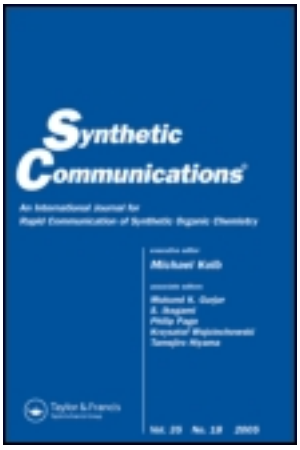

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Synthesis and Characterization of Exo-endo and Endo-endo Benzenesulfonylaziridines

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Synthesis and Characterization of Exo-endo and Endo-endo Benzenesulfonylaziridines

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ABSTRACT

In the search for structural cyclic imide analogues of therapeutic interest, the synthesis, separation, and characterization of exo-endo **3** and endo-endo **4** stereoisomers of benzenesulfonylaziridines, not found in the literature, are described in this study. The benzenesulfonylaziridines were synthesized through a 1,3-dipolar-type reaction of *p*-toluenesulfonylazide and different norbornenesuccinimides.

Key Words: Benzenesulfonylaziridines.

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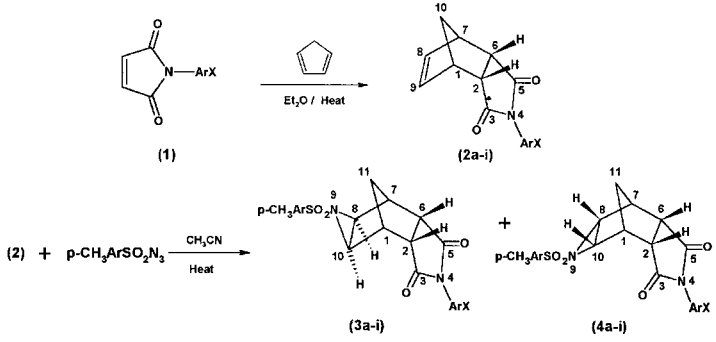
INTRODUCTION

The aziridines or azacyclopropanes are generally prepared through cyclic reactions.[1,2] In the present study a series of benzenesulfonylaziridines was synthesized through a method adapted by Nunes,[3] from a method described by Zalkow.[4,5]

This study aimed to synthesize and characterize exo-endo **3** and endo-endo **4** stereoisomers of a series of benzenesulfonylaziridines. The benzenesulfonylaziridines (Sch. 1) were obtained through a 1,3-dipolar-type reaction between *p*-toluenesulfonylazide (previously prepared) and different endonorbornenesuccinimides **2**. The endo-norbornenesuccinimides (Table 1) were prepared through the Diels-Alder reaction between substituted *N*-phenylmaleimides **1** and cyclopentadiene according to the method described in the literature for similar structures.[6] The *N*-phenylmaleimides were prepared through the reaction of a substituted aniline and maleic anhydride in acetic anhydride.[7]

The endo-norbornenesuccinimides **2** showed only one spot on thin layer chromatography (t. l. c.). The formation of exo-norbornenesuccinimide was not observed at any time. Their structures were confirmed through ^{1}H NMR and ^{13}C NMR spectroscopic analysis, CNH elemental analysis, and comparison of their ^{1}H NMR spectra with those of the exo- and endo-norbornenesuccinimides and similar compounds given in the literature.[6,8–10] The signal, in the form of a doublet, exhibited by the $H_{2,6}$ hydrogens of all of the endo-norbornenesuccinimides synthesized in this study, indicates the existence of a coupling with the $H_{1,7}$ hydrogens, which was not observed in the case of exo-norbornenesuccinimide, due to the dihedral angle being approximately 90°.



X = H (a); 4-Cl (b); 3,4-Cl_2 (c); 4-CH_3 (d); 4-OCH_3 (e); 4-Br (f); 4-NO_2 (g); 2,3-dimethyl (h) and 3-ethyl (i).

Scheme 1.

Table 1. Yield, mp, and CNH of endo-norbornenesuccinimides 2.

Compound X	Y (%)	mp (°C) mp Literature [10–12]	Formula mass	Calcd. (%) found (%) C	H	N
2a	71	143.9–144.9	$C_{15}H_{13}NO_2$	75.30	5.48	5.85
H		144	239.27	74.94	4.96	5.95
2b	63	141.4–142.9	$C_{15}H_{12}NO_2Cl$	65.82	4.42	5.12
4-Cl		—	273.71	65.50	4.52	5.10
2c	67	163.8–164.6	$C_{15}H_{11}NO_2Cl_2$	58.46	3.60	4.55
3,4-diCl		—	308.16	58.51	3.68	4.49
2d	73	158.2–158.6	$C_{16}H_{15}NO_2$	75.87	5.97	5.53
4-CH_3		157–158	253.30	75.80	6.02	5.45
2e	75	171.6–173.0	$C_{16}H_{15}NO_3$	71.36	5.61	5.20
4-OCH_3		169–170	269.29	71.23	5.72	5.11
2f	62	153.4–154.6	$C_{15}H_{12}NBrO_2$	56.62	3.80	4.40
4-Br		156	318.16	57.23	3.30	4.26
2g	70	188.9–189.2	$C_{15}H_{12}N_2O_4$	63.38	4.25	9.85
4-NO_2		190–191	284.27	63.28	4.91	9.43
2h	79	188.3–188.7	$C_{17}H_{17}NO_2$	76.38	6.41	5.24
2,3-Dimethyl		—	267.32	76.37	6.72	5.33
2i	90	108.5–108.8	$C_{17}H_{17}NO_2$	76.38	6.41	5.24
3-Ethyl		—	267.32	76.47	6.65	5.21

The *p*-toluenesulfonylazide was prepared from *p*-toluenesulfonyl chloride and sodium azide, and its structure was confirmed through the ^{1}H NMR spectroscopie (δ ppm: -C***H***$_3$-Ph [(s: 2.48) e Ar-***H*** (d: 7.38 7.85 J = 8.2 Hz)] and melting point (20°C).[3]

The formation of isomers was initially detected by t. l. c. in all the reactions of the benzenesulfonylaziridines and later confirmed through ^{1}H NMR and ^{13}C NMR spectroscopies and CHN elemental analysis. The yield of the reactions was 65% to 90%, as described in the experimental section. The stereoisomers were separated and purified through column chromatography and successive recrystalizations.

The ^{1}H NMR spectrum in two dimensions (COSY) of the endo-endo-aziridines shows a broad singlet for the $H_{1,7}$ hydrogens and shows coupling between these hydrogens and the $H_{2,6}$ and $H_{8,10}$ hydrogens. The $H_{2,6}$ and $H_{8,10}$ hydrogens show multiplets due to a W coupling between them and consequently to the coupling with the $H_{1,7}$ hydrogens.

On the other hand, the ^{1}H NMR spectrum in two dimension (COSY) of the exo-endo-aziridines shows coupling of $H_{1,7}$ hydrogens only with the

$H_{2,6}$ hydrogens. The spectrum also shows a sharp singlet for the $H_{8,10}$ hydrogens with no coupling with the $H_{1,7}$ hydrogens since the dihedral angle between them is approximately 90°. This is the principal difference between the stereoisomers.

The results obtained with the aziridines synthesized in this study are consistent with the results found in the literature for related structures.[4,5,13,14] In the reaction of benzenesulfonylazides with *cis*-endo or *cis*-exo norbornene-5,6-dicarboxylic anhydride, the authors obtained exo- and endo-aziridines, where the endo isomer was obtained in greater proportion (approximately in the proportions of 70% : 30%). In the present study the endo-endo aziridine was also obtained in greater proportion as described in the experimental part.

EXPERIMENTAL

Analytical-grade reagents were utilized and purified according to methods cited in the literature.[15] For the determination of the melting point (mp) a Microquímica device model MQRPF-301 (Florianópolis, Brazil) was utilized. For the CHN analysis, a CHN elemental analyzer Perkin Elmer 2400 (Boston, MA, USA) was utilized. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Brucker AC-200F (Rheinstetten, Germany) (at 200 MHz and 50 MHz, respectively). $CDCl_3$ was used as the solvent with tetramethylsilane (TMS) as the internal standard; chemical shifts (δ) were in parts per million. In the t. l. c., aluminium sheets with silica gel 60 F-254 with 0.2 mm thickness were utilized. All benzenesulfonylaziridines were purified by column chromatography with silica gel 60 (230–400 mesh) purchased from Merck.

General Experimental Procedure

(2R,6S,8S,10R) **3a** and (2R,6S,8R,10S) **4a** 9-(4′-Methylphenylsulfonyl)-4-phenyl-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$]undecane-3,5-dione

p-Toluenesulfonylazide (4.14 g, 0.0210 mol) was added to a mixture of 4-phenyl-4-aza-tricycle[5.2.1.02,6-endo]dec-8-ene-3,5-dione **2a** (4.00 g, 0.0167 mol) in acetonitrile (20 mL). The reaction was refluxed (15 hours) and the solvent was evaporated in vacuo. The solid residue was triturated with methanol: chloroform (3 : 7) and filtered off with suction to give the mixture of **3a** and **4a.** The two products were isolated by column chromatography (silica gel, ethyl acetate : acetone : hexane, 6 : 3 : 11). Yield: 91%. Ratio **3a**/**4a** = 35%/65%. mp 250.1–251.3°C **3a** and 253.0–254.9°C **4a**. Anal. Calcd. for C_{22} H_{20} N_2 O_4 S: C, 64.69; H, 4.94; N, 6.86; O, 15.66; S,

7.85. Found: C, 63.85; H, 4.98; N, 6.72 **3a** and C, 64.59; H, 4.97; N, 6.92 **4a**. ^{1}H NMR δ ppm: CH_2-11 (d: 1.22 and 1.85, J = 10.5 Hz); CH_3-Ph (s: 2.46); CH-8 (s sharp: 3.06); CH-7 (s broad: 3.12); CH-6 (m: 3.32); ArH (m: 7.15–7.80). ^{13}C NMR δ ppm: CH_3-Ph (22.39); CH_2-11 (32.31); CH-7 (38.05); CH-8 (39.49); CH-6 (47.89); C Ar (127.41; 128.73; 129.84; 130.13; 130.54; 135.06; 145.62); C═O (175.98) **3a**. ^{1}H NMR δ ppm: CH_2-11 (m: 2.01 and 2.41); CH_3-Ph (s: 2.32); CH-7 (s broad: 3.11); CH-8 (t: 3.24 J = 2.5 Hz); CH-6 (t: 3.59 J = 2.0 Hz); ArH (m: 7.00–7.56). ^{13}C NMR δ ppm: CH_3-Ph (22.30); CH_2-11 (40.74); CH-7 (48.76); CH-8 (50.36); CH-6 (55.98); C Ar (126.70; 127.68; 128.04; 128.34; 129.14; 129.35; 129.88; 130.09); C═O (175.76) **4a**.

By this procedure the following benzenesulfonylaziridines were prepared:

(2R,6S,8S,10R) **3b** and (2R,6S,8R,10S) **4b** 9-(4′-Methylphenylsulfonyl)-4-(4″-chlorophenyl)-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$]undecane-3,5-dione

Yield: 70%. Ratio **3b**/**4b** = 30%/70%. mp 230.3–231.8°C **3b** and 249.7–251.3°C **4b**. Anal. Calcd. for C_{22} H_{19} Cl N_2 O_4 S: C, 59.66; H, 4.33; N, 6.33; O, 14.44; S, 7.24; Cl, 8.00. Found: C, 59.76; H, 4.40; N, 6.05; **3b** and C, 59.88; H, 4.72; N, 6.16 **4b**. ^{1}H NMR δ ppm: CH_2-11(d: 1.19 and 1.86, J = 10,6 Hz); CH_3-Ph (s: 2.46); CH-8 (s sharp: 3.03); CH-7 (s broad: 3.11); CH-6 (m: 3.31); ArH (d: 7.11 and 7.46, J = 8.6); ArH (d: 7.35 and 7.77, J = 8.2). ^{13}C NMR δ ppm: CH_3-Ph (21.64); CH_2-11 (31.51); CH-7 (37.25); CH-8 (38.75); CH-6 (47.12); C Ar (127.93; 129.58; 129.81; 134.28; 134.92; 144.95); C═O (174.99) **3b**. ^{1}H NMR δ ppm: CH_2-11 (d: 1.93 and 2.32, J = 10.0); CH_3-Ph (s: 2.34); CH-7 (s broad: 3.10); CH-8 (m: 3.22); CH-6 (s: 3.56); ArH (m: 7.04–7.54). ^{13}C NMR δ ppm: CH3-Ph (21.58); CH_2-11 (40.03); CH-7 (47.98); CH-8 (49.63); CH-6 (55.17); C Ar (127.22; 128.26; 128.72; 129.43; 131.10; 132.52; 133.12; 145.08); C═O (174.86) **4b**.

(2R,6S,8S,10R) **3c** and (2R,6S,8R,10S) **4c** 9-(4′-Methylphenylsulfonyl)-4-(3″,4″-dichloro phenyl)-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$] undecane-3,5-dione

Yield: 75%. Ratio **3c**/**4c** = 40%/60%. mp 203.5–204.9°C **3c** and 206.9–207.5°C **4c**. Anal. Calcd. for C_{22} H_{18} Cl_2 N_2 O_4 S: C, 55.35; H, 3.81; N, 5.87; O, 13.40; S, 6.72; Cl, 14.85. Found: C, 55.05; H, 3.77; N, 6.02 **3c** and C, 55.15; H, 3.84; N, 5,79 **4c**. ^{1}H NMR δ ppm: CH_2-11(m: 1.22 and 1.83); CH_3-Ph (s: 2.45); CH-8 (s sharp: 3.01); CH-7 (s broad: 3.11); CH-6 (m: 3.31); ArH (m: 7.04–7.79). ^{13}C NMR δ ppm: CH_3-Ph (21.95); CH_2-11 (32.30); CH-7 (38.08); CH-8 (39.47); CH-6 (47.87); C Ar

(127.19; 128.72; 130.53; 130.79; 135.09; 139.99); C═O (176.12) **3c**. ^{1}H NMR δ ppm: CH_2-11 (m: 1.97 and 2.35); CH_3-Ph (s: 2.35); CH-7 (s broad: 3.13); CH-8 (s: 3.24); CH-6 (s: 3.60); ArH (m: 7.08–7.65). ^{13}C NMR δ ppm: CH_3-Ph (21.60); CH_2-11 (40.16); CH-7 (47.98); CH-8 (49.67); CH-6 (55.13); C Ar (125.11; 127.60; 128.05; 129.46; 130.13; 131.36; 131.89; 132.66; 145.14); C═O (174.59) **4c**.

(2R,6S,8S,10R) **3d** and (2R,6S,8R,10S) **4d** 9-(4′-Methylphenylsulfonyl)-4-(4″-methylphenyl)-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$]undecane-3,5-dione

Yield: 80%. Ratio **3d**/**4d** = 40%/60%. mp 230.7–231.2°C **3d** and 244.9–246.4°C **4d**. Anal. Calcd. for C_{23} H_{22} N_2 O_4 S: C, 65.37; H, 5.26; N, 6.63; O, 15.15; S, 7.59. Found: C, 64.79; H, 5.17; N, 6.69 **3d** and C, 64.80; H, 5.19; N, 6.70 **4d**. ^{1}H NMR δ ppm: CH_2-11(d: 1.20 and 1.82 J = 10.0); CH_3-Ph (s: 2.39); CH_3-Ph (s: 2.45); CH-8 (s sharp: 3.03); CH-7 (s broad: 3.09); CH-6 (m: 3.28); ArH (d: 7.00 and 7.27 J = 8.10); ArH (d: 7.34 and 7.77 J = 8.10). ^{13}C NMR δ ppm: CH_3-Ph (21.19); CH_3-Ph (21.61); CH_2-11 (31.49); CH-7 (37.33); CH-8 (38.67); CH-6 (47.08); C Ar (126.44; 127.95; 128.69; 129.78; 130.00; 134.24; 139,19; 144.85); C═O (175.40) **3d**. ^{1}H NMR δ ppm: CH_2-11 (d: 1.93 and 2.33 J = 9.90); CH_3-Ph (s: 2.33); CH_3-Ph (s: 2.41); CH-7 (s broad: 3.08); CH-8 (m: 3.22); CH-6 (m: 3.55); ArH (m: 7.03–7.47). ^{13}C NMR δ ppm: CH_3-Ph (21.90); CH_2-11 (40.66); CH-7 (48.73); CH-8 (50.36); CH-6 (55.96); C Ar (126.55; 129.15; 129.94; 130.09; 130.72; 133.34; 138.21; 145.61); C═O (175.89) **4d**.

(2R,6S,8S,10R) **3e** and (2R,6S,8R,10S) **4e** 9-(4′-Methylphenylsulfonyl)-4-(4″-methoxyphenyl)-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$] undecane-3,5-dione

Yield: 70%. Ratio **3e**/**4e** = 30%/70%. mp 232.3–233.6°C **3e** and 224.6–225.3°C **4e**. Anal. Calcd. For: C_{23} H_{22} N_2 O_5 S: C, 63.00; H, 5.07; N, 6.39; O, 18.23; S, 7.31. Found: C, 63.50; H, 4.97; N, 6.57 **3e** and C, 62.90; H, 5.21; N, 6.76 **4e**. ^{1}H NMR δ ppm: CH_2-11(m: 1.26 and 1.61); CH_3-Ph (s: 2.46); CH-8 (s sharp: 3.04); CH-7 (s broad: 3.10); CH-6 (m: 3.29); O-CH_3 (s: 3.83); ArH (m: 7.00–7.80). ^{13}C NMR δ ppm: CH_3-Ph (21.66); CH_2-11 (31.56); CH-7 (37.38); CH-8 (38.74); CH-6 (47.10); O-CH_3 (55.49); C Ar (114.75; 128.00; 129.82; 144.88); C═O (175.59) **3e**. ^{1}H NMR δ ppm: CH_2-11 (d: 1.95 and 2.30 J = 10.0); CH_3-Ph (s: 2.33); CH-7 (s broad: 3.10); CH-8 (s: 3.22); CH-6 (s: 3.54); O-CH_3 (s: 3.85); ArH (d: 7.00 and 7.50 J = 8.4); ArH (d: 7.08 and 7.42 J = 8.0). ^{13}C NMR δ ppm: CH_3-Ph (21.72); CH_2-11 (40.05); CH-7 (48.08); CH-8 (49.75); CH-6

(55.33); O-CH_3 (55.53); C Ar (113.96; 125.59; 127.51; 128.53; 129.49; 132.73; 145.03; 159.92); C═O (175.89) **4e**.

(2R,6S,8S,10R) **3f** and (2R,6S,8R,10S) **4f** 9-(4′-Methylphenylsulfonyl)-4-(4″-bromophenyl)-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$]undecane-3,5-dione

Yield: 65%. Ratio **3f**/**4f** = 25%/75%. mp 217.2–218.1°C **3f** and 219.2–220.0°C **4f**. Anal. Calcd. for: $C_{22}H_{19}BrN_2O_4S$: C, 54.22; H, 3.94 N, 5.75; O, 13.12; S, 6.58; Br, 6.39. Found: C, 54.42; H, 4.21; N, 6.02 **3f** and C, 54.55; H, 3.98; N, 5.64 **4f**. ^{1}H NMR δ ppm: CH_2-11(d: 1.20 and 1.88 J = 10.7); CH_3-Ph (s: 2.46); CH-8 (s sharp: 3.02); CH-7 (s broad: 3.11); CH-6 (m: 3.30); ArH (d: 7.05 and 7.61 J = 8.6); ArH (d: 7.34 and 7.77 J = 8.2). ^{13}C NMR δ ppm: CH_3-Ph (21.66); CH_2-11 (31.55); CH-7 (37.24); CH-8 (38.79); CH-6 (47.16); O-CH_3 (55.49); C Ar (123.00; 127.99; 128.19; 129.83; 130.00; 132.61; 134.33; 144.88); C═O (174.94) **3f**. ^{1}H NMR δ ppm: CH_2-11 (d: 1.95 and 2.35 J = 9.0); CH_3-Ph (s: 2.35); CH-7 (s broad: 3.10); CH-8 (m: 3.23); CH-6 (m: 3.57); ArH (d: 7.07 and 7.36 J = 8.0); ArH (d: 7.45 and 7.59 J = 8.7). ^{13}C NMR δ ppm: CH_3-Ph (21.62); CH_2-11 (40.06); CH-7 (48.00); CH-8 (49.65); CH-6 (55.19); C Ar (121.20; 127.50; 128.26; 129.45; 131.73; 132.54; 145.09); C═O (174.80) **4f**.

(2R,6S,8S,10R) **3g** and (2R,6S,8R,10S) **4g** 9-(4′-Methylphenylsulfonyl)-4-(4″-nitrophenyl)-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$]undecane-3,5-dione

Yield: 65%. Ratio **3g**/**4g** = 20%/80%. mp 266.7–266.9°C **3g** and 216.9–217.1°C **4g**. Anal. Calcd. for: $C_{22}H_{19}N_3O_6S$: C, 58.27; H, 4.23; N, 9.27; O, 21.16; S, 7.07. Found: C, 58.81; H, 4.58; N, 7.54 **3g** and C, 58.11; H, 4.69; N, 6.66 **4g**. ^{1}H NMR δ ppm: CH_2-11(d: 1.25 and 1.90 J = 10.0); CH_3-Ph (s: 2.46); CH-8 (s sharp: 3.04); CH-7 (s broad: 3.14); CH-6 (m: 3.37); ArH (d: 7.26 and 7.48 J = 8.6); ArH (d: 7.76 and 8.37 J = 8.6). ^{13}C NMR δ ppm: CH_3-Ph (21.65); CH_2-11 (31.55); CH-7 (37.13); CH-8 (38.91); CH-6 (47.23); C Ar (124.55; 127.27; 127.92; 129.83; 134.34; 136.75; 145.05; 147.31); C═O (174.47) **3g**. ^{1}H NMR δ ppm: CH_2-11 (d: 2.00 and 2.33 J = 10.0); CH_3-Ph (s: 2.32); CH-7 (s broad: 3.14); CH-8 (m: 3.29); CH-6 (m: 3.59); ArH (d: 7.02 and 7.34 J = 8.3); ArH (d: 7.77 and 8.35 J = 9.1). ^{13}C NMR δ ppm: CH_3-Ph (21.56); CH_2-11 (40.22); CH-7 (48.05); CH-8 (49.63); CH-6 (55.09); C Ar (123.87; 126.25; 128.12; 129.47; 132.34; 138.20; 145.24; 146.08); C═O (174.50) **4g**.

(2R,6S,8S,10R) **3h** and (2R,6S,8R,10S) **4h** 9-(4′-Methylphenylsulfonyl)-4-(2″,3″-dimethylphenyl)-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$] undecane-3,5-dione

Yield: 75%. Ratio **3h**/**4h** = 40%/60%. mp 225.6–225.9°C **3h** and dec 232.0°C **4h**. ^{1}H NMR δ ppm: CH_2-11(d: 1.21 and 1.88 J = 10.5); 2-CH_3-Ph (m: 2.11); 3-CH_3-Ph (s: 2.33); 4-CH_3-Ph (s: 2.46); CH-8 (s sharp: 3.11); CH-7 (s broad: 3.20); CH-6 (m: 3.35); ArH (m: 6.67–7.81). ^{13}C NMR δ ppm: 2-CH_3-Ph (14.88); 3-CH_3-Ph (22.36); 4-CH_3-Ph (21.14); CH_2-11 (32.38); CH-7 (38.08); CH-8 (38.90); CH-6 (47.93); C Ar (125.84; 126.17; 127.09; 128.55; 130.53; 132.01; 134.88; 135.47; 139.35; 144.61); C═O (176.08) **3h**. ^{1}H NMR δ ppm: 3-CH_3-Ph and CH_2-11 (s: 1.94); 4-CH_3-Ph and CH_2-11 (s: 2.11); 2-CH_3-Ph (s: 2.35); CH-7 (s broad: 3.10); CH-8 (s: 3.32); CH-6 (m: 3.56); ArH (m: 7.14–7.76). ^{13}C NMR δ ppm: 2-CH_3-Ph (15.07); 3-CH_3-Ph (22.32); 4-CH_3-Ph (21.16); CH_2-11 (40.54); CH-7 (48.96); CH-8 (50.55); CH-6 (56.24); C Ar (126.62; 129.26; 130.24; 130.99; 131.99; 133.33; 134.05; 138.32; 145.76); C═O (175.76) **4h**.

(2R,6S,8S,10R) **3i** and (2R,6S,8R,10S) **4i** 9-(4′-Methylphenylsulfonyl)-4-(3″-ethylphenyl)-4,9-diazatetracycle[5.3.1.$0^{2,6}$. $0^{8,10}$]undecane-3,5-dione

Yield: 73%. Ratio **3i**/**4i** = 40%/60%. mp 189.1–191.0°C **3i** and 155.7–156.5°C **4i**. ^{1}H NMR δ ppm: CH_2-11 and 3-CH_2CH_3-Ph (s broad: 1.25); CH_2-11 (m: 1.82); CH_3-Ph (s: 2.44); CH-8 (s sharp: 2.69); CH-7 and 3-CH_2CH_3-Ph (s broad: 3.09); CH-6 (s: 3.29); ArH (m: 6.99–7.76). ^{13}C NMR δ ppm: 3-CH_2CH_3-Ph (15.78 and 29.26); 4-CH_3-Ph (22.36); CH_2-11 (32.26); CH-7 (38.11); CH-8 (39.45); CH-6 (47.86); C Ar (126.63; 126.87; 128.65; 129.49; 129.99; 130.49; 132.02; 135.22; 145.56; 146.47); C═O (176.11) **3i**. ^{1}H NMR δ ppm: 3-CH_2CH_3-Ph (t: 1.29); CH_2-11 (d: 1.97 and 2.33 J = 14.00); CH_3-Ph (s: 2.33); CH_3CH_2-Ph (m: 2.72); CH-7 (s broad: 3.09); CH-8 (s: 3.24); CH-6 (s: 3.57); ArH (m: 7.02–7.50). ^{13}C NMR δ ppm: 3-CH_2CH_3-Ph (16.12 and 29.48); CH_3-Ph (22.28); CH_2-11 (40.70); CH-7 (48.73); CH-8 (50.32); CH-6 (55.97); C Ar (124.04; 124.62; 126.31; 126.80; 127.99; 129.17; 130.04; 133.30; 135.26; 145.57); C═O (175.84) **4i**.

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