Synthesis Y.-k. Sugiyama et al. Special Topic

# Iron-Catalyzed Reductive Metalation–Allylation and Metalative Cyclization of 2,3-Disubstituted Oxetanes and Their Stereoselectivity

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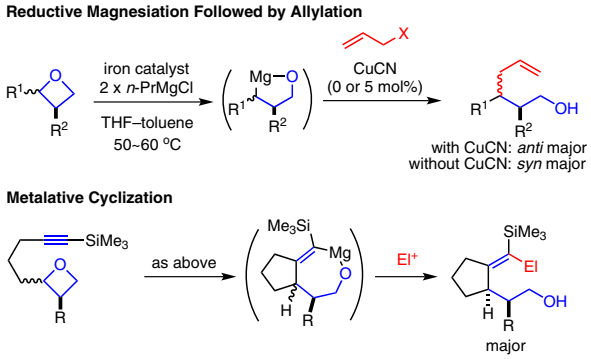


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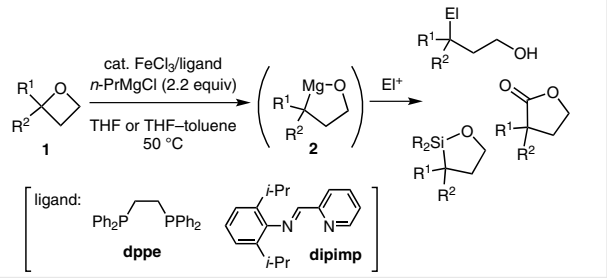
**Abstract** A novel process for the reductive magnesiation of 2-substituted oxetanes and the metalative cyclization of ω-alkynyl oxetanes is developed using *n*-propylmagnesium chloride in the presence of an iron catalyst. The generated intermediate organomagnesium compounds react with electrophiles. The reactions of 2,3-disubstituted oxetanes and their subsequent allylation with allyl halides in the presence or absence of copper(I) cyanide as the catalyst is studied with a unique switching of stereoselectivity being observed in the absence or presence of copper(I) cyanide . In addition, it is found that the metalative cyclization of 3-substituted 2-alkynyl oxetanes proceeds in an *anti*-selective manner starting from both *syn*- and *anti*-substrates. In all cases, the stereochemistry at the 2-position of the oxetanes is lost during the reactions suggesting the involvement of a radical process.

**Key words** iron catalyst, oxetanes, reductive magnesiation, metalative cyclization, (3-oxidopropyl)magnesium, diastereoselective reaction

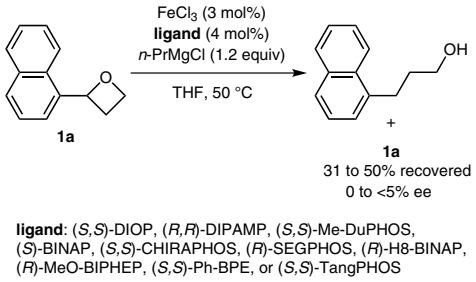
We have recently developed an iron-catalyzed reductive magnesiation reaction of 2-substituted oxetanes **1**, which generates substituted (3-oxidopropyl)magnesium compounds **2** (Scheme 1).[1,2] It was found that the reaction of aryl-substituted oxetanes could be performed with either an iron–dppe or an iron–dipimp catalyst, but the latter was necessary for the reactions of alkyl-substituted oxetanes; [dppe: 1,2-bis(diphenylphosphino)ethane; dipimp: 2-(2,6-diisopropylphenylimino)methylpyridine]. The generated organomagnesium compounds **2** reacted smoothly with a variety of electrophiles to produce the corresponding alcohols, lactones, and cyclic silyl ethers in good to excellent yields (Scheme 1). Herein we describe a novel process for the reductive magnesiation of 2-substituted oxetanes and the metalative cyclization of ω-alkynyl oxetanes, and discuss the stereochemical outcomes.



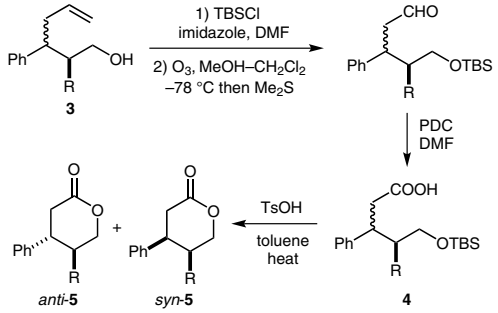

**Scheme 1** Iron-catalyzed reductive magnesiation of 2-substituted oxetanes and their subsequent reactions with electrophiles

First, to study the reductive magnesiation reaction extensively, we attempted the kinetic resolution of racemic 2-(naphthalen-1-yl)oxetane (**1a**) in the presence of a chiral diphosphine ligand instead of dppe (Scheme 2). Thus, the reactions of **1a** in the presence of $FeCl_3$ and a chiral ligand were performed with 1.2 equivalents of *n*-PrMgCl to control the conversion to around 50%. All the reactions using a chiral ligand, such as (*S*,*S*)-DIOP, (*R*,*R*)-DIPAMP, (*S*,*S*)-Me-DuPHOS, (*S*)-BINAP, (*S*,*S*)-CHIRAPHOS, (*R*)-SEGPHOS, (*R*)-H8-BINAP, (*R*)-MeO-BIPHEP, (*S*,*S*)-Ph-BPE, and (*S*,*S*)-TangPHOS, proceeded at 50 °C in THF and 31–50% of **1a** was recovered. Chiral HPLC analyses of the remaining **1a** confirmed the ee to be less than 5%, and all attempts at the kinetic resolution of **1a** were unsuccessful.

Next, the reductive magnesiation reactions of 2,3-disubstituted oxetanes **1b–d** along with the subsequent allylations were performed, and the stereochemistry was investigated (Scheme 3). Initially, we found that in the presence of the $FeCl_3$/dppe catalyst, the reaction of *anti*-**1b** was rapid and complete within six hours, while the reaction of *syn*-**1b** proceeded very slowly (41% conversion in 72 h). In contrast,

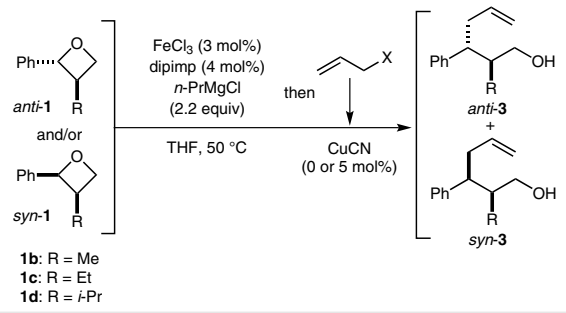



**Scheme 2** Kinetic resolution of **1a** using chiral diphosphine ligands




**Scheme 4** Confirmation of the stereochemistry of compounds **3** by their conversion into known lactones **5**

when $FeCl_3$/dipimp was used as the catalyst, both stereoisomers reacted smoothly and subsequent treatment with allyl bromide afforded **3b** in good yields. Thus, *anti*-**1**, *syn*-**1**, or a mixture of *anti*- and *syn*-**1** were subjected to the $FeCl_3$/dipimp-catalyzed reaction with *n*-PrMgCl (2.2 equiv) to generate the corresponding organomagnesium compounds **2**, after which the mixture was treated with an allyl halide in the absence or presence of CuCN as the catalyst (0 or 5 mol%).




**Scheme 3** Reductive magnesiation and subsequent diastereoselective allylation

The stereochemistries of the resulting allylated products **3** were determined by their conversion into the known lactones **5** through hydroxy acid derivatives **4**, according to the conventional procedure depicted in Scheme 4. The stereochemistries of **3b** and **3c** were confirmed by comparison of the NMR spectra of products **5b**[3,4] and **5c**,[4] respectively, with those reported in the literature. The stereochemistries of **3d** were assigned by analogy with **3b** and **3c**.

The results of the reductive metalation and the subsequent allylation are summarized in Table 1. In the absence of the CuCN catalyst, the allylation proceeded smoothly to afford products **3** in good yields. Note that the isomeric products were obtained in the same ratio (*anti*/*syn* = 23:77) starting from both *syn*-**1b** and *anti*-**1b** (Table 1, entries 1 and 2). In contrast, in the presence of the CuCN catalyst, *anti*-**3b** was produced as the major product, but the ratios (*anti*/*syn* = 77:23) were similar starting from both *syn*-**1b** and *anti*-**1b** (Table 1, entries 3 and 4). Similar diastereomeric ratios and the trend of switching selectivity in the absence or presence of CuCN were observed in the reactions with allyl chloride (Table 1, entries 5 and 6). The presence of halogen atoms in the allylating agents did not affect the selectivity. In summary, the present iron-catalyzed reductive magnesiation lacked stereochemistry at the cleaving carbon atom, and the stereochemistry of the subsequent reaction with electrophiles varied depending on the conditions. Hence, for **1c** and **1d**, mixtures of *syn* and *anti* substrates were subjected to the reaction. The switch in diastereoselectivity in the absence/presence of CuCN was observed again in the reaction of **1c** (Table 1, entries 7 and 8). In the presence of CuCN, **1d** carrying a bulky *i*-Pr substituent showed somewhat better selectivity (85:15) (Table 1, entry 10).

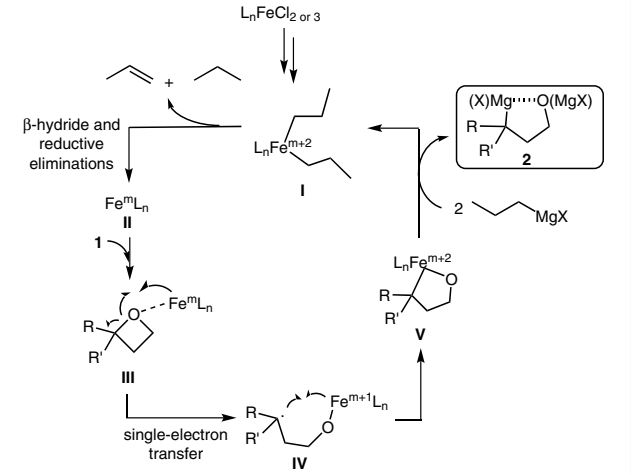
**Table 1** Results of the Reductive Magnesiation/Allylation in the Absence or Presence of CuCN

| Entry | Oxetane | X | CuCN (mol%) | *anti*-**3**/*syn*-**3** | Yield (%)[a] |
|---|---|---|---|---|---|
| 1[b] | *syn*-**1b** (R = Me) | Br | 0 | 23:77 | 81 |
| 2[b] | *anti*-**1b** | Br | 0 | 23:77 | 85 |
| 3[b] | *syn*-**1b** | Br | 5 | 77:23 | 85 |
| 4[b] | *anti*-**1b** | Br | 5 | 78:22 | 92 |
| 5 | *anti*-**1b** | Cl | 0 | 27:73 | 76 |
| 6 | *anti*-**1b** | Cl | 5 | 77:23 | 82 |
| 7 | *mix*-**1c**[c] (R = Et) | Br | 0 | 37:63 | 73 |
| 8 | *mix*-**1c**[c] | Br | 5 | 76:24 | 92 |
| 9 | *mix*-**1d**[c] (R = *i*-Pr) | Br | 0 | 55:45 | 59 |
| 10 | *mix*-**1d**[c] | Br | 5 | 85:15 | 89 |

[a] Combined yield.
[b] See ref. 1.
[c] Mixture (~1:1) of *anti* and *syn* isomers.

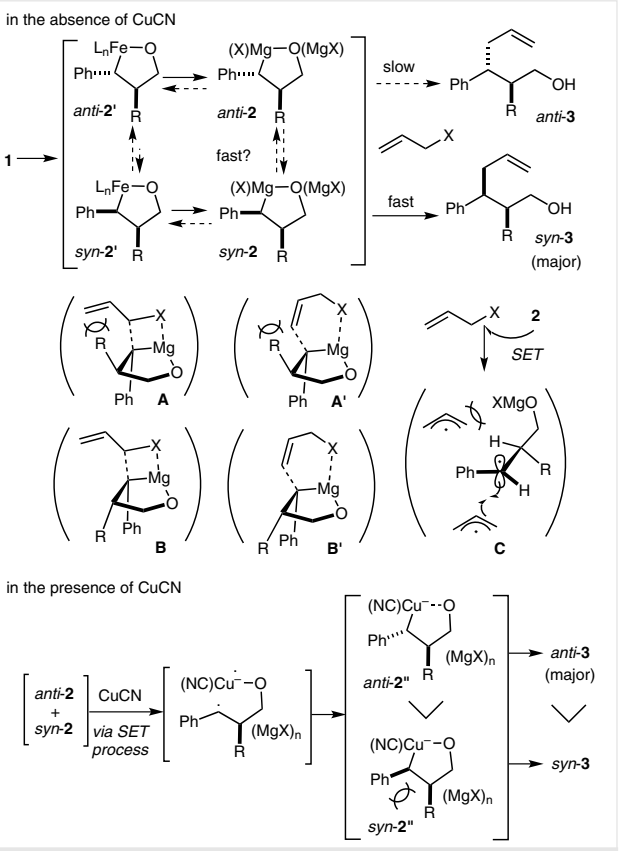
As proposed in a previous paper, this magnesiation of oxetanes catalyzed by an iron complex might involve a single-electron transfer (SET) process to generate a radical species at the cleaving carbon atom during which the stereochemical information is lost (Scheme 5).[1] The low-valent

iron species **II**, generated from the $FeCl_3$–ligand complex through complex **I** by the reaction with two equivalents of *n*-PrMgCl, may react with oxetane **1** through coordination and subsequent single-electron transfer to provide γ-oxidoradical **IV**, which would then form cyclic iron complex **V**. Subsequent transmetalation of **V** with two equivalents of the Grignard reagent would afford (3-oxidopropyl)magnesium compound **2** as the product and simultaneously regenerate complex **I**. Coordination of the oxygen atom in the oxetanes **1** to the iron atom in structure **III** increases the electron-deficiency of the oxetanes while making the iron complex more electron-rich, thus allowing a facile electron transfer. As it can be assumed that dppe might be more Lewis basic than dipimp, the higher reactivity attained using the iron–dipimp complex compared with that of the iron–dppe complex can be attributed to the higher Lewis acidity of the former relative to that of the latter. Steric effects of ligands might also be considered; the relatively sterically demanding dppe complex was less reactive than the dipimp complex.



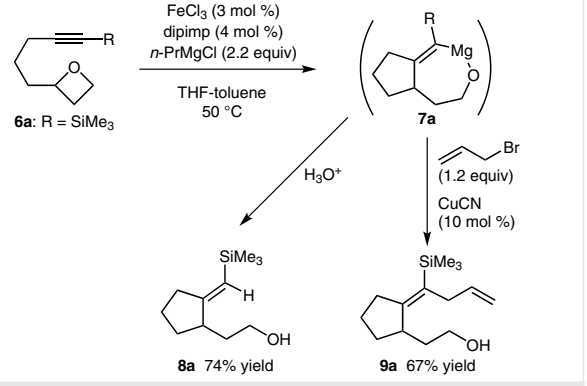

**Scheme 5** Proposed mechanism for the generation of **2** from **1**

For the resulting organomagnesium **2**, there seems to be an equilibrium between *anti*-**2** and *syn*-**2**, which may occur between organomagnesiums **2** themselves and/or via iron complexes **2′** (Scheme 6). Presumably, *anti*-**2** exists predominantly because *syn*-**2** may be comparably less stable due to steric repulsion between the Ph and R substituents. In the absence of CuCN, the allylation of **2a** may proceed via the four-membered Grignard metathesis (**A** and **B**) and/or the six-membered substitution reaction (**A′** and **B′**) in an $S_N2'$ fashion. Possible transition structures **A** or **A′** may be less stable than those of **B** or **B′** due to repulsion between the R and allyl moieties, respectively. When the rate of the allylation step is expected to be slower than the equilibrium rate, the reaction of *syn*-**2** to afford *syn*-**3** is faster than that of *anti*-**2**. In addition, the allylation through SET from **2** to the allyl halide should be considered. A stable conformer of an intermediate radical species may be assumed (**C**), owing to minimization of steric repulsion against the Ph substituent, and the diastereofacial selection for a radical coupling depends on the difference in the bulk of the $CH_2OMgX$ and R substituents. However, Hoffmann suggested that the ratio of the polar reaction(s) versus the SET process can be varied by the allyl halide employed, and that the polar reaction was predominant with allyl chloride and bromide having higher reduction potential than allyl iodide.[5] In this investigation, it seems that the SET process has little influence because allyl chloride and bromide were employed and both showed the same selectivity. Meanwhile, in the presence of the CuCN catalyst, the selectivity was opposite to that of the reaction without CuCN. Hoffmann reported that transmetalation between a Grignard reagent and CuCN occurs mainly through an SET process.[6] The transmetalation of **2** with CuCN via the SET process proceeds regardless of the stereochemistry of magnesium complexes **2** and may generate the predominantly more stable cuprate *anti*-**2″** rather than *syn*-**2″**. The subsequent allylation proceeds with retention of stereochemistry to provide *anti*-**3** as the major product.[6]




**Scheme 6** Proposed mechanism for the allylation reaction

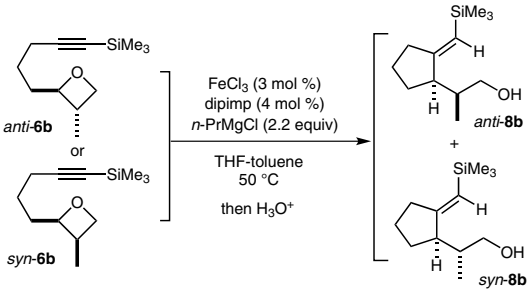
During our extensive investigations, we found that the catalyst system enables carbo-metalative cyclization of ω-alkynyl oxetanes **6** to generate the corresponding alkenylmagnesium compounds **7**, that react with electrophiles (Scheme 7). Since **6a** is a 2-alkyl-substituted oxetane, the catalysis requires the use of dipimp as the ligand. Indeed, when dppe was used as the ligand, the reaction did not proceed. Thus, the reaction of **6a** with *n*-PrMgCl (2.2 equiv) in the presence of $FeCl_3$ (3 mol%) and dipimp (4 mol%) in THF–toluene proceeded smoothly via a metalative cyclization pathway at 50 °C to generate cyclized organomagnesium compound **7a**, which was confirmed by hydrolysis and allylation reactions. The protonated and allylated products **8a** and **9a** were obtained in 74% and 67% isolated yields, respectively (Scheme 7).




**Scheme 7** Iron-catalyzed metalative cyclization of ω-alkynyl oxetanes **6** followed by reactions with electrophiles

On the basis of these results, we were interested in the reactions of 3-substituted ω-alkynyl oxetanes **6b** and their diastereoselectivity (Table 2). Thus, *anti*- and *syn*-**6b** were separately subjected to the iron-catalyzed carbo-metalative cyclization using dipimp as the ligand in THF–toluene at 50 °C. The reaction of *anti*-**6b** was complete after 12 hours and produced the cyclized product **8b** after hydrolysis of the reaction mixture. Compound **8b** was obtained in 76% total yield in an *anti*/*syn* ratio of 83:17.[7] Conversely, the reaction of *syn*-**6b** was much slower than that of *anti*-**6b** and was complete after 24 hours. However, the reaction was highly diastereoselective and afforded exclusively *anti*-**8b** in 69% yield. In these reactions, the stereochemistries at the oxetane 2-position were lost and the production of the *anti* product was predominant starting from both *anti*- and *syn*-**6b**. From the similarity of the analytical values ($^1$H NMR, $^{13}$C NMR, and polarity) of analogous compounds,[8] the stereochemistries of the resulting products **8b** were assigned tentatively as shown in Table 2. The explanation for these selectivities must await further study.

**Table 2** Diastereoselective Metalative Cyclizations of **6b** Catalyzed by an Iron Complex




| Oxetane | Time | *anti*-**8b**/*syn*-**8b** | Yield (%)[a] |
|---|---|---|---|
| *anti*-**6b** | 12 h | 83:17 | 76 |
| *syn*-**6b** | 24 h | >99:1 | 69 |

[a] Combined yield.

In summary, we have developed a novel reductive metalation of 2-substituted oxetanes and metalative cyclization of ω-alkynyl oxetanes catalyzed by an iron complex. The generated intermediate organomagnesium compounds react with electrophiles. The reactions of 2,3-disubstituted oxetanes and the subsequent allylations were carried out in the presence and absence of CuCN as the catalyst, and the stereochemical outcomes were investigated. Unique switching of stereoselectivity in the absence or presence of CuCN was observed. In addition, the metalative cyclization of 3-substituted 2-alkynyl oxetanes was found to proceed in an *anti*-selective manner. In all cases, during the reactions, the stereochemistry at the 2-position in the substrate oxetanes was lost. Further investigations related to the scope and application of these reactions are underway in our laboratory.

All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. Dry solvents were purchased from Kanto Chemicals. 2-(2,6-Diisopropylphenyliminomethyl)pyridine (dipimp) was prepared from pyridine 2-carboxaldehyde and 2,6-diisopropylaniline using the reported procedure.[9] The substrate oxetanes **1a**–**d** and **6a**,**b** were prepared according to a procedure similar to that reported in our previous paper.[1] IR spectra were recorded on a JASCO IR FT/IR 4100 spectrometer. NMR spectra were recorded in $CDCl_3$ at 600 MHz or 500 MHz for $^1$H and 150 MHz or 125 MHz for $^{13}$C on JEOL JNM-ECA600 and -ECA500 spectrometers, respectively. Chemical shifts (δ) are reported in parts per million (ppm) relative to $Me_4Si$ (δ 0.00) or residual $CHCl_3$ (δ 7.26) for $^1$H NMR, and $CDCl_3$ (δ 77.0) for $^{13}$C NMR. In the $^{13}$C NMR peak listings, * denotes peaks attributed to the *anti*-isomer. High-resolution mass spectra (HRMS) were measured on a JEOL Accu TOF T-100 spectrometer equipped with an ESI unit.

**Reductive Magnesiation and Allylation of 2,3-Disubstituted Oxetanes; General Procedure**

To a solution of $FeCl_3$ (2.5 mg, 0.015 mmol) and dipimp (5.3 mg, 0.02 mmol) in THF (1.0 mL) was added *n*-PrMgCl (0.85 mL, 1.3 M in THF, 1.1 mmol) at r.t. The resulting mixture was stirred at ambient temperature for 5 min. A solution of oxetane **1** (0.5 mmol) in THF (1.0 mL) was added and the mixture was stirred at 50 °C. After ensuring complete consumption of **1** by TLC analysis, the reaction mixture was added to a mixture of allyl bromide (0.05 mL, 0.6 mmol) and CuCN (2.1 mg, 0.025 mmol) in THF (1 mL). After 2 h at r.t., aq sat. $NH_4Cl$ was added and the mixture was extracted with $Et_2O$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered through a pad of Celite and concentrated in vacuo. The crude residue was purified by chromatography on silica gel to afford **3** as a colorless oil.

**2-Methyl-3-phenylhex-5-en-1-ol (3b)**

IR (neat, *anti* + *syn*): 3357, 3026, 2960, 2927, 2877, 1601, 1492, 1383 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): δ (*anti*) = 7.31–7.26 (m, 2 H, Ar), 7.22–7.11 (m, 3 H, Ar), 5.68–5.59 (m, 1 H, C*H*=$CH_2$), 5.02–4.87 (m, 2 H, CH=C*H*$_2$), 3.56–3.41 (m, 2 H, $CH_2CH_2OH$), 2.88–2.79 (m, 1 H, PhC*H*$CH_2$), 2.63–2.33 (m, 2 H, C*H*$_2$CH=$CH_2$), 2.01–1.92 (m, 1 H, CHC*H*$CH_3$), 1.27 (t, *J* = 6.0 Hz, 1 H, $CH_2OH$), 0.77 (d, *J* = 8.4 Hz, 3 H, CC*H*$_3$); δ (*syn*, selected peaks) = 5.61–5.51 (m, 1 H, C*H*=$CH_2$), 4.95–4.83 (m, 2 H, CH=C*H*$_2$), 3.30–3.21 (m, 1 H, PhC*H*$CH_2$), 1.93–1.84 (m, 1 H, CHC*H*$CH_3$), 1.07 (d, *J* = 8.4 Hz, 3 H, CC*H*$_3$).

$^{13}C$ NMR (150 MHz, $CDCl_3$): δ (*anti* + *syn*) = 143.4, 142.1*, 137.2*, 137.0, 128.8*, 128.30, 128.29, 128.0*, 126.21, 126.16*, 115.87*, 115.85, 66.4, 66.2*, 48.4, 46.5*, 40.8, 39.7*, 37.6*, 36.9, 15.1, 13.2*.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{18}NaO$: 213.1255; found: 213.1250.

**2-Ethyl-3-phenylhex-5-en-1-ol (3c)**

IR (neat, *anti* + *syn*): 3366, 3062, 2961, 2873, 1601, 1493, 1452, 1415 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): δ (*anti*) = 7.30–7.26 (m, 2 H, Ar), 7.20–7.15 (m, 3 H, Ar), 5.66–5.57 (m, 1 H, C*H*=$CH_2$), 4.99–4.86 (m, 2 H, CH=C*H*$_2$), 3.78–3.69 (m, 1 H, $CH_2CH_2OH$), 3.62–3.55 (m, 1 H, $CH_2CH_2OH$), 2.93–2.85 (m, 1 H, PhC*H*$CH_2$), 2.60–2.36 (m, 2 H, C*H*$_2$CH=$CH_2$), 1.73–1.63 (m, 1 H, CHC*H*$CH_2$), 1.43–1.33 (m, 1 H, $CHCH_2CH_3$), 1.12–1.02 (m, 1 H, $CHCH_2CH_3$), 0.86 (t, *J* = 7.2 Hz, 3 H, $CH_2CH_3$); δ (*syn*, selected peaks) = 3.55–3.47 (m, 1 H, $CH_2CH_2OH$), 3.39–3.31 (m, 1 H, $CH_2CH_2OH$), 2.76–2.68 (m, 1 H, PhC*H*$CH_2$), 1.52–1.44 (m, 1 H, $CHCH_2CH_3$), 0.97 (t, *J* = 7.2 Hz, 3 H, $CH_2CH_3$).

$^{13}C$ NMR (150 MHz, $CDCl_3$): δ (*anti* + *syn*) = 143.3, 143.0*, 137.3*, 137.2, 128.7*, 128.4, 128.3, 128.1*, 126.2, 126.1*, 115.80, 115.78*, 62.7, 62.3*, 46.8, 46.7*, 46.4, 45.9*, 37.3, 37.0*, 21.1, 20.5*, 11.9*, 11.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{20}NaO$: 227.1412; found: 227.1408.

**2-Isopropyl-3-phenylhex-5-en-1-ol (3d)**

IR (neat, *anti* + *syn*): 3375, 3054, 2941, 2928, 2788, 1594, 1485, 1351 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): δ (*anti*) = 7.32–7.26 (m, 2 H, Ar), 7.23–7.15 (m, 3 H, Ar), 5.61–5.55 (m, 1 H, C*H*=$CH_2$), 4.96–4.83 (m, 2 H, CH=C*H*$_2$), 3.86–3.74 (m, 2 H, $CH_2CH_2OH$), 2.92–2.84 (m, 1 H, PhC*H*$CH_2$), 2.66–2.59 (m, 1 H, C*H*$_2$CH=$CH_2$), 2.48–2.40 (m, 1 H, C*H*$_2$CH=$CH_2$), 1.64–1.56 (m, 2 H, CHC*H*$CH_2$ and $CH_3CHCH_3$), 0.94 (d, *J* = 6.6 Hz, 3 H, $CHCH_3$), 0.76 (d, *J* = 6.6 Hz, 3 H, $CHCH_3$); δ (*syn*, selected peaks) = 3.58–3.48 (m, 2 H, $CH_2CH_2OH$), 2.84–2.78 (m, 1 H, PhC*H*$CH_2$), 1.07 (d, *J* = 6.6 Hz, 3 H, $CHCH_3$), 0.95 (d, *J* = 6.6 Hz, 3 H, $CHCH_3$).

$^{13}C$ NMR (150 MHz, $CDCl_3$): δ (*anti* + *syn*) = 144.0), 143.6, 137.5*, 137.0, 128.54, 128.46, 128.38*, 128.2*, 125.5, 126.0*, 115.9, 115.6*, 61.6, 61.1*, 51.4*, 51.2, 46.08*, 46.05, 38.1, 37.3*, 27.4, 27.2*, 22.2), 22.0, 18.0, 17.9*.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{22}NaO$: 241.1564; found: 241.1564.

**Metalative Cyclization and Protonation of Oxetanes; General Procedure**

To a solution of $FeCl_3$ (2.5 mg, 0.015 mmol) and dipimp (5.3 mg, 0.02 mmol) in toluene (1.0 mL) was added *n*-PrMgCl (0.85 mL, 1.3 M in THF, 1.1 mmol) at r.t. The resulting mixture was stirred at ambient temperature for 5 min. A solution of alkynyl oxetane **6** (0.5 mmol) in toluene (1.0 mL) was added and the mixture was stirred at 50 °C. After ensuring complete consumption of **6** by TLC analysis, the reaction mixture was quenched by adding aq sat. $NH_4Cl$ and then extracted with $Et_2O$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered through a pad of Celite and concentrated in vacuo. The crude residue was purified by chromatography on silica gel to afford **8** as a colorless oil.

**2-{2-[(Trimethylsilyl)methylene]cyclopentyl}ethanol (8a)**

IR (neat): 3352, 2952, 2904, 2864, 1436, 1246, 1167 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): δ = 5.31 (dd, *J* = 1.8, 3.0 Hz, 1 H, C=C*H*), 3.80–3.60 (m, 2 H, $CH_2CH_2OH$), 2.45–2.35 (m, 2 H, C*H*$_2$C=CH), 2.33–2.24 (m, 1 H, C*H*C=CH), 1.96–1.87 (m, 2 H, $CH_2CH_2$), 1.81–1.74 (m, 1 H, $CH_2CH_2$), 1.62–1.43 (m, 3 H, $CH_2CH_2$), 1.30–1.22 (m, 2 H, $CH_2CH_2$), 0.08 (s, 9 H, $SiMe_3$).

$^{13}C$ NMR (150 MHz, $CDCl_3$): δ = 165.8, 117.3, 61.9, 43.8, 37.3, 32.5, 32.1, 24.5, –0.32.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{22}NaOSi$: 221.1338; found: 221.1333.

**(*E*)-2-{2-[(Trimethylsilyl)methylene]cyclopentyl}propan-1-ol (8b)**

IR (neat, *anti*-**8b**): 3625, 2954, 1681 $cm^{-1}$.

IR (neat, *syn*-**8b**): 3626, 2960, 1651 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): δ (*anti*) = 5.28 (br s, 1 H, C=C*H*Si), 3.54 (dd, *J* = 7.2, 10.2 Hz, 1 H, C*H*$_2$O), 3.49 (dd, *J* = 6.6, 9.6 Hz, 1 H, C*H*$_2$O), 2.53–2.47 (m, 1 H, allylic C*H*), 2.44–2.38 (m, 1 H, allylic C*H*$_2$), 2.20–2.13 (m, 1 H, allylic C*H*$_2$), 2.03–1.96 (m, 1 H), 1.79–1.72 (m, 1 H), 1.67–1.61 (m, 1 H), 1.55–1.46 (m, 1 H), 1.39–1.33 (m, 1 H), 0.75 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$), 0.07 (s, 9 H, $SiMe_3$); δ (*syn*) = 5.39 (br s, 1 H, C=C*H*Si), 3.98–3.92 (m, 1 H), 3.66–3.60 (m, 1 H), 3.43–3.38 (m, 1 H, C*H*$_2$O), 2.48–2.38 (m, 2 H), 2.29–2.19 (m, 1 H), 2.09–1.70 (m, 4 H), 0.97 (d, *J* = 7.2 Hz, 3 H, $CH_3$), 0.09 (s, 9 H, $SiCH_3$).

$^{13}C$ NMR (150 MHz, $CDCl_3$): δ (*anti*) = 164.7, 117.4, 67.7, 48.1, 37.8, 33.5, 26.1, 24.8, 11.6, –0.3; δ (*syn*) = 163.5, 118.5, 65.7, 50.2, 37.7, 33.7, 27.3, 24.9, 11.1, –0.8.

**Metalative Cyclization and Allylation of Oxetanes; General Procedure**

To a solution of $FeCl_3$ (2.5 mg, 0.015 mmol) and dipimp (5.3 mg, 0.02 mmol) in toluene (1.0 mL) was added *n*-PrMgCl (0.85 mL, 1.3 M in THF, 1.1 mmol) at r.t. The resulting mixture was stirred at ambient temperature for 5 min. A solution of oxetane **6a** (98 mg, 0.5 mmol) in toluene (1.0 mL) was added and the mixture was stirred at 50 °C. Af-

ter ensuring complete consumption of **6a** by TLC analysis, the reaction mixture was added to a mixture of allyl bromide (0.05 mL, 0.6 mmol) and CuCN (4.2 mg, 0.05 mmol) in THF (1 mL). After 6 h at r.t., aq sat. $NH_4Cl$ solution was added and the mixture was extracted with hexane. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered through a pad of Celite and concentrated in vacuo. The crude residue was purified by chromatography on silica gel to afford **9a** (80 mg, 67%) as a pale yellow oil.

**(*E*)-2-{2-[1-(Trimethylsilyl)but-3-en-1-ylidene]cyclopentyl}ethanol (9a)**

IR (neat): 3333, 3077, 2950, 2864, 1824, 1433, 1246 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): δ = 5.81 (ddd, *J* = 5.4, 10.8, 15.6 Hz, 1 H, C*H*=$CH_2$), 4.99–4.92 (m, 2 H, CH=C$H_2$), 3.73–3.61 (m, 2 H, $CH_2CH_2OH$), 2.97 (dd, *J* = 5.4, 16.2 Hz, 1 H, =CC$H_2$CH=$CH_2$), 2.86 (dd, *J* = 5.4, 15.6 Hz, 1 H, =CC$H_2$CH=$CH_2$), 2.83–2.78 (m, 1 H, C*H*C=CH), 2.38–2.32 (m, 2 H, C$H_2$C=CSi), 1.76–1.61 (m, 4 H, C$H_2$), 1.55–1.42 (m, 2 H, C$H_2$), 0.11 (s, 9 H, $SiMe_3$).

$^{13}C$ NMR (150 MHz, $CDCl_3$): δ = 159.9, 138.3, 126.8, 114.3, 61.8, 38.7, 37.5, 36.7, 32.2, 30.6, 23.9, 0.09.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{26}NaOSi$: 261.1651; found: 261.1650.

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## Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561627.

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