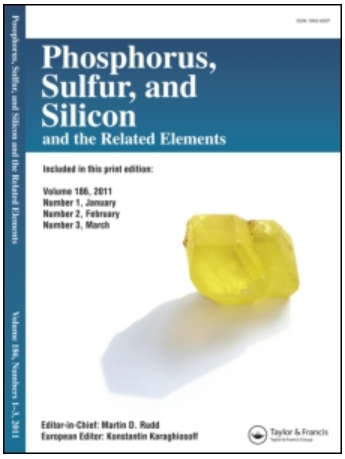

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SYNTHESIS OF NOVEL SUBSTITUTED 6aλ⁴-THIA-1,6-DIAZAPENTALENES AND THEIR COMPLEXATION BEHAVIOUR TOWARD SODIUM (I), SILVER(I) AND MERCURY(II)

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SYNTHESIS OF NOVEL SUBSTITUTED 6aλ^4-THIA-1,6-DIAZAPENTALENES AND THEIR COMPLEXATION BEHAVIOUR TOWARD SODIUM (I), SILVER(I) AND MERCURY(II)

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Herein we describe the synthesis of novel substituted 6aλ^4-thia-1,6-diazapentalenes by a base-induced dimerisation of two isothiazolium salts. It was possible to introduce benzo crown ether substituents for the first time according to the well established reaction procedure for the synthesis of the thiadiazapentalenes. The complex formation behaviour of the 6aλ^4-thia-1,6-diazapentalenes towards Ag(I), Hg(II) and Na(I) in solution was studied in terms of the influence of several substituents. The combination of 6aλ^4-thia-1,6-diazapentalenes with benzo crown ether substituents results in a simultaneous binding of one hard and one soft metal ion by one molecule.

Keywords: 6aλ^4-thia-1,6-diazapentalenes; isothiazolium salts; benzo crown ether; complexation behaviour; host-guest chemistry; silver(I) mercury(II) and sodium(I) complexes

INTRODUCTION

The host-guest chemistry of appropriate functionalized macrocycles reveals novel aspects in the field of supramolecular chemistry. To date, all attempts to use novel macrocyclic host systems for the selective complexation of metal ions have focused on the modification of the molecular rec-

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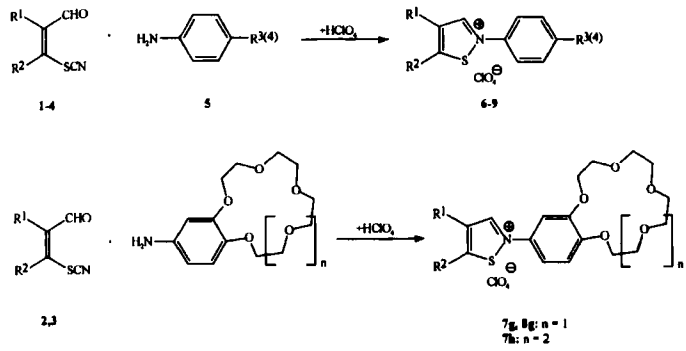
ognition properties. The 1,6,6aλ^4-trithia-3,4-diaza- and the 6aλ^4-thia-1,6-diazapentalene units represent novel building blocks in macrocycles which show interesting structure and binding properties.[1] Theoretical studies on the trithia-[2] and thiadiazapentalene[3] system have shown the significant influence of different substituents on the electronic character of the pentalene system. Recently, we reported on the graduated complex formation of crown compounds containing a 1,6,6aλ^4-trithia-3,4-diazapentalene unit in the macrocyclic ring system toward Ag(I) and Hg(II) depending on the cavity size.[4] In this paper we describe the synthesis of novel 6aλ^4-thia-1,6-diazapentalenes including those with benzo crown ether substituents, and their complex formation behaviour towards Na(I), Ag(I) and Hg(II) in solution.

RESULTS AND DISCUSSION

The synthesis of thiadiazapentalene compounds was easily accomplished by the base-induced dimerization of isothiazolium salts. The isothiazolium salts can be obtained by the reaction of β-thiocyanatovinylaldehydes **1–4** with substituted anilines **5** (scheme 1).[5,6]

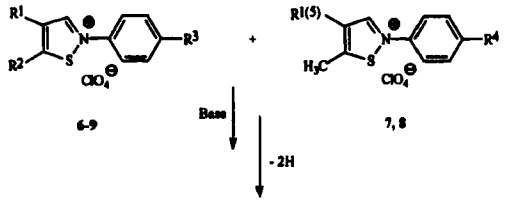


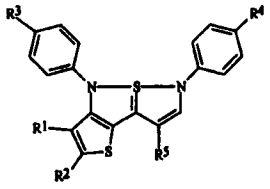
	R^1	R^2
1,6	-$(CH_2)_4$-	
2,7	CH_3	CH_3
3,8	C_6H_5	CH_3
4,9	C_6H_5	C_6H_5

5-9	$R^{3(4)}$
a	OCH_3
b	CH_3
c	H
d	CF_3
e	Cl
f	Br
g	15-crown-5
h	18-crown-6

SCHEME 1

Accordingly we prepared the N-phenyl-substituted isothiazolium salts **6–9, 7g, 7h** and **8g** bearing a benzo crown ether substituent. Furthermore, the 6aλ^4-thia-1,6-diazapentalenes **10–15** were obtained by the reaction of the active methyl group in 5-position of **7** or **8** with the sulfur atom of the isothiazolium salts **6–9** followed by a consecutive oxidative ring closure (scheme 2).[5–7] The yields obtained for the benzo crown ether substituted pentalenes are comparable with the reaction yields of the other compounds.





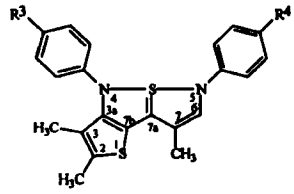
10-15

	R^1	R^3	R^5
10	CH_3	CH_3	CH_3
11	C_6H_5	CH_3	C_6H_5
12		$-(CH_2)_4-$	CH_3
13		$-(CH_2)_4-$	C_6H_5
14	C_6H_5	C_6H_5	CH_3
15	C_6H_5	C_6H_5	C_6H_5

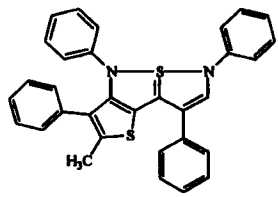
R^3 and R^4 see Scheme 3 and 4

SCHEME 2

The reaction of isothiazolium salts **7** or **8** containing an active methyl group in the 5-position and similar substituents $R^3 = R^4$ affords the pentalene compounds **10a-c** and **11** (scheme 3). To date it was not possible to obtain a 6aλ^4-thia-1,6-diazapentalene with two benzo crown ether substituents.



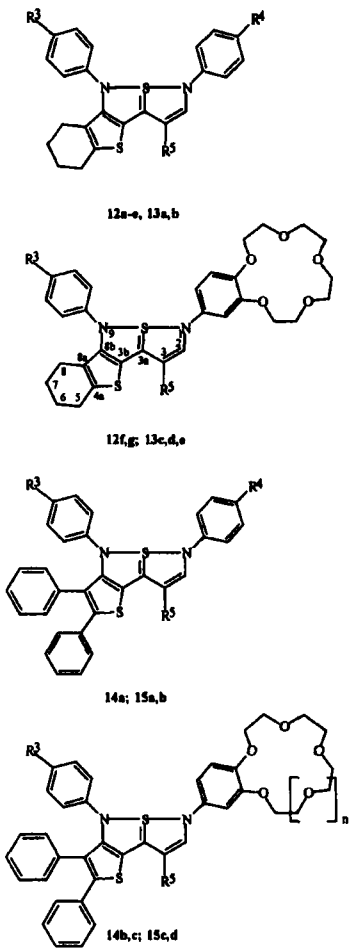
10a: $R^3 = R^4 = CH_3$
10b: $R^3 = R^4 = H$
10c: $R^3 = R^4 = Cl$



11

SCHEME 3

The highest yields of thiadiazapentalenes **12–15** with $R^3 \neq R^4$ are observed with electron-withdrawing groups in position R^3, e.g. $R^3 = Cl$, Br, CF_3 and electron-donating substituents in R^4 like CH_3, OCH_3 (scheme 4)[6].



	R^3	R^4	R^5	n
12a	H	OCH_3	CH_3	
b	CF_3	OCH_3	CH_3	
c	CF_3	CF_3	CH_3	
d	Br	H	CH_3	
e	Cl	OCH_3	CH_3	
f	Cl	--	CH_3	
g	CF_3	--	CH_3	
13a	H	OCH_3	C_6H_5	
b	Cl	OCH_3	C_6H_5	
c	Cl	--	C_6H_5	
d	CF_3	--	C_6H_5	
e	H	--	C_6H_5	
14a	Cl	OCH_3	CH_3	
b	Cl	--	CH_3	1
c	Cl	--	CH_3	2
15a	Cl	OCH_3	C_6H_5	
b	CF_3	OCH_3	C_6H_5	
c	Cl	--	C_6H_5	1
d	CF_3	--	C_6H_5	1

SCHEME 4

The complex formation behaviour of the new synthesized 6aλ^4-thia-1,6-diazapentalenes **10–15** was studied by liquid-liquid extraction experiments in the system metal salt-picric acid-water as the aqueous

phase and the thiadiazapentalene dissolved in chloroform as the organic phase.[8,9] Due to the basic character of the nitrogen atom in the thiadiazapentalene unit a buffer system (pH = 7.5) was used to prevent its protonation, which would cause a ring opening reaction.[10]

The extractabilities of Ag(I) and Hg(II) for all studied pentalene compounds are presented in figure 1 and table I.

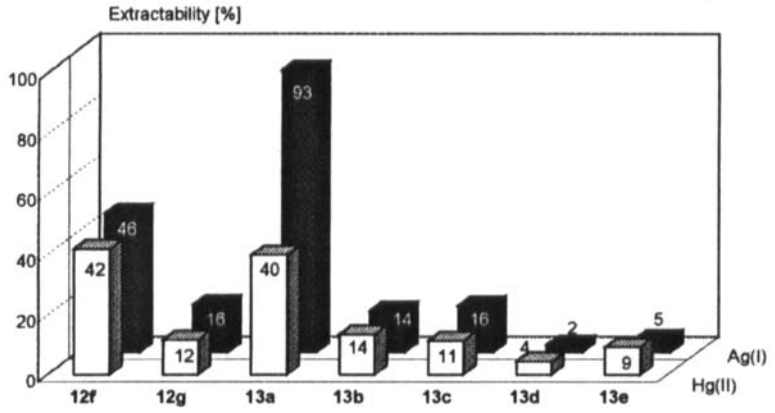


FIGURE 1 Extraction behaviour of the benzo-15-crown-5 substituted thiadiazapentalenes **12f, g** and **13a-e** with Ag(I) and Hg(II); $c_{(Ag(I)/Hg(II)} = 1 \cdot 10^{-4}$ M; $c_{HPic} = 5 \cdot 10^{-3}$ M and TRIS/HCl (pH = 7.5) for Hg(II); HEPES/LiOH (pH = 7.5) for Ag(I); $c_{ligand} = 1 \cdot 10^{-3}$ M in chloroform

The complex formation of the compounds **10–15** strongly depends on the nature of the substituents R^1 – R^5, especially in position R^5. This observation reveals the interpretation that the soft metal ions are favourably complexed by the thiophene sulfur adjacent to R^5. The thiadiazapentalenes **10a-c** with $R^3 = R^4$ (Cl, H or CH_3) and $R^5 = CH_3$ exhibit only low extractabilities (table I). The same phenomenon could also be observed with the tetracyclic compounds **12a-e** (table I).

The introduction of a benzo crown ether function attached at the nitrogen atom of the pentalene unit (**12f,g**) leads to a significant increase of the extractability, whereas **12f** and **12g** differ significantly in their extraction capability. Probably, this finding is determined by electronic effects of the R^3 substituent. In compound **12f**, R^3 is a chloro-substituent with a small positive mesomeric effect and the change to the strongly electron-withdrawing trifluoromethyl group results in a decrease of the extractabilities

for both, Ag(I) and Hg(II). Interestingly in the case of type **13** compounds a phenyl substituent in position R^5 only leads to a strong extraction especially of Ag(I) for **13a** with $R^3 = H$ and $R^4 = OCH_3$. In contrast to this a lower extractability is observed for **13b** ($R^3 = Cl$). The introduction of an additional benzo crown ether substituent does not result in higher extractabilities, neither if R^3 is an electron-withdrawing substituent like Cl or CF_3 (see **13c, d**), nor in case of $R^3 = H$ (**13e**).

TABLE I Extraction behaviour of the investigated thiadiazapentalenes **10–15** toward Ag(I) and Hg(II) $c_{(Ag(I)/Hg(II)} = 1 \cdot 10^{-4}$ M; $c_{HPic} = 5 \cdot 10^{-3}$ M and TRIS/HCl (pH = 7.5) for Hg(II); HEPES/LiOH (pH = 7.5) for Ag(I); $c_{ligand} = 1 \cdot 10^{-3}$ M in chloroform

Compound	*Extractabilities [%]*	
	Ag(I)	*Hg(II)*
10 a	2.7	2.9
10 b	6.5	5.6
10 c	5.0	2.5
11	21.4	10.5
12 a	1.0	1.9
12 b	1.5	4.2
12 c	1.8	2.1
12 d	3.6	6.6
12 e	4.0	5.4
12 f	46.2	41.9
12 g	16.0	11.7
13 a	93.4	40.0
13 b	13.9	13.6
13 c	15.6	11.4
13 d	2.5	4.5
13 e	4.6	9.3
14 a	6.3	5.9
14 b	3.4	1.9
14 c	6.8	4.5
15 a	0.9	0.5
15 b	3.0	1.6
15 c	24.2	23.0
15 d	14.3	8.3

To study the influence of further phenyl substituents, we have synthesized compounds of different types **11, 14** and **15** with phenyl groups in position R^1, R^2 and R^5. The thiadiazapentalenes **15d** and **15c** with $R^5 = C_6H_5$ and a benzo crown ether substituent give the best results for the complex formation with Ag(I) and Hg(II) (see table I). These extractabilities are comparable with those of the pentalene type **11** ($R^3 = R^4 = H$).

The investigated thiadiazapentalenes **10–15** containing a phenyl group in position R^5 show a beneficial influence of that group on the extraction of Ag(I) and Hg(II) (see **11, 13a** and **15c**). Obviously, the complex formation of both metal ions is promoted by the thieno sulfur and the π-system of the phenyl substituent, respectively. Furthermore, the introduction of a benzo crown ether unit leads to a significant increase of the extractabilities (**12f,g 13c** and **15c**), whereas the strongly electron-withdrawing trifluoromethyl-group in position R^3 drastically decreases the complexation capability.

Generally electron-donating substituents in positions R^1, R^2, R^3 and R^4 promote the extractabilities of Ag(I) and Hg(II) by the increase of the electron density in the thienopentalene system. But the access of compounds with electron donating substituents in R^3 together with a phenyl group in R^5 is limited.

TABLE II Extraction behaviour of selected thiadiazapentalenes **12–15** toward Na(I) $c_{Na(I)} = 1 \cdot 10^{-4}$ M; $c_{HPic} = 5 \cdot 10^{-3}$ M and TRIS/HCl (pH = 7.5); $c_{ligand} = 1 \cdot 10^{-3}$ M in chloroform

Compound	*Extractabilities [%]*
	Na(I)
12 f	0.5
12 g	0.3
13 b	0
13 c	0.4
13 d	0.4
13 e	0.6
14 a	0
14 b	0.4
15 c	0.5
15 d	0.3
Benzo-15-crown-5	0.6

Besides the extraction of the soft metal ions Ag(I) and Hg(II) the introduced benzo crown ether substituents are also interesting for the complexation of alkaline metals like Na(I). The studies have shown, that the complex formation of benzo-15-crown-5 with Na(I) is low but comparable with the extraction behaviour of benzo-15-crown-5 substituted pentalene compounds (see table II).

Thiadiazapentalenes without a benzo crown substituent do not extract sodium to any extent. It can be concluded, that the introduction of a benzo-15-crown-5 substituent offers the simultaneous complexation of the hard alkali cation Na(I) as well as the complexation of the thiophilic metals Ag(I) and Hg(II) by the thieno sulfur. This result has been confirmed by competitive liquid-liquid extraction experiments for Na(I) and Hg(II) with **13e**. The results are shown in figure 2.

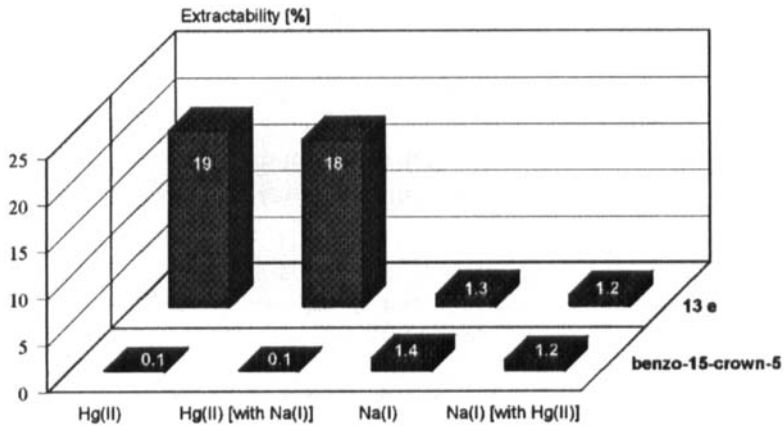


FIGURE 2 Comparison of the Hg(II) and Na(I) extraction with the thiadiazapentalene **13e** and benzo-15-crown-5 [Hg(II) and Na(I) separate or together in a mixture] $c_{(Na(I)/Hg(II))} = 1 \cdot 10^{-4}$ M; $C_{HPic} = 5 \cdot 10^{-3}$ M and TRIS/HCl (pH = 7.5), $C_{ligand} = 2{,}5 \cdot 10^{-3}$ M in chloroform

In both cases the extraction of the metal ions is not influenced by the presence of the other metal. The distribution ratios are the same and the resulting complexes composition is allways 1:1.

CONCLUSION

We have synthesized novel substituted 6aλ^4-thia-1,6-diazapentalenes with a high diversity of different substituents, especially benzo crown ethers, by using base-induced dimerization of two isothiazolium salts.

Solvent extraction experiments have shown that the modification of the general molecule structure by different substitution leads to significant changes of the complexing properties toward silver and mercury. A remarkable result represents the simultaneous binding of one hard and one soft metal ion by the benzo crown ether substituent compounds.

EXPERIMENTAL

Liquid-liquid extraction

The extraction studies were performed at room temperature in 2 cm^3 micro-reaction vessels by means of mechanical shaking. The phase ration was $v_{(org)}:v_{(aqu)}$ = 1:1 (0.5 cm^3 each), the shaking time was 30 min. The extraction equilibrium was attained within few minutes. The used concentrations are given in table I and II and figure 1. The measurements of the metal concentrations in both phases were carried out radiometrically using Na(TI) scintillation counter (Cobrall, Canberra-Packard) for ^{22}Na, ^{110m}Ag and ^{203}Hg. The radioisotopes were purchased by Medgenix Diagnostics GmbH Rathingen. $D = c_{M(org)} / c_{M(aqu)}$; $E_M[\%] = D.100 / (D+1)$ see[9].

SYNTHESIS

General

IR: Specord M 80, Carl-Zeiss, Jena; UV/VIS: Specord UVVIS, Specord M 40, Carl-Zeiss, Jena; NMR: Varian Gemini 200 (200 MHz ^1H, 50 MHz ^{13}C), TMS internal Standard; Elemental analyses: Foss-Heraeus CHN-O-S-Rapid; melting points: system Boetius.

Isothiazolium perchlorates 6–9

Isothiazolium perchlorates **6c-f, 7a-e** and **8c** were described in[5,6,11]. **7g,h; 8a,g** and **9d,e** were prepared according to literature procedure[5].

2-(Benzo-1,4,7,10,13-pentaoxacyclopentadecano)-4,5-dimethyl-isothiazolium perchlorate 7g

59 %; m.p. 140–144°C. IR (KBr): ν = 1100 cm^{-1}(O-Cl-O). UV(ethanol): λ_{max} (log ε) = 266(3.85), 333(3.73) nm. ^{1}H-NMR (DMSO-d_6): δ = 2.38 (s, 3H; 4-CH_3); 2.70 (s, 3H; 5-CH_3); 3.73 (s, 8H; O-CH_2); 3.89 (m, 4H; O-CH_2); 4.14 (m, 2H; O-CH_2); 4.24 (m, 2H; O-CH_2); 6.90 (d, 1H; arom H); 7.12 (d, 1H; arom H); 7.29 (s, 1H; arom H); 8.96 (s, 1H; CH=N) ppm. ^{13}C-NMR ($CDCl_3$): δ = 11.3 (4-CH_3); 13.6 (5-CH_3); 69.6, 69.8, 70.4, 70.6, 71.4, 71.6 (O-CH_2); 108.0, 113.4, 116.7, 130.3 (i-C); 135.2 (C-4); 150.8, 151.9; 155.3 (C-3); 166.3 (C-5). $C_{19}H_{26}ClNO_9S$ (479.92) calcd. C 47,55; H 5.46; N 2.92; S 6.68, found C 47.41; H 5.51; N 2.86; S 6.75.

2-(Benzo-1,4,7,10,13,16-hexaoxacyclooctadecano)-4,5-dimethyl-isothiazolium perchlorate 7h

53 %; m.p. 79–85°C. IR (KBr): ν = 1070 cm^{-1}(O-Cl-O). UV (ethanol): λ_{max} (log ε) = 233(3.94), 269(3.77), 346(3.94) nm. ^{1}H-NMR (DMSO-d_6): δ = 2.36 (s, 3H; 4-CH_3); 2.71 (s, 3H; 5-CH_3); 3.65 (m, 12H; O-CH_2); 3.89 (m, 4H; O-CH_2); 4.17 (m, 2H; O-CH_2); 4.28 (m, 2H; O-CH_2); 6.90 – 7.32 (m, 3H; arom H); 8.99 (s, 1H; CH=N) ppm. ^{13}C-NMR ($CDCl_3$): δ = 11.5 (4-CH_3); 13.1 (5-CH_3); 68.9, 69.4, 69.5, 70.6, 70.8, 71.0 (O-CH_2); 108.1, 113.7, 116.1, 130.3 (i-C); 134.9 (C-4); 149.6, 150.7; 156.0 (C-3); 166.6 (C-5). $C_{21}H_{30}ClNO_{10}S$ (523.97) calcd. C 48.13; H 5.77; N 2.67; S 6.12, found C 48.01; H 5.87; N 2.51; S 6.35.

2-(4-Methoxyphenyl)-5-methyl-4-phenyl-isothiazolium perchlorate 8a

70 %; m.p.145–147°C. IR (KBr): ν = 1170 cm-1 (O-Cl-O). UV (ethanol): λ_{max} (log ε) = 228(3.94), 291 (3.39), 328(3.40) nm. ^{1}H-NMR (DMSO-d_6): δ = 2.86 (s, 3H; 5-CH_3); 3.86 (s, 3H; O-CH_3); 7.23; 7.86 (4H, J_{AB} = 5 Hz; o/m-H); 7.56–7.72 (m, 5H; arom H); 9.73 (s, 1H; CH=N) ppm. ^{13}C-NMR (DMSO-d_6): δ = 14.8 (5-CH_3); 56.8 (OCH_3); 116.4; 126.0, 130.1, 130.2, 130.3, 130.4, 130.8; 137.6 (C-4); 156.9 (C-3); 162.2 (p-C); 166.5 (C-5). $C_{17}H_{16}ClNO_5S$ (381.83) calcd. C 53.47; H 4.22; N 3.67; S 8.40, found C 53.29; H 4.15; N 3.85; S 8.21.

2-(Benzo-1,4.7.10.13-pentaoxacyclopentadecano)-5-methyl-4-phenyl-isothiazolium perchlorate 8g

60 %; m.p. 150–152°C. IR (KBr): ν = 1100 cm-1 (O-Cl-O). UV (ethanol): λ_{max} (log ε) = 228(4.26), 306(3.56), 357(3.50) nm. ^{1}H-NMR (DMSO-d_6): δ = 2.89 (s, 3H; 5-CH_3); 3.76 (s, 8H; O-CH_2); 3.83 (m, 4H; O-CH_2); 4.08

(m, 2H; O-CH_2); 4.19 (m, 2H; O-CH_2); 6.92 (d, 1H; arom H); 7.04 (d, 1H; arom H); 7.23 (s, 1H; arom H); 7.44–7.75 (m, 5H; arom H); 9.76 (s, 1H; CH=N) ppm. ^{13}C-NMR (DMSO-d_6): δ = 14.2 (5-CH_3); 68.7, 68.8, 68.9, 69.1, 69.2, 69.9, 70.7, 70.8 (O-CH_2); 109.0, 113.9, 116.0, 129.4, 129.5, 129.7, 130.1 (i-C); 136.9 (C-4); 148.6, 149.4, 150.8; 155.8 (C-3); 165.6 (C-5). $C_{24}N_{28}ClNO_9S$ (541.98) calcd. C 53.18; H 5.21; N 2.58; S 5.92, found C 53.31; H 5.44; N 2.51; S 5.74.

2-(4-Trifluormethylphenyl)-4,5-diphenyl-isothiazolium perchlorate 9d

46 %; m.p. 222–224°C. IR (KBr): ν = 1170 cm-1 (O-Cl-O). UV (ethanol): λ_{max} (log ε) = 248(3.86), 345(3.70) nm. ^{1}H-NMR (200 MHz, DMSO-d_6): δ = 7.47–7.62 (m, 10H; arom H); 8.19 (2H, J_{AB} = 7.4 Hz; o/m H); 8.26 (2H, J_{AB} = 7.4 Hz; o/m H); 10.19 (s, 1H; CH=N) ppm. ^{13}C-NMR (50 MHz, DMSO-d_6): δ = 125.8; 128.3 (d, CF_3, $^1J_{C,F}$ = 148 Hz); 128.8, 130.1, 130.4, 130.6, 130.6, 131.9, 133.3; 136.4 (C-4); 140.6; 159.1 (C-3); 167.6 (C-5). $C_{22}H_{15}ClF_3NO_4S$ (481.88) calcd. C 54.83; H 3.14; N 2.91; S 6.65, found C 54.61; H 3.01; N 3.05; S 6.45.

2-(4-Chlorophenyl)-4,5-diphenyl-isothiazolium perchlorate 9e

45 % m.p. 223–225°C. IR (KBr): ν = 1030 cm-1 (O-Cl-O). UV (ethanol): λ_{max} (log ε) = 287(3.90), 344(3.96) nm. ^{1}H-NMR (DMSO-d_6): δ = 7.47–7.61 (m, 10H; arom. H); 7.86, 8.06 (4H, J_{AB} = 8.8 Hz, o/m-H); 9.96 (s, 1H; CH=N) ppm. ^{13}C-NMR (50 MHz, DMSO-d_6): δ = 126.4, 126.8, 129.8, 130.1, 130.2, 130.3, 130.5, 130.6, 131.4, 133.2, 136.3, 136.4; 137.1 (C-4); 158.9 (C-3); 166.8 (C-5). $C_{21}H_{15}Cl_2NO_4S$ (448.32) calcd. C 56.26; H 3.37; N 3.12; S 7.15, found C 56.02; H 3.20; N 3.18; S 7.31.

6aλ^4-Thia-1,6-diazapentalenes 10–15

6aλ^4-Thia-1,6-diazapentalenes **10a-c** and **11** were described in ref.[5]; respectively **12a-e** in ref.[6,10]. **12f,g; 13a-e; 14a-c** and **15a-d** were prepared according to literature procedure[6].

9-(4-Chlorphenyl)-1-(benzo-1,4,7,10,13-pentaoxacyclopentadecano)-3-methyl-[4,5,6,7]-tetrahydrobenzo[d]thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 12f

16.8 % m.p. 143–146°C; red powder. MS (El, 70 eV) m/z (%): 625 (5) [M-H$^+$]; 626 (100) [M]; 627 (40); 628 (45); 629 (15); 630 (5). HR-MS (El,

70 eV): calcd. 626.1676; found 626.1650. ^{1}H-NMR ($CDCl_3$): δ = 1.69 (m, 2H, CH_2); 1.85 (m, 2H, CH_2); 2.25 (t, 2H, CH_2); 2.55 (s, 3H, 3-CH_3); 2.86 (t, 2H, CH_2); 3.76 (s, 8H; OCH_2); 3.93 (m, 4H; OCH_2); 4.14 (m, 4H; OCH_2); 6.86 (m, 3H; arom H); 7.04; 7.31 (4H, J_{AB} = 7.8 Hz; o/m H); 7.98 (s, 1H; 2-H). ^{13}C-NMR ($CDCl_3$): δ = 14.4 (3-CH_3); 23.0, 23.4, 26.5, 27.3 (CH_2); 69.6, 70.0, 70.2, 71.0, 71.1, 71.5 (O-CH_2); 108.0; 110.9 (C-3b); 111.9; 113.9; 115.9; 123.8 (C-8a); 125.8, 129.0, 129,5, 137.2; 142.0 (C-2); 146.0; 146.2 (C-4a); 147.2; 150.4 (C-3a); 152.0; 152.5 (C-8b). $C_{32}H_{35}ClN_2O_5S_2$ (627.19) calcd. C 61.27; H 5.62; N 4.47; S 10.22, found C 60.60; H 5.70; N 4.20; S 9.72.

9-(4-Trifluormethylpheny)-1-(benzo-1,4,7,10,13-pentaoxacyclopentadecano)-3-methyl-[4,5,6,7]-tetrahydrobenzo[d]thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 12g

88 %; m.p. 171–176°C; red powder, MS(El, 70 eV) m/z (%): 659 (5) [M-H$^+$]; 660 (100) [M]; 661 (40); 662 (15); 663 (5). HR-MS (El, 70 eV): calcd. 660.1940; found 660.1951. ^{1}H-NMR ($CDCl_3$): δ = 1.69 (m, 2H, CH_2); 1.81 (m, 2H, CH_2); 2.30 (m, 2H, CH_2); 2.56 (s, 3H, 3-CH_3); 2.90 (m, 2H, CH_2); 3.76 (s, 8H; OCH_2); 3.91 (m, 4H; OCH_2); 4.14 (m, 4H; OCH_2); 6.87 (m, 3H; arom H); 7.14; 7.57 (4H, J_{AB} = 8.3 Hz; o/m H);; 7.98 (s, 1H; 2-H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 14.4 (3-CH_3); 23.0, 23.4, 26.7, 27.3 (CH_2); 69.5, 69.9, 70.0, 70.17, 70.20, 71.0, 71.1, 71.5 (O-CH_2); 108.2; 111.7 (C-3); 112.2 (C-3b); 114.0; 115.8; 123.6 (C-8a); 124.2, 126.1, 136.7; 142.0 (C-2); 146.4 (C-4a); 146.8; 147.5; 150.4 (C-3a); 152.6; 152.8 (C-8b). $C_{33}H_{35}F_3N_2O_5S_2$ (660.78) calcd. C 59.98; H 5.34; N 4.24; S 9.71, found C 59.50; H 4.95; N 4.38; S 9.45.

9-(Phenyl)-1-(4-methoxyphenyl)-3-phenyl-[4,5,6,7]-tetrahydrobenzo[d]thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 13a

38.9 %; m.p. 80-85°C; red powder; MS(EL, 70 eV) m/z (%): 493 (15) [M-H$^+$]; 494 (100) [M]; 495 (30); 496 (15); 497 (5). HR-MS (El, 70 eV): calcd. 494.1487; found 494.1456. ^{1}H-NMR ($CDCl_3$): δ = 1.64 (m, 2H, CH_2); 1.77 (m, 2H, CH_2); 2.17 (m, 2H, CH_2); 2.72 (m, 2H, CH_2); 3.81 (s, 3H, O-CH_3); 6.92; 7.31 (4H, J_{AB} = 8.7 Hz; o/m H); 7.20 – 7.60 (m, 10H; arom H); 8.17 (s, 1H; 2-H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 23.0, 23.3, 25.7, 26.1 (CH_2); 56.0 (O-CH_3) 114.9 (C-3); 115.3; 115.8 (C-3b); 122.5 (C-8a); 125.2, 126.4, 127.8, 128.7, 128.9, 129.1, 130.6, 136.3, 137.2, 142.1; 142.4 (C-2); 145.6 (C-4a); 150.0 (C-3a); 153.4 (C-8b); 157.5 (p-C).

$C_{30}H_{26}N_2OS_2$ (494.68) calcd. C 72.84; H 5.30; N 5.66; S 12.96, found C 72.61; H 5.25; N 5.40; S 13.02.

9-(4-Chlorphenyl)-1-(4-methoxyphenyl)-3-phenyl-[4,5,6,7]-tetrahydro-benzo[d]thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 13b

41.2 %; m.p. 167–173°C; red powder. MS(El, 70 eV) m/z (%): 527 (25) [M-H$^+$]; 528 (100) [M]; 529 (40); 530 (45); 531 (20); 532 (5). HR-MS (El, 70 eV): calcd. 528.1097; found 528.1077. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.63 (m, 2H, CH_2); 1.78 (m, 2H, CH_2); 2.18 (t, 2H, CH_2); 2.72 (t, 2H, CH_2); 3.83 (s, 3H, O-CH_3); 6.93 (2H, J_{AB} = 9.0 Hz; o/m H); 7.10 (2H, J_{AB} = 8.7 Hz; o/m H); 7.30 (2H, J_{AB} = 8.7 Hz; o/m H); 7.35 (2H, AB, J_{AB} = 8.6 Hz; o/m H); 7.49 – 7.55 (m, 5H; arom H); 8.16 (s, 1H; 2-H) ppm. $C_{30}H_{25}ClN_2OS_2$ (529.10) calcd. C 68.10; H 4.76; N 5.29; S 12.12, found C 68.31; H 4.83; N 5.17; S 12.41.

9-(4-Chlorphenyl)-1-(benzo-1,4,7,10,13-pentaoxacyclopentadecano)-3-phenyl-[4,5,6,7]-tetrahydrobenzo[d]thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 13c

30.2 %; m.p. 169–173°C; red powder. UV (ethanol): $\lambda_{(max)}$ (log ε) = 329.5 (3.64), 467,0 (3.95). MS(El, 70 eV) m/z (%): 687 (5) [M-H$^+$]; 688 (100) [M]; 689 (40); 690 (45); 691 (15); 692 (5). HR-MS (El, 70 eV): calcd 688.1832; found 688.1813. ^{1}H-NMR ($CDCl_3$): δ = 1.60–1.87 (m, 4H; CH_2); 2.20 (m, 2H; CH_2); 2.75 (m, 2H; CH_2); 3.75 (s, 8H; OCH_2); 3.90 (m, 4H; OCH_2); 4.14 (m, 4H; OCH_2); 6.89 (m, 3H; arom. H); 7.10; 7.33 (4H, J_{AB} = 8.8 Hz, o/m-H); 7.44–7.57 (m, 5H, arom. H); 8.13 (s, 1H; 2-H) ppm. $C_{37}H_{37}ClN_2O_5S_2$ (689.25) calcd. C 64.38; H 5.55; N 4.06; S 9.29, found C 64.51; H 5.68; N 4.15; S 9.41.

9-(4-Trifluormethylpheny)-1-(benzo-1,4,7,10,13-pentaoxacyclopenta-decano)-3-phenyl-[4,5,6,7]-tetrahydrobenzo[d]thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 13d

44.9 %; m.p. 199–204°C; red powder. MS(El, 70 eV) m/z (%): 721 (5) [M-H$^+$]; 722 (100) [M]; 723 (40); 724 (15); 725 (5). HR-MS (El, 70 eV): calcd. 722.2096; found 722.2089. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.64 (m, 2H, CH_2); 1.79 (m, 2H, CH_2); 2.20 (m, 2H, CH_2); 2.72 (m, 2H, CH_2); 3.75 (s, 8H; OCH_2); 3.89 (m, 4H; OCH_2); 4.11 (m, 4H; OCH_2); 6.89 (m, 3H; arom H); 7.20 (2H, J_{AB} = 8.2 Hz; o/m H); 7.47 – 7.54 (m, 5H; arom

H); 7.60 (2H, J_{AB} = 8.2 Hz; o/m H); 8.12 (s, 1H; 2-H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 22.8, 23.2, 26.5, 27.1 (CH_2); 69.4, 69.8, 70.1, 70.9, 71.0, 71.5 (O-CH_2); 108.0 (CH); 114.1 (CH); 114.2 (C-3); 115.6 (C-3b); 117.5 (CH); 123.2 (C-8a); 124.4, 126.1, 126.2; 126.8 (CF_3; $^1J_{C,F}$ = 125 Hz); 128.3, 129.1, 130.7, 135.7, 142.3 (C-2); 146.0 (C-4a); 146.4; 147.6; 150.5 (C-3a); 151.0; 153.6 (8b). $C_{38}H_{37}F_3N_2O_5S_2$(722.85) calcd. C 63.14; H 5.16; N 3.88; S 8.87, found C 63.02; H 5.11; N 3.97; S 8.71.

1-(Benzo-1,4,7,10,13-pentaoxacyclopentadecano)-3,9-diphenyl-[4,5,6,7]-tetrahydrobenzo[d]thieno-[2,3-b][6aλ^4]-thia-1,6-diazapentalene 13e

54%; m.p. 174–176°C. MS(El, 70 eV) m/z (%): 652 (20) [M-H$^+$]; 654 (100) [M]. ^{1}H-NMR ($CDCl_3$): δ = 1.64 (m, 2H, CH_2); 1.76 (m, 2H, CH_2); 2.18 (m, 2H, CH_2); 2.71 (m, 2H, CH_2); 3.76 (s, 8H, OCH_2); 3.93 (m, 4H, OCH_2); 4.14 (m, 4H, OCH_2); 6.89 (m, 3H, arom. H), 7.17–7.54 (m, 10H, arom. H); 8.17 (s, 1H, 2-H). $C_{37}H_{38}N_2O_5S_2$ (654,82) calcd. C 67.85; H 5.99; N 4.27; S 9.78, found C 67.57; H 6.05; N 4.11; S 9.65.

4-(4-Chlorphenyl)-5-(4-methoxyphenyl)-2,3-diphenyl-7-methyl-thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 14a

54 %; m.p. 204–208°C; red powder. MS(El, 70 eV) m/z (%): 563 (15) [M-H$^+$] 564 (100) [M]; 565 (40); 566 (45); 567 (15); 568 (5). HR-MS (El, 70 eV): calcd 564.1097; found 564.1084. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 2.67 (s, 3H, 7-CH_3); 3.82 (s, 3H, O-CH_3); 6.60 – 6.64 (m, 4H; arom H); 6.84 – 7.02 (m, 9H; arom H); 7.22 – 7.32 (m, 5H; arom H); 8.08 (s, 1H; 6-H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 14.7 (CH_3); 56.0 (O-CH_3); 111.4 (C-7); 113.5 (C-7b); 115.3; 122.8, 122.9; 125.3 (C-3); 126.0, 127.2, 128.2, 128.3, 128.5, 128.8, 129.9; 130.6, 134.7, 135.0, 136.4; 140.7 (C-2); 142.6 (C-6); 146.7; 151.2 (C-7a); 151.6 (C-3a); 157.8 (C-OCH_3). $C_{33}H_{25}ClN_2OS_2$ (565.16) calcd. C 70.13; H 4.46; N 4.96; S 11.35, found C 69.83; H 4.88; N 4.85; S 11.57.

4-(4-Chlorphenyl)-5-(benzo-1,4,7,10,13-pentaoxacyclopentadecano)-2,3-diphenyl-7-methyl-thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 14b

16.5 %; m.p. 159–161°C red powder. MS(El, 70 eV) m/z (%): 723 (10) [M-H$^+$]; 724 (100) [M]; 725 (45); 726 (50); 727 (20); 728 (10). HR-MS (El, 70 eV): calcd. 724.1832; found 724.1833. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 2.65 (s, 3H, 7-CH_3); 3.76 (s, 8H; OCH_2); 3.90 – 3.92 (m, 4H;

OCH_2); 4.12 – 4.14 (m, 4H; OCH_2); 6.59 (s, 1H; arom H); 6.64 (s, 1H; arom H); 6.83 (s, 1H; arom H); 6.87 – 6.99 (m, 9H; arom H); 7.26 (m, 5H; arom H); 8.06 (s, 1 H; 6-H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 14.6 (CH_3); 69.4, 69.9, 70.1, 70.9, 71.0, 71.5 (O-CH_2); 108.5 (CH); 111.5 (C-7); 113.8 (C-7b); 114.0, 115.8 (CH); 125.2 (C-3); 126.1, 127.3, 128.2, 128.4, 128.6, 128.9, 129.9; 130.6, 134.7, 135.0, 137.2; 140.6 (C-2); 142.4 (C-6); 146.9; 147.4; 150.5 (C-7a); 151.2; 151.6 (C-3a). $C_{40}H_{37}ClN_2O_5S_2$ (725.29) calcd. C 66.23; H 5.14; N 3.86; S 8.83, found C 65.60; H 5.02; N 3.52; S 8.20.

4-(4-Chlorphenyl)-5-(benzo-1,4,7,10,13,16-hexaoxacyclooctadecano)-2,3-diphenyl-7-methyl-thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 14c

34 %; m.p. 165–168°C; red powder. UV (ethanol): $\lambda_{(max)}$ (log ε) = 309.5 (4.22), 343.5 (4.14), 489.0 (4.34). MS(El, 70 eV) m/z (%): 767 (5) [M-H$^+$]; 768 (100) [M]; 769 (50); 770 (50); 771 (20); 772 (5). HR-MS (El, 70 eV): calcd. 768.2095; found 768.2088. ^{1}H-NMR ($CDCl_3$): δ = 2.67 (s, 3H; 7-CH_3); 3.69–3.78 (m, 12H; OCH_2); 3.92 (m, 4H; OCH_2); 4.17 (m, 4H; OCH_2); 6.60; 6.84 (4H, J_{AB} = 7.5 Hz, o/m-H); 6.87 (s, 3H; arom. H); 6.92–7.05 (m, 5H; arom. H); 7.25 (s, 5H; arom. H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 14.7 (7-CH_3); 69.6, 70.0, 71.1, 71.3 (OCH_2); 108.3; 111.4 (C-7); 113.8 (C-7b); 114.0; 115.9; 125.2 (C-3); 126.0; 127.3; 128.2; 128.4; 128.6; 128.7; 128.9; 129.9; 130.6; 134.7; 135.0; 137.2; 140.6 (C-6); 142.3 (C-2); 146,9; 147.3; 150.3 (C-7a); 151.2; 151.6 (C-3a) ppm. $C_{42}H_{41}ClN_2O_6S_2$ (769.35) calcd. C 65.58; H 5.37; N 3.64; S 8.32, found C 65.29; H 5.21; N 3.23; S 8.20.

4-(4-Chlorphenyl)-5-(4-methoxyphenyl)-2,3,7-triphenyl-thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 15a

51.6 %; m.p. 207–209°C; red powder. UV (ethanol): $\lambda_{(max)}$ (log ε) = 472.5 (3.58). MS(El, 70 eV) m/z (%): 625 (20) [M-H$^+$]; 626 (100) [M]; 627 (50); 628 (50); 629 (20); 630 (5). HR-MS (El, 70 eV): calcd. 626.1253; found 626.1243. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.83 (s, 3H, O-CH_3); 6.67 (2H, J_{AB} = 8.7 Hz; o/m H); 6.83 – 7.05 (m, 10H; arom H); 7.17 (m, 5H; arom H); 7.33 (2H, J_{AB}= 8.9 Hz; o/m H); 7.52 (2H, J_{AB} = 7.4 Hz; o/m H); 7.64 (2H, J_{AB} = 8.2 Hz; o/m H); 8.25 (s, 1H; 6-H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 56.0 (OCH_3); 113.0 (C-7); 115.4 (C-7b); 117.4; 122.8, 125.5; 125.9 (C-3); 127.2, 128.2, 128.3, 128.5, 128.7, 129.2, 129.4, 129.9; 130.5; 130.6, 134.5, 134.8, 135.8, 136.5; 140.0 (C-2); 142.8 (C-6);

146.6; 149.9 (C-7a); 152.4 (C-3a); 158.0 (C-OCH_3). $C_{38}H_{27}ClN_2OS_2$ (627.20) calcd. C 72.76; H 4.34; N 4.47; S 10.23, found C 72.41; H 4.21; N 4.23; S 10.51.

4-(4-Trifluormethylphenyl)-5-(4-methoxyphenyl)-2,3,7-triphenyl-thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 15b

31.7 %; m.p. 220–223°C; red powder. UV (ethanol): $\lambda_{(max)}$ (log ε) = 324.0 (4.14), 483.0 (4.13). MS(El, 70 eV) m/z (%): 659 (20) [M-H$^+$]; 660 (100) [M]; 661 (45); 662 (15); 663 (5). HR-MS (El, 70 eV): calcd. 660.1517; found 660.1539. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.83 (s, 3H; O-CH_3); 6.76 – 7.60 (m, 23H; arom H); 8.24 (s, 1H; 6-H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 56.0 (OCH_3); 113.8 (C-7); 115.3 (C-7b); 118.2; 123.0 (C-3); 123.6 (CF_3, $^1J_{C,F}$ = 115 Hz); 124.2, 125.2, 125.3, 125.4, 125.6, 127.3, 128.4, 128.5, 128.6, 128.8, 129.3, 130.0; 130.6, 134.5, 134.8, 135.5, 136.0; 142.9 (C-2); 144.9 (C-6); 146.8; 150.5 (C-7a); 152.7 (C-3a); 158.3 (C-OCH_3). $C_{39}H_{27}F_3N_2OS_2$ (660.8) calcd. C 70.89; H 4.12; N 4.24; S 9.71, found C 70.50; H 4.34; N 3.84; S 9.52.

4-(4-Chlorphenyl)-5-(benzo-1,4,7,10,13-pentaoxacyclopentadecano)-2,3,7-triphenyl-thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 15c

40.5 %; m.p. 252–256°C; red powder. MS(El, 70 eV) m/z (%): 785 (10) [M-H$^+$]; 786 (100) [M]; 787 (40); 788 (40); 789 (20); 790 (10). HR-MS (El, 70 eV): calcd. 786.1989; found 786.1988. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.76 (s, 8H; OCH_2); 3.91 (m, 4H; OCH_2); 4.15 (m, 4H; OCH_2); 6.67 (2H, J_{AB} = 8.5 Hz; o/m H); 6.84 – 7.00 (m, 10H; arom H); 7.17 (m, 5H; arom H); 7.49 – 7.61 (m, 5H; arom H); 8.24 (s, 1H; 6-H) ppm. $C_{45}H_{39}ClN_2O_5S_2$ (787.36) calcd. C 68.64; H 4.99; N 3.56; S 8.15, found C 68.54; H 5.12; N 3.41; S 8.01.

4-(4-Trifluormethylphenyl)-5-(benzo-1,4,7,10,13-pentaoxacyclopenta-decano)-2,3,7-triphenyl-thieno-[3,2-b][6aλ^4]-thia-1,6-diazapentalene 15d

19.5 %; m.p. 221–224°C; red powder. UV (ethanol): $\lambda_{(max)}$ (log ε) = 310.5 (3.34), 343.0 (3.24), 486.0 (3.38). MS(El, 70 eV) m/z (%): 819 (10) [M-H$^+$]; 820 (100) [M]; 821 (50); 822 (20); 823 (5). HR-MS (El, 70 eV): calcd. 820.2253; found 820.2256. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.76 (s, 8H; OCH_2); 3.92 (m, 4H; OCH_2); 4.14 (m, 4H; OCH_2); 6.77 – 6.99 (m,

10H; arom H); 7.13 – 7.18 (m, 7H; arom H); 7.50 – 7.61 (m, 5H; arom H); 8.24 (s, 1H; 6-H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 69.4, 69.5, 69.9, 70.1, 70.9, 71.0, 71.4, 71.5 (O-CH_2); 108.1 (CH); 113.9 (CH); 114.2 (C-7); 115.7 (C-7b); 118.2 (CH); 124.1 (C-3); 125.2, 125.3, 125.6; 126.2 (CF_3, $^1J_{C,F}$ = 140 Hz); 127.3, 128.4, 128.5, 128.7, 128.8, 129.3, 130.0, 130.5; 130.6, 134.6, 134.8, 135.4, 136.8; 142.7 (C-2); 144.9 (C-6); 146.9; 147.9; 150.4 (C-7a); 150.6; 152.6 (C-3a). $C_{46}H_{39}F_3N_2O_5S_2$ (820.95) calcd. C 67.22; H 4.79; N 3.41; S 7.81, found C 66.50; H 4.60; N 3.14; S 7.34.

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