

Cycloaddition Reactions of Azatrienes with Sulfene

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ABSTRACT

Unprecedented cycloaddition reactions of azatrienes (**1**) with sulfene leading to the synthesis of functionalized thiazine-dioxide derivatives (**5**) are described. The reactions were found to be highly regioselective resulting in the formation of only [4 + 2] cycloadducts.

Keywords: Azadiene; Azatriene; Cycloaddition; Sulfene; Thiazine-Dioxide

1. Introduction

1-Azadienes are remarkably efficient precursors for the synthesis of nitrogen-containing heterocycles [1-10]. The presence of multiple reactive sites makes them excellent candidates for various synthetic manipulations. For example, α,β -unsaturated imine can participate as a dienophile in a Michael type 1,4-addition (Rxn 1, **Figure 1**), or in a 1,2-addition (Rxn 2, **Figure 1**). Moreover, depending upon the reaction partner, 1-azadiene can react as 2π (Rxn 3, **Figure 1**) or 4π (Rxn 4, **Figure 1**) component in the cycloaddition reactions. It is believed that the electron density in the 1-azadiene system is a significant factor that defines its reactivity. The presence of electron-donating groups (-NR₂, -OR, -R, -OSi) typically on nitrogen atom increases their reactivity towards electrophiles (Rxn 5, **Figure 1**) or electron deficient dienophiles in the hetero Diels-Alder (HDA) reactions [11-13]. On the other hand, the presence of electron-withdrawing groups (-COR, -COOR, -SO₂) makes them prone to the attack of nucleophiles or electron rich dienophiles in the inverse electron-demand HDA reactions [14,15]. However, the 4π participation of the 1-azadienes is reported to suffer from low conversion, competitive [2 + 2] addition, and low diene reactivity due to an unfavorable *s-cis/s-trans* equilibrium [16,17]. In addition the tautomerization of substituted 1-azadienes to enamines precludes the [4 + 2] cycloaddition due to the instability of endocyclic enamine products. Consequently, only a limited number of 1-aza-but-1,3-diene structural variations and modified or restricted reaction conditions have been introduced that have permitted the productive 4π participation of α,β -unsaturated imines in [4 + 2] cycloaddition reactions.

Literature study reveals that the cycloaddition reactions of highly reactive heterodienophile sulfene have not

extensively been explored with the C=N double bond [18].

Recently, we reported a single pot synthesis of stable cross-conjugated azatrienes **1** (**Scheme 1**) along with the tandem [2 + 2] cycloaddition and highly facile [3,3]-sigmatropic rearrangements in their reactions with conjugated ketenes, leading to facile synthesis of functionalized azocinone derivatives [19]. In connection with our ongoing interest in this research area, we widened our study to the cycloaddition reactions of azatrienes with sulfene dienophile. To the best of our knowledge, this is a first report where the [4 + 2] cycloadditions of 1-azadienes are carried out with the sulfene.

2. Results and Discussion

The cycloadditions were realized by the dropwise addition of a solution of methanesulfonyl chloride (2eq.) to a cooled dichloromethane solution of azatrienes **1** [19,20] and triethylamine (3eq.). The reactions were found to be highly regioselective leading to the exclusive formation of cycloadducts **5** without any traces of corresponding [2 + 2] adducts **6** (**Scheme 1**).

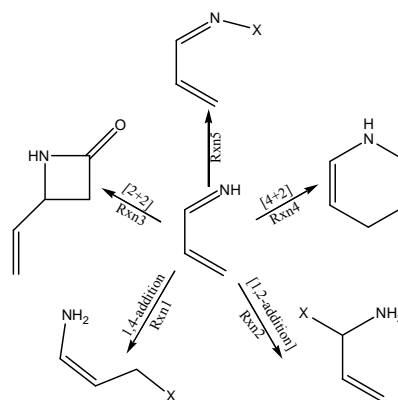
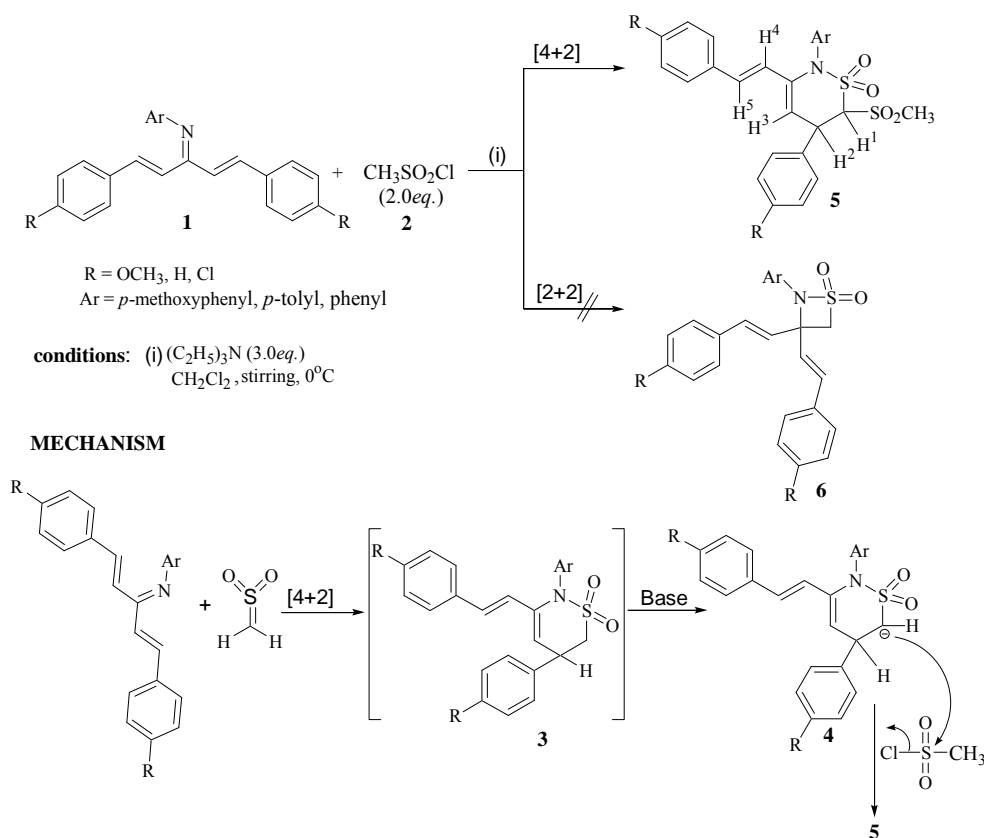


Figure 1. Different reaction types of 1-azadiene system.

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Scheme 1. Synthetic route and mechanism for the preparation of thiazine-dioxide derivatives from cycloaddition reactions of azatrienes (**1**) with sulfene.

The solid compounds, isolated after column chromatography, were characterized as thiazine-dioxide derivatives **5** on the basis of their available spectral data and analytical evidence. The plausible mechanistic pathway followed in these reactions involved the initial formation of [4 + 2] cycloadduct **3** as an intermediate that upon loss of proton under basic conditions get transformed into another intermediate **4** (Scheme 1). The intermediate **4** subsequently underwent sulfenylation under reaction conditions resulting in thiazine derivatives **5** in reasonable yields (Table 1). The treatment of azatrienes **5** with equimolar ratio of methanesulfonyl chloride and triethylamine led to the incompleteness of reaction with the partial generation of compound **5** (TLC based), clearly ruling out any possibility of compound **6** formed in the reaction. Moreover, the reaction did not proceed between **5** and methanesulfonyl chloride (TLC based) in the absence of triethylamine.

The detailed spectral features of the compounds **5** are given in the experimental section; however, the significant features are mentioned here. The compound **5a**, for example, analyzed for $\text{C}_{28}\text{H}_{29}\text{NO}_7\text{S}_2$, exhibited a molecular ion peak at m/z 555 (M^+) in its mass spectrum. The ^1H spectrum showed a characteristic doublet at δ 4.51 ($J = 10.7$ Hz) for one methine proton (H^1), one doublet of dou-

blet (dd) at δ 4.76 ($J = 10.7$ Hz & 3.3 Hz) for another methine proton (H^2), a doublet at δ 5.75 ($J = 3.3$ Hz) for olefinic proton (H^3) and two doublets at δ 6.21 and 6.52 ($J = 16.0$ Hz) corresponding to two *trans* olefinic protons (H^4 & H^5) respectively. The characteristic four singlets at δ 2.97, 3.76, 3.82 and 3.83 confirmed the presence of single $-\text{SO}_2\text{CH}_3$ and three methoxy groups in the compound.

3. Conclusion

The highly regioselective cycloadditions reactions of azatrienes (**1**) with sulfene dienophile is described, and a series of new functionalized thiazine-dioxide scaffolds has been prepared. This is a first report, to the best of our knowledge, in which the [4 + 2] cycloadditions of 1-azabutadienes are explored with the sulfene dienophile.

4. Experimental Section

4.1. General

The cross-conjugated azatrienes **1** were prepared according to the reported procedure [19,20]. Thionyl chloride and methanesulfonyl chloride used were commercially available. Dichloromethane dried over *di*-phosphorus pentoxide and stored over molecular sieves (4 Å). Mass

Table 1. Reactions of azatrienes (1) with the sulfene.

S.No.	Compound	R	Ar	Yield (%)	M.P. (°C)
1	5a	-OCH ₃	<i>p</i> -methoxyphenyl	79	113 - 114
2	5b	-OCH ₃	<i>p</i> -tolyl	76	134 - 135
3	5c	-OCH ₃	phenyl	69	121 - 122
4	5d	H	<i>p</i> -methoxyphenyl	77	118 - 119
5	5e	H	<i>p</i> -tolyl	68	125 - 126
6	5f	H	phenyl	71	130 - 131
7	5g	Cl	<i>p</i> -methoxyphenyl	75	136 - 137
8	5h	Cl	<i>p</i> -tolyl	72	132 - 133
9	5i	Cl	phenyl	78	116 - 117

spectra were recorded on Shimadzu GCMS-QP-2000 mass spectrometer. IR spectra were recorded on a Shimadzu D-8001 spectrophotometer. ¹H NMR spectra were recorded in deuteriochloroform (CDCl₃) with Bruker AC-E 300 (300 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shift values are expressed as ppm downfield from TMS and *J* values are in Hz. Splitting patterns are indicated as s: singlet, d: doublet and dd: doublet of doublet. ¹³C-NMR spectra were also recorded on AC-E 300 (75.0 MHz) spectrometer in a deuteriochloroform (CDCl₃) using tetramethylsilane (TMS) as an internal standard. Melting points were determined by open capillary method using Veego Precision Digital Melting Point apparatus (MP-D) and are uncorrected. Elemental analyses were performed on Heraeus CHN-O-Rapid Elemental Analyzer.

4.2. General Procedure for the Cycloaddition Reactions of Azatrienes (1) with Sulfene

To a well-stirred solution of azatrienes **1** (10 mmol) and triethylamine (30 mmol) in dry methylene chloride (30 mL) was added drop wise a solution of methanesulfonyl chloride (20 mmol) in dry methylene chloride (30 mL) over a period of 0.5 hour at 0°C. After completion of the reaction (TLC), the reaction mixture was first washed with the saturated sodium bicarbonate solution (2 × 25 mL) and water (2 × 50 mL) and the organic layer dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (2:10, v/v).

6-Methanesulfonyl-2,5-bis-(4-methoxy-phenyl)-3-[2-(4-methoxy-phenyl)-vinyl]-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5a). Light yellow solid, yield 79%; mp 113°C - 114°C; IR (KBr) 1604, 1510, 1463 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.97 (s, 3H, -SO₂CH₃), 3.76 (s, 3H, -OCH₃), 3.82 (s, 3H, -OCH₃), 3.83 (s, 3H, -OCH₃), 4.51 (d, *J* = 10.7 Hz, 1H, H¹), 4.76 (dd, *J* = 10.7 & 3.3 Hz, 1H, H²), 5.75 (d, *J* = 3.3 Hz, 1H, H³), 6.21 (d,

J = 16.0 Hz, 1H, H⁴), 6.52 (d, *J* = 16.0 Hz, 1H, H⁵), 6.78 (d, *J* = 8.6 Hz, 2H, ArH), 6.97 (d, *J* = 8.6 Hz, 2H, ArH), 7.15 (d, *J* = 8.6 Hz, 4H, ArH), 7.36 (d, *J* = 8.7 Hz, 2H, ArH), 7.44 (d, *J* = 8.7 Hz, 2H, ArH) ppm; ¹³C NMR (CDCl₃): δ 43.1 (-CH), 44.1 (-SO₂CH₃), 55.2 (-OCH₃), 55.3 (-OCH₃), 55.4 (-OCH₃), 75.9 (-CH), 96.1, 114.0, 114.5, 119.7, 120.8, 127.8, 127.9, 128.5, 129.6, 130.1, 131.1, 132.6, 136.3, 159.2, 159.4, 159.8 ppm; MS (EI) *m/z*: 555 (M⁺). Anal. Calcd. for C₂₈H₂₉NO₇S₂: C, 60.52; H, 5.26; N, 2.52%. Found: C, 60.71; H, 5.19; N, 2.47%.

6-Methanesulfonyl-5-(4-methoxy-phenyl)-3-[2-(4-methoxy-phenyl)-vinyl]-2-*p*-tolyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5b). Colorless solid, yield 76%; mp 134°C - 135°C; IR (KBr) 1603, 1510, 1463 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.05 (s, 3H, -CH₃), 3.00 (s, 3H, -SO₂CH₃), 3.76 (s, 3H, -OCH₃), 3.83 (s, 3H, -OCH₃), 4.49 (d, *J* = 10.8 Hz, 1H, H¹), 4.75 (dd, *J* = 10.8 & 3.4 Hz, 1H, H²), 5.77 (d, *J* = 3.4 Hz, 1H, H³), 6.22 (d, *J* = 16.0 Hz, 1H, H⁴), 6.50 (d, *J* = 16.0 Hz, 1H, H⁵), 6.77 (d, *J* = 8.6 Hz, 2H, ArH), 6.96 (d, *J* = 8.6 Hz, 2H, ArH), 7.14 (d, *J* = 8.6 Hz, 2H, ArH), 7.23 - 7.43 (m, 6H, ArH) ppm; ¹³C NMR (CDCl₃): δ 21.0 (-CH₃), 43.2 (-CH), 44.2 (-SO₂CH₃), 55.3 (-OCH₃), 55.4 (-OCH₃), 76.1 (-CH), 96.1, 114.0, 114.6, 120.2, 120.8, 126.4, 127.9, 128.3, 128.5, 129.6, 132.7, 135.8, 136.3, 138.4, 159.5, 159.8 ppm; MS (EI) *m/z*: 539 (M⁺). Anal. Calcd. for C₂₈H₂₉NO₆S₂: C, 62.32; H, 5.42; N, 2.60%. Found: C, 62.25; H, 5.51; N, 2.53%.

6-Methanesulfonyl-5-(4-methoxy-phenyl)-3-[2-(4-methoxy-phenyl)-vinyl]-2-phenyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5c). Pale yellow solid, yield 69%; mp 121°C - 122°C; IR (KBr) 1604, 1510, 1462 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.99 (s, 3H, -SO₂CH₃), 3.79 (s, 3H, -OCH₃), 3.82 (s, 3H, -OCH₃), 4.47 (d, *J* = 10.8 Hz, 1H, H¹), 4.73 (dd, *J* = 10.8 & 3.3 Hz, 1H, H²), 5.76 (d, *J* = 3.3 Hz, 1H, H³), 6.21 (d, *J* = 16.0 Hz, 1H, H⁴), 6.51 (d, *J* = 16.0 Hz, 1H, H⁵), 6.79 (d, *J* = 8.6 Hz, 2H, ArH), 6.94 (d, *J* = 8.6 Hz, 2H, ArH), 7.11 - 7.46 (m, 9H, ArH) ppm; ¹³C NMR (CDCl₃): δ 42.9 (-CH), 44.1 (-SO₂CH₃), 55.1 (-OCH₃), 55.2 (-OCH₃), 76.0 (-CH), 96.1,

114.0, 114.3, 120.1, 121.2, 125.8, 127.4, 128.2, 129.3, 130.8, 132.1, 134.9, 135.8, 138.6, 159.2, 159.6 ppm; MS (EI) m/z : 525 (M^+). Anal. Calcd. for $C_{27}H_{27}NO_6S_2$: C, 61.69; H, 5.18; N, 2.66%. Found: C, 61.78; H, 5.11; N, 2.56%.

6-Methanesulfonyl-2-(4-methoxy-phenyl)-5-phenyl-3-styryl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5d). Yellow solid, yield 77%; mp 118°C - 119°C; IR (KBr) 1607, 1517, 1460 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 3.01 (s, 3H, $-SO_2CH_3$), 3.82 (s, 3H, $-OCH_3$), 4.57 (d, $J = 10.5$ Hz, 1H, H^1), 4.77 (dd, $J = 10.5$ & 2.9 Hz, 1H, H^2), 5.82 (d, $J = 2.9$ Hz, 1H, H^3), 6.34 (d, $J = 16.0$ Hz, 1H, H^4), 6.58 (d, $J = 16.0$ Hz, 1H, H^5), 6.85 (d, $J = 8.5$ Hz, 2H, ArH), 6.97 (d, $J = 8.5$ Hz, 2H, ArH), 7.22 - 7.44 (m, 10H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 42.7 ($-CH$), 43.8 ($-SO_2CH_3$), 55.4 ($-OCH_3$), 76.1 ($-CH$), 96.0, 113.8, 114.2, 119.9, 122.8, 125.4, 126.3, 128.1, 128.4, 130.2, 131.7, 132.8, 133.6, 135.9, 155.1, 159.8 ppm; MS (EI) m/z : 495 (M^+). Anal. Calcd. for $C_{26}H_{25}NO_5S_2$: C, 63.01; H, 5.08; N, 2.83%. Found: C, 62.94; H, 5.17; N, 2.76%.

6-Methanesulfonyl-5-phenyl-3-styryl-2-p-tolyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5e). Colorless solid, yield 68%; mp 125°C - 126°C; IR (KBr) 1605, 1511, 1460 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 2.12 (s, 3H, $-CH_3$), 3.00 (s, 3H, $-SO_2CH_3$), 4.55 (d, $J = 10.6$ Hz, 1H, H^1), 4.74 (dd, $J = 10.6$ & 3.1 Hz, 1H, H^2), 5.82 (d, $J = 3.1$ Hz, 1H, H^3), 6.33 (d, $J = 16.0$ Hz, 1H, H^4), 6.54 (d, $J = 16.0$ Hz, 1H, H^5), 6.92 (d, $J = 8.6$ Hz, 2H, ArH), 7.10 (d, $J = 8.6$ Hz, 2H, ArH), 7.15 - 7.48 (m, 10H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 20.9 ($-CH_3$), 42.4 ($-CH$), 44.1 ($-SO_2CH_3$), 76.3 ($-CH$), 96.1, 114.1, 114.6, 120.4, 123.1, 124.9, 126.1, 128.6, 129.5, 130.2, 130.8, 131.6, 133.2, 133.9, 142.7, 159.5 ppm; MS (EI) m/z : 479 (M^+). Anal. Calcd. for $C_{26}H_{25}NO_4S_2$: C, 65.11; H, 5.25; N, 2.92%. Found: C, 65.23; H, 5.17; N, 2.86%.

6-Methanesulfonyl-2,5-diphenyl-3-styryl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5f). Colorless solid, yield 71%; mp 130°C - 131°C; IR (KBr) 1603, 1510, 1460 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 3.01 (s, 3H, $-SO_2CH_3$), 4.54 (d, $J = 10.5$ Hz, 1H, H^1), 4.71 (dd, $J = 10.5$ & 2.8 Hz, 1H, H^2), 5.82 (d, $J = 2.8$ Hz, 1H, H^3), 6.36 (d, $J = 16.0$ Hz, 1H, H^4), 6.53 (d, $J = 16.0$ Hz, 1H, H^5), 6.79 - 7.53 (m, 15H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 42.9 ($-CH$), 44.4 ($-SO_2CH_3$), 76.6 ($-CH$), 96.1, 114.0, 114.5, 120.6, 121.5, 122.5, 124.7, 126.7, 129.2, 130.5, 132.4, 133.4, 133.4, 135.7, 144.7, 159.6 ppm; MS (EI) m/z : 465 (M^+). Anal. Calcd. for $C_{25}H_{23}NO_4S_2$: C, 64.49; H, 4.98; N, 3.01%. Found: C, 64.59; H, 5.10; N, 2.96%.

5-(4-Chloro-phenyl)-3-[2-(4-chloro-phenyl)-vinyl]-6-methanesulfonyl-2-(4-methoxy-phenyl)-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5g). Yellow solid, yield 75%; mp 136°C - 137°C; IR (KBr) 1605, 1512, 1460 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 2.98 (s, 3H, $-SO_2CH_3$), 3.83 (s, 3H, $-OCH_3$), 4.55 (d, $J = 10.5$ Hz, 1H, H^1), 4.76 (dd, J

= 10.5 & 3.2 Hz, 1H, H^2), 5.82 (d, $J = 3.2$ Hz, 1H, H^3), 6.38 (d, $J = 16.0$ Hz, 1H, H^4), 6.59 (d, $J = 16.0$ Hz, 1H, H^5), 6.83 (d, $J = 8.7$ Hz, 2H, ArH), 6.97 (d, $J = 8.7$ Hz, 2H, ArH), 6.99 - 7.45 (m, 8H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 42.6 ($-CH$), 43.9 ($-SO_2CH_3$), 55.4 ($-OCH_3$), 76.2 ($-CH$), 96.0, 114.1, 114.4, 120.3, 122.6, 125.3, 126.8, 127.8, 128.8, 129.5, 131.2, 131.9, 133.4, 135.2, 154.2, 159.6 ppm; MS (EI) m/z : 563 (M^+). Anal. Calcd. for $C_{26}H_{23}Cl_2NO_5S_2$: C, 55.32; H, 4.11; N, 2.48%. Found: C, 55.26; H, 4.22; N, 2.52%.

5-(4-Chloro-phenyl)-3-[2-(4-chloro-phenyl)-vinyl]-6-methanesulfonyl-2-p-tolyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5h). Pale yellow solid, yield 72%; mp 132°C - 133°C; IR (KBr) 1603, 1510, 1460 cm^{-1} ; 1H NMR (300MHz, $CDCl_3$): δ 2.21 (s, 3H, $-CH_3$), 3.01 (s, 3H, $-SO_2CH_3$), 4.53 (d, $J = 10.5$ Hz, 1H, H^1), 4.71 (dd, $J = 10.5$ & 3.1 Hz, 1H, H^2), 5.80 (d, $J = 3.1$ Hz, 1H, H^3), 6.36 (d, $J = 16.0$ Hz, 1H, H^4), 6.53 (d, $J = 16.0$ Hz, 1H, H^5), 6.90 (d, $J = 8.7$ Hz, 2H, ArH), 7.06 (d, $J = 8.7$ Hz, 2H, ArH), 7.13 - 7.49 (m, 8H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 21.0 ($-CH_3$), 42.6 ($-CH$), 44.4 ($-SO_2CH_3$), 76.6 ($-CH$), 96.0, 114.0, 114.3, 120.5, 123.4, 123.8, 125.4, 127.1, 127.8, 131.7, 131.9, 133.4, 133.9, 134.5, 142.5, 159.8 ppm; MS (EI) m/z : 547 (M^+). Anal. Calcd. for $C_{26}H_{23}Cl_2NO_4S_2$: C, 56.93; H, 4.23; N, 2.55%. Found: C, 57.03; H, 4.29; N, 2.61%.

5-(4-Chloro-phenyl)-3-[2-(4-chloro-phenyl)-vinyl]-6-methanesulfonyl-2-phenyl-5,6-dihydro-2H-[1,2]thiazine 1,1-dioxide (5i). Colorless solid, yield 78%; mp 116°C - 117°C; IR (KBr) 1604, 1510, 1460 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 2.99 (s, 3H, $-SO_2CH_3$), 4.51 (d, $J = 10.4$ Hz, 1H, H^1), 4.71 (dd, $J = 10.4$ & 3.1 Hz, 1H, H^2), 5.82 (d, $J = 3.1$ Hz, 1H, H^3), 6.33 (d, $J = 16.0$ Hz, 1H, H^4), 6.50 (d, $J = 16.0$ Hz, 1H, H^5), 6.69 - 7.49 (m, 15H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 43.0 ($-CH$), 44.9 ($-SO_2CH_3$), 76.8 ($-CH$), 96.0, 114.1, 114.3, 120.9, 122.2, 122.9, 123.8, 126.6, 129.2, 131.4, 132.3, 133.2, 133.6, 134.4, 143.1, 159.7 ppm; MS (EI) m/z : 533 (M^+). Anal. Calcd. for $C_{25}H_{21}Cl_2NO_4S_2$: C, 56.18; H, 3.96; N, 2.62%. Found: C, 56.26; H, 4.09; N, 2.53%.

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