Supplementary Information:

Organic base effects in NHC promoted *O*- to *C*-carboxyl transfer; chemoselectivity profiles, mechanistic studies and domino catalysis

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I EXPERIMENTAL PROCEDURES

I.2 General information

^{1}H NMR Spectra were recorded using a Bruker Avance 400 spectrometer and Bruker Avance 300 spectrometer at 400 MHz and 300 MHz respectively, using residual protonated solvent as a reference for internal lock. The chemical shift information (δ_H) for each resonance signal are given in units of parts per million (ppm) relative to tetramethylsilane (TMS) where δ_H TMS = 0.00 ppm, or to residual (protonated) solvent. The number of protons (*n*) for a reported resonance signal are indicated by *n*H from their integral value and their multiplicity is reported with their coupling constants (*J*) quoted in Hz. Coupling constants are determined by analysis using iNMR® and Topspin®.

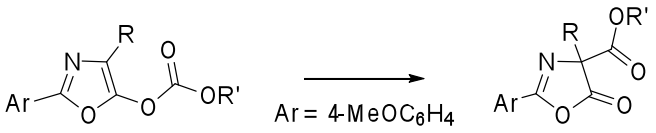
^{13}C NMR Spectra were recorded using a Bruker Avance 300 and Bruker Avance 400 spectrometer using the PENDANT sequence at 75.5 MHz and 100 MHz respectively with internal deuterated solvent lock. The chemical shift information (δ_C) for each resonance signal is given in units of parts per million (ppm) relative to tetramethylsilane (TMS) where δ_C TMS = 0.00 ppm, or to the relevant solvent.

^{19}F NMR Spectra were recorded using a Bruker Avance 400 spectrometer at 282 MHz. The chemical shift information (δ_F) for each resonance signal are given in units of parts per million (ppm) relative to trichlorofluoromethane ($CFCl_3$) where δ_F = 0.00.

HPLC was performed on either a Varian ProStar or Gilson apparatus, using a CHIRALPAK OD-H, AD-H or AS-H silica column, 0.46 cm ϕ × 25 cm, using hexane and isopropanol as eluents.

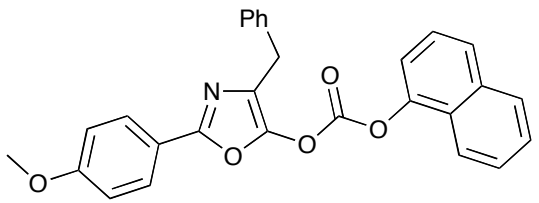
I.2 Known Substrates and Rearrangement Products

Known azlactone precursors, carbonate substrates and their *C*-carboxyazlactone isomers were prepared following literature procedures with physical and spectroscopic data in agreement with the literature,[1-5] which can be found at the following references. Spectroscopic data of purified materials were used to identify product distributions in crossover experiments.



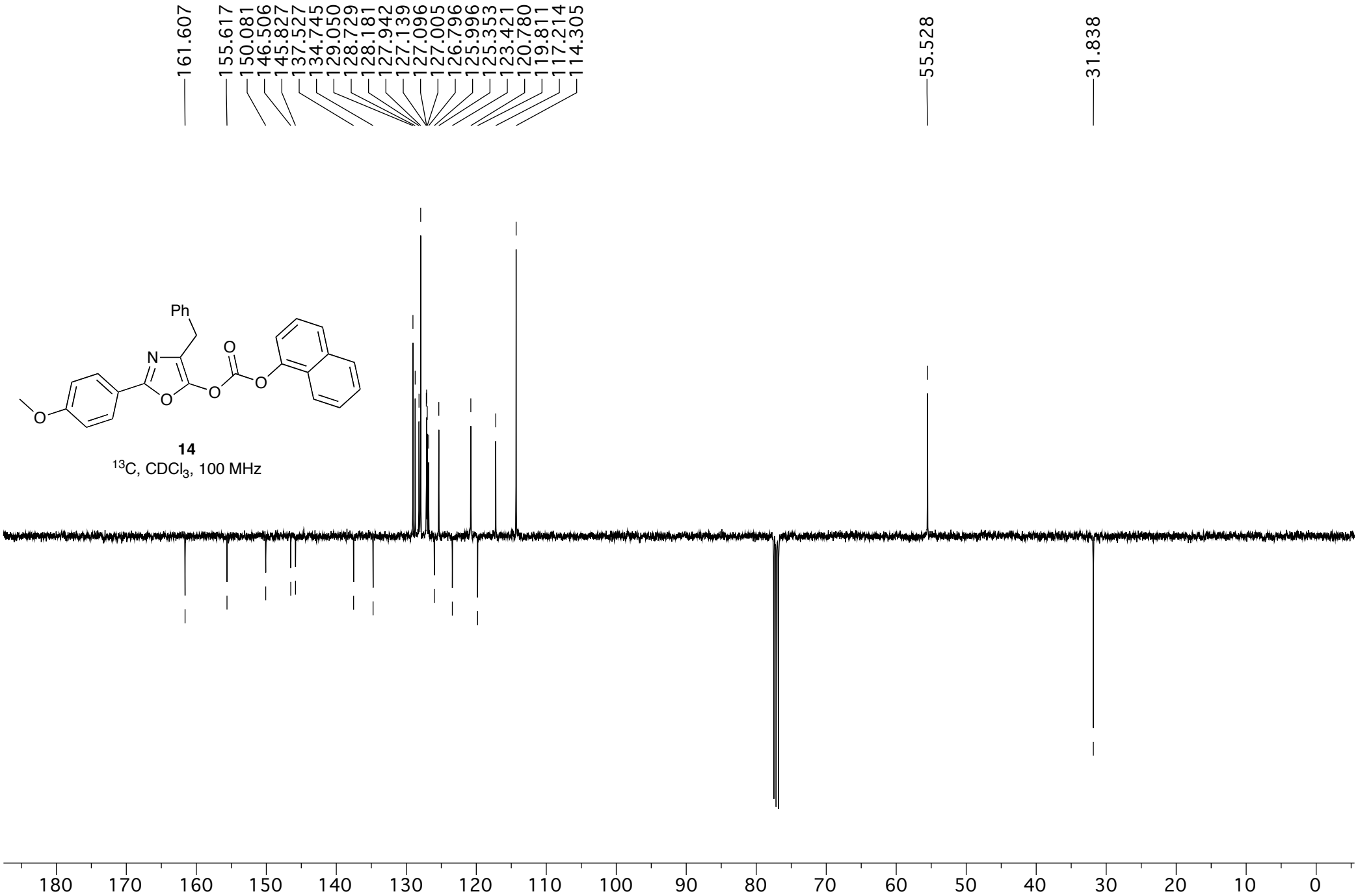
R	OR'	Carbonate	*C*-Carboxy azlactone	Reference
Bn	OPh	**4**	**5**	**1**
Bn	OMe	**11**	**17**	**1**
Bn	OBn	**12**	**18**	**2**
Bn	$OCMe_2CCl_3$	**13**	**19**	**2**
Me	OPh	**23**	**30**	**3**
n-Bu	OPh	**24**	**31**	**2,4**
i-Bu	OPh	**25**	**32**	**2**
Ph	OPh	**26**	**33**	**2**
4-$PhOCO_2C_6H_4CH_2$	OPh	**27**	**34**	**3**
CH_2CH_2SMe	OPh	**28**	**35**	**2**
i-Pr	OPh	**29**	**36**	**2**
Me	OMe	**37**	**38**	**2**
Me	$OCMe_2CCl_3$	**39**	**40**	**2**

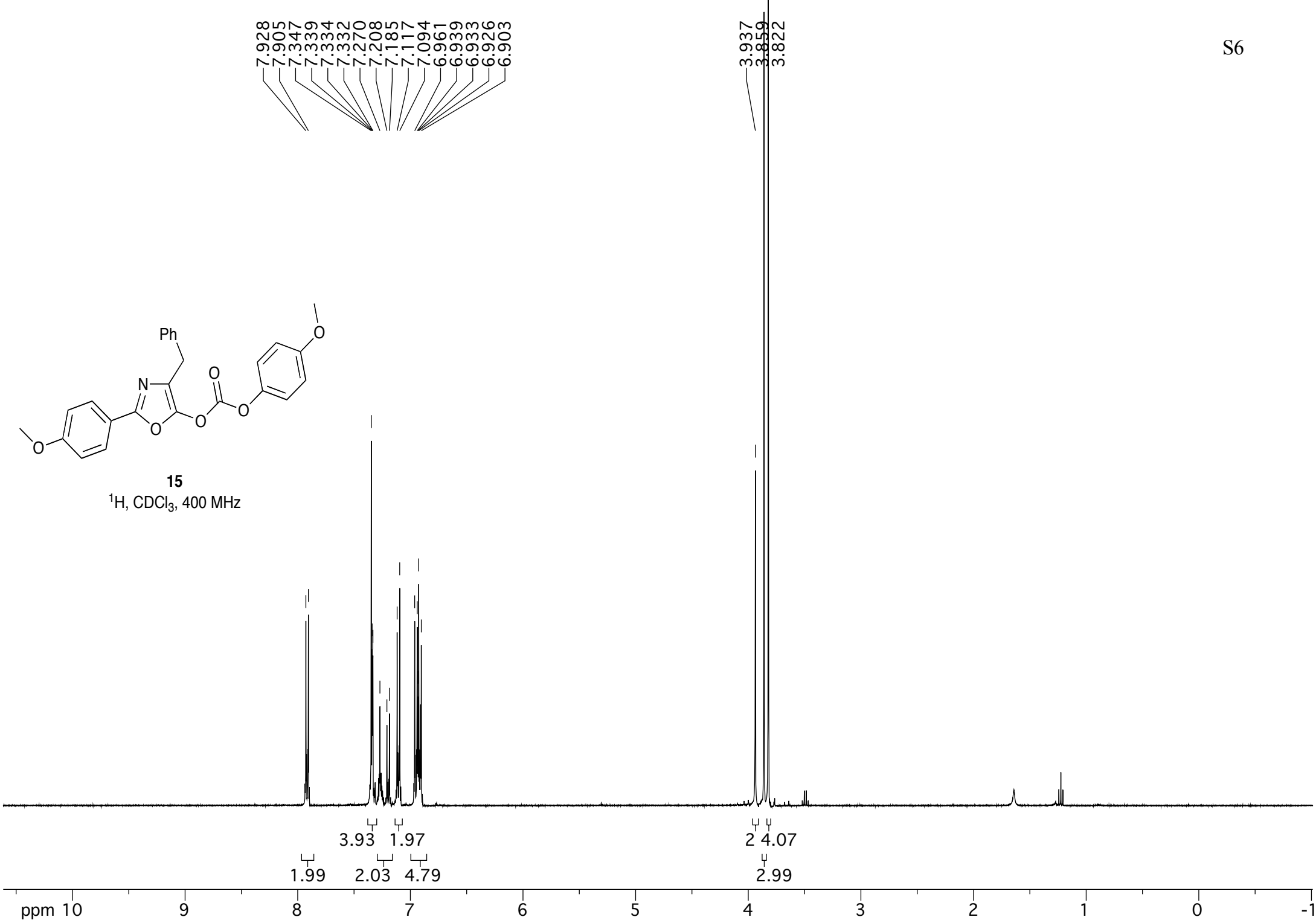
Literature procedures were used for the preparation of compounds **2**,[1] **6**,[1] **7**,[1] **9**,[1] **10**,[1] **47**[5] and **48**,[6] giving analytical and spectroscopic data in accordance with the literature.



14

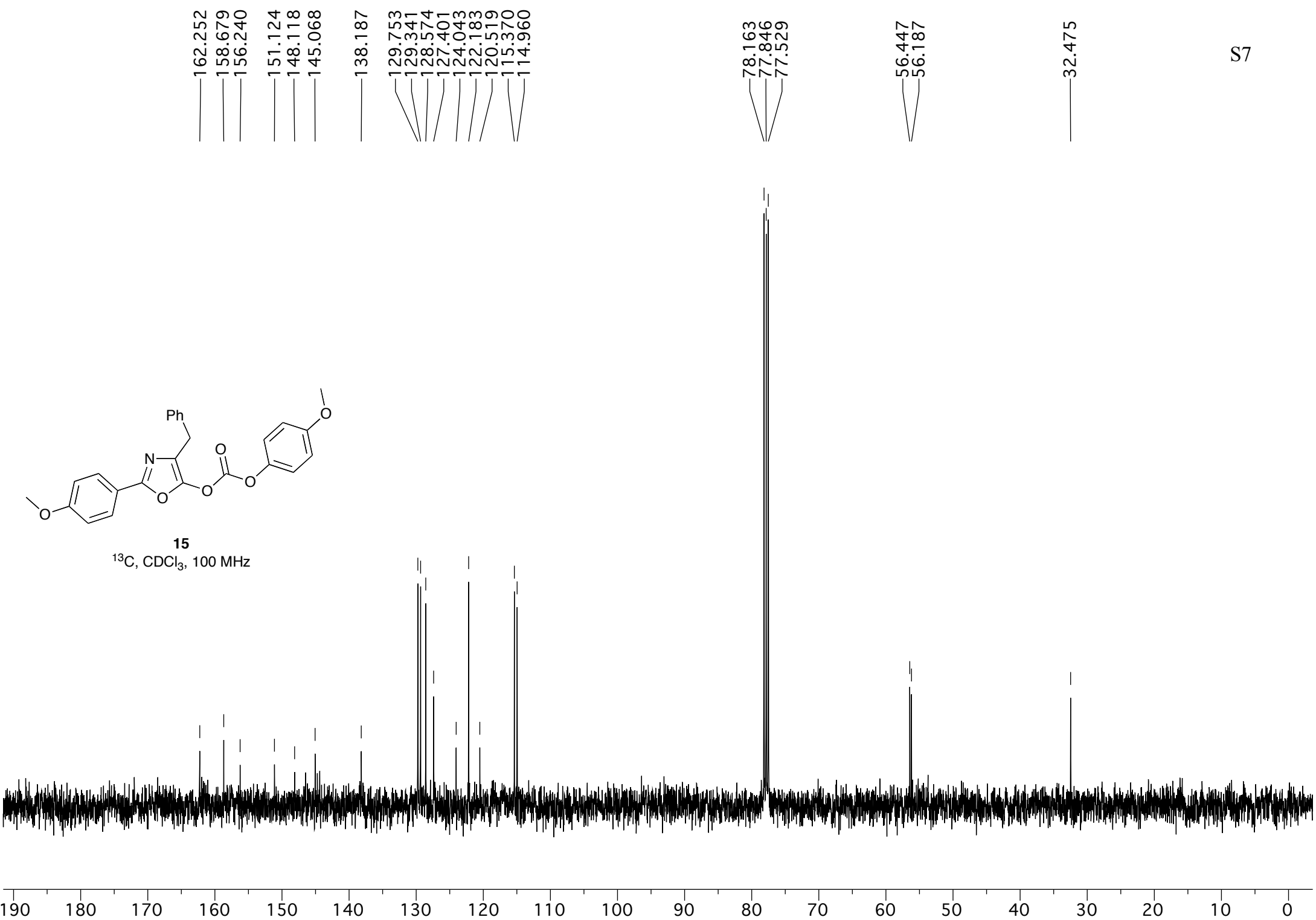
^{1}H, $CDCl_3$, 400 MHz

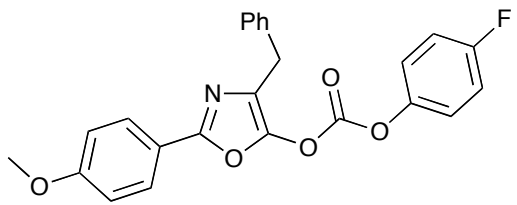

161.607
155.617
150.081
146.506
145.827
137.527
134.745
129.050
128.729
128.181
127.942
127.139
127.096
127.005
126.796
125.996
125.353
123.421
120.780
119.811
117.214
114.305
55.528
31.838
Ph
N
O
O
O
O
O
14
13C, CDCl3, 100 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



15

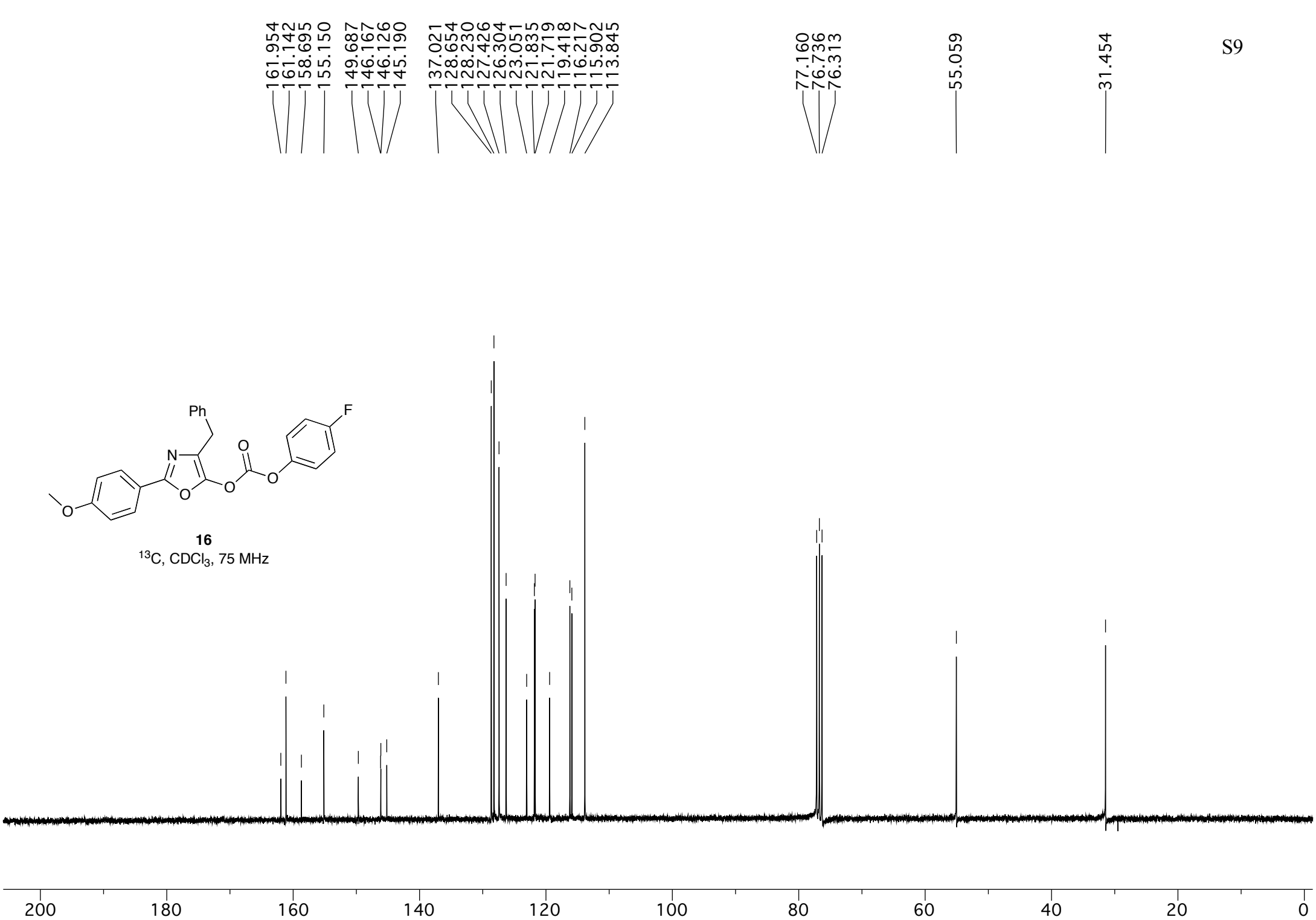
^{1}H, $CDCl_3$, 400 MHz

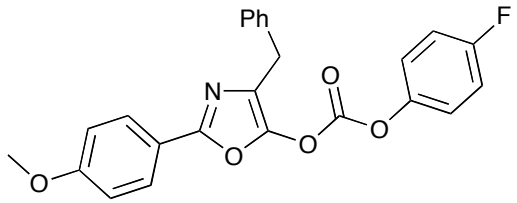

162.252
158.679
156.240
151.124
148.118
145.068
138.187
129.753
129.341
128.574
127.401
124.043
122.183
120.519
115.370
114.960
78.163
77.846
77.529
56.447
56.187
32.475
Ph
N
O
O
O
O
O
O
15
13C, CDCl3, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



16

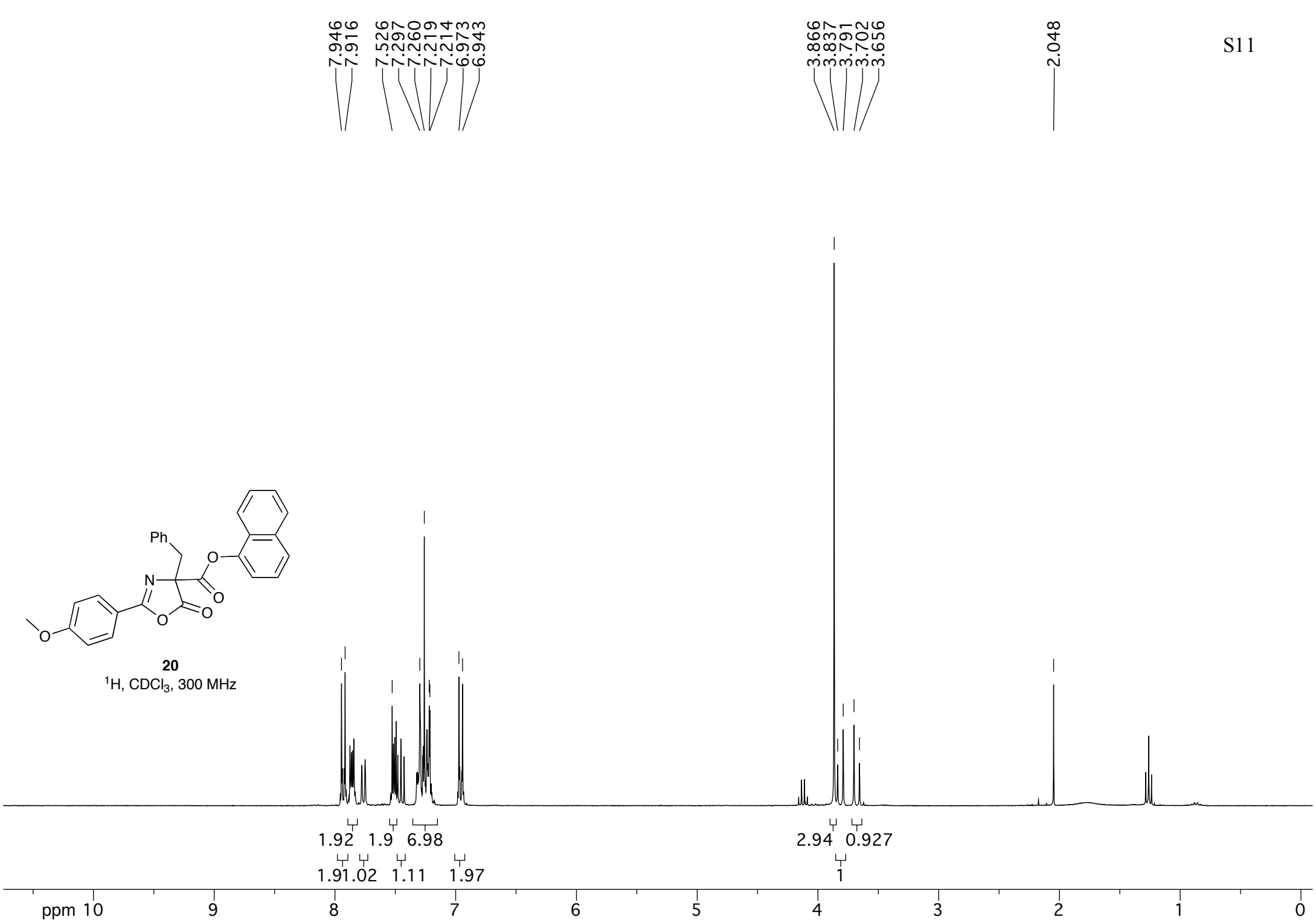
^{1}H, $CDCl_3$, 300 MHz

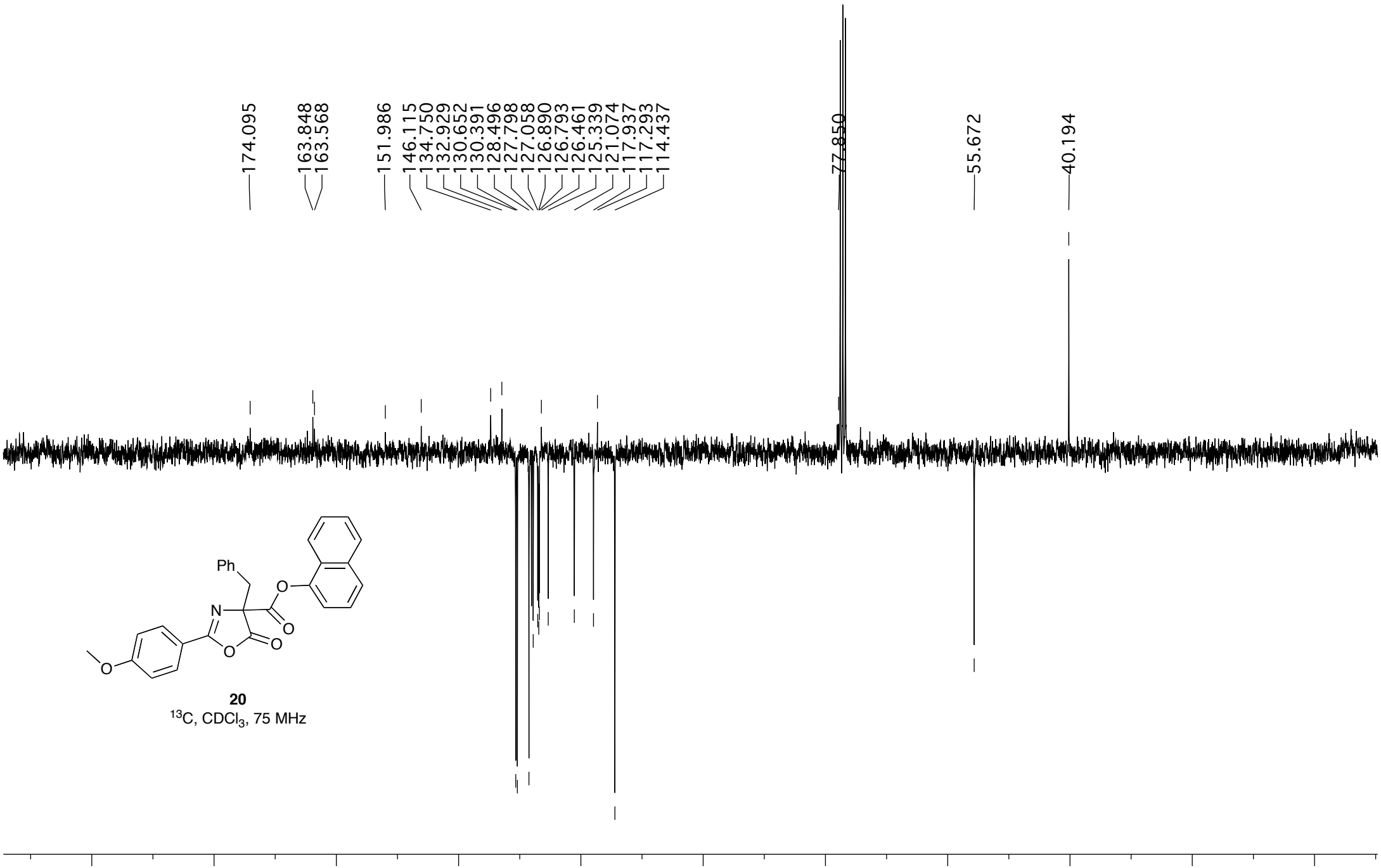

161.954
161.142
158.695
155.150
149.687
146.167
146.126
145.190
137.021
128.654
128.230
127.426
126.304
123.051
121.835
121.719
119.418
116.217
115.902
113.845
77.160
76.736
76.313
55.059
31.454
Ph
F
N
O
O
O
O
O
16
13C, CDCl3, 75 MHz
200
180
160
140
120
100
80
60
40
20
0



16

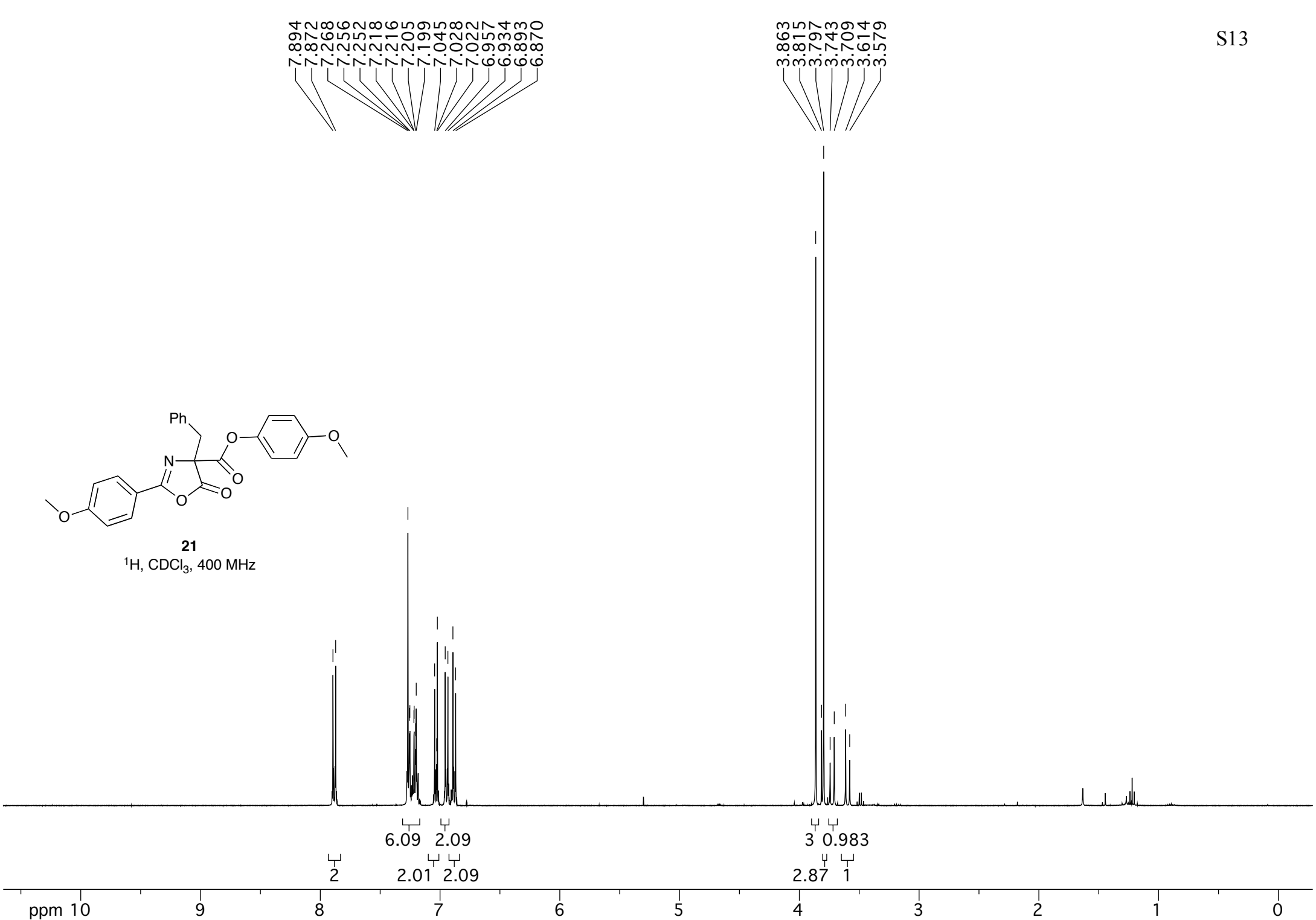
^{19}F, $CDCl_3$, 282 MHz


7.946
7.916
7.526
7.297
7.260
7.219
7.214
6.973
6.943
3.866
3.837
3.791
3.702
3.656
2.048
Ph
N
O
O
O
O
O
20
1H, CDCl3, 300 MHz
1.92
1.9
6.98
2.94
0.927
1.91
1.02
1.11
1.97
1
ppm 10
9
8
7
6
5
4
3
2
1
0



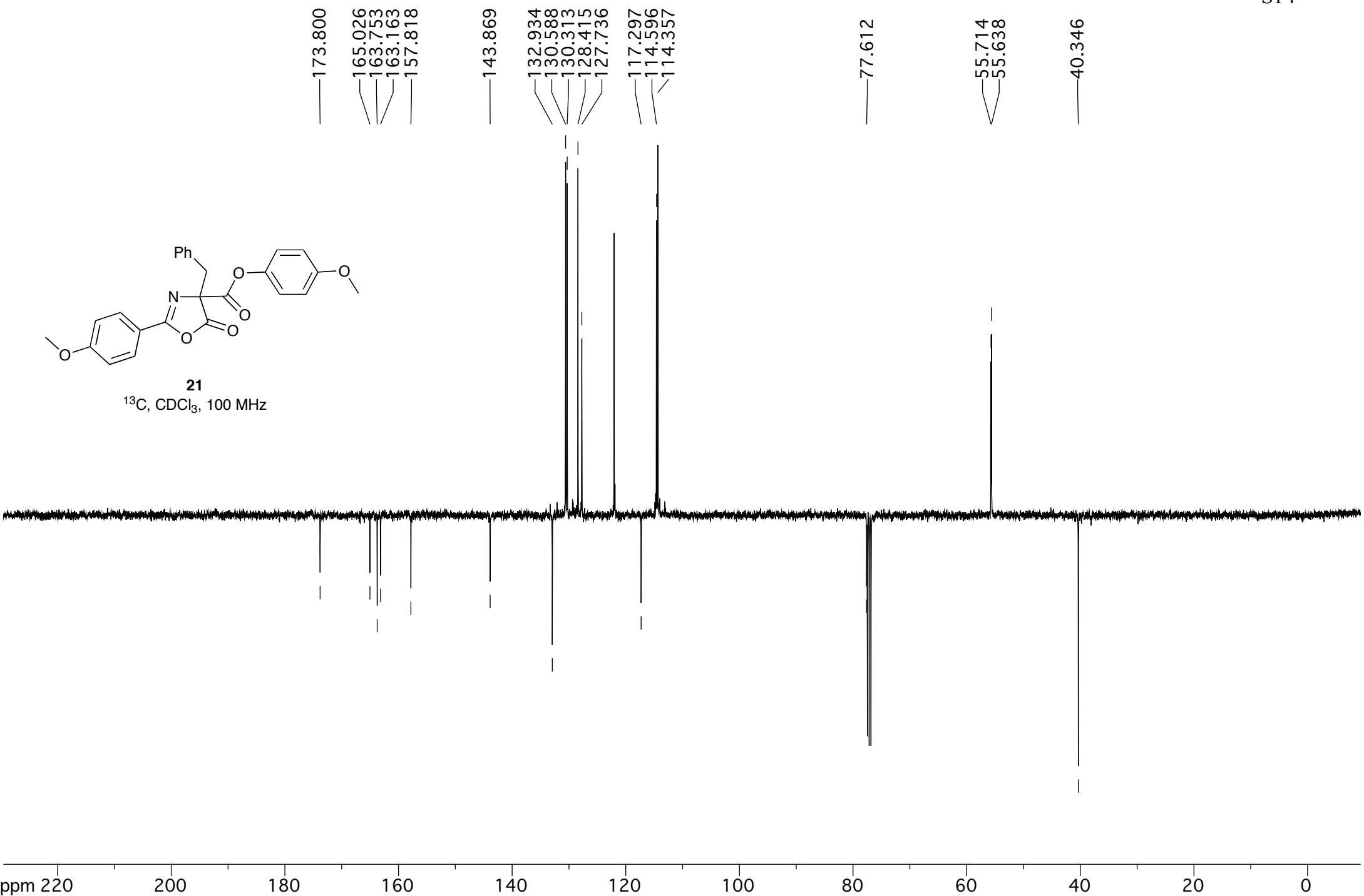
20

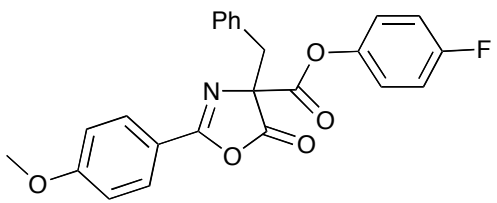
^{13}C, $CDCl_3$, 75 MHz



21

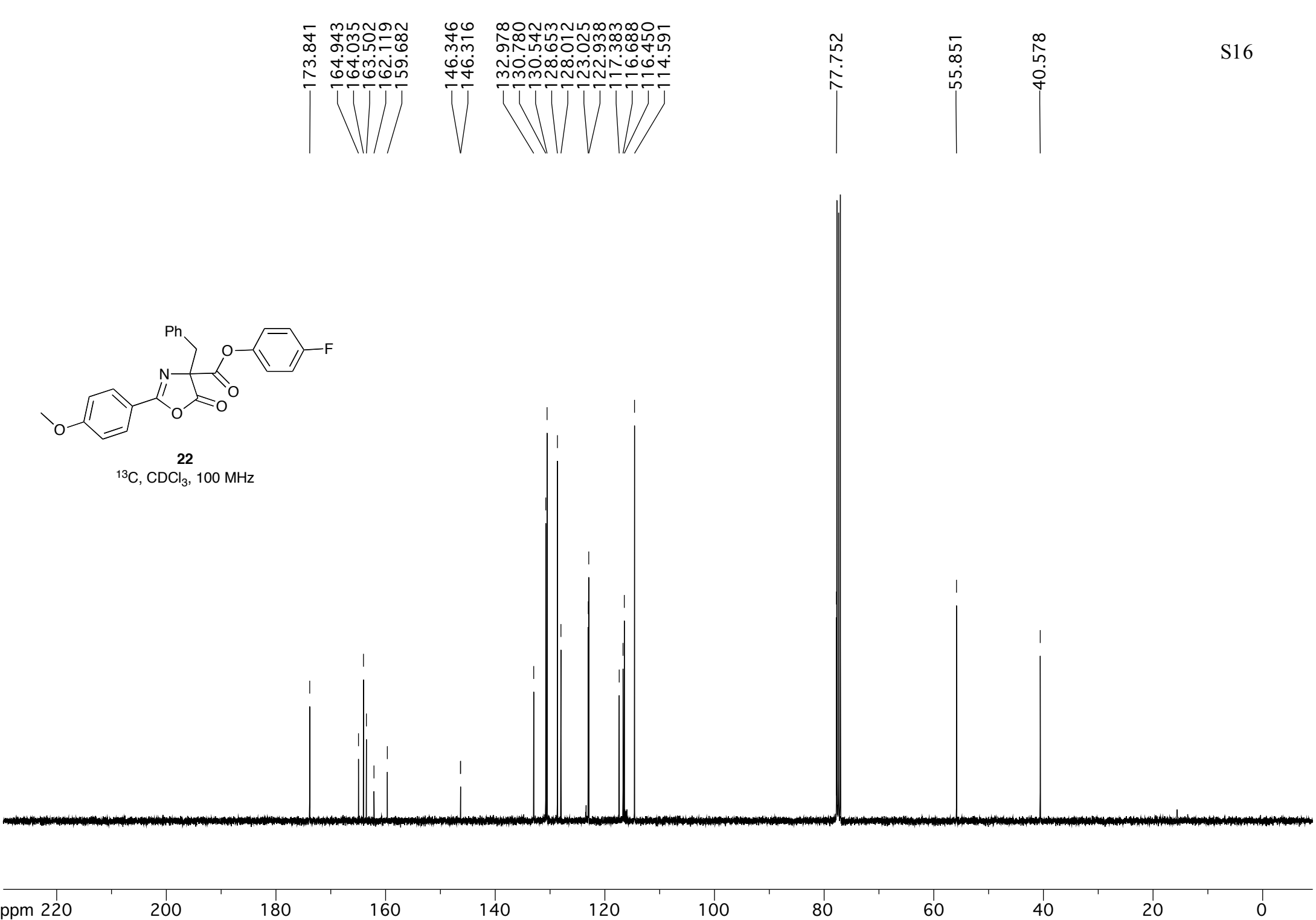
^{1}H, $CDCl_3$, 400 MHz

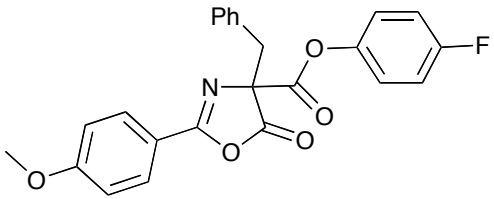

173.800
165.026
163.753
163.163
157.818
143.869
132.934
130.588
130.313
128.415
127.736
117.297
114.596
114.357
77.612
55.714
55.638
40.346
Ph
N
O
O
O
O
O
O
21
13C, CDCl3, 100 MHz
ppm 220
200
180
160
140
120
100
80
60
40
20
0



22

^{1}H, $CDCl_3$, 400 MHz


173.841
164.943
164.035
163.502
162.119
159.682
146.346
146.316
132.978
130.780
130.542
128.653
128.012
123.025
122.938
117.383
116.688
116.450
114.591
77.752
55.851
40.578
Ph
N
O
O
O
O
O
F
O
22
13C, CDCl3, 100 MHz
ppm 220
200
180
160
140
120
100
80
60
40
20
0



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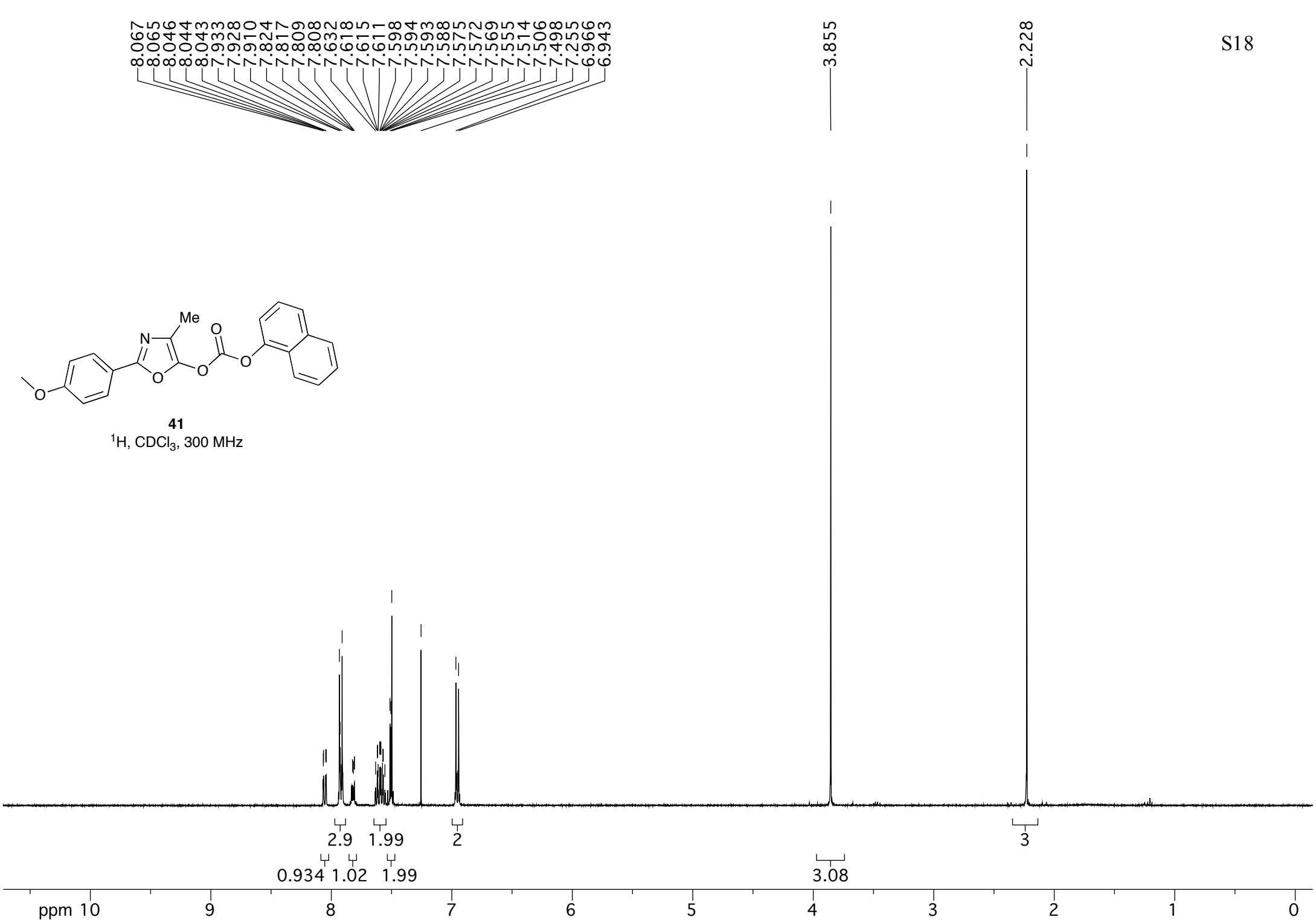
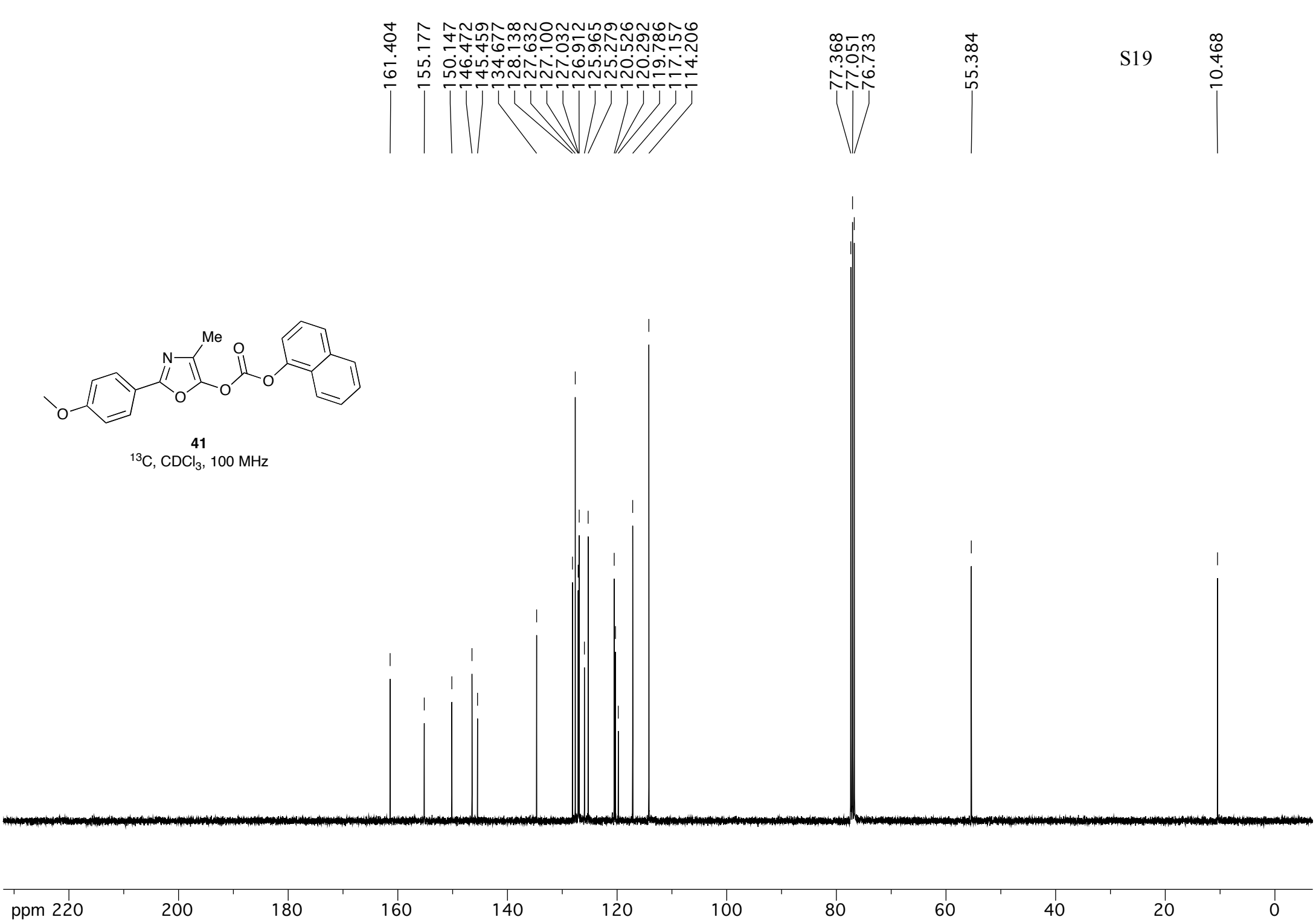
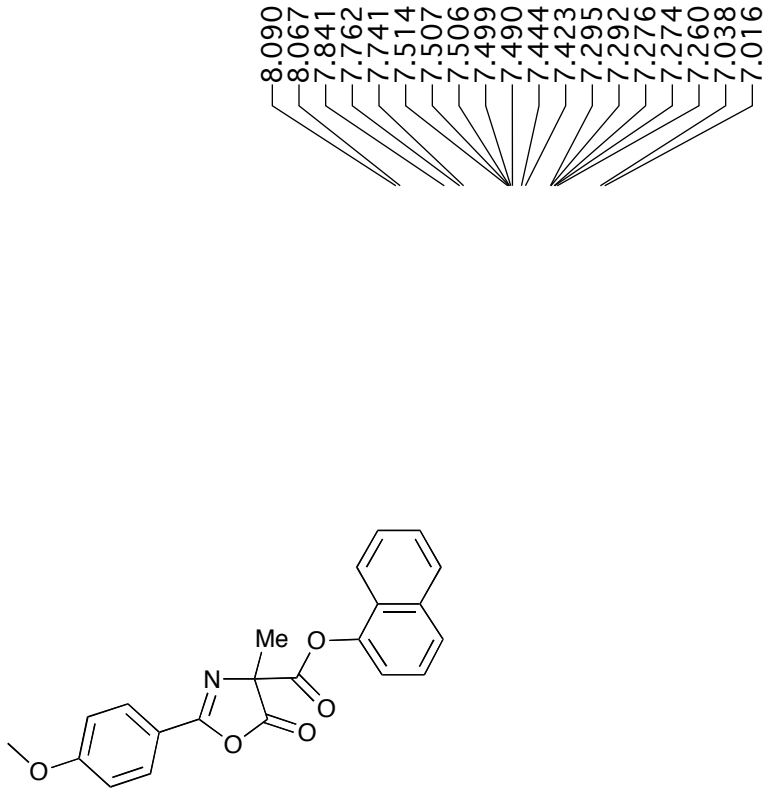
^{19}F, $CDCl_3$, 282 MHz



41

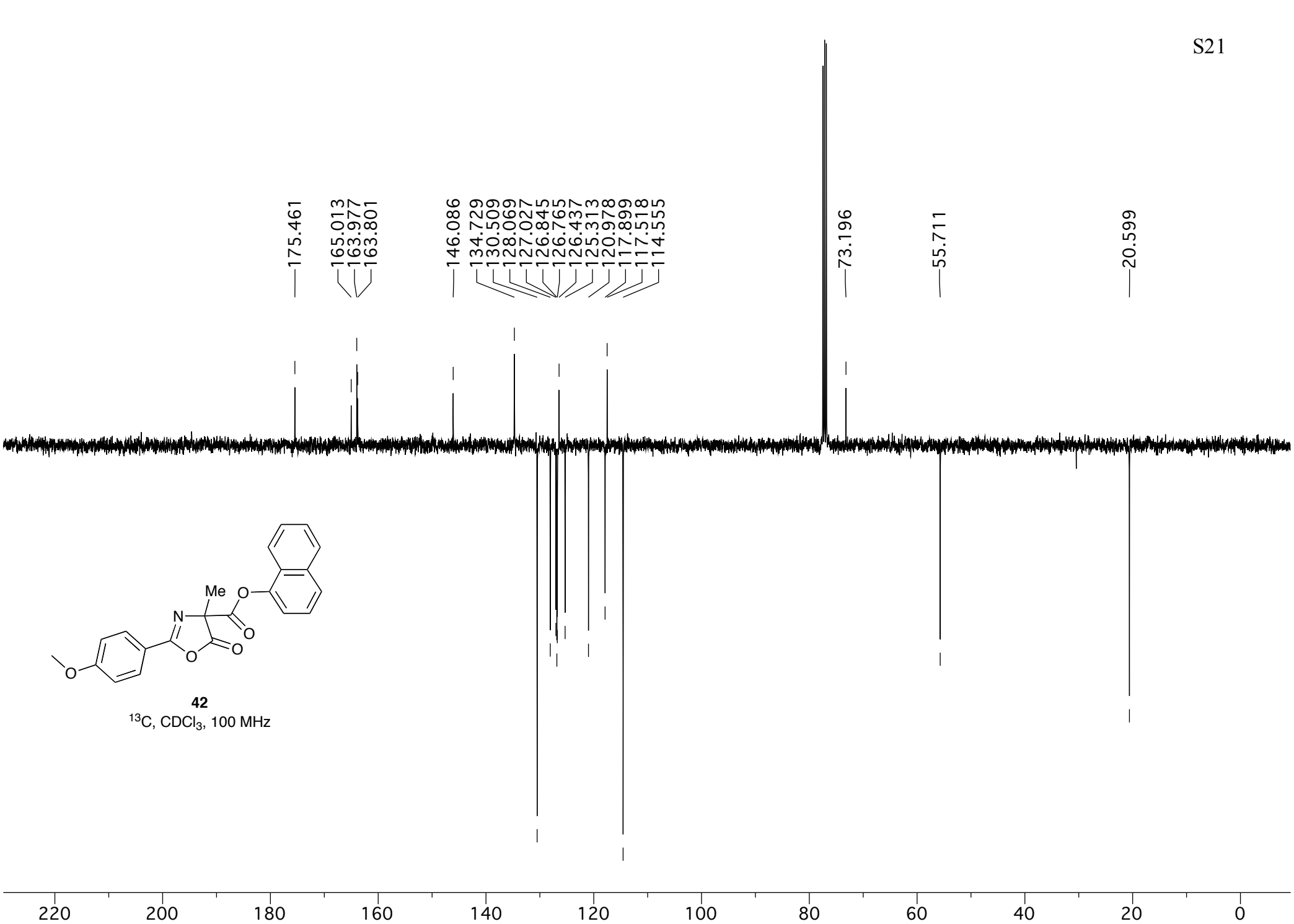
^{1}H, $CDCl_3$, 300 MHz


161.404
155.177
150.147
146.472
145.459
134.677
128.138
127.632
127.100
127.032
126.912
125.965
125.279
120.526
120.292
119.786
117.157
114.206
77.368
77.051
76.733
55.384
10.468
Me
N
O
O
O
O
O
41
13C, CDCl3, 100 MHz
ppm 220
200
180
160
140
120
100
80
60
40
20
0



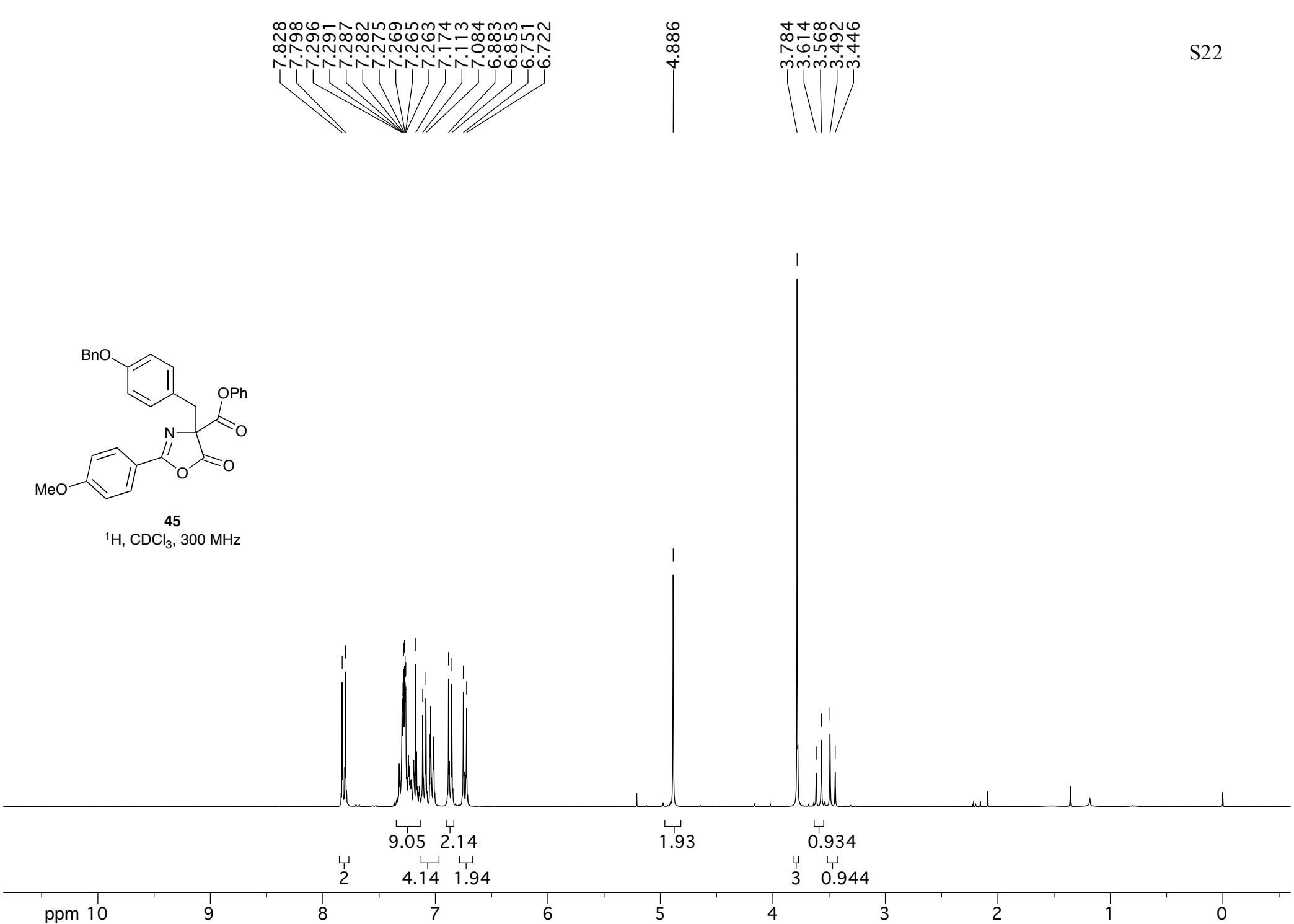
42

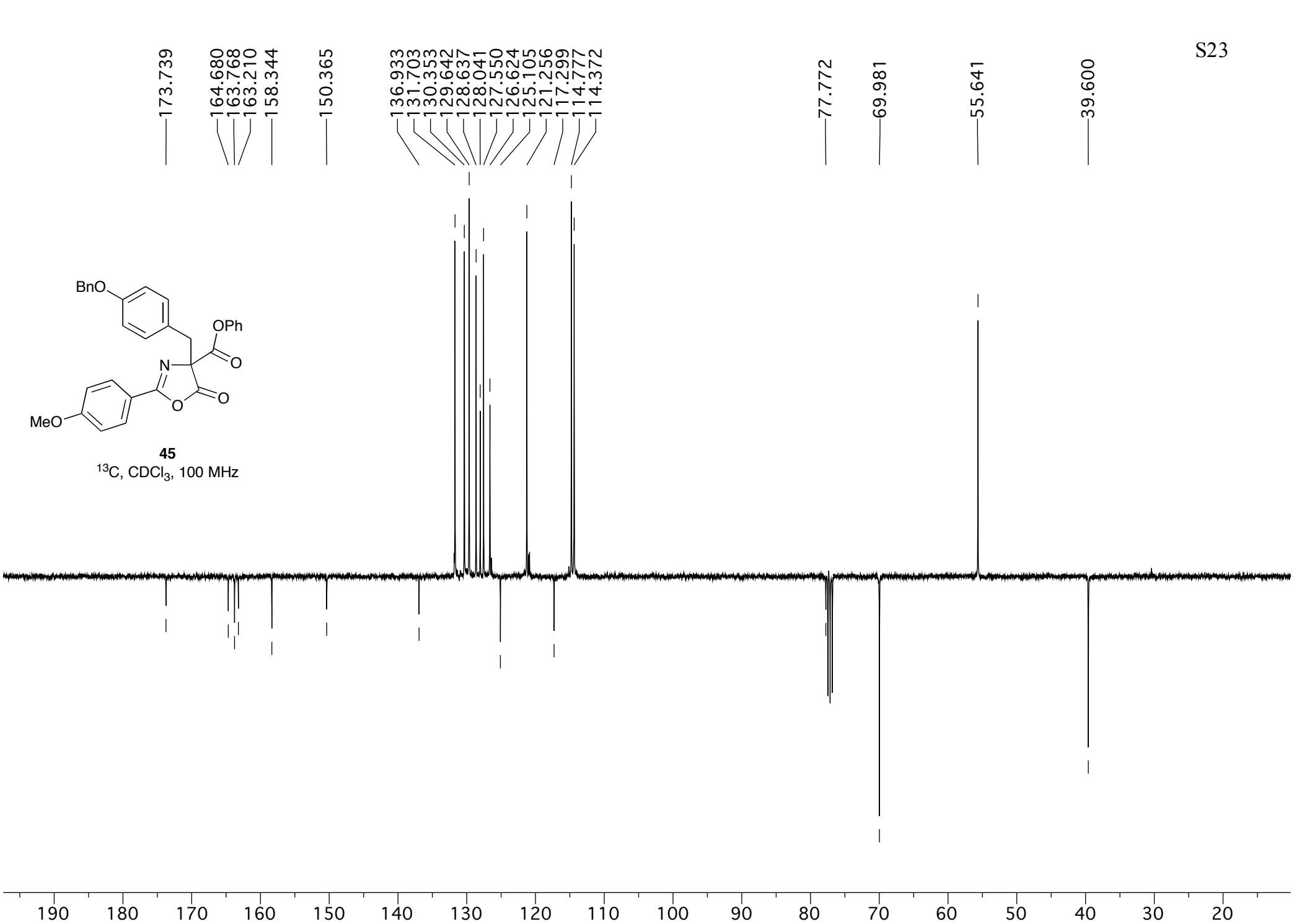
^{1}H, $CDCl_3$, 400 MHz



42

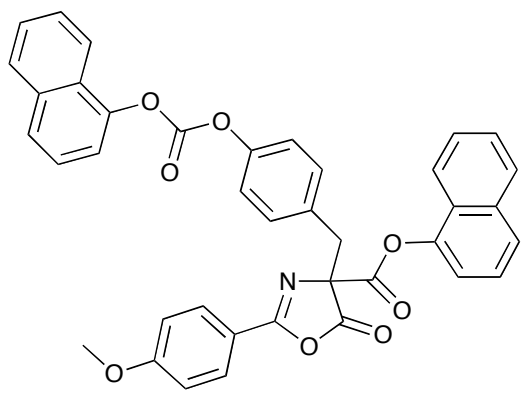
^{13}C, $CDCl_3$, 100 MHz


7.828
7.798
7.296
7.291
7.287
7.282
7.275
7.269
7.265
7.263
7.174
7.113
7.084
6.883
6.853
6.751
6.722
4.886
3.784
3.614
3.568
3.492
3.446
BnO
OPh
O
N
O
O
MeO
45
1H, CDCl3, 300 MHz
9.05
2.14
1.93
0.934
2
4.14
1.94
3
0.944
ppm 10
9
8
7
6
5
4
3
2
1
0



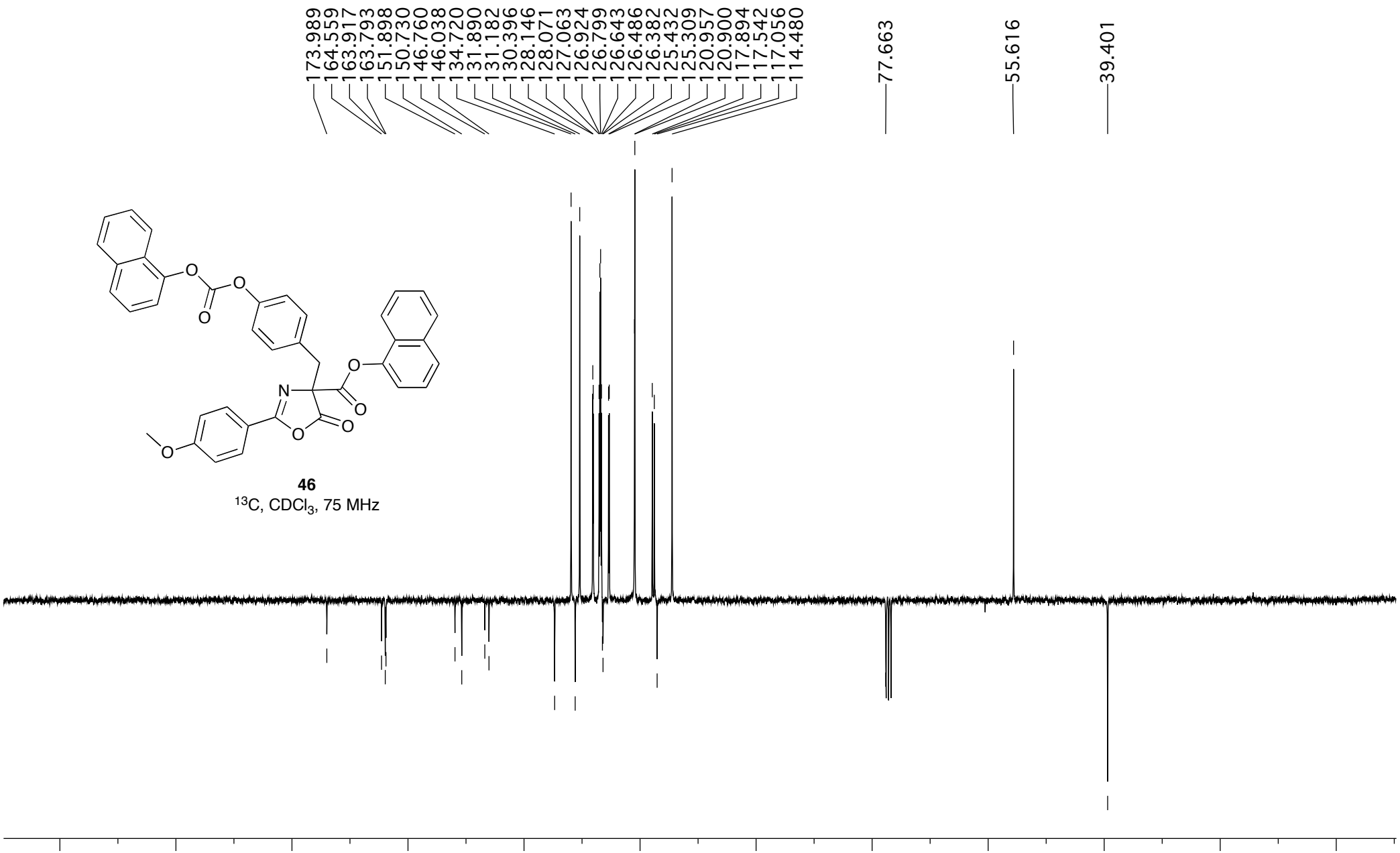
45

^{13}C, $CDCl_3$, 100 MHz



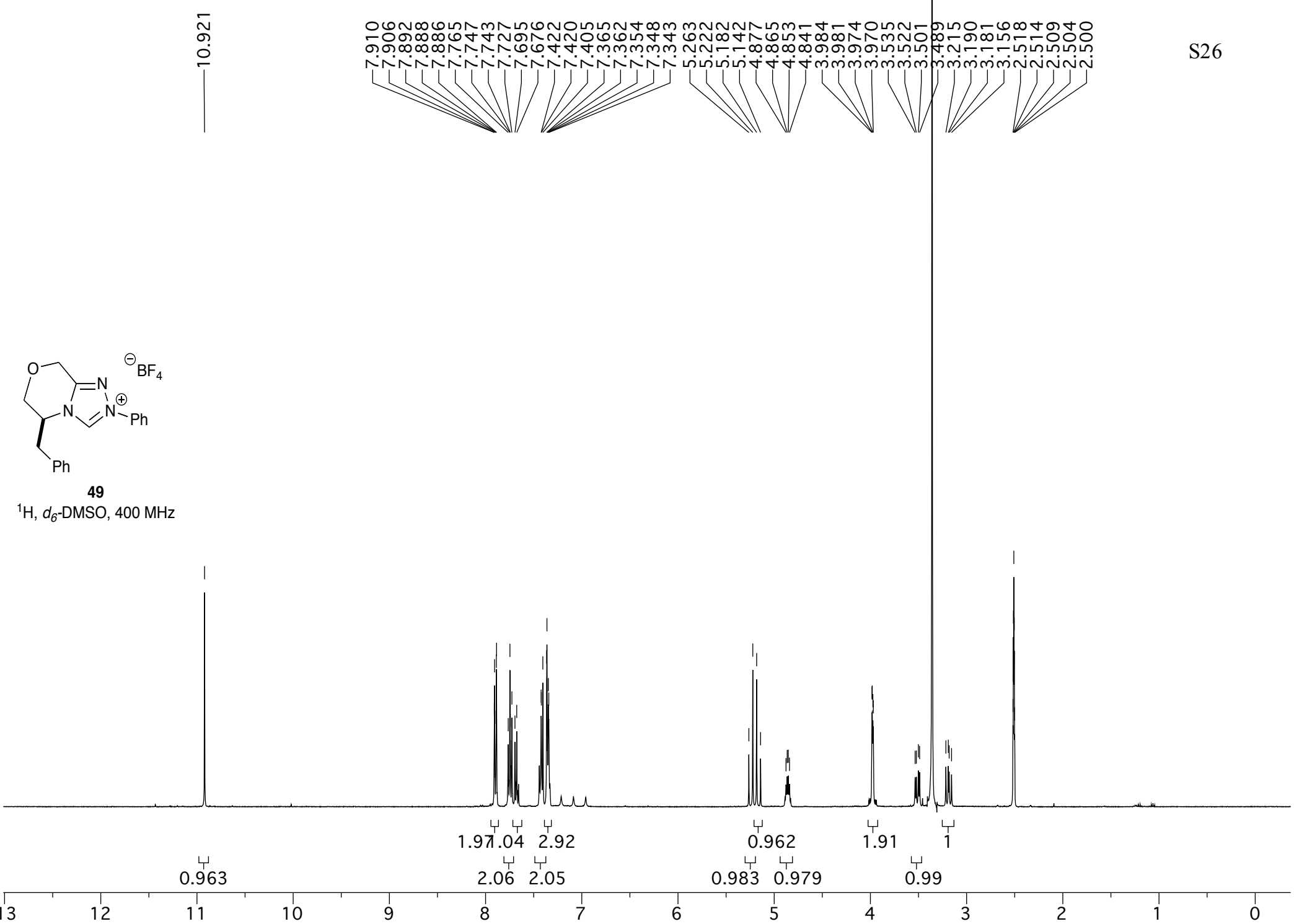
46

^{1}H, $CDCl_3$, 300 MHz



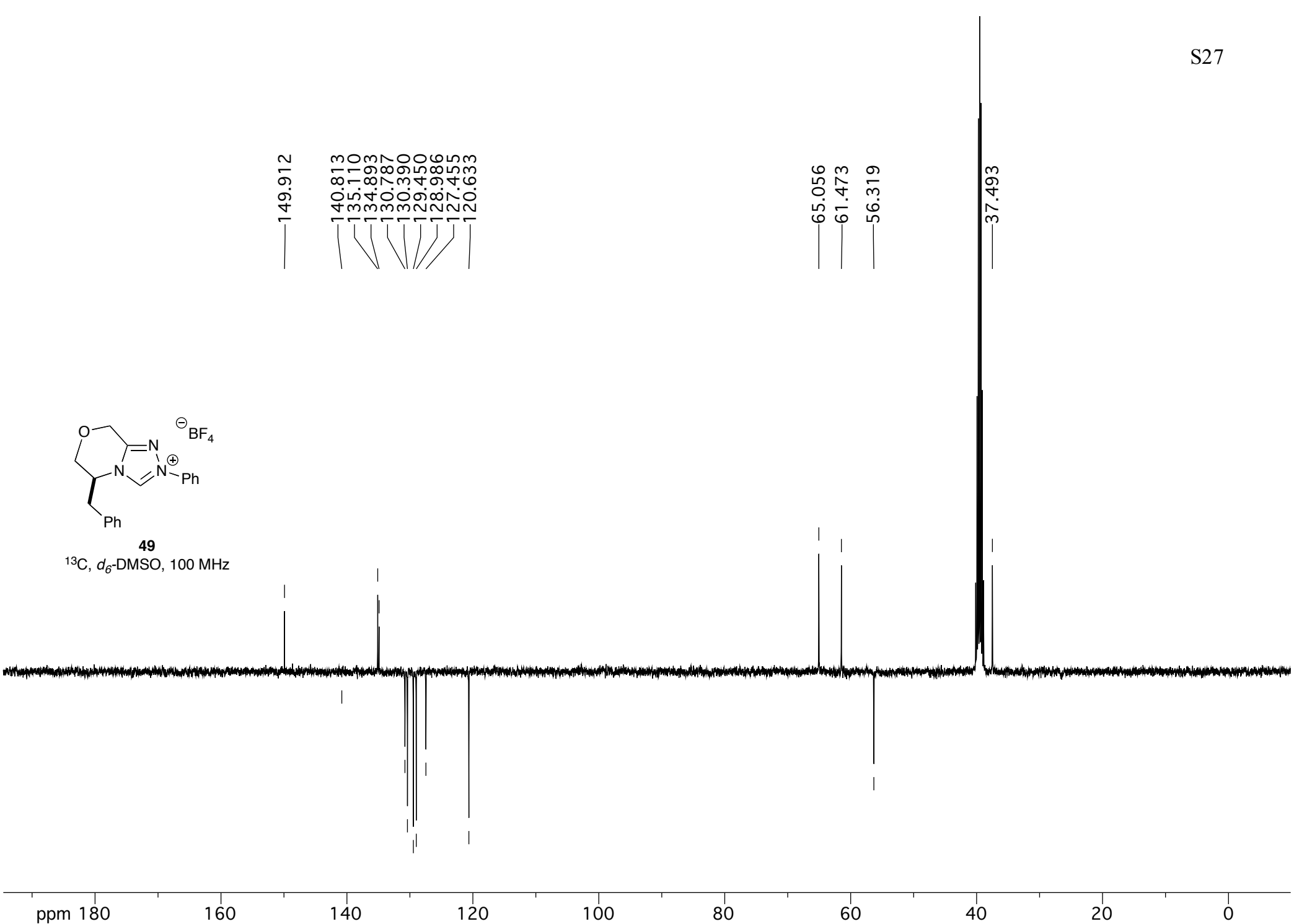
46

^{13}C, $CDCl_3$, 75 MHz



49

^{1}H, d_6-DMSO, 400 MHz



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^{13}C, d_6-DMSO, 100 MHz

III REFERENCES

[1] Thomson, J. E.; Campbell, C. D.; Concellón, C.; Duguet, N.; Rix, K.; Slawin, A. M. Z.; Smith, A. D. *J. Org. Chem.* **2008**, *73*, 2784–2791.
[2] Joannesse, C.; Simal, C.; Concellón, C.; Thomson, J. E.; Campbell, C. D.; Slawin, A. M. Z.; Smith, A. D. *Org. Biomol. Chem.* **2008**, *6*, 2900–2907.
[3] Shaw, S. A.; Aleman, P.; Vedejs, E. *J. Am. Chem. Soc.* **2003**, *125*, 13368–13369.
[4] Campbell, C. D.; Duguet, N.; Gallagher, K. A.; Thomson, J. E.; Lindsay, A. G.; O'Donoghue, A. C.; Smith, A. D. *Chem. Commun.* **2008**, 3528–3530.
[5] Duguet, N.; Campbell, C. D.; Slawin, A. M. Z.; Smith, A. D. *Org. Biomol. Chem.* **2008**, *6*, 1108–1113.
[6] Kerr, M. S.; de Alaniz, J. R.; Rovis, T. *J. Am. Chem. Soc.* **2002**, *124*, 10298–10299.