Generation of Stereocenters via Single-Carbon-Atom Doping Using *N*-Isocyanides

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Abstract

Among the electronically unsaturated carbon species, atomic carbon is the most challenging to use for the synthesis of organic molecules, despite its potential to forge four distinct covalent bonds at a carbon center in a single process.[1] Single-carbon-atom doping (SCAD) into organic molecules without loss of atoms in the reactant is highly attractive because it allows for a remarkable increase in molecular complexity in a single process. We have previously reported that *N*-heterocyclic carbenes (NHCs) can serve as an atomic carbon equivalent suitable for SCAD reactions.[2,3] However, that method is limited to the formation of methylene carbons, leaving the full potential of

the concept unrealized. Here, we report an SCAD reaction that results in the formation of stereocenters by unlocking the reactivity of (*N*-isocyanoimino)triphenylphosphorane as an atomic carbon equivalent. This reagent enables the single-step conversion of a range of acyl chlorides into homologated α-chloro cyclic ketones, which proceeds via the generation of four different bonds, *i.e.*, one C–Cl, one C–H, and two C–C bonds at the incorporated carbon atom.

Main text

Since the skeleton of many natural and synthetic organic molecules consists primarily of tetravalent carbons, the introduction of four substituents into a given carbon center represents a central issue in organic chemistry. Traditionally, this has been achieved via stepwise substitution and/or addition reactions at the carbon center; however, despite its reliability, this method often lacks efficiency. The overall efficiency of introducing four substituents at the carbon center can be dramatically enhanced by using electronically unsaturated carbon species such as carbenes[4,5] and carbynes.[6–14] Depending on their degree of unsaturation, these species can form multiple covalent bonds at the carbon center in a single step. For example, a divalent carbon atom in carbenes can generate two new covalent bonds in a single step via cyclopropanation or insertion reactions.[15] The development of suitable precursors and synthetic equivalents has led to significant advances in the synthetic chemistry of carbenes and carbynes, enabling the regulation of the high reactivity and

short lifetimes of these electronically unsaturated species for various synthetic applications. Among the noncharged carbon species, atomic carbon possesses the lowest valence and provides a promising platform in organic synthesis for the formation of four new covalent bonds at the carbon center. Atomic carbon can induce numerous modes of reactivity, among which insertion into a reactant molecule represents the simplest and most powerful tool because four covalent bonds can be forged at the carbon center with no loss of atoms in the reactant. In one of our previous papers, we have termed this process single-carbon-atom doping (SCAD; **Fig. 1a**).[1] Although naked atomic carbons that can be generated by physical methods (e.g., arc discharge) have already been demonstrated to undergo SCAD reactions with organic molecules, such techniques require atomic carbons to be dispersed on a paraffin matrix at −196 °C, which is unsuitable for synthetic applications. Reagents that can generate naked atomic carbons (or their equivalent) under simple thermal or photoirradiation conditions, including carbon suboxide[16,17], diazotetrazole,[18,19] and chromium carbide complexes,[20] have also been developed, albeit that the efficiency of these chemical processes remains low. Stable carbon(0) complexes, the so-called carbones, have also attracted attention as atomic carbon equivalents (**Fig. 1b**).[21–23] However, these reagents are used only in the deoxygenative functionalization of carbonyl compounds based on the nature of ylides and have not been applied to SCAD reactions. Recently, we discovered that *N*-heterocyclic carbenes (NHCs) can function as atomic-carbon equivalents by eliminating a 1,2-diimine moiety, which can be applied to the synthesis of γ-lactam derivatives with reasonable scalability (**Fig.**

1c).[2,3] However, SCAD reactions involving NHCs are, in principle, limited to simple polar reactions, which restricts the substrate scope and the substituents that can be introduced at the carbon center. Therefore, finding a more versatile atomic-carbon equivalent remains a crucial objective.

Inspired by Cummins's *N*-isocyanide reagent (**Fig. 1d**), which has been reported to serve as a carbon-atom source for the synthesis of a metal-carbide complex,[24] we turned our attention to (*N*-isocyanoimino)triphenylphosphorane (PINC) as an atomic-carbon equivalent.[25] PINC is a bench-stable solid that can be readily prepared from formohydrazide in one step[26] (**Fig. 1e**) and that has been used as a reagent for the synthesis of various *N*-heterocyclic scaffolds.[27–29] We envisioned that the release of dinitrogen and triphenylphosphine from PINC could unlock its reactivity mode as an atomic carbon equivalent applicable to SCAD reactions. This could be realized through two consecutive processes. First, the isocyanide moiety of PINC would behave as a simple isocyanide and insert into a suitable covalent bond[30] to generate a metastable phosphazine intermediate (**Fig. 1d**). Subsequently, this intermediate would be activated by an appropriate metal catalyst to generate a metal–carbene species, which is akin to the decomposition of diazo compounds. The as-generated metal–carbene species could undergo additional insertion reactions. This approach would enable the single-step generation of a chiral center by introducing four substituents into the carbon atom in PINC. As a proof-of-concept study to demonstrate that PINC can serve as an atomic carbon

equivalent, we describe here the SCAD reactions of acyl chlorides for the synthesis of homologated α-chloro ketones (**Fig. 1e**).

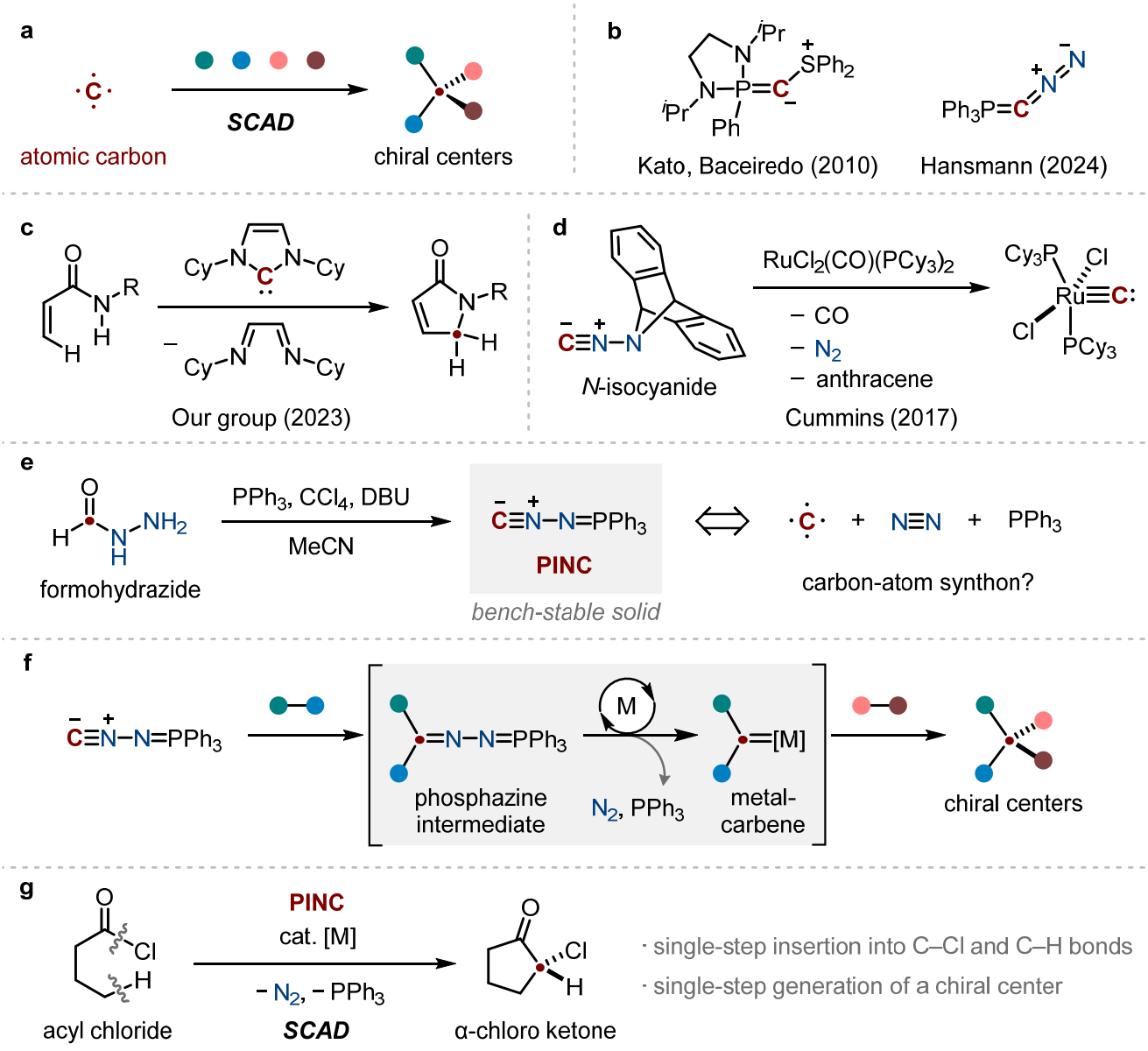


Fig. 1. Background and potential of PINC as an atomic-carbon equivalent.

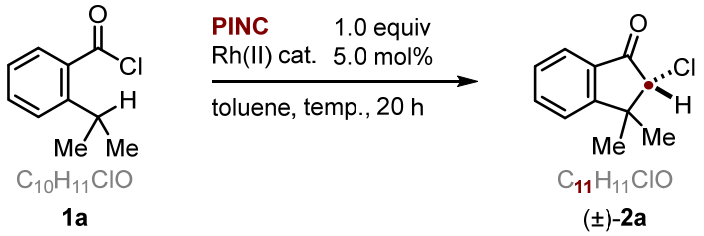
a, New disconnection approach for the construction of chiral centers with an atomic-carbon equivalent: single-carbon-atom doping (SCAD). **b**, Zero-valent carbon species as carbon-atom transfer reagents. **c**, NHCs as an atomic-carbon equivalent. **d**, Carbon-atom transfer into a metal

complex using *N*-isocyanide. **e**, Potential of PINC as an atomic-carbon equivalent. **f**, Strategy for the construction of a chiral carbon center with PINC. **g**, This work: SCAD reaction of acyl chlorides.

To investigate the feasibility of our hypothesis (**Fig. 1f**) and considering that isocyanides can insert into the C–Cl bonds of acyl chlorides (Nef isocyanide-type reaction),[31] we initially examined the reaction of 2-isopropylbenzoyl chloride (**1a**) with PINC (1.0 equiv) in the presence of rhodium(II) acetate dimer ($Rh_2(OAc)_4$, 5.0 mol%) in toluene at 80 °C. To our delight, the reaction afforded the expected α-chloro cyclic ketone **2a** in 29% yield via sequential insertion into C–Cl and C–H bonds (entry 1, **Table 1**). Using other rhodium(II) catalysts, such as $Rh_2(TPA)_4$ (entry 2), $Rh_2(TFA)_4$ (entry 3), and $Rh_2(esp)_2$ (entry 4), did not improve the reaction efficiency. The reaction did not proceed in the absence of a rhodium catalyst (entry 5). Increasing the reaction temperature to 120 °C and 140 °C improved the yield to 53% (entry 6) and 62% (entry 7), respectively. The reproducibility was also improved, and the yield further increased to 74% by pre-stirring the acyl chloride and PINC in THF instead of toluene, due presumably to the higher solubility of PINC in THF. This reaction forges four covalent bonds, i.e., one C–Cl, one C–H, and two C–C bonds at the carbon center in a single step without atom loss from the reactant, demonstrating the inherent power of the SCAD reaction.[1] In these reactions, a stoichiometric amount of triphenylphosphine was also formed, thus confirming the fate of the cleaved phosphorus residue. SCAD product **2a** was

formed even in the absence of a rhodium catalyst at 140 °C (entry 8), which implies that a metal-free carbene can be generated thermally from the phosphazine intermediate at temperatures above 120 °C (for details, see the Supplementary Information). However, we used a rhodium catalyst for subsequent investigations because this generally provided the SCAD products in higher yield.

Table 1. Rh-catalyzed and thermal carbon-atom-doping reaction into acyl chloride 1a



$C_{10}H_{11}ClO$ **1a**

$C_{11}H_{11}ClO$ (±)-**2a**

entry	catalyst	temperature (ºC)	yield (%)[a]
1	$Rh_2(OAc)_4$	80	29
2	$Rh_2(TPA)_4$	80	1
3	$Rh_2(TFA)_4$	80	4
4	$Rh_2(esp)_2$	80	10
5	none	80	0
6	$Rh_2(OAc)_4$	120	53
7[b]	$Rh_2(OAc)_4$	140	62 (74)[c]
8[b]	none	140	58

[a]Reaction conditions: **1a** (0.20 mmol), PINC (0.20 mmol), toluene (1.0 mL) at room temperature for 1 h; catalyst (0.01 mmol), toluene (1.0 mL) at 80 °C for 20 h; NMR yield. [b]Xylene was used instead of toluene. [c]Pre-stirring **1a** and PINC in THF instead of toluene; isolated yield.

This SCAD reaction was successfully applied for the conversion of a diverse array of acyl chlorides into the corresponding α-chloro cyclic ketones (**Fig. 2**). Benzoyl chloride bearing cyclopentyl (**1b**), cyclohexyl (**1c**), cycloheptyl (**1d**), and xanthyl (**1e**) groups readily participated in this SCAD reaction to form the corresponding α-chloro cyclic ketones that bear various spiro rings. Not only C–H bonds in tertiary alkyl groups but also those in secondary (**1f**) and primary (**1g**, **1h**) alkyl groups participated in this reaction, enabling the synthesis of indanones with diverse substitution patterns. In the case of **1f**, the carbon-atom insertion occurred in a stereospecific manner to afford indanone **2f** as a single diastereomer. Regarding the substituent on the aromatic ring, chloro (**1h**), fluoro (**1j**), bromo (**1k**), and methoxy (**1l**) groups were compatible. Acyl chlorides with heteroaryl (**1m**) and π-extended aryl (**1n**) groups also underwent the SCAD reaction successfully. In addition, this SCAD reaction was also applicable to the annulation of aliphatic acyl chlorides to yield multi-substituted cyclopentenone derivatives, such as **2p**. The method also enabled the synthesis of six-membered cyclic ketones, as exemplified by **2p**, further demonstrating its versatility in accessing diverse scaffolds.

The α-chloro cyclic ketones synthesized by the SCAD reaction serve as versatile intermediates for producing an array of value-added compounds. For example, the α-chloro group in **2** can be used for the introduction of different functional groups via nucleophilic substitution (*e.g.*, thiolation to give **3a**) or reductive radical functionalization (*e.g.*, reductive trifluoromethylation to give **4a**).[32] The α-C–H bond in **2** can also be functionalized via an enolate

intermediate without loss of the chloro moiety, thereby generating quaternary stereocenters, as exemplified by the formation of **5a**.[33,34] Notably, the enantioselective α-C–H bond functionalization of SCAD product **2h** was achieved via a chiral zinc complex-catalyzed Mannich reaction,[35] resulting in the formation of enantioenriched (–)-**6h**. Furthermore, the asymmetric transfer hydrogenation employing a Noyori–Ikariya-type ruthenium catalyst under dynamic kinetic-resolution conditions[36] produced chlorohydrin (+)-**7h** in an enantiopure form. These SCAD/enantioconvergent functionalization strategies facilitate the straightforward construction of a chiral carbon center by the enantioselective formation of four covalent bonds at a single carbon atom.

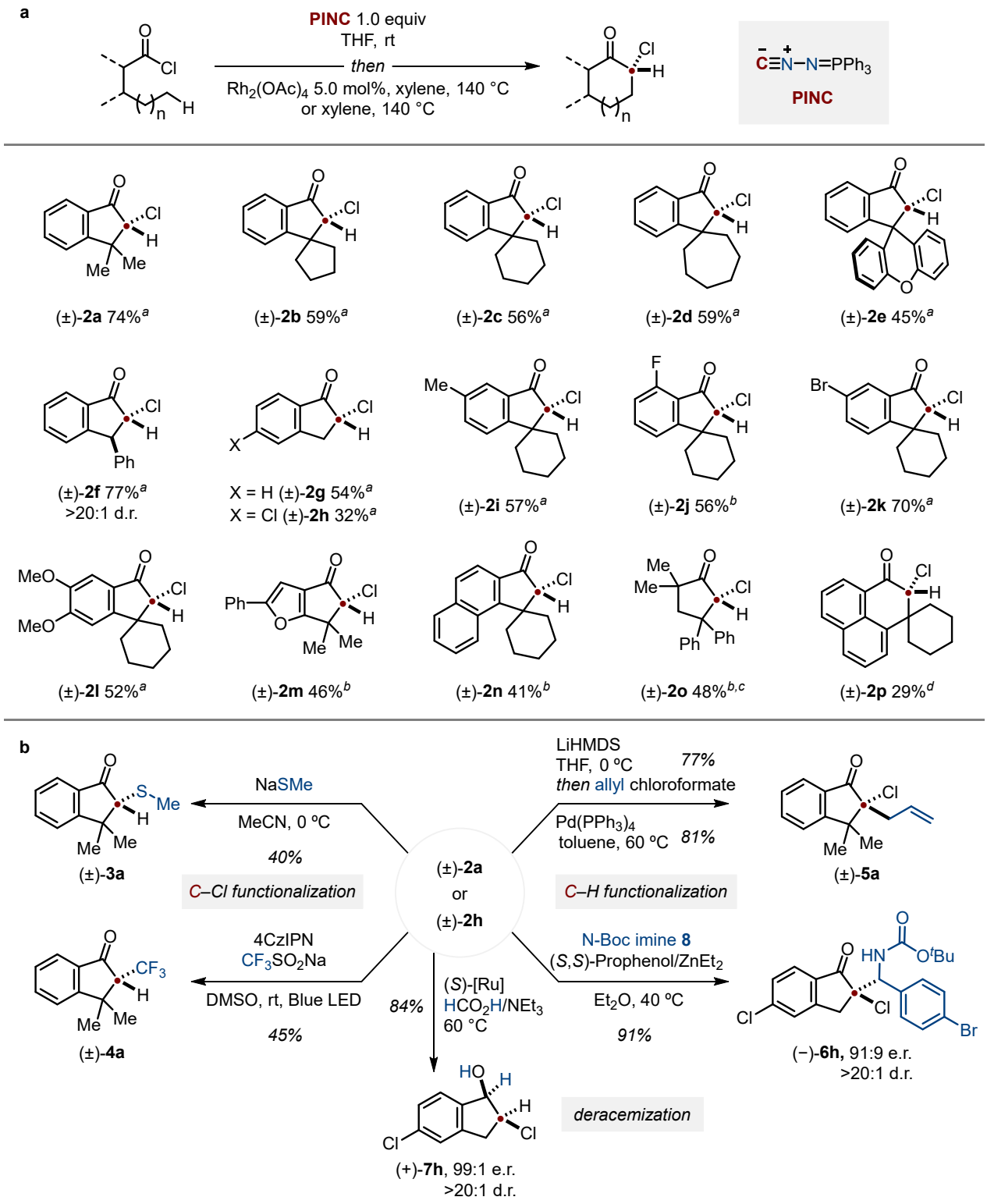


Fig. 2. Scope of the SCAD reaction of acyl chlorides using PINC.

[a]Reaction conditions: acyl chloride (0.20 mmol), PINC (0.20 mmol), THF (1.0 mL), room temperature, 1 h; $Rh_2(OAc)_4$ (0.01 mmol), xylene (1.0 mL), 140 °C, 20 h; isolated yield.

[b]Reaction was performed in the absence of $Rh_2(OAc)_4$; [c]NMR yield; [d]Pre-stirring was performed at 60 °C for 20 h; (*S*)-[Ru] = RuCl[(*S*,*S*)-Tsdpen](*p*-cymene).

A plausible mechanism for this reaction is illustrated in **Fig. 3a**. The reaction begins with the insertion of the isocyano moiety of PINC into the C–Cl bond of the acyl chloride to produce phosphazine intermediate **int-I**. This intermediate is activated by a rhodium(II) catalyst to generate rhodium carbene **Int-II** with concomitant release of dinitrogen and triphenylphosphine. Subsequently, rhodium carbene **Int-II** inserts into the intramolecular C–H bond to yield the homologated α-chloro ketone. Several mechanistic studies were conducted to test the feasibility of the proposed mechanism. When the reaction of **1a** was performed using PINC labeled with ^{13}C at the isocyano carbon (PINC-^{13}C), the resulting product contained ^{13}C at the α-position of the ketone, as confirmed by ^{13}C NMR spectroscopy (**Fig. 3b**). This result unequivocally proves that PINC acts as the carbon-atom source. Moreover, this protocol also serves as a useful method for the core-labeling of cyclic ketones.[37] Next, the key phosphazine intermediate was successfully isolated. The reaction of acyl chloride **1a** with PINC in THF at room temperature afforded a white solid precipitate, which was subjected to a single-crystal X-ray diffraction analysis, revealing the structure of phosphazine intermediate **9a** (**Fig. 3c**). We confirmed that **9a** was converted to **2a** under the rhodium-catalyzed conditions described above, demonstrating that the reaction proceed via phosphazine **7a** as an intermediate.

Density-functional-theory (DFT) calculations were carried out to gain insights into the carbene-transfer process. Two pathways were considered for the formation of the rhodium–carbene species from the phosphazine (**Fig. 3d**). One pathway involves the direct reaction of phosphazine with the rhodium complex to form intermediate **A**, which subsequently eliminates triphenylphosphine and dinitrogen to form the rhodium–carbene (path A). The second pathway consists of the thermal dissociation of triphenylphosphine from the phosphazine to generate a diazoalkane[38], followed by its decomposition to the rhodium–carbene species via release of dinitrogen from intermediate **B** (path B). The calculation results revealed that a stable rhodium–phosphazine adduct **A** was not formed, whereas stable rhodium–diazoalkane adduct **B** was observed. We also conducted relaxed-scan calculations using acetyl derivatives as a model substrate, in which the potential-energy surface was calculated by progressively decreasing the distance (in 0.05 Å increments) between the Rh and C atoms (**Fig. 3e**). The free energy of the rhodium–diazoalkane adduct decreases with decreasing Rh–C bond distance. In contrast, the rhodium–phosphazine species proved to be unstable, whereby the potential energy increasing upon shortening the Rh–C bond. These results indicate that the generation of the rhodium–carbene most likely proceeds through path B rather than path A.

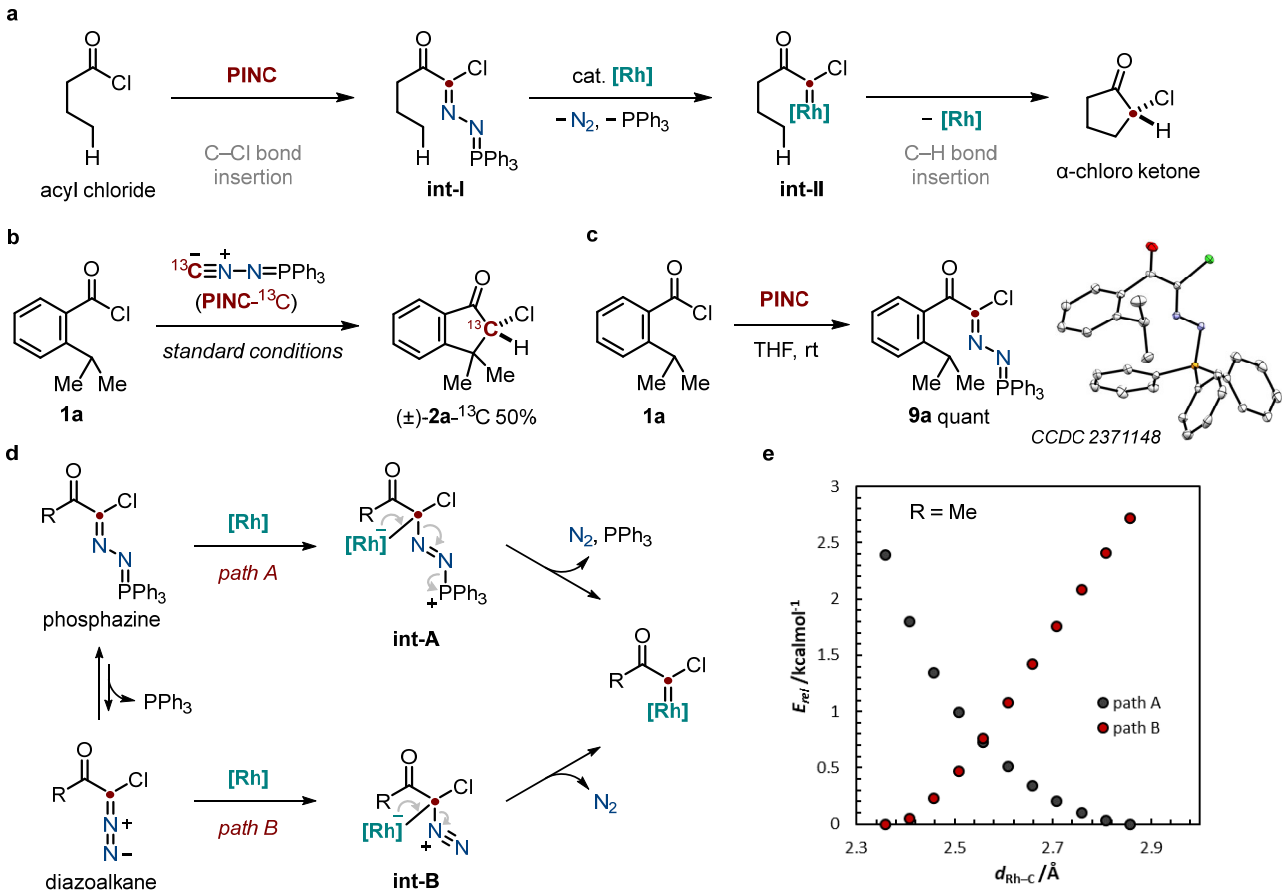


Fig. 3. Mechanistic studies.

a, Generation of stereocenters by single-carbon-atom doping using PINC. **b**, ^{13}C-Labeling experiment. **c**, Isolation of a phosphazine intermediate. **d**, Mechanism for the generation of a rhodium–carbene species. **e**, Relaxed-scan calculations of rhodium–carbon bonds using acetyl derivatives; [Rh] = $Rh_2(OAc)_4$.

In summary, we have disclosed a single-carbon-atom insertion reaction to generate chiral centers, a conceptually novel method for the construction of molecular skeletons. A key aspect of this study is the use of PINC as an atomic carbon equivalent in synthetic organic reactions. This protocol enables the formation of four distinct covalent bonds at a carbon center in a single step, thereby providing

the maximum increase in molecular complexity. This method is of synthetic value as an efficient tool for the straightforward conversion of a range of acyl chlorides, which are readily accessible from ubiquitous carboxylic acids, to homologated α-chloro cyclic ketones with the concomitant generation of new stereocenters in a single step. We anticipate that this SCAD approach will serve as a powerful tool for synthesizing a library of complex molecules with potential applications in various fields and will provide a solid framework for the future development of reactions involving atomic-carbon equivalents.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers JP22K20532 (H.F.) in Research Activity Start-up, JP23K13747 (H.F.) in Early-Career Scientists, JP24H02206 (M.T.) and JP24H02207 (M.T.) in Transformative Research Areas (A) JP24A202 Integrated Science of Synthesis by Chemical Structure Reprogramming (SReP) from MEXT, and TOBE MAKI Foundation (23-JA-008) (H.F.). The authors thank Mr. Satoshi Ogawa, Mr. Ryota Shiraki, Mr. Tomoya Emmei, and Mr. Takayuki Enomoto for the synthesis of acyl chlorides, and Mr. Hikaru Noguchi for HPLC analysis of **6h** and **7h**. We also thank the Instrumental Analysis Center, Graduate School of Engineering, Osaka University, for HRMS analysis.

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