Supporting Information

A green protocol for the synthesis of conformationally rigid sulfur linked bisquinolines by double Friedlander reaction in water

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Experimental

General

All melting points reported in this work were measured in open capillaries. The ^{1}H, ^{13}C NMR and 2D NMR spectra have been measured at 300 and 75 MHz respectively using Bruker 300 MHz (Avance) instrument in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Chemical shifts are reported as δ values (ppm). For compounds **5a-e**, all the carbon signals are not picked up. All one- and two-dimensional NMR spectra were obtained using standard Bruker software throughout. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of petroleum ether (60–80 ^{o}C) and ethyl acetate as eluent. Elemental analyses were performed on a Perkin Elmer 2400 Series II Elemental CHNS analyzer. IR spectra were recorded on a JASCO FT IR instrument (KBr pellet method).

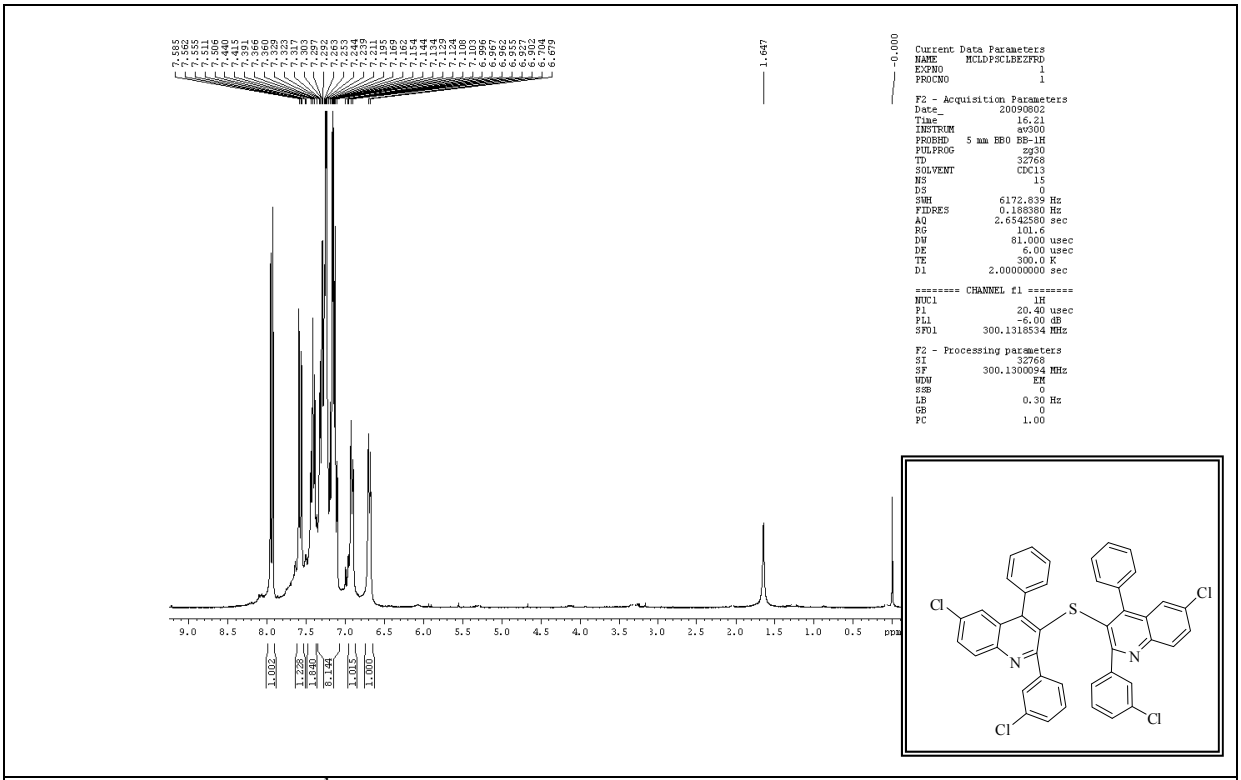
Crystallographic Investigations

Crystals suitable for X-ray crystallographic studies were obtained by crystallization from 1:1 mixture of dichloromethane and DMF. Crystallographic data for compounds **3h**, **3c** and **5e** are given in table below.

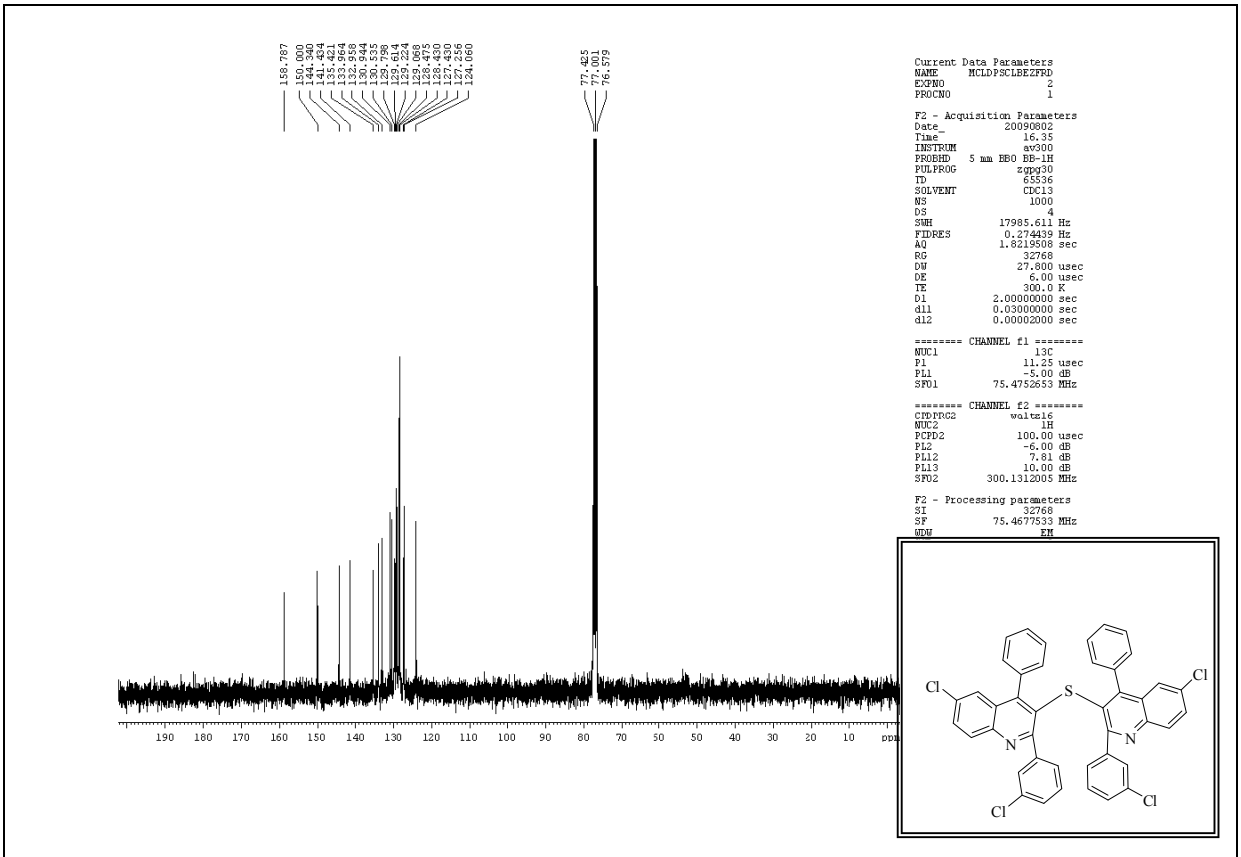
Compound	**3h**	**3c**	**5e**
Empirical formula	C_{42} H_{26} Cl_2 N_2 S	C_{42} H_{26} Cl_2 N_2 S	C_{42} H_{24} Cl_4 N_2 S_2
Formula weight	661.62	661.62	762.55
Temperature	110(2) K	100(2) K	110(2) K
Wavelength	1.54178 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/n	P-1	P-1
Unit cell dimensions	a = 20.036(3) Å; α= 90°; b = 8.2313(13) Å; β=115.113(8)°; c = 21.197(5) Å; γ = 90°.	a = 11.115(5) Å; α = 67.905(5)°; b = 12.085(5) Å; β = 86.187(5)°; c = 13.476(5) Å; γ = 73.358(4)°.	a = 10.422(5) Å; α = 76.543(5)°; b = 13.304(6) Å; β = 83.590(5)°; c = 13.766(6) Å γ = 70.965(4)°.
Volume	3165.4(10) $Å^3$	1605.2(12) $Å^3$	1753.5(13) $Å^3$
Z	4	2	2
Density (calculated)	1.388 Mg/m^3	1.369 Mg/m^3	1.444 Mg/m^3
Absorption coefficient	2.728 mm^{-1}	0.302 mm^{-1}	0.492 mm^{-1}
F(000)	1368	684	780
Crystal size	0.13 x 0.06 x 0.03 mm^3	0.20 x 0.16 x 0.14 mm^3	0.50 x 0.20 x 0.20 mm^3
Theta range for data collection	2.54 to 60.00°.	2.28 to 27.90°.	1.52 to 27.43°.
Index ranges	-22<=h<=22, -9<=k<=9, -23<=l<=23	-14<=h<=14, -12<=k<=16, -13<=l<=17	-13<=h<=13, -17<=k<=17, -17<=l<=17
Reflections collected	17717	10483	19832
Independent reflections	4584 [R(int) = 0.0984]	7581 [R(int) = 0.0246]	7807 [R(int) = 0.0228]
Completeness to theta = 60.00°	97.5 %	98.9 %	97.6 %
Max. and min. transmission	0.9226 and 0.7181	0.9590 and 0.9440	0.9080 and 0.7910
Data / restraints / parameters	4584 / 0 / 424	7581 / 0 / 424	7807 / 0 / 451
Goodness-of-fit on F^2	1.041	1.173	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1179	R1 = 0.0657, wR2 = 0.1754	R1 = 0.0401, wR2 = 0.0951
R indices (all data)	R1 = 0.0783, wR2 = 0.1304	R1 = 0.0913, wR2 = 0.2521	R1 = 0.0463, wR2 = 0.0986
Largest diff. peak and hole	0.289 and -0.303 e.$Å^{-3}$	0.684 and -0.749 e.$Å^{-3}$	0.352 and -0.369 e.$Å^{-3}$

General procedure for synthesis of quinoline derivatives (**3/5**)

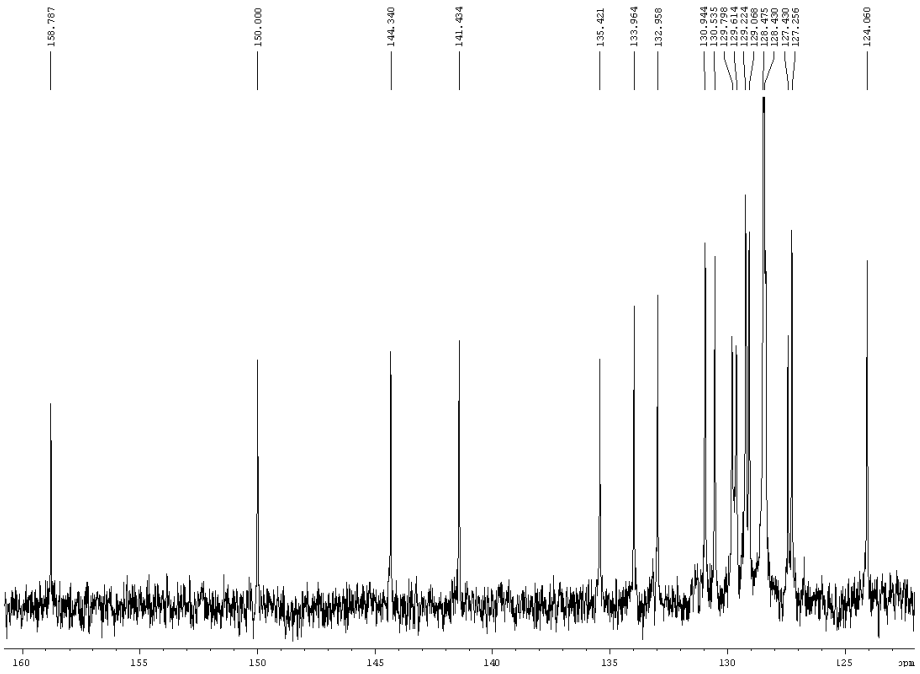
2-[(2-Oxo-2-arylethyl)sulfanyl]-1-aryl-1-ethanone/ 2-[(2-oxo-2-phenylethyl)disulfanyl]-1-aryl-1-ethanone **2/4** (0.1 mole) and 2-amino benzophenone **1** (0.2 mole) were taken in 15 mL water followed by the addition of *p*-toluenesulphonic acid (10 mol%) and refluxed for 1-2 h. After the completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and the solid was filtered out and recrystallised from dichloromethane-ethyl acetate (8:2) mixture to yield pure product.



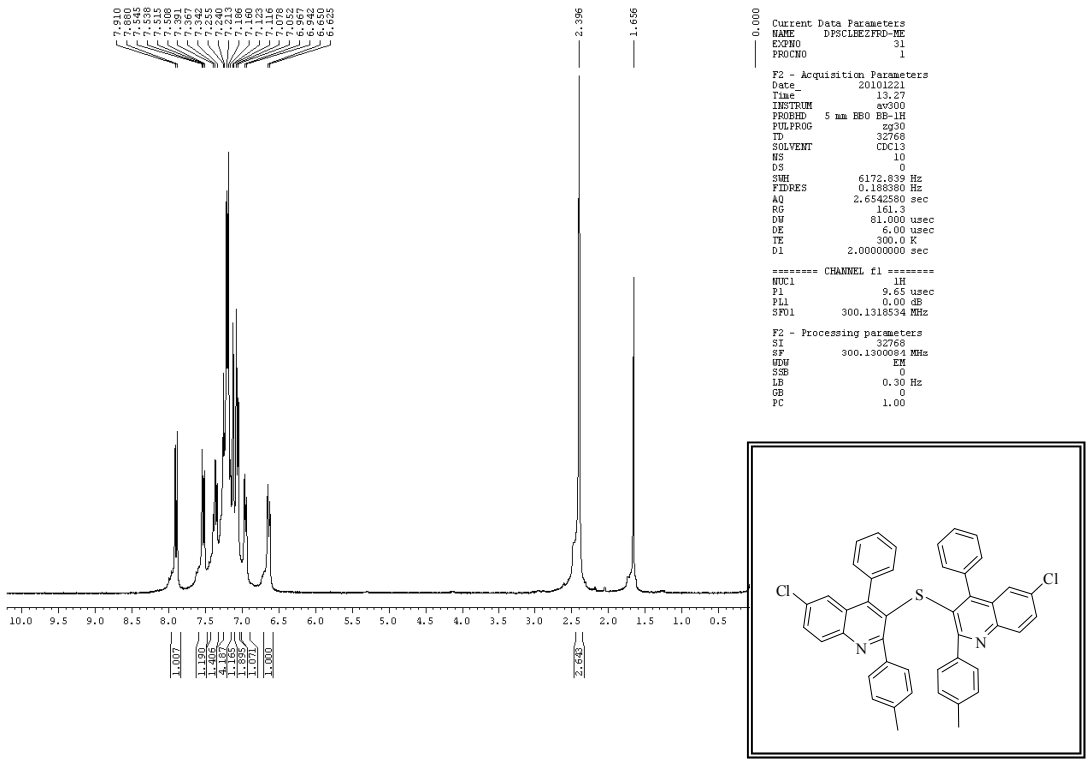
^{1}H NMR Spectrum of **3m** (recorded in $CDCl_3$)



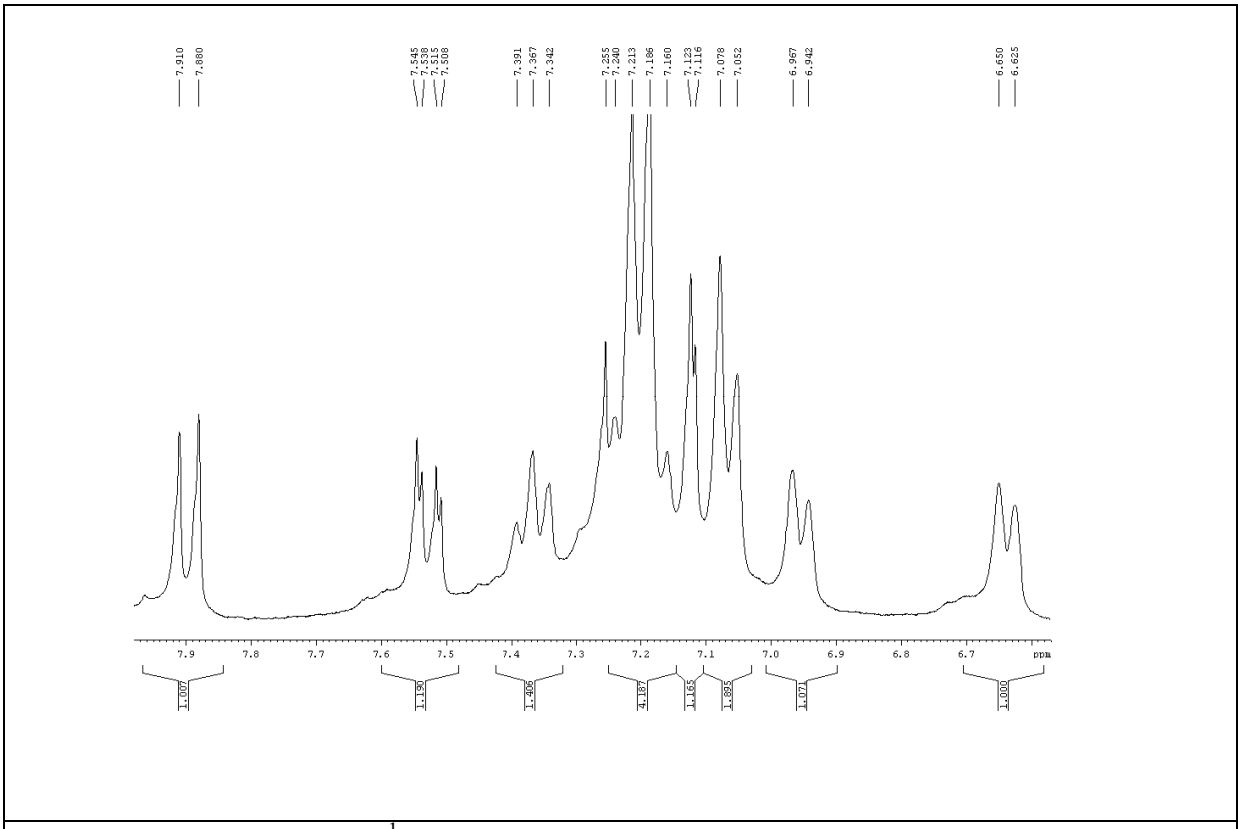
^{13}C NMR Spectrum of **3m** (recorded in $CDCl_3$)



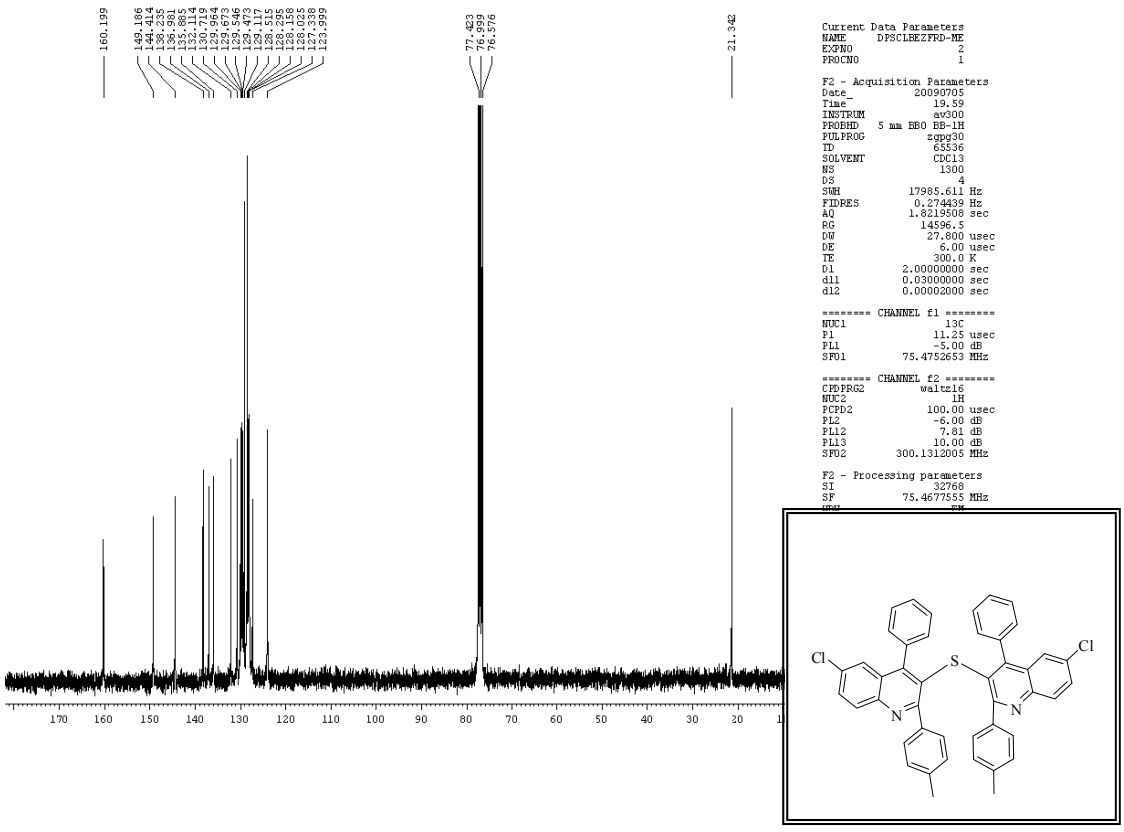
^{13}C NMR Spectrum of **3m** (expanded)



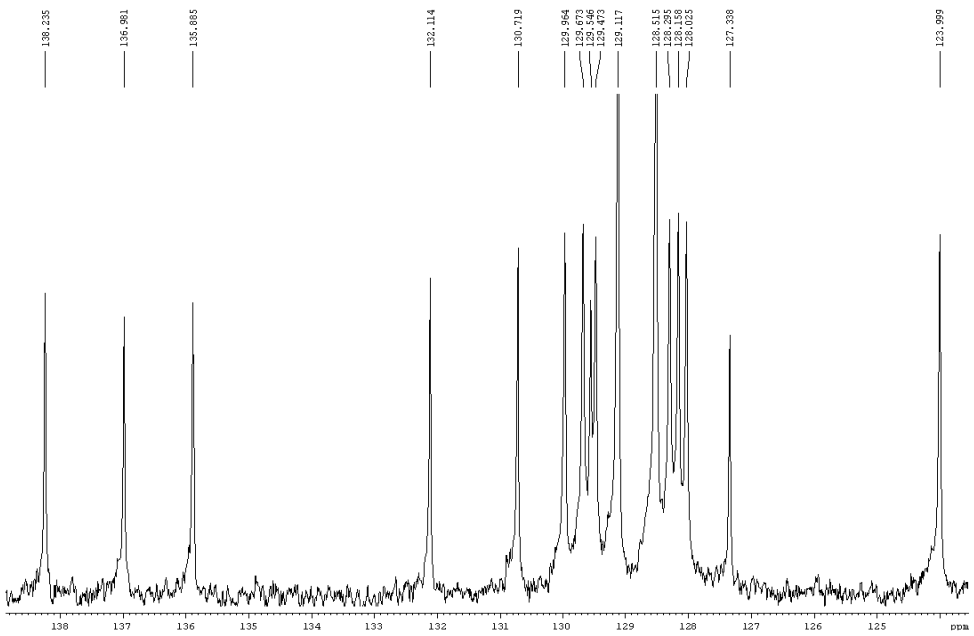
^{1}H NMR Spectrum of **3i** (recorded in $CDCl_3$)



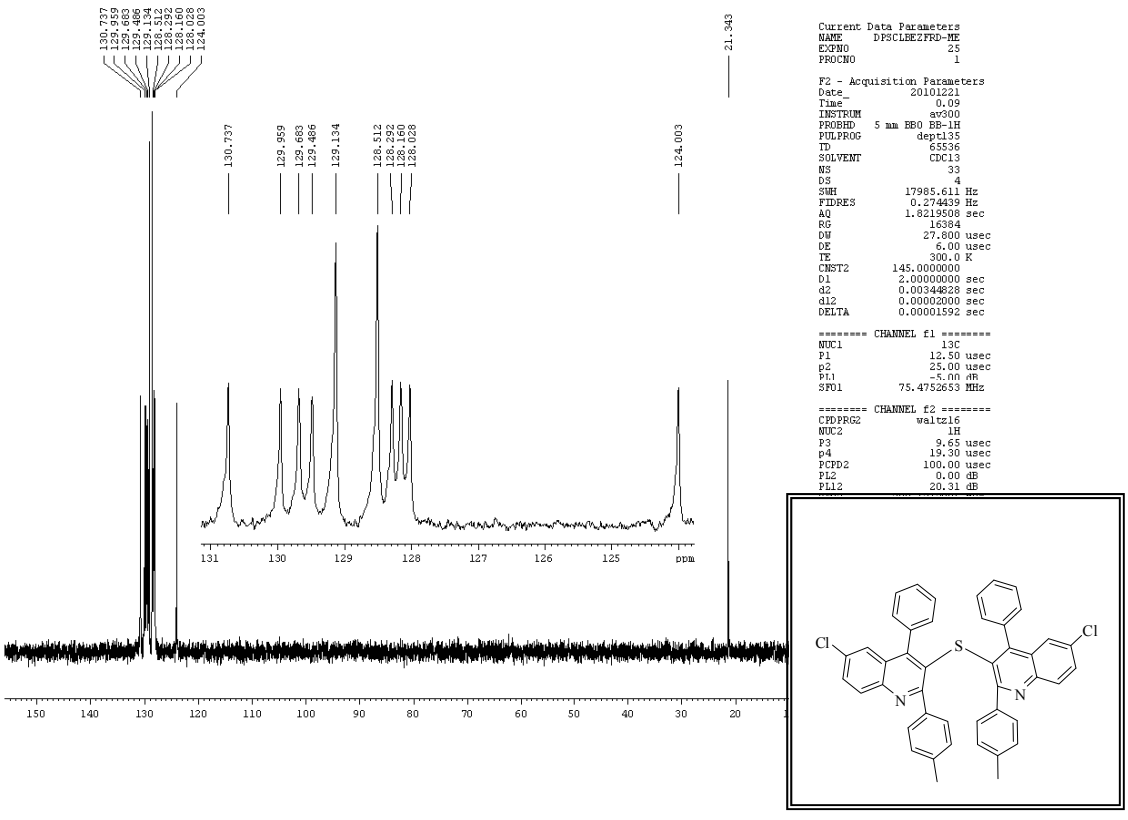
^{1}H NMR Spectrum of **3i** (expanded)



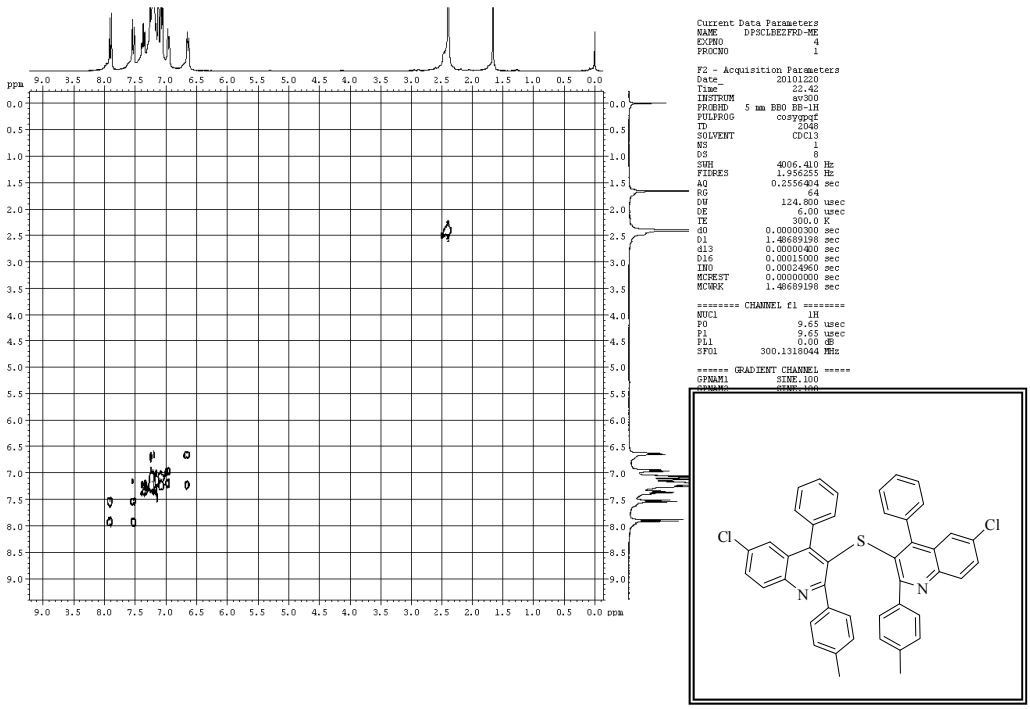
^{13}C NMR Spectrum of **3i** (recorded in $CDCl_3$)



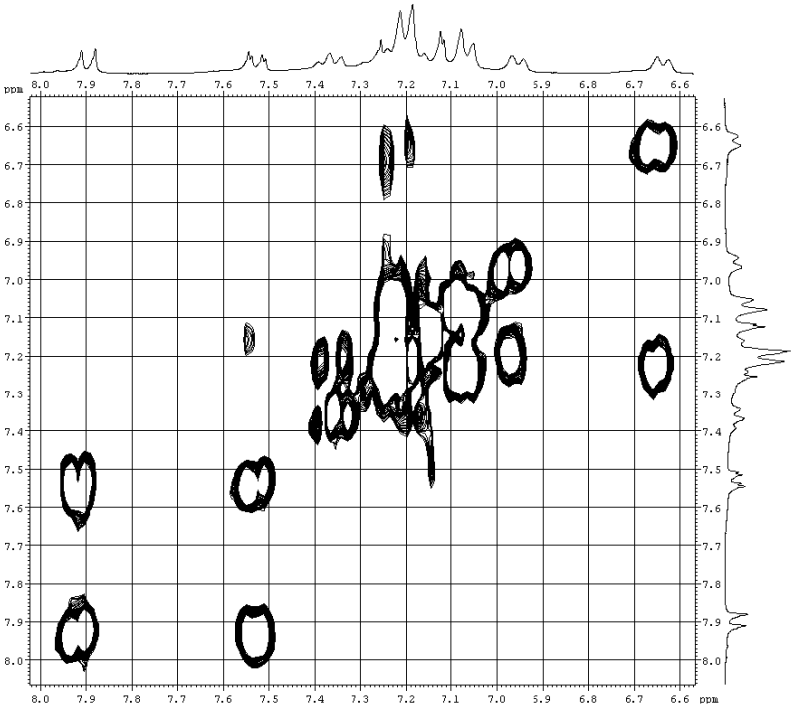
^{13}C NMR Spectrum of **3i** (expanded)



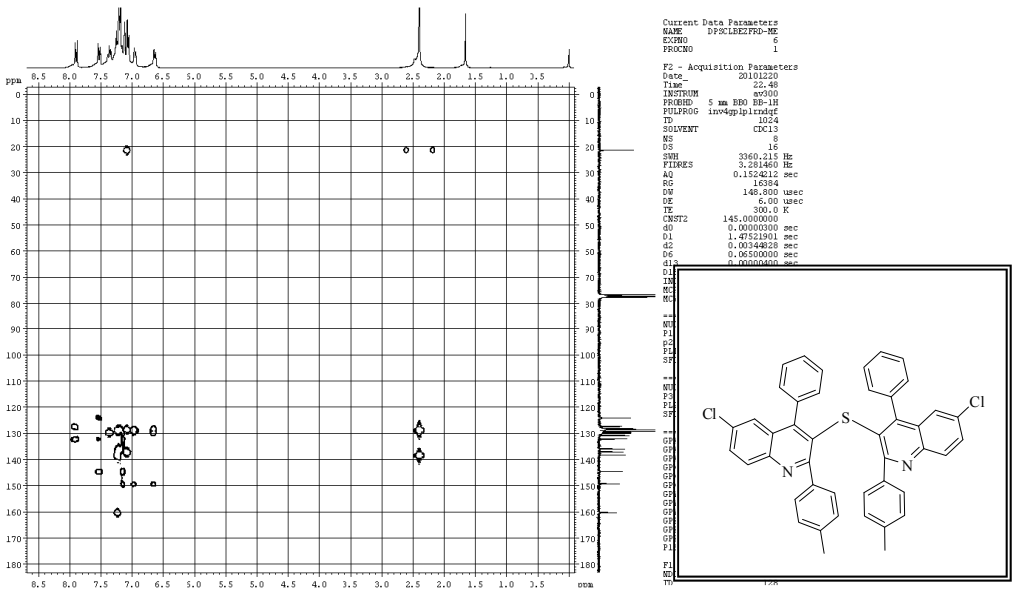
DEPT-135 Spectrum of **3i** ($CDCl_3$)



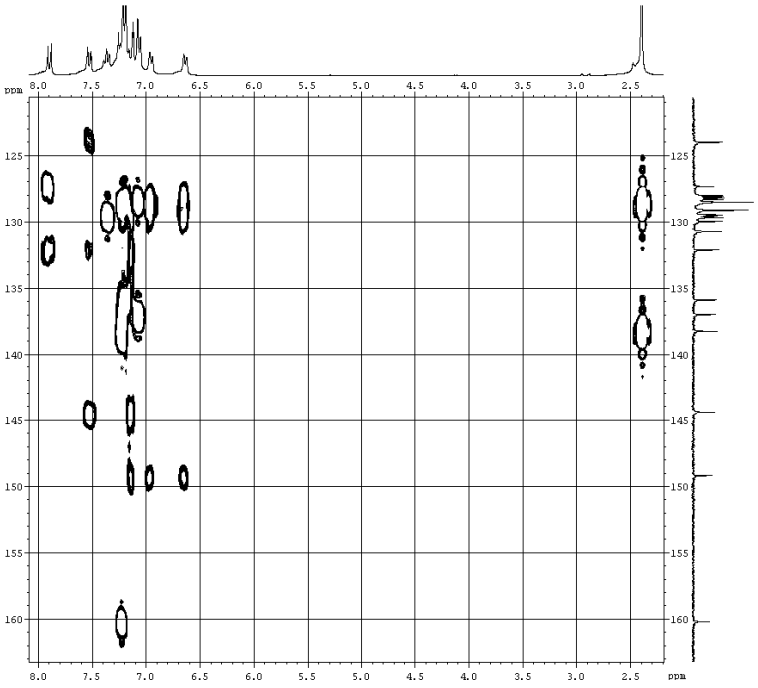
H,H-COSY Spectrum of **3i** (recorded in $CDCl_3$)



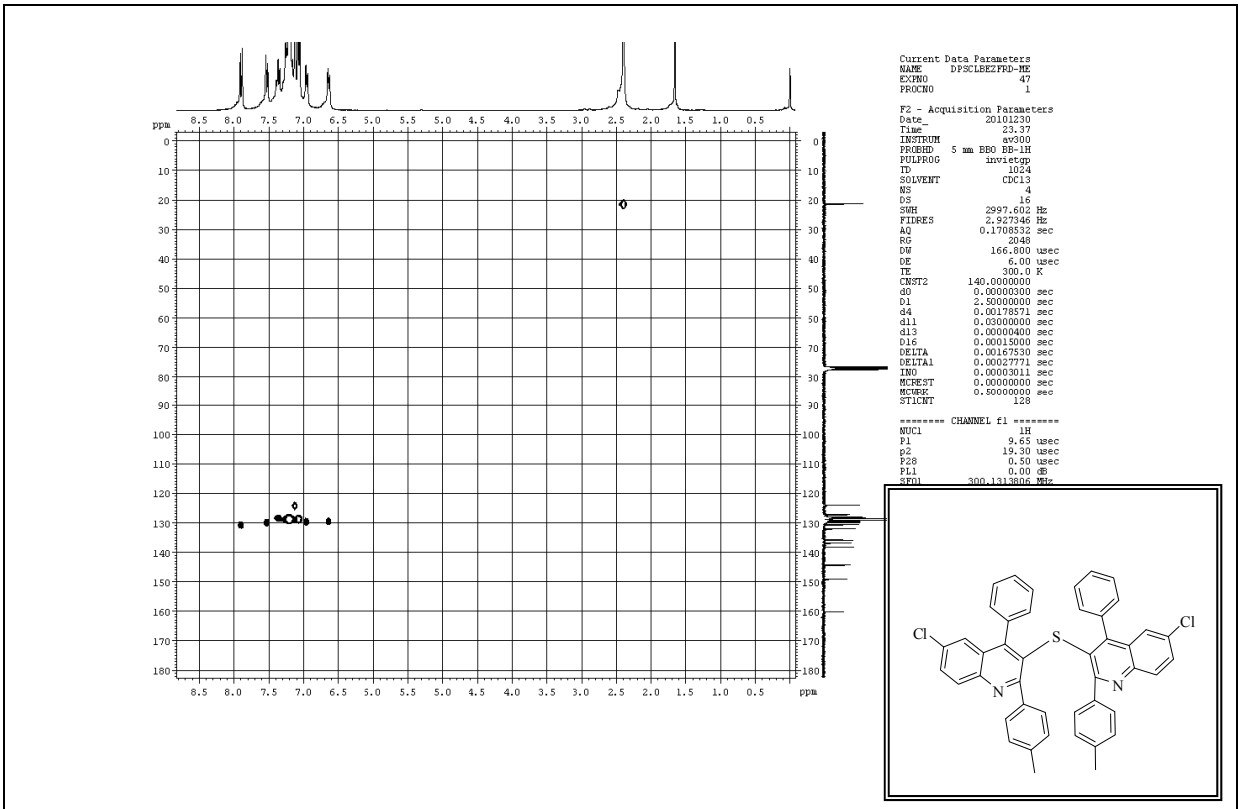
H,H-COSY Spectrum of **3i** (expanded)



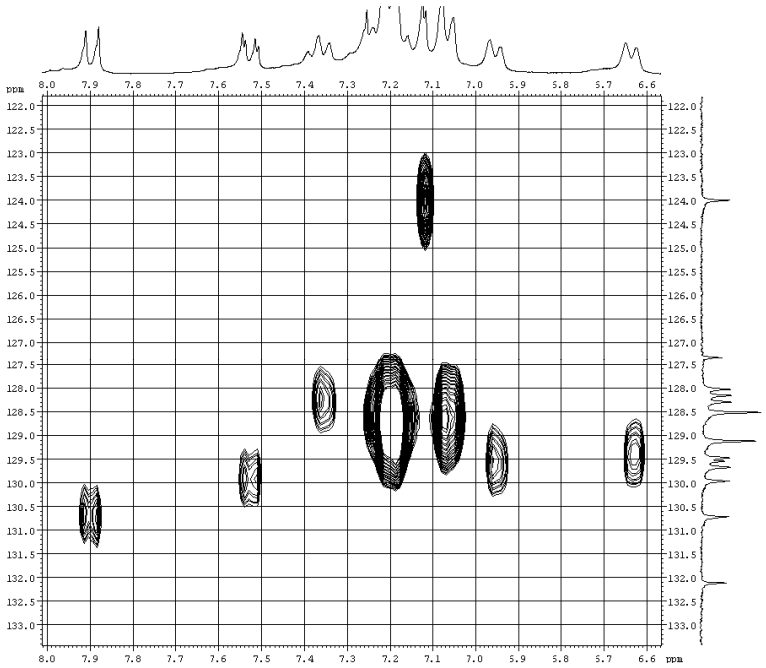
HMBC Spectrum of **3i** (recorded in $CDCl_3$)



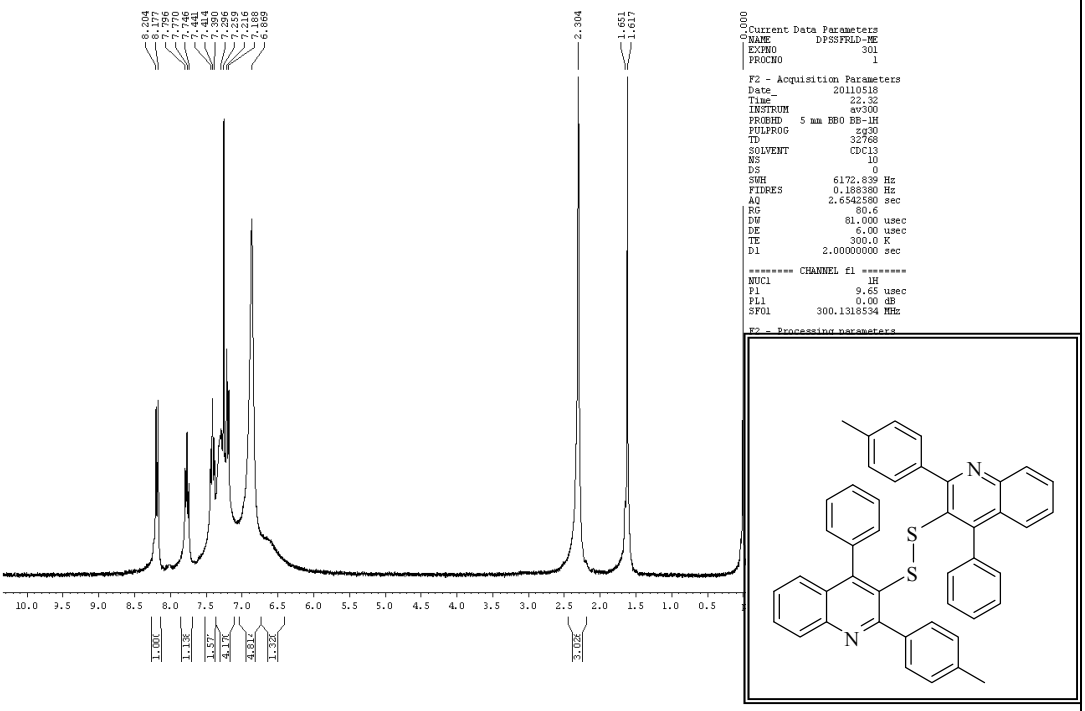
HMBC Spectrum of **3i** (expanded)



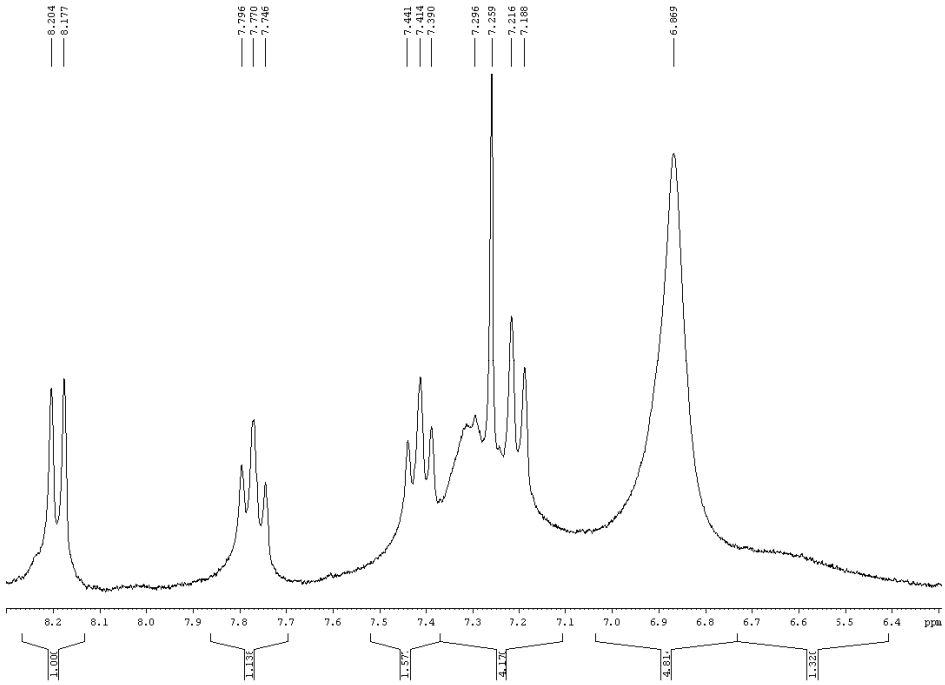
C,H-COSY Spectrum of **3i** (recorded in $CDCl_3$)



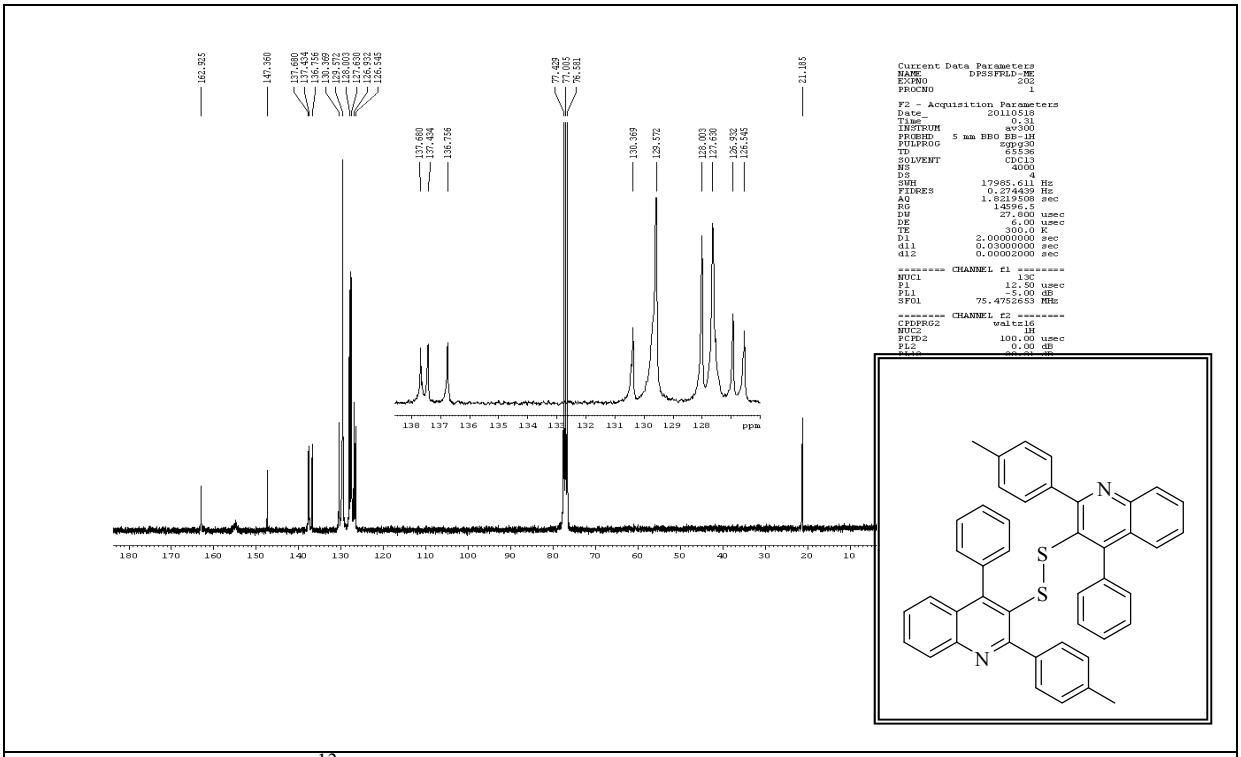
C,H-COSY Spectrum of **3i** (expanded)



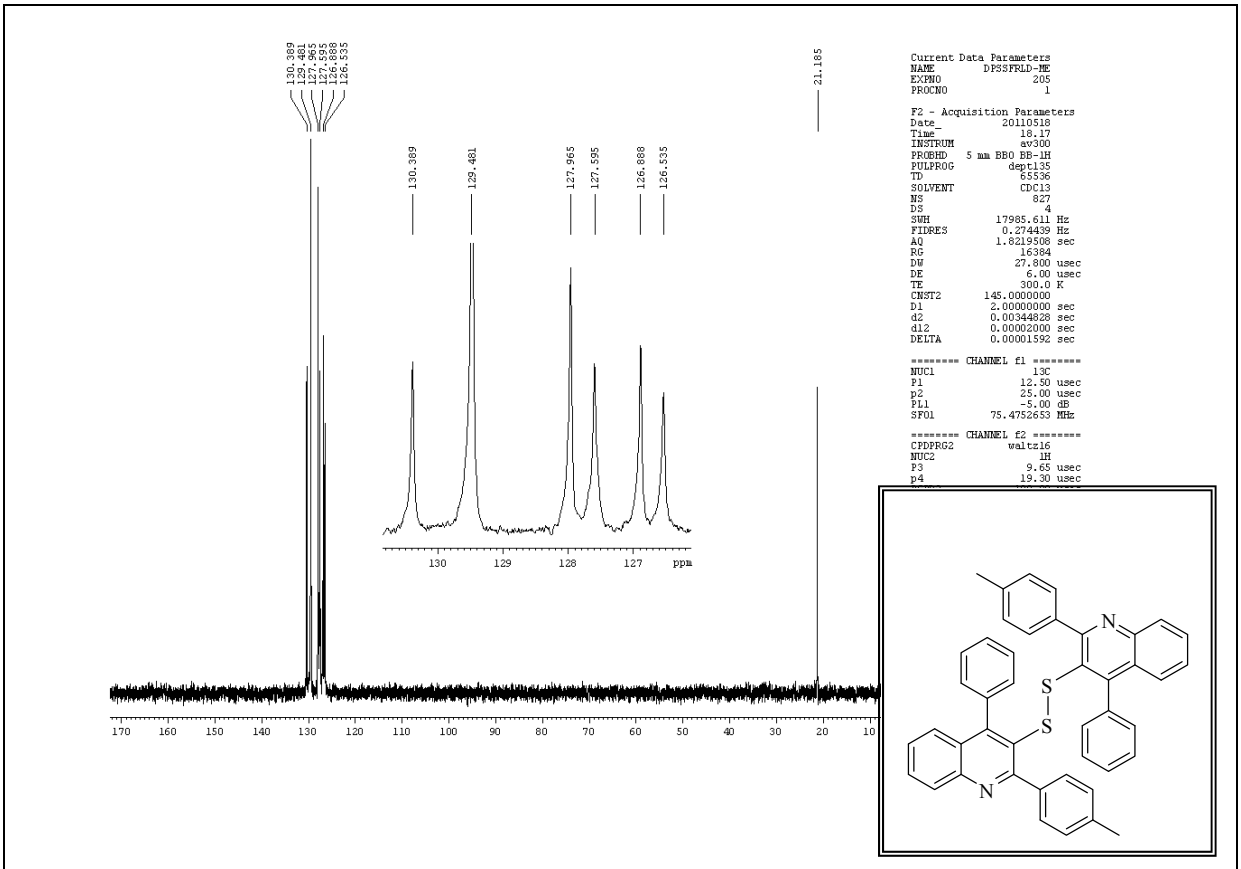
^{1}H NMR Spectrum of **5b** (recorded in $CDCl_3$)



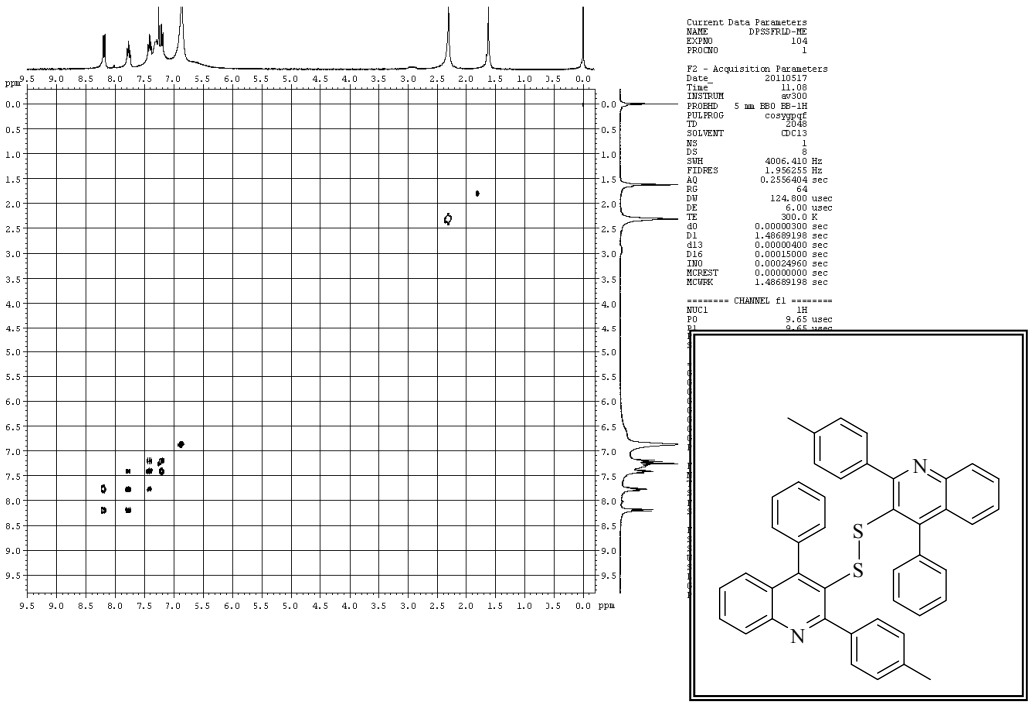
^{1}H NMR Spectrum of **5b** (expanded)



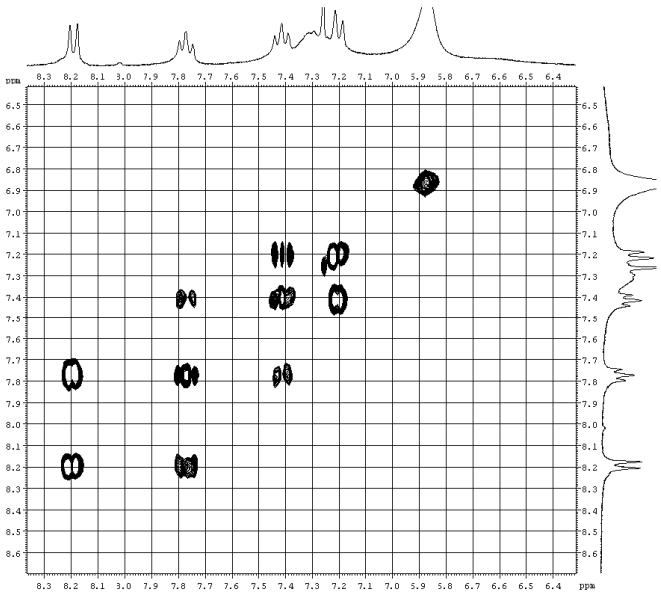
^{13}C NMR Spectrum of **5b** (recorded in $CDCl_3$)



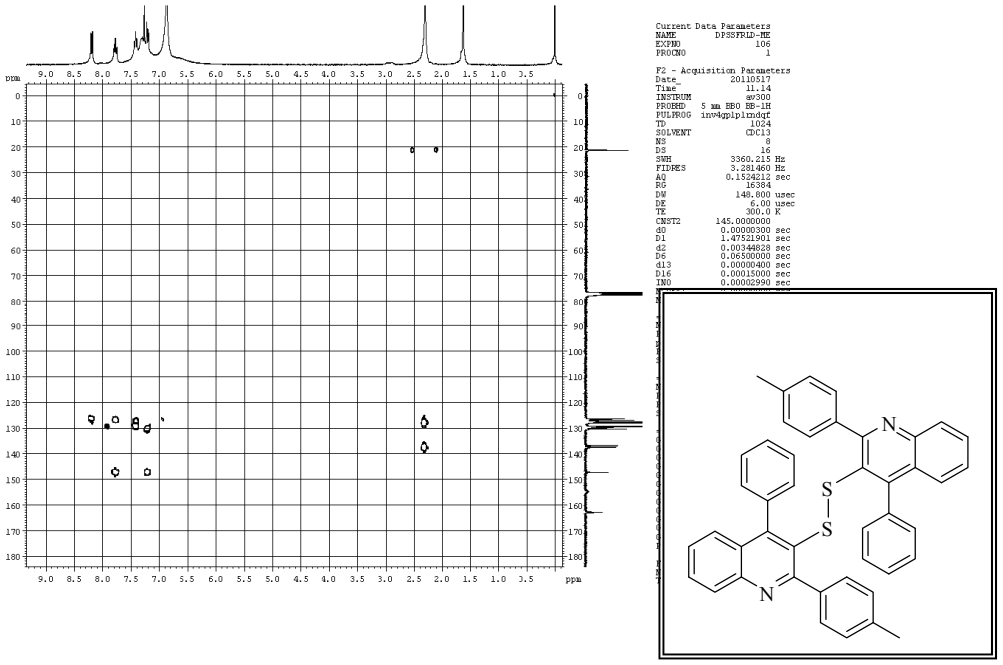
DEPT-135 Spectrum of **5b** ($CDCl_3$)



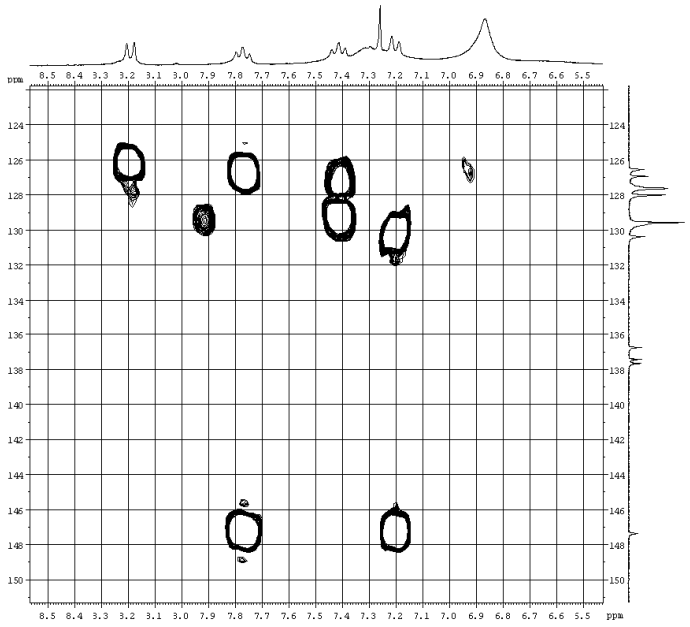
H,H-COSY Spectrum of **5b** (recorded in $CDCl_3$)



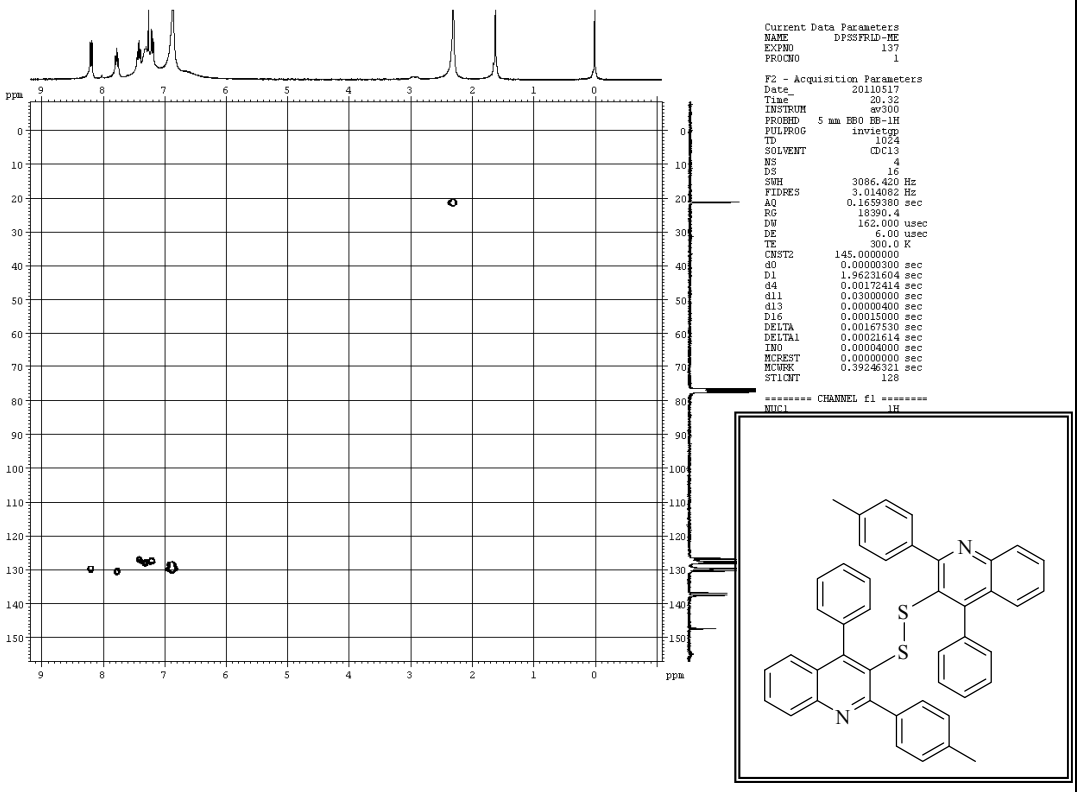
H,H-COSY Spectrum of **5b** (expanded)



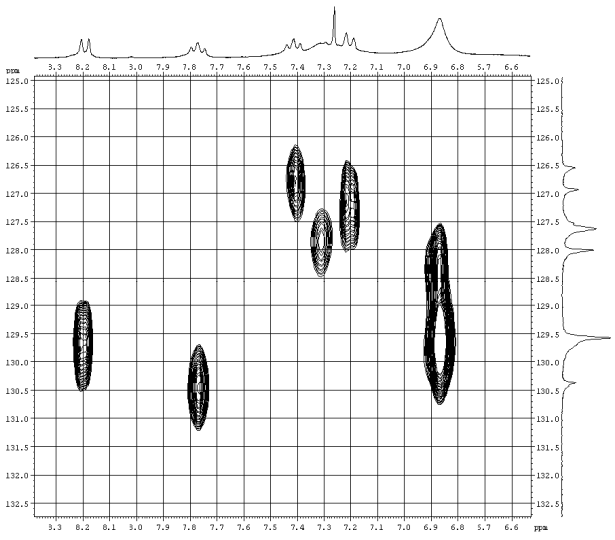
HMBC Spectrum of **5a** (recorded in $CDCl_3$)



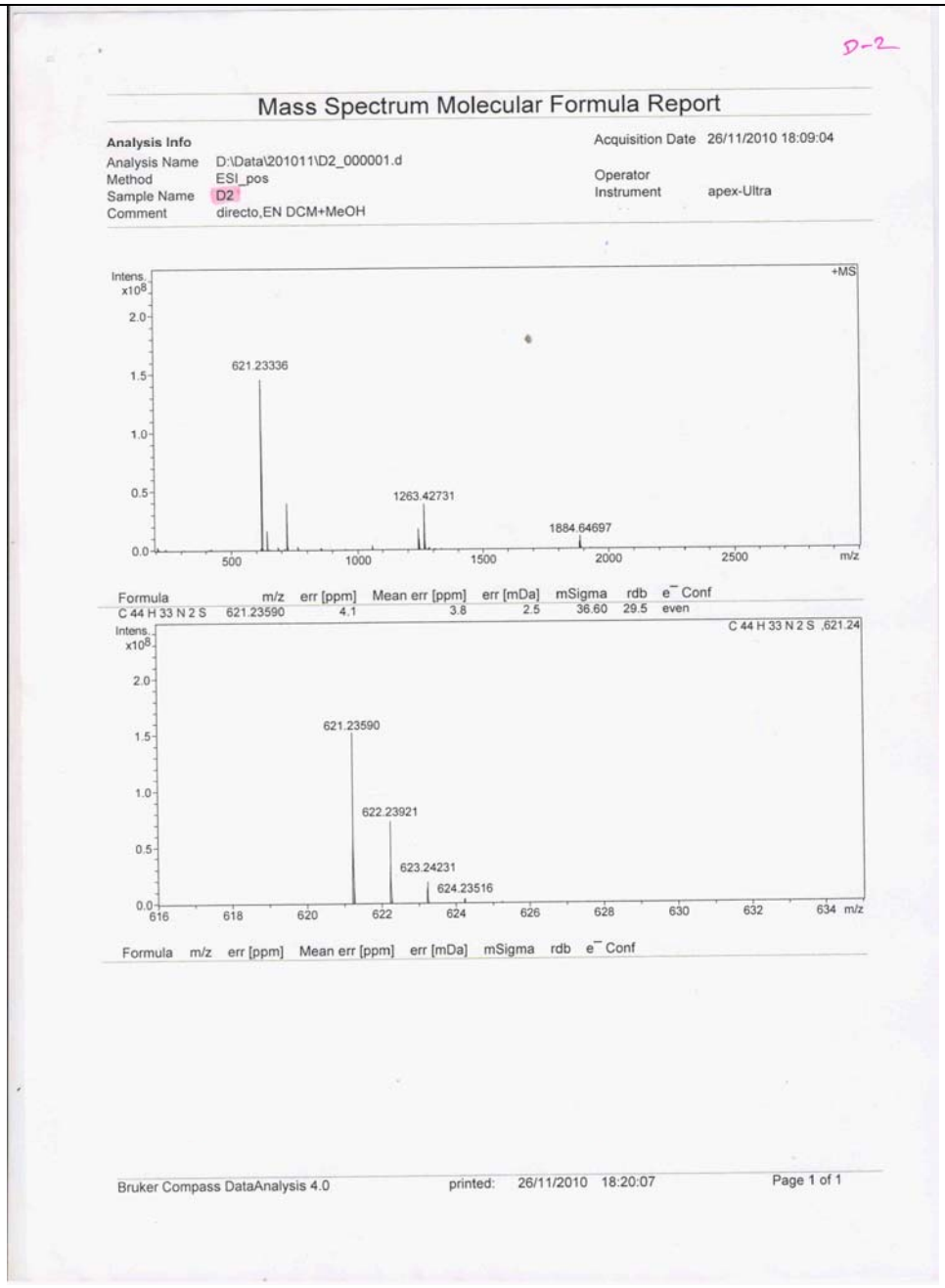
HMBC Spectrum of **5b** (expanded)



C,H-COSY Spectrum of **5b** (recorded in $CDCl_3$)



C,H-COSY Spectrum of **5b** (expanded)



D-2

Mass Spectrum Molecular Formula Report

Analysis Info

Analysis Name D:\Data\201011\D2_000001.d
Method ESI_pos
Sample Name D2
Comment directo,EN DCM+MeOH

Acquisition Date 26/11/2010 18:09:04
Operator
Instrument apex-Ultra

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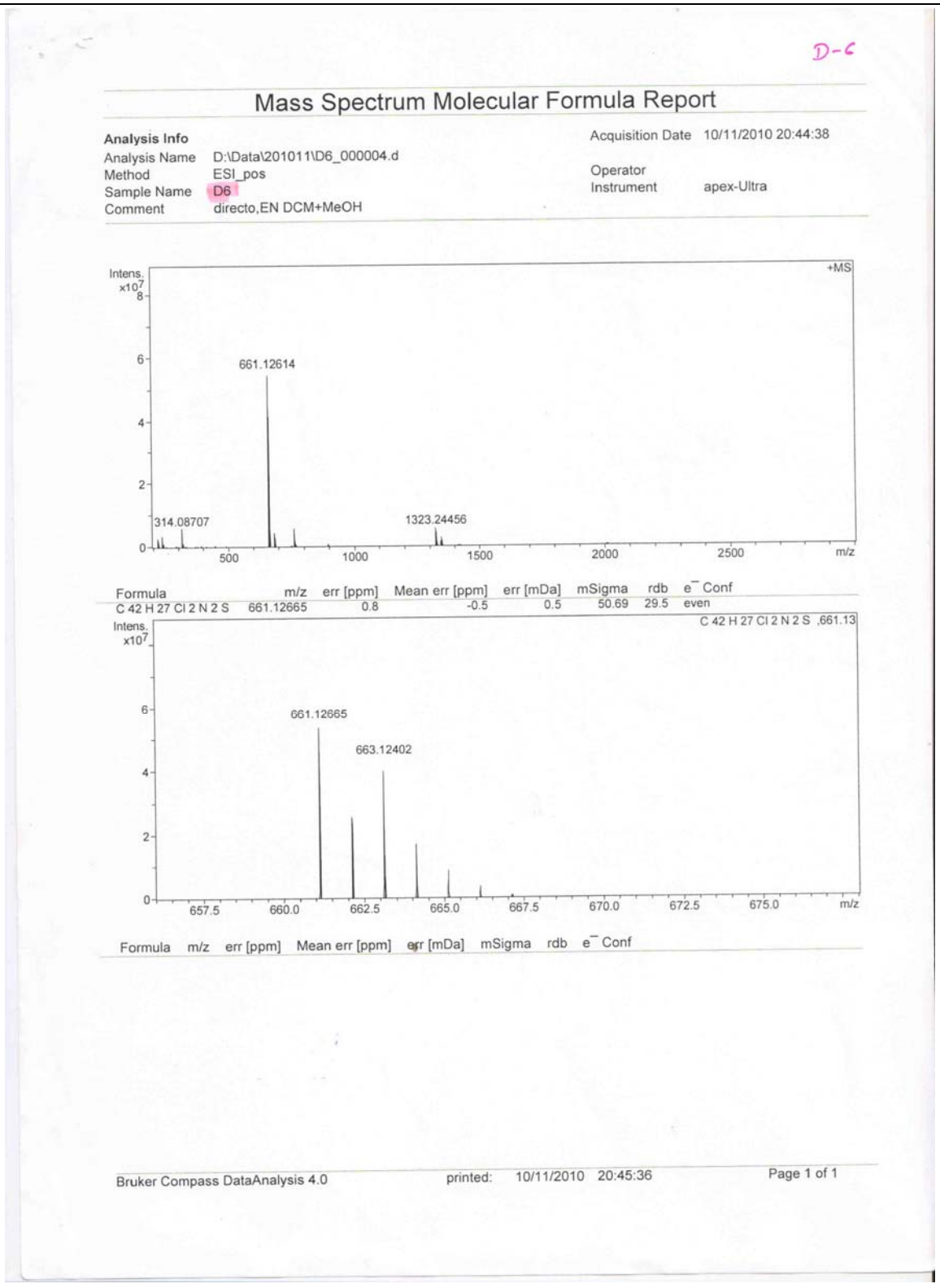
Formula	m/z	err [ppm]	Mean err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf

Bruker Compass DataAnalysis 4.0 printed: 26/11/2010 18:20:07 Page 1 of 1

Mass spectrum of **3b**



D-C

Mass Spectrum Molecular Formula Report

Analysis Info

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Method ESI_pos
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Comment directo,EN DCM+MeOH

Acquisition Date 10/11/2010 20:44:38
Operator
Instrument apex-Ultra

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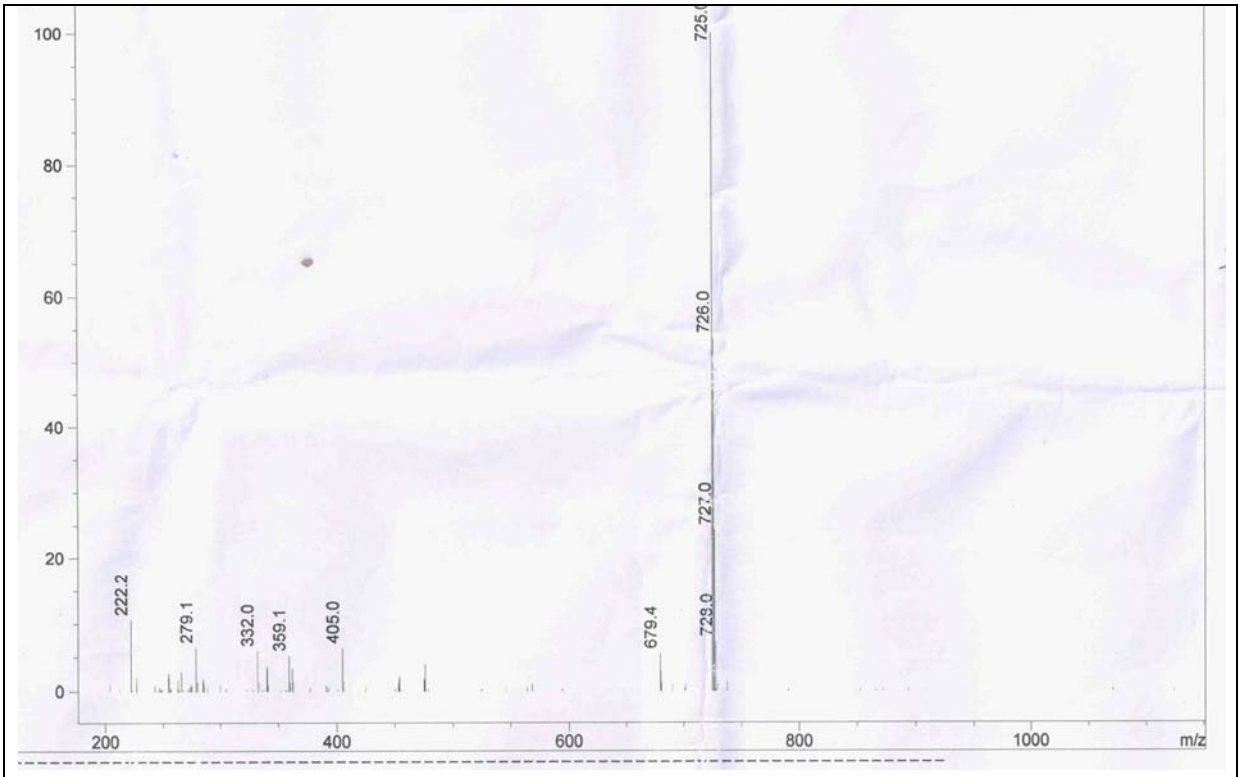
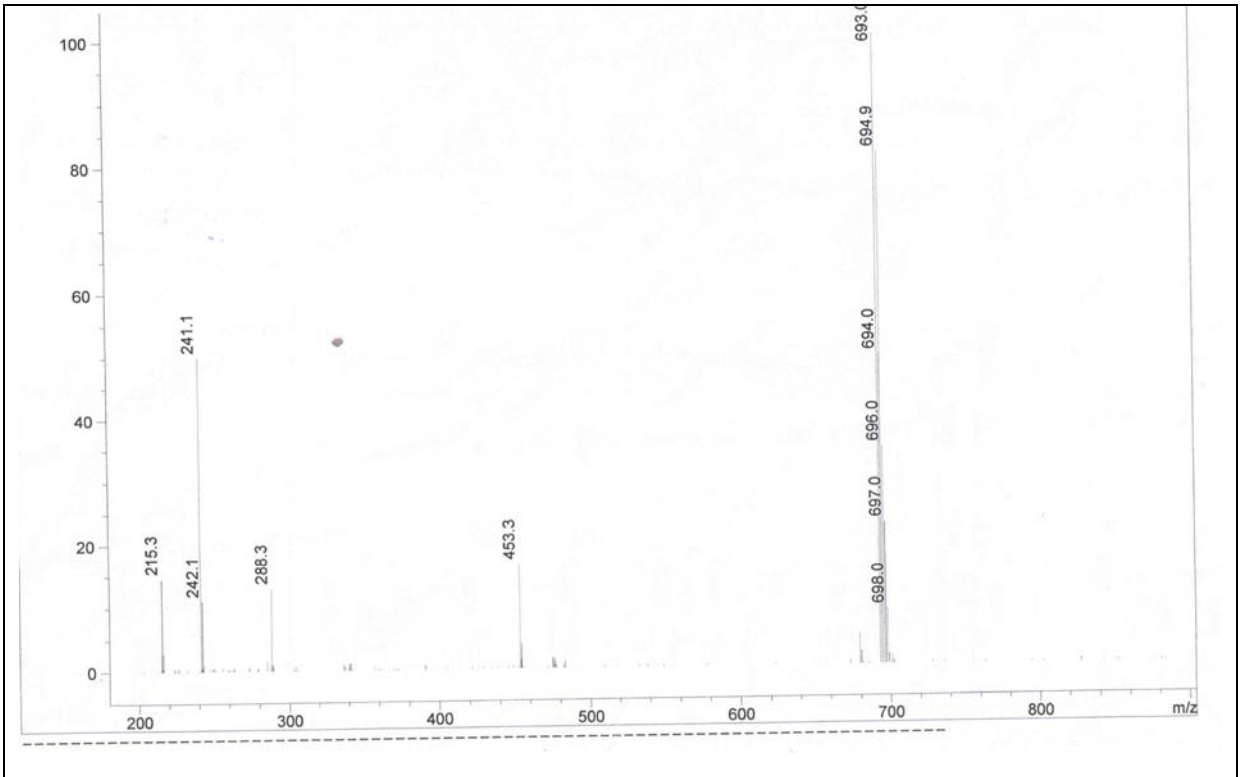
Formula	m/z	err [ppm]	Mean err [ppm]	err [mDa]	mSigma	rdb	e⁻ Conf

Bruker Compass DataAnalysis 4.0 printed: 10/11/2010 20:45:36 Page 1 of 1

Mass Spectrum of **3f**



Mass Spectrum of **5a**



Mass Spectrum of **5c**