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Reaction of 1-Bromovinyl and 1-Bromo-2-phenylvinyl Sulfones with Some CH Acids

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Abstract—Benzyl, methyl, and phenyl α-bromovinyl sulfones reacted with malononitrile and dimethyl malonate sodium enolates in THF to give sulfonyl-substituted cyclopropanes. Reactions of the same sulfones with methyl acetoacetate sodium enolate afforded the corresponding sulfonyl-substituted cyclopropanes as mixtures of *cis* and *trans* isomers with a small impurity of 5-sulfonyl-4,5-dihydrofuran derivative. Phenyl and *p*-tolyl 1-bromo-2-phenylvinyl sulfones reacted with methyl acetoacetate sodium salt to produce a mixture of *trans*-isomeric 5-sulfonyl-4,5-dihydrofuran and Michael adduct of the CH acid with activated acetylene generated by concurrent 1,2-dehydrobromination of the initial α-bromovinyl sulfone.

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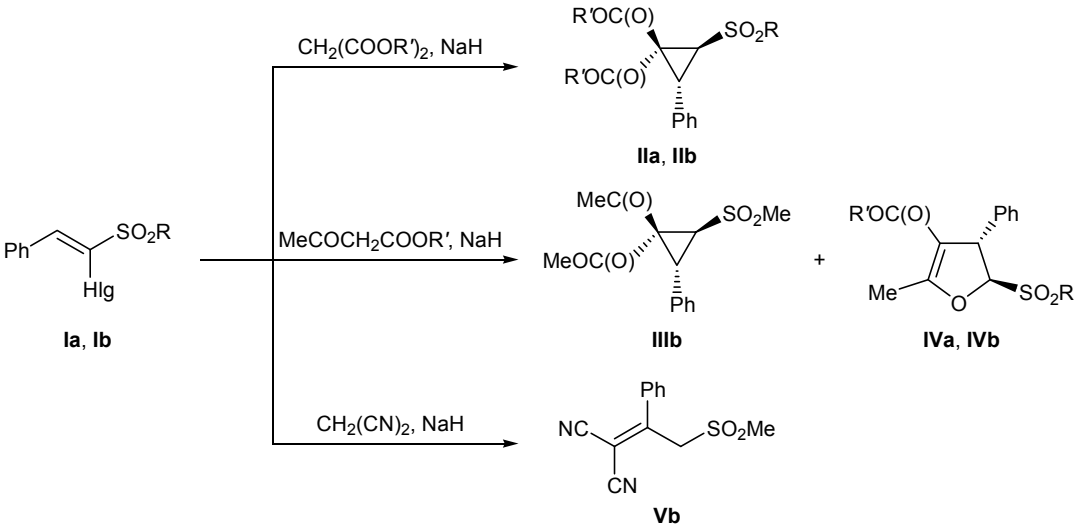
α-Halo α,β-unsaturated esters, nitriles, and ketones are known to react with dialkyl malonates and malononitrile in the presence of a base to give substituted cyclopropanecarboxylates, cyclopropanecarbonitriles, and cyclopropyl ketones, respectively [1–6]. Reactions of the same activated alkenes with alkyl acetoacetate or 1,3-diketones lead to the formation of mixtures of the corresponding cyclopropanes and dihydrofuran derivative; in some cases, the latter is formed as the major product [7–9]. These transformations can be regarded as MIRC reactions (Michael-Induced Ring Closure) where the Michael addition is followed by 1,3- and/or 1,5-cyclization.

A few published data are available on analogous transformations involving α-halovinyl sulfones. As shown in [10, 11], 1-halo-2-phenylvinyl sulfones **Ia** and **Ib** react with dialkyl malonates in the presence of sodium hydride according to the MIRC reaction pat-

Scheme 1.



Ia, **Ib** **IIa**, **IIb** **IIIb** **IVa**, **IVb** **Vb**

I, R = Ph, Hlg = Cl (**a**); R = Me, Hlg = Br (**b**); **II**, **IV**, R = Ph, R′ = Et (**a**); R = R′ = Me (**b**).

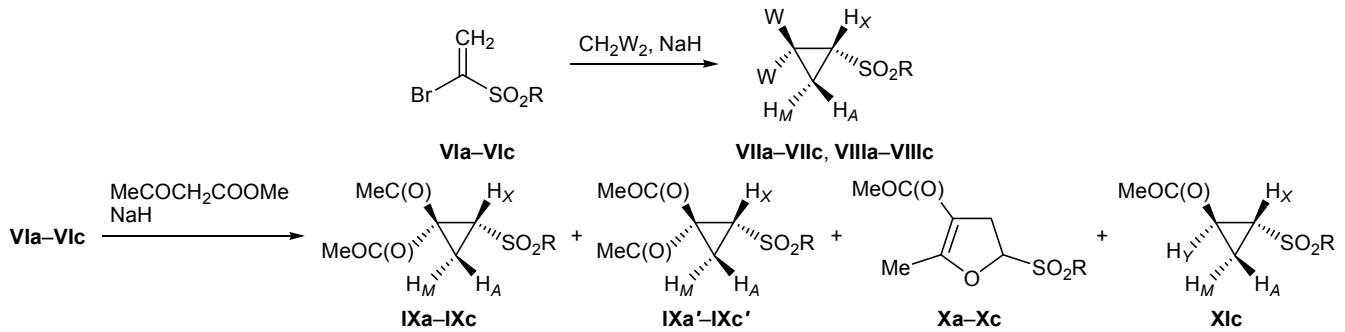
tern with formation of cyclopropyl sulfones **IIa** and **IIb** (Scheme 1). The reaction of 1-bromo-2-phenylvinyl sulfone (**Ib**) with methyl acetoacetate gave a mixture of cyclopropane and dihydrofuran derivatives **IIIb** and **IVb** at a ratio of 3 : 1, whereas 1-chloro-2-phenylvinyl sulfone (**Ia**) reacted with ethyl acetoacetate to produce substituted dihydrofuran **IVa** as the only product. Unexpectedly, in the reaction of α-bromo sulfone **Ib** with malononitrile we isolated allyl sulfone **Vb**, presumably as a result of synchronous process including 1,2-dehydrobromination, Michael addition, and isomerization [12].

In the present work we studied reactions of 1-bromovinyl sulfones **VIa**–**VIc** with malononitrile, dimethyl malonate, and methyl acetoacetate with a view to comparison of their behavior with the behavior of 1-halo-2-phenylvinyl sulfones **I** with different substitution pattern of the C=C double bond. Reactions of sulfones **VIa** and **VIc** with CH acids have already been reported. For example, the MIRC reaction of sulfone **VIa** with diethyl malonate and ethyl acetoacetate in the presence of sodium hydride in THF gave the corresponding substituted cyclopropyl sulfone [13]. Interesting results were obtained in the reaction of sulfone **VIc** with dimethyl 2-methylmalonate [14]. In this case, MIRC reaction is impossible, and MIRB reaction (Michael-Induced Ramberg–Bäcklund rearrangement) leads to diethyl 2-cinnamoyl-2-methylmalonate.

The reactions of bromovinyl sulfones **VIa**–**VIc** with CH acids were carried out in THF at 20–50°C using sodium hydride as base to generate the corresponding CH acid enolate. In the reactions with dimethyl malonate and malononitrile we isolated in all cases the only product, the corresponding cyclopropyl sulfone **VIIa**–**VIIc** or **VIIIa**–**VIIIc** (Scheme 2). Much more complicated pattern was observed in the reactions with methyl acetoacetate. Bromovinyl sulfone **VIa** gave rise to a mixture of stereoisomeric cyclopropanes **IXa** and **IXa′** at a ratio of 1 : 1 with a small impurity of dihydrofuran **Xa**. This result differs from the data of [13], according to which the reaction of sulfone **VIa** with ethyl acetoacetate afforded an analog of **IXa** as a single stereoisomer whose configuration was not determined. From vinyl sulfone **VIb** we obtained cyclopropanes **IXb** and **IXb′** at a ratio of 1 : 2 and a small amount (3.5%) of dihydrofuran **Xb**. In the reaction of vinyl sulfone **VIc** with methyl acetoacetate stereoisomeric cyclopropanes **IXc** and **IXc′** were formed at a ratio of 1 : 3. In addition, the reaction mixture contained small amounts of dihydrofuran derivative **Xc** and cyclopropane **XIc** which were detected by ^{1}H NMR. Presumably, the latter was formed as a result of partial decomposition of acetyl-substituted cyclopropane **IVc′** under alkaline conditions during the isolation procedure (treatment with water). No products that could arise from *a priori* possible MIRB reactions were identified in the reactions of vinyl sulfones **VIb** and **VIc** with all the CH acids used.

Except for **Xb**, compounds **VII**–**XI** were isolated in the pure state by silica gel column chromatography and/or crystallization. Dihydrofuran **Xb** was detected in the product mixture by ^{1}H NMR. Chromatographic purification of cyclopropane **IXa** was accompanied by its partial transformation into dihydrofuran **Xa** (cf. [15]). The structure of the isolated compounds was determined on the basis of their IR, ^{1}H and ^{13}C NMR, and mass spectra. Cyclopropanes **VIIIa**–**VIIIc** characteristically showed in the ^{13}C NMR spectra anomalously upfield position of the C^1 signal (δ_C ~6 ppm) despite two cyano groups attached to that carbon atom. Signals from carbon nuclei were assigned using ^{13}C–^{1}H HMBC technique. In the ^{1}H NMR spectra of **VII**–**IX** multiplet signals from protons on the cyclopropane ring were reliably recognized as an *AMX* spin system. These protons were assigned, and the con-

Scheme 2.



R = Ph (**a**), Me (**b**), $PhCH_2$ (**c**); **VII**, W = CO_2Me; **VIII**, W = CN.

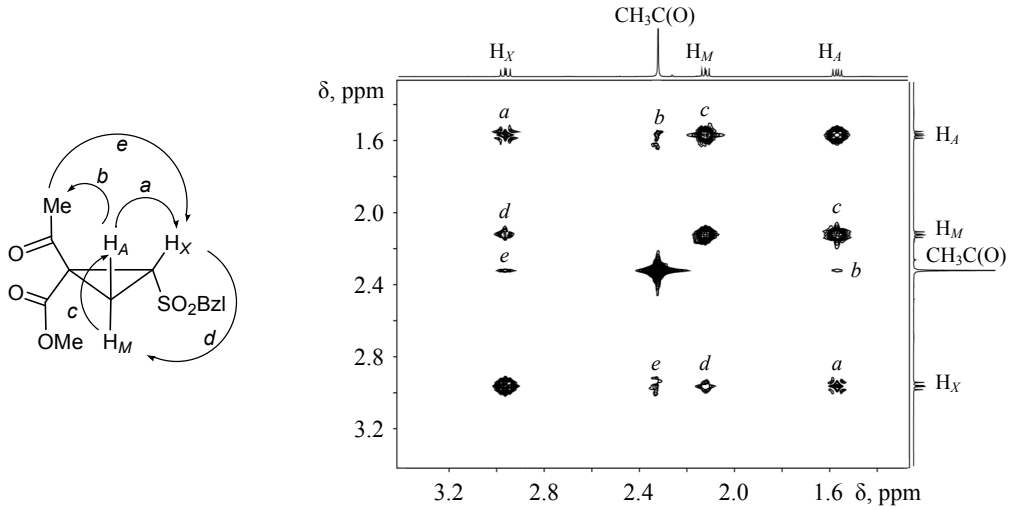


Fig. 1. A fragment of the ^{1}H–^{1}H NOESY spectrum of methyl 1-acetyl-2*c*-(phenylmethanesulfonyl)cyclopropane-1*r*-carboxylate (**IXc**).

figuration of stereoisomers **IX** and **IX′**, was determined with account taken of the known relation for spin–spin coupling constants in cyclopropanes: $^3J_{cis} > {}^3J_{trans} > {}^2J_{gauche}$ [16, 17]. The assumed configurations of **IXa**–**IXc** and **IXa′**–**IXc′** were consistent with the observed differences in the chemical shifts of protons in the methoxycarbonyl and acetyl group due to deshielding effect of the oppositely faced sulfonyl group. The ^{1}H–^{1}H NOESY data (Figs. 1, 2) provided additional proofs for the assigned configurations of **IXc** and **IXc′**. In the NOESY spectrum of **IXc**, cross-peaks *a* correspond to the interaction between H_A and H_X, cross-peaks *b* reflect coupling of protons in the acetyl group with H_A, correlations H_A/H_M and H_X/H_M give rise to cross-peaks *c* and *d*, respectively, and cross-peaks *e* belong to coupling of H_X with methyl protons in the acetyl group. In the ^{1}H–^{1}H NOESY spectrum of **XIc′** (Fig. 2) we observed the following correlations: H_M–MeCO (*a*), H_A–H_M (*b*), H_X–H_A (*c*), and H_X–H_M (*d*). Cyclopropane **XIc** was assigned *trans* configuration [16] on the basis of the spin–spin coupling constant between H_X and H_Y (^3J = 7.4 Hz), which was determined by decoupling from H_A and H_M.

Comparison of our results with the data of [13] on the reactions of α-bromovinyl sulfones **VIa**–**VIc** with CH acids and with the results of the reactions of sulfones **Ia** and **Ib** with the same CH acids [10–12] shows almost complete similarity with respect to the reaction pattern, except for the reaction of **Ib** with malononitrile. One more notable feature is the behavior of chlorostyryl sulfone **Ia** in the reaction with alkyl acetoacetate, which, unlike the reactions with bromovinyl

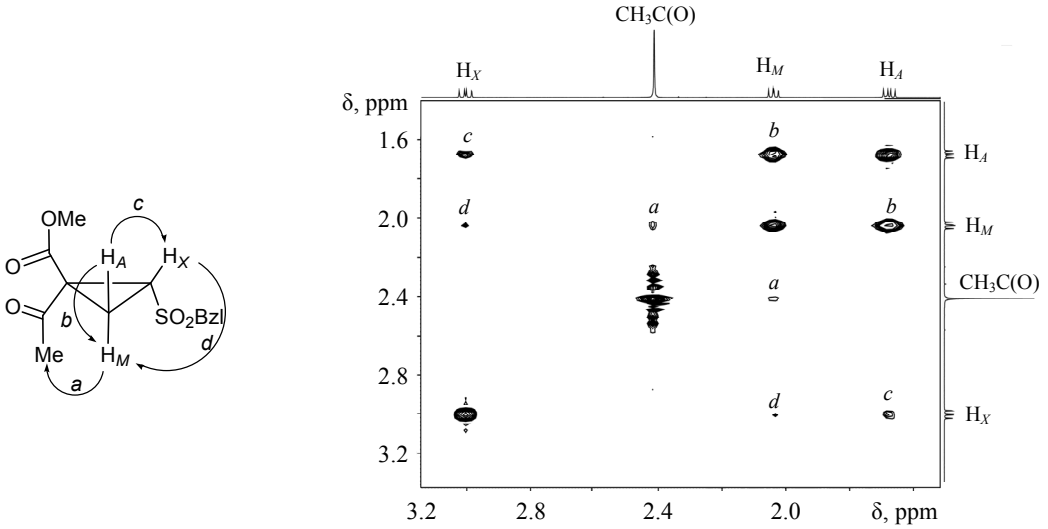
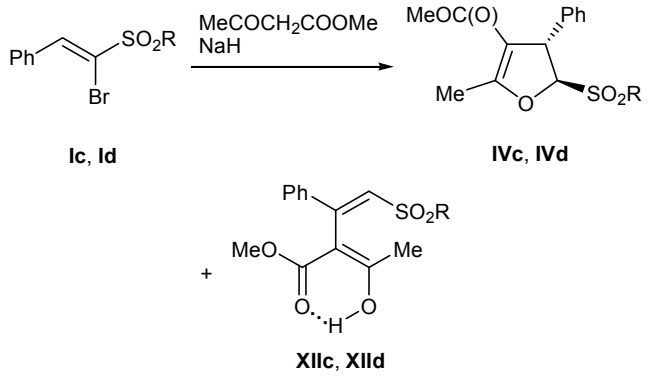


Fig. 1. A fragment of the ^{1}H–^{1}H NOESY spectrum of methyl 1-acetyl-2*t*-(phenylmethanesulfonyl)cyclopropane-1*r*-carboxylate (**IXc′**).

sulfones **Ib** and **VIa**–**VIc**, led to the formation of dihydrofuran derivative **IVa** as the only product.

We also examined reactions of analogs of **Ia** and **Ib**, aryl 1-bromo-2-phenyl sulfones **Ic** and **Id**, with methyl acetoacetate. The products of these reactions were mixtures of dihydrofurans **IVc** and **IVd** and vinyl sulfones **XIIc** and **XIId** at ratios of 2:1 and 1:1.2, respectively (Scheme 3). Pure compounds **IVc**, **IVd**, **XIIc**, and **XIId** were isolated by silica gel column chromatography. The configuration of **IVc** and **IVd** was assumed to be the same as that of their analogs **IVa** and **IVb** [10] on the basis of the expected similarity of their ^{1}H NMR spectra. Sulfones **XIIc** and **XIId** were identified by comparison with authentic samples [18].

Scheme 3.



Ic, **Id** **IVc**, **IVd**

XIIc, **XIId**

R = Ph (**c**), 4-MeC_6H_4 (**d**).

Presumably, the presence of a phenyl group in sulfone **Ib** facilitates its 1,2-dehydrobromination which becomes preferred to Michael addition; therefore, the reaction of **Ib** with malononitrile yields allylic derivative **Vb** in contrast to sulfones **VIa**–**VIc** whose reaction with malononitrile leads to the formation of cyclopropyl sulfones **VIIIa**–**VIIIc**.

The different behaviors of halostyryl sulfone **Ia**, on the one hand, and **Ic** and **Id**, on the other, can also be rationalized taking into account that dehydrobromination is more favorable than dehydrochlorination. Then, bromo sulfones **Ic** and **Id** are involved in both MIRC reaction and tandem dehydrobromination–Michael addition with formation of compounds **Vc**, **Vd** and **XIIc**, **XIId**, respectively, whereas chloro sulfone **Ia** reacts exclusively according to the MIRC pattern to produce dihydrofuran derivative **IVa**.

Finally, somewhat different stereoselectivities in the MIRC reactions of vinyl sulfones **VIa**–**VIc** may be interpreted as follows. The reaction with sulfone **VIa** is not selective. The reaction with sulfone **VIc** containing a bulkier (than $PhSO_2$) $PhCH_2SO_2$ group clearly shows *trans* selectivity, i.e., the major product is cyclopropane **IXc′** in which the $PhCH_2SO_2$ is faced to smaller acetyl group rather than ester group (cf. conformational energies of the COMe and CO_2Me substituents, 1.02 and 1.2 kcal/mol, respectively [19]).

In summary, we can state that Michael-induced tandem reactions of 1-bromovinyl sulfones and 1-bromo-2-phenylvinyl sulfones with CH acids should be regarded as a convenient method for the preparation of functionally substituted cyclopropane derivatives which are difficult to obtain by other methods. On the other hand, there exist some limitations related to specific structural features of the initial α-bromo sulfones.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Jeol JNM-ECX400 spectrometer at 400 and 100 MHz, respectively; the chemical shifts were measured relative to the residual proton and carbon signals of the solvent ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.0 ppm). The IR spectra were recorded from thin films or KBr pellets on an InfraLYuM FT-02 spectrometer with Fourier transform. The elemental compositions were determined on a VarioMICRO CHNS-analyzer. The mass spectra (electron impact, 70 eV) were obtained using a KONIK RBK-HRGC5000B-MSQ12 instrument (Spain). Silufol UV-254 plates were used for analytical TLC; eluent light petroleum ether–ethyl acetate (2:1), development with iodine vapor. Silica gel L (40–100 μm) was used for column chromatography; eluent light petroleum ether–ethyl acetate (5:1).

α-Bromovinyl sulfones **VIa**, **VIc** [20], and **VIb** [21] were synthesized by known procedures.

1-Bromo-2-phenylvinyl sulfones Ic and Id (*general procedure*). (*E*)-1-Benzenesulfonyl-2-phenylethene [22] or (*E*)-1-(4-methylbenzenesulfonyl)-2-phenylethene [23], 12 mmol, was dissolved in 12 mL of anhydrous methylene chloride, a solution of 13.2 mmol (2.11 g) of bromine in 4 mL of the same solvent was gradually added, and the mixture was stirred for 40 h at 20°C. The solvent was distilled off under reduced pressure (water-jet pump). The oily residue was treated with 30 mL of aqueous dioxane (1:1) and 1.53 g (14 mmol) of sodium carbonate, the mixture was stirred for 25 h at 40–45°C and diluted with 150 mL of water, and the crystals were filtered

off, dried in air, and recrystallized from diethyl ether–hexane (1:4).

(*Z*)-1-(Benzenesulfonyl)-1-bromo-2-phenylethene (Ic). Yield 83%, R_f 0.56, mp 101–102°C; published data [24]: mp 101–103°C. ^{1}H NMR spectrum, δ, ppm: 7.40–7.47 m (3H, H_{arom}), 7.54–7.60 m (2H, H_{arom}), 7.63–7.68 m (1H, H_{arom}), 7.77–7.87 m (2H, H_{arom}), 7.98–8.00 m (2H, H_{arom}), 8.36 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 120.6 weak, 128.7 (2C), 129.05 (2C), 129.11 (2C), 130.1 (2C), 131.1, 131.8 weak, 134.0, 137.3 weak, 138.9. Found, %: C 52.14; H 3.51; S 9.89. $C_{14}H_{11}BrO_2S$. Calculated, %: C 52.03; H 3.43; S 9.92.

(*Z*)-1-Bromo-1-(4-methylbenzenesulfonyl)-2-phenylethene (Id). Yield 85%, R_f 0.68, mp 105–106°C; published data [25]: mp 109–111°C. IR spectrum, ν, cm^{-1}: 1593 m, 1323 s, 1312 m, 1150 v.s, 756 m, 687 m, 667 s, 606 m, 544 v.s. ^{1}H NMR spectrum, δ, ppm: 2.46 s (3H, CH_3), 7.36 d (2H, H_{arom}, J = 8.2 Hz), 7.38–7.47 m (3H, H_{arom}), 7.79–7.84 m (2H, H_{arom}), 7.88 d (2H, H_{arom}, J = 8.2 Hz), 8.34 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 21.7 (CH_3), 121.0 weak, 128.5 (2C), 129.1 (2C), 129.8 (2C), 130.0 (2C), 131.0, 131.9 weak, 134.2 weak, 138.5, 145.1. Found, %: C 53.45; H 3.68; S 9.39. $C_{13}H_{14}O_6S$. Calculated, %: C 53.42; H 3.89; S 9.51.

Reaction of α-bromovinyl sulfones VIa–VIc with dimethyl malonate and malononitrile (*general procedure*). Sodium hydride, 6 mmol (prepared by washing a 60% suspension of NaH in mineral oil with hexane), was added under argon to 5 mL of anhydrous THF, a solution of 4.5 mmol of dimethyl malonate or malononitrile in 10 mL of THF was added dropwise over a period of 15 min under stirring at 20°C, and the mixture was stirred for 1 h at 20°C. A solution of 4.0 mmol of α-bromovinyl sulfone **VIa–VIc** in 10 mL of anhydrous THF was added dropwise over a period of 15 min under stirring at 20°C, and the mixture was stirred for 15 h at 20°C, diluted with water (200 mL), neutralized with dilute (1:1) aqueous HCl, and extracted with methylene chloride (3×30 mL). The combined extracts were washed with water and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel.

Dimethyl 2-(benzenelsulfonyl)cyclopropane-1,1-dicarboxylate (VIIa). Yield 55%, mp 118–119°C (from Et_2O). IR spectrum, ν, cm^{-1}: 3029 w, 1748 v.s, 1736 v.s, 1443 m, 1346 m, 1308 s, 1262 s, 1208 m, 1157 s, 725 m, 613 m. ^{1}H NMR spectrum, δ, ppm: 1.73 d.d (1H, H_A, J = 5.6, 9.2 Hz), 2.24 d.d (1H, H_M, J = 5.6, 7.1 Hz), 3.35 d.d (1H, H_X, J = 7.1, 9.2 Hz), 3.72 s and 3.85 s (3H each, OCH_3), 7.57 t (2H, H_{arom}, J = 7.9 Hz), 7.67 t (1H, H_{arom}, J = 7.5 Hz), 7.92 d (2H, H_{arom}, J = 7.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.7 (C^3), 36.5 weak (C^1), 44.6 (C^2), 53.4 and 53.5 (OCH_3), 127.9 (2C, C_{arom}), 129.3 (2C, C_{arom}), 134.1 (C_{arom}), 139.6 weak (C_{arom}), 164.7 and 167.9 (C=O). Found, %: C 52.44; H 4.61; S 10.79. $C_{13}H_{14}O_6S$. Calculated, %: C 52.34; H 4.73; S 10.75.

Dimethyl 2-(methanesulfonyl)cyclopropane-1,1-dicarboxylate (VIIb). Yield 59%, mp 81–82°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 1747 s, 1740 v.s, 1724 s, 1443 m, 1319 s, 1311 v.s, 1257 v.s, 1215 m, 1142 s, 791 m. ^{1}H NMR spectrum, δ, ppm: 1.81 d.d (1H, H_A, J = 5.8, 9.2 Hz), 2.26 d.d (1H, H_M, J = 5.8, 6.8 Hz), 3.12 s (3H, CH_3SO_2), 3.30 d.d (1H, H_X, J = 6.8, 9.2 Hz), 3.79 s and 3.81 s (3H each, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 15.8 (C^3), 35.7 weak (C^1), 41.6 (C^2), 42.4 (SO_2CH_3), 53.4 and 53.7 (OCH_3), 164.7 and 167.8 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 236 (0.7) $[M]^{+\cdot}$, 205 (90), 157 (92), 156 (84), 125 (84), 98 (90), 83 (90), 69 (93), 67 (92), 59 (99), 55 (100). Found, %: C 40.64; H 5.21; S 13.64. $C_8H_{12}O_6S$. Calculated, %: C 40.67; H 5.12; S 13.57.

Dimethyl 2-(phenylmethanesulfonyl)cyclopropane-1,1-dicarboxylate (VIIc). Yield 68%, mp 110–111°C (from EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1755 s, 1732 v.s, 1443 m, 1338 s, 1311 s, 1273 s, 1211 m, 1200 m, 1142 s, 1126 s, 1011 m, 694 m, 505 m. ^{1}H NMR spectrum, δ, ppm: 1.72 d.d (1H, H_A, J = 5.7, 9.3 Hz), 2.20 d.d (1H, H_M, J = 5.7, 6.9 Hz), 2.94 d.d (1H, H_X, J = 6.9, 9.3 Hz), 3.77 s and 3.85 s (3H each, OCH_3), 4.36 d and 4.53 d (1H each, SO_2CH_2, J = 13.6 Hz), 7.37–7.41 m (3H, H_{arom}), 7.42–7.47 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 15.8 (C^3), 35.5 weak (C^1), 39.8 (C^2), 53.5 and 53.6 (OCH_3), 60.1 (SO_2CH_2), 127.3 weak (C_{arom}), 129.0 (2C, C_{arom}), 129.1 (C_{arom}), 130.9 (2C, C_{arom}), 165.0 and 167.6 (C=O). Found, %: C 53.75; H 5.12; S 10.29. $C_{14}H_{16}O_6S$. Calculated, %: C 53.84; H 5.16; S 10.26.

2-(Benzenesulfonyl)cyclopropane-1,1-dicarbonitrile (VIIIa). Yield 43%, mp 126–127°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 3040 m, 2253 w, 1346 m, 1319 s, 1165 v.s, 1157 s, 1084 m, 744 m, 687 m, 548 m. ^{1}H NMR spectrum, δ, ppm: 2.33 d.d (1H, H_A, J = 6.7, 9.3 Hz), 2.66 d.d (1H, H_M, J = 6.7, 7.9 Hz), 3.46 d.d (1H, H_X, J = 7.9, 9.3 Hz), 7.69 t (2H, H_{arom}, J = 7.4 Hz), 7.82 t (1H, H_{arom}, J = 7.5 Hz), 8.05 d (2H, H_{arom}, J = 7.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 6.2 weak (C^1), 20.5 (C^3), 45.2 (C^2), 110.2 and

112.5 (CN) 128.4 (2C, C_{arom}), 130.1 (2C, C_{arom}), 135.6 (C_{arom}), 137.2 weak (C_{arom}). Found, %: C 56.76; H 3.40; N 11.96; S 13.86. $C_{11}H_8N_2O_6S$. Calculated, %: C 56.89; H 3.47; N 12.06; S 13.80.

2-(Methanesulfonyl)cyclopropane-1,1-dicarbonitrile (VIIIb). Yield 61%, mp 129–130°C (from EtOH). IR spectrum, ν, cm^{-1}: 2256 w, 1335 m, 1311 s, 1165 m, 1146 v.s, 1099 m, 1088 m, 783 m, 536 m, 509 m. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.43 d.d (1H, H_M, J = 6.8, 8.2 Hz), 2.71 d.d (1H, H_A, J = 6.8, 9.3 Hz), 3.34 s (3H, CH_3), 4.45 d.d (1H, H_X, J = 8.2, 9.3 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 5.6 weak (C^1), 20.3 (C^3), 42.0 (SO_2CH_3), 43.4 (C^2), 112.2 and 114.2 (C≡N). Found, %: C 42.42; H 3.50; N 16.54; S 18.72. $C_6H_6N_2O_2S$. Calculated, %: C 42.35; H 3.55; N 16.46; S 18.84.

2-(Phenylmethanesulfonyl)cyclopropane-1,1-dicarbonitrile (VIIIc). Yield 56%, mp 106–107°C (from EtOH). IR spectrum, ν, cm^{-1}: 3024 m, 2256 w, 1331 s, 1315 v.s, 1153 m, 1126 v.s, 698 m, 540 m, 517 s. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.25 d.d (1H, H_M, J = 6.8, 8.3 Hz), 2.66 d.d (1H, H_A, J = 6.8, 9.5 Hz), 4.40 d.d (1H, H_X, J = 8.3, 9.5 Hz), 4.85 d and 4.90 d (1H each, SO_2CH_2, J = 14.0 Hz), 7.41–7.48 m (3H, H_{arom}), 7.48–7.52 m (2H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 6.2 weak (C^1), 19.6 (C^3), 41.6 (C^2), 59.9 (SO_2CH_2), 111.5 and 113.9 (C≡N), 127.7 weak (C_{arom}), 129.4 (2C, C_{arom}), 129.5 (C_{arom}), 131.8 (2C, C_{arom}). Found, %: C 58.49; H 4.15; N 11.39; S 12.99. $C_{12}H_{10}N_2O_2S$. Calculated, %: C 58.52; H 4.09; N 11.37; S 13.02.

Reaction of sulfones Ic, Id, and VIa–VIc with methyl acetoacetate (*general procedure*). The reactions of α-bromo sulfones **Ic**, **Id**, and **VIa–VIc** with methyl acetoacetate were carried out at the same reactant ratio as in the reactions with malonic acid derivatives. The mixture was stirred for 22–24 h at 50°C and treated as described above. The crude product was analyzed by ^1H NMR. From bromovinyl sulfone **Ic** we obtained dihydrofuran **IVc** and vinyl sulfone **XIIc** at a ratio of 2:1; from sulfone **Id** a mixture of dihydrofuran **IVd** and vinyl sulfone **XIId** at a ratio of 1:1.2 was formed. The reaction with **VIa** gave a 1:1 mixture of **IXa** and **IXa′** and <8% of dihydrofuran **Xa**. Sulfone **VIb** gave rise to compounds **IXb** and **IXb′** at a ratio of 1:2 and 3.5% of dihydrofuran **Xb**; and the reaction with **VIc** produced sulfones **IXc** and **IXc′** at a ratio of 1:3 and ~5% of **Xc** and **XIc** each. The pure products were isolated by column chromatography on silica gel.

Methyl *trans*-5-(benzenesulfonyl)-2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (IVc). Yield 49%, R_f 0.37, mp 148–149°C (from EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1701 v.s, 1659 s, 1458 m, 1451 m, 1439 m, 1327 s, 1308 m, 1238 m, 1208 m, 1188 m, 1150 m, 1088 m, 1022 m, 992 m, 814 m, 760 m, 721 m, 706 m, 687 m, 594 s, 540 m. ^1H NMR spectrum, δ, ppm: 2.28 d (3H, CH_3, J = 1.4 Hz), 3.55 s (3H, OCH_3), 4.91 d.q (1H, 4-H, J = 1.4, 3.2 Hz), 5.11 d (1H, 5-H, J = 3.2 Hz), 7.19 d (2H, H_{arom}, J = 7.0 Hz), 7.25 t (1H, H_{arom}, J = 7.3 Hz), 7.32 t (2H, H_{arom}, J = 6.9 Hz), 7.58 t (2H, H_{arom}, J = 7.8 Hz), 7.70 t (1H, H_{arom}, J = 7.5 Hz), 7.94 d (2H, H_{arom}, J = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.8 (CH_3), 48.9 (C^4), 51.2 (OCH_3), 99.9 (C^5), 107.6 (C^3); 127.1 (2C, C_{arom}), 127.7 (C_{arom}), 129.0 (2C, C_{arom}), 129.2 (2C, C_{arom}), 129.5 (2C, C_{arom}), 134.6 (C_{arom}), 135.5 weak (C_{arom}), 140.5 weak (C_{arom}), 164.3 (C^2), 167.4 (C=O). Found, %: C 63.61; H 5.13; S 8.99. $C_{19}H_{18}O_5S$. Calculated, %: C 63.67; H 5.06; S 8.95.

Methyl (2*Z*,3*Z*)-4-(benzenesulfonyl)-2-(1-hydroxyethylidene)-3-phenylbut-2-enoate (XIIc). Yield 17%, R_f 0.24, mp 118–119°C (from acetone–hexane). The NMR spectra of **XIIc** were identical to those given in [18].

Methyl *trans*-2-methyl-5-(4-methylbenzenesulfonyl)-4-phenyl-4,5-dihydrofuran-3-carboxylate (IVd). Yield 34%, R_f 0.54, mp 153–154°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 1697 m, 1659 v.s, 1435 m, 1335 m, 1323 m, 1311 m, 1215 m, 1184 s, 1153 s, 1088 s, 1018 s, 694 m, 660 v.s, 590 v.s, 528 m, 521 m. ^1H NMR spectrum, δ, ppm: 2.28 d (3H, CH_3, J = 1.4 Hz), 3.54 s (3H, OCH_3), 4.89 d.q (1H, 4-H, J = 1.4, 3.9 Hz), 5.08 d (1H, 5-H, J = 3.9 Hz), 7.19 d (2H, H_{arom}, J = 7.0 Hz), 7.23–7.27 m (1H, H_{arom}), 7.29–7.33 m (2H, H_{arom}), 7.36 d and 7.81 d (2H each, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.8 (CH_3), 21.7 ($\mathbf{C}H_3C_6H_4$), 48.8 (C^4), 51.2 (OCH_3), 99.9 (C^5), 107.6 (C^3), 127.1 (2C, C_{arom}), 127.6 (C_{arom}), 128.9 (2C, C_{arom}), 129.5 (2C, C_{arom}), 129.9 (2C, C_{arom}), 132.4 weak (C_{arom}), 140.6 weak (C_{arom}), 145.8 weak (C_{arom}), 164.4 (C^2), 167.4 (C=O). Found, %: C 64.57; H 5.53; S 8.68. $C_{20}H_{20}O_5S$. Calculated, %: C 64.50; H 5.41; S 8.61.

Methyl (2*Z*,3*Z*)-2-(1-hydroxyethylidene)-4-(4-methylbenzenesulfonyl)-3-phenylbut-2-enoate (XIId). Yield 35%, R_f 0.38, mp 109–110°C (from acetone–hexane). The NMR spectra of **XIId** were identical to those given in [18].

Methyl 1-acetyl-2*c*-(benzenesulfonyl)cyclopropane-1*r*-carboxylate (IXa). Yield 30%, R_f 0.25, mp 83–84°C (from EtOAc–hexane). IR spectrum, ν,

cm^{-1}: 1748 v.s, 1709 s, 1443 m, 1362 m, 1350 m, 1331 m, 1312 s, 1296 s, 1223 s, 1204 s, 1173 s, 1154 s, 1127 m, 737 m, 725 m, 598 v.s. ^{1}H NMR spectrum, δ, ppm: 1.63 d.d (1H, H_A, J = 5.2, 9.0 Hz), 2.22 d.d (1H, H_M, J = 5.2, 7.1 Hz), 2.33 s (3H, CH_3), 3.35 d.d (1H, H_X, J = 7.1, 9.0 Hz), 3.92 s (3H, OCH_3), 7.59 t (2H, H_{arom}, J = 7.2 Hz), 7.68 t (1H, H_{arom}, J = 7.9 Hz), 7.92 d (2H, H_{arom}, J = 6.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.5 (C^3), 28.4 (CH_3), 43.0 weak (C^1), 45.8 (C^2), 53.5 (OCH_3), 127.8 (2C, C_{arom}), 129.3 (2C, C_{arom}), 134.1 (C_{arom}), 139.6 weak (C_{arom}), 166.8 (C=O), 199.0 (Me**C**=O). Mass spectrum, m/z (I_{rel}, %): 282 (0.7) $[M]^{+\cdot}$, 267 (13), 240 (43), 209 (29), 208 (100), 141 (25), 125 (34), 116 (20), 105 (15), 99 (16), 77 (51), 59 (13), 51 (16), 43 (63). Found, %: C 55.37; H 5.05; S 11.46. $C_{13}H_{14}O_5S$. Calculated, %: C 55.31; H 5.00; S 11.36.

Methyl 1-acetyl-2*t*-(benzenesulfonyl)cyclopropane-1*r*-carboxylate (IXa′). Yield 36%, R_f 0.15, mp 80–81°C (from EtOAc–hexane). IR spectrum, ν, cm^{-1}: 2924 weak, 1747 v.s, 1716 s, 1450 m, 1357 m, 1292 s, 1265 s, 1257 v.s, 1153 v.s, 1061 s, 729 s, 698 s, 544 s. ^{1}H NMR spectrum, δ, ppm: 1.66 d.d (1H, H_A, J = 5.5, 8.8 Hz), 2.16 d.d (1H, H_M, J = 5.5, 7.1 Hz), 2.57 s (3H, CH_3), 3.39 d.d (1H, H_X, J = 7.1, 8.8 Hz), 3.76 s (3H, OCH_3), 7.59 t (2H, H_{arom}, J = 7.0 Hz), 7.69 t (1H, H_{arom}, J = 7.5 Hz), 7.90 d (2H, H_{arom}, J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.1 (C^3), 30.7 (CH_3), 42.1 (C^1), 46.0 (C^2), 53.4 (OCH_3), 127.8 (2C, C_{arom}), 129.4 (2C, C_{arom}), 134.2 (C_{arom}), 139.4 weak (C_{arom}), 168.5 (C=O), 197.1 (Me**C**=O). Found, %: C 55.40; H 5.15; S 11.41. $C_{13}H_{14}O_5S$. Calculated, %: C 55.31; H 5.00; S 11.36.

Methyl 5-(benzenesulfonyl)-4,5-dihydrofuran-3-carboxylate (Xa). Yield 10%, R_f 0.32, mp 122–123°C (acetone–hexane). IR spectrum, ν, cm^{-1}: 2985 m, 1701 v.s, 1662 v.s, 1446 s, 1435 s, 1342 s, 1327 v.s, 1254 s, 1153 s, 1142 s, 1084 s, 1018 s, 733 s, 586 v.s. ^{1}H NMR spectrum, δ, ppm: 2.11 t (3H, CH_3, J = 1.8 Hz), 3.20–3.30 m and 3.38–3.48 m (1H each, CH_2), 3.67 s (3H, OCH_3), 5.34 d.d (1H, 5-H, J = 5.1, 10.9 Hz), 7.57 t (2H, H_{arom}, J = 7.8 Hz), 7.69 t (1H, H_{arom}, J = 7.5 Hz), 7.92 d (2H, H_{arom}, J = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.5 (CH_3), 30.8 (C^4), 51.2 (OCH_3); 93.0 (C^5), 102.9 (C^3), 129.2 (2C, C_{arom}), 129.5 (2C, C_{arom}), 134.6 (C_{arom}), 135.2 weak (C_{arom}), 164.6 (C^2), 166.4 (C=O). Mass spectrum, m/z (I_{rel}, %): 268 (0.6), 251 (22), 250 (13), 209 (14), 208 (44), 186 (32), 176 (13), 171 (16), 141 (100), 140 (22), 125 (42), 116 (14), 115 (11), 109 (20), 78 (11), 77 (83), 67 (14), 59 (23), 43 (81). Found, %: C 55.38; H 5.09; S 11.50. $C_{13}H_{14}O_5S$. Calculated, %: C 55.31; H 5.00; S 11.36.

Methyl 1-acetyl-2*c*-(methanesulfonyl)cyclopropane-1*r*-carboxylate (IXb). Yield 21%, R_f 0.43 (light petroleum ether–EtOAc, 1 : 1), mp 93–94°C (from EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1716 s, 1662 s, 1446 m, 1385 m, 1338 m, 1311 s, 1257 s, 1219 m, 1196 m, 1161 m, 1142 v.s, 1080 s, 1026 m, 1003 m, 914 s, 779 m, 760 m, 513 m, 482 m. ^{1}H NMR spectrum, δ, ppm: 1.64 d.d (1H, H_A, J = 5.6, 8.9 Hz), 2.19 d.d (1H, H_M, J = 5.6, 6.6 Hz), 2.33 s (3H, CH_3), 3.03 s (3H, SO_2CH_3), 3.28 d.d (1H, H_X, J = 6.6, 8.9 Hz), 3.82 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 16.3 (C^3), 30.5 (CH_3), 40.3 (C^1), 42.0 (C^2), 43.6 (SO_2CH_3), 53.6 (OCH_3), 168.4 (C=O), 198.3 (Me**C**=O). Found, %: C 43.54; H 5.54; S 14.62. $C_8H_{12}O_5S$. Calculated, %: C 43.63; H 5.49; S 14.56.

Methyl 1-acetyl-2*t*-(methanesulfonyl)cyclopropane-1*r*-carboxylate (IXb′). Yield 40%, R_f 0.35 (light petroleum ether–EtOAc, 1 : 1), oily substance. IR spectrum, ν, cm^{-1}: 1747 m, 1740 s, 1732 s, 1724 v.s, 1716 s, 1311 s, 1257 s, 1142 s. ^{1}H NMR spectrum, δ, ppm: 1.80 d.d (1H, H_A, J = 5.4, 9.0 Hz), 2.18 d.d (1H, H_M, J = 5.4, 6.7 Hz), 2.42 s (3H, CH_3), 3.08 s (3H, SO_2CH_3), 3.33 d.d (1H, H_X, J = 6.7, 9.0 Hz), 3.77 s (3H, OCH_3). ^{13}C NMR spectrum, δ, ppm: 17.6 (C^3), 28.3 (CH_3), 41.5 weak (C^1), 42.3 (C^2), 43.4 (SO_2CH_3), 53.5 (OCH_3), 166.8 (C=O), 198.8 (Me**C**=O). Found, %: C 43.59; H 5.53; S 14.64. $C_8H_{12}O_5S$. Calculated, %: C 43.63; H 5.49; S 14.56.

Methyl 5-(methanesulfonyl)-4,5-dihydrofuran-3-carboxylate (Xb). ^{1}H NMR spectrum (from the spectrum of the reaction mixture), δ, ppm: 2.24 d (3H, CH_3, J = 1.8 Hz), 2.91 s (3H, SO_2CH_3), 3.70 s (3H, OCH_3), 5.31 d.d (1H, 5-H, J = 5.5, 11.0 Hz).

Methyl 1-acetyl-2*c*-(phenylmethanesulfonyl)cyclopropane-1*r*-carboxylate (IXc). Yield 10%, R_f 0.22, oily substance. IR spectrum, ν, cm^{-1}: 1740 v.s, 1720 v.s, 1335 s, 1308 v.s, 1257 v.s, 1153 v.s, 1122 s, 598 m, 544 m. ^{1}H NMR spectrum, δ, ppm: 1.57 d.d (1H, H_A, J = 5.4, 9.1 Hz), 2.13 d.d (1H, H_M, J = 5.4, 6.9 Hz), 2.33 s (3H, CH_3), 2.97 d.d (1H, H_X, J = 6.9, 9.1 Hz), 3.87 s (3H, OCH_3), 4.30 d and 4.44 d (1H each, CH_2SO_2, J = 13.7 Hz), 7.38 br.s (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 17.4 (C^3), 28.1 (CO**Me**), 35.6 (C^2), 42.0 weak (C^1), 53.5 (OMe), 60.0 (CH_2SO_2), 127.1 (C_{arom}), 128.9 (2C, C_{arom}), 129.1 (C_{arom}), 130.7 (2C, C_{arom}), 167.0 (C=O), 198.5 (Me**C**=O). Found, %: C 56.57; H 5.38; S 10.80. $C_{14}H_{16}O_5S$. Calculated, %: C 56.74; H 5.44; S 10.82.

Methyl 1-acetyl-2*t*-(phenylmethanesulfonyl)cyclopropane-1*r*-carboxylate (IXc′). Yield 36%, R_f 0.20, mp 87–88°C (from EtOAc–hexane). IR spec-

trum, ν, cm^{-1}: 3048 m, 1736 s, 1728 s, 1709 s, 1439 s, 1335 s, 1316 s, 1308 v.s, 1300 v.s, 1265 v.s, 1258 v.s, 1123 s, 1115 v.s, 795 m, 698 s, 536 s, 478 s. ^{1}H NMR spectrum, δ, ppm: 1.69 d.d (1H, H_A, J = 5.5, 9.1 Hz), 2.06 d.d (1H, H_M, J = 5.5, 6.7 Hz), 2.43 s (3H, CH_3), 3.01 d.d (1H, H_X, J = 6.7, 9.1 Hz), 3.76 s (3H, OCH_3), 4.34 d and 4.47 d (1H each, CH_2SO_2, J = 13.7 Hz), 7.35–7.41 m (3H, H_{arom}), 7.42–7.46 (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 16.4 (C^3), 30.5 (CO**Me**), 40.0 (C^1), 41.1 (C^2), 53.5 (OMe), 60.6 (CH_2SO_2), 127.2 weak (C_{arom}), 129.0 (2C, C_{arom}), 129.2 (C_{arom}), 130.9 (2C, C_{arom}), 68.3 (C=O), 198.4 (Me**C**=O). Found, %: C 56.55; H 5.35; S 10.71. $C_{14}H_{16}O_5S$. Calculated, %: C 56.74; H 5.44; S 10.82.

Methyl 2*t*-(phenylmethanesulfonyl)cyclopropane-1*r*-carboxylate (XIc). Yield 2%, R_f 0.13, mp 116–117°C (from EtOAc–hexane). IR spectrum, ν, cm^{-1}: 2947 w, 1732 v.s, 1319 s, 1296 s, 1223 s, 1130 s, 910 m, 729 m, 702 m. ^{1}H NMR spectrum, δ, ppm: 1.32–1.38 m (1H, H_A), 1.96–2.01 m (1H, H_Y), 2.19–2.25 m (1H, H_X), 2.38–2.44 m (1H, H_M), 3.80 s (3H, CH_3), 4.30 d and 4.42 d (1H each, CH_2SO_2, J = 13.7 Hz), 7.35–7.42 m (3H, H_{arom}), 7.46–7.53 (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 8.3 (C^3), 15.4 (C^1), 22.3 (C^2), 52.9 (OMe), 60.2 (CH_2SO_2), 127.8 weak (C_{arom}), 129.0 (3C, C_{arom}), 130.9 (2C, C_{arom}), 167.7 (C=O). Found, %: C 56.62; H 5.58; S 12.69. $C_{12}H_{14}O_4S$. Calculated, %: C 56.68; H 5.55; S 12.61.

Methyl 5-(phenylmethanesulfonyl)-4,5-dihydrofuran-3-carboxylate (Xc). Yield 7%, R_f 0.27, mp 133–134°C (from EtOAc–hexane). IR spectrum, ν, cm^{-1}: 2955 w, 1701 v.s, 1662 v.s, 1435 m, 1323 s, 1273 s, 1223 s, 1134 s, 1088 s, 1018 m, 760 m, 505 m. ^{1}H NMR spectrum, δ, ppm: 2.29 d.d (3H, CH_3, J = 1.4, 1.6 Hz), 3.04–3.15 m and 3.37–3.45 m (1H each, 4-H), 3.71 s (3H, OCH_3), 4.23 d and 4.48 d (1H each, CH_2SO_2, J = 14.1 Hz), 5.19 d.d (1H, 5-H, J = 5.5, 11.0 Hz), 7.37–7.45 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.7 (CH_3), 28.9 (C^4), 51.3 (OCH_3), 55.7 (CH_2SO_2), 87.6 (C^5), 103.3 (C^3), 126.9 weak (C_{arom}), 129.1 (2C, C_{arom}), 129.2 (C_{arom}), 130.9 (2C, C_{arom}), 164.7 (C^2), 166.2 (C=O). Found, %: C 56.82; H 5.41; S 10.71. $C_{14}H_{16}O_5S$. Calculated, %: C 56.74; H 5.44; S 10.82.

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