Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis and photophysics of selective functionalized π-conjugated, blue light emitting highly fluorescent C7-imidazo indolizine derivatives

Rajib Sarkar,[a] Tandrima Chaudhuri,[b] Animesh Karmakar[b] and Chhanda Mukhopadhyay*[a]

[a]Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata-700009, India
E-mail: cmukhop@yahoo.co.in

[b]Department of Chemistry, Dr. B. N. Dutta Smriti Mahavidyalaya, Burdwan-713407, India.

Table of contents

Table S1. Absoptivity variation data along with quantum yield of the compounds **3a** to **3e** and **4a** to **4r** studied in acetonitrile at 25 ^{0}C.

Entry	Fluorophore	Φ_{fl}±0.009*	ε at Λ=312nm
1	3a	0.97	18860.3
2	3b	0.94	21030.6
3	3c	0.49	18282.1
4	3d	0.49	21184.3
5	3e	1.00	11130.3
6	4a	1.00	13471.0
7	4b	0.88	17489.5
8	4c	0.87	23466.5
9	4d	0.93	22254.0
10	4e	0.91	11688.3
11	4f	1.00	12887.0
12	4g	0.51	24949.0
13	4h	0.92	20657.0
14	4i	0.81	18604.6
15	4j	0.91	23557.2
16	4k	0.88	24038.5
17	4l	0.87	14570.1
18	4m	0.82	13946.6
19	4n	0.82	14409.4
20	4o	1.00	18406.5
21	4p	0.86	15174.4
22	4q	0.87	18080.0
23	4r	0.77	18251.9

*for OD = 0.09 at λ_{ex} = 315 nm, referance used 9,10-diphenylanthracene.

Table S2. Detailed photophysical data of the compounds **6a** to **6f** and **7a** to **7e** studied in acetonitrile at 25 ^{0}C.

Entry	Fluorophore	λ_{abs} [nm]	λ_{em} [nm]	Δλ (λ_{em}- λ_{abs}) [nm]	Φ_{fl}±0.009*	ε at Λ=312nm
1	6a	387.4	448.0	60.6	0.98	15456.8
2	6b	387.6	448.2	60.6	0.99	12073.5
3	6c	388.2	448.2	60.0	0.98	14819.7
4	6d	388.0	448.2	60.2	0.97	13613.9
5	6e	385.4	449.2	63.8	1.00	11851.2
6	6f	388.6	448.6	60.0	0.98	16544.7
7	7a	364.0	423.0	59.0	0.95	15758.4
8	7b	370.7	429.4	58.7	0.99	24859.3
9	7c	371.5	430.0	58.5	0.92	13423.6
10	7d	370.5	425.6	55.1	1.00	16961.9
11	7e	367.0	423.4	56.4	0.97	13323.0

*for OD = 0.09 at λ_{ex} = 315 nm, referance used 9,10-diphenylanthracene.

Detailed photophysical results of the compounds **6a** to **6f** and **7a** to **7e** were illustrated in Table S2. From the results it was clearly observed that the compounds derived (**6a-6f**) from 9,10-phenanthraquinone absorption comparatively in the longer wavelengths (λ_{abs}) region (385.4-388.6 nm), and also emit comparatively in longer wavelengths (λ_{em}) region (448.0-449.2 nm) with high absorptivity and quantum yields Φ_{fl}. The derivatives prepared from o-phenelenediamine (**7a-7e**) show similar types of absorption spectra in the UV region (364.0-371.5 nm), and comparatively emission occurs in shorter wavelengths (λ_{em}) region (423.0-430.0 nm) with high quantum yields Φ_{fl} (Table S2).

Table S3. Detailed photophysical properties and data of the compounds **2a** and **2b** studied in acetonitrile at 25 ^{0}C.

Entry	Compound	λ_{abs} [nm]	λ_{em} [nm]	Φ_{fl}±0.009*	ε at Λ=312nm
1	2a	362.0	437.2	0.06	4000.0
2	2b	365.6	439.6	0.09	5427.8

*for OD = 0.09 at λ_{ex} = 315 nm, referance used 9,10-diphenylanthracene.

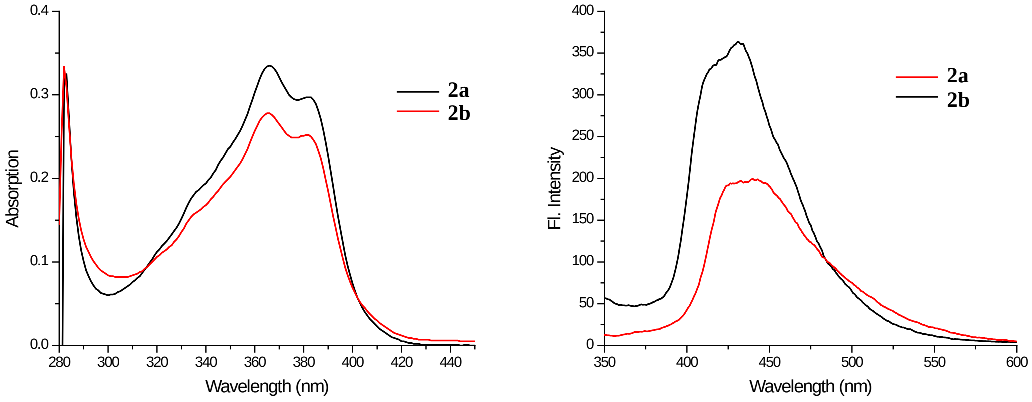


Figure S1. Normalized absorption and emission spectra of **2a** and **2b**, in air-equilibrated solutions of acetonitrile at 25 ^{0}C.

A comparative photophysical study of the fluorophores (**3a**, **4c** and **4k**) were also investigated in a wide variety of solvents starting from aprotic polar DMSO to nonpolar xylene and protic methanol also at 25 ^{0}C by UV/Vis and fluorescence spectroscopy. The absorption and emission spectra has been given in the Figure S2.

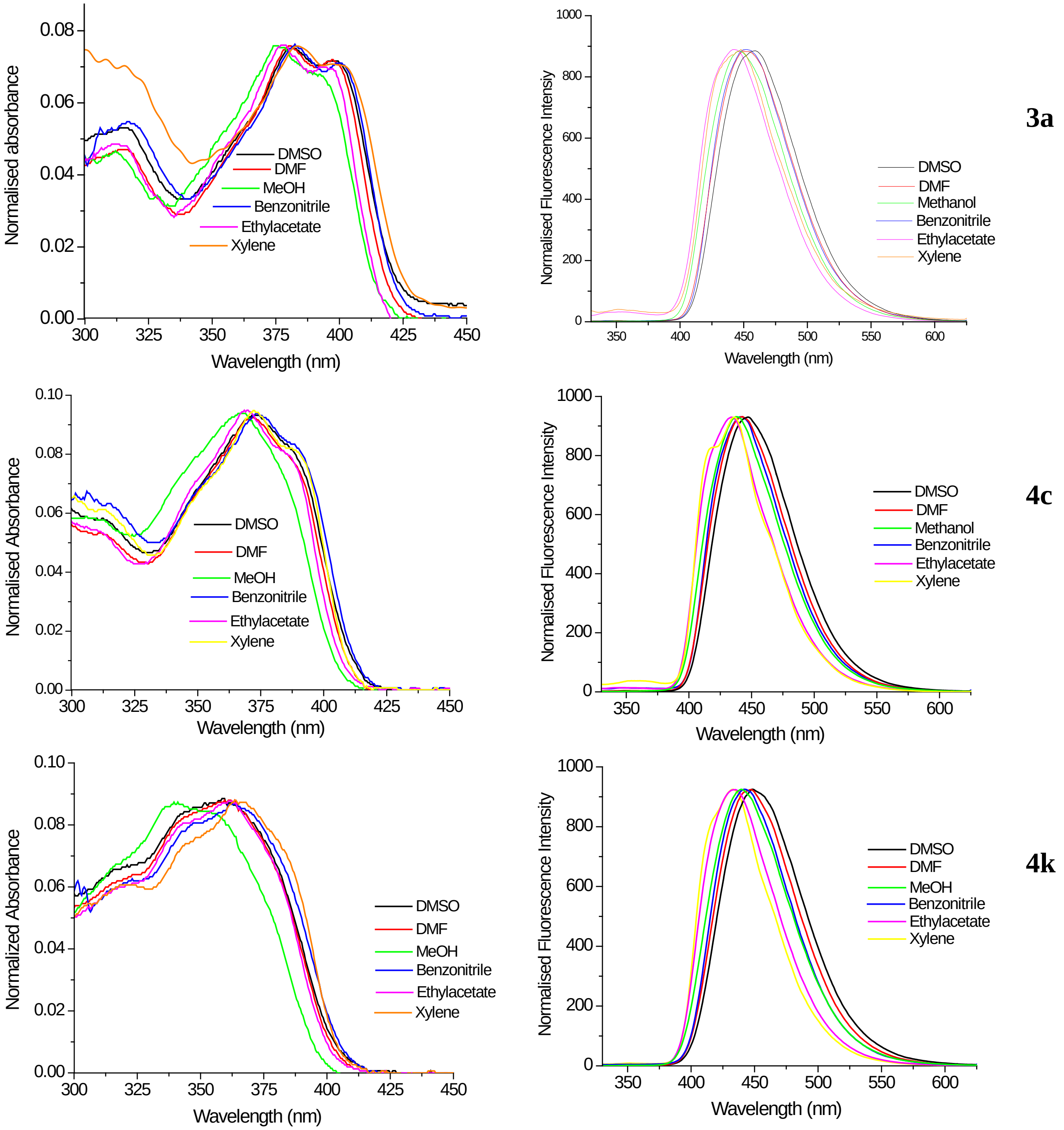
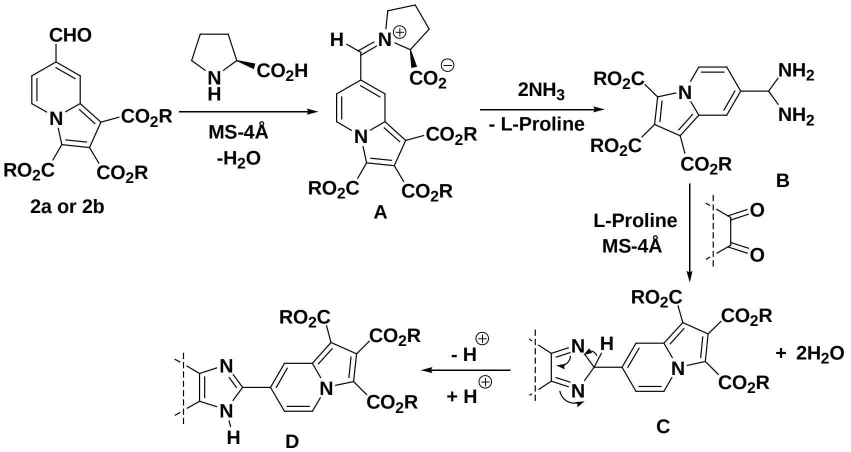


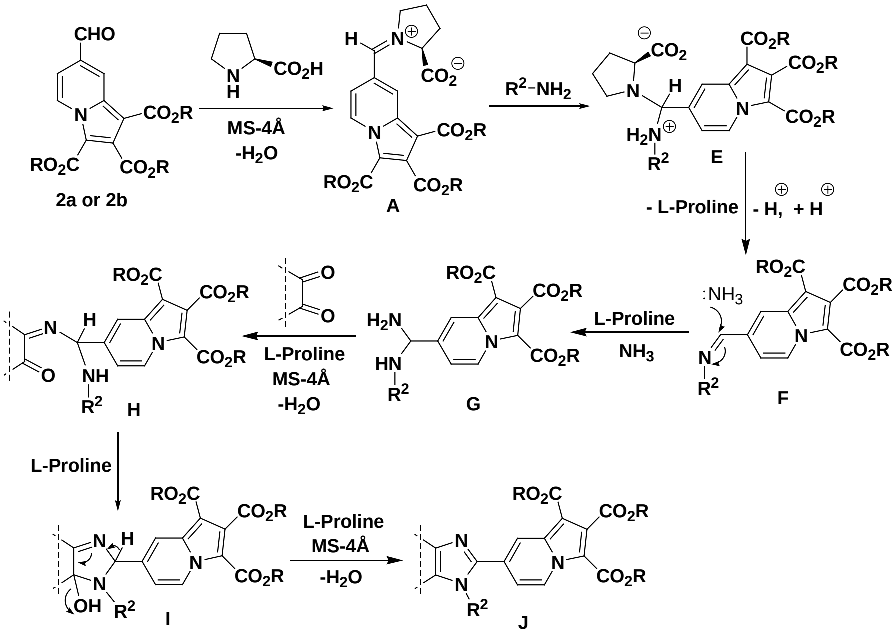
Figure S2. Normalized absorption spectra and emission spectra of **3a** (Top), **4c** (middle) and **4k** (below) respectively, in air-equilibrated solutions of various solvents at 25 ^{0}C.

A most plausible reaction mechanism was proposed for this L-proline mediated synthesis of C7-imidazo indolizine derivatives has been illustrated in Scheme S1.[1] Initially, amination of trialkyl-7-formylindolizine-1,2,3-tricarboxylate (**2a** or **2b**) to a diamine intermediate **B**, through the formation of **A**, catalyzed by L-proline in presence of molecular sieves (4Å). In the next step, the diamine intermediate **B** condenses with the carbonyl carbons of the 1,2-diketone to afford the intermediate **C**, catalyzed by L-proline. Finally, it (**C**) rearranges to the ultimate tri substituted C7-imidazo indolizine derivatives, **D** (**3a**-**3e**) as a product.



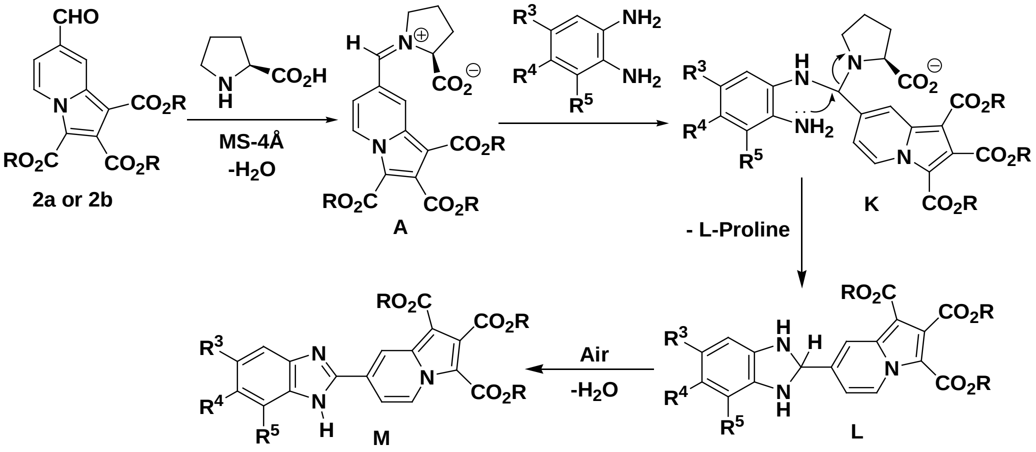
Scheme S1. Mechanism of the formation of 2,4,5-trisubstituted C7-imidazo indolizines, **3a**-**3e**.

In the case of tetrasubstituted C7-imidazo indolizine derivatives (**4a**-**4r** and **6a**-**6f**) the reaction precedes through almost the similar pathway as for trisubstituted C7-imidazo indolizine derivatives, **J** shown in Scheme S2.[2]



Scheme S2. Mechanism of the formation of C7-imidazo indolizine derivatives **4a**-**4r** and **6a**-**6f**.

The formation of tri-substituted benzimidazo indolizine derivatives (**7a**-**7e**) catalyzed by L-proline in presence of 4Å molecular sieves also dscribed in Scheme S3.[2] Here, simple dehydration followed by proton rearrangement furnishes the corresponding product, **M** (**7a**-**7e**).

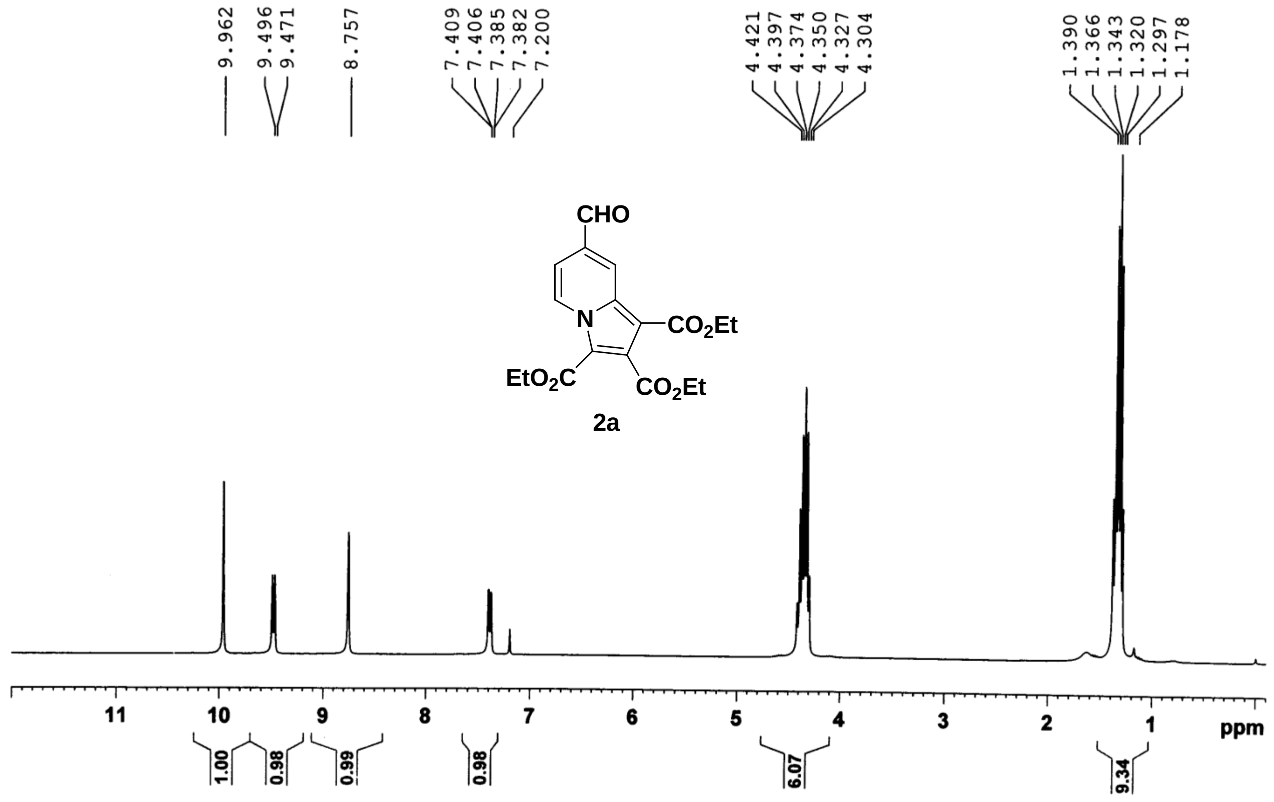


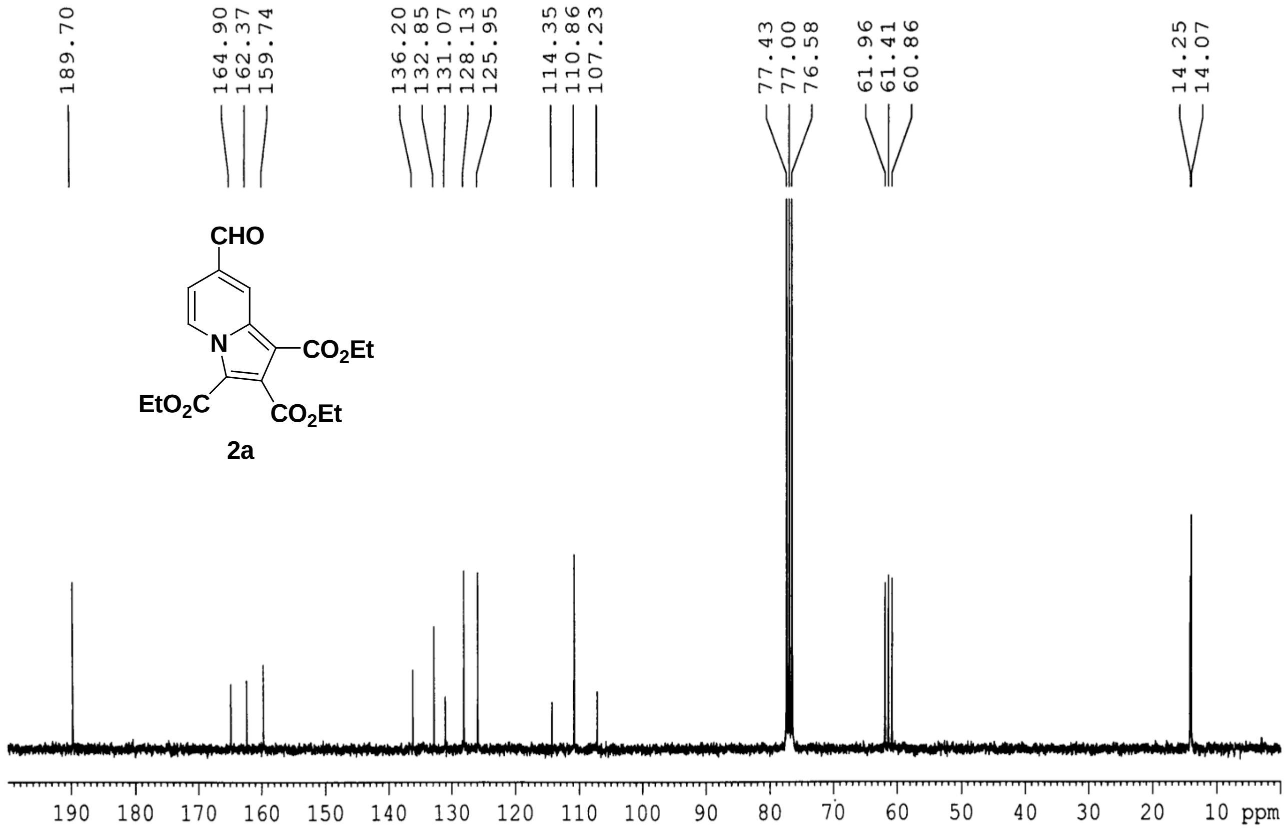
Scheme S3. Mechanism of the formation of 2-substituted C7-benzimidazo indolizines, **7a**-**7e**.

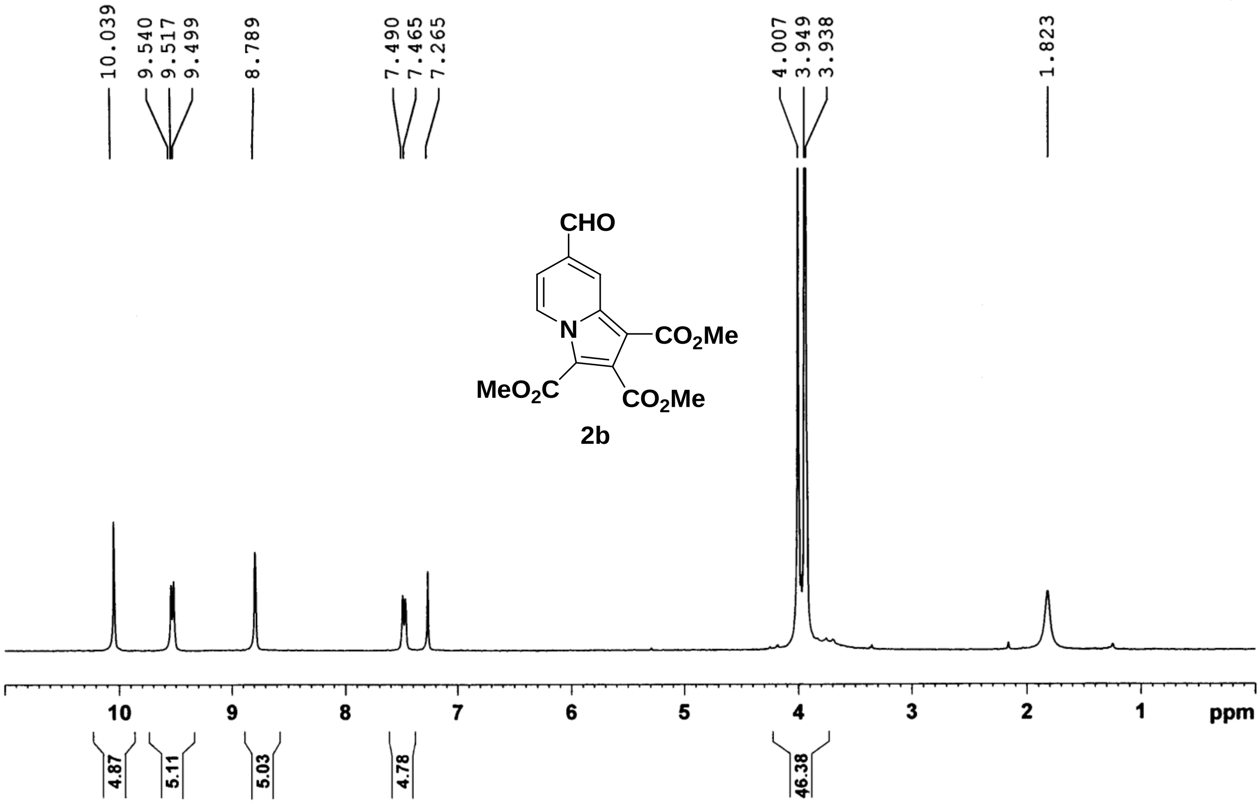
Reference

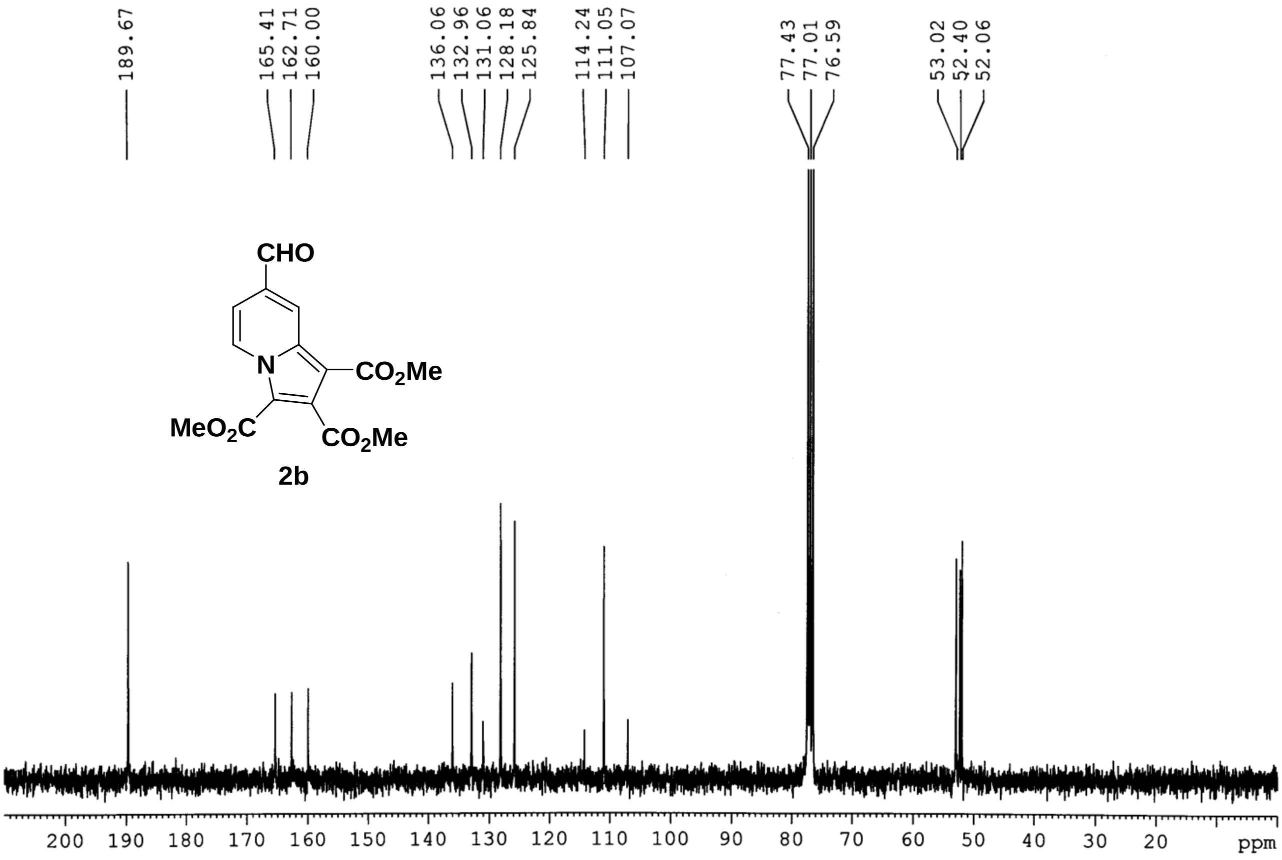
1. (a) A. Hasaninejad, A. Zare, M. Shekouhy and J. A. Rad, *J. Comb. Chem.*, 2010**,** **12**, 844; (b) C. Mukhopadhyay, P. K. Tapaswi, *Green. Chem. Lett. Rev.*, 2012, **5**, 109; (c) S. D. Sharma, P. Hazarika and D. Konwar, *Tetrahedron Lett.*, 2008, **49**, 2216; (d) S. N. Murthy, B. Madhav and Y. V. D. Nageswar, *Tetrahedron Lett.*, 2010, **51**, 5252; (e) S. Samai, G. C. Nandi, P. Singh and M.S. Singh, *Tetrahedron Lett.*, 2009, **65**, 10155.

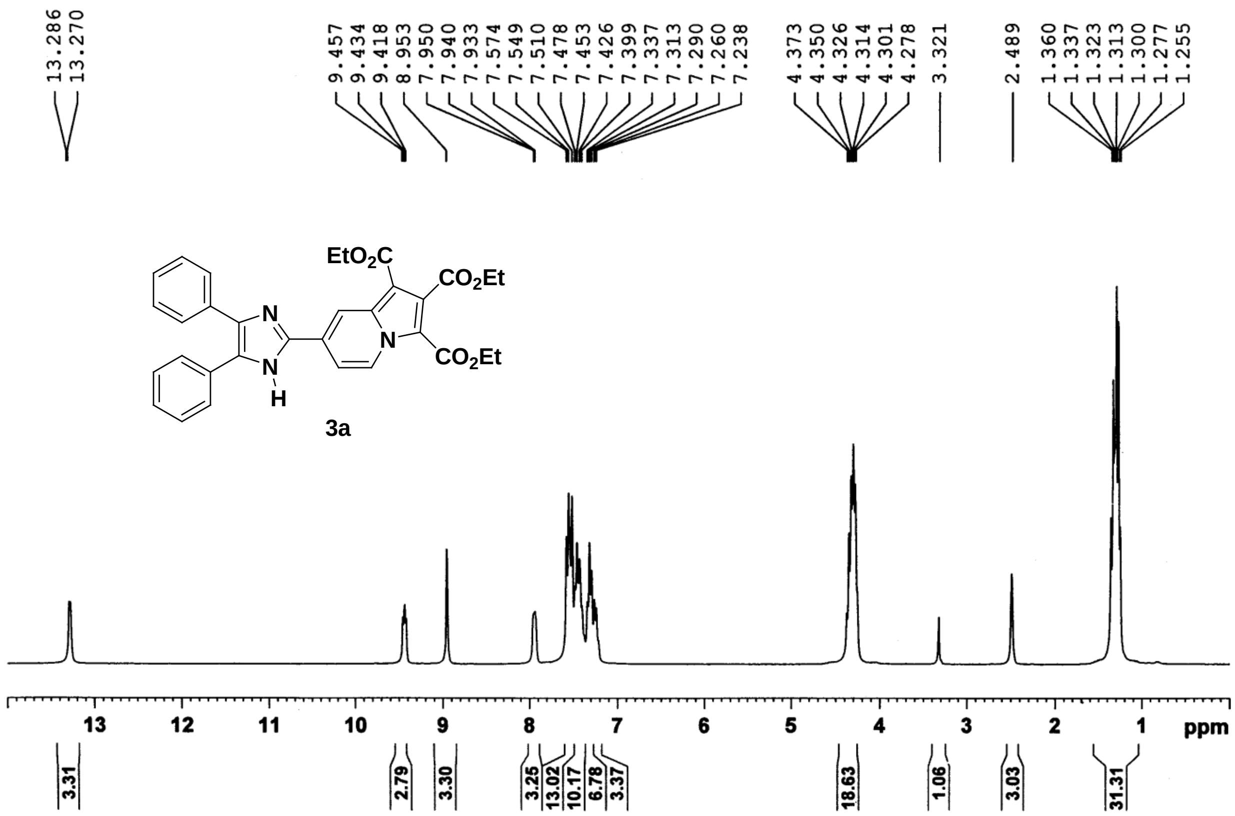
2. (a) M. A. Chari, D. Shobha and T. Sasaki, *Tetrahedron Lett.*, 2011, **52**, 5575; (b) H. Sharghi, M. H. Beyzavi and M. M. Doroodmand, *Eur. J. Org. Chem.*, 2008, 4126; (c) H. Sharma, N. Singh and D. O. Jang, *Green Chem.*, 2014, **16**, 4922; (d) A. Kumar, R. A. Maurya and P. Ahmad, *J. Comb. Chem.*, 2009**,** **11**, 198; (e) K. Bahrami, M. M. Khodaei and F. Naali, *J. Org. Chem.*, 2008, **73**, 6835.

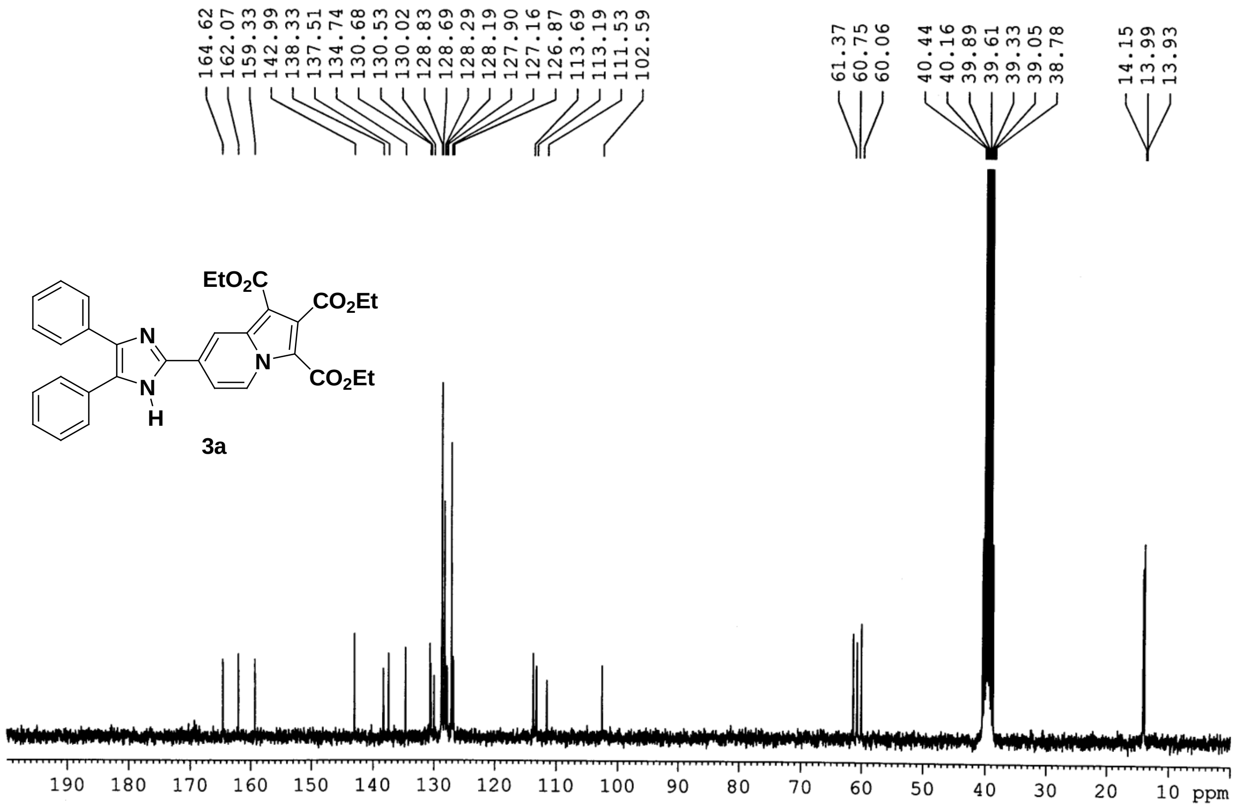

9.962
9.496
9.471
8.757
7.409
7.406
7.385
7.382
7.200
4.421
4.397
4.374
4.350
4.327
4.304
1.390
1.366
1.343
1.320
1.297
1.178
CHO
N
CO2Et
EtO2C
CO2Et
2a
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
0.99
0.98
6.07
9.34

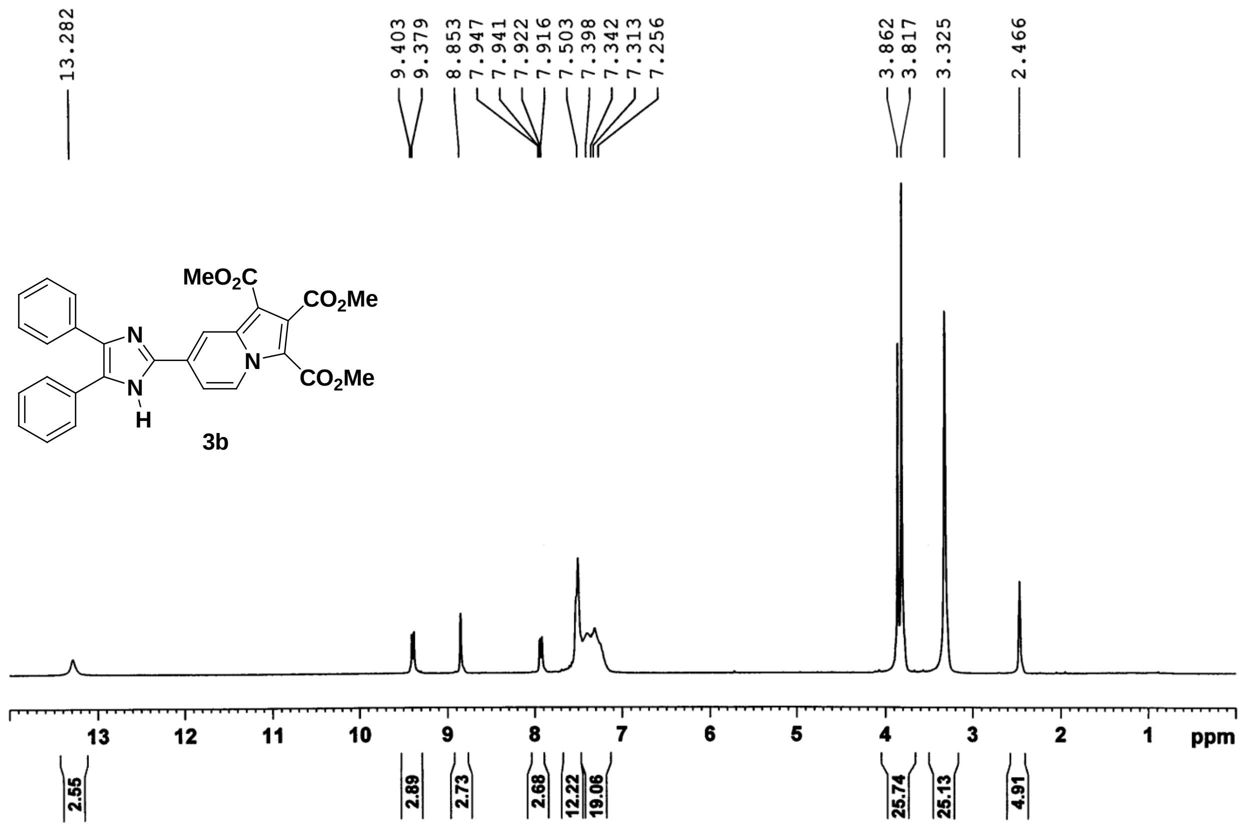

189.70
164.90
162.37
159.74
136.20
132.85
131.07
128.13
125.95
114.35
110.86
107.23
77.43
77.00
76.58
61.96
61.41
60.86
14.25
14.07
CHO
N
CO2Et
EtO2C
CO2Et
2a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

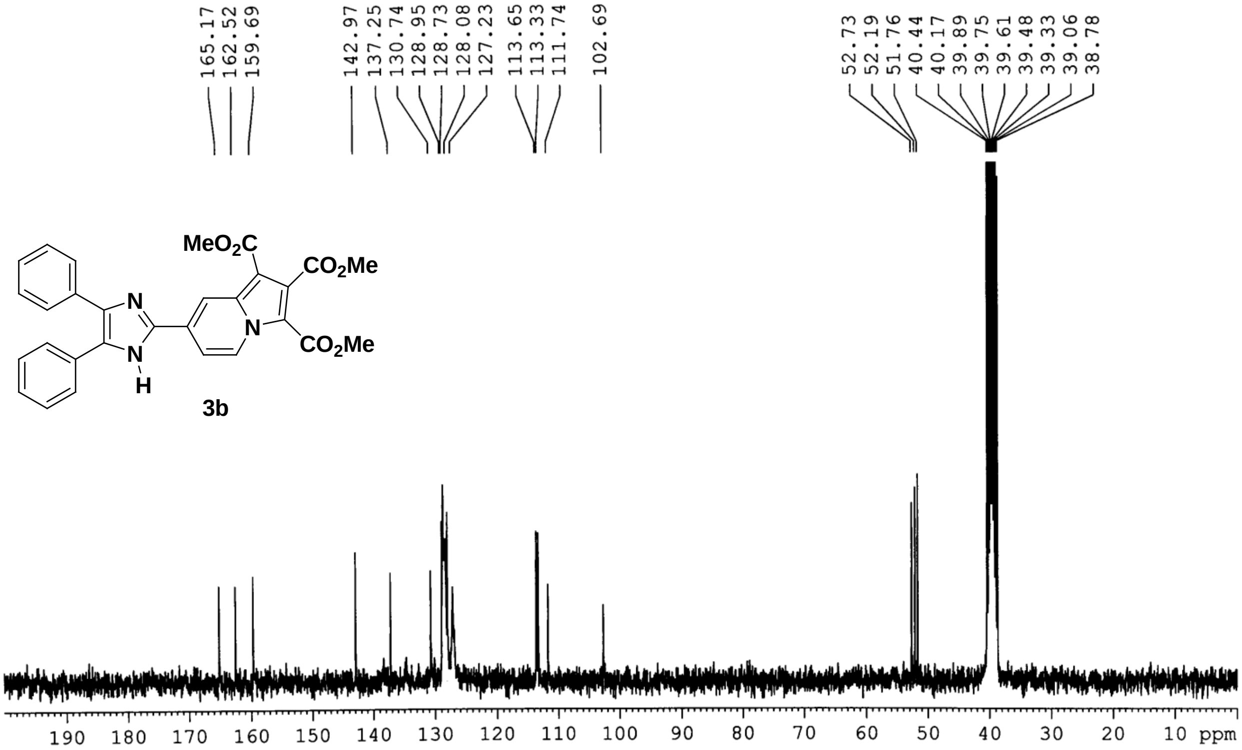

10.039
9.540
9.517
9.499
8.789
7.490
7.465
7.265
4.007
3.949
3.938
1.823
CHO
N
CO2Me
MeO2C
CO2Me
2b
10
9
8
7
6
5
4
3
2
1
ppm
4.87
5.11
5.03
4.78
46.38

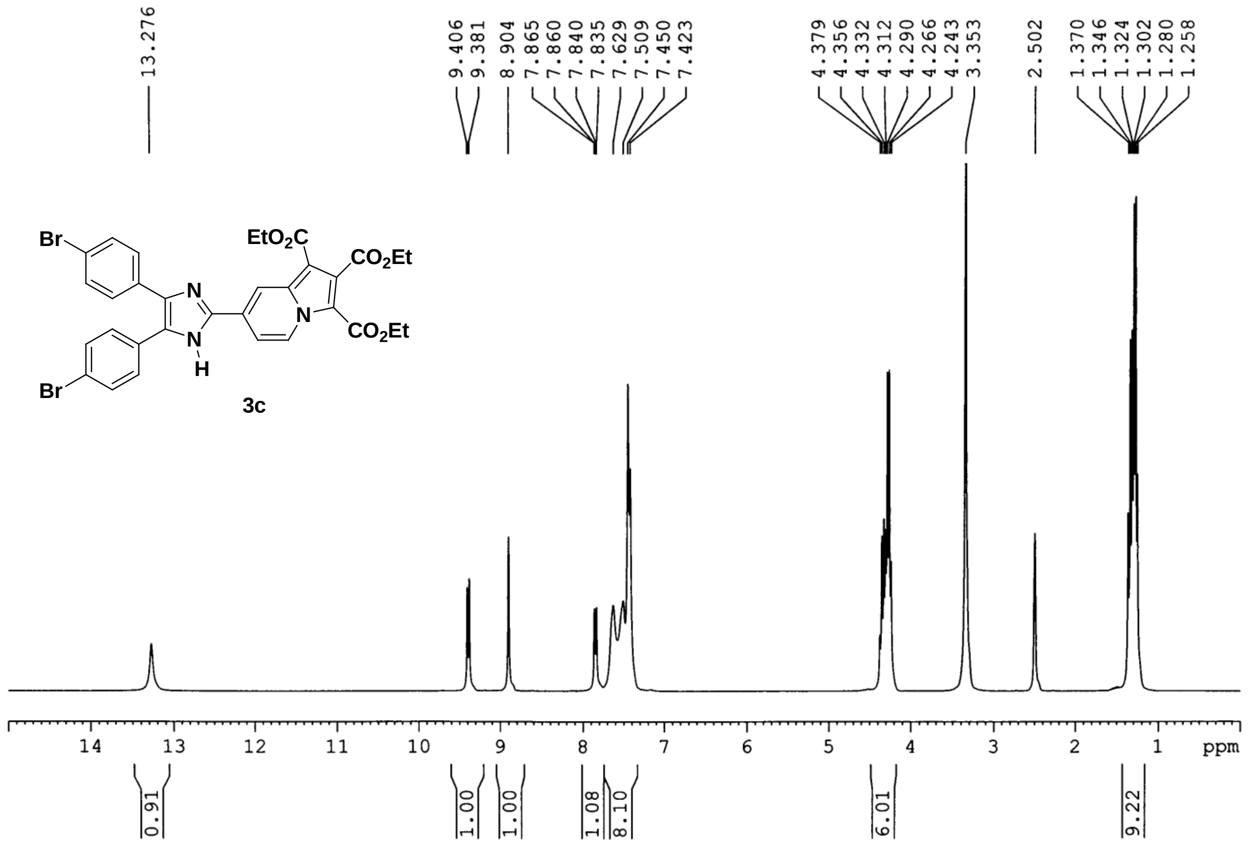

189.67
165.41
162.71
160.00
136.06
132.96
131.06
128.18
125.84
114.24
111.05
107.07
77.43
77.01
76.59
53.02
52.40
52.06
CHO
N
CO2Me
MeO2C
CO2Me
2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

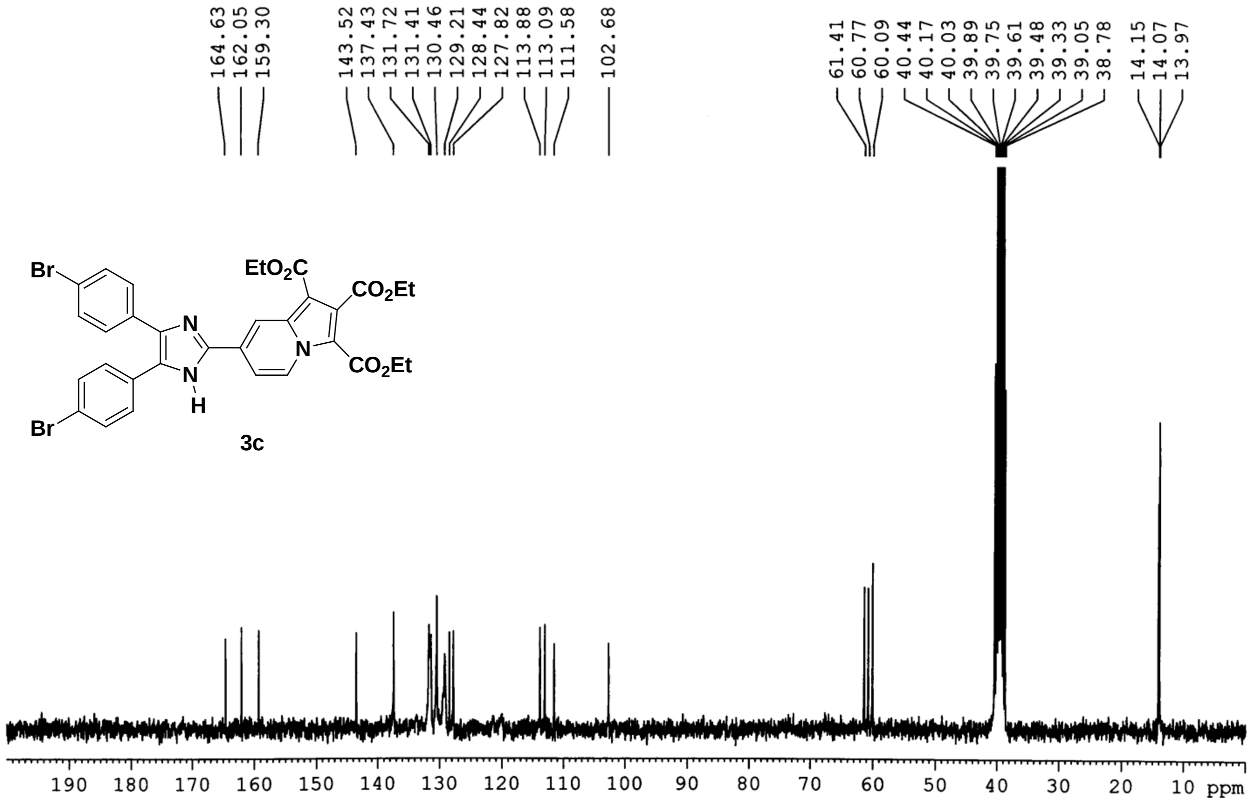

13.286
13.270
9.457
9.434
9.418
8.953
7.950
7.940
7.933
7.574
7.549
7.510
7.478
7.453
7.426
7.399
7.337
7.313
7.290
7.260
7.238
4.373
4.350
4.326
4.314
4.301
4.278
3.321
2.489
1.360
1.337
1.323
1.313
1.300
1.277
1.255
EtO2C
CO2Et
CO2Et
N
N
N
H
3a
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
3.31
2.79
3.30
3.25
13.02
10.17
6.78
3.37
18.63
1.06
3.03
31.31

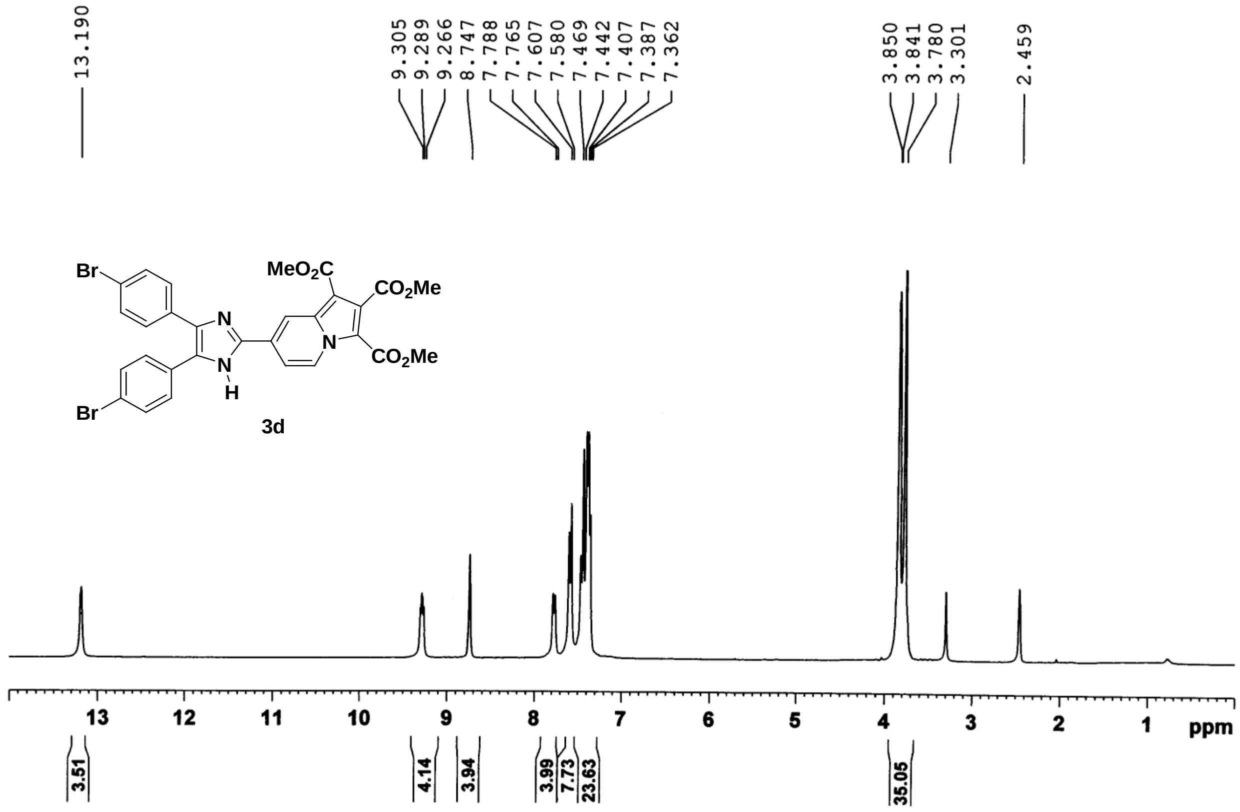

164.62
162.07
159.33
142.99
138.33
137.51
134.74
130.68
130.53
130.02
128.83
128.69
128.29
128.19
127.90
127.16
126.87
113.69
113.19
111.53
102.59
61.37
60.75
60.06
40.44
40.16
39.89
39.61
39.33
39.05
38.78
14.15
13.99
13.93
EtO2C
CO2Et
CO2Et
N
N
N
H
3a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

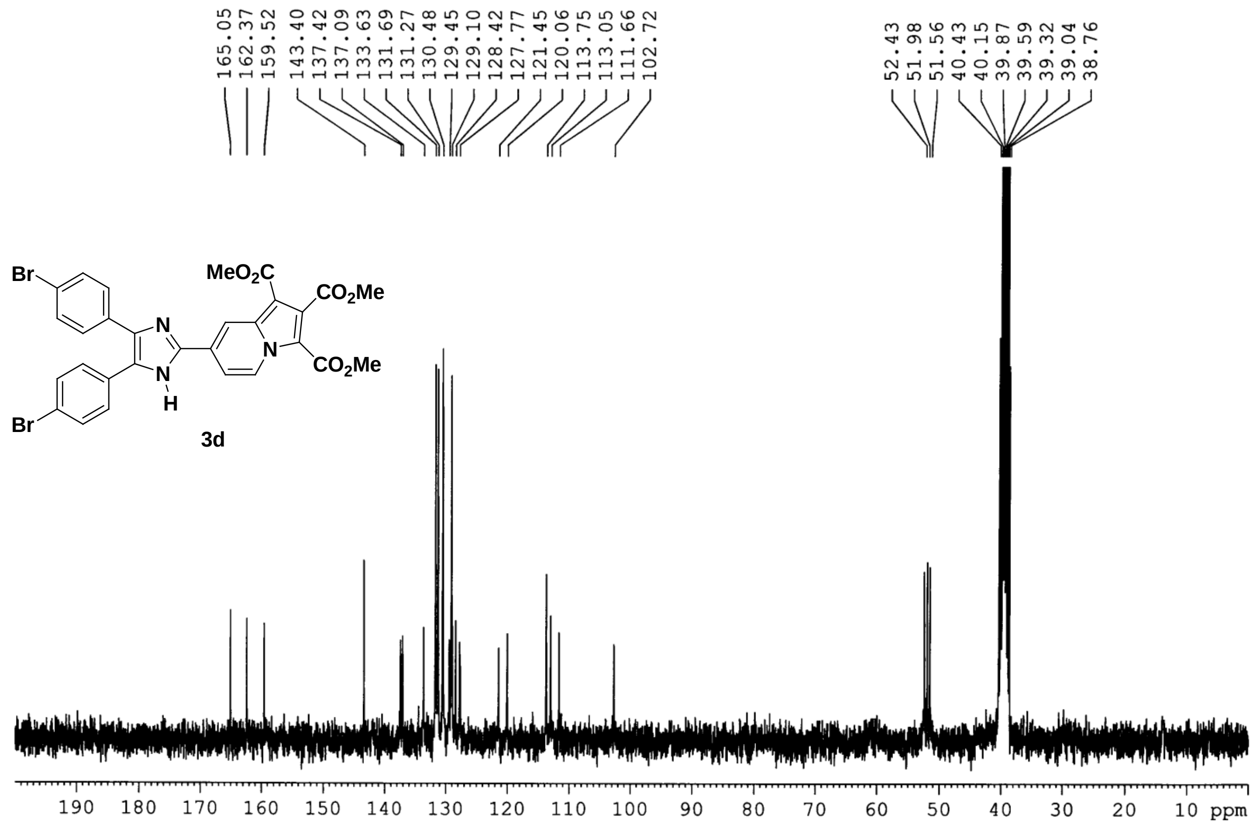

13.282
9.403
9.379
8.853
7.947
7.941
7.922
7.916
7.503
7.398
7.342
7.313
7.256
3.862
3.817
3.325
2.466
MeO2C
CO2Me
CO2Me
N
N
H
N
3b
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.55
2.89
2.73
2.68
12.22
19.06
25.74
25.13
4.91

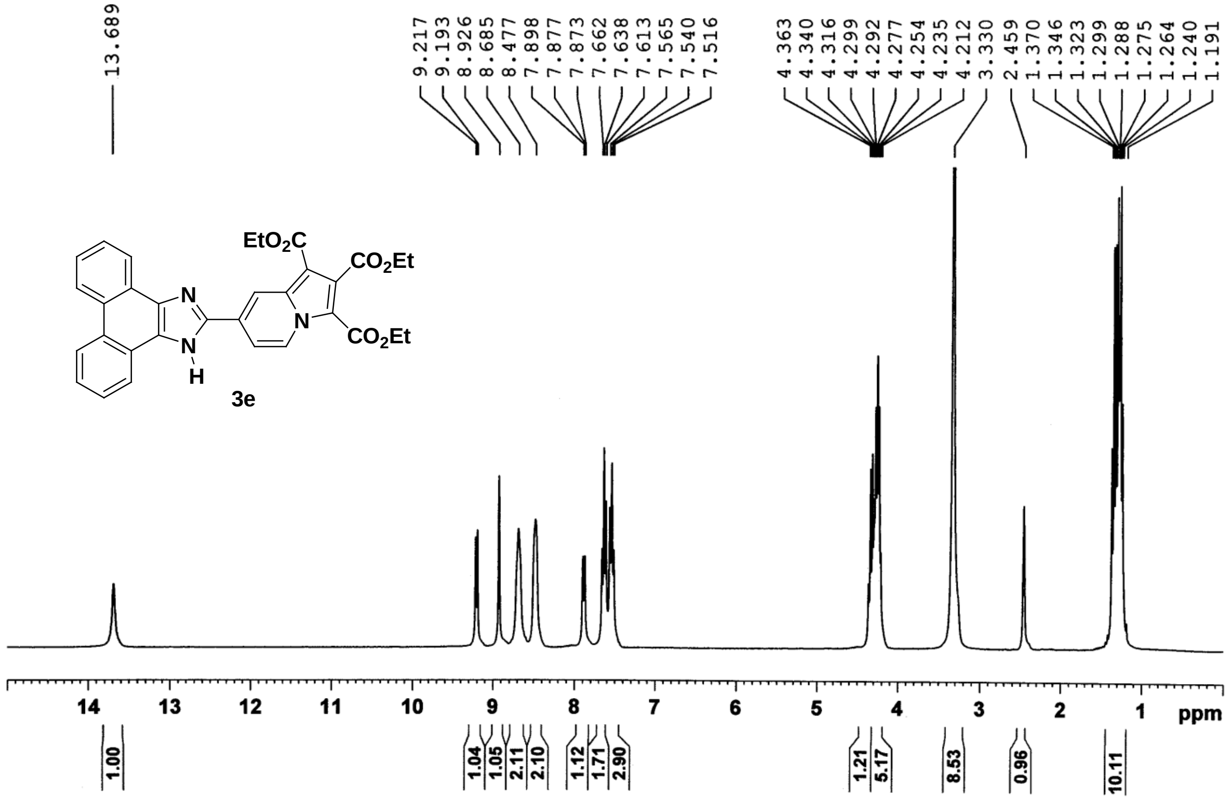

165.17
162.52
159.69
142.97
137.25
130.74
128.95
128.73
128.08
127.23
113.65
113.33
111.74
102.69
52.73
52.19
51.76
40.44
40.17
39.89
39.75
39.61
39.48
39.33
39.06
38.78
MeO2C
CO2Me
CO2Me
N
N
H
N
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

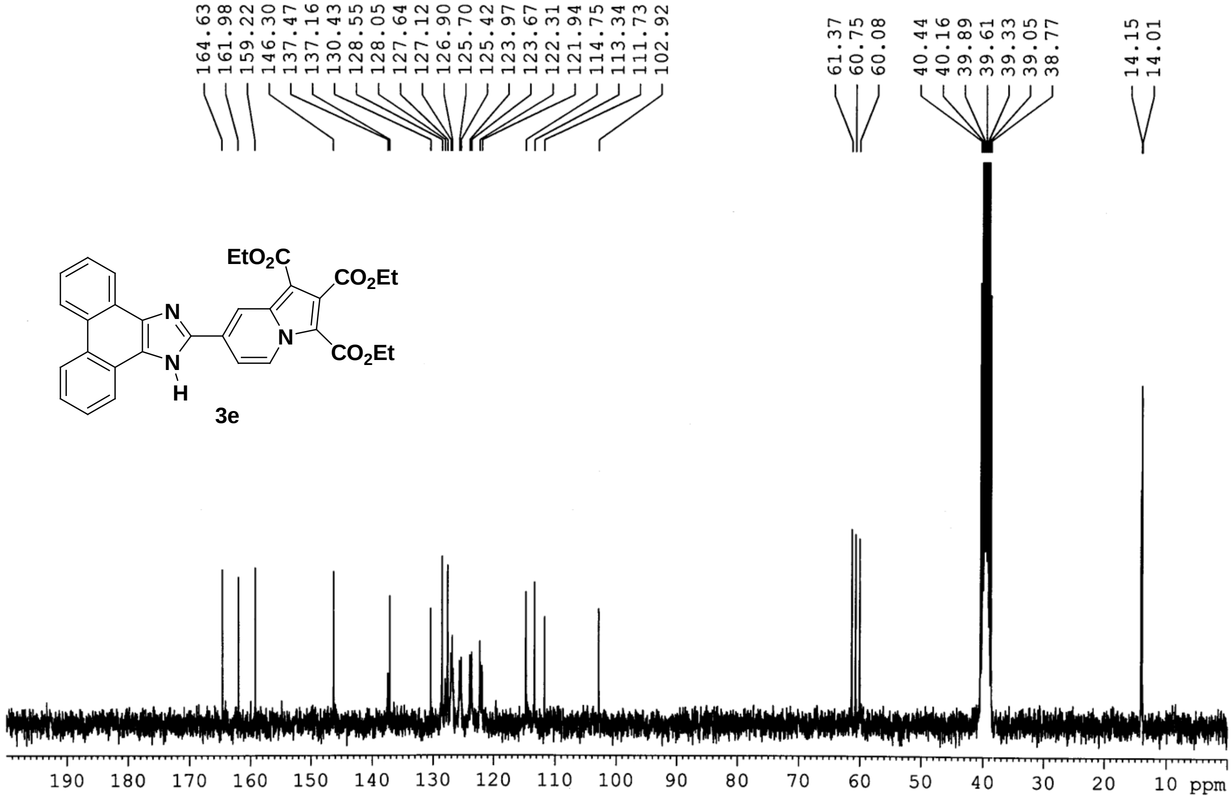

13.276
9.406
9.381
8.904
7.865
7.860
7.840
7.835
7.629
7.509
7.450
7.423
4.379
4.356
4.332
4.312
4.290
4.266
4.243
3.353
2.502
1.370
1.346
1.324
1.302
1.280
1.258
Br
Br
EtO$_2$C
CO$_2$Et
CO$_2$Et
N
N
N
H
3c
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.91
1.00
1.00
1.08
8.10
6.01
9.22

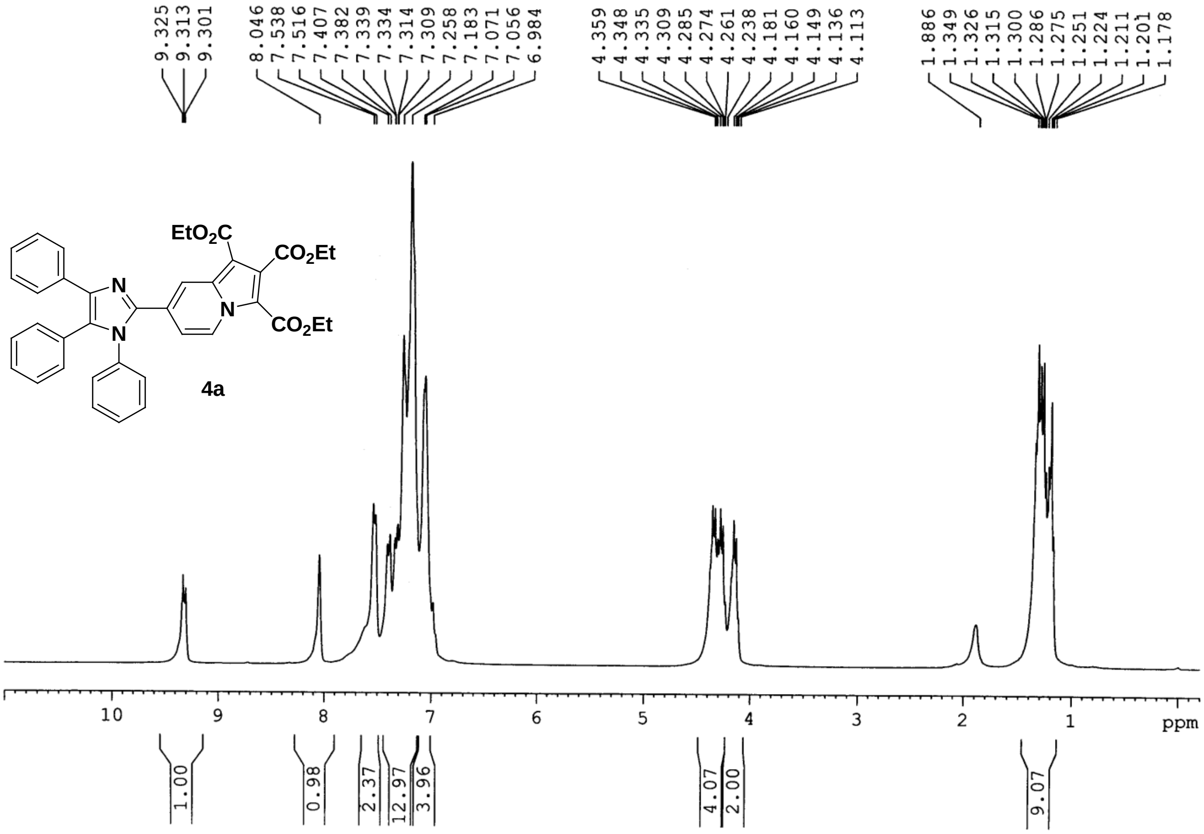

164.63
162.05
159.30
143.52
137.43
131.72
131.41
130.46
129.21
128.44
127.82
113.88
113.09
111.58
102.68
61.41
60.77
60.09
40.44
40.17
40.03
39.89
39.75
39.61
39.48
39.33
39.05
38.78
14.15
14.07
13.97
Br
Br
EtO$_2$C
CO$_2$Et
CO$_2$Et
N
N
N
H
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

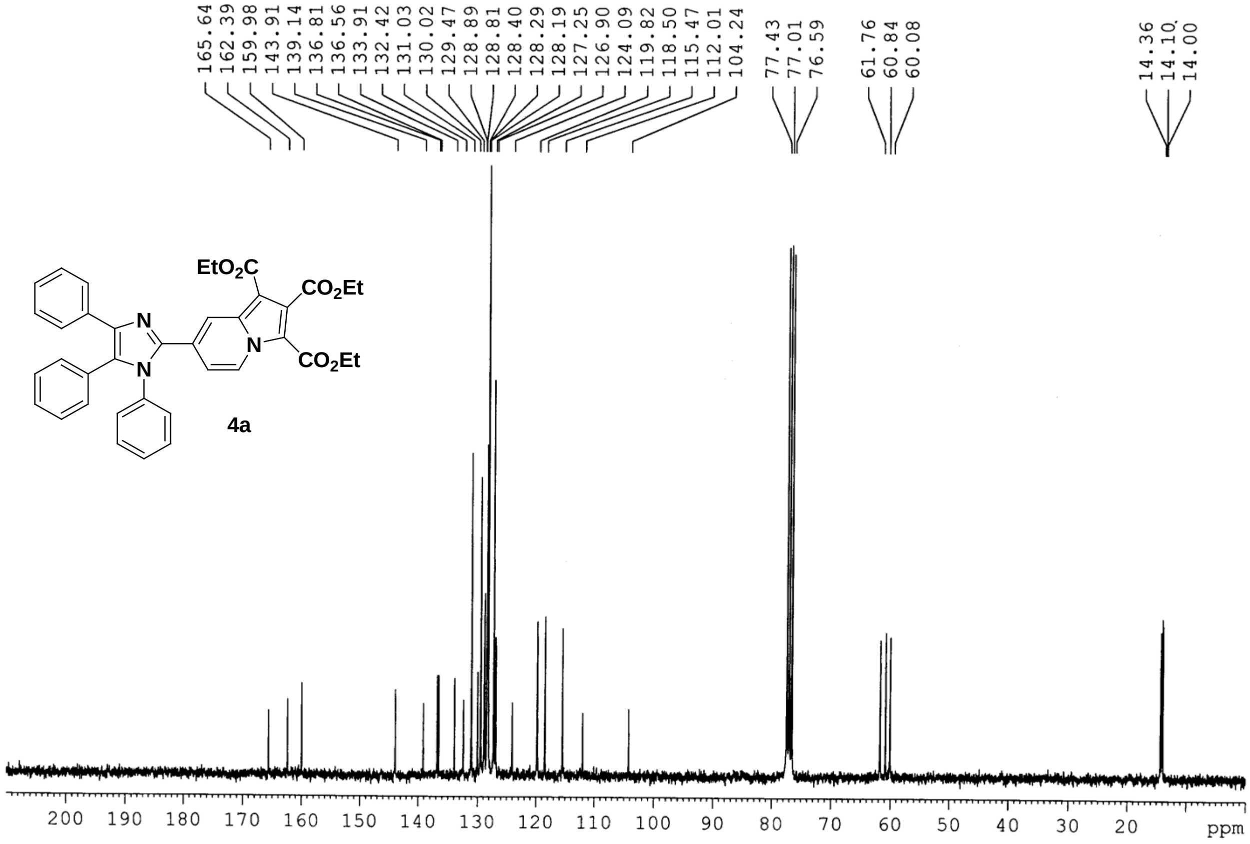

13.190
9.305
9.289
9.266
8.747
7.788
7.765
7.607
7.580
7.469
7.442
7.407
7.387
7.362
3.850
3.841
3.780
3.301
2.459
Br
Br
MeO$_2$C
CO$_2$Me
CO$_2$Me
N
N
H
3d
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
3.51
4.14
3.94
3.99
7.73
23.63
35.05

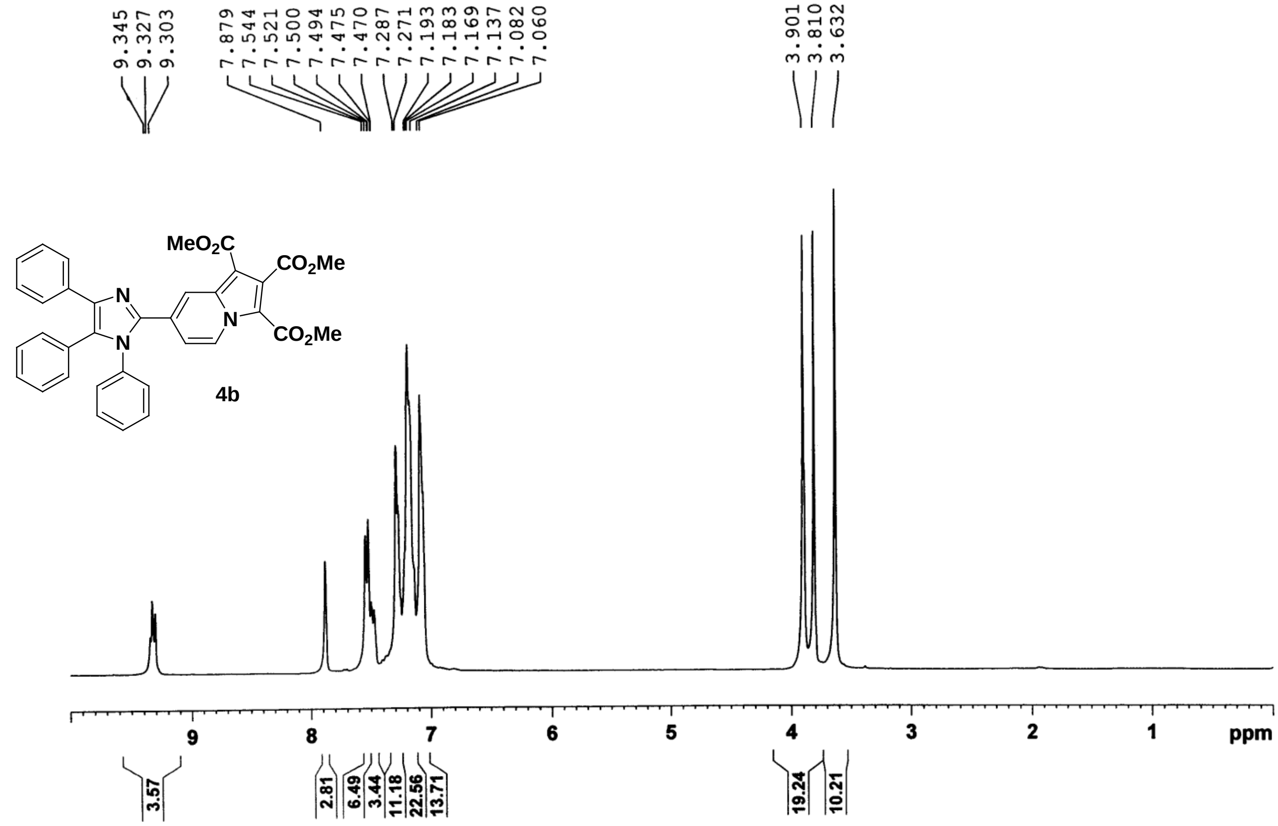

165.05
162.37
159.52
143.40
137.42
137.09
133.63
131.69
131.27
130.48
129.45
129.10
128.42
127.77
121.45
120.06
113.75
113.05
111.66
102.72
52.43
51.98
51.56
40.43
40.15
39.87
39.59
39.32
39.04
38.76
Br
Br
MeO$_2$C
CO$_2$Me
CO$_2$Me
N
N
H
3d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

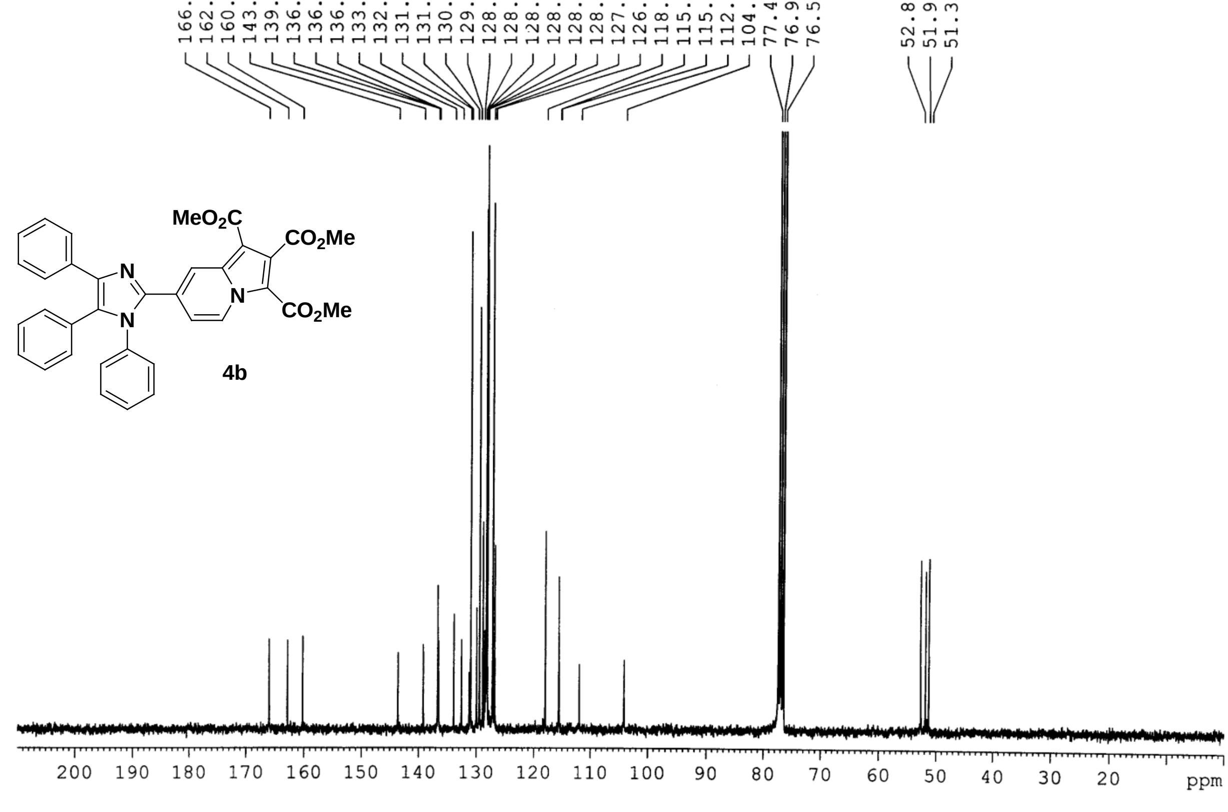

13.689
9.217
9.193
8.926
8.685
8.477
7.898
7.877
7.873
7.662
7.638
7.613
7.565
7.540
7.516
4.363
4.340
4.316
4.299
4.292
4.277
4.254
4.235
4.212
3.330
2.459
1.370
1.346
1.323
1.299
1.288
1.275
1.264
1.240
1.191
EtO2C
CO2Et
CO2Et
N
N
H
N
3e
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.04
1.05
2.11
2.10
1.12
1.71
2.90
1.21
5.17
8.53
0.96
10.11

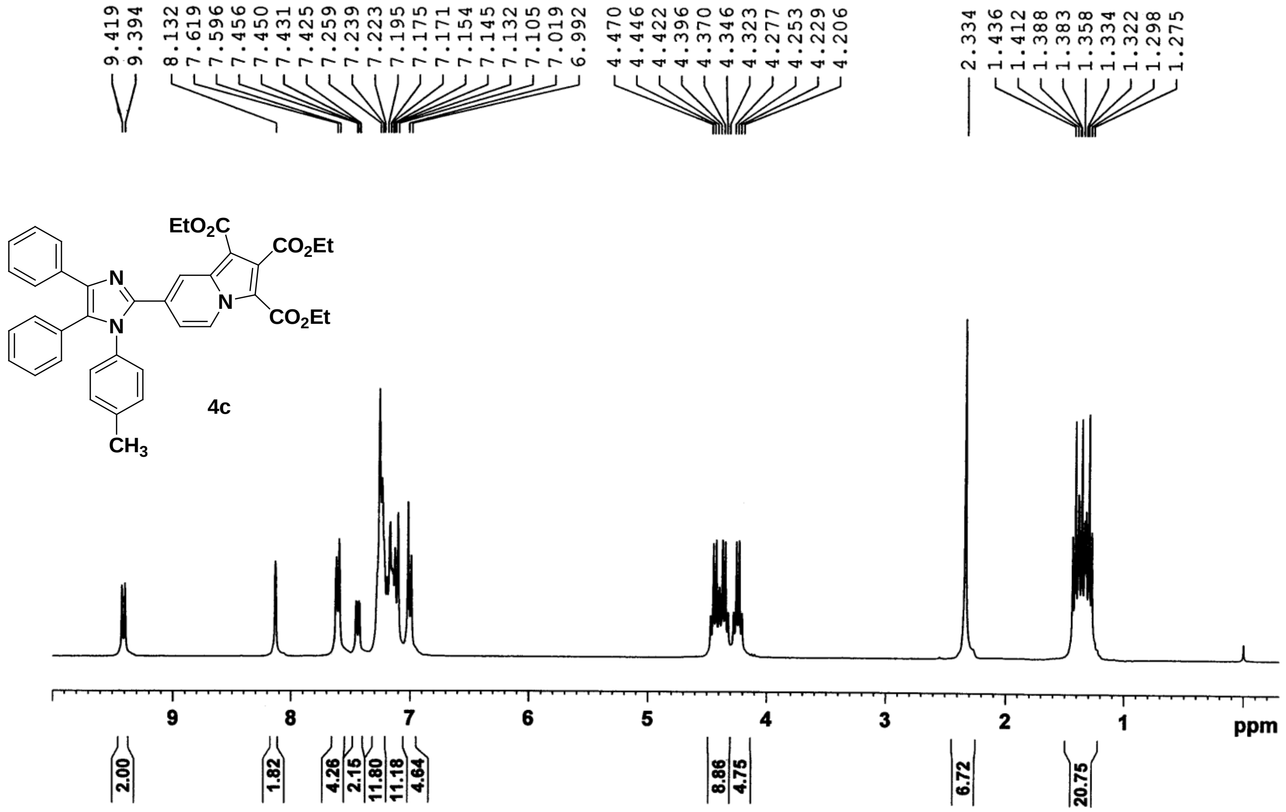

164.63
161.98
159.22
146.30
137.47
137.16
130.43
128.55
128.05
127.64
127.12
126.90
125.70
125.42
123.97
123.67
122.31
121.94
114.75
113.34
111.73
102.92
61.37
60.75
60.08
40.44
40.16
39.89
39.61
39.33
39.05
38.77
14.15
14.01
EtO2C
CO2Et
CO2Et
N
N
H
N
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

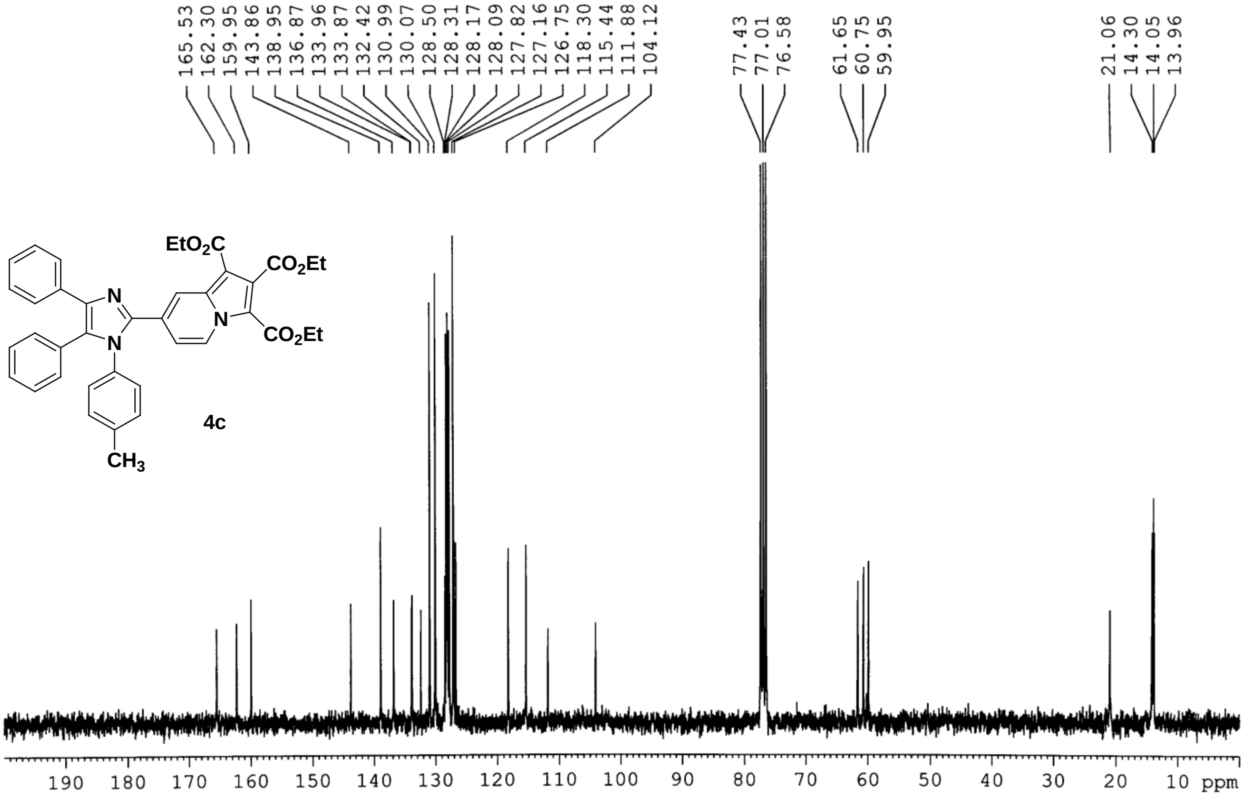

9.325
9.313
9.301
8.046
7.538
7.516
7.407
7.382
7.339
7.334
7.314
7.309
7.258
7.183
7.071
7.056
6.984
4.359
4.348
4.335
4.309
4.285
4.274
4.261
4.238
4.181
4.160
4.149
4.136
4.113
1.886
1.349
1.326
1.315
1.300
1.286
1.275
1.251
1.224
1.211
1.201
1.178
EtO2C
CO2Et
CO2Et
N
N
N
4a
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
2.37
12.97
3.96
4.07
2.00
9.07

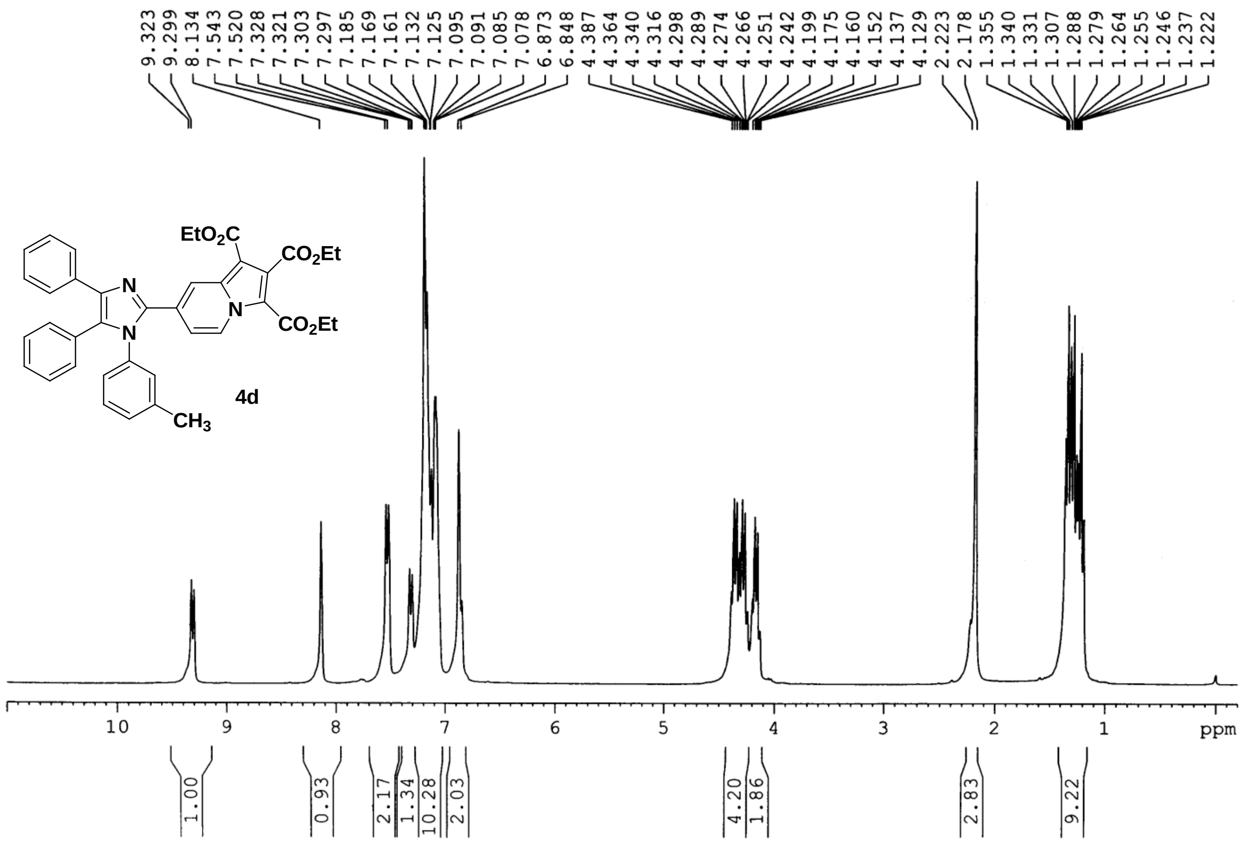

165.64
162.39
159.98
143.91
139.14
136.81
136.56
133.91
132.42
131.03
130.02
129.47
128.89
128.81
128.40
128.29
128.19
127.25
126.90
124.09
119.82
118.50
115.47
112.01
104.24
77.43
77.01
76.59
61.76
60.84
60.08
14.36
14.10
14.00
EtO2C
CO2Et
CO2Et
N
N
N
4a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

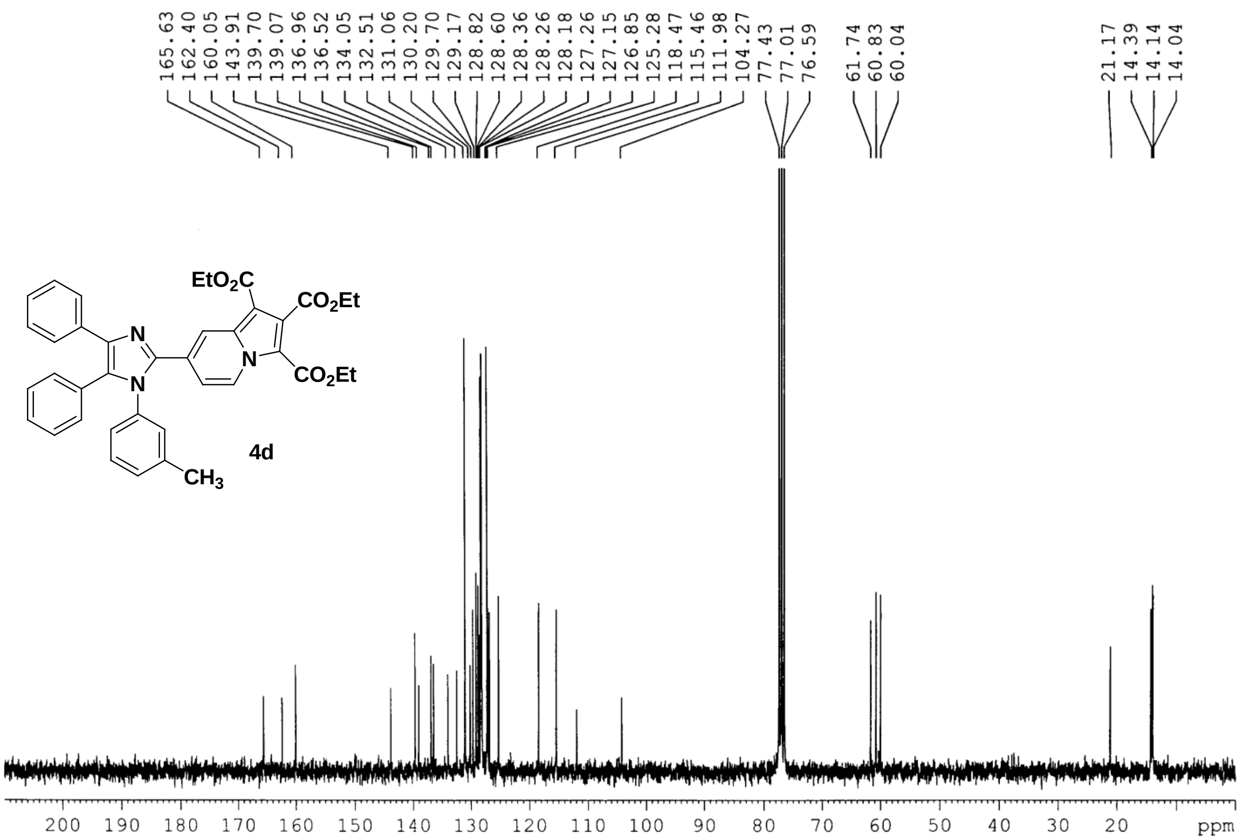

9.345
9.327
9.303
7.879
7.544
7.521
7.500
7.494
7.475
7.470
7.287
7.271
7.193
7.183
7.169
7.137
7.082
7.060
3.901
3.810
3.632
MeO$_2$C
CO$_2$Me
CO$_2$Me
N
N
N
4b
9
8
7
6
5
4
3
2
1
ppm
3.57
2.81
6.49
3.44
11.18
22.56
13.71
19.24
10.21

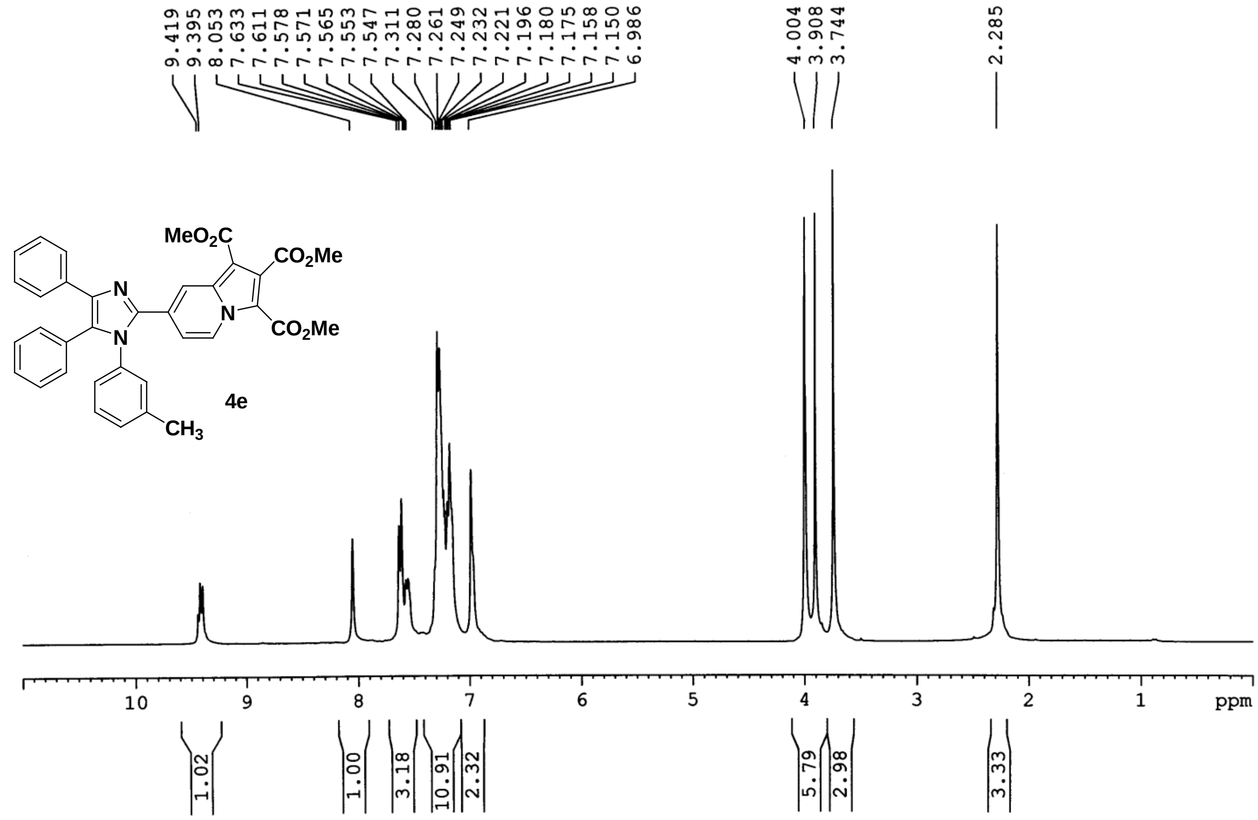

166.04
162.87
160.27
143.62
139.23
136.71
136.57
136.51
133.92
132.60
131.29
131.05
130.01
129.51
128.95
128.63
128.53
128.41
128.30
128.20
127.27
126.94
118.04
115.66
115.57
112.07
104.17
77.42
76.99
76.57
52.82
51.94
51.35
MeO$_2$C
CO$_2$Me
CO$_2$Me
N
N
N
4b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

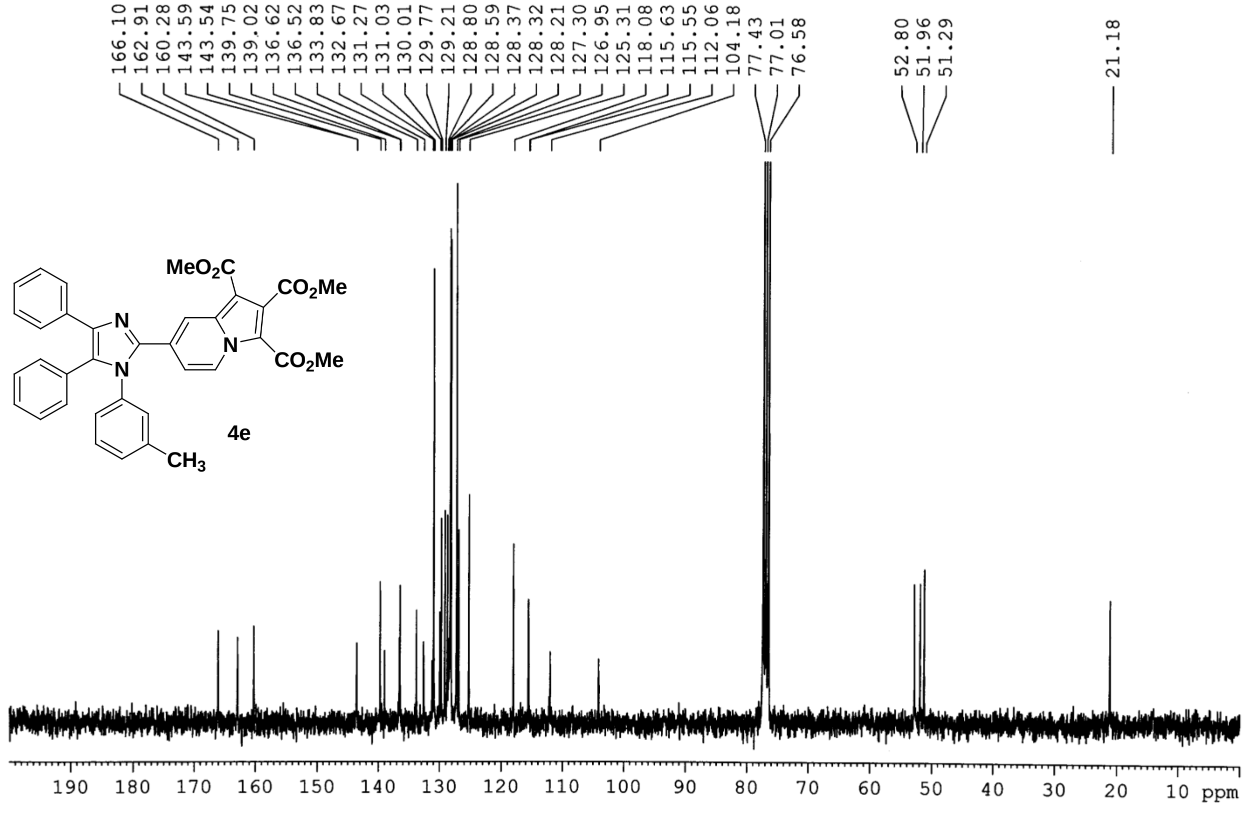

9.419
9.394
8.132
7.619
7.596
7.456
7.450
7.431
7.425
7.259
7.239
7.223
7.195
7.175
7.171
7.154
7.145
7.132
7.105
7.019
6.992
4.470
4.446
4.422
4.396
4.370
4.346
4.323
4.277
4.253
4.229
4.206
2.334
1.436
1.412
1.388
1.383
1.358
1.334
1.322
1.298
1.275
EtO₂C
CO₂Et
CO₂Et
N
N
N
CH₃
4c
9
8
7
6
5
4
3
2
1
ppm
2.00
1.82
4.26
2.15
11.80
11.18
4.64
8.86
4.75
6.72
20.75

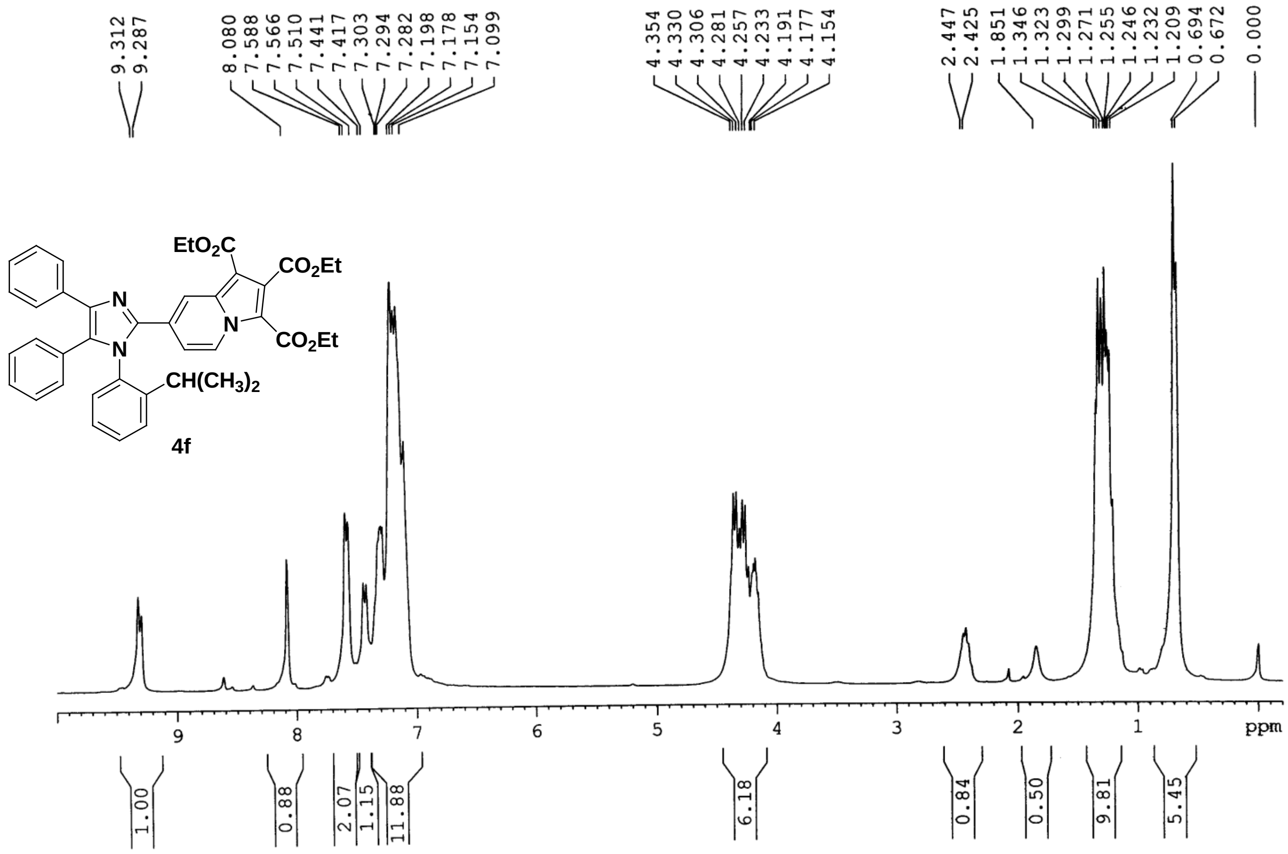

165.53
162.30
159.95
143.86
138.95
136.87
133.96
133.87
132.42
130.99
130.07
128.50
128.31
128.17
128.09
127.82
127.16
126.75
118.30
115.44
111.88
104.12
77.43
77.01
76.58
61.65
60.75
59.95
21.06
14.30
14.05
13.96
EtO₂C
CO₂Et
CO₂Et
N
N
N
CH₃
4c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

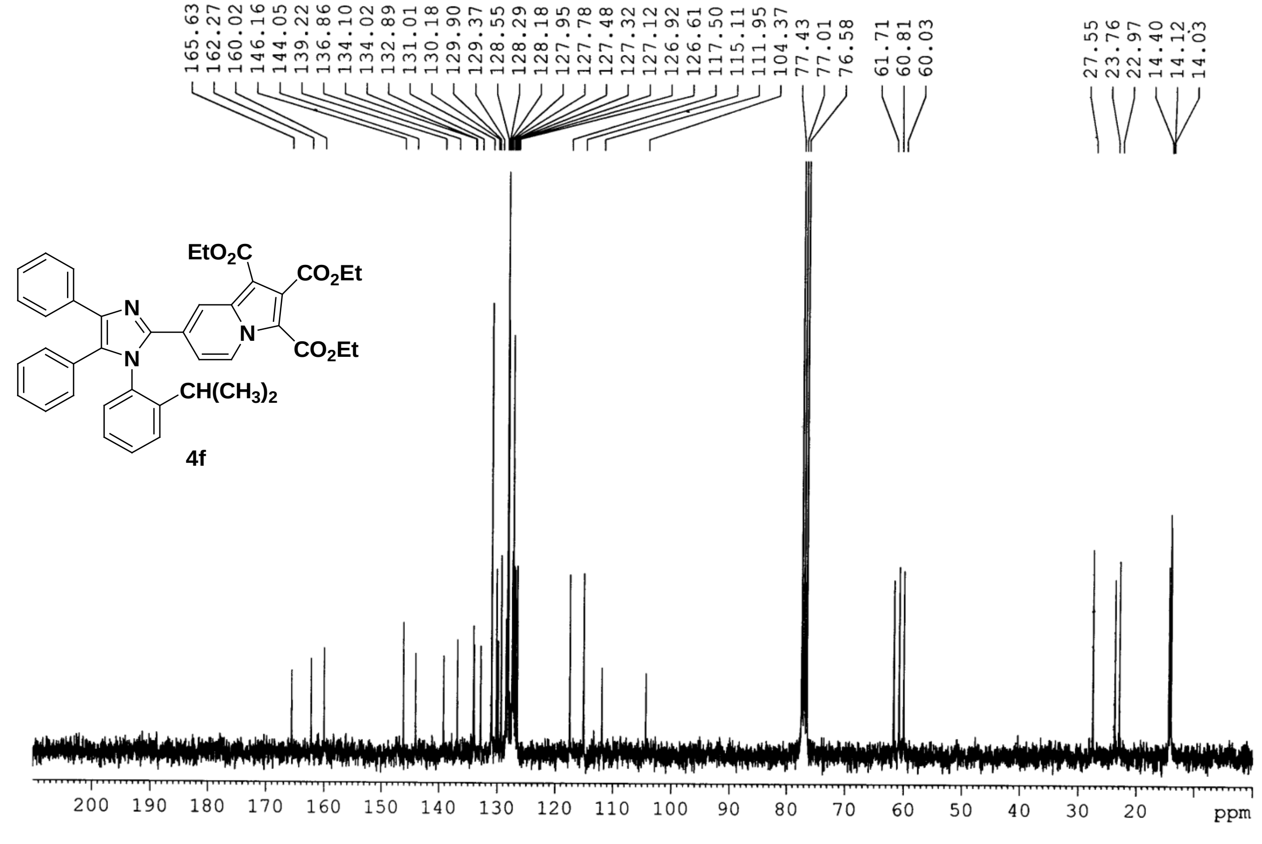

9.323
9.299
8.134
7.543
7.520
7.328
7.321
7.303
7.297
7.185
7.169
7.161
7.132
7.125
7.095
7.091
7.085
7.078
6.873
6.848
4.387
4.364
4.340
4.316
4.298
4.289
4.274
4.266
4.251
4.242
4.199
4.175
4.160
4.152
4.137
4.129
2.223
2.178
1.355
1.340
1.331
1.307
1.288
1.279
1.264
1.255
1.246
1.237
1.222
EtO2C
CO2Et
CO2Et
N
N
N
CH3
4d
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.93
2.17
1.34
10.28
2.03
4.20
1.86
2.83
9.22

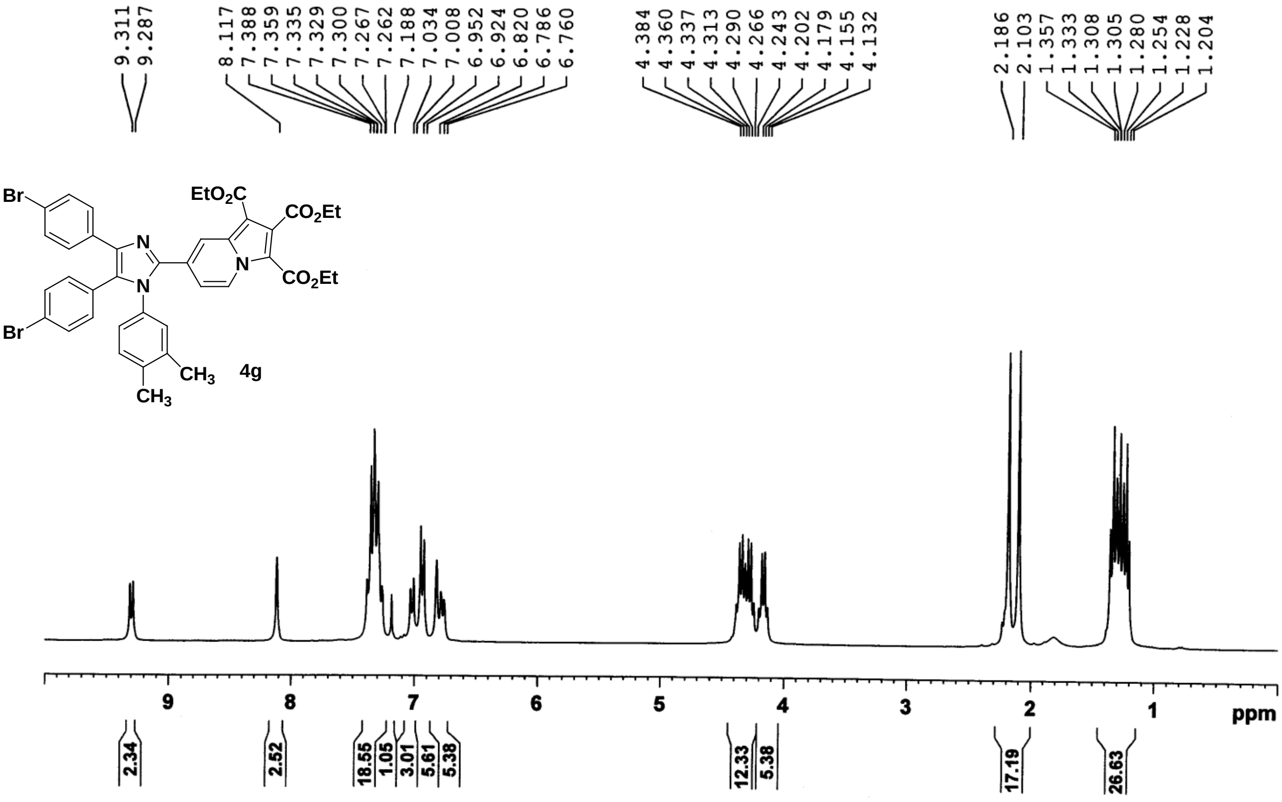

165.63
162.40
160.05
143.91
139.70
139.07
136.96
136.52
134.05
132.51
131.06
130.20
129.70
129.17
128.82
128.60
128.36
128.26
128.18
127.26
127.15
126.85
125.28
118.47
115.46
111.98
104.27
77.43
77.01
76.59
61.74
60.83
60.04
21.17
14.39
14.14
14.04
EtO2C
CO2Et
CO2Et
N
N
N
CH3
4d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

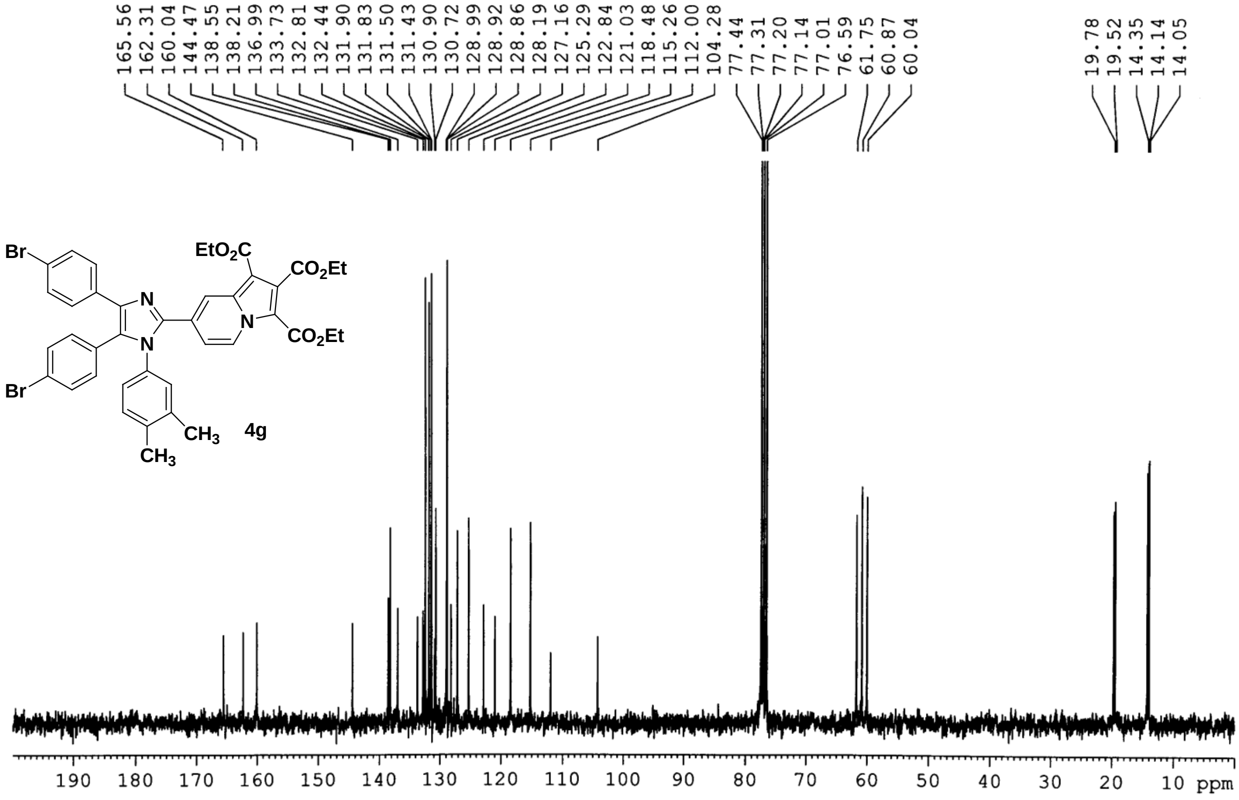

9.419
9.395
8.053
7.633
7.611
7.578
7.571
7.565
7.553
7.547
7.311
7.280
7.261
7.249
7.232
7.221
7.196
7.180
7.175
7.158
7.150
6.986
4.004
3.908
3.744
2.285
MeO2C
CO2Me
CO2Me
N
N
N
CH3
4e
10
9
8
7
6
5
4
3
2
1
ppm
1.02
1.00
3.18
10.91
2.32
5.79
2.98
3.33

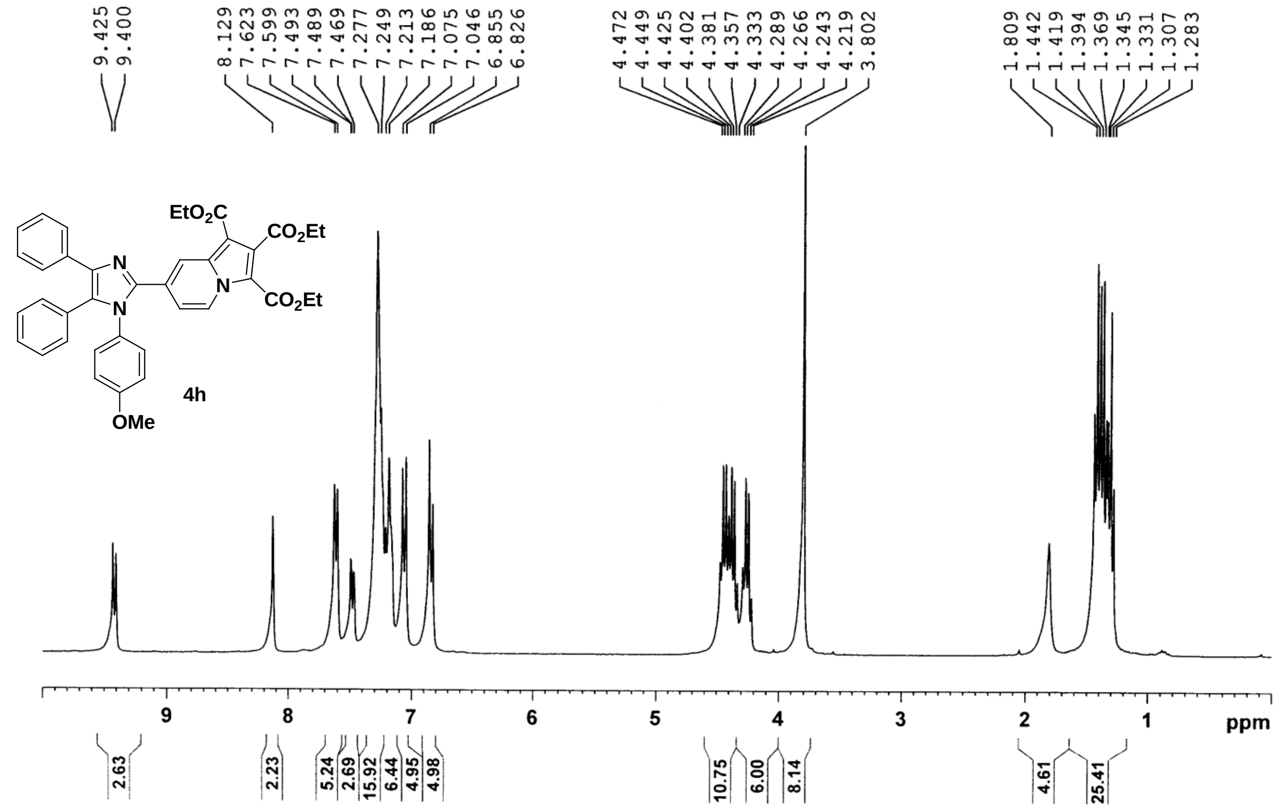

166.10
162.91
160.28
143.59
143.54
139.75
139.02
136.62
136.52
133.83
132.67
131.27
131.03
130.01
129.77
129.21
128.80
128.59
128.37
128.32
128.21
127.30
126.95
125.31
118.08
115.63
115.55
112.06
104.18
77.43
77.01
76.58
52.80
51.96
51.29
21.18
MeO2C
CO2Me
CO2Me
N
N
N
CH3
4e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

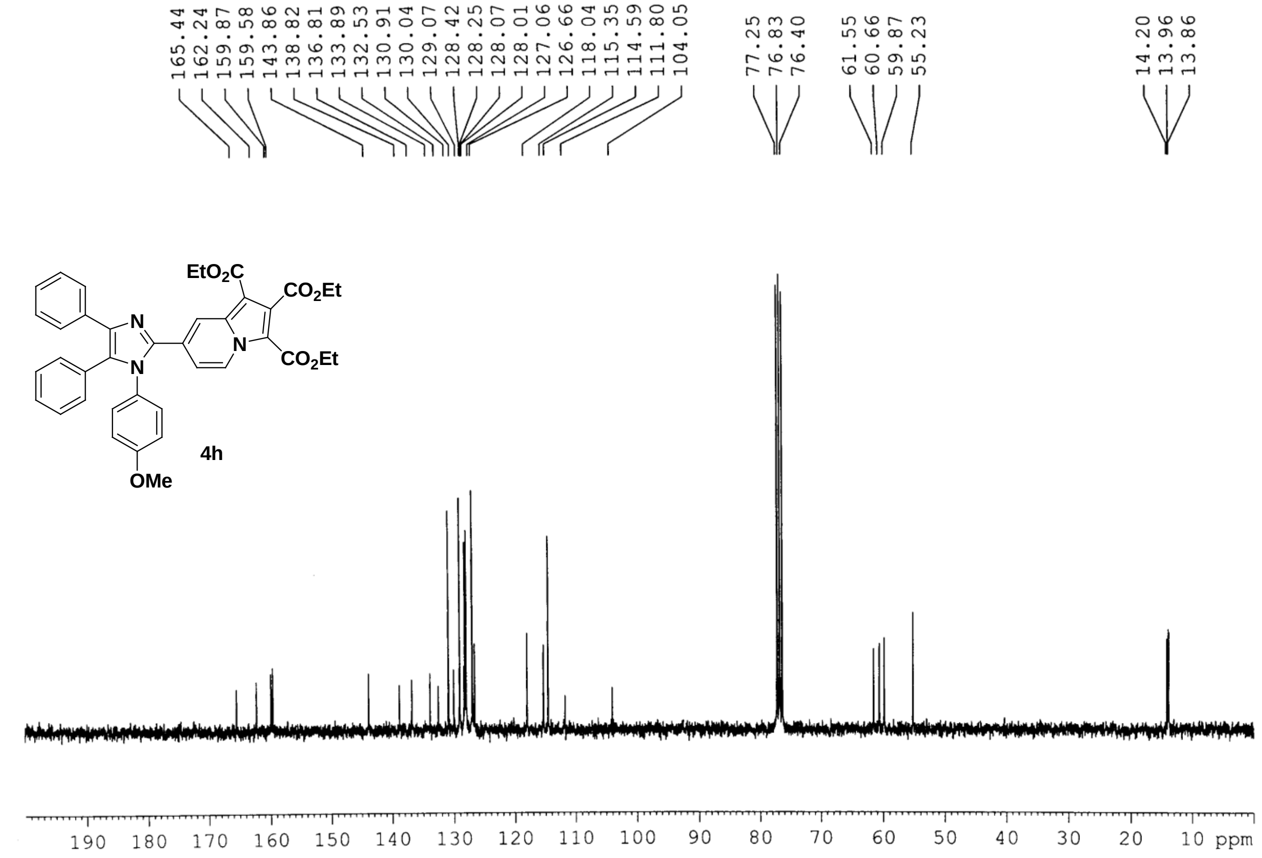

9.312
9.287
8.080
7.588
7.566
7.510
7.441
7.417
7.303
7.294
7.282
7.198
7.178
7.154
7.099
4.354
4.330
4.306
4.281
4.257
4.233
4.191
4.177
4.154
2.447
2.425
1.851
1.346
1.323
1.299
1.271
1.255
1.246
1.232
1.209
0.694
0.672
0.000
EtO2C
CO2Et
CO2Et
N
N
N
CH(CH3)2
4f
9
8
7
6
5
4
3
2
1
ppm
1.00
0.88
2.07
1.15
11.88
6.18
0.84
0.50
9.81
5.45

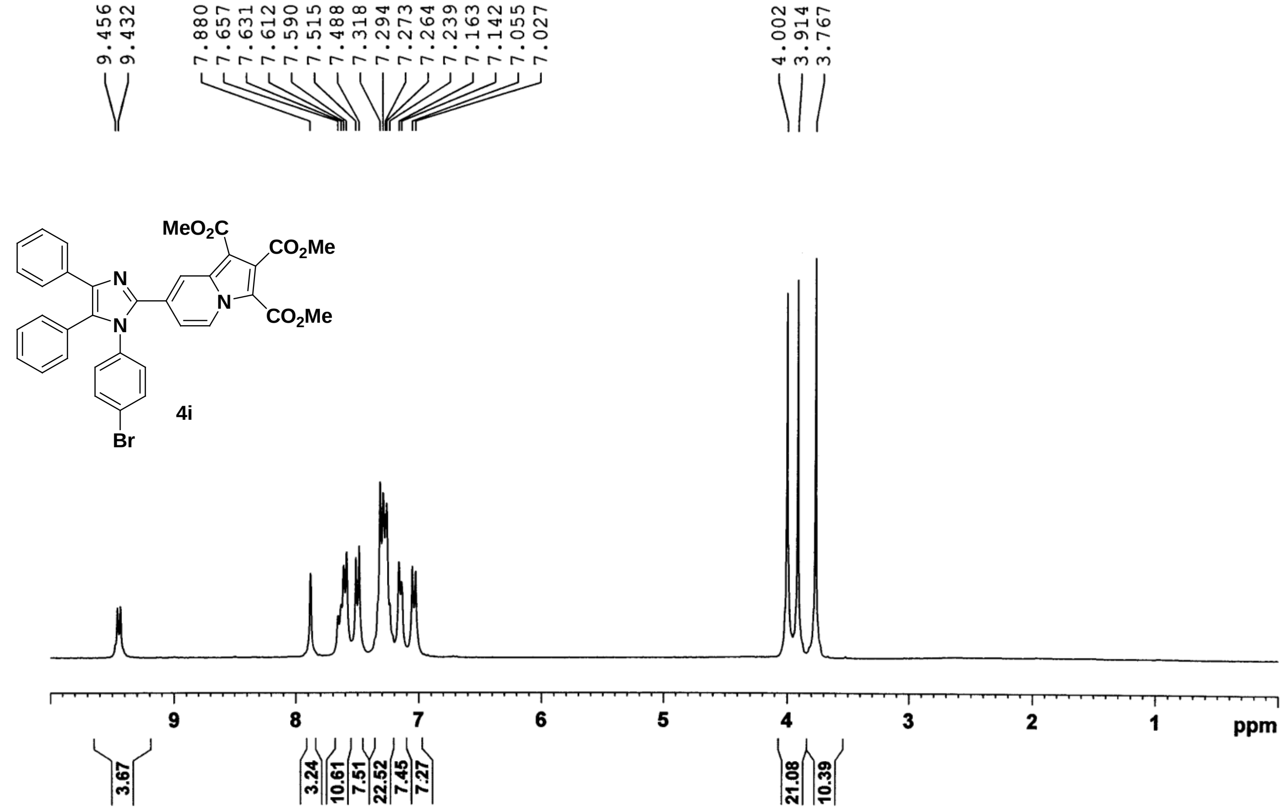

165.63
162.27
160.02
146.16
144.05
139.22
136.86
134.10
134.02
132.89
131.01
130.18
129.90
129.37
128.55
128.29
128.18
127.95
127.78
127.48
127.32
127.12
126.92
126.61
117.50
115.11
111.95
104.37
77.43
77.01
76.58
61.71
60.81
60.03
27.55
23.76
22.97
14.40
14.12
14.03
EtO2C
CO2Et
CO2Et
N
N
N
CH(CH3)2
4f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

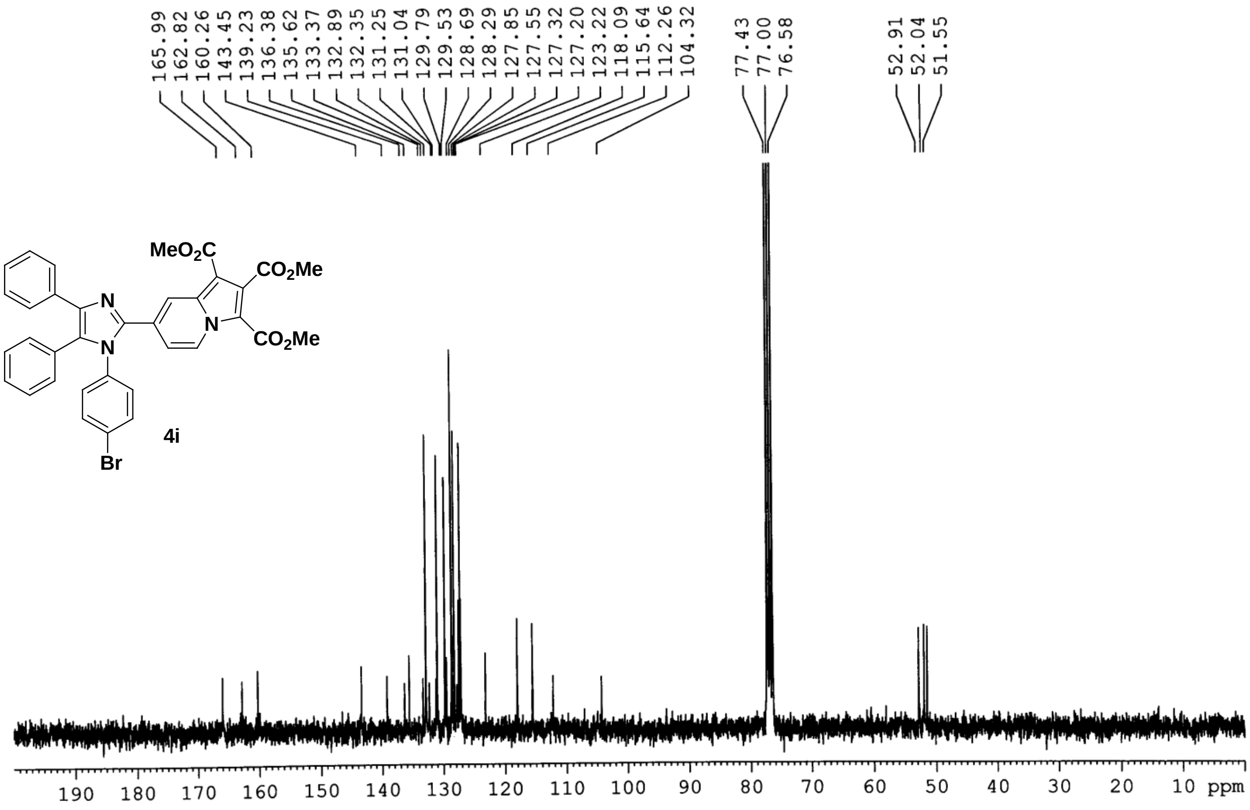

9.311
9.287
8.117
7.388
7.359
7.335
7.329
7.300
7.267
7.262
7.188
7.034
7.008
6.952
6.924
6.820
6.786
6.760
4.384
4.360
4.337
4.313
4.290
4.266
4.243
4.202
4.179
4.155
4.132
2.186
2.103
1.357
1.333
1.308
1.305
1.280
1.254
1.228
1.204
Br
EtO2C
CO2Et
N
N
N
CO2Et
Br
CH3
CH3
4g
9
8
7
6
5
4
3
2
1
ppm
2.34
2.52
18.55
1.05
3.01
5.61
5.38
12.33
5.38
17.19
26.63

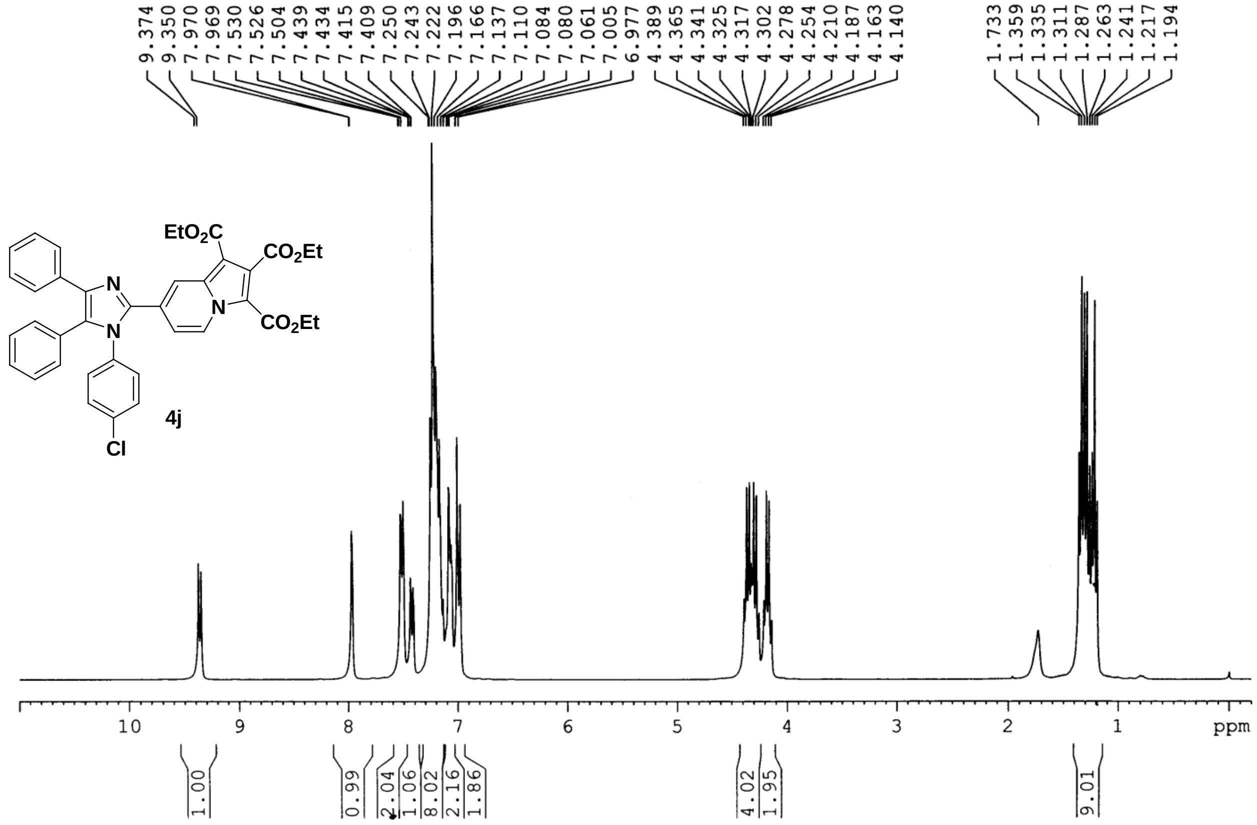

165.56
162.31
160.04
144.47
138.55
138.21
136.99
133.73
132.81
132.44
131.90
131.83
131.50
131.43
130.90
130.72
128.99
128.92
128.86
128.19
127.16
125.29
122.84
121.03
118.48
115.26
112.00
104.28
77.44
77.31
77.20
77.14
77.01
76.59
61.75
60.87
60.04
19.78
19.52
14.35
14.14
14.05
Br
EtO2C
CO2Et
N
N
N
CO2Et
Br
CH3
CH3
4g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

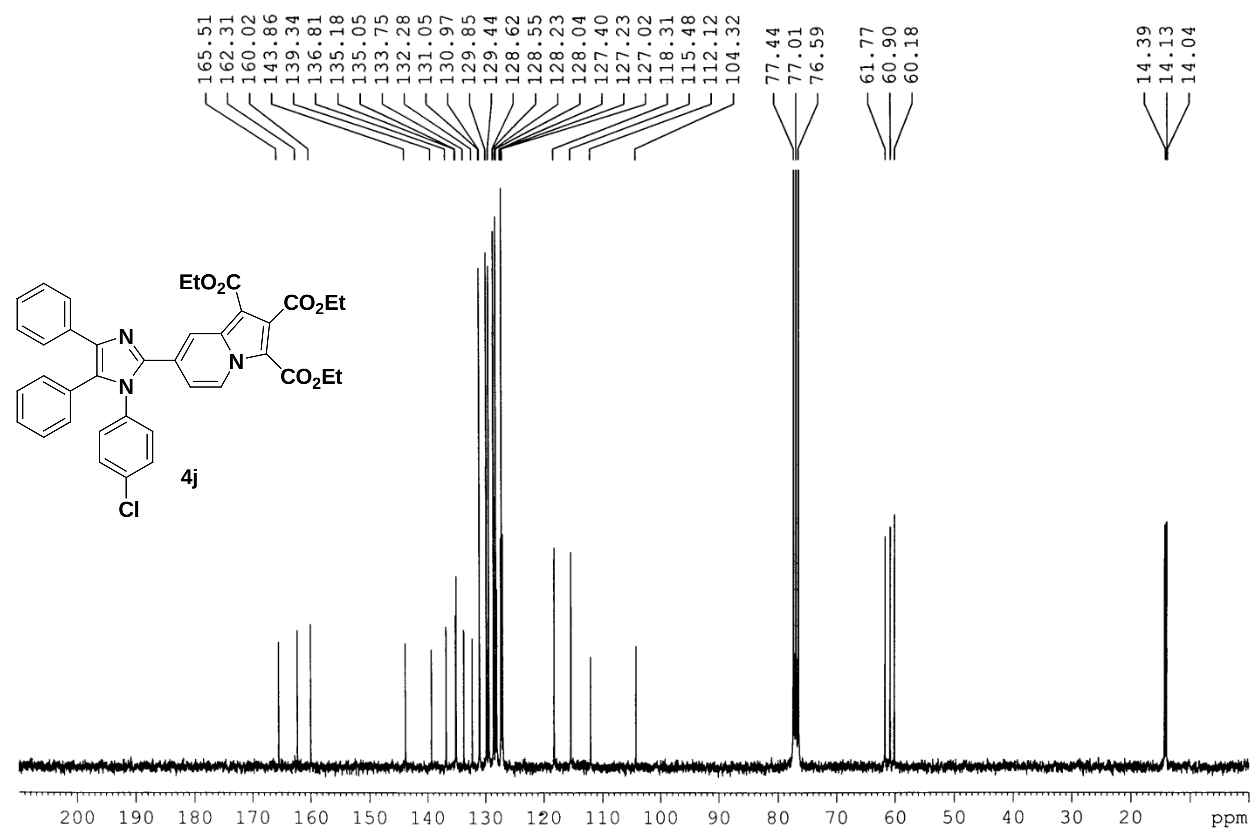

9.425
9.400
8.129
7.623
7.599
7.493
7.489
7.469
7.277
7.249
7.213
7.186
7.075
7.046
6.855
6.826
4.472
4.449
4.425
4.402
4.381
4.357
4.333
4.289
4.266
4.243
4.219
3.802
1.809
1.442
1.419
1.394
1.369
1.345
1.331
1.307
1.283
EtO2C
CO2Et
CO2Et
N
N
N
OMe
4h
9
8
7
6
5
4
3
2
1
ppm
2.63
2.23
5.24
2.69
15.92
6.44
4.95
4.98
10.75
6.00
8.14
4.61
25.41

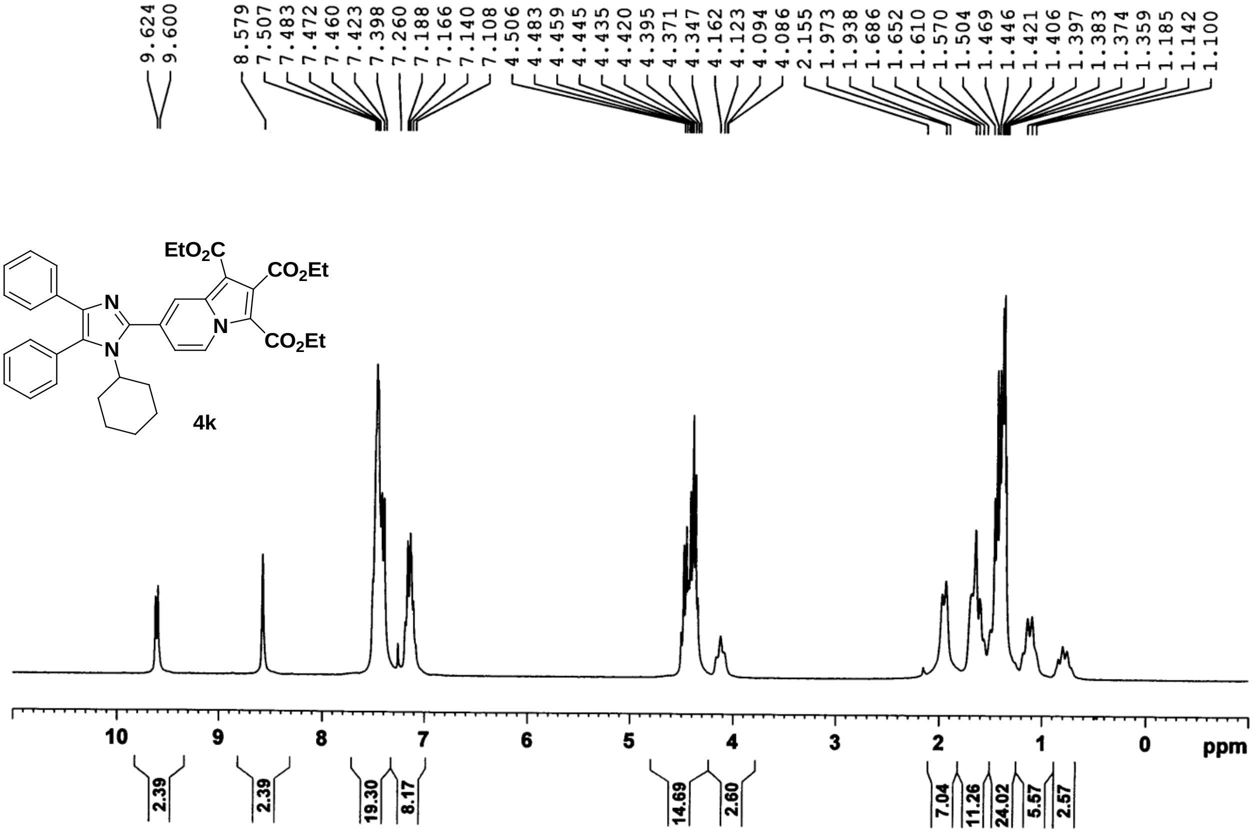

165.44
162.24
159.87
159.58
143.86
138.82
136.81
133.89
132.53
130.91
130.04
129.07
128.42
128.25
128.07
128.01
127.06
126.66
118.04
115.35
114.59
111.80
104.05
77.25
76.83
76.40
61.55
60.66
59.87
55.23
14.20
13.96
13.86
EtO2C
CO2Et
CO2Et
N
N
N
OMe
4h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

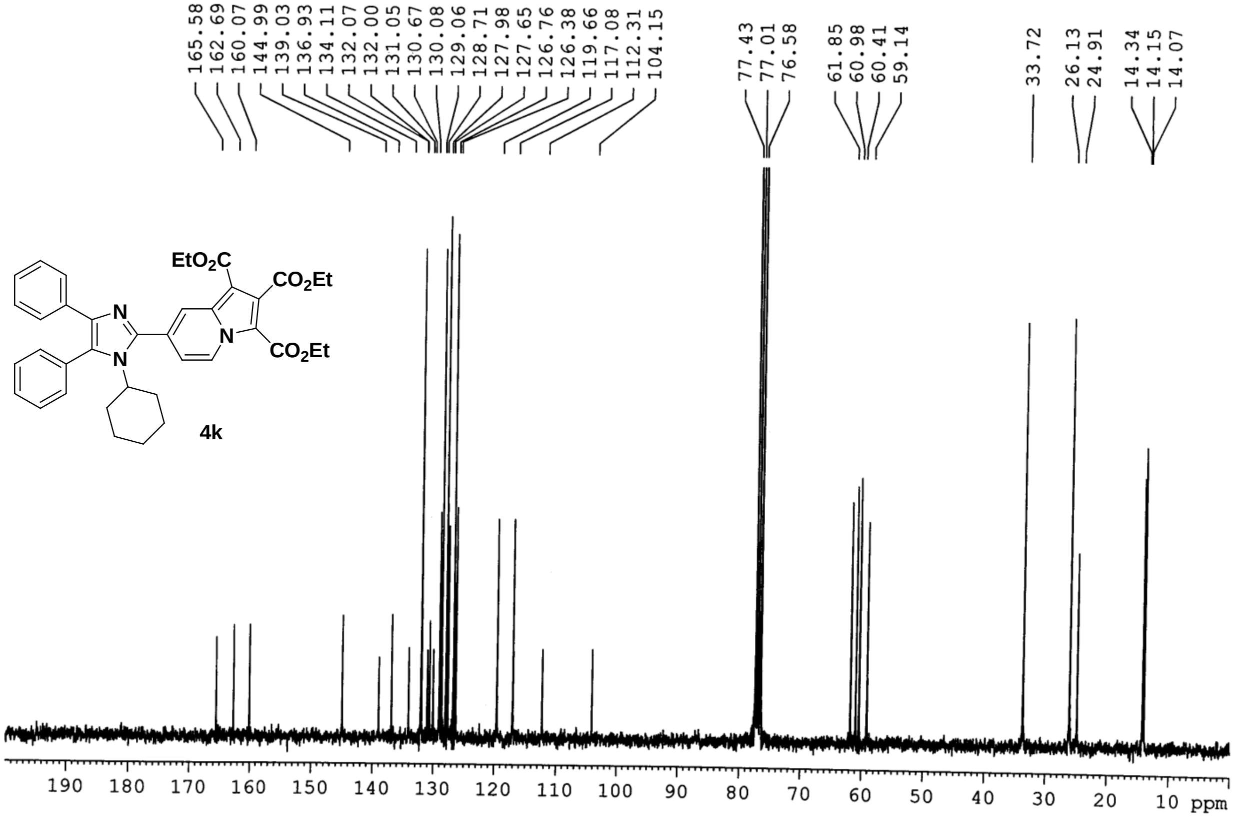

9.456
9.432
7.880
7.657
7.631
7.612
7.590
7.515
7.488
7.318
7.294
7.273
7.264
7.239
7.163
7.142
7.055
7.027
4.002
3.914
3.767
MeO$_2$C
CO$_2$Me
CO$_2$Me
N
N
N
4i
Br
9
8
7
6
5
4
3
2
1
ppm
3.67
3.24
10.61
7.51
22.52
7.45
7.27
21.08
10.39

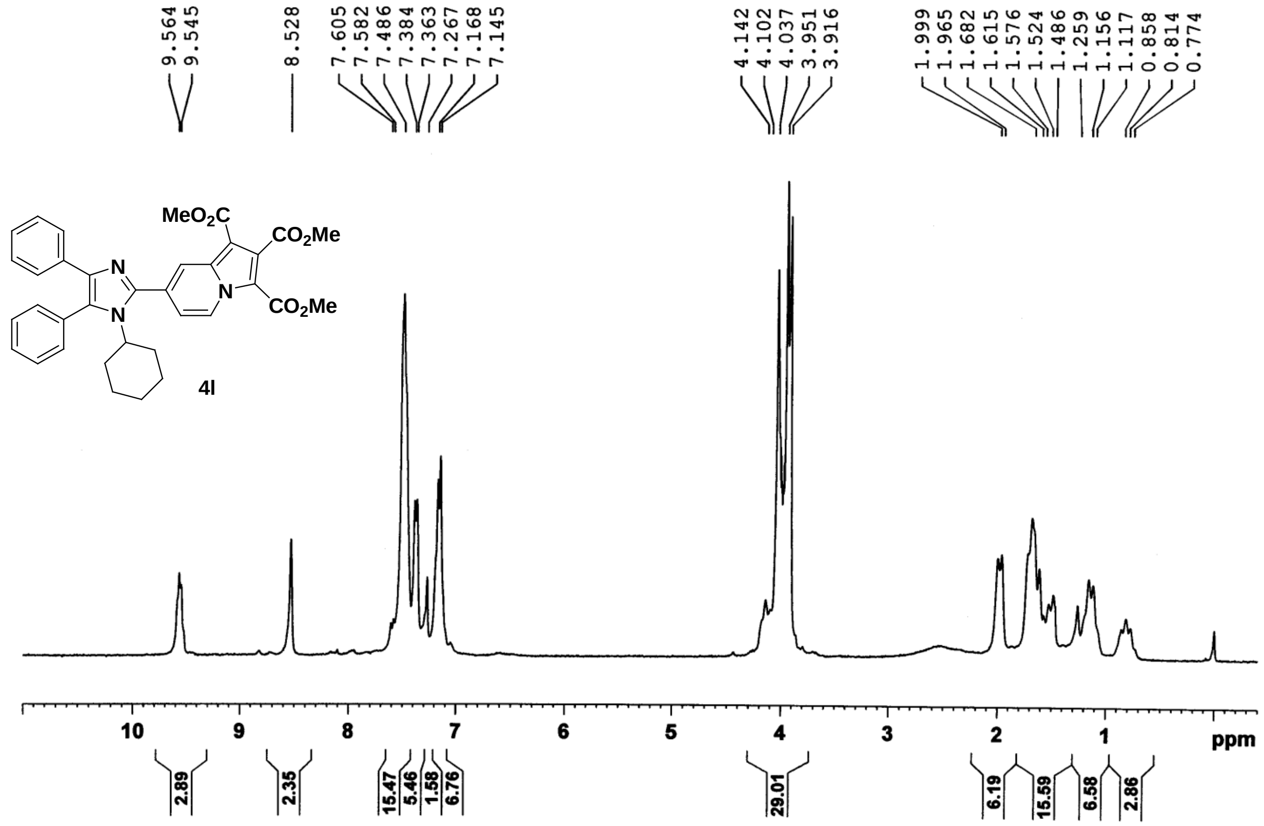

165.99
162.82
160.26
143.45
139.23
136.38
135.62
133.37
132.89
132.35
131.25
131.04
129.79
129.53
128.69
128.29
127.85
127.55
127.32
127.20
123.22
118.09
115.64
112.26
104.32
77.43
77.00
76.58
52.91
52.04
51.55
MeO$_2$C
CO$_2$Me
CO$_2$Me
N
N
N
4i
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

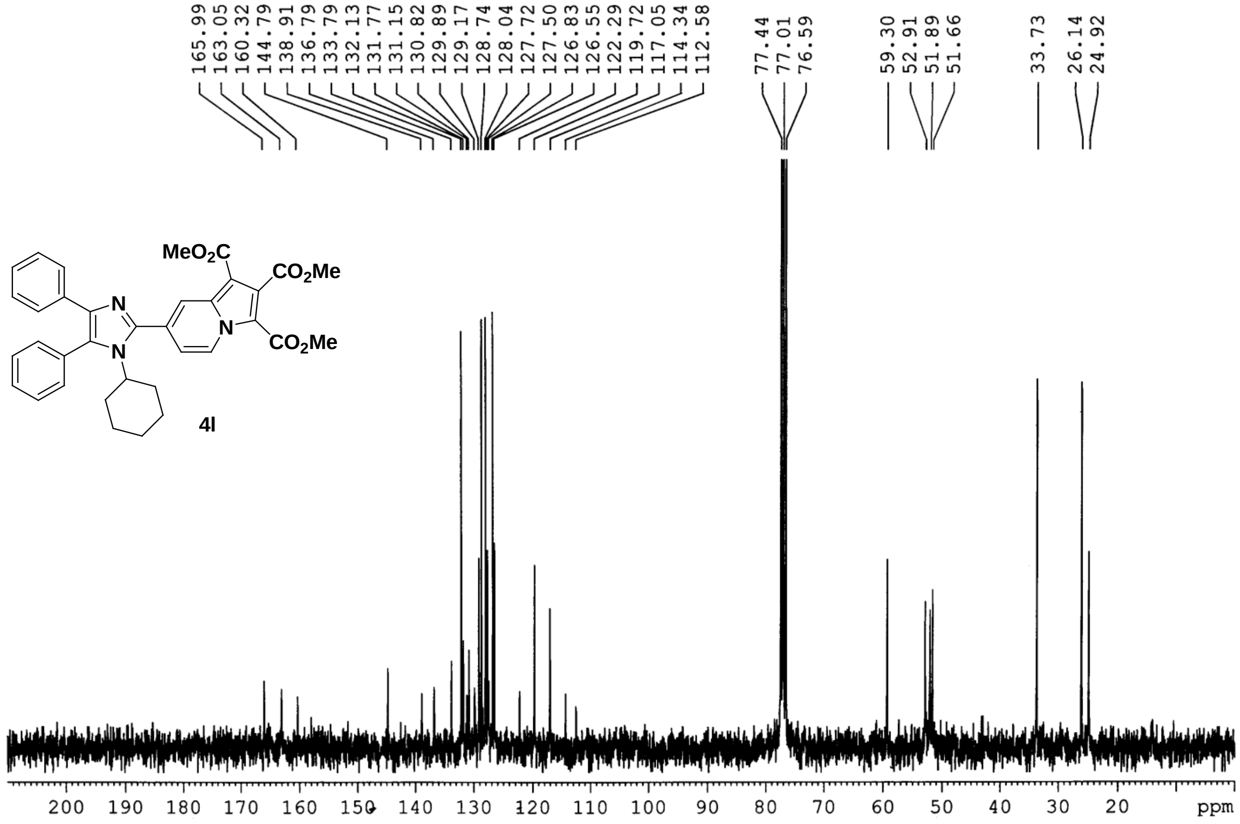

9.374
9.350
7.970
7.969
7.530
7.526
7.504
7.439
7.434
7.415
7.409
7.250
7.243
7.222
7.196
7.166
7.137
7.110
7.084
7.080
7.061
7.005
6.977
4.389
4.365
4.341
4.325
4.317
4.302
4.278
4.254
4.210
4.187
4.163
4.140
1.733
1.359
1.335
1.311
1.287
1.263
1.241
1.217
1.194
EtO$_2$C
CO$_2$Et
CO$_2$Et
N
N
N
Cl
4j
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.99
2.04
1.06
8.02
2.16
1.86
4.02
1.95
9.01

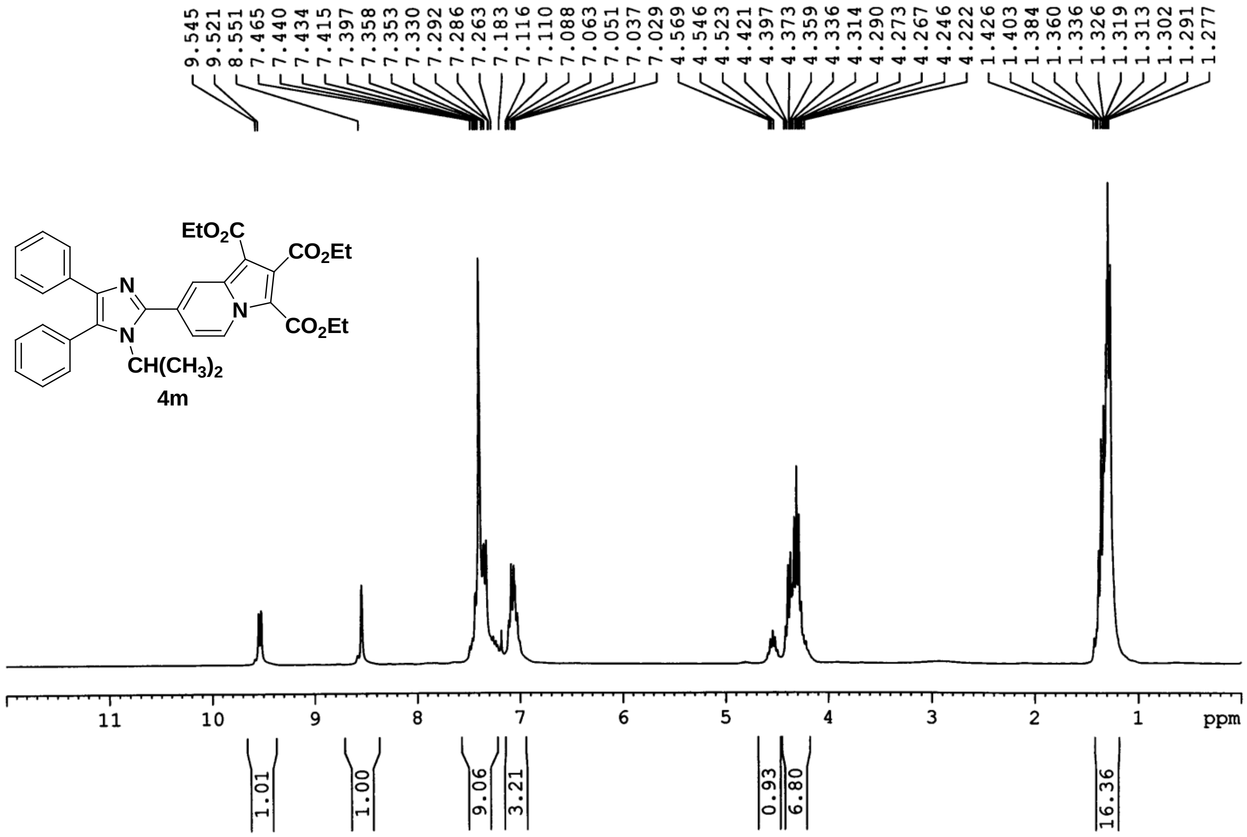

165.51
162.31
160.02
143.86
139.34
136.81
135.18
135.05
133.75
132.28
131.05
130.97
129.85
129.44
128.62
128.55
128.23
128.04
127.40
127.23
127.02
118.31
115.48
112.12
104.32
77.44
77.01
76.59
61.77
60.90
60.18
14.39
14.13
14.04
EtO$_2$C
CO$_2$Et
CO$_2$Et
N
N
N
Cl
4j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


9.624
9.600
8.579
7.507
7.483
7.472
7.460
7.423
7.398
7.260
7.188
7.166
7.140
7.108
4.506
4.483
4.459
4.445
4.435
4.420
4.395
4.371
4.347
4.162
4.123
4.094
4.086
2.155
1.973
1.938
1.686
1.652
1.610
1.570
1.504
1.469
1.446
1.421
1.406
1.397
1.383
1.374
1.359
1.185
1.142
1.100
EtO$_2$C
CO$_2$Et
CO$_2$Et
N
N
N
4k
10
9
8
7
6
5
4
3
2
1
0
ppm
2.39
2.39
19.30
8.17
14.69
2.60
7.04
11.26
24.02
5.57
2.57

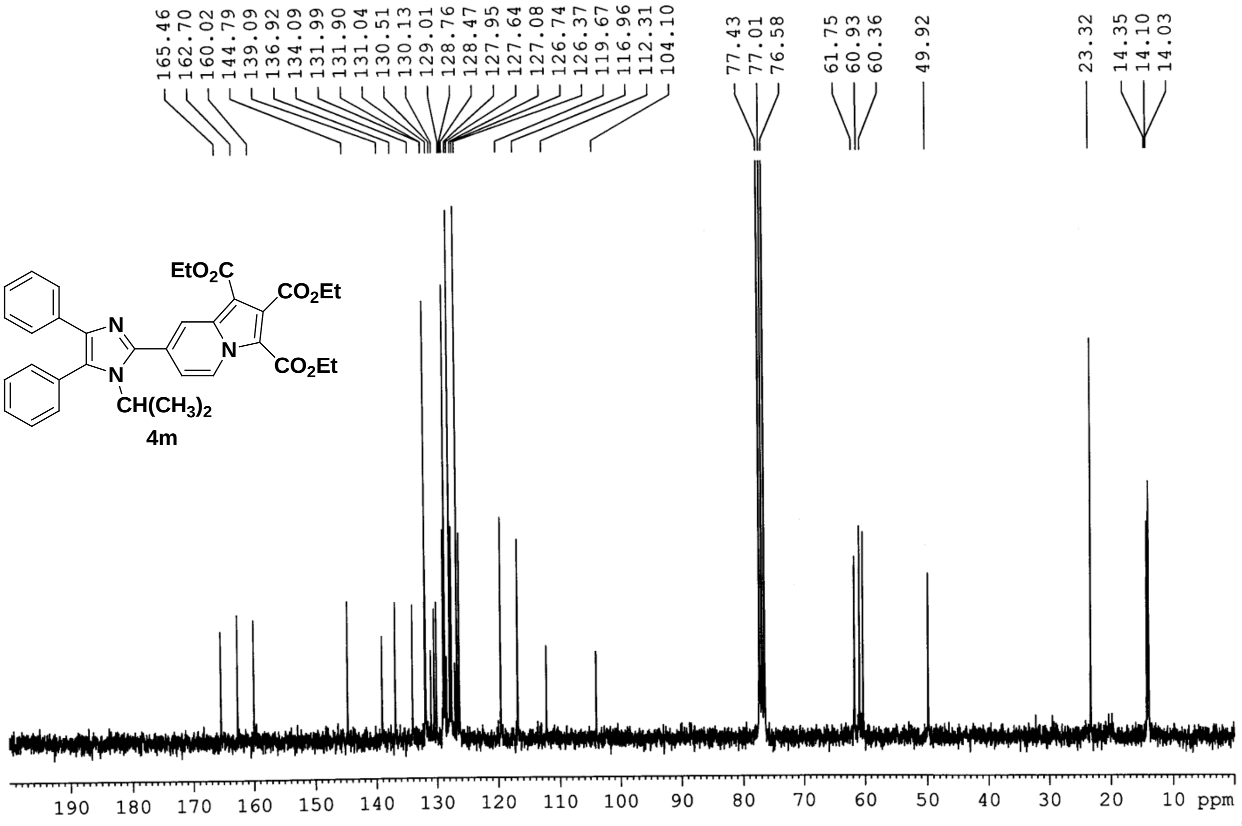

165.58
162.69
160.07
144.99
139.03
136.93
134.11
132.07
132.00
131.05
130.67
130.08
129.06
128.71
127.98
127.65
126.76
126.38
119.66
117.08
112.31
104.15
77.43
77.01
76.58
61.85
60.98
60.41
59.14
33.72
26.13
24.91
14.34
14.15
14.07
EtO$_2$C
CO$_2$Et
CO$_2$Et
N
N
N
4k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.564
9.545
8.528
7.605
7.582
7.486
7.384
7.363
7.267
7.168
7.145
4.142
4.102
4.037
3.951
3.916
1.999
1.965
1.682
1.615
1.576
1.524
1.486
1.259
1.156
1.117
0.858
0.814
0.774
MeO2C
CO2Me
CO2Me
N
N
N
4l
10
9
8
7
6
5
4
3
2
1
ppm
2.89
2.35
15.47
5.46
1.58
6.76
29.01
6.19
15.59
6.58
2.86

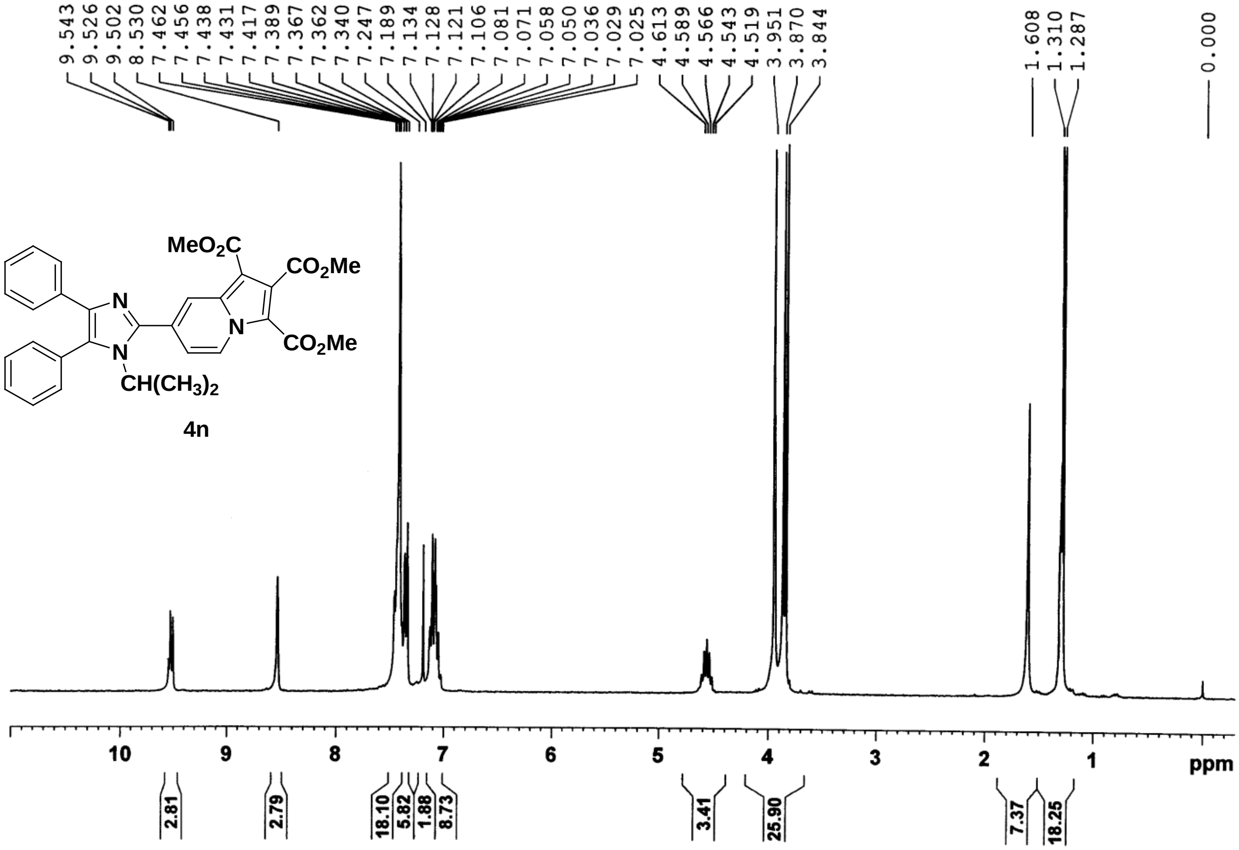

165.99
163.05
160.32
144.79
138.91
136.79
133.79
132.13
131.77
131.15
130.82
129.89
129.17
128.74
128.04
127.72
127.50
126.83
126.55
122.29
119.72
117.05
114.34
112.58
77.44
77.01
76.59
59.30
52.91
51.89
51.66
33.73
26.14
24.92
MeO2C
CO2Me
CO2Me
N
N
N
4l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

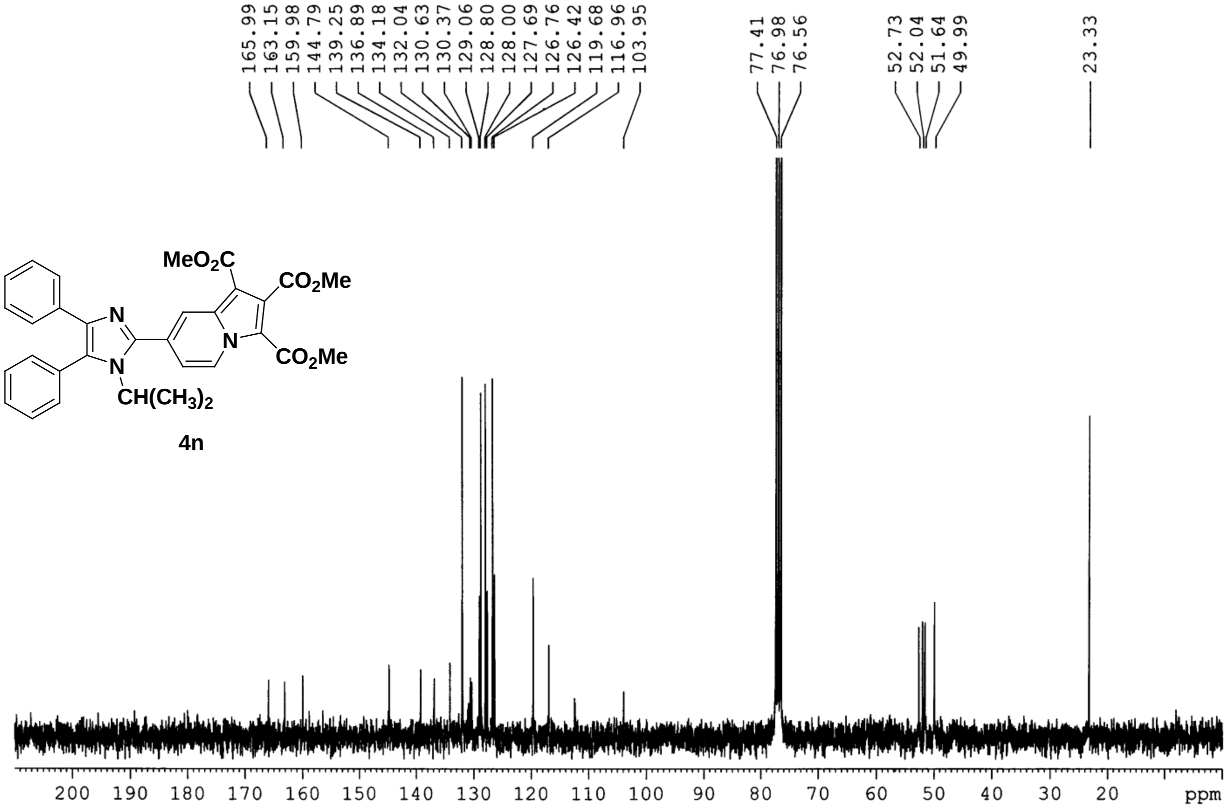

9.545
9.521
8.551
7.465
7.440
7.434
7.415
7.397
7.358
7.353
7.330
7.292
7.286
7.263
7.183
7.116
7.110
7.088
7.063
7.051
7.037
7.029
4.569
4.546
4.523
4.421
4.397
4.373
4.359
4.336
4.314
4.290
4.273
4.267
4.246
4.222
1.426
1.403
1.384
1.360
1.336
1.326
1.319
1.313
1.302
1.291
1.277
EtO2C
CO2Et
CO2Et
N
N
N
CH(CH3)2
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.00
9.06
3.21
0.93
6.80
16.36

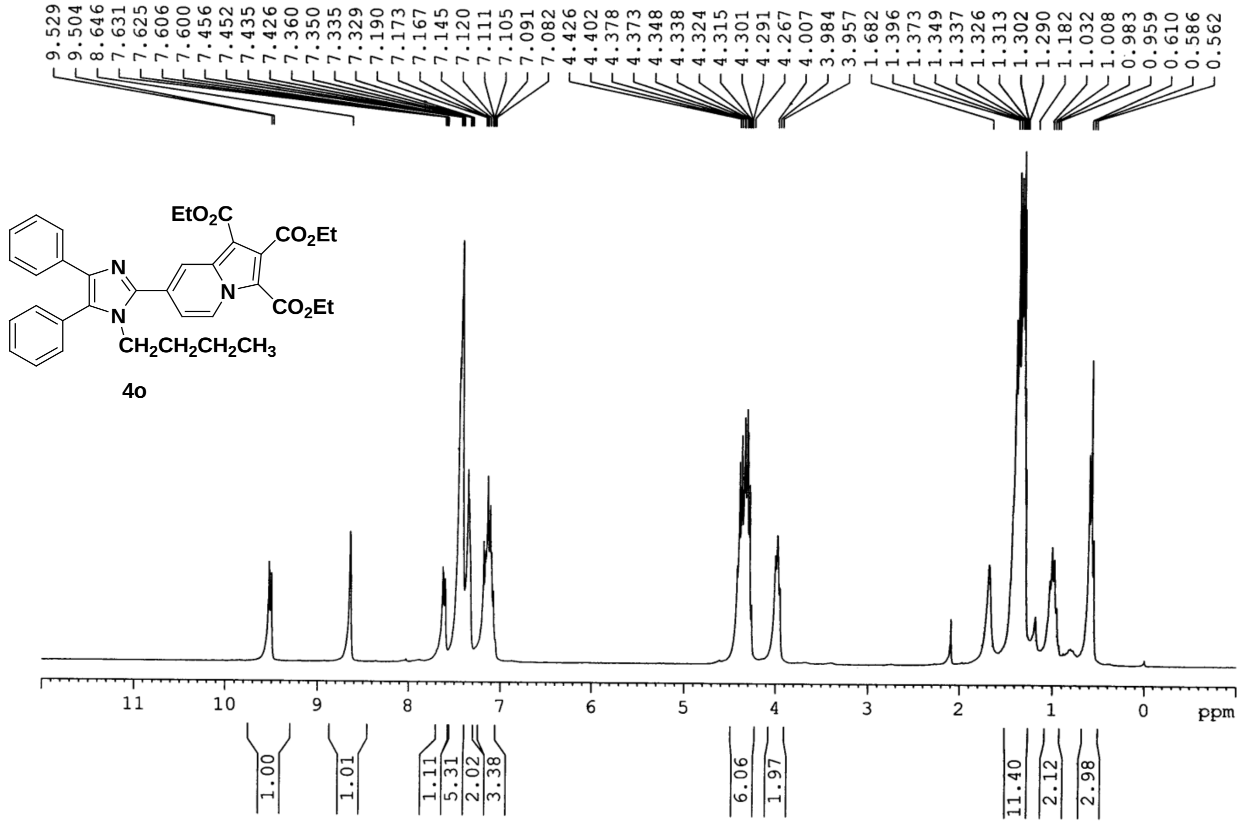
4m

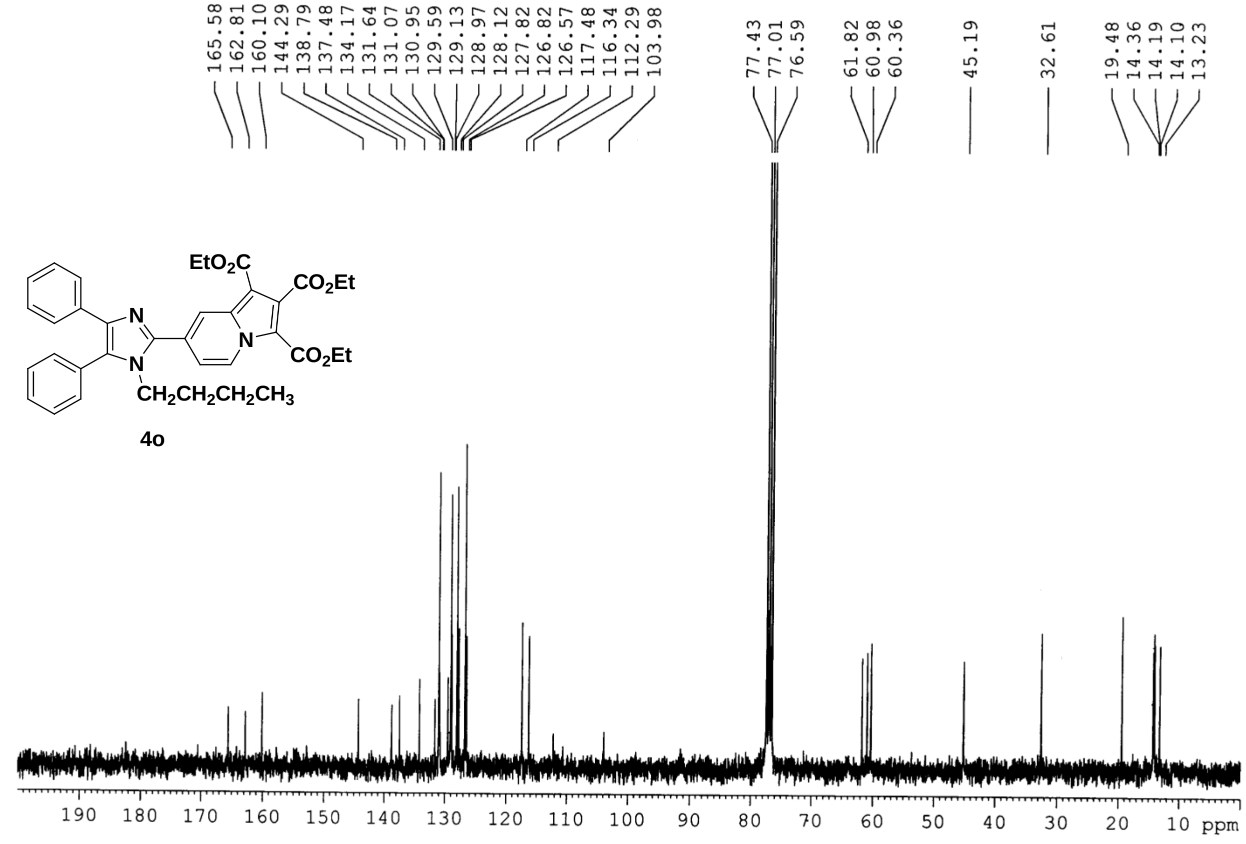

165.46
162.70
160.02
144.79
139.09
136.92
134.09
131.99
131.90
131.04
130.51
130.13
129.01
128.76
128.47
127.95
127.64
127.08
126.74
126.37
119.67
116.96
112.31
104.10
77.43
77.01
76.58
61.75
60.93
60.36
49.92
23.32
14.35
14.10
14.03
EtO2C
CO2Et
CO2Et
N
N
N
CH(CH3)2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

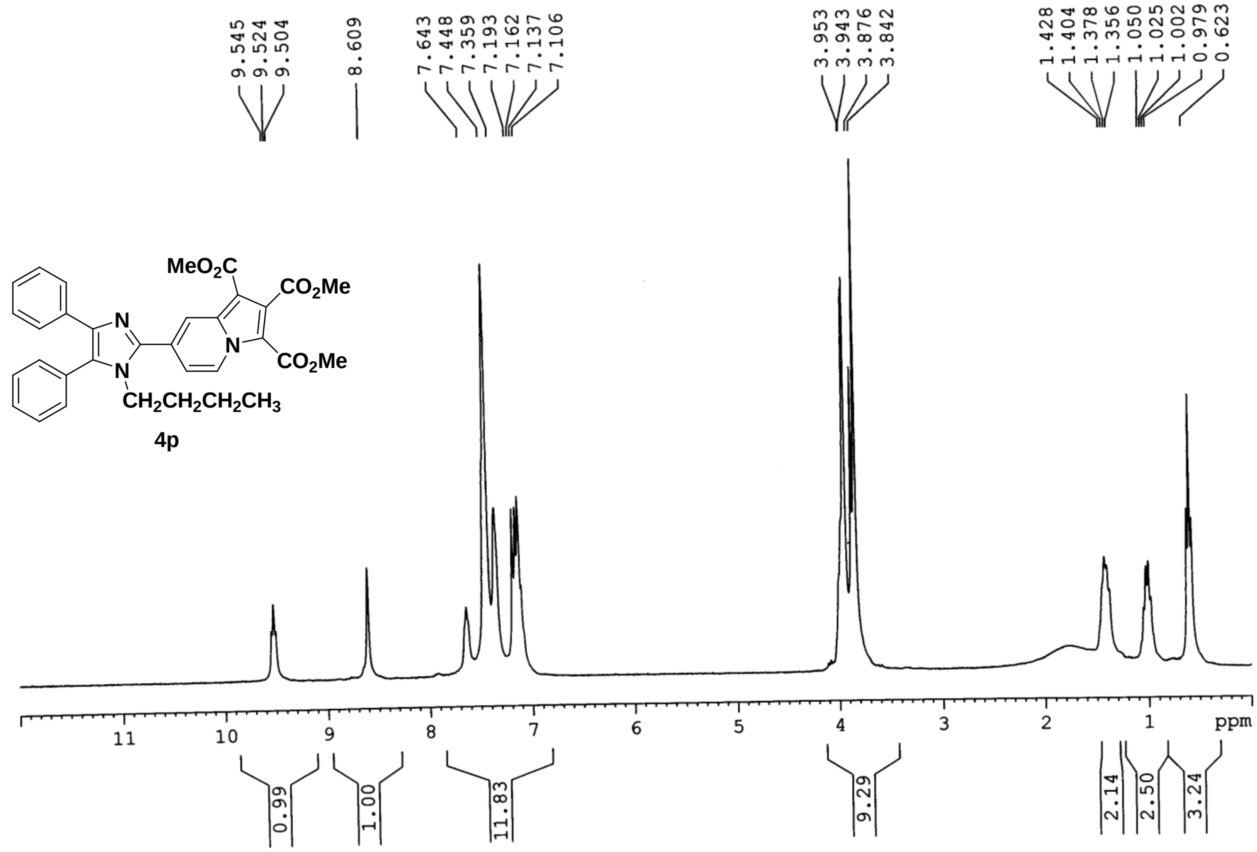
4m

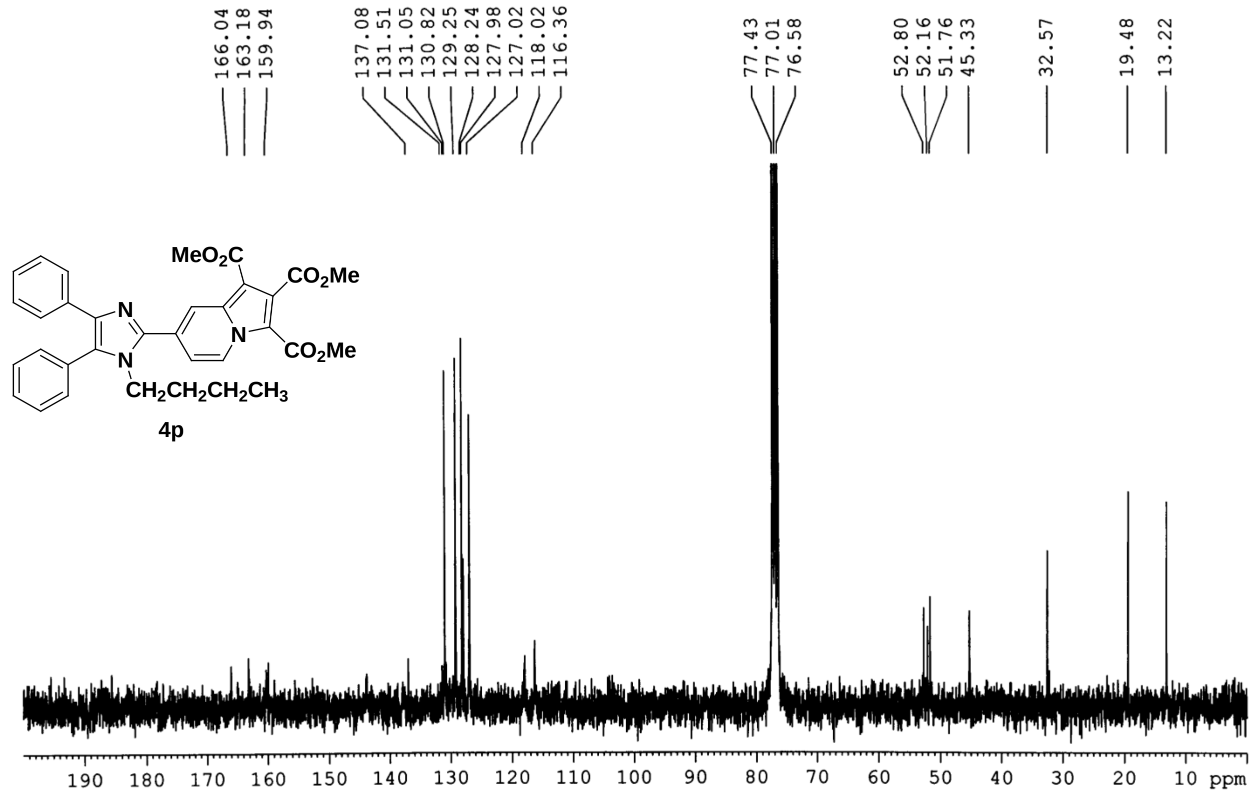

9.543
9.526
9.502
8.530
7.462
7.456
7.438
7.431
7.417
7.389
7.367
7.362
7.340
7.247
7.189
7.134
7.128
7.121
7.106
7.081
7.071
7.058
7.050
7.036
7.029
7.025
4.613
4.589
4.566
4.543
4.519
3.951
3.870
3.844
1.608
1.310
1.287
0.000
MeO2C
CO2Me
CO2Me
N
N
N
CH(CH3)2
4n
10
9
8
7
6
5
4
3
2
1
ppm
2.81
2.79
18.10
5.82
1.88
8.73
3.41
25.90
7.37
18.25

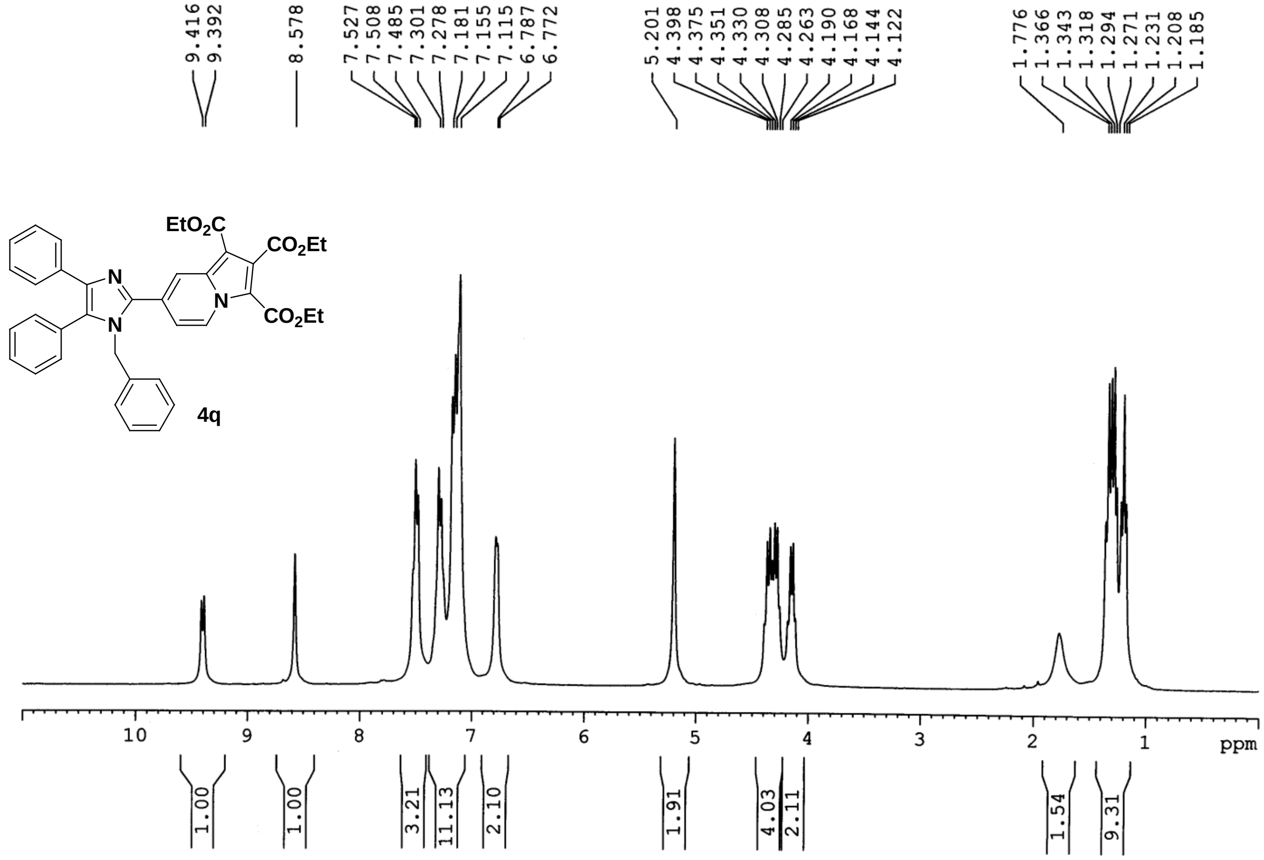

165.99
163.15
159.98
144.79
139.25
136.89
134.18
132.04
130.63
130.37
129.06
128.80
128.00
127.69
126.76
126.42
119.68
116.96
103.95
77.41
76.98
76.56
52.73
52.04
51.64
49.99
23.33
MeO2C
CO2Me
CO2Me
N
N
N
CH(CH3)2
4n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

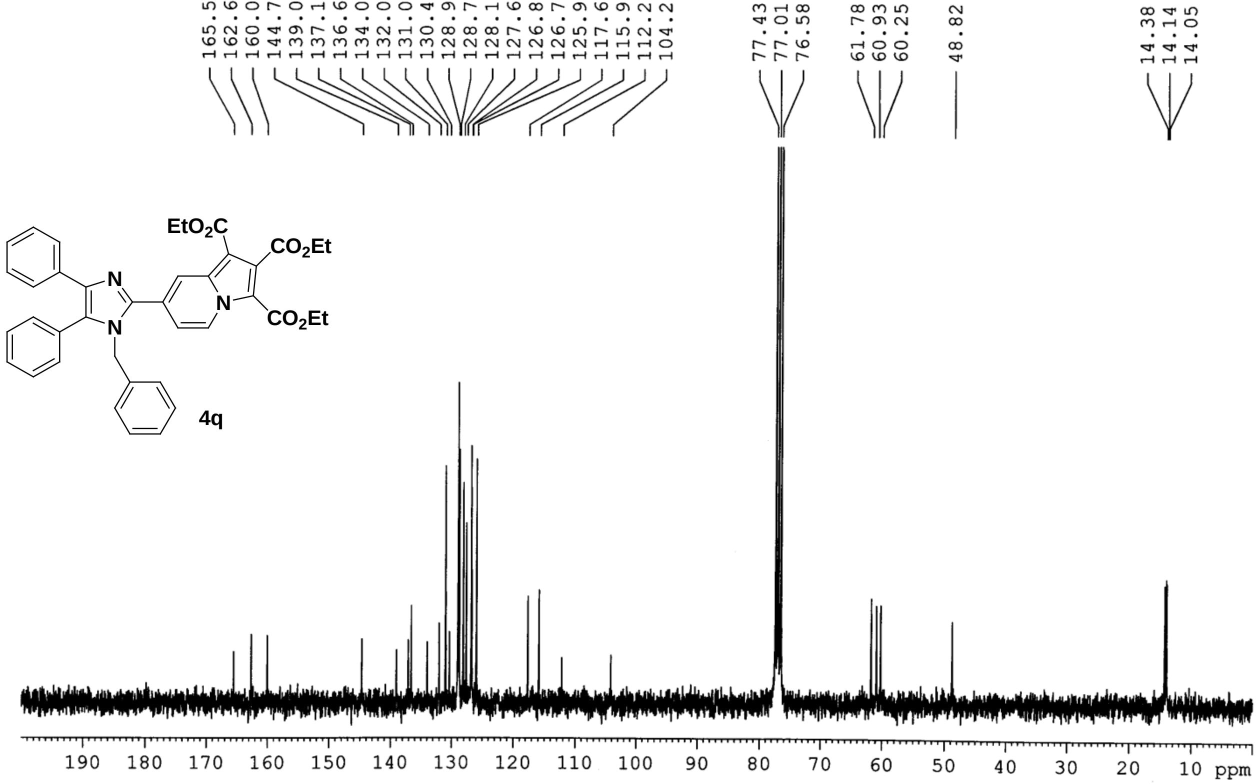

9.529
9.504
8.646
7.631
7.625
7.606
7.600
7.456
7.452
7.435
7.426
7.360
7.350
7.335
7.329
7.190
7.173
7.167
7.145
7.120
7.111
7.105
7.091
7.082
4.426
4.402
4.378
4.373
4.348
4.338
4.324
4.315
4.301
4.291
4.267
4.007
3.984
3.957
1.682
1.396
1.373
1.349
1.337
1.326
1.313
1.302
1.290
1.182
1.032
1.008
0.983
0.959
0.610
0.586
0.562
EtO2C
CO2Et
CO2Et
N
N
N
CH2CH2CH2CH3
4o
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.11
5.31
2.02
3.38
6.06
1.97
11.40
2.12
2.98

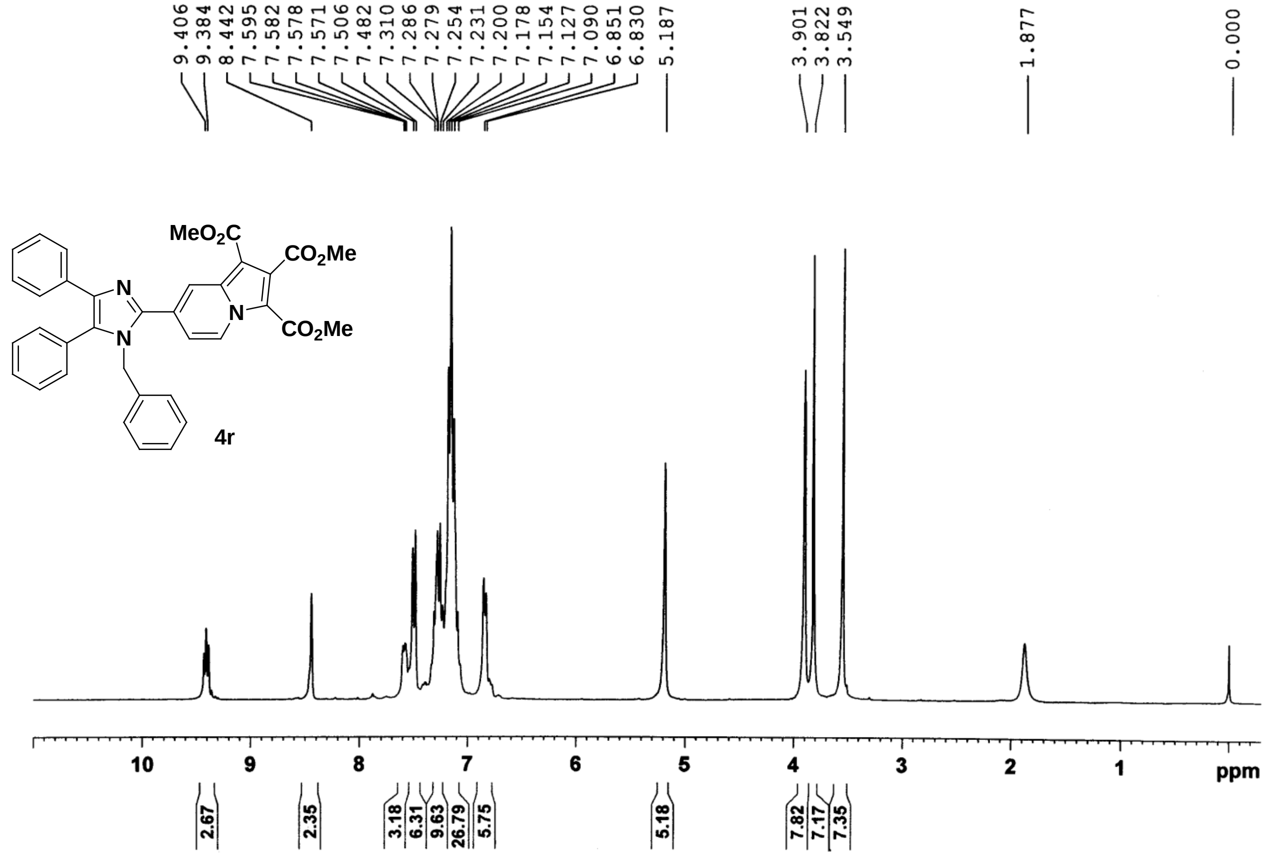

165.58
162.81
160.10
144.29
138.79
137.48
134.17
131.64
131.07
130.95
129.59
129.13
128.97
128.12
127.82
126.82
126.57
117.48
116.34
112.29
103.98
77.43
77.01
76.59
61.82
60.98
60.36
45.19
32.61
19.48
14.36
14.19
14.10
13.23
EtO2C
CO2Et
CO2Et
N
N
N
CH2CH2CH2CH3
4o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

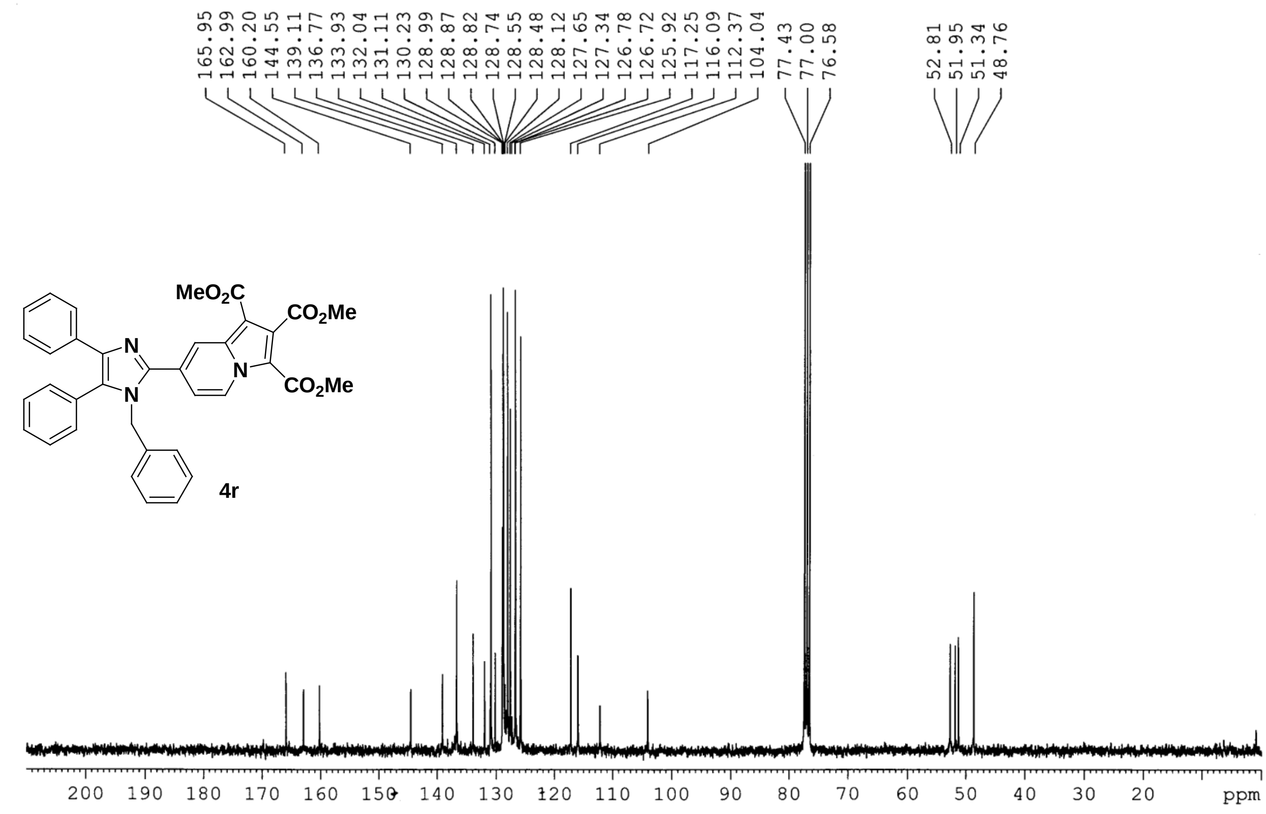

9.545
9.524
9.504
8.609
7.643
7.448
7.359
7.193
7.162
7.137
7.106
3.953
3.943
3.876
3.842
1.428
1.404
1.378
1.356
1.050
1.025
1.002
0.979
0.623
MeO₂C
CO₂Me
N
N
CO₂Me
N
CH₂CH₂CH₂CH₃
4p
11
10
9
8
7
6
5
4
3
2
1
ppm
0.99
1.00
11.83
9.29
2.14
2.50
3.24

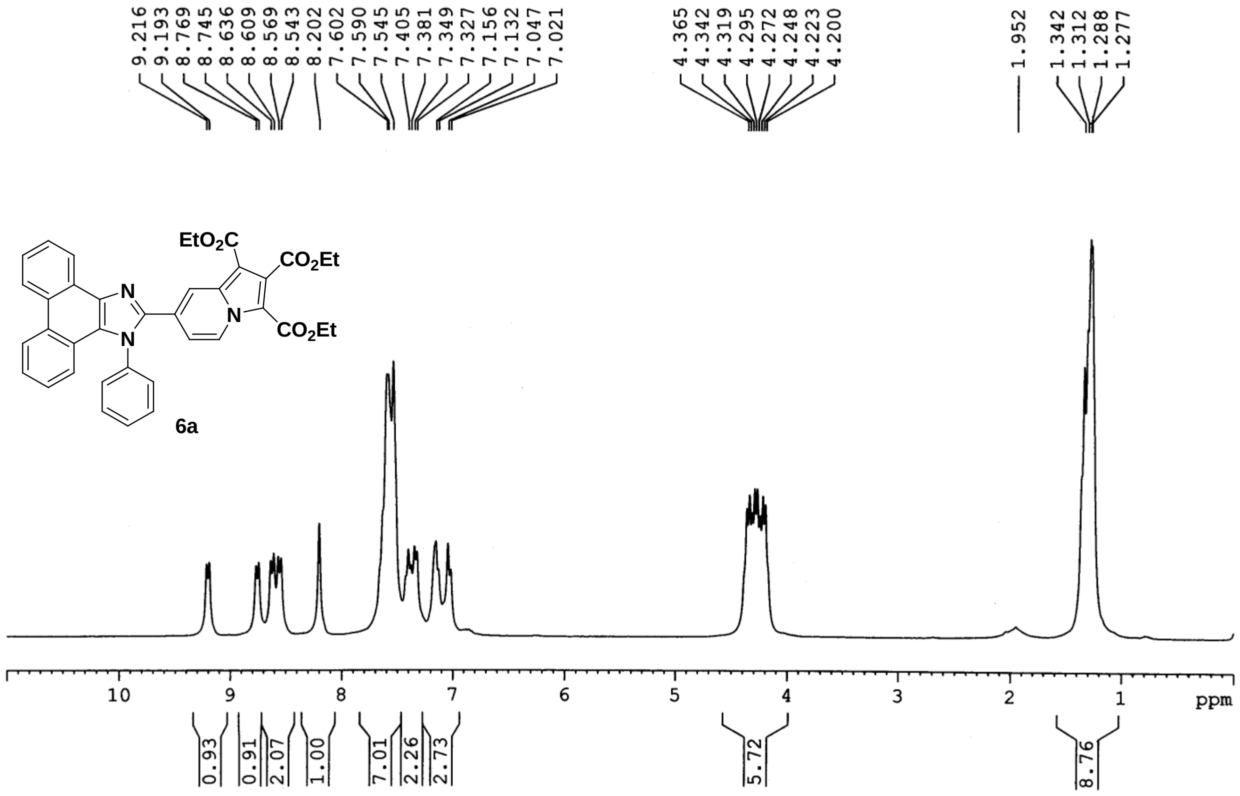

166.04
163.18
159.94
137.08
131.51
131.05
130.82
129.25
128.24
127.98
127.02
118.02
116.36
77.43
77.01
76.58
52.80
52.16
51.76
45.33
32.57
19.48
13.22
MeO₂C
CO₂Me
N
N
CO₂Me
N
CH₂CH₂CH₂CH₃
4p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

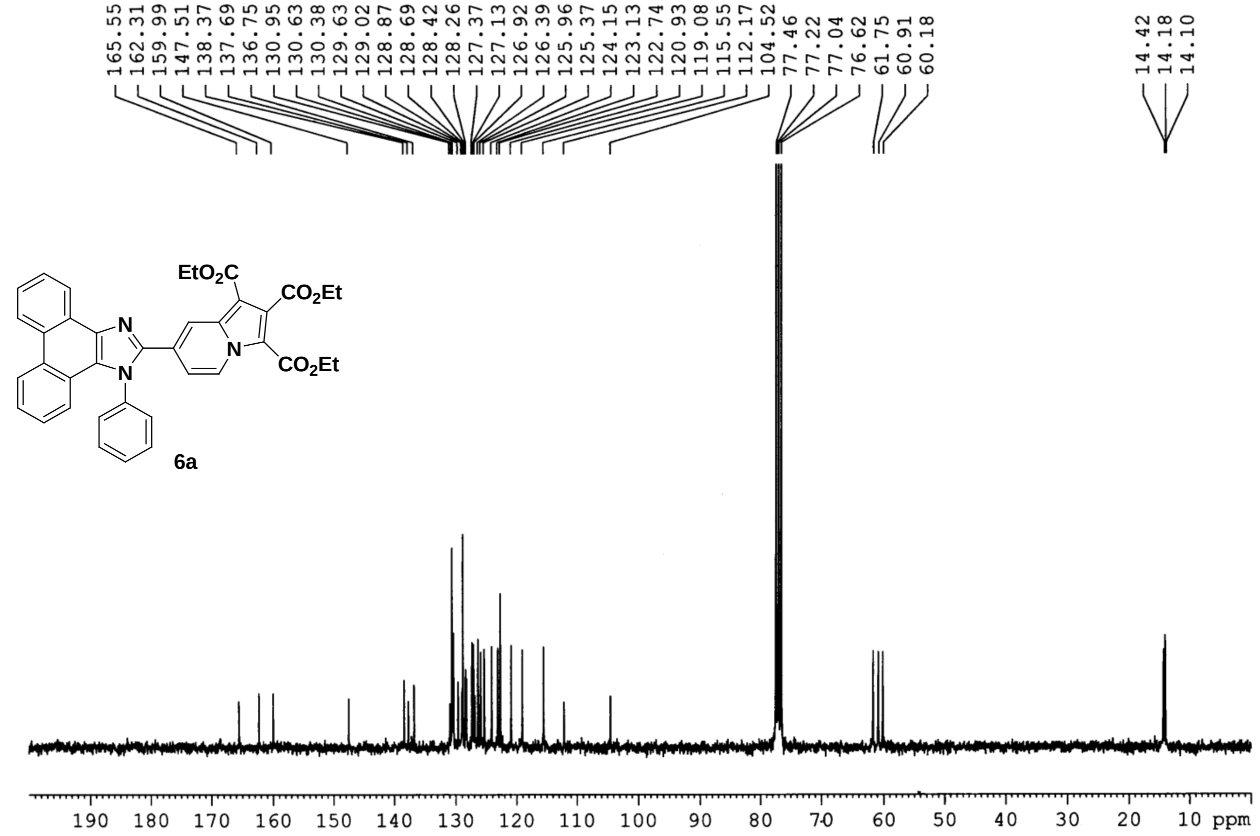

9.416
9.392
8.578
7.527
7.508
7.485
7.301
7.278
7.181
7.155
7.115
6.787
6.772
5.201
4.398
4.375
4.351
4.330
4.308
4.285
4.263
4.190
4.168
4.144
4.122
1.776
1.366
1.343
1.318
1.294
1.271
1.231
1.208
1.185
EtO2C
CO2Et
CO2Et
N
N
N
4q
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
3.21
11.13
2.10
1.91
4.03
2.11
1.54
9.31

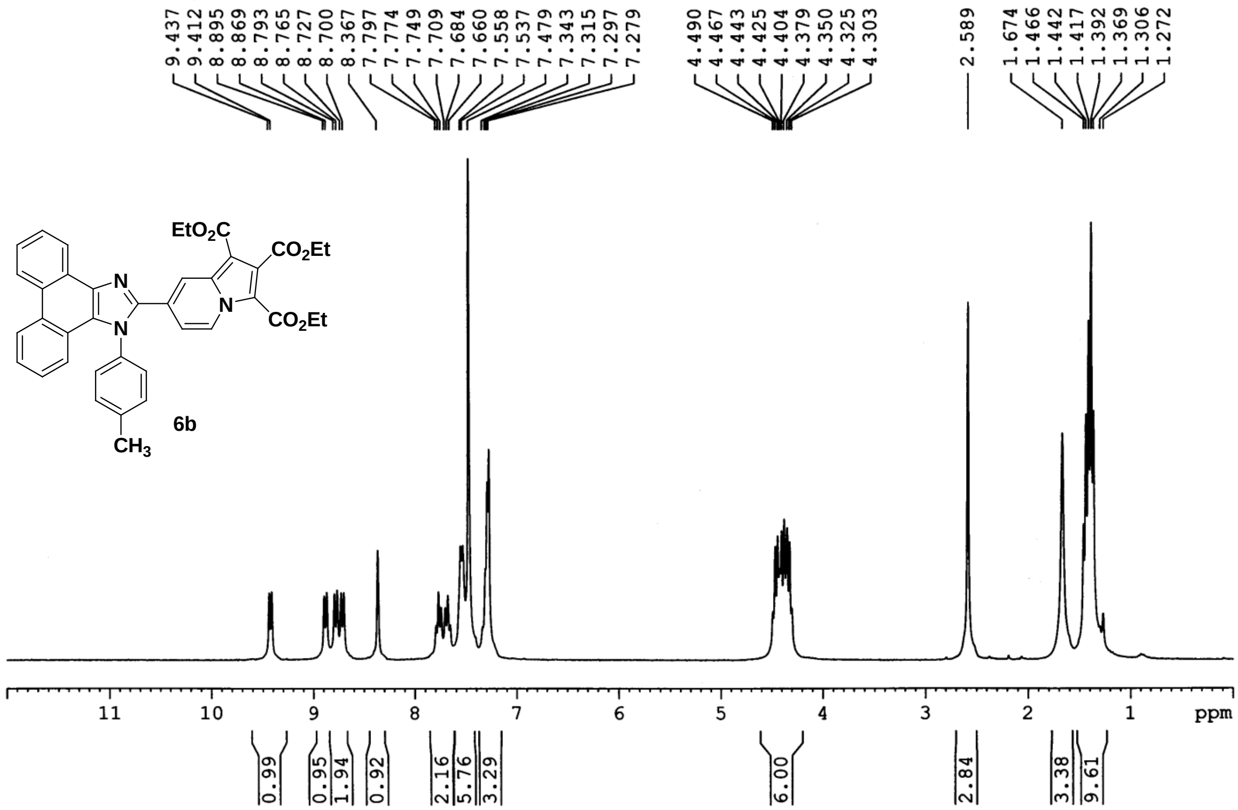

165.53
162.65
160.02
144.74
139.05
137.13
136.63
134.02
132.06
131.02
130.40
128.96
128.78
128.16
127.66
126.84
126.74
125.99
117.69
115.92
112.25
104.21
77.43
77.01
76.58
61.78
60.93
60.25
48.82
14.38
14.14
14.05
EtO2C
CO2Et
CO2Et
N
N
N
4q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

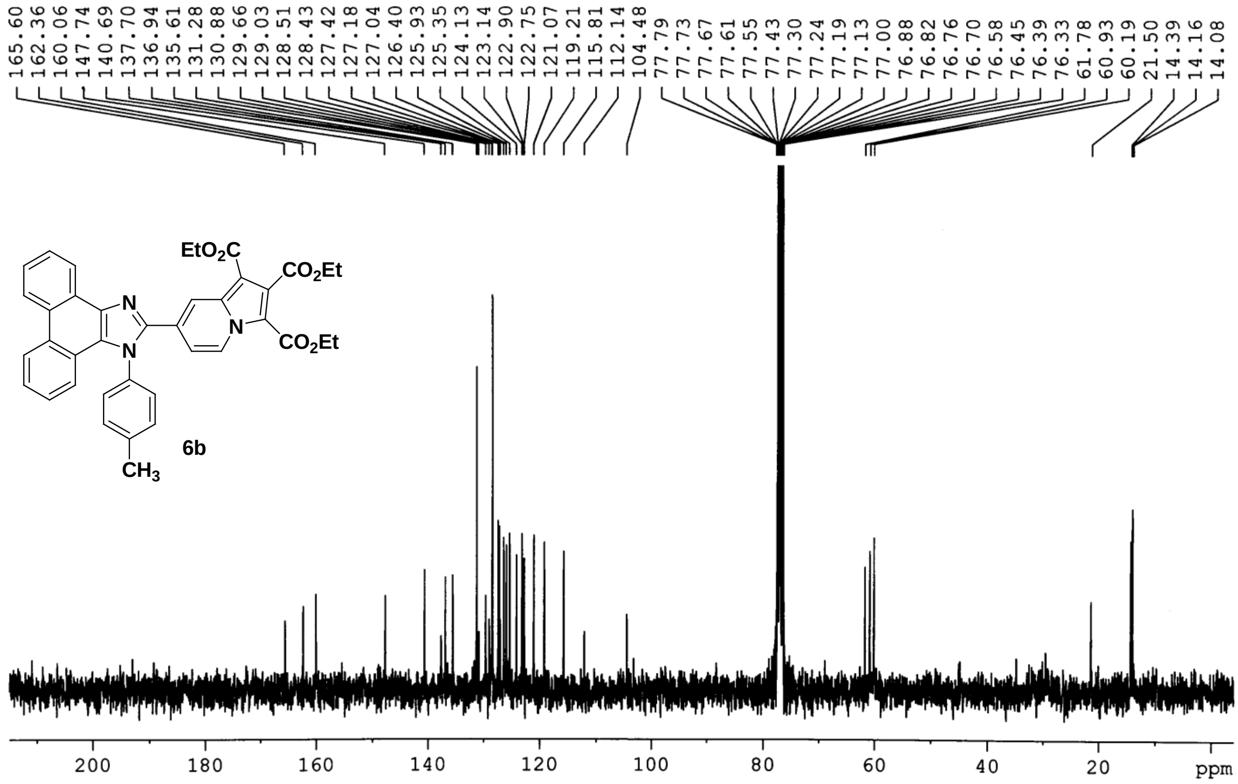

9.406
9.384
8.442
7.595
7.582
7.578
7.571
7.506
7.482
7.310
7.286
7.279
7.254
7.231
7.200
7.178
7.154
7.127
7.090
6.851
6.830
5.187
3.901
3.822
3.549
1.877
0.000
MeO2C
CO2Me
CO2Me
N
N
N
4r
10
9
8
7
6
5
4
3
2
1
ppm
2.67
2.35
3.18
6.31
9.63
26.79
5.75
5.18
7.82
7.17
7.35

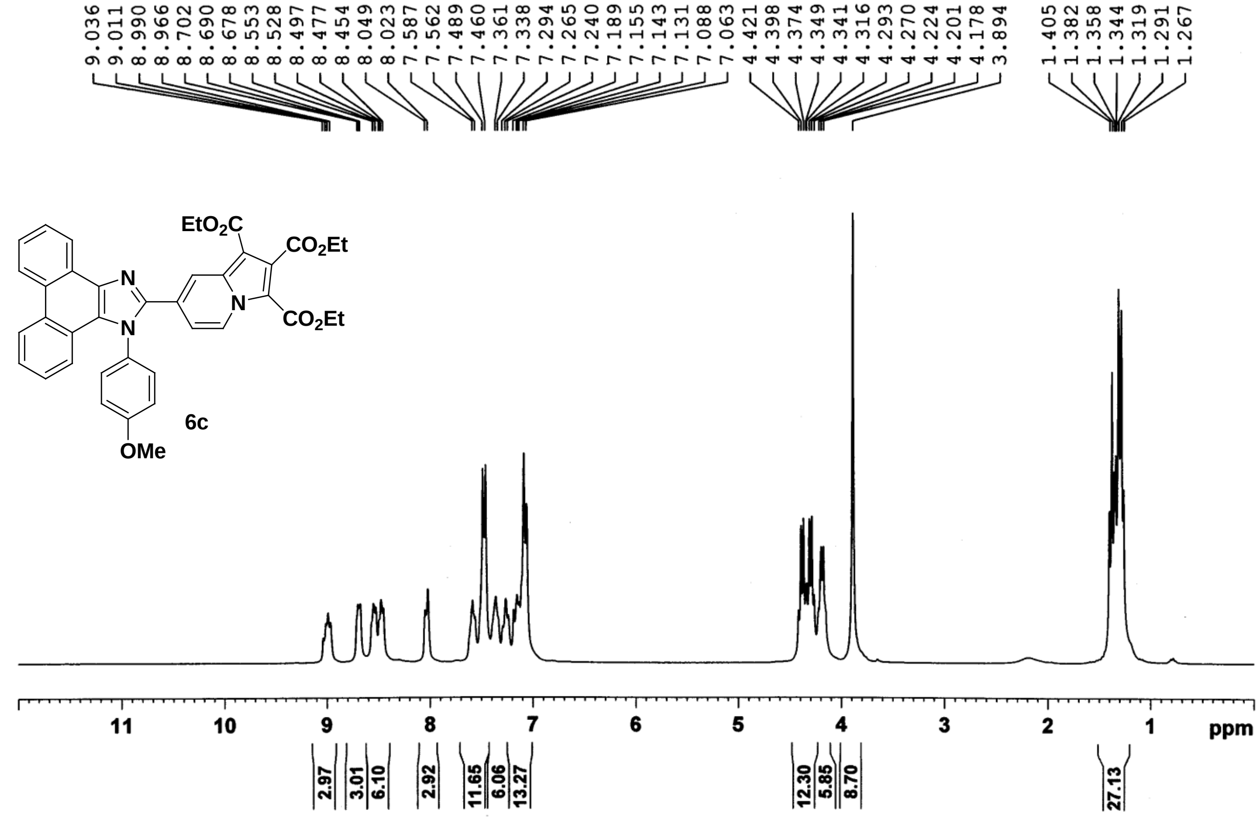

165.95
162.99
160.20
144.55
139.11
136.77
133.93
132.04
131.11
130.23
128.99
128.87
128.82
128.74
128.55
128.48
128.12
127.65
127.34
126.78
126.72
125.92
117.25
116.09
112.37
104.04
77.43
77.00
76.58
52.81
51.95
51.34
48.76
MeO2C
CO2Me
CO2Me
N
N
N
4r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

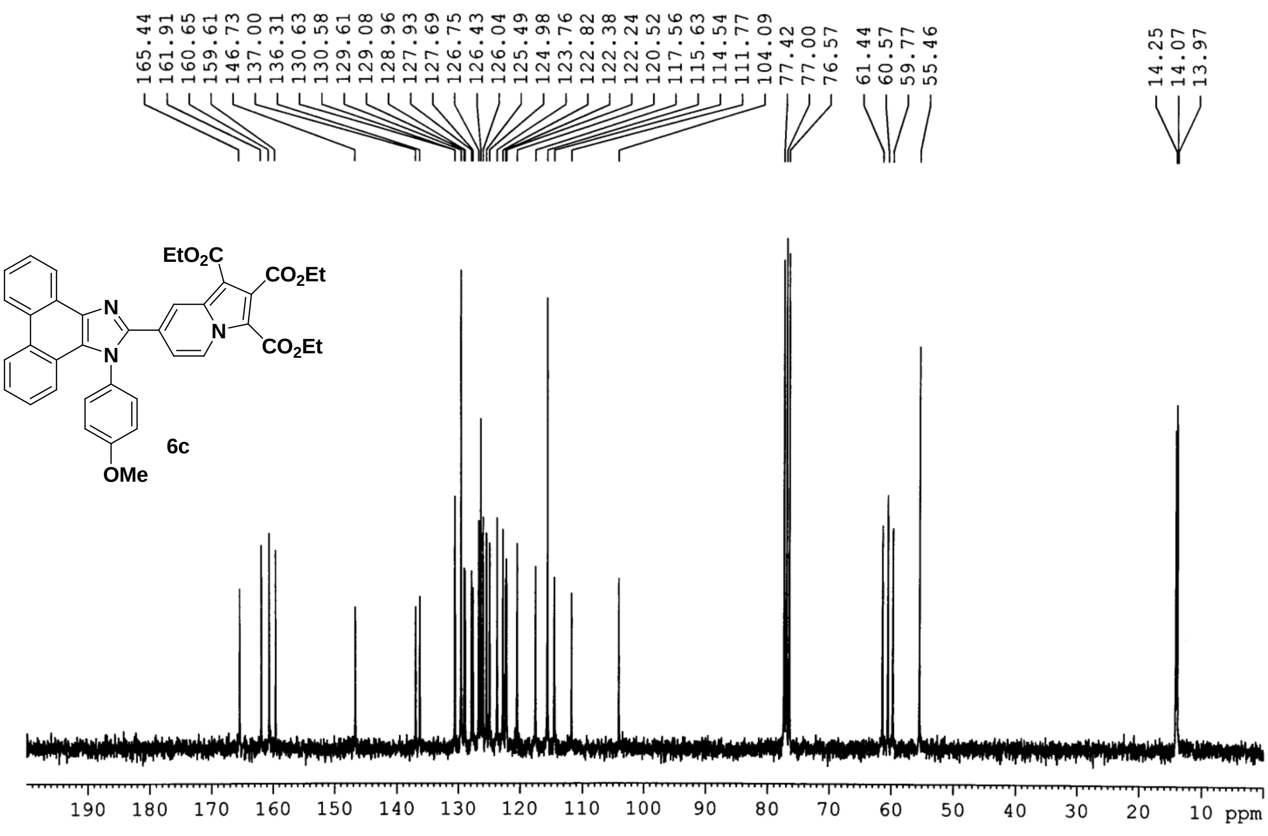

9.216
9.193
8.769
8.745
8.636
8.609
8.569
8.543
8.202
7.602
7.590
7.545
7.405
7.381
7.349
7.327
7.156
7.132
7.047
7.021
4.365
4.342
4.319
4.295
4.272
4.248
4.223
4.200
1.952
1.342
1.312
1.288
1.277
EtO_2C
CO_2Et
CO_2Et
N
N
N
6a
10
9
8
7
6
5
4
3
2
1
ppm
0.93
0.91
2.07
1.00
7.01
2.26
2.73
5.72
8.76

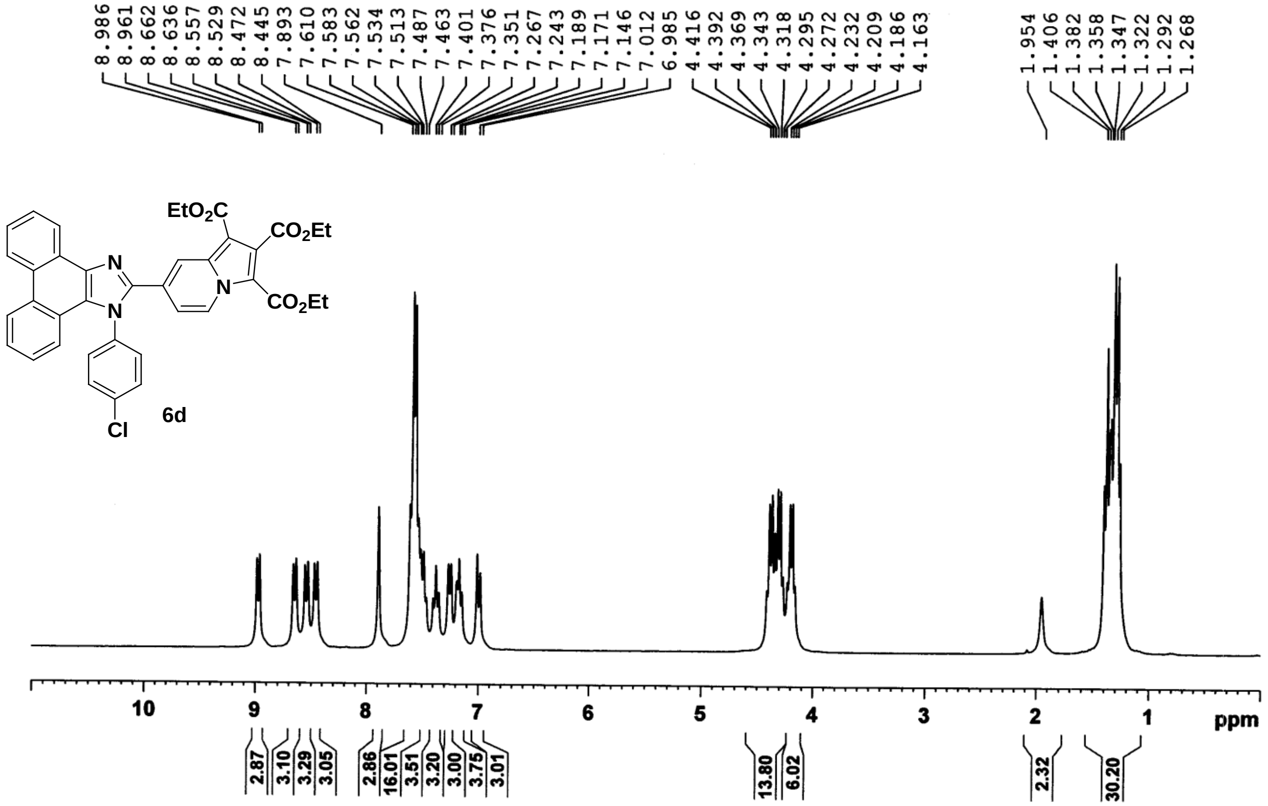

165.55
162.31
159.99
147.51
138.37
137.69
136.75
130.95
130.63
130.38
129.63
129.02
128.87
128.69
128.42
128.26
127.37
127.13
126.92
126.39
125.96
125.37
124.15
123.13
122.74
120.93
119.08
115.55
112.17
104.52
77.46
77.22
77.04
76.62
61.75
60.91
60.18
14.42
14.18
14.10
EtO_2C
CO_2Et
CO_2Et
N
N
N
6a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

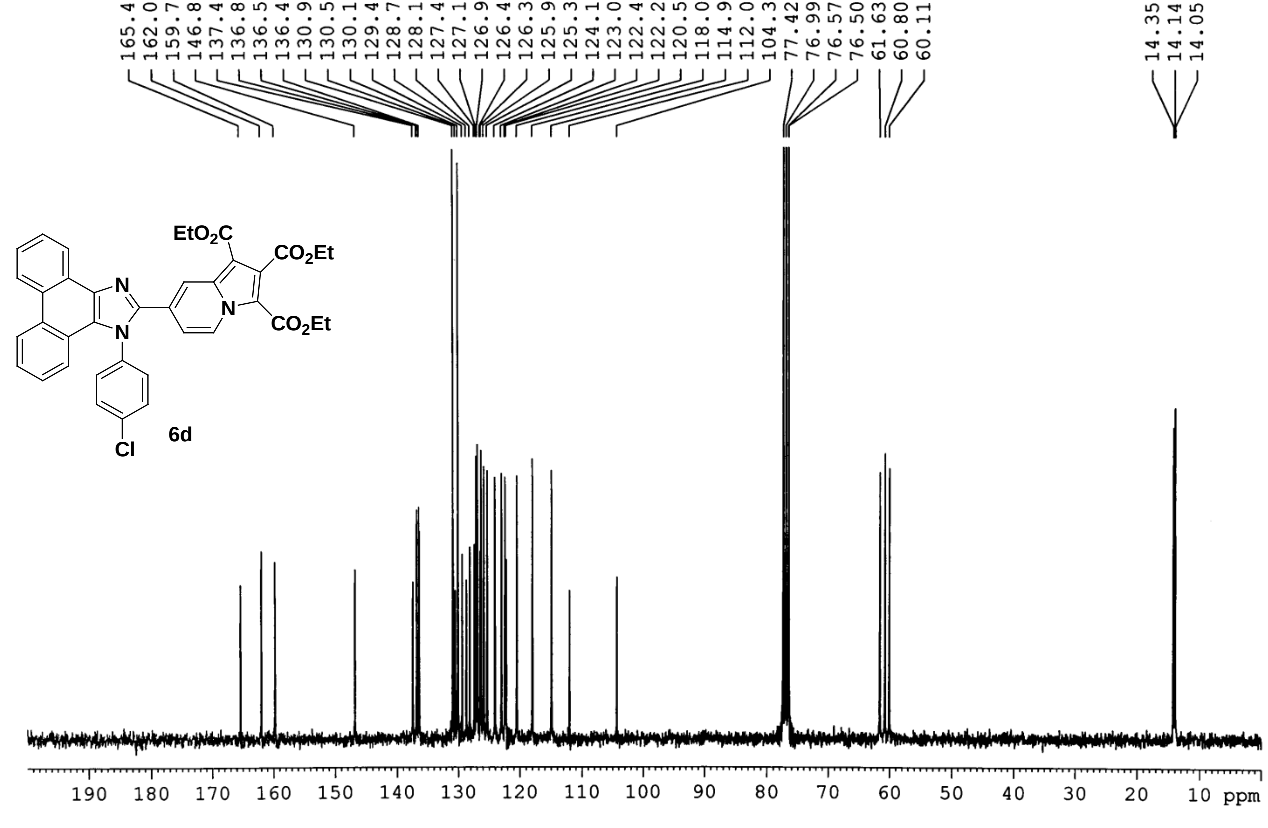

9.437
9.412
8.895
8.869
8.793
8.765
8.727
8.700
8.367
7.797
7.774
7.749
7.709
7.684
7.660
7.558
7.537
7.479
7.343
7.315
7.297
7.279
4.490
4.467
4.443
4.425
4.404
4.379
4.350
4.325
4.303
2.589
1.674
1.466
1.442
1.417
1.392
1.369
1.306
1.272
EtO$_2$C
CO$_2$Et
CO$_2$Et
N
N
N
CH$_3$
6b
11
10
9
8
7
6
5
4
3
2
1
ppm
0.99
0.95
1.94
0.92
2.16
5.76
3.29
6.00
2.84
3.38
9.61

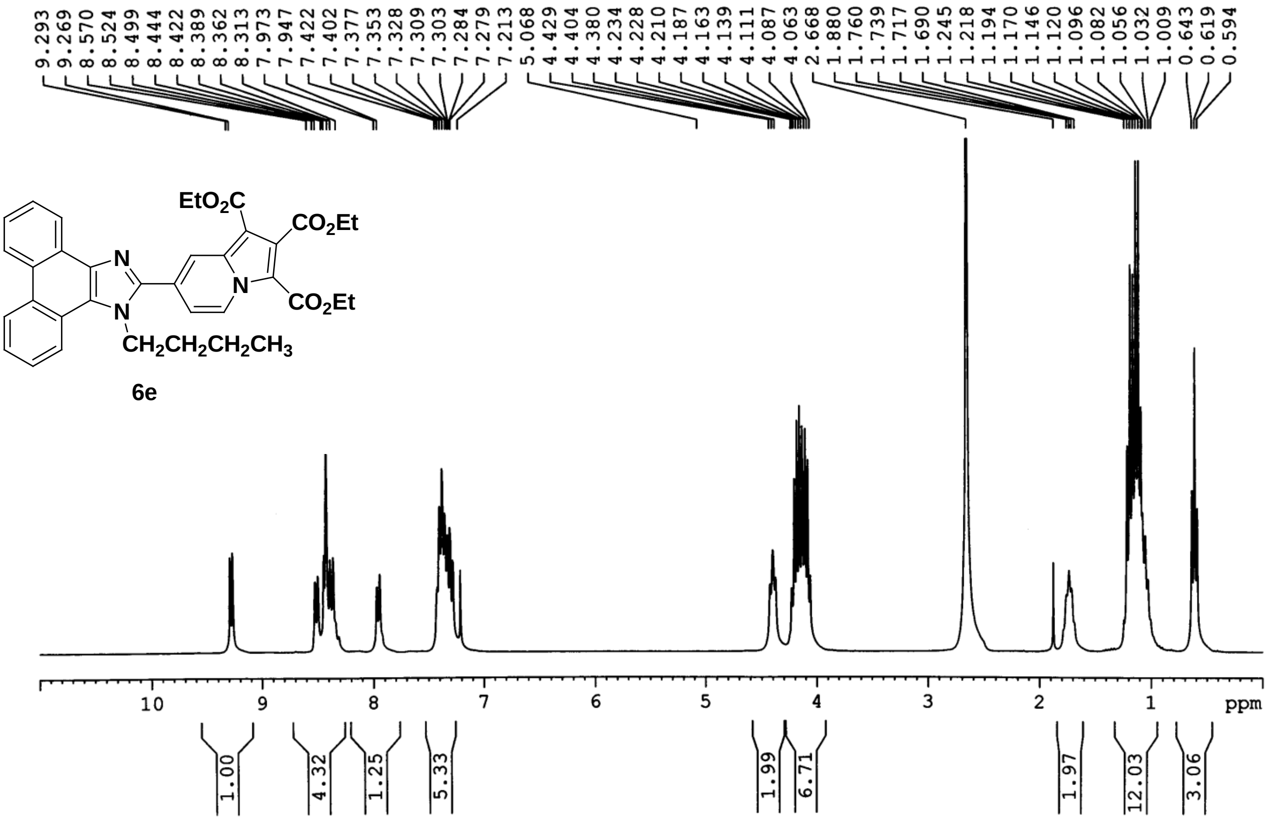

165.60
162.36
160.06
147.74
140.69
137.70
136.94
135.61
131.28
130.88
129.66
129.03
128.51
128.43
127.42
127.18
127.04
126.40
125.93
125.35
124.13
123.14
122.90
122.75
121.07
119.21
115.81
112.14
104.48
77.79
77.73
77.67
77.61
77.55
77.43
77.30
77.24
77.19
77.13
77.00
76.88
76.82
76.76
76.70
76.58
76.45
76.39
76.33
61.78
60.93
60.19
21.50
14.39
14.16
14.08
EtO$_2$C
CO$_2$Et
CO$_2$Et
N
N
N
CH$_3$
6b
200
180
160
140
120
100
80
60
40
20
ppm

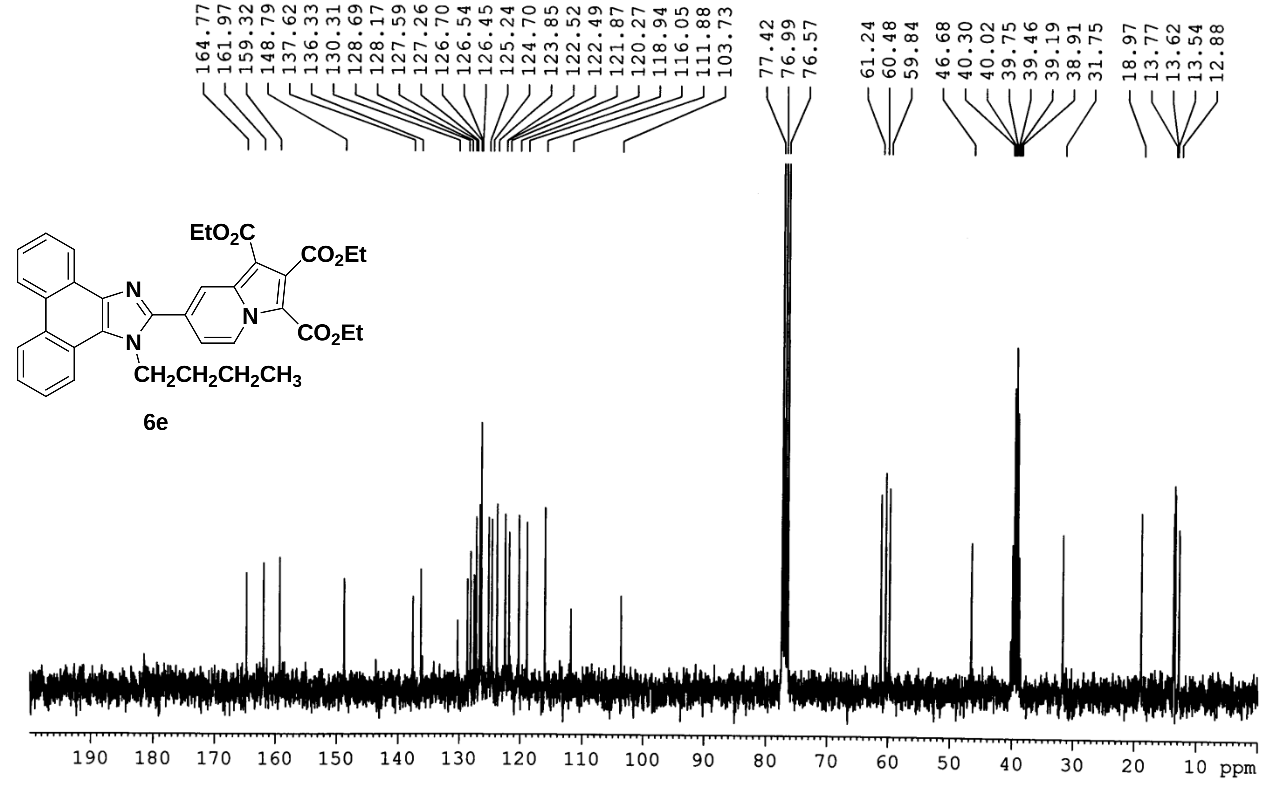

9.036
9.011
8.990
8.966
8.702
8.690
8.678
8.553
8.528
8.497
8.477
8.454
8.049
8.023
7.587
7.562
7.489
7.460
7.361
7.338
7.294
7.265
7.240
7.189
7.155
7.143
7.131
7.088
7.063
4.421
4.398
4.374
4.349
4.341
4.316
4.293
4.270
4.224
4.201
4.178
3.894
1.405
1.382
1.358
1.344
1.319
1.291
1.267
EtO2C
CO2Et
CO2Et
N
N
N
OMe
6c
11
10
9
8
7
6
5
4
3
2
1
ppm
2.97
3.01
6.10
2.92
11.65
6.06
13.27
12.30
5.85
8.70
27.13

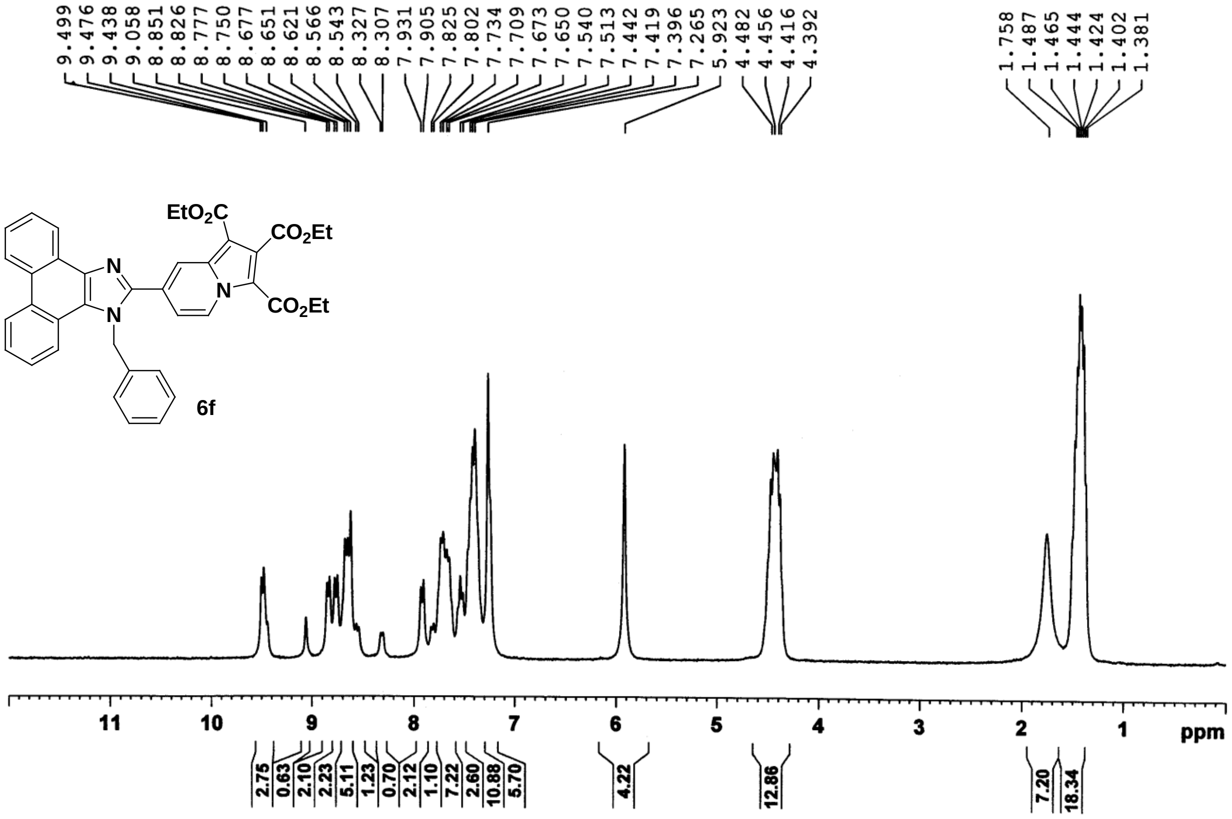

165.44
161.91
160.65
159.61
146.73
137.00
136.31
130.63
130.58
129.61
129.08
128.96
127.93
127.69
126.75
126.43
126.04
125.49
124.98
123.76
122.82
122.38
122.24
120.52
117.56
115.63
114.54
111.77
104.09
77.42
77.00
76.57
61.44
60.57
59.77
55.46
14.25
14.07
13.97
EtO2C
CO2Et
CO2Et
N
N
N
OMe
6c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

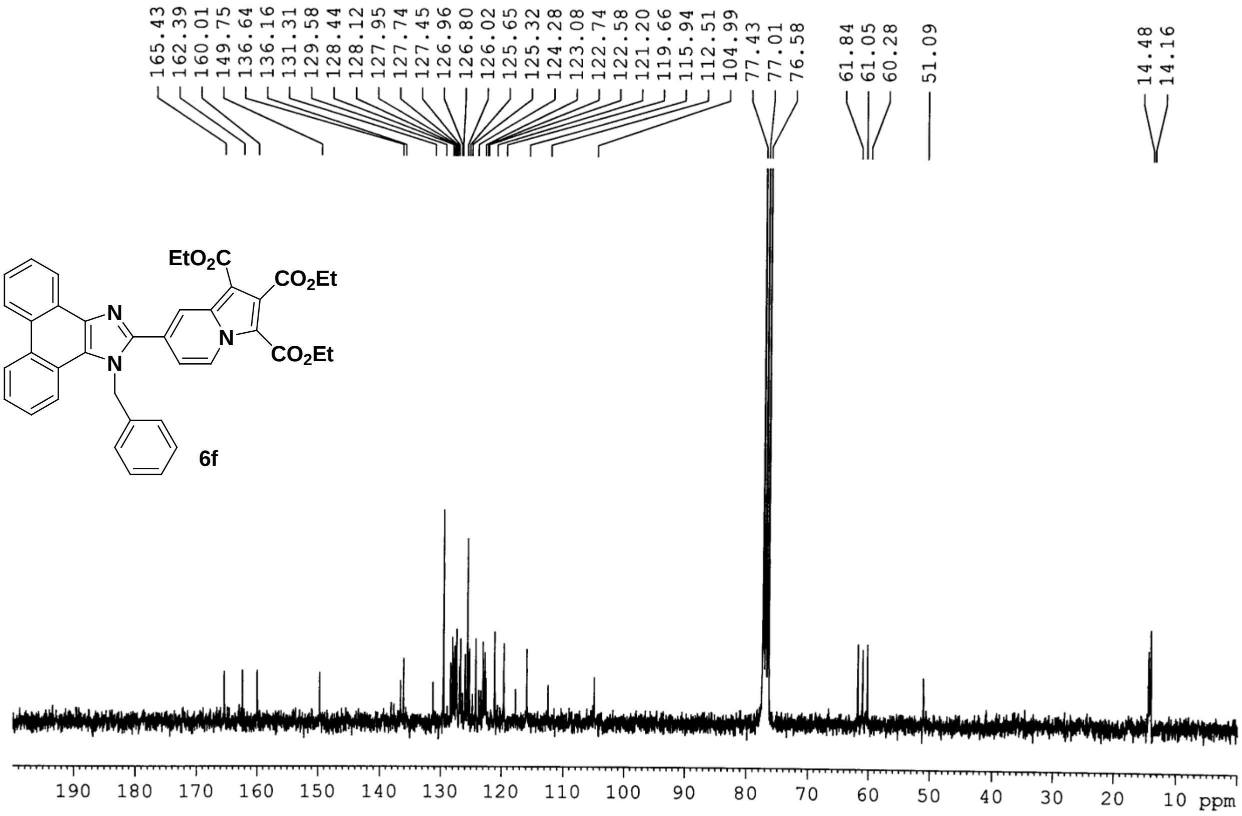

8.986
8.961
8.662
8.636
8.557
8.529
8.472
8.445
7.893
7.610
7.583
7.562
7.534
7.513
7.487
7.463
7.401
7.376
7.351
7.267
7.243
7.189
7.171
7.146
7.012
6.985
4.416
4.392
4.369
4.343
4.318
4.295
4.272
4.232
4.209
4.186
4.163
1.954
1.406
1.382
1.358
1.347
1.322
1.292
1.268
EtO2C
CO2Et
CO2Et
N
N
N
Cl
6d
10
9
8
7
6
5
4
3
2
1
ppm
2.87
3.10
3.29
3.05
2.86
16.01
3.51
3.20
3.00
3.75
3.01
13.80
6.02
2.32
30.20

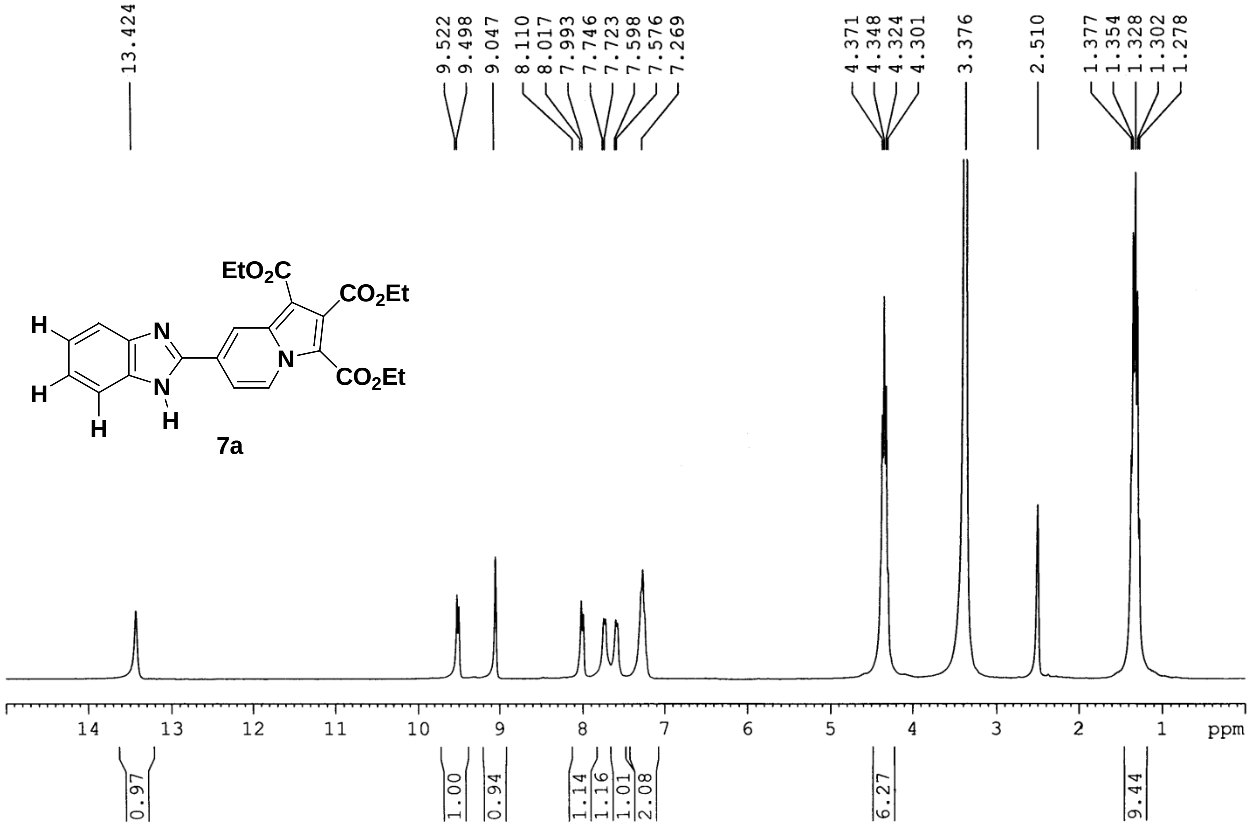

165.41
162.00
159.78
146.89
137.47
136.87
136.50
136.43
130.94
130.56
130.11
129.41
128.74
128.18
127.44
127.17
126.92
126.49
126.35
125.91
125.34
124.10
123.02
122.44
122.26
120.53
118.04
114.98
112.07
104.34
77.42
76.99
76.57
76.50
61.63
60.80
60.11
14.35
14.14
14.05
EtO2C
CO2Et
CO2Et
N
N
N
Cl
6d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.293
9.269
8.570
8.524
8.499
8.444
8.422
8.389
8.362
8.313
7.973
7.947
7.422
7.402
7.377
7.353
7.328
7.309
7.303
7.284
7.279
7.213
5.068
4.429
4.404
4.380
4.234
4.228
4.210
4.187
4.163
4.139
4.111
4.087
4.063
2.668
1.880
1.760
1.739
1.717
1.690
1.245
1.218
1.194
1.170
1.146
1.120
1.096
1.082
1.056
1.032
1.009
0.643
0.619
0.594
EtO2C
CO2Et
CO2Et
N
N
N
CH2CH2CH2CH3
6e
10
9
8
7
6
5
4
3
2
1
ppm
1.00
4.32
1.25
5.33
1.99
6.71
1.97
12.03
3.06

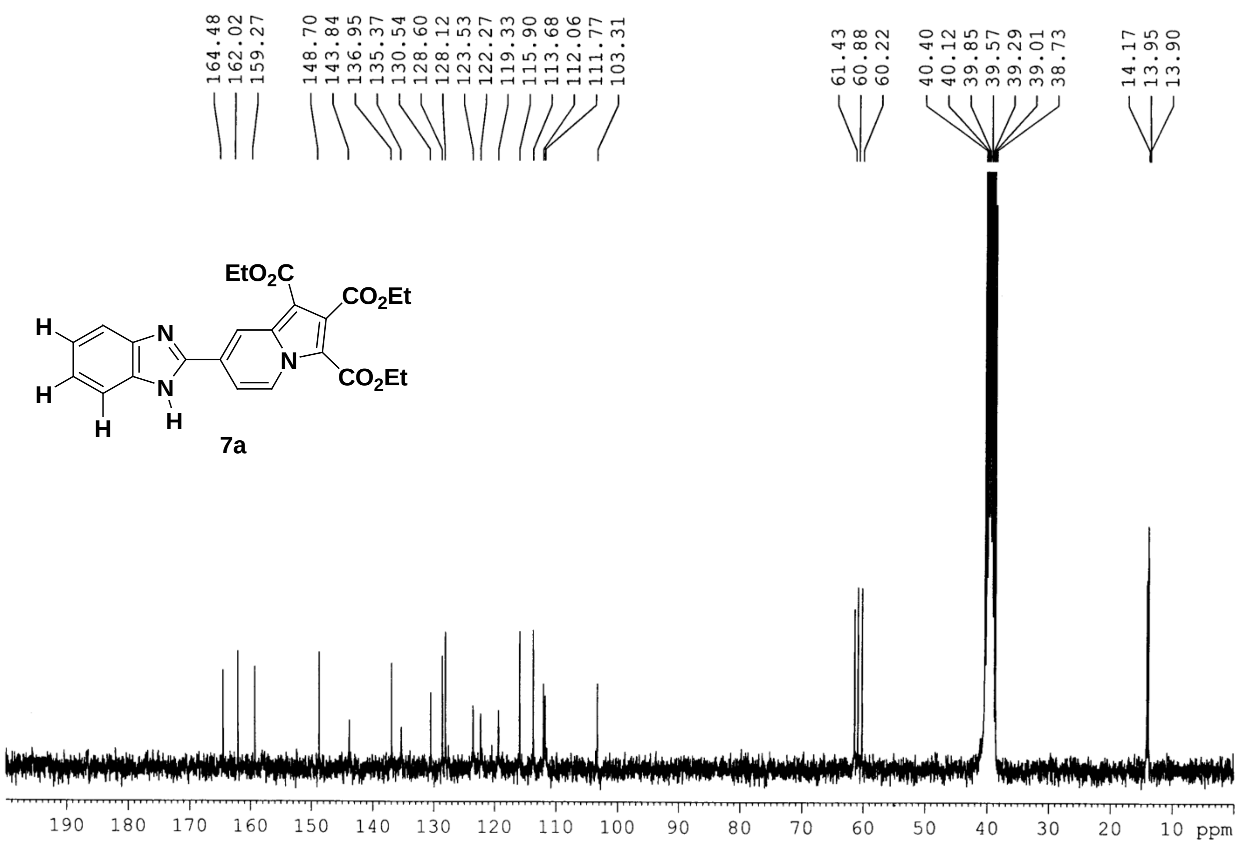

164.77
161.97
159.32
148.79
137.62
136.33
130.31
128.69
128.17
127.59
127.26
126.70
126.54
126.45
125.24
124.70
123.85
122.52
122.49
121.87
120.27
118.94
116.05
111.88
103.73
77.42
76.99
76.57
61.24
60.48
59.84
46.68
40.30
40.02
39.75
39.46
39.19
38.91
31.75
18.97
13.77
13.62
13.54
12.88
EtO2C
CO2Et
CO2Et
N
N
N
CH2CH2CH2CH3
6e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.499
9.476
9.438
9.058
8.851
8.826
8.777
8.750
8.677
8.651
8.621
8.566
8.543
8.327
8.307
7.931
7.905
7.825
7.802
7.734
7.709
7.673
7.650
7.540
7.513
7.442
7.419
7.396
7.265
5.923
4.482
4.456
4.416
4.392
1.758
1.487
1.465
1.444
1.424
1.402
1.381
EtO2C
CO2Et
CO2Et
N
N
N
6f
11
10
9
8
7
6
5
4
3
2
1
ppm
2.75
0.63
2.10
2.23
5.11
1.23
0.70
2.12
1.10
7.22
2.60
10.88
5.70
4.22
12.86
7.20
18.34

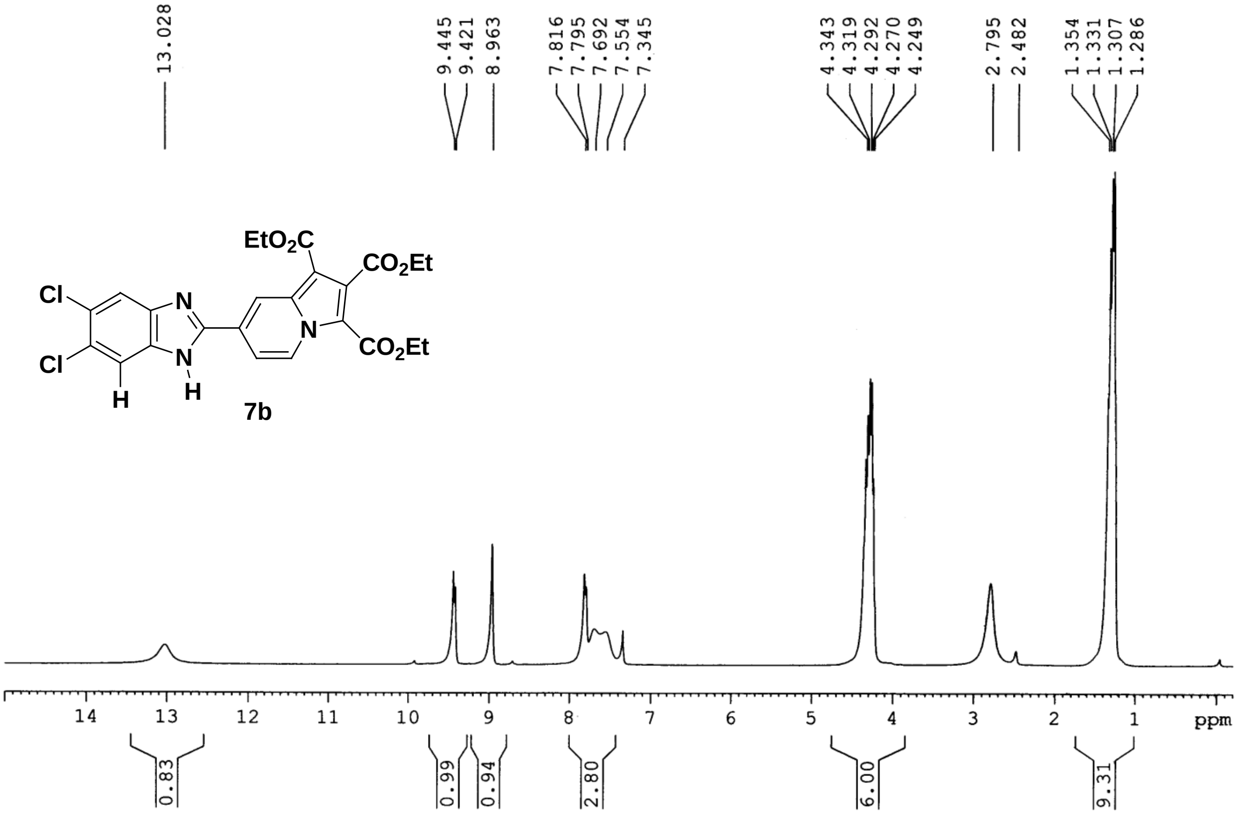

165.43
162.39
160.01
149.75
136.64
136.16
131.31
129.58
128.44
128.12
127.95
127.74
127.45
126.96
126.80
126.02
125.65
125.32
124.28
123.08
122.74
122.58
121.20
119.66
115.94
112.51
104.99
77.43
77.01
76.58
61.84
61.05
60.28
51.09
14.48
14.16
EtO2C
CO2Et
CO2Et
N
N
N
6f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

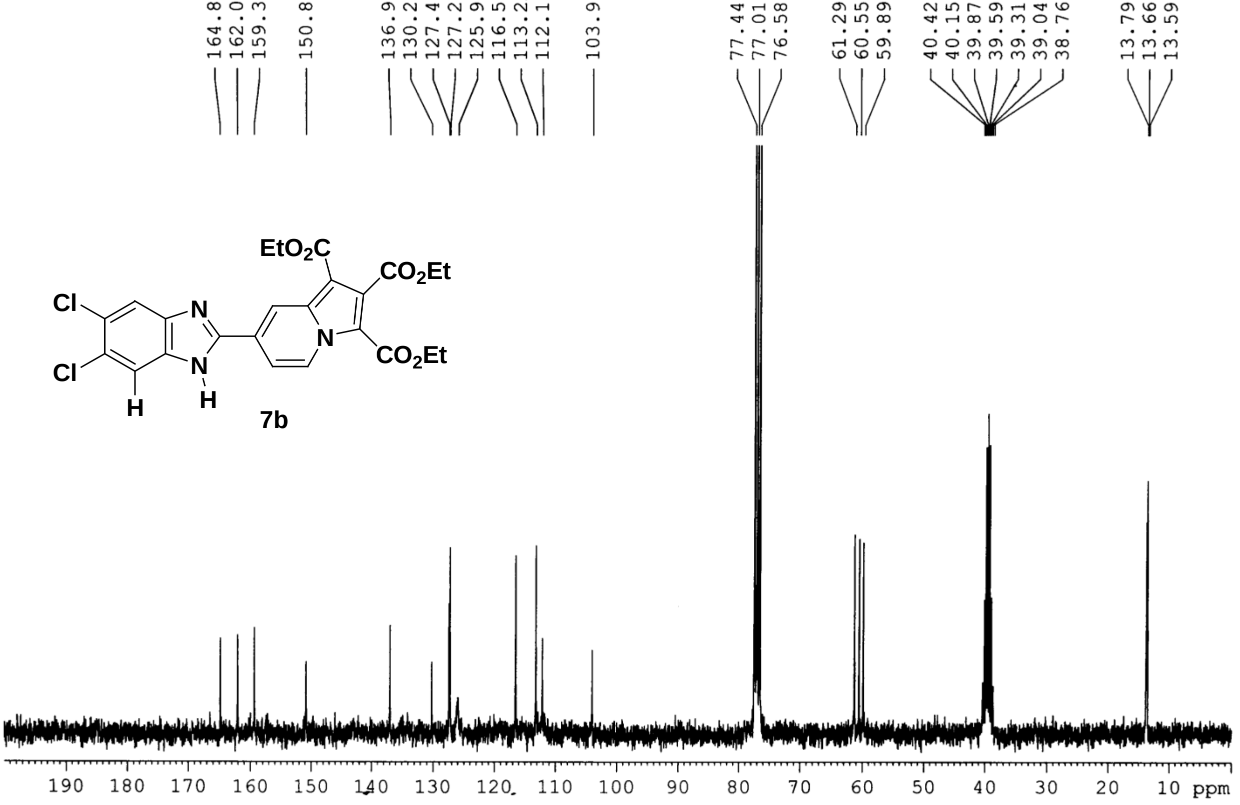

13.424
9.522
9.498
9.047
8.110
8.017
7.993
7.746
7.723
7.598
7.576
7.269
4.371
4.348
4.324
4.301
3.376
2.510
1.377
1.354
1.328
1.302
1.278
EtO$_2$C
CO$_2$Et
CO$_2$Et
H
H
H
N
N
H
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.97
1.00
0.94
1.14
1.16
1.01
2.08
6.27
9.44

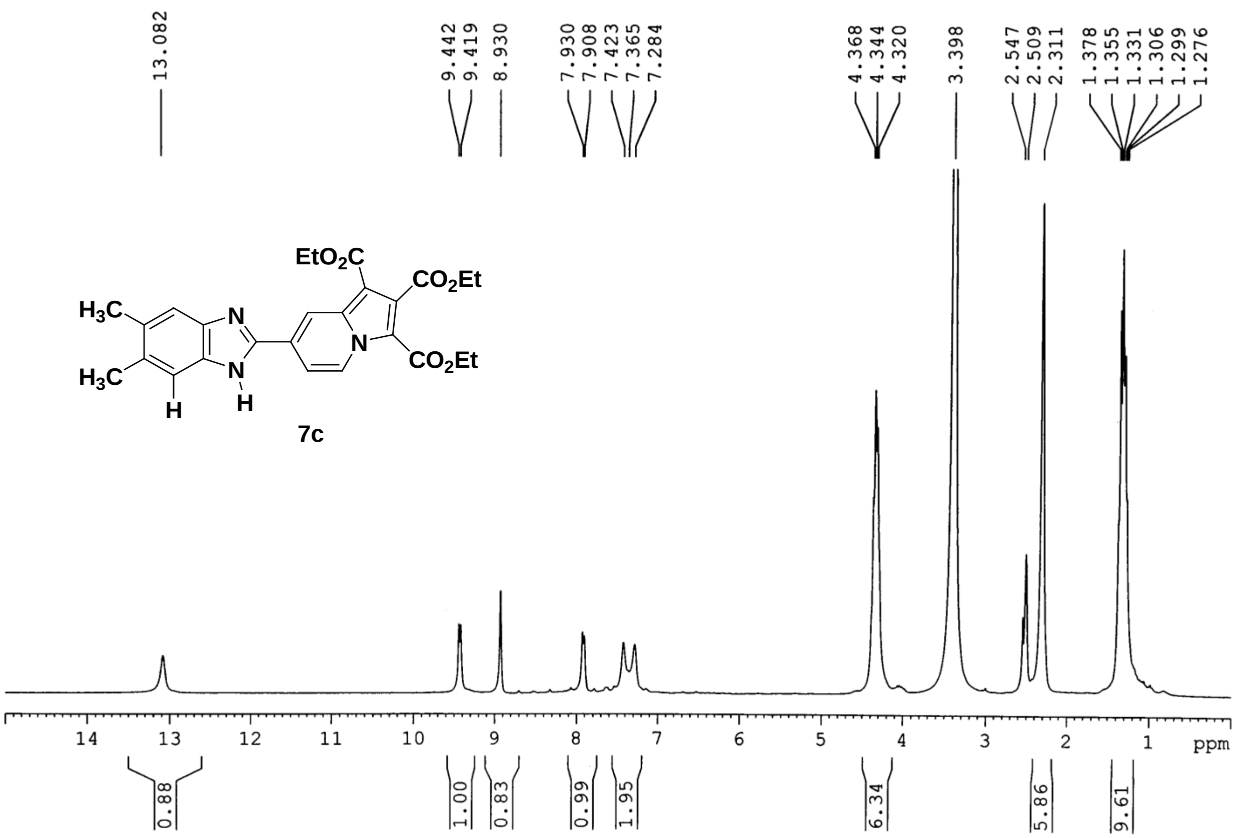
7a

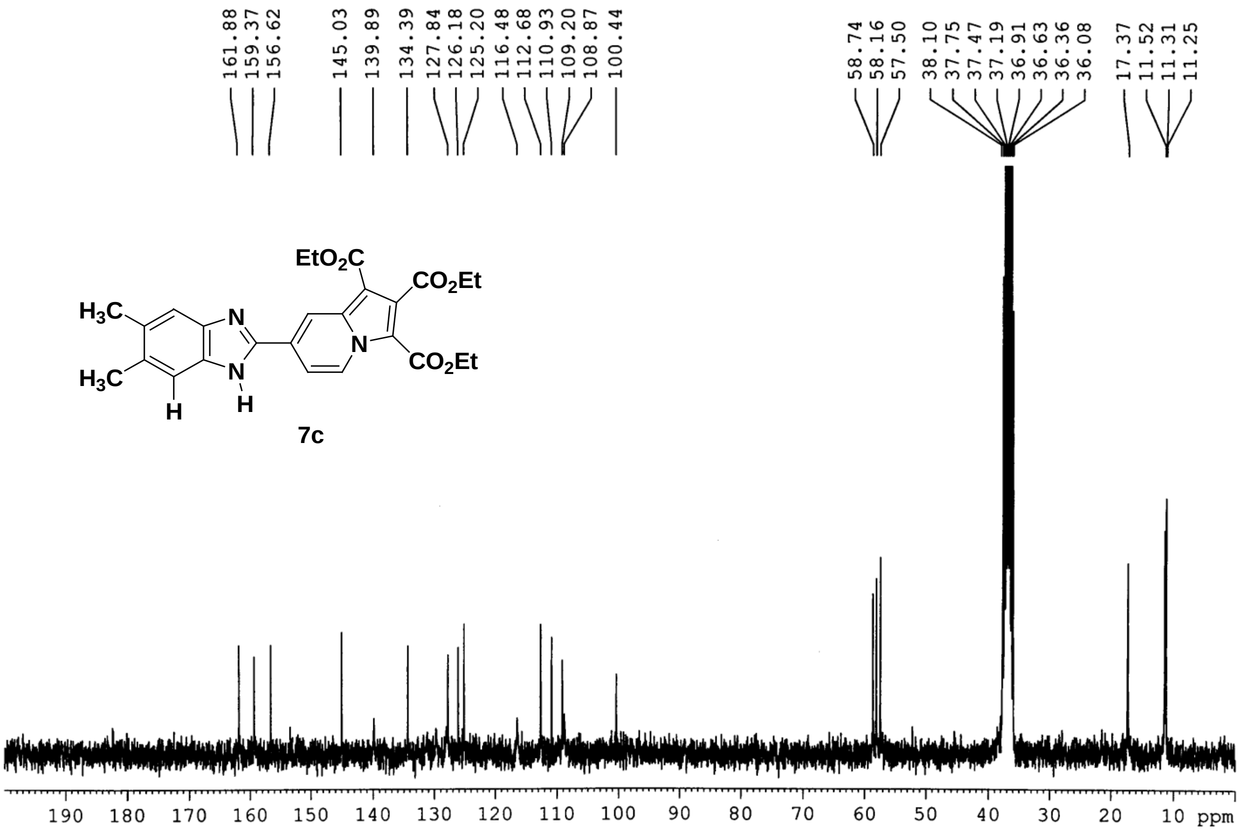

164.48
162.02
159.27
148.70
143.84
136.95
135.37
130.54
128.60
128.12
123.53
122.27
119.33
115.90
113.68
112.06
111.77
103.31
61.43
60.88
60.22
40.40
40.12
39.85
39.57
39.29
39.01
38.73
14.17
13.95
13.90
EtO$_2$C
CO$_2$Et
CO$_2$Et
H
H
H
N
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

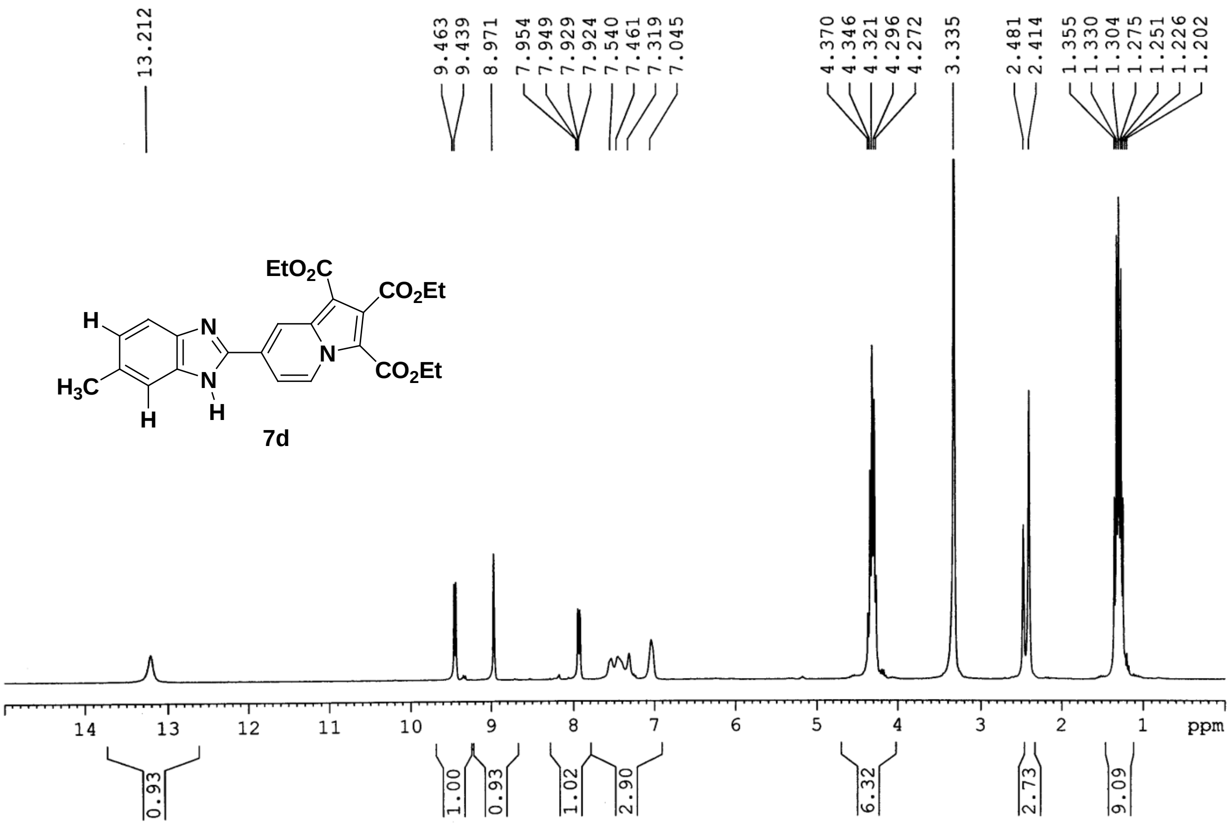
7a

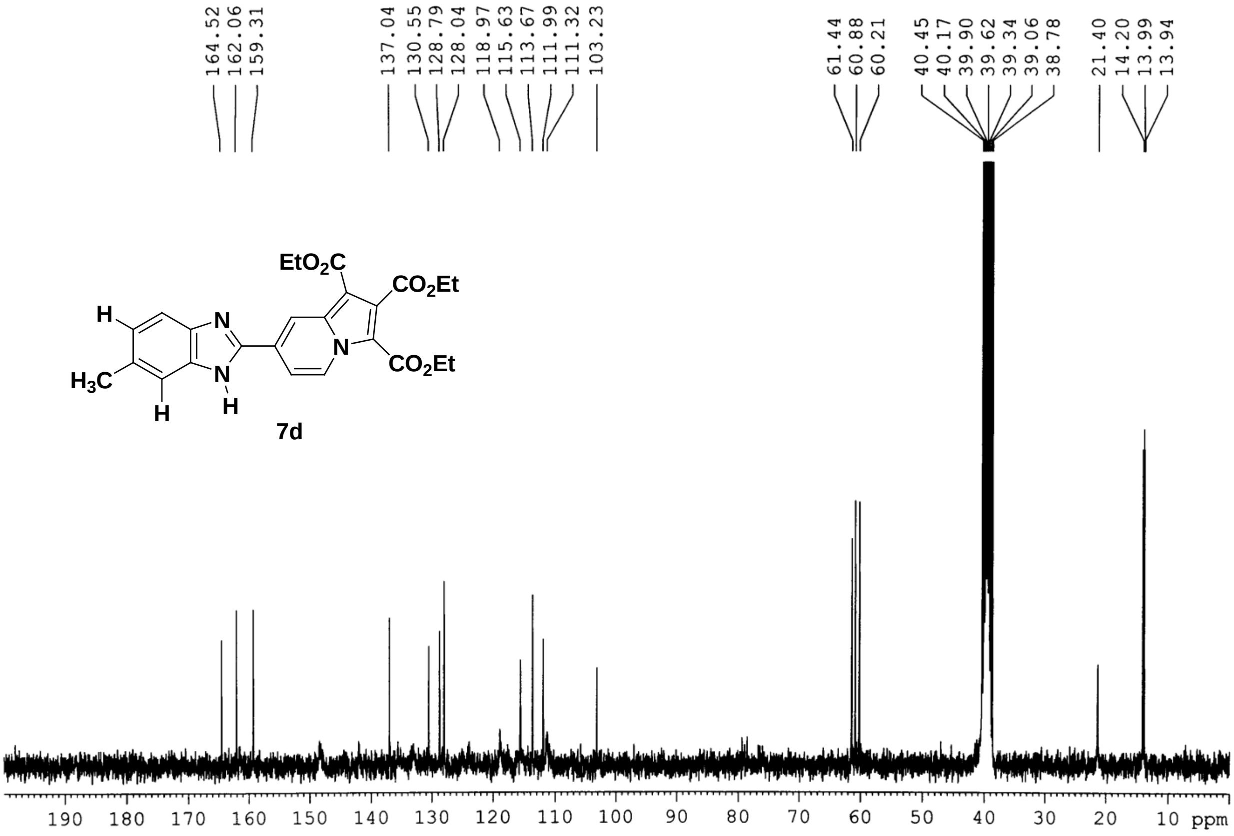

13.028
9.445
9.421
8.963
7.816
7.795
7.692
7.554
7.345
4.343
4.319
4.292
4.270
4.249
2.795
2.482
1.354
1.331
1.307
1.286
EtO₂C
CO₂Et
CO₂Et
Cl
Cl
N
N
N
H
H
7b
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.83
0.99
0.94
2.80
6.00
9.31

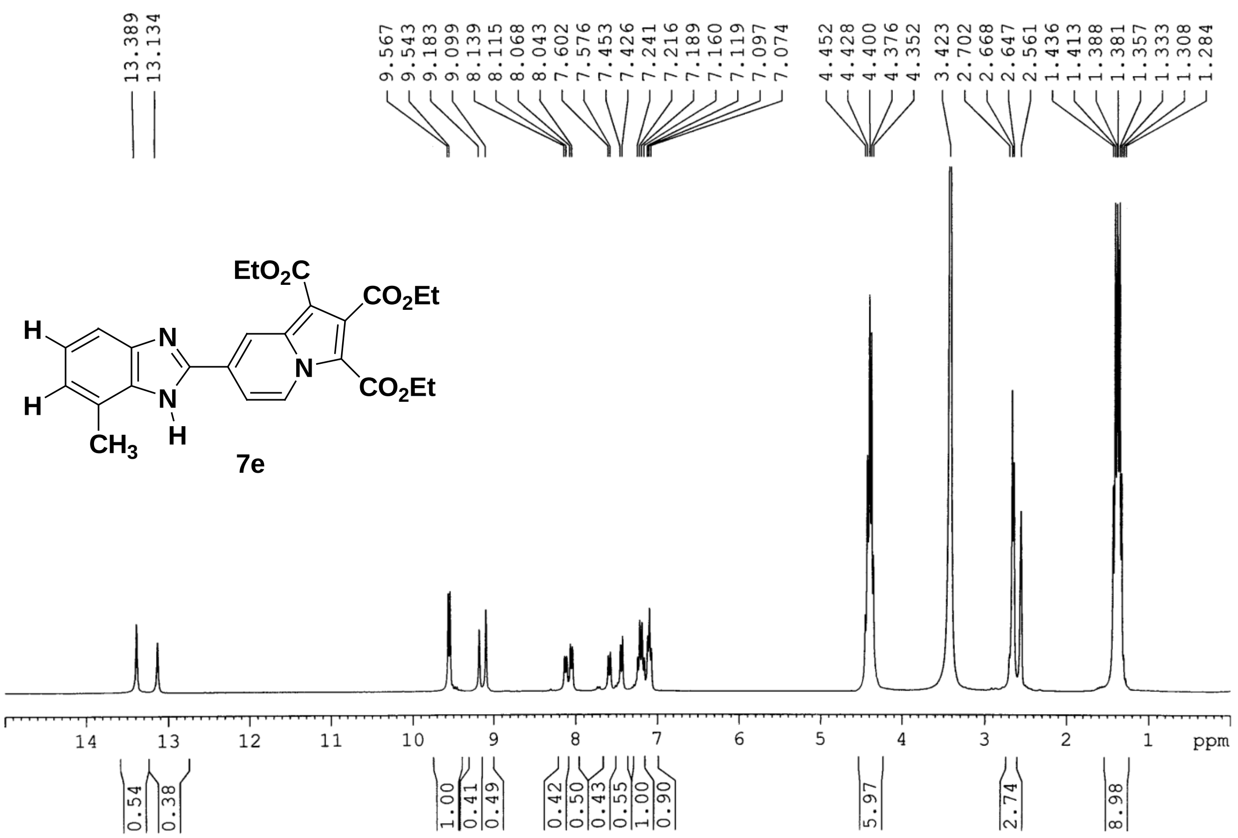

164.85
162.05
159.35
150.86
136.93
130.22
127.44
127.26
125.94
116.55
113.22
112.16
103.96
77.44
77.01
76.58
61.29
60.55
59.89
40.42
40.15
39.87
39.59
39.31
39.04
38.76
13.79
13.66
13.59
EtO₂C
CO₂Et
CO₂Et
Cl
Cl
N
N
N
H
H
7b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

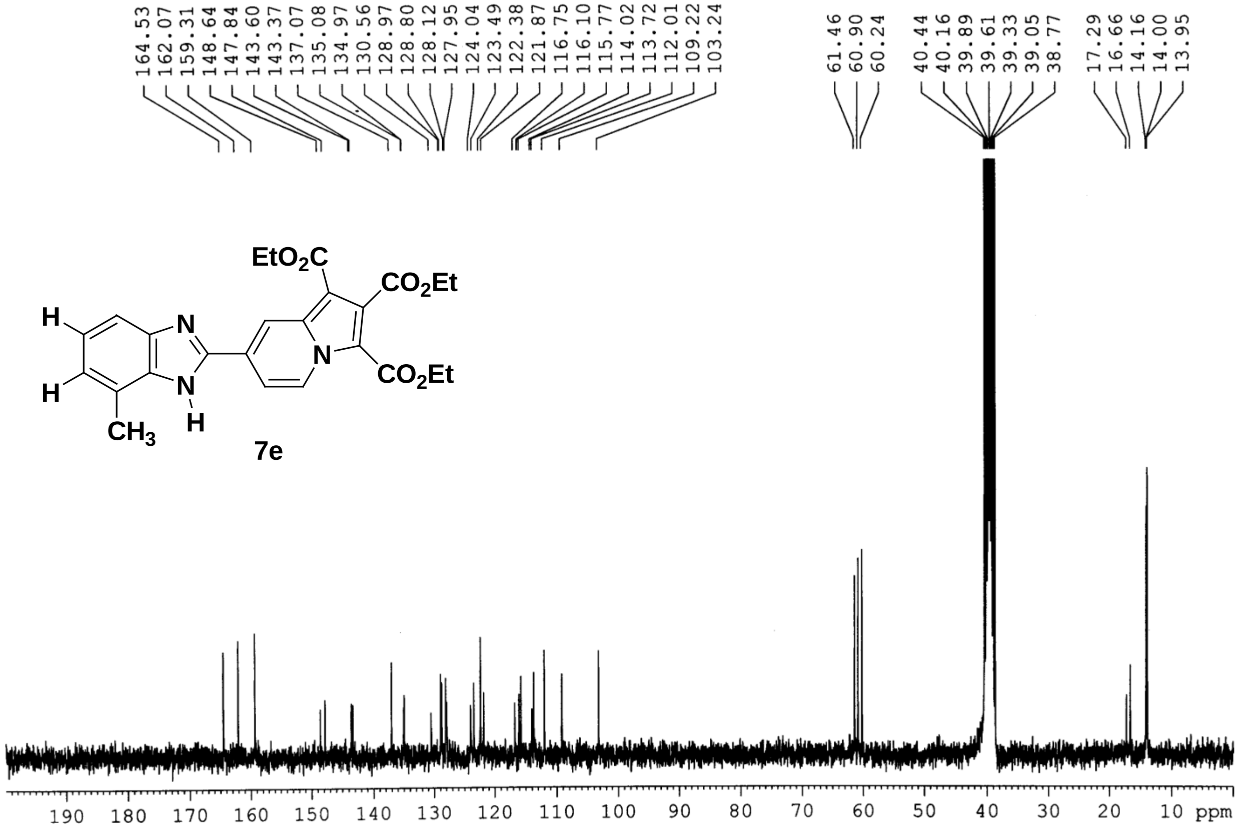

13.082
9.442
9.419
8.930
7.930
7.908
7.423
7.365
7.284
4.368
4.344
4.320
3.398
2.547
2.509
2.311
1.378
1.355
1.331
1.306
1.299
1.276
EtO_2C
CO_2Et
H_3C
N
N
CO_2Et
H_3C
N
H
H
7c
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.88
1.00
0.83
0.99
1.95
6.34
5.86
9.61


161.88
159.37
156.62
145.03
139.89
134.39
127.84
126.18
125.20
116.48
112.68
110.93
109.20
108.87
100.44
58.74
58.16
57.50
38.10
37.75
37.47
37.19
36.91
36.63
36.36
36.08
17.37
11.52
11.31
11.25
EtO_2C
CO_2Et
H_3C
N
N
CO_2Et
H_3C
N
H
H
7c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13.212
9.463
9.439
8.971
7.954
7.949
7.929
7.924
7.540
7.461
7.319
7.045
4.370
4.346
4.321
4.296
4.272
3.335
2.481
2.414
1.355
1.330
1.304
1.275
1.251
1.226
1.202
EtO$_2$C
CO$_2$Et
CO$_2$Et
H
N
N
H$_3$C
N
H
H
7d
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.93
1.00
0.93
1.02
2.90
6.32
2.73
9.09


164.52
162.06
159.31
137.04
130.55
128.79
128.04
118.97
115.63
113.67
111.99
111.32
103.23
61.44
60.88
60.21
40.45
40.17
39.90
39.62
39.34
39.06
38.78
21.40
14.20
13.99
13.94
EtO$_2$C
CO$_2$Et
CO$_2$Et
H
N
N
H$_3$C
N
H
H
7d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13.389
13.134
9.567
9.543
9.183
9.099
8.139
8.115
8.068
8.043
7.602
7.576
7.453
7.426
7.241
7.216
7.189
7.160
7.119
7.097
7.074
4.452
4.428
4.400
4.376
4.352
3.423
2.702
2.668
2.647
2.561
1.436
1.413
1.388
1.381
1.357
1.333
1.308
1.284
EtO$_2$C
CO$_2$Et
CO$_2$Et
H
H
N
N
H
CH$_3$
7e
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.54
0.38
1.00
0.41
0.49
0.42
0.50
0.43
0.55
1.00
0.90
5.97
2.74
8.98


164.53
162.07
159.31
148.64
147.84
143.60
143.37
137.07
135.08
134.97
130.56
128.97
128.80
128.12
127.95
124.04
123.49
122.38
121.87
116.75
116.10
115.77
114.02
113.72
112.01
109.22
103.24
61.46
60.90
60.24
40.44
40.16
39.89
39.61
39.33
39.05
38.77
17.29
16.66
14.16
14.00
13.95
EtO$_2$C
CO$_2$Et
CO$_2$Et
H
H
N
N
H
CH$_3$
7e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm