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Regio- and stereoselective synthesis of tetrasubstituted allylic alcohols by three-component reaction of acetylenic sulfone, dialkylzinc, and aldehyde

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ABSTRACT

(*Z*)-Tetrasubstituted allylic alcohols bearing sulfonyl group were synthesized regio- and stereoselectively by alkylzincation of acetylenic sulfone followed by addition to aldehyde.

1. Introduction

Allylic alcohols are useful intermediates in many synthetic applications such as palladium-catalyzed π-allyl chemistry [1], Claisen rearrangements and related sigmatropic processes [2], enantio- and diastereoselective hydroxyl-directed additions to alkene and so on [3–7]. Stereodefined allylic alcohols are also important building blocks in many natural products [8–10]. Therefore, stereoselective synthesis of allylic alcohols has drawn the attention of organic chemists and addition of an alkenylmetallic reagent to a carbonyl compound is a commonly used method [11–14].

Organozinc reagents are useful and versatile reagents for a variety of transformations in organic synthesis since they show high tolerance for a wide variety of functional groups [15–19]. Synthesis of di- or trisubstituted allylic alcohols by addition of alkenylzinc to aldehydes has been extensively studied and the alkenylzinc reagents are mainly generated in situ by reaction of dialkylzinc with alkenylboranes or alkenylzirconium, or by metal exchange of zinc chloride with alkenylmagnesium bromide and zinc bromide with alkenyllithium [20–23]. However, the direct synthesis of tetrasubstituted allylic alcohols remains a formidable challenge and synthesis of tetrasubstituted allylic alcohols by direct carbozincation of alkynes followed by addition to aldehyde is scarce [24]. Recently, we have reported a stereoselective synthesis of tetrasubstituted allylic alcohols by carbomagnesium of acetylenic sulfone followed by reaction with aldehyde [25]. In the course of our study, we found that the stereoselectivity is poor and a mixture of stereoisomers are obtained when alkylmagnesium bromide was used. As an extension of our research interest in the application of organozinc reagents in organic synthesis [26,27], we investigated the alkylzincation of acetylenic sulfone and its further reaction with aldehyde. Herein, we wish to report the regio- and stereoselective synthesis of (*Z*)-tetrasubstituted allylic alcohols by three-component tandem reaction of acetylenic sulfone, dialkylzinc reagent and aldehyde.

2. Results and discussion

Firstly, we examined the ethylzincation reaction of acetylenic sulfones followed by hydrolysis. Upon treatment of 1-phenyl-2-(*p*-tolylsulfonyl)ethyne (**1a**) with Et_2Zn (1.2 mol per 1 mol of **1a**) in toluene at room temperature, the expected vinyl sulfone **3a** was obtained only in 10% yield (entry 1, Table 1). When the reaction was performed in the presence of 10 mol% CuI, product **3a** was obtained in 60% yield (entry 2, Table 1). The yield of **3a** was improved to 85% and the reaction time was decreased dramatically when the reaction proceeded in refluxing toluene (entry 3, Table 1). Increasing the molar ratio of Et_2Zn/**1a** from 1.2 to 2.0 led to an increasing in yield from 85% to 94% (entries 3–5, Table 1). Decreasing the amount of CuI from 10 mol% to 5 mol% diminished the yield of **3a** (entry 6, Table 1). On the basis of the above experimental results, we can see that the general reaction condition is that acetylenic sulfone react with 2.0 equiv. diethylzinc in the presence of 10 mol% CuI in refluxing toluene. Further investigation show that carbozincation product **3b**–**3d** can be prepared in high

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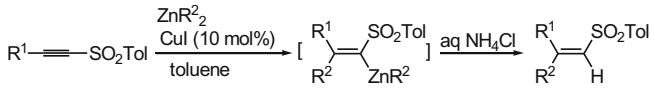
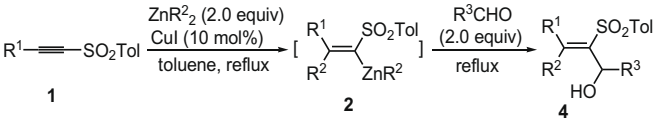
Table 1
Reaction of dialkylzinc with acetylenic sulfone.



Entry	R^1	ZnR^2_2 (equiv.)	Time (min)	T (°C)	Yield (%)[a]
1[b]	Ph–	$(CH_3CH_2)_2Zn$ (1.2)	100	RT	**3a** (10)
2	Ph–	$(CH_3CH_2)_2Zn$ (1.2)	80	RT	**3a** (60)
3	Ph–	$(CH_3CH_2)_2Zn$ (1.2)	25	Reflux	**3a** (85)
4	Ph–	$(CH_3CH_2)_2Zn$ (1.5)	20	Reflux	**3a** (89)
5	Ph–	$(CH_3CH_2)_2Zn$ (2.0)	10	Reflux	**3a** (94)
6[c]	Ph–	$(CH_3CH_2)_2Zn$ (2.0)	12	Reflux	**3a** (85)
7	n-C_4H_9	$(CH_3CH_2)_2Zn$ (2.0)	12	Reflux	**3b** (88)
8	Ph–	$(CH_3)_2Zn$ (2.0)	5	Reflux	**3c** (96)
9	n-C_4H_9	$(CH_3)_2Zn$ (2.0)	8	Reflux	**3d** (90)

[a] Isolated yield based on **1**.
[b] No catalyst was used.
[c] 5 mol% catalyst was used.

Table 2
Reaction of alkenylzinc **2** with aldehyde.



Entry	R^1	R^2	R^3	Yield (%)[a]
1	Ph–	CH_3CH_2–	Ph–	**4a** (70)
2	Ph–	CH_3CH_2–	4-$CH_3OC_6H_4$–	**4b** (75)
3	Ph–	CH_3CH_2–	2,4-$CH_3OC_6H_3$–	**4c** (71)
4	Ph–	CH_3CH_2–	4-Br-C_6H_4–	**4d** (60)
5	Ph–	CH_3CH_2–	4-Cl-C_6H_4–	**4e** (55)
6	n-C_4H_9–	CH_3CH_2–	Ph–	**4f** (50)
7	n-C_4H_9–	CH_3CH_2–	4-$CH_3OC_6H_4$–	**4g** (60)
8	n-C_4H_9–	CH_3CH_2–	4-Br-C_6H_4–	**4h** (45)
9	n-C_4H_9–	CH_3CH_2–	4-Cl-C_6H_4–	**4i** (55)
10	Ph–	CH_3–	Ph–	**4j** (93)
11	Ph–	CH_3–	4-$CH_3OC_6H_4$–	**4k** (90)
12	Ph–	CH_3–	2,4-$CH_3OC_6H_3$–	**4l** (93)
13	Ph–	CH_3–	4-Br-C_6H_4–	**4m** (82)
14	Ph–	CH_3–	4-Cl-C_6H_4–	**4n** (85)
15	n-C_4H_9–	CH_3–	Ph–	**4o** (82)
16	n-C_4H_9–	CH_3–	4-$CH_3OC_6H_4$–	**4p** (78)
17	n-C_4H_9–	CH_3–	2,4-$CH_3OC_6H_3$–	**4q** (87)
18	n-C_4H_9–	CH_3–	4-Br-C_6H_4–	**4r** (84)
19	n-C_4H_9–	CH_3–	4-Cl-C_6H_4–	**4s** (73)

[a] Isolated yield based on **1**.

yield in the optimized reaction conditions (entries 7–9, Table 1). Compound (*Z*)-**3b** was a known compound and the ^{1}H NMR data observed here are identical to what was published in the literature [19]. The carbozincation of acetylenic sulfone in the optimized reaction conditions lead to a single regio- and stereoisomer. No *anti*-adduct was observed.

Having in hand the easy and reproducible protocol for the alkylzincation of acetylenic sulfone, we examined addition of the in situ formed alkenylzinc reagent to aldehydes, hoping to synthesize tetrasubstituted allylic alcohols stereoselectively. The experimental results show that the reaction of alkenylzinc reagent with aldehyde is quite general and the expected tetrasubstituted allylic alcohols **4** were obtained in moderate to high yield. The results are summarized in Table 2. Table 2 shows that R^1 in acetylenic sulfone can be phenyl or *n*-butyl, ZnR^2_2 can be $Zn(CH_2CH_3)_2$ or $Zn(CH_3)_2$, R^3 in aldehydes can be phenyl (entries 1, 6, 10 and 15, Table 2), electron-rich aryl (entries 2, 3, 7, 11, 12, 16 and 17, Table 2) or electron-poor aryl (entries 4, 5, 8, 9, 13, 14, 18 and 19, Table 2).

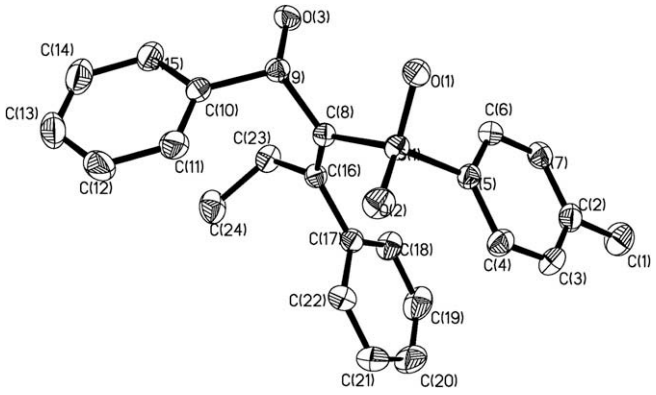


Fig. 1. The molecular structure of compound **4a**.

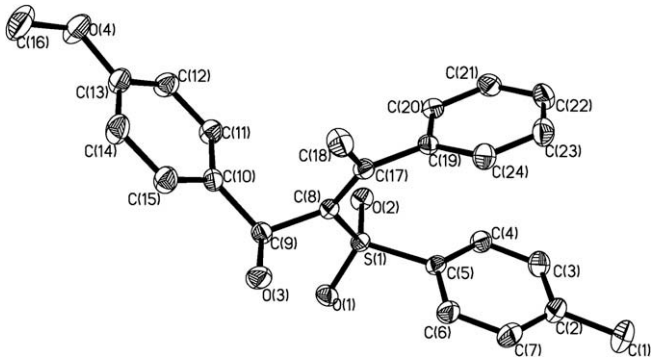


Fig. 2. The molecular structure of compound **4k**.

However, no expected allylic alcohol was obtained when *n*-butyraldehyde reacted with alkenylzinc **2**. In the case of dimethylzinc, a higher yield was obtained as compared to the yield with diethylzinc, this may be due to the less steric effect of methyl than ethyl.

The configurations of compounds **4a**, **4h**, **4k** and **4s** were verified by the NOESY spectra. The NOESY spectra of these compounds show that CH(OH) is in a *cis* orientation with ethyl or methyl. The molecular structures of **4a** [28] and **4k** [29] (Figs. 1 and 2) were also affirmatively characterized by X-ray diffraction analysis, which show that the double bonds in **4a** and **4k** are in *Z*-configuration. The fact that all of the compounds **4** shared almost the same NMR patterns suggests the stereochemistry of compounds **4** to be identical. Therefore, the tandem reaction of acetylenic sulfone, dialkylzinc reagent and aldehyde is in a *syn*-fashion and the double bond in compounds **4** is in *Z*-configuration.

In conclusion, (*Z*)-tetrasubstituted allylic alcohols were conveniently prepared as single isomers by one-pot tandem reaction of acetylenic sulfone, dialkylzinc and aldehyde. The methods are direct and experimentally simple with readily accessible reagents and excellent regio- and stereoselectivity.

3. Experimental

All solid products were recrystallized from ethyl acetate and hexane, and the melting points are uncorrected. All reactions were carried out under an argon atmosphere. Toluene was distilled from sodium–benzophenone immediately before use. ^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR spectra were measured at 75 MHz in $CDCl_3$ with TMS as the internal standard. Acetylenic sulfones were prepared according to previously described procedures [30].

3.1. General procedure for the synthesis of trisubstituted alkenes **3a–3d**

Dialkylzinc (1.0 mmol, 1.2 M in toluene) was added to the solution of acetylenic sulfone (0.5 mmol) and CuI (10 mol%) in toluene (2 mL) at room temperature. The reaction mixture was stirred at refluxing temperature for 5–12 min. After the alkylzincation was complete (monitored by TLC), the reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. After filtration and removal of solvent in vacuo, the crude product was purified with flash chromatography (silica/hexane–ethyl acetate 10:1 v/v). The desired products **3a–3d** were obtained.

3.1.1. (Z)-2-Phenyl-1-tosylbut-1-ene (**3a**)

White solid; m.p. 71–73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.2 Hz, 2H), 7.32–7.22 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 7.02–7.00 (m, 2H), 6.49 (s, 1H), 2.43–2.36 (m, 5H), 1.01 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 143.6, 138.6, 136.9, 129.3, 128.2, 128.1, 127.8, 127.6, 127.5, 34.0, 21.6, 11.7; Anal. Calc. for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; found: C, 71.15; H, 6.43; IR (KBr) ν (cm^{-1}) 3049, 1616, 1444, 1288, 1145, 1083.

3.1.2. (Z)-2-Ethyl-1-tosylhex-1-ene (**3b**) [19]

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81–7.78 (m, 2H), 7.32 (d, J = 7.2 Hz, 2H), 6.11 (s, 1H), 2.57–2.54 (m, 2H), 2.44 (s, 3H), 2.18 (q, J = 7.3 Hz, 2H), 1.41–1.23 (m, 4H), 1.03 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 143.8, 139.8, 129.7, 127.1, 125.1, 31.1, 30.5, 30.4, 22.9, 21.5, 13.8, 11.7; Anal. Calc. for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; found: C, 67.45; H, 8.49; IR (KBr) ν (cm^{-1}) 2960, 2931, 1620, 1462, 1313, 1145.

3.1.3. (Z)-2-Phenyl-1-tosylprop-1-ene (**3c**)

White solid; m.p. 93–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 7.7 Hz, 2H), 7.31–7.27 (m, 4H), 7.18–7.09 (m, 3H), 6.54 (s, 1H), 2.38 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 143.7, 138.5, 137.6, 129.3, 129.2, 128.4, 127.9, 127.6, 127.3, 27.8, 21.6; Anal. Calc. for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; found: C, 70.25; H, 5.61; IR (KBr) ν (cm^{-1}) 3061, 2987, 1620, 1435, 1300, 1083.

3.1.4. (Z)-2-Methyl-1-tosylhex-1-ene (**3d**)

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.15 (s, 1H), 2.57 (t, J = 7.5 Hz, 2H), 2.44 (s, 3H), 1.86 (s, 3H), 1.42–1.28 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7, 143.8, 139.7, 129.7, 127.1, 126.4, 32.2, 30.0, 24.5, 22.8, 21.5, 13.9; Anal. Calc. for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; found: C, 66.35; H, 7.63; IR (KBr) ν (cm^{-1}) 2956, 2931, 1624, 1597, 1440, 1300, 1145.

3.2. General procedure for the synthesis of tetrasubstituted allylic alcohols **4a–4s**

Alkenylzinc intermediate was prepared in situ according to the procedure described above. Once the alkylzincation was complete, aldehyde (1.0 mmol) was added. The reaction mixture was stirred for another 35–90 minutes at reflux temperature. After the reaction was complete (monitored by TLC), the reaction was quenched with a saturated NH_4Cl solution. After usual workup, the crude product was purified with flash chromatography (silica/hexanes–ethyl acetate 8:1 v/v). The desired product **4** was obtained.

3.2.1. (Z)-1,3-Diphenyl-2-tosylpent-2-en-1-ol (**4a**)

White solid; m.p. 136–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2H), 7.47–7.42 (m, 2H), 7.36–7.32 (m, 1H), 7.22–7.09 (m, 4H), 6.99–6.93 (m, 5H), 6.16 (d, J = 10.8 Hz, 1H), 4.45 (d, J = 10.8 Hz, 1H), 2.61–2.45 (m, 2H), 2.33 (s, 3H), 0.87 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 143.2, 141.8, 141.7, 138.8, 137.9, 128.8, 128.5, 128.2, 127.7, 127.5, 127.4, 125.5, 71.3, 31.4, 21.5, 11.9; Anal. Calc. for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16; found: C, 73.65; H, 6.21; IR (KBr) ν (cm^{-1}) 3454, 2960, 1597, 1492, 1350, 1274, 1132.

3.2.2. (Z)-1-(4-Methoxyphenyl)-3-phenyl-2-tosylpent-2-en-1-ol (**4b**)

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 7.1 Hz, 2H), 7.33–7.08 (m, 6H), 7.01 (d, J = 9.4 Hz, 5H), 6.12 (d, J = 10.7 Hz, 1H), 4.47 (d, J = 10.8 Hz, 1H), 3.87 (s, 3H), 2.58–2.46 (m, 2H), 2.34 (s, 3H), 0.90 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 157.6, 143.2, 141.6, 138.9, 137.9, 133.9, 128.8, 128.6, 127.6, 127.5, 127.4, 126.8, 113.9, 71.1, 55.3, 31.3, 21.5, 12.1; Anal. Calc. for $C_{25}H_{26}O_4S$: C, 71.06; H, 6.20; found: C, 71.45; H, 6.41; IR (KBr) ν (cm^{-1}) 3481, 2916, 1510, 1274, 1247, 1139.

3.2.3. (Z)-1-(2,4-Dimethoxyphenyl)-3-phenyl-2-tosylpent-2-en-1-ol (**4c**)

Yellow solid; m.p. 138–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 8.5 Hz, 1H), 7.22–7.15 (m, 4H), 6.99–6.85 (m, 5H), 6.61–6.58 (m, 1H), 6.37 (d, J = 2.2 Hz, 1H), 6.22 (d, J = 10.0 Hz, 1H), 4.31 (d, J = 9.7 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 2.69–2.49 (m, 2H), 2.32 (s, 3H), 0.82 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 157.9, 157.4, 142.8, 140.3, 139.2, 138.9, 128.6, 128.2, 127.5, 127.4, 127.3, 121.7, 103.9, 98.1, 67.7, 55.4, 54.9, 31.4, 21.5, 11.4; Anal. Calc. for $C_{26}H_{28}O_5S$: C, 69.00; H, 6.24; found: C, 69.35; H, 6.51; IR (KBr) ν (cm^{-1}) 3523, 2935, 1612, 1492, 1282, 1136, 1082.

3.2.4. (Z)-1-(4-Bromophenyl)-3-phenyl-2-tosylpent-2-en-1-ol (**4d**)

White solid; m.p. 150–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.49 (m, 4H), 7.28–7.21 (m, 3H), 7.11–6.95 (m, 5H), 6.72–6.56 (br, 1H), 6.08 (d, J = 10.9 Hz, 1H), 4.52 (d, J = 10.0 Hz, 1H), 2.65–2.56 (m, 1H), 2.49–2.39 (m, 1H), 2.34 (s, 3H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 143.4, 141.1, 140.9, 138.5, 137.6, 131.6, 128.9, 128.6, 127.8, 127.6, 127.4, 127.3, 121.5, 70.9, 31.4, 21.6, 12.2; Anal. Calc. for $C_{24}H_{23}BrO_3S$: C, 61.15; H, 4.92; found: C, 61.45; H, 4.81; IR (KBr) ν (cm^{-1}) 3495, 2962, 1489, 1340, 1282, 1083.

3.2.5. (Z)-1-(4-Chlorophenyl)-3-phenyl-2-tosylpent-2-en-1-ol (**4e**)

White solid; m.p. 145–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.28–7.14 (m, 4H), 7.02–6.95 (m, 5H), 6.11 (d, J = 10.9 Hz, 1H), 4.49 (d, J = 10.9 Hz, 1H), 2.62–2.57 (m, 1H), 2.48–2.41 (m, 1H), 2.35 (s, 3H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 143.3, 141.3, 140.5, 138.6, 137.7, 133.3, 128.9, 128.6, 127.8, 127.5, 127.3, 127.0, 70.9, 31.4, 21.5, 12.1; Anal. Calc. for $C_{24}H_{23}ClO_3S$: C, 67.51; H, 5.43; found: C, 67.82; H, 5.40; IR (KBr) ν (cm^{-1}) 3481, 2962, 1591, 1485, 1340, 1282, 1134.

3.2.6. (Z)-3-Ethyl-1-phenyl-2-tosylhept-2-en-1-ol (**4f**)

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7. 47 (d, J = 7.4 Hz, 2H), 7.39–7.24 (m, 5H), 5.95 (d, J = 10.8 Hz, 1H), 4.32 (d, J = 11.1 Hz, 1H), 2.48–2.42 (m, 5H), 2.35–2.23 (m, 2H), 1.33–1.14 (m, 4H), 1.06 (t, J = 7.5 Hz, 3H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 143.7, 142.0, 140.5, 138.4, 129.4, 128.4, 127.3, 127.1, 125.7, 71.4, 33.6, 29.9, 27.4, 23.2, 21.5, 13.8, 13.0; Anal. Calc. for $C_{22}H_{28}O_3S$: C, 70.93; H, 7.58; found: C, 70.65; H, 7.31; IR (KBr) ν (cm^{-1}) 3500, 2953, 1606, 1514, 1409, 1242, 1141.

3.2.7. (Z)-3-Ethyl-1-(4-methoxyphenyl)-2-tosylhept-2-en-1-ol (**4g**)

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 5.89 (d, J = 11.2 Hz, 1H), 4.30 (d, J = 11.3 Hz, 1H), 3.82 (s, 3H), 2.47–2.39 (m, 5H), 2.31–2.24 (m, 2H), 1.38–1.22 (m, 4H),

1.05 (t, J = 7.5 Hz, 3H), 0.82 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.6, 158.9, 143.6, 140.6, 138.3, 134.2, 129.5, 127.0, 126.9, 113.7, 71.1, 55.3, 33.6, 29.9, 27.3, 23.2, 21.5, 13.8, 13.1; Anal. Calc. for $C_{23}H_{30}O_4S$: C, 68.62; H, 7.51; found: C, 68.65; H, 7.33; IR (KBr) ν (cm^{-1}) 3504, 2933, 1608, 1510, 1379, 1247, 1136.

3.2.8. (Z)-1-(4-Bromophenyl)-3-ethyl-2-tosylhept-2-en-1-ol ***(4h)***

White solid; m.p. 96–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7.49–7.45 (m, 2H), 7.34–7.22 (m, 4H), 5.86 (d, J = 10.8 Hz, 1H), 4.30 (d, J = 11.0 Hz, 1H), 2.45–2.43 (m, 5H), 2.28 (q, J = 7.6 Hz, 2H), 1.27–1.23 (m, 4H), 1.06 (t, J = 7.5 Hz, 3H), 0.83 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 143.9, 141.2, 140.3, 137.9, 131.4, 129.5, 127.5, 127.0, 121.3, 70.9, 33.7, 30.0, 27.5, 23.2, 21.5, 13.8, 13.1; Anal. Calc. for $C_{22}H_{27}BrO_3S$: C, 58.53; H, 6.03; found: C, 58.68; H, 6.16; IR (KBr) ν (cm^{-1}) 3471, 2962, 1606, 1467, 1377, 1280, 1130.

3.2.9. (Z)-1-(4-Chlorophenyl)-3-ethyl-2-tosylhept-2-en-1-ol ***(4i)***

White solid; m.p. 73–76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 7.8 Hz, 2H), 7.40–7.27 (m, 6H), 5.88 (d, J = 10.7 Hz, 1H), 4.31 (d, J = 10.9 Hz, 1H), 2.59–2.41 (m, 5H), 2.29–2.25 (m, 2H), 1.36–1.18 (m, 4H), 1.05 (t, J = 7.3 Hz, 3H), 0.83 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 143.9, 140.7, 140.4, 138.0, 133.1, 129.5, 128.5, 127.2, 127.0, 70.9, 33.7, 30.0, 27.4, 23.2, 21.5, 13.8, 13.1; Anal. Calc. for $C_{22}H_{27}ClO_3S$: C, 64.93; H, 6.69; found: C, 65.20; H, 6.86; IR (KBr) ν (cm^{-1}) 3469, 2962, 1606, 1490, 1350, 1280, 1130.

3.2.10. (Z)-1,3-Diphenyl-2-tosylbut-2-en-1-ol ***(4j)***

White solid; m.p. 139–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 7.3 Hz, 2H), 7.48–7.43 (m, 2H), 7.38–7.36 (m, 1H), 7.21–7.16 (m, 5H), 6.98–6.92 (m, 4H), 6.20 (d, J = 10.0 Hz, 1H), 4.46 (d, J = 10.5 Hz, 1H), 2.34 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2, 143.3, 142.1, 141.8, 139.9, 138.7, 128.9, 128.6, 127.8, 127.7, 127.6, 127.5, 127.4, 125.5, 71.3, 25.7, 21.5; Anal. Calc. for $C_{23}H_{22}O_3S$: C, 72.99; H, 5.86; found: C, 72.68; H, 5.75; IR (KBr) ν (cm^{-1}) 3477, 2916, 1597, 1492, 1355, 1278, 1134.

3.2.11. (Z)-1-(4-Methoxyphenyl)-3-phenyl-2-tosylbut-2-en-1-ol ***(4k)***

White solid; m.p. 166–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.5 Hz, 2H), 7.25–7.10 (m, 4H), 7.02–6.87 (m, 7H), 6.12 (d, J = 10.7 Hz, 1H), 4.43 (d, J = 10.8 Hz, 1H), 3.84 (s, 3H), 2.32 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 152.5, 143.2, 141.9, 139.9, 138.8, 133.6, 128.8, 127.7, 127.6, 127.4, 126.7, 113.9, 71.4, 55.3, 25.5, 21.5; Anal. Calc. for $C_{24}H_{24}O_4S$: C, 70.56; H, 5.92; found: C, 70.28; H, 5.77; IR (KBr) ν (cm^{-1}) 3469, 2954, 1597, 1458, 1361, 1249, 1136.

3.2.12. (Z)-1-(2,4-Dimethoxyphenyl)-3-phenyl-2-tosylbut-2-en-1-ol ***(4l)***

White solid; m.p. 133–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 8.5 Hz, 1H), 7.22–7.13 (m, 3H), 6.98–6.92 (m, 4H), 6.86 (d, J = 7.2 Hz, 2H), 6.64–6.61 (m, 1H), 6.43 (s, 1H), 6.23 (d, J = 10.0 Hz, 1H), 4.59 (d, J = 10.1 Hz, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 157.4, 152.8, 142.9, 140.9, 140.1, 139.2, 128.6, 128.2, 127.6, 127.4, 127.3, 121.4, 104.1, 98.2, 68.2, 55.4, 55.2, 25.9, 21.5; Anal. Calc. for $C_{25}H_{26}O_5S$: C, 68.47; H, 5.98; found: C, 68.37; H, 5.88; IR (KBr) ν (cm^{-1}) 3489, 2956, 1587, 1496, 1417, 1139, 1083.

3.2.13. (Z)-1-(4-Bromophenyl)-3-phenyl-2-tosylbut-2-en-1-ol ***(4m)***

White solid; m.p. 121–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H), 7.47–7.44 (m, 2H), 7.25–7.11 (m, 3H), 7.01–6.94 (m, 4H), 6.90–6.82 (br, 2H), 6.09 (d, J = 10.5 Hz, 1H), 4.42 (d, J = 10.5 Hz, 1H), 2.32 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.6, 143.5, 141.7, 140.9, 139.7, 138.4, 131.6, 128.9, 127.8, 127.6, 127.5, 127.4, 121.3, 70.8, 25.6, 21.6; Anal. Calc. for $C_{23}H_{21}BrO_3S$: C, 60.40; H, 4.63; found: C, 60.62; H, 4.77; IR (KBr) ν (cm^{-1}) 3481, 2918, 1595, 1485, 1340, 1284, 1132.

3.2.14. (Z)-1-(4-Chlorophenyl)-3-phenyl-2-tosylbut-2-en-1-ol ***(4n)***

White solid; m.p. 130–132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.28–7.13 (m, 4H), 7.04–6.96 (m, 3H), 6.90–6.78 (br, 2H), 6.14 (d, J = 10.1 Hz, 1H), 4.46 (d, J = 10.7 Hz, 1H), 2.35 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 143.4, 141.7, 140.2, 139.7, 138.5, 133.3, 128.9, 128.7, 127.8, 127.7, 127.4, 126.9, 71.1, 25.6, 21.5; Anal. Calc. for $C_{23}H_{21}ClO_3S$: C, 66.90; H, 5.13; found: C, 66.50; H, 5.22; IR (KBr) ν (cm^{-1}) 3529, 2954, 1595, 1489, 1340, 1294, 1083.

3.2.15. (Z)-3-Methyl-1-phenyl-2-tosylhept-2-en-1-ol ***(4o)***

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.1 Hz, 2H), 7.45–7.24 (m, 7H), 5.98 (d, J = 10.7 Hz, 1H), 4.32 (d, J = 10.8 Hz, 1H), 2.48 (q, J = 4.6 Hz, 2H), 2.42 (s, 3H), 1.96 (s, 3H), 1.32–1.21 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 143.8, 141.8, 140.2, 138.7, 129.5, 128.4, 127.3, 127.2, 125.6, 71.6, 36.3, 29.7, 23.1, 21.6, 21.5, 13.9; Anal. Calc. for $C_{21}H_{26}O_3S$: C, 70.36; H, 7.31; found: C, 70.65; H, 7.65; IR (KBr) ν (cm^{-1}) 3568, 2953, 1560, 1490, 1344, 1276, 1122.

3.2.16. (Z)-1-(4-Methoxyphenyl)-3-methyl-2-tosylhept-2-en-1-ol ***(4p)***

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 5.92 (d, J = 10.7 Hz, 1H), 4.29 (d, J = 10.7 Hz, 1H), 3.83 (s, 3H), 2.49–2.42 (m, 5H), 1.94 (s, 3H), 1.27–1.20 (m, 3H), 1.10–1.08 (m, 1H), 0.83 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 155.7, 143.7, 140.4, 138.6, 133.8, 129.5, 127.1, 126.9, 113.8, 71.4, 55.3, 36.2, 29.7, 23.0, 21.5, 21.4, 13.9; Anal. Calc. for $C_{22}H_{28}O_4S$: C, 68.01; H, 7.26; found: C, 68.35; H, 7.41; IR (KBr) ν (cm^{-1}) 3498, 2937, 1583, 1510, 1354, 1199, 1085.

3.2.17. (Z)-1-(2,4-Dimethoxyphenyl)-3-methyl-2-tosylhept-2-en-1-ol ***(4q)***

White solid; m.p. 82–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.43 (m, 3H), 7.14 (d, J = 7.2 Hz, 2H), 6.54 (d, J = 8.3 Hz, 1H), 6.25 (s, 1H), 6.01 (d, J = 9.7 Hz, 1H), 4.31 (d, J = 9.7 Hz, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 2.76–2.57 (m, 1H), 2.47–2.40 (m, 1H), 2.38 (s, 3H), 2.02 (s, 3H), 1.38–1.19 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 157.4, 156.8, 143.1, 140.1, 136.6, 129.1, 128.5, 126.6, 121.6, 103.9, 97.9, 68.1, 55.4, 54.9, 36.4, 30.3, 23.0, 22.1, 21.4, 13.9; Anal. Calc. for $C_{23}H_{30}O_5S$: C, 66.00; H, 7.22; found: C, 66.29; H, 7.09; IR (KBr) ν (cm^{-1}) 3535, 2951, 1558, 1490, 1298, 1207, 1136.

3.2.18. (Z)-1-(4-Bromophenyl)-3-methyl-2-tosylhept-2-en-1-ol ***(4r)***

White solid; m.p. 119–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 6.8 Hz, 2H), 7.48–7.46 (m, 2H), 7.30–7.26 (m, 4H), 5.89 (d, J = 10.5 Hz, 1H), 4.25 (d, J = 9.3 Hz, 1H), 2.53–2.49 (m, 2H), 2.44 (s, 3H), 1.95 (s, 3H), 1.28–1.22 (m, 3H), 1.13–1.10 (m, 1H), 0.84 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 143.9, 140.9, 140.0, 138.2, 131.5, 129.6, 127.4, 127.0, 121.3, 71.1, 36.3, 29.8, 23.0, 21.6, 21.5, 13.9; Anal. Calc. for $C_{21}H_{25}BrO_3S$: C, 57.67; H, 5.76; found: C, 57.87; H, 5.83; IR (KBr) ν (cm^{-1}) 3486, 2960, 1610, 1485, 1392, 1269, 1138.

3.2.19. (Z)-1-(4-Chlorophenyl)-3-methyl-2-tosylhept-2-en-1-ol ***(4s)***

White solid; m.p. 109–111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 7.7 Hz, 2H), 7.38–7.28 (m, 6H), 5.91 (d, J = 10.7 Hz, 1H), 4.26 (d, J = 10.8 Hz, 1H), 2.51–2.46 (m, 2H), 2.43 (s, 3H), 1.95 (s, 3H), 1.33–1.21 (m, 3H), 1.12–1.09 (m, 1H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 143.9, 140.4, 140.1, 138.3, 133.1, 129.6, 128.5, 127.1, 127.0, 71.1, 36.3, 29.8, 23.0, 21.6, 13.9; Anal.

Calc. for $C_{21}H_{25}ClO_3S$: C, 64.19; H, 6.41; found: C, 64.37; H, 6.17; IR (KBr) ν (cm^{-1}) 3508, 2958, 1616, 1487, 1377, 1282, 1132.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.01.003.

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[28] The CCDC deposition number for compound **4a** is 740766; crystal data: $C_{24}H_{24}O_3S_1$, $M_W = 392.49$, monoclinic, space group $P2(1)/n$, $a = 7.9248(8)$, $b = 22.178(2)$, $c = 12.3117(12)$ Å; $\alpha = 90°$, $\beta = 106.8700(10)°$, $\gamma = 90°$. $V = 2070.7(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, $D_{calc.} = 1.259$ g cm^{-1}, $\mu = 0.178$ mm^{-1}, $\lambda = 0.71073$ Å; $F(0\,0\,0)$ 832, 4794 independent reflections ($R_{int} = 0.0239$), 17774 reflections collected; refinement method, Full-matrix least-squares on F^2; goodness-of-fit on $F^2 = 1.038$; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0465$, $wR_2 = 0.1063$.
[29] The CCDC deposition number for compound **4k** is 740765; $C_{24}H_{24}O_4S_1$, $M_W = 408.49$, monoclinic, space group $P2(1)/c$, $a = 13.5000(11)$, $b = 14.7630(12)$, $c = 11.2969(9)$ Å; $\alpha = 90°$, $\beta = 112.3020(10)°$, $\gamma = 90°$. $V = 2083.1(3)$ Å^3, $T = 293(2)$ K, $Z = 4$, $D_{calc.} = 1.303$ g cm^{-1}, $\mu = 0.183$ mm^{-1}, $\lambda = 0.71073$ Å; $F(0\,0\,0)$ 864, 4801 independent reflections ($R_{int} = 0.0421$), 17875 reflections collected; refinement method, Full-matrix least-squares on F^2; goodness-of-fit on $F^2 = 1.026$; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0679$, $wR_2 = 0.1078$.
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