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Meso – *Aryl* Heptaphyrins: The First 30π Aromatic Expanded Porphyrins with an Inverted Structure

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Supporting information

S1. Spectroscopic data (^{1}H NMR and Mass Spectra) for selected compounds.

S2. UV-Vis absorption data for Heptaphyrins.

S3. Electronic absorption spectra of **2b**, **3d** and **4b**.

S4. Cyclic voltammogram of **3b**, **3d** and **4d**.

S5. ^{1}H NMR spectra of **3a**, **3c** and **3d** in the aromatic region.

S6. Temperature dependent ^{1}H NMR spectra of inverted β-CH protons of **3d** in free base (a) and protonated (b) forms

S7. Temperature dependent ^{1}H NMR spectra of inverted β-CH protons of **3c** in free base (a) and protonated (b) forms

S8. Temperature dependent ^{1}H NMR spectrum of inverted β-CH protons of **3b** in its protonated form.

S9. ^{1}H NMR spectrum of protonated **4d** in CD_2Cl_2.

S10. FAB Mass spectrum of **2b**.

S11. FAB Mass spectrum of **3a**.

S12. FAB Mass spectrum of **3b**.

S13. ES Mass spectrum of **4b**.

S1: Spectroscopic data for selected compounds

2a: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = -3.33(d, J = 4.8Hz, 2H), -3.21(d, J = 5.2Hz, 2H), 2.05(s, 12H), 2.08(s, 12H), 2.12(s, 6H), 2.14(s, 6H), 7.4(s, 4H), 7.42(s, 4H), 9.49(d, J = 4.4Hz, 2H), 9.62(d, J = 4.4Hz, 2H), 01.37(d, J = 4.Hz, 2H), 10.59(d, J = 4.8Hz,,2H), 10.72(s, 2H). **ES-MS**: *m/z*(%): 1009 (100%) [$(M+1)^+$].

2b: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = -3.54(d, J = 4.8Hz, 2H), -3.4(d, J = 5.2Hz, 2H), 2.09(s, 12H), 2.11(s, 12H), 2.7(s, 6H), 2.73(s, 6H), 7.44(s, 4H), 7.47(s, 4H), 9.33(d, J = 3.6Hz, 2H), 9.53(d, J = 4.4Hz, 2H), 10.32(d, J = 3.6Hz, 2H), 10.52(d, J = 4.4Hz, 2H), 10.6(s, 2H). **MS (FAB)**: *m/z* (%) =1108(70)[$(M+2)^+$]

3a: Anal.cacld. For $C_{68}H_{58}S_5N_2$: C, 76.76; H, 5.49; N, 2.63, found C, 76.69, H, 5.52, N, 2.62%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.93(d, J = 4.4Hz, 1H), 10.78(d, J = 6Hz, 1H), 10.76(d, J = 4.4Hz, 1H), 10.5(d, J = 4Hz, 1H), 10.31(d, J = 5.2Hz, 1H), 9.69(d, J = 4.8Hz, 1H), 9.58(d, J = 4.4Hz, 1H), 9.5(d, J = 4.8Hz, 1H), 8.48(d, J = 4.8Hz, 1H), 8.45(d, J = 4.8Hz, 1H), 8.32(m, 2H), 7.48 – 7.37(m, 8H), -0.6(d, J = 5.2Hz, 1H), -1.7(d, J = 5.2Hz, 1H). **^{1}H NMR** (400 MHz, $CDCl_3$\TFA 243K): δ = 12.97(d, 3.6Hz, 1H), 12.82(d, J = 4Hz, 1H). 12.72(d, J = 4.4Hz, 1H), 12.37(d, J = 4Hz, 1H), 11.94(d, J = 4.4Hz, 1H), 11.46(d, J = 3.2Hz, 1H), 11.3(d, J = 3.6Hz, 1H), 11.07(d, J = 3.6Hz, 1H), 10.06(s, 1H), 10.02(s, 1H), 9.91(d, J = 4Hz, 2H), 7.75–7.72(m, 8H), -5.22(d, J = 4Hz, 1H), -5.39(d, J = 4Hz, 1H), -6.64(brs, 1H, NH), -7.08(brs, 1H, NH). **MS (FAB)**: *m/z* (%) = 1065(80)[$(M+1)^+$]

3b: Anal.cacld. For $C_{56}H_{34}N_2S_5$: C, 75.13; H, 3.82; N, 3.13, found C, 75.09; H, 3.85; N, 3.03%. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 10.87(d, *J* = 4Hz, 1H), 10.74(d, *J* = 4Hz, 1H), 10.71(d, *J* = 4Hz, 1H), 10.49(d, *J* = 4Hz, 1H), 10.36(d, *J* = 4Hz, 1H), 9.83(d, *J* = 4Hz, 1H), 9.75(d, *J* = 4Hz, 1H), 9.7(d, *J* = 4Hz, 1H), 8.71(d, *J* = 4Hz, 1H), 8.61(d, *J* = 4Hz, 1H), 8.52(d, *J* = 4Hz, 1H), 8.30(d, *J* = 4Hz, 1H), 7.86-8.0(m, 15H), 8.35-8.6(m, 5H), -1.12(d, *J* = 4Hz, 1H), -2.03(d, *J* = 4Hz, 1H). **^{1}H NMR** (300 MHz, $CDCl_3$\TFA 243K): δ = 12.39(d, *J* = 4Hz, 1H), 12.22(d, *J* = 4Hz, 1H), 12.13(s, 1H), 11.76(d, *J* = 4Hz, 1H), 11.28(d, *J* = 4Hz, 1H), 11.12(s, 1H), 11.03(d, *J* = 4Hz, 1H), 10.6(d, *J* = 4Hz, 1H), 9.7(d, 1H, 8Hz), 9.65(s, 2H), 9.56(d, *J* = 8Hz, 1H), 9.43(d, *J* = 8Hz, 1H), 9.04-8.89(m, 6H), 8.44-8.22(m, 13H), -3.83 (d, *J* = 4Hz, 1H), -4.16(d, *J* = 4Hz, 1H), -4.88(brs, 2NH). **MS (FAB)**: *m/z* (%) = 895(75)[M^+]

3c: Anal.cacld for $C_{56}H_{34}N_2S_3O_2$: C, 77.89; H, 3.97; N, 3.24, found C, 78.12; H, 3.95; N, 3.21%. **^{1}H NMR** (400 MHz, $CDCl_3$\TFA 228K): δ = 10.98(brs, 1H), 10.79(brs, 2H), 10.49(brs, 1H), 10.17(brs, 1H). 9.94(brs, 1H), 9.8(brs, 1H), 9.16(brs, 1H). 8.49(d, J = 7.2Hz, 2H), 7.98(d, J = 6.8Hz, 2H), 8.87(m, 6H), 8.35(m, 8H), 7.93(m 6H), -1.22(brs, 1H), -1.69(brs, 1H). **^{1}H NMR** (400 MHz, $CDCl_3$\TFA 253K): δ = 11.91(brs, 1H), 11.64(d, J = 4Hz, 1H), 11.02(d, J = 4.4Hz, 1H), 11.97(d, J = 4Hz, 1H), 10.58(d, J = 4.4Hz, 1H), 9.97(d, J = 4.8Hz, 1H), 9.52(d, J = 4.8Hz, 1H), 9.45(d, 5.2Hz, 1H), 9.35(m, 2H), 9.03(d, J = 7.2Hz, 2H), 8.71 – 8.65(m, 5H), 8.43 – 8.12(m, 15H), -2.95(brs, 1H, NH), -3.275(s, 2H), -3.77(brs, 1H, NH). **MS (FAB)**: *m/z* (%) = 863(100)[M^+].

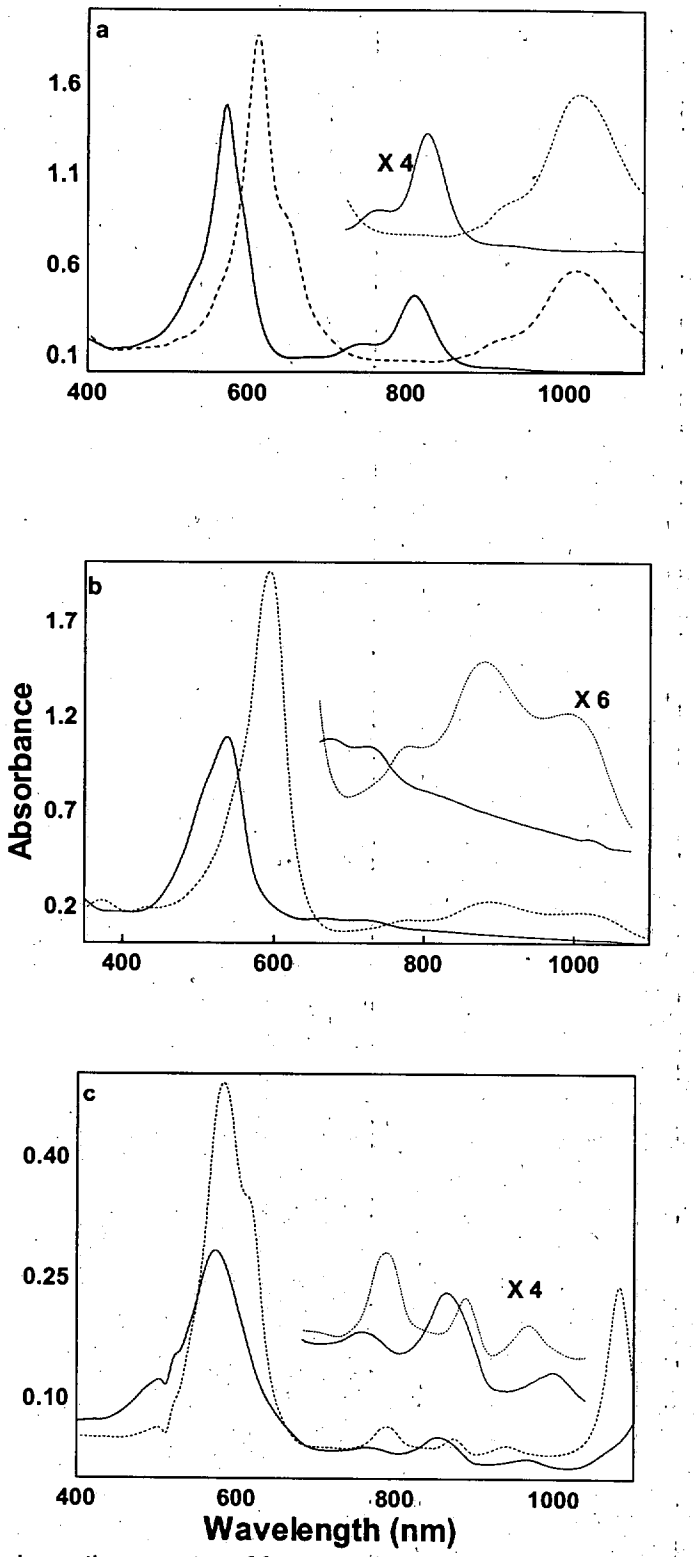
3d: Anal.cacld for $C_{56}H_{34}N_2S_3Se_2$: C, 67.95; H, 3,46; N, 2.83, found C, 68.01; H, 3.43; N, 2.79%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.2(d, *J* = 4Hz, 1H), 10.09(d, *J* = 4Hz, 1H), 10.07(d, *J* = 4Hz, 1H), 9.90(d, *J* = 4Hz, 1H), 9.78(d, *J* = 4Hz, 1H), 9.42(d, *J* = 4Hz, 1H), 9.30(d, *J* = 4Hz, 1H), 9.22(d, *J* = 4Hz, 1H), 8.34(d, *J* = 4Hz, 1H), 8.31(d, *J* = 4Hz, 1H), 8.23-8.19(m, 4h), 8.18(d, *J* = 4Hz, 1H), 8.14-8.12(m, 2H) 8.08(d, *J* = 4Hz, 1H), 7.7-7.9(m, 14H), 0.6(s, 1H), -0.65(s, 1H). **^{1}H NMR** (400 MHz, $CDCl_3$\TFA 243K): δ = 12.22(d, *J* = 4Hz, 1H), 12.09(d, *J* = 4Hz, 1H), 11.96(d, *J* = 4Hz, 1H), 11.66(d, *J* = 4Hz, 1H), 11.2(d, *J* = 4Hz, 1H), 11.04(d, *J* = 4Hz, 1H), 10.94(d, *J* = 4Hz, 1H), 10.79(d, *J* = 4Hz, 1H), 9.62(d, *J* = 4Hz, 1H), 9.54(d, *J* = 4Hz, 1H), 9.5(d, *J* = 4Hz, 1H), 9.48(d, *J* = 4Hz, 1H), 9.0-8.9(m, 6H), 8.4-8.3(m, 14H),
-3.39(d, *J* = 4Hz, 1H), -3.71(d, *J* = 4Hz, 1H), -4.2(brs, 1H), -4.52(brs, 1H). **MS (FAB)**: *m/z* (%) = 989(10)[M^+]

4b: Anal.cacld for $C_{56}H_{36}N_4S_2Se$: C, 74.07; H, 3.99; N, 6.17, found, C, 73.95; H, 4.02; N, 6.19%. **^{1}H NMR** (400 MHz, CD_2Cl_2 \ TFA): δ = 9.55-9.54(m, 4H), 9.15(d, J = 3.6Hz, 2H), 8.54(s, 4H), 8.4(brs, 2H), 8.2(d, 6.4Hz, 4H), 8.04-8.02(m, 6H), 7.84-7.8(m, 6H), 7.32(brs, 2H), 6.94(brs, 2H), 2.3(s, 2H), 2.042(s, 2H, NH), 0.52(s, 2H). **ES-MS**: *m/z* (%): 909(100)[$(M+1)^+$].

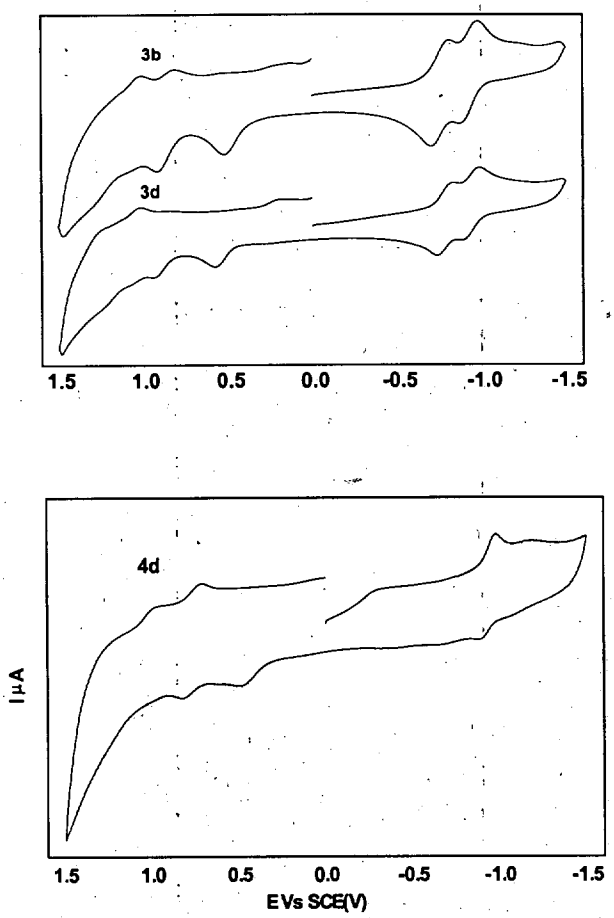
4d: Anal.cacld for $C_{56}H_{36}N_4Se_3$: C, 67.14, H, 3.62; N, 5.59, found, C, 67.76; H, 3.47; N, 5.55%. **^{1}H NMR** (400 MHz, CD_2Cl_2 \ TFA): δ = 10.17-10.14(m, 4H), 9.63(d, J = 4Hz, 2H), 9.18(brs, 2H), 9.07(d, J = 4Hz, 2H), 8.89-8.8(m, 4H), 8.74(brs, 2H), 8.51(d, J = 6.8Hz, 4H), 8.18-8.16(m 6H), 8.01-7.93(m, 6H), 0.02(s, 2H, NH), -0.47(s, 2H, NH), -1.62(s, 2H). **ES-MS**: *m/z*(%): 1003(100)[$(M+2)^+$]

S2: UV-Vis absorption data for the heptaphyrins 2-4 in Dichloromethane

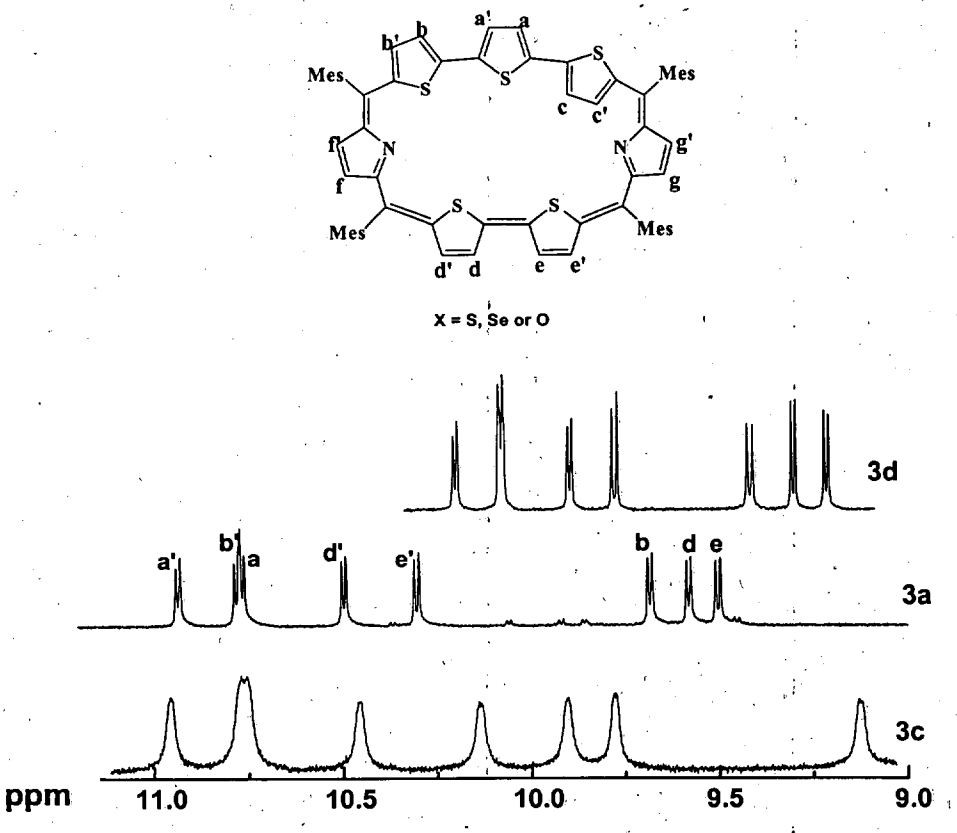
	Soret λ_{nm} (ε x 10^4 $M^{-1}cm^{-1}$)		Q-Bands λ_{nm} (ε x 10^3 $M^{-1}cm^{-1}$)	
	Free Base	Dication	Free Base	Dication
2a	571(0.157)	577 (0.354)	740(0.028), 808(0.024), 950(0.014), 1058(0.016). 1100(0.025)	777(0.056), 859(0.041), 925(0.03), 1068(0.143)
2b	572(0.077)	582 (0.135), 614sh (0.093)	764(0.01), 854(0.014), 965(0.006),1100(0.019)	790(0.017), 873(0.013), 941(0.011), 1082(0.065)
3a	565 (33.2), 590sh(21.2)	602(28.4)	742(0.87), 813(3.8), 938(0.4)	645(5.2), 672(5.2), 924(1.9), 998(2.9), 1037(2.9).
3b	567(30.7) 594sh(20.38)	598(37.12)	757(2.7), 826(10.42), 945(2), 1090(2.5)	639(15.01), 914(3.27), 1014(12.7)
3c	586(12.09), 586(sh, 8.8)	595(9.4)	822(3.77), 928(0.6), 1026(0.5)	646(6.4), 911(br, 2.35), 992(3.33), 1025(3.37).
3d	574(11.71)	612(14.9)	747(1.2), 810(3.5), 916(0.2)	925(1.5), 1014(4.48)
4b	538(9)	594(16.25)	660(0.013), 720(0.012), 797(0.007), 1037(0.002)	781(0.012), 889(0.002), 1007(0.016).
4d	552(9.9)	598(19.26)	674(0.013), 727(0.009), 828(0.006), 993(0.004)	789(0.19), 884(0.014), 1066(0.02)



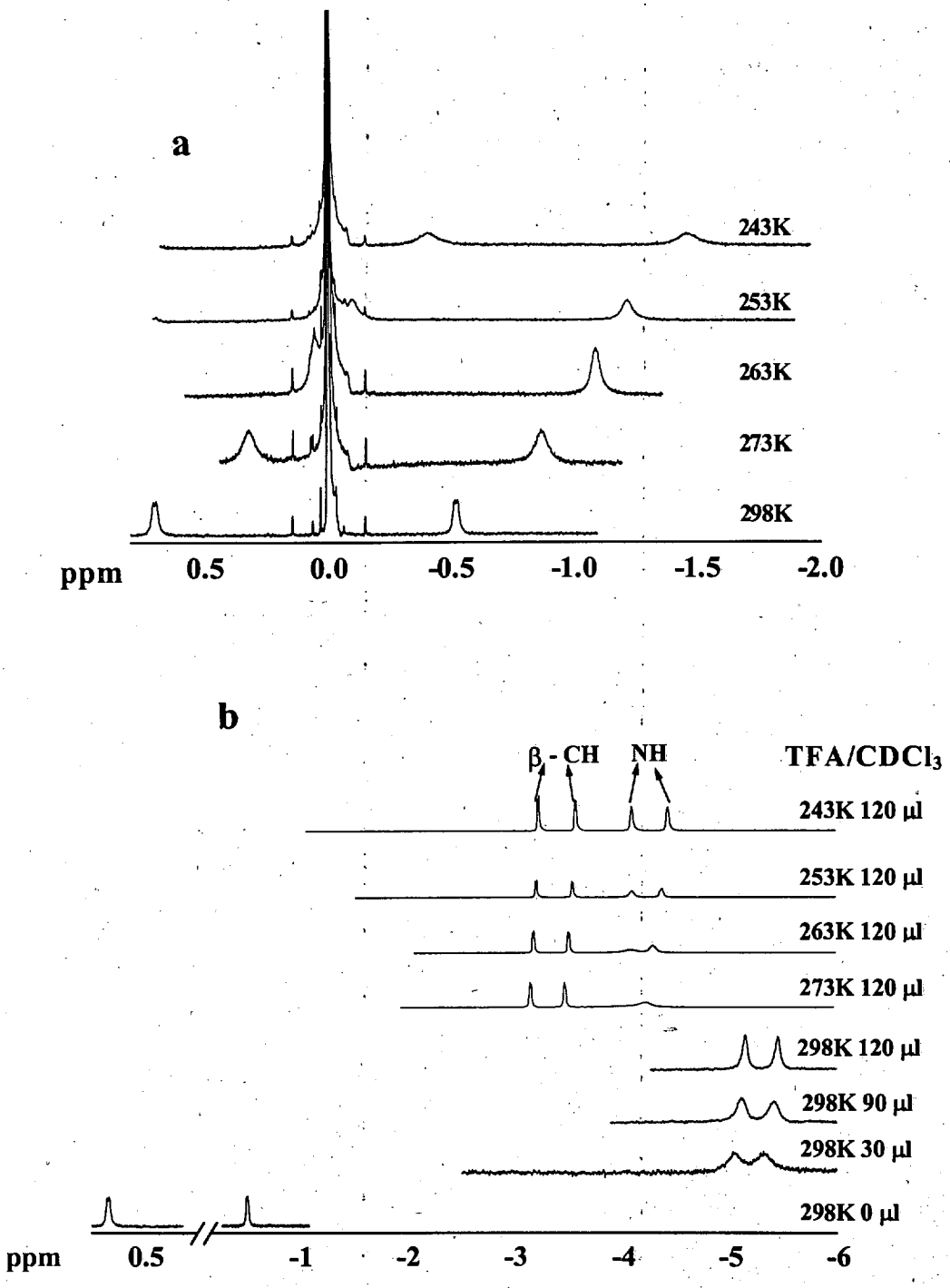
S3: Electronic absorption spectra of freebase (—) and diprotonated (.....) forms of **3d**(a), **4b**(b) and **2b**(c) in dichloromethane.



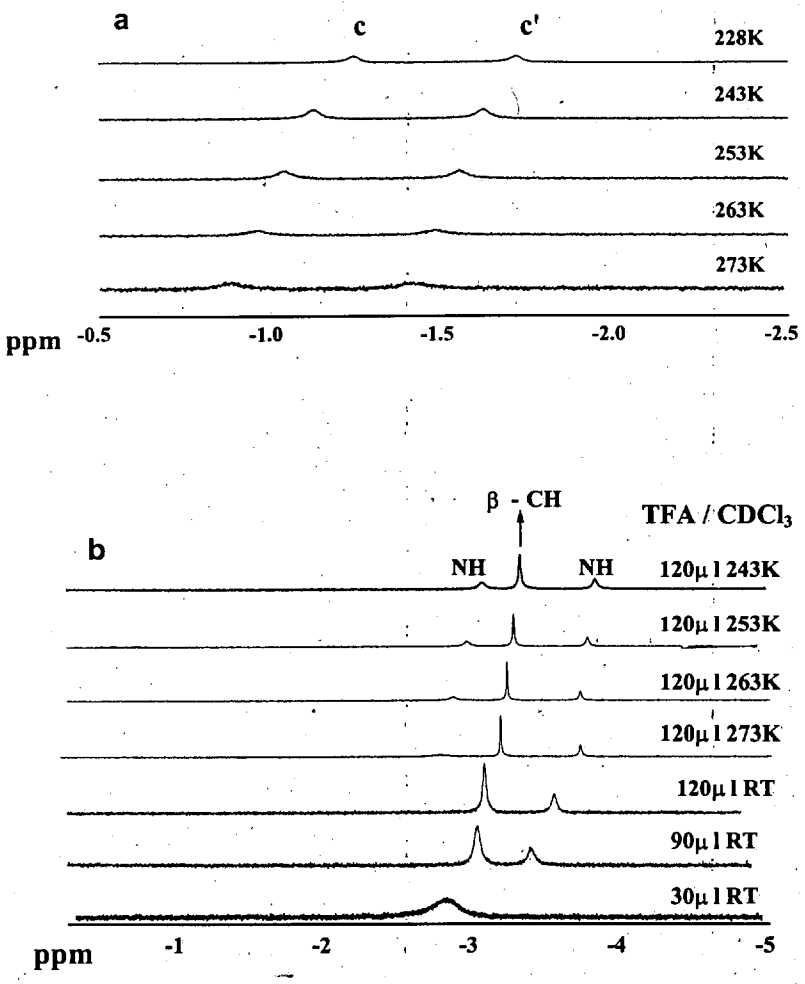
S4: Cyclic Voltammogram of **3b**, **3d** and **4d** in CH_2Cl_2 containing $TBAPF_6$ (0.01M) recorded at 100mVs^{-1}. The concentrations of the heptaphyrins were ~10^{-3}M



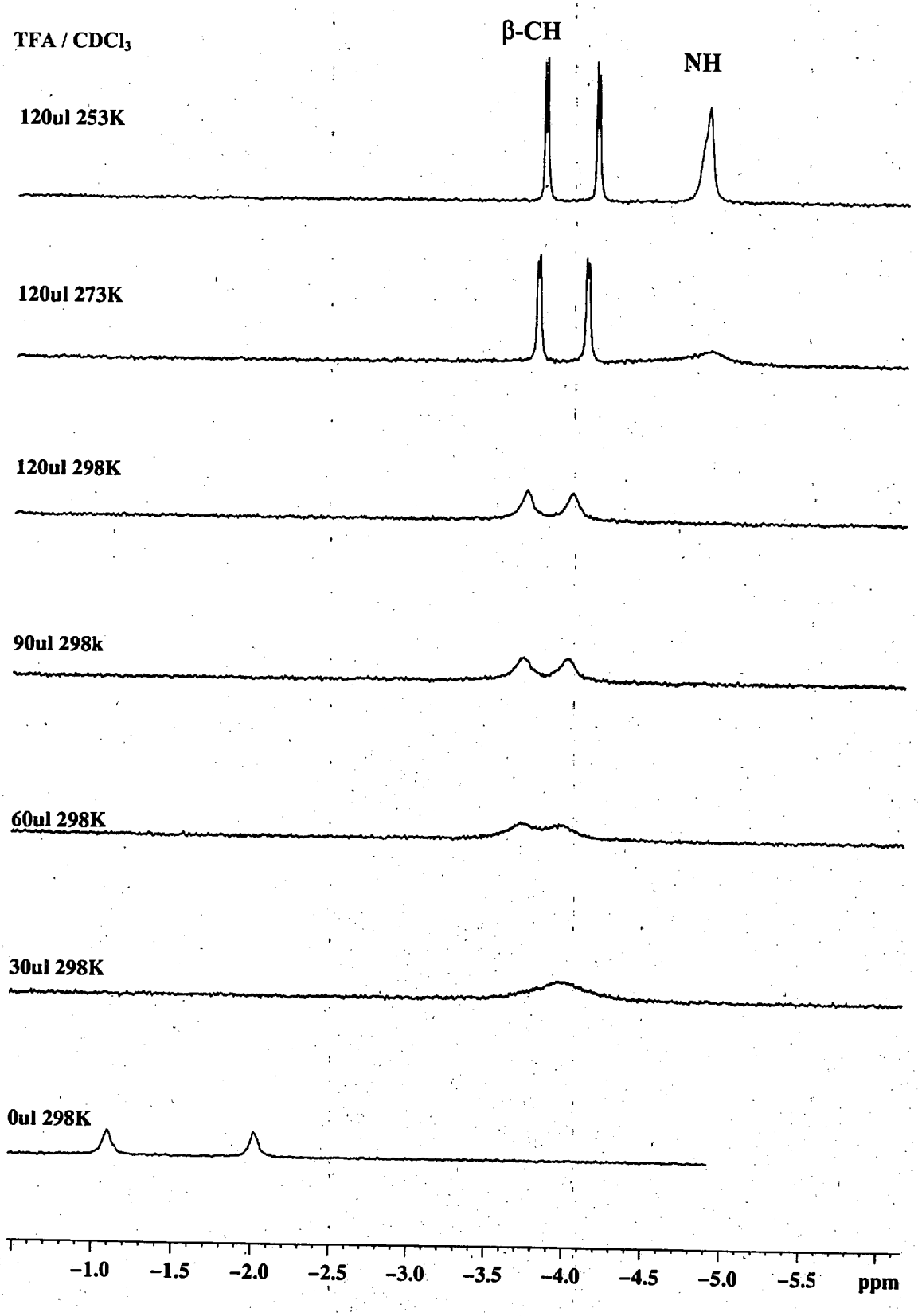
S5: ^{1}H NMR spectra of **3a**, **3c** and **3d** in the aromatic region in $CDCl_3$.



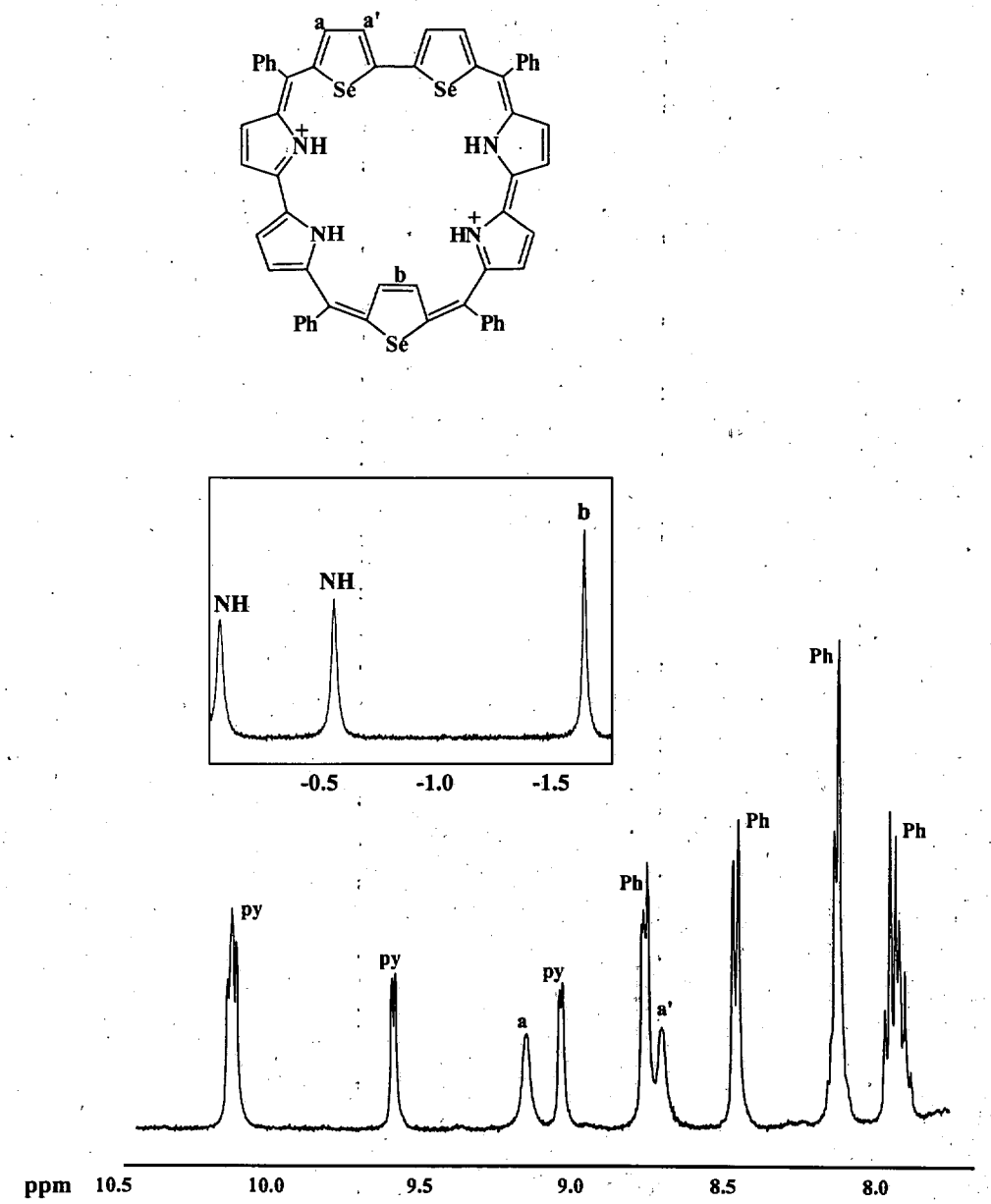
S6: Temperature dependent ^{1}H NMR spectra of inverted β-CH protons of **3d** in (a) freebase and (b) protonated form in $CDCl_3$.



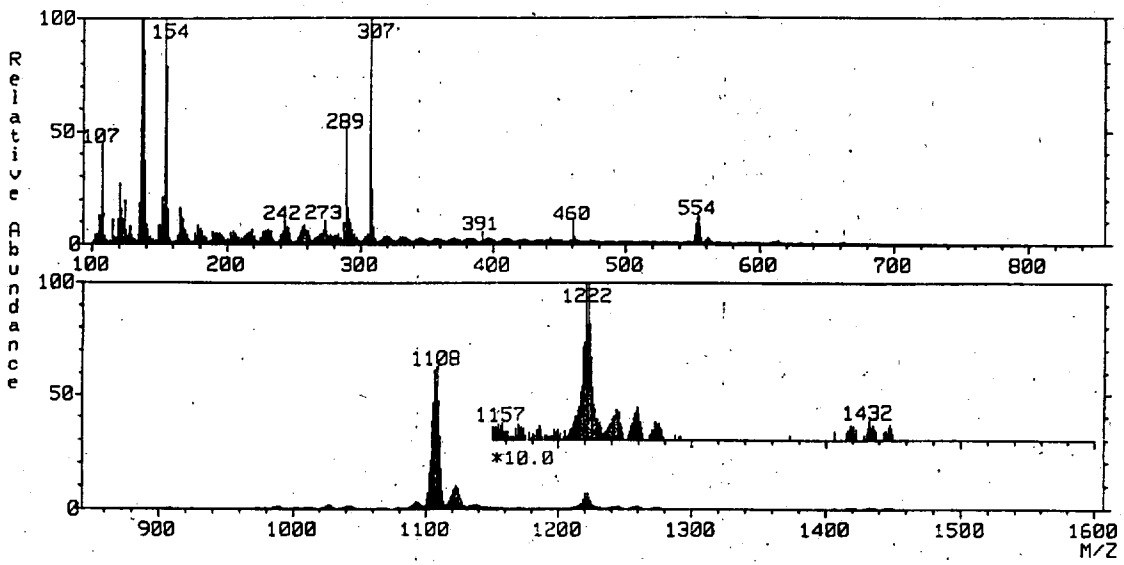
S7: Temperature dependent ^{1}H NMR spectra of inverted β-CH protons of **3c** in (a) freebase and (b) protonated form in $CDCl_3$.



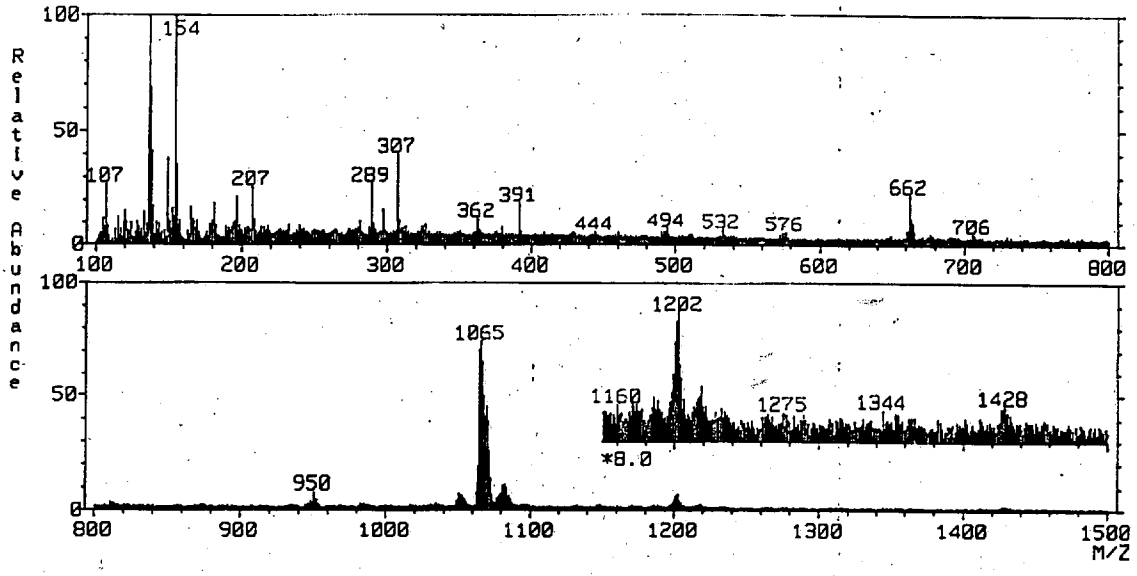
S8: Temperature dependent ^{1}H NMR spectrum of inverted β-CH protons of **3b** in protonated form in $CDCl_3$.



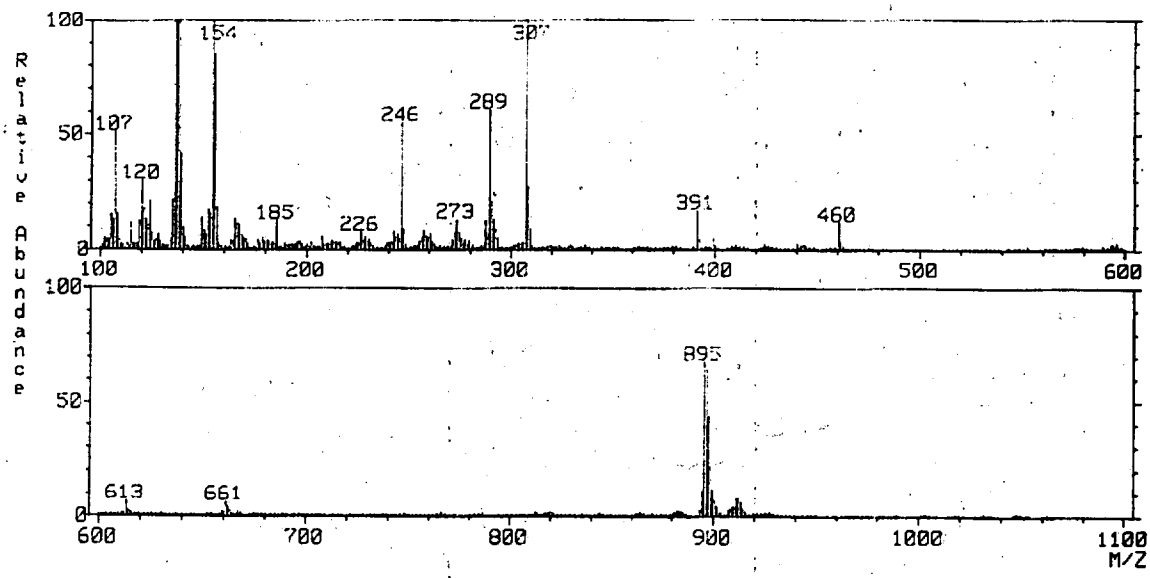
S9: ^{1}H NMR spectrum of protonated **4d** in CD_2Cl_2 : py = pyrrole protons



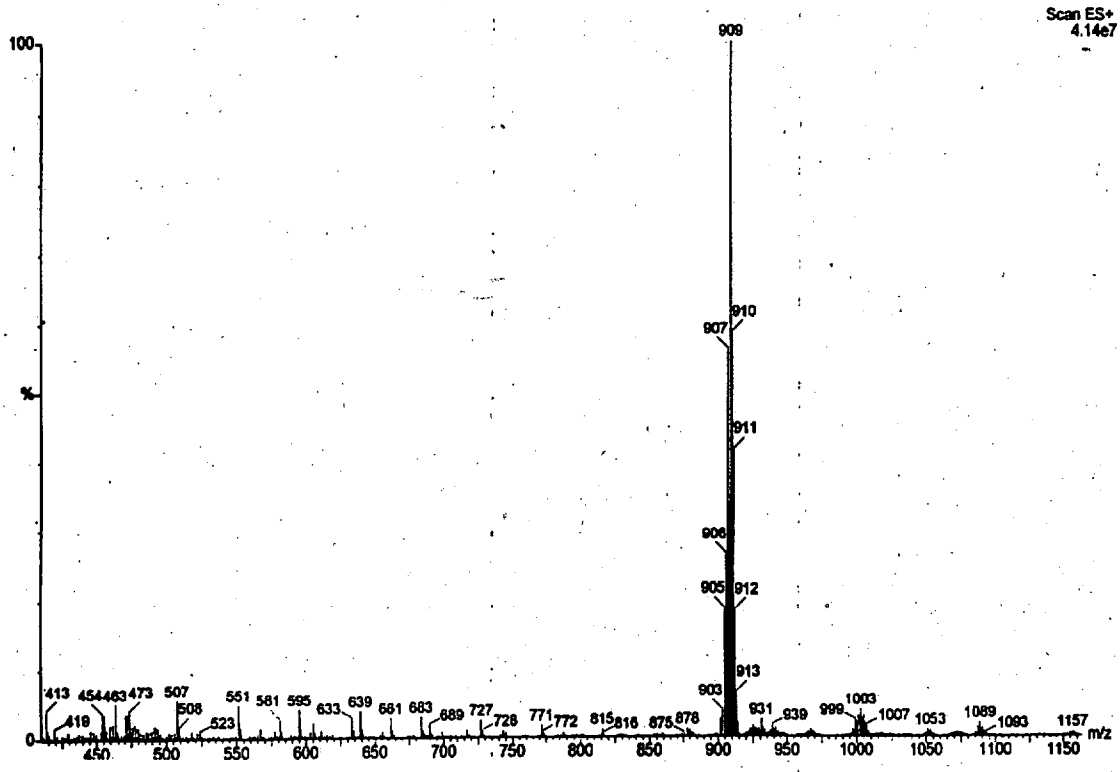
S10-FAB Mass Spectrum of **2b.**



S11- FAB Mass spectrum of **3a**



S12- FAB Mass spectrum of **3b**.



S13- ES Mass spectrum of **4b**.