Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPLEMENTARY SECTION

Single step incorporation of carboxylic acid groups in the lower rim of calix[4]arenes: a recyclable catalyst towards assembly of diverse five ring fused acridines

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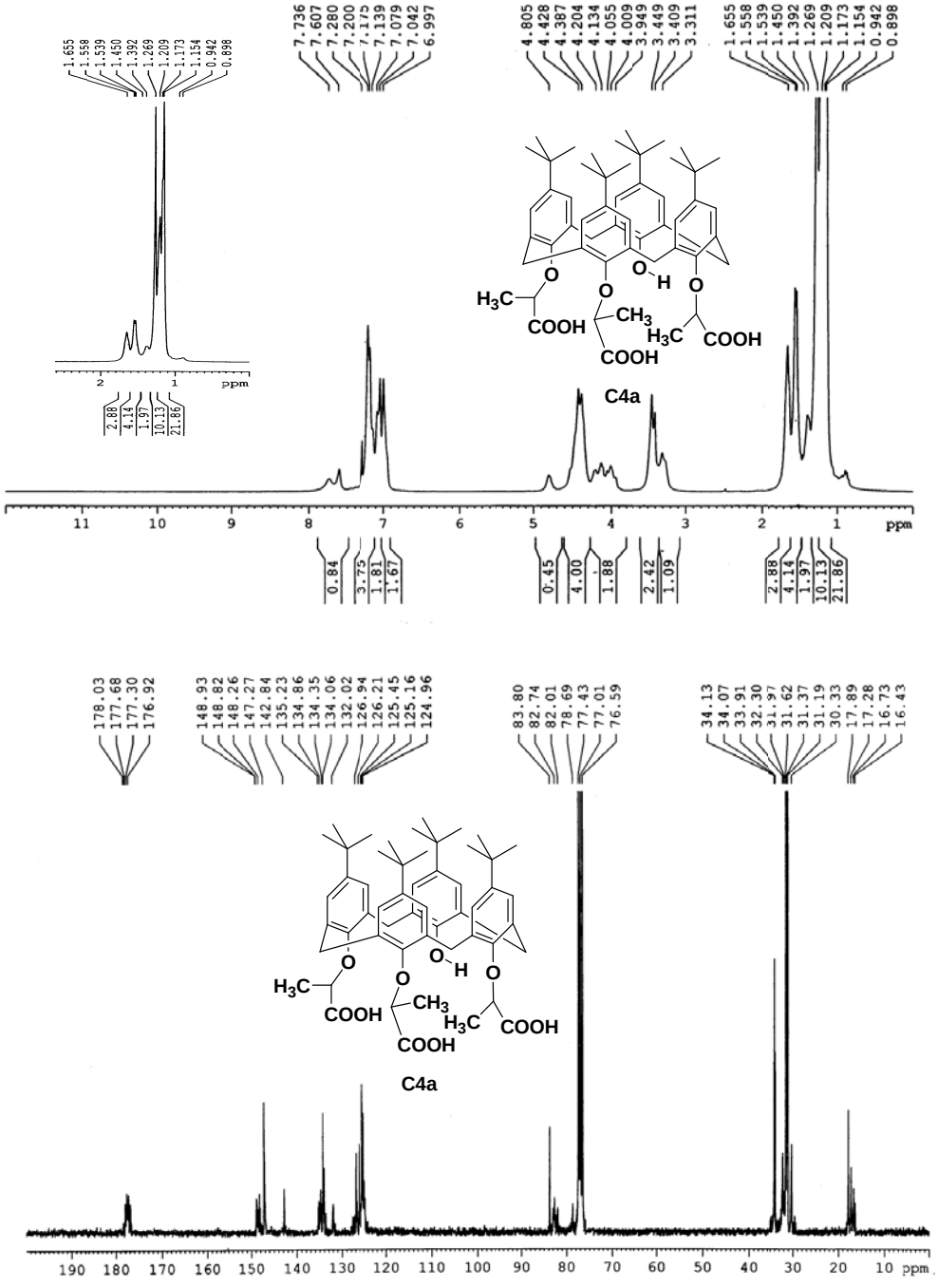
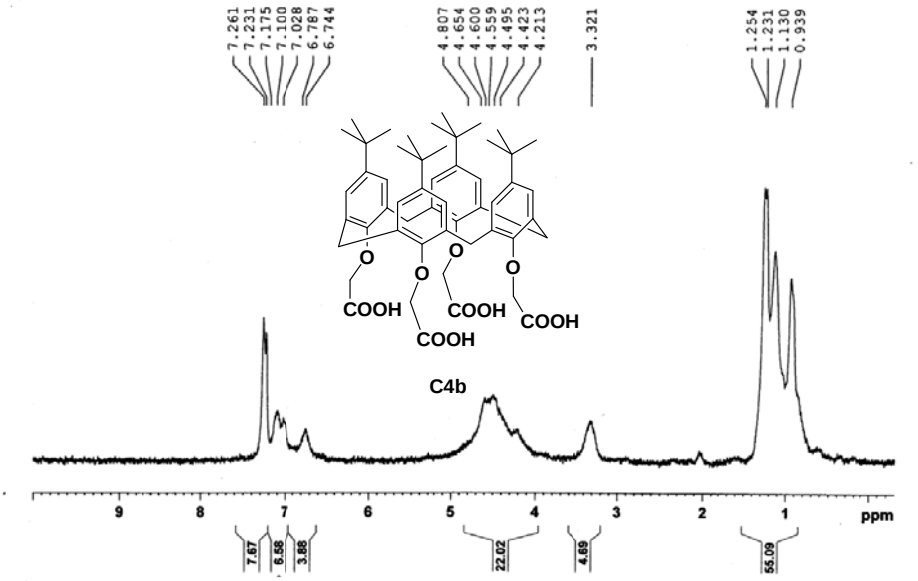
Contents:

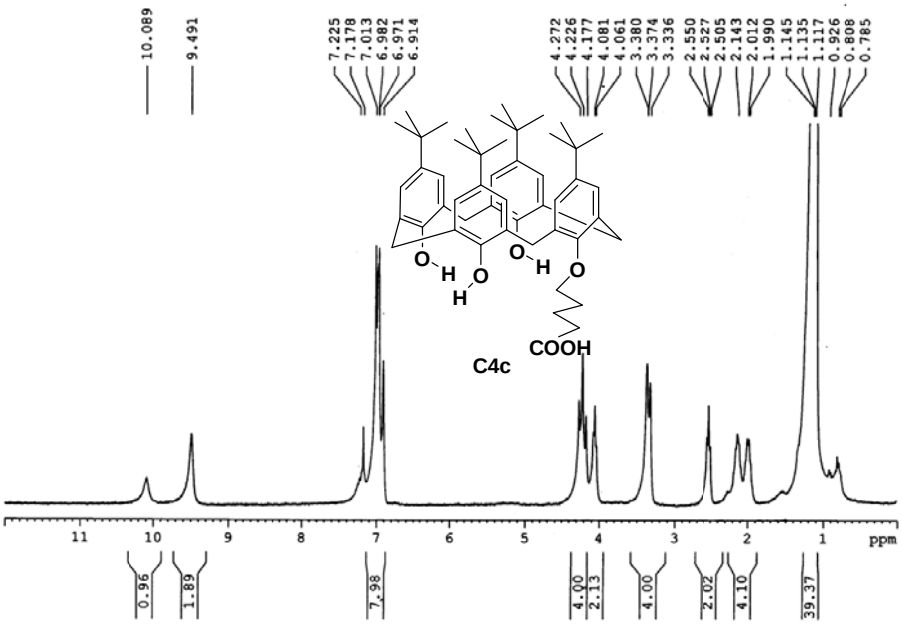
1. ^{1}H and ^{13}C spectra of **C4a** (scheme 1):

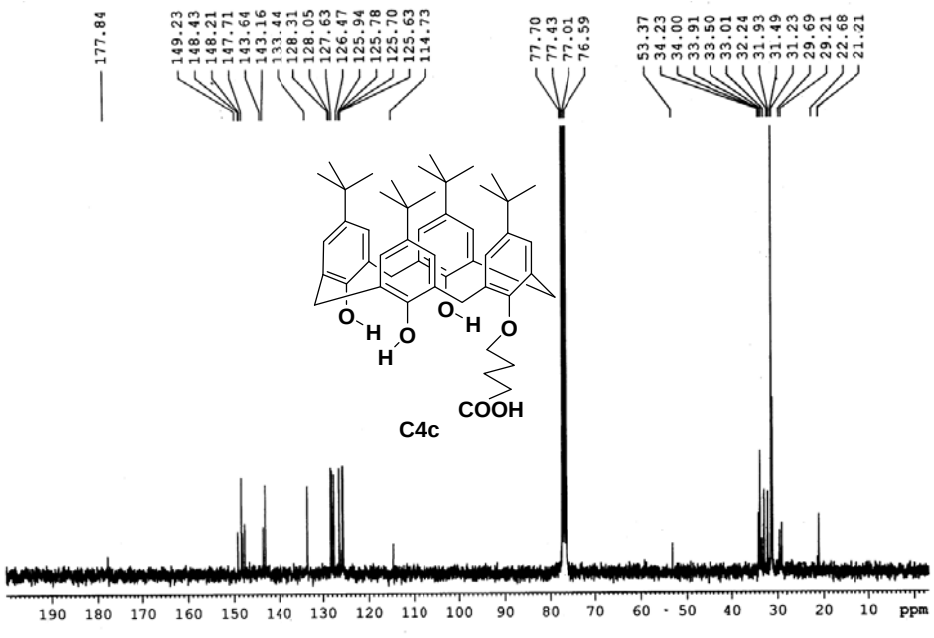


2. ^{1}H spectra of **C4b** (scheme 2):

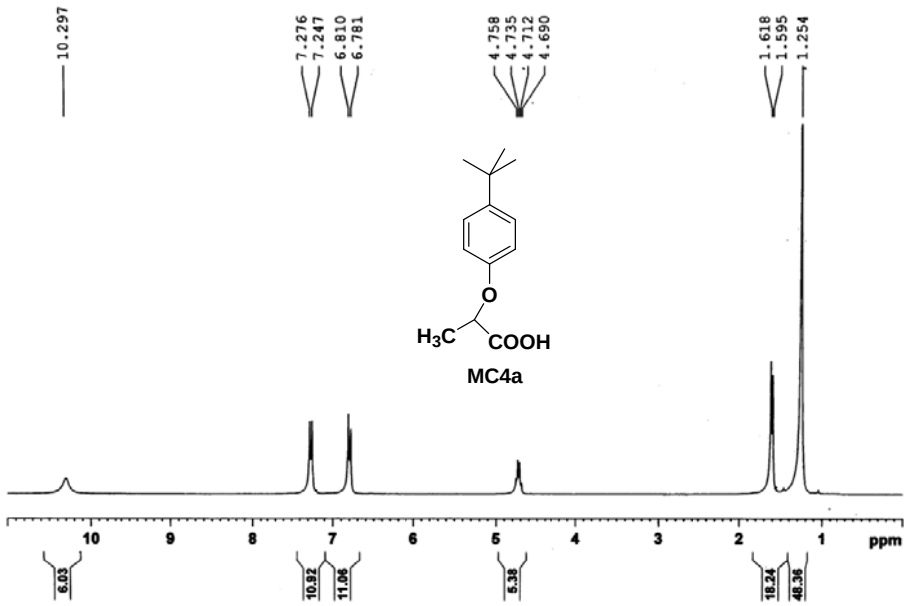


3. ^{1}H and ^{13}C spectra of **C4c** (scheme 2):





4. **Synthesis of the monomer unit of the parent calixarene (C4a), 1-(p-tert-butylphenoxy)-1-methylacetic acid (MC4a):** 4-tert-Butylphenol (150mg, 1 mmol) was mixed with NaH (48 mg, 2 mmol) in a 25 ml round bottom flask, 10 ml of dry DMF was added to it. The mixture was allowed to stir for 30 mins at room temperature (25-30 ºC). 2-Bromopropionic acid (0.9 ml, 1 mmol) was added drop wise maintaining the temperature at 20-25 ºC. After the complete addition the reaction mixture was stirred for 4 h. As the reaction progressed, the suspended particles changed into a form of viscous mass. The disappearance of starting 4-tert-Butylphenol was checked by TLC. After complete conversion the reaction mixture was placed in an ice bath and was quenched via acidification using 5% HCl solution. Then 20 ml of chilled water was added to it and we got the crude product by filtration. 210 mg (95%) pure product, color less solid was gained via column chromatography at 10% ethyl acetate in petroleum ether as eluent. mp. 64 ºC; IR (KBr, υ cm^{-1}): 3394, 2963, 2865, 1738, 1654, 1362, 1199, 1068. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.30 (br s,, 1H, -COOH), 7.26 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.80 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.72 (q, *J* = 6.8 Hz, 1H, -CH), 1.61 (d, *J* = 6.9 Hz, 3H, $-CH_3$), 1.25 (s, 9H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.9, 154.6, 144.2, 126.1,126.0, 114.2, 71.8, 33.7, 31.1, 18.1; Anal. calcd. for $C_{13}H_{18}O_3$; C: 70.24; H: 8.16. Found: C: 70.29; H: 8.15.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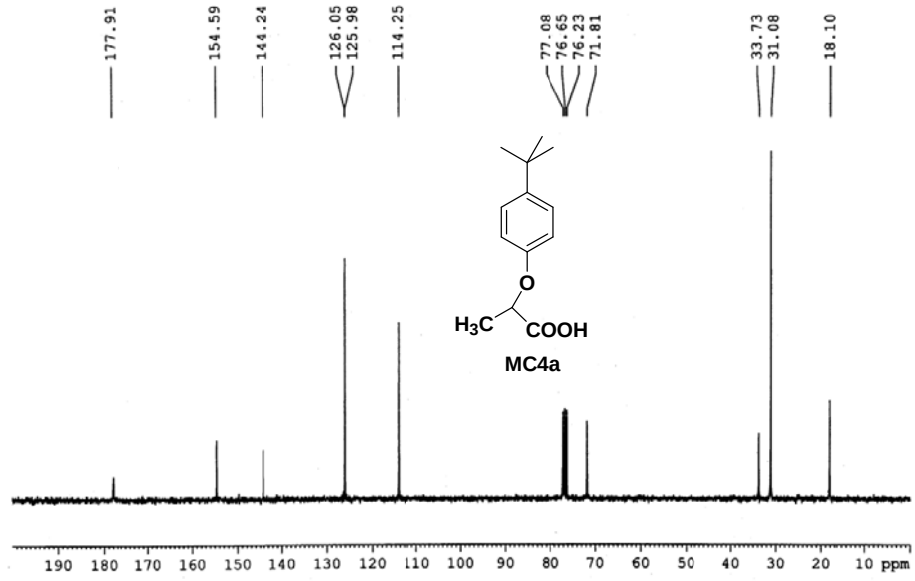
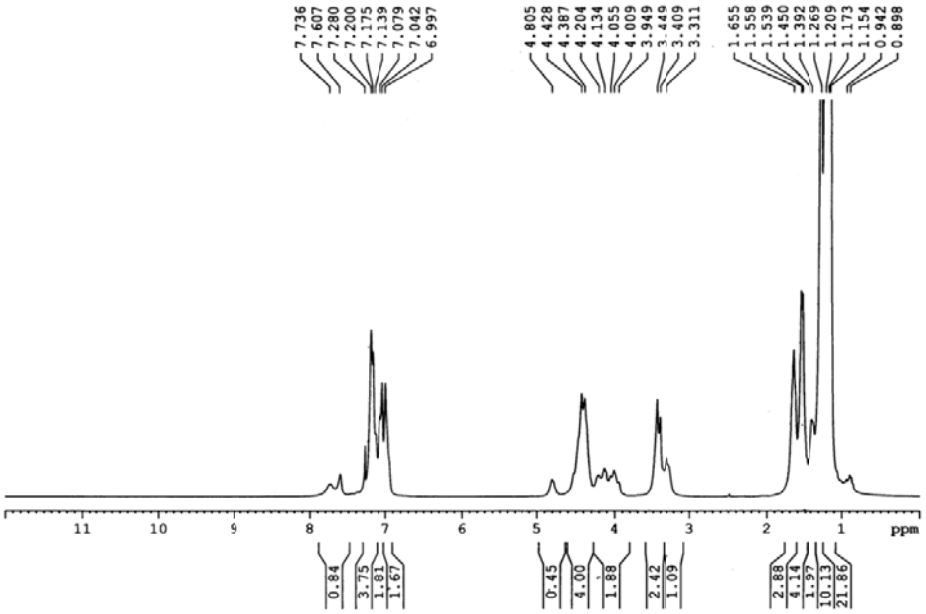
7.276
7.247
6.810
6.781
4.758
4.735
4.712
4.690
1.618
1.595
1.254
O
H3C
COOH
MC4a
10
9
8
7
6
5
4
3
2
1
ppm
6.03
10.82
11.06
5.38
18.24
48.36


177.91
154.59
144.24
126.05
125.98
114.25
77.08
76.65
76.23
71.81
33.73
31.08
18.10
O
H3C
COOH
MC4a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

5. The ^{1}H NMR of the catalyst after each 2 cycles :

Initially :



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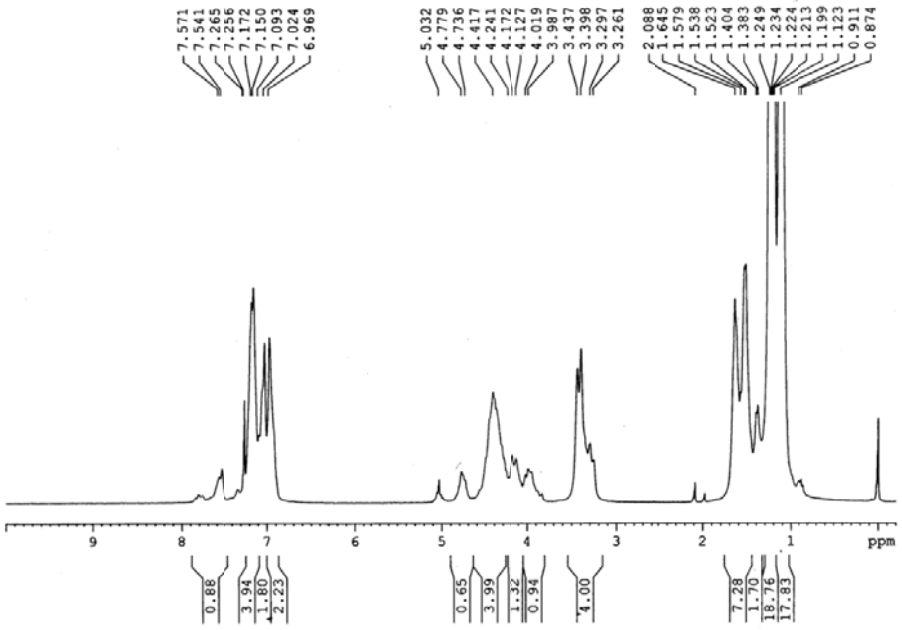
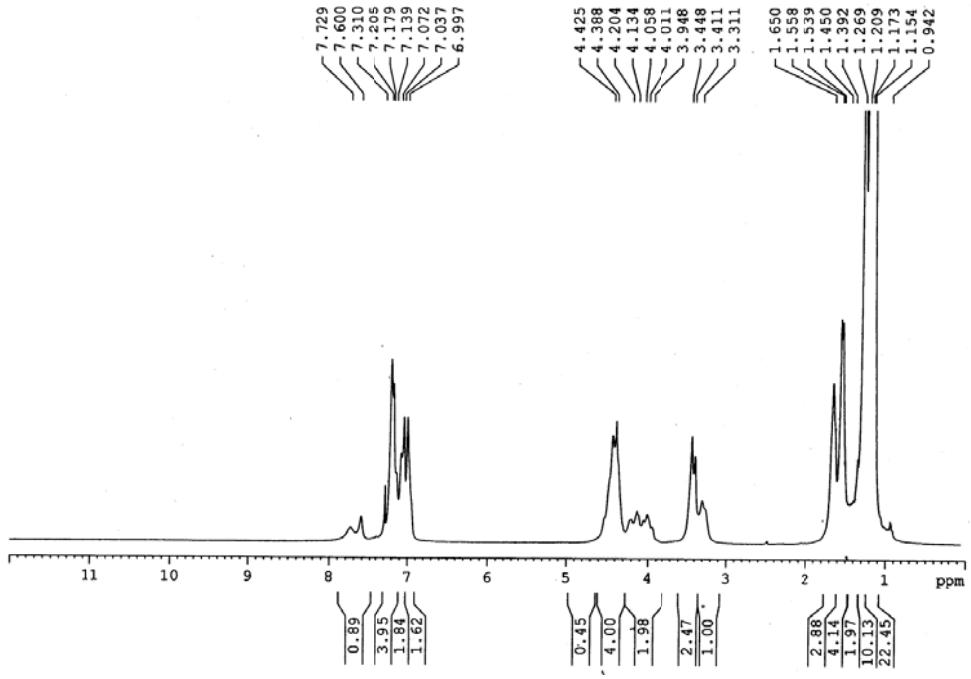
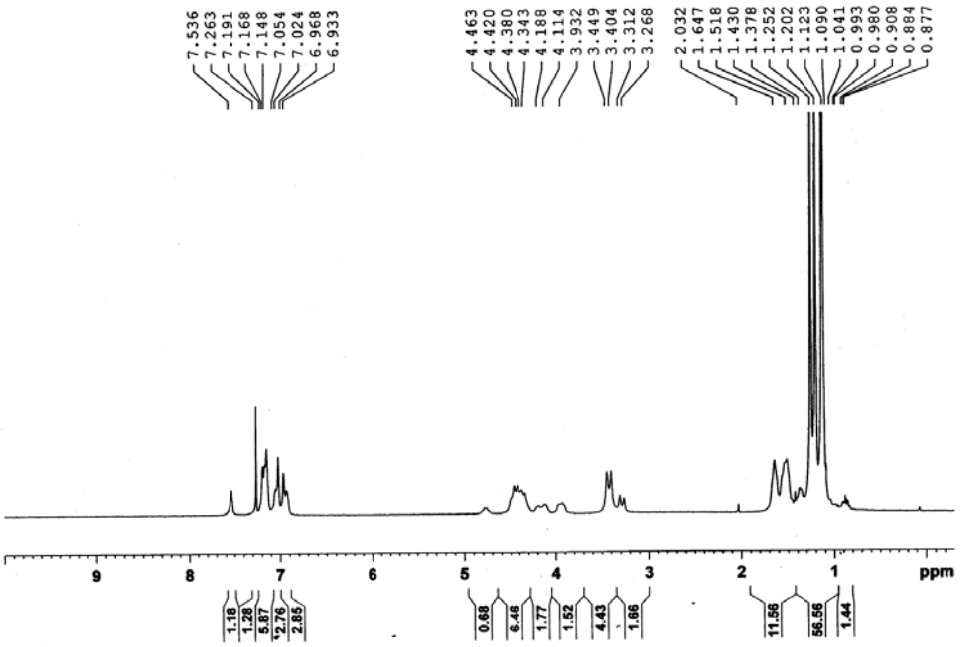


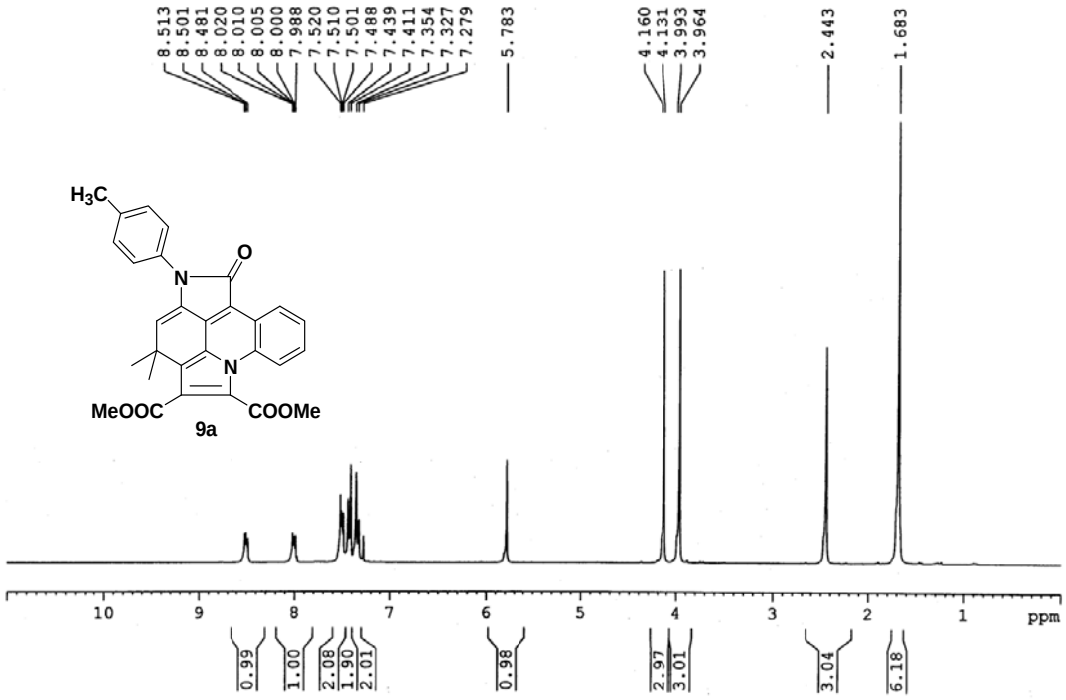
After 4th run:

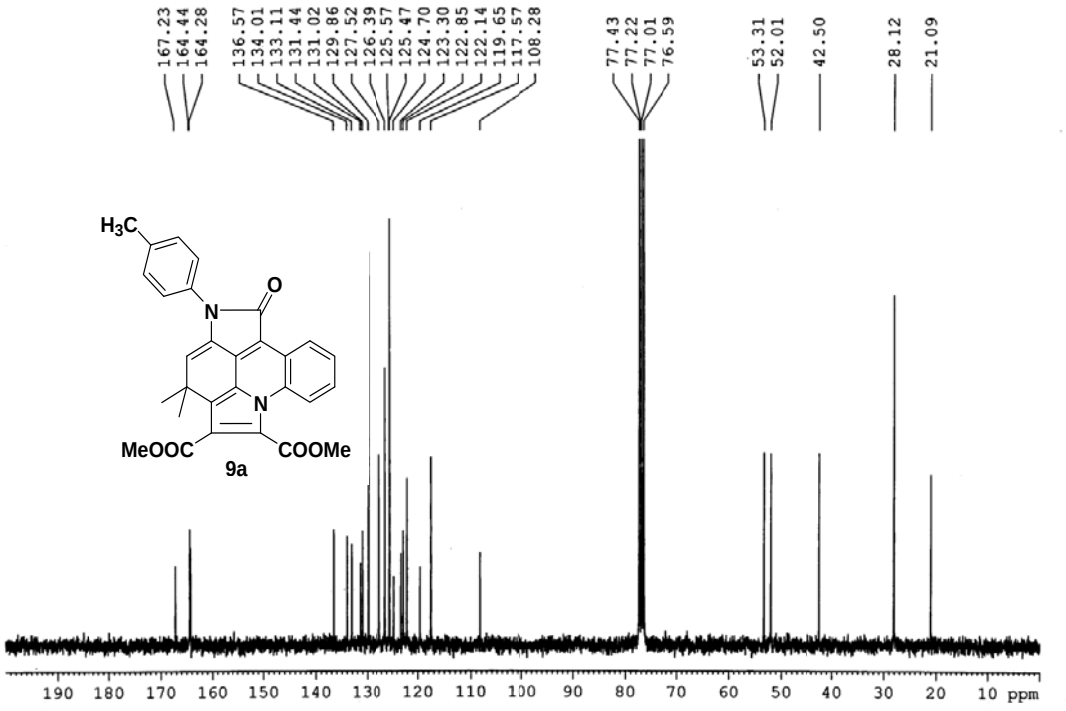


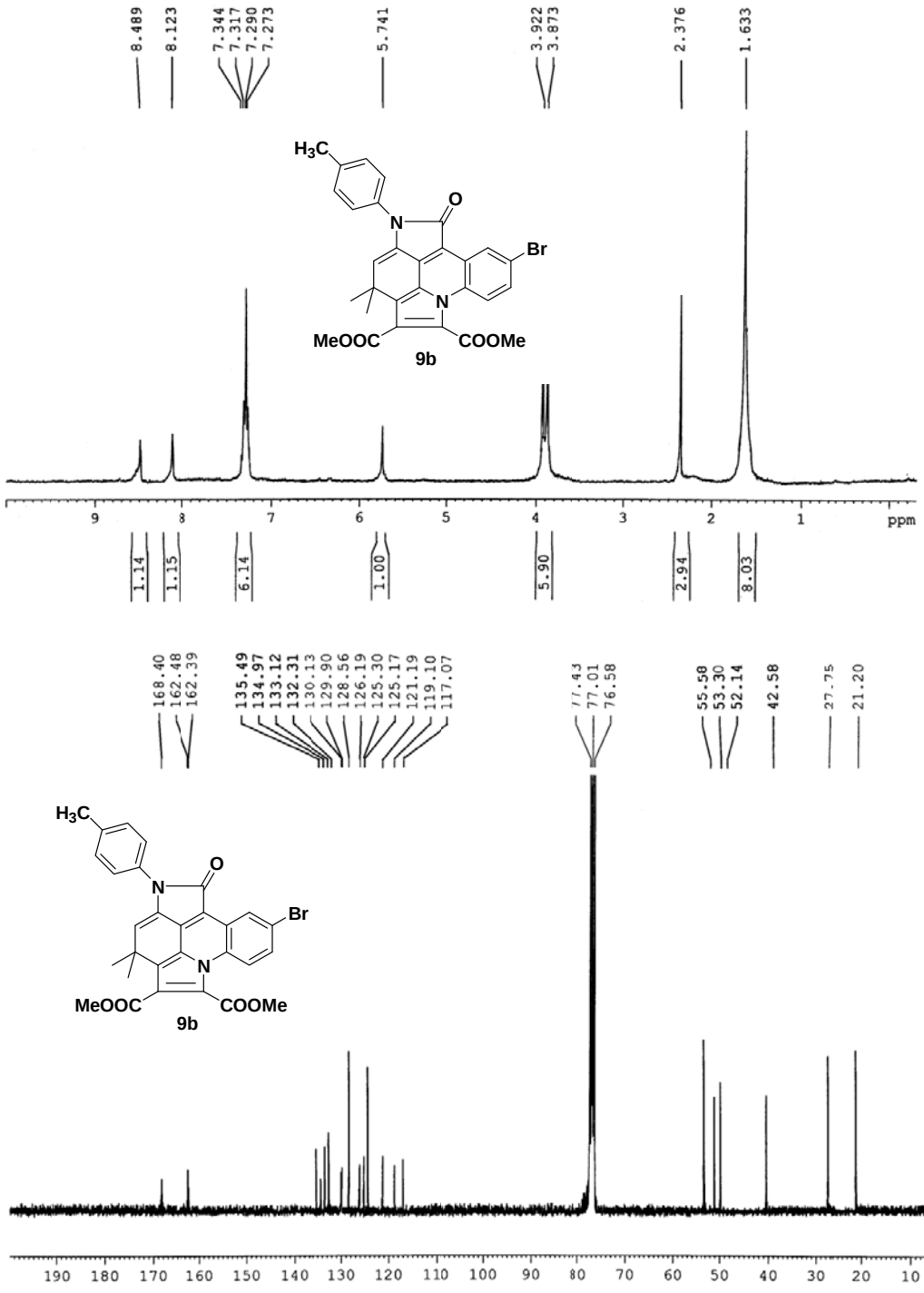
After 6th run:



6. ^{1}H and ^{13}C spectra of **9a-9z** and **9a'-9e'** (scheme 3):



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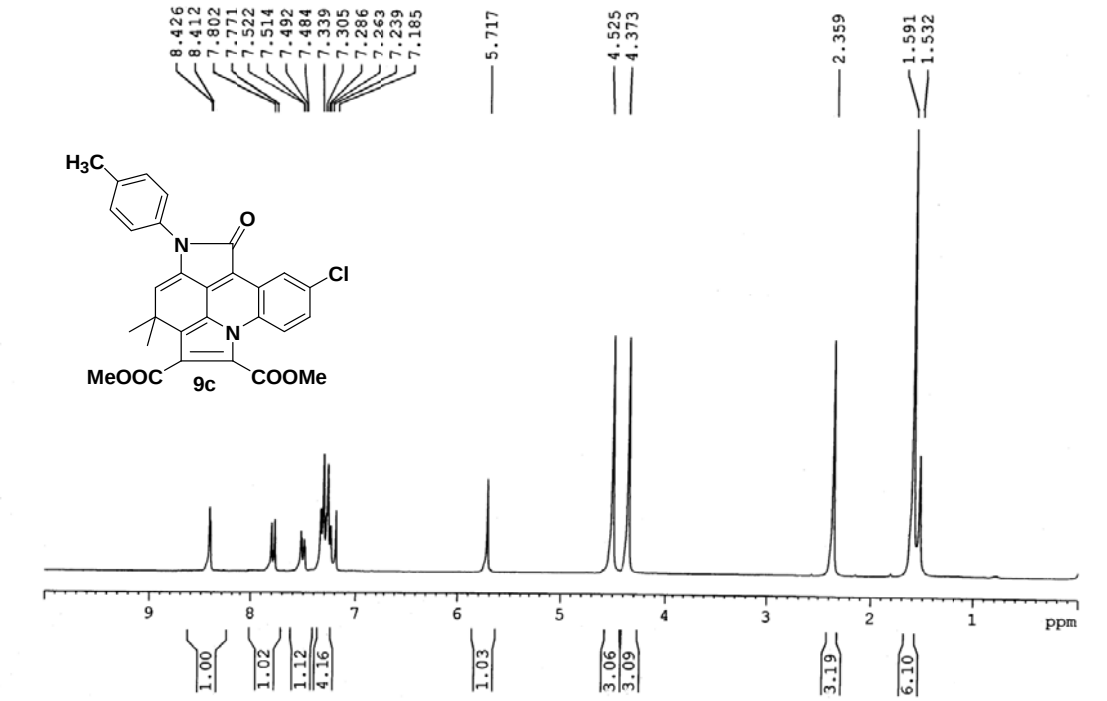
7.344
7.317
7.290
7.273
5.741
3.922
3.873
2.376
1.633
H3C
O
N
Br
N
MeOOC
COOMe
9b
ppm
1.14
1.15
6.14
1.00
5.90
2.94
8.03
168.40
162.48
162.39
135.49
134.97
133.12
132.31
130.13
129.90
128.56
126.19
125.30
125.17
121.19
119.10
117.07
77.01
76.58
55.58
53.30
52.14
42.58
27.75
21.20
H3C
O
N
Br
N
MeOOC
COOMe
9b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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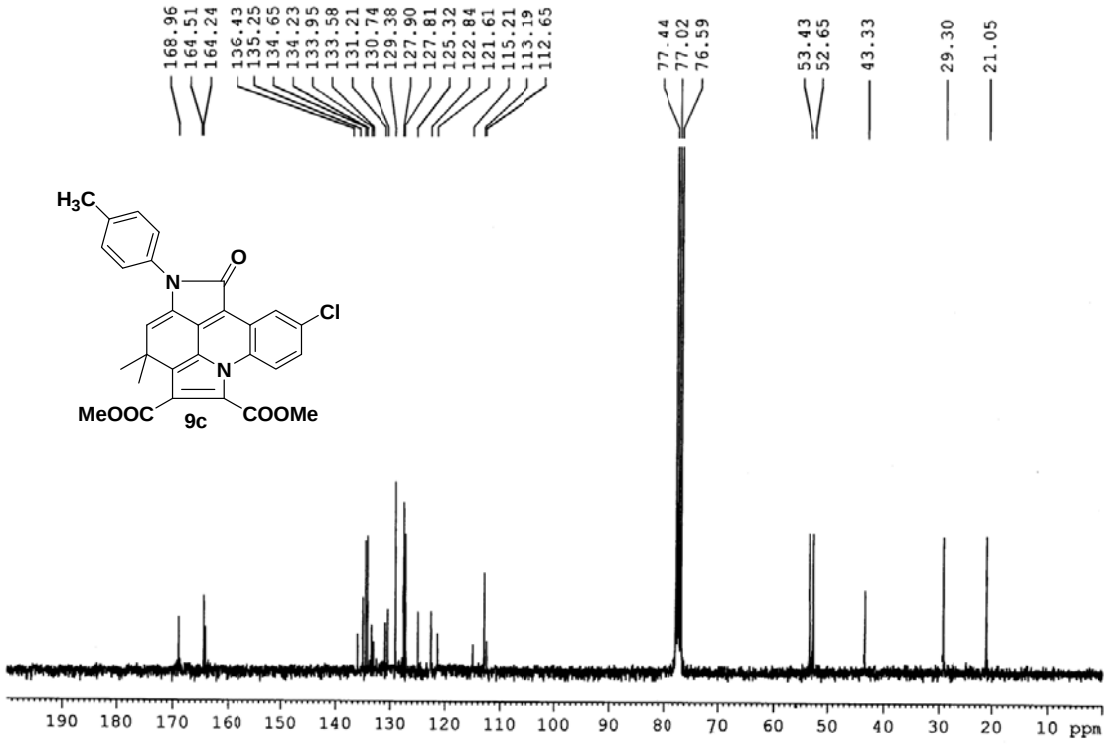
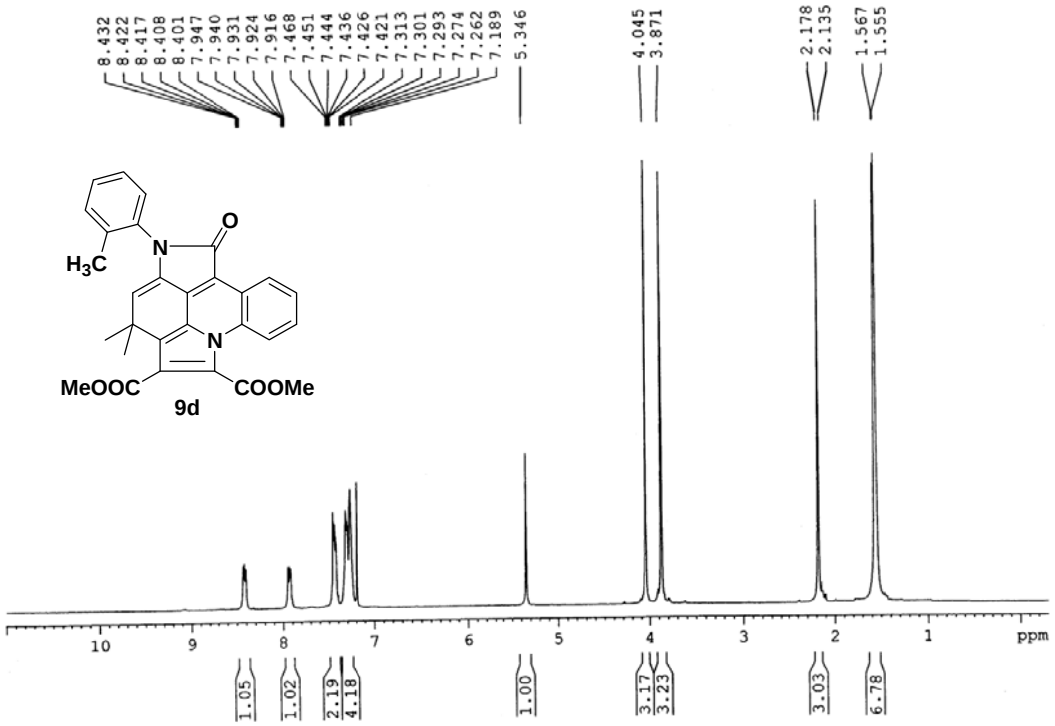
8.412
7.802
7.771
7.522
7.514
7.492
7.484
7.339
7.305
7.286
7.263
7.239
7.185
5.717
4.525
4.373
2.359
1.591
1.532
H3C
O
N
Cl
N
MeOOC
9c
COOMe
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.12
4.16
1.03
3.06
3.09
3.19
6.10


168.96
164.51
164.24
136.43
135.25
134.65
134.23
133.95
133.58
131.21
130.74
129.38
127.90
127.81
125.32
122.84
121.61
115.21
113.19
112.65
77.44
77.02
76.59
53.43
52.65
43.33
29.30
21.05
H3C
O
N
Cl
N
MeOOC
9c
COOMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.408
8.401
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7.931
7.924
7.916
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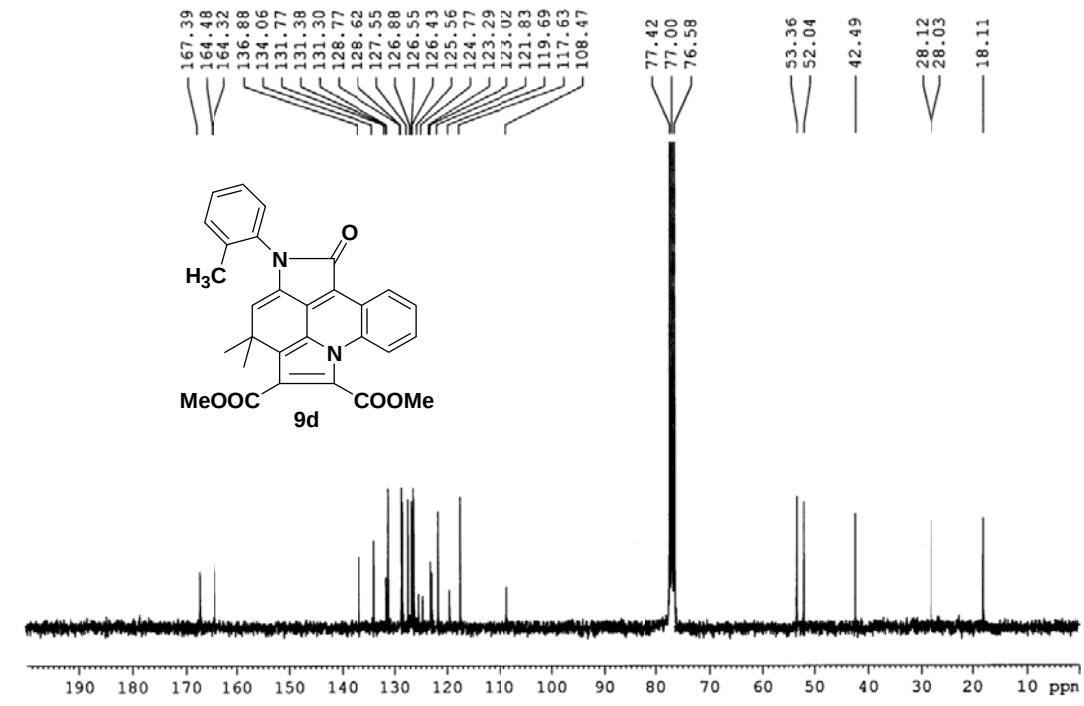
7.451
7.444
7.436
7.426
7.421
7.313
7.301
7.293
7.274
7.262
7.189
5.346
4.045
3.871
2.178
2.135
1.567
1.555
O
N
H3C
N
MeOOC
COOMe
9d
10
9
8
7
6
5
4
3
2
1
ppm
1.05
1.02
2.19
4.18
1.00
3.17
3.23
3.03
6.78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131.77
131.38
131.30
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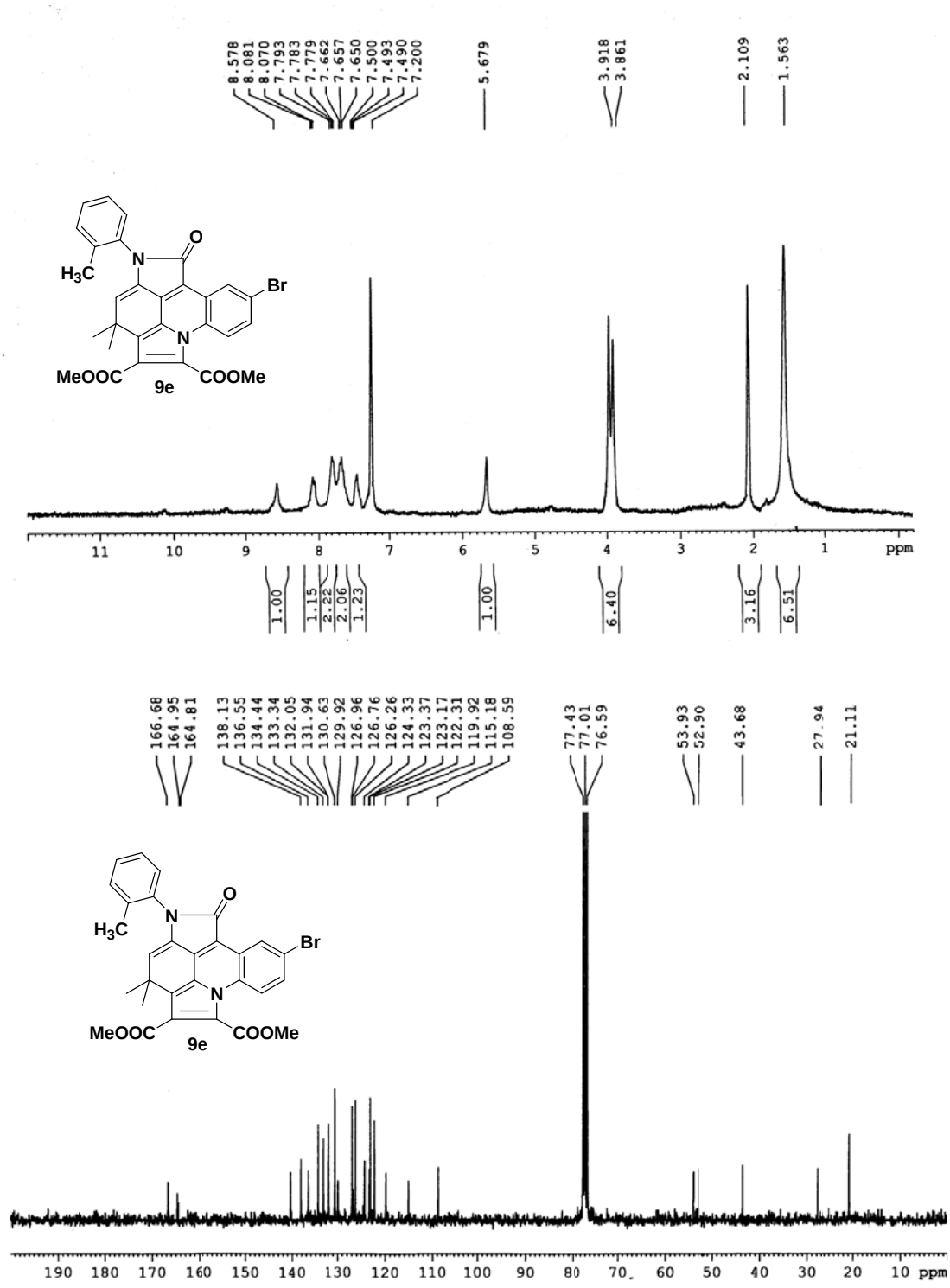
128.62
127.55
126.88
126.55
126.43
125.56
124.77
123.29
123.02
121.83
119.69
117.63
108.47
77.42
77.00
76.58
53.36
52.04
42.49
28.12
28.03
18.11
O
N
H3C
N
MeOOC
COOMe
9d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.070
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7.779
7.662
7.657
7.650
7.500
7.493
7.490
7.200
5.679
3.918
3.861
2.109
1.563
H3C
N
O
Br
N
MeOOC
COOMe
9e
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.15
2.22
2.06
1.23
1.00
6.40
3.16
6.51
166.68
164.95
164.81
138.13
136.55
134.44
133.34
132.05
131.94
130.63
129.92
126.96
126.76
126.26
124.33
123.37
123.17
122.31
119.92
115.18
108.59
77.43
77.01
76.59
53.93
52.90
43.68
27.94
21.11
H3C
N
O
Br
N
MeOOC
COOMe
9e
190
180
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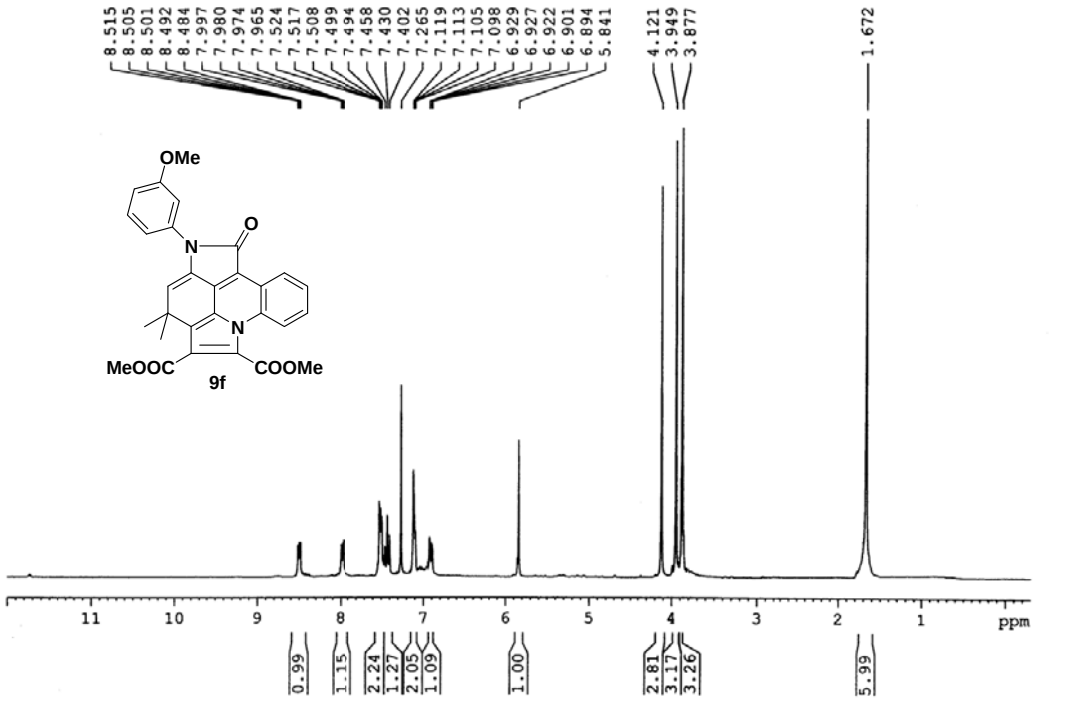
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.501
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8.484
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7.980
7.974
7.965
7.524
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7.508
7.499
7.494
7.458
7.430
7.402
7.265
7.119
7.113
7.105
7.098
6.929
6.927
6.922
6.901
6.894
5.841
4.121
3.949
3.877
1.672
OMe
O
N
N
MeOOC
COOMe
9f
11
10
9
8
7
6
5
4
3
2
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1.00
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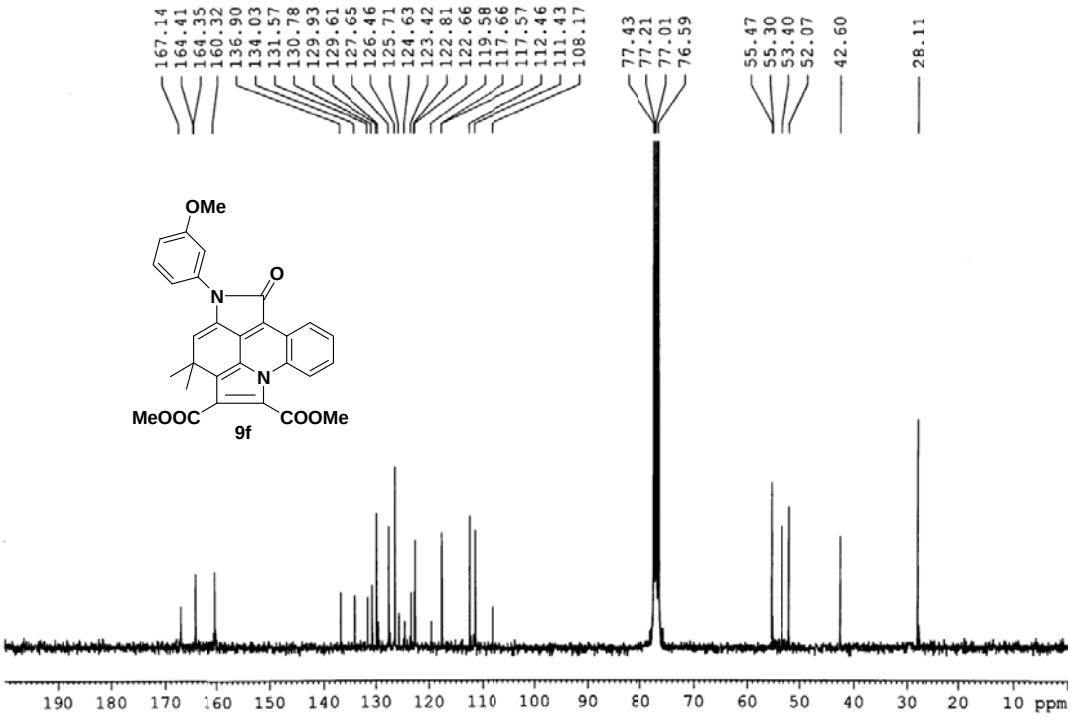
3.26
5.99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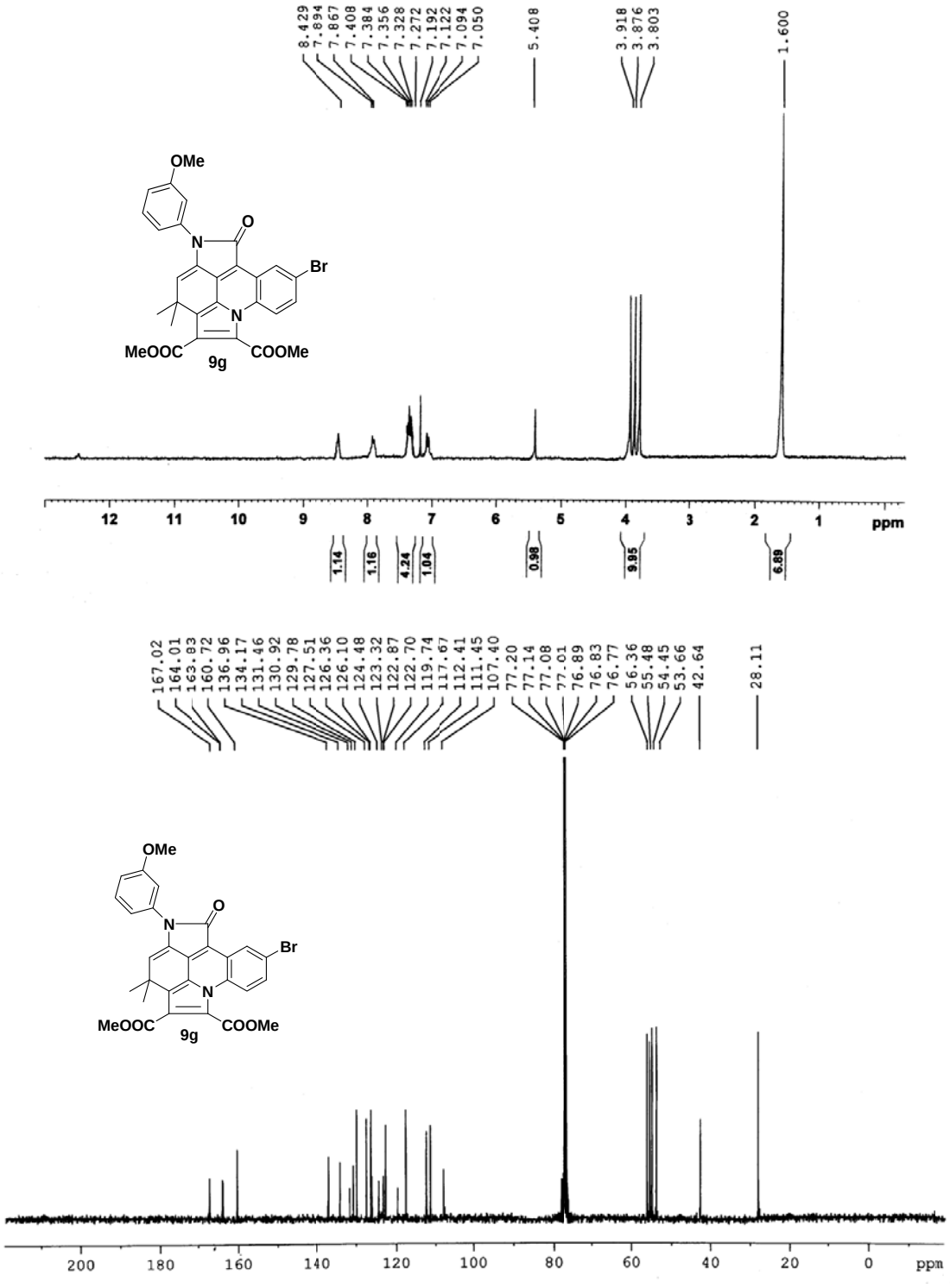
164.35
160.32
136.90
134.03
131.57
130.78
129.93
129.61
127.65
126.46
125.71
124.63
123.42
122.81
122.66
119.58
117.66
117.57
112.46
111.43
108.17
77.43
77.21
77.01
76.59
55.47
55.30
53.40
52.07
42.60
28.11
OMe
O
N
N
MeOOC
COOMe
9f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.867
7.408
7.384
7.356
7.328
7.272
7.192
7.122
7.094
7.050
5.408
3.918
3.876
3.803
1.600
OMe
O
N
Br
N
MeOOC
COOMe
9g
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.14
1.16
4.24
1.04
0.98
9.95
6.89
167.02
164.01
163.83
160.72
136.96
134.17
131.46
130.92
129.78
127.51
126.36
126.10
124.48
123.32
122.87
122.70
119.74
117.67
112.41
111.45
107.40
77.20
77.14
77.08
77.01
76.89
76.83
76.77
56.36
55.48
54.45
53.66
42.64
28.11
OMe
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COOMe
9g
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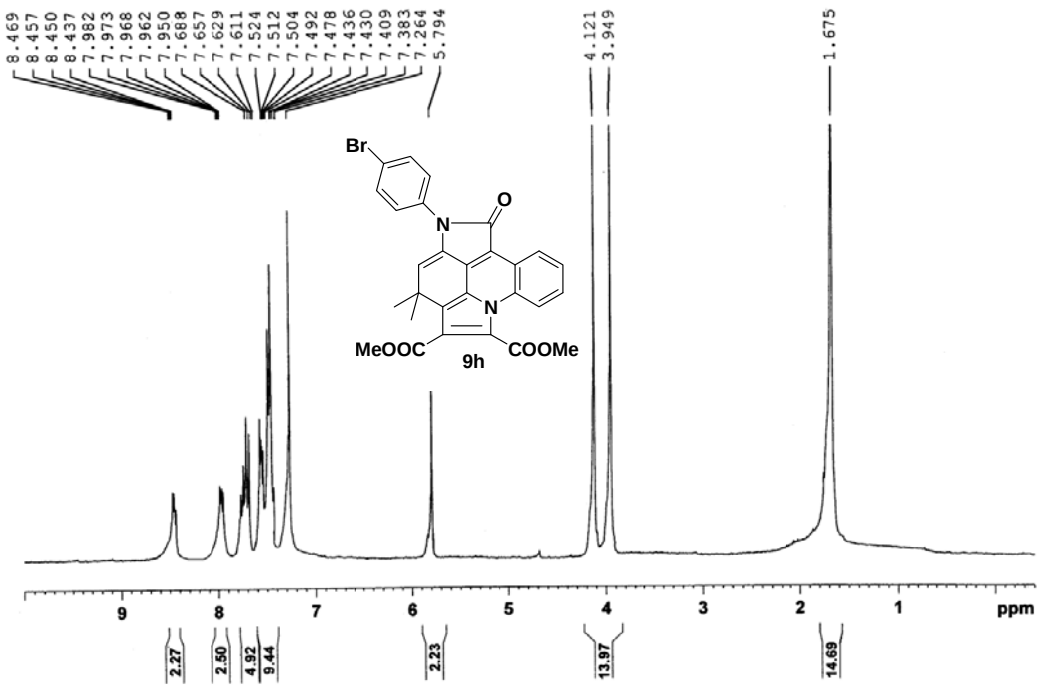
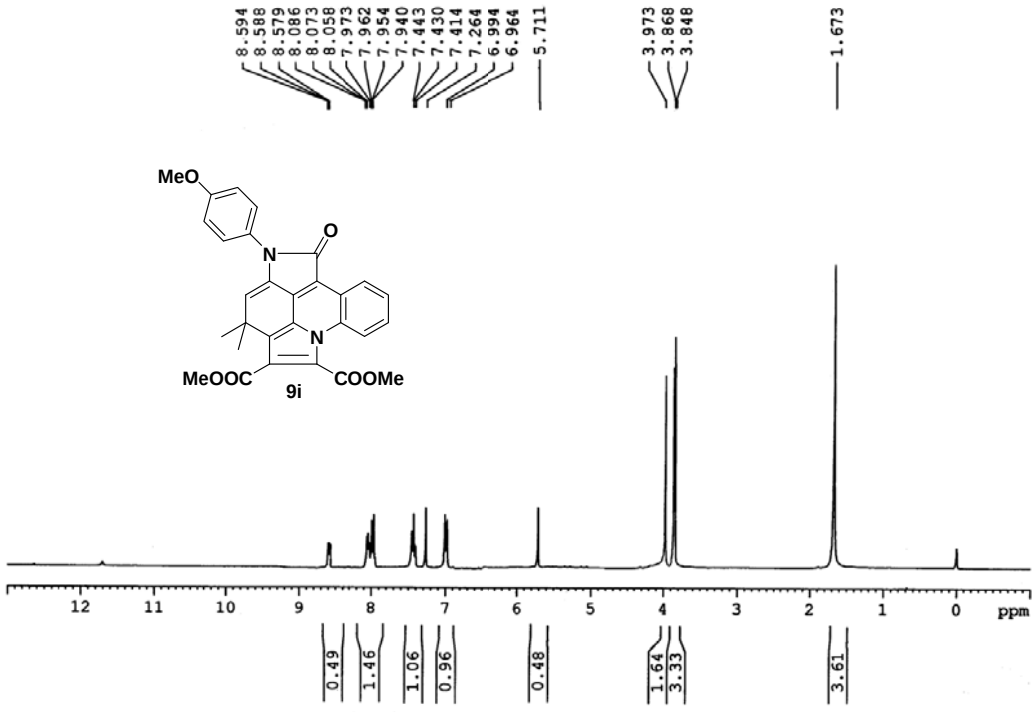
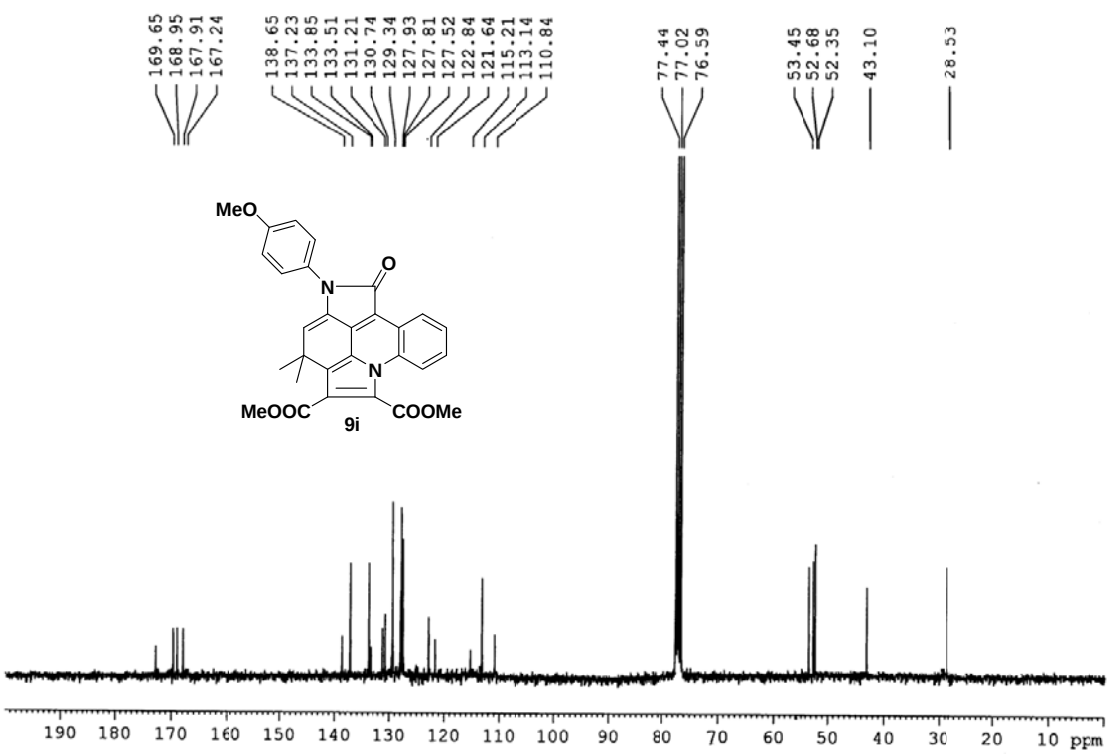
180
160
140
120
100
80
60
40
20
0
ppm



The solubility of this compound, 9h is too low to collect the ^{13}C data. We got the ^{1}H-NMR after several scans.

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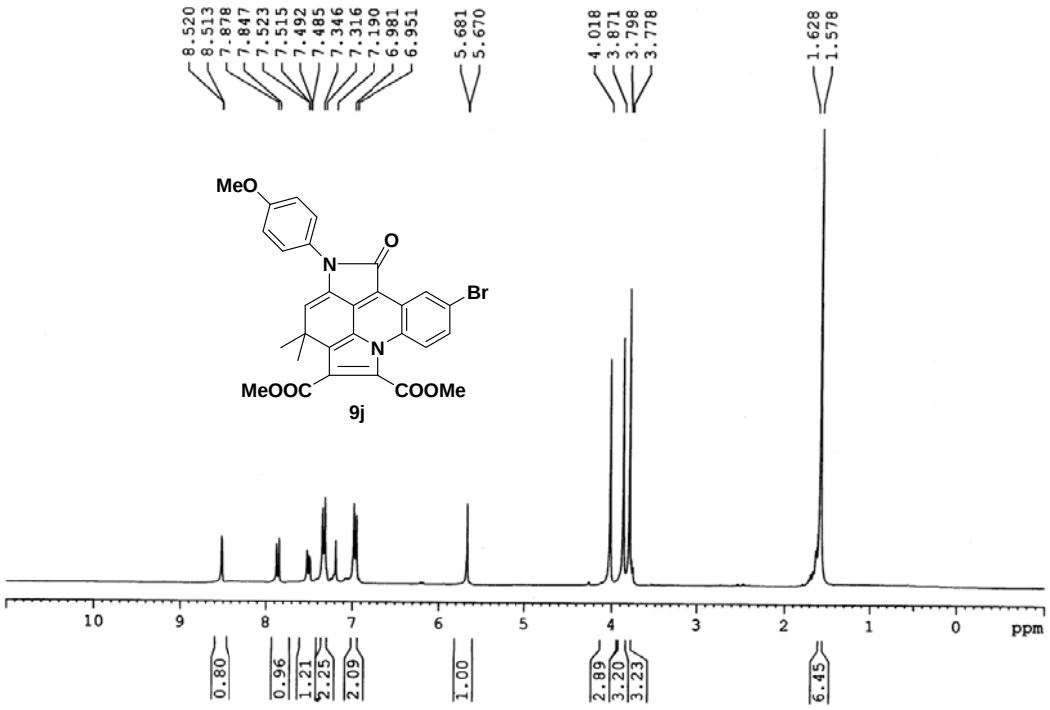
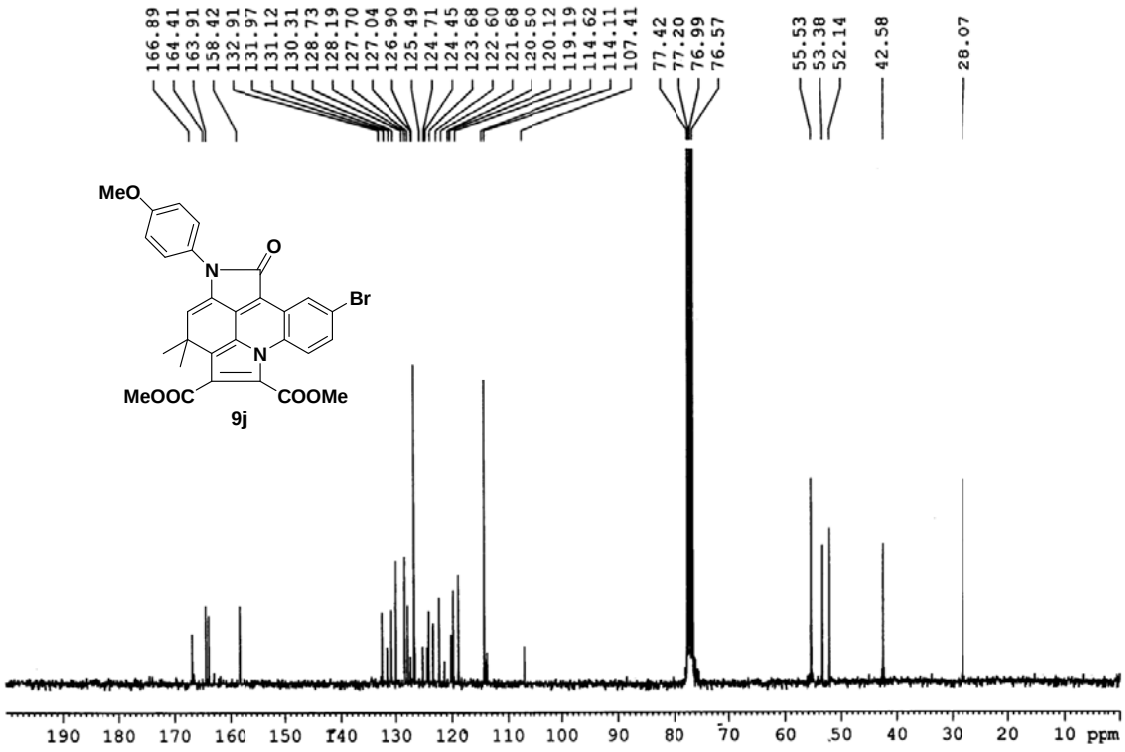
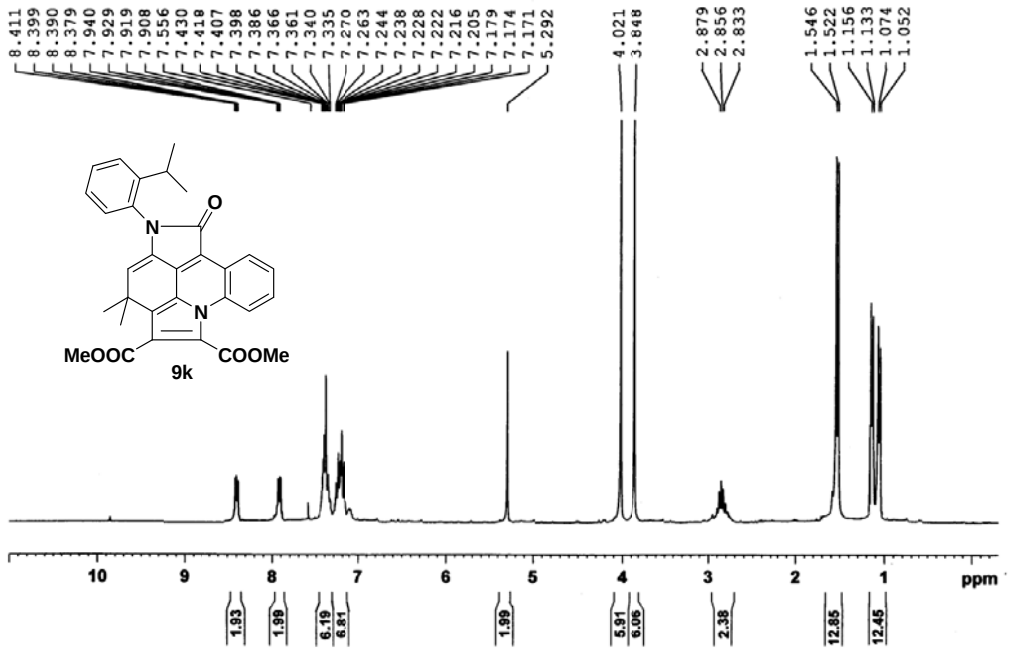
168.95
167.91
167.24
138.65
137.23
133.85
133.51
131.21
130.74
129.34
127.93
127.81
127.52
122.84
121.64
115.21
113.14
110.84
77.44
77.02
76.59
53.45
52.68
52.35
43.10
28.53
MeO
O
N
N
MeOOC
COOMe
9i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.520
8.513
7.878
7.847
7.523
7.515
7.492
7.485
7.346
7.316
7.190
6.981
6.951
5.681
5.670
4.018
3.871
3.798
3.778
1.628
1.578
MeO
O
N
Br
N
MeOOC
COOMe
9j
10 9 8 7 6 5 4 3 2 1 0 ppm
0.80
0.96
1.21
2.25
2.09
1.00
2.89
3.20
3.23
6.45


166.89
164.41
163.91
158.42
132.91
131.97
131.12
130.31
128.73
128.19
127.70
127.04
126.90
125.49
124.71
124.45
123.68
122.60
121.68
120.50
120.12
119.19
114.62
114.11
107.41
77.42
77.20
76.99
76.57
55.53
53.38
52.14
42.58
28.07
MeO
O
N
Br
N
MeOOC
COOMe
9j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.411
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7.940
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7.398
7.386
7.366
7.361
7.340
7.335
7.270
7.263
7.244
7.238
7.228
7.222
7.216
7.205
7.179
7.174
7.171
5.292
4.021
3.848
2.879
2.856
2.833
1.546
1.522
1.156
1.133
1.074
1.052
O
N
N
MeOOC
COOMe
9k
10 9 8 7 6 5 4 3 2 1 ppm
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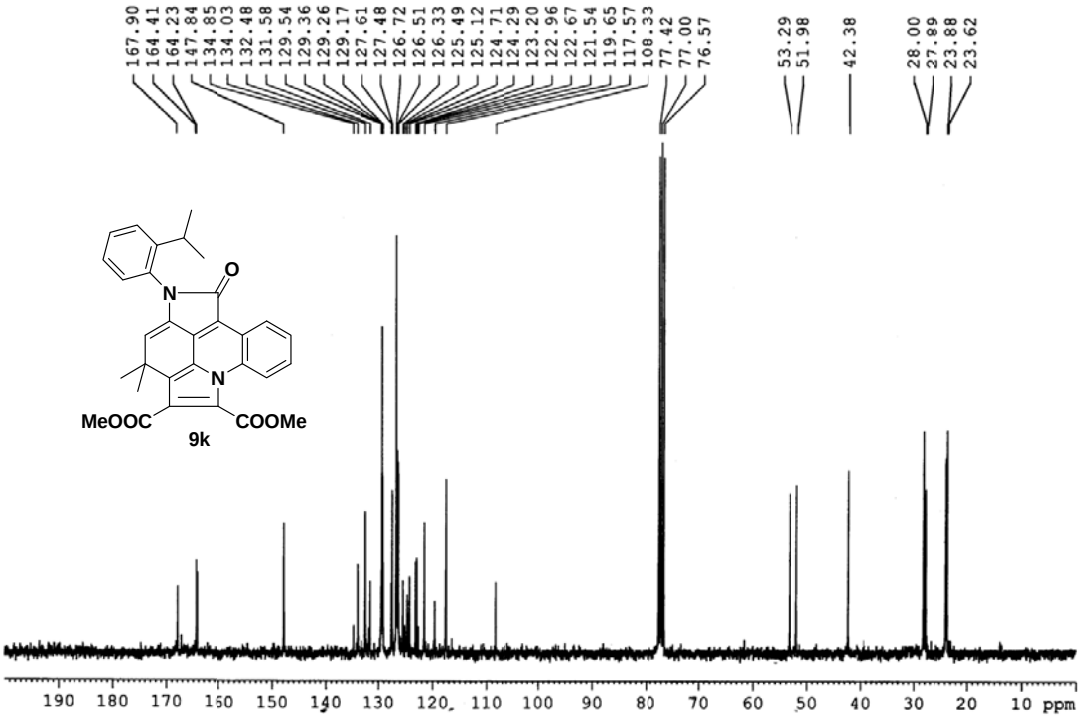
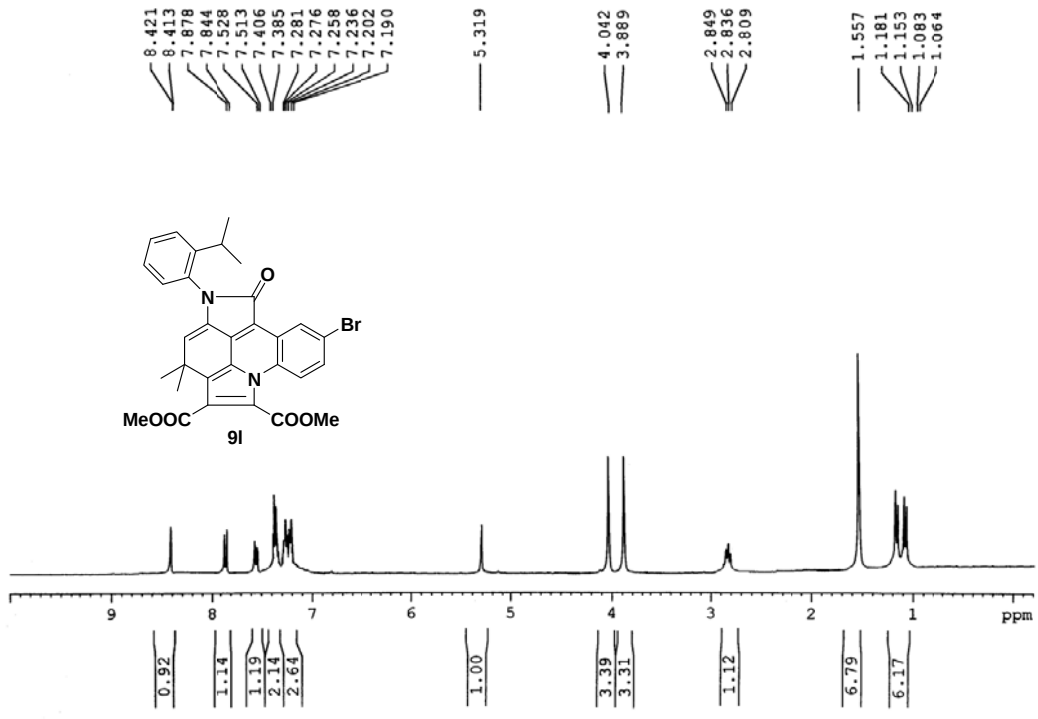
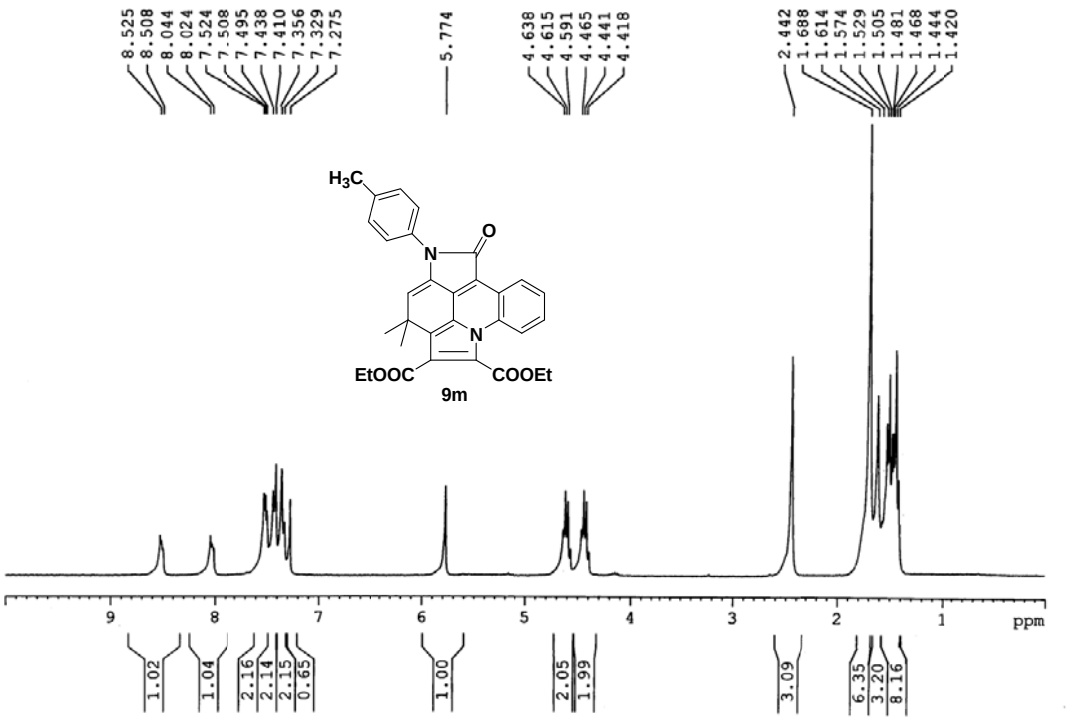
6.81
1.99
5.91
6.06
2.38
12.85
12.45





The solubility of this compound, 9l is too low to collect the ^{13}C data. We got the ^{1}H-NMR after several scans.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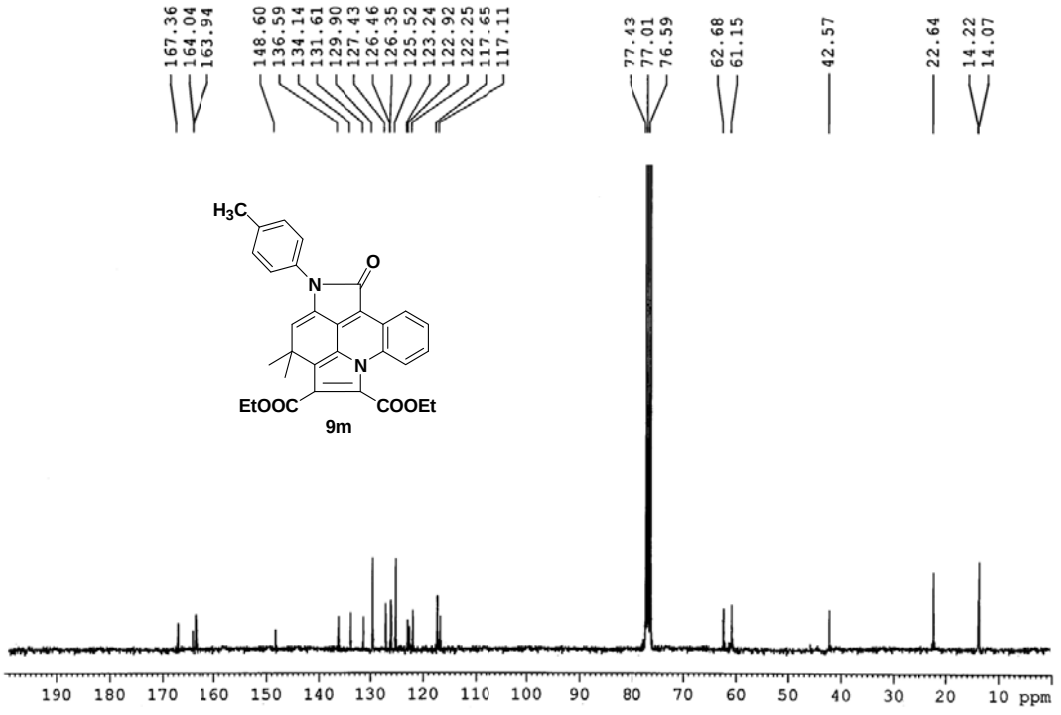
7.438
7.410
7.356
7.329
7.275
5.774
4.638
4.615
4.591
4.465
4.441
4.418
2.442
1.688
1.614
1.574
1.529
1.505
1.481
1.468
1.444
1.420
H3C
O
N
N
EtOOC
COOEt
9m
ppm
1.02
1.04
2.16
2.14
2.15
0.65
1.00
2.05
1.99
3.09
6.35
3.20
8.16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131.61
129.90
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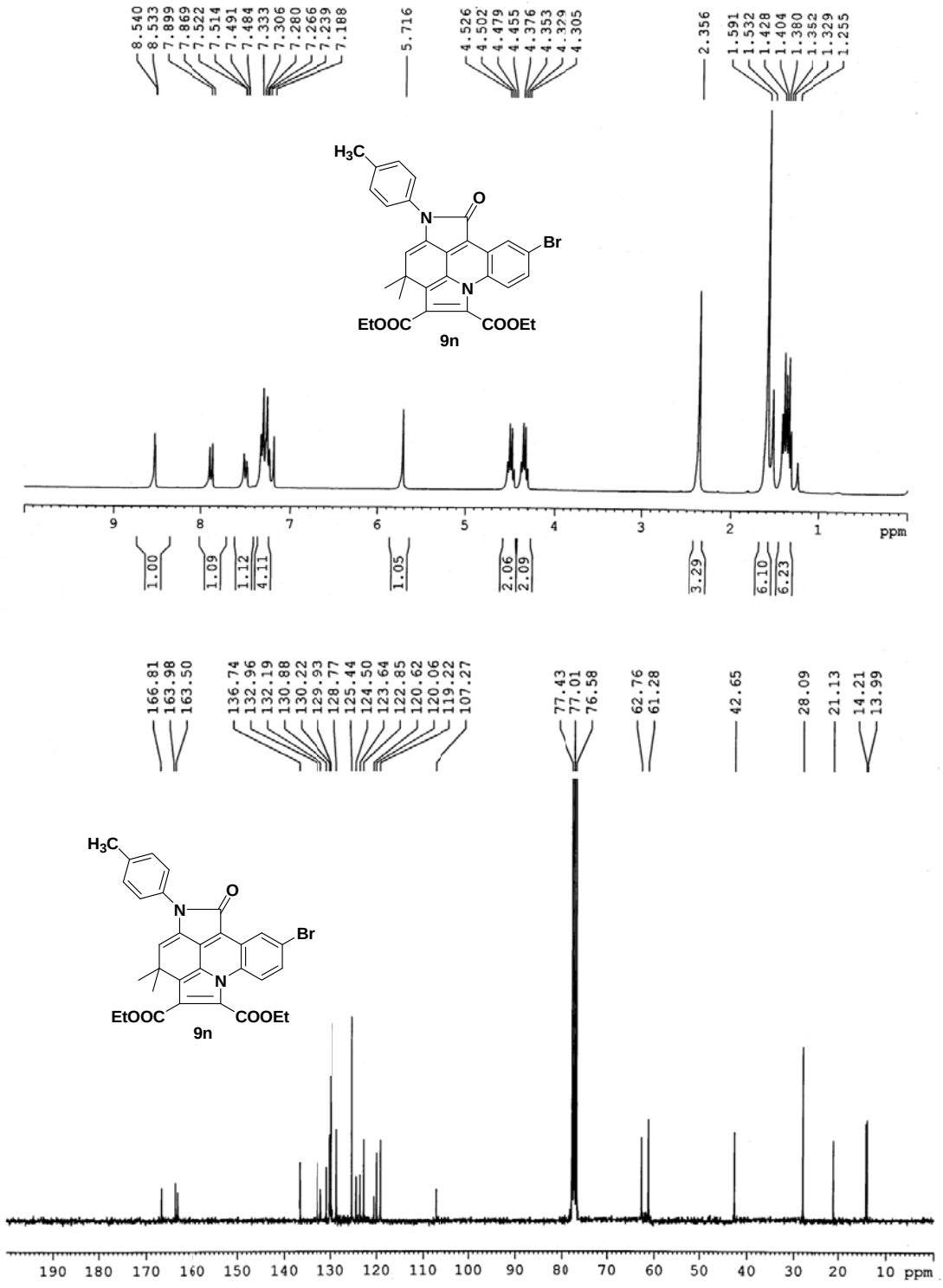
126.46
126.35
125.52
123.24
122.92
122.25
117.65
117.11
77.43
77.01
76.59
62.68
61.15
42.57
22.64
14.22
14.07
H3C
O
N
N
EtOOC
COOEt
9m
ppm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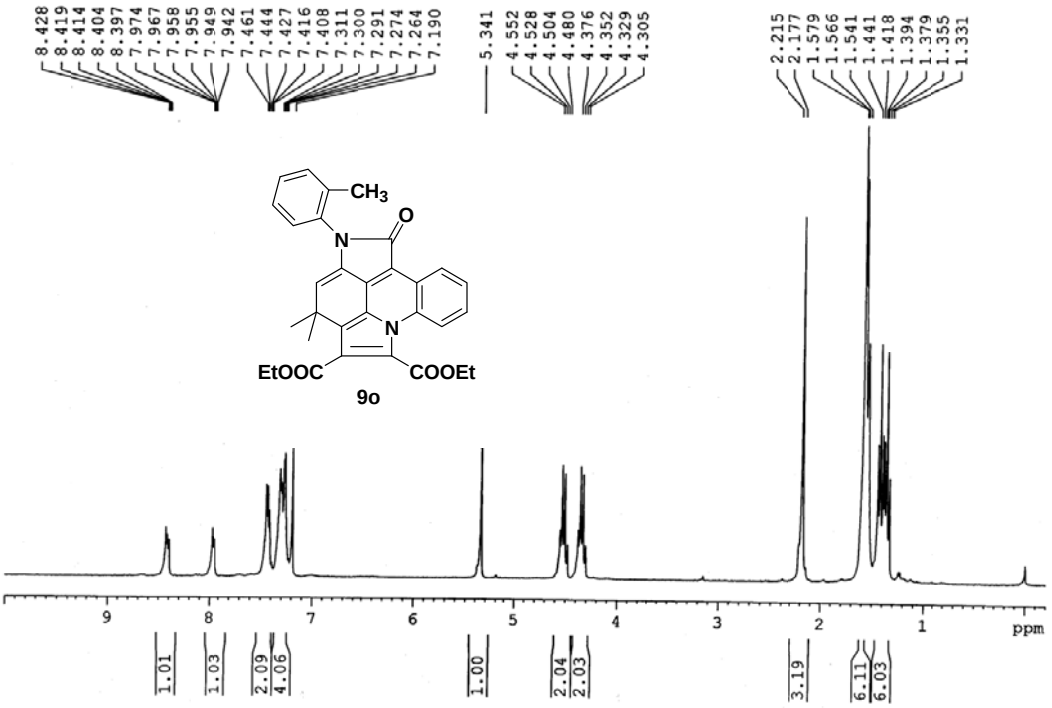
7.484
7.333
7.306
7.280
7.266
7.239
7.188
5.716
4.526
4.502
4.479
4.455
4.376
4.353
4.329
4.305
2.356
1.591
1.532
1.428
1.404
1.380
1.352
1.329
1.255
H3C
O
N
Br
N
EtOOC
COOEt
9n
ppm
1.00
1.09
1.12
4.11
1.05
2.06
2.09
3.29
6.10
6.23
166.81
163.98
163.50
136.74
132.96
132.19
130.88
130.22
129.93
128.77
125.44
124.50
123.64
122.85
120.62
120.06
119.22
107.27
77.43
77.01
76.58
62.76
61.28
42.65
28.09
21.13
14.21
13.99
H3C
O
N
Br
N
EtOOC
COOEt
9n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.404
8.397
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7.967
7.958
7.955
7.949
7.942
7.461
7.444
7.427
7.416
7.408
7.311
7.300
7.291
7.274
7.264
7.190
5.341
4.552
4.528
4.504
4.480
4.376
4.352
4.329
4.305
2.215
2.177
1.579
1.566
1.541
1.441
1.418
1.394
1.379
1.355
1.331
CH3
O
N
N
EtOOC
COOEt
9o
9
8
7
6
5
4
3
2
1
ppm
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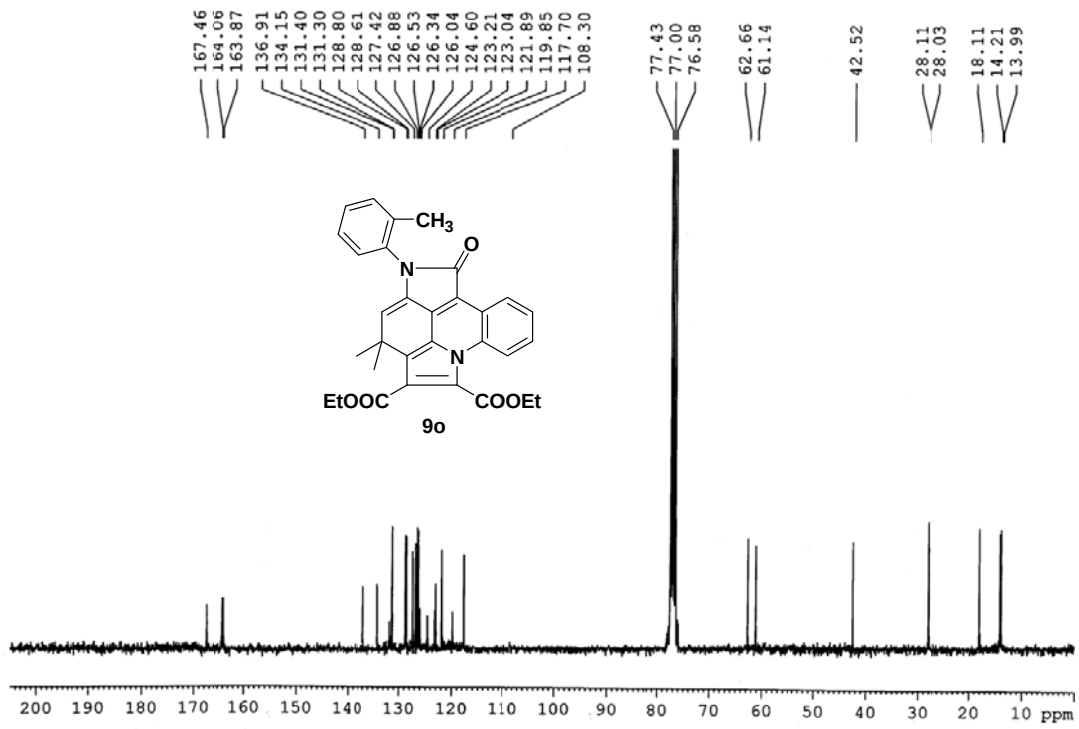
1.03
2.09
4.06
1.00
2.04
2.03
3.19
6.11
6.03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131.40
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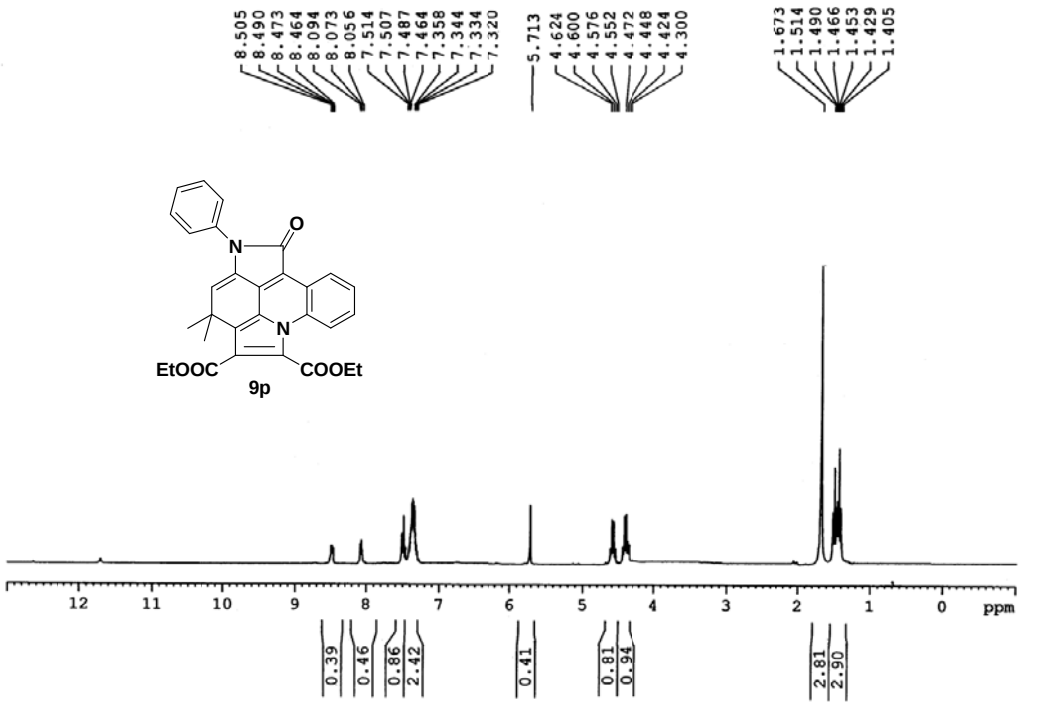
128.80
128.61
127.42
126.88
126.53
126.34
126.04
124.60
123.21
123.04
121.89
119.85
117.70
108.30
77.43
77.00
76.58
62.66
61.14
42.52
28.11
28.03
18.11
14.21
13.99
CH3
O
N
N
EtOOC
COOEt
9o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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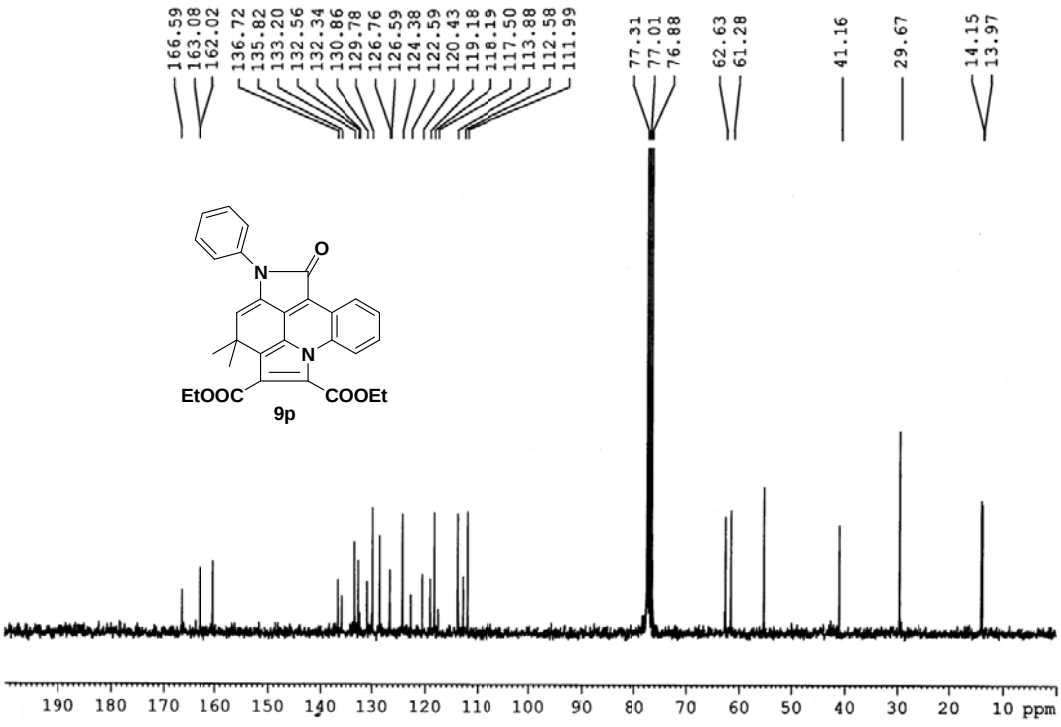
8.473
8.464
8.094
8.073
8.056
7.514
7.507
7.487
7.464
7.358
7.344
7.334
7.320
5.713
4.624
4.600
4.576
4.552
4.472
4.448
4.424
4.300
1.673
1.514
1.490
1.466
1.453
1.429
1.405
EtOOC
COOEt
9p
ppm
0.39
0.46
0.86
2.42
0.41
0.81
0.94
2.81
2.90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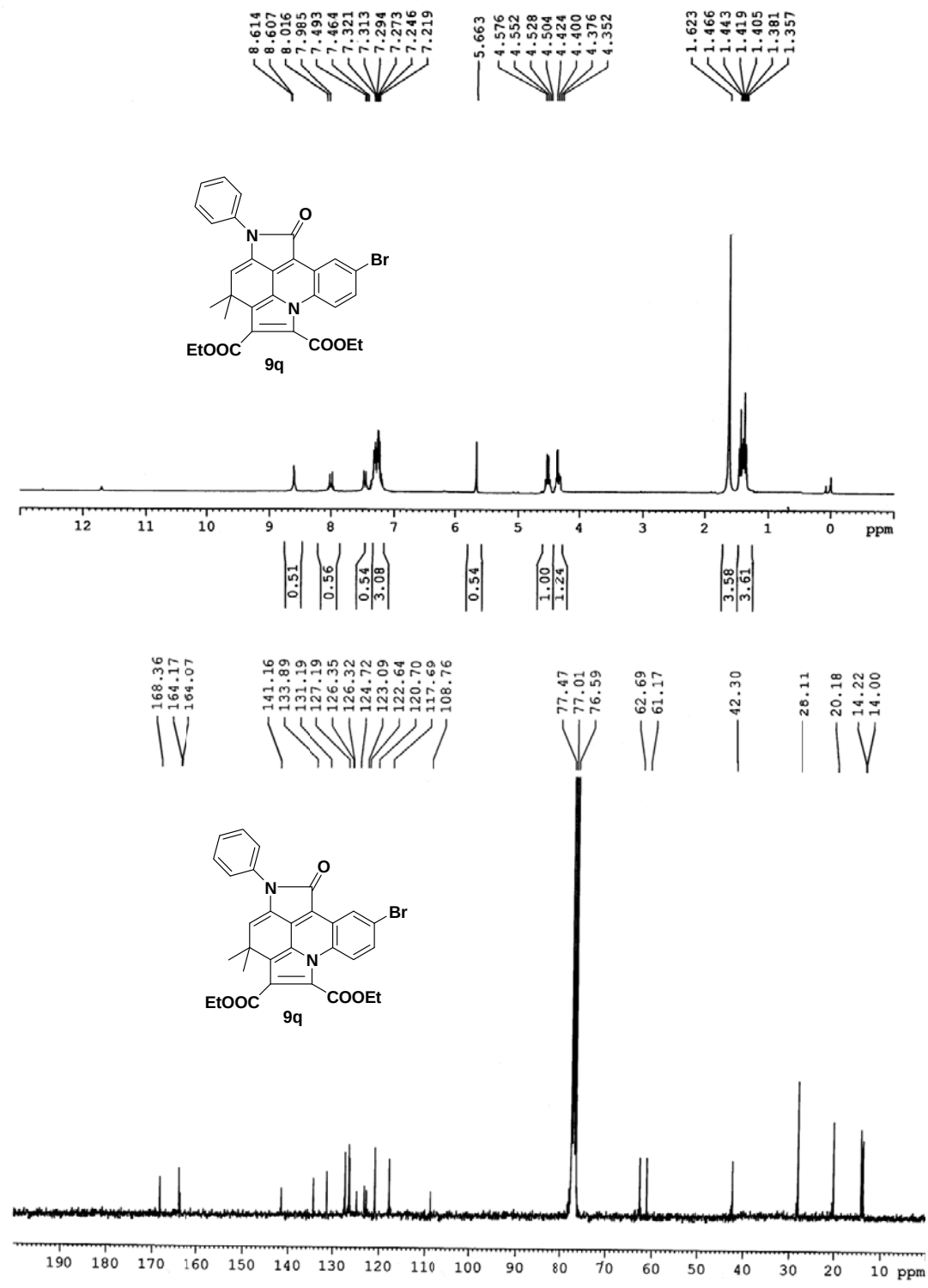
133.20
132.56
132.34
130.86
129.78
126.76
126.59
124.38
122.59
120.43
119.18
118.19
117.50
113.88
112.58
111.99
77.31
77.01
76.88
62.63
61.28
41.16
29.67
14.15
13.97
EtOOC
COOEt
9p
ppm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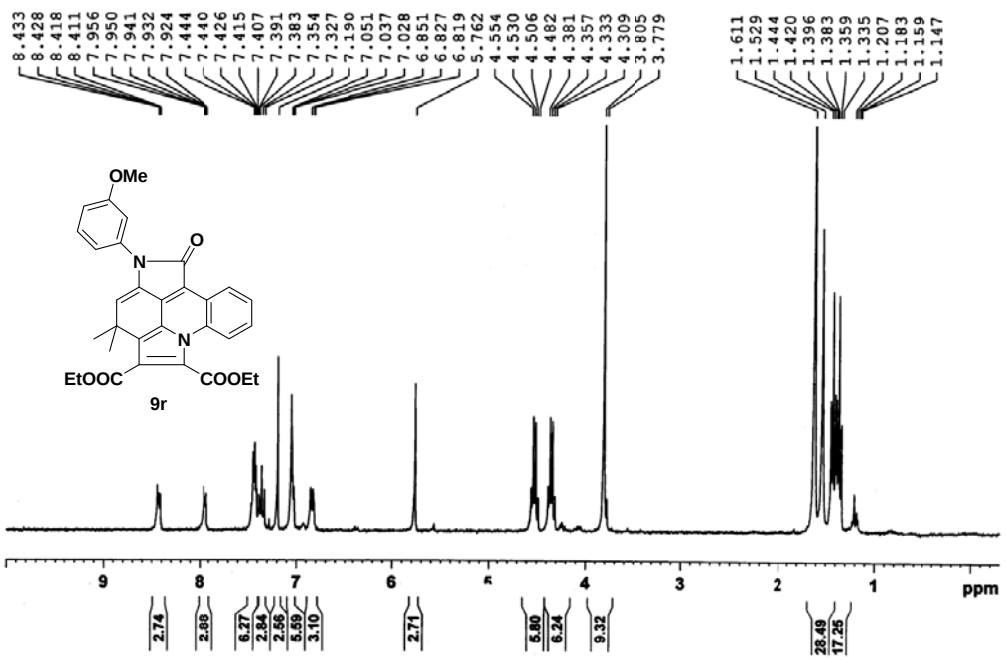
8.016
7.985
7.493
7.464
7.321
7.313
7.294
7.273
7.246
7.219
5.663
4.576
4.552
4.528
4.504
4.424
4.400
4.376
4.352
1.623
1.466
1.443
1.419
1.405
1.381
1.357
O
N
Br
N
EtOOC
COOEt
9q
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.51
0.56
0.54
3.08
0.54
1.00
1.24
3.58
3.61
168.36
164.17
164.07
141.16
133.89
131.19
127.19
126.35
126.32
124.72
123.09
122.64
120.70
117.69
108.76
77.47
77.01
76.59
62.69
61.17
42.30
28.11
20.18
14.22
14.00
O
N
Br
N
EtOOC
COOEt
9q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.932
7.924
7.444
7.440
7.426
7.415
7.407
7.391
7.383
7.354
7.327
7.190
7.051
7.037
7.028
6.851
6.827
6.819
5.762
4.554
4.530
4.506
4.482
4.381
4.357
4.333
4.309
3.805
3.779
1.611
1.529
1.444
1.420
1.396
1.383
1.359
1.335
1.207
1.183
1.159
1.147
OMe
O
N
N
EtOOC
COOEt
9r
9
8
7
6
5
4
3
2
1
ppm
2.74
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2.56
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5.80
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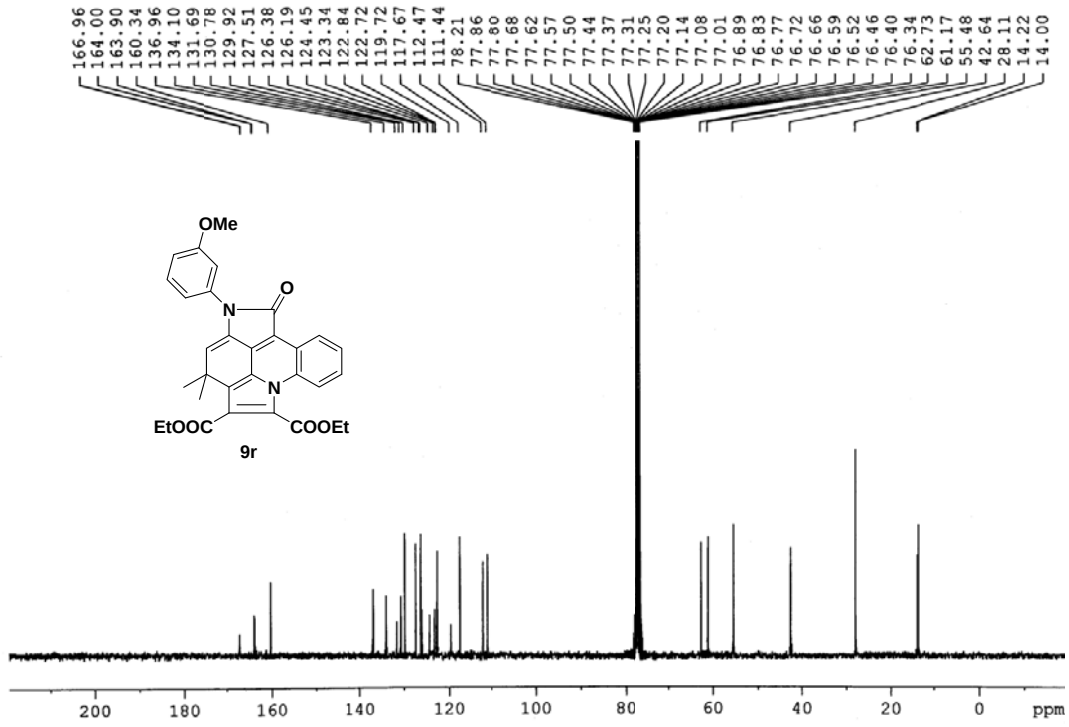
17.25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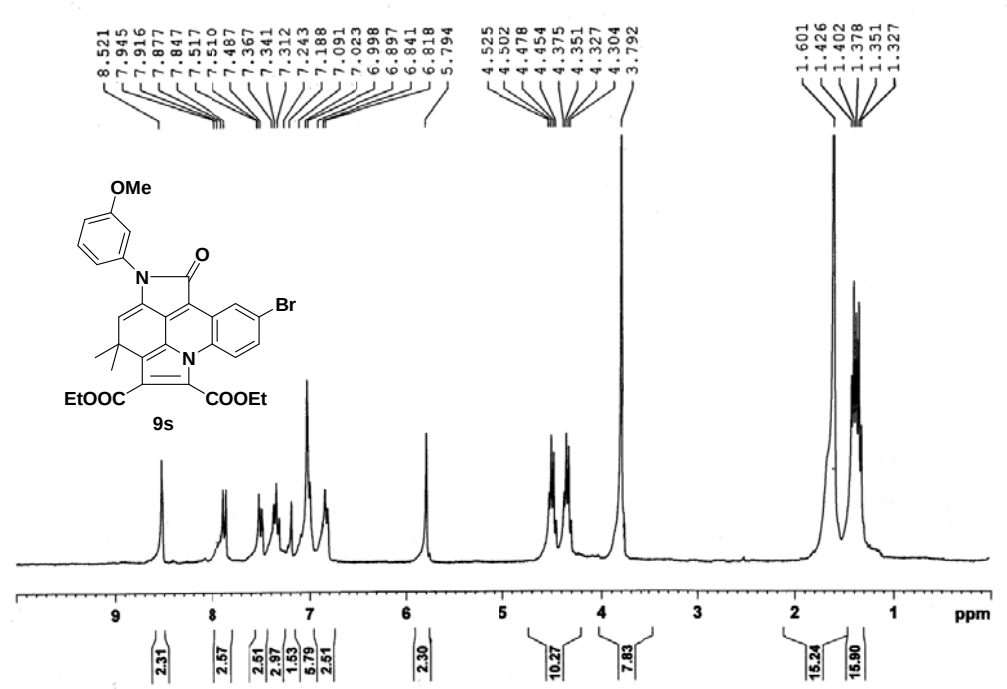
129.92
127.51
126.38
126.19
124.45
123.34
122.84
122.72
119.72
117.67
112.47
111.44
78.21
77.86
77.80
77.68
77.62
77.57
77.50
77.44
77.37
77.31
77.25
77.20
77.14
77.08
77.01
76.89
76.83
76.77
76.72
76.66
76.59
76.52
76.46
76.40
76.34
62.73
61.17
55.48
42.64
28.11
14.22
14.00
OMe
O
N
N
EtOOC
COOEt
9r
200
180
160
140
120
100
80
60
40
20
0
ppm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7.487
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7.312
7.243
7.188
7.091
7.023
6.998
6.897
6.841
6.818
5.794
4.525
4.502
4.478
4.454
4.375
4.351
4.327
4.304
3.792
1.601
1.426
1.402
1.378
1.351
1.327
OMe
O
N
Br
N
EtOOC
COOEt
9s
9
8
7
6
5
4
3
2
1
ppm
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2.57
2.61
2.97
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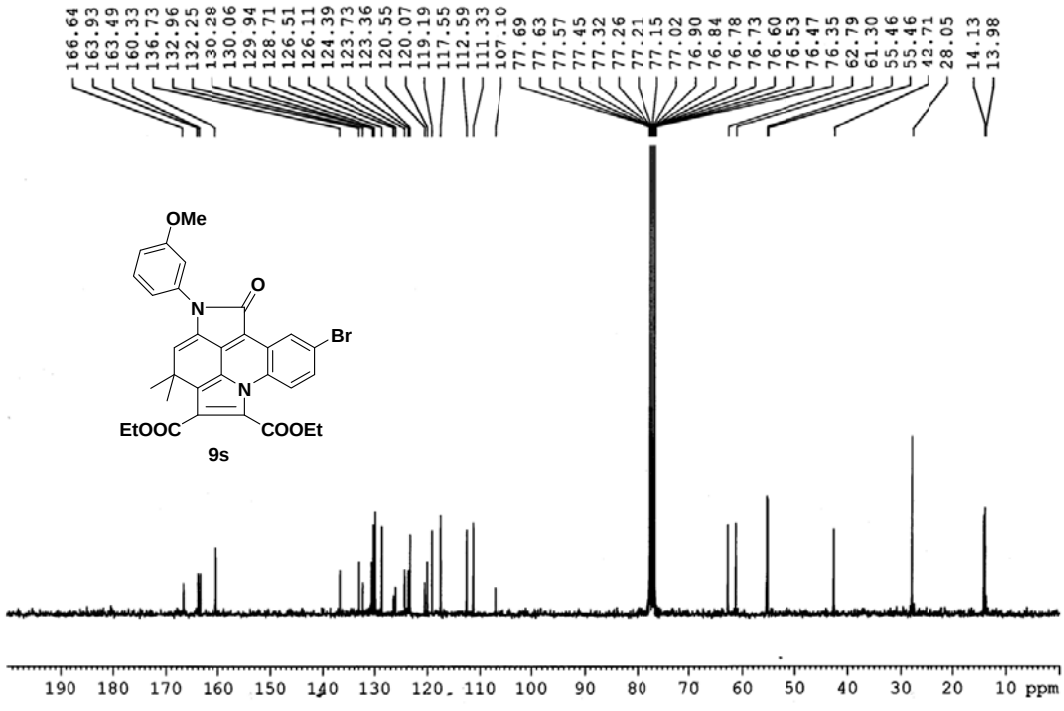
2.61
2.30
10.27
7.83
15.24
15.90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130.28
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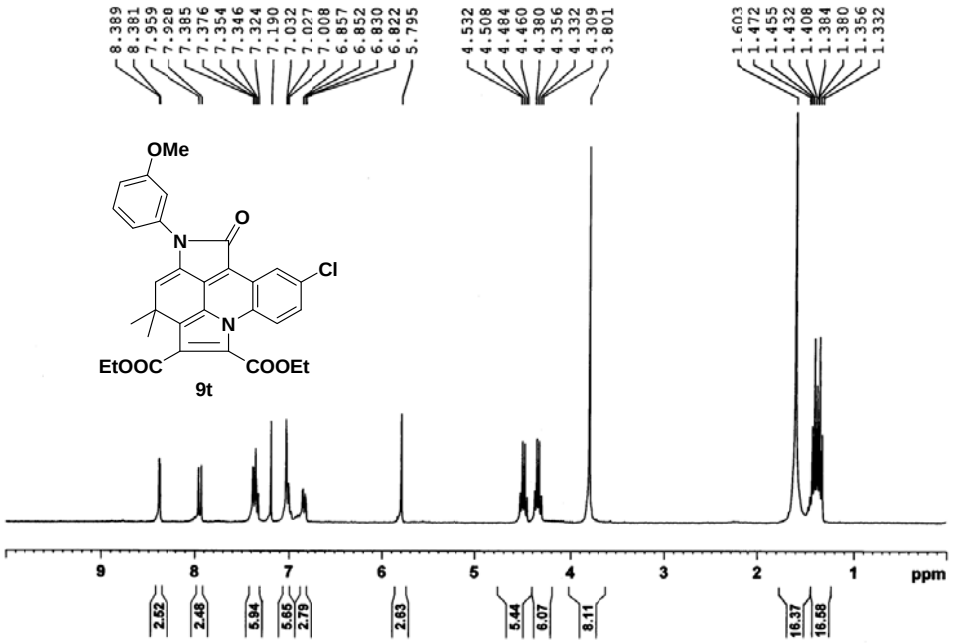
126.11
124.39
123.73
123.36
120.55
120.07
119.19
117.55
112.59
111.33
107.10
77.69
77.63
77.57
77.45
77.32
77.26
77.21
77.15
77.02
76.90
76.84
76.78
76.73
76.60
76.53
76.47
76.35
62.79
61.30
55.46
55.46
42.71
28.05
14.13
13.98
OMe
O
N
Br
N
EtOOC
COOEt
9s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.032
7.027
7.008
6.857
6.852
6.830
6.822
5.795
4.532
4.508
4.484
4.460
4.380
4.356
4.332
4.309
3.801
1.603
1.472
1.455
1.432
1.408
1.384
1.380
1.356
1.332
OMe
O
N
Cl
N
EtOOC
COOEt
9t
9
8
7
6
5
4
3
2
1
ppm
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5.94
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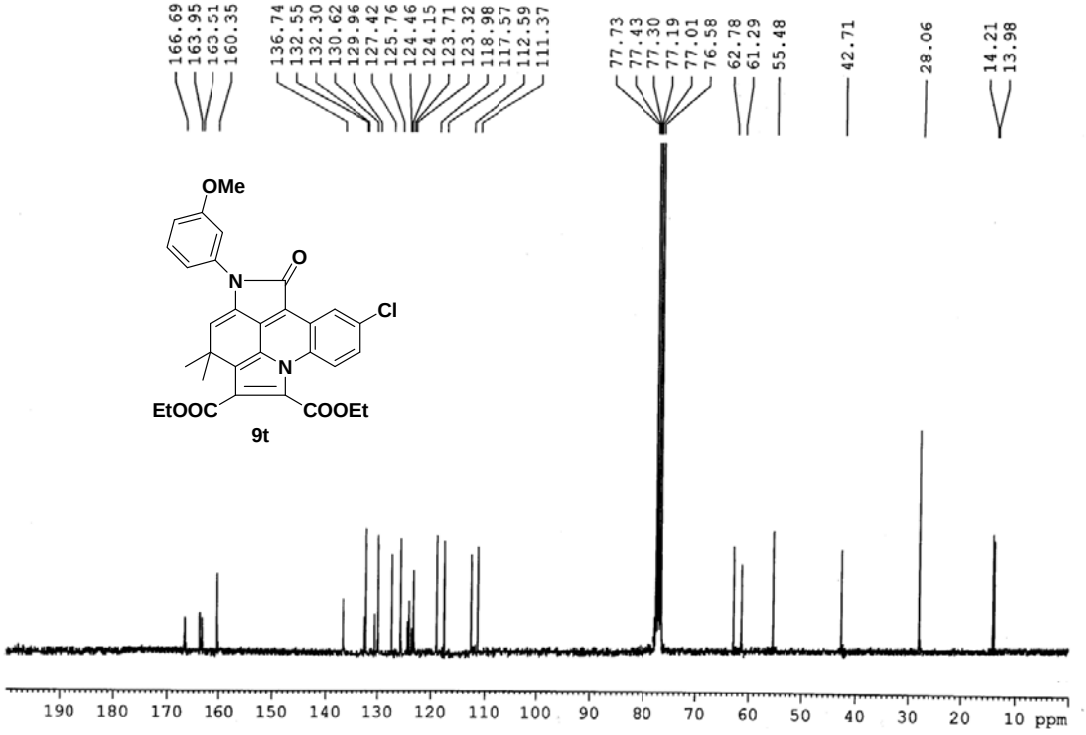
2.79
2.83
5.44
6.07
8.11
16.37
16.58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129.96
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125.76
124.46
124.15
123.71
123.32
118.98
117.57
112.59
111.37
77.73
77.43
77.30
77.19
77.01
76.58
62.78
61.29
55.48
42.71
28.06
14.21
13.98
OMe
O
N
Cl
N
EtOOC
COOEt
9t
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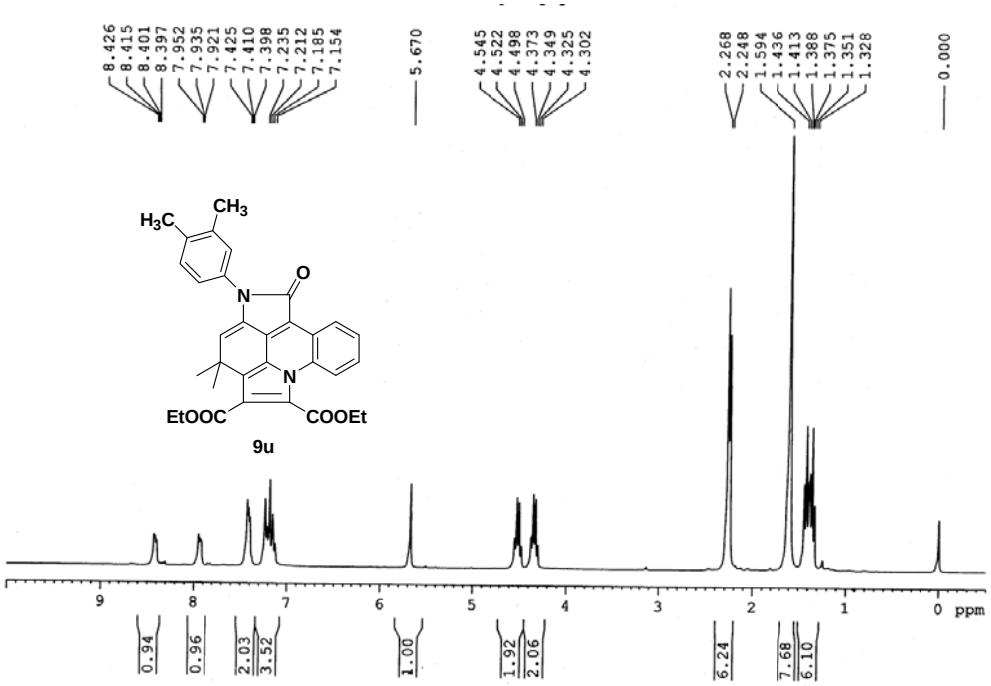
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.397
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7.425
7.410
7.398
7.235
7.212
7.185
7.154
5.670
4.545
4.522
4.498
4.373
4.349
4.325
4.302
2.268
2.248
1.594
1.436
1.413
1.388
1.375
1.351
1.328
0.000
H3C
CH3
O
N
N
EtOOC
COOEt
9u
9
8
7
6
5
4
3
2
1
0 ppm
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0.96
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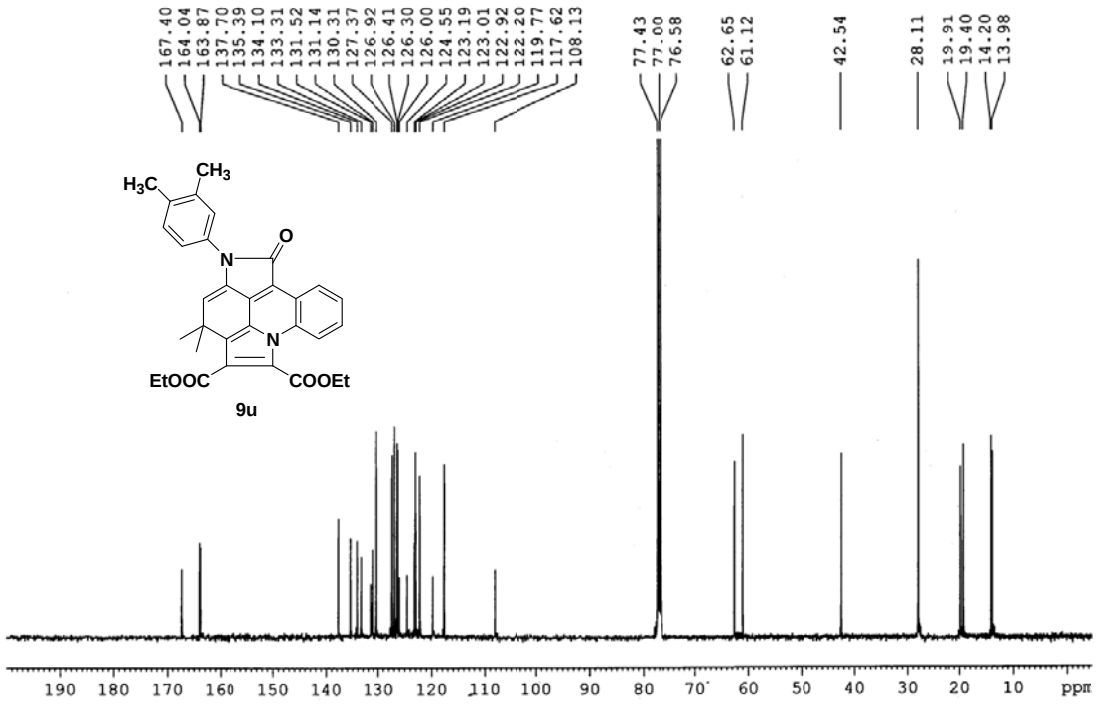
7.68
6.10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137.70
135.39
134.10
133.31
131.52
131.14
130.31
127.37
126.92
126.41
126.30
126.00
124.55
123.19
123.01
122.92
122.20
119.77
117.62
108.13
77.43
77.00
76.58
62.65
61.12
42.54
28.11
19.91
19.40
14.20
13.98
H3C
CH3
O
N
N
EtOOC
COOEt
9u
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150
140
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120
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70
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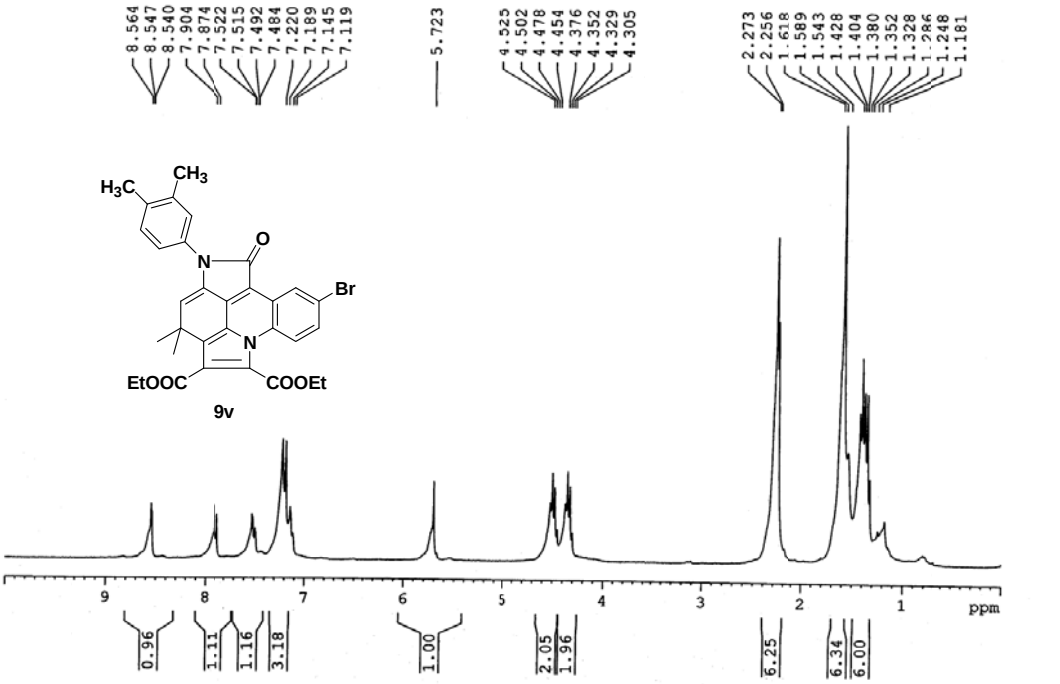
30
20
10
ppm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7.492
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7.189
7.145
7.119
5.723
4.525
4.502
4.478
4.454
4.376
4.352
4.329
4.305
2.273
2.256
1.589
1.543
1.428
1.404
1.380
1.352
1.328
1.248
1.181
H3C
CH3
O
N
Br
N
EtOOC
COOEt
9v
9
8
7
6
5
4
3
2
1
ppm
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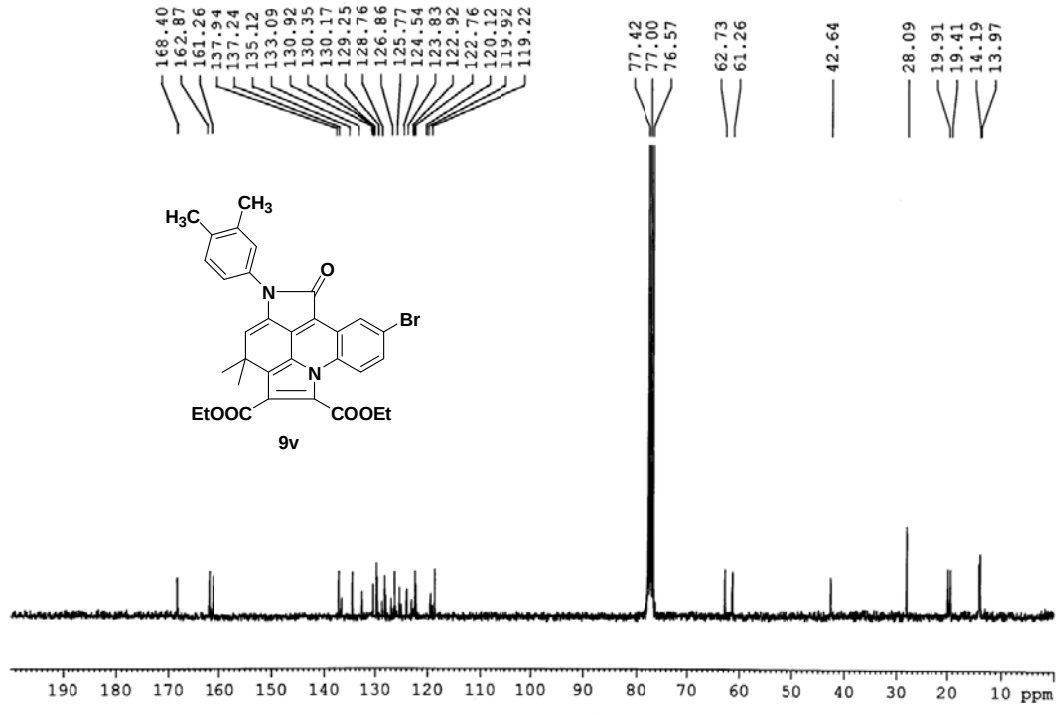
1.16
3.18
1.00
2.05
1.96
6.25
6.34
6.00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161.26
137.94
137.24
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133.09
130.92
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130.17
129.25
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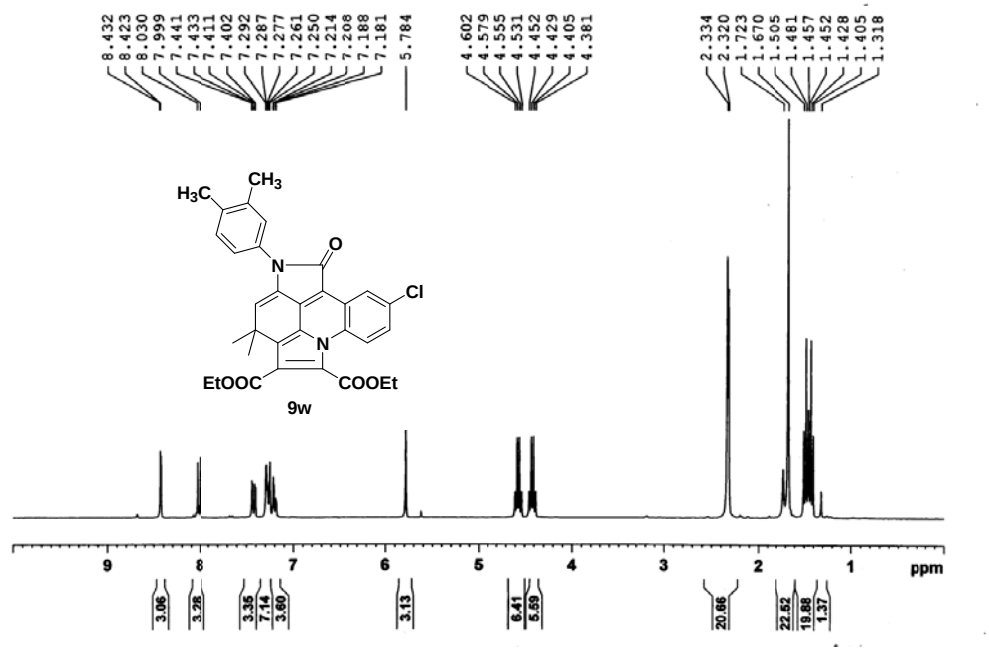
126.86
125.77
124.54
123.83
122.92
122.76
120.12
119.92
119.22
77.42
77.00
76.57
62.73
61.26
42.64
28.09
19.91
19.41
14.19
13.97
H3C
CH3
O
N
Br
N
EtOOC
COOEt
9v
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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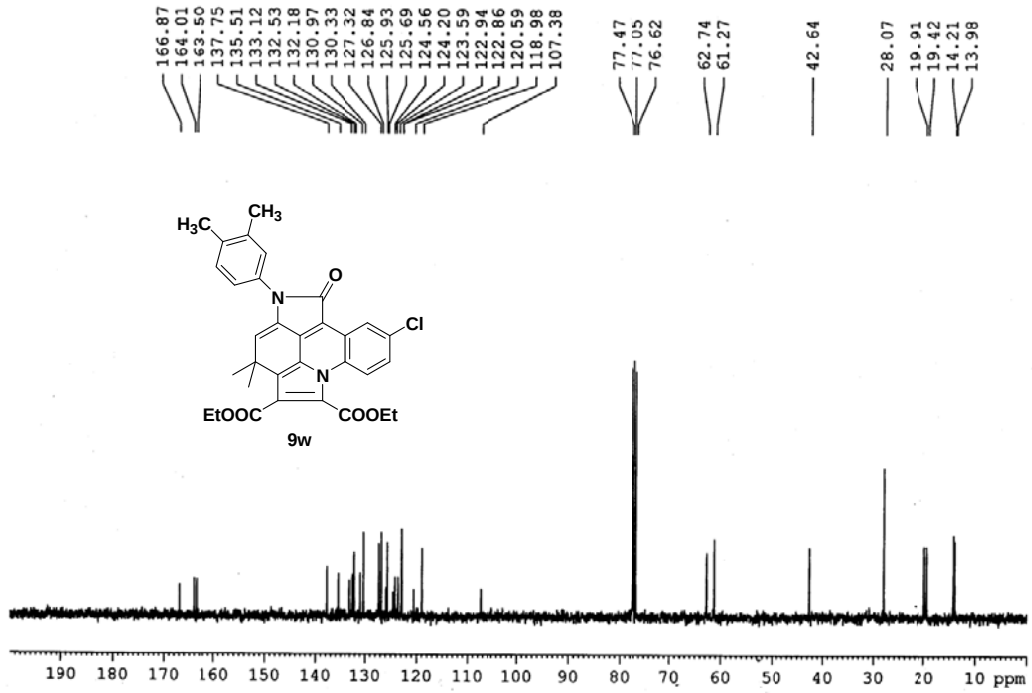
7.433
7.411
7.402
7.292
7.287
7.277
7.261
7.250
7.214
7.208
7.188
7.181
5.784
4.602
4.579
4.555
4.531
4.452
4.429
4.405
4.381
2.334
2.320
1.723
1.670
1.505
1.481
1.457
1.452
1.428
1.405
1.318
H3C
CH3
O
N
Cl
N
EtOOC
COOEt
9w
9
8
7
6
5
4
3
2
1
ppm
3.06
3.28
3.35
7.14
3.60
3.13
6.41
5.69
20.66
22.52
19.88
1.37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125.93
125.69
124.56
124.20
123.59
122.94
122.86
120.59
118.98
107.38
77.47
77.05
76.62
62.74
61.27
42.64
28.07
19.91
19.42
14.21
13.98
H3C
CH3
O
N
Cl
N
EtOOC
COOEt
9w
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170
160
150
140
130
120
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100
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80
70
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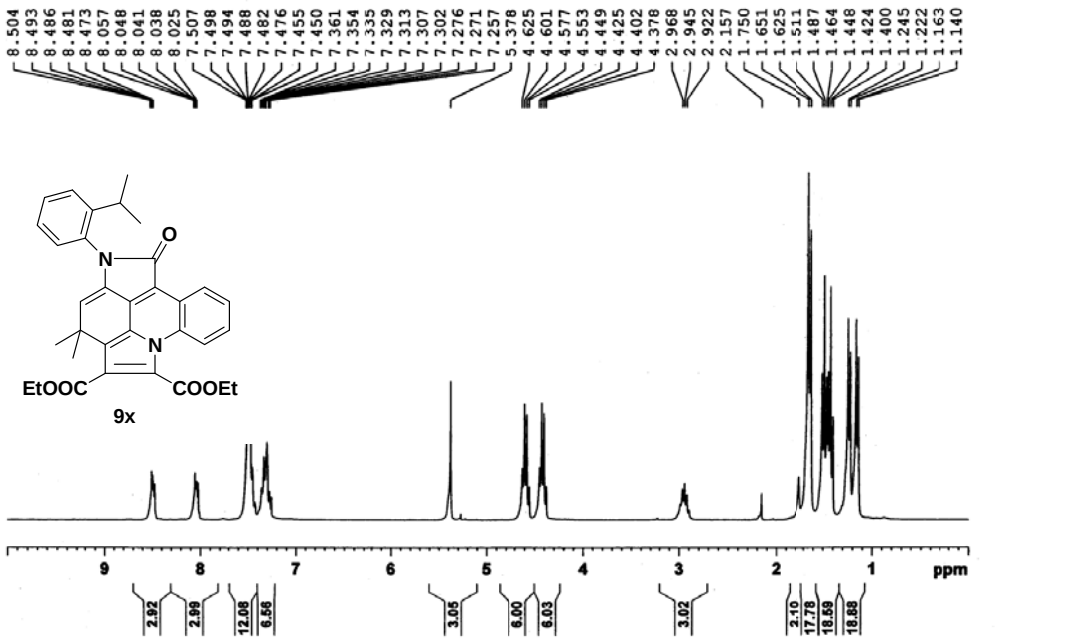
50
40
30
20
10 ppm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8.041
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7.494
7.488
7.482
7.476
7.455
7.450
7.361
7.354
7.335
7.329
7.313
7.307
7.302
7.276
7.271
7.257
5.378
4.625
4.601
4.577
4.553
4.449
4.425
4.402
4.378
2.968
2.945
2.922
2.157
1.750
1.651
1.625
1.511
1.487
1.464
1.448
1.424
1.400
1.245
1.222
1.163
1.140
O
N
N
EtOOC
COOEt
9x
9
8
7
6
5
4
3
2
1
ppm
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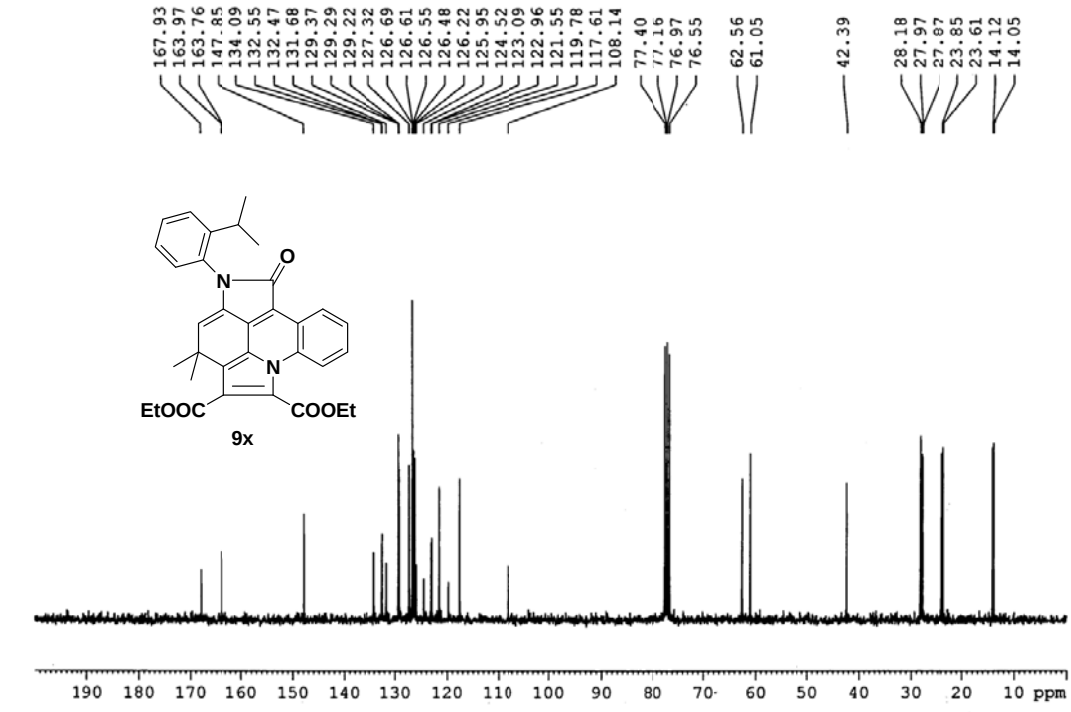
6.56
3.05
6.00
6.03
3.02
2.10
17.78
18.59
18.88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147.85
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131.68
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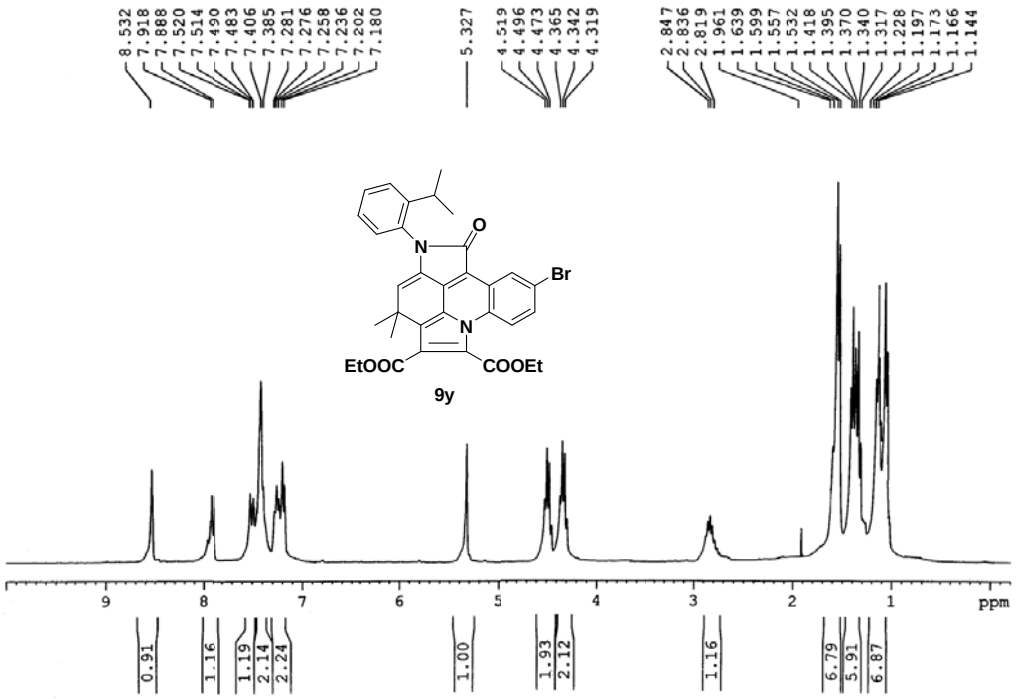
129.29
129.22
127.32
126.69
126.61
126.55
126.48
126.22
125.95
124.52
123.09
122.96
121.55
119.78
117.61
108.14
77.40
76.97
76.55
62.56
61.05
42.39
28.18
27.97
27.87
23.85
23.61
14.12
14.05
O
N
N
EtOOC
COOEt
9x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.406
7.385
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7.276
7.258
7.236
7.202
7.180
5.327
4.519
4.496
4.473
4.365
4.342
4.319
2.847
2.836
2.819
1.961
1.639
1.599
1.557
1.532
1.418
1.395
1.370
1.340
1.317
1.228
1.197
1.173
1.166
1.144
O
N
Br
N
EtOOC
COOEt
9y
9
8
7
6
5
4
3
2
1
ppm
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2.14
2.24
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2.12
1.16
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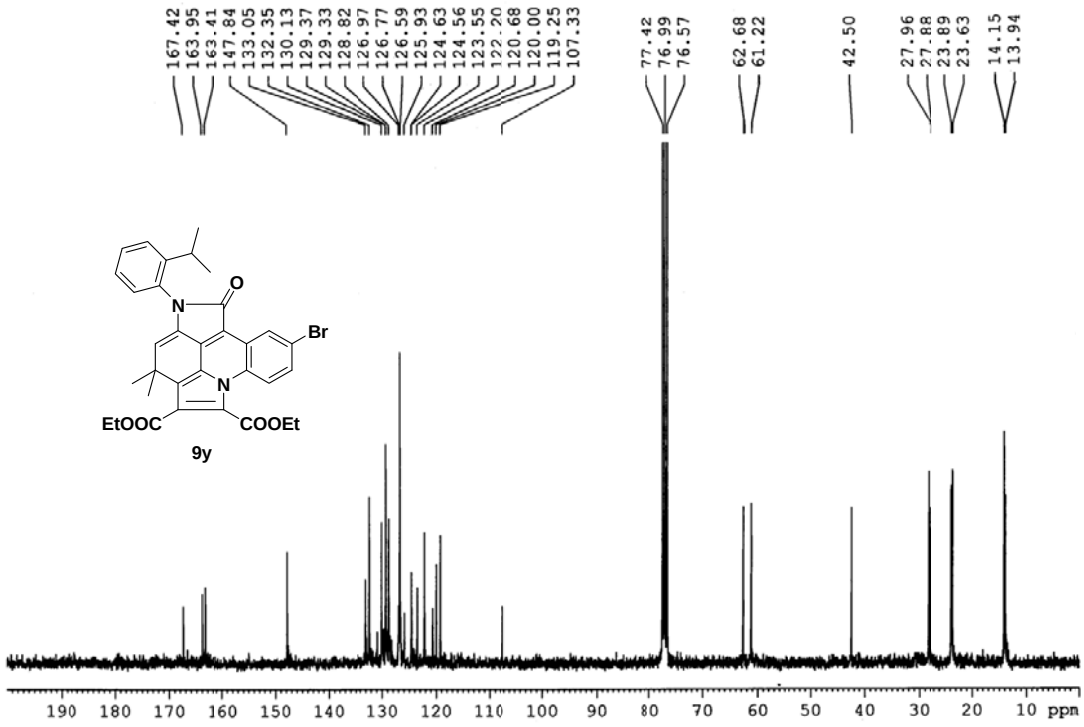
5.91
6.87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132.35
130.13
129.37
129.33
128.82
126.97
126.77
126.59
125.93
124.63
124.56
123.55
120.68
120.00
119.25
107.33
77.42
76.99
76.57
62.68
61.22
42.50
27.96
27.88
23.89
23.63
14.15
13.94
O
N
Br
N
EtOOC
COOEt
9y
190
180
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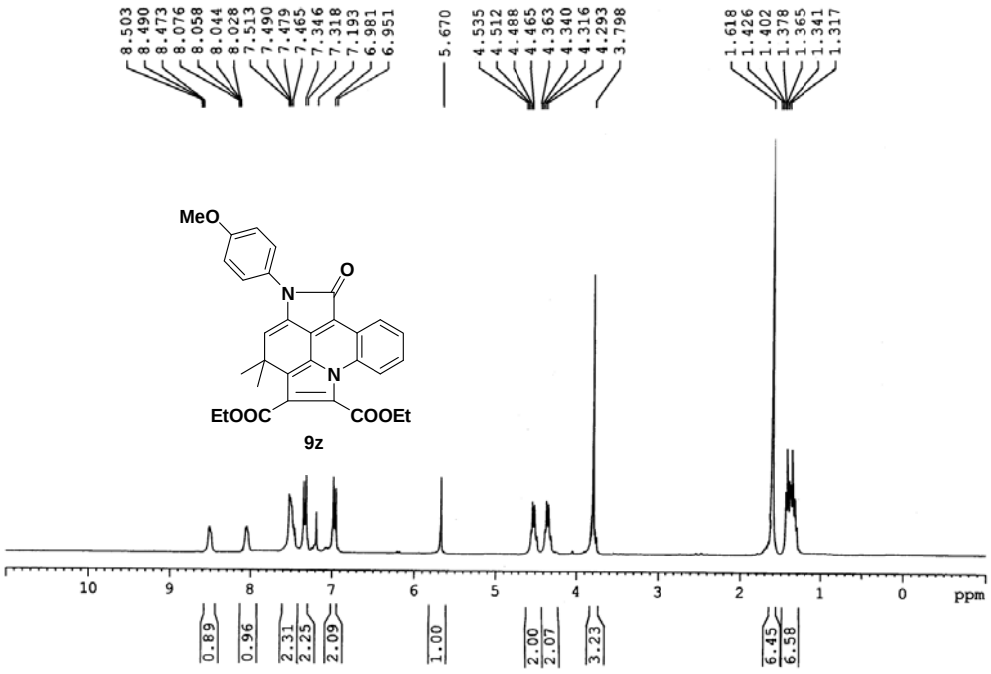
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.473
8.076
8.058
8.044
8.028
7.513
7.490
7.479
7.465
7.346
7.318
7.193
6.981
6.951
5.670
4.535
4.512
4.488
4.465
4.363
4.340
4.316
4.293
3.798
1.618
1.426
1.402
1.378
1.365
1.341
1.317
MeO
O
N
N
EtOOC
COOEt
9z
10
9
8
7
6
5
4
3
2
1
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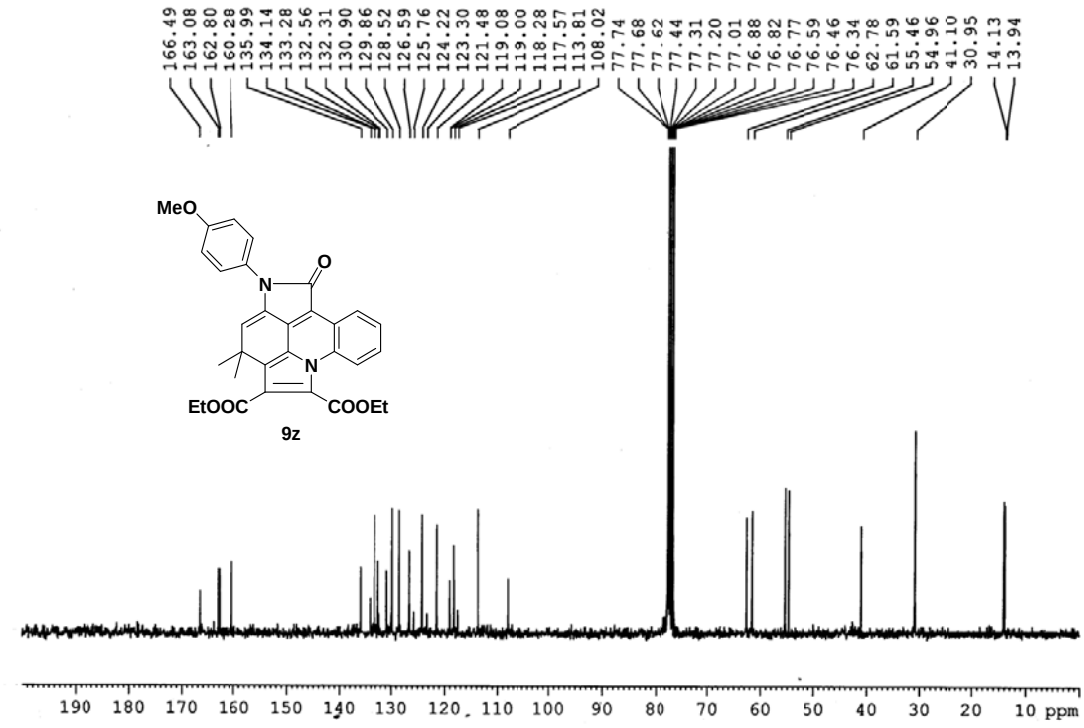
2.00
2.07
3.23
6.45
6.58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134.14
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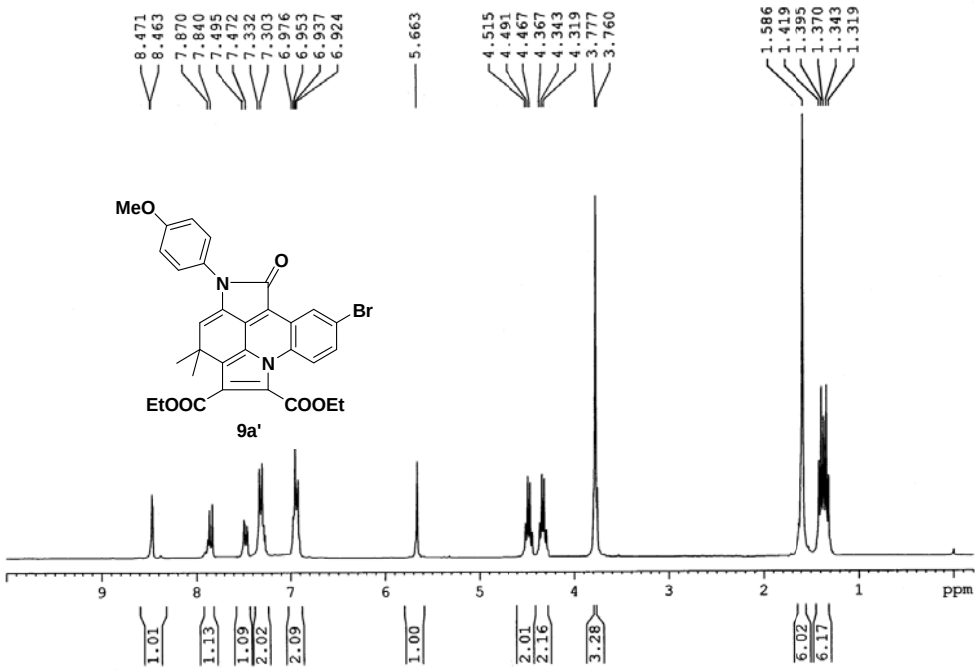
132.56
132.31
130.90
129.86
128.52
126.59
125.76
124.22
123.30
121.48
119.08
119.00
118.28
117.57
113.81
108.02
77.74
77.68
77.62
77.44
77.31
77.20
77.01
76.88
76.82
76.77
76.59
76.46
76.34
62.78
61.59
55.46
54.96
41.10
30.95
14.13
13.94
MeO
O
N
N
EtOOC
COOEt
9z
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.495
7.472
7.332
7.303
6.976
6.953
6.937
6.924
5.663
4.515
4.491
4.467
4.367
4.343
4.319
3.777
3.760
1.586
1.419
1.395
1.370
1.343
1.319
MeO
O
N
Br
N
EtOOC
COOEt
9a'
9
8
7
6
5
4
3
2
1
ppm
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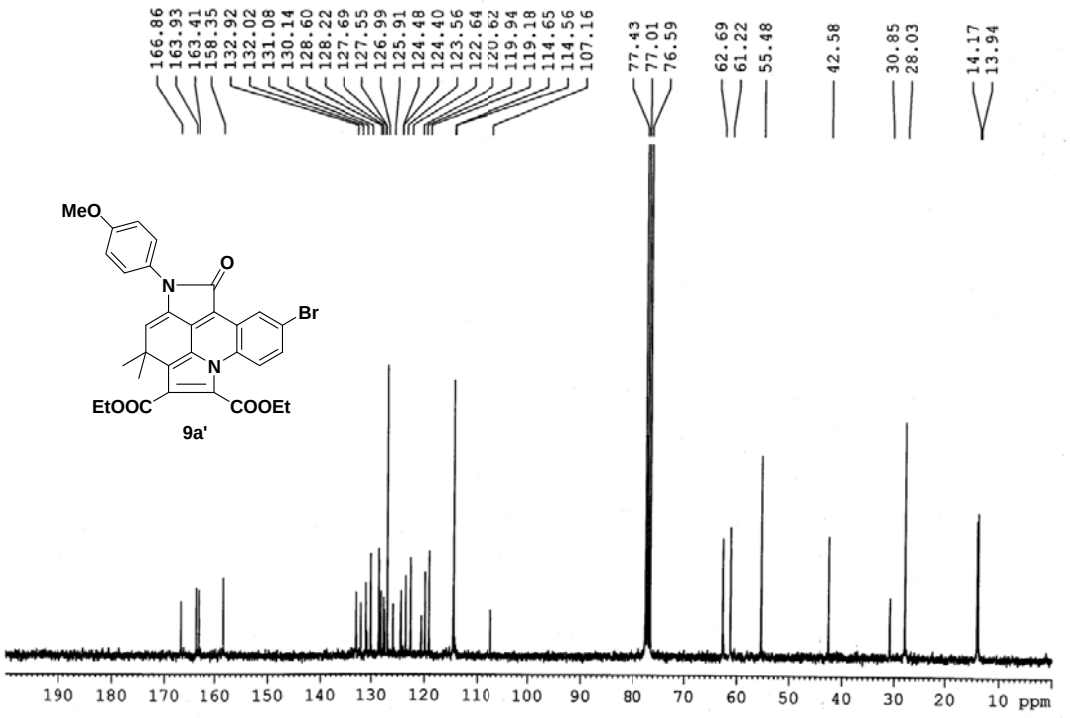
1.13
1.09
2.02
2.09
1.00
2.01
2.16
3.28
6.02
6.17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131.08
130.14
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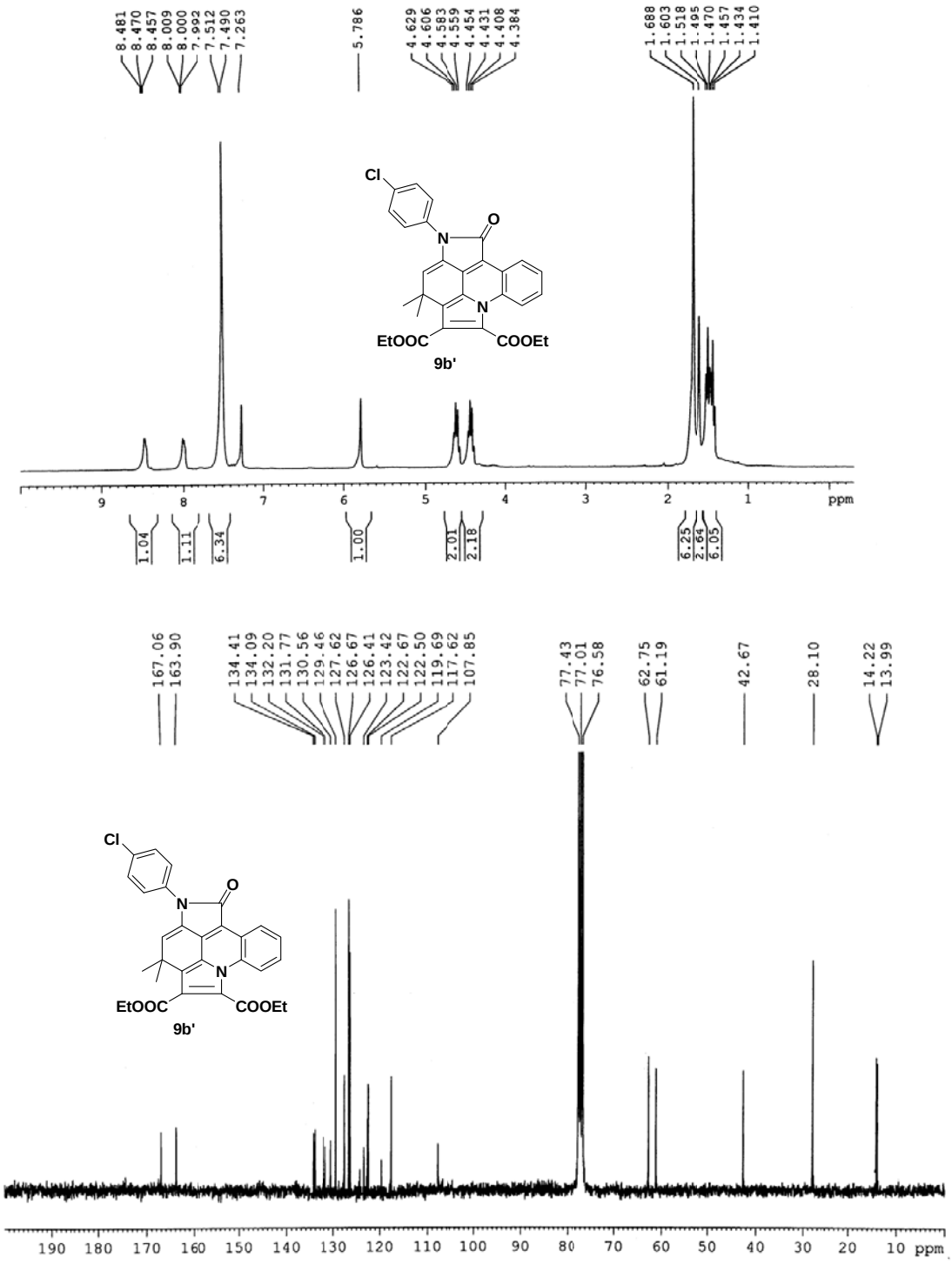
128.22
127.69
127.55
126.99
125.91
124.48
124.40
123.56
122.64
120.62
119.94
119.18
114.65
114.56
107.16
77.43
77.01
76.59
62.69
61.22
55.48
42.58
30.85
28.03
14.17
13.94
MeO
O
N
Br
N
EtOOC
COOEt
9a'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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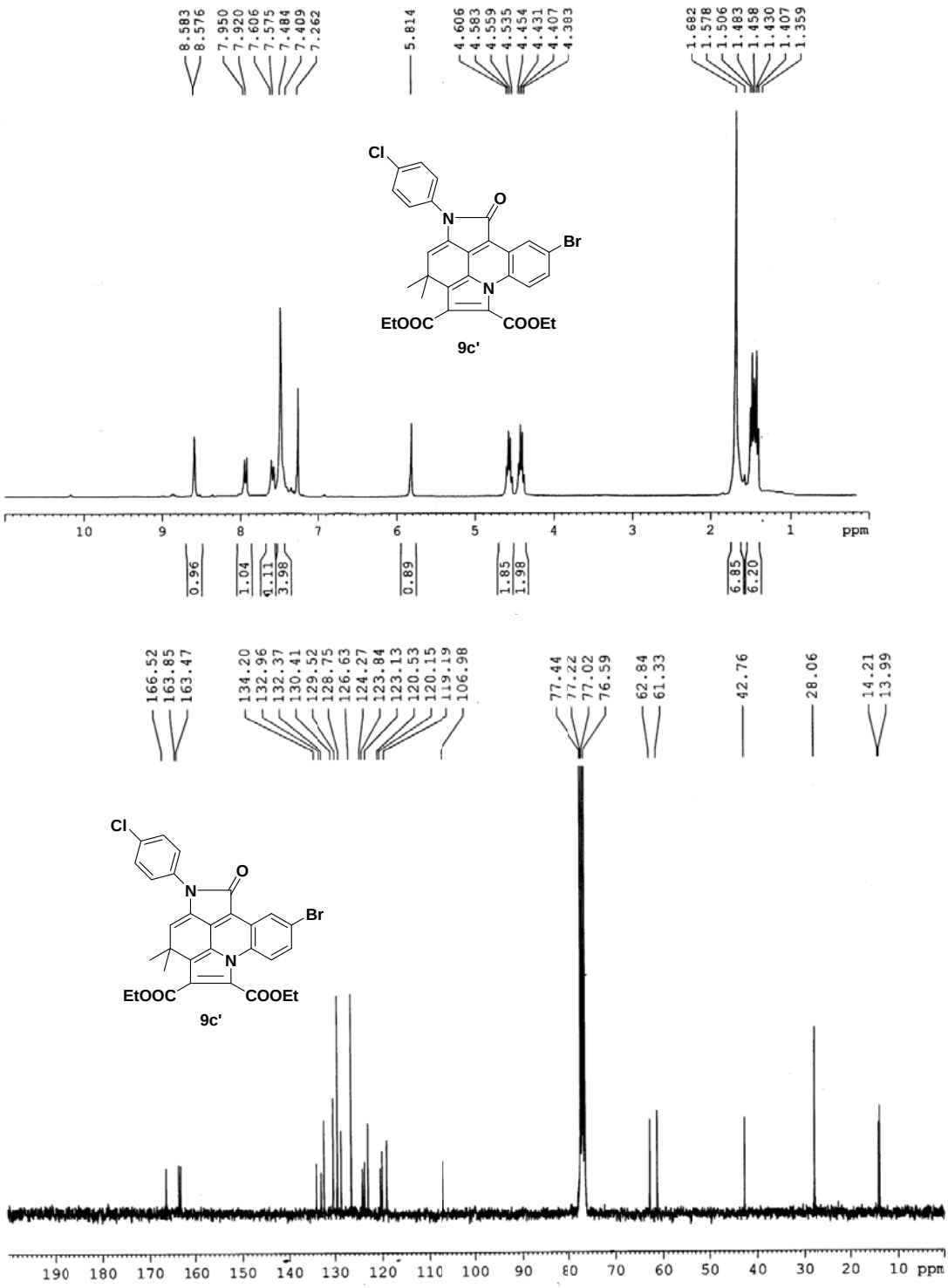
7.490
7.263
5.786
4.629
4.606
4.583
4.559
4.454
4.431
4.408
4.384
1.688
1.603
1.518
1.495
1.470
1.457
1.434
1.410
Cl
O
N
N
EtOOC
COOEt
9b'
ppm
1.04
1.11
6.34
1.00
2.01
2.18
6.25
2.64
6.05
167.06
163.90
134.41
134.09
132.20
131.77
130.56
129.46
127.62
126.67
126.41
123.42
122.67
122.50
119.69
117.62
107.85
77.43
77.01
76.58
62.75
61.19
42.67
28.10
14.22
13.99
Cl
O
N
N
EtOOC
COOEt
9b'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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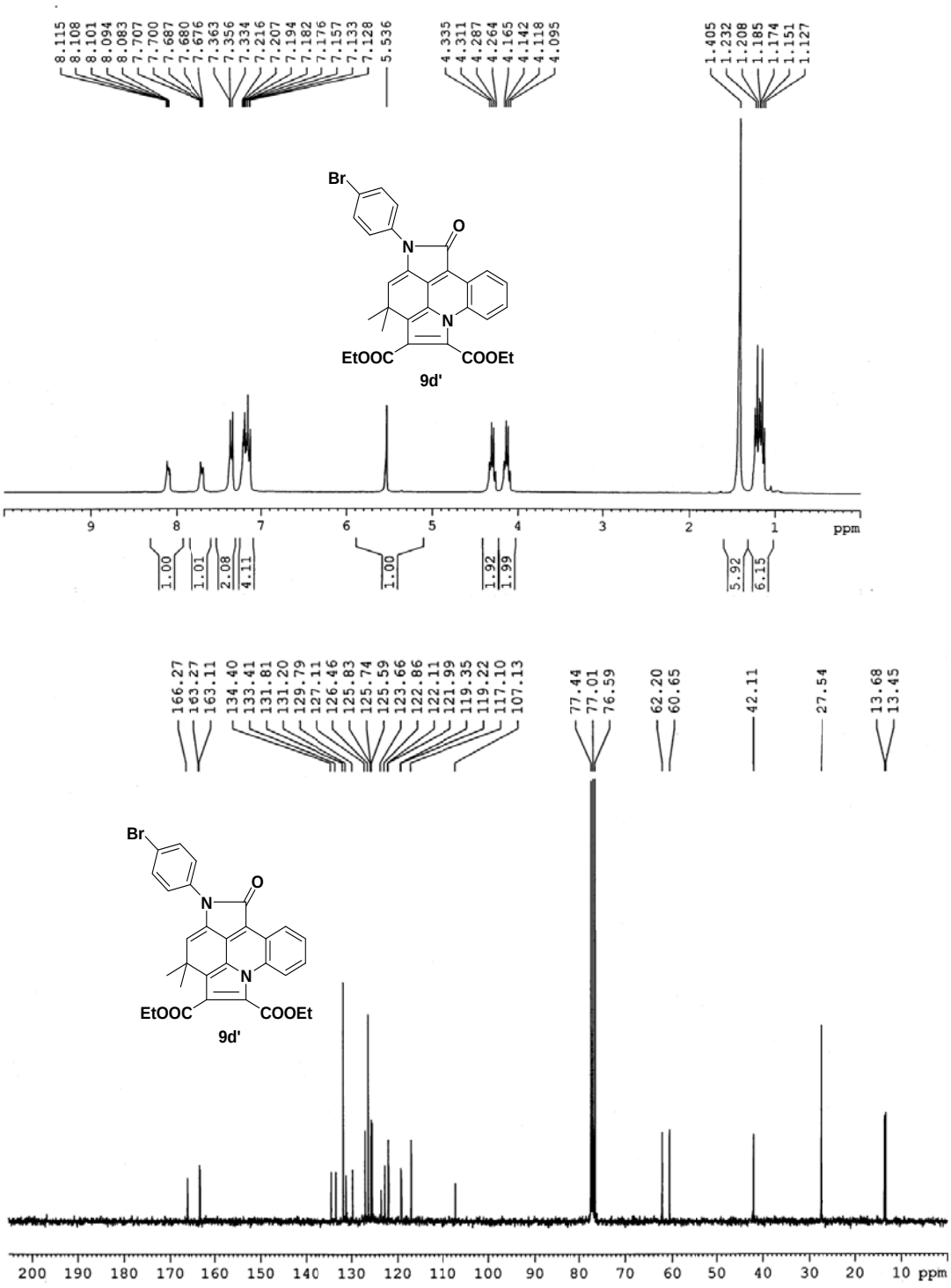
7.920
7.606
7.575
7.484
7.409
7.262
5.814
4.606
4.583
4.559
4.535
4.454
4.431
4.407
4.383
1.682
1.578
1.506
1.483
1.458
1.430
1.407
1.359
Cl
O
N
Br
N
EtOOC
COOEt
9c'
ppm
0.96
1.04
1.11
3.98
0.89
1.85
1.98
6.85
6.20
166.52
163.85
163.47
134.20
132.96
132.37
130.41
129.52
128.75
126.63
124.27
123.84
123.13
120.53
120.15
119.19
106.98
77.44
77.22
77.02
76.59
62.84
61.33
42.76
28.06
14.21
13.99
Cl
O
N
Br
N
EtOOC
COOEt
9c'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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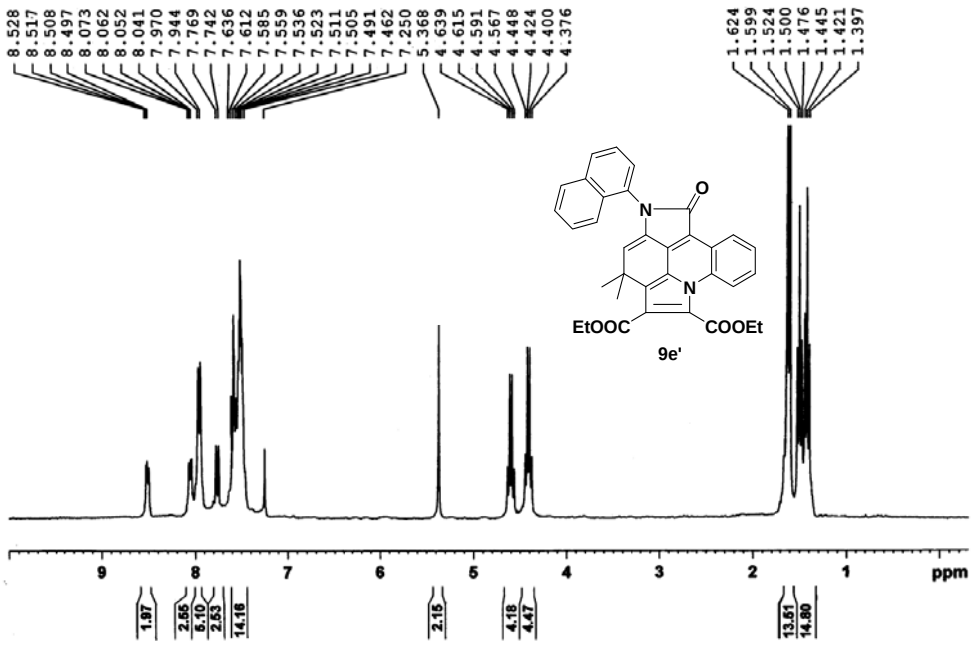
7.680
7.676
7.363
7.356
7.334
7.216
7.207
7.194
7.182
7.176
7.157
7.133
7.128
5.536
4.335
4.311
4.287
4.264
4.165
4.142
4.118
4.095
1.405
1.232
1.208
1.185
1.174
1.151
1.127
Br
O
N
N
EtOOC
COOEt
9d'
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
2.08
4.11
1.00
1.92
1.99
5.92
6.15
166.27
163.27
163.11
134.40
133.41
131.81
131.20
129.79
127.11
126.46
125.83
125.74
125.59
123.66
122.86
122.11
121.99
119.35
119.22
117.10
107.13
77.44
77.01
76.59
62.20
60.65
42.11
27.54
13.68
13.45
Br
O
N
N
EtOOC
COOEt
9d'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.041
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7.944
7.769
7.742
7.636
7.612
7.585
7.559
7.536
7.523
7.511
7.505
7.491
7.462
7.250
5.368
4.639
4.615
4.591
4.567
4.448
4.424
4.400
4.376
1.624
1.599
1.524
1.500
1.476
1.445
1.421
1.397
N
O
N
EtOOC
COOEt
9e'
9
8
7
6
5
4
3
2
1
ppm
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2.55
6.10
2.53
14.16
2.15
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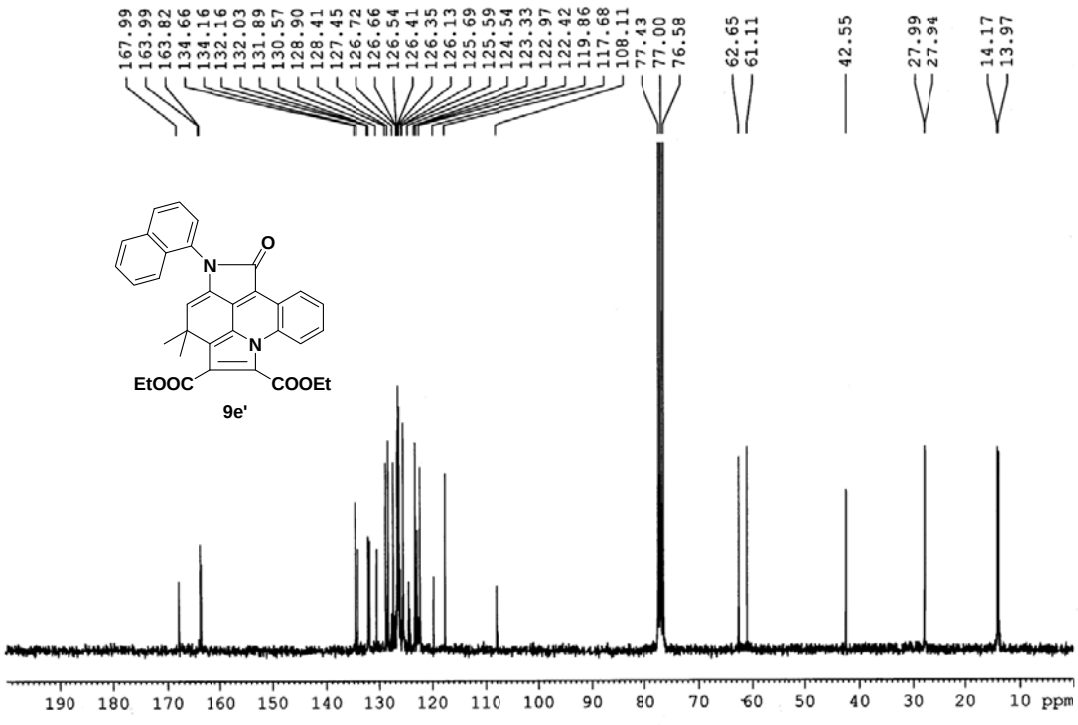
14.80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128.41
127.45
126.72
126.66
126.54
126.41
126.35
126.13
125.69
125.59
124.54
123.33
122.97
122.42
119.86
117.68
108.11
77.43
77.00
76.58
62.65
61.11
42.55
27.99
27.94
14.17
13.97
N
O
N
EtOOC
COOEt
9e'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm