View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. Liu and M. Szostak, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC00271A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Published on 30 January 2018. Downloaded by University of Reading on 31/01/2018 00:16:58.



COMMUNICATION

Decarbonylative Thioetherification by Nickel Catalysis using Airand Moisture-Stable Nickel Precatalysts

Received 00th January 20xx, Accepted 00th January 20xx

Chengwei Liu^a and Michal Szostak^{a,}*

DOI: 10.1039/x0xx00000x

www.rsc.org/

A general, highly selective method for decarbonylative thioetherification of aryl thioesters by C–S cleavage is reported. These reactions are promoted by a commercially-available, userfriendly, inexpensive, air- and moisture-stable nickel precatalyst. The process occurs with broad functional group tolerance, including free anilines, cyanides, ketones, halides and aryl esters, to efficiently generate thioethers using ubiquitous carboxylic acids as ultimate cross-coupling precursors (cf. conventional aryl halides or pseudohalides). Selectivity studies and site-selective orthogonal cross-coupling/thioetherification are described. This thioester activation/coupling has been highlighted in the expedient synthesis of biorelevant drug analogues. In light of the synthetic utility of thioethers and Ni(II) precatalysts, we anticipate that this user-friendly method will be of broad interest.

The thioether functional group represents one of the privileged structural motifs in the synthesis of pharmaceuticals (Fig. 1A).^{1,2} Most synthetic disconnections for the synthesis of aryl thioethers capitalize on transition-metal-catalyzed crosscoupling of aryl halides or pseudohalides with thiols (Fig. 1B).^{3,4} Recently, significant progress has been made in the development of transition-metal-catalyzed decarbonylative processes that utilize ubiquitous carboxylic acids as ultimate cross-coupling precursors in the oxidant free, redox-neutral decarbonylative pathway.⁵ Carboxylic acids are among the most appealing chemical building blocks in organic synthesis.^{5b} Of note, carboxylic acids are (1) cheaper and there are more carboxylic acids commercially available than aryl halides; (2) derived from a different pool of precursors than aryl halides and pseudohalides; (3) inert to a variety of reaction conditions allowing for ring prefunctionalization.⁶ Likewise, significant effort has been devoted to the cross-coupling of inert C-S bonds.⁷ Notably, Morandi and co-workers have developed a versatile method for carbon-sulfur bond metathesis,⁸ while

Yorimitsu and co-workers have shown that Pd-NHC systems catalyze the coupling of aromatic thioethers with N- and C-nucleophiles.⁹ In another important development, Niwa, Hosoya and co-workers established the feasibility of Rh-catalyzed decarbonylative borylation of thioesters.¹⁰ The recent surge of efforts to capture sulfur intermediates in metal-free pathways¹¹ engenders the appeal of assembling thioethers from carboxylic acid-based substrates using robust, operationally-simple protocols that could be widely adapted in various areas of chemical science.

In the past decade, there has been an increasing interest in nickel catalysis due to more facile oxidative addition, abundance and economic advantages compared with Pd catalysis.¹² Generally speaking, the use of air- and moisture-stable precatalysts is strongly preferred in modern cross-coupling applications.¹³ In this context, the groups of Monteiro,¹⁴ Percec,¹⁵ Buchwald,¹⁶ Jamison,¹⁷ Doyle,¹⁸ Monfette¹⁹ and others¹⁵⁻¹⁹ have reported well-defined Ni(II) precatalysts, which enable a variety of cross-coupling transformations. The fact that the use of robust, bench-stable Ni(II) precatalysts enables broad applications of metal catalysis in industrial research¹³ in lieu of the limited options available with air-sensitive and capricious Ni(0)-complexes.

Inspired by our recent studies in decarbonylative olefination,²⁰ arylation,²¹ cyanation²² and phosphorylation²³ of amides,²⁴ in this report we communicate our findings on decarbonylative thioetherification of aryl thioesters by selective C-S cleavage enabled by user-friendly, air- and moisture-stable nickel precatalysts (Fig. 1C). While this work was in progress, a Ni(0)-catalyzed decarbonylative thioether synthesis by C-S cleavage using a combination of air-sensitive Ni(cod)₂ (10 mol%) and PCy₃ (20 mol%) was reported.²⁵ Since our method (1) utilizes Ni(II) precatalysts that are air-stable, easy to handle and manipulate, (2) is significantly broader in scope, and (3) enables the use of operationally-simple and robust decarbonylative thioetherification for wide applications within both industry and academia, we anticipate that the protocol will be of general interest to the broad synthetic community.1-4,13

^aDepartment of Chemistry, Rutgers University, 73 Warren Street, Newark, NJ 07102, United States. Fax: (+1)-973-353-1264; Tel:(+1)-973-353-532. E-mail: michal.szostak@rutgers.edu. Homepage: http://chemistry.rutgers.edu/szostak/

^{*}Electronic Supplementary Information (ESI) available: Experimental details and characterization data. See DOI: 10.1039/x0xx00000x

COMMUNICATION

Published on 30 January 2018. Downloaded by University of Reading on 31/01/2018 00:16:58



Fig. 1 (a) Examples of pharmaceutically important aryl thioethers. (b) Conventional synthesis. (c) Decarbonylative thioetherification using air- and moisture-stable Ni precatalysts (this study).

The reaction was optimized using S-phenyl benzothioate as a model substrate. Key optimization experiments are summarized in Table 1. Using our optimized conditions, Ni(dppp)Cl₂, (10 mol%), Na₂CO₃ (1.5 equiv), dioxane, 160 °C, Sphenyl benzothioate undergoes selective C-S insertion/CO extrusion in excellent yield (entry 1). Under these conditions, $Ni(PCy_3)_2Cl_2$ is also a highly effective catalyst (entry 2). As expected, no reaction is observed in the absence of base (entries 3-4) or nickel precatalyst (entry 5). Examination of various reaction parameters revealed a significant dependence on the Ni(II) complex used (entries 6-10), with Ni(dppp)Cl₂, Ni(dppe)Cl₂, and Ni(PCy₃)₂Cl₂ showing similar performance. As expected, no reaction was observed in the absence of phosphine ligand (entry 11). An extensive screen of bases revealed that the best results were obtained with Na₂CO₃ (entries 12-14). Dioxane was identified as the optimal solvent (entries 15-17). We were pleased to find that decreasing the nickel loading to 5 mol% delivered the product under the optimized conditions (entries 18-19). Low conversions were observed in the presence of oxygen (not shown). Finally, we note that substantial conversion was observed as 120 °C, consistent with facile decarbonylation by this catalytic system (entry 20).

Table 1ReactionOptimization:Ni-CatalyzedDecarbonylativeThioetherification a

	o V S S Ph -	[Ni], -CO	S Ph	
Entry	Catalyst	Base	<i>Т</i> (°С)	Yield (%) ^b
1	Ni(dppp)Cl ₂	Na ₂ CO ₃	160	>95
2	Ni(PCy ₃) ₂ Cl ₂	Na ₂ CO ₃	160	>95
3	Ni(dppp)Cl ₂	-	160	<2
4	Ni(PCy ₃) ₂ Cl ₂	-	160	<2
5	-	Na ₂ CO ₃	160	<2
6	Ni(dppp)Cl ₂	Na ₂ CO ₃	140	>95
7	Ni(PCy ₃) ₂ Cl ₂	Na ₂ CO ₃	140	>95
8	Ni(PPh ₃) ₂ Cl ₂	Na ₂ CO ₃	140	43
9	Ni(dppe)Cl ₂	Na ₂ CO ₃	140	>95
10	Ni(dppf)Cl ₂	Na ₂ CO ₃	140	18
11	Ni(OAc) ₂	Na ₂ CO ₃	140	<5
12	Ni(PCy ₃) ₂ Cl ₂	K ₂ CO ₃	140	27
13	Ni(PCy ₃) ₂ Cl ₂	Cs ₂ CO ₃	140	<5
14	Ni(PCy ₃) ₂ Cl ₂	K ₃ PO ₄	140	15
15 [°]	Ni(PCy ₃) ₂ Cl ₂	Na ₂ CO ₃	140	87
16^d	Ni(PCy ₃) ₂ Cl ₂	Na ₂ CO ₃	140	>95
17 ^e	Ni(PCy ₃) ₂ Cl ₂	Na ₂ CO ₃	140	>95
18 ^f	Ni(PCy ₃) ₂ Cl ₂	Na ₂ CO ₃	140	27
19 ^f	Ni(PCy ₃) ₂ Cl ₂	Na ₂ CO ₃	160	>95
20	$Ni(PCy_3)_2Cl_2$	Na ₂ CO ₃	120	52

^aConditions: thioester (1.0 equiv), catalyst (10 mol%), base (1.5 equiv), 1,4-dioxane (0.20 M), *T*, 15 h. ^bGC/¹H NMR yields. ^ctoluene. ^dCH₃CN. ^eDMF. ^fcatalyst (5 mol%). See ESI for details.

The reaction exhibits broad substrate scope (Scheme 1). Electron-rich (2b-c) and electron-deficient (2d) substrates performed well in this protocol. Notable examples include halides (2e-f) and electrophilic functional groups (2g-i), providing handles for further functionalization. Orthosubstitution was well-tolerated under these conditions (2j-k). Furthermore, this protocol could be extended to polyaromatic (2I), heterocyclic (2m-n) and vinyl substrates (2o), providing the desired products in good to excellent yields. Finally, the scope of the thiol component was briefly examined (Table 2). A selection of electron-rich (entry 2), electron-deficient (entry 3), halide-containing (entry 4) and sterically-hindered (entry 5) substrates were converted into the desired thioethers in high yields. Important from a practical point of view, all of these reactions were conveniently set-up on a bench-top, which provides a very attractive feature of this protocol. 13-19 Furthermore, the scope supersedes the $Ni(cod)_2$ system²⁵ in that cyanides, ketones, halides, unprotected anlines (vide infra) and aryl esters (vide infra) are readily tolerated.

Preliminary studies demonstrate that cross-coupling of an aryl-alkyl thioester is also feasible (Scheme 2), providing another advantage of this user-friendly method. Note that alkyl thioesters are not tolerated using air-sensitive Ni(cod)₂.²⁵ Studies to expand the scope of aryl–alkyl coupling to chiral thioesters are ongoing and will be reported in due course.

To investigate the potential utility of this cross-coupling method, we tested this protocol in the rapid derivatization of

Chemical Communications

flufenamic acid, a selective COX-2 inhibitor (Scheme 3).²⁶ As shown, the reaction proceeded uneventfully, delivering the desired thioether product in high overall yield.¹⁰



^{*a*}Conditions: thioester (1.0 equiv), Ni(dppp)Cl₂ (10 mol%), Na₂CO₃ (1.5 equiv), dioxane (0.20 M), 160 °C, 15 h. ^{*b*}Isolated yields. ^{*c*}Ni(PCy₃)₂Cl₂. ^{*d*}140 °C. See ESI for details.

Table 2SubstrateScope:Ni-CatalyzedDecarbonylativeThioetherification^a

Ar Ni(dppp)Cl₂ (10 mol%) `Ar Na₂CO₃ (1.5 equiv) 160 °C, 15 h 2 1 Yield Entry Thioester 1 Product 2 (%) 1 1a 2a 98 2 1p 2c' 85 1q 3 2ď 98 1r 2e' 91 5 2k' 96 **1**s

^aConditions: thioester (1.0 equiv), Ni(dppp)Cl₂ (10 mol%), Na₂CO₃ (1.5 equiv), dioxane (0.20 M), 160 °C, 15 h. ^bIsolated yields. See ESI for details.

Scheme 2 Ni-Catalyzed Decarbonylative Thioetherification of *S*-Alkyl Benzothioate

$$\begin{array}{c} 0 \\ \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

Scheme 3 Expedient Synthesis of Flufenamic Acid Thioether



Scheme 4 Selective Decarbonylative Thioetherification









Yamaguchi, Itami and co-workers recently reported a Nicatalyzed decarbonylative diaryl ether synthesis by C–O cleavage.²⁷ We were intrigued to find that the present coupling proceeds in the presence of the sensitive aryl ester linkage (Scheme 4), demonstrating high chemoselectivity of the present method.

To further showcase the utility of this new thioetherification, sequential orthogonal cross-couplings were investigated (Scheme 5). This sequence highlights the potential

Page 3 of 4

of decarbonylative thioetherification to selectively generate thioethers from readily available carboxylic acids. 5,6,10

In conclusion, we have reported a general method for decarbonylative thioetherification by C–S cleavage using a commercially-available, user-friendly, inexpensive, air- and moisture-stable nickel(II) precatalyst. The process provides a synthetic entry to the biologically-relevant thioether functional group exploiting abundant carboxylic acids as ultimate cross-coupling precursors. In view of the synthetic utility of thioethers and Ni(II) precatalysts, we anticipate that the method will be of broad interest.²⁸ Further studies on related decarbonylative cross-coupling transformations are ongoing.

Rutgers University and the NSF (CAREER CHE-1650766) are acknowledged for support.

Notes and references

Published on 30 January 2018. Downloaded by University of Reading on 31/01/2018 00:16:58

- For leading reviews on biological activity of thioethers, see: (a) E. A. Ilardi, E. Vitaku and J. T. Njardson, *J. Med. Chem.*, 2014, **57**, 2832; (b) M. Feng, B. Tang, S. H. Liang and X. Jiang, *Curr. Top. Med. Chem.*, 2016, **16**, 1200.
- 2 L. Brunton, B. Chabner and B. Knollman, *Goodman and Gilman's The Pharmacological Basis of Therapeutics*; MacGraw-Hill, New York, 2010.
- 3 For excellent reviews on C–S bond formation, see: (*a*) C. C. Eichman and J. P. Stambuli, *Molecules*, 2011, **16**, 590; (*b*) J. P. Stambuli, In *New Trends in Cross-Coupling*, T. J. Colacot, The Royal Society of Chemistry, 2015, p. 254; (*c*) I. P. Beletskaya and V. P. Ananikov, *Chem. Rev.*, 2011, **111**, 1596.
- 4 For recent selected examples of thioether synthesis, see: (a) M. Jouffroy, C. B. Kelly and G. A. Molander, Org. Lett., 2016, **18**, 876; (b) M. S. Oderinde, M. Frenette, D. W. Robbins, B. Aquila and J. W. Johannes, J. Am. Chem. Soc., 2016, **138**, 1760; (c) B. Liu, C. H. Lim and G. M. Miyaka, J. Am. Chem. Soc., 2017, **139**, 13616; (d) C. Uyeda, Y. Tan, G. C. Fu and J. C. Peters, J. Am. Chem. Soc., 2013, **135**, 9548; (e) M. A. Fernandez-Rodriguez, Q. Shen and J. F. Hartwig, J. Am. Chem. Soc., 2006, **128**, 2180; For a leading report on C–S construction by C–H activation, see: (f) P. Saravanan and P. Anbarasan, Org. Lett., 2014, **16**, 848.
- 5 For reviews, see: (a) R. Takise, K. Muto and J. Yamaguchi, *Chem. Soc. Rev.*, 2017, **46**, 5864; (b) W. I. Dzik, P. P. Lange and L. J. Gooßen, *Chem. Sci.*, 2012, **3**, 2671; For the seminal decarbonylative cross-coupling of aryl esters, see: (c) K. Amaike, K. Muto, J. Yamaguchi and K. Itami, *J. Am. Chem. Soc.*, 2012, **134**, 13573; For additional examples, see: (d) A. Dermenci and G. Dong, *Sci. China Chem.*, 2013, **56**, 685.
- 6 For a comprehensive review, see: L. J. Gooßen, N. Rodriguez and K. Gooßen, *Angew. Chem. Int. Ed.*, 2008, **47**, 3100.
- For reviews, see: (a) S. G. Modha, V. P. Mehta and E. V. Van der Eycken, *Chem. Soc. Rev.*, 2013, **42**, 5042; (b) L. Wang, W. He and Z. Yu, *Chem. Soc. Rev.*, 2013, **42**, 599; (c) S. R. Dubbaka and P. Vogel, *Angew. Chem. Int. Ed.*, 2005, **44**, 7674; For selected relevant examples, see: (d) K. Osakada, T. Yamamoto and A. Yamamoto, *Tetrahedron Lett.*, 1987, **28**, 6321; (e) E. Wenkert and D. Chianelli, *J. Chem. Soc., Chem. Commun.*, 1991, 627; (f) Y. Minamo, H. Kuniyasu, K. Miyafuji and N. Kambe, *Chem. Commun.*, 2009, 3080.
- (a) Z. Lian, B. N. Bhawal, P. Yu and B. Morandi, *Science*, 2017, 356, 1059; For a pertinent reversible process involving decarbonylation, see: (b) X. Fang, B. Cacherat and B. Morandi, *Nat. Chem.*, 2017, 9, 1105 and references cited therein.
- (a) T. Sugahara, K. Murakami, H. Yorimitsu and A. Osuka, Angew. Chem. Int. Ed., 2014, 53, 9329; (b) K. Gao, H. Yorimitsu and A. Osuka, Angew. Chem. Int. Ed., 2016, 55, 4573; See, also: (c) S. Otsuka, D. Fujino, K. Murakami, H.

4 | Chem. Commun., 2018, 00, 1-3

Yorimitsu and A. Osuka, *Chem. Eur. J.*, 2014, **20**, 13146; (*d*) M. Bhanuchandra, A. Baralle, S. Otsuka, K. Nogi, H. Yorimitsu and A. Osuka, *Org. Lett.*, 2016, **18**, 2966.

- (a) H. Ochiai, Y. Uetake, T. Niwa and T. Hosoya, Angew. Chem. Int. Ed., 2017, 56, 2482; See, also: (b) Y. Uetake, T. Niwa and T. Hosoya, Org. Lett., 2016, 18, 2758.
- 11 (a) J. A. Fernandez-Salas, A. J. Eberhart and D. J. Procter, J. Am. Chem. Soc., 2016, **138**, 790; (b) L. Shang, Y. Chang, F. Luo, J. N. He, X. Huang, L. Zhang, L. Kong, K. Li and B. Peng, J. Am. Chem. Soc., 2017, **139**, 4211; (c) T. Yanagi, S. Otsuka, Y. Kasuga, K. Fujimoto, K. Murakami, K. Nogi, H. Yorimitsu and A. Otsuka, J. Am. Chem. Soc., 2016, **138**, 14582; For excellent study on metal-free fluoroalkylthiolation, see: (d) D. Zhu, Y. Gu, L. Lu and Q. Shen, J. Am. Chem. Soc., 2015, **137**, 10547.
- 12 (a) S. Z. Tasker, E. A. Standley and T. F. Jamison, Nature, 2014, 509, 299; (b) V. P. Ananikov, ACS Catal., 2015, 5, 1964.
- 13 For an excellent monograph on cross-couplings, see: (a) T. J. Colacot, New Trends in Cross-Coupling, RSC, 2015; For leading reviews, see: (b) P. G. Gildner and T. J. Colacot, Organometallics, 2015, 34, 5497; (c) H. Li, C. C. C. Johansson-Seechurn and T. J. Colacot, ACS Catal., 2012, 2, 1147.
- 14 D. Zim, V. R. Lando, J. Dupont and A. L. Monteiro, *Org. Lett.*, 2001, **3**, 3049.
- 15 R. L. Jezorek, N. Zhang, P. Leowanawat, M. H. Bunner, N. Gutsche, A. K. R. Pesti, J. T. Olsen and V. Percec, *Org. Lett.*, 2014, **16**, 6326.
- 16 N. H. Park, G. Teverovskiy and S. L. Buchwald, Org. Lett., 2014, 16, 220.
- 17 E. A. Stadley, S. J. Smith, P. Müller and T. F. Jamison, Organometallics, 2014, 33, 2012.
- 18 J. D. Shields, E. E. Gray and A. G. Doyle, Org. Lett., 2015, 17, 2166.
- (a) J. Magano and S. Monfette, ACS Catal., 2015, 5, 3120; For a review on well-defined, bench-stable precatalysts, see: (b) N. Hazari, P. R. Melvin and M. M. Beromi, Nat. Rev. Chem., 2017, 1, 25.
- 20 (a) G. Meng and M. Szostak, Angew. Chem. Int. Ed., 2015, 54, 14518; (b) C. Liu, and G. Meng and M. Szostak, J. Org. Chem., 2016, 81, 12023.
- 21 (a) S. Shi, G. Meng and M. Szostak, Angew. Chem. Int. Ed., 2016, 55, 6959; (b) G. Meng and M. Szostak, Org. Lett., 2016, 18, 796; (c) G. Meng and M. Szostak, ACS Catal., 2017, 7, 7251.
- 22 S. Shi and M. Szostak, Org. Lett., 2017, 19, 3095.
- 23 C. Liu and M. Szostak, Angew. Chem. Int. Ed., 2017, 56, 12718.
- 24 For reviews, see: (a) G. Meng, S. Shi and M. Szostak, Synlett, 2016, 27, 2530; (b) C. Liu and M. Szostak, Chem. Eur. J., 2017, 23, 7157; For selected examples of decarbonylative cross-coupling of amides, see: (c) A. Dey, S. Sasmai, K. Seth, G. K. Lahiri and D. Maiti, ACS Catal., 2017, 7, 433; (d) H. Yue, L. Guo, H. H. Liao, Y. Cai, C. Zhu and M. Rueping, Angew. Chem. Int. Ed., 2017, 56, 4282; (e) H. Yue, L. Guo, S. C. Lee, X. Liu and M. Rueping, Angew. Chem. Int. Ed., 2017, 56, 3972; (f) W. Srimontree, A. Chatupheeraphat, H. H. Liao and M. Rueping, Org. Lett., 2017, 19, 3091; For selected examples of decarbonylative cross-coupling of esters, see: (g) K. Muto, J. Yamaguchi, D. G. Musaev and K. Itami, Nat. Commun., 2015, 6, 7508; (h) T. Okita, K. Kumazawa, R. Takise, K. Muto, K. Itami and J. Yamaguchi, Chem. Lett., 2017, 46, 218.
- 25 N. Ichiishi, C. A. Malapit, L. Wozniak and M. S. Sanford, *Org. Lett.*, 2018, **20**, 44.
- 26 B. Cryer and M. Feldman, Am. J. Med., 1998, 104, 413.
- 27 R. Takise, R. Isshiki, K. Muto, K. Itami and J. Yamaguchi, J. Am. Chem. Soc., 2017, **139**, 3340.
- 28 We hypothesize that the mechanism involves selective oxidative addition into the C–S bond (cf. C(aryI)–C(carbonyI)). For precedent reports on C–S oxidative addition, see: refs. 7a–c, f and references cited therein.

Decarbonylative Coupling via Selective C–S Cleavage



carboxylic acid precursors broad tolerance high generality

■ selective C–S cleavage ■ modular, air-stable Ni precatalyst