One-Pot Diastereoselective Synthesis of Polysubstituted Δ^1-Dyrroline Derivatives from in situ Generated Nitrile Ylides

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Supporting Information

1. General Methods:

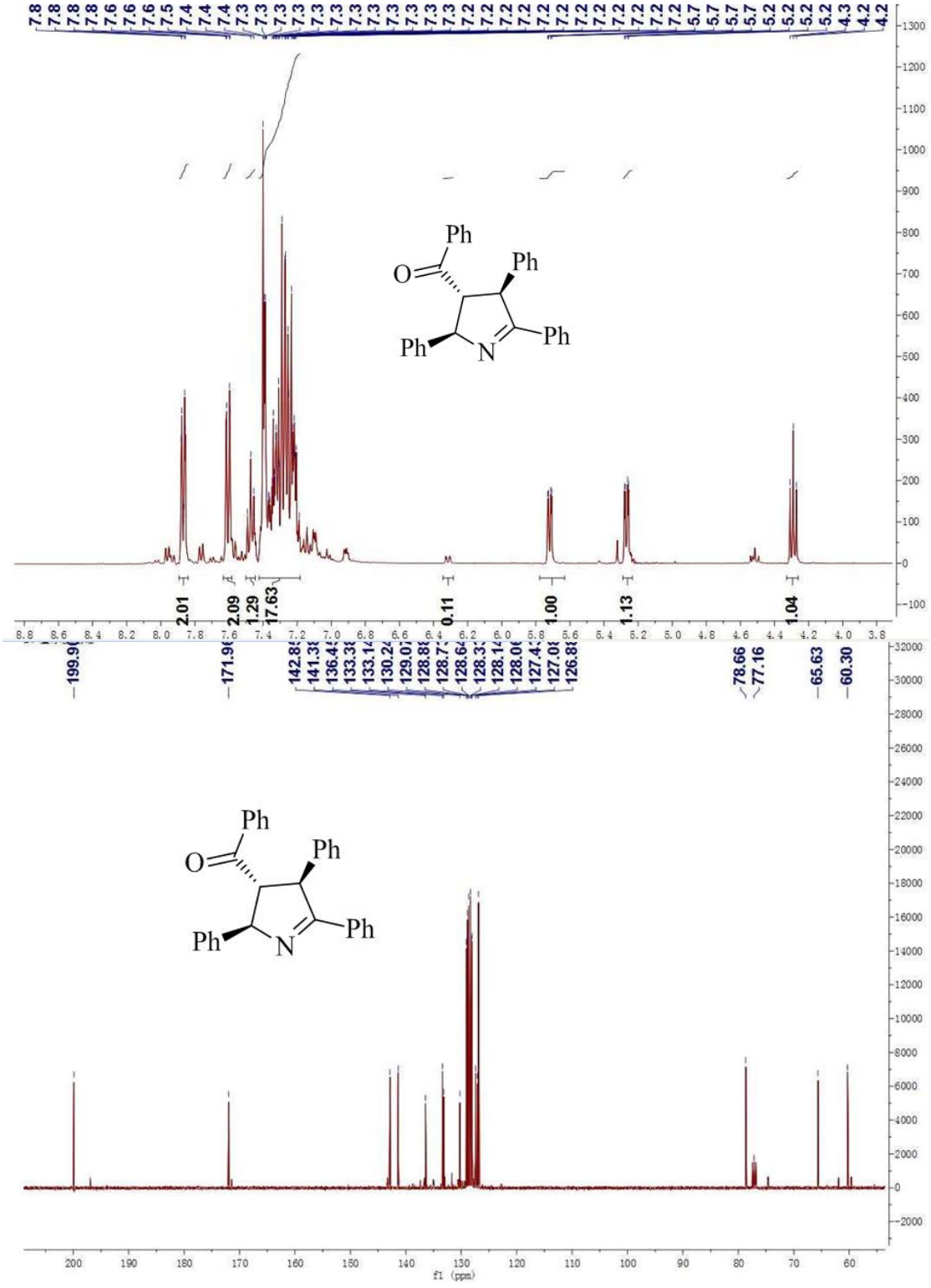
Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX 400 or 600 spectrometer at room temperature in $CDCl_3$ as solvent. Chemical shifts for protons are reported using residual $CHCl_3$ as internal reference (=7.26 ppm). Carbon spectra were referenced to the shift of the ^{13}C signal of $CDCl_3$ (=77.0 ppm). Coupling constants (*J*) are given in Hz. ESI-HRMS spectrometer was measured with a Finnigan LCQ^{DECA} ion trap mass spectrometer. Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997).

General procedure for the one-pot reaction of benzamides 1 with *α,β*-unsaturated ketones 2

Benzamide (**1a**, 316 mg, 1.5 mmol) was stirred in thionyl chloride (7.5 mmol, 0.54 mL) at the temperature of 80 ^{o}C for 12 h under N_2. The excessive thionyl chloride was removed in vacuo, the obtained residue was re-dissolved in dry THF (3 mL) and concentrated for three times to remove remaining thionyl chloride. Then chalcone (**2a**, 208 mg, 1.0 mmol) in 6 mL THF was added and cooled to 0 ^{o}C. *t*-BuOK (168 mg, 1.5 mmol) in 3 mL THF was added dropwisely over 2 min at 0 ^{o}C. The mixture was stirring for another 10 min. Concentration of solvent under reduced pressure, and purified by column chromatography (5%~10% ethyl ether/ petroleum ether) to give **3a** (340 mg, 85% yield).

1. NMR spectra

3a



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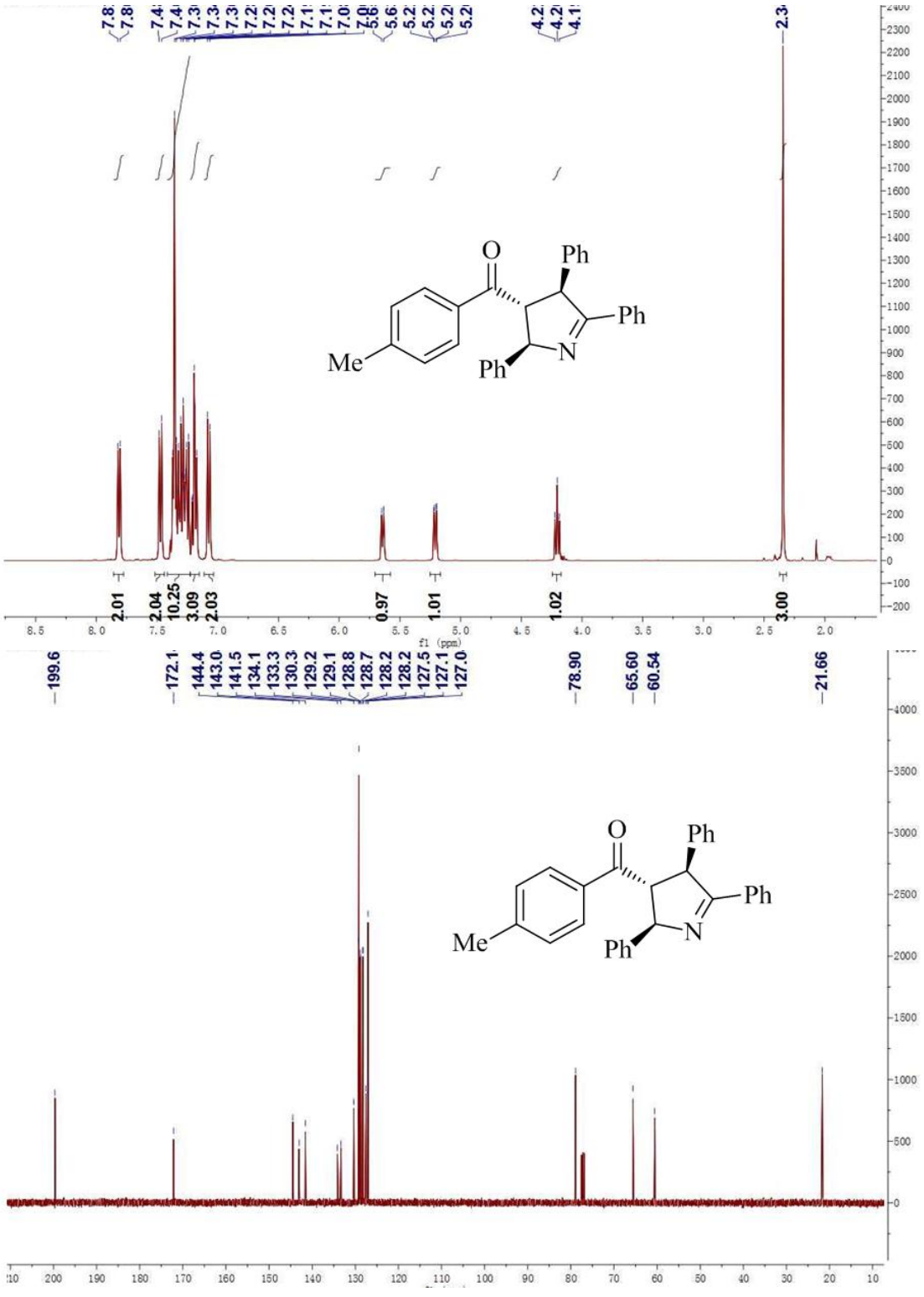

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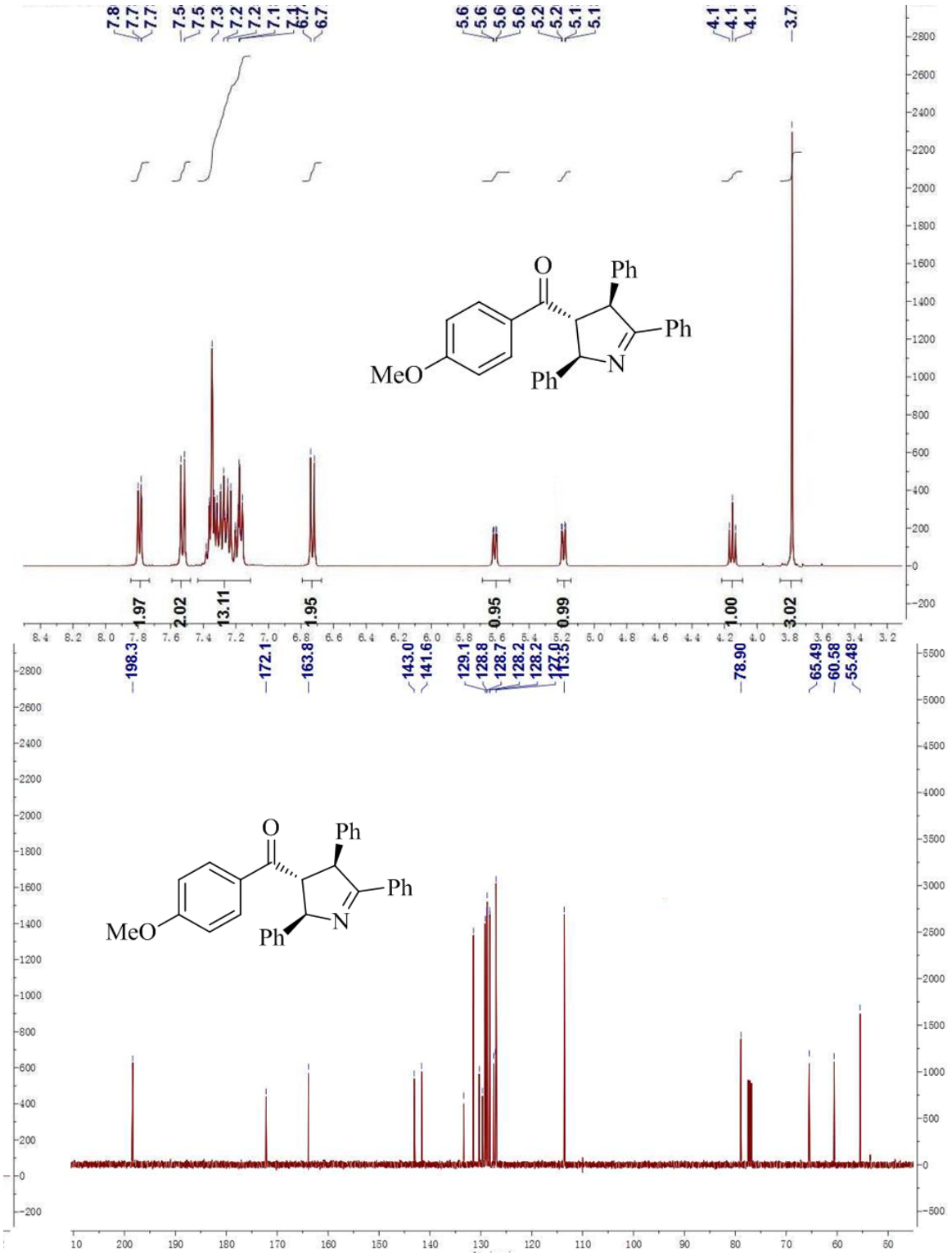
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Ph
MeO
Ph
N
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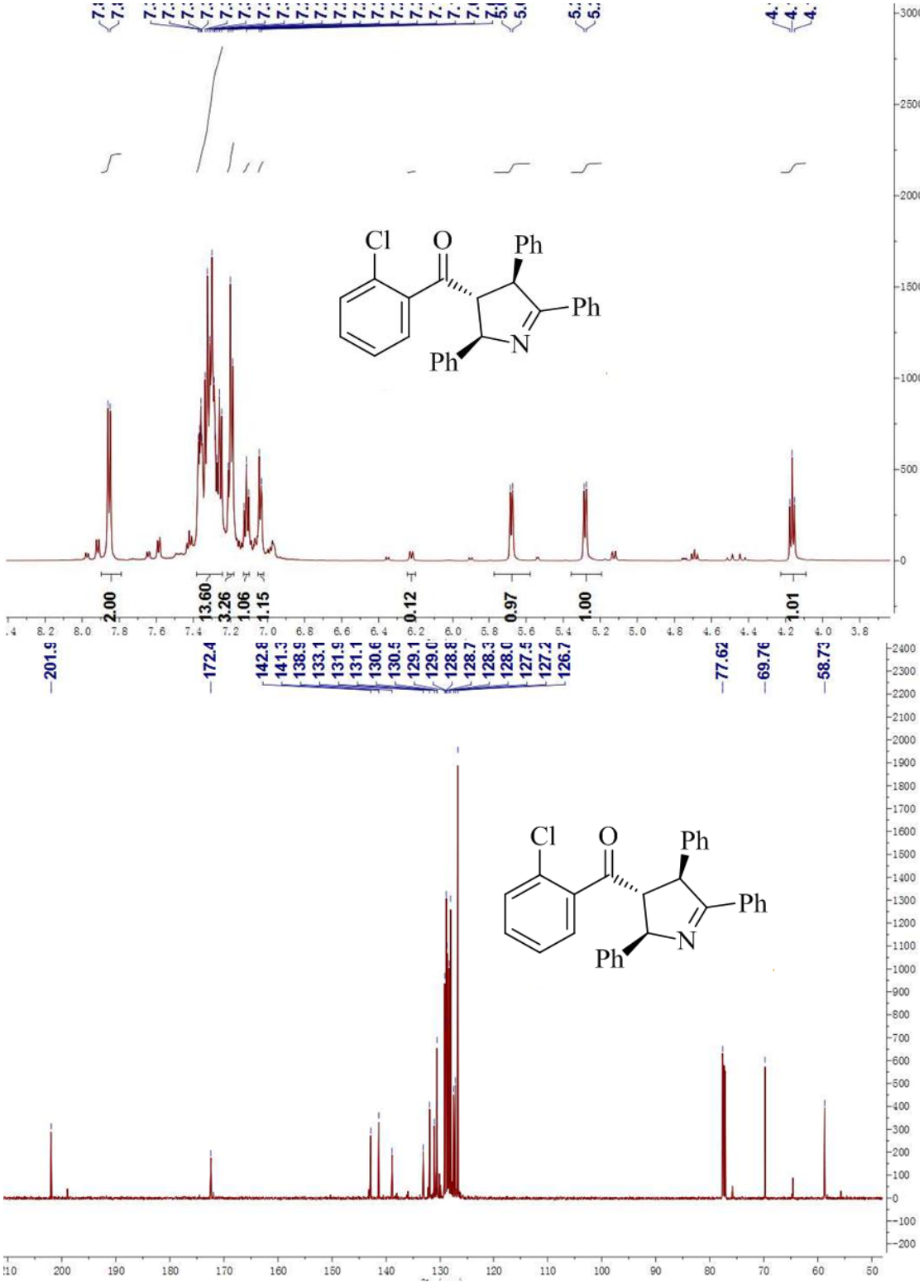
7.3
7.2
7.2
7.1
6.7
6.7
5.6
5.6
5.6
5.6
5.2
5.2
5.1
5.1
4.1
4.1
4.1
3.7
1.97
2.02
13.11
1.95
0.95
0.99
1.00
3.02
198.3
172.1
163.8
143.0
141.6
129.1
128.8
128.7
128.2
128.2
127.0
113.5
78.90
65.49
60.58
55.48

3d



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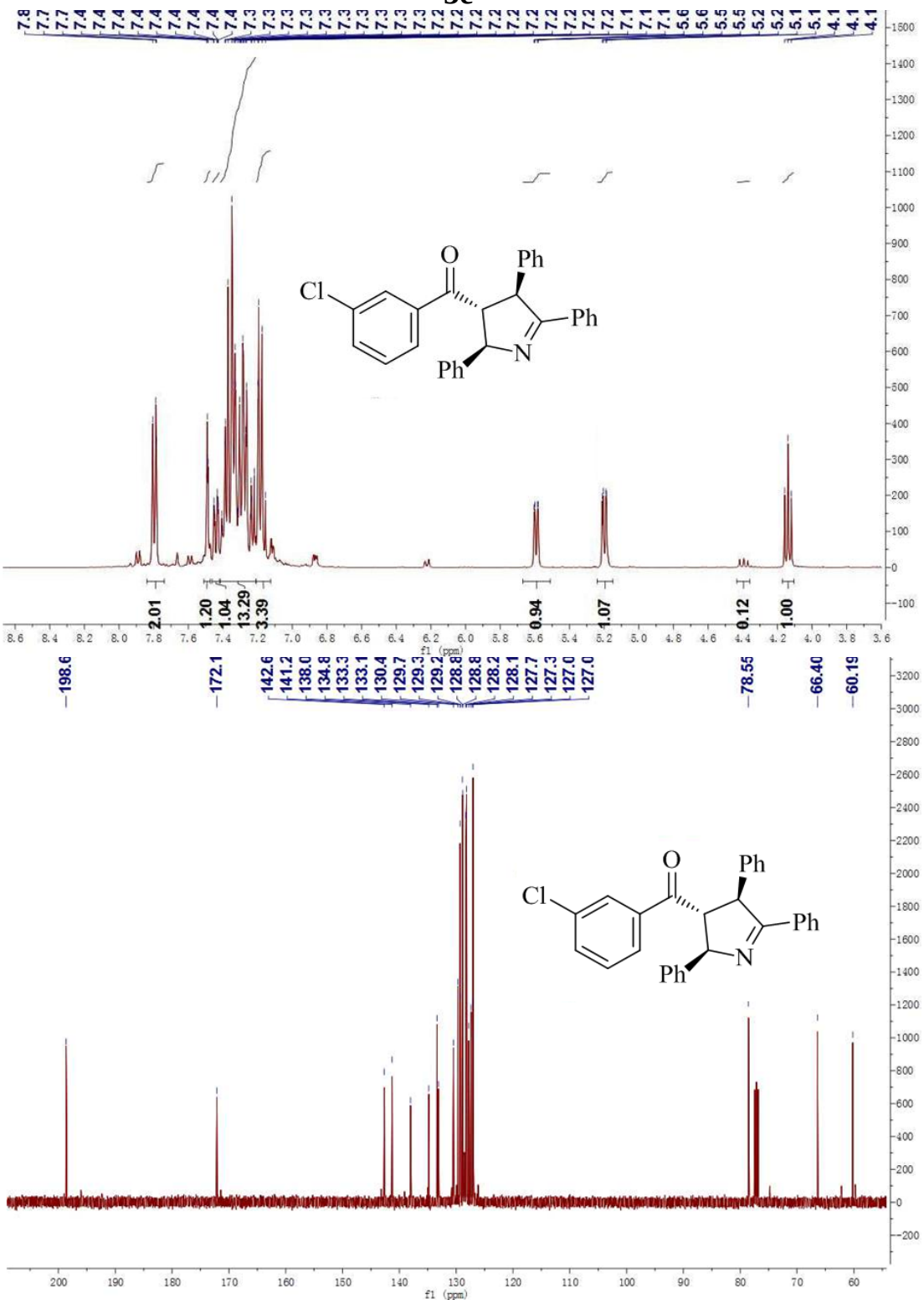
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Ph
N
Ph
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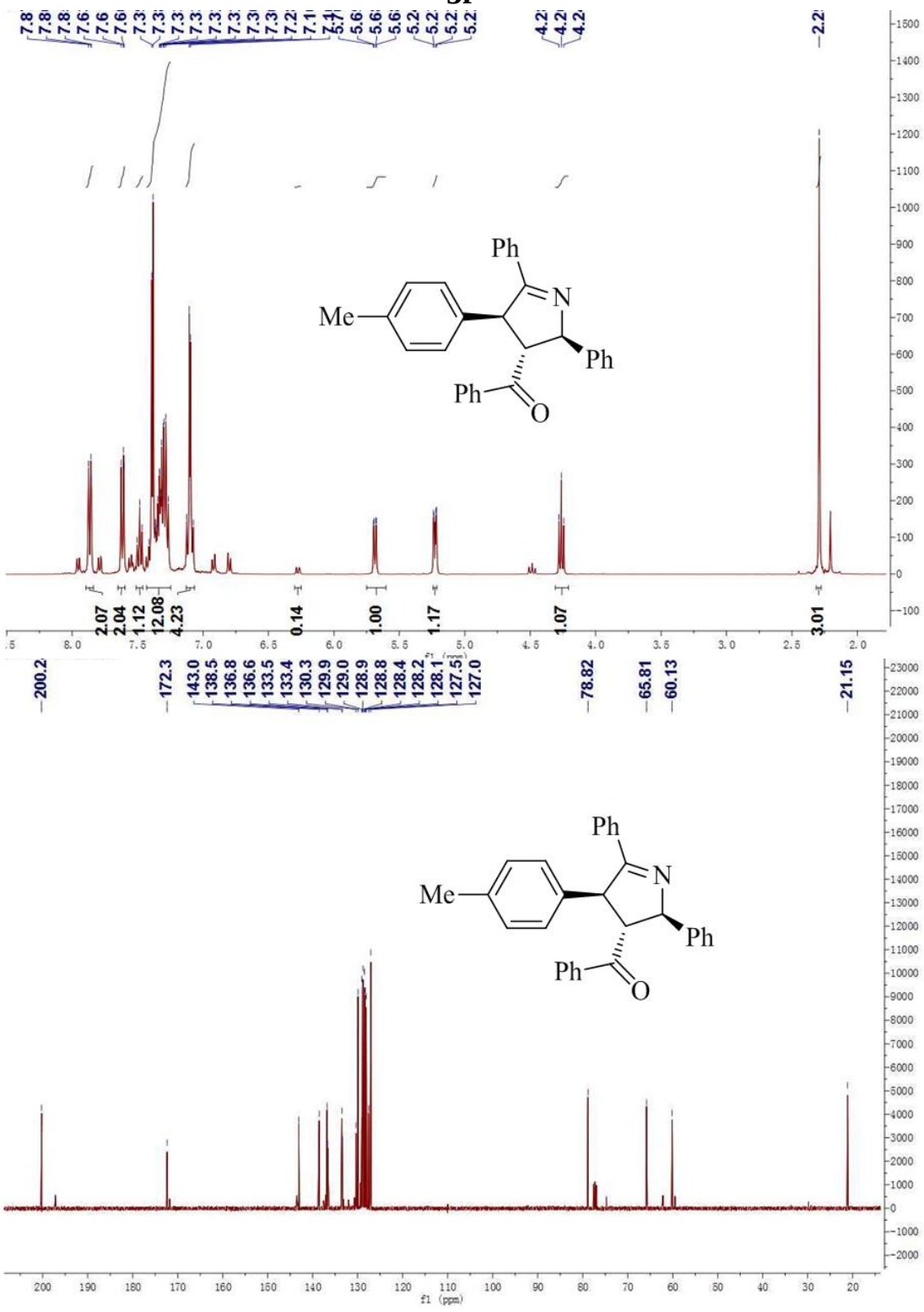
1.00
f1 (ppm)
198.6
172.1
142.6
141.2
138.0
134.8
133.3
133.1
130.4
129.7
128.8
128.2
128.1
127.7
127.3
127.0
127.0
78.55
66.40
60.19
f1 (ppm)

3f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Me
Ph
Ph
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12.08
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0.14
1.00
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1.07
3.01
200.2
172.3
143.0
138.5
136.8
136.6
133.5
133.4
130.3
129.9
129.0
128.9
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128.4
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128.1
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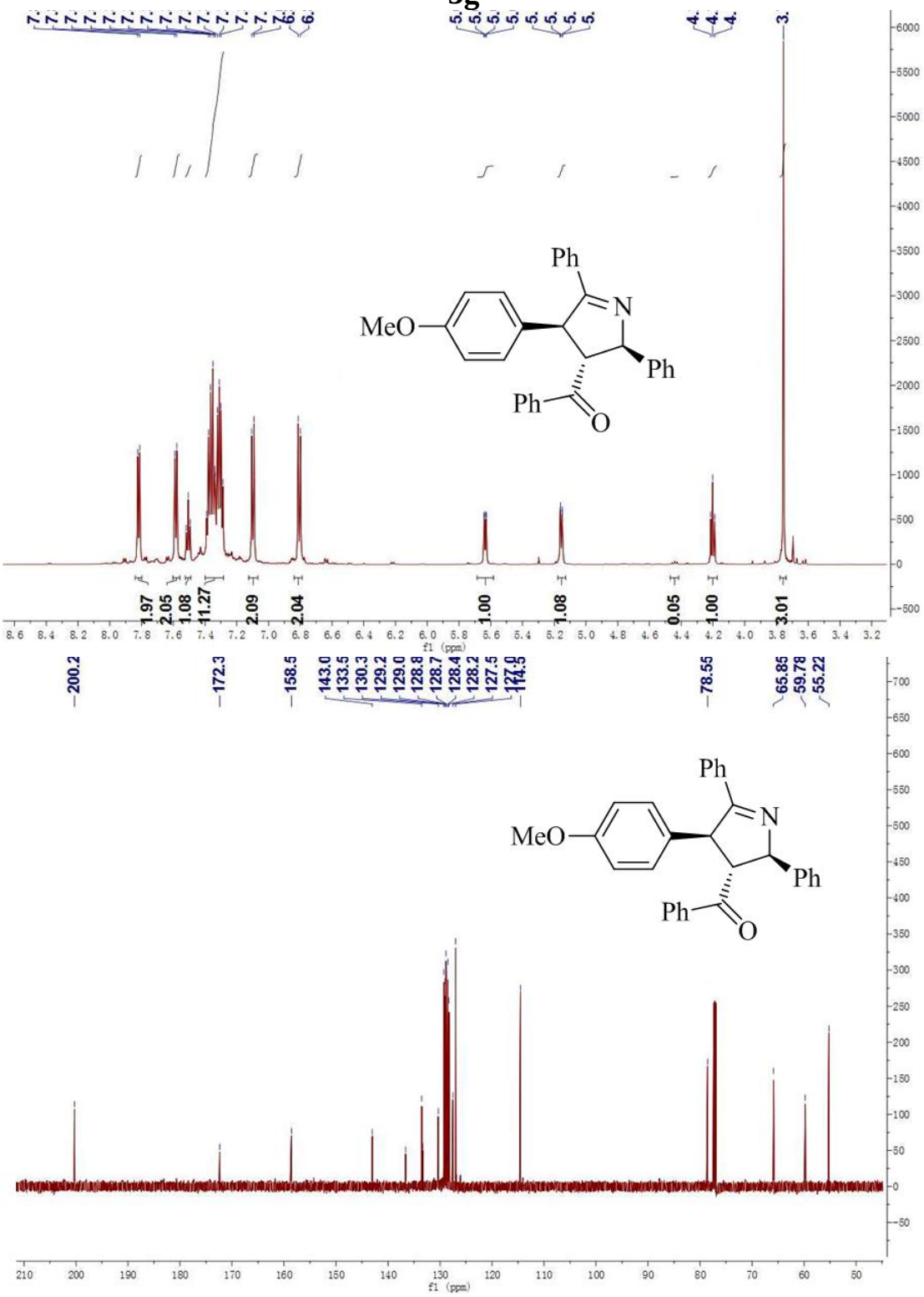
60.13
21.15
f1 (ppm)

3g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MeO
Ph
Ph
O
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11.27
2.09
2.04
1.00
1.08
0.05
1.00
3.01
f1 (ppm)
200.2
172.3
158.5
143.0
133.5
130.3
129.2
129.0
128.8
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128.4
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127.5
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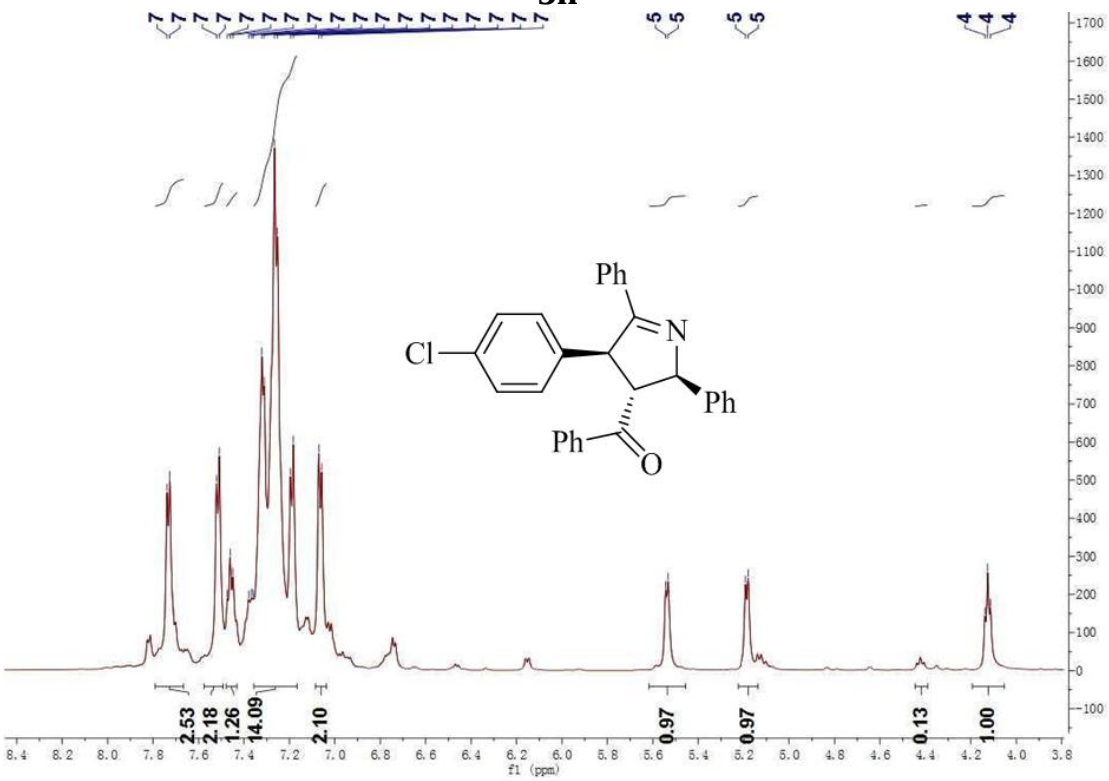
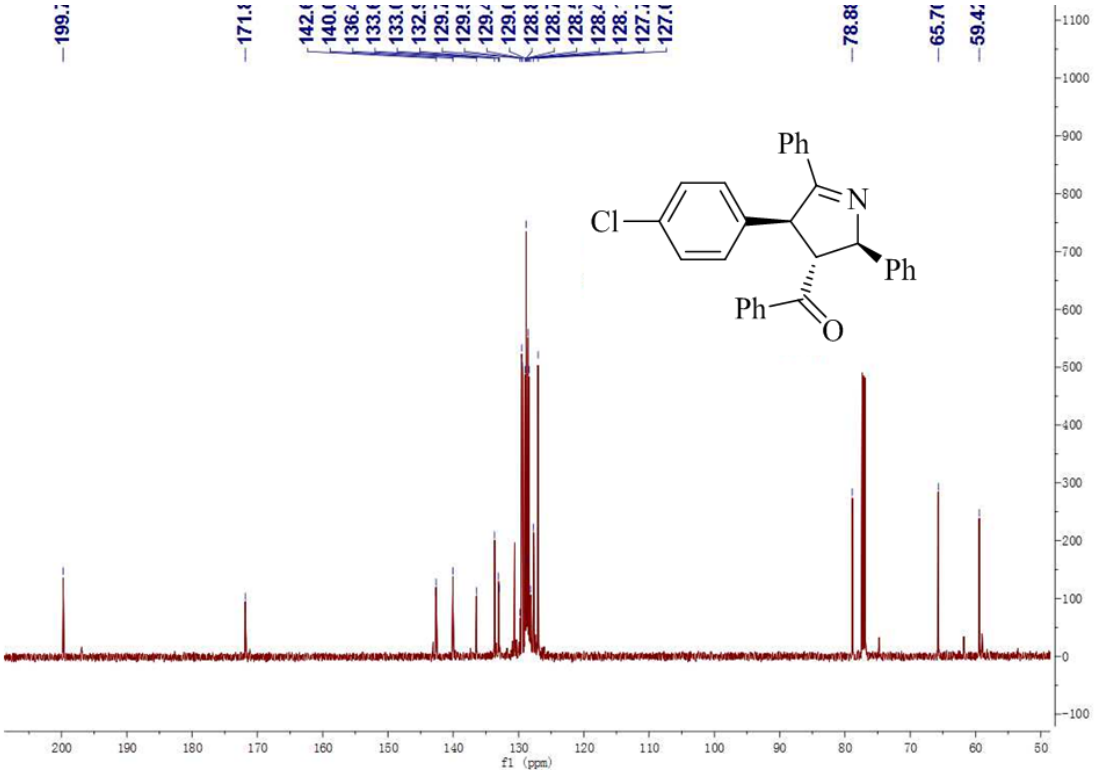
65.85
59.78
55.22
f1 (ppm)

3h





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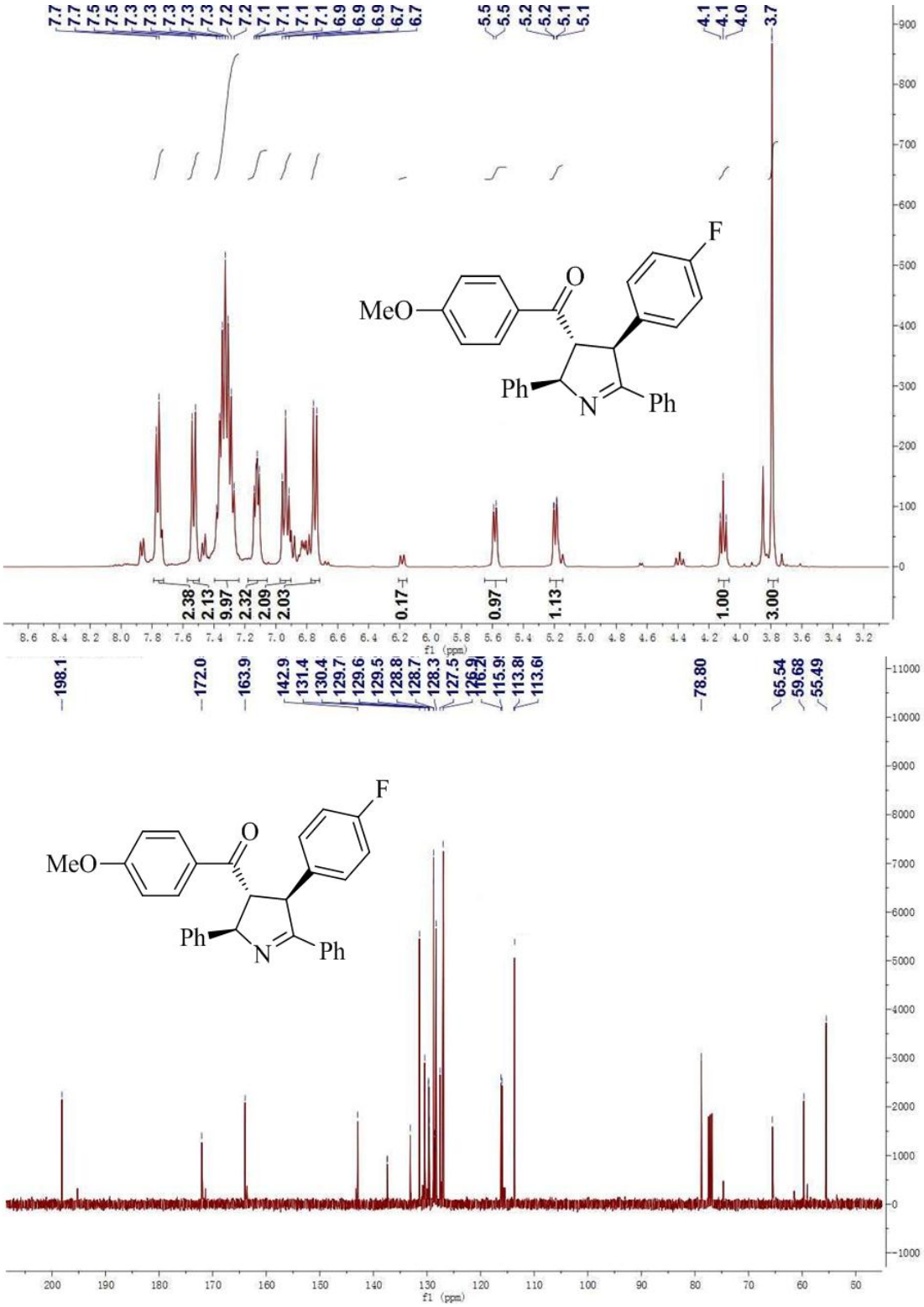

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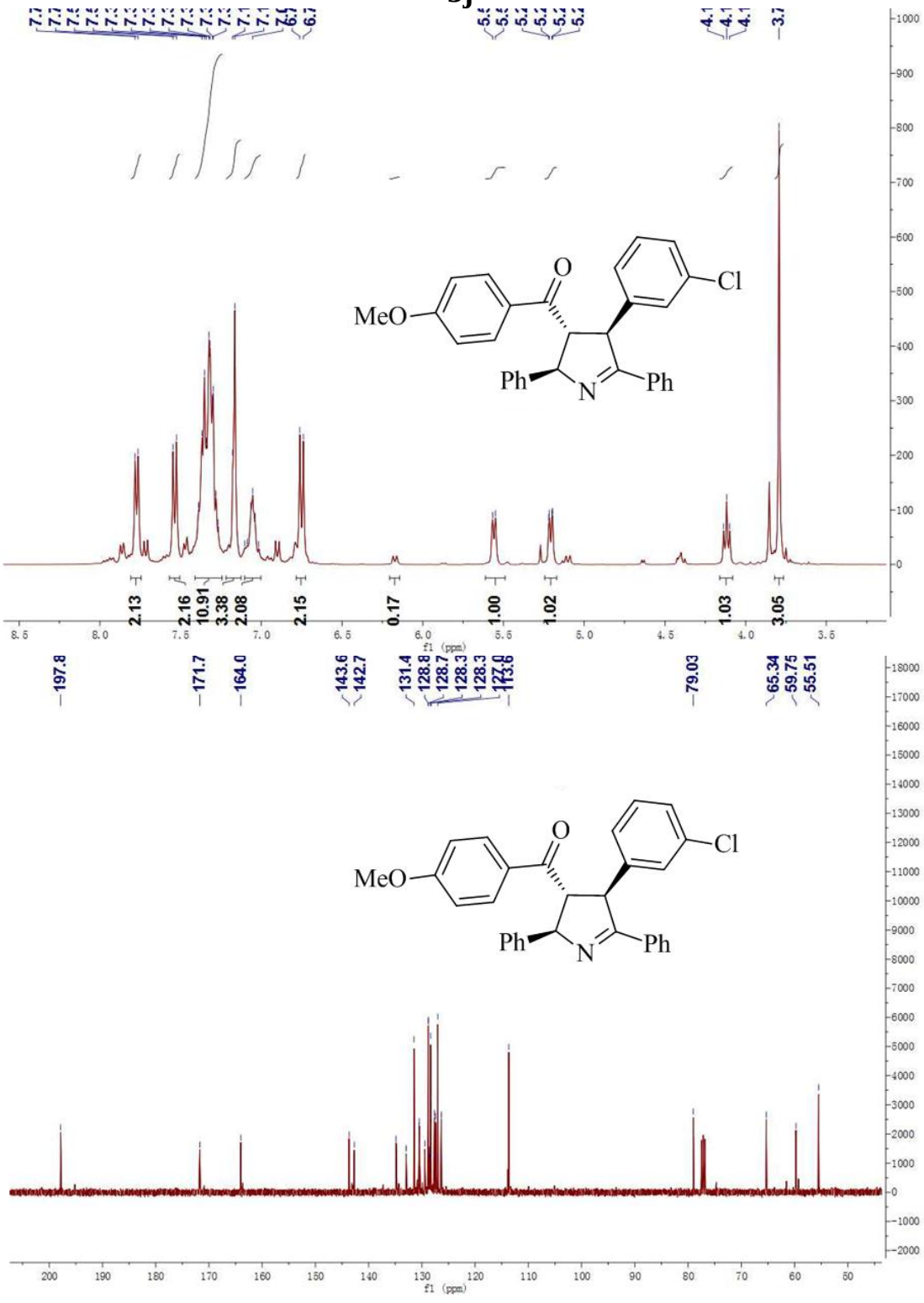

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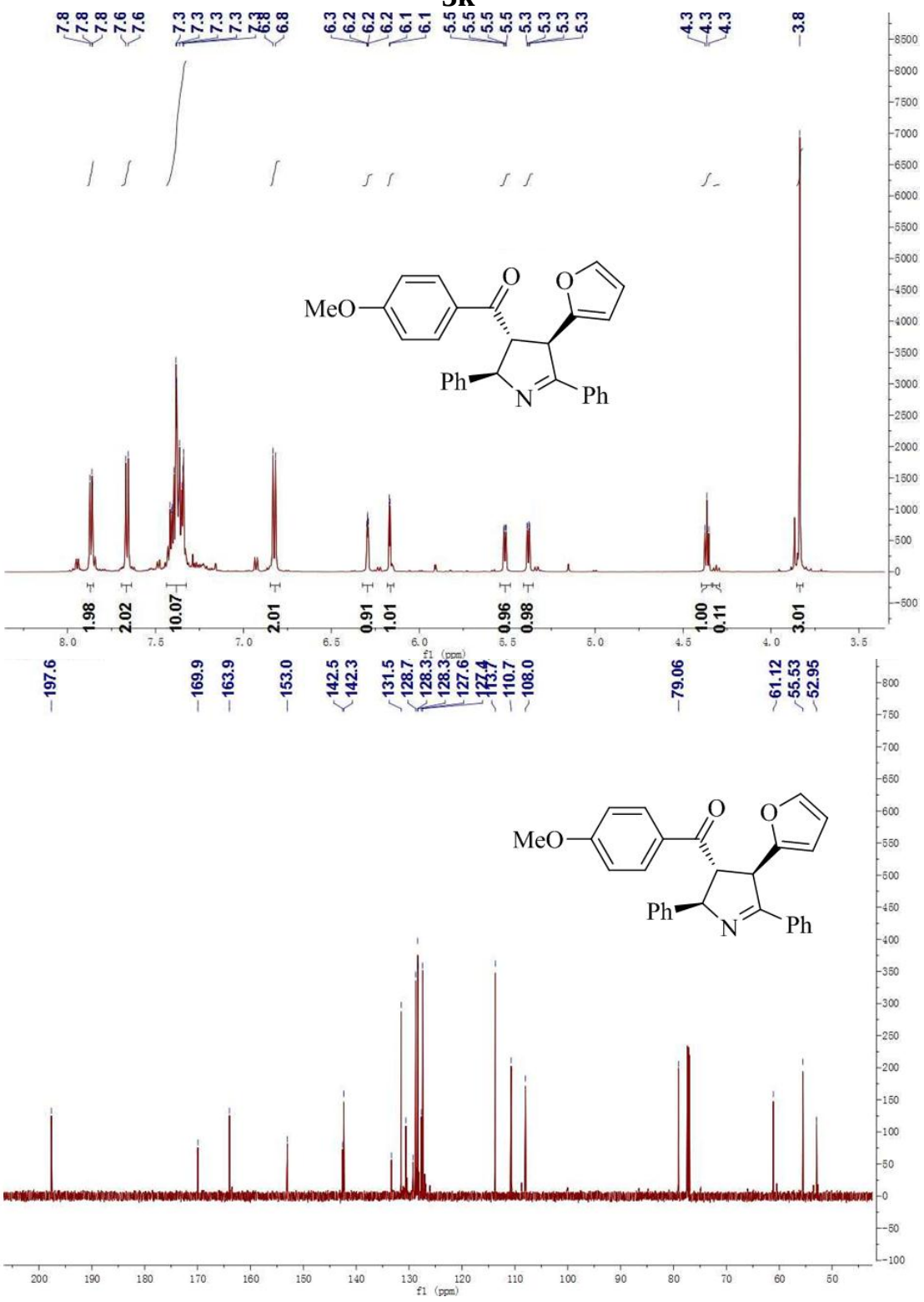

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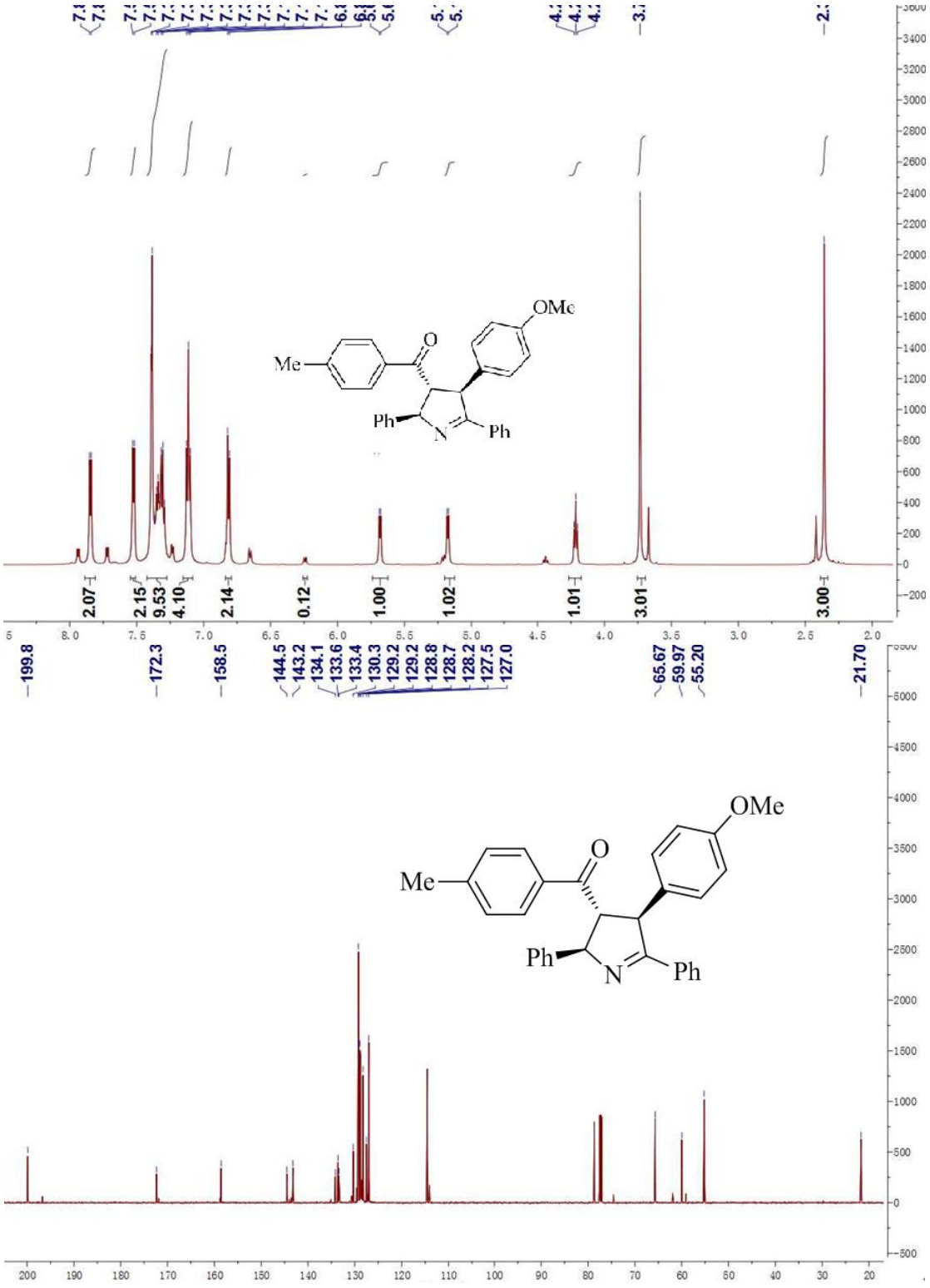
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N
Ph
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4.10
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1.01
3.01
3.00
199.8
172.3
158.5
144.5
143.2
134.1
133.6
133.4
130.3
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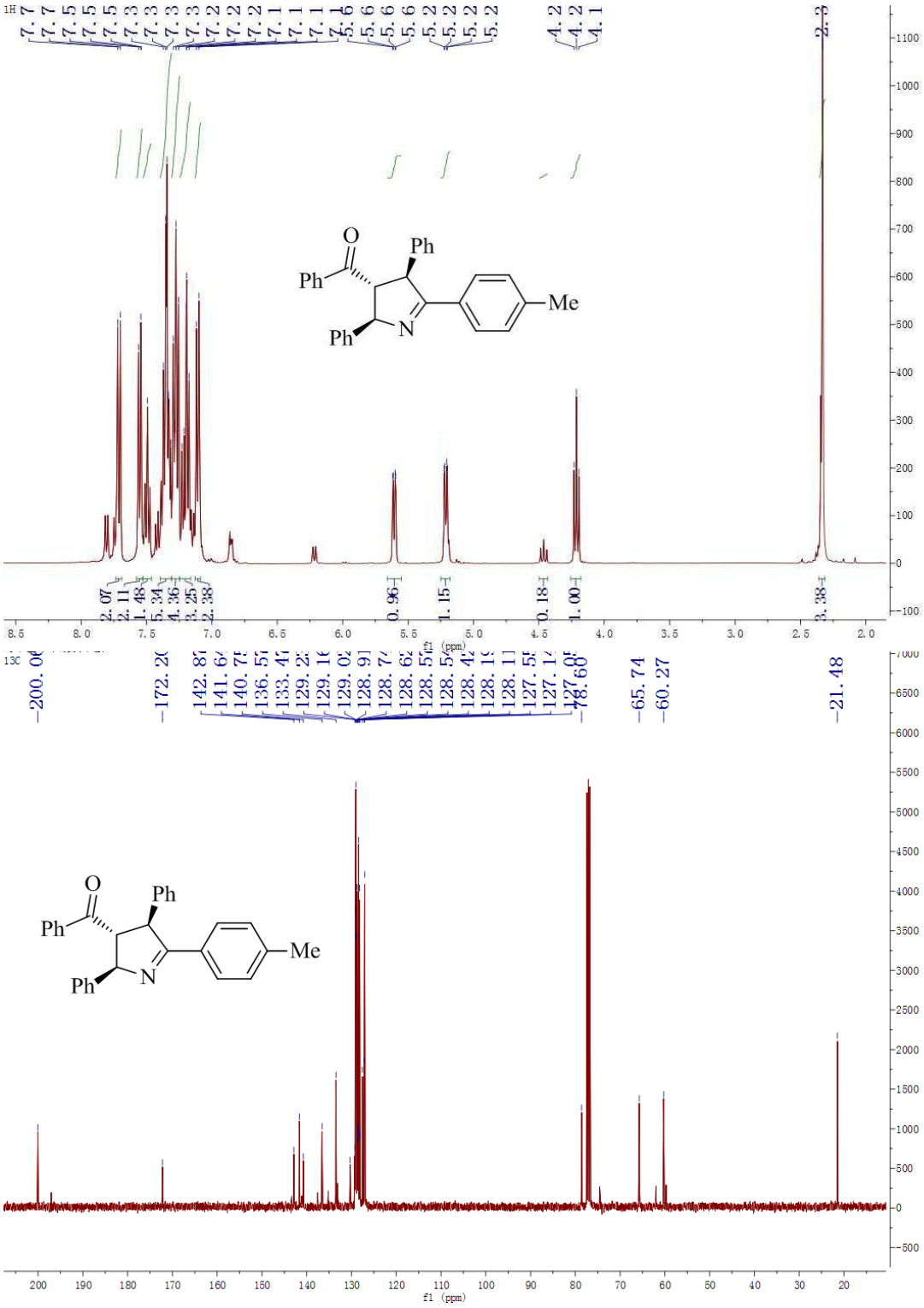
3m



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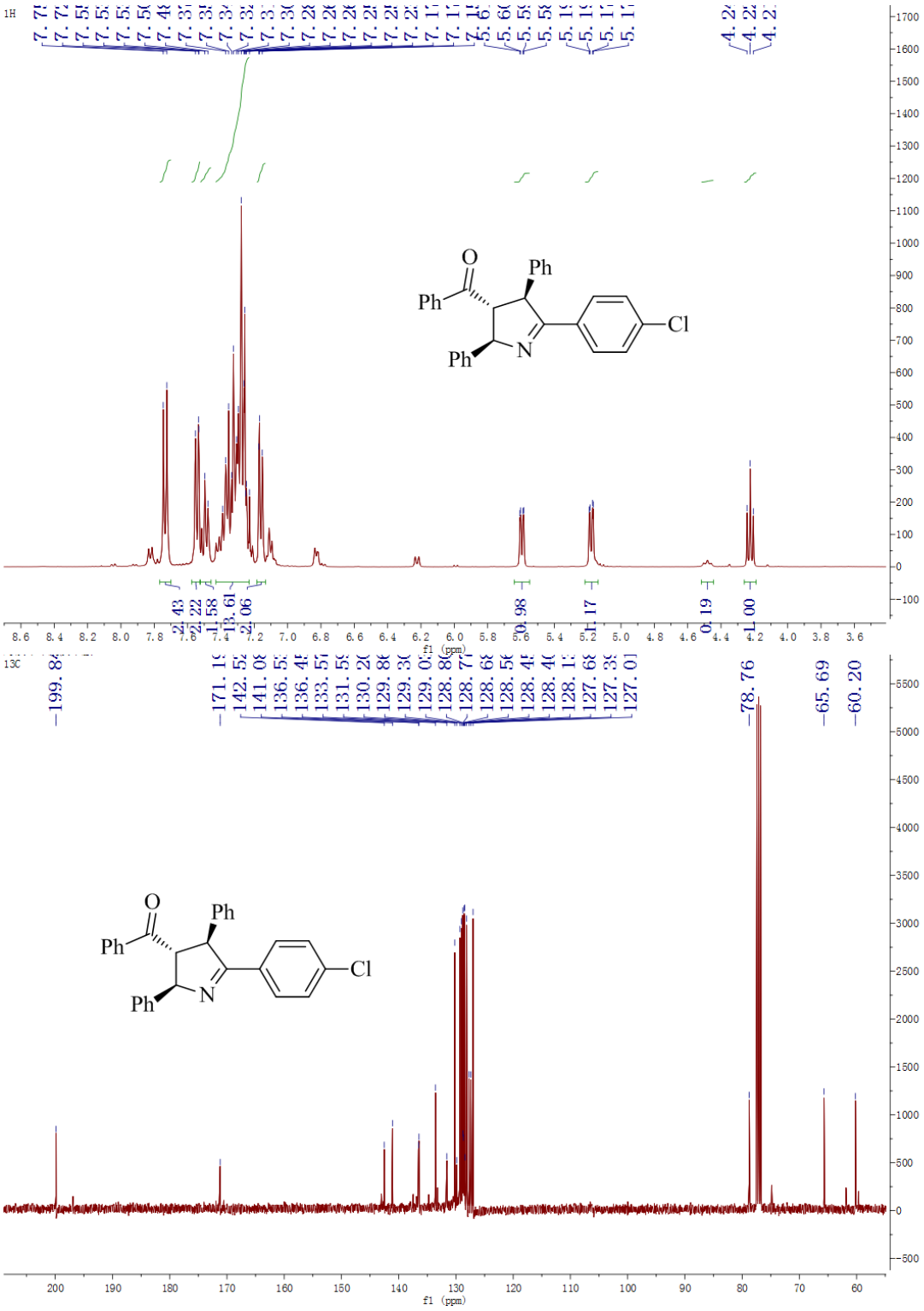

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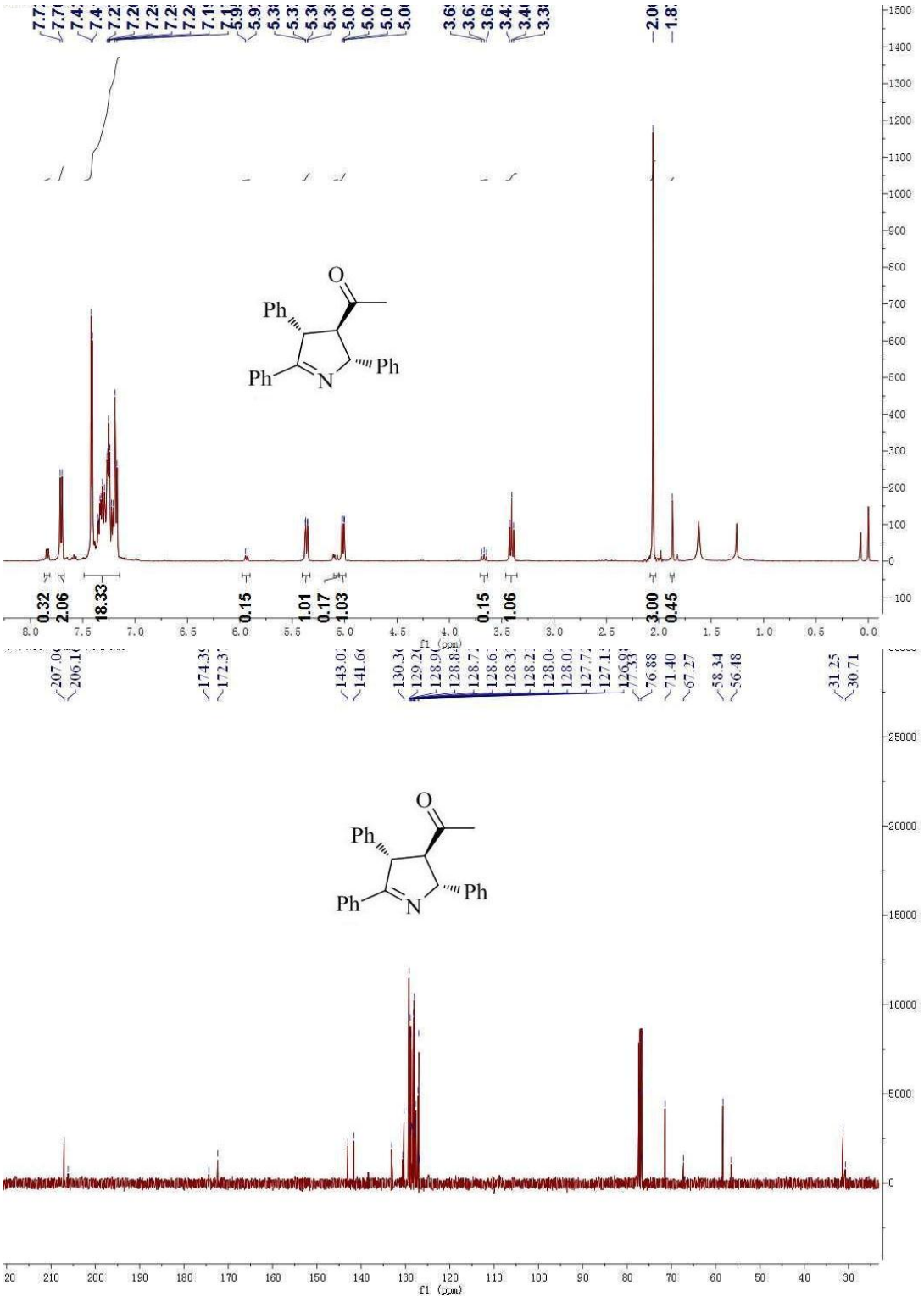

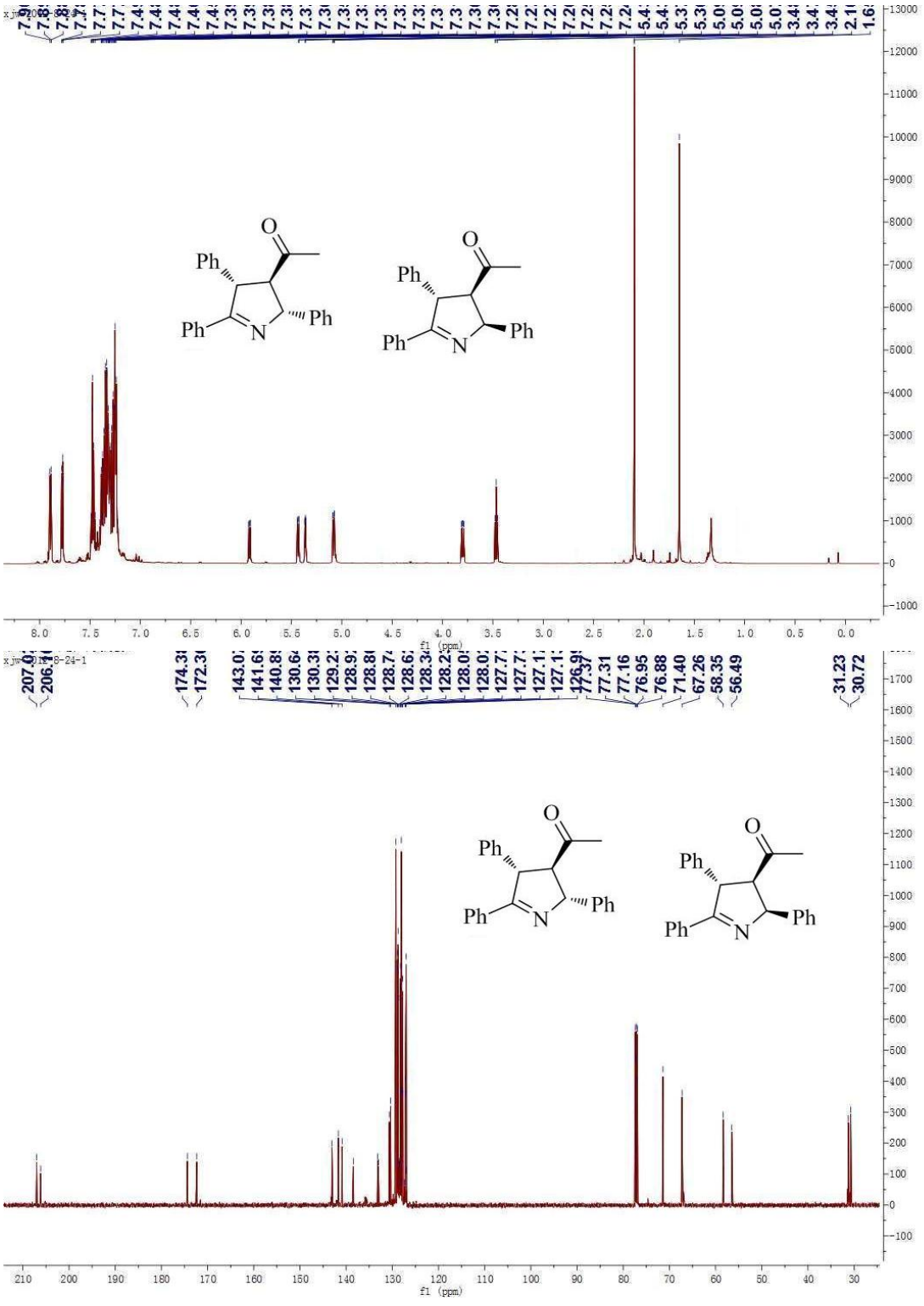
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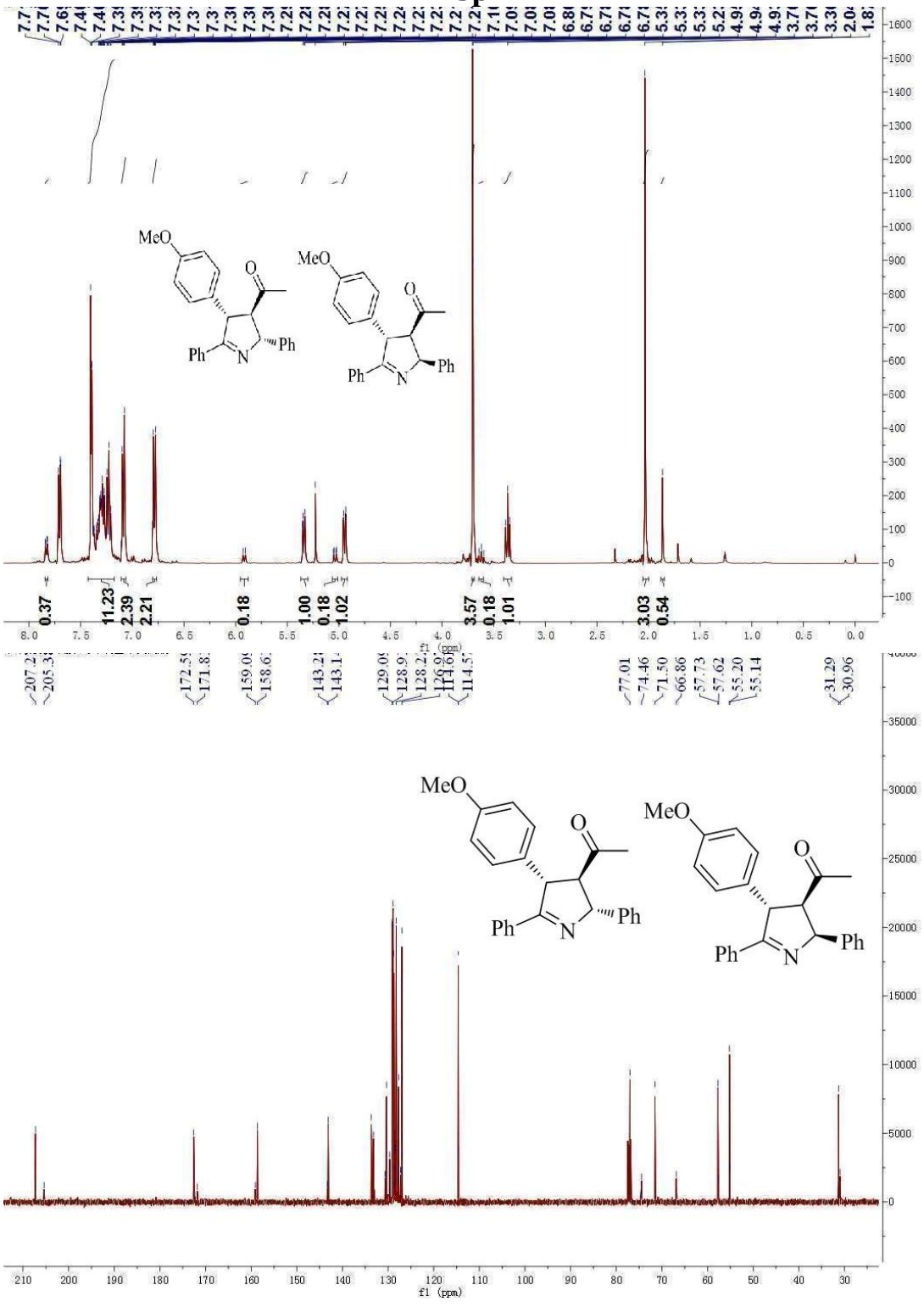
Ph
Ph
N
Ph
Ph
O
Ph
Ph
N
Ph
f1 (ppm)
O
Ph
Ph
N
Ph
Ph
O
Ph
Ph
N
Ph
f1 (ppm)

3p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Ph
N
Ph
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3.03
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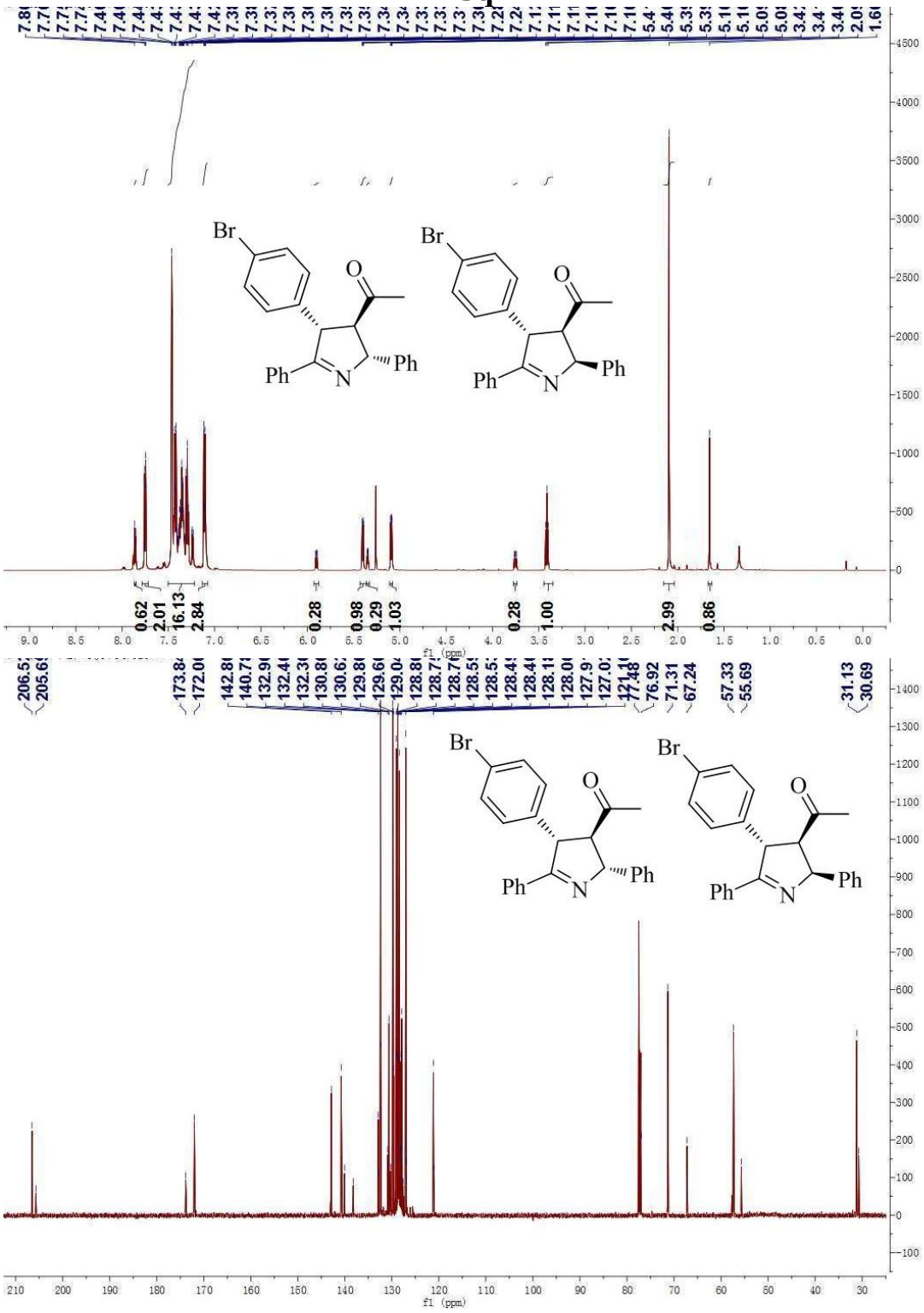
f1 (ppm)

3q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2.99
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f1 (ppm)
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205.6
173.8
172.0
142.8
140.7
132.9
132.4
132.3
130.8
130.6
129.8
129.6
129.0
128.8
128.7
128.5
128.4
128.1
128.0
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127.0
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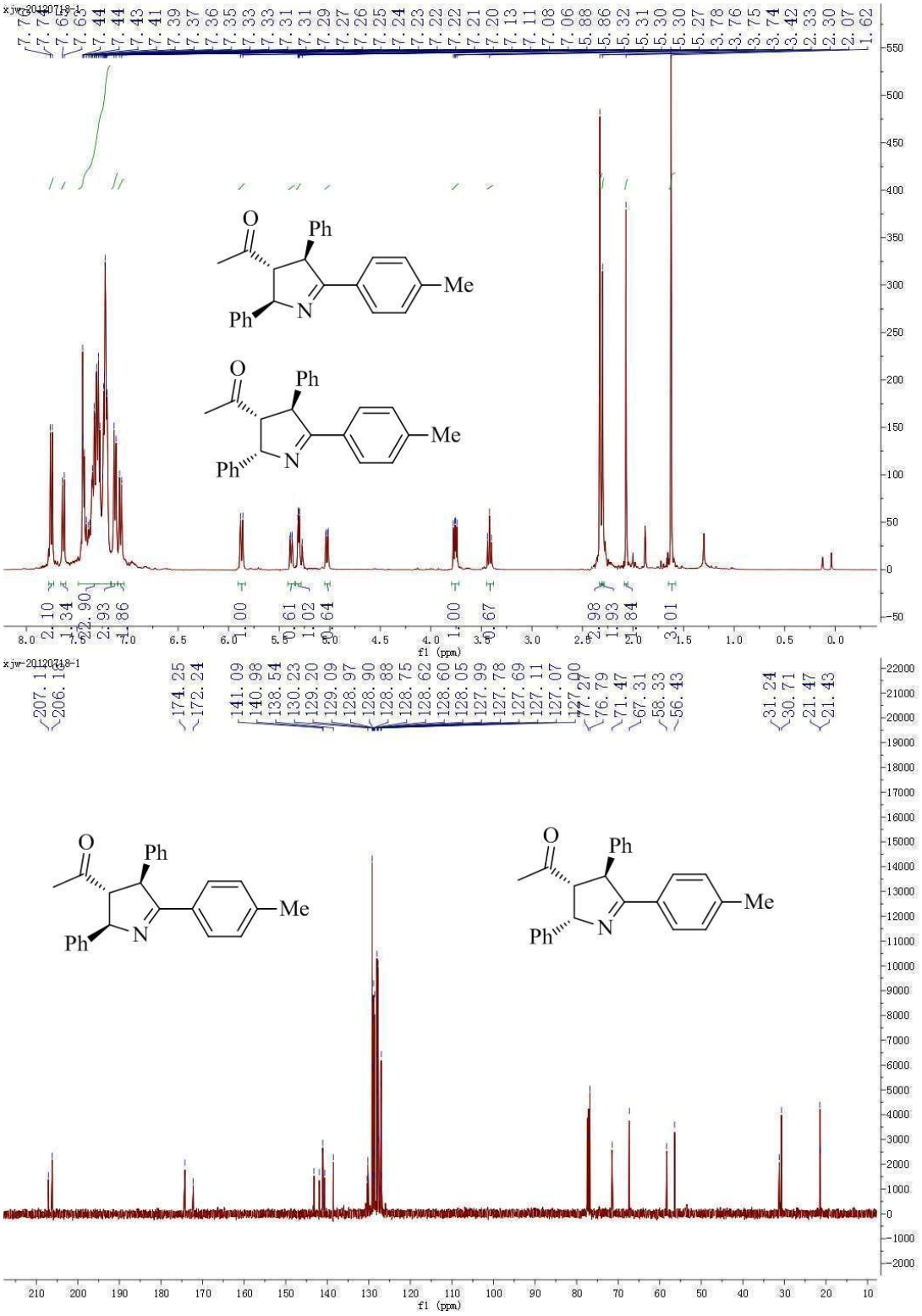
67.24
57.33
55.69
31.13
30.69
f1 (ppm)

3r



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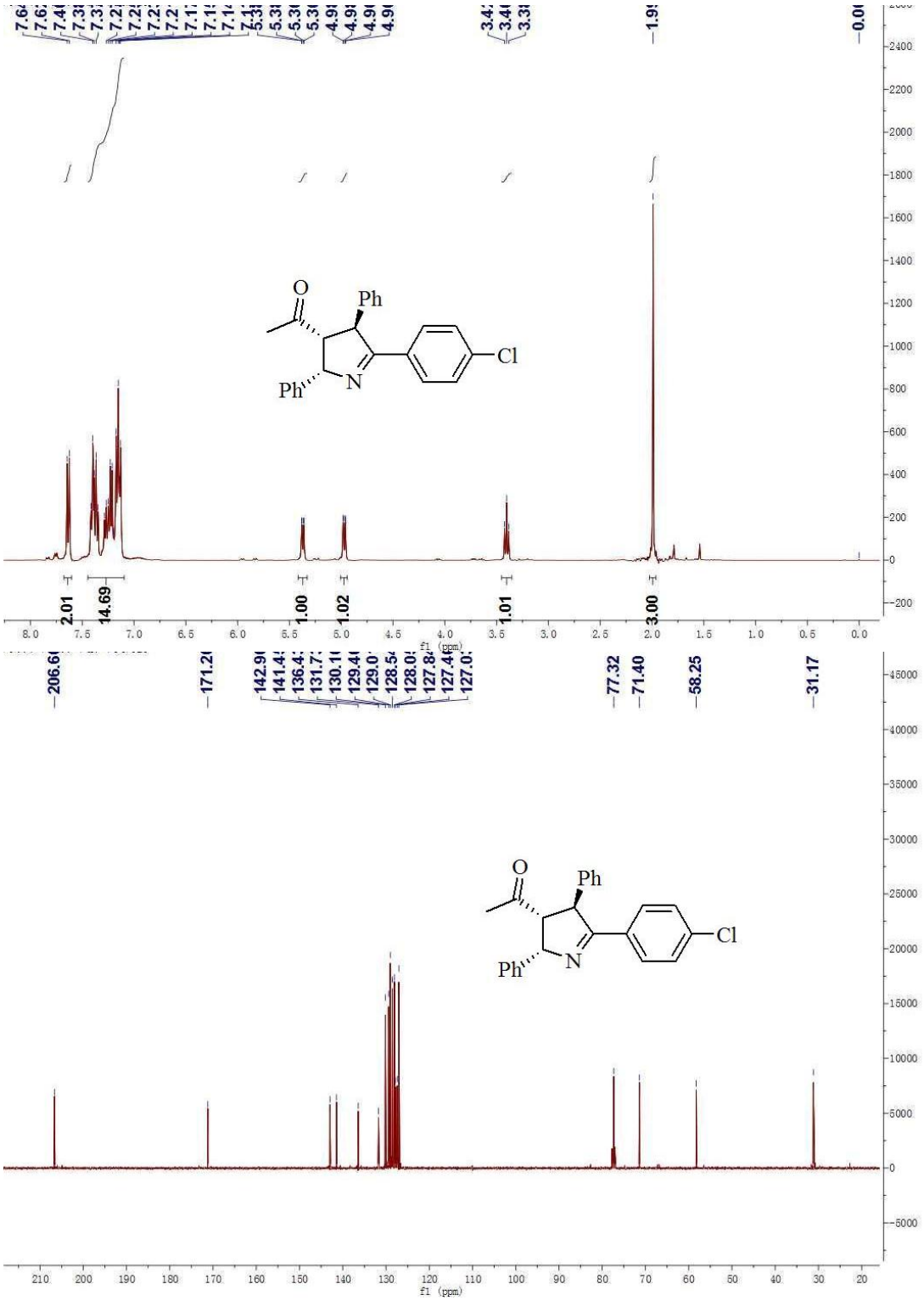
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Cl
Ph
N
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1.00
1.02
1.01
3.00
f1 (ppm)
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171.2
142.9
141.4
136.4
131.7
130.1
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128.0
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127.0
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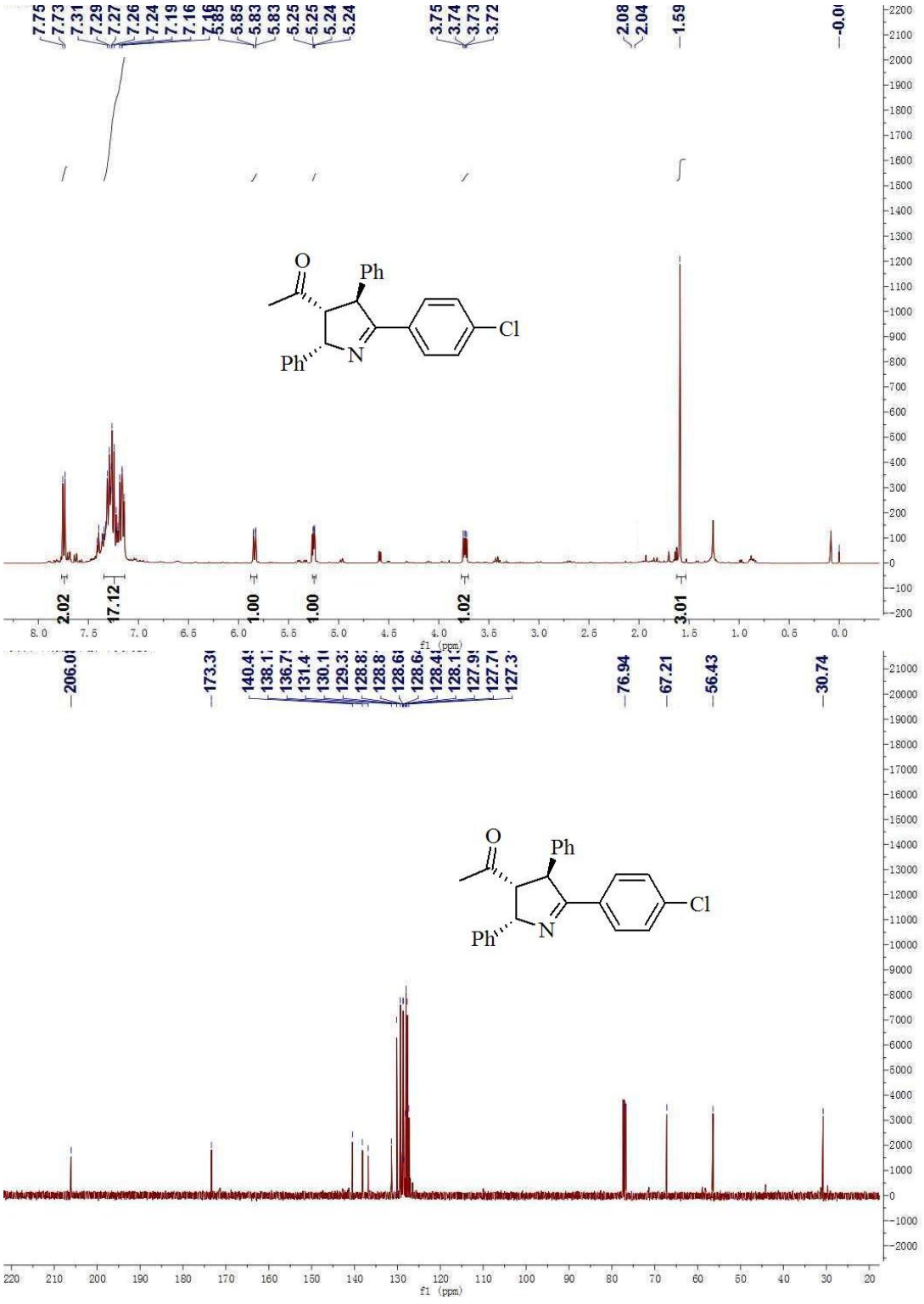
58.25
31.17
f1 (ppm)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5.85
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5.83
5.25
5.25
5.24
5.24
3.75
3.74
3.73
3.72
2.08
2.04
1.59
0.00
O
Ph
Cl
Ph
N
2.02
17.12
1.00
1.00
1.02
3.01
f1 (ppm)
206.08
173.38
140.45
138.13
136.75
131.47
130.11
129.32
128.82
128.81
128.61
128.61
128.44
128.11
127.95
127.71
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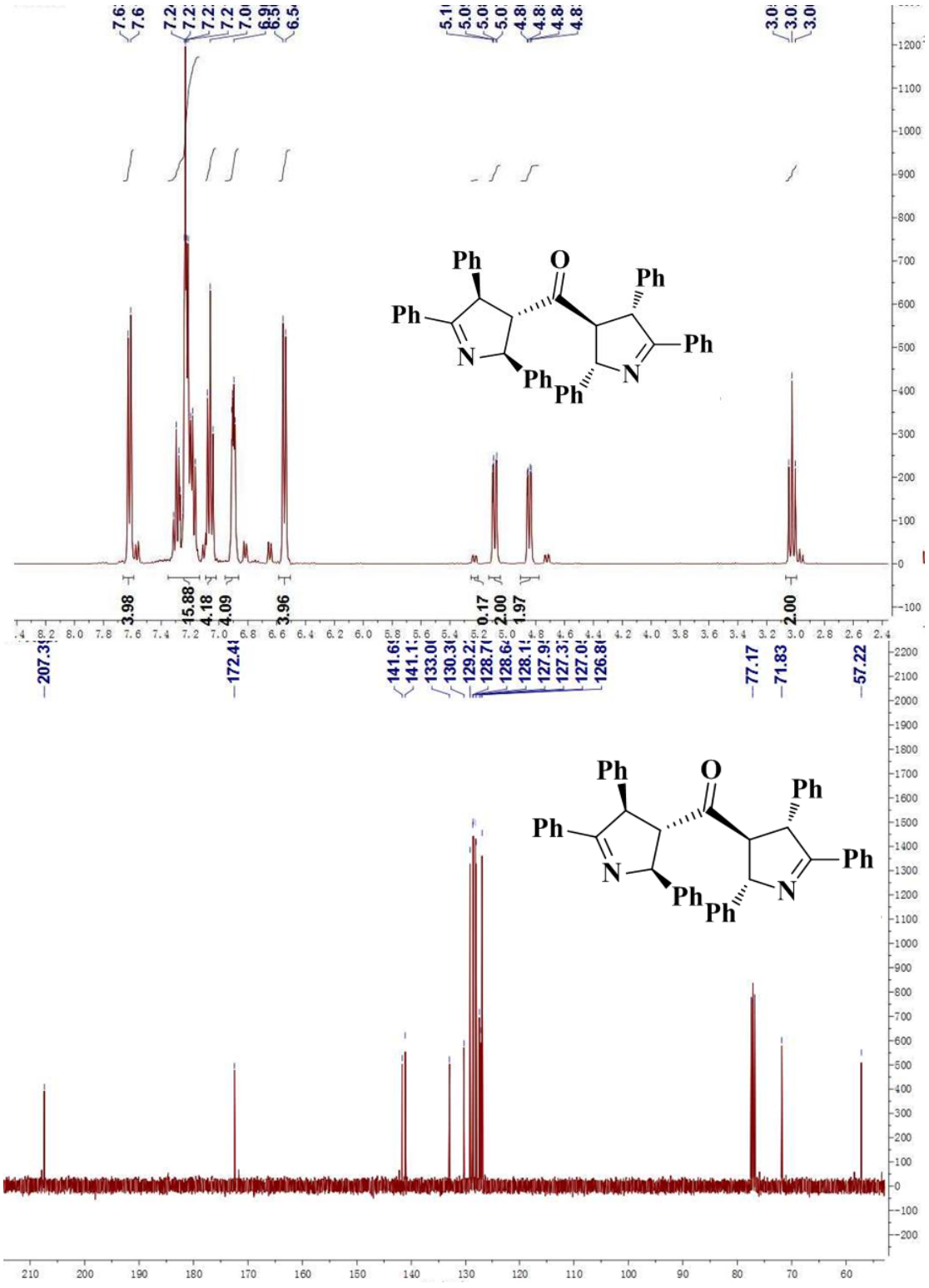
56.43
30.74
O
Ph
Cl
Ph
N
f1 (ppm)

3t



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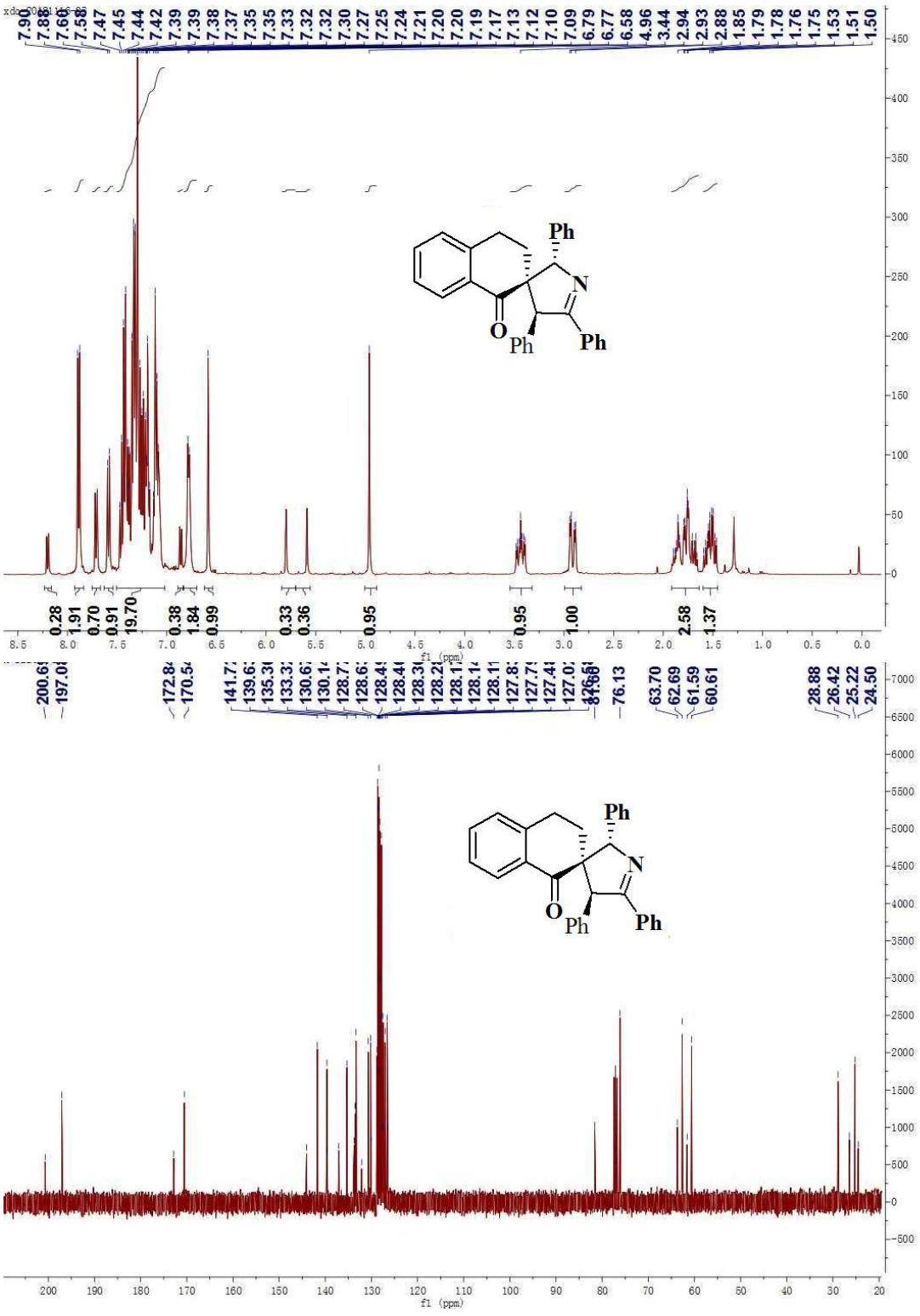
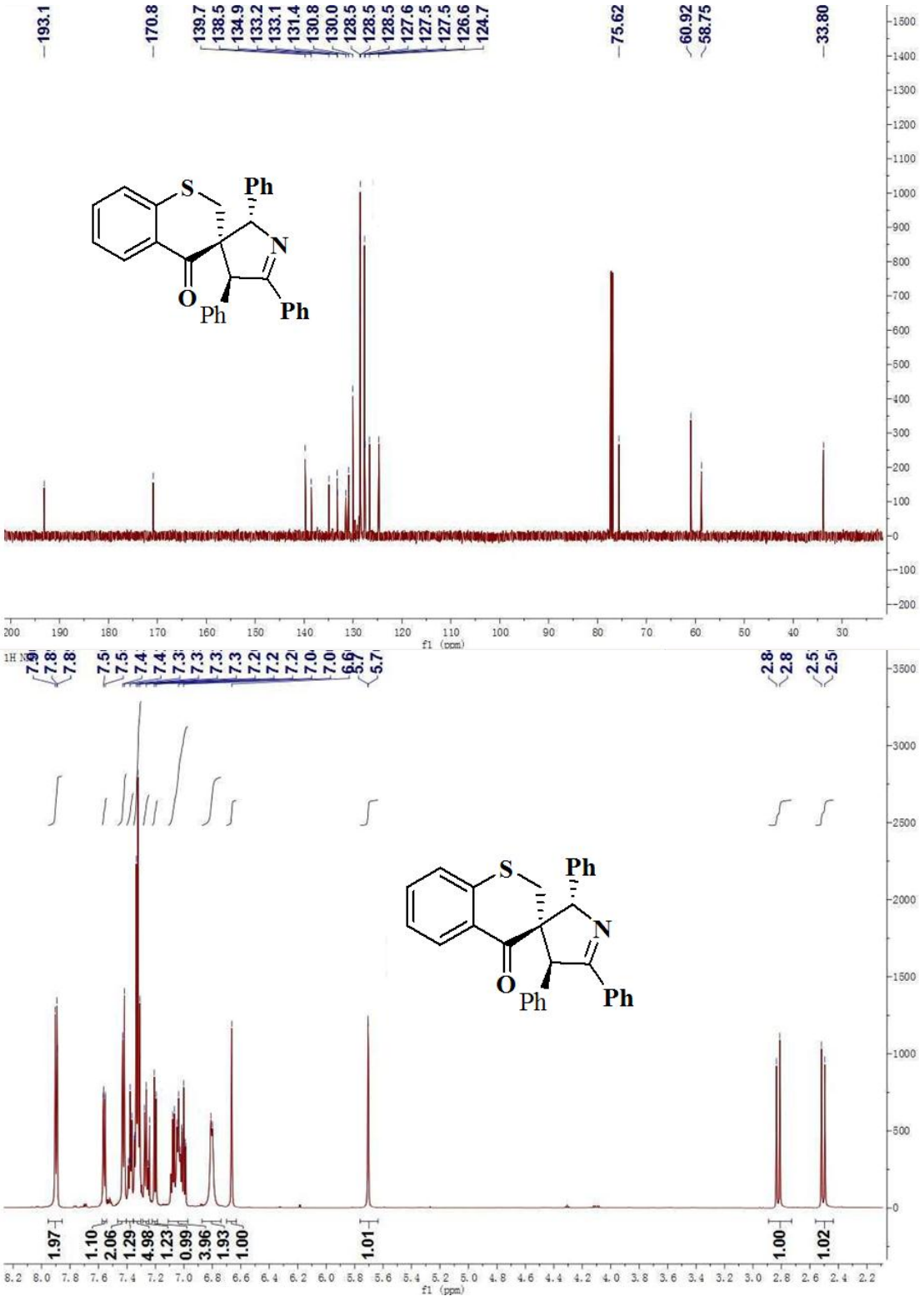


3v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128.5
128.5
127.6
127.5
127.5
126.6
124.7
75.62
60.92
58.75
33.80
S
Ph
N
O
Ph
Ph
f1 (ppm)
7.9
7.8
7.8
7.5
7.5
7.4
7.4
7.3
7.3
7.3
7.3
7.2
7.2
7.2
7.0
7.0
6.6
5.7
5.7
2.8
2.8
2.5
2.5
1.97
1.10
2.06
1.29
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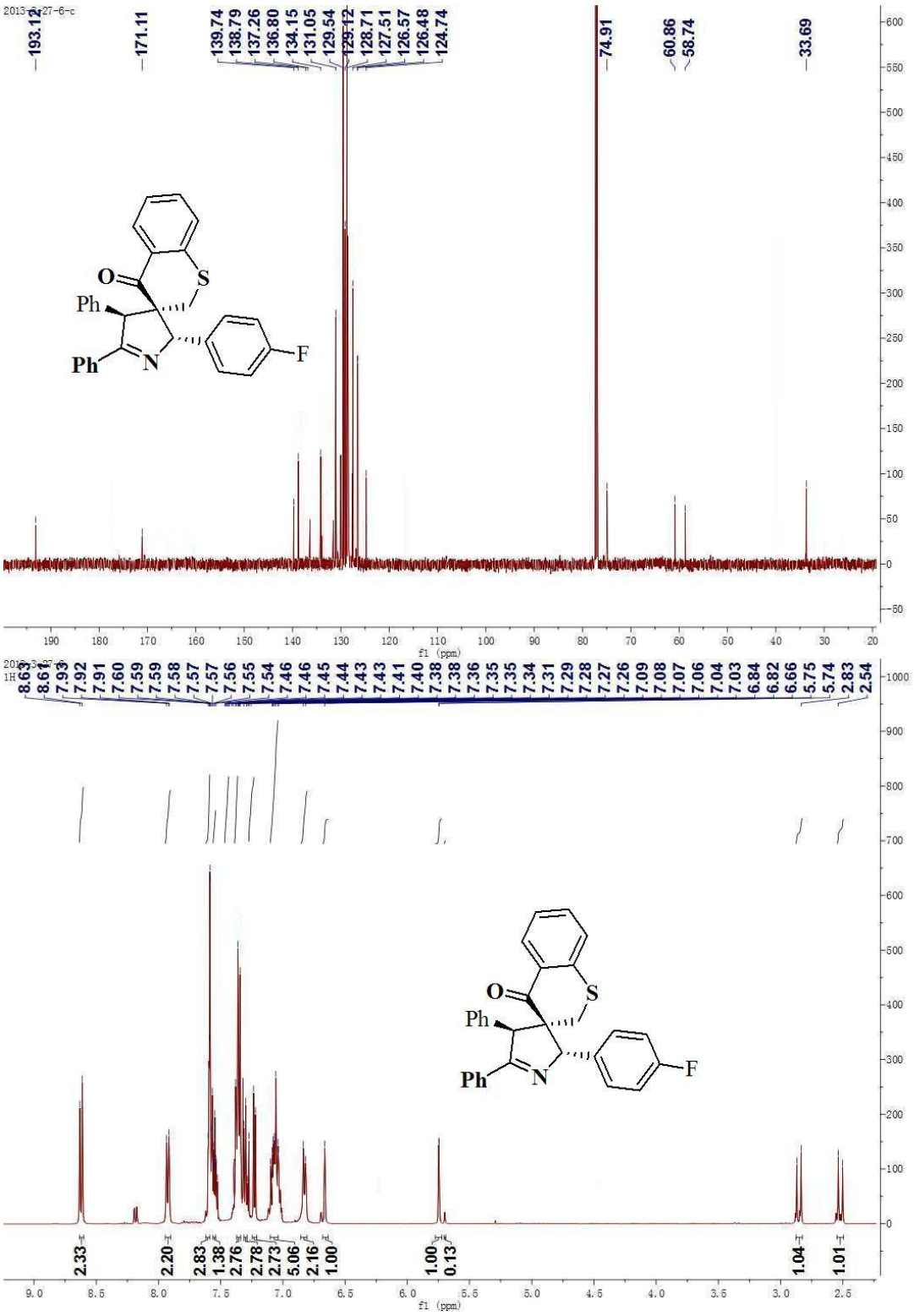
1.93
1.00
1.01
1.00
1.02
f1 (ppm)

3w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131.05
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129.12
128.71
127.51
126.57
126.48
124.74
74.91
60.86
58.74
33.69
O
S
Ph
Ph
N
F
f1 (ppm)
8.63
8.61
7.93
7.92
7.91
7.60
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.54
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7.45
7.44
7.43
7.43
7.41
7.40
7.38
7.38
7.36
7.35
7.35
7.34
7.31
7.29
7.28
7.27
7.26
7.09
7.08
7.07
7.06
7.04
7.03
6.84
6.82
6.66
5.75
5.74
2.83
2.54
2.33
2.20
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1.00
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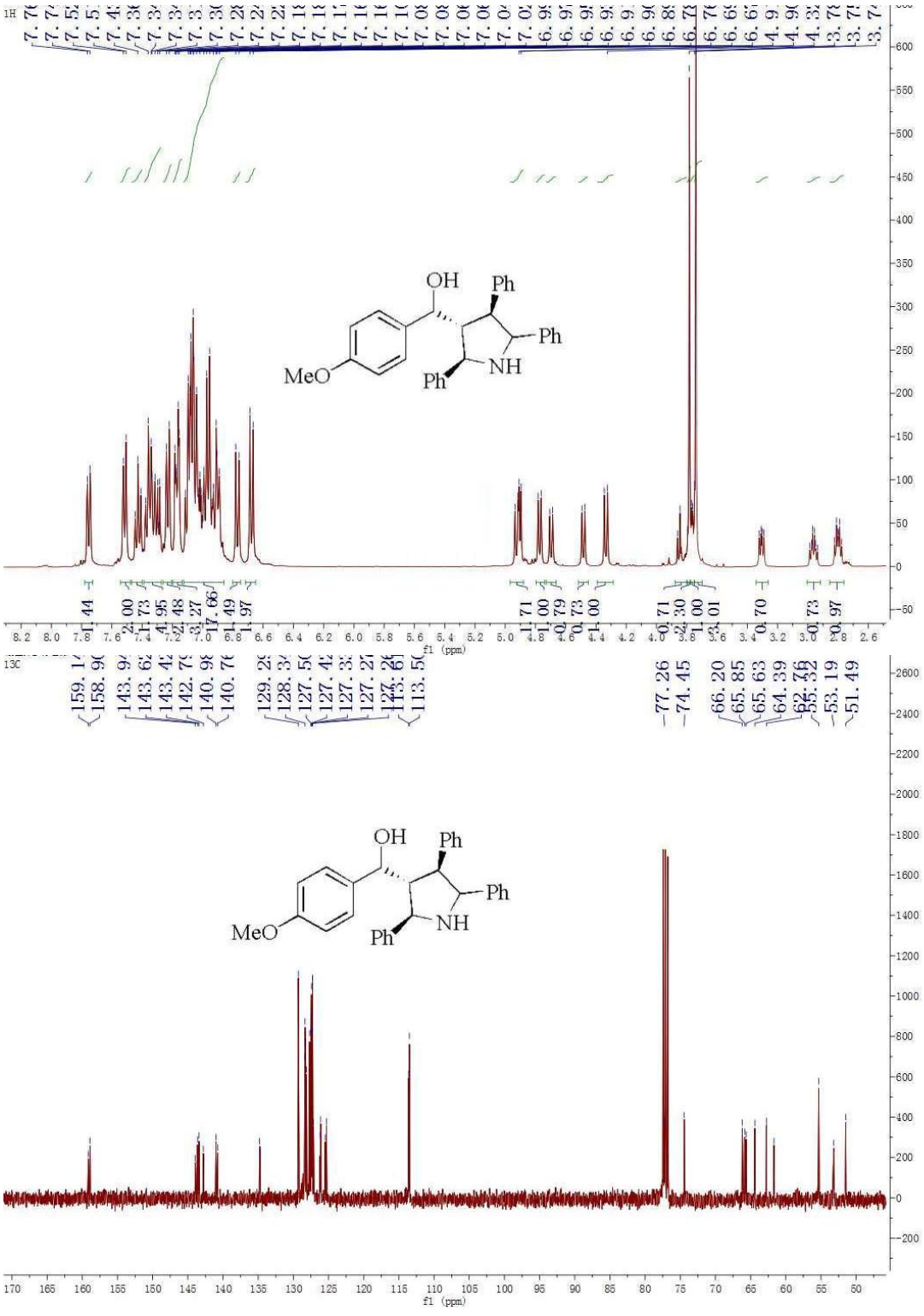
1.04
1.01

4



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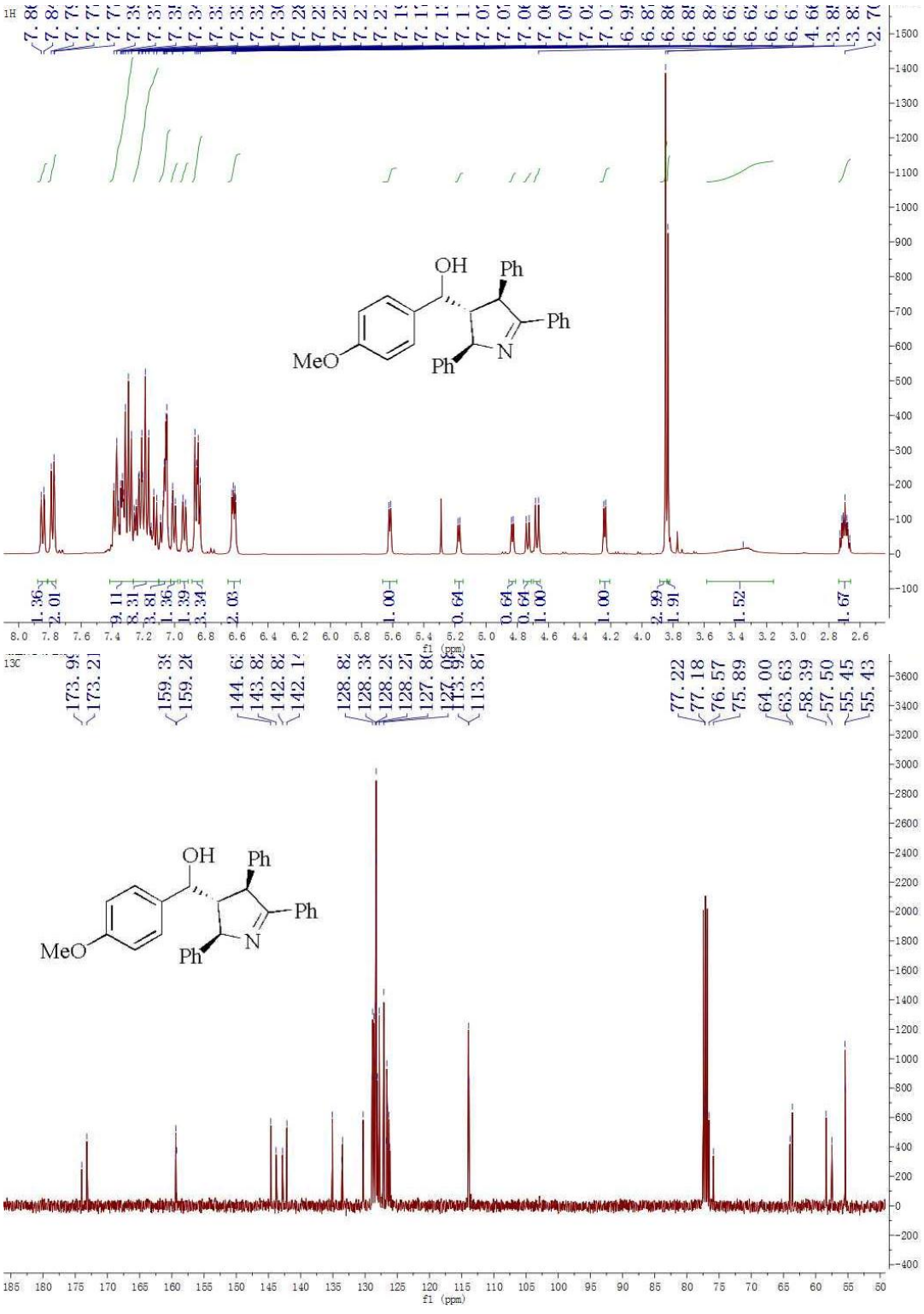

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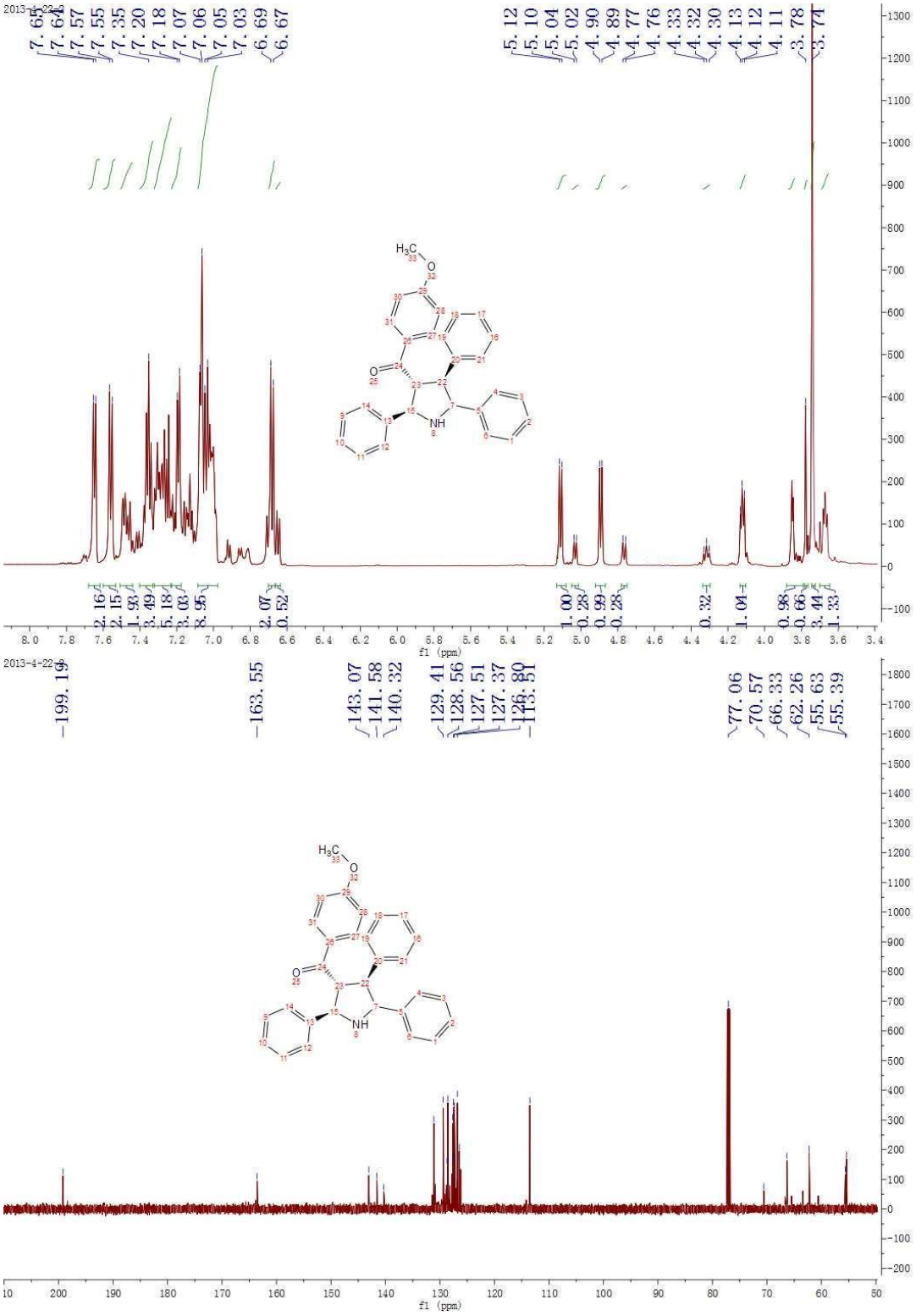
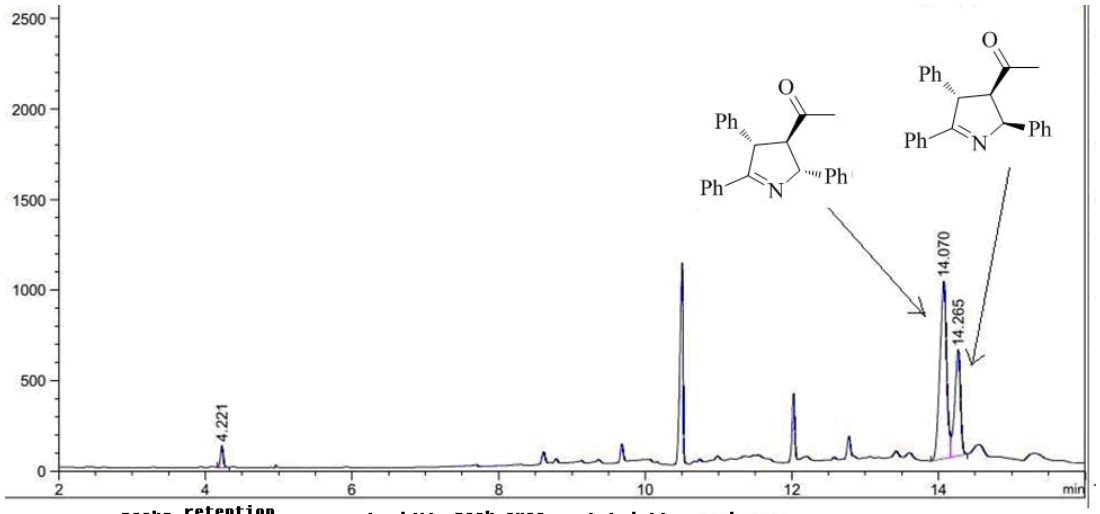

7.65
7.64
7.57
7.55
7.35
7.20
7.18
7.07
7.06
7.05
7.03
6.69
6.67
5.12
5.10
5.04
5.02
4.90
4.89
4.77
4.76
4.33
4.32
4.30
4.13
4.12
4.11
3.78
3.74
f1 (ppm)
199.19
163.55
143.07
141.58
140.32
129.41
128.56
127.51
127.37
126.80
115.51
77.06
70.57
66.33
62.26
55.63
55.39
f1 (ppm)

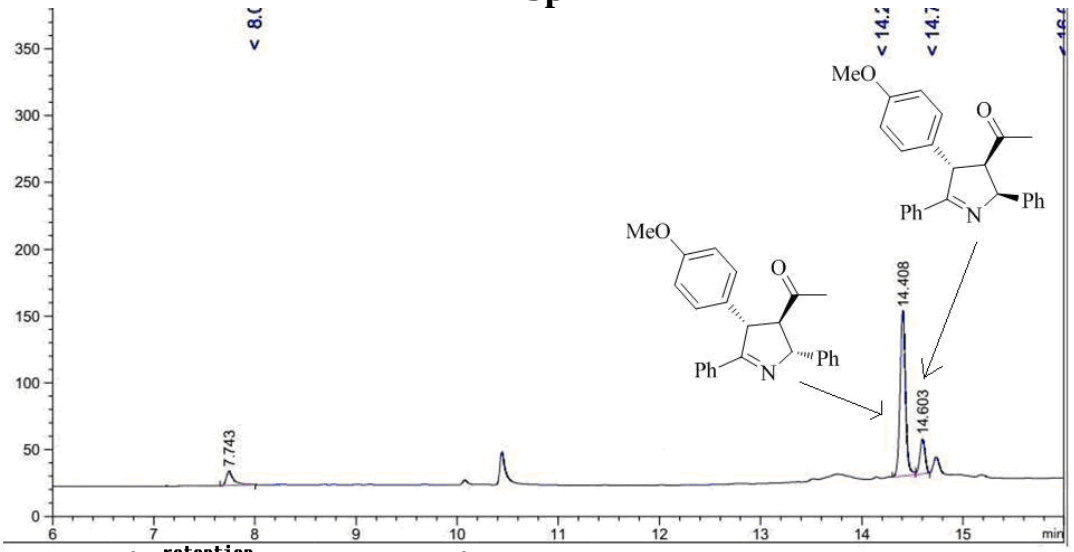
2. GC spectra of 3ao-3co

3o



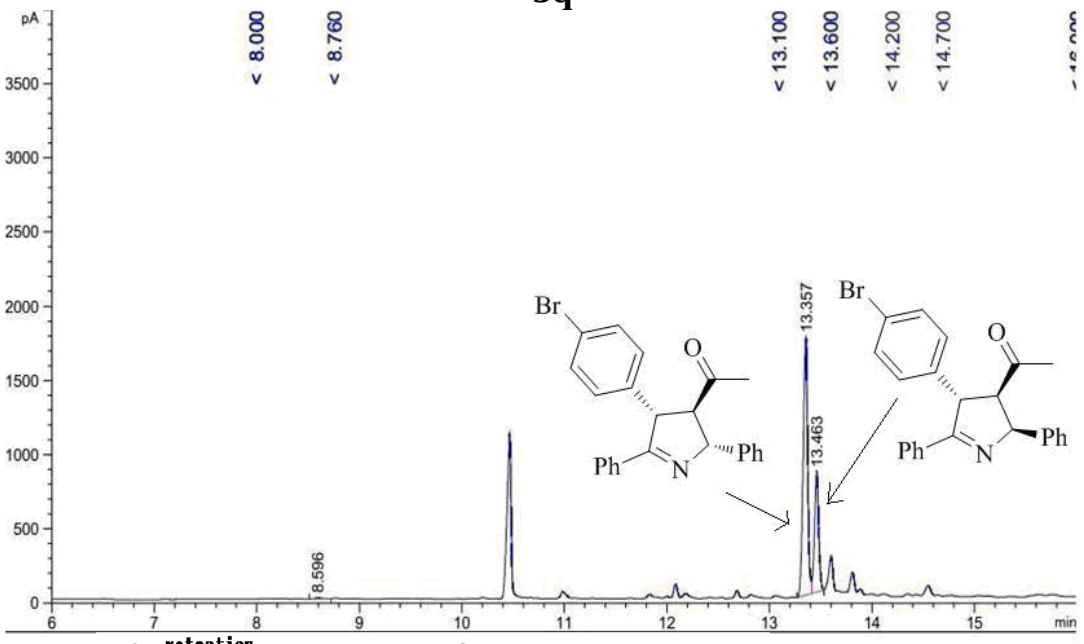
peaks #	retention time [min]		peak width [min]	peak area [pA*s]	peak height [pA]	peak area %
1	4.221	VV	0.0413	324.00232	120.63481	3.32338
2	14.070	BV	0.0886	6242.26221	976.60394	64.02862
3	14.265	VB	0.0784	3182.91040	585.58417	32.64800

3p



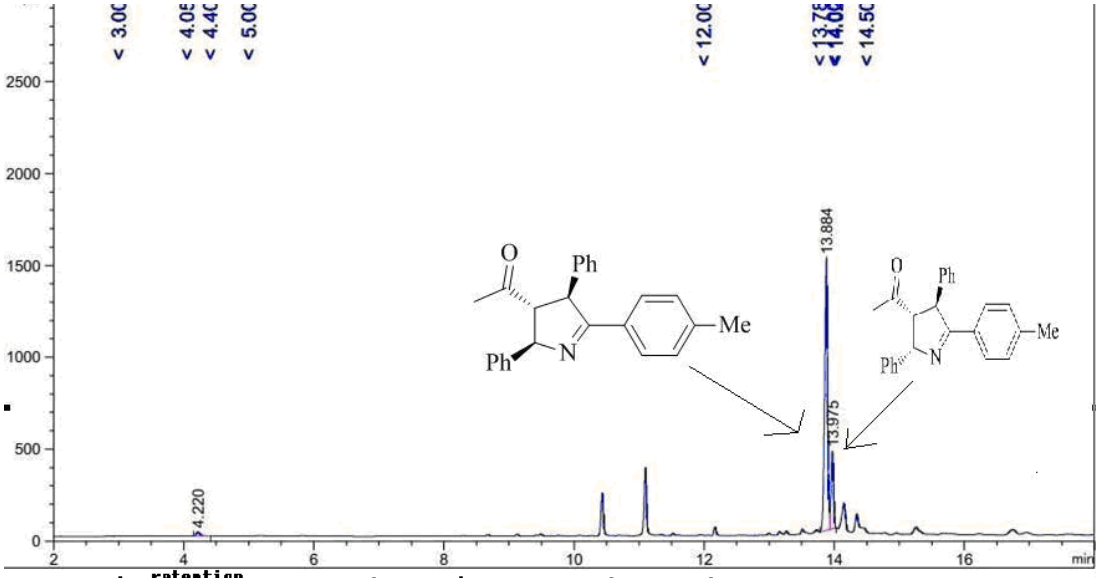
peaks #	retention time [min]		peak width [min]	peak area [pA*s]	peak height [pA]	peak area %
1	7.743	BBA	0.0723	55.38268	10.71849	9.07626
2	14.408	BV	0.0556	461.24826	123.52940	75.59060
3	14.603	VB	0.0563	93.56167	25.79592	15.33314

3q



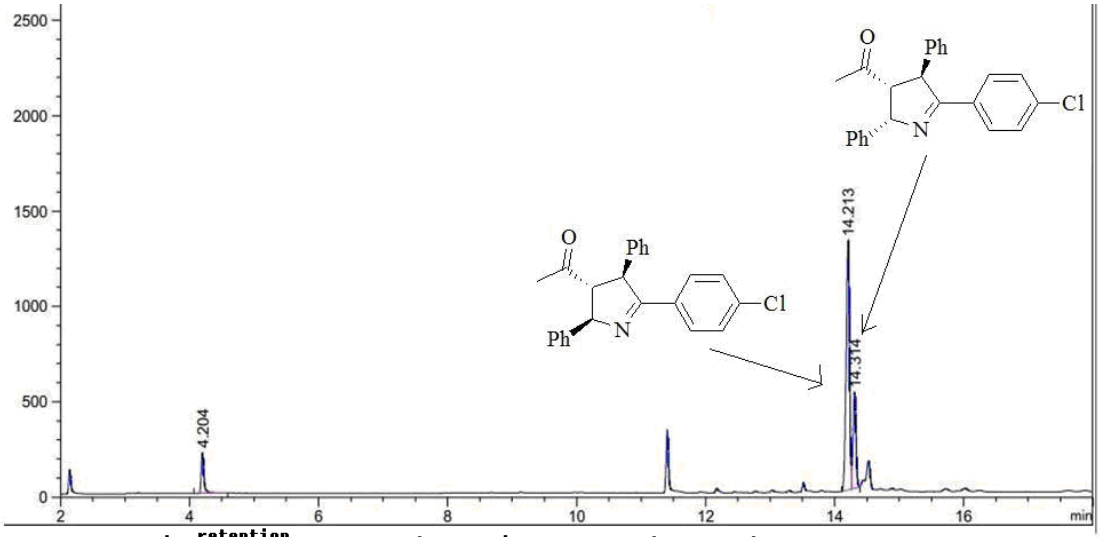
peaks #	retention time [min]		peak width [min]	peak area [pA*s]	peak height [pA]	peak area %
1	8.596	BB	0.0612	39.03310	9.65267	0.51333
2	13.357	BV	0.0465	5281.03271	1733.61658	69.45225
3	13.463	VB	0.0428	2283.76709	812.15955	30.03442

3r



peaks #	retention time [min]		peak width [min]	peak area [pA*s]	peak height [pA]	peak area %
1	4.220	BBA	0.0580	96.32767	24.42641	1.64032
2	13.884	BV	0.0462	4594.16064	1479.32654	78.23195
3	13.975	VBA	0.0427	1181.99792	421.30643	20.12773

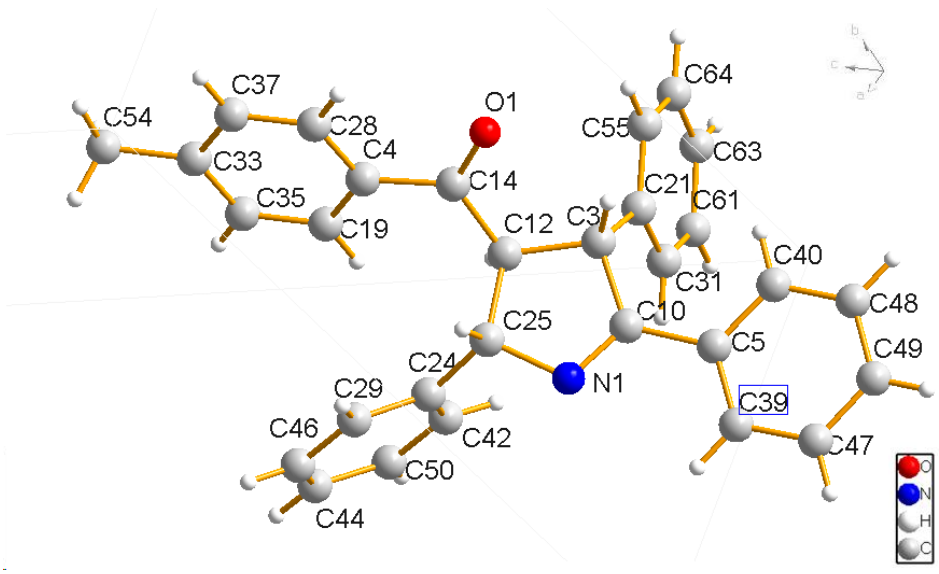
3s

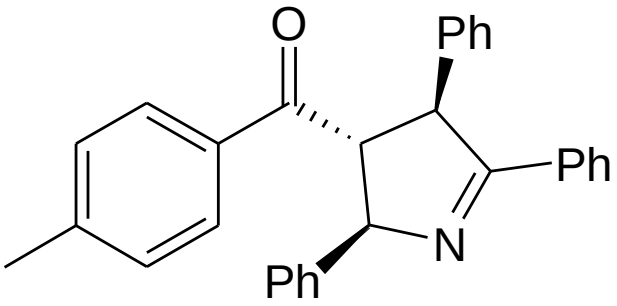


peaks #	retention time [min]		peak width [min]	peak area [pA*s]	peak height [pA]	peak area %
1	4.204	BB	0.0465	653.63824	214.83203	9.20424
2	14.213	BV	0.0541	4814.56396	1302.87073	67.79654
3	14.314	VB	0.0502	1633.28674	505.11649	22.99922

3. X-ray data of 3ab, 3ao, 3ar and 3at

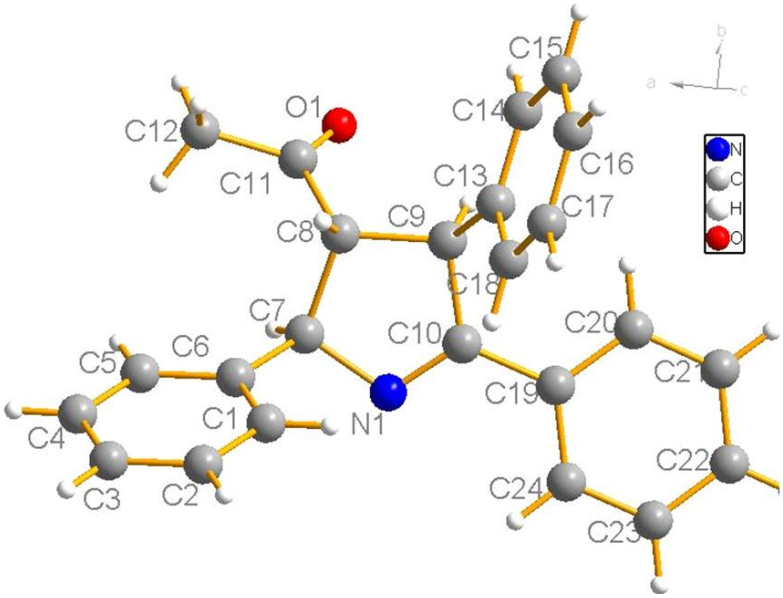
3b

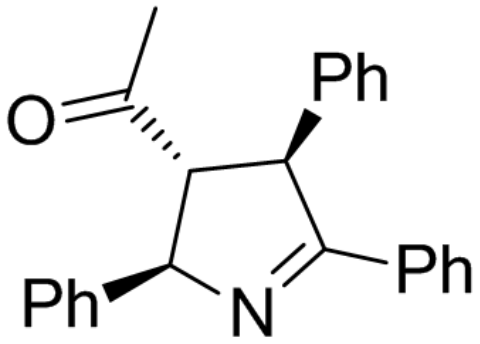




Crystal data for 3b: $C_{30}H_{27}NO$ (417.21), Triclinic, P-1, a = 9.6811(7) Å, alpha = 67.492(4) deg. b = 14.0805(11) Å, beta = 88.996(4) deg. c = 18.2882(14) Å, gamma = 83.445(4) deg. *U* = 2287.1(3) $Å^3$, Z = 4, *T* = 296(2) K, absorption coefficient 0.069 mm^{-1}, reflections collected 37416, unique 10498 [R(int) = 0.0768], refinement by Full-matrix least-squares on F^2, data/ restraints/ parameters 10498 / 0 / 579, goodness-of-fit on F^2 = 1.003, final *R* indices [*I>2sigma(I)*] R1 = 0.0556, wR2 = 0.1254, *R* indices (all data) R1 = 0.1346, wR2 = 0.1607, largest diff. peak and hole 0.193 and -0.350 e. $Å^{-3}$.

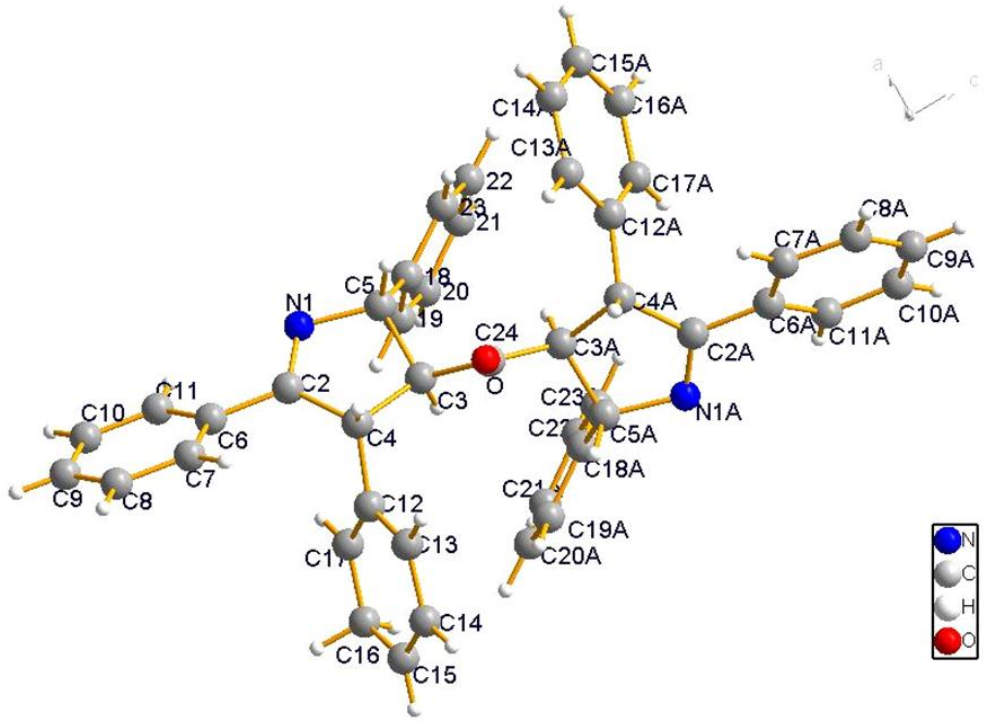
3o

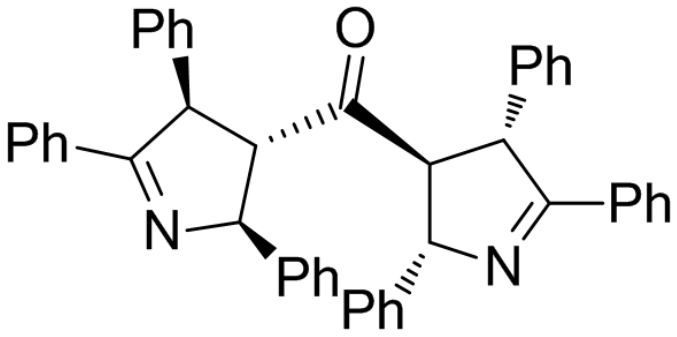




Crystal data for 3o: $C_{24}H_{21}NO$ (339.16), Monoclinic, P2(1)/n, a = 8.7440(2) Å, alpha = 90.00 deg. b = 16.3482(3) Å, beta = 96.6940 deg. c = 13.1750(7) Å, gamma = 90.00 deg. *U* = 1870.51(7) $Å^3$, Z = 12, *T* = 296(2) K, absorption coefficient 0.073 mm^{-1}, reflections collected 29598, unique 4285 [R(int) = 0.0383], refinement by Full-matrix least-squares on F^2, data/ restraints/ parameters 4285 / 0 / 236, goodness-of-fit on F^2 = 1.076, final *R* indices [*I>2sigma(I)*] R1 = 0.0506, wR2 = 0.1555, *R* indices (all data) R1 = 0.0736, wR2 = 0.1403, largest diff. peak and hole 0.172 and -0.492 e. $Å^{-3}$.

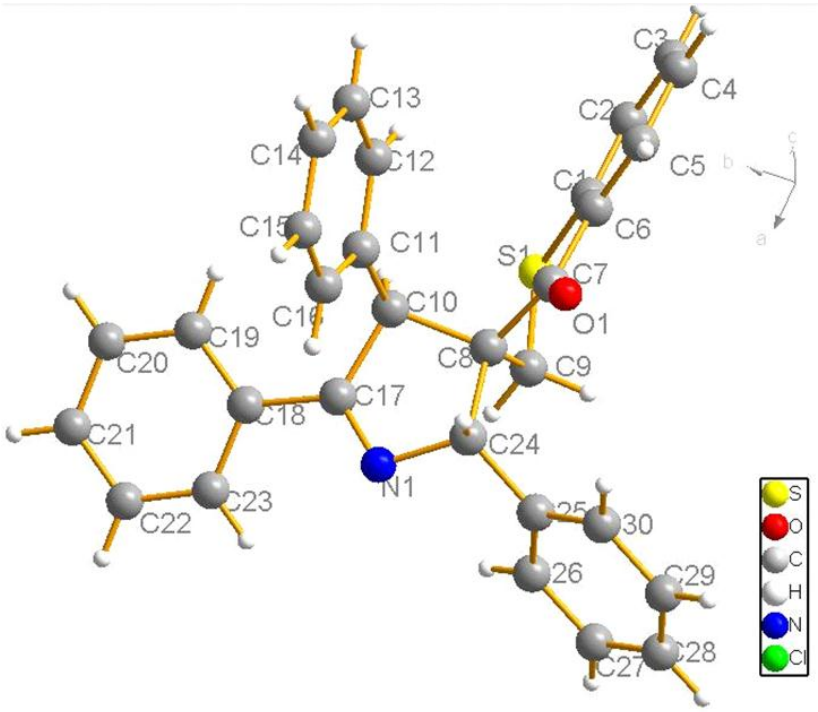
3t

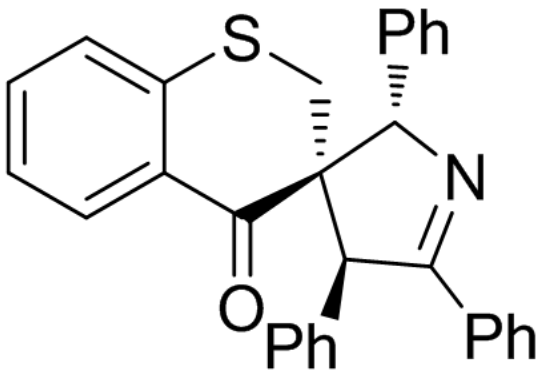




Crystal data for 3t: $C_{45}H_{36}N_2O$ (620.28), Trigonal, P3(2), a = 9.2770(3) Å, alpha = 90 deg. b = 9.2770(3) Å, beta = 90 deg. c = 34.749(3) Å, gamma = 120 deg. *U* = 2589.9(2) $Å^3$, Z = 17, *T* = 296(2) K, absorption coefficient 0.071 mm^{-1}, reflections collected 13698, unique 6868 [R(int) = 0.0787], refinement by Full-matrix least-squares on F^2, data/ restraints/ parameters 6868 / 1 / 434, goodness-of-fit on F^2 = 0.921, final *R* indices [*I>2sigma(I)*] R1 = 0.0596, wR2 = 0.1175, *R* indices (all data) R1 = 0.1998, wR2 = 0.1684, largest diff. peak and hole 0.139 and -0.134 e. $Å^{-3}$.

3v





Crystal data for 3v $C_{30}H_{23}NOS+0.5\ CCl_2H_2$ (488.02), Triclinic, P-1, a = 39.108(4) Å, alpha = 90 deg. b = 8.1605(8) Å, beta = 111.789(8) deg. c = 16.4308(15) Å, gamma = 90 deg. *U* = 4869.1(8) $Å^3$, Z = 8, *T* = 293(2) K, absorption coefficient 0.267 mm^{-1}, reflections collected 36193, unique 5614 [R(int) = 0.0587], refinement by Full-matrix least-squares on F^2, data/ restraints/ parameters 5614 / 0 / 313, goodness-of-fit on F^2 = 1.125, final *R* indices [*I>2sigma(I)*] R1 = 0.0463, wR2 = 0.1272, *R* indices (all data) R1 = 0.0767, wR2 = 0.1416, largest diff. peak and hole 0.451 and -0.471 e. $Å^{-3}$.