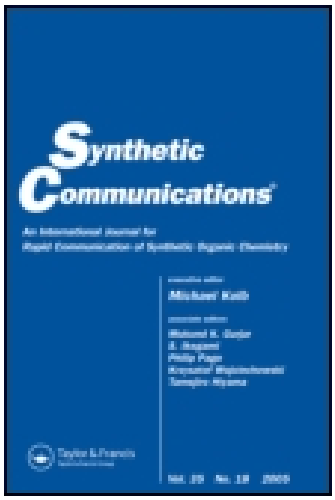

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 16 Aug 2006.

To cite this article: Suk-Ku Kang , Byung-Su Ko & Dong-Min Lee (2002) HIGHLY REGIOSELECTIVE AND STEREOSELECTIVE RADICAL ADDITION OF p-TsBr TO α-ALLENIC ALCOHOLS AND THEIR ELIMINATION REACTION: SYNTHESIS OF β-p-TOSYL-SUBSTITUTED α,β-UNSATURATED KETONES, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:21, 3263-3271, DOI: 10.1081/SCC-120014030

To link to this article: http://dx.doi.org/10.1081/SCC-120014030

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SYNTHETIC COMMUNICATIONS
Vol. 32, No. 21, pp. 3263–3271, 2002

HIGHLY REGIOSELECTIVE AND STEREOSELECTIVE RADICAL ADDITION OF *p*-TsBr TO α-ALLENIC ALCOHOLS AND THEIR ELIMINATION REACTION: SYNTHESIS OF β-*p*-TOSYL-SUBSTITUTED α,β-UNSATURATED KETONES

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ABSTRACT

Regio- and stereoselective radical addition of α-allenic alcohols with *p*-TsBr in the presence of a catalytic amount of AIBN afforded (*E*)-γ-bromo-β-sulfonyl allylic alcohols in moderate yields. The base-promoted 1,4-elimination followed by isomerization to give β-sulfonyl-α,β-unsaturated ketones is described.

Key Words: Radical addition reactions; *p*-TsBr; α-Allenic alcohols; 1,4-Elimination; Tosyl-substituted α,β-unsaturated ketones

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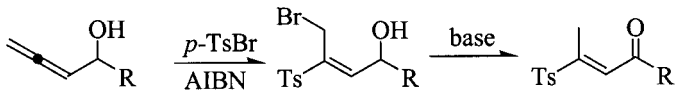
DOI: 10.1081/SCC-120014030 0039-7911 (Print); 1532-2432 (Online)

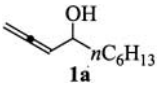
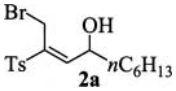
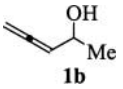
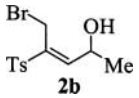
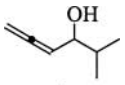
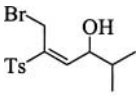
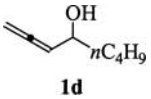
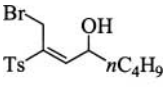
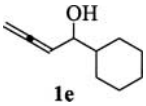
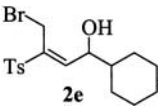
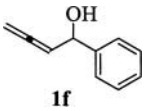
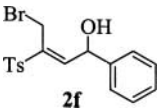
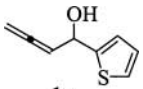
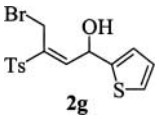
Although the radical chemistry of sulfonyl halides has been extensively investigated, and has concentrated on the readily available sulfonyl chlorides,[1] much less work has been done with relatively stable, but less readily available sulfonyl bromides.[2] Most of the work has involved the free-radical addition of sulfonyl halides to alkenes and alkynes. However, the radical addition reaction of sulfonyl halides to allenes is rare,[3] and the reason is explained by the complexity associated with the addition reaction to allenes in terms of chemo-, regio-, and stereoselectivity. The radical cyclization of enallenes with *p*-TsBr to form five-membered ring system is known.[3a] Alternatively, the light-initiated addition of sulfonyl iodides, which is highly reactive and unstable, to various allenes have been reported.[4] The photo-induced addition of sulfonyl iodides to allenes yielded a mixture of products including the two 1 : 1 adducts resulting from attack by the sulfonyl radical on both the central and terminal positions of the allenic unit. The product distribution was highly dependent on the substituents attached to the allene and reaction conditions, even if in some cases the products derived from central attack on allene bearing one or more substituents were formed.[4] Recently we have reported radical addition of *p*-toluenesulfonyl bromide to simple terminal allenes and allenic alcohols and sulfonamides in the presence of AIBN to give regioselective and stereoselective adducts (*E*)-allylic bromides and/or the cyclized ethers.[5,6] Our ongoing programs to utilize radical addition of *p*-TsBr to allenic alcohols we reasoned that γ-bromo-β-tosyl substituted (*E*)-allylic alcohols from α-allenic alcohol and *p*-TsBr reaction could be intermediates for organic synthesis and 1,4-elimination would give (*E*)-β-tosyl-substituted α,β-unsaturated ketones, which is shown in Scheme 1. The resulting enones and unsaturated sulfones could be useful as a Michael acceptor and a dienophile in Diels–Alder reaction.[2] Herein we wish to report the regioselective radical addition of *p*-TsBr to the allenic alcohols and their 1,4-elimination to form tosyl-substituted α,β-unsaturated enones.

The results of regioselective and stereoselective radical addition α-allenic alcohols with *p*-TsBr in the presence of AIBN to give γ-bromo-β-sulfonyl allylic alcohols to form γ-bromo-β-tosyl substituted (*E*)-allylic alcohols are summarized in Table 1. The α-hydroxyallene **1a** reacted with *p*-TsBr in the presence of a catalytic amount of AIBN in toluene at 90°C for 2 h to afford the (*E*)-adduct as a sole product **2a** in 75% yield



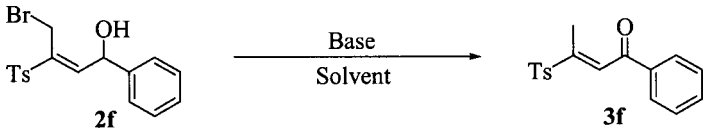
Scheme 1.

Table 1. Radical Addition of *p*-TsBr to α-Allenic Alcohols

Entry	α-Allenic Alcohols	Radical Adducts	Isolated Yield (%)
1	 **1a**	 **2a**	75
2	 **1b**	 **2b**	71
3	 **1c**	 **2c**	71
4	 **1d**	 **2d**	73
5	 **1e**	 **2e**	75
6	 **1f**	 **2f**	70
7	 **1g**	 **2g**	67

(Entry 1 in Table 1). The stereochemistry of **2a** was unambiguously determined by the observation of a nOe effect between vinyl proton and aromatic protons in ^{1}H NMR.[7] Under the same conditions for α-hydroxyallene **1b** treated with *p*-TsBr gave (*E*)-tosyl-substituted alcohol **2b** in 71% yield (Entry 2). The alkyl-substituted α-hydroxyallenes **1c** and **1d** were reacted with *p*-TsBr to give the corresponding allylic bromides **2c** and **2d** in 71 and 73% yields, respectively (Entries 3 and 4). When the cyclohexyl-substituted

Table 2. Optimum Conditions for 1,4-Elimination



2f **3f**

Entry	Base	Solvent	Time (h)	Temp. (°C)	Yield (%)
1	K_2CO_3 (1.1 equiv.)	THF	2	40	48
2	K_2CO_3 (5 equiv.)	THF	2	40	50
3	NaH (1.1 equiv.)	THF	2	rt	0
4	TEA (1.1 equiv.)	THF	3	rt	68
5	TEA (2 equiv.)	THF	3	rt	66
6	TEA (1.1 equiv.)	Toluene	3	rt	67
7	TEA (1.1 equiv.)	DMF	3	rt	60

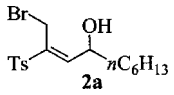
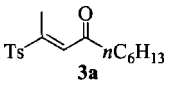
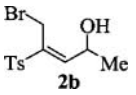
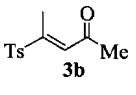
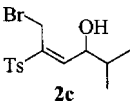
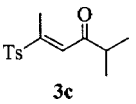
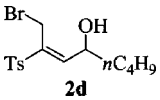
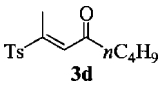
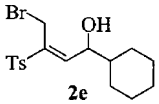
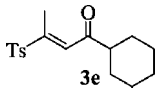
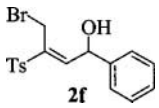
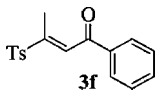
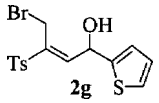
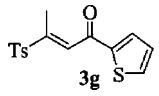
α-hydroxyallene **1e** was treated with *p*-TsBr in the presence of AIBN the (*E*)-adduct **2e** was afforded (Entry 5). The aryl-substituted α-hydroxyallenes **1f** and **1g** were coupled with *p*-TsBr under the same conditions to provide **2f**[7] and **2g** in 70 and 67% yields, respectively (Entries 6 and 7).

To find optimum conditions for 1,4-elimination of the (*E*)-adduct **2f**, a series of experiments has been carried out (Table 2). Of the base Et_3N was the best of choice and as a suitable solvent THF and toluene were effective. Nevertheless THF was utilized for further studies.

The (*E*)-adducts **2** were good substrates for the 1,4-elimination to form tosyl-substrated α,β-unsaturated enones (Table 3). The (*E*)-adduct **2a** reacted with Et_3N (1.1 equiv.) in THF for 3 h at rt to afford the enone **3a** in 68% yield (Entry 1 in Table 3). For the substrate **2b** under the same conditions enone **3b** was provided in 80% yield (Entry 2). The alkyl-substituted (*E*)-allylic bromides **2c** and **2d** were treated under the same conditions to provide the corresponding **3c** and **3d** in 78 and 83% yields, respectively (Entries 3 and 4). The cyclohexyl-substituted adduct **2e** was subjected to base-promoted elimination to give tosyl-substituted enone **3e** in 66% yield (Entry 5). The aryl-substituted (*E*)-allylic bromides **2f** and **2g** were readily converted into enones **3f** and **3g** in 68 and 84% yields, respectively (Entries 6 and 7).

In summary, the regioselective radical addition of α-allenic alcohol with *p*-TsBr in the presence of AIBN to give (*E*)-unsaturated γ-bromo-β-sulfonyl allylic alcohols and base-promoted 1,4-elimination of the resulting allylic bromides to afford β-sulfonyl-α,β-unsaturated ketones were accomplished.

Table 3. 1,4-Elimination of the Radical Adducts

Entry	Radical Adducts	Unsaturated Ketones	Isolated Yield (%)
1	 **2a**	 **3a**	68
2	 **2b**	 **3b**	80
3	 **2c**	 **3c**	78
4	 **2d**	 **3d**	83
5	 **2e**	 **3e**	66
6	 **2f**	 **3f**	68
7	 **2g**	 **3g**	84

EXPERIMENTAL SECTION

Typical Procedure

Preparation of 1-bromo-2-(toluene-4-sulfonyl)dec-2-en-4-ol (2a): To a stirred solution of allenic alcohol **1a** (50 mg, 0.32 mmol) and AIBN (11 mg, 0.06 mmol) in toluene (3 mL) was added *p*-TsBr (84 mg, 0.36 mmol) and heated at 90°C for 2 h. Toluene was evaporated in vacuo and the crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 3, $R_f = 0.28$) to give 1-bromo-2-(toluene-4-sulfonyl)dec-2-en-4-ol

(2a) (95 mg, 75%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.29 (m, 7H), 1.43 (m, 1H), 1.66 (m, 2H), 2.30 (d, 1H, $J = 4.4$ Hz), 2.45 (s, 3H), 4.22 (d, 1H, $J = 11.4$ Hz), 4.26 (d, 1H, $J = 11.4$ Hz), 4.55 (m, 1H), 7.02 (d, 1H, $J = 7.9$ Hz), 7.35 (d, 2H, $J = 8.2$ Hz), 7.78 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 21.3, 22.3, 23.2, 25.6, 29.7, 32.3, 36.7, 69.5, 129.2, 130.6, 137.1, 140.1, 145.6, 147.9; IR (KBr, cm^{-1}) 3500, 2929, 2858, 1661, 1630, 1313, 1144, 1085; HRMS (EI) m/z 388.0729 (calcd. for $C_{17}H_{25}BrO_3S$ 388.0708).

5-Bromo-4-(toluene-4-sulfonyl)pent-3-en-2-ol (2b): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.31$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.40 (d, 3H, $J = 7.1$ Hz), 2.44 (s, 3H), 2.73 (d, 1H, $J = 4.5$ Hz), 4.18 (d, 1H, $J = 11.6$ Hz), 4.25 (d, 1H, $J = 11.6$ Hz), 4.74 (m, 1H), 7.03 (d, 1H, $J = 7.9$ Hz), 7.35 (d, 2H, $J = 8.2$ Hz), 7.78 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 22.4, 22.6, 65.6, 129.2, 129.8, 130.7, 139.2, 145.8, 148.8; IR (neat, cm^{-1}) 3498, 2977, 2926, 1639, 1595, 1450, 1315, 1187, 1143, 1085; HRMS (EI) m/z 317.9913 (calcd. for $C_{12}H_{15}BrO_3S$ 317.9925).

6-Bromo-2-methyl-5-(toluene-4-sulfonyl)hex-4-en-3-ol (2c): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.28$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.94 (d, 2H, $J = 6.8$ Hz), 1.01 (d, 2H, $J = 6.8$ Hz), 1.91 (m, 1H), 2.23 (d, 1H, $J = 4.5$ Hz), 2.45 (s, 3H), 4.26 (d, 1H, $J = 11.4$ Hz), 4.28 (d, 1H, $J = 11.4$ Hz), 4.30 (m, 1H), 7.05 (d, 1H, $J = 8.3$ Hz), 7.35 (d, 2H, $J = 8.2$ Hz), 7.79 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.5, 16.0, 18.5, 19.4, 31.6, 71.0, 126.1, 127.7, 134.1, 137.7, 142.7, 144.0; IR (neat, cm^{-1}) 3493, 3013, 2918, 2863, 1632, 1596, 1316, 1143, 1084; HRMS (EI) m/z 346.0222 (calcd. for $C_{14}H_{19}BrO_3S$ 346.0238).

5-Bromo-4-(toluene-4-sulfonyl)pent-3-en-2-ol (2d): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.31$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, 3H, $J = 6.7$ Hz), 1.31 (m, 4H), 1.65 (m, 2H), 2.44 (s, 3H), 3.32 (s, 1H), 4.20 (d, 1H, $J = 11.5$ Hz), 4.27 (d, 1H, $J = 11.5$ Hz), 4.52 (m, 1H), 7.02 (d, 1H, $J = 7.9$ Hz), 7.34 (d, 2H, $J = 8.2$ Hz), 7.78 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.6, 18.4, 19.3, 20.2, 24.8, 33.2, 66.1, 126.1, 127.7, 133.9, 136.3, 142.7, 145.7; IR (KBr, cm^{-1}) 3518, 3056, 2959, 2862, 1634, 1597, 1465, 1267, 1143, 1018; HRMS (EI) m/z 360.0379 (calcd. for $C_{15}H_{21}BrO_3S$ 360.0395).

4-Bromo-1-cyclohexyl-3-(toluene-4-sulfonyl)but-2-en-1-ol (2e): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.30$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.14 (m, 6H), 1.60 (m, 4H), 1.90 (m, 1H), 2.44 (s, 3H), 2.78 (d, 1H, $J = 4.7$ Hz), 4.19 (d, 1H, $J = 11.5$ Hz), 4.26 (d, 1H, $J = 11.5$ Hz), 4.28 (m, 1H), 7.04 (d, 1H, $J = 8.3$ Hz), 7.34 (d, 2H, $J = 8.2$ Hz), 7.77 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 26.5, 27.0, 29.0, 29.4, 44.2, 73.4, 129.2, 130.7, 137.0, 140.5, 145.7, 147.2; IR (KBr, cm^{-1}) 3483, 3054, 2930, 2855, 1597, 1449, 1315, 1265, 1145, 1084; HRMS (EI) m/z 386.0534 (calcd. for $C_{17}H_{23}BrO_3S$ 386.0551).

4-Bromo-1-phenyl-3-(toluene-4-sulfonyl)but-2-en-1-ol (2f): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.25$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3H), 2.52 (d, 1H, $J = 4.2$ Hz), 4.22 (d, 1H, $J = 11.8$ Hz), 4.26 (d, 1H, $J = 11.8$ Hz), 5.60 (dd, 1H, $J = 7.5$, 4.2 Hz), 7.23 (d, 1H, $J = 7.5$ Hz), 7.32–7.42 (m, 7H), 7.75 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 22.4, 71.8, 127.3, 129.3, 129.6, 129.8, 130.7, 136.8, 139.9, 140.5, 146.1, 146.2; IR (KBr, cm^{-1}) 3478, 3031, 2921, 1637, 1595, 1492, 1452, 1400, 1309, 1143, 1082; HRMS (EI) m/z 380.0005 (calcd. for $C_{17}H_{17}BrO_3S$ 380.0082).

4-Bromo-1-thiophen-2-yl-3-(toluene-4-sulfonyl)but-2-en-1-ol (2g): TLC, SiO_2, EtOAc/hexanes 1 : 2, $R_f = 0.35$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3H), 2.62 (d, 1H, $J = 3.6$ Hz), 4.20 (d, 1H, $J = 11.3$ Hz), 4.30 (d, 1H, $J = 11.3$ Hz), 5.87 (d, 1H, $J = 7.9$, 3.6 Hz), 7.00 (dd, 1H, $J = 3.8$, 1.1 Hz), 7.07 (dd, 1H, $J = 3.8$, 4.6 Hz), 7.25 (dd, 1H, $J = 4.6$, 1.1 Hz), 7.35 (m, 3H), 7.78 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 22.1, 71.3, 128.2, 128.4, 129.0, 129.1, 130.4, 130.6, 136.4, 140.5, 142.8, 145.5; IR (neat, cm^{-1}) 3454, 3102, 2918, 2856, 1652, 1596, 1419, 1323, 1146, 1090; HRMS (EI) m/z 385.9643 (calcd. for $C_{15}H_{15}BrO_3S_2$ 385.9646).

Typical Procedure

Preparation of 2-(toluene-4-sulfonyl)dec-2-en-4-one (3a): To a stirred solution of radical adduct **2a** (50 mg, 0.13 mmol) in THF (3 mL) was added Et_3N (14 mg, 0.14 mmol) at rt for 3 h. The reaction mixture was stirred for room temperature and quenched with saturated NH_4Cl solution (5 mL) and then extracted with ether (3 × 30 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes = 1 : 3, $R_f = 0.45$) to give 2-(toluene-4-sulfonyl)dec-2-en-4-one **(3a)** (27 mg, 68%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.89 (t, 3H, $J = 6.8$ Hz), 1.30 (m, 6H), 1.60 (m, 2H), 2.17 (d, 3H, $J = 1.2$ Hz), 2.45 (s, 3H), 2.60 (t, 2H, $J = 7.0$ Hz), 7.24 (q, 1H, $J = 1.2$ Hz), 7.36 (d, 2H, $J = 8.2$ Hz), 7.75 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.7, 22.4, 23.2, 29.6, 32.3, 45.8, 129.4, 130.5, 130.7, 135.2, 145.9, 151.5, 201.3; IR (neat, cm^{-1}) 3057, 2930, 2858, 1701, 1621, 1597, 1428, 1312, 1266, 1154; HRMS (EI) m/z 308.1457 (calcd. for $C_{17}H_{24}O_3S$ 308.1446).

4-(Toluene-4-sulfonyl)pent-3-en-2-one (3b): TLC, SiO_2, EtOAc/hexanes 1 : 3 $R_f = 0.50$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (d, 3H, $J = 1.2$ Hz), 2.36 (s, 3H), 2.46 (s, 3H), 7.24 (q, 1H, $J = 1.2$ Hz), 7.36 (d, 2H, $J = 8.2$ Hz), 7.75 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.4, 33.0, 129.4, 130.5, 130.8, 135.1, 146.0, 151.9, 198.5; IR (neat, cm^{-1}) 3062, 2925, 1705,

1660, 1621, 1360, 1308, 1186, 1019; HRMS (EI) m/z 238.0662 (calcd. for $C_{12}H_{14}O_3S$ 238.0664).

4-(Toluene-4-sulfonyl)pent-3-en-2-one (3c): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.45$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.29 (m, 7H), 1.43 (m, 1H), 1.66 (m, 2H), 2.30 (d, 1H, $J = 4.4$ Hz), 2.45 (s, 3H), 4.22 (d, 1H, $J = 11.4$ Hz), 4.26 (d, 1H, $J = 11.4$ Hz), 4.55 (m, 1H), 7.02 (d, 1H, $J = 7.9$ Hz), 7.35 (d, 2H, $J = 8.2$ Hz), 7.78 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.0, 15.3, 19.4, 40.1, 126.3, 126.8, 127.8, 132.2, 142.9, 149.7, 197.6; IR (neat, cm^{-1}) 3033, 2968, 2845, 1701, 1621, 1596, 1314, 1156, 1051; HRMS (EI) m/z 266.0973 (calcd. for $C_{14}H_{18}O_3S$ 266.0977).

4-(Toluene-4-sulfonyl)pent-3-en-2-one (3d): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.51$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91 (t, 3H, $J = 6.8$ Hz), 1.33 (qt, 2H, $J = 6.8$, 6.7 Hz), 1.62 (tt, 2H, $J = 6.7$, 6.9 Hz), 2.18 (d, 3H, $J = 0.9$ Hz), 2.45 (s, 3H), 2.63 (t, 2H, $J = 6.9$ Hz), 7.25 (q, 1H, $J = 0.9$ Hz), 7.37 (d, 2H, $J = 8.2$ Hz), 7.76 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.9, 11.5, 19.3, 19.8, 23.3, 42.4, 126.3, 127.5, 127.8, 132.2, 142.9, 148.5, 198.2; IR (KBr, cm^{-1}) 3055, 2962, 2874, 1701, 1621, 1597, 1315, 1265, 1157, 1055; HRMS (EI) m/z 280.1131 (calcd. for $C_{15}H_{20}O_3S$ 280.1133).

1-Cyclohexyl-3-(toluene-4-sulfonyl)but-2-en-1-one (3e): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.45$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.21 (m, 2H), 1.32 (m, 3H), 1.70 (m, 2H), 1.80 (m, 2H), 1.90 (m, 2H), 2.15 (d, 3H, $J = 1.2$ Hz), 2.45 (s, 3H), 2.50 (m, 1H), 7.28 (q, 1H, $J = 1.2$ Hz), 7.34 (d, 2H, $J = 8.2$ Hz), 7.75 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.4, 26.0, 26.4, 28.6, 52.8, 129.3, 130.1, 130.8, 135.2, 145.9, 151.7, 204.1; IR (KBr, cm^{-1}) 3021, 2921, 2840, 1709, 1601, 1588, 1426, 1311, 1122, 1038; HRMS (EI) m/z 306.1248 (calcd. for $C_{17}H_{22}O_3S$ 306.1290).

1-Phenyl-3-(toluene-4-sulfonyl)but-2-en-1-one (3f): TLC, SiO_2, EtOAc/hexanes 1 : 3, $R_f = 0.42$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (d, 3H, $J = 1.2$ Hz), 2.46 (s, 3H), 7.38 (d, 2H, $J = 8.2$ Hz), 7.51 (dd, 2H, $J = 7.5$, 7.2 Hz), 7.63 (dd, 1H, $J = 7.2$, 2.3 Hz), 7.81 (d, 2H, $J = 8.2$ Hz), 7.92 (q, 1H, $J = 1.2$ Hz), 7.98 (dd, 2H, $J = 7.5$, 2.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.4, 129.3, 129.4, 129.7, 129.9, 130.1, 130.8, 134.8, 137.6, 145.9, 152.0, 191.3; IR (KBr, cm^{-1}) 3042, 2936, 2847, 1698, 1620, 1599, 1439, 1315, 1259, 1124, 1099; HRMS (EI) m/z 300.0826 (calcd. for $C_{17}H_{17}O_3S$ 300.0820).

1-Thiophen-2-yl-3-(toluene-4-sulfonyl)but-2-en-1-one (3g): TLC, SiO_2, EtOAc/hexanes 1 : 2, $R_f = 0.51$. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.15 (d, 6H, $J = 6.7$ Hz), 2.16 (d, 3H, $J = 1.2$ Hz), 2.45 (s, 3H), 2.77 (m, 1H), 7.32 (q, 1H, $J = 1.2$ Hz), 7.37 (d, 2H, $J = 8.2$ Hz), 7.76 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 21.3, 22.3, 23.2, 25.6, 29.7, 32.3, 36.7, 69.5, 129.2, 130.6, 137.1, 140.1, 145.6, 147.9; IR (neat, cm^{-1}) 2961, 2925, 2847, 1659, 1649, 1418, 1305, 1241, 1149, 1067; HRMS (EI) m/z 388.0729 (calcd. for $C_{15}H_{14}O_3S$ 388.0708).

ACKNOWLEDGMENTS

This paper was supported by Samsung Research Fund, Sungkyunkwan University, 2000. B.-S. Ko and D.-M. Lee thanks financial support from BK21 School of Molecular Science.

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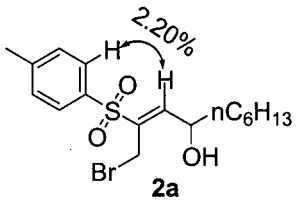
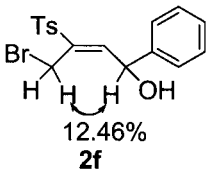


2a



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Received in the Netherlands October 20, 2001

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