Synthesis of 2-Amino-4,5-dihydro-3-methanesulfonylfurans (and -thiophenes)

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2-Amino-4,5-dihydro-3-methanesulfonylfurans **7** and 2-amino-4,5-dihydro-3-methanesulfonylthiophenes **8** were prepared by deamidation of tetrahydro-2-imino-3-methanesulfonyl-3-furancarboxamides **3** and of tetrahydro-2-imino-3-methanesulfonyl-3-thiophenecarboxamides **4** with bases. Compounds **3** and **4** were obtained by reaction of 2-amino-4,5-dihydro-3-furancarboxamides **1** and 2-amino-4,5-dihydro-3-thiophenecarboxamides **2** with methanesulfonyl chloride in the presence of triethylamine.

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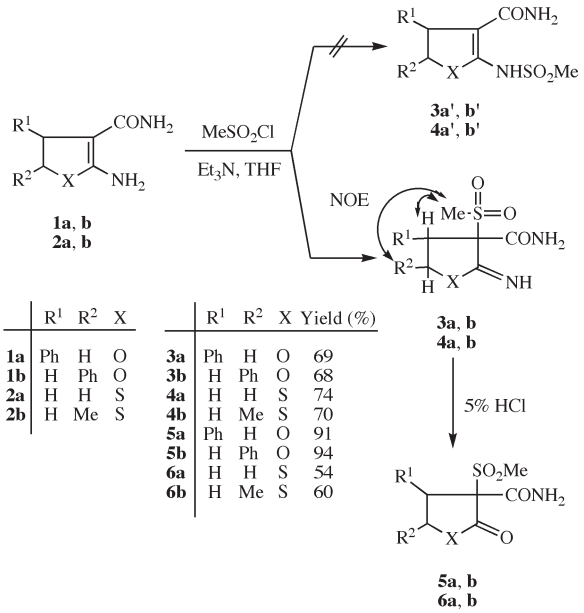
Five-membered ring heterocyclic enamines containing electron withdrawing substituent such as alkoxycarbonyl [1], cyano [2-6] or carbamoyl group [7] at the 3-position have widely been used as building blocks for the construction of several heterocycles. We report in this paper on a simple method for the preparation of 2-amino-4,5-dihydrofurans **7** and 2-amino-4,5-dihydrothiophenes **8** having a methanesulfonyl group at the 3-position, involving deamidation of tetrahydro-2-imino-3-methanesulfonyl-3-furancarboxamides **3** and tetrahydro-2-imino-3-methanesulfonyl-3-thiophenecarboxamides **4** with bases.

The ir and ^{1}H nmr spectra of 2-amino-4,5-dihydro-3-furancarboxamides **1** [8] and 2-amino-4,5-dihydro-3-thiophenecarboxamides **2** [9] indicate that **1** and **2** exist as the primary enaminoamide forms. Therefore, electrophilic reagents are anticipated to attack at either the enamino nitrogen atom or the β-carbon atom (the 3-position of **1** and **2**) in the enamine. The reactions of compounds **1a**,**b** and **2a**,**b** with methanesulfonyl chloride in the presence of triethylamine in tetrahydrofuran yielded the corresponding tetrahydro-2-imino-3-methanesulfonyl-3-furancarboxamides **3a**,**b** and tetrahydro-2-imino-3-methanesulfonyl-3-thiophenecarboxamides **4a**,**b** (C_3-SO_2CH_3) in 68-74% yields. The stereochemistry of **3a** was assigned by means of NOE between C_3-SO_2CH_3 and C_4-H. In the NOESY spectrum of **3a**, the NOE showed that these groups are located on the same side of the tetrahydrofuran ring system, which corresponded to the *cis* form. Similarly, from the NOESY spectra of **3b** and **4b**, the NOE observed between C_3-SO_2CH_3 and C_5-C_6H_5, and C_3-SO_2CH_3 and C_5-CH_3 indicated a *cis* configuration of these groups. In order to confirm the structures of **3a**,**b** and **4a**,**b** hydrolysis of **3a**,**b** and **4a**,**b** with hydrochloric acid resulted in the formation of the corresponding tetrahydro-3-methanesulfonyl-2-oxo-3-

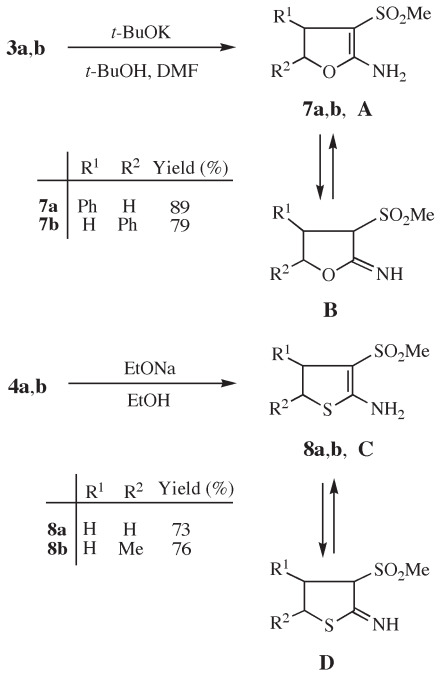
Scheme 1



	R^1	R^2	X
1a	Ph	H	O
1b	H	Ph	O
2a	H	H	S
2b	H	Me	S

	R^1	R^2	X	Yield (%)
3a	Ph	H	O	69
3b	H	Ph	O	68
4a	H	H	S	74
4b	H	Me	S	70
5a	Ph	H	O	91
5b	H	Ph	O	94
6a	H	H	S	54
6b	H	Me	S	60

Scheme 2



	R^1	R^2	Yield (%)
7a	Ph	H	89
7b	H	Ph	79

	R^1	R^2	Yield (%)
8a	H	H	73
8b	H	Me	76

furancarboxamides **5a**,**b** and tetrahydro-3-methanesulfonyl-2-oxo-3-thiophenecarboxamides **6a**,**b**. These experimental results are consistent with the 2-imino-3-methanesulfonyl-3-furancarboxamides **3a**,**b** and 2-imino-3-methanesulfonyl-3-thiophenecarboxamides **4a**,**b** rather than the 2-methanesulfonamido-3-furancarboxamides **3a'**,**b'** and 2-methanesulfonamido-3-thiophenecarboxamides **4a'**, **b'** (C_2-N-SO_2CH_3) (Scheme 1).

Subsequently, we examined the deamidation of compounds **3a**,**b** and **4a**,**b** with bases. Treatment of **3a**,**b** with potassium *tert*-butoxide in *tert*-butanol-DMF (1:4) underwent deamidation to give the expected 2-amino-4,5-dihydro-3-methanesulfonylfurans **7a**,**b** in good yields (Scheme 2). Compounds **4a**,**b** were allowed to react with sodium ethoxide in ethanol to yield the desired 2-amino-4,5-dihydro-3-methanesulfonylthiophenes **8a**,**b**. The structures of **7a**,**b** and **8a**,**b** were determined by means of analytical and spectral data. The ^{1}H nmr spectra of **7a**,**b** in DMSO-d_6 and **8a**,**b** in deuteriochloroform show the presence of a mixture of the enamine **A**, **C** and imine **B**, **D** form (see EXPERIMENTAL).

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were taken with a JASCO A-302 spectrometer or JASCO FT/IR-230 spectrometer. The ^{1}H nmr and ^{13}C nmr spectra were measured with a JEOL JNM-A500 instrument (500.00 MHz for ^{1}H, 125.65 MHz for ^{13}C) in DMSO-d_6 and $CDCl_3$ with TMS as internal standard. ^{13}C signal assignments were confirmed by the DEPT and ^{13}C-^{1}H COSY techniques. Mass spectra were recorded with a JEOL JMS-HX100 instrument at 70 eV. Elemental analyses were performed using a YANACO MT-6 elemental analyzer.

General Procedures for the Preparation of Tetrahydro-2-imino-3-methanesulfonyl-3-furancarboxamides **3a**,**b** and Tetrahydro-2-imino-3-methanesulfonyl-3-thiophenecarboxamides **4a**,**b**.

Methanesulfonyl chloride (1.27 g, 11 mmoles) was added to an ice-cooled and stirred suspension of **1a,b** or **2a,b** (10 mmoles) and triethylamine (1.21 g, 12 mmoles) in THF (15 ml). The mixture was stirred at room temperature (in the case of the preparation **3a,b**) or 40° (**4a,b**) for 3 hours. The solvent was removed in vacuo and cold water was added to the residue. The precipitate was collected, washed with water and dried to give **3a,b** and **4a,b**.

trans-Tetrahydro-2-imino-3-methanesulfonyl-4-phenyl-3-furancarboxamide (**3a**).

This compound was obtained as colorless prisms (1.94 g, 69%), mp 149-150° (acetone-petroleum ether); ir (potassium bromide): ν 3340, 3290, 3200 (NH), 1690 (C=O) cm^{-1}; ^{1}H nmr (DMSO-d_6): δ, 3.42 (s, 3H, SO_2CH_3), 4.19 (dd, J = 2.1, 8.8 Hz, 1H, 5-H), 4.44 (dd, J = 2.1, 6.4 Hz 1H, 4-H), 4.66 (dd, J = 6.4, 8.8 Hz 1H, 5-H), 7.20-7.32 (m, 5H, aryl H), 7.76 (br. s, 1H, NH), 8.37 (br. s, 1H, NH), 9.16 ppm (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ, 38.2 (SO_2CH_3), 46.5 (4-C), 73.3 (5-C), 80.0 (3-C), 127.4, 127.6, 128.3, 139.2 (C aryl), 162.8 (2-C), 162.9 (C=O) ppm; ms: m/z 283 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_{14}N_2O_4S$ (MW 282.2): C, 51.05; H, 5.00; N, 9.92. Found: C, 51.02; H, 4.98; N, 9.86.

cis-Tetrahydro-2-imino-3-methanesulfonyl-5-phenyl-3-furancarboxamide (**3b**).

This compound was obtained as colorless prisms (1.93 g, 68%), m.p. 168-169° (acetone); ir (potassium bromide): ν 3350, 3300, 3220 (NH), 1690 (C=O) cm^{-1}; ^{1}H nmr (DMSO-d_6): δ, 2.75 (dd, J = 9.5, 15.3 Hz, 1H, 4-H) 3.33 (s, 3H, SO_2CH_3), 3.40 (dd, J = 6.7, 15.3 Hz, 1H, 4-H), 5.53 (dd, J = 6.7, 9.5 Hz, 1H, 5-H) 7.34-7.47 (m, 5H, aryl H), 8.05 (br. s, 1H, NH), 8.30 (br. s, 1H, NH), 9.05 ppm (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ, 37.1 (4-C), 37.2 (SO_2CH_3), 76.2 (3-C), 79.3 (5-C), 126.0, 128.5, 128.6, 138.7 (C aryl), 162.0 (2-C), 163.7 (C=O) ppm; ms: m/z 283 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_{14}N_2O_4S$ (MW 282.2): C, 51.05; H, 5.00; N, 9.92. Found: C, 51.02; H, 5.03; N, 9.88.

Tetrahydro-2-imino-3-methanesulfonyl-3-thiophenecarboxamide (**4a**).

This compound was obtained as colorless prisms (1.64 g, 74%) mp 155-156° (acetone); ir (potassium bromide): ν 3400, 3340, 3280 (NH), 1690 (C=O) cm^{-1}; ^{1}H nmr (DMSO-d_6): δ, 2.86-2.97 (m, 2H, 4-H), 3.08-3.13 (m, 1H, 5-H), 3.21 (s, 3H, SO_2CH_3), 3.26-3.31 (m, 1H, 5-H), 7.87 (s, 1H, NH), 7.91 (s, 1H, NH), 11.3 ppm (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ, 28.7 (4-C), 33.4 (5-C), 38.3 (SO_2CH_3), 80.8 (3-C), 163.8 (2-C), 173.4 (C=O) ppm; ms: m/z 223 $[M+H]^+$.

Anal. Calcd. for $C_6H_{10}N_2O_3S_2$ (MW 222.3): C, 32.42; H, 4.53; N, 12.60. Found: C, 32.48; H, 4.49; N, 12.61.

cis-Tetrahydro-2-imino-3-methanesulfonyl-5-methyl-3-thiophenecarboxamide (**4b**).

This compound was obtained as colorless prisms, (1.65 g, 70%), mp166-167° (acetone); ir (potassium bromide): ν 3440, 3280, 3200 (NH), 1705 (C=O) cm^{-1}; ^{1}H nmr (DMSO-d_6): δ, 1.34 (d, J = 6.5 Hz, 3H, CH_3), 2.56 (dd, J = 9.5, 15.0 Hz, 1H, 4-H), 3.12 (dd, J = 5.8, 15.0 Hz 1H, 4-H), 3.19 (s, 3H, SO_2CH_3), 3.90-3.97 (m, 1H, 5-H), 7.89 (br.s, 1H, NH), 8.18 (br.s, 1H, NH), 11.35 ppm (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ, 20.6 (CH_3), 38.0 (SO_2CH_3), 40.3 (5-C), 41.8 (4-C), 82.4 (3-C), 164.7 (2-C), 173.6 (C=O) ppm; ms: m/z 237 $[M+H]^+$

Anal. Calcd. for $C_7H_{12}N_2O_3S_2$ (MW 236.3): C, 35.58; H, 5.12; N, 11.85. Found: C, 35.52; H, 5.02; N, 11.83.

General Procedure for the Preparation of Tetrahydro-3-methanesulfonyl-2-oxo-3-furancarboxamides **5a**,**b** and Tetrahydro-3-methanesulfonyl-2-oxo-3-thiophenecarboxamides **6a**,**b**.

A solution of **3a**,**b** or **4a**,**b** (5 mmoles) and 5% hydrochloric acid (15 ml) was stirred at room temperature for 2 hours. The precipitate was collected, washed with water and dried to give **5a**,**b** and **6a**,**b**.

trans-Tetrahydro-3-methanesulfonyl-2-oxo-4-phenyl-3-furancarboxamide (**5a**).

This compound was obtained as colorless prisms (1.27 g, 91%), mp 214-215° (acetone); ir (potassium bromide): ν 3480, 3370 (NH), 1775, 1690 (C=O) cm^{-1}; ^{1}H nmr (DMSO-d_6): δ, 3.42 (s, 3H, SO_2CH_3), 4.56 (dd, J = 8.0, 8.8 Hz 1H, 5-H), 4.63 (t, J = 8.0 Hz, 1H, 4-H), 4.82 (dd, J = 8.0, 8.8 Hz 1H, 5-H), 6.83 (br. s, 1H, NH), 7.32-7.36 (m, 5H, aryl H), 7.99 ppm (br. s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ, 38.9 (SO_2CH_3), 44.6 (4-C), 70.9 (5-C), 79.5 (3-C), 128.2, 128.3, 129.0, 134.8 (C aryl), 162.1 (C=O), 168.6 (C=O) ppm; ms: m/z 284$[M+H]^+$.

Anal. Calcd. for $C_{12}H_{13}NO_5S$ (MW 283.3): C, 50.88; H, 4.63; N, 4.94. Found: C, 50.83; H, 4.50; N, 4.93.

cis-Tetrahydro-3-methanesulfonyl-2-oxo-5-phenyl-3-furancarboxamide (**5b**).

This compound was obtained as colorless needles (1.33 g, 94%), mp 150-151° (acetone); ir (potassium bromide): ν 3430, 3397 (NH), 1764, 1677 (C=O) cm^{-1}; ^1H nmr (DMSO-d_6): δ, 2.94 (dd, J = 7.8, 15.1 Hz 1H, 4-H), 3.34 (s, 3H, SO_2CH_3), 3.50 (dd, J = 7.8, 15.1 Hz, 1H, 4-H), 5.74 (t, J = 7.8 Hz, 1H, 5-H), 7.38-7.48 (m, 5H, aryl H), 7.51 (br. s, 1H, NH), 8.13 ppm (br. s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ, 35.5 (4-C), 38.1 (SO_2CH_3), 76.3 (3-C), 78.9 (5-C), 126.1, 128.6, 128.8, 137.8 (C aryl), 162.4 (C=O), 167.6 (C=O) ppm; ms: m/z 284 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_{13}NO_5S$ (MW 283.3): C, 50.87; H, 4.63; N, 4.94. Found: C, 50.89; H, 4.57; N, 4.98.

Tetrahydro-3-methanesulfonyl-2-oxo-3-thiophenecarboxamide (**6a**).

This compound was obtained as colorless needles (0.60 g, 54%), mp 142-143° (acetone); ir (potassium bromide): ν 3423, 3391 (NH), 1720, 1686 (C=O)cm^{-1}; ^1H nmr (DMSO-d_6): δ, 2.90 (ddd, J = 7.0, 9.0, 14.0 Hz, 1H, 4-H), 3.08 (ddd, J = 3.9, 6.0, 14.0 Hz, 1H, 4-H), 3.20 (s, 3H, SO_2CH_3), 3.36 (ddd, J = 6.0, 9.0, 11.2 Hz, 1H, 5-H), 3.54 (ddd, J = 3.9, 7.0, 11.2 Hz, 1H, 5-H), 7.56 (br. s, 1H, NH), 8.10 ppm (br. s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ, 28.2 (4-C), 30.7 (5-C), 38.8 (SO_2CH_3), 82.9 (3-C), 162.0 (C=O), 198.7 (C=O) ppm; ms: m/z 224 $[M+H]^+$.

Anal. Calcd. for $C_6H_9NO_4S_2$ (MW 223.3): C, 32.28; H, 4.06; N, 6.27. Found: C, 32.22; H, 4.05; N, 6.33.

cis-Tetrahydro-5-methyl-3-methanesulfonyl-2-oxo-3-thiophenecarboxamide (**6b**).

This compound was obtained as colorless columns (0.71 g, 60%), mp 153-154° (acetone); ir (potassium bromide): ν 3427, 3286 (NH), 1682, 1662 (C=O) cm^{-1}; ^1H nmr (DMSO-d_6): δ, 1.45 (d, J = 6.7 Hz, 3H, CH_3), 2.77 (dd, J = 6.7, 14.8 Hz, 1H, 4-H), 3.17 (dd, J = 6.7, 14.8 Hz, 1H, 4-H), 3.19 (s, 3H, SO_2CH_3), 4.10-4.20 (m, 1H, 5-H), 7.45 (br. s, 1H, NH), 8.06 ppm (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ, 21.3 (CH_3), 38.6 (4-C), 38.8 (SO_2CH_3), 40.5 (5-C), 84.4 (3-C), 163.3 (C=O), 198.9 (C=O) ppm; ms: m/z 238 $[M+H]^+$.

Anal. Calcd. for $C_7H_{11}NO_4S_2$ (MW 237.3): C, 35.43; H, 4.67; N, 5.90. Found: C, 35.37; H, 4.64; N, 6.02.

General Procedures for the Preparation of 2-Amino-4,5-dihydro-3-methanesulfonylfurans **7a**,**b** and 2-Amino-4,5-dihydro-3-methanesulfonylthiophenes **8a**,**b**.

Procedure A.

A mixture of **3a**,**b** (1.41 g, 5 mmoles), potassium *tert*-butoxide (0.56 g, 5 mmoles), *tert*-butyl alcohol (1 ml) and DMF (4 ml) was stirred at 60° for 4 hours. After removal of the solvent *in vacuo* ice-water was added to the residue. The precipitate was collected, washed with water and dried to yield **7a**,**b**.

Procedure B.

A mixture of **4a**,**b** (10 mmoles) and sodium ethoxide (0.14 g, 2 mmoles) in ethanol (30 ml) was refluxed for 5 hours. The solvent was removed *in vacuo*, and then cold water was added to the residue. The mixture was extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on alumina with dichloromethane as the eluent to give **8a**,**b**.

2-Amino-4,5-dihydro-3-methanesulfonyl-4-phenylfuran (**7a**).

This compound was obtained as colorless columns (1.06 g, 89%), mp 135-137° (acetone-petroleum ether); ir (potassium bromide): ν 3440, 3300 (NH) cm^{-1}; ^1H nmr (DMSO-d_6): δ, 2.39 (s, 2.4H, SO_2CH_3), 3.29 (s, 0.6H, SO_2CH_3), 4.14 (dd, J = 5.5, 8.4 Hz, 0.2H, 5-H), 4.20 (dd, J = 4.3, 9.2 Hz, 0.8H, 5-H), 4.28 (dd, J = 4.3, 9.2 Hz, 0.8H, 4-H), 4.56 (dd, J = 7.7, 8.4 Hz, 0.2H, 5-H), 4.70 (t, J = 9.2 Hz, 0.8H, 5-H), 4.76 (d, J = 5.8 Hz 0.2H, 3-H), 6.77 (br. s, 1.6H, NH_2), 7.23-7.39 (m, 5H, aryl H), 8.48 ppm (s, 0.2H, NH); ^{13}C nmr (DMSO-d_6): δ, 39.2 (SO_2CH_3), 41.5 (4-C), 44.2 (SO_2CH_3), 46.8 (4-C), 67.2 (3-C), 74.0 (5-C), 76.6 (5-C), 80.4 (3-C), 126.9, 127.17, 127.19, 127.3, 128.4, 128.7, 139.5, 143.5 (C aryl), 162.9 (2-C), 164.2 (2-C) ppm; ms: m/z 240 $[M+H]^+$.

Anal. Calcd. for $C_{11}H_{13}NO_3S$ (MW 239.3): C, 55.21, H, 5.48; N, 5.85. Found: C, 55.31; H, 5.40; N, 5.74.

2-Amino-4,5-dihydro-3-methanesulfonyl-5-phenylfuran (**7b**).

This compound was obtained as colorless columns (0.94 g, 79%), mp 98-100° (acetone); ir (potassium bromide): ν 3440, 3180 (NH) cm^{-1}; ^1H nmr (DMSO-d_6): δ, 2.30-2.38 (m, 0.2H, 4-H), 2.54 (ddd, J = 8.6, 9.8, 14.5 Hz, 0.4H, 4-H), 2.76 (dd, J = 7.3, 11.6 Hz, 0.4H, 4-H), 2.90 (s, 0.6H, SO_2CH_3), 2.93-2.98 (m, 0.2H, 4-H), 3.06 (ddd, J = 3.1, 7.1, 14.5 Hz, 0.4H, 4-H), 3.25-3.32 (m, 0.4H, 4-H), 3.29 (s, 2.4H, SO_2CH_3), 4.68 (dd, J = 3.1, 9.8 Hz, 0.4H, 3-H), 4.87 (t, J = 10.1Hz, 0.2H, 3-H), 5.43 (dd, J = 7.4, 8.6 Hz, 0.2H, 5-H), 5.52 (dd, J = 7.1, 8.6 Hz, 0.4H, 5-H), 5.65 (dd, J = 7.3, 9.5 Hz, 0.2H, 5-H), 6.66 (br. s, 0.8H, NH_2), 7.34-7.44 (m, 5H, aryl H), 8.41 (br. s 0.3H, NH), 8.46 ppm (br. s, 0.3H, NH); ^{13}C nmr (DMSO-d_6): δ, 30.8 (4-C), 31.1 (4-C), 36.1 (4-C), 38.9 (SO_2CH_3), 39.2 (SO_2CH_3), 42.8 (SO_2CH_3), 61.7 (3-C), 62.7 (3-C), 73.6 (3-C), 78.9 (5-C), 80.8 (5-C), 80.9 (5-C), 125.7, 125.9, 126.0, 128.2, 128.4, 128.47, 128.53, 125.6, 139.0, 139.3, 140.6 (C aryl), 162.0 (2-C), 162.6 (2-C) ppm; ms: m/z 240 $[M+H]^+$.

Anal. Calcd. for $C_{11}H_{13}NO_3S$ (MW 239.3): C, 55.21, H, 5.48; N, 5.85. Found: C, 55.22; H, 5.50; N, 5.75.

2-Amino-4,5-dihydro-3-methanesulfonylthiophene (**8a**).

This compound was obtained as colorless prisms (1.31 g, 73%), mp 95-97° (acetone-petroleum ether); ir (potassium bromide): ν 3450, 3340 (NH) cm^{-1}; ^1H nmr ($CDCl_3$): δ, 2.60-2.68 (m, 0.5H, 4-H), 2.92 (s, 1.5H, SO_2CH_3), 3.02-3.07 (m, 0.5H, 4-H), 3.06-3.12 (m, 1H, 4-H), 3.18 (s, 1.5H, SO_2CH_3), 3.19-3.23 (m, 1H, 5-H), 3.23-3.27 (m, 0.5H, 5-H), 3.66 (ddd, J = 6.1, 9.8, 10.8 Hz, 0.5H, 5-H), 4.05 (dd, J = 3.7, 8.2 Hz, 0.5H, 3-H), 5.56 (br. s, 0.5H, NH_2), 7.27 ppm (br. s, 0.5H, NH); ^{13}C nmr ($CDCl_3$): δ, 28.3 (4-C), 29.8 (4-C), 33.0 (5-C), 34.3 (5-C), 40.0 (SO_2CH_3) 42.6 (SO_2CH_3), 70.8 (3-C), 93.3 (3-C), 159.2 (2-C), 176.9 (2-C) ppm; ms: m/z 180 $[M+H]^+$.

Anal. Calcd. for $C_5H_9NO_2S_2$ (MW 179.3): C, 33.50; H, 5.06; N, 7.81. Found: C, 33.38; H, 5.03; N, 7.79.

2-Amino-4,5-dihydro-3-methanesulfonyl-5-methylthiophene (**8b**).

This compound was obtained as colorless columns, (1.47 g, 76%), mp 92-93° (acetone-petroleum ether); ir (potassium bromide): ν 3440, 3320 (NH) cm^{-1}; ^1H nmr ($CDCl_3$): δ, 1.44 (d, J = 6.4Hz, 0.9H, CH_3), 1.45 (d, J = 6.4 Hz, 2.1H, CH_3), 2.23 (ddd, J = 8.4, 10.4, 14.3 Hz, 0.3H, 4-H), 2.73 (dd, J = 5.8, 13.4 Hz, 0.7H, 4-H), 2.91(s, 2.1H, SO_2CH_3), 3.08-3.13 (m, 0.3H, 4-H), 3.17 (s, 0.9H, SO_2CH_3), 3.22 (dd, J = 7.6, 13.4Hz, 0.7H, 4-H), 3.85-3.94

(m, 0.7H, 5-H), 4.14 (dd, J = 2.1, 8.4Hz, 0.3H, 3-H), 4.26-4.35 (m, 0.3H, 5-H), 5.56 ppm (br. s, 1.7H, NH_2, NH); ^{13}C nmr ($CDCl_3$): δ, 20.8 (CH_3), 21.7 (CH_3), 36.6 (4-C), 40.0 (SO_2CH_3), 42.1 (4-C), 42.2 (5-C), 42.5 (SO_2CH_3), 45.5 (5-C), 72.6 (3-C), 92.4 (3-C), 158.4 (2-C), 176.9 (2-C) ppm; ms: m/z 194 $[M+H]^+$.

Anal. Calcd. for $C_6H_{11}NO_2S_2$ (MW 193.3): C, 37.28; H, 5.74; N, 7.25. Found: C, 37.20; H, 5.63; N, 7.13.

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