Supporting Information

Structures, Reactivities, and Antibiotic Activities of the Marinopyrroles A-F

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General. Diazomethane was prepared according to the method of Arndt (Arndt, F. *Org. Synth.* **1943**, Coll. Vol. 2, 165). Ethyl 2,5-dioxopentanoate (**28**) was synthesized via ozonolysis of ethyl 2-oxohex-5-enoate (Macritchie, J. A.; Silcock, A.; Willis, C. L. *Tetrahedron Asym.* **1997**, *8*, 3895-3902). Ethyl 3-amino-1*H*-pyrrole-2-carboxylate (**29**) was prepared according to literature procedures (Furneaux, R. H.; Tyler, P. C. *J. Org. Chem.* **1999**, *64*, 8411-8412). Pyridine was distilled from calcium hydride prior to use, and tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl. All other reagents and solvents were purchased commercially and were used without further purification. Column chromatography was performed using 60 Å 230-400 mesh silica gel. RP-HPLC purification was performed on a C8(2) Phenomenex® Luna column (5 µm, 250 x 10 mm) at 3 mL min^{-1} with UV detection (254 nm). Unless otherwise stated, ^{1}H NMR spectra were recorded at 500 MHz in $CDCl_3$ (residual $CHCl_3$ referenced to 7.26 ppm), DMSO-d_6 (residual DMSO referenced to 2.50 ppm), or CD_3CN (residual CH_3CN referenced to 1.94 ppm) on a Varian Inova spectrometer. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ (referenced to 77.0 ppm) or DMSO-d_6 (referenced to 39.4 ppm) on a Varian Inova NMR spectrometer.

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Marinopyrrole A (**1**)	
^{1}H NMR spectrum (500 MHz, $CDCl_3$)	S1
^{13}C NMR spectrum (75 MHz, $CDCl_3$)	S2
COSY spectrum (500 MHz, $CDCl_3$)	S3
HSQC spectrum (500 MHz, $CDCl_3$)	S4
HMBC spectrum (500 MHz, $CDCl_3$)	S5
HRESI-TOF	S6

Marinopyrrole B (**2**)
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S7
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S8
COSY spectrum (500 MHz, $CDCl_3$) S9
HSQC spectrum (500 MHz, $CDCl_3$) S10
HMBC spectrum (500 MHz, $CDCl_3$) S11
HRESI-TOF S12

Marinopyrrole C (**3**)
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S13
COSY spectrum (500 MHz, $CDCl_3$) S14
HSQC spectrum (500 MHz, $CDCl_3$) S15
HMBC spectrum (500 MHz, $CDCl_3$) S16
HRESI-TOF S17

Marinopyrrole D (**4**)
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S18
COSY spectrum (500 MHz, $CDCl_3$) S19
HSQC spectrum (500 MHz, $CDCl_3$) S20
HMBC spectrum (500 MHz, $CDCl_3$) S21
HRESI-TOF S22

Marinopyrrole E (**5**)
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S23
COSY spectrum (500 MHz, $CDCl_3$) S24
HSQC spectrum (500 MHz, $CDCl_3$) S25
HMBC spectrum (500 MHz, $CDCl_3$) S26
HRESI-TOF S27

Marinopyrrole F (**6**)
^{1}H NMR spectrum (500 MHz, DMSO-d_6) S28
HRESI-TOF S29

Synthetic marinopyrrole F (**6**)
^{1}H NMR spectrum (500 MHz, DMSO-d_6) S30
^{13}C NMR spectrum (75 MHz, DMSO-d_6) S31
COSY spectrum (500 MHz, DMSO-d_6) S32
HSQC spectrum (500 MHz, DMSO-d_6) S33
HMBC spectrum (500 MHz, DMSO-d_6) S34

CD spectra for **1**-**6** (CH_3CN) S35

O,*O*-Diacetyl marinopyrrole A (**11**)
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S36
^{13}C NMR spectrum (125 MHz, $CDCl_3$) S37
HRESI-TOF S38

O,*O*,*N*-Trimethyl marinopyrrole A (**12**)
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S39
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S40
HRESI-TOF S41

N-Methyl marinopyrrole A (**13**)
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S42
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S43
HRESI-TOF S44

Methoxide adduct **14**
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S45
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S46
COSY spectrum (500 MHz, $CDCl_3$) S47
HSQC spectrum (500 MHz, $CDCl_3$) S48
HMBC spectrum (500 MHz, $CDCl_3$) S49
HMBC spectrum (500 MHz, $CDCl_3$) S50
HRESI-TOF S51

Cysteamine adduct **15**
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S52
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S53
COSY spectrum (500 MHz, $CDCl_3$) S54
HSQC spectrum (500 MHz, $CDCl_3$) S55
HMBC spectrum (500 MHz, $CDCl_3$) S56
HMBC spectrum (500 MHz, $CDCl_3$) S57
HRESI-TOF S58

Dimethylamine adduct **16**
^{1}H NMR spectrum (600 MHz, $CDCl_3$) S59
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S60
COSY spectrum (600 MHz, $CDCl_3$) S61
HSQC spectrum (600 MHz, $CDCl_3$) S62
HMBC spectrum (600 MHz, $CDCl_3$) S63
HMBC spectrum (600 MHz, $CDCl_3$) S64
HRESI-TOF S65

Lysine adduct **17**
^{1}H NMR spectrum (600 MHz, CD_3CN) S66
COSY spectrum (600 MHz, CD_3CN) S67
HSQC spectrum (600 MHz, CD_3CN) S68
HMBC spectrum (600 MHz, CD_3CN) S69
HRESI-TOF S70

Bromoacetate **22**
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S71
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S72
HRESI-TOF S73

Bromophenol **19**
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S74
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S75
HRESI-TOF S76

Iodoacetate **23**
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S77
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S78
HRESI-TOF S79

Iodophenol **20**
^{1}H NMR spectrum (500 MHz, $CDCl_3$) S80
^{13}C NMR spectrum (75 MHz, $CDCl_3$) S81
HRESI-TOF S82

N-Bromoacetate **24**
^{1}H NMR spectrum (500 MHz, $CDCl_3$) **S**83
^{13}C NMR spectrum (75 MHz, $CDCl_3$) **S**84
HRESI-TOF S85

Chromene **25**
^{1}H NMR spectrum (500 MHz, DMSO-d_6) S86
^{13}C NMR spectrum (75 MHz, DMSO-d_6) S87
COSY spectrum (500 MHz, DMSO-d_6) S88
HSQC spectrum (500 MHz, DMSO-d_6) S89
HMBC spectrum (500 MHz, DMSO-d_6) S90
HRESI-TOF S91

Tabulated ^{1}H, ^{13}C, and HMBC NMR spectral data for **30** and **31** S92

Bipyrrole **30**
^{1}H NMR spectrum (600 MHz, $CDCl_3$) **S**93
^{13}C NMR spectrum (75 MHz, $CDCl_3$) **S**94
COSY spectrum (600 MHz, $CDCl_3$) **S**95
HSQC spectrum (600 MHz, $CDCl_3$) **S**96
HMBC spectrum(600 MHz, $CDCl_3$) **S**97
HRESI-TOF S98

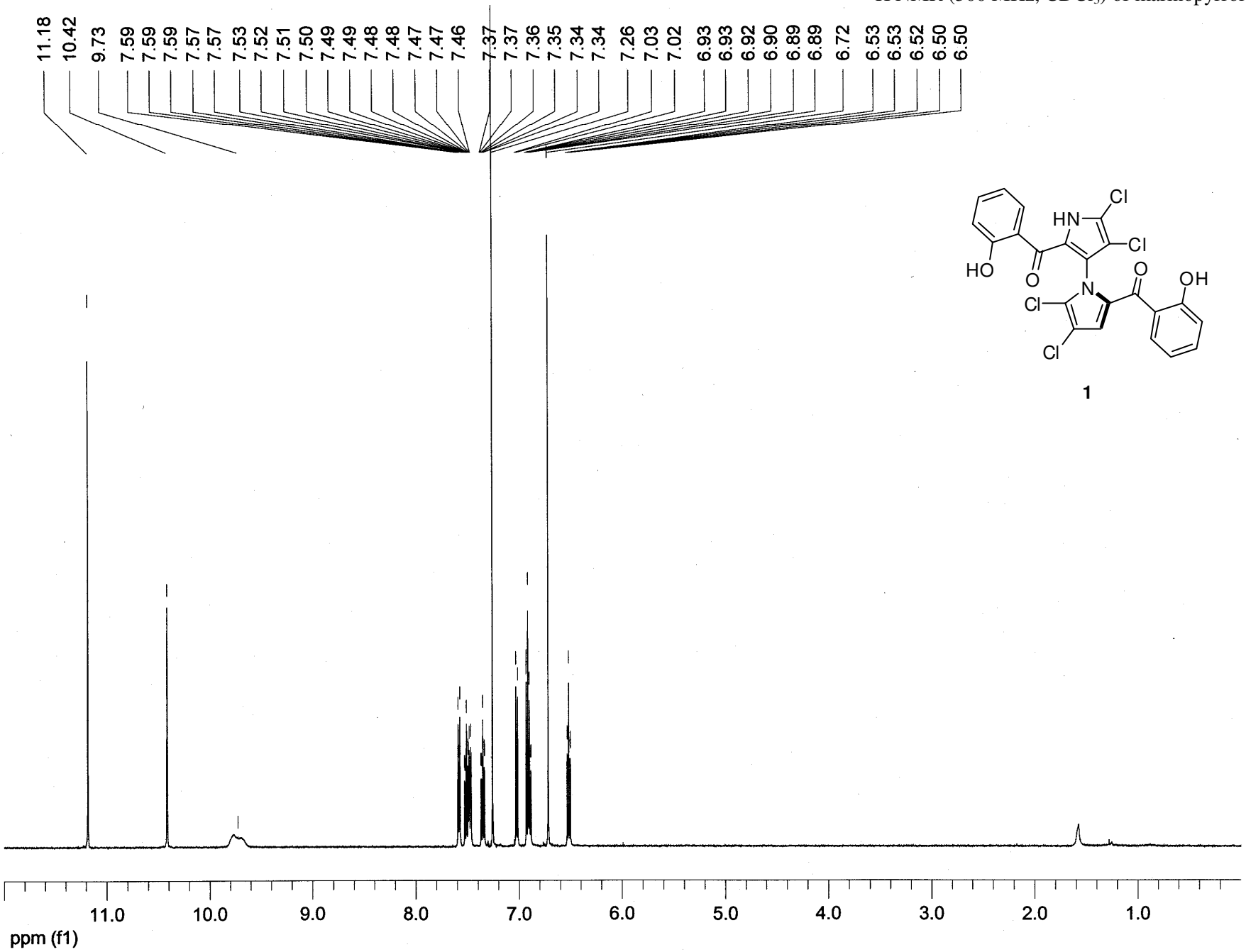
Bipyrrole **31**
^{1}H NMR spectrum (600 MHz, $CDCl_3$) **S**99
^{13}C NMR spectrum (75 MHz, $CDCl_3$) **S**100
COSY spectrum (600 MHz, $CDCl_3$) **S**101
HSQC spectrum (600 MHz, $CDCl_3$) **S**102
HMBC spectrum (600 MHz, $CDCl_3$) S103
HRESI-TOF S104

Figure S1. ORTEP of marinopyrrole F (**6**) S105

Figure S2. ORTEP of bromophenol **19** S106

Figure S3. ORTEP of bipyrrole **31** S107

^{1}H NMR (500 MHz, $CDCl_3$) of marinopyrrole A (**1**)



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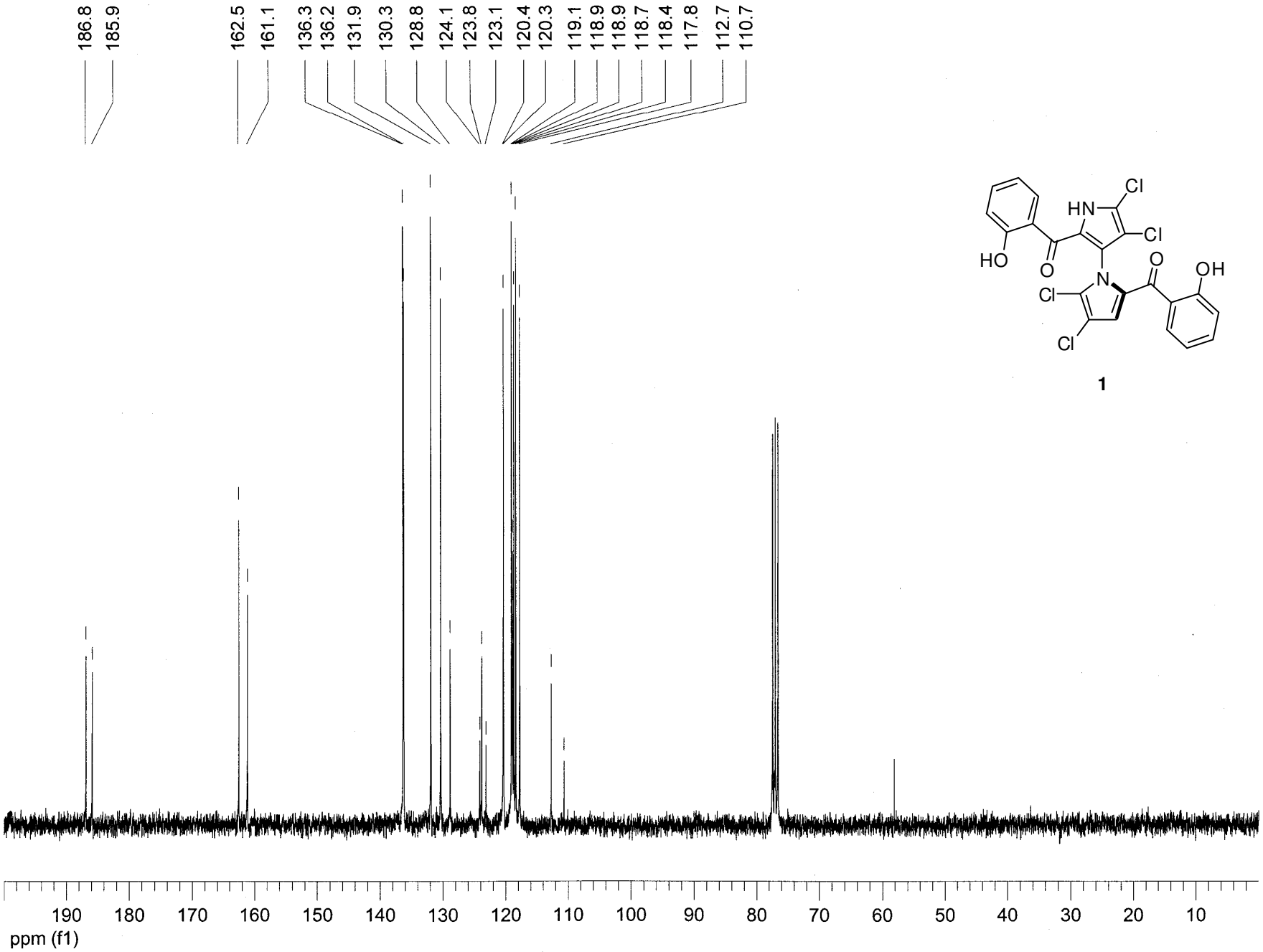
^{13}C NMR (75 MHz, $CDCl_3$) of marinopyrrole A (**1**)



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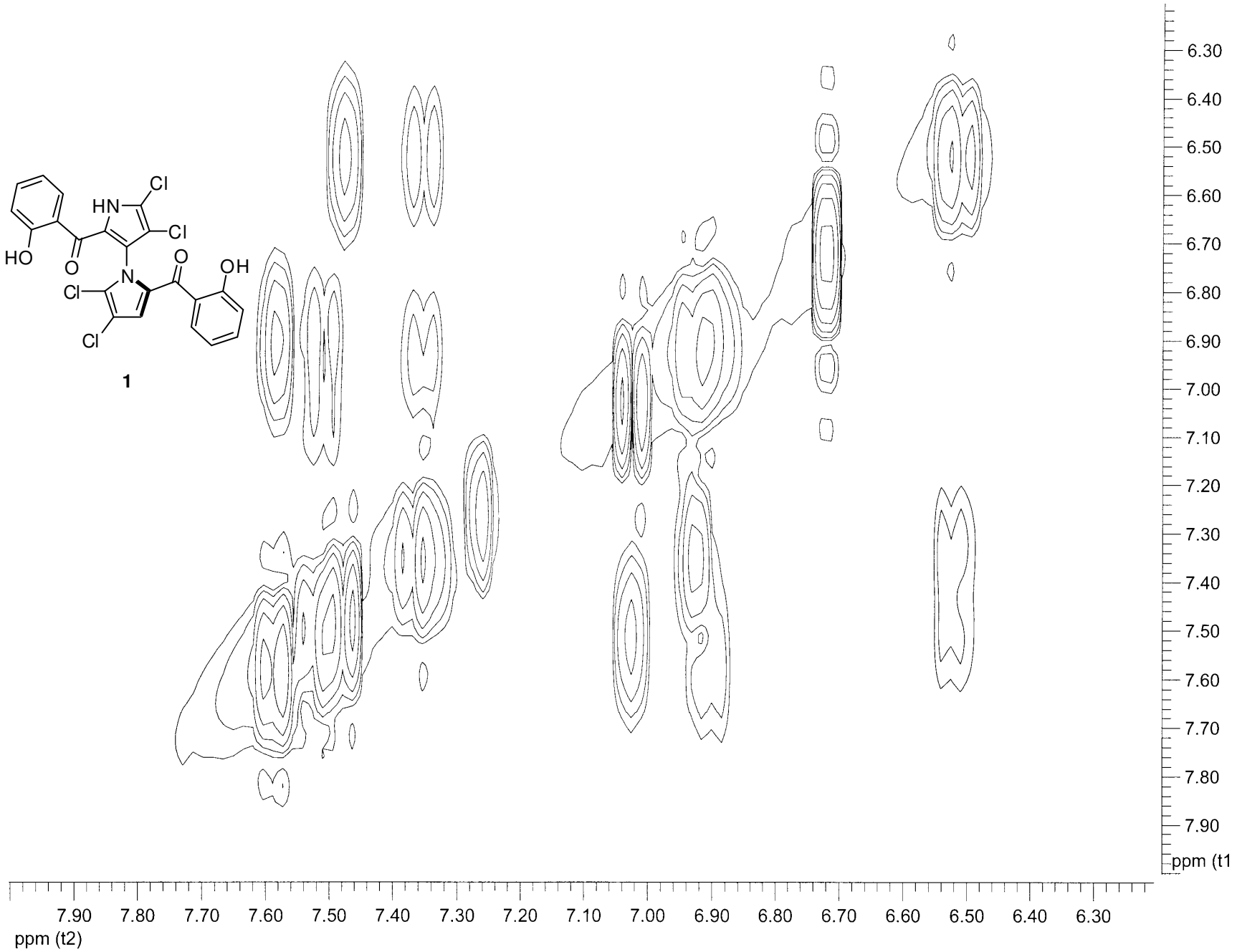
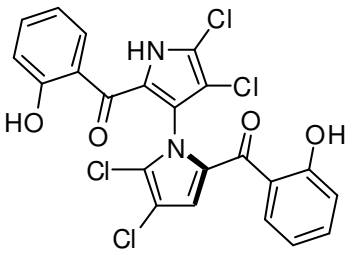
COSY (500 MHz, $CDCl_3$) of marinopyrrole A (**1**)



HSQC (500 MHz, $CDCl_3$) of marinopyrrole A (**1**)



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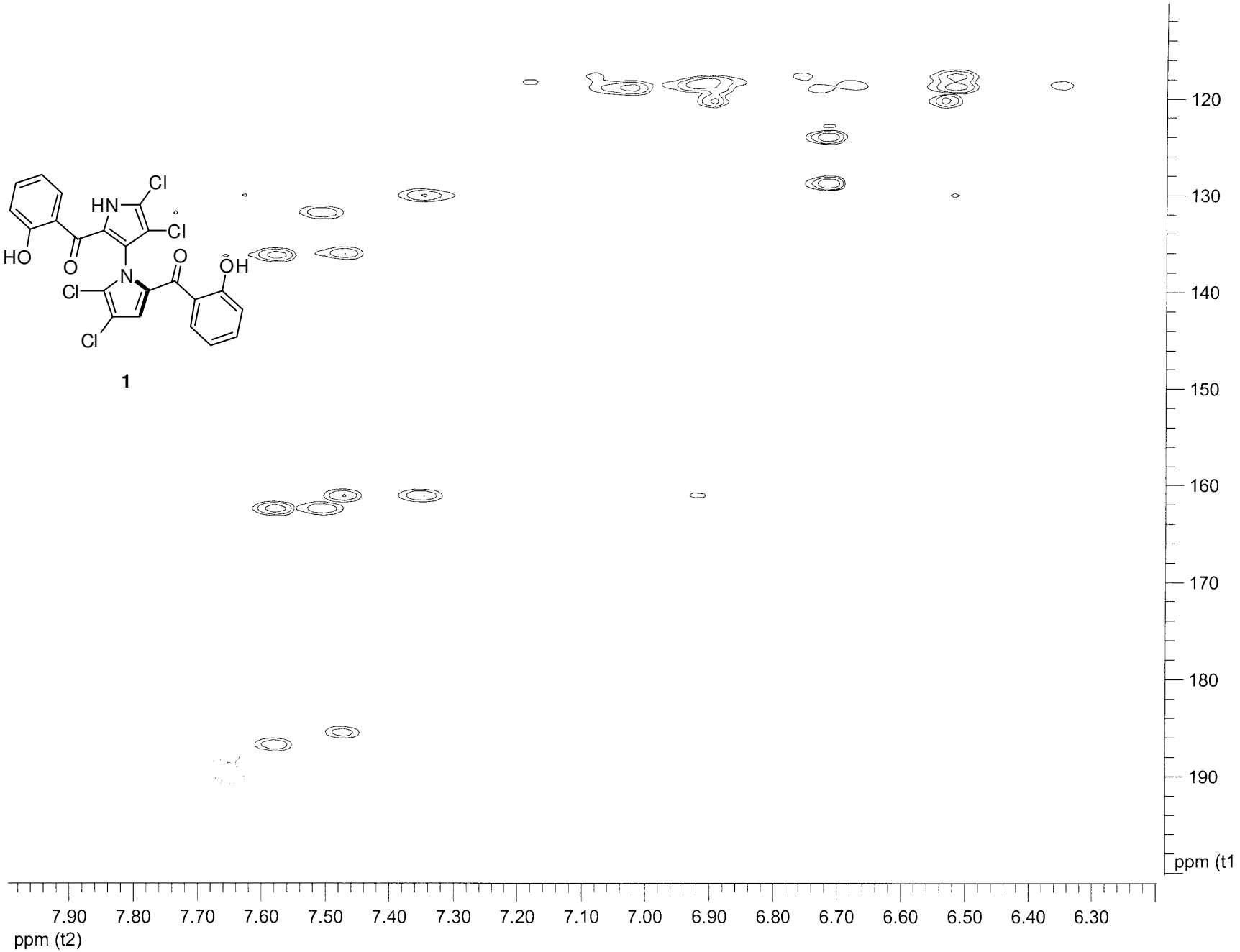
HMBC (500 MHz, $CDCl_3$) of marinopyrrole A (**1**)



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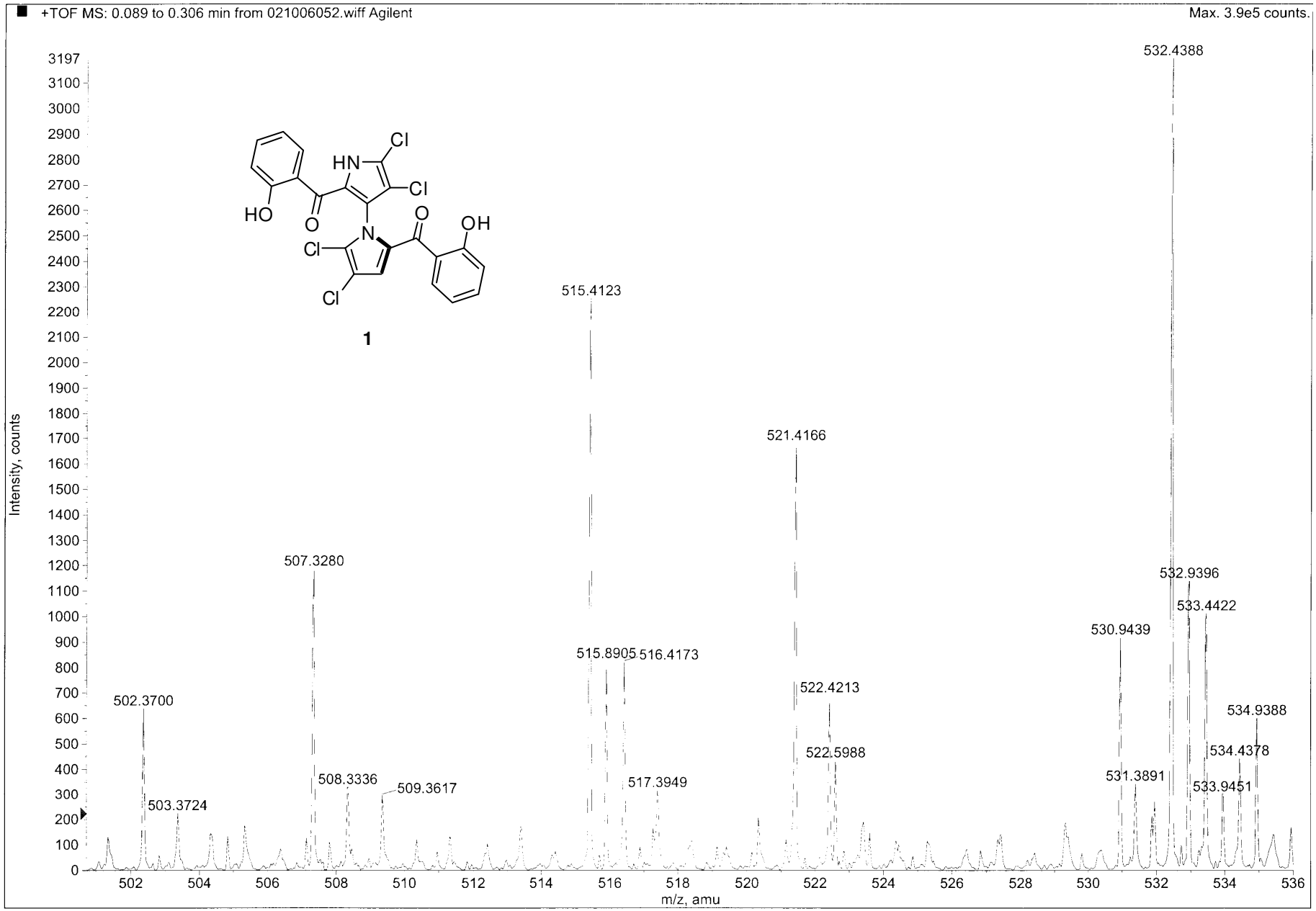
Acq. File: 021006052.wiff



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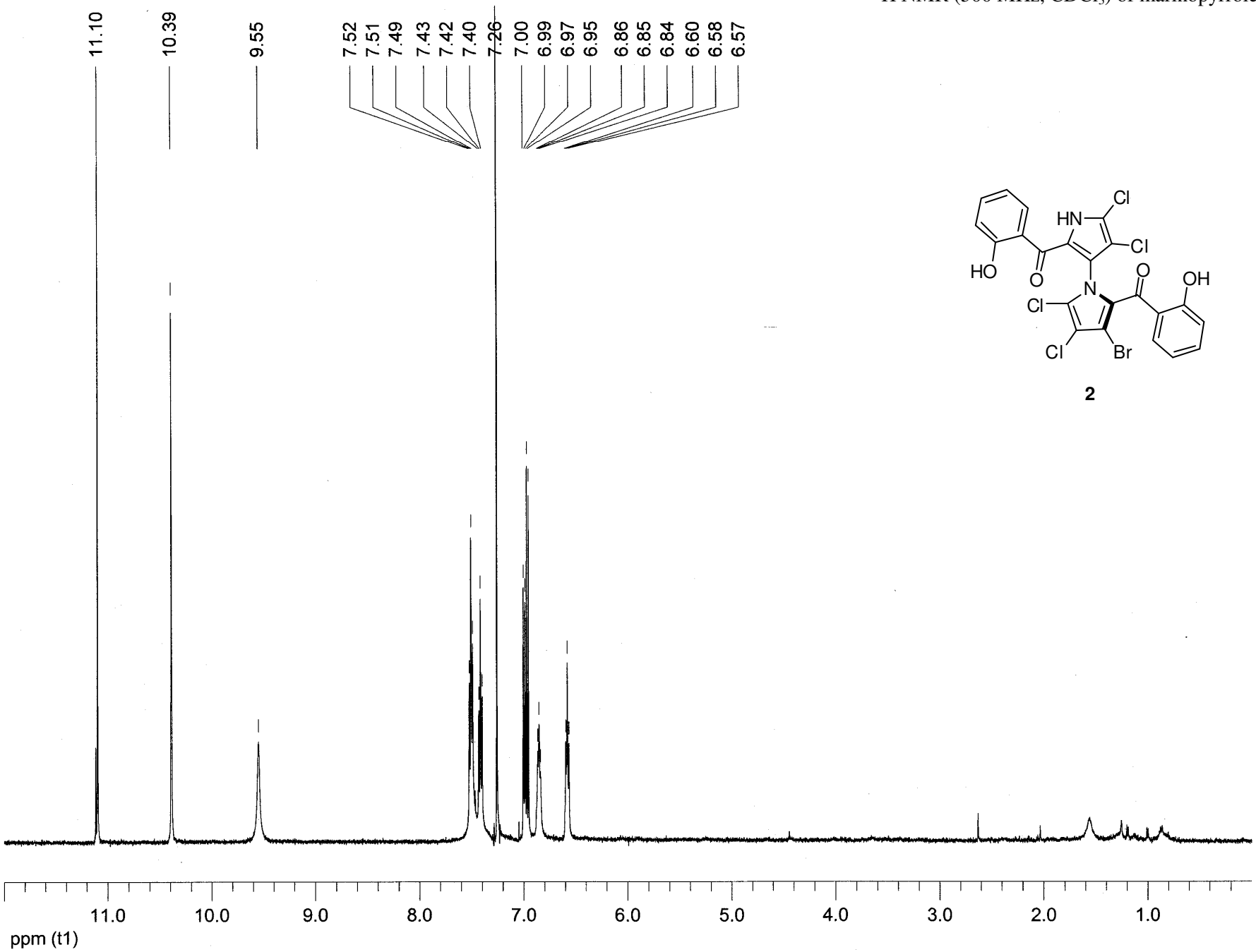
^{1}H NMR (500 MHz, $CDCl_3$) of marinopyrrole B (**2**)



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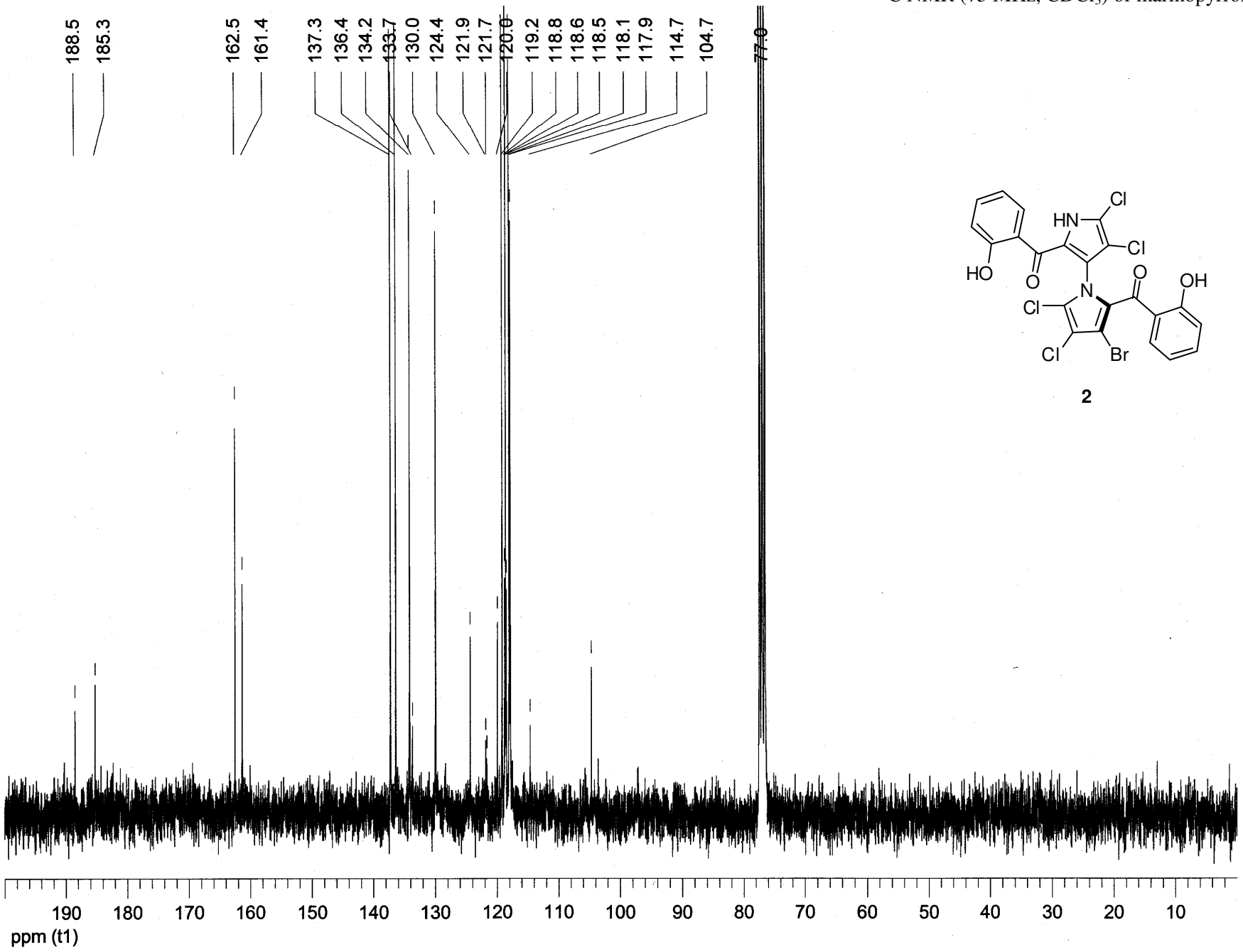
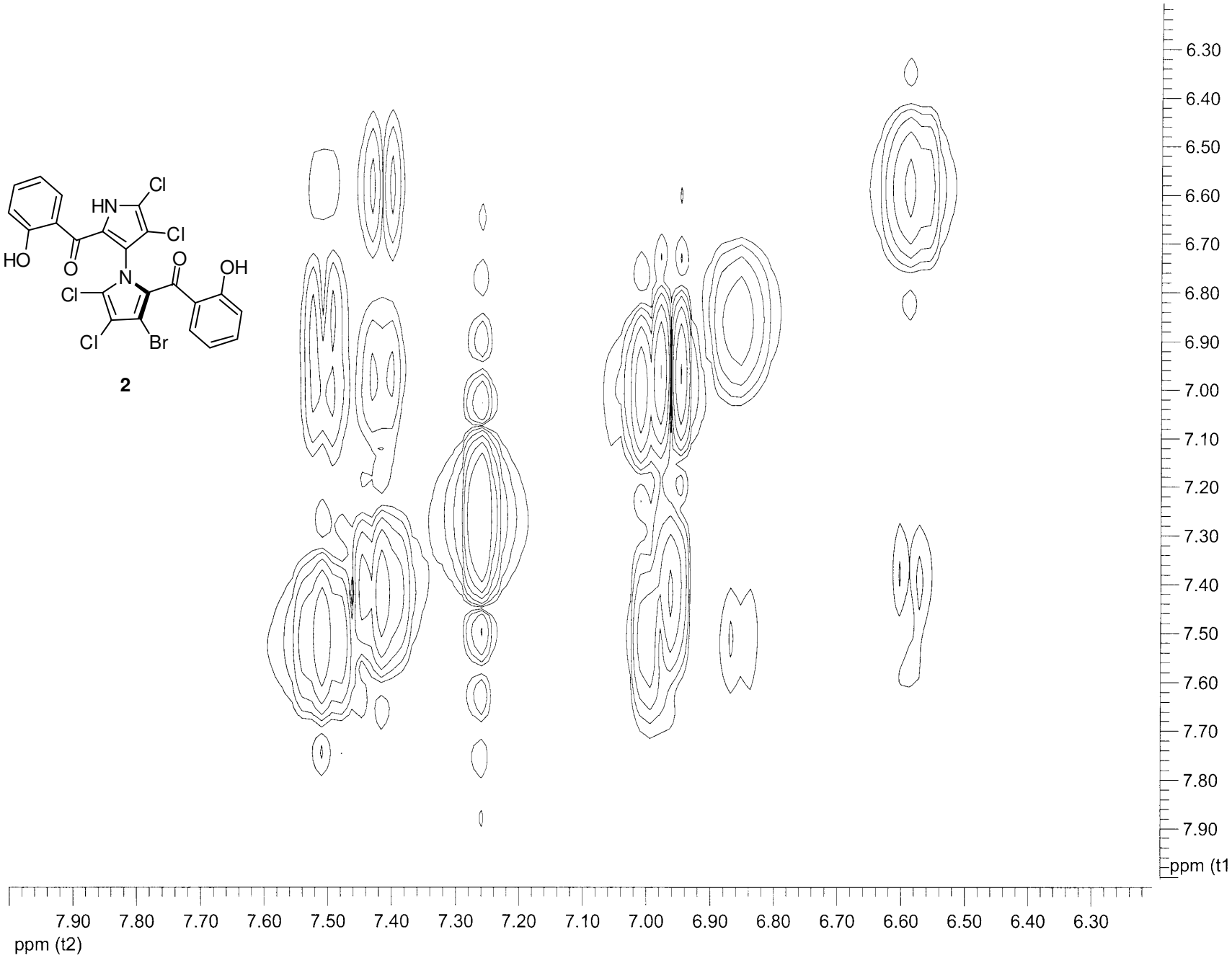
^{13}C NMR (75 MHz, $CDCl_3$) of marinopyrrole B (**2**)



2

COSY (500 MHz, $CDCl_3$) of marinopyrrole B (**2**)



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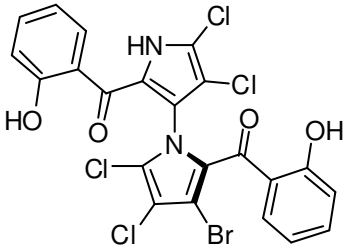
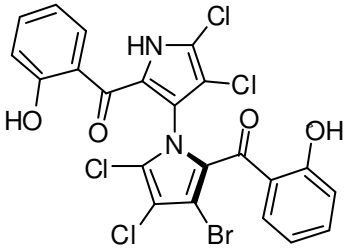
HSQC (500 MHz, $CDCl_3$) of marinopyrrole B (**2**)



2

HMBC (500 MHz, $CDCl_3$) of marinopyrrole B (**2**)



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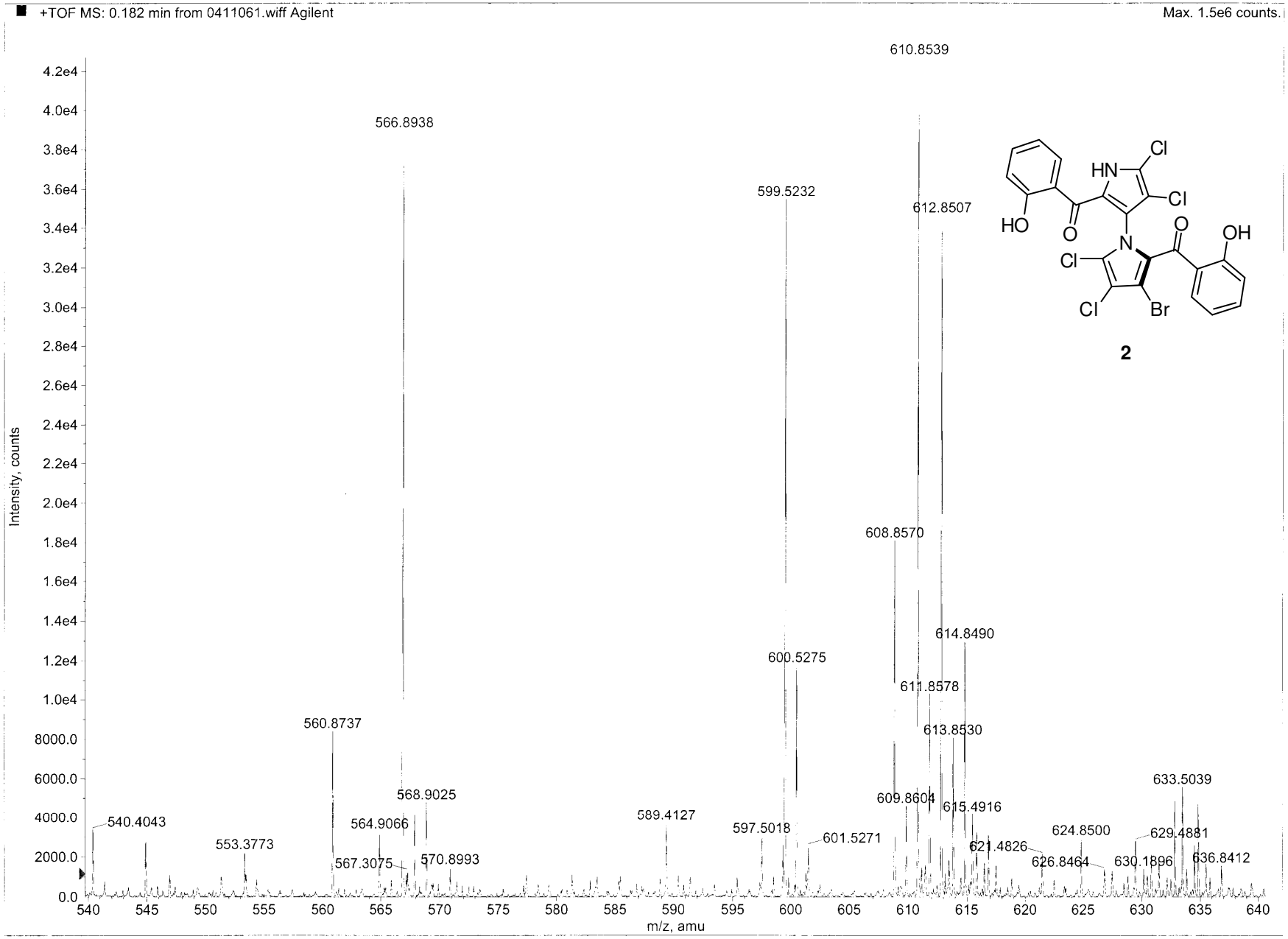
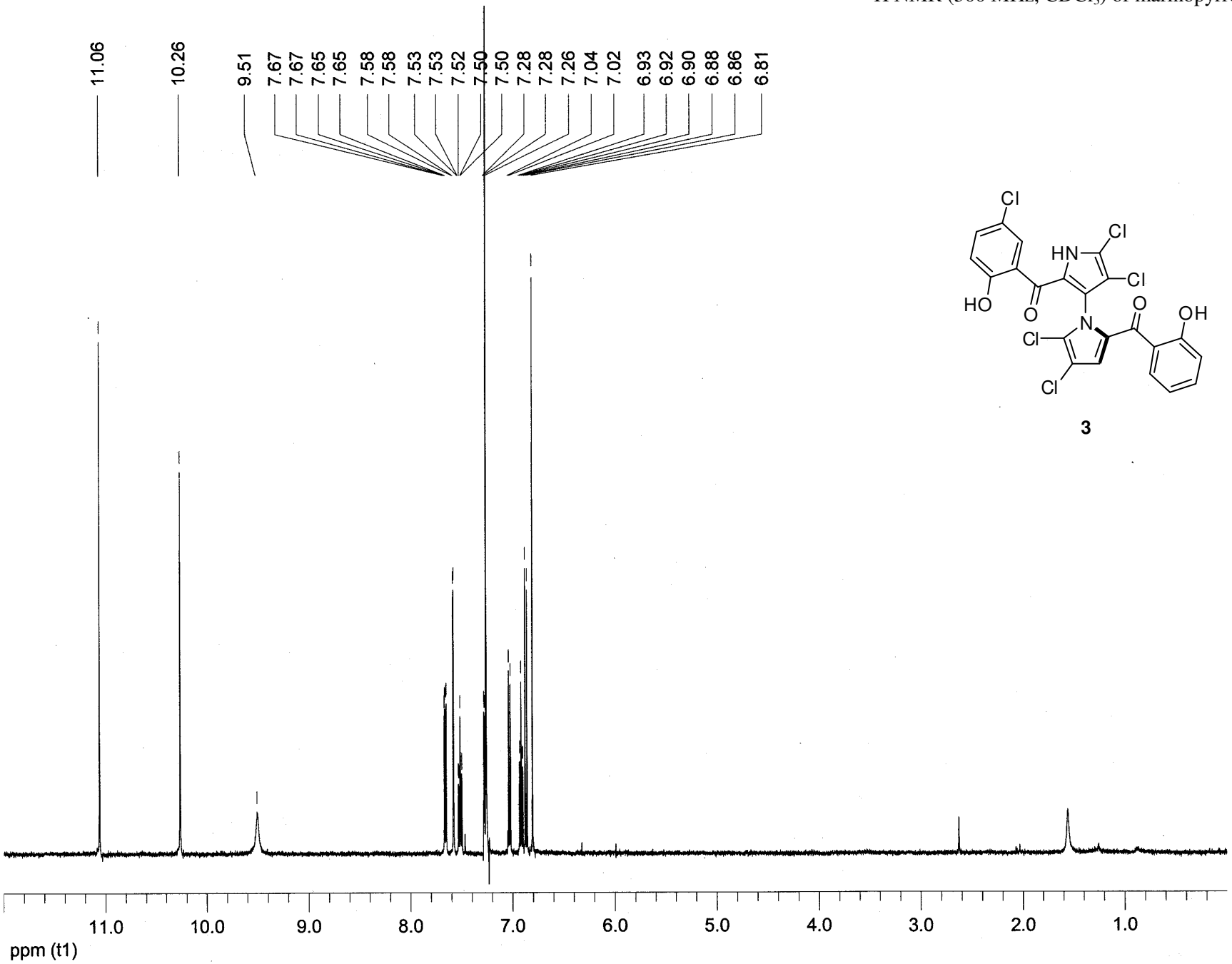
Acq. File: 0411061.wiff



^{1}H NMR (500 MHz, $CDCl_3$) of marinopyrrole C (**3**)



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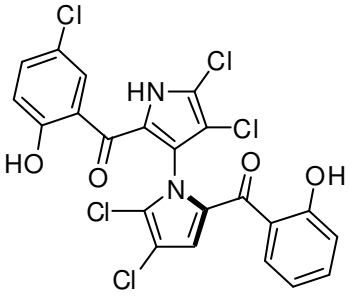
COSY (500 MHz, $CDCl_3$) of marinopyrrole C (**3**)



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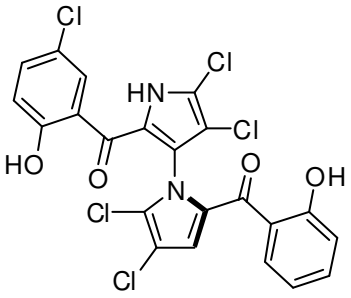
HSQC (500 MHz, $CDCl_3$) of marinopyrrole C (**3**)



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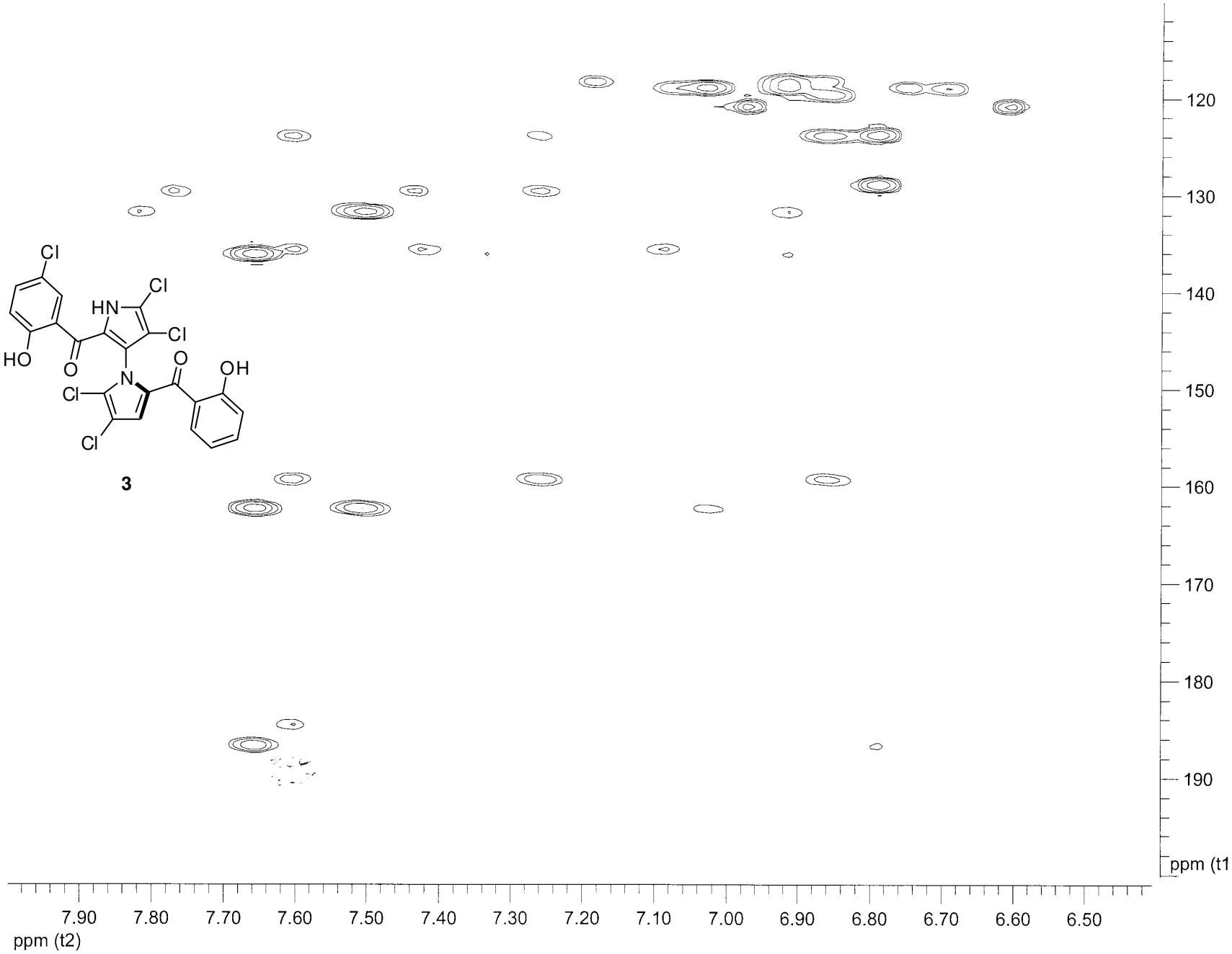
HMBC (500 MHz, $CDCl_3$) of marinopyrrole C (**3**)



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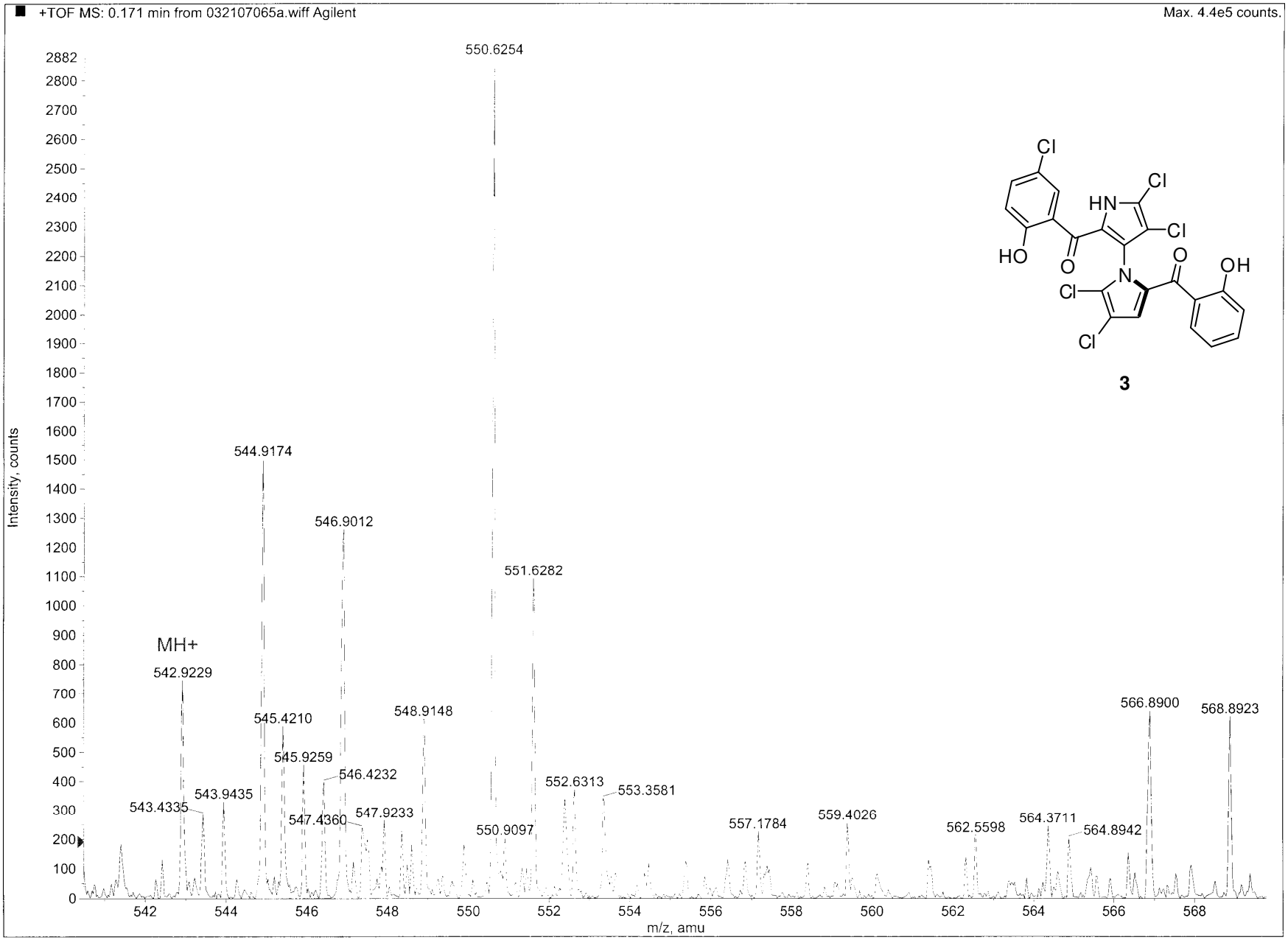
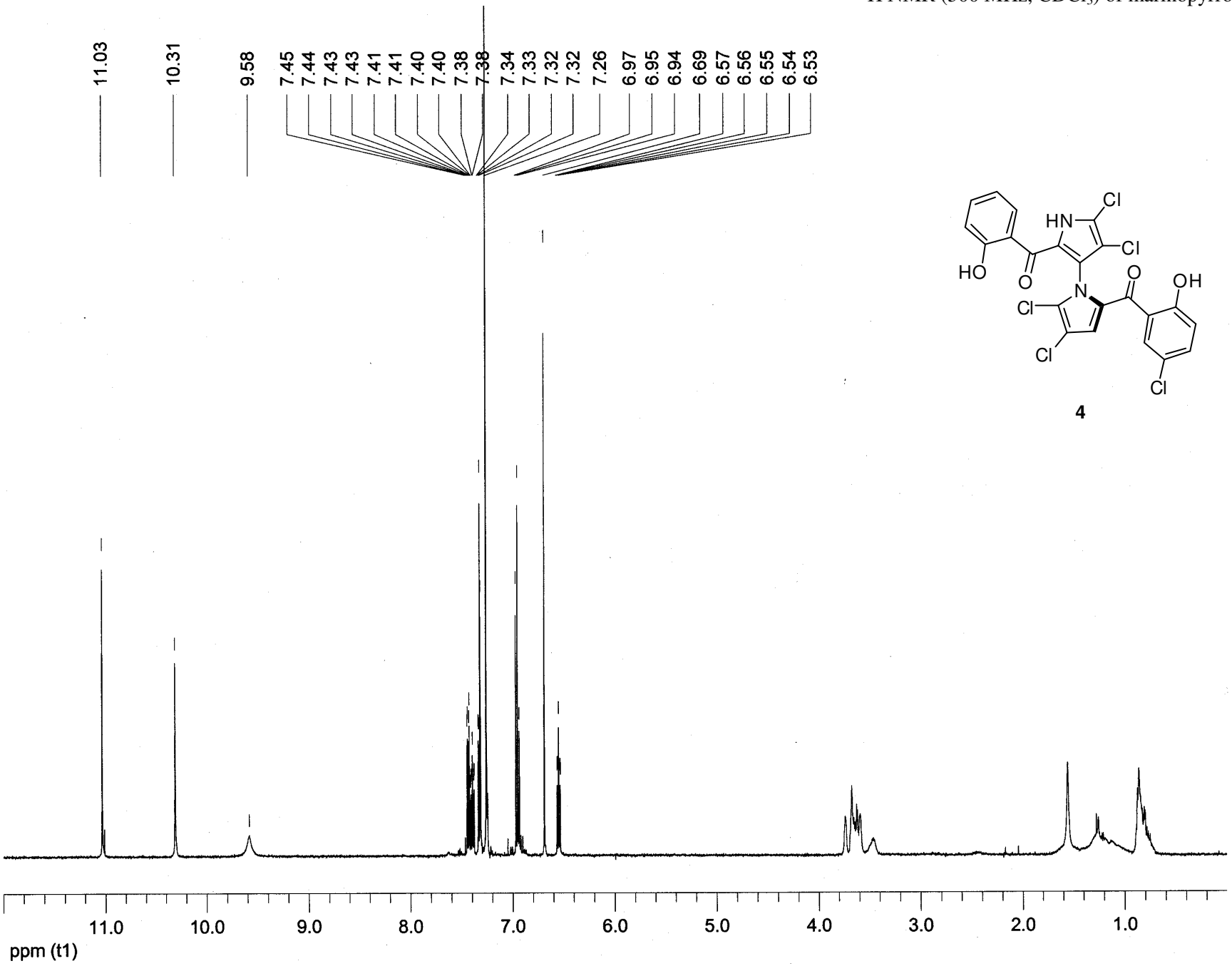
Acq. File: 032107065a.wiff



^{1}H NMR (500 MHz, $CDCl_3$) of marinopyrrole D (**4**)



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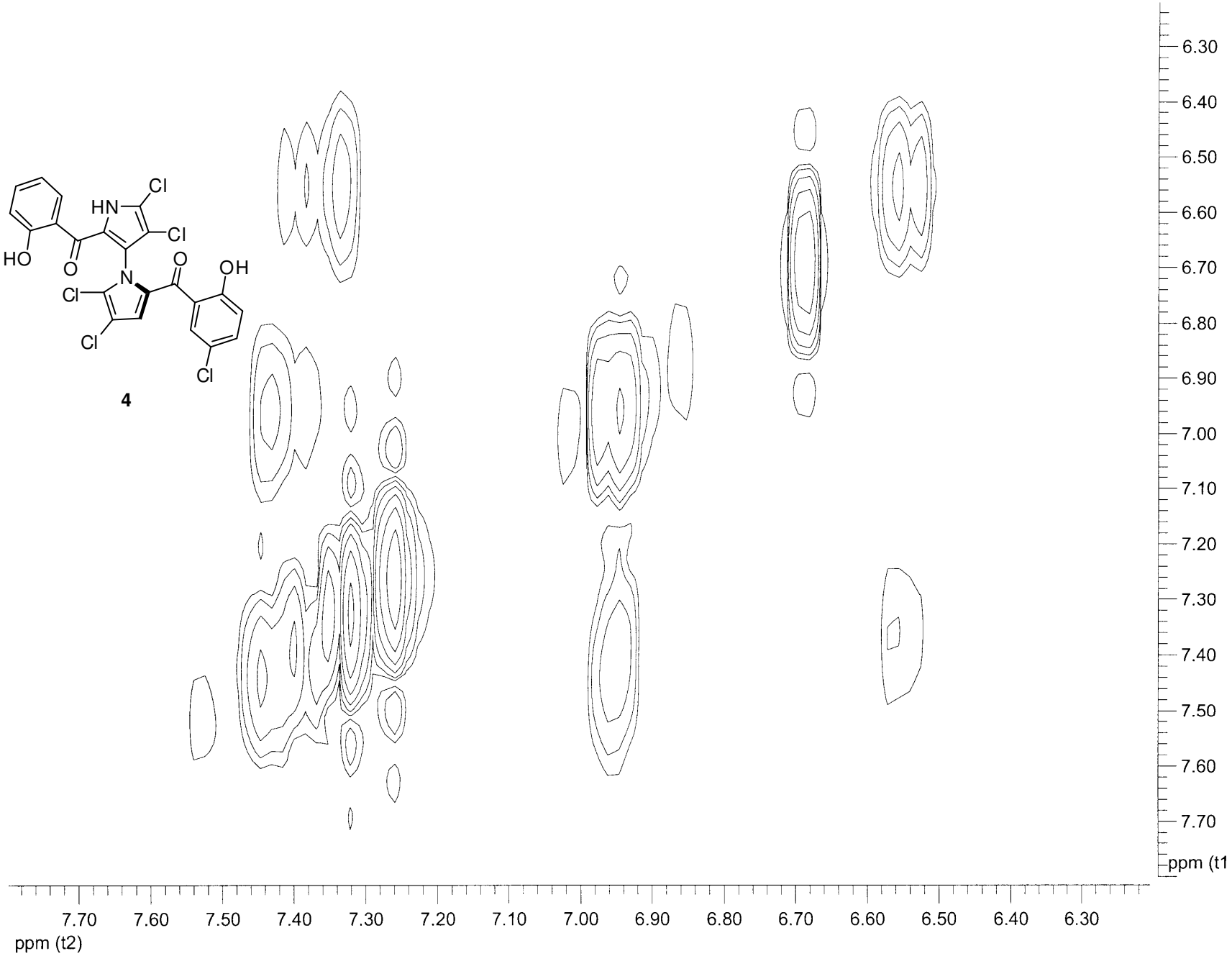
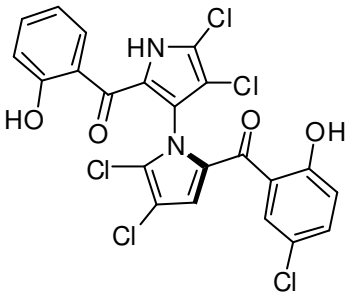
COSY (500 MHz, $CDCl_3$) of marinopyrrole D (**4**)



HSQC (500 MHz, $CDCl_3$) of marinopyrrole D (**4**)



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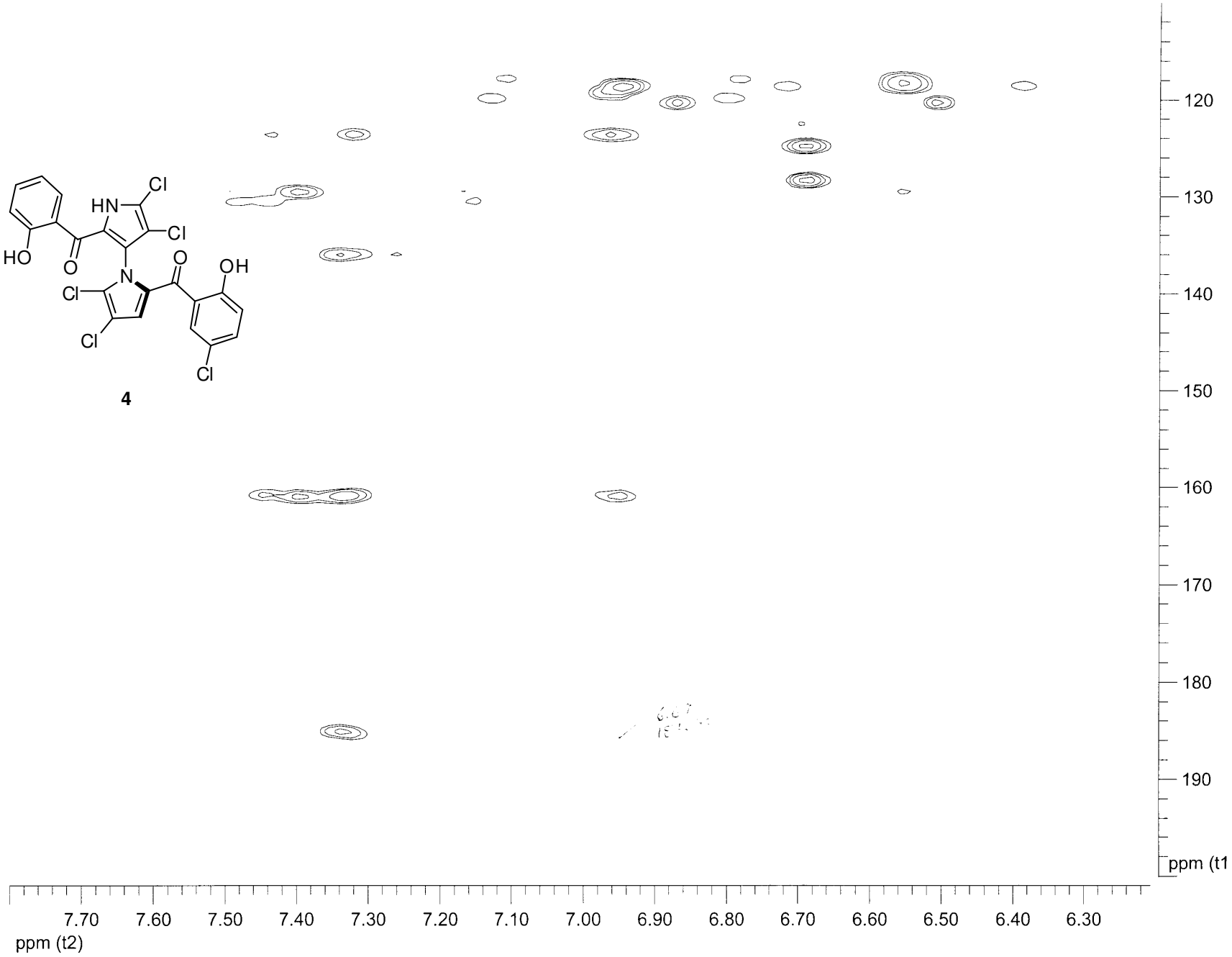
HMBC (500 MHz, $CDCl_3$) of marinopyrrole D (**4**)



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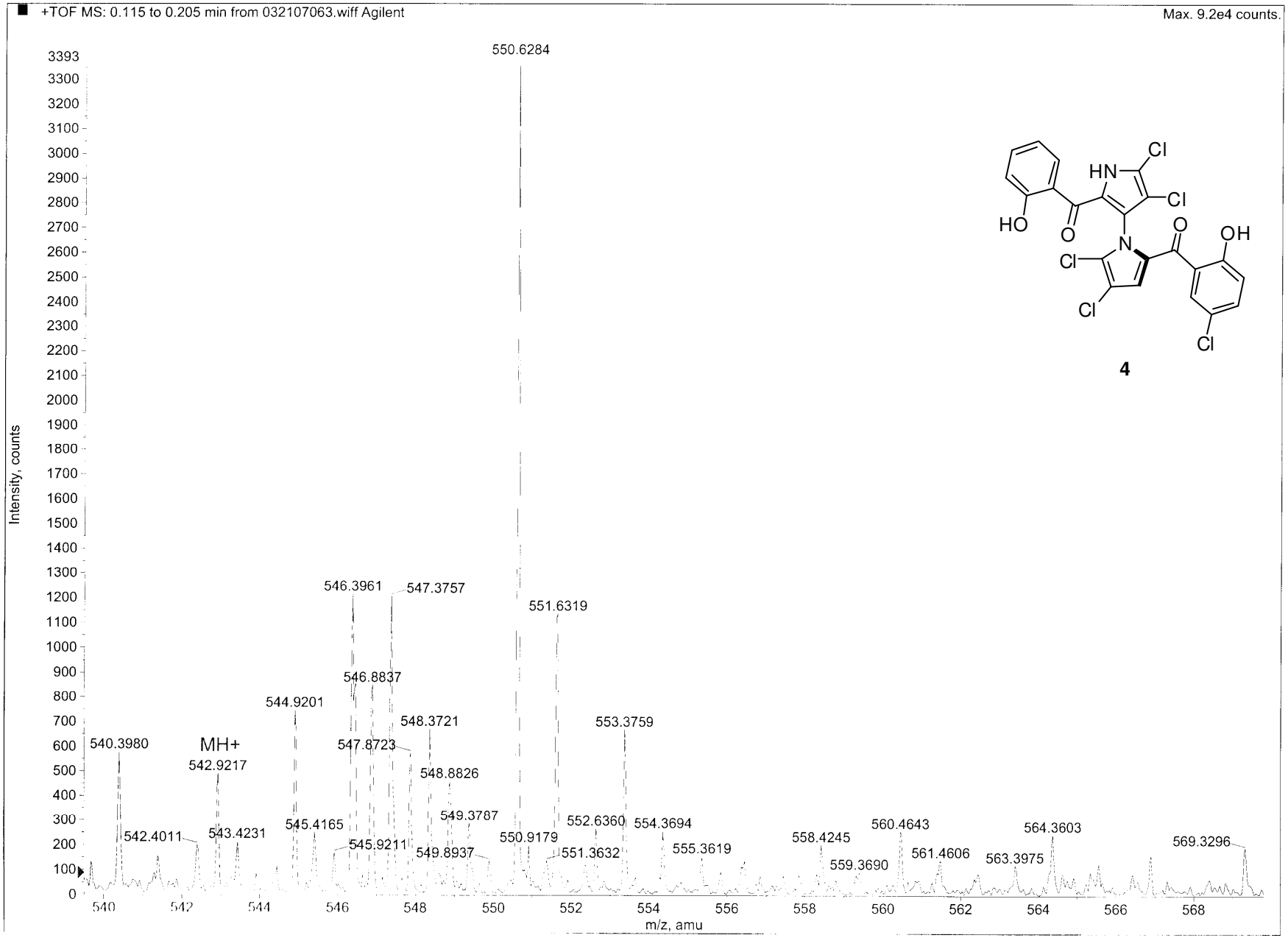
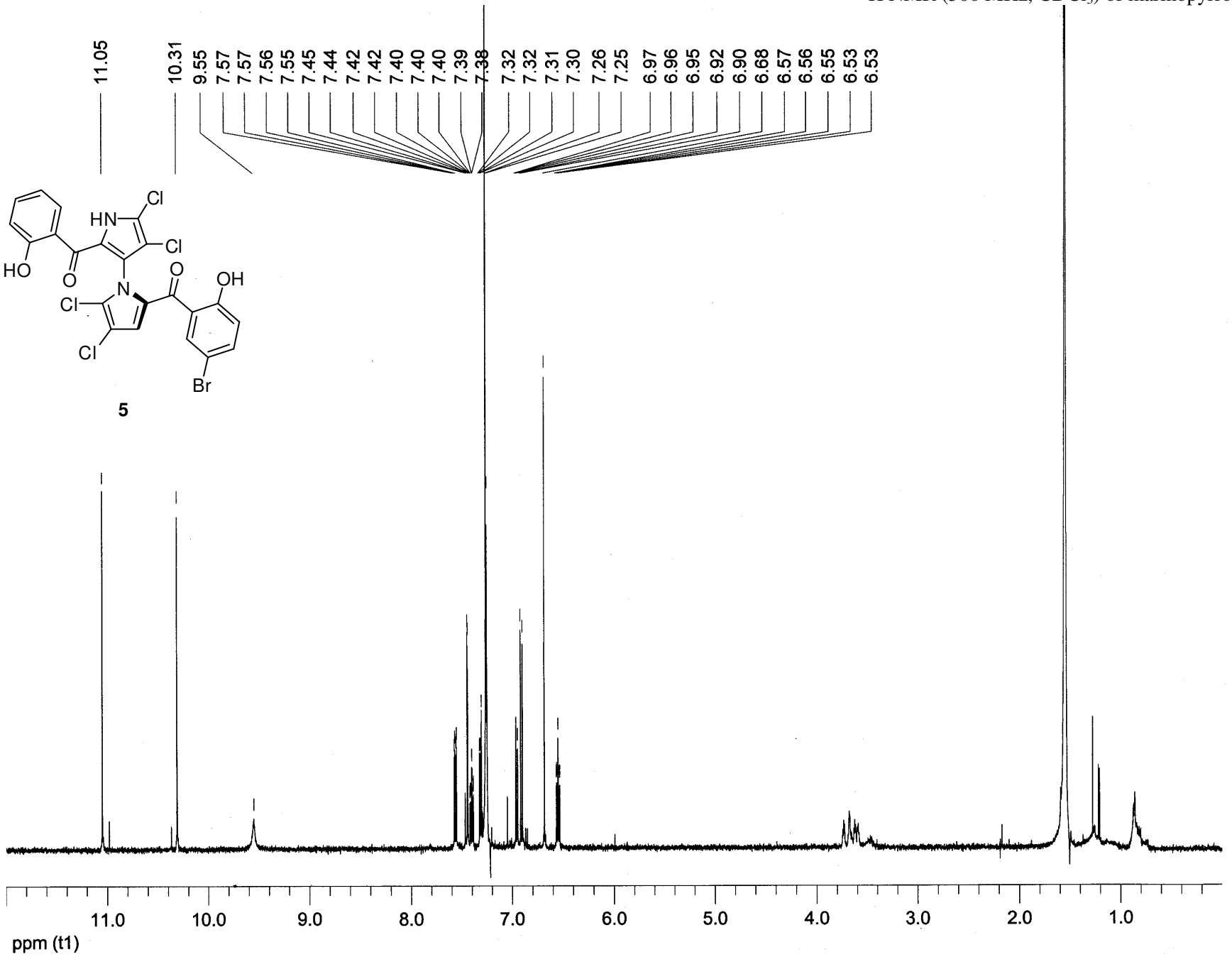
Acq. Date: Wednesday, March 21, 2007

Acq. File: 032107063.wiff



^{1}H NMR (500 MHz, $CDCl_3$) of marinopyrrole E (**5**)



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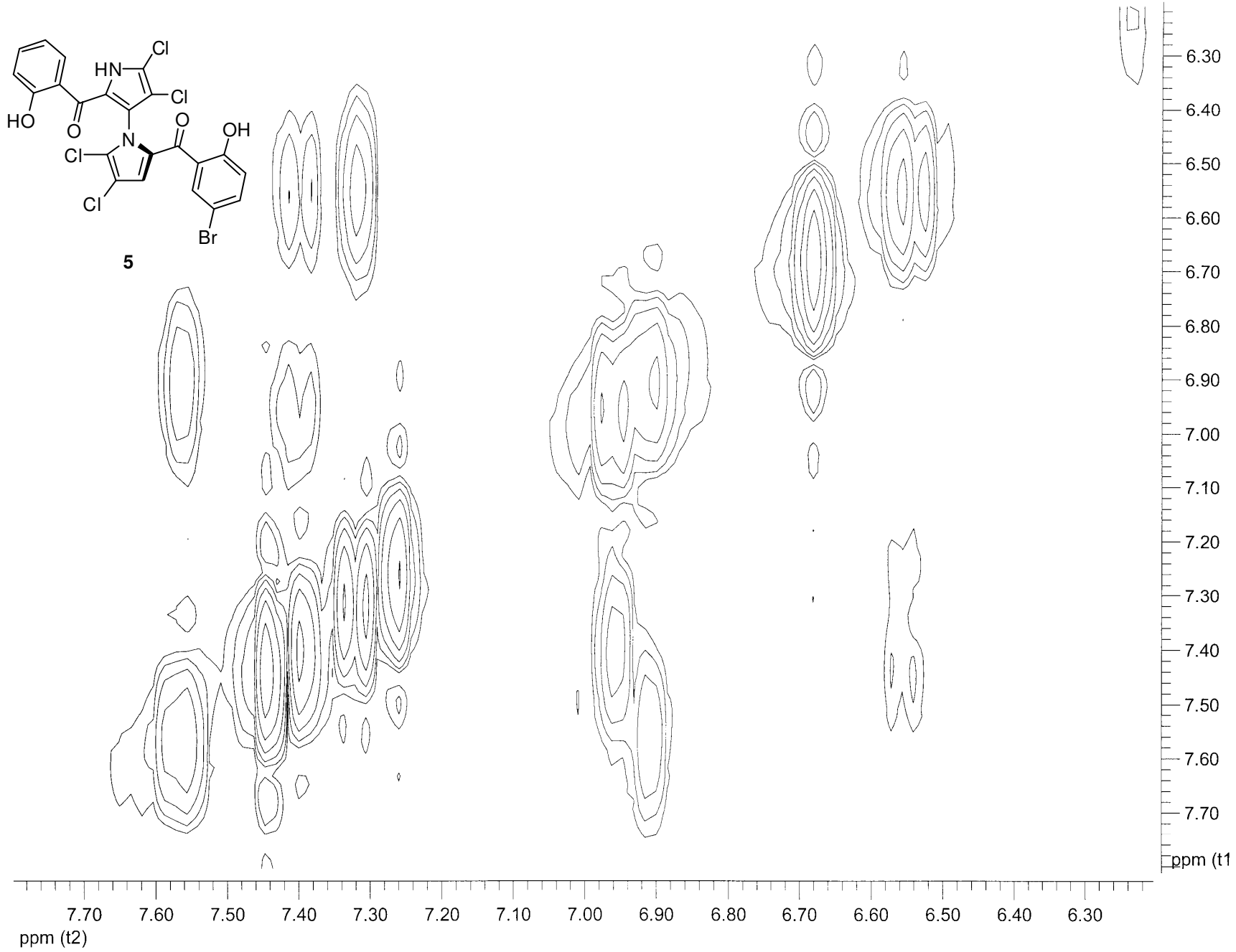
COSY (500 MHz, $CDCl_3$) of marinopyrrole E (**5**)



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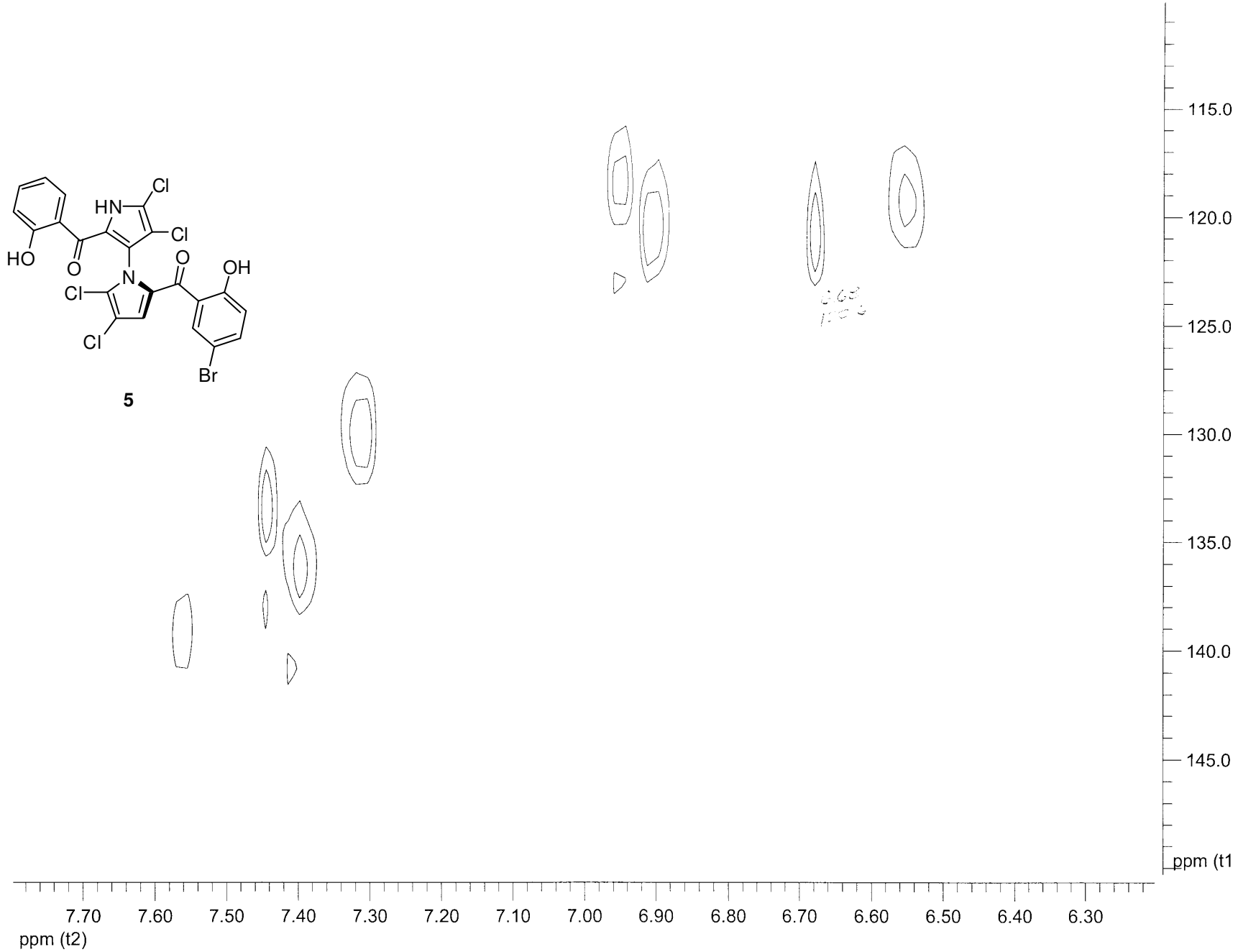
HSQC (500 MHz, $CDCl_3$) of marinopyrrole E (**5**)



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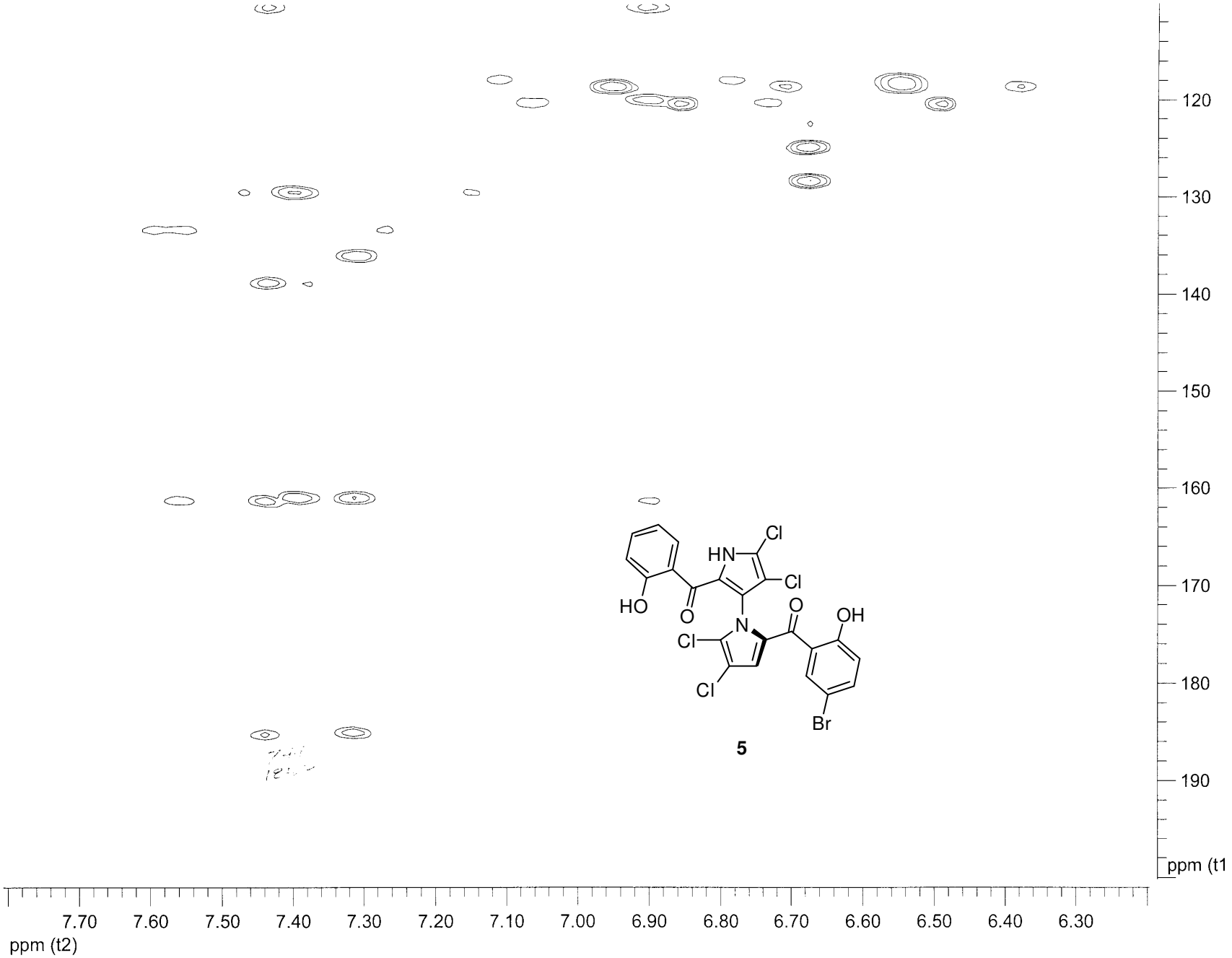
HMBC (500 MHz, $CDCl_3$) of marinopyrrole E (**5**)



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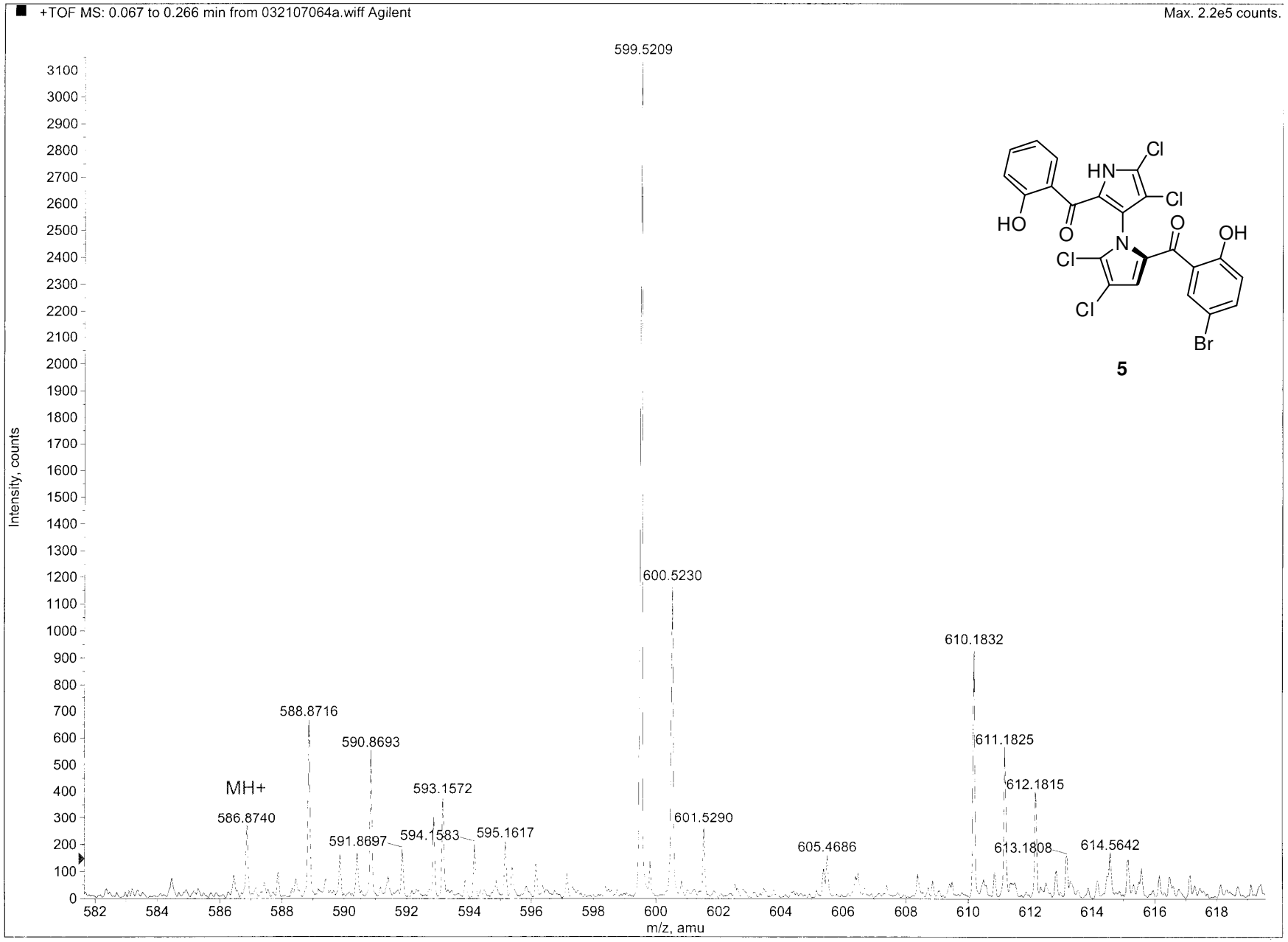
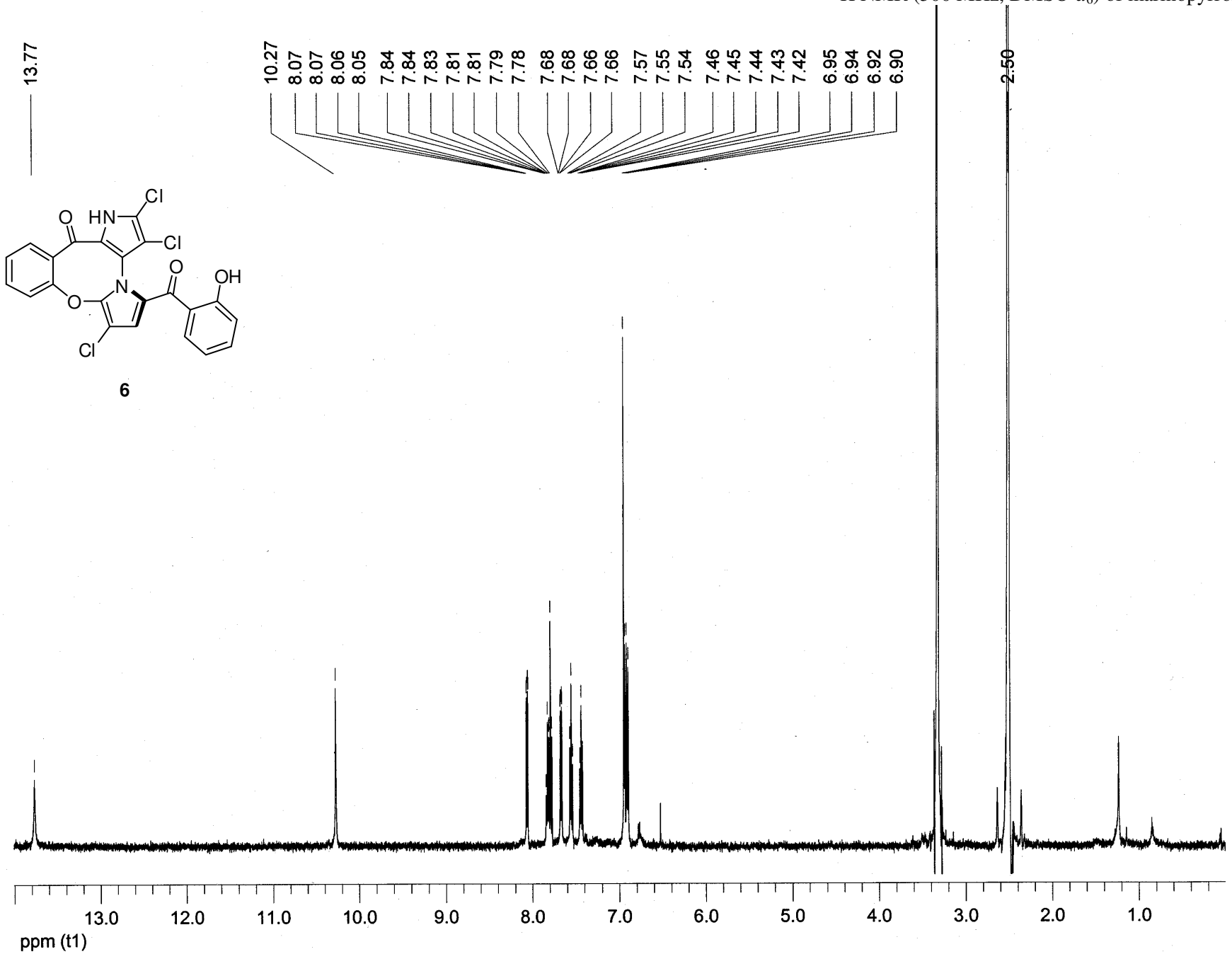
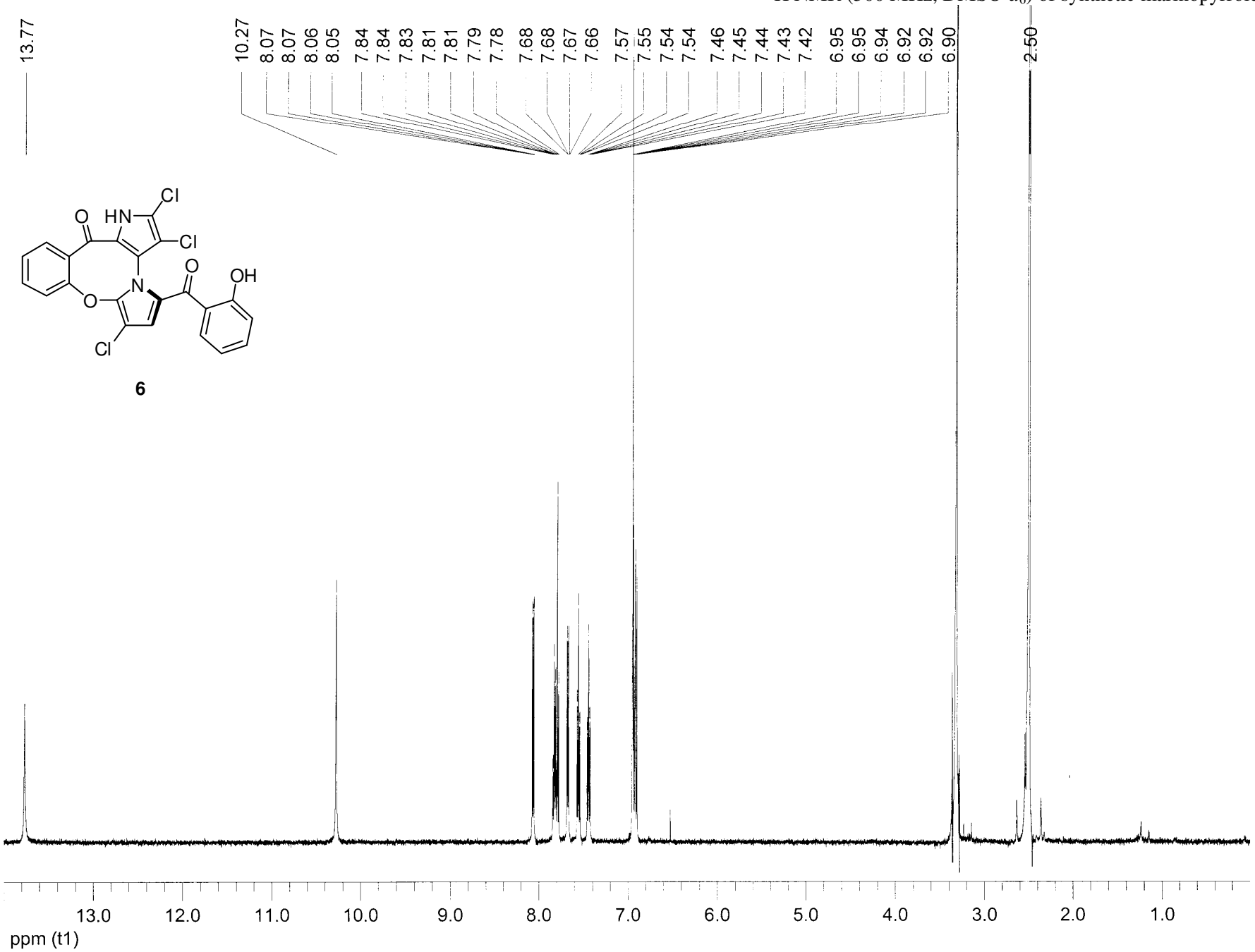


^{1}H NMR (500 MHz, DMSO-d_6) of marinopyrrole F (**6**)



^{1}H NMR (500 MHz, DMSO-d_6) of synthetic marinopyrrole F (**6**)



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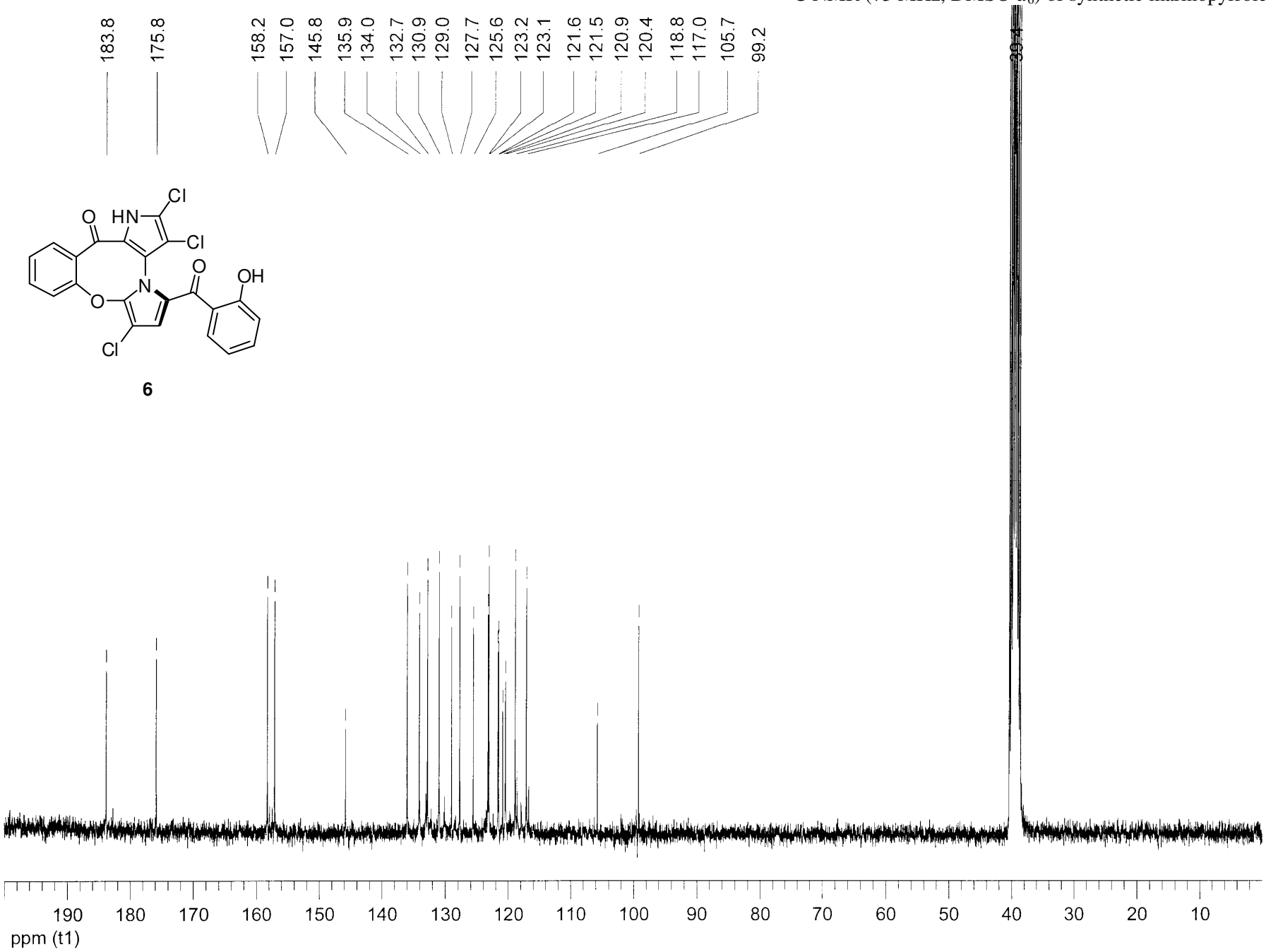
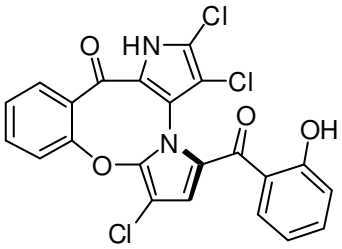
^{13}C NMR (75 MHz, DMSO-d_6) of synthetic marinopyrrole F (**6**)



COSY NMR (500 MHz, DMSO-d_6) of synthetic marinopyrrole F (**6**)



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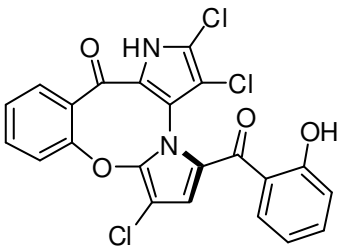
HSQC NMR (500 MHz, DMSO-d_6) of synthetic marinopyrrole F (**6**)



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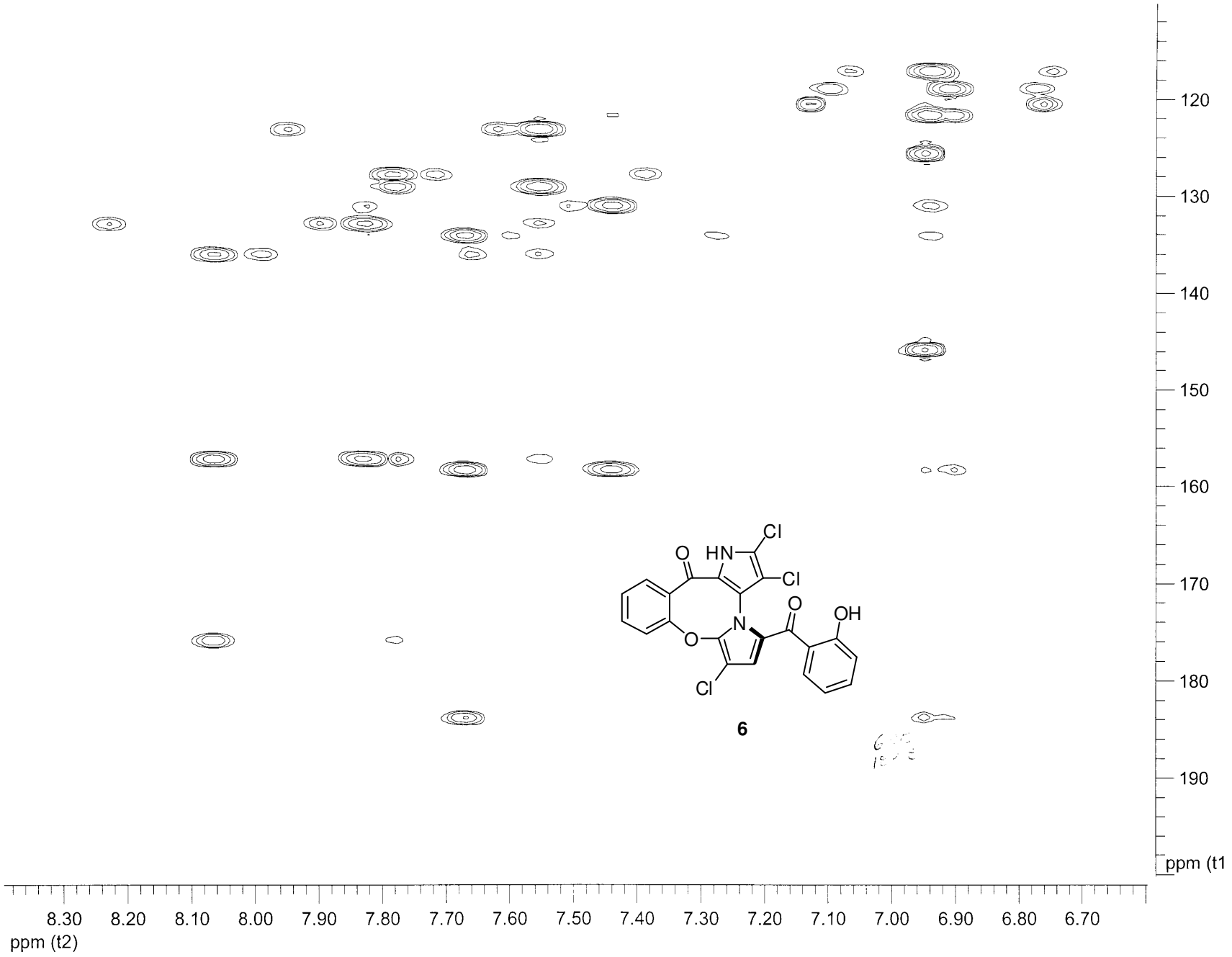
HMBC NMR (500 MHz, DMSO-d_6) of synthetic marinopyrrole F (**6**)



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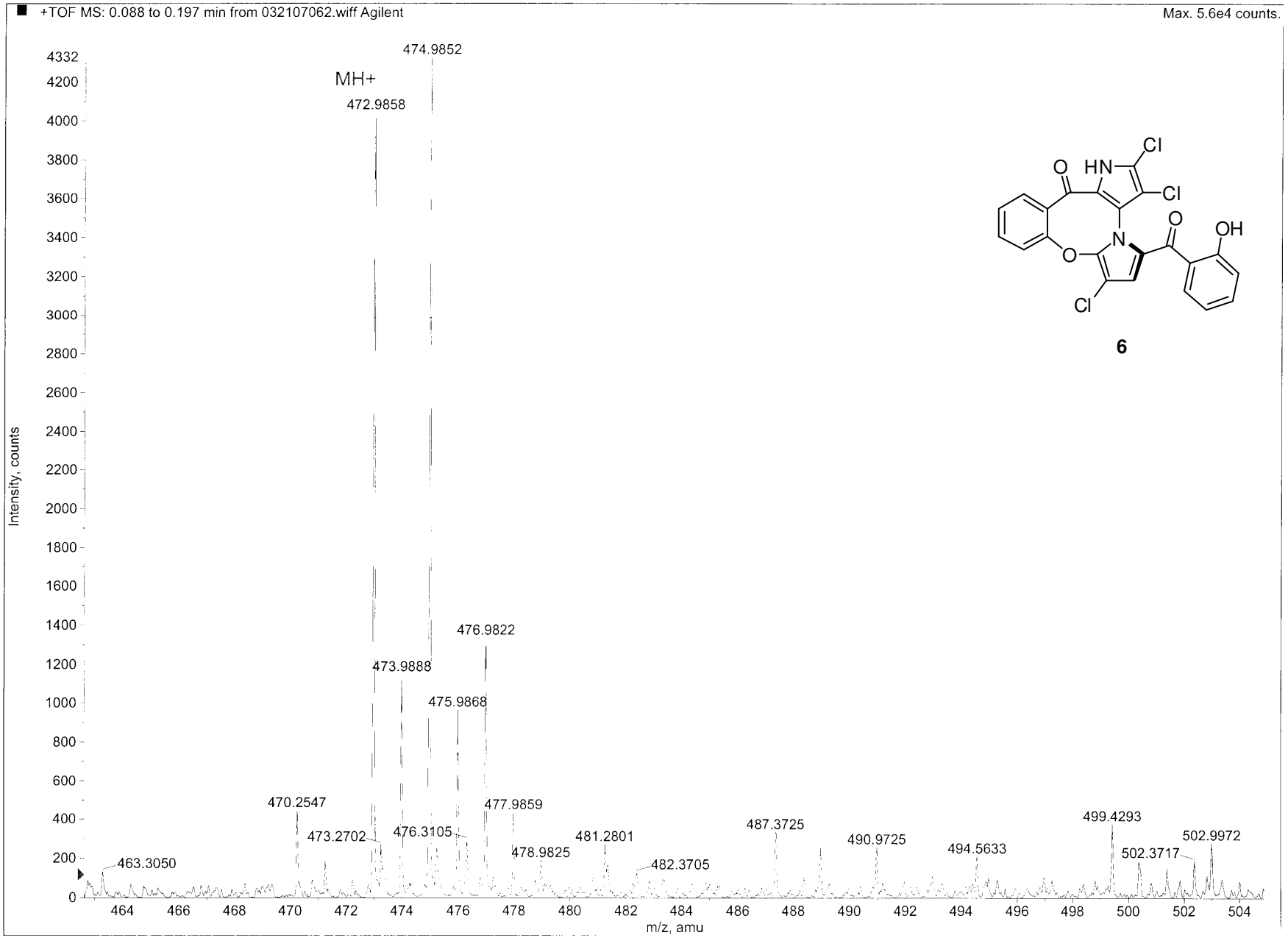

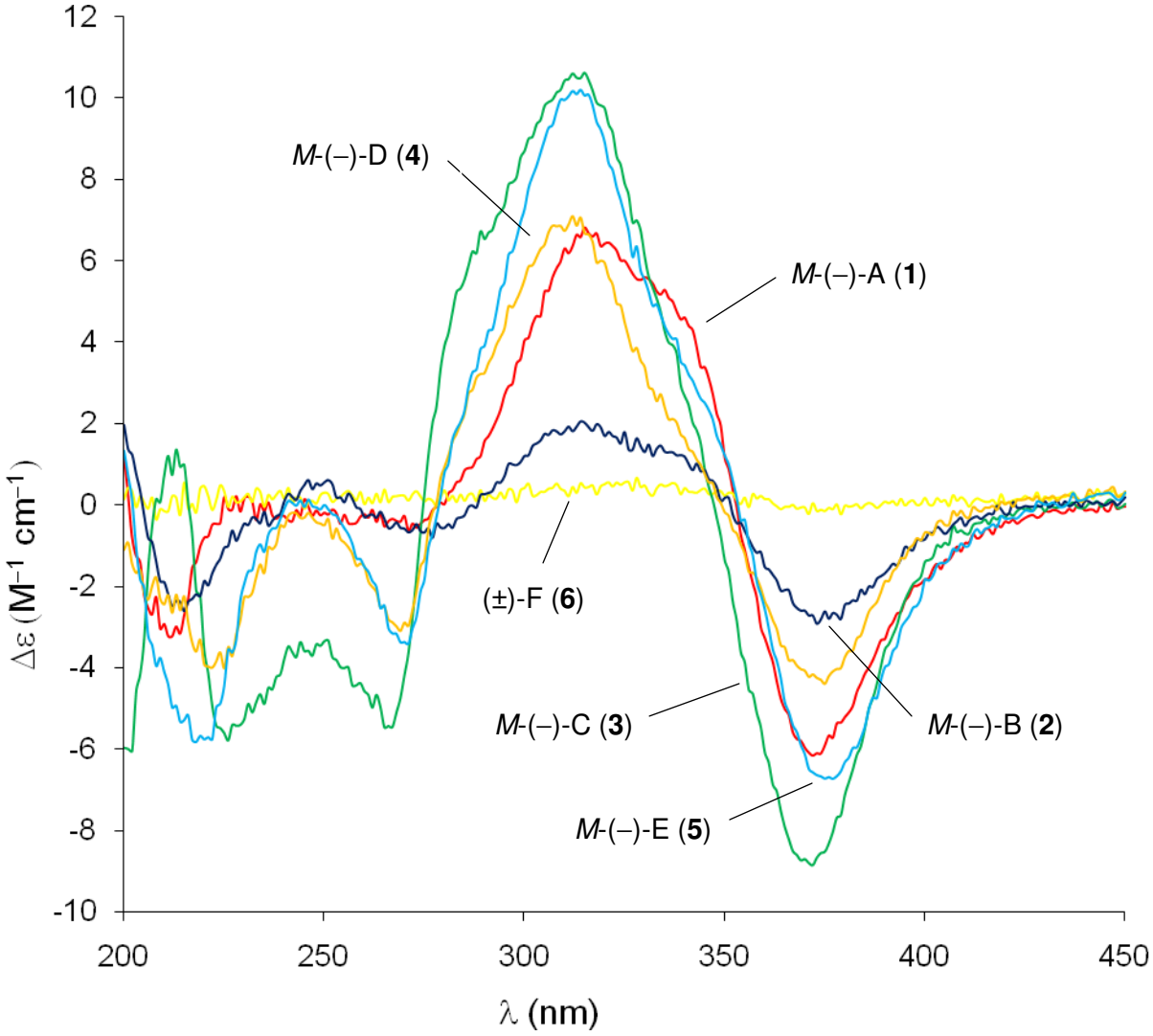
12
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8
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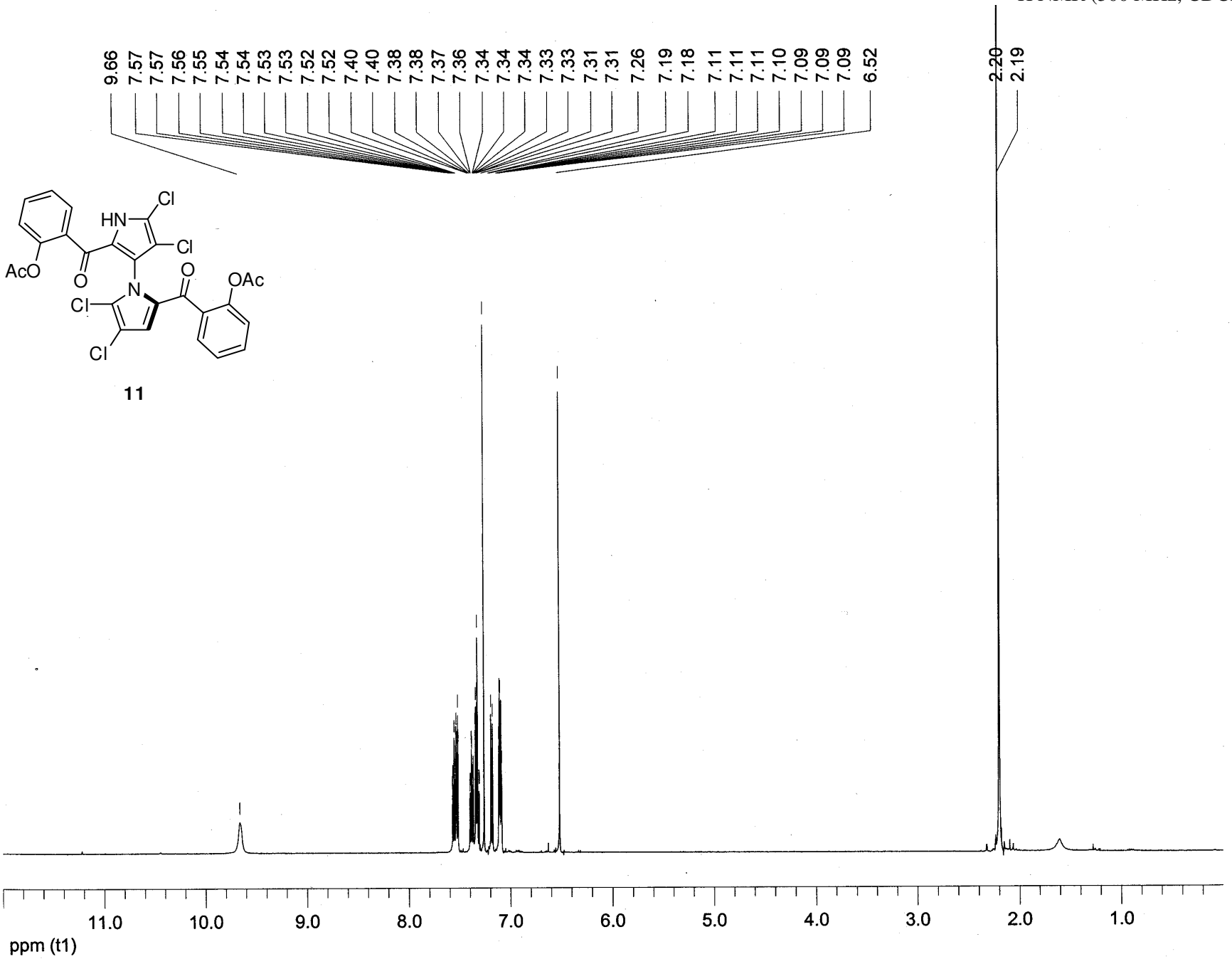
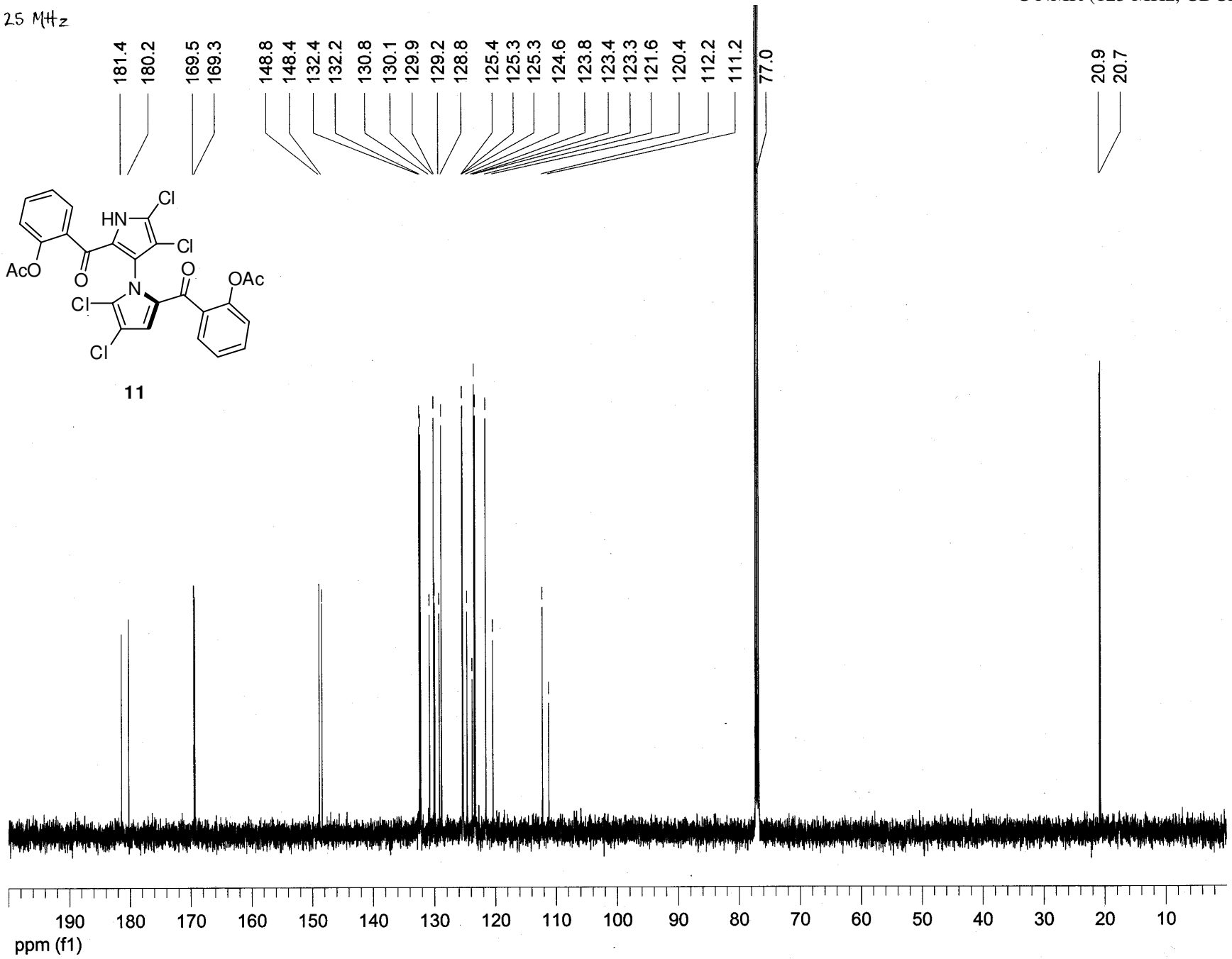
-2
-4
-6
-8
-10
200
250
300
350
400
450
Δε (M⁻¹ cm⁻¹)
λ (nm)
M-(–)-D (4)
M-(–)-A (1)
(±)-F (6)
M-(–)-C (3)
M-(–)-B (2)
M-(–)-E (5)

^{1}H NMR (500 MHz, $CDCl_3$) of **11**



^{13}C NMR (125 MHz, $CDCl_3$) of **11**

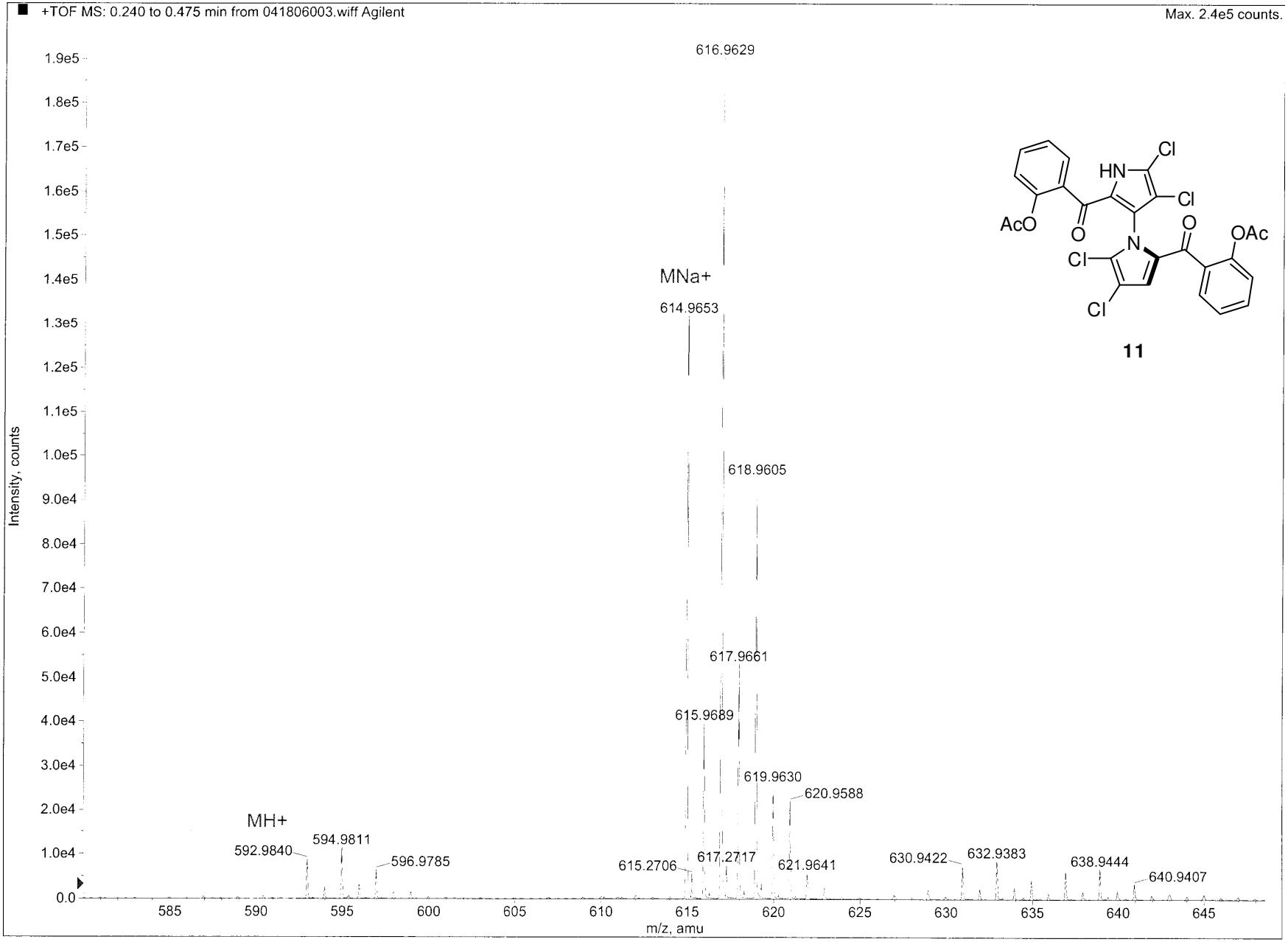


Polarity/Scan Type: Positive

Sample Name: flch3144

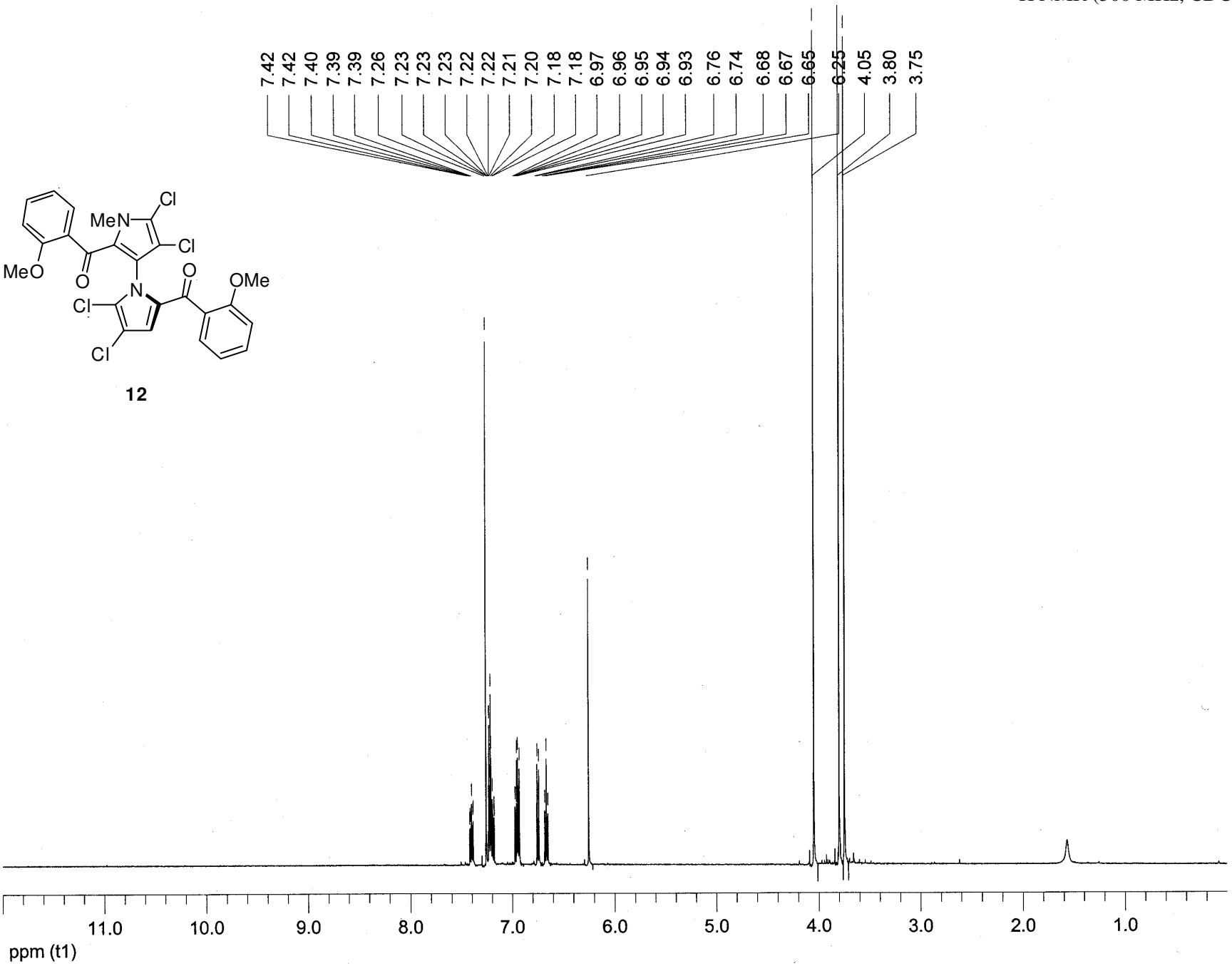
Acq. Date: Tuesday, April 18, 2006

Acq. File: 041806003.wiff



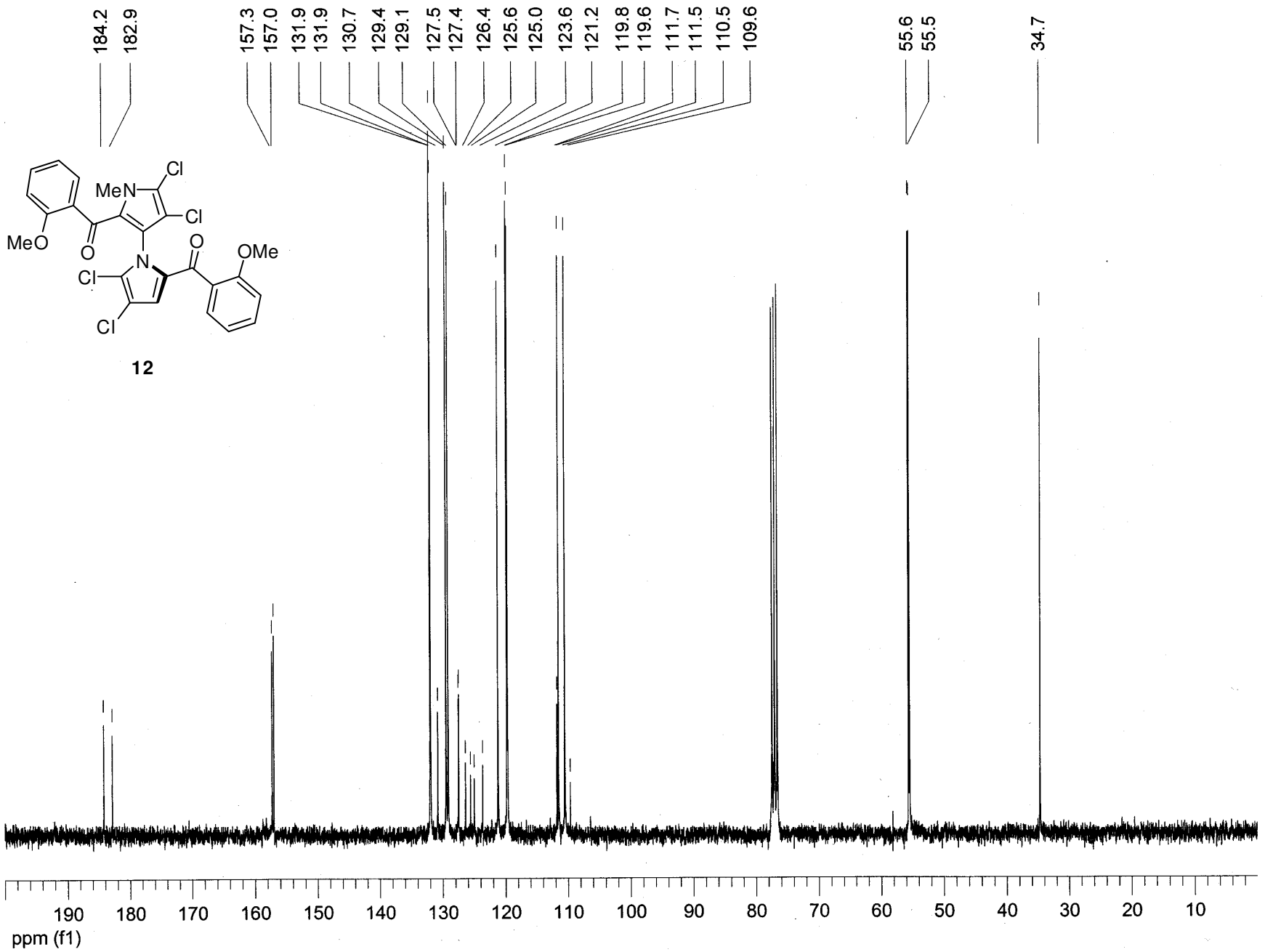
11

^{1}H NMR (500 MHz, $CDCl_3$) of **12**



12

^{13}C NMR (75 MHz, $CDCl_3$) of **12**



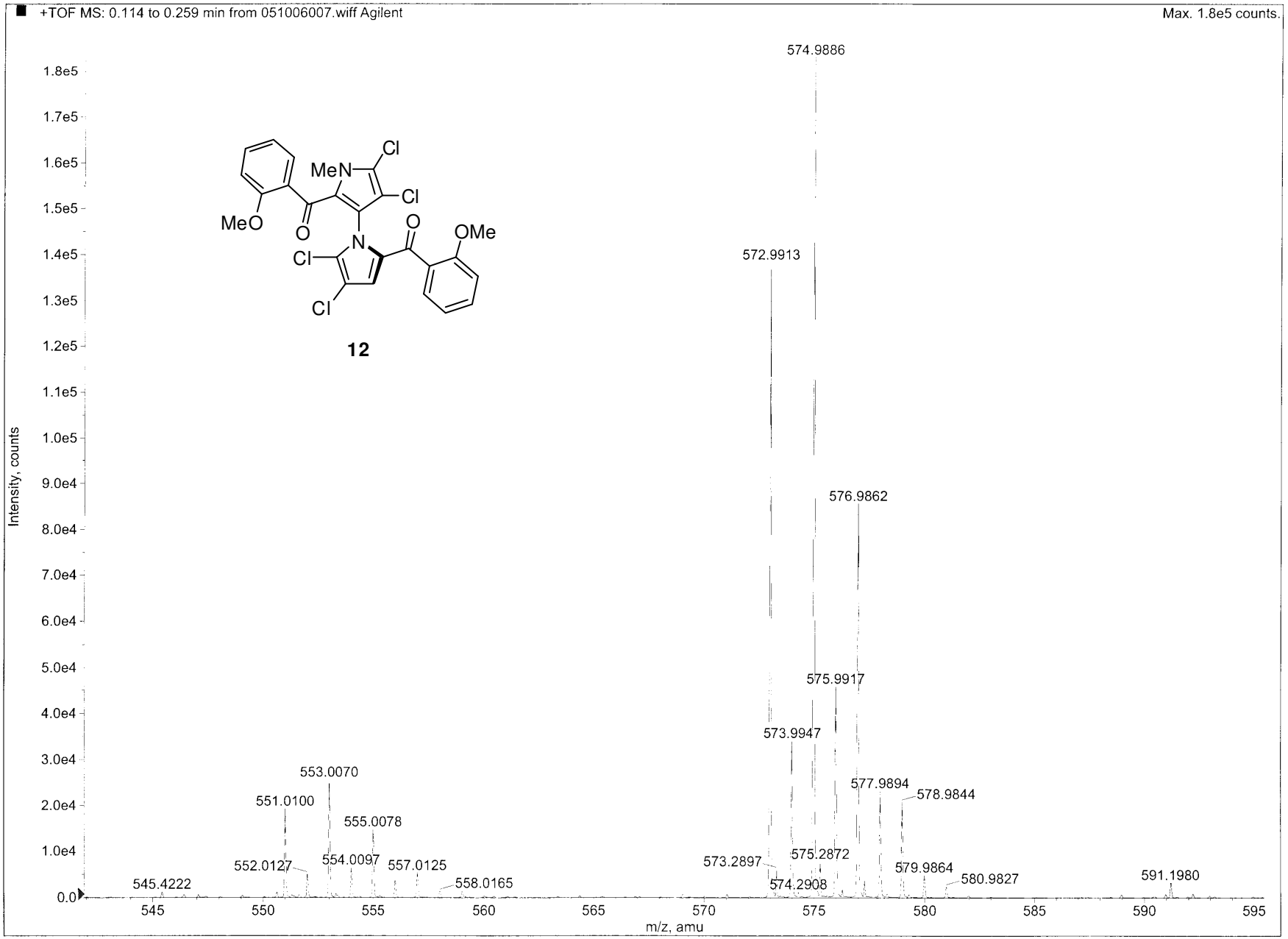
12

Polarity/Scan Type: Positive

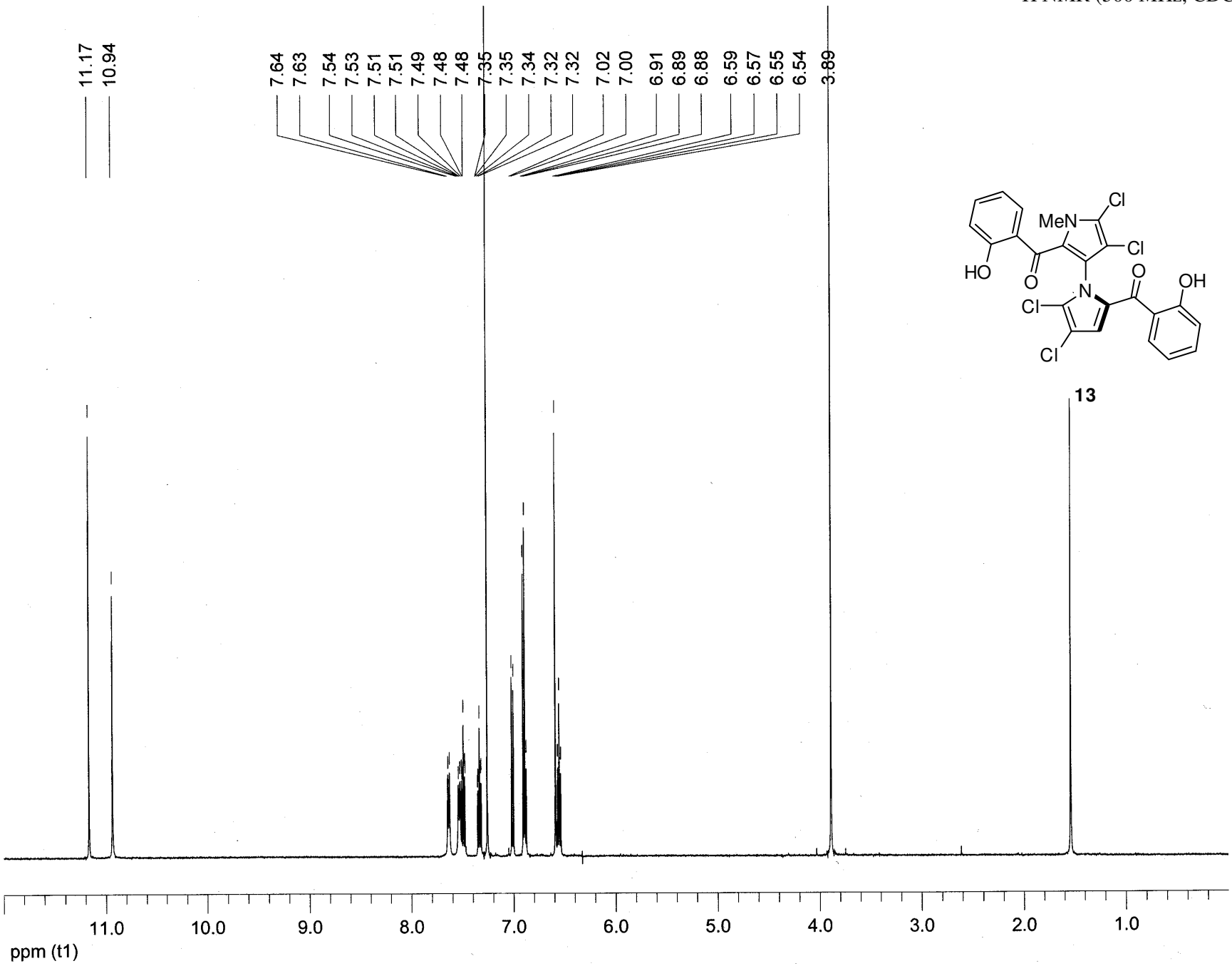
Sample Name: flch3956

Acq. Date: Wednesday, May 10, 2006

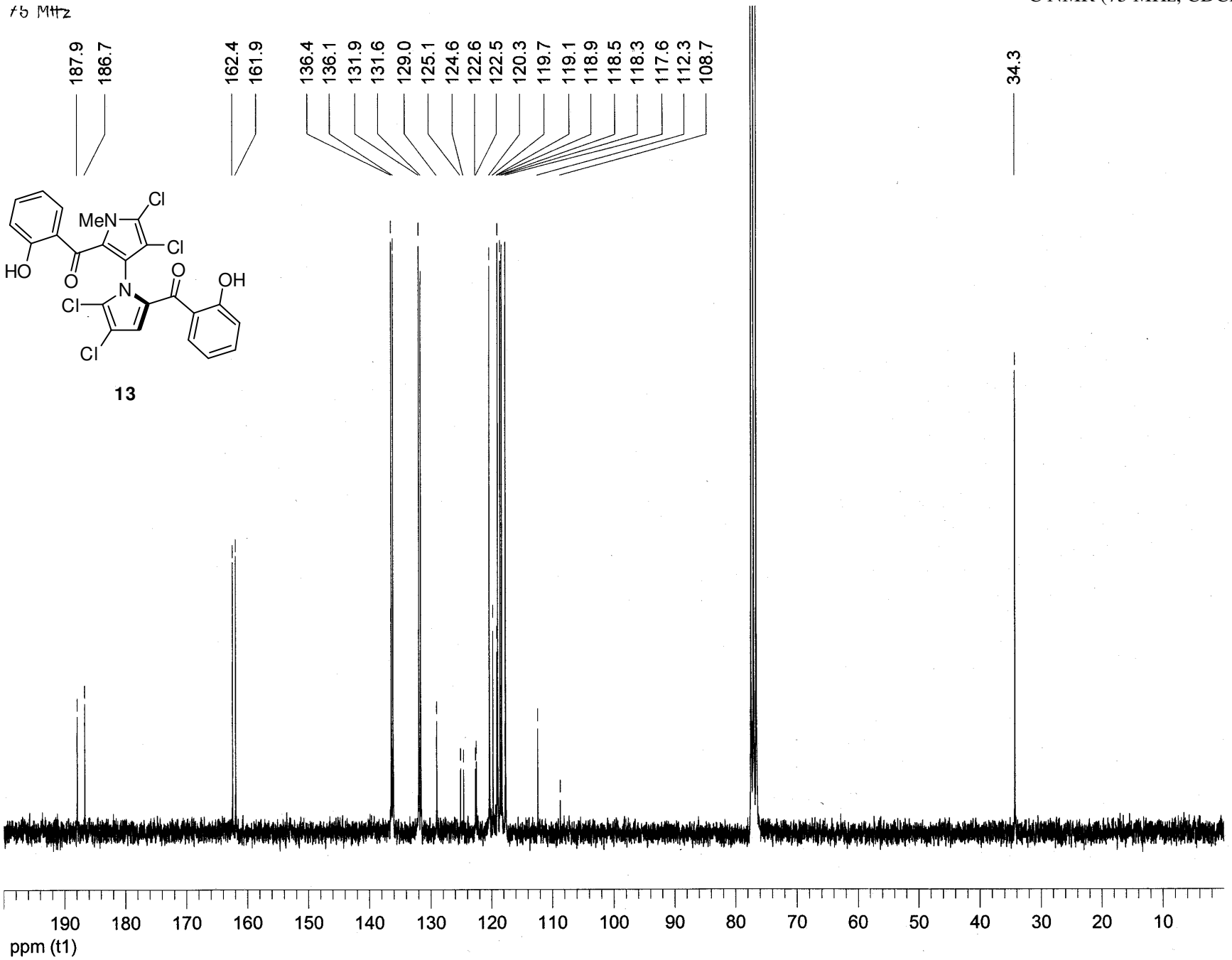
Acq. File: 051006007.wiff



^{1}H NMR (500 MHz, $CDCl_3$) of **13**



^{13}C NMR (75 MHz, $CDCl_3$) of **13**

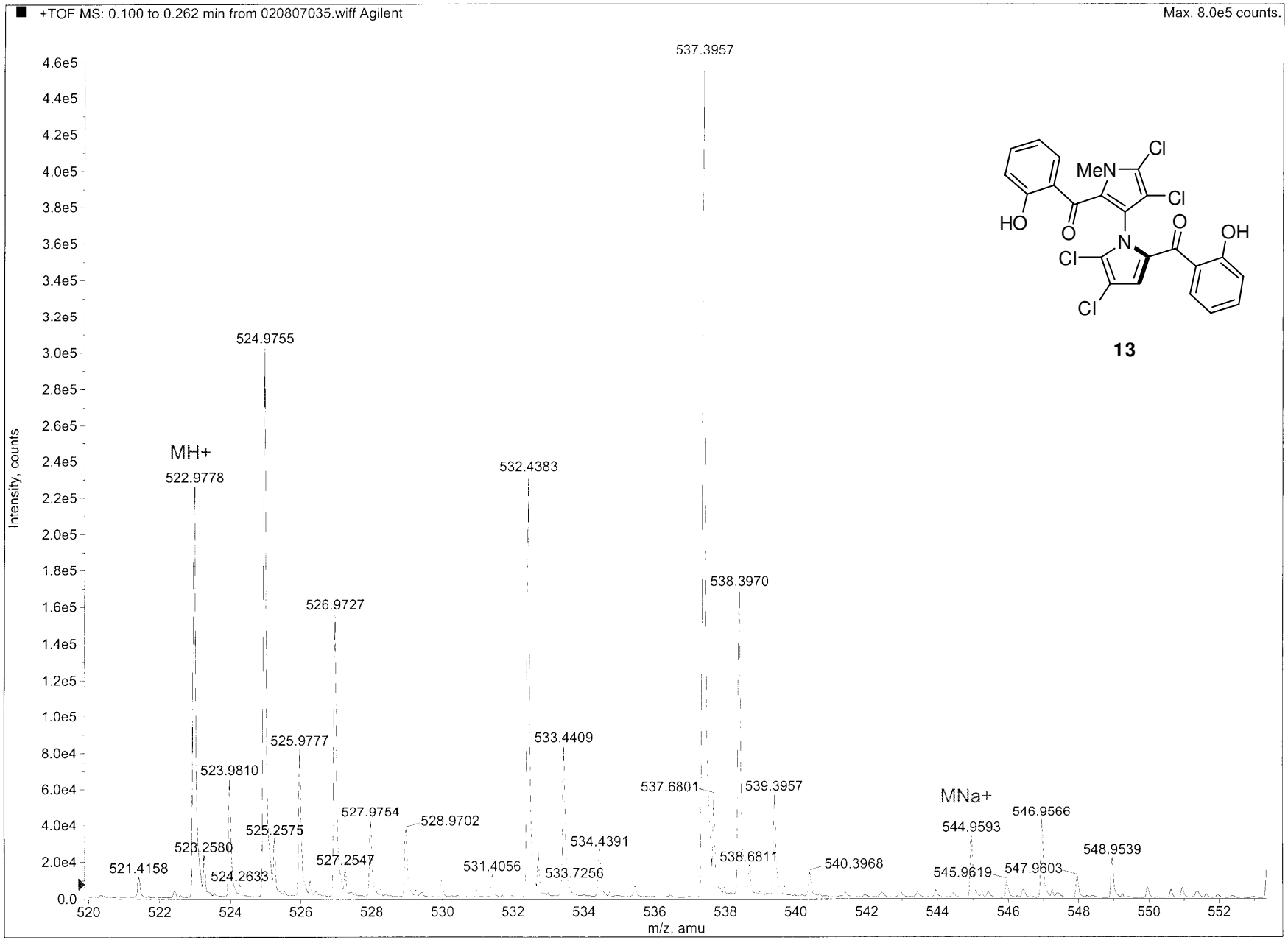


Polarity/Scan Type: Positive

Sample Name: flch2178

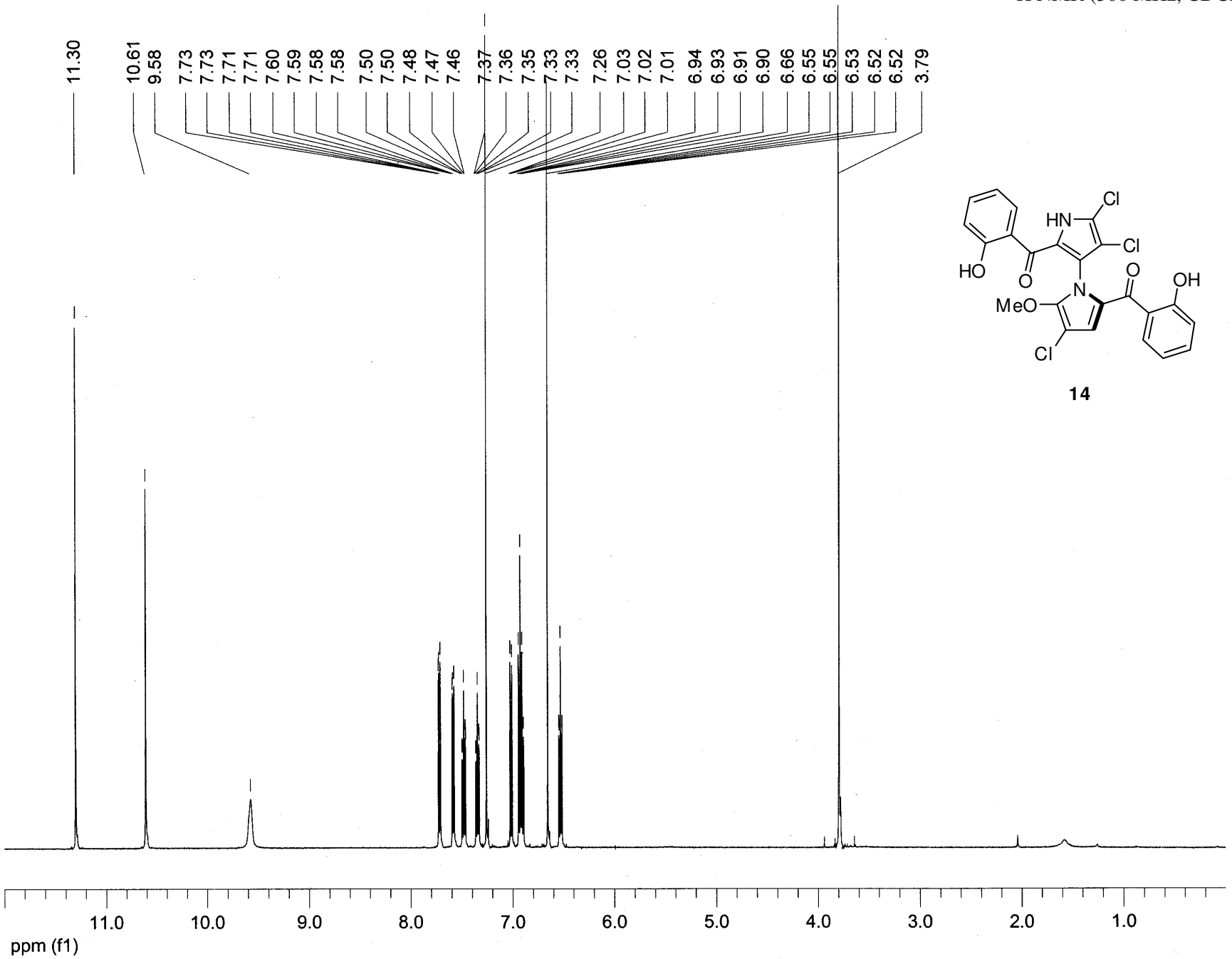
Acq. Date: Thursday, February 08, 2007

Acq. File: 020807035.wiff



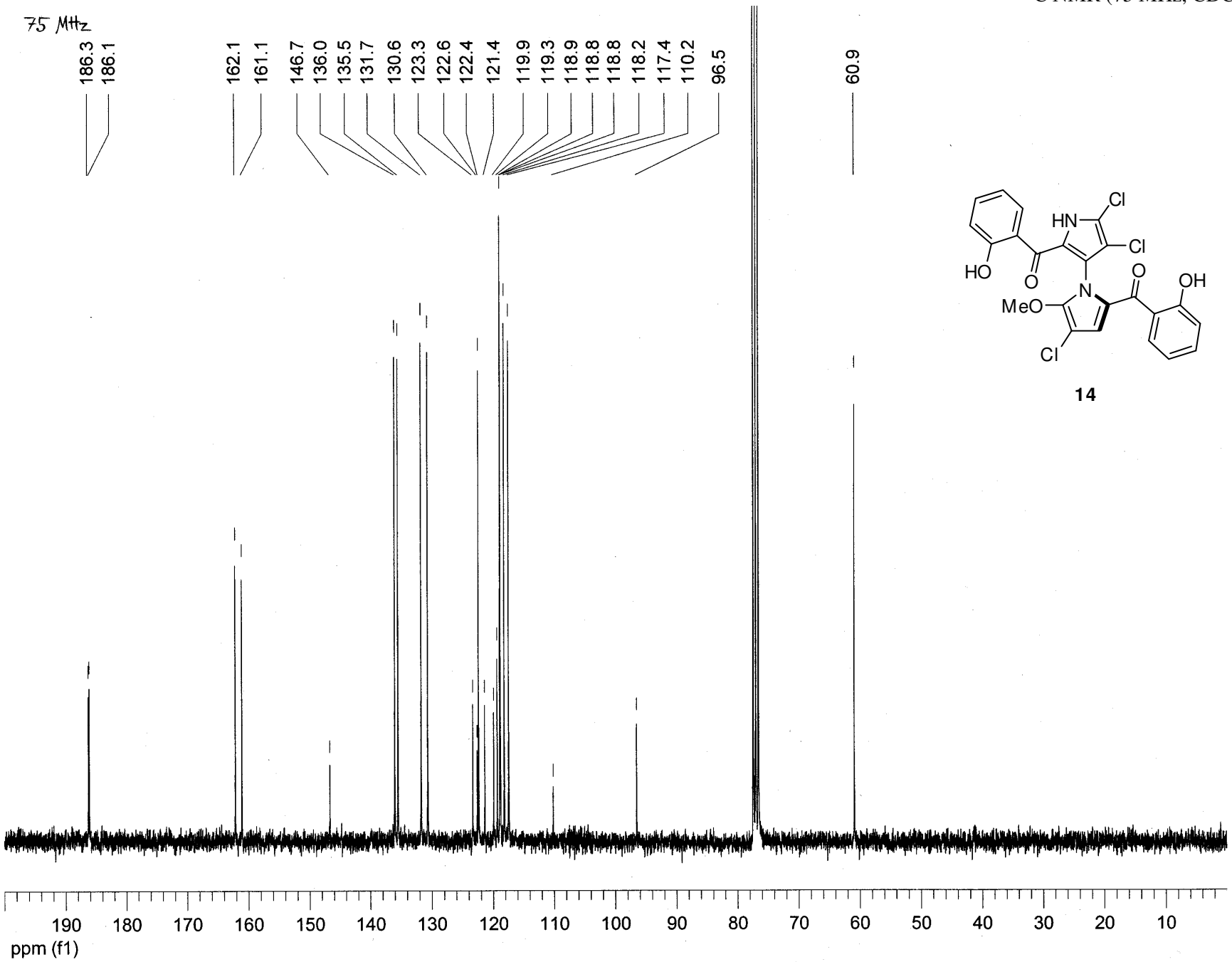
13

^{1}H NMR (500 MHz, $CDCl_3$) of **14**



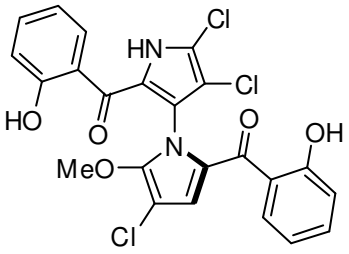
14

^{13}C NMR (75 MHz, $CDCl_3$) of **14**



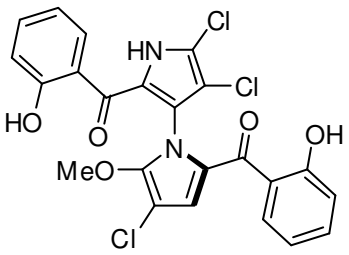
14

COSY (500 MHz, $CDCl_3$) of **14**



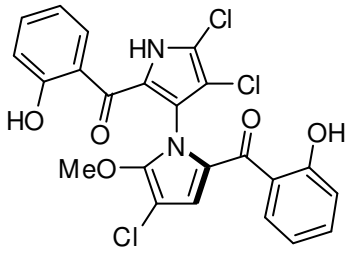
14

HSQC (500 MHz, $CDCl_3$) of **14**

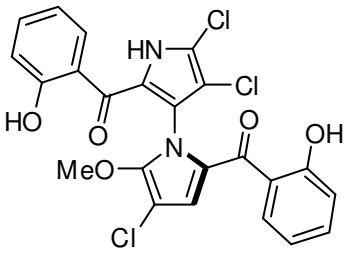


14

HMBC (500 MHz, $CDCl_3$) of **14**



14


Cl
HN
Cl
HO
O
O
OH
N
MeO
Cl

14

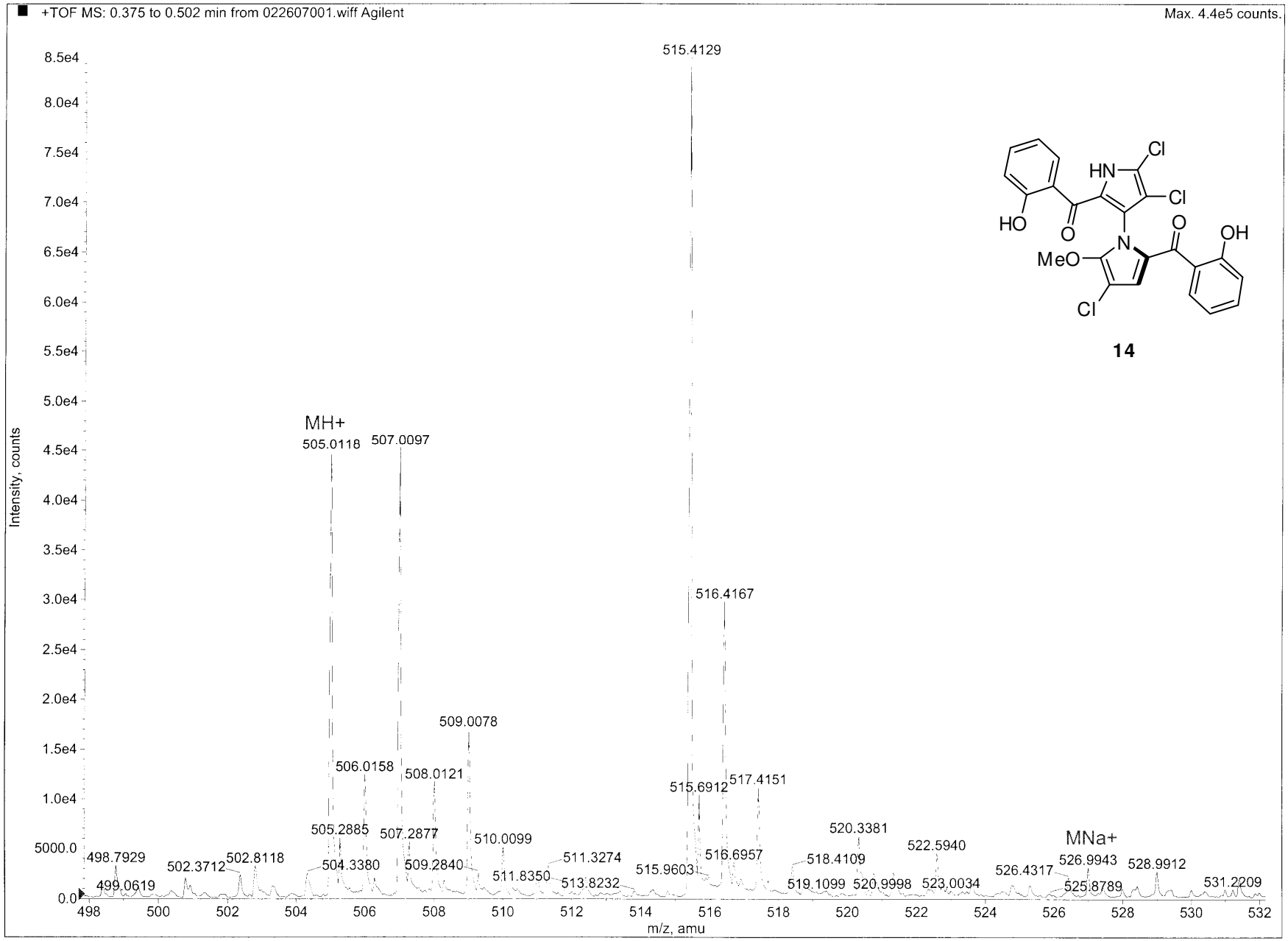
60
70
80
90
100
110
120
130
140
150
ppm (t1
4.40
4.30
4.20
4.10
4.00
3.90
3.80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
ppm (t2)

Polarity/Scan Type: Positive

Sample Name: flch2488

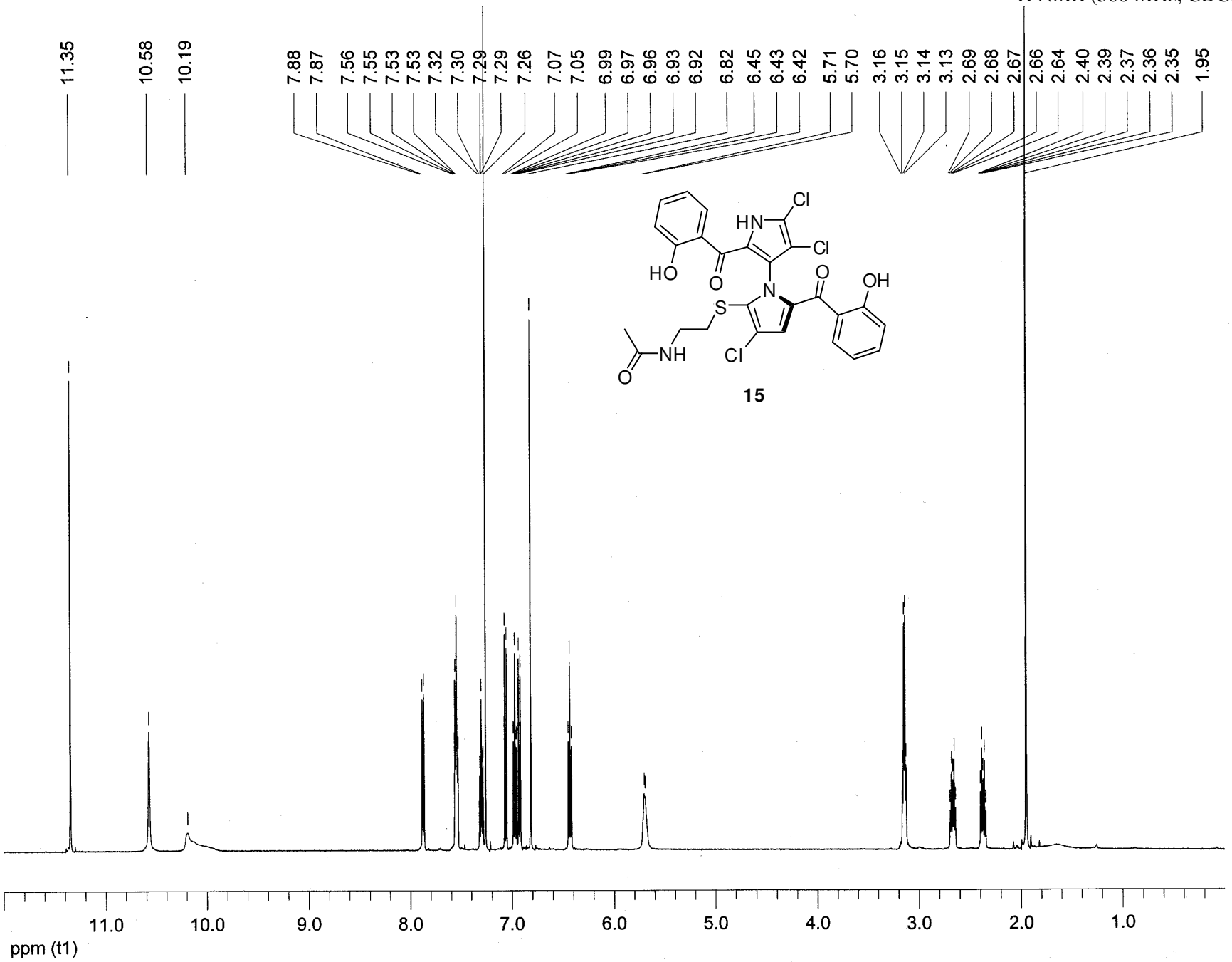
Acq. Date: Monday, February 26, 2007

Acq. File: 022607001.wiff



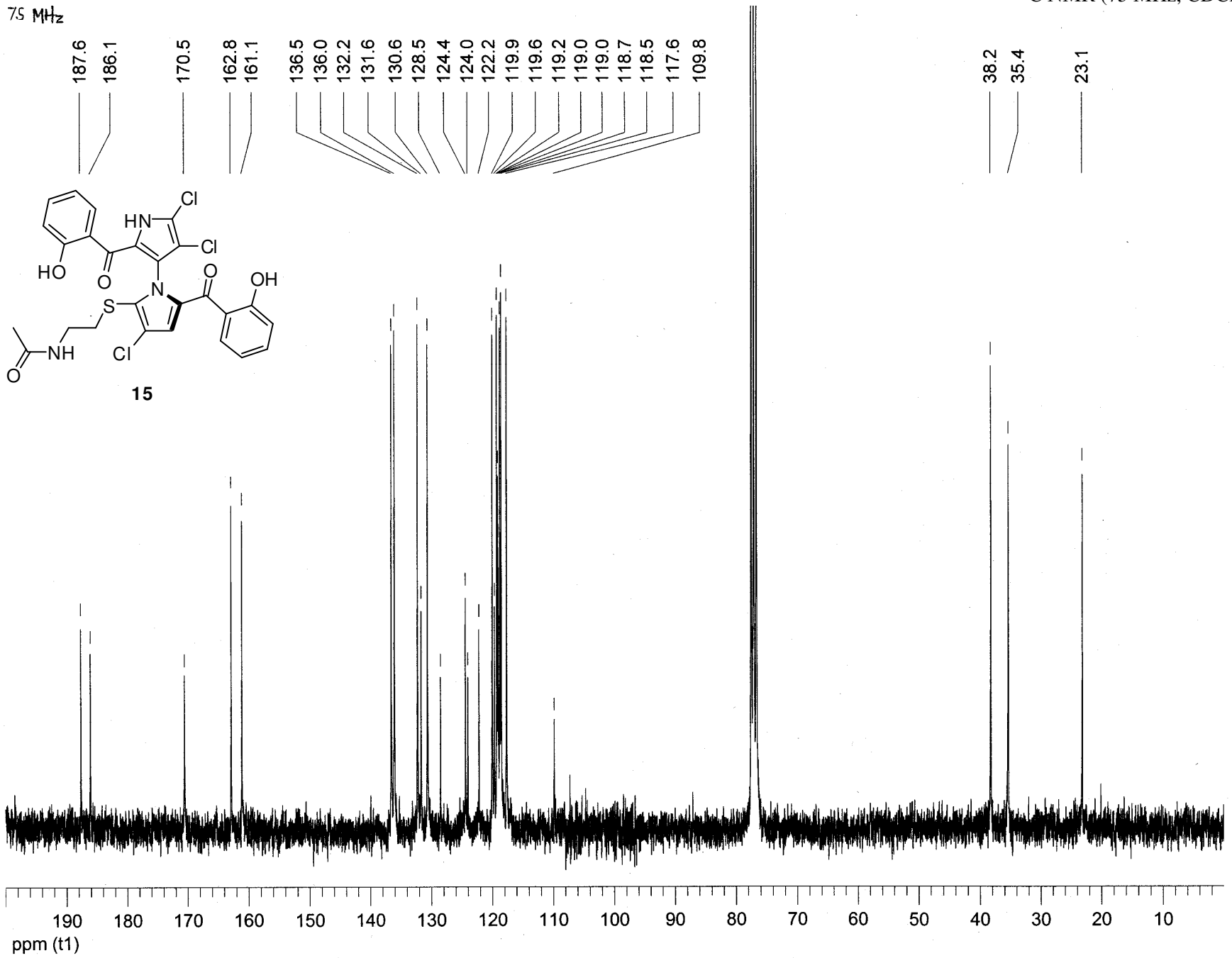
14

^{1}H NMR (500 MHz, $CDCl_3$) of **15**

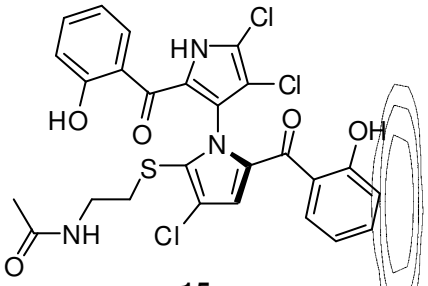


15

^{13}C NMR (75 MHz, $CDCl_3$) of **15**

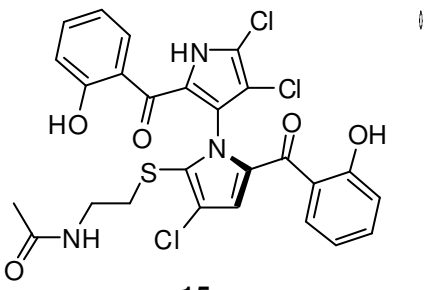


COSY (500 MHz, $CDCl_3$) of **15**



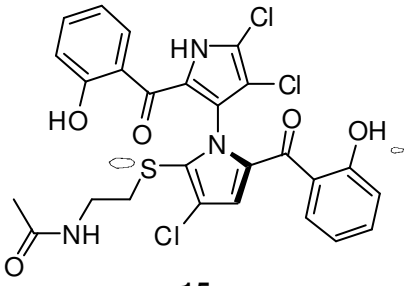
15

HSQC (500 MHz, $CDCl_3$) of **15**



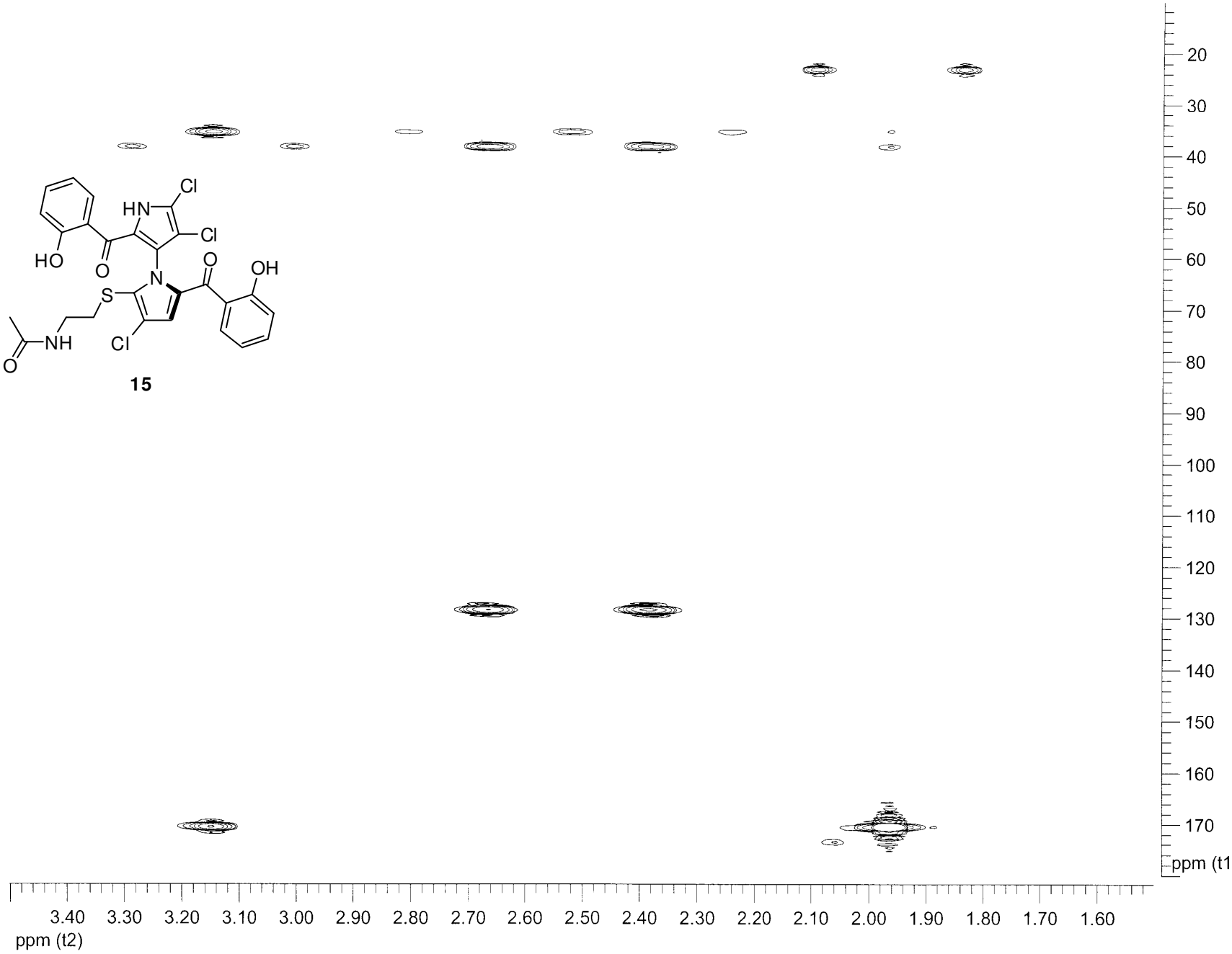
15

HMBC (500 MHz, $CDCl_3$) of **15**



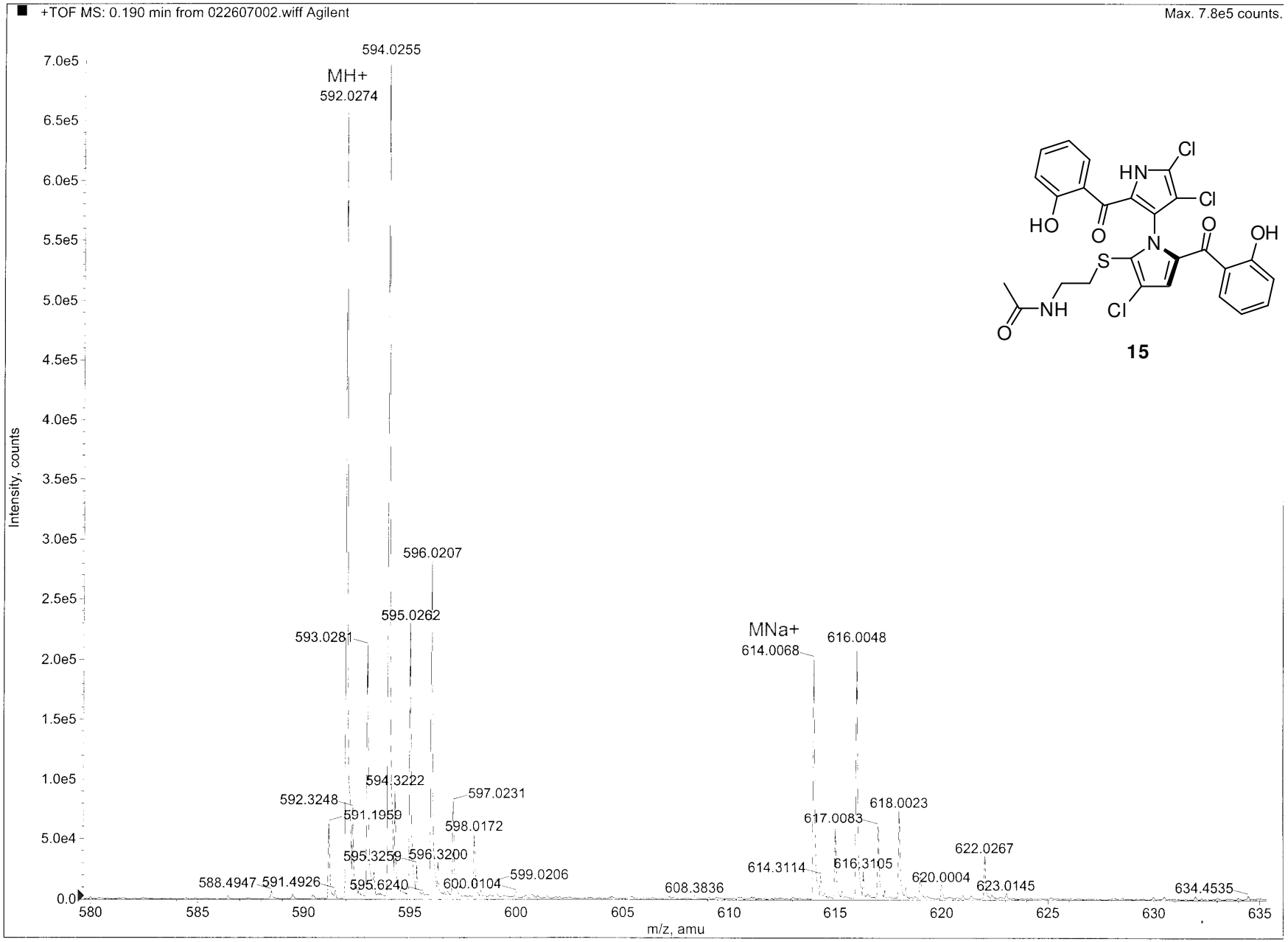
15

HMBC (500 MHz, $CDCl_3$) of **15**



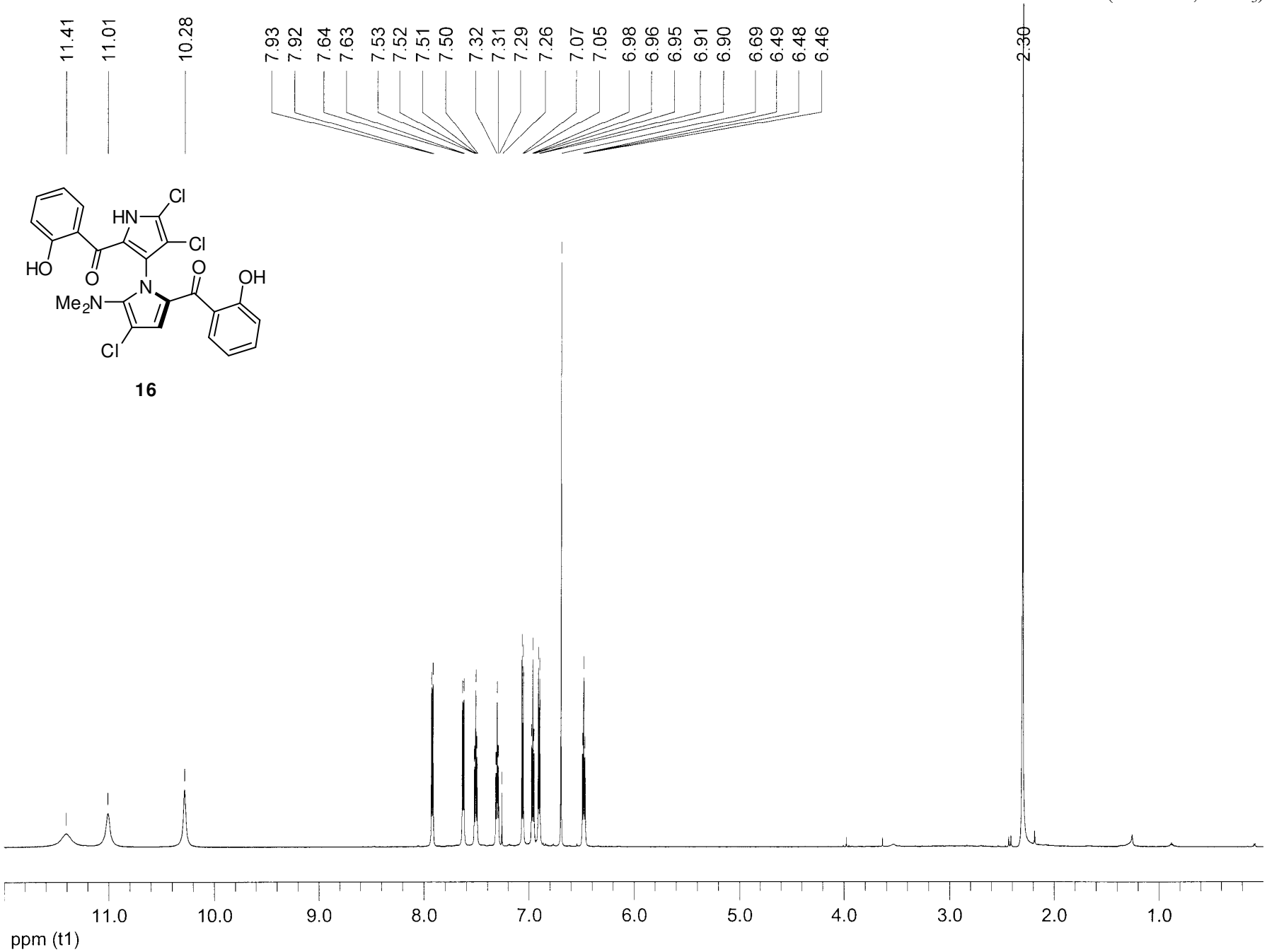
Polarity/Scan Type: Positive Sample Name: flch2489 Acq. Date: Monday, February 26, 2007

Acq. File: 022607002.wiff

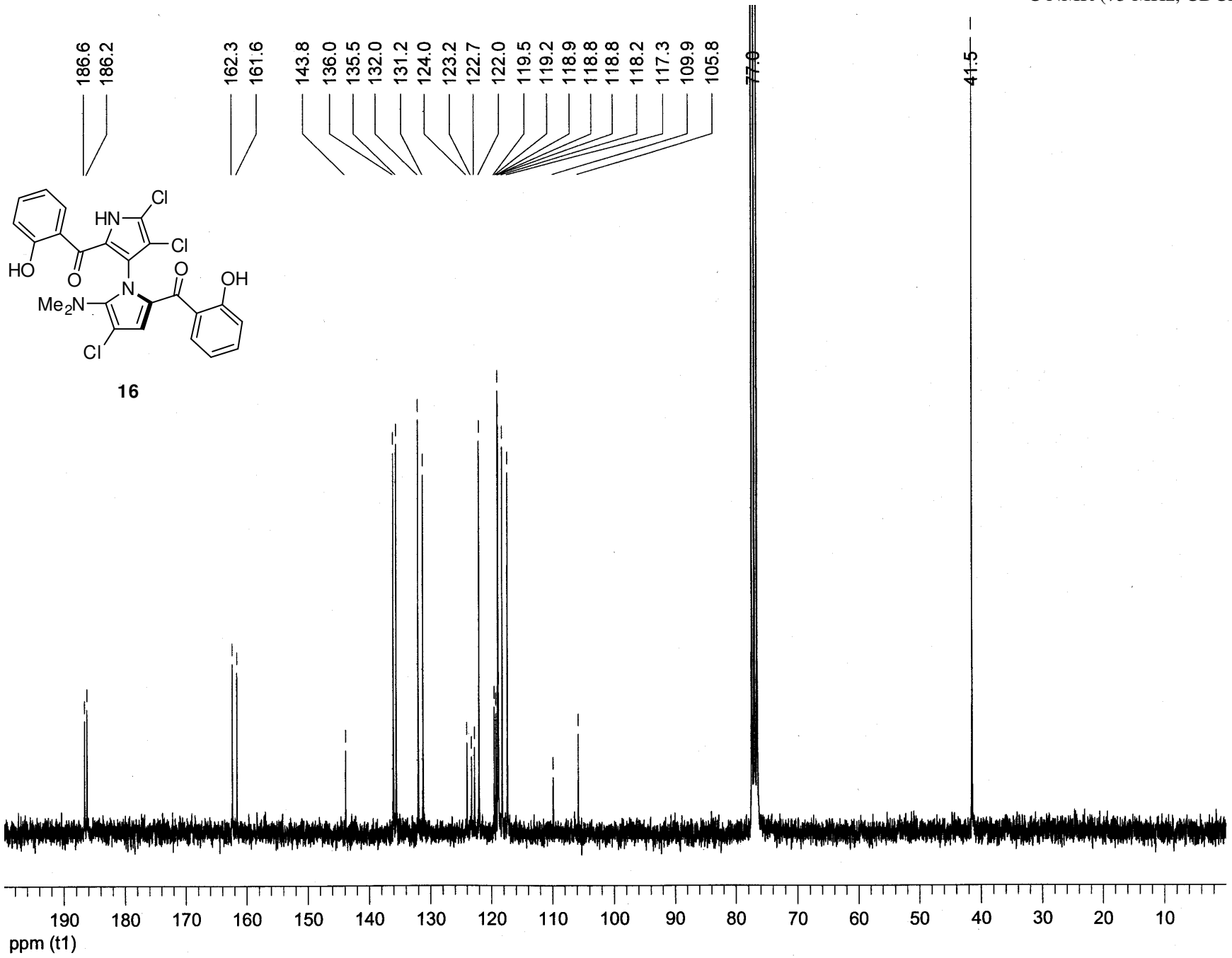


15

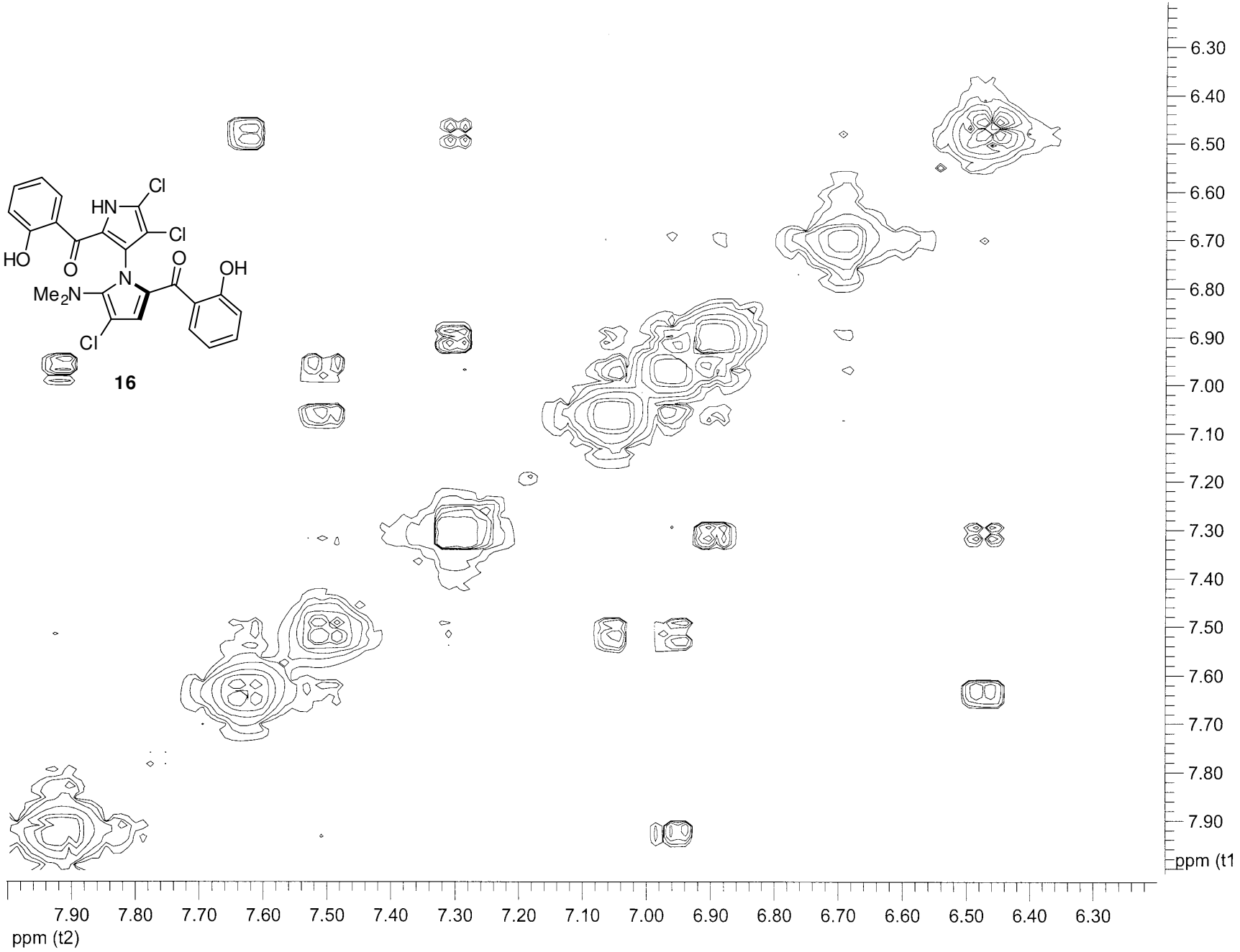
^{1}H NMR (600 MHz, $CDCl_3$) of **16**



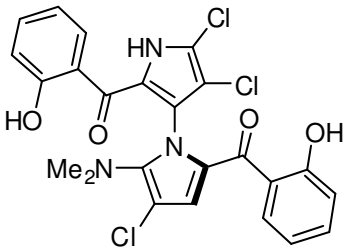
^{13}C NMR (75 MHz, $CDCl_3$) of **16**



COSY (600 MHz, $CDCl_3$) of **16**

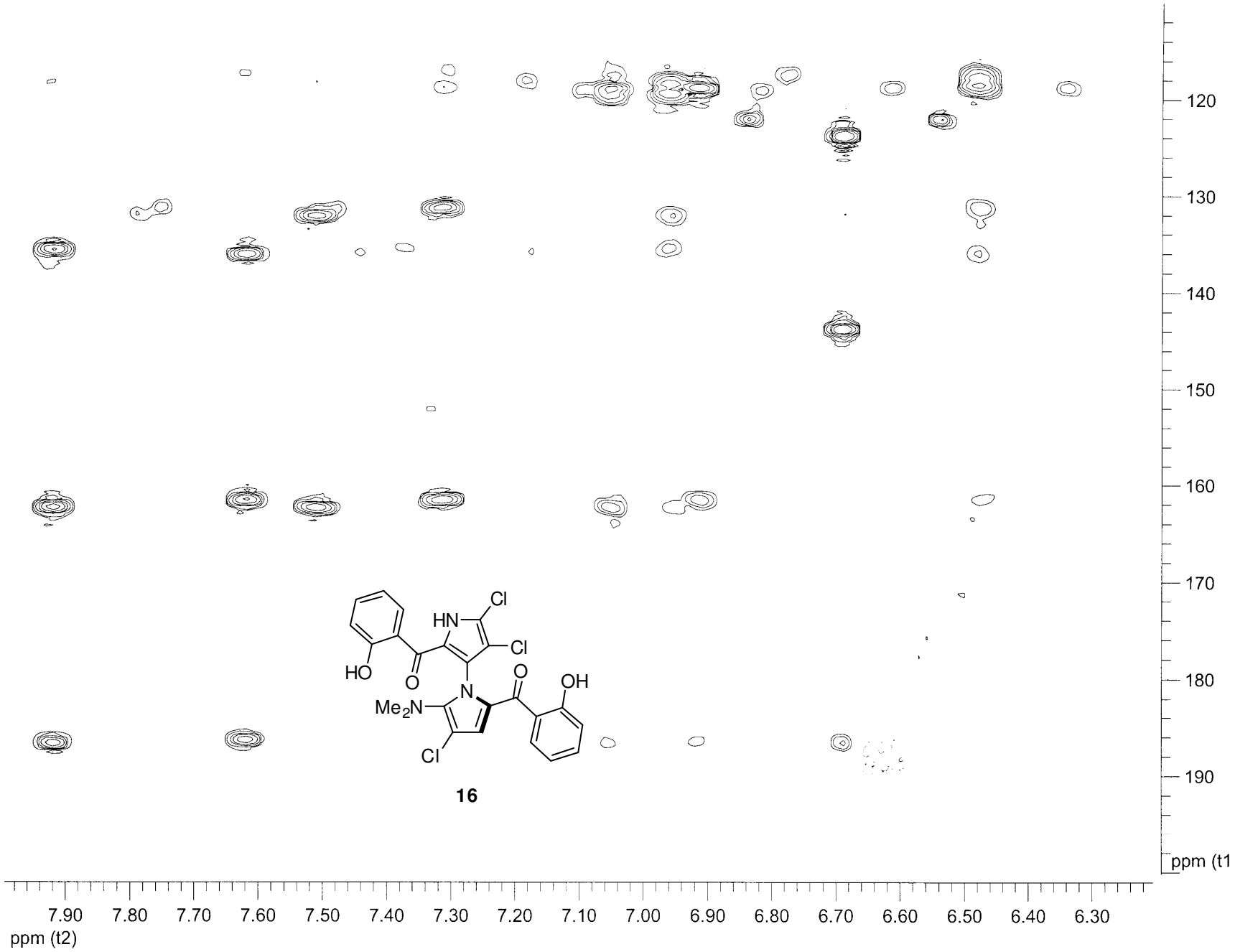


HSQC (600 MHz, $CDCl_3$) of **16**

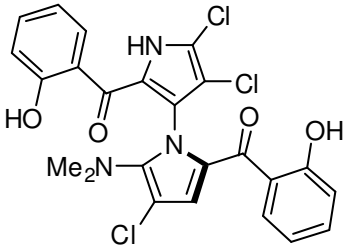


16

HMBC (600 MHz, $CDCl_3$) of **16**



16

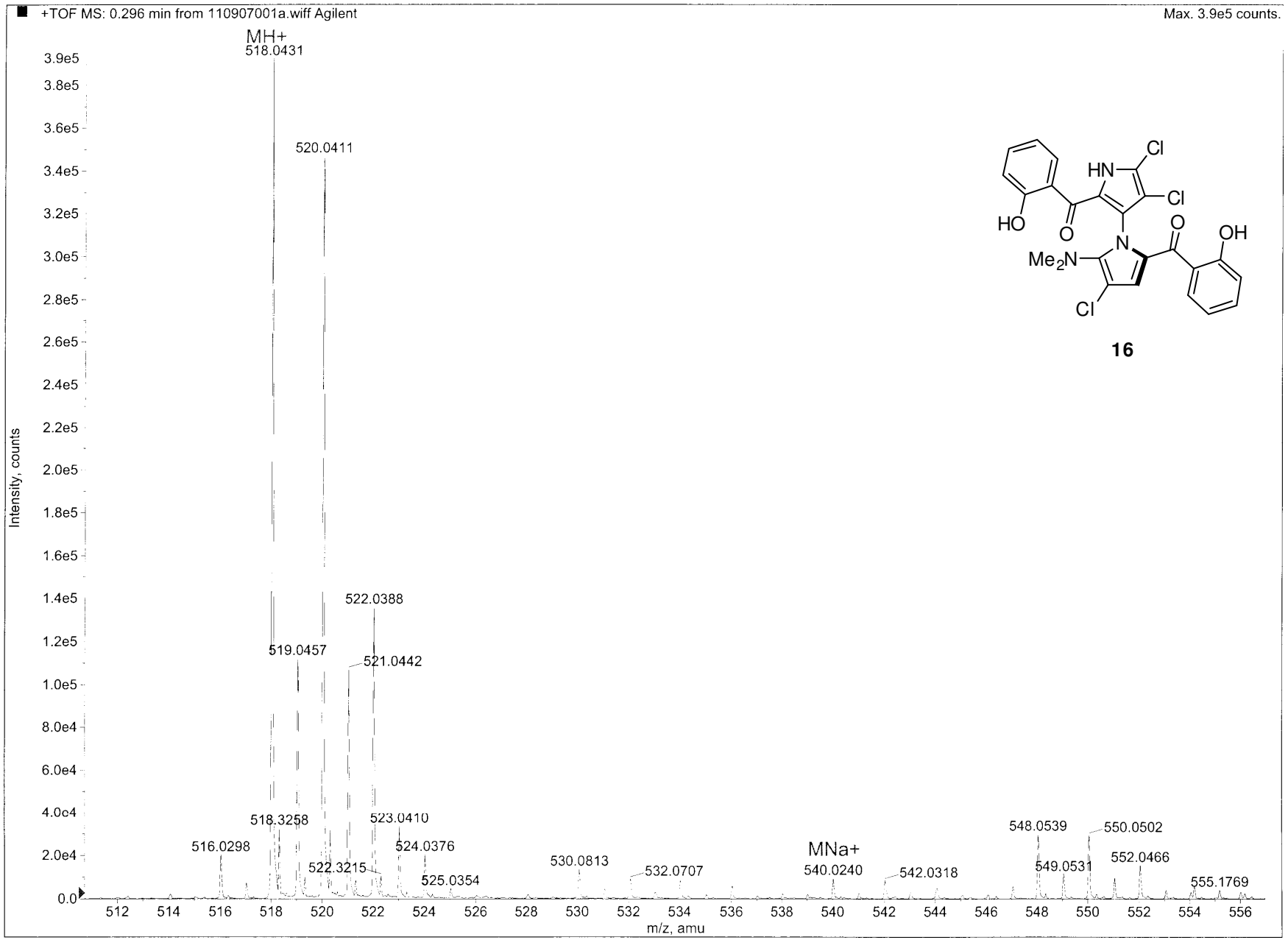

Cl
HN
Cl
HO
O
O
OH
N
Me2N
Cl

16

30
40
50
60
70
80
90
100
110
120
130
140
150
ppm (t1
2.70
2.60
2.50
2.40
2.30
2.20
2.10
2.00
1.90
ppm (t2)

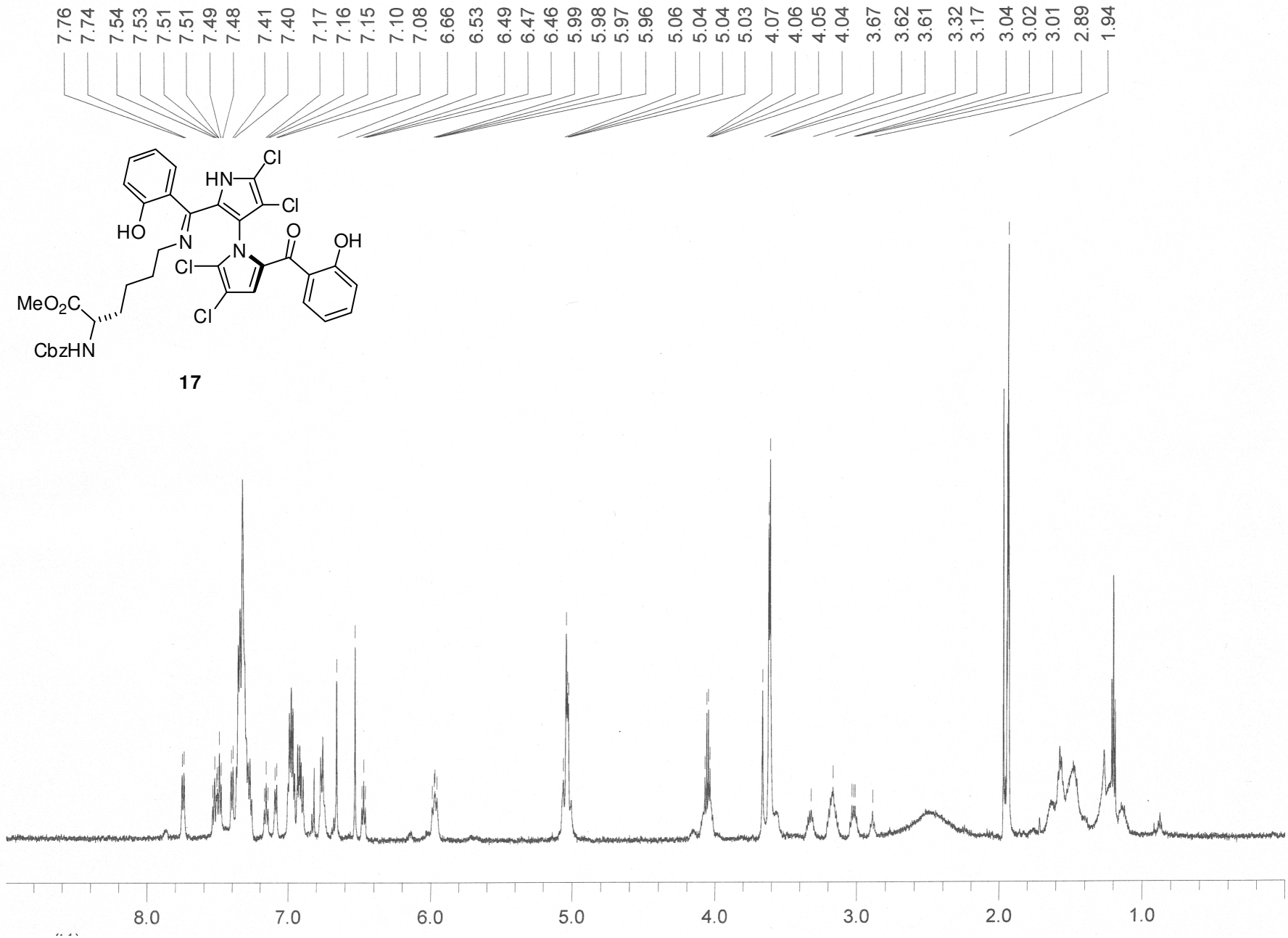
Polarity/Scan Type: Positive Sample Name: flch8669 Acq. Date: Friday, November 09, 2007

Acq. File: 110907001a.wiff



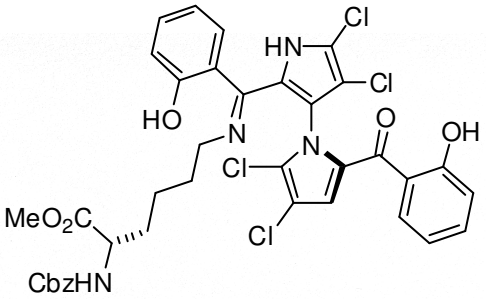
16

^{1}H NMR (600 MHz, $CDCl_3$) of **17**



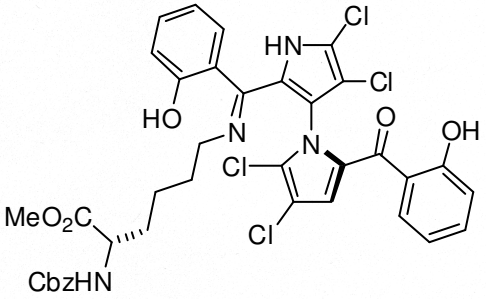
17

COSY (600 MHz, $CDCl_3$) of **17**



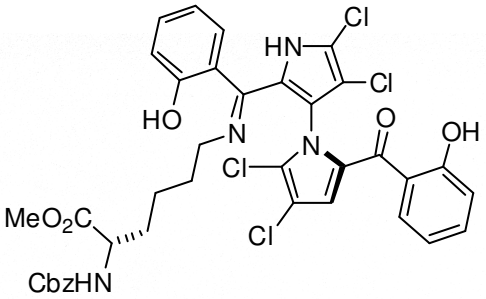
17

HSQC (600 MHz, $CDCl_3$) of **17**



17

HMBC (600 MHz, $CDCl_3$) of **17**



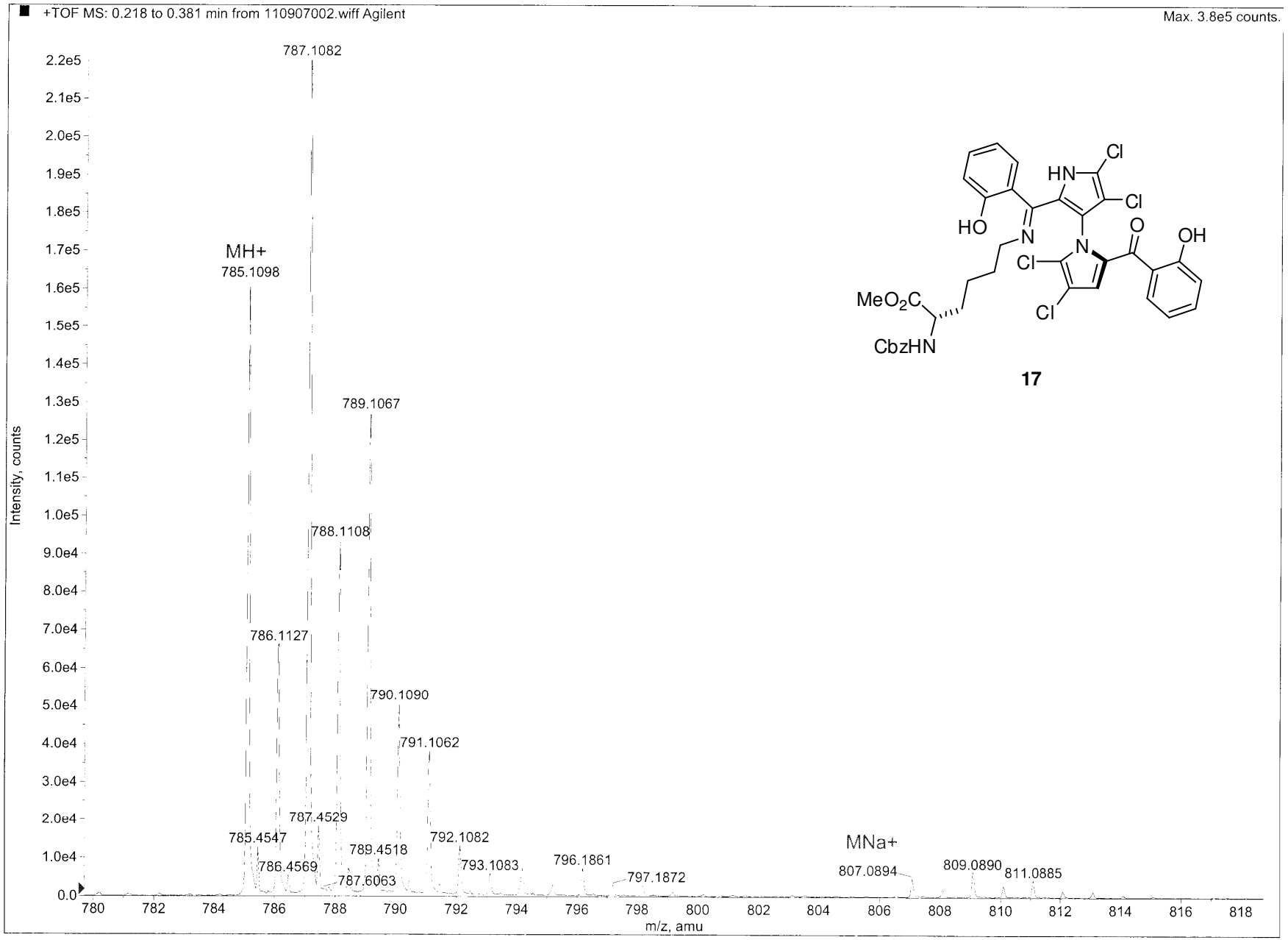
17

Polarity/Scan Type: Positive

Sample Name: flch8670

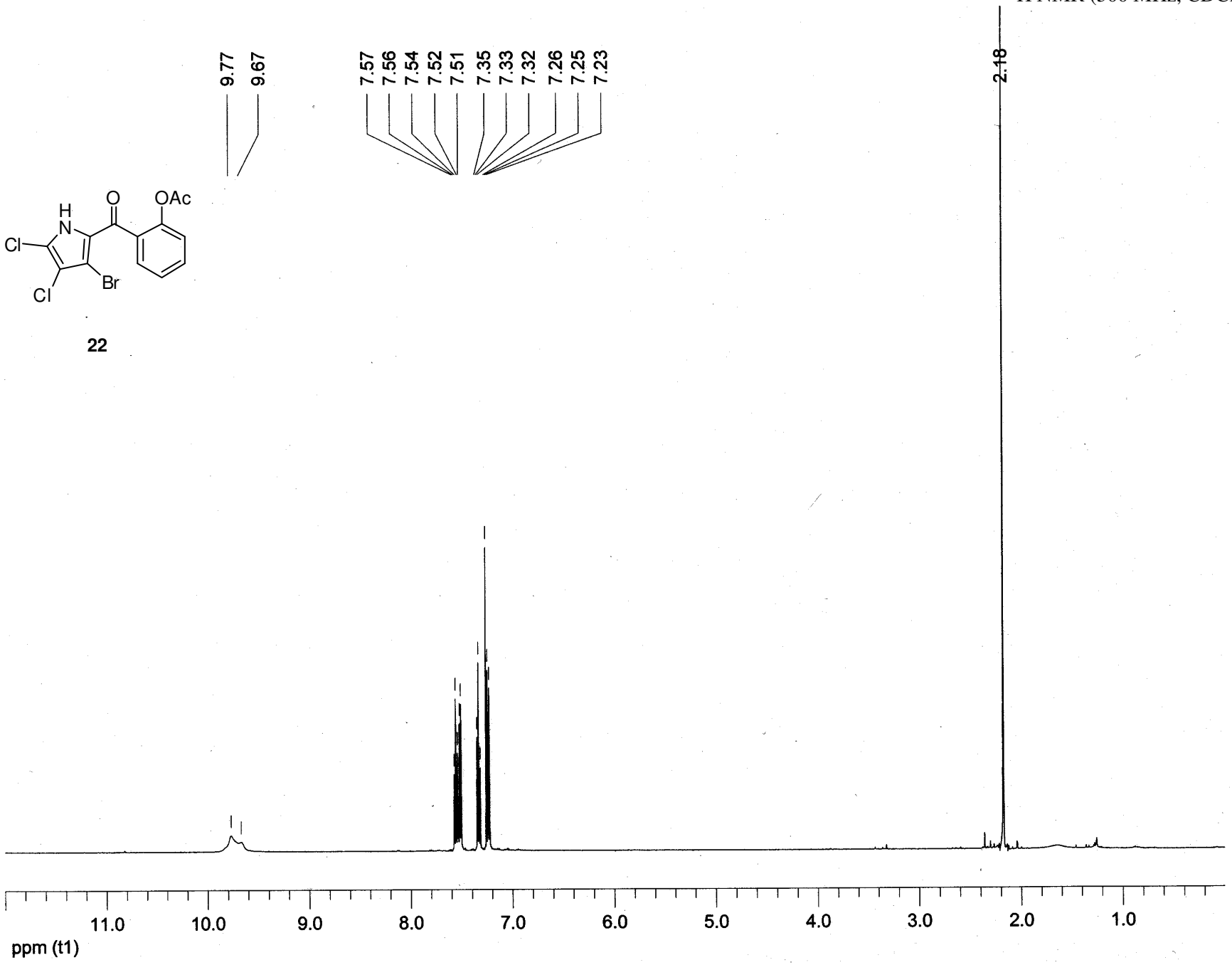
Acq. Date: Friday, November 09, 2007

Acq. File: 110907002.wiff



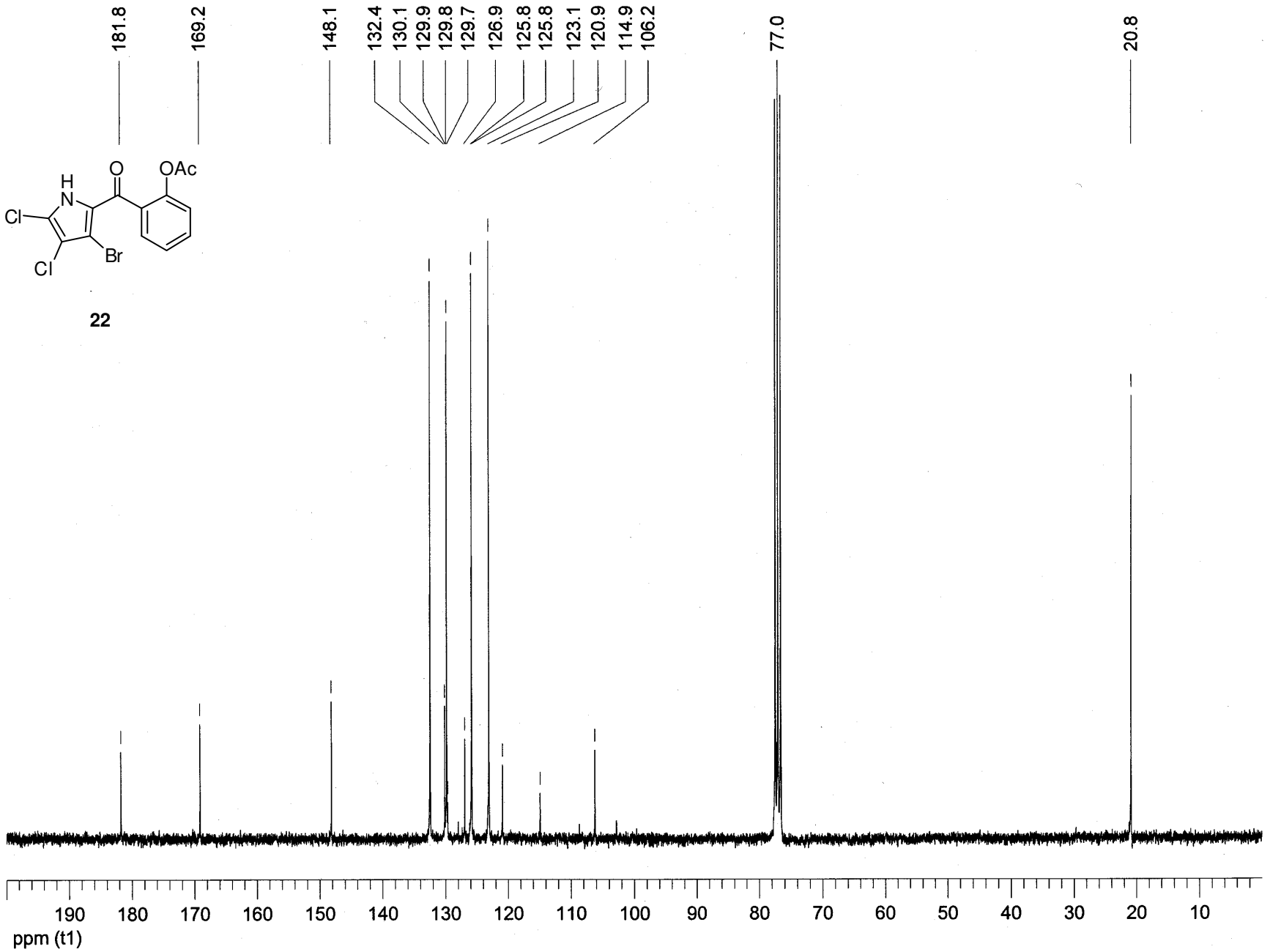
17

^{1}H NMR (500 MHz, $CDCl_3$) of **22**

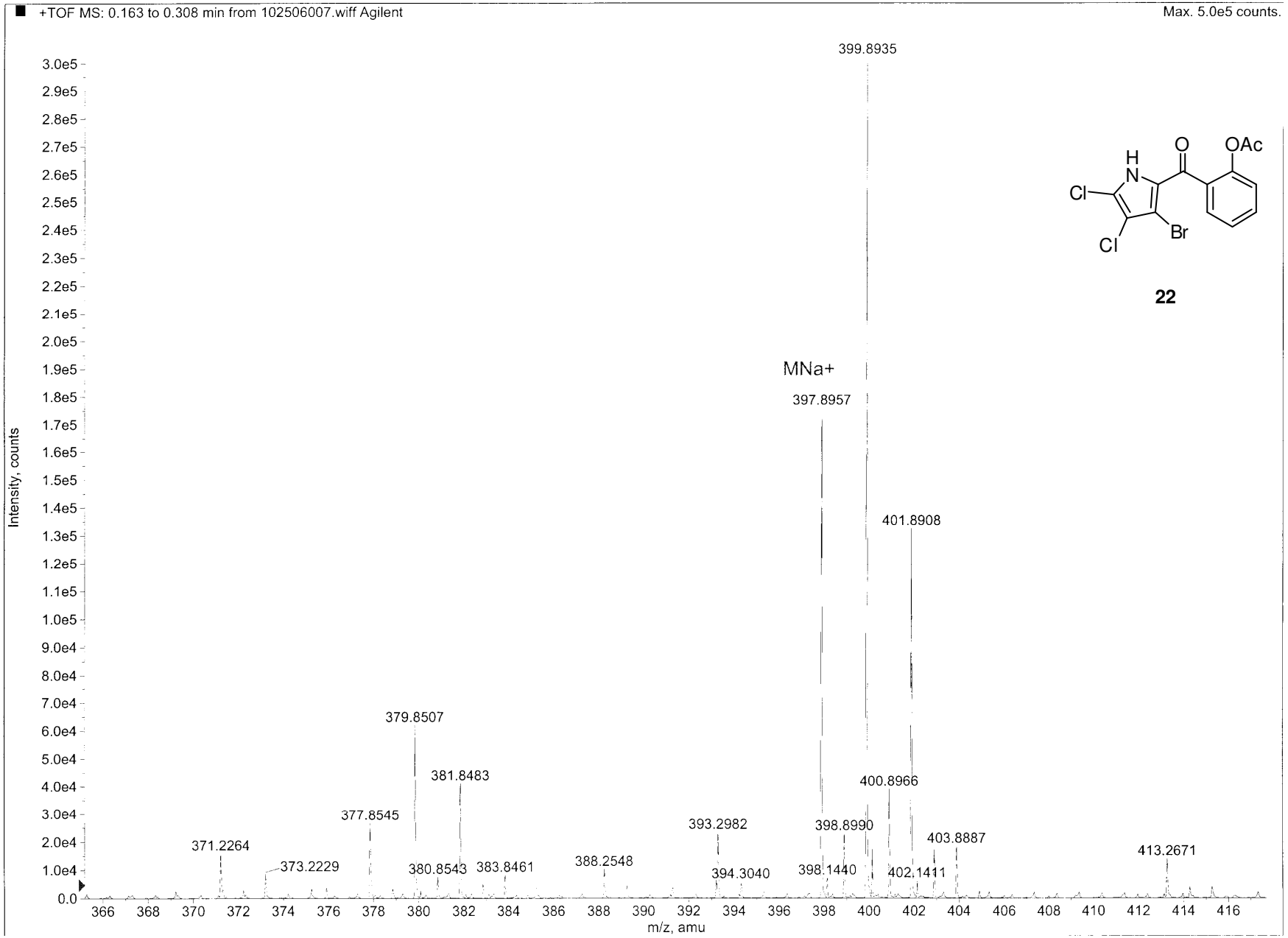


22

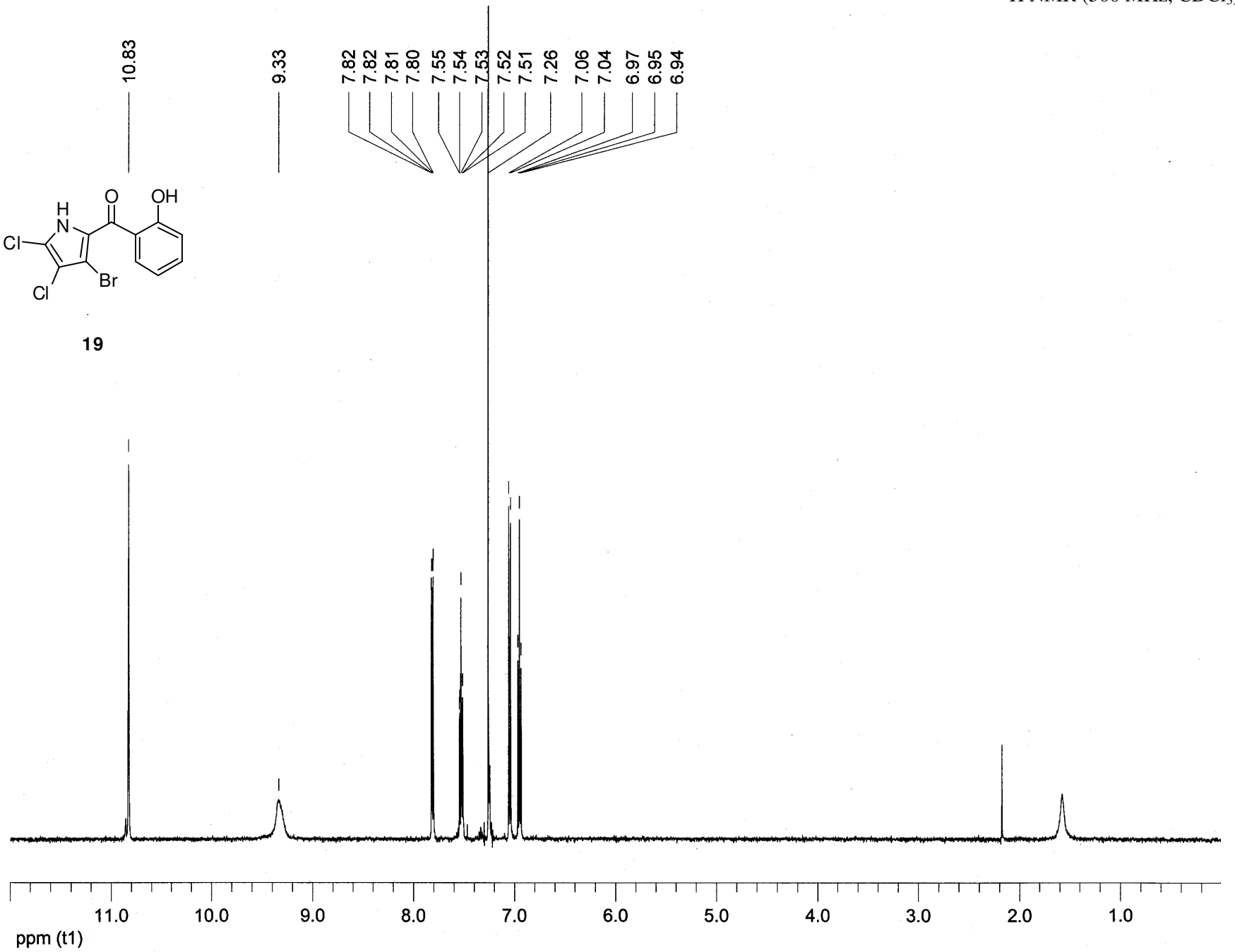
^{13}C NMR (75 MHz, $CDCl_3$) of **22**



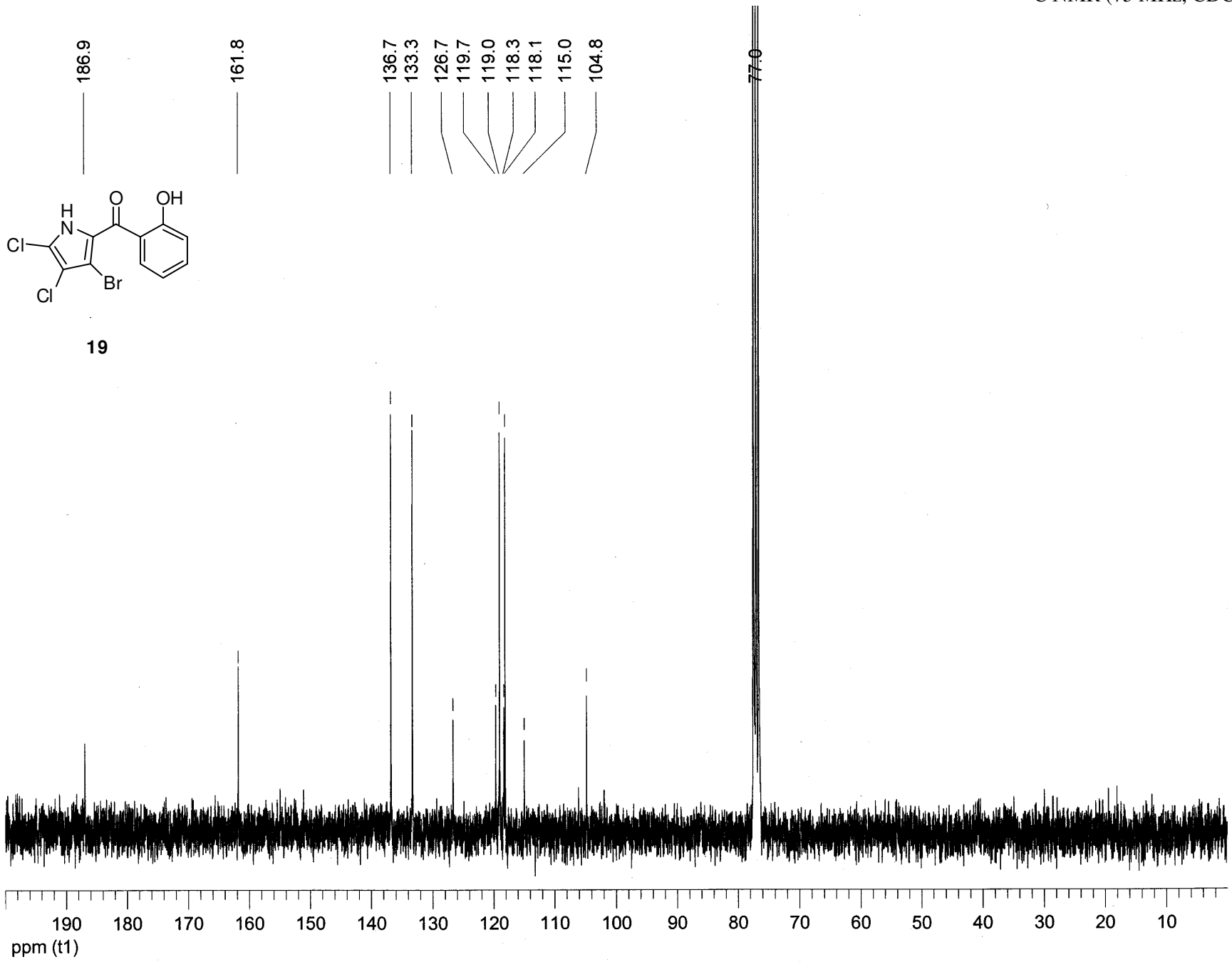
Polarity/Scan Type: Positive Sample Name: flch8550 Acq. Date: Wednesday, October 25, 2006
Acq. File: 102506007.wiff



^{1}H NMR (500 MHz, $CDCl_3$) of **19**



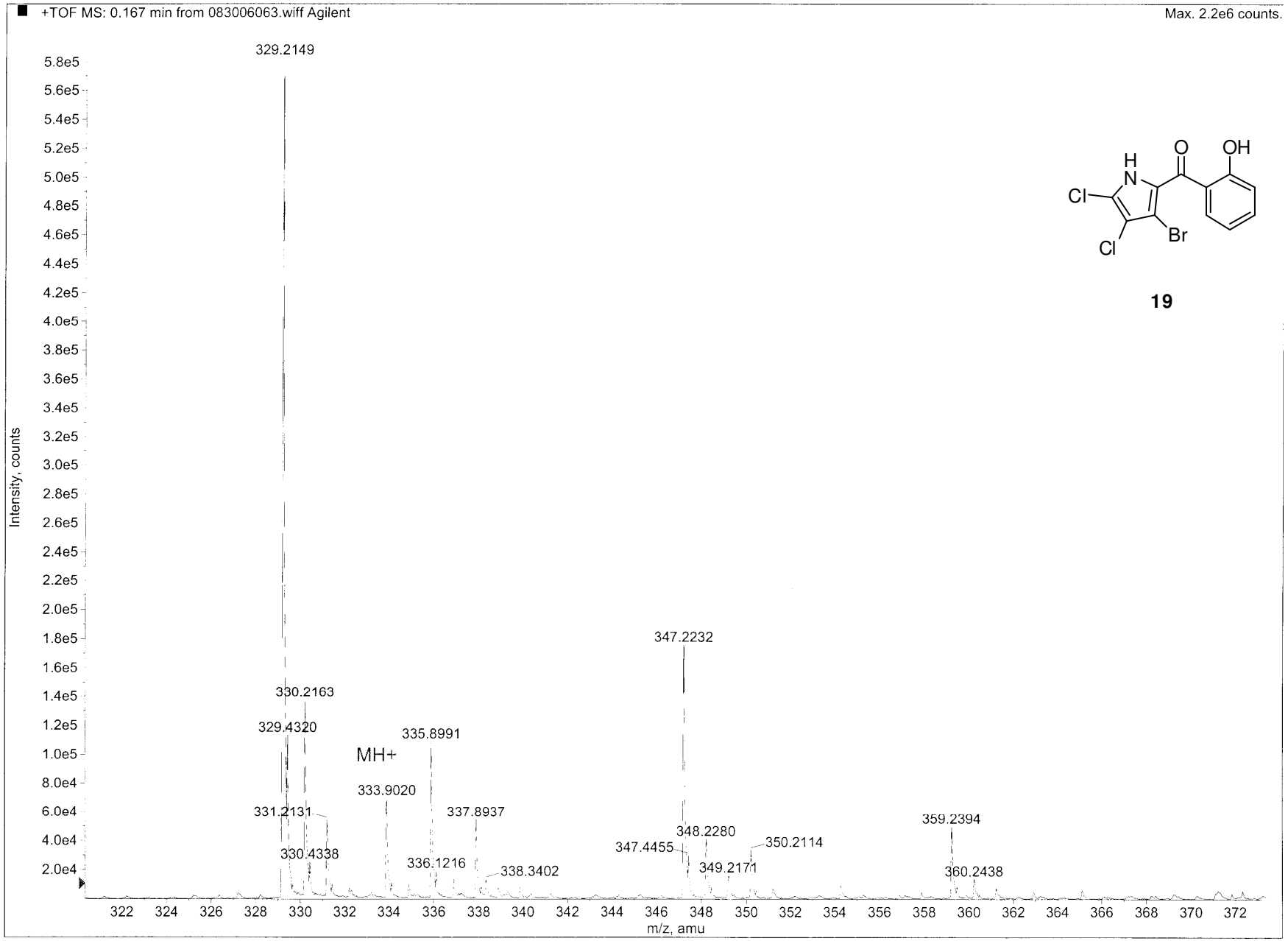
^{13}C NMR (75 MHz, $CDCl_3$) of **19**



19

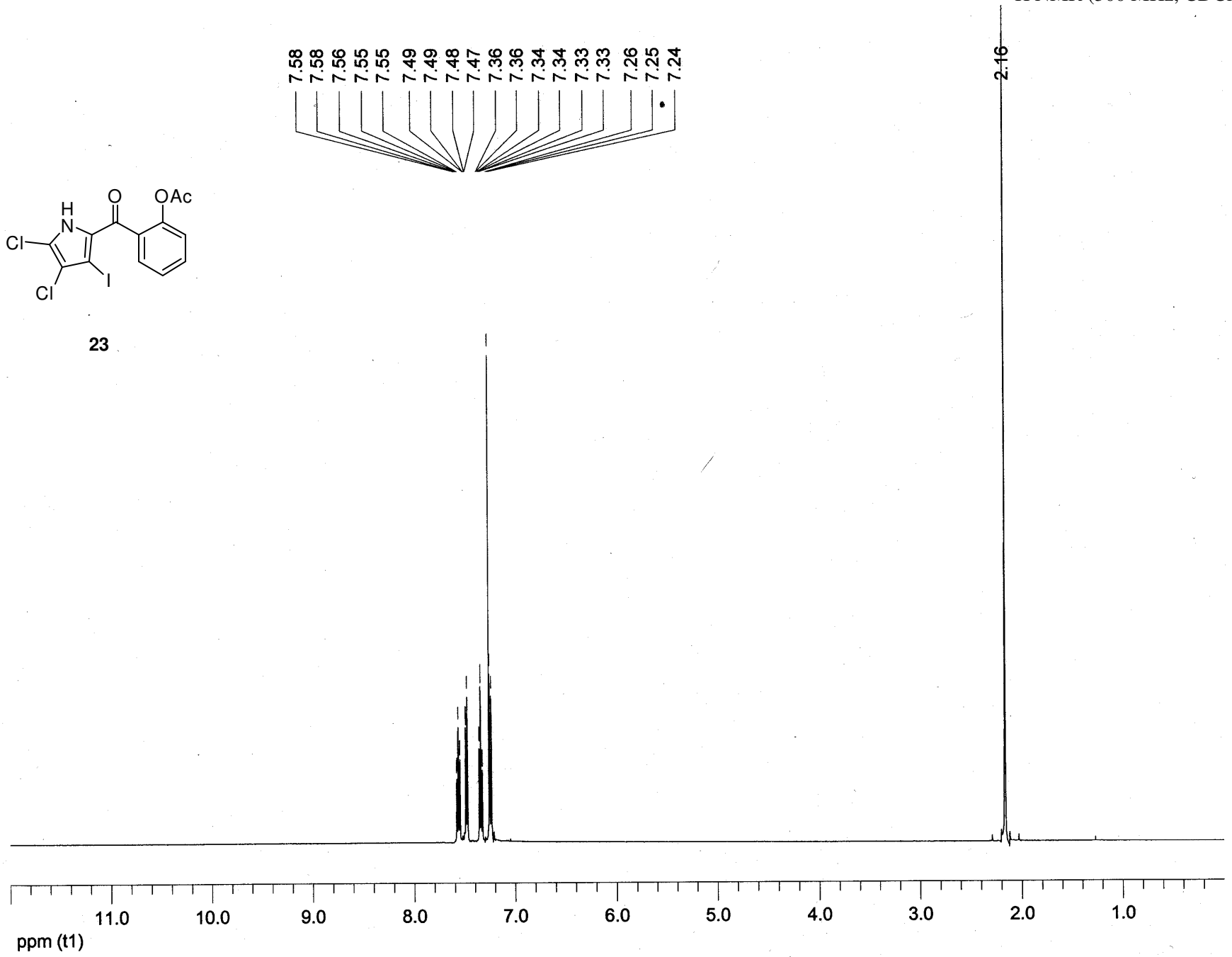
Polarity/Scan Type: Positive Sample Name: flch6844 Acq. Date: Wednesday, August 30, 2006

Acq. File: 083006063.wiff



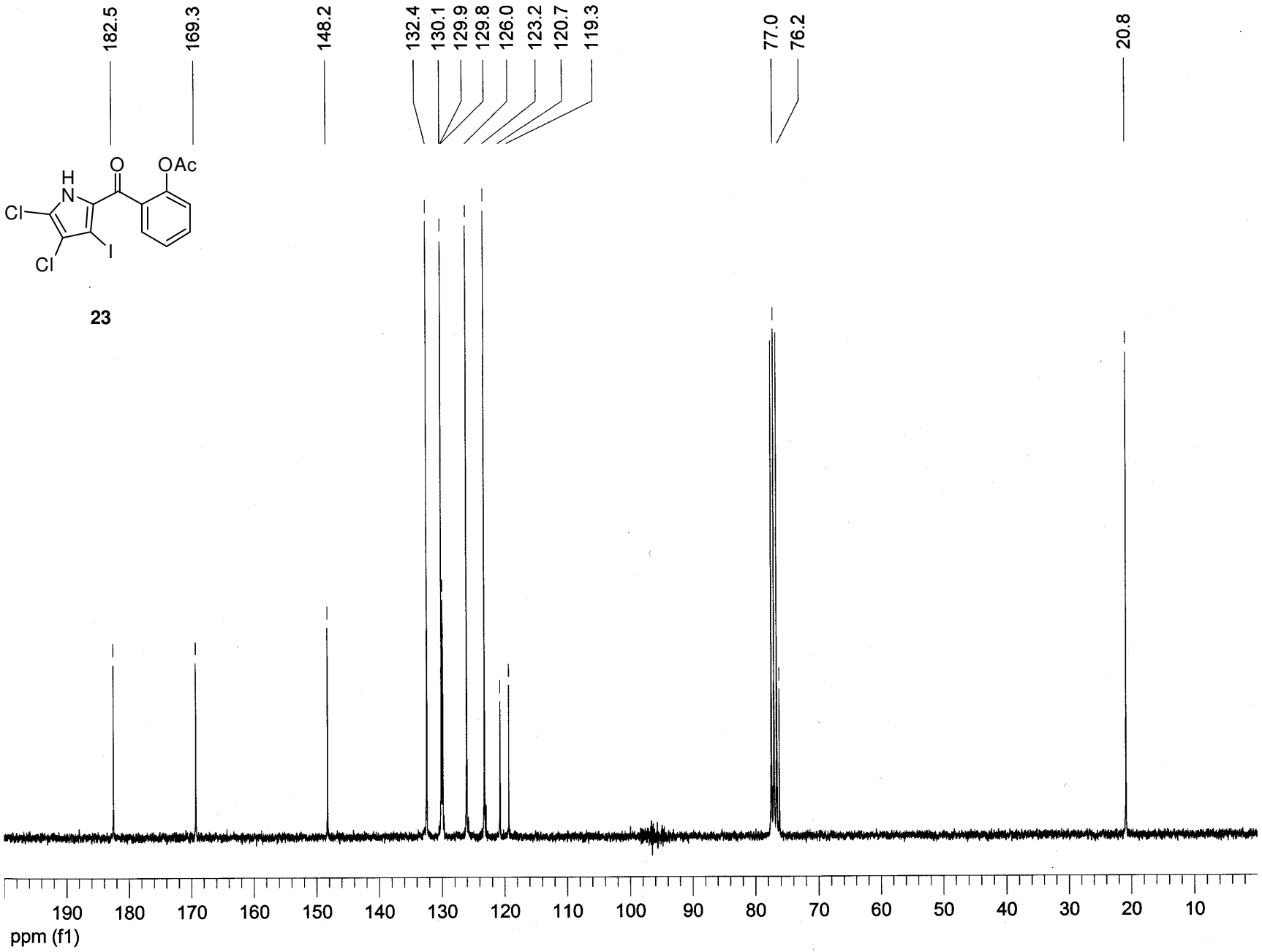
19

^{1}H NMR (500 MHz, $CDCl_3$) of **23**



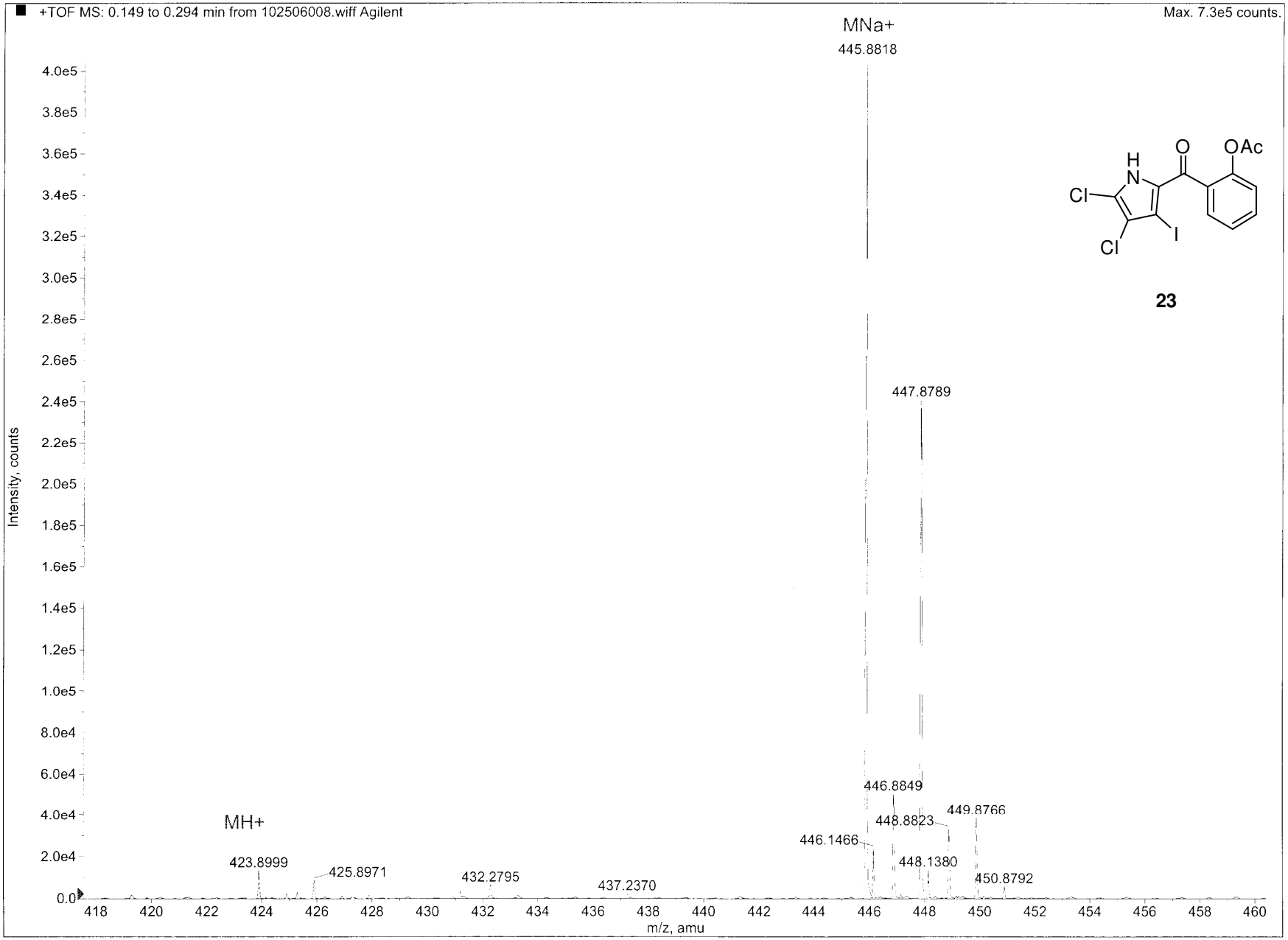
23

^{13}C NMR (75 MHz, $CDCl_3$) of **23**



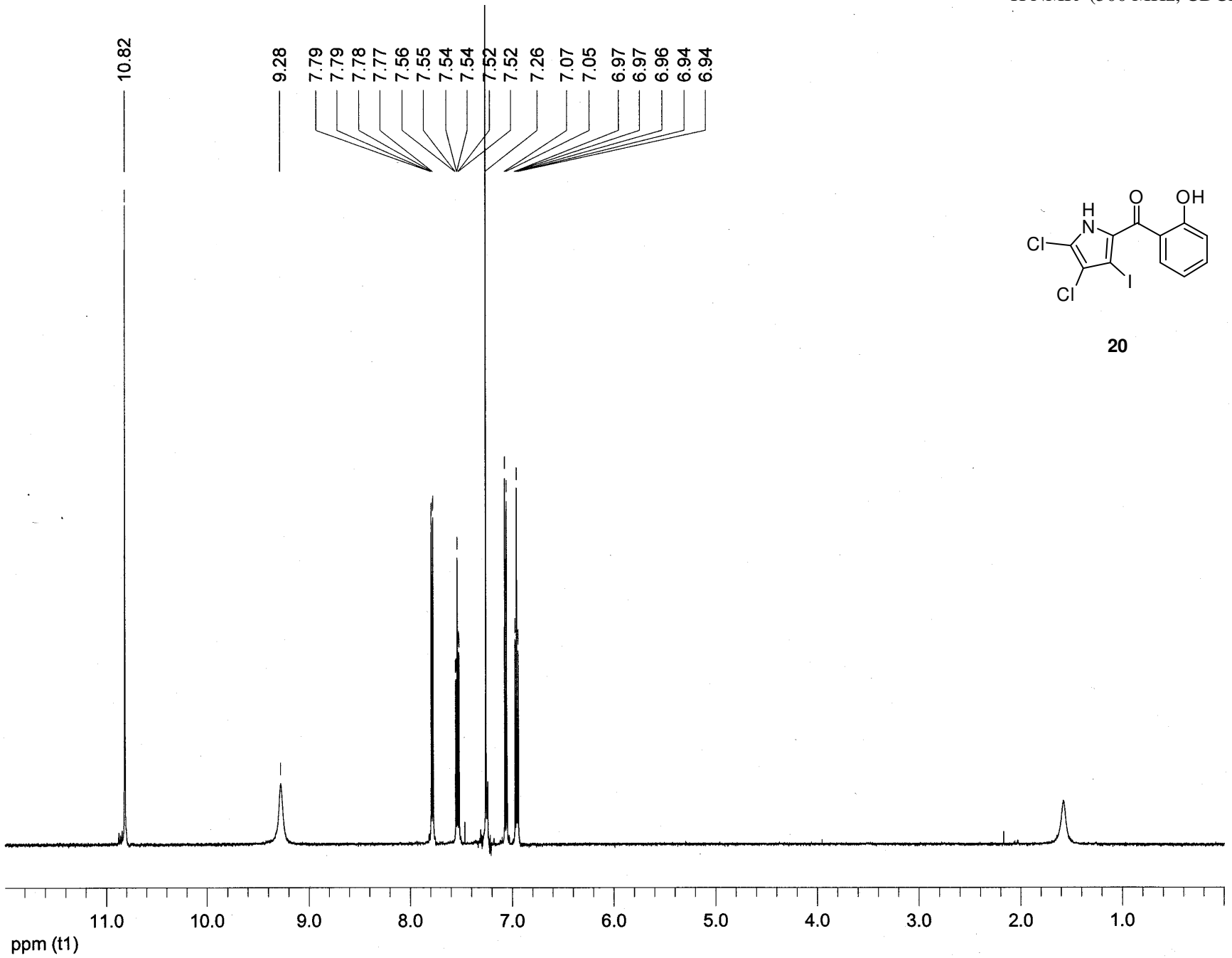
Polarity/Scan Type: Positive Sample Name: flch8551 Acq. Date: Wednesday, October 25, 2006

Acq. File: 102506008.wiff



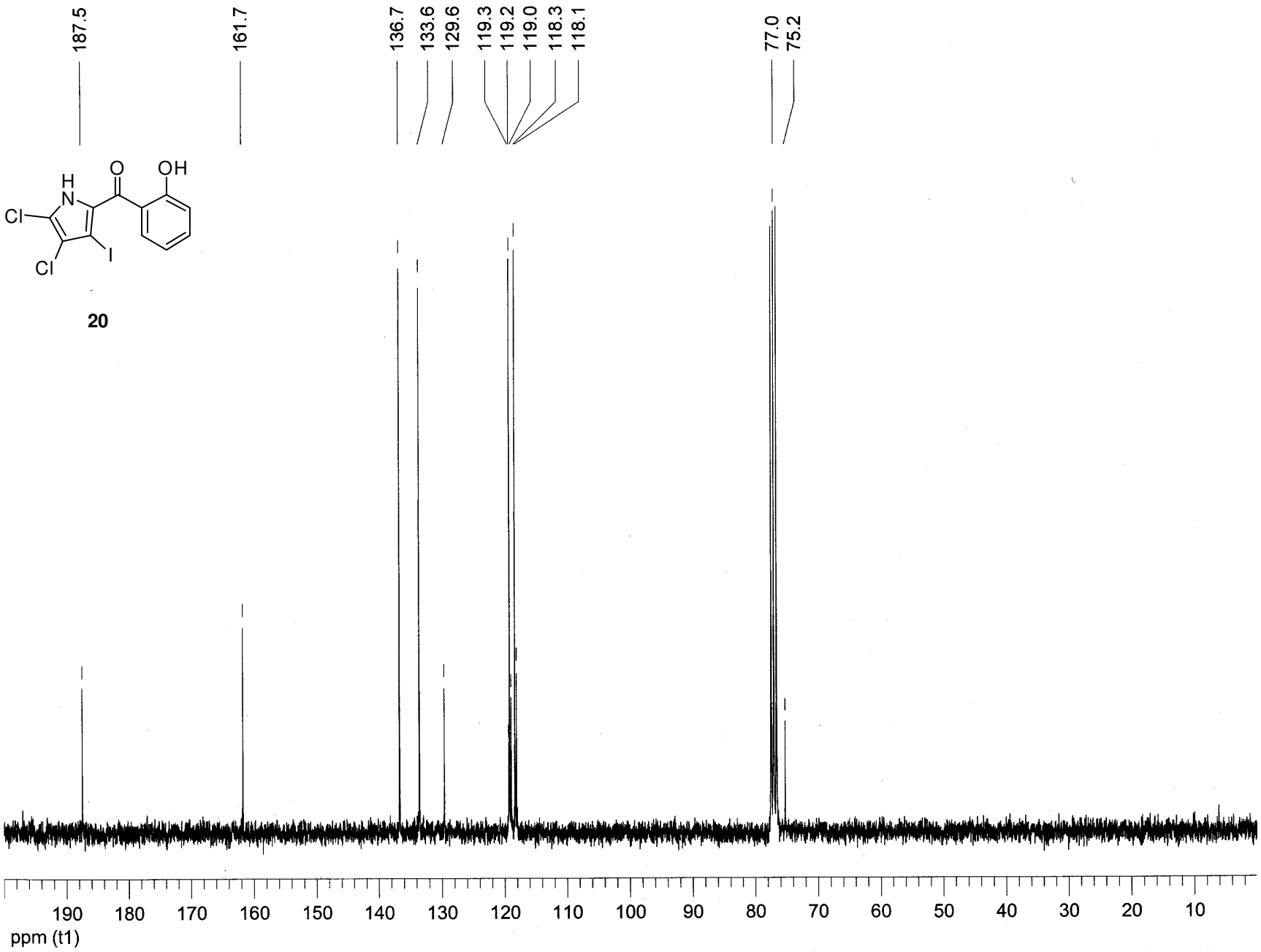
23

^{1}H NMR (500 MHz, $CDCl_3$) of **20**



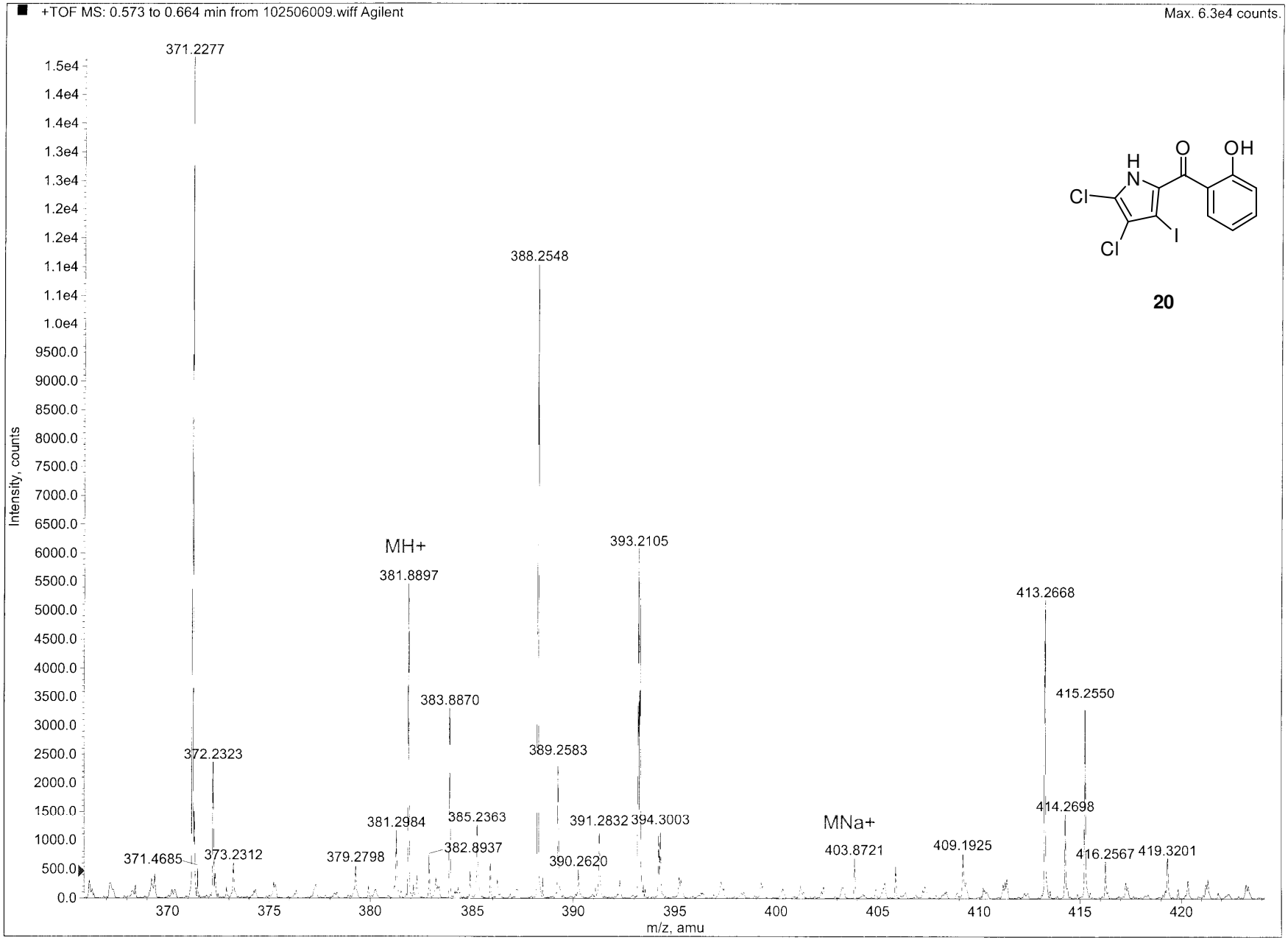
20

^{13}C NMR (75 MHz, $CDCl_3$) of **20**

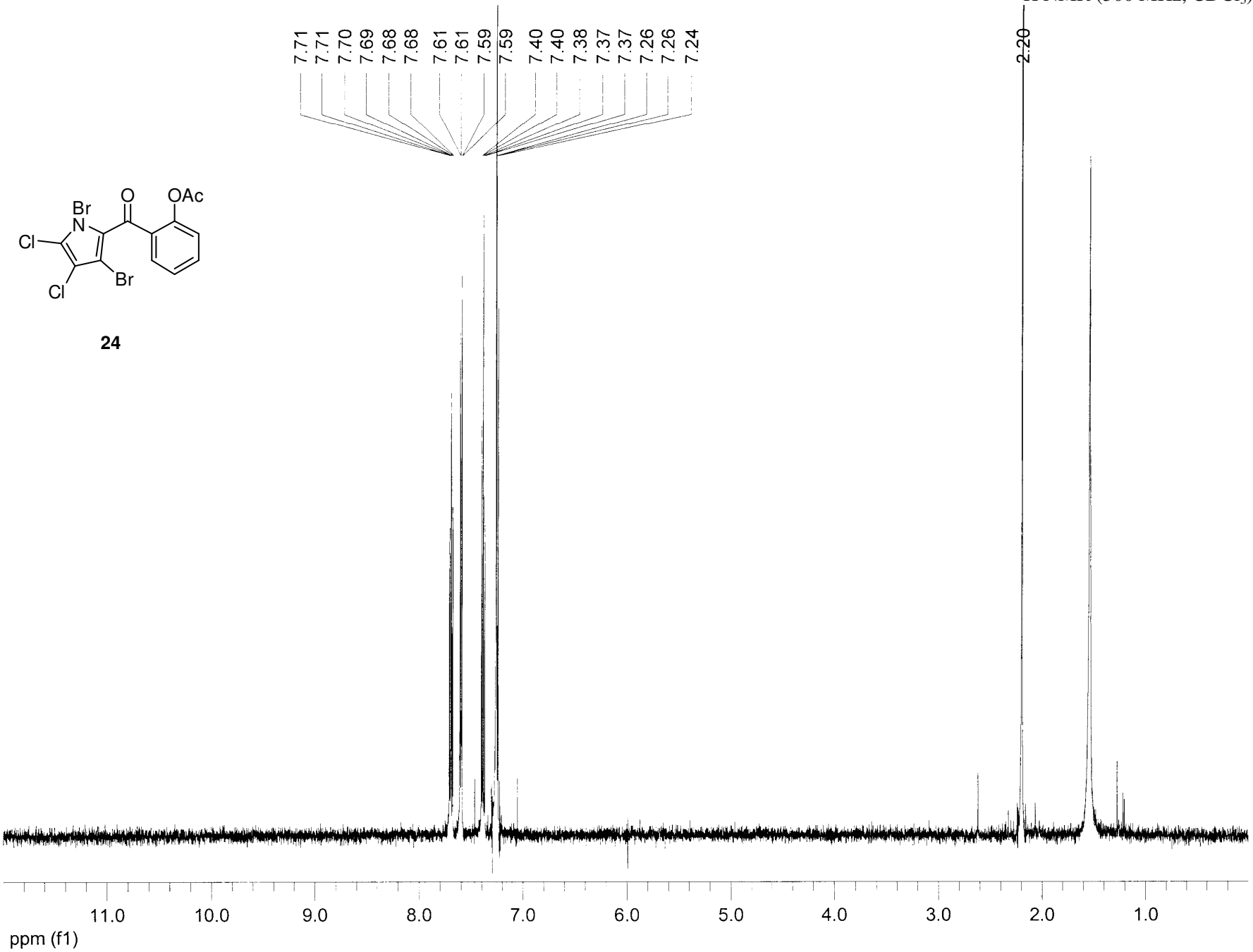


Polarity/Scan Type: Positive Sample Name: flch8552 Acq. Date: Wednesday, October 25, 2006

Acq. File: 102506009.wiff

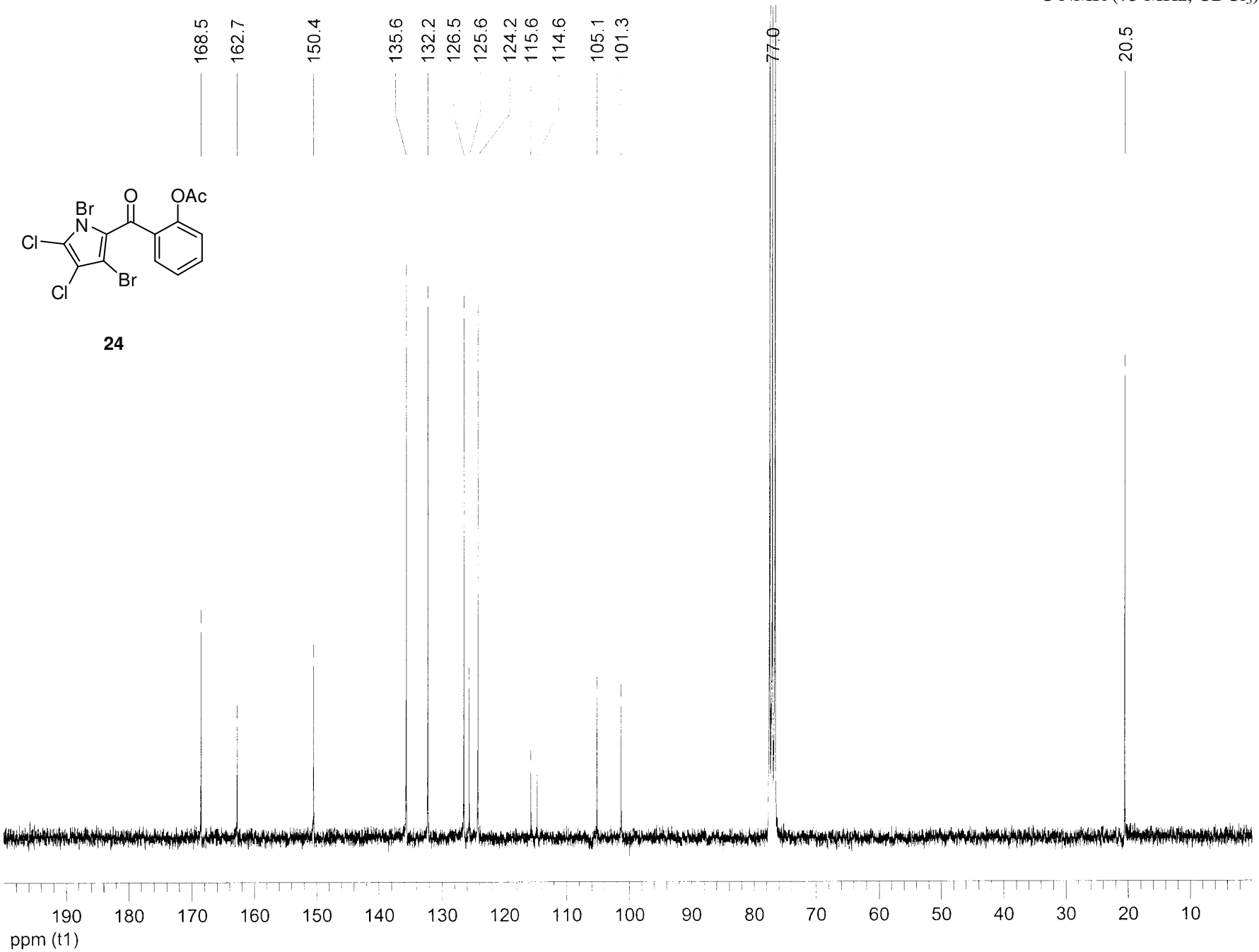


^{1}H NMR (500 MHz, $CDCl_3$) of **24**



24

^{13}C NMR (75 MHz, $CDCl_3$) of **24**

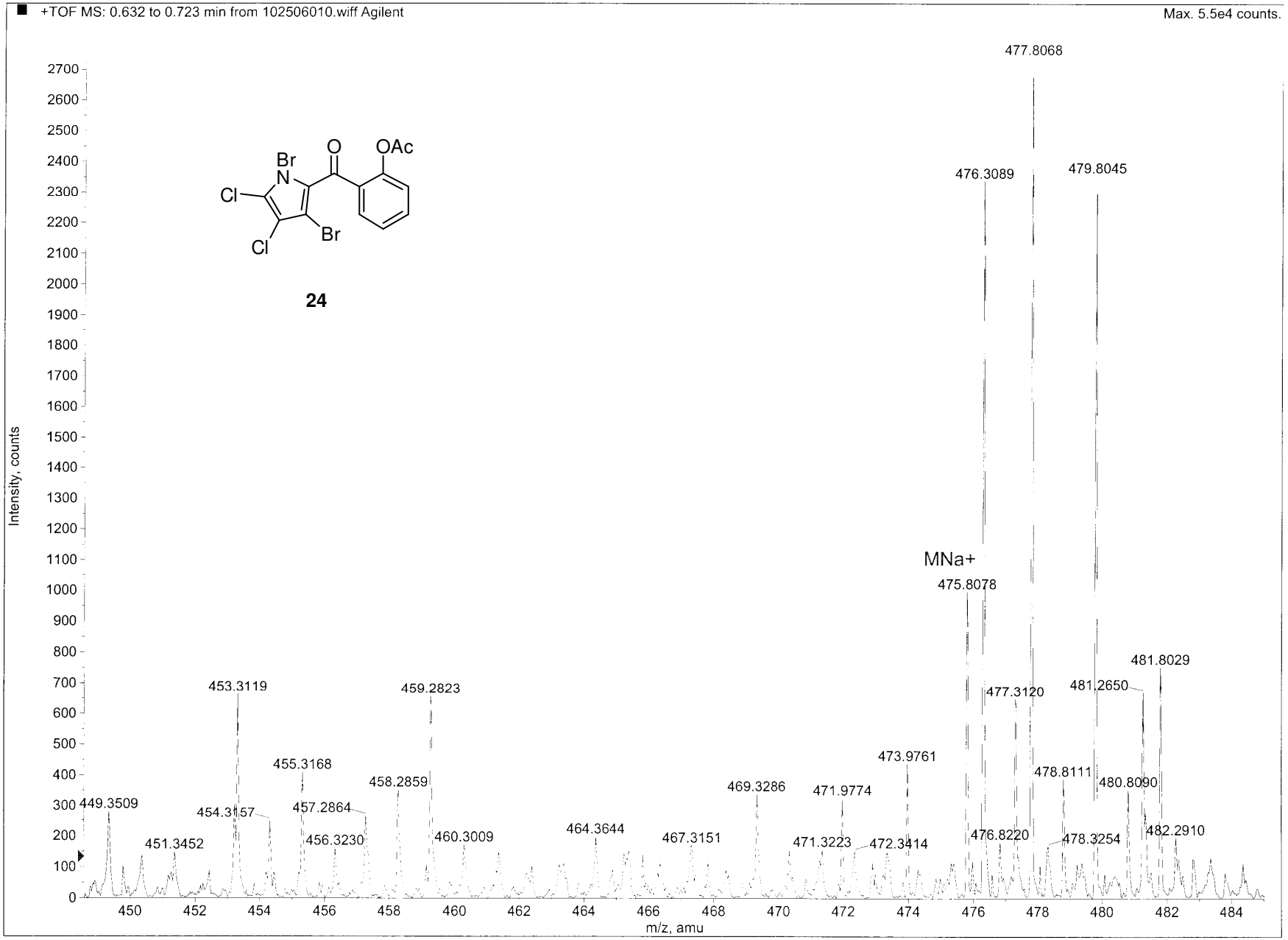


Polarity/Scan Type: Positive

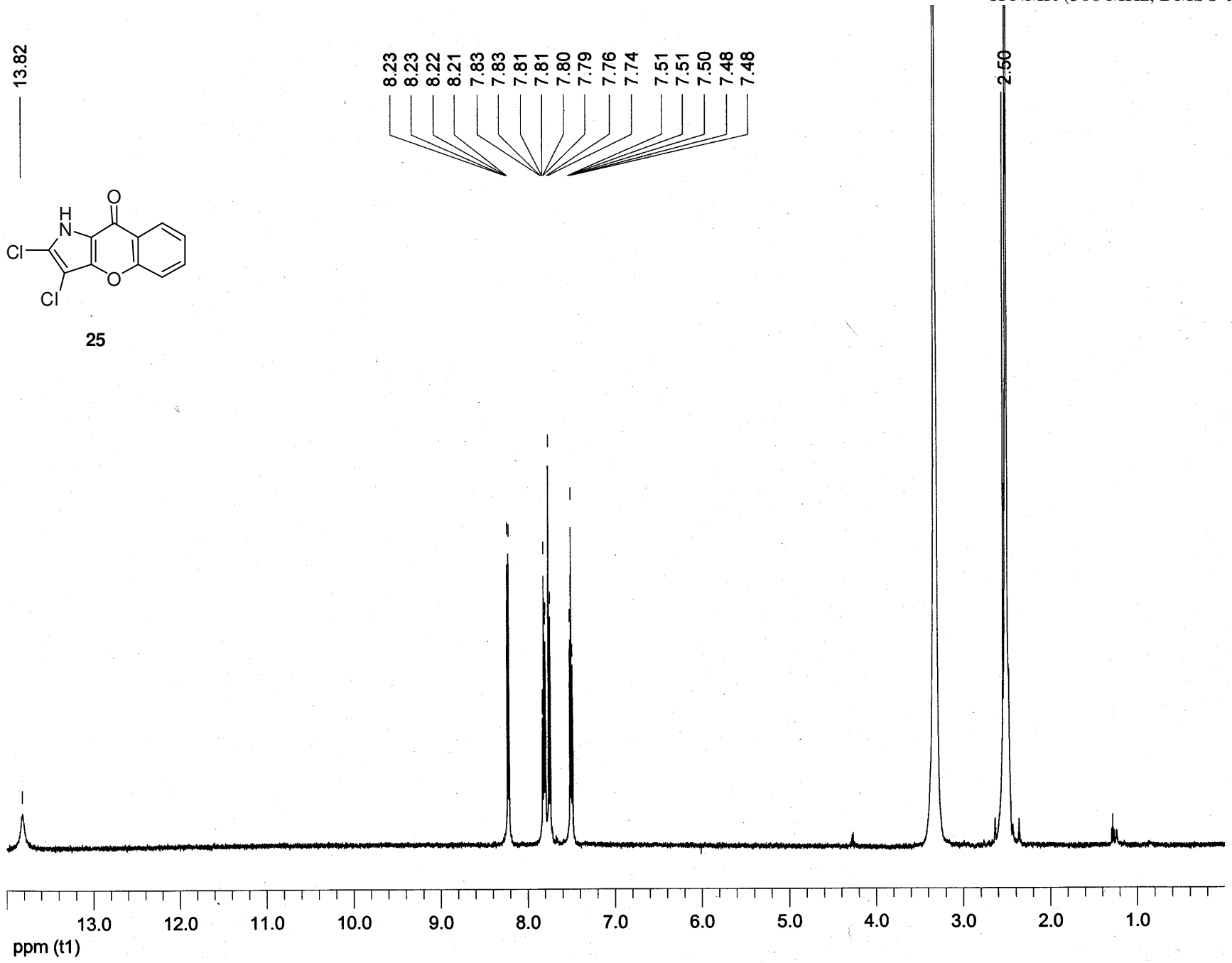
Sample Name: flch8553

Acq. Date: Wednesday, October 25, 2006

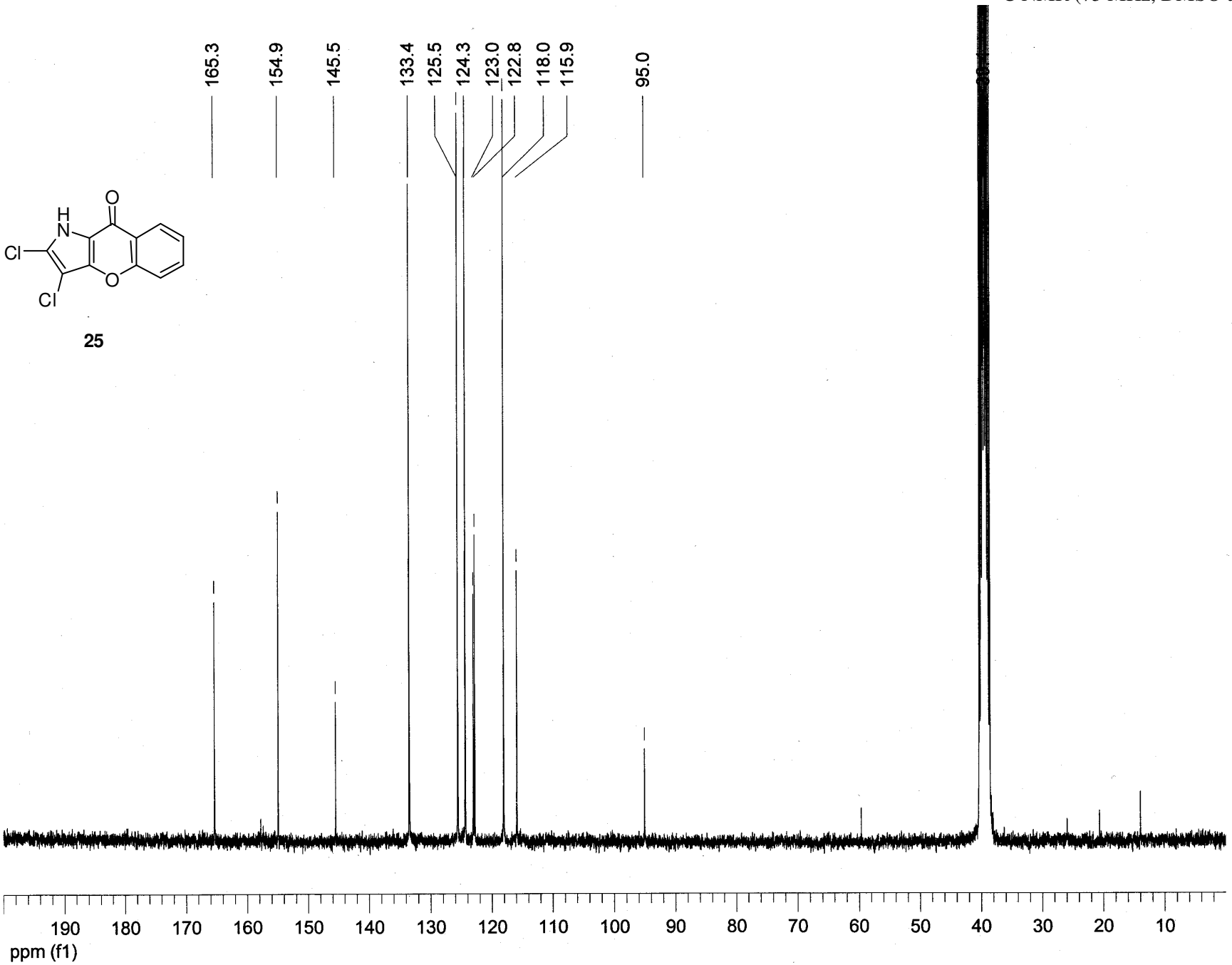
Acq. File: 102506010.wiff



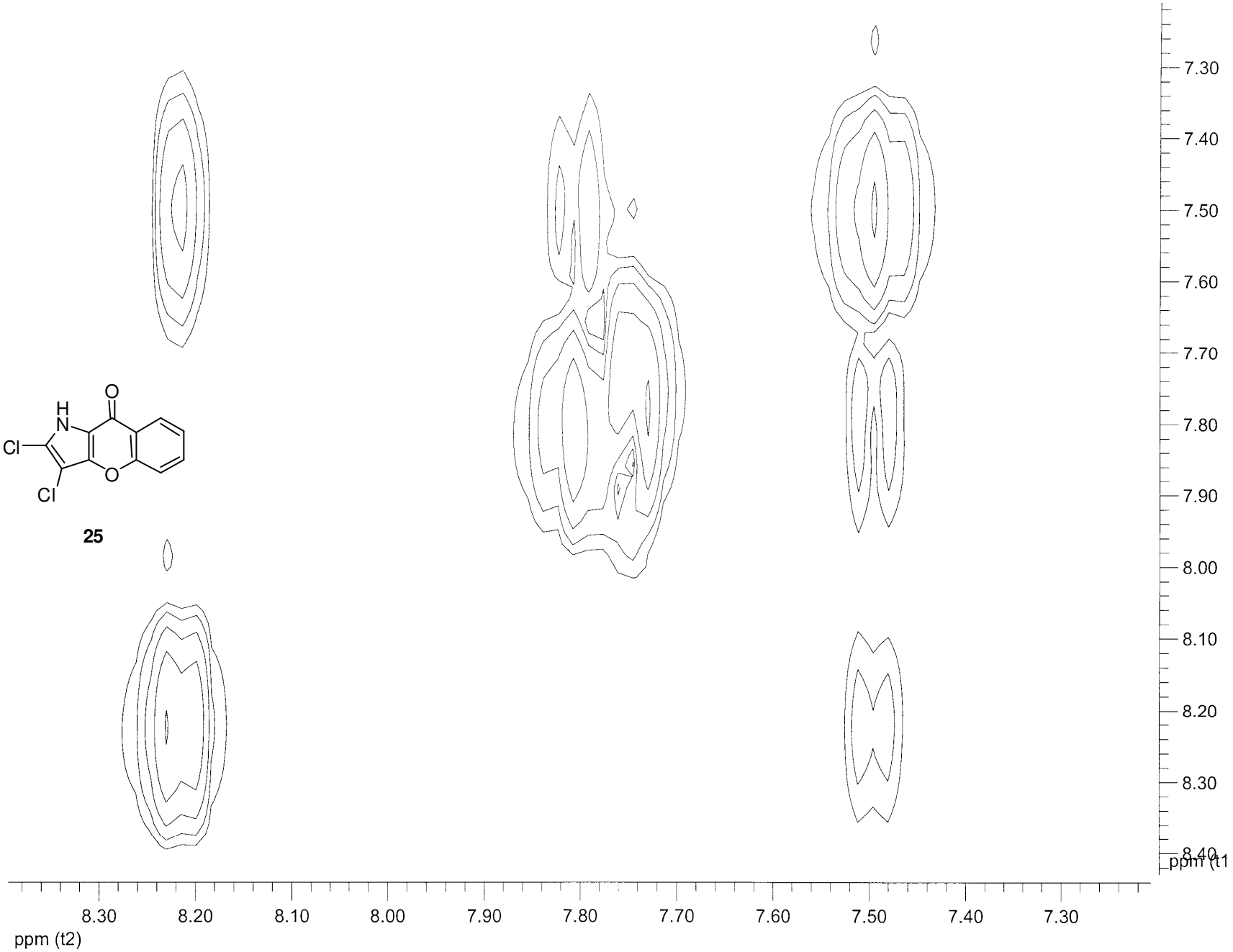
^{1}H NMR (500 MHz, DMSO-d_6) of **25**



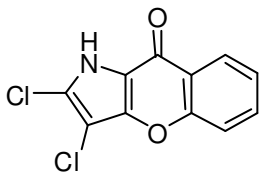
^{13}C NMR (75 MHz, DMSO-d_6) of **25**



COSY (500 MHz, DMSO-d_6) of **25**



HSQC (500 MHz, DMSO-d_6) of **25**



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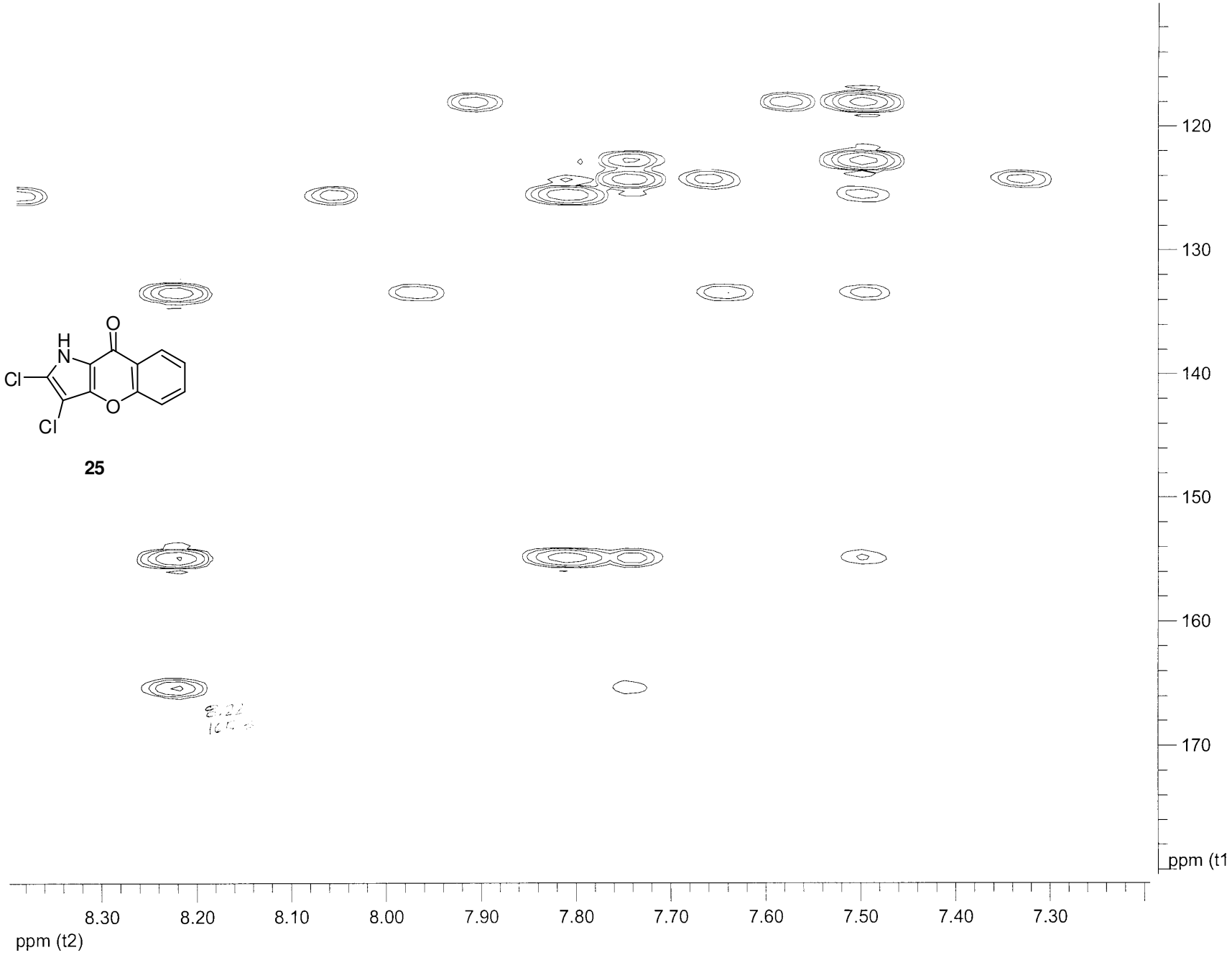
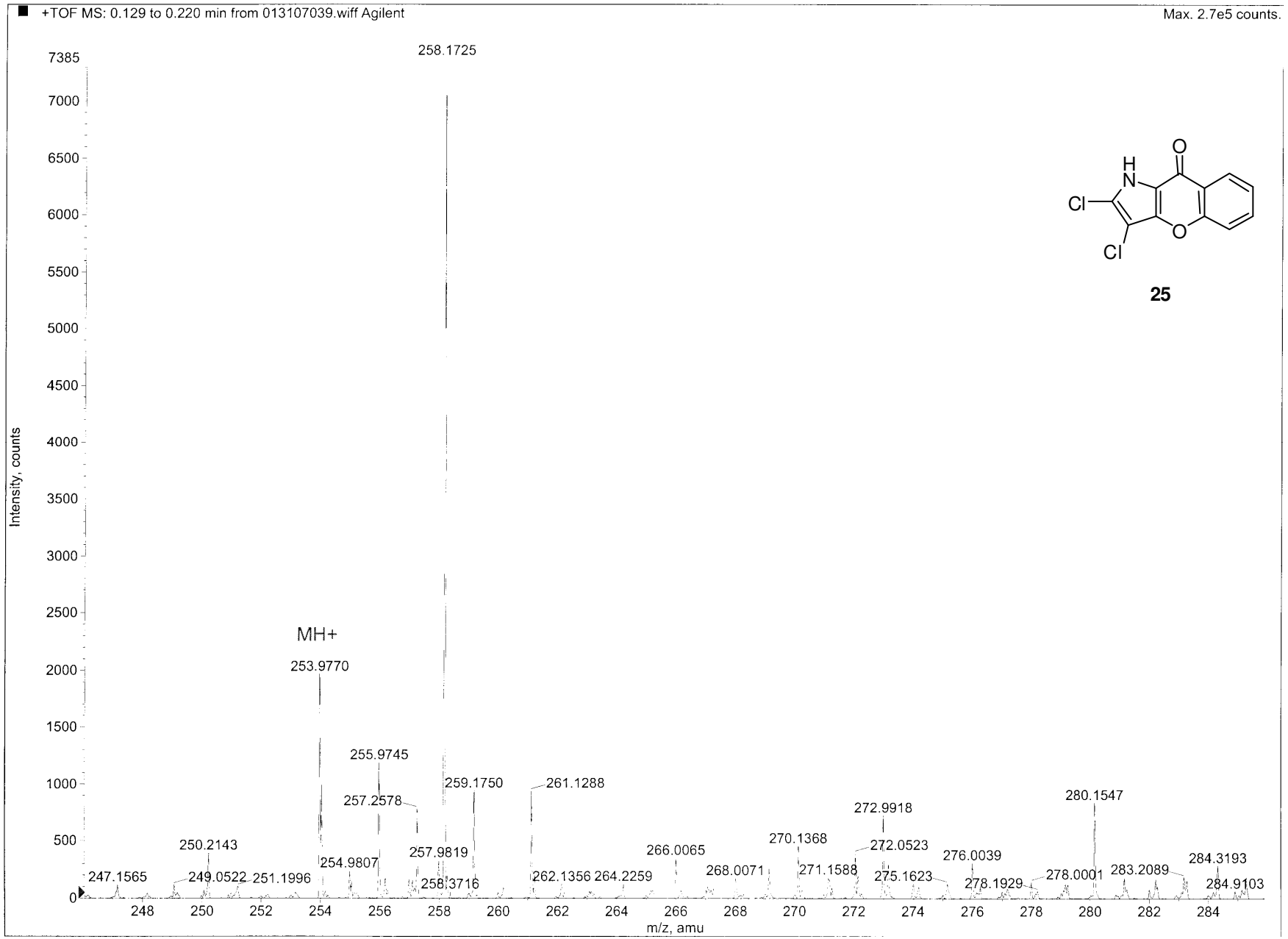
HMBC (500 MHz, DMSO-d_6) of **25**



Polarity/Scan Type: Positive Sample Name: flch2013 Acq. Date: Wednesday, January 31, 2007

Acq. File: 013107039.wiff



25

^{1}H, ^{13}C, and HMBC NMR Spectral Data for **30** ($CDCl_3$)

position	δ_C[a]	δ_H, mult. (*J*, Hz)[b]	HMBC
1		9.42, br s	
2	129.7		
3	117.5		
4	109.9	6.29, m	3,5
5	120.4	6.89, m	2-4
6	160.0		
7	60.3	4.12, q (7.2)	6,8
8	13.9	1.10, t (7.2)	7
2'	124.6		
3'	117.8	7.06, m	2',4'-6'
4'	108.5	6.25, m	2',3',5'
5'	130.0	6.88, m	2'-4'
6'	160.6		
7'	59.6	4.16, q (7.2)	6',8'
8'	14.2	1.22, t (7.2)	7'

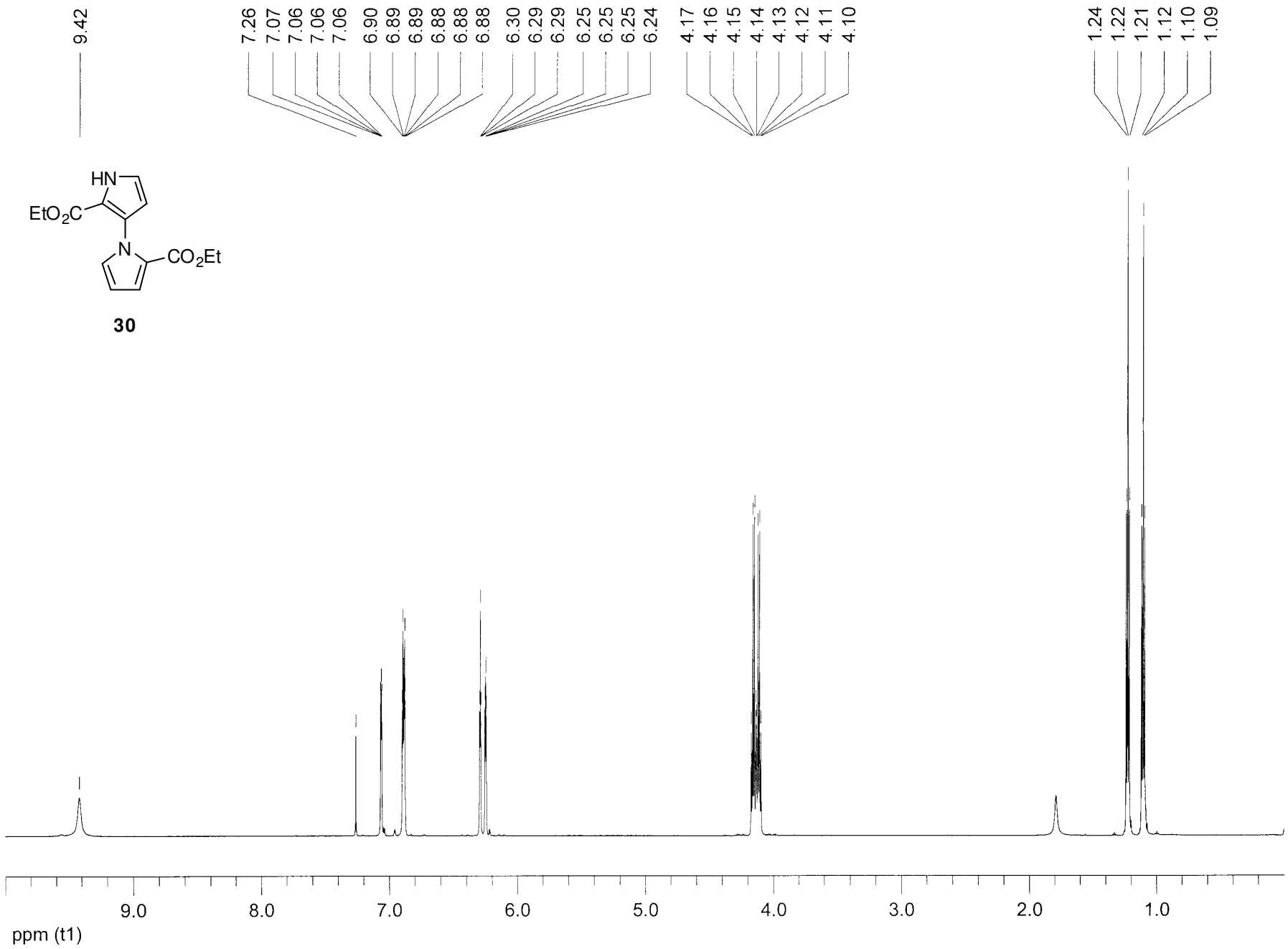
[a] 75 MHz. [b] 600 MHz.

^{1}H, ^{13}C, and HMBC NMR Spectral Data for **31** ($CDCl_3$)

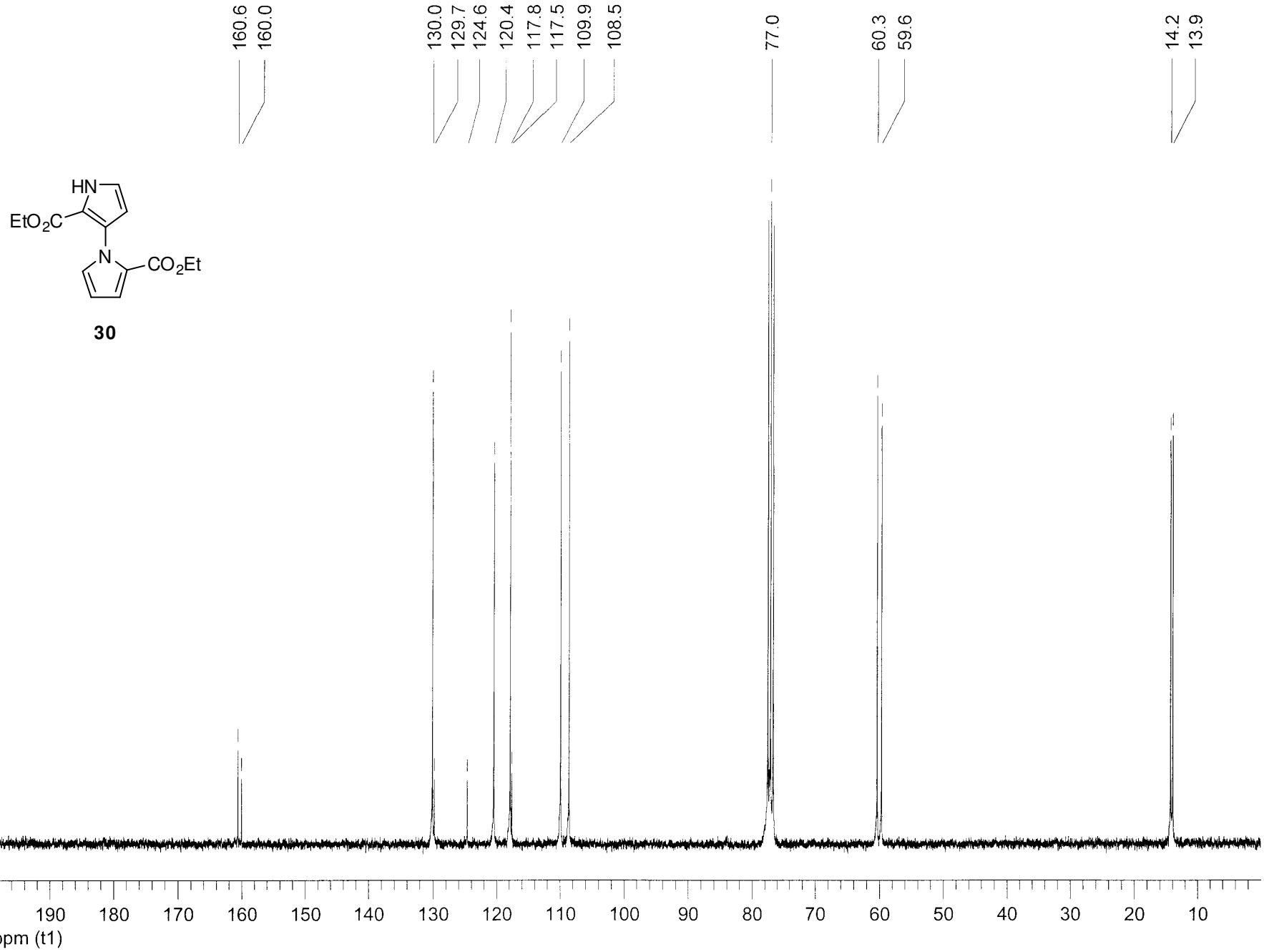
position	δ_C[a]	δ_H, mult. (*J*, Hz)[b]	HMBC
1		10.45, br s	2,4
2	126.8		
3	120.5[c]		
4	102.2		
5	106.0[c]		
6	158.2		
7	61.3	4.13, m	6,8
8	13.8	1.08, t (7.2)	7
2'	125.9		
3'	120.0	7.17, s	2',5',6'
4'	100.5[c]		
5'	114.3		
6'	158.6		
7'	60.7	4.20, q (7.2)	6',8'
8'	14.1	1.26, t (7.2)	7'

[a] 75 MHz. [b] 600 MHz. [c] Carbon assignments were based on ^{13}C data for **30**.

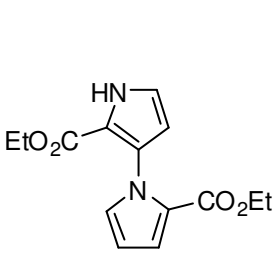
^{1}H NMR (600 MHz, $CDCl_3$) of **30**



^{13}C NMR (75 MHz, $CDCl_3$) of **30**

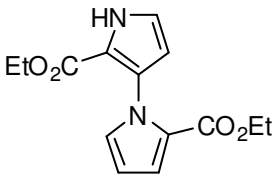


COSY (600 MHz, $CDCl_3$) of **30**



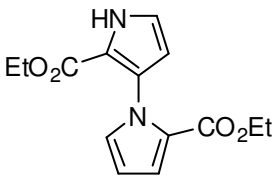
30

HSQC (600 MHz, $CDCl_3$) of **30**



30

HMBC (600 MHz, $CDCl_3$) of **30**



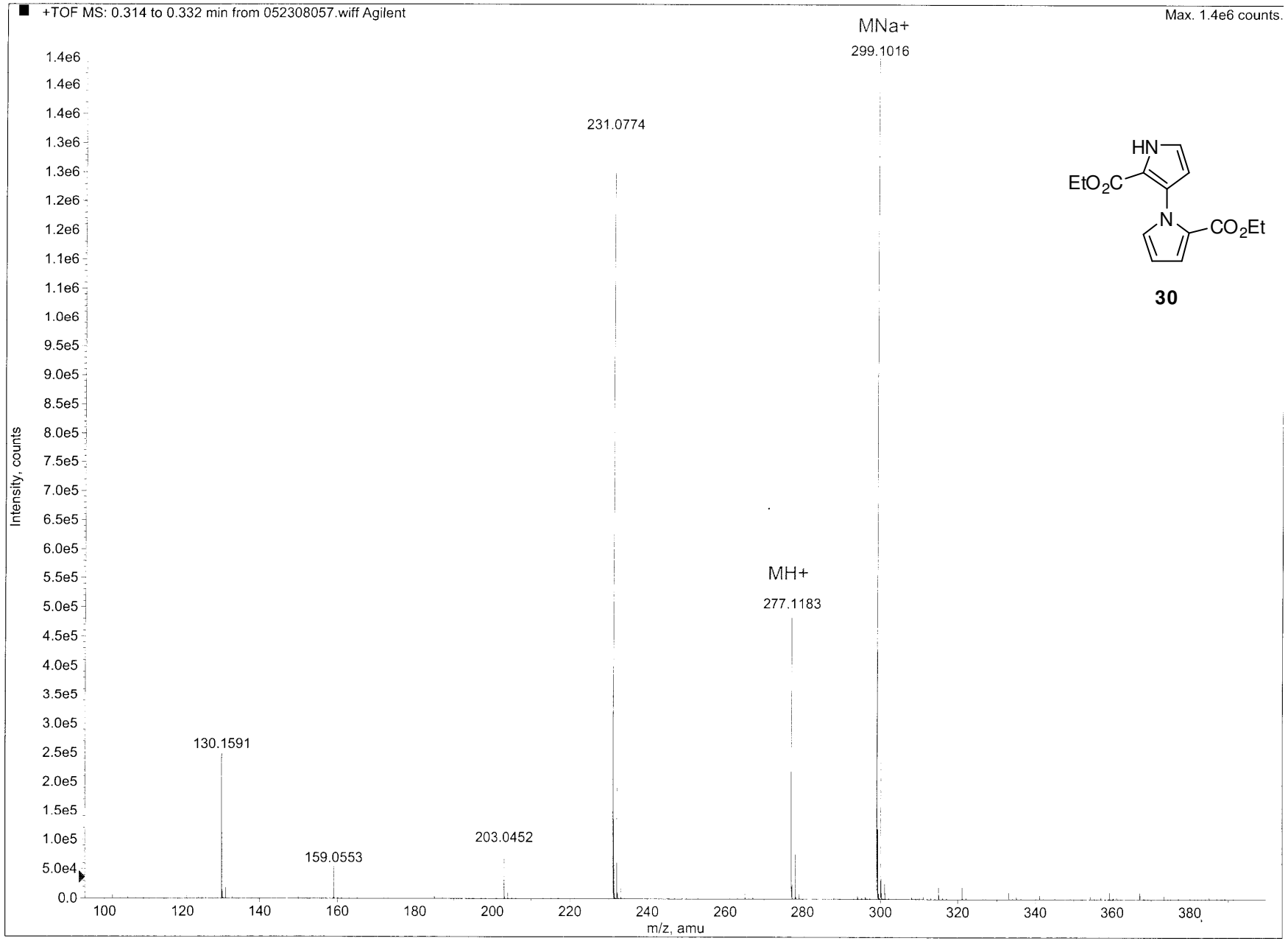
30

Polarity/Scan Type: Positive

Sample Name: flch4384

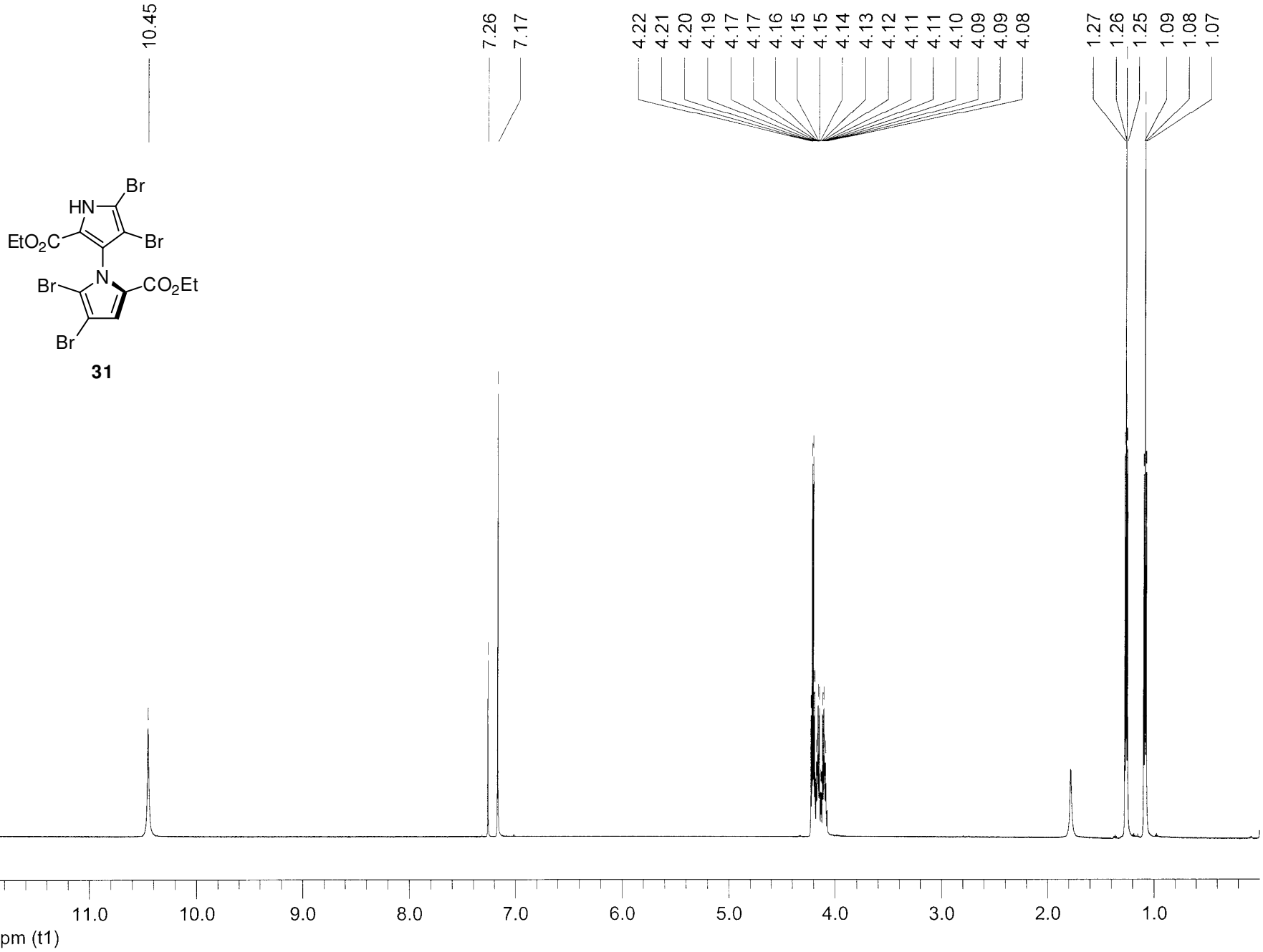
Acq. Date: Friday, May 23, 2008

Acq. File: 052308057.wiff

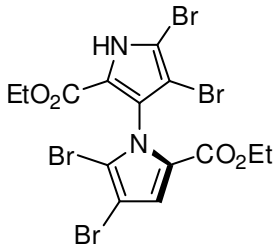


30

^{1}H NMR (600 MHz, $CDCl_3$) of **31**

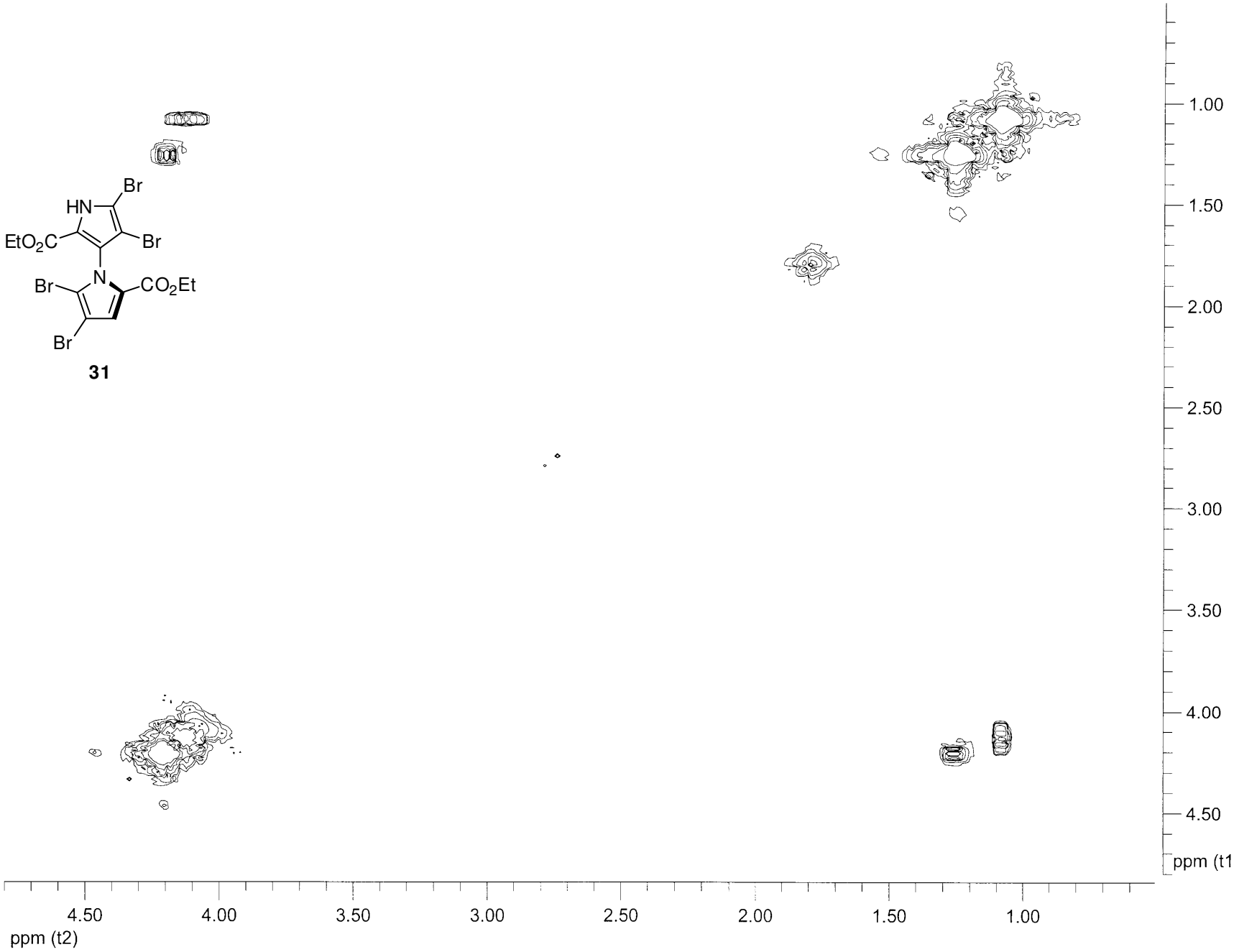


^{13}C NMR (75 MHz, $CDCl_3$) of **31**

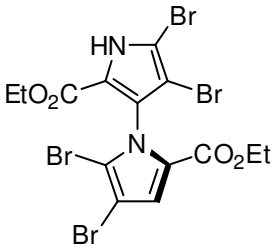


31

COSY (600 MHz, $CDCl_3$) of **31**

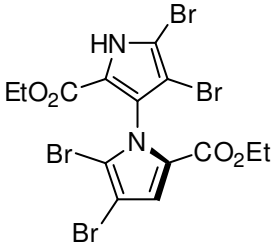


HSQC (600 MHz, $CDCl_3$) of **31**



31

HMBC (600 MHz, $CDCl_3$) of **31**



31

Polarity/Scan Type: Positive Sample Name: flch4385 Acq. Date: Friday, May 23, 2008

Acq. File: 052308058.wiff

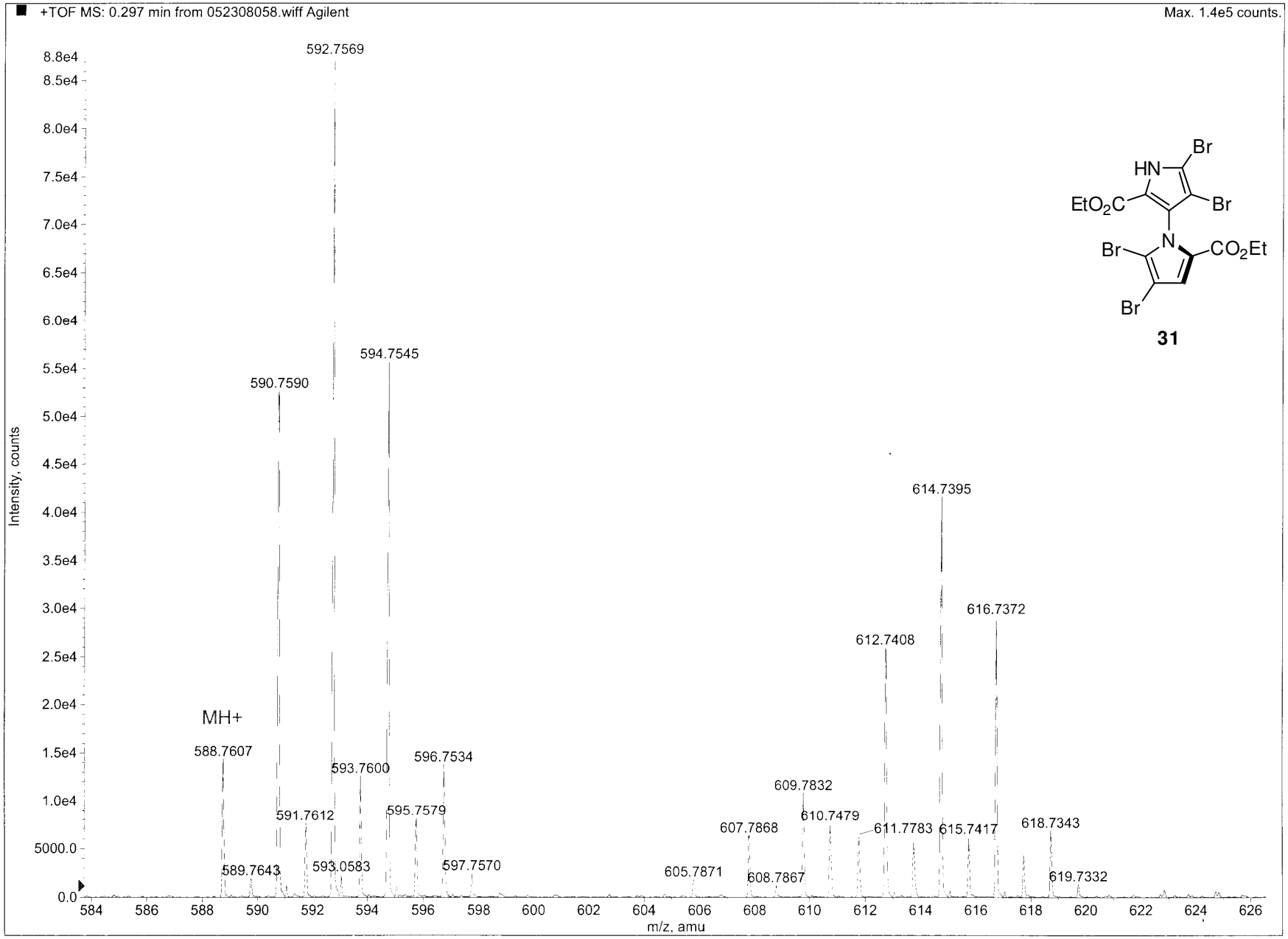


Figure S1. ORTEP of marinopyrrole F (**6**)

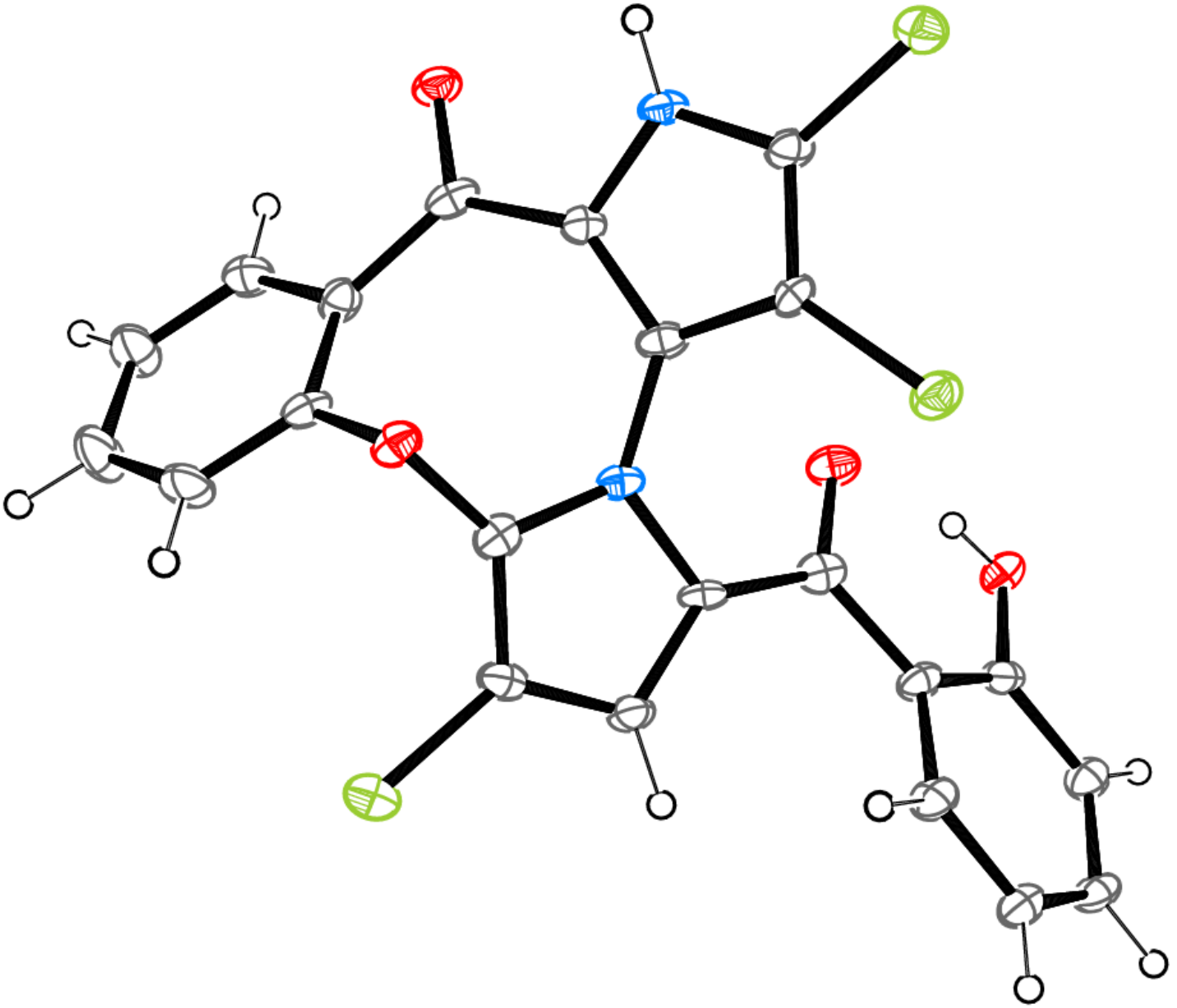


Figure S2. ORTEP of bromophenol **19**

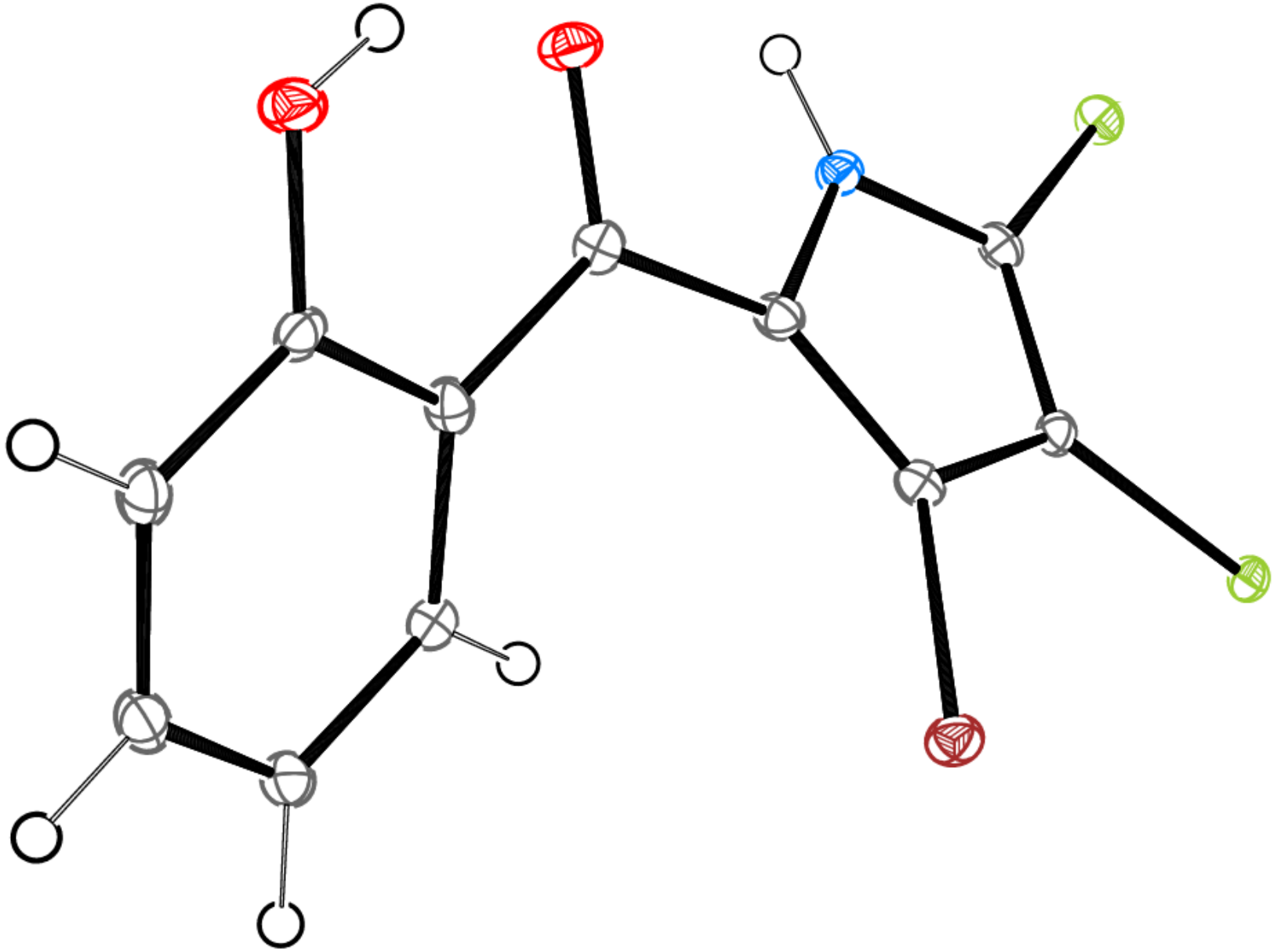


Figure S3. ORTEP of bipyrrole **31**