Electronic Supplementary Material (ESI) for Faraday Discussions.
This journal is © The Royal Society of Chemistry 2015

SUPPORTING INFORMATION for:

Water oxidation catalysis upon evolution of Co(III) cubanes in aqueous media

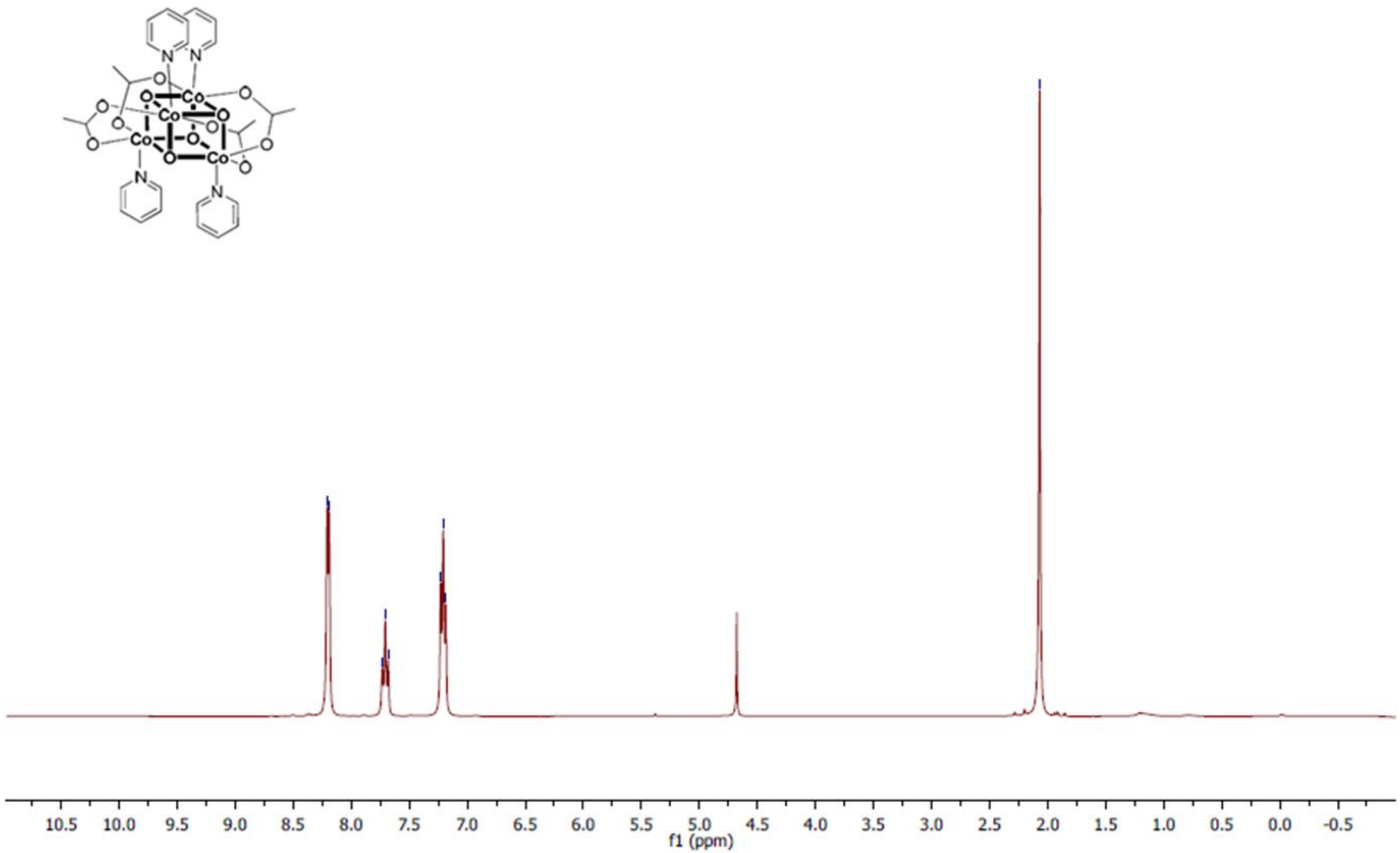
Andrea Genoni,[a] Giuseppina La Ganga,[c] Andrea Volpe,[a] Fausto Puntoriero,[c] Marilena Di Valentin,[a] Marcella Bonchio,[a] Mirco Natali[b*] and Andrea Sartorel[a*]

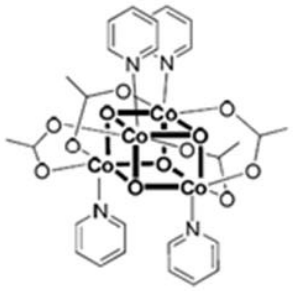
[a.] *Department of Chemical Sciences, University of Padova and ITM-CNR, via Marzolo 1, 35131 Padova (Italy).*

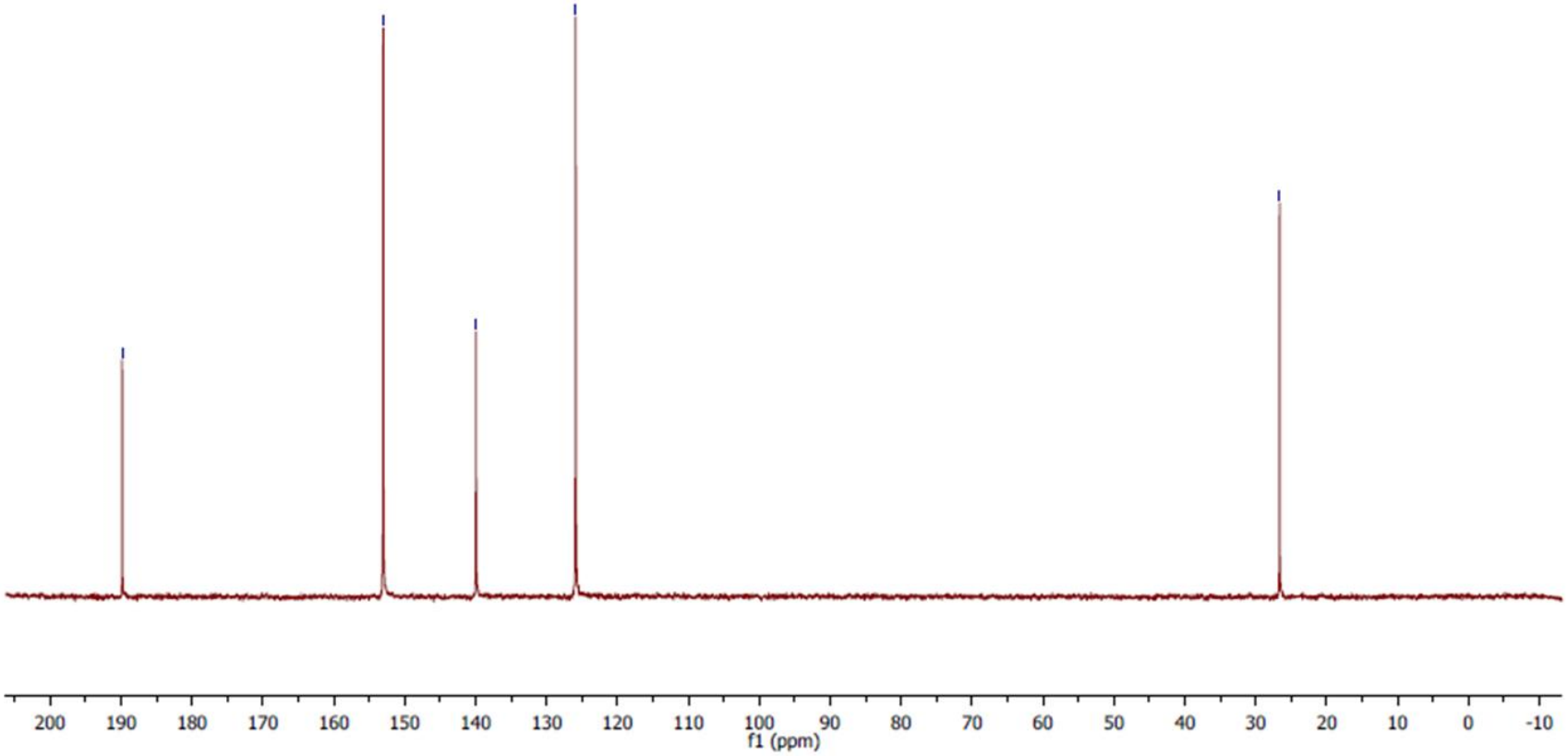
[b.] *Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara and Centro Interuniversitario per la Conversione Chimica dell'Energia Solare, sezione di Ferrara, Via Fossato di Mortara 17-19, 44121 Ferrara, Italy.*

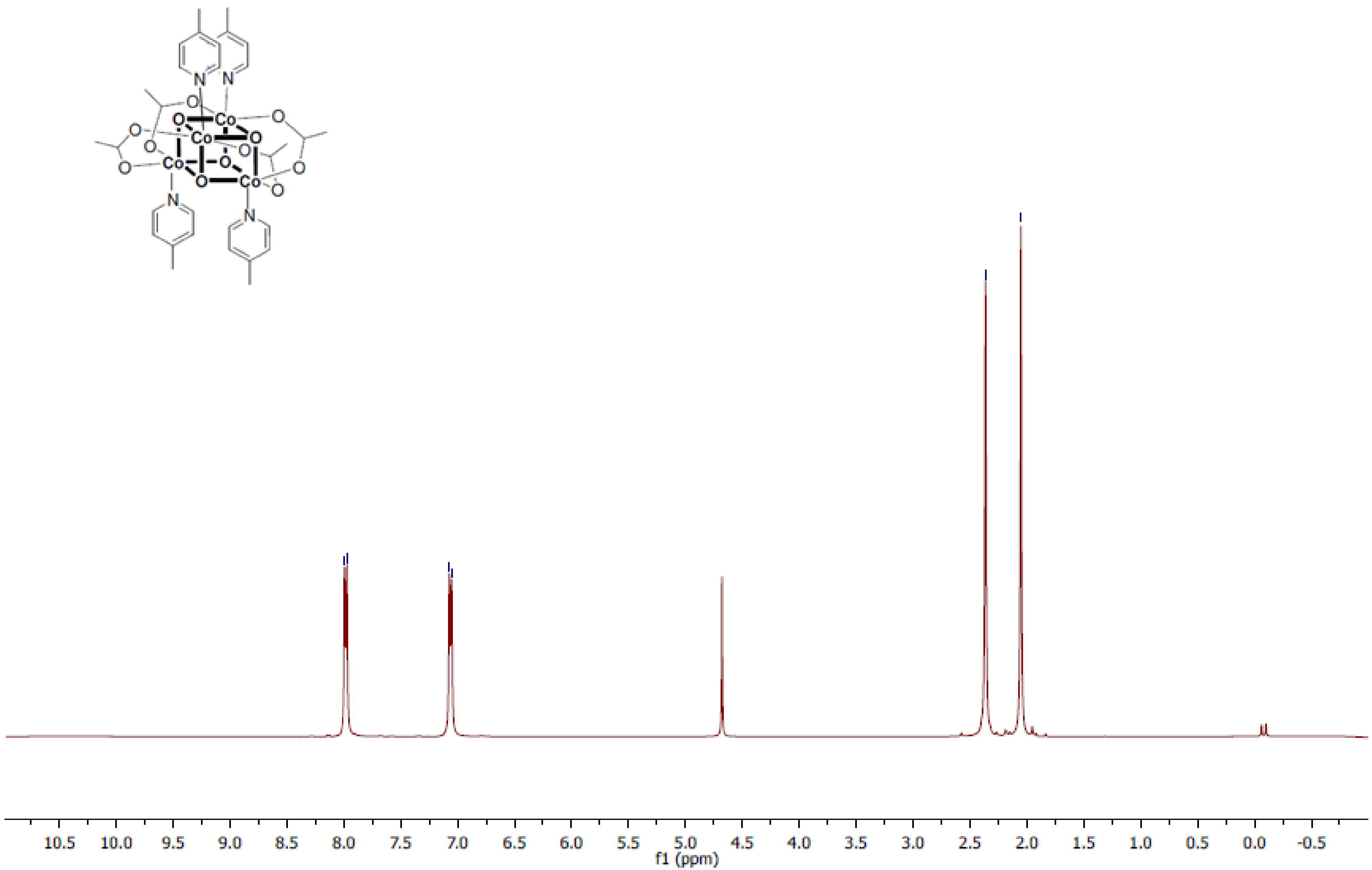
[c.] *Dipartimento di Scienze Chimiche, Università di Messina and Centro Interuniversitario per la Conversione Chimica dell'Energia Solare, sezione di Messina, Via Sperone 31, 98166 Messina, Italy.*

Content

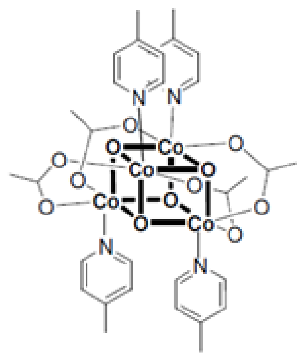

Co
O
N
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

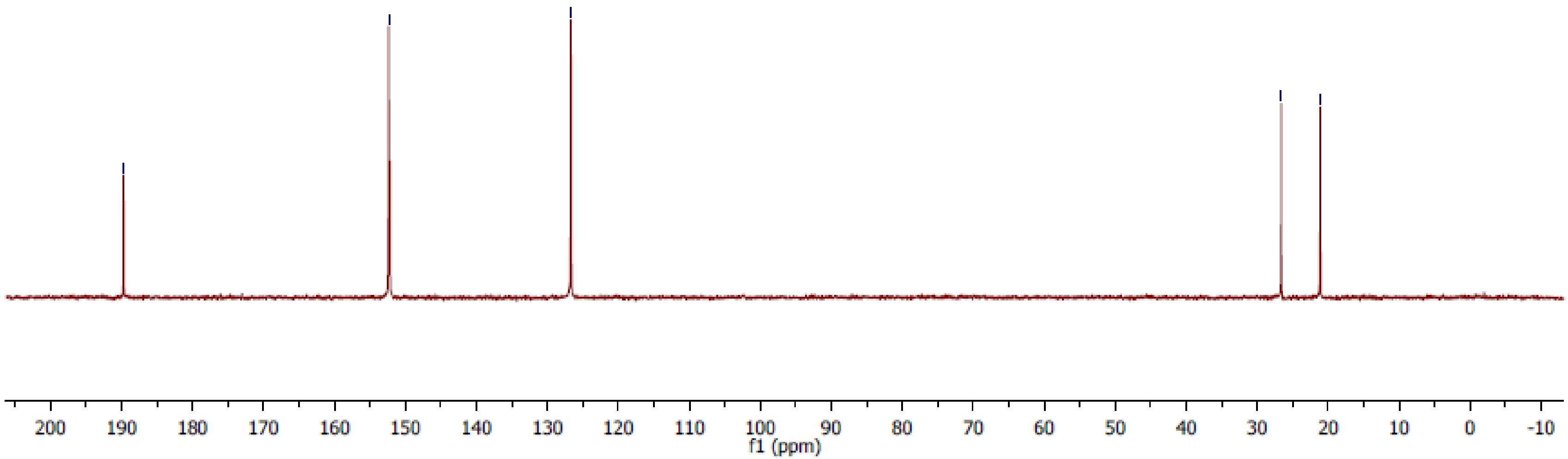


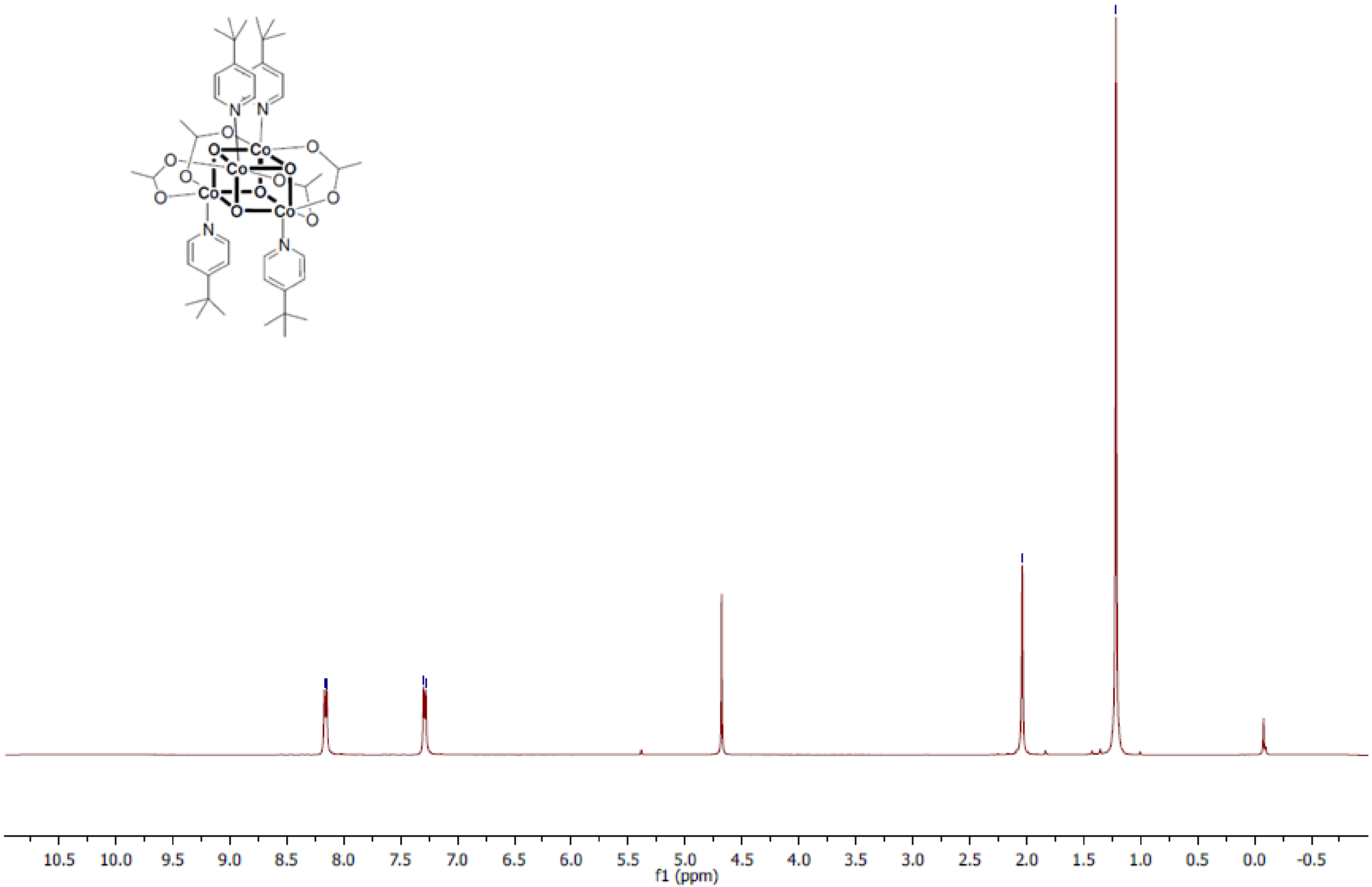

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



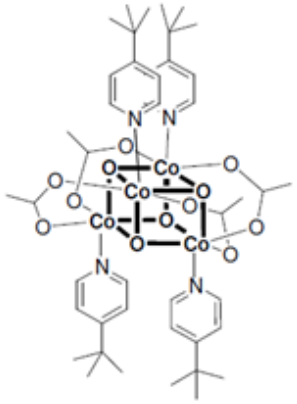
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

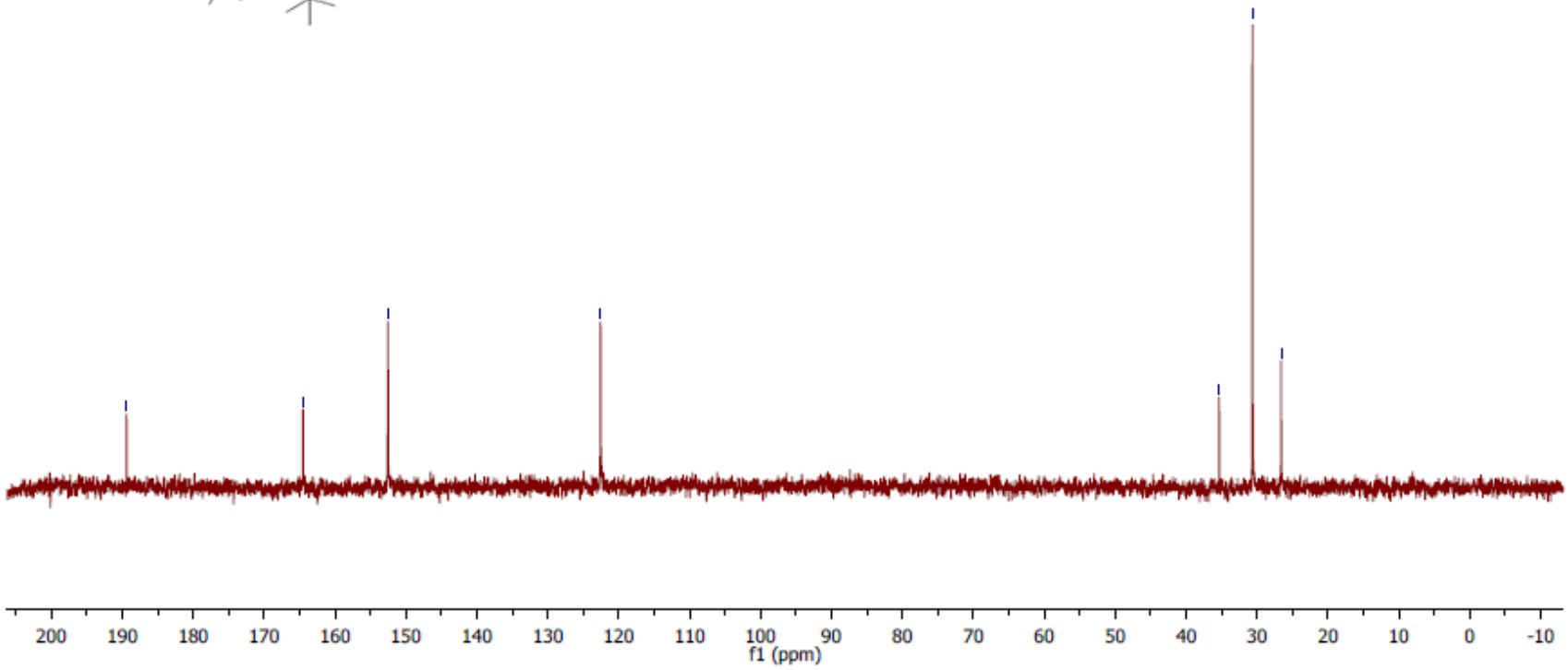

Co
N
O

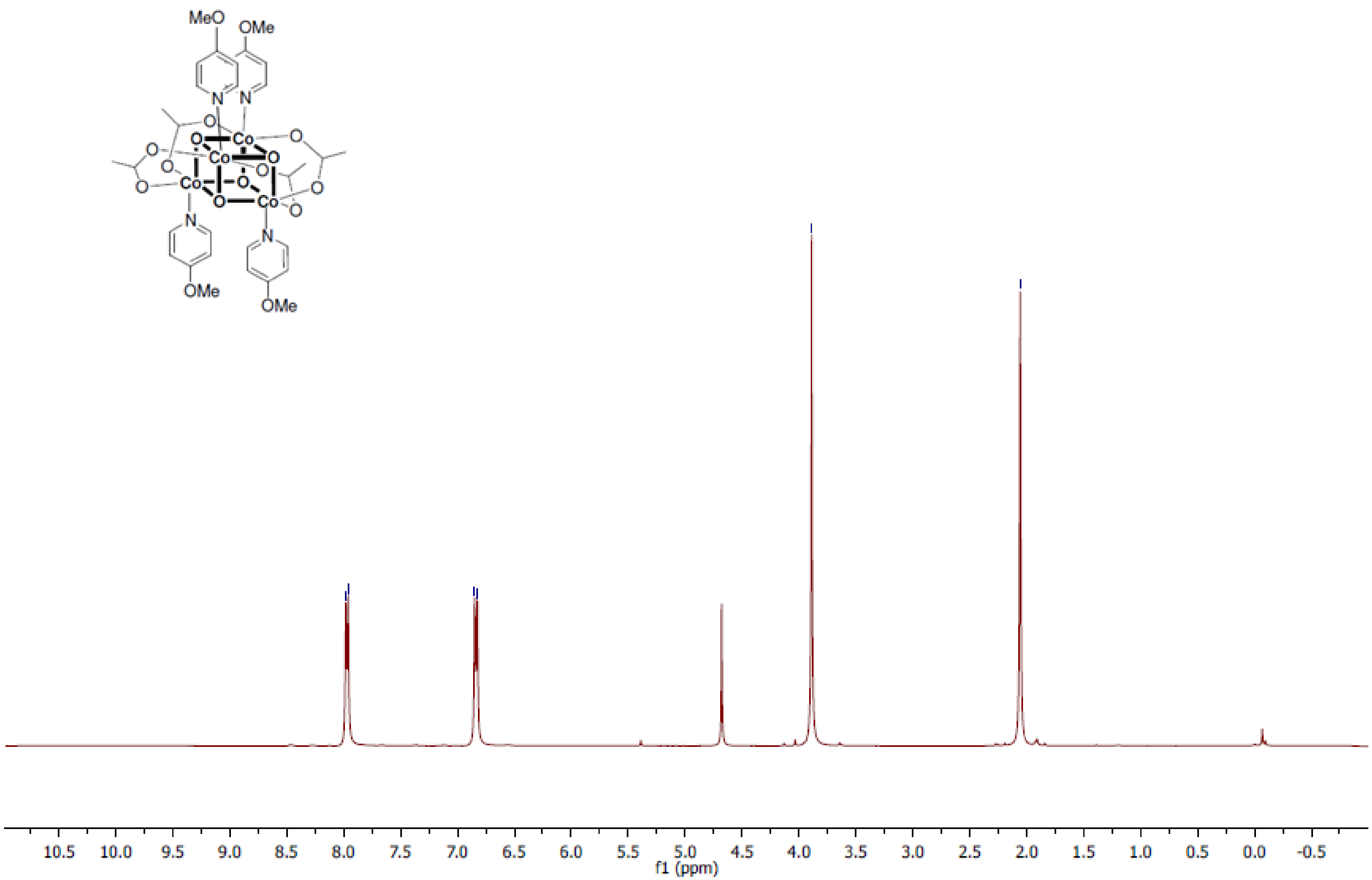

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

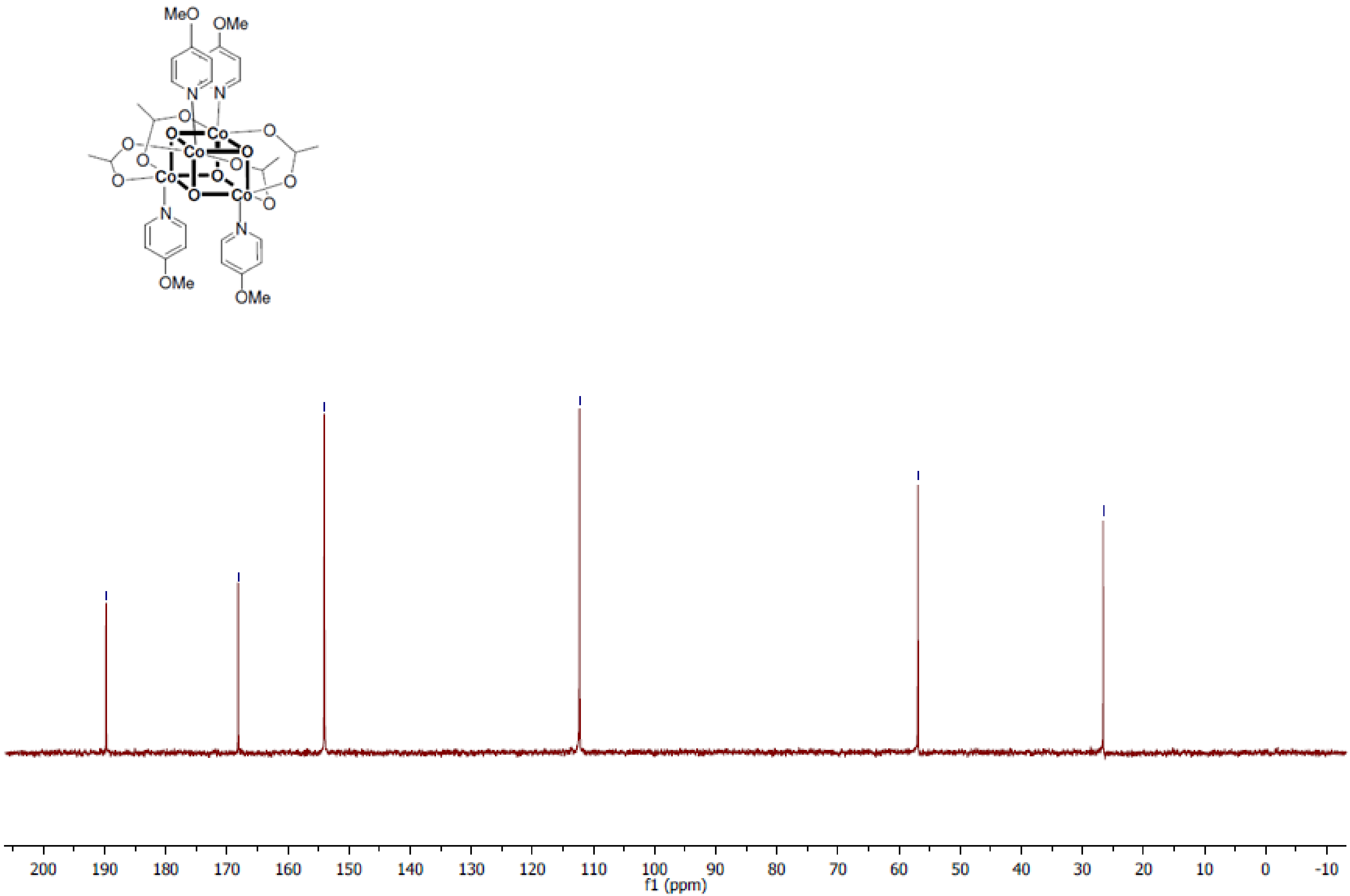


Co
O
N
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

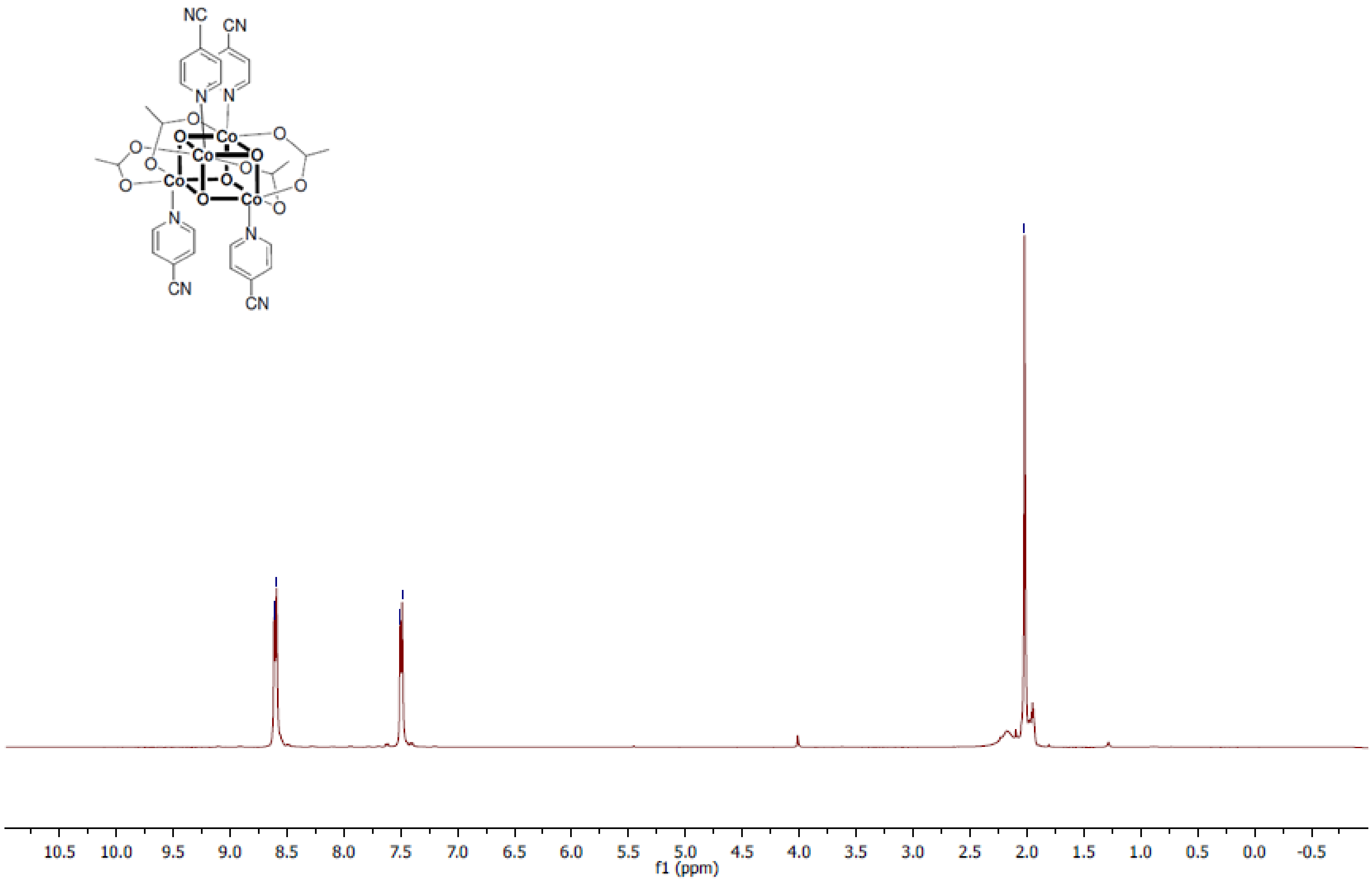

N
N
O
Co
O
O
Co
O
O
O
Co
O
O
O
O
Co
O
O
N
N


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

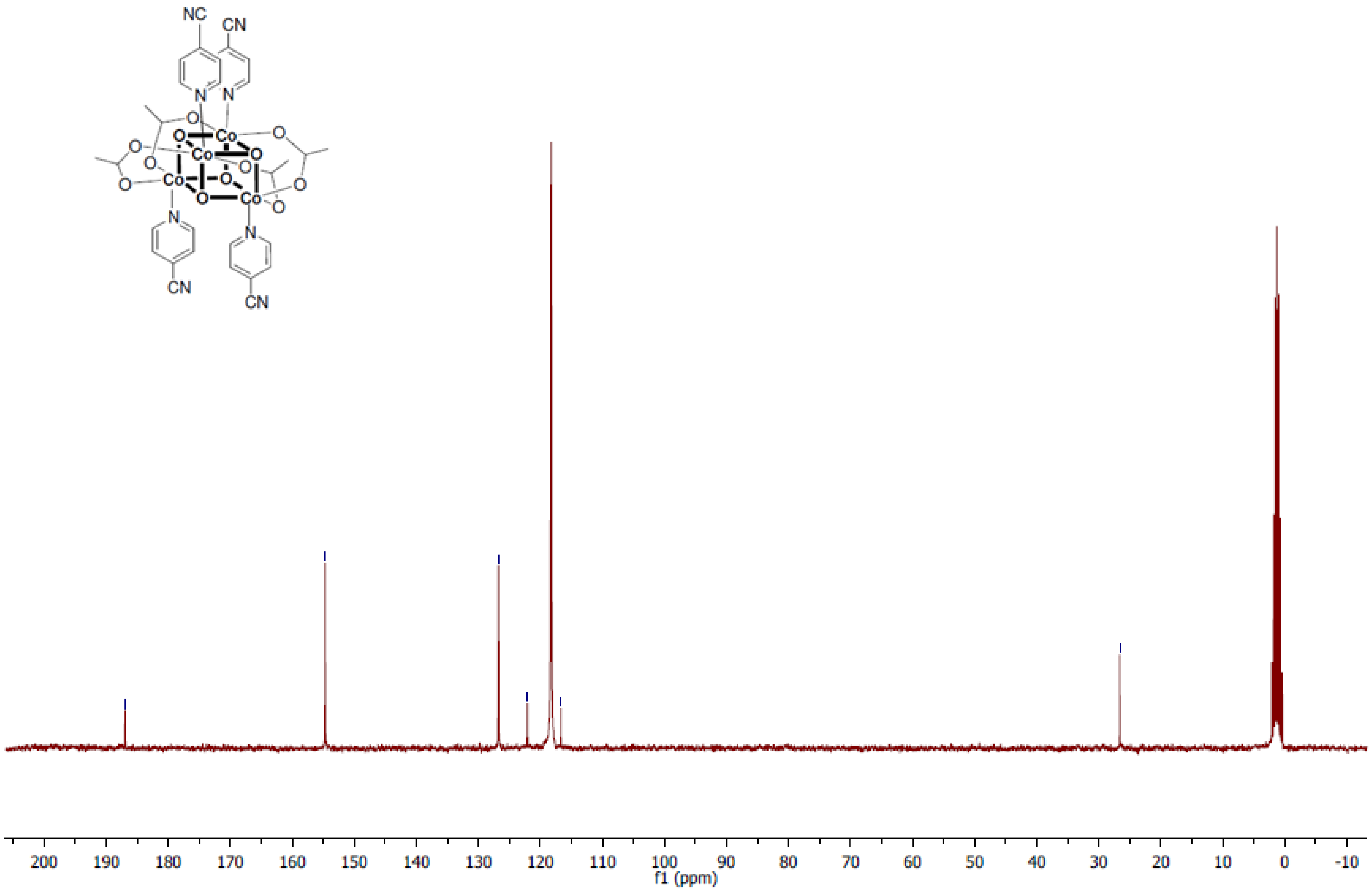

MeO
OMe
OMe
OMe
Co
O
N
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

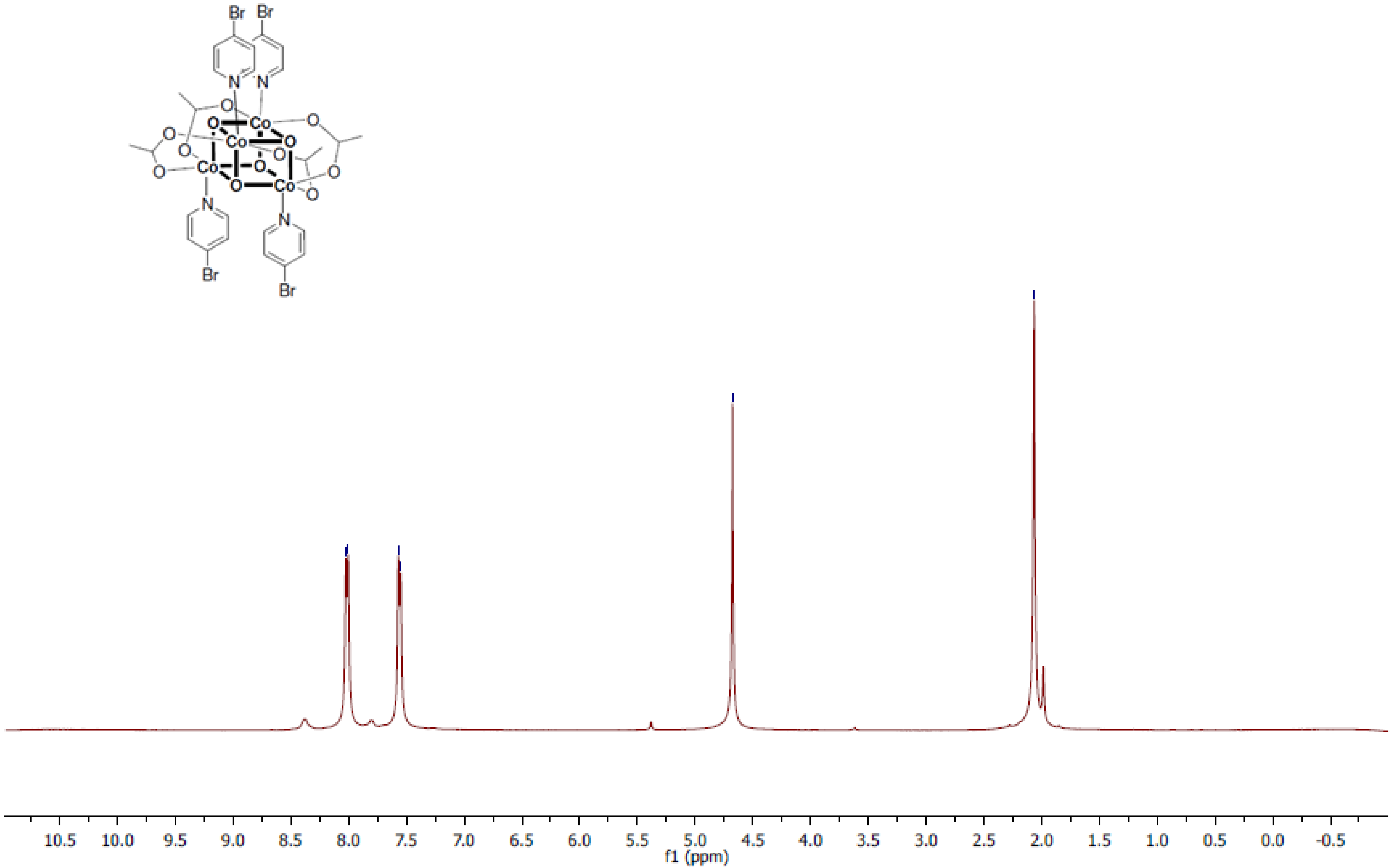


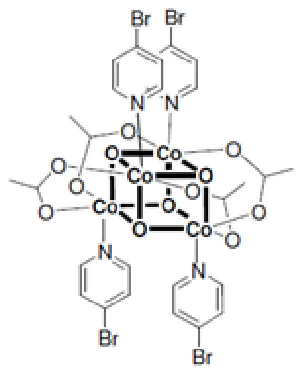
MeO
OMe
N
Co
O
OMe
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

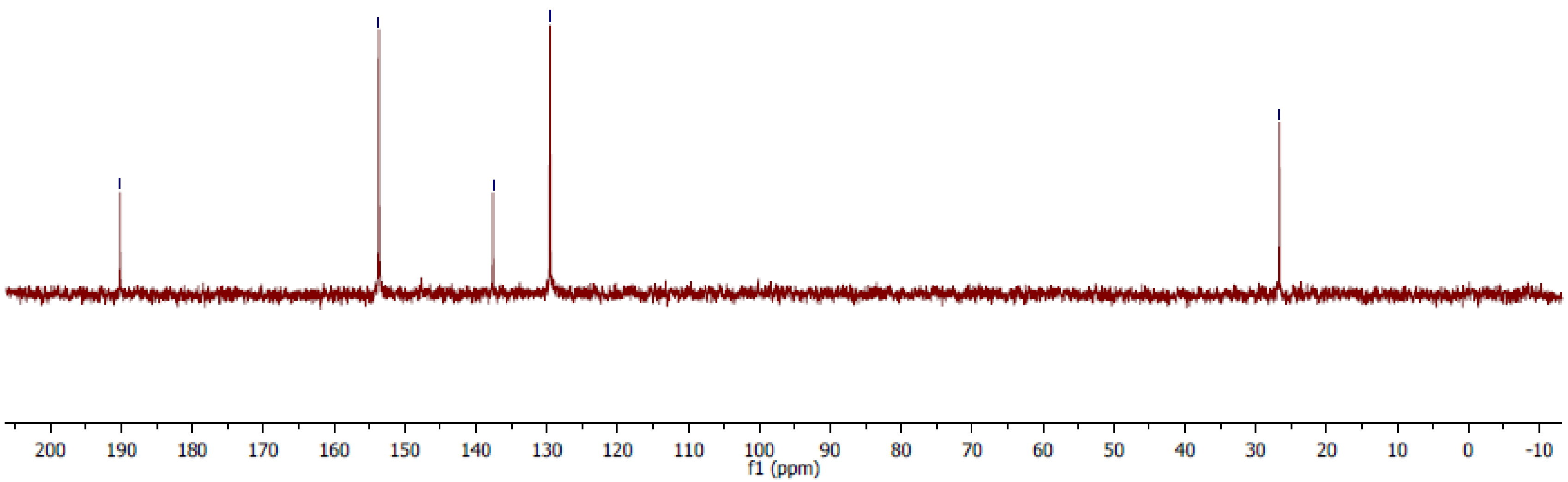


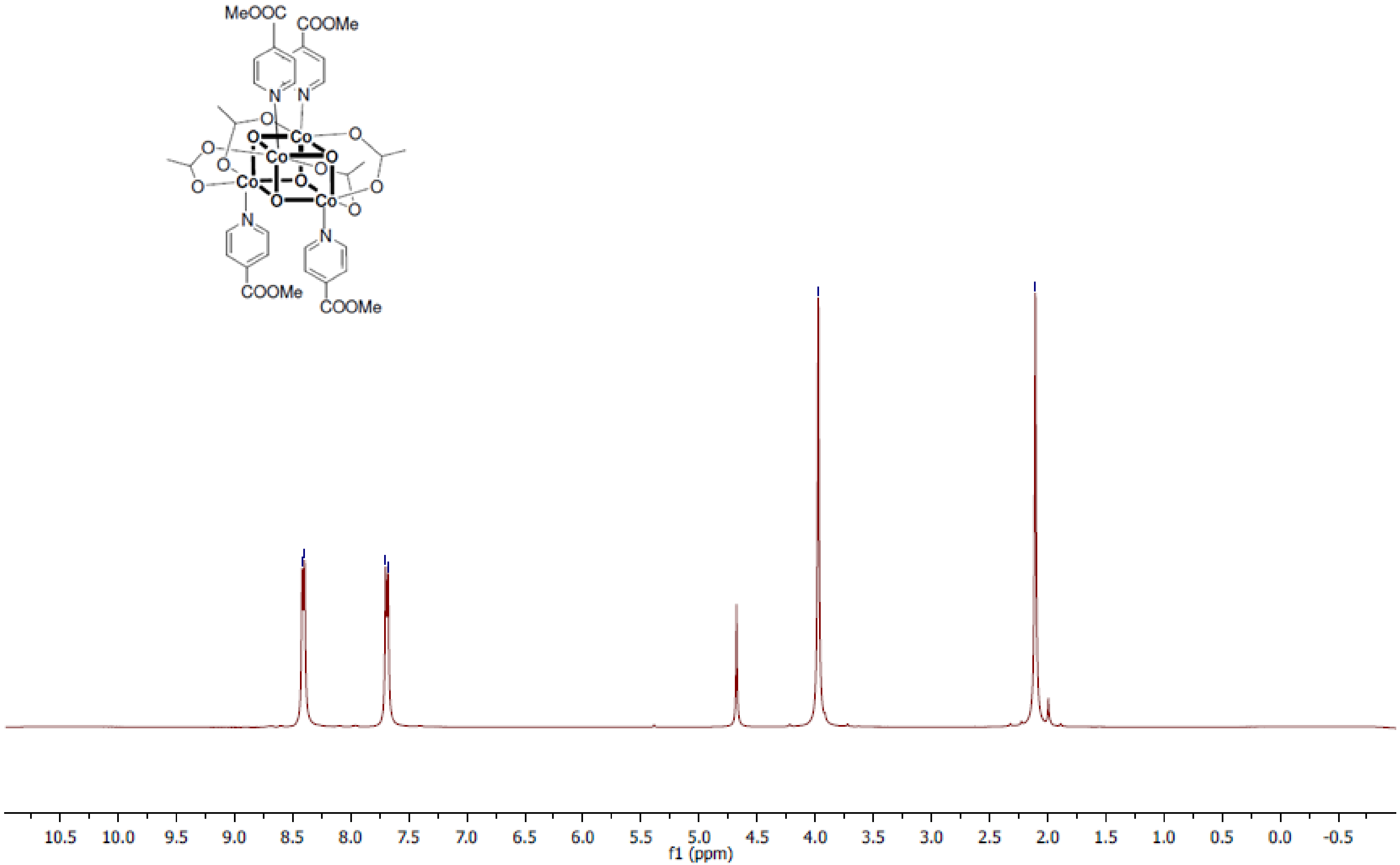
NC
CN
N
Co
O
CN
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

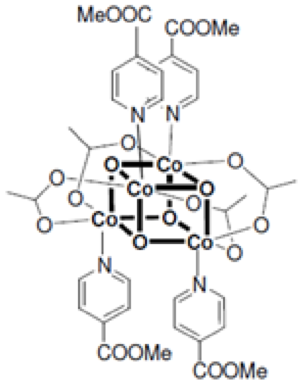

NC
CN
CN
CN
Co
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

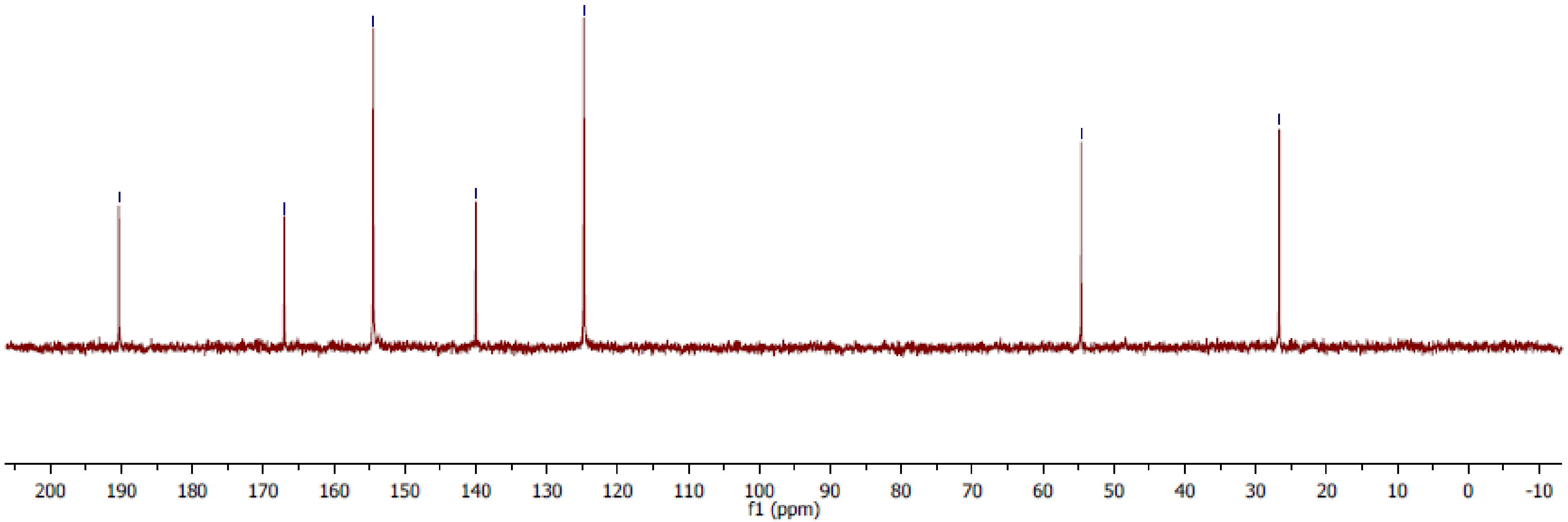

Br
Br
N
N
Co
Co
Co
Co
Br
Br
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

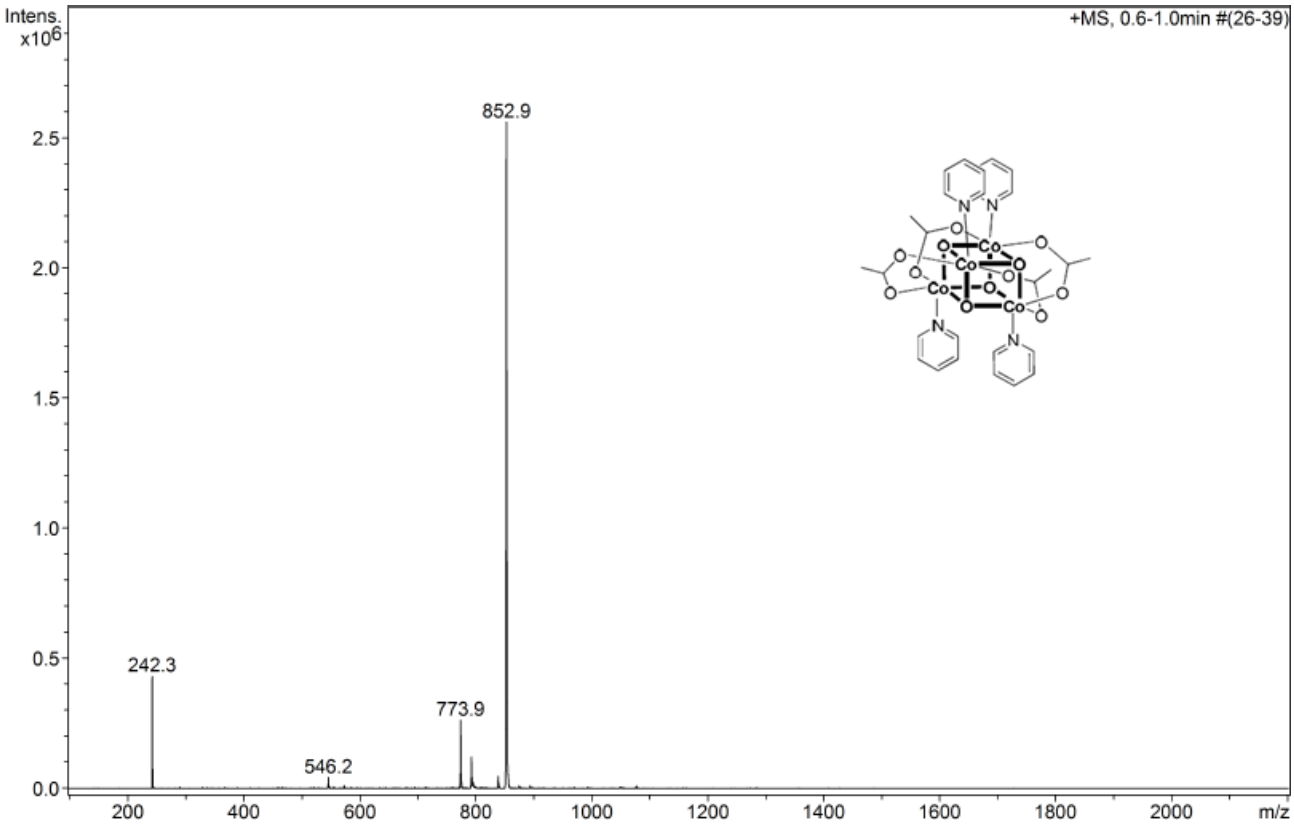

Br
Br
N
N
O
O
Co
Co
O
O
O
Co
O
O
O
O
Co
O
O
O
Co
O
O
N
N
Br
Br

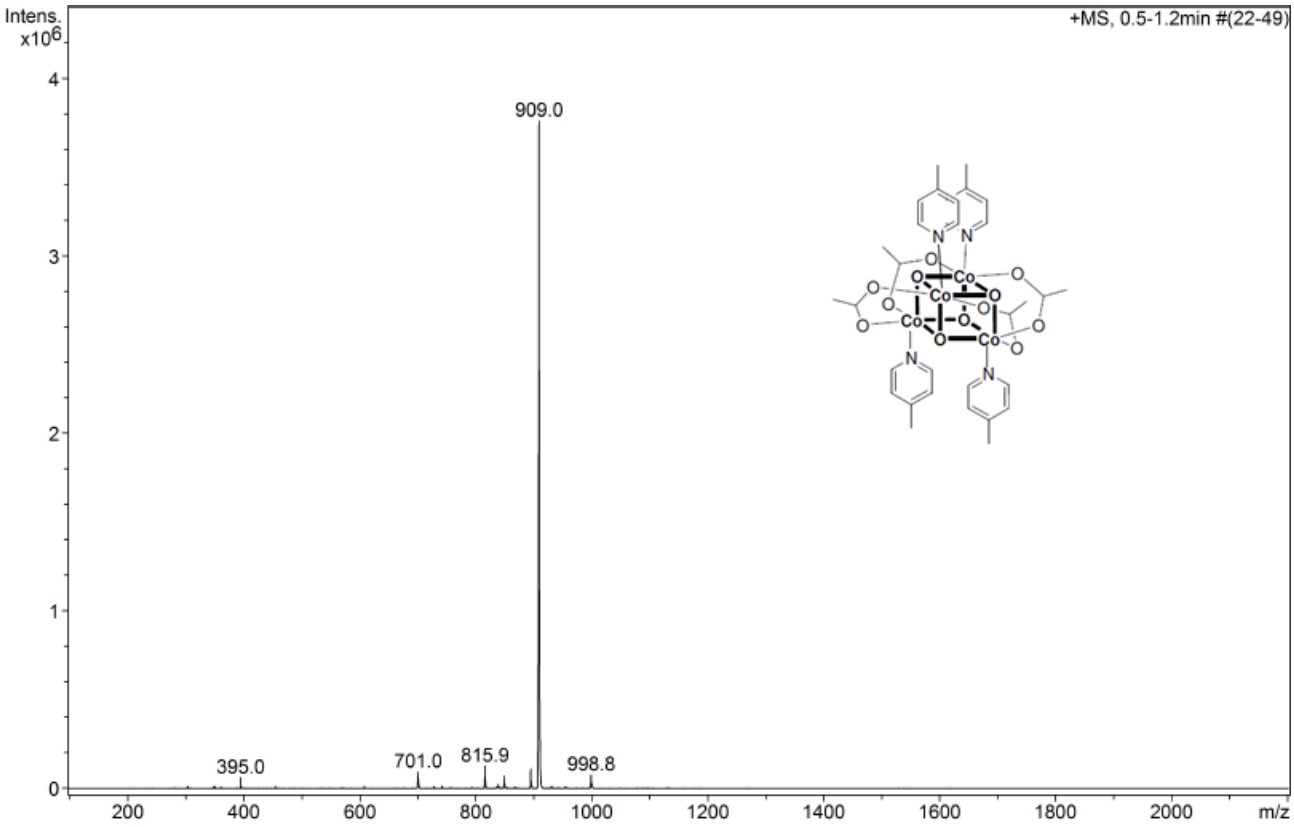

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

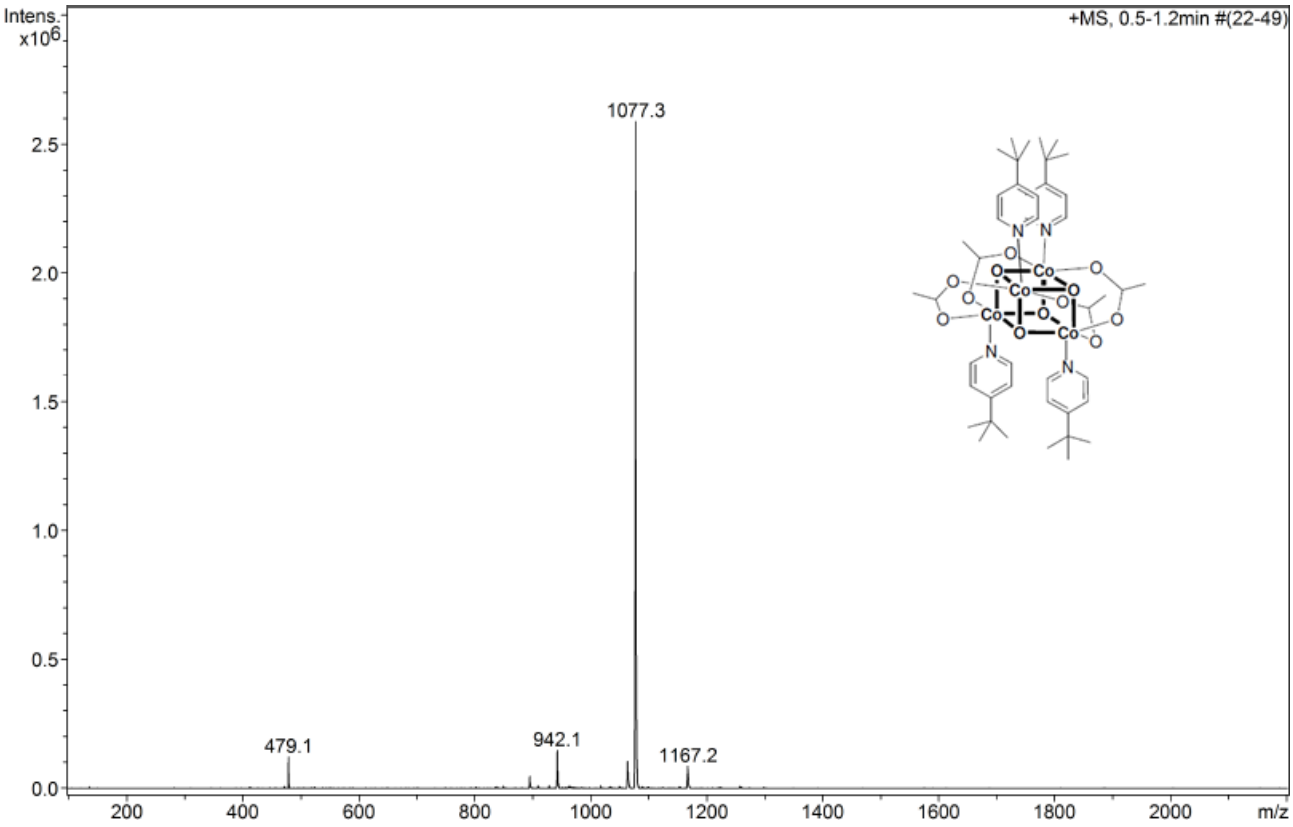

MeOOC
COOMe
COOMe
COOMe
Co
O
N
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

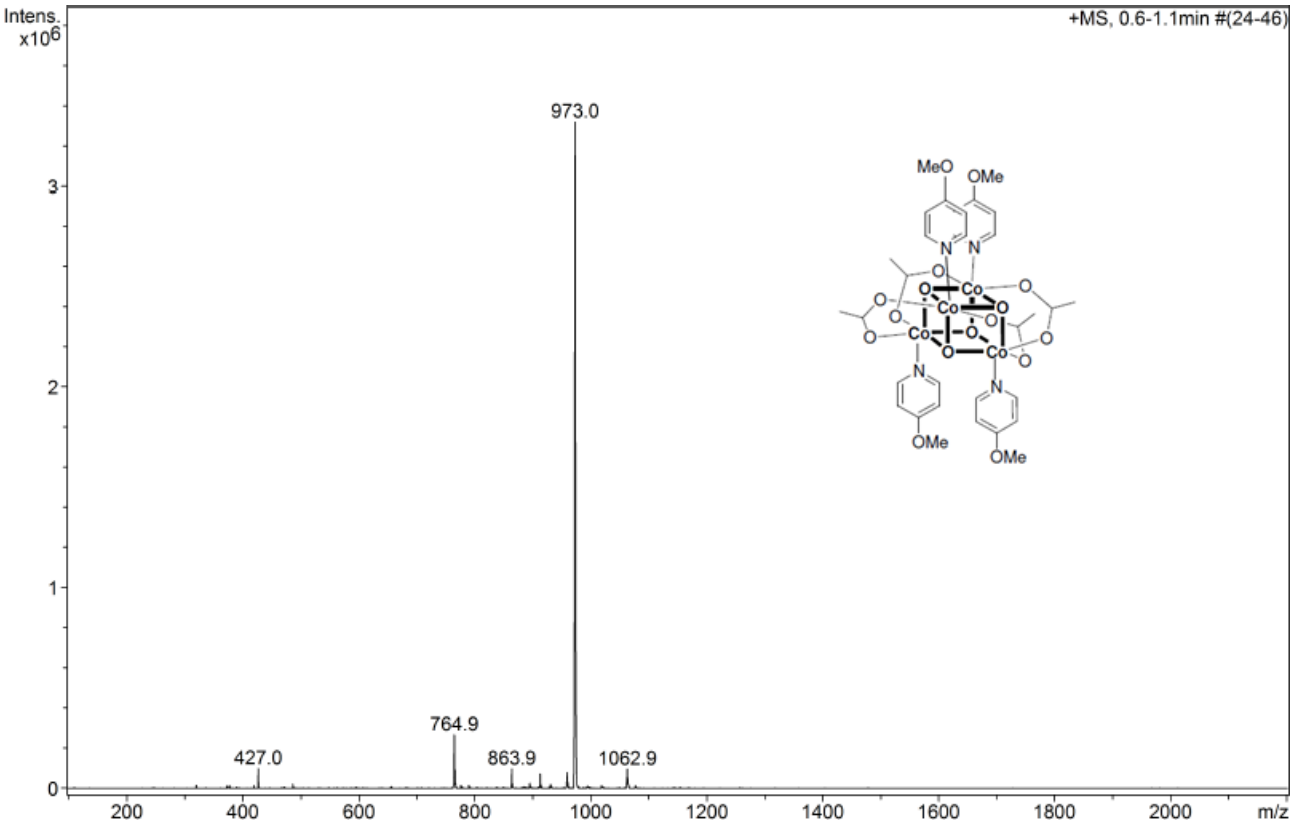

MeOOC
COOMe
COOMe
COOMe
Co
O
N

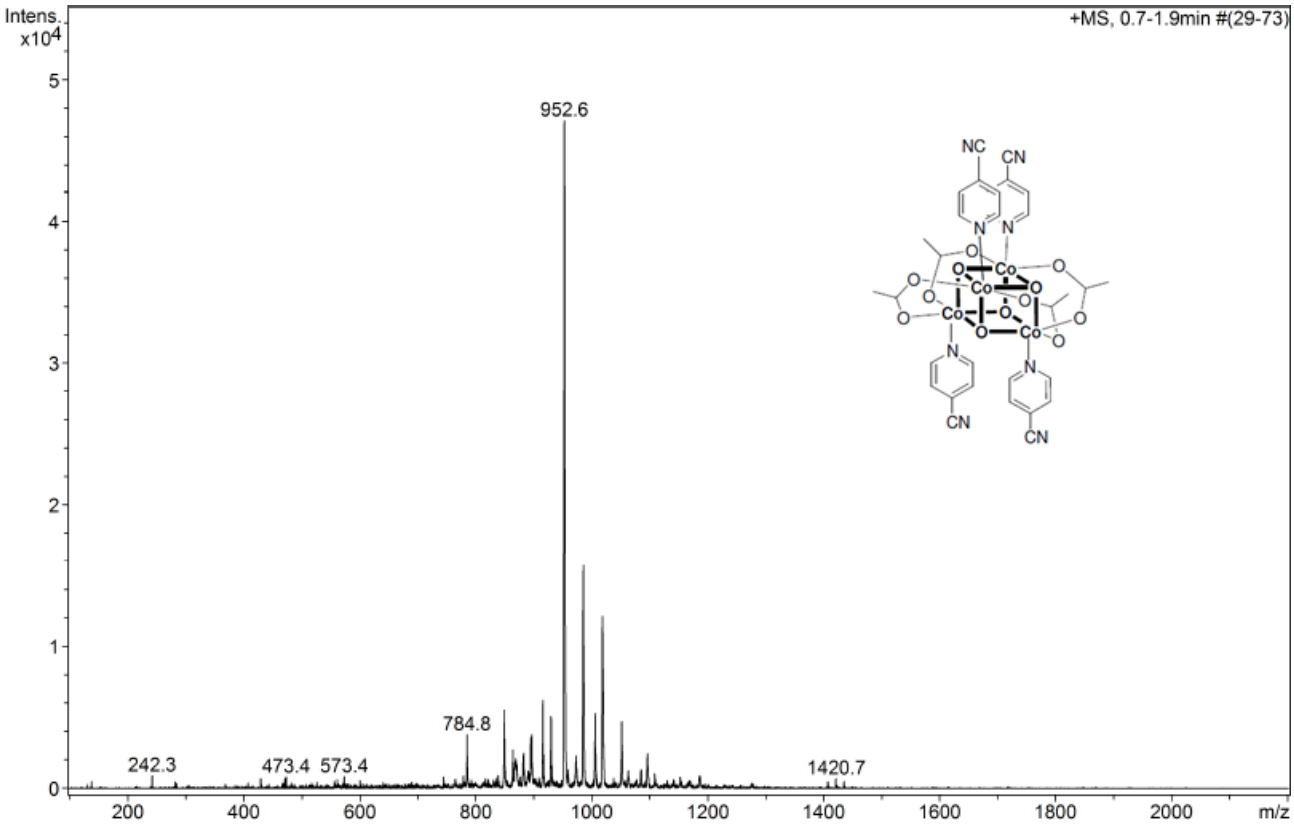

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

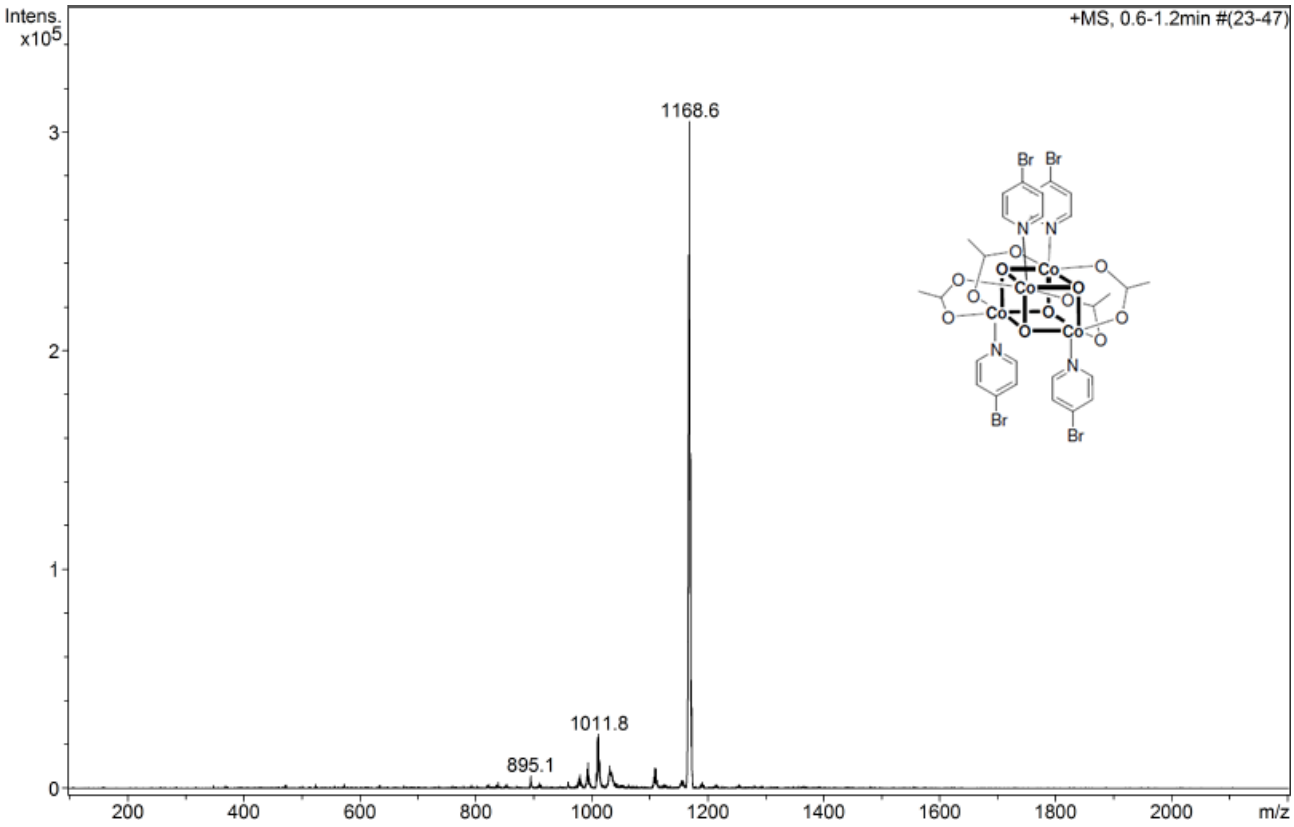

Intens.
x10^6
+MS, 0.6-1.0min #(26-39)
852.9
242.3
773.9
546.2
m/z

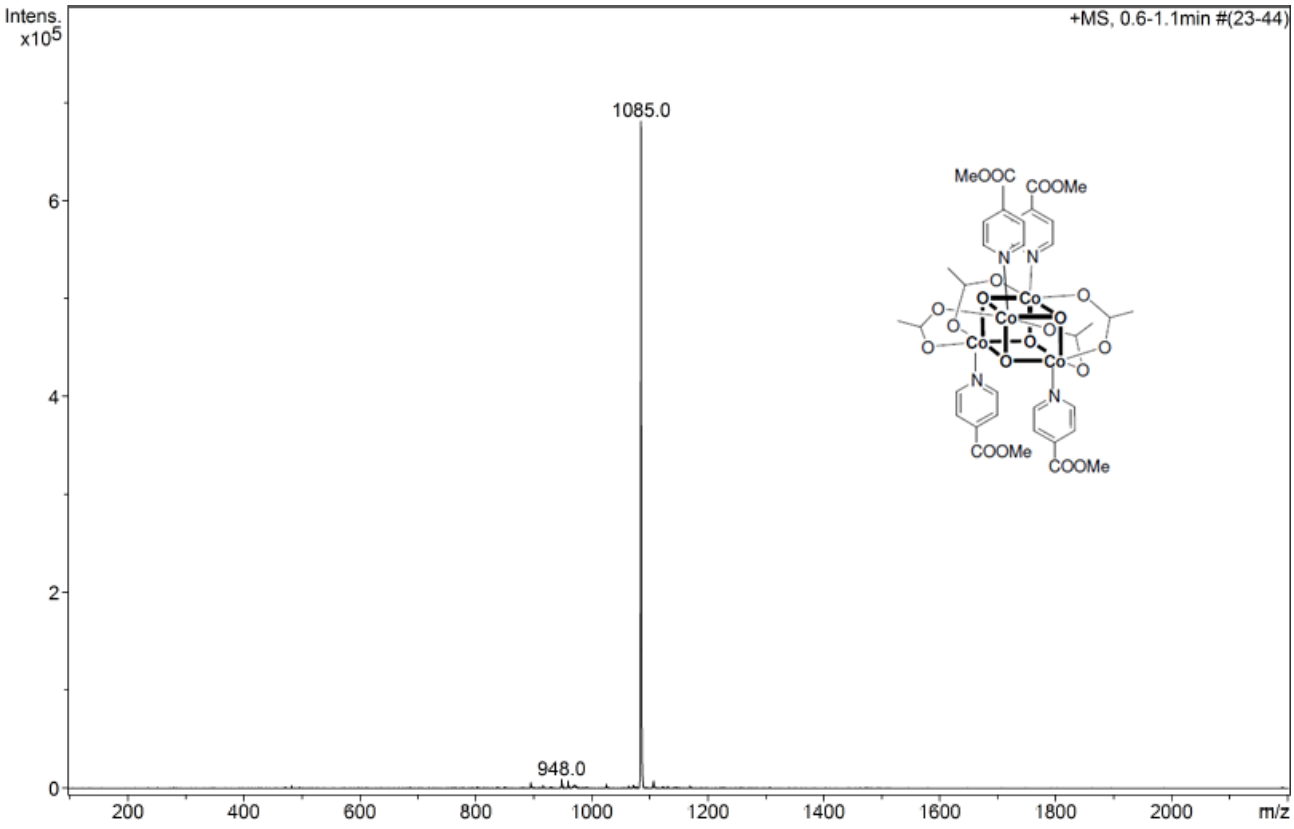

Intens.
x10^6
+MS, 0.5-1.2min #(22-49)
909.0
395.0
701.0
815.9
998.8
m/z

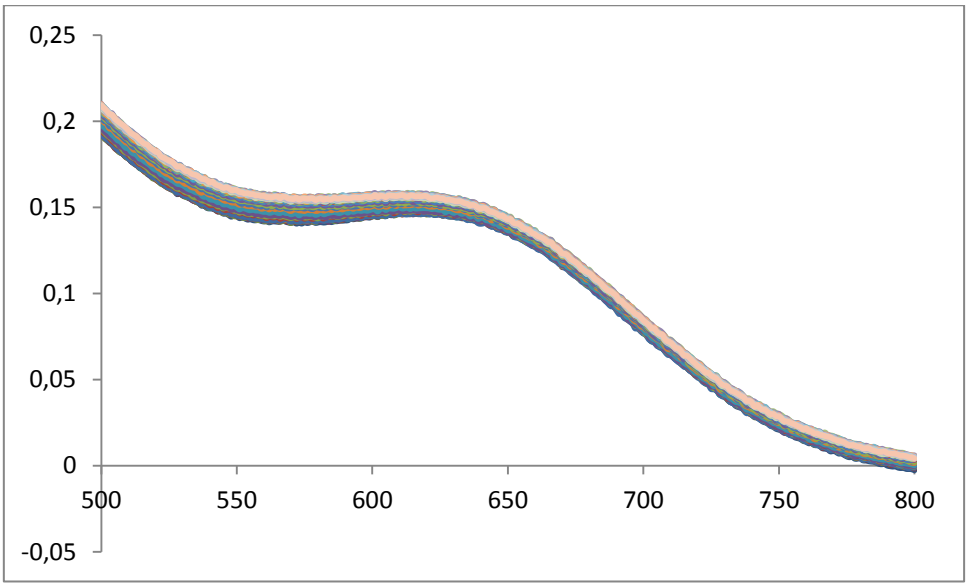

Intens.
x10^6
+MS, 0.5-1.2min #(22-49)
1077.3
479.1
942.1
1167.2
m/z


Intens.
x10^6
+MS, 0.6-1.1min #(24-46)
973.0
764.9
427.0
863.9
1062.9
m/z


Intens.
x10^4
+MS, 0.7-1.9min #(29-73)
952.6
784.8
242.3
473.4
573.4
1420.7
m/z


Intens.
x10^5
+MS, 0.6-1.2min #(23-47)
1168.6
1011.8
895.1
m/z

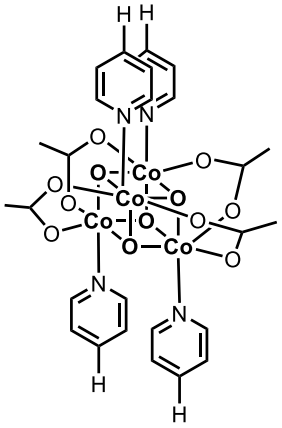


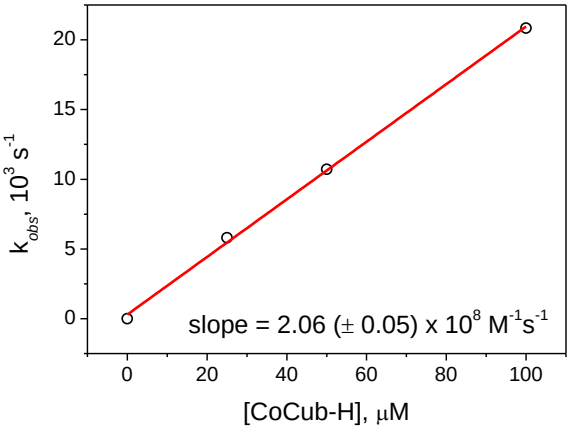


UV-Vis evolution of **1-H** (5 mM) in 10 mM borate buffer, pH 8, over the course of 12 hours. Optical path of the cuvette: 1 mm.

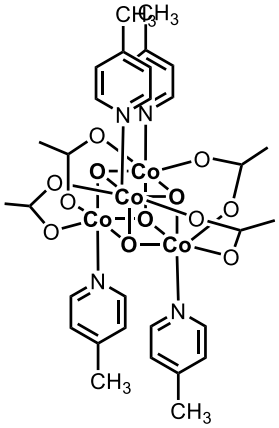
Hole scavenging in 50:50 acetonitrile:10 mM borate buffer, pH 8 (50μM $Ru(bpy)_3Cl_2$, 5 mM $Na_2S_2O_8$, 0-100 μM **1-X**

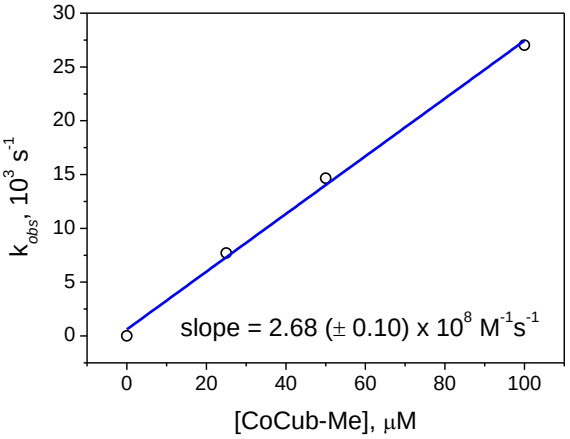
1-H



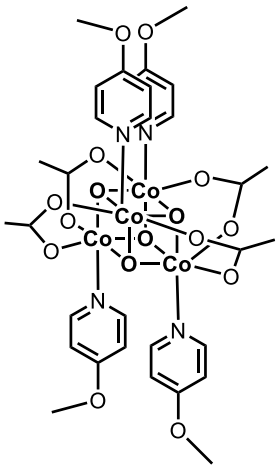


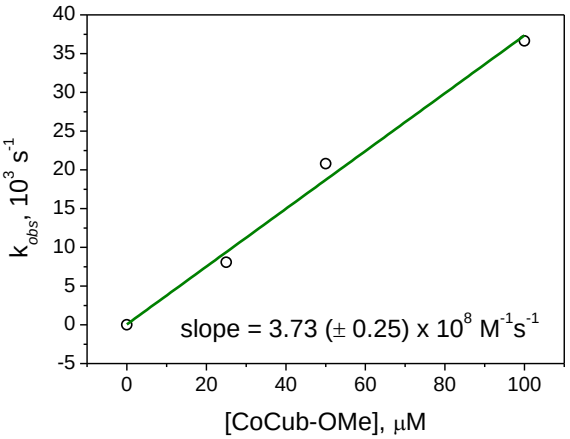
1-Me



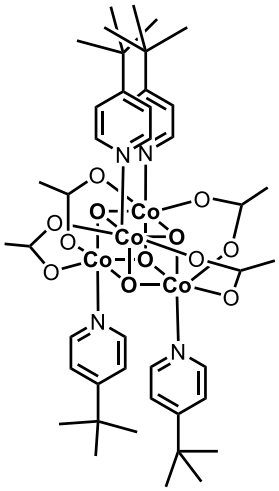


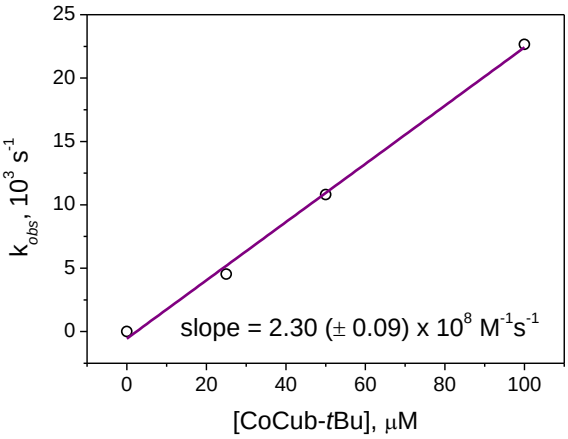
1-OMe



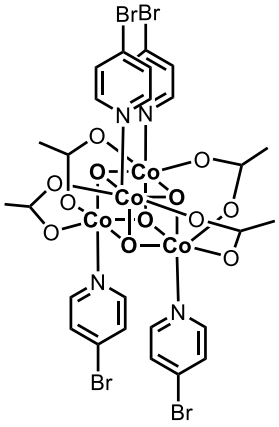


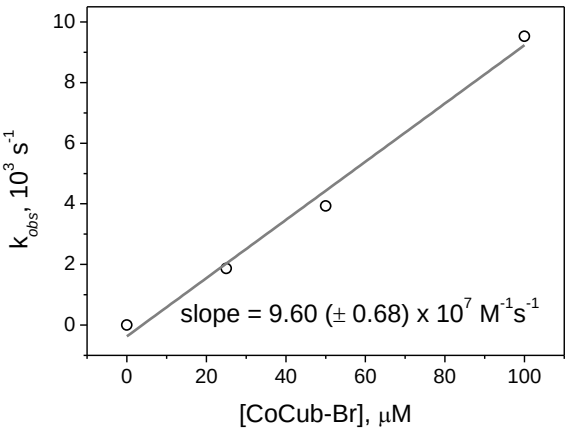
1-*t*Bu



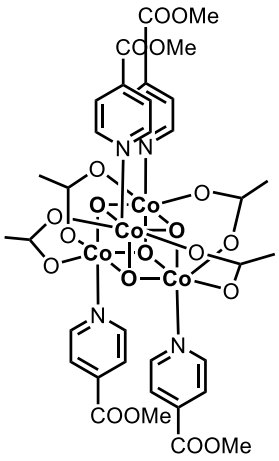


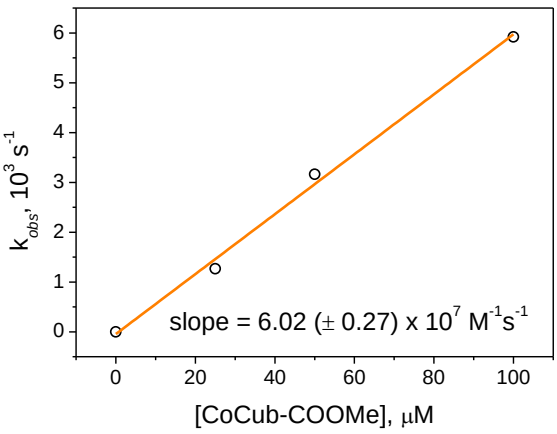
1-Br



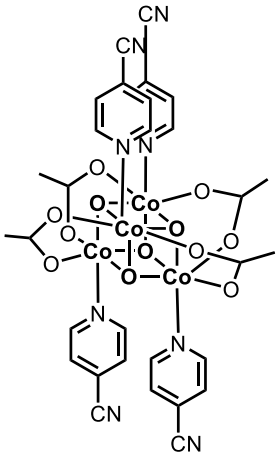


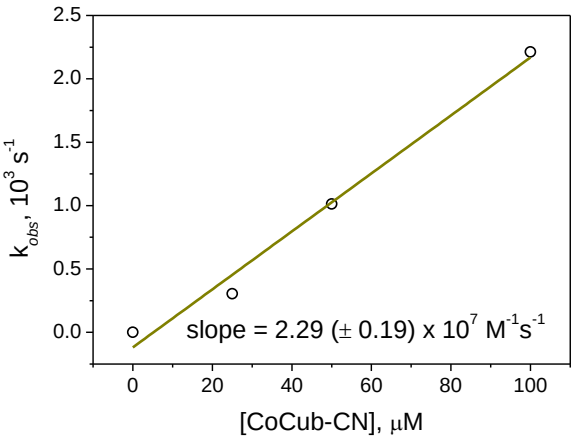
1-COOMe





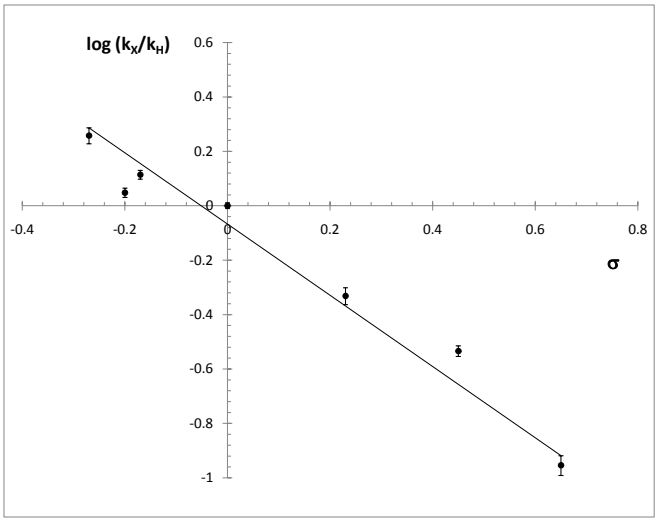
1-CN



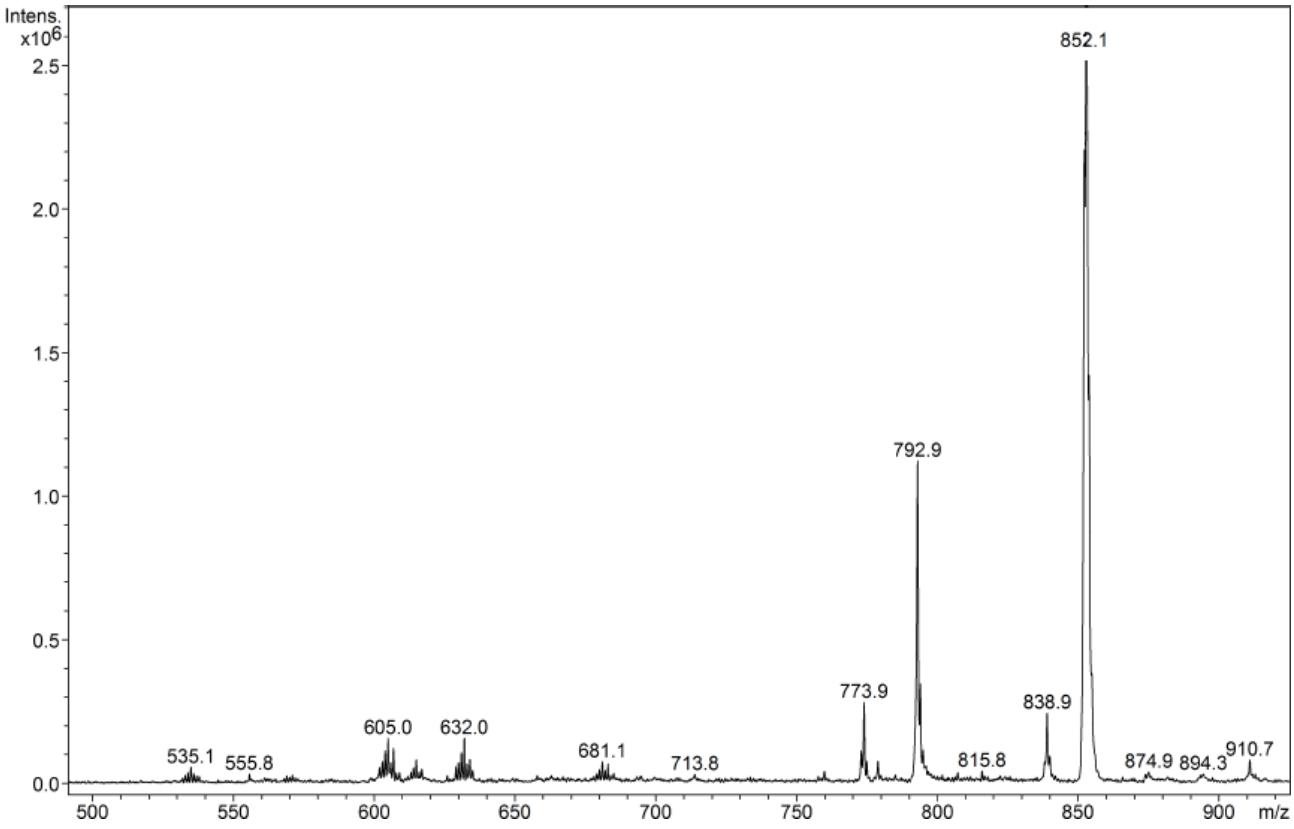


X	σ	k_X (10^8 $M^{-1}s^{-1}$)	log (k_X / k_H)
H	0	2.06 (± 0.05)	0
Me	-0.17	2.68 (± 0.10)	0.114
OMe	-0.27	3.73 (± 0.25)	0.258
***t*Bu**	-0.2	2.30 (± 0.09)	0.048
Br	0.23	0.96 (± 0.07)	-0.331
COOMe	0.45	0.60 (± 0.03)	-0.534
CN	0.65	0.23 (± 0.02)	-0.954

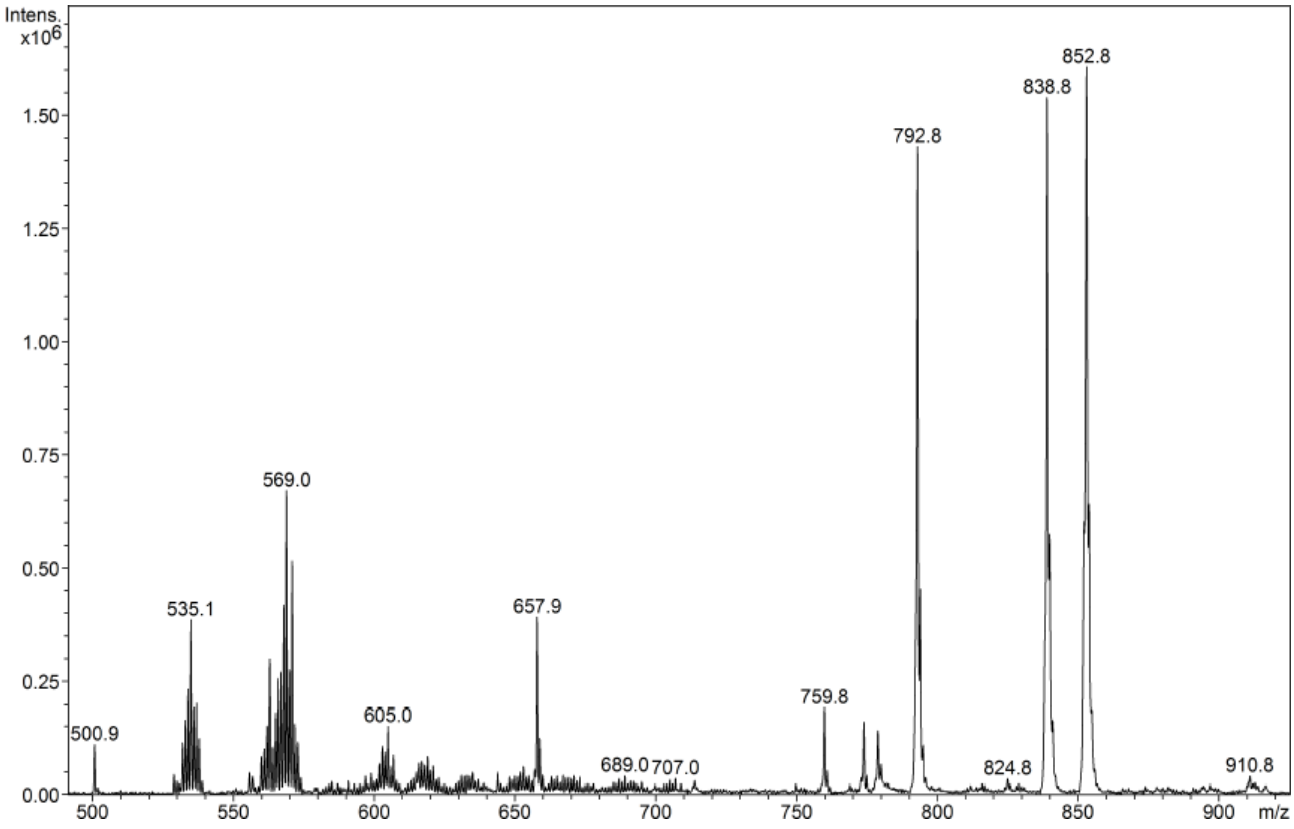
Hammet plot



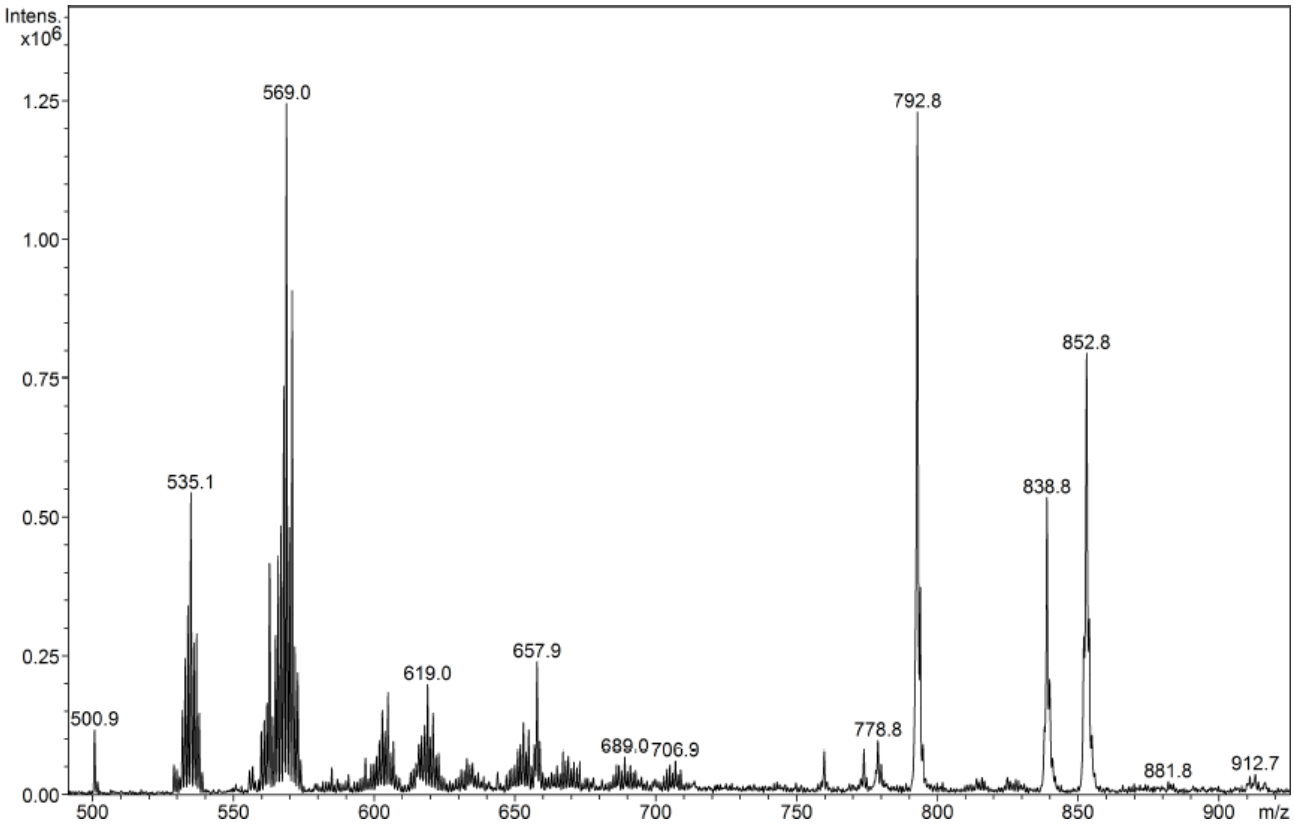
a)


Intens.
x10^6
2.5
2.0
1.5
1.0
0.5
0.0
852.1
792.9
773.9
838.9
605.0
632.0
535.1
555.8
681.1
713.8
815.8
874.9
894.3
910.7
500
550
600
650
700
750
800
850
900
m/z

b)


Intens.
x10^6
1.50
1.25
1.00
0.75
0.50
0.25
0.00
852.8
838.8
792.8
569.0
535.1
657.9
759.8
605.0
500.9
689.0
707.0
824.8
910.8
500
550
600
650
700
750
800
850
900
m/z

c)



ESI-MS spectra (5 x 10^{-5} M in acetonitrile, + 0.1% formic acid) of a catalytic test carried out under the conditions reported in Table 1 Entry 4, recorded on aliquots sampled at different times (respectively: a) 0 min; b) 30 min; c) 60 min.).