Support Information

LEWIS ACID CATALYZED DIASTEREOSELECTIVE 1,3-DIPOLAR CYCLOADDITION BETWEEN DIAZOACETOACETATE ENONES AND AZOMETHINE YLIDES

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Department of Chemistry & Biochemistry, University of Maryland, College Park MD, 20742, U. S. A.

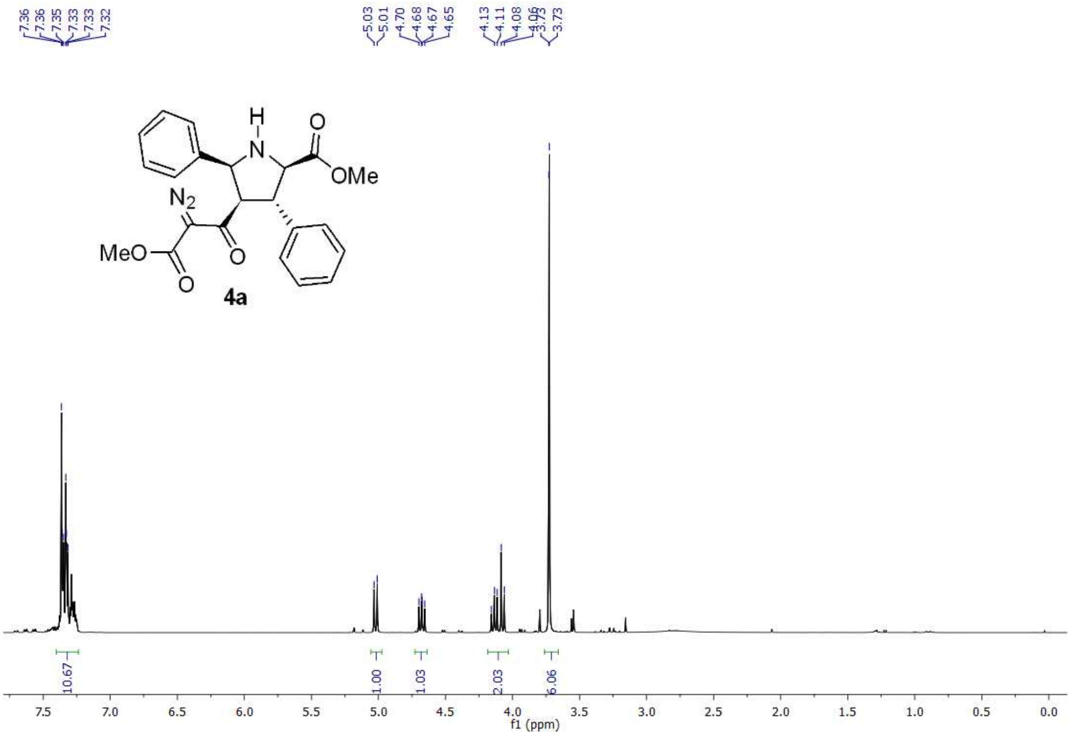
Crystal Structure for the tosylamide of 4a: A clear colourless plate-like specimen of $C_{29}H_{27}N_3O_7S$, approximate dimensions 0.10 mm × 0.41 mm × 0.55 mm was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoKα sealed tube ($\lambda = 0.71073$ Å). Data collection temperature was 200 K.

The total exposure time was 20.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 59484 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 10877 were independent (average redundancy 5.469, completeness = 100.0%, $R_{int} = 4.35\%$) and 8278 (76.11%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 20.889(3)$ Å, $b = 12.7021(18)$ Å, $c = 22.956(3)$ Å, $\beta = 114.809(2)°$, $V = 5528.9(14)$ Å^3, are based upon the refinement of the XYZ-centroids of 9988 reflections above 20 σ(I) with $4.716° < 2\theta < 52.73°$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8820 and 0.9830.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 8 for the formula unit, $C_{29}H_{27}N_3O_7S$. The final anisotropic full-matrix least-squares refinement on F^2 with 978 variables converged at $R_1 = 5.56\%$, for the observed data and $wR_2 = 13.83\%$ for all data. The goodness-of-fit was 1.006. The largest peak in the final difference electron density synthesis was 0.619 $e^-/Å^3$ and the largest hole was -0.414 $e^-/Å^3$ with an RMS deviation of 0.054 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.349 g/cm^3 and F(000), 2352 e^-.

This structure shows whole molecule disorder where each of 2 symmetrically independent molecules (A and B) have "shadow" shifted along b axis for 0.55. Apparently molecules form distinctive layers in ac plane which could be easily shifted along b axis. Thus what is observed as shadow structure is actually stacking fault. The portion of "shadow" molecules is only 7.21(6)%, yet it is significant enough to drop R-factor from 9.0% to 5.5% when accounting for. During refinement, geometry of shadow molecules was restrained to be close to that of normal molecules and adps to be equal.

The $COOCH_3$ group attached to the central ring is disordered in two alternative orientations in about 2:1 ratio so only C37B or C39B is present. H atoms where positioned from geometric consideration and refined as riding on the attached atom with Uiso constrained to 20% larger than Ueqv for attached atom (30% for CH_3 group).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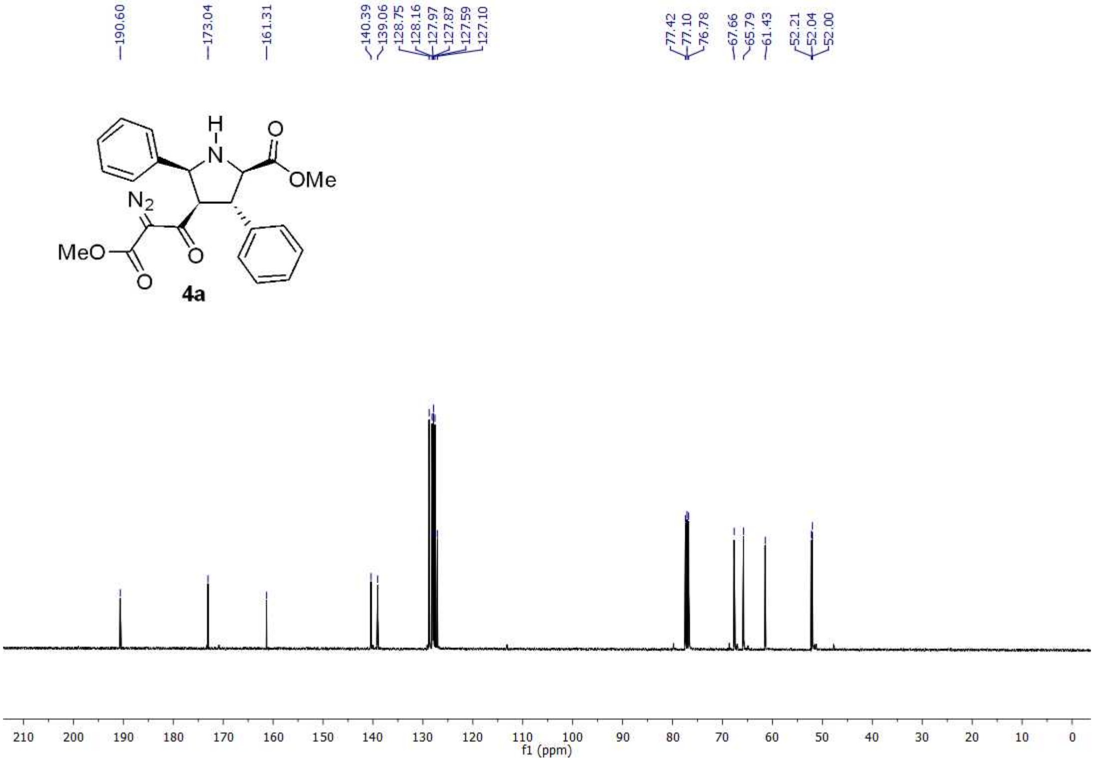
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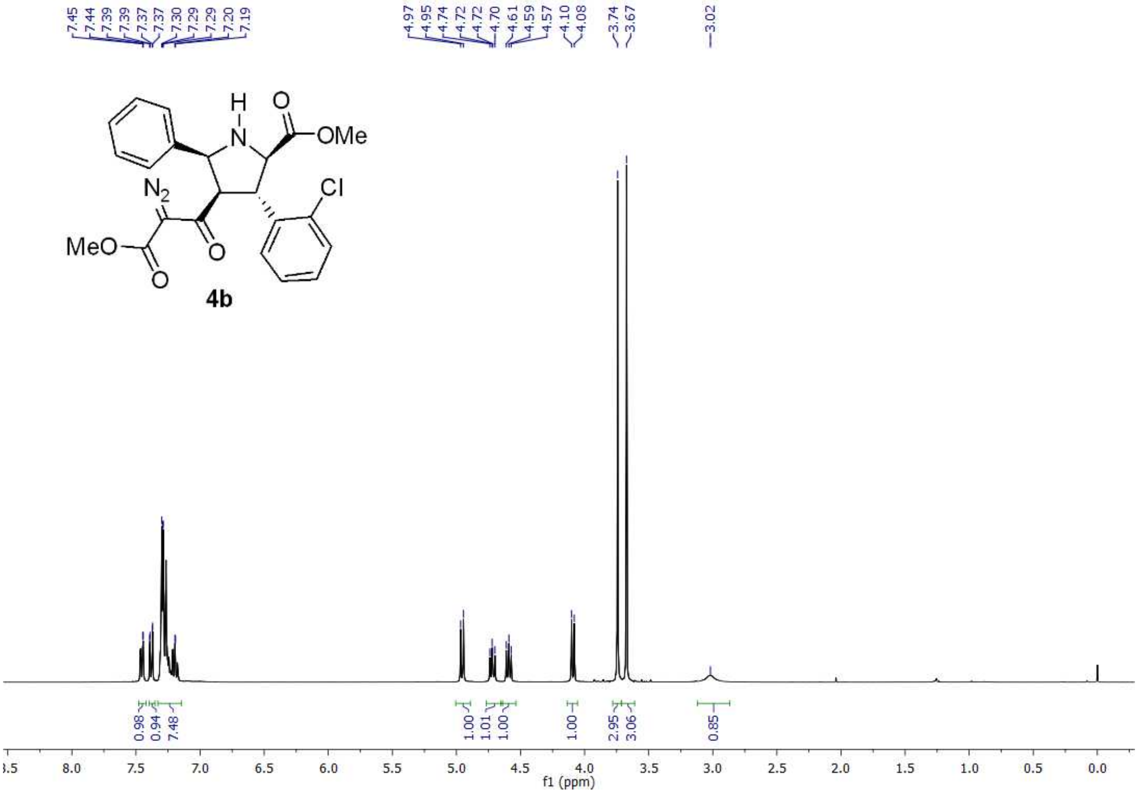
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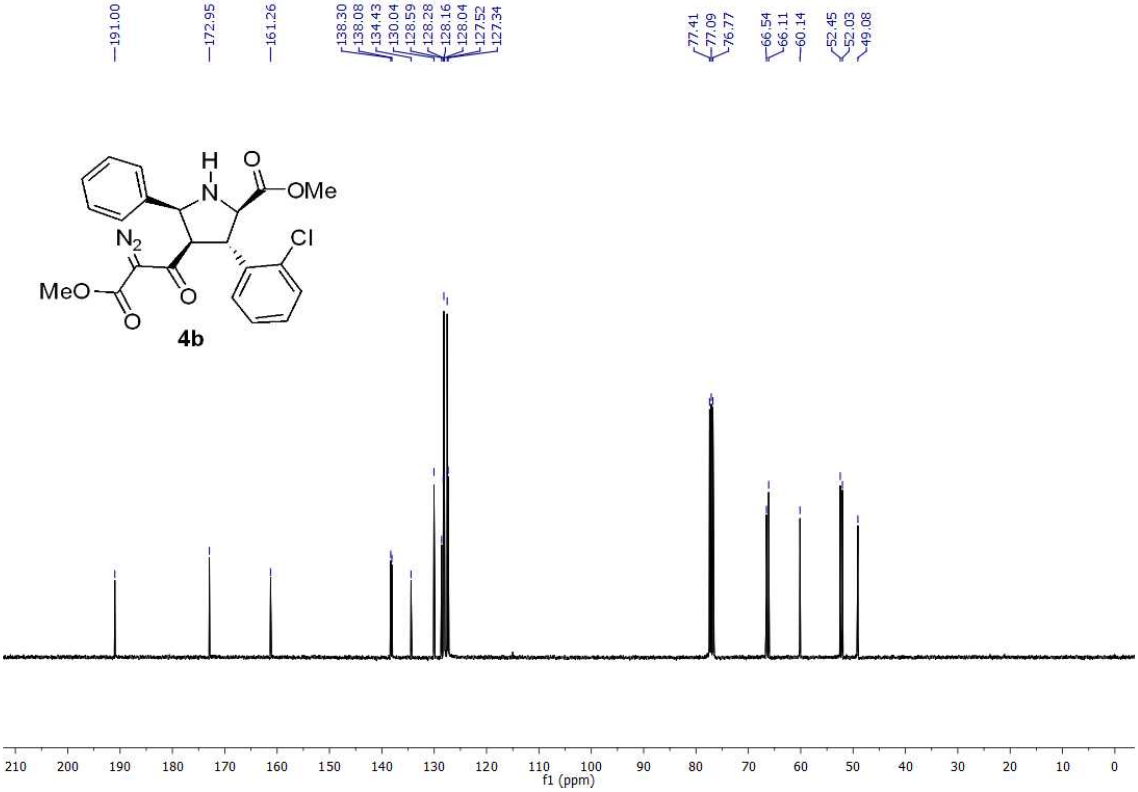
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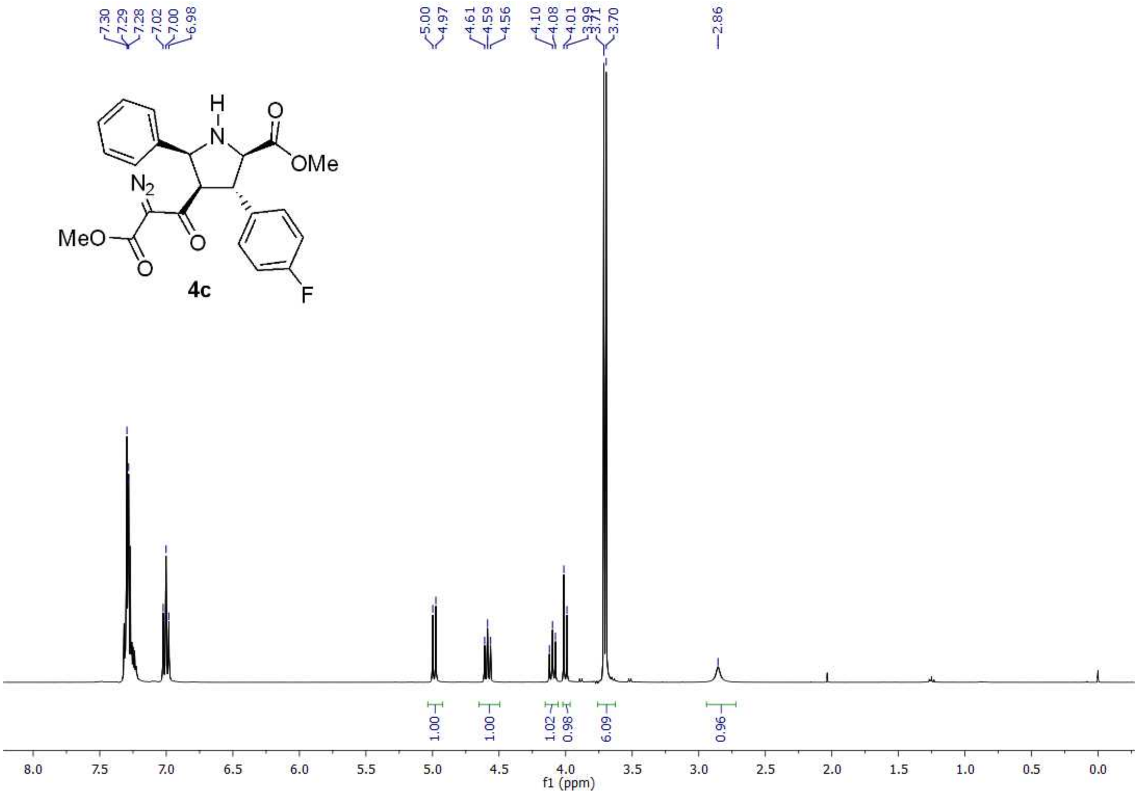
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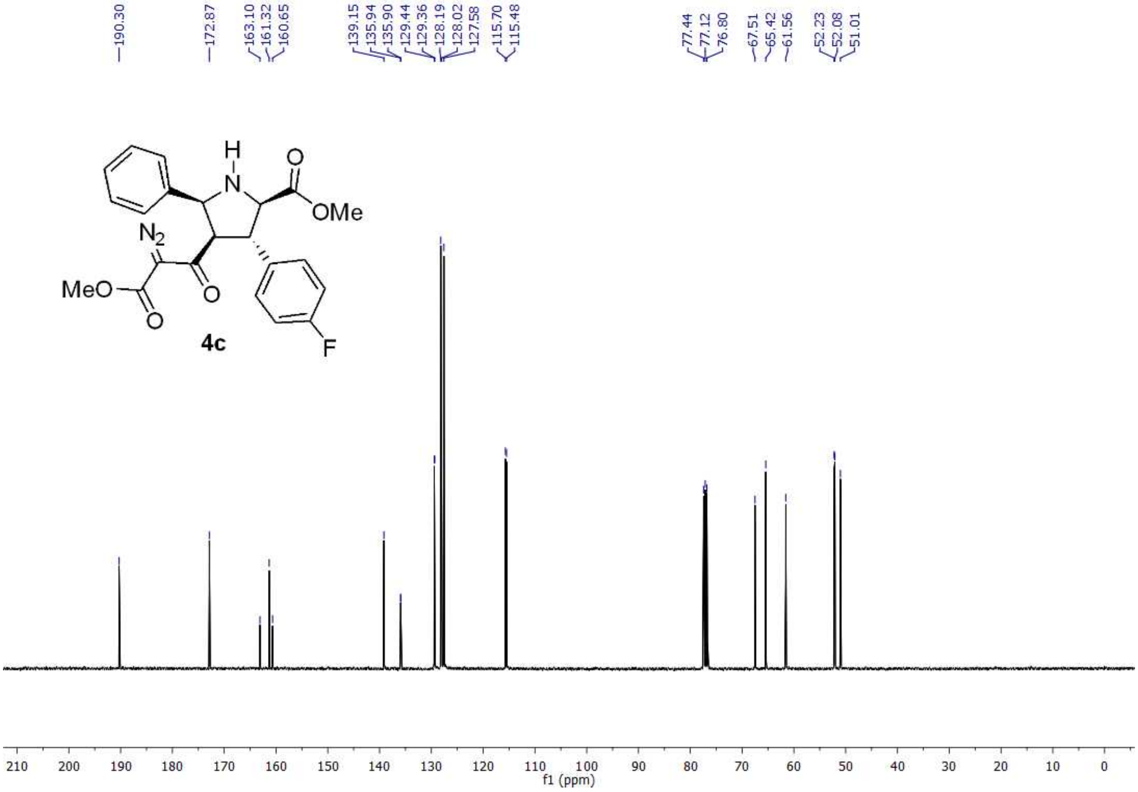
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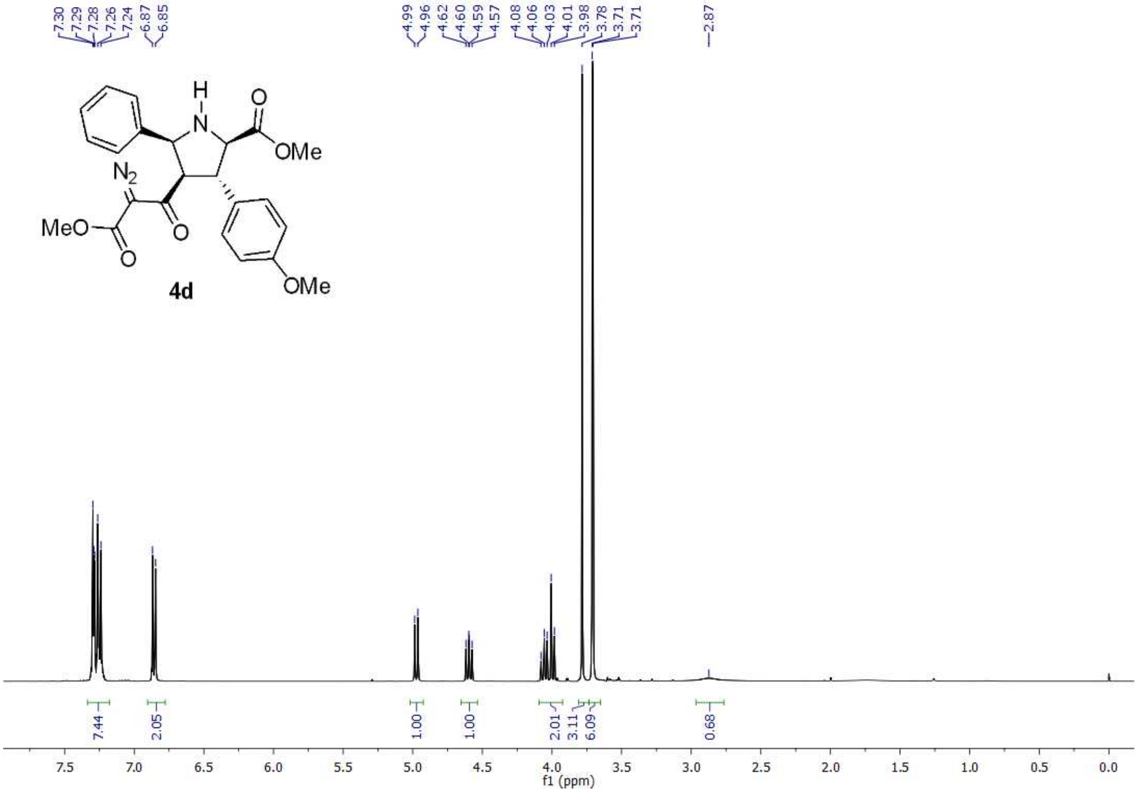
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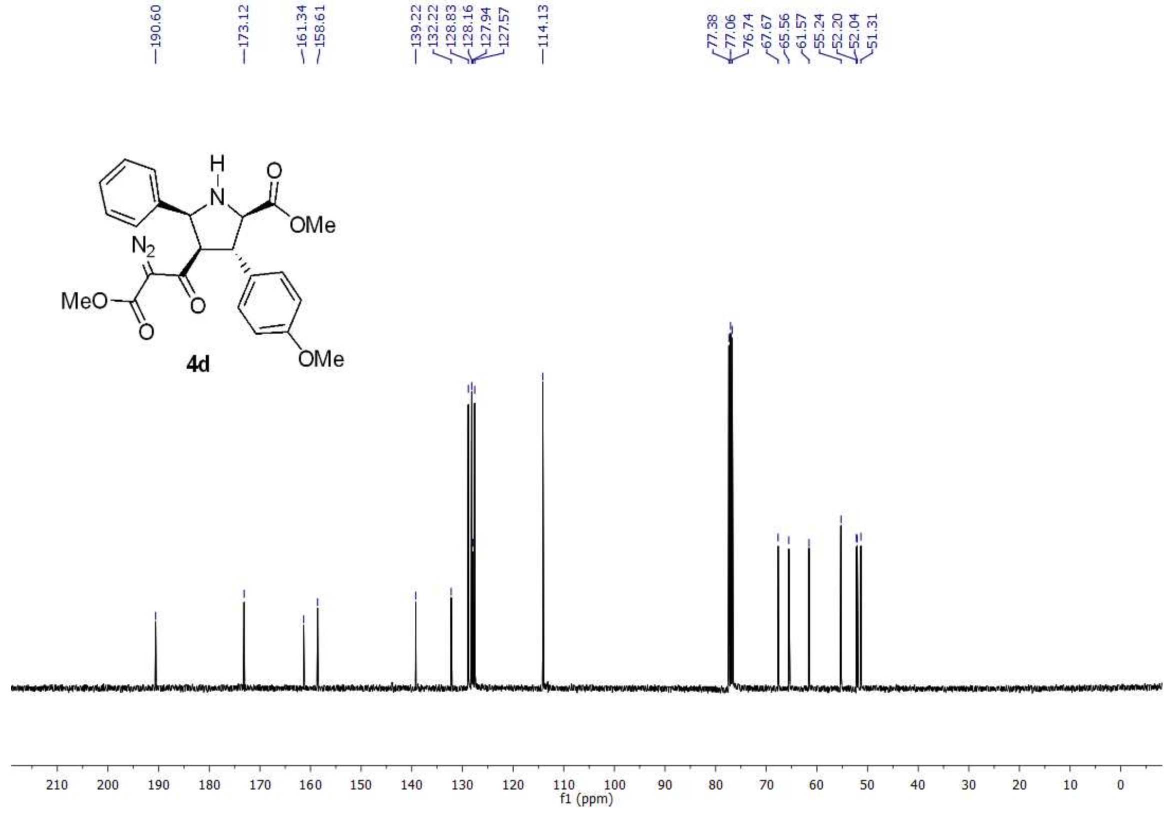
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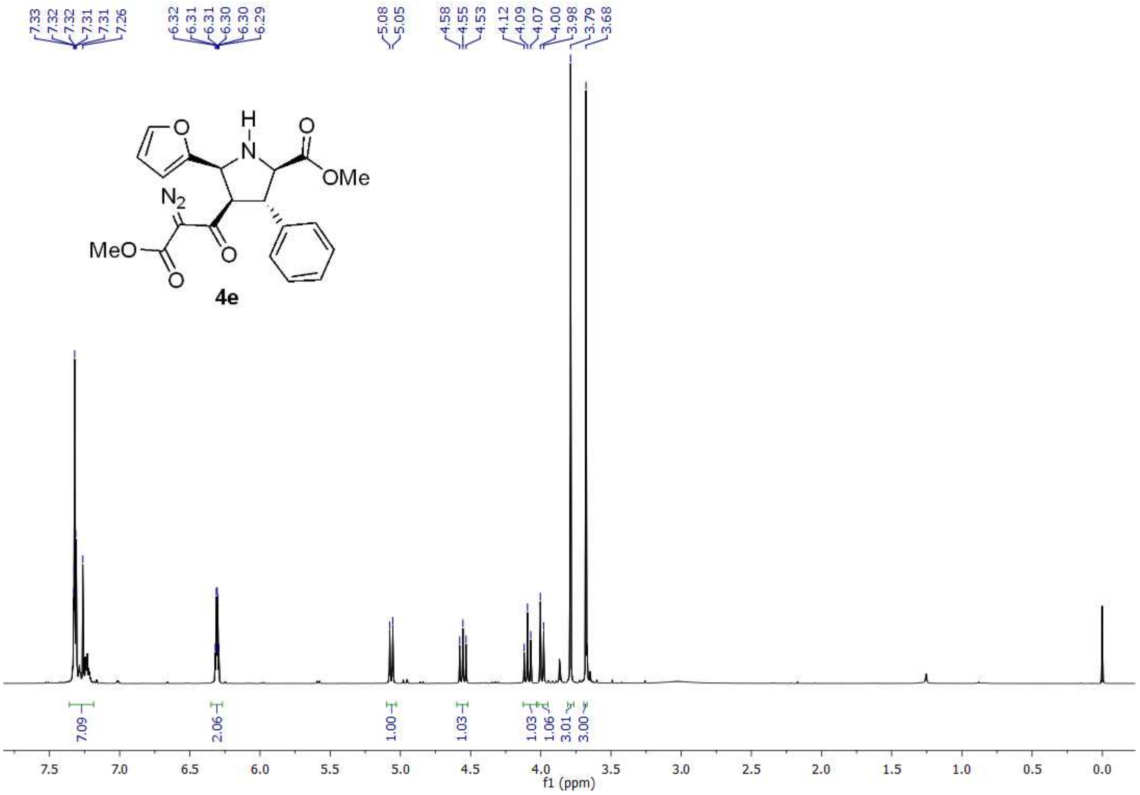
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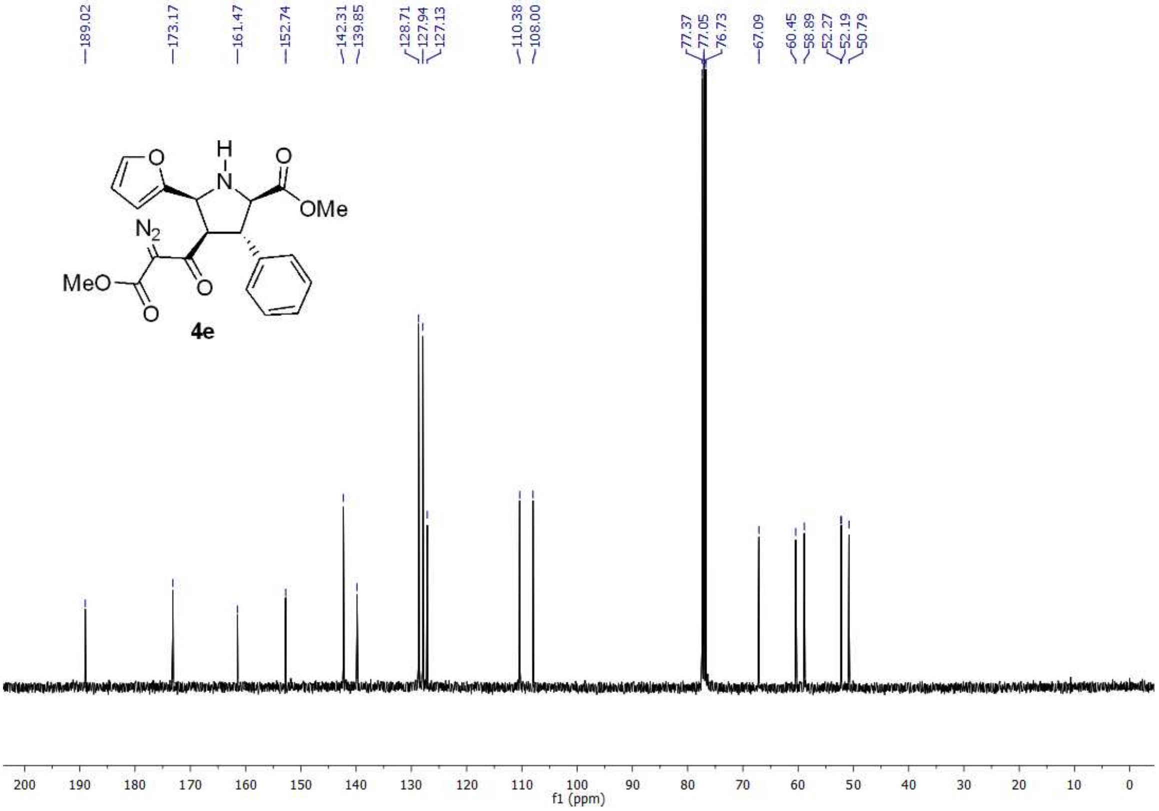
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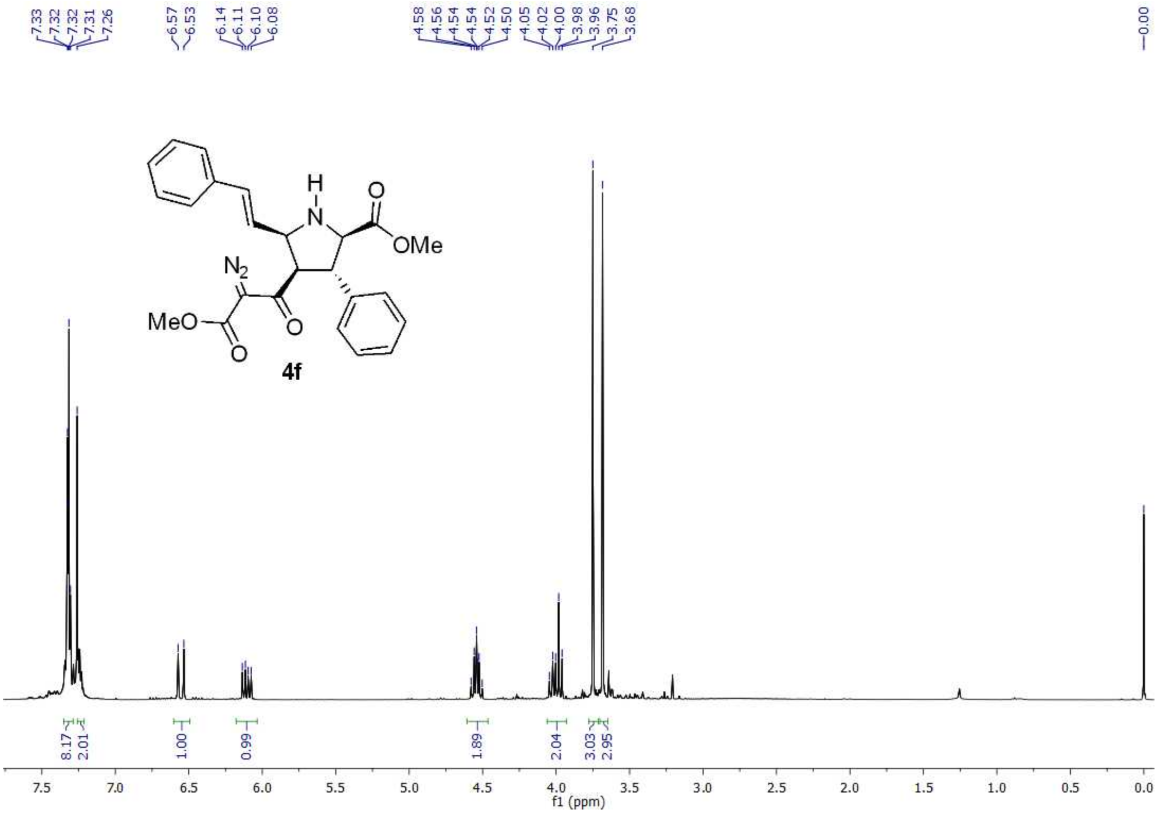
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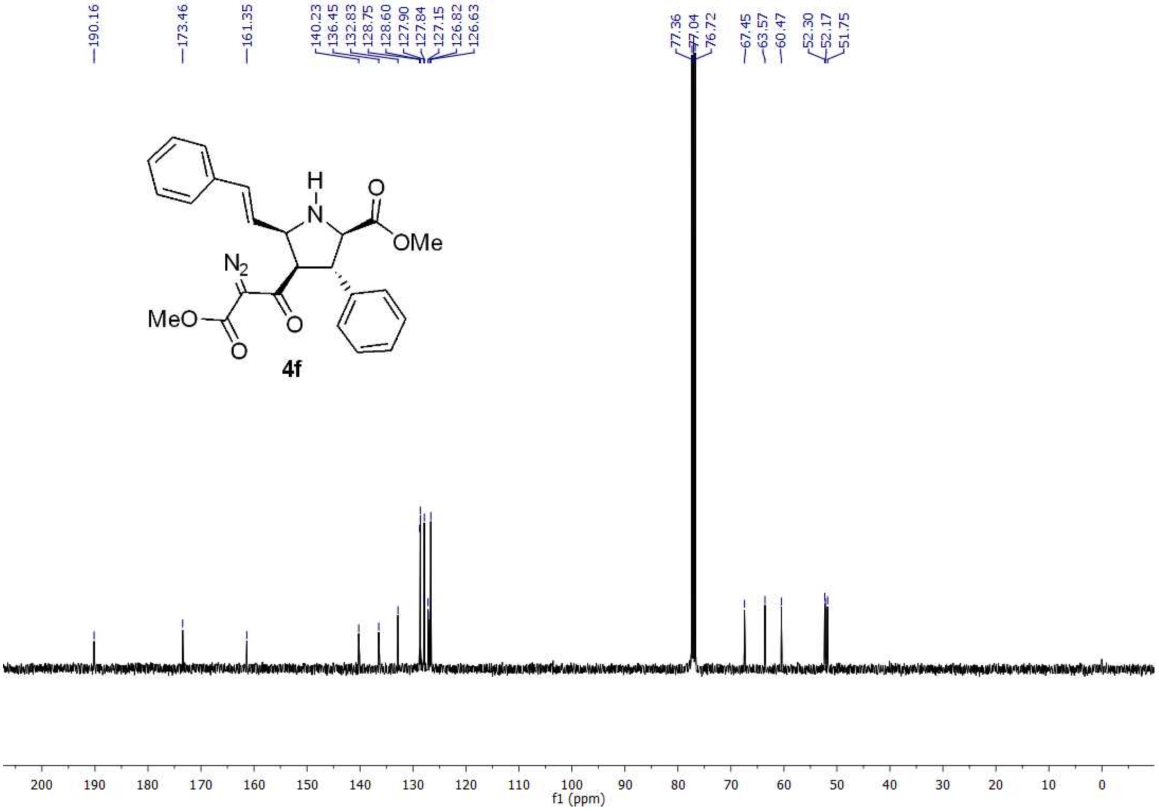
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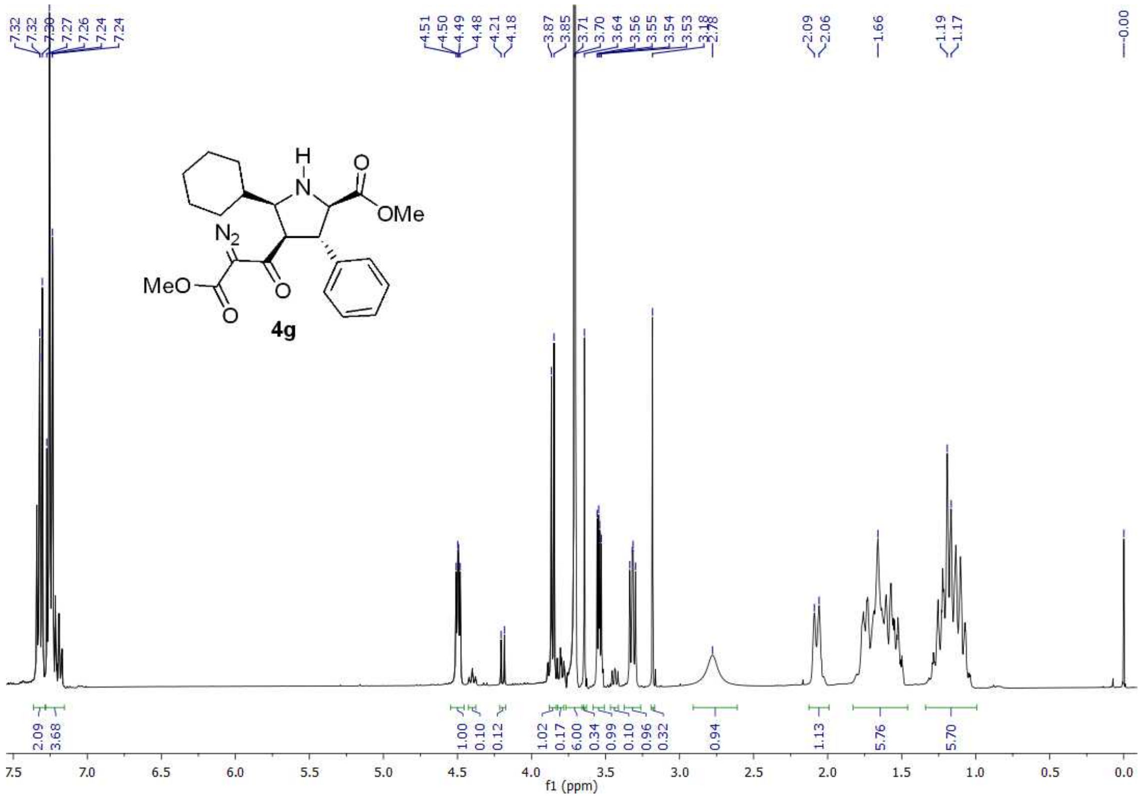
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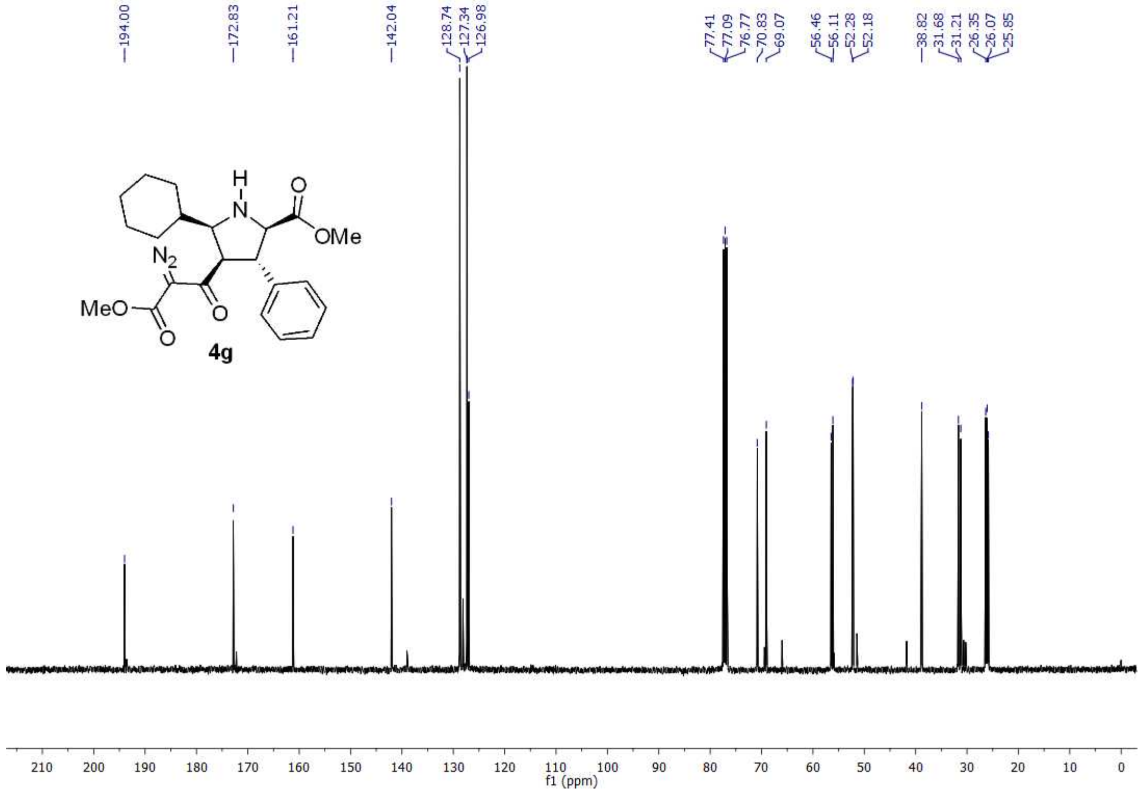
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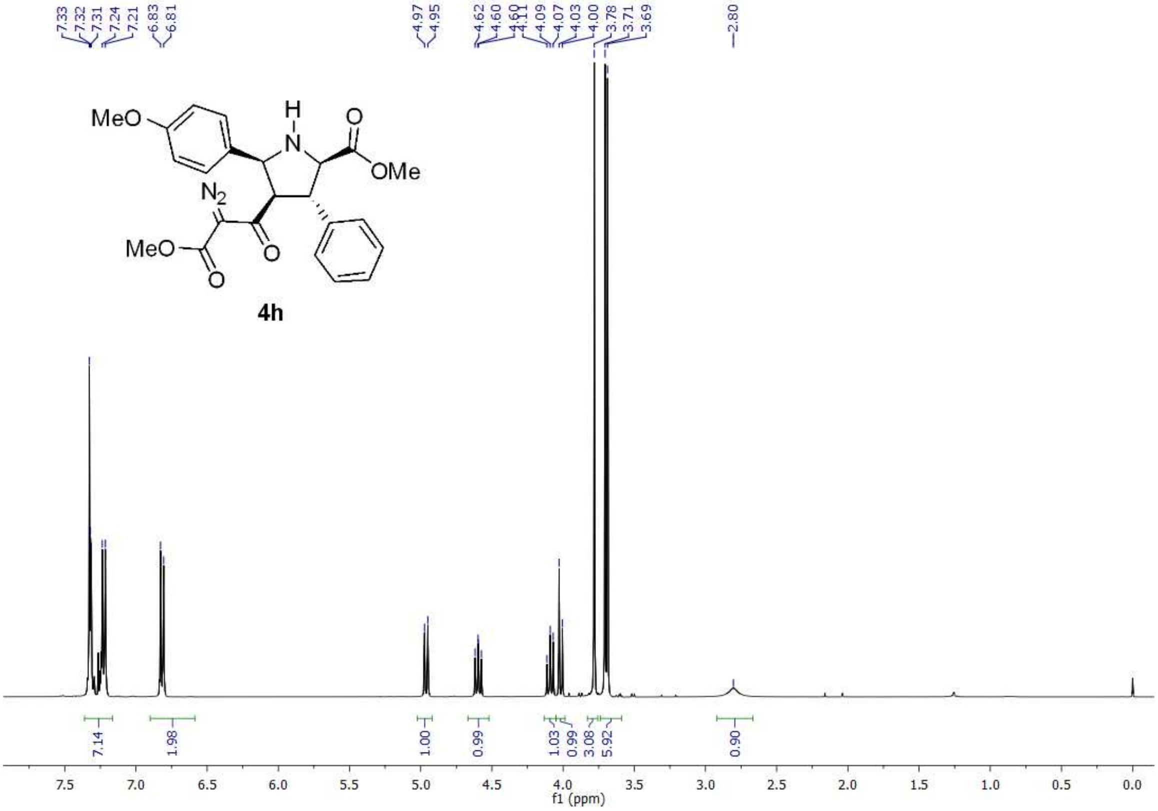
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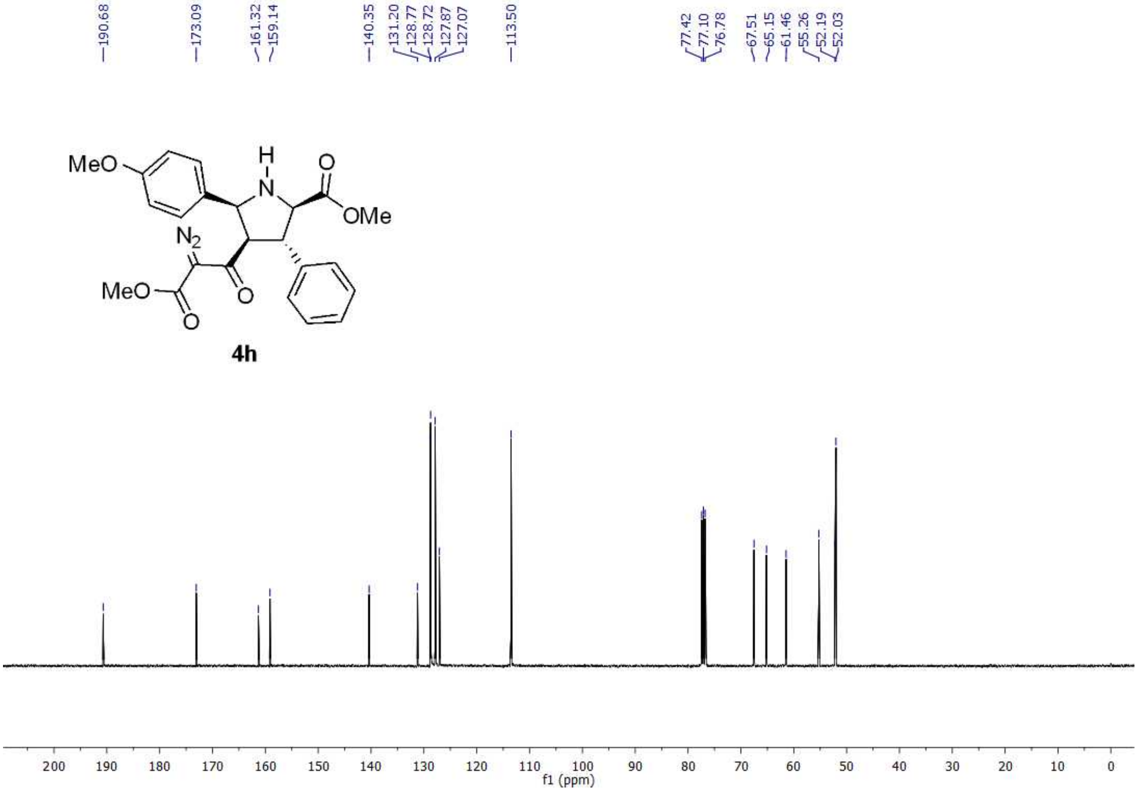
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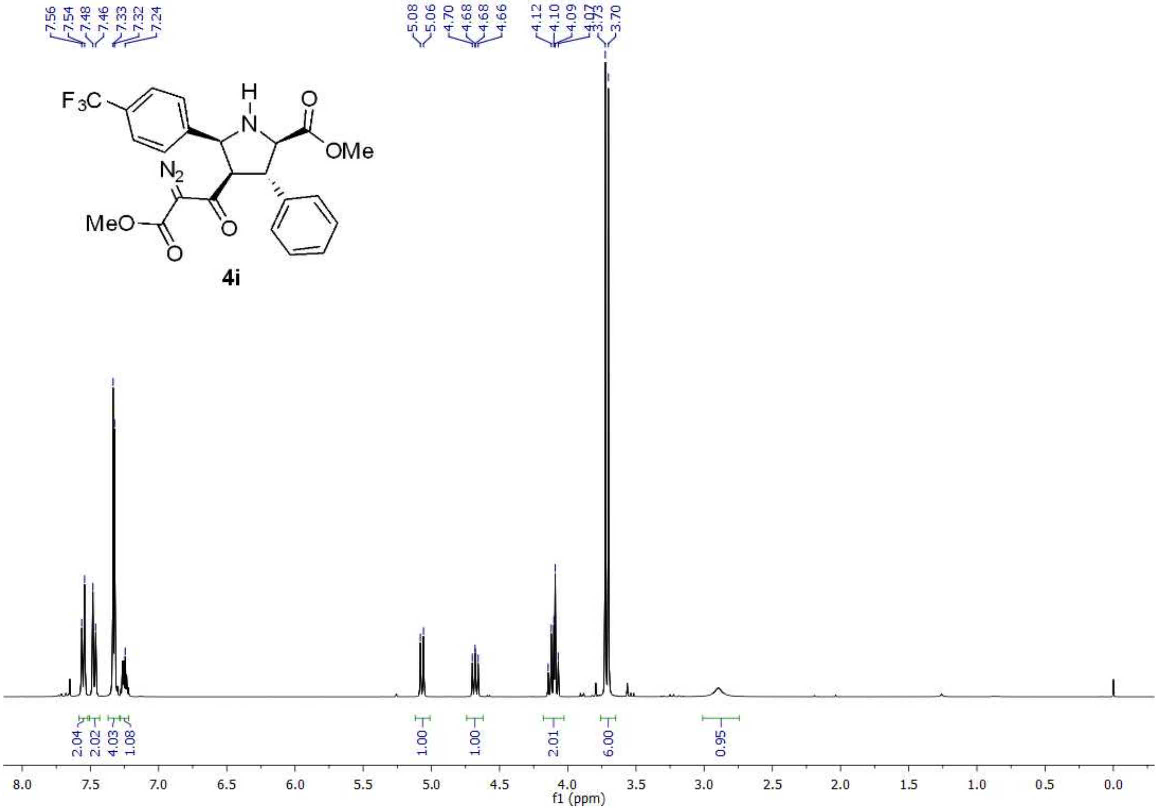
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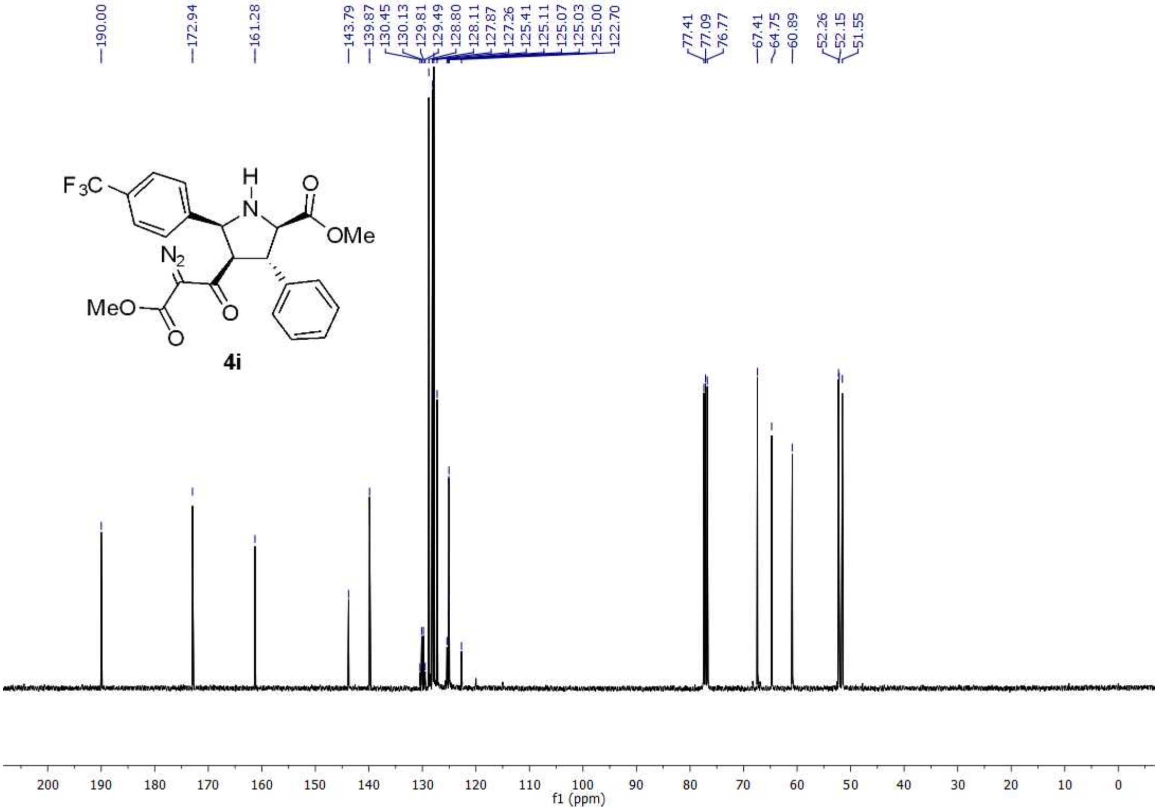
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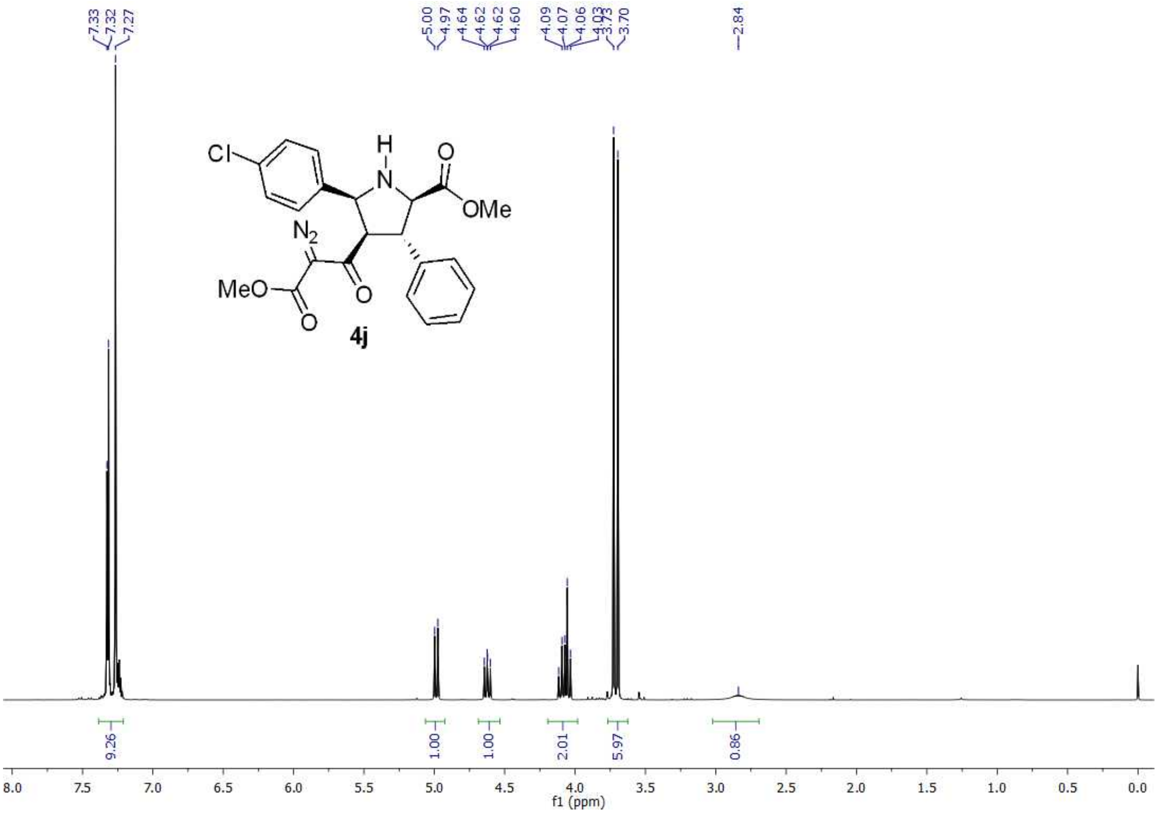
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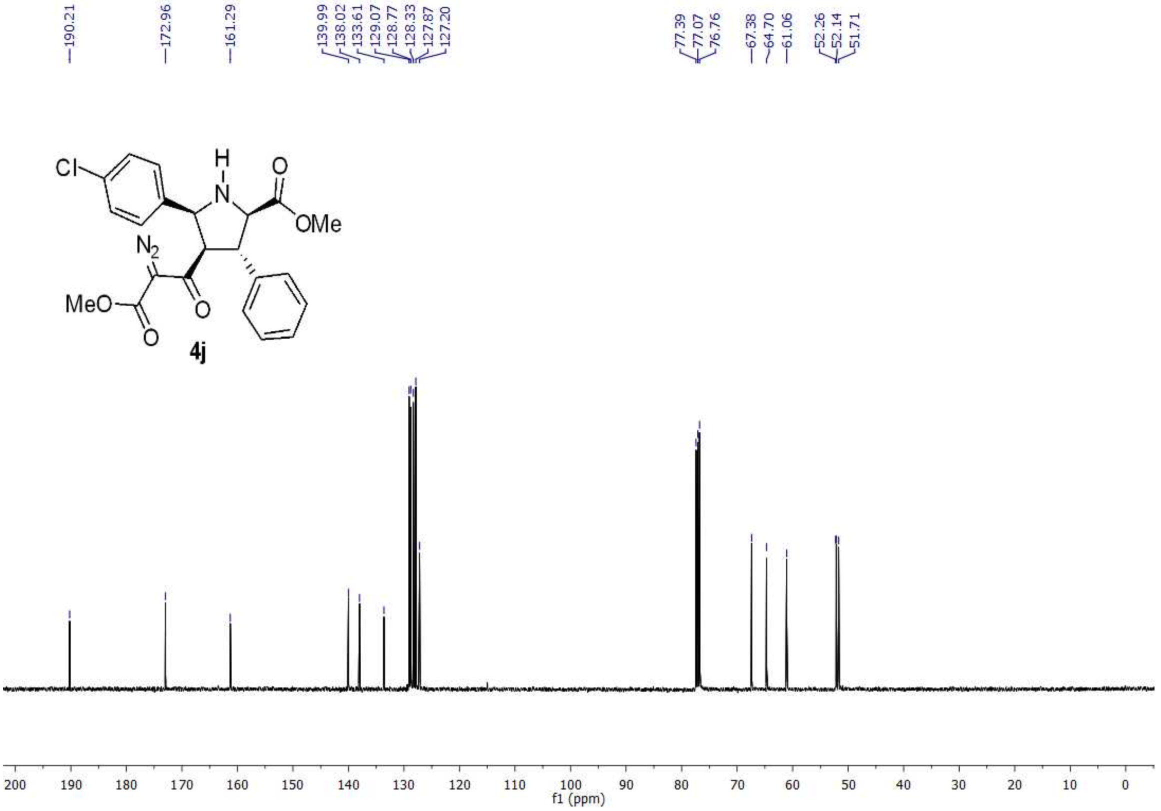
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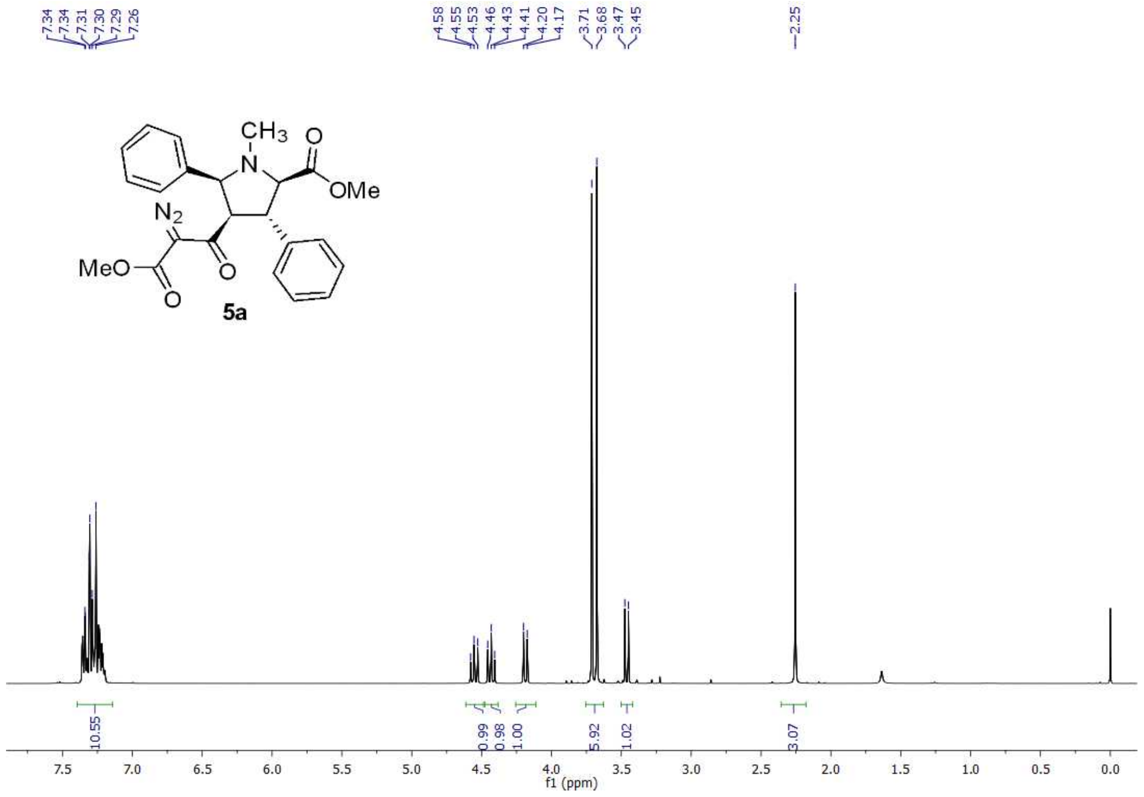
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6.5
6.0
5.5
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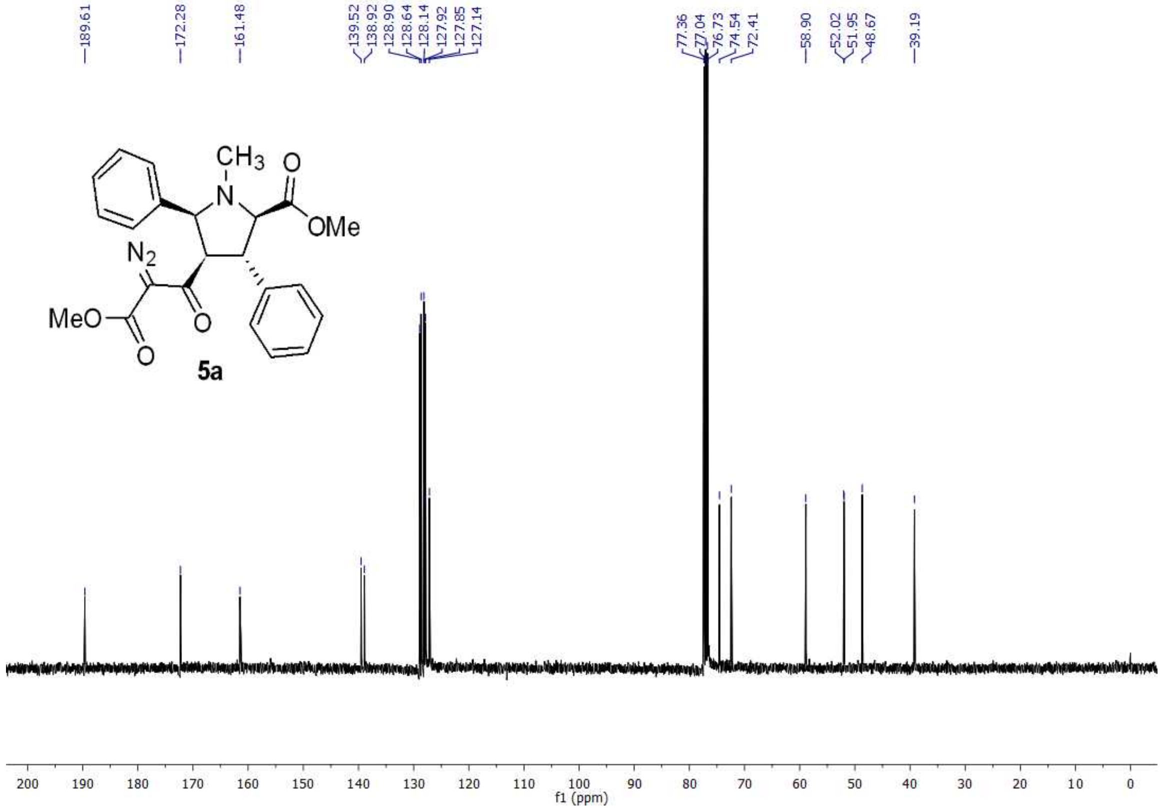
f1 (ppm)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128.14
127.92
127.85
127.14
77.36
77.04
76.73
74.54
72.41
58.90
52.02
51.95
48.67
39.19
CH3
N
O
OMe
N2
MeO
O
O
5a
200
190
180
170
160
150
140
130
120
110
100
90
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50
40
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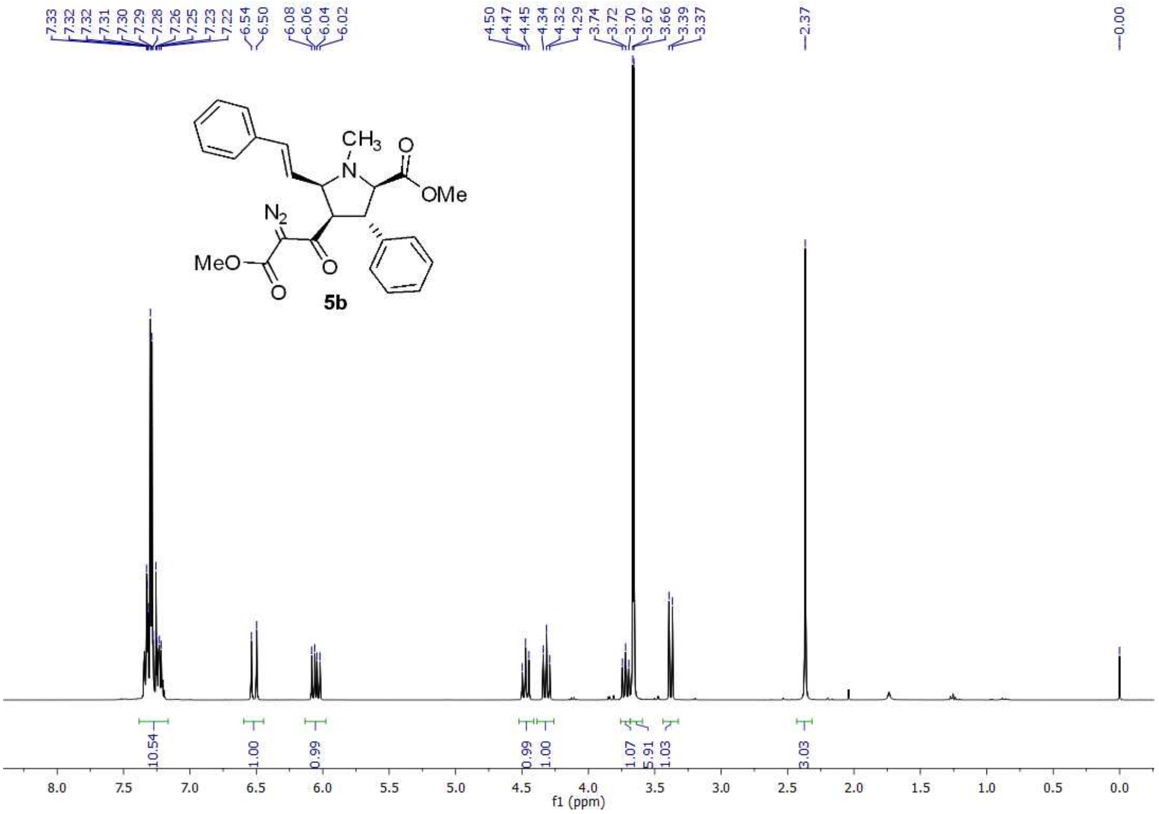
f1 (ppm)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6.54
6.50
6.08
6.06
6.04
6.02
4.50
4.47
4.45
4.34
4.32
4.29
3.74
3.72
3.70
3.67
3.66
3.39
3.37
2.37
0.00
CH3
N
O
OMe
N2
O
MeO
O
5b
10.54
1.00
0.99
0.99
1.00
1.07
5.91
1.03
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
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2.5
2.0
1.5
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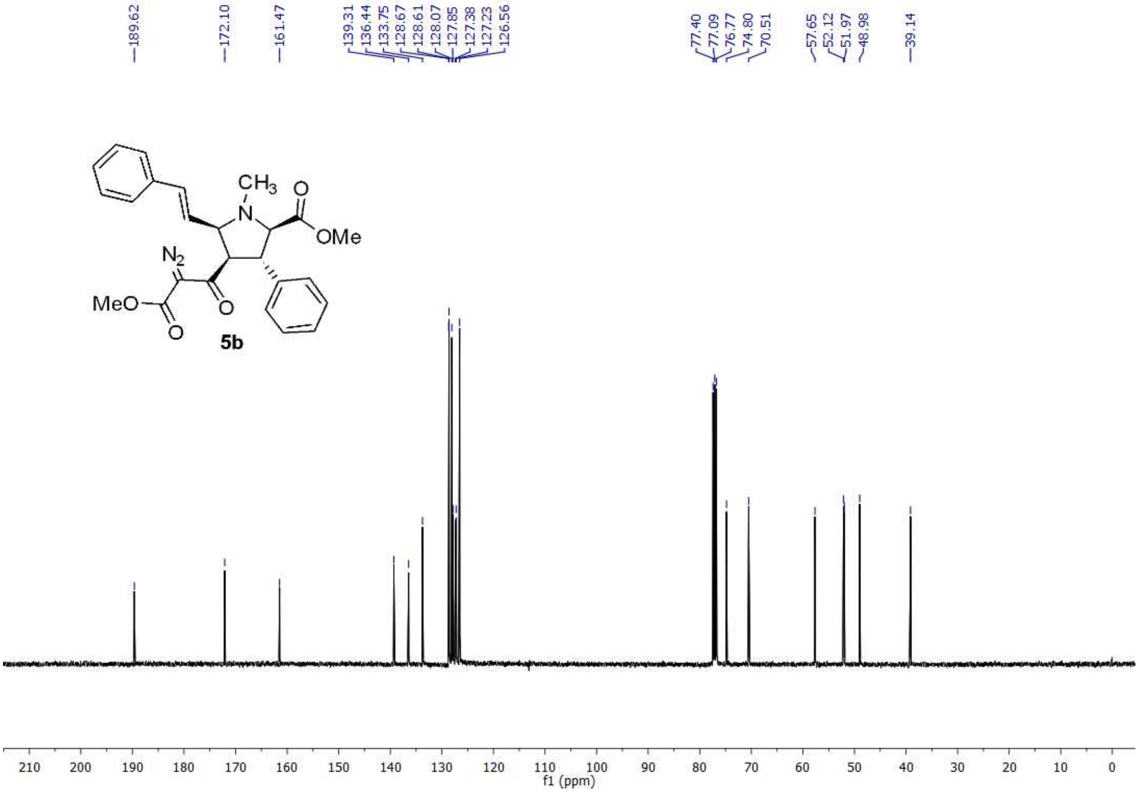
0.0
f1 (ppm)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127.38
127.23
126.56
77.40
77.09
76.77
74.80
70.51
57.65
52.12
51.97
48.98
39.14
CH3
N
O
OMe
N2
O
MeO
O
5b
210
200
190
180
170
160
150
140
130
120
110
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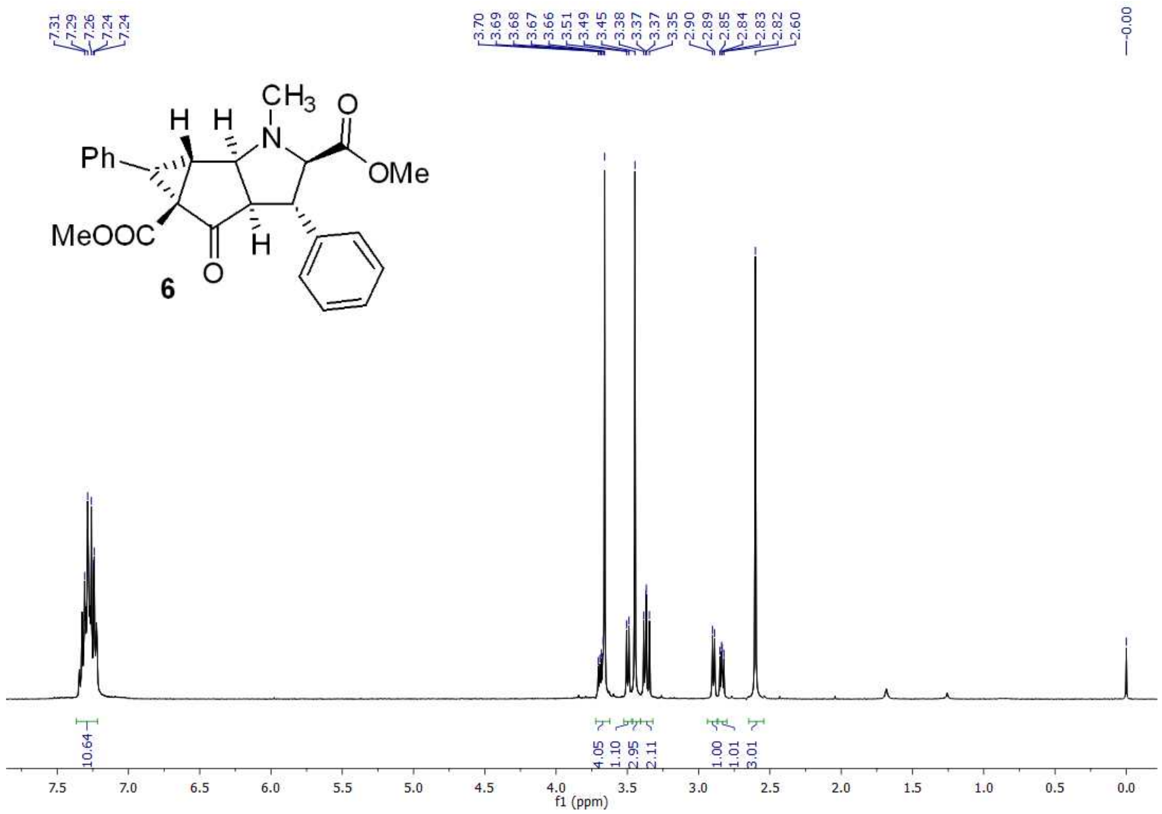
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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3.68
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3.66
3.51
3.49
3.45
3.38
3.37
3.37
3.35
2.90
2.89
2.85
2.84
2.83
2.82
2.60
0.00
H
H
CH3
N
O
Ph
OMe
MeOOC
H
O
6
10.64
4.05
1.10
2.95
2.11
1.00
1.01
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
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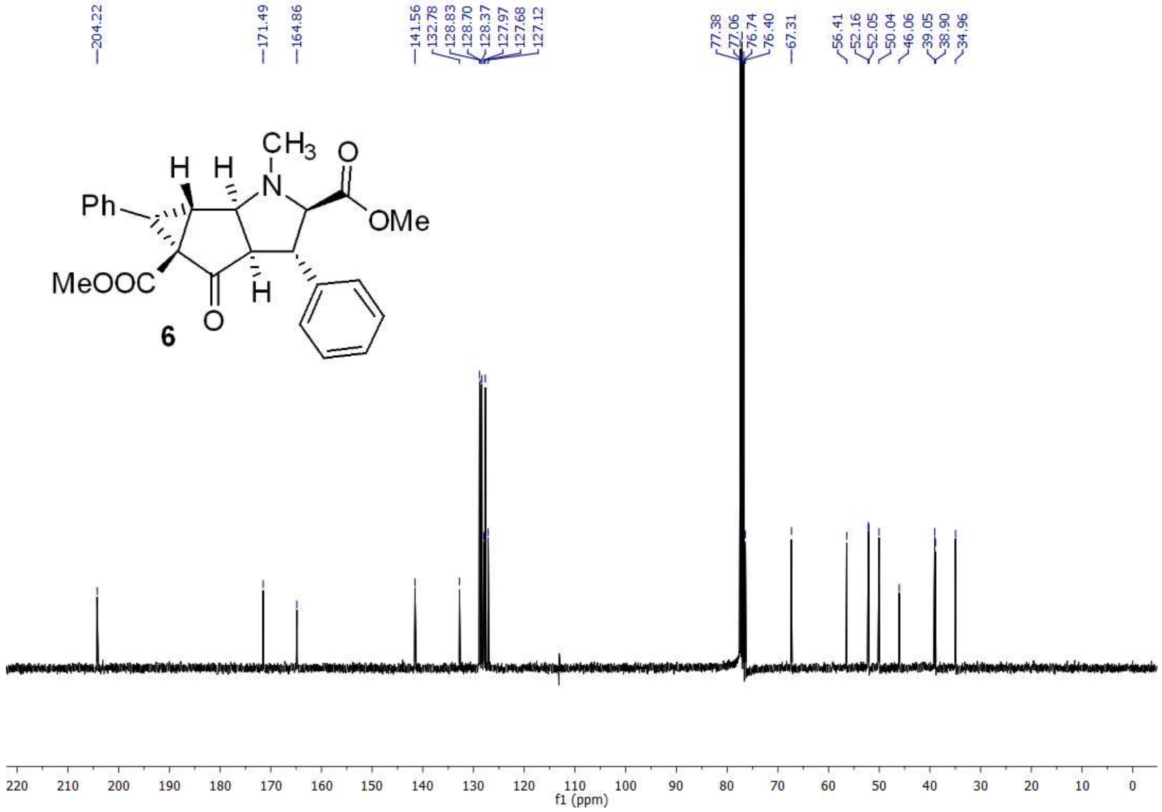
0.0
f1 (ppm)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127.68
127.12
77.38
77.06
76.74
76.40
67.31
56.41
52.16
52.05
50.04
46.06
39.05
38.90
34.96
H
H
CH3
N
O
Ph
OMe
MeOOC
H
O
6
220
210
200
190
180
170
160
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140
130
120
110
100
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50
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10
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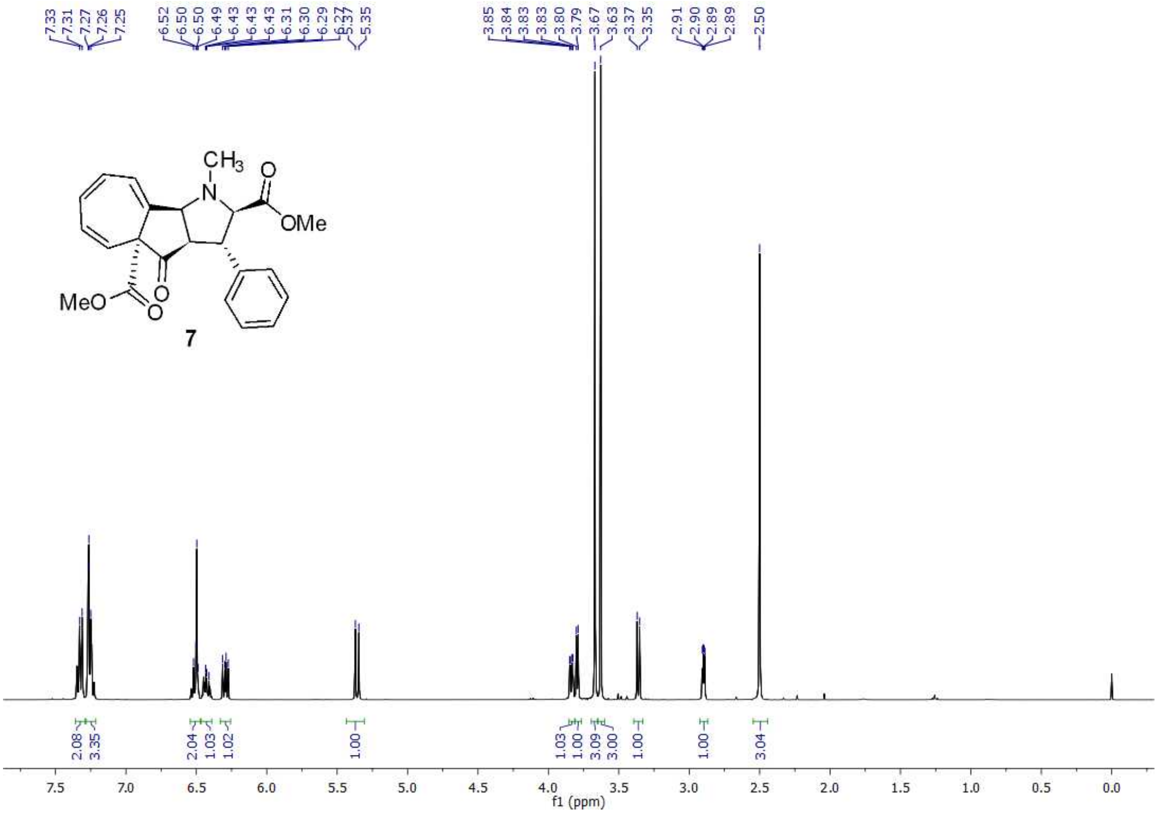
f1 (ppm)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6.31
6.30
6.29
6.27
5.37
5.35
3.85
3.84
3.83
3.83
3.80
3.79
3.67
3.63
3.37
3.35
2.91
2.90
2.89
2.89
2.50
CH3
N
O
OMe
MeO
O
O
7
2.08
3.35
2.04
1.03
1.02
1.00
1.03
1.00
3.09
3.00
1.00
1.00
3.04
7.5
7.0
6.5
6.0
5.5
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4.5
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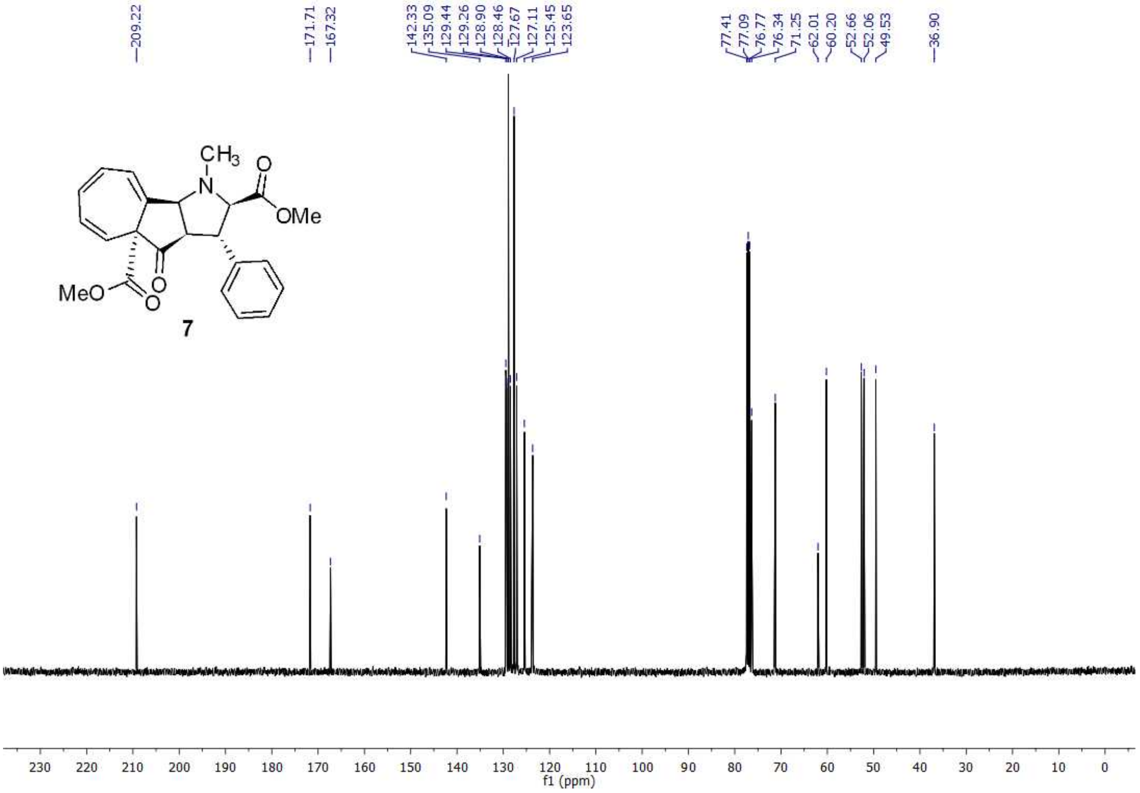
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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167.32
142.33
135.09
129.44
129.26
128.90
128.46
127.67
127.11
125.45
123.65
77.41
77.09
76.77
76.34
71.25
62.01
60.20
52.66
52.06
49.53
36.90
CH3
N
O
OMe
MeO
O
O
7
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
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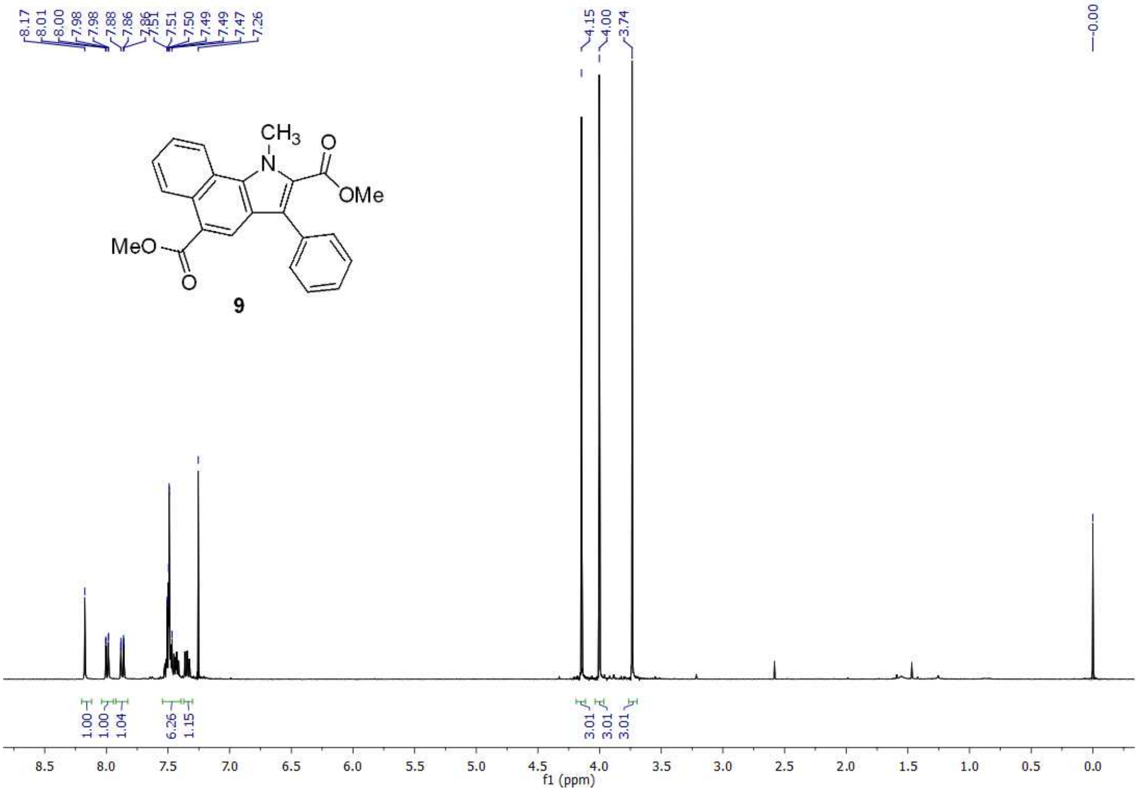
70
60
50
40
30
20
10
0
f1 (ppm)


9

8.17
8.01
8.00
7.98
7.98
7.88
7.86
7.86
7.51
7.51
7.50
7.49
7.49
7.47
7.26
4.15
4.00
3.74
0.00
CH3
N
O
OMe
MeO
O
1.00
1.00
1.04
6.26
1.15
3.01
3.01
3.01
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
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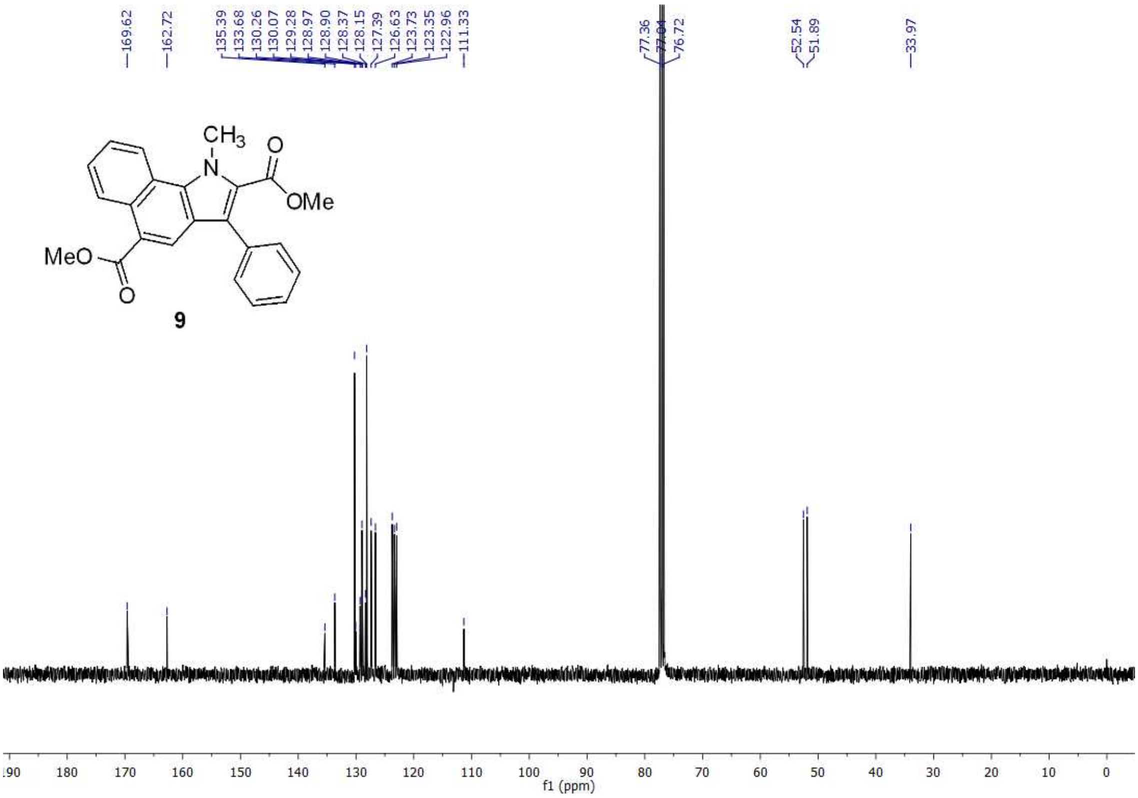
0.0
f1 (ppm)


9

169.62
162.72
135.39
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130.26
130.07
129.28
128.97
128.90
128.37
128.15
127.39
126.63
123.73
123.35
122.96
111.33
77.36
77.04
76.72
52.54
51.89
33.97
CH3
N
O
OMe
MeO
O
190
180
170
160
150
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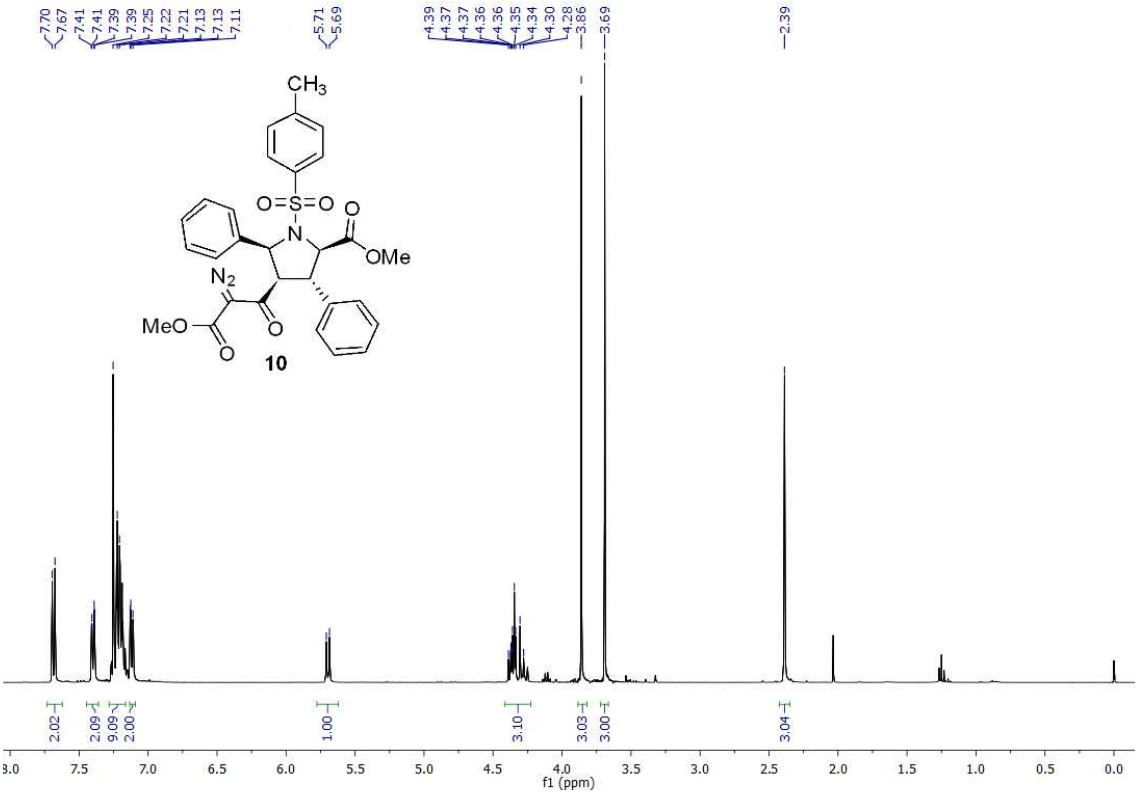
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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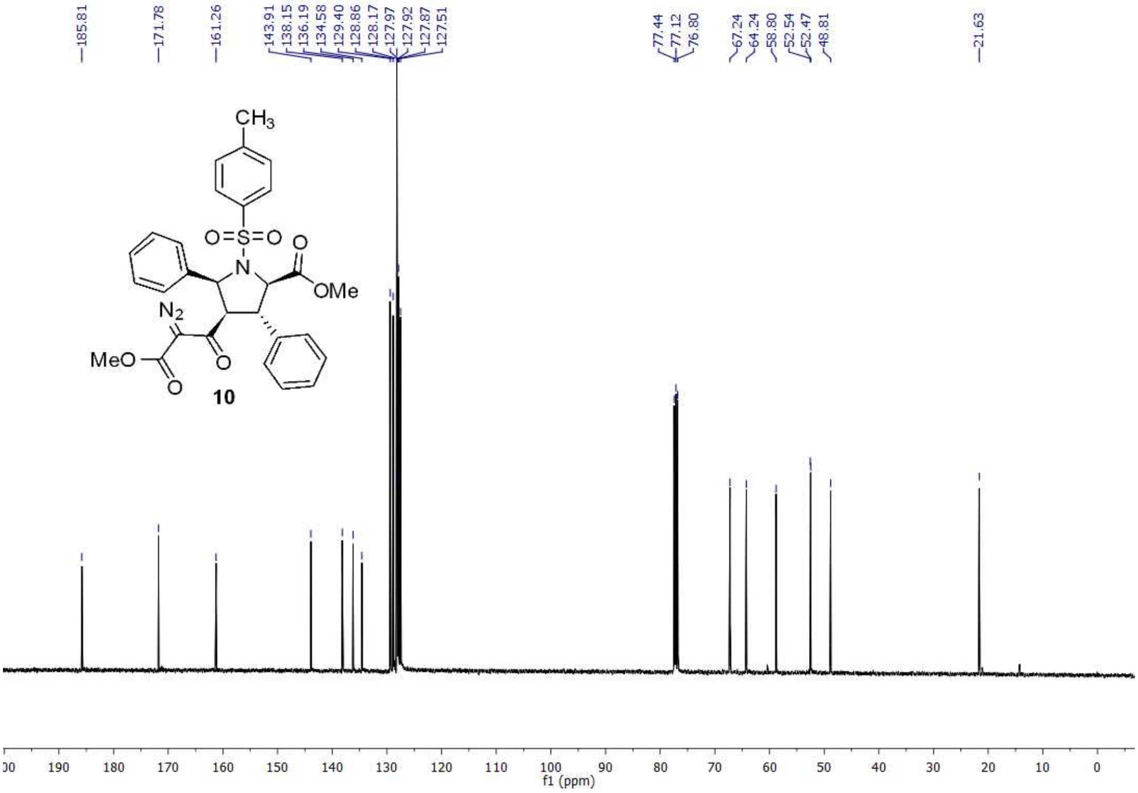
7.39
7.25
7.22
7.21
7.13
7.13
7.11
5.71
5.69
4.39
4.37
4.37
4.36
4.36
4.35
4.34
4.30
4.28
3.86
3.69
2.39
CH3
O=S=O
N
O
OMe
N2
MeO
O
O
10
2.02
2.09
9.09
2.00
1.00
3.10
3.03
3.00
3.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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143.91
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128.86
128.17
127.97
127.92
127.87
127.51
77.44
77.12
76.80
67.24
64.24
58.80
52.54
52.47
48.81
21.63
CH3
O=S=O
N
O
OMe
N2
MeO
O
O
10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)