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Zinc diiodide-promoted synthesis of trisubstituted allenes from propargylic amines†

Jinqiang Kuang,[a] Xinjun Tang[a] and Shengming Ma*[a,b]

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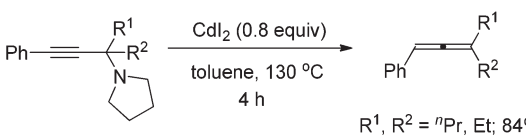
Zinc diiodide has been identified as an effective reagent for the efficient synthesis of trisubstituted allenes from propargylic amines. Compared to CdI_2 this protocol offers a green approach. Due to the easy preparation of propargylic amines through the method developed by this group, this method provides a two-step synthesis of trisubstituted allenes from 1-alkynes, ketones, and pyrrolidine. Finally, an efficient synthesis of such trisubstituted allenes from 1-alkynes, ketones, and pyrrolidine *via* simple filtration has been developed. Compared with the CdI_2-mediated protocol, the current protocol enjoys a much wider scope for ketones and affords functionalized allenes without further cyclization in some substrates.

Introduction

Allenes are playing more and more important roles in organic synthesis as many attractive transformations of allenes have been discovered,[1] thus, efficient synthetic methods of preparation of allenes from readily available starting materials are highly desirable.[2] With such a consideration, we have been paying close attention to the allenylation of terminal alkyne (ATA) reactions since its starting materials, *i.e.*, terminal alkynes, aldehydes (or ketones) and amines, are readily available. Based on the pioneering contribution of Crabbé *et al.* with paraformaldehyde,[3,4] in the last few years, we have developed a methodology for the synthesis of mono-substituted and 1,3-disubstituted allenes from terminal alkynes, aldehydes and amines.[5,6] However, it should be noted that these reactions are limited to paraformaldehyde or aldehydes: no or only a trace amount of allene was formed when ketones were used. There are only limited reports on synthesis of trisubstituted allenes from terminal alkynes. Bertrand *et al.* employed a cationic gold(I) complex for the catalytic coupling of enamines, which are derived from aldehydes or ketones, and terminal alkynes to non-terminal allenes,[7] however, only one example of ketone, *i.e.*, phenyl isopropyl ketone, was reported. Wang *et al.* developed a Cu(I)-catalyzed protocol for the reaction of 1-alkynes with *N*-tosylhydrazones of aldehydes or ketones to afford 1,3-disubstituted or trisubstituted allenes.[8] Recently, this group reported that the allenylation of terminal alkyne (ATA) reactions with methyl alkyl ketones or cyclic ketones may be realized to afford trisubstituted allenes efficiently when promoted by CdI_2,[9] in which propargylic amines derived from 1-alkynes, ketones and pyrrolidine were believed to be key intermediates. However, it should be noted that CdI_2 is a relatively toxic chemical, which is harmful to the environment and human beings. In this report, we would like to report that ZnI_2, cheaper, non-toxic and environmentally benign, is very effective for converting corresponding propargylic amines derivatized from ketones to trisubstituted allenes. Finally a practical two-step protocol from terminal alkynes and ketones to trisubstituted allenes *via* simple filtration has also been developed.

Results and discussion

We have recently developed a CuBr-catalyzed method for the efficient synthesis of propargylic amines.[10] Through this method, various propargylic amines derived from terminal alkynes, ketones and pyrrolidine could be obtained in excellent yields. Under the mediation of CdI_2, these types of propargylic amines may be converted into trisubstituted allenes efficiently (eqn (1)).[9]



R^1, R^2 = ^{n}Pr, Et; 84%
R^1, R^2 = ^{i}Pr, Me; 81%
R^1, R^2 = ^{n}Pr, ^{n}Pr; 88%
R^1, R^2 = Ph, Me; 45%

(1)

To our delight, ZnI_2 could also promote the transformation effectively (entry 1, Table 1), which nicely provides chemists an

[a]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China. E-mail: masm@sioc.ac.cn*
[b]*Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, P. R. China*

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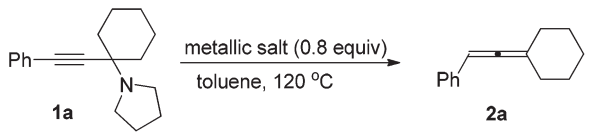
environmentally friendly choice to produce trisubstituted allenes. In comparison, $ZnBr_2$, $Zn(OTf)_2$, CuBr, and $CuBr_2$ might also be a choice, however, much less effective (entries 2–4 and 9, Table 1). CuI, $KAuCl_4{\cdot}2H_2O$,[11a] and $AgNO_3$ [11b] are extremely ineffective for such transformation (entries 10–12, Table 1). Further screening of reaction temperature and loading of ZnI_2 led to a set of optimal conditions: 0.6 equiv. of ZnI_2 in toluene at 120 °C (entry 5, Table 1). As a comparison, CdI_2 provided the product in 88% NMR yield (entry 13, Table 1).

Table 1 Identifying the best reagent for the synthesis of allene **2a** from propargylic amine **1a** [a]

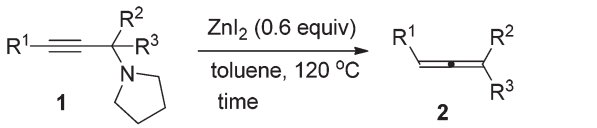


Entry	Metallic salt (*X* equiv.)	Time (h)	Yield of **2a** [b] (%)	Recovery of **1a** [b] (%)
1	ZnI_2 (0.8)	1.1	78	—
2	$ZnBr_2$ (0.8)	1.1	74	—
3	$Zn(OTf)_2$ (0.8)	1.1	69	—
4	CuBr (0.8)	14.5	18	8
5	**ZnI_2 (0.6)**	**0.9**	77	—
6	ZnI_2 (0.5)	1.6	65	—
7[c]	ZnI_2 (0.6)	1.6	72	—
8[d]	ZnI_2 (0.6)	2.5	64	—
9	$CuBr_2$ (0.6)	10	17	6
10	CuI (0.6)	3	Trace	75
11	$AgNO_3$ (0.6)	3	2	45
12	$KAuCl_4{\cdot}2H_2O$ (0.1)	3	4	60
13	CdI_2 (0.8)	2	88	—

[a] The reaction was carried out on a 0.5 mmol scale in 1.5 mL of toluene. [b] Determined by ^1H NMR analysis of the crude reaction mixture with CH_2Br_2 as the internal standard. [c] The reaction was carried out at 110 °C. [d] The reaction was carried out at 100 °C.

With the optimal conditions in hand, we then investigated the scope of the transformation. Under the mediation of ZnI_2, propargylic amine **1a** afforded trisubstituted allene **2a** in 63% isolated yield (entry 1, Table 2). Propargylic amines **1b–1f** derived from phenylacetylene, pyrrolidine, and different methyl ketones were transformed to allenes **2b–2f** smoothly in moderate yields (entries 2–6, Table 2). Notably, the reaction of substrate **1c** bearing an isopropyl group proceeded smoothly, albeit with a longer reaction time, which may be due to the steric hindrance of *i*-Pr (entry 3, Table 2). Surprisingly, propargylic amines **1g–1i** also require longer reaction times (entries 7–9, Table 2). Since ethyl and *n*-propyl groups are generally considered as not so bulky, it indicates that the reaction rate is very sensitive to the steric effect of R^2 and R^3. It should be noted that acyclic non-methyl ketones are not suitable for our previously reported CdI_2-mediated ATA reaction to afford trisubstituted allenes.[9] When propargylic amines **1j–1q**, which were prepared from differently substituted arylacetylenes, were applied in the reaction, allenes bearing different aryl groups were obtained in 50–65% isolated yields (entries 10–17, Table 2). Substitutes on the phenyl group have only a slight impact on the yields; a halogen substituent survived in the reaction (entries 11, 12 and 14–16, Table 2), affording products ready for further elaborations. When propargylic amines derived from alkyl-substituted acetylenes were treated under the standard conditions, the corresponding allene products were produced in higher yields (entries 18–21, Table 2), as compared to the arylacetylene-based propargylic amines.

Table 2 ZnI_2-mediated synthesis of trisubstituted allenes from propargylic amines[a]

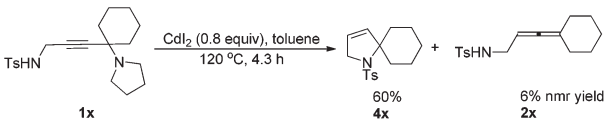


	1			
Entry	R^1	R^2; R^3	Time (h)	Yield of **2**[b] (%)
1	Ph	$-(CH_2)_5-$ (**1a**)	0.8	63 (**2a**)
2	Ph	Me; Et (**1b**)	1.1	57 (**2b**)
3	Ph	Me; *i*-Pr (**1c**)	5.3	62 (**2c**)
4	Ph	Me; *n*-Bu (**1d**)	1.5	53 (**2d**)
5	Ph	Me; *n*-Hex (**1e**)	1.0	55 (**2e**)
6	Ph	Me; $BnCH_2$ (**1f**)	1.0	56 (**2f**)
7	Ph	Et; *n*-Pr (**1g**)	7.8	52 (**2g**)
8	Ph	*n*-Pr; *n*-Pr (**1h**)	5.0	56 (**2h**)
9	Ph	Et; Et (**1i**)	4.0	60 (**2i**)
10	4-$MeOC_6H_4$	$-(CH_2)_5-$ (**1j**)	2.0	65 (**2j**)
11	4-BrC_6H_4	$-(CH_2)_5-$ (**1k**)	2.0	63 (**2k**)
12	3-BrC_6H_4	$-(CH_2)_5-$ (**1l**)	2.0	60 (**2l**)
13	4-$MeOC_6H_4$	Me; *n*-Bu (**1m**)	0.9	50 (**2m**)
14	4-BrC_6H_4	Me; *n*-Bu (**1n**)	2.7	52 (**2n**)
15	3-BrC_6H_4	Me; *n*-Bu (**1o**)	1.0	55 (**2o**)
16	2-ClC_6H_4	Me; *n*-Bu (**1p**)	1.0	56 (**2p**)
17	4-MeC_6H_4	Me; *n*-Bu (**1q**)	1.7	57 (**2q**)
18	*n*-C_6H_{13}	Me; *n*-Bu (**1r**)	2.0	67 (**2r**)
19	*n*-C_8H_{17}	$-(CH_2)_5-$ (**1s**)	1.3	81 (**2s**)
20	*n*-C_8H_{17}	Me; Me (**1t**)	1.3	61 (**2t**)
21	*n*-C_8H_{17}	$-(CH_2)_4-$ (**1u**)	1.6	58 (**2u**)

[a] The reaction was carried out on a 1.0 mmol scale in 3 mL of toluene. [b] Isolated yield.

The method could also tolerate substrates bearing reactive functional groups such as hydroxyl and amide functionalities (Table 3), which could easily undergo further transformations for the preparation of other functionalized allenes.[1,2c,12]

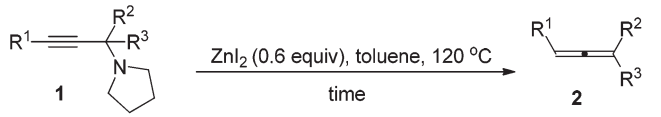
In fact, as a comparison, when **1x** was treated with CdI_2, in addition to the corresponding allenyl amide **2x**, the related cyclization product **4x** was also obtained in 60% yield as the major product (eqn (2)).



(2)

Furthermore, it is interesting to observe that the reaction depends highly on the structure of the amine applied: pro-

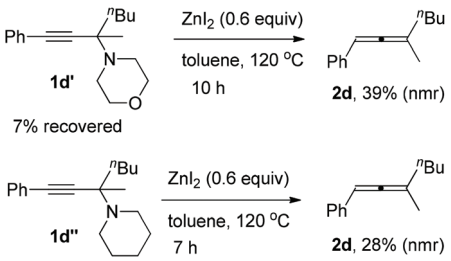
Table 3 ZnI_2-mediated synthesis of trisubstituted allenes bearing a hydroxyl or an amide group[a]



	1		
Entry	R^1; R^2; R^3	Time (h)	Yield of 2 (%)
1	$Me_2C(OH)$; Me; *n*-Bu (**1v**)	2.0	58[b] (**2v**)
2	$HO(CH_2)_2$; Me; *n*-Bu (**1w**)	1.0	53[b] (**2w**)
3	$TsNHCH_2$; $-(CH_2)_5-$ (**1x**)	1.0	79[b] (**2x**)
4	$TsNHCH(n\text{-}C_7H_{15})$; $-(CH_2)_5-$ (**1y**)	1.8	92[b] (**2y**)
5	TsNHPhCH; $-(CH_2)_5-$ (**1z**)	1.3	85[b] (**2z**)

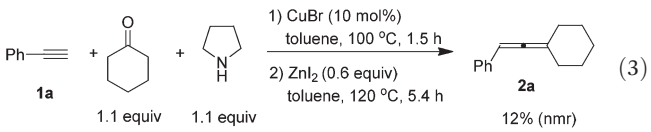
[a] The reaction was carried out on a 1.0 mmol scale in 3 mL of toluene. Ts = *p*-toluenesulfonyl. [b] Isolated yield.

pargylic amines **1d′** and **1d″** from phenylacetylene, 2-hexanone, and six-membered morpholine or piperidine may also afford corresponding trisubstituted allenes, however, with a very low efficiency (Scheme 1).



Scheme 1 Synthesis of trisubstituted allenes from propargylic amines derived from morpholine or piperidine.

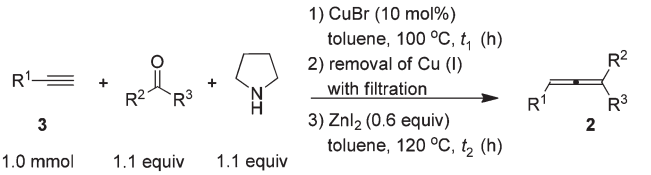
Since CuBr-catalyzed synthesis of propargylic amines from 1-alkynes, ketones, and pyrrolidine[10] and ZnI_2-promoted the synthesis of trisubstituted allenes from propargylic amines both proceeded smoothly in the same solvent, we tried to combine them in one pot, however, a poor result was obtained (eqn (3)).



(3)

After careful study and optimizations, we found that filtration to remove Cu(I) after the first step is essential for a successful second step. Based on this, we developed a convenient two-step synthesis of trisubstituted allenes from 1-alkynes, ketones, and pyrrolidine. Propargylic amines were firstly synthesized through the CuBr-catalyzed KA[2] reaction[10] and then subjected to the ZnI_2-mediated transformation after a simple filtration through a short pad of silica gel to remove Cu(I). The substrate scope of the reaction was evaluated for various 1-alkynes and ketones and the typical results are summarized in Table 4. Besides phenylacetylene **3a**, substituted phenylacetylenes bearing 4-Cl, 4-Br, and 4-Me substituents reacted with cyclohexanone to afford the corresponding allenes in moderate yields (entries 1–4, Table 4). Alkyl-substituted 1-alkyne **3f** could react with cyclohexanone to afford alkyl-substituted allene **2s** in 74% isolated yield (entry 5, Table 4). Since 2,3-allenols and 2,3-allenyl amines are useful in organic synthesis,[1,2c,11] we also investigated the tolerance of amino and hydroxyl groups in the reaction: encouragingly, terminal propargylic toluenesulfonylamide **3g** may be applied, affording 2,3-allenyl tosylamide **2x** in 30% isolated yield (entry 6, Table 4). The reaction of terminal homopropargylic alcohol **3h** with cyclohexanone afforded 2,3-allenol **2w** in 53% isolated yield (entry 7, Table 4). Moreover, terminal alkynes with common protecting groups such as THP and TBS were also tolerated, producing corresponding allenes **2ad** and **2ae** in moderate yields (entries 8 and 9, Table 4). Cyclopentanone reacted with 1-decyne **3f** to afford trisubstituted allene **2u** smoothly, however, with an obviously decreased yield as compared to that of cyclohexanone (entry 10 *vs.* 5, Table 4). When acetone was used, allene **2t** bearing two methyl groups on the allene moiety could be obtained in 49% isolated yield, although two equivalents of acetone were required to ensure the yield due to the lower boiling point of acetone (entry 11, Table 4). 2-Octanone may also be used in the reaction, affording allene **2af** in moderate yield (entry 12, Table 4). Meanwhile, aromatic ketones gave a disappointing result in this reaction.

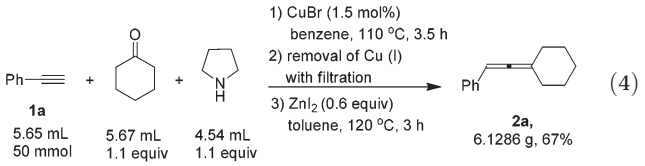
Table 4 Two-step synthesis of trisubstituted allenes from 1-alkynes, ketones, and pyrrolidine



	3[a]			
Entry	R^1	R^2; R^3	t_1/t_2 (h)	Yield of 2[b] (%)
1	Ph (**3a**)	$-(CH_2)_5-$	1.1/1.5	61 (**2a**)
2	4-ClC_6H_4 (**3c**)	$-(CH_2)_5-$	1.5/1.5	57 (**2aa**)
3	4-BrC_6H_4 (**3d**)	$-(CH_2)_5-$	1.5/0.5	51 (**2k**)
4	4-MeC_6H_4 (**3e**)	$-(CH_2)_5-$	1.1/0.8	51 (**2ab**)
5	*n*-C_8H_{17} (**3f**)	$-(CH_2)_5-$	1.0/0.7	74 (**2s**)
6	$TsNHCH_2$ (**3g**)	$-(CH_2)_5-$	1.9/3.5	30 (**2x**)
7	$HO(CH_2)_2$ (**3h**)	$-(CH_2)_5-$	0.9/1.0	53 (**2ac**)
8	$TBSOCH_2$ (**3i**)	$-(CH_2)_5-$	1.2/0.8	52 (**2ad**)
9	$THPOCH_2$ (**3j**)	$-(CH_2)_5-$	1.1/0.9	43 (**2ae**)
10	*n*-C_8H_{17} (**3f**)	$-(CH_2)_4-$	1.3/1.3	50 (**2u**)
11[c]	*n*-C_8H_{17} (**3f**)	Me; Me	3.1/0.9	49 (**2t**)
12[d]	*n*-C_8H_{17} (**3f**)	Me; *n*-C_6H_{13}	1.9/0.6	45 (**2af**)

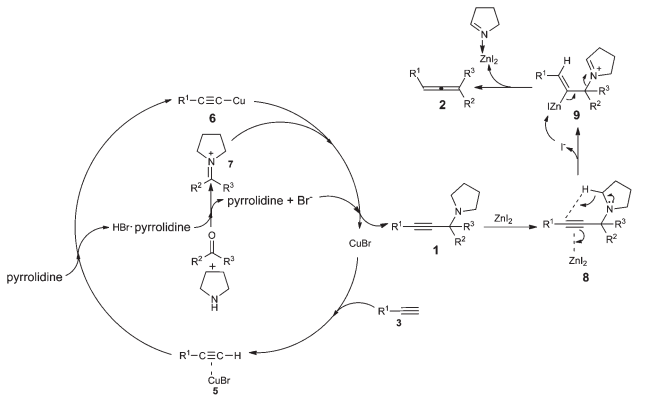
[a] Ts = *p*-toluenesulfonyl; THP = 2-tetrahydropyranyl; TBS = *t*-butyldimethylsilyl. [b] Isolated yield. [c] 2.0 equiv. of acetone were used. [d] 1.3 equiv. of 2-octanone were used.

When the reaction was carried out on a 50 mmol-scale, only 1.5 mol% of CuBr was needed[10] and allene **2a** was afforded in 67% isolated yield (eqn (4)).



(4)

Based on recent reports of the ATA reactions,[9] we proposed a plausible mechanism for this reaction. In the first place, ketoniminium **7**, formed *in situ* from ketone and pyrrolidine, would react with alkynyl copper species **6** to give propargylic amine **1**. Then the triple in propargylic amine **1** coordinates with ZnI_2 which was followed by 1,5-hydride transfer and β-elimination to afford the corresponding trisubstituted allene **2** (Scheme 2). We reasoned that the coordination of Zn^{2+} with the *in situ* generated imine makes the Zn^{2+} much less active after the reaction.



Scheme 2 Proposed mechanism for the reaction.

Conclusions

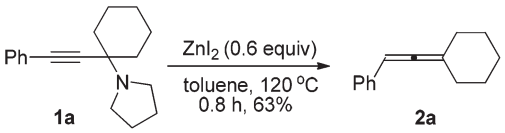
In conclusion, we have developed an efficient ZnI_2-mediated method for the synthesis of trisubstituted allenes from propargylic amines bearing a quaternary carbon center, which are readily available from 1-alkynes, ketones and amines through our recently established method.[10] This ZnI_2-mediated method meets our long-term goal of efficient synthesis of allenes from readily available chemicals in common chemistry laboratories. Based on this, a two-step synthesis of trisubstituted allenes from terminal alkynes and ketones has been developed. Due to the fact that ZnI_2 is cheaper, non-toxic and environmentally benign, and enjoys a much wider scope as compared to CdI_2, the method constitutes an urgent supplement to the previously reported CdI_2-promoted synthesis of trisubstituted allenes and will be of great interest to chemists. Further studies including the asymmetric version of this reaction are being pursued in our laboratory.

Experimental section

General information

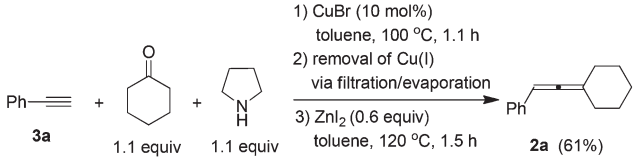
CuBr (98.5%) and pyrrolidine were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further treatment. ZnI_2 (98%) was purchased from Acros and kept in a glove box. Toluene was dried over a sodium wire with benzophenone as the indicator and distilled freshly before use. Anhydrous benzene was purchased from Aladdin and used without further treatment. Other reagents were used without further treatment. All the temperatures are referred to the oil baths used.

Synthesis of 1,1-pentamethylene-3-phenylpropadiene 2a from propargylic amine 1a.



To a flame-dried Schlenk tube was added anhydrous ZnI_2 (191.3 mg, 0.6 mmol). The Schlenk tube was then taken out and dried under vacuum with a heating gun. **1a** (252.9 mg. 1.0 mmol) and 3 mL of toluene were added sequentially under an Ar atmosphere. The Schlenk tube was then equipped with a condenser and placed in a pre-heated oil bath of 120 °C with stirring for 0.8 h and monitored by TLC. After cooling to room temperature, the crude reaction mixture was filtered through a short pad of silica gel with a sand-core funnel eluted with ethyl acetate (15 mL). After evaporation, the residue was purified by chromatography on silica gel (eluent: 30–60 °C petroleum ether) to afford **2a**[13] (116.7 mg, 63%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.23 (m, 4 H, ArH), 7.18–7.10 (m, 1 H, ArH), 6.02–5.96 (m, 1 H, =CH), 2.32–2.12 (m, 4 H, 2 × CH_2), 1.77–1.48 (m, 6 H, 3 × CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 199.6, 136.1, 128.5, 126.5, 126.2, 106.4, 92.3, 31.3, 27.7, 26.1; MS (EI) *m*/*z* 184 (M^+, 70.53), 141 (100); IR (neat) 3030, 2929, 2887, 2853, 1951, 1598, 1496, 1459, 1446, 1256, 1237, 1198, 1069, 1027 cm^{-1}.

Synthesis of 1,1-pentamethylene-3-phenylpropadiene 2a from phenylacetylene, cyclohexanone, and pyrrolidine.

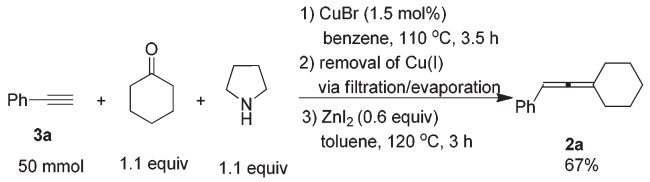


To a flame-dried Schlenk tube were added CuBr (14.6 mg, 0.1 mmol), phenyl acetylene **3a** (102.4 mg, 1.0 mmol)/toluene (0.5 mL), cyclohexanone (107.8 mg, 1.1 mmol)/toluene (0.5 mL), and pyrrolidine (93.0 μL, d = 0.8618 g mL^{-1}, 80.1 mg, 1.1 mmol) sequentially. The Schlenk tube was then stirred at 100 °C until the completion of the reaction as monitored by TLC (1.0 h). After cooling to room temperature, the crude reaction mixture was filtered through a short pad of silica gel with a sand-core funnel eluted with acetone (20 mL). After evapo-

ration, the crude product was used in the next step without further treatment.

To another Schlenk tube was added anhydrous ZnI_2 (191.4 mg, 0.6 mmol). The Schlenk tube was then dried under vacuum with a heating gun. The above crude product was then dissolved in toluene (3 mL) and transferred to the Schlenk tube *via* a syringe under an Ar atmosphere. The Schlenk tube was then equipped with a condenser and placed in a pre-heated oil bath of 120 °C with stirring. After 1.5 h, the reaction was complete as monitored by TLC, the crude reaction mixture was cooled to room temperature and filtrered through a short pad of silica gel with a sand-core funnel eluted with ethyl ether (20 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **2a**[13] (112.1 mg, 61%) as a liquid (eluent: petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.22 (m, 4 H, ArH), 7.20–7.10 (m, 1 H, ArH), 6.02–5.96 (m, 1 H, =CH), 2.34–2.12 (m, 4 H, 2 × CH_2), 1.80–1.46 (m, 6 H, 3 × CH_2).

Fifty mmol-scale reaction for the synthesis of 1,1-pentamethylene-3-phenylpropadiene from phenyl acetylene, cyclohexanone, and pyrrolidine (2a).



To a three-necked flask equipped with a Dean-Stark trap and a condenser dried under vacuum with a heating gun, were added CuBr (11 mg, 0.75 mmol), **3a** (5.65 mL, d = 0.93 g mL^{-1}, 5.25 g, 97%, 50 mmol), cyclohexanone (5.67 mL, d = 0.95 g mL^{-1}, 5.39 g, 55 mmol), pyrrolidine (4.54 mL, d = 0.86 g mL^{-1}, 3.90 g, 55 mmol), and benzene (50 mL) sequentially under an Ar atmosphere. The flask was then placed in a pre-heated oil bath at 110 °C with stirring for 3.5 h and monitored by TLC. After cooling to room temperature, the crude reaction mixture was filtered through a short pad of silica gel with a sand-core funnel eluted with ethyl acetate (120 mL). After evaporation, the crude product was used in the next step without further treatment.

To another three-necked flask equipped with a condenser was added anhydrous ZnI_2 (9.78 g, 30 mmol). The flask was then dried under vacuum with a heating gun. The above crude product was then dissolved in toluene (150 mL) and transferred to the flask *via* a syringe under an Ar atmosphere. The flask was then placed in a pre-heated oil bath of 120 °C with stirring. After 3.0 h, the reaction was complete as monitored by TLC, the crude reaction mixture was cooled to room temperature and filtered through a short pad of silica gel with a sand-core funnel eluted with ethyl ether (100 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **2a**[13] (6.13 g, 67%) as a liquid (eluent: petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 4 H, ArH), 7.20–7.12 (m, 1 H, ArH), 6.02–5.97 (m, 1 H, =CH), 2.32–2.12 (m, 4 H, 2 × CH_2), 1.77–1.47 (m, 6 H, 3 × CH_2).

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