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Nickel(0)-Catalyzed Enantioselective [3+2] Annulation of Cyclopropenones and α,β-Unsaturated Ketones/Imines

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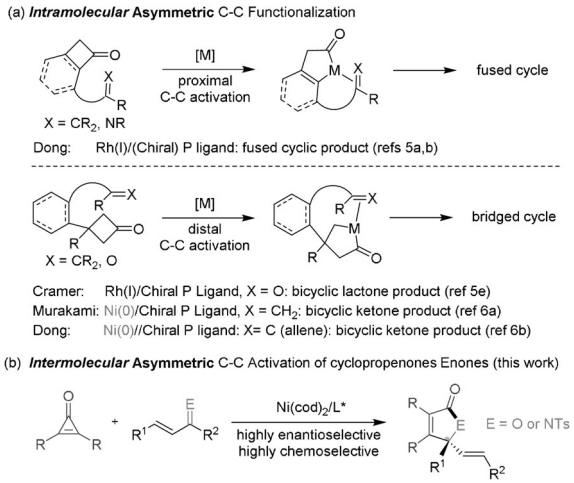
Dedicated to Prof. Li-Xin Dai on the occasion of his 95th birthday

Abstract: *Ni^0-catalyzed chemo- and enantioselective [3+2] cycloaddition of cyclopropenones and α,β-unsaturated ketones/imines is described. This reaction integrates C–C bond cleavage of cyclopropenones and enantioselective functionalization by carbonyl/imine group, offering a mild approach to γ-alkenyl butenolides and lactams in excellent enantioselectivity (88–98 % ee) through intermolecular C–C activation.*

In the past decade, catalytic C–C bond activation has received increasing attention, allowing facile reconstruction and reorganization of carbon skeletons.[1] The C–C bond activation is typically fulfilled through two elementary, non-radical reaction pathways, namely the C–C oxidative addition and β-carbon elimination.[1] Despite the advancement, the majority of reported systems rely on noble metal catalysis.[2–4] In addition, the development of asymmetric catalytic C–C bond activation systems severely lags behind,[5,6] even for activated C–C bonds, and previously reported systems are predominantly initiated by chelation-assisted C–C bond oxidative addition, followed by intramolecular insertion into a C=C, C=O, or C=N bond (Schemes 1 a).

Despite the tremendous progress, integration of base metals and asymmetric C–C functionalization would significantly increase the competitiveness and sustainability of C–C activation. Ni^0 catalysts are known to activate C–C bonds,[6,7] but enantioselective systems remain underexplored.[6] Two notable examples have been reported by Murakami[6a] and by Dong[6b] on asymmetric intramolecular insertion of alkene or allene into a cyclobutanone (Scheme 1 a). However, Ni-catalyzed intermolecular asymmetric C–C activation systems are highly rare. Besides cyclobutanones, strained cyclopropenones are also prominent reagents in cycloaddition reactions dated back to 1972.[8] Both organo-[9] and metal-catalyzed[10–12] activation of the C–C single bonds of cyclopropenones has drawn increasing attention with different π-bonds being the coupling partner. Nevertheless, only racemic couplings have been disclosed by metal catalysis. This limitation is likely related to the narrow arsenal of coupling reagents in delivering chiral centers with high efficiency. We now report mild and enantioselective formal [3+2] annulation between cyclopropenones and enones/imines (Scheme 1 b), where the C=O or C=N group participated chemoselectively to afford γ-alkenylbutenolides or lactams, respectively (Scheme 1 c). γ-Butenolides are prominent motifs in bioactive natural products.[13] However, to the best of our knowledge, only limited examples of their enantioselective synthesis have been reported.[14]



Scheme 1. Metal-catalyzed (enantioselctive) C–C functionalization of strained rings.

Unlike in intramolecular coupling systems, the issues of both chemo- and enantioselectivity arise when a multifunctional π component such as enone is used in intermolecular couplings. Previously, the C=C bond of enones participated preferentially in various coupling reactions.[7d–f] This is especially the case for low-valent metal catalysis where propensity of insertion into a polar C=O group is reduced due to less polarized M–C bonds. However, insertion of C=O might be facilitated by the conjugate C=C bond. To explore the chemoselectivity, we selected diphenylcyclopropenone (**1a**) and enone **2a** as model substrates (Table 1). Our initial attempts using a $Ni(cod)_2$/Pybox **L1** catalyst afforded the

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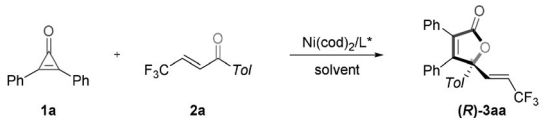
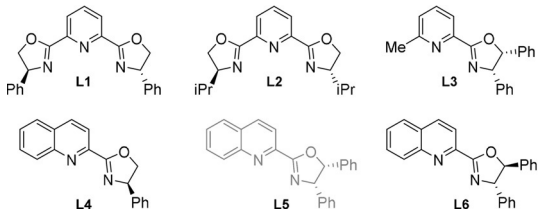
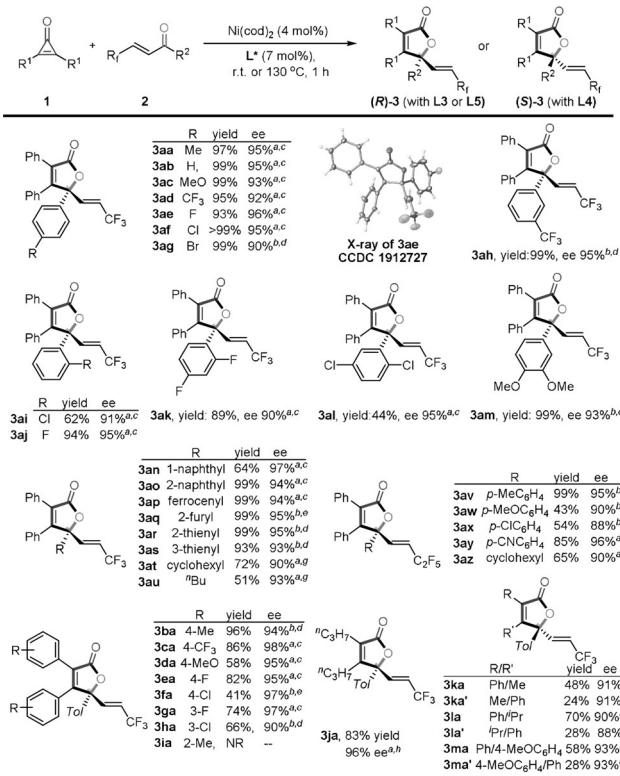
Table 1: Optimization of reaction conditions[a]



Entry	Catalyst (mol %)	L* (mol %)	Solvent	T (°C)	Yield (%)	ee (%)
1	$Ni(cod)_2$ (9)	**L1** (14)	EtOH	130	37	75
2	$Ni(cod)_2$ (9)	**L1** (14)	DCE	130	trace	--
3	$Ni(cod)_2$ (9)	**L1** (14)	DMF	130	52	50
4	$Ni(cod)_2$ (9)	**L1** (14)	dioxane	130	75	84
5	$Ni(cod)_2$ (9)	**L1** (14)	toluene	130	88	87
6	$Ni(cod)_2$ (9)	**L2** (14)	toluene	130	39	37
7	$Ni(cod)_2$ (9)	**L3** (14)	toluene	130	93	87
8	$Ni(cod)_2$ (9)	**L4** (14)	toluene	130	79	-87
9	$Ni(cod)_2$ (9)	**L5** (14)	toluene	130	76	95
10	$Ni(cod)_2$ (9)	**L6** (14)	toluene	130	82	87
11	$Ni(cod)_2$ (4)	**L5** (7)	toluene	130	78	94
12	$Ni(cod)_2$ (4)	**L5** (7)	toluene	60	88	95
13	$Ni(cod)_2$ (4)	**L5** (7)	toluene	r.t.	98	95
14	$Ni(cod)_2$ (4)	**L5** (5)	toluene	r.t.	97	93
15	--	**L5** (7)	toluene	r.t.	0	--
16[b]	$Ni(cod)_2$ (0.1)	**L5** (0.18)	toluene	r.t.	44	95



[a] Reaction conditions: **1a** (0.2 mmol), enone **2a** (0.2 mmol), $Ni(cod)_2$, and chiral ligand in toluene (2.0 mL) for 1 h under Ar, yields of isolated products. The *ee* was determined by HPLC on a chiral stationary phase. [b] 48 h.



	R	yield	ee
3aa	Me	97%	95%[a,c]
3ab	H,	99%	95%[a,c]
3ac	MeO	99%	93%[a,c]
3ad	CF_3	95%	92%[a,c]
3ae	F	93%	96%[a,c]
3af	Cl	>99%	95%[a,c]
3ag	Br	99%	90%[b,d]

	R	yield	ee
3ai	Cl	62%	91%[a,c]
3aj	F	94%	95%[a,c]

	R	yield	ee
3an	1-naphthyl	64%	97%[a,c]
3ao	2-naphthyl	99%	94%[a,c]
3ap	ferrocenyl	99%	94%[a,c]
3aq	2-furyl	99%	95%[b,e]
3ar	2-thienyl	99%	95%[b,d]
3as	3-thienyl	93%	93%[b,d]
3at	cyclohexyl	72%	90%[a,g]
3au	^{n}Bu	51%	93%[a,g]

	R	yield	ee
3av	*p*-MeC_6H_4	99%	95%[b,d]
3aw	*p*-$MeOC_6H_4$	43%	90%[b,d]
3ax	*p*-ClC_6H_4	54%	88%[b,d]
3ay	*p*-CNC_6H_4	85%	96%[a,c]
3az	cyclohexyl	65%	90%[a,g]

	R	yield	ee
3ba	4-Me	96%	94%[b,d]
3ca	4-CF_3	86%	98%[a,c]
3da	4-MeO	58%	95%[a,c]
3ea	4-F	82%	95%[a,c]
3fa	4-Cl	41%	97%[b,e]
3ga	3-F	74%	97%[a,c]
3ha	3-Cl	66%,	90%[b,d]
3ia	2-Me,	NR	--

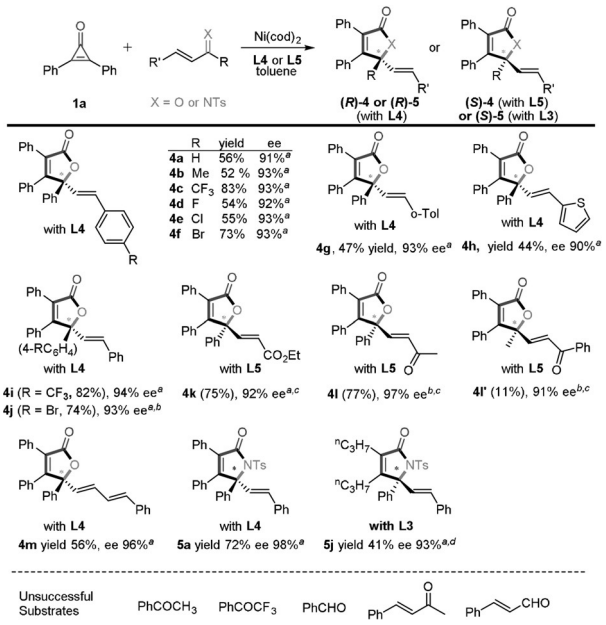
	R/R'	yield	ee
3ka	Ph/Me	48%	91%[a,f]
3ka'	Me/Ph	24%	91%[a,f]
3la	Ph/^{i}Pr	70%	90%[a,f]
3la'	^{i}Pr/Ph	28%	88%[a,f]
3ma	Ph/4-$MeOC_6H_4$	58%	93%[a,c]
3ma'	4-$MeOC_6H_4$/Ph	28%	93%[a,c]

Scheme 2. Scope of β-fluoroalkylenones in asymmetric [3+2] cycloaddition. [a] **1** (0.20 mmol), **2** (0.20 mmol), $Ni(cod)_2$ (0.008 mmol), and **L5** (0.014 mmol), in PhMe (2.0 mL) for 1 h. [b] **1** (0.20 mmol), **2** (0.24 mmol), $Ni(cod)_2$ (0.008 mmol), **L5** (0.014 mmol) in toluene (2.0 mL) for 1 h. [c] 25 °C. [d] 130 °C. [e]100 °C. [f] **L4**, 130 °C. [g] **L3** and 1,4-dioxane were used. [h] EtOH was used.

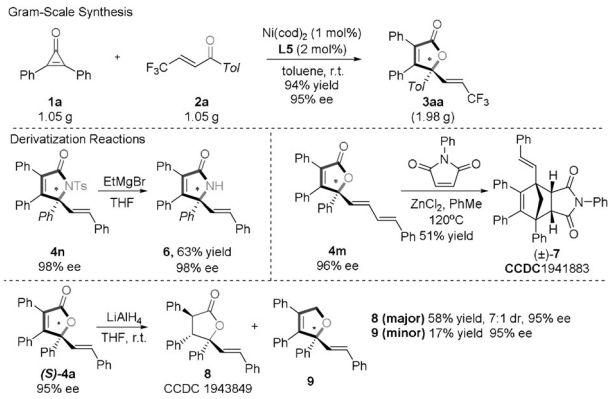
desired [3+2] cycloaddition product (*R*)-**3aa** in 37 % yield and 75 % *ee* in EtOH (entry 1), and no C=C insertion product was detected. Solvent screening indicated that toluene offered the best result (entries 1–5). Screening of ligand revealed that **L5** with *cis* vicinal diphenyl substituents in the oxazoline ring was highly efficient, providing (*R*)-**3aa** in 76 % yield and 95 % *ee* (entry 9). The absolute configuration of the product **3aa** was found to be dictated by that of the 5-position in the ligand (entries 8–10). Thus, employment of chiral ligand **L4** delivered the (*S*)-**3aa** product in high, complementary enantioselectivity (entry 8). Decreasing the temperature to 25 °C or lowering the catalyst loading resulted in excellent yield and enantioselectivity (entries 11–14). The reaction was highly efficient, and a TON of up to 440 was attained when the catalyst loading was reduced to 0.1 mol % (48 h, entry 16). Moreover, the catalyst could be used 4 times without loss of efficiency by introducing new batches of substrates (see Supporting Information).

Having identified the optimal conditions, we next explored the scope of this coupling system (Scheme 2). The reaction turned out to accommodate β-CF_3 enones bearing diverse electron-donating and electron-withdrawing groups at the *para* position of the benzene ring (93–99 % and 90–96 % *ee*). The reaction also worked well for *meta*- and *ortho*-substituted (**3ah–3am,** 44–99 % yield, 90–96 % *ee*) and for other (hetero)aryl-substituted enones (**3an–3as**) although slightly lower yields were isolated for several *ortho*-substituted aryl ketones (**3ai** and **3al**), possibly due to steric effects. Cyclohexyl- and *n*Bu-substituted enones also worked well on the premise of using **L3** as ligand in dioxane (**3at,** 71 % yield, 90 % *ee*, and **3au**, 51 % yield, 93 % *ee*, see Table S1 in the Supporting Information). Extension of the β-CF_3 group to -C_2F_5 was also successful (**3av–3az**, 88–96 % *ee*). Moreover, symmetrical diarylcyclopropenones bearing both electron-donating and electron-withdrawing groups at the *meta* and *para* position all coupled with excellent enantioselectivity (**3ba–3ha**, 41–96 % yield and 90–98 % *ee*). Besides diarylcyclopropononones, a dialkylcyclopropenone coupled with high yield and excellent enantioselectivity in EtOH (**3ja**, 83 % yield and 96 % *ee*, also see Table S2 in the Supporting Information). Nonsymmetrical cyclopropenones also proved viable, and high enantioselectivities were realized for each product although the regioselectivity was moderate (**3ka**/**3ka′, 3la**/**3la′,** and **3ma**/**3ma′**).

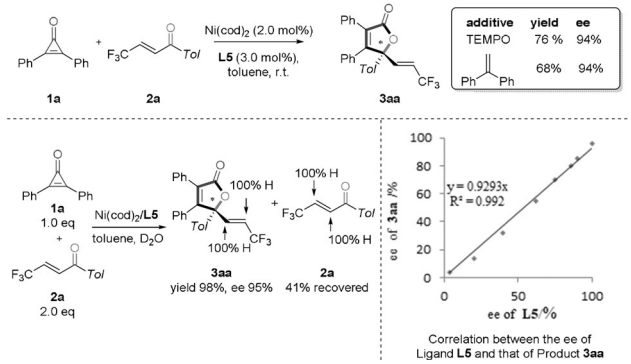
To better define the scope of this coupling system, the enone was extended to less reactive chalcones (Scheme 3) which had exhibited poor reactivity under our initially optimal conditions. To our delight, switching the **L5** to **L4** led to isolation of (*S*)-**4a** in 56 % yield and 91 % *ee.* Introduction of Me, halogen, and CF_3 into the *para* position



Scheme 3. Scope of other enones and α, β-unsaturated imines in [3+2] annulation. [a] Reaction conditions: **1** (0.2 mmol), acceptor **2** (0.24 mmol), $Ni(cod)_2$ (0.008 mmol), and **L4** (0.014 mmol) in toluene (2.0 mL) at 25 °C. for 24 h. [b]130 °C.[c] **L5** instead of **L4**. [d] **L3** and EtOH were used.



Scheme 4. Scale-up synthesis and derivatization.



Scheme 5. Mechanistic studies.

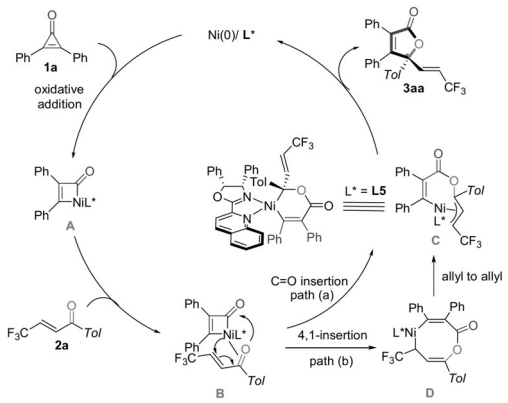
of the β-phenyl ring of the chalcone afforded the desired products in moderate to high yield and excellent *ee*. Similarly, electron-poor enones generally showed higher reactivity (**4a**–**4f**, 54–83% yield, 91–93% *ee*), and an *ortho*-substituted phenyl and a 2-thienyl group were also tolerated (**4g**, **4h**). As expected, employment of a β-EWG resulted in smooth coupling even using the **L5** ligand (**4k**, 75% yield and 92% *ee*). When (*E*)-1-phenylpent-2-ene-1,4-dione was employed in this reaction, the chemoselectivity was 7:1 (130 °C) favoring insertion of the benzoyl carbonyl group (**4l** and **4l′**). Of note, a dienone coupled smoothly in 56% yield and 96% *ee* (**4m**). To our delight, an imine substrate also worked well in this reaction, affording the corresponding lactam in excellent enantioselectivity (**5a** and **5j**). In contrast, acetophenone, $PhC(O)CF_3$, benzaldehyde, benzylideneacetone, and cinnamaldehyde all failed to undergo any coupling even under harsh conditions.

The coupling system turned out to be synthetically useful. The [3+2] coupling of **1a** and **2a** was readily scaled up to a gram-scale with 1 mol% catalyst loading, affording product (*R*)-**3aa** in excellent yield and enantioselectivity (Scheme 4). Deprotection of the Ts group in **4n** was achieved when treated with an alkyl Grignard reagent. The reaction of diene **4m** and a maleimide afforded a racemic tricyclic product through decarboxylation–Diels–Alder addition. $LiAlH_4$ reduction of (*S*)-**4a** at room temperature afforded a lactone with three contiguous chiral centers in moderate yield with retention of the enantiopurity, and a 2,5-dihydrofuran **9** was obtained as a minor product.

To gain insight into the reaction mechanism, preliminary studies were carried out (Scheme 5). The reaction of **1a** and **2a** was found to be essentially unaffected by TEMPO (2,2,6,6-tetramethyl-1-piperidyloxy) or 1,1-diphenylethylene, indicating an ionic instead of a radical reaction pathway (see Supporting Information). When D_2O was introduced to this coupling, no deuterium incorporation was detected in the product and the recovered starting material **2a**, which argues against a nickel hydride pathway. A linear correlation between the enantiomeric excesses of the ligand **L5** and that of the product **3aa** suggested 1:1 binding of the chiral ligand to the nickel center.[15]

On the basis of our studies and previous reports, a plausible pathway is proposed to account for the cycloaddition pathway (Scheme 6).[10,16] Oxidative addition of diphenylcyclopenone to Ni^0 affords intermediate A, which is proposed to undergo enantioselective Ni–C(acyl) migratory insertion into the C=O bond via intermediate **B** (path a). The resulting Ni^{II}-allyl intermediate **C** reductively eliminates the final product **3aa**, thus regenerating the catalyst. Alternatively[17] or even more likely, **B** may undergo concerted 4,1-insertion of the Ni–acyl into the enone to give a 8-membered nickelacycle **D** which is a direct precursor to **C** (path b). In either pathway, the olefin unit participates to allow for allyl stabilization.

In summary, we have realized Ni^0-catalyzed enantioselective [3+2] cycloaddition of enones/imines with cyclopropenones through C–C bond activation. This atom-economic reaction is both highly chemo- and enantioselective (88–99% *ee*), with the C=O or C=N bond exclusively participating in the cycloaddition, affording γ-alkenyl butenolides or



Scheme 6. Proposed mechanism.

-lactams, respectively, bearing a *tetra*-substituted carbon. The high chemo- and enantioselectivity and the intermolecularity of this system may provide insight into development of new asymmetric C–C bond activation systems.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cyclopropenones · enantioselective C–C activation · enones · lactones · nickel

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[17] See the Supporting InformationI for other proposed possible pathways.

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