Nickel-Catalyzed C-S Bond Formation via Decarbonylative Thioetherification of Esters, Amides and Intramolecular Recombination Fragment Coupling of Thioesters

Item Type	Article
Authors	Lee, Shao-Chi; Liao, Hsuan-Hung; Chatupheeraphat, Adisak; Rueping, Magnus
Citation	Lee S-C, Liao H-H, Chatupheeraphat A, Rueping M (2018) Nickel-Catalyzed C-S Bond Formation via Decarbonylative Thioetherification of Esters, Amides and Intramolecular Recombination Fragment Coupling of Thioesters. Chemistry - A European Journal. Available: http://dx.doi.org/10.1002/chem.201705842.
Eprint version	Post-print
DOI	10.1002/chem.201705842
Publisher	Wiley
Journal	Chemistry - A European Journal
Rights	This is the peer reviewed version of the following article: Nickel-Catalyzed C-S Bond Formation via Decarbonylative Thioetherification of Esters, Amides and Intramolecular Recombination Fragment Coupling of Thioesters, which has been published in final form at http://doi.org/10.1002/chem.201705842. This article may be used for non-commercial purposes in accordance With Wiley Terms and Conditions for self-archiving.
Download date	04/08/2022 17:29:08

| Link to Item | http://hdl.handle.net/10754/626876 |

Accepted Article

Authors: Shao-Chi Lee, Hsuan-Hung Liao, Adisak Chatupheeraphat, and Magnus Rueping

FULL PAPER

Nickel-Catalyzed C-S Bond Formation via Decarbonylative Thioetherification of Esters, Amides and Intramolecular Recombination Fragment Coupling of Thioesters

Shao-Chi Lee,[a] Hsuan-Hung Liao,[a] Adisak Chatupheeraphat,[a] and Magnus Rueping*[a,b]

Abstract: A nickel catalyzed cross-coupling protocol for the straightforward C-S bond formation has been developed. Various mercaptans and a wide range of ester and amide substrates bearing various substituents were tolerated in this process which afforded products in good to excellent yields. Furthermore, an intramolecular protocol for the synthesis of thioethers starting from thioesters has been developed. The utility of this protocol has been demonstrated in a new synthesis protocol of benzothiophene.
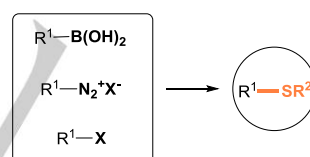
Introduction

Sulfur-containing molecules,[1] especially thioethers, are important structural motifs present in nature and numerous natural products including bioactive and pharmaceutically active compounds are sulfur-derived compounds.[2] Furthermore, various sulfur based, tailor-made molecules including artificial enzymes as well as synthetic drugs and therapeutics have been designed and produced. Therefore, the development of efficient methods for the construction of C-S bonds continues to attract attention. Regarding the introduction of arylthio moieties into aromatic compounds, this process is mainly achieved by Chan-Lam, Leuckart thiophenol, Ullmann and Sandmeyer-type reactions with reactive electrophiles as coupling partners.[3] However, recent studies revealed that first row transition metals, such as nickel,[4] are effective in harnessing less reactive electrophiles, resulting in the exploration of less toxic and more economic cross-coupling partners. Due to their non-toxic and environmental friendly nature, particular attention has been drawn to the use of carboxylic acid derivatives, such as esters and amides, which proved successful especially in decarbonylative processes.[5,6] Although nickel catalyzed decarbonylative reactions have been explored extensively among various research groups,[5-8] the glove-box is often a must in order to enable the use of moisture- and air-sensitive ligands and/or catalysts. Most of the developed methodologies are taking advantage of the high reactivity of catalysts and ligands, such as Ni(cod)$_2$/dcype[7a-d,j-m,8b] for inert bond activation,

which requires manipulation in a glove-box. In sharp contrast, finding stable nickel catalysts and ligands, especially without storage in an inert atmosphere,[7a] is more challenging but essential for the exploration of further cross-coupling reactions. Given the usefulness of thioethers, the development of a decarbonylative thioetherification protocol, in particular as a glove-box-free manipulation strategy, is highly desirable (Scheme 1). One subtle approach for avoiding the use of a glove-box is to prepare "paraffin capsules" which allow air and moisture sensitive transition metal catalyzed reactions to be performed on the bench top.[9] However, the additional process for preparing the capsules may have limitations.[10]

With these considerations in mind, we decided to examine a glove-box and paraffin capsule-free strategy for the challenging nickel catalyzed decarbonylative thioetherification process.
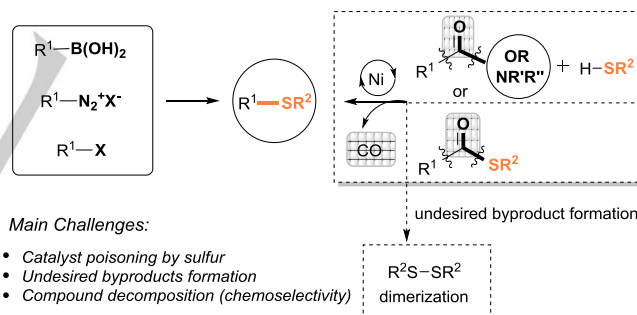

Scheme 1. Thioether formation: Classical *vs.* innovation and its challenges.

Results and Discussion

Initially, we started to investigate the decarbonylative cross-coupling reaction between phenyl naphthalene-2-carboxylate (**1a**) and commercially available 4-methylthiophenol (**2a**) as reaction partners (Table 1). NiCl$_2$ was selected as catalyst, based on economical considerations and its stability under air and moisture conditions. Since ligands typically play an important role in nickel-catalyzed transformations, preliminary experiments were conducted with a series of air stable ligands, including triphenyl phosphine (PPh$_3$), 1,3-bis(2,6-diisopropylphenyl)-imidazolidin-2-ylidene (SIPr) carbene ligand, and 1,1′-ferrocenediyl-bis(diphenylphosphine) (dppf). However, no desired product was obtained (entries 1-3). The product was obtained in 18% GC yield using the bidentate phosphine ligand

[a]   M. Sc. S.-C. Lee, Dr. H.-H. Liao, M. Sc. A. Chatupheeraphat, Prof.
        Dr. M. Rueping
        Institut für Organische Chemie, RWTH Aachen
        Landoltweg 1, 52074 Aachen (Germany)
        E-mail: magnus.rueping@rwth-aachen.de
[b]   Prof. Dr. M. Rueping
        King Abdullah University of Science and Technology (KAUST)
        KAUST Catalysis Center (KCC), Thuwal, 23955-6900 (Saudi
        Arabia); E-mail: magnus.rueping@Kaust.edu.sa
[**]   Supporting information for this article is given via a link at the end of
        the document.

dppp [1,3-bis(diphenylphosphino)-propane] (entry 4). A considerable increase in the yield was observed upon changing the base from K_2CO_3 to Na_2CO_3 (93% GC yield, entry 5). Next, another air stable Ni catalyst, $NiBr_2$, was examined, however, a similar result was obtained (93% GC yield, entry 6). Decreasing the ratio of $NiCl_2$/dppp from 1:4 to 1:2 resulted in a considerably lower yield (entry 7). Under these new conditions, a slightly higher yield was obtained when raising the temperature (29% yield, entry 8 vs 7) whereas extending the reaction time gave a rather unsatisfactory result (entry 9). In order to achieve a better yield, Zn and Mn were used as reducing reagents and Mn was found to be superior (entries 10 and 11). Furthermore, when the amount of base was changed from stoichiometric to catalytic amount, a dramatic increase in the yield was observed (43% vs 71% entry 12 vs 13). Notably, the use of Mg instead of Mn provides even a better result (75% GC yield, entry 14). Finally, decreasing the amount of Mg significantly improved the yield to 92% GC yield (89% yield, entry 15).

range of aromatic and heteroaromatic esters **1** provided the corresponding sulfanes **3** with high to excellent yields. For example simple unsubstituted 2-naphthyl (**1a**) and phenyl fluoride (**1b**) derived esters underwent this nickel catalyzed procedure and could be efficiently converted into the appropriate products **3a** and **3b** in high yields. Functional groups such as ketone and methyl ester groups (**1c**, **1d**) were nicely tolerated, which illustrates the chemoselectivity profile of this method. As anticipated, our decarbonylative thioetherification transformation could be successfully extended to heterocyclic esters derived from furan, thiophene and quinoline, affording the corresponding heteroaryl sulfanes **3e-h** in excellent yields. In addition, the $C(sp^3)$ ester **1j** was suitable for our protocol, leading to the corresponding product, albeit in lower yield. Furthermore, representative chain and nonaromatic mercaptan sources were applied in reaction with the quinoline derived ester substrate **1g**, resulting in high yields of the desired decarbonylative thioetherification products **3k** and **3l**.

Table 1. Optimization of the nickel catalyzed decarbonylative thioetherification cross-coupling reaction.[a]
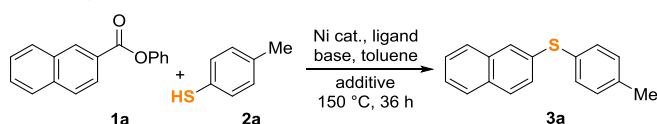
| Entry	Ni cat.	Ligand (mol%)	Base	Additive (x equiv.)	Yield (%)[b]
1	$NiCl_2$	PPh_3 (40)	K_2CO_3	-	0
2	$NiCl_2$	SIPr (40)	K_2CO_3	-	0
3	$NiCl_2$	dppf (40)	K_2CO_3	-	0
4	$NiCl_2$	dppp (40)	K_2CO_3	-	18
5	$NiCl_2$	dppp (40)	Na_2CO_3	-	93
6	$NiBr_2$	dppp (40)	Na_2CO_3	-	93
7	$NiCl_2$	dppp (20)	Na_2CO_3	-	<5
8[c]	$NiCl_2$	dppp (20)	Na_2CO_3	-	29
9[d]	$NiCl_2$	dppp (20)	Na_2CO_3	-	<5
10	$NiCl_2$	dppp (20)	Na_2CO_3	Zn (2)	<5
11	$NiCl_2$	dppp (20)	Na_2CO_3	Mn (2)	25
12[e]	$NiCl_2$	dppp (20)	Na_2CO_3	Mn (2)	43
13[f]	$NiCl_2$	dppp (20)	Na_2CO_3	Mn (2)	71
14[f]	$NiCl_2$	dppp (20)	Na_2CO_3	Mg (2)	75
15[f]	$NiCl_2$	dppp (20)	Na_2CO_3	Mg (1)	92 (89)[g]
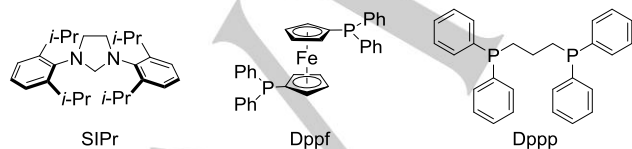
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Ni] (0.02 mmol, 10 mol%), toluene (1 ml), base (3 equiv.), 150 °C, 36 h. [b] GC yields, decane as internal standard. [c] 170 °C. [d] 48 h. [e] Base (0.5 equiv.). [f] Base (0.2 equiv.). [g] Isolated yield.

With the optimal conditions in hands, we then studied the scope of this newly developed nickel catalyzed decarbonylative thioetherification of esters (Table 2). The results show that a

Table 2. The scope of nickel catalyzed decarbonylative thioetherification cross-coupling with aryl ester.
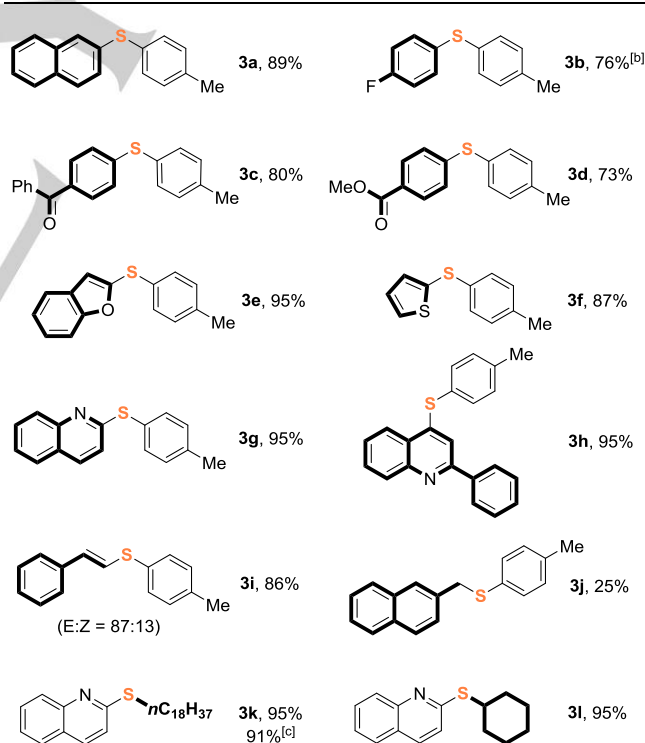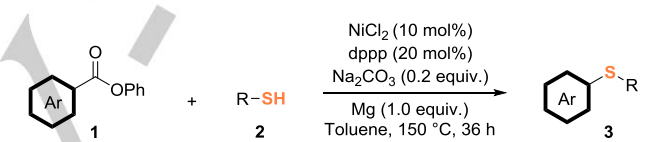

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $NiCl_2$ (0.02 mmol, 10 mol%), dppp (0.04 mmol, 20 mol%), Na_2CO_3 (0.04 mmol, 0.2 equiv.), Mg (0.2 mmol, 1 equiv.), toluene(1 ml), 150 °C, 36 h, isolated yields. [b] 170 °C. [c] 1 g scale.

Prompted by our successful results, we next focused our attention on the decarbonylative thioetherification of amides

(Table 3). Applying 10 mol% NiCl$_2$ and 40 mol% dppp ligand with Na$_2$CO$_3$ as base, afforded the expected thioether product in a good yield of 75% (Table 3, entry 1). Changing the catalyst to ligand ratio provided the product in an unsatisfactory yield (entry 3). Neither increasing the temperature (entry 4) nor extending the reaction time (entry 5) provided superior results. The use of additives as reducing agents, especially Mn, had a beneficial effect on the reaction yield (entries 6-8). Notably, performing the reaction in the absence of base, provided the product in a comparable yield (entry 9). The yield dropped slightly upon reducing the amount of additive (entry 10).

Having optimized the reaction conditions, we then evaluated the scope of the reaction with respect to a wide range of amide substrates (Table 4). Electron-neutral as well as electron-rich and poor aromatic amides **4a-g** successfully provided the desired products **5a-g** in good to high yields. Notably, substrates bearing phenyl, fluorine, methyl ester and methoxy groups efficiently underwent this transformation. Furthermore, heterocyclic benzofuran derivative **4h** and amide **4i** containing an extended pi-electron system are also tolerated under our reaction conditions, providing the desired products **5h** and **5i** in good to high yields. Finally, applying an aliphatic mercaptan, resulted in a high yield of the desired decarbonylative thioetherification product **5j**. In addition, subjecting an unactivated *N*-Boc, *N*-Ph amide substrate to our optimized reaction conditions resulted in a superior yield (90%) for the desired product.

Table 3. Optimization of the nickel catalyzed decarbonylative thioetherification cross-coupling reaction.[a]
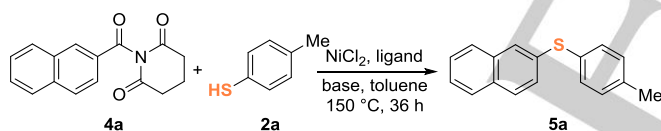
Entry	Ligand (mol%)	Base	Additive (x equiv.)	Yield (%)[b]
1	dppp (40)	Na$_2$CO$_3$	-	75
2	dppp (40)	Na$_3$PO$_4$	-	86
3	dppp (20)	Na$_3$PO$_4$	-	<5
4[c]	dppp (20)	Na$_3$PO$_4$	-	35
5[d]	dppp (20)	Na$_3$PO$_4$	-	35
6	dppp (20)	Na$_3$PO$_4$	Zn (2)	28
7	dppp (20)	Na$_3$PO$_4$	Mn (2)	84
8	dppp (20)	Na$_3$PO$_4$	Mg (2)	69
9	dppp (20)	-	Mn (2)	83
10	dppp (20)	-	Mn (1)	81

[a] Reaction conditions: **4a** (0.2 mmol), **2a** (0.4 mmol), NiCl$_2$ (10 mol%), base (3 equiv.), toluene (1 ml), at 150 °C 36 h. [b] GC yields, decane as internal standard. [c] 170 °C. [d] 48 h.

Table 4. The scope of nickel catalyzed decarbonylative sulfenylation cross-coupling with aryl amides.
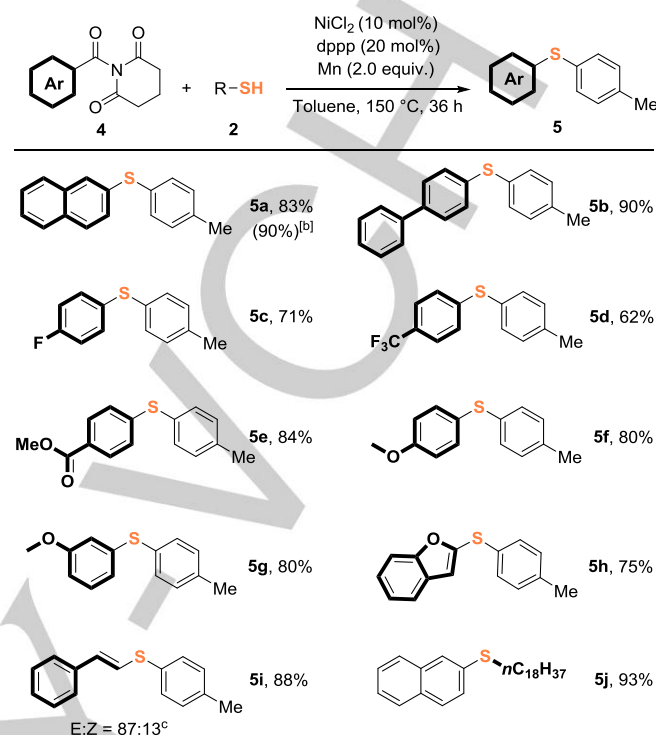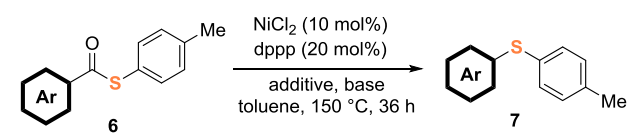

[a] Reaction conditions: **4** (0.2 mmol), **2** (0.4 mmol), NiCl$_2$ (0.02 mmol, 10 mol%), dppp (0.04 mmol, 20 mol%), Mn (0.4 mmol, 2 equiv), toluene (1 ml) at 150 °C, 36 h. [b] From *N*-Ph, *N*-Boc amide. [d] Determined by NMR.

Based on the success of the decarbonylative thioetherification reaction[11] with esters and amides, we envisioned that the developed conditions might work as well for thioester substrates,[12,13] enabling an intramolecular version of this highly practical reaction. In this context, in 1987 Yamamoto and coworkers reported the Pd catalyzed decarbonylation of thioesters for the synthesis of diaryl, alkyl, aryl and alkenyl, aryl sulfides.[11b,c] However, a limited substrate scope was described. In addition, the reaction was also described with stoichiometric amounts of Ni[11a] and Rh[11b] and during the preparation of our manuscript with a Ni- and Pd- catalyzed procedure.[11d]
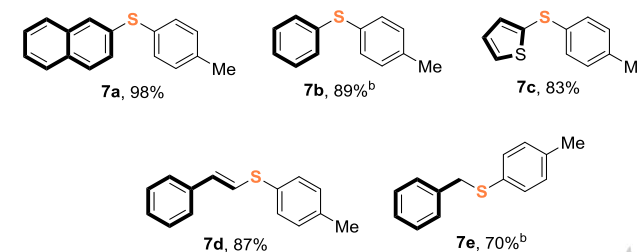
With these considerations in mind we focused our attention on a catalytic decarbonylative transformation, and aimed at a broad functional group tolerance (Table 5). Applying the optimal conditions developed for ester substrates to thioester **6a**, the desired product **7a** was obtained in an excellent yield (98%). Without magnesium as an additive a considerably lower yield (35%) was obtained. In the absence of the base, a slightly lower yield (92%) was obtained. To assess the utility of this protocol, a series of representative thioesters was employed to determine the scope of the Ni-catalyzed intramolecular decarbonylative reaction. The 2-naphthyl (**6a**) and phenyl (**6b**) thioesters underwent the decarbonylative diaryl sufide synthesis to give the corresponding products in excellent yields. Next, thiophene derivative **6c** was evaluated and performed great to afford heteroarenethiol **7c** in a high yield. Remarkably, the challenging

styryl and benzyl sulfanes **7d** and **7e** were also formed under our reaction conditions.

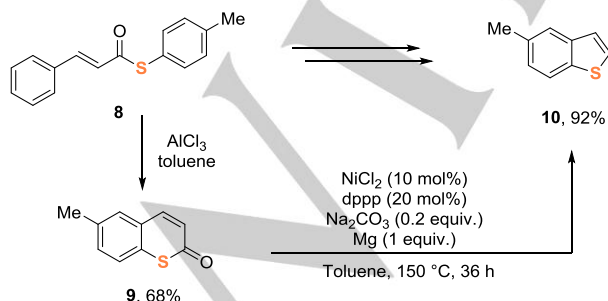**Table 5.** Nickel catalyzed decarbonylation of thioesters.[a]

Entry	Base	Additive (x equiv.)	Yield **7a** (%)[b]
1	Na$_2$CO$_3$	Mg	98
2	Na$_2$CO$_3$	-	35
3	-	Mg	92

7a, 98%   **7b**, 89%b   **7c**, 83%

7d, 87%   **7e**, 70%b

[a] Reaction conditions: **6** (0.2 mmol), NiCl$_2$ (0.02 mmol, 10 mol%), dppp (0.04 mmol, 20 mol%), Mg (0.2 mmol, 1 equiv.), toluene(1 ml) at 150 °C, 36 h. [b] Isolated yield.

Lastly, in order to show the applicability of our newly developed method, we devised an innovative synthetic route for the preparation of benzothiophene[13] via an intramolecular decarbonylative strategy (Scheme 2). A survey of the previous literature,[14] showed that most studies for benzothiophene synthesis focus on either S$_N$Ar reactions or electrophilic cyclization of alkynes with various thiol surrogates. Herein, we devised a new synthetic route for substituted benzothiophene **10** from easily available starting material **8**. Preparation of thiacoumarin **9** can be achieved easily via Friedel-Crafts type intramolecular cyclization of **8**. The desired benzothiophene **10** can subsequently be obtained by applying our newly designed intramolecular decarbonylative reaction.

Scheme 2. Preparation of 5-methyl benzothiophene via an intramolecular decarbonylative strategy.

Regarding the mechanism we propose the following mechanism for this nickel-catalyzed decarbonylative thioetherification reaction: Ni^{II} is firstly reduced to be L$_n$Ni^0 **A** by the reducing reagent. Oxidative addition of the C(acyl)-S bond of the thioester **B**, which is formed by reaction of the thiol with the ester or imide or preformed, to the L$_n$Ni^0 complex **A** gives an acyl nickel(II) intermediate **C**. Subsequently decarbonylation affords the intermediate **D**. Finally, the C-S bond formation by reductive elimination provides the thioether and the active catalyst.
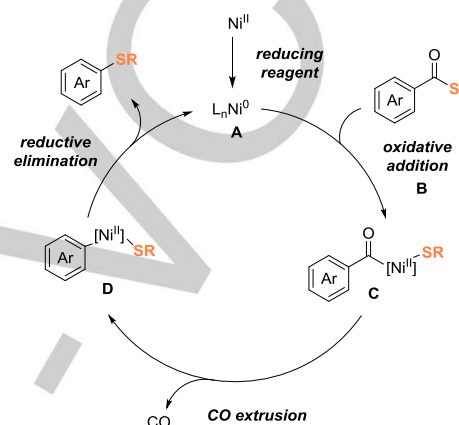
Scheme 3. Proposed mechanism for the decarbonylative thioetherification.

Conclusions

In summary, we have developed a new and selective cross-coupling reaction of esters and amides with mercaptans as coupling partners. The transformation of aryl, alkenyl and alkyl esters/amides to the corresponding thioethers was previously not known and is, with conventional methods, difficult to achieve. Thus, the newly developed methodology enables a facile route for C-S bond formation in a straightforward fashion. Various mercaptans and a wide range of ester and amide substrates bearing various substituents are tolerated in this process which afforded products in good to excellent yields. In addition, an intramolecular version of this reaction has also been developed. The utility of this newly designed protocol has been demonstrated in the synthesis of benzothiophene on the bench top. Given the simplicity and generality of the protocol it is anticipated that it should find application in synthesis, retrosynthesis and late stage modification.

Acknowledgements

WILEY-VCH

[1]   a) R. J. Cremlyn, *An Introduction to Organosulfur Chemistry*, Wiley: New York, **1996**; b) *Organosulfur Chemistry I*, Ed.: P. C. B. Page, Springer: Heidelberg, 1999; c) *Organosulfur Chemistry II*, Ed.: P. C. B. Page, Springer: Heidelberg, **1999**; d) C. M. Rayner, *Advances in Sulfur Chemistry*, JAI Press: Greenwich, **2000**, Vol. 2; e) *Sulfur Compounds: Advances in Research and Application*, Ed.: A. Q. Acton, Atlanta, GA, **2012**.

[2]   a) G. Liu, J. R. Huth, E. T. Olejniczak, R. Mendoza, P. DeVries, S. Leitza, E. B. Reilly, G. F. Okasinski, S. W. Fesik, T. W. von Geldern, *J. Med. Chem.* **2001**, *44*, 1202; b) S. W. Kaldor, V. J. Kalish, J. F. Davies, II, B. V. Shetty, J. E. Fritz, A. J. Appelt, J. A. Burgess, K. M. Campanale, N. Y. Chirgadze, D. K. Clawson, B. A. Dressman, S. D. Hatch, D. A. Khalil, M. B. Kosa, P. P. Lubbehusen, M. A. Muesing, A. K. Patick, S. H. Reich, K. S. Su, J. H. Tatlock, *J. Med. Chem.* **1997**, *40*, 3979; c) S. F. Nielsen, E. O. Nielsen, G. M. Olsen, T. Liljefors, D. Peters, *J. Med. Chem.* **2000**, *43*, 2217; d) L. Liu, J. E. Stelmach, S. R. Natarajan, M.-H. Chen, S. B. Singh, C. D. Schwartz, C. E. Fitzgerald, S. J. O'Keefe, D. M. Zaller, D. M. Schmatz, J. B. Doherty, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3979.

[3]   For selected reviews on C-S bond formation, see: a) T. Kondo, T.-A. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205; b) I. P. Beletskaya, V. P. Ananikov, *Eur. J. Org. Chem.* **2007**, 3431; c) P. Bichler, J. A. Love, *Top. Organomet. Chem.* **2010**, *31*, 39; d) C. C. Eichman, J. P. Stambuli, *Molecules* **2011**, *16*, 590; e) A. Postigo, *RSC Adv.* **2011**, *1*, 14; f) I. P. Beletskaya, V. P. Ananikov, *Chem. Rev.* **2011**, *111*, 1596; g) Liu, W.; Zhao, X. *Synthesis* **2013**, 2051; h) P. Chauhan, S. Mahajan, D. Enders, *Chem. Rev.* **2014**, *114*, 8807; i) C.-F. Lee, Y.-C. Liu, S. S. Badsara, *Chem. Asian J.* **2014**, *9*, 706; j) A. Sujatha, A. M. Thomas, A. P. Thankachan, G. Anilkumar, *ARKIVOC* **2015**, 1; k) C. Shen, P. Zhang, Q. Sun, S. Bai, T. S. A. Hor, X. Liu, *Chem. Soc. Rev.* **2015**, *44*, 291; l) A. Ghaderi, *Tetrahedron* **2016**, *72*, 4758; m) K. L. Dunbar, D. H. Scharf, A. Litomska, C. Hertweck, *Chem. Rev.* **2017**, *117*, 5521.

[4]   a) B. M. Rosen, K. W. Quasdorf, D. A. Wilson, N. Zhang, A.-M. Resmerita, N. K. Garg, V. Percec, *Chem. Rev.* **2011**, *111*, 1346; b) S. Z. Tasker, E. A. Standley, T. F. Jamison, *Nature* **2014**, *509*, 299; c) V. P. Ananikov, *ACS Catal.* **2015**, *5*, 1964.

[5]   R. Takise, K. Muto, J. Yamaguchi, *Chem. Soc. Rev.* **2017,** *46*, 5864.

[6]   a) G. Meng, S. Shi, M. Szostak, *Synlett* **2016**, *27*, 2530; b) J. E. Dander, N. K. Garg, *ACS Cat.* **2017**, *7*, 1413; c) C. Liu, M. Szostak, *Chem. Eur. J.* **2017**, *23*, 7157.

[7]   For examples of Ni-catalyzed decarbonylative transformations of esters, see: a) K. Amaike, K. Muto, J. Yamaguchi, K. Itami, *J. Am. Chem. Soc.* **2012**, *134*, 13573; b) A. Correa, J. Cornella, R. Martin, *Angew. Chem. Int. Ed.* **2013**, *52*, 1878; c) L. Meng, Y. Kamada, K. Muto, J. Yamaguchi, K. Itami, *Angew. Chem., Int. Ed.* **2013**, *52*, 10048; d) K. Muto, J. Yamaguchi, D. G. Musaev, K. Itami, *Nat. Commun.* **2015**, *6*, 7508; e) N. A. LaBerge, J. A. Love, *Eur. J. Org. Chem.* **2015**, 5546; f) A. N. Desnoyer, F. W. Friese, W. Chiu, M. W. Drover, B. O. Patrick, J. A. Love, *Chem. Eur. J.* **2016**, *22*, 4070; g) K. Amaike, K. Itami, J. Yamaguchi, *Chem.-Eur. J.* **2016**, *22*, 4384; h) L. Guo, A. Chatupheeraphat, M. Rueping, *Angew. Chem. Int. Ed.* **2016**, *55*, 11810; i) L. Guo, M. Rueping, *Chem. Eur. J.* **2016**, *22*, 16787; j) X. Pu, J. Hu, Y. Zhao, Z. Shi, *ACS Catal.* **2016**, *6*, 6692; k) H. Yue, L. Guo, H.-H. Liao, Y. Cai, C. Zhu, M. Rueping, *Angew. Chem. Int. Ed.* **2017**, *56*, 4282; l) A. Chatupheeraphat, H.-H. Liao, S.-C. Lee, M. Rueping, *Org. Lett.* **2017**, *19*, 4255; m) X. Liu, J. Jia, M. Rueping, *ACS Catal.* **2017**, *7*, 4491; n) H. Yue, L. Guo, S.-C. Lee, X. Liu, M. Rueping, *Angew. Chem. Int. Ed.* **2017**, *56*, 3972; o) R. Takise, R. Isshiki, K. Muto, K. Itami, J. Yamaguchi, *J. Am. Chem. Soc.* **2017**, *139*, 3340; For theoretical studies, see: p) X. Hong, Y. Liang, K. N. Houk, *J. Am. Chem. Soc.* **2014**, *136*, 2017; q) Q. Lu, H. Yu, Y. Fu, *J. Am. Chem. Soc.* **2014**, *136*, 8252; r) for a related Pd-catalyzed ester to ketone reaction, see: T. B. Halima, W. Zhang, I. Yalaoui, I.; X. Hong, Y.-F. Yang, K. N. Houk, S. G. Newman, *J. Am. Chem. Soc.* **2017**, *139*, 1311.

[8]   For examples of Ni-catalyzed decarbonylative transformations of amides, see: a) S. Shi, G. Meng, M. Szostak, *Angew. Chem., Int. Ed.* **2016**, *55*, 6959; b) W. Srimontree, A. Chatupheeraphat, H.-H. Liao, M. Rueping, *Org. Lett.* **2017**, *19*, 3091; c) J. Hu, Y. Zhao, J. Liu, Y. Zhang, Z. Shi, *Angew. Chem., Int. Ed.* **2016**, *55*, 8718; d) A. Dey, S. Sasmal, K. Seth, G. K. Lahiri, D. Maiti, *ACS Catal.* **2017**, *7*, 433; e) Hu, J.; Wang, M.; Pu, X.; Shi, Z. *Nat. Commun.* **2017**, *8*, 14993; f) X. Liu, H. Yue, J. Jia, L. Guo, M. Rueping, *Chem. Eur. J.* **2017**, *23*, 11771; g) C. Liu, M. Szostak, *Angew. Chem. Int. Ed.* **2017**, *56*, 12718; h) S.-C. Lee, L. Guo, H. Yue, H.-H. Liao, M. Rueping, M. *Synlett* **2017**, DOI: 10.1055/s-0036-1591495. For examples of Pd and Rh-catalyzed decarbonylative transformations of amides, see: i) G. Meng, M. Szostak, *Angew. Chem., Int. Ed.* **2015**, *54*, 14518; j) C. Liu, G. Meng, M. Szostak, *J. Org. Chem.* **2016**, *81*, 12023; k) G. Meng, M. Szostak, *Org. Lett.* **2016**, *18*, 796; l*)* H. Wu, T. Liu, M. Cui, Y. Li, J. Jian, H. Wang, Z. Zeng, *Org. Biomol. Chem.* **2017**, *15*, 536; m) S. Shi, M. Szostak, *Org. Lett.* **2017**, *19*, 3095.

[9]   a) J. E. Dander, N. A. Weires, N. K. Garg, *Org. Lett.* **2016**, *18*, 3934; b) A. C. Sather, H. G. Lee, J. R. Colombe, A. Zhang, S. L. Buchwald, *Nature* **2015**, *524*, 208.

[10]   a) E. D. Scudder, R. E. Lyons, *The Production of Hydrogen Sulphide by Heating Paraffine and Other Hydrocarbon Mixtures with Sulphur, Vol. 40*, Proceedings of the Indiana Academy of Science, Indiana, **1930**; b) H. A. Wiebe, A. R. Knight, O. P. Strausz, H. E. Gunning, *J. Am. Chem. Soc.* **1965**, *87*, 1443. c) G. Schmitt*, Corrosion* **1991**, *47*, 285.

[11]   For decarbonylative thioetherification of thioesters: Ni-mediated: a) E. Wenkert, D. Chianelli, *J. Chem. Soc., Chem. Commun.* **1991**, *9*, 627; Pd- and Rh-catalysis: b) K. Osakada, T. Yamamoto, A. Yamamoto, *Tetrahedron Lett.* **1987**, *28*, 6321; c) T. Kato, H. Kuniyasu, T. Kajiura, Y. Minami, A. Ohtaka, M. Kinomoto, J. Terao, H. Kurosawa, N. Kambe, *Chem. Commun.* **2006**, 868; for a Pd- and Ni-catalysis: d) N. Ichiishi, C. A. Malapit, Ł. Wozniak, M. S. Sanford, *Org. Lett.* **2018**, *20*, 44.

[12]   For recent use of thioesters in decarbonylative couplings, see: a) H. Ochiai, Y. Uetake, T. Niwa, T. Hosoya*, Angew. Chem. Int. Ed.* **2017**, *56*, 2482; b) T. Niwa, H. Ochiai, M. Isoda, T. Hosoya *Chem. Lett.* **2017**, *46*, 1315.

[13]   a) T. Y. Zhang, J. O'Toole, C. S. Proctor, *J. Sulfur Chem.* **1999**, *22*, 1; b) S. Yamaguchi, C. Xu, T. Okamoto, *Pure Appl. Chem.* **2006**, *78*, 721; c) T. Yamamoto, K. Takimiya, *J. Am. Chem. Soc.* **2007**, *129*, 2224; d) J. Schatz, T. Brendgen, D. Schühle in *Comprehensive Heterocyclic Chemistry III, Vol. 3* (Eds.: A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor), Elsevier, Amsterdam, **2008**, pp. 931-974; e) D. Gramec; L. P. Mašič; M. S. Dolenc, *Chem. Res. Toxicol.* **2014**, *27*, 1344; f) T. Liang, L. Xiao, K. Guo, W. Xu, X. Peng, Y. Cao, *ACS Appl. Mater. Interfac,* **2017**, *9*, 7131.

[14]   For selected recent examples, see: a) B. Wu, N. Yoshikai, *Org. Biomol. Chem.* **2016**, *14*, 5402; b) E. R. Biehl, *Top. Heterocycl. Chem.* **2012**, *29*, 347; c) O. Sato, J. Nakayama in *Comprehensive Heterocyclic Chemistry III, Vol. 3* (Eds.: A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor), Elsevier, Amsterdam, **2008**, pp. 843-930; d) T. Kashiki, S. Shinamura, M. Kohara, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, *Org. Lett.* **2009**, *11*, 2473; e) B. Godoi, R. F. Shumacher, G. Zeni, *Chem. Rev.* **2011**, *111*, 2937; f) Z. Qiao, H. Liu, X. Xiao, Y. Fu, J. Wei, Y. Li, X. Jiang, *Org. Lett.* **2013**, *15*, 2594; g) A. J. Eberhart, H. Shrives, Y. Zhang, A. Carrër, A. V. S. Parry, D. J. Tate, M. L. Turner, D. J. Procter, *Chem. Sci.* **2016**, *7*, 1281.

FULL PAPER

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

FULL PAPER
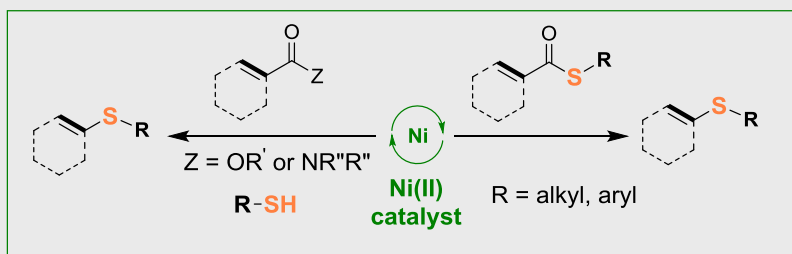
S.-C. Lee, H.-H. Liao, A.
Chatupheeraphat, M. Rueping*

Nickel-Catalyzed C-S Bond Formation
via Decarbonylative Thioetherification of
Esters, Amides and Intramolecular
Recombination Fragment Coupling of
Thioesters

Page No. – Page No.