

Palladium-Catalyzed Synthesis of *N*-Benzoyl-2-arylethenesulfonamides from [2-(Benzoylsulfamoyl)ethyl]pyridinium Chloride and Aryl Halides

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Synopsis. A new, general synthesis of *N*-benzoyl-2-arylethenesulfonamides by the reaction of aryl halides including heteroaryl halides with [2-(benzoylsulfamoyl)ethyl]pyridinium chloride in the presence of palladium acetate is described.

Although palladium-catalyzed vinylation of aryl halides with olefinic derivatives, known as the Heck reaction,¹⁾ has been widely investigated for its usefulness in organic synthesis, there has been no report concerning a vinylation reaction of aryl halides with saturated ethane derivatives as a versatile vinyl synthon. We have been studying the chemistry of 2-arylethenesulfonamides regarding their biological activity and important precursors of 2-arylethynyl-sulfonamides.²⁾ Only their benzene derivatives have been known,³⁾ because heteroaryl derivatives are difficult to prepare by the known method.⁴⁾ Then, for the synthesis of these compounds, palladium-catalyzed ethenesulfonamidation of aryl halides by applying the Heck reaction was examined. We found that aryl halides react with [2-(benzoylsulfamoyl)ethyl]pyridinium chloride (**1**) as a versatile vinyl synthon in the presence of a catalytic amount of palladium acetate (Pd(OAc)₂) and triethylamine (NEt₃) in dry *N,N*-dimethylformamide (DMF) to give *N*-benzoyl-2-arylethenesulfonamides. It is the first example, to our knowledge, of such a coupling reaction. Here, we wish to report on general syntheses of the *N*-benzoyl-2-arylethenesulfonamides by two procedures.

A two-step synthesis of *N*-benzoyl-2-arylethenesulfonamides was successfully achieved as follows. Ethenesulfonamide (**2**)⁵⁾ reacted with various aryl halides in the presence of palladium acetate⁶⁾ to give the *E*-form of 2-aryl ethenesulfonamides **7–14**. The

E-configuration of these compounds was confirmed by their ¹H-NMR spectral data, such as the ¹H–¹H coupling constants (*J*=14–15.5 Hz) of the protons on the vinyl moiety. In this reaction, a great improvement in the yields of 2-arylethenesulfonamide **7**, **8**, and 4-phenyl-1,3-butadiene-1-sulfonamide **9**⁷⁾ was obtained, compared to those of the former method (Table 1). Furthermore, 2-(heteroaryl)ethenesulfonamides **10–14** could be prepared only by this method. 2-(2,4-Dimethoxy-5-pyrimidinyl)ethenesulfonamide (**13**) and its 6-methyl derivatives **14** were transformed to the uracil derivative of ethenesulfonamides **15** and its 6-methyl derivative **16**, respectively. They are of interest regarding their antitumor activity because of their structural similarity to the sparsomicine⁸⁾ and potential precursor for 5-uracilethynesulfonamides, which is known to have an antitumor activity.⁹⁾ Since the generality and superiority of this method were verified, compounds **7**, **10**, and **11**, chosen as typical examples for comparing the yields of the following one-step synthesis, were benzoylated with benzoyl chloride to give **22–24** (Table 1). Similarly, 3-aryl-2-propene-1-sulfonamides **17–21**, homo-derivatives of 2-arylethenesulfonamides, were prepared without isomerization of the double bond by the reaction of aryl halides with 2-propene-1-sulfonamide (**4**)¹⁰⁾ in the place of **3**.

Since it was considered that the use of *N*-benzoyl-ethenesulfonamide (**3**) would shorten the preparation steps of *N*-benzoyl-2-arylethenesulfonamides **22–24**, benzoylation of ethenesulfonamide **2** in the presence of pyridine used as a base was attempted. However, this benzoylation reaction gave only unexpected pyridinium salt **1** in 56% yield.

It was incidentally found that the reaction of this salt **1** with aryl halides in the presence of a catalytic

Table 1. Synthesis of 2-Arylethenesulfonamides **7–14** and 3-Aryl-2-propene-1-sulfonamides **17–21**

Aryl Halide	2-Arylethene-sulfonamide	Yield/%	3-Aryl-2-propene-sulfonamide	Yield/%
Iodobenzene	7	55 (21) ^{a)}		
Bromobenzene	7	61	17	42
1-Bromonaphthalene	8	72 (19) ^{b)}	18	38
2-Bromostyrene	9	56 (13) ^{a)}		
2-Bromothiophene	10	56	19	39
3-Bromopyridine	11	54	20	30
4-Bromopyridine	12	30		
5-Bromo-2,4-dimethoxy-pyrimidine	13	10	21	10
5-Bromo-2,4-dimethoxy-6-methylpyrimidine	14	16		

a) Yield from Ref. 6. b) Our own result obtained by using Culbertson's method.

amount of $\text{Pd}(\text{OAc})_2$ and triethylamine in dry DMF gave *N*-benzoyl-2-arylethenesulfonamides **22**–**24** in better yields than those of the former two-step synthesis (Table 1), and that 20–30% of the unreacted aryl halides were recovered in all cases. The use of **1** is better than that of **2**, not only regarding yields but also in view of the easiness of preparation of **1**, though it was derived from **2**.

A detailed examination of this reaction in order to obtain more information about its mechanism revealed that the salt **1** does not change in the absence of triphenylphosphine and triethylamine at 140 °C. However, the treatment of **1** with triethylamine as a base in DMF at 140 °C gave *N*-benzoyl-ethenesulfonamide (**3**) in 65.8% yield. In consideration of this result, benzylation of **2** in the presence of NEt_3 (but not pyridine) successfully gave **3** in 13.4% yield. The reaction of **3** with a typical aryl halide of bromobenzene under similar conditions as above gave an expected *N*-benzoyl-2-phenylethenesulfonamide (**22**), but in low yield (16%), which is rather lower yield than that of the case used pyridinium salt **1**. Thus, the above results suggest that the salt **1** was generated *N*-benzoylethenesulfonamide (**3**) in situ under the conditions and that it reacted with aryl halides to give *N*-Benzoyl-2-arylethenesulfonamides **22**–**24**.

Experimental

All melting points are uncorrected. The IR spectra were taken on a IR-810 spectrometer. The ^1H NMR spectra were taken on Hitachi R-24 (60 MHz) and JEOL-FX 90 (90 MHz) spectrometers in chloroform-*d* (TMS as internal standard), and dimethyl-*d*₆ sulfoxide (TMS). The ^{13}C NMR spectra were taken on a JEOL-FX 90 (23 MHz) spectrometer in chloroform-*d* (TMS) and dimethyl-*d*₆ sulfoxide (TMS). The Mass spectra were taken on a JEOL-OISG-2 mass spectrometer.

General Procedures for the Preparation of 2-Arylethenesulfonamides 7–14 and 3-Aryl-2-propene-1-sulfonamides 17–21. A solution of triphenylphosphine (61 mg, 0.23 mmol) and palladium acetate (26 mg, 0.116 mmol) in DMF (16 mL) was stirred at room temperature for a few min under a nitrogen atmosphere. To this solution, a mixture of aryl bromide (5.88 mmol), **2** (or **4** for **17**–**21**) (7.01 mmol), and triethylamine (1.480 g, 14.7 mmol) was added. The mixture was heated at 140 °C for 24 h under a nitrogen atmosphere with stirring and, after cooling, filtered. The filtrate was concentrated under reduced pressure. The residue was dissolved in 50 mL of 1 M-sodium hydroxide (1M=1 mol dm⁻³). The resulting solution was heated with 5 g of active carbon and filtered. The filtrate was brought to pH 3 with dil hydrochloric acid and the precipitate was collected by filtration.

7: Colorless needles; mp 140–142 °C (water), (lit.³) 143 °C).

2-(1-Naphthyl)ethenesulfonamide (8): Colorless needles, mp 162–165 °C (ethanol); IR (KBr) 3345s, 3230s, 3050w, 1625m, 1495m, 1445m, 1319vs, 1308vs, 1172s, 989m, 908s, 748s cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =8.23 (m, 1H), 8.00–7.20 (m, 10H); MS *m/z* 217 (M^+ , 57%). Anal. ($\text{C}_{12}\text{H}_{11}\text{NO}_2\text{S}$) C, H.

4-Phenyl-1,3-butadienesulfonamide (9): Colorless needles, mp 193–194 °C, (lit.⁷) 198–199 °C).

2-(2-Thienyl)ethenesulfonamide (10): Colorless needles, mp 144–145 °C (by adding ethyl acetate dropwise to a solution of **10** in water); IR (KBr) 3360s, 3260s, 3080w, 1600m, 1520w, 1400w, 1300s, 1270s, 1140s, 960w, 900w, 820m, 780w, 720m cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =7.69 (d,

J =5.0 Hz, 1H, H-3), 7.53 (d, J =15.5 Hz, 1H, H-b, $\text{CH}_2=\text{CH}_2\text{SO}_2$), 7.52 (d, J =3.2 Hz, 1H, H-5), 7.15 (dd, J =5.0 & 3.2 Hz, 1H, H-4), 7.14 (s, 2H, NH_2), 6.90 (d, J =15.5 Hz, 1H, H-a); ^{13}C NMR δ =136.9 (s), 131.2 (d), 129.7 (d), 129.2 (d), 128.4 (d), 128.3 (d); MS *m/z* 189 (M^+ , 41%), 108 (100%). Anal. ($\text{C}_6\text{H}_7\text{NO}_2\text{S}_2$) C, H.

2-(3-Pyridyl)ethenesulfonamide (11): Pale yellow needles, mp 167–169 °C (water); IR (KBr) 3300s, 3050w, 2900m, 2650w, 1615m, 1590m, 1475m, 1421m, 1331vs, 1202m, 1139vs, 1122m, 969s, 900m, 870s, 815s, 778s cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =8.83 (bs, 1H, H-2), 8.60 (bd, J =6.5 Hz, 1H, H-6), 8.15 (dt, J =1.0 & 7.5 Hz, 1H, H-4), 7.43 (m, 3H, H-5, H-a, b, $\text{CH}_2=\text{CH}_2\text{SO}_2$), 7.28 (bs, 2H, NH_2); ^{13}C NMR (DMSO-*d*₆) δ =150.7 (d), 149.4 (d), 134.9 (d), 133.4 (d), 132.2 (d), 128.9 (s), 122.9 (d); MS *m/z* 184 (M^+ , 53%), 104 (100%); Anal. ($\text{C}_7\text{H}_8\text{N}_2\text{O}_2\text{S}$) C, H.

2-(4-Pyridyl)ethenesulfonamide (12): Colorless needles, mp 180 °C (decomp) (water); IR (KBr) 3320s, 3060w, 2980w, 2420w, 1596s, 1410m, 1322vs, 1135vs, 990m, 972vs, 932m, 810m, 795s cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =8.59 (dd, J =1.2 & 6.2 Hz, 2H, H-2, 6), 7.59 (dd, J =1.2 & 6.2 Hz, 2H, H-5, 3), 7.51 (dd, J =1.0 & 15.7 Hz, 1H, H-b, $\text{CH}_2=\text{CH}_2\text{SO}_2$), 7.24 (bs, 2H, NH_2), 7.22 (d, J =15.7 Hz, 1H, H-a); MS *m/z* 184 (M^+ , 74%), 104 (92%). Anal. ($\text{C}_7\text{H}_8\text{N}_2\text{O}_2\text{S}$) C, H.

2-(2,4-Dimethoxy-5-pyrimidinyl)ethenesulfonamide (13): Colorless crystals, mp 172–173 °C (ethyl acetate); IR (KBr) 3300m, 3220m, 1590s, 1540s, 1470s, 1400m, 1380m, 1320s, 1300s, 1230m, 1130s, 1060m, 1000m, 850m, 809m, 759m cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =8.61 (s, 1H, H-6), 7.23 (s, 2H, H-a, b, $\text{CH}_2=\text{CH}_2\text{SO}_2$), 7.08 (s, 2H, NH_2), 4.01 (s, 3H, OMe), 3.92 (s, 3H, OMe); ^{13}C NMR (DMSO-*d*₆) δ =168.2 (s), 165.0 (s), 160.1 (d), 130.9 (d), 128.2 (d), 108.4 (s), 54.9 (q), 54.4 (q); MS *m/z* 245 (M^+ , 100%), 164 (72%). Anal. ($\text{C}_8\text{H}_{11}\text{N}_3\text{O}_4\text{S}$) C, H.

2-(2,4-Dimethoxy-6-methyl-5-pyrimidinyl)ethenesulfonamide (14): Colorless needles, mp 195–197 °C (ethyl acetate); IR (KBr) 3300m, 3140w, 3020w, 1610m, 1560s, 1470s, 1450m, 1370s, 1130s, 1060m, 910m, 800m, 785m cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =7.33 (d, J =15.6 Hz, 1H, H-b, $\text{CH}_2=\text{CH}_2\text{SO}_2$), 7.09 (d, J =15.6 Hz, 1H, H-a), 7.06 (s, 2H, NH_2), 4.00 (s, 3H, OMe), 3.90 (s, 3H, OMe), 2.46 (s, 3H, Me); ^{13}C NMR (DMSO-*d*₆) δ =168.9 (s), 168.7 (s), 163.3 (s), 132.5 (d), 126.9 (d), 105.8 (s), 54.6 (q), 54.4 (q), 22.3 (q); MS *m/z* 259 (M^+ , 100%), 178 (93%). Anal. ($\text{C}_9\text{H}_{13}\text{N}_3\text{O}_4\text{S}$) C, H.

3-Phenyl-2-propene-1-sulfonamide (17): Colorless crystals, mp 110–111 °C (benzene) (lit.¹⁰) 126–127 °C).

3-(1-Naphthyl)-2-propene-1-sulfonamide (18): Pale yellow needles, mp 176–178 °C (EtOH); IR (KBr) 3350s, 3260s, 3050w, 1596w, 1416m, 1310vs, 1145vs, 975s, 890m, 820m, 800s, 772s cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =8.18 (m, 1H), 7.90–7.50 (m, 7H), 6.69 (s, 2H, NH_2), 6.25 (dt, J =15.0 & 6.0 Hz, 1H, H-b, $\text{CH}_2=\text{CH}_2\text{CH}_2\text{SO}_2$), 3.50 (d, J =6.0 Hz, 2H, CH_2); MS *m/z* 247 (M^+ , 8%), 116 (100%). Anal. ($\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}$) C, H.

3-(2-Thienyl)-2-propene-1-sulfonamide (19): Pale yellow crystals, mp 141–142 °C (benzene); IR (KBr) 3390vs, 3280s, 3040w, 1642m, 1550m, 1400m, 1328vs, 1138vs, 1125vs, 965s, 930m, 842m, 810m, 739m, 700s cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =7.42 (d, J =5.0 Hz, 1H, H-5), 7.00 (m, 2H, H-2, 4), 6.92 (bs, 2H, NH_2), 6.82 (d, J =14.5 Hz, 1H, H-b, $\text{CH}_2=\text{CH}_2\text{CH}_2\text{SO}_2$), 5.98 (dt, J =14.5 & 7.2 Hz, 1H, H-c), 3.85 (d, J =7.2 Hz, 1H, H-a); MS *m/z* 203 (M^+ , 3%), 122 (100%). Anal. ($\text{C}_7\text{H}_9\text{NO}_2\text{S}_2$) C, H.

3-(3-Pyridyl)-2-propene-1-sulfonamide (20): Colorless needles, mp 120–121 °C (H_2O); IR (KBr) 3260vs, 3050w, 2900s, 2620s, 1640w, 1580m, 1558m, 1460m, 1318vs, 1285vs, 1232s, 1150s, 1128vs, 962s, 800m, 780s, 718 cm⁻¹; ^1H NMR (DMSO-*d*₆) δ =8.62 (bs, 1H, H-2), 8.43 (bd, J =7.0 Hz, 1H, H-6), 7.89 (dt, J =9.5 & 1.1 Hz, 1H, H-4), 7.35 (dd, J =9.5 & 7.0 Hz, 1H, H-5), 6.93 (bs, 2H, NH_2), 6.72 (d, J =14.5 Hz, 1H, H-c, $\text{CH}_2=\text{CH}_2-\text{CH}_2$), 6.40 (dt, J =14.5 & 8.0 Hz, 1H, H-b), 3.92

(d, $J=8.0$ Hz, 2H, H-a); MS m/z 200 (M^+ , 7%), 118 (100%). Anal. ($C_8H_{10}N_2O_2S$) C, H.

3-(2,4-Dimethoxy-5-pyrimidinyl)-2-propene-1-sulfonamide (21): Colorless crystals, mp 273°C (decomp AcOEt); IR (KBr) 3280m, 3160w, 1590s, 1480s, 1400s, 1380s, 1330s, 1160m, 1000s, 960m, 780m cm^{-1} ; ^1H NMR (DMSO- d_6) $\delta=8.44$ (s, 1H, H-6), 6.88 (s, 2H, NH_2), 6.60 (d, $J=15.8$ Hz, 1H, H-c, $\text{CH}_2=\text{CH}_b-\text{CH}_{a2}$), 6.30 (dt, $J=15.8$ & 7.9 Hz, 1H, H-b), 3.98 (s, 3H, OMe), 3.89 (s, 2H, H-a), 3.80 (s, 3H, OMe); MS m/z 259 (M^+ , 43%), 179 ($-\text{SO}_2\text{NH}_2$, 100%). Anal. ($C_9H_{13}N_3O_4S$) C, H.

2-(1,2,3,4-Tetrahydro-2,4-dioxo-5-pyrimidinyl)ethenesulfonamide (15): A solution of **13** (1.00 g, 4.00 mmol) and sodium iodide (1.84 g, 12 mmol) in acetic acid (9 mL) was heated at 100°C with stirring for 4 h. After cooling, the solvent was evaporated in vacuo and the residue was dissolved in water (9 mL). To this solution was added dil sodium thiosulfate until the color of the solution disappeared. The precipitate was collected by filtration to give **15** (83%): colorless crystals, mp $266\text{--}268^\circ\text{C}$ decomp (water); IR (KBr) 3320s, 3220m, 3020w, 1710s, 1690vs, 1670vs, 1620m, 1500w, 1420m, 1320s, 1230s, 1150s, 810m, 769m cm^{-1} ; ^1H NMR (DMSO- d_6) $\delta=11.45$ (m, 2H, NH), 8.02 (d, $J=7.0$ Hz, 1H, H-6), 7.49 (d, $J=15.1$ Hz, 1H, H-b, $\text{CH}_b=\text{CH}_a-\text{SO}_2$), 7.01 (d, $J=15.1$ Hz, 1H, H-a), 6.88 (s, 2H, NH_2); ^{13}C NMR (DMSO- d_6) $\delta=162.7$ (s), 150.2 (s), 145.7 (d), 130.1 (d), 128.3 (d), 105.9 (s); MS m/z 217 (M^+ , 3%), 137 (100%). Anal. ($C_6H_7N_3O_4S$) C, H.

2-(1,2,3,4-Tetrahydro-2,4-dioxo-6-methyl-5-pyrimidinyl)-ethenesulfonamide (16): Similarly 6-methyl derivative **16** was obtained from **14** by the above method: Colorless crystals, mp $269\text{--}272^\circ\text{C}$ decomp (water); IR (KBr) 3300s, 3220s, 3080m, 1700vs, 1660vs, 1580m, 1540m, 1412s, 1310s, 1140s, 900m, 760m cm^{-1} ; ^1H NMR (DMSO- d_6) $\delta=11.21$ (bs, 2H, NH), 7.56 (d, $J=15.1$ Hz, 1H, H-b, $\text{CH}_b=\text{CH}_a-\text{SO}_2$), 7.02 (d, $J=15.1$ Hz, 1H, H-a), 6.89 (s, 2H, NH_2), 2.26 (s, 3H, Me); ^{13}C NMR (DMSO- d_6) $\delta=162.7$ (s), 155.6 (s), 149.9 (s), 129.0 (d), 127.9 (d), 102.3 (s), 16.6 (q); MS m/z 231 (M^+ , 7%), 151 (100%). Anal. ($C_7H_9N_3O_4S$) C, H.

[2-(Benzoylsulfamoyl)ethyl]pyridinium Chloride (1): To a solution of **2** (9.29 g, 86.8 mmol) and dry pyridine (14.73 g, 186 mmol) in dry acetone (30 mL) was added benzoyl chloride (25.95 g, 184 mmol) dissolved in dry benzene (10 mL). The mixture was refluxed for 30 min and, after cooling, the precipitate was collected by filtration to give salt **1** (15.38 g, 53%): Pale yellow prisms; mp $186\text{--}187^\circ\text{C}$ (DMF); IR (KBr) 3128m, 1690s, 1343s, 1150s cm^{-1} ; ^1H NMR (DMSO- d_6) $\delta=9.42$ (d, $J=5.8$ Hz, 2H, H-2, 6), 8.63 (t, $J=7.7$ Hz, 1H, H-4), 8.54—7.45 (m, 4H, H-3,5, and NH_2), 5.26 (t, $J=6.4$ Hz, 2H, $\text{CH}_2-\text{C}-\text{SO}_2$), 4.42 (t, $J=6.4$ Hz, 2H, CH_2SO_2); ^{13}C NMR (DMSO- d_6) $\delta=166.6$, 146.1, 145.8, 133.2, 131.4, 128.9, 128.3, 127.6, 54.7, 52.4. Anal. ($C_{14}H_{15}N_2O_3S$) C, H.

N-Benzoylthienenesulfonamide (3): To a solution of **2** (10.8 g, 0.10 mol) and triethylamine (12.7 g, 0.12 mol) in acetone (55 mL) was added benzoyl chloride (17.8 g, 0.13 mol) dropwise with stirring at room temperature. After the addition, the reaction mixture was stirred at room temperature for 30 min. The salt was removed by filtration and the filtrate was evaporated in vacuo. The residue was chromatographed on silica gel with dichloromethane as eluent to give **3** (2.7 g, 13%): Colorless needles, mp $87\text{--}92^\circ\text{C}$ (ether); IR (KBr) 3274m, 1710s, 1336s, 1151s, 1060m, 899m, 848m, 733m, 842m cm^{-1} ; ^1H NMR (CDCl_3) $\delta=9.50$ (bs, 1H, NH), 7.92 (m, 2H, ortho protons on Ph), 7.28 (m, 3H, m - & p -protons on Ph), 6.99 (dd, $J=16.6$ & 9.7 Hz, 1H, H-a), 6.49 (d, $J=16.6$ Hz, 1H, H-b), 6.14 (d, $J=9.7$ Hz, 1H, H-c); ^{13}C NMR $\delta=165.5$, 135.3, 133.6, 131.0, 130.4, 128.9, 128.1; MS m/z 211 (M^+ , 5%), 105 ($-\text{PhCO}^+$, 100%). Anal. ($C_9H_9NO_3S$) C, H.

N-Benzoyl-2-arylethenesulfonamide (22—24). Method A: The procedure for the preparation of **22**, **23**, and **24** is similar to that described in general procedure for the arylethenesulfonamides, except for using **1** in place of ethenesulfonamide **2**.

Method B: 2-Arylethenesulfonamides **7**, **10**, and **11** were treated with benzoyl chloride in a manner similar to the case of **3**, giving **22**.

22: (A: 23%; B: 19%) Colorless needles, mp $232\text{--}232.5^\circ\text{C}$; IR (KBr) 3290s, 1692s, 1418s, 1335s, 1159s, 1061s, 870m, 839m, 752m, 703m cm^{-1} ; ^1H NMR (DMSO- d_6) $\delta=12.1\text{--}12.5$ (bm, 1H), 8.01—7.34 (m, 12H); ^{13}C NMR (DMSO- d_6) $\delta=165.6$, 143.2, 133.0, 132.1, 131.6, 131.1, 128.9, 128.8, 128.5, 125.8; MS m/z 223 ($M^+ - \text{SO}_2$, 0.7%). Anal. ($C_{15}H_{13}NO_3S$) C, H.

23: (A: 24%; B: 9%) Colorless needles, mp $191\text{--}192^\circ\text{C}$ (methanol); IR (KBr) 3290m, 1695s, 1418vs, 1335s, 1159s, 840s, 718s, 702s cm^{-1} ; ^1H NMR (DMSO- d_6) $\delta=12.0\text{--}12.5$ (bm, 1H, NH), 8.00—7.40 (m, 8H), 7.35—7.05 (m, 2H); ^{13}C NMR (DMSO- d_6) $\delta=165.7$, 136.1, 133.3, 133.1, 131.6, 131.3, 128.6, 128.5, 128.4, 123.2; MS m/z 229 ($M^+ - \text{SO}_2$), 126 (100%), 105 (64%), 77 (88%). Anal. ($C_{13}H_{11}NO_3S_2$) C, H.

24: (A: 21%; B: 16%) Pale brown crystals, mp $224\text{--}225^\circ\text{C}$ (DMF); IR (KBr) 3060w, 3020w, 2850m, 1696s, 1623m, 1596m, 1509m, 1349s, 1260s, 1157vs, 843m, 791s, 718s cm^{-1} ; ^1H NMR (DMSO- d_6) $\delta=8.97$ (d, $J=1.8$ Hz, 1H, H-2), 8.65 (dd, $J=4.8$ & 1.8 Hz, 1H, H-5), 8.30 (dt, $J=7.4$ & 1.8 Hz, 1H, H-4), 7.95 (bd, $J=5.1$ Hz, 2H, ortho protons on Ph), 7.73 (s, 2H, $\text{CH}_b=\text{CH}_a-\text{SO}_2$), 7.50 (m, 4H, NH & m -, p -protons on Ph); ^{13}C NMR (DMSO- d_6) $\delta=165.8$, 151.5, 150.1, 139.9, 135.4, 133.7, 133.1, 128.5, 128.4, 128.3, 128.0, 124.0; MS m/z 289 ($M^+ + 1$, 0.3%), 224 (1.2%), 121 (100%). Anal. ($C_{14}H_{12}N_2O_3S$) C, H.

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