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Palladium-catalyzed cascade reactions of benzyl halides with *N*,*N*-diallyl-*p*-toluenesulfonamide

Abstract: Reaction of *N*,*N*-diallyl-*p*-toluenesulfonamide **1** with benzyl halides **2** in the presence of a palladium catalyst afforded a series of novel dihydropyrroles **3** in moderate yields. A palladium-catalyzed self-cyclization reaction of the diene **1** may take place to give a cyclic dihydropyrrole **4** during the reaction. It is proposed that the cyclic products **4** are formed via a palladium-catalyzed cascade cyclization-coupling process. Reaction of phenyl iodide **5** with **1** in the same condition afforded normal Heck vinylation products **6**.

Keywords: alkylation; cyclic cascade reactions; dihydropyrrole; Heck reaction.

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Introduction

Many heterocyclic compounds with pyrrole ring, as biologically or pharmacologically active compounds, have been used in various fields, especially medical fields (Yuan and Xia, 1984). Developing new and effective synthetic methods for the construction of cyclic compounds has attracted great interest in recent years. Many annulation methods, including ring-closing metathesis (Furstner and Langemann, 1996; Pernerstorfer et al., 1997; Furstner and Muller, 1999), cyclic cascade reactions (Lee et al., 2000; Miura et al., 2000; Grigg et al., 2001; Wang et al., 2001), and Mizoroki-Heck reactions (Negishi et al., 1996), have been discovered. Palladium-catalyzed reaction for the construction of heterocyclic compounds has become one of the most powerful methods. Aryl or olefinic halides have been used as starting materials in various cases, but few examples of palladium catalyzed cyclization reactions of alkyl halides are known. In fact, the palladium-catalyzed alkylation of olefins by alkyl halides is one of the important aspects of the Heck reaction (Heck, 1968, 1982; Grigg, 1994; de Meijere and Meyer, 1995; Tsuji, 1995). We have reported the palladium-catalyzed reactions of various benzyl halides with a variety of olefins (Zhang et al., 1990; Pan et al., 1995; Wang et al., 2000; Hu et al., 2003). Negishi reported some interesting examples of intramolecular Heck reactions of benzyl halides (Wu et al., 1989). We also found (Hu et al., 2003) the first example of a palladium-catalyzed cascade reaction of benzylic halides with diene such as *N*-allyl-*N*-(2-butenyl)-*p*-toluenesulfonamide, in which a dihydropyrrole cyclic product was obtained via a novel palladium-catalyzed cascade cyclization-coupling process. As part of our continuing efforts in the study of palladium-catalyzed reactions of alkyl halides with olefins, we report here the palladium catalyzed reaction of benzyl halides with *N, N*-diallyl-*p*-toluenesulfonamide leading to dihydropyrroles.

Results and discussion

The benzyl chloride (**2a**) was allowed to react with *N,N*-diallyl-*p*-toluenesulfonamide (**1**) in the presence of palladium acetate in DMF at 130°C under a nitrogen atmosphere for 15 h to give a dihydropyrrole product **3a**, as the main identifiable product, in moderate yield (Scheme 1). The reaction yields depend on the substituents on the phenyl ring of benzylic halides. The use of benzylic chlorides with electron-donating groups, such as a methyl or methoxy, afford higher yields than the substrates with deactivating electron-withdrawing groups such as CN, Cl, Br. The steric effects of the substituents such as *ortho*-CH_3 suppress the reaction, whereas strong electron-withdrawing groups, such as NO_2, almost completely inhibit the reaction.

It is believed that the cyclic products **3** are formed via a cascade cyclization-coupling process as described in the literature (Hu et al., 2003). The ring-closure reaction should involve at least two additions of organopalladium intermediates to the double bonds of the diene substrate **1**. Once the benzylic palladium species is formed, it reacts with one of the double bonds of the diene to form a new palladium intermediate, which reacts with the other

double bond intramolecularly resulting in the formation of a ring in a cascade.

Another cyclization product, 3,4-dimethyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (**4**), was also isolated in all cases. This is the first example for self-cyclization reaction of the diene **1**, although similar self-cyclization reactions of other dienes have been described in the literature (Takacs et al., 1992; Goj et al., 2003). The structure of **4** was characterized by FT-IR, ^{1}H NMR, and MS. A simplified reaction mechanism is proposed in Scheme 2.

When phenyl iodide **5** was allowed to react with diene **1,** normal Heck vinylation product **6** was only isolated, and no expected cyclization product could be found (Scheme 3). This may be due to the fact that organopalladium iodide intermediate products have higher Heck reaction activities than analogous organopalladium chlorides.

Conclusions

A series of novel dihydropyrroles **3** were synthesized in moderate yields by palladium-catalyzed cascade reactions of *N,N*-diallyl-*p*-toluenesulfonamide (**1**) with benzyl halides **2** in the presence of palladium acetate and tributylamine in DMF. A palladium-catalyzed self-cyclization reaction of the diene **1** also takes place to give a cyclic dihydropyrrole **4**. The mechanism of formation of the cyclic product **4** obviously involves a palladium-catalyzed cascade cyclization-coupling process. Reaction of phenyl iodide (**5**) with **1** under similar conditions afforded normal Heck vinylation products **6** (Scheme 3).

Experimental

Reactions were monitored by TLC on Silufol UV-254 plates in the ethyl acetate-petroleum ether (1:7 and 1:4) solvent systems. ^{1}H NMR spectra were recorded on a Bruker Avance spectrometer (500 MHz) in $CDCl_3$ relatively to Me_4Si as an internal standard. FT-IR spectra were recorded on a Nicolet NEXUS870 spectrometer using KBr pellets. Mass spectra (EI, 70 eV) were recorded on a VG ZAB-HS instrument. Elemental analysis was performed on a Elemental Vario MICRO analyzer.

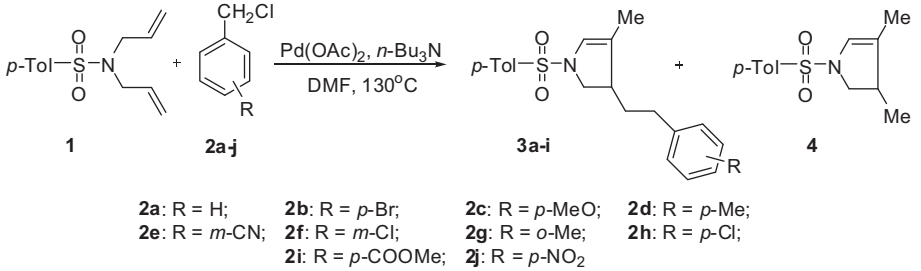
Preparation of 4-methyl-3-phenethyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (3a)

A dried 50 mL Schlenk flask was filled with nitrogen and charged with *N,N*-diallyl-*p*-toluenesulfonamide (**1**) (1.25 g, 5 mmol), a benzyl chloride (**2**) (0.70 g, 5.5 mmol), tributylamine (2.0 mL), $Pd(OAc)_2$ (12 mg, 0.05 mmol, 1 mol%), and 2 mL DMF. The mixture was heated at 130°C with stirring for 15 h, then cooled to room temperature. The resultant yellow-orange mixture was poured into water (20 mL). The mixture was extracted with ether (3×10 mL). The extract was washed with HCl (1%) and water, then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (6:1) to give 4-methyl-3-phenethyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (**3a**) and 3,4-dimethyl-1-tosyl-2,3- dihydro-1*H*-pyrrole (**4**). Other products **3** were obtained in a similar manner.

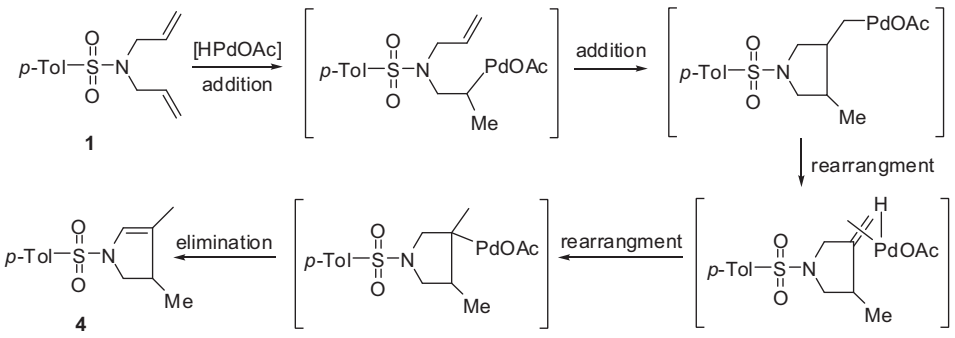
Compound 3a Yield 53%; mp 91–92°C; IR: 3031(m), 2956(w), 2925(s), 2875(w), 1662(v), 1600(m), 1494(m), 1450(m), 1344(s), 1156(m), 819(m), 756(m), 700(m), 663(s), 589(s) cm^{-1}; ^{1}H NMR: δ 7.64 (d, 2H, J = 8.0 Hz, ArH), 7.31 (d, 2H, J = 8.0 Hz, ArH), 6.99–7.28 (m, 5H, ArH), 6.06 (s, 1H, $ArSO_2N$-CH=C), 3.59 (t, 1H, J = 10.5 Hz, $ArSO_2N$-CH_2), 3.19 (dd, 1H, J_1 = 10.5 Hz, J_2 = 6.0 Hz, $ArSO_2N$-CH_2), 2.58 (m, 1H, $CH_2C\underline{H}_2Ar$), 2.44 (m, 1H, $CH_2C\underline{H}_2Ar$), 2.40 (s, 3H, $ArCH_3$), 2.26 (m, 1H, $ArSO_2N$-CH_2CH-C), 1.68 (m, 1H, $C\underline{H}_2CH_2Ar$), 1.61 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.15 (m, 1H, $C\underline{H}_2CH_2Ar$); MS: m/z 341(M$^+$, 21), 236(98), 155(31), 94(18), 91(100). Anal. Calcd for $C_{20}H_{23}NO_2S$: C, 70.35; H, 6.79; N, 4.10. Found: C, 70.44; H, 6.95; N, 4.32%.

Compound 3b Yield 40%; mp 104–105°C; IR: 3019(m), 2981(m), 2931(s), 2863(w), 1669(v), 1600(m), 1494(m), 1444(m), 1344(3), 1156(m), 850(m), 813(m), 775(m), 706(m), 656(s) cm^{-1}; ^{1}H NMR: δ 7.64 (d, 2H, J = 8 Hz, ArH), 7.34 (d, 2H, J = 8 Hz, ArH), 7.29 (d, 2H, J = 8 Hz, ArH), 6.89 (d, 2H, J = 8Hz, ArH), 6.06 (s, 1H, $ArSO_2N$-CH=C), 3.57 (t, 1H, J = 10.5 Hz, $ArSO_2N$-CH_2), 3.18 (dd, 1H, J_1 = 10.5, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.56 (m, 1H, $CH_2C\underline{H}_2Ar$), 2.41 (m, 1H, $CH_2C\underline{H}_2Ar$), 2.38 (s, 3H, $ArCH_3$), 2.23 (m, 1H, $ArSO_2N$-CH_2CH-C), 1.64 (m, 1H, $C\underline{H}_2CH_2Ar$), 1.60 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.13 (m, 1H, $C\underline{H}_2CH_2Ar$). MS: m/z 421(M$^+$2, 13), 419(M$^+$, 13), 236(100), 155(30), 94(23), 91(60). Anal. Calcd for $C_{20}H_{22}BrNO_2S$: C, 57.14; H, 5.27; N, 3.33. Found: C, 57.05; H, 5.50; N, 3.63.

Compound 3c Yield 47%; mp 79–80°C; IR: 3044(m), 2975(m), 2931(s), 2850(w), 1656(v), 1606(m), 1512(m), 1456(m), 1337(m) 1156(m), 1244(m), 1031(m), 969(m), 850(m), 812(m), 668(s) cm^{-1}; ^{1}H NMR: δ 7.63 (d, 2H,



Scheme 1 Reaction of benzyl halides with *N,N*-diallyl-*p*-toluenesulfonamide.



Scheme 2 Palladium catalyzed self-cyclization reaction mechanism of *N,N*-diallyl-*p*-toluenesulfonamide.

J = 8 Hz, ArH), 7.31 (d, 2H, *J* = 8Hz, ArH), 6.95 (d, 2H, *J* = 8 Hz, ArH), 6.71 (d, 2H, *J* = 8 Hz, ArH), 6.03 (s, 1H, $ArSO_2N$-CH=C), 3.75 (s, 3H, $ArOCH_3$), 3.56 (t, 1H, *J* = 10.5 Hz, $ArSO_2N$-CH_2), 3.21 (dd, 1H, J_1 = 10.5, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.60 (m, 1H, CH_2CH_2Ar), 2.41 (m, 1H, CH_2CH_2Ar), 2.39 (s, 3H, $ArCH_3$), 2.34 (m, 1H, $ArSO_2N$-CH_2CH-C), 1.64 (m, 1H, CH_2CH_2Ar), 1.59 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.13 (m, 1H, CH_2CH_2Ar); MS: m/z 371(M^+, 33), 236(100), 155(33), 121(93), 94(16), 91(72). Anal. Calcd for $C_{21}H_{25}NO_3S$: C, 67.90; H, 6.78; N, 3.77. Found: C, 68.32; H, 7.07; N, 3.58.

Compound 3d Yield 50%; mp 72–73°C; IR: 3019(m), 2937(s), 2856(w), 1656(v), 1600(m), 1513(m), 1450(m), 1344(m), 1163(m), 950(m), 856(m), 873(m), 750(m), 706(m), 669(s) cm^{-1}; ^1H NMR: δ 7.64 (d, 2H, *J* = 8 Hz, ArH), 7.31 (d, 2H, *J* = 8 Hz, ArH), 7.03 (d, 2H, *J* = 8 Hz, ArH), 6.90 (d, 2H, *J* = 8 Hz, ArH), 6.05 (s, 1H, $ArSO_2N$-CH=C), 3.62 (t, 1H, *J* = 10.5 Hz, $ArSO_2N$-CH_2), 3.18 (dd, 1H, J_1 = 10.5, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.57 (m, 1H, CH_2CH_2Ar), 2.41 (m, 1H, CH_2CH_2Ar), 2.39 (s, 3H, $ArCH_3$), 2.30 (s, 3H, $ArCH_3$), 2.22 (m, 1H, $ArSO_2N$-CH_2CH-C), 1.64 (m, 1H, CH_2CH_2Ar), 1.59 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.11 (m, 1H, CH_2CH_2Ar); MS: m/z 355(M^+, 24), 236(100), 155(35), 105(36), 96(30), 94(19), 91(78). Anal. Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09; N, 3.94. Found: C, 71.39; H, 7.49; N, 4.25.

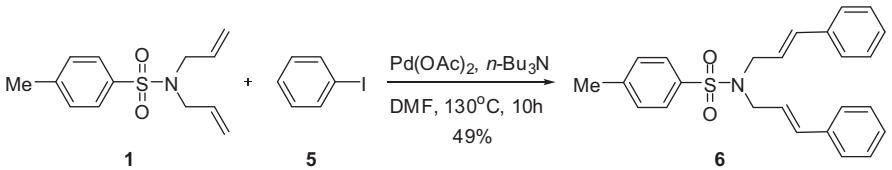
Compound 3e Yield 43%; mp 123–124°C; IR: 3050(m), 2924(s), 2861(w), 2221(m), 1666(v), 1602(m), 1490(m), 1441(m), 1342(m) 1159(m), 857(m), 807(m), 667(s)cm^{-1}; ^1H NMR: δ 7.65 (d, 2H, *J* = 8 Hz, ArH), 7.28–7.47 (m, 6H, ArH), 6.09 (s, 1H, $ArSO_2N$-CH=C), 3.61 (t, 1H, *J* = 10.5 Hz, $ArSO_2N$-CH_2), 3.22 (dd, 1H, J_1 = 10.5, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.61 (m, 1H, CH_2CH_2Ar), 2.44 (m, 1H, CH_2CH_2Ar), 2.40 (s, 3H, $ArCH_3$), 2.31 (m, 1H, $ArSO_2N$-CH_2CH-C), 1.65 (m, 1H, CH_2CH_2Ar), 1.61 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.14 (m, 1H, CH_2CH_2Ar); MS: m/z 366(M^+, 23), 236(100), 155(32), 94(31), 91(65). Anal. Calcd for $C_{21}H_{22}N_2O_2S$: C, 68.83; H, 6.05; N, 7.64. Found: C, 68.30; H, 6.18; N, 7.83.

Compound 3f Yield 39%; mp 95–96°C; IR: 3037(m), 2944(m), 2913(s), 2856(w), 1662(v), 1600(m), 1475(m), 1350(m) 1156(m), 900(m), 863(m), 813(m), 781(m), 700(m), 669(s) cm^{-1}; ^1H NMR: δ 7.67 (d, 2H, *J* = 8 Hz, ArH), 7.32 (d, 2H, *J* = 8 Hz, ArH), 6.91–7.20 (m, 4H, ArH), 6.08 (s, 1H, $ArSO_2N$-CH=C), 3.63 (t, 1H, *J* = 10.5 Hz, $ArSO_2N$-CH_2), 3.20 (dd, 1H, J_1 = 10.5, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.61 (m, 1H, CH_2CH_2Ar), 2.41 (s, 3H, $ArCH_3$), 2.36 (m, 1H, CH_2CH_2Ar), 2.22 (m, 1H, $ArSO_2N$-CH_2CH-C), 1.62 (m, 1H, CH_2CH_2Ar), 1.61 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.10 (m, 1H, CH_2CH_2Ar). MS: m/z 375(M^+, 16), 236(100), 155(33), 94(29), 91(66). Anal. Calcd for $C_{20}H_{22}ClNO_2S$: C, 63.89; H, 5.90; N, 3.73. Found: C, 63.52; H, 6.05; N, 3.94.

Compound 3g Yield 33%; mp 56–57°C; IR: 3012(m), 2925(s), 2856(w), 1656(v), 1600(m), 1500(m), 1450(m), 1381(m), 1344(m), 1163(m), 981(m), 844(m), 819(m), 763(m), 669(s) cm^{-1}; ^1H NMR: δ 7.65 (d, 2H, *J* = 8 Hz, ArH), 7.31 (d, 2H, *J* = 8 Hz, ArH), 6.91–7.06 (m, 4H, ArH), 6.07 (s, 1H, $ArSO_2N$-CH=C), 3.64 (t, 1H, *J* = 10.5 Hz, $ArSO_2N$-CH_2), 3.20 (dd, 1H, J_1 = 10.5, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.62 (m, 1H, CH_2CH_2Ar), 2.44 (m, 1H, CH_2CH_2Ar), 2.41 (s, 3H, $ArCH_3$), 2.27 (m, 1H, $ArSO_2N$-CH_2CH-C), 2.20 (s, 3H, $ArCH_3$), 1.63 (m, 1H, CH_2CH_2Ar), 1.61 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.11 (m, 1H, CH_2CH_2Ar); MS: m/z 355(M^+, 31), 236(100), 155(32), 105(42), 94(17), 91(69). Anal. Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09; N, 3.94. Found: C, 71.58; H, 7.38; N, 4.16.

Compound 3h Yield 42%; mp 89–90°C; IR: 3062(m), 2975(m), 2931(s), 2863(w), 1669(v), 1594(m), 1488(m), 1344(m), 1281(m), 1163(m), 1100(m), 963(m), 856(m), 825(m), 756(m), 706(m), 663(s)cm^{-1}; ^1H NMR: δ 7.57 (d, 2H, *J* = 8 Hz, ArH), 6.60–7.40 (m, 6H, ArH), 6.08 (s, 1H, $ArSO_2N$-CH=C), 3.62 (t, 1H, *J* = 10.5 Hz, $ArSO_2N$-CH_2), 3.20 (dd, 1H, J_1 = 10.5, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.60 (m, 1H, CH_2CH_2Ar), 2.41 (s, 3H, $ArCH_3$), 2.36 (m, 1H, CH_2CH_2Ar), 2.22 (m, 1H, $ArSO_2N$-CH_2CH-C), 1.61 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.60 (m, 1H, CH_2CH_2Ar), 1.12 (m, 1H, CH_2CH_2Ar); MS: m/z 375(M^+, 18), 236(100), 155(37), 94(17), 91(55). Anal. Calcd for $C_{20}H_{22}ClNO_2S$: C, 63.89; H, 5.90; N, 3.73. Found: C, 64.39; H, 6.04; N, 3.51.

Compound 3i Yield 49%; mp 123–124°C; IR: 3031(m), 2962(m), 2944(s), 1719(v), 1669(v), 1600(m), 1344(m), 1281(m), 1100(v), 963(m), 856(m), 825(m), 756(m), 706(m), 663(s) cm^{-1}; ^1H NMR: δ 7.78 (d, 2H, *J* = 8 Hz, ArH), 7.58 (d, 2H, *J* = 8 Hz, ArH), 7.24 (d, 2H, *J* = 8 Hz, ArH), 7.06 (d, 2H, *J* = 8 Hz, ArH), 6.09 (s, 1H, $ArSO_2N$-CH=C), 3.78 (s, 3H, $COOCH_3$), 3.64 (t, 1H, *J* = 10.5 Hz, $ArSO_2N$-CH_2), 3.20 (dd, 1H,



Scheme 3 Palladium catalyzed reaction of phenyl iodide with *N,N*-diallyl-*p*-toluenesulfonamide.

J_1 = 10.5, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.64 (m, 1H, $CH_2C\underline{H}_2Ar$), 2.44 (m, 1H, $CH_2C\underline{H}_2Ar$), 2.41 (s, 3H, $ArCH_3$), 2.31 (m, 1H, $ArSO_2N$-CH_2CH-C), 1.62 (m, 1H, $C\underline{H}_2CH_2Ar$), 1.61 (s, 3H, $ArSO_2N$-C=C-CH_3), 1.13 (m, 1H, $C\underline{H}_2CH_2Ar$); MS: m/z 399(M^+, 20), 236(100), 155(34), 94(22), 91(57). Anal. Calcd for $C_{22}H_{25}NO_4S$: C, 66.14; H, 6.31; N, 3.51. Found: C, 66.96; H, 6.55; N, 3.40.

3,4-Dimethyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (4) Yield 10%; mp 67–68°C; IR: 3094(m), 1663(m), 1600(m), 1450(m), 1344(s), 1156(m), 850(m), 819(m) cm^{-1}; ^{1}H NMR: δ 7.70 (d, 2H, J = 8 Hz, ArH), 7.24 (d, 2H, J = 8 Hz, ArH), 6.04 (s, 1H, $ArSO_2N$-CH=C), 3.59 (t, 1H, J = 10.5 Hz, $ArSO_2N$-CH_2), 2.94 (dd, 1H, J_1 = 10.5 Hz, J_2 = 6 Hz, $ArSO_2N$-CH_2), 2.51 (m, 1H, CH_2Ar), 2.40 (s, 3H, $ArCH_3$), 1.63 (s, 3H, $ArSO_2N$-CH=CH-C$\underline{H}_3$), 0.87 (d, 3H, J = 6 Hz, $ArSO_2NCH_2CHC\underline{H}_3$); MS: m/z 251($M^+$, 61), 236(74), 155(42), 94(18), 96(100). Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.56; H, 6.51; N, 5.23.

Synthesis of *N,N*-dicinnamyl-4-methylbenzenesulfonamide (6)

Compound **6** was prepared by the reaction of substrate **1** with iodobenzene (**5**) under the conditions that are similar to the procedure for the preparation of **3a**. The reaction time was reduced to 10 h: Yield 49%; mp 84–85°C; IR: 3025(m), 2925(s), 2856(w), 1656(m), 1600(m), 1500(m), 1450(m), 1337(s), 1156(m), 963(m), 900(m), 856(s), 813(m), 756(s), 725(m) cm^{-1}; ^{1}H NMR: δ 7.66 (d, 2H, J = 8 Hz, ArH), 7.00–7.33 (m, 12H, ArH), 6.47 (d, 2H, J = 18 Hz, $ArSO_2NCH_2CH$=C$\underline{H}$), 5.90 (tt, 2H, J_1 = 18 Hz, J_2 = 7 Hz, $ArSO_2NCH_2C\underline{H}$=CH), 3.90 (d, 4H, J = 7 Hz, $ArSO_2N$-C$\underline{H}_2$), 2.35 (s, 3H, $ArCH_3$). Anal. Calcd for $C_{25}H_{25}NO_2S$: C, 74.47; H, 6.24; N, 3.25. Found: C, 74.76; H, 6.41; N, 3.53.

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