

Synthesis of coumarin sulfonamides and sulfonylurea

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Dedicated to Professor R.A. Abramovitch on the occasion of his 70th birthday

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Abstract

4-Coumarinsulfonamide **5c** and 4-hydroxy-3-coumarinsulfonamide **7b**, were prepared from 4-hydroxycoumarin **1**. Coumarinsulfonamide **5c** was served as intermediate for the synthesis of *N*-(isopropylphenyl)-*N*-(coumarin-4-sulfonyl)urea **9** and *N*-(4-bromophenyl)-, **8a**, *N*-(1,3,4-thiadiazol-2-yl)-, **8b**, and *N*-(4-isopropylphenyl)-4-aminocoumarin **8c**.

Keywords: Coumarin sulfonamides, coumarin sulfonylureas, aminocoumarins

Introduction

Sulfonylurea herbicides possess herbicidal activity at unprecedented levels combined with very low mammalian toxicity and desirable environmental properties.² The synthesis and SAR-study of a great number of sulfonylureas have shown that maximum herbicidal activity is found in compound having an ortho substituted aryl group next to unmodified sulfonylurea bridge and with the heterocycle as a pyrimidine or 1,3,5-triazine with methyl or methoxy in the 4 and 6 positions.³

ARYL-SO₂-NH-CO-NH-HETEROCYCLE

I

Our research effort has been focused on substitution of the ARYL part of general formula **I** by the coumarin moiety.

A comprehensive review of the syntheses of sulfonylureas and their intermediates has been published by Beyer et. al.⁴ The overall synthesis of these sulfonylureas involves preparation of the sulfonamide and their coupling reactions with isocyanate derivatives.

Results and Discussion

The coumarinsulfonamide **5c** is a key intermediate that required to prepare the target product of type **I**. 4-Chlorocoumarin **2a** was prepared from 4-hydroxycoumarin **1**. It is known, that the selectivity of the reaction of **1** with POCl₃ is low,^{6,7} because a considerable amount of 4-chloro-3,4',3',4''-tercoumarin **3** was formed as a by-product. Our method improved the yield of the **2a** and significantly decreased yield of the **3**. ¹H-NMR of the **3** clearly shows three doublets with a typical ortho interaction constant (5,5',5''-H) and a singlet for 3''-H. ¹³C-NMR (DEPT) spectra indicate the presence of 14 quaternary carbons and 13 tertiary (C-H) ones. Quaternary carbons are in positions 3 and 4 on the two of three α -pyrone skeletons. Mass spectrum showed a molecular weight of 468, which was consistent with the elemental analysis.

The key intermediate, 4-isopropylthiocoumarin **2c** was easily prepared from 4-chlorocoumarin **2a** using sodium 2-propanethiol. Oxidation of **2c** by chlorine in acetic acid, and subsequent transformation of the sulfonylchloride **5a** by different amines led to the sulfonamides **5b**, **5c**. Attempted oxidation of the 4-ethylthiocoumarin **2b** under the same condition led mainly to the 3,4-dichlorocoumarin **4**.

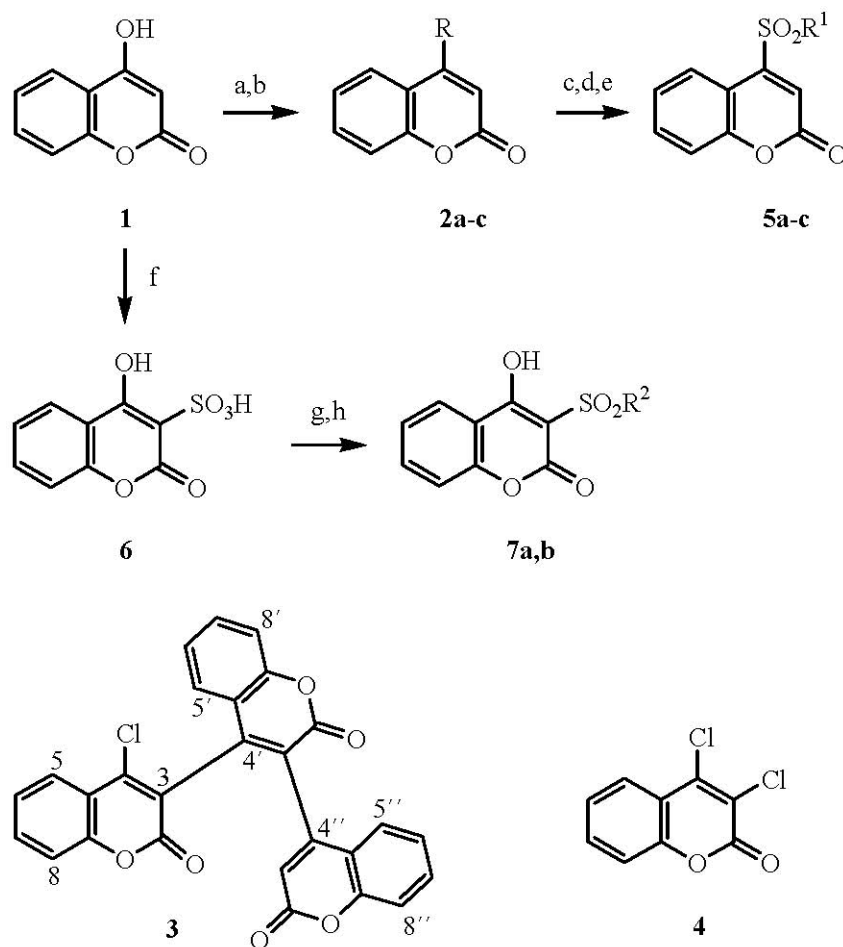
The most selective and effective way to the sulfonamide **5c** was via the preparation of N-*t*-butyl coumarinsulfonamide **5b**, with subsequent removal of the *t*-butyl group with trifluoroacetic acid (TFA).

Chlorosulfonation of **1** exclusively produced 3-coumarinsulfonic acid **6** which was further converted to sulfonamide **7b** (Scheme 1).

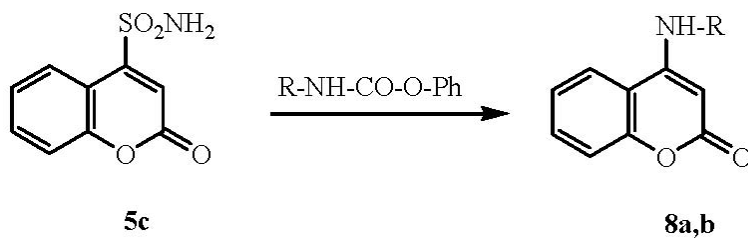
A very convenient method for the preparation of sulfonylureas is the diazabicycloundecene (DBU) catalyzed condensation of an arylsulfonamide with a phenoxycarbamate. Other route (Meyer and Fory method) involved the heating of a phenylcarbamate of the sulfonamide with arylamines and heteroamines.⁵

According to the method reported by Meyer and Fory, we have obtained 4-substituted aminocoumarins **8a** and **8b** (Scheme 2).

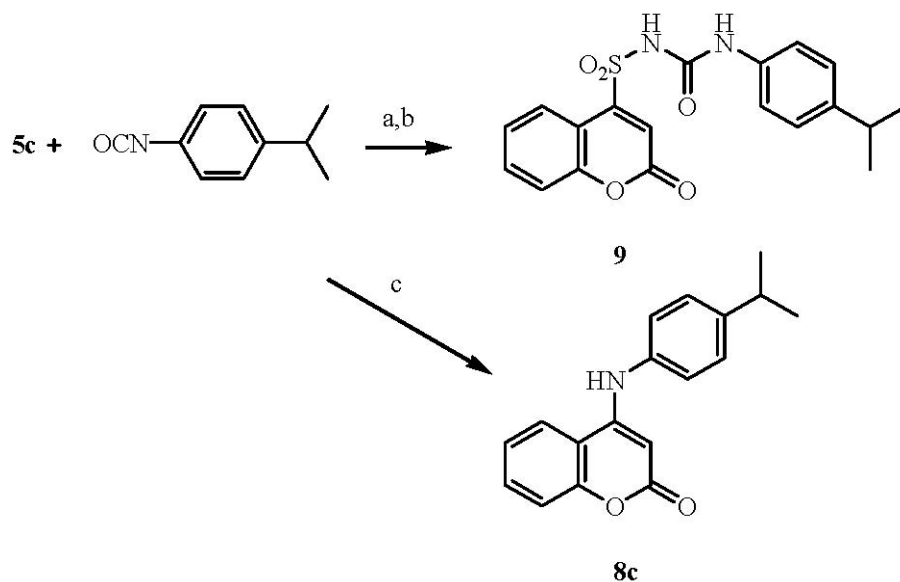
The attempted condensation of coumarinsulfonamide **5c** with 4-isopropylphenylisocyanate using diazabicyclononene (DBN) led only to 4-aminosubstituted coumarin **8c**. The SnCl₄ catalyzed reaction of **5c** with the isocyanate provides desired sulfonylurea **9** (Scheme 3).



Scheme 1. (a) POCl_3 , $\text{R} = \text{Cl}$ **2a**; (b) RSNa/MeOH , $\text{R} = \text{SC}_2\text{H}_5$ **2b**, $\text{i/C}_3\text{H}_7\text{S}$ **2c**; (c) $\text{Cl}_2/\text{AcOH/H}_2\text{O}$, $\text{R}^1 = \text{Cl}$ **5a**; (d) $\text{R}^1 = \text{t/C}_4\text{H}_9\text{NH}$ **5b**; (e) TFA , $\text{R}^1 = \text{NH}_2$ **5c**; (f) ClSO_3H ; (g) SOCl_2 , $\text{R}^2 = \text{Cl}$ **7a**; (h) $\text{NH}_3/\text{Et}_2\text{O}$, $\text{R}^2 = \text{NH}_2$ **7b**.



Scheme 2. $\text{R} = 4\text{-bromophenyl-}$, **8a**; $1,3,4\text{-thiadiazol-2-yl-}$, **8b**.



Scheme 3. (a) SnCl_4 ; (b) H_3O^+ ; (c) DBN

Experimental Section

General Procedures. Flash chromatography was carried out on 0.04–0.063 mm (Merck) silica gel, thin layer chromatography was carried out on aluminum back silica plates by Merck and plates were viewed in UV254 light. IR-spectra were recorded on a Philips Analytical PU 9800 spectrometer. $^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra were recorded on a Varian VXR 300 instrument at 293 °K in CDCl_3 or DMSO D-6. Spectra were internally referenced to TMS. Peaks are reported in ppm downfield of TMS. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), some combinations of these were made by DEPT editing of the spectra. The MS-spectra were recorded on a AEI MS 902 S electron ionization spectrometer (EI = 70 eV). The elemental analysis, were performed on a Perkin-Elmer 2400 spectrometer.

Materials. The 4-hydroxycoumarin **1**, ethanethiol, 2-propanethiol, trifluoroacetic acid (TFA), chlorosulfonic acid (ClSO_3H), POCl_3 were purchased from Fluka, and Bu_tNH_2 was purified, dried and distilled prior to use.

4-Chlorocoumarin (2a). 4-hydroxycoumarin **1** (30 g, 0.185 mol) and 60 mL POCl_3 were refluxed for 1 h, cooled, and slowly poured onto crushed ice (700 g) with vigorous stirring. The solid was collected by filtration and washed successively with ice–water. Azeotropic distillation with i-hexane, hot filtration of the by–product (15 g, 17%),⁷ followed by evaporation of solvent and crystallization yielded 21.9 g (65%) of 4-chlorocoumarin with mp 87–89 °C (lit.⁶ 89–91 °C). $^1\text{H-NMR}$ δ 7.88–7.30 (4H, m, ar-H), 6.62 (1H, s, 3-H); IR ν 3098, 3069, 3040, 1754, 1721, 1611, 1603, 1449, 1348, 1273, 1177 cm^{-1} ; MS m/z : 182 (23), 180 (MH^+ , 77), 154 (31), 152 (100), 89 (85), 63 (46), 62 (31), 39 (19).

4-Chloro-3,4',3',4''-tercoumarin (by-product) (3). Crystallization from acetic acid gave yellowish crystals, mp 321–325 °C (lit.⁷ 324–327 °C). ¹H-NMR δ 8.11 (1H, d, *J* = 7.92), 8.01 (1H, d, *J* = 7.92), 7.93 (1H, d, *J* = 7.92), 7.81–7.41 (9H, m), 7.26 (1H, s, 3''-H); ¹³C-NMR δ 170.84, 169.80, 160.10, 153.75, 153.73, 152.96, 159.65, 151.80, 151.20, 149.20, 146.15, 134.74, 134.37, 133.96, 126.83, 126.64, 126.36, 125.52, 125.15, 123.95, 122.47, 121.54, 119.87, 118.96, 117.63, 117.21, 116.79; IR ν 3088, 3068, 3039, 1718, 1625, 1593, 1538, 1352, 1187 cm⁻¹; MS *m/z*: 470 (31), 468 (MH⁺, 86), 440 (9), 434 (18), 433 (56), 405 (22), 389 (13), 361 (11), 349 (8), 313 (36), 289 (100), 285 (36), 261 (11), 257 (13), 229 (16), 220 (7), 200 (20), 92 (9), 85 (29), 83 (40). Anal. Calcd for C₂₇H₁₃ClO₆: C, 69.16; H, 2.79. Found: C, 69.30; H, 2.75.

4-Ethylthiocoumarin (2b). To a stirred solution of 4-chlorocoumarin (0.5 g, 2.8 mmol) in methanol (10 mL) was added dropwise sodium ethanethiol (prepared from Na (0.07 g, 3 mmol) in 4 mL of methanol and 0.17 g (0.2 mL, 2.8 mmol) of ethanethiol). The mixture was refluxed for 30 minutes, followed by hot filtration. After cooling to 0 °C the product was filtered and dried (60 °C/15 torr). We have obtained 0.49 g (85%) of **2b** with mp 111–114 °C (lit.⁸ 120–121 °C). ¹H-NMR δ 7.8–7.2 (4H, m, ar-H), 6.2 (1H, s, 3-H), 3.1 (2H, q, *J* = 7.5, 11-H), 1.5 (3H, t, *J* = 7.5, 12-H); IR ν 3067, 2967, 2909, 2868, 1761, 1730, 1607, 1447, 1350, 1260, 1165 cm⁻¹.

4-Isopropylthiocoumarin (2c). Method A: To a refluxed solution of 4-chlorocoumarin (20 g, 0.11 mol) in methanol (350 mL) was added dropwise sodium 2-propanethiol (prepared from 2.56 g of Na (0.11 mol) in 150 mL of methanol and 8.44 g (10.3 mL, 0.11 mol) of 2-propanethiol). The mixture was refluxed for 20 minutes, followed by hot filtration. After cooling to 0 °C the product was filtered and dried (60 °C/15 torr). We have obtained 15.65 g (64%) of **2c** with mp 123–125 °C. Method B: A mixture of 4-chlorocoumarin (1 g, 5.6 mmol), Et₃N (0.56 g, 0.8 mL, 5.6 mmol), DMAP (0.1 g, 0.8 mmol) and 2-propanethiol (0.76 g, 0.9 mL, 10 mmol) in acetone (10 mL) was refluxed for 3.5 h. After treating with HCl (4 mL HCl/30 mL H₂O), the formed solid was collected by filtration. Recrystallization from MeOH gave 0.34 g (28%) of product **2c** with mp 121–124 °C (lit.⁸ 131–132 °C). ¹H-NMR δ 7.7–7.2 (4H, m, ar-H), 6.2 (1H, s, 3-H), 3.6 (1H, k, 11-H), 1.5 (6H, d, 12-H, 12'-H); IR ν 3061, 2975, 2926, 2826, 1755, 1705, 1601, 1595, 1545, 1346, 1192, 1180 cm⁻¹; MS *m/z*: 220 (MH⁺, 62), 221 (10), 179 (10), 178 (100), 177 (28), 150 (52), 122 (14), 121 (22), 89 (14), 90 (14).

3,4-Dichlorocoumarin (4). Chlorine was added to a mixture of **2b** (0.45 g, 2.2 mmol) and 1 mL of H₂O in 4 mL of glacial acetic acid over 10 minutes at 10 °C. After addition of 1 mL of H₂O to the mixture, introducing of chlorine was continued for another 20 minutes. The formed solid was filtered and quenched with cold water. Recrystallization from CHCl₃ gave 0.26 g (55%) of product with mp 107–108 °C (lit.⁹ 106.7–107.5 °C). ; ¹H-NMR δ 7.88 (1H, dd, *J* = 7.8, 1.5, 5-H), 7.64 (1H, td, *J* = 7.9, 1.5, 7-H), 7.42 (1H, td, *J* = 7.8, 1.1, 6-H), 7.39 (1H, d, *J* = 7.9, 8-H); ¹³C-NMR δ 155.89 (2-C), 150.76 (9-C), 145.71 (4-C), 132.97 (7-C), 125.76 (5-C), 125.40 (6-C), 121.37 (3-C), 118.08 (10-C), 116.91 (8-C); IR ν 3094, 3069, 3038, 1736, 1595, 1448, 1304, 1275, 1009 cm⁻¹; MS *m/z*: 218 (34), 216 (68), 214 (MH⁺, 100), 190 (6), 188 (29), 186 (46), 160 (13), 158 (20), 125 (16), 123 (46).¹⁰

4-Coumarinsulfonyl chloride (5a). Chlorine (prepared in reaction between K₂Cr₂O₇ (20 g,

0.07 mol) and 36% HCl (80 mL) was introduced into a mixture of **2c** (6.5 g, 0.03 mol) and 20 mL of H₂O in glacial acetic acid (50 mL) over 20 minutes at 5–10 °C. The formed solid was filtered and quenched with cold water. Recrystallization from CHCl₃ provided 6.15 g (84%) of product with mp 119–121 °C; ¹H-NMR δ 8.29 (1H, d, *J* = 7.9, 5-H), 7.73 (1H, t, *J* = 7.3, 7-H), 7.45 (2H, m, 6-H, 8-H), 7.21 (1H, s, 3-H); IR ν 3073, 1759, 1732, 1607, 1450, 1385, 1366, 1198, 1167 cm⁻¹; MS *m/z*: 246 (34), 244 (MH⁺, 85), 218 (11), 216 (26), 209 (64), 181 (11), 154 (13), 152 (40), 146 (21), 145 (66), 117 (15), 101 (100), 89 (74). Anal. Calcd for C₉H₅ClO₄S: C, 44.18; H, 2.06; S 13.13. Found: C, 44.32; H, 2.15; S, 12.96.

***N*-(1,1-Dimethylethyl)-4-coumarinsulfonamide (5b)**. To a stirred and cooled solution at –10 °C of 4-coumarinsulfochloride (2.46 g, 0.01 mol) in 7 mL of CHCl₃ was added dropwise the solution of Bu₄NH₂ (1.46 g, 0.02 mol) in CHCl₃ (3.5 mL) over 30 minutes. The reaction mixture was stirred 45 minutes at 20 °C. Formed hydrochloride was separated by filtration. The solvent was removed and the product was crystallized from MeOH. We have obtained 0.95 g (34%) of product with mp 135 °C; ¹H-NMR δ 8.3–7.3 (4H, m, ar-H), 7.1 (1H, s, 3-H), 4.9 (1H, s_{br}, NH), 1.4 (9H, s, 11-H); IR ν 3231, 3090, 2982, 1759, 1717, 1607, 1341, 1196, 1154, 1007 cm⁻¹; MS *m/z*: 281 (MH⁺, 21), 266 (100), 254 (4), 145 (12), 101 (27), 89 (12), 57 (30), 56 (65), 55 (25), 41 (99). Anal. Calcd for C₁₃H₁₅NO₄S: C, 55.50; H, 5.37; N, 4.98. Found: C, 55.40; H, 5.21; N, 4.90.

4-Coumarinsulfonamide (5c). A solution of *N*-(1,1-dimethylethyl)-4-coumarinsulfonamide (0.33 g, 1.2 mmol) in TFA (10 mL) was refluxed for 3 h. The solvent was then rotary evaporated to leave a solid. Crystallization from MeOH gave 0.1 g (40%) of product **5c** with mp 174–176 °C; ¹H-NMR δ 8.24 (2H, s, NH₂), 8.18 (1H, d, *J* = 8.1, 5-H), 7.73 (1H, t, *J* = 7.9, 7-H), 7.51 (1H, d, *J* = 8.4, 8-H), 7.45 (1H, t, *J* = 7.9, 6-H), 6.88 (1H, s, 3-H); ¹³C-NMR δ 159.23 (2-C), 153.7 (9-C), 153.54 (4-C), 133.22 (7-C), 126.47 (5-C), 124.93 (6-C), 117.32, 115.44 (3-C, 8-C), 113.38 (10-C); IR ν 3304, 3220, 3086, 1763, 1720, 1603, 1448, 1344, 1203, 1163 cm⁻¹; MS *m/z*: 225 (MH⁺, 89), 161 (5), 145 (24), 133 (21), 118 (100), 116 (13), 101 (36), 90 (18), 89 (47), 63 (34). Anal. Calcd for C₉H₇NO₄S: C, 47.99; H, 3.13; N, 6.22; S, 14.24. Found: C, 48.19; H, 3.16; N, 6.47; S, 14.08.

4-Hydroxy-3-coumarinsulfonic acid (6). To a solution of 20 mL of ClSO₃H in 80 mL of dioxane was added **1** (24 g, 0.15 mol) at 50 °C.¹¹ After 20 minutes the formed solid was filtered, washed with cold Et₂O and air-dried. We have obtained 32.6 g (91%) of **6** with mp 92 °C; ¹H-NMR δ 14.1 (2H, s_{br}, OH), 7.87 (1H, d, *J* = 7.8, 5-H), 7.69 (1H, t, *J* = 8.1, 7-H), 7.41–7.34 (2H, m, 6-H, 8-H), 2.56 (8H, s, dioxane-CH₂); ¹³C-NMR δ 162.34 (4-C), 157.03 (2-C), 152.57 (9-C), 133.61 (7-C), 124.44 (5-C), 124.19 (6-C), 116.27 (8-C), 114.9 (10-C), 107.71 (3-C), 66.38 (dioxane-C); IR ν 3500–2500, 1726, 1705, 1676, 1608, 1556, 1493, 1439, 1348, 1327, 1242, 1213, 1157, 1030 cm⁻¹.

4-Hydroxy-3-coumarinsulfonamide (7b). Mixture of **6** (5 g, 21 mmol) and SOCl₂ (20 mL) was refluxed for 3 h.¹¹ After distillation of SOCl₂, the residue was diluted with AcOEt. The sulfochloride **7a** was filtered and air-dried (mp 125–145 °C). 2 g of crude coumarinsulfochloride was added to a solution of 25% NH₃ in MeOH (5 mL) at –10 °C. After 2 h of standing at room temperature, the volume of mixture was reduced for one-half and treated

with HCl (5 mL). The product was filtered and recrystallized from EtOH (40 mL). We have obtained 0.2 g (10%) of **7b** with mp 238 °C; $^1\text{H-NMR}$ δ 7.96 (1H, d, $J = 7.4$, 5-H), 7.76 (1H, t, $J = 7.6$, 7-H), 7.46–7.40 (2H, m, 6-H, 8-H), 4.50 (3H, s, NH_2 , OH); $^{13}\text{C-NMR}$ δ 165.47 (4-C), 157.16 (2-C), 153.0 (9-C), 135.03 (7-C), 125.05 (5-C), 124.84 (6-C), 116.76 (8-C), 115.24 (10-C), 105.41 (3-C); IR ν 3420, 3361, 3259, 3088, 1703, 1619, 1606, 1553, 1436, 1350, 1329, 1293, 1126 cm^{-1} ; MS m/z : 241 (MH^+ , 51), 224 (37), 162 (11), 121 (39), 120 (100), 105 (7), 104 (5), 92 (34), 76 (10), 77 (10). Anal. Calcd for $\text{C}_9\text{H}_7\text{NO}_5\text{S}$: C, 44.80; H, 2.82; N 5.83. Found: C, 44.98; H, 2.84; N, 5.88.

***N*-(4-Bromophenyl)-4-aminocoumarin 8a and *N*-(1,3,4-thiadiazol-2-yl)-4-aminocoumarin (8b)**. A solution of 4-coumarinsulfonamide **5c** (0.1 g, 0.4 mmol), DBU (0.06 mL, 0.4 mmol) and 0.4 mmol of phenoxy *N*-(4-bromophenyl)carbamate or phenoxy *N*-(1,3,4-thiadiazol-2-yl)carbamate was reflux for 3 h. After evaporating of solvent (two third of volume), the residue was then stirred with the same volume of water contained 1 mL of HCl. The formed solid products **8a** or **8b** was filtered and recrystallized from EtOH. We have obtained 59 mg (42%) of **8a** with mp 240 °C (subl.) or 89 mg (82%) of **8b** with mp 290 °C; **8a**: $^1\text{H-NMR}$ δ 9.33 (1H, s, NH), 8.22 (1H, d, $J = 7.3$, 5-H), 7.68–7.67 (1H, m, 7-H), 7.66 (2H, d, $J = 8.6$, 12-H, 12'-H), 7.42–7.40 (2H, m, 6-H, 8-H), 7.36 (2H, d, $J = 8.6$, 13-H, 13'-H), 5.38 (1H, s, 3-H); $^{13}\text{C-NMR}$ δ 161.34 (2-C), 153.37 (9-C), 151.98 (4-C), 137.78 (11-C), 132.47 (7-C), 132.40 (13-C, 13'-C), 126.77 (12-C, 12'-C), 123.66 (5-C), 122.84 (6-C), 117.88 (14-C), 117.07 (8-C), 114.45 (10-C), 85.13 (3-C); IR ν 3281, 3113, 3065, 1665, 1618, 1613, 1582, 1534, 1491, 1404, 1262, 1202 cm^{-1} ; MS m/z : 317 (100), 315 (MH^+ , 100), 300 (12), 298 (12), 289 (22), 287 (22), 275 (14), 273 (14), 260 (5), 258 (5), 247 (5), 245 (5), 236 (38), 235 (63), 208 (38), 180 (26), 157 (16), 155 (16), 118 (19), 96 (18), 90 (30). Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{BrNO}_2$: C, 56.98; H, 3.19; N, 4.32. Found: C, 55.84; H, 3.13; N, 4.32. **8b**: $^1\text{H-NMR}$ δ 11.0 (1H, s, NH), 9.23 (1H, s, 12-H), 8.38 (1H, d, $J = 7.32$, 5-H), 7.69 (1H, t, $J = 7.5$, 7-H), 7.5–7.4 (2H, m, 6-H, 8-H), 5.44 (1H, s, 3-H); $^{13}\text{C-NMR}$ δ 163.13 (4-C), 161.50 (2-C), 153.04 (9-C), 148.76 (11-C), 147.43 (12-C), 132.44 (7-C), 123.97 (6-C), 123.02 (5-C), 117.24 (8-C), 114.08 (10-C), 94.68 (3-C); IR ν 3270, 3106, 3079, 3036, 1668, 1578, 1557, 1501, 1497, 1254 cm^{-1} ; MS m/z : 245 (MH^+ , 41), 228 (29), 217 (59), 190 (10), 175 (9), 163 (7), 144 (8), 132 (41), 127 (21), 124 (83), 123 (100), 103 (12), 101 (90), 96 (17), 89 (17), 74 (64), 69 (38), 68 (45). Anal. Calcd for $\text{C}_{11}\text{H}_7\text{N}_3\text{O}_2\text{S}$: C, 53.86; H, 2.88; N, 17.13. Found: C, 52.78; H, 2.81; N, 16.87.

***N*-(4-Isopropylphenyl)-4-aminocoumarin (8c)**. To a solution of 4-coumarinsulfonamide **5c** (0.5 g, 2.2 mmol) in 10 mL of dioxane was added 4-isopropylphenyl isocyanate (0.53 g, 3.3 mmol) and DBN (0.41 g, 0.4 ml, 3.3 mmol) at 40 °C, following the reflux for 15 minutes. After cooling, treating with 1 mL of HCl and removing of solvent, the product was purified by column chromatography (SiO_2 , 40 g; CHCl_3). We have obtained 0.39 g (65%) of **8c**; $^1\text{H-NMR}$ δ 9.28 (1H, s, NH), 8.25 (1H, d, 5-H), 7.64 (1H, t, 7-H), 7.43–7.28 (6H, m, ar-H), 5.26 (1H, s, 3-H), 2.93 (1H, k, 15-H), 1.23 (6H, d, 16-H, 16'-H); $^{13}\text{C-NMR}$ δ 161.47 (2-C), 153.39 (9-C), 152.62 (4-C), 146.29 (11-C), 135.77 (14-C), 132.32 (7-C), 127.29 (13-C, 13'-C), 125.14 (12-C, 12'-C), 123.55 (6-C), 122.74 (5-C), 117.04 (8-C), 114.48 (10-C), 83.99 (3-C), 33.01 (15-C),

24.02, 23.86 (16-C, 16'-C); IR ν 3302, 3069, 3030, 2961, 2928, 1666, 1620, 1537, 1261, 1198 cm^{-1} ; MS m/z : 279 (MH^+ , 86), 264 (91), 237 (30), 236 (32), 146 (40), 145 (23), 135 (43), 128 (20), 120 (100), 91 (23), 77 (26). Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$: C, 77.42; H, 6.09; N, 5.02. Found: C, 76.82; H, 5.87; N, 4.98.

***N*-(4-isopropylphenyl)-*N*-(coumarin-4-sulfonyl)urea (9).** A mixture of 4-coumarinsulfonamide **5c** (0.5 g, 2.2 mmol), 4-isopropylphenyl isocyanate (0.53 g, 3.3 mmol) and SnCl_4 (0.4 mL, 3.3 mmol) was heated to (100 ± 10) °C for 1.3 h. After cooling the mixture was poured into ice-water (10 g) and 1 mL of HCl and 30 mL of AcOEt was added. The stirring was continued until two clear phases was disappeared. Organic layer was separated, dried and the solvent was evaporated. Purification by column chromatography (SiO_2 , 50 g; CHCl_3) gave 0.39 g (46%) of **9** with mp 174–176 °C; $^1\text{H-NMR}$ δ 9.04 (1H, s, NH), 8.26 (1H, d, 5-H), 7.74 (1H, t, 7-H), 7.55 (1H, d, 8-H), 7.50 (1H, t, 6-H), 7.27 (2H, d, $J = 8.66$, 13-H, 13'-H), 7.11 (2H, d, $J = 8.66$, 14-H, 14'-H), 7.06 (1H, s, 3-H), 4.02 (1H, s_{br}, NH), 2.80 (1H, k, 16-H), 1.12 (6H, d, 17-H, 17'-H); $^{13}\text{C-NMR}$ δ 158.55 (2-C), 153.59 (9-C), 150.26 (4-C), 149.25 (11-C), 143.73 (12-C), 135.50 (15-C), 133.27 (CH), 126.54 (2 x CH), 125.65 (CH), 124.97 (CH), 119.56 (2 x CH), 118.33 (CH), 117.42 (CH), 112.95 (10-C), 32.81 (16-C), 24.05, 23.91 (17-C, 17'-C); IR ν 3312, 3193, 3112, 2963, 2928, 1757, 1728, 1665, 1607, 1530, 1451, 1366, 1352, 1159 cm^{-1} ; MS m/z : 251 (6), 225 (3), 185 (3), 170 (9), 161 (6), 159 (8), 146 (9), 135 (31), 120 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_5\text{S}$: C, 59.07; H, 4.66; N, 7.25; S, 8.29. Found: C, 57.92; H, 4.64; N, 7.18; S, 8.37.

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