Iron(III)-Catalyzed Dehydration C(sp^2)–C(sp^2) Coupling of Tertiary Propargyl Alcohols and α-Oxo Ketene Dithioacetals: A New Route to *gem*-Bis(alkylthio)-Substituted Vinylallenes

Qian Li,[a] Yeming Wang,[c] Zhongxue Fang,[b] Peiqiu Liao,[b] Badru-Deen Barry,[b] Guangbo Che,*[a,c] Xihe Bi*[b,c,d]

[a] College of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, P. R. of China

[b] Department of Chemistry, Northeast Normal University, 5268 Renmin Street, 130024 Changchun, P. R. of China

[c] Key Laboratory of Preparation and Applications of Environmental Friendly Materials (Jilin Normal University), Chinese Ministry of Education, Siping 136000, P. R. of China

[d] State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. of China
Fax +86(431)85099759; E-mail: bixh507@nenu.edu.cn; E-mail: guangbochejl@yahoo.com

Received: 09.01.2013; Accepted after revision: 23.01.2013

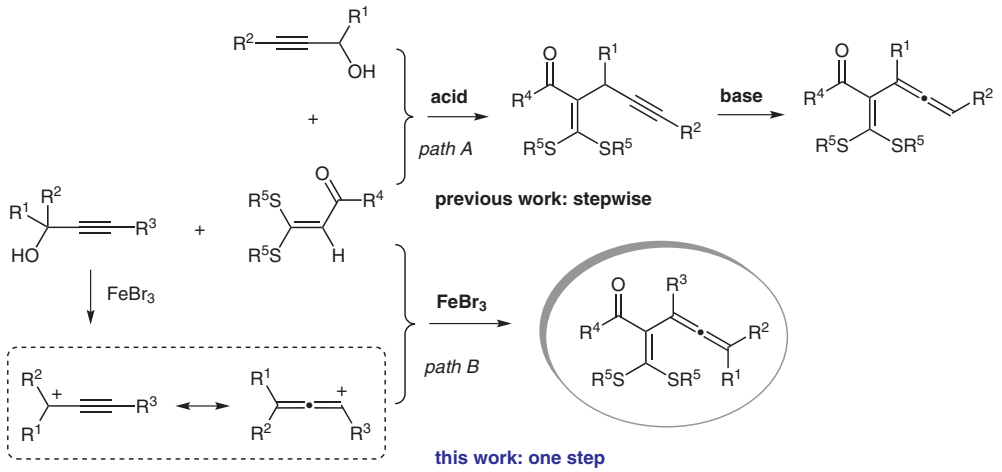
Abstract: A new and efficient synthetic approach to [*gem*-bis(alkylthio)vinyl]allenes has been developed involving iron(III)-catalyzed dehydration C(sp^2)–C(sp^2) coupling of tertiary propargyl alcohols and α-oxo ketene dithioacetals, affording a variety of [*gem*-bis(alkylthio)vinyl]allenes in good to excellent yields.

Key words: iron catalysis, tertiary propargyl alcohols, α-oxo ketene dithioacetals, allenic carbocation, [*gem*-bis(alkylthio)vinyl]allenes

Vinylallenes have attracted great interest as building blocks in organic cyclization reactions. Examples include Diels–Alder reactions,[1] [4+1]-cycloaddition reactions,[2] thermal electrocyclic reactions,[3] [1,5]-H sigmatropic rearrangement,[4] and several other tautomerization/isomerization reactions.[5] Although a good number of dynamic routes to vinylallenes have been developed over the past few decades,[6] efforts toward the discovery of novel and more efficient synthetic methods, particularly with attention to the introduction of novel substitution patterns to modulate the reactivity of vinylallenes, are still ongoing.[7]

Recently, [*gem*-bis(alkylthio)vinyl]allenes, with inherent features of the ketene dithioacetals[8] and allenes,[9] were efficiently synthesized by our group. Based on the regulation effect of the alkylthio group, these intrinsic synthetic synthons have led our team to establish conceptually new procedures for the divergent synthesis of fully substituted pyrrole and thiophene heterocycles.[10]

The introduction of two alkylthio groups to the vinylic terminus of vinylallenes has brought unprecedented synthetic utility, however, in this approach, synthesis of the [*gem*-bis(alkylthio)vinyl]allenes involved two principal steps: (1) the Lewis acid catalyzed formation of *gem*-bis(alkylthio)penten-4-yne derivatives from α-oxo ketene dithioacetals and secondary propargyl alcohols;[11] and (2) transformation of these derivatives into [*gem*-bis(alkylthio)vinyl]allenes through base-promoted propargyl isomerization (Scheme 1, path A). Even though construction of these compounds was efficiently accomplished by this route, the variation of substituents was limited to the use of secondary propargyl alcohols. As a result, production of multifunctional [*gem*-bis(alkylthio)vinyl]allenes



Scheme 1 Synthetic strategies for [*gem*-bis(alkylthio)vinyl]allenes

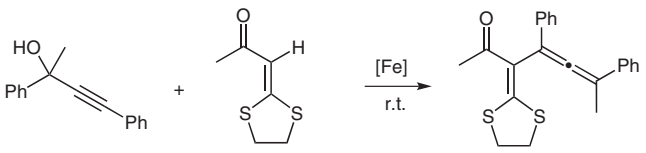
SYNTHESIS 2013, 45, 0609–0614
Advanced online publication: 06.02.2013
DOI: 10.1055/s-0032-1316855; Art ID: SS-2012-H0024-OP

via a straightforward and step-economic approach still remains a demanding goal in vinylallene chemistry.

As a continuation of our studies on the exploration of the potential applicability of vinylallenes in organic synthesis, we sought a more practical protocol to assemble [*gem*-bis(alkylthio)vinyl]allenes based upon the synthetic advantages of the reaction of propargyl tertiary alcohols with α-oxo ketene dithioacetals as a new approach. Tertiary propargyl alcohols are efficient precursors for allenes bearing functionalities[12] due to the resonance between propargylic and allenic carbocations.[13] The Wang[14] and Chan[15] groups and others[16] have disclosed the potential transformation of allenic carbocations into a diverse class of carbocyclic and heterocyclic compounds via reaction with suitable nucleophiles under either Lewis acid [such as $BF_3{\cdot}OEt_2$ and $Yb(OTf)_3$] or Brønsted acid (such as TfOH and TsOH) catalysis. As part of our efforts to develop non-precious-metal-catalyzed organic transformations,[17] and in continuation of our previously reported synthesis of *gem*-bis(alkylthio)penten-4-ynes and their subsequent synthetic conversion into methyl pent-4-ynoates, pyrroles, and thiophenes under varied conditions,[10,11] we disclose herein a new and facile iron(III)-catalyzed dehydration $C(sp^2)$–$C(sp^2)$ coupling reaction route (Scheme 1, path B) of tertiary propargyl alcohols and α-oxo ketene dithioacetals leading to the synthesis of [*gem*-bis(alkylthio)vinyl]allenes in a single step.[18] This currently rapid and step-economic procedure is functionally straightforward and utilizes economically benign, low-cost, and readily available reagents and catalysts. Under catalysts by iron(III) salts, tertiary propargyl alcohols reacted expediently with electron-rich α-oxo ketene dithioacetals to furnish the desired functionalized [*gem*-bis(alkylthio)vinyl]allenes.

In our proposed strategy, tertiary propargyl alcohol **1a** and α-oxo ketene dithioacetal **2a** were chosen as model substrates. Investigation of optimal conditions commenced with the screening for solvent suitability using the reaction of **1a** with **2a**; the results are summarized in Table 1. With 20 mol% of either iron(III) chloride, bromide, or triflate catalyst in toluene, transformation to the target **3a** was successfully accomplished in 85%, 91% and 88% yields, respectively, within five minutes (entries 1, 7, and 8). Although the reaction catalyzed by iron(III) chloride in both acetonitrile and dichloromethane afforded comparably similar yields of 80% and 73%, respectively, these reactions proceeded with much longer reaction times, one and six hours, respectively (entries 2 and 3). While 1,4-dioxane (entry 4) only gave trace amounts of **3a**, the reaction did not proceed in solvents like dimethyl sulfoxide and methanol (entries 5 and 6). The results as outlined in Table 1 distinctly illustrate the effect that the choice of solvent has on both the kinetics and yield of **3a**. Thus as toluene has manifestly better solvent activity, it was more closely scrutinized in the model reaction using different iron(III) salts. In general, reactions in toluene at room temperature with iron(III) chloride, bromide, or triflate as the catalyst promoted the reaction efficiently (entries 1, 7, and 8) whereas those using $Fe(acac)_3$, iron(II) chloride, and iron failed to initiate any transformation even after prolonged reaction times (entries 9–11). Thus the best yields of **3a** and shortest reaction times were obtained with iron(III) chloride, bromide, or triflate as the catalyst and using nonpolar toluene as the solvent. Of these catalysts, transformation with iron(III) bromide in toluene furnished the best results, thus we selected the conditions in entry 7 for further use.

Table 1 Optimization of the Conditions[a]



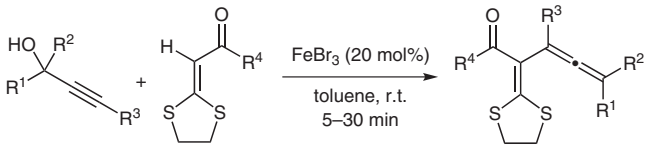
1a **2a** **3a**

Entry	Catalyst	Solvent	Time (min)	Yield[b] (%)
1	$FeCl_3$	toluene	5	85
2	$FeCl_3$	MeCN	60	80
3	$FeCl_3$	CH_2Cl_2	360	73
4	$FeCl_3$	1,4-dioxane	360	trace
5	$FeCl_3$	DMSO	360	0
6	$FeCl_3$	MeOH	360	0
7	$FeBr_3$	toluene	5	91
8	$Fe(OTf)_3$	toluene	5	88
9	$Fe(acac)_3$	toluene	360	0
10	$FeCl_2$	toluene	360	0
11	Fe	toluene	360	0

[a] Reaction conditions: **1a** (0.55 mmol), **2a** (0.5 mmol), [Fe] (20 mol%), solvent (1 mL), r.t.
[b] Isolated yield.

With the optimal conditions established, we immediately explored the scope of our reaction for substrate suitability. First, functional tertiary propargyl alcohol **1** with varying substituents (R^1 = Et, Ph, Me and R^2 = Ph, 2-ClC_6H_4, 3-ClC_6H_4, 1-naphthyl) was subjected to reaction with the five-membered cyclic α-oxo ketene dithioacetal **2**; the results are summarized in Table 2. Regardless of whether the substituents are electron-withdrawing or electron-releasing, the transformations proceeded smoothly providing the corresponding [*gem*-bis(alkylthio)vinyl]allenes **3b**–**f** in good to high yields (entries 1–5). Importantly however, the reaction of **1** with R^3 = 4-FC_6H_4 (entry 6), afforded a slightly lower yield (79%) compared to the others. A similarly easy transformation that afforded **3h** in 89% yield was realized when R^4 of the ketene dithioacetal was changed to phenyl (entry 7). Further, alkyl-substituted propargyl alcohols were also applied in this coupling reaction with **1a**; to our delight, the corresponding vinylallene **3i** was obtained 95% yield (entry 8). When using a

Table 2 Synthesis of [*gem*-Bis(alkylthio)vinyl]allenes **3**[a]



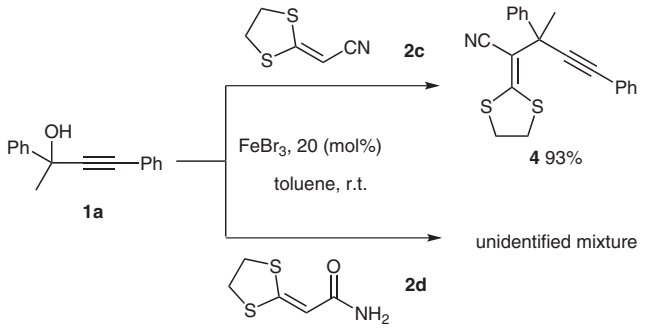
1 2 3

Entry	R^1	R^2	R^3	R^4	Product	Yield[b] (%)
1	Et	Ph	Ph	Me	**3b**	84
2	Ph	Ph	Ph	Me	**3c**	92
3	Me	2-ClC_6H_4	Ph	Me	**3d**	90
4	Me	3-ClC_6H_4	Ph	Me	**3e**	88
5	Me	1-naphthyl	Ph	Me	**3f**	85
6	Me	Ph	4-FC_6H_4	Me	**3g**	79
7	Me	Ph	Ph	Ph	**3h**	89
8	Me	Ph	Pr	Me	**3i**	95
9	$(CH_2)_5$		Ph	Me	**3j**	–[c]

[a] Reaction conditions: **1** (0.55 mmol), **2** (0.5 mmol), $FeBr_3$ (20 mol%), toluene (1 mL), r.t.
[b] Isolated yield.
[c] No reaction.

tertiary propargyl alcohol prepared from cyclohexanone, no reaction took place (entry 9). These results demonstrated the limitation and scope of tertiary propargyl alcohols.

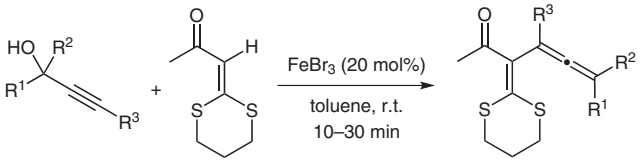
Furthermore, other α-functionalized ketene dithioacetals were examined in the dehydration coupling reaction with tertiary propargyl alcohol **1a** (Scheme 2). Unexpectedly, the reaction of α-cyano ketene dithioacetal **2c** with **1a** afforded 1,1-bis(alkylthio)penten-4-yne **4** in 93% yield. Notably, no corresponding [*gem*-bis(alkylthio)vinyl]allene product was formed. The reaction using α-aminoacyl ketene dithioacetal **2d** resulted in an unidentified mixture.



Scheme 2

Based on our previous observations[11] and the findings of Okuyama[19] that the reactivity of α-oxo ketene dithioacetals is greatly influenced by the choice of alkylthio groups, we decided to explore the nature of this effect on the less activated six-membered cyclic α-oxo ketene dithioacetal **2′** as substrate (Table 3). Indeed, comparable results to the five-membered cases were realized with a kinetic range of 10–30 minutes (entries 1–4).

Table 3 Synthesis of [*gem*-Bis(alkylthio)vinyl]allenes **3′**[a]

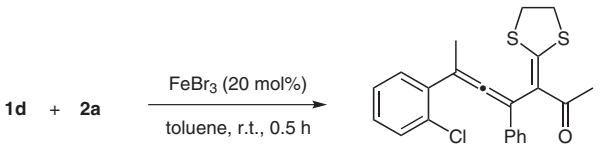


1 2′ 3′

Entry	R^1	R^2	R^3	**3′**	Yield[b] (%)
1	Me	Ph	Ph	**3a′**	87
2	Me	2-ClC_6H_4	Ph	**3b′**	89
3	Ph	Ph	Ph	**3c′**	88
4	4-ClC_6H_4	4-ClC_6H_4	Ph	**3d′**	89

[a] Reaction conditions: **1** (0.55 mmol), **2′** (0.5 mmol), $FeBr_3$ (20 mol%), toluene (1 mL), r.t.
[b] Isolated yield.

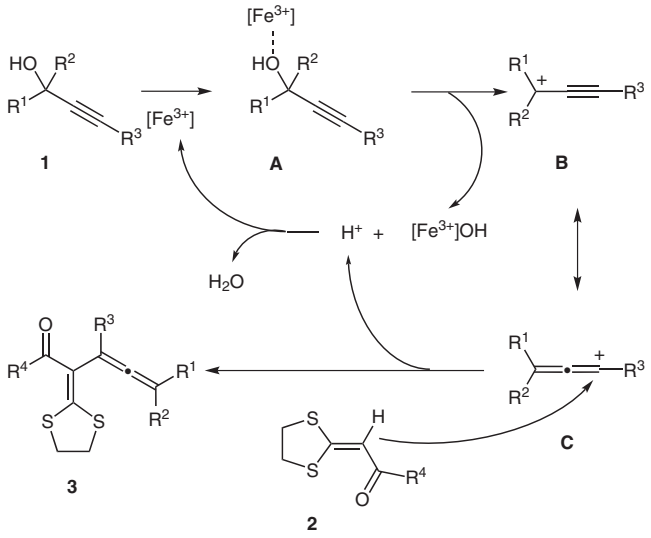
To demonstrate the synthetic potential of the method, the reaction of tertiary propargyl alcohol **1d** and ketene dithioacetal **2a** was carried out on a gram scale (Scheme 3). Gratifyingly, the corresponding product **3d** was isolated in 87% yield.



3d
2.0 g, 87%

Scheme 3 Gram-scale experiment

A plausible mechanism for the reaction is tentatively proposed and depicted in Scheme 4. The polarity of the OH group in **1** was enhanced by the interaction between the ferric ion (Fe^{3+}) and the hydroxy group leading to the formation of the complex **A**, which was subsequently converted into propargylic carbocation **B** with the loss of [Fe^{3+}]OH species.[15a] A resonance exists between propargylic carbocation **B** and allenic carbocation **C**, and here the later is preferably attacked by the electron-rich α-carbon of α-oxo ketene dithioacetal **2**, leading to the target [*gem*-bis(alkylthio)vinyl]allenes **3**. The released H^+ was picked up by [Fe^{3+}]OH species to furnish side product H_2O and ferric ion, hence preparing the latter for the next catalytic cycle.



Scheme 4 A plausible reaction mechanism

In summary, we have described a straightforward and step-economic method for the potent synthesis of [*gem*-bis(alkylthio)vinyl]allenes utilizing readily available starting materials and environmentally benign iron catalyst as the catalyst. This procedure constitutes a direct and practical route to fully substituted vinylallenes, which would find synthetic utility in cyclization reactions. Toward this end, the exploration of the intrinsically embedded features of these vinylallenes products is ongoing in our laboratory, and will be reported in due course.

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C at 500 MHz and 125 Hz, respectively, with TMS as internal standard. Mass spectra were recorded on Bruker AutoflexIII Smartbeam MS spectrometer. HRMS were recorded on Bruck microTof by using ESI method. IR spectra (KBr) were recorded on FTIR spectrophotometer in the range of 400–4000 cm^{-1}.

3-(1,3-Dithiolan-2-ylidene)-4,6-diphenylhepta-4,5-dien-2-one (3a); Typical Procedure

To a soln of **1a** (122 mg, 0.55 mmol) in toluene (1.0 mL) at r.t., **2a** (80 mg, 0.5 mmol) and $FeBr_3$ (30 mg, 0.10 mmol) were added in succession and the mixture stirred for 5 min at r.t. (20 °C) without exclusion of air. After the reaction was complete (monitored by TLC), the mixture was diluted with CH_2Cl_2 (10 mL) and aq NaCl soln (10 mL). The mixture was stirred for an additional 30 min and the two layers separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel, PE–EtOAc,10:1) to afford **3a** as a white solid; yield: 166 mg (91%); mp 144–145 °C.

IR (KBr): 1643, 1481, 1270, 767, 691 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 2.28 (s, 3 H), 3.23–3.29 (m, 2 H), 3.44–3.47 (m, 2 H), 7.24–7.27 (m, 2 H), 7.25–7.36 (m, 6 H), 7.49 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.7, 27.9, 35.5, 39.6, 104.5, 108.6, 120.0, 125.9, 126.1, 127.3, 127.4, 128.5, 128.8, 134.9, 136.0, 165.6, 193.8, 206.5.

MS (ESI): *m*/*z* = 365 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{22}H_{21}OS_2$: 365.1034; found: 365.1022.

3-(1,3-Dithiolan-2-ylidene)-4,6-diphenylocta-4,5-dien-2-one (3b)

White solid; yield: 160 mg (84%); mp 154–155 °C.

IR (KBr): 1625, 1453, 1279, 754, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.0 Hz, 3 H), 2.15 (s, 3 H), 2.61–2.66 (m, 1 H), 2.74–2.79 (m, 1 H), 3.22 (q, *J* = 7.0 Hz, 2 H), 3.42–3.44 (m, 2 H), 7.24–7.25 (m, 2 H), 7.26–7.33 (m, 4 H), 7.33–7.39 (m, 2 H), 7.40–7.45 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 24.0, 35.4, 39.4, 109.5, 111.5, 119.9, 125.6, 126.7, 127.2, 127.3, 128.3, 128.8, 134.8, 135.4, 165.7, 193.9, 205.9.

MS (ESI): *m*/*z* = 379 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{23}H_{23}OS_2$: 379.1190; found: 379.1190.

3-(1,3-Dithiolan-2-ylidene)-4,6,6-triphenylhexa-4,5-dien-2-one (3c)

White solid; yield: 195 mg (92%); mp 164–165 °C.

IR (KBr): 1637, 1462, 1267, 759, 672 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 3.21 (t, *J* = 6.0 Hz, 2 H), 3.45 (t, *J* = 6.0 Hz, 2 H), 7.25–7.29 (m, 1 H), 7.30–7.32 (m, 2 H), 7.35 (m, 6 H), 7.40–7.42 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.8, 35.6, 39.5, 109.5, 113.3, 119.0, 125.9, 127.6, 127.7, 128.3, 128.5, 128.8, 128.9, 134.1, 135.4, 166.3, 193.8, 207.4.

MS (ESI): *m*/*z* = 427 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{27}H_{23}OS_2$: 427.1190; found: 427.1182.

6-(2-Chlorophenyl)-3-(1,3-dithiolan-2-ylidene)-4-phenylhepta-4,5-dien-2-one (3d)

White solid; yield: 179 mg (90%); mp 135–136 °C.

IR (KBr): 1655, 1472, 1280, 772, 683 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 2.26 (s, 3 H), 3.15–3.25 (m, 2 H), 3.43–3.47 (m, 2 H), 7.18–7.25 (m, 3 H), 7.32–7.35 (m, 3 H), 7.38–7.40 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.7, 27.6, 35.4, 39.5, 102.5, 106.6, 119.8, 126.2, 126.6, 127.2, 128.4, 128.6, 129.8, 129.9, 132.6, 134.6, 136.1, 165.5, 193.9, 204.3.

MS (ESI): *m*/*z* = 399 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{22}H_{20}ClOS_2$: 399.0644; found: 399.0387.

6-(3-Chlorophenyl)-3-(1,3-dithiolan-2-ylidene)-4-phenylhepta-4,5-dien-2-one (3e)

White solid; yield: 175 mg (88%); mp 144–145 °C.

IR (KBr): 1643, 1475, 1266, 780, 687 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 2.25 (s, 3 H), 3.24–3.28 (m, 2 H), 3.43–3.46 (m, 2 H), 7.20–7.22 (m, 1 H), 7.24–7.28 (m, 2 H), 7.34–7.37 (m, 5 H), 7.48 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.6, 27.7, 35.5, 39.6, 103.6, 109.1, 119.6, 124.2, 125.9, 126.3, 127.2, 127.6, 128.9, 129.6, 134.4, 134.4, 138.1, 165.9, 193.5, 206.5.

MS (ESI): *m*/*z* = 399 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{22}H_{20}ClOS_2$: 399.0644; found: 399.0646.

3-(1,3-Dithiolan-2-ylidene)-6-(naphthalen-1-yl)-4-phenylhepta-4,5-dien-2-one (3f)
White solid; yield: 175 mg (85%); mp 166–167 °C.

IR (KBr): 1632, 1462, 1274, 812, 683 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.89 (s, 3 H), 2.36 (s, 3 H), 3.04–3.13 (m, 2 H), 3.36–3.38 (m, 2 H), 7.19–7.22 (m, 1 H), 7.29–7.32 (m, 2 H), 7.35–7.43 (m, 5 H), 7.45–7.49 (m, 1 H), 7.73–7.75 (m, 1 H), 7.79–7.81 (m, 1 H), 8.13–8.15 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.9, 27.6, 35.2, 39.5, 102.3, 106.0, 119.9, 125.1, 125.2, 125.3, 125.6, 125.9, 126.0, 127.1, 127.6, 128.2, 128.6, 130.8, 133.6, 135.1, 135.3, 165.6, 193.9, 204.4.

MS (ESI): *m*/*z* = 415 $[M + H]^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{26}H_{23}OS_2$: 415.1190; found: 415.1185.

3-(1,3-Dithiolan-2-ylidene)-4-(4-fluorophenyl)-6-phenylhepta-4,5-dien-2-one (3g)
White solid; yield: 150 mg (79%); mp 164–165 °C.

IR (KBr): 1637, 1468, 1270, 1242, 840, 585 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.19 (s, 3 H), 2.28 (s, 3 H), 3.27–3.28 (m, 2 H), 3.46 (t, *J* = 6.5 Hz, 2 H), 7.00–7.04 (m, 2 H), 7.23–7.29 (m, 1 H), 7.30–7.39 (m, 4 H), 7.47–7.49 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.7, 27.8, 35.5, 39.6, 104.7, 107.7, 115.7, 115.9, 126.1, 127.4, 127.4, 127.5, 128.5, 130.8, 130.8, 135.8, 161.2, 163.2, 165.9, 193.5, 206.1.

MS (ESI): *m*/*z* = 383 $[M + H]^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{22}H_{20}FOS_2$: 383.0940; found: 383.0940.

2-(1,3-Dithiolan-2-ylidene)-1,3,5-triphenylhexa-3,4-dien-1-one (3h)
Yellow solid; yield: 189 mg (89%); mp 122–123 °C.

IR (KBr): 1634, 1467, 1269, 720, 694 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.80 (s, 3 H), 3.31–3.34 (m, 2 H), 3.44–3.49 (m, 2 H), 7.19–7.25 (m, 8 H), 7.30 (t, *J* = 7.5 Hz, 2 H), 7.33–7.38 (m, 3 H), 7.52 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.0, 36.1, 39.2, 104.6, 109.3, 119.4, 126.1, 126.3, 127.1, 127.1, 127.6, 127.9, 128.3, 128.7, 130.3, 135.5, 135.8, 139.9, 168.8, 191.1, 207.3.

MS (ESI): *m*/*z* = 427 $[M + H]^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{27}H_{23}OS_2$: 427.1190; found: 427.1231.

3-(1,3-Dithiolan-2-ylidene)-6-phenyl-4-propylhepta-4,5-dien-2-one (3i)
Yellow liquid; yield: 157 mg (95%).

IR (KBr): 1604, 1445, 1278, 762, 693 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 1.5, 8.0 Hz, 2 H), 7.32 (t, *J* = 8.0 Hz, 2 H), 7.20 (t, *J* = 7.5 Hz, 1 H), 3.36 (t, *J* = 6.5 Hz, 2 H), 3.30–3.21 (m, 2 H), 2.39–2.29 (m, 4 H), 2.26–2.18 (m, 1 H), 2.15 (s, 3 H), 1.59 (q, *J* = 7.5, 15.0 Hz, 2 H), 0.99 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 203.1, 193.1, 163.1, 136.9, 128.1, 126.5, 125.8, 122.8, 106.7, 101.8, 39.2, 35.3, 34.9, 27.5, 20.9, 15.9, 13.8.

MS (ESI): *m*/*z* = 331 $[M + H]^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{23}OS_2$: 331.1190; found: 331.1191.

3-(1,3-Dithian-2-ylidene)-4,6-diphenylhepta-4,5-dien-2-one (3a′)
White solid; yield: 164 mg (87%); mp 165–166 °C.

IR (KBr): 1635, 1465, 1262, 763, 691 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.17–2.18 (m, 2 H), 2.19 (s, 3 H), 2.29 (s, 3 H), 2.86–2.96 (m, 4 H), 7.23–7.28 (m, 2 H), 7.31–7.38 (m, 6 H), 7.51–7.53 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.7, 23.8, 29.0, 29.2, 29.8, 104.2, 106.9, 125.8, 126.2, 127.3, 127.4, 128.2, 128.4, 128.8, 135.1, 136.1, 161.6, 194.5, 207.2.

MS (ESI): *m*/*z* = 379 $[M + H]^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{23}H_{23}OS_2$: 379.1190; found: 379.1214.

6-(2-Chlorophenyl)-3-(1,3-dithian-2-ylidene)-4-phenylhepta-4,5-dien-2-one (3b′)
White solid; yield: 183 mg (89%); mp 150–151 °C.

IR (KBr): 1637, 1462, 1267, 761, 677 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.01 (s, 3 H), 2.14–2.19 (m, 2 H), 2.26 (s, 3 H), 2.83–2.85 (m, 2 H), 2.86–2.89 (m, 1 H), 2.95–2.96 (m, 1 H), 7.17–7.27 (m, 3 H), 7.31–7.37 (m, 3 H), 7.38–7.40 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.7, 23.8, 28.8, 29.0, 29.6, 102.4, 105.0, 126.2, 126.6, 127.2, 128.2, 128.4, 128.6, 129.9, 132.6, 134.9, 136.3, 161.2, 176.2, 194.5, 204.9.

MS (ESI): *m*/*z* = 413 $[M + H]^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{23}H_{22}ClOS_2$: 413.0801; found: 413.0797.

3-(1,3-Dithian-2-ylidene)-4,6,6-triphenylhexa-4,5-dien-2-one (3c′)
White solid; yield: 193 mg (88%); mp 153–154 °C.

IR (KBr): 1635, 1440, 1270, 770, 696 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.01 (s, 3 H), 2.15–2.18 (m, 2 H), 2.85 (t, *J* = 7.0 Hz, 2 H), 2.91 (t, *J* = 7.0 Hz, 2 H), 7.25–7.27 (m, 1 H), 7.30–7.33 (m, 2 H), 7.33–7.38 (m, 6 H), 7.40–7.44 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.7, 29.0, 29.1, 29.7, 108.2, 113.2, 125.8, 127.3, 127.6, 127.7, 128.3, 128.9, 128.9, 134.5, 135.5, 162.5, 194.5, 207.8.

MS (ESI): *m*/*z* = 441 $[M + H]^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{28}H_{25}OS_2$: 441.1347; found: 441.1365.

6,6-Bis(4-chlorophenyl)-3-(1,3-dithian-2-ylidene)-4-phenylhexa-4,5-dien-2-one (3d′)
White solid; yield: 226 mg (89%); mp 162–163 °C.

IR (KBr): 1641, 1481, 1267, 1089, 838, 556 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.01 (s, 3 H), 2.17–2.20 (m, 2 H), 2.86 (t, *J* = 7.0 Hz, 2 H), 2.92 (t, *J* = 7.0 Hz, 2 H), 7.26–7.30 (m, 2 H), 7.31–7.33 (m, 6 H), 7.33–7.35 (m, 1 H), 7.35–7.36 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.7, 23.8, 29.0, 29.8, 108.9, 111.3, 125.9, 126.8, 127.8, 127.9, 128.7, 128.8, 129.1, 129.2, 130.0, 133.7, 133.7, 133.9, 162.9, 194.1, 207.7.

MS (ESI): *m*/*z* = 509 $[M + H]^+$.

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{28}H_{23}Cl_2OS_2$: 509.0567; found: 509.0552.

2-(1,3-Dithiolan-2-ylidene)-3-methyl-3,5-diphenylpent-4-ynenitrile (4)
Yellow solid; yield: 161 mg (93%); mp 186–187 °C.

IR (KBr): 1611, 1250, 1113, 889, 721, 507 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.5 Hz, 2 H), 7.54–7.49 (m, 2 H), 7.38–7.31 (m, 5 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 3.47–3.40 (m, 1 H), 3.40–3.36 (m, 2 H), 3.35–3.29 (m, 1 H), 1.96 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.3, 143.4, 131.6, 128.37, 128.3, 128.2, 127.1, 126.4, 122.9, 118.6, 101.4, 90.2, 85.6, 42.9, 41.4, 37.0, 33.2.

MS (ESI): m/z = 348 $[M + H]^+$.

HRMS (ESI): m/z [M + H] calcd for $C_{21}H_{18}NS_2$: 348.0881; found: 348.0883.

Acknowledgment

This work was supported by NSFC (21172029, 21202016, 31101010), Fundamental Research Funds for the Central Universities (11CXPY005), Research Fund for the Doctoral Program of Higher Education of China (RFDP 20100043120008) and China Postdoctoral Science Foundation (2012M51854).

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

References

(1) (a) Robinson, J. M.; Sakai, T.; Okano, K.; Kitawaki, T.; Danheiser, R. L. *J. Am. Chem. Soc.* **2010**, *132*, 11039. (b) Regás, D.; Ruiz, J. M.; Afonso, M. M.; Palenzuela, J. A. *J. Org. Chem.* **2006**, *71*, 9153. (c) Ruiz, J. M.; Regás, D.; Afonso, M. M.; Palenzuela, J. A. *J. Org. Chem.* **2008**, *73*, 7246.

(2) (a) Souto, J. A.; López, C. S.; Faza, O. N.; Alvarez, R.; de Lera, A. R. *Org. Lett.* **2005**, *7*, 1565. (b) Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2691.

(3) Delas, C.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2001**, *123*, 7937.

(4) (a) Faza, O. N.; López, C. S.; de Lera, A. R. *J. Org. Chem.* **2007**, *72*, 2617. (b) Knudsen, C. G.; Carey, S. C.; Okamura, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 6355.

(5) (a) Wu, Y.; West, F. G. *J. Org. Chem.* **2010**, *75*, 5410. (b) Funami, H.; Kusama, H.; Iwasawa, N. *Angew. Chem. Int. Ed.* **2007**, *46*, 909. (c) Lee, J. H.; Toste, F. D. *Angew. Chem. Int. Ed.* **2007**, *46*, 912. (d) Cergol, K. M.; Newton, C. G.; Lawrence, A. L.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. *Angew. Chem. Int. Ed.* **2011**, *50*, 10425.

(6) (a) Krause, N.; Purpura, M. *Angew. Chem. Int. Ed.* **2000**, *39*, 4355. (b) Purpura, M.; Krause, N. *Eur. J. Org. Chem.* **1999**, 267. (c) Dulcere, J.-P.; Grimaldi, J.; Santelli, M. *Tetrahedron Lett.* **1981**, *22*, 3179. (d) Dulcere, J. P.; Roumestant, M. L.; Gore, J. *Tetrahedron Lett.* **1972**, *13*, 4465.

(7) For examples of the substituent-regulated reactivity of vinylallenes, see: (a) Murakami, M.; Amii, H.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1476. (b) Murakami, M.; Ashida, S.; Matsuda, T. *J. Am. Chem. Soc.* **2004**, *126*, 10838.

(8) For a recent review on the chemistry of ketene dithioacetals, see: Pan, L.; Bi, X.; Liu, Q. *Chem. Soc. Rev.* **2013**, *42*, 1251.

(9) For selected reviews of allenes, see: (a) *Modern Allene Chemistry*; Krause, N.; Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, **2004**. (b) Ma, S. *Chem. Rev.* **2005**, *105*, 2829. (c) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133.

(10) Fang, Z.; Yuan, H.; Liu, Y.; Tong, Z.; Li, H.; Yang, J.; Barry, B.; Liu, J.; Liao, P.; Zhang, J.; Liu, Q.; Bi, X. *Chem. Commun.* **2012**, *48*, 8802.

(11) Song, J.; Fang, Z.; Liu, Y.; Li, R.; Xu, L.; Barry, B.; Liu, Q.; Bi, X. *Synlett* **2011**, 2551.

(12) Yoshida, M.; Gotou, T.; Ihara, M. *Tetrahedron Lett.* **2004**, *45*, 5573.

(13) (a) Swaminathan, S.; Narayanan, K. V. *Chem. Rev.* **1971**, *71*, 429. (b) Edens, M.; Boerner, D.; Chase, C. R.; Nass, D.; Schiavelli, M. D. *J. Org. Chem.* **1977**, *42*, 3403.

(14) (a) Wang, S.; Zhu, Y.; Wang, Y.; Lu, P. *Org. Lett.* **2009**, *11*, 2615. (b) Zhu, Y.; Yin, G.; Hong, D.; Lu, P.; Wang, Y. *Org. Lett.* **2011**, *13*, 1024. (c) Yin, G.; Zhu, Y.; Lu, P.; Wang, Y. *J. Org. Chem.* **2011**, *76*, 8922. (d) Zhu, Y.; Wen, S.; Yin, G.; Hong, D.; Lu, P.; Wang, Y. *Org. Lett.* **2011**, *13*, 3553. (e) Yin, G.; Zhu, Y.; Zhang, L.; Lu, P.; Wang, Y. *Org. Lett.* **2011**, *13*, 940. (f) Chen, X.; Wang, H.; Jin, X.; Feng, J.; Wang, Y.; Lu, P. *Chem. Commun.* **2011**, *47*, 2628. (g) Zhang, L.; Zhu, Y.; Yin, G.; Lu, P.; Wang, Y. *J. Org. Chem.* **2012**, *77*, 9510.

(15) (a) Zhang, X.; Teo, W. T.; Chan, P. W. H. *Org. Lett.* **2009**, *11*, 4990. (b) Zhang, X.; Teo, W. T.; Chan, P. W. H. *J. Org. Chem.* **2010**, *75*, 6290. (c) Rao, W.; Chan, P. W. H. *Org. Biomol. Chem.* **2010**, *8*, 4016. (d) Kothandaraman, P.; Mothe, S. R.; Toh, S. S. M.; Chan, P. W. H. *J. Org. Chem.* **2011**, *76*, 7633. (e) Mothe, S. R.; Lauw, S. J. L.; Kothandaraman, P.; Chan, P. W. H. *J. Org. Chem.* **2012**, *77*, 6937. (f) Susanti, D.; Koh, F.; Kusuma, J. A.; Kothandaraman, P.; Chan, P. W. H. *J. Org. Chem.* **2012**, *77*, 7166.

(16) (a) Yao, L.-F.; Tan, D.; Miao, X.; Huang, K.-W. *RSC Adv.* **2012**, *2*, 7594. (b) Guo, L.-N.; Duan, X.-H.; Liang, Y.-M. *Acc. Chem. Res.* **2011**, *44*, 111. (c) Zhu, H.-T.; Ji, K.-G.; Yang, F.; Wang, L.-J.; Zhao, S.-C.; Ali, S.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2011**, *13*, 684. (d) Wang, T.; Chen, X.; Chen, L.; Zhan, Z. *Org. Lett.* **2011**, *13*, 3324. (e) Pan, Y.; Zhao, S.; Ji, W.; Zhan, Z. *J. Comb. Chem.* **2009**, *11*, 103.

(17) (a) Wang, Y.; Li, W.; Che, G.; Bi, X.; Liao, P.; Zhang, Q.; Liu, Q. *Chem. Commun.* **2010**, *46*, 6843. (b) Wang, Y.; Bi, X.; Li, D.; Liao, P.; Wang, Y.; Yang, J.; Zhang, Q.; Liu, Q. *Chem. Commun.* **2011**, *47*, 809. (c) Xiong, T.; Li, Y.; Bi, X.; Lv, Y.; Zhang, Q. *Angew. Chem. Int. Ed.* **2011**, *50*, 7140. (d) Wang, Y.; Bi, X.; Li, W.; Li, D.; Zhang, Q.; Liu, Q.; Ondon, B. S. *Org. Lett.* **2011**, *13*, 1722. (e) Hu, Y.; Fu, X.; Barry, B.-D.; Bi, X.; Dong, D. *Chem. Commun.* **2012**, *48*, 690. (f) Wang, Z.; Bi, X.; Liao, P.; Zhang, R.; Liang, Y.; Dong, D. *Chem. Commun.* **2012**, *48*, 7076. (g) Xiang, D.; Bi, X.; Liao, P.; Fang, G.; Wang, Z.; Xin, X.; Dong, D. *RSC Adv.* **2013**, *3*, 386. (h) Wang, Z.; Bi, X.; Liao, P.; Lin, X.; Dong, D. *Chem. Commun.* **2013**, *49*, 1309.

(18) For reviews on the iron-catalyzed organic reactions, see: *Iron Catalysis in Organic Chemistry: Reactions and Applications*; Plietker, B., Ed.; Wiley-VCH: Weinheim, **2008**.

(19) (a) Okuyama, T. *Acc. Chem. Res.* **1986**, *19*, 370. (b) Okuyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 7134.

