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Study on halolactamization-γ-hydroxylation or haloiminolactonization of 2,3-alkadienamides

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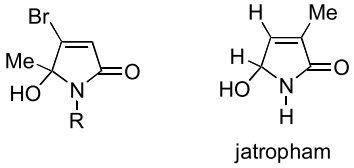
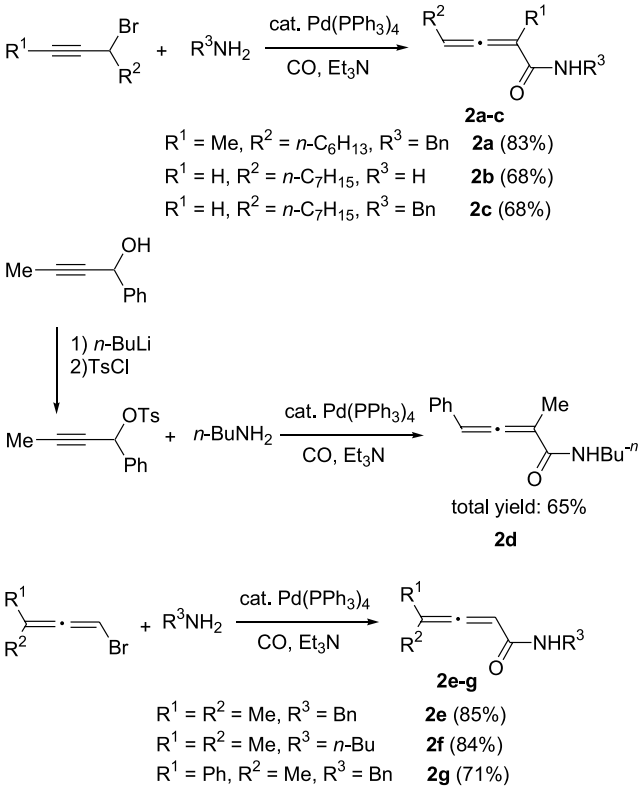
Abstract—The reactions of 4-mono- or 4-unsubstituted 2,3-alkadienamides with CuX_2 afforded 5-hydroxypyrrol-2(5*H*)-ones via the sequential lactamization and γ-hydroxylation process in aqueous THF while those of 4,4-disubstituted 2,3-alkadienamides with CuX_2 in THF afforded iminolactones in high yields. Iodoiminolactonization and iodolactamization/γ-hydroxylation were achieved by the corresponding reaction with I_2 in THF at rt. The structures of the products depend on the steric hindrance at the 4-position of the starting allenamides. Relatively electron-rich allenes afforded the corresponding products in much higher yields under milder reaction conditions implying the intramolecular electrophilic nature of the cyclization reaction.

1. Introduction

Allenes are a class of compounds with interesting chemical and physical properties due to the presence of the unique cumulated diene unit.[1,2] For a long period of time or even now they are still considered unstable, which limits the study of their chemistry as compared to the chemistry of alkenes and alkynes.[1,2] During the last 5–10 years, much attention has been paid to the chemistry of allenes probably due to the observed fact during research that they are not so unstable and showed nice reactivities and selectivity in some cases.[3–5] We have developed some methodologies based on the ionic addition of allenes.[6] We have also develop the transition metal-mediated cyclization of allenes with an α-functionality, which provides efficient and diverse routes for the selective synthesis of aminoalcohols, carbocycles, and heterocycles.[7] Lactams especially 5-membered lactams are a class of important heterocycles, which exhibit interesting biological activities. Thus, we turned our attention to the chemistry of 2,3-allenamides, which may provide new methods for the synthesis of pyrrol-2(5*H*)-ones (Scheme 1).[1,8] In a preliminary communication,[9] we have shown that the reaction of 2,3-allenamides with CuX_2



Scheme 1.



Scheme 2.

Keywords: γ-Hydroxylation; Iminolactones; Allenes.
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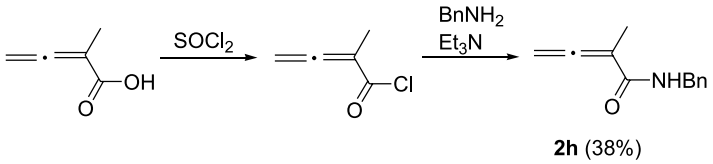


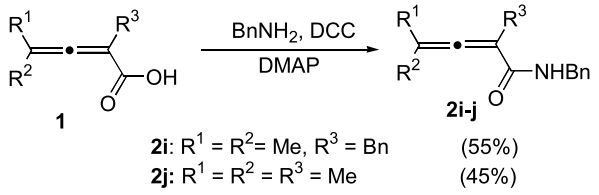
Scheme 3.

(X=Br, Cl) afforded 5-hydroxypyrrol-2(5*H*)-ones in THF–H_2O. In this paper we wish to disclose the details of this reaction.

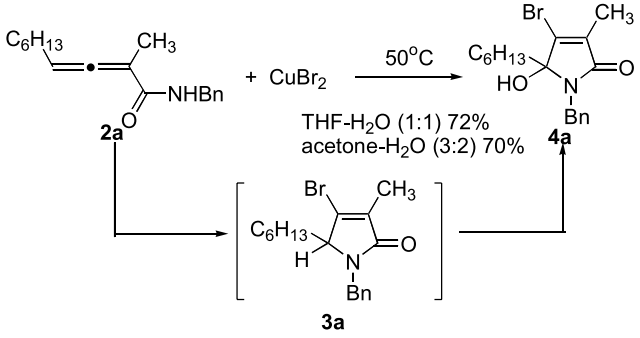
2. Results and discussion

2.1. Synthesis of starting materials

2,3-Allenamides **2a–g** were prepared by the $Pd(PPh_3)_4$-catalyzed carbonylation of 1,2-allenylic bromides or propargylic bromides/tosylate and amines in the presence of Et_3N and CO (Scheme 2).[10,11]



Scheme 4.



Scheme 5.

N-Benzyl 2-methyl-2,3-butadienamide **2h** was prepared by the reaction of 2-methyl-2,3-butadienoyl chloride with $BnNH_2$ (Scheme 3).[12]

2,3-Allenamides **2i–j** were synthesized by the DMAP-catalyzed amidation of the related carboxylic acids with amines (Scheme 4).[10]

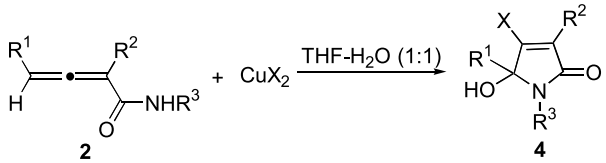
2.2. Cyclization of 2,3-allenamides with $CuBr_2$

Following our study of 2,3-allenoic acids with $CuBr_2$,[13,14] we studied the halolactamization of *N*-benzyl 2-methyl-deca-2,3-dienamide **2a** with 1.1 equiv of $CuBr_2$. After some screening, it was observed that the solvent is important. The reaction proceeded in aqueous THF or acetone to afford 5-hydroxypyrrol-2(5*H*)-one **4a** in ~70% yield. Obviously, a 5-hydoxylation reaction occurred to the initially formed pyrrol-2(5*H*)-one **3a** (Scheme 5).

Some typical results are summarized in Table 1. From the results in Table 1, it should be noted that (1) R^1 can be alkyl or aryl; R^2 can be H or alkyl; R^3 can be H, benzyl, or alkyl, (2) the reaction with $CuBr_2$ is usually faster than that with $CuCl_2$, (3) the yields are from moderate to good.

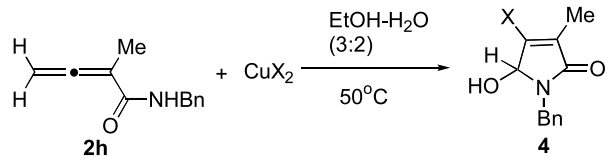
The reaction of $CuBr_2$ and a substrate without a substituent at 4-position, i.e. **2h**, afforded the corresponding products **4h** in THF/H_2O (1:1) in only 48% yield. Thus, optimization of the reaction condition was conducted. Finally EtOH–H_2O (3:2) was found to be a better reaction medium for this transformation with the results shown in Scheme 6.

Table 1. Halolactamization–hydroxylation reaction of 2,3-allenamides with CuX_2

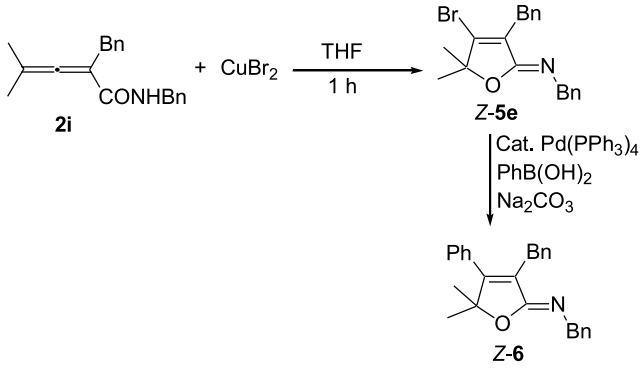


Entry	2			CuX_2, X (equiv)	Temperature (°C)	Time (h)	Yield of **4** (%)[a]
	R^1	R^2	R^3				
1	*n*-C_6H_{13}	Me	Bn (**2a**)	Br (1.1)	50	18.5	72 (**4a**)
2	*n*-C_6H_{13}	Me	Bn (**2a**)	Cl (1.1)	Reflux	21	57 (**4b**)
3	*n*-C_7H_{15}	H	H (**2b**)	Br (1.1)	50	22	69 (**4c**)
4	*n*-C_7H_{15}	H	Bn (**2c**)	Br (1.1)	50	32	78 (**4d**)
5	*n*-C_7H_{15}	H	Bn (**2c**)	Cl (2)	50	36	78 (**4e**)
6	Ph	Me	*n*-C_4H_9 (**2d**)	Br (2)	Reflux	24	94 (**4f**)
7	Ph	Me	*n*-C_4H_9 (**2d**)	Cl (4)	Reflux	60	71 (**4g**)

[a] Isolated yields.



Scheme 6.



Scheme 7.

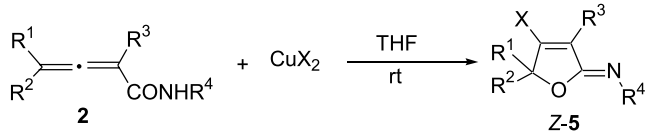
Furthermore, when we ran this reaction with 4,4-disubstituted 2,3-alkadienamides, instead of 5-hydroxypyrrol-2(5*H*)-one, iminolactones **5**[15] were formed smoothly in THF at rt in fairly high yield. In the preliminary communication,[9] we assigned it to pyrrol-2(5*H*)-ones, which was proven to be a wrong structure based on the further ^{13}C NMR analysis and its conversion to the known derivative **6**[16] by the related Pd-catalyzed coupling reaction (Scheme 7). It should be noted that only *Z*-**5e** was obtained in this reaction. The configuration of C=N bond in others products **5** was tentatively assigned based on this coupling result. From the typical results shown in Table 2, it can be concluded that the reaction was very fast (completed within 2 h) and the scope is broad.

2.3. Iodoiminolactonization/lactamization–hydroxylation of 2,3-alkadienamides

The reaction of 4,4-disubstituted 2,3-alkadienamides with I_2 in THF at rt also proceeded to produce 4-iodoiminolactones *Z*-**5k–n** in good yields (Table 3).

The reaction of 4-mono or 4-unsubstituted 2,3-alkadienamides with I_2 in THF followed by oxidation with O_2 at rt afforded 5-hydroxypyrrol-2(5*H*)-ones **4j–k** (Scheme 8).

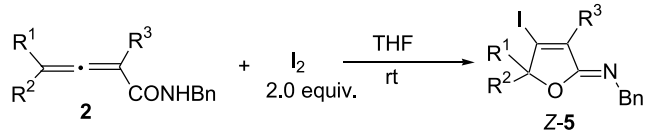
Table 2. Synthesis of iminolactones via the reaction of 4,4-disubstituted 2,3-alkadienamides with CuX_2



Entry	2				CuX_2		Time (h)	Yield of **5** (%)[a] (*Z*-**5**:*E*-**5**)[b]
	R^1	R^2	R^3	R^4	X=	(equiv)		
1	Me	Me	H	Bn (**2e**)	Br	1.1	1	85 (**5a**) (>97:3)
2	Me	Me	H	Bn (**2e**)	Cl	1.1	1	85 (**5b**) (>98:2)
3	Ph	Me	H	Bn (**2g**)	Br	3	1	99 (**5c**) (>99:1)
4	Ph	Me	H	Bn (**2g**)	Cl	3	2	98 (**5d**) (96:4)
5	Me	Me	Bn	Bn (**2i**)	Br	3	1	94 (**5e**) (100:0)
6	Me	Me	Bn	Bn (**2i**)	Cl	3	1	97 (**5f**) (100:0)
7	Me	Me	H	*n*-Bu (**2f**)	Br	1.1	1	78 (**5g**) (>98:2)
8	Me	Me	H	*n*-Bu (**2f**)	Cl	1.1	1	68 (**5h**) (>96:4)
9	Me	Me	Me	Bn (**2j**)	Br	1.1	2	82 (**5i**) (100:0)
10	Me	Me	Me	Bn (**2j**)	Cl	1.1	1	95 (**5j**) (100:0)

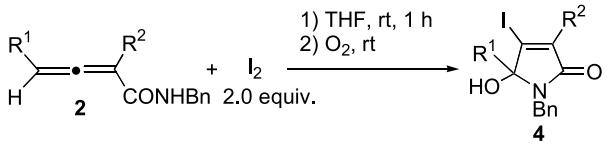
[a] Isolated yield.
[b] The ratios were determined by ^1H NMR spectra.

Table 3. Synthesis of 4-iodoiminolactones via the reaction of I_2 with 4,4-disubstituted 2,3-alkadienamides



Entry	2			Time (h)	Yield of **5** (%)[a] (*Z*-**5**:*E*-**5**)[b]
	R^1	R^2	R^3		
1	Me	Me	H (**2e**)	3	75 (**5k**) (95:5)
2	Me	Ph	H (**2g**)	26	84 (**5l**) (96:4)
3	Me	Me	Bn (**2i**)	16	92 (**5m**) (100:0)
4	Me	Me	Me (**2j**)	16	99 (**5n**) (100:0)

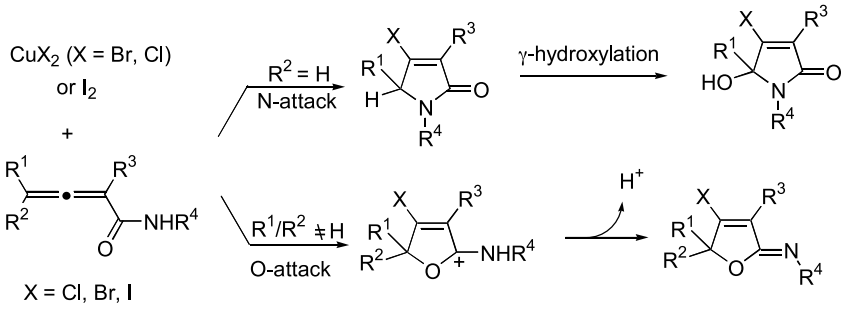
[a] Isolated yield.
[b] The ratios were determined by ^1H NMR spectra.



R^1	R^2	Time (h)	Yield (%)
n-C_7H_{15}	H (**2b**)	24	89 (**4j**)
H	Me (**2h**)	42	58 (**4k**)

Scheme 8.

It is quite obvious that the reaction is electrophilic in nature since the relatively electron richer amides provided the corresponding products in generally higher yields at a lower temperature (compare the results of Tables 1 and 2). Both the nitrogen and the carbonyl oxygen in starting materials may act as the intramolecular nucleophile. The selectivity clearly depends on the steric hindrance of 4-position of the amides, i.e. with 4-mono or 4-non-substituted 2,3-alkadienamides, pyrrol-2(5*H*)-ones were formed highly selectively, which was followed by γ-hydroxylation affording 5-hydroxypyrrol-2(5*H*)-ones while the reaction of 4,4-disubstituted 2,3-alkadienamides afforded iminolactones (Scheme 9).



Scheme 9.

In conclusion, we have developed the haloiminolactonization and halolactamization–hydroxylation reaction of 2,3-allenanimdes providing an efficient route for the highly selective synthesis of iminolactones or 5-hydroxypyrrol-2(5*H*)-ones, respectively, depending on the steric hindrance of 4-position of 2,3-allenamides. Further studies in this area are being carried out in our laboratory.

3. Experimental

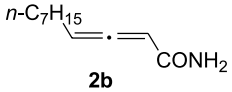
3.1. Synthesis of starting materials

The known compounds **2e**–**2g**, and **2i**–**2j** were prepared according to the reported procedure.[10]

3.1.1. *N*-Benzyl 2-methyl-2,3-decadienamide (2a). *Typical procedure A*. A stainless steel autoclave (250 mL) fitted with a glass reactor with a stirring bar inside was charged with THF (20 mL), 3-bromo-2-decyne (1.09 g, 5 mmol), $BnNH_2$ (0.6 mL, 5.5 mmol), Et_3N (0.77 mL, 5.5 mmol), and $Pd(PPh_3)_4$ (64 mg, 0.05 mmol) sequentially. The autoclave was charged with CO with a pressure of 18 atm. After the mixture was stirred for 1 h at rt, CO was released. The reaction was quenched with water followed by the addition of CH_2Cl_2. After separation, the organic phase was washed sequentially with 1 N HCl and brine. After evaporation, the residue was purified by flash chromatography on silica gel to afford 1.12 g (83%) of allenamide **2a**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 6.32 (bs, 1H), 5.52–5.45 (m, 1H), 4.48 (d, J=6 Hz, 2H), 2.08 (q, J=7 Hz, 2H), 1.91 (d, J=2.7 Hz, 3H), 1.45–1.18 (m, 8H), 0.87 (t, J=6.6 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 205.0, 166.8, 138.5, 128.5, 127.4, 127.2, 98.1, 96.0, 43.6, 31.4, 28.7, 28.7, 28.3, 22.5, 14.4, 14.0; MS m/z 271 (M^+, 19.43), 91 (100); IR (neat) 3347, 1955, 1655 cm^{-1}; HRMS cacld for $C_{18}H_{25}NO$ 271.1936; found 271.1949.

The following compounds **2b**–**2c** were prepared according to Typical procedures A.

3.1.2. 2,3-Undecadienamide (2b).



2b

The reaction of 3-bromo-1-decyne (1.02 g, 4.7 mmol), $NH_3\cdot H_2O$ (0.4 mL, 5.2 mmol), Et_3N (0.72 mL, 5.2 mmol), and $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) in THF (25 mL) at rt for 2 h afforded 0.58 g (68% yield) of **2b**; white solid; mp 88–99 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (bs, 1H), 5.67–5.52 (m, 3H), 2.18–2.10 (m, 2H), 1.55–1.20 (m, 10H), 0.87 (t, J=6.6 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 208.4, 168.2, 96.5, 90.7, 31.6, 28.9, 28.9, 28.7, 27.7, 22.5, 13.9; MS m/z 180 (M^+-1, 1.46), 96 (100); IR (KBr) 3339, 3176, 1962, 1658 cm^{-1}. Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.82; H, 10.64; N, 7.52.

3.1.3. *N*-Benzyl 2,3-undecadienamide (2c). The reaction of 3-bromo-1-decyne (1.09 g, 5.0 mmol), $BnNH_2$ (0.6 mL, 5.5 mmol), Et_3N (0.77 mL, 5.5 mmol), and $Pd(PPh_3)_4$ (64 mg, 0.05 mmol) in THF (20 mL) at rt for 1.5 h afforded 0.92 g (68% yield) of **2c**; white solid; mp 88–90 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.20 (m, 5H), 6.22 (bs, 1H), 5.63–5.57 (m, 2H), 4.47 (d, J=5.7 Hz, 2H), 2.15–2.06 (m, 2H), 1.50–1.20 (m, 10H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 207.5, 165.1, 138.3, 128.6, 127.5, 127.3, 96.9, 91.2, 43.5, 31.6, 29.0, 28.9,

28.7, 27.8, 22.5, 14.0; MS *m/z* 271 (M^+, 22.04), 186 (100); IR (KBr) 3279, 1961, 1629 cm^{-1}. Anal. Calcd for $C_{18}H_{25}NO$: C, 79.66; H, 9.28; N, 5.16. Found: C, 79.67; H, 9.23; N, 4.94.

3.1.4. *N*-Benzyl 4-phenyl-2,3-pentadienamide (2g). The reaction of 1-bromo-3-phenyl-1,2-butadiene (0.87 g, 4.1 mmol), $BnNH_2$ (0.5 mL, 4.5 mmol), Et_3N (0.65 mL, 4.5 mmol), and $Pd(PPh_3)_4$ (49 mg, 0.04 mmol) in THF (25 mL) at rt for 1.5 h afforded 0.77 g (71% yield) of **2g**; white solid; mp 139–140 °C (Et_2O–CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.26 (m, 10H), 6.04 (bs, 1H), 5.98 (q, $J=2.7$ Hz, 1H), 4.59–4.43 (m, 2H), 2.21 (d, $J=2.7$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 208.6, 164.5, 138.2, 134.0, 128.5, 128.5, 127.8, 127.4, 127.2, 125.9, 106.4, 92.9, 43.4, 16.3; MS *m/z* 263 (M^+, 19.88), 91 (100); IR (KBr) 3273, 1947, 1639 cm^{-1}. Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.03; H, 6.26; N, 5.12.

3.1.5. *N*-Butyl 2-methyl-4-phenyl-2,3-butadienamide (2d). In a dry flask containing 1-phenyl-2-butyn-1-ol (580 mg, 4.0 mmol) in 40 mL THF was added *n*-BuLi (2.5 mL (1.6 M in hexane), 4.0 mmol) dropwise at −60 °C. After stirring for 30 min at −60 °C, TsCl (762 mg, 4.0 mmol) was added. The mixture was stirred for 15 min at −60 °C and then for 2 h at rt. Then, *n*-$BuNH_2$ (0.35 mL, 4.0 mmol), Et_3N (0.56 mL, 4.0 mmol), and $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) were added sequentially at −78 °C. The autoclave was charged with CO with a pressure of 25 atm. After the mixture was stirred for 1 h at rt, CO was released. The reaction was quenched with water followed by the addition of CH_2Cl_2. After separation, the organic phase was washed sequentially with 1 N HCl and brine. After evaporation, the residue was purified by flash chromatography on silica gel to afford 0.59 g (65%) of **2d**: oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.20 (m, 5H), 6.48 (q, $J=3$ Hz, 1H), 6.07 (bs, 1H), 3.33–3.14 (m, 2H), 1.99 (d, $J=3$ Hz, 3H), 1.48–1.39 (m, 2H), 1.33–1.21 (m, 2H), 0.87 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 206.6, 165.3, 132.3, 128.7, 127.7, 126.9, 102.0, 98.4, 39.4, 31.5, 19.8, 14.2, 13.5; MS *m/z* 229 (M^+, 10.01), 84 (100); IR (neat) 3333, 1943, 1651 cm^{-1}; HRMS cacld for $C_{15}H_{19}NO$ 229.14666, found 229.14891.

3.1.6. *N*-Benzyl 2-methyl-2,3-butadienamide (2h). In a dry flask containing 2-methylbuta-2,3-dienoic acid (922 mg, 9.4 mmol) was added $SOCl_2$ (1.4 mL, 18.8 mmol). After stirring for 30 min at rt, the excess $SOCl_2$ was removed under reduced pressure to afford 2-methylbuta-2,3-dienoyl chloride, which was dissolved in dry ether (30 mL) for conversion in the next step.

To a mixture of benzylamine (1.1 mL, 10.3 mmol) and Et_3N (1.4 mL, 10.3 mmol) in dry ether (30 mL) was added 2-methyl buta-2,3-dienoyl chloride in dry ether dropwise at rt. After the mixture was stirred overnight, the reaction was quenched with water followed by the addition of ether. After separation, the water phase was extracted twice with ether and the combined organic layer was dried over $MgSO_4$. After evaporation, the residue was purified by flash chromatography on silica gel to afford 655 mg (38%) of **2h** white solid; mp 76–78 °C (*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.26 (m, 5H), 6.30 (bs, 1H), 5.09 (q, $J=3.0$ Hz, 2H), 4.48 (d, $J=6.0$ Hz, 2H), 1.92 (t, $J=3.0$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 209.7, 166.1, 138.4, 128.6, 127.6, 127.3, 97.6, 79.7, 43.7, 13.9; MS *m/z* 187 (M^+, 18.39), 91 (100); IR (KBr) 3422, 1944, 1641 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.91; H, 7.13; N, 7.35.

3.2. Halolactamization-γ-hydroxylation of 2,3-allenamides with CuX_2. General procedure B

A solution of 2,3-allenamide (**2**) (0.5 mmol) and CuX_2 (1.1–4 equiv) in THF/H_2O (1:1) (or enthanol/H_2O (3:2)) (8 mL) was stirred at 50 °C. When the reaction was complete, the mixture was then quenched with saturated NH_4Cl and extracted five times with chloroform. The organic layer was combined and dried over Na_2SO_4. After evaporation, the residue was purified via flash chromatography on silica gel to afford **4a**–**g**. All of the solid products were recrystallized from petroleum ether.

3.2.1. 4-Bromo-1-benzyl-5-*n*-hexyl-5-hydroxy-3-methyl-pyrrol-2(5*H*)-one (4a). The reaction of **1a** (75 mg, 0.28 mmol) and $CuBr_2$ (68 mg, 0.30 mmol) in THF (4 mL) and H_2O (4 mL) at 50 °C for 18.5 h afforded 73 mg (72% yield) of **2a**: white solid; mp 119–119.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43–7.35 (m, 2H), 7.35–7.25 (m, 3H), 4.65 (d, $J=15.00$ Hz, 1H), 4.42 (d, $J=15.00$ Hz, 1H), 2.98 (s, 1H), 1.92 (s, 32H), 2.10–1.59 (m, 2H), 1.12–0.45 (m, 8H), 0.79 (t, $J=7.14$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 168.8, 139.2, 137.9, 134.1, 128.8, 128.5, 127.5, 92.5, 42.7, 34.3, 31.4, 28.5, 22.6, 22.4, 14.0, 10.5; MS *m/z* 368 ($M^+(^{81}Br)+1$, 22.17), 366 ($M^+(^{79}Br)+1$, 23.76), 91 (100); IR (KBr) 3303, 1677, 1072, 1026 cm^{-1}. Anal. Calcd for $C_{18}H_{24}BrNO_2$: C 59.02, H 6.60, N 3.82. Found: C 59.15, H 6.74, N 3.82.

The compounds **4b**–**4i**[9] were prepared according to Typical procedure B in the text, and the data of these compounds can be found in the supporting information of Ref. 2.

3.3. Haloiminolactonization of 2,3-alkadienamide. General procedure C

A solution of 2,3-allenamide (0.5 mmol) and CuX_2 (1.1–3 equiv) in THF (5 mL) was stirred at rt. When the reaction was complete, 10 mL of Et_2O and 10 mL of saturated NH_4Cl were added. The mixture was stirred for 5 min and extracted three times with Et_2O. The organic layer was combined and dried over Na_2SO_4. After evaporation, the residue was purified via flash chromatography on silica gel to afford **5a**–**5j**.

3.3.1. *Z*-2-Benzylimino-4-bromo-5,5-dimethyl-2,5-dihydrofuran (5a). The reaction of **2e** (112 mg, 0.56 mmol) and $CuBr_2$ (137 mg, 0.61 mmol) in THF (5 mL) at rt for 1 h afforded 132 mg (85% yield) of **5a** (*Z*-**5a**:*E*-**5a** > 97:3); light yellow oil; ^1H NMR (300 MHz, $CDCl_3$) *Z*-**5a**: δ 7.37–7.22 (m, 5H), 6.25 (s, 1H), 4.51 (s, 2H), 1.51 (s, 6H). The following data were discernible for the *E* isomer, *E*-**5a**: 6.54 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 160.5, 144.3, 140.5, 128.3, 127.8, 126.4, 123.7, 90.8, 50.8, 25.4; MS *m/z* 281 ($M^+(^{81}Br)$, 30.18), 279 ($M^+(^{79}Br)$, 32.65), 91 (100); IR

(neat) 1687 cm^{-1}; HRMS cacld for $C_{13}H_{14}^{79}BrNO$ 279.0259; found 279.0264.

3.3.2. *Z*-2-Benzylimino-4-chloro-5,5-dimethyl-2,5-dihydrofuran (5b). The reaction of **2e** (119 mg, 0.59 mmol) and $CuCl_2 \cdot 2H_2O$ (111 mg, 0.65 mmol) in THF (5 mL) at rt for 1 h afforded 119 mg (85% yield) of **5b** (*Z*-**5b**:*E*-**5b**> 98:2), colorless oil; ^1H NMR (300 MHz, $CDCl_3$) *Z*-**5b**: δ 7.37–7.25 (m, 5H), 6.09 (s, 1H), 4.53 (s, 2H), 1.51 (s, 6H). The following data were discernible for the *E* isomer, *E*-**5b**: δ 6.38 (s, 1H), 4.50 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.6, 154.1, 140.5, 128.3, 127.8, 126.4, 119.2, 89.5, 50.8, 25.0; MS *m/z* 237 ($M^+(^{37}Cl)$, 12.82), 235 ($M^+(^{35}Cl)$, 38.02), 91 (100); IR (neat) 1689, 1631 cm^{-1}; HRMS cacld for $C_{13}H_{14}^{35}ClNO$ 235.0764; found 235.0757.

3.3.3. *Z*-2-Benzylimino-4-bromo-5-phenyl-5-methyl-2,5-dihydrofuran (5c). The reaction of **2g** (67 mg, 0.25 mmol) and $CuBr_2$ (168 mg, 0.75 mmol) in THF (5 mL) at rt for 1 h afforded 86 mg (99% yield) of **5c** (*Z*-**5c**:*E*-**5c**>99:1); light yellow oil; ^1H NMR (300 MHz, $CDCl_3$) *Z*-**5c**: δ 7.43–7.26 (m, 10H), 6.38 (s, 1H), 4.63 (s, 2H), 1.95 (s, 3H). The following data were discernible for the *E* isomer, *E*-**5c**: δ 6.63 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 160.7, 144.6, 140.3, 138.4, 128.6, 128.5, 128.3, 127.9, 126.5, 125.5, 123.8, 92.5, 51.1, 23.8; MS *m/z* 344 ($M^+(^{81}Br)+1$, 5.47), 342 ($M^+(^{79}Br)+1$, 6.58), 105 (100); IR (neat) 1687, 1602 cm^{-1}; HRMS cacld for $C_{18}H_{16}^{79}BrNO$ 341.04153; found 341.04516.

3.3.4. *Z*-2-Benzylimino-4-chloro-5-phenyl-5-methyl-2,5-dihydrofuran (5d). The reaction of **2g** (85 mg, 0.32 mmol) and $CuCl_2 \cdot 2H_2O$ (165 mg, 0.97 mmol) in THF (5 mL) at rt for 2 h afforded 94 mg (98% yield) of **5d** (*Z*-**5d**:*E*-**5d**= 96:4); light yellow oil; ^1H NMR (300 MHz, $CDCl_3$) *Z*-**5d**: δ 7.34–7.20 (m, 5H), 6.14 (s, 1H), 4.57 (s, 2H), 1.87 (s, 3H). The following data were discernible for the *E* isomer, *E*-**5d**: δ 6.39 (s, 1H), 4.53 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.7, 154.0, 140.4, 138.4, 128.6, 128.5, 128.3, 127.8, 126.5, 125.3, 119.3, 91.2, 51.0, 23.6; MS *m/z* 299 ($M^+(^{37}Cl)$, 0.79), 297 ($M^+(^{35}Cl)$, 1.92), 105 (100); IR (neat) 1687, 1612 cm^{-1}; HRMS cacld for $C_{18}H_{16}^{35}ClNO$ 297.0920; found 297.0932.

3.3.5. *Z*-2-Benzylimino-3-benzyl-4-bromo-5,5-dimethyl-2,5-dihydrofuran (5e). The reaction of **2i** (62 mg, 0.21 mmol) and $CuBr_2$ (143 mg, 0.61 mmol) in THF (4 mL) at rt for 1 h afforded 74 mg (94% yield) of *Z*-**5e**; yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48–7.22 (m, 10H), 4.51 (s, 2H), 3.70 (s, 2H), 1.48 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.9, 141.0, 140.0, 137.7, 132.5, 128.8, 128.3, 128.1, 127.3, 126.3, 126.1, 88.4, 50.2, 31.1, 25.7; MS *m/z* 371 ($M^+(^{81}Br)$, 52.32), 369 ($M^+(^{79}Br)$, 54.98), 91 (100); IR (neat) 1682 cm^{-1}. Anal. Calcd for $C_{20}H_{20}BrNO$: C 64.87, H 5.44, N 3.78. Found: C 64.75, H 5.50, N 3.97.

3.3.6. *Z*-2-Benzylimino-3-benzyl-4-chloro-5,5-dimethyl-2,5-dihydrofuran (5f). The reaction of **2i** (48 mg, 0.16 mmol) and $CuCl_2 \cdot 2H_2O$ (84 mg, 0.45 mmol) in THF (4 mL) at rt for 1 h afforded 52 mg (97% yield) of *Z*-**5f**; yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43–7.24 (m, 10H), 4.64 (s, 2H), 3.75 (s, 2H), 1.53 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.5, 148.2, 141.0, 137.8, 128.8, 128.8, 128.3, 128.1, 127.3, 126.3, 126.1, 87.3, 50.2, 29.8, 25.2; MS *m/z* 327 ($M^+(^{37}Cl)$, 36.93), 325 ($M^+(^{35}Cl)$, 84.57), 91 (100); IR (neat) 1683 cm^{-1}. Anal. Calcd for $C_{20}H_{20}ClNO$: C 73.72, H 6.19, N 4.30. Found: C 73.36, H 6.09, N 4.20.

3.3.7. *Z*-2-*n*-Butylimino-4-bromo-5,5-dimethyl-2,5-dihydrofuran (5g). The reaction of **2f** (119 mg, 0.71 mmol) and $CuBr_2$ (175 mg, 0.78 mmol) in THF (5 mL) at rt for 1 h afforded 137 mg (78% yield) of **5g** (*Z*-**5g**:*E*-**5g**>98:2); light yellow oil; ^1H NMR (300 MHz, $CDCl_3$) *Z*-**5g**: δ 6.14 (s, 1H), 3.25 (t, J=6.9 Hz, 2H), 1.56–1.51 (m, 2H), 1.44 (s, 6H), 1.38–1.30 (m, 2H), 0.90 (t, J=7.4 Hz, 3H). The following data were discernible for the *E* isomer, *E*-**5g**: δ 6.42 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.7, 143.8, 123.7, 90.4, 46.4, 32.9, 25.4, 20.5, 13.8; MS *m/z* 248 ($M^+(^{81}Br)+1$, 23.52), 246 ($M^+(^{79}Br)+1$, 27.67), 160 (100); IR (neat) 1692, 1604 cm^{-1}; HRMS cacld for $C_{10}H_{16}^{79}BrNO$ 245.0415; found 245.0370.

3.3.8. *Z*-2-*n*-Butylimino-4-chloro-5,5-dimethyl-2,5-dihydrofuran (5h). The reaction of **2f** (126 mg, 0.75 mmol) and $CuCl_2 \cdot 2H_2O$ (142 mg, 0.83 mmol) in THF (6 mL) at rt for 1 h afforded 103 mg (68% yield) of **5h** (*Z*-**5h**:*E*-**5h**>96:4); colorless oil; ^1H NMR (300 MHz, $CDCl_3$) *Z*-**5h**: δ 5.96 (s, 1H), 3.24 (t, J=7.1 Hz, 2H), 1.52–1.46 (m, 2H), 1.41 (s, 6H), 1.34–1.27 (m, 2H), 0.86 (t, J=7.2 Hz, 3H). The following data were discernible for the *E* isomer, *E*-**5h**: δ 6.23 (s, 1H), 3.19 (t, J=7.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.8, 153.5, 119.1, 88.9, 46.3, 32.9, 24.9, 20.5, 13.8; MS *m/z* 203 ($M^+(^{37}Cl)$, 4.27), 201 ($M^+(^{35}Cl)$, 12.79), 130 (100); IR (neat) 1694, 1614 cm^{-1}; HRMS cacld for $C_{10}H_{16}^{35}ClNO$ 201.09204; found 201.08779.

3.3.9. *Z*-2-Benzylimino-3-methyl-4-bromo-5,5-dimethyl-2,5-dihydrofuran (5i). The reaction of **2i** (96 mg, 0.45 mmol) and $CuBr_2$ (110 mg, 0.49 mmol) in THF (5 mL) at rt for 2 h afforded 108 mg (82% yield) of *Z*-**5i**; light yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41–7.22 (m, 5H), 4.57 (s, 2H), 1.91 (s, 3H), 1.47 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.0, 140.8, 139.1, 129.7, 128.2, 127.6, 126.3, 88.4, 50.5, 25.6, 10.9; MS *m/z* 294 ($M^+(^{81}Br)-1$, 37.11), 292 ($M^+(^{79}Br)-1$, 36.26), 105 (100); IR (neat) 1691, 1655 cm^{-1}; HRMS cacld for $C_{13}H_{13}^{79}BrNO$ (M^+-CH_3) 278.0179; found 278.0177.

3.3.10. *Z*-2-Benzylimino-3-methyl-4-chloro-5,5-dimethyl-2,5-dihydrofuran (5j). The reaction of **2j** (105 mg, 0.49 mmol) and $CuCl_2 \cdot 2H_2O$ (92 mg, 0.54 mmol) in THF (5 mL) at rt for 1 h afforded 116 mg (95% yield) of *Z*-**5j**; light yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.23 (m, 5H), 4.60 (s, 2H), 1.92 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 160.7, 147.4, 140.8, 128.1, 127.6, 126.3, 125.8, 87.3, 50.4, 25.1, 9.3; MS *m/z* 251 ($M^+(^{37}Cl)$, 30.49), 249 ($M^+(^{35}Cl)$, 58.32), 91 (100); IR (neat) 1693,1664 cm^{-1}; HRMS cacld for $C_{14}H_{16}^{35}ClNO$ 249.0920; found 249.0932.

3.4. Iodoiminolactonization of 2,3-alkadienamide. General procedure D

A solution of 2,3-allenamide (0.5 mmol) and I_2 (2 equiv) in

THF (4 mL) was stirred at rt. When the reaction was complete, 10 mL of Et_2O was added, and then a solution of $Na_2S_2O_3$ was added to remove the excess I_2. After extraction with Et_2O, drying over Na_2SO_4, and evaporation, the residue was purified via flash chromatography on silica gel to afford **5k–5n**.

3.4.1. *Z*-2-Benzylimino-4-iodo-5,5-dimethyl-2,5-dihydrofuran (5k). The reaction of **2e** (106 mg, 0.53 mmol) and I_2 (268 mg, 1.06 mmol) in THF (4 mL) at rt for 3 h afforded 129 mg (75% yield) of **5k** (*Z*-**5k**:*E*-**5k**=95:5); light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) *Z*-**5k**: δ 7.37–7.20 (m, 5H), 6.43 (s, 1H), 4.50 (s, 2H), 1.47 (s, 6H). The following data were discernible for the *E* isomer, *E*-**5k**: 6.73 (s, 1H), 4.49 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.03, 140.37, 131.86, 128.19, 127.70, 126.35, 119.54, 92.67, 50.75, 25.92; MS *m*/*z* 327 (M^+, 42.23), 95 (100); IR (neat) 1758, 1681 cm^{-1}; HRMS cacld for $C_{13}H_{14}INO$ 327.0120; found 327.0128.

3.4.2. *Z*-2-Benzylimino-4-iodo-5-methyl-5-phenyl-2,5-dihydrofuran (5l). The reaction of **2g** (47 mg, 0.18 mmol) and I_2 (91 mg, 0.36 mmol) in THF (5 mL) at rt for 26 h afforded 59 mg (84% yield) of **5l** (*Z*-**5l**:*E*-**5l**=96:4); light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.22 (m, 10H), 6.56 (s, 1H), 4.60 (s, 2H), 1.91 (s, 3H). The following data were discernible for the *E* isomer, *E*-**5l**: δ 6.84 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.4, 140.3, 138.6, 131.8, 128.6, 128.5, 128.3, 127.9, 126.5, 125.8, 120.7, 94.5, 51.1, 24.2; MS *m*/*z* 389 (M^+, 5.86), 129 (100); IR (neat) 1680 cm^{-1}; HRMS cacld for $C_{18}H_{16}INO$ 389.0277; found 389.0318.

3.4.3. *Z*-2-Benzylimino-3-benzyl-4-iodo-5,5-dimethyl-2,5-dihydrofuran (5m). The reaction of **2i** (78 mg, 0.27 mmol) and I_2 (136 mg, 0.54 mmol) in THF (5 mL) at rt for 16 h afforded 103 mg (92% yield) of *Z*-**5m**; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.26 (m, 10H), 4.63 (s, 2H), 3.77 (s, 2H), 1.50 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 160.5, 141.0, 139.3, 137.7, 128.9, 128.2, 128.1, 127.3, 126.3, 126.1, 118.4, 89.8, 50.3, 33.4, 26.3; MS *m*/*z* 417 (M^+, 25.25), 91 (100); IR (neat) 1681, 1629 cm^{-1}; HRMS cacld for $C_{20}H_{20}INO$ 417.0590; found 417.0569.

3.4.4. *Z*-2-Benzylimino-3-methyl-4-iodo-5,5-dimethyl-2,5-dihydrofuran (5n). The reaction of **2j** (21 mg, 0.10 mmol) and I_2 (50 mg, 0.20 mmol) in THF (3 mL) at rt for 16 h afforded 33 mg (99% yield) of *Z*-**5n**; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.21 (m, 5H), 4.55 (s, 2H), 1.94 (s, 3H), 1.45 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.5, 140.8, 136.7, 128.2, 127.7, 126.3, 117.3, 89.7, 50.6, 26.3, 13.8; MS *m*/*z* 341 (M^+, 43.86), 81 (100); IR (neat) 1686, 1639 cm^{-1}; HRMS cacld for $C_{14}H_{16}INO$ 341.0277; found 341.0253.

3.5. Iodolactamization-γ-hydroxylation of 2,3-allenamides. General procedure E

A solution of 2,3-allenamide (0.5 mmol) and I_2 (2 equiv) in THF (4 mL) was stirred at rt for 1 h, then 1 atm of O_2 was charged. When the reaction was complete, 10 mL of Et_2O was added, and then a solution of $Na_2S_2O_3$ was added to remove the excess I_2. After extraction with Et_2O, drying over Na_2SO_4, and evaporation, the residue was purified via flash chromatography on silica gel to afford **4j–k**.

3.5.1. 1-Benzyl-5-hydroxy-5-heptyl-4-iodopyrrol-2(5*H*)-one (4j). The reaction of **2b** (63 mg, 0.23 mmol) and I_2 (118 mg, 0.46 mmol) in THF (5 mL) at rt for 24 h afforded 85 mg (89% yield) of **4j**: light yellow solid; mp 106–108 °C (*n*-hexane–Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.19 (m, 5H), 6.52 (s, 1H), 4.58 (d, J=15 Hz, 1H), 4.42 (d, J=15 Hz, 1H), 2.78 (s, 1H), 1.76–1.58 (m, 2H), 1.19–0.45 (m, 10H), 0.79 (t, J=7.4 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 169.0, 137.6, 135.3, 128.8, 128.4, 127.5, 123.1, 95.0, 42.8, 34.8, 31.5, 28.8, 28.7, 22.5, 22.2, 14.0; MS *m*/*z* 413 (M^+, 1.66), 91 (100); IR (KBr) 3197, 1673, 1652 cm^{-1}. Anal. Calcd for $C_{18}H_{24}INO_2$: C, 52.31; H, 5.85; N, 3.39. Found: C, 52.45; H, 6.02; N, 3.19.

3.5.2. 1-Benzyl-5-hydroxy-4-iodo-3-methylpyrrol-2(5*H*)-one (4k). The reaction of **2k** (70 mg, 0.37 mmol) and I_2 (191 mg, 0.75 mmol) in THF (5 mL) at rt for 42 h afforded 71 mg (58% yield) of **4k**: white solid; mp 108–109 °C (*n*-hexane–Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.26 (m, 5H), 5.03 (d, J=6.9 Hz, 1H), 4.94 (d, J=14.4 Hz, 1H), 4.26 (d, J=14.4 Hz, 1H), 4.11 (bs, 1H), 1.86 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 167.3, 142.0, 136.5, 128.7, 128.3, 127.7, 112.5, 84.7, 43.5, 13.3; MS *m*/*z* 329 (M^+, 11.56), 124 (100); IR (KBr) 3317, 1678 cm^{-1}. Anal. Calcd for $C_{12}H_{12}INO_2$: C, 43.79; H, 3.67; N, 4.26. Found: C, 43.89; H, 3.67; N, 4.06.

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