Reactions of (*E*)-2-Iodo-1-tosyl-1-alkenes as Useful Synthetic Intermediates

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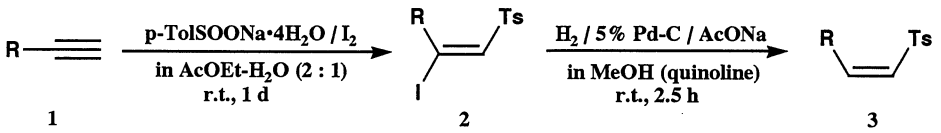
(*E*)-2-Iodo-1-tosyl-1-alkenes readily available by iodosulfonization of 1-alkynes were found to be useful synthons for the regio- and/or stereoselective preparation of 1-tosyl-1-alkynes, 1-tosyl-2-alkynes, (*Z*)-vinyl and (*Z*)-allyl sulfones, β-tosyl enamines, α-tosyl ketones, α-tosyl aldehyde acetal, and β-disubstituted vinyl sulfones.

We have been investigating the preparations and the reactions of vinyl sulfones[1] and the related allyl sulfones[2] to extend the synthetic utility of sulfones and to elucidate the origin of "syn-effect".[1,3] In the previous paper,[2b] we briefly reported the regio- and stereoselective synthesis of (*E*)- and (*Z*)-allyl sulfones from aldehydes and alkynes. The preparation of (*Z*)-allyl sulfones was achieved through propargyl sulfone derivatives (**4**) which were derived from (*E*)-2-iodo-1-tosyl-1-alkenes (**2**)[2b] readily available by iodosulfonization of 1-alkynes (**1**). The compounds **2** have been also found to be the useful intermediates for the regio- and stereoselective preparation of (*Z*)-vinyl sulfones.[1a] In this report, the various kinds of reactions of **2** were described including the detail of its application to the synthesis of (*Z*)-vinyl and (*Z*)-allyl sulfones.

Results and Discussion

Iodosulfonization of 1-alkynes (**1**) was accomplished by the similar manner described for 1-alkenes[1b] to yield **2** in high yields as listed in Table 1.[4a] (*Z*)-Vinyl sulfones (**3**) were readily prepared by selective catalytic hydrogenation of **2** by the use of Pd–C in excellent yields (Table 1). The abbreviation Ts means *p*-toluenesulfonyl (=tosyl, *p*-$CH_3C_6H_4SO_2$-) group in the following.

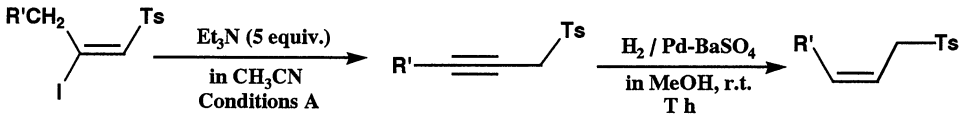
On the other hand, the preparation of (*Z*)-allyl sulfones (**5**) was achieved through propargyl sulfones (**4**) which



1 **2** **3**

Table 1. Preparation of (*E*)-2-Iodo-1-tosyl-1-alkenes (**2**) and (*Z*)-1-Tosyl-1-alkenes (**3**)

Run	**1**,	R	Yield of **2** %	Yield of **3** %
1	**a**,	$Ph(CH_2)_2$	75	98
2	**b**,	$CH_3(CH_2)_2$	88	98
3	**c**,	$CH_3(CH_2)_3$	95	98
4	**d**,	$CH_3(CH_2)_5$	92	96
5	**e**,	$CH_3(CH_2)_8$	79	96



2 **4** **5**

Table 2. Preparation of 1-Tosyl-2-alkynes (**4**) and (*Z*)-1-Tosyl-2-alkenes (**5**)

Run	**2**,	R′	Conditions A	Yield of **4** %	Time h	Yield of **5** %
1	**a**,	$PhCH_2$	r.t., 3 d	87	1.0	93
2	**b**,	CH_3CH_2	50°C, 1 d	95	3.0	89
3	**c**,	$CH_3(CH_2)_2$	50°C, 1 d	94	0.5	91
4	**d**,	$CH_3(CH_2)_4$	50°C, 2.5 d	89	0.5	94
5	**e**,	$CH_3(CH_2)_7$	50°C, 2 d	92	4.0	94

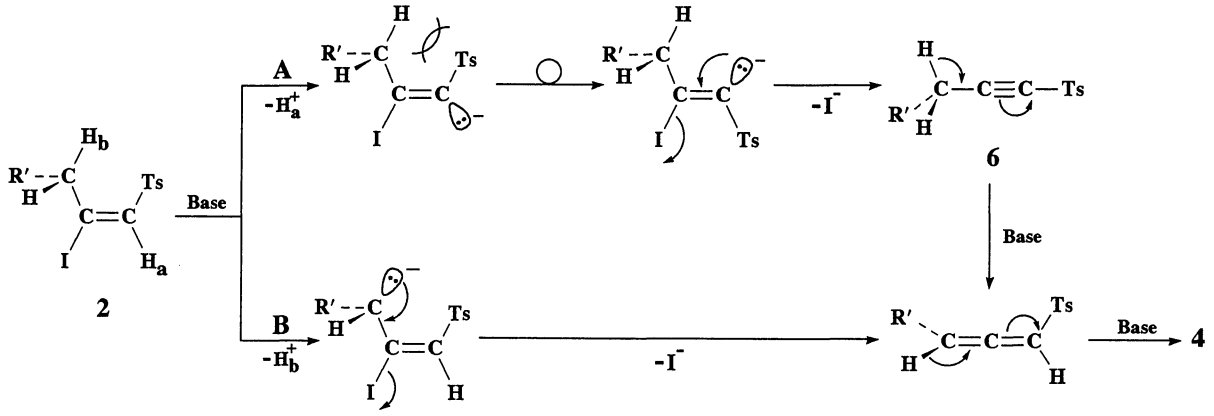
were derived from **2** by treatment with triethylamine. Catalytic hydrogenation of **4** afforded **5** in excellent yields as summarized in Table 2.

In order to elucidate the reaction mechanism from **2** to **4**, (*E*)-2-iodo-4-phenyl-1-tosyl-1-butene (**2a**) was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) instead of triethylamine in acetonitrile at 0 °C for 10 min, and the corresponding 1-tosyl-1-alkyne (**6a**) was isolated in low yield (29%).[2b] This fact seemed to suggest that the reaction proceeded through the path A in Scheme 1. The rapid inversion of the initially formed vinyl α-anion having unfavorable steric hindrance is supported by the fact that electron-withdrawing substituents lower a barrier to the inversion[5] different from the case of unactivated vinyl anion in which the syn β-elimination is possible as described for potassium *t*-butoxide induced dehydrochlorination of the isomeric chlorodiphenylethenes.[6]

Such a consideration prompted us to investigate the experimental conditions under which the synthetically useful **6**[7] is formed selectively, since the previous attempts using potassium carbonate as a base were not so promising.[4a] Ultimately, it was found that when **2** was treated with *t*-BuOK in THF at −78 °C for a short time, the corresponding **6** was obtained in excellent yield as summarized in Table 3 (Runs 3—8).

4-Phenyl-1-tosyl-1-butyne (**6a**) thus prepared could be quantitatively converted to 4-phenyl-1-tosyl-2-butyne (**4a**) by treatment with triethylamine in acetonitrile at room temperature for 30 h. Though this result looks to support the path A in Scheme 1 again, the reaction mechanism is still ambiguous since the use of triethylamine for **2** did not allow us to observe the formation of the intermediate **6**, but always directly afforded only **4**.

It was further found that when the above reaction of **2** with *t*-BuOK (4 equiv) was carried out at higher temparature (−16 °C), the dimerized products (**7**) were



Scheme 1.

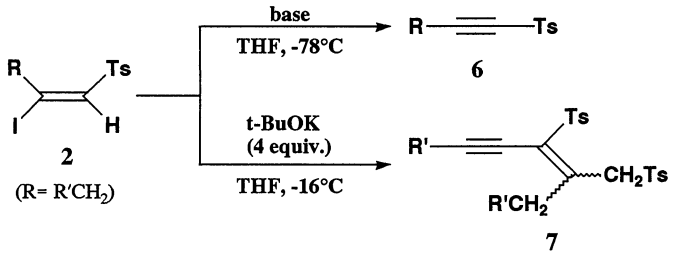


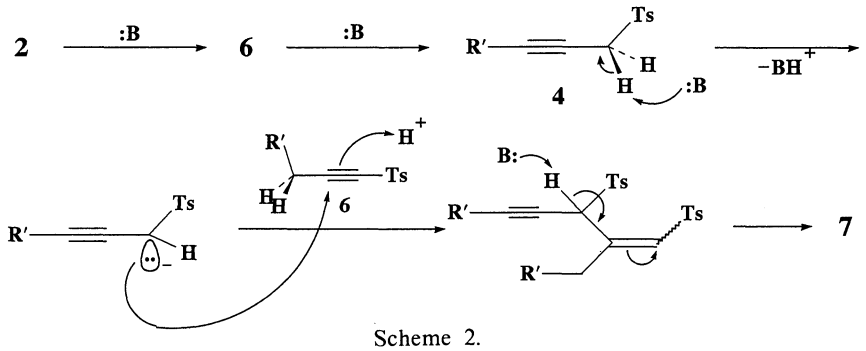
Table 3. Preparation of 1-Tosyl-1-alkynes (**6**) and Their Dimers (**7**)

Run	2,	R	Base (equiv)	Time (min)	Yield of **6** (%)	Time (min)	Yield of **7** (%)
1	**a**,	$Ph(CH_2)_2$	*n*-BuLi (1.0)	30	8	—	—
2	**a**,	$Ph(CH_2)_2$	*t*-BuLi (2.0)	30	50	—	—
3	**a**,	$Ph(CH_2)_2$	*t*-BuOK (2.5)	5	94	60	83
4	**b**,	$CH_3(CH_2)_2$	*t*-BuOK (2.5)	3	90	40	80
5	**c**,	$CH_3(CH_2)_3$	*t*-BuOK (2.5)	5	95	25	94
6	**d**,	$CH_3(CH_2)_5$	*t*-BuOK (2.5)	10	95	20	92
7	**e**,	$CH_3(CH_2)_8$	*t*-BuOK (2.5)	10	94	30	87
8	**f**,	H	*t*-BuOK (6.0)	10	84	—	—

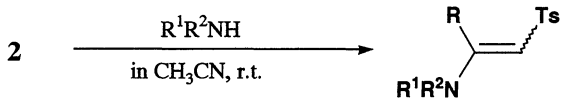
obtained as mixtures of (*E*)- and (*Z*)-isomers in high yields (Table 3). A possible reaction pathway is shown in Scheme 2.

The reaction of **2** with a primary amine (methylamine) and a secondary amine (pyrrolidine) in acetonitrile at room temperature produced the corresponding β-tosyl enamines (**8** and **8′**) in almost quantitative yields as shown in Table 4. The products **8** with monomethylamine were mixtures of (*E*)- and (*Z*)-isomers except **8f**, while pyrrolidine gave only (*E*)-isomers (**8′**) probably due to its bulkiness.

Acidic hydrolysis of β-tosyl enamines (**8**) gave the corresponding α-tosyl ketones (**9**) in excellent yields. The yields of **9** in Table 5 were based on **2** and the



Scheme 2.



8, $R^1R^2N=CH_3NH$
8′, $R^1R^2N=(CH_2)_4N$

Table 4. Preparation of 2-Amino-1-tosyl-1-alkenes (**8** and **8′**)

Run	2,	R	R^1	R^2	Time	Yield of **8**, **8′** %	Ratio of *E*/*Z*
1	**a**,	$Ph(CH_2)_2$	CH_3	H	1.5 h	100	42/58
2	**b**,	$CH_3(CH_2)_2$	CH_3	H	40 min	99	33/67
3	**c**,	$CH_3(CH_2)_3$	CH_3	H	1.0 h	100	35/65
4	**d**,	$CH_3(CH_2)_5$	CH_3	H	1.0 h	97	36/64
5	**e**,	$CH_3(CH_2)_8$	CH_3	H	1.0 h	100	32/68
6	**f**,	H	CH_3	H	30 min	100	100/0
7	**a**,	$Ph(CH_2)_2$	$-(CH_2)_4-$		1.0 d	91	100/0
8	**b**,	$CH_3(CH_2)_2$	$-(CH_2)_4-$		2.0 h	100	100/0
9	**c**,	$CH_3(CH_2)_3$	$-(CH_2)_4-$		2.0 h	100	100/0
10	**d**,	$CH_3(CH_2)_5$	$-(CH_2)_4-$		2.0 h	99	100/0
11	**e**,	$CH_3(CH_2)_8$	$-(CH_2)_4-$		3.0 h	97	100/0
12	**f**,	H	$-(CH_2)_4-$		1.0 h	100	100/0

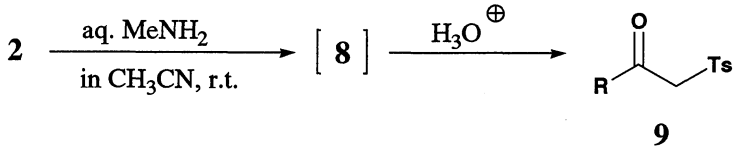


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Table 5. Preparation of 1-Tosyl-2-alkanones (**9**)

Run	2,	R	Time	Yield of **9** %
1	**a**,	$Ph(CH_2)_2$	50 min	100
2	**b**,	$CH_3(CH_2)_2$	1.0 h	98
3	**c**,	$CH_3(CH_2)_3$	1.0 h	100
4	**d**,	$CH_3(CH_2)_5$	1.0 h	96
5	**e**,	$CH_3(CH_2)_8$	1.0 h	100
6	**f**,	H	15 min	—

intermediary enamines (**8**) were not isolated. Tosylacetaldehyde (**9f**) could not be obtained. It may be unstable under the conditions employed.

Compound **2f** was readily converted to the corresponding tosylacetaldehyde acetal (**10**) by treatment with excess amounts of sodium methoxide quantitatively (Scheme 3), while **2a**—**e** afforded the mixture consisting of **11**, **12**, and/or **13** (X=O) even when the amount of methoxide was varied under various conditions.

Treatment of **2d** with an equimolar amount of methanethiolate gave the corresponding β-(methythio)-vinyl sulfone (**14**) in high yield as shown in Scheme 3, but the use of excess amounts of the thiolate resulted in the formation of the mixture of **11** and **12** (X=S). The geometry of **14** was confirmed to be *E*-form by NOE measurement as shown in the Scheme.

It was also found that **2b** reacts stereospecifically with "higher-order" cuprates[8] to give the β-alkylated products (**15** and **16**)[4] as shown in Scheme 4. The structures of **15** and **16** were confirmed by NOE measurement and the empirical rule that the protons of alkyl group syn to the tosyl group in a vinyl sulfone appear at lower field in NMR spectrum than those of alkyl group anti to the tosyl group.[9]

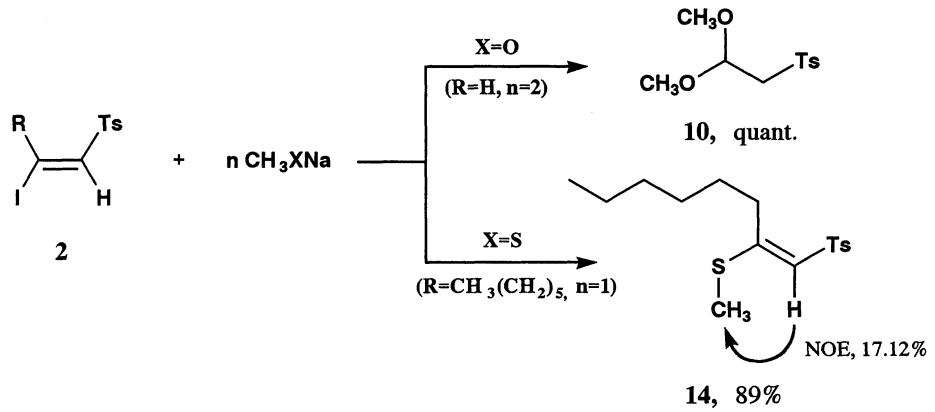
As described above, (*E*)-2-iodo-1-tosyl-1-alkenes (**2**) have proved to be useful synthetic intermediates and were readily converted to the corresponding 1-tosyl-1-alkynes, 1-tosyl-2-alkynes, (*Z*)-vinyl and (*Z*)-allyl sulfones, β-tosyl enamines, α-tosyl ketones, α-tosyl aldehyde acetal, and β-disubstituted vinyl sulfones as summarized in Fig. 1.

Experimental

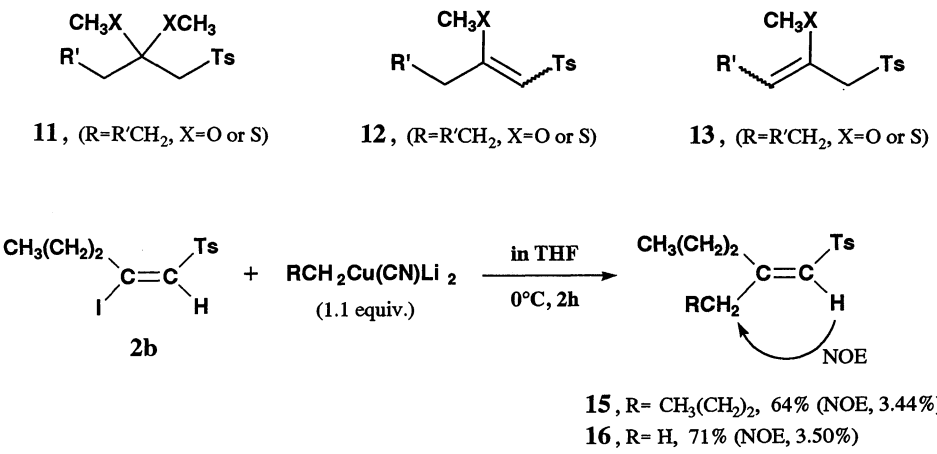
All the melting points were determined with a micro melting apparatus (Yanagimoto-Seisakusho) and were uncorrected. The ^{1}H NMR, IR, and MS spectra were recorded on JEOL JNM-GX 400 (400 MHz) FT-NMR spectrometer, JASCO IRA-1 diffraction grating infrared spectrometer and Hitachi M-80 mass spectrometer, respectively. The chemical shifts of NMR are reported in the δ-scale relative to TMS as an internal standard.

Materials. All the solvents were distilled and stored over a drying agent. Thin-layer chromatography (TLC) and flash column chromatography were performed by the use of Merck's silica gel 60 PF_{254} (Art. 7749) and Wakogel C-300, respectively.

Preparation of (*E*)-2-Iodo-1-tosyl-1-alkenes (2): An aqueous solution (1 ml) of sodium *p*-toluenesulfinate (*p*-



Scheme 3.



Scheme 4.

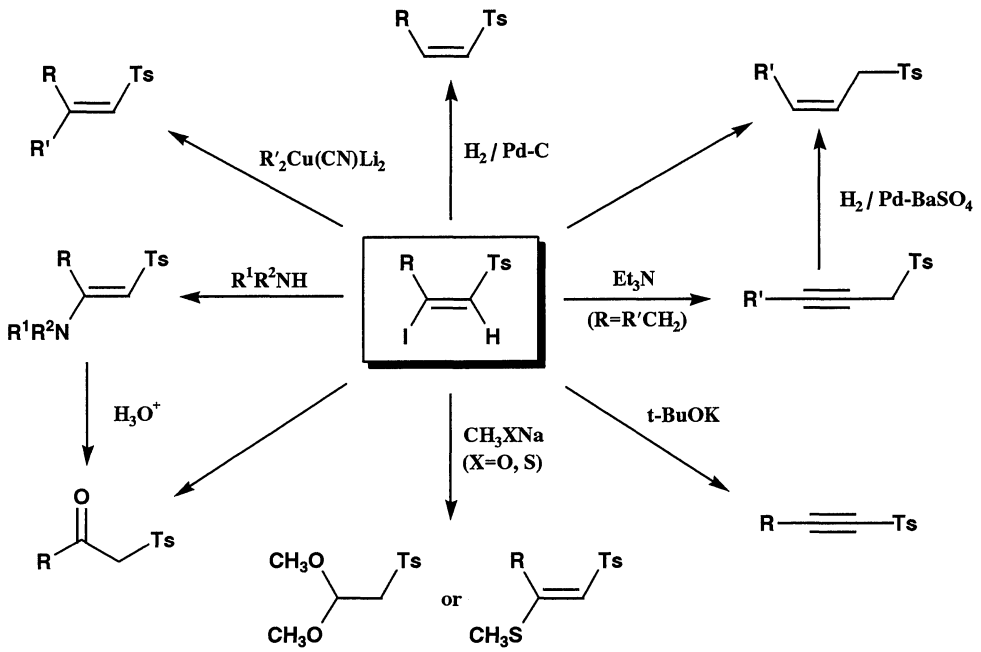


Fig. 1.

$CH_3C_6H_4SOONa \cdot 4H_2O$, 375 mg, 1.5 mmol) was vigorously stirred with a solution of iodine (254 mg, 1 mmol) and 1-alkyne (1 mmol) in ethyl acetate (2 ml) at room temperature for 1 d. The product was extracted with ethyl acetate and washed successively with aq $NaHCO_3$ containing a small amount of $NaHSO_3$, brine, and dried over Na_2SO_4. After evaporation of the solvents, the resulting residue was subjected to preparative TLC [solvent; hexane/ethyl acetate=5/1, v/v (for **2a**) or hexane/ethyl acetate/ether=10/1/1, v/v/v (for **2b—e**)] to afford (**2**) in the yields listed in Table 1.

Physical and spectral data of **2a—e** and **2f** are shown in the following.

(*E*)-2-Iodo-4-phenyl-1-tosyl-1-butene (2a): Mp 89—90°C (from 2-propanol); MS *m/z* 413 (M^++1, 0.05%), 412 (M^+, 0.08), 257 (M^++1−^{127}I, 19.81), 256 (M^+−^{127}I, 66.33), 130 (20.34), 129 (31.96), 91 (100.00); IR (KBr) 3020, 2920, 1585, 1480, 1440, 1310, 1140, 1075, 1005, 960, 800, 755, 740, 690, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.43 (s, 3H), 2.89 (t, 2H, *J*=7.6 Hz), 3.38 (t, 2H, *J*=7.6 Hz), 6.98 (s, 1H), 7.20—7.38 (m, 7H), 7.63 (d, 2H, *J*=8.2 Hz). Found: C, 49.36; H, 4.12%. Calcd for $C_{17}H_{17}IO_2S$: C, 49.53; H, 4.16%.

(*E*)-2-Iodo-1-tosyl-1-pentene (2b): An oil; MS *m/z* 351 (M^++1, 0.31%), 350 (M^+, 0.37), 223 (M^+−^{127}I, 92.21), 157 (39.71), 155 (57.80), 139 (26.38), 91 (100.00); IR (neat) 3040, 2950, 2920, 2860, 1585, 1450, 1310, 1290, 1280, 1145, 1105, 1080, 970, 950, 805, 775, 760, 740, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.95 (t, 3H, *J*=7.6 Hz), 1.59 (sx, 2H, *J*=7.6 Hz), 2.45 (s, 3H), 3.02 (t, 2H, *J*=7.6 Hz), 7.02 (s, 1H), 7.36 (d, 2H, *J*=8.1 Hz), 7.79 (d, 2H, *J*=8.1 Hz).

(*E*)-2-Iodo-1-tosyl-1-hexene (2c): Mp 48.5—49.0°C (from hexane, lit,[4a] 50.0—50.5°C); MS *m/z* 365 (M^++1, 0.41%), 364 (M^+, 0.42), 237 (M^+−^{127}I, 81.83), 157 (52.83), 155 (57.54), 139 (35.47), 91 (100.00); IR (neat) 3040, 2950, 2920, 2850, 1585, 1450, 1320, 1295, 1140, 1080, 805, 760, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.94 (t, 3H, *J*=7.3 Hz), 1.37 (sx, 2H, *J*=7.3 Hz), 1.52 (p, 2H, *J*=7.3 Hz), 2.45 (s, 3H), 3.03 (t, 2H, *J*=7.3 Hz), 7.00 (s, 1H), 7.36 (d, 2H, *J*=8.1 Hz), 7.78 (d, 2H, *J*=8.1 Hz). Found: C, 43.06; H, 4.67%. Calcd for $C_{13}H_{17}IO_2S$: C, 42.87; H, 4.70%.

(*E*)-2-Iodo-1-tosyl-1-octene (2d): Mp 56°C (from 2-propanol, lit,[4a] 55—56°C); MS *m/z* 265 (M^+−^{127}I, 57.23%), 157 (71.74), 155 (51.07), 139 (33.56), 109 (27.16), 91 (100.00); IR (KBr) 3030, 2950, 2900, 2840, 1580, 1450, 1310, 1135, 1075, 805, 790, 780, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, 3H, *J*=7.0 Hz), 1.24—1.39 (m, 6H), 1.47—1.58 (m, 2H), 2.45 (s, 3H), 3.01 (t, 2H, *J*=7.6 Hz), 7.00 (s, 1H), 7.36 (d, 2H, *J*=8.1 Hz), 7.78 (d, 2H, *J*=8.1 Hz). Found: C, 45.72; H, 5.28%. Calcd for $C_{15}H_{21}IO_2S$: C, 45.93; H, 5.40%.

(*E*)-2-Iodo-1-tosyl-1-undecene (2e): An oil; MS *m/z* 307 (M^+−^{127}I, 100.00%), 279 (9.20), 195 (17.10), 157 (100.00), 155 (100.00), 151 (44.70), 139 (91.61), 95 (57.56), 91 (100.00), 81 (51.95); IR (neat) 3030, 2910, 2840, 1585, 1450, 1310, 1140, 1080, 805, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, 3H, *J*=7.3 Hz), 1.19—1.38 (m, 12H), 1.46—1.56 (m, 2H), 2.45 (s, 3H), 3.01 (t, 2H, *J*=7.3 Hz), 7.00 (s, 1H), 7.36 (d, 2H, *J*=8.1 Hz), 7.78 (d, 2H, *J*=8.1 Hz).

(*E*)-2-Iodo-1-tosylethene (2f): Mp 79.6—80.0°C (from 2-propanol); MS *m/z* 308 (M^+, 12.91%), 244 (4.11), 155 (25.25), 139 (71.99), 91 (100.00), 65 (16.06); IR (KBr) 3050, 1580, 1550, 1315, 1270, 1240, 1155, 1130, 1075, 915, 810, 790, 780, 745, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.45 (s, 3H), 7.27 (d, 1H, *J*=14.5 Hz), 7.36 (d, 2H, *J*=8.4 Hz), 7.77 (d, 2H, *J*=8.4 Hz), 7.96 (d, 1H, *J*=14.5 Hz). Found: C, 35.17; H, 2.89%. Calcd for $C_9H_9IO_2S$: C, 35.08; H, 2.94%.

Preparation of (*Z*)-1-Tosyl-1-alkenes (3): The iodosulfonization product (**2**, 1 mmol) from alkyne (**1**) was treated with 5% Pd–C (25 mg) deactivated with a small amount of quinoline in methanol in the presence of sodium acetate (165 mg, 2 mmol) under hydrogen atmosphere for 2.5 h at room temperature. After the usual work-up, the reduced products **3**, were isolated by preparative TLC [solvent; benzene/ethyl acetate=100/1, v/v (for **3a—c**) or hexane/ethyl acetate/ether=10/1/1, v/v/v (for **3d,e**)] in almost quantitative yields as summarized in Table 1.

Physical and spectral data of **3a—e** are shown in the

following.

(*Z*)-4-Phenyl-1-tosyl-1-butene (3a): An oil; MS *m/z* 286 (M^+, 1.33%), 131 (100.00), 130 (100.00), 91 (100.00); IR (neat) 3050, 3020, 2920, 2850, 1610, 1590, 1485, 1440, 1305, 1295, 1280, 1140, 1080, 805, 750, 715, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.43 (s, 3H), 2.75 (t, 2H, *J*=7.6 Hz), 3.01 (m, 2H), 6.22 (dt, 1H, *J*=7.0, 11.3 Hz), 6.27 (d, 1H, *J*=11.3 Hz), 7.15—7.37 (m, 7H), 7.71 (d, 2H, *J*=8.2 Hz).

(*Z*)-1-Tosyl-1-pentene (3b): An oil; MS *m/z* 224 (M^+, 100.00%), 209 (65.43), 157 (41.21), 139 (70.47), 92 (49.24), 91 (64.79), 68 (85.16), 41 (54.41); IR (neat) 3040, 2960, 2920, 2860, 1610, 1590, 1450, 1305, 1140, 1080, 805, 740, 710, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (t, 3H, *J*=7.3 Hz), 1.45 (sx, 2H, *J*=7.3 Hz), 2.44 (s, 3H), 2.64 (q, 2H, *J*=7.3 Hz), 6.22 (dt, 1H, *J*=7.3, 11.2 Hz), 6.29 (d, 1H, *J*=11.2 Hz), 7.34 (d, 2H, *J*=8.2 Hz), 7.80 (d, 2H, *J*=8.2 Hz).

(*Z*)-1-Tosyl-1-hexene (3c): An oil; MS *m/z* 238 (M^+, 55.03%), 209 (100.00), 157 (65.68), 139 (62.33), 92 (32.78), 91 (55.57), 83 (22.25), 82 (77.80), 67 (49.12), 55 (33.83), 41 (35.59); IR (neat) 3040, 2955, 2920, 2860, 1610, 1590, 1455, 1305, 1295, 1280, 1140, 1080, 805, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, 3H, *J*=7.3 Hz), 1.28—1.45 (m, 4H), 2.44 (s, 3H), 2.66 (q, 2H, *J*=7.3 Hz), 6.21 (dt, 1H, *J*=7.3, 11.0 Hz), 6.27 (d, 1H, *J*=11.0 Hz), 7.34 (d, 2H, *J*=8.1 Hz), 7.80 (d, 2H, *J*=8.1 Hz).

(*Z*)-1-Tosyl-1-octene (3d): An oil; MS *m/z* 266 (M^+, 26.73%), 209 (78.87), 157 (100.00), 139 (52.90), 92 (36.63), 91 (38.21), 81 (39.79), 69 (29.99), 68 (28.72), 54 (28.82); IR (neat) 3040, 2910, 2840, 1610, 1590, 1450, 1305, 1280, 1140, 1080, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=7.0 Hz), 1.17—1.34 (m, 6H), 1.35—1.45 (m, 2H), 2.44 (s, 3H), 2.64 (q, 2H, *J*=7.3 Hz), 6.21 (dt, 1H, *J*=7.0, 11.2 Hz), 6.28 (d, 1H, *J*=11.2 Hz), 7.33 (d, 2H, *J*=8.3 Hz), 7.80 (d, 2H, *J*=8.3 Hz).

(*Z*)-1-Tosyl-1-undecene (3e): Mp 28—30 °C (not recrystallized); MS *m/z* 308 (M^+, 11.08%), 209 (50.02), 196 (28.26), 157 (100.00), 139 (35.35), 92 (33.06); IR (neat) 3030, 2910, 2840, 1605, 1580, 1450, 1300, 1290, 1135, 1075, 800, 750, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=7.0 Hz), 1.16—1.35 (m, 12H), 1.35—1.45 (m, 2H), 2.44 (s, 3H), 2.64 (q, 2H *J*=7.3 Hz), 6.21 (dt, 1H, *J*=7.0, 11.0 Hz), 6.28 (d, 1H, *J*=11.0 Hz), 7.33 (d, 2H, *J*=8.1 Hz), 7.80 (d, 2H, *J*=8.1 Hz).

Preparation of 1-Tosyl-2-alkynes (4): To a solution of **2** (0.43 mmol) in acetonitrile (18 ml) was added a solution of triethylamine (214 mg, 2.15 mmol) in acetonitrile (3 ml). After stirring under the conditions shown in Table 2, the reaction mixture was added dropwise into a diluted methanolic HCl (5.5 equiv, 2.37 mmol) solution at 0 °C. The residue obtained by evaporation of the solvent was dissolved in ethyl acetate and successively washed with water and brine, and dried over sodium sulfate. After evaporation of the solvent, the residue was separated by preparative TLC or a flash column chromatography to afford **4** in the yields shown in Table 2.

Physical and spectral data of **4a—e** are shown in the following.

4-Phenyl-1-tosyl-2-butyne (4a): Mp 84.0 °C (from 2-propanol); MS *m/z* 285 (M^++1, 1.19%), 284 (M^+, 4.45), 205 (11.41), 145 (17.11), 139 (16.06), 129 (68.74), 128 (100.00), 127 (33.75), 91 (24.20); IR (KBr) 3000, 2970, 2930, 2240, 1595, 1490, 1450, 1400, 1315, 1305, 1290, 1255, 1165, 1145, 1130, 1085, 875, 810, 750, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.44 (s, 3H), 3.56 (m, 2H), 3.98 (t, 2H, *J*=2.5 Hz), 7.19 (d, 2H, *J*=7.3 Hz), 7.23—7.31 (m, 3H), 7.28 (d, 2H, *J*=7.6 Hz), 7.80 (d, 2H, *J*=8.2 Hz). Found: C, 71.73; H, 5.57%. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67%.

1-Tosyl-2-pentyne (4b): An oil; MS *m/z* 223 (M^++1, 1.43%), 222 (M^+, 0.76), 174 (6.44), 158 (72.68), 139 (100.00), 123 (30.53), 91 (72.75), 67 (52.95), 65 (32.05), 41 (46.42); IR (neat) 2970, 2910, 2870, 2230, 1590, 1485, 1450, 1400, 1395, 1320, 1310, 1300, 1280, 1250, 1180, 1160, 1145, 1130, 1080, 1010, 870, 810, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (t, 3H, *J*=7.6 Hz), 2.17 (m, 2H), 2.47 (s, 3H), 3.90 (t, 2H, *J*=2.4 Hz), 7.36 (d, 2H, *J*=8.1 Hz), 7.85 (d, 2H, *J*=8.1 Hz).

1-Tosyl-2-hexyne (4c): An oil; MS *m/z* 237 (M^++1, 0.44%), 208 (7.28), 172 (20.69), 157 (48.92), 155 (25.46), 140 (29.00), 139 (100.00), 137 (21.37), 123 (35.16), 91 (61.42), 81 (36.47), 79 (57.37), 53 (32.29), 41 (26.09); IR (neat) 2960, 2850, 2220, 1590, 1485, 1455, 1440, 1390, 1320, 1300, 1280, 1160, 1140, 1130, 1080, 870, 805, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, 3H, *J*=7.3 Hz), 1.46 (sx, 2H, *J*=7.3 Hz), 2.13 (m, 2H), 2.46 (s, 3H), 3.92 (t, 2H, *J*=2.4 Hz), 7.36 (d, 2H, *J*=8.2 Hz), 7.84 (d, 2H, *J*=8.2 Hz).

1-Tosyl-2-octyne (4d): An oil; MS *m/z* 265 (M^++1, 0.61%), 264 (M^+, 0.61), 208 (9.41), 157 (42.49), 139 (100.00), 123 (33.63), 109 (43.26), 91 (62.02), 67 (76.35), 55 (37.21); IR (neat) 2960, 2920, 2850, 2220, 1590, 1480, 1460, 1320, 1300, 1280, 1245, 1160, 1140, 1130, 1080, 865, 800, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=7.0 Hz), 1.24—1.28 (m, 4H), 1.43 (p, 2H, *J*=7.0 Hz), 2.14 (m, 2H), 2.46 (s, 3H), 3.91 (t, 2H, *J*=2.1 Hz), 7.36 (d, 2H, *J*=8.2 Hz), 7.84 (d, 2H, *J*=8.2 Hz).

1-Tosyl-2-undecyne (4e): An oil; MS *m/z* 307 (M^++1, 0.46%), 306 (M^+, 0.48), 209 (3.57), 157 (36.73), 139 (51.68), 109 (33.64), 95 (100.00), 81 (63.72), 67 (35.94), 55 (29.39); IR (neat) 2920, 2840, 2220, 1590, 1460, 1390, 1370, 1320, 1300, 1280, 1245, 1180, 1160, 1140, 1130, 1080, 1010, 865, 805, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, 3H, *J*=7.0 Hz), 1.24—1.38 (m, 10H), 1.42 (p, 2H, *J*=7.0 Hz), 2.14 (m, 2H), 2.46 (s, 3H), 3.91 (t, 2H, *J*=2.4 Hz), 7.36 (d, 2H, *J*=8.4 Hz), 7.84 (d, 2H, *J*=8.4 Hz).

Preparation of (*Z*)-1-Tosyl-2-alkenes (5): To a suspension of 5% Pd–$BaSO_4$ (106 mg, 5 mol%) in methanol (20 ml) was added a solution of **4** (1 mmol) in methanol (5 ml) under hydrogen atmosphere at room temperature. After completion of the reduction and the usual work-up, the products (**5**) were isolated by preparative TLC.

Physical and spectral data of **5a—e** are shown in the following.

(*Z*)-4-Phenyl-1-tosyl-2-butene (5a): An oil; MS *m/z* 288 (M^++2, 2.47%), 131 (64.76), 130 (100.00), 129 (22.48), 116 (8.27), 115 (8.34), 104 (7.68), 91 (32.16); IR (neat) 3020, 2920, 1580, 1480, 1440, 1420, 1390, 1370, 1295, 1270, 1240, 1220, 1150, 1120, 1070, 1060, 800, 730, 700, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.45 (s, 3H), 3.14 (d, 2H, *J*=7.5 Hz), 3.94 (d, 2H, *J*=8.1 Hz), 5.55 (dt, 1H, *J*=8.1, 9.6 Hz), 5.90 (dt, 1H, *J*=7.5, 9.6 Hz), 6.93 (d, 2H, *J*=7.3 Hz), 7.17—7.27 (m, 3H), 7.34 (d, 2H, *J*=7.9 Hz), 7.79 (d, 2H, *J*=7.9 Hz).

(*Z*)-1-Tosyl-2-pentene (5b): An oil; MS *m/z* 224 (M^+, 0.50%), 209 (0.43), 157 (37.78), 139 (10.63), 92 (28.36), 91 (22.31), 69 (88.92), 68 (49.28), 41 (100.00); IR (neat) 3020, 2960, 2920, 2870, 1590, 1485, 1450, 1400, 1310, 1300, 1280, 1165, 1135, 1080, 805, 705, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.76 (t, 3H, *J*=7.3 Hz), 1.78 (dq, 2H, *J*=7.3, 7.6 Hz), 2.44 (s, 3H), 3.83 (d, 2H, *J*=7.9 Hz), 5.36 (dt, 1H, *J*=7.9, 10.7 Hz), 5.71 (dt, 1H, *J*=7.3, 10.7 Hz), 7.33 (d, 2H, *J*=8.2 Hz), 7.76 (d, 2H, *J*=8.2 Hz).

(*Z*)-1-Tosyl-2-hexene (5c): An oil; MS *m/z* 239 (M^++1, 0.73%), 157 (100.00), 139 (11.99), 92 (16.02), 91 (20.63), 83 (49.98), 82 (86.00), 67 (20.03), 55 (62.53), 41 (23.48); IR (neat)

3020, 2950, 2920, 2860, 1590, 1485, 1450, 1400, 1310, 1295, 1280, 1230, 1160, 1130, 1080, 805, 705, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.76 (t, 3H, *J*=7.3 Hz), 1.16 (sx, 2H, *J*=7.3 Hz), 1.73 (q, 2H, *J*=7.3 Hz), 2.44 (s, 3H), 3.83 (d, 2H, *J*=7.9 Hz), 5.40 (dt, 1H, *J*=7.9, 10.7 Hz), 5.71 (dt, 1H, *J*=7.3, 10.7 Hz), 7.33 (d, 2H, *J*=8.2 Hz), 7.76 (d, 2H, *J*=8.2 Hz).

(*Z*)-1-Tosyl-2-octene (5d): An oil; MS *m/z* 267 (M^++1, 0.52%), 157 (75.44), 111 (23.45), 110 (71.32), 91 (14.95), 81 (14.78), 69 (100.00), 55 (43.64), 41 (17.83); IR (neat) 2960, 2920, 2850, 1590, 1450, 1315, 1300, 1285, 1230, 1160, 1140, 1080, 890, 810, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84 (t, 3H, *J*=7.3 Hz), 1.08—1.12 (m, 4H), 1.20 (p, 2H, *J*=7.0 Hz), 1.72—1.73 (m, 2H), 2.44 (s, 3H), 3.83 (d, 2H, *J*=7.9 Hz), 5.40 (dt, 1H, *J*=7.9, 10.7 Hz), 5.71 (dt, 1H, *J*=7.3, 10.7 Hz), 7.33 (d, 2H, *J*=8.2 Hz), 7.76 (d, 2H, *J*=8.2 Hz).

(*Z*)-1-Tosyl-2-undecene (5e): An oil; MS *m/z* 309 (M^++1, 3.13%), 157 (100.00), 152 (97.28), 97 (56.91), 83 (62.68), 69 (42.49), 55 (41.81), 43 (17.10); IR (neat) 2920, 2840, 1585, 1450, 1400, 1310, 1295, 1280, 1225, 1135, 1080, 880, 800, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=7.3 Hz), 1.08—1.29 (m, 12H), 1.72 (q, 2H, *J*=7.2 Hz), 2.44 (s, 3H), 3.83 (d, 2H, *J*=7.8 Hz), 5.39 (dt, 1H, *J*=7.8, 10.7 Hz), 5.71 (dt, 1H, *J*=7.2, 10.7 Hz), 7.33 (d, 2H, *J*=8.2 Hz), 7.76 (d, 2H, *J*=8.2 Hz).

Preparation of 1-Tosyl-1-alkynes (6) and Their Dimerized Products (7): To a solution of **2** (0.35 mmol) in THF (8 ml) was added dropwise a cooled (−78 °C) solution of *t*-BuOK (98 mg, 0.875 mmol) in THF (2 ml) at −78 °C. After stirring for the period shown in Table 3, a cooled (−78 °C) methanolic 1 M HCl solution (0.875 ml) was added. The residue obtained by evaporation of the solvent was dissolved in ethyl acetate, and successively washed by water, brine, and dried over sodium sulfate. After evaporation of the solvent, the residual oil was subjected to preparative TLC to afford the corresponding 1-tosyl-1-alkynes (**6**) in excellent yields as summarized in Table 3.

When the similar reaction was carried out with 4 equimolar amounts of *t*-BuOK at −16 °C, the dimerized products (**7**) were obtained in high yields (Table 3).

Physical and spectral data of **6a**—**f** and **7a**—**e** are shown in the following.

4-Phenyl-1-tosyl-1-butyne (6a): An oil; MS *m/z* 285 (M^++1, 2.00%), 284 (M^+, 3.05), 256 (3.60), 219 (7.42), 205 (5.69), 204 (5.57), 129 (25.42), 128 (28.81), 91 (100.00), 65 (2.36); IR (neat) 3015, 2900, 2840, 2210, 1585, 1485, 1440, 1310, 1290, 1140, 1080, 1020, 1010, 820, 800, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.46 (s, 3H), 2.63 (t, 2H, *J*=7.3 Hz), 2.83 (t, 2H, *J*=7.3 Hz), 7.10 (d, 2H, *J*=7.6 Hz), 7.18—7.26 (m, 3H), 7.34 (d, 2H, *J*=8.1 Hz), 7.82 (d, 2H, *J*=8.1 Hz).

1-Tosyl-1-pentyne (6b): An oil; MS *m/z* 224 (M^++2, 5.61%), 223 (M^++1, 14.97), 222 (M^+, 100.00), 201 (21.25), 143 (32.97), 139 (73.04), 129 (38.63), 107 (33.38), 91 (21.62), 85 (20.14); IR (neat) 2940, 2920, 2850, 2180, 1585, 1440, 1320, 1300, 1280, 1170, 1150, 1080, 1010, 985, 870, 805, 700, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (t, 3H, *J*=7.1 Hz), 1.58 (sx, 2H, *J*=7.1 Hz), 2.33 (t, 2H, *J*=7.1 Hz), 2.46 (s, 3H), 7.36 (d, 2H, *J*=8.1 Hz), 7.88 (d, 2H, *J*=8.1 Hz).

1-Tosyl-1-hexyne (6c): An oil; MS *m/z* 237 (M^++1, 17.35%), 236 (M^+, 100.00), 201 (27.46), 194 (68.46), 157 (22.86), 155 (40.99), 139 (57.21), 129 (29.02), 107 (12.56), 85 (9.51); IR (neat) 2910, 2840, 2200, 1580, 1480, 1440, 1410, 1370, 1315, 1290, 1280, 1170, 1145, 1080, 1030, 1005, 970, 945, 850, 800, 700, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=7.3 Hz), 1.36 (sx, 2H, *J*=7.3 Hz), 1.53 (p, 2H, *J*=7.3 Hz), 2.35 (t, 2H, *J*=7.0 Hz), 2.46 (s, 3H), 7.36 (d, 2H, *J*=8.2 Hz), 7.88 (d, 2H, *J*=8.2 Hz).

1-Tosyl-1-octyne (6d): An oil; MS *m/z* 265 (M^++1, 2.07%), 264 (M^+, 1.72), 196 (22.22), 157 (41.00), 139 (100.00), 129 (28.14), 119 (51.28), 109 (60.54), 93 (59.54), 92 (28.43), 91 (56.67), 79 (44.13), 67 (63.20), 55 (25.93): IR (neat) 2920, 2860, 2200, 1595, 1460, 1325, 1185, 1160, 1090, 815, 710, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (t, 3H, *J*=7.0 Hz), 1.18—1.35 (m, 6H), 1.54 (p, 2H, *J*=7.0 Hz), 2.34 (t, 2H, *J*=7.0 Hz), 2.46 (s, 3H), 7.36 (d, 2H, *J*=8.2 Hz), 7.87 (d, 2H, *J*=8.2 Hz).

1-Tosyl-1-undecyne (6e): An oil; MS *m/z* 307 (M^++1, 5.48%), 306 (1.95), 236 (29.72), 196 (34.20), 157 (100.00), 139 (94.10), 121 (56.55), 109 (32.56), 107 (33.77), 105 (40.25), 95 (88.06), 94 (38.17), 93 (40.28), 91 (50.48), 81 (86.24), 79 (42.32), 67 (39.06), 55 (24.53); IR (neat) 2900, 2840, 2180, 1580, 1440, 1320, 1290, 1180, 1170, 1150, 1080, 1010, 800, 700, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=7.0 Hz), 1.23—1.31 (m, 12H), 1.54 (p, 2H, *J*=7.3 Hz), 2.34 (t, 2H, *J*=7.3 Hz), 2.46 (s, 3H), 7.36 (d, 2H, *J*=8.1 Hz), 7.87 (d, 2H, *J*=8.1 Hz).

1-Tosylethyne (6f): Mp 75.0 °C (from hexane, lit,[10] 74—75 °C); MS *m/z* 180 (M^+, 37.35%), 155 (29.29), 139 (76.77), 115 (44.15), 91 (100.00), 65 (33.52); IR (KBr) 3230, 2050, 1580, 1315, 1290, 1145, 1075, 805, 790, 725, 705, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.48 (s, 3H), 3.46 (s, 1H), 7.39 (d, 2H, *J*=8.3 Hz), 7.89 (d, 2H, *J*=8.3 Hz).

1,7-Diphenyl-4-tosyl-5-(tosylmethyl)-4-hepten-2-yne (7a): An oil; MS *m/z* 569 (M^++1, 0.61%), 568 (M^+, 1.32), 413 (36.33), 258 (30.43), 257 (100.00), 256 (38.37), 179 (17.45), 165 (13.08), 141 (21.75), 139 (34.68), 129 (22.70), 91 (63.98); IR (neat) 3080, 3040, 2940, 2230, 1600, 1495, 1450, 1320, 1300, 1290, 1265, 1150, 1080, 810, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$) of major isomer (M) δ=2.41 (s, 3H), 2.47 (s, 3H), 2.84 (t, 2H, *J*=7.2 Hz), 3.03 (t, 2H, *J*=7.2 Hz), 3.69 (s, 2H), 4.78 (s, 2H), 7.05 (d, 2H, *J*=7.9 Hz), 7.37 (d, 2H, *J*=7.9 Hz), 7.13—7.38 (m, 10H), 7.76 (d, 2H, *J*=8.4 Hz), 7.87 (d, 2H, *J*=8.4 Hz). ^1H NMR ($CDCl_3$) of minor isomer (m) δ=2.25 (s, 3H), 2.45 (s, 3H), 2.92 (t, 2H, *J*=7.8 Hz), 3.36 (t, 2H, *J*=7.8 Hz), 3.46 (s, 2H), 4.07 (s, 2H), 6.94 (d, 2H, *J*=7.9 Hz), 7.05 (d, 2H, *J*=7.9 Hz), 7.22 (m, 10H), 7.46 (d, 2H, *J*=8.2 Hz), 7.64 (d, 2H, *J*=8.2 Hz). M/m=65/35.

5-Tosyl-6-(tosylmethyl)-5-nonen-3-yne (7b): An oil; MS *m/z* 446 (M^++2, 0.16%), 445 (M^++1, 0.34), 444 (M^+, 1.17), 289 (43.14), 225 (4.04), 139 (100.00), 133 (24.74), 105 (10.34), 91 (10.79); IR (neat) 3020, 2960, 2920, 2880, 2200, 1585, 1480, 1450, 1395, 1310, 1290, 1280, 1240, 1140, 1075, 800, 720, 690 cm^{-1}; ^1H NMR ($CDCl_3$) of major isomer (M) δ=0.94 (t, 3H, *J*=7.3 Hz), 1.04 (t, 3H, *J*=7.3 Hz), 1.57 (sx, 2H, *J*=7.3 Hz), 2.27 (q, 2H, *J*=7.3 Hz), 2.43 (s, 3H), 2.47 (s, 3H), 2.70 (t, 2H, *J*=7.3 Hz), 4.90 (s, 2H), 7.30 (d, 2H, *J*=8.1 Hz), 7.38 (d, 2H, *J*=8.1 Hz), 7.86 (d, 2H, *J*=8.1 Hz), 7.90 (d, 2H, *J*=8.1 Hz). ^1H NMR ($CDCl_3$) of minor isomer (m) δ=0.90 (t, 3H, *J*=7.3 Hz), 1.04 (t, 3H, *J*=7.3 Hz), 1.57 (sx, 2H, *J*=7.3 Hz), 2.01 (q, 2H, *J*=7.3 Hz), 2.38 (s, 3H), 2.47 (s, 3H), 3.03 (t, 2H, *J*=7.3 Hz), 4.17 (s, 2H), 7.11 (d, 2H, *J*=8.1Hz), 7.34 (d, 2H, *J*=8.1 Hz), 7.57 (d, 2H, *J*=8.1 Hz), 7.69 (d, 2H, *J*=8.1 Hz). M/m=73/27.

6-Tosyl-7-(tosylmethy)-6-undecen-4-yne (7c): An oil; MS *m/z* 473 (M^++1, 0.58%), 472 (M^+, 1.98), 317 (50.33), 161 (48.10), 139 (100.00), 119 (19.93), 105 (17.08), 91 (11.25), 71 (7.69); IR (neat) 3030, 2960, 2920, 2880, 2210, 1585, 1480, 1450, 1400, 1370, 1320, 1300, 1250, 1140, 1080, 1010, 860, 800, 790, 720, 700 cm^{-1}; ^1H NMR ($CDCl_3$) of major isomer (M) δ=0.86 (t, 3H, *J*=7.3 Hz), 0.90 (t, 3H, *J*=7.3 Hz), 1.34 (sx, 2H, *J*=7.3 Hz), 1.43 (sx, 2H, *J*=7.3 Hz), 1.51 (p, 2H, *J*=7.3 Hz), 2.24 (t, 2H,

J=7.3 Hz), 2.43 (s, 3H), 2.47 (s, 3H), 2.72 (t, 2H, J=7.3 Hz), 4.90 (s, 2H), 7.30 (d, 2H, J=8.1 Hz), 7.38 (d, 2H, J=8.1 Hz), 7.86 (d, 2H, J=8.1 Hz), 7.91 (d, 2H, J=8.1 Hz). ^{1}H NMR ($CDCl_3$) of minor isomer (m) δ=0.79 (m, 6H), 1.28—1.54 (m, 6H), 1.99 (t, 2H, J=7.0 Hz), 2.38 (s, 3H), 2.46 (s, 3H), 3.03 (t, 2H, J=7.0 Hz), 4.18 (s, 2H), 7.11 (d, 2H, J=8.1 Hz), 7.31 (m, 2H), 7.57 (d, 2H, J=8.1 Hz), 7.69 (d, 2H, J=8.1 Hz). M/m =80/20.

8-Tosyl-9-(tosylmethyl)-8-pentadecen-6-yne (7d): An oil; MS m/z 529 (M^++1, 1.50%), 528 (M^+, 3.77), 374 (26.63), 373 (100.00), 217 (58.93), 161 (12.90), 139 (99.83), 105 (14.04), 91 (8.77); IR (neat) 3020, 2960, 2920, 2860, 2200, 1585, 1480, 1450, 1390, 1370, 1310, 1290, 1280, 1140, 1070, 900, 800, 720, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) of major isomer (M) δ=0.86 (t, 3H, J=7.0 Hz), 0.87 (t, 3H, J=7.3 Hz), 1.16—1.30 (m, 10H), 1.39 (p, 2H, J=7.3 Hz), 1.48—1.53 (m, 2H), 2.25 (t, 2H, J=7.3 Hz), 2.43 (s, 3H), 2.47 (s, 3H), 2.71 (t, 2H, J=7.9 Hz), 4.89 (s, 2H), 7.30 (d, 2H, J=8.2 Hz), 7.38 (d, 2H, J=8.2 Hz), 7.86 (d, 2H, J=8.2 Hz), 7.91 (d, 2H, J=8.2 Hz). ^{1}H NMR ($CDCl_3$) of minor isomer (m) δ=0.84—0.92 (m, 6H), 1.16—1.53 (m, 14H), 2.00 (t, 2H, J=7.0 Hz), 2.38 (s, 3H), 2.46 (s, 3H), 3.03 (m, 2H), 4.18 (s, 2H), 7.11 (d, 2H, J=8.2 Hz), 7.13 (m, 2H), 7.57 (d, 2H, J=8.2 Hz), 7.68 (d, 2H, J=8.2 Hz). M/m=89/11.

11-Tosyl-12-(tosylmethyl)-11-heneicosen-9-yne (7e): An oil; MS m/z 614 (M^++2, 1.95%), 613 (M^++1, 4.41), 457 (95.73), 301 (100.00), 203 (12.17), 139 (78.08), 105 (11.55), 91 (8.75), 81 (8.38); IR (neat) 3020, 2920, 2850, 2200, 1585, 1480, 1450, 1390, 1370, 1310, 1290, 1280, 1240, 1140, 1080, 1005, 900, 800, 720, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) of major isomer (M) δ=0.86 (t, 3H, J=7.0 Hz), 0.89 (t, 3H, J=6.4 Hz), 1.24—1.53 (m, 26H), 2.25 (t, 2H, J=7.0 Hz), 2.43 (s, 3H), 2.47 (s, 3H), 2.70 (t, 2H, J=7.9 Hz), 4.89 (s, 2H), 7.31 (d, 2H, J=8.2 Hz), 7.38 (d, 2H, J=8.2 Hz), 7.86 (d, 2H, J=8.2 Hz), 7.91 (d, 2H, J=8.2 Hz). ^{1}H NMR ($CDCl_3$) of minor isomer (m) δ=0.85—0.90 (m, 6H), 1.24—1.53 (m, 26H), 2.00 (t, 2H, J=6.7 Hz), 2.40 (s, 3H), 2.46 (s, 3H), 3.02 (m, 2H), 4.18 (s, 2H), 7.11 (d, 2H, J=8.1 Hz), 7.31 (m, 2H), 7.57 (d, 2H, J=8.1 Hz), 7.68 (d, 2H, J=8.1 Hz). M/m=93/7.

Preparation of 2-Amino-1-tosyl-1-alkenes (8 and 8′): To a solution of **2** (0.2 mmol) in acetonitrile (3—4 ml) was added an aqueous methylamine (ca. 40%, 1 ml, ca. 12 equiv) solution or an acetonitrile solution (1 ml) of pyrrolidine (56 mg, 0.8 mmol, 4 equiv) at room temperature under nitrogen with stirring. After completion of the reaction, the organic solvent was evaporated. The residue was dissolved in ether, and successively washed with water, brine, and dried over sodium sulfate. Evaporation of the solvent afforded **8** or **8′**, respectively.

Physical and spectral data of **8a**—**f** and **8′a**—**f** are shown in the following.

2-Methylamino-4-phenyl-1-tosyl-1-butene (8a): An oil; MS m/z 316 (M^++1, 2.20%), 315 (M^+, 9.57), 251 (11.30), 160 (100.00), 159 (74.12), 158 (55.71), 146 (48.74), 144 (16.20), 129 (14.72), 105 (15.22), 91 (32.96), 82 (12.66), 56 (76.57); IR (neat) 3300, 2860, 1570, 1530, 1510, 1410, 1250, 1110, 1060, 930, 800, 735, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) of E isomer δ=2.40 (s, 3H), 2.41—2.45 (m, 2H), 2.58 (d, 3H, J=4.9 Hz), 2.75—2.85 (m, 2H), 4.24 (br, 1H), 4.91 (s, 1H), 7.15—7.35 (m, 7H), 7.77 (d, 2H, J=8.2 Hz). ^{1}H NMR ($CDCl_3$) of Z isomer δ=2.42 (s, 3H), 2.43 (t, 2H, J=7.6 Hz), 2.77 (t, 2H, J=7.6 Hz), 2.84 (d, 3H, J=5.2 Hz), 4.57 (s, 1H), 7.07 (d, 2H, J=7.9 Hz), 7.15—7.35 (m, 6H), 7.70 (d, 2H, J=8.2 Hz). E/Z=42/58.

2-Methylamino-1-tosyl-1-pentene (8b): Mp 86.5—87.5°C (from hexane, E/Z mixture); MS m/z 254 (M^++1, 3.04%), 253 (M^+, 15.62), 225 (7.66), 210 (8.81), 188 (22.77), 161 (67.60), 160 (29.69), 139 (15.92), 105 (15.12), 98 (36.14), 91 (18.13), 84 (100.00), 70 (26.52), 56 (94.26); IR (KBr) 3280, 2940, 2840, 1560, 1530, 1410, 1280, 1255, 1110, 1060, 1030, 935, 800, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) of E isomer δ=0.88 (t, 3H, J=7.3 Hz), 1.42—1.48 (m, 2H), 2.40 (s, 3H), 2.52 (t, 2H, J=7.9 Hz), 2.67 (d, 3H, J=4.9 Hz), 4.46 (br, 1H), 4.92 (s, 1H), 7.25 (d, 2H, J=8.1 Hz), 7.77 (d, 2H, J=8.1 Hz). ^{1}H NMR ($CDCl_3$) of Z isomer δ=0.93 (t, 3H, J=7.3 Hz), 1.51 (sx, 2H, J=7.3 Hz), 2.11 (t, 2H, J=7.3 Hz), 2.40 (s, 3H), 2.86 (d, 3H, J=8.2 Hz), 4.55 (s, 1H), 7.23 (br, 1H), 7.25 (d, 2H, J=8.1 Hz), 7.73 (d, 2H, J=8.1 Hz). E/Z=33/67 (before recrystallization).

2-Methylamino-1-tosyl-1-hexene (8c): Mp 68.5—70.0°C (from hexane, E/Z mixture); MS m/z 268 (M^++1, 2.18%), 267 (M^+, 4.63), 238 (17.20), 225 (20.92), 161 (100.00), 160 (42.56), 98 (39.79), 70 (23.88), 56 (79.23); IR (KBr) 3320, 3040, 2920, 2840, 1570, 1520, 1400, 1290, 1250, 1220, 1150, 1105, 1060, 1005, 930, 890, 800, 720, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) of E isomer δ=0.85 (t, 3H, J=7.3 Hz), 1.23—1.40 (m, 4H), 2.40 (s, 3H), 2.53 (t, 2H, J=7.9 Hz), 2.67 (d, 3H, J=4.9 Hz), 4.46 (br, 1H), 4.92 (s, 1H), 7.25 (d, 2H, J=8.4 Hz), 7.77 (d, 2H, J=8.4 Hz). ^{1}H NMR ($CDCl_3$) of Z isomer δ=0.90 (t, 3H, J=7.3 Hz), 1.34 (sx, 2H, J=7.3 Hz), 1.46 (p, 2H, J=7.3 Hz), 2.13 (t, 2H, J=7.3 Hz), 2.40 (s, 3H), 2.87 (d, 3H, J=5.2 Hz), 4.56 (s, 1H), 7.23 (br, 1H), 7.25 (d, 2H, J=8.4 Hz), 7.73 (d, 2H, J=8.4 Hz). E/Z=35/65 (before recrystallization).

2-Methylamino-1-tosyl-1-octene (8d): Mp 96.5—98.5°C (from benzene–hexane, E/Z mixture); MS m/z 296 (M^++1, 2.08%), 295 (M^+, 8.20), 238 (44.86), 225 (13.32), 161 (100.00), 160 (36.96), 140 (30.15), 126 (31.47), 105 (13.13), 70 (25.85), 56 (78.96); IR (KBr) 3310, 2840, 1560, 1530, 1510, 1400, 1250, 1110, 1060, 1035, 930, 810, 800, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) of E isomer δ=0.85 (t, 3H, J=7.0 Hz), 1.14—1.34 (m, 6H), 1.35—1.41 (m, 2H), 2.39 (s, 3H), 2.52 (t, 2H, J=7.9 Hz), 2.67 (d, 3H, J=4.9 Hz), 4.52 (br, 1H), 4.93 (s, 1H), 7.25 (d, 2H, J=8.1 Hz), 7.77 (d, 2H, J=8.1 Hz). ^{1}H NMR ($CDCl_3$) of Z isomer δ=0.86 (t, 3H, J=7.0 Hz), 1.14—1.34 (m, 6H), 1.47 (p, 2H, J=7.6 Hz), 2.12 (t, 2H, J=7.6 Hz), 2.40 (s, 3H), 2.86 (d, 3H, J=5.2 Hz), 4.56 (s, 1H), 7.23 (br, 1H), 7.25 (d, 2H, J=8.1 Hz), 7.73 (d, 2H, J=8.1 Hz). E/Z=36/64 (before recrystallization).

2-Methylamino-1-tosyl-1-undecene (8e): An oil; MS m/z 338 (M^++1, 1.27%), 337 (M^+, 4.22), 238 (36.88), 182 (24.23), 168 (21.45), 161 (100.00), 160 (26.88), 139 (12.04), 70 (15.50), 56 (69.95); IR (neat) 3320, 2900, 2840, 1560, 1530, 1410, 1260, 1115, 1065, 930, 800, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) of E isomer δ=0.88 (t, 3H, J=7.0 Hz), 1.20—1.50 (m, 14H), 2.40 (s, 3H), 2.53 (t, 2H, J=7.9 Hz), 2.68 (d, 3H, J=5.0 Hz), 4.37 (br, 1H), 4.95 (s, 1H), 7.25 (d, 2H, J=8.1 Hz), 7.77 (d, 2H, J=8.1 Hz). ^{1}H NMR ($CDCl_3$) of Z isomer δ=0.88 (t, 3H, J=7.0 Hz), 1.20—1.50 (m, 14H), 2.12 (t, 2H, J=7.6 Hz), 2.40 (s, 3H), 2.86 (d, 3H, J=5.2 Hz), 4.57 (s, 1H), 7.23 (br, 1H), 7.25 (d, 2H, J=8.1 Hz), 7.74 (d, 2H, J=8.1 Hz). E/Z=32/68.

(*E*)-2-Methylamino-1-tosylethene (8f): Mp 120.0—122.0°C (from 2-propanol–benzene–hexane, lit,[11] 122—123°C); MS m/z 212 (M^++1, 12.33%), 211 (M^+, 100.0), 147 (93.80), 146 (60.99), 132 (19.31), 120 (10.45), 105 (28.71), 91 (52.20), 55 (80.96), 42 (28.77); IR (KBr) 3340, 3070, 3040, 2940, 1620, 1520, 1500, 1420, 1290, 1260, 1120, 1080, 1020, 990, 970, 900, 810, 730, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.40 (s, 3H), 2.71 (d, 3H, J=4.9 Hz), 4.91 (br, 1H), 5.05 (d, 1H, J=12.6 Hz), 7.26 (d, 2H, J=8.1 Hz), 7.46 (dd, 1H, J=7.6, 12.6 Hz), 7.73 (d, 2H,

J=8.1 Hz). Found: C, 56.87; H, 6.42; N, 6.73%. Calcd for $C_{10}H_{13}NO_2S$: C, 56.83; H, 6.20; N, 6.63%.

(*E*)-4-Phenyl-2-(1-pyrrolidinyl)-1-tosyl-1-butene (8'a): Mp 157.5—158.0°C (from ethanol); MS m/z 356 (M^++1, 1.46%), 335 (M^+, 5.81), 200 (100.00), 129 (3.27), 96 (15.07), 70 (4.54); IR (KBr) 2920, 2860, 1540, 1440, 1420, 1260, 1120, 1070, 840, 810, 740, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.91 (br, 4H), 2.38 (s, 3H), 2.78 (m, 2H), 2.88 (m, 2H), 3.15 (br, 2H), 3.19 (br, 2H), 4.89 (s, 1H), 7.18—7.31 (m, 7H), 7.81 (d, 2H, J=8.2 Hz). Found: C, 70.67; H, 7.16; N, 3.82%. Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09; N, 3.94%.

(*E*)-2-(1-Pyrrolidinyl)-1-tosyl-1-pentene (8'b): Mp 78.5—79.0°C (from hexane); MS m/z 294 (M^++1, 1.37%), 293 (M^+, 6.73), 265 (3.27), 201 (29.53), 200 (27.16), 138 (100.00), 122 (9.72), 110 (8.24), 96 (16.48), 70 (14.35); IR (KBr) 2950, 2840, 1535, 1450, 1410, 1340, 1300, 1260, 1120, 1070, 1030, 990, 820, 800, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92 (t, 3H, J=7.3 Hz), 1.39 (m, 2H), 1.91 (br, 4H), 2.40 (s, 3H), 2.55 (m, 2H), 3.14 (br, 2H), 3.32 (br, 2H), 4.81 (s, 1H), 7.24 (d, 2H, J=8.1 Hz), 7.78 (d, 2H, J=8.1 Hz). Found: C, 65.29; H, 8.18; N, 4.74%. Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77%.

(*E*)-2-(1-Pyrrolidinyl)-1-tosyl-1-hexene (8'c): Mp 65.5—66.5°C (from hexane); MS m/z 308 (M^++1, 1.69%), 307 (M^+, 7.52), 278 (28.27), 265 (23.96), 201 (96.87), 200 (100.00), 152 (92.93), 138 (24.96), 110 (27.00), 96 (36.58), 70 (25.02); IR (KBr) 2900, 2840, 1530, 1410, 1260, 1115, 1065, 820, 710, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.85 (t, 3H, J=7.0 Hz), 1.30—1.31 (m, 4H), 1.91 (br, 4H), 2.39 (s, 3H), 2.57 (t, 2H, J=7.3 Hz), 3.15 (br, 2H), 3.35 (br, 2H), 4.83 (s, 1H), 7.24 (d, 2H, J=8.1 Hz), 7.78 (d, 2H, J=8.1 Hz). Found: C, 66.38; H, 8.15; N, 4.60%. Calcd for $C_{17}H_{25}NO_2S$: C, 66.39; H, 8.20; N, 4.56%.

(*E*)-2-(1-Pyrrolidinyl)-1-tosyl-1-octene (8'd): An oil; MS m/z 336 (M^++1, 1.97%), 335 (M^+, 8.02), 278 (42.14), 201 (91.05), 200 (84.80), 180 (100.00), 166 (20.01), 124 (17.68), 110 (20.43), 96 (28.06), 70 (15.73); IR (neat) 2900, 2840, 1530, 1440, 1410, 1260, 1120, 1070, 980, 820, 800, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=7.3 Hz), 1.18—1.28 (m, 8H), 1.91 (br, 4H), 2.39 (s, 3H), 2.56 (t, 2H, J=7.6 Hz), 3.12 (br, 2H), 3.33 (br, 2H), 4.82 (s, 1H), 7.24 (d, 2H, J=8.1 Hz), 7.77 (d, 2H, J=8.1 Hz).

(*E*)-2-(1-Pyrrolidinyl)-1-tosyl-1-undecene (8'e): An oil; MS m/z 378 (M^++1, 1.94%), 377 (M^+, 7.26), 278 (42.86), 222 (87.55), 201 (100.00), 124 (14.23), 110 (12.85), 96 (17.30), 70 (8.38); IR (neat) 2900, 2840, 1540, 1410, 1265, 1120, 1070, 825, 800, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7.0 Hz), 1.26 (m, 14H), 1.91 (br, 4H), 2.39 (s, 3H), 2.56 (t, 2H, J=7.0 Hz), 3.18 (br, 2H), 3.33 (br, 2H), 4.81 (s, 1H), 7.23 (d, 2H, J=8.1 Hz), 7.78 (d, 2H, J=8.1 Hz).

(*E*)-2-(1-Pyrrolidinyl)-1-tosylethene (8'f): Mp 134.5—135.0°C [from benzene–hexane, lit,[12] 136°C (benzene–ligroin)]; 251 (M^+, 52.45%), 187 (7.56), 160 (3.36), 96 (27.84), 95 (100.00), 94 (53.52), 69 (6.66), 54 (13.23); IR (KBr) 3040, 2940, 2910, 2840, 1590, 1445, 1390, 1270, 1245, 1120, 1070, 955, 880, 840, 800, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.93 (br, 4H), 2.40 (s, 3H), 3.03 (br, 2H), 3.45 (br, 2H), 4.81 (d, 1H, J=12.5 Hz), 7.24 (d, 2H, J=8.1 Hz), 7.49 (d, 1H, J=12.5 Hz), 7.72 (d, 2H, J=8.1 Hz). Found: C, 62.06; H, 7.01; N, 5.55%. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57%.

Preparation of 1-Tosyl-2-alkanones (9): To a solution of **2** (0.2 mmol) in acetonitrile (4 ml) was added an aqueous methylamine (ca. 40%, 1 ml, ca. 12 equiv) solution at room temperature under nitrogen. After stirring for 15 min—1.0 h, aqueous 1 M HCl solution was added at room temperature followed by evaporation of the acetonitrile. The extract of ethyl acetate was successively washed with water, brine, and dried over sodium sulfate. Evaporation of the solvent afforded 1-tosyl-2-alkanones (**9**).

Physical and spectral data of **9a**—**e** are shown in the following.

4-Phenyl-1-tosyl-2-butanone (9a): An oil; MS m/z 302 (M^+, 0.31%), 147 (22.58), 146 (100.00), 129 (21.56), 105 (43.68), 91 (35.11); IR (neat) 3020, 2900, 1705, 1580, 1480, 1440, 1390, 1300, 1140, 1080, 1050, 1010, 805, 720, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.43 (s, 3H), 2.87 (t, 2H, J=7.3 Hz), 3.40 (t, 2H, J=7.3 Hz), 4.08 (s, 2H), 7.15—7.21 (m, 2H), 7.25—7.29 (m, 3H), 7.31 (d, 2H, J=8.4 Hz), 7.64 (d, 2H, J=8.4 Hz).

1-Tosyl-2-pentanone (9b): Mp 56°C (from hexane, lit,[13] an oil); MS m/z 241 (M^++1, 1.81%), 240 (M^+, 8.16), 222 (4.62), 176 (14.93), 154 (53.67), 138 (15.37), 90 (63.92), 70 (100.00), 42 (28.27); IR (KBr) 3010, 2970, 2940, 2880, 1710, 1585, 1395, 1380, 1365, 1310, 1290, 1235, 1205, 1160, 1140, 1080, 1040, 1030, 890, 805, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, 3H, J=7.3 Hz), 1.59 (sx, 2H, J=7.3 Hz), 2.46 (s, 3H), 2.68 (t, 2H, J=7.3 Hz), 4.12 (s, 2H), 7.36 (d, 2H, J=8.1 Hz), 7.75 (d, 2H, J=8.1 Hz). Found: C, 59.90; H, 6.68%. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71%.

1-Tosyl-2-hexanone (9c): Mp 56.0—56.5°C (from hexane); MS m/z 255 (M^++1, 0.75%), 254 (M^+, 1.74), 212 (14.34), 155 (60.55), 148 (45.13), 139 (74.16), 98 (37.18), 91 (75.97), 85 (100.00), 57 (51.84); IR (KBr) 3000, 2960, 2940, 2880, 1715, 1585, 1390, 1370, 1360, 1305, 1285, 1240, 1200, 1160, 1140, 1080, 1040, 805, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, 3H, J=7.3 Hz), 1.28 (sx, 2H, J=7.3 Hz), 1.54 (p, 2H, J=7.3 Hz), 2.45 (s, 3H), 2.70 (t, 2H, J=7.3 Hz), 4.12 (s, 2H), 7.36 (d, 2H, J=8.1 Hz), 7.75 (d, 2H, J=8.1 Hz). Found: C, 61.34; H, 7.13%. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13%.

1-Tosyl-2-octanone (9d): Mp 35.5—36.0°C (from hexane); MS m/z 282 (M^+, 0.58%), 264 (6.34), 213 (24.32), 155 (54.87), 148 (55.75), 139 (100.00), 126 (58.74), 113 (54.46), 91 (58.24), 43 (49.89); IR (KBr) 3000, 2930, 2860, 1715, 1585, 1390, 1310, 1285, 1150, 1140, 805, 740, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86 (t, 3H, J=7.0 Hz), 1.25—1.31 (m, 6H), 1.50—1.56 (m, 2H), 2.45 (s, 3H), 2.68 (t, 2H, J=7.3 Hz), 4.12 (s, 2H), 7.36 (d, 2H, J=8.3 Hz), 7.55 (d, 2H, J=8.3 Hz). Found: C, 63.62; H, 7.74%. Calcd for $C_{15}H_{22}O_3S$: C, 63.80; H, 7.85%.

1-Tosyl-2-undecanone (9e): Mp 70.0—70.5°C (from hexane); MS m/z 325 (M^++1, 0.73%), 306 (5.46), 213 (37.64), 168 (44.41), 155 (42.15), 148 (60.10), 139 (100.00), 91 (33.57), 71 (21.42), 43 (23.01); IR (KBr) 2900, 2840, 1700, 1580, 1460, 1390, 1370, 1305, 1280, 1230, 1155, 1135, 1070, 1035, 900, 805, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7.0 Hz), 1.25 (m, 12H), 1.55 (m, 2H), 2.46 (s, 3H), 2.69 (t, 2H, J=7.3 Hz), 4.11 (s, 2H), 7.36 (d, 2H, J=8.2 Hz), 7.75 (d, 2H, J=8.2 Hz). Found: C, 66.54; H, 8.65%. Calcd for $C_{18}H_{28}O_3S$: C, 66.63; H, 8.70%.

2-Tosylethanal Dimethyl Acetal (10): Compound **2f** (77 mg, 0.25 mmol) in methanol (2 ml) was treated with 3 M sodium methoxide (1 ml, 3 mmol) for 1 h at room temperature under nitrogen. After evaporation of the solvent, the extract of ethyl acetate was washed with brine and dried over sodium sulfate, followed by evaporation of the solvent. The product (**10**) was separated by a flash column chromatography with Merck's aluminum oxide 90 active basic (Merck 1076, activity stage IV. Solvent; hexane/ethyl acetate=4/1, v/v) in quantitative yield (61 mg). Mp 49.0—49.5°C [from hexane,

lit, 49.5—50°C (from hexane, cyclohexane),[14a] 50—51°C (from ligroin)[14b]]; IR (melted) 2960, 2920, 2820, 1585, 1440, 1390, 1370, 1300, 1295, 1280, 1240, 1135, 1110, 1075, 1055, 980, 960, 810, 790, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.45 (s, 3H), 3.41 (d, 2H, J=5.2 Hz), 4.86 (t, 1H, J=5.2 Hz), 7.35 (d, 2H, J=8.2 Hz), 7.78 (d, 2H, J=8.2 Hz). Found: C, 54.02; H, 6.48%. Calcd for $C_{11}H_{16}O_4S$: C, 54.08; H, 6.60%.

(*E*)-2-Methylthio-1-tosyl-1-octene (14): To a solution of **2d** (39 mg, 0.1 mmol) in acetonitrile (1 ml) was added a 15% aqueous sodium methanethiolate (0.05 ml, 0.11 mmol) solution at room temperature under nitrogen. After refluxing for 2 h, the reaction mixture was filtered through a small amount of aluminum oxide (Merck 1076, basic) and dried over sodium sulfate. After evaporation of the solvent, the resulting residue was subjected to preparative TLC [solvent; hexane/ethyl acetate=5/1, v/v] to afford 28 mg (89% yield) of **14**. Mp 54.0—54.5°C (from hexane); IR (KBr) 2920, 2840, 1590, 1550, 1410, 1300, 1270, 1140, 1080, 1020, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7.3 Hz), 1.22—1.34 (m, 6H), 1.50 (p, 2H, J=7.9 Hz), 2.26 (s, 3H), 2.43 (s, 3H), 2.73 (t, 2H, J=7.9 Hz), 5.77 (s, 1H), 7.94 (d, 2H, J=8.1 Hz), 8.24 (d, 2H, J=8.1 Hz). Found: C, 61.34; H, 7.66%. Calcd for $C_{16}H_{24}O_2S_2$: C, 61.50; H, 7.74%.

(*E*)-2-Propyl-1-tosyl-1-hexene (15): "Higher order" cuprate[8] was prepared from copper (I) cyanide (10 mg, 0.11 mmol) and butyllithium (0.22 mmol) in THF (3 ml) at −78 to 0°C for 1 h under argon. To the solution was added a solution of **2b** (35 mg, 0.1 mmol) in THF (1 ml) at 0°C. After stirring for 2 h at the temperature, the reaction mixture was treated with a saturated aqueous ammonium chloride solution, followed by evaporation of THF. The extract of ethyl acetate was successively washed with water and brine, and dried over sodium sulfate. The residue obtained by evaporation of the solvent was subjected to preparative TLC [solvent; hexane/ethyl acetate=5/1, v/v] to afford 18 mg (64% yield) of **15**. An oil; MS m/z 281 (M^++1, 15.04%), 280 (M^+, 83.45), 245 (36.47), 214 (20.07), 185 (22.58), 171 (53.10), 157 (94.30), 139 (41.64), 109 (25.76), 96 (34.93), 95 (61.22), 83 (47.06), 82 (100.00), 81 (53.28), 69 (31.36), 67 (37.58), 55 (34.84); IR (neat) 3040, 2960, 2930, 2870, 1610, 1590, 1450, 1370, 1305, 1290, 1280, 1140, 1080, 800, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7.0 Hz), 0.92 (t, 3H, J=7.0 Hz), 1.23—1.32 (m, 2H), 1.35—1.48 (m, 4H), 2.11 (t, 2H, J=7.3 Hz), 2.43 (s, 3H), 2.54 (t, 2H, J=7.0 Hz), 6.12 (s, 1H), 7.32 (d, 2H, J=8.1 Hz), 7.78 (d, 2H, J=8.1 Hz).

(*Z*)-2-Methyl-1-tosyl-1-pentene (16): An oil; MS m/z 239 (M^++1, 3.61%), 238 (M^+, 22.59), 203 (25.17), 172 (57.27), 171 (52.53), 157 (55.48), 143 (41.29), 139 (77.51), 131 (25.70), 119 (29.45), 92 (48.81), 91 (47.80), 82 (58.35), 67 (100.00), 55 (47.11); IR (neat) 3040, 2960, 2930, 2880, 1610, 1590, 1490, 1430, 1370, 1305, 1290, 1280, 1140, 1080, 850, 800, 770, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (t, 3H, J=7.3 Hz), 1.45 (sx, 2H, J=7.3 Hz), 1.86 (s, 3H), 2.43 (s, 3H), 2.57 (t, 2H, J=7.3 Hz), 6.12 (s, 1H), 7.32 (d, 2H, J=8.1 Hz), 7.78 (d, 2H, J=8.1 Hz).

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