# Direct and Asymmetric Nickel(II) Catalyzed Construction of Carbon–Carbon Bonds from *N*-Acyl Thiazinanethiones

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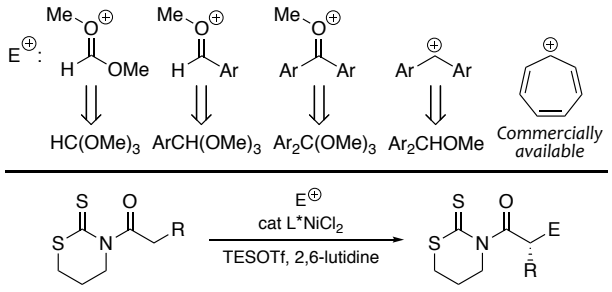
*Supporting Information Placeholder*

**ABSTRACT:** A wide array of new *N*-acyl thiazinanethiones are employed in a number of direct and enantioselective carbon–carbon bond forming reactions catalyzed by nickel(II) complexes. The electrophilic species are mostly prepared in situ from ortho esters, methyl ethers, acetals, and ketals, which makes the overall process highly efficient and experimentally straightforward. Theoretical calculations indicate that the reactions proceed through an open transition state in a $S_N1$-like mechanism. The utility of this novel procedure has been demonstrated by the asymmetric preparation of synthetically useful intermediates and the total synthesis of peperomin D.

The stereocontrolled construction of carbon–carbon bonds from metal enolates holds a prominent position among carbon backbone forming methods in asymmetric synthesis.[1] Unfortunately, most of the reported methods hinge on the stoichiometric generation of the enolate and subsequent reaction with the chosen electrophile, so they do not meet the current demands for economy in synthesis.[2] Organocatalysis does meet such challenges,[3] but the source of nucleophiles is often restricted to aldehydes and a few privileged compounds.[4] Hence, there is a lack of direct, catalytic, and asymmetric transformations based on metal enolates from non–activated carboxylic derivatives. In this context, pioneering studies underlined the benefits of working with easily removable scaffolds attached to the carboxylic moiety.[5–7] This led Kobayashi to use amides in highly enantioselective aldol and Michael additions,[8] similarly Evans described aldol reactions and orthoester alkylations from *N*-acyl thiazolidinethiones,[9] Kumagai and Shibasaki also reported a number of reactions based on 7-azaindoline amides.[10,11] Inspired by such precedents and taking advantage of our own experience in $S_N1$-like stereoselective transformations[12] and the *isolobal principle*,[13] we envisaged that treatment of *N*-acyl thioimides with easy to handle chiral nickel(II) complexes might catalytically produce the corresponding metal enolates. These would then be capable of taking part in asymmetric carbon–carbon bond forming reactions with cationic intermediates. According to such ideas, we herein report that the direct TESOTf-mediated addition of *N*-acyl thiazinanethiones to a wide array of electrophiles catalyzed by chiral nickel(II) complexes and the ensuing removal of the thiazinanethione scaffold provides enantiomerically pure compounds in high yields and in a straightforward manner (Scheme1).

**Scheme 1. Direct, Asymmetric, and Catalytic C–C Bond Forming Reactions**

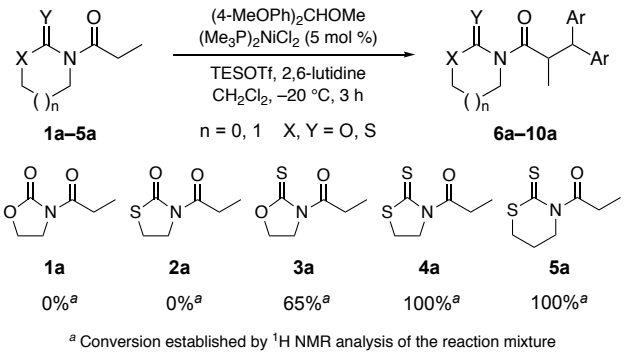



We were aware from the very beginning that such a challenging process called for: (a) the catalytic formation of an enolate possessing the necessary chiral environment in parallel to (b) the generation of the required electrophile for (c) the installation of up to two

new stereocenters whilst (d) minimizing undesired reactions. Therefore, we carried out a careful examination of all the species involved in such a process.

Exploratory studies on the addition of *N*-propanoyl derivatives **1a–5a** to 4,4'-dimethoxybenzhydryl methyl ether in the presence of commercially available $(Me_3P)_2NiCl_2$ demonstrated the crucial role of the exocyclic C=S bond (Scheme 2). Indeed, oxazolidinone **1a** and thiazolidinone **2a** did not react at all, whereas thiazolidinethione **4a** and thiazinanethione **5a** were converted into the alkylated products quantitatively.

**Scheme 2. Assessment of the Scaffold**

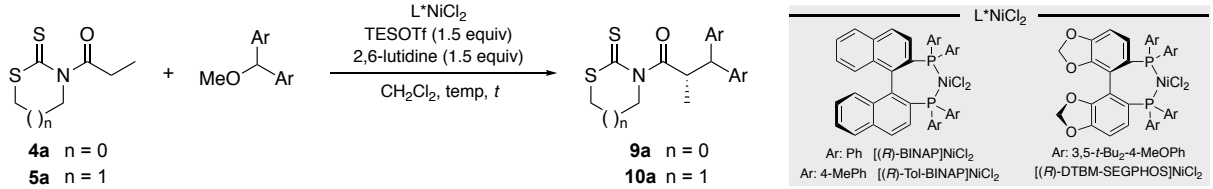



[a] Conversion established by $^1$H NMR analysis of the reaction mixture

Therefore, we focused our attention on the alkylation of **4a** and **5a** promoted by a few chiral complexes (L*$NiCl_2$ in Table 1), easily prepared by simple heating of mixtures of $NiCl_2$ and the corresponding diphosphines in $CH_3CN$.[9b] Initial screening of the reaction conditions revealed that both substrates were appropriate platforms to carry out such alkylations. Thereby, treatment of thiazolidinethione **4a** with 4,4'-dimethoxybenzhydryl methyl ether, TESOTf, and 2,6-lutidine in the presence of 5 mol % L*$NiCl_2$ at –20 °C for 15 h produced the quantitative and enantioselective (ee up to 96%) conversion into the alkylated adduct **9a** (entries 1–3 in Table 1). Even better, parallel reactions from thiazinanethione **5a** afforded adduct **10a** as a single enantiomer (entries 4–6 in Table 1). Importantly, the temperature could be raised to 0 °C without any detrimental effect, which enabled us to dramatically reduce the reaction time and to scale down the catalyst loading (compare entries 6–9 in Table 1). Eventually, the alkylation of **5a** with a mere 1 mol % of [(*R*)-DTBM-SEGPHOS]$NiCl_2$ took place at 0 °C in just 10 min and gave **10a** with a 98% ee and a 96% yield after chromatographic purification (entry 8 in Table 1).

The optimized conditions were then applied to a broad array of *N*-acyl thiazinanethiones **5** (Table 2). The reaction proved to be sensitive to the bulk of the acyl group, so the catalyst loading had to be increased to 10 mol % for the sterically hindered (R: *i*-Pr) thiazinanethione **5d** (compare entries 1–4 in Table 2). Otherwise, it tolerated the presence of common functional groups as alkenes, alkynes, and carboxylic esters as well as Cα-benzyl or phenyl ethers, in most cases with an outstanding enantiocontrol (ee up to 98%) and yields from 78 to 96% (entries 5–9 in Table 2). Unfortunately, the synthesis of the azidoacetyl thiazinanethione counterpart proved troublesome, but a parallel alkylation reaction was carried out successfully with the *N*-azidoacetyl thiazolidinethione **4j**

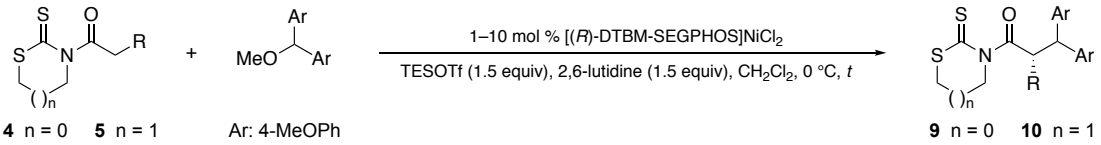
**Table 1. Initial Trials on the Direct and Asymmetric Reactions Catalyzed by Chiral Nickel(II) Complexes**




| entry | substrate | L*$NiCl_2$ | mol % | temp (°C) | *t* (h) | ee (%)[a] | conversion (%)[b] | yield (%)[c] |
|---|---|---|---|---|---|---|---|---|
| 1 | **4a** | [(*R*)-BINAP]$NiCl_2$ | 5 | –20 | 15 | 94 | > 97 | |
| 2 | **4a** | [(*R*)-TolBINAP]$NiCl_2$ | 5 | –20 | 15 | 95 | > 97 | |
| 3 | **4a** | [(*R*)-DTBM-SEGPHOS]$NiCl_2$ | 5 | –20 | 15 | 96 | > 97 | |
| 4 | **5a** | [(*R*)-BINAP]$NiCl_2$ | 5 | –20 | 15 | 96 | > 97 | |
| 5 | **5a** | [(*R*)-TolBINAP]$NiCl_2$ | 5 | –20 | 15 | 98 | > 97 | |
| 6 | **5a** | [(*R*)-DTBM-SEGPHOS]$NiCl_2$ | 5 | –20 | 15 | 98 | > 97 | |
| 7 | **5a** | [(*R*)-DTBM-SEGPHOS]$NiCl_2$ | 2 | –20 | 1 | 98 | > 97 | |
| 8 | **5a** | [(*R*)-DTBM-SEGPHOS]$NiCl_2$ | 1 | 0 | 0.2 | 98 | > 97 | 96 |
| 9 | **5a** | [(*R*)-DTBM-SEGPHOS]$NiCl_2$ | 1 | 20 | 0.2 | 92 | > 97 | |

[a] Established by chiral HPLC. [b] Established by $^1$H NMR. [c] Isolated yield after column chromatography.

**Table 2. Direct and Enantioselective Alkylation with (4-MeOPh)$_2$CHOMe Catalyzed by a Chiral Nickel(II) Complex**




| entry | substrate | R | mol % L*$NiCl_2$ | *t* (h) | adduct | ee (%) | yield (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | **5a** | Me | 1 | 0.2 | **10a** | 98 | 96 |
| 2 | **5b** | Et | 2 | 2 | **10b** | 95 | 88 |
| 3 | **5c** | Bn | 2 | 2 | **10c** | 96 | 81 |
| 4 | **5d** | *i*-Pr | 10 | 2 | **10d** | 98 | 78 |
| 5 | **5e** | $(CH_2)_2CH{=}CH_2$ | 2 | 2 | **10e** | 98 | 78 |
| 6 | **5f** | $(CH_2)_3CCH$ | 2 | 2 | **10f** | 98 | 96 |
| 7 | **5g** | $(CH_2)_2CO_2Me$ | 2 | 2 | **10g** | 95 | 78 |
| 8 | **5h** | OPh | 10 | 2.5 | **10h** | 95 | 85 |
| 9 | **5i** | OBn | 2 | 4 | **10**i | 95 | 93 |
| 10 | **4j** | $N_3$ | 2 | 2 | **9j** | 95 | 93 |

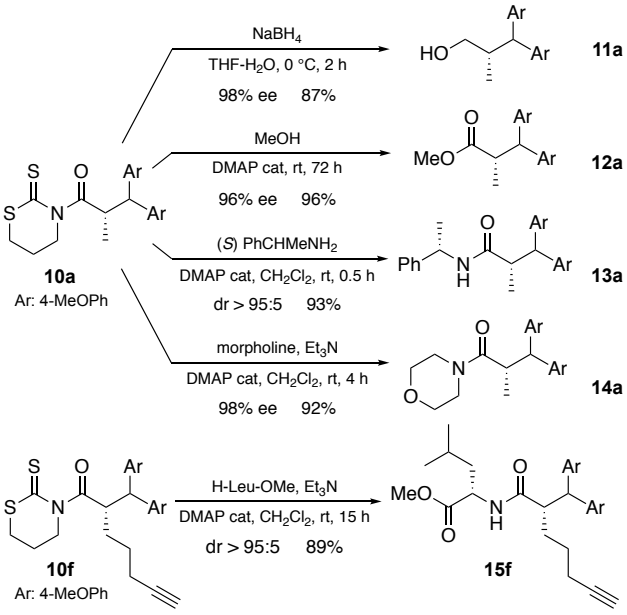
[a] Established by chiral HPLC. [b] Isolated yield after column chromatography.

(entry 10 in Table 2). Significantly, the results for **10i** and **9j** make this alkylation a new approach to the asymmetric synthesis of α-hydroxy and α-amino acids respectively (entries 9 and 10 in Table 2).

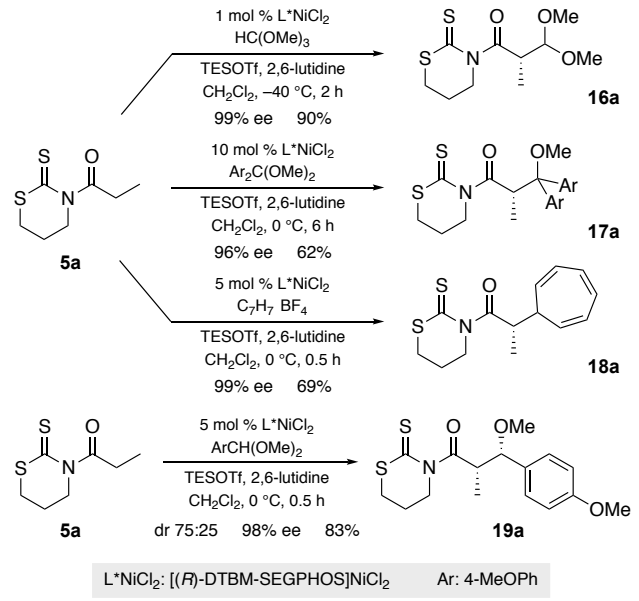
The thiazinanethione scaffold of the products **10** was easily removed to release alkylated products (Scheme 3).[14–16] Indeed, reduction of **10a** with $NaBH_4$ led to alcohol **11a** with a yield of 87%, whereas treatment of **10a** with methanol afforded ester **12a** with a 96% yield. In turn, (*S*)-α-methylbenzylamine and morpholine reacted smoothly with **10a** to produce amides **13a** and **14a** respectively in yields up to 96%. At this point, absolute configuration of adducts **10** was firmly established by chemical correlation of **11a–12a** and X-ray analysis of amide **13a**.[17] Interestingly, thiazinanethione may also act as a coupling reagent and permitted us to obtain diastereomerically pure *N*-acyl amino acid **15f** by simple addition of methyl (*S*) leucinate to adduct **10f** with an 89% yield.

Once the feasibility of the catalytic and asymmetric alkylation of **5** with 4,4'-dimethoxybenzhydryl methyl ether was established, we examined the synthetic potential of such a transformation through the use of other electrophiles represented in Scheme 1. The reactions with trimethyl orthoformate, a dimethyl ketal, and a tropylium salt, which involve the installation of a single stereocenter, proceeded smoothly and led to enantiomerically pure adducts **16a–18a** (ee ≥97%) after slight adjustments of the former experimental conditions (Scheme 4). More concretely, the reaction with trimethyl orthoformate was carried out at –40 °C to suppress the competitive alkylation of the exocyclic C=S bond, whereas the addition to the dimethyl ketal lasted for six hours, probably because of the steric bulk of the oxo carbenium intermediate. Besides these results, it is important to highlight that the related reaction with 4-MeOPhCH(OMe)$_2$, which involves the simultaneous construction of two new stereocenters, was also satisfactory and afforded the *syn* adduct **19a** (dr 75:25, 98% ee for the *syn* diastereomer) and with a high overall yield (Scheme 4).

**Scheme 3. Removal of the Thiazinanethione Scaffold**



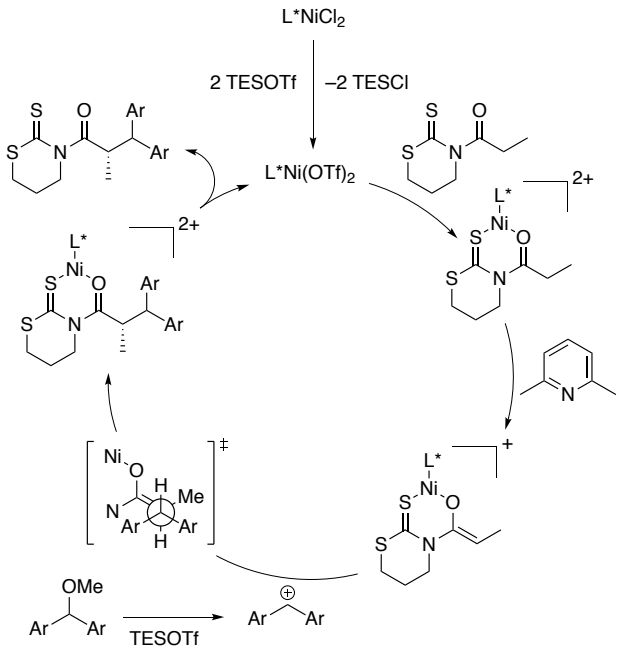
**Scheme 4. Reactions with other electrophiles**



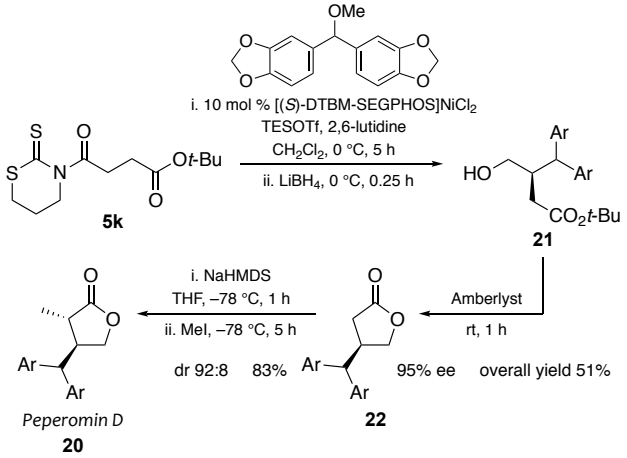

An $S_N1$-like mechanism based on the approach of cationic reagents to the *Re* face of a putative chiral nickel enolate accounts for all these results. [(*R*)-DTBM-SEGPHOS]$NiCl_2$ is a robust and bench stable nickel(II) complex with a distorted square planar geometry which can be seen in the crystal structure obtained;[17] it does not catalyse the alkylation reaction but it is easily activated in situ with TESOTf to produce the true catalyst containing two triflate ligands.[18] Coordination of this species to the thioimide moiety enhances the acidity of **5** and facilitates the deprotonation of the Cα position. At the same time, the TESOTf reacts with the benzhydryl methyl ether and produces the corresponding carbocation, which in turn adds to the nickel(II) enolate.[19] Once the carbon-carbon bond is formed, the alkylated adduct **10a** is released and the nickel(II) complex may start a new catalytic cycle (Scheme 5).

Eventually, we considered the synthesis of peperomin D (**20** in Scheme 6), a secolignan metabolite isolated from *Peperomia glabielle*.[20] Featuring a five membered lactone with a benzhydryl appendage at the β position, we envisaged that it might be synthesized through alkylation of thiazinanethione **5k** with the appropriate benzhydryl methyl ether in the presence of [(*S*)-DTBM-SEGPHOS]$NiCl_2$.[21] Indeed, quenching the reaction mixture with $LiBH_4$ gave chemoselectivily the hydroxy ester **21**, which was then treated with Amberlyst resin to obtain the desired lactone **22** with an excellent stereocontrol (95% ee) and a 51% yield. Remarkably, just a single chromatographic purification was required. The installation of the α-stereocenter was next accomplished by substrate-controlled alkylation of **22** with MeI, which allowed us the isolation of enantiomerically pure peperomin D **20** with an overall yield of 42% over three steps.

**Scheme 5. Mechanistic Model**




**Scheme 6. Synthesis of Peperomin D**




In summary, we have demonstrated the utility of *N*-acyl thiazinanethiones in a number of direct, chemo- and enantioselective carbon-carbon bond forming reactions usually promoted by 1–5 mol % of [DTBM-SEGPHOS]$NiCl_2$. The thiazinanethione scaffold can be smoothly released from the resulting adducts to provide a broad array of enantiomerically pure intermediates. Theoretical studies suggest that these transformations proceed through an open transition state in an $S_N1$-like mechanism, in which the configuration of the α-stereocenter is absolutely controlled by the chiral biphosphine. The efficiency of such an alkylation has been proved in the total synthesis of peperomin D, a five membered lactone containing two stereocenters.

## ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and characterization data (PDF).

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Dedicated to the memory of recently deceased Professor Josep Castells.


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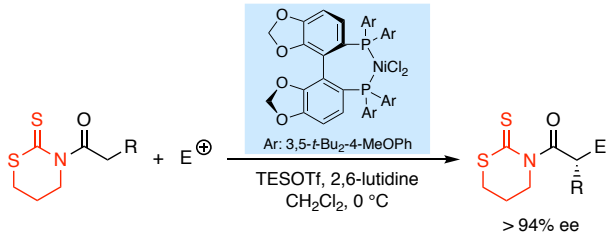
Ar
Ar
P
NiCl2
P
Ar
Ar
Ar: 3,5-t-Bu2-4-MeOPh
TESOTf, 2,6-lutidine
CH2Cl2, 0 °C
> 94% ee