

Double Michael addition reactions of methyl-3-aryl-2-(Z-styrylsulfonyl)acrylate

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The double Michael addition of active methylene compounds, *viz.*, dimethyl malonate, ethyl cyanoacetate and malononitrile to methyl-3-aryl-2-(Z-styrylsulfonyl)-acrylate is described.

Keywords: Methyl-3-aryl-2-(Z-styrylsulfonyl)acrylate, dimethyl malonate, ethyl cyanoacetate, malononitrile, Triton B, double Michael addition

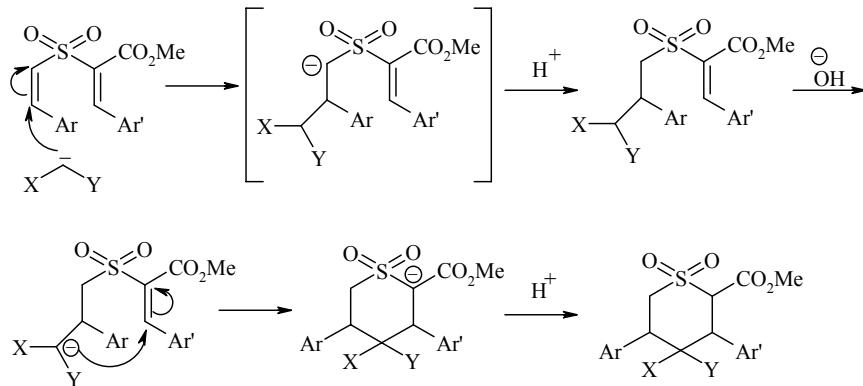
The Michael addition is the reaction between a compound having enolizable hydrogen and an activated olefin. It is known that under the influence of a base the activated olefins combine with a variety of substances having active hydrogens¹. The mode of addition in all the cases is same but the ease of addition depends upon the nature of groups at β -position. If these groups are aromatic the substituent in the nucleus has a quite remarkable effect on the reaction. Thus, Michael addition is one of the useful processes in organic synthesis. During the last one decade this group has been actively involved in the development of cyclic Michael adducts exploiting various Michael acceptors and utilized them for the development of different spiro heterocycles^{2,3}. In fact, Michael addition of malonic esters and a variety of active methylene compounds to sulfonyl activated olefins produced different adducts in the presence of catalytic amounts of base^{4,5}. However, Otto and

Yamamura reported that the double Michael addition of malonic esters to bis(styryl)sulfones in the presence of sodium methoxide or ethoxide led to an open-chain addition product before it undergoes cyclization⁶. On the other hand, the same reaction when carried out in the presence of Triton-B directly gave a cyclic product⁷. Thus, the double Michael addition of active methylene compounds to sulfonyl activated Michael acceptors in the presence of Triton-B appears to be a facile method for the synthesis of thiandioxides. However, reports about such compounds are scanty.

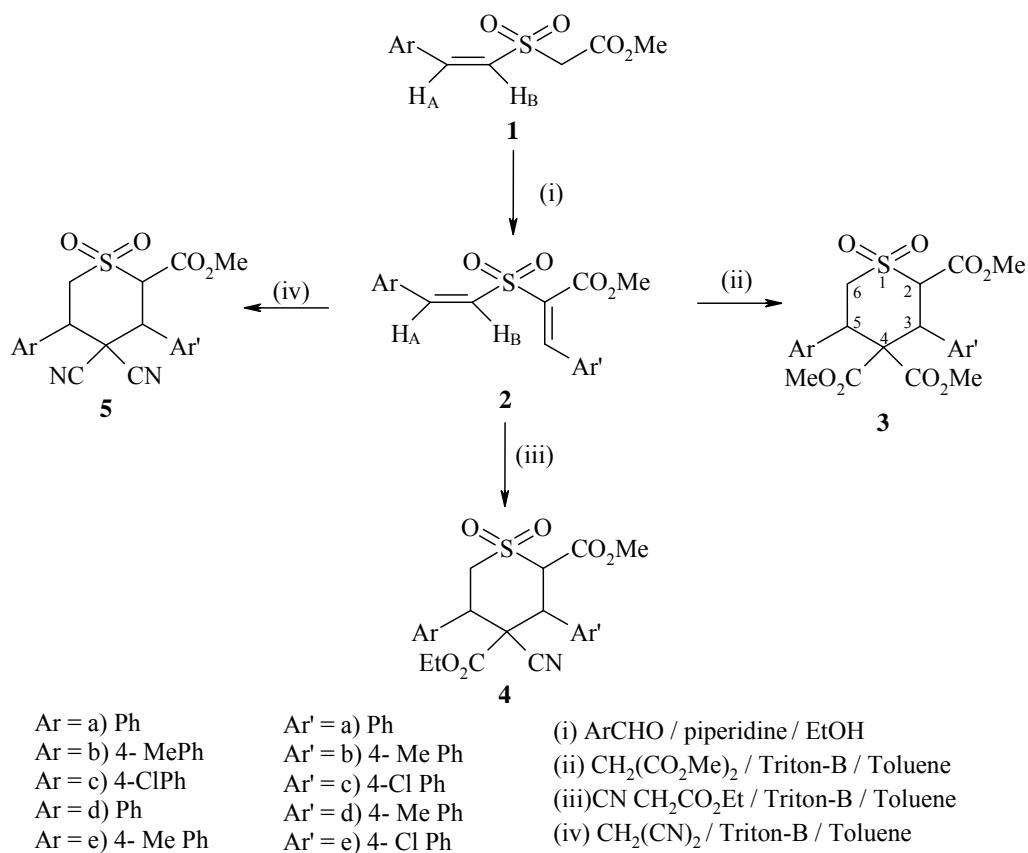
Results and Discussion

The present communication deals with the double Michael addition of active methylene compounds to methyl-3-aryl-2-(Z-arylethenesulfonyl)acrylate **2**. The synthetic intermediate **2** is prepared by the Knoevenagel condensation of *Z*-styrylsulfonylacetic acid methyl ester **1** with araldehyde in the presence of

Mechanism



X = Y = CO₂Me; X = CO₂Et, Y = CN; X = Y = CN



Scheme I

a catalytic amount of piperidine in absolute ethanol. The IR spectra of **2** displayed absorption bands in the regions 1640-1655 ($\text{C}=\text{C}$), 1120-1140, 1325-1340 (SO_2) and 1730- 1745 cm^{-1} (CO_2Me). The ^1H NMR spectra of **2** exhibited two singlets at δ_{H} 8.10 for $\text{Ar}'\text{CH}$ and at δ_{H} 3.62 for methoxy protons of carbomethoxy group and two doublets at δ_{H} 7.61, and 6.62 for H_A and H_B protons. The coupling constant values ($J = 9.7$ Hz) indicates that they possess *cis* geometry. The double Michael addition of dimethyl malonate, ethyl cyanoacetate and malononitrile to **2** in the presence of Triton-B in toluene produced 2,4,4-tricarbomethoxy-3, 5 - diphenyltetrahydrothiopyran-1,1-dioxide **3**, 2-carbomethoxy-4-cyano-4-carboethoxy-3,5-diphenyltetrahydrothiopyran-1,1-dioxide **4**, 2-carbomethoxy-4,4-dicyano-3,5-diphenyltetrahydrothiopyran-1,1-dioxide **5** (Scheme I, Table I).

The IR spectra of **3-5** exhibited absorption bands at 1130-1150 and 1330-1350 (SO_2), 1730-1750 cm^{-1} (CO_2Me). Apart from these, compounds **4** and **5** displayed a characteristic absorption band for CN at 2235-2250 cm^{-1} . The ^1H NMR spectra of **3a**, **4a** and **5a** showed three double doublets for methylene and methine protons, thus exhibiting an AMX splitting

pattern. The axial methylene proton, H_M , due to the deshielding effect of sulfonyl group absorbs at a more downfield region than the equatorial methylene proton, H_X . Thus, the double doublets observed at δ_{H} 4.31, 3.77, 3.09 in **3a**, at δ_{H} 4.24, 3.84, 3.22 in **4a** and at δ_{H} 4.23, 3.69, 3.18 in **5a** are assigned to H_A , H_M and H_X , respectively. The coupling constant values are found to be $J_{\text{AM}} = 9.8$ Hz, $J_{\text{MX}} = 14.5$ Hz, $J_{\text{AX}} = 5.3$ Hz. Besides, two doublets are observed at δ_{H} 4.61, 4.63, 4.59 (C_3H) and at δ_{H} 4.11, 4.09, 4.06 (C_2H) in **3a**, **4a** and **5a**. The coupling constant values ($J = 10.6$ Hz) indicates that they possess *trans* geometry (Table II). Hence, it is presumed that the two aryl groups at C-3 and C-5 positions are in *cis* orientation of the chair conformation of 4,4-disubstituted thiandioxide ring, while the carbomethoxy group at C-2 is in equatorial position (Figure 1). In fact, Otto and Yamamura have pointed out that in 3,5-diaryl-4,4-dialkoxy carbonyl-1,1-dioxides, the two aryl groups at 3 and 5 positions have diequatorial arrangement based on the NMR spectra^{2a}.

Three sharp singlets are observed in **3a** around δ_{H} 3.58, 3.74 and 3.87 which are assigned to methoxy

Table I — Physical characterization data of compounds **2-5**

Compd	m.p. °C	Yield (%)	Mol. formula (Mol. wt.)	Found % (Calcd.)		
				C	H	N
2a	79-80	69	C ₁₈ H ₁₆ O ₄ S (328.38)	65.79 (65.84)	4.84 4.91)	-
2b	104-06	66	C ₂₀ H ₂₀ O ₄ S (356.44)	67.28 (67.39)	5.57 5.66)	-
2c	98-99	72	C ₁₈ H ₁₄ Cl ₂ O ₄ S (397.27)	54.36 (54.42)	3.48 3.55)	-
2d	117-19	65	C ₁₉ H ₁₈ O ₄ S (342.41)	66.58 (66.65)	5.29 5.30)	-
2e	126-28	70	C ₁₉ H ₁₇ ClO ₄ S (376.85)	60.43 (60.55)	4.36 4.55)	-
3a	122-24	75	C ₂₃ H ₂₄ O ₈ S (460.5)	59.87 (59.99)	5.31 5.25)	-
3b	143-45	79	C ₂₅ H ₂₈ O ₈ S (488.55)	61.55 (61.46)	5.66 5.78)	-
3c	149-51	76	C ₂₃ H ₂₂ Cl ₂ O ₈ S (529.39)	52.14 (52.18)	4.17 4.19)	-
3d	136-38	72	C ₂₄ H ₂₆ O ₈ S (474.52)	60.69 (60.75)	5.55 5.52)	-
3e	129-31	74	C ₂₄ H ₂₅ ClO ₈ S (508.97)	56.69 (56.64)	4.99 4.95)	-
4a	132-34	76	C ₂₃ H ₂₃ NO ₆ S (441.5)	62.52 (62.57)	5.21 5.25	3.23 3.17)
4b	156-58	78	C ₂₅ H ₂₇ NO ₆ S (469.55)	64.04 (63.95)	5.83 5.80	3.04 2.98)
4c	151-53	75	C ₂₃ H ₂₁ Cl ₂ NO ₆ S (510.39)	54.16 (54.12)	4.17 4.15	2.79 2.74)
4d	148-50	71	C ₂₄ H ₂₅ NO ₆ S (455.52)	63.22 (63.28)	5.49 5.53	3.12 3.07)
4e	142-44	74	C ₂₄ H ₂₄ ClNO ₆ S (489.97)	58.74 (58.83)	4.91 4.94	2.89 2.86)
5a	166-68	65	C ₂₁ H ₁₈ N ₂ O ₄ S (394.44)	63.99 (63.94)	4.65 4.60	7.02 7.10)
5b	171-73	62	C ₂₃ H ₂₂ N ₂ O ₄ S (422.5)	65.42 (65.38)	5.28 5.25	6.69 6.63)
5c	158-60	66	C ₂₁ H ₁₆ Cl ₂ N ₂ O ₄ S (463.33)	54.41 (54.44)	3.53 3.48	6.12 6.05)
5d	182-84	67	C ₂₂ H ₂₀ N ₂ O ₄ S (408.47)	64.75 (64.69)	4.99 4.94	6.79 6.86)
5e	177-79	63	C ₂₂ H ₁₉ ClN ₂ O ₄ S (442.92)	59.60 (59.66)	4.28 4.32	6.27 6.32)

protons of three carbomethoxy groups. However, **4a** and **5a** showed a sharp singlet at δ_H 3.64, 3.54 for methoxy protons. Apart from these, **4a** displayed a quartet at δ_H 3.84 and a triplet at δ_H 1.28 for carboethoxy group.

The ^{13}C NMR spectra of **3a**, **4a** and **5a** showed δ_C values for methylene, methine and tertiary carbons of thiandioxide ring in the regions 58.6, 57.2, 56.6 (C-6),

24.6, 25.8, 25.3 (C-3), 59.9, 59.6, 60.1 (C-2), 27.3, 27.9, 27.2 (C-5) and 67.3, 68.8, 67.6, (C-4). The δ_C values for other carbons are given in **Table II**.

Experimental Section

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The homogeneity of the compounds was checked by TLC

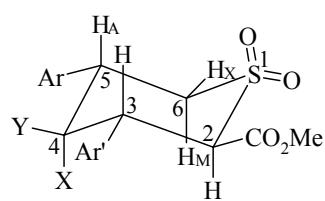
Table II — Spectral characterization data for **2-5**

Compd	¹ H NMR (δ ppm) (J in Hz)	¹³ C NMR (δ ppm)
2a	3.62 (s, 3H, OCH ₃), 6.62 (d, 1H, H _B , J = 9.7 Hz), 7.61 (d, 1H, H _A , J = 9.7 Hz), 8.10 (s, 1H, Ar'-CH), 7.12-7.48 (m, 10H, Ar-H)	53.1 (OCH ₃), 125.4 (=CHSO ₂), 129.7 (SO ₂ -C=(CO ₂ Me), 142.1 (=CH-Ar'), 145.4 (=CH-Ar), 176.1 (C=O), 128.2, 128.9, 129.4, 130.2, 130.8, 131.4, 131.6, 131.9 (aromatic carbons)
2b	2.28 (s, 6H, Ar-CH ₃ & Ar'-CH ₃), 3.58 (s, 3H, OCH ₃), 6.60 (d, 1H, H _B , J = 9.6 Hz), 7.58 (d, 1H, H _A , J = 9.6 Hz), 8.09 (s, 1H, Ar'-CH), 7.10-7.45 (m, 8H, Ar-H)	21.2 (Ar-CH ₃ & Ar'-CH ₃), 53.8 (OCH ₃), 125.9 (=CHSO ₂), 129.1 (SO ₂ -C=(CO ₂ Me), 141.8 (=CH-Ar'), 144.9 (=CH-Ar), 174.8 (C=O), 128.6, 129.1, 129.7, 130.4, 130.9, 131.2, 131.9, 132.4 (aromatic carbons)
2c	3.60 (s, 3H, OCH ₃), 6.64 (d, 1H, H _B , J = 9.9 Hz), 7.63 (d, 1H, H _A , J = 9.9 Hz), 7.90 (s, 1H, Ar'-CH), 7.32-7.53 (m, 8H, Ar-H)	51.7 (OCH ₃), 124.7 (=CHSO ₂), 129.3 (SO ₂ -C=(CO ₂ Me), 142.8 (=CH-Ar'), 145.6 (=CH-Ar), 174.1 (C=O), 128.8, 129.4, 129.9, 131.4, 131.8, 132.0, 132.4, 132.8 (aromatic carbons)
2d	2.35 (s, Ar'-CH ₃), 3.56 (s, 3H, OCH ₃), 6.65 (d, 1H, H _B , J = 9.8 Hz), 7.64 (d, 1H, H _A , J = 9.8 Hz), 7.96 (s, 1H, Ar'-CH), 7.28-7.50 (m, 9H, Ar-H)	22.4 (Ar'-CH ₃), 53.3 (-OCH ₃), 125.3 (=CHSO ₂), 128.8 (SO ₂ -C=(CO ₂ Me), 142.1 (=CH-Ar'), 146.9 (=CH-Ar), 174.6 (C=O), 128.0, 128.6, 129.2, 129.8, 131.1, 131.4, 131.8, 132.5 (aromatic carbons)
2e	2.29 (s, Ar-CH ₃), 3.59 (s, 3H, OCH ₃), 6.63 (d, 1H, H _B , J = 9.6 Hz), 7.60 (d, 1H, H _A , J = 9.6 Hz), 7.92 (s, 1H, Ar'-CH), 7.24-7.51 (m, 8H, Ar-H)	21.8 (Ar-CH ₃), 53.4 (-OCH ₃), 125.9 (=CHSO ₂), 127.9 (SO ₂ -C=(CO ₂ Me), 142.9 (=CH-Ar'), 147.4 (=CH-Ar), 173.8 (C=O), 128.2, 128.8, 129.6, 130.4, 130.8, 131.6, 132.0, 132.4 (aromatic carbons)
3a	3.09 (dd, 1H, H _X , J_{AX} = 5.6 Hz, J_{MX} = 15.2 Hz), 3.58 (s, 3H, OCH ₃), 3.74 (s, 3H, OCH ₃), 3.87 (s, 3H, OCH ₃), 4.11 (d, 1H, C ₂ -H), 3.37 (dd, 1H, H _M), 4.31 (dd, 1H, H _A , J_{AM} = 10.2 Hz), 4.61 (d, 1H, C ₃ -H, J = 10.6 Hz), 7.03-7.27 (m, 10H, Ar-H)	24.6 (C-3), 27.3 (C-5), 51.3, 54.6, 55.9 (3-OCH ₃), 58.6 (C-6), 59.9 (C-2), 67.3 (C-4), 173.9, 176.6, 179.3 (C=O), 126.6, 127.9, 128.6, 129.3, 129.9, 136.6, 139.3 (aromatic carbons)
3b	2.31 (s, 6H, Ar-CH ₃ & Ar'-CH ₃), 3.12 (dd, 1H, H _X , J_{AX} = 5.8 Hz, J_{MX} = 15.5 Hz), 3.52 (s, 3H, OCH ₃), 3.68 (s, 3H, OCH ₃), 3.82 (s, 3H, OCH ₃), 4.14 (d, 1H, C ₂ -H), 3.34 (dd, 1H, H _M), 4.26 (dd, 1H, H _A , J_{AM} = 10.4 Hz), 4.65 (d, 1H, C ₃ -H, J = 10.8 Hz), 7.08-7.36 (m, 8H, Ar-H)	20.9 (Ar-CH ₃ & Ar'-CH ₃), 24.2 (C-3), 27.9 (C-5), 50.7, 53.2, 54.7 (3-OCH ₃), 56.8 (C-6), 59.5 (C-2), 67.7 (C-4), 174.7, 175.6, 177.8 (C=O), 127.9, 127.7, 128.1, 128.9, 129.1, 129.6, 137.5, 138.7 (aromatic carbons)
3c	3.08 (dd, 1H, H _X , J_{AX} = 5.8 Hz, J_{MX} = 15.5 Hz), 3.58 (s, 3H, OCH ₃), 3.71 (s, 3H, OCH ₃), 3.84 (s, 3H, OCH ₃), 4.12 (d, 1H, C ₂ -H), 3.36 (dd, 1H, H _M), 4.22 (dd, 1H, H _A , J_{AM} = 10.6 Hz), 4.64 (d, 1H, C ₃ -H, J = 10.7 Hz), 7.02-7.31 (m, 8H, Ar-H)	24.7 (C-3), 27.1 (C-5), 50.2, 51.3, 51.4 (3-OCH ₃), 56.4 (C-6), 58.6 (C-2), 66.7 (C-4), 173.2, 175.1, 178.4 (C=O), 128.4, 129.0, 129.3, 129.6, 131.2, 137.9, 138.2 (aromatic carbons)
3d	2.35 (s, 3H, Ar'-CH ₃), 3.11 (dd, 1H, H _X , J_{AX} = 5.7 Hz, J_{MX} = 15.8 Hz), 3.54 (s, 3H, OCH ₃), 3.68 (s, 3H, OCH ₃), 3.73 (s, 3H, OCH ₃), 4.12 (d, 1H, C ₂ -H), 3.38 (dd, 1H, H _M), 4.28 (dd, 1H, H _A , J_{AM} = 10.6 Hz), 4.59 (d, 1H, C ₃ -H, J = 10.5 Hz), 7.10-7.39 (m, 9H, Ar-H)	22.7 (Ar'-CH ₃), 24.6 (C-3), 27.8 (C-5), 50.6, 51.4, 52.6 (3-OCH ₃), 56.7 (C-6), 59.5 (C-2), 67.8 (C-4), 174.0, 175.1, 177.1 (C=O), 128.5, 129.6, 131.4, 131.9, 132.7, 136.2, 138.5 (aromatic carbons)
3e	2.33 (s, 3H, Ar-CH ₃), 3.13 (dd, 1H, H _X , J_{AX} = 5.5 Hz, J_{MX} = 15.6 Hz), 3.49 (s, 3H, OCH ₃), 3.69 (s, 3H, OCH ₃), 3.76 (s, 3H, OCH ₃), 4.11 (d, 1H, C ₂ -H), 3.41 (dd, 1H, H _M), 4.27 (dd, 1H, H _A , J_{AM} = 10.6 Hz), 4.62 (d, 1H, C ₃ -H, J = 10.7 Hz), 7.11-7.42 (m, 8H, Ar-H)	21.3 (Ar-CH ₃), 24.2 (C-3), 28.4 (C-5), 50.6, 52.9, 55.7 (3-OCH ₃), 56.2 (C-6), 59.2 (C-2), 67.2 (C-4), 174.3, 175.5, 177.2 (C=O), 127.1, 127.4, 128.4, 128.8, 129.6, 130.1, 137.1, 138.5 (aromatic carbons)
4a	1.28 (t, 3H, OCH ₂ CH ₃), 3.22 (dd, 1H, H _X , J_{AX} = 5.5 Hz, J_{MX} = 15.1 Hz), 3.64 (s, 3H, OCH ₃), 3.75 (dd, 1H, H _M), 3.84 (q, 2H, OCH ₂), 4.09 (d, 1H, C ₂ -H), 4.24 (dd, 1H, H _A , J_{AM} = 10.1 Hz), 4.63 (d, 1H, C ₃ -H, J = 10.6 Hz), 7.12-7.60 (m, 10H, Ar-H)	13.4 (OCH ₂ CH ₃), 25.8 (C-3), 27.9 (C-5), 51.8 (CO ₂ CH ₃), 52.5 (OCH ₂ CH ₃), 57.2 (C-6), 59.6 (C-2), 68.8 (C-4), 114.8 (CN), 174.9, 175.8 (C=O), 127.7, 128.1, 128.9, 129.3, 129.8, 130.5, 137.4, 138.0 (aromatic carbons)

— *Contd*

Table II — Spectral characterization data for **2-5** — *Contd*

Compd	¹ H NMR (δ ppm) (<i>J</i> in Hz)	¹³ C NMR (δ ppm)
4b	1.24 (t, 3H, OCH ₂ CH ₃), 2.30 (s, 6H, Ar-CH ₃ & Ar'-CH ₃), 3.20 (dd, 1H, H _X , <i>J</i> _{AX} = 5.4 Hz, <i>J</i> _{MX} = 4.9 Hz), 3.57 (s, 3H, OCH ₃), 3.75 (dd, 1H, H _M), 3.81 (q, 2H, OCH ₂), 4.10 (d, 1H, C ₂ -H), 4.27 (dd, 1H, H _A , <i>J</i> _{AM} = 10.0 Hz), 4.65 (d, 1H, C ₃ -H, <i>J</i> = 10.9 Hz), 7.11-7.56 (m, 8H, Ar-H)	13.8 (OCH ₂ CH ₃), 21.6 (Ar-CH ₃ & Ar'-CH ₃), 24.5 (C-3), 27.9 (C-5), 52.0 (CO ₂ CH ₃), 53.9 (OCH ₂ CH ₃), 56.1 (C-6), 58.9 (C-2), 67.1 (C-4), 121.2 (CN), 174.3, (COO) 176.1 (C=O), 128.2, 129.1, 129.3, 129.9, 131.1, 132.3, 134.3, 134.6, (aromatic carbons)
4c	1.27 (t, 3H, OCH ₂ CH ₃), 3.17 (dd, 1H, H _X , <i>J</i> _{AX} = 5.3 Hz, <i>J</i> _{MX} = 14.7 Hz), 3.54 (s, 3H, OCH ₃), 3.71 (dd, 1H, H _M), 3.85 (q, 2H, OCH ₂), 4.12 (d, 1H, C ₂ -H), 4.24 (dd, 1H, H _A , <i>J</i> _{AM} = 10.0 Hz), 4.62 (d, 1H, C ₃ -H, <i>J</i> = 10.8 Hz), 7.15-7.58 (m, 8H, Ar-H)	13.6 (OCH ₂ CH ₃), 25.2 (C-3), 28.1 (C-5), 52.7 (CO ₂ CH ₃), 54.1 (OCH ₂ CH ₃), 56.9 (C-6), 59.1 (C-2), 67.9 (C-4), 115.6 (CN), 173.8, 176.8 (C=O), 127.4, 127.9, 128.7, 128.9, 129.4, 130.6, 137.8, 138.2 (aromatic carbons)
4d	1.25 (t, 3H, OCH ₂ CH ₃), 2.35 (s, 3H, Ar'-CH ₃), 3.22 (dd, 1H, H _X , <i>J</i> _{AX} = 5.6 Hz, <i>J</i> _{MX} = 15.1 Hz), 3.56 (s, 3H, OCH ₃), 3.74 (dd, 1H, H _M), 3.81 (q, 2H, OCH ₂), 4.09 (d, 1H, C ₂ -H), 4.25 (dd, 1H, H _A , <i>J</i> _{AM} = 10.2 Hz), 4.64 (d, 1H, C ₃ -H, <i>J</i> = 10.9 Hz), 7.11-7.49 (m, 9H, Ar-H)	13.5 (OCH ₂ CH ₃), 22.6 (Ar'-CH ₃), 24.4(C-3), 28.7 (C-5), 51.5 (CO ₂ CH ₃), 55.5 (OCH ₂ CH ₃), 56.2 (C-6), 58.6 (C-2), 66.6 (C-4), 115.2 (CN), 172.4, 176.2 (C=O), 127.1, 127.6, 128.3, 128.6, 129.8, 130.9, 137.4, 138.5 (aromatic carbons)
4e	1.21 (t, 3H, OCH ₂ CH ₃), 2.30 (s, 3H, Ar-CH ₃), 3.21 (dd, 1H, H _X , <i>J</i> _{AX} = 5.5 Hz, <i>J</i> _{MX} = 15.1 Hz), 3.55 (s, 3H, OCH ₃), 3.77 (dd, 1H, H _M), 4.13 (d, 1H, C ₂ -H), 3.83 (q, 2H, OCH ₂), 4.22 (dd, 1H, H _A , <i>J</i> _{AM} = 9.9 Hz), 4.61 (d, 1H, C ₃ -H, <i>J</i> = 10.7 Hz), 7.13-7.61 (m, 8H, Ar-H)	14.1 (OCH ₂ CH ₃), 21.8 (Ar-CH ₃), 23.7(C-3), 28.2 (C-5), 52.7 (CO ₂ CH ₃), 54.9 (OCH ₂ CH ₃), 57.1 (C-6), 59.2 (C-2), 67.2 (C-4), 122.8 (CN), 172.9, (COO) 175.2 (C=O), 128.4, 129.9, 130.7, 131.2, 132.4, 133.1, 133.8, 134.0 (aromatic carbons)
5a	3.18 (dd, 1H, H _X , <i>J</i> _{AX} = 5.3 Hz, <i>J</i> _{MX} = 14.5 Hz), 3.54 (s, 3H, OCH ₃), 3.69 (dd, 1H, H _M), 4.06 (d, 1H, C ₂ -H), 4.23 (dd, 1H, H _A , <i>J</i> _{AM} = 9.8 Hz), 4.59 (d, 1H, C ₃ -H, <i>J</i> = 10.6 Hz), 7.06-7.52 (m, 10H, Ar-H)	25.3 (C-3), 27.2 (C-5), 52.6 (CO ₂ CH ₃), 56.6 (C-6), 60.1 (C-2), 67.6 (C-4), 119.2 & 120.8 (CN), 175.8 (C=O), 128.1, 129.3, 129.8, 130.4 131.9, 132.6, 133.2, 133.9 (aromatic carbons)
5b	2.26 (s, 6H, Ar-CH ₃ & Ar'-CH ₃), 3.15 (dd, 1H, H _X , <i>J</i> _{AX} = 5.1 Hz, <i>J</i> _{MX} = 14.3 Hz), 3.46 (s, 3H, OCH ₃), 3.67 (dd, 1H, H _M), 4.01 (d, 1H, C ₂ -H), 4.26 (dd, 1H, H _A , <i>J</i> _{AM} = 9.7 Hz), 4.55 (d, 1H, C ₃ -H, <i>J</i> = 10.5 Hz), 7.08-7.56 (m, 8H, Ar-H)	21.7 (Ar-CH ₃ & Ar'-CH ₃), 25.7 (C-3), 27.4 (C-5), 53.9 (CO ₂ CH ₃), 57.1 (C-6), 58.9 (C-2), 69.2 (C-4), 119.8 & 121.2 (CN), 175.1 (C=O), 128.4, 129.0, 129.4, 130.1 131.6, 132.5, 133.0, 133.3 (aromatic carbons)
5c	3.19 (dd, 1H, H _X , <i>J</i> _{AX} = 5.3 Hz, <i>J</i> _{MX} = 14.6 Hz), 3.49 (s, 3H, -OCH ₃), 3.64 (dd, 1H, H _M), 4.08 (d, 1H, C ₂ -H), 4.25 (dd, 1H, H _A , <i>J</i> _{AM} = 9.9 Hz), 4.58 (d, 1H, C ₃ -H, <i>J</i> = 10.7 Hz), 7.26-7.66 (m, 8H, Ar-H)	26.1 (C-3), 27.9 (C-5), 52.5 (CO ₂ CH ₃), 57.3 (C-6), 60.3 (C-2), 68.9 (C-4), 118.6 & 121.8 (CN), 174.8 (C=O), 128.6, 129.3, 129.7, 130.5 131.8, 132.4, 133.6, 135.4 (aromatic carbons)
5d	2.34 (s, 3H, Ar'-CH ₃), 3.21 (dd, 1H, H _X , <i>J</i> _{AX} = 5.6 Hz, <i>J</i> _{MX} = 14.8 Hz), 3.51 (s, 3H, OCH ₃), 3.66 (dd, 1H, H _M), 4.09 (d, 1H, C ₂ -H), 4.22 (dd, 1H, H _A , <i>J</i> _{AM} = 10.2 Hz), 4.61 (d, 1H, C ₃ -H, <i>J</i> = 10.8 Hz), 7.18-7.60 (m, 9H, Ar-H)	22.9 (Ar'-CH ₃), 26.8 (C-3), 27.4 (C-5), 52.8 (CO ₂ CH ₃), 57.9 (C-6), 59.3 (C-2), 68.6 (C-4), 118.9 & 122.4 (CN), 175.1 (C=O), 128.8, 129.1, 129.4, 130.2, 131.3, 132.4, 133.2, 136.8 (aromatic carbons)
5e	2.29 (s, 3H, Ar-CH ₃), 3.18 (dd, 1H, H _X , <i>J</i> _{AX} = 5.4 Hz, <i>J</i> _{MX} = 14.5 Hz), 3.46 (s, 3H, OCH ₃), 3.68 (dd, 1H, H _M), 4.04 (d, 1H, C ₂ -H), 4.21 (dd, 1H, H _A , <i>J</i> _{AM} = 9.8 Hz), 4.59 (d, 1H, C ₃ -H, <i>J</i> = 10.6 Hz), 7.17-7.69 (m, 8H, Ar-H)	21.3 (Ar-CH ₃), 26.2 (C-3), 27.8 (C-5), 52.3 (CO ₂ CH ₃), 57.4 (C-6), 60.3 (C-2), 68.9 (C-4), 119.1 & 122.8 (CN), 175.6 (C=O), 126.8, 128.1, 129.0, 130.1, 131.4, 132.3, 133.1, 133.8 (aromatic carbons)

**Figure 1**

(silica gel H, BDH, ethyl acetate/hexane, 3:1). The IR spectra were recorded on a Thermo Nicolet IR 200 FT-IR spectrometer as KBr pellets and the wave numbers were given in cm^{-1} . The ¹H NMR spectra were recorded in CDCl₃ /DMSO-*d*₆ on a Varian EM-360 spectrometer (300 MHz). The ¹³C NMR spectra were recorded in CDCl₃ /DMSO-*d*₆ on a Varian VXR spectrometer operating at 75.5 MHz. All chemical shifts were reported in δ (ppm) using TMS as an

internal standard. The microanalyses were performed on Perkin-Elmer 240C elemental analyzer. The starting compound Z-styrylsulfonylacetic acid methyl ester **1** was prepared by the literature procedure⁸.

General procedure for the preparation of methyl-3-aryl-2-(Z-arylethenesulfonyl)acrylate, 2

To an equimolar (0.01 mole) of Z-styrylsulfonylacetic acid methyl ester **1**, araldehyde and absolute ethanol (10 mL), piperidine (0.3 mL) was added. The contents were refluxed for 6-8 hr. The solid separated on cooling was collected and purified by recrystallization from 2-propanol.

General procedure for the preparation of 2,4,4-tricarbomethoxy-3, 5 - diaryltetrahydrothiopyran-1,1-dioxide, 3/2-carbomethoxy-4-cyano-4-carboethoxy-3,5-diphenyltetrahydrothiopyran-1,1-dioxide, 4/2- carbomethoxy-4, 4-dicyano-3, 5-diphenyltetrahydrothiopyran-1,1-dioxide, 5

A mixture of **2** (0.01 mole), dimethyl malonate/ethyl cyanoacetate/malononitrile (0.015 mole), toluene (10 mL) and catalytic amount of Triton-B (0.3 mL) was refluxed for 3-4 hr. The reaction mixture was cooled and the solvent was removed under reduced

pressure. The solid obtained was purified by recrystallization from 2-propanol.

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