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Homodimeric coupling–cyclization reaction of 2,3-allenamides

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ABSTRACT

The $PdCl_2/NaI/K_2CO_3$-catalyzed highly stereoselective homodimeric coupling–cyclization reaction of 2,3-allenamides afforded *Z*-bis(furanimine) derivatives. The addition of K_2CO_3 is crucial for this reaction and a possible mechanism is proposed.

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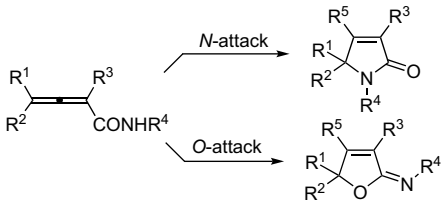
1. Introduction

The chemistry of allenes has been becoming one of the hottest research areas in organic chemistry.[1,2] Especially, the transition metal-catalyzed cyclization of functionalized allenes provides many efficient routes for the synthesis of cyclic products.[1,2] Recently, the transition metal-catalyzed cyclizative dimerization reaction of two functionalized allenes has started to provide new pathways for the preparation of cyclic compounds with unique structural features. For example, Hashmi et al. first reported the $PdCl_2(MeCN)_2$ or $AuCl_3$ catalyzed homodimerization reaction of 1,2-allenyl ketones.[3,4] In our research group, the homodimerization reactions of 2,3-allenoic acids[5] and 2,3-allenols[6] have been studied to provide bisbutenolides and 1,3-alkadien-2-yl-2,5-dihydrofunans, respectively. As it is known that the cyclizations of 2,3-allenamides have two types of reactions: *N*-attack forming the γ-lactams and O-attack furnishing furanimines (Scheme 1),[7] it is interesting to see, which reaction type would occur in the dimerization of 2,3-allenamides. Herein, we wish to report the homodimeric coupling–cyclization reaction of 2,3-allenamides.

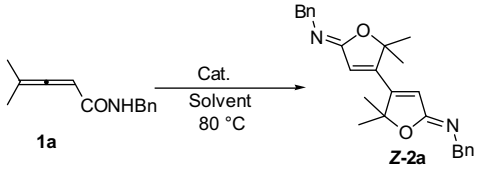


Scheme 1.

2. Results and discussion

Initially, we used *N*-benzyl 4-methyl-penta-2,3-dienamide **1a** to try the dimerization reaction. The corresponding results under different conditions are summarized in Table 1. At first, different catalytic systems were tested for this homodimerization coupling–cyclization reaction. Although $PdCl_2$ failed to catalyze this reaction (entry 1, Table 1), fortunately, when we used the $PdCl_2$/NaI catalytic system, which has been used for the dimeric cyclization of 2,3-allenols,[6] bis(furanimine) **2a** was formed in 29% yield with 32% recovery of the starting material **1a** within 16 h (entry 2, Table 1). After analyzing the NMR spectra of crude and pure product after the reaction, it

Table 1
Homodimeric coupling–cyclization reaction of *N*-benzyl 4-methyl-penta-2,3-dienamide (**1a**)[a]



1a **Z-2a**

Entry	Cat.[b]	Solvent	*T* (h)	Yield of *Z*-**2a**[c]	Recovery of **1a**[c]
1	$PdCl_2$	DMF	12	0	58
2	$PdCl_2$/NaI	DMF	16	29	32
3	*$PdCl_2/NaI/K_2CO_3$*	*DMF*	*8*	*77*	*0*
4	$PdCl_2/K_2CO_3$	DMF	12	26	0
5	PdI_2/K_2CO_3	DMF	12	59	0
6	*$PdCl_2/NaI/K_2CO_3$*	*DMA*	*14*	*67*	*0*
7	$PdCl_2/NaI/K_2CO_3$	DMSO	22	46	5
8	$PdCl_2/NaI/K_2CO_3$	MeCN	22	53	4
9	$PdCl_2/NaI/K_2CO_3$	THF	23	15	30
10	$PdCl_2/NaI/K_2CO_3$	DCE	23	9	49

[a] The reaction was carried out using 0.2 mmol of **1a** and 5 mol% of Pd at 80 °C.
[b] NaI (50 mol%) or K_2CO_3 (1.0 equiv) was used, if any.
[c] Yields were determined by ^1H NMR analysis with mesitylene as the internal standard.

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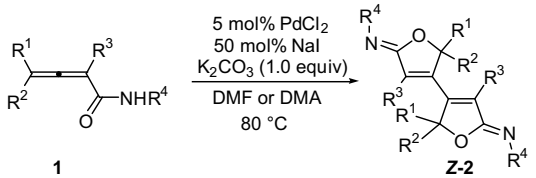
Table 2
Homodimeric coupling–cyclization reaction of 2,3-allenamides[a]



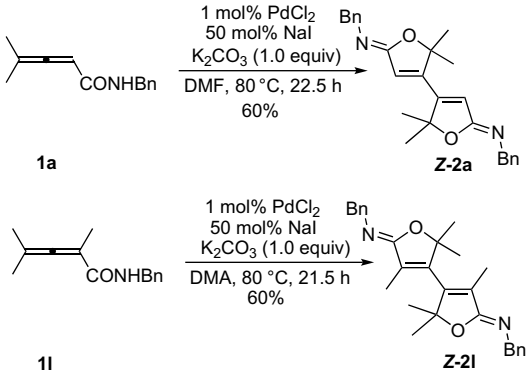
1 Z-2

Entry	R^1	R^2	R^3	R^4	Solvent	T (h)	Yield[b] (%)
1	Me	Me	H	Bn (**1a**)	DMF	8	68 (**2a**)
2	Me	Me	H	*n*-Bu (**1b**)	DMF	11	66 (**2b**)
3	Me	Me	H	*t*-Bu (**1c**)	DMA	14	65 (**2c**)
4	Me	Me	H	*i*-Pr (**1d**)	DMA	10	73 (**2d**)
5	Et	Et	H	Bn (**1e**)	DMA	21	58 (**2e**)
6	Et	Et	H	*n*-Bu (**1f**)	DMA	15	66 (**2f**)
7	*n*-Pr	*n*-Pr	H	Bn (**1g**)	DMA	10	72 (**2g**)
8	*n*-Pr	*n*-Pr	H	*n*-Bu (**1h**)	DMA	28	64 (**2h**)
9	*n*-Bu	*n*-Bu	H	Bn (**1i**)	DMA	14	66 (**2i**)
10	$-(CH_2)_5-$		H	Bn (**1j**)	DMF	14	74 (**2j**)
11	Me	Et	H	Bn (**1k**)	DMA	14	69 (**2k**)[c]
12	Me	Me	Me	Bn (**1l**)	DMA	14	88 (**2l**)

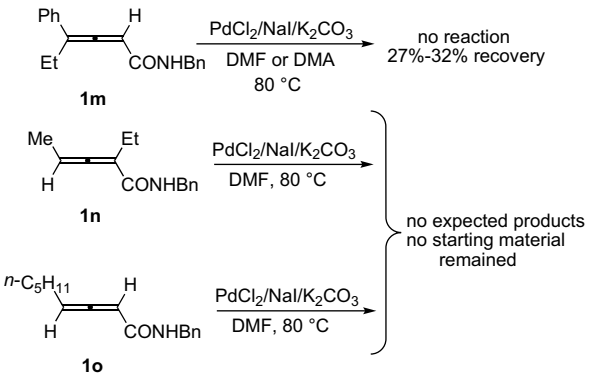
[a] The reaction was carried out using 0.2 mmol of **1**, 5 mol % of $PdCl_2$, 50 mol % of NaI and 1.0 equiv of K_2CO_3 in DMF or DMA at 80 °C.
[b] Isolated yield.
[c] A 1:1 mixture of two diastereomers.

was confirmed that only bis(furanimine) was formed. To enhance the nucleophilicity of amide functionality, 1.0 equiv of K_2CO_3 was added to afford **2a** in 77% yield with complete conversion of the starting material **1a** within 8 h (entry 3, Table 1). Although the combination of $PdCl_2$ or PdI_2 with K_2CO_3 smoothly consumed the starting allene, the yield was much lower (entries 4 and 5, Table 1). The solvent effect was also tested. From Table 1, it is noted that the reaction in DMA yielded the product **2a** in 67% yield (entry 6, Table 1). Other solvents such as DMSO, MeCN, THF, DCE led to inferior results with some of the starting material **1a** remaining (entries 7–10, Table 1).

With the optimized reaction conditions in hand, the scope of the reaction was explored with some typical results summarized in Table 2. In some cases, the solvent was changed to DMA for higher yield or consuming the starting material more efficiently. The substituents at 4-position, i.e., R^1 and R^2, can be an alkyl group such as methyl, ethyl, propyl, butyl; the α-substituent R^3 can be H and alkyl group; the substituent R^4 can be benzyl, butyl, *tert*-butyl, *iso*-propyl group. When R^1 is different with R^2 such as methyl and ethyl group, a 1:1 diastereoisomeric mixture was formed as expected (entry 11, Table 2). The structure of the product **2e** was further confirmed by the X-ray diffraction studies (Fig. 1).[8] When the amount of catalyst $PdCl_2$ was reduced to 1 mol %, the reaction of allenamides **1a** and **1l** also completed to afford *Z*-**2a** and *Z*-**2l** in 60% yields (Scheme 2).



Scheme 2.



Scheme 3.

However, when *N*-benzyl 4-phenyl-2,3-hexadienamide **1m** was applied, no reaction occurred. In addition, 2,4-disubstituted 2,3-allenamide **1n** or 4-substituted 2,3-allenamide **1o** failed to afford the corresponding products under the standard reaction conditions although the starting materials were completely consumed (Scheme 3).

A rationale for this reaction is depicted in Scheme 4. The interaction of allenamides with Pd(II) would form a coordination complex, which may undergo an oxypalladation to form iminyllactonyl palladium(II) intermediate **M1**. Then the Pd(II) intermediate **M1** may promote the second oxypalladation with another molecule of the allenamide to form bis(iminyllactonyl) palladium intermediate **M2**. The addition of K_2CO_3 increased the nucleophilicity of the amide functionality. Subsequent reductive elimination generates the bis(furanimine)s and Pd(0). Finally, the in

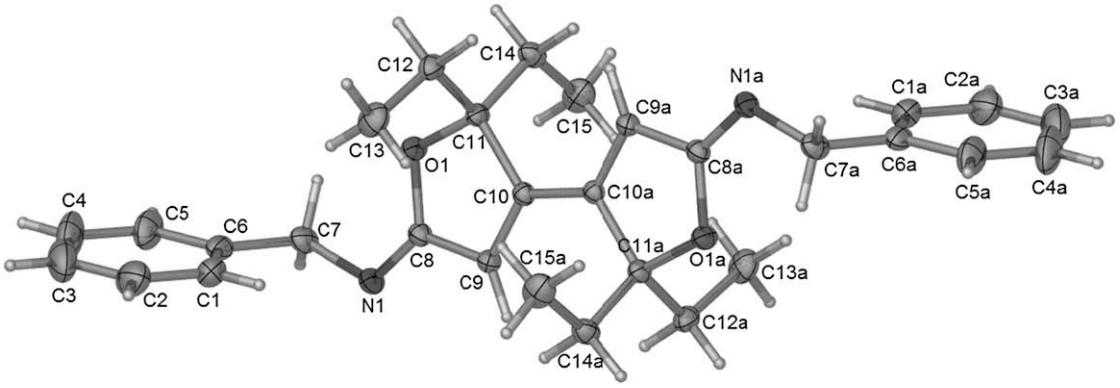
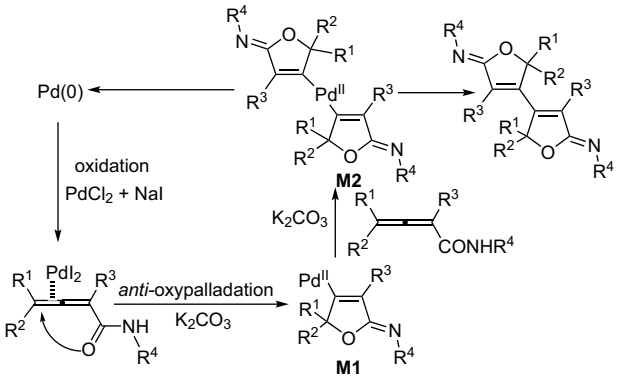


Figure 1.



Scheme 4.

situ generated Pd(0) was oxidized to Pd(II) to finish the catalytic cycle via the oxidation with the in situ generated I_2 from NaI and O_2 in air.[5b] The *Z*-selectivity referring to the C=N bond may be explained by the steric interaction of R^3 and R^4 in the *E*-products.[7]

3. Conclusions

We have developed a $PdCl_2$/NaI/K_2CO_3-catalyzed highly stereoselective homodimeric coupling-cyclization reaction of 2,3-allenamides, which provides an efficient route to *Z*-bis(furanimine) derivatives. The addition of K_2CO_3 is crucial for this reaction. Further studies in this area are being carried out in our laboratory.

4. Experimental

4.1. Preparation of 2,2′-bis(benzylimino)-5,5,5′,5′-tetramethyl-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2a). General procedure

K_2CO_3 (27.6 mg, 0.20 mmol), $PdCl_2$ (1.9 mg, 0.011 mmol), NaI (15.0 mg, 0.10 mmol), **1a** (40.0 mg, 0.20 mmol) and 2 mL of DMF were added sequentially to a reaction tube. The resulting solution was heated at 80 °C with stirring. After 8 h as monitored by TLC, the reaction was quenched with 10 mL of H_2O, extracted with ether (25 mL×3), washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, chromatography on neutral Al_2O_3 (eluent: petroleum ether/ethyl acetate=4:1) of the crude product afforded *Z*-**2a** (27.2 mg, 68%) as a white solid. Mp: 164.2–165.3 °C (Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.29 (m, 8H), 7.28–7.20 (m, 2H), 6.23 (s, 2H), 4.56 (s, 4H), 1.61 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4, 151.2, 140.6, 128.4, 127.9, 126.6, 123.0, 90.4, 51.6, 26.7; MS (*m*/*z*): 400 (M^+, 74.35), 91 (100); IR (KBr, cm^{-1}): 3072, 2983, 2939, 2855, 1670, 1449, 1289, 1132, 1044, 1023. Anal. Calcd for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99. Found: C, 77.92; H, 7.08; N, 6.91.

The reaction of 40.3 mg (0.20 mmol) of **1a**, 0.4 mg (0.002 mmol) of $PdCl_2$, 15.7 mg (0.10 mmol) of NaI and 28.1 mg (0.20 mmol) of K_2CO_3 in DMF (2 mL) afforded 23.9 mg (60%) of *Z*-**2a** (Scheme 2).

4.2. 2,2′-Bis(*n*-butylimino)-5,5,5′,5′-tetramethyl-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2b)

The reaction of 34.0 mg (0.20 mmol) of **1b**, 1.9 mg (0.011 mmol) of $PdCl_2$, 15.7 mg (0.10 mmol) of NaI and 27.6 mg (0.20 mmol) of K_2CO_3 in DMF (2 mL) afforded 22.4 mg (66%) of *Z*-**2b**. White solid, mp: 109.0–110.0 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.12 (s, 2H), 3.31 (t, *J*=6.9 Hz, 4H), 1.62–1.50 (m, 4H), 1.54 (s, 12H), 1.44–1.30 (m, 4H), 0.91 (t, *J*=7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.9, 150.8, 122.8, 90.0, 47.1, 33.1, 26.6, 20.6, 13.9; MS (*m*/*z*): 332 (M^+, 31.44), 289 (100); IR (KBr, cm^{-1}): 2958, 2932, 2871, 1670, 1460, 1369, 1276, 1194, 1130. Anal. Calcd for $C_{20}H_{32}N_2O_2$: C, 72.25; H, 9.70; N, 8.43. Found: C, 72.23; H, 9.75; N, 8.52.

4.3. 2,2′-Bis(*tert*-butylimino)-5,5,5′,5′-tetramethyl-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2c)

The reaction of 33.1 mg (0.20 mmol) of **1c**, 1.7 mg (0.010 mmol) of $PdCl_2$, 14.7 mg (0.10 mmol) of NaI and 27.6 mg (0.20 mmol) of K_2CO_3 in DMA (2 mL) afforded 21.3 mg (65%) of *Z*-**2c**. White solid, mp: 228.9–230.3 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.08 (s, 2H), 1.53 (s, 12H), 1.29 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 149.9, 124.4, 90.5, 53.7, 29.6, 26.5; MS (*m*/*z*): 332 (M^+, 2.73), 317 (100); IR (KBr, cm^{-1}): 2975, 2930, 2869, 1677, 1454, 1371, 1361, 1270, 1228, 1190, 1115. Anal. Calcd for $C_{20}H_{32}N_2O_2$: C, 72.25; H, 9.70; N, 8.43. Found: C, 72.37; H, 9.65; N, 8.45.

4.4. 2,2′-Bis(isopropylimino)-5,5,5′,5′-tetramethyl-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2d)

The reaction of 31.8 mg (0.21 mmol) of **1d**, 1.7 mg (0.010 mmol) of $PdCl_2$, 14.8 mg (0.10 mmol) of NaI and 28.0 mg (0.20 mmol) of K_2CO_3 in DMA (2 mL) afforded 23.2 mg (73%) of *Z*-**2d**. White solid, mp: 161.9–162.9 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.10 (s, 2H), 3.87 (heptet, *J*=6.3 Hz, 2H), 1.53 (s, 12H), 1.12 (d, *J*=6.3 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 150.7, 123.2, 90.0, 47.3, 26.6, 23.7; MS (*m*/*z*): 304 (M^+, 13.06), 289 (100); IR (KBr, cm^{-1}): 2966, 2934, 2870, 1672, 1458, 1386, 1369, 1344, 1282, 1270, 1195, 1120. Anal. Calcd for $C_{18}H_{28}N_2O_2$: C, 71.02; H, 9.27; N, 9.20. Found: C, 71.10; H, 9.26; N, 9.13.

4.5. 2,2′-Bis(benzylimino)-5,5,5′,5′-tetraethyl-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2e)

The reaction of 45.6 mg (0.20 mmol) of **1e**, 2.0 mg (0.011 mmol) of $PdCl_2$, 14.4 mg (0.10 mmol) of NaI and 27.6 mg (0.20 mmol) of K_2CO_3 in DMA (2 mL) afforded 26.4 mg (58%) of *Z*-**2e**. White solid, mp: 176.6–177.2 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.29 (m, 8H), 7.27–7.20 (m, 2H), 6.35 (s, 2H), 4.58 (s, 4H), 2.10–1.95 (m, 4H), 1.95–1.78 (m, 4H), 0.76 (t, *J*=7.4 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6, 147.4, 140.5, 128.4, 127.9, 126.5, 125.2, 96.2, 51.7, 31.2, 7.4; MS (*m*/*z*): 456 (M^+, 26.91), 91 (100); IR (KBr, cm^{-1}): 3076, 2971, 2935, 2857, 1670, 1494, 1450, 1343, 1284, 1224, 1137, 1045, 1021. Anal. Calcd for $C_{30}H_{36}N_2O_2$: C, 78.91; H, 7.95; N, 6.13. Found: C, 78.96; H, 7.97; N, 6.11.

4.6. 2,2′-Bis(*n*-butylimino)-5,5,5′,5′-tetraethyl-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2f)

The reaction of 38.9 mg (0.20 mmol) of **1f**, 1.8 mg (0.010 mmol) of $PdCl_2$, 15.0 mg (0.10 mmol) of NaI and 26.8 mg (0.19 mmol) of K_2CO_3 in DMA (2 mL) afforded 25.4 mg (66%) of *Z*-**2f**. White solid, mp: 99.4–100.1 °C (*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.25 (s, 2H), 3.34 (t, *J*=7.1 Hz, 4H), 2.04–1.73 (m, 8H), 1.63–1.50 (m, 4H), 1.46–1.30 (m, 4H), 0.92 (t, *J*=7.2 Hz, 6H), 0.72 (t, *J*=7.4 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 147.0, 125.0, 95.7, 47.2, 33.1, 31.2, 20.6, 13.9, 7.3; MS (*m*/*z*): 388 (M^+, 100); IR (KBr, cm^{-1}): 3071, 2971, 2953, 2936, 2871, 1665, 1453, 1378, 1333, 1270, 1216, 1137, 1111, 1061, 1035. Anal. Calcd for $C_{24}H_{40}N_2O_2$: C, 74.18; H, 10.38; N, 7.21. Found: C, 74.12; H, 10.40; N, 7.18.

4.7. 2,2′-Bis(benzylimino)-5,5,5′,5′-tetra(*n*-propyl)-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2g)

The reaction of 50.4 mg (0.20 mmol) of **1g**, 1.9 mg (0.011 mmol) of $PdCl_2$, 14.5 mg (0.10 mmol) of NaI and 27.9 mg (0.20 mmol) of

K_2CO_3 in DMA (2 mL) afforded 36.3 mg (72%) of *Z*-**2g**. White solid, mp: 146.5–147.7 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44–7.29 (m, 8H), 7.27–7.20 (m, 2H), 6.31 (s, 2H), 4.55 (s, 4H), 2.01–1.86 (m, 4H), 1.84–1.66 (m, 4H), 1.35–1.14 (m, 4H), 1.13–0.94 (m, 4H), 0.87 (t, J=7.1 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6, 148.4, 140.5, 128.4, 127.9, 126.6, 124.5, 95.8, 51.7, 40.6, 16.3, 13.9; MS (*m*/*z*): 512 (M^+, 5.88), 91 (100); IR (KBr, cm^{-1}): 2960, 2942, 2908, 2873, 1674, 1603, 1582, 1493, 1445, 1347, 1284, 1230, 1212, 1138, 1046, 1014. Anal. Calcd for $C_{34}H_{44}N_2O_2$: C, 79.65; H, 8.65; N, 5.46. Found: C, 79.68; H, 8.68; N, 5.42.

4.8. 2,2′-Bis(*n*-butylimino)-5,5,5′,5′-tetra(*n*-propyl)-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2h)

The reaction of 43.6 mg (0.20 mmol) of **1h**, 1.9 mg (0.011 mmol) of $PdCl_2$, 15.6 mg (0.10 mmol) of NaI and 27.3 mg (0.20 mmol) of K_2CO_3 in DMA (2 mL) afforded 27.8 mg (64%) of *Z*-**2h**. White solid, mp: 102.5–103.2 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.21 (s, 2H), 3.32 (t, J=7.1 Hz, 4H), 1.94–1.80 (m, 4H), 1.78–1.65 (m, 4H), 1.63–1.50 (m, 4H), 1.45–1.31 (m, 4H), 1.30–1.11 (m, 4H), 1.09–0.90 (m, 4H), 0.92 (t, J=7.2 Hz, 6H), 0.84 (t, J=7.1 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.1, 148.0, 124.4, 95.3, 47.2, 40.6, 33.1, 20.6, 16.3, 13.95, 13.91; MS (*m*/*z*): 444 (M^+, 95.50), 401 (100); IR (KBr, cm^{-1}): 3065, 2956, 2932, 2872, 1666, 1465, 1338, 1272, 1255, 1213, 1142, 1046. Anal. Calcd for $C_{28}H_{48}N_2O_2$: C, 75.62; H, 10.88; N, 6.30. Found: C, 75.66; H, 10.80; N, 6.25.

4.9. 2,2′-Bis(benzylimino)-5,5,5′,5′-tetra(*n*-butyl)-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2i)

The reaction of 56.3 mg (0.20 mmol) of **1i**, 1.8 mg (0.010 mmol) of $PdCl_2$, 14.5 mg (0.10 mmol) of NaI and 27.4 mg (0.20 mmol) of K_2CO_3 in DMA (2 mL) afforded 37.0 mg (66%) of *Z*-**2i**. White solid, mp: 179.7–180.6 °C (*n*-hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.29 (m, 8H), 7.27–7.19 (m, 2H), 6.31 (s, 2H), 4.56 (s, 4H), 2.02–1.88 (m, 4H), 1.87–1.72 (m, 4H), 1.35–1.09 (m, 12H), 1.06–0.89 (m, 4H), 0.83 (t, J=7.1 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.7, 148.3, 140.5, 128.4, 128.0, 126.6, 124.7, 95.7, 51.8, 38.4, 25.2, 22.6, 14.0; MS (*m*/*z*): 568 (M^+, 8.94), 91 (100); IR (KBr, cm^{-1}): 3065, 3022, 2951, 2927, 2867, 1664, 1495, 1464, 1451, 1441, 1378, 1345, 1284, 1234, 1205, 1143, 1086, 1045, 1018. Anal. Calcd for $C_{38}H_{52}N_2O_2$: C, 80.24; H, 9.21; N, 4.92. Found: C, 80.24; H, 9.28; N, 4.99.

4.10. 2,2′-Bis(benzylimino)[4,4′]bi[1-oxa-spiro[4.5]dec-3-enyl] (*Z*-2j)

The reaction of 48.4 mg (0.20 mmol) of **1j**, 1.7 mg (0.010 mmol) of $PdCl_2$, 15.2 mg (0.10 mmol) of NaI and 26.8 mg (0.20 mmol) of K_2CO_3 in DMF (2 mL) afforded 35.7 mg (74%) of *Z*-**2j**. White solid, mp: 187.7–188.2 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.29 (m, 8H), 7.28–7.20 (m, 2H), 6.34 (s, 2H), 4.58 (s, 4H), 2.00–1.60 (m, 18H), 1.33–1.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.8, 151.4, 140.7, 128.3, 127.9, 126.5, 123.1, 92.4, 51.7, 34.8, 24.6, 22.1; MS (*m*/*z*): 480 (M^+, 37.74), 91 (100); IR (KBr, cm^{-1}): 3023, 2939, 2861, 1680, 1497, 1450, 1355, 1305, 1287, 1270, 1212, 1135, 1043. Anal. Calcd for $C_{32}H_{36}N_2O_2$: C, 79.96; H, 7.55; N, 5.83. Found: C, 79.82; H, 7.53; N, 5.83.

4.11. 2,2′-Bis(benzylimino)-5,5′-diethyl-5,5′-dimethyl-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2k)

The reaction of 43.9 mg (0.20 mmol) of **1k**, 1.8 mg (0.010 mmol) of $PdCl_2$, 14.9 mg (0.10 mmol) of NaI and 27.3 mg (0.20 mmol) of K_2CO_3 in DMA (2 mL) afforded 30.3 mg (69%) of *Z*-**2k**. White solid, mp: 162.6–164.0 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44–7.28 (m, 16H), 7.28–7.18 (m, 4H), [6.28 (s), 6.27 (s), 4H], 4.57 (s, 8H), 2.10–1.78 (m, 8H), [1.59 (s), 1.58 (s), 12H], 0.81–0.68 (m, 12H); MS (*m*/*z*): 428 (M^+, 34.51), 91 (100); IR (KBr, cm^{-1}): 3076, 2977, 2934, 2876, 2858, 1669, 1602, 1494, 1451, 1441, 1376, 1343, 1313, 1284, 1228, 1134, 1043, 1034, 1016. Anal. Calcd for $C_{28}H_{32}N_2O_2$: C, 78.47; H, 7.53; N, 6.54. Found: C, 78.49; H, 7.46; N, 6.53.

4.12. 2,2′-Bis(benzylimino)-3,5,5,3′,5′,5′-hexamethyl-2,5,2′,5′-tetrahydro[4,4′]bifuranyl (*Z*-2l)

The reaction of 43.3 mg (0.20 mmol) of **1l**, 1.8 mg (0.010 mmol) of $PdCl_2$, 15.1 mg (0.10 mmol) of NaI and 28.4 mg (0.21 mmol) of K_2CO_3 in DMA (2 mL) afforded 38.1 mg (88%) of *Z*-**2l**. Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, J=7.5 Hz, 4H), 7.39–7.29 (m, 4H), 7.29–7.20 (m, 2H), 4.61 (s, 4H), 1.79 (s, 6H), 1.50 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 148.9, 140.9, 131.6, 128.2, 127.7, 126.3, 89.5, 50.9, 27.5, 10.9; MS (*m*/*z*): 428 (M^+, 41.82), 91 (100); IR (KBr, cm^{-1}): 3027, 2979, 2929, 2869, 1762, 1682, 1495, 1453, 1379, 1353, 1328, 1291, 1255, 1191, 1087, 1029. Anal. Calcd for $C_{28}H_{32}N_2O_2$: C, 78.47; H, 7.53; N, 6.54. Found: C, 78.48; H, 7.52; N, 6.55.

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Supplementary data

Supplementary data in association with this article can be found in the online version, at doi:10.1016/j.tet.2009.03.083.

References and notes

1. For books, see: (a) *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic: London, 1982; Vol. 1; (b) *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004; Vols. 1–2; (c) *Allenes in Organic Synthesis*; Schuster, H. F., Coppola, G. M., Eds.; Wiley: New York, NY, 1984; (d) *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Wiley: New York, NY, 1980.
2. For some of the most recent reviews, see: (a) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067; (b) Hoffmann-Röder, A.; Krause, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 1196; (c) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701; (d) Ma, S. *Chem. Rev.* **2005**, *105*, 2829; (e) Ma, S. *Aldrichimica Acta* **2007**, *40*, 91.
3. (a) Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1581; (b) Hashmi, A. S. K.; Ruppert, T. L.; Knöfel, T.; Bats, J. W. *J. Org. Chem.* **1997**, *62*, 7295; (c) Hashmi, A. S. K.; Schwarz, L.; Choi, J. H.; Frost, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2285; (d) Hashmi, A. S. K.; Schwarz, L.; Bolte, M. *Eur. J. Org. Chem.* **2004**, 1923.
4. For a recent report, see: Alcaide, B.; Almendros, P.; Martínez del Campo, T. *Eur. J. Org. Chem.* **2007**, 2844.
5. (a) Ma, S.; Yu, Z. *Org. Lett.* **2003**, *5*, 1507; (b) Ma, S.; Yu, Z.; Gu, Z. *Chem.—Eur. J.* **2005**, *11*, 2351.
6. For an selective homodimerization rection of 2,3-allenols, see: Deng, Y.; Yu, Y.; Ma, S. *J. Org. Chem.* **2008**, *73*, 585; Hashmi, A. S. K.; Blanco, M. C.; Fischer, D.; Bats, J. W. *Eur. J. Org. Chem.* **2006**, 1387.
7. (a) Ma, S.; Xie, H. *Org. Lett.* **2000**, *2*, 3801; (b) Ma, S.; Xie, H. *J. Org. Chem.* **2002**, *67*, 6575; (c) Ma, S.; Xie, H. *Tetrahedron* **2005**, *61*, 251; (d) Ma, S.; Gu, Z.; Yu, Z. *J. Org. Chem.* **2005**, *70*, 6291.
8. Crystal data for compound **2e**: $C_{15}H_{18}ON$, M_w=228.30, orthorhombic, space group *Pbca*, Mo Kα, final *R* indices [$I>2\sigma(I)$], R_1=0.0364, wR_2=0.0951, a=7.8526 (3) Å, b=12.3101 (5) Å, c=26.5628 (10) Å, α=90°, β=90°, γ=90°, V=2567.73 (17) Å^3, T=296 (2) K, Z=8, number of reflections collected/unique: 27,674/2265 (R_{int}=0.0260), number of observations: 1961 [$I>2\sigma(I)$], parameters 155. CCDC 702814 contains the supplementary crystallographic data.