Supplementary Material for:

π-Conjugated Macrocycles From Thiophenes and Benzenes

J. Sreedhar Reddy[a] and Venkataramanarao G. Anand[b]

[a]Chemical Sciences & Technology Division,
National Institute for Interdisciplinary Science & Technology, NIST (Formerly RRL Trivandrum) CSIR, Trivandrum-695019,
India.

[b]Department of Chemistry,
Indian Institute of Science Education & Research, (IISER)
900, NCL Innovation Park, Dr. Homi Bhabha Road,
Pune - 411 008. Fax: +91-20-25898022; Tel: +91-20-25898021; India.
E-mail: vg.anand@iiserpune.ac.in

General notes and procedure:

^{1}H NMR spectra were recorded on a 300 MHz Bruker Advance DPX spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent ($CHCl_3$, s, δ, 7.26). Mass spectroscopic analysis was carried out on JEOL JMS 600H spectrometer. Electronic spectra were recorded on a Perkin-Elmer Lambda 20 spectrophotometer. Chromatographic separations were performed on basic alumina and silica gel (100-200) in glass columns.

Single Crystal Structure Determination: The single crystal X-ray diffraction data were collected on a Bruker AXS Kappa Apex 2 CCD diffractometer at 173(2) K.

References:

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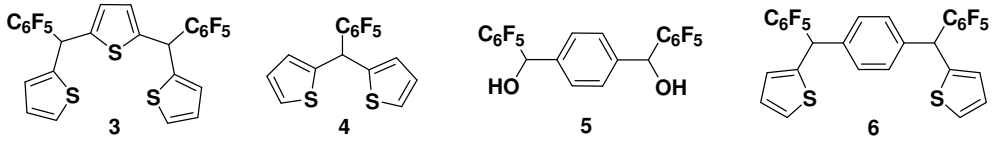
Synthesis & Spectral data for **1,2,3 & 6**

Thiophene and all aldehydes were purchased from Sigma-Aldrich and used as such. Synthesis was carried out under an inert atmosphere using standard Schlenk line techniques. Dry CH_2Cl_2 was used throughout. All other reagents were used as received unless otherwise specified.

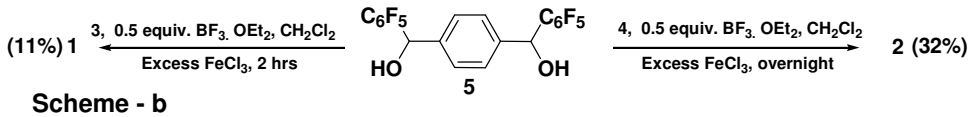
Synthetic Procedure for 1:

A solution of1,4 – bis(pentafluorophenylhydroxy methyl) benzene, **5,** (235 mg, 0.5 mmol) and 2,5-bis((pentafluorophenyl)(thiophen-2yl)methyl)thiophene, **3,** (304 mg, 0.5 mmol) in 100 ml of dry dichloromethane was placed in 250 ml flask under nitrogen. $BF_3.OEt_2$ (0.03 ml, 0.25 mmol) was added under dark, and the resulting solution was stirred for 2h. After adding excess $FeCl_3$, solution was opened to air and stirred for 2 more hrs. The reaction mixture was washed with water and passed through a short alumina column. This mixture was separated by silica gel column chromatography by using CH_2Cl_2/n-hexane as eluant. Light pink color fraction was obtained; it was repeatedly purified by silica gel column chromatography by using 5% CH_2Cl_2 in n-hexane as eluant. (Scheme – a)

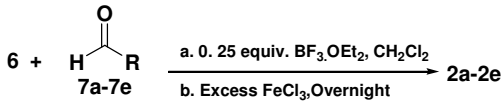
^{1}H NMR (300MHz, $CDCl_3$, 298K): $\delta = 7.53$ (s, 4H), $\delta = 6.69$ (d, J= 6.0Hz, 2H), $\delta = 6.59$ (d, J= 6.0Hz, 2H), $\delta = 6.47$ (s, 2H); **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 398$ (4.3 x 10^4), 543 (0.6 x 10^4), 569(0.6 x 10^4); **FAB MS** m/z: Calcd For $C_{46}H_{10}F_{20}S_3$ 1038.74; Observed 1040 (100.0%, M +1).



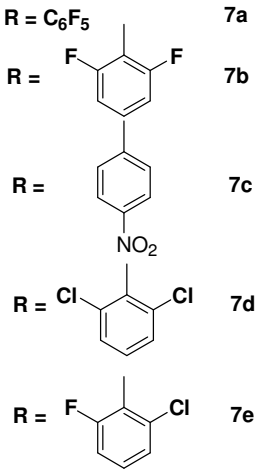
Scheme - a



Scheme - b



Yield (%)
2a = 36, 2b = 31
2c = 10, 2d = 24
2e = 26



Synthetic Procedure for 2: (Scheme – a)

A solution of 5-pentafluorophenyldithienylmethane, **4**, (173 mg, 0.5 mmol) and 1,4–bis (pentafluorophenylhydroxy methyl)benzene, **5,** (235 mg, 0.5 mmol) in 100 ml of dry dichloromethane was placed in 250 ml flask under nitrogen. $BF_3.OEt_2$ (0.03 ml, 0.25 mmol) was added under dark, and the resulting solution was stirred for 2h. After adding excess $FeCl_3$, solution was opened to air and stirred for overnight (12 hrs). The reaction mixture was washed with water and passed through a short alumina column. This mixture was separated by silica gel column chromatography by using CH_2Cl_2/n-hexane as eluant. Pink color fraction was obtained; it was repeatedly purified by silica gel column chromatography by using 10% CH_2Cl_2 in n-hexane as eluant.

Synthetic Procedure for 2: (Scheme – b)

A solution of aldehyde (**7a–e**) (0.25 mmol) and 1,4-bis((pentafluorophenyl)(thiophen-2-yl)methyl)benzene (150.5 mg, 0.25 mmol) in 100 ml of dry dichloromethane was placed in 250 ml flask under nitrogen. $BF_3.OEt_2$ (0.008 ml, 0.0625 mmol) was added under dark, and the resulting solution was stirred for 2h. After adding excess $FeCl_3$, solution was opened to air and stirred for overnight (12hrs). The reaction mixture was washed with water and passed through a short alumina column. This mixture was separated by silica gel column chromatography by using CH_2Cl_2/n-hexane as eluant. Pink color fraction was obtained; it was repeatedly purified by silica gel column chromatography by using 10% CH_2Cl_2 in n-hexane as eluant.

2a: ^{1}**H NMR** (300MHz, $CDCl_3$, 298K): $\delta = 8.82$ (d, J=4.8Hz, 4H), $\delta = 8.76$ (d, J=5.4Hz, 4H), $\delta = 4.74$ (s,8H) ; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 520(30.2 \times 10^4)$, $540(30.8 \times 10^4)$, $613(4.8 \times 10^4)$, $664(6.8 \times 10^4)$, $721(13.1 \times 10^4)$; **FAB MS** m/z: Calcd for $C_{70}H_{16}F_{30}S_4$ 1553.97; Observed 1555(100.0%, M+1).

2b: ^{1}**H NMR** (300MHz, $CDCl_3$, 298K): $\delta = 9.0$ (d, J=5.4Hz, 4H), $\delta = 8.9$ (d, J=4.8Hz, 4H), $\delta = 7.88$ (m, 2H), $\delta = 7.48$ (m, 4H), $\delta = 4.53$ (s,8H) ; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 521(19.9 \times 10^4)$, $541(20.7 \times 10^4)$, $614(1.3 \times 10^4)$, $666(2 \times 10^4)$, $722(4.2 \times 10^4)$; **FAB MS** m/z: Calcd for $C_{70}H_{22}F_{24}S_4$ 1447.15; Observed 1448(100.0%, M+1).

2c: ^{1}**H NMR** (300MHz, $CDCl_3$, 298K): $\delta = 8.73$ (m, 12H), $\delta = 8.40$ (d, J=8.4Hz, 4H), $\delta = 4.72$ (s,8H) ; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 529(17.7 \times 10^4)$, $543(19.2 \times 10^4)$, $727(3.9 \times 10^4)$; **FAB MS** m/z: Calcd for $C_{70}H_{24}F_{20}N_2O_4S_4$ 1465.18; Observed 1466 (100.0%, M+1).

2d: ^{1}**H NMR** (300MHz, $CDCl_3$, 298K): $\delta = 9.0$ (d, J=5.4Hz, 4H), $\delta = 8.9$ (d, J=4.8Hz, 4H), $\delta = 7.90$ (d, J= 8.4Hz, 4H), $\delta = 7.79$ (m, 2H), $\delta = 4.51$ (s, 8H) ; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 524(17.6 \times 10^4)$, $543(20 \times 10^4)$, $725(4.1 \times 10^4)$; **FAB MS** m/z: Calcd for $C_{70}H_{22}Cl_4F_{20}S_4$ 1510.90; Observed 1512 (100.0%, M+1).

2e: ^{1}**H NMR** (300MHz, $CDCl_3$, 298K): $\delta = 9.0$ (d, J=4.5Hz, 4H), $\delta = 8.9$ (d, J=5.4Hz, 4H), $\delta = 7.81$ (m, 4H), δ =7.60 (m, 2H),$\delta = 4.50$ (s,8H) ; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 522(17.1 x 10^4), 542(17.8 x 10^4), 724(3.6 x 10^4); **FAB MS** m/z: Calcd. for $C_{70}H_2Cl_2F_{22}S_4$ 1480.05; Observed 1481(100.0%, M+1).

Synthetic procedure for 3(2,5-bis((pentafluorophenyl)(thiophen-2yl)methyl)thiophene)**:**

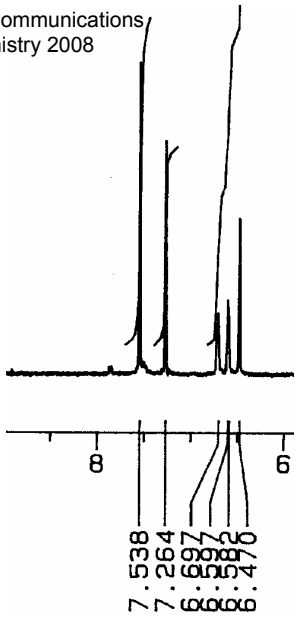
A mixture of 2, 5-(pentafluourophenylhydroxy methyl) thiophene (238 mg, 0.5 mmol) and thiophene (3.0 ml, 37 mmol) was degassed with argon for 10 min, then $BF_3.O(Et)_2$ (0.06 ml, 0.5 mmol) was added. The resulting solution was stirred at room temperature and the progress of the reaction was carefully monitored by TLC (~ 30 min), the mixture was poured in to CH_2Cl_2 (50 ml) and washed with aqueous NaOH (0.1 N).The organic layer was washed with water and dried ($MgSO_4$). The excess thiophene and solvent was removed in vacuum and resulting solid was chromatographed on silica (1%EtOAc in hexane) the desired product obtained as light yellow solid. Yield 216 mg (71%).

^{1}**H NMR** (300MHz, $CDCl_3$, 298K): $\delta = 7.23$ (m, 2H), δ =6.94 (m, 4H), $\delta = 6.78$(s, 2H), $\delta = 6.15$ (s,2H). **FAB MS** m/z: Calcd for $C_{26}H_{10}F_{10}S_3$ 607.98; Observed 608.1(20.0%, M+1).

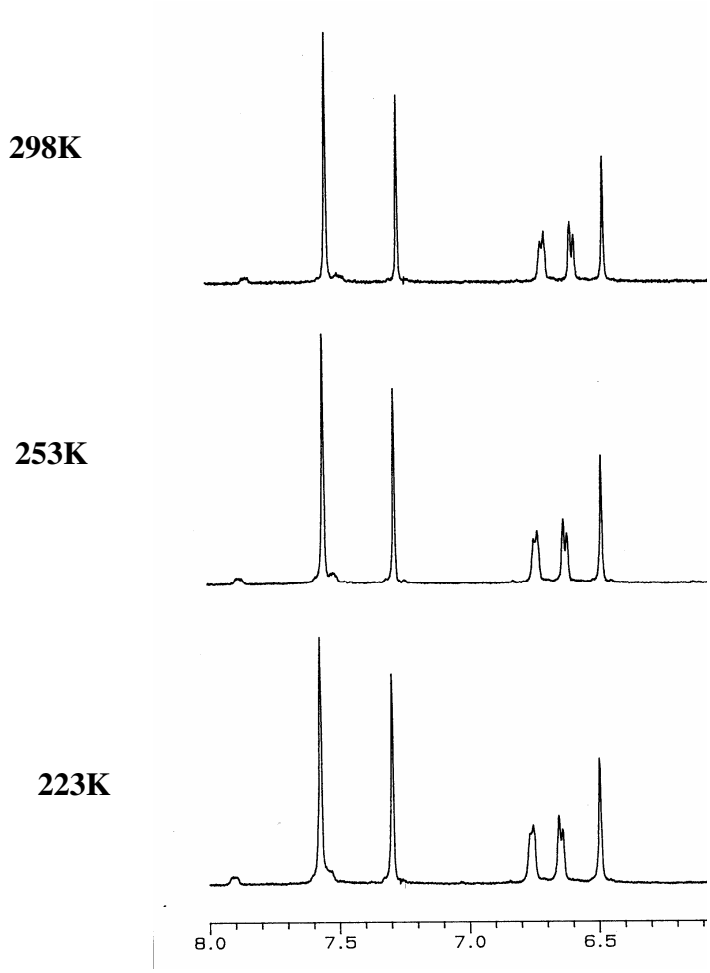
Synthetic procedure for 6 (1,4 -bis((pentafluorophenyl)(thiophen-2-yl)methyl)benzene)**:**

A mixture of 1,4 – bis (perfluorophenylhydroxymethyl)benzene(235 mg, 0.5 mmol) and thiophene (3.0 ml, 37 mmol)was degassed with argon for 10min, then $BF_3.O(Et)_2$ (0.06 ml, 0.5 mmol)was added. The resulting solution was stirred at room temperature and the progress of the reaction was carefully monitored by TLC (~ 30 min), the mixture was poured in to CH_2Cl_2 (50 ml) and washed with aqueous NaOH (0.1N).The organic layer was washed with water and dried ($MgSO_4$). The excess thiophene and solvent was removed in vacuum and resulting solid was chromatographed on silica (1% EtOAc in hexane) the desired product obtained as white solid. Yield 185 mg (61%).

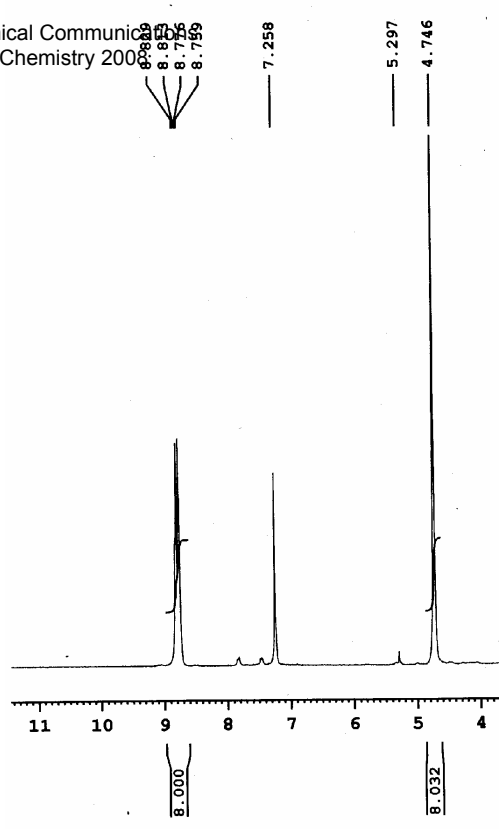
^{1}**H NMR** (300MHz, $CDCl_3$, 298K): $\delta = 7.23$ (m, Phenyl 4H and thiophene -2H), δ =6.95 (m, thiophene – 2H), $\delta = 6.78$(d, J=3Hz, thiophene α–2H) $\delta = 6.01$ (s, *meso* - 2H). **FAB MS** m/z: Calcd for $C_{28}H_{12}F_{10}S_2$ 602.02; Observed 601.04(20.0%, M-1$^+$).



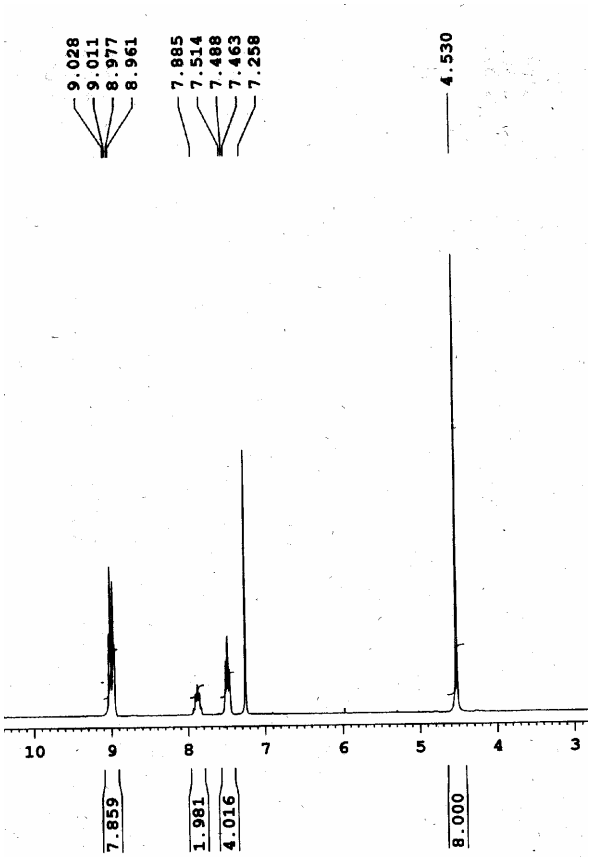
^{1}H NMR Spectrum of 1 in $CDCl_3$ at 298K



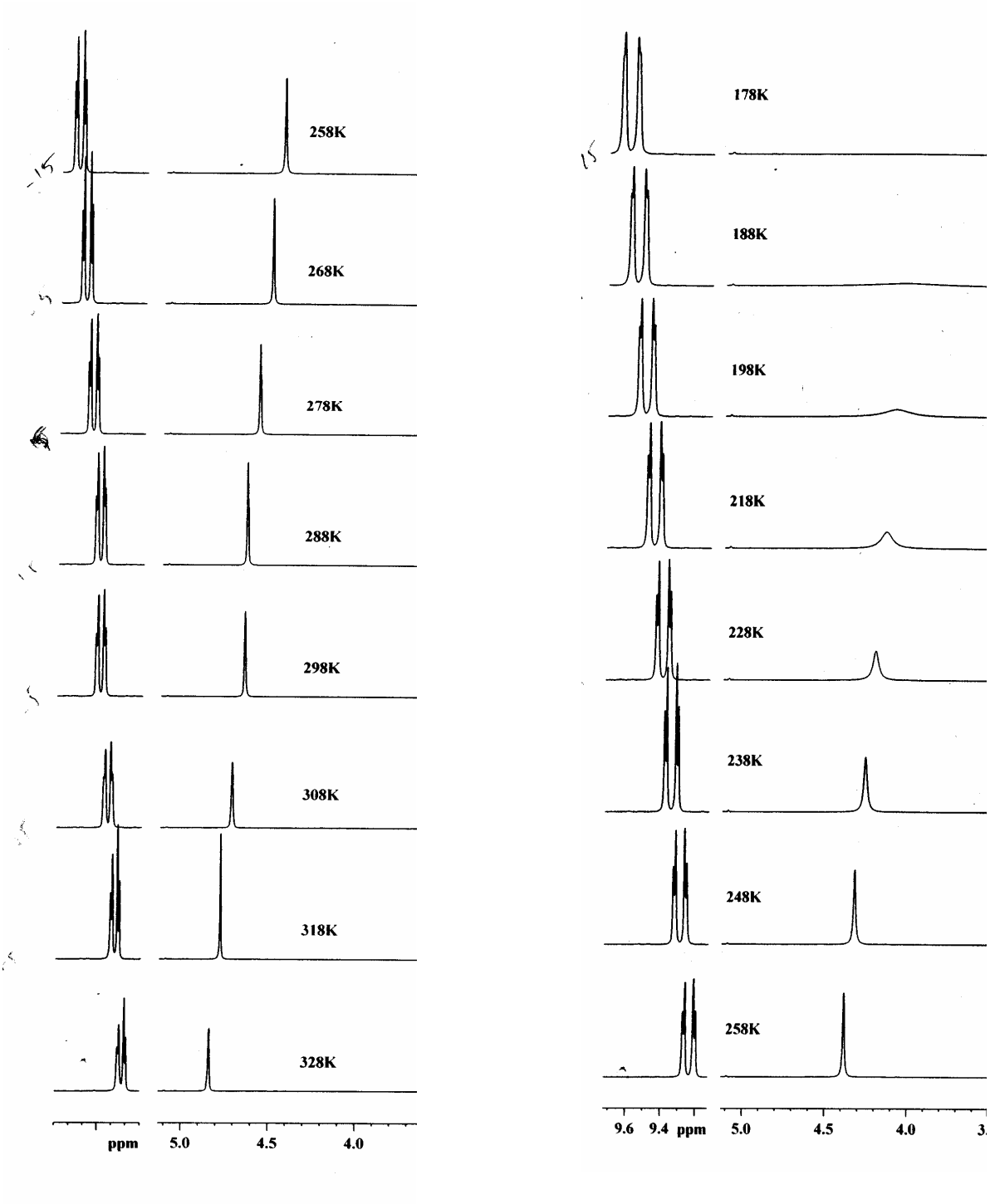
Variable temperature ^{1}H NMR Spectrum of 1 in $CDCl_3$



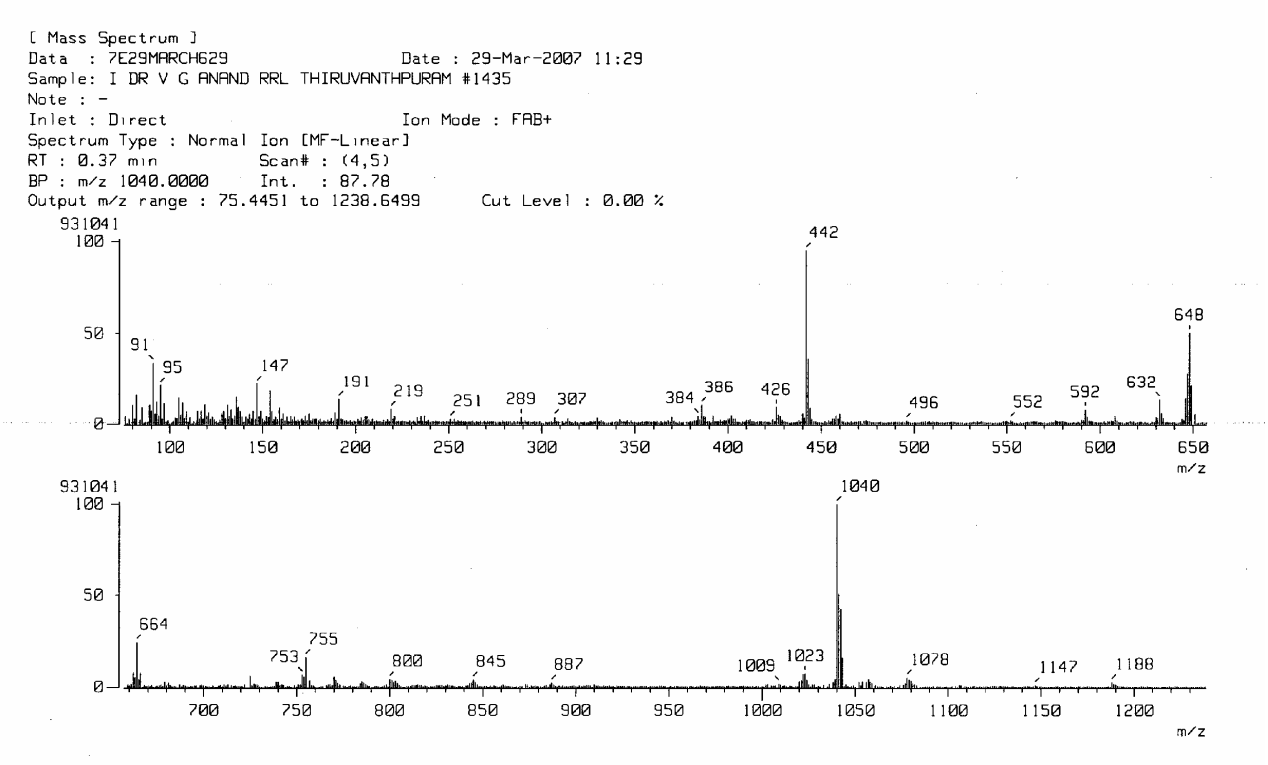
^{1}H NMR Spectrum of 2a in $CDCl_3$:



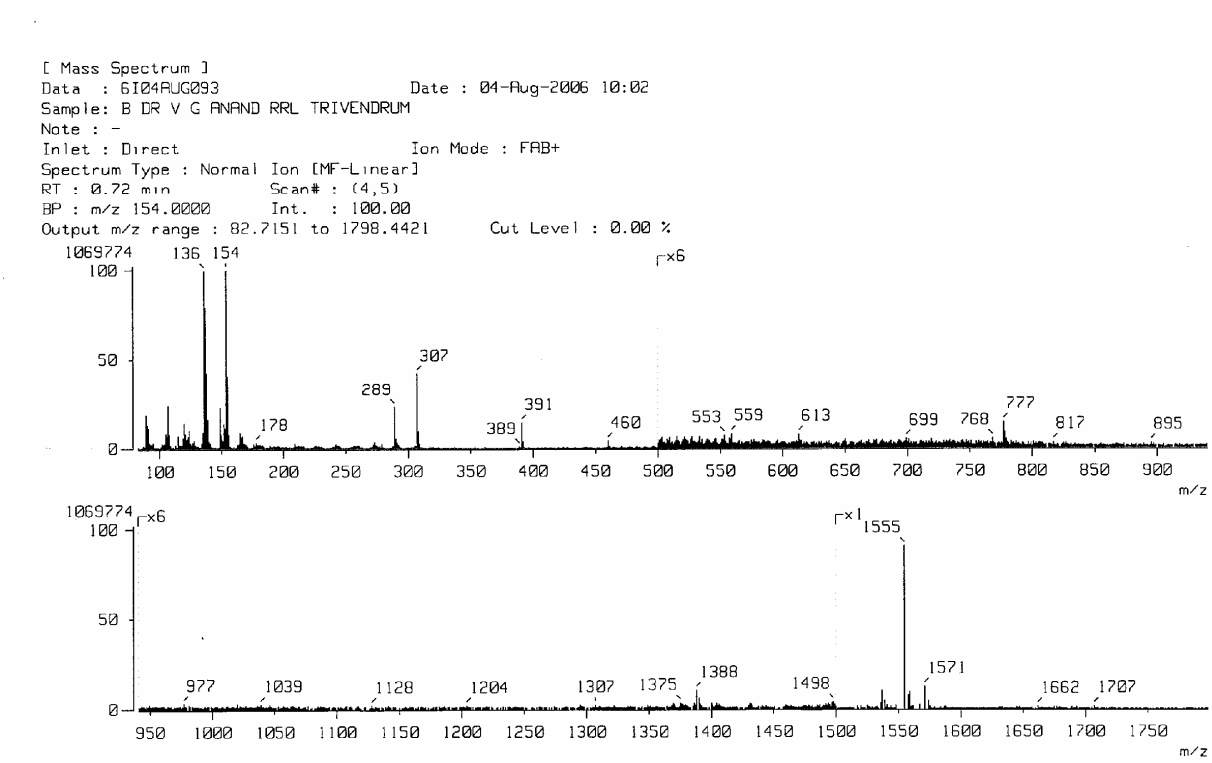
^{1}H NMR Spectrum of 2b in $CDCl_3$:



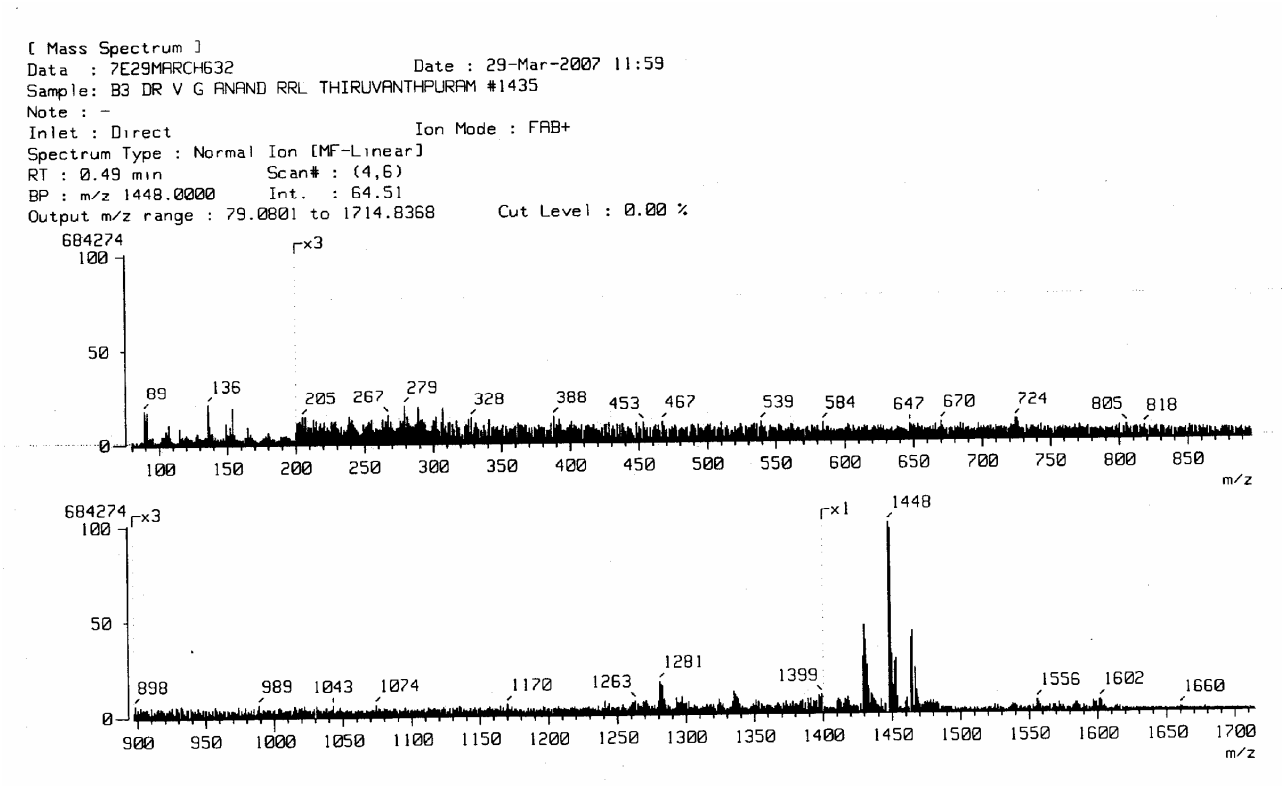
Variable temperature ^{1}H NMR Spectrum of 2a in CD_2Cl_2:



FAB Mass spectrum of 1

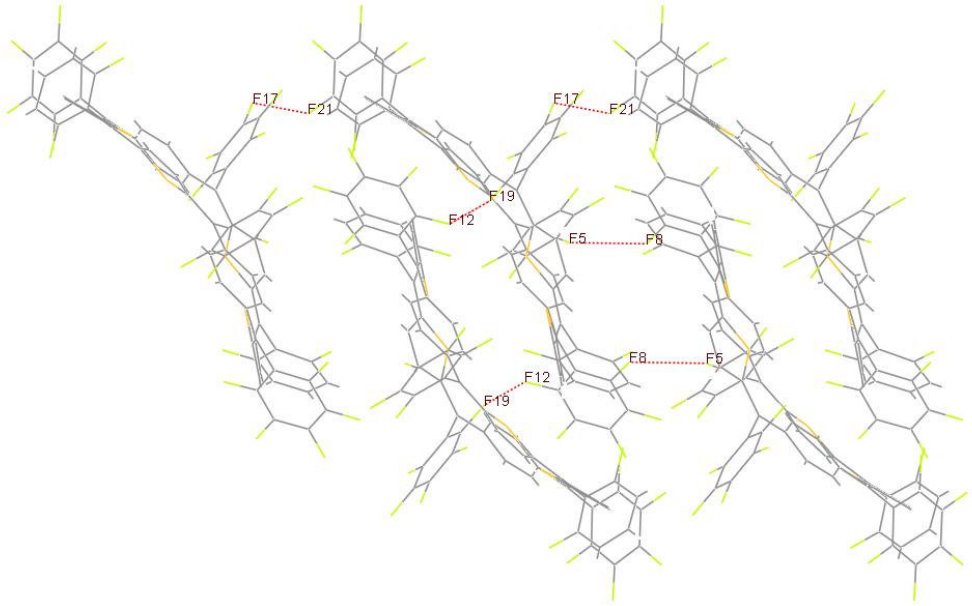


FAB Mass spectrum of 2a



FAB Mass spectrum of 2b

F…F Non –bonded interactions in 2b



F19…F12 (2.813Å); F17…F21 (2.697Å); F8…F5 (2.829Å).