

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

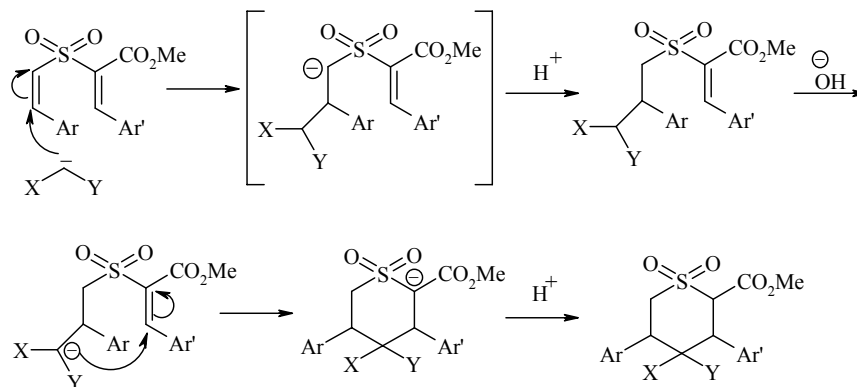
The Michael addition is the reaction between a compound having enolizable hydrogen and an activated olefin. It is known that under the influence of a base the activated olefins combine with a variety of substances having active hydrogens¹. The mode of addition in all the cases is same but the ease of 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)sulfonyls 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





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 carbomethoxy 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	^1H 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)

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)

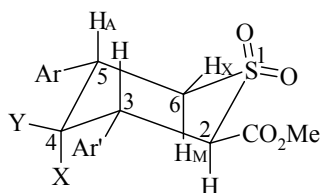

$$X = Y = \text{CO}_2\text{Me}; X = \text{CO}_2\text{Et}, Y = \text{CN}; X = Y = \text{CN}$$

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 $\text{CDCl}_3/\text{DMSO}-d_6$ on a Varian EM-360 spectrometer (300 MHz). The ^{13}C NMR spectra were recorded in $\text{CDCl}_3/\text{DMSO}-d_6$ 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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