Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION FOR:

Synthesis of highly functionalized [3]dendralenes and their Diels-Alder reaction displaying unexpected regioselectivity

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1. X-ray Crystallographic Studies:

Single crystal X-ray diffraction data were collected on Agilent Supernova system equipped with a microfocus Cu-source (λ = 1.5418 Å) and a Titan CCD detector. The crystals were separated, coated with paraffin oil and mounted on a loop for X-ray diffraction data collection at specified temperature. The data reduction and analysis were carried out with CrysAlisPro software suit. Analytical absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid[1] and as implemented in the CrysAlisPro software suit was carried out for both the crystals. The structures were solved by direct method using Shelxs and refined using Shelxl softwares[2] using Olex2 interface[3]. All the nonhydrogen atoms were refined anisotropically and hydrogens were generated at their idealized positions and refined isotropically according to riding model.

2. X-ray Crystallographic Data (Table 1):

Compounds	**11a**	**15**	**16**	**19**
Formula	$C_{29}H_{28}O_3$	$C_{34}H_{32}BrNO_5$	$C_{33}H_{29}BrClNO_4$	$C_{26}H_{27}NO_4$
Formula Wt	424.51	614.51	618.93	417.48
Crystal System	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space Group	$P2_1/n$	$P2_1/c$	Pbca	$P2_1/c$
T,K	293	293	150.15	293(2)
Z	4	4	8	4
a, Å	10.4846(6)	13.0988(11)	10.4479(2)	14.7213(14)
b, Å	15.8614(8)	27.6314(14)	20.6292(3)	12.0482(10)
c, Å	14.7350(8)	8.4212(5)	27.0817(4)	13.0935(10)
α, deg	90	90	90	90
β, deg	99.128(5)	93.631(7)	90	109.305(11)
γ, deg	90	90	90	90
V, $Å^3$	2419.4(2)	3041.8(4)	5836.97(16)	2191.8(4)
$\rho_{calc,}$ mg/mm^3	1.165	1.342	1.409	1.265
μ, m/mm^{-1}	0.585	2.179	3.072	0.683
θ range, deg	4.123-69.930	3.199-70.246	4.29-72.13	3.181-70.164

GOF (F^2)	1.041	1.049	1.045	1.053
R_1[a] (wR_2[b]), %	0.0464 (0.1220)	0.0787 (0.2324)	0.0430 (0.1152)	0.0524 (0.1452)

3. X-ray Crystal Structures (50% ellipsoid contour percent probability):

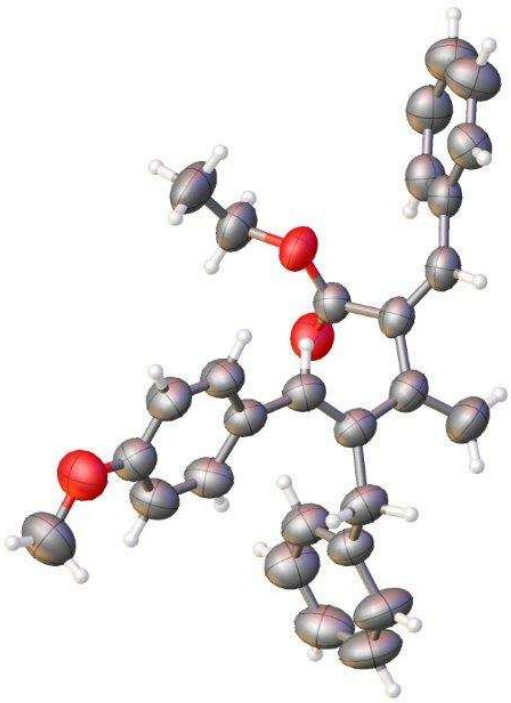


Figure S1: X-ray structure of **11a**, CCDC No. 1427878

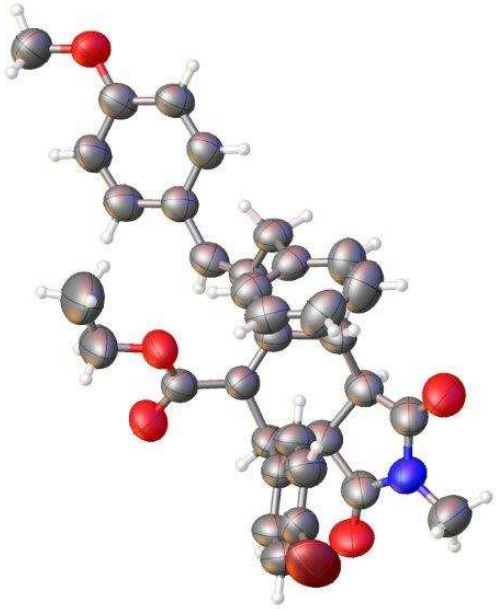


Figure S2: X-ray structure of **15**, CCDC No. 1427914

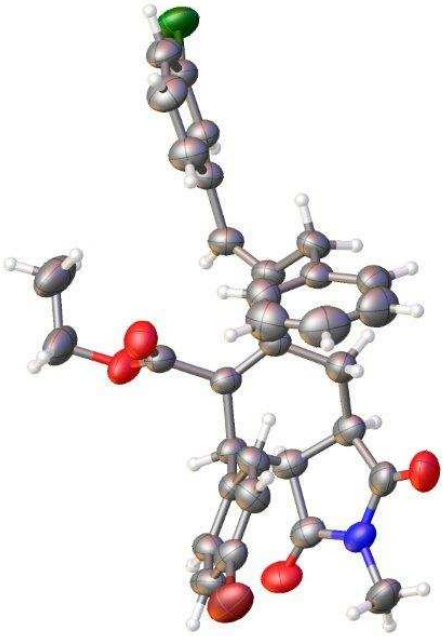


Figure S3: X-ray structure of **16**, CCDC No. 1427900

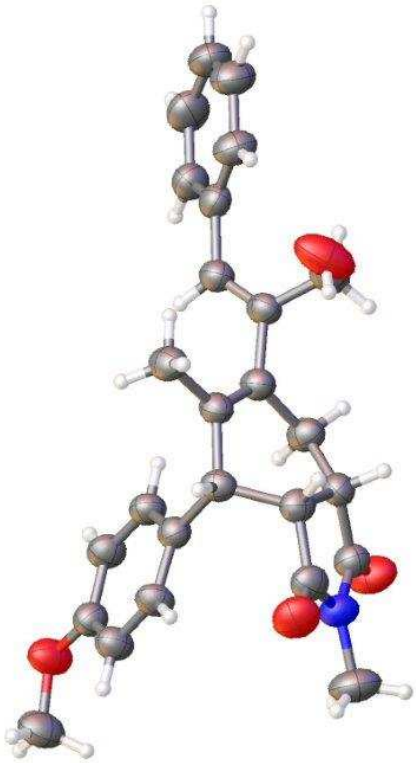


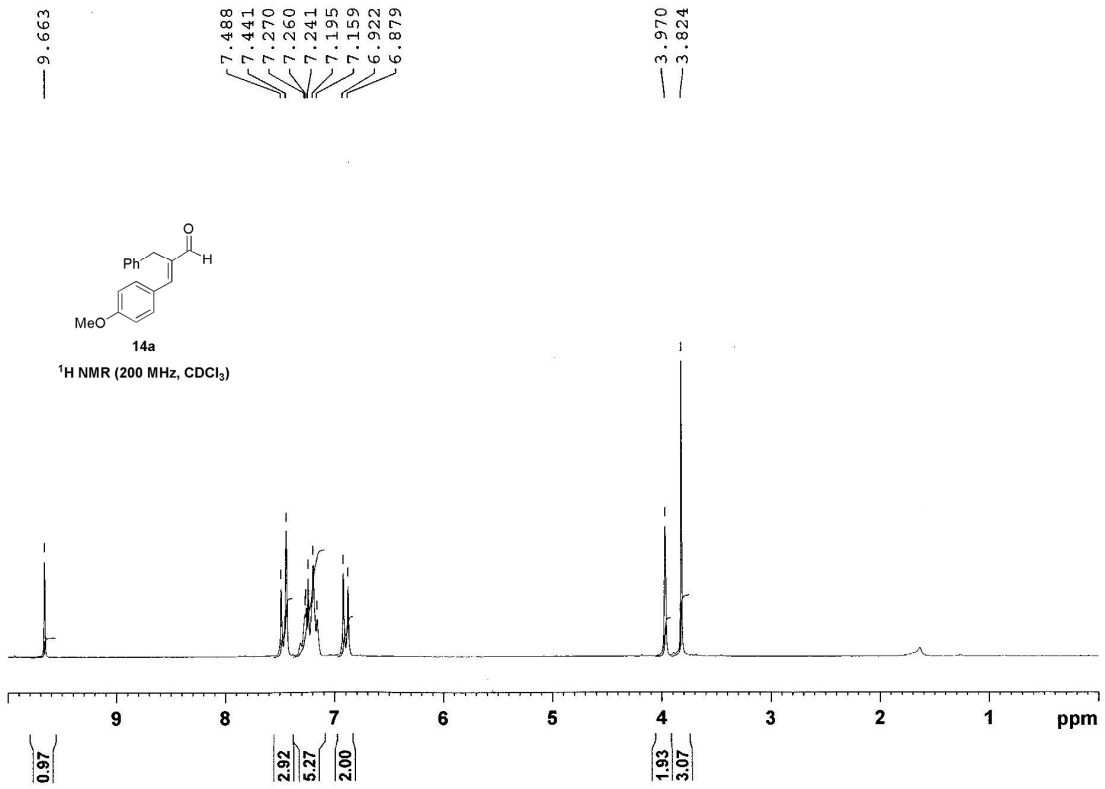
Figure S4: X-ray structure of **19**, CCDC No. 1427915

4. References:

1) R.C. Clark, J. S. Reid, *Acta Cryst.* **1995**, *A51*, 887.

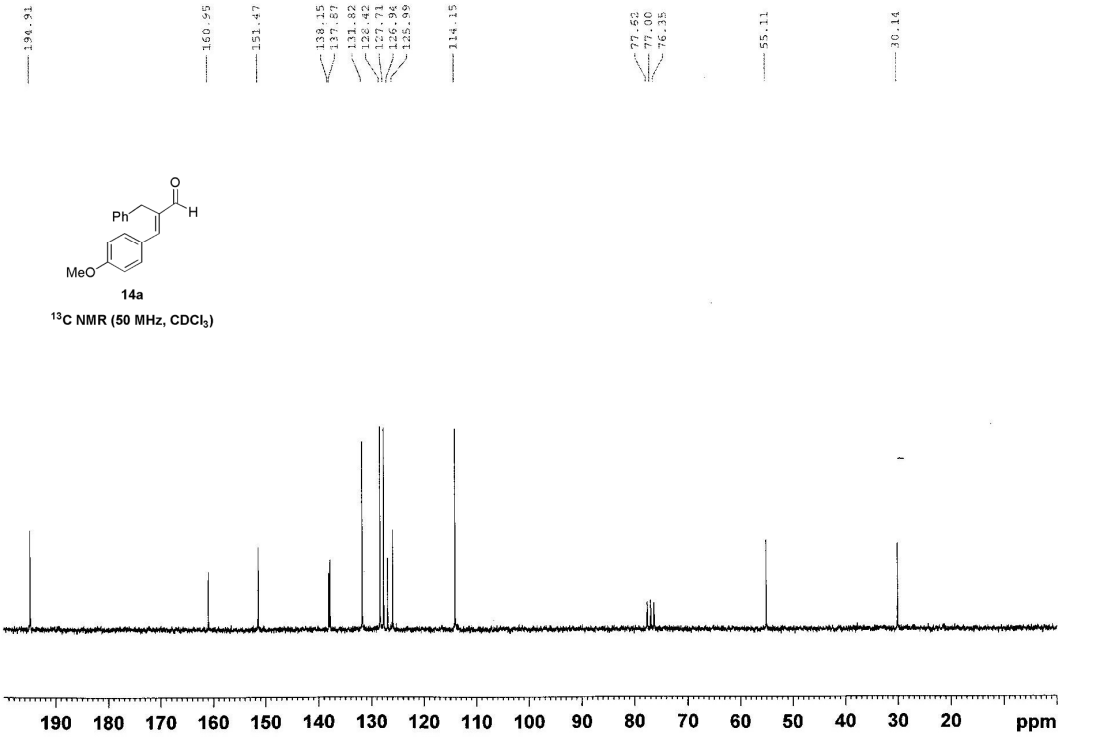
2) G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.

3) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.



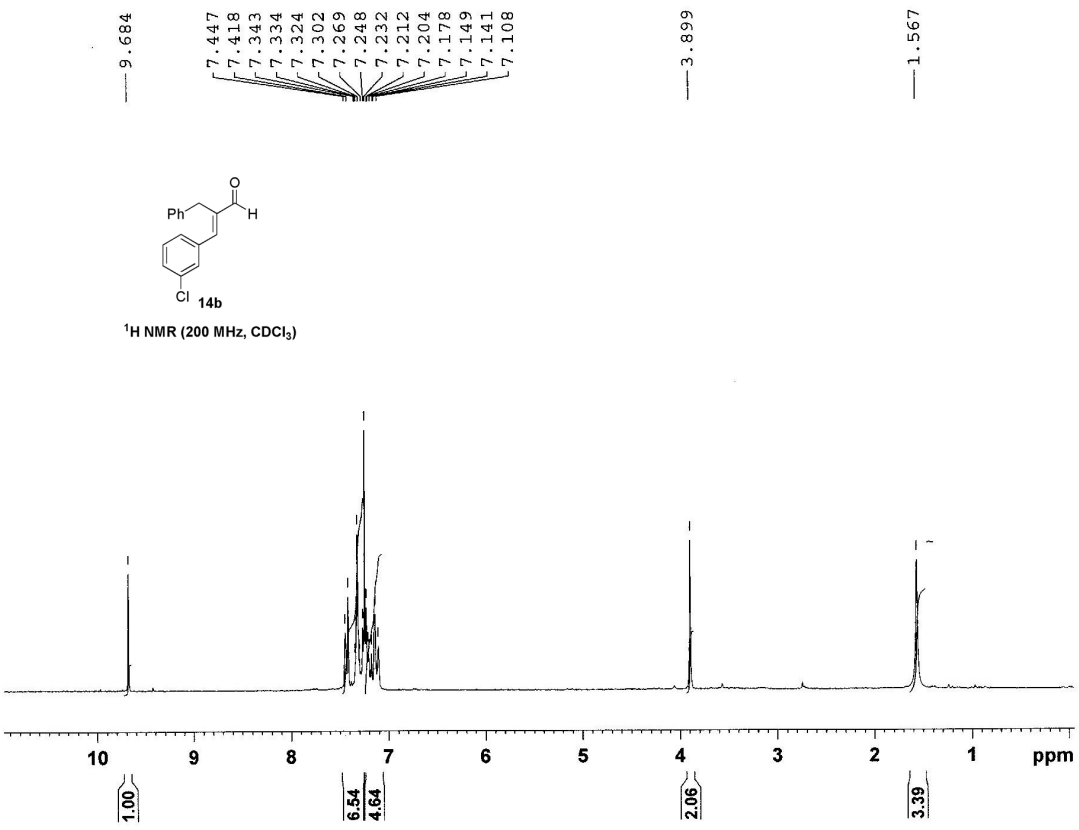
14a

^{1}H NMR (200 MHz, $CDCl_3$)

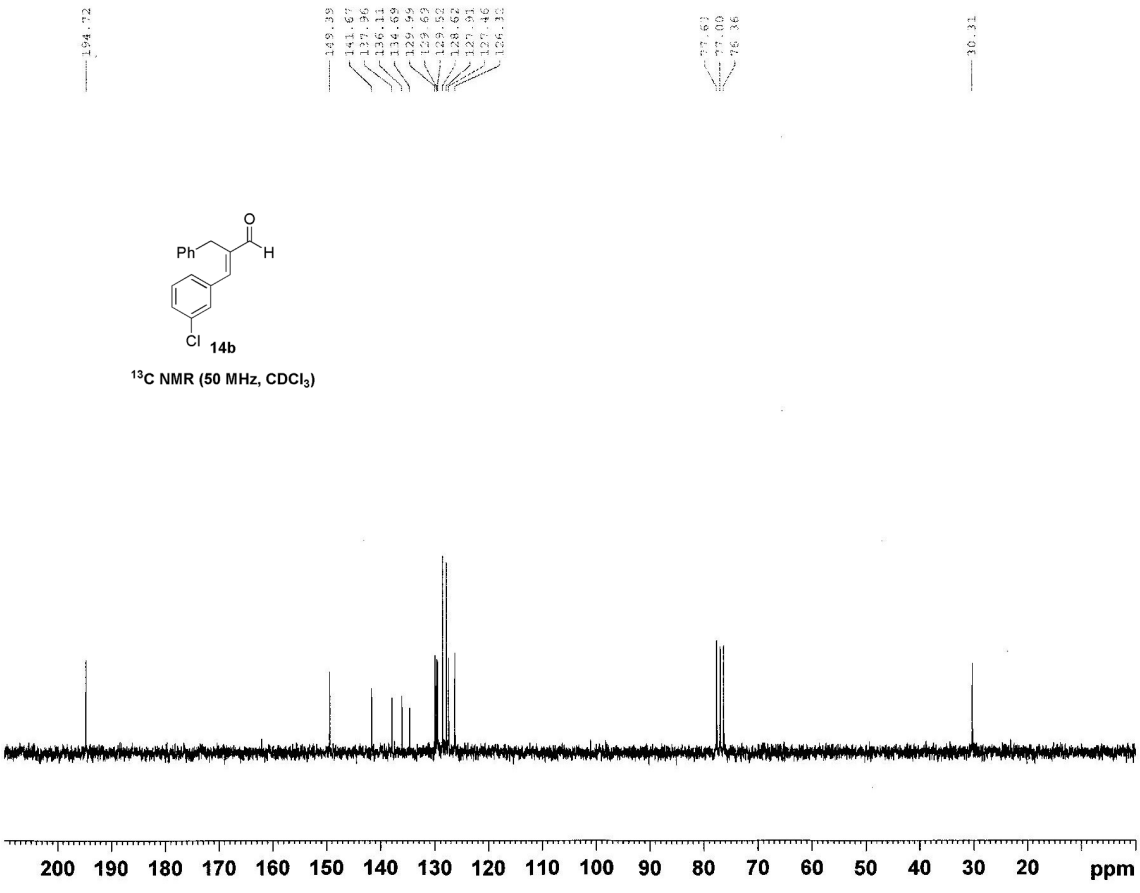


14a

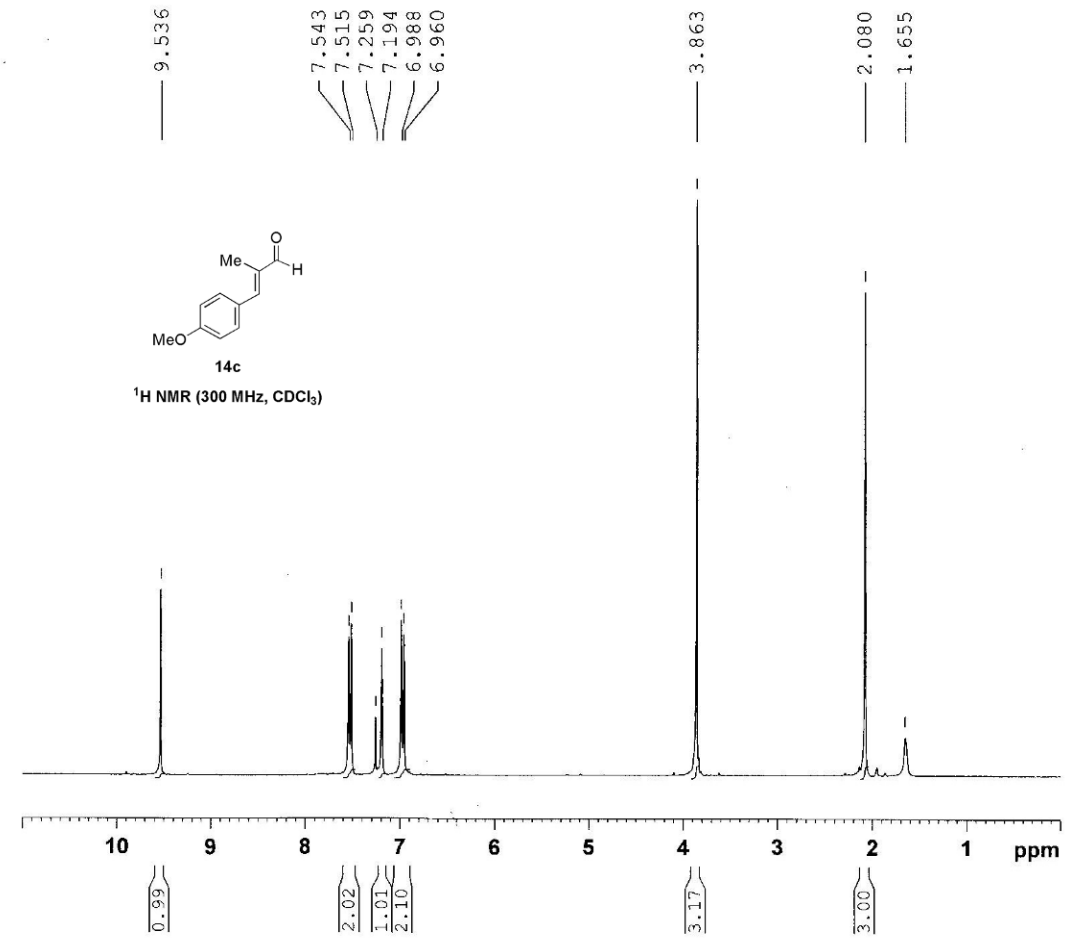
^{13}C NMR (50 MHz, $CDCl_3$)



^{1}H NMR (200 MHz, $CDCl_3$)



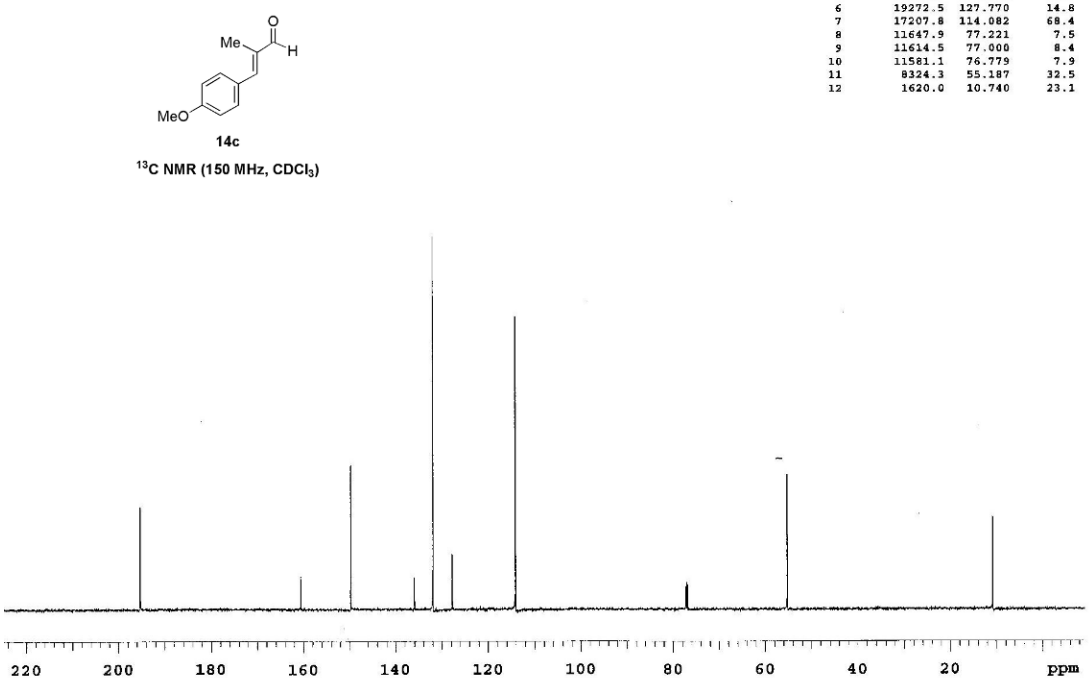
^{13}C NMR (50 MHz, $CDCl_3$)



14c

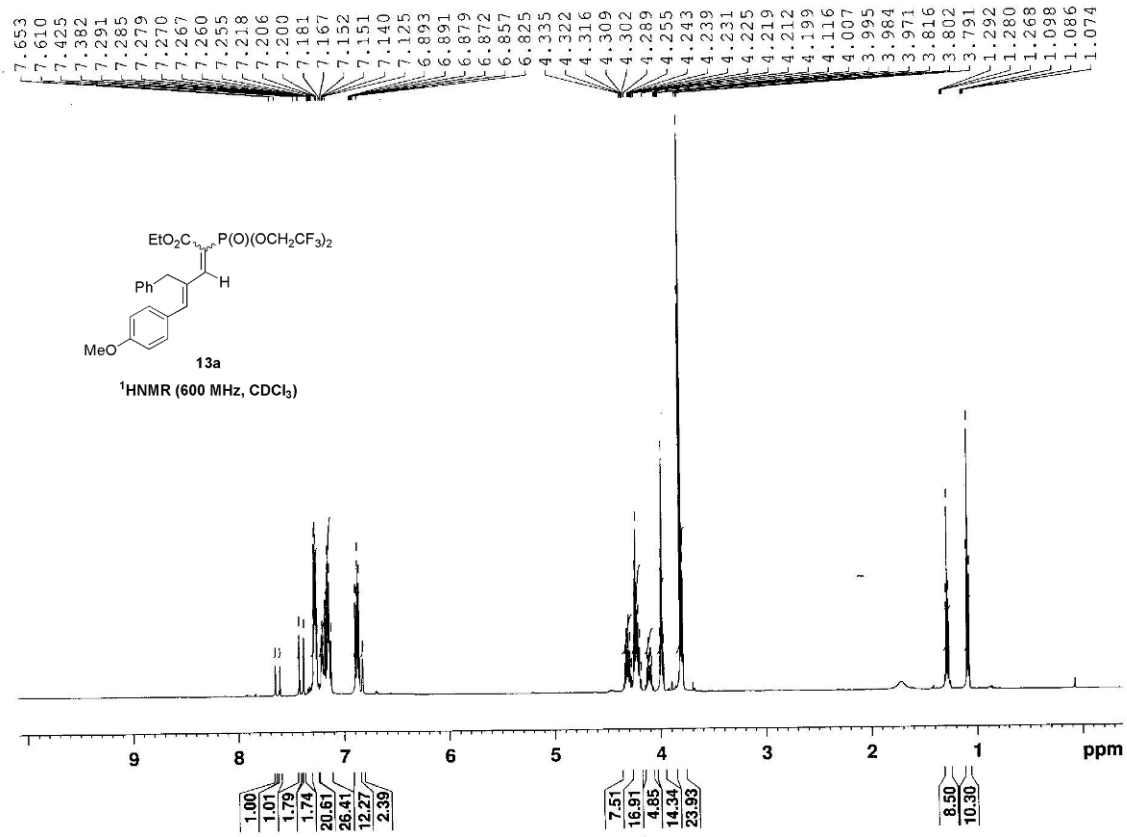
^{1}H NMR (300 MHz, $CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	29453.0	195.263	25.5
2	24226.8	160.615	9.8
3	22577.0	149.677	34.8
4	20507.5	135.958	9.6
5	19897.2	131.911	86.6
6	19272.5	127.770	14.8
7	17207.8	114.082	68.4
8	11647.9	77.221	7.5
9	11614.5	77.000	8.4
10	11581.1	76.779	7.9
11	8324.3	55.187	32.5
12	1620.0	10.740	23.1



14c

^{13}C NMR (150 MHz, $CDCl_3$)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7.382
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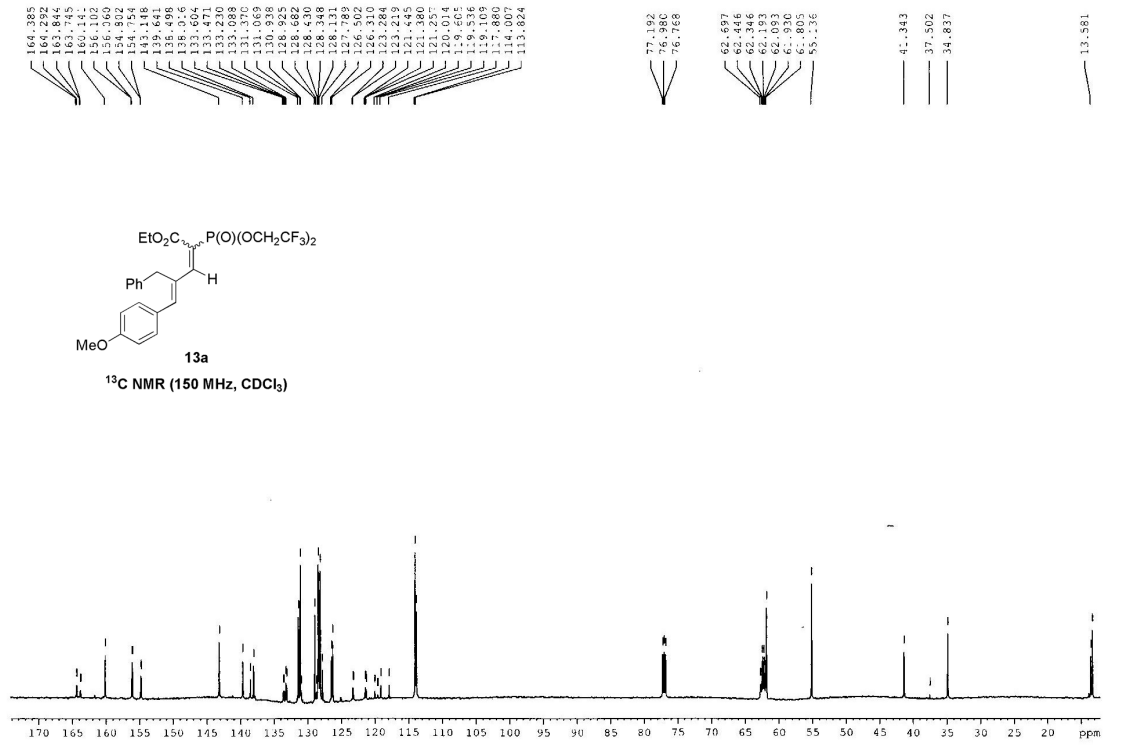
7.285
7.279
7.270
7.267
7.260
7.255
7.218
7.206
7.200
7.181
7.167
7.152
7.151
7.140
7.125
6.893
6.891
6.879
6.872
6.857
6.825
4.335
4.322
4.316
4.309
4.302
4.289
4.255
4.243
4.239
4.231
4.225
4.219
4.212
4.199
4.116
4.007
3.995
3.984
3.971
3.816
3.802
3.791
1.292
1.280
1.268
1.098
1.086
1.074
EtO2C
P(O)(OCH2CF3)2
Ph
H
MeO
13a
1HNMR (600 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.79
1.74
20.61
26.41
12.27
2.39
7.51
16.91
4.85
14.34
23.93
8.50
10.30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164.292
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156.102
156.060
154.802
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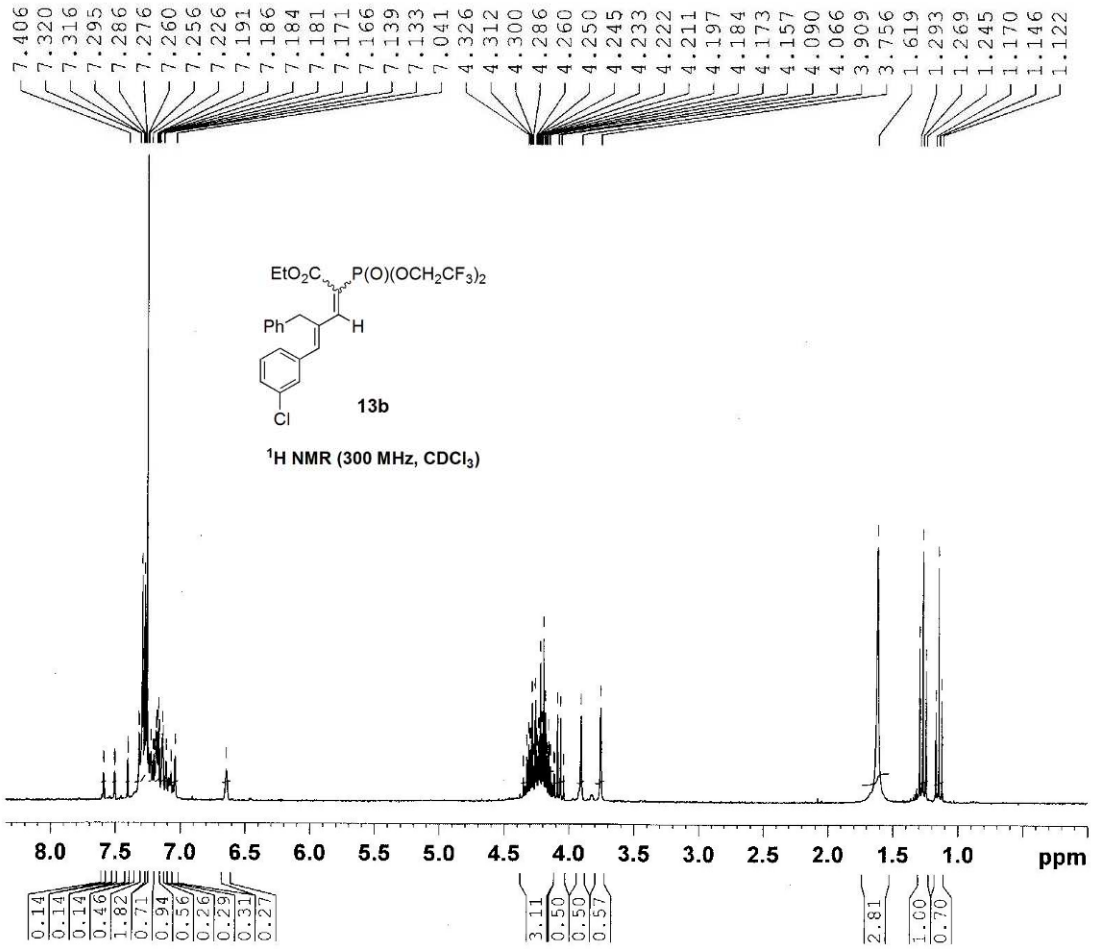
138.076
133.604
133.471
133.230
133.088
131.370
131.069
130.938
128.925
128.682
128.630
128.348
128.131
127.789
126.502
126.310
123.284
123.219
121.445
121.380
121.257
120.014
119.605
119.536
119.109
117.880
114.007
113.824
77.192
76.980
76.768
62.697
62.446
62.346
62.193
62.093
61.930
61.805
55.236
41.343
37.502
34.837
13.581

EtO2C
P(O)(OCH2CF3)2
Ph
H
MeO
13a
13C NMR (150 MHz, CDCl3)
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
ppm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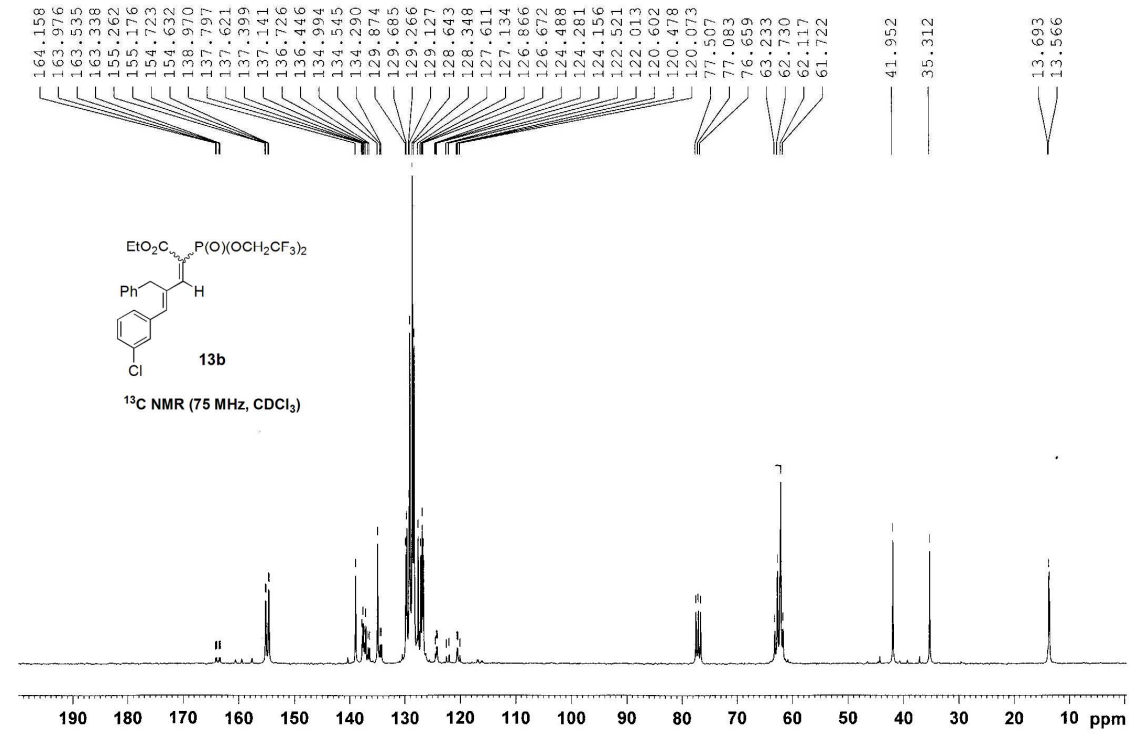
7.295
7.286
7.276
7.260
7.256
7.226
7.191
7.186
7.184
7.181
7.171
7.166
7.139
7.133
7.041
4.326
4.312
4.300
4.286
4.260
4.250
4.245
4.233
4.222
4.211
4.197
4.184
4.173
4.157
4.090
4.066
3.909
3.756
1.619
1.293
1.269
1.245
1.170
1.146
1.122
EtO2C
P(O)(OCH2CF3)2
Ph
H
Cl
13b
1H NMR (300 MHz, CDCl3)
8.0
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
ppm
0.14
0.14
0.14
0.46
1.82
0.71
0.94
0.56
0.26
0.29
0.31
0.27
3.11
0.50
0.50
0.57
2.81
1.00
0.70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155.262
155.176
154.723
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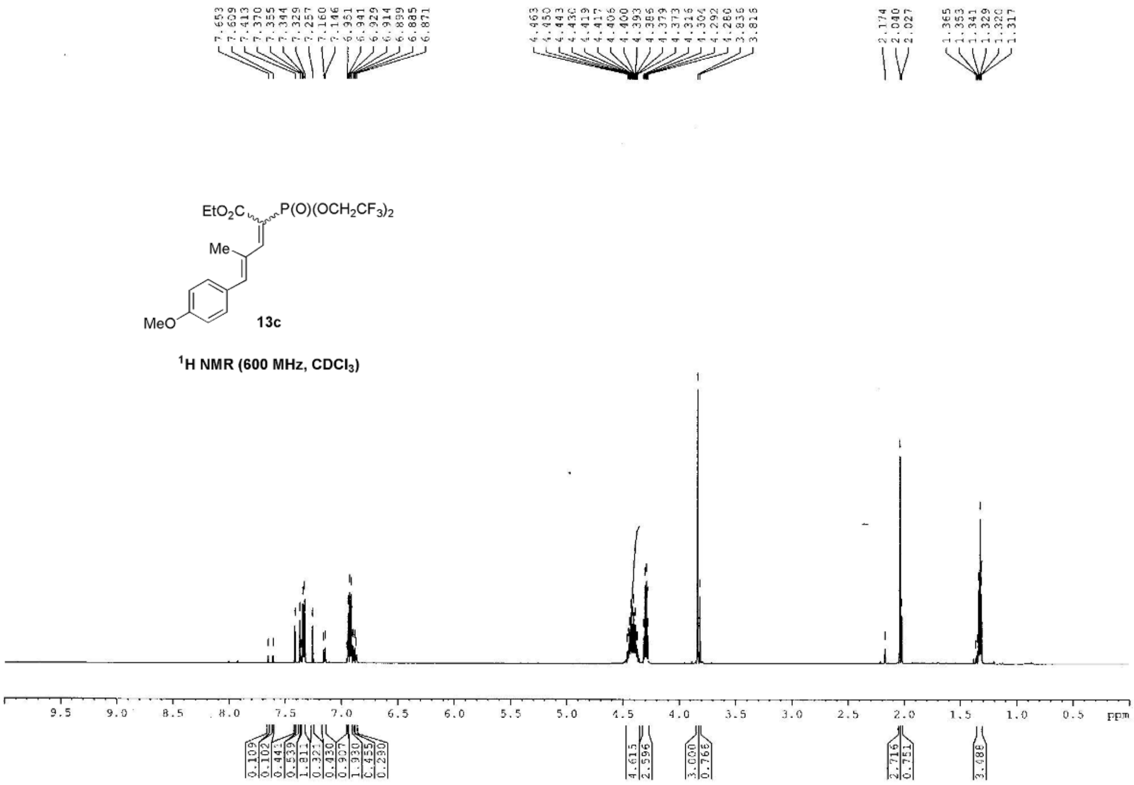
137.141
136.726
136.446
134.994
134.545
134.290
129.874
129.685
129.266
129.127
128.643
128.348
127.611
127.134
126.866
126.672
124.488
124.281
124.156
122.521
122.013
120.602
120.478
120.073
77.507
77.083
76.659
63.233
62.730
62.117
61.722
41.952
35.312
13.693
13.566
EtO2C
P(O)(OCH2CF3)2
Ph
H
Cl
13b
13C NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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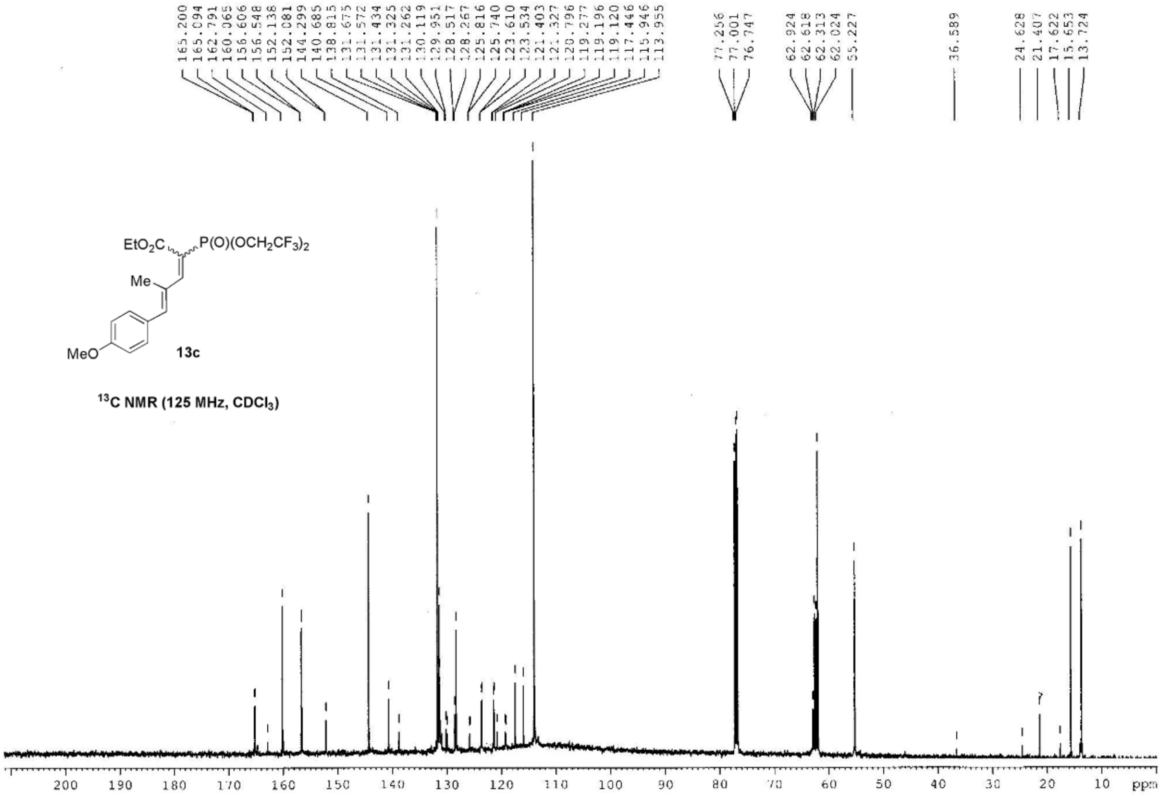
2.174 2.040 2.027
1.365 1.353 1.341 1.329 1.320 1.317
EtO2C P(O)(OCH2CF3)2
Me
MeO
13c
1H NMR (600 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.109 0.102 0.441 0.833 1.811 0.322 0.430 0.907 1.930 0.455 0.230
4.615 2.596 3.000 0.766 2.716 0.751 3.088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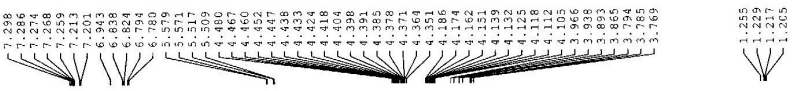
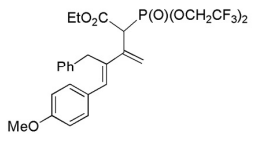
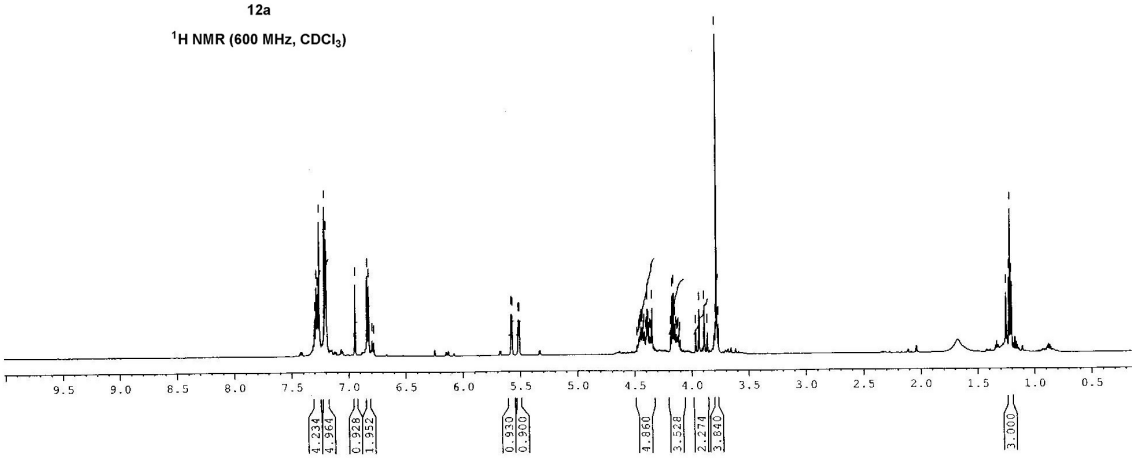
77.256 77.001 76.747
62.924 62.618 62.313 62.024 55.227
36.589
24.628 21.407 17.622 15.653 13.724
EtO2C P(O)(OCH2CF3)2
Me
MeO
13c
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

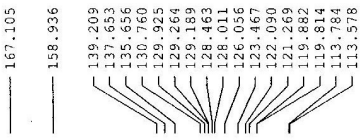




12a

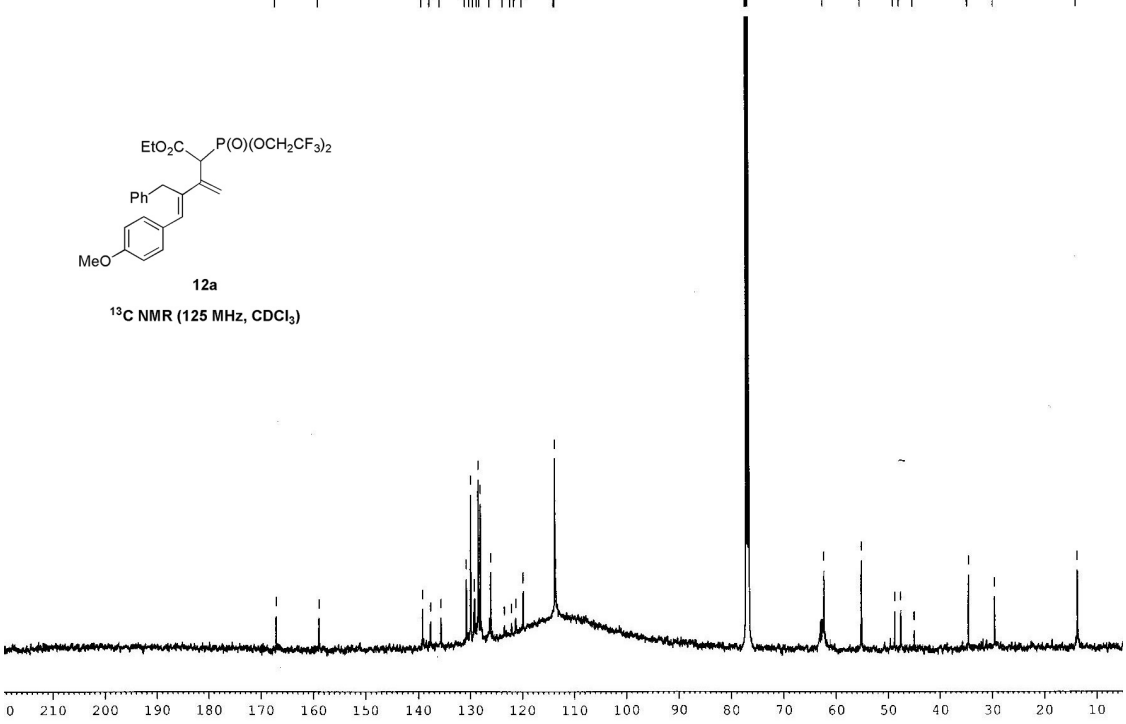
^{1}H NMR (600 MHz, $CDCl_3$)

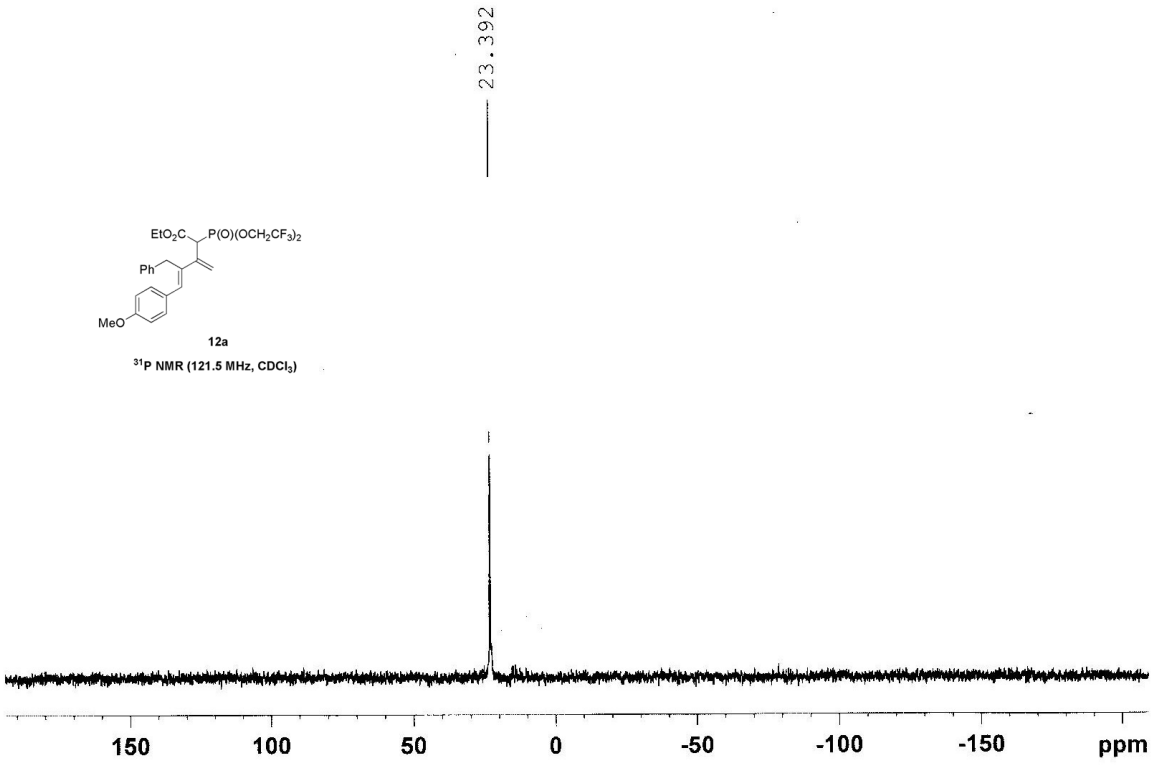




12a

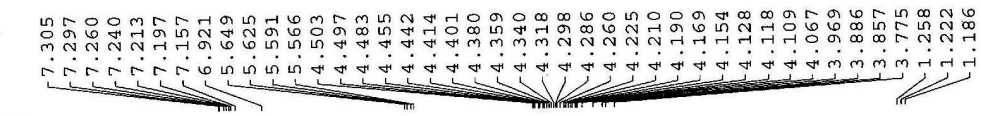
^{13}C NMR (125 MHz, $CDCl_3$)

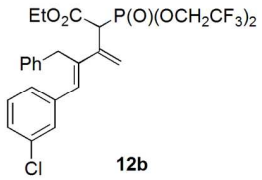




12a

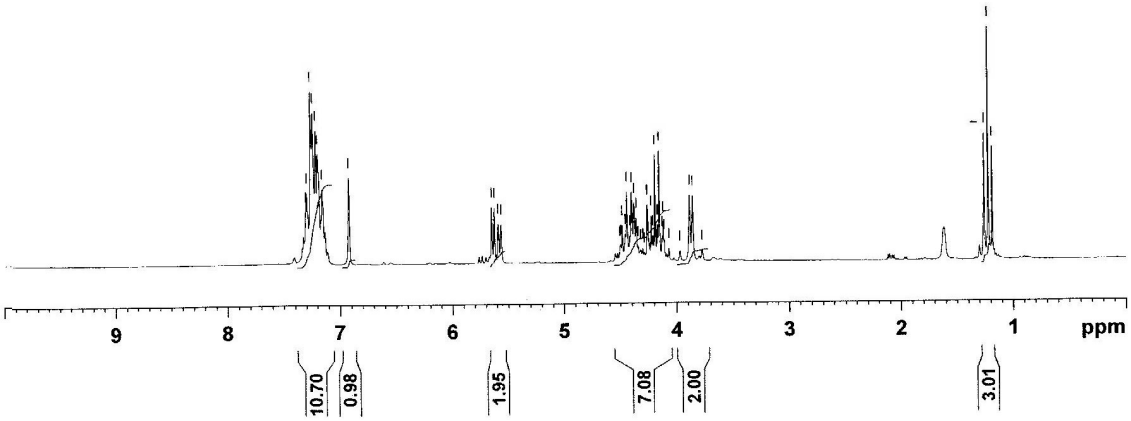
^{31}P NMR (121.5 MHz, $CDCl_3$)

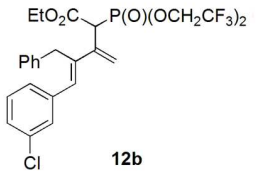




12b

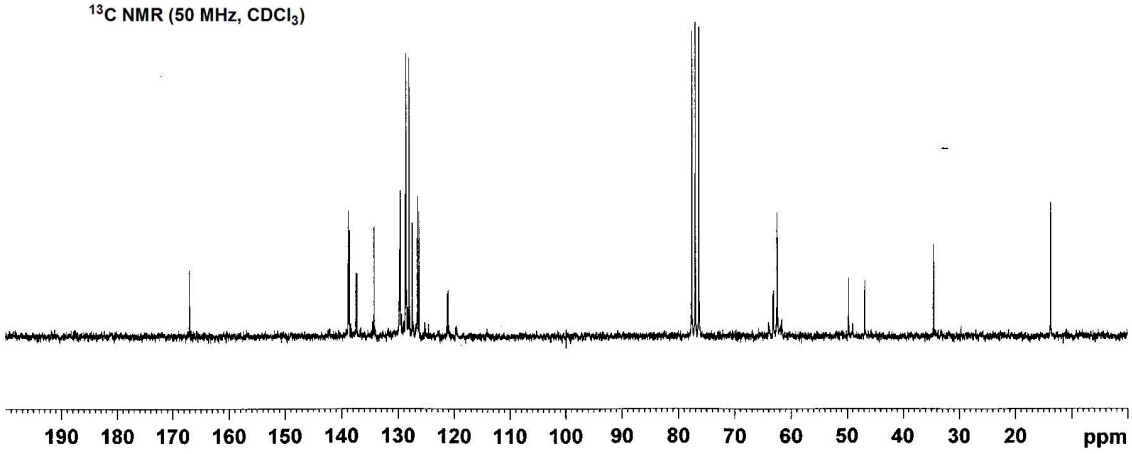
^{1}H NMR (200 MHz, $CDCl_3$)

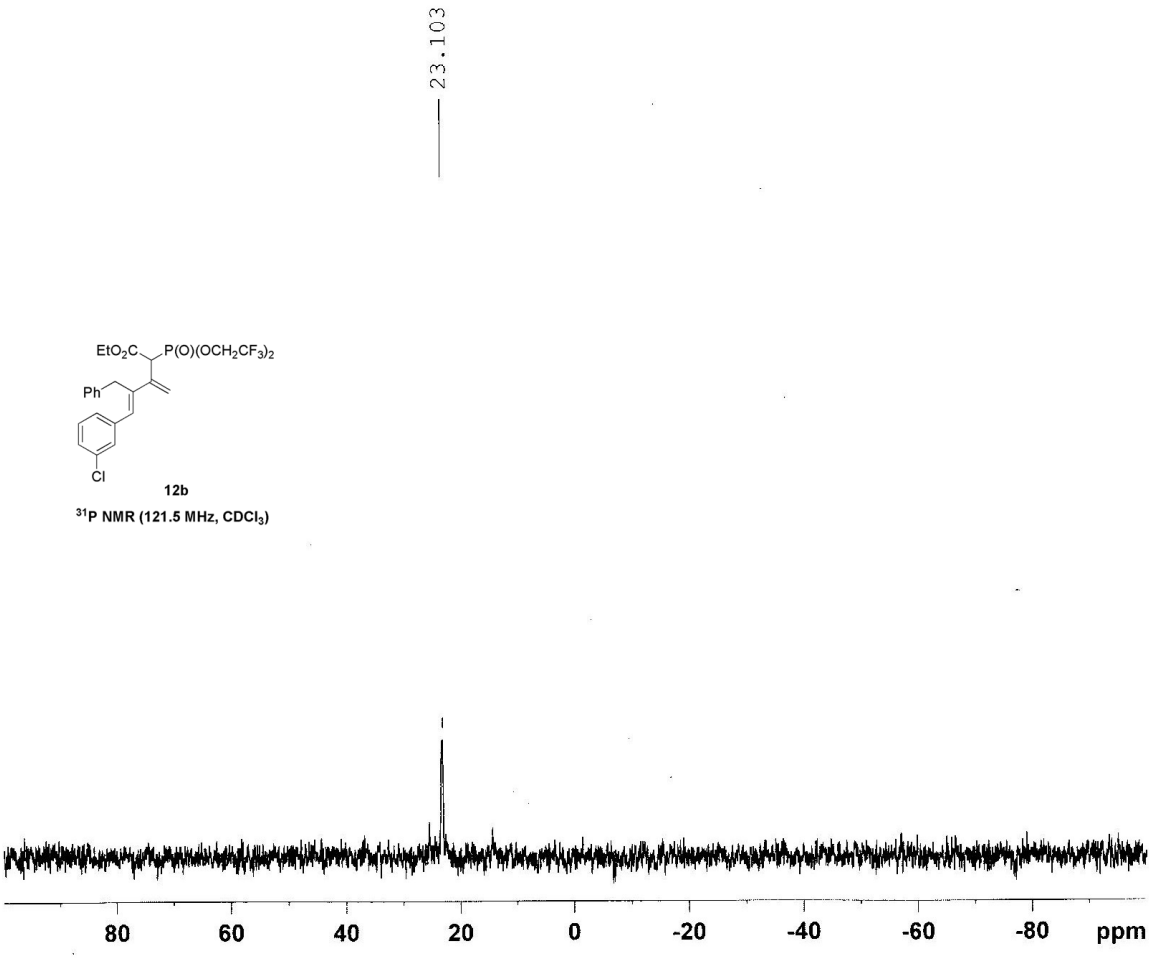




12b

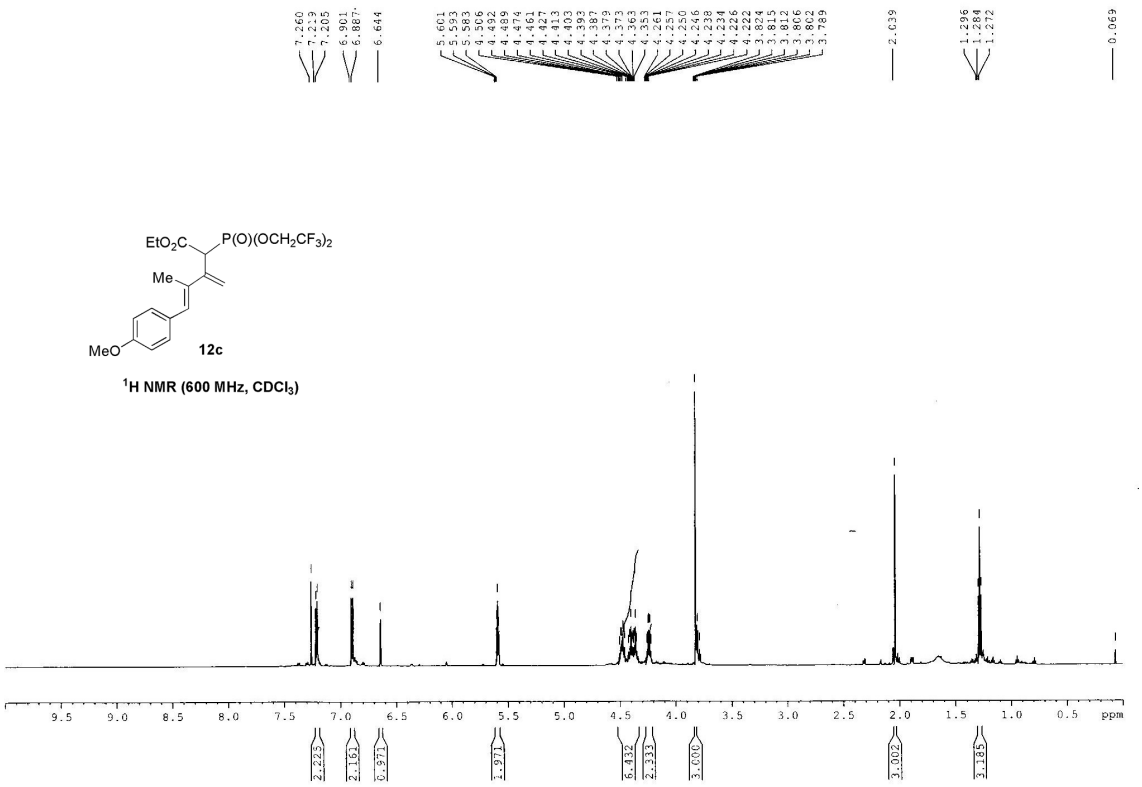
^{13}C NMR (50 MHz, $CDCl_3$)





12b

^{31}P NMR (121.5 MHz, $CDCl_3$)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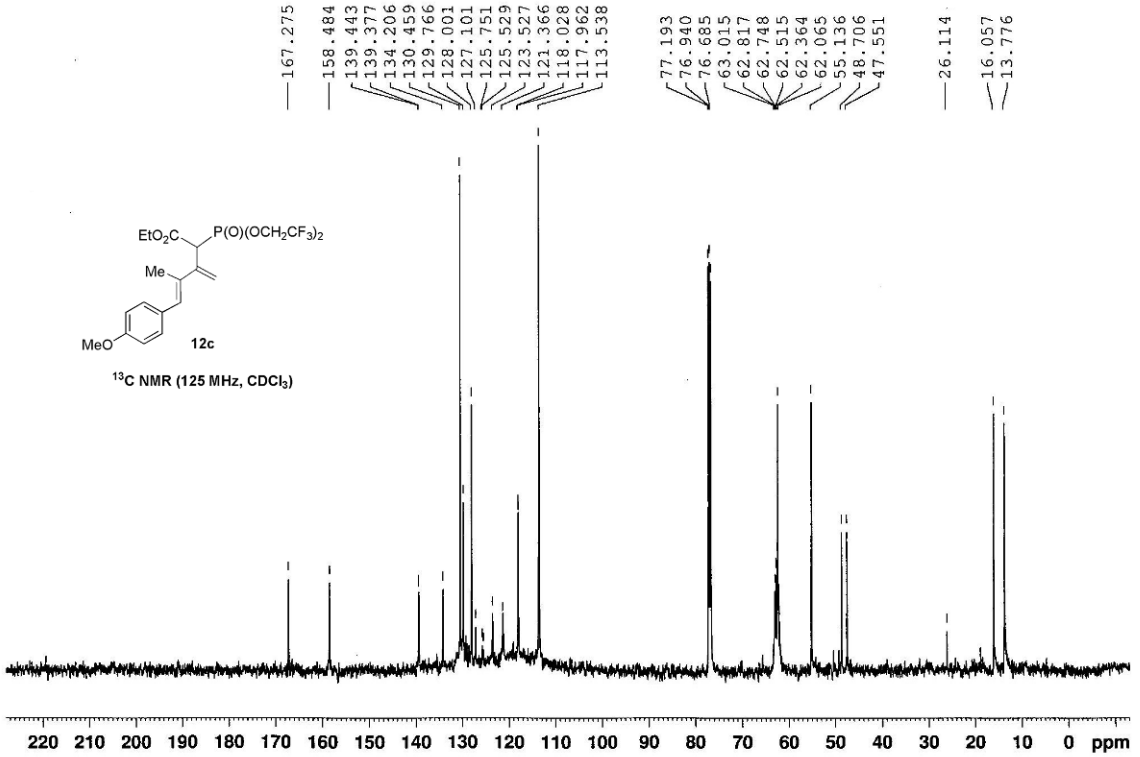
6.901
6.887
6.644
5.601
5.593
5.583
4.506
4.492
4.488
4.474
4.461
4.427
4.413
4.403
4.393
4.387
4.379
4.373
4.363
4.353
4.261
4.257
4.250
4.246
4.238
4.234
4.226
4.222
3.824
3.815
3.812
3.806
3.802
3.789
2.039
1.296
1.284
1.272
0.069
EtO2C
P(O)(OCH2CF3)2
Me
MeO
12c
1H NMR (600 MHz, CDCl3)
9.5 9.0 8.5 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 ppm
2.225
2.161
0.971
1.971
6.432
2.333
3.000
3.002
3.185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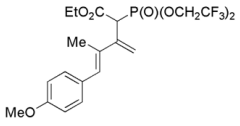
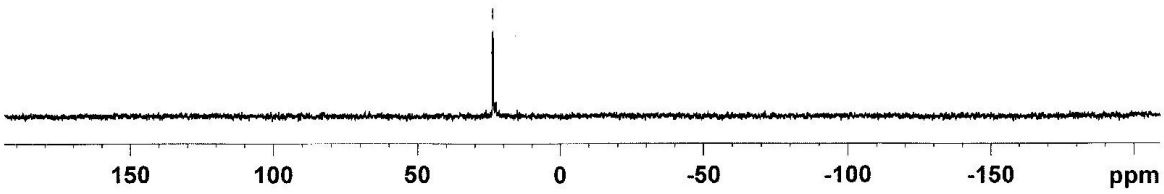
158.484
139.443
139.377
134.206
130.459
129.766
128.001
127.101
125.751
125.529
123.527
121.366
118.028
117.962
113.538
77.193
76.940
76.685
63.015
62.817
62.748
62.515
62.364
62.065
55.136
48.706
47.551
26.114
16.057
13.776
EtO2C
P(O)(OCH2CF3)2
Me
MeO
12c
13C NMR (125 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

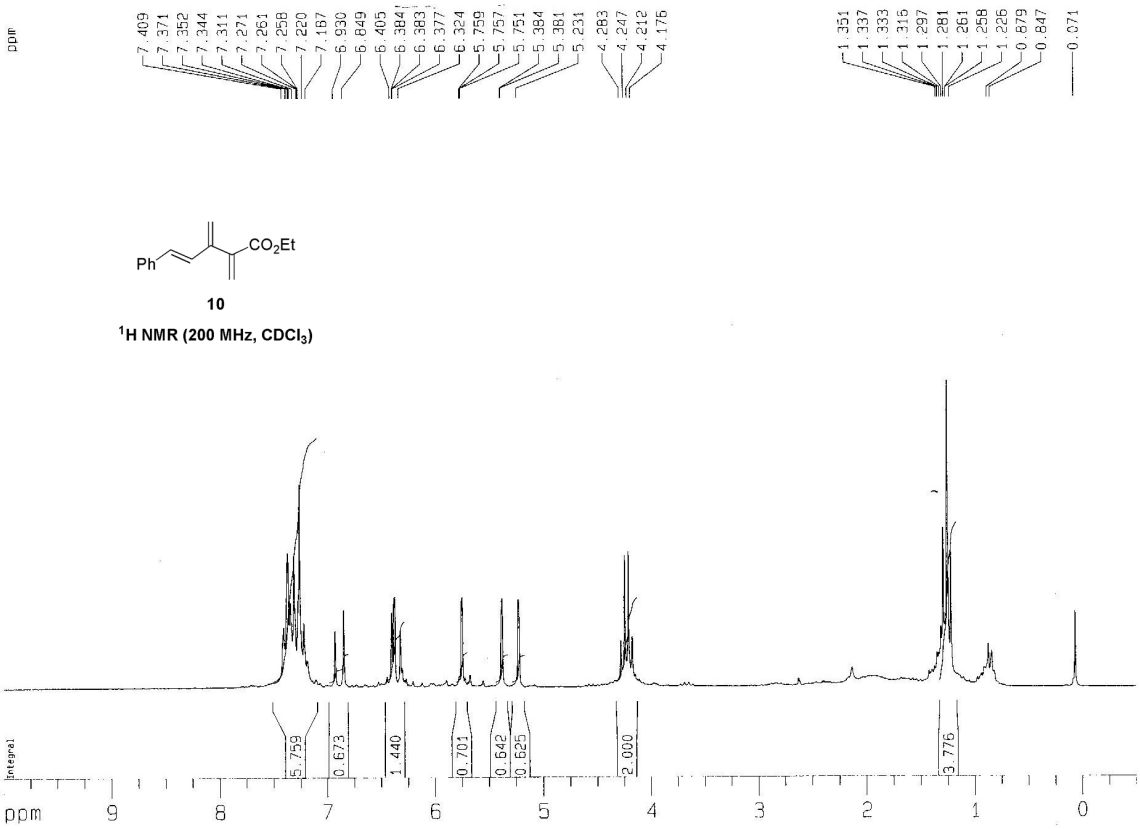
23.715



12c

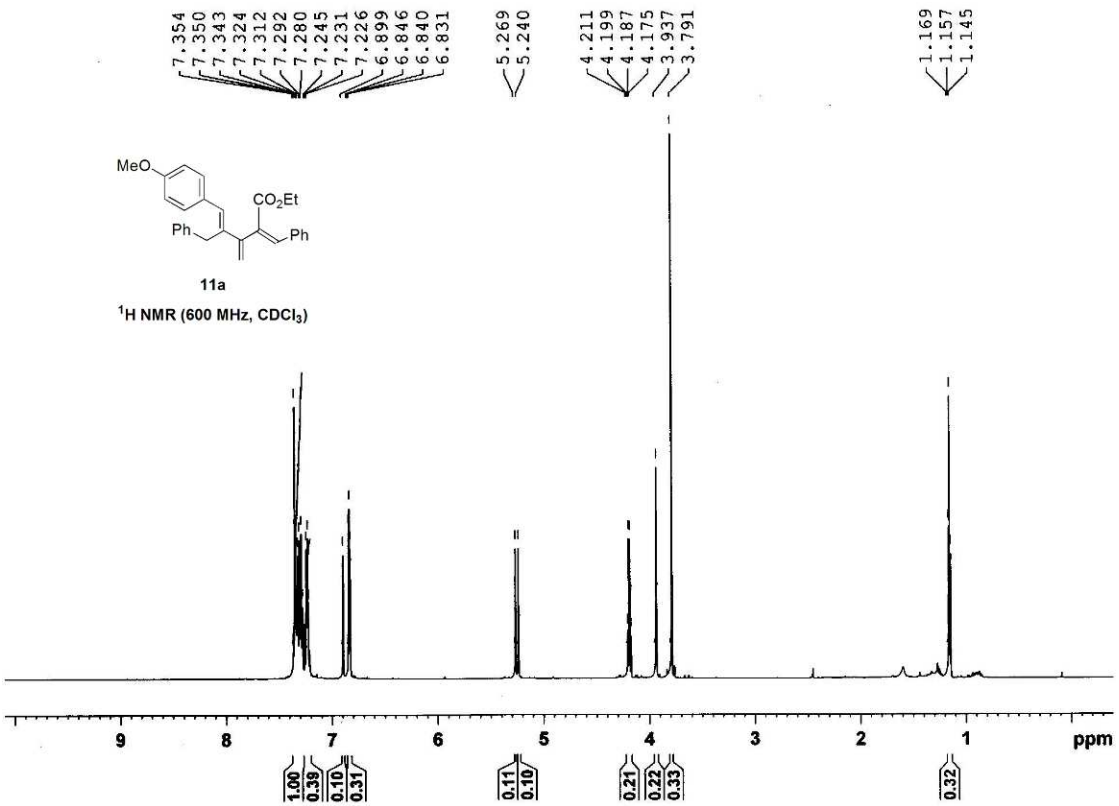
^{31}P NMR (121.5 MHz, C_6D_6)

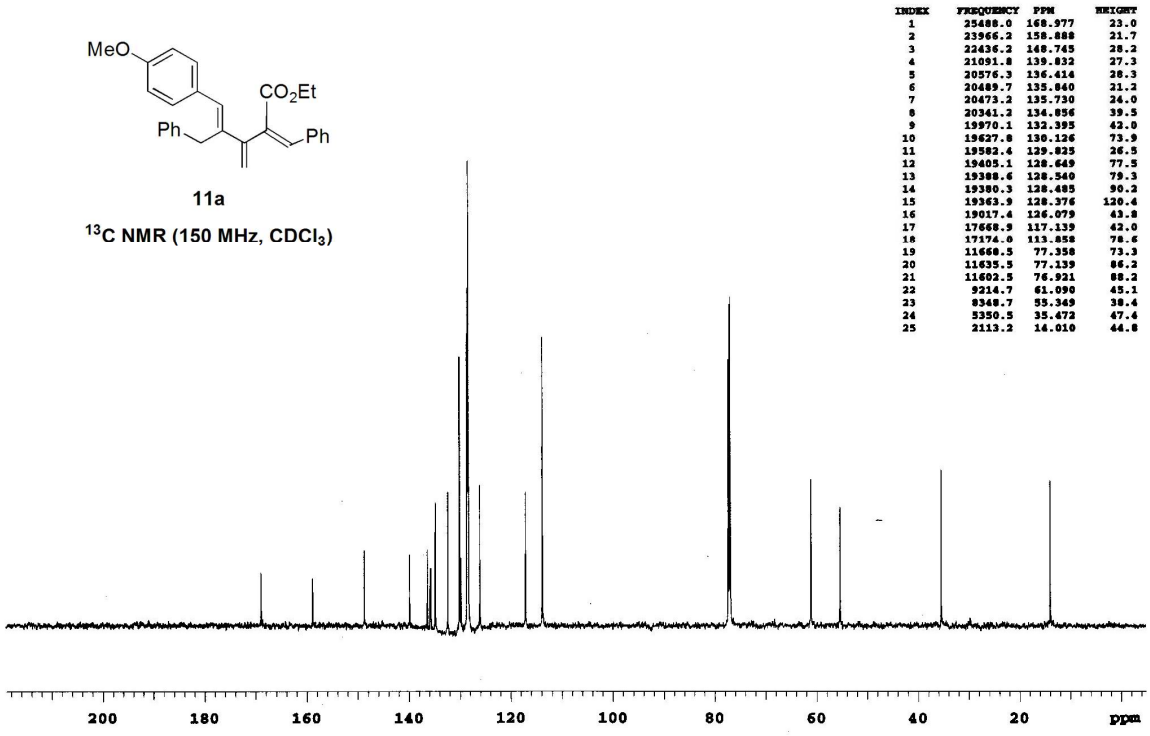




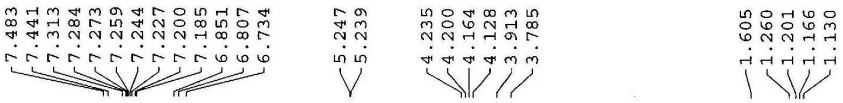
10

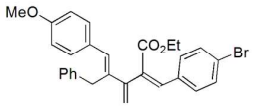
^{1}H NMR (200 MHz, $CDCl_3$)





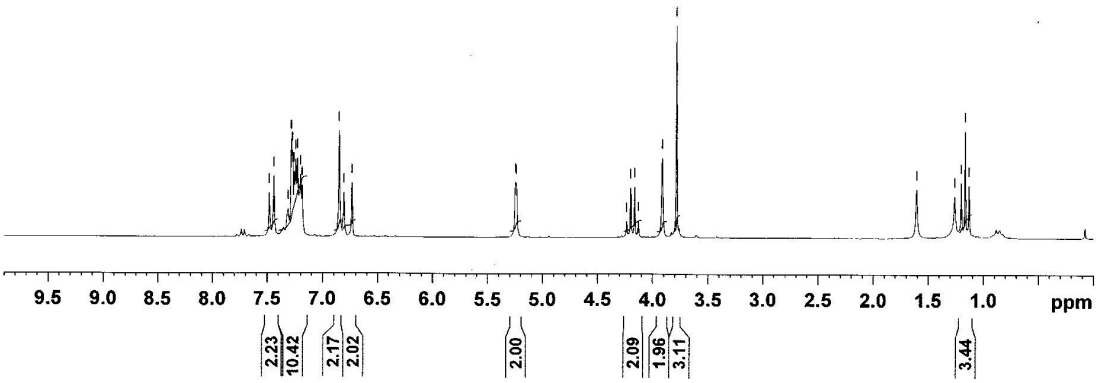
INDEX	FREQUENCY	PPM	HEIGHT
1	25488.0	168.977	23.0
2	23966.2	158.888	21.7
3	22436.2	148.745	28.2
4	21091.8	139.832	27.3
5	20576.3	136.414	28.3
6	20489.7	135.840	21.2
7	20473.2	135.730	24.0
8	20341.2	134.856	39.5
9	19970.1	132.395	42.0
10	19627.8	130.126	73.9
11	19582.4	129.825	26.5
12	19405.1	128.649	77.5
13	19388.6	128.540	79.3
14	19380.3	128.485	90.2
15	19363.9	128.376	120.4
16	19017.4	126.079	43.8
17	17668.9	117.139	42.0
18	17174.0	113.858	78.6
19	11660.5	77.358	73.3
20	11635.5	77.139	86.2
21	11602.5	76.921	88.2
22	9214.7	61.090	45.1
23	8348.7	55.349	38.4
24	5350.5	35.472	47.4
25	2113.2	14.010	44.8

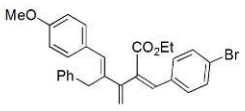




11b

^{1}H NMR (200 MHz, $CDCl_3$)

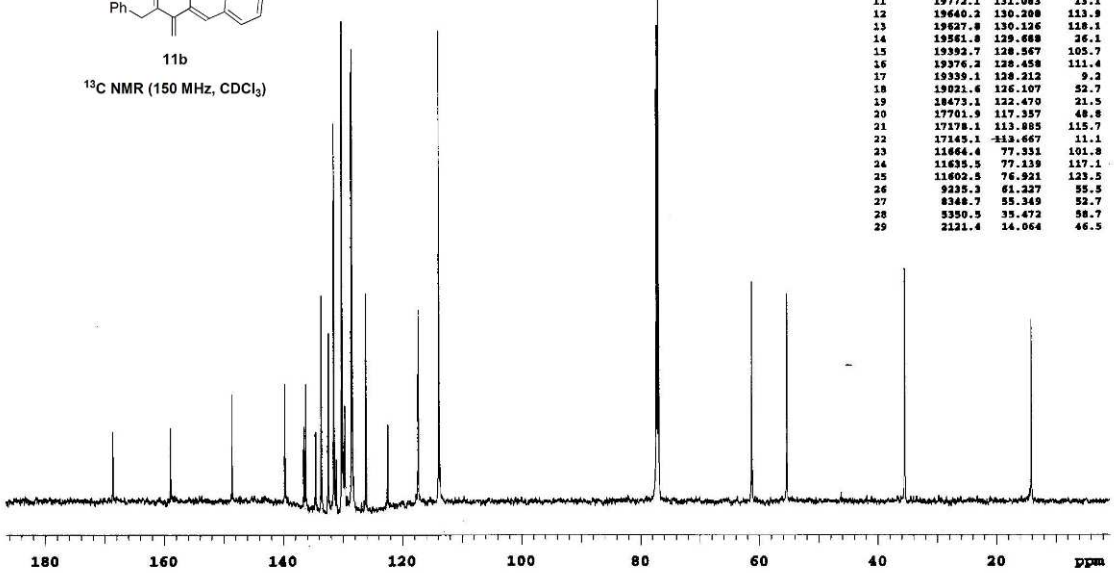


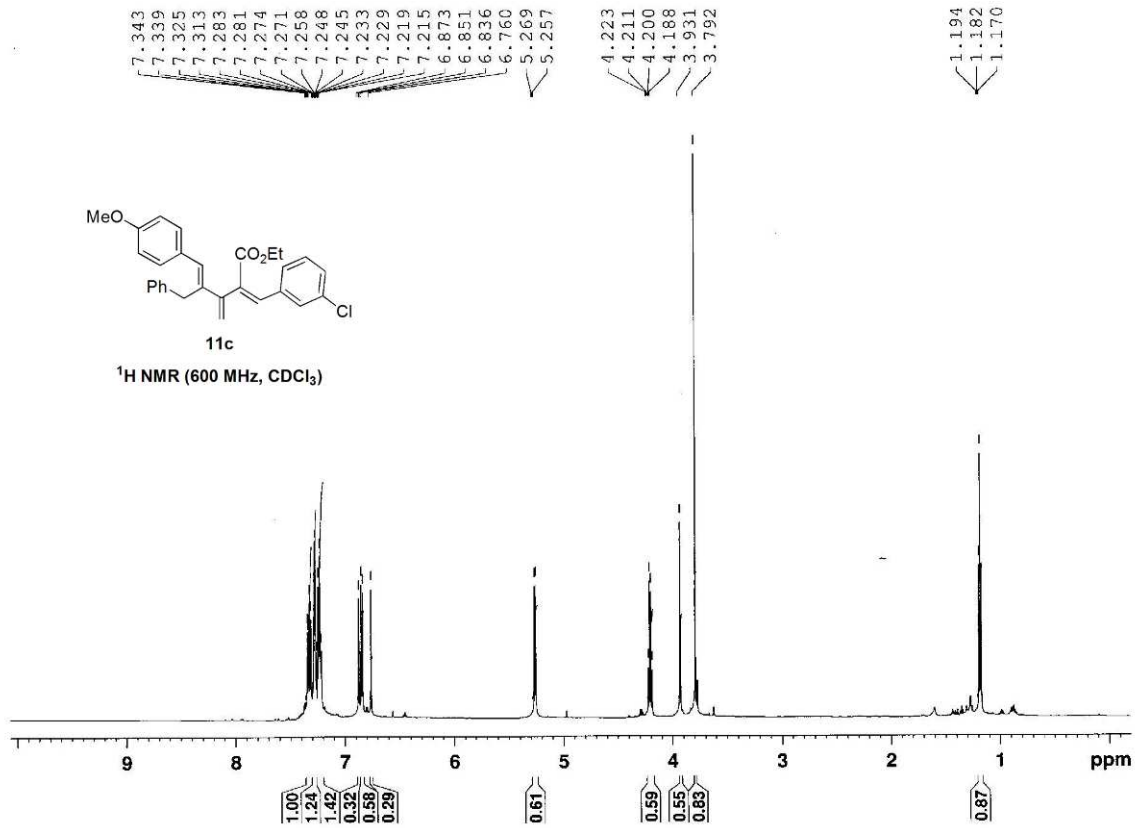


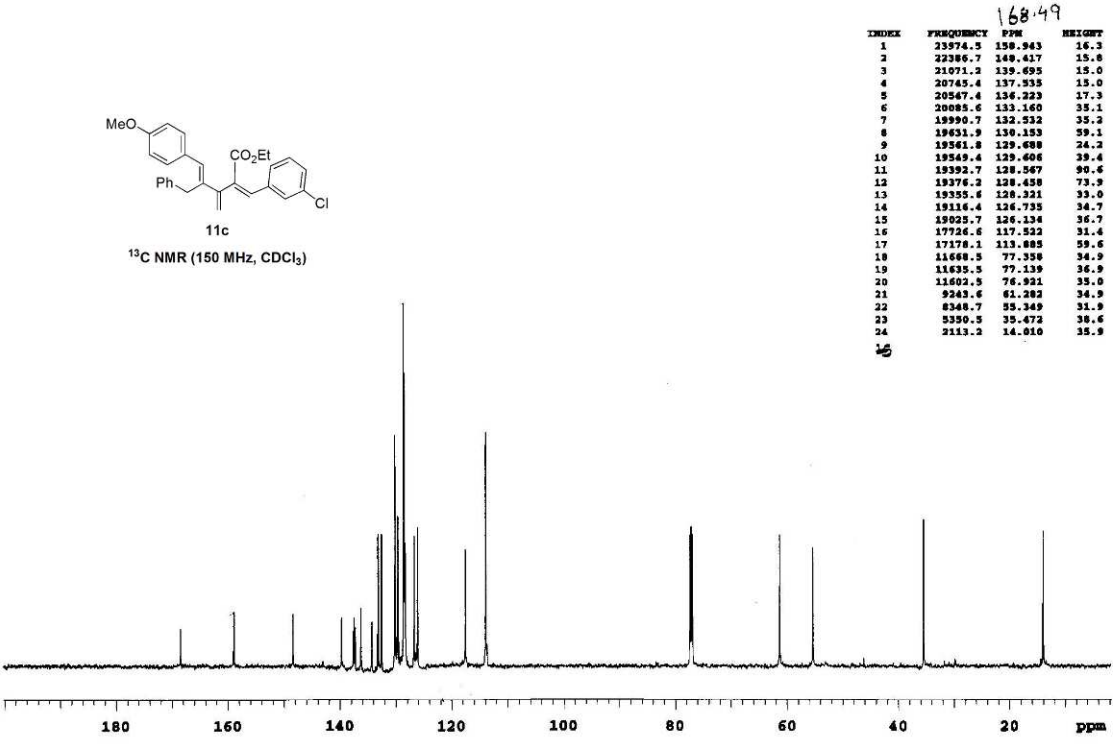
11b

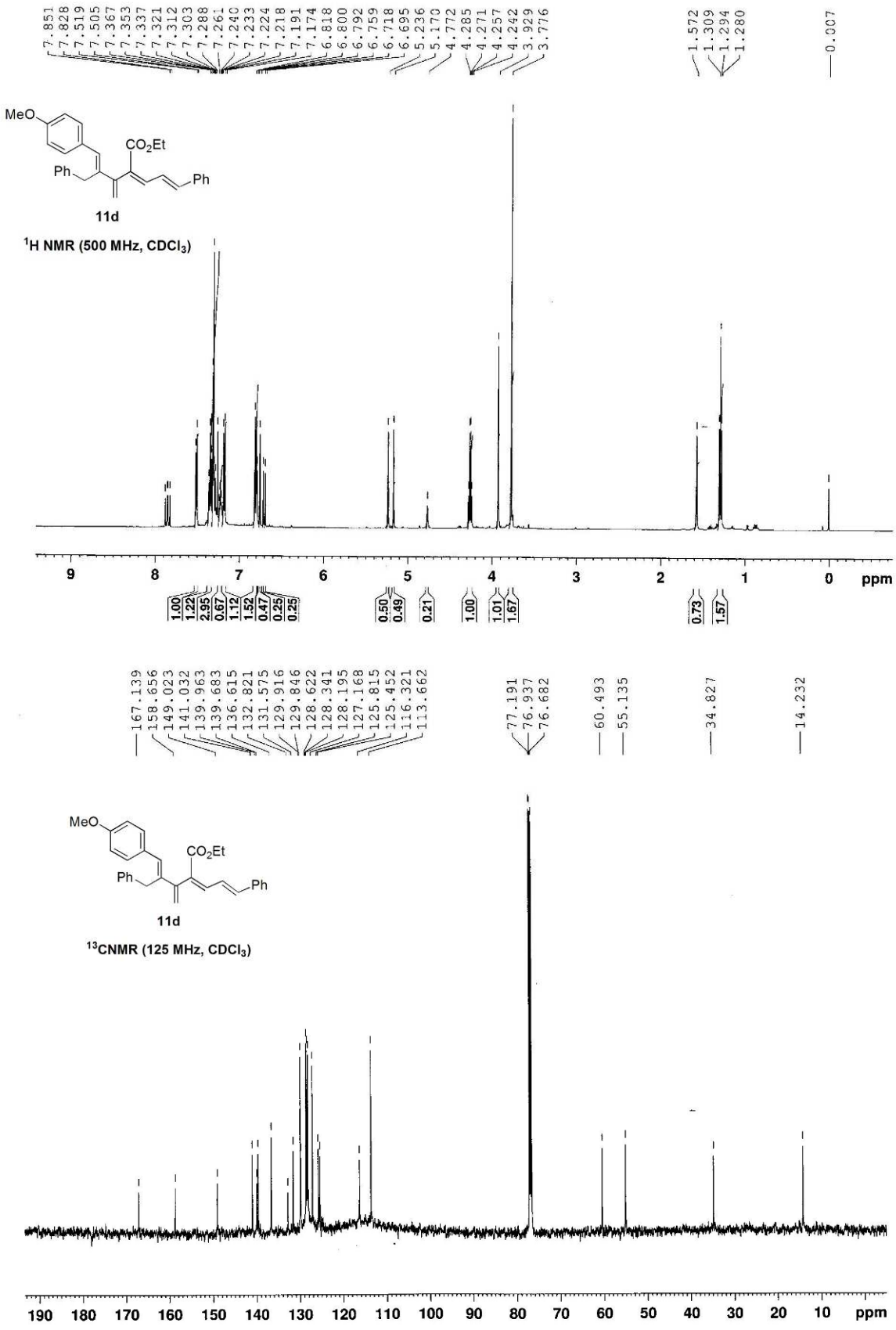
^{13}C NMR (150 MHz, $CDCl_3$)

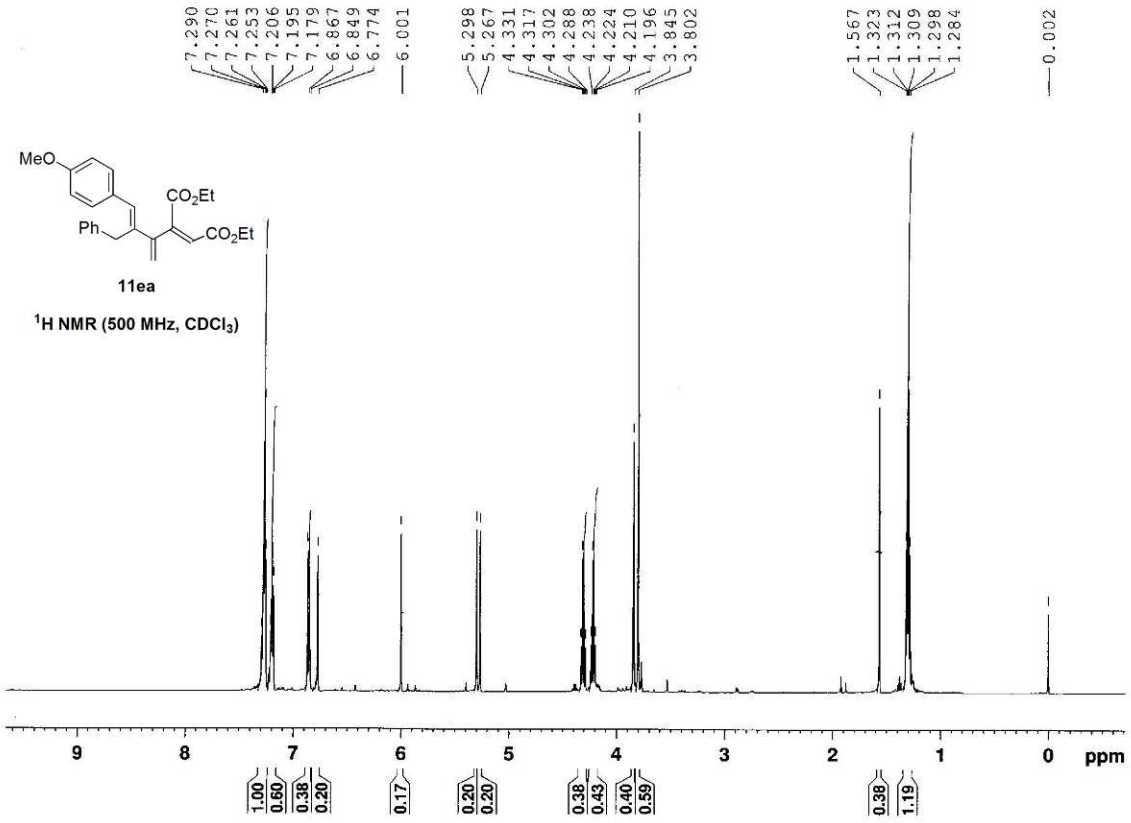
INDEX	FREQUENCY	PPM	HEIGHT
1	25438.5	168.649	19.7
2	23970.4	158.915	20.6
3	22411.5	148.581	28.8
4	21075.3	139.722	31.2
5	20596.9	136.551	20.9
6	20551.6	136.250	31.2
7	20308.2	134.637	19.8
8	20155.7	133.625	92.3
9	19978.3	132.450	43.3
10	19838.1	131.520	93.6
11	19772.1	131.083	13.1
12	19640.2	130.208	113.9
13	19627.8	130.126	118.1
14	19561.8	129.688	26.1
15	19392.7	128.567	105.7
16	19376.2	128.458	111.4
17	19339.1	128.212	9.2
18	19021.6	126.107	52.7
19	18473.1	122.470	21.5
20	17701.9	117.357	48.8
21	17178.1	113.885	115.7
22	17145.1	113.667	11.1
23	11664.4	77.331	101.8
24	11635.5	77.139	117.1
25	11602.5	76.921	123.5
26	9235.3	61.227	55.5
27	8348.7	55.349	52.7
28	5350.5	35.472	58.7
29	2121.4	14.064	46.5

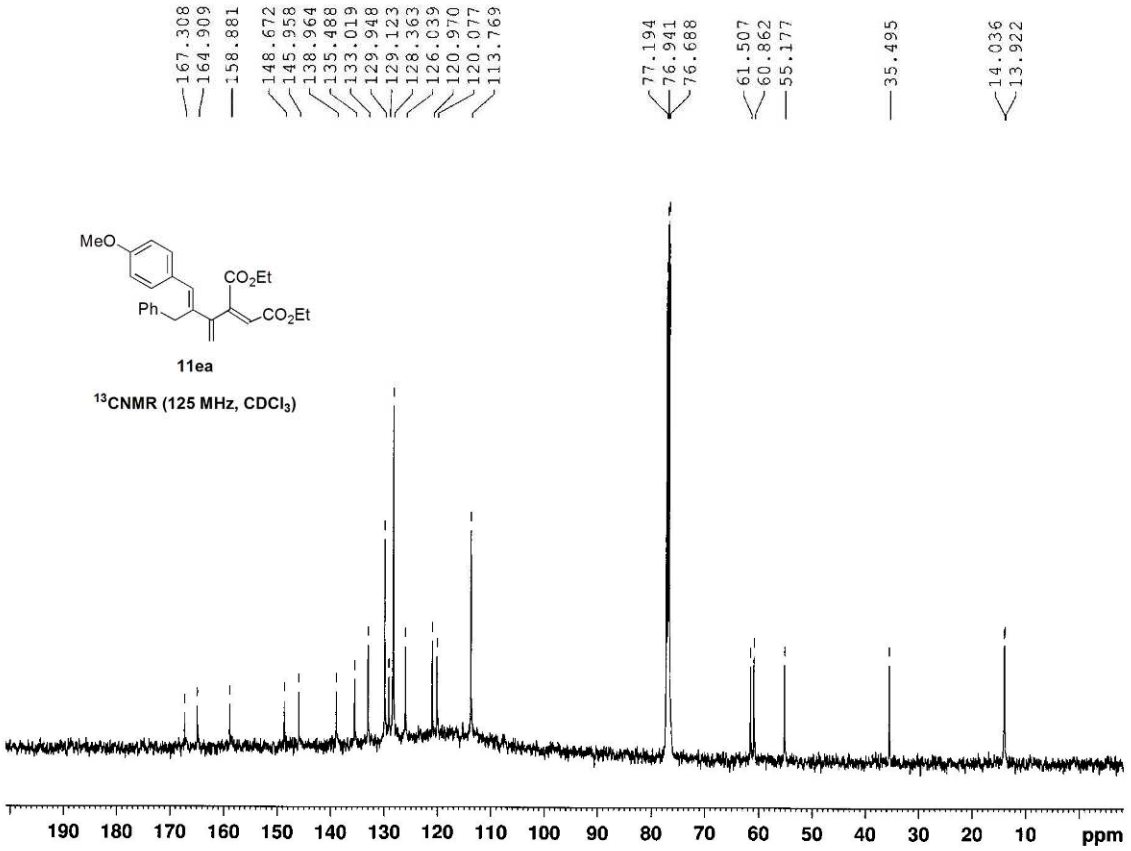


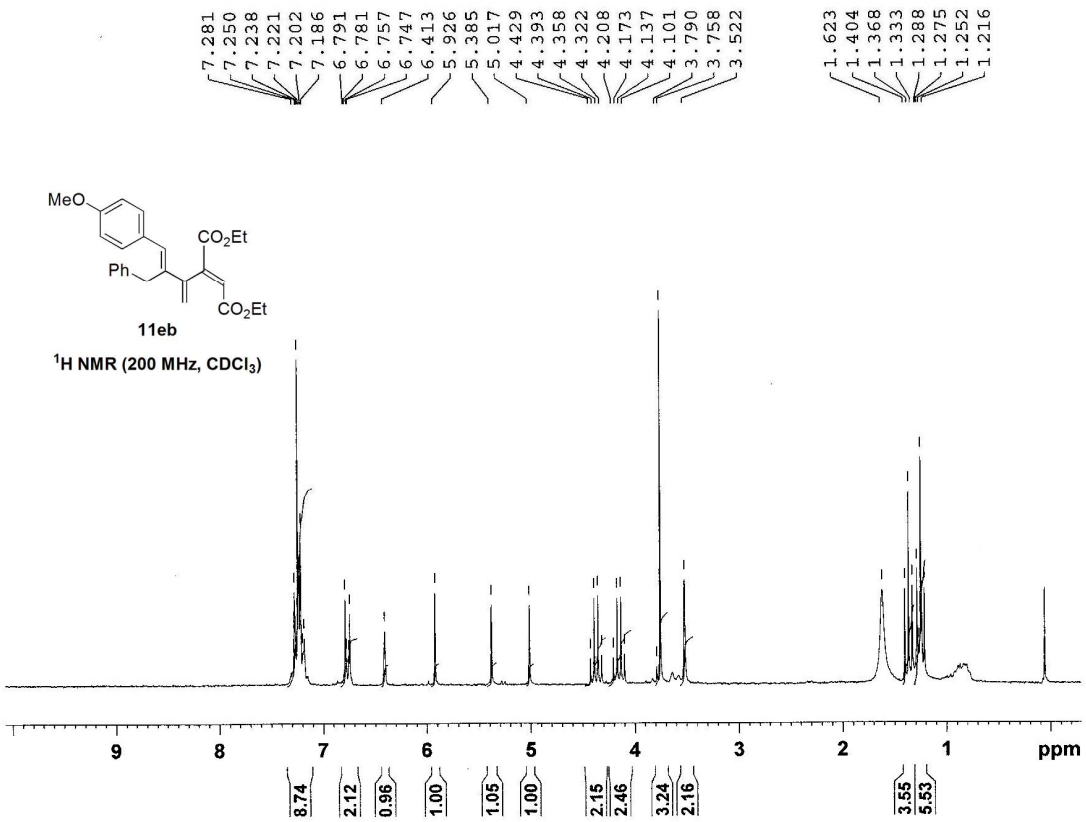

7.343
7.339
7.325
7.313
7.283
7.281
7.274
7.271
7.258
7.248
7.245
7.233
7.229
7.219
7.215
6.873
6.851
6.836
6.760
5.269
5.257
4.223
4.211
4.200
4.188
3.931
3.792
1.194
1.182
1.170
MeO
CO2Et
Ph
Cl
11c
1H NMR (600 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
ppm
1.00
1.24
1.42
0.32
0.58
0.29
0.61
0.59
0.55
0.83
0.87

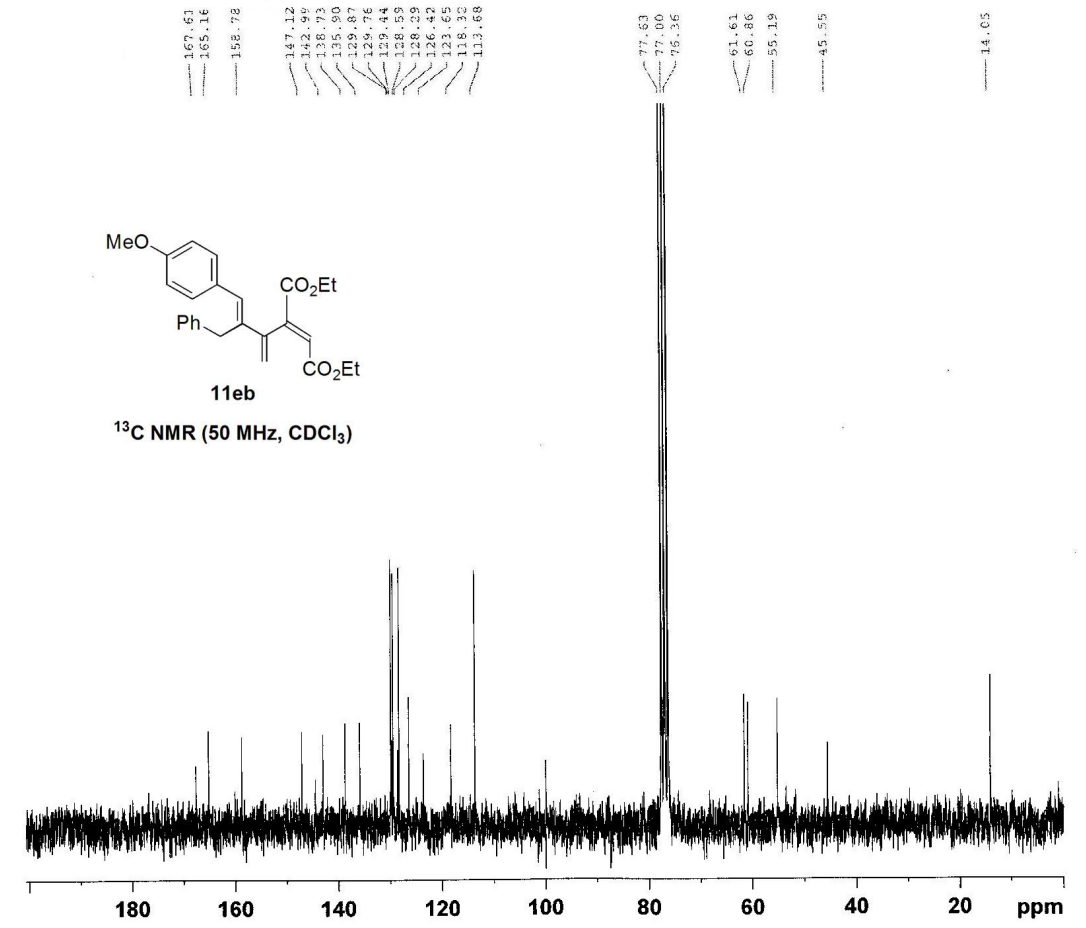

168.49
INDEX FREQUENCY PPM HEIGHT
1 23974.5 158.943 16.3
2 22386.7 148.417 15.8
3 21071.2 139.695 15.0
4 20745.4 137.535 15.0
5 20547.4 136.223 17.3
6 20085.6 133.160 35.1
7 19990.7 132.532 35.2
8 19631.9 130.153 39.1
9 19561.8 129.688 24.2
10 19549.4 129.606 39.4
11 19392.7 128.567 90.6
12 19376.2 128.458 73.9
13 19355.6 128.321 93.0
14 19116.4 126.735 34.7
15 19025.7 126.134 36.7
16 17726.6 117.522 31.4
17 17178.1 113.885 59.6
18 11668.5 77.358 34.9
19 11635.5 77.139 36.9
20 11602.5 76.921 35.0
21 9243.6 61.282 34.9
22 8348.7 55.349 31.9
23 5350.5 35.472 38.6
24 2113.2 14.010 35.9
MeO
CO2Et
Ph
Cl
11c
13C NMR (150 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
ppm

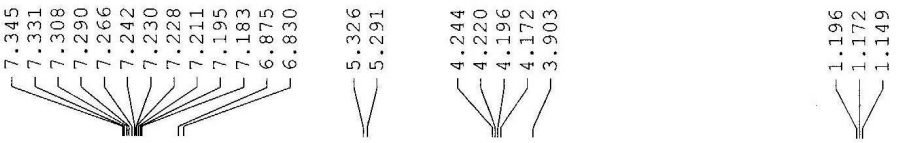

7.851
7.828
7.519
7.505
7.367
7.353
7.337
7.321
7.312
7.303
7.288
7.261
7.240
7.233
7.224
7.218
7.191
7.174
6.818
6.800
6.792
6.759
6.718
6.695
5.236
5.170
4.772
4.285
4.271
4.257
4.242
3.929
3.776
1.572
1.309
1.294
1.280
0.007
MeO
CO2Et
Ph
Ph
11d
1H NMR (500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.22
2.95
0.67
1.12
1.52
0.47
0.25
0.25
0.50
0.49
0.21
1.00
1.01
1.67
0.73
1.57
167.139
158.656
149.023
141.032
139.963
139.683
136.615
132.821
131.575
129.916
129.846
128.622
128.341
128.195
127.168
125.815
125.452
116.321
113.662
77.191
76.937
76.682
60.493
55.135
34.827
14.232
MeO
CO2Et
Ph
Ph
11d
13CNMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

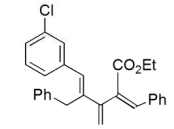

7.290
7.270
7.261
7.253
7.206
7.195
7.179
6.867
6.849
6.774
6.001
5.298
5.267
4.331
4.317
4.302
4.288
4.238
4.224
4.210
4.196
3.845
3.802
1.567
1.323
1.312
1.309
1.298
1.284
0.002
MeO
CO2Et
Ph
CO2Et
11ea
1H NMR (500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.60
0.38
0.20
0.17
0.20
0.20
0.38
0.43
0.40
0.59
0.38
1.19


167.308
164.909
158.881
148.672
145.958
138.964
135.488
133.019
129.948
129.123
128.363
126.039
120.970
120.077
113.769
77.194
76.941
76.688
61.507
60.862
55.177
35.495
14.036
13.922
MeO
CO2Et
Ph
CO2Et
11ea
13CNMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.281
7.250
7.238
7.221
7.202
7.186
6.791
6.781
6.757
6.747
6.413
5.926
5.385
5.017
4.429
4.393
4.358
4.322
4.208
4.173
4.137
4.101
3.790
3.758
3.522
1.623
1.404
1.368
1.333
1.288
1.275
1.252
1.216
MeO
CO2Et
Ph
CO2Et
11eb
1H NMR (200 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
ppm
8.74
2.12
0.96
1.00
1.05
1.00
2.15
2.46
3.24
2.16
3.55
5.53

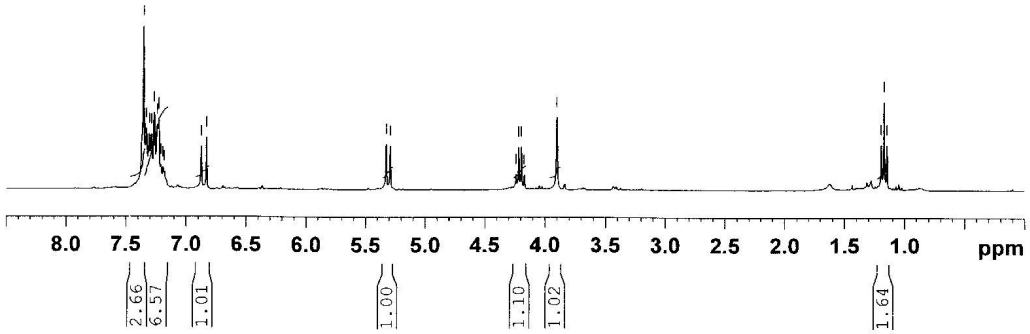

167.61
165.16
158.78
147.12
142.99
138.73
135.90
129.87
129.76
129.44
128.59
128.29
126.42
123.65
118.30
113.68
77.63
77.00
75.36
61.61
60.86
55.19
45.55
14.05
MeO
CO2Et
Ph
CO2Et
11eb
13C NMR (50 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
ppm

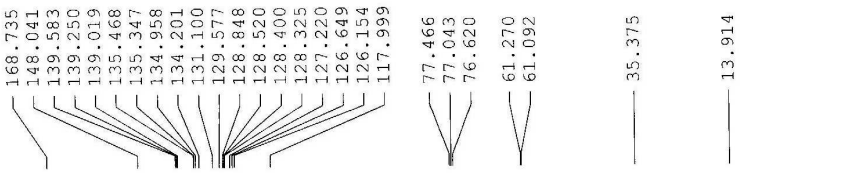




11f

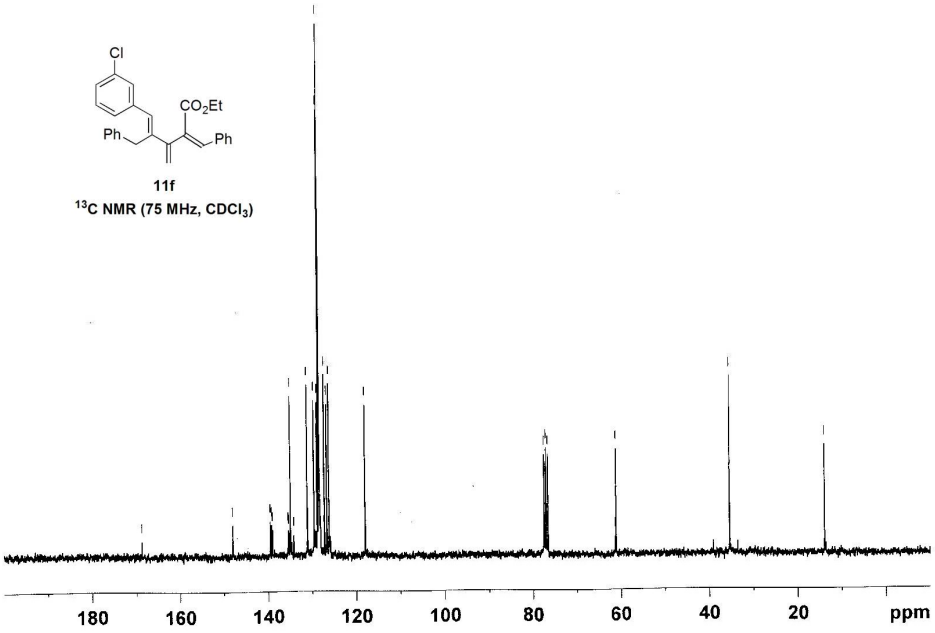
^{1}H NMR (300 MHz, $CDCl_3$)

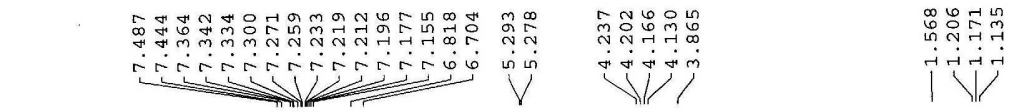


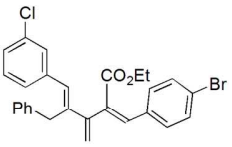


11f

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

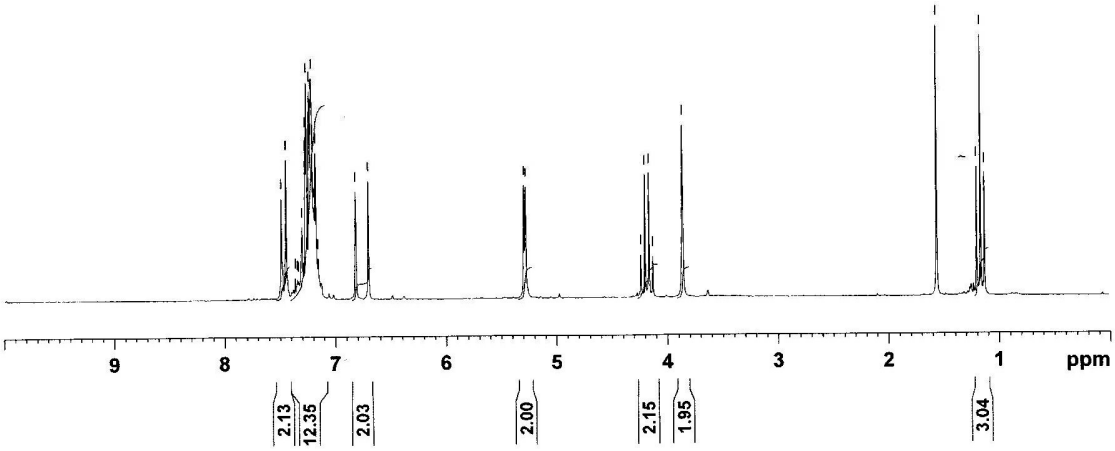


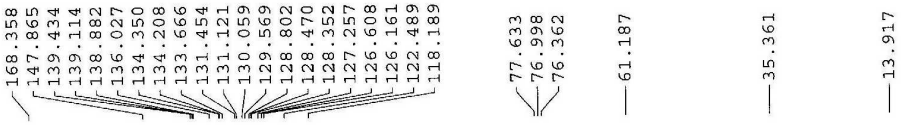


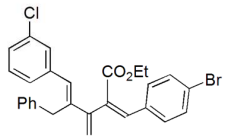


11g

^{1}H NMR (200 MHz, $CDCl_3$)

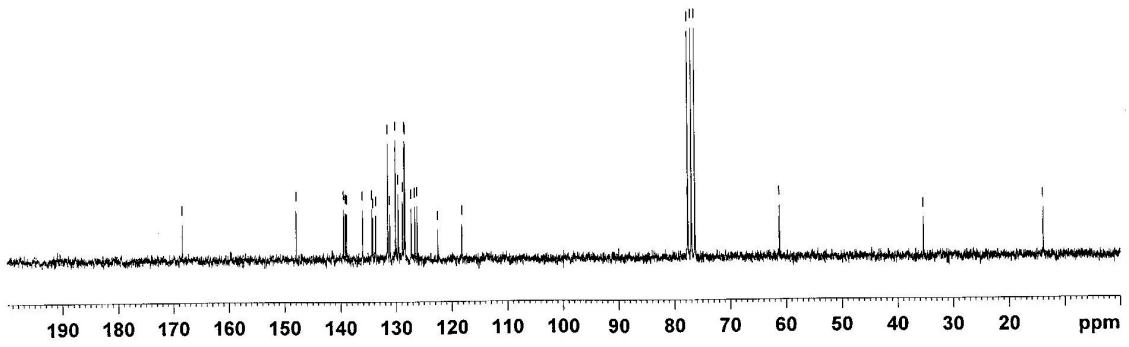


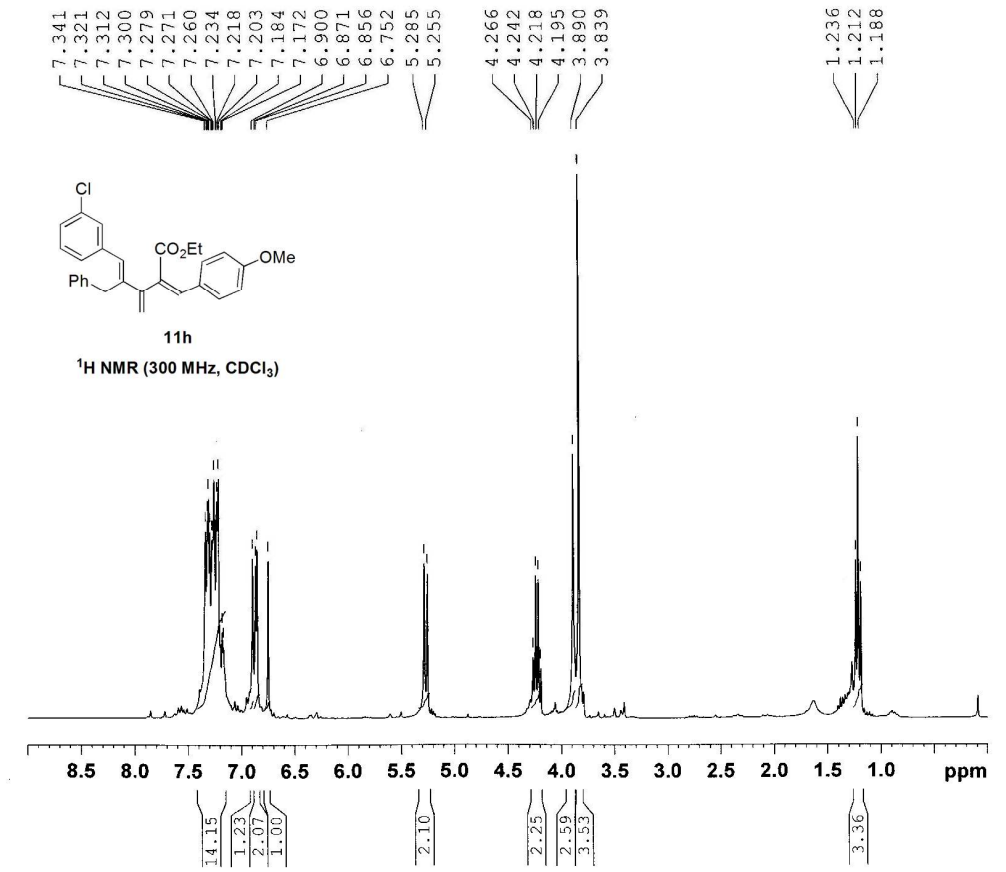


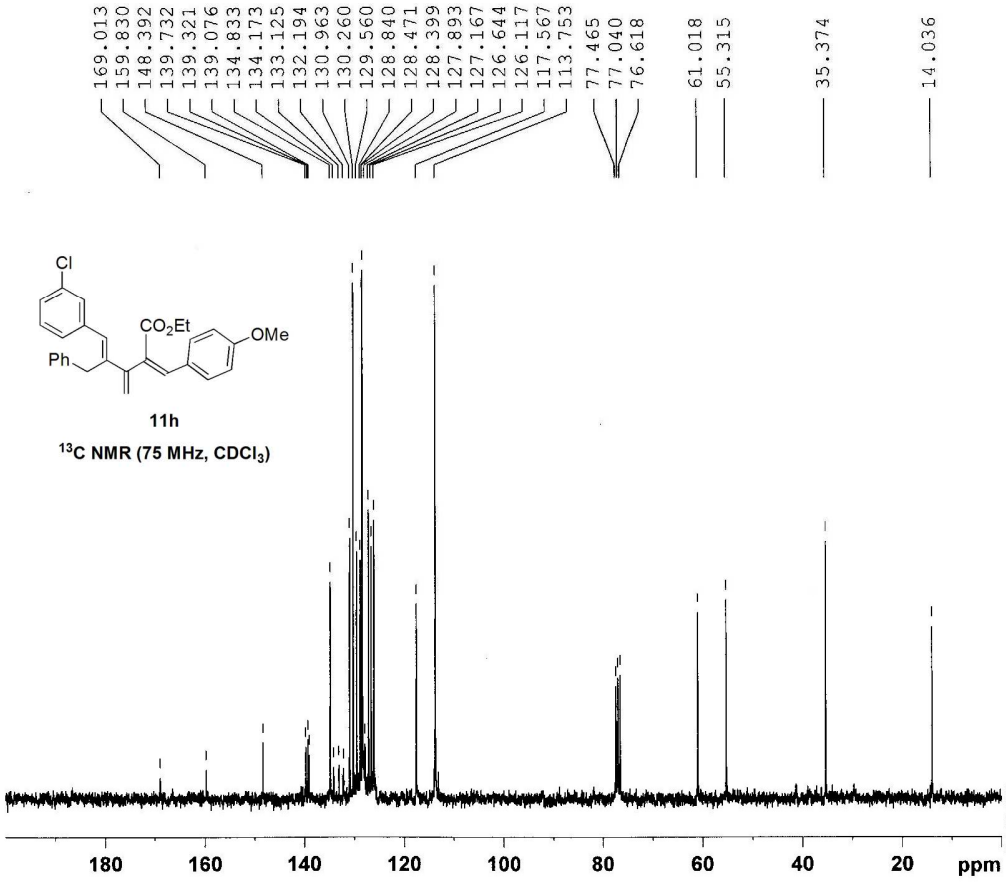


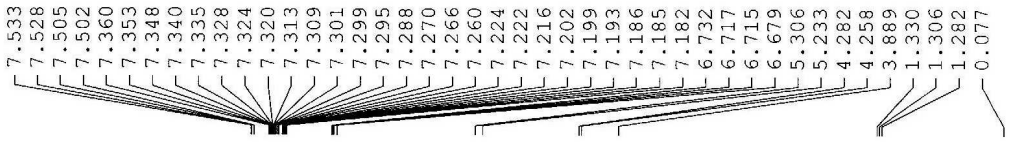
11g

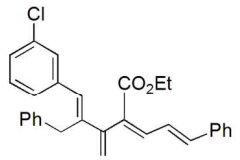
^{13}C NMR (50 MHz, $CDCl_3$)




7.341
7.321
7.312
7.300
7.279
7.271
7.260
7.234
7.218
7.203
7.184
7.172
6.900
6.871
6.856
6.752
5.285
5.255
4.266
4.242
4.218
4.195
3.890
3.839
1.236
1.212
1.188
Cl
CO2Et
OMe
Ph
11h
1H NMR (300 MHz, CDCl3)
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 ppm
14.15
1.23
2.07
1.00
2.10
2.25
2.59
3.53
3.36

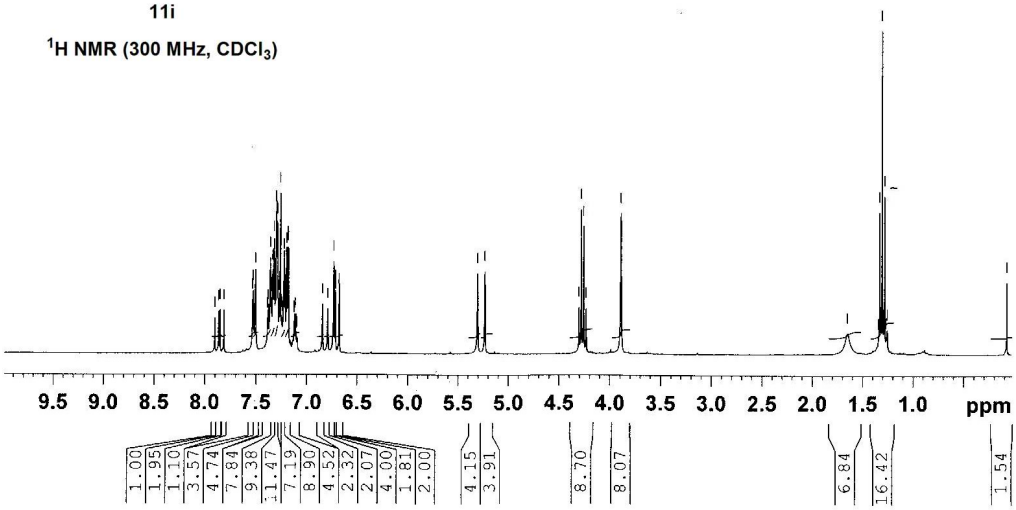

169.013
159.830
148.392
139.732
139.321
139.076
134.833
134.173
133.125
132.194
130.963
130.260
129.560
128.840
128.471
128.399
127.893
127.167
126.644
126.117
117.567
113.753
77.465
77.040
76.618
61.018
55.315
35.374
14.036
Cl
CO2Et
OMe
Ph
11h
13C NMR (75 MHz, CDCl3)
180 160 140 120 100 80 60 40 20 ppm

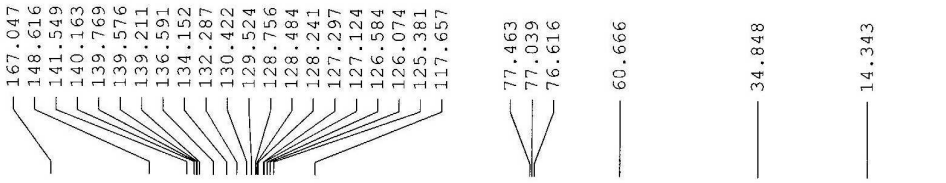




11i

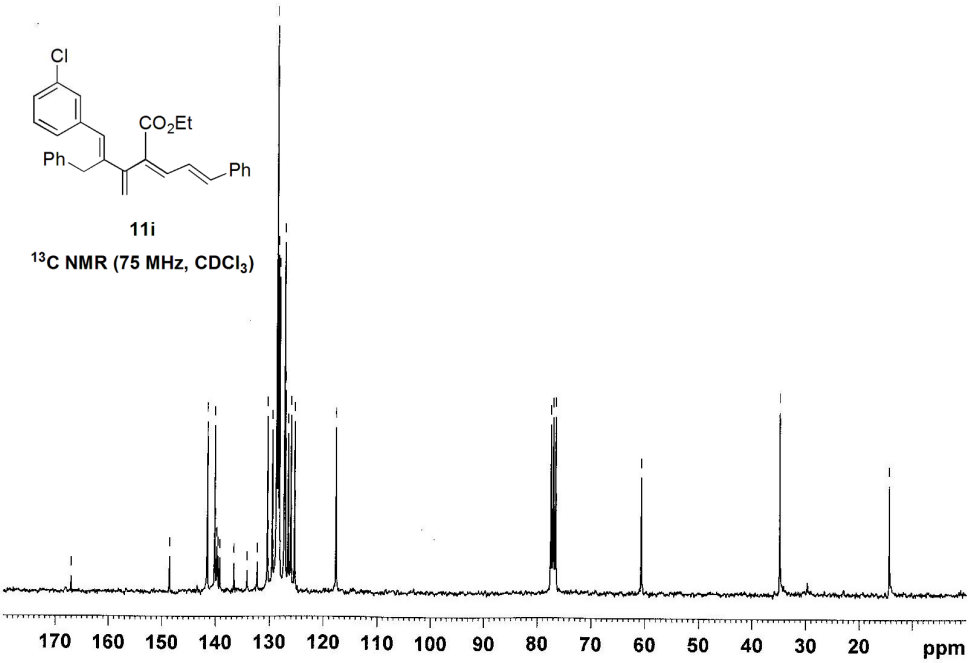
^{1}H NMR (300 MHz, $CDCl_3$)

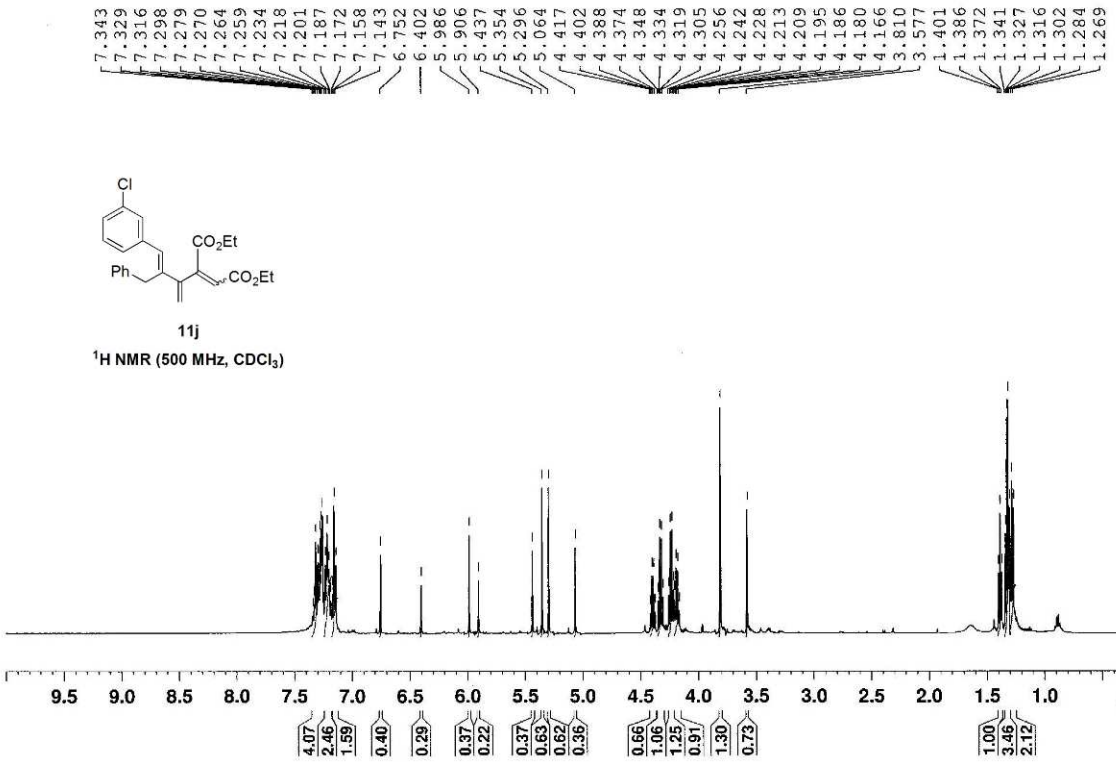


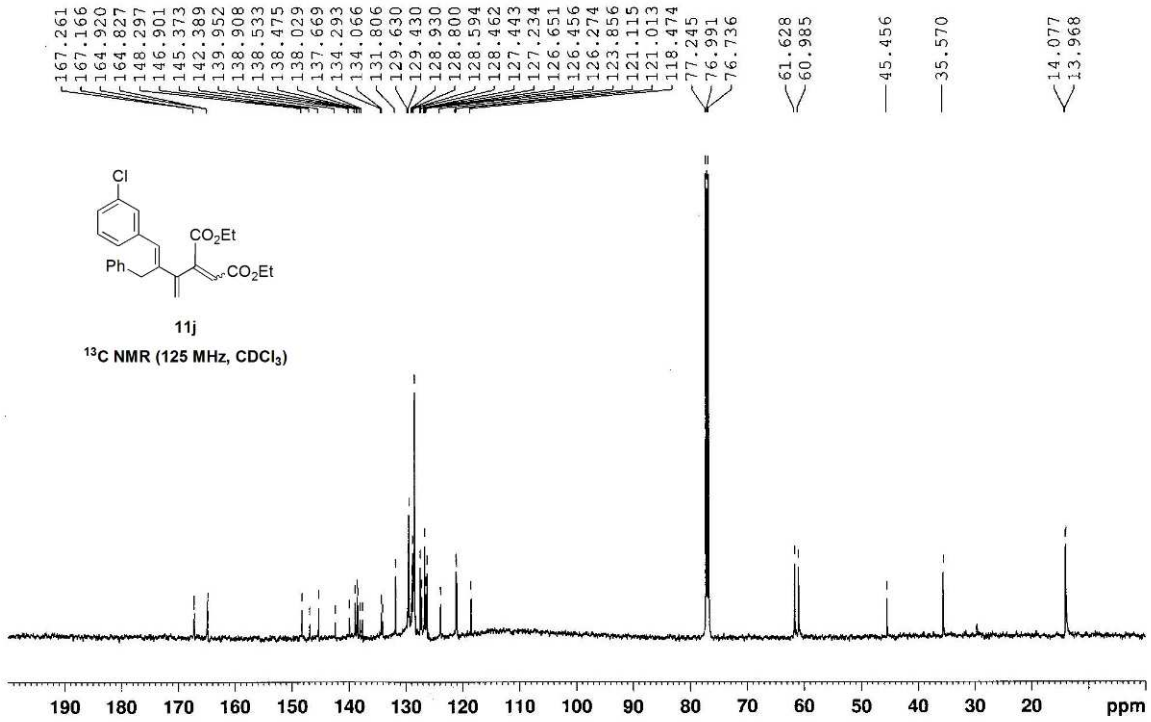


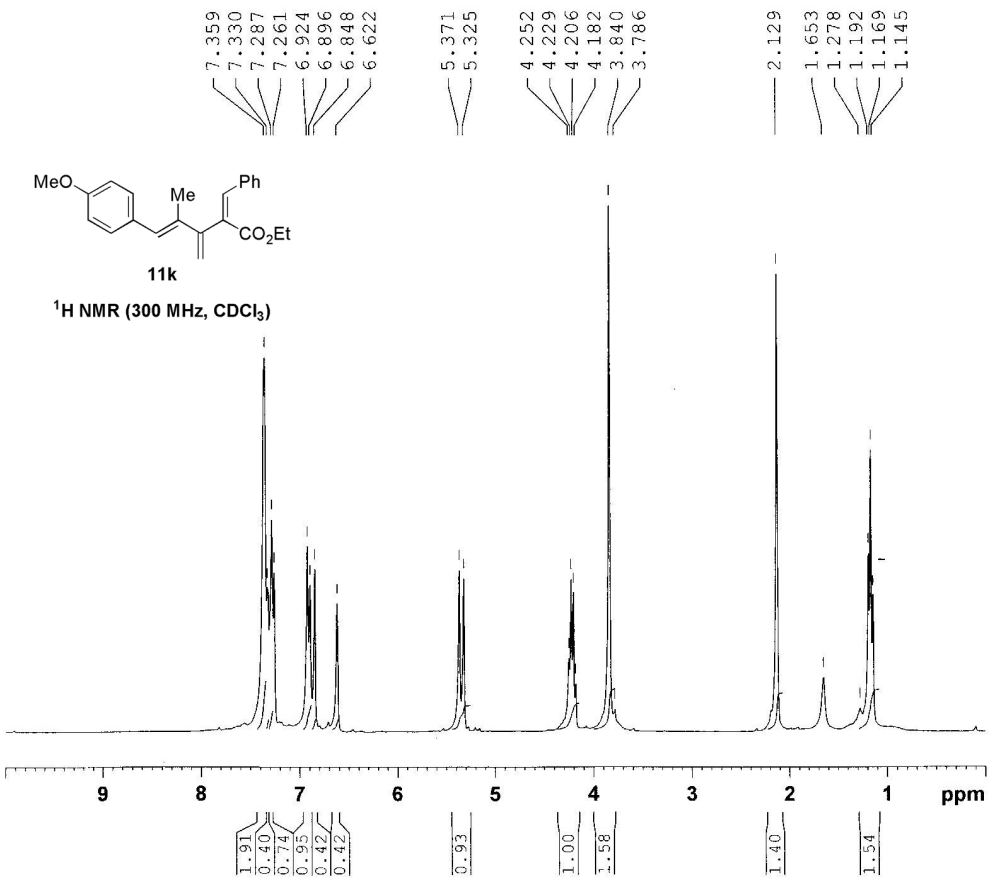
11i

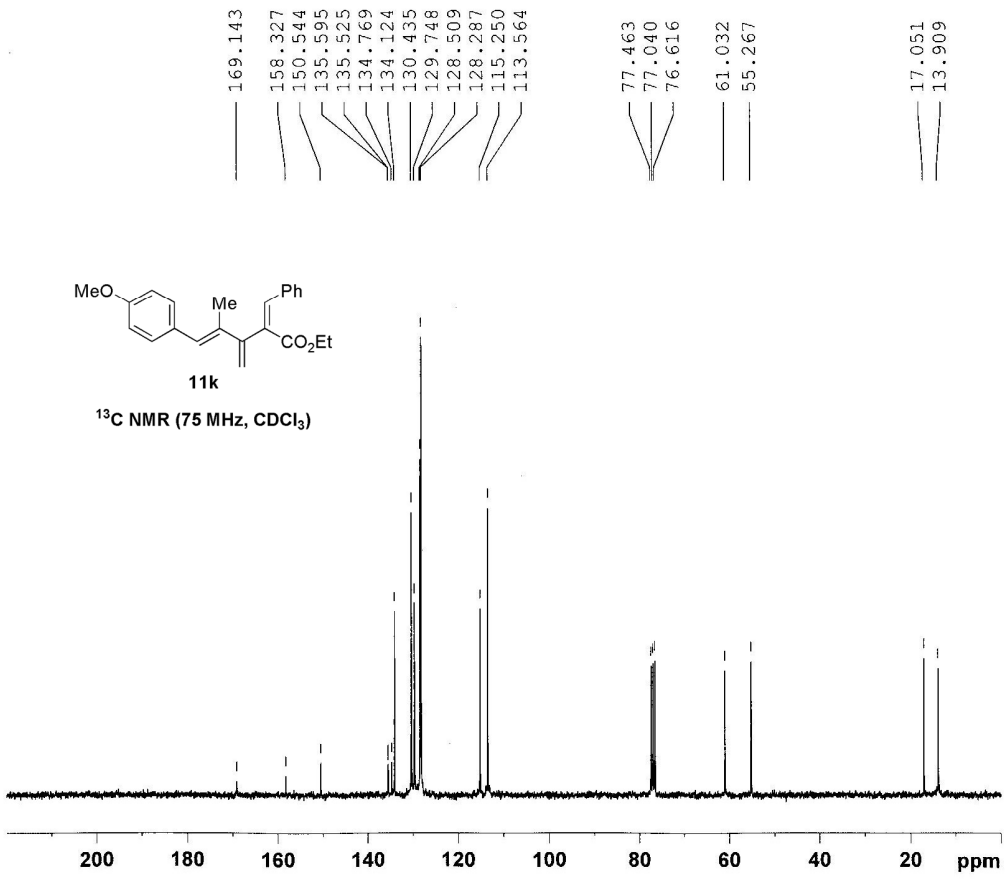
^{13}C NMR (75 MHz, $CDCl_3$)

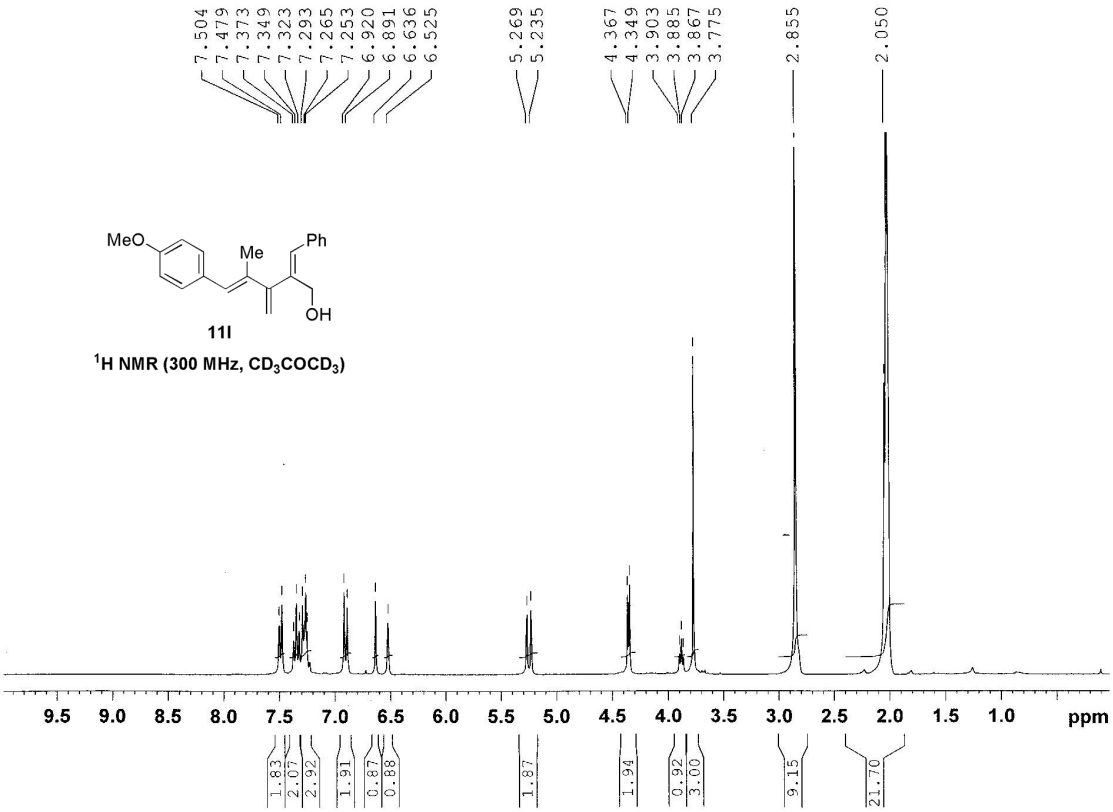



7.343
7.329
7.316
7.298
7.279
7.270
7.264
7.259
7.234
7.218
7.201
7.187
7.172
7.158
7.143
6.752
6.402
5.986
5.906
5.437
5.354
5.296
5.064
4.417
4.402
4.388
4.374
4.348
4.334
4.319
4.305
4.256
4.242
4.228
4.213
4.209
4.195
4.186
4.180
4.166
3.810
3.577
1.401
1.386
1.372
1.341
1.327
1.316
1.302
1.284
1.269
Cl
CO2Et
Ph
CO2Et
11j
1H NMR (500 MHz, CDCl3)
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 ppm
4.07 2.46 1.59 0.40 0.29 0.37 0.22 0.37 0.63 0.62 0.36 0.66 1.06 1.25 0.91 1.30 0.73 1.00 3.46 2.12


167.261
167.166
164.920
164.827
148.297
146.901
145.373
142.389
139.952
138.908
138.533
138.475
138.029
137.669
134.293
134.066
131.806
129.630
129.430
128.930
128.800
128.594
128.462
127.443
127.234
126.651
126.456
126.274
123.856
121.115
121.013
118.474
77.245
76.991
76.736
61.628
60.985
45.456
35.570
14.077
13.968
Cl
CO2Et
Ph
CO2Et
11j
13C NMR (125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

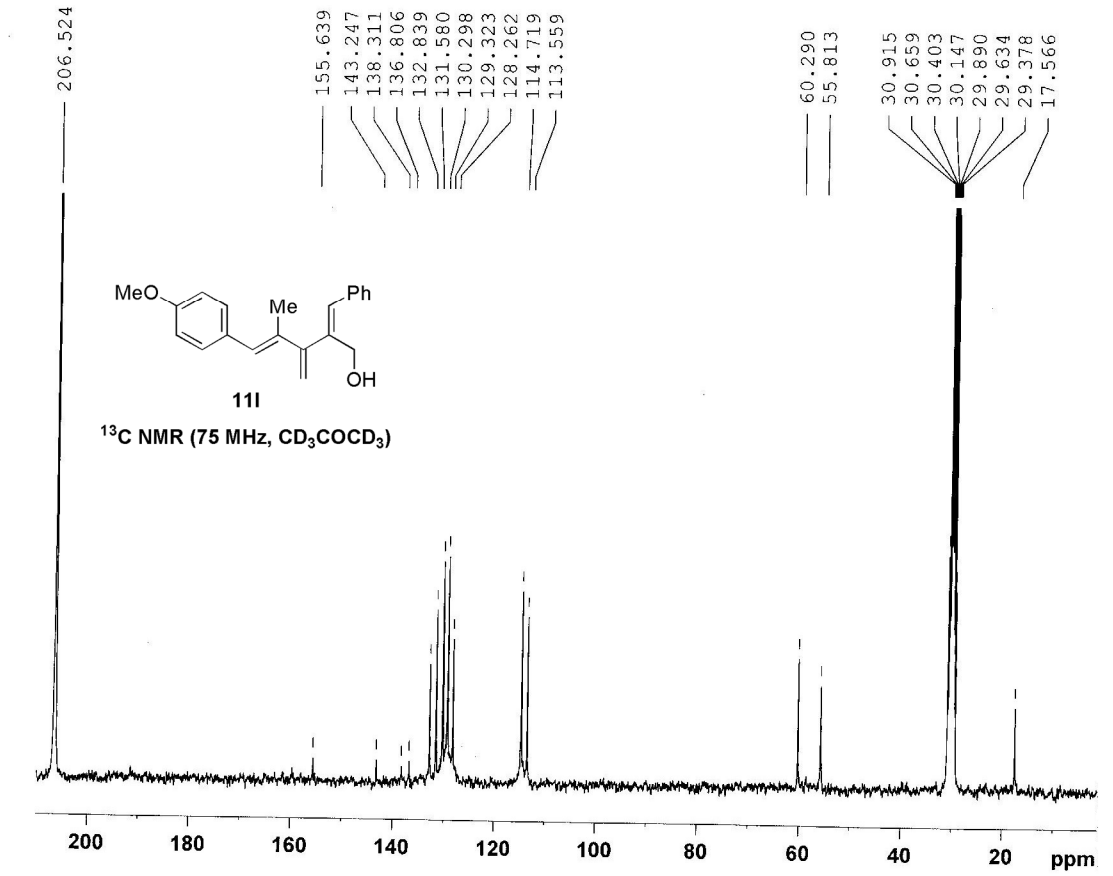

7.359
7.330
7.287
7.261
6.924
6.896
6.848
6.622
5.371
5.325
4.252
4.229
4.206
4.182
3.840
3.786
2.129
1.653
1.278
1.192
1.169
1.145
MeO
Me
Ph
CO2Et
11k
1H NMR (300 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
ppm
1.91
0.40
0.74
0.95
0.42
0.42
0.93
1.00
1.58
1.40
1.54


169.143
158.327
150.544
135.595
135.525
134.769
134.124
130.435
129.748
128.509
128.287
115.250
113.564
77.463
77.040
76.616
61.032
55.267
17.051
13.909
MeO
Me
Ph
CO2Et
11k
13C NMR (75 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm



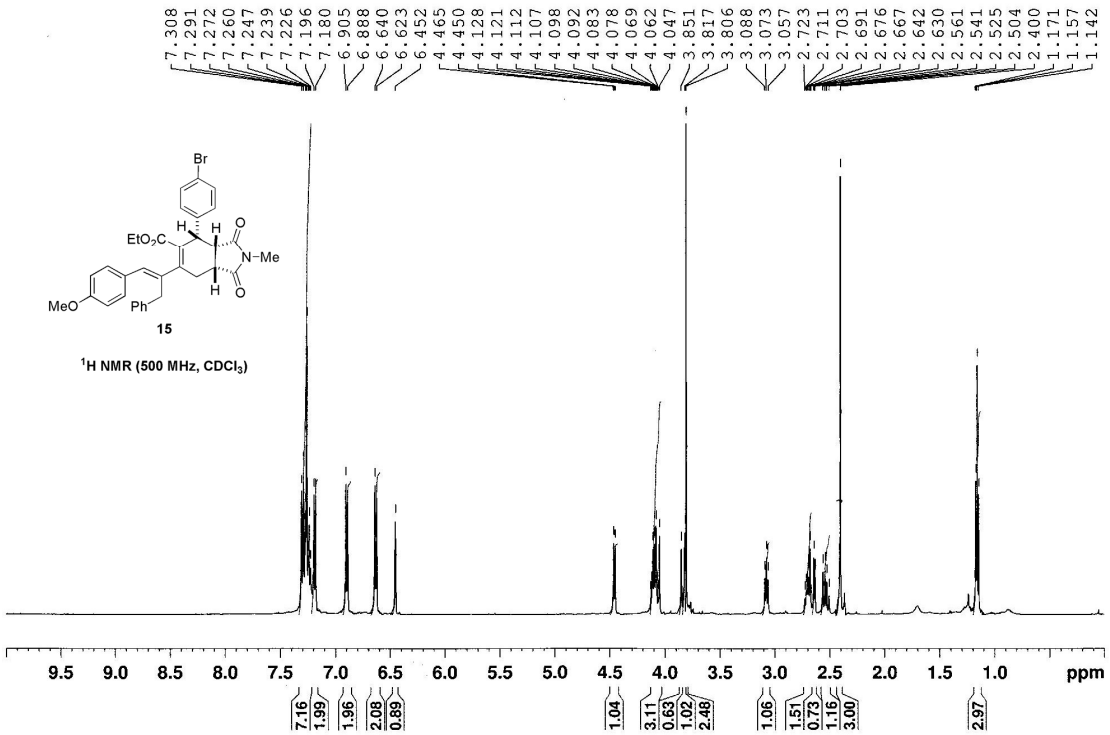
11l

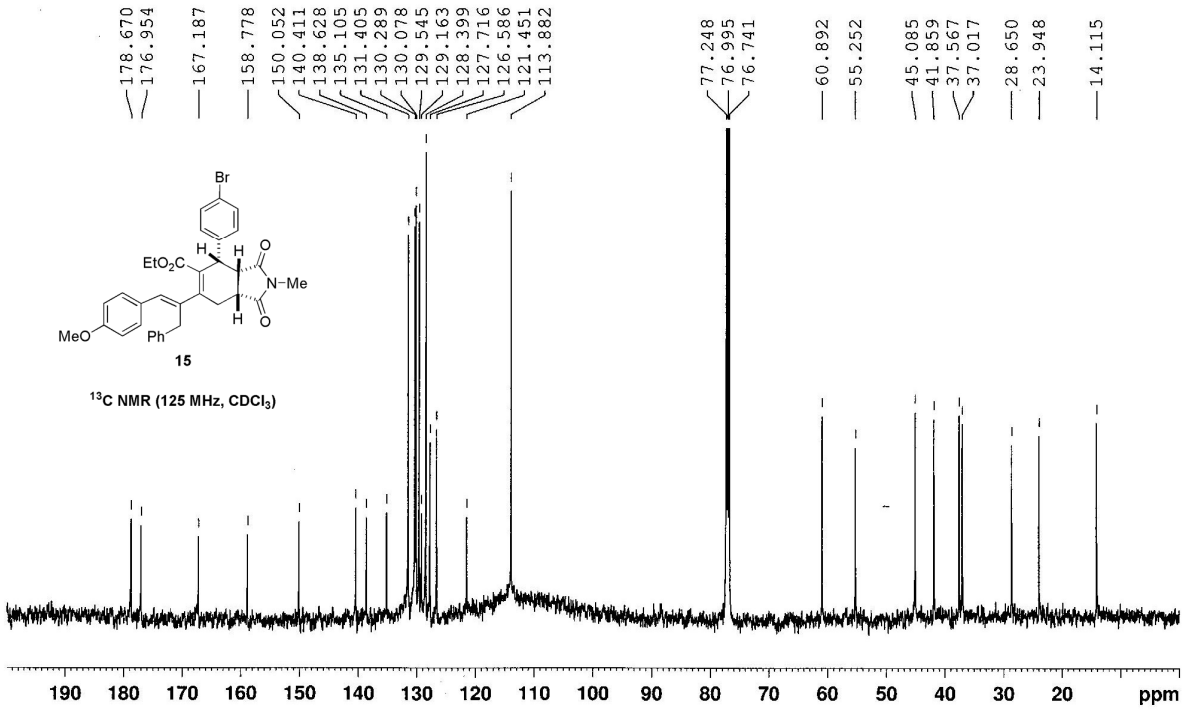
^{1}H NMR (300 MHz, CD_3COCD_3)

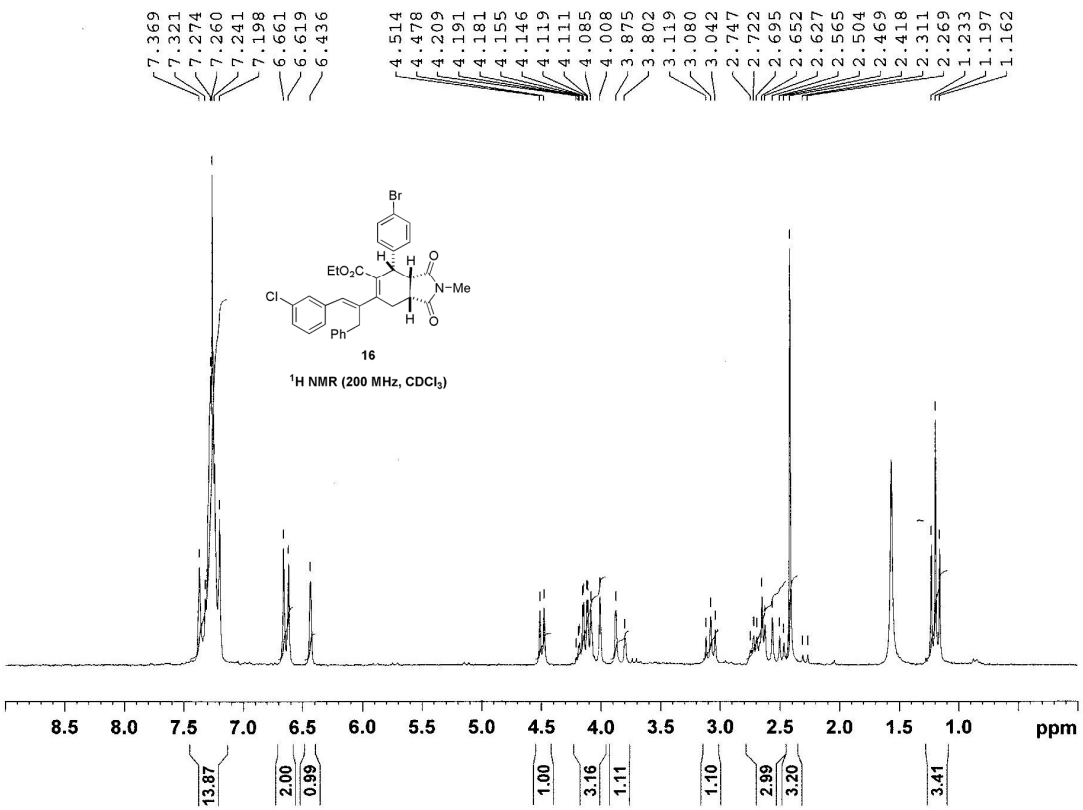


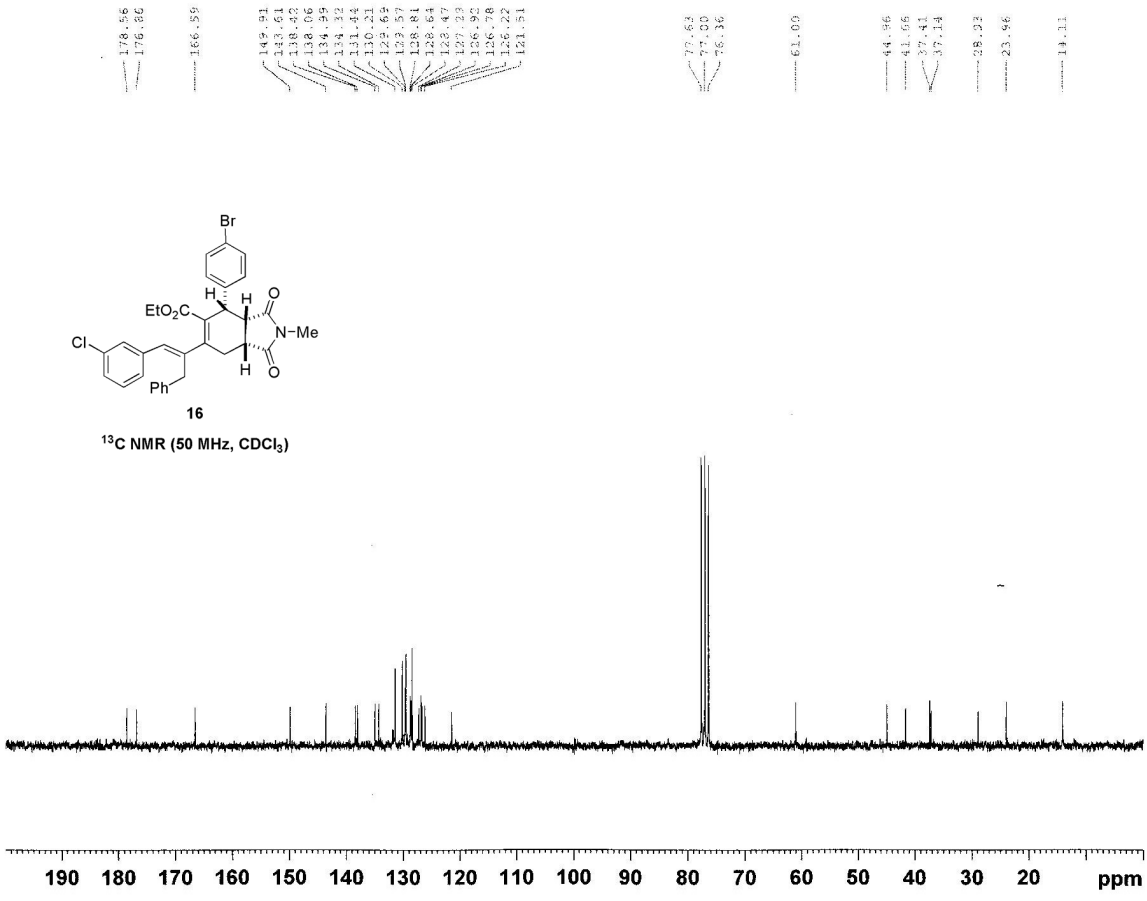
11l

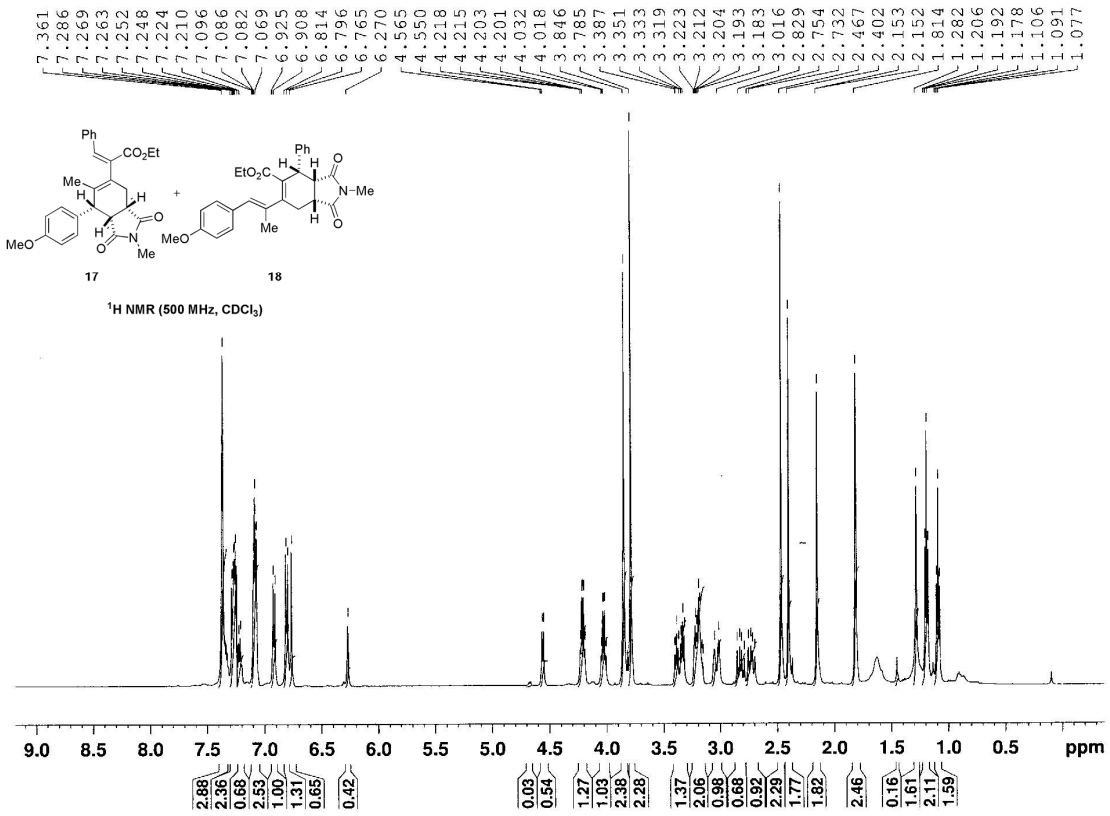
^{13}C NMR (75 MHz, CD_3COCD_3)


7.308
7.291
7.272
7.260
7.247
7.239
7.226
7.196
7.180
6.905
6.888
6.640
6.623
6.452
4.465
4.450
4.128
4.121
4.112
4.107
4.098
4.092
4.083
4.078
4.069
4.062
4.047
3.851
3.817
3.806
3.088
3.073
3.057
2.723
2.711
2.703
2.691
2.676
2.667
2.642
2.630
2.561
2.541
2.525
2.504
2.400
1.171
1.157
1.142
Br
EtO2C
N–Me
MeO
Ph
15
1H NMR (500 MHz, CDCl3)
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 ppm
7.16 1.99 1.96 2.08 0.89 1.04 3.11 0.63 1.02 2.48 1.06 1.51 0.73 1.16 3.00 2.97

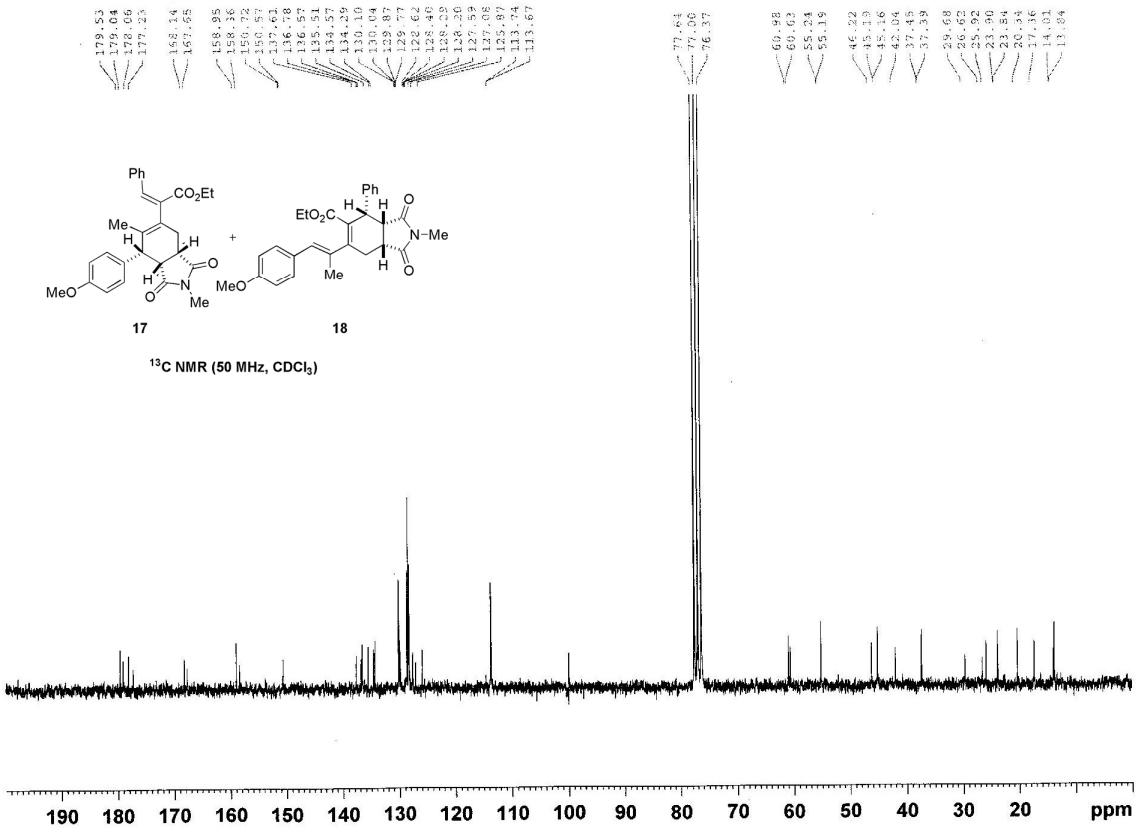

178.670
176.954
167.187
158.778
150.052
140.411
138.628
135.105
131.405
130.289
130.078
129.545
129.163
128.399
127.716
126.586
121.451
113.882
77.248
76.995
76.741
60.892
55.252
45.085
41.859
37.567
37.017
28.650
23.948
14.115
Br
EtO2C
N–Me
MeO
Ph
15
13C NMR (125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.369
7.321
7.274
7.260
7.241
7.198
6.661
6.619
6.436
4.514
4.478
4.209
4.191
4.181
4.155
4.146
4.119
4.111
4.085
4.008
3.875
3.802
3.119
3.080
3.042
2.747
2.722
2.695
2.652
2.627
2.565
2.504
2.469
2.418
2.311
2.269
1.233
1.197
1.162
Br
EtO2C
H
H
O
N–Me
O
Cl
H
Ph
16
1H NMR (200 MHz, CDCl3)
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
ppm
13.87
2.00
0.99
1.00
3.16
1.11
1.10
2.99
3.20
3.41

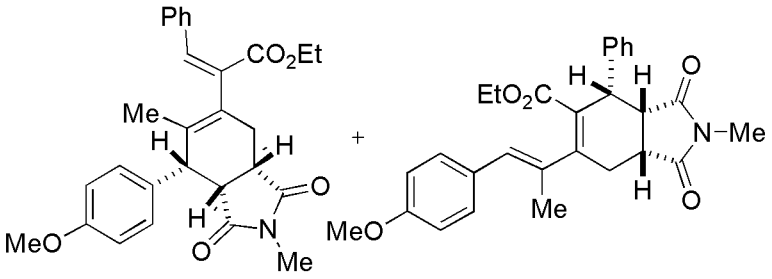

178.56
176.86
166.59
149.91
143.61
138.42
138.06
134.99
134.32
131.44
130.21
129.69
129.57
128.81
128.64
128.47
127.23
126.90
126.78
126.22
121.51
77.63
77.00
76.36
61.09
44.96
41.66
37.41
37.14
28.02
23.96
19.11
Br
EtO2C
H
H
O
N–Me
O
Cl
H
Ph
16
13C NMR (50 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



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

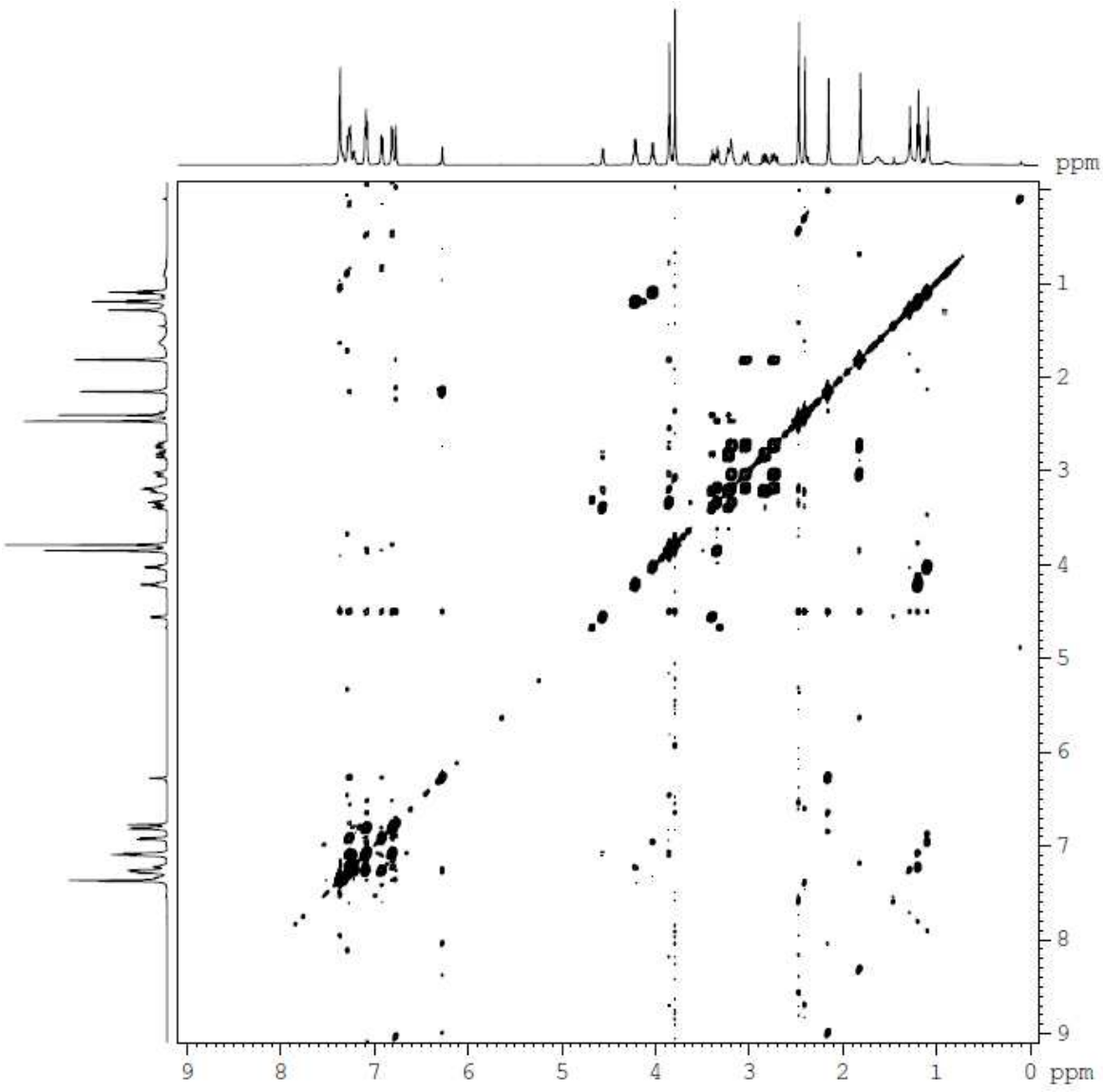


^{13}C NMR (50 MHz, $CDCl_3$)



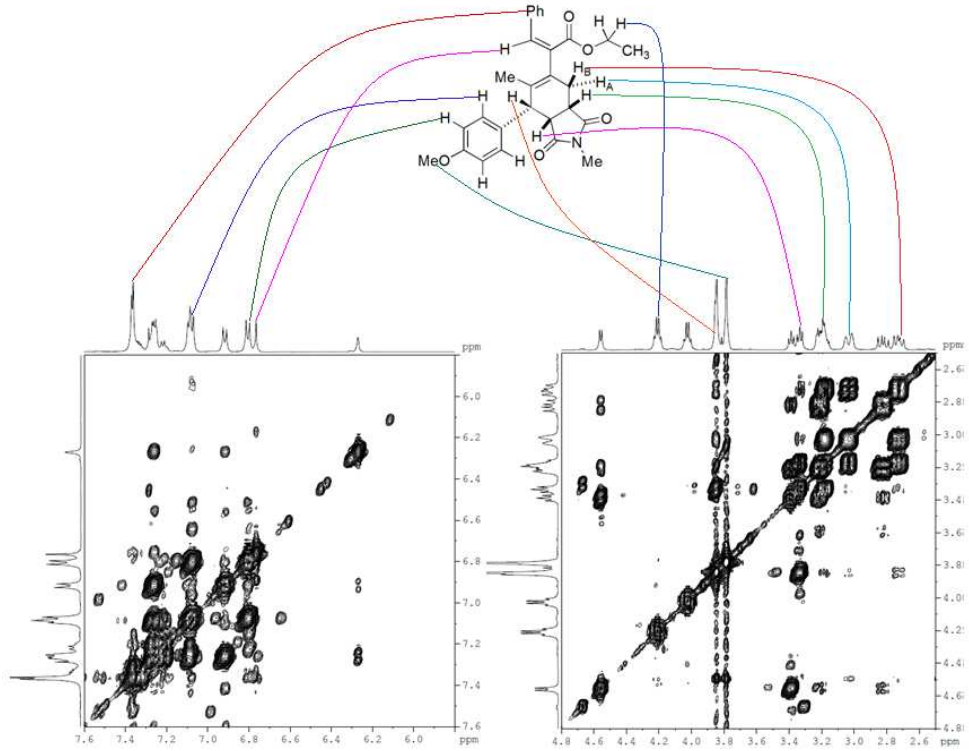
17 **18**

^{1}H/^{1}H COSY (500 MHz, $CDCl_3$)



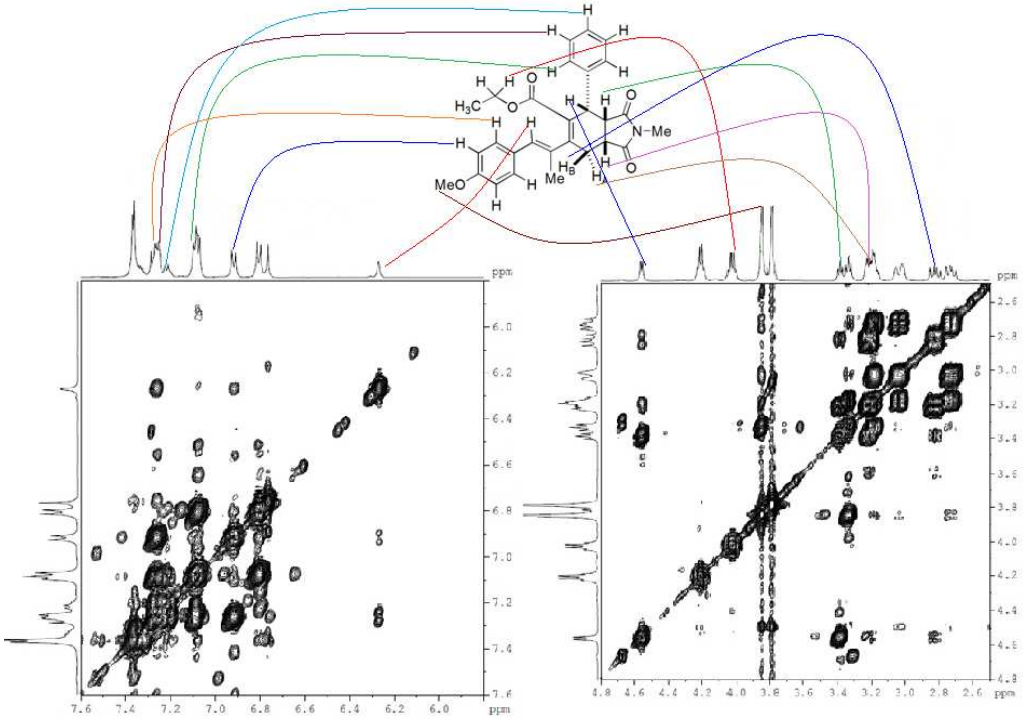
Expansions of $^{1}H/^{1}H$ COSY spectrum for the interpretation of peaks of **17**

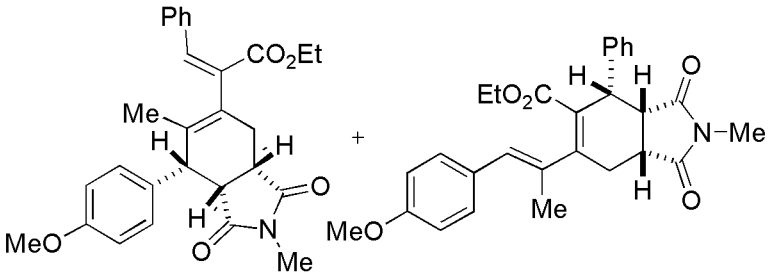
Unmarked peaks belong to the other regioisomer **18**



Expansions of $^{1}H/^{1}H$ COSY spectrum for the interpretation of peaks of **18**

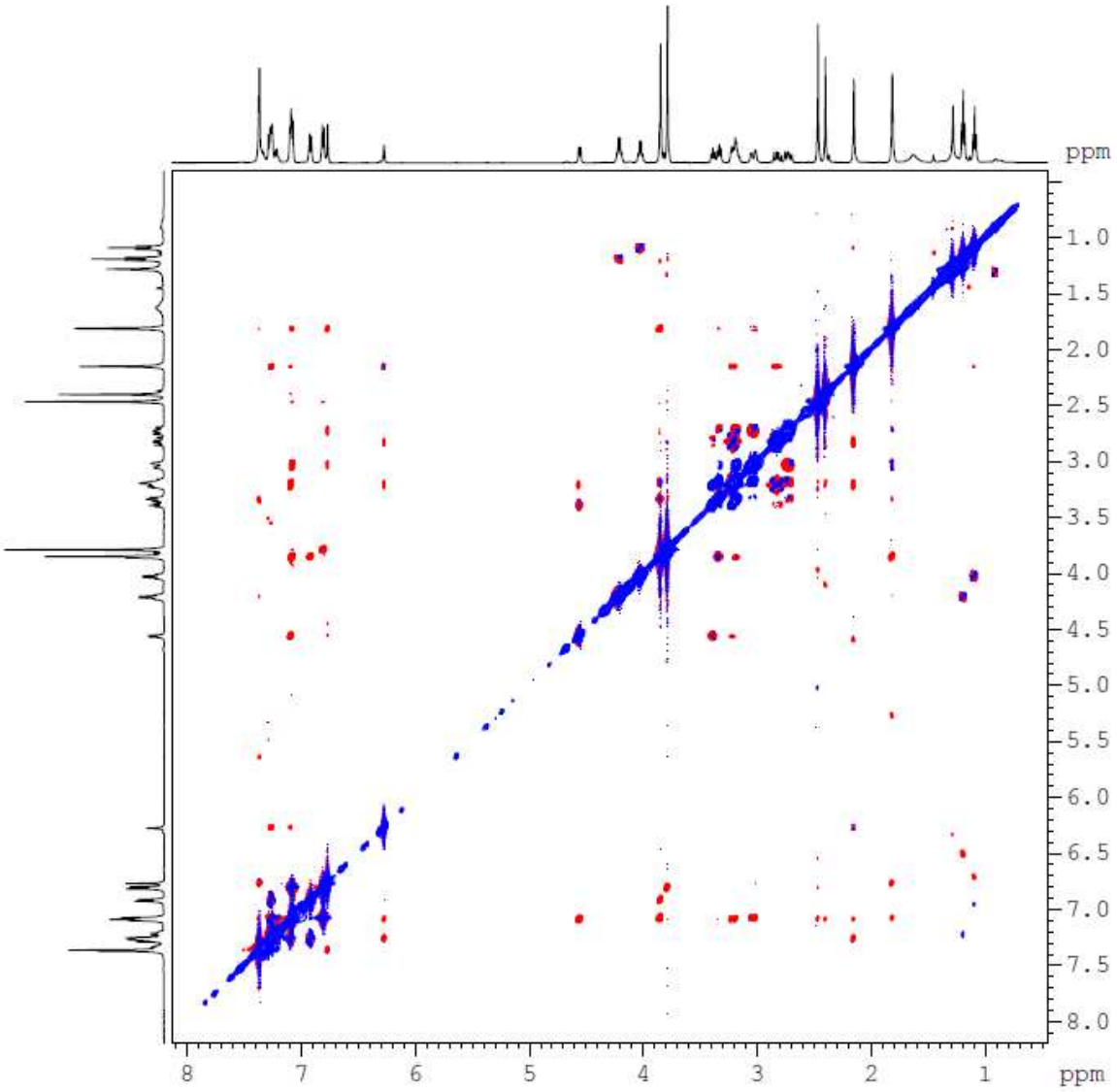
Unmarked peaks belong to the other regioisomer **17**



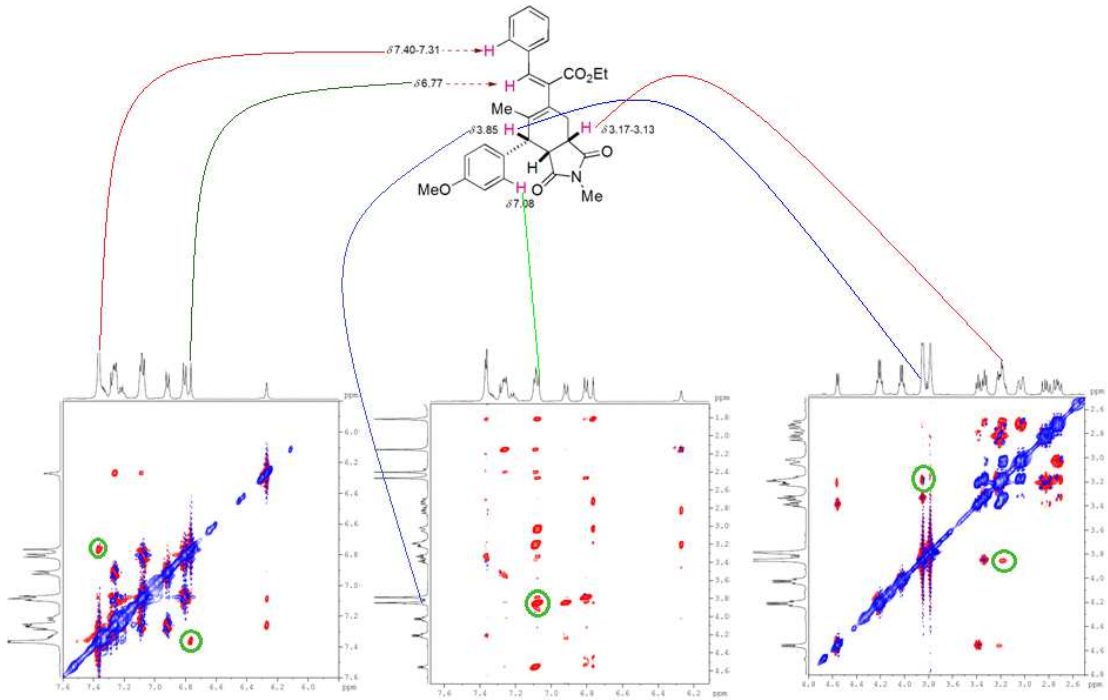


17 **18**

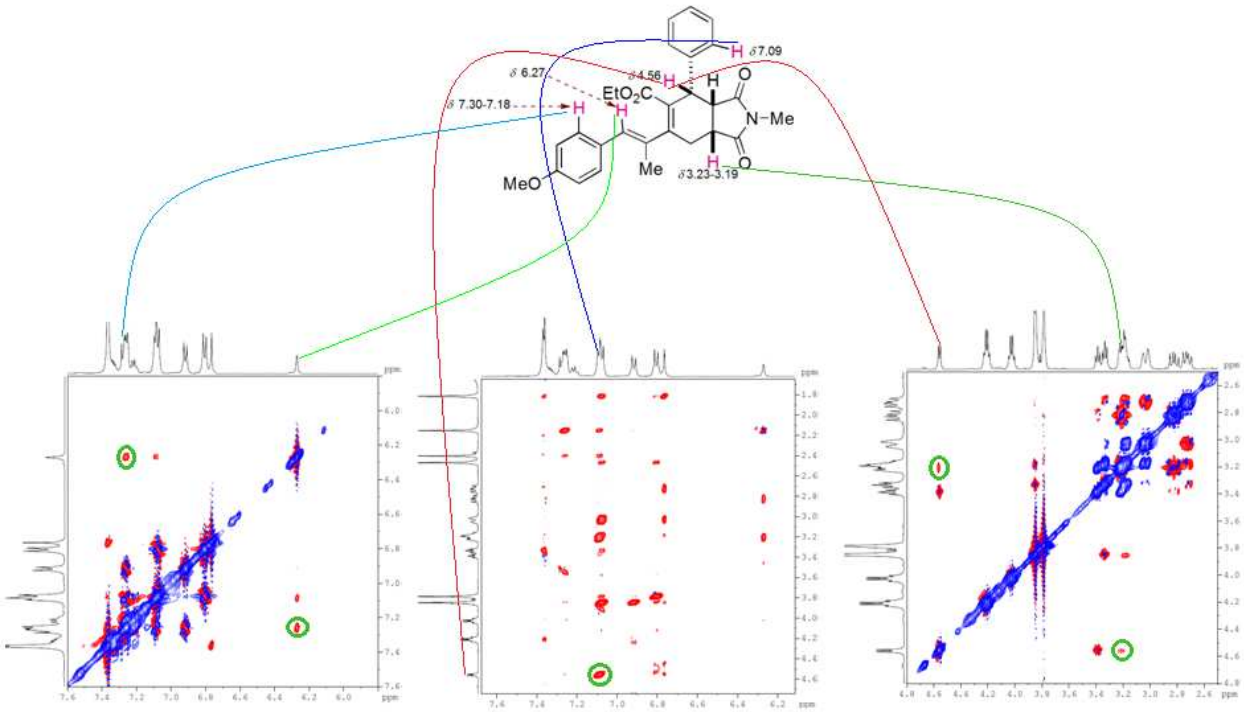
^{1}H/^{1}H ROESY (500 MHz, $CDCl_3$)

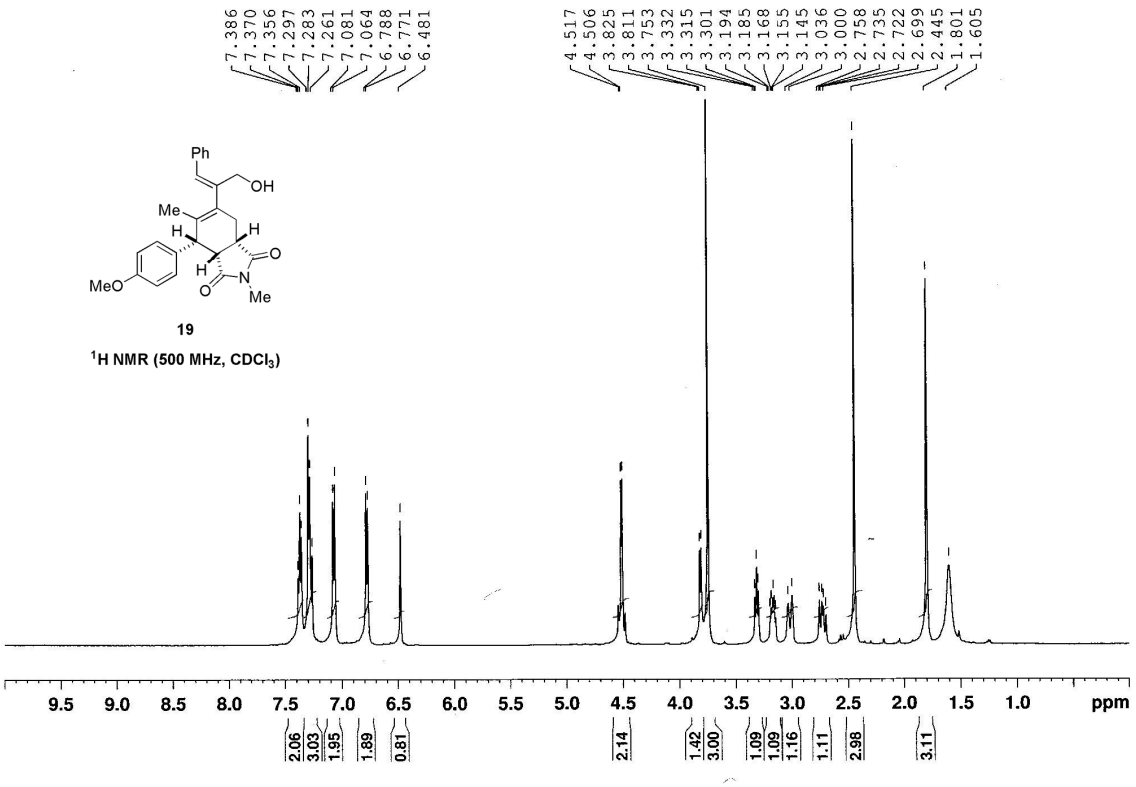


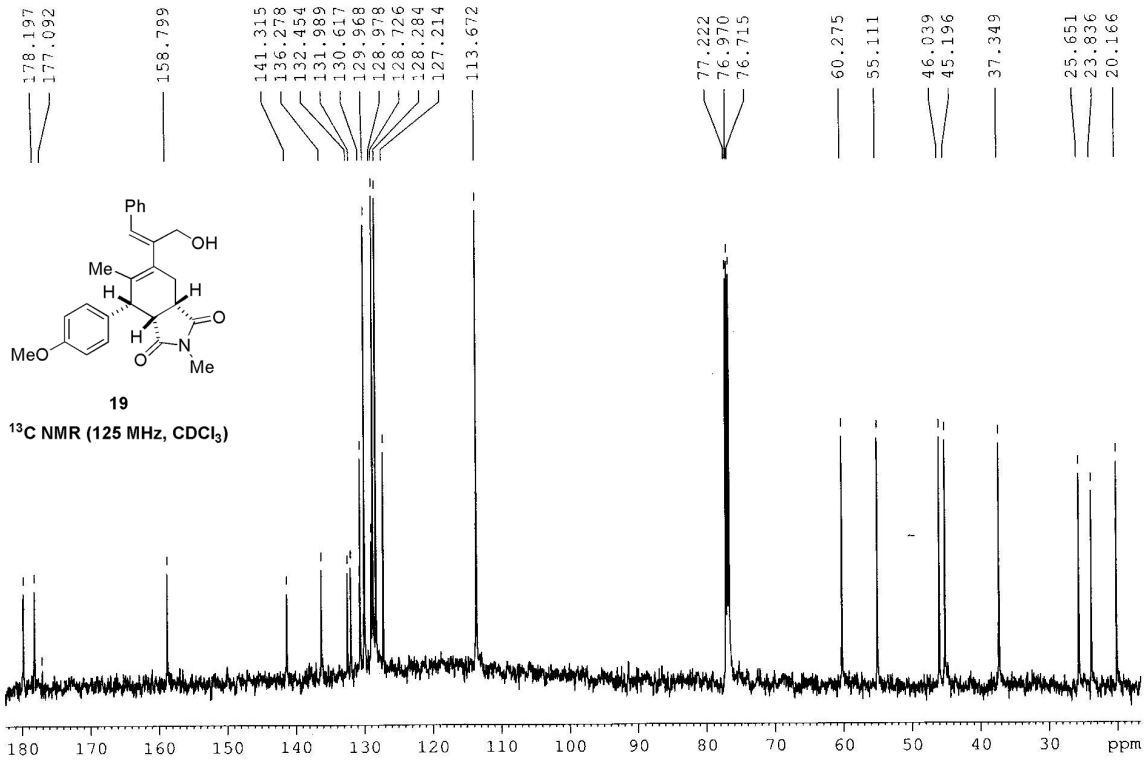
Expansions of $^{1}H/^{1}H$ ROESY for the assignment of stereo and regiochemistry **17**

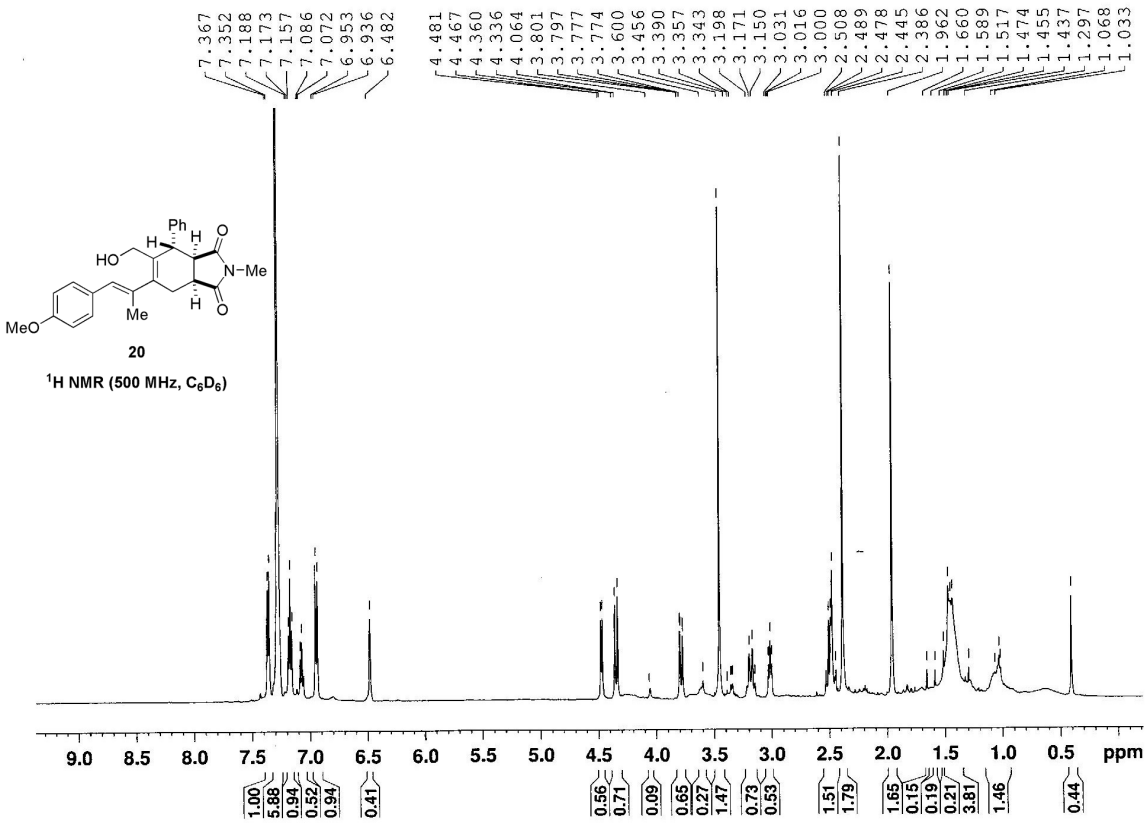


Expansions of $^{1}H/^{1}H$ ROESY for the assignment of stereo and regiochemistry of **18**



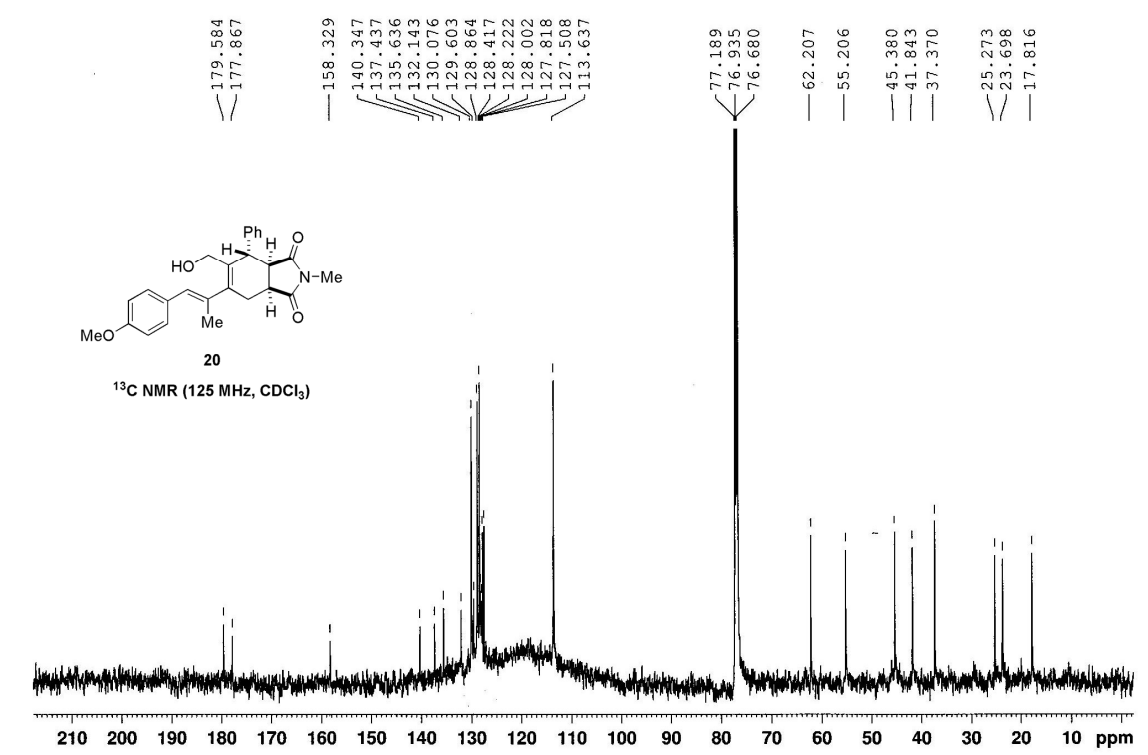

7.386
7.370
7.356
7.297
7.283
7.261
7.081
7.064
6.788
6.771
6.481
4.517
4.506
3.825
3.811
3.753
3.332
3.315
3.301
3.194
3.185
3.168
3.155
3.145
3.036
3.000
2.758
2.735
2.722
2.699
2.445
1.801
1.605
Ph
OH
Me
H
H
O
H
N
Me
MeO
O
19
1H NMR (500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06
3.03
1.95
1.89
0.81
2.14
1.42
3.00
1.09
1.09
1.16
1.11
2.98
3.11


178.197
177.092
158.799
141.315
136.278
132.454
131.989
130.617
129.968
128.978
128.726
128.284
127.214
113.672
77.222
76.970
76.715
60.275
55.111
46.039
45.196
37.349
25.651
23.836
20.166
Ph
OH
Me
H
H
O
H
N
Me
MeO
O
19
13C NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm



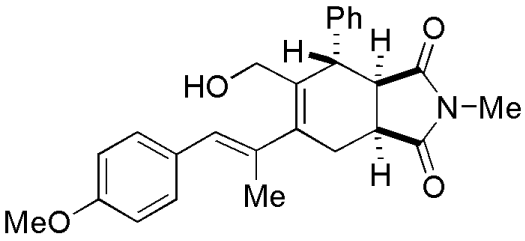
20

^{1}H NMR (500 MHz, C_6D_6)



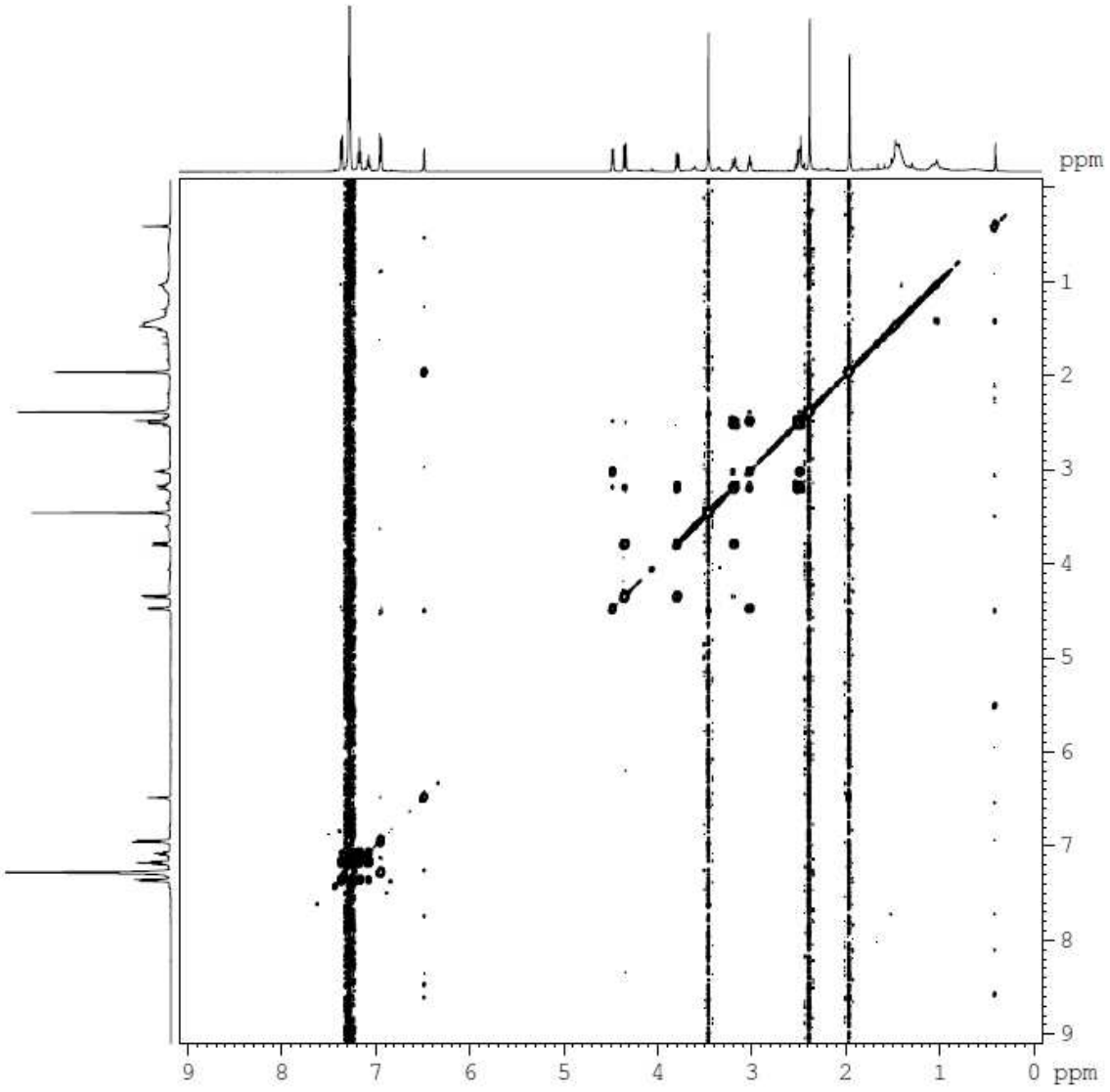
20

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

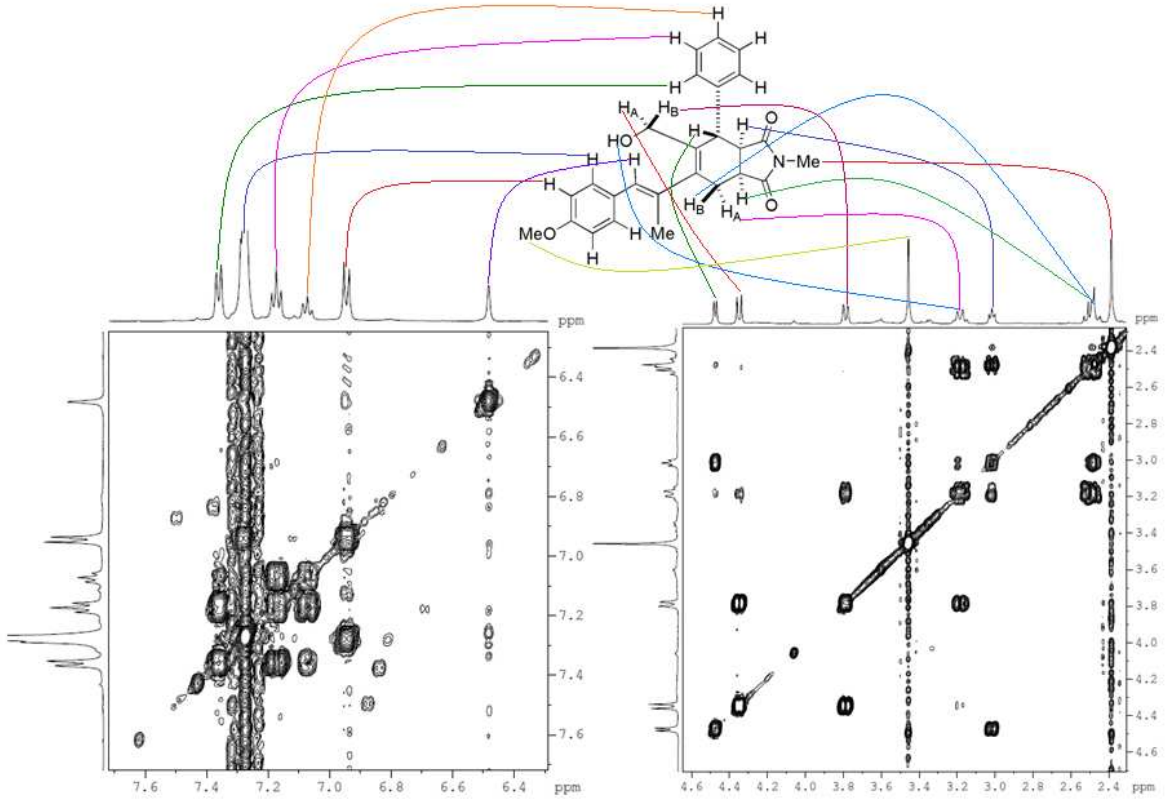


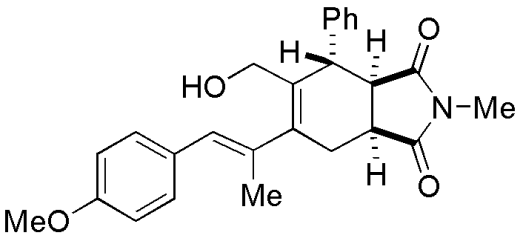
20

^{1}H/^{1}H COSY (500 MHz, C_6D_6)



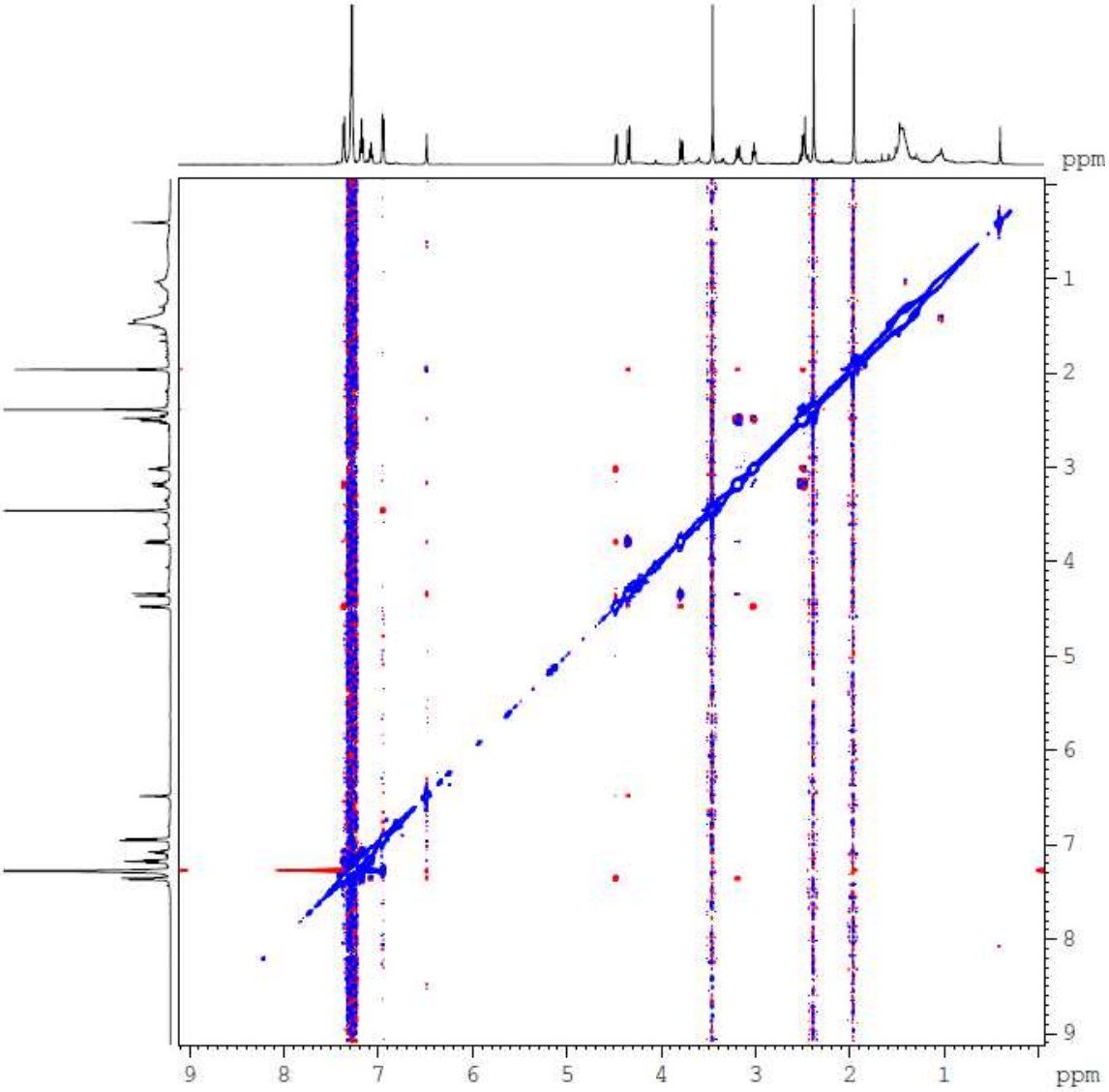
Expansions of $^{1}H/^{1}H$ COSY spectrum for the interpretation of peaks of **20**



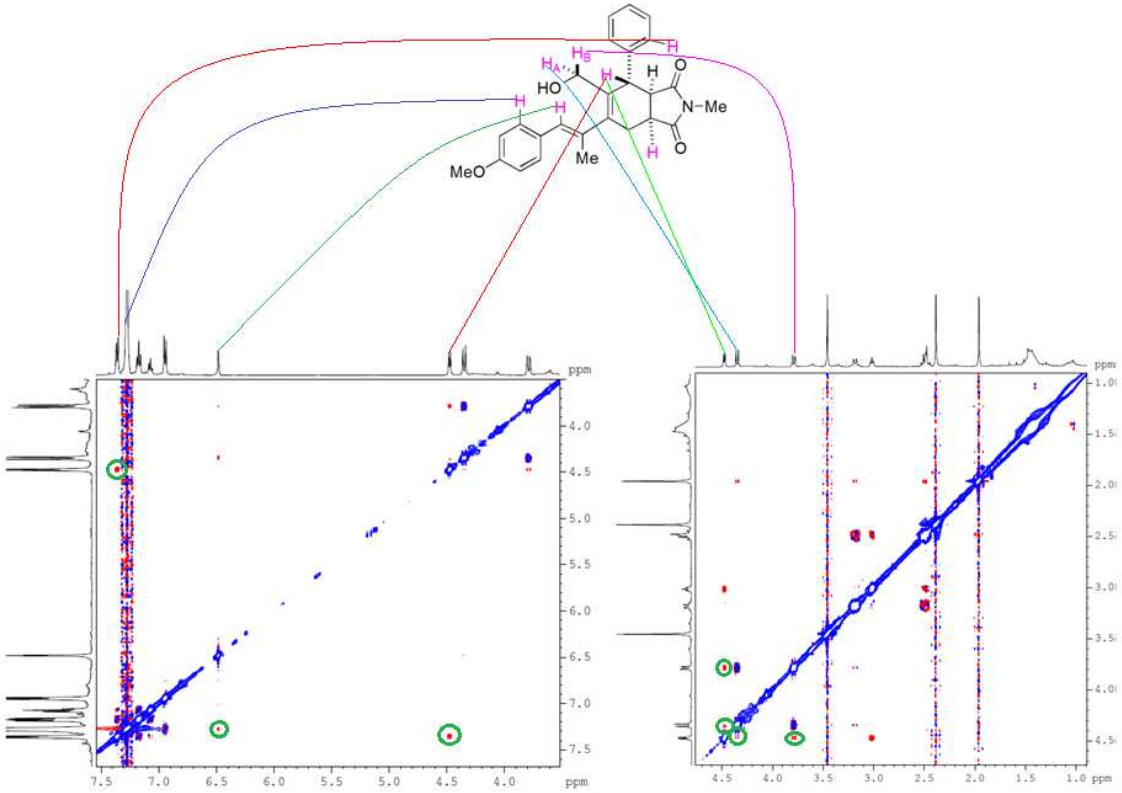


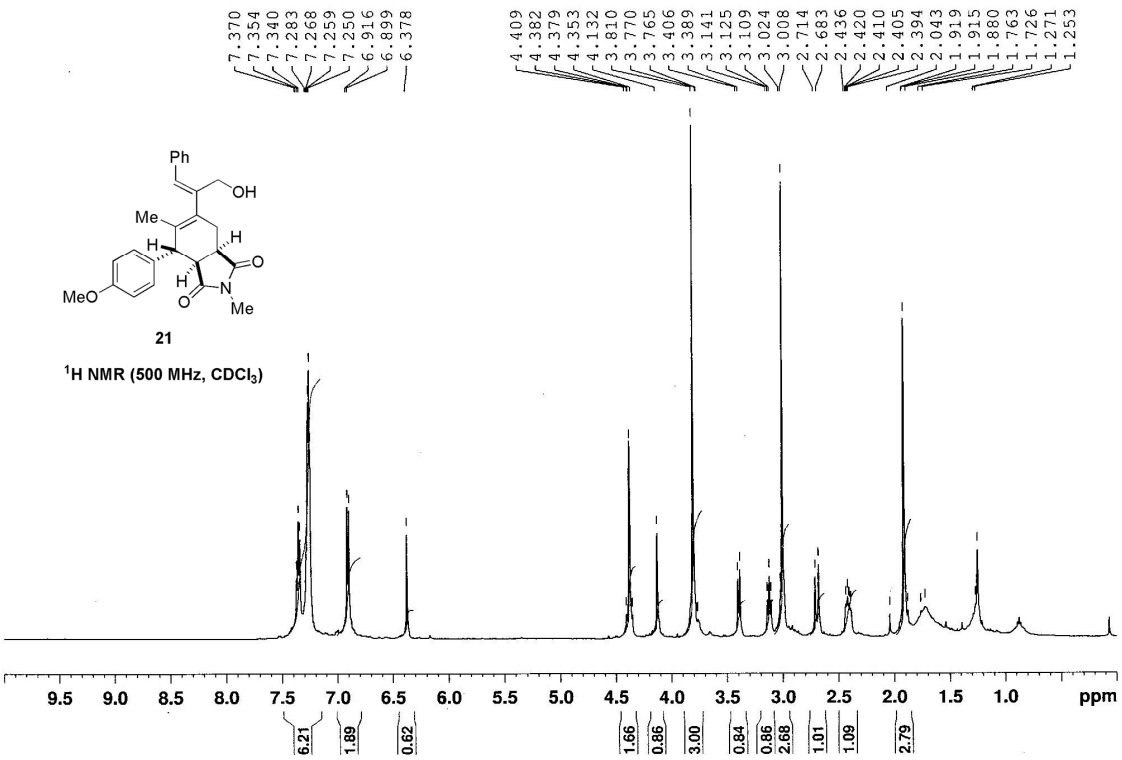
20

^{1}H/^{1}H ROESY (500 MHz, C_6D_6)



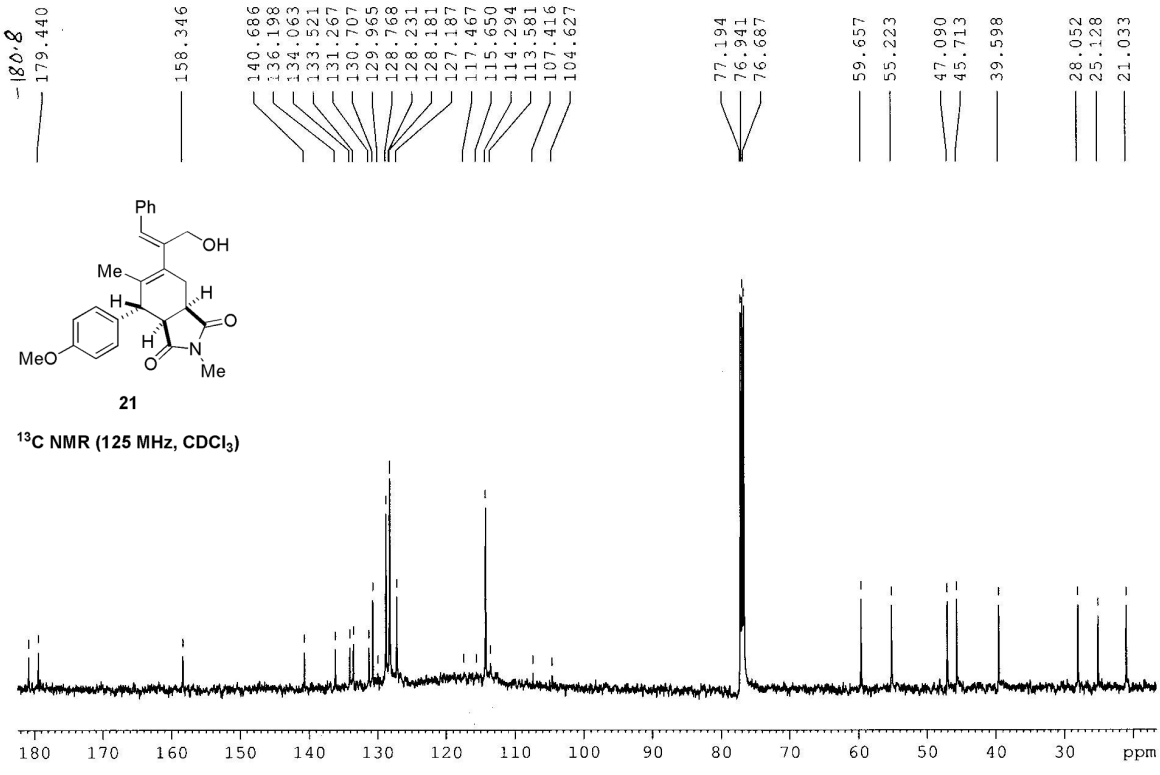
Expansions of $^{1}H/^{1}H$ ROESY for the assignment of stereo and regiochemistry of **20**





21

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



21

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