

THE  
UNIVERSITY  
OF RHODE ISLAND

University of Rhode Island  
DigitalCommons@URI

---

Chemistry Faculty Publications

Chemistry

---

2019

## FeCl<sub>2</sub>-Mediated Rearrangement of Allylic Alcohols

Anita A. Opping-Quaicoe  
*University of Rhode Island*

Brenton DeBoef  
*University of Rhode Island, [bdeboef@uri.edu](mailto:bdeboef@uri.edu)*

Follow this and additional works at: [https://digitalcommons.uri.edu/chm\\_facpubs](https://digitalcommons.uri.edu/chm_facpubs)

---

### Citation/Publisher Attribution

Opping-Quaicoe, A. A. & DeBoef, B. (2019). FeCl<sub>2</sub>-Mediated Rearrangement of Allylic Alcohols. *ACS Omega*, 4(3), 6077-6083. doi: 10.1021/acsomega.9b00163  
Available at: <https://doi.org/10.1021/acsomega.9b00163>

This Article is brought to you for free and open access by the Chemistry at DigitalCommons@URI. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact [digitalcommons@etal.uri.edu](mailto:digitalcommons@etal.uri.edu).

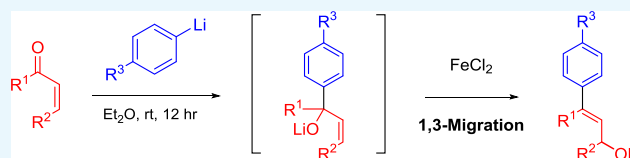
# FeCl<sub>2</sub>-Mediated Rearrangement of Allylic Alcohols

Anita A. Oppong-Quaicoo and Brenton DeBoef\*<sup>1</sup>

Department of Chemistry, University of Rhode Island, 140 Flagg Road, Kingston, Rhode Island 02881, United States

**S** Supporting Information

**ABSTRACT:** A mild, one-pot procedure to produce 3-substituted allylic alcohols from  $\alpha,\beta$ -unsaturated ketones is described. The addition of an organolithium nucleophile produces a tertiary allylic alcohol as an intermediate, which undergoes a 1,3-OH-migration assisted by FeCl<sub>2</sub>. The proposed mechanism indicates that a *syn*-facial migration occurs for the major product. Yields as high as 98% for the one-pot reaction are reported.



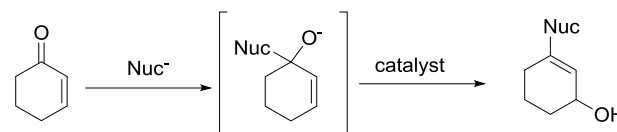
## INTRODUCTION

Allylic alcohols are indispensable functional groups in the synthesis of structurally complex organic molecules.<sup>1–8</sup> 3,3'-Disubstituted allylic alcohols, in particular, are often more difficult to synthesize than their monosubstituted counterparts. Though methods such as the conjugate addition of nucleophiles to ynones and the addition of organometallic reagents to propargylic alcohols have been described,<sup>9–13</sup> one method that has received little attention is the 1,3-migration of the hydroxy group in tertiary allylic alcohols. This transformation has been primarily catalyzed by oxo catalysts,<sup>14–16</sup> though oxidative palladium catalysis has also been employed to perform the migration and oxidize the allylic alcohol to a  $\beta$ -disubstituted enone.<sup>17</sup> This rearrangement can be performed by enzymes to form enones.<sup>2</sup> A rhenium-assisted rearrangement has also been used in the synthesis of semisquarates.<sup>18</sup> Trifluoroacetic acid has also been used to isomerize allylic alcohols, and this method has been applied to the synthesis of valerenic acid, which binds to both the GABA<sub>A</sub> and 5-HT<sub>5A</sub> receptors, and is used as a treatment of insomnia.<sup>19</sup> Acid-assisted allylic alcohol rearrangement was also used in the synthesis of two quinolone natural products isolated from *Pseudonocardia* sp.<sup>20</sup> Additionally, one can envision that this rearrangement could be used to create artemisinin-like antimalarial drugs via Singh's synthetic scheme (Scheme 1).<sup>21</sup>

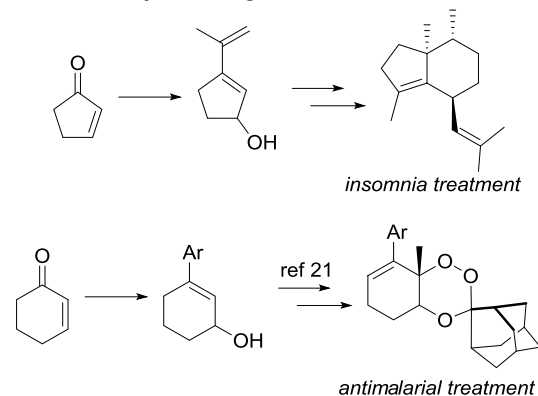
Iron has recently been studied as a catalyst for a number of coupling reactions.<sup>12–28</sup> The most widely used of these processes are alternatives to traditional palladium-catalyzed transformations, such as the Kumada coupling and C–H arylation and alkylation reactions.<sup>22,29,30</sup> Even a few examples of substitution reactions via  $\pi$ -allyl iron intermediates have been reported.<sup>31–35</sup> Iron is preferable to late transition metal catalysts due to its low expense and toxicity. Additionally, iron catalysts are often capable of performing synthetic steps that conventional late transition metal catalysts cannot perform, such as breaking and functionalizing strong C–O bonds. Herein, we describe a one-pot addition of an organolithium reagent to an  $\alpha,\beta$ -unsaturated ketone, followed by an iron-mediated 1,3-rearrangement reaction. We propose that the

## Scheme 1. Application of Allylic 1,3-Migrations

### 1,2-Addition/1,3-migration



### Applications of allylic 1,3-migration



novel reaction proceeds via the formal cleavage of a C–O bond and the intermediacy of an allylic cation.

## RESULTS AND DISCUSSION

During the course of our studies on iron-mediated reactions involving organolithium and organomagnesium nucleophiles,<sup>30,36</sup> we discovered that the addition of an organolithium reagent to an  $\alpha,\beta$ -unsaturated ketone in the presence of an iron salt does not result in the expected 1,4-addition products, but rather an isomeric allylic alcohol is formed (2).

Cyclohex-2-enone, (1) was chosen as a reliable and simple substrate for reaction optimization (Table 1). A number of

Received: January 17, 2019

Accepted: February 26, 2019

Published: March 29, 2019

Table 1. Evaluation of Catalytic Conditions<sup>a</sup>

entry	iron species	solvent	temp (°C)	yield (%) 2	yield (%) 3
1 <sup>b</sup>	FeCl <sub>2</sub>	Et <sub>2</sub> O	25	55	4
2	FeCl <sub>2</sub>	Et <sub>2</sub> O	25	87	17
3	Fe(OAc) <sub>2</sub>	Et <sub>2</sub> O	25	35	27
4	FeF <sub>3</sub>	Et <sub>2</sub> O	25	25	40
5	Fe(acac) <sub>2</sub>	Et <sub>2</sub> O	25	41	44
6	Fe(acac) <sub>3</sub>	Et <sub>2</sub> O	25	30	29
7	FeCl <sub>2</sub>	THF	25		5
8	FeCl <sub>2</sub>	2-methyl THF	25	4	91
9	FeCl <sub>2</sub>	MBTE	25	23	32
10	FeCl <sub>2</sub>	Et <sub>2</sub> O	-78		73
11 <sup>c</sup>	FeCl <sub>2</sub>	Et <sub>2</sub> O	25	36	
12 <sup>d</sup>	FeCl <sub>2</sub>	Et <sub>2</sub> O	25	8	83
13 <sup>e</sup>	FeCl <sub>2</sub>	Et <sub>2</sub> O	25	71	

<sup>a</sup>Standard conditions: 0.2 M in Et<sub>2</sub>O (stabilized with 5 ppm BHT), -78 °C to room temperature (rt), 1 equiv of FeCl<sub>2</sub> and 3 equiv of nucleophile. <sup>b</sup>1 equiv of the aryllithium was used. <sup>c</sup>1 equiv of BHT was added. <sup>d</sup>10 mol % of FeCl<sub>2</sub>. <sup>e</sup>Solvent was diethyl ether without BHT.

both iron(II) and iron(III) salts were selected, out of which FeCl<sub>2</sub> was determined as the most efficient reagent. In general, iron(III) salts were inferior to iron(II) salts. Diethyl ether (with or without butylated hydroxytoluene (BHT) stabilization) was the most desirable solvent for the rearrangement, and the other common ether solvents, THF and Me-THF, produced low or no yields of 2.

Colder temperatures (entry 10) allowed for the formation of the 1,2-addition product, 3, but hindered the formation of the desired rearranged product, 2. Although the reaction proceeded in both inhibited and purified Et<sub>2</sub>O, the addition of 1 equiv of BHT further hindered the reaction (entry 11), indicating that the BHT preservative was not involved in the reaction, and that commercial, stabilized ether was a suitable solvent for the addition/migration. The reduction of the loading of FeCl<sub>2</sub> from 1 equiv to 10 mol % resulted in an 8% yield (entry 13), indicating that the reaction required a stoichiometric amount of the iron reagent.

The scope and limitations of the addition-rearrangement with respect to both linear and cyclic  $\alpha,\beta$  unsaturated ketone substrates were also investigated (Table 2). Cycloalkenones were found to be the best substrates, with cyclohex-2-enone (1) giving the highest yield. Linear  $\alpha,\beta$ -unsaturated ketones (entries 3–5) produced only the 1,2-addition product.

We then investigated the scope and limitation of organolithium and Grignard nucleophiles (Table 3). Alkylolithium reagents did not yield any results, presumably due to their basicity. The naphthyllithium reagent produced only the 1,2-addition product 15, indicating that the 1,3 migration may be inhibited due to steric hindrance. Only trace amounts of the product were obtained from the Grignard reagent (entry 6). We investigated the feasibility of this method using heterocyclic aryllithiums, and we obtained only a trace amount of products 20 and 22.

Table 2. Substrate Scope<sup>a</sup>

En try	Substrate	1,3-Migration	1,2-Addition
1			
2			
3			
4			
5			

<sup>a</sup>Conditions: 0.2 M in Et<sub>2</sub>O (stabilized with 5 ppm BHT), -78 °C to rt, 1 equiv of FeCl<sub>2</sub> and 3 equiv of nucleophile.

To probe the mechanism of the reaction, the biphenyl lithium reagent was added to 1 and stirred for 3 h. Purification by flash chromatography gave 3. FeCl<sub>2</sub> (1 equiv) was then added to a solution of 3 (1 equiv), and the reaction was stirred at room temperature for 3 h, providing 2 after column chromatography (Scheme 2). This confirmed that the tertiary allylic alcohol (3) was an intermediate for the rearrangement.

Furthermore, the use of a chiral  $\alpha,\beta$ -unsaturated ketone indicated that the OH-migration was diastereoselective. 6-Methylcyclohexenone, 23, was reacted with phenyllithium to produce a 1:1 mixture of diastereomers 24 and 25 (as judged by 1H NMR of the crude reaction mixture). Of the two possible diastereomers, only 24 could be isolated by flash chromatography. When this stereoisomer was reacted with FeCl<sub>2</sub>, a 2:1 mixture of the two diastereomeric migration products (26 and 27) was obtained. NOESY NMR spectroscopy revealed that the major diastereomer retained the anti-relationship between the methyl group and the alcohol. This indicates that the 1,3-migration proceeded primarily via a *syn*-facial pathway due to less energy needed for the iron-oxo species to approach from the same face of the allylic cation than to approach from the opposite face as the methyl group to give the *syn* product (Scheme 3).

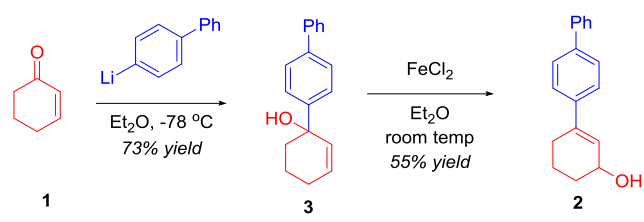
Based on these data and the previous work by McCubbin,<sup>37</sup> we propose the mechanism shown in Scheme 4. The organolithium reagent reacts with the  $\alpha,\beta$ -unsaturated ketone to give the tertiary alkoxide (1,2-addition). The FeCl<sub>2</sub> coordinates to the alkoxide (28), and LiCl is formed. The iron-oxo species (29) cleaves the C–O bond, forming an allylic carbocation (30), and the iron-oxo species then attacks the 3-position of the allylic cation, forming a new C–O bond. The major product of this process arises from the *syn* migration of the iron-oxo species. We hypothesize that the intimate ionic

Table 3. Nucleophile Scope<sup>a,b</sup>

Entry	Nucleophile	Product
1		
2 <sup>a</sup>		
3 <sup>a</sup>		
4 <sup>a</sup>		
5 <sup>a</sup>		
6 <sup>a</sup>		
7 <sup>a</sup>		
8 <sup>a</sup>		

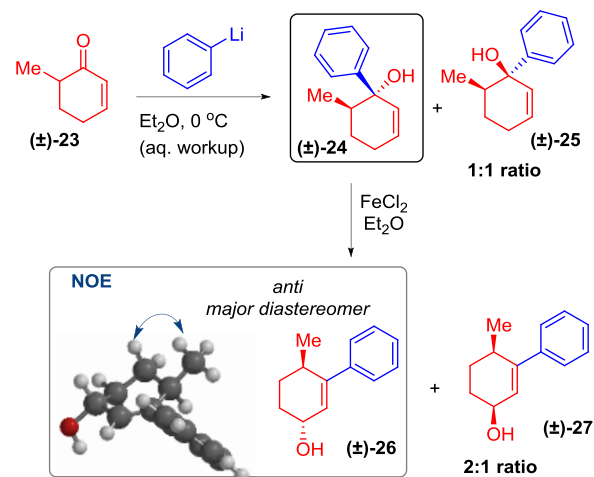
<sup>a</sup>Conditions: 0.2 M in Et<sub>2</sub>O (stabilized with 5 ppm BHT), -78 °C to rt, 1 equiv of FeCl<sub>2</sub> and 3 equiv of nucleophile. <sup>b</sup>Aryllithium was synthesized via lithium-halogen exchange from arylbromide and butyllithium.

## Scheme 2. Stepwise Reaction

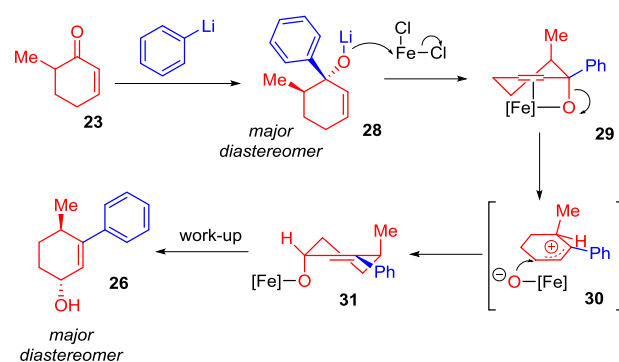


pair shown in Scheme 4 (30) could explain the formation of both diastereomers (26 and 27) and the preference for the *trans* isomer (26). Density functional theory calculations indicate that both the *trans* (26) and *cis* (27) rearranged products have similar ground-state energies, so the observed 2:1 selectivity likely arises from kinetic control. When

## Scheme 3. Diastereoselective OH-Migration



## Scheme 4. Proposed Mechanism for the 1,3-OH-Migration



aryllithium nucleophiles are used, the final allylic alcohol is conjugated which we believe is the overall driving force for the reaction.

Finally, the extent of the OH-migration was investigated. Phenyllithium was added to a solution of the conjugated dieneone, 32, then after an hour FeCl<sub>2</sub> was added. The mixture was then stirred at room temperature for 24 h, producing 33, a 1,2-addition product, and 34, the product of a 1,5-OH-migration. The 1,3-migration product (35) was not observed, likely because it was less conjugated than 33 or 34. This result corroborates the proposed OH-migration mechanism and confirms that the overall driving force for the reaction is the creation of an extended conjugated system (Scheme 5).

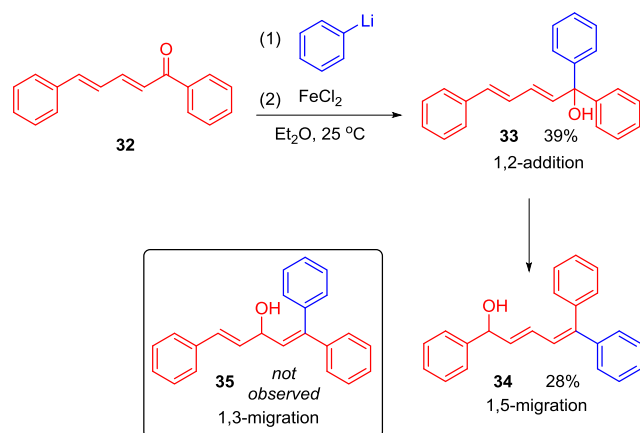
## CONCLUSIONS

In summary, we have developed a novel iron-mediated process that isomerizes allylic alcohols. The system can be used to effect the transformation of cyclic  $\alpha,\beta$ -unsaturated enones to 3,3'-disubstituted allylic alcohols. Future work in this field could involve the enhancement of the diastereoselectivity of the process and its application to the synthesis of medicinal compounds.

## EXPERIMENTAL SECTION

All reactions were carried out in an oven-dried glassware under a nitrogen atmosphere, unless stated otherwise. Yields refer to chromatographically and spectroscopically pure compounds unless stated otherwise. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 400 MHz and Bruker Avance 300

Scheme 5. Extent of Migration



MHz spectrometers. NMR spectra were measured in dimethyl sulfoxide (DMSO) and CDCl<sub>3</sub> solutions. The chemical shifts  $\delta$  are reported relative to the residual solvent peaks (<sup>1</sup>H,  $\delta$  DMSO = 2.50 ppm; <sup>13</sup>C,  $\delta$  DMSO = 39.52 ppm <sup>1</sup>H,  $\delta$  CDCl<sub>3</sub> = 7.26 ppm; <sup>13</sup>C,  $\delta$  CDCl<sub>3</sub> = 77.16 ppm). All <sup>1</sup>H and <sup>13</sup>C shifts are given in ppm (s = singlet; d = doublet; t = triplet; q = quadruplet; m = multiplet; bs = broad signal). High-resolution mass spectrometry was performed using a Thermo Scientific LTQ Orbitrap XL instrument.

**General Procedure (Method A).**<sup>38</sup> *n*-Butyllithium (0.32 mL, 0.6 mmol, 3 equiv) was slowly added to a solution of aryllhalide (1.0 equiv) in anhydrous diethyl ether (0.20 M) precooled to  $-78$  °C. The resulting slightly turbid solution was stirred for 30 min allowing it to warm to ambient temperature. Then, the aryllithium solution was added to the substrate (1 equiv) dissolved in anhydrous diethyl ether in a glovebox dropwise and the reaction mixture was stirred for 3 h, and then iron species (1 equiv) were added to the reaction mixture. The reaction was allowed to run overnight at room temperature. Silica was then added to the reaction. Purification by flash column chromatography using hexanes and ethyl acetate provided the desired 1,3-rearranged allylic alcohol.

**General Procedure (Method B).**<sup>39</sup>  $\alpha,\beta$ -Unsaturated ketone (1.0 equiv) was dissolved in an anhydrous diethyl ether (0.20 M) in a glovebox dropwise. Then, aryllithium solution (3.0 equiv) was added to the substrate solution in a dropwise manner, and the reaction mixture was stirred for 3 h and FeCl<sub>2</sub> (1.0 equiv) was added. The reaction was allowed to run at room temperature overnight. Silica was then added to the reaction. Purification by flash column chromatograph using hexane and ethyl acetate provided the corresponding desired 1,3-rearranged allylic alcohols.

**3-Biphenylcyclohex-2-en-1-ol (2).** According to method A, 1.44 mL of *n*-butyllithium (1.6 M, 0.9 mmol) was slowly added to a solution of 4-bromobiphenyl (210 mg, 0.9 mmol) dissolved in anhydrous diethyl ether (0.20 M) and precooled to  $-78$  °C. After 30 min, this solution was added to 2-cyclohexen-1-one (97%, 29.1  $\mu$ L, 0.3 mmol) dropwise. After stirring for 3 h, FeCl<sub>2</sub> (anhydrous, 37.9 mg, 0.3 mmol) was added to the reaction mixture. After 12 h, purification (column chromatography: 17% ethyl acetate in hexane) of reaction mixture gave 216 mg of 3-biphenylcyclohex-2-en-1-ol (2) as a white powder (87% yield). <sup>1</sup>H NMR (400 MHz, chloroform-*d*)  $\delta$  7.51 (m, 4H), 7.37 (m, 4H), 7.26 (m, 1H), (dt,  $J$  = 3.6, 1.8, 1.8 Hz, 1H), 4.33 (bs, 1H), 2.51 (m, 1H), 2.42 (m, 1H),

1.86 (m, 2H), 1.65 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, chloroform-*d*)  $\delta$  140.68, 140.23, 139.67, 128.84, 128.78, 127.56, 127.39, 127.30, 127.05, 127.00, 126.97, 126.58, 125.78, 66.41, 31.74, 27.47, 19.48. HRMS (ESI-TOF)  $m/z$ : [M – OH]<sup>+</sup> calcd for C<sub>18</sub>H<sub>17</sub><sup>+</sup>: 233.1325; found: 233.1322.

**3-([1,1'-Biphenyl]-4-yl)cyclopent-2-en-1-ol (4).** According to method A, 1.44 mL of *n*-butyllithium (1.6 M, 0.9 mmol) was slowly added to a solution of 4-bromobiphenyl (210 mg, 0.9 mmol) dissolved in an anhydrous diethyl ether (0.20 M) and precooled to  $-78$  °C and stirred for 30 min. This solution was then added to 2-cyclohexen-1-one (97%, 29.1  $\mu$ L, 0.3 mmol) dropwise. After stirring for 3 h, FeCl<sub>2</sub> (anhydrous, 37.9 mg, 0.3 mmol) was added to the reaction mixture. After 12 h, purification (column chromatography: 17% ethyl acetate in hexane) of the reaction mixture gave 38 mg of 3-([1,1'-biphenyl]-4-yl)cyclopent-2-en-1-ol as a yellowish powder. (53% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.67 (t,  $J$  = 7.9, 7.9 Hz, 4H), 7.58 (d,  $J$  = 8.2 Hz, 2H) 7.46 (t,  $J$  = 7.6, 7.6 Hz, 2H), 7.36 (t,  $J$  = 7.3, 7.3 Hz, 1H), 6.30 (d,  $J$  = 1.9 Hz, 1H), 4.83 (s, 1H), 2.81 (m, 1H), 2.56 (m, 1H), 2.30 (m, 1H), 1.71 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  143.05, 140.18, 140.07, 139.62, 135.31, 135.25, 130.20, 129.42, 127.94, 127.79, 127.26, 127.24, 127.07, 126.93, 126.91, 126.80, 76.36, 33.86, 31.38. HRMS (ESI-TOF)  $m/z$ : [M – OH]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub><sup>+</sup>: 219.1168; found: 219.1154.

**(E)-2-([1,1'-Biphenyl]-4-yl)-3-methylpent-3-en-2-ol (5).** According to method A, 1.88 mL of *n*-butyllithium (1.6 M, 1 mmol) was slowly added to a solution of 4-bromobiphenyl (699 mg, 3 mmol) dissolved in an anhydrous diethyl ether (0.20 M) and precooled to  $-78$  °C. After 30 min, this solution was then added to 3-methyl-2-penten-1-one (98%, 99  $\mu$ L, 1 mmol, 1 equiv) dropwise. After 3 h, FeCl<sub>2</sub> (anhydrous, 126 mg, 1 mmol, 1 equiv) was added. After 12 h, purification (column chromatography: 14% ethyl acetate in hexane) of reaction mixture gave 81 mg (0.32 mmol) of (E)-2-([1,1'-biphenyl]-4-yl)-3-methylpent-3-en-2-ol (5) as a white powder. (32% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.65 (m, 2H), 7.58 (m, 2H), 7.45 (m, 4H), 7.34 (t,  $J$  = 7.3, 7.3 Hz, 1H), 5.70 (m, 1H), 5.13 (s, 1H), 1.60 (m, 6H), 1.43 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  147.79, 141.96, 140.60, 138.33, 129.31, 127.60, 126.99, 126.46, 126.41, 117.25, 76.08, 29.26, 13.69, 13.23. HRMS (ESI-TOF)  $m/z$ : [M – OH]<sup>+</sup> calcd for C<sub>18</sub>H<sub>19</sub><sup>+</sup>: 235.1487; found: 235.1481.

**2-([1,1'-Biphenyl]-4-yl)-4-methylpent-3-en-2-ol (6).** According to method A, 1.9 mL of *n*-butyllithium (1.6 M, 31 mmol) was slowly added to a solution of 4-bromobiphenyl (699 mg, 3 mmol) dissolved in an anhydrous diethyl ether (0.20 M) and precooled to  $-78$  °C. After 30 min, this solution was then added to 4-methyl-2-penten-1-one (98%, 99  $\mu$ L, 1 mmol, 1 equiv) was added. After 12 h, purification (column chromatography: 14% ethyl acetate in hexane) of reaction mixture gave 171 mg (0.68 mmol) of 2-([1,1'-biphenyl]-4-yl)-4-methylpent-3-en-2-ol (6) as a white powder. (68% yield). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.65 (m, 2H), 7.58 (m, 2H), 7.48 (m, 4H), 7.35 (m, 1H), 5.62 (p,  $J$  = 1.4, 1.4, 1.4, 1.4 Hz, 1H), 5.09 (s, 1H), 1.67 (d,  $J$  = 1.4 Hz, 3H), 1.52 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  149.90, 140.59, 138.01, 133.66, 133.61, 129.32, 127.58, 126.96, 126.42, 126.18, 72.77, 33.65, 27.18, 19.37. HRMS (ESI-TOF)  $m/z$ : [M + Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>20</sub>ONa<sup>+</sup>: 275.1412; found: 275.1406.

**(E)-2-([1,1'-Biphenyl]-4-yl)-4-phenylbut-3-en-2-ol (7).** According to method A, 3.8 mL of *n*-butyllithium (1.6 M, 6

mmol) was slowly added to a solution of 4-bromobiphenyl (1250 mg, 6 mmol) dissolved in an anhydrous diethyl ether (0.20 M) and precooled to  $-78$  °C. 4-Methyl-2-penten-1-one (98%, 294  $\mu$ L, 2 mmol) and  $\text{FeCl}_2$  (anhydrous, 255 mg, 2 mmol) were added. After 12 h, purification (column chromatography: 14% ethyl acetate in hexane) of reaction mixture gave 460 mg (1.5 mmol) of (*E*)-2-([1,1'-biphenyl]-4-yl)-4-phenylbut-3-en-2-ol (**7**) as a white powder. (77% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.64 (m, 6H), 7.45 (m, 4H), 7.34 (m, 3H), 7.23 (m, 1H), 6.62 (d,  $J = 2.8$  Hz, 2H), 5.53 (s, 1H), 1.66 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{DMSO}$ )  $\delta$  147.87, 140.54, 138.63, 138.45, 137.31, 129.34, 129.04, 127.68, 127.04, 126.74, 126.69, 126.26, 126.00, 73.47, 40.86, 40.58, 40.30, 40.03, 39.75, 39.47, 39.19, 31.14, 30.30. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{20}\text{ONa}^+$ : 323.1412; found: 323.1406.

**3-Phenylcyclohex-2-en-1-ol (9)**. According to method B, 2-cyclohexen-1-one (97%, 29.1  $\mu$ L, 0.3 mmol) was dissolved in 2 mL of ether (stabilized with BHT) reacted with phenyllithium (2.1 mL, 1.9 M, 0.9 mmol). The reaction mixture was stirred for 3 h, and  $\text{FeCl}_2$  (anhydrous, 38 mg, 0.3 mmol) was added. After 12 h, purification (column chromatography: 17% ethyl acetate in hexane) of reaction mixture gave 41 mg of 3-phenylcyclohex-2-en-1-ol (**9**) as an off-white powder (54% yield).  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  7.31 (m, 2H), 7.25 (m, 2H), 7.17 (m, 1H), 6.03 (dt,  $J = 3.6, 1.8, 1.8$  Hz, 1H), 4.29 (bs, 1H), 2.35 (m, 1H), 2.27 (m, 1H), 1.93 (s, 1H), 1.81 (s, 1H), 1.61 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, chloroform-*d*)  $\delta$  141.40, 140.03, 128.33, 127.43, 126.67, 125.41, 66.34, 31.69, 27.52, 19.53. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{20}\text{ONa}^+$ : 197.0937; found: 197.0938.<sup>37</sup>

**4'-(*tert*-Butyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (11)**. According to method A, 0.94 mL of *n*-butyllithium (1.6 M, 1.5 mmol) was slowly added to a solution of 4-bromotertbutylbenzene (320 mg, 1.5 mmol) dissolved in an anhydrous diethyl ether (0.20 M) and precooled to  $-78$  °C. After 30 min, this solution was added to 2-cyclohexen-1-one (97%, 49.0  $\mu$ L, 0.5 mmol) and stirred for 3 h, and then  $\text{FeCl}_2$  (anhydrous, 63 mg, 0.5 mmol) was added. Purification (column chromatography: 17% ethyl acetate in hexane) of reaction mixture after 12 h gave 114 mg (0.49 mmol) of 4'-(*tert*-butyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (**11**) as a pale yellowish powder (98% yield).  $^1\text{H}$  NMR (300 MHz, chloroform-*d*)  $\delta$  7.31 (s, 4H) 6.13 (dt,  $J = 3.6, 1.8, 1.8$  Hz, 1H), 4.39 (bs, 1H), 2.51 (m, 1H), 2.42 (m, 1H), 1.92 (m, 2H), 1.72 (m, 2H), 1.33 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, chloroform-*d*)  $\delta$  150.48, 139.88, 138.36, 125.86, 125.22, 125.04, 66.38, 34.50, 31.76, 31.32, 27.45, 19.45. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} - \text{OH}]^+$  calcd for  $\text{C}_{16}\text{H}_{21}^+$ : 213.1638; found: 213.1634.

**4'-Methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (13)**. According to method A, 3.8 mL of *n*-butyllithium (1.6 M, 6 mmol) was slowly added to a solution of 4-bromotoluene (0.7 mL, 6 mmol) dissolved in an anhydrous diethyl ether (0.20 M) and precooled to  $-78$  °C. After 30 min, this solution was added to 2-cyclohexen-1-one (97%, 17.0  $\mu$ L, 0.2 mmol) and stirred for 3 h, and then  $\text{FeCl}_2$  (anhydrous, 25 mg, 0.2 mmol) was added. Purification (column chromatography: 17% ethyl acetate in hexane) of reaction mixture after 12 h gave 22 mg (0.12 mmol) of 4'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (**13**) as a white powder (59% yield).  $^1\text{H}$  NMR (300 MHz, chloroform-*d*)  $\delta$  7.32 (m, 2H), 7.14 (d,  $J = 8.1$  Hz, 2H), 6.11 (dt,  $J = 3.5, 1.8, 1.8$  Hz, 1H), 4.39 (bs, 1H), 2.51 (m, 1H), 2.42 (m, 1H), 2.35 (s, 3H), 1.92 (m, 2H), 1.70 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$

NMR (101 MHz, chloroform-*d*)  $\delta$  150.49, 139.92, 138.35, 125.92, 125.82, 125.74, 125.23, 125.04, 124.71, 66.40, 37.29, 34.50, 31.75, 31.32, 31.19, 31.10, 27.97, 27.52, 27.45, 22.83, 19.45. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{16}\text{H}_{21}\text{ONa}^+$ : 211.1099, found 211.1093.<sup>17</sup>

**(Naphthalen-1-yl)cyclohex-2-en-1-ol (15)**. According to method A, 0.94 mL of *n*-butyllithium (1.6 M, 1.5 mmol) was slowly added to a solution of 1-bromonaphthalene (311 mg, 1.5 mmol) dissolved in an anhydrous diethyl ether (0.20 M) and precooled to  $-78$  °C. After 30 min, this solution was added to 2-cyclohexen-1-one (97%, 49.0  $\mu$ L, 0.5 mmol) and stirred for 3 h, and then  $\text{FeCl}_2$  (anhydrous, 63 mg, 0.5 mmol) was added. After 12 h, purification (column chromatography: 14% ethyl acetate in hexane) of the reaction mixture gave 97 mg (0.43 mmol) of (naphthalen-1-yl)cyclohex-2-en-1-ol (**15**) as a white powder. (87% yield).  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  8.67 (dd,  $J = 7.4, 2.8$  Hz, 1H), 7.89 (m, 1H), 7.80 (m, 2H), 7.47 (m, 3H), 6.11 (ddd,  $J = 10.0, 3.7, 3.7$  Hz, 1H), 5.99 (dt,  $J = 10.0, 2.3, 2.3$  Hz, 1H), 2.49 (ddd,  $J = 13.7, 10.6, 3.2$  Hz, 1H), 2.24 (m, 3H), 2.11 (m, 1H), 1.91 (m, 1H), 1.64 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, chloroform-*d*)  $\delta$  142.15, 134.80, 133.87, 130.45, 129.97, 129.08, 128.49, 126.54, 125.20, 125.13, 124.89, 124.73, 73.51, 37.21, 25.04, 19.49. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} - \text{OH}]^+$  calcd for  $\text{C}_{16}\text{H}_{15}^+$ : 207.1174, found 207.1179.<sup>40</sup>

**6-Methylcyclohex-2-en-1-one (23)**. Diisopropylamine (1.5 equiv) was dissolved in 3.2 mL of THF and placed in a sealed nitrogen filled vial with a stir bar. The vial was cooled to 0 °C, and *n*-butyllithium (1.6 M, 10.5 mmol) was added dropwise. After stirring for 20 min, the reaction was then cooled to  $-78$  °C; then, the cyclohexenone (1 equiv) was added dropwise, and the reaction was stirred for 30 min. At the same temperature, 1.3 mL of methyl iodide was added, and the reaction was stirred for another 30 min. Hexamethylphosphoramide (6.3 mL) was then added, and the reaction was then stirred for 2 h. The reaction was then warmed to 0 °C before 8 mL of ether was added, and the organic layer was washed with saturated ammonium chloride (5 mL  $\times$  3) and saturated sodium chloride (5 mL  $\times$  3) and then dried over sodium sulfate. The product 6-methylcyclohex-2-en-1-one (**23**, 542 mg) was obtained after purification by flash chromatography (10:1 Hex/EtOAc) as a clear solid. (47% yield).  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  6.91 (m, 1H), 5.96 (dq,  $J = 10.0, 1.9, 1.8, 1.8$  Hz, 1H), 2.37 (m, 3H), 2.04 (dddd,  $J = 16.7, 13.2, 6.2, 4.9$  Hz, 1H), 1.71 (dddd,  $J = 13.4, 12.0, 8.3, 6.8$  Hz, 1H), 1.12 (dd,  $J = 6.8, 1.1$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, chloroform-*d*)  $\delta$  202.35, 149.71, 129.34, 41.60, 30.80, 25.50, 15.04. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_7\text{H}_{11}\text{O}^+$ : 111.0811;  $[\text{M} + \text{H}]^+$  found: 111.0804.

**2-Methyl-3,4-dihydro-[1,1'-biphenyl]-1(2H)-ol (24)**. According to method B, 0.2 mmol (22  $\mu$ L) of **23** was dissolved in 1 mL of anhydrous diethyl ether (stabilized with BHT). Phenyllithium (316  $\mu$ L, 1.9 M, 0.6 mmol) was added dropwise to the reaction mixture and stirred for 3 h at room temperature. Purification (column chromatography: 17% ethyl acetate in hexane) of reaction mixture gave 15 mg of 2-methyl-3,4-dihydro-[1,1'-biphenyl]-1(2H)-ol as a clear liquid (37% yield).  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  7.45 (m, 2H), 7.35 (m, 2H), 7.26 (m, 1H), 6.00 (m, 1H), 5.76 (dt,  $J = 9.9, 2.1, 2.1$  Hz, 1H), 2.22 (m, 2H), 1.88 (m, 1H), 1.64 (dt,  $J = 3.9, 2.4, 2.4$  Hz, 2H), 0.85 (d,  $J = 6.7$  Hz, 3H). LRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{17}\text{O}^+$ : 189.13;  $[\text{M} + \text{H}]^+$  found: 189.14.

**6-Methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (26) and (27).** In 1 mL of anhydrous diethyl ether, 0.2 mmol of **24** was dissolved, and FeCl<sub>2</sub> (25 mg, 0.2 mmol) was then added in the glovebox. The reaction was stirred overnight at room temperature. Purification (column chromatography: 17% ethyl acetate in hexane) of the reaction mixture gave 20 mg of (3*R*,6*R*)-6-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (**26**) and (3*S*,6*R*)-6-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (**27**) as a clear solid with 52% yield. This diastereomeric mixture was impossible to separate by flash chromatography, but <sup>1</sup>H NMR analysis of the crude mixture indicated a 2:1 ratio of the two isomers, **26** and **27** (determined by comparing the integrals of the two peaks corresponding to the methyl groups in each isomer). <sup>1</sup>H NMR (400 MHz, chloroform-*d*) δ 7.24 (m, 5H) (both), 5.82 (dd, *J* = 3.7, 1.5 Hz, 2H) (**26**), 5.79 (dd, *J* = 3.7, 1.5 Hz 1H) (**27**), 4.26 (m, 1H) (both), 2.75 (m, 1H) (both), 1.97 (m, 1H) (both), 1.85 (m, 1H) (both), 1.60 (m, 1H) (both), 1.41 (m, 1H) (both), 0.90 (d, *J* = 7.1 Hz, 3H) (**27**), 0.83 (d, *J* = 7.1 Hz, 6H) (**26**). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, chloroform-*d*) δ 146.38, 141.52, 128.24, 127.24, 127.20, 126.53, 66.26, 30.93, 29.03, 27.13, 19.42. LRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>17</sub>O<sup>+</sup>: 189.13. [M + H]<sup>+</sup> found: 189.14.

**(*E*)-1,5,5-Triphenylpenta-2,4-dien-1-ol (33) and (2*E*,4*E*)-1,1,5-Triphenylpenta-2,4-dien-1-ol (34).** Anhydrous diethyl ether (2 mL) was added to cinnamylideneacetophenone (234 mg, 1 mmol), and the solution was cooled to -78 °C. Phenyllithium (1.6 mL, 3 mmol, 1.9 M) was then added dropwise, and the reaction mixture was stirred for 1 h before FeCl<sub>2</sub> (126 mg, 1 mmol) was added in the glovebox. After 12 h, purification (column chromatography: 14% ethyl acetate in hexane) of reaction mixture isolated two isomers.

87 mg of (*E*)-1,5,5-triphenylpenta-2,4-dien-1-ol (**33**) was obtained as a yellow powder with 28% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.31 (m, 9H), 7.22 (m, 4H), 7.16 (m, 3H), 6.81 (d, *J* = 11.0 Hz, 1H), 6.29 (m, 1H), 6.09 (m, 1H), 5.51 (d, *J* = 4.3 Hz, 1H), 5.08 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 144.73, 142.02, 141.79, 140.30, 139.63, 130.40, 129.04, 128.91, 128.79, 128.58, 127.93, 127.84, 127.43, 127.31, 126.60, 126.37, 73.24. HRMS (ESI-TOF) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>23</sub>H<sub>20</sub>ONa<sup>+</sup>: 335.1412; found: 335.1406.

**(2*E*,4*E*)-1,1,5-Triphenylpenta-2,4-dien-1-ol (34, 123 mg)** was obtained as a yellow powder with 39% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.47 (m, 6H), 7.34 (dd, *J* = 8.5, 6.8 Hz, 6H), 7.25 (m, 3H), 7.09 (dd, *J* = 15.7, 10.6 Hz, 1H), 6.62 (dd, *J* = 29.7, 15.4 Hz, 2H), 6.43 (dd, *J* = 15.1, 10.6 Hz, 1H), 6.18 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 147.72, 141.57, 137.55, 132.37, 129.21, 129.12, 129.07, 128.27, 127.92, 127.24, 127.07, 126.70, 78.23. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>21</sub>O<sup>+</sup>: 313.1587; found: 313.1583.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00163.

Preparations of the compounds, characterization data sets and copies of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: bdeboef@uri.edu.

## ORCID

Brenton DeBoef: 0000-0002-9270-2557

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (Grant # 1566392).

## ■ REFERENCES

- (1) Cai, S.; Tian, Y.; Zhang, J.; Liu, Z.; Lu, M.; Weng, W.; Huang, M. Carbotrifluoromethylation of Allylic Alcohols via 1,2-Aryl Migration Promoted by Visible-Light-Induced Photoredox Catalysis. *Adv. Synth. Catal.* **2018**, *360*, 4084–4088.
- (2) Brenna, E.; Crotti, M.; De Pieri, M.; Gatti, F. G.; Manenti, G.; Monti, D. Chemo-Enzymatic Oxidative Rearrangement of Tertiary Allylic Alcohols: Synthetic Application and Integration into a Cascade Process. *Adv. Synth. Catal.* **2018**, *360*, 3677–3686.
- (3) Hanson, J. R. Stereochemical Aspects of the Hydrogenolysis of Derivatives of Terpenoid and Steroidal Allylic Alcohols. *J. Chem. Res.* **2018**, *42*, 1–6.
- (4) Motokura, K.; Ikeda, M.; Kim, M.; Nakajima, K.; Kawashima, S.; Nambo, M.; Chun, W.-J.; Tanaka, S. Silica Support-Enhanced Pd-Catalyzed Allylation Using Allylic Alcohols. *ChemCatChem* **2018**, *10*, 4476.
- (5) Sanz-Marco, A.; Možina, Š.; Martínez-Erro, S.; Iskra, J.; Martín-Matute, B. Synthesis of  $\alpha$ -Iodoketones from Allylic Alcohols through Aerobic Oxidative Iodination. *Adv. Synth. Catal.* **2018**, *360*, 3884–3888.
- (6) Wang, G.; Gan, Y.; Liu, Y. Nickel-Catalyzed Direct Coupling of Allylic Alcohols with Organoboron Reagents. *Chin. J. Chem.* **2018**, *36*, 916–920.
- (7) Vu, M. D.; Foo, C. Q.; Sadeer, A.; Shand, S. S.; Li, Y.; Pullarkat, S. A. Triflic-Acid-Catalyzed Tandem Allylic Substitution-Cyclization Reaction of Alcohols with Thiophenols - Facile Access to Polysubstituted Thiochromans. *ACS Omega* **2018**, *3*, 8945–8951.
- (8) Ukaji, Y.; Watanabe, Y.; Sakai, T.; Maeda, H.; Segi, M. Magnesium-Alkoxide Directed Photoaddition of Tetrahydrofurans to  $\gamma,\gamma$ -Disubstituted Allylic Alcohols. *Heterocycles* **2016**, *93*, 833.
- (9) Wuest, F. R.; Berndt, M. 11C–C Bond Formation by Palladium-Mediated Cross-Coupling of Alkenylzirconocenes with [11C]Methyl Iodide. *J. Labelled Compd. Radiopharm.* **2006**, *49*, 91–100.
- (10) Hosoya, T.; Sumi, K.; Doi, H.; Wakao, M.; Suzuki, M. Rapid Methylation on Carbon Frameworks Useful for the Synthesis of 11CH<sub>3</sub>-Incorporated PET Tracers: Pd(0)-Mediated Rapid Coupling of Methyl Iodide with an Alkenyltributylstannane Leading to a 1-Methylalkene. *Org. Biomol. Chem.* **2006**, *4*, 410.
- (11) Candito, D. A.; Dobrovolsky, D.; Lautens, M. Development of an Intramolecular Aryne Ene Reaction and Application to the Formal Synthesis of ( $\pm$ )-Crinine. *J. Am. Chem. Soc.* **2012**, *134*, 15572–15580.
- (12) Choi, S.; Breugst, M.; Houk, K. N.; Poulter, C. D.  $\delta$ -Deuterium Isotope Effects as Probes for Transition-State Structures of Isoprenoid Substrates. *J. Org. Chem.* **2014**, *79*, 3572–3580.
- (13) Chen, H.; Jia, X.; Yu, Y.; Qian, Q.; Gong, H. Nickel-Catalyzed Reductive Allylation of Tertiary Alkyl Halides with Allylic Carbonates. *Angew. Chem., Int. Ed.* **2017**, *56*, 13103–13106.
- (14) Morrill, C.; Grubbs, R. H. Highly Selective 1,3-Isomerization of Allylic Alcohols via Rhenium Oxo Catalysis. *J. Am. Chem. Soc.* **2005**, *127*, 2842–2843.
- (15) Shibuya, M.; Ito, S.; Takahashi, M.; Iwabuchi, Y. Oxidative Rearrangement of Cyclic Tertiary Allylic Alcohols with IBX in DMSO. *Org. Lett.* **2004**, *6*, 4303–4306.
- (16) Shibuya, M.; Tomizawa, M.; Iwabuchi, Y. Oxidative Rearrangement of Tertiary Allylic Alcohols Employing Oxoammonium Salts. *J. Org. Chem.* **2008**, *73*, 4750–4752.
- (17) Li, J.; Tan, C.; Gong, J.; Yang, Z. Palladium-Catalyzed Oxidative Rearrangement of Tertiary Allylic Alcohols to Enones with Oxygen in Aqueous Solvent. *Org. Lett.* **2014**, *16*, 5370–5373.

- (18) Yamamoto, Y.; Kurohara, T.; Shibuya, M. CF<sub>3</sub>-Substituted Semisquarate: A Pluripotent Building Block for the Divergent Synthesis of Trifluoromethylated Functional Molecules. *Chem. Commun.* **2015**, *51*, 16357–16360.
- (19) Ramharter, J.; Mulzer, J. Total Synthesis of Valerenic Acid, a Potent GABA<sub>A</sub> Receptor Modulator. *Org. Lett.* **2009**, *11*, 1151–1153.
- (20) Geddis, S. M.; Carro, L.; Hodgkinson, J. T.; Spring, D. R. Divergent Synthesis of Quinolone Natural Products from *Pseudonocardia* sp. CL38489. *Eur. J. Org. Chem.* **2016**, 5799–5802.
- (21) Singh, C.; Gupta, N.; Puri, S. K. Photooxygenation of 3-Aryl-2-Cyclohexenols: Synthesis of a New Series of Antimalarial 1,2,4-Trioxanes. *Tetrahedron Lett.* **2005**, *46*, 205–207.
- (22) Shang, R.; Ilies, L.; Nakamura, E. Iron-Catalyzed Directed C(Sp(2))-H and C(Sp(3))-H Functionalization with Trimethylaluminum. *J. Am. Chem. Soc.* **2015**, *137*, 7660–7663.
- (23) Shang, R.; Ilies, L.; Nakamura, E. Iron-Catalyzed C–H Bond Activation. *Chem. Rev.* **2017**, *117*, 9086–9139.
- (24) Adams, C. J.; Bedford, R. B.; Carter, E.; Gower, N. J.; Haddow, M. F.; Harvey, J. N.; Huwe, M.; Cartes, M. Á.; Mansell, S. M.; Mendoza, C.; et al. Iron(I) in Negishi Cross-Coupling Reactions. *J. Am. Chem. Soc.* **2012**, *134*, 10333–10336.
- (25) Bedford, R. B. How Low Does Iron Go? Chasing the Active Species in Fe-Catalyzed Cross-Coupling Reactions. *Acc. Chem. Res.* **2015**, *48*, 1485–1493.
- (26) Jiang, X.; Zhang, J.; Ma, S. Iron Catalysis for Room-Temperature Aerobic Oxidation of Alcohols to Carboxylic Acids. *J. Am. Chem. Soc.* **2016**, *138*, 8344–8347.
- (27) Cheng, B.; Liu, W.; Lu, Z. Iron-Catalyzed Highly Enantioselective Hydrosilylation of Unactivated Terminal Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 5014–5017.
- (28) Piontek, A.; Bisz, E.; Szostak, M. Iron-Catalyzed Cross-Couplings in the Synthesis of Pharmaceuticals: In Pursuit of Sustainability. *Angew. Chem., Int. Ed.* **2018**, *57*, 11116–11128.
- (29) Ilies, L.; Matsubara, T.; Ichikawa, S.; Asako, S.; Nakamura, E. Iron-Catalyzed Directed Alkylation of Aromatic and Olefinic Carboxamides with Primary and Secondary Alkyl Tosylates, Mesylates, and Halides. *J. Am. Chem. Soc.* **2014**, *136*, 13126–13129.
- (30) Sirois, J. J.; Davis, R.; DeBoef, B. Iron-Catalyzed Arylation of Heterocycles via Directed C–H Bond Activation. *Org. Lett.* **2014**, *16*, 868–871.
- (31) Holzwarth, M.; Dieskau, A.; Tabassam, M.; Plietker, B. Preformed  $\pi$ -Allyl Iron Complexes as Potent, Well-Defined Catalysts for the Allylic Substitution. *Angew. Chem., Int. Ed.* **2009**, *48*, 7251–7255.
- (32) Qi, L.; Ma, E.; Jia, F.; Li, Z. Iron-Catalyzed Allylic Substitution Reactions of Allylic Ethers with Grignard Reagents. *Tetrahedron Lett.* **2016**, *57*, 2211–2214.
- (33) Dieskau, A. P.; Plietker, B. A Mild Ligand-Free Iron-Catalyzed Liberation of Alcohols from Allylcarbonates. *Org. Lett.* **2011**, *13*, 5544–5547.
- (34) Casitas, A.; Krause, H.; Lutz, S.; Goddard, R.; Bill, E.; Fürstner, A. Ligand Exchange on and Allylic C–H Activation by Iron(0) Fragments:  $\pi$ -Complexes, Allyliron Species, and Metallacycles. *Organometallics* **2018**, *37*, 729–739.
- (35) Sundararaman, P.; Herz, W. Oxidative Rearrangements of Tertiary and Some Secondary Allylic Alcohols with Chromium(VI) Reagents. A New Method for 1,3-Functional Group Transposition and Forming Mixed Aldol Products. *J. Org. Chem.* **1977**, *42*, 813–819.
- (36) Sirois, J. J.; DeBoef, B. Transition-Metal Free Umpolung Carbon–nitrogen versus Carbon–chlorine Bond Formation. *Tetrahedron Lett.* **2015**, *56*, S610–S612.
- (37) McCubbin, J. A.; Hosseini, H.; Krokhin, O. V. Boronic Acid Catalyzed Friedel-Crafts Reactions of Allylic Alcohols with Electron-Rich Arenes and Heteroarenes. *J. Org. Chem.* **2010**, *75*, 959–962.
- (38) Yamamoto, H.; Fujita, T. *Thiadiazole Compound for Light-Emitting Elements, Light-Emitting Element, Light-Emitting Apparatus, Authentication Apparatus, And Electronic Device*. United States Patent Application: 0130221334. 13/773033, 2013, DOI: CAN157:619441.
- (39) Ramharter, J.; Mulzer, J. Efficient and Scalable One-Pot Synthesis of 2,4-Dienols from Cycloalkenones: Optimized Total Synthesis of Valerenic Acid. *Org. Lett.* **2011**, *13*, 5310–5313.
- (40) McCubbin, J. A.; Voth, S.; Krokhin, O. V. Mild and Tunable Benzoic Acid Catalysts for Rearrangement Reactions of Allylic Alcohols. *J. Org. Chem.* **2011**, *76*, 8537–8542.