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Toward Green Acylation of (Hetero)arenes: Palladium-Catalyzed Carbonylation of Olefins to Ketones

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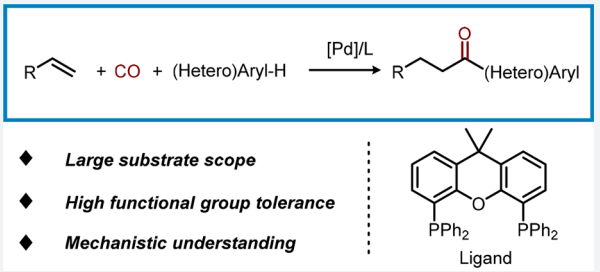
Supporting Information

ABSTRACT: Green Friedel–Crafts acylation reactions belong to the most desired transformations in organic chemistry. The resulting ketones constitute important intermediates, building blocks, and functional molecules in organic synthesis as well as for the chemical industry. Over the past 60 years, advances in this topic have focused on how to make this reaction more economically and environmentally friendly by using green acylating conditions, such as stoichiometric acylations and catalytic homogeneous and heterogeneous acylations. However, currently well-established methodologies for their synthesis either produce significant amounts of waste or proceed under harsh conditions, limiting applications. Here, we present a new protocol for the straightforward and selective introduction of acyl groups into (hetero)arenes without directing groups by using available olefins with inexpensive CO. In the presence of commercial palladium catalysts, inter- and intramolecular carbonylative C–H functionalizations take place with good regio- and chemoselectivity. Compared to classical Friedel–Crafts chemistry, this novel methodology proceeds under mild reaction conditions. The general applicability of this methodology is demonstrated by the direct carbonylation of industrial feedstocks (ethylene and diisobutene) as well as of natural products (eugenol and safrole). Furthermore, synthetic applications to drug molecules are showcased.



INTRODUCTION

Carbonylation reactions are widely used in industrial production of fine and bulk chemicals as well as organic synthesis since they can efficiently introduce the synthetically versatile carbonyl group and easily expand carbon chains.[1−3] In terms of production scale, carbonylation reactions nowadays constitute the largest industrial applications in the area of homogeneous catalysis. In addition to the well-known Monsanto[4] or Cativa processes,[5] which produce acetic acid by the carbonylation of methanol, carbonylative transformations of simple olefins have been shown to be core processes in industry for the production of aldehydes (hydroformylation, such as "oxo process")[6] and esters (alkoxycarbonylation, such as "Lucite α process").[7,8] Since the original work of Reppe in the past century,[9] carbonylation of alkenes with various nucleophiles such as H_2O and alcohols (*O*-nucleophiles),[10−13] thiols (*S*-nucleophiles),[14] and amines and amides (*N*-nucleophiles)[15−19] have been extensively studied, and nowadays a plethora of catalysts is available for producing all kinds of carboxylic acid derivatives (Scheme 1a). On the other hand, the use of *C*-nucleophiles, which creates important C–C bonds, has been investigated to a lesser extent. Since the pioneering work by Heck and co-workers in the 1970s,[20] enormous efforts have gone into the synthesis of ketones through the carbonylations of organometallic reagents as the *C*-nucleophiles, such as organic zinc, boron, tin, silanes, etc.[21−23]

Unfortunately, all these procedures generate stoichiometric amounts of metal salts as waste. Obviously, the most ideal bond-formation mode—carbonylation directly utilizing C–H as the nucleophile—would be more straightforward to construct a synthetically versatile carbonyl group with high efficiency and selectivity. Based on the Mayr scale on the nucleophilicity of various (hetero)arenes (Scheme 1b),[24] we had the idea to apply (Het)Ar–H as the nucoleophile in the Reppe type carbonylation of olefins.

Among the various carbonyl compounds, (hetero)aromatic ketones are important motifs for industrial chemistry and drug discovery, the synthesis of advance materials and polymers.[25] At present, the most common approach for the introduction of a carbonyl group to (hetero)arenes is the well-known Friedel–Crafts acylation reactions (Scheme 1c, path I).[26] In general, this method utilizes unstable and corrosive acyl halides or anhydrides, resulting in stoichiometric amounts of corrosive waste, and substantial amounts of Lewis acids are required for the activation of the acyl substrate. To overcome this problem, Arndtsen, Skrydstrup, and Gu independently developed a strategy to utilize aryl halides as the electrophiles in carbonylation of (hetero)arenes (Scheme 1c, path II).[27−30] Additionally, examples based on ruthenium cluster catalyzed C–H carbonylation of heteroarenes were also investigated. However, these methodologies require directing groups or specific activation on heteroarenes (Scheme 1c, path III).[31−37] To the best of our knowledge, Reppe type carbonylation

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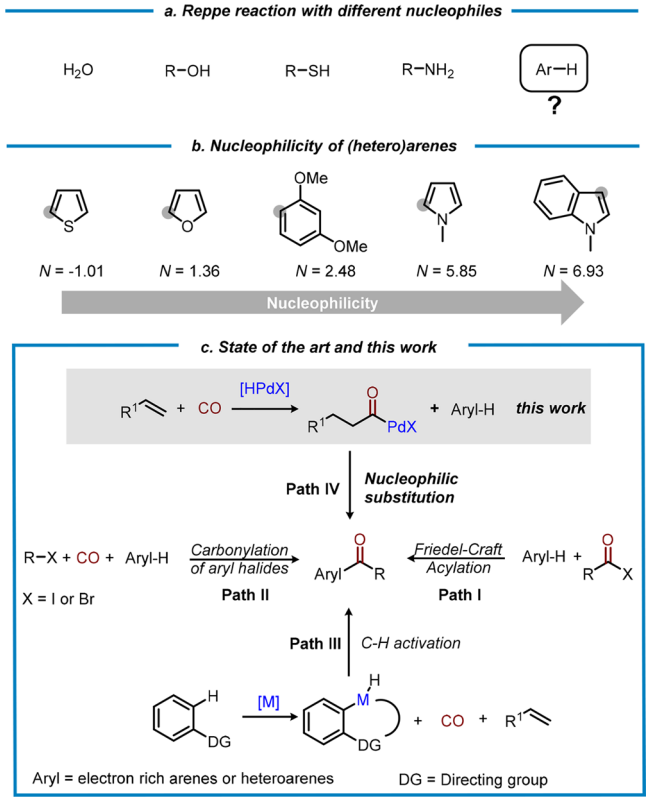
Scheme 1. (a) Reppe Type Carbonylation with Various Nucleophiles. (b) Nucleophilicity of Representative (Hetero)arenes. (c) State of the Art Work and Our Proposal



utilizing indoles and pyrroles as *C*-nucleophiles has thus far been only achieved with alkynes reported by Alper as well as our group.[38,39] Therefore, selective carbonylation of olefins with simple (hetero)arenes is basically unknown, even though the potential products that would arise from such reactions have broad utility in organic synthesis.

Based on our long-standing interest in carbonylation reactions,[40] we report herein a novel protocol for the general and efficient synthesis of ketones via selective carbonylation of ubiquitous available olefins to the corresponding acyl palladium complex and subsequent reaction with simple (hetero)arenes (Scheme 1c, path IV).

RESULTS AND DISCUSSION

Recently, several innovative and selective C−H functionalization reactions of unfunctionalized (hetero)arenes have been disclosed.[41−50] Notably, good regio- and chemoselectivities were observed in some of these reactions without the necessity of additional directing groups. Meanwhile, considering prior reports of alkoxycarbonylation and aminocarbonylation by our group, we questioned whether the direct C−H carbonylation of (hetero)arenes with easily available olefins can be developed to a general methodology. At the outset of our studies, the palladium-catalyzed carbonylation of 1-octene with *N*-methylindole as nucleophile was chosen as the benchmark system. To ensure sufficient reactivity *p*-TsOH was added as acid cocatalyst. Compared to other C−H functionalization reactions, the control of selectivity is crucial in this transformation. Apart from the different isomers resulting from the attack on the (hetero)arene, olefin insertion might lead to linear and branched products. In order to control this selectivity, we studied the ligand effect in detail (Table S1). For alkoxycarbonylation reactions it is well-known that bidentate phosphines preferentially form linear products from both internal and terminal olefins.[51−53] Hence, different bidentate ligands were tested with our model substrates. To our delight, Xantphos was identified as the most effective ligand to afford the product **3a** in excellent yield (determined by GC) of 92% and selectivity (*l*:*b* = 88:12). Notably, the carbonylation was selectively performed at the C3 position on indole with >20:1 regioselectivity.

Having a reliable C−H carbonylation protocol in hand, we explored the reactivity of different olefins (Scheme 2). Both short and longer chain aliphatic olefins were able to give good yields and good linear selectivities (**3a** to **3e**, 54% to 89% yields, *l*:*b* up to 92%). Increasing the steric bulk of a terminal olefin led to higher linear selectivity of products in moderate to good yields (**3f** to **3h**). Interestingly, cyclic olefins including cyclohexene and norbornene were found to be suitable substrates to afford the corresponding ketones in high yields (**3i** and **3j**). Applying aromatic olefins as the substrates under the acidic reaction conditions, Friedel−Crafts alkylation was observed as the main side reaction, nevertheless, the desired ketones were obtained in 33%−48% yields with excellent linear selectivity (**3k** to **3n**, *l*:*b* up to 98%). Furthermore, alkenes bearing −CN, −OAc, −COOMe, and −Cl were compatible with the conditions and gave the corresponding ketones in moderate yields with 84−95% linear selectivity (**3o** to **3r**). In addition to terminal olefins, also 2-octene gave the desired product **3s** with 89% branched selectivity. Gratifyingly, 1,1-disubstituted olefins were found to be suitable substrates under similar conditions to afford the corresponding carbonylative products in good yields and excellent selectivity (**3t** and **3u**). Tetrasubstituted olefins are known to be highly challenging substrates. However, tetramethylethylene was converted to the corresponding ketone **3u** successfully (81% yield and >99:1 linear selectivity). Finally, when (−)-*β*-citronellene was used as the substrate, the internal bond remained intact and only the double bond in the terminal position was selectively carbonylated to the linear ketone (**3v**). To note, all the C−H carbonylation preferentially occurred at the C3 position on the indole with regioselectivities >20:1.

Next, we examined the substrate scope by employing structurally diverse arenes and heteroarenes. Benzyl (Bn) protected indole also led to regioselective C3 carbonylation in excellent yield (**4a**). Various substituents including −OMe (**4b**), −Me (**4c**), −Ph (**4d**), −CN (**4e** and **4f**), −F (**4g** and **4h**), −Cl (**4i** and **4j**), and −Br (**4k**) at different positions of the indole nucleus are well compatible with this methodology and give the desired ketones in 41%−97% yield exclusively at C3. Interestingly, when this position was blocked by a methyl group, the carbonylation product was obtained in good yield (80%) at the C2 position selectively (**4l**). To demonstrate a broader scope of substrates, C−H functionalization of diverse N-, O-, and S-containing heteroaromatics was investigated. The carbonylation of *N*-methylpyrrole and *N*-benzylpyrrole with industrially important ethylene afforded the corresponding 2-propionylpyrrole (**4m** and **4n**) in good yields. In addition, furans, containing substituents at various positions, underwent this transformation smoothly with excellent regioselectivity at the C2 position (**4o** to **4q**). Interestingly, similarly to 1,3-dimethylindole, 2,5-dimethylfuran, with both the C2 and C5 positions blocked by methyl groups, participated in this transformation at the C3 position selectively, and a synthetically

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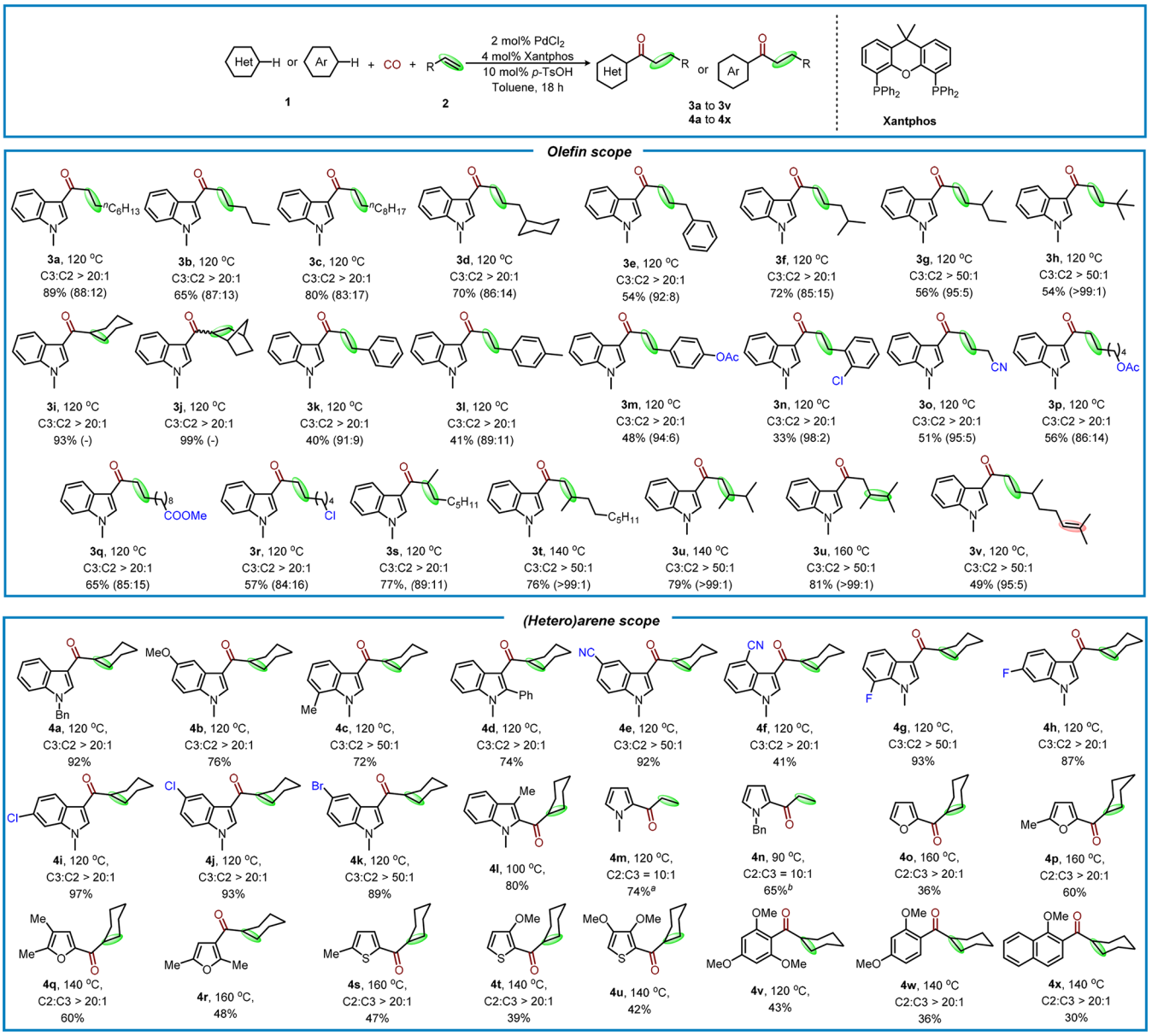
Scheme 2. Substrate scope of Different Olefins and (Hetero)arenes[a]



[a]General reaction conditions: (hetero)arene **1** (0.5 mmol), olefin **2** (1.0 mmol), $PdCl_2$ (2.0 mol %), Xantphos (4.0 mol %), *p*-TsOH (10 mol %), CO (40 bar), toluene (1 mL), 18 h. Isolated yield. The ratios of isomers were determined by GC analysis. Green shading, the original double bond in olefin. Red shading, double bond is well tolerated. (a) For **4m**: *N*-methylpyrrole (20 mmol), ethylene (2.0 g), $Pd_2(dba)_3$ (0.1 mol % Pd), Xantphos (0.2 mol %), *p*-TsOH (0.4 mol %), CO (40 bar), toluene (20 mL), 120 °C, 48 h. GC yield. The ratios of isomers were determined by GC analysis. (b) For **4n**: *N*-benzylpyrrole (2.0 mmol), ethylene (0.2 g), $PdCl_2$ (2.0 mol %), Xantphos (4.0 mol %), *p*-TsOH (10 mol %), CO (40 bar), toluene (4 mL), 90 °C, 18 h. Isolated yield. The ratios of isomers were determined by GC analysis.

useful yield was obtained (**4r**). Furthermore, 2-methylthiophene, 3-methoxythiophene, and 3,4-dimethoxythiophene were found to be suitable substrates and underwent this carbonylation smoothly with excellent regioselectivity (**4s** to **4u**). Last but not least, electron-rich arenes also showed good reactivity as well. For example, benzenes bearing methoxy groups at various positions are well-tolerated and the corresponding products are obtained in moderate yields (**4v** and **4w**). Similarly, 1-methoxynaphthalene proved to be suitable and furnished a moderate yield of the desired product (**4x**).

As shown in Scheme 3 carbonylation reaction of *N*-methylindole with diisobutene takes place to give the corresponding pure ketones **3w** in high yields. Notably, this industrially important olefin consists of a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (ratio of 4:1), which is obtained by dimerizing butenes. Nevertheless, we succeeded to convert this mixture in both cases in excellent selectivity (*l*:*b* > 99:1; C3:C2 > 50:1). Gratifyingly, in most cases shown in Scheme 2, *N*-methyl- or *N*-benzylpyrroles are carbonylated highly selectively at the C2 position because of the natural reactivity of pyrrole. We speculated that it is possible to change the position of C−H bond functionalization by additional steric and/or electronic control (Scheme 4). Accordingly, pyrroles *N*-substituted with sterically hindered groups (**5a**, **5b**, and **5c**) gave mainly carbonylation products at the C3 position. This switch in selectivity is attributed to the

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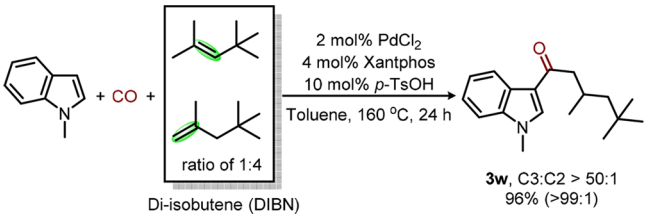
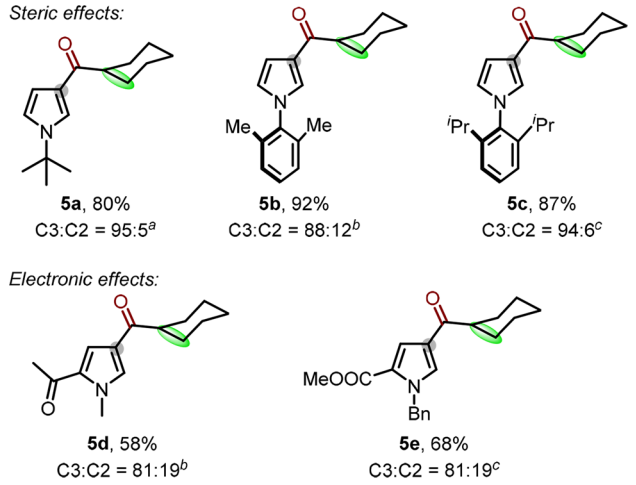
Scheme 3. Selective Carbonylation of Diisobutene[a]



[a]Reaction conditions: *N*-methylindole (0.5 mmol), diisobutene (1.0 mmol), $PdCl_2$ (2.0 mol %), Xantphos (4.0 mol %), *p*-TsOH (10 mol %), CO (40 bar), toluene (1 mL), 160 °C, 24 h. Isolated yield. The ratios of isomers were determined by GC analysis.

Scheme 4. Reversing the Carbonylation of Substituted Pyrroles and Cyclohexene



[a]Reaction conditions: *N*-[t]butylpyrrole (0.5 mmol), cylohexene (1.0 mmol), $PdCl_2$ (2.0 mol %), Xantphos (4.0 mol %), *p*-TsOH (10 mol %), CO (40 bar), toluene (1 mL), 100 °C, 18 h. Isolated yield. The ratios of isomers were determined by GC analysis. [b]Reaction conditions: substituted pyrrole (0.5 mmol), cylohexene (1.0 mmol), $PdCl_2$ (2.0 mol %), Xantphos (4.0 mol %), *p*-TsOH (10 mol %), CO (40 bar), toluene (1 mL), 140 °C, 18 h. Isolated yields. The ratios of isomers were determined by GC analysis. [c]Reaction conditions: substituted pyrrole (0.5 mmol), cylohexene (1.0 mmol), $PdCl_2$ (2.0 mol %), Xantphos (4.0 mol %), *p*-TsOH (10 mol %), CO (40 bar), toluene (1 mL), 160 °C, 18 h. Isolated yields. The ratios of isomers were determined by GC analysis.

sterically demanding nature of the bulky groups that shields the C2 position from reaction with the palladium catalyst, forcing the reactive pyrrole to palladate at C3. Noteworthily, in the case of **5a**, the *tert*-butyl group can be easily removed and thereby serves as a traceless directing group.

In addition, introduction of an electron withdrawing group (such as acyl **5d** and ester group **5e**) allows reversing the reactivity of the pyrrole and yields selective C3 acylation.

Remarkably, this catalyst system can also be applied for the intramolecular acylation to 1-teralone derivatives. Thus, substituted allylbenzenes, e.g., eugenol methyl ether (4-allyl-1,2-dimethoxybenzene) and safrole, a class of natural products extracted from essential oil, underwent this transformation selectively to give the corresponding C−H carbonylation−annulation products in good yields (Scheme 5, **6a** and **6b**). These products can be further converted to aminonaphthalene **8** according to a reported method.[54] Compound **8** is an intermediate in the synthesis of the antitumor/antiviral alkaloid, norallonitidine. The present method provides an alternative route for such pharmaceutically active compounds.

Allylic alcohols were also found to be versatile substrates in this novel carbonylation transformation. For example, indoles first underwent a Pd catalyzed allylic substitution reaction at the C3 position. Subsequently, intramolecular carbonylation afforded directly the tricyclic ketone in good yield (75% yield of **7a**) (Scheme 6). To the best of our knowledge, this is the most convenient synthesis of this key intermediate, which has been applied for the synthesis of tetracyclic necrostatin-21, a novel necroptosis inhibitor.[55] Interestingly, when using 2-cyclohexen-1-ol, the polycyclic ketone **7b** containing a six membered ring was identified as the only product in this reaction. This annulation process works well and provides a facile method for the generation of complex polycyclic ring products.

In general, different mechanisms are possible for this novel acylation reaction: (1) Pd(II) precursor is presumably reduced in situ to a Pd(0) species in the presence of an excess amount of phosphine ligands.[56] In the presence of acid, the key hydride complex $[LPd-H]^+$ is generated.[57] After coordination of the alkene to this complex followed by migratory insertion into the Pd−H bond, the corresponding alkyl complex $[LPd-CH_2CH_2R]^+$ is obtained, which is transformed into the corresponding acyl complex $[LPd-CO-CH_2CH_2R]^+$ via CO coordination and insertion. Finally, inter- or intramolecular nucleophilic attack of (hetero)arene on the acyl carbonyl leads to the formation of the desired ketone and regeneration of the $[Pd-H]^+$ species (Scheme 7a, hydride mechanism). (2) Alternatively, the intermediate acyl complex forms the corresponding acyl halide or acid, which then undergoes a traditional Friedel−Crafts-like reaction (Scheme S2).[27−30] (3) In contrast, this reaction may also proceed via C−H activation mechanism (Scheme S3).[58] In the last case, a Pd^{II} catalyst would initially activate the arene C−H bond to give the aryl palladium complex, followed by CO insertion to give the Pd acyl species. Subsequently, olefin coordination, insertion, and finally protolysis take place to give the desired product and regenerate the Pd catalyst. In order to understand this novel carbonylation reaction, the mechanism of the palladium-catalyzed carbonylation cycle was investigated in more detail and several control experiments were performed.

As we discussed above, we assumed that related Friedel−Crafts acylations with the corresponding acid or acyl chloride as the possible intermediates might take place under our reaction conditions. However, when nonanoic acid or the corresponding acyl chloride was applied under the standard conditions with and without palladium catalyst, no desired product was observed (Scheme 7b). Therefore, we exclude a traditional Friedel−Crafts acylation, which is not related to this carbonylation of (hetero)arenes with olefins.

In order to prove the nature of the active catalyst, next the carbonylation of ethylene and *N*-methylpyrrole was carried out with different Pd(II) and Pd(0) precatalysts (Scheme 7c). When using $PdCl_2$, an induction period of around 1 h was observed, indicating that Pd(II) is not the true active species. Meanwhile, almost no induction period was observed for $Pd_2(dba)_3$, and the substrate conversion started immediately. These results indicate that no initial C−H activation of the heterocycle takes place; instead it is most likely that this reaction goes through the hydride mechanism in Scheme 1.

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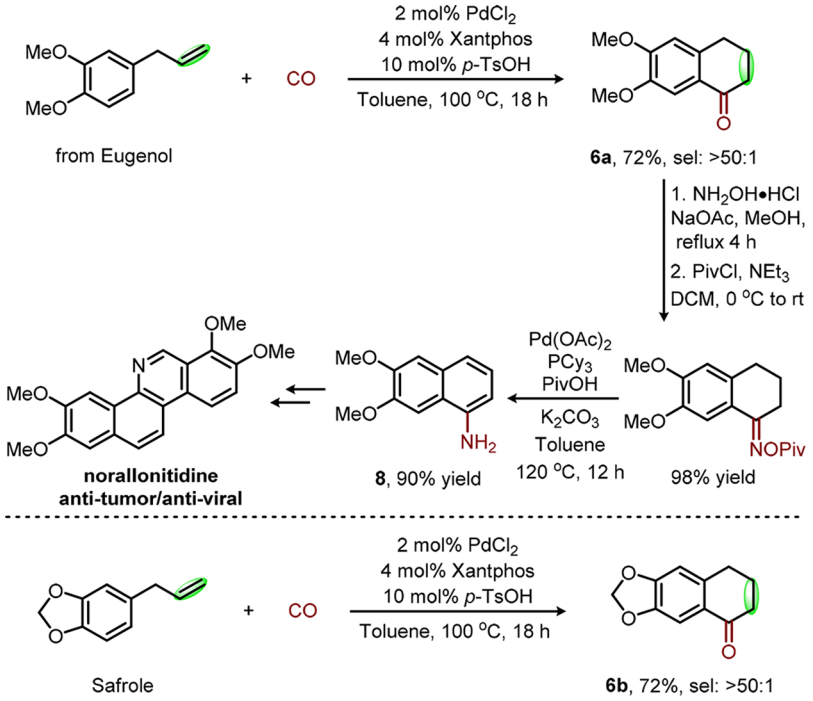
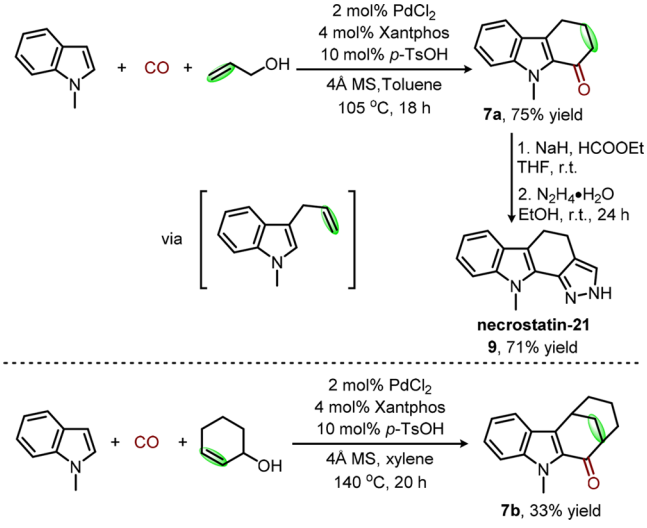
Scheme 5. Intramolecular Carbonylation to 1-Tetralone Derivatives and Synthetic Application[a]



[a]Reaction conditions: substituted allylbenzene (0.5 mmol), $PdCl_2$ (2.0 mol %), Xantphos (4.0 mol %), *p*-TsOH (10 mol %), CO (40 bar), toluene (1 mL), 100 °C, 18 h. Isolated yields. The ratios of isomers were determined by GC analysis. For procedures of synthetic applications please see the Supporting Information.

Scheme 6. Carbonylation of Allylic Alcohols with *N*-Methylindoles[a]



[a]Reaction conditions: *N*-methylindole (0.5 mmol), allylic alcohol (1.0 mmol), $PdCl_2$ (2.0 mol %), Xantphos (4.0 mol %), *p*-TsOH (10 mol %), 4 Å molecular sieves (20 mg), CO (40 bar), toluene (1 mL), 105 or 140 °C, 18 or 20 h. Isolated yields. For procedures of synthetic applications, please see the Supporting Information.

To understand this mechanism in more detail, we carried out B3PW91[59] density functional theory computations both in the gas phase and under the consideration of toluene solvation based on solute electron density (SMD).[60] In our computation we used the cationic $[LPd-H]^+$ (L = Xantphos) complex as active catalyst as well as ethene, CO, and *N*-methylpyrrole as substrates. All results and the full potential energy surfaces are given the Supporting Information. Since the results in the gas phase and toluene solution are qualitatively similar (Schemes S5 and S6), we present only the results in toluene solution. In addition, we carried out single-point calculations by adding GD3BJ dispersion correction and by using the M06 functional in combination with triple-ζ basis sets for Pd (Table S6). It is found that GD3BJ dispersion (Scheme S7) lowers the energy barrier. However, the regioselectivity is highly overestimated by about 6×10^3. As we are much more interested in the difference of the barriers between different reaction pathways as well as to distinguish the selectivity between the C2- and C3-*N*-methylpyrrole, therefore, we used the B3PW91-SCRF results for discussion and comparison.

As shown in Figure 1, the simplified potential energy surface can be divided into two parts; the first part is the formation of the ethyl complex via ethene coordination and Pd−H migratory insertion as well as the formation of the acyl complex via CO coordination and insertion to the alkyl complex. The second part is the selective C−H activation via C−C coupling between the acyl carbon and the C2 (or C3) carbon of *N*-methylpyrrole as well as the H transfer from *N*-methylpyrrole to Pd center resulting in the formation of the corresponding ketone and the $[LPd-H]^+$ regeneration.

At first, it is noted that no stable complex of side-on ethene coordination could be located. All attempts to optimize ethene coordination result in the spontaneous ethene insertion and the formation of the ethyl complex $[LPd(C_2H_5)]^+$, which is slightly endergonic by 0.5 kcal/mol. Next, CO coordination leading to $[LPd(CO)(C_2H_5)]^+$ is exergonic by 1.9 kcal/mol. Starting from $LPd(CO)(C_2H_5)]^+$, $[LPd(-CO-C_2H_5)]^+$ formation from CO insertion has free energy barrier of 4.9 kcal/mol and is exergonic by 22.5 kcal/mol. Totally, the formation of acyl

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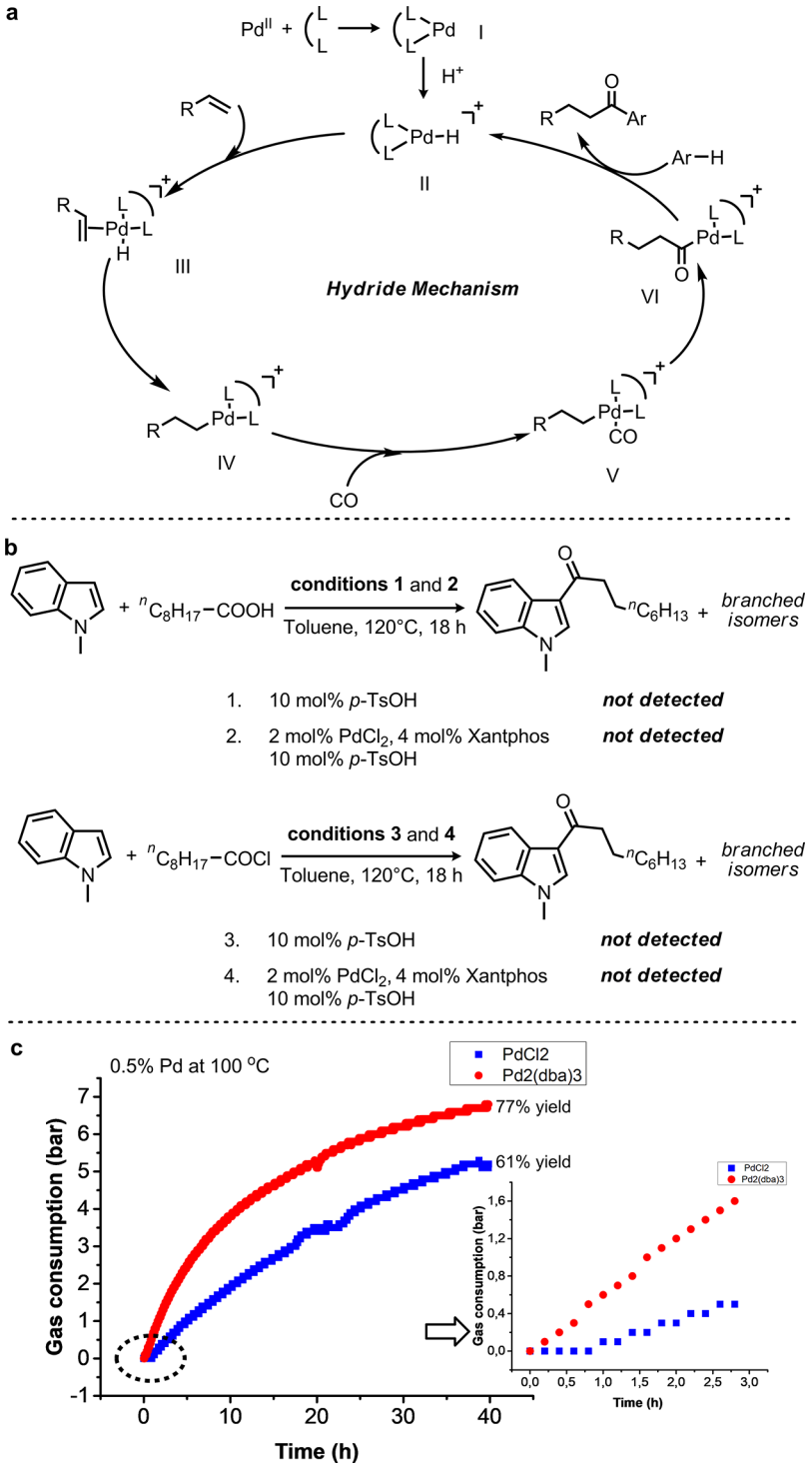
Scheme 7. (a) Proposed Mechanism. (b) Control Experiments Applying Nonanoic Acid and Nonanoyl Chloride. (c) Gas Consumption versus Time for the Carbonylation of *N*-Methylpyrrole with Ethylene with $PdCl_2$ or $Pd_2(dba)_3$ (0.5 mol % Pd Catalyst)



complex is exergonic by 23.9 kcal/mol, indicating a kinetically very facile and thermodynamically very favored process.

Starting from the acyl complex $[LPd(-CO-C_2H_5)]^+$ and *N*-methylpyrrole, the C−C coupling between the acyl carbon and the C2 carbon has a barrier of 43.9 kcal/mol and is endergonic by 41.1 kcal/mol, while the C−C coupling between the acyl carbon and the C3 carbon has a barrier of 46.7 kcal/mol and is endergonic by 46.1 kcal/mol. Alternatively, we also computed the barrier of the OSO_2CH_3 anion stabilized C−C coupling as well as the concerted metalation deprotonation (CMD) step.[61] As given in Table S7, the barrier of OSO_2CH_3 anion stabilized C−C coupling (43.5 kcal/mol) is close to that of our proposed route (43.9 kcal/mol), while the concerted metalation deprotonation mechanism has a much higher barrier (49.1 kcal/mol).

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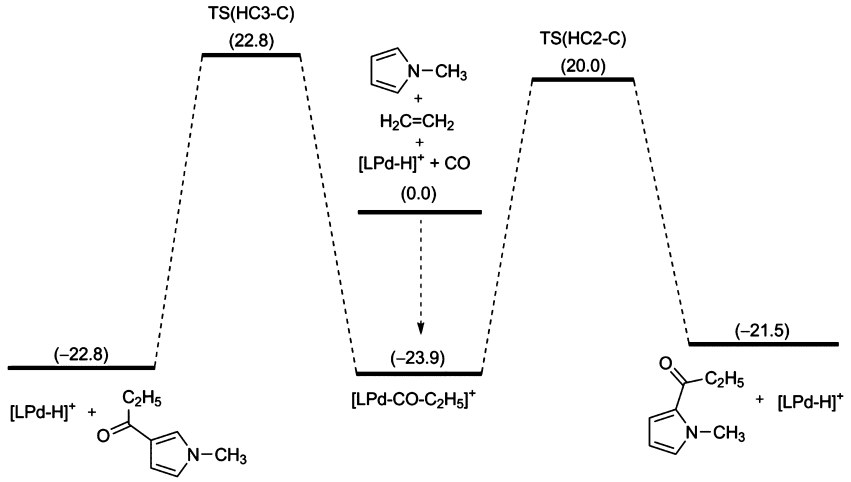

Figure 1. Simplified B3PW91-SCRF (SMD/toluene) potential energy surface of carbonylation of ethylene and *N*-methylpyrrole (kcal/mol).

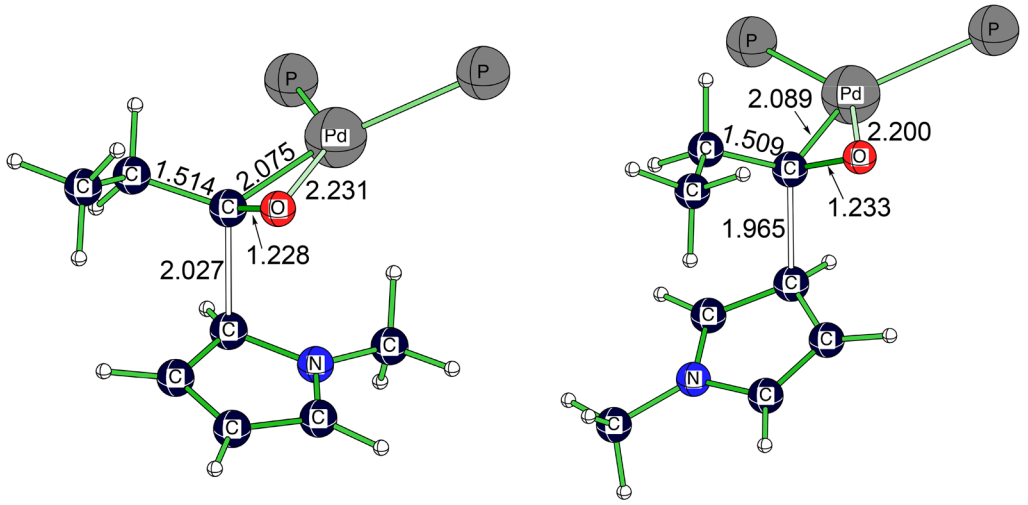

Figure 2. Optimized transition state structures of C−C coupling between the acyl carbon and the C2 (left)/C3 (right) carbon of *N*-methylpyrrole (only the central part is presented; and the other parts are omitted for clarity).

The subsequent C−H transfer resulting in the formation of the corresponding ketone and the $[LPd-H]^+$ regeneration is found barrierless and exergonic by 38.7 and 45.0 kcal/mol for the C2 and C3 carbon, respectively. Totally, the acyl complex is the resting state and the C−C coupling step is rate-determining. The overall reaction is exergonic by 21.5 and 22.8 kcal/mol for the formation of 2-propionyl-1-methylpyrrole and 3-propionyl-1-methylpyrrole, respectively. The energy difference between the two transition states is 2.8 kcal/mol (4.3 kcal/mol in gas phase); and the computed rate constant ratio k(C2−H)/k(C3−H) of C−C bond coupling based on standard transition state theory is 1.1×10^2. This indicates the selective activation of the C2−H carbon from kinetic aspect. The computed selectivity is in agreement with the experimental observation.

On the basis of the optimized transition state structures (Figure 2), it is hard to get information on origin of the observed regioselectivity, since the bond parameters between the acyl group and the Pd center are very similar on one hand; and on the other hand, the forming C−C distance for C2 carbon coupling is even longer than that for C3 carbon coupling (2.027 vs 1.965 Å).

To understand the regioselectivity in favoring of the C2 carbon of *N*-methylpyrrole, we dissected the electronic activation energy of the C2/C3 transition states by using the proposed activation strain model (ASM)[62−64] (Figure S1 and Table S8). It is found that the C−C2 transition state has lower strain energy than the C−C3 transition state; and this energy difference determines the regioselectivity.

CONCLUSION

In our work, we developed a novel type of catalytic acylation reaction complementary to the classic Friedel−Crafts methodologies. Key for the success is the use of a $PdCl_2$/Xantphos catalyst, which allows for selective carbonylation of (hetero)-arenes with olefins. Using ethene and *N*-methylpyrrole as substrates, the regioselectivity comes from the kinetic differentiation in the C−C coupling step as revealed by detailed B3PW91-SCRF density functional theory computations. This novel transformation can be applied to an array of privileged heteroaromatic scaffolds and permits the acylation with industrially important aliphatic olefins (more than 50 examples, 30−99% yield and up to >99% linear selectivity). The applicability of this methodology is further highlighted by the synthesis of active pharmaceutical intermediates and the

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selective construction of polycyclic ring compounds. We believe that these procedures can broaden the currently known methods for carbonylation reactions in organic synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.7b00368.

Additional experimental results and procedures and characterization data (PDF)

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Author Contributions

M.B. and J.L. conceived and designed the experiments. J.L. performed the experiments and analyzed the data. Z.W. and H.J. performed the DFT study. R.J. participated in the discussions and supported the project. M.B., H.J., Z.W., and J.L. cowrote the paper.

Notes

The authors declare no competing financial interest.

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