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Pincer-Nickel Catalyzed Selective Guerbet-Type Reactions

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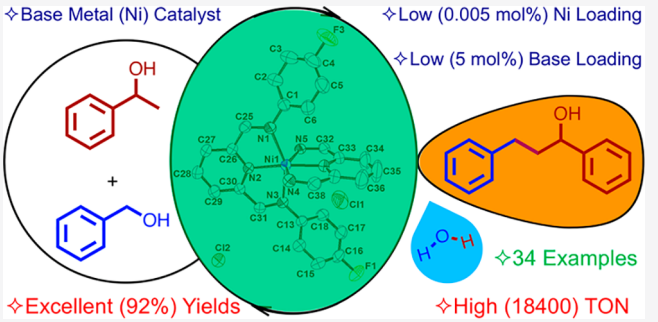
ABSTRACT: We report here the synthesis and characterization of a series of NNN pincer-nickel complexes of the type (^{R2}NNN)-$NiCl_2(CH_3CN)$ (R = ^{i}Pr, ^{t}Bu, Cy, Ph, and *p*-F-C_6H_4) based on *bis*(imino)pyridine ligands. In solution, these complexes are found to be equilibrium mixtures containing one and two pincer ligands, respectively. While the crystal structure of the former was reported by us recently for R = ^{i}Pr, we report the crystal structure of the latter in this study for R = *p*-F-C_6H_4. The considered NNN pincer-Ni complexes have been successfully employed to accomplish the catalytic β-alkylation of several secondary alcohols with a variety of benzyl alcohols at 140 °C with high yields and unprecedented turnovers. A maximum of 92% yield of the β-alkylated product at 18 400 TON was obtained in the reaction of benzyl alcohol with 1-(4-(trifluoromethyl)phenyl)ethane-1-ol in the presence of 0.005 mol % of (^{Ph2}NNN)$NiCl_2(CH_3CN)$ and 5 mol % of NaO^{t}Bu at 140 °C after 24 h. The reaction exhibits zero-order dependence of rate on catalyst concentration and first-order dependence on the concentration of base, benzyl alcohol, and 1-phenyl ethanol which points to the base-mediated aldol condensation as the rate-determining step. Most of the intermediates involved in catalysis have been identified by HRMS. To the best of our knowledge, this is the first report on a pincer-Ni catalyzed β-alkylation of alcohols and, hitherto, such unprecedented turnovers have not been reported with a homogeneous molecular nickel-based catalyst.



INTRODUCTION

The formation of C−C bonds plays an important role in synthetic organic chemistry having varied applications in fuel, fine chemicals, medicinal, agrochemicals, pharmaceuticals, and many others.[1] A plethora of reactions that lead to C−C bonds majorly involve transition-metal catalyzed C-H or C-X (X = Cl, Br, I) activation operating via radical[2] or purely organometallic pathways.[3] The direct coupling of primary and secondary alcohols to yield β-alkylated alcohols has been extensively studied in the past decade via the hydrogen borrowing pathway[4] which has been pegged as one of the most important green chemistry research areas recently.[5] It is a useful and an environmentally friendly process, in which alcohols are used as an alkyl precursor and water is the sole byproduct.

In the absence of any metal-based catalysts, the β-alkylation of alcohols[6] requires a stoichiometric amount of base that results in an equivalent amount of waste formation. The β-alkylation of alcohols has been widely reported with catalysts based on precious metals such as Ru,[7] Rh,[8] Ir,[7a,m,n,9] and Pd.[10] Recently, first-row transition-metal catalysts have also been employed for these Guerbet-type reaction.[11] Considering the fact that one of the early and finest examples of the Guerbet reaction came from the use of Raney nickel in the presence of a strong base;[12] it is interesting to note that the corresponding reports with homogeneous Ni catalysts are very sparse and mainly devoted to α-alkylation of alcohols and ketones apart from related C−C bond forming reactions.[13] The C-C cross-coupling of alcohols was recently reported by Lang and co-workers (Figure 1) in which they utilized a Ni(II) 4,6-dimethylpyrimidine-2-thiolate cluster catalyst toward the synthesis of α,β-unsaturated ketones, α-alkylated ketones, and β-alkylated alcohols by simple tuning of the reaction conditions.[14] Very recently, Balaraman reported excellent yields (up to 90%) in the β-alkylation of various alcohols using $NiBr_2$ (5 mol %)/TMEDA (5 mol %) in the presence of an equivalent of KOH using *n*-octane as solvent at 130 °C (Figure 1).[15] To the best of our knowledge, there are no other homogeneous Ni systems (none with pincer-Ni,[13r,16] in particular) that have been reported for this reaction (Figure 1).

Encouraged by our recent success in obtaining unprecedented turnovers in the *N*-alkylation of alcohols using the NNN pincer-nickel catalyst (^{iPr2}NNN)$NiCl_2(CH_3CN)$ (**2a**) under solvent-free conditions,[17] we wished to probe the activity of these pincer-nickel systems toward the synthetically valuable β-alkylation of alcohols. In this study, we report the synthesis of a series of pincer-nickel complexes of the type (^{R2}NNN)$NiCl_2(CH_3CN)$ (**2a**, R = ^{i}Pr; **2b**, R = ^{t}Bu; **2c**, R =

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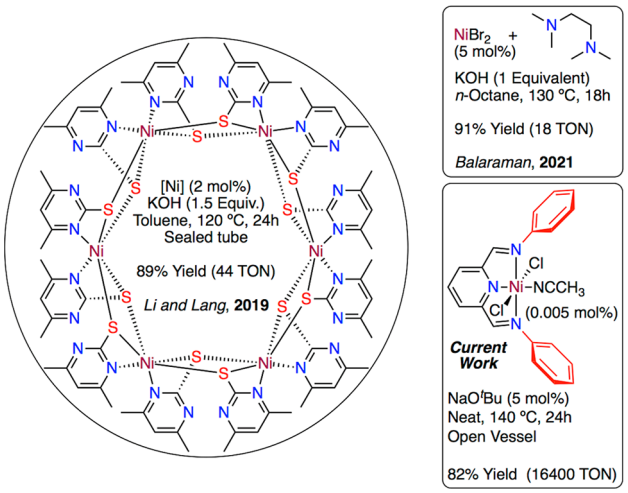


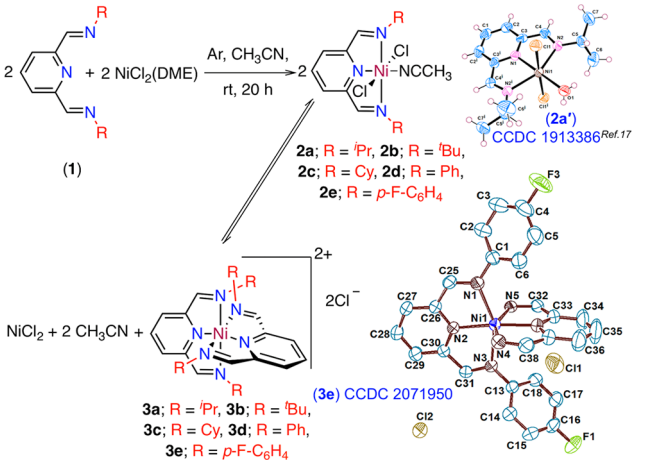
Figure 1. Homogeneous Ni catalysts reported for β-alkylation of 1-phenyl ethanol with benzyl alcohol.

Cy; **2d**, R = Ph; and **2e**, R = *p*-F-C_6H_4) and their utility in catalyzing the β-alkylation of alcohols (Figure 2). It is gratifying to note that among **2a**−**2e**, the catalyst **2d** (0.005 mol %) is highly active toward the Guerbet-type reaction of various benzyl alcohols with several 1-phenyl ethanols at 140 °C under neat conditions in the presence of only 5 mol % NaO^{t}Bu. In particular, 18 400 TON (ca. 92% yield) was obtained in the β-alkylation of benzyl alcohol with 1-(4-(trifluoromethyl)phenyl)ethane-1-ol at 140 °C after 24 h.

RESULTS AND DISCUSSION

Synthesis and Characterization of Pincer-Nickel Complexes Based on *Bis*(imino)pyridine Ligands. The NNN pincer ligands[18] and their corresponding Ni complexes[17] were synthesized according to our recently reported protocol. Treatment of anhydrous $NiCl_2$(DME) (DME = dimethoxyethane) with (^{R2}NNN) ligand in acetonitrile at room temperature for 20 h, followed by washing with diethyl ether, afforded the corresponding Ni(II) pincer complexes (**2a**−**e**) in good yields (Scheme 1). While NMR analysis was not possible for these paramagnetic complexes, the magnetic susceptibility measurements of these complexes provided evidence for their octahedral structure and paramagnetic nature (**2a**, μ_{eff} = 3.21 μ_B; **2b**, μ_{eff} = 3.20 μ_B; **2c**, μ_{eff} = 3.28 μ_B; **2d**, μ_{eff} = 3.01 μ_B; **2e**, μ_{eff} = 4.24 μ_B).[19] The EPR signals of the octahedral complexes **2a**−**e** were broad and hard to detect

Scheme 1. A General Pathway to the Synthesis of (^{R2}NNN)$NiCl_2(CH_3CN)$ (2a−e)[a]



[a]The molecular structure of **3e** is provided as an ORTEP drawn at 50% probability. All the hydrogen atoms and the aromatic groups on two N atoms of one of the pincer fragment are omitted for the sake of clarity. The molecular structure of previously reported **2a′**, an aqua-derivative of **2a**, is also provided.

(even at very low temperatures, Figures S95−S98) which is typical of an octahedral d^8 Ni(II) species.[20]

The single-crystal X-ray analysis of **2a′** (obtained by the substitution of acetonitrile in **2a** by a water molecule) reported by us earlier[17] showed Ni is in an octahedral environment having the pincer ligand bound in a meridional fashion with the two chlorides *trans* to each other. Surprisingly, crystallization of **2e** via slow evaporation from methanol led to the isolation of a dicationic complex **3e** (presumably formed due to its equilibration with **2e** in the mother liquor (Scheme 1)) where the Ni is in an octahedral environment with two pincer ligands attached to it in a meridional geometry (Scheme 1, Tables S1 and S2). While the complex (^{iPr2}NNN)$NiCl_2(H_2O)$ (**2a′**) crystallized in the *C*2/*c* space group, the dicationic complex **3e** crystallized in the triclinic $P\bar{1}$ space group. The Ni−N(pyridyl) bond distance was slightly longer in the case of neutral complex **2a′** (**2a′**, 2.008(6) Å; **3e**, 1.983(3) Å). On the other hand, the Ni−N(imine) bond length was similar in both the complexes (**2a′**, 2.171(5) Å; **3e**, 2.172(3) Å). The (pyridyl)N−Ni−N(imine) bond angles in both the complexes were comparable (**2a′**: 77.60(5)°; **3e**:

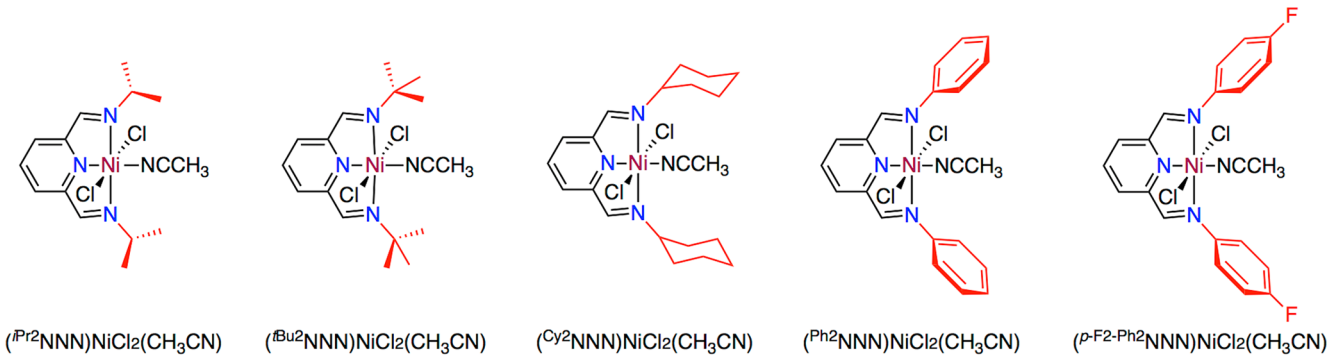


Figure 2. Pincer-nickel complexes investigated in the current study for the β-alkylation of 1-phenyl ethanol with benzyl alcohol.

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Organometallics XXXX, XXX, XXX−XXX

77.73(12)°). A detailed comparison of the crystallographic parameters of **2a′** and **3e** is provided in Tables S1 and S2.

Interesting observations were made from the HRMS analysis that provided evidence for the presence of fragments originating from both **2** and **3** (Figures 3 and S57–S79).

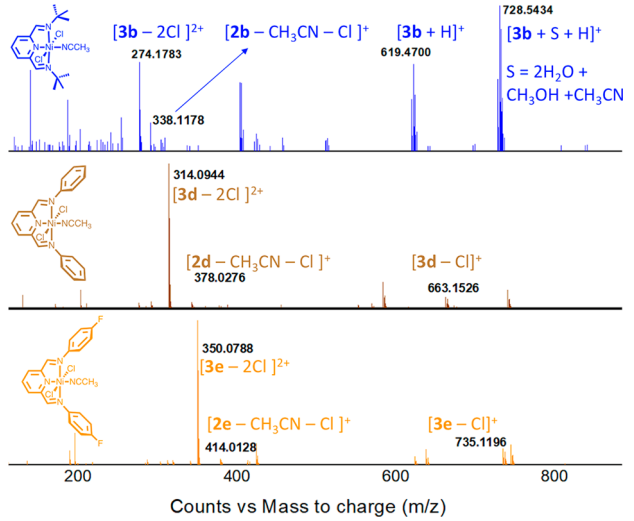


Figure 3. HRMS analysis of pincer-Ni complexes **2**/**3**. Also see Figures S57–S79.

For instance, the HRMS analysis of **2b** showed peaks at m/z values 274.1783 and 338.1178 that correspond to $[\mathbf{3b} - 2\mathrm{Cl}]^{2+}$ and $[\mathbf{2b} - \mathrm{CH_3CN} - \mathrm{Cl}]^{+}$, respectively. Similar observations were made in the HRMS analysis of the other considered complexes (Figures 3 and S57–S79). Single-crystal X-ray analysis and HRMS studies thus clearly indicate that, in solution, the complex **2** exists in equilibrium with **3** (Scheme 1), the extent of which is likely to be different for various complexes based on the nature of the R group (R = ^{i}Pr, ^{t}Bu, Cy, Ph, and p-F-C_6H_4). The pincer-Ni complexes (**2a**–**e**)/(**3a**–**e**) demonstrated very good thermal stability as indicated by the TGA analysis (Figure 4). The mass loss[21] could be correlated to loss of fragments either from **2** or from **3** (Figure 4 and Figure S56). The TGA profile of **2a** has been previously discussed.[17]

Investigations on the Pincer-Nickel Catalyzed β-Alkylation of 1-Phenyl Ethanol with Benzyl Alcohol.

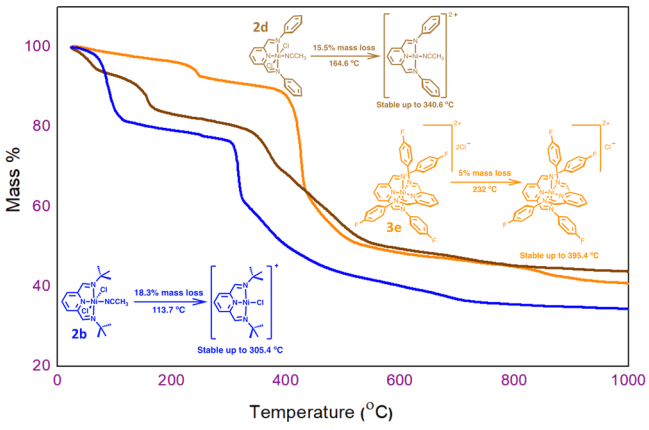
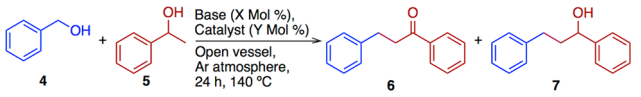


Figure 4. TGA analysis of pincer-Ni complexes **2**/**3**. Also see Figure S56.

To arrive at the optimal conditions, the catalytic β-alkylation reactions were initiated in the presence of **2a**–**e** along with a variety of bases using 1-phenyl ethanol and benzyl alcohol as a model secondary and primary alcohol, respectively, at 140 °C (Table 1 and Table S3). At a loading of 0.01 mol % of **2d**, the

Table 1. Solvent-Free β-Alkylation of 1-Phenyl Ethanol with Benzyl Alcohol under Varying Conditions[a]



Entry	Base (X mol%)	Ni (Y mol%)	% Yield[b] [TON] 6	7
1	Na_2CO_3 (5)	**2d** (0.01)	0 [0]	0 [0]
2	K_2CO_3 (5)	**2d** (0.01)	1 [100]	0 [0]
3	KO^{t}Bu (5)	**2d** (0.01)	2 [200]	23 [2300]
4	KOH (5)	**2d** (0.01)	3 [300]	31 [3100]
5	NaOH (5)	**2d** (0.01)	2 [200]	68 [6800]
6	NaOH (2.5)	**2d** (0.01)	2 [200]	37 [3700]
7	NaOH (1.25)	**2d** (0.01)	2 [200]	15 [1500]
8	Na (5)	**2d** (0.01)	9 [900]	62 [6200]
9	NaO^{t}Bu (5)	**2d** (0.01)	14 [1400]	75 [7500]
10	NaO^{t}Bu (2.5)	**2d** (0.01)	3 [300]	47 [4700]
11	NaO^{t}Bu (1.25)	**2d** (0.01)	7 [700]	18 [1800]
12[c]	NaO^{t}Bu (5)	**2d** (0.005)	10±1 [2000]	82±1 [16400]
13[d]	NaO^{t}Bu (5)	**2d** (0.005)	2 [400]	51 [10200]
14	—	**2d** (0.005)	0 [0]	0 [0]
15	NaOH (5)	**2d** (0.005)	23 [4600]	71 [14200]
16[c]	NaO^{t}Bu (5)	**2a** (0.005)	12±3 [2400]	78±1 [15600]
17[c]	NaO^{t}Bu (5)	**2b** (0.005)	9±1 [1800]	80±2 [16000]
18[c]	NaO^{t}Bu (5)	**2c** (0.005)	11±0 [2200]	76±3 [15200]
19[c]	NaO^{t}Bu (5)	**2e** (0.005)	13±1 [2600]	77±2 [15400]
20	NaO^{t}Bu (5)	$NiCl_2$ (0.005)	2 [400]	50 [10000]
21	NaO^{t}Bu (5)	$NiCl_2$.DME (0.005)	3 [600]	77 [15400]
22[c]	NaO^{t}Bu (5)	**3e** (0.005)	16±1 [3200]	72±2 [14400]
23	K_3PO_4 (5)	**2d** (0.005)	1 [200]	3 [600]

[a]Reaction conditions: 4.14 mmol of **4**, 4.14 mmol of **5**, X mol % of base, and Y mol % of Ni catalyst at 140 °C. For selectivity of **7**, please see Table S3. [b]Yield determined from ^{1}H NMR using toluene as external standard. [c]Yield reported as an average of two runs. [d]Reaction was performed at 120 °C.

reaction of **4** with **5** did not proceed when 5 mol % of either Na_2CO_3 or K_2CO_3 was used (entries 1 and 2, Table 1). Poor yields of β-alkylated product **7** was observed when the **2d** (0.01 mol %) catalyzed reaction was performed independently with KO^{t}Bu (5 mol %) and KOH (5 mol %) (entries 3 and 4, Table 1). On the other hand, use of 5 mol % of NaOH provided moderate yields (68%) of **7** in the **2d** (0.01 mol %) catalyzed reaction (entry 5, Table 1). The yields of **7** dropped steadily upon lowering the NaOH loading (entries 6 and 7, Table 1). Employing Na (5 mol %) to generate the base *in situ*[22] (prior to addition of **2d**) resulted in yields that are comparable to that obtained with the use of NaOH (5 mol %) (entry 5 vs entry 8, Table 1). The yield of **7** improved (75%) with the use of NaO^{t}Bu (5 mol %) in the **2d** (0.01 mol %) catalyzed β-alkylation of **5** with **4** (entry 9, Table 1).

Similar to the observations made during the use of NaOH, lowering the amounts of NaO^{t}Bu led to reduced yields (entries 10 and 11, Table 1). Lowering the loading of **2d** to 0.005 mol

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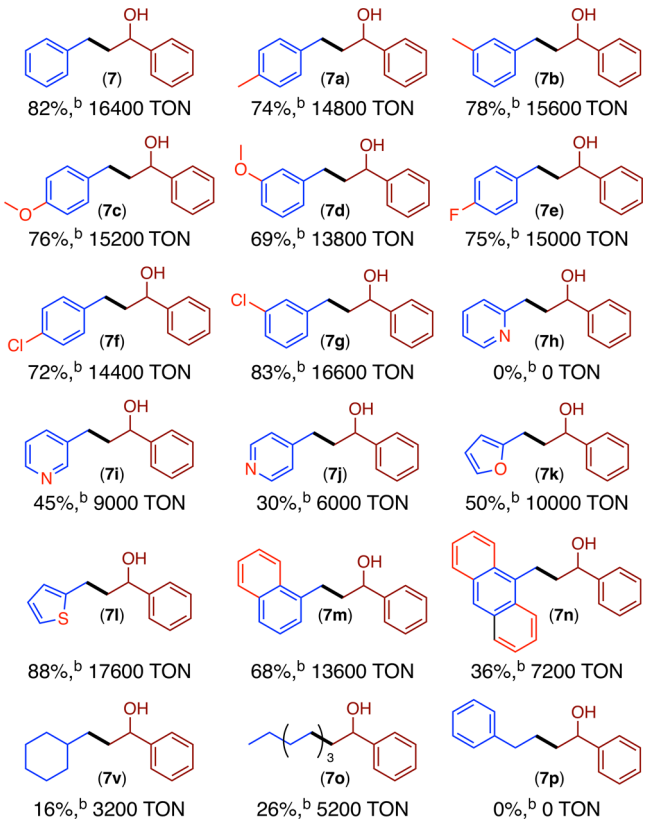
Organometallics XXXX, XXX, XXX–XXX

% while maintaining NaO^{t}Bu at 5 mol % resulted in about 82% of **7** and 11% of **6** that amounts to a total of 18 600 TON (**6** + **7**) (entry 12, Table 1). Repeating the same reaction at a lower temperature (120 °C) or with a different base (5 mol % NaOH) resulted in a decrease in productivity of **7** (entries 13 and 15, Table 1). The β-alkylation of **5** with **4** did not proceed either in the absence of a base (entry 14, Table 1) or in the absence of a catalyst.[7d] Under the optimized conditions comprising 0.005 mol % of Ni catalyst in the presence of NaO^{t}Bu (5 mol %) at 140 °C, the total turnovers (**6** + **7**) obtained were clearly lower with the other considered catalysts (entries 16−21, Table 1) in comparison with **2d** (entry 12, Table 1).

The practical utility of this reaction was confirmed by carrying out the **2d** (0.005 mol %) catalyzed β-alkylation of 1 g of **5** with 0.895 g of **4** in the presence of 5 mol % of NaO^{t}Bu at 140 °C to obtain 1.301 g of **7** in 74% isolated yield and 85% selectivity. The synthetic utility of the optimized catalytic system (entry 12, Table 1) was further investigated for the catalytic β-alkylation of several 1-phenyl ethanol derivatives with a variety of benzyl alcohols (Table 2, Table S4, Table 3, and Table S5).

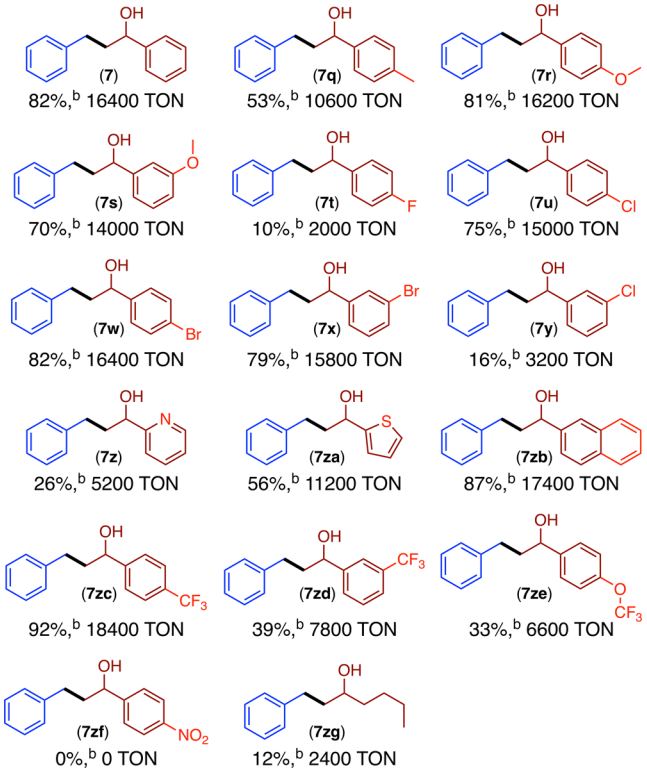
In most cases, good tolerance was observed for the electron-withdrawing (−Cl, −F) and electron-donating (−Me, −OMe) groups at the *para* and *meta* positions of the phenyl ring in primary alcohols, affording good yields of the desired products (**7a**−**7g**, Table 2) with high selectivity (up to 98%, Table S4).

Table 2. 2d Catalyzed Solvent-Free β-Alkylation of 1-Phenyl Ethanol with a Variety of Benzyl Alcohols[a]



[a]Reaction conditions: 4.14 mmol of **4**, 4.14 mmol of **5**, 5 mol % of NaO^{t}Bu, and 0.005 mol % of **2d** at 140 °C (Table S4). [b]Yield determined from ^{1}H NMR using toluene as external standard.

Table 3. 2d Catalyzed Solvent-Free β-Alkylation of 1-Phenyl Ethanol Derivatives with Benzyl Alcohol[a]



[a]Reaction conditions: 4.14 mmol of **4**, 4.14 mmol of **5**, 5 mol % of NaO^{t}Bu, and 0.005 mol % of **2d** at 140 °C (Table S5). [b]Yield determined from ^{1}H NMR using toluene as external standard.

A decrease in product yield (**7h**−**7l**, Table 2) barring **7l** was observed when heteroaromatic primary alcohols were used as alkylating agents presumably due to inhibition of Ni by the heteroatoms. The inhibition affect appears to be more pronounced in the case of **7h** that is capable of forming a chelate with the Ni center. The formation of **7l** in good yields points to the poor inhibition of the Ni(II) by the relatively soft S. Aromatic primary alcohols consisting of naphthyl and anthracyl groups could be used as alkylating agents with moderate yields (**7m**,**n**, Table 2). Lower yields were observed upon use of primary aliphatic alcohols (**7v**, **7o**, and **7p**, Table 2).

A general trend of good yields was observed across various 1-phenylethanol substrates using benzyl alcohol as alkylating agent in the **2d** (0.005 mol %) catalyzed β-alkylation at 140 °C (Table 3 and Table S5). However, in particular, the presence of electron-withdrawing groups in the *meta* position (−Cl and CF_3 in **7y** and **7zd**, respectively, Table 3) and in the *para* position (−F, $-OCF_3$, and NO_2 in **7t**, **7ze**, and **7zf**, respectively, Table 3) leads to lower yields of products. A lower yield was also obtained for the β-alkylation of an aliphatic secondary alcohol (**7zg**, Table 3).

Mechanistic studies (*vide infra*) have indicated that the aldol condensation of benzaldehyde **4′** with acetophenone **5′** is the rate-determining step (RDS). Apparently, electron-withdrawing groups on **5** are likely to have a detrimental effect on the overall yield of the reaction. Accordingly, very poor yields of **7t** were obtained as a result of the highly electronegative fluoro group in the *para* position that withdraws electrons by an inductive effect. The compound **7u** that had a less electro-

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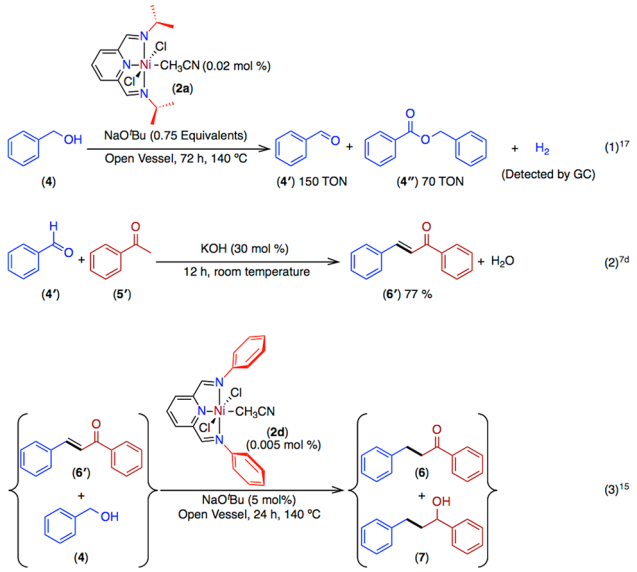
Organometallics XXXX, XXX, XXX−XXX

negative chloro group was obtained in better yields. The higher yields of **7u** in comparison with **7y** can be traced to the fact that the inductive effect of the chloro group is more pronounced at the *meta* position as compared to the *para* position considering the fact that the inductive effect of a substituent is directly proportional to the distance.[23] However, upon replacement of chloro with a poorer electron-withdrawing and less electronegative bromo substituent, the inductive effect is hardly noticeable. Not surprisingly, the yields of the corresponding *para*- and *meta*-substituted bromo derivatives **7w** and **7x** are comparable. The $-CF_3$ group demonstrates an electron-withdrawing nature only by an inductive effect which is more significant in the *meta* position in comparison to the *para* position. Rightly, the yield of **7zd** was poorer than that of **7zc**. However, in the case of **7zf**, the nitro group exhibits a very strong electron-withdrawing character due to the involvement of both inductive and resonance activities that result in a complete mitigation of reactivity.

Control Experiments and Mechanistic Insights. We have recently demonstrated the hydrogen evolution in the **2a** catalyzed dehydrogenation of **4** with an associated formation of benzaldehyde **4′** (eq 1, Scheme 2).[17] Similarly, one could

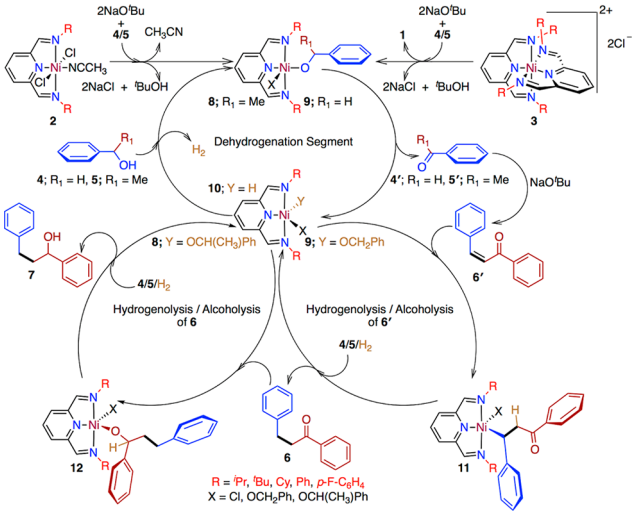
Scheme 2. Control Experiments



anticipate formation of **5′** and hydrogen in the **2** catalyzed dehydrogenation of **5**. The reaction of **4′** and **5′** in the presence of catalytic amounts of base yields the *α,β*-unsaturated ketone **6′** (eq 2, Scheme 2).[7d] Furthermore, **6′** has been detected in the reaction mixture by HRMS experiments (Figures S89, S92, and S93). Transfer hydrogenation of **6′** with **4** results in the formation of a mixture of **6** (9% isolated yield with respect to **6′**) and **7** (40% isolated yield with respect to **6′**) (eq 3, Scheme 2). The above observations in addition to the fact that both **6** and **7** are isolated in minor and major amounts, respectively (Table 1), form the basis of the proposed mechanism (Scheme 3) for the **2** catalyzed *β*-alkylation of **5** with **4** under open-vessel conditions.

Treatment of the NNN pincer-Ni complex with NaO^{t}Bu in the presence of **4**/**5** results in the formation of **9**/**8** by the dissociation of either CH_3CN from **2** or the ligand **1** from **3** along with the formation of NaCl (Scheme 3).[17] The *β*-

Scheme 3. Plausible Mechanism Involved in the 2/3 Catalyzed *β*-Alkylation of 5 with 4



hydride elimination from **9**/**8**, followed by extrusion of **4′**/**5′**, results in the formation of a pincer Ni-H species **10** similar to that reported by us recently (Scheme 3).[17] The active species **9**/**8** is regenerated by the alcoholysis of **10** with **4**/**5** along with the liberation of H_2. In the presence of NaO^{t}Bu, the aldol reaction of **4′** with **5′** results in the formation of *α,β*-unsaturated ketone **6′**.

Insertion[7d] of the C−C double bond in **6′** into the Ni−H bond of **10** results in the formation of intermediate **11** (Scheme 3). The carbonyl compound **6** is obtained from **11** either by the hydrogenolysis with H_2 or by the alcoholysis with **4**/**5** while regenerating **10**/**9**/**8**. A similar insertion, followed by a hydrogenolysis/alcoholysis pathway involving **10**→**12**→**10**/**9**/**8**, can account for the transformation of **6** to **7** (Scheme 3). We have previously shown that both hydrogenolysis and alcoholysis contribute to the **2a** catalyzed *N*-alkylation reactions under open-vessel conditions.[17] The fact that we observed **7** as a major product in our current studies that are performed in an open-vessel further fortifies the involvement of alcoholysis.

Valuable information on the intermediates proposed in Scheme 3 was obtained from the HRMS(ESI) analysis performed by periodic sampling of the reaction between **4** and **5** in the presence of 0.5 mol % of **2d** and 5 mol % of NaO^{t}Bu. The HRMS analysis of the reaction mixture at t = 0 (Figure 5) contained several adducts of **4**/**5** with pincer-Ni species such as $[\mathbf{8a} + CH_3CN + K + H]^{2+}$, $[\mathbf{8b} + CH_3CN + H_2O + H]^+$, $[\mathbf{8b} + CH_3OH + CH_3OK]^+$, and $[\mathbf{8b} + CH_3CN + CH_3OK + H]^+$ corresponding to peaks at m/z 326.1919, 645.4985, 687.3524, and 697.3808, respectively. The HRMS profile at t = 2 h (Figure 5) provided key evidence to the intermediates proposed in Scheme 3 and demonstrated peaks at m/z 681.3039, 764.5815, 771.3520, and 859.3856 that correspond to $[\mathbf{12b} + CH_3CN + 3H_2O + H]^+$, $[\mathbf{12a} + CH_3OH + H_2O + K]^+$, $[\mathbf{12a} + 3CH_3OH]^+$, and $[\mathbf{12a} + \mathbf{5'} + 2CH_3OH]^+$, respectively. The profile of HRMS analysis at t = 4, 8, 16, and 24 h (Figures S80−S94) were similar to that observed at t = 2 h, and some of them contained an additional peak at m/z = 209.0986 corresponding to $[\mathbf{6'} + H]^+$ (Figures S89, S92, and S93).

Kinetic studies were carried out for the **2d** catalyzed reaction of **4** with **5** in the presence of 5 mol % of NaO^{t}Bu at 140 °C

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Organometallics XXXX, XXX, XXX−XXX

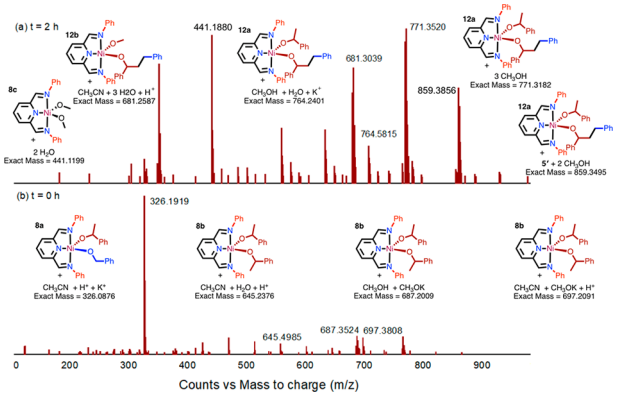

Figure 5. HRMS analysis of the reaction mixture containing **4** and **5** in the presence of 0.5 mol % **2d** and 5 mol % Na^{t}BuO at t = 0 h at room temperature and at t = 2 h at 140 °C. Also see Figures S80–S94.

(Figures S99–S108). Notably, upon use of 0.005 mol % of **2d**, a very high initial rate of 3200 TOh^{-1} was observed (Figure S99). Using the initial rate method, we observed that the plot of initial rate vs [**2d**] was a straight line that ran parallel to the X-axis, implying a zero-order dependence of rate on catalyst concentration (Figure 6). On the other hand, the corresponding plots of initial rate vs concentrations of base, **4**, and **5** were all linear and nearly passing through the origin. This indicates that the rate has a first-order dependence on the concentrations of base and primary and secondary alcohols.

This can be explained only if one invokes the possibility of a fast dehydrogenation (**4**/**5**→**4′**/**5′** + H_2) and hydrogenolysis (**6′** and **6** with H_2)/alcoholysis (**6′** and **6** with **4**/**5**) steps. Apparently, the base mediated coupling of benzaldehyde **4′** and acetophenone **5′** that gives α,β-unsaturated ketone **6′** is the rate-determining step. Not surprisingly, **6′** (Figures S89, S92, and S93) and its Ni-adducts **11a** and **11b** (Figures S89–S94) are detected in HRMS analysis.

CONCLUSIONS

We have accomplished the synthesis of a series of NNN pincer-nickel complexes of the type (^{R2}NNN)NiCl$_2$(CH$_3$CN) (R = ^{i}Pr, ^{t}Bu, Cy, Ph, and p-F-C$_6$H$_4$) based on *bis*(imino)-pyridine ligands. Single-crystal, HRMS, and TGA analyses reveal that these complexes exist as equilibrium mixtures of neutral and dicationic pincer-nickel complexes containing one and two pincer ligands, respectively. Among the five pincer-Ni

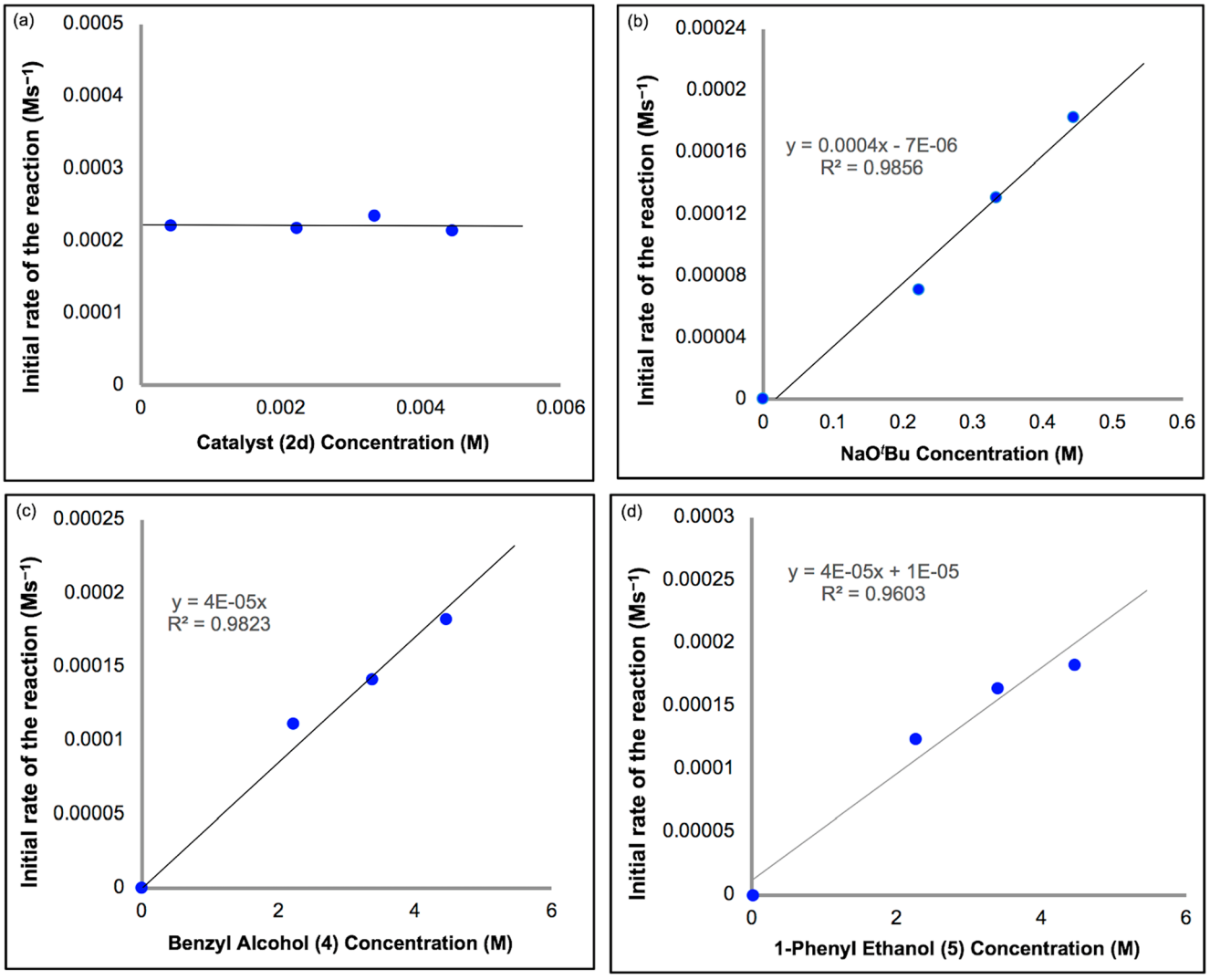

Figure 6. Variation of initial rate of Guerbet reaction with concentration of (a) **2d**, (b) NaO^{t}Bu, (c) benzyl alcohol, and (d) 1-phenyl ethanol.

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Organometallics XXXX, XXX, XXX−XXX

complexes that have been screened for the catalytic β-alkylation in the presence of 5 mol % of NaO^{t}Bu at 140 °C, (^{Ph2}NNN)NiCl$_2$(CH$_3$CN) (0.005 mol %) was the most efficient catalyst, giving up to 92% yield (ca. 18 400 TON) for a combination of benzyl alcohol and 1-(4-(trifluoromethyl)phenyl)ethane-1-ol. Kinetic studies on the (^{Ph2}NNN)NiCl$_2$(CH$_3$CN) catalyzed β-alkylation of 1-phenyl ethanol with benzyl alcohol revealed a first-order dependence of rate on the concentration of base, first-order dependence on both the alcohols, and zero-order dependence on catalyst concentration. This is indicative of a base-mediated aldol condensation as the rate-determining step. HRMS analysis proved to be a useful tool in the identification of several intermediates that are involved in the catalytic cycle. For the first time, we have reported the application of a pincer-Ni catalyst for the Guerbet-type reactions which gives the highest TON reported hitherto among homogeneous Ni-based β-alkylation systems.

EXPERIMENTAL SECTION

General Procedure and Materials. All manipulations were carried out under an Ar atmosphere in a glovebox or by using a standard double manifold. The nickel precursor, NiCl$_2$(DME), was purchased from Sigma-Aldrich. Benzyl alcohol, acetonitrile, and hexane were purchased from MERCK and were dried according to a literature procedure prior to experiment.[24] Other chemicals were purchased from MERCK or Sigma-Aldrich and used as such. All catalytic reactions were carried out under an argon atmosphere using dried glassware. The ligands (**1a**−**e**)[18] and complex **2a**[17] were prepared according to literature procedures.

Physical Measurements. ^{1}H, ^{13}C{H}, and ^{19}F NMR were recorded on a Bruker ASCEND 600 operating at 600 MHz for ^{1}H, 150 MHz for ^{13}C{H}, and 565 MHz for ^{19}F or on a Bruker AVANCE 400 operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C{H}, 377 MHz for ^{19}F or on a Bruker AVANCE 500 operating at 500 MHz for ^{1}H, 125 MHz for ^{13}C{H}, 471 MHz for ^{19}F. Spin−spin coupling constants (J) are expressed in Hz; chemical shifts (δ) are reported in ppm. Other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, and br s = broad singlet. HRMS measurements were done using an Agilent Accurate-Mass Q-TOF ESI−MS 6520. X-ray crystallographic data were acquired on a Bruker D8 Venture single-crystal X-ray diffractometer using graphite-monochromated Mo Kα radiation. The data refinement and cell reductions were carried out by the Bruker SAINT program.[25] Structures were further solved and refined by the full matrix least-squares method using SHELXS-14.[26] A JES-FA200 ESR spectrometer was use to record the X-band EPR spectra. Thermogravimetric analyses were performed using a thermal analyzer (SDTQ600) with a simultaneous DTA/TGA system, under nitrogen with a heating rate of 10 °C min^{-1}. Solid-state magnetic susceptibilities of the complexes at room temperature were recorded using a Sherwood Scientific magnetic balance MSB-1.

Synthesis of (1*E*,1′*E*)-1,1′-(Pyridine-2,6-diyl)*bis*(*N*-(4-fluorophenyl)methanimine) (1e). The ligand **1e** was prepared according to the procedure reported in literature.[18] The reaction of pyridine-2,6-dicarbaldehyde (0.1 g, 0.529 mmol) with 4-fluoroaniline (0.117 g, 1.06 mmol) in anhydrous dichloromethane containing molecular sieves (4 Å) for 12 h at 40 °C, followed by filtration and removal of solvent, afforded the ligand **1e** as light-yellow powder (0.102 g) in 60% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.66 (s, 2H), 8.27 (d, J = 7.8 Hz, 2H), 7.94 (t, J = 7.8 Hz, 1H), 7.35−7.29 (m, 4H), 7.12 (t, J = 8.6 Hz, 4H). ^{13}C{H} NMR (101 MHz, CDCl$_3$): δ 163.25, 160.81, 159.85, 154.71, 146.90, 137.52, 123.40, 122.98, 122.90, 116.34, 116.12. ^{19}F NMR (377 MHz, CDCl$_3$): δ −115.59. HRMS (ESI): m/z calculated for [**1e** + 4H$_2$O]$^+$: 393.1500, found 393.1826.

Synthesis of Complex (^{tBu2}NNN)NiCl$_2$(CH$_3$CN) (2b). The ligand **1b** (0.037 g, 0.154 mmol) was stirred with NiCl$_2$(DME) (0.034 g, 0.15 mmol) in anhydrous acetonitrile (2 mL) for 20 h at room temperature. The solvent was evaporated under reduced pressure, and the mustard solid was washed with diethyl ether (3 × 3 mL). The solid was dried under vacuum and isolated as a light mustard solid (0.039 g) in 61% yield. HRMS (ESI): m/z calculated for [**3b** − 2Cl]$^{2+}$: 274.1569, found 274.1783; m/z calculated for [**2b** − Cl − CH$_3$CN]$^+$: 338.0934, found 338.1178; m/z calculated for [(**2b** − 2Cl − CH$_3$CN) + HCOO]$^+$: 348.1222, found 348.1521; m/z calculated for [**3b** + H]$^+$: 619.2593, found 619.4700. m/z calculated for [**3b** + H + 2H$_2$O + CH$_3$OH + CH$_3$CN]$^+$: 728.3332, found 728.5434. Magnetic susceptibility μ_{eff} = 3.20 μ_B

Synthesis of Complex (^{Cy2}NNN)NiCl$_2$(CH$_3$CN) (2c). The ligand **1c** (0.077 g, 0.26 mmol) was stirred with NiCl$_2$(DME) (0.057 g, 0.26 mmol) in anhydrous acetonitrile (2 mL) for 20 h at room temperature. The solvent was evaporated under reduced pressure, and the light green solid was washed with diethyl ether (3 × 3 mL). The solid was dried under vacuum and isolated as a light green solid (0.057 g) in 47% yield. HRMS (ESI): m/z calculated for [**3c** − 2Cl]$^{2+}$: 326.1882, found 326.1894; m/z calculated for [**2c** − Cl − CH$_3$CN]$^+$: 390.1247, found 390.1240; m/z calculated for [**3c** − Cl]$^+$: 687.3452, found 687.3447. Magnetic susceptibility μ_{eff} = 3.28 μ_B

Synthesis of Complex (^{Ph2}NNN)NiCl$_2$(CH$_3$CN) (2d). The ligand **1d** (0.057 g, 0.20 mmol) was stirred with NiCl$_2$(DME) (0.044 g, 0.20 mmol) in anhydrous acetonitrile (2 mL) for 20 h at room temperature. The solvent was evaporated under reduced pressure, and the light orange solid was washed with diethyl ether (3 × 3 mL). The solid was dried under vacuum and isolated as a light orange solid (0.041 g) in 89% yield. HRMS (ESI): m/z calculated for [**3d** − 2Cl]$^{2+}$: 314.0943, found 314.0944; m/z calculated for [**2d** − Cl − CH$_3$CN]$^+$: 378.0808, found 378.0276; m/z calculated for [**3d** − Cl]$^+$: 663.1574, found 663.1526. Magnetic susceptibility μ_{eff} = 3.01 μ_B

Synthesis of Complex ($^{(p\text{-}F\text{-}Ph)2}$NNN)$_2$Ni]Cl$_2$ (2e). The ligand **1e** (0.048 g, 0.15 mmol) was stirred with NiCl$_2$(DME) (0.033 g, 0.15 mmol) in anhydrous acetonitrile (2 mL) for 20 h at room temperature. The solvent was evaporated under reduced pressure, and the orange solid was washed with diethyl ether (3 × 3 mL). The solid was dried under vacuum and isolated as an orange solid (0.040 g) in 69% yield. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution containing **2e** (10 mg) in 1 mL of methanol under noninert conditions. HRMS (ESI): m/z calculated for [**3e** − 2Cl]$^{2+}$: 350.0755, found 350.0788; m/z calculated for [**2e** − Cl − CH$_3$CN]$^+$: 414.0120, found 414.0128; m/z calculated for [**3e** − Cl]$^+$: 735.1197, found 735.1196. Magnetic susceptibility μ_{eff} = 4.24 μ_B.

General Procedure for the Pincer-Nickel Catalyzed β-Alkylation of Alcohols. In a 10 mL two-neck round-bottom flask was added NaO^{t}Bu (0.04 g, 0.416 mmol) inside the glovebox. This was followed by addition of 0.005 mol % of **2d** (0.0002 g, 0.44 μmol) (from a stock solution in either benzyl alcohol or 1-phenyl ethanol) under an Ar atmosphere. Subsequently, the reaction mixture as made up with the required amounts of benzyl alcohol (**4**) and 1-phenyl ethanol (**5**). Ultimately, the reaction mixture contained 0.430 mL of **4** (4.14 mmol) and 0.500 mL of **5** (4.14 mmol). The mixture was heated at 140 °C for 24 h and was then cooled down to room temperature. An aliquot (10 mg) was withdrawn from the reaction mixture, and the NMR yield was determined by ^{1}H NMR using CDCl$_3$ as solvent and toluene as external standard (10 μL added in the NMR tube). The rest of the reaction mixture was quenched with water, followed by extraction of the organic fraction with dichloromethane. The organic phase was separated and was dried over anhydrous Na$_2$SO$_4$. The solvent was removed from the organic fraction under reduced pressure. Silica gel column chromatography using 0−5% ethyl acetate in hexane as eluent gave the product **7** in a pure form.

*1,3-Diphenylpropan-1-ol (**7**).* ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.39−7.36 (m, 4H), 7.32−7.29 (m, 3H), 7.22−7.20 (m, 3H), 4.69 (m, J = 6.0 Hz, 1H), 2.79−2.74 (m, 1H), 2.71−2.66 (m, 1H), 2.18−2.12 (m, 1H), 2.07−2.02 (m, 1H). ^{13}C{H} NMR (151 MHz, CDCl$_3$): δ 144.65, 141.88, 128.63, 128.55, 128.50, 127.75, 126.04,

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Organometallics XXXX, XXX, XXX−XXX

125.96, 73.97, 40.55, 32.15. HRMS (ESI): m/z calculated for $[M + Na]^+$: 235.1099, found 235.0846.

*1-Phenyl-3-(p-tolyl)propan-1-ol (**7a**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.38 (m, 4H), 7.34 (ddd, J = 8.6, 3.7, 2.1 Hz, 1H), 7.15 (brs, 4H), 4.72 (ddd, J = 8.1, 5.3, 3.1 Hz, 1H), 2.80−2.64 (m, 2H), 2.39 (s, 3H), 2.22−2.02 (m, 3H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 144.72, 138.76, 135.42, 129.20, 128.63, 128.43, 127.74, 126.06, 74.02, 40.68, 31.72, 21.12.

*1-Phenyl-3-(m-tolyl)propan-1-ol (**7b**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 4.3 Hz, 4H), 7.21−7.16 (m, 1H), 7.11−7.06 (m, 1H), 6.93−6.89 (m, 4H), 4.58 (ddd, J = 7.9, 5.3, 2.3 Hz, 1H), 2.67−2.48 (m, 2H), 2.23 (s, 3H), 2.08−1.92 (m, 2H), 1.91 (brs, J = 3.0 Hz, 1H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 144.71, 141.82, 137.98, 129.34, 128.56, 128.37, 127.66, 126.67, 126.03, 125.53, 73.99, 40.57, 32.06, 21.46.

*3-(4-Methoxyphenyl)-1-phenylpropan-1-ol (**7c**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.35 (m, 5H), 7.20−7.18 (m, 2H), 6.93−6.91 (m, 2H), 4.70 (t, J = 4.0 Hz, 1H), 3.83 (s, 3H), 2.80−2.65 (m, 2H), 2.19−2.04 (m, 2H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 157.87, 144.73, 133.91, 129.44, 128.62, 127.72, 126.05, 113.91, 73.94, 55.37, 40.80, 31.24. HRMS (ESI): m/z calculated for $[M + Na]^+$: 265.1204, found 265.1055.

*3-(3-Methoxyphenyl)-1-phenylpropan-1-ol (**7d**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 4.3 Hz, 4H), 7.32−7.25 (m, 1H), 7.20 (td, J = 7.4, 1.7 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.74 (d, J = 7.0 Hz, 2H), 4.70 (ddd, J = 8.1, 5.3, 2.8 Hz, 1H), 3.79 (s, 3H), 2.79−2.61 (m, 2H), 2.20−1.98 (m, 2H), 1.93 (brs, J = 3.2 Hz, 1H). ^{13}C{H} NMR (101 MHz, $CDCl_3$): δ 159.83, 144.70, 143.57, 129.47, 128.65, 127.77, 126.05, 120.99, 114.35, 111.35, 74.00, 55.27, 40.47, 32.24. HRMS (ESI): m/z calculated for $[M + H]^+$: 265.1204, found 265.1198.

*3-(4-Fluorophenyl)-1-phenylpropan-1-ol (**7e**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−7.34 (m, 4H), 7.30−7.28 (m, 1H), 7.15−7.13 (m, 2H), 6.96 (t, J = 6 Hz, 2H), 4.67 (brs, 1H), 2.75−2.70 (m, 1H), 2.67−2.60 (m, 1H), 2.14−2.08 (m, 1H), 2.02−1.97 (m, 1H), 1.87 (brs, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 162.21, 144.61, 137.48, 129.91, 129.86, 128.71, 127.88, 126.03, 115.31, 115.17, 73.92, 40.72, 31.37. ^{19}F NMR (377 MHz, $CDCl_3$): δ −117.65.

*3-(4-Chlorophenyl)-1-phenylpropan-1-ol (**7f**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29−7.25 (m, 4H), 7.23−7.20 (m, 1H), 7.18−7.16 (m, 2H), 7.04 (d, J = 6.0 Hz, 2H), 4.58 (t, J = 6.0 Hz, 1H), 2.66−2.61 (m, 1H), 2.59−2.54(m, 1H), 2.05−1.99 (m, 1H), 1.94−1.88 (m, 1H), 1.85−1.82 (m, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 144.52, 140.34, 131.68, 129.92, 128.71, 128.59, 127.89, 126.01, 73.84, 40.44, 31.51. HRMS (ESI): m/z calculated for $[M + Na]^+$: 285.0448, found 285.1295.

*3-(3-Chlorophenyl)-1-phenylpropan-1-ol (**7g**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.17 (m, 5H), 7.14−7.07 (m, 3H), 6.99 (d, J = 4.0 Hz, 1H), 4.61−4.57 (m, 1H), 2.69−2.53 (m, 2H), 2.08−1.83 (m, 3H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 144.49, 143.99, 134.25, 129.76, 128.73, 127.92, 126.79, 126.20, 126.01, 73.85, 40.32, 31.86.

*1-Phenyl-3-(pyridin-3-yl)propan-1-ol (**7i**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.43−8.37 (m, 2H), 7.51−7.50 (m, 1H), 7.35−7.34 (m, 4H), 7.29−7.28 (m, 1H), 7.20−7.18 (m, 1H), 4.68−4.66 (m, 1H), 2.77−2.65 (m, 2H), 2.15−2.08 (m, 1H), 2.02−1.98 (m, 1H), 1.71 (s, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 149.91, 147.30, 144.60, 137.34, 136.14, 128.70, 127.84, 125.99, 123.50, 73.50, 40.21, 29.29.

*1-Phenyl-3-(pyridin-4-yl)propan-1-ol (**7j**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32−8.30 (m, 2H), 7.27−7.26 (m 4H), 7.21−7.19 (m, 1H), 7.02−7.01 (m, 2H), 4.61−4.58 (m, 1H), 2.70−2.64 (m 1H), 2.62−2.56 (m 1H), 2.07−2.00 (m, 1H), 1.97−1.90 (m, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 151.16, 149.70, 144.43, 128.75, 127.95, 125.97, 124.08, 73.65, 39.38, 31.50. HRMS (ESI): m/z calculated for $[M + H]^+$: 214.1232, found 214.1273.

*3-(Furan-2-yl)-1-phenylpropan-1-ol (**7k**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, 4H), 7.31−7.28 (m, 2H), 6.28 (brs, 1H), 6.06−6.01 (s, 1H), 4.73−4.70 (m, 1H), 2.79−2.68 (m, 2H), 2.17−2.03 (m, 3H), 1.93 (brs, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 155.66, 144.46, 141.10, 128.68, 128.65, 127.83, 126.02, 110.27, 105.17, 73.84, 37.30, 24.54.

*1-Phenyl-3-(thiophen-2-yl)propan-1-ol (**7l**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27−7.19 (m, 5H), 7.02−7.01 (m, 1H), 6.83−6.82 (m, 1H), 6.71 (s, 1H), 4.61 (s, 1H), 2.88−2.77 (m, 2H), 2.11−1.94 (m, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ 144.73, 144.46, 128.66, 127.81, 126.87, 126.00, 124.43, 123.20, 73.60, 40.78, 26.32.

*3-(Naphthalen-1-yl)-1-phenylpropan-1-ol (**7m**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, J = 6.0 Hz, 1H), 7.85−7.81 (m, 1H), 7.71 (d, J = 12.0 Hz, 1H), 7.49−7.45 (m, 2H), 7.40−7.34 (m, 5H), 7.31−7.28 (m, 1H) 4.81−4.80 (m, 1H), 3.28−3.23 (m, 1H), 3.14−3.09 (m, 1H), 2.29−2.23(m, 1H), 2.19−2.14 (m, 1H), 1.93 (d, J = 3.1 Hz, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 144.65, 138.13, 134.04, 131.96, 128.90, 128.69, 127.84, 126.82, 126.09, 125.93, 125.68, 125.59, 123.91, 74.34, 39.97, 29.26.

*3-(Anthracen-9-yl)-1-phenylpropan-1-ol (**7n**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.18 (d, J = 8.6 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H), 7.46 (dt, J = 16.6, 7.0 Hz, 6H), 7.39 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 4.94 (p, J = 3.7 Hz, 1H), 3.78 (ddd, J = 13.4, 11.2, 5.0 Hz, 1H), 3.65 (ddd, J = 13.8, 10.9, 6.0 Hz, 1H), 2.34−2.26 (m, 1H), 2.22 (ddd, J = 13.9, 10.6, 5.4 Hz, 1H), 2.05 (brs, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$) δ 144.60, 134.47, 131.76, 129.72, 129.33, 128.73, 127.92, 126.10, 125.92, 125.66, 124.96, 124.46, 74.57, 40.18, 24.12.

*3-Phenyl-1-(p-tolyl)propan-1-ol (**7q**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18−7.15 (t, J = 7.5 Hz, 2H), 7.12−7.10 (m, 2H), 7.08−7.03 (m, 5H), 4.50 (t, J = 5.0 Hz, 1H), 2.64−2.58 (m, 1H), 2.56−2.50 (m, 1H), 2.23 (s, 3H), 2.03−1.96 (m, 2H), 1.92−1.85 (m, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$): δ 141.94, 141.65, 137.33, 129.24, 128.53, 128.44, 126.00, 125.88, 73.73, 40.41, 32.15, 21.21. HRMS (ESI): m/z calculated for $[M + Na]^+$: 249.1255, found 249.1276.

*1-(4-Methoxyphenyl)-3-phenylpropan-1-ol (**7r**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (d, J = 5.0 Hz, 3H), 7.19 (d, J = 7.1 Hz, 3H), 6.89 (d, J = 8.6 Hz, 2H), 4.64 (brs, 1H), 3.81 (s, 3H), 2.68 (d, J = 79.0 Hz, 2H), 2.17−1.98 (m, 2H). ^{13}C{H} NMR (101 MHz, $CDCl_3$): δ 159.28, 141.98, 128.57, 128.51, 127.35, 125.97, 114.05, 73.65, 55.44, 32.27. HRMS (ESI): m/z calculated for $[M + Na]^+$: 265.1204, found 265.1384.

*1-(3-Methoxyphenyl)-3-phenylpropan-1-ol (**7s**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (q, J = 7.9 Hz, 3H), 7.09 (d, J = 7.7 Hz, 3H), 6.82 (d, J = 7.0 Hz, 2H), 6.72 (d, J = 8.4 Hz, 1H), 4.59−4.54 (m, 1H), 3.70 (s, 3H), 2.69−2.53 (m, 2H), 2.06−1.89 (m, 2H), 1.85 (brs, 1H). ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ 159.95, 146.45, 141.90, 129.66, 128.57, 128.51, 125.98, 118.37, 113.22, 111.56, 73.94, 55.36, 40.52, 32.16.

*1-(4-Bromophenyl)-3-phenylpropan-1-ol (**7w**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49−7.46 (m, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.24−7.17 (m, 5H), 4.65 (ddd, J = 8.2, 5.1, 3.0 Hz, 1H), 2.77−2.63 (m, 2H), 2.13−1.96 (m, 2H), 1.95 (brs, J = 3.4 Hz, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$) δ 143.62, 141.56, 131.70, 128.58, 128.54, 127.78, 126.09, 121.46, 73.28, 40.57, 32.01.

*1-(3-Bromophenyl)-3-phenylpropan-1-ol (**7x**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (brs, 1H), 7.33−7.31 (d, J = 10.0 Hz, 1H), 7.22−7.16 (m, 3H), 7.14−7.09 (m, 4H), 4.55 (brs, 1H), 2.69−2.59 (m, 2H), 2.04−1.88 (m, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ 147.10, 141.57, 130.76, 130.21, 129.17, 128.59, 128.55, 126.11, 124.64, 122.77, 73.25, 40.60, 32.03.

*3-Phenyl-1-(thiophen-2-yl)propan-1-ol (**7za**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.20 (m, 3H), 7.16 (d, J = 7.5 Hz, 3H), 6.97−6.90 (m, 2H), 4.88 (t, J = 6.7 Hz, 1H), 2.79−2.63 (m, 2H), 2.25−2.05 (m, 2H), 1.95 (s, 1H). ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 148.67, 141.60, 128.63, 128.59, 126.82, 126.11, 124.83, 124.06, 69.69, 40.86, 32.16.

*1-(Naphthalen-2-yl)-3-phenylpropan-1-ol (**7zb**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71−7.68 (m, 3H), 7.62 (brs, 1H), 7.37−7.32 (m, 3H), 7.18−7.15 (m, 2H), 7.09−7.07 (m, 3H), 4.68 (brs, 1H), 2.67−2.60 (m, 1H), 2.58−2.53 (m, 1H), 2.12−2.06 (m, 2H), 2.01−1.94 (m, 1H). ^{13}C{H} NMR (151 MHz, $CDCl_3$) δ 141.93, 141.82, 133.31, 133.06, 128.56, 128.51, 128.48, 128.03, 127.80, 126.29, 125.98, 124.79, 124.14, 74.03, 40.38, 32.12. HRMS (ESI): m/z calculated for $[M + Na]^+$: 285.1255, found 285.1200.

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Organometallics XXXX, XXX, XXX−XXX

*3-Phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol (**7zc**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.8 Hz, 3H), 4.78 (b rs, J = 3.7 Hz, 1H), 2.83−2.70 (m, 2H), 2.17−2.03 (m, 2H), 2.03 (brs, J = 3.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.61, 141.42, 129.83 (q, J = 32.4 Hz), 128.62, 128.54, 126.27, 126.17, 125.57 (q, J = 3.7 Hz), 125.14, 123.34, 73.27, 40.69, 31.96. ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.45.

*3-Phenyl-1-(3-(trifluoromethyl)phenyl)propan-1-ol (**7zd**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.47−7.45 (m, 2H), 7.40−7.37 (m, 1H), 7.23−7.18 (m, 2H), 7.13−7.11 (m, 3H), 4.70−4.67 (m, 1H), 2.73−2.60 (m, 2H), 2.06−1.91 (m, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 145.77, 141.48, 129.38, 129.09, 128.65, 128.57, 126.20, 124.53 (q, J = 3.8 Hz), 122.86 (q, J = 3.7 Hz), 73.38, 40.76, 32.08. ^{19}F NMR (471 MHz, $CDCl_3$): δ −62.60.

*3-Phenyl-1-(4-(trifluoromethoxy)phenyl)propan-1-ol (**7ze**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30−7.29 (m, 2H), 7.22−7.18 (m, 2H), 7.12−7.11 (m, 5H), 4.63 (s, 1H), 2.71−2.57 (m, 2H), 2.07−2.00 (m, 1H), 1.97−1.90 (m, 1H), 1.86 (s, 1H). ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ 148.70, 143.42, 141.59, 128.61, 128.55, 127.44, 126.14, 121.13, 73.23, 40.71, 32.09. ^{19}F NMR (471 MHz, $CDCl_3$): δ −57.88.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00328.

X-ray crystallographic parameters, NMR spectra, and computational data (PDF)

Accession Codes

CCDC 2071950 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

V.A. performed the experiments. H.N. purified the derivatives of **7** by column chromatography. A.K. conceptualized, compiled the work, and wrote the manuscript.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Ashoka G. Samuelson (IISc, Bangalore, India) on the occasion of his 65th birthday and his superannuation from service.

■ ABBREVIATIONS

TON,turnover number; THF,tetrahydrofuran; RDS,rate-determining step

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Organometallics XXXX, XXX, XXX−XXX

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