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ORGANIC CHEMISTRY

A general alkyl-alkyl cross-coupling enabled by redox-active esters and alkylzinc reagents

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Alkyl carboxylic acids are ubiquitous in all facets of chemical science, from natural products to polymers, and represent an ideal starting material with which to forge new connections. This study demonstrates how the same activating principles used for decades to make simple C–N (amide) bonds from carboxylic acids with loss of water can be used to make C–C bonds through coupling with dialkylzinc reagents and loss of carbon dioxide. This disconnection strategy benefits from the use of a simple, inexpensive nickel catalyst and exhibits a remarkably broad scope across a range of substrates (>70 examples).

The heart of chemical synthesis relies on forging new C–C bonds, with the evolution and advancement of the field being easily correlated to new developments on this front. For example, pioneering work on the cross-coupling of halogenated aromatic or vinylic (sp^2) systems (Heck, Suzuki, Negishi, and Stille) has transformed the practice of organic synthesis (*1*). Similarly, a general and practical approach to C(sp^3)–C(sp^3) variants would have the potential to open up new vistas in retrosynthetic analysis. Indeed, such transformations have been on organic chemists' wish list for well over a century (*2*, *3*). Historically, alkyl-alkyl transition metal–catalyzed cross-coupling reactions have been difficult to accomplish, but exam-

ples can be traced to the early work of Kharasch in the 1950s (*4*), followed by Noller (*5*, *6*) and Kochi and Tamura (*7*, *8*) in the 1960s to more recent work from the groups of Suzuki (*9*), Fu (*10*), Knochel (*11*), Kambe (*12*), Oshima (*13*), and many others (*14*). Thus far, the vast majority of approaches to this problem have involved the coupling of alkyl halides (or related species) to organometallic reagents (*15–18*). However, the limited availability, perceived instability, and frequent toxicity of alkyl halides has perhaps prevented the area of alkyl cross-coupling from blossoming. If one only considers convenience, stability, and availability as desired attributes in a functional group for such a coupling, the carboxylic acid reigns supreme (Fig. 1A). Alkyl carboxylic acids are ubiquitous in every aspect of chemistry and can be readily found in medicines, materials, and natural products and in the pages of commercial chemical supplier catalogs. They are a stable functional group, nontoxic, and eminently diversifiable owing to the field of combinatorial chemistry, in which they are the "workhorse" building block. Although

certain carboxylic acids have already been demonstrated to engage in cross-coupling reactions (*19*), the use of alkyl carboxylic acids in alkyl-alkyl cross-coupling remains elusive.

Carboxylic acids can be primed for reaction through a process known as activation (such as formation of an active ester, –OA*), dating back to the classic work of Sheehan in the synthesis of penicillin (*20*). Once activated, a gateway opens to access a myriad of related functional groups such as amides, ketones, esters, or alcohols via addition of a nucleophile or alternative oxidation states by the formal addition of hydrogen. In this Report, we present a broadly useful transform that is able to forge C(sp^3)–C(sp^3) bonds via this age-old activation process.

We recently reported a Ni-catalyzed decarboxylative cross-coupling of alkyl carboxylic acids with arylzinc reagents to forge C(sp^3)–C(sp^2) bonds by repurposing activating methods more typically associated with amide-bond formation (*21*, *22*). Certain active esters [such as HOAt (*N*-hydroxy-7-azabenzotriazole), HOBt (*N*-hydroxybenzotriazole), NHPI (*N*-hydroxyphthalimide), and TCNHPI (*N*-hydroxytetrachlorophthalimide)] can accept an electron to trigger an ensuing cascade of events that liberates CO$_2$ from the parent alkyl group (Alk$_1$); such esters (*23*) are termed redox-active (*21*, *22*). The application of this chemistry to sp^3-sp^3 C–C bond formation poses a number of substantial challenges, with potentially unproductive pathways far outnumbering the desired reaction (Fig. 1B) (*15–18*). For example, β-hydride elimination from the alkyl metal intermediates, dimerization of the organometallic reagent, reduction of the electrophile, and proto-demetallation are problems that also historically plague traditional C(sp^3)–C(sp^3) cross-coupling reactions. With a redox-active ester as an electrophile, oxidative addition of low-valent Ni into the activated C–O bond could result in the formation of an acyl-Ni complex, which could reductively eliminate and ultimately result in undesired ketone by-products. These fundamental challenges notwithstanding, we describe a straightforward solution to this problem.

Dialkylzinc reagents were chosen for the organometallic coupling partner because of their

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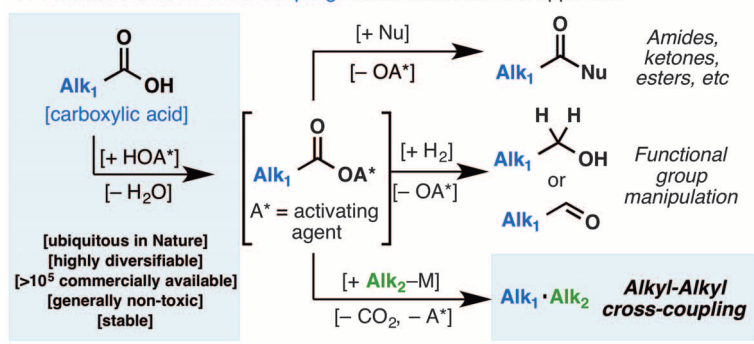
ease of preparation from the parent alkyl halide, high functional group tolerance, and their propensity for facile transmetallation. Over the years, mono and dialkylzinc reagents have been shown to be viable cross-coupling partners in Negishi cross-coupling through use of alkyl halides, and related species with Ni-based catalysts (*16, 18*). Thus, an exploration of the coupling of redox-active esters **1a** and **1b** (Fig. 1C) with diethylzinc (**2**) was undertaken. An exhaustive screen of ligands, including bipy (**L1**, entries 1 and 2) and di-*t*Bubipy (**L2**, entries 3 and 4) showed that the electron-deficient TCNHPI ester **1b** with **L2** afforded the desired product in 84% isolated yield (entry 4). TCNHPI can be easily prepared from tetrachlorophthalic anhydride, an industrial nontoxic flame retardant [~$48/kg from VWR (Radnor, PA)] (*24*), and it has recently been commercialized by Aldrich (catalog no. ALD00564). Additional screening of ligands based on phenanthroline (**L3** to **L5**, entries 5 to 7) and terpyridine (**L6** and **L7**, entries 8 and 9) did not improve the yield and were in many cases detrimental. When the reaction was performed in the absence of NiCl₂·glyme, the desired product was not formed (entry 10).

With an optimized set of conditions in hand, we explored the scope of this new reaction and found it to be remarkably broad. First, we explored a range of 16 dialkylzinc reagents (Fig. 2A) with piperidine esters **1a** and **1b**. With the exception of dibenzylzinc reagents, all primary dialkylzinc reagents explored were viable in the cross-coupling. From dimethylzinc (**4**) and simple alkyl chains (**3**, **5**, **6**, **9**, and **10**) to derivatives harboring olefins (**7** and **8**), alkynes (**11** and **12**), acetals (**16**), ethers (**14** and **15**), and even alkyl halides (**13**) were tolerated. The reaction was easily run on a gram scale (as exemplified by **3**) and could even be used to produce isotopically labeled piperidine **4**-^{13}C. In addition to **3**, this example highlights that a lower loading of dialkylzinc reagent (0.5 equivalent) could be used when a highly valuable alkyl group is involved. Secondary alkylzinc reagents such as cyclopropylzinc could also be accommodated, as exemplified by **17**.
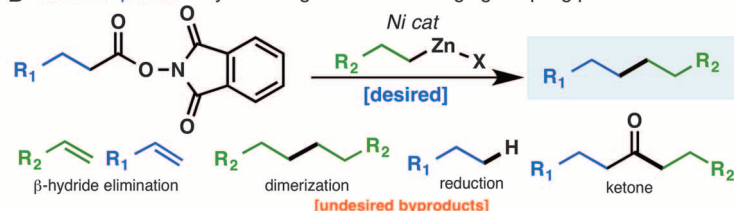
Next, we explored 15 secondary alkyl carboxylic acids (Fig. 2B). Cyclic (**18**, **19**, and **21**), heterocyclic (**20**, **22**, **26** to **28**, and **31**), bridging (**25**), indane (**24**), acyclic (**29**), and even fluorinated (**23** and **30**) alkyl carboxylic acids were all viable coupling partners. Substrates **30** through **32** are particularly striking and open the door to access a vast array of fluorinated building blocks and optically pure tartrate-derived materials. Many of these products would be either inconvenient or chemically intractable to access from the corresponding alkyl halide starting materials (**27**, **28**, **30**, **31**, and **32**).

Primary alkyl carboxylic acids, representing some of the most inexpensive organic materials available, could also be readily used. Of the eight examples depicted in Fig. 2C, most notable are the use of mono-methyladipic acid (**34**; 2.5 billion kg of adipic acid are produced per year) (*25*), a pyridine-containing substrate (**36**), and a polyfluorinated acid (**40**). Tertiary alkyl carboxylic acids (Fig. 2D) could also be
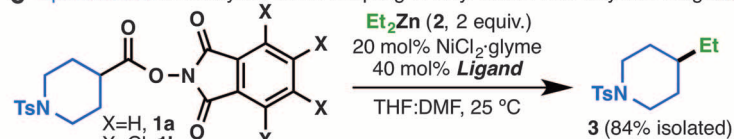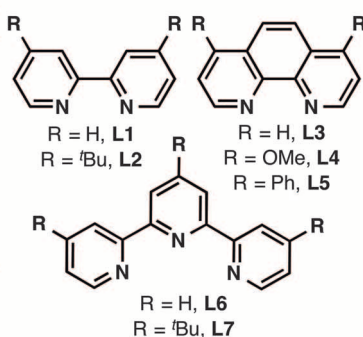

Fig. 1. Development of a Ni-catalyzed decarboxylative alkyl-alkyl cross-coupling. (**A**) Activation of carboxylic acids in organic synthesis. (**B**) Potential side products. (**C**) Ni-catalyzed cross-coupling of redox-active esters and alkylzinc reagents.

used to generate quaternary centers. Although limited in scope, bridgehead systems such as adamantane (**41** and **42**) or bicyclo[2.2.2]octane (**43**) smoothly participated in the cross-coupling. The preparation of such bridged systems is traditionally performed via a three-step Wittig/hydrogenation sequence from the parent aldehyde (*26*). Although pivalic acid (**44**) did not couple in this context, its failure led to a distinct type of coupling (vide infra).

Simple primary and secondary α-oxyacids could also be used (Fig. 2E, **45** to **49**), representing a practical route to form ethers that would not be possible by using alkyl halides. The classic Williamson ether synthesis is still the staple transform for constructing ethers, but in many cases, the S$_N$2 reaction is either sluggish or unworkable because of steric hindrance. This cross-coupling opens a distinct disconnection

strategy for ether synthesis by using easily obtained α-oxyacids (either commercial or derived via alkylation with bromoacetic acid) as progenitors for a virtually limitless array of new ethers.

Redox-active esters enable the cross-coupling of alkylzinc reagents with high chemoselectivity (Fig. 2F) even in complex contexts, reminiscent of that exhibited in classic amide-bond formation. For example, a variety of sensitive fatty acids reacted smoothly to give the corresponding alkyl chains (**50**, **57**, and **58**) without olefin isomerization or epoxide opening. Naturally occurring carboxylic acids such as biotin, cholic acid, and dehydrocholic acid were also amenable to alkylation (**54** to **56**). Pharmaceuticals and agrochemicals such as pregabalin, 2,4-D, cetirizine, and atorvastatin smoothly reacted with alkylzinc reagents to afford good yields of the alkyl coupling products (**51** to **53** and **59**).
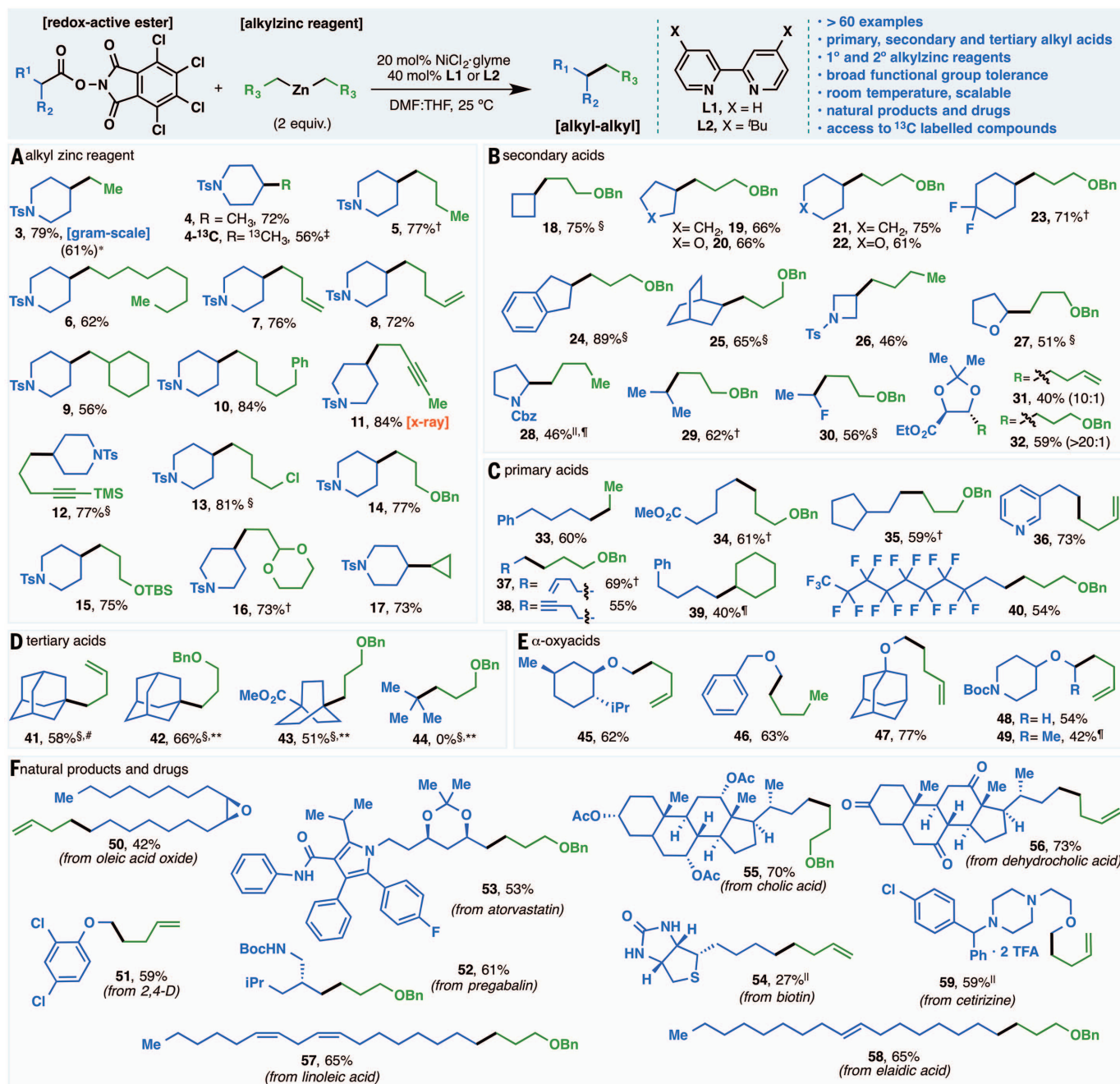
Fig. 2. Scope of the Ni-catalyzed decarboxylative alkyl-alkyl cross-coupling. (**A**) Alkyl zinc reagent. (**B**) Secondary acids. (**C**) Primary acids. (**D**) Tertiary acids. (**E**) α-oxyacids. (**F**) Natural products and drugs. Standard conditions were redox-active ester (1 eq), dialkylzinc reagent (2 eq), NiCl₂·glyme (20 mol %), L2 (40 mol %), THF:DMF, 25°C, 8–14 hours. THF, tetrahydrofuran; DMF, dimethylformamide.

In perhaps the most impressive feat of chemoselectivity for this methodology, the cross-coupling could be conducted on solid phase in the context of peptide synthesis. On-resin coupling of dialkylzinc reagents to proteinogenic amino acids (both side-chain and α-carboxylic acids) facilitates the late-stage introduction of designer amino acids, which would otherwise require de novo synthesis. Valuable synthetic handles including alkenes (**60** and **62**) and alkyl ethers (**63**) could be readily incorporated into resin-bound substrates (Fig. 3), and the installation of an aliphatic side chain (**61**) provides a facile approach to the modulation of peptide lipophilicity (27). Double activation of a peptide substrate bearing both Asp and Glu residues also enables the simultaneous introduction of multiple nonproteinogenic side chains (**64** and **65**). This convenient approach to diversely functionalized peptides provides a tool for the construction of therapeutic peptide leads and stapled peptides (28, 29) and for applications in bioconjugation (30).

Returning to the limitations posed by tertiary systems, mechanistic studies involving 5-exo-trig cyclization, racemization, and ring-strain opening experiments clearly point to the radical nature of this reaction (figs. S1 to S3). We reasoned that the steric limitations encountered could be overcome by engaging these reactive species with a radical trap that could subsequently combine
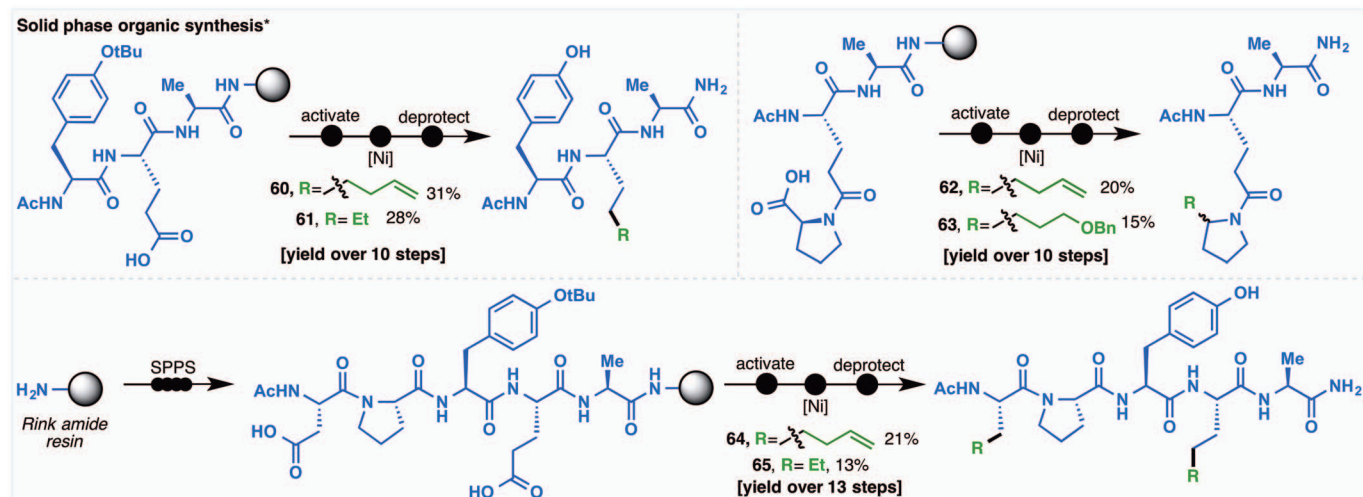
Fig. 3. Ni-catalyzed decarboxylative alkyl-alkyl coupling in solid-phase synthesis. Experimental details are provided in the supplementary materials.
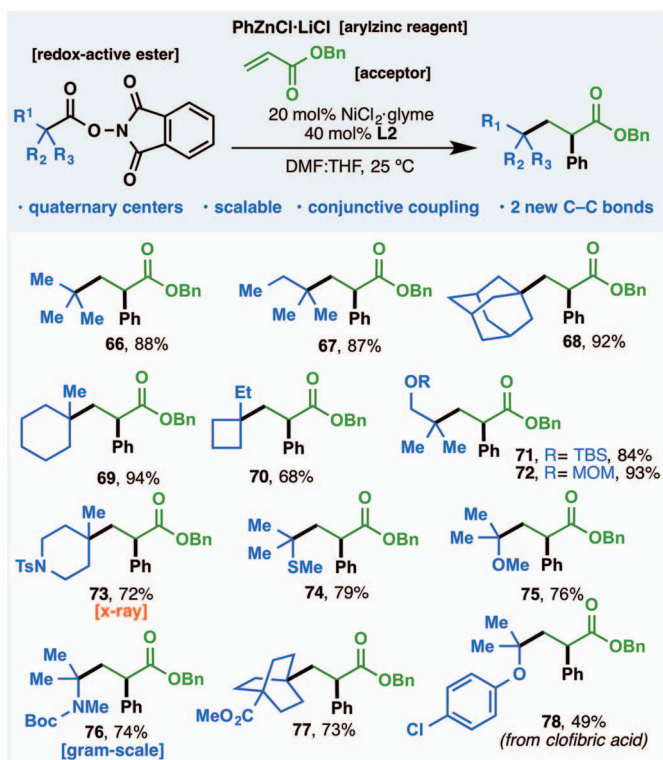
Fig. 4. Scope of the Ni-catalyzed three-component conjunctive cross-coupling. Standard conditions were redox-active ester (1 eq), acceptor (2.5 eq), PhZnCl·LiCl complex (3 eq), NiCl₂·glyme (20 mol %), **L2** (40 mol %), THF:DMF, 25°C, 8 hours. All the products shown were obtained in racemic form.

with an organozinc reagent. Remarkably, such a conjunctive cross-coupling could be realized, as shown in Fig. 4 (*31*). By using benzylacrylate as a radical trap and phenylzinc as a coupling partner, 13 different tertiary alkyl carboxylic acids could be smoothly engaged in a three-component cross-coupling to generate useful building blocks that would be extremely difficult to access in any other way (**66** to **78**). This reaction is scalable (as exemplified by **76**), generates two new C–C bonds, and is a rare example of a multicomponent

cross-coupling reaction that forms quaternary centers in high yield. In addition to the broad functional group tolerance [heteroatom containing substrates, Boc (*tert*-butoxycarbonyl), TBS (*tert*-butyldimethylsilyl), and MOM (methoxymethyl) groups], this reaction features the use of electronically different radical precursors, such as α-heteroatom acids or electronically unbiased and neutral alkyl acids such as pivalic acid.

As with any methodology, there are obvious drawbacks. For example, the atom-economy is

low because of the use of an activating group. We do note, however, that such considerations are ignored in the enormous field of peptide chemistry, in which expensive coupling agents are regularly used to make a simple amide bond (*32*). The activating agents used here, NHPI ($19.5/mol) and TCNHPI, are both commercially available and derived from cheap, readily available materials and open a gateway of reactivity heretofore inaccessible. The use of two equivalents of the dialkylzinc reagent is another disadvantage in cases in which the zinc-derived fragment is valuable. However, as shown in **3** and **4**-¹³**C**, the reaction proceeds with workable yields when simply equimolar amounts of alkylzinc reagents and 5 mole percent (mol %) catalyst were used.

The data presented here suggests that the advantages associated with this method far outweigh its limitations. Without exception, the carboxylic acids used represent the most inexpensive sources of these carbon frameworks; all of these were commercially available. In contrast, in the cases in which an alkyl halide would be chemically stable, only a handful are commercially available. Conceptually, carboxylic acids can perhaps be considered nature's version of a boronic acid. For the past seven decades, these ubiquitous functional groups have usually been dehydrated with incorporation of a nucleophile (such as an amine to make an amide). This method extends the native diversification of this functional group (*33*) to allow for the addition of a new carbon framework via extrusion of CO₂. As such, it is anticipated that this technique will greatly expand planning options in retrosynthetic analysis.

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APPLIED PHYSICS

On-chip noninterference angular momentum multiplexing of broadband light

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Angular momentum division has emerged as a physically orthogonal multiplexing method in high-capacity optical information technologies. However, the typical bulky elements used for information retrieval from the overall diffracted field, based on the interference method, impose a fundamental limit toward realizing on-chip multiplexing. We demonstrate noninterference angular momentum multiplexing by using a mode-sorting nanoring aperture with a chip-scale footprint as small as 4.2 micrometers by 4.2 micrometers, where nanoring slits exhibit a distinctive outcoupling efficiency on tightly confined plasmonic modes. The nonresonant mode-sorting sensitivity and scalability of our approach enable on-chip parallel multiplexing over a bandwidth of 150 nanometers in the visible wavelength range. The results offer the possibility of ultrahigh-capacity and miniaturized nanophotonic devices harnessing angular momentum division.

I n the age of information technology, optical multiplexing using physical dimensions of light, including space (*1*), frequency (*2*), brightness (*3*), color (*1*, *4*), polarization (*1*, *5*, *6*), mode (*7*), and lifetime (*8*), has played a crucial role in high-definition displaying (*3–5*), high-capacity data storage (*1*, *6*), high-speed communications (*7*), and highly sensitive biological sensing (*8*). As one of the most fundamental physical properties in both classical and quantum optics, angular momentum (AM) of light—including spin angular momentum (SAM) possessed by circularly polarized light and orbital angular momentum (OAM) manifested by the helical wavefront of light—has emerged as a physically orthogonal multiplexing approach to high-capacity optical communications ranging from free-space (*9*) to compact optical fibers (*10*). However, macro-scale interference-based detection methods through hologram-coding (*9*, *10*) or phase-shifting (*11*, *12*) of AM-carrying beams have imposed a fundamental physical limit for realizing such a principle at a chip-scale footprint.

The advance of strong light-confinement nanophotonic approaches has been a major propellant of miniaturized optical circuits to harness AM of light. The chip-scale generation and transmission of AM-carrying beams on silicon-integrated circuits have been realized through whispering gallery mode resonators (*13*) and resonant microring fibers (*10*). However, these approaches are resonant in nature, leading to a narrow bandwidth down to several nanometers. Surface plasmon polaritons (SPPs) capable of strong light confinements have long been pursued to overcome the size limitation of nanophotonic devices and, hence, potentially facilitate the chip-scale multiplexing of SAM through the SAM-distinguishing nanostructures (*14–18*). Even though the OAM generators mediated by SPPs have been demonstrated either through digitalized metasurfaces with a helical phase (*19*) or geometric metasurfaces based on spin-orbit interaction (*20*), the extrinsic nature of OAM (*21*) with helical wavefronts restricts its detection to a phase-sensitive interference-based method through a holographic metasurface (*22*), which inevitably degrades the perceptive devices for on-chip applications.

The concept of our on-chip noninterference AM multiplexing of broadband light is illustrated in Fig. 1. Without losing the generality, coaxially superposed AM-carrying beams with four selected AM modes [$l_0 = -4$, $s = -1$ (AM$_1$); $l_0 = -2$, $s = -1$ (AM$_2$); $l_0 = +2$, $s = +1$ (AM$_3$); and $l_0 = +4$, $s = +1$ (AM$_4$); where l_0 and s are the modal indices for OAM and SAM, respectively (Fig. 1A)] propagate through a nanoring aperture (NRA) multiplexing unit that consists of shallow nanogrooves and the spatially shifted mode-sorting nanoring slits of different sizes (Fig. 1B and fig. S1A). The nanogroove structures act as the metal-dielectric interfaces to convert the AM modes carried by photons into SPPs and to spatially route the excited plasmonic AM modes to the locations of the nanoring slits. A set of AM-carrying beams of $l_0 = \pm1$, ±2, ±3, ±4 and $s = \pm1$ (fig. S2) can be adopted to excite a range of plasmonic AM modes (determined by total AM $L = l_0 + s + l_s$, where l_s is the geometrical topological charge arising from the nanogrooves), with a distinguished spatial separability from

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Editor's Summary

Carbon links without helpful neighbors

It's an irony of modern organic chemistry that the simplest-looking carbon-carbon bonds are often the hardest to make. Most reactions owe their efficiency to neighboring double bonds or oxygen and nitrogen atoms that linger in the products. Qin *et al.* now present a broadly applicable protocol for making C-C bonds in the absence of such surrounding help. The nickel-catalyzed process couples a zinc-activated carbon center to an ester that's poised to lose CO_2. The ready availability of numerous carboxylic acids (which are easily converted to esters) contributes to the reaction's versatility.

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