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Ligand Exchange Reaction of Sulfoxides in Organic Synthesis: A Novel Method for Synthesizing Acetylenes and Allenes from Carbonyl Compounds through Sulfoxides Having a Trifluoromethanesulfonyloxy Group on the β-Carbon

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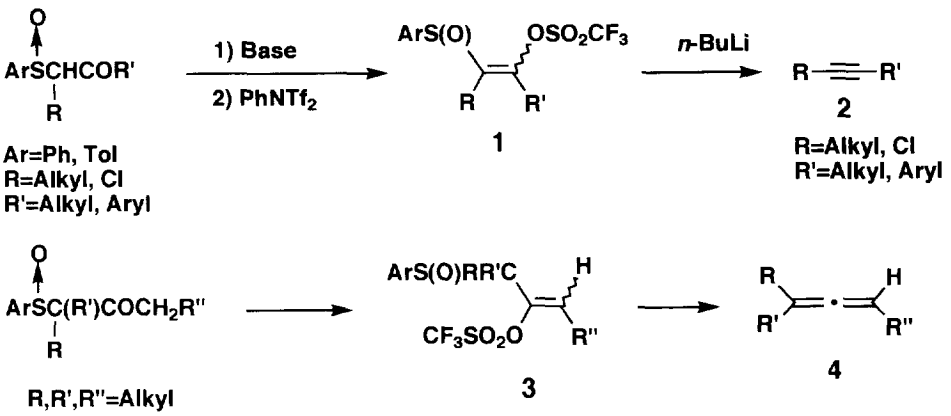
Abstract: *A novel method for synthesizing acetylenes and allenes from carbonyl compounds is described. Ligand exchange reaction of alkenylsulfoxides having a trifluoromethanesulfonyloxy group on the β-carbon, which were derived from α-alkyl β-ketosulfoxides, with n-BuLi gave disubstituted acetylenes in good yields. In the case of alkenylsulfoxides having both the trifluoromethanesulfonyloxy and aryl groups on the β-carbon, aryl acetylenes were obtained without treatment with n-BuLi. On the other hand, the enol triflates derived from α, α-dialkyl β-ketosulfoxides gave trisubstituted allenes on treatment with n-BuLi. This procedure was applied to the synthesis of chloroacetylenes, macrocyclic acetylenes and macrocyclic allenes.*

Acetylenes and allenes are quite important compounds in organic chemistry and innumerable studies have been reported on their chemistry and synthesis.[1] One method for synthesis of acetylenes and allenes is alkylation of the carbanionic intermediates of acetylenes and allenes. Transition metal-promoted reaction of alkylhalides with acetylenes is a useful recent method for preparing acetylenes.[2] In the synthesis of allenes, base-promoted interconversion of acetylenes to allenes is a useful procedure. Another useful method for synthesizing acetylenes and allenes is 1,n-elimination of olefins; for example, 1,2-elimination of hydrogen halide from vinylhalides.[1d,3]

Bartlett and Lythgoe reported a reductive 1,2-elimination of enol phosphonates derived from β-ketosulfones.[4] As the β-ketosulfones were synthesized from sulfones and esters with carbon-carbon bond formation, this procedure is useful for the construction of compounds having an acetylenic group. However, one drawback of this method is the use of liquid ammonia or toxic mercury.

Recently, our studies have focused on the development of the ligand exchange reaction of sulfoxides[5] in organic synthesis, and a useful β-elimination reaction was found.[6] In continuation of these studies we report here a new method for synthesizing acetylenes **2** and allenes **4** from carbonyl compounds via the ligand exchange reaction of sulfoxides having a trifluoromethanesulfonyloxy group on the β-carbon **1** and **3** (Scheme 1).[7]



Scheme 1

RESULTS AND DISCUSSION

Synthesis of Acetylenes from Carbonyl Compounds.

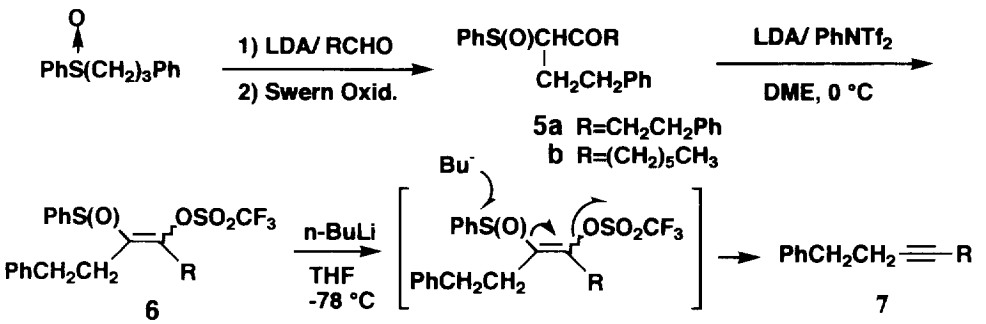
It has already been known that treatment of alkyl aryl sulfoxides with alkyllithium resulted in sulfur-aryl bond-cleavage to give aryllithium.[8] However, from our own experiences[5e, f] as well as reports from other chemists,[9] we expected that the sulfur-alkyl (and/or alkenyl) bond cleavage takes place in some particular compounds such as alkenylsulfoxides having a leaving group on its β-position.

α-Sulfinyl ketone **5a** was synthesized from phenyl 3-phenylpropyl sulfoxide and hydrocinnamaldehyde in two steps in quantitative yield (Scheme 2, Table 1). For the substituent having good leaving ability on β-position, we chose diethoxyphosphinyloxy[4] and trifluoromethanesulfonyloxy group.[10] Enol phosphorylation of α-sulfinyl ketone **5** according to Bartlett's procedure,[4] however, always gave less than 60% yield of enol phosphonates. On the other hand, enol triflates **6** were synthesized from **5** in almost quantitative yields by McMurry's procedure.[10]

Enol triflate **6a** was treated with 1.4 equivalents of *n*-BuLi in THF at -78 °C for 5 min. Fortunately, this reaction gave the desired acetylene **7a** in 82% yield.[11] Slightly lower yield (79%) was obtained when this reaction was carried out with *t*-BuLi. The mechanism of this reaction is shown in Scheme 2. Butyl anion attacks sulfinyl sulfur to give sulfur-alkenyl carbon bond cleavage, then the formed carbanion kicks out the trifluoromethanesulfonyloxy group. In this reaction no product derived from the sulfur-phenyl bond cleavage was observed. Two examples of this procedure are summarized in Table 1.

Next, α-sulfinyl ketone **8** was synthesized (Scheme 3). Enol triflation was carried out in DME containing 5 equivalents of HMPA. The enol triflate **9** was found to be unstable; upon chromatography on silica gel, it decomposed to give sulfinylallene **10** in about 30% yield. To overcome this problem, 2.1 equivalents of *n*-BuLi were added to the crude enol triflate **9** in THF at -78 °C. This two-step reaction gave the desired acetylene **11** in 55% overall yield from **8**.

This procedure was next applied to the α-sulfinyl ketones derived from aromatic aldehydes (Table 2). α-Sulfinyl ketones **12** were synthesized in high yields from aromatic aldehydes and sulfoxides in a similar way as

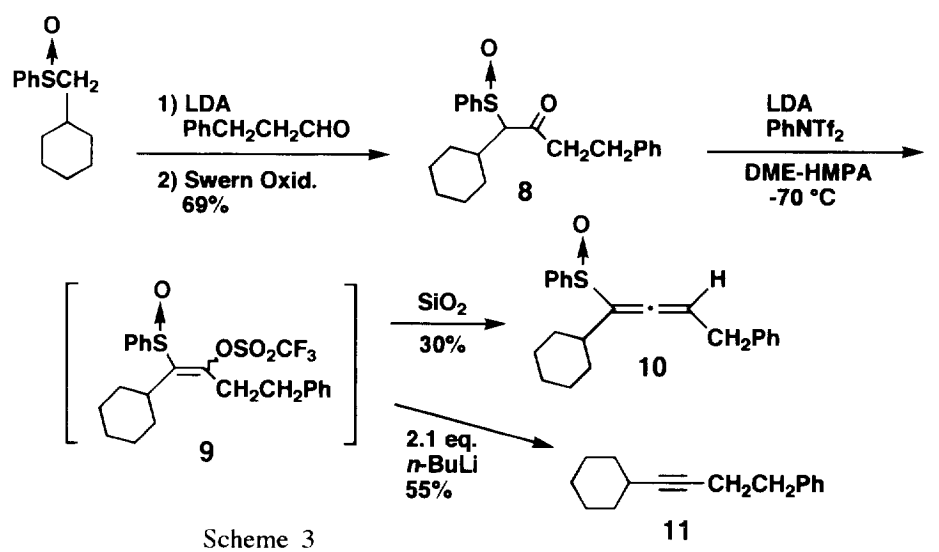


Scheme 2

Table 1. Synthesis of Acetylene **7** from Aldehydes through β-Trifluoromethanesulfonyloxy Vinyl Sulfoxide **6**

Aldehyde	**5** Yield (%)[a]	**6** Yield (%)	**7** Yield (%)
$PhCH_2CH_2CHO$	**5a** (99)	**6a** (99)[b]	**7a** (82)[c]
$CH_3(CH_2)_5CHO$	**5b** (93)	**6b** (95)[b]	**7b** (94)

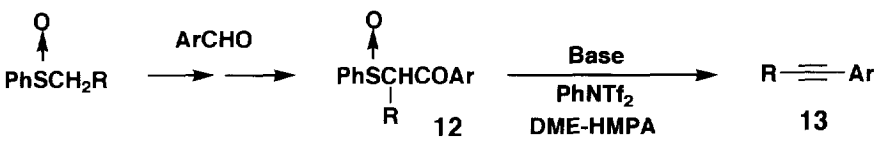
a) Two-step overall yield from phenyl 3-phenylpropyl sulfoxide and aldehyde. Isolate yield. b) E/Z-isomeric mixture. c) Slightly lower yield (79%) was obtained when this reaction was carried out with *t*-BuLi.

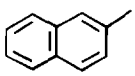
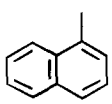
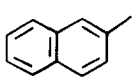


Scheme 3

described above (yields of **12** are summarized in Table 2). Enol triflation of **12a** was carried out under the same conditions as described for the synthesis of **6** at -78 °C. However, the reaction was found to be quite sluggish and a complex mixture was obtained. After some investigation we found that the reaction took place much more smoothly on addition of 5-7 equivalents of HMPA in the solution. This time, it was found that the produced enol triflate was slowly converted to acetylene **13a**. This reaction was completed at room temperature within 20 h and 67% of **13a** was obtained.

Table 2. Synthesis of Aryl Acetylene **13** from Aryl Aldehydes and Sulfoxide



R	12 Ar	(Yield/%)[a]	Base	13 (Yield/%)
$PhCH_2CH_2$	12a	Ph (98)	LDA	13a (67)
			KH	(56)
$PhCH_2CH_2$	12b	 (96)	LDA	13b (55)
			KH	(34)
$PhCH_2CH_2$	12c	 (81)	LDA	13c (55)
			KH	(47)
	12d	 (89)	LDA	13d (57)

a) Two-step overall yield from aromatic aldehyde and sulfoxide.

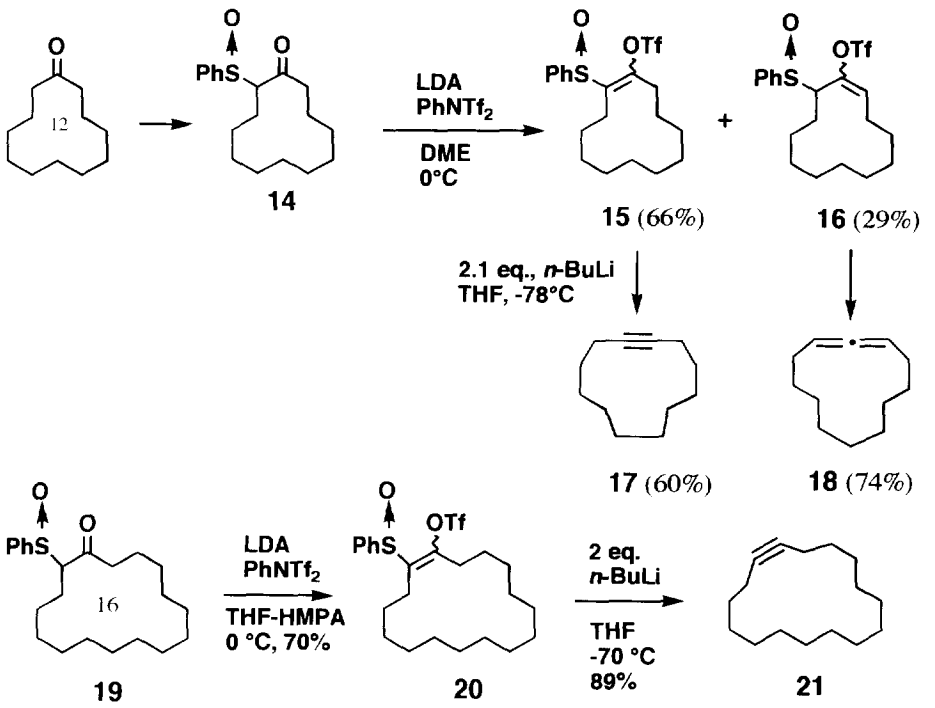
The mechanism of this reaction was thought to be similar to that mentioned in Scheme 2. However, obviously no *n*-BuLi was present in the reaction mixture, the ligand exchange reaction proceeded with a nucleophile other than *n*-BuLi. This reaction also proceeded with potassium hydride (KH) as a base in somewhat lower yield. From this fact, it is inferred that the nucleophile for the ligand exchange reaction is $PhNTf^-$.[12]

Four examples of the results for the transformation of the aromatic aldehydes to aryl acetylenes **13** through α-sulfinyl ketones **12** are summarized in Table 2. Though the overall yields are moderate, this three-step synthesis of acetylenes from aldehydes is useful for construction of aryl acetylenes.

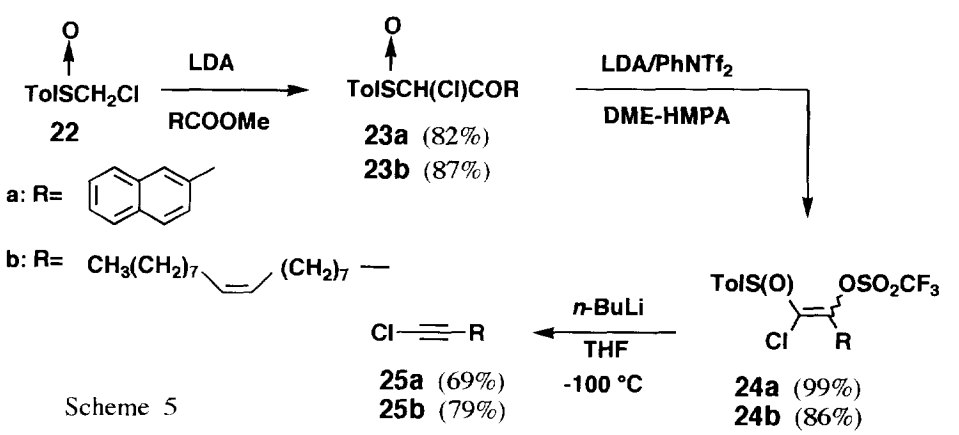
We next applied this procedure to a synthesis of cyclic acetylenes (Scheme 4). Cyclododecanone was converted to α-sulfinyl ketone **14** by sulfenylation[13] followed by oxidation with *m*-chloroperbenzoic acid in good yield. Enol triflation of **14** under the usual conditions gave the expected **15** and, somewhat surprisingly, another enol triflate **16**. The two enol triflates were separated by silica gel column chromatography. On treatment of **15**

with 2.1 equivalents of *n*-BuLi in THF at -78 °C, the expected cyclododecyne **17** was obtained in 60% yield. On the other hand, the same treatment of **16** gave cyclic allene **18** in 74% yield.

α-Sulfinyl ketone **19**, derived from cyclohexadecanone, was converted to enol triflate **20**. In this case only **20** was obtained. Treatment of **20** with 2-equivalents of *n*-BuLi in THF at -70 °C gave cyclohexadecyne **21** in high yield.

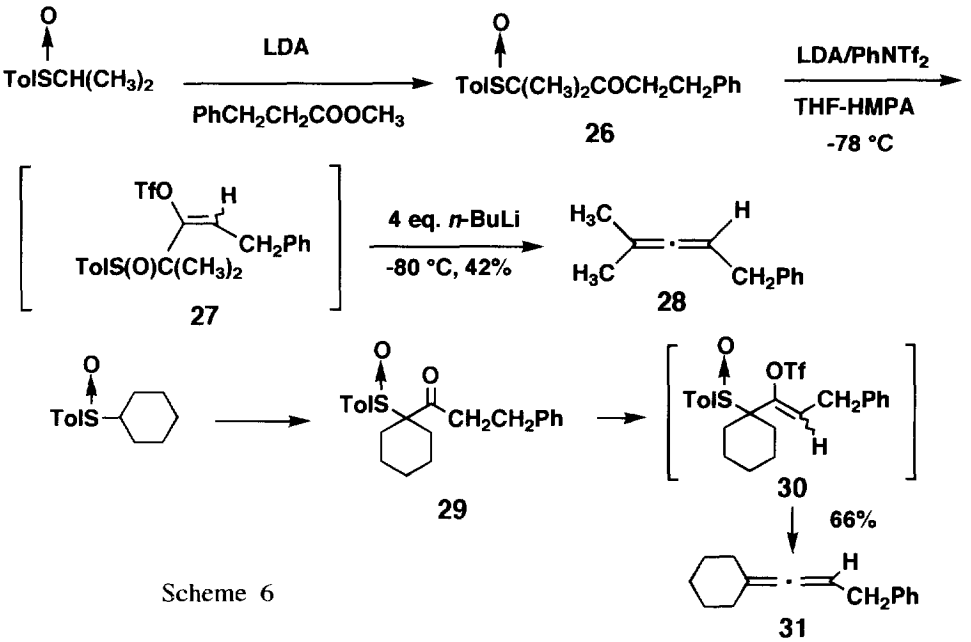


Scheme 4

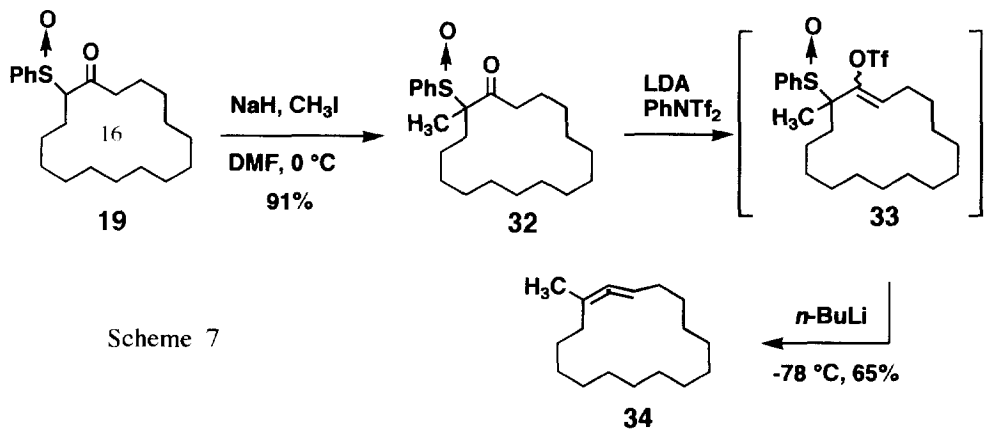


Scheme 5

Next, this procedure was applied to the synthesis of chloroacetylenes (Scheme 5).[1a] Chloromethyl *p*-tolyl sulfoxide **22** was treated with 2.4 equivalents of LDA in THF at -70 °C, then addition of a methyl ester afforded α-chloro α-sulfinyl ketone **23** in good yield. The enol triflation of **23** took place smoothly in DME-HMPA at room temperature to give **24** in high yield. The conditions of the desulfinylative β-elimination were found to be subtle. Treatment of **24** with 1.4 equivalents of *n*-BuLi in THF at -100 °C for 2 min proved to be the conditions of choice for the reaction. The desired chloroacetylenes **25a** and **b** were obtained in moderate to good yields.[14]



Scheme 6



Scheme 7

Synthesis of Allenes from Carbonyl Compounds.

As already mentioned above, the ligand exchange reaction of the sulfoxide having enol triflate group **16** gave allene **18** in good yield (see Scheme 4). This result implied that treatment of enol triflate **27** and **30** with *n*-BuLi would afford allenes **28** and **31**. To substantiate of this presumption, α-sulfinyl ketones having two alkyl groups on the α-carbon (**26** and **29**) were synthesized from isopropyl *p*-tolyl sulfoxide and cyclohexyl *p*-tolyl sulfoxide (Scheme 6).

The desired enol triflate **27** was easily synthesized at -78 °C with LDA, $PhNTf_2$ in THF-HMPA. However, **27** was found to be very unstable on contact with silica gel. In this case, after all the starting material **26** was gone, excess *n*-BuLi was added to the reaction mixture at -78 °C. This treatment gave the desired trisubstituted allene **28** in 42% yield. A similar treatment of ketone **29** gave allene **31** in 66% yield.

Finally, this method was applied to synthesis of trisubstituted macrocyclic allenene (Scheme 7). 2-Phenylsulfinylcyclohexadecanone **19** was alkylated with iodomethane in DMF by the use of sodium hydride as a base to afford α-methyl α-sulfinyl ketone **32** in high yield. Enol triflation and the ligand exchange reaction of **32** were carried out in a similar way as described for the synthesis of **28** and **31** to afford macrocyclic allene **34** in 65% yield from **32**.

In conclusion, we have established a novel method for synthesizing acetylenes and allenes from carbonyl compounds. The key reaction is β-elimination via the ligand exchange reaction of sulfoxides. These results extend the usefulness of sulfoxides in organic synthesis.

Experimental Section

All melting points are uncorrected. ^1H and ^{13}C NMR spectra were measured in a $CDCl_3$ solution with JEOL FX-100 or GX-270 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Devison) containing 2% 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 a dry solvent, THF was distilled from diphenylketyl; diisopropylamine, HMPA and DMF were dried over CaH_2 and distilled. DME was dried with $LiAlH_4$ and distilled.

1,6-Diphenyl-4-(phenylsulfinyl)-3-hexanone (5a). A solution of 3-phenylpropyl phenyl sulfoxide (1.22 g; 5 mmol) in 5 ml of dry THF was added to a solution of LDA (5.5 mmol) in 5 ml of THF at 0 °C with stirring. After 30 min, the solution was cooled to -65 °C and hydrocinnamaldehyde (6 mmol) was added dropwise with stirring and the reaction mixture was stirred at -65 °C for 10 min. The reaction was quenched with sat. aq. NH_4Cl. The whole was extracted with CH_2Cl_2, washed once with sat. aq. NH_4Cl. The organic layer was dried and the solvent was evaporated to afford the crude adduct, which was purified over silica gel column chromatography to give the adduct, which was used immediately in the next reaction.

To a solution of oxalyl chloride (7.5 mmol) in dry CH_2Cl_2 (12 ml) at -65 °C was added dimethylsulofoxide (15 mmol). After 5 min, a solution of the above mentioned adduct in 10 ml of CH_2Cl_2 was slowly added to the reaction mixture with stirring. The mixture was stirred at -65 °C for 15 min, then triethylamine (25 mmol) was added. The reaction mixture was stirred for 5 min, then gradually allowed to warm to 0 °C (about 2 h). The reaction was quenched by adding 10 ml of water. The whole was extracted with CH_2Cl_2 and the organic layer was washed once with sat. aq. NH_4Cl. The product was purified by silica gel column chromatography to afford 1.86 g (99%) of **5a** as colorless crystals. Mp 58-62 °C (AcOEt-hexane); IR (KBr) 1705 (CO), 1085, 1050 (SO) cm^{-1}; ^1H NMR δ 1.9-2.8 (8H, m), 3.58 (1H, dd, *J*=8, 6 Hz), 6.9-7.5 (15H, m); *Anal.* Calcd for $C_{24}H_{24}O_2S$: C, 76.56; H, 6.42; S, 8.51%. Found: C, 76.55; H, 6.40; S, 8.40%.

1-Phenyl-3-(phenylsulfinyl)-4-decanone (5b). Colorless oil; IR (neat) 1705 (CO), 1085, 1045 (SO) cm^{-1}; ^1H NMR δ 0.85 (3H, t, *J*=7 Hz), 1.0-1.5 (8H, m), 1.9-2.8 (6H, m), 3.5-3.8 (1H, m), 6.9-7.3 (5H, m),

7.48 (5H, s); MS *m/z* (%) 357 ([M+H]$^+$, 0.4), 145 (92), 91 (100). Calcd for $C_{22}H_{29}O_2S$: M, 357.1887. Found: *m/z* 357.1893.

1,6-Diphenyl-3-(phenylsulfinyl)-4-(trifluoromethanesulfonyloxy)-3-hexene (6a) A solution of **5a** (134 mg; 0.36 mmol) in dry DME (1.5 ml) was added dropwise to a solution of LDA (0.39 mmol) in 1 ml of DME at 0 °C. The mixture was stirred for 30 min, then a solution of *N*-phenyltrifluoromethanesulfonimide ($PhNTf_2$; 139 mg; 0.39 mmol) in 1 ml of DME was added. The reaction mixture was stirred for 3 h at 0 °C and quenched with sat. aq. NH_4Cl. The whole was extracted with CH_2Cl_2. The product was purified over silica gel column chromatography to give 179 mg (99%) of enol triflate **6a** as a light yellow oil. IR (neat) 1660 (C=C), 1425, 1220, 1145 cm^{-1}; ^{1}H NMR δ 1.9-2.8 (4H, m), 2.9-3.5 (4H, m), 6.8-7.8 (15H, m); MS *m/z* (%) 508 (M$^+$, trace), 490 (0.2), 417 (0.2), 91 (100). Calcd for $C_{25}H_{23}F_3O_4S_2$: M, 508.0988. Found: *m/z* 508.0975.

1-Phenyl-3-(phenylsulfinyl)-4-(trifluoromethanesulfonyloxy)-3-decene (6b). Light yellow oil; IR (neat) 1655 (C=C), 1410, 1210, 1135 cm^{-1}; ^{1}H NMR δ 0.84, 0.92 (each triplet, CH_3), 1.0-3.3 (14H, m), 6.9-7.8 (10H, m); MS *m/z* (%) 489 ([M+H]$^+$, 0.6), 471 (1.2), 91 (100). Calcd for $C_{23}H_{28}F_3O_4S_2$: M, 489.1379. Found: *m/z* 489.1383.

1,6-Diphenyl-3-hexyne (7a). A solution of *n*-BuLi (1.6 M in hexane; 0.33 mmol; 1.4 equivalents) was added dropwise with stirring to a solution of **6a** (118 mg; 0.23 mmol) at -78 °C under Ar atmosphere. After 5 min the reaction was quenched with sat. aq. NH_4Cl and the whole was extracted with CH_2Cl_2. The product was purified by silica gel column chromatography to give acetylene **7a** (46 mg; 82%) as a colorless oil. IR; no signal due to acetylenic stretching vibration could be observed. ^{1}H NMR δ 2.42, 2.78 (each 4H, t, *J*=7 Hz), 7.0-7.4 (10H, m); ^{13}C NMR δ 20.94, 35.45, 80.21 (acetylene), 126.13, 128.41, 140.93; MS *m/z* (%) 234 (M$^+$, 5), 206 (7), 143 (31), 91 (100). Calcd for $C_{18}H_{18}$: M, 234.1407. Found: *m/z* 234.1413.

1-Phenyl-3-decyne (7b). Colorless oil; IR; no signal due to acytylenic stretching vibration could be observed. ^{1}H NMR δ 0.89 (3H, t, *J*=7 Hz), 1.1-1.6 (8H, m), 2.0-2.2 (2H, m), 2.3-2.6 (2H, m), 2.79 (2H, t, *J*=7 Hz), 7.0-7.3 (5H, m); MS *m/z* (%) 214 (M$^+$, 1), 186 (1.5), 129 (28), 91 (100). Calcd for $C_{16}H_{22}$: M, 214.1720. Found: *m/z* 214.1720.

1-Cyclohexyl-4-phenyl-1-(phenylsulfinyl)-2-butanone (8). This compound was synthesized from cyclohexylmethyl phenyl sulfoxide and hydrocinnamaldehyde in a similar way as described for **5a**. Light yellow viscous oil; IR (neat) 1705 (CO), 1085, 1050 cm^{-1}; ^{1}H NMR δ 0.9-2.7 (15H, m), 3.12 (0.4H, d, *J*=10 Hz), 3.68 (0.6H, d, *J*=6 Hz), 6.8-7.3 (5H, m), 7.3-7.6 (5H, m); MS *m/z* (%) 354 (M$^+$, 5), 228 (88), 123 (100). Calcd for $C_{22}H_{26}O_2S$: M, 354.1655. Found: *m/z* 354.1650.

1-Cyclohexyl-4-phenyl-1-butyne (11). A solution of **8** (142 mg; 0.4 mmol) in DME (0.7 ml) and HMPA (0.35 ml) was added to a solution of LDA (0.48 mmol) in 0.5 ml of DME at -70 °C. The reaction mixture was stirred for 20 min. To the reaction mixture was added a solution of $PhNTf_2$ (200 mg; 0.56 mmol) in 1 ml of DME. The solution was stirred at -70 °C for 10 min then sat. aq. NH_4Cl was added. The whole was extracted with ether-benzene and the organic layer was washed once with sat. aq. NH_4Cl. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was dissolved in 4 ml of dry THF and the solution was cooled to -78 °C. To this solution was added *n*-BuLi (0.84 mmol) and the reaction mixture was stirred at -78 °C for 5 min. The reaction was quenched by adding sat. aq. NH_4Cl and the usual workup followed by purification by silica gel column chromatography gave 47 mg (55%) of the desired acetylene **11** as a colorless oil. IR; no signal due to acetylenic stretching vibration could be observed. ^{1}H NMR δ 1.0-1.9 (10H, m), 2.1-2.5 (3H, m), 2.78 (2H, t, *J*=7 Hz), 7.10 (5H, m); ^{13}C NMR δ 21.86, 24.92, 25.98, 29.13, 33.11, 35.75, 79.33 (acetylene), 85.41 (acetylene), 126.87, 128.24, 128.54, 141.10. MS *m/z* (%) 212 (M$^+$, 24), 184 (11), 169 (18), 130 (50), 91 (100). Calcd for $C_{16}H_{20}$: M, 212.1564. Found: *m/z* 212.1567.

Upon purification of the enol triflate in this reaction over silica gel, about 30% of sulfinylallene **10** was obtained. **10**: Colorless oil (diastereomeric mixture); IR (neat) 1960 (allene) cm^{-1}; ^{1}H NMR δ 0.8-2.7 (11H, m), 3.4 0 (2H, d, *J*=7 Hz), 5.85 (1H, q, *J*=7 Hz), 6.9-7.6 (10H, m); ^{13}C NMR δ 201.13, 201.83 (each allene-carbon). MS *m/z* (%) 336 (M$^+$, 15), 211 (40), 91 (100). Calcd for $C_{22}H_{24}OS$: M, 336.1546. Found: *m/z* 336.1544.

β-Ketosulfoxide (12). These ketones were synthesized in a similar way as described for **5a**. 1,4-Diphenyl-2-(phenylsulfinyl)-1-butanone (**12a**). Light yellow viscous oil; IR (neat) 1670 (CO), 1085, 1050 (SO) cm^{-1}; ^{1}H NMR δ 2.1-2.8 (4H, m), 4.5-4.8 (1H, m), 6.9-7.8 (15H, m); MS *m/z* (%) 349 ([M+H]$^+$, trace), 222

(86), 105 (100). 1-(2-Naphthyl)-4-phenyl-2-(phenylsulfinyl)-1-butanone (**12b**). Light yellow viscous oil; IR (neat) 1670 (CO), 1085, 1055 (SO) cm^{-1}; ^1H NMR δ 2.2-2.9 (4H, m), 4.6-4.9 (1H, m), 7.0-7.9 (17H, m); MS *m/z* (%) 398 (M^+, 0.4), 272 (100). 1-(1-Naphthyl)-4-phenyl-2-(phenylsulfinyl)-1-butanone (**12c**). Light yellow viscous oil; IR (neat) 1675 (CO), 1090, 1055 (SO) cm^{-1}; ^1H NMR δ 2.2-2.9 (4H, m), 4.5-4.8 (1H, m), 6.9-8.0 (16H, m), 8.4-8.6 (1H, m); MS *m/z* (%) 274 ([M-PhSOH]$^+$, 80), 181 (92), 155 (100). 2-Cyclohexyl-1-(2-naphthyl)-2-(phenylsulfinyl)-1-ethanone (**12d**). Colorless crystals (diastereomeric mixture); IR (KBr) 1660 (CO), 1050, 1030 (SO) cm^{-1}; ^1H NMR δ 0.9-2.7 (11H, m), 4.34 (0.3H, d, *J*=11H), 4.71 (0.7H, d, *J*=7 Hz), 7.0-8.0 (12H, m). A part of the crystals were recrystallized from AcOEt-hexane; mp 142-144 °C. Anal. Calcd for $C_{24}H_{24}O_2S$: C, 76.56; H, 6.43; S, 8.52%. Found: C, 76.37; H, 6.47; S, 8.58%.

1,4-Diphenyl-1-butyne (13a). A solution of **12a** (174 mg; 0.5 mmol) in 0.5 ml of DME and 0.4 ml of HMPA was added to a solution of LDA (0.6 mmol) in 0.5 ml of DME at -65 °C with stirring under Ar atmosphere. The solution was stirred at -65 °C for 15 min, then a solution of $PhNTf_2$ (250 mg; 0.7 mmol) in 0.8 ml of DME was added. The reaction mixture was stirred at -70 °C for 5 min and allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 3 h and the reaction was quenched with sat. aq. NH_4Cl. The whole was extracted with ether-benzene and the product was purified by silica gel column chromatography to afford 69 mg (67%) of acetylene **13a** as a colorless oil. IR (neat) 2250 (acetylene) cm^{-1}; ^1H NMR δ 2.6-2.8 (2H, m), 2.8-3.0 (2H, m), 7.1-7.6 (10H, m); ^{13}C NMR δ 21.65, 35.16, 81.21 (acetylene), 89.45 (acetylene). MS *m/z* (%) 206 (M^+, 91), 91 (100). Calcd for $C_{16}H_{14}$: M, 206.1094. Found: *m/z* 206.1097.

Potassium hydride (1.5 mmol) was added to a dry flask and DME (0.5 ml) was added. To this suspension was added a solution of **12a** (174 mg; 0.5 mmol) in 0.3 ml of DME and 0.5 ml of HMPA at 0 °C. The reaction mixture was stirred at 0 °C for 20 min. A solution of $PhNTf_2$ (250 mg; 0.7 mmol) in 0.5 ml of DME and 0.1 ml of HMPA was added to the reaction mixture and the solution was stirred at room temperature for 3.5 h. The usual workup followed by purification gave 58 mg (56%) of **13a** as a colorless oil.

1-(2-Naphthyl)-4-phenyl-1-butyne (13b). Colorless crystals; mp 53-55 °C (MeOH). IR (KBr) the signal due to acetylenic stretching vibration could not be observed; ^1H NMR δ 2.6-2.8 (2H, m), 2.8-3.0 (2H, m), 7.1-7.5 (8H, m), 7.6-7.9 (4H, m); ^{13}C NMR δ 21.76, 35.22, 81.73 (acetylene), 89.92 (acetylene); MS *m/z* (%) 256 (M^+, 99), 165 (100). *Anal.* Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29 %. Found: C, 93.57; H, 6.25 %.

1-(1-Naphthyl)-4-phenyl-1-butyne (13c). Colorless crystals; mp 40-43 °C (MeOH). IR (KBr) the signal due to acetylenic stretchingvibration could not be observed; ^1H NMR δ 2.6-3.1 (4H, m), 7.0-8.2 (12H, m); ^{13}C NMR δ 21.88, 35.22, 79.45 (acetylene), 94.48 (acetylene). MS *m/z* (%) 256 (M^+, 26), 165 (100). Calcd for $C_{20}H_{16}$: M, 256.1251. Found: *m/z* 256.1253.

2-Cyclohexyl-1-(2-naphthyl)ethyne (13d). Colorless crystals; mp 56-57 °C (MeOH); IR (KBr) 2240 (acetylene) cm^{-1}; ^1H NMR δ 1.1-2.1 (10H, m), 2.4-2.8 (1H, m), 7.1-7.9 (7H, m); ^{13}C NMR δ 24.92, 25.92, 29.78, 32.76, 88.99 (acetylene), 94.77 (acetylene). MS *m/z* (%) 234 (M^+, 100), 205 (33). *Anal.* Calcd for $C_{18}H_{16}$: C, 92.26; H, 7.74%. Found: C, 92.25; H, 7.62%.

1-(Phenylsulfinyl)-2-trifluoromethanesulfonyloxy)cyclododecene (15) and 3-(Phenylsulfinyl)-2-(trifluoromethanesulfonyloxy)cyclododecene (16). These enol triflates were synthesized from **14** in a similar way as described for **6a**. **15**: Light yellow oil; IR (neat) 1645 (C=C), 1420, 1220, 1140, 1090, 1055 cm^{-1}; ^1H NMR δ 0.9-2.2 (16H, m), 2.4-2.7 (4H, m), 7.0-7.7 (5H, m); MS *m/z* (%) 438 (M^+, 6), 421 (25), 305 (21), 126 (100). Calcd for $C_{19}H_{25}F_3O_4S_2$: M, 438.1134. Found: *m/z* 438.1139. **16**: Light yellow oil; IR (neat) 1615 (C=C), 1425, 1110, 1050 cm^{-1}; ^1H NMR δ 1.0-1.9 (15H, m), 2.0-2.2 (2H, m), 2.4-2.5 (1H, m), 3.25, 3.47 (total 1H, each dd, *J*=10.5, 5.5 Hz and *J*=12.5, 3.5 Hz), 5.76 (1H, dd, *J*=10.5, 8.5 Hz), 7.5-7.7 (5H, m); MS *m/z* (%) 439 ([M+H]$^+$, 1), 422 (1), 218 (41). Calcd for $C_{19}H_{26}F_3O_4S_2$: M, 439.1210. Found: *m/z* 439.1216.

Cyclododecyne (17). Colorless oil; IR (neat) 2235 (acetylene) cm^{-1}; ^1H NMR δ 1.1-1.7 (16H, m), 2.0-2.3 (4H, m); ^{13}C NMR δ 18.51, 24.60, 24.92, 25.59, 25.70, 81.58 (acetylene); MS *m/z* (%) 164 (M^+, 7), 121 (57), 67 (100). Calcd for $C_{12}H_{20}$: M, 164.1564. Found: *m/z* 164.1570.

1,2-Cyclododecadiene (18). Colorless oil; IR (neat) 1970 (allene) cm^{-1}; ^1H NMR δ 0.8-1.8 (14H, m), 1.8-2.2 (4H, m), 4.7-5.0 (2H, m); ^{13}C NMR δ 21.68, 22.85, 26.16, 21.86, 27.06, 88.93, 206.59 (allene); MS *m/z* (%) 164 (M^+, 8), 121 (23), 67 (100). Calcd for $C_{12}H_{20}$: M, 164.1564. Found: *m/z* 164.1564.

1-(Phenylsulfinyl)-2-(trifluoromethanesulfonyloxy)cyclohexadecene (20). A solution of **19** (323 mg; 1 mmol) in 2 ml of THF and 1 ml of HMPA was added to a solution of LDA (1.2 mmol) in THF (2 ml) at 0 °C with stirring. The solution was stirred for 30 min and then a solution of $PhNTf_2$ (464 mg; 1.3 mmol) in 3 ml of THF was added to the reaction mixture. The reaction mixture was stirred at 0 °C for 3 h. The reaction was quenched with sat. aq. NH_4Cl and the whole was extracted with CH_2Cl_2. The product was purified by silica gel column chromatography to afford 347 mg (70%) of **20** as a light yellow oil. IR (neat) 1650 (C=C), 1420, 1210, 1140, 1085, 1050 cm^{-1}; ^1H NMR δ 0.8-1.8 (24H, m), 1.9-2.6 (4H, m), 7.4-7.7 (5H, m); ^{13}C NMR δ 139.46, 142.33, 151.86 (CF_3).

Cyclohexadecyne (21). Colorless oil; IR (neat) no signal due to acetylenic stretching vibration could be observed; ^1H NMR δ 1.2-1.6 (24H, m), 2.2 (4H, m); ^{13}C NMR δ 18.53, 25.91, 26.27, 27.24, 27.35 (2C), 28.36, 80.54 (acetylene). MS *m/z* (%) 220 (M^+, 23), 149 (8), 121 (27), 80 (100). Calcd for $C_{16}H_{28}$: M, 220.2190. Found: *m/z* 220.2197.

2-Chloro-2-(*p*-tolylsulfinyl)-1-(2-naphthyl)-1-ethanone (23a). A solution of chloromethyl *p*-tolyl sulfoxide (192 mg; 1 mmol) in THF (1 ml) was added dropwise with stirring to a solution of LDA (2.2 mmol) in 3 ml of THF at -70 °C. The solution was stirred for 30 min. To this solution was added a solution of methyl 2-naphthoate (206 mg; 1.1 mmol) in 1 ml of THF. The reaction mixture was stirred at -70 °C for 30 min and the reaction was quenched with sat. aq. NH_4Cl. The whole was extracted with CH_2Cl_2 and the product was purified over silica gel column chromatography to afford **23a** (288 mg; 83%) as light yellow crystals. Mp 153-156 °C (AcOEt-hexane); IR (KBr) 1675, 1660 (CO), 1090, 1065 (SO) cm^{-1}; ^1H NMR δ 2.29, 2.40 (total 3H, each singlet, CH_3), 5.99, 6.00 (total 1H, each singlet), 7.0-8.5 (11H, m); MS *m/z* (%) 342 (M^+, 7), 204 (8), 155 (100). *Anal.* Calcd for $C_{19}H_{15}ClO_2S$: C, 66.60; H, 4.40%. Found: C, 66.40; H, 4.41%.

(Z)-1-Chloro-1-(*p*-tolylsulfinyl)-10-nonadecen-2-one (23b). Light yellow oil; IR (neat) 1720 (CO), 1080, 1055 (SO) cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.0-2.8 (28H, m), 2.43 (3H, s), 4.95, 4.97 (total 1H, each singlet), 5.33 (2H, m), 7.2-7.6 (4H, m); MS *m/z* (%) 452 (M^+, 1.5), 313 (5), 139 (100). Calcd for $C_{26}H_{41}ClO_2S$: M, 452.2513. Found: *m/z* 452.2501.

Enol triflate (24a). A solution of **23a** (754 mg; 2.2 mmol) in DME (10 ml) and HMPA (1.6 ml) was added to a solution of LDA (2.85 mmol) in 10 ml of DME at -78 °C under Ar atmosphere. The cooling bath was replaced to ice bath and the reaction mixture was stirred at 0 °C for 30 min. To the reaction mixture was added a solution of $PhNTf_2$ (1.1 g; 3.07 mmol) in 1 ml of DME was added and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched by sat. aq. NH_4Cl and usual workup followed by silica gel column chromatography gave **24a** (1.04 g; 99%) as a light yellow oil; IR (neat) 1440, 1230, 1220, 1140, 1095, 1060, 1035 cm^{-1}; ^1H NMR δ 2.43 (3H, s), 7.1-8.2 (11H, m).

Enol triflate (24b). Light yellow oil; IR (neat) 1440, 1250, 1225, 1210, 1120 cm^{-1}; ^1H NMR δ 0.88 (3H, t, *J*=7 Hz), 2.43 (3H, s), 5.34 (2H, m), 7.2-7.6 (4H, m).

(2-Naphthyl)chloroacetylene (25a). A solution of *n*-Bu:Li (0.65 mmol) in hexane was added dropwise with stirring to a solution of **24a** (217 mg; 0.46 mmol) in 3 ml of THF at -100 °C. After 2 min, the reaction was quenched with sat. aq. NH_4Cl and the whole was extracted with benzene-ether. The product was purified by silica gel column chromatography to give **25a** (59 mg; 69%) as a light yellow solid. IR (KBr) 2200 (acetylene) cm^{-1}; ^1H NMR δ 7.3-8.0 (m); MS *m/z* (%) 186 (M^+, 100), 151 (50). Calcd for $C_{12}H_7Cl$: M, 186.0236. Found: *m/z* 186.0233.

(Z)-1-Chloro-10-nonadecene-1-yne (25b). Colorless oil; IR (neat) 2250 (acetylene) cm^{-1}; ^1H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.0-1.6 (24H, m), 1.8-2.2 (4H, m), 5.33 (2H, m). Calcd for $C_{19}H_{33}Cl$: M, 296.2269. Found: *m/z* 296.2286.

5-Phenyl-2-(*p*-tolylsulfinyl)-3-pentanone (26). A solution of 1.08 g (6 mmol) of isopropyl *p*-tolyl sulfoxide in 5 ml of THF was added to a solution of LDA (10.7 mmol) in 10 ml of THF at -78 °C. After 5 min HMPA (2.1 ml) was added to the reaction mixture and the mixture was stirred for 15 min. Methyl hydrocinnamate (1.76 g) was added to the reaction mixture and the solution was stirred for 50 min. The reaction was quenched by adding sat. aq. NH_4Cl and the whole was extracted with ether-benzene. After purification over silica gel column chromatography, 1.067 g (57%; conversion yield 72%) of **26** and the recovered starting material were obtained. **26:** Light yellow oil; IR (neat) 1700 (CO), 1083, 1047 (SO) cm^{-1}; ^1H NMR δ 1.35, 1.39, 2.39

(each 3H, s), 2.75 (4H, bs), 7.0-7.4 (9H, m); MS *m/z* (%) 314 (M^+, trace), 174 (95), 140 (73), 91 (100). Calcd for $C_{19}H_{22}O_2S$: M, 314.1330. Found: *m/z* 314.1346.

1-(3-Phenyl-1-propanoyl)-1-(*p*-tolylsulfinyl)cyclohexane (29). Colorless solid; IR (KBr) 1690 (CO), 1095, 1050 (SO) cm^{-1}; ^1H NMR δ 1.1-2.2 (10H, m), 2.39 (3H, s), 2.6-3.0 (4H, m), 7.1-7.4 (9H, m).

1,1-Dimethyl-4-phenyl-1,2-butadiene (28). To a solution of LDA (2 mmol) in 4 ml of THF at -78 °C was added a solution of **26** (490 mg; 1.56 mmol) in THF (3 ml) with stirring. After 5 min, 1.36 ml of HMPA was added dropwise to the reaction mixture. The solution was stirred at -78 °C for 20 min and a solution of $PhNTf_2$ (670 mg) in 4 ml of THF was added. The reaction mixture was stirred at -78 °C for 50 min. The reaction mixture was cooled to -83 °C and *n*-BuLi (6.24 mmol) was added. After 5 min, the reaction was quenched by adding sat. aq. NH_4Cl. Usual workup followed by silica gel column chromatography gave the allene **28** (104 mg; 42%) as a colorless oil. IR (neat) 1967 (allene) cm^{-1}; ^1H NMR δ 1.66, 1.69 (each 3H, s), 3.28 (2H, d, *J*=7 Hz), 5.08 (1H, m), 7.21 (5H, m); ^{13}C NMR δ 20.59 (CH_3), 36.21, 88.28, 95.42, 125.96, 128.24, 128.47, 141.05, 202.48 (allene); MS *m/z* (%) 158 (M^+, 38), 143 (100). Calcd for $C_{12}H_{14}$: M, 158.1095. Found: *m/z* 158.1096.

Allene (31). Colorless oil; IR (neat) 1965 (allene) cm^{-1}; ^1H NMR δ 1.3-1.7 (6H, m), 2.0-2.2 (4H, m), 3.30 (2H, d, *J*=7 Hz), 5.12 (1H, m), 7.1-7.4 (5H, m); ^{13}C NMR δ 26.10, 27.35, 31.64, 36.35, 88.32, 103.00, 125.89, 128.21, 128.59, 140.99, 199.17 (allene); MS *m/z* (%) 198 (M^+, 67), 183 (12), 169 (24), 91 (100). Calcd for $C_{15}H_{18}$: M, 198.1407. Found: *m/z* 198.1418.

2-Methyl-2-(phenylsulfinyl)cyclohexadecanone (32). To a solution of **19** (168 mg; 0.46 mmol) in 3 ml of DMF at 0 °C was added NaH (0.62 mmol) with stirring under Ar atmosphere. The reaction mixture was stirred at 0 °C until H_2 gas evolution ceased (30 min). Iodomethane (0.72 mmol) was added to the solution and the reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched with sat. aq. NH_4Cl and the DMF was evaporated under vacuum. The residue was extracted with benzene, washed with water and dried over $MgSO_4$. The product was purified over silica gel column chromatography to afford **32** (158 mg; 91%) as a colorless oil. This compound is somewhat unstable due to thermal elimination of the sulfinyl group. IR (neat) 1697 (CO), 1080, 1045 (SO) cm^{-1}; ^1H NMR δ 1.0-1.8 (26H, m), 1.22 (3H, s), 2.2-2.7 (2H, m), 7.3-7.7 (5H, m); MS *m/z* (%) 176 (M^+, 0.2), 159 (12), 250 (79), 125 (100). Calcd for $C_{23}H_{36}O_2S$: M, 376.2433. Found: *m/z* 376.2428.

1-Methylcyclohexadeca-1,2-diene (34). To a solution of LDA (0.5 mmol) in 2 ml of THF at -80 °C was added a solution of HMPA (0.44 mmol) in 1 ml of THF. A solution of **32** (158 mg; 0.42 mmol) in 1 ml of THF was slowly added to the solution of LDA and stirred at -80 °C for 30 min. To the reaction mixture was added a solution of $PhNTf_2$ (257 mg; 0.71 mmol) in 3 ml of THF and the reaction mixture was stirred for 1 h. To this reaction mixture was added *n*-BuLi (1.68 mmol) at -80 °C with stirring and after 10 min the reaction was quenched with sat. aq. NH_4Cl. The product was purified by silica gel column chromatography to give 64 mg (65%) of **34** as a colorless oil. IR (neat) 1963 (allene) cm^{-1}; ^1H NMR δ 1.2-1.5 (22H, m), 1.66 (3H, d, *J*=3 Hz), 1.8-2.2 (4H, m), 4.97 (1H, m); ^{13}C NMR δ 19.03 (CH_3), 25.02, 25.41, 25.66, 25.73, 26.08, 26.70, 27.44, 27.53, 27.75, 27.84, 28.32, 29.56, 34.22, 90.10, 98.99, 201.54 (allene); MS *m/z* (%) 234 (M^+,25), 219 (3), 95 (81), 82 (100). Calcd for $C_{17}H_{30}$: M, 234.2346. Found: *m/z* 234.2346.

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11. This reaction gave butyl phenyl sulfoxide as a side product in less than 50% yield (not 82%). The reason is that the produced butyl phenyl sulfoxide reacted with *n*-BuLi to give dibutyl sulfoxide (see ref. 8).
12. Several trials to isolate the expected sulfinamide (PhNTf(SOPh)) was failed. We think that the sulfinamide is not stable in our workup conditions. We expect that the reason why **12** directly gave **13** (and **6** did not yield **7**) is the formation of thermodynamically stable acetylenes conjugated with aryl group. We did not observe any acetylenes in the formation of enol triflate **6** at 0 °C.
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14. We also tried to synthesize fluoroacetylenes by this method starting from fluoromethyl phenyl sulfoxide. The enol triflates **24** (fluorine and phenyl instead of chlorine and tolyl) were synthesized in a similar way as described for **24** without any problem. However, the final step gave a complex mixture.

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