ORGANOMETALLICS

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Ruthenium(III)-Catalyzed β-Alkylation of Secondary Alcohols with Primary Alcohols

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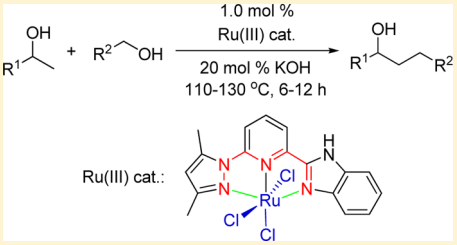
Supporting Information

ABSTRACT: A Ru(III)-NNN complex bearing a pyridyl-supported pyrazolyl-imidazolyl ligand was synthesized and utilized as the catalyst for the direct β-alkylation of secondary alcohols with primary alcohols. β-Alkylated secondary alcohols were obtained in moderate to high yields with water formed as the byproduct through a hydrogen borrowing pathway. The present protocol provides a concise atom-economical and environmentally benign method for C−C bond formation.

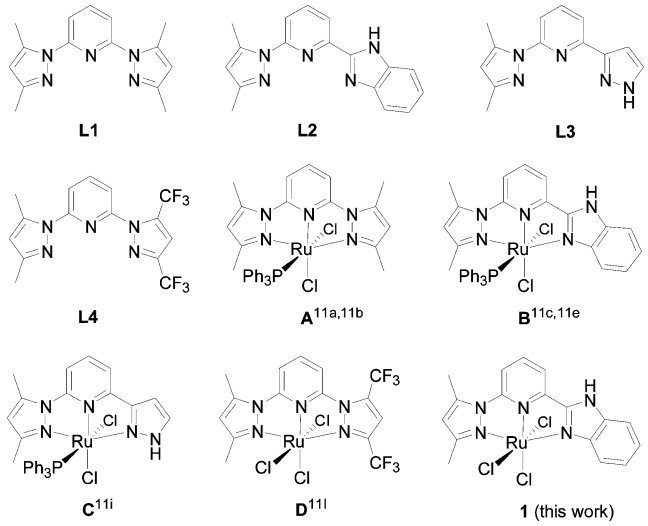


INTRODUCTION

Alcohols are one of the most important intermediates that have been widely used in organic synthesis and chemical industry. Traditional routes to access β-alkylated alcohols from secondary alcohols usually require a multistep process that involves oxidation of secondary alcohols, alkylation with alkyl halides, and reduction of β-alkylated ketones. Considering the demand of environmentally benign processes, transition-metal-catalyzed direct β-alkylation of secondary alcohols with primary alcohols has been widely studied as a greener route through a hydrogen borrowing or hydrogen autotransfer strategy in recent years.[1] This alternative method involves a dehydrogenation of alcohol to ketone or aldehyde, followed by aldol reaction, generating the corresponding enone intermediate, and subsequent hydrogenation of the enone to afford β-alkylated alcohols with high atom efficiency by producing water as the only byproduct. Cho et al. reported such a direct β-alkylation with $RuCl_2(PPh_3)_3$ as the catalyst, but sacrificial hydrogen acceptor and hydrogen donor were needed.[2] $RuCl_2(DMSO)_4$ was found to be a more efficient catalyst for the same purpose.[3] Ruthenium complexes containing a chelating N-heterocyclic carbene and other types of ligands were efficiently used for direct β-alkylation of secondary alcohols with primary alcohols.[4] Highly active iridium complexes, such as $[Cp^*IrCl_2]_2$ and iridium-NHC complexes, have also been applied in this area.[5] Tris(acetylacetonato)rhodium(III) was shown to be a suitable catalyst for the alkylation of secondary alcohols in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO).[6] β-Alkylation of secondary alcohols can also be realized by using palladium,[7] copper,[8] and iron[9] complex catalysts or under metal-free conditions.[10]

Recently, we have reported a series of versatile symmetrical and unsymmetrical pyridyl-based N-heterocylic ligands and the application of their corresponding ruthenium complexes as the catalysts for transfer hydrogenation of ketones and Oppenauer-type oxidation of secondary alchohols (Scheme 1).[11] Ru(II) complexes **A**−**C** and their analogues have exhibited very high catalytic activities in these transformations. Unexpectedly, Ru(III) complex **D** also acted as an efficient catalyst for the transfer hydrogenation of ketones.[11] As compared to the extensively investigated Ru(II) complexes,[12] Ru(III) complexes have been paid much less attention.[13] In the latter case, Ru(III) complexes were reported as the catalysts for C−H activation,[14] heterocycle synthesis,[15] and transfer hydrogenation of

Scheme 1. Selected NNN Ligands and Their Corresponding Ruthenium Complexes



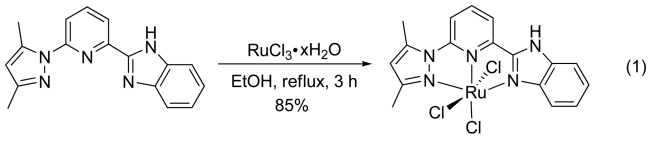
Received: February 15, 2016
Published: April 21, 2016

DOI: 10.1021/acs.organomet.6b00130
Organometallics 2016, 35, 1251−1256

ketones.[16] During our ongoing exploration of ruthenium-catalyzed transfer hydrogenation of ketones, we reasonably envisioned that the ruthenium(III) complex of ligand **L2**, that is, complex **1**, might be used as the catalyst for β-alkylation of secondary alcohols with primary alcohols. Herein, we report ruthenium(III)-NNN complex-catalyzed β-alkylation of secondary alcohols with primary alcohols through a hydrogen borrowing pathway.

RESULTS AND DISCUSSION

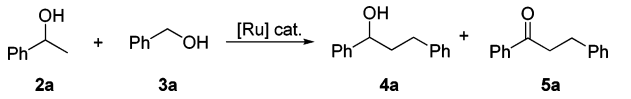
Synthesis and Characterization of Ru(III) Complex 1. Reacting equimolar amounts of ligand **L2** with $RuCl_3{\cdot}xH_2O$ in refluxing ethanol gave Ru(III) complex **1** in 85% yield (eq 1). Ru(III) complex **1** is paramagnetic, and its NMR spectra could not be successfully collected. Complex **1** was characterized by HRMS, elemental analysis, and IR. The HRMS analysis of complex **1** revealed a peak corresponding to value of 460.9750 ($[M - Cl]^+$), which is consistent with the calculated value of 460.9748 for the composition of the $RuCl_3{\cdot}$**L2** adduct. Compared with the ligand **L2** infrared spectrum, the C═N stretching vibration of complex **1** moved from 1580 to 1609 cm^{-1} due to the coordination effect of the ligand with the ruthenium metal center.



(1)

β-Alkylation of Secondary Alcohols with Primary Alcohols. Initially, the reaction of 1-phenylethanol (**2a**) with benzyl alcohol (**3a**) was conducted to optimize the reaction conditions (Table 1). By using 1 mol % $RuCl_3{\cdot}xH_2O$ as the catalyst and 100 mol % KOH as the base in toluene at 110 °C, the corresponding β-alkylated product **4a** was obtained in 30% yield, with formation of ketone **5a** as the minor product (Table 1, entry 1). The conversions and selectivities were obviously improved by addition of a pyridyl-based NNN ligand, that is, one of **L1**–**L4** (Table 1, entries 2–5). Encouraged by **L2** as a promising ligand to stabilize the Ru(III) catalyst (Table 1, entry 3), complex **1** was synthesized and tested as the catalyst for the same reaction. To our delight, complex **1** (1.0 mol %) promoted the reaction to reach 95% conversion for **2a** and 90% selectivity for **4a** (Table 1, entry 6). Under the solvent-free conditions, the conversion and selectivity were further improved (Table 1, entry 7). Among the screened bases, KOH acted as the most suitable base for the desired reaction (Table 1, entries 7–10). A catalytic amount of the base, that is, 20 mol % KOH, also effected the reaction to reach the best reaction efficiency: >99% conversion for **2a** with a 93:7 molar ratio of **4a**:**5a**. Thus, **4a** was isolated in 90% yield (Table 1, entry 11). Both the Ru(II) complexes $RuCl_2(PPh_3)_3$ and $[RuCl_2(p\text{-cymene})]_2$ demonstrated poor catalytic activity for the reaction (Table 1, entries 12 and 13). Under atmospheric oxygen, the reaction efficiency was obviously deteriorated (Table 1, entry 14).

Table 1. Screening of the Reaction Conditions[a]



2a **3a** **4a** **5a**

entry	catalyst	base	conversion of **2a**[b] (%)	**4a**:**5a** (molar ratio)[b]
1	$RuCl_3{\cdot}xH_2O$	KOH	30	67:33
2	$RuCl_3{\cdot}xH_2O$/**L1**	KOH	60	75:25
3	$RuCl_3{\cdot}xH_2O$/**L2**	KOH	89	86:14
4	$RuCl_3{\cdot}xH_2O$/**L3**	KOH	49	72:28
5	$RuCl_3{\cdot}xH_2O$/**L4**	KOH	52	65:35
6	**1**	KOH	95	90:10
7[c]	**1**	KOH	>99	93:7
8[c]	**1**	*t*BuOK	81	91:9
9[c]	**1**	NaOH	75	77:23
10[c]	**1**	K_3PO_4	<5	n.d.
11[c,d]	**1**	KOH	>99	93:7 (90)[e]
12[c,d]	$RuCl_2(PPh_3)_3$	KOH	15	55:45
13[c,d]	$[RuCl_2(p\text{-cymene})]_2$	KOH	<5	n.d.
14[c,d,f]	**1**	KOH	80	80:20

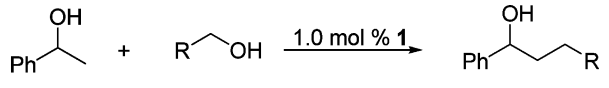
[a]Conditions: **2a** (2.0 mmol), **3a** (2.0 mmol), catalyst (1.0 mol %), base (2.0 mmol), toluene (1 mL), 0.1 MPa N_2, 110 °C, 6 h. The reaction was performed in a 25 mL sealed tube. [b]Determined by GC analysis. [c]Solvent-free. [d]Using 0.2 equiv of KOH. [e]Isolated yield of **4a** given in parentheses. [f]Under 0.1 MPa O_2 atmosphere.

Under the optimized conditions, the protocol generality was explored by using a variety of primary alcohols (Table 2). Benzylic alcohols bearing an electron-donating methyl, methoxy, or 3,4-methylenedioxy substituent reacted with **2a** to form the desired products **4b**–**4f** in 81–91% yields. Electron-deficient substituent-bearing benzylic alcohols, that is, 2-, 3-, or 4-chlorobenzyl alcohols, also smoothly reacted with **2a** to afford products **4g**–**4i** in good yields (78–91%). However, the reactions of the alcohol substrates bearing an ester, amide, aldehyde, or cyanide substituent on the aryl moiety gave no identified products. Such substituents underwent decomposition to mess the reactions under the reaction conditions. In the case of benzylic alcohol bearing a benzoyl substituent, its reaction with 1-phenylethanol formed the intermediate ketone product **5j** in 52% yield. The reaction of **2a** with 2-naphthylmethanol efficiently underwent, forming **4k** in 88% yield. Use of 2-pyridylmethanol decreased the yield of **4l** to 64%, whereas the corresponding 4-pyridylmethanol reacted with **2a** to give the desired product **4m** in 75% yield, which reveals an electronic effect from the pyridyl moiety. Unexpectedly, 2-furylmethanol reacted to give **4n** in a good yield (76%). Somehow, use of chain-varying aliphatic primary alcohols only led to the desired products **4o**–**4s** in 52–70% yields by increasing the catalyst loading to 2.0 mol % and extending the reaction time to 12 h.

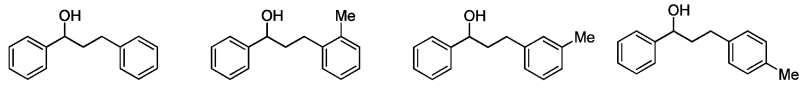
Next, the scope of the secondary alcohols (**2**) was investigated (Table 3). The present catalytic system could be tolerant with various functional groups. Steric hindrance from the aryl moieties of **2** had no obvious impact on the reaction efficiency. Thus, 1-(2-methylphenyl)ethanol reacted with **3a** to afford the desired product **6a** in 93% yield. Secondary alcohols bearing a *meta*-Me, or -OMe or *para*-OMe group also underwent the reaction efficiently to form **6b**–**6d** in 87–90% yields. Electron-withdrawing substituents such as bromo and chloro lessened the reaction efficiency to some extent, leading to the desired products **6e**–**6g** in 74–82% yields. In the same fashion, treatment of 1-(2-naphthyl)ethanol with **3a** resulted in **6h** in 91% yield. 1-(2-Pyridyl)ethanol reacted with **3a** to give **6i** in a good yield (80%). However, the long-chain secondary alcohols only exhibited relatively low reactivity to **3a**, and their reactions had to be performed to form **6j**–**6l** in 53–76% yields in the presence of 2.0 mol % catalyst over a period of 12 h.

DOI: 10.1021/acs.organomet.6b00130
Organometallics 2016, 35, 1251–1256

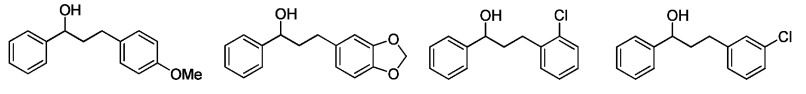
Table 2. Scope of Primary Alcohols (3)[a,b]



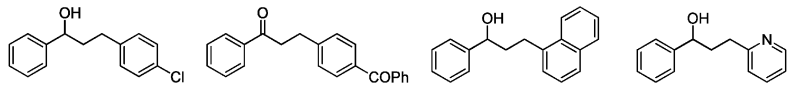
2a **3** **4**



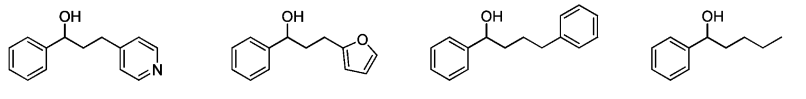
4a, 90% **4b**, 91% **4c**, 88% **4d**, 81%



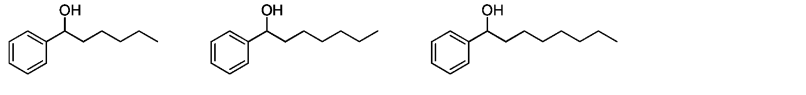
4e, 82% **4f**, 83% **4g**, 78% **4h**, 91%



4i, 82% **5j**, 52% **4k**, 88% **4l**, 64%



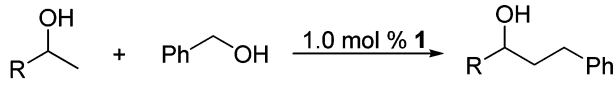
4m, 75% **4n**, 76% **4o**, 70%[c] **4p**, 65%[c]



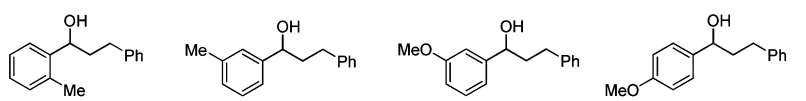
4q, 67%[c] **4r**, 65%[c] **4s**, 52%[c]

[a]Conditions: **2a** (2.0 mmol), **3** (2.0 mmol), 1.0 mol % **1**, 20 mol % KOH, 0.1 MPa N_2, 110 °C, 6 h. [b]Isolated yields. [c]2.0 mol % **1**, 12 h.

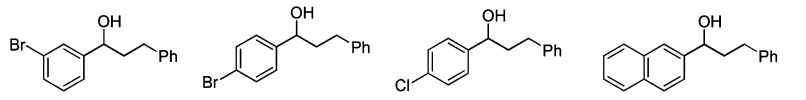
Table 3. Generality of Secondary Alcohols (2)[a,b]



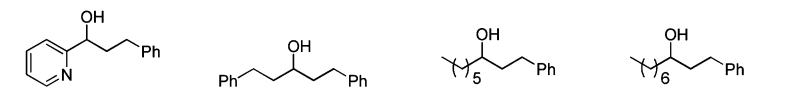
2 **3a** **6**



6a, 93% **6b**, 90% **6c**, 87% **6d**, 88%



6e, 74% **6f**, 80% **6g**, 82% **6h**, 91%

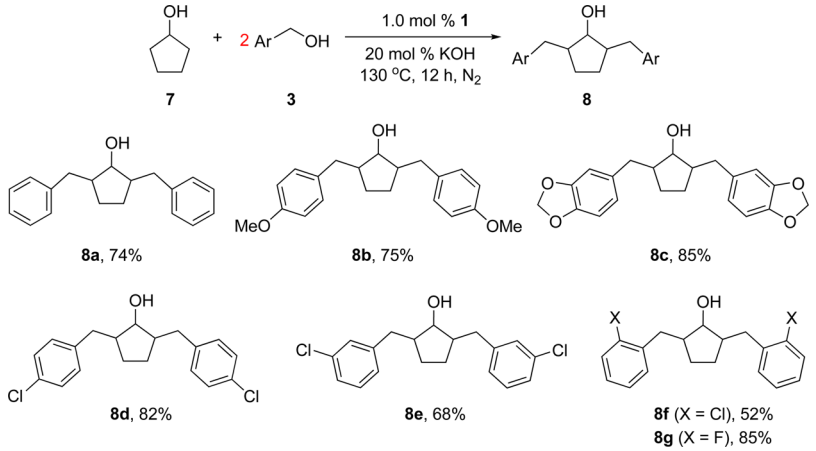


6i, 80% **6j**, 53%[c] **6k**, 76%[c] **6l**, 65%[c]

[a]Conditions: **2** (2.0 mmol), **3a** (2.0 mmol), 1.0 mol % **1**, 20 mol % KOH, 0.1 MPa N_2, 110 °C, 6 h. [b]Isolated yields. [c]2.0 mol % **1**, 12 h.

DOI: 10.1021/acs.organomet.6b00130
Organometallics 2016, 35, 1251−1256

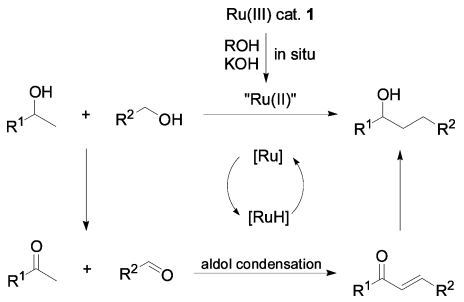
Scheme 2. Reactions of Cyclopentanol with Benzylic Alcohols



Then, cyclic secondary alcohols, that is, cyclopentanol **7**, was employed to react with various primary alcohols in the same fashion (Scheme 2). Interestingly, **7** reacted with benzyl alcohols to afford dialkylated secondary alcohol products of type **8**. The reaction of cyclopentanol with benzylic alcohol formed 2,5-dibenzylcyclopentanol **8a** (74%). The electron-donating 4-methoxy and 3,4-methylenedioxy substituents varied the product yields of **8b** (75%) and **8c** (85%). The electronic and steric effects are obvious for the electron-withdrawing chloro and fluoro substituents on the aryl moiety of the benzylic alcohols, rendering formation of **8d**–**8g** in 52–82% yields.

Reaction Mechanism. A simplified mechanism is proposed in Scheme 3. Initially, the precatalyst Ru(III) complex **1** was

Scheme 3. Proposed Mechanism



transformed to a pentacoordinated complex by extrusion of one molecule of HCl in the presence of KOH and then reduced to Ru(II) species under the reaction conditions.[11l] The Ru(II) species generated in situ promotes oxidation of the secondary and primary alcohols to the corresponding ketone and aldehyde by generation of a ruthenium hydride species.[1g] Then, the base mediated cross-aldol condensation of the in situ formed ketone and aldehyde to form the α,β-unsaturated ketone intermediate. Subsequent transfer hydrogenation of the resultant enone with the ruthenium hydride species yields the coupled alcohol. The possible catalytically RuH species was not successfully prepared from complex **1** under the reported basic conditions.[11j]

CONCLUSIONS

In summary, we have developed an efficient Ru(III)-NNN complex-catalyzed direct β-alkylation of secondary alcohols with primary alcohols. The present protocol provides a potential strategy that combines simple metal salts with polydentate ligands to explore the catalytic activity of the possible catalyst systems.

EXPERIMENTAL SECTION

General Considerations. The solvents were dried and distilled prior to use by the literature methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX–400 spectrometer, and all chemical shift values refer to δ_{TMS} = 0.00 ppm, $CDCl_3$ ($\delta(^1H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm). The HRMS analysis was obtained on an Agilent 6540 UHD Q-TOF mass spectrometer. All the melting points were uncorrected. TLC analysis was performed by using glass-backed plates coated with 0.2 mm of silica gel. Flash column chromatography was performed on silica gel. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Ligands **L1**,[11b] **L2**,[11c] **L3**,[11i] and **L4**[11l] were prepared as reported.

*Synthesis of Complex **1**.* Under a nitrogen atmosphere, a mixture of $RuCl_3{\cdot}xH_2O$ (262 mg, 1.0 mmol) and ligand **L2** (289 mg, 1.0 mmol) in ethanol (20 mL) was refluxed for 3 h. After it cooled to ambient temperature, the mixture was filtered and the residue was rinsed with diethyl ether (3 × 10 mL), and dried in vacuo to afford **1** as a brown powder (421 mg, 85% yield). Mp: > 300 °C dec. IR (KBr pellets, cm^{-1}): ν 3528, 3136, 1609, 1559, 1470, 1405, 1356, 1322, 1235, 1160, 1095, 1058, 984, 798, 764, 434. Anal. Calcd for $C_{17}H_{15}Cl_3N_5Ru$: C, 41.10; H, 3.04; N, 14.10. Found: C, 40.64; H, 2.89; N, 14.11. HRMS: calcd for $C_{17}H_{15}Cl_3N_5Ru$, $[M - Cl]^+$ 460.9748, found 460.9750.

*General Procedure for Ru(III)-Catalyzed β-Alkylation of Secondary Alcohols with Primary Alcohols: Synthesis of 1,3-Diphenylpropan-1-ol (**4a**).* Under a nitrogen atmosphere, a mixture of complex **1** (10 mg, 0.02 mmol), KOH (22 mg, 0.4 mmol), 1-phenylethanol (**2a**) (244 mg, 2.0 mmol), and benzyl alcohol (**3a**) (216 mg, 2.0 mmol) was loaded in a 25 mL sealed tube and stirred at 110 °C for 6 h. After it cooled to ambient temperature, the mixture was filtered through a short pad of Celite and rinsed with 20 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure, and the resulting residue was purified by column chromatography on silica gel (eluent petroleum ether (60–90 °C)/ethyl acetate: 20:1, v/v) to afford **4a** as a white solid (382 mg, 90%).

*General Procedure for Ru(III)-Catalyzed β-Alkylation of Cyclopentanol with Primary Alcohols: Synthesis of 2,5-Dibenzylcyclopentanol (**8a**).* Under a nitrogen atmosphere, a mixture of complex **1** (10 mg, 0.02 mmol), KOH (11 mg, 0.2 mmol), cyclopentanol (**7**) (86 mg, 1.0 mmol), and benzyl alcohol (**3a**) (216 mg, 2.0 mmol) was loaded in a 25 mL sealed tube and stirred at 130 °C for 12 h. After it cooled to ambient temperature, the mixture was filtered through a short pad of Celite and rinsed with 20 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure, and the resulting residue was purified by column chromatography on silica gel (eluent petroleum ether (60–90 °C)/ethyl acetate: 20:1, v/v) to afford **8a** as a white solid (197 mg, 74%).

DOI: 10.1021/acs.organomet.6b00130
Organometallics 2016, 35, 1251–1256

*Synthesis of 2,5-Bis(4-methoxybenzyl)cyclopentanol (**8b**).* In a fashion similar to the synthesis of **8a**, cyclopentanol (**7**) (86 mg, 1.0 mmol) reacted with 4-methoxybenzyl alcohol (**3b**) (276 mg, 2.0 mmol) to afford **8b** as a white solid (244 mg, 75% yield). Mp: 65−66 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13 and 6.85 (d each, J = 8.5 Hz, 4:4 H, aromatic CH), 3.79 (s, 6 H, 2 × OCH_3), 3.42 (t, J = 8.2 Hz, 1 H, C*H*OH), 2.84 and 2.52 (q each, 2:2 H, 2 × CH_2), 2.01 (m, 2 H, 2 × CH), 1.73 and 1.28 (m each, 2:2 H, 2 × CH_2), 1.41 (br, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.0 and 133.2 (Cq each), 129.8 and 113.9 (aromatic CH), 83.2 (*C*HOH), 55.3 (OCH_3), 48.9, 39.2, and 27.2. HRMS: calcd for $C_{21}H_{26}O_3$ 326.1882, found 326.1877.

*Synthesis of 2,5-Bis(benzo[d][1,3]dioxol-5-ylmethyl)cyclopentanol (**8c**).* In a fashion similar to the synthesis of **8a**, cyclopentanol (**7**) (86 mg, 1.0 mmol) reacted with 3,4-(methylenedioxy)benzyl alcohol (**3c**) (304 mg, 2.0 mmol) to afford **8c** as a white solid (301 mg, 85% yield). Mp: 124−125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.74 (m, 6 H, aromatic CH), 5.93 (d, J = 3.5 Hz, 4 H, 2 × OCH_2O), 3.84 (m, 1 H, C*H*OH), 2.82, 2.65, 2.57, and 2.48 (q each, 1:1:1:1 H, 2 × CH_2), 2.15 (m, 2 H, 2 × CH), 1.92, 1.70, 1.50, and 1.24 (m each, 1:2:1:1 H, 2 × CH_2 and OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 147.61, 147.59, 145.7, 145.6, 135.6, and 134.9 (Cq each), 121.6, 121.4, 109.20, 109.19, 108.14, and 108.12 (aromatic CH), 100.8 and 100.7 (2 × OCH_2O), 78.5 (*C*HOH), 49.7, 45.6, 40.4, 35.0, 29.0, and 28.8. HRMS: calcd for $C_{21}H_{22}O_5$ 354.1467, found 354.1466.

*Synthesis of 2,5-Bis(4-chlorobenzyl)cyclopentanol (**8d**).* In a fashion similar to the synthesis of **8a**, cyclopentanol (**7**) (86 mg, 1.0 mmol) reacted with 4-chlorobenzyl alcohol (**3d**) (285 mg, 2.0 mmol) to afford **8d** as a white solid (275 mg, 82% yield). Mp: 141−142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16 (m, 4 H, aromatic CH), 7.66 and 7.01 (d each, J = 8.4 Hz, 2:2 H, aromatic CH), 3.71 (m, 1 H, C*H*OH), 2.76, 2.60, 2.48, and 2.40 (q each, 1:1:1:1 H, 2 × CH_2), 2.07 (m, 2 H, 2 × CH), 1.82, 1.60, 1.40, and 1.08 (m each, 1:1:1:1 H, 2 × CH_2), 1.20 (br, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 140.3, 139.5, 131.9, and 131.6 (Cq each), 130.24, 130.22, 128.62, and 128.58 (aromatic CH), 78.6 (*C*HOH), 49.7, 45.5, 40.1, 34.8, 29.1, and 29.0. HRMS: calcd for $C_{19}H_{20}Cl_2O$ 334.0891, found 334.0887.

*Synthesis of 2,5-Bis(3-chlorobenzyl)cyclopentanol (**8e**).* In a fashion similar to the synthesis of **8a**, cyclopentanol (**7**) (86 mg, 1.0 mmol) reacted with 3-chlorobenzyl alcohol (**3e**) (285 mg, 2.0 mmol) to afford **8e** as a white solid (228 mg, 68% yield). Mp: 125−126 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19 (m, 6 H, aromatic CH), 7.08 and 7.06 (s, 1:1 H, aromatic CH), 3.40 (m, 1 H, C*H*OH), 2.91 and 2.50 (q each, 2:2 H, 2 × CH_2), 2.02 (m, 2 H, 2 × CH), 1.74 and 1.28 (m each, 2:3 H, 2 × CH_2 and OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 143.2 and 134.3 (Cq each), 129.8, 129.1, 127.1, and 126.3 (aromatic CH), 83.2 (*C*HOH), 48.6, 39.7, and 27.0. HRMS: calcd for $C_{19}H_{20}Cl_2O$ 334.0891, found 334.0881.

*Synthesis of 2,5-Bis(2-chlorobenzyl)cyclopentanol (**8f**).* In a fashion similar to the synthesis of **8a**, cyclopentanol (**7**) (86 mg, 1.0 mmol) reacted with 2-chlorobenzyl alcohol (**3f**) (285 mg, 2.0 mmol) to afford **8f** as a white solid (174 mg, 52% yield). Mp: 106−107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25, 7.15, and 7.10 (m each, 2:2:4 H, aromatic CH), 3.47 (m, 1 H, C*H*OH), 3.00 and 2.63 (q each, 2:2 H, 2 × CH_2), 2.08 (m, 2 H, 2 × CH), 1.65 and 1.28 (m each, 2:3 H, 2 × CH_2 and OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 138.8 and 134.2 (Cq each), 131.0, 129.7, 127.5, and 126.8 (aromatic CH), 83.6 (CHOH), 47.3, 37.4, and 27.2. HRMS: calcd for $C_{19}H_{20}Cl_2O$ 334.0891, found 334.0884.

*Synthesis of 2,5-Bis(2-fluorobenzyl)cyclopentanol (**8g**).* In a fashion similar to the synthesis of **8a**, cyclopentanol (**7**) (86 mg, 1.0 mmol) reacted with 2-fluorobenzyl alcohol (**3g**) (252 mg, 2.0 mmol) to afford **8g** as a white solid (257 mg, 85% yield). Mp: 122−123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 and 7.03 (m each, 4:4 H, aromatic CH), 3.46 (t, J = 8.3 Hz, 1 H, C*H*OH), 2.94 and 2.64 (q each, 2:2 H, 2 × CH_2), 2.08 (m, 2 H, 2 × CH), 1.74 and 1.33 (m each, 2:2 H, 2 × CH_2), 1.52 (br, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.6 (d and Cq, J = 242.8 Hz, aromatic C-F), 131.2 (d, J = 5.0 Hz, aromatic CH), 128.0 (d and Cq, J = 15.9 Hz, aromatic CH), 127.8 (d, J = 8.0 Hz), 124.1 (d, J = 3.5 Hz) and 115.5 (d, J = 22.4 Hz) (aromatic CH), 83.2 (CHOH), 47.7, 32.7 (d, J = 1.7 Hz) and 27.0. HRMS: calcd for $C_{19}H_{20}F_2O$ 302.1482, found 302.1471.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00130.

NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (21272232).

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DOI: 10.1021/acs.organomet.6b00130
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