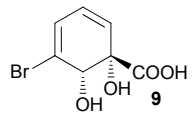
Supplementary Material (ESI) for Organic & Biomolecular Chemistry

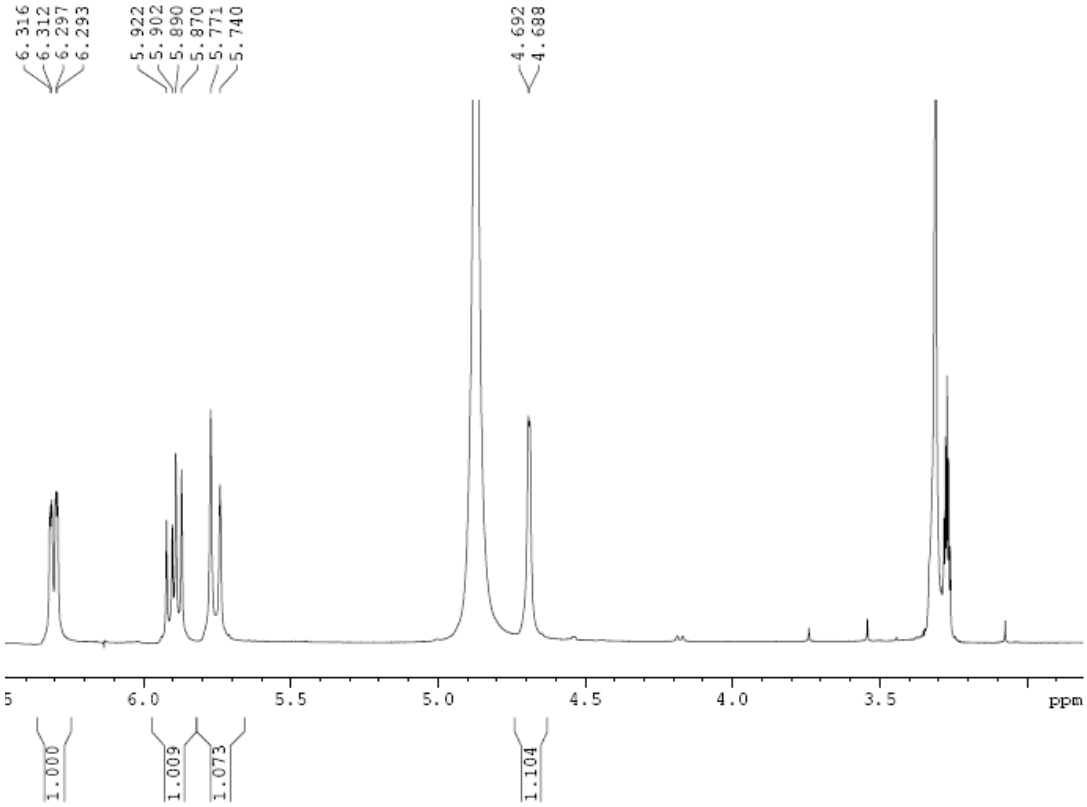
Electronic Supporting Information

Expanding the chiral pool: oxidation of 3-bromobenzoic acid by *R. eutrophus* B9 allows access to new reaction manifolds.

Julia A. Griffen, Amélie M. Le Coz, Gabriele Kociok-Köhn, Monika Ali Khan, Alan J. W. Stewart and Simon E. Lewis*


Br
COOH
OH
OH

9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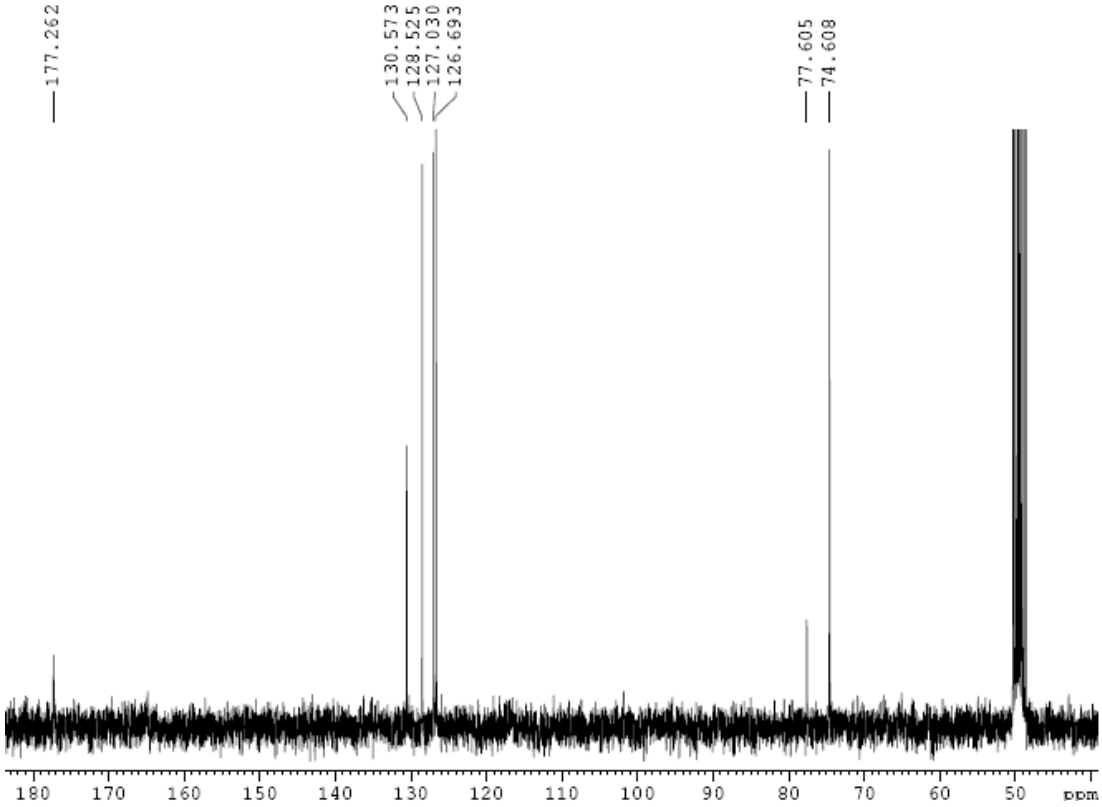
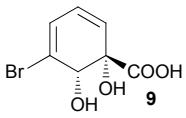
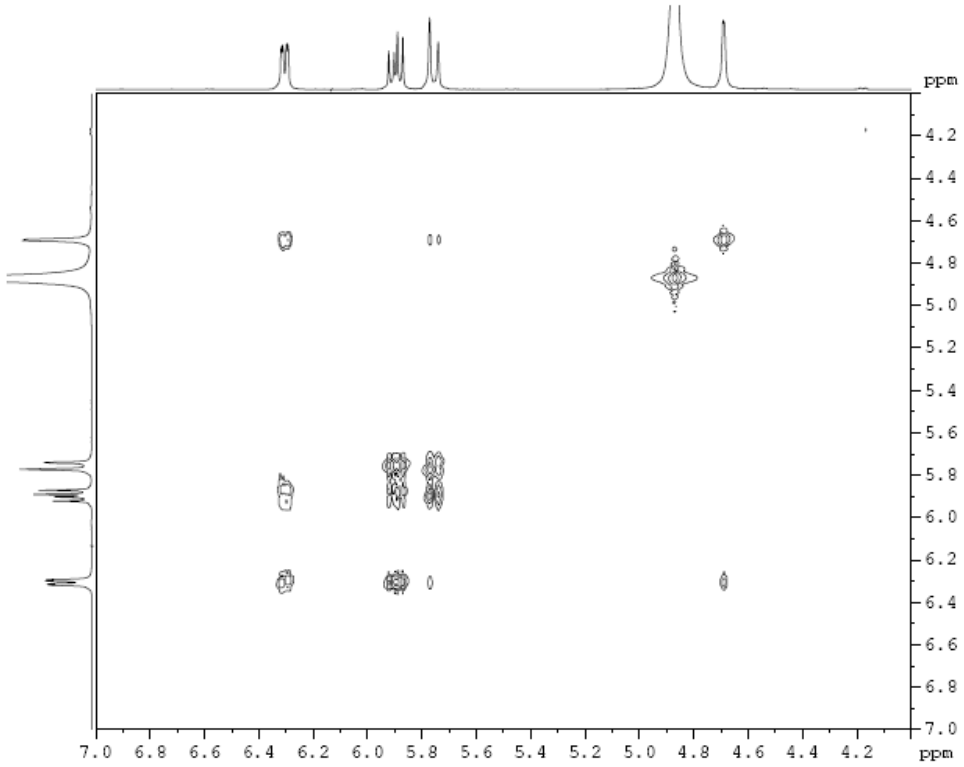
6.312
6.297
6.293
5.922
5.902
5.890
5.870
5.771
5.740
4.692
4.688
6.0
5.5
5.0
4.5
4.0
3.5
ppm
1.000
1.009
1.073
1.104

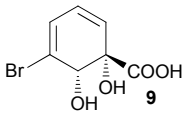

177.262
130.573
128.525
127.030
126.693
77.605
74.608
180
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm


Br
COOH
OH
OH

9

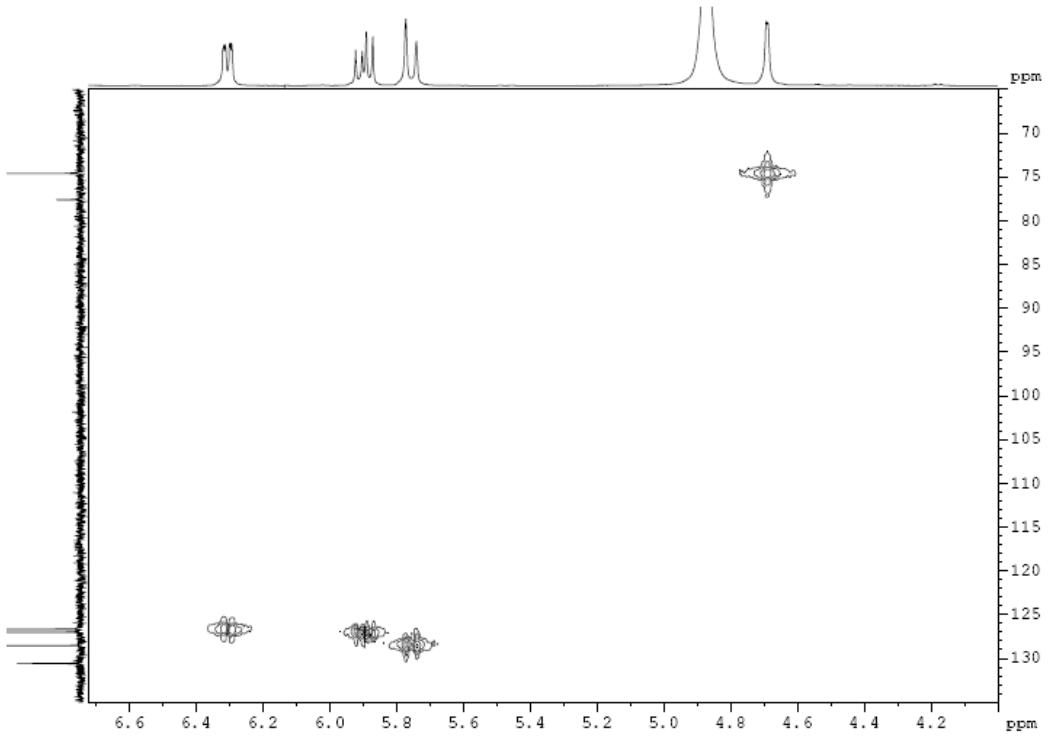
COSY

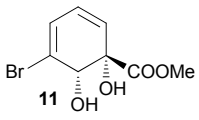

ppm
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2
ppm


Br
COOH
OH
OH

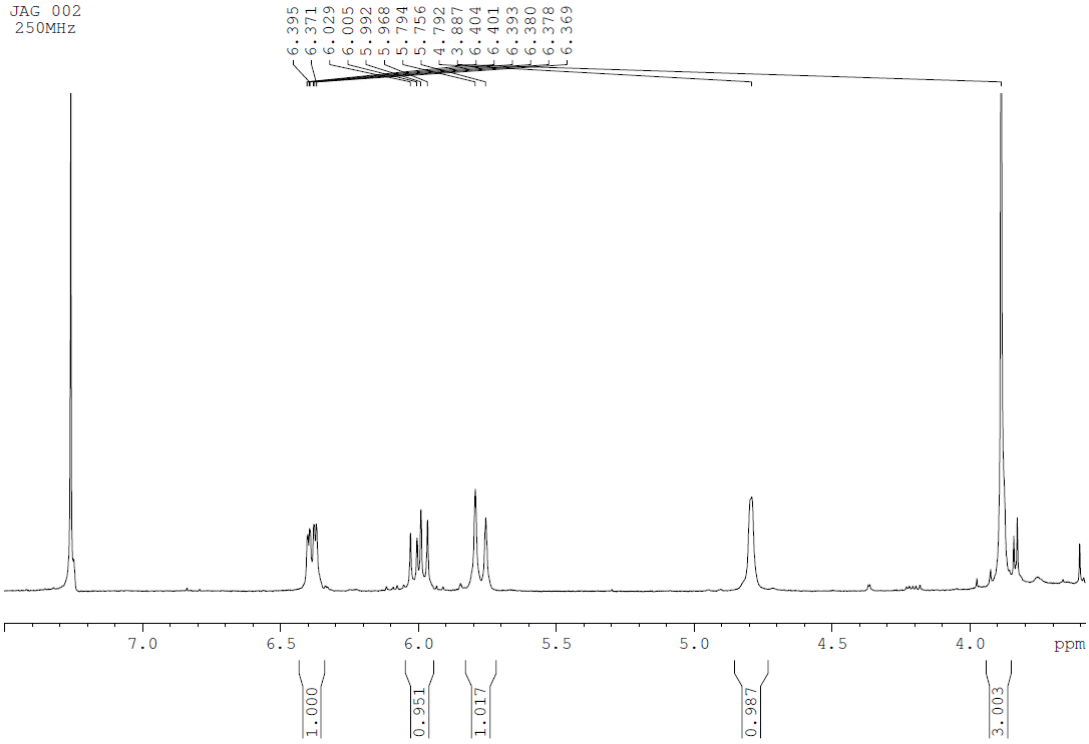
9

HMQC


ppm
70
75
80
85
90
95
100
105
110
115
120
125
130
6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2
ppm


Br
COOMe
OH
OH

11 *crude*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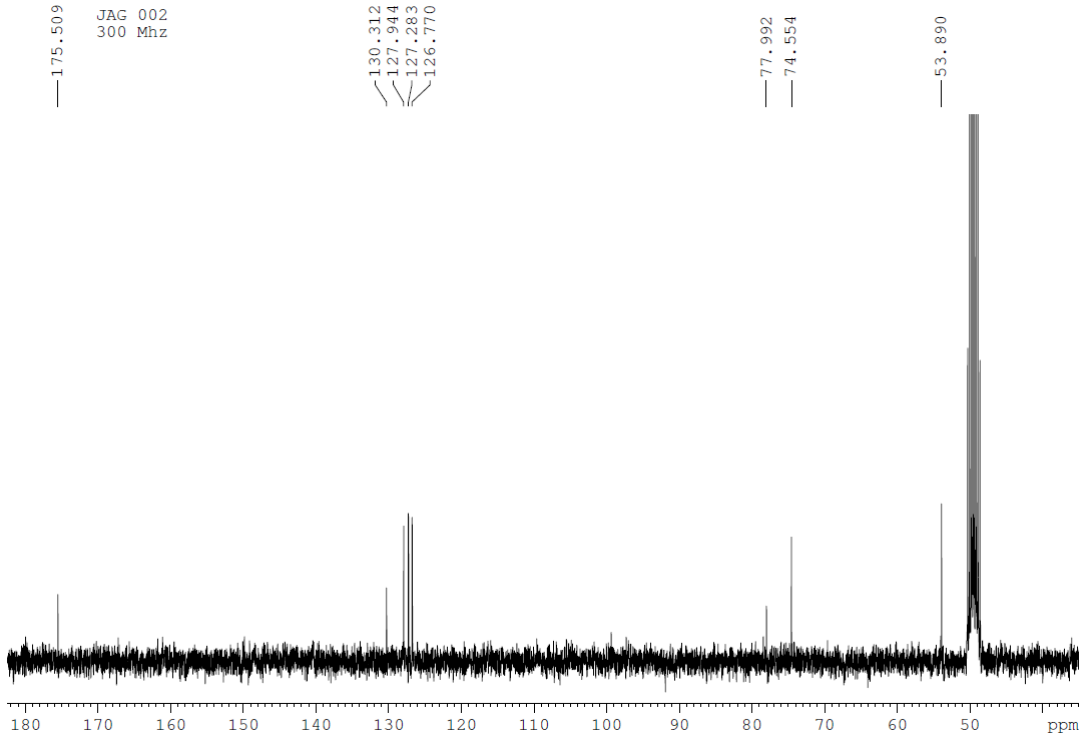
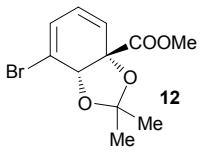
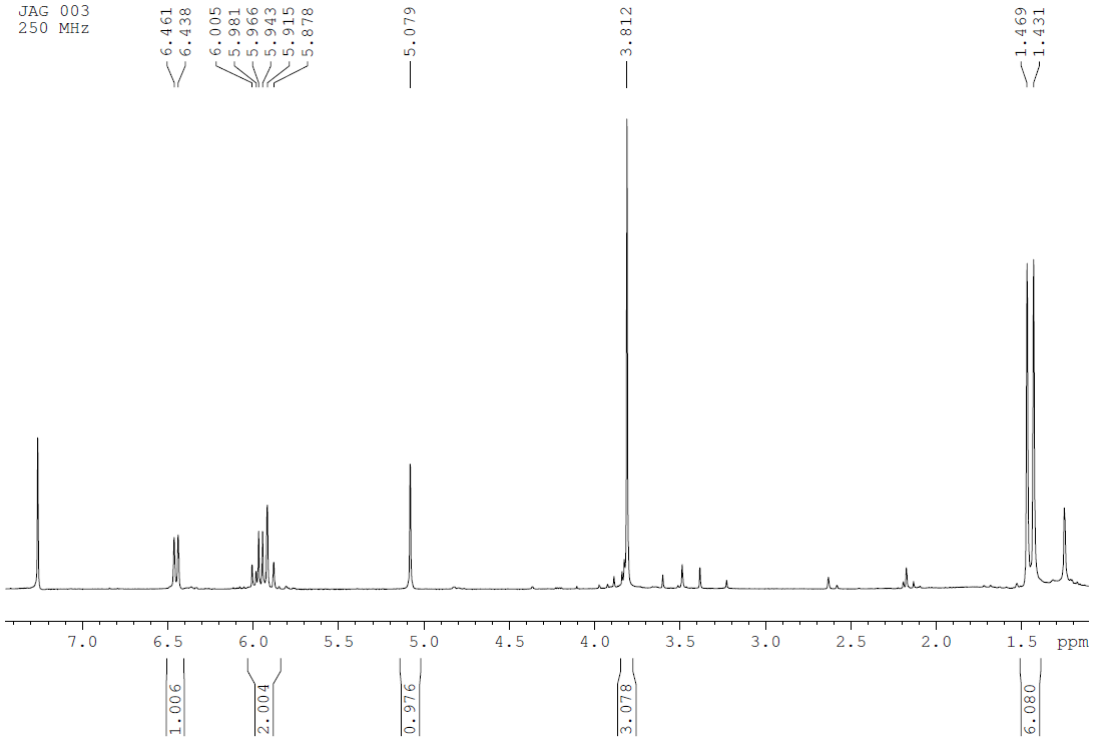
250MHz
6.395
6.371
6.029
6.005
5.992
5.968
5.794
5.756
4.792
3.887
6.404
6.401
6.393
6.380
6.378
6.369
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
1.000
0.951
1.017
0.987
3.003


175.509
JAG 002
300 Mhz
130.312
127.944
127.283
126.770
77.992
74.554
53.890
180
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm


COOMe
Br
O
O
Me
Me

12

crude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250 MHz
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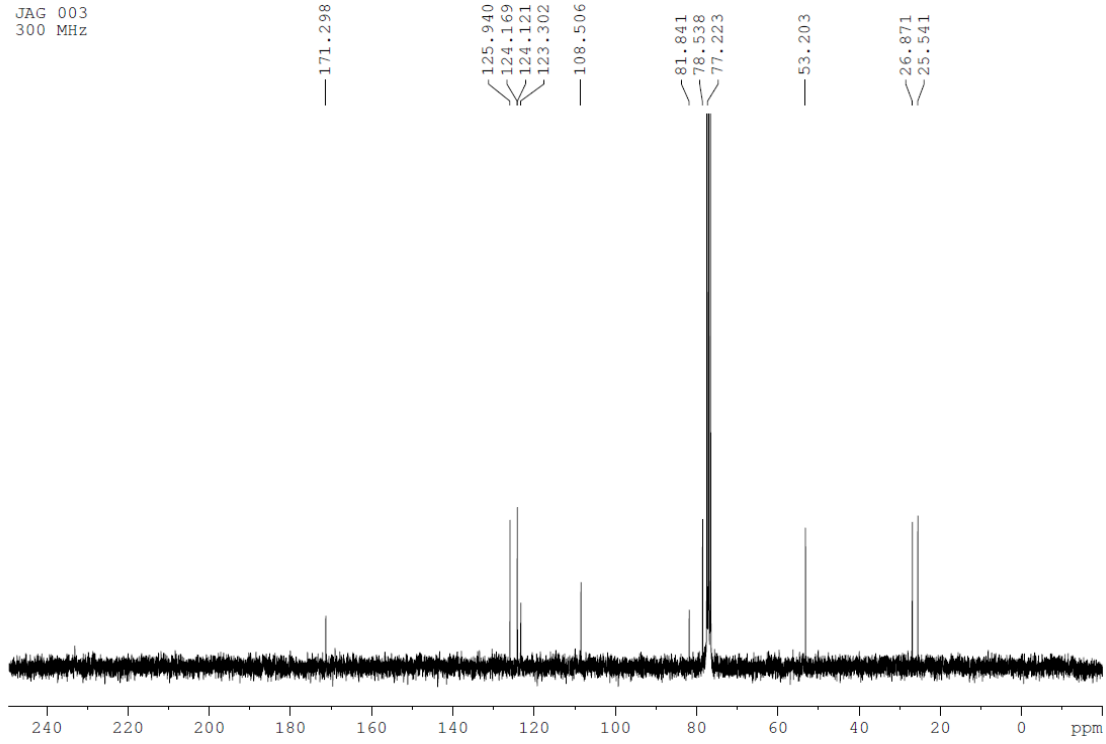
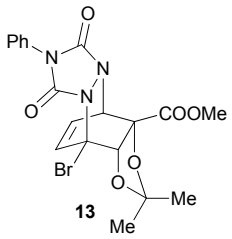
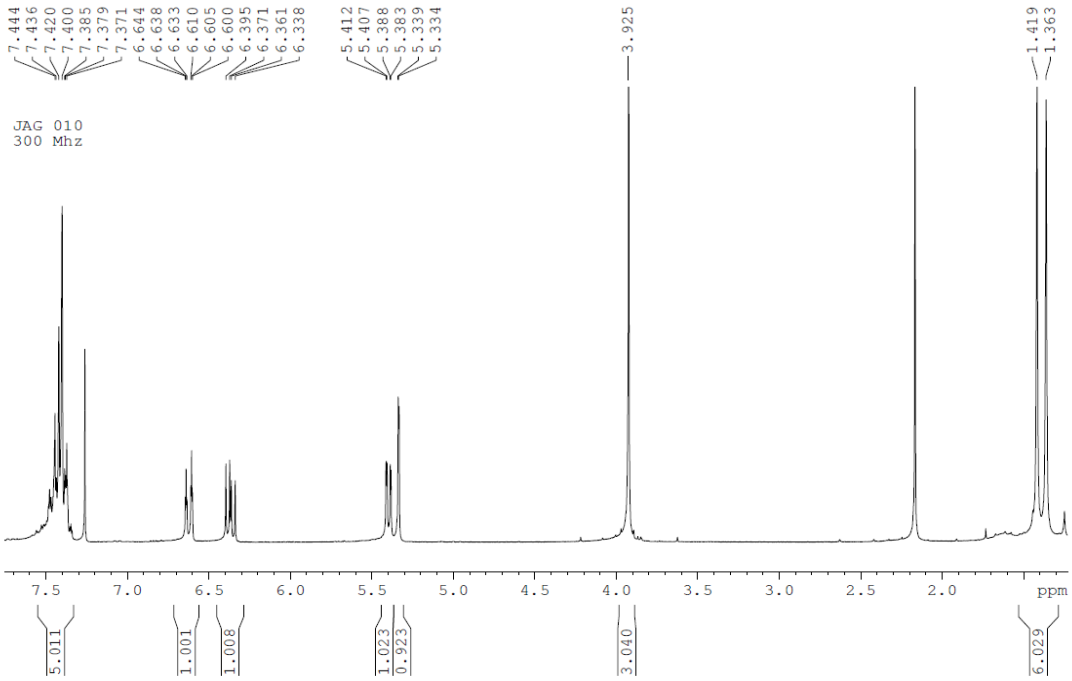
6.438
6.005
5.981
5.966
5.943
5.915
5.878
5.079
3.812
1.469
1.431
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.006
2.004
0.976
3.078
6.080


JAG 003
300 MHz
171.298
125.940
124.169
124.121
123.302
108.506
81.841
78.538
77.223
53.203
26.871
25.541
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
N
O
N
N
O
COOMe
Br
O
O
Me
Me

13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7.436
7.420
7.400
7.385
7.379
7.371
6.644
6.638
6.633
6.610
6.605
6.600
6.395
6.371
6.361
6.338
5.412
5.407
5.388
5.383
5.339
5.334
3.925
1.419
1.363
JAG 010
300 Mhz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
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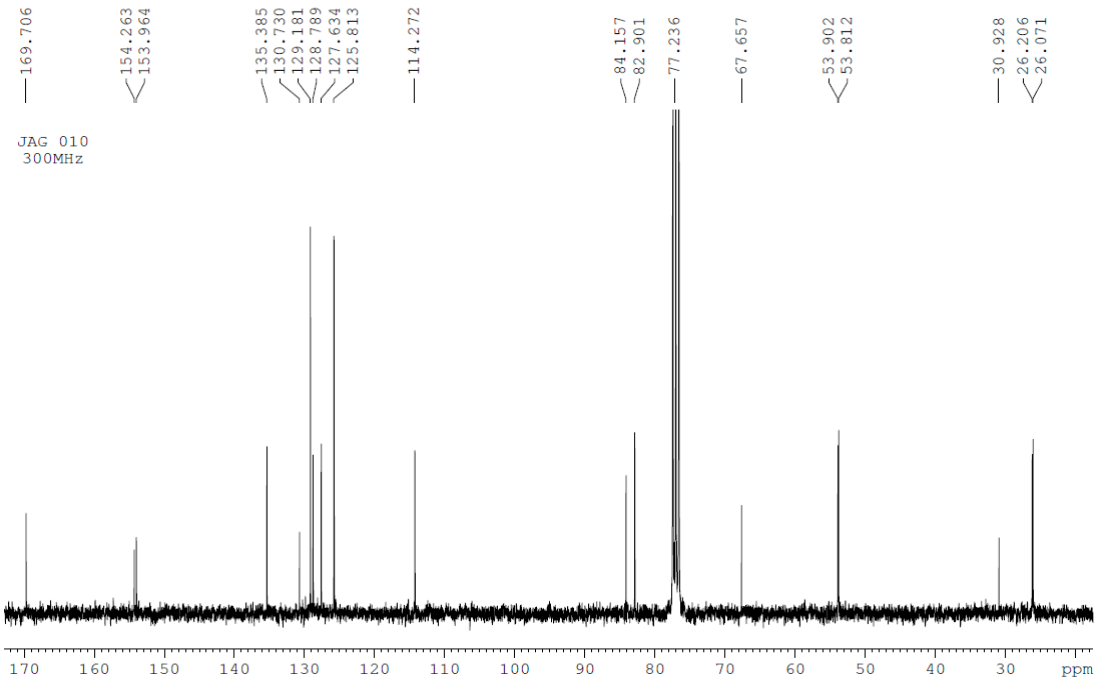
1.001
1.008
1.023
0.923
3.040
6.029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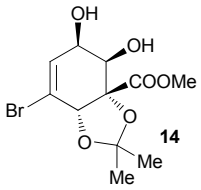
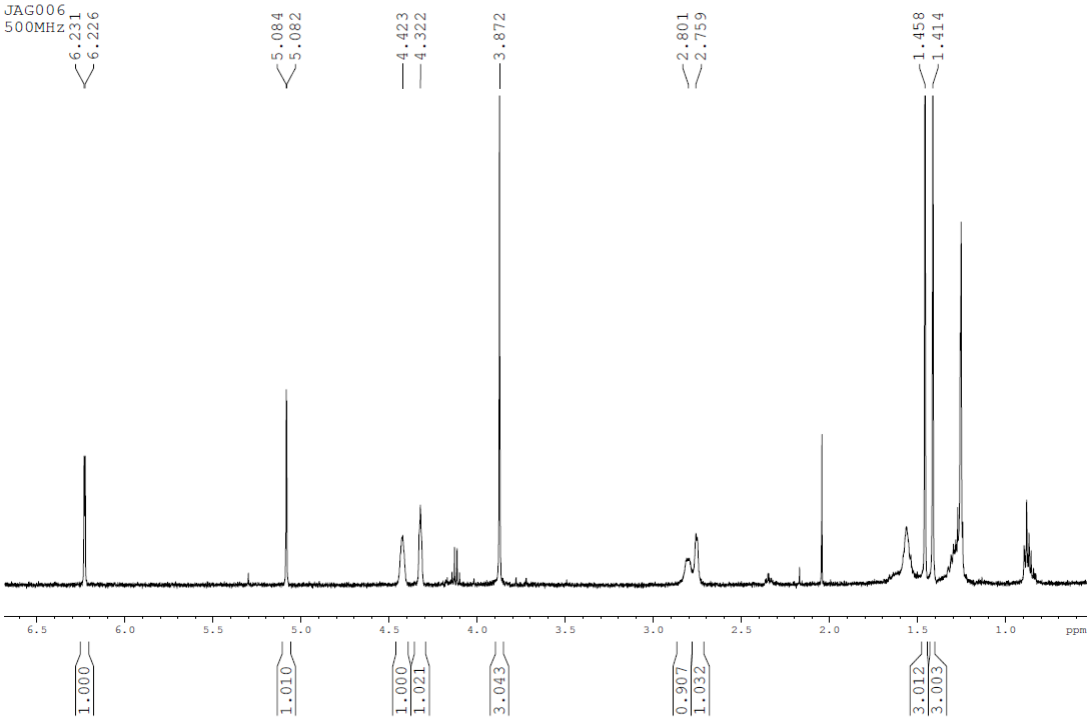
154.263
153.964
135.385
130.730
129.181
128.789
127.634
125.813
114.272
84.157
82.901
77.236
67.657
53.902
53.812
30.928
26.206
26.071
JAG 010
300MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


OH
OH
COOMe
Br
O
O
Me
Me

14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500MHz
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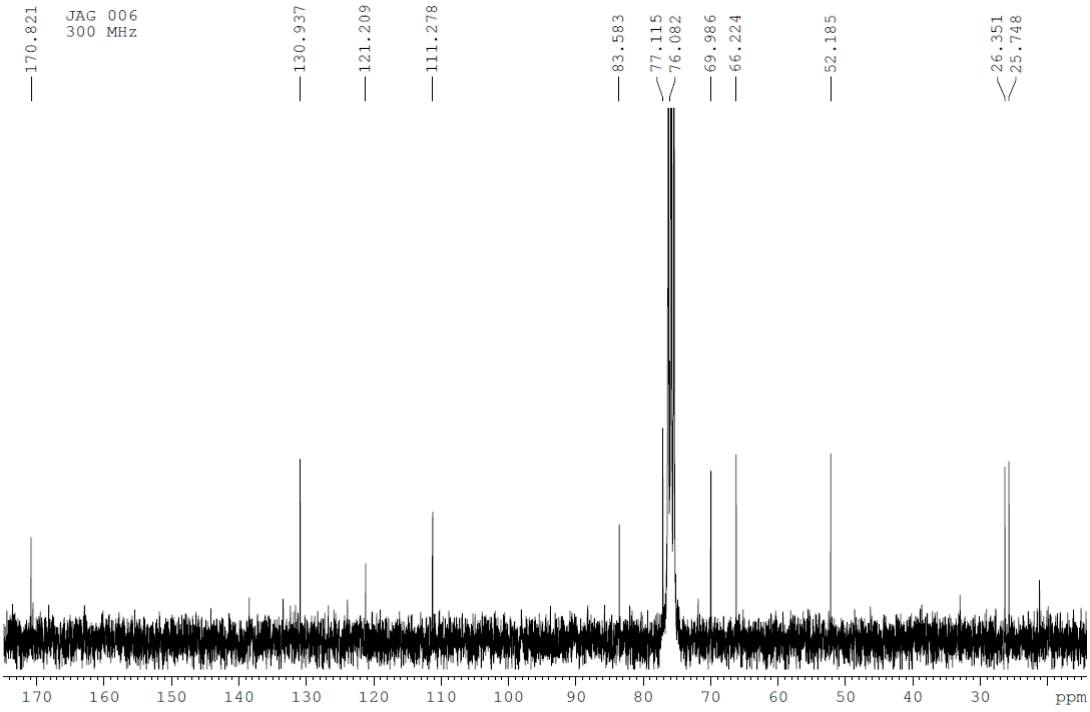
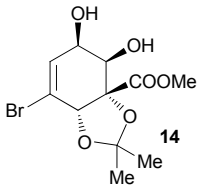
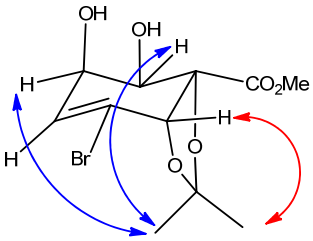
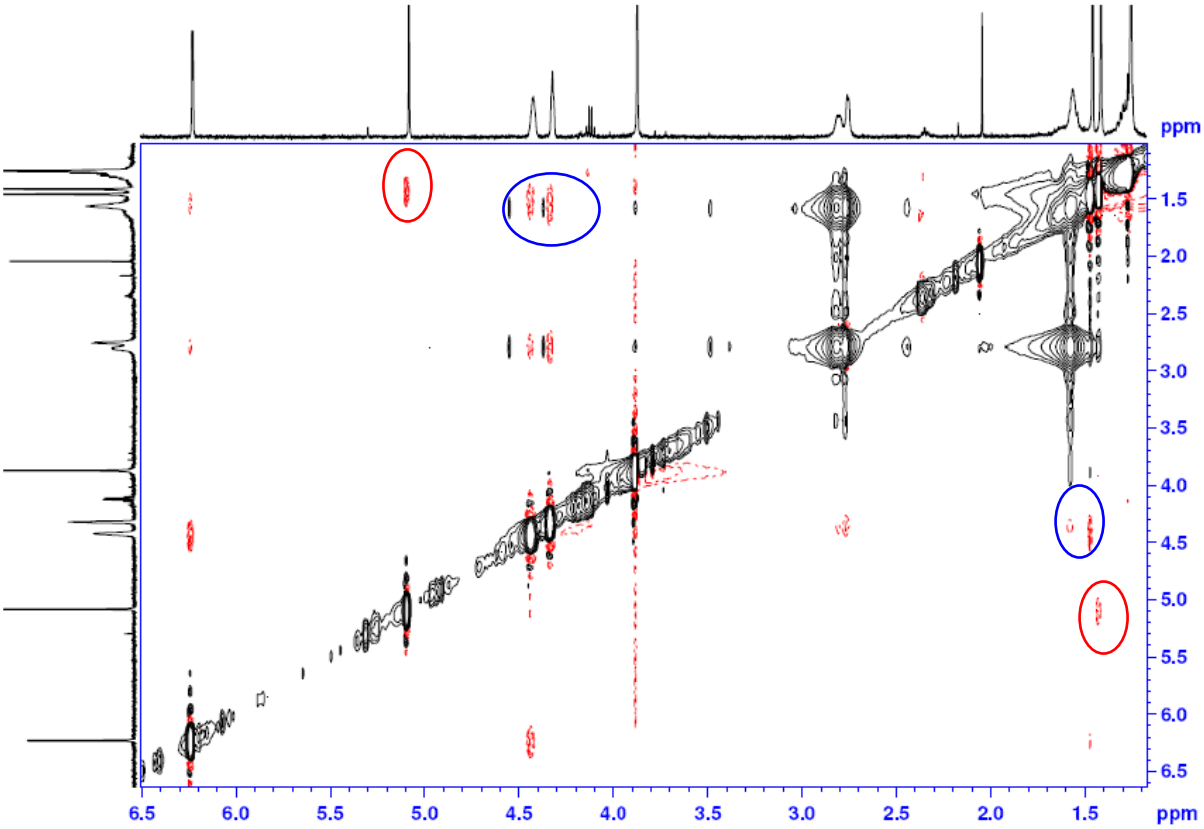
6.226
5.084
5.082
4.423
4.322
3.872
2.801
2.759
1.458
1.414
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.000
1.010
1.000
1.021
3.043
0.907
1.032
3.012
3.003


JAG 006
300 MHz
170.821
130.937
121.209
111.278
83.583
77.115
76.082
69.986
66.224
52.185
26.351
25.748
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


OH
OH
COOMe
Br
O
O
Me
Me

14


OH
OH
H
H
CO2Me
H
H
Br
O
O


ppm
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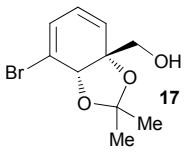
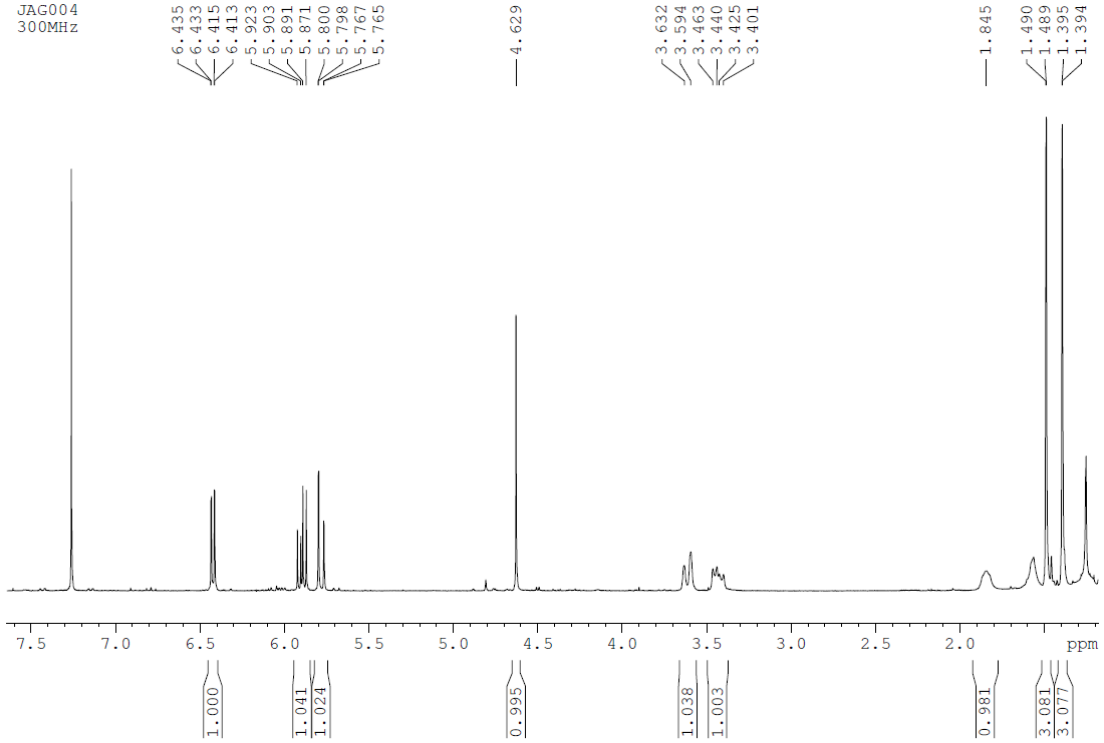
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


Br
OH
O
O
Me
Me

17


JAG004
300MHz
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6.413
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5.891
5.871
5.800
5.798
5.767
5.765
4.629
3.632
3.594
3.463
3.440
3.425
3.401
1.845
1.490
1.489
1.395
1.394
7.5
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5.5
5.0
4.5
4.0
3.5
3.0
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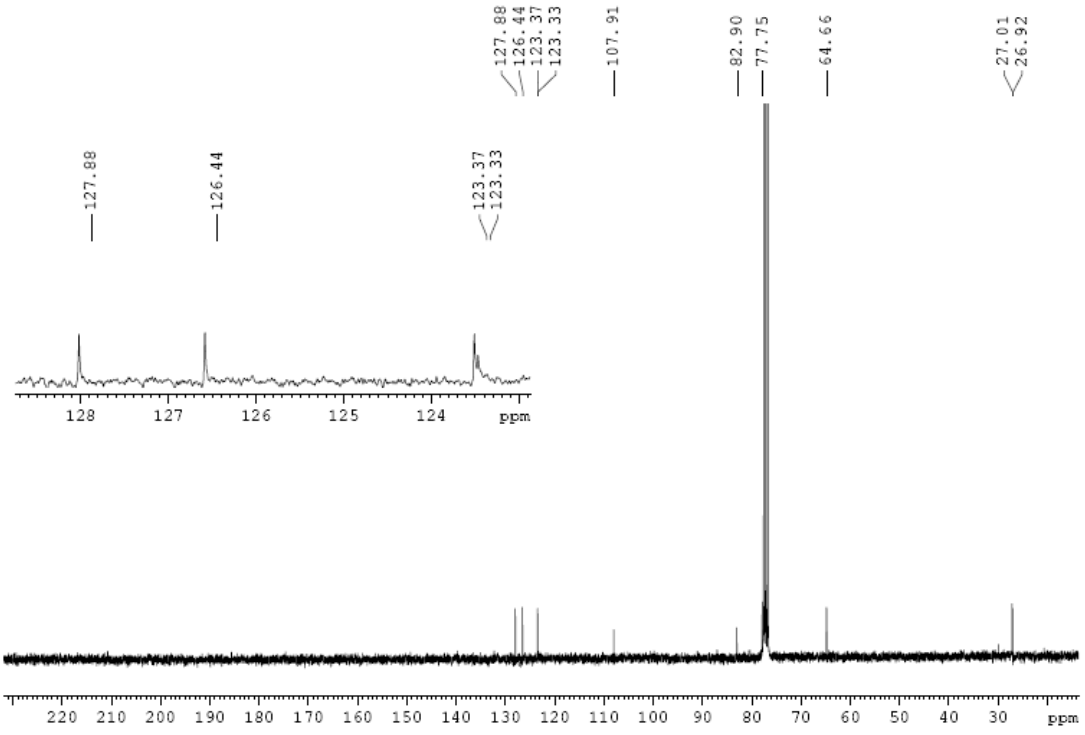
3.077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107.91
82.90
77.75
64.66
27.01
26.92
127.88
126.44
123.37
123.33
128
127
126
125
124
ppm
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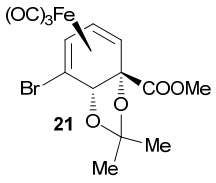
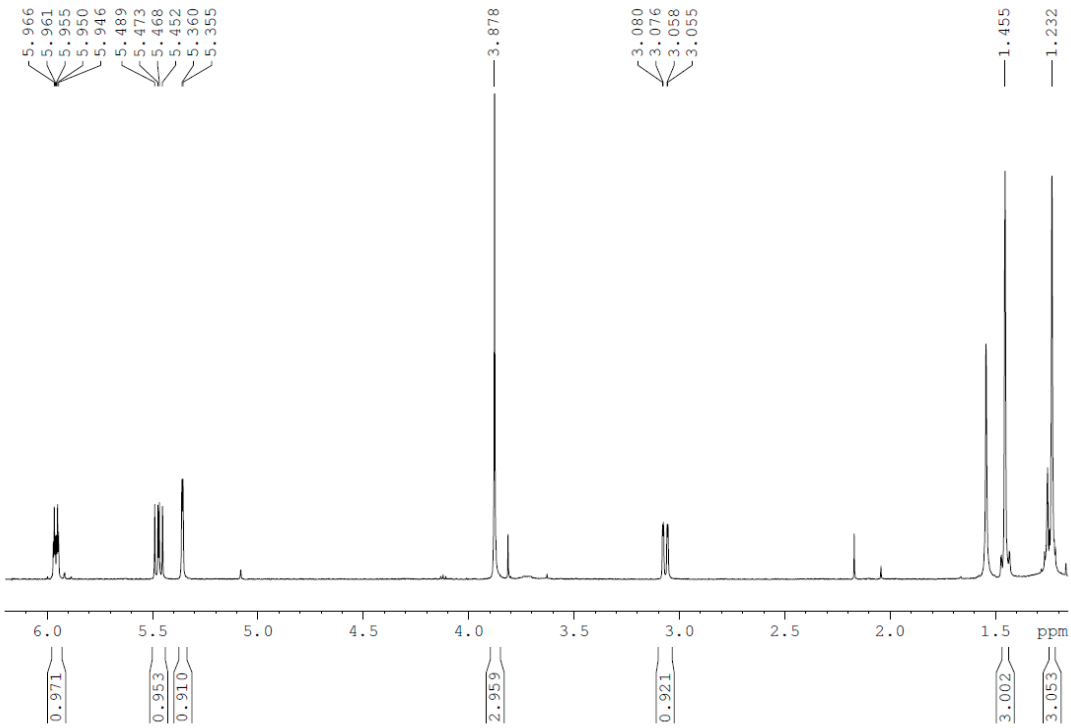
ppm


(OC)3Fe
Br
COOMe
O
21
O
Me
Me


5.966
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5.955
5.950
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5.473
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5.452
5.360
5.355
3.878
3.080
3.076
3.058
3.055
1.455
1.232
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
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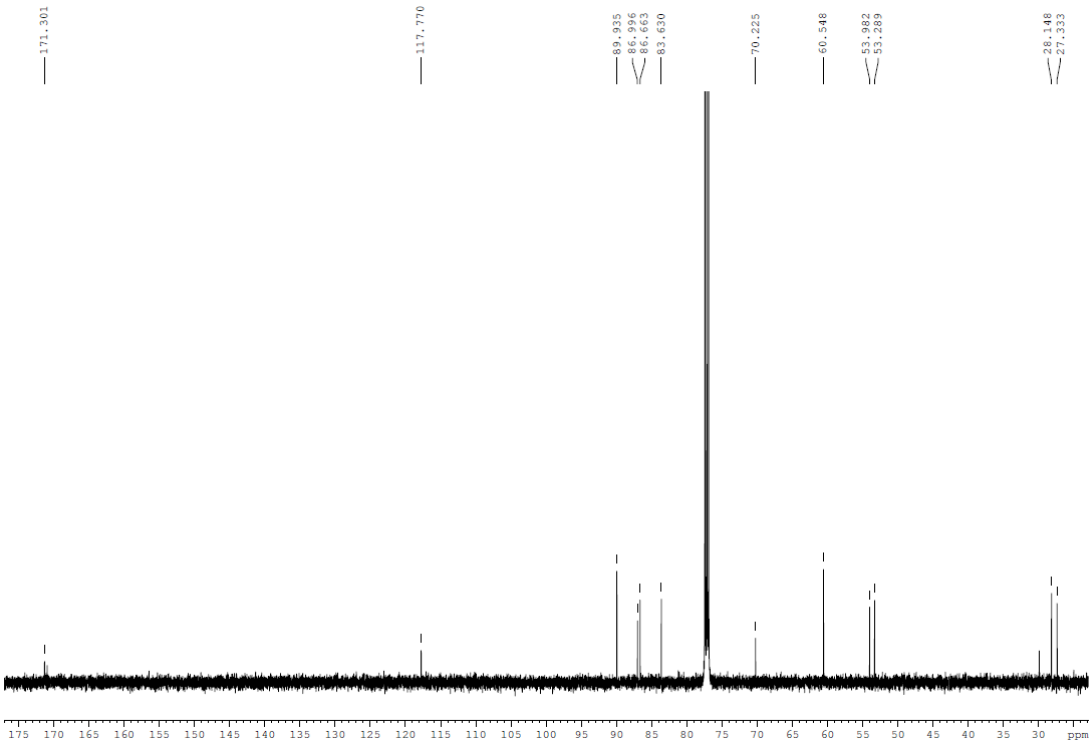
3.053


171.301
117.770
89.935
86.996
86.663
83.630
70.225
60.548
53.982
53.289
28.148
27.333
175
170
165
160
155
150
145
140
135
130
125
120
115
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105
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95
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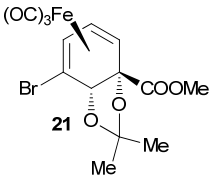
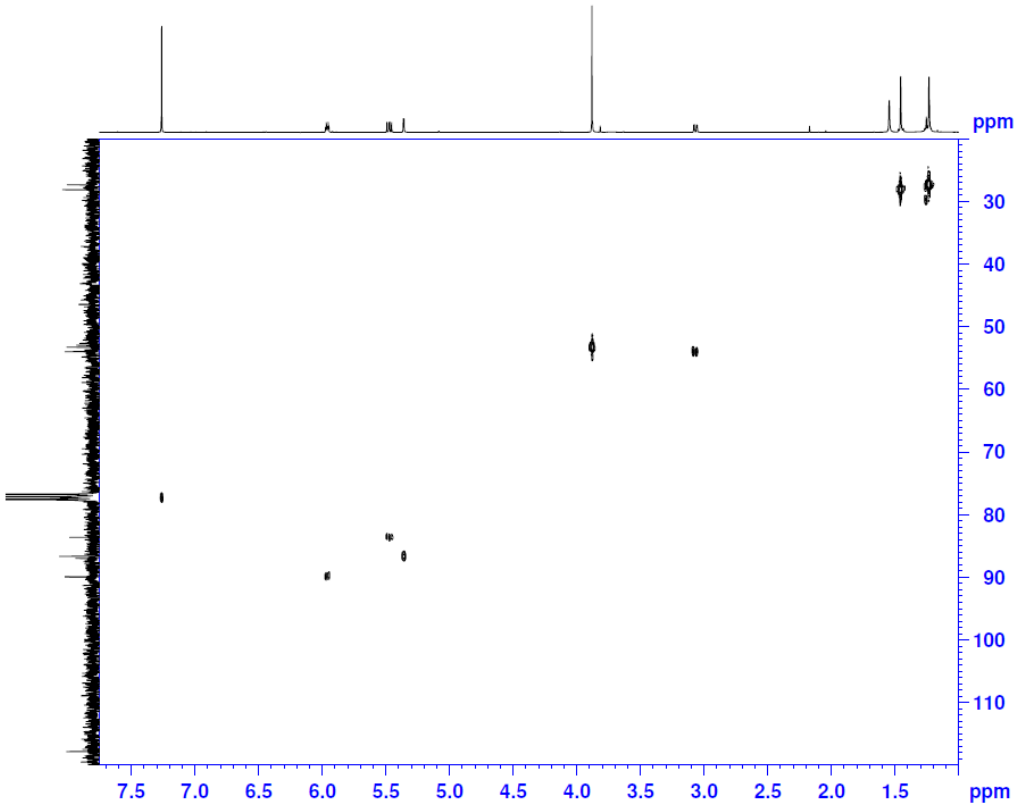
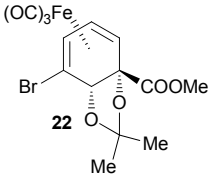
85
80
75
70
65
60
55
50
45
40
35
30
ppm

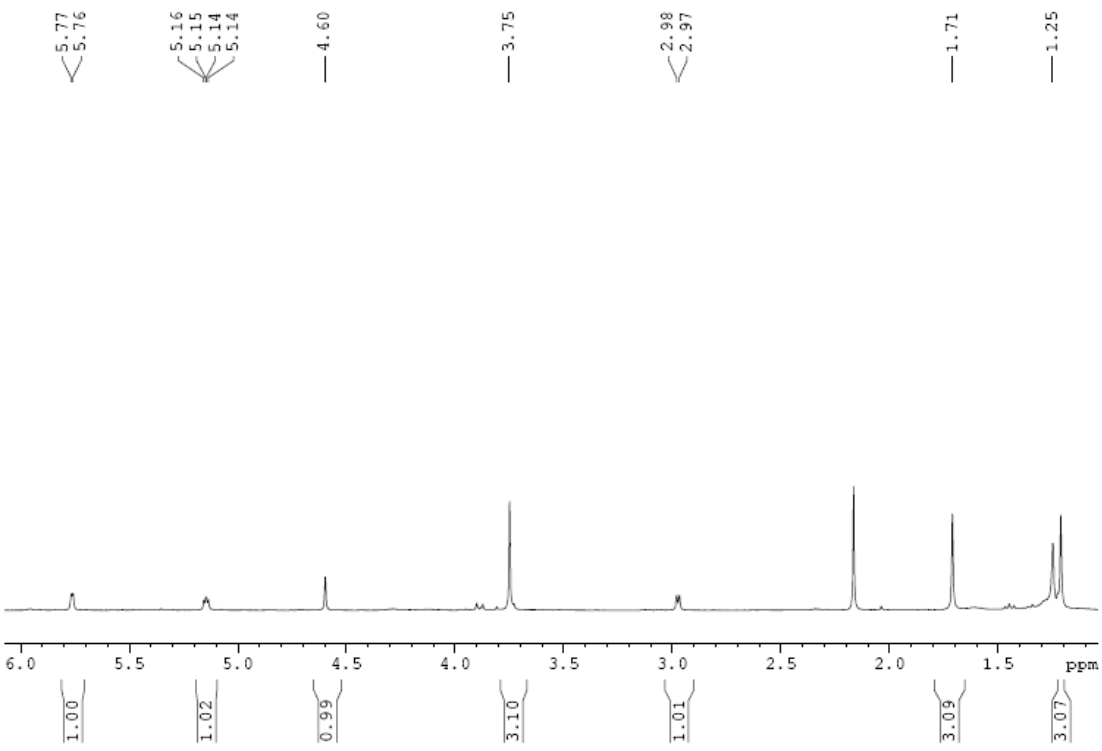

(OC)3Fe
Br
COOMe
O
21
O
Me
Me

HMQC


ppm
30
40
50
60
70
80
90
100
110
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


(OC)3Fe
Br
COOMe
O
O
Me
Me

22


5.77
5.76
5.16
5.15
5.14
5.14
4.60
3.75
2.98
2.97
1.71
1.25
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
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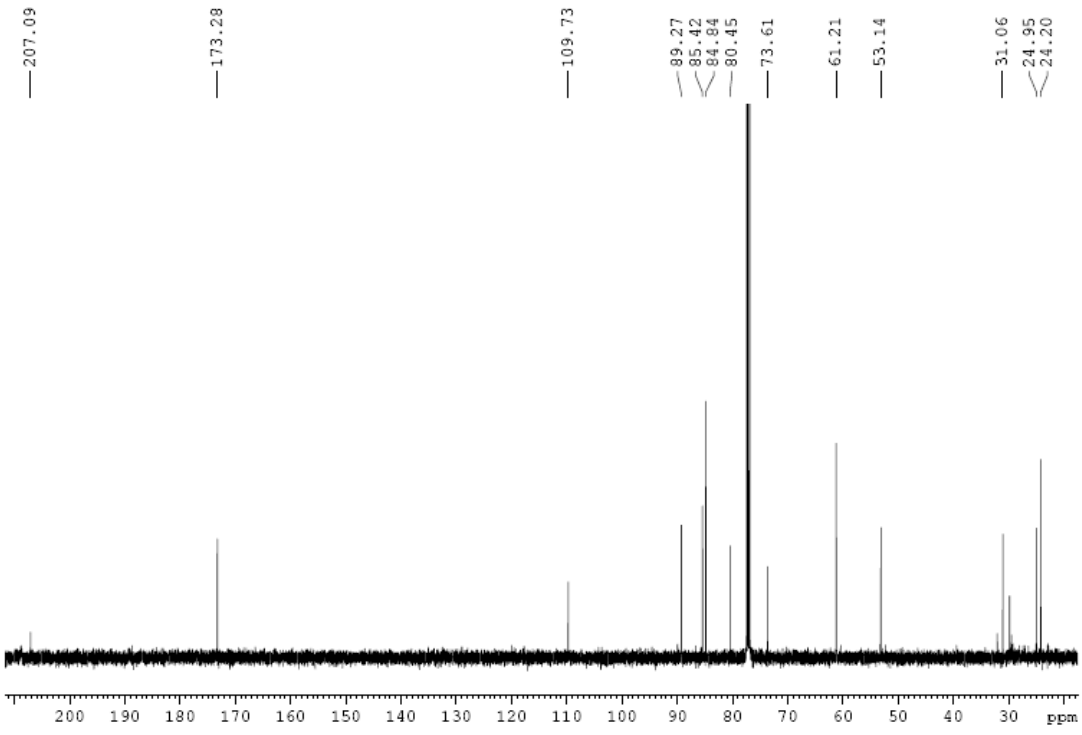
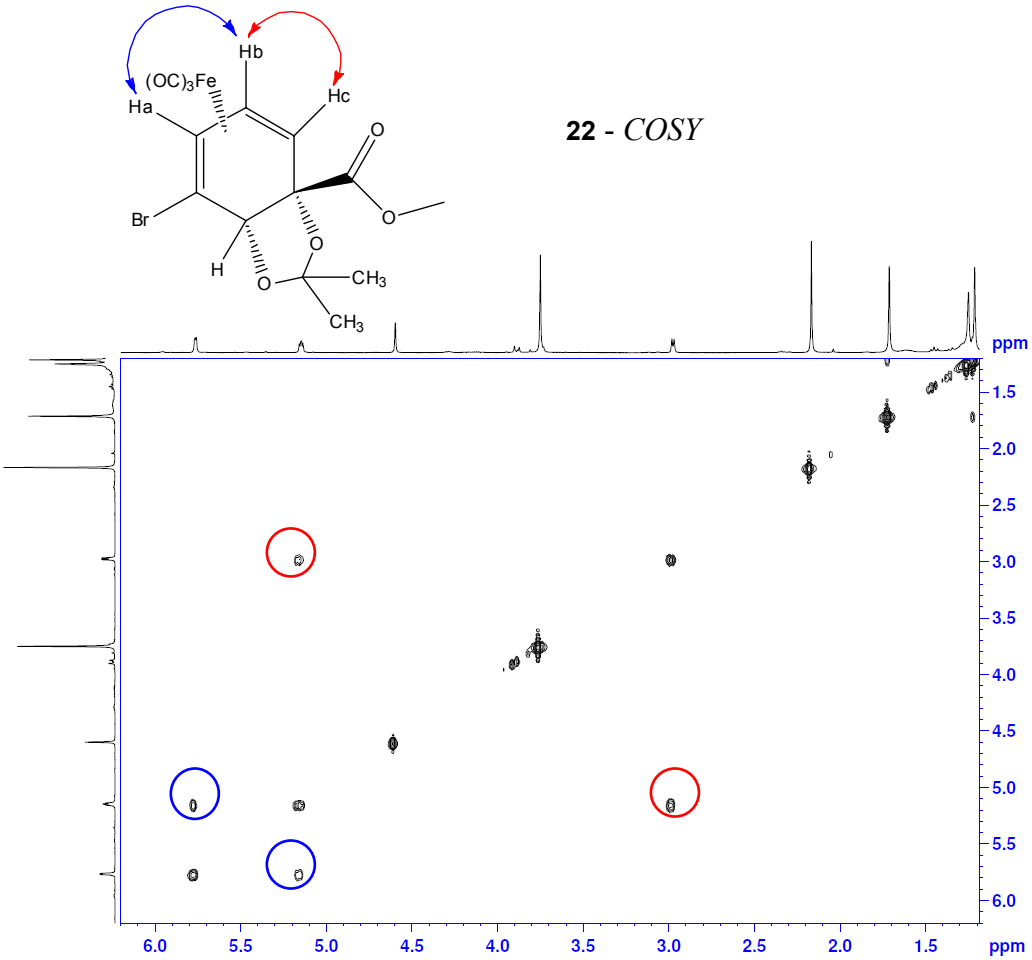
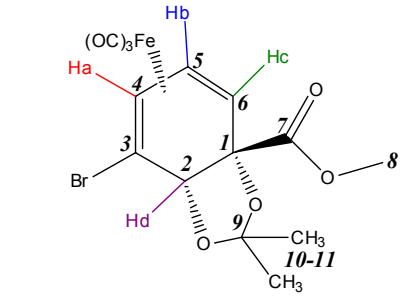
1.02
0.99
3.10
1.01
3.09
3.07

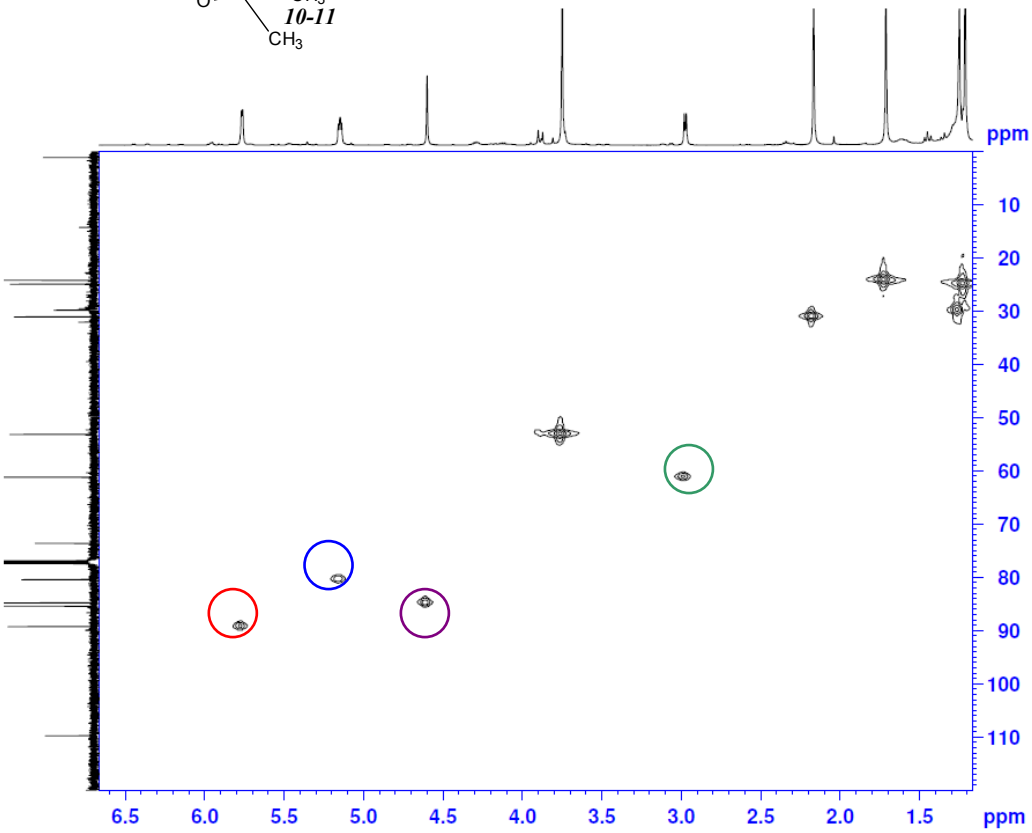

207.09
173.28
109.73
89.27
85.42
84.84
80.45
73.61
61.21
53.14
31.06
24.95
24.20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

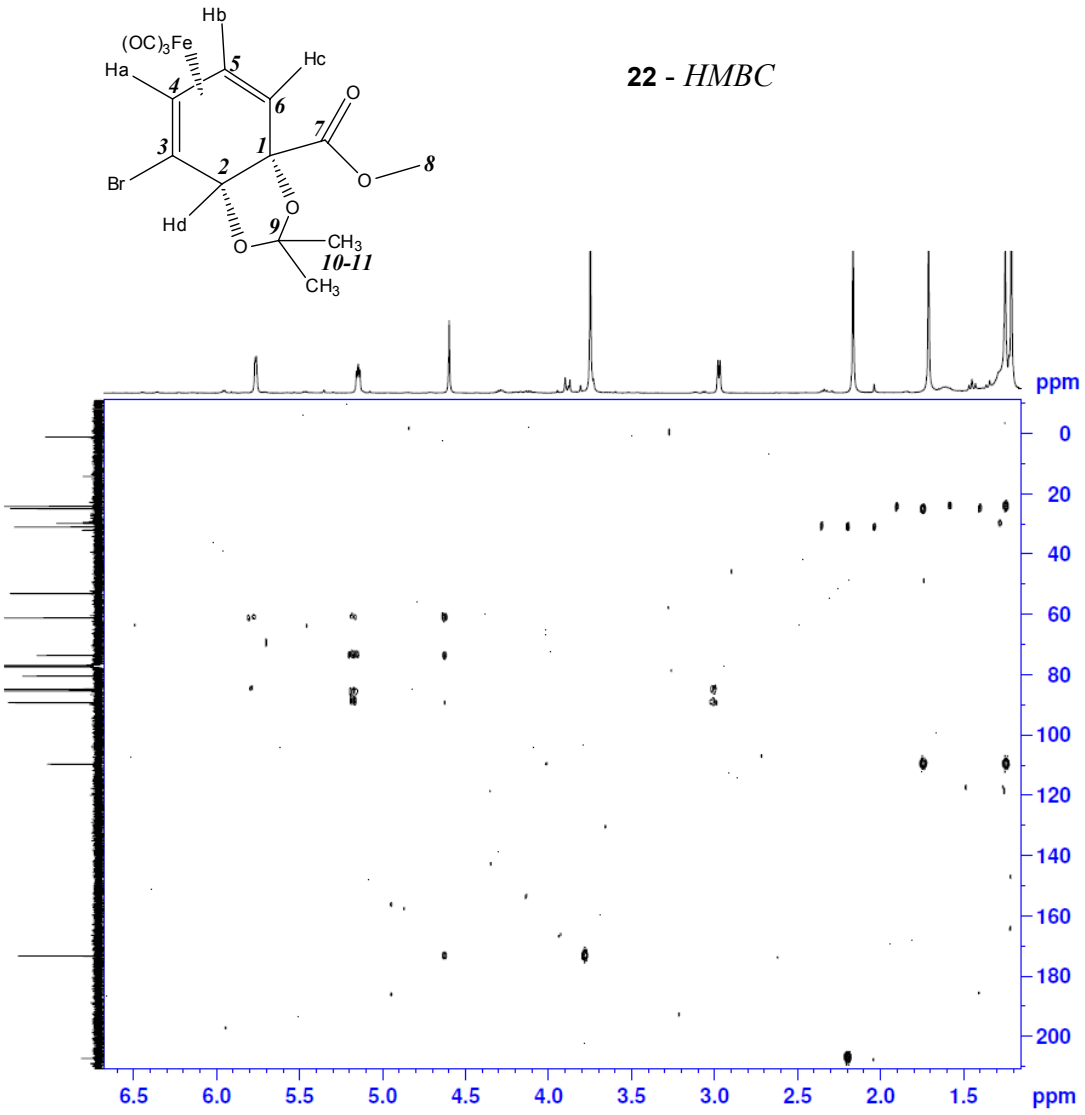

Hb
(OC)3Fe
Ha
Hc
O
O
Br
O
H
O
CH3
CH3
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

22 - *COSY*

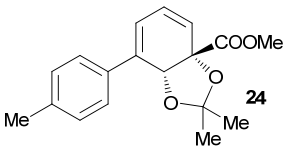

Hb
(OC)3Fe
Ha
Hc
5
4
6
7
O
3
1
8
Br
2
O
Hd
9
O
CH3
10-11
CH3

22 - *HMQC*

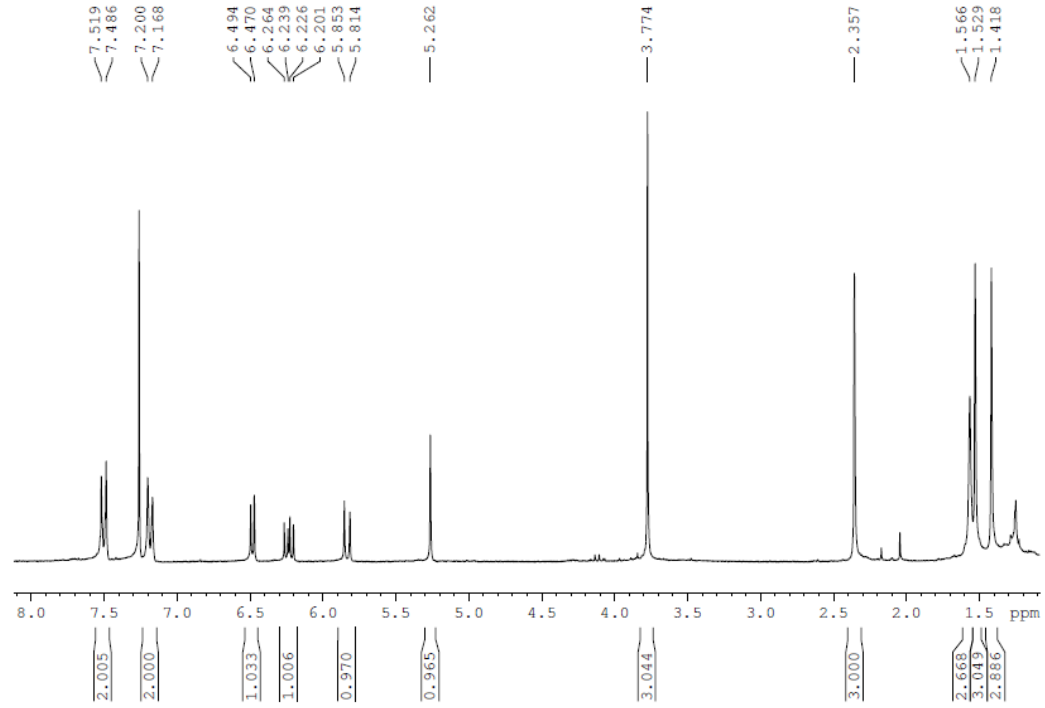

ppm
10
20
30
40
50
60
70
80
90
100
110
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

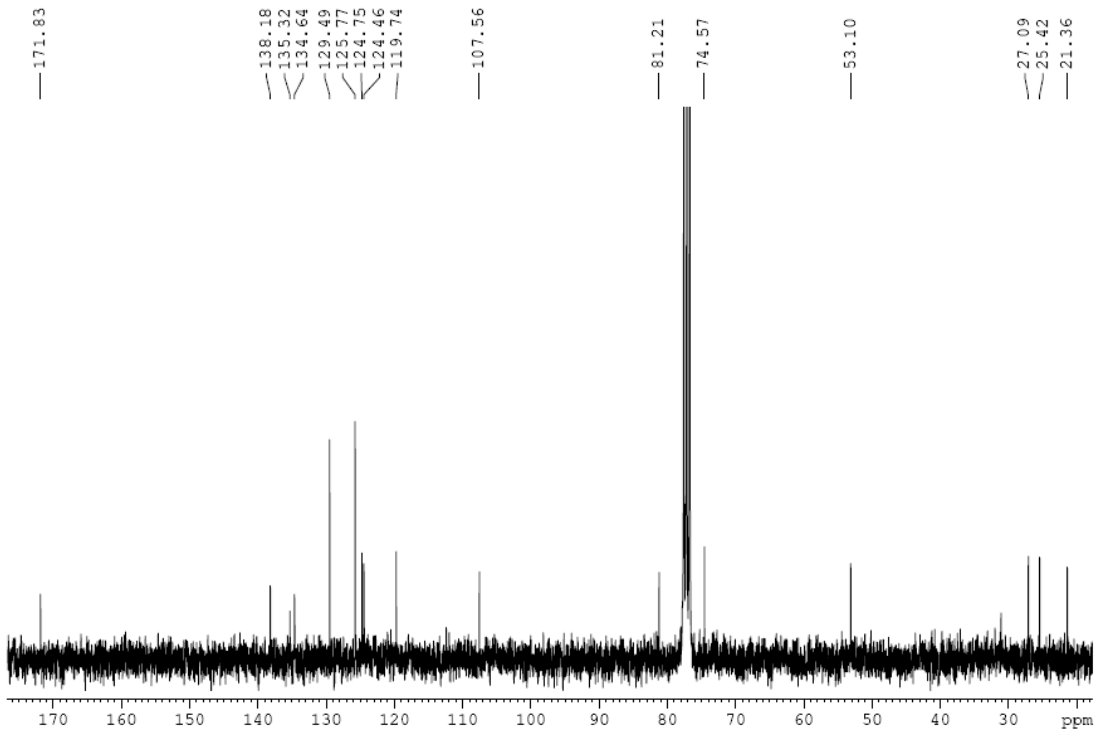

Hb
(OC)3Fe
Ha
Hc
5
4
6
7
O
3
1
8
Br
2
O
Hd
9
O
CH3
10-11
CH3
ppm
0
20
40
60
80
100
120
140
160
180
200
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

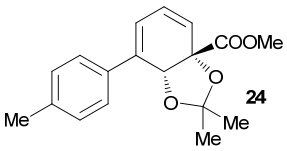
22 - *HMBC*


COOMe
O
O
Me
Me
Me

24

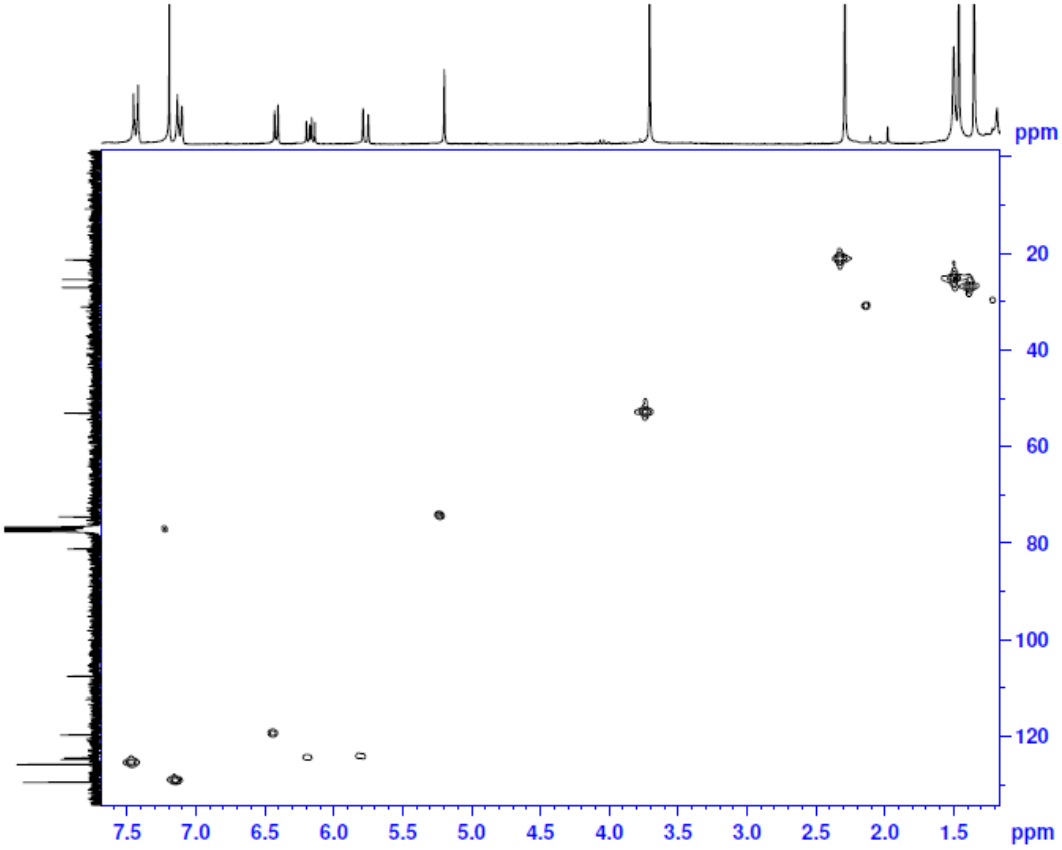

7.519
7.486
7.200
7.168
6.494
6.470
6.264
6.239
6.226
6.201
5.853
5.814
5.262
3.774
2.357
1.566
1.529
1.418
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.005
2.000
1.033
1.006
0.970
0.965
3.044
3.000
2.668
3.049
2.886

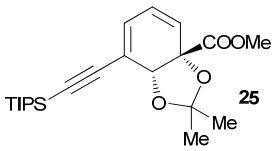

171.83
138.18
135.32
134.64
129.49
125.77
124.75
124.46
119.74
107.56
81.21
74.57
53.10
27.09
25.42
21.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


COOMe
O
O
Me
Me
Me

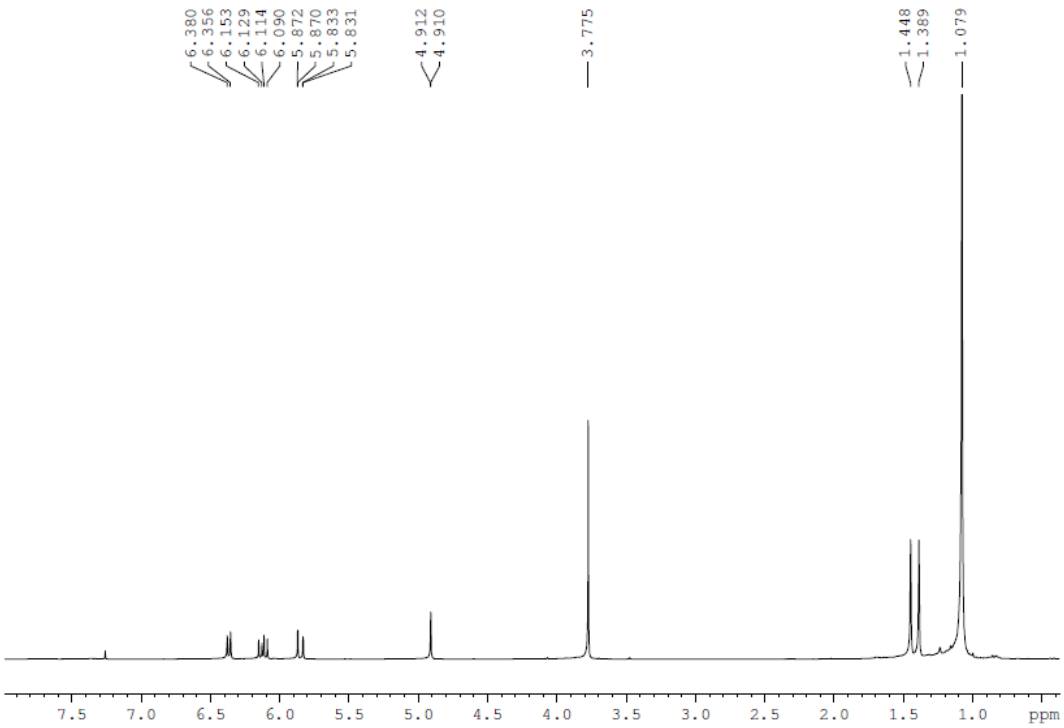
24

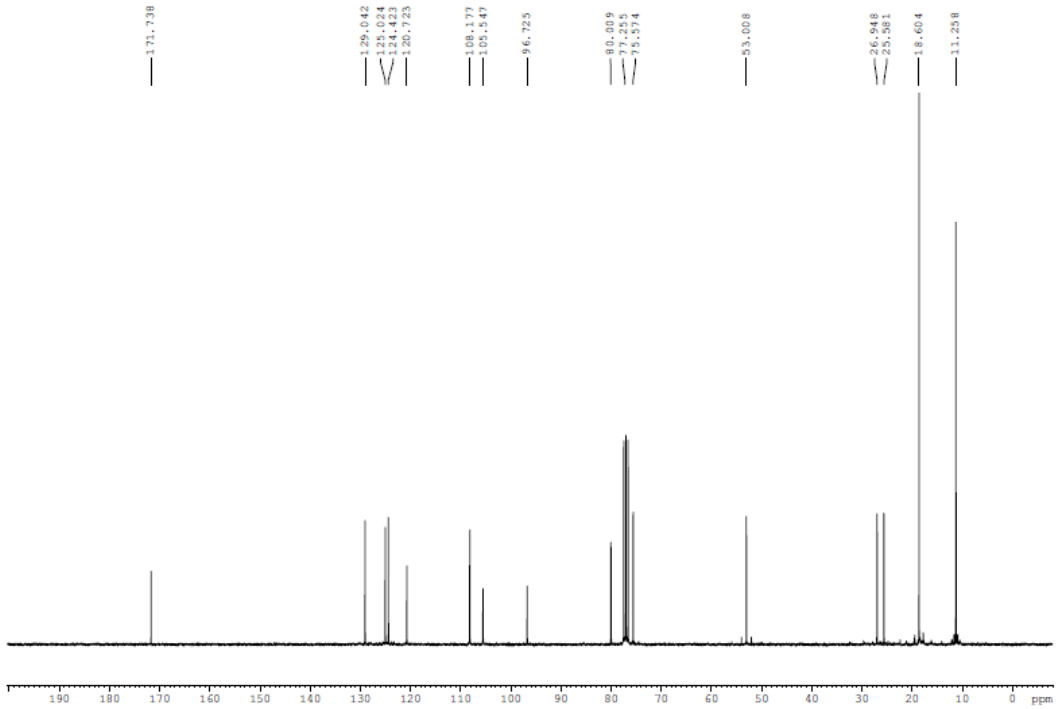
HMQC

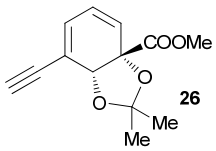

ppm
20
40
60
80
100
120
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


COOMe
O
O
TIPS
Me
Me

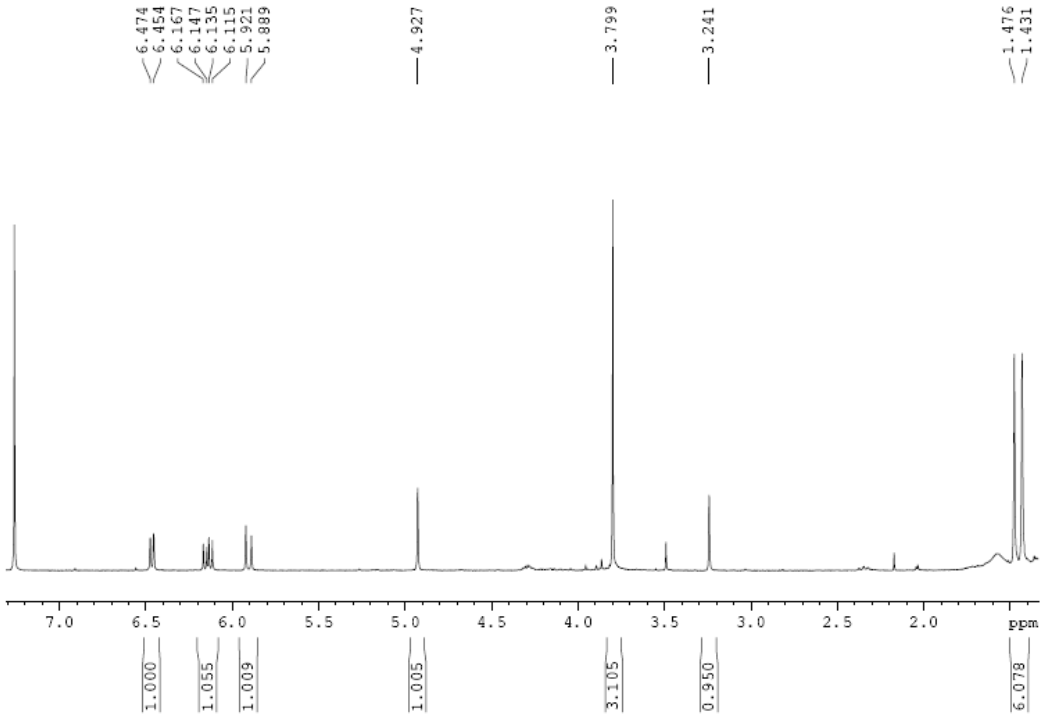
25

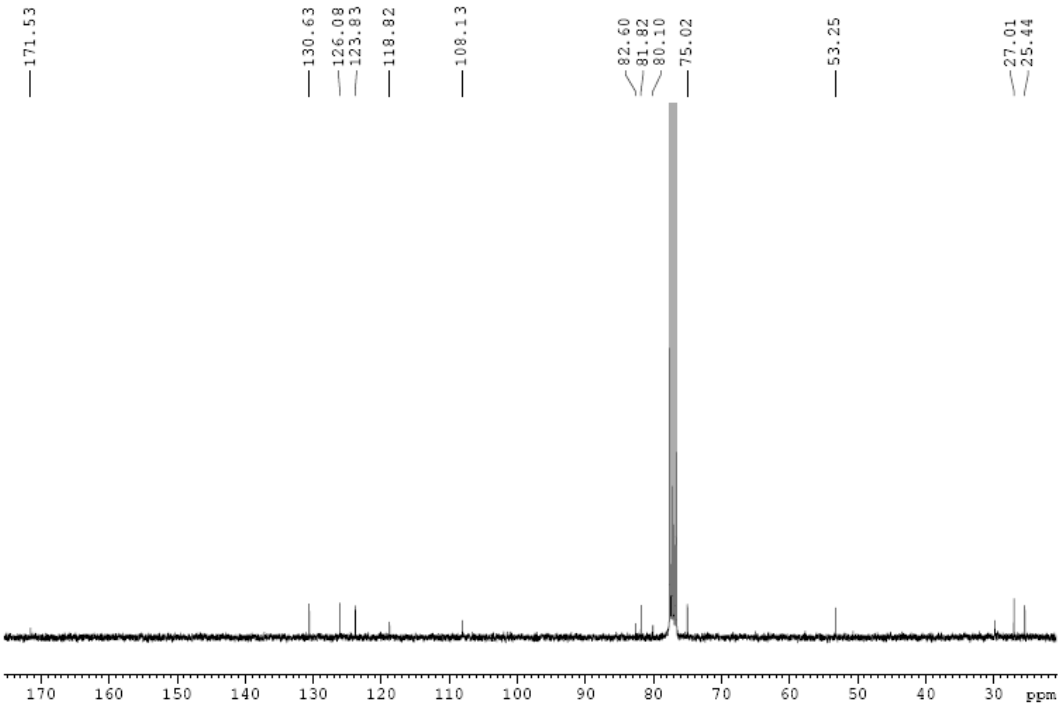

6.380
6.356
6.153
6.129
6.114
6.090
5.872
5.870
5.833
5.831
4.912
4.910
3.775
1.448
1.389
1.079
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

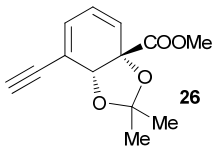

171.738
129.642
125.024
124.423
120.723
108.177
105.547
96.725
80.009
77.255
75.574
53.008
26.948
25.581
18.604
11.258
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


COOMe
O
O
Me
Me

26

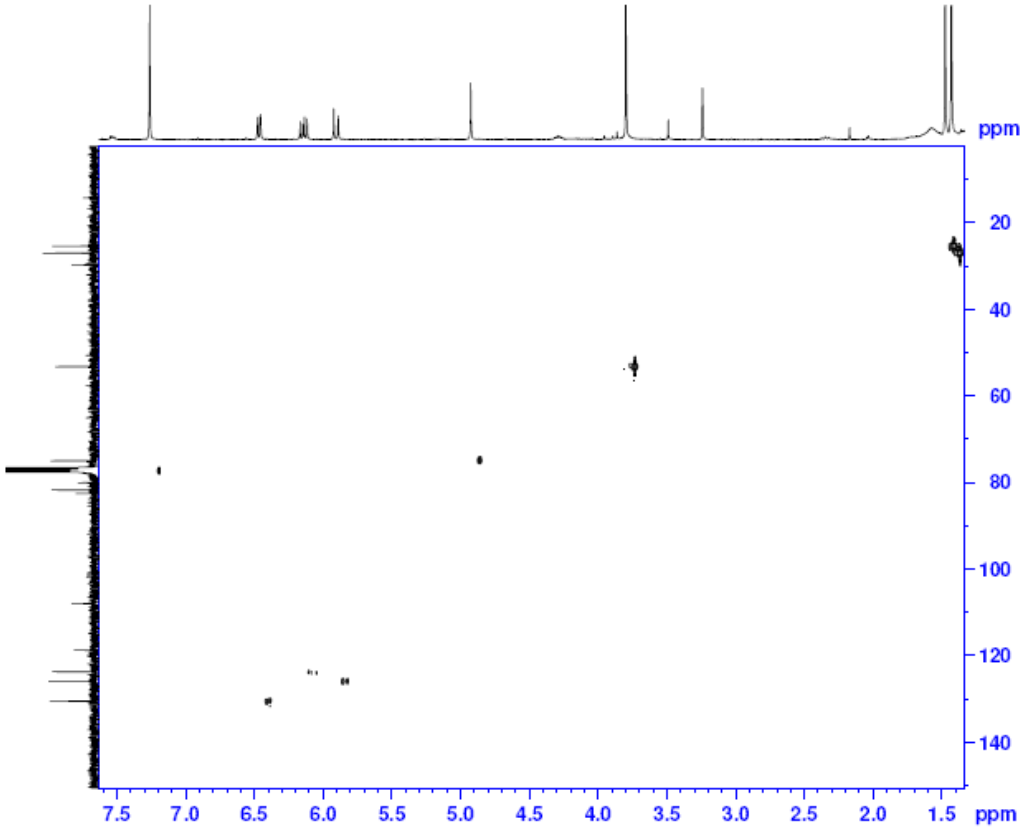

6.474
6.454
6.167
6.147
6.135
6.115
5.921
5.889
4.927
3.799
3.241
1.476
1.431
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
1.000
1.055
1.009
1.005
3.105
0.950
6.078

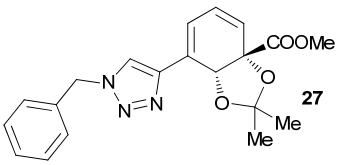

171.53
130.63
126.08
123.83
118.82
108.13
82.60
81.82
80.10
75.02
53.25
27.01
25.44
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


COOMe
O
O
Me
Me

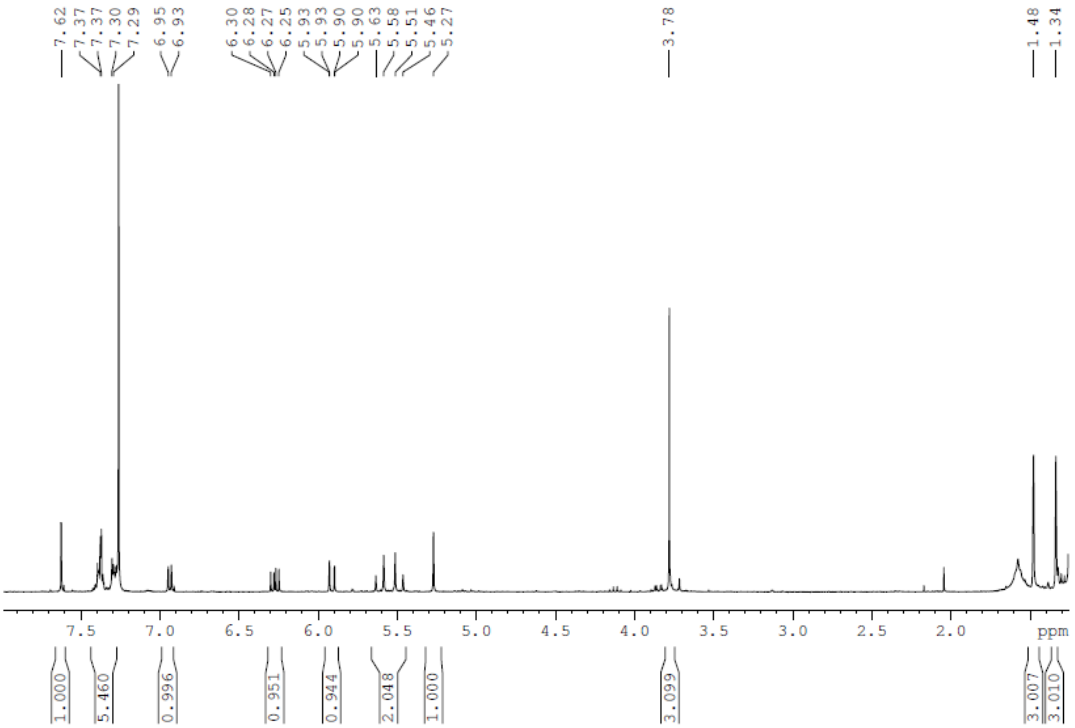
26

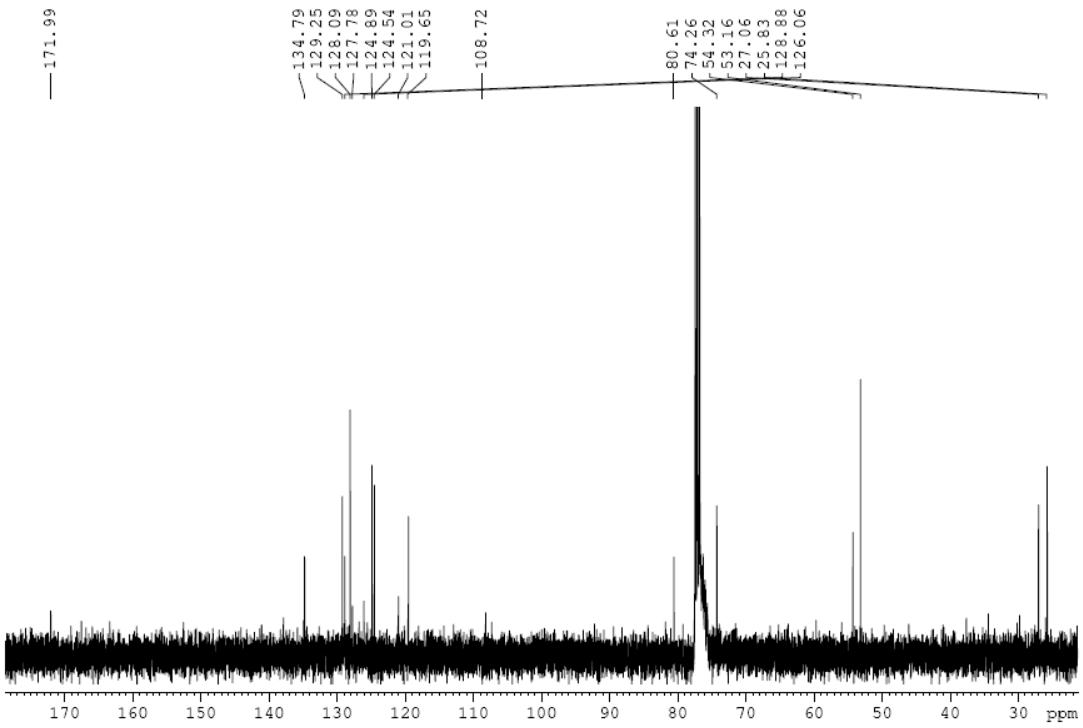
HMQC

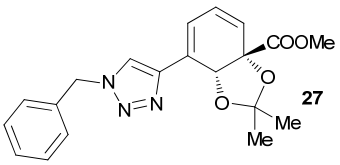

ppm
20
40
60
80
100
120
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


COOMe
N
N
N
O
O
Me
Me

27

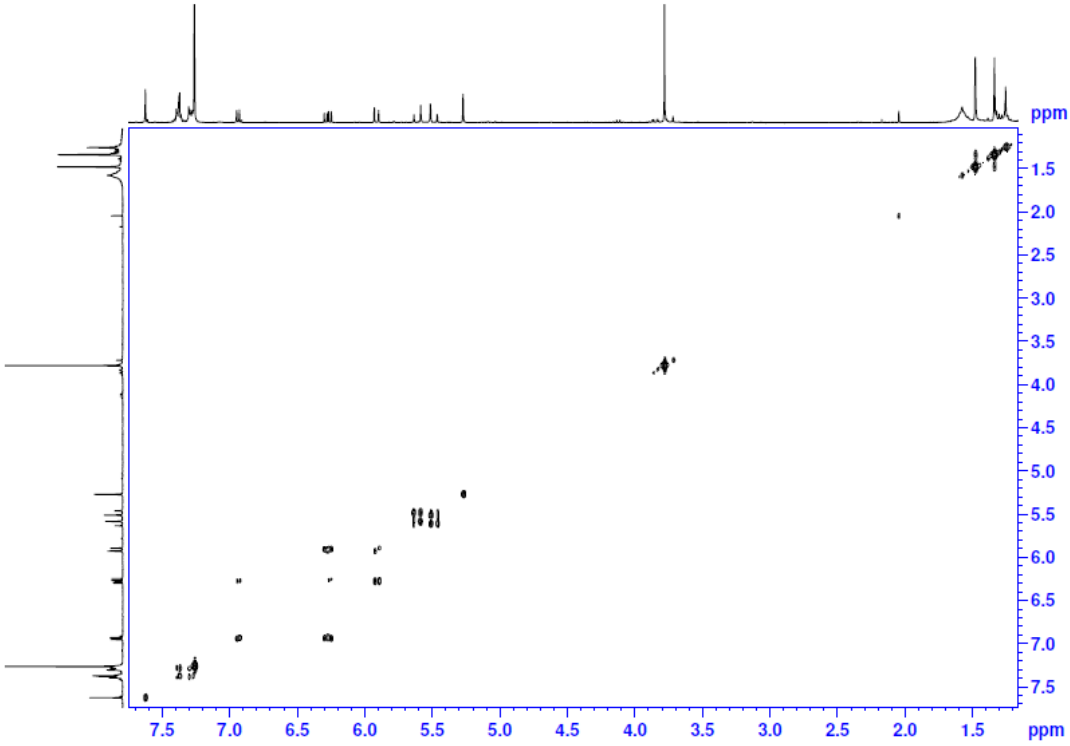

7.62
7.37
7.37
7.30
7.29
6.95
6.93
6.30
6.28
6.27
6.25
5.93
5.93
5.90
5.90
5.63
5.58
5.51
5.46
5.27
3.78
1.48
1.34
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
1.000
5.460
0.996
0.951
0.944
2.048
1.000
3.099
3.007
3.010

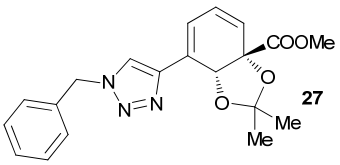

171.99
134.79
129.25
128.09
127.78
124.89
124.54
121.01
119.65
108.72
80.61
74.26
54.32
53.16
27.06
25.83
128.88
126.06
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


COOMe
N
N
N
O
O
Me
Me

27

COSY


ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


COOMe
N
N
N
O
O
Me
Me

27

HMQC

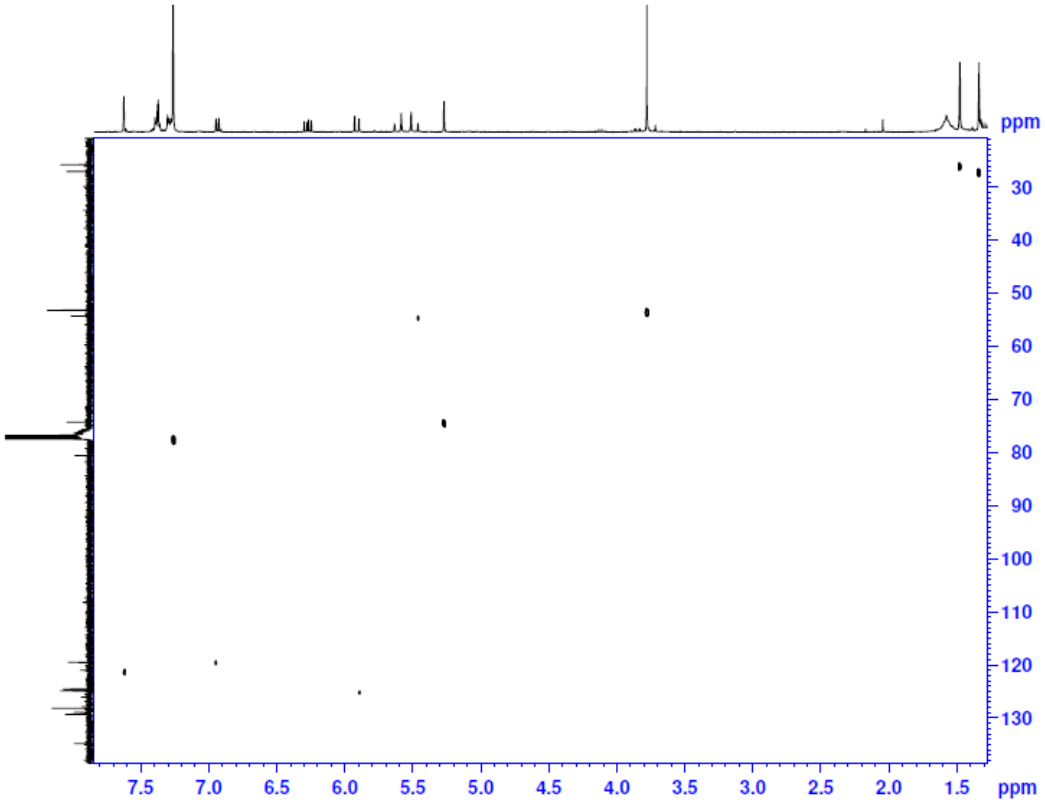

ppm
30
40
50
60
70
80
90
100
110
120
130
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

Table S1. Crystal data and structure refinement for **13**.

Identification code	p10sel1
Empirical formula	C19 H18 Br N3 O6
Formula weight	464.27
Temperature	150(2) K
Wavelength	1.54184 A
Crystal system, space group	Hexagonal, P 6_5
Unit cell dimensions	a = 27.8075(4) A alpha = 90 deg. b = 27.8075(4) A beta = 90 deg. c = 6.47080(10) A gamma = 120 deg.
Volume	4333.24(11) A^3
Z, Calculated density	6, 1.067 Mg/m^3
Absorption coefficient	2.196 mm^-1
F(000)	1416
Crystal size	0.40 x 0.20 x 0.10 mm
Theta range for data collection	4.86 to 66.74 deg.
Limiting indices	-29<=h<=33, -33<=k<=33, -7<=l<=6
Reflections collected / unique	52878 / 4920 [R(int) = 0.0752]
Completeness to theta = 66.74	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8103 and 0.4737
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4920 / 1 / 265
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0850
R indices (all data)	R1 = 0.0418, wR2 = 0.0864
Absolute structure parameter	-0.003(17)
Largest diff. peak and hole	0.324 and -0.221 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **13**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br	2656(1)	3496(1)	1396(1)	43(1)
N(1)	3443(1)	4763(1)	5658(4)	32(1)
N(2)	3363(1)	4342(1)	4164(4)	31(1)
N(3)	3941(1)	4384(1)	6624(4)	32(1)
O(1)	3353(1)	5646(1)	1551(5)	52(1)
O(2)	3505(1)	5901(1)	4867(5)	58(1)
O(3)	2296(1)	4960(1)	4150(4)	39(1)
O(4)	2154(1)	4293(1)	1759(4)	41(1)
O(5)	3900(1)	5036(1)	8774(4)	48(1)
O(6)	3680(1)	3703(1)	4114(4)	39(1)
C(1)	3764(2)	6209(2)	931(9)	78(2)
C(2)	3265(1)	5555(1)	3586(6)	41(1)
C(3)	2808(1)	4963(1)	4040(5)	34(1)
C(4)	1944(1)	4643(1)	2445(6)	39(1)
C(5)	1985(2)	5028(2)	692(6)	52(1)
C(6)	1368(1)	4292(2)	3254(8)	57(1)
C(7)	2709(1)	4514(1)	2396(5)	30(1)
C(8)	2780(1)	4053(1)	3469(5)	32(1)
C(9)	2394(1)	3820(1)	5281(6)	41(1)
C(10)	2475(1)	4202(2)	6661(6)	40(1)
C(11)	2924(1)	4773(1)	6118(5)	34(1)
C(12)	3773(1)	4758(1)	7250(5)	36(1)
C(13)	3653(1)	4085(1)	4888(5)	32(1)
C(14)	4364(1)	4322(1)	7660(5)	31(1)
C(15)	4269(1)	4105(1)	9630(6)	36(1)
C(16)	4688(1)	4064(1)	10624(5)	38(1)
C(17)	5191(1)	4233(1)	9630(6)	38(1)
C(18)	5280(1)	4448(1)	7676(5)	35(1)
C(19)	4868(1)	4502(1)	6662(5)	35(1)

Table S3. Bond lengths [A] for **13**.

Br-C(8)	1.945(3)
N(1)-C(12)	1.384(4)
N(1)-N(2)	1.447(3)
N(1)-C(11)	1.487(4)
N(2)-C(13)	1.398(4)
N(2)-C(8)	1.475(4)
N(3)-C(13)	1.389(4)
N(3)-C(12)	1.396(4)
N(3)-C(14)	1.438(4)
O(1)-C(2)	1.340(5)
O(1)-C(1)	1.458(5)
O(2)-C(2)	1.189(5)
O(3)-C(3)	1.419(3)
O(3)-C(4)	1.446(4)
O(4)-C(7)	1.408(4)
O(4)-C(4)	1.432(4)
O(5)-C(12)	1.193(4)
O(6)-C(13)	1.210(4)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.523(5)
C(3)-C(11)	1.538(5)
C(3)-C(7)	1.557(4)
C(4)-C(6)	1.491(5)
C(4)-C(5)	1.524(5)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-C(8)	1.555(4)
C(7)-H(7)	1.0000
C(8)-C(9)	1.501(5)
C(9)-C(10)	1.320(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.490(5)
C(10)-H(10)	0.9500
C(11)-H(11)	1.0000
C(14)-C(15)	1.378(5)
C(14)-C(19)	1.390(4)
C(15)-C(16)	1.385(5)
C(15)-H(15)	0.9500
C(16)-C(17)	1.390(5)
C(16)-H(16)	0.9500
C(17)-C(18)	1.368(5)
C(17)-H(17)	0.9500
C(18)-C(19)	1.391(4)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500

Table S4. Bond angles [deg] for **13**.

C(12)-N(1)-N(2)	108.9(2)
C(12)-N(1)-C(11)	120.4(3)
N(2)-N(1)-C(11)	113.0(2)
C(13)-N(2)-N(1)	107.1(2)
C(13)-N(2)-C(8)	125.5(2)
N(1)-N(2)-C(8)	109.1(2)
C(13)-N(3)-C(12)	111.9(2)
C(13)-N(3)-C(14)	124.6(2)
C(12)-N(3)-C(14)	123.5(3)
C(2)-O(1)-C(1)	116.4(4)
C(3)-O(3)-C(4)	109.7(2)
C(7)-O(4)-C(4)	110.1(2)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(2)-C(2)-O(1)	123.8(3)
O(2)-C(2)-C(3)	124.5(4)
O(1)-C(2)-C(3)	111.7(3)
O(3)-C(3)-C(2)	108.0(2)
O(3)-C(3)-C(11)	109.7(3)
C(2)-C(3)-C(11)	109.6(3)
O(3)-C(3)-C(7)	104.8(2)
C(2)-C(3)-C(7)	116.8(3)
C(11)-C(3)-C(7)	107.7(2)
O(4)-C(4)-O(3)	105.6(2)
O(4)-C(4)-C(6)	109.5(3)
O(3)-C(4)-C(6)	108.0(3)
O(4)-C(4)-C(5)	109.4(3)
O(3)-C(4)-C(5)	110.4(3)
C(6)-C(4)-C(5)	113.6(3)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(4)-C(7)-C(8)	109.5(2)
O(4)-C(7)-C(3)	105.4(2)
C(8)-C(7)-C(3)	108.2(2)
O(4)-C(7)-H(7)	111.2
C(8)-C(7)-H(7)	111.2
C(3)-C(7)-H(7)	111.2
N(2)-C(8)-C(9)	110.6(3)
N(2)-C(8)-C(7)	104.2(2)
C(9)-C(8)-C(7)	110.3(2)
N(2)-C(8)-Br	110.71(19)
C(9)-C(8)-Br	113.0(2)
C(7)-C(8)-Br	107.7(2)
C(10)-C(9)-C(8)	112.5(3)
C(10)-C(9)-H(9)	123.8
C(8)-C(9)-H(9)	123.8
C(9)-C(10)-C(11)	114.4(3)
C(9)-C(10)-H(10)	122.8
C(11)-C(10)-H(10)	122.8
N(1)-C(11)-C(10)	109.4(2)

N(1)-C(11)-C(3)	101.9(3)
C(10)-C(11)-C(3)	111.3(3)
N(1)-C(11)-H(11)	111.3
C(10)-C(11)-H(11)	111.3
C(3)-C(11)-H(11)	111.3
O(5)-C(12)-N(1)	126.2(3)
O(5)-C(12)-N(3)	128.6(3)
N(1)-C(12)-N(3)	105.2(3)
O(6)-C(13)-N(3)	126.1(3)
O(6)-C(13)-N(2)	128.0(3)
N(3)-C(13)-N(2)	105.8(2)
C(15)-C(14)-C(19)	121.7(3)
C(15)-C(14)-N(3)	119.6(3)
C(19)-C(14)-N(3)	118.6(3)
C(14)-C(15)-C(16)	118.7(3)
C(14)-C(15)-H(15)	120.6
C(16)-C(15)-H(15)	120.6
C(15)-C(16)-C(17)	120.2(3)
C(15)-C(16)-H(16)	119.9
C(17)-C(16)-H(16)	119.9
C(18)-C(17)-C(16)	120.6(3)
C(18)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(17)-C(18)-C(19)	120.2(3)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(14)-C(19)-C(18)	118.6(3)
C(14)-C(19)-H(19)	120.7
C(18)-C(19)-H(19)	120.7

Table S5. Anisotropic displacement parameters (A^2 x 10^3) for **13**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br	49(1)	43(1)	40(1)	-13(1)	-11(1)	25(1)
N(1)	34(1)	40(1)	29(1)	-8(1)	-8(1)	25(1)
N(2)	32(1)	37(1)	29(1)	-6(1)	-7(1)	22(1)
N(3)	35(1)	43(1)	28(1)	-7(1)	-6(1)	26(1)
O(1)	53(1)	39(1)	56(2)	7(1)	10(1)	18(1)
O(2)	63(2)	44(1)	61(2)	-12(1)	-15(2)	22(1)
O(3)	33(1)	51(1)	41(1)	-9(1)	-8(1)	28(1)
O(4)	38(1)	49(1)	45(2)	-9(1)	-14(1)	27(1)
O(5)	54(1)	65(2)	41(2)	-22(1)	-22(1)	42(1)
O(6)	48(1)	44(1)	37(1)	-5(1)	-4(1)	31(1)
C(1)	74(3)	45(2)	96(4)	21(2)	30(3)	15(2)
C(2)	39(2)	40(2)	50(2)	-5(2)	-4(2)	25(2)
C(3)	34(2)	43(2)	33(2)	-3(1)	-2(1)	25(1)
C(4)	38(2)	49(2)	36(2)	-5(2)	-10(1)	26(2)
C(5)	56(2)	59(2)	50(2)	3(2)	-10(2)	36(2)
C(6)	38(2)	69(2)	66(3)	-7(2)	-4(2)	28(2)
C(7)	29(1)	40(2)	25(2)	0(1)	-4(1)	21(1)
C(8)	33(1)	34(2)	30(2)	2(1)	-1(1)	18(1)
C(9)	36(2)	43(2)	41(2)	4(2)	-1(2)	19(2)
C(10)	41(2)	60(2)	26(2)	-3(2)	-2(1)	31(2)
C(11)	37(2)	47(2)	29(2)	-3(1)	-3(1)	28(1)
C(12)	37(2)	44(2)	33(2)	-8(1)	-11(1)	25(1)
C(13)	35(1)	39(2)	26(2)	0(1)	3(1)	22(1)
C(14)	29(1)	39(2)	31(2)	-2(1)	-4(1)	22(1)
C(15)	35(2)	40(2)	37(2)	7(2)	6(2)	22(1)
C(16)	41(2)	43(2)	31(2)	9(1)	4(1)	23(1)
C(17)	37(2)	44(2)	39(2)	8(2)	-4(2)	24(1)
C(18)	33(2)	41(2)	35(2)	7(1)	5(1)	22(1)
C(19)	40(2)	44(2)	27(2)	2(1)	-1(1)	26(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **13**.

	x	y	z	U(eq)
H(1A)	3660	6471	1488	117
H(1B)	3780	6233	-580	117
H(1C)	4129	6299	1469	117
H(5A)	2376	5267	312	77
H(5B)	1829	5258	1144	77
H(5C)	1778	4806	-507	77
H(6A)	1372	4061	4391	86
H(6B)	1127	4054	2145	86
H(6C)	1228	4532	3757	86
H(7)	2970	4680	1204	36
H(9)	2121	3438	5419	49
H(10)	2264	4121	7898	48
H(11)	2983	5043	7245	41
H(15)	3923	3986	10293	43
H(16)	4631	3919	11988	45
H(17)	5474	4198	10313	46
H(18)	5625	4562	7009	42
H(19)	4930	4658	5316	41

Table S7. Crystal data and structure refinement for **21**.

Identification code	h10sel3
Empirical formula	C14 H13 Br Fe O7
Formula weight	429.00
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 2_1 2_1 2_1
Unit cell dimensions	a = 8.6252(3) A alpha = 90 deg. b = 8.6773(3) A beta = 90 deg. c = 43.7286(16) A gamma = 90 deg.
Volume	3272.8(2) A^3
Z, Calculated density	8, 1.741 Mg/m^3
Absorption coefficient	3.394 mm^-1
F(000)	1712
Crystal size	0.45 x 0.30 x 0.15 mm
Theta range for data collection	3.31 to 27.56 deg.
Limiting indices	-11<=h<=11, -10<=k<=11, -56<=l<=56
Reflections collected / unique	25844 / 6937 [R(int) = 0.0663]
Completeness to theta = 27.56	95.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6300 and 0.3104
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6937 / 0 / 429
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.0788
R indices (all data)	R1 = 0.0677, wR2 = 0.0860
Absolute structure parameter	0.011(9)
Largest diff. peak and hole	0.554 and -0.567 e.A^-3

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **21**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	10630(1)	3004(1)	1789(1)	29(1)
C(10)	11952(6)	4506(7)	1691(1)	37(1)
O(10)	12725(4)	5543(5)	1637(1)	55(1)
C(20)	9414(5)	3129(5)	1460(1)	33(1)
O(20)	8621(4)	3203(5)	1252(1)	48(1)
C(30)	11935(7)	1555(7)	1656(1)	49(1)
O(30)	12798(6)	659(6)	1564(1)	82(2)
Br(1)	9092(1)	-631(1)	1945(1)	40(1)
O(1)	5849(4)	4037(4)	1661(1)	45(1)
O(2)	7164(4)	6167(4)	1767(1)	34(1)
O(3)	6991(3)	4460(4)	2354(1)	26(1)
O(4)	7042(3)	1862(4)	2372(1)	32(1)
C(1)	7613(5)	2229(5)	2075(1)	25(1)
C(2)	9181(5)	1552(5)	2031(1)	28(1)
C(3)	10416(5)	2056(5)	2218(1)	27(1)
C(4)	10515(5)	3662(5)	2237(1)	27(1)
C(5)	9388(5)	4487(6)	2071(1)	26(1)
C(6)	7726(5)	4003(5)	2075(1)	24(1)
C(7)	6801(5)	4696(5)	1809(1)	27(1)
C(8)	6394(5)	6928(6)	1514(1)	39(1)
C(9)	6190(5)	3148(5)	2481(1)	29(1)
C(11)	6334(6)	3219(7)	2823(1)	43(1)
C(12)	4525(5)	3111(6)	2376(1)	40(1)
Fe(2)	10537(1)	8236(1)	709(1)	31(1)
C(40)	12113(8)	9453(7)	814(1)	49(1)
C(50)	10325(5)	7159(6)	1058(1)	34(1)
C(60)	9096(8)	9641(7)	804(1)	52(2)
O(40)	13210(6)	10130(5)	881(1)	80(2)
O(50)	10073(5)	6542(4)	1279(1)	54(1)
O(60)	8167(6)	10514(6)	869(1)	86(2)
Br(2)	6891(1)	6719(1)	544(1)	39(1)
O(5)	11603(4)	3692(5)	904(1)	59(1)
O(6)	13814(4)	4496(4)	706(1)	36(1)
O(7)	11983(3)	4543(4)	163(1)	27(1)
O(8)	9357(4)	4498(4)	165(1)	34(1)
C(21)	9769(5)	5174(5)	451(1)	27(1)
C(22)	9099(5)	6770(5)	470(1)	29(1)
C(23)	9665(5)	7941(5)	278(1)	29(1)
C(24)	11290(6)	8018(5)	265(1)	32(1)
C(25)	12078(6)	6912(6)	448(1)	29(1)
C(26)	11539(5)	5273(5)	446(1)	24(1)
C(27)	12292(5)	4390(5)	715(1)	25(1)
C(28)	14656(6)	3757(6)	952(1)	37(1)
C(29)	10673(5)	3691(5)	53(1)	29(1)
C(31)	10679(7)	3765(6)	-290(1)	47(1)
C(32)	10713(6)	2062(5)	174(1)	44(1)

Table S9. Bond lengths [A] for **21**.

Fe(1)-C(30)	1.785(6)
Fe(1)-C(10)	1.785(6)
Fe(1)-C(20)	1.785(5)
Fe(1)-C(4)	2.044(4)
Fe(1)-C(3)	2.054(4)
Fe(1)-C(2)	2.066(5)
Fe(1)-C(5)	2.079(5)
C(10)-O(10)	1.143(6)
C(20)-O(20)	1.141(5)
C(30)-O(30)	1.149(6)
Br(1)-C(2)	1.933(4)
O(1)-C(7)	1.193(5)
O(2)-C(7)	1.326(5)
O(2)-C(8)	1.451(5)
O(3)-C(6)	1.432(5)
O(3)-C(9)	1.444(5)
O(4)-C(9)	1.420(5)
O(4)-C(1)	1.423(5)
C(1)-C(2)	1.487(6)
C(1)-C(6)	1.543(6)
C(2)-C(3)	1.410(6)
C(3)-C(4)	1.399(6)
C(4)-C(5)	1.410(6)
C(5)-C(6)	1.494(6)
C(5)-H(5)	0.85(4)
C(6)-C(7)	1.532(6)
C(9)-C(11)	1.500(6)
C(9)-C(12)	1.509(6)
Fe(2)-C(40)	1.782(7)
Fe(2)-C(60)	1.790(6)
Fe(2)-C(50)	1.799(5)
Fe(2)-C(23)	2.042(4)
Fe(2)-C(24)	2.057(5)
Fe(2)-C(22)	2.061(4)
Fe(2)-C(25)	2.096(5)
C(40)-O(40)	1.151(7)
C(50)-O(50)	1.125(5)
C(60)-O(60)	1.139(7)
Br(2)-C(22)	1.933(4)
O(5)-C(27)	1.184(5)
O(6)-C(27)	1.317(5)
O(6)-C(28)	1.447(5)
O(7)-C(29)	1.433(5)
O(7)-C(26)	1.441(5)
O(8)-C(29)	1.421(5)
O(8)-C(21)	1.426(5)
C(21)-C(22)	1.503(6)
C(21)-C(26)	1.528(6)
C(22)-C(23)	1.404(6)
C(23)-C(24)	1.405(7)
C(24)-C(25)	1.422(7)
C(25)-C(26)	1.496(7)
C(25)-H(25)	0.93(4)
C(26)-C(27)	1.547(6)
C(29)-C(31)	1.500(6)
C(29)-C(32)	1.509(6)

Table S10. Bond lengths [A] and angles [deg] for **21**.

C(30)-Fe(1)-C(10)	91.9(2)
C(30)-Fe(1)-C(20)	98.7(2)
C(10)-Fe(1)-C(20)	97.8(2)
C(30)-Fe(1)-C(4)	122.7(2)
C(10)-Fe(1)-C(4)	93.3(2)
C(20)-Fe(1)-C(4)	136.7(2)
C(30)-Fe(1)-C(3)	94.1(2)
C(10)-Fe(1)-C(3)	124.7(2)
C(20)-Fe(1)-C(3)	135.03(19)
C(4)-Fe(1)-C(3)	39.93(17)
C(30)-Fe(1)-C(2)	96.8(2)
C(10)-Fe(1)-C(2)	162.8(2)
C(20)-Fe(1)-C(2)	95.5(2)
C(4)-Fe(1)-C(2)	69.49(17)
C(3)-Fe(1)-C(2)	40.01(17)
C(30)-Fe(1)-C(5)	162.6(2)
C(10)-Fe(1)-C(5)	91.1(2)
C(20)-Fe(1)-C(5)	97.92(19)
C(4)-Fe(1)-C(5)	39.97(17)
C(3)-Fe(1)-C(5)	70.20(18)
C(2)-Fe(1)-C(5)	76.24(18)
O(10)-C(10)-Fe(1)	175.0(5)
O(20)-C(20)-Fe(1)	179.1(4)
O(30)-C(30)-Fe(1)	177.6(5)
C(7)-O(2)-C(8)	115.8(4)
C(6)-O(3)-C(9)	108.9(3)
C(9)-O(4)-C(1)	108.1(3)
O(4)-C(1)-C(2)	110.1(3)
O(4)-C(1)-C(6)	104.3(4)
C(2)-C(1)-C(6)	109.7(4)
C(3)-C(2)-C(1)	119.4(4)
C(3)-C(2)-Br(1)	116.6(3)
C(1)-C(2)-Br(1)	112.1(3)
C(3)-C(2)-Fe(1)	69.5(3)
C(1)-C(2)-Fe(1)	112.0(3)
Br(1)-C(2)-Fe(1)	121.4(2)
C(4)-C(3)-C(2)	113.0(4)
C(4)-C(3)-Fe(1)	69.6(3)
C(2)-C(3)-Fe(1)	70.4(3)
C(3)-C(4)-C(5)	115.6(4)
C(3)-C(4)-Fe(1)	70.4(3)
C(5)-C(4)-Fe(1)	71.4(3)
C(4)-C(5)-C(6)	120.9(4)
C(4)-C(5)-Fe(1)	68.7(3)
C(6)-C(5)-Fe(1)	109.1(3)
O(3)-C(6)-C(5)	110.9(3)
O(3)-C(6)-C(7)	107.9(3)
C(5)-C(6)-C(7)	112.4(4)
O(3)-C(6)-C(1)	104.3(4)
C(5)-C(6)-C(1)	109.9(4)
C(7)-C(6)-C(1)	111.1(4)
O(1)-C(7)-O(2)	123.3(4)
O(1)-C(7)-C(6)	125.6(4)
O(2)-C(7)-C(6)	111.1(4)
O(4)-C(9)-O(3)	104.0(3)
O(4)-C(9)-C(11)	109.0(4)
O(3)-C(9)-C(11)	108.3(4)
O(4)-C(9)-C(12)	111.9(4)
O(3)-C(9)-C(12)	110.7(4)
C(11)-C(9)-C(12)	112.6(4)
C(40)-Fe(2)-C(60)	93.8(3)
C(40)-Fe(2)-C(50)	99.6(2)
C(60)-Fe(2)-C(50)	95.0(2)
C(40)-Fe(2)-C(23)	126.4(2)
C(60)-Fe(2)-C(23)	92.5(2)

C(50)-Fe(2)-C(23)	132.8(2)
C(40)-Fe(2)-C(24)	93.3(2)
C(60)-Fe(2)-C(24)	120.1(2)
C(50)-Fe(2)-C(24)	141.8(2)
C(23)-Fe(2)-C(24)	40.08(18)
C(40)-Fe(2)-C(22)	162.9(2)
C(60)-Fe(2)-C(22)	96.9(2)
C(50)-Fe(2)-C(22)	92.8(2)
C(23)-Fe(2)-C(22)	40.00(18)
C(24)-Fe(2)-C(22)	69.78(18)
C(40)-Fe(2)-C(25)	88.9(2)
C(60)-Fe(2)-C(25)	160.1(2)
C(50)-Fe(2)-C(25)	104.0(2)
C(23)-Fe(2)-C(25)	70.30(18)
C(24)-Fe(2)-C(25)	40.04(18)
C(22)-Fe(2)-C(25)	76.53(17)
O(40)-C(40)-Fe(2)	174.2(6)
O(50)-C(50)-Fe(2)	174.2(4)
O(60)-C(60)-Fe(2)	178.4(6)
C(27)-O(6)-C(28)	116.6(4)
C(29)-O(7)-C(26)	107.8(3)
C(29)-O(8)-C(21)	107.8(3)
O(8)-C(21)-C(22)	109.3(4)
O(8)-C(21)-C(26)	105.1(4)
C(22)-C(21)-C(26)	109.5(4)
C(23)-C(22)-C(21)	120.1(4)
C(23)-C(22)-Br(2)	117.4(3)
C(21)-C(22)-Br(2)	111.5(3)
C(23)-C(22)-Fe(2)	69.3(3)
C(21)-C(22)-Fe(2)	111.4(3)
Br(2)-C(22)-Fe(2)	121.4(2)
C(22)-C(23)-C(24)	114.0(4)
C(22)-C(23)-Fe(2)	70.7(3)
C(24)-C(23)-Fe(2)	70.5(3)
C(23)-C(24)-C(25)	114.9(4)
C(23)-C(24)-Fe(2)	69.4(3)
C(25)-C(24)-Fe(2)	71.5(3)
C(24)-C(25)-C(26)	119.3(4)
C(24)-C(25)-Fe(2)	68.5(3)
C(26)-C(25)-Fe(2)	109.0(3)
O(7)-C(26)-C(25)	109.8(3)
O(7)-C(26)-C(21)	104.7(4)
C(25)-C(26)-C(21)	111.4(4)
O(7)-C(26)-C(27)	108.9(3)
C(25)-C(26)-C(27)	109.6(4)
C(21)-C(26)-C(27)	112.3(4)
O(5)-C(27)-O(6)	123.8(4)
O(5)-C(27)-C(26)	125.0(4)
O(6)-C(27)-C(26)	111.2(4)
O(8)-C(29)-O(7)	105.1(3)
O(8)-C(29)-C(31)	109.0(4)
O(7)-C(29)-C(31)	108.1(4)
O(8)-C(29)-C(32)	111.0(4)
O(7)-C(29)-C(32)	110.4(4)
C(31)-C(29)-C(32)	112.9(4)

Table S11. Anisotropic displacement parameters (A^2 x 10^3) for **21**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	30(1)	36(1)	20(1)	-1(1)	1(1)	3(1)
C(10)	29(3)	52(3)	32(3)	-6(3)	-4(2)	2(3)
O(10)	37(2)	68(3)	59(3)	3(2)	3(2)	-20(2)
C(20)	37(3)	30(3)	32(3)	-5(2)	11(2)	-6(3)
O(20)	48(2)	76(3)	19(2)	0(2)	-8(2)	-13(2)
C(30)	58(3)	61(4)	27(3)	6(3)	15(3)	19(3)
O(30)	109(4)	78(3)	58(3)	13(3)	42(3)	52(3)
Br(1)	59(1)	28(1)	34(1)	-3(1)	-5(1)	7(1)
O(1)	46(2)	37(2)	53(2)	3(2)	-30(2)	-7(2)
O(2)	37(2)	30(2)	33(2)	9(1)	-10(2)	-9(2)
O(3)	24(2)	28(2)	25(2)	0(1)	3(1)	-1(2)
O(4)	31(2)	28(2)	35(2)	6(2)	7(2)	2(2)
C(1)	24(2)	26(3)	23(2)	2(2)	-2(2)	-2(2)
C(2)	40(3)	26(2)	18(2)	-1(2)	-2(2)	0(2)
C(3)	30(2)	37(3)	15(2)	2(2)	3(2)	7(2)
C(4)	26(2)	38(3)	18(2)	-5(2)	-3(2)	-2(2)
C(5)	24(2)	29(3)	24(2)	-4(2)	1(2)	-8(2)
C(6)	22(2)	31(3)	19(2)	1(2)	-3(2)	1(2)
C(7)	28(2)	29(3)	24(2)	0(2)	-1(2)	-1(2)
C(8)	42(3)	34(3)	40(3)	13(2)	-11(2)	-6(2)
C(9)	26(2)	28(3)	33(2)	1(2)	5(2)	-1(2)
C(11)	39(3)	56(3)	34(3)	6(3)	9(2)	2(3)
C(12)	28(3)	40(3)	53(3)	4(3)	2(2)	-6(3)
Fe(2)	48(1)	24(1)	21(1)	0(1)	-1(1)	1(1)
C(40)	82(4)	32(3)	32(3)	2(3)	8(3)	-9(4)
C(50)	40(3)	35(3)	27(3)	1(2)	1(2)	3(2)
C(60)	79(4)	46(4)	33(3)	-8(3)	-19(3)	11(4)
O(40)	101(4)	79(4)	58(3)	-20(2)	6(3)	-54(3)
O(50)	72(3)	53(3)	36(2)	16(2)	7(2)	-2(2)
O(60)	108(4)	73(3)	76(4)	-33(3)	-25(3)	54(3)
Br(2)	34(1)	50(1)	33(1)	4(1)	2(1)	11(1)
O(5)	34(2)	84(3)	59(3)	46(2)	7(2)	4(2)
O(6)	34(2)	39(2)	33(2)	9(2)	-10(2)	-1(2)
O(7)	29(2)	30(2)	22(2)	-1(1)	3(1)	-3(2)
O(8)	33(2)	29(2)	39(2)	-10(2)	-7(2)	0(2)
C(21)	33(3)	20(2)	29(3)	1(2)	2(2)	2(2)
C(22)	32(2)	32(2)	22(2)	-2(2)	-1(2)	3(2)
C(23)	37(3)	30(3)	21(2)	-1(2)	-1(2)	9(2)
C(24)	52(3)	20(2)	23(2)	2(2)	5(2)	-4(2)
C(25)	28(2)	25(3)	32(2)	2(2)	3(2)	-3(2)
C(26)	27(3)	23(3)	23(2)	0(2)	3(2)	0(2)
C(27)	28(3)	26(2)	22(2)	1(2)	-2(2)	2(2)
C(28)	39(3)	37(3)	34(3)	2(2)	-19(2)	0(2)
C(29)	30(2)	26(2)	30(3)	-3(2)	-2(2)	-2(2)
C(31)	57(3)	51(3)	34(3)	-6(2)	-11(3)	-11(3)
C(32)	44(3)	21(2)	67(4)	-3(2)	5(3)	0(2)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **21**.

	x	y	z	U(eq)
H(1)	6883	1862	1913	30
H(3)	11108	1375	2319	33
H(4)	11291	4164	2355	33
H(8A)	6639	6388	1323	58
H(8B)	6753	7998	1500	58
H(8C)	5271	6914	1547	58
H(11A)	5835	2313	2913	65
H(11B)	5829	4155	2899	65
H(11C)	7433	3234	2880	65
H(12A)	4493	2989	2153	61
H(12B)	4012	4078	2433	61
H(12C)	3988	2244	2473	61
H(21)	9404	4523	625	33
H(23)	9008	8622	168	35
H(24)	11823	8752	142	38
H(28A)	14395	4257	1147	55
H(28B)	15772	3849	915	55
H(28C)	14370	2665	962	55
H(31A)	9735	3281	-369	71
H(31B)	11589	3218	-369	71
H(31C)	10717	4844	-355	71
H(32A)	10663	2080	397	66
H(32B)	11676	1561	109	66
H(32C)	9824	1487	93	66
H(25)	13140(50)	7050(50)	436(9)	17(10)
H(5)	9480(40)	5460(50)	2082(9)	13(11)