HIGHLY STEREOSELECTIVE SYNTHESIS OF SOME β-BRANCHED α-(PHENYLSULFONYLMETHYL) ACRYLIC COMPOUNDS

Sonia Khamri, Taoufik Turki, Hassen Amri *

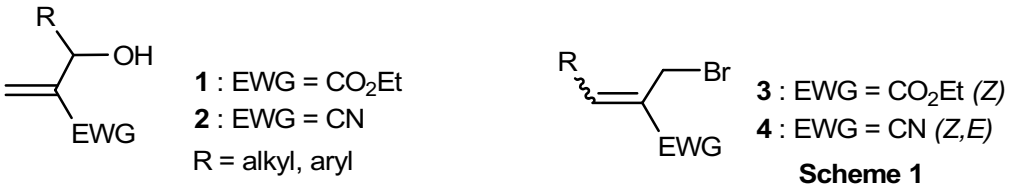
Laboratoire de Chimie Organique et Organométallique
Faculté des Sciences de Tunis, Campus Universitaire, 2092 Tunis, Tunisie

(Reçu le 8 Novembre 2008, accepté le 12 Janvier 2009)

ABSTRACT : Substitution reaction of β-branched Baylis-Hillman bromides with sodium benzenesulfinate in absolute ethanol at room temperature, produces in S_N2 process and high stereoselectivity, the corresponding allyl phenyl sulfinates in good yields.

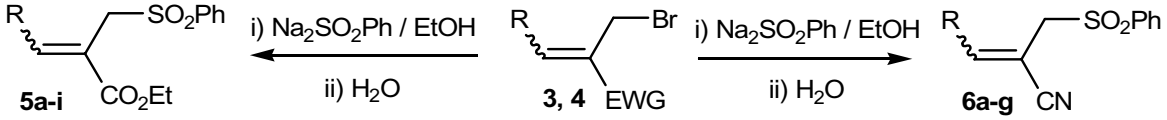
Key words: Baylis-Hillman derivatives, nucleophilic substitution, allyl phenyl sulfones.

The Baylis-Hillman method is now considered as a simple organic reaction leading to carbon-carbon formation [1-3]. In most cases, the reaction provides functionalized alcohols **1** and **2** [4-7] which can be transformed into polyfunctionalized derivatives. In order to extend the potential synthetic utility of this class of acrylic compounds, we investigated the electrophilic reactivity of some allyl bromides **3** and **4** [8-12].



Scheme 1

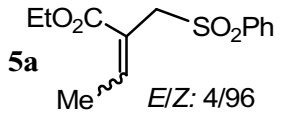
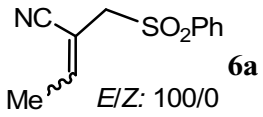
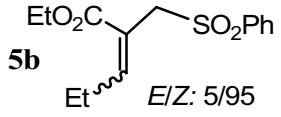
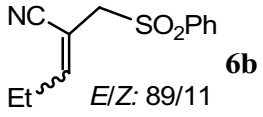
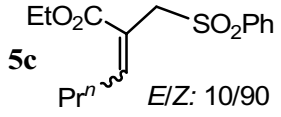
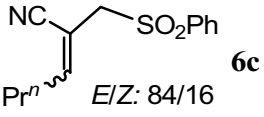
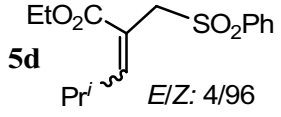
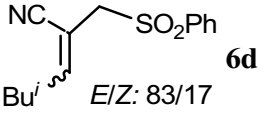
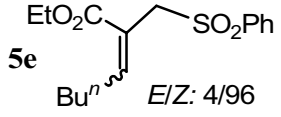
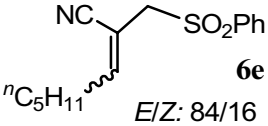
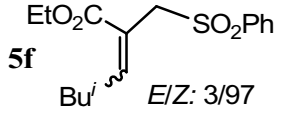
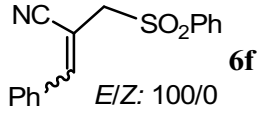
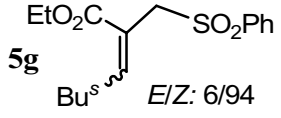
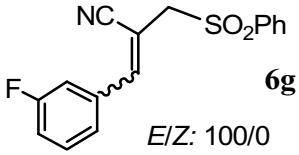
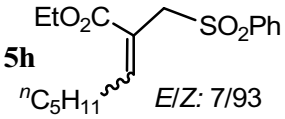
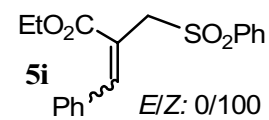
Due to their easy conversion into homoallyl alcohols and α,β-unsaturated ketones or ketones [13] *via* a reductive desulfonylation using low-valent Titanium reagents [14]; we have shown that the reaction-coupling of functional allyl bromides **3** or **4** and commercially available benzenesulfinate, in absolute ethanol, and at room temperature, could be appropriate for the easy synthesis of various β-branched α-(phenylsulfonylmethyl) acrylic compounds **5** and **6** in good yields (Scheme 1, Table 1).



Scheme 2

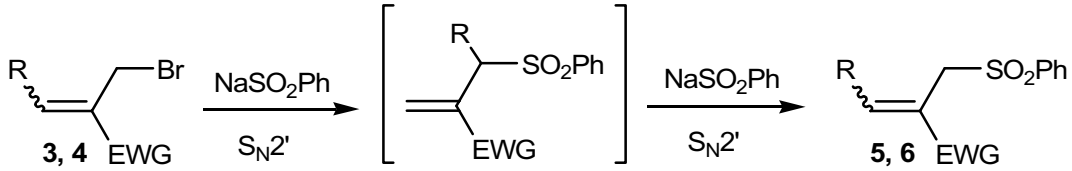
* corresponding author, e-mail: hassen.amri@fst.rnu.tn , tél.: +216 71872600 , fax: +216 71883424

Table 1: β-Branched α-(phenylsulfonylmethyl) acrylic compounds **5** and **6** synthetised.

Entry	R	Allyl sulfones **5a-i***	Yield (%)	R	Allyl sulfones **6a-g***	Yield(%)
1	Me	**5a**  *E/Z:* 4/96	92	Me	 **6a** *E/Z:* 100/0	88
2	Et	**5b**  *E/Z:* 5/95	90	Et	 **6b** *E/Z:* 89/11	85
3	^{n}Pr	**5c**  *E/Z:* 10/90	85	^{n}Pr	 **6c** *E/Z:* 84/16	85
4	^{i}Pr	**5d**  *E/Z:* 4/96	65	^{i}Bu	 **6d** *E/Z:* 83/17	71
5	^{n}Bu	**5e**  *E/Z:* 4/96	71	$^{n}C_5H_{11}$	 **6e** *E/Z:* 84/16	75
6	^{i}Bu	**5f**  *E/Z:* 3/97	66	Ph	 **6f** *E/Z:* 100/0	52
7	^{s}Bu	**5g**  *E/Z:* 6/94	65	$^{m}FC_6H_4$	 **6g** *E/Z:* 100/0	45
8	$^{n}C_5H_{11}$	**5h**  *E/Z:* 7/93	69			
9	Ph	**5i**  *E/Z:* 0/100	42			

(*) Stereochemical assignments and isomeric purities were based on the difference in chemical shifts and integration ratio of vinylic protons in ^{1}H NMR analysis.

Several methods for the synthesis of simple ally sulfones have been reported from the reaction of alcohols or allyl acetates and sodium benzenesulfinate in the presence of a catalytic amounts of $Pd(OAc)_2$ [15] or Pd-Graphite [16] in refluxing THF [17]. However, functionalized allyl sulfones of type **5** and **6** were either rarely described, or required relatively delicate operating conditions [18,19]. Initial investigation on the prepared allyl sulfones **5** and **6** indicated that the reaction proceeds through an usual tandem nucleophilic addition-elimination reactions $2x(S_N2')$ [19-21] leading to the most substituted sulfones in the presence of an excess of sodium sulfinate which undergoes an isomerisation leading to compounds **5** and **6**.



Scheme 3

Moreover, it seems that the stereochemistry of the obtained allyl sulfones **5** or **6** depends on the size of the alkyl or aryl group R. The ethoxycarbonyl one, being more bulky than the corresponding cyano group, allowed the isolation of allyl sulfones **5** in *Z* configuration in the first case and *E* in the second family of allyl sulfones **6**.

In conclusion, this work shows that the nucleophilic substitution of functional allyl bromide of type **3** or **4** in the presence of sodium phenylsulfinate proceeds *via* a double Michael reaction. The examination of the experimental conditions showed that it was possible to use a polar protic solvent as the ethanol instead of a complexant like polyethylene oxide 400 (PEO 400) [19].

EXPERIMENTAL

Reaction progress and purity of products were monitored by TLC on silica gel plates (Fluka Kieselgel $60F_{254}$) and Merck silica gel 60 (70-230 mesh) for flash chromatography. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 (^1H: 300 MHz, ^{13}C: 75 MHz) in $CDCl_3$ solution as solvent with TMS as an internal reference. The allyl products were obtained in satisfactory to excellent yields by using 2.1 equivalents of the benzenesulfinic acid sodium salt (97%) purchased from Fluka Chemie GmbH.

Allyl Bromides 3 or 4; General Procedure:

Phosporus tribromide (PBr_3) (5.7g, 1.9 mL, 20 mmol) was added to a stirred solution of 2-(1-hydroxyalkyl) acrylic compound **1** or **2** in anhydrous ether Et_2O (40 mL) at -10°C. The temperature was allowed to rise to 20° C and stirring was continued for 1 h. Water (25 mL) was then added at -10°C and the mixture was extracted with hexane (3 x 20 mL). The organic layer was washed with brine (2 x 15 mL) and dried over $MgSO_4$. The solvent was evaporated and the remaining oil was distilled in vacuo.

Phenyl allyl sulphones 5 and 6: Typical procedure:

To benzenesulfinic acid sodium salt 2.1 eq (0.832 g; 5.07 mmol) dissolved in 6 mL of absolute ethanol was added dropwise to ethyl α-(bromomethyl) acrylate (0.5 g; 2.42 mmol) diluted in 5 mL of dry dichloromethane. The mixture was stirred during 6 h at room temperature then concentrated to reduce the excess of ethanol. After quenching with water (10 mL) and extraction with dichloromethane, the combined organic layers were washed with brine, dried over $MgSO_4$,

filter and evaporate under reduce pressure. The crude product was purified by column chromatography on silica gel (diethyl ether / petroleum ether, 2:8).

(E,Z)-Ethyl 2-(phenylsulfonylmethyl)but-2-enoate **5a**

^{1}H NMR (300 MHz, $CDCl_3$): δ 1,14 (t, 3H, C*H*$_3$CH$_2$O, *J* = 7.35 Hz); 1.83 (d, 3H, C*H*$_3$CH=C, *J* = 7.35 Hz); 3.94 (q, 2H, -OC*H*$_2$CH$_3$, *J* = 7.35 Hz); 4.26 (s, 2H, -C*H*$_2$-SO$_2$); 6.28 (q, 1H, CH$_3$C*H*=C, *J* = 7.35 Hz (*E*-isomer)); 7.24 (q, 1H, CH$_3$C*H*=C, *J* = 7.35 Hz (*Z*-isomer)); 7.53-7.86 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.03 (*C*H$_3$CH=C); 15.30 (*C*H$_3$CH$_2$O); 53.70 (-*C*H$_2$-SO$_2$); 61.10 (CH$_3$*C*H$_2$O); 122.01 (aromatic CH); 129.00 (aromatic CH); 129.40 (CH$_3$CH=*C*); 133.80 (aromatic CH); 138.80 (CH$_3$*C*H=C); 146.30 (aromatic C); 165.40 (CH$_3$CH$_2$O*C*O).

(E,Z)-Ethyl 2-(phenylsulfonylmethyl)pent-2-enoate **5b**

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (t, 3H, C*H*$_3$-CH$_2$-CH=, *J* = 7.35 Hz); 1.14 (t, 3H, C*H*$_3$-CH$_2$-O, *J* = 7.35 Hz); 2.24 (qd, 2H, CH$_3$-C*H*$_2$CH=, *J* = 7.35 Hz, *J* = 7.35 Hz); 3.94 (q, 2H, O-C*H*$_2$-CH$_3$, *J* = 7.35 Hz); 4.25 (s, 2H, -C*H*$_2$-SO$_2$); 6.08 (t, 1H, CH$_3$-CH$_2$-C*H*=C, *J* = 7.35 Hz (*E*-isomer)); 7.10 (t, 1H, CH$_3$-CH$_2$-C*H*=C, *J* = 7.35 Hz (*Z*-isomer)); 7.53-7.85(m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.21 (*C*H$_3$CH$_2$O); 14.22 (*C*H$_3$CH$_2$CH=C); 23.02 (CH$_3$*C*H$_2$CH=C); 53.93 (-*C*H$_2$-SO$_2$); 61.11 (CH$_3$*C*H$_2$O); 120.24 (aromatic CH); 128.71 (aromatic CH); 128.93 (CH$_3$CH$_2$CH=*C*); 133.72 (aromatic CH); 138.94 (aromatic C); 152.80 (CH$_3$CH$_2$*C*H=C); 165.62 (CH$_3$CH$_2$O*C*O).

(E,Z)-Ethyl 2-(phenylsulfonylmethyl)hex-2-enoate **5c**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, 3H, C*H*$_3$-CH$_2$-CH$_2$, *J* = 7.35 Hz); 1.14 (t, 3H, C*H*$_3$-CH$_2$-O, *J* = 6.99 Hz); 1.46 (qt, 2H, CH$_3$-C*H*$_2$- CH$_2$, *J* = 7.35 Hz, *J* = 7.35 Hz); 2.19 (td, 2H, CH$_2$-C*H*$_2$-CH=, *J* = 7.35, *J* = 7.71 Hz); 3.94 (q, 2H,O-C*H*$_2$-CH$_3$, *J* = 6.99 Hz); 4.26 (s, 2H, -C*H*$_2$-SO$_2$); 6.12 (t, 1H, CH$_3$-CH$_2$-CH$_2$-C*H*=C, *J* = 7.71 Hz *(E*-isomer*)*); 7.12 (t, 1H, CH$_3$-CH$_2$-CH$_2$-C*H*=C, *J* = 7.71 Hz *(Z*-isomer*)*); 7.53-7.85 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.80 (*C*H$_3$CH$_2$O); 13.87 (*C*H$_3$(CH$_2$)$_2$CH=C); 21.60 (CH$_3$*C*H$_2$CH$_2$); 31.20 (CH$_3$CH$_2$*C*H$_2$); 54.65 (-*C*H$_2$-SO$_2$); 60.82 (CH$_3$*C*H$_2$O); 120.84 (aromatic CH); 128.81 (aromatic CH); 128.96 CH$_3$(CH$_2$)$_2$CH=*C*); 133.7 (aromatic CH); 138.91 (aromatic C); 151.44 (CH$_3$(CH$_2$)$_2$*C*H=C); 165.61 (CH$_3$CH$_2$O*C*O).

(E,Z)-Ethyl 4-methyl-2-(phenylsulfonylmethyl)pent-2-enoate **5d**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.47 (d, 6H, (C*H*$_3$)$_2$CH, *J* = 6.60 Hz); 0.63 (t, 3H, C*H*$_3$CH$_2$O, *J* = 6.99 Hz); 2.21 (m, 1H, =CH-C*H*(CH$_3$)$_2$); 3.42 (q, 2H, OC*H*$_2$CH$_3$, *J* = 6.99 Hz); 3.80 (s, 2H, -C*H*$_2$-SO$_2$); 5.12 (d, 1H, (CH$_3$)$_2$CH-C*H*=C, *J* = 10.65 Hz (*E*-isomer)); 6.37 (d,1H, (CH$_3$)$_2$CH-C*H*=C, *J* = 10.65 Hz (*Z*-isomer)); 7.02-7,35 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.82 (*C*H$_3$CH$_2$O); 21.05 ((*C*H$_3$)$_2$CH=); 28.44 ((CH$_3$)$_2$*C*H); 54.62 (-*C*H$_2$-SO$_2$); 60.46 (CH$_3$*C*H$_2$O); 118.47 (CH=*C*); 128.80 (aromatic CH); 128.90 (aromatic CH); 133.60 (aromatic CH); 139.09 (aromatic C);156.32 (*C*H=C) ; 165.46 (CH$_3$CH$_2$O*C*O).

(E,Z)-Ethyl 2-(phenylsulfonylmethyl)hept-2-enoate **5e**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, 3H, C*H*$_3$CH$_2$(CH$_2$)$_2$), *J* = 6.96 Hz); 1.14 (t, 3H, C*H*$_3$CH$_2$O, *J* = 6.99 Hz); 1.37 (m, 4H, CH$_3$(C*H*$_2$)$_2$-CH$_2$); 2.21 (dt, 2H, CH$_2$-C*H*$_2$CH=, *J* = 7.71 Hz, *J* = 7.71 Hz); 3.94 (q, 2H, O-C*H*$_2$CH$_3$, *J* = 6.99 Hz); 4.26 (s, 2H, -C*H*$_2$-SO$_2$); 6.12 (t, 1H, -CH$_2$C*H*=C, *J* = 7.71 Hz *(E*-isomer*)*); 7.12 (t, 1H, -CH$_2$C*H*=C, *J* = 7.71 Hz *(Z*-isomer*)*); 7.53-7.85 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.81 (*C*H$_3$CH$_2$O); 14.05 (*C*H$_3$(CH$_2$)$_3$CH); 22.45 (CH$_3$*C*H$_2$(CH$_2$)$_2$); 29.30 (CH$_3$(CH$_2$)$_2$*C*H$_2$CH); 30.34 (CH$_3$CH$_2$*C*H$_2$CH$_2$CH); 54.04 (-*C*H$_2$-SO$_2$); 61.10 (CH$_3$*C*H$_2$O); 120.68 (aromatic CH); 129.00 (aromatic CH); 129.12 (CH=*C*); 133.73 (aromatic CH); 138.92 (aromatic C); 151.61 (*C*H=C); 165.61 (CH$_3$CH$_2$O*C*O).

(E,Z)-Ethyl 4-methyl-2-(phenylsulfonylmethyl)hex-2-enoate **5f**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.76 (t, 3H, C*H*$_3$CH$_2$CHCH$_3$, *J* = 7.35 Hz); 0.92 (d, 3H, C*H*$_3$CHCH$_2$CH$_3$, *J* = 6.60 Hz); 1.04 (t, 3H, C*H*$_3$CH$_2$O, *J* = 6.99 Hz); 1.29 (m, 2H, CH$_3$C*H*$_2$CHCH$_3$); 2.41 (m, 1H, (CH$_3$CH$_2$C*H*(CH$_3$)-CH=); 3.81 (s, 2H, -C*H*$_2$-SO$_2$); 4.18 (q, 2H, OC*H*$_2$CH$_3$, *J* = 6.99 Hz); 6.17 (d, 1H, CH$_3$CH$_2$C*H*(CH$_3$)-C*H*=C, *J* = 11.01 Hz *(E*-isomer); 6.77 (d, 1H, CH$_3$CH$_2$C*H*(CH$_3$)-C*H*=C, *J* = 11.01 Hz, *(Z*-isomer)); 7.43-7.76 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.66 (*C*H$_3$CH$_2$CH); 14.06 (*C*H$_3$CH$_2$O); 18.95 (CH$_3$CH$_2$CH(*C*H$_3$); 29.94 (CH$_3$*C*H$_2$CH); 35.64 (CH$_3$CH$_2$*C*H); 54.01 (-*C*H$_2$-SO$_2$); 61.03 (CH$_3$*C*H$_2$O); 119.47 (CH=*C*); 128.96 (aromatic CH); 129.18 (aromatic CH); 134.03 (aromatic CH); 139.05 (aromatic C); 156.21 (*C*H=C); 165.70 (CH$_3$CH$_2$O*C*O).

(E,Z)-Ethyl 5-methyl-2-(phenylsulfonylmethyl)hex-2-enoate **5g**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (d, 6H, (C*H*$_3$)$_2$CH, *J* = 6.63 Hz); 1.13 (t, 3H, C*H*$_3$CH$_2$O, *J* = 7.35 Hz); 1.74 (m, 1H, CH$_2$C*H*(CH$_3$)$_2$); 2.11 (dd, 2H, (CH$_3$)$_2$-CH-C*H*$_2$-CH=, *J* = 7.35 Hz, *J* = 7.55 Hz); 3.93 (q, 2H, OC*H*$_2$CH$_3$, *J* = 7.35 Hz); 4.25 (s, 2H, -C*H*$_2$-SO$_2$); 5.70 (t, 1H, (CH$_3$)$_2$CH-CH$_2$C*H*=C, *J* = 7.55 Hz *(E*-isomer)); 6.77 (t, 1H, (CH$_3$)$_2$CH-CH$_2$C*H*=C, *J* = 7.55 Hz *(Z*-isomer)); 7.50-7.85 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.97 (*C*H$_3$CH$_2$O); 22.36 ((*C*H$_3$)$_2$CH); 28.02 ((CH$_3$)$_2$*C*H); 38.24 ((CH$_3$)$_2$CH*C*H$_2$); 54.07 (-*C*H$_2$-SO$_2$); 61.05 (CH$_3$*C*H$_2$O); 121.29 (CH=*C*); 128.67 (aromatic CH); 128.95 (aromatic CH); 133.65 (aromatic CH); 138.89 (aromatic C); 150.55 (*C*H=C); 165.49 (CH$_3$CH$_2$O*C*O).

(E,Z)-Ethyl 2-(phenylsulfonylmeyhyl)oct-2-enoate **5h**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, C*H*$_3$CH$_2$(C*H*$_2$)$_3$, *J* = 6.60 Hz) ; 1.14 (t, 3H, C*H*$_3$CH$_2$O, *J* = 6.99 Hz); 1.25-1.50 (m, 6H, CH$_3$(C*H*$_2$)$_3$- CH$_2$); 2.19 (dt, 2H, CH$_2$-C*H*$_2$-CH=, *J* = 7.35 Hz, *J* = 7.35 Hz); 3.95 (q, 2H, OC*H*$_2$CH$_3$, *J* = 6.99 Hz); 4.26 (s, 2H, -C*H*$_2$-SO$_2$); 6.11 (t, 1H,-CH$_2$-C*H*=, *J* = 7.35 Hz (*E*-isomer)); 7.12 (t, 1H,-CH$_2$-C*H*=, *J* = 7.35 Hz (*Z*-isomer)); 7.53-7.85 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.89 (*C*H$_3$(CH$_2$)$_4$CH); 13.94 (*C*H$_3$CH$_2$O); 22.41 (CH$_3$*C*H$_2$(CH$_2$)$_3$); 27.93 (CH$_3$(CH$_2$)$_3$*C*H$_2$CH); 30.06 (CH$_3$(CH$_2$)$_2$*C*H$_2$CH$_2$CH); 31.51 (CH$_3$CH$_2$*C*H$_2$(CH$_2$)$_2$CH); 54.04 (-*C*H$_2$-SO$_2$); 60.80 (CH$_3$*C*H$_2$O); 120.67 (CH=*C*); 128.82 (aromatic CH); 129.02 (aromatic CH); 133.74 (aromatic CH); 138.31 (aromatic C); 151.67 (*C*H=C); 165.62 (CH$_3$CH$_2$O*C*O).

(Z)-Ethyl 3-phenyl-2-(phenylsulfonylmethyl)acrylate **5i**

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (t, 3H, C*H*$_3$CH$_2$O, *J* = 6.99 Hz); 4.05 (q, 2H, CH$_3$C*H*$_2$O, *J* = 6.99 Hz); 4.49 (s, 2H, -C*H*$_2$-SO$_2$); 7.35-7.85 (m,10H, aromatic H); 7.93 (s, 1H, PhC*H*=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.11 (*C*H$_3$CH$_2$O); 55.05 (-*C*H$_2$-SO$_2$); 61.53 (CH$_3$*C*H$_2$O); 121.21(CH=*C*); 128.76 (aromatic CH); 128.90 (aromatic CH); 129.03 (aromatic CH); 129.14 (aromatic CH); 129.37 (aromatic CH); 129.63 (aromatic CH); 133.70 (aromatic C); 139.40 (aromatic C); 145.00 (*C*H=C); 166.41 (CH$_3$CH$_2$O*C*O).

(E)-2-(Phenylsulfonylmethyl)but-2-enenitrile **6a**

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (d, 3H, C*H*$_3$-CH=, *J* = 6.99 Hz); 3.88 (s, 2H, -C*H*$_2$-SO$_2$); 6.51 (q, 1H, CH$_3$-C*H*=, *J* = 6.99 Hz); 7.61-7.90 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.97 (*C*H$_3$CH=); 59.63 (-*C*H$_2$- SO$_2$); 104.03 (CH=*C*); 115.34 (*C*N); 128.66 (aromatic CH); 129.54 (aromatic CH); 134.59 (aromatic CH); 137.55 (aromatic C); 153.38 (*C*H=C).

(E,Z)-2-(Phenylsulfonylmethyl)pent-2-enenitrile **6b**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (t, 3H, C*H*$_3$-CH$_2$-CH=, *J* = 7.53 Hz); 2.36 (qd, 2H, CH$_3$-C*H*$_2$-CH=, *J* = 7.53 Hz, *J* = 7.53 Hz); 3.92 (s, 2H, -C*H*$_2$-SO$_2$); 6.31 (t, 1H, CH$_3$-CH$_2$-C*H*=, *J* = 7.71 Hz

(*E*-isomer)); 6.65 (t, 1H, CH_3-CH_2-C*H*=, *J* = 7.71 Hz (*Z*-isomer)); 7.61-7.90 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.44 (*C*H_3CH_2); 25.49 (CH_3*C*H_2); 59.50 (-*C*H_2- SO_2); 102.39 (CH=*C*); 115.50 (*C*N); 128.88 (aromatic CH); 129.78 (aromatic CH); 134.51 (aromatic CH); 137.24 (aromatic C); 159.60 (*C*H=C).

***(E,Z)-2-(Phenylsulfonylmethyl)hex-2-enenitrile* 6c**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, 3H, C*H*$_3$-CH_2-CH_2-CH=, *J* = 6.96 Hz); 1.35(m, 2H, CH_3-C*H*$_2$-CH_2-CH=); 2.29 (td, 2H, CH_3-CH_2-C*H*$_2$-CH=, *J* = 7.35 Hz, *J* = 7.71 Hz); 3.97 (s, 2H, -C*H*$_2$-SO_2); 6.31 (t, 1H, CH_3-CH_2-CH_2-C*H*=, *J* = 7.71 Hz (*E*-isomer)); 6.68(t, 1H, CH_3-CH_2-CH_2-C*H*=, *J* = 7.71 Hz (*Z*-isomer)); 7. 61-7.90(m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.44 (*C*$H_3CH_2CH_2$); 21.26 (CH_3*C*H_2CH_2); 33.82 (CH_3CH_2*C*H_2); 59.43 (-*C*H_2- SO_2); 102.91 (CH=*C*); 115.74 (*C*N); 128.56 (aromatic CH); 129.56 (aromatic CH); 134.45 (aromatic CH); 137.24 (aromatic C); 158.31 (*C*H=C).

***(E,Z)-5-Methyl-2-(phenylsulfonylmethyl)hex-2-enenitrile* 6d**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (d, 6H, (C*H*$_3$)$_2$-CH-CH_2-CH=, *J* = 6.99 Hz); 1.68 (m, 1H, $(CH_3)_2$-C*H*-CH_2-CH=); 2.23 (dd, 2H, $(CH_3)_2$-CH-C*H*$_2$-CH=, *J* = 7.35, *J* = 7.74); 3,98 (s, 2H, -C*H*$_2$-SO_2); 6. 38 (t, 1H, $(CH_3)_2$-CH-CH_2-C*H*=, *J* = 7.74 (*E*-isomer)); 6.70 (t, 1H, $(CH_3)_2$-CH-CH_2-C*H*=, *J* = 7.74 (*Z*-isomer)); 7. 56-7.91 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.08 ((*C*H_3)$_2$CH); 28.02 ((CH_3)$_2$*C*H); 40.79 ((CH_3)$_2$CH*C*H_2); 59.45 (-*C*H_2- SO_2); 103.46 (CH=*C*); 118.14 (*C*N); 128.61 (aromatic CH); 129.54 (aromatic CH); 134.42 (aromatic CH); 137.40 (aromatic C); 157.44 (*C*H=C).

***(E,Z)-2-(Phenylsulfonylmethyl)oct-2-enenitrile* 6e**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78 (t, 3H, C*H*$_3$- CH_2-(CH_2)$_3$-CH=, *J* = 6.81 Hz); 1.08-1.27 (m, 6H, CH_3-(C*H*$_2$)$_3$-CH_2-CH=); 2.25 (td, 2H, CH_3-(CH_2)$_2$-CH_2-C*H*$_2$-CH=, *J* = 7.35 Hz, *J* = 7.71 Hz); 3.84 (s, 2H, -C*H*$_2$-SO_2); 6.25 (t, 1H, CH_3-(CH_2)$_2$-CH_2-CH_2-C*H*=, *J* = 7.71 Hz (*E*-isomer)); 6.58 (t, 1H, CH_3-(CH_2)$_2$-CH_2-CH_2-C*H*=, *J* = 7.71 Hz (*Z*-isomer)); 7.48-7.82 (m, 5H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.42 (*C*H_3CH_2); 22.55 (CH_3*C*H_2); 27.56 (CH_3(CH_2)$_3$*C*H_2CH); 31.13 (CH_3(CH_2)$_2$*C*H_2CH_2CH); 32.11 (CH_3CH_2*C*H_2(CH_2)$_2$CH); 59.66 (-*C*H_2-SO_2); 102.99 (CH=*C*); 118.20 (*C*N); 129.58 (aromatic CH); 129.99 (aromatic CH); 134.70 (aromatic CH); 137.48 (aromatic C); 158.63 (*C*H=C).

***(E)-3-Phenyl-2-(phenylsulfonylmethyl)acrylonitrile* 6f**

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05 (s, 2H, -C*H*$_2$-SO_2); 7.09 (s, 1H, PhC*H*=); 7.43-7.94 (m, 10H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.38 (-*C*H_2-SO_2); 98.03 (CH=*C*); 117.05 (*C*N); 128.84 (aromatic CH); 129.07 (aromatic CH); 129.30 (aromatic CH); 129.61 (aromatic CH); 131.66 (aromatic CH); 132.45 (aromatic CH); 134.66 (aromatic C); 137.53 (aromatic C); 151.89 (*C*H=C).

***(E)-3-(3-Fluorophenyl)-2-(phenylsulfonylmethyl)acrylonitrile* 6g**

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.06 (s, 2H, -C*H*$_2$-SO_2); 7.10 (s, 1H, PhC*H*=); 7.13-7.94 (m, 9H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.27 (-*C*H_2-SO_2); 97.67 (CH=*C*); 97.70 (*C*N); 116.23 (aromatic CH); 116.52 (aromatic CH); 117.12 (aromatic CH); 128.81 (aromatic CH); 129.67 (aromatic CH); 131.58 (aromatic CH); 134.73 (aromatic CH); 137.58 (aromatic C); 150.57 (aromatic C); 162.66 (*C*H=C); 166.03(aromatic CF).

REFERENCES

[1] Baylis, A. B.; Hillman, M. E. D. *German Patent* 2155113 (1972), *Chem. Abstr*. **1972**, *77*, 34174q.
[2] Ciganek, E. *Org. React*. **1977**, *51*, 201.
[3] Basavaiah, D.; Rao, P. D.; Hyma, R., S. *Tetrahedron* **1996**, *52*, 8001.
[4] Drewes, S. E.; Roos, G. H. P. *Tetrahedron* **1988**, *44*, 4653.
[5] Morita, K.; Suziki, Z.; *Bull. Chem. Soc. Jpn* **1968**, *41*, 2815.
[6] Amri, H.; Villiéras, J. *Tetrahedron Lett*. **1986**, *27*, 4307.
[7] Basavaiah, D.; Gowriswari, V. V. L. *Tetrahedron Lett*. **1986**, *27*, 2031.
[8] Beltaïef, I.; Besbes, R. ; Amri, H. ; Villiéras, J. *Tetrahedron Lett*. **1997**, *38*, 813
[9] Hbaïeb, S.; Ben Ayed, T.; Amri, H. *Synth. Commun*. **1997**, *27*, 2825.
[10] Hbaïeb, S.; Amri, H. *J. Soc. Chim. Tunisie* **2000**, *7*, 671.
[11] Beltaïef, I.; Hbaïeb, S. ; Besbes, R. ; Amri, H. ; Villiéras, M.; Villiéras, J. *Synthesis* **1998**, 1765.
[12] Lee, JY; Kim, S. *Bull. Korean Chem. Soc*. **2006**, *27*, 189.
[13] Guo, H; Ye, S; Wang, J.; Zhang, Y. *J. Chem. Research (S),* **1997**, 114.
[14] McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.
[15] Chandrasekhard, S.; Jagadeshwar, V. ; Saritha, B. ; Narsihmulu, C. *J. Org. Chem*. **2005**, *70*, 6506.
[16] Savoia, D.; Trombini, C. ; Umani-Ronchi, A. *Pure & Appl. Chem*. **1985**, *57*, 1887.
[17] Kabalka, G. W.; Venkataiah, B.; Dong, G. *Tetrahedron Lett*. **2003**, *44*, 4673.
[18] Darmency, V.; Scanlan, E. M.; Schaffner, A. P.; Renaud, P. *Org. Synth*. **2006**, *83*, 24.
[19] Colombani, D.; Navarro, C.; Degueil-Castaing, M.; Maillard, B. *Synth. Commun*. **1991**, *21*, 1481.
[20] Anderson, R. J.; Hendrick, C. A.; Sidall, J. B. *J. Am. Chem. Soc.* **1970**, *90*, 735.
[21] Goering, H. L.; Kantner, S. S.; Seitz Jr, E. P. *J. Org. Chem.* **1985**, *50*, 549.