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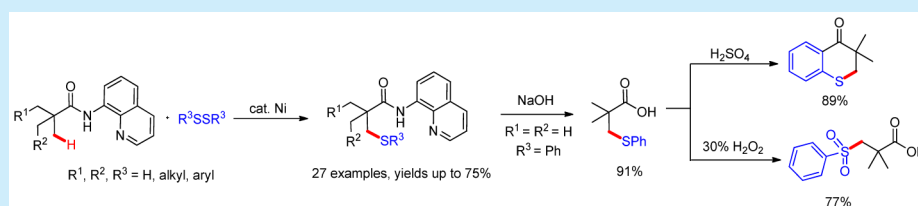
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Nickel-Catalyzed Direct Thiolation of C(sp³)–H Bonds in Aliphatic AmidesXie Wang,[†] Renhua Qiu,^{*,†,‡} Chunyang Yan,[†] Vutukuri Prakash Reddy,[‡] Longzhi Zhu,[†] Xinhua Xu,^{*,†} and Shuang-Feng Yin^{*,†}[†]State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, P. R. China[‡]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Osaka, 565-0871, Japan

Supporting Information



ABSTRACT: Nickel-catalyzed thiolation of the inactivated methyl C(sp³)–H bonds of aliphatic amides with disulfide is described. It is a novel strategy for the synthesis of thioethers with the ultimate goal of generating thioether carboxylic acids with various functional groups.

Organosulfur compounds are ubiquitous in organic and pharmaceutical research.^{1,2} There are recent efforts targeting thiol-based transformation for the formation of thiochromane analogues³ (A–D) and sulfones (E–F) (Figure 1). Song et al. reported that the 3,3'-diindolylmethane analogues,

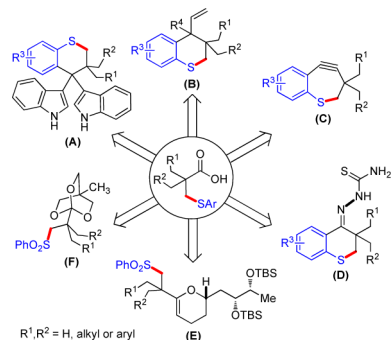


Figure 1. Thiol-based bioactive molecules.

such as thiochromane (A), showed in vitro antitumor activities.⁴ Grassi and Alexakis demonstrated that the well-established catalytic asymmetric methods can be further extended by enforcing the S-carbon quaternary centers (B) with a vinyl group.⁵ Almeida et al. noted that thiacycloalkynes (C) are promising new reagents for click chemistry.⁶ Furthermore, thiosemicarbazone analogues (D) were found to be potent inhibitors of cathepsin L,⁷ whereas in the synthesis of bryostatin, which is used in the treatment of lymphoma, sulfones (E) serve as central glycol intermediates.⁸ In addition, 2,6,7-trioxabicyclo-[2.2.2]octane sulfone (F) is a new reagent that enables the rapid

assembly of pyranone intermediates.⁹ Given the significant biological potential of these compounds, the development of a general route for their efficient generation is urgent. The synthesis of these sulfur-containing compounds requires a key precursor, and the precursors can be formed by the oxidation or ring-closing reaction of carboxylic acid intermediates.^{7,10} Herein, we provide a strategy for the synthesis of thioether carboxylic acids with the ultimate goal of generating these natural and synthetic compounds (Scheme 1).

Scheme 1. Synthetic Route to the Key Precursors



Thiolysis and the addition of various sulfur nucleophiles to a C–C unsaturated bond involved in the direct coupling of organic halides with thiols are convenient methods for the formation of C–S bonds, but these methods have critical issues, such as the use of highly prefucionalized organic halides.^{11,12} The thiolation of the C(sp²)–H bond of reactive arenes has been reported.¹³ It is easy to deprotonate acidic arenes and heteroarenes with a strong base to give the thiolated products.¹⁴ There are reports on the direct thiolation of the C(sp²)–H bond to construct intermolecular skeletons as well as intramolecular benzothiophene and benzothiazole using catalysts that are based on transition metals.^{15–20} In recent years, there have been reports on approaches that are free of transition metals.²¹

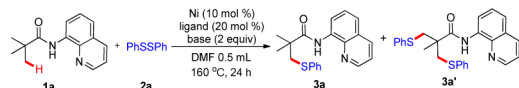
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However, the direct thiolation of an inactivated methyl C(sp³)–H bond has yet to be established due to its thermodynamic stability (calcd 440 kJ mol^{−1} for a primary C–H bond). It is believed that the chelation-assisted transformation is facilitated by a bidentate directing group, which leads to the site-selective functionalization of the C(sp³)–H bonds.²² The method has shown prime synthetic potential for exploring new types of transformations of C(sp³)–H bonds that cannot be achieved using conventional synthetic methods.²³ In this work, we applied the chelation-assisted method using amides as bidentate directing groups for the direct thiolation of inactivated methyl C(sp³)–H bonds.

To verify the proposed strategy, our initial investigation focused on the thiolation of *N*-(quinolin-8-yl)pivalamide **1a** (0.2 mmol) with diphenyl disulfide **2a** (0.4 mmol) over Ni catalysts (Table 1). 2,4,6-Trimethylbenzoic acid, Na₂CO₃, and DMF were

Table 1. Optimization of Reaction Conditions^a



entry	catalyst	ligand	base	yields (3a/3a') ^b
1	Ni(OAc) ₂	MesCOOH	Na ₂ CO ₃	40/5
2	Ni(OTf) ₂	MesCOOH	Na ₂ CO ₃	51/20
3	Ni(cod) ₂	MesCOOH	Na ₂ CO ₃	57/17
4	Ni(acac) ₂	MesCOOH	Na ₂ CO ₃	20/0
5	NiF ₂	MesCOOH	Na ₂ CO ₃	47/18
6	NiCl ₂	MesCOOH	Na ₂ CO ₃	55/10
7	NiBr ₂	MesCOOH	Na ₂ CO ₃	72/8
8	NiBr ₂	PPh ₃	Na ₂ CO ₃	45/0
9	NiBr ₂	PCy ₃	Na ₂ CO ₃	55/0
10	NiBr ₂	xantphos	Na ₂ CO ₃	47/23
11	NiBr ₂	Dppbz	Na ₂ CO ₃	34/0
12	NiBr ₂	P(2-furyl) ₃	Na ₂ CO ₃	41/8
13	NiBr ₂	BINAP	Na ₂ CO ₃	47/7
14	NiBr ₂	Dppe	Na ₂ CO ₃	18/0
15	NiBr ₂	MesCOOH	K ₂ CO ₃	7/0
16	NiBr ₂	MesCOOH	Cs ₂ CO ₃	12/0
17	NiBr ₂	MesCOOH	NaHCO ₃	60/5
18	NiBr ₂	MesCOOH	KHCO ₃	14/0
19	NiBr ₂	MesCOOH	NaOAc	31/0
20	NiBr ₂	MesCOOH	NaOH	0

^aReaction conditions: amide (0.2 mmol), diphenyl disulfides (0.4 mmol), catalyst (0.02 mmol), ligand (0.04 mmol), base (0.4 mmol) in solvent (0.5 mL) at 160 °C for 24 h in 10 mL screw-capped vials. ^bNMR yield.

handled under N₂. After screening the catalysts, thioarylated product **3a** was obtained in 72% NMR yield over NiBr₂ (entry 7). Further optimization showed that, with variation of the ligands, such as bidentate phosphines and bulky 2,4,6-trimethylbenzoic acid (MesCOOH), there is a discrepancy in the catalytic activity (entries 7–14). The efficiency of the reaction was also significantly affected by the choice of bases (entries 15–20). Na₂CO₃ and NaHCO₃ result in good yields of the thiolated products, but other bases have poor yields. In these reactions, DMF was the solvent of choice (see Supporting Information). Figure 2 shows the directing groups that are not effective (giving no desired products). The results indicate the importance of quinoline species for bidentate direction.

The approach was then applied to different amides under the optimal reaction conditions (Scheme 2). The reaction was

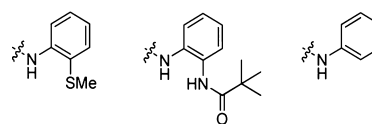
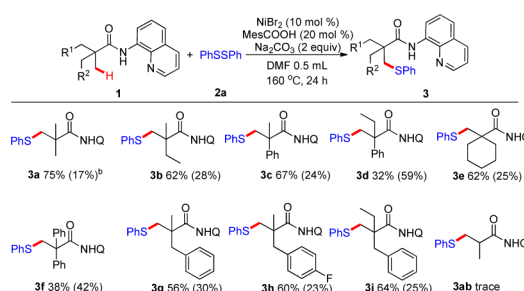


Figure 2. Ineffective directing groups.

Scheme 2. Investigation of Aliphatic Amides Scope^a

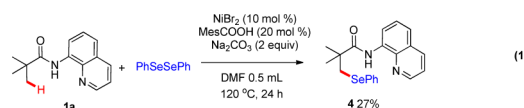


^aReaction conditions: amide **1** (0.2 mmol), diphenyl disulfides **2a** (0.4 mmol), NiBr₂ (0.02 mmol), MesCOOH (0.04 mmol), Na₂CO₃ (0.4 mmol) in DMF (0.5 mL) at 160 °C for 24 h in 10 mL screw-capped vials. ^bIsolated yields; the number in the parentheses is the isolated yield of the recovered starting amide **1**.

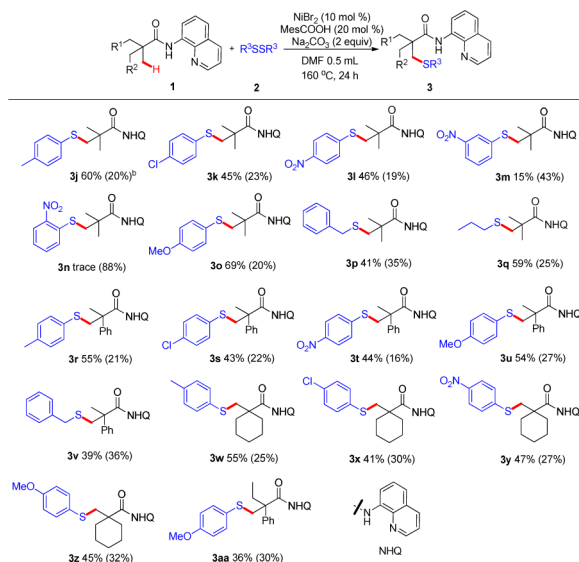
sensitive to the structure of the amides (**3ab**).²² As expected, the disulfides react with the methyl groups in the α-position of the amide, giving both mono- and dithiolated products, with the monothiolated product (**3a**) being the most favorable. The reactions proceed exclusively at the methyl group in a highly regioselective manner, as in the cases of **3b**, **3c**, and **3d**. The reactions show a predominant preference for the C(sp³)–H bonds of the methyl groups over the methylene and benzene groups. This fact indicates that, for the cyclometalation step, the five-membered ring intermediate is favored over the six- or seven-membered ring intermediates. The reaction of cyclohexane carboxamide **1e** results in selective monothiolation at the methyl group. Again, in the case of 2,2'-diphenylpropionamide **1f**, the reaction occurs exclusively on the methyl group, and there is no thiolation of the benzene C–H bonds. As for the tertiary alkyl carboxamides bearing a benzylic group (**1g–1i**), only monothiolated products (**3g–3i**) are obtained (56%–64% yields).

Next, the scope of the disulfides with various substituents was examined using different amides (Scheme 3). As expected, diaryl disulfides show high compatibility under the optimized thiolation conditions, and the reactions tolerate a variety of functional groups, such as methoxy, chloro, nitro, benzyl, and even propyl groups.

Encouraged by the viability of the approach for direct C–S bond formation, we applied the system to diaryl diselenide with an aliphatic amide, and the desired cross-coupling compound (**4**) was obtained in moderate yield (eq 1).

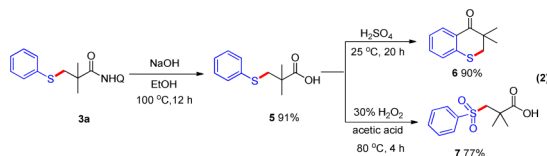


Having successfully achieved the synthesis of highly functionalized thioethers, we explored their conversion to carboxylic acids, which are the building blocks for the synthesis of the targeted key precursors. The 8-aminoquinoline group was readily hydrolyzed in a one-step procedure using NaOH in EtOH, as

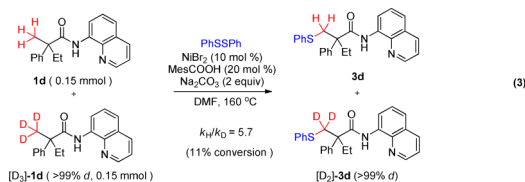
Scheme 3. Investigation of Disulfides Scope^a

^aReaction conditions: amide **1** (0.2 mmol), diphenyl disulfides **2** (0.4 mmol), NiBr₂ (0.02 mmol), MesCOOH (0.04 mmol), Na₂CO₃ (0.4 mmol) in DMF (0.5 mL) at 160 °C for 24 h in 10 mL screw-capped vials. ^bIsolated yields; the number in parentheses is the yield of the recovered starting amide **1**.

reported by Shabashov and Daugulis,²⁴ giving phenyl sulfide carboxylic acid in excellent yield (eq 2). The carboxylic acid could be applied as a key precursor for the construction of biological molecules (Figure 1).

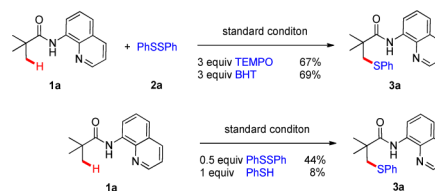


To probe the mechanism of the reaction further, a deuterium-labeling experiment was performed. The mixture of amide **1d** and deuterated amide **1d-D₃** was reacted with **2a** under standard reaction conditions in one pot (eq 3), and a *k_H*/*k_D* isotope effect up to 5.7 was observed, providing evidence that C–H cleavage is the rate-determining step.



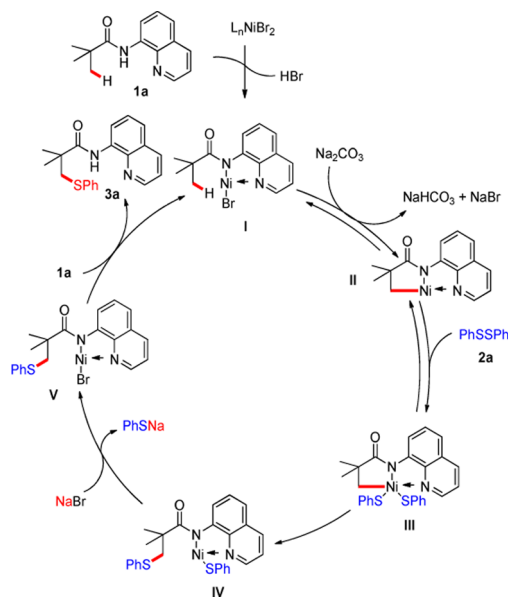
In addition, we performed four control experiments (Scheme 4) for understanding the pathway of the present reactions. When 3 equiv of 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) as the radical-trapping reagent were added under the standard conditions, the reaction is not inhibited but gives **3a** in 67% and 69% isolated yield, respectively. The results suggest that the reaction does not involve single-electron transfer. Additionally, when 0.5 equiv of phenyl disulfide **1a** or 1 equiv of benzenethiol was employed, the desired product **3a** is isolated in 44% and 8% yield, which confirmed the role of the disulfide as an active reagent.

Scheme 4. Preliminary Mechanistic Study



On the basis of the above results and those reported previously,²⁵ a possible reaction mechanism of **1a** with **2a** is proposed (Scheme 5). Coordination of **1a** to the nickel center

Scheme 5. Proposed Catalytic Mechanism



followed by ligand exchange with the concomitant generation of HBr gives the nickel intermediate **I**, which undergoes C–H cleavage and reversible cyclometalation to give **II**. The oxidative addition of **2a** gives the high-valent Ni(IV) complex **III**, which undergoes reductive elimination to give **IV** and the C–S bond. After neutralization with NaBr, nickel bromide species **V** and sodium thiophenolate form. Finally, ligand exchange of **V** with **1a** results in product **3a** and regeneration of nickel complex **I**.

In summary, we reported the first example of nickel-catalyzed direct thiolation of inactivated methyl C(sp³)–H bonds in aliphatic amides having an 8-aminoquinoline moiety (as a bidentate group). It is a novel strategy for the synthesis of thioethers with the ultimate goal of generating thioether carboxylic acids with various functional groups.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and copies of the ¹H, ¹³C spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Hansch, C.; Sammes, P. G.; Taylor, J. B. *Comprehensive medicinal chemistry; the rational design, mechanistic study & therapeutic application of chemical compounds*; Pergamon Press: Oxford, NY, 1990; pp 12–27.
- (2) (a) Sawyer, J. S.; Schmittling, E. A.; Palkowitz, J. A.; Smith, W. J. *J. Org. Chem.* **1998**, *63*, 6338. (b) Mellah, M.; Voituriez, A.; Schulz, E. *Chem. Rev.* **2007**, *107*, 5133. (c) Tian, M.; Guo, F.; Sun, Y.; Zhang, W.; Miao, F.; Liu, Y.; Song, G.; Ho, C.-L.; Yu, X.; Sun, J.-Z.; Wong, W.-Y. *Org. Biomol. Chem.* **2014**, *12*, 6128. (d) Poon, S.-Y.; Wong, W.-Y.; Cheah, K.-W.; Shi, J.-X. *Chem.—Eur. J.* **2006**, *12*, 2550. (e) Babu, G.; Orita, A.; Otera, J. *Org. Lett.* **2005**, *7*, 4641. (f) Dong, W.; Wang, L.; Parthasarathy, K.; Pan, F.; Bolm, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 11573.
- (3) (a) Wang, W.; Li, H.; Wang, J.; Zu, L. *J. Am. Chem. Soc.* **2006**, *128*, 10354. (b) Kinf, H.-H.; Mebrahtu, F.-M.; Makolo, F.-L.; Moshapo, P.-T.; Manana, M.-M. *J. Org. Chem.* **2014**, *79*, 3111. (c) Xu, F.; Peng, L.; Shinohara, K.; Morita, T.; Yoshida, S.; Hosoya, T.; Orita, A.; Otera, J. *J. Org. Chem.* **2014**, *79*, 11592.
- (4) Song, Y.-L.; Dong, Y.-F.; Yang, T.; Zhang, C.-C.; Su, L.-M.; Huang, X.; Zhang, D.-N.; Yang, G.-L.; Liu, Y.-X. *Bioorg. Med. Chem.* **2013**, *21*, 7624.
- (5) Grassi, D.; Alexakis, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 13642.
- (6) Almeida, G.; Sletten, E. M.; Nakamura, H.; Palaniappan, K. K.; Bertozzi, C. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 2443.
- (7) Song, J.; Jones, L. M.; Kumar, G. D. K.; Conner, E. S.; Bayeh, L.; Chavarria, G. E.; Charlton-Sevcik, A. K.; Chen, S.-E.; Chaplin, D. J.; Trawick, M. L.; Pinney, K. G. *ACS Med. Chem. Lett.* **2012**, *3*, 450.
- (8) Hale, K. J.; Frigerio, M.; Manaviazar, S. *Org. Lett.* **2001**, *3*, 3791.
- (9) Grove, C. I.; Maso, M. J. D.; Jaipuri, F. A.; Kim, M. B.; Shaw, J. T. *Org. Lett.* **2012**, *14*, 4338.
- (10) Parham, W. E.; Mckown, W. D.; Nelson, V.; Kajigaeshi, S.; Ishikawa, N. *J. Org. Chem.* **1973**, *38*, 1361.
- (11) For recent reviews on metal-catalyzed C–S bond formations, see: (a) Shen, C.; Zhang, P.-F.; Sun, Q.; Bai, S.-Q.; Andy Hor, T. S.; Liu, X.-G. *Chem. Soc. Rev.* **2015**, *44*, 291. (b) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596. (c) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (d) Postigo, A. *RSC Adv.* **2011**, *1*, 14. (e) Eichman, C. C.; Stambuli, J. P. *Molecules* **2011**, *16*, 590. (f) Kondo, T.; Mitsudo, T.-A. *Chem. Rev.* **2000**, *100*, 3205. (g) Geramita, K.; McBee, J.; Shen, Y.; Radu, N.; Tilley, T. D. *Chem. Mater.* **2006**, *18*, 3261. (h) Karshtedt, D.; Bell, A.-T.; Tilley, T.-D. *J. Am. Chem. Soc.* **2005**, *127*, 12640. (i) Han, L.-B.; Tilley, T. D. *J. Am. Chem. Soc.* **2006**, *128*, 13698.
- (12) For selected reviews on organocatalytic C–S bond formations, see: (a) Nielsen, M.; Jacobsen, C. B.; Holub, N.; Paixão, M. W.; Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 2668. (b) Chauhan, P.; Mahajan, S.; Enders, D. *Chem. Rev.* **2014**, *114*, 8807. (c) Alba, A.-N. R.; Companyó, X.; Rios, C. *Chem. Soc. Rev.* **2010**, *39*, 2018.
- (13) For works on thiolation of C(sp²)–H bonds, see: (a) Iwasaki, M.; Iyanaga, M.; Tsuchiya, Y.; Nishimura, Y.; Li, W.-J.; Li, Z.-P.; Nishihara, Y. *Chem.—Eur. J.* **2014**, *20*, 2459. (b) Xu, C.; Shen, Q. *Org. Lett.* **2014**, *16*, 2046. (c) Wu, Z.; Song, H.; Cui, X.; Pi, C.; Du, W.; Wu, Y. *Org. Lett.* **2013**, *15*, 1270. (d) Yang, Y.; Hou, W.; Qin, L.; Du, J.; Feng, H.; Zhou, B.; Li, Y. *Chem.—Eur. J.* **2014**, *20*, 416. (e) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 8249. (f) Yu, S.; Wan, B.; Li, X. *Org. Lett.* **2015**, *17*, 58. (g) Lin, C.; Li, D.; Wang, B.; Yao, J.; Zhang, Y. *Org. Lett.* **2015**, *17*, 1328.
- (14) (a) Popov, I.; Do, H.-Q.; Daugulis, O. *J. Org. Chem.* **2009**, *74*, 8309. (b) Zou, L.-H.; Reball, J.; Mottweiler, J.; Bolm, C. *Chem. Commun.* **2012**, *48*, 11307.
- (15) For palladium-catalyzed thiolation: (a) Samanta, R.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 5217. (b) Joyce, L. L.; Batey, R. A. *Org. Lett.* **2009**, *11*, 2792. (c) Inamoto, K.; Arai, Y.; Hiroya, K.; Doi, T. *Chem. Commun.* **2008**, *43*, 5529. (d) Iwasaki, M.; Kaneshika, W.; Tsuchiya, Y.; Nakajima, K.; Nishihara, Y. *J. Org. Chem.* **2014**, *79*, 11330.
- (16) For copper-catalyzed thiolation: (a) Deng, H.; Li, Z.; Ke, F.; Zhou, X. *Chem.—Eur. J.* **2012**, *18*, 4840. (b) Tran, L. D.; Popov, I.; Daugulis, O. *J. Am. Chem. Soc.* **2012**, *134*, 18237. (c) Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790. (d) Wang, L.; Priebbenow, D.-L.; Dong, W.; Bolm, C. *Org. Lett.* **2014**, *16*, 2661. (e) Ali, W.; Guin, S.; Rout, S. K.; Gogoi, A.; Patel, B. K. *Adv. Synth. Catal.* **2014**, *356*, 3099. (f) Riduan, S. N.; Ying, J. Y.; Zhang, Y. *Org. Lett.* **2012**, *14*, 1780. (g) Wu, X.; Zhao, Y.; Zhang, G.; Ge, H. *Angew. Chem., Int. Ed.* **2014**, *53*, 3706.
- (17) For ruthenium-catalyzed thiolation: Cheng, Y.; Yang, J.; Qu, Y.; Li, P. *Org. Lett.* **2012**, *14*, 98.
- (18) For iron-catalyzed thiolation: (a) Wang, H.; Wang, L.; Shang, J.; Li, X.; Wang, H.; Gui, J.; Lei, A. *Chem. Commun.* **2012**, *48*, 76. (b) Cheng, Y.; Dong, W.; Wang, L.; Parthasarathy, K.; Bolm, C. *Org. Lett.* **2014**, *16*, 2000. (c) Iwasaki, M.; Fujii, T.; Nakajima, K.; Nishihara, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 13880.
- (19) For silver-catalyzed thiolation: Wang, P.-F.; Wang, X.-Q.; Dai, J.-J.; Feng, Y.-S.; Xu, H.-J. *Org. Lett.* **2014**, *16*, 4586.
- (20) For nickel-catalyzed thiolation: (a) Yan, S.-Y.; Liu, Y.-J.; Liu, B.; Liu, Y.-H.; Shi, B.-F. *Chem. Commun.* **2015**, *51*, 4069. (b) Yang, K.; Wang, Y.; Chen, X.; Kadi, A.-A.; Fun, H.-K.; Sun, H.; Zhang, Y.; Lu, H. *Chem. Commun.* **2015**, *51*, 3582.
- (21) (a) Kang, X.; Yan, R.; Yu, G.; Pang, X.; Liu, X.; Li, X.; Xiang, L.; Huang, G. *J. Org. Chem.* **2014**, *79*, 10605. (b) He, L.; Guo, H.; Li, Y.-Z.; Du, G.-F.; Dai, B. *Chem. Commun.* **2014**, *50*, 3719. (c) Ge, W.; Wei, Y. *Green Chem.* **2012**, *14*, 2066. (d) Zhu, Y.-P.; Lian, M.; Jia, F.-C.; Liu, M.-C.; Yuan, J.-J.; Gao, Q.-H.; Wu, A.-X. *Chem. Commun.* **2012**, *48*, 9086. (e) Guo, S.-R.; Yuan, Y.-Q.; Xiang, J.-N. *Org. Lett.* **2014**, *15*, 4654. (f) Yuan, J.; Ma, X.; Yi, H.; Liu, C.; Lei, A. *Chem. Commun.* **2014**, *50*, 14386. (g) Zhao, J.; Fang, H.; Han, J.; Pan, Y.; Li, G. *Adv. Synth. Catal.* **2014**, *356*, 2719.
- (22) (a) Aihara, Y.; Chatani, N. *J. Am. Chem. Soc.* **2014**, *136*, 898. (b) Shang, R.; Ilies, L.; Matsumoto, A.; Nakamura, E. *J. Am. Chem. Soc.* **2013**, *135*, 6030. (c) Wu, X.; Zhao, Y.; Ge, H. *J. Am. Chem. Soc.* **2014**, *136*, 1789. (d) Wang, Z.; Ni, J.; Kuninobu, Y.; Kanai, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 3496. (e) Zhang, S.-Y.; Li, Q.; He, G.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2015**, *137*, 531.
- (23) (a) Zaitsev, V. G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154. (b) Rouquet, G.; Chatani, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 11726. (c) Hasegawa, N.; Charra, V.; Inoue, S.; Fukumoto, Y.; Chatani, N. *J. Am. Chem. Soc.* **2011**, *133*, 8070. (d) Qiu, R.; Reddy, V. P.; Iwasaki, T.; Kambe, N. *J. Org. Chem.* **2015**, *80*, 367. (e) He, G.; Zhang, S.-Y.; Nack, W. A.; Li, Q.; Chen, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 11124. (f) Zhang, S.-Y.; Li, Q.; He, G.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2013**, *135*, 12135.
- (24) Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2010**, *132*, 3965.
- (25) (a) Aihara, Y.; Chatani, N. *J. Am. Chem. Soc.* **2013**, *135*, 5308. (b) Higgs, A. T.; Zinn, P. J.; Sanford, M. S. *Organometallics* **2010**, *29*, 5446. (c) Iwasaki, M.; Tsuchiya, Y.; Nakajima, K.; Nishihara, Y. *Org. Lett.* **2014**, *16*, 4920.