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# THE FREE RADICAL CYCLIZATION REACTION OF 1,6-DIENES WITH ALLYLSULFONES[1]

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*Key words*: free radical reaction; allylsulfone; 1,6-dienes; sulfonyl radical.

***Abstract***: A sulfonyl radical induced addition-cyclization reaction of 1,6-dienes with allylsulfones giving functionalized cyclopentane systems is described.

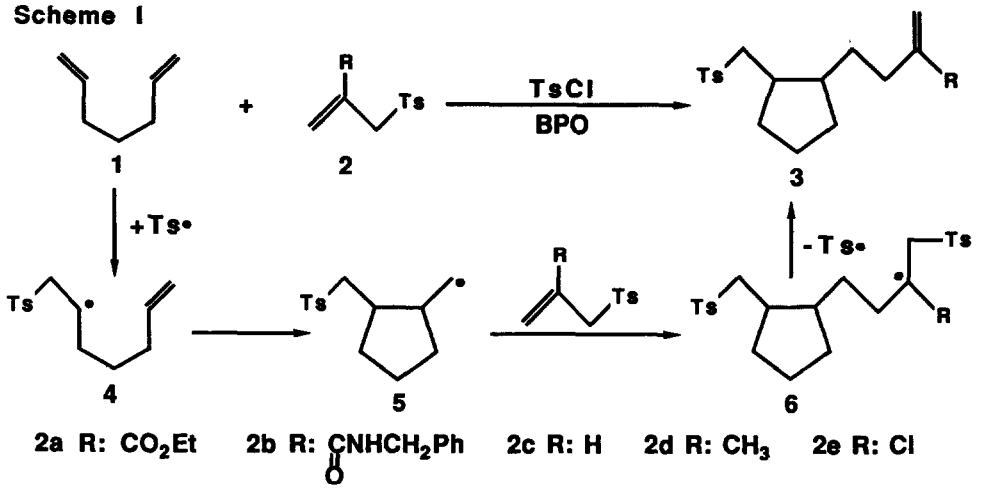
## INTRODUCTION:

Ring formation by free radical cyclization reaction has attracted particular interest and these cyclization reactions frequently occur with high, predictable, regio- and stereoselectivity[2]. The free radical addition reactions of allylsulfone have been studied[3]. These reactions are recongnized to undergo $S_H2'$ substitution of allylsulfone with carbon centered radicals. Free radical cyclization reactions mediated by sulfonyl radical have been reported by several groups [4,5]. We report here the results of sulfonyl radical induced addition-cyclization reaction of 1,6-dienes and allylsulfones.

## RESULTS AND DISCUSSION:

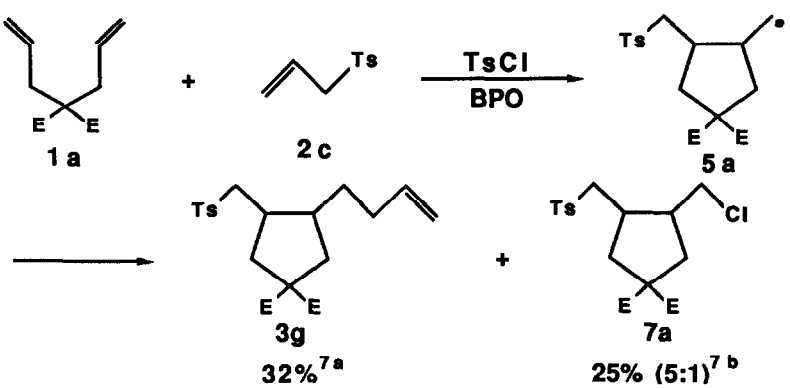
Treatment of a toluene solution of diene and allylsulfone (2 eq) with *p*-toluenesulfonyl chloride as a radical precursor furnished cyclopentane in modest yield (Scheme I). The results of this reaction are shown in Table I. In most case, the cyclopentane products were obtained as a mixture of cis- and trans-stereoisomers and the cis-isomer predominates[6].

**Scheme I**

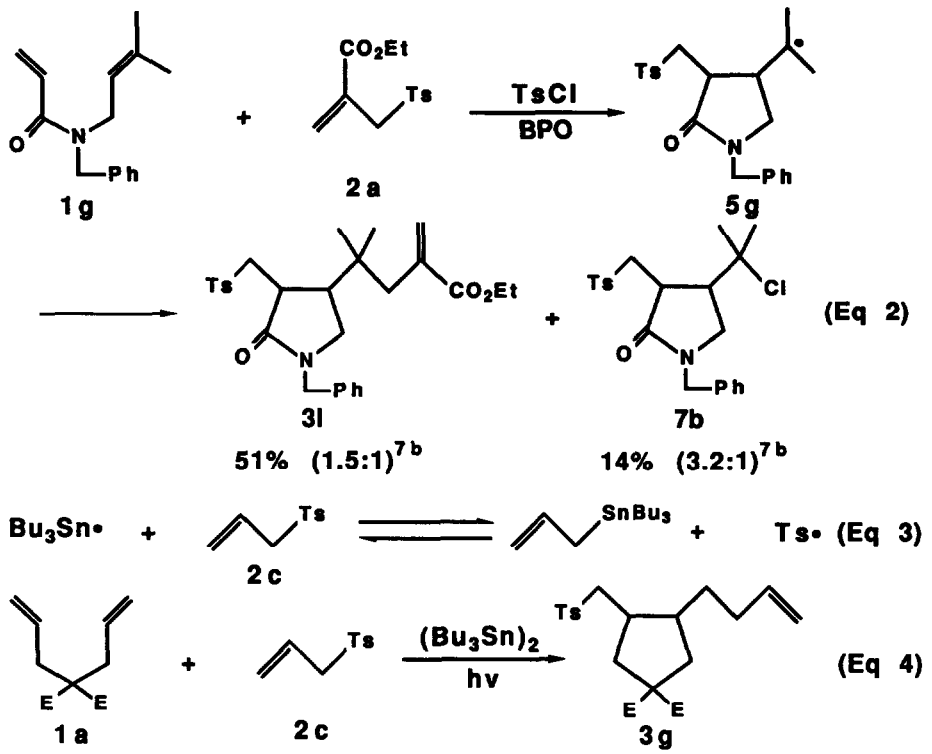



A possible mechanism for this three component coupling reaction is shown in Scheme I. Initiation occurs by *p*-toluenesulfonyl radical addition to diene **1**, followed by 5-exo cyclization to cyclopentylmethyl radical **5**, bimolecular addition of allylsulfone **2** to produce radical **6**, and termination via ejection of *p*-toluenesulfonyl radical to give cyclopentane product **3**.

When dienes **1a** and **1g** were treated with allylsulfone **2c** (10 eq) under BPO (dibenzoylperoxide) conditions, in addition to the desired products (**3g**, **3l**) the chloro products (**7a**, **7b**) were also obtained (Eq 1 and 2). These unexpected chloro products are derived from the chlorine atom abstraction of radical intermediate **5a** and **5g** from *p*-toluenesulfonyl chloride. These results suggest that this sulfonyl chloride induced free radical reaction is not feasible for unactivated allylsulfones (e.g. **2c**) and hindered radicals (e.g. **5g**). To overcome these limitations, another method for the generation of sulfonyl radical has to be used. It has been reported that sulfonyl radical can be generated from the reaction of



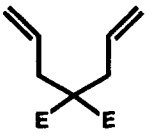
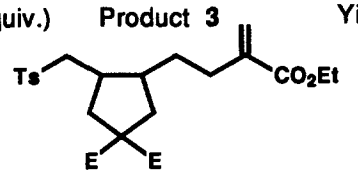
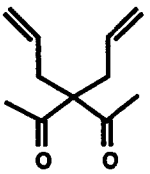
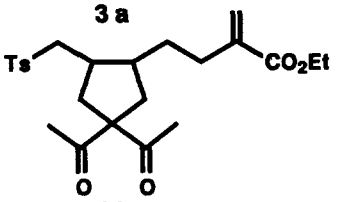
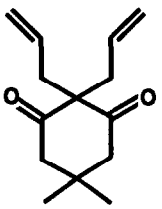
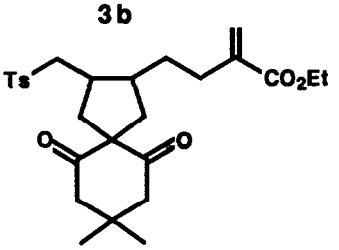
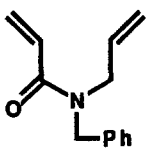
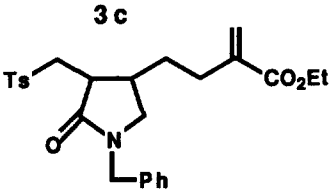
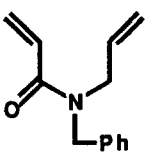
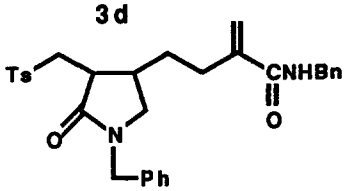
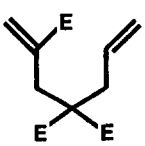
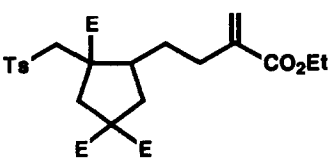

(Eq 1)




tin radical with allylsulfone (Eq 3)[8]. On this basis, we next examined the feasibility of bis(tributyltin) as tin radical precursor for this reaction. Thus, a benzene solution of **1a**, allylsulfone **2c** and bis(tributyltin) was irradiated at 300 nm giving **3g** in 49% and none of chloro product **7a** could be found (Eq 4). As shown in Table II, this tin radical induced reaction with either unreactive allylsulfone (Entry 1,2,3,5) or hindered radical (Entry 4,6,7,8) gave three component coupling product in modest to good yield and no chloro product could be found.

In conclusion, this three component coupling reaction can be achieved by using either p-toluenesulfonyl chloride or bis(tributyltin) as radical precursor and provides a method for the synthesis of functionalized carbocycles and heterocycles. Further application of this reaction in organic synthesis is promising.

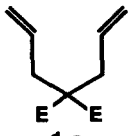
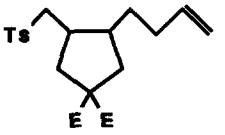
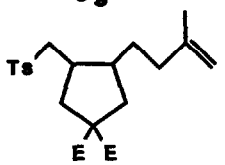
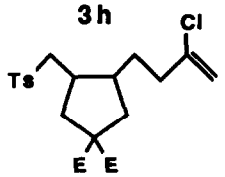
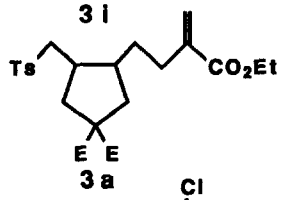
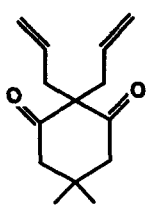
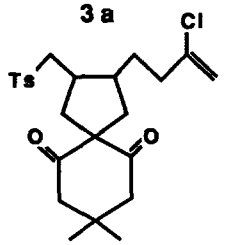
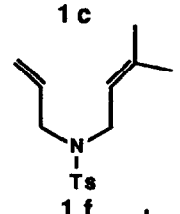
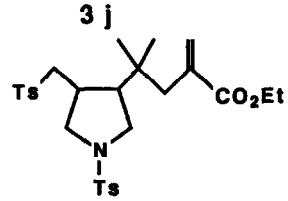
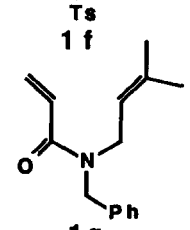
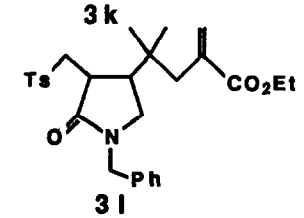
**Table I:** Free Radical Cyclization Reaction Induced By Sulfonyl Radical Generated From *p*-Toluenesulfonyl Chloride and BPO

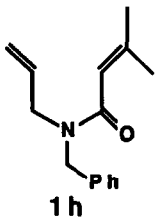
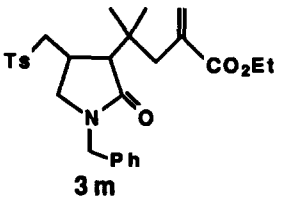
| Entry | Diene 1 | Sulfone 2 (mol. equiv.) | Product 3 | Yield (Ratio) |
|---|---|---|---|---|
| 1 |  1a | 2a (2) |  3a | 64%[a] |
| 2 |  1b | 2a (2) |  3b | 60% (9.6:1)[b] |
| 3 |  1c | 2a (2) |  3c | 63% (6.7:1)[b] |
| 4 |  1d | 2a (2) |  3d | 51% (3.6:1)[c] |
| 5 |  1d | 2b (2) |  3e | 46% (3.5:1)[c] |
| 6 |  1e | 2a (2) |  3f | 53% (1.1:1)[c] |

E: $CO_2Me$ Bn: $CH_2Ph$

(a)One stereoisomer was obtained . (b)The ratio was based on HPLC analysis. (c)The ratio was based on isolated yield.

**Table II.** Free Radical Cyclization Reaction Induced By Sulfonyl Radical Generated From Allylsufone and Bis(tributyltin)

| Entry | Diene 1 | Sulfone 2 (mol. equiv.) | Product 3 | Yield (Ratio) |
|---|---|---|---|---|
| 1 |  1 a | 2c (10) |  3 g | 49%[a] |
| 2 | 1 a | 2d (10) |  3 h | 65%[a] |
| 3 | 1 a | 2e (10) |  3 i | 86%[a] |
| 4 | 1 a | 2a (10) |  3 a | 51%[a] |
| 5 |  1 c | 2e (10) |  3 j | 81% (7.5:1)[b] |
| 6 |  1 f | 2a (2) |  3 k | 68% (1.8:1)[b] |
| 7 |  1 g | 2a (2) |  3 l | 54% (2:1)[c] |

8  **2a** (2)  70% (1.4:1)[c]

**1h** **3m**

(a)One stereoisomer was obtained . (b)The ratio was based on HPLC analysis. (c)The ratio was based on isolated yield.

## EXPERIMENTAL SECTION:

Melting points were taken with a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken with Hitachi 260-30 spectrometer. Nuclear magnetic resonance spectra were recorded on Bruker Wp100 FT-NMR spectrometer. NMR data were reported as follows: chemical shift [mutiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=mutiplet), coupling constant, integration, interpretation]. Mass spectra were recorded with Jeol JMS-HX 110 mass spectrometer. Elemental analysis was performed on a Heraeus CHN-Rapid Analyzer. High-performance liquid chromatography (HPLC) was conducted with a Shimadzu LC 6A and SPD-6A UV Spectrophotometric Detector using a TSK-gel Silica 150 column (4.6 mm x 25 cm) (Toyo Soda). Photochemical reaction was performed with a Rayonet reactor RPR-100. All reactions were carried out under an atmosphere of nitrogen. Anhydrous benzene and toluene were freshly distilled from calcium hydride. Analytical thin-layer chromatography was perfomed by precoated silica gel 60 F-254 plates (0.25 mm thick) of EM Laboratories. The reaction mixtures were purified by column chromatography over EM Laboratories silica gel (230-400 mesh) using a ethyl acetate-hexane mixture as eluent.

*General procedure for BPO initiation method.*

A solution of 161 mg (0.76 mmol) of methyl diallyl malonate, 417 mg (1.56 mmol) of allylsulfone **2a**, 50 mg (0.26 mmol) of *p*-toluenesulfonyl chloride and 50 mg (0.20 mmol) of benzoylperoxide in 6 ml of toluene was heated under reflux for 4 h. The reaction mixture was diluted with 50 ml of ethyl acetate, washed with three 25-mL portions of water, dried ($Na_2SO_4$) and concentrated in vacuo. The residue was chromatographed over 20 g silica gel (eluted with ethyl acetate-hexane, 1:3) to give 235 mg (64%) of **3a** as a single product.

*General procedure for the tin radical initiation method.*

A solution of 123 mg (0.54 mmol) of amide **1g**, 301 mg (1.12 mmol) of allylsulfone **2a** and 115 mg (0.20 mmol) of bis(tributyltin) in 6 ml of benzene

was irradiated at 300 nm for 4 h. The product was purified by the same procedure as above (eluted with ethyl acetate-hexane, 1:1.5) to give 145 mg (54%) of **3l** as 2:1 separable mixture.

**Methyl 3-(3-ethoxycarbonyl-3-buten-1-yl)-4-*p*-toluenesulfonylmethyl-cyclopentane-1,1-dicarboxylate 3a.** (cis isomer) colorless oil: IR ($CHCl_3$) 2980, 1731, 1299 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.29 (t, J=7.0Hz, 3H, $CH_3$), 1.1-1.7 (m, 2H), 1.8-2.8 (m, 8H), 2.45 (s, 3H, $CH_3$), 2.8-3.3 (m, 2H), 3.72 (s, 6H, $OCH_3$), 4.20 (q, J=7.0Hz, 2H, $OCH_2$), 5.44-5.57 (m, 1H, =CH), 6.06-6.2 (m , 1H, =CH), 7.36 (d, J=8.0Hz, 2H, ArH), 7.8 (d, J=8.0Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 13.9(q), 21.3(q), 28.1(t), 30.1(t), 36.1(d), 38.1(t), 41.9(d), 52.6(q), 55.5(t), 58.1(s), 60.4(t), 124.8(t), 127.8(d), 129.7(d), 136.5(s), 139.9(s), 144.5(s), 166.5(s), 172.4(s), 172.7(s); mass spectrum, m/e (relative intensity) 480($M^+$), 434(16), 233(13), 132(28), 91(100); exact mass calcd for $C_{24}H_{32}O_8S$ m/e 480.1818, found m/e 480.1804.

**1,1-Diacetyl-3-(3-ethoxycarbonyl-3-buten-1-yl)-4-*p*-toluenesulfonylmethyl-cyclopentane 3b.** (cis isomer) colorless oil: IR ($CHCl_3$) 2932, 1701, 1149 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.8-3.3 (m, 12H), 1.03 (t, J=7.1Hz, 3H, $CH_3$), 1.82 (s, 3H, $CH_3$), 1.83 (s, 3H, $CH_3$), 2.2 (s, 3H, $CH_3$), 3.93 (q, J=7.1Hz, 2H, $OCH_2$), 5.13-5.35 (m, 1H, =CH), 5.76-5.95 (m, 1H, =CH), 7.11 (d, J=8.2Hz, 2H, ArH), 7.55 (d, J=8.2Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 13.4 (q), 20.8(q), 25.6(q), 25.9(q), 27.5(t), 29.5(t), 33.8(t), 35.6(d), 41.3(d), 54.9(t), 59.9(t), 72.9(s), 124.3(t), 127.6(d), 129.2(d), 136.0(s), 139.4(s), 144.0(s), 166.0(s), 203.3(s), 204.0(s); mass spectrum, m/e (relative intensity) 449($M^+$+1), 406(43), 294(46), 251(55), 138(62), 91(100); exact mass calcd for $C_{24}H_{33}O_6S$ m/e 449.1998, found m/e 449.1982.

**2-(3-Ethoxycarbonyl-3-buten-1-yl)-3-*p*-toluenesulfonylmethyl-8,8-dimethyl-spiro[4,5]octa-6,10-dione 3c.** (cis isomer) colorless oil: IR ($CDCl_3$) 1715, 1708, 1695, 1146 $cm^{-1}$, $^1H$ NMR ($CDCl_3$) δ 0.92 (s, 3H, $CH_3$), 1.02 (s, 3H, $CH_3$), 1.28 (t, J=7.1Hz, 3H, $CH_3$), 1.0-1.55 (m, 2H), 1.75-2.9 (m, 12H), 2.45 (s, 3H, $CH_3$), 2.95-3.2 (m, 2H, $CH_2SO_2$), 4.18 (q, J=7.1Hz, 2H, $OCH_2$), 5.44-5.56 (m, 1H, =CH), 6.04-6.17 (m, 1H, =CH), 7.36 (d, J=8.1Hz, 2H, ArH), 7.79 (d, J=8.1Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$ ) δ 14.0(q), 21.4(q), 27.7(q), 28.4(t), 28.7(q), 30.2(t), 30.3(s), 34.3(t), 36.8(d), 37.6(t), 42.8(d), 51.2(t), 51.7(t),54.8(t), 60.4(t), 69.7(s), 124.8(t), 127.8(s), 129.8(s), 136.9(s), 140.1(s), 144.5(s), 166.7(s), 207.1(s), 208.0(s); mass spectrum, m/e (relative intensity) 488($M^+$, 9), 442(13), 333(10), 259(22), 91(47), 83(100); exact mass calcd for $C_{27}H_{36}O_6S$ m/e 488.2233, found m/e 488.2237.

***N*-Benzyl-4-(3-ethoxycarbonyl-3-buten-1-yl)-3-*p*-toluenesulfonylmethyl-pyrrolidin-2-one 3d.** (cis isomer) colorless oil: IR

($CHCl_3$) 1708, 1698, 1149 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.1-3.9 (m, 10H), 1.28 (t, J=7.2Hz, 3H, $CH_3$), 2.44 (s, 3H, $CH_3$), 4.18 (q, J=7.2Hz, 2H, $OCH_2$), 4.3-4.53 (m, 2H, $NCH_2$), 5.5-5.67 (m, 1H, =CH), 6.07-6.25 (m, 1H, =CH), 7.0-7.5 (m, 5H, ArH), 7.35 (d, J=8.3Hz, 2H, ArH), 7.82 (d, J=8.3Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.0(q), 21.4(q), 27.0(t), 28.9(t), 34.0(d), 41.1(d), 46.9(t), 48.7(t), 52.2(t), 60.5(t), 124.9(t), 127.6(d), 127.8(d), 128.1(d), 128.6(d), 129.8(d), 135.8(s), 136.4(s), 139.7(s), 144.7(s), 166.6(s), 171.8(s); mass spectrum, m/e (relative intensity) 469($M^+$, 7), 314(36), 286(12), 91(100); exact mass calcd for $C_{26}H_{31}O_5NS$ m/e 469.1923, found m/e 469.1931. (trans isomer) colorless oil: IR ($CHCl_3$) 2953, 1701, 1149 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ1.0-2.9 (m, 4H), 1.29 (t, J=7.0Hz, 3H, $CH_3$), 2.45 (s, 3H, $CH_3$), 2.95-3.85 (m, 6H), 4.19 (q, J=7.0Hz, 2H, $OCH_2$), 4.42 (s, 2H, $CH_2N$), 5.39-5.52 (m, 1H, =CH), 6.06-6.18 (m, 1H, =CH), 7.08-7.47 (m, 5H), 7.36 (d, J=8.3Hz, 2H, ArH), 7.82 (d, J=8.3Hz, 2H, ArH); mass spectrum, m/e (relative intensity) 469($M^+$, 12), 154(12), 129(21), 91(100); exact mass calcd for $C_{26}H_{31}NO_5S$ m/e 469.1923, found m/e 469.1916.

***N*-Benzyl-4-(3-*N*-benzylcarbamoyl-3-buten-1-yl)-3-*p*-toluenesulfonylmethyl-pyrrolidin-2-one 3e.** (cis isomer) colorless oil: IR (neat) 1683, 1302, 1152 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.35-1.9 (m, 2H), 1.95-3.85 (m, 8H), 2.45 (s, 3H, $CH_3$), 4.25-4.7 (m, 4H, $NCH_2$), 5.23-5.4 (m, 1H, =CH), 5.5-5.7 (m, 1H, =CH), 6.3-6.6 (m, 1H, NH), 7.0-7.5 (m, 10H, ArH), 7.35 (d, J=8.3Hz, 2H, ArH), 7.77 (d, J=8.3Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.1(q), 21.5(q), 29.1(t), 32.3(t), 37.2(d), 43.2(d), 46.9(t), 50.4(t), 57.2(t), 60.6(t), 125.0(t), 127.7(d), 127.8(d), 128.0(d), 128.7(d), 129,8(d), 135.7(s), 136.6(s), 139.7(s), 144.8(s), 166.8(s), 172.6(s); mass spectrum, m/e (relative intensity) 530($M^+$), 375(29), 213(13), 105(20), 91(100); exact mass calcd for $C_{31}H_{34}N_2O_4S$ m/e 530.2239, found m/e 530.2244. (trans isomer) colorless oil: IR ($CHCl_3$) 1683, 1305, 1151 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.0-2.8 (m, 6H), 2.44 (s, 3H, $CH_3$), 2.9-3.9 (m, 4H), 4.2-4.7 (m, 4H, $CH_2N$), 5.14-5.3 (m, 1H, =CH), 5.48-5.64 (m, 1H, =CH), 6.2-6.5 (m, 1H, NH), 7.0-7.6 (m, 10H, ArH), 7.34 (d, J=8.3Hz, 2H, ArH), 7.77 (d, J=8.3Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.0(q), 21.4(q), 29.8(t), 32.2(t), 36.9(d), 43.0(d), 43.4(t), 47.1(t), 50.3(t), 57.0(t), 117.9(t), 127.1(d), 127.6(d), 127.7(d), 127.9(d), 128.4(d), 128.6(d), 129.8(d), 135.7(s), 136.6(s), 138.3(s), 144.4(s), 144.7(s), 168.7(s), 172.8(s); mass spectrum, m/e (relative intensity) 530($M^+$), 469(11), 406(25), 360(17), 251(31), 177(29), 91(100); exact mass calcd for $C_{31}H_{34}N_2O_4S$ m/e 530.2239, found m/e 530.2228.

**Methyl 3-(3-ethoxycarbonyl-3-buten-1-yl)-4-methoxycarbonyl-4-*p*-toluenesulfonylmethyl-cyclopentane-1,1-dicarboxylate 3f.** (cis isomer) colorless oil: IR ($CHCl_3$) 2956, 1731, 1272, 1152 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.8-2.53 (m, 7H), 1.26 (t, J=7.2Hz, 3H, $CH_3$), 2.45 (s, 3H, $CH_3$), 2.8 and 3.32 (AB system, J=14Hz, 2H, $CH_2$), 3.17 and 4.0 (AB system, J=13Hz, 2H, $CH_2$), 3.63 (s, 3H,

$OCH_3$), 3.74 (s, 3H, $OCH_3$), 3.79 (s, 3H, $OCH_3$), 4.16 (q, J=7.2Hz, 2H, $OCH_2$), 5.42-5.52 (m, 1H, =CH), 6.06-6.16 (m, 1H, =CH), 7.35 (d, J=8.2Hz, 2H, ArH), 7.78 (d, J=8.2Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.1(q), 21.5(q), 29.0(t), 30.6(t), 37.7(t), 40.6(t), 49.8(d), 52.0(q), 52.7(q), 53.0(q), 54.0(s), 58.4(s), 60.6(t), 63.5(t), 124.9(t), 127.7(d), 129.8(d), 138.2(s), 139.9(s), 144.6(s), 166.6(s), 171.6(s), 172.3(s), 173.3(s); mass spectrum, m/e (relative intensity) 539($M^+$, 13), 460(58), 305(74), 217(72), 91(100); exact mass calcd for $C_{26}H_{34}O_{10}S$ m/e 538.1873, found m/e 538.1863. (trans isomer) colorless oil: IR ($CHCl_3$) 1731, 1269, 1152 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.0-2.6 (m, 7H), 1.27 (t, J=7.0Hz, 3H, $CH_3$), 2.45 (s, 3H, $CH_3$), 3.07 and 3.40 (AB system, J=15Hz, 2H, $CH_2$), 3.27 and 3.69 (AB system, J=15Hz, 2H, $CH_2SO_2$), 3.69 (s, 3H, $OCH_3$), 3.78 (s, 6H, $OCH_3$), 4.17 (q, J=7.0Hz, 2H, $OCH_2$), 5.4-5.55 (m, 1H, =CH), 6.02-6.18 (m, 1H, =CH), 7.35 (d, J=8.2Hz, 2H, ArH), 7.77 (d, J=8.2Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.1(q), 21.5(q), 28.2(t), 30.4(t), 38.0(t), 39.4(t), 48.5(d), 52.5(q), 52.9(q), 53.1(q), 53.4(s), 57.7(s), 57.9(t), 60.6(t), 124.9(t), 127.8(d), 129.7(d), 138.3(s), 139.9(s), 144.5(s), 166.6(s), 172.1(s), 172.4(s), 173.4(s); mass spectrum, m/e (relative intensity) 538($M^+$, 13), 383(67), 245(57), 216(73), 91(100); exact mass calcd for $C_{26}H_{34}O_{10}S$ m/e 538.1873, found m/e 538.1868.

**Methyl 3-(3-buten-1-yl)-4-*p*-toluenesulfonylmethyl-cyclopentane-1,1-dicarboxylate 3g.** (cis isomer) colorless oil: IR ($CHCl_3$) 2956, 1731, 1271 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.0-1.5 (m, 2H), 1.7-2.8 (m, 8H), 2.46 (s, 3H, $CH_3$), 2.9-3.2 (m, 2H, $CH_2SO_2$), 3.71 (s, 6H, $OCH_3$), 4.8-5.1 (m, 2H, =CH), 5.45-5.96 (m, 1H, =CH), 7.37 (d, J=8.3Hz, 2H, ArH), 7.79 (d, J=8.3Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 21.4(q), 28.0(t), 31.6(t), 36.3(d), 38.1(t), 41.6(d), 52.6(q), 55.8(t), 58.2(s), 114.8(t), 127.8(d), 129.8(d), 136.5(s), 137.6(d), 144.5(s), 172.4(s), 172.8(s); mass spectrum, m/e (relative intensity) 376(24), 344(14), 316(19), 252(100), 221(44), 192(30).

**Methyl 3-(3-methyl-3-buten-1-yl)-4-*p*-toluenesulfonylmethyl-cyclopentane-1,1-dicarboxylate 3h.** (cis isomer) colorless oil: IR ($CHCl_3$) 2956, 1731, 1272, 1146 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.0-1.5 (m, 2H), 1.67 (s, 3H, $CH_3$), 1.75-2.75 (m, 8H), 2.46 (s, 3H, $CH_3$), 2.8-3.3 (m, 2H, $CH_2SO_2$), 3.72 (s, 6H, $OCH_3$), 4.5-7.5 (m, 2H, =CH), 7.37 (d, J=8.1Hz, 2H, ArH), 7.80 (d, J=8.1Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 21.5(q), 22.1(q), 26.9(t), 35.6(t), 36.4(d), 38.2(t), 41.9(d), 52.7(q), 55.9(t), 58.3(s), 110.3(t), 127.9(d), 129.9(d), 136.6(s), 144.6(s), 144.9(s), 172.6(s), 172.9(s); mass spectrum, m/e (relative intensity) 422($M^+$), 390(28), 330(16), 266(100), 235(50), 206(56); exact mass calcd for $C_{22}H_{30}O_6S$ m/e 422.1763, found 422.1738.

**Methyl 3-(3-chloro-3-buten-1-yl)-4-*p*-toluenesulfonylmethyl-cyclopentane-1,1-dicarboxylate 3i.** (cis isomer) pale yellow oil: IR (CHCl3) 2956, 1731, 1272 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.2-1.7 (m, 2H), 1.84-3.76 (m, 8H),

2.46 (s, 3H, $CH_3$), 3.0-3.23 (m, 2H, $CH_2SO_2$), 3.72 (s, 6H, $OCH_3$), 5.12 (s, 2H, =CH), 7.37 (d, J=8.0Hz, 2H, ArH), 7.80 (d, J=8.0Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 21.4(q), 26.5(t), 36.3(d), 37.1(t), 38.0(t), 38.2(t), 41.2(d), 52.7(q), 55.8(t), 58.2(s), 112.5(t), 127.8(d), 129.8(d), 136.5(s), 141.8(s), 144.7(s), 172.4(s), 172.7(s); mass spectrum, m/e (relative intensity) 442($M^+$, 13), 410(74), 374(29), 255(100), 211(35); exact mass cacld for $C_{21}H_{27}ClO_6S$ m/e 442.1217 found m/e 442.1207.

**2-(3-Chloro-3-buten-1-yl)-3-*p*-toluenesulfonylmethyl-8,8-dimethyl-spiro[4,5]octa-6,10-dione 3j.** (cis isomer) pale yellow oil: iR ($CHCl_3$) 2962, 1728, 1695, 1146 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.91 (s, 3H, $CH_3$), 1.02 (s, 3H, $CH_3$), 1.3-1.6 (m, 2H), 1.77-2.84 (m, 12H), 2.45 (s, 3H, $CH_3$), 2.85-3.26 (m, 2H, $CH_2SO_2$), 5.11 (s, 2H, =CH), 7.36 (d, J=8.2Hz, 2H, ArH), 7.78 (d, J=8.2Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 21.3(q), 26.5(t), 27.5(q), 28.4(q), 32.1(s), 33.9(t), 36.6(d), 37.0(t), 37.4(t), 41.8(d), 50.9(t), 51.4(t), 54.8(t), 69.4(s), 112.3(d), 127.6(d), 129.7(d), 136.4(s), 141.7(s), 144.5(s), 207.0(s), 207.9(s); mass spectrum, m/e (relative intensity) 450($M^+$, 100), 415(8), 294(36), 259(26), 218(12); exact mass calcd for $C_{24}H_{31}ClO_4S$ m/e 450.1631, found m/e 450.1636.

***N*-*p*-Toluenesulfonyl-3-(1,1-dimethyl-3-ethoxycarbonyl-3-buten-1-yl)-4-*p*-toluenesulfonylmethyl-pyrrolidine 3k.** (cis isomer) colorless oil: IR ($CHCl_3$) 2974, 1713, 1161 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.74 (s, 6H, $CH_3$), 1.27 (t, J=7.1Hz, 3H, $CH_3$), 1.6-3.95 (m, 8H), 2.16 (s, 2H, $CH_2$), 2.45 (s, 6H, $CH_3$), 4.16 (q, J=7.1Hz, 2H, $CH_2O$), 5.3-5.45 (m, 1H, =CH), 6.1-6.23 (m, 1H, =CH), 7.35 (d, J=8.1Hz, 2H, ArH), 7.75 (d, J=8.1Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.0(q), 21.4(q), 21.5(q), 24.7(q), 25.7(q), 34.2(s), 34.9(d), 41.4(t), 46.2(t), 51.5(d), 52.3(t), 53.6(t), 60.8(t), 127.3(d) ,127.9(d), 128.0(t), 129.7(d), 129.8(d), 133.6(s), 136.2(s), 137.0(s), 143.5(s), 144.8(s), 167.5(s); mass spectrum, m/e (relative intensity) 547($M^+$), 434(20), 392(100), 278(13), 236(97); exact mass calcd for $C_{28}H_{37}NO_6S_2$ m/e 547.2062, found m/e 547.2048.

***N*-Benzyl-4-(1,1-dimethyl-3-ethoxycarbonyl-3-buten-1-yl)-3-*p*-toluenesulfonylmethyl-pyrrolidin-2-one 3l.** (cis isomer) colorless oil: IR ($CHCl_3$) 1710, 1689, 1146 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.76 (s, 3H, $CH_3$), 0.84 (s, 3H, $CH_3$), 1.26 (t, J=7.0Hz, 3H, $CH_3$), 2.26 (s, 2H, $CH_2$), 2.44 (s, 3H, $CH_3$), 2.52-3.66 (m, 6H), 4.16 (q, J=7.0Hz, $CH_2O$), 4.41 (s, 2H, $CH_2N$), 5.4-5.6 (m, 1H, =CH), 6.14-6.28 (m, 1H, =CH), 7.1-7.48 (m, 5H, ArH), 7.34 (d, J=8.0Hz, 2H, ArH), 7.81 (d, J=8.0Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 13.9(q), 21.4(q), 22.4(q), 23.5(q), 36.5(s), 39.6(t), 40.0(d), 43.5(d), 46.5(t), 46.8(t), 56.9(t), 60.6(t), 127.5(d), 127.6(d), 127.9(t), 128.1(d), 128.5(d), 129.6(d), 135.7(s), 137.3(s), 144.5(s), 167.5(s), 172.8(s); mass spectrum, m/e (relative intensity) 497($M^+$, 78), 384(21), 342 (100); exact mass calcd for $C_{28}H_{35}NO_5S$ m/e 497.2236, found m/e 497.2223. (trans isomer) colorless oil: IR ($CHCl_3$) 2926, 1698, 1149 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.77 (s, 3H, $CH_3$), 0.84 (s, 3H, $CH_3$), 1.26 (t, J=7.2Hz, 3H, $CH_3$), 2.27 (s, 2H, $CH_2$) , 2.44 (s, 3H,

$CH_3$), 2.53-3.8 (m, 6H), 4.17 (q, J=7.2Hz, 2H, $OCH_2$), 4.41 (s, 2H, $CH_2N$), 5.38-5.5 (m, 1H, =CH) , 6.12-6.3 (m, 1H, =CH), 7.05-7.5 (m, 5H, ArH), 7.35 (d, J=8.2Hz, 2H, ArH), 7.82 (d, J=8.2Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.1(q), 21.6(q), 24.5(q), 25.8(q), 40.2(t), 40.4(d), 45.3(d), 47.0(t), 53.2(t), 60.8(t), 127.8(d), 128.1(d), 128.3(t), 128.5 (d), 128.7(d), 129.8(d), 135.8(s), 136.6(s), 137.4(s), 144.7(s), 167.8(s), 172.3(s); mass spectrum, m/e (relative intensity) 497($M^+$, 46), 384(20), 342(100) 269(12); exact mass calcd for $C_{28}H_{35}NO_5S$ m/e 497.2236, found m/e 497.2213.

***N*-Benzyl-3-(1,1-dimethyl-3-ethoxycarbonyl-3-buten-1-yl)-4-*p*-toluenesulfonylmethyl-pyrrolidin-2-one 3m.** (cis isomer) colorless oil: IR ($CHCl_3$) 2992, 1710, 1686, 1149 $cm^{-1}$; $^1H$ NMR (CDCl3) δ 0.97 (s, 6H, $CH_3$), 1.28 (t, J=7.0Hz, 3H, $CH_3$), 2.2-3.9 (m, 8H), 2.43 (s, 3H, $CH_3$), 4.18 (q, J=7.0Hz, 2H, $CH_2O$), 4.44 and 4.57 (AB system, J=15Hz, 2H, $CH_2N$), 5.45-5.6 (m, 1H, =CH), 6.12-6.28 (m, 1H, =CH), 7.1-7.45 (m, 5H, ArH), 7.27 (d, J=8.2Hz, 2H, ArH), 7.69 (d, J=8.2Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.0(q), 21.5(q), 25.0(q), 25.2(q), 32.1(d), 34.5(s), 40.0(t), 46.5(t), 48.5(t), 53.7(d), 54.6(t), 60.6(t), 127.5(d), 127.9(d), 128.2(d), 128.3(t), 128.6(d), 129.8(d), 136.2(s), 136.3(s), 137.5(s), 144.7(s), 167.9(s), 172.4(s); mass spectrum, m/e (relative intensity) 497($M^+$, 100), 384(36), 343(30), 328(11), 279(35); exact mass calcd for $C_{28}H_{35}NO_5S$ m/e 497.2236 found m/e 497.2227. (trans isomer) colorless oil: IR ($CHCl_3$) 2974, 1713, 1677, 1149 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.8 (s, 3H, $CH_3$), 0.85 (s, 3H, $CH_3$), 1.29 (t, J=7.1Hz, 3H, $CH_3$), 2.0-3.0 (m, 2H), 2.44 (s, 3H, $CH_3$), 2.6 (s, 2H, $CH_2$), 3.0-3.8 (m, 4H), 4.16 (q, J=7.1Hz, 2H, $OCH_2$), 4.27 and 4.58 (AB system, J=15Hz, 2H, $CH_2N$), 5.56-5.7 (m, 1H, =CH), 6.14-6.3 (m, 1H, =CH), 7.1-7.5 (m, 5H, ArH), 7.34 (d, J=8.2Hz, 2H, ArH), 7.72 (d, J=8.2Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$) δ 14.0(q), 21.5(q), 23.5(q), 24.1(q), 28.1(d), 37.6(s), 39.4(t), 46.6(t), 50.2(t), 55.0(d), 60.6(t), 61.9(t), 127.6(d), 127.7(d), 128.2(d), 128.5(t), 128.6(d), 130.0(d), 136.0(s), 137.7(s), 145.0(s), 167.9(s), 172.7(s); mass spectrum, m/e (relative intensity) 497($M^+$, 100), 384(17), 342(66), 279(80); exact mass calcd for $C_{28}H_{35}NO_5S$ m/e 497.2236, found m/e 497.2223.

**Methyl 3-chloromethyl-4-*p*-toluenesulfonylmethyl-cyclopentane-1,1-dicarboxylate 7a.** (cis isomer) colorless oil: IR (neat) 2950, 1730, 1380 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.6-2.9 (m, 6H), 2.46 (s, 3H, $CH_3$), 3.0-3.35 (m, 2H, $CH_2SO_2$), 3.35-3.6 (m, 2H, $CH_2Cl$), 3.73 (s, 6H, $OCH_3$), 7.37 (d, J=8.0Hz, 2H, ArH), 7.79 (d, J=8.0Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$), δ 21.5(q), 35.7(d), 36.9(t), 38.4(t), 43.5(d), 44.2(t), 52.8(q), 55.7(t), 58.3(s), 127.9(d), 129.9(d), 136.3(s), 144.8(s), 172.1(s), 172.2(s); mass spectrum, m/e (relative intensity) 402($M^+$, 3), 367(11), 247(100), 215(51), 187(84), 139(31), 91(77); exact mass calcd for $C_{18}H_{23}ClO_6S$ m/e 402.0434, found m/e 402.0410.

***N*-Benzyl-4-(2-chloro-2-propyl)-3-*p*-toluenesulfonylmethyl-pyrrolidin-2-one 7b.** (cis isomer) white solid, m.p. 115$^0$C, IR ($CHCl_3$) 2914, 1683, 1314 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 1.55 (s, 3H, $CH_3$), 1.64 (s, 3H, $CH_3$), 2.44 (s, 3H, $CH_3$), 3.0-3.9 (m, 6H), 4.35 and 4.66 (AB system, J=14Hz, 2H, $CH_2N$), 7.0-7.6 (m, 5H, ArH), 7.35 (d, J=8.3Hz, 2H, ArH), 7.83 (d, J=8.3Hz, 2H, ArH); $^{13}$C NMR ($CDCl_3$) δ 21.3(q), 30.3(q), 40.8(d), 45.4(d), 46.6(t), 47.2(t), 56.1(t), 72.1(s), 127.4(d), 127.5(d), 127.8(d), 128.4(d), 129.6(d), 135.4(s), 137.1(s), 144.7(s), 171.9(s).

Anal. calcd for $C_{22}H_{26}ClNO_3S$: C,62.92; H,6.24; N,3.34. Found: C,62.67; H,6.22; N,3.39.

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