Tetrahedron 67 (2011) 3081–3090

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of conjugated enynes from ketones and aldehydes by 1,2-CC insertion and 1,2-CH insertion of carbenoids as the key reactions

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ARTICLE INFO

Article history:
Received 11 January 2011
Received in revised form 25 February 2011
Accepted 28 February 2011
Available online 5 March 2011

Keywords:
Magnesium carbenoid
Lithium carbenoid
Sulfoxide–magnesium exchange reaction
Conjugated enyne
1,2-Carbon–carbon insertion

ABSTRACT

The addition reactions of 1-chlorovinyl *p*-tolyl sulfoxides, which were derived from ketones and chloromethyl *p*-tolyl sulfoxide, with lithium acetylides gave adducts in moderate to good yields. Treatment of the adducts with Grignard reagents resulted in the formation of conjugated enynes in good to high yields via the 1,2-carbon–carbon insertion (1,2-CC insertion) reaction of the generated magnesium carbenoid intermediates. On the other hand, the addition reactions of 1-chlorovinyl *p*-tolyl sulfoxides derived from aldehydes with lithium acetylides directly gave conjugated enynes bearing a *p*-tolyl sulfinyl group at the 1-position through the 1,2-carbon–hydrogen insertion (1,2-CH insertion) reaction of the generated lithium carbenoid intermediates. These procedures provide a good way for the synthesis of multi-substituted conjugated enynes from ketones and aldehydes.

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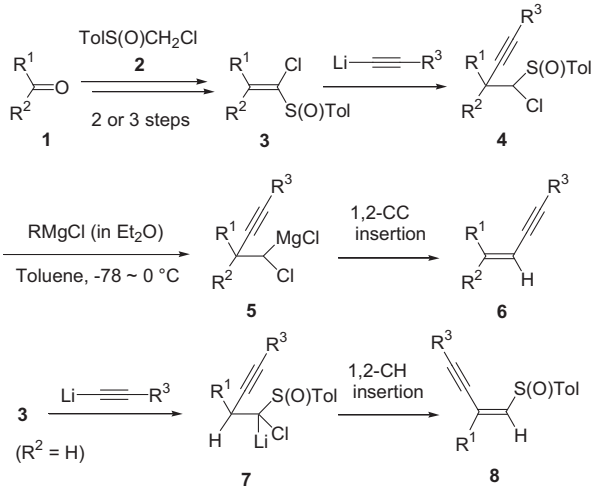
1. Introduction

Recently, conjugated enynes are of great interest in organic, synthetic organic, and bioorganic chemistry. The enediyne anticancer antibiotics, such as calicheamicine, dynemicin, and esperamicin, have conjugated enyne moiety as the essential structure for their biological activities.[1] Conjugated enynes are also very important compounds in synthetic organic chemistry.[2]

The synthesis of conjugated enynes has received considerable attention in these days and some methods have already been published. The cross-coupling of vinyl halides with terminal acetylenes in the presence of Pd(0) or Pd(II)/Cu is known as Sonogashira coupling.[3] Oxidative Pd(II)-catalyzed Heck-type coupling of alkynes with α,β-unsaturated carbonyl compounds is also the method for the coupling of acetylenes with olefins.[4] Rhodium- or palladium-catalyzed hydroalkynylation of internal alkynes with silylacetylenes,[5] and dimerization of terminal alkynes[6] are the methods for the synthesis of conjugated enynes from two acetylenes. Some other methods for the synthesis of conjugated enynes have been reported.[7] We also reported a synthesis of conjugated enynes based on the reaction of magnesium alkylidene carbenoids with lithium acetylides.[8]

We have been interested in the chemistry of carbenoids, especially magnesium carbenoids, in the development of new synthetic methods.[9] In continuation of our studies for the chemistry and synthetic uses of magnesium carbenoids, we recently found a versatile method for the synthesis of conjugated enynes starting from ketones and aldehydes as shown in Scheme 1.



Scheme 1.

Thus, the addition reactions of 1-chlorovinyl *p*-tolyl sulfoxides **3**, synthesized from ketones **1** and chloromethyl *p*-tolyl sulfoxide **2**, with lithium acetylides gave adducts **4** in moderate to good yields.

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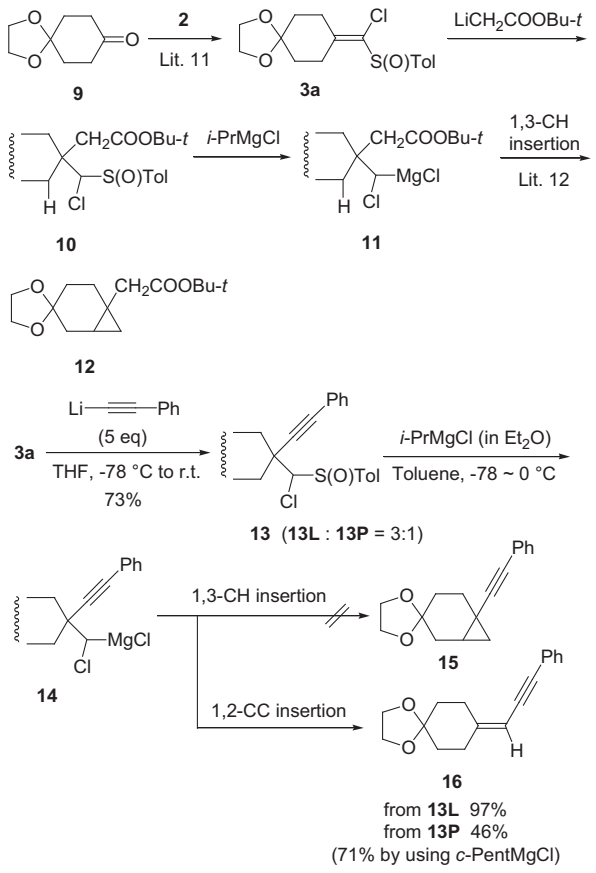
0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.02.079

Treatment of the adducts **4** with Grignard reagents resulted in the formation of conjugated enynes **6** via the 1,2-CC insertion reaction of the generated magnesium carbenoid intermediates **5**. On the other hand, the addition reactions of 1-chlorovinyl *p*-tolyl sulfoxides **3** (R^2=H) derived from aldehydes **1** (R^2=H) and chloromethyl *p*-tolyl sulfoxide **2** with lithium acetylides directly gave conjugated enynes bearing a *p*-tolyl sulfinyl group at the 1-position **8** through the 1,2-CH insertion reaction of the generated lithium carbenoid intermediates **7**. In this paper we would like to report, in detail, the results described above.[10]

2. Results and discussion

2.1. Synthesis of conjugated enynes from ketones with chloromethyl *p*-tolyl sulfoxide and acetylenes

In our previous study, we reported the synthesis of bicyclo[n.1.0]alkanes from ketones by 1,3-CH insertion reaction of magnesium carbenoids as the key reaction. For example, as shown in Scheme 2, addition reaction of 1-chlorovinyl *p*-tolyl sulfoxide **3a**, which was synthesized from ketone **9** with chloromethyl *p*-tolyl sulfoxide in high overall yield,[11] with lithium enolate of *tert*-butyl acetate to give adduct **10** in quantitative yield. Treatment of adduct **10** with *i*-PrMgCl resulted in the formation of magnesium carbenoid intermediate **11**, from which 1,3-CH insertion reaction took place to afford bicyclo[4.1.0]heptane bearing a *tert*-butyl acetate moiety on the bridgehead carbon **12** in quantitative yield.[12]



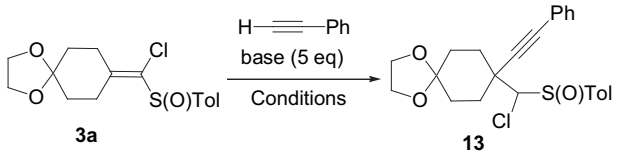
Scheme 2.

As an application of this chemistry into the synthesis of bicyclo[n.1.0]alkanes bearing an alkyne moiety on the bridgehead carbon, we planned the procedure shown in Scheme 2. Thus, 1-chlorovinyl *p*-tolyl sulfoxide **3a**[11] was treated with 5 equiv of lithium acetylide (derived from phenylacetylene with *n*-BuLi) to give adduct **13** in 73% yield as an easily separable mixture of two diastereomers (less polar adduct **13L** and more polar adduct **13P** on silica gel TLC; the ratio 3:1, respectively). Main diastereomer **13L** was treated with 5 equiv of *i*-PrMgCl (in ether) in toluene at −78 °C to result in the formation of magnesium carbenoid intermediate **14**. The reaction mixture was slowly allowed to warm to 0 °C to give a clean reaction mixture from which a single product was obtained. Initially, as described above, bicyclo[4.1.0]heptane **15** was expected to be formed by the 1,3-CH insertion reaction of magnesium carbenoid **14**.[12] However, very interestingly, the product had an olefinic hydrogen and was confirmed to be conjugated enyne **16** (97% yield) and no bicyclo[4.1.0]heptane **15** was observed. The same reaction of the minor diastereomer **13P** gave the same conjugated enyne **16**; however, the yield was moderate (46%). Significant difference about the yields of **16** from diastereomers **13P** and **13L** was observed; however, the real reason for this difference is still not clear at present.[10]

Although the expected bicyclo[4.1.0]heptane **15** could not be obtained, we recognized that this reaction is unprecedented and would become quite interesting way for preparing conjugated enynes. At first, we investigated to obtain better yield of **16** from the minor diastereomer **13P** and cyclopentylmagnesium chloride (*c*-PentMgCl; in ether solution) was found to be the Grignard reagent of choice and 71% yield of **16** was obtained.[10] We use *i*-PrMgCl and *c*-PentMgCl for the reaction of the less polar adduct (**L**) and the more polar adduct (**P**), respectively, throughout in this study.

Next, an investigation to find the best conditions for the addition reaction of **3a** with lithium phenylacetylide was carried out and the results are summarized in Table 1. The conditions in entry 1 have been mentioned already in the text. As shown in entries 2–7, the addition reaction could be started at −30 °C and somewhat better yield was obtained (entry 2). Starting the reaction at 0 °C gave diminished yield (entry 3). Using LDA, instead of *n*-BuLi, as the base gave much better yield of **13** (entry 4). Toluene and diethyl ether were proved to be unsuitable solvents in this reaction (entries 6 and 7). As a result, we decided that the conditions in entry 4 were the conditions of choice in this study.

Table 1
Investigation for the addition reaction of lithium acetylide derived from phenylacetylene to 1-chlorovinyl *p*-tolyl sulfoxide **3a**



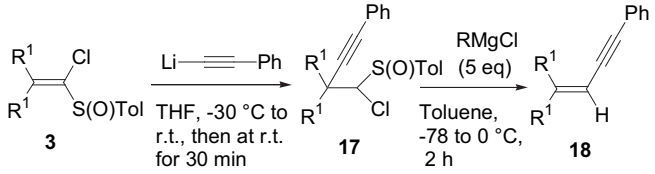
Entry	Conditions				**13**
	Temp/°C	Time/h	Solvent	Base	Yield/%
1	−78 to rt	3	THF	*n*-BuLi	73
2	−30 to rt	2	THF	*n*-BuLi	75
3	0 to rt	1	THF	*n*-BuLi	60
4	*−30 to rt*	*2*	*THF*	*LDA*	*80*
5	−30 to rt	2	THF	LHMDS	48
6	−30 to rt	2	Toluene	LDA	20[a]
7	−30 to rt	2	Et_2O	LDA	19[b]

[a] Starting material **3a** was recovered in 69% yield.
[b] Starting material **3a** was recovered in 64% yield.

Next, the substrate scope of this procedure was investigated with some 1-chlorovinyl *p*-tolyl sulfoxides derived from symmetrical ketones (**3b**–**e**) by using above-mentioned best conditions and the results are summarized in Table 2. Thus, 1-chlorovinyl *p*-tolyl sulfoxides **3** derived from cyclohexanone, cyclododecanone, cyclopentadecanone, and 4-heptanone, were used as the representative examples for the substrates and phenylacetylene was

used as the representative example for the alkyne. The addition reaction of 1-chlorovinyl *p*-tolyl sulfoxides derived from large membered cyclic ketones and an acyclic ketone was not completed; however, about 30% yield of adducts **17b**–**d** were obtained (entries 3–8). In these cases, significant amount of the staring materials were recovered and the yields calculated based on the consumed starting material were moderate.

Table 2
Addition reaction of **3** with lithium acetylide generated from phenylacetylene with LDA followed by the treatment with Grignard reagents to give conjugated enynes **18**



Entry	**3**	**17**	RMgCl	**18**
	R^1	Yield/% (diastereomeric ratio)[a]		Yield/%
1	**3b** $-(CH_2)_5-$	**17a** 73 (2:1)	*i*-PrMgCl	**18a** 98 (from **17aL**)
2			*c*-PentMgCl	**18a** 42 (from **17aP**)
3	**3c** $-(CH_2)_{11}-$	**17b** 36 (3:2)[b]	*i*-PrMgCl	**18b** 93 (from **17bL**)
4			*c*-PentMgCl	**18b** 96 (from **17bP**)
5	**3d** $-(CH_2)_{14}-$	**17c** 33 (3:2)[c]	*i*-PrMgCl	**18c** 91 (from **17cL**)
6			*c*-PentMgCl	**18c** 99 (from **17cP**)
7	**3e** $CH_3(CH_2)_2$	**17d** 29 (9:2)[d,e]	*i*-PrMgCl	**18d** 98 (from **17dL**)
8			*c*-PentMgCl	**18d** 99 (from **17dP**)

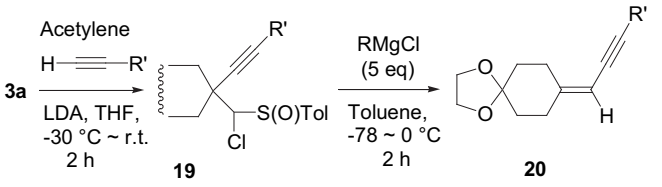
[a] The ratio for less polar product (**L**) and more polar product (**P**) on silica gel TLC.
[b] Starting material was recovered in 27% yield.
[c] Starting material was recovered in 42% yield.
[d] Starting material was recovered in 59% yield.
[e] The reaction mixture was slowly allowed to warm from −30 °C to room temperature for 2 h, then stirred at room temperature for 2 h.

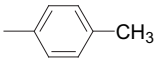
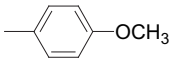
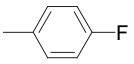
Treatment of adducts **17a**–**d** with Grignard reagents was conducted in the same way as described above. The reaction of **17a**, which has six-membered cyclic carbon chain, showed again significant difference in the reactivity with respect to the two diastereomers (entries 1 and 2). Quite interestingly, in the reaction with the adducts bearing a large cyclic carbon chain (**17b**,**c**) or acyclic carbon chain (**17d**), both diastereomers gave almost quantitative yields of the desired conjugated enynes **18** (entries 3–8). In other words, the differences in the reactivity appear only when the reaction is carried out with adducts **17** derived from medium-sized cyclic ketones. From the results shown in Table 2, the generality of this procedure was verified.

Further, substrate scope about the alkynes was investigated with 1-chlorovinyl *p*-tolyl sulfoxide **3a** and the results are summarized in Table 3. The addition reaction of lithium acetylides derived from arylacetylenes and (trimethylsilyl)acetylene with 1-chlorovinyl *p*-tolyl sulfoxide **3a** proceeded smoothly to afford moderate to good yields of adducts **19a**–**d** (entries 1–8). However, quite interestingly, addition reaction of lithium acetylide derived from an alkylacetylene, 4-phenyl-1-butyne, with **3a** did not proceed at all (entry 9). Generation of the magnesium carbenoids from the adducts was conducted with *i*-PrMgCl or *c*-PentMgCl, and similar results (less polar adducts gave almost quantitative yields of conjugated enynes **20** and more polar adducts gave somewhat lower yields) were observed (compare the results in Table 3 with those shown in Scheme 2 and Table 2, entries 1 and 2).

As the addition reaction of 1-chlorovinyl *p*-tolyl sulfoxides with lithium acetylide itself did not give the desired adducts, the conjugated enynes without a substituent on the acetylenic carbon was synthesized from the adducts with (trimethylsilyl)acetylene.

Table 3
Addition reaction of **3a** with lithium acetylide generated from acetylenes with LDA and the reaction of the adducts **19** with Grignard reagents to give conjugated enynes **20**



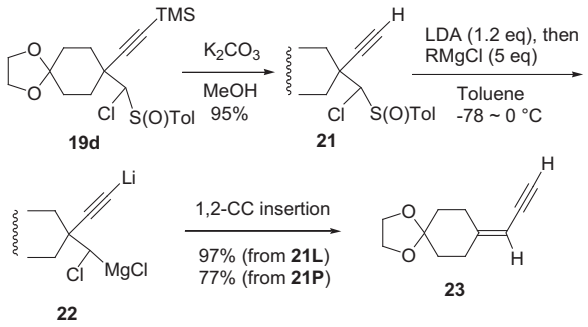
Entry	Acetylene	**19**	RMgCl	**20**
	R'	Yield/% (diastereomeric ratio)[a]		Yield/%
1		**19a** 69[b]	*i*-PrMgCl	**20a** 93 (from **19aL**)
2		(2:1)	*c*-PentMgCl	**20a** 54 (from **19aP**)
3		**19b** 55[c]	*i*-PrMgCl	**20b** 93 (from **19bL**)
4		(2:1)	*c*-PentMgCl	**20b** 80 (from **19bP**)
5		**19c** 66	*i*-PrMgCl	**20c** 95 (from **19cL**)
6		(2:1)	*c*-PentMgCl	**20c** 56 (from **19cP**)
7	$-Si(CH_3)_3$	**19d** 77	*i*-PrMgCl	**20d** 99 (from **19dL**)
8		(5:2)	*c*-PentMgCl	**20d** 52 (from **19dP**)
9	$-CH_2CH_2Ph$	—[d]		

[a] The ratio for less polar product (**L**) and more polar product (**P**) on silica gel TLC.
[b] The reaction mixture was slowly allowed to warm from −30 °C to room temperature for 2 h and then stirred for 30 min at the temperature.
[c] Starting material was recovered in 15% yield.
[d] No addition reaction was observed.

Representative procedure from **19d** is reported as shown in Scheme 3. Thus, trimethylsilyl groups of adduct **19dL** and **19dP** were cleaved with potassium carbonate in methanol to give terminal acetylene **21L** and **21P**, respectively, in almost quantitative yields. At first, alkynes **21** were treated with 1.2 equiv of LDA (to remove the acidic hydrogen on the terminal acetylene) to give lithium acetylides. The lithium acetylide derived from **21L** was treated with 5 equiv of *i*-PrMgCl to give smoothly the desired conjugated enyne **23** in 97% yield by the 1,2-CC insertion of the generated magnesium carbenoid intermediate **22L**. In the same way, the treatment of **21P** with LDA followed by *c*-PentMgCl gave **23** in 77% yield.

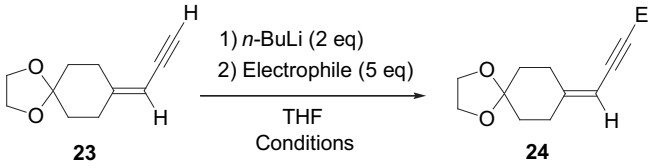
As mentioned in Table 3 entry 9, the addition reaction of lithium acetylide derived from an alkylacetylene to 1-chlorovinyl *p*-tolyl sulfoxide **3a** did not proceed. This result implied that by the presented procedure conjugated enynes bearing an alkyl group on the acetylenic carbon could not be obtained. To overcome this problem, we tried to alkylate the aforementioned conjugated enyne bearing a terminal acetylenic group **23**. The results for the treatment of **23** with *n*-BuLi followed by electrophiles including iodoalkanes are summarized in Table 4.

Thus, at first, conjugated enyne **23** was treated with 2 equiv of *n*-BuLi followed by 5 equiv of iodomethane in THF at 0 °C and the



Scheme 3.

Table 4
Synthesis of conjugated enynes **24** by treatment of **23** with *n*-BuLi followed by electrophiles



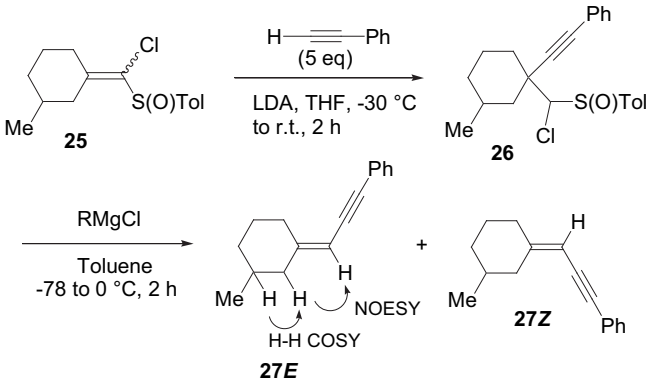
Entry	Electrophile	Additive	Conditions		**24**	
			Temp °C	Time	E	Yield/%
1	CH_3I	non	0	30 min	CH_3	**24a** 69
2	CH_3CH_2I	HMPA (6 equiv)	rt	12 h	CH_3CH_2	**24b** 52
3	$CH_3(CH_2)_5I$	HMPA (6 equiv)	rt	12 h	$CH_3(CH_2)_5$	**24c** 82
4	PhCOCl	non	0	30 min	PhCO	**24d** 64
5	$ClCOOC_2H_5$	non	0	30 min	$COOC_2H_5$	**24e** 57
6	PhCHO	non	0	30 min	PhCH(OH)	**24f** 65
7	I_2	non	0	30 min	I	**24g** 79

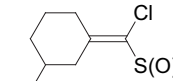
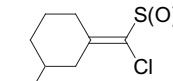
reaction mixture was stirred at 0 °C for 30 min to give conjugated enyne bearing a methyl group on the acetylenic carbon **24a** in 69% yield (entry 1). The alkylation with iodoethane and 1-iodohexane required somewhat forcing conditions. In these cases, HMPA was found to be an effective additive and the desired conjugated enynes having ethyl (**24b**) or *n*-hexyl group (**24c**) were obtained in moderate to good yields (entries 2 and 3). The reaction with benzoyl chloride and ethyl chloroformate gave the desired products **24d** and **24e**, respectively, in up to 64% yield (entries 4 and 5). Benzaldehyde reacted with the lithium acetylide to give adduct **24f** in 65% yield (entry 6). Iodoacetylene **24g** could be obtained in 79% yield by adding iodine in the reaction mixture (entry 7).

Next, we investigated this procedure starting with an unsymmetrical ketone, 3-methylcyclohexanone, and the results are summarized in Table 5. Thus, geometrical isomers **25*E*** and **25*Z*** were synthesized from 3-methylcyclohexanone in the same way as described above[11] in high overall yield. The structure of both isomers was easily determined by ^{1}H NMR (H–H COSY spectra and chemical shift of the allylic hydrogen[11a]). 1-Chlorovinyl *p*-tolyl sulfoxide **25*E*** was treated with lithium acetylide of phenylacetylene to afford adducts **26aL** and **26aP** (**26aL**/**26aP**=3:2) in 70% yield. In the same manner, treatment of **25*Z*** with lithium acetylide of phenylacetylene afforded adducts **26bL** and **26bP** (**26aL**/**26aP**=3:2) in 76% yield.

The sulfoxide–magnesium exchange reaction of **26aL** with 5 equiv of *i*-PrMgCl in toluene smoothly afforded the desired conjugated enyne **27** in 92% yield (entry 1). Somewhat surprisingly, the product was a mixture of two geometrical isomers and the ratio of **27*E*** to **27*Z*** was found to be 1:14, respectively. Treatment of **26aP** with *c*-PentMgCl gave conjugated enyne **27** in 88% yield as a mixture of two geometrical isomers, **27*E*** and **27*Z***. In this case, the ratio of **27*E*** to **27*Z*** was found to be 9:1, respectively (entry 2). Obviously, relatively high stereospecificity was obtained. Higher stereospecificity

Table 5
Synthesis of conjugated enynes **27** from 1-chlorovinyl *p*-tolyl sulfoxides **25** derived from unsymmetrical ketone, 3-methylcyclohexanone



Entry	**25**	**26** Yield/% (diastereomeric ratio)[a]	RMgCl	**27** Yield %	(*E*:*Z*)[b]
1	 **25*E***	**26a** 70 (3:2)	*i*-PrMgCl	92	(1:14)[c]
2			*c*-PentMgCl	88	(9:1)[d]
3	 **25*Z***	**26b** 76 (3:2)	*i*-PrMgCl	98	(20:1)[c]
4			*c*-PentMgCl	85	(1:16)[d]

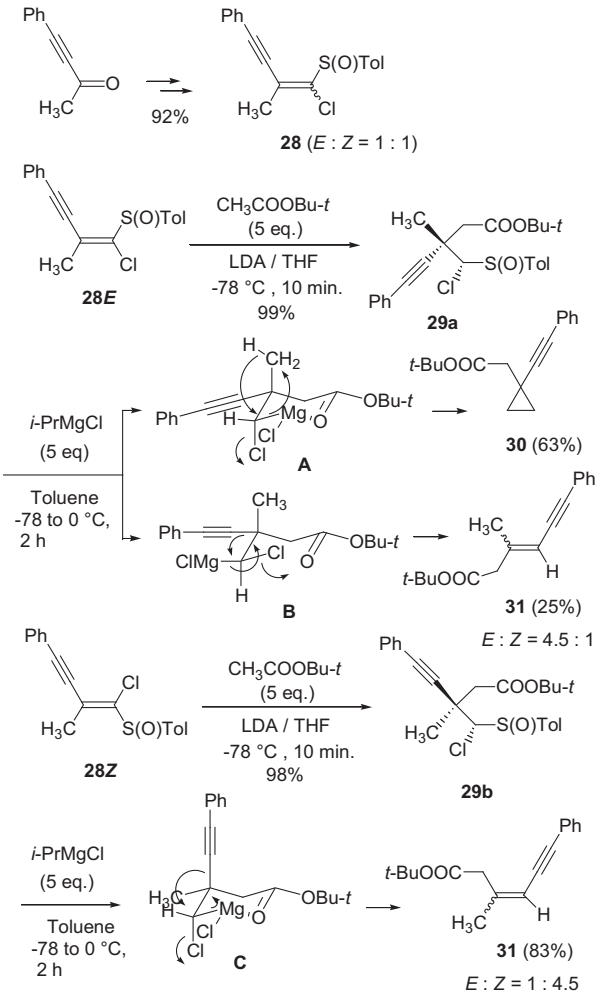
[a] The ratio for less polar product (**L**) and more polar product (**P**) on silica gel TLC.
[b] The ratio of *E*/*Z* was determined by ^{1}H NMR.
[c] The yield from less polar adduct.
[d] The yield from more polar adduct.

was observed in the reaction of **26bL** and **26bP** with Grignard reagents as shown in entries 3 and 4 in Table 5. The specificity of the reactions is very interesting; however, we still find it very difficult to propose a rational mechanism for explaining this specificity.

Finally, this procedure was carried out starting with unsymmetrical ketone, 4-phenyl-3-butyn-2-one, and the results are summarized in Scheme 4. Thus, 1-chlorovinyl *p*-tolyl sulfoxide **28** was synthesized from 4-phenyl-3-butyn-2-one in three steps in 92% overall yield as an equal mixture of two diastereomers. The geometrical isomers (**28*E*** and **28*Z***) were easily separated by silica gel column chromatography. Addition reaction of **28*E*** with lithium enolate of *tert*-butyl acetate gave adduct **29a** in quantitative yield as a single product. In the same way **28*E*** gave adduct **29b** in quantitative yield as a single product. The products **29a** and **29b** are diastereomers to each other. The configuration of the products, **29a** and **29b**, was confirmed to be as shown in Scheme 4 based on the study reported previously.[12b]

These two diastereomers **29a** and **29b** showed quite interesting specificity in the reaction with Grignard reagent. Thus, the sulfoxide–magnesium exchange reaction of **29a** was conducted with 5 equiv of *i*-PrMgCl in toluene to afford cyclopropane **30** (63%) and the desired conjugated enyne **31** (25%) as a mixture of two geometrical isomers (*E*/*Z*=4.5:1). Obviously, cyclopropane **30** was formed by the 1,3-CH insertion reaction of the generated magnesium carbenoid intermediate (between the magnesium carbenoid and the hydrogen at the methyl group).[12] In the same way, **29b** was treated with *i*-PrMgCl to give the desired conjugated enyne **31** in 83% yield as a mixture of two geometrical isomers (*E*/*Z*=1:4.5) and no cyclopropane **30** was observed.

This specificity of the reactions can be explained as follows. As the sulfoxide–magnesium exchange reaction is proved to take place



Scheme 4. Synthesis of conjugated enynes bearing a *tert*-butyl acetate moiety **31** from 4-phynyl-3-butyn-2-one.

with retention of the configuration of the carbon bearing the sulfinyl group,[13] treatment of **29a** with *i*-PrMgCl gives magnesium carbenoid having *R**-configuration. The magnesium and carbonyl oxygen atom of the ester group must make six-membered intermediate **A**, in which the bulkiest *tert*-butoxy group would occupy equatorial-like position. In this intermediate, the chlorine atom was attacked by the C–H bond of the methyl group from back side (1,3-CH insertion reaction) to afford cyclopropane **30**. On the other hand, rearrangement of the acetylenic group (1,2-CC insertion) would occur simultaneously via the conformation **B** to give conjugated enyne **31** in low yield.

The sulfoxide–magnesium exchange reaction of **29b** again gives magnesium carbenoid having *R**-configuration. The magnesium and carbonyl oxygen atom of the ester group must make six-membered intermediate **C**, in which the acetylenic group occupies axial position. In this case, the rearrangement of the acetylenic group (1,2-CC insertion) is expected to be easily taken place from back side of the carbon–chlorine bond to afford conjugated enyne **31** in good yield. However, the *E*/*Z* ratio of the produced enyne **31** is still very difficult to be rationalized.

2.2. Synthesis of conjugated enynes bearing a sulfinyl group at the 1-position from aldehydes with chloromethyl *p*-tolyl sulfoxide and acetylenes

Finally, the procedure described above was developed with aldehydes and quite interesting results were obtained. The representative example is reported by using pivalaldehyde **32** as an aldehyde (Scheme 5). Thus, 1-chlorovinyl *p*-tolyl sulfoxide **33** was synthesized from **32** in two steps in 85% overall yield as a mixture of easily separable two geometrical isomers (**33*E*** and **33*Z***).[14] Main product **33*E*** was treated with 5 equiv of lithium acetylide, derived from phenylacetylene with LDA, in THF and the temperature of the reaction mixture was allowed to warm to 0 °C. The reaction mixture was very clean and a single product was obtained. Initially, we anticipated that the product was adduct **36**; however, the product had an olefinic hydrogen and the structure was confirmed to be conjugated enyne bearing a sulfinyl group at the 1-position **35** (yield was found to be 95%). Obviously, product **35** was produced by the 1,2-CH insertion reaction of lithium carbenoid intermediate **34** that generated from the addition reaction of **33** with lithium acetylide.

The configuration of **35** was confirmed to be *Z* by NOESY spectrum. Neither anticipated adduct **36** nor the corresponding *E* isomer were observed as the product. The same treatment of **33*Z*** gave the same product **35** in somewhat lower yield. Again, neither anticipated adduct **36** nor the *E* isomer were observed. Very interestingly, these reactions were found to be highly stereoselective.

The presumed mechanism of this stereoselectivity is shown in Scheme 5. Thus, addition reaction of **33*E*** with a carbanion is expected to give lithium carbenoid intermediate **A**.[12b] As the chlorine and the hydrogen atoms are trans to each other, 1,2-CH insertion reaction (rearrangement of the hydrogen atom) would smoothly take place to give **35** in high yield. In this event, the acetylenic group and the sulfinyl group must be placed cis to each other. On the other hand, the reaction of **33*Z*** gave lithium carbenoid intermediate **B**. As the chlorine and the hydrogen atoms are cis to each other, the 1,2-CH insertion is though to be difficult. In this case, the configuration of the carbenoid carbon must be inverted to give intermediate **C**. From this intermediate the 1,2-CH insertion would take place to give the same product **35**.

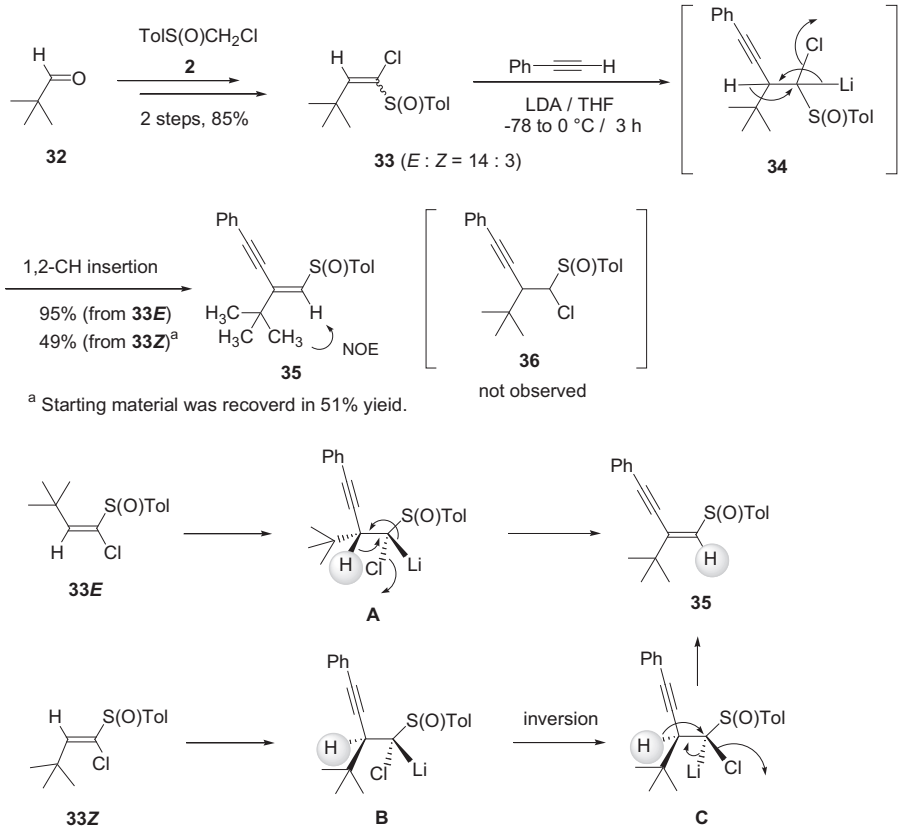
Generality of this reaction was investigated and the results are summarized in Table 6. As shown in the table, 1-chlorovinyl *p*-tolyl sulfoxides **37** could be synthesized from aldehydes in good yields. The reaction of **37** with some lithium acetylides was carried out and again it was found that *E* isomer of **37** gave much better yields of conjugated enynes **38** (entries 1–8).

In conclusion, we have found that the magnesium carbenoids bearing an acetylenic group on the β-position, which were derived from ketones, gave conjugated enynes via 1,2-CC insertion reaction in good to high yields. A highly stereospecific reactions were observed in this case. Both conjugated enynes bearing an aromatic group and an alkyl group on the acetylenic carbon can be obtained by the presented procedure. On the other hand, the addition reactions of 1-chlorovinyl *p*-tolyl sulfoxides derived from aldehydes with lithium acetylides directly gave conjugated enynes bearing a *p*-tolyl sulfinyl group at the 1-position through the 1,2-CH insertion reaction of the generated lithium carbenoid intermediates. In this case, high stereoselectivity was observed. These procedures provide a good way for the synthesis of multi-substituted conjugated enynes from ketones and aldehydes. The chemistry presented here is unprecedented and would contribute to the synthesis of conjugated enynes.

3. Experimental

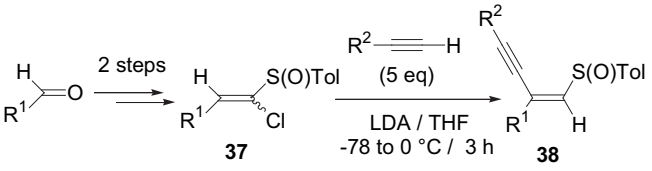
3.1. General

All melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 300, 500, Bruker DPX 400, and AV 600 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion by HITACHI M-80B mass spectrometer. IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR instrument. Silica gel 60N (KANTO CHEMICAL) containing 0.5%



Scheme 5. Synthesis of conjugated enyne bearing a sulfinyl group at the 1-position **35** by the reaction of **33** with lithium phenylacetylide and the presumed mechanism for the stereoselectivity.

Table 6
Synthesis of conjugated enynes bearing a sulfinyl group at the 1-position **38** from aldehydes and acetylenes



Entry	**37**		**38**	
	R^1	Yield/%[a]	R^2	Yield/%
1	$Ph(CH_2)_2$	**37a*E*** 53	Ph	**38a** 55
2	$Ph(CH_2)_2$	**37a*Z*** 35	Ph	**38a** 27
3		**37b*E*** 32	Ph	**38b** 78
4		**37b*Z*** 41	Ph	**38b** 38
5	$(CH_3)_3C$	**33*E*** 70	$Ph(CH_2)_2$	**38c** 69
6	$(CH_3)_3C$	**33*Z*** 15	$Ph(CH_2)_2$	—[b]
7	$(CH_3)_3C$	**33*E*** 70	H	**38d**[c] 82
8	$(CH_3)_3C$	**33*Z*** 15	H	**38d**[c] 9[b]

[a] Two-step overall yield from aldehydes.
[b] Starting material was mainly recovered.
[c] Trimethylsilylacetylene was used as the acetylene.

fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring dry solvents and reagents, THF and diethyl ether were distilled from diphenylketyl. Diisopropylamine, toluene, and HMPA were distilled from CaH_2. All reactions involving air- or water-sensitive compounds were routinely conducted in glassware, which was flame-dried under a positive pressure of argon. Compounds **18a**[7b] and **18c**[8] are known.

*3.1.1. 8-[Chloro-(p-tolylsulfinyl)methyl]-8-phenylethynyl-1,4-dioxaspiro[4.5]decane (**13**).* Phenylacetylene (0.055 mL; 0.5 mmol) was added to a solution of LDA (0.5 mmol) in 1 mL of dry THF in a flame-dried flask under argon atmosphere dropwise at 0 °C with stirring. The reaction mixture was stirred for 10 min at 0 °C and cooled to −30 °C. A solution of **3a** (33 mg; 0.1 mmol) in 1 mL of THF was added to the solution and the reaction mixture was slowly allowed to warm to room temperature for 2 h. The reaction was quenched with satd aq NH_4Cl and the whole mixture was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography (hexane/AcOEt) to give **13L** (25.7 mg; 60%) as colorless crystals and **13P** (8.5 mg; 20%) as colorless oil. Compound **13L**: mp 137.5–138 °C (hexane/AcOEt); IR (KBr) 2957, 2884, 1152, 1110, 1087, 1054, 809, 758, 693 cm^{-1}; ^1H NMR δ 1.75–1.93 (3H, m), 2.07–2.25 (5H, m), 2.41 (3H, s), 3.92–4.02 (4H, m), 4.40 (1H, s), 7.29–7.37 (5H, m), 7.46–7.55 (4H, m). Anal. Calcd for $C_{24}H_{25}ClO_3S$: C, 67.20; H, 5.87; Cl, 8.26; S, 7.48. Found: C, 67.06; H, 6.02; Cl, 8.14; S, 7.39. Compound **13P**: IR (neat) 2954, 2883, 2232, 1164, 1107, 1083, 1052, 809, 757, 692 cm^{-1}; ^1H NMR δ 1.70–1.90 (3H, m), 1.94–2.25 (4H, m), 2.40 (3H, s), 2.72–2.80 (1H, m), 3.90–4.02 (4H, m), 4.40 (1H, s), 7.27–7.34 (5H, m), 7.44–7.48 (2H, m), 7.70–7.75 (2H, m). MS *m*/*z* (%) 428 (M^+, 2), 289 (38), 253 (100), 167 (61), 139 (33), 99 (40). Calcd for $C_{24}H_{25}ClO_3S$: M, 428.1213. Found: *m*/*z* 428.1219.

*3.1.2. 8-(3-Phenylprop-2-ynylidene)-1,4-dioxaspiro[4.5]decane (**16**).* To a flame-dried flask under argon atmosphere was added dry toluene (3 mL) followed by *i*-PrMgCl (2.0 M solution in diethyl ether; 0.195 mL, 0.39 mmol) at −78 °C. A solution of **13L** (33.6 mg; 0.078 mmol) in toluene (1 mL) was added dropwise to the solution of the Grignard reagent with stirring and the reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction was quenched with satd aq NH_4Cl and the whole mixture was extracted three

times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography (hexane/AcOEt) to give **16** (19.2 mg; 97%) as colorless oil. IR (neat) 2951, 2882, 2197, 1120, 1087, 1034, 906, 756, 690 cm^{-1}; ^1H NMR δ 1.72–1.79 (4H, m), 2.36–2.42 (2H, m), 2.63–2.68 (2H, m), 3.97–4.00 (4H, m), 5.50 (1H, s), 7.27–7.32 (3H, m), 7.41–7.44 (2H, m). MS *m*/*z* (%) 254 (M^+, 100), 209 (20), 192 (20), 167 (57), 153 (20), 115 (19). Calcd for $C_{17}H_{18}O_2$: M, 254.1307. Found: *m*/*z* 254.1303.

*3.1.3. 1-[Chloro(p-tolylsulfinyl)methyl]-1-phenylethynylcyclohexane (**17a**).* Compound **17aL**; colorless crystal; mp 112.5–113 °C (hexane/AcOEt); IR (KBr) 2941, 2855, 1491, 1087, 1058, 813, 755, 613, 516 cm^{-1}; ^1H NMR δ 1.70–1.90 (9H, m), 2.14–2.21 (1H, m), 2.41 (3H, s), 4.37 (1H, s), 7.29–7.36 (5H, m), 7.48–7.54 (4H, m). Anal. Calcd for $C_{22}H_{23}ClOS$: C, 71.24; H, 6.25; Cl, 9.56; S, 8.64. Found: C, 71.07; H, 6.21; Cl, 9.43; S, 8.54. Compound **17aP**; colorless crystal; mp 85–85.5 °C (hexane/AcOEt); IR (KBr) 2942, 2863, 2079, 1490, 1084, 1047, 812, 755, 691, 508 cm^{-1}; ^1H NMR δ 1.54–1.62 (2H, m), 1.66–1.85 (6H, m), 2.10–2.15 (1H, m), 2.40 (3H, s), 2.58–2.64 (1H, m), 4.42 (1H, s), 7.28–7.32 (5H, m), 7.43–7.47 (2H, m), 7.71–7.75 (2H, m). Anal. Calcd for $C_{22}H_{23}ClOS$: C, 71.24; H, 6.25; Cl, 9.56; S, 8.64. Found: C, 71.21; H, 6.09; Cl, 9.45; S, 8.52.

*3.1.4. 1-[Chloro(p-tolylsulfinyl)methyl]-1-phenylethynylcyclododecane (**17b**).* Compound **17bL**; colorless crystal; mp 119.5–120 °C (hexane/AcOEt); IR (KBr) 2926, 2861, 2113, 1596, 1490, 1468, 1443, 1079, 1060, 815, 753, 689 cm^{-1}; ^1H NMR δ 1.23–1.54 (16H, m), 1.65–1.74 (2H, m), 1.78–1.86 (1H, m), 1.95–2.08 (2H, m), 2.37 (3H, s), 2.39–2.47 (1H, m), 4.45 (1H, s), 7.24–7.34 (5H, m), 7.39–7.43 (2H, m), 7.71–7.75 (2H, m). Anal. Calcd for $C_{29}H_{37}ClOS$: C, 73.90; H, 7.75; Cl, 7.79; S, 7.05. Found: C, 73.45; H, 7.69; Cl, 8.08; S, 6.99. Compound **17bP**; colorless crystal; mp 177.5–178 °C (hexane/AcOEt); IR (KBr) 2850, 1597, 1490, 1467, 1446, 1088, 1063, 811, 765, 695 cm^{-1}; ^1H NMR δ 1.24–1.76 (18H, m), 1.89–2.04 (4H, m), 2.41 (3H, s), 4.31 (1H, s), 7.27–7.34 (5H, m), 7.48–7.55 (4H, m). Anal. Calcd for $C_{29}H_{37}ClOS$: C, 73.90; H, 7.75; Cl, 7.79; S, 7.05. Found: C, 73.79; H, 7.72; Cl, 7.66; S, 7.03.

*3.1.5. 1-[Chloro(p-tolylsulfinyl)methyl]-1-phenylethynylcyclopentadecane (**17c**).* Compound **17cL**; colorless crystal; mp 107–108 °C (hexane/AcOEt); IR (KBr) 2929, 2857, 1491, 1460, 1083, 1060, 811, 756, 691 cm^{-1}; ^1H NMR δ 1.15–1.62 (24H, m), 1.80–1.95 (2H, m), 2.03–2.11 (1H, m), 2.25–2.33 (1H, m), 2.38 (3H, s), 4.51 (1H, s), 7.25–7.31 (5H, m), 7.39–7.43 (2H, m), 7.74 (2H, d, *J*=8.1 Hz). MS *m*/*z* (%) 496 (M^+, 8), 357 (38), 321 (95), 309 (37), 167 (59), 141 (64), 91 (100). Calcd for $C_{31}H_{41}ClOS$: M, 496.2567. Found: *m*/*z* 496.2564. Anal. Calcd for $C_{31}H_{41}ClOS$: C, 74.89; H, 8.31; Cl, 7.13; S, 6.45. Found: C, 74.68; H, 8.28; Cl, 7.03; S, 6.41. Compound **17cP**; colorless oil; IR (neat) 2929, 2857,2330, 1491, 1459, 1091, 1065, 809, 756, 691 cm^{-1}; ^1H NMR δ 1.25–1.60 (24H, m), 1.81–1.96 (3H, m),2.03–2.12 (1H, m) 2.40 (3H, s), 4.40 (1H, s), 7.29–7.34 (5H, m), 7.43–7.53 (4H, m). MS *m*/*z* (%) 496 (M^+, 17), 357 (58), 321 (100), 309 (26), 167 (59), 139 (67), 115 (46), 91(92). Calcd for $C_{31}H_{41}ClOS$: M, 496.2567. Found: *m*/*z* 496.2559.

*3.1.6. 1-Chloro-2-phenylethynyl-2-propyl-1-(p-tolylsulfinyl)pentane (**17d**).* Compound **17dL**; colorless oil; IR (neat) 2961, 2932, 2873, 1598, 1491, 1083, 1059, 756, 691 cm^{-1}; ^1H NMR δ 0.96 (3H, t, *J*=7.2 Hz), 1.02 (3H, t, *J*=7.2 Hz), 1.38–1.66 (4H, m), 1.72–2.18 (4H, m), 2.41 (3H, s), 4.64 (1H, s), 7.27–7.33 (5H, m), 7.40–7.46 (2H, m), 7.70–7.76 (2H, m). MS *m*/*z* (%) 386 (M^+, 8), 247 (44), 211 (52), 169 (100), 155 (55), 141 (52), 139 (59), 115 (75). Calcd for $C_{23}H_{27}ClOS$: M, 386.1471. Found: *m*/*z* 386.1480. Compound **17dP**; colorless oil; IR (neat) 2960, 2932, 2873, 1492, 1090, 1065, 756, 691 cm^{-1}; ^1H NMR δ 0.96 (3H, t, *J*=7.2 Hz), 1.02 (3H, t, *J*=7.2 Hz), 1.32–1.86 (7H, m), 2.01–2.12 (1H, m) 2.41 (3H, s), 4.48 (1H, s), 7.28–7.37 (5H, m), 7.45–7.55 (4H, m). MS *m*/*z* (%) 386 (M^+, 11), 247 (78), 211 (49), 169 (100), 155 (56), 141 (50), 139 (58), 129 (41), 115 (78). Calcd for $C_{23}H_{27}ClOS$: M, 386.1471. Found: *m*/*z* 386.1462.

*3.1.7. (3-Phenylprop-2-ynylidene)cyclododecane (**18b**).* Colorless oil; IR (neat) 2939, 2862, 2198, 1489, 1469, 1443, 754, 690 cm^{-1}; ^1H NMR δ 1.24–1.44 (14H, m), 1.52–1.66 (4H, m), 2.18–2.24 (2H, m), 2.43–2.49 (2H, m), 5.59 (1H, s), 7.24–7.32 (3H, m), 7.40–7.43 (2H, m). MS *m*/*z* (%) 280 (M^+, 100), 181 (10), 167, (25), 155 (22), 128 (18), 115 (17). Calcd for $C_{21}H_{28}$: M, 280.2191. Found: *m*/*z* 280.2191.

*3.1.8. 1-Phenyl-4-propylhept-3-en-1-yne (**18d**).* Colorless oil; IR (neat) 2960, 2932, 2872, 2199, 1595, 1489, 755, 690 cm^{-1}; ^1H NMR δ 0.92 (3H, t, *J*=7.4 Hz), 0.97 (3H, t, *J*=7.4 Hz), 1.41–1.61 (4H, m), 2.07–2.15 (2H, m), 2.33–2.42 (2H, m), 5.49 (1H, s), 7.25–7.34 (3H, m), 7.39–7.44 (2H, m). MS *m*/*z* (%) 212 (M^+, 100), 183 (57), 169 (30), 155 (71), 141 (35), 128 (25), 115 (35). Calcd for $C_{16}H_{20}$: M, 212.1565. Found: *m*/*z* 212.1566.

*3.1.9. 8-[Chloro(p-tolylsulfinyl)methyl]-8-(p-tolylethynyl)-1,4-dioxaspiro[4.5]decane (**19a**).* Compound **19aL**; colorless crystal; mp 167.5–168 °C (hexane/AcOEt); IR (KBr) 2954, 2880, 2101, 1509, 1151, 1112, 1055, 947, 893, 819, 704 cm^{-1}; ^1H NMR δ 1.74–1.89 (3H, m), 2.08–2.22 (5H, m), 2.36 (3H, s), 2.41 (3H, s), 3.94–3.98 (4H, m), 4.40 (1H, s), 7.14 (2H, d, *J*=7.9 Hz), 7.32 (2H, d, *J*=7.9 Hz), 7.36–7.40 (2H, m), 7.50–7.54 (2H, m). Anal. Calcd for $C_{25}H_{27}ClO_3S$: C, 67.78; H, 6.14; Cl, 8.00; S, 7.24. Found: C, 67.62; H, 6.28; Cl, 7.78; S, 7.15. Compound **19aP**; colorless oil; IR (neat) 2954, 2883, 2231, 1510, 1163, 1107, 1082, 1052, 816, 757 cm^{-1}; ^1H NMR δ 1.68–1.88 (3H, m), 1.92–2.23 (4H, m), 2.35 (3H, s), 2.40 (3H, s), 2.70–2.79 (1H, m), 3.93–3.98 (4H, m), 4.39 (1H, s), 7.08–7.14 (2H, m), 7.27–7.32 (2H, m), 7.32–7.37 (2H, m), 7.69–7.75 (2H, m). MS *m*/*z* (%) 442 (M^+, 4), 379 (52), 303 (38), 276 (50), 267 (100), 254 (71), 223 (30), 181 (79), 135 (47), 119 (36), 99 (58). Calcd for $C_{25}H_{27}ClO_3S$: M, 442.1369. Found: *m*/*z* 442.1367.

*3.1.10. 8-[Chloro(p-tolylsulfinyl)methyl]-8-[(4-methoxyphenyl)ethynyl]-1,4-dioxaspiro[4.5]decane (**19b**).* Compound **19bL**; colorless crystal; mp 136.5–137 °C (hexane/AcOEt); IR (KBr) 2964, 2883, 2222, 1605, 1508, 1246, 1087, 1053, 830, 807 cm^{-1}; ^1H NMR δ 1.75–1.82 (2H, m), 1.84–1.88 (1H, m), 2.07–2.21 (5H, m), 2.41 (3H, s), 3.83 (3H, s), 3.94–4.00 (4H, m), 4.39 (1H, s), 6.84–6.87 (2H, m), 7.30–7.34 (2H, m), 7.41–7.45 (2H, m), 7.50–7.53 (2H, m). Anal. Calcd for $C_{25}H_{27}ClO_5S\ H_2O$: C, 62.95; H, 6.13; Cl, 7.43; S, 6.72. Found: C, 62.74; H, 5.69; Cl, 7.59; S, 6.87. Compound **19bP**; colorless oil; IR (neat) 2955, 2933, 2885, 1606, 1509, 1249, 1084, 1052, 733 cm^{-1}; ^1H NMR δ 1.66–1.94 (4H, m), 1.96–2.22 (3H, m), 2.41 (3H, s), 2.68–2.78 (1H, m), 3.81 (3H, s), 3.90–4.00 (4H, m), 4.39 (1H, s), 6.80–6.87 (2H, m), 7.27–7.33 (2H, m), 7.37–7.42 (2H, m), 7.70–7.75 (2H, m). MS *m*/*z* (%) 458 (M^+, 2), 395 (53), 283 (58), 307 (25), 270 (54), 242 (49), 209 (47), 197 (61), 151 (100), 139 (28), 99 (70). Calcd for $C_{25}H_{27}ClO_4S$: M, 458.1319. Found: *m*/*z* 458.1315.

*3.1.11. 8-[Chloro(p-tolylsulfinyl)methyl]-8-[(4-fluorophenyl)ethynyl]-1,4-dioxaspiro[4.5]decane (**19c**).* Compound **19cL**; colorless crystal; mp 116–116.5 °C (hexane/AcOEt); IR (KBr) 2965, 2884, 1506, 1234, 1116, 1087, 1054, 838, 812 cm^{-1}; ^1H NMR δ 1.73–1.86 (2H, m), 1.91–1.97 (1H, m), 2.04–2.23 (5H, m), 2.42 (3H, s), 3.93–4.01 (4H, m), 4.37 (1H, s), 6.99–7.06 (2H, m), 7.33 (2H, d, *J*=8.2 Hz), 7.45–7.53 (2H, m). Anal. Calcd for $C_{24}H_{24}ClFO_3S$: C, 64.49; H, 5.41; Cl, 7.93; F, 4.25; S, 7.17. Found: C, 64.38; H, 5.56; Cl, 7.82; F, 4.04; S, 7.11. Compound **19cP**; colorless crystal; mp 109.5–110 °C (hexane/AcOEt); IR (KBr) 2954, 2932, 2884, 2244, 1506, 1234, 1107, 1083, 1052, 838, 733 cm^{-1}; ^1H NMR δ 1.72–1.88 (3H, m), 1.95–2.13 (3H, m), 2.17–2.24 (1H, m), 2.41 (3H, s), 2.71–2.79 (1H, m), 3.93–4.01 (4H, m), 4.38 (1H, s), 7.01 (2H, t, 8.6 Hz), 7.30 (2H, d, *J*=8.1 Hz), 7.40–7.48 (2H, m) 7.73 (2H, d, *J*=8.1 Hz). Anal. Calcd for

$C_{24}H_{24}ClFO_3S$: C, 64.49; H, 5.41; Cl, 7.93; F, 4.25; S, 7.17. Found: C, 64.53; H, 5.26; Cl, 7.82; F, 4.06; S, 6.89.

*3.1.12. 8-[Chloro(p-tolylsulfinyl)methyl]-8-[(2-trimethylsilyl)ethynyl]-1,4-dioxaspiro[4.5]decane (**19d**).* Compound **19dL**; colorless crystal; mp 164–164.5 °C (hexane/AcOEt); IR (KBr) 2961, 2931, 2884, 2167, 1250, 1091, 1061, 861, 846 cm^{-1}; ^1H NMR δ 0.22 (9H, s), 1.65–1.80 (3H, m), 1.98–2.12 (5H, m), 2.42 (3H, s), 3.90–4.01 (4H, m), 4.32 (1H, s), 7.33 (2H, d, J=8.2 Hz), 7.50 (2H, d, J=8.2 Hz). Anal. Calcd for $C_{21}H_{29}ClO_3SSi$: C, 59.34; H, 6.88; Cl, 8.34; S, 7.54; Si, 6.61. Found: C, 59.53; H, 6.90; Cl, 8.03; S, 7.22. Compound **19dP**; colorless oil; IR (neat) 2957, 2932, 2884, 2166, 1251, 1109, 1084, 1055, 845, 761 cm^{-1}; ^1H NMR δ 0.20 (9H, s), 1.64–2.10 (7H, m), 2.43 (3H, s), 2.60–2.68 (1H, m), 3.89–4.01 (4H, m), 4.27 (1H, s), 7.28–7.34 (2H, m), 7.67–7.73 (2H, m). MS m/z (%) 424 (M^+, 3), 408 (11), 285 (39), 257 (25), 249 (100), 177 (17), 99 (48), 73 (77). Calcd for $C_{21}H_{29}ClO_3SSi$: M, 424.1295. Found: m/z 424.1291.

*3.1.13. 8-[3-(p-Tolyl)prop-2-ynylidene]-1,4-dioxaspiro[4.5]decane (**20a**).* Colorless crystal; mp 57–58 °C (hexane/AcOEt); IR (KBr) 2951, 2881, 2196, 1120, 1087, 1034, 906, 817 cm^{-1}; ^1H NMR δ 1.70–1.80 (4H, m), 2.34 (3H, s), 2.35–2.42 (2H, m), 2.61–2.68 (2H, m), 3.96–4.01 (4H, m), 5.49 (1H, s), 7.07–7.13 (2H, m), 7.29–7.34 (2H, m). MS m/z (%) 268 (M^+, 100), 223 (24), 206 (16), 181 (38), 167 (33), 152 (17). Calcd for $C_{18}H_{20}O_2$: M, 268.1463. Found: m/z 268.1461. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.28; H, 7.13. Found: C, 80.20; H, 7.60.

*3.1.14. 8-[3-(4-Methoxyphenyl)-2-ynylidene]-1,4-dioxaspiro[4.5]decane (**20b**).* Light yellow oil; IR (neat) 2950, 2883, 2839, 2197, 1508, 1247, 1034, 831 cm^{-1}; ^1H NMR δ 1.70–1.79 (4H, m), 2.38 (2H, dt, J=1.1, 6.5 Hz), 2.60–2.68 (2H, m), 3.81 (3H, s), 3.98 (4H, s), 5.48 (1H, t, J=1.1 Hz), 6.80–6.86 (2H, m), 7.33–7.39 (2H, m). MS m/z (%) 284 (M^+, 100), 239 (30), 222 (11), 197 (28), 183 (13), 165 (11). Calcd for $C_{18}H_{20}O_3$: M, 284.1412. Found: m/z 284.1410.

*3.1.15. 8-[3-(4-Fluorophenyl)-2-ynylidene]-1,4-dioxaspiro[4.5]decane (**20c**).* Colorless oil; IR (neat) 2952, 2883, 2198, 1506, 1228, 1120, 1087, 853 cm^{-1}; ^1H NMR δ 1.70–1.80 (4H, m), 2.35–2.42 (2H, m), 2.80–2.87 (2H, m), 3.99 (4H, s), 5.48 (1H, s), 6.96–7.03 (2H, m), 7.37–7.43 (2H, m). MS m/z (%) 272 (M^+, 100), 227 (19), 210 (18), 185 (59), 171 (19), 157 (11) 133 (20). Calcd for $C_{17}H_{17}FO_2$: M, 272.1213. Found: m/z 272.1211.

*3.1.16. 8-[3-(Trimethylsilyl)prop-2-ynyliden]-1,4-dioxaspiro[4.5]decane (**20d**).* Colorless oil; IR (neat) 2955, 2883, 2144, 2124, 1249, 1098, 843 cm^{-1}; ^1H NMR δ 0.19 (9H, s), 1.67–1.77 (4H, m), 2.32 (2H, dt, J=1.1, 6.5 Hz), 2.54–2.61 (2H, m), 3.97 (4H, s), 5.31 (1H, t, J=1.1 Hz). MS m/z (%) 250 (M^+, 100), 235 (11), 221 (42), 191 (18), 163 (18), 73 (23). Calcd for $C_{14}H_{22}O_2Si$: M, 250.1389. Found: m/z 250.1389.

*3.1.17. 8-[Chloro(p-tolylsulfinyl)methyl]-8-ethynyl-1,4-dioxaspiro[4.5]decane (**21**).* Compound **21L**; colorless crystal; mp 141.5–142 °C (hexane/AcOEt); IR (KBr) 3253, 2956, 2939, 2893, 2113, 1437, 1277, 1088, 1058, 808, 692 cm^{-1}; ^1H NMR δ 1.72–1.80 (2H, m), 1.87–2.17 (6H, m), 2.42 (3H, s), 2.56 (1H, s) 3.90–4.01 (4H, m), 4.28 (1H, s), 7.29–7.37 (2H, m), 7.48–7.54 (2H, m). Anal. Calcd for $C_{18}H_{21}ClO_3S$: C, 61.27; H, 6.00; Cl, 10.05; S, 9.09. Found: C, 61.31; H, 5.96; Cl, 9.96; S, 8.98. Compound **21P**; colorless oil; IR (neat) 3294, 2955, 2931, 2886, 2107, 1107, 1036 cm^{-1}; ^1H NMR δ 1.67–2.19 (7H, m), 2.43 (3H, s), 2.47 (1H, s), 2.66–2.75 (1H, m), 3.89–4.00 (4H, m), 4.29 (1H, s), 7.29–7.35 (2H, m), 7.69–7.75 (2H, m). MS m/z (%) 352 (M^+, 9), 213 (100), 185 (60), 177 (81), 169 (24), 139 (38), 105 (60), 99 (80) 91 (58). Calcd for $C_{18}H_{21}ClO_3S$: M, 352.0900. Found: m/z 352.0886.

*3.1.18. 8-(Prop-2-ynylidene)-1,4-dioxaspiro[4.5]decane (**23**).* Colorless oil; IR (neat) 3289, 2953, 2883, 2577, 2097, 1121, 1088, 686 cm^{-1}; ^1H NMR δ 1.67–1.79 (4H, m), 2.30–2.38 (2H, m), 2.55–2.63 (2H, m), 2.98 (1H, d, J=2.2 Hz), 3.98 (4H, s), 5.27 (1H, t, J=1.0 Hz). MS m/z (%) 178 (M^+, 88), 163 (63), 149 (100), 119 (19), 105 (30), 99 (15), 91 (60), 86 (19). Calcd for $C_{11}H_{14}O_2$: M, 178.0994. Found: m/z 178.0996.

*3.1.19. 8-(But-2-ynylidene)-1,4-dioxaspiro[4.5]decane (**24a**).* Colorless oil; IR (neat) 2952, 2880, 2236, 1120, 1083, 1035, 908 cm^{-1}; ^1H NMR δ 1.66–1.75 (4H, m), 1.97 (3H, d, J=2.3 Hz), 2.26–2.35 (2H, m), 2.50–2.58 (2H, m), 3.97 (4H, s), 5.23 (1H, t, J=1.0 Hz). MS m/z (%) 192 (M^+, 100), 177 (18), 163 (42), 133 (20), 119 (22), 105 (51), 91 (50). Calcd for $C_{12}H_{16}O_2$: M, 192.1150. Found: m/z 192.1149.

*3.1.20. 8-(Pent-2-ynylidene)-1,4-dioxaspiro[4.5]decane (**24b**).* Colorless oil; IR (neat) 2951, 2880, 1120, 1084, 1035, 907 cm^{-1}; ^1H NMR δ 1.17 (3H, t, J=7.6 Hz), 1.67–1.74 (4H, m), 2.28–2.37 (4H, m), 2.55 (2H, dt, J=0.8, 6.6 Hz), 3.95–3.99 (4H, m), 5.26 (1H, t, J=1.1 Hz). MS m/z (%) 206 (M^+, 100), 177 (39), 133 (18), 119 (29), 105 (44), 91 (39), 77 (18). Calcd for $C_{13}H_{18}O_2$: M, 206.1307. Found: m/z 206.1308.

*3.1.21. 8-(Non-2-ynylidene)-1,4-dioxaspiro[4.5]decane (**24c**).* A solution of **23** (20.6 mg; 0.12 mmol) in 1 mL of THF and HMPA (0.12 mL; 0.72 mmol) was added to a solution of *n*-BuLi (1.57 M solution in hexane, 0.15 mL; 0.24 mmol) in 1.3 mL of dry THF in a flame-dried flask under argon atmosphere at 0 °C and the reaction mixture was stirred for 10 min to generate lithium acetylide. Iodohexane (0.09 mL; 0.6 mmol) was added to the reaction mixture dropwise with stirring and the whole mixture was stirred at room temperature overnight. The reaction was quenched with satd aq NH_4Cl and the whole mixture was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography (hexane/AcOEt) to give **24c** (25.7 mg; 82%) as light yellow oil; IR (neat) 2931, 2858, 1120, 1083, 1035, 908, 684 cm^{-1}; ^1H NMR δ 0.89 (3H, t, J=6.8 Hz), 1.24–1.59 (8H, m), 1.66–1.78 (4H, m), 2.27–2.36 (4H, m), 2.50–2.58 (2H, m), 3.97 (4H, s), 5.26 (1H, s). MS m/z (%) 262 (M^+, 100), 233 (14), 191 (12), 147 (13), 119 (14), 105 (19), 91 (24), 80 (14). Calcd for $C_{17}H_{26}O_2$: M, 262.1933. Found: m/z 262.1941.

*3.1.22. 4-(1,4-Dioxaspiro[4.5]dec-8-ylidene)-1-phenylbut-2-yn-1-one (**24d**).* Colorless oil; IR (neat) 2953, 2884, 2404, 2177, 1640, 1266, 1120, 1083, 701 cm^{-1}; ^1H NMR δ 1.75–1.84 (4H, m), 2.47 (2H, dt, J=1.0, 6.5 Hz), 2.70–2.78 (2H, m), 4.00 (4H, s), 5.57 (1H, t, J=1.0 Hz), 7.45–7.53 (2H, m), 7.57–7.64 (1H, m), 8.12–8.18 (2H, m). MS m/z (%) 282 (M^+, 54), 239 (58), 196 (57), 181 (100), 167 (87), 105 (80), 86 (55), 77 (58). Calcd for $C_{18}H_{18}O_3$: M, 282.1256. Found: m/z 282.1247.

*3.1.23. Ethyl 4-(1,4-dioxaspiro[4.5]dec-8-ylidene)but-2-ynoate (**24e**).* Colorless oil; IR (neat) 2955, 2203, 1705, 1256, 1122, 1077, 1034 cm^{-1}; ^1H NMR δ 1.32 (3H, t, J=7.2 Hz), 1.69–1.79 (4H, m), 2.40 (2H, dt, J=0.9, 6.5 Hz), 2.59–2.68 (2H, m), 3.98 (4H, s), 4.24 (2H, q, J=7.2 Hz), 5.38 (1H, t, J=0.9 Hz). MS m/z (%) 250 (M^+, 18), 205 (35), 178 (16), 134 (28), 120 (100), 105 (12), 91(22), 86 (20). Calcd for $C_{14}H_{18}O_4$: M, 250.1205. Found: m/z 250.1204.

*3.1.24. 4-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-1-phenylbut-2-yn-1-ol (**24f**).* Colorless oil; IR (neat) 3420, 2952, 2885, 2208, 1119, 1082, 1033, 908, 699 cm^{-1}; ^1H NMR δ 1.66–1.76 (4H, m), 2.34 (2H, dt, J=0.8, 6.4 Hz), 2.30–2.40 (1H, m), 2.52–2.62 (2H, m), 3.96 (4H, s), 5.35 (1H, t, J=0.8 Hz), 5.60 (1H, s), 7.29–7.42 (3H, m), 7.53–7.59 (2H, m). MS m/z (%) 284 (M^+, 84), 267 (58), 198 (74), 181 (51), 165 (60), 105 (100), 91 (46), 77 (57). Calcd for $C_{18}H_{20}O_3$: M, 284.1412. Found: m/z 284.1409.

*3.1.25. 8-(3-Iodoprop-2-ynylidene)-1,4-dioxapiro[4.5]decane (**24g**).* Light yellow oil; IR (neat) 2949, 2879, 1646, 1120, 1089, 1030, 904 cm^{-1}; ^1H NMR δ 1.72–1.81 (4H, m), 2.23–2.32 (4H, m), 4.00 (4H, s), 5.60 (1H, t, J=1.0 Hz). MS m/z (%) 304 (M^+, 25), 260 (17), 105

(21), 99(19), 91 (22), 71 (13). Calcd for $C_{11}H_{13}O_2I$: M, 303.9960. Found: *m*/*z* 303.9960.

*3.1.26. (E)-[Chloro(p-tolylsulfinyl)methylidene]-3-methylcyclohexane (**25E**).* Colorless crystal; mp 153.5–154 °C (hexane/AcOEt); IR (KBr) 2947, 2918, 2860, 1600, 1492, 1086, 1056, 807 cm^{-1}; ^1H NMR δ 1.08 (3H, d, *J*=6.6 Hz), 1.17–1.25 (1H, m), 1.36 (1H, tq, *J*=4.2, 12.0 Hz), 1.57–1.67 (1H, m), 1.78–1.85 (1H, m), 1.89 (1H, dt, *J*=13.8, 4.2 Hz), 1.97–2.05 (2H, m), 2.41 (3H, s), 2.82–2.88 (1H, m), 3.36 (1H, dquint, *J*=13.8, 1.8 Hz), 7.28–7.35 (2H, m), 7.44–7.50 (2H, m). Anal. Calcd for $C_{15}H_{19}ClOS$: C, 63.70; H, 6.77; Cl, 12.53; S, 11.34. Found: C, 63.69; H, 6.77; Cl, 12.54; S, 11.33.

*3.1.27. (Z)-[Chloro(p-tolylsulfinyl)methylidene]-3-methylcyclohexane (**25Z**).* Colorless crystal; mp 122.5–123.0 °C (hexane/AcOEt); IR (KBr) 2950, 2919, 2864, 1600, 1491, 1084, 1054, 805 cm^{-1}; ^1H NMR δ 0.98 (3H, d, *J*=6.6 Hz), 1.17–1.25 (1H, m), 1.43 (1H, tq, *J*=4.2, 13.2 Hz), 1.51–1.60 (1H, m), 1.76 (1H, dd, *J*=11.4, 13.2 Hz), 1.78–1.84 (1H, m), 2.03–2.08 (1H, m), 2.27 (1H, dt, *J*=4.2, 13.2 Hz), 2.41 (3H, s), 2.86 (1H, dt, *J*=13.2, 1.8), 3.36–3.42 (1H, m), 7.29–7.35 (2H, m), 7.44–7.51 (2H, m). Anal. Calcd for $C_{15}H_{19}ClOS$: C, 63.70; H, 6.77; Cl, 12.53; S, 11.34. Found: C, 63.68; H, 6.78; Cl, 12.48; S, 11.32.

*3.1.28. 1-[Chloro(p-tolylsulfinyl)methyl]-3-methyl-1-phenylethynylcyclohexane (**26**).* Compound **26aL**; colorless oil; IR (neat) 2927, 2866, 1597, 1492, 1090, 1063, 756, 692 cm^{-1}; ^1H NMR δ 0.91 (3H, d, *J*=6.1 Hz), 0.92–1.08 (1H, m), 1.35–1.94 (6H, m), 2.29–2.39 (1H, m), 2.39 (3H, s), 2.97–3.08 (1H, m), 4.78 (1H, s), 7.26–7.33 (5H, m), 7.40–7.46 (2H, m), 7.71–7.77 (2H, m). MS *m*/*z* (%) 384 (M^+, 2), 349 (5), 266 (10), 230 (24), 209 (100), 181 (32), 167 (51), 151 (52), 139 (40), 115 (77), 105 (41), 91 (58). Calcd for $C_{23}H_{25}ClOS$: M, 384.1315. Found: *m*/*z* 384.1313. Compound **26aP**; colorless oil; IR (neat) 2929, 2867, 1598, 1492, 1093, 1067, 757, 692 cm^{-1}; ^1H NMR δ 1.10 (3H, d, *J*=6.1 Hz), 1.28–1.44 (1H, m), 1.53–1.86 (6H, m), 2.18–2.30 (1H, m), 2.42 (3H, s), 2.44–2.52 (1H, m), 4.59 (1H, s), 7.25–7.32 (3H, m), 7.34 (2H, d, *J*=8.1 Hz), 7.47–7.55 (4H, m). MS *m*/*z* (%) 384 (M^+, 2), 232 (62), 209 (97), 181 (36), 167 (61), 151 (60), 139 (65), 115 (100), 91 (78). Calcd for $C_{23}H_{25}ClOS$: M, 384.1315. Found: *m*/*z* 384.1315. Compound **26bL**; colorless oil; IR (neat) 2928, 2866, 1598, 1491, 1082, 1059, 756, 692 cm^{-1}; ^1H NMR δ 1.01 (3H, d, *J*=6.3 Hz), 1.24–1.45 (1H, m), 1.57–1.89 (6H, m), 2.30–2.44 (1H, m), 2.39 (3H, s), 2.93–3.04 (1H, m), 4.81 (1H, s), 7.25–7.32 (5H, m), 7.38–7.45 (2H, m), 7.74 (2H, d, *J*=8.1 Hz). MS *m*/*z* (%) 384 (M^+, 6), 349 (8), 321 (7), 232 (60), 209 (100), 181 (34), 167 (56), 151 (53), 139 (43), 115 (79), 91 (60). Calcd for $C_{23}H_{25}ClOS$: M, 384.1315. Found: *m*/*z* 384.1308. Compound **26bP**; colorless oil; IR (neat) 2927, 2866, 1598, 1492, 1093, 1067, 757, 692 cm^{-1}; ^1H NMR δ 1.03 (3H, d, *J*=6.0 Hz), 1.08–1.20 (1H, m), 1.33–1.73 (3H, m), 1.79–2.09 (3H, m), 2.24–2.32 (1H, m), 2.37–2.46 (1H, m), 2.42 (3H, s), 4.57 (1H, s), 7.26–7.36 (5H, m), 7.49–7.55 (4H, m). MS *m*/*z* (%) 384 (M^+, 2), 349 (10), 321 (8), 245 (27), 232 (64), 209 (100), 181 (38), 167 (59), 151 (58), 139 (50), 115 (89), 91 (63). Calcd for $C_{23}H_{25}ClOS$: M, 384.1315. Found: *m*/*z* 384.1316.

*3.1.29. (E)-1-(3-Phenylprop-2-ynylidene)-3-ethycyclohexane (**27E**).* Colorless oil; IR (neat) 2924, 2197, 1596, 1489, 1442, 754, 690 cm^{-1}; ^1H NMR δ 0.94 (3H, d, *J*=6.4 Hz), 1.07–1.16 (1H, m), 1.40 (1H, tq, *J*=3.6, 12.6 Hz), 1.50–1.60 (1H, m), 1.72–1.78 (1H, m), 1.79 (1H, t, *J*=12.6 Hz), 1.83–1.89 (1H, m), 1.92–2.00 (1H, m), 2.31 (1H, dt, *J*=13.2, 1.8 Hz), 2.94 (1H, dt, *J*=13.8, 3.6 Hz), 5.42 (1H, s), 7.25–7.31 (3H, m), 7.41–7.44 (2H, m). MS *m*/*z* (%) 210 (M^+, 100), 195 (18), 167 (31), 154 (25), 141 (13), 128 (38), 115 (22), 95 (20). Calcd for $C_{16}H_{18}$: M, 210.1409. Found: *m*/*z* 210.1410.

*3.1.30. (Z)-1-(3-Phenylprop-2-ynylidene)-3-ethycyclohexane (**27Z**).* Colorless oil; IR (neat) 2926, 2198, 1595, 1489, 1443, 754, 690 cm^{-1}; ^1H NMR δ 0.99 (3H, d, *J*=6.6 Hz), 1.07–1.15 (1H, m), 1.37 (1H, tq, *J*=4.2, 12.6 Hz), 1.53–1.62 (1H, m), 1.69 (1H, t, *J*=12.6 Hz), 1.71–1.78 (1H, m), 1.79–1.88 (1H, m), 2.06 (1H, dt, *J*=4.2, 13.2 Hz), 2.25–2.30 (1H,m), 2.96 (1H, dt, *J*=13.2, 1.8 Hz), 5.44 (1H, s), 7.24–7.31 (3H, m), 7.41–7.44 (2H, m). MS *m*/*z* (%) 210 (M^+, 100), 195 (19), 167 (36), 154 (30), 141 (18), 128 (43), 115 (31), 95 (26). Calcd for $C_{16}H_{18}$: M, 210.1409. Found: *m*/*z* 210.1406.

*3.1.31. (E)-1-Chloro-2-methyl-4-phenyl-1-(p-tolylsulfinyl)but-1-en-3-yne (**28E**).* Colorless crystal; mp 102.5–103.5 °C (hexane/AcOEt); IR (KBr) 3056, 3019, 2921, 2207, 2184, 1492, 1083, 1064, 760, 687 cm^{-1}; ^1H NMR δ 2.16 (3H, s), 2.39 (3H, s), 7.27–7.32 (2H, m), 7.34–7.40 (3H, m) 7.49–7.54 (2H, m), 7.58–7.63 (2H, m). Anal. Calcd for $C_{18}H_{15}ClOS$: C, 68.67; H, 4.80; Cl, 11.26; S, 10.18. Found: C, 68.50; H, 4.74; Cl, 11.33; S, 10.14.

*3.1.32. (Z)-1-Chloro-2-methyl-4-phenyl-1-(p-tolylsulfinyl)but-1-en-3-yne (**28Z**).* Colorless crystal; mp 94.0–95.0 °C (hexane/AcOEt); IR (KBr) 3079, 3000, 2223, 2180, 1489, 1087, 1060, 758, 687 cm^{-1}; ^1H NMR δ 2.40 (3H, s), 2.47 (3H, s), 7.28–7.36 (5H, m), 7.43–7.48 (2H, m), 7.49–7.54 (2H, m). Anal. Calcd for $C_{18}H_{15}ClOS$: C, 68.67; H, 4.80; Cl, 11.26; S, 10.18. Found: C, 68.53; H, 4.81; Cl, 11.09; S, 10.04.

3.1.33. (3S,4R*,S*)-tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methyl-5-phenylpent-4-ynoate (**29a**).* Colorless oil; IR (neat) 2980, 2936, 2234, 1722, 1368, 1159, 1083, 1056, 757 cm^{-1}; ^1H NMR δ 1.49 (9H, s), 1.64 (3H, s), 2.41 (3H, s), 2.91 (1H, d, *J*=15.8 Hz) 3.50 (1H, d, *J*=15.8 Hz), 5.32 (1H, s), 7.28–7.34 (5H, m), 7.43–7.52 (2H, m), 7.72–7.79 (2H, m). MS *m*/*z* (%) 430 (M^+, 4), 414 (5), 357 (28), 207 (19), 199 (16), 187 (65), 171 (20), 140 (80), 115 (19), 105 (30), 57 (100). Calcd for $C_{24}H_{21}ClOS$: M, 430.1369. Found: *m*/*z* 430.1367.

3.1.34. (3R,4R*,S*)-tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methyl-5-phenyl-pent-4-ynoate (**29b**).* Colorless oil; IR (neat) 2979, 2935, 2238, 1726, 1160, 1084, 1055, 757 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 1.89 (3H, s), 2.42 (3H, s), 2.91 (1H, d, *J*=15.7 Hz), 3.16 (1H, d, *J*=15.7 Hz), 5.25 (1H, s), 7.25–7.35 (5H, m), 7.38–7.44 (2H, m), 7.73–7.79 (2H, m). MS *m*/*z* (%) 430 (M^+, 2), 357 (20), 235 (20), 207 (18), 199 (19), 187 (20), 171 (19), 140 (100), 105 (20), 57 (90). Calcd for $C_{24}H_{21}ClOS$: M, 430.1369. Found: *m*/*z* 430.1372.

*3.1.35. tert-Butyl 2-(1-phenylethynylcyclopropyl)acetate (**30**).* Colorless oil; IR (neat) 2978, 2930, 2220, 1726, 1368, 1147, 756 cm^{-1}; ^1H NMR δ 0.86 (1H, d, *J*=7.2 Hz), 0.87 (1H, d, *J*=6.6 Hz), 1.10 (1H, d, *J*=6.6 Hz), 1.11 (1H, d, *J*=7.2 Hz), 1.49 (9H, s), 2.36 (2H, s), 7.22–7.28 (3H, m), 7.32–7.39 (2H, m). MS *m*/*z* (%) 256 (M^+, 8), 200 (48), 183 (12), 155 (100), 127 (22) 57 (31). Calcd for $C_{17}H_{20}O_2$: M, 256.1463. Found: *m*/*z* 256.1459.

*3.1.36. (E)-tert-Butyl 3-methyl-6-phenylhex-3-en-5-ynoate (**31E**).* Colorless oil; IR (neat) 2979, 2932, 2199, 1732, 1368, 1145, 756, 691 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 2.05 (3H, d, *J*=1.1 Hz), 3.05 (2H, d, *J*=0.9 Hz), 5.59–6.62 (1H, m), 7.27–7.33 (3H, m), 7.40–7.47 (2H, m). MS *m*/*z* (%) 256 (M^+, 23), 200 (62), 155 (78), 115 (19) 57 (100), 41 (11). Calcd for $C_{17}H_{20}O_2$: M, 256.1463. Found: *m*/*z* 256.1463.

*3.1.37. (Z)-tert-Butyl 3-methyl-6-phenylhex-3-en-5-ynoate (**31Z**).* Colorless oil; IR (neat) 2978, 2933, 2199, 1732, 1368, 1145, 757, 691 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 1.94 (3H, d, *J*=1.5 Hz), 3.35 (2H, s), 5.64 (1H, d, *J*=1.5 Hz), 7.26–7.33 (3H, m), 7.40–7.46 (2H, m). MS *m*/*z* (%) 256 (M^+, 36), 200 (97), 183 (30), 155 (89), 115 (24) 57 (100). Calcd for $C_{17}H_{20}O_2$: M, 256.1463. Found: *m*/*z* 256.1464.

*3.1.38. (Z)-2-tert-Butyl-4-phenyl-1-(p-tolylsulfinyl)but-1-en-3-yne (**35**).* Phenylacetylene (0.38 mL; 1.3 mmol) was added to a solution of LDA (1.3 mmol) in 3 mL of dry THF in a flame-dried flask under argon atmosphere dropwise at 0 °C with stirring. The reaction mixture was

stirred for 10 min at 0 °C and cooled to −78 °C. A solution of **35** (69 mg; 0.27 mmol) in 3 mL of THF was added to the solution and the reaction mixture was slowly allowed to warm to 0 °C for 3 h. The reaction was quenched with satd aq NH_4Cl and the whole mixture was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography (hexane/AcOEt) to give **35** (83.2 mg; 95%) as colorless oil; IR (neat) 2968, 2870, 2210, 1490, 1082, 1060, 1041, 1016, 757 cm^{-1}; ^1H NMR δ 1.22 (9H, s), 2.41 (3H, s), 6.42 (1H, s), 7.28–7.41 (5H, m), 7.51–7.63 (4H, m). MS *m*/*z* (%) 322 (M^+, 10), 306 (21), 291 (13), 229 (12), 199 (100), 115 (12) 105 (79), 91 (18), 77 (11). Calcd for $C_{21}H_{22}OS$: M, 322.1391. Found: *m*/*z* 322.1392.

*3.1.39. (Z)-2-(2-Phenylethyl)-4-phenyl-1-(p-tolylsulfinyl)but-1-en-3-yne (**38a**).* Colorless oil; IR (neat) 3027, 2922, 2858, 2196, 1490, 1080, 1042, 757 cm^{-1}; ^1H NMR δ 2.41 (3H, s), 2.56–2.71 (2H, m), 2.94 (2H, t, *J*=6.3 Hz), 6.33 (1H, t, *J*=1.2 Hz), 7.13–7.20 (3H, m), 7.22–7.29 (4H, m), 7.36–7.41 (3H, m), 7.46–7.50 (2H, m), 7.53–7.56 (2H, m). MS *m*/*z* (%) 370 (M^+, 26), 265 (18), 247 (80), 229 (40), 215 (50), 141 (19) 115 (21), 105 (50), 91 (100). Calcd for $C_{25}H_{22}OS$: M, 370.1391. Found: *m*/*z* 370.1397.

*3.1.40. (Z)-2-Cyclohexyl-4-phenyl-1-(p-tolylsulfinyl)but-1-en-3-yne (**38b**).* Colorless oil; IR (neat) 2928, 2853, 2194, 1490, 1449. 1080, 1044, 808, 757 cm^{-1}; ^1H NMR δ 1.10–1.44 (5H, m), 1.63–1.74 (1H, m), 1.74–1.94 (4H, m), 2.14–2.27 (1H, m), 2.41 (3H, s), 6.39 (1H, d, *J*=1.0 Hz), 7.28–7.33 (2H, m), 7.36–7.41 (3H, m), 7.51–7.61 (4H, m). MS *m*/*z* (%) 348 (M^+, 9), 332 (28), 225 (100), 141 (18), 129 (18) 115 (25), 105 (81), 91 (40), 81 (22). Calcd for $C_{23}H_{24}OS$: M, 348.1548. Found: *m*/*z* 348.1550.

*3.1.41. (Z)-2-tert-Butyl-6-phenyl-1-(p-tolylsulfinyl)hex-1-en-3-yne (**38c**).* Colorless oil; IR (neat) 2967, 2930, 2214, 1493, 1455, 1080, 1043, 810, 700 cm^{-1}; ^1H NMR δ 1.07 (9H, s), 2.40 (3H, s), 2.75–2.82 (2H, m), 2.89–2.97 (2H, m), 6.27 (1H, s), 7.17–7.33 (7H, m), 7.47 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 350 (M^+, 7), 302 (15), 259 (75), 246 (23), 231 (26), 211 (20), 155 (18), 135 (32), 105 (21), 91 (100), 57 (29). Calcd for $C_{23}H_{26}OS$: M, 350.1704. Found: *m*/*z* 350.1705.

*3.1.42. (Z)-2-tert-Butyl-1-(p-tolylsulfinyl)but-1-en-3-yne (**38d**).* Colorless oil; IR (neat) 3202, 2969, 2901, 1493, 1082, 1040, 812, 787 cm^{-1}; ^1H NMR δ 1.13 (9H, s), 2.39 (3H, s), 3.55 (1H, s), 6.41 (1H, s), 7.29 (2H, d, *J*=8.1 Hz), 7.54 (2H, d, *J*=8.1 Hz). MS *m*/*z* (%) 246 (M^+, 5), 231 (21), 215 (24), 198 (53), 183 (100), 141 (56), 91 (60), 41 (30). Calcd for $C_{15}H_{18}OS$: M, 246.1078. Found: *m*/*z* 246.1078.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research No. 19590018 and 22590021 from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and TUS Grant for Research Promotion from Tokyo University of Science, which are gratefully acknowledged.

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