

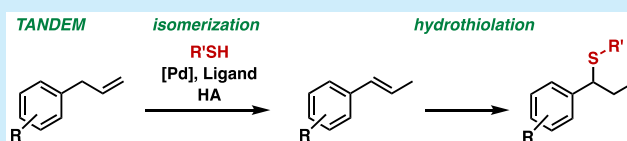
Palladium-Catalyzed Tandem Isomerization/Hydrothiolation of Allylarenes

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S Supporting Information

ABSTRACT: Herein we report a tandem olefin migration/hydrothiolation of allyl benzenes facilitated by an *in situ* generated palladium hydride. A catalyst system composed of palladium acetate and bidentate ligand dtbpx (1,2-bis(di-*tert*-butylphosphinomethyl)benzene) in the presence of catalytic amounts of triflic acid led to the tandem transformation, which furnished benzylic thioethers. The reaction exhibits high regioselectivity and can be conducted under mild conditions. The robustness of the catalyst is displayed through reactions with coordinating thiols.



The conjugative migration of a double bond of allyl benzenes (migration over one carbon atom) is a well-understood and extensively investigated process.¹ In general, transition metal hydrides have enabled the use of mild reaction conditions in alkene isomerizations.² A large portion of work in this field was essentially intended toward developing additional reactivity in a tandem process, which is often referred to as remote functionalization.³ Allylic isomerization was combined with various functionalizations of the benzylic position, which enabled formation of new C–C⁴ or C–heteroatom⁵ bonds from easily available precursors. To the best of our knowledge, this strategy was not applied in the formation of new C–S bonds.

The ubiquity of branched thioethers in a range of biologically relevant compounds (Figure 1) has triggered

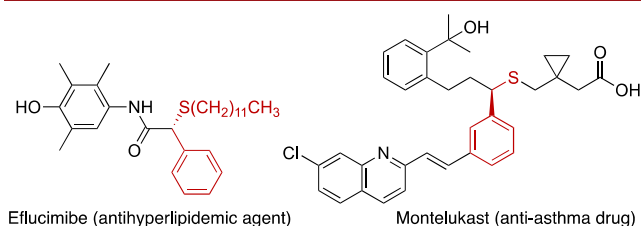


Figure 1. Thioether moiety in biologically relevant compounds.

efforts directed toward catalytic C–S bond formation through hydrothiolation of olefins.⁶ This method complements other strategies for catalytic C–S bond construction,⁷ such as couplings⁸ or carbonylations.⁹ Barring some exceptions,¹⁰ a radical pathway is proposed to give rise to an anti-Markovnikov product.¹¹ This, also called a thiol–ene “click” reaction, has been exploited as a synthetic tool mostly in materials chemistry.¹² In contrast, an acid- or metal-catalyzed cationic pathway usually provides the Markovnikov product.¹³

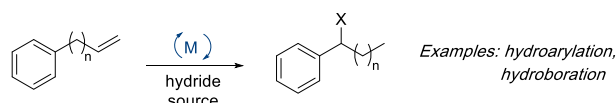
Palladium-catalyzed alkene hydrothiolations are rare,¹⁴ probably due to catalyst poisoning by formation of strong M–S bonds.¹⁵ However, based on our experience with Pd-catalyzed transformations of thiols,^{9c} we envisaged a process that would enable a tandem conjugative migration–hydrothiolation using a palladium hydride precursor (Scheme 1b). This would stand out as an atom and step economic transformation furnishing benzylic thioethers.

We started our investigation by employing 4-allyl-1,2-dimethoxybenzene (1a) and heptane-1-thiol (2a) as reaction

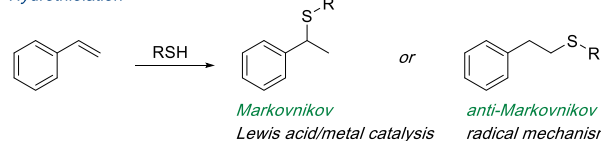
Scheme 1. (a) Prior Work in Hydrothiolation and Conjugative Migration/Hydrofunctionalization; (b) This Work

a) Literature

Metal hydride-catalyzed isomerization/hydrofunctionalization

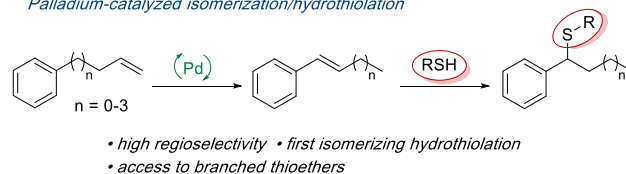


Hydrothiolation



b) This work


Palladium-catalyzed isomerization/hydrothiolation



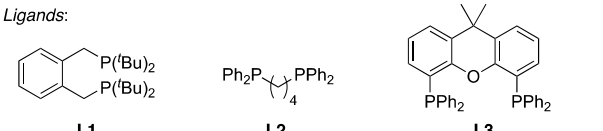
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partners (Table 1). The initial choice of the catalyst system depended on its activity in the isomerization. We confirmed

Table 1. Optimization of Reaction Conditions^a



Ligands:



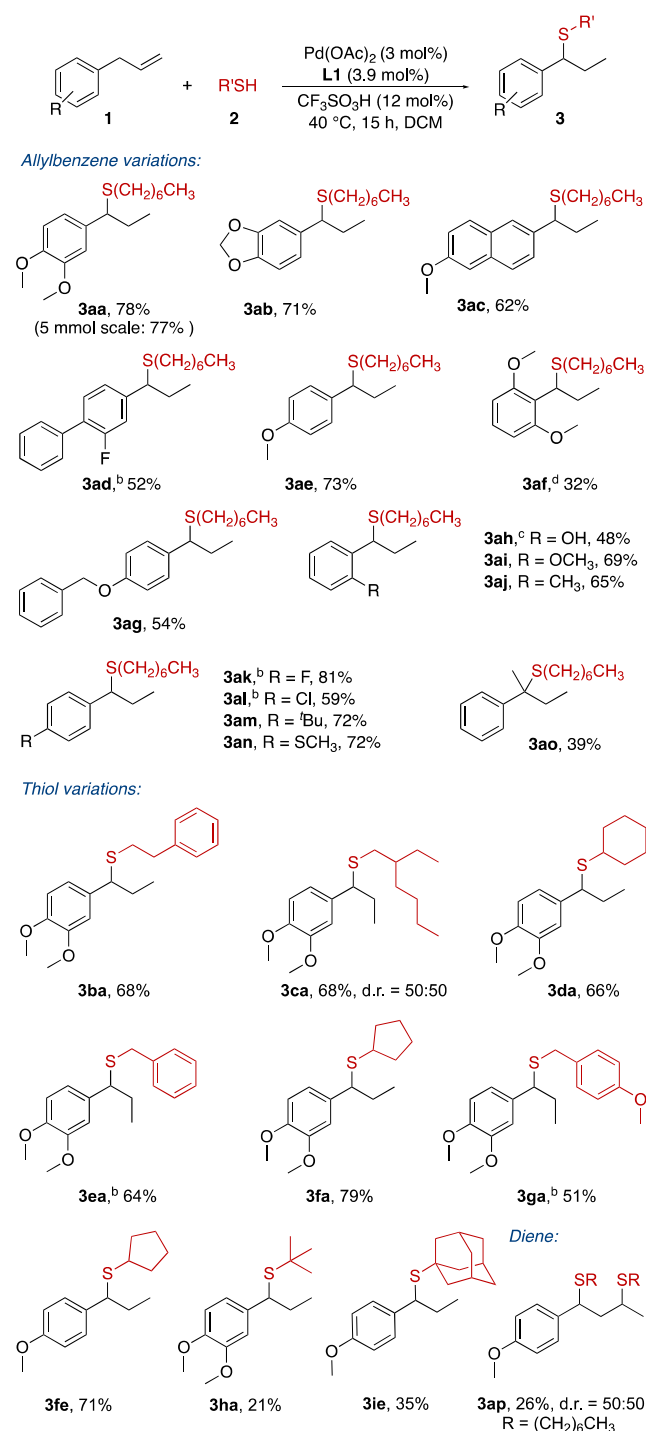
entry	Pd cat. (mol %)	ligand (mol %)	conv (%) ^b	yield (%) ^b
1	Pd(OAc) ₂ (5)	L1 (9.4)	100	94
2	Pd(OAc) ₂ (3)	L1 (5.4)	100	93
3	Pd(OAc) ₂ (2)	L1 (3.4)	100	51
4	Pd(OAc) ₂ (3)	L2 (3.9)	85	74
5	Pd(acac) ₂ (5)	L1 (9.4)	—	—
6	Pd(OAc) ₂ (3)	L3 (6)	—	—
7 ^c	Pd(OAc) ₂ (3)	L1 (3.9)	100	94
8 ^d	Pd(OAc) ₂ (3)	L1 (3.9)	99	97

^aReaction conditions: **1a** (0.5 mmol), **2a** (0.55 mmol), CF₃SO₃H (12 mol %), toluene (1 mL), 50 °C, 18 h. ^bDetermined by GC-FID analysis using pentadecane as the internal standard. ^cSolvent: DCM. ^dSolvent: DCM, CF₃SO₃H (12 mol %), 40 °C, 15 h.

that palladium acetate in combination with a strong acid as a hydride source and L1 as a ligand resulted in rapid conjugative migration, which was known to occur during carbonylations.¹⁶ Employing the standard isomerization conditions to hydrothiolation, we were delighted to observe conversion to the product arising from Markovnikov hydrothiolation of the isomerized double bond (entry 1). Only a small amount (<5%) of anti-Markovnikov regioisomer was detected. This was avoided by the use of freshly distilled heptanethiol (stored under argon). The amount of catalyst could be reduced to 3 mol %, while diminished activity was observed using 2 mol % of catalyst (entries 2, 3). Further optimization including use of other palladium salts as catalyst precursors led to little or no conversion (entry 5, only 1 example shown). Ligand L1 displayed superior reactivity when compared to other bidentate ligands such as L2 (entry 4). The strong ligand effects point to the significance of stability of the catalytic metal hydride in this transformation.¹⁶ Use of bulky and rigid phosphine such as L3 resulted in no yield (entry 6). Solvent screening revealed that polar, chlorinated solvents offer high yields. In the presence of DCM, the reaction could be carried out under much milder conditions and relatively lower loadings of catalyst and ligand (entries 7, 8 and Supporting Information for more details). Another important aspect was the use of a partially oxidized ligand in different purchased samples. Fortunately, the use of pure ligand also led to complete conversion and comparable yields to the batch with partially oxidized phosphine. Hence, there appears to be no influence of the oxide on the reactivity.

The scope of this transformation was investigated by employing a variety of substituted allyl benzenes (Scheme 2). Substrates with alkoxy substituents such as **3aa**, **3ab**, **3ae** gave good yields in the range 71–78%. The model reaction of **1a** with **2a** was also tested at a 5 mmol scale. Product isolation and purification by column chromatography provided 1.2 g,

Scheme 2. Tandem Isomerization–Hydrothiolation of Various Allylbenzenes and Thiols^a



^aReaction conditions: **1** (0.5 mmol), **2** (0.55 mmol), Pd (3 mol %), L1 (3.9 mol %), CF₃SO₃H (12 mol %), DCM (1 mL), 40 °C, 15 h. ^b**1** (0.25 mmol), **2** (0.27 mmol), Pd (6 mol %), L1 (12 mol %), CF₃SO₃H (16 mol %), 50 °C, 64 h. ^cToluene (1 mL), L1 (6 mol %), 24 h, 50 °C. ^dCF₃SO₃H (16 mol %).

77% of **3a**. Substrates with –Cl and –F required higher catalyst loadings and slightly elevated temperature and time to achieve full conversion. Such products can be used in downstream chemistry.

1-Allylnaphthalene showed no reactivity possibly due to steric effects. However, the use of 2-allyl-6-methoxy naph-

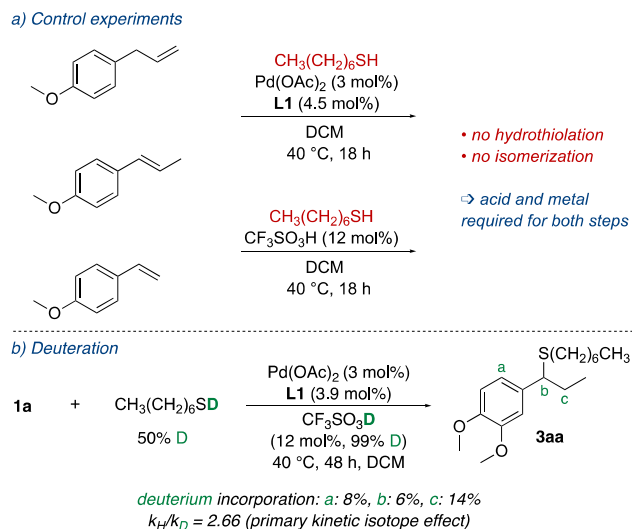
thalene resulted in complete conversion and afforded the corresponding thioether **3ac** in 62% yield. A striking influence of solvent was observed in the case of **3ah**, wherein the reaction with DCM resulted in no conversion; however, under the same reaction conditions, switching the solvent to toluene led to a 49% yield of **3ah**. Substrates with amino functionality showed very poor reactivity to give corresponding thioethers, although conjugative migration did take place. An obvious reason is the formation of an ammonium cation, hence deactivating the aromatic system. Similar behavior was observed for electron-poor allylbenzenes containing CF₃, CN functionalities. Notably, also *o*-substituted alkenes furnished the corresponding products (**3ai**, **3aj**) in good yields. The presence of a methyl substituent in the benzylic position still allowed for the tandem transformation; however, the product **3ao** was obtained in lower yield. Interestingly, the use of (buta-1,3-dien-1-yl)-4-methoxybenzene led to dihydrothiolation and resulted in formation of **3ap** in 26% yield.

Furthermore, aliphatic thiols with differing steric and electronic attributes were tested in the hydrothiolation of **1a**. It became clear that more nucleophilic thiols are the most effective in catalysis. Under identical reaction conditions, the similar reactivity of primary and secondary thiols was noted, with products **3ca**, **3da**, and **3fa** obtained in yields of 68%, 66%, and 74%, respectively. Thiols with higher acidity (benzyl mercaptan with a pK_a in the range 8–9) displayed poorer reactivity. Thus, **3ea** and **3ga** were synthesized from corresponding benzyl mercaptan derivatives in 64% and 51% yields under more forcing reaction conditions. Thiols possessing high steric bulk resulted in rather low yields albeit with complete conversion of starting material. Dimerization of the isomerized internal olefin was confirmed by MS.

Control experiments were conducted in the absence of triflic acid or catalyst precursor and ligand using 4-allylanisole as the substrate (Scheme 3a). In both cases, no product was formed. Similar experiments carried out with *trans*-anethole and 4-methoxystyrene resulted in the same outcome. This shows that neither the isomerization nor the following hydrothiolation are acid- or purely metal-catalyzed.

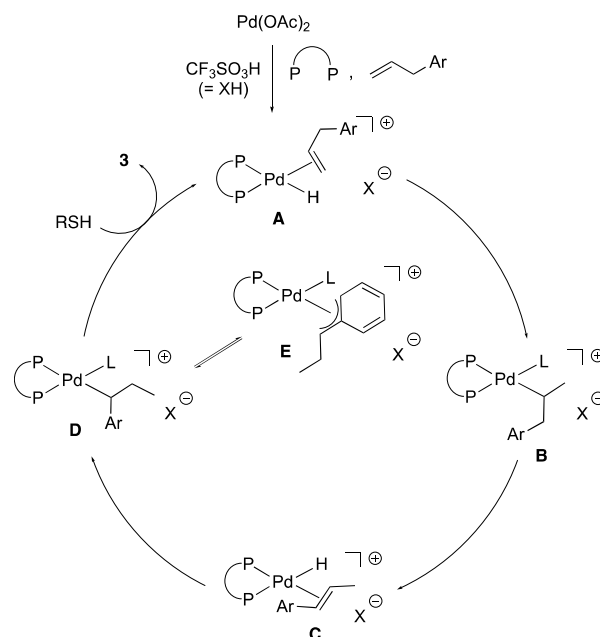
Moreover, preliminary mechanistic investigations were performed through deuteration experiments, which were

Scheme 3. Isomerizing Hydrothiolation: (a) Control Experiments Catalyst Components; (b) Deuteration



conducted using partially deuterated heptane-1-thiol and deuterated triflic acid (Scheme 3b). Varying amounts of deuterium incorporation were found on all three carbon atoms of the propyl group (b, c and CH₃ group, which could not be quantified due to overlap; see SI). This suggests a reversible insertion of alkene into the Pd–H bond and isomerization. Interestingly, deuterium was also found in the *ortho*-position (a) on benzene. This observation hints toward the existence of a π -benzylic Pd-intermediate (**F**, Scheme 4). However, when

Scheme 4. Proposed Catalytic Cycle



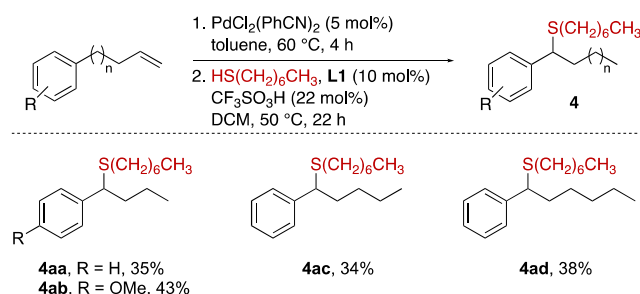
2,6-dimethoxy-1-allylbenzene was subjected to the same reaction conditions, we observed the formation of Markovnikov product **3af** albeit in lower yield. This indicates that the presence of the benzylic intermediate is not a precondition for the hydrothiolation to take place.

In addition, a comparison of kinetic profiles of reaction with deuterated and nondeuterated acid and thiol showed a significant primary kinetic isotope effect. However, cleavage of X–H and M–H bonds may be involved in many steps of the catalytic cycle. In accordance to the above experiments and accepted mechanism for related reactions,¹⁶ we propose a catalytic cycle based on the formation of palladium hydride **A** from triflic acid. Insertion of olefin into the Pd–H bond results in the alkyl complex **B**, which undergoes β -hydride elimination to furnish the complex **C** with a conjugated aromatic system. The repeated insertion leads to complex **D**, which can be stabilized by the η^3 -coordination mode in **E**. The incorporation of deuterium in the alkyl chain is indicative of a chain walking mechanism of isomerization. The reaction of **D** with the thiol leads to the formation of **3** and the regeneration of the palladium hydride. It is unclear if this proceeds via coordination of thiol, which can also occur earlier in the cycle, or direct substitution.

To extend the scope of this reactivity, we directed our efforts toward increasing the chain length of the olefin. Under the conditions developed for allylbenzenes, no isomerization of 1-phenyl-4-butene was observed. PdCl₂(PhCN)₂ has been established as an efficient precatalyst for double bond migration in similar systems.¹⁷ Thus, we envisioned a simple

approach to accomplish the desired reactivity for longer chain substrates (Scheme 5). PdCl₂(PhCN)₂ was employed for

Scheme 5. One-Pot Isomerization–Hydrothiolation of Longer Chain Olefins^a



^aReaction Conditions: (1) PdCl₂(PhCN)₂ (5 mol %), toluene (0.3 mL), alkene (0.5 mmol), 4 h, 60 °C; (2) L1 (10 mol %), CF₃SO₃H (22 mol %), heptane-1-thiol (0.55 mmol), DCM (0.7 mL), 50 °C, 22 h.

double bond migration to generate β -substituted styrenes. In this case, the isomerization occurs without the need of an external hydride source. This was followed by the sequential addition of the ligand L1, acid, and thiol. Indeed, this one-pot approach proved to be suitable for the conversion of terminal alkenes with varying chain lengths and furnished the corresponding benzylic thioethers **4** in moderate yields.

In conclusion, we have developed a methodology for efficient Pd-catalyzed tandem isomerization/hydrothiolation of allylbenzenes. The catalyst system consisting of a Pd(II) precursor, bidentate phosphine ligand, and strong Brønsted acid was able to convert a variety of 3-arylpropenes and thiols to branched benzylic thioethers in a highly regioselective manner. The stability and activity of palladium hydride in the presence of highly coordinating thiols was demonstrated. Overall this transformation serves as a convenient strategy in achieving benzylic functionalization starting from allylated aromatic precursors. Further efforts to render this transformation asymmetric are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00504.

Experimental procedures, analytical data, and mechanistic discussion (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Tolman, C. A. Chemistry of tetrakis(triethyl phosphite) nickel hydride, HNi[P(OEt)₃]₄⁺. IV. Mechanism of olefin isomerization. *J. Am. Chem. Soc.* **1972**, *94*, 2994–2999. (b) McGrath, D. V.; Grubbs, R. H. The mechanism of aqueous ruthenium(II)-catalyzed olefin isomerization. *Organometallics* **1994**, *13*, 224–235. (c) Gauthier, D.; Lindhardt, A. T.; Olsen, E. P. K.; Overgaard, J.; Skrydstrup, T. In Situ Generated Bulky Palladium Hydride Complexes as Catalysts for the Efficient Isomerization of Olefins. Selective Transformation of Terminal Alkenes to 2-Alkenes. *J. Am. Chem. Soc.* **2010**, *132*, 7998–8009. (d) Spallek, M. J.; Stockinger, S.; Goddard, R.; Trapp, O. Modular Palladium Bipyrazoles for the Isomerization of Allylbenzenes – Mechanistic Considerations and Insights into Catalyst Design and Activity, Role of Solvent, and Additive Effects. *Adv. Synth. Catal.* **2012**, *354*, 1466–1480. (e) Lee, W.-C.; Wang, C.-H.; Lin, Y.-H.; Shih, W.-C.; Ong, T.-G. Tandem Isomerization and C–H Activation: Regioselective Hydroheteroarylation of Allylarenes. *Org. Lett.* **2013**, *15*, 5358–5361. (f) Hassam, M.; Taher, A.; Arnott, G. E.; Green, I. R.; van Otterlo, W. A. L. Isomerization of Allylbenzenes. *Chem. Rev.* **2015**, *115*, 5462–5569. (g) Chuc, L. T. N.; Chen, C.-S.; Lo, W.-S.; Shen, P.-C.; Hsuan, Y.-C.; Tsai, H.-H. G.; Shieh, F.-K.; Hou, D.-R. Long-Range Olefin Isomerization Catalyzed by Palladium(0) Nanoparticles. *ACS Omega* **2017**, *2*, 698–711. (h) Kapat, A.; Sperger, T.; Guven, S.; Schoenebeck, F. E-Olefins through intramolecular radical relocation. *Science* **2019**, *363*, 391–396.
- (2) Larionov, E.; Li, H.; Mazet, C. Well-defined transition metal hydrides in catalytic isomerizations. *Chem. Commun.* **2014**, *50*, 9816–9826.
- (3) (a) Vasseur, A.; Bruffaerts, J.; Marek, I. Remote functionalization through alkene isomerization. *Nat. Chem.* **2016**, *8*, 209. (b) Sommer, H.; Juliá-Hernández, F.; Martin, R.; Marek, I. Walking Metals for Remote Functionalization. *ACS Cent. Sci.* **2018**, *4*, 153–165.
- (4) (a) Yamakawa, T.; Yoshikai, N. Alkene Isomerization–Hydroarylation Tandem Catalysis: Indole C2-Alkylation with Aryl-Substituted Alkenes Leading to 1,1-Diarylalkanes. *Chem. - Asian J.* **2014**, *9*, 1242–1246. (b) He, Y.; Cai, Y.; Zhu, S. Mild and Regioselective Benzylic C–H Functionalization: Ni-Catalyzed Reductive Arylation of Remote and Proximal Olefins. *J. Am. Chem. Soc.* **2017**, *139*, 1061–1064. (c) Peng, L.; Li, Y.; Li, Y.; Wang, W.; Pang, H.; Yin, G. Ligand-Controlled Nickel-Catalyzed Reductive Relay Cross-Coupling of Alkyl Bromides and Aryl Bromides. *ACS Catal.* **2018**, *8*, 310–313.
- (5) (a) Scheuermann, M. L.; Johnson, E. J.; Chirik, P. J. Alkene Isomerization–Hydroboration Promoted by Phosphine-Ligated Cobalt Catalysts. *Org. Lett.* **2015**, *17*, 2716–2719. (b) Huang, J.; Yan, W.; Tan, C.; Wu, W.; Jiang, H. Palladium-catalyzed regioselective hydroboration of aryl alkenes with B₂pin₂. *Chem. Commun.* **2018**, *54*, 1770–1773.
- (6) (a) Yang, Y.; Rioux, R. M. Highly stereoselective anti-Markovnikov hydrothiolation of alkynes and electron-deficient alkenes by a supported Cu-NHC complex. *Green Chem.* **2014**, *16*, 3916–3925. (b) Kuciński, K.; Pawluć, P.; Marciniak, B.; Hreczycho, G. Highly Selective Hydrothiolation of Unsaturated Organosilicon Compounds Catalyzed by Scandium(III) Triflate. *Chem. - Eur. J.* **2015**, *21*, 4940–4943. (c) Kennemur, J. L.; Kortman, G. D.; Hull, K. L. Rhodium-Catalyzed Regiodivergent Hydrothiolation of Allyl Amines and Imines. *J. Am. Chem. Soc.* **2016**, *138*, 11914–11919. (d) Mosafari, E.; Ripsman, D.; Stephan, D. W. The air-stable carbocation salt [(MeOC₆H₄)CPh₂][BF₄] in Lewis acid catalyzed hydrothiolation of alkenes. *Chem. Commun.* **2016**, *52*, 8291–8293. (e) Yang, X.-H.; Davison, R. T.; Dong, V. M. Catalytic Hydrothiolation: Regio- and Enantioselective Coupling of Thiols and Dienes. *J. Am. Chem. Soc.* **2018**, *140*, 10443–10446.
- (7) Lee, C.-F.; Basha, R. S.; Badsara, S. S. Engineered C–S Bond Construction. *Top. Curr. Chem.* **2018**, *376*, 25.

- (8) (a) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.-i.; Kato, Y.; Kosugi, M. The Palladium Catalyzed Nucleophilic Substitution of Aryl Halides by Thiolate Anions. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1385–1389. (b) Fernández-Rodríguez, M. A.; Shen, Q.; Hartwig, J. F. A General and Long-Lived Catalyst for the Palladium-Catalyzed Coupling of Aryl Halides with Thiols. *J. Am. Chem. Soc.* **2006**, *128*, 2180–2181. (c) Oderinde, M. S.; Frenette, M.; Robbins, D. W.; Aquila, B.; Johannes, J. W. Photoredox Mediated Nickel Catalyzed Cross-Coupling of Thiols With Aryl and Heteroaryl Iodides via Thiyl Radicals. *J. Am. Chem. Soc.* **2016**, *138*, 1760–1763. (d) Ichiishi, N.; Malapit, C. A.; Woźniak, Ł.; Sanford, M. S. Palladium- and Nickel-Catalyzed Decarbonylative C–S Coupling to Convert Thioesters to Thioethers. *Org. Lett.* **2018**, *20*, 44–47. (e) Jones, K. D.; Power, D. J.; Bierer, D.; Gericke, K. M.; Stewart, S. G. Nickel Phosphite/Phosphine-Catalyzed C–S Cross-Coupling of Aryl Chlorides and Thiols. *Org. Lett.* **2018**, *20*, 208–211. (f) Liu, C.; Szostak, M. Decarbonylative thioetherification by nickel catalysis using air- and moisture-stable nickel precatalysts. *Chem. Commun.* **2018**, *54*, 2130–2133. (g) Gehrtz, P. H.; Geiger, V.; Schmidt, T.; Sršan, L.; Fleischer, I. Cross-Coupling of Chloro(hetero)arenes with Thiolates Employing a Ni(0)-Precatalyst. *Org. Lett.* **2019**, *21*, 50–55.
- (9) (a) Xiao, W.-J.; Vasapollo, G.; Alper, H. Highly Regioselective Thiocarbonylation of Conjugated Dienes via Palladium-Catalyzed Three-Component Coupling Reactions. *J. Org. Chem.* **2000**, *65*, 4138–4144. (b) Xiao, W.-J.; Alper, H. Highly Stereoselective Palladium-Catalyzed Dithiocarbonylation of Propargylic Mesylates with Thiols and Carbon Monoxide. *J. Org. Chem.* **2005**, *70*, 1802–1807. (c) Burhardt, M. N.; Taaning, R. H.; Skrydstrup, T. Pd-Catalyzed thiocarbonylation with stoichiometric carbon monoxide: Scope and applications. *Org. Lett.* **2013**, *15*, 948–951. (d) Burhardt, M. N.; Ahlburg, A.; Skrydstrup, T. Palladium-Catalyzed Thiocarbonylation of Aryl, Vinyl, and Benzyl Bromides. *J. Org. Chem.* **2014**, *79*, 11830–11840. (e) Hirschbeck, V.; Gehrtz, P. H.; Fleischer, I. Regioselective Thiocarbonylation of Vinyl Arenes. *J. Am. Chem. Soc.* **2016**, *138*, 16794–16799.
- (10) (a) Weiwer, M.; Coulombel, L.; Duñach, E. Regioselective indium(iii) trifluoromethanesulfonate-catalyzed hydrothiolation of non-activated olefins. *Chem. Commun.* **2006**, 332–334. (b) Kuciński, K.; Pawluć, P.; Hreczycho, G. Scandium(III) Triflate-Catalyzed anti-Markovnikov Hydrothiolation of Functionalized Olefins. *Adv. Synth. Catal.* **2015**, *357*, 3936–3942. (c) Kristensen, S. K.; Laursen, S. L. R.; Taarning, E.; Skrydstrup, T. Ex Situ Formation of Methanethiol: Application in the Gold(I)-Promoted Anti-Markovnikov Hydrothiolation of Olefins. *Angew. Chem., Int. Ed.* **2018**, *57*, 13887–13891. (d) Tamai, T.; Fujiwara, K.; Higashimae, S.; Nomoto, A.; Ogawa, A. Gold-Catalyzed Anti-Markovnikov Selective Hydrothiolation of Unactivated Alkenes. *Org. Lett.* **2016**, *18*, 2114–2117.
- (11) (a) Griesbaum, K. Problems and Possibilities of the Free-Radical Addition of Thiols to Unsaturated Compounds. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 273–287. (b) Biermann, U.; Metzger, J. O. Regioselectivity of Radical Addition of Thiols to 1-Alkenes. *Eur. J. Org. Chem.* **2018**, *2018*, 730–734. (c) Sinha, A. K.; Equbal, D. Thiol–Ene Reaction: Synthetic Aspects and Mechanistic Studies of an Anti-Markovnikov-Selective Hydrothiolation of Olefins. *Asian J. Org. Chem.* **2019**, *8*, 32–47.
- (12) (a) Hoyle, C. E.; Bowman, C. N. Thiol-Ene Click Chemistry. *Angew. Chem., Int. Ed.* **2010**, *49*, 1540–1573. (b) Dondoni, A.; Marra, A. Recent applications of thiol-ene coupling as a click process for glycoconjugation. *Chem. Soc. Rev.* **2012**, *41*, 573–586. (c) Lowe, A. B. Thiol-ene “click” reactions and recent applications in polymer and materials synthesis: a first update. *Polym. Chem.* **2014**, *5*, 4820–4870.
- (13) (a) Cabrero-Antonino, J. R.; Leyva-Pérez, A.; Corma, A. Iron-Catalyzed Markovnikov Hydrothiolation of Styrenes. *Adv. Synth. Catal.* **2012**, *354*, 678–687. (b) Savolainen, M. A.; Wu, J. Markovnikov-Selective Hydrothiolation of Styrenes: Application to the Synthesis of Stereodefined Trisubstituted Olefins. *Org. Lett.* **2013**, *15*, 3802–3804. (c) Ma, H.; Ren, X.; Zhou, X.; Ma, C.; He, Y.; Huang, G. Palladium and copper co-catalyzed Markovnikov hydrothiolation of terminal olefins and alkynes. *Tetrahedron Lett.* **2015**, *56*, 6022–6029.
- (14) Tamai, T.; Ogawa, A. Regioselective Hydrothiolation of Alkenes Bearing Heteroatoms with Thiols Catalyzed by Palladium Diacetate. *J. Org. Chem.* **2014**, *79*, 5028–5035.
- (15) DuBois, M. R. Catalytic applications of transition-metal complexes with sulfide ligands. *Chem. Rev.* **1989**, *89*, 1–9.
- (16) (a) Jimenez Rodriguez, C.; Foster, D. F.; Eastham, G. R.; Cole-Hamilton, D. J. Highly selective formation of linear esters from terminal and internal alkenes catalysed by palladium complexes of bis-(di-tert-butylphosphinomethyl)benzene. *Chem. Commun.* **2004**, 1720–1721. (b) Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. Mechanistic Features of Isomerizing Alkoxy carbonylation of Methyl Oleate. *J. Am. Chem. Soc.* **2012**, *134*, 17696–17703.
- (17) (a) Harrod, J. F.; Chalk, A. J. Homogeneous Catalysis. I. Double Bond Migration in n-Olefins, Catalyzed by Group VIII Metal Complexes. *J. Am. Chem. Soc.* **1964**, *86*, 1776–1779. (b) Sparke, M. B.; Turner, L.; Wenham, A. J. M. The isomerization of olefins by palladium complexes. *J. Catal.* **1965**, *4*, 332–340. (c) Tan, E. H. P.; Lloyd-Jones, G. C.; Harvey, J. N.; Lennox, A. J. J.; Mills, B. M. [(RCN)₂PdCl₂]-Catalyzed E/Z Isomerization of Alkenes: A Non-Hydride Binuclear Addition–Elimination Pathway. *Angew. Chem., Int. Ed.* **2011**, *50*, 9602–9606.