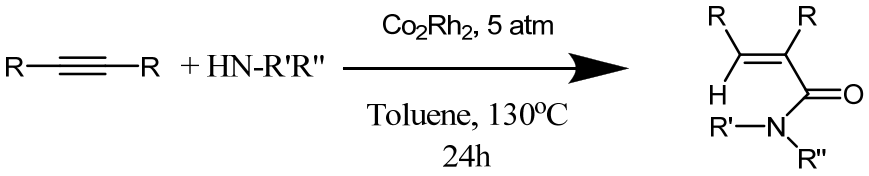
Scheme 5. Co_2Rh_2 NP/C catalyzed reaction of synthesis for coumarins from a reaction of alkynes with 2-iodophenol under 1 atm of CO[6c]



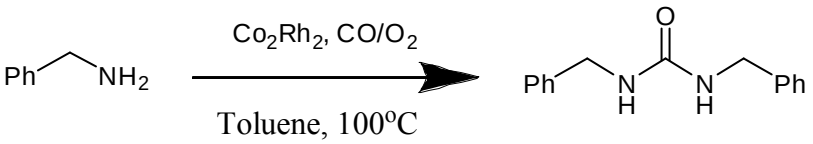
Scheme 6. Cyclohydrocarbonylation of substituted alkynes catalyzed by immobilized Co–Rh heterobimetallic nanoparticles[6d]



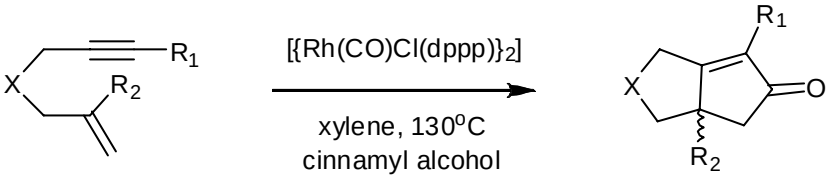
Scheme 7. Immobilized Co/Rh-catalyzed intramolecular Pauson–Khand reaction using a substitute for carbon monoxide.[6e]



Scheme 8. The first example of cobalt-rhodium heterobimetallic nanoparticle-catalyzed synthesis of alkenyl amides from alkynes, amines, and carbonmonoxide is described.[7a]



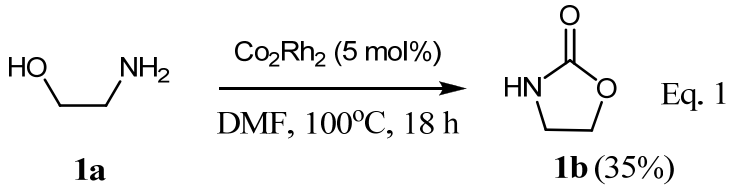
Scheme 9. Cobalt/Rhodium Heterobimetallic Nanoparticle-Catalyzed Oxidative Carbonylation of Amines in the Presence of Carbon Monoxide and Molecular Oxygen to Ureas.[7b]



Scheme 10. Rhodium-Catalyzed Pauson–Khand-Type reaction using alcohol as a source of carbon monoxide.[9]

Results and Discussion

A catalytic synthesis of oxazoldinones was studied using β-amino alcohol **1a** as a model substrate and Co_2Rh_2 NP/C as a catalyst. β-Amino alcohols used in this study were commercially available and used without further purification. The treatment of **1a** (31 mg, 0.5 mmol) with 5 atm of carbon monoxide and 2 atm of oxygen in the presence of Co_2Rh_2 NP/C (5 mol%, 45 mg) in 5 mL of ethanol at 100℃ for 18 h gave an oxazolidinone **1b** in 35% yield (eq 1).



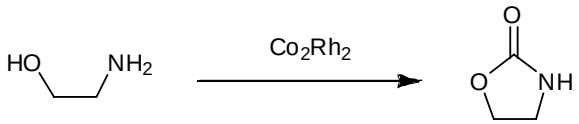
Eq. 1

1a **1b** (35%)

The formation of the oxazolidinone was confirmed by IR and ^{1}H and ^{13}C NMR studies. We were pleased to find that the desired product **1b** was obtained in 35% in the initial study. Encouraged by the formation of **1b**, we further optimized the reaction conditions. The representative optimization experiments are summarized in Table 1. The yield was highly dependent upon the reaction solvent (entries 1-9), the reaction temperature (entries 3 and 10-12), the amount of the reaction catalyst (entries 3 and 13-14), the reaction time (entries 3 and 15-16), and the pressure of CO and O_2 (entries 17-21). The reaction in THF and dioxane gave a trace amount of **1b**, in water no reaction was observed. DMF was chosen as a reaction solvent. The yield of **1b** was rather insensitive to the reaction temperature. The yield of **1b** was also dependent upon the pressures of CO and O_2. Interestingly, the reaction could

be carried out in the presence of CO without oxygen. The best yield was obtained when the pressures of CO and O_2 were 3 and 4 atm, respectively. Considering the reaction yield based on the reaction solvent, the reaction temperature, the pressures of CO and O_2, and the amount of the catalyst used, the optimized reaction conditions were established as follows: 4ml DMF, 2.5 atm of O_2 and 4 atm of CO, 100℃, and 18 h. Recent concern about the Green Chemistry urged us to study aldehydes or alcohols as CO surrogates.[6e,9] Thus, we examined cinnamyl aldehyde, cinnamyl alcohol, ethanol, and ethylene glycol as CO source under our reaction conditions. However, the yield of **1b** was negligible for cinnamyl aldehyde, cinnamyl alcohol, and ethanol. In case of ethylene glycol, **1b** was obtained in 30% yield.

Table 1. Screen of reaction conditions.



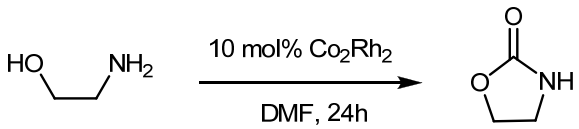
1a **1b**

Entry	mol% of Cat.	Solvent	Temp. (^oC)	Time (h)	O_2 (atm)	CO (atm)	Yield (%)
1	5	EtOH	100	18	1.5	5	35
2	5	DMF	100	18	1.5	5	59
3[a)]	5	DMF	100	18	1.5	5	60
4	5	THF	100	18	1.5	5	Trace
5	5	dioxane	100	18	1.5	5	Trace
6	5	MeOH	100	18	1.5	5	44
7	5	H_2O	100	18	1.5	5	N.R
8	5	toluene	100	18	1.5	5	30
9	5	DMSO	100	18	1.5	5	35
10	5	DMF	150	18	1.5	5	64
11	5	DMF	50	18	1.5	5	61
12	5	DMF	20	18	1.5	5	55
13	10	DMF	100	18	1.5	5	88

14	15	DMF	100	18	1.5	5	>99
15	5	DMF	100	12	1.5	5	46
16	5	DMF	100	24	1.5	5	81
17	10	DMF	100	18	0	7	64
18	10	DMF	100	18	0.5	6	76
19	10	DMF	100	18	0.5	4	71
20	10	DMF	100	18	2.5	4	95
21	10	DMF	100	18	3.5	3	35

[a] In the presence of molecular sieves 4Å.

Table 2. Co_2Rh_2 NP/C-catalyzed oxidative cyclocarbonylation using a substitute for carbon monoxide.



1a **1b**

Entry	CO Source	Time (h)	Temp. (^oC)	Yield (%)
1	cinnamyl aldehyde	24	100	Trace
2	cinnamyl alcohol	24	100	Trace
3	ethanol	24	70	Trace
4	ethylene glycol	24	100	30

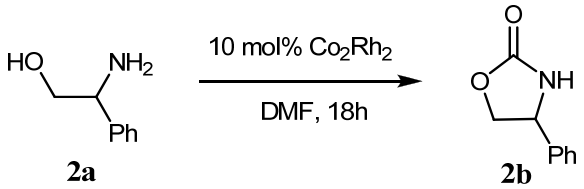
To check for recyclability, the catalyst was separated and reused several times. The catalyst maintained its high level of activity even after being recycled five times (the substrate used was 2-amino-2-phenylethanol, **2a**: 99%, 98%, 96%, 92%, and 95%, respectively). The maximum reusuability has not been tested. In order to recycle the catalyst, the catalyst was separated from the reaction mixture by centrifugation, washed several times by CH_2Cl_2, and dried in vacuum. It could then be reused for further catalytic reactions. The catalyst is stable under reaction conditions as reflected by its activity in the recovered material.

To examine the scope of the present reaction, various β-amino alcohols were

screened under the optimized reaction conditions. The results are summarized in Table 2, which shows that oxazolidinones **b** are obtained in satisfactory yields (83-99%) for all β-amino alcohols, which have the amino and alcohol groups are close enough to make ring formation. Interestingly, β-amino alcohols with a phenyl substituent (entries 2, 3, and 10) gave relatively higher yields than those having an alkyl substituent.

Chiral β-amino alcohols were transformed into chiral oxazoldiinones without loss of stereochemical information (entries 2 and 3). Reaction of 2-aminophenol afforded 84% of an oxazoldiinone derivative (entry 11), but in case of 4-aminophenol no reaction was observed. 2-Aminobenzyl alcohol also produced the corresponding oxazoldiinone in 99% yield under our optimized reaction conditions (entry 12), but the same product was obtained in 45% yield (by GC analysis) in the presence of $Pd(OAc)_2$, PPh_3, and Et_3N under 27 atm CO.[10] The trend of the yields (84% and 99%) of five- and six-membered benzo-fused heterocycles (entries 11 and 12) were opposite to that observed (95% and 45%) in Pd-catalyzed reactions.[10]

Table 3. Reuse of Co_2Rh_2 NP/C catalyst for oxidative cyclocarbonylation reaction of **2b**[a)]



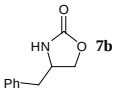
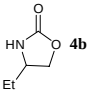
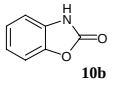
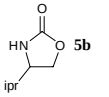
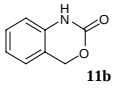
2a **2b**

Entry	catalyst	Yield (%)
1	Co_2Rh_2 NP/C 10 mol%	99

2	Recovered from #1	98
3	Recovered from #2	96
4	Recovered from #3	92
5	Recovered from #4	95

[a] In order to recycle the catalyst, the catalyst was separated from the reaction mixture by centrifugation, washed several times by CH_2Cl_2, and dried in vacuum. It could then be reused for further catalytic reactions.

Table 4. Co_2Rh_2 NP/C-catalyzed oxidative cyclocarbonylation of β-amino alcohols [a]

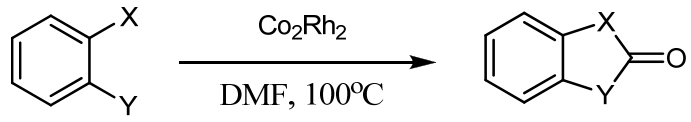
entry	product	Yield (%)[a]	ee (%)	entry	product	Yield (%)[b]
1	 **1b**	95		7	 **6b**	83
2[c]	 **2b**	99	99	8	 **7b**	83
3[d]	 **2b**	99	99	9	 **8b**	83
4	 **3b**	88		10	 **9b**	96
5	 **4b**	91		11	 **10b**	84
6	 **5b**	94		12	 **11b**	99

[a] Reactions were carried out using 0.5 mmol of substrate in DMF (4 mL) at 100 °C for 18 h under 6.5 atm of a mixture of CO/O_2 (4:2.5) in the presence of 10 mol% Co_2Rh_2 NP/C. [b] Isolated yield. [c] *S* enantiomer. [d] *R* enantiomer

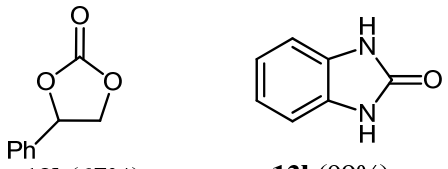
As an extension of the Co_2Rh_2 NP/C-catalyzed oxidative carbonylation

reactions, we examined also the conversion of 1,2-diol, 1,2-diamine, and 1,2-aminothiol into cyclic carbonate, dithiocarbonate, benzimidazolone, and 2(3*H*)-benzothiazolone, respectively (Table 3).

Table 5. Co_2Rh_2 NP/C-catalyzed cyclocarbonylation of 1,2-diol, 1,2-diamine, and 1,2-aminothiol[a)]



X, Y = NH, S, O



12b(67%) **13b**(99%) **14b**(97%)

[a)] Reactions were carried out using 0.5 mmol of substrate in 4 mL DMF at 100°C for 18 h under 6.5 atm of a mixture of CO and O_2 (4:2.5) in the presence of 10 mol% Co_2Rh_2 NP/C.

The oxidative carbonylation of diols to cyclic carbonates is a well-known reaction in the presence of a palladium catalyst.[11] A Co_2Rh_2 NP/C-catalyzed oxidative carbonylation of 1-phenylethane-1,2-diol gave a cyclic carbonate in 67% yield. The oxidative carbonylation reactions of o-phenylenediamine

and 1,2-aminothiol are also a well-known process in the presence of palladium catalyst with some additives under relatively high pressure (20-68 atm) of CO and O_2 (or air).[10] The Co_2Rh_2 NP/C–catalyzed reaction under 6.5 atm of CO and O_2 led to isolation of benzimidazolone and 2(3*H*)-benzothiazolone in 99% and 97% yields, respectively. Therefore, our catalytic system is active for the aerobic oxidative carbonylation of β-amino alcohols, 1,2-diol, 1,2-diamine, and 1,2-aminothiol.

Conclusion

we demonstrated that Co_2Rh_2 NP/C can be used as an effective catalyst in the oxidatice carbonylative cyclization of β-amino alcohols in the presence of carbon monoxide and oxygen. No chirality loss is encountered during the catalytic reaction. This reaction permits the formation of oxazolinones, which are versatile synthetic intermediates as well as important structural units in a variety of biologically active natural products. In addition, the Co_2Rh_2 NP catalyst has been also successfully applied to the oxidative carbonylative cyclization reactions of 1-phenylethane-1,2-diol, o-phenylenediamine, and 2-aminobenzenethiol which have great pharmaceutical and agrochemical interest.

Experimental

General Remarks. All solvents were dried and distilled according to standard methods before use. Reactions were carried out in a high pressure reactor equipped with a stirring bar. The reactor was charged with 6.5 atm of CO and O_2 (4:2.5). unless otherwise indicated. Elevated temperatures were maintained in thermostat-controlled oil baths. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and acidic *p*-anisaldehyde, and heat as a developing agent. Workup procedures were done in air. All solvents were dried and distilled according to standard methods before use. Liquid was transferred via syringe or cannula. Flash chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ^{1}H and ^{13}C NMR spectra were recorded with Bruker (300 MHz) spectrometer. ^{1}H NMR spectra were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity(s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.23 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu). Infrared spectra were recorded on an iS10 Smart iTR Basic spectrometer. HPLC analysis was performed on a Hewlett-Packard 1100 Series HPLC, UV detection monitored at 254.4 nm, using a Chiralpak® Chiralcel OD-H column (25 cm).

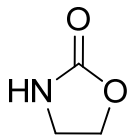
All the heterocyclic compounds reported herein have been previously prepared by other groups and characterized: oxazolidin-2-one (**1b**),[1] 4-phenyloxazolidin-2-one (**2b**),[12] 4-methyloxazolidin-2-one (**3b**),[12] 4-

ethyloxazolidin-2-one (**4b**),[12] 4-isopropyloxazolidin-2-one (**5b**),[12] 4,4-dimethyloxazolidin-2-one (**6b**),[12] 4-benzyloxazolidin-2-one (**7b**),[12] 5-methyl oxazolidin-2-one (**8b**),[13] 5-phenyloxazolidin-2-one (**9b**),[14] benzo[d]oxazol-2(3*H*)-one (**10b**),[15] 1*H*-benzo[d][1,3]oxazin-2(4*H*)-one (**11b**),[15] 4-phenyl-1,3-dioxolan-2-one (**12b**),[16] 1H-benzo[d]imidazol-2(3H)-one (**13b**),[17] benzo[d]thiazol-2(3*H*)-one (**14b**).[18]

General procedure for the Co_2Rh_2 NP/C -catalyzed oxidative cyclocarbonylation of β–amino alcohols:

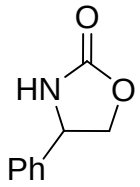
To a high pressure reactor were added a substrate (0.5 mmol), Co_2Rh_2 NP/C (10 mol%, 90 mg), and 4 mL of DMF. The reactor was charged with 6.5 atm of CO and O_2 (4:2.5). The resulting solution was heated at 100^{o}C for 18 h. After the soultion was cooled to room temperature, the reaction mixture was washed with dichloromethane. In order to recycle the catalyst, the catalyst was seprated from the reaction mixture by using a centrifuge. The supernatant solution was concentrated by a rotary evaporator and the remaining DMF was distilled off under vaccum. The product was purified by flash chromatography on a silica gel column by eluting with n-hexane/ethyl acetate.(v/v=3:1) The recovered catalyst was dried in vacuum. It could then be reused for further catalytic reactions.

Characterization of Compounds:



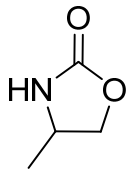
oxazolidin-2-one (1b)

IR ($CDCl_3$) (νCO) = 1754㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.28 (s, 1 H), 4.43 (t, J = 7.9 Hz, 2 H) 3.63 (t, J = 7.9 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 161.0, 65.1, 40.8 ppm. Exact mass for $C_3H_5NO_2$: 87.0320 (calc), 87.0321 (found).



4-phenyloxazolidin-2-one (2b)

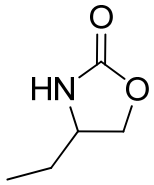
IR ($CDCl_3$) (νCO) = 1756㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.38 (m, 5 H), 6.02 (s, 1 H), 4.96 (t, J = 7.8 Hz, 1 H), 4.74 (t, J = 7.7 Hz, 1 H), 4.18 (t, J = 7.7 Hz, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.9, 139.6, 129.4, 129.3, 126.2, 72.7, 56.5 ppm. Exact mass for $C_9H_9NO_2$: 163.0633 (calc), 163.0632 (found).



4-methyloxazolidin-2-one (3b)

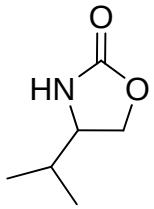
IR ($CDCl_3$) (νCO) = 1753㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.87 (s, 1 H),

4.51 (t, J = 7.7 Hz, 1 H), 3.99 (m, 2 H), 1.30 (d, J = 5.9 Hz , 3 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.8, 71.8, 48.4, 21.0 ppm. Exact mass for $C_4H_7NO_2$: 101.0477 (calc), 101.0479 (found).



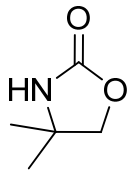
4-ethyloxazolidin-2-one (4b)

IR ($CDCl_3$) (νCO) = 1750㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.58 (s, 1 H), 4.47 (t, J = 8.4 Hz, 1 H), 4.01 (dd, J = 6.1, 8.4 Hz, 1 H), 3.80 (m, 1 H), 1.59 (m, 2 H), 0.94 (t, J = 7.4 Hz, 3 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 160.4, 70.2, 54.0, 28.3, 9.4 ppm. Exact mass for $C_5H_9NO_2$: 115.0633 (calc), 115.0632 (found).



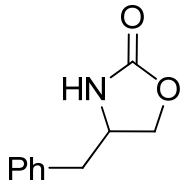
4-isopropyloxazolidin-2-one (5b)

IR ($CDCl_3$) (νCO) = 1750㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.50 (s, 1 H), 4.44 (m, 1 H), 4.10 (m, 1 H), 3.60 (m, 1 H), 1.72 (m, 1 H), 0.96 (d, J = 6.6 Hz, 3 H) 0.89 (d, J = 6.7 Hz, 3 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 160.6, 68.8, 58.5, 32.8, 18.1, 17.8 ppm. Exact mass for $C_6H_{11}NO_2$: 129.0790 (calc), 129.0788 (found).



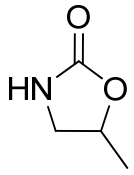
4,4-dimethyloxazolidin-2-one (6b)

IR ($CDCl_3$) (νCO) = 1751㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.29 (s, 1 H), 4.09 (s, 2 H), 1.37 (s, 6 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.5, 76.8, 55.4, 27.7 ppm. Exact mass for $C_5H_9NO_2$: 115.0633 (calc), 115.0636 (found).



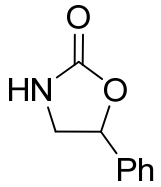
4-benzyloxazolidin-2-one (7b)

IR ($CDCl_3$) (νCO) = 1753㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.33 (m, 3 H), 7.18 (d, J = 6.8 Hz, 2 H), 5.78 (s, 1 H), 4.44 (t, J = 8.0 Hz, 1 H), 4.12 (m, 2H), 2.87 (d, J = 6.3 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.5, 136.1, 129.1, 127.4, 69.7, 53.9, 41.6 ppm. Exact mass for $C_{10}H_{11}NO_2$: 177.0790 (calc), 177.0787 (found).



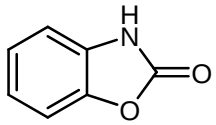
5-methyloxazolidin-2-one (8b)

IR ($CDCl_3$) (νCO) = 1747㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.35 (s, 1 H), 4.79 (m, 1 H), 3.71 (t, J = 8.3 Hz, 1 H), 3.21 (t, J = 7.8 Hz, 1 H), 1.45 (d, J = 6.0 Hz, 3 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 160.5, 73.6, 47.6, 20.7 ppm. Exact mass for $C_4H_7NO_2$: 101.0477 (calc), 101.0478 (found).



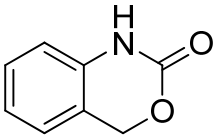
5-phenyloxazolidin-2-one (9b)

IR ($CDCl_3$) (νCO) = 1756㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.30 (s, 5 H), 6.56 (s, 1 H), 5.53 (t, J = 8.1 Hz, 1 H), 3.89 (t, J = 8.7 Hz, 1 H), 3.46 (t, J = 8.1 Hz, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 160.4, 138.6, 129.0, 125.8, 78.0, 48.5 ppm. Exact mass for $C_9H_9NO_2$: 163.0633 (calc), 163.0632 (found).



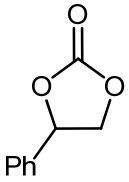
benzo[d]oxazol-2(3H)-one (10b)

IR ($CDCl_3$) (νCO) = 1774㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.06 (s, 1 H), 7.17 (m, 4H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 156.0, 144.1, 129.4, 124.3, 122.9, 110.4, 110.2 ppm. Exact mass for $C_7H_5NO_2$: 135.0320 (calc), 135.0319 (found).



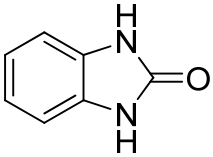
1H-benzo[d][1,3]oxazin-2(4H)-one (11b)

IR ($CDCl_3$) (νCO) = 1718㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.63 (m, 1 H), 7.27 (t, J = 7.4 Hz, 1 H), 7.08 (m, 2 H), 6.86 (d, J = 7.9 Hz, 1 H), 5.33 (s, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.7, 135.7, 129.4, 124.4, 123.5, 118.1, 114.3 68.9 ppm. Exact mass for $C_8H_7NO_2$: 149.0477 (calc), 149.0475 (found).



4-phenyl-1,3-dioxolan-2-one (12b)

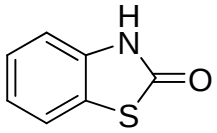
IR ($CDCl_3$) (νCO) = 1814㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.40 (m, 5 H), 5.68 (t, J = 8.0 Hz, 1 H), 4.80 (t, J = 8.4 Hz, 1 H), 4.35 (t, J = 8.2 Hz, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.0, 135.9, 129.9, 129.4, 126.0, 71.3 ppm. Exact mass for $C_9H_8O_3$: 164.0473 (calc), 164.0473 (found).



1H-benzo[d]imidazol-2(3H)-one (13b)

IR (KBr) (νCO) = 1754㎝$^{-1}$. **^{1}H NMR (300 MHz, DMSO)** δ 10.58 (s, 2 H),

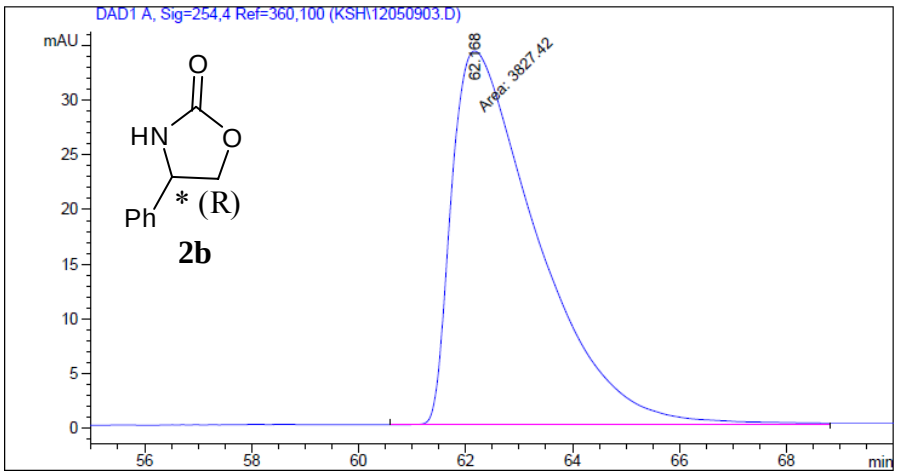
6.91 (s, 4 H) ppm. **^{13}C NMR (75 MHz, DMSO)** δ 155.2, 159.6, 120.3, 108.4 ppm. Exact mass for $C_7H_6N_2O$: 134.0480 (calc), 134.0479 (found).

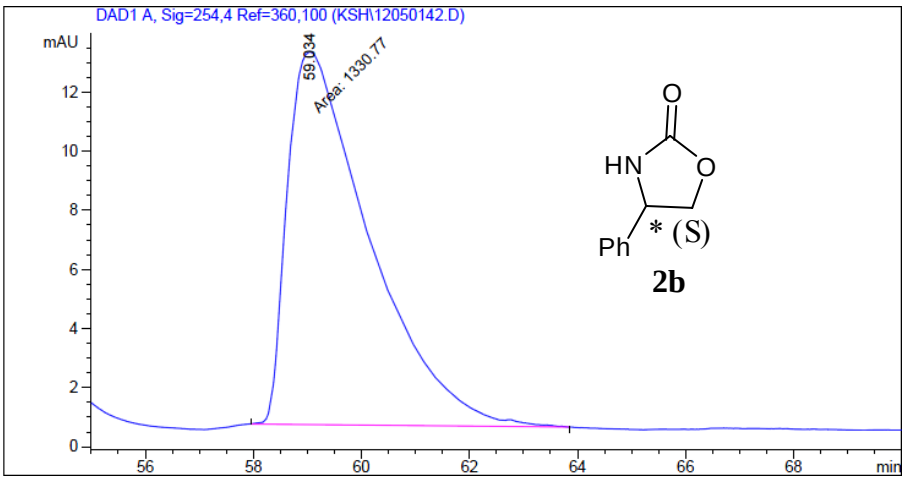


benzo[d]thiazol-2(3H)-one (14b)

IR ($CDCl_3$) (νCO) = 1672㎝$^{-1}$. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.62 (s, 1 H), 7.38 (d, J = 7.7 Hz, 1 H), 7.27 (m, 1 H), 7.18 (d, J = 10.2 Hz, 1 H), 7.12 (d, J = 7.3 Hz, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 173.7, 135.7, 126.6, 124.0, 123.3, 122.5, 112.1 ppm. Exact mass for C_7H_5NOS: 151.0092 (calc), 151.0091 (found).

HPLC chromatograms for S- and R-enantiomers of 2b





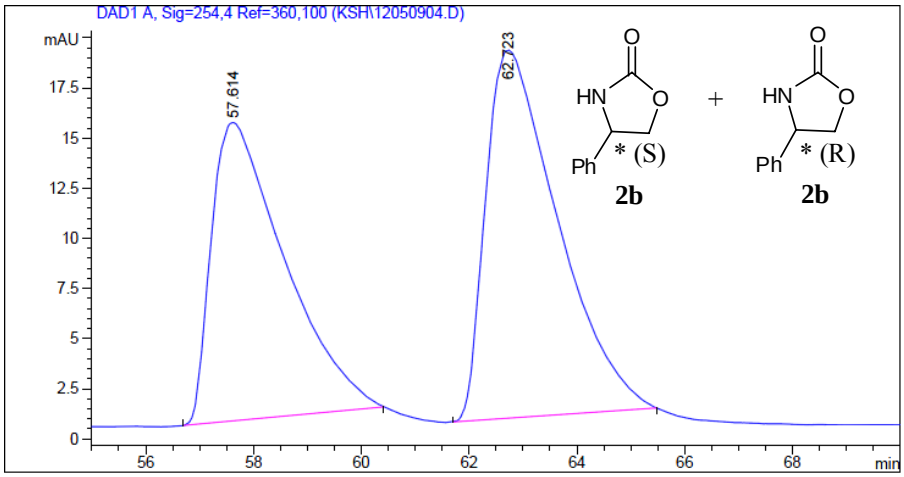


Figure 2. HPLC chromatograms for S- and R-enantiomers of **2b.** Chiralcel OD-H column (25 cm), hexane:isopropyl alcohol = 90 : 10, flow rate = 0.9 ml/min.

Chiralcel OD-H column (25 cm), hexane:isopropyl alcohol = 90 : 10, flow rate = 0.9 ml/min.

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국문초록

코발트-로듐 이핵 나노입자를 촉매로 하는 산화-카보닐화 반응을 통해 이전의 반응 조건보다 마일드한 조건으로 일산화탄소와 산소조건하에서 베타-아미노 알코올로부터 옥사졸리디논을 합성할 수 있었다. 1-페닐에탄-1,2-다이올, 올쏘-페닐렌다이아민, 2-아미노 벤조싸이올의 산화-카노닐화반응도 좋은 수율로 합성할 수 있었다.

주요어: 베타-아미노 알코올, 옥사졸리디논, 나노 촉매, 산화, 고리화카보닐화 반응, 고리 카보네이트, 다이싸이오카보네이트, 벤즈이미다졸론, 2(3*H*)-벤조싸이아졸론.

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