Supporting Information

$ZnCl_2$-promoted Domino Reaction of 2-Hydroxybenzonitriles with Ketones for Synthesis of Benzoxazinones

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Content

Crystal data and structure refinement for 3a

The crystal structure of **3a** was assigned to THF. A summary of the crystal data is given in Table **S1** and **S2**. with the structure depicted in the main text, where ellipsoids have been drawn at the 50% probability level. Single crystals of **3a** were mounted with glue on glass fiber and crystal data were collected on the Xcalibur, Eos, Gemini diffractometer equipped with graphite-monochromated MoKα radiation (λ = 0.7107 Å). Empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 (Sheldrick, 1997) program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1536185 (**3a**). Copies of the data can be obtained, free of charge, on application to CCDC,12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table S1

Crystallographic Data and Structure Refinement for compound **3a**

Identification code	**3a**
Empirical formula	$C_{13}H_{15}NO_2$
Formula weight	217.26
Temperature / K	104.9
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å, b / Å, c / Å	6.8238(3), 14.8389(7), 10.8490(3)
α/°, β/°, γ/°	90.00, 96.975(3), 90.00

Volume / $Å^3$	1090.41(8)
Z	4
ρ_{calc} / mg mm^{-3}	1.323
μ / mm^{-1}	0.089
F(000)	464
Crystal size / mm^3	0.45 × 0.45 × 0.40
2Θ range for data collection	3.3 to 29.6°
Index ranges	$-8 \le h \le 8$, $-12 \le k \le 18$, $-13 \le l \le 8$
Reflections collected	4531
Independent reflections	2146[R(int) = 0.0216 (inf-0.9Å)]
Data/restraints/parameters	2146/0/145
Goodness-of-fit on F^2	1.050
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0396, wR_2 = 0.0877
Final R indexes [all data]	R_1 = 0.0486, wR_2 = 0.0930
Largest diff. peak/hole / e $Å^{-3}$	0.209/-0.256
Flack Parameters	N
Completeness	0.999

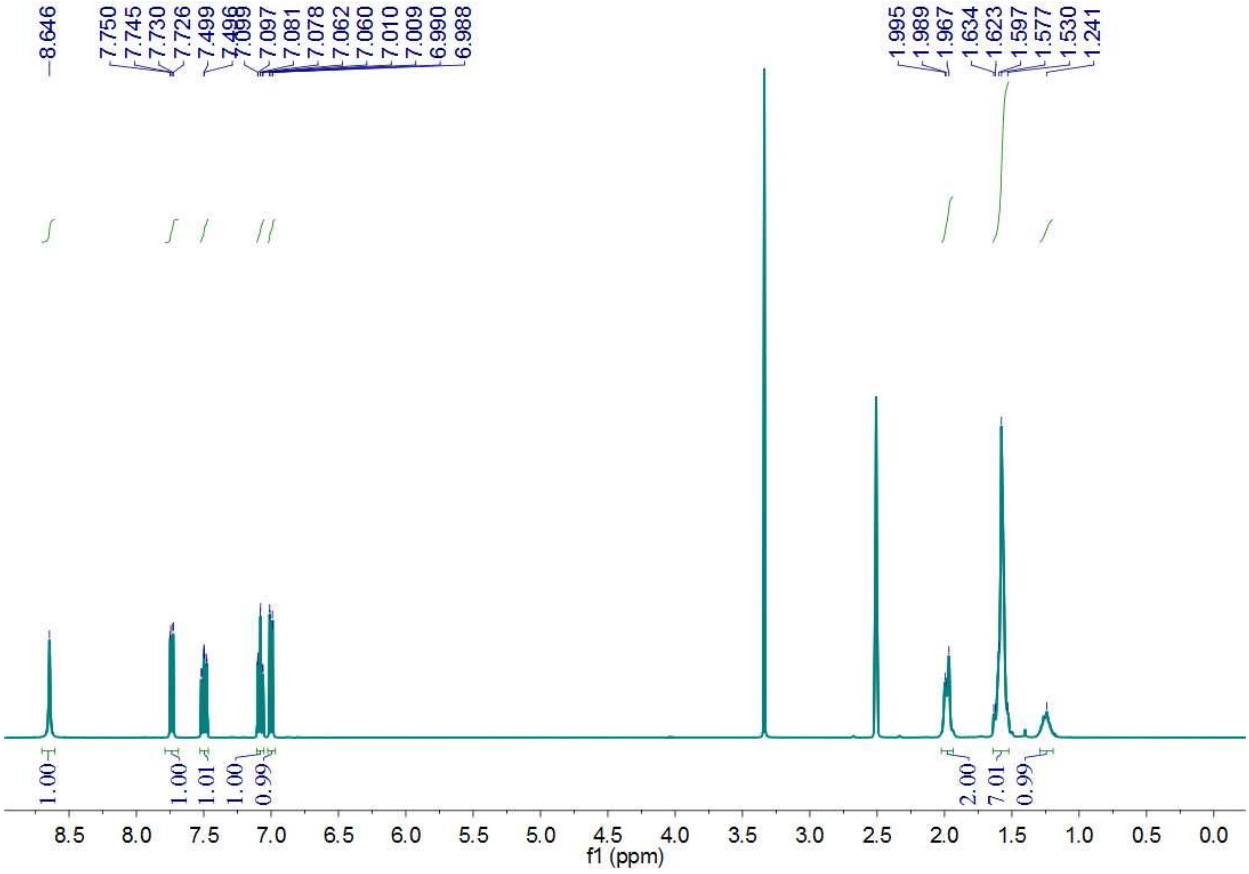
Table S2

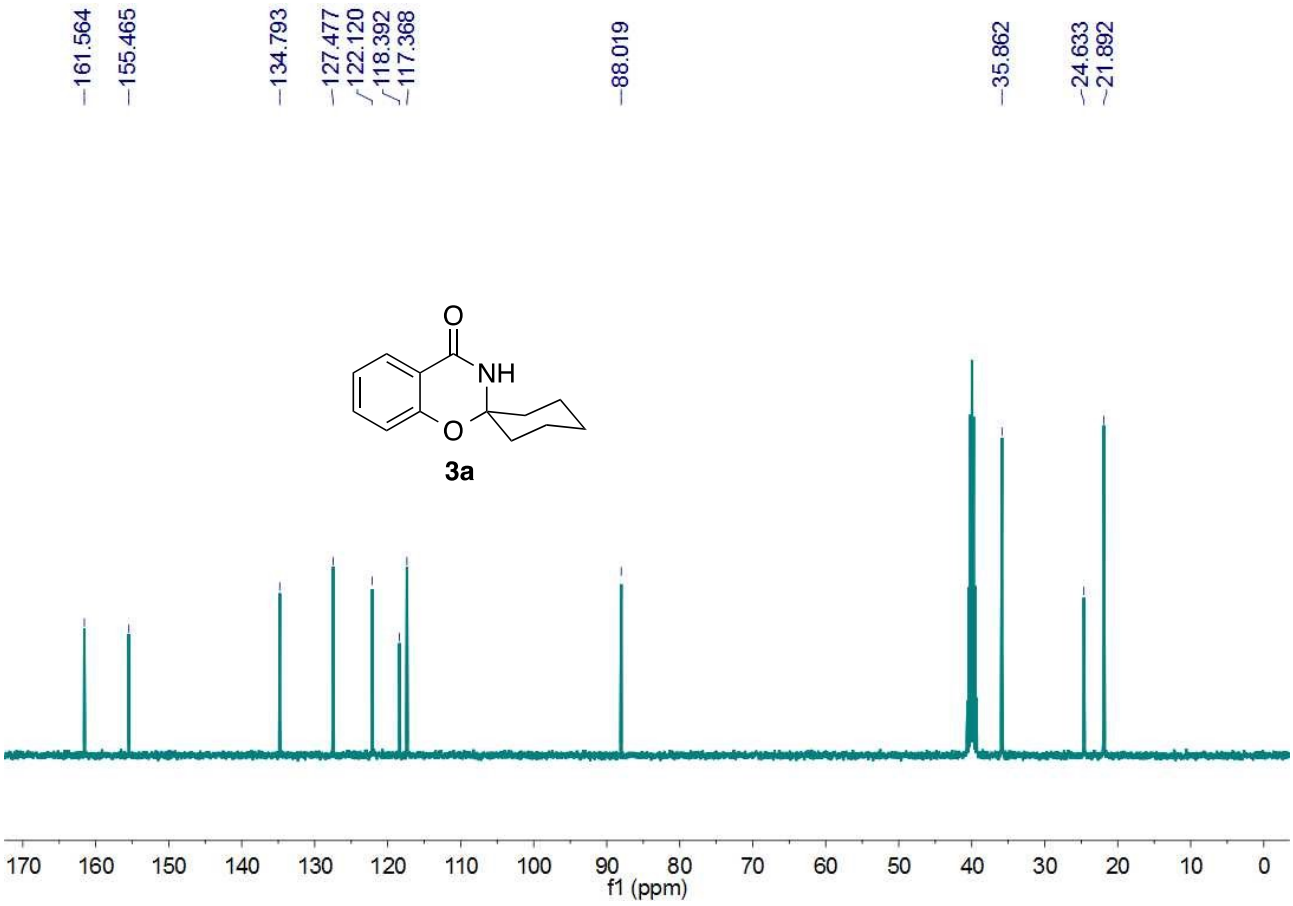
Bond Lengths (Å) and Bond Angles (°) of **3a**

Bond	Dist.	Bond	Dist.
O2-C1	1.2424(16)	C4-C5	1.386(2)
O1-C3	1.3748(16)	C9-C10	1.5248(18)
O1-C8	1.4484(16)	C9-C8	1.5286(19)
N1-C1	1.3449(17)	C10-C11	1.5268(19)
N1-C8	1.4617(16)	C13-C12	1.5275(18)
C2-C3	1.3954(19)	C13-C8	1.5180(18)
C2-C1	1.4820(19)	C5-C6	1.395(2)

C2-C7	1.3979(19)	C11-C12	1.5294(19)
C4-C3	1.3921(19)	C7-C6	1.386(2)
Angle	(°)	Angle	(°)
C1-O1-C8	114.23(10)	O2-C1-N1	122.57(12)
C1-N1-C8	122.15(11)	O2-C1-C2	122.83(12)
C3-C2-C1	118.86(12)	N2-C1-C2	114.54(12)
C3-C2-C7	119.38(12)	C10-C11-C12	110.19(11)
C7-C2-C1	121.72(13)	C6-C7-C2	120.13(14)
C5-C4-C3	118.80(13)	C13-C12-C11	111.45(11)
C10-C9-C8	111.79(11)	O1-C8-N1	108.11(10)
O1-C3-N2	120.52(12)	O1-C8-C9	110.29(10)
O1-C3-C2	118.58(12)	O1-C8-C13	106.42(10)
C4-C3-C2	120.88(13)	N1-C8-C9	111.19(11)
C9-C10-C11	110.80(11)	N1-C8-C13	109.34(11)
C8-C13-C12	112.46(11)	C13-C8-C9	111.33(11)
C4-C5-C6	121.13(13)	C7-C6-C5	119.59(13)

The ^{1}H-NMR and^{13}C-NMR Spectra of products

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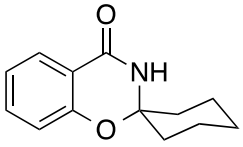
f1 (ppm)

3a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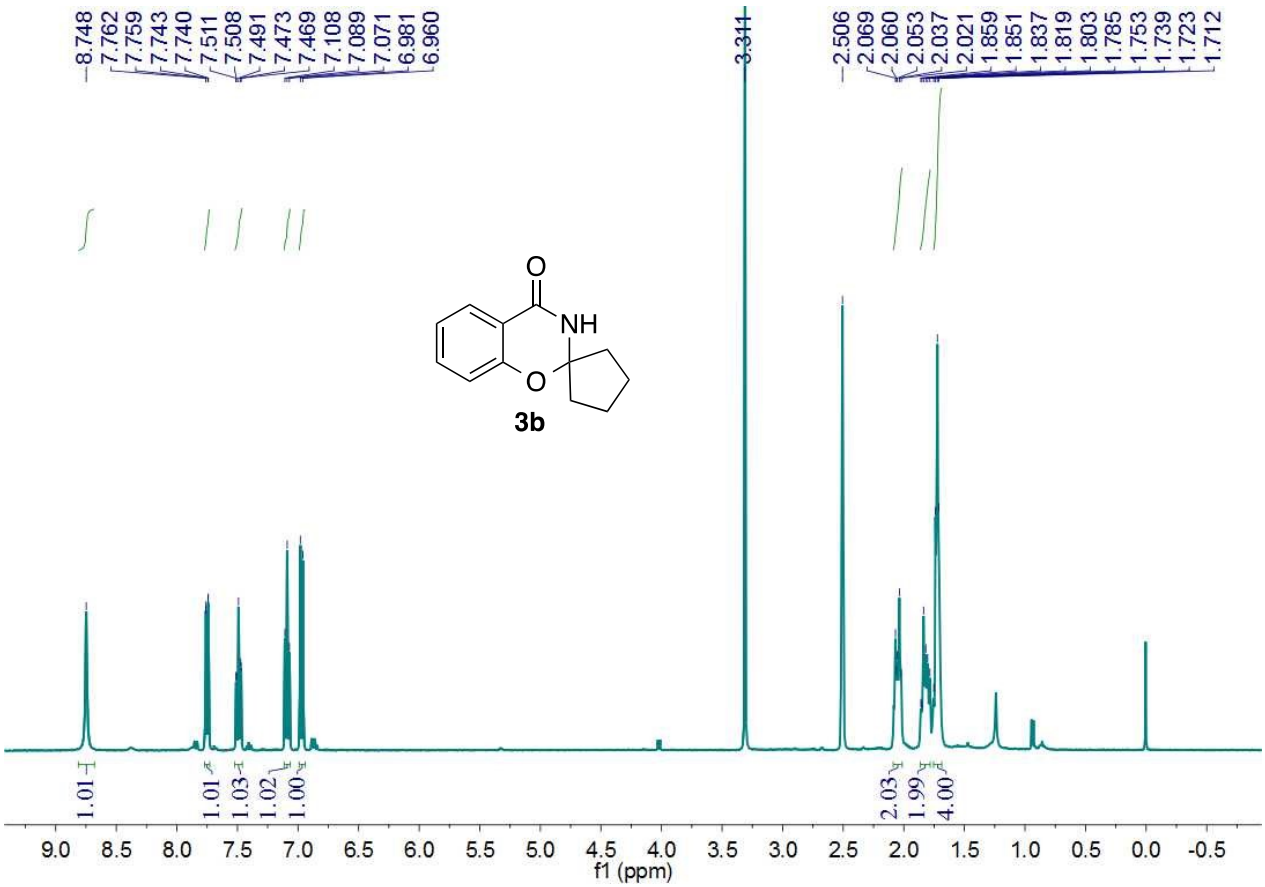
3a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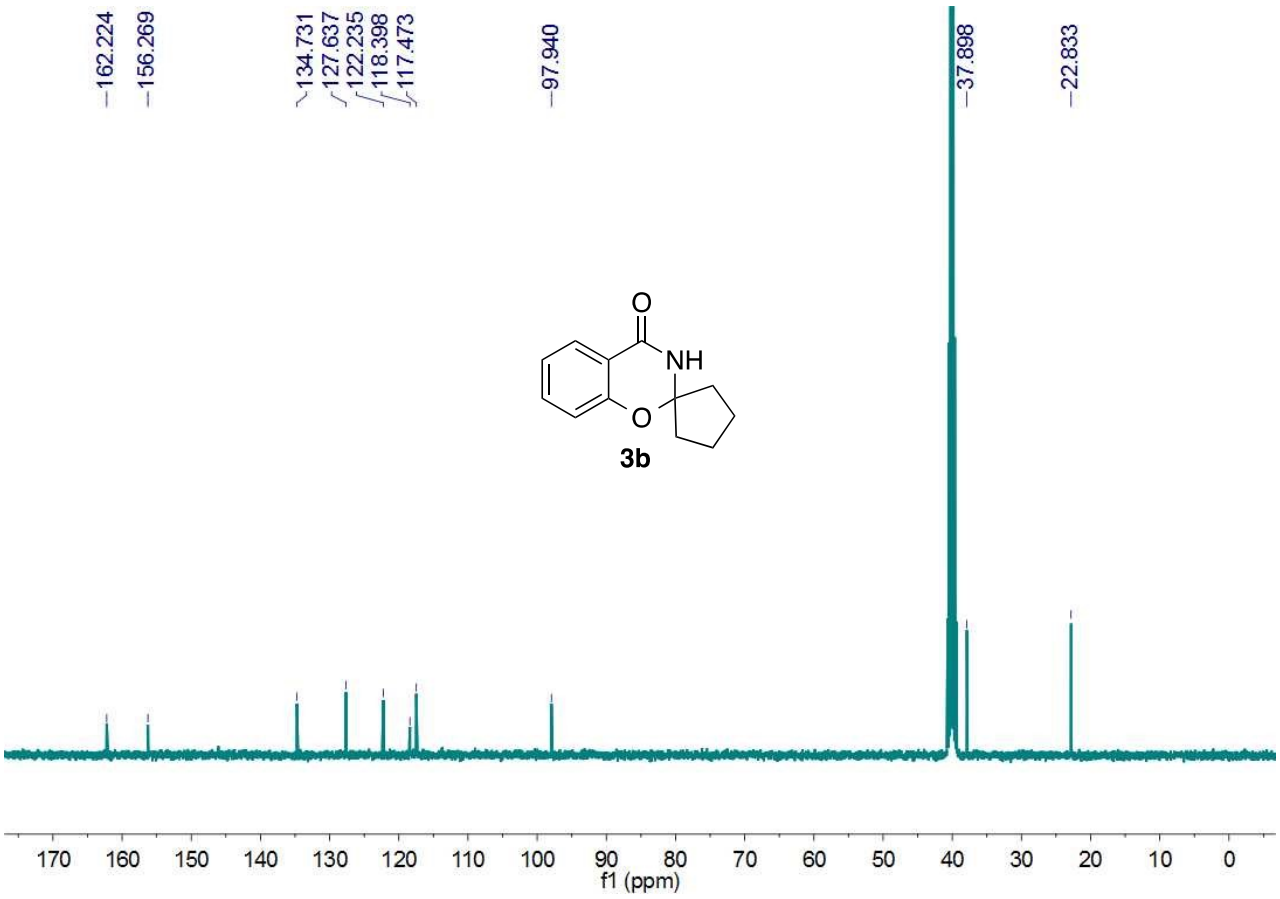
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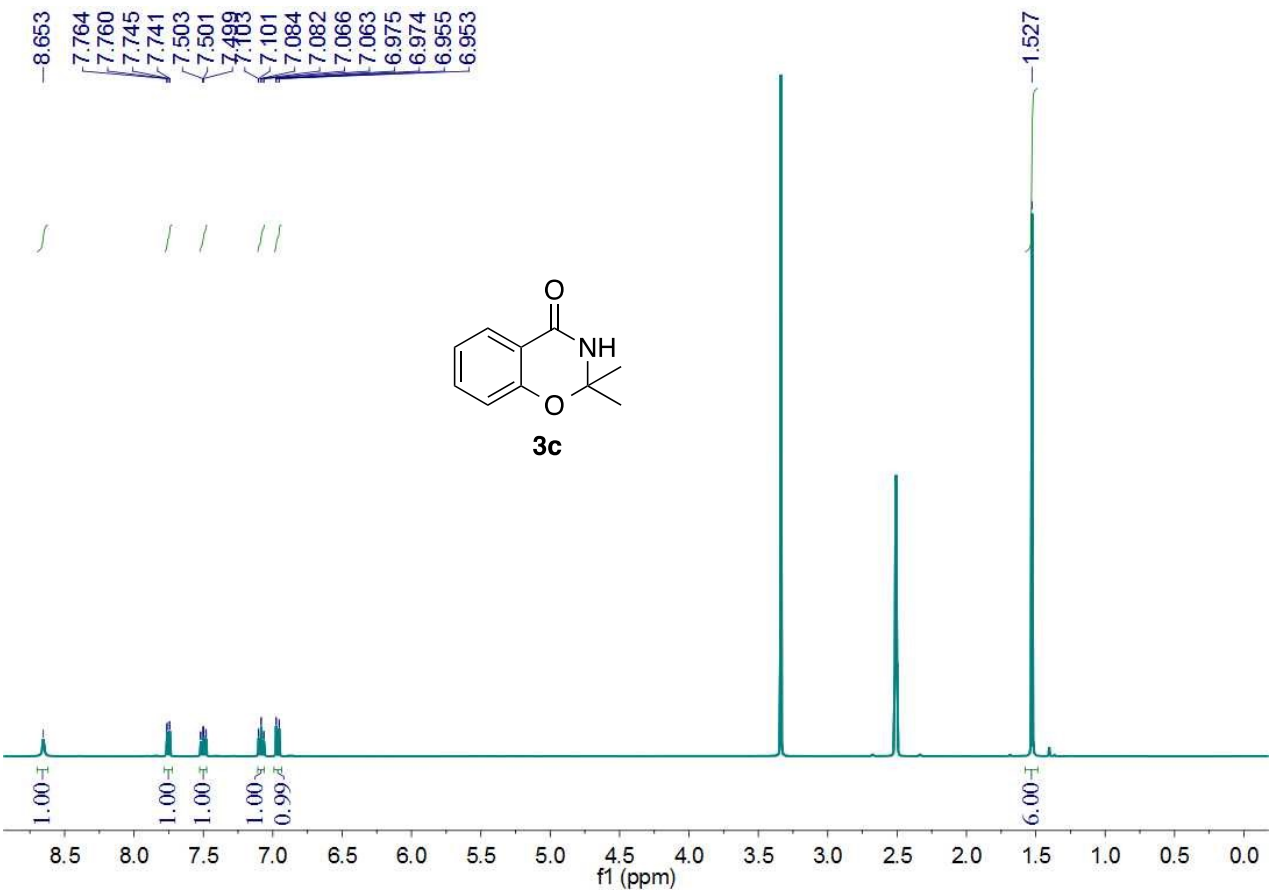
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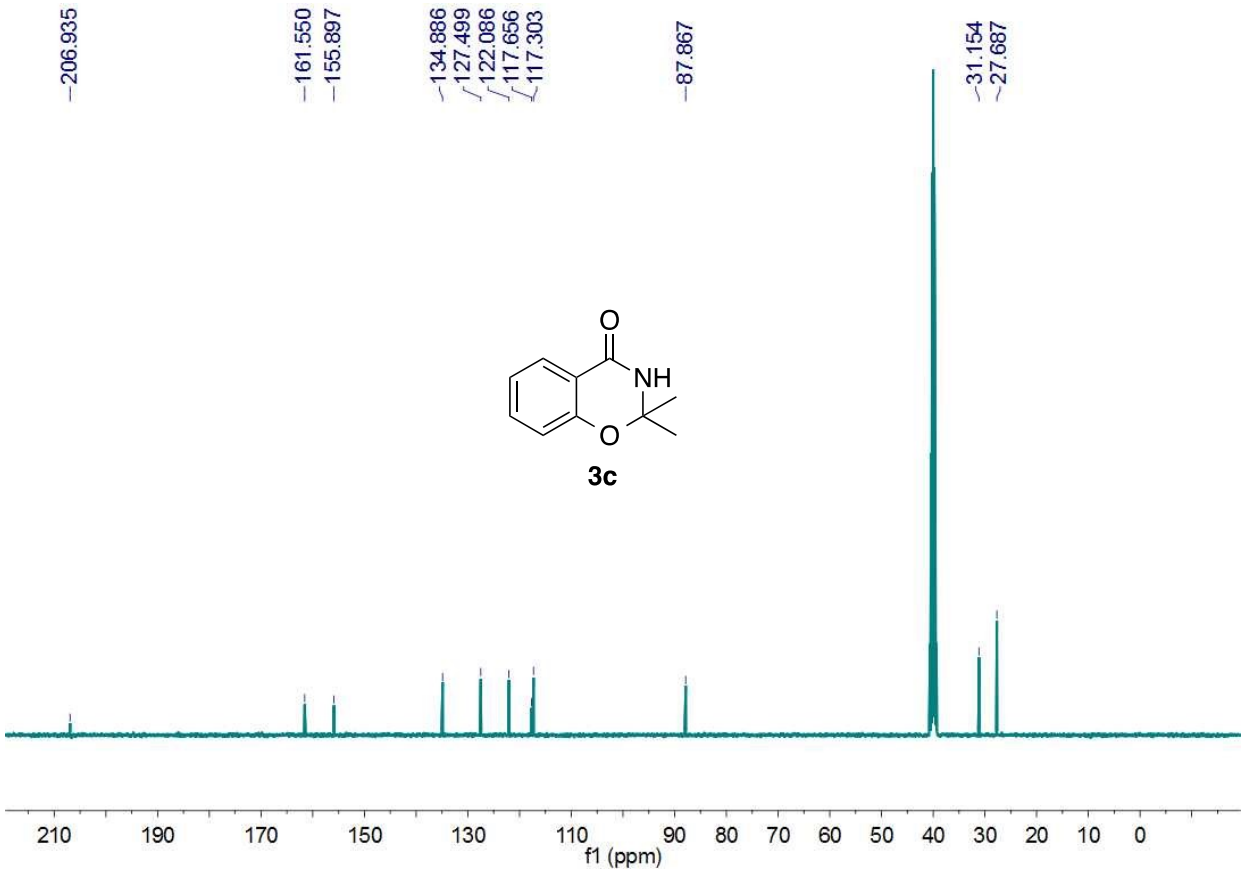
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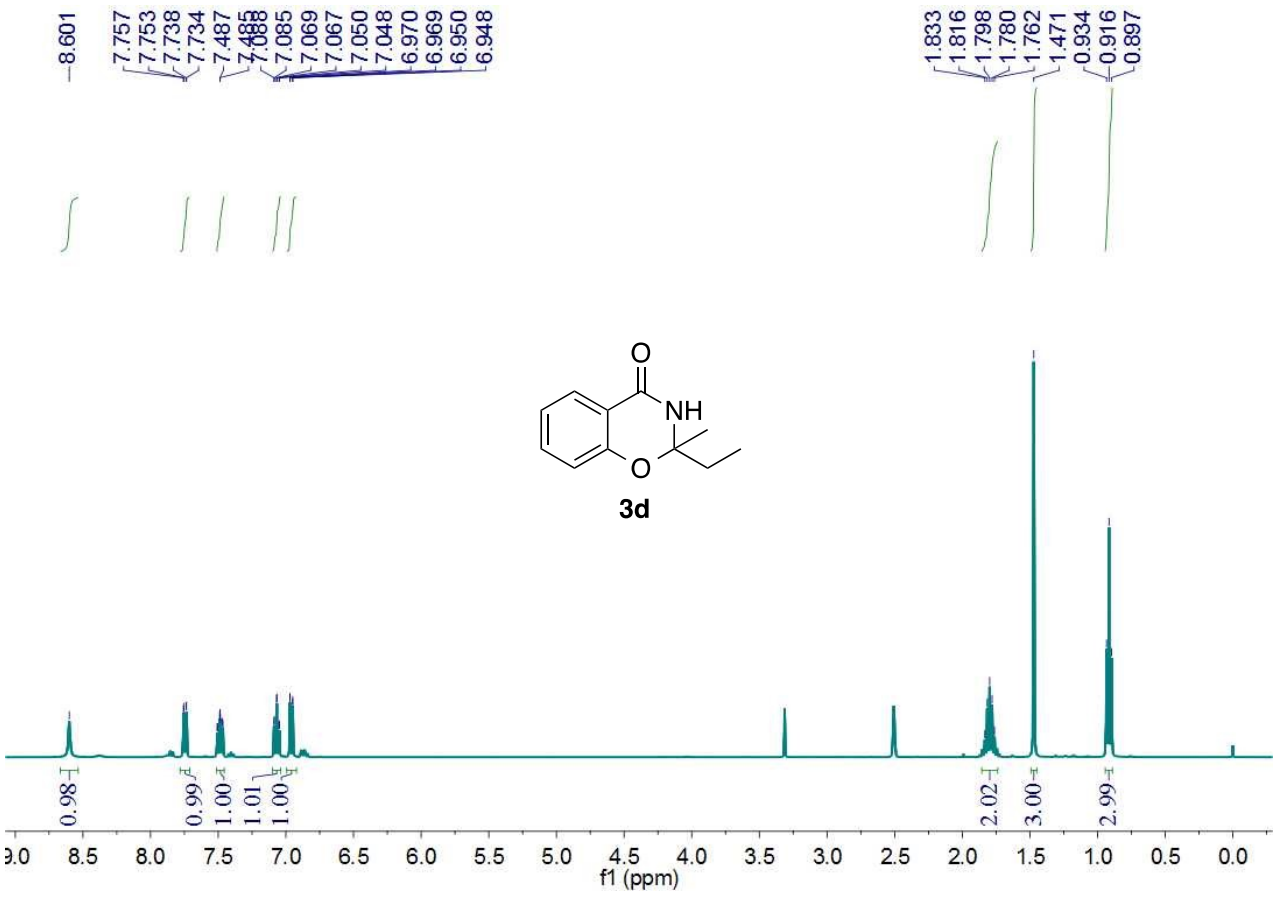
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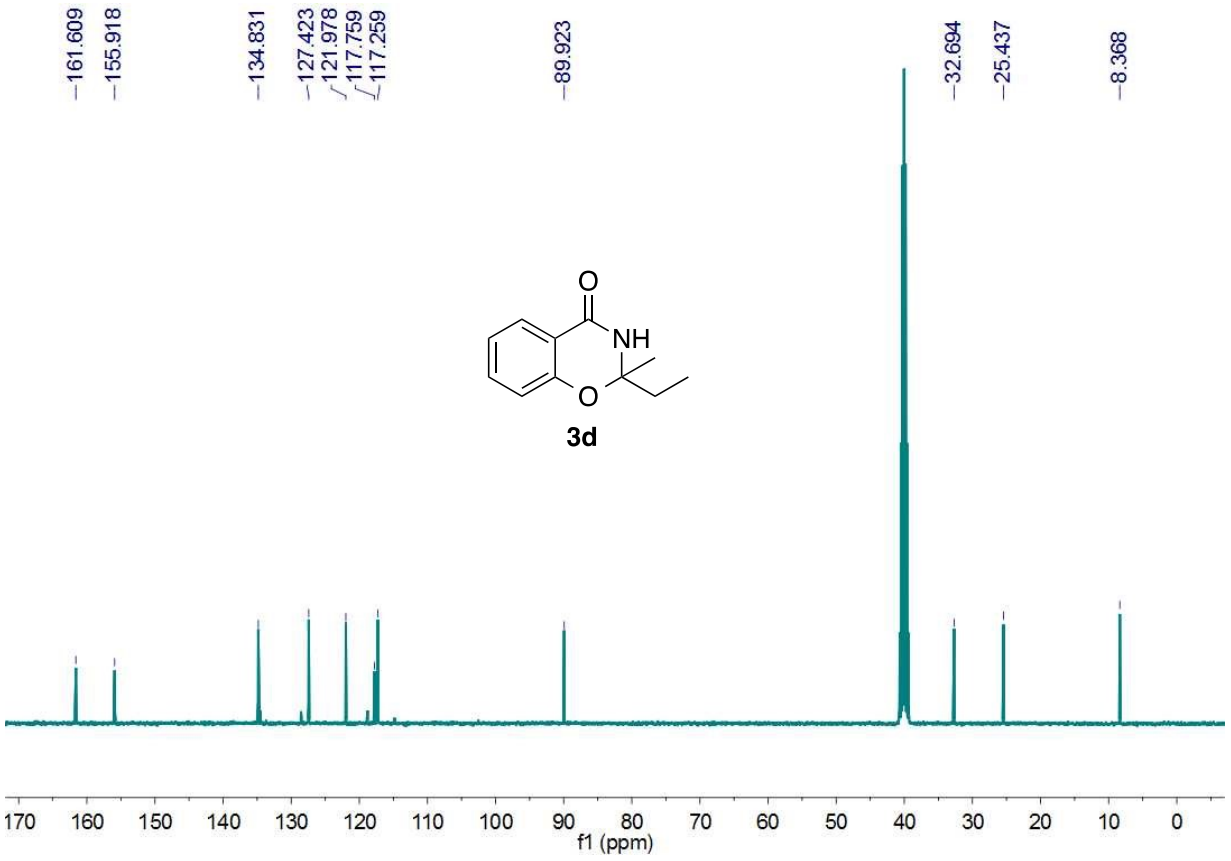
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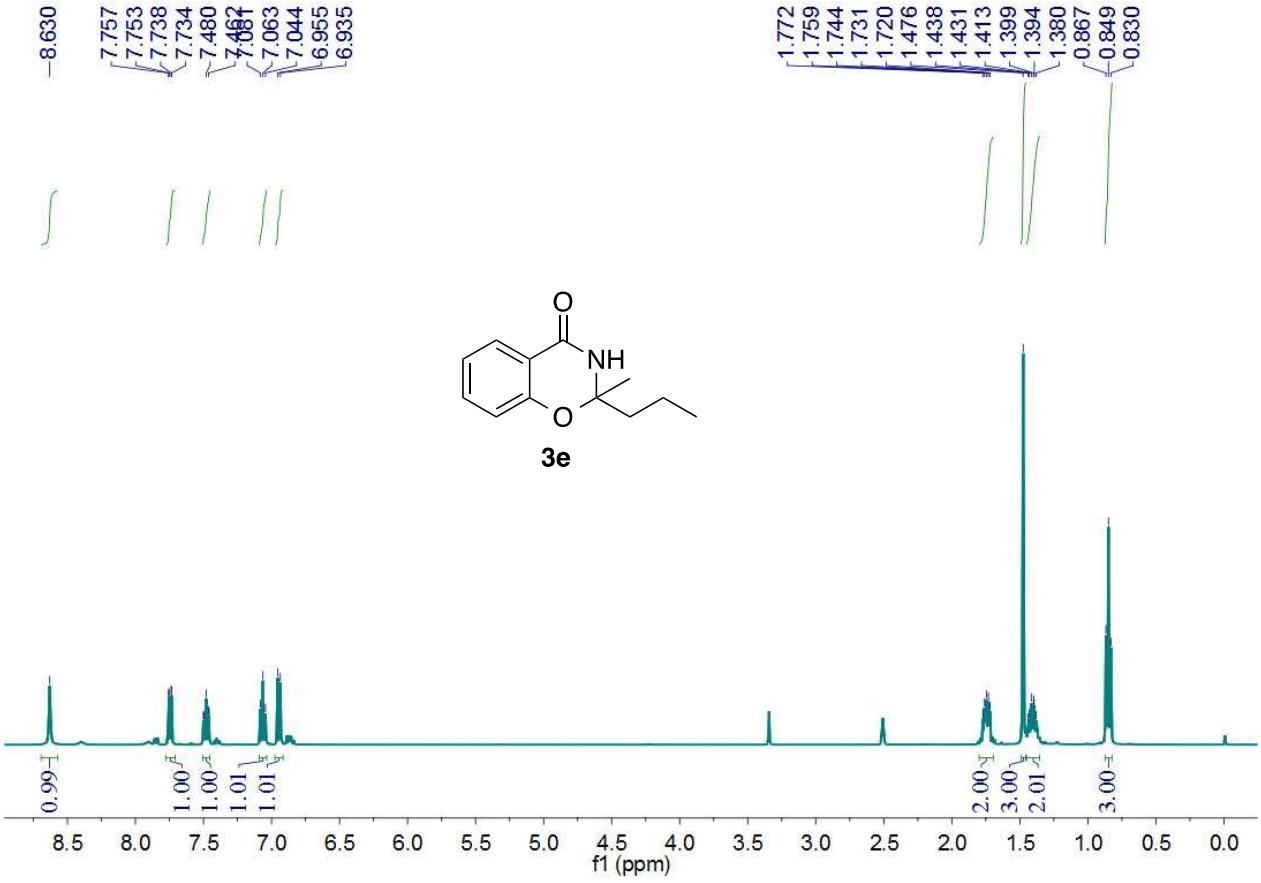
3d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2.01
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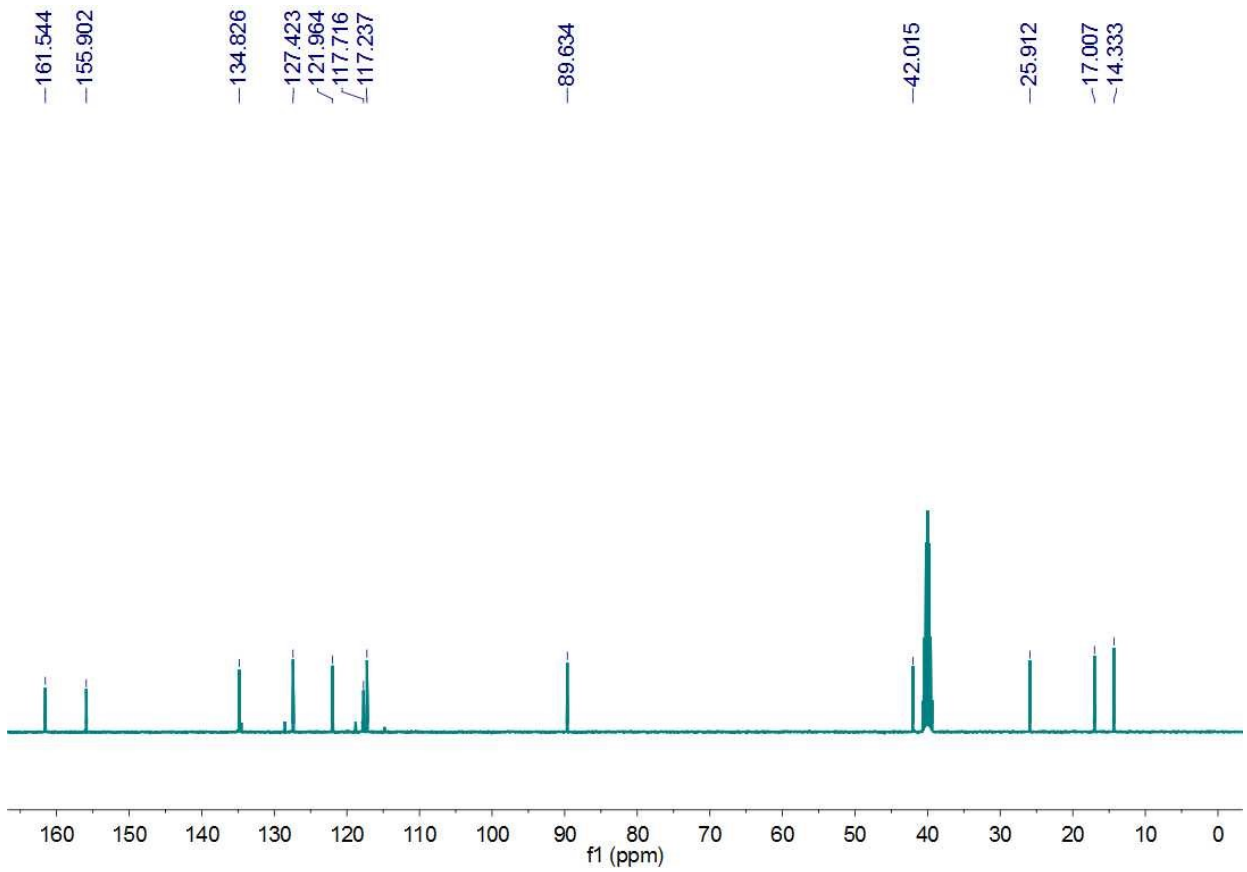
3e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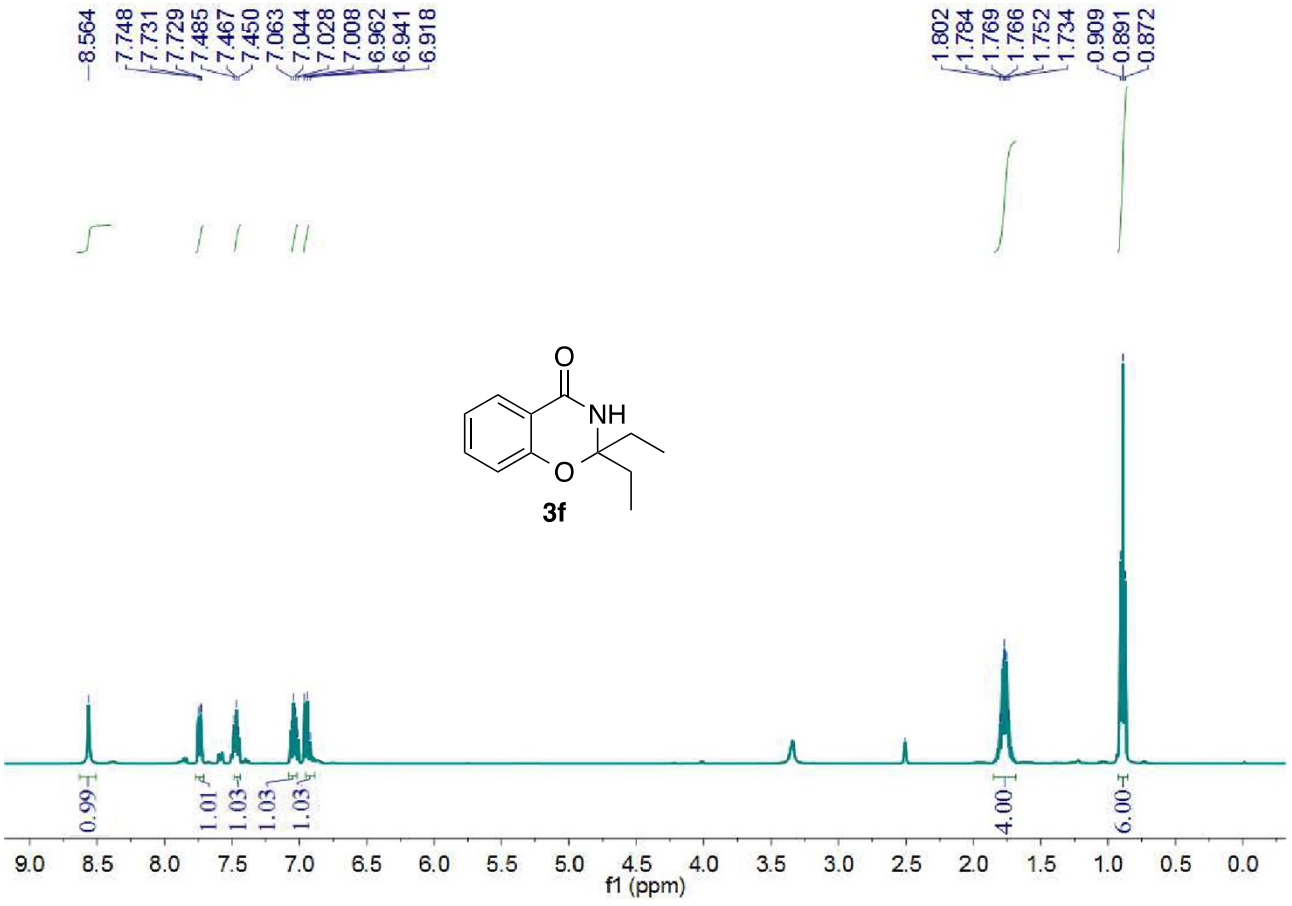
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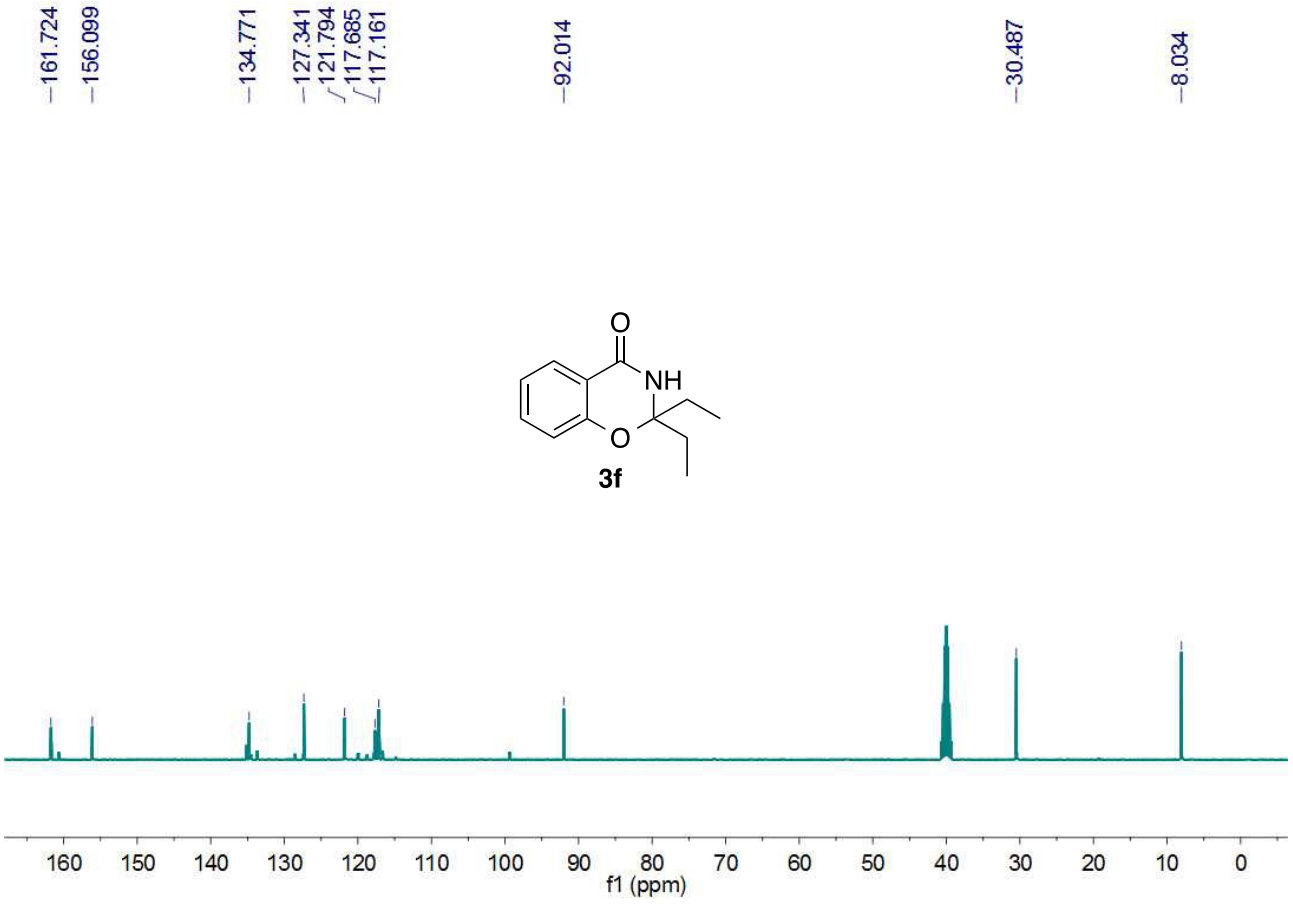
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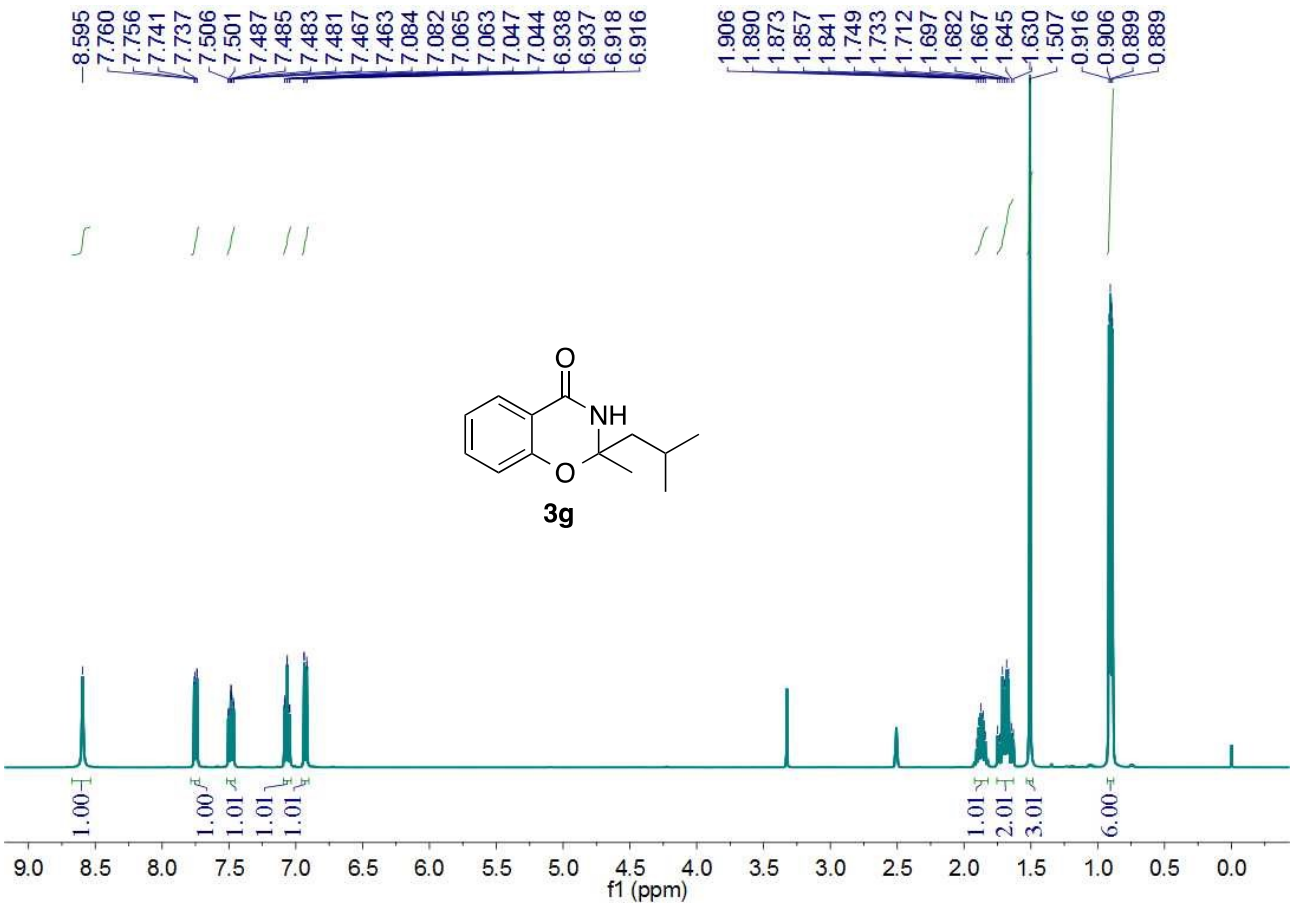
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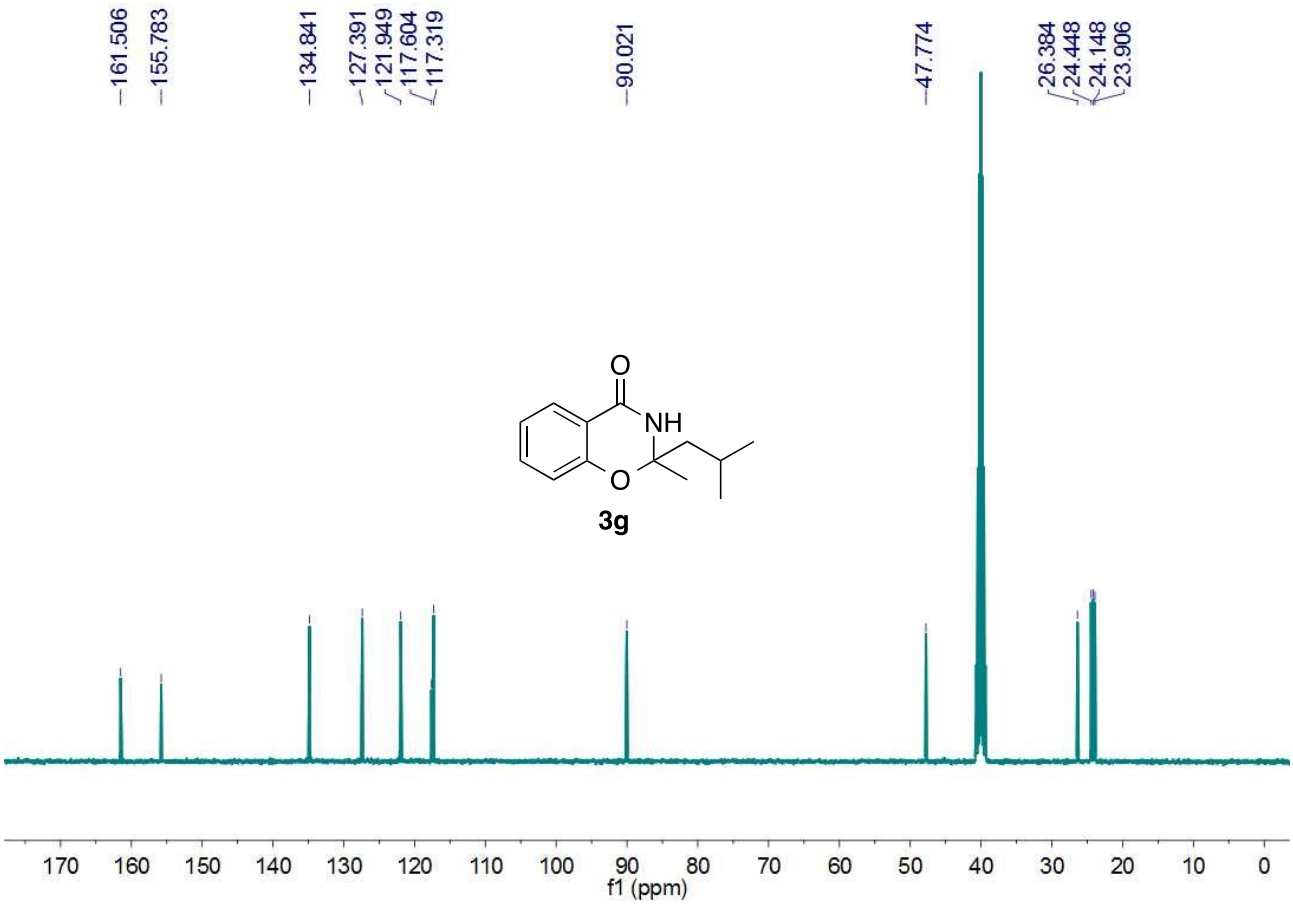
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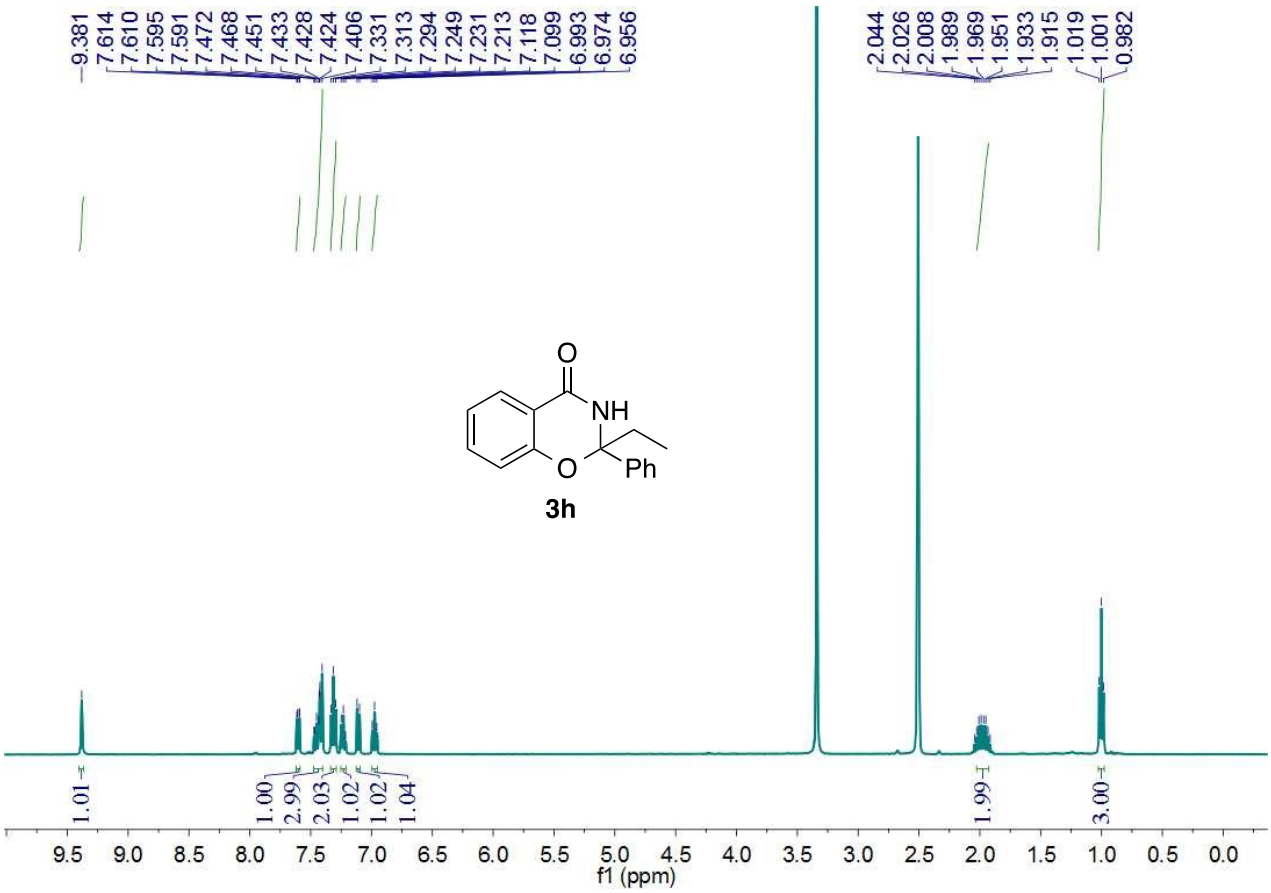
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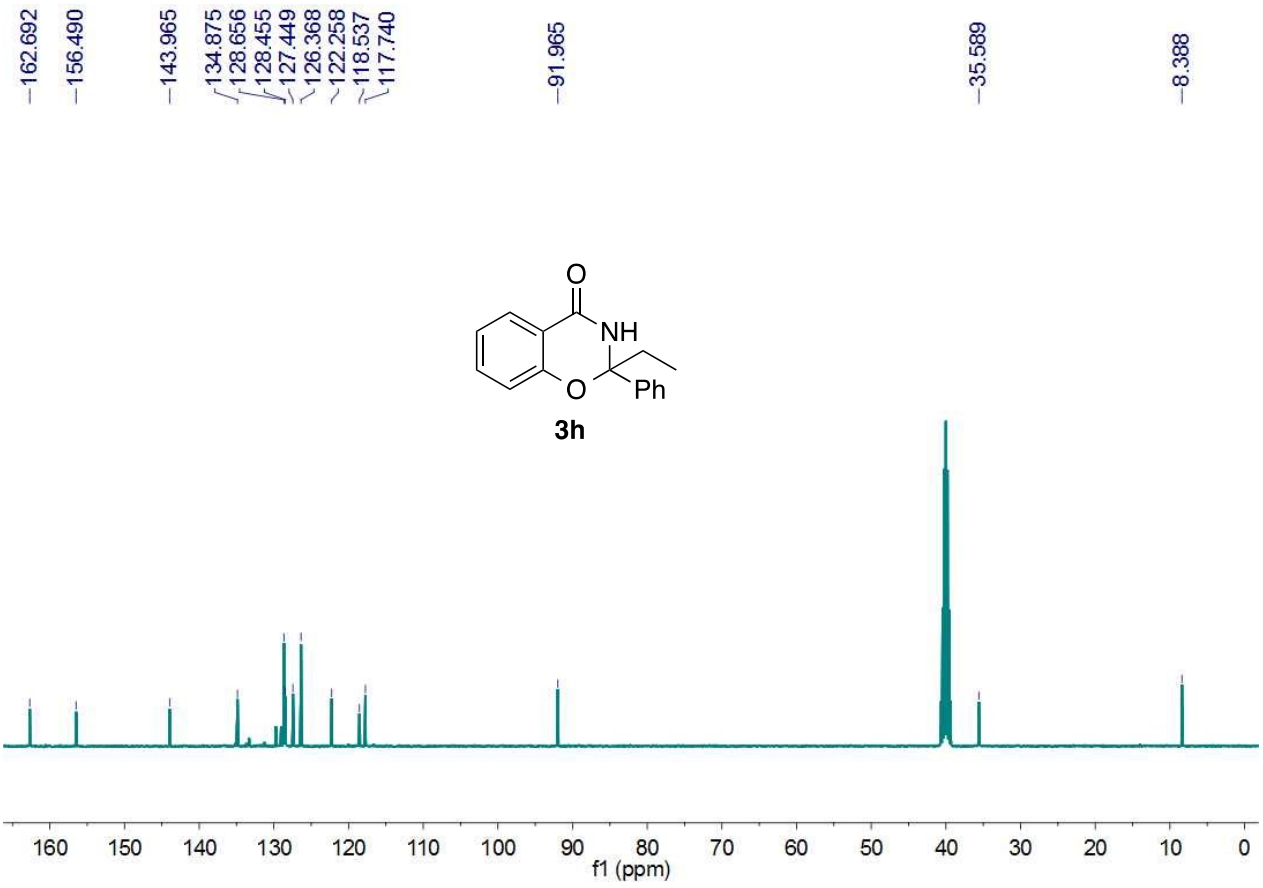
3h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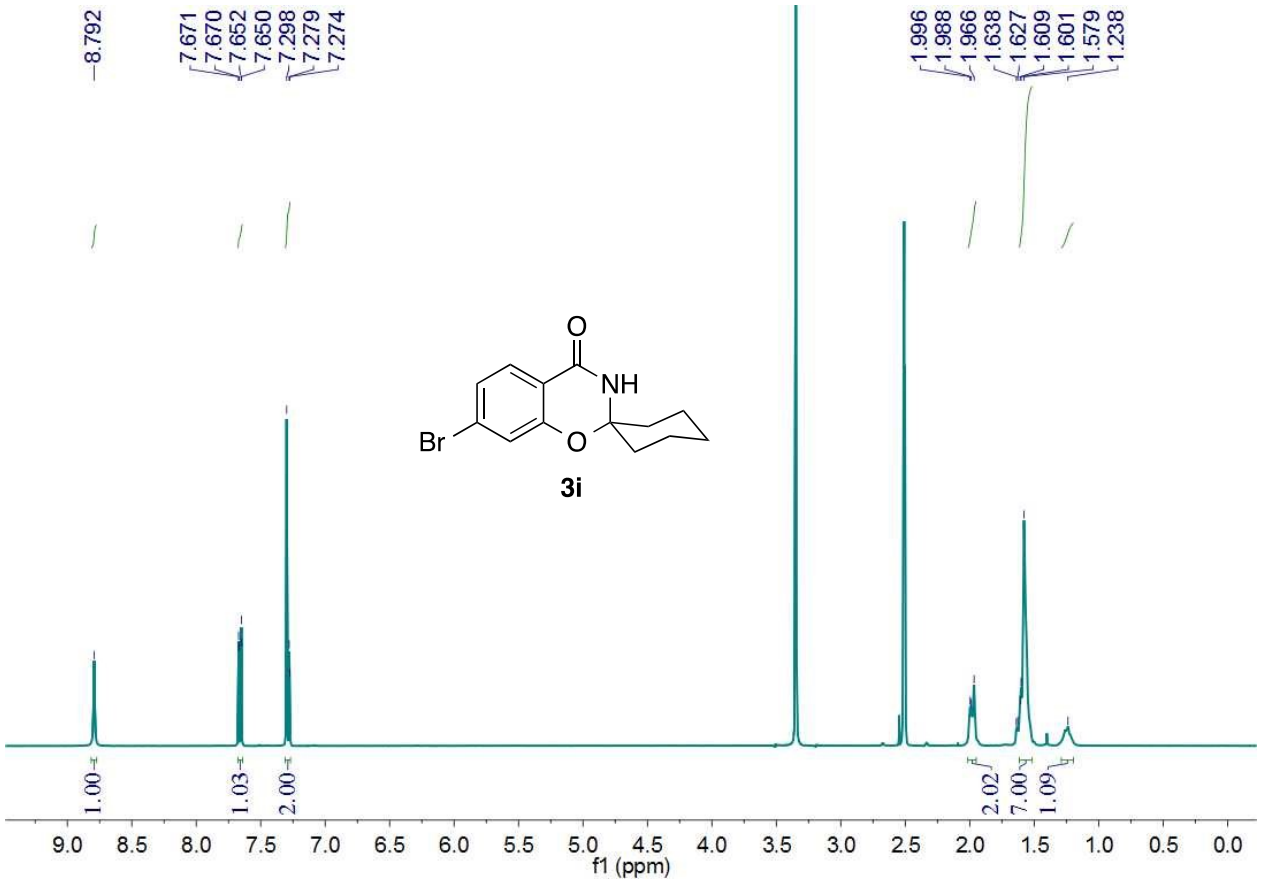
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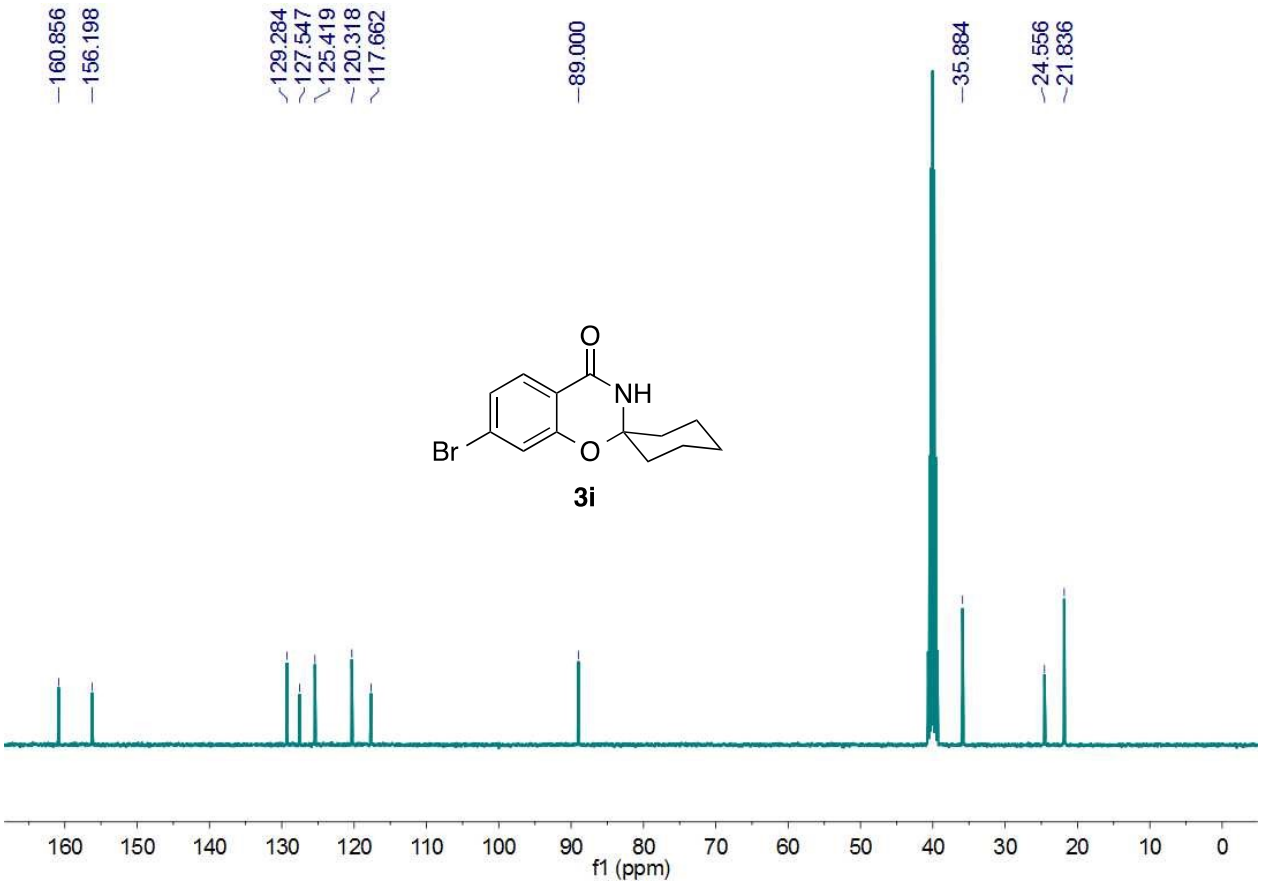
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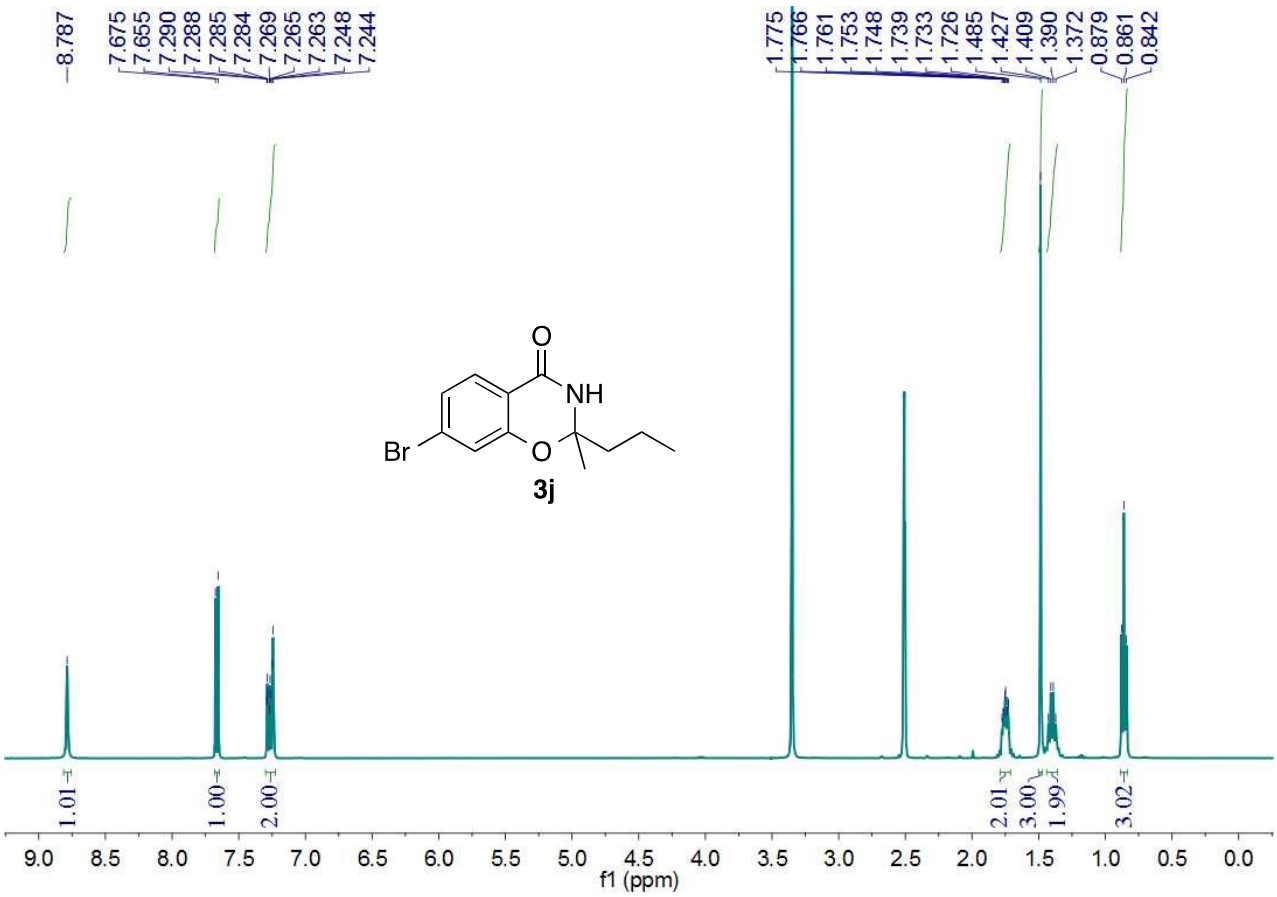
3i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2.01
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3.02
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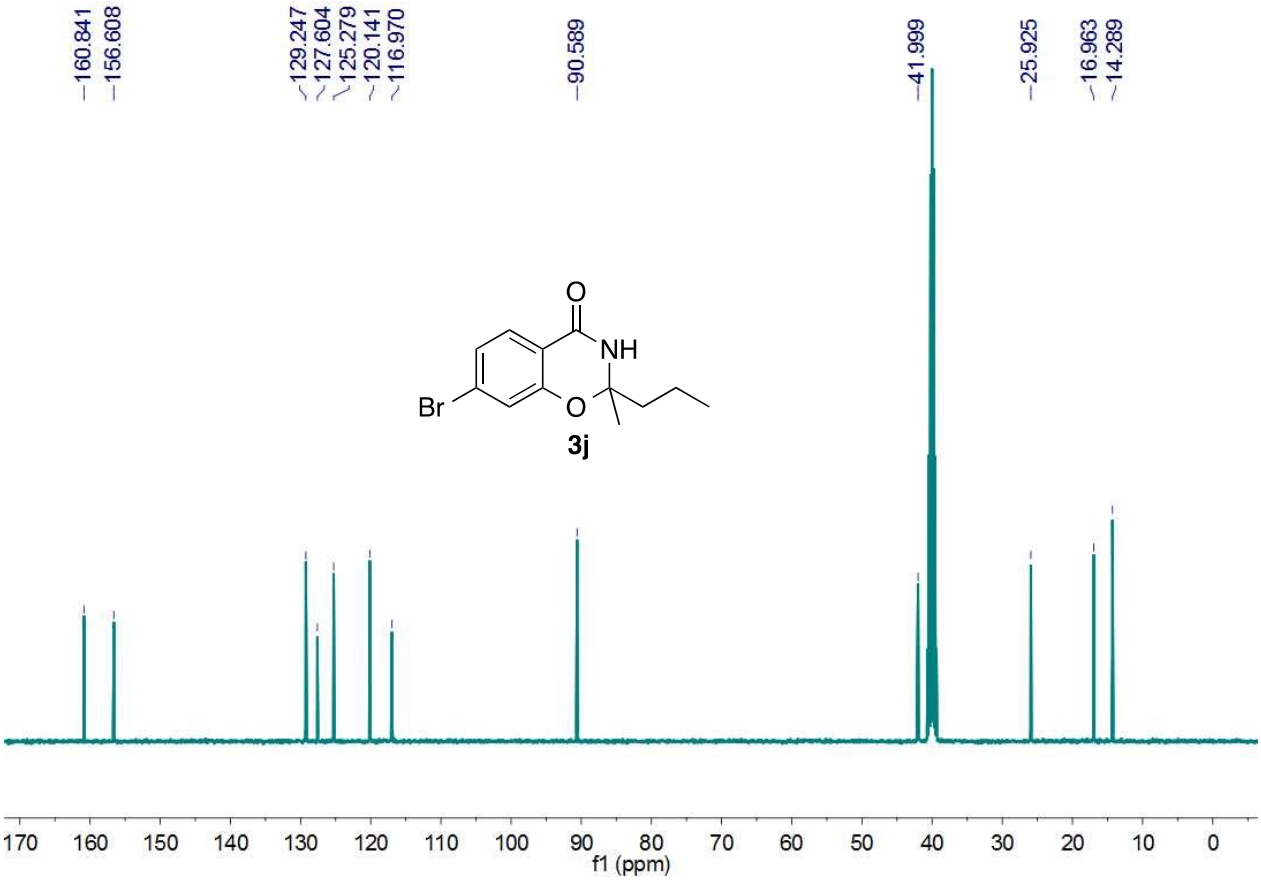
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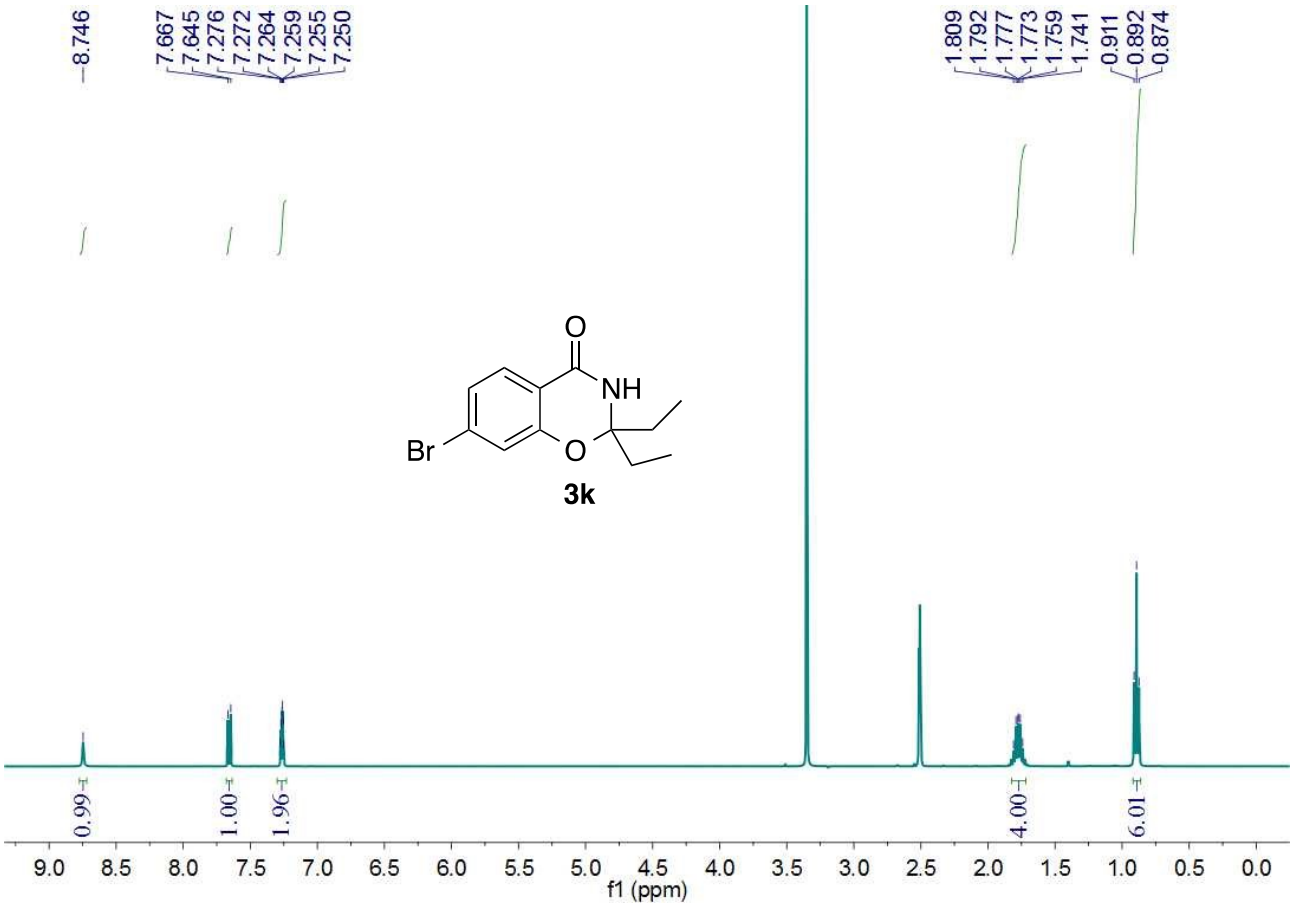
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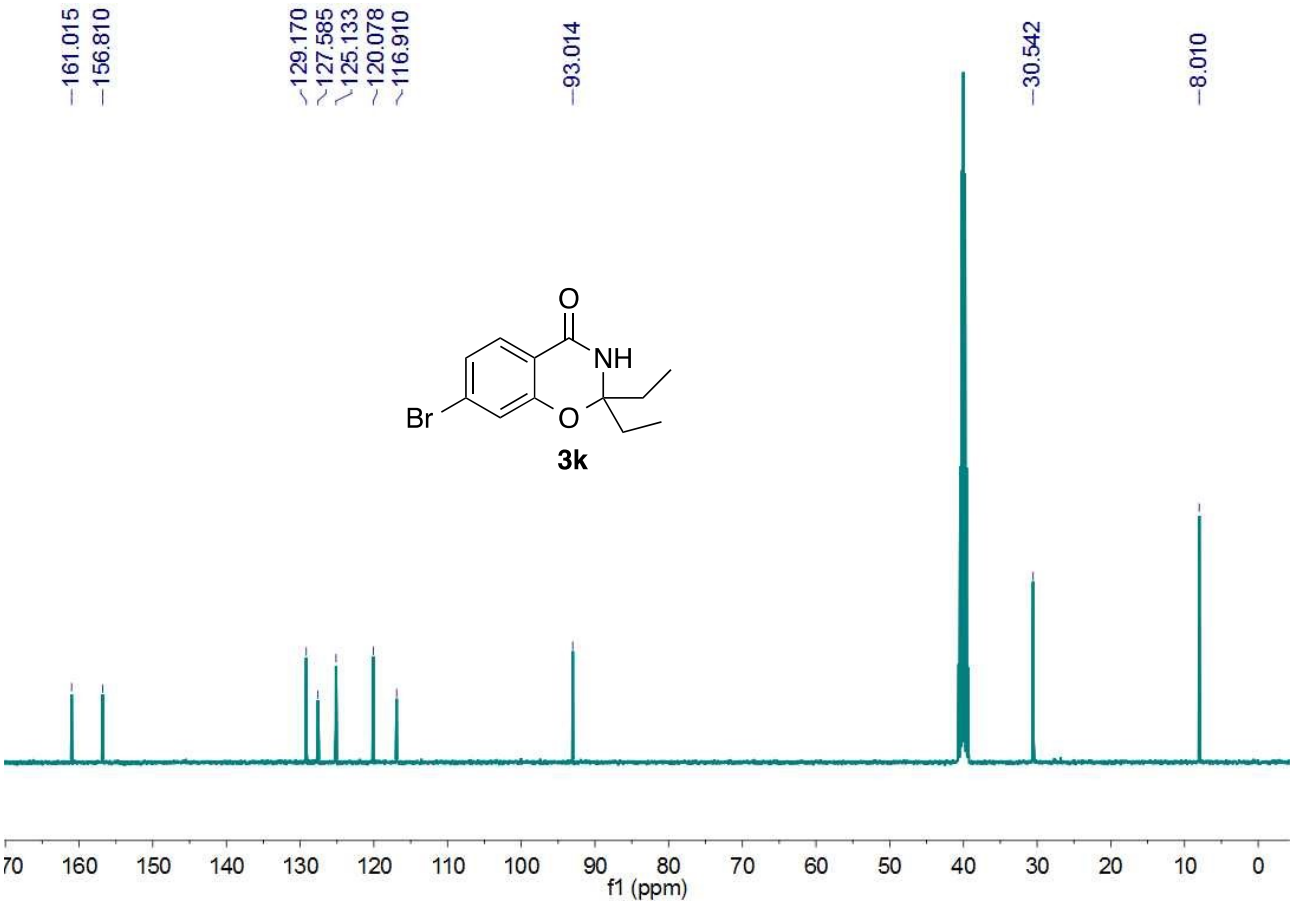
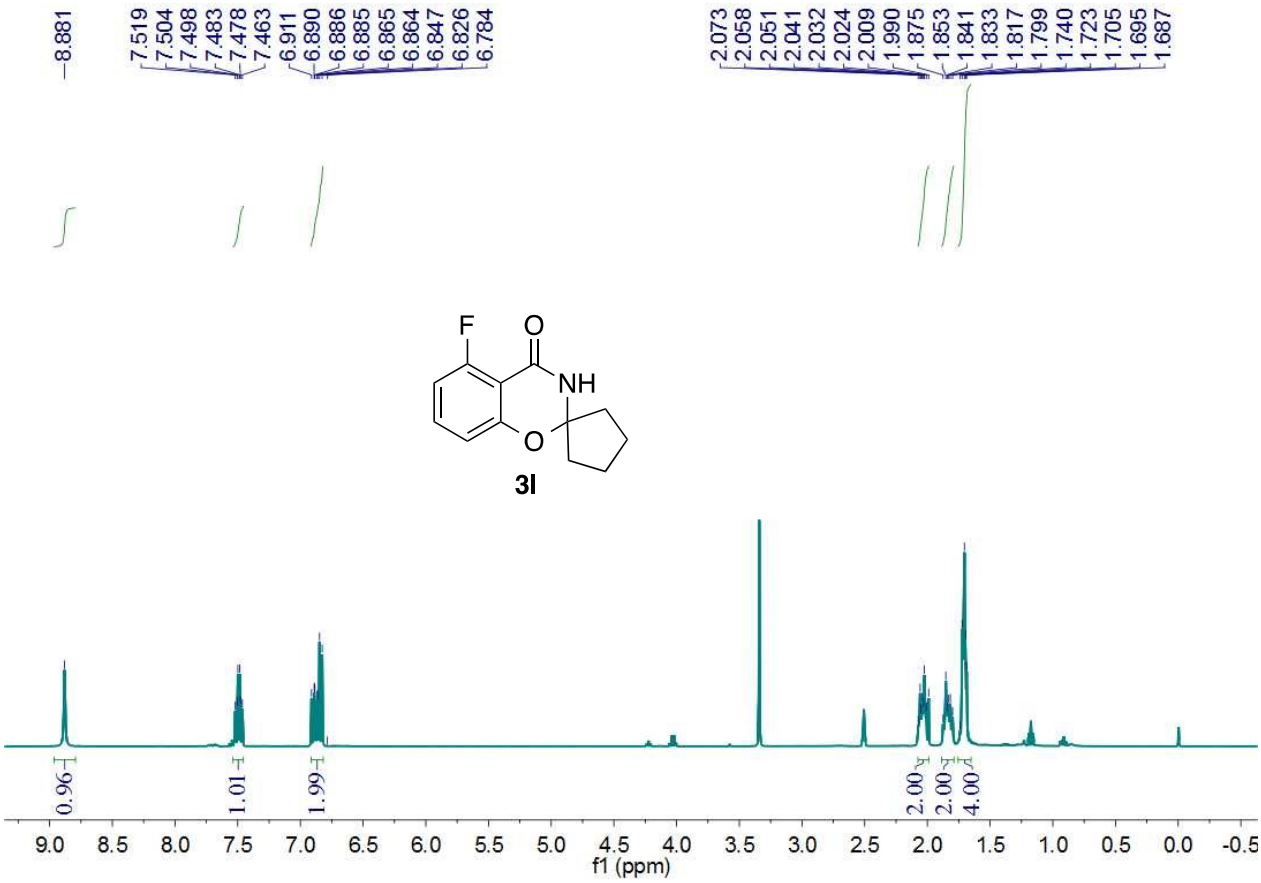
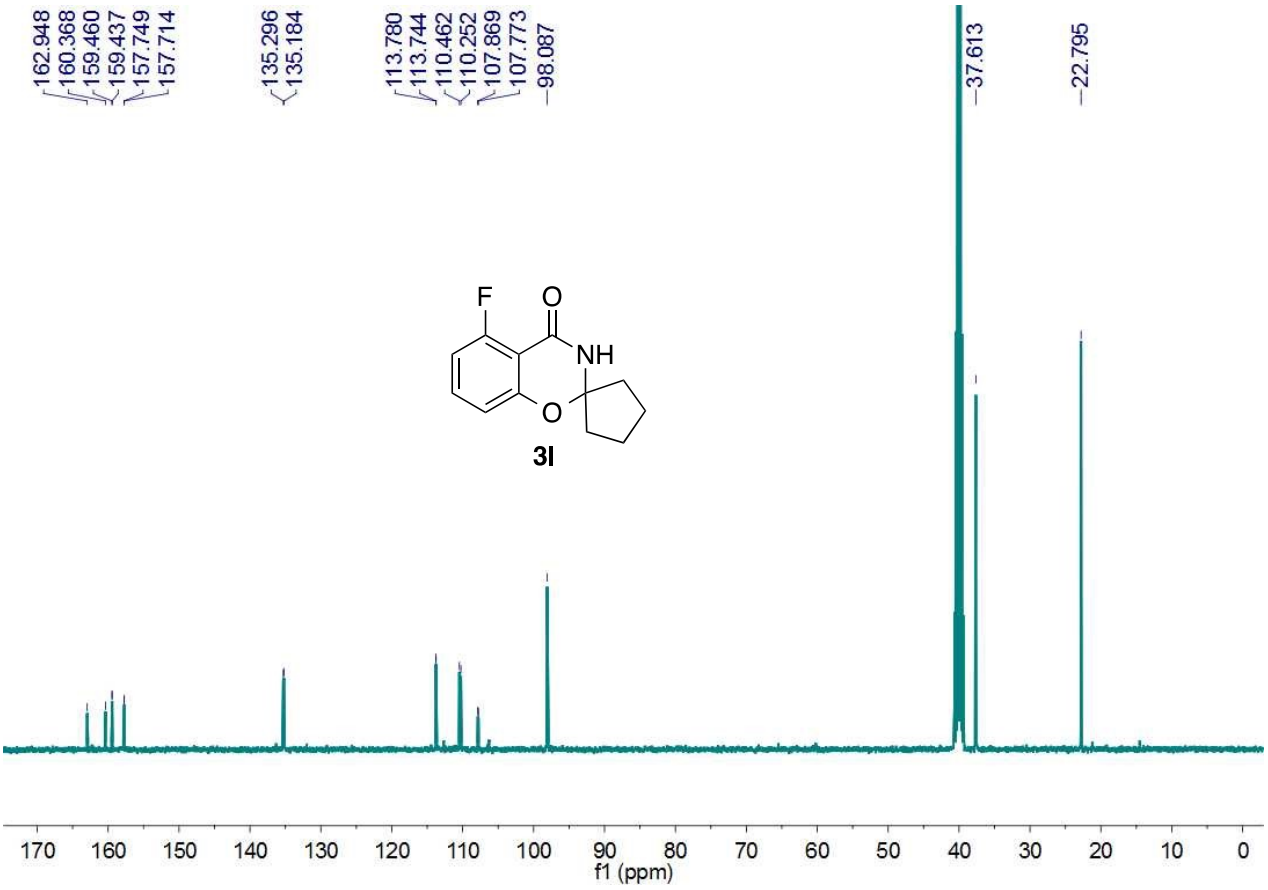
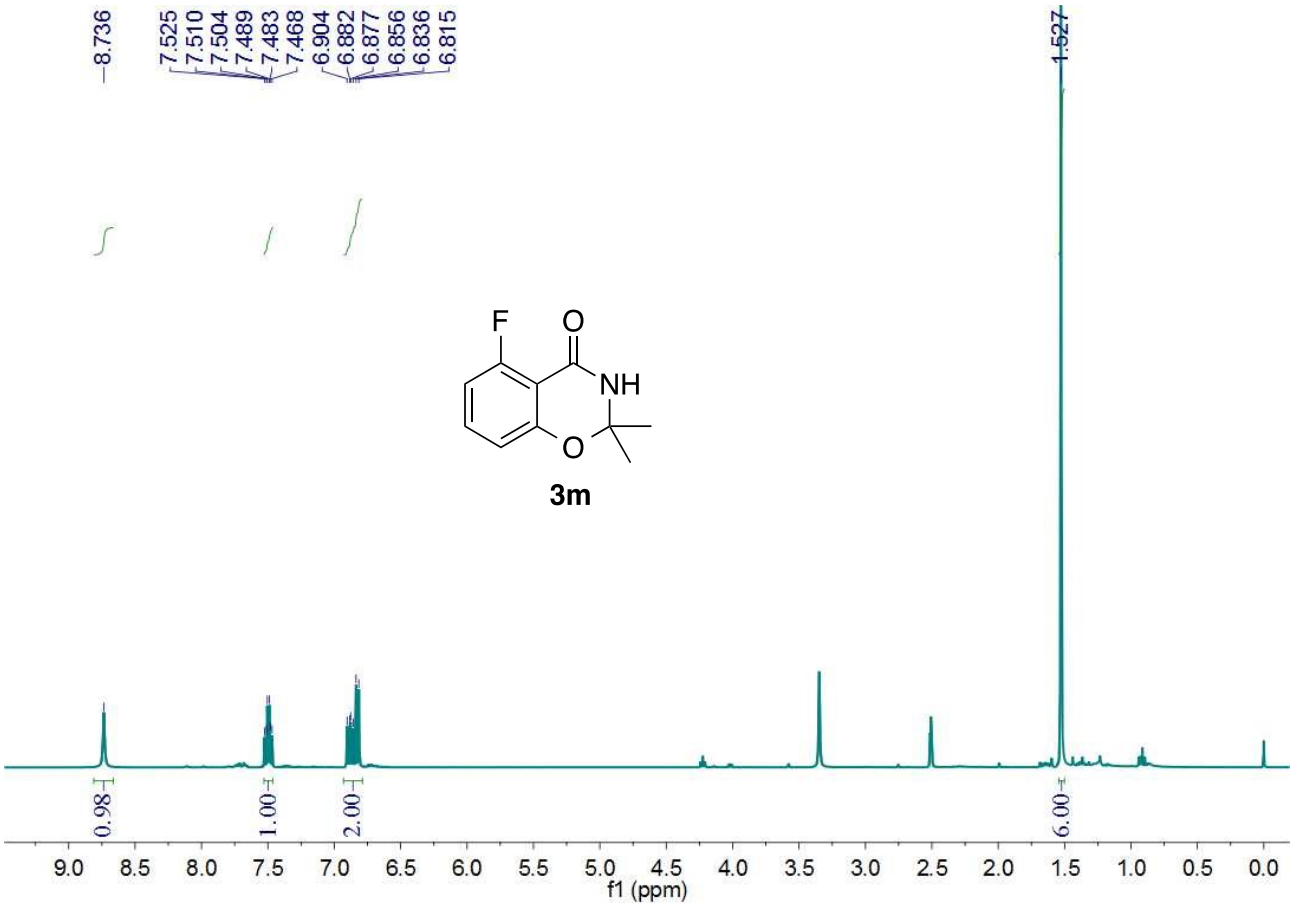
1.759
1.741
0.911
0.892
0.874
O
NH
Br
O
3k
0.99
1.00
1.96
4.00
6.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

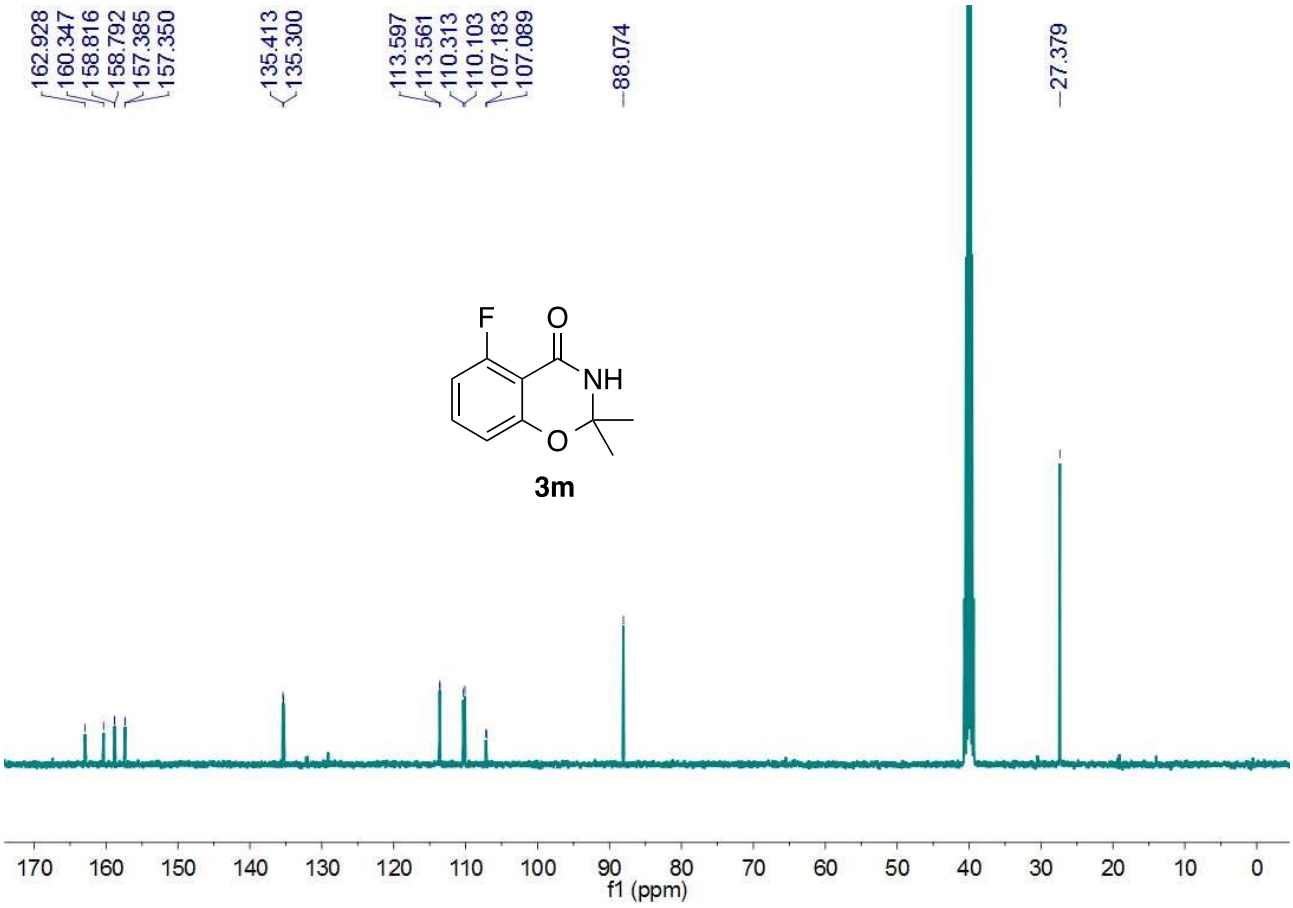

161.015
156.810
129.170
127.585
125.133
120.078
116.910
93.014
30.542
8.010
O
NH
Br
O
3k
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.881
7.519
7.504
7.498
7.483
7.478
7.463
6.911
6.890
6.886
6.885
6.865
6.864
6.847
6.826
6.784
2.073
2.058
2.051
2.041
2.032
2.024
2.009
1.990
1.875
1.853
1.841
1.833
1.817
1.799
1.740
1.723
1.705
1.695
1.687
F
O
NH
O
3l
0.96
1.01
1.99
2.00
2.00
4.00
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
0.0
-0.5
f1 (ppm)

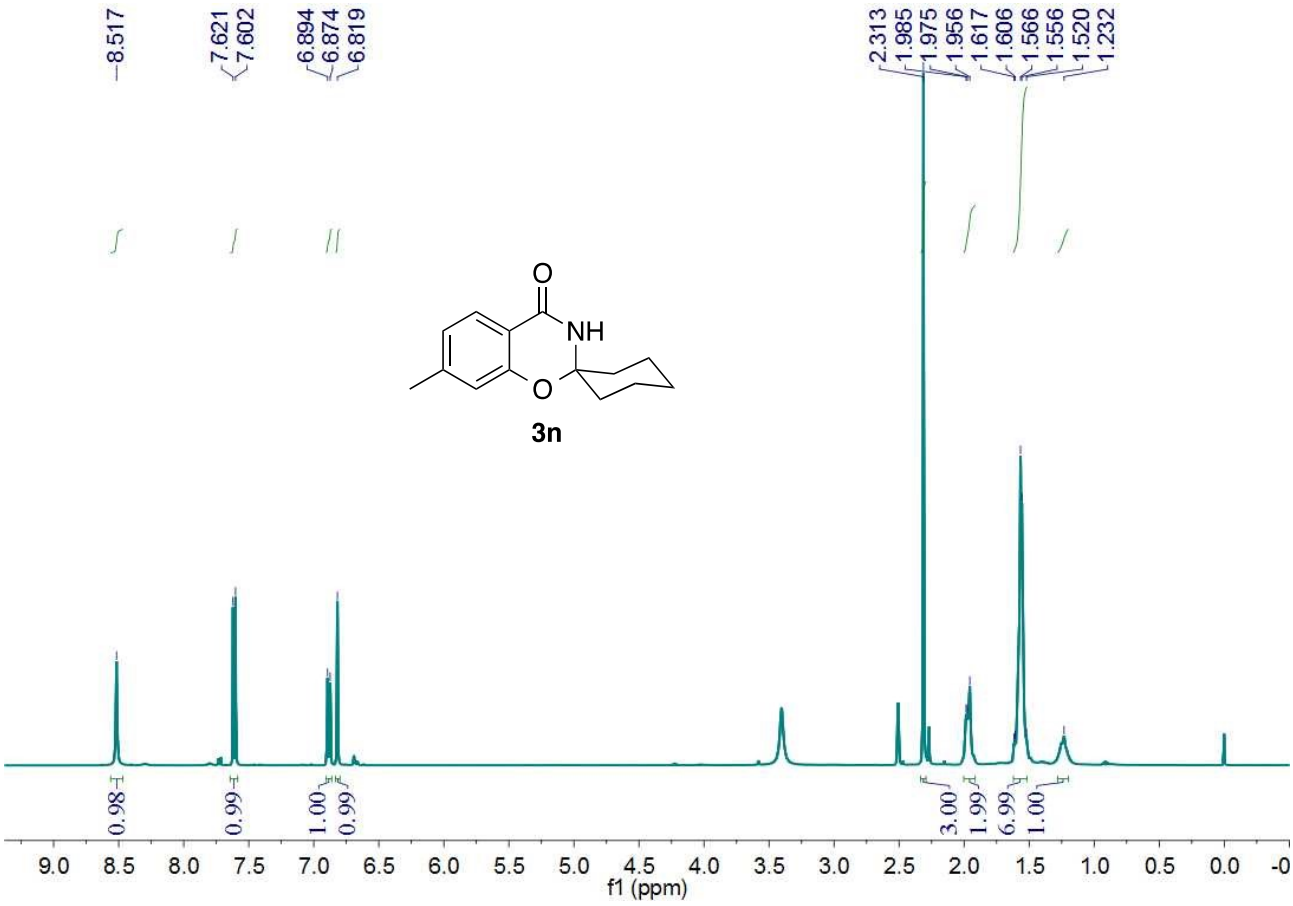

162.948
160.368
159.460
159.437
157.749
157.714
135.296
135.184
113.780
113.744
110.462
110.252
107.869
107.773
98.087
37.613
22.795
F
O
NH
O
3l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

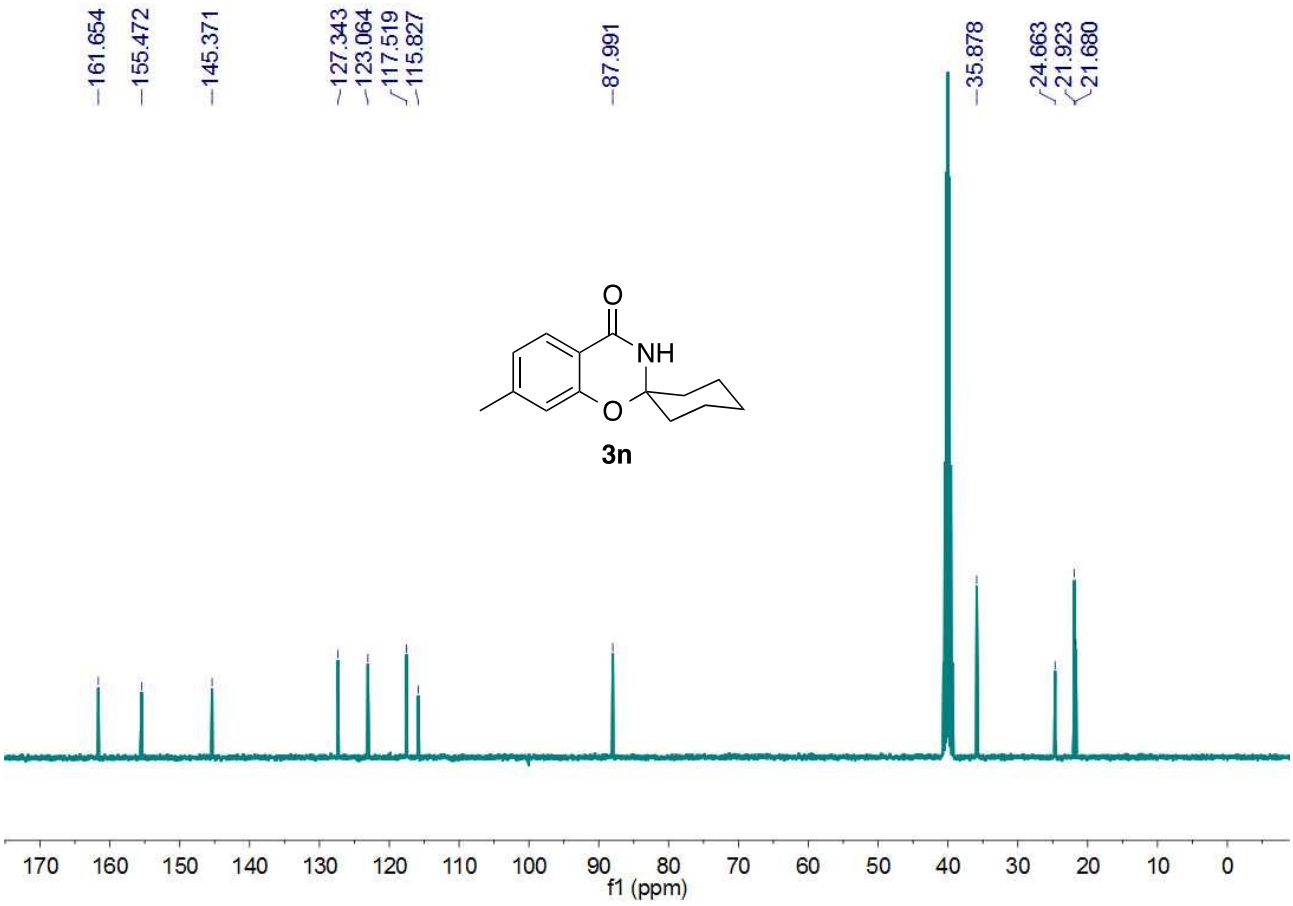

8.736
7.525
7.510
7.504
7.489
7.483
7.468
6.904
6.882
6.877
6.856
6.836
6.815
1.527
F
O
NH
O
0.98
1.00
2.00
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

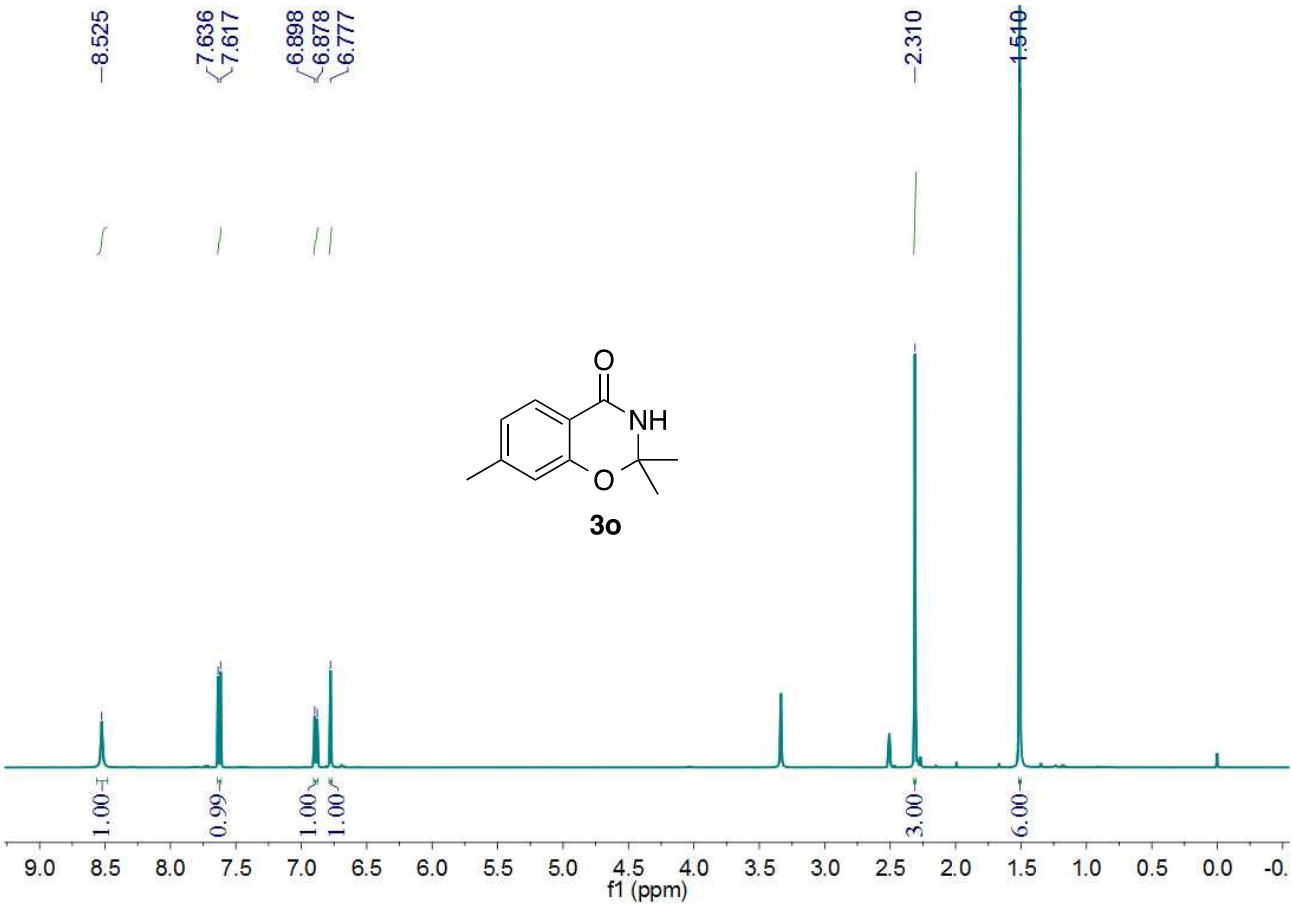
3m


162.928
160.347
158.816
158.792
157.385
157.350
135.413
135.300
113.597
113.561
110.313
110.103
107.183
107.089
88.074
27.379
F
O
NH
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

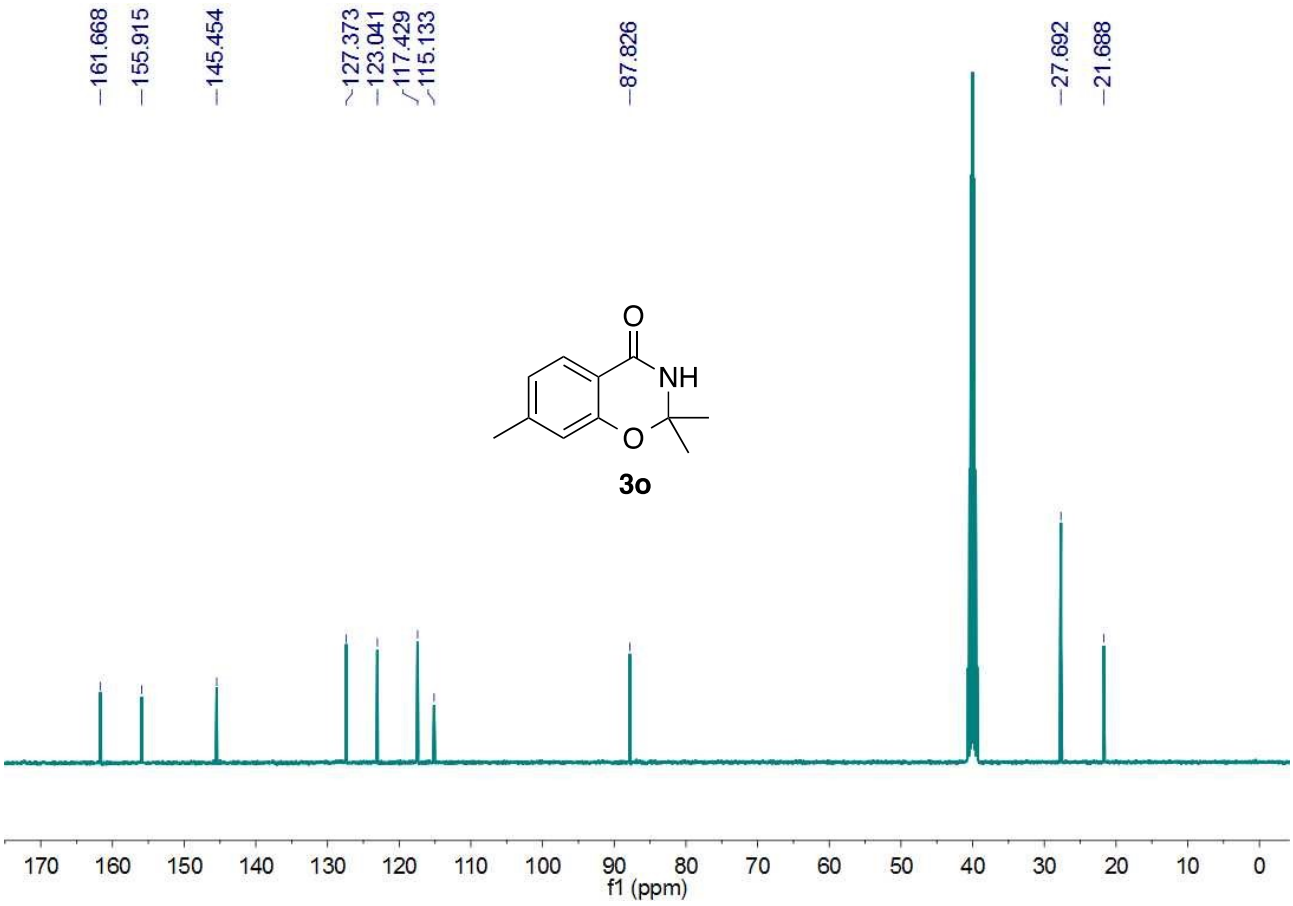
3m


8.517
7.621
7.602
6.894
6.874
6.819
2.313
1.985
1.975
1.956
1.617
1.606
1.566
1.556
1.520
1.232
O
NH
O
3n
0.98
0.99
1.00
0.99
3.00
1.99
6.99
1.00
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 0.0 -0
f1 (ppm)

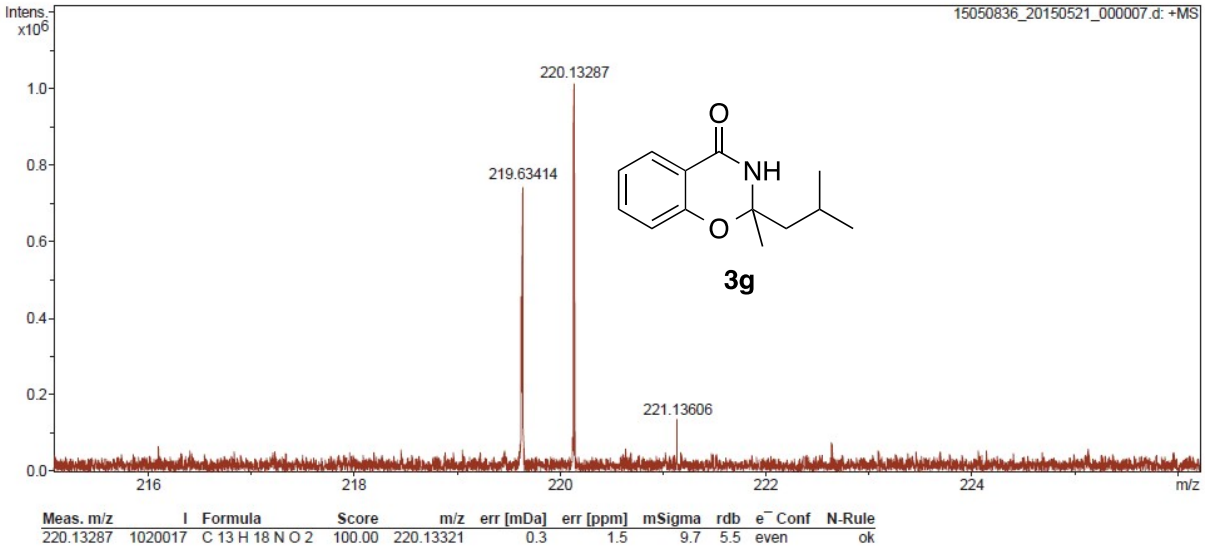

161.654
155.472
145.371
127.343
123.064
117.519
115.827
87.991
35.878
24.663
21.923
21.680
O
NH
O
3n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.525
7.636
7.617
6.898
6.878
6.777
2.310
1.510
O
NH
O
1.00
0.99
1.00
1.00
3.00
6.00
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 0.0 -0.
f1 (ppm)

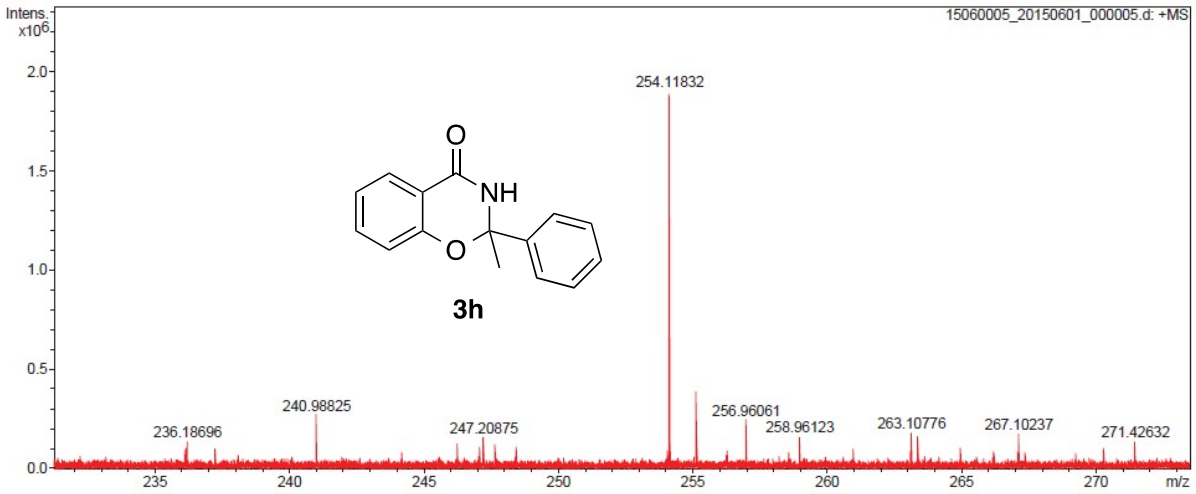
3o



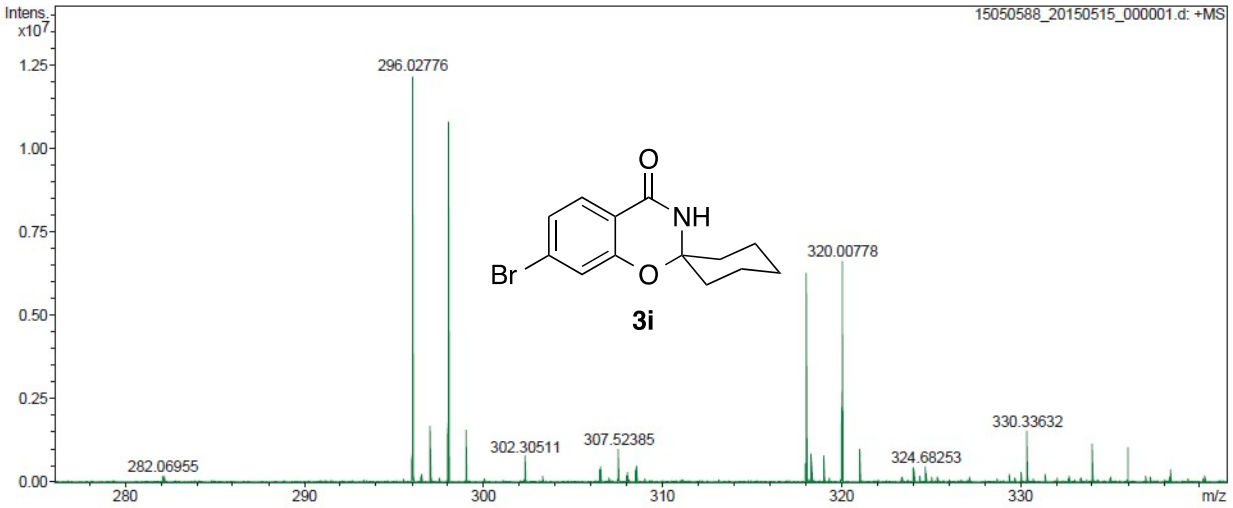
HR-MS of new products



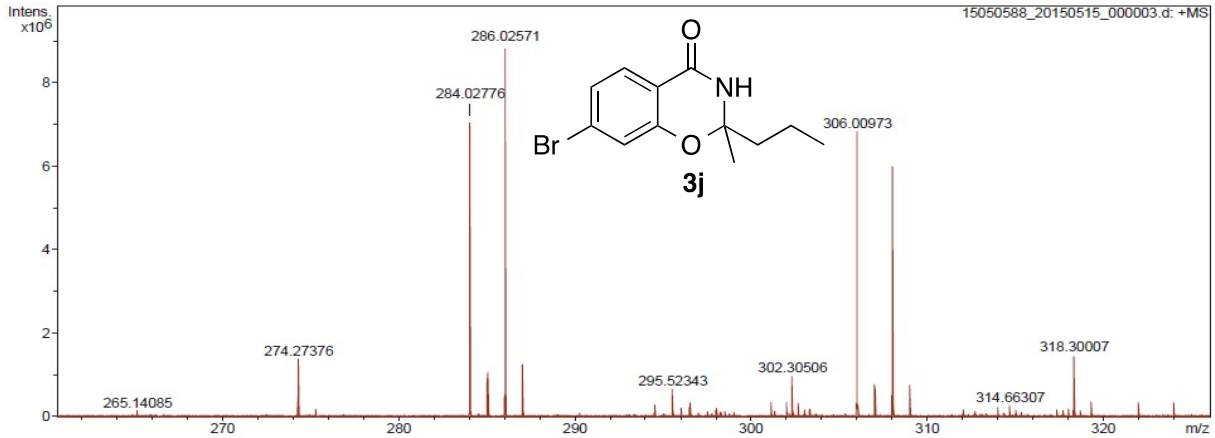
Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
220.13287	1020017	C 13 H 18 N O 2	100.00	220.13321	0.3	1.5	9.7	5.5	even	ok



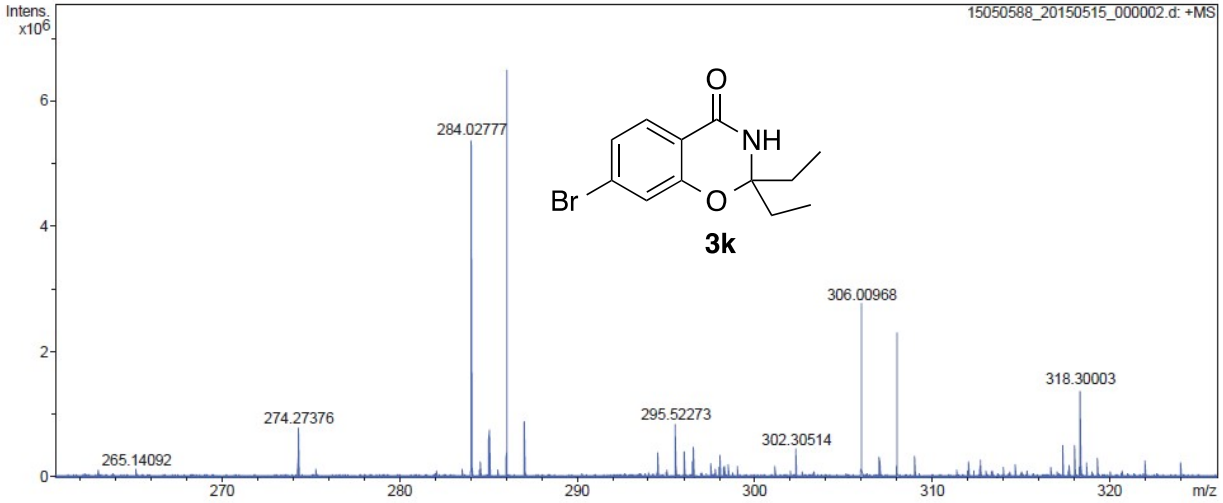
Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
254.11832	1906181	C 16 H 16 N O 2	100.00	254.11756	-0.8	-3.0	19.2	9.5	even	ok



Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
296.02776	12190080	C 13 H 15 Br N O 2	100.00	296.02807	0.3	1.0	30.1	6.5	even	ok

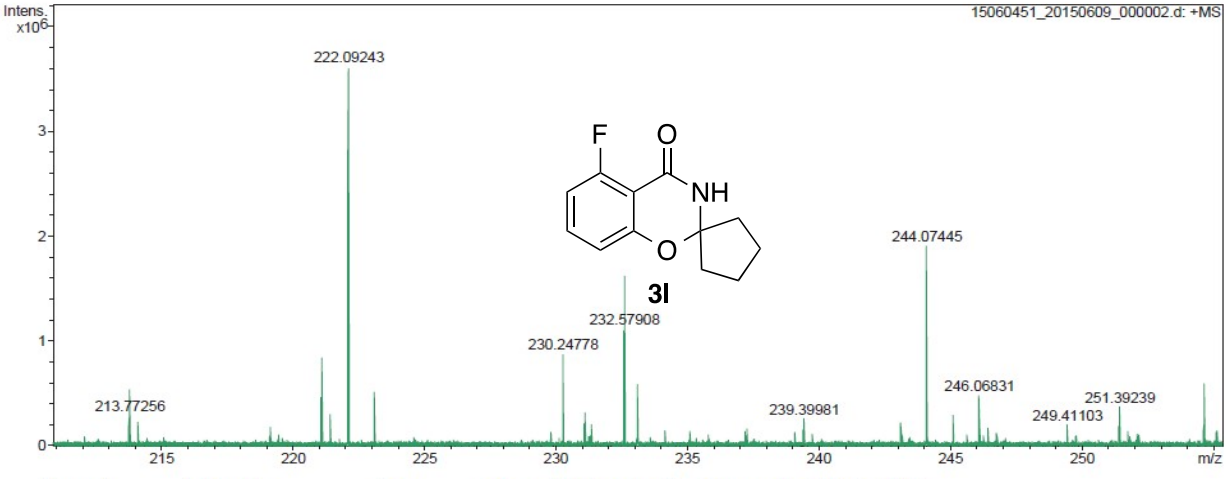


Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
284.02776	7086408	C 12 H 15 Br N O 2	100.00	284.02807	0.3	1.1	93.3	5.5	even	ok



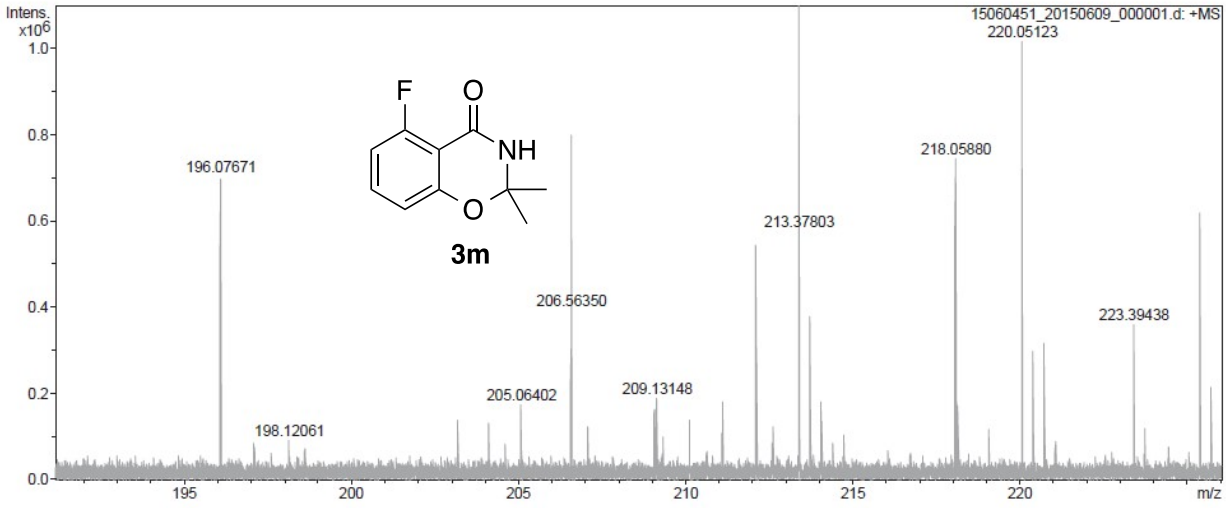
3k

Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
284.02777	5400549	C 12 H 15 Br N O 2	100.00	284.02807	0.3	1.1	440.9	5.5	even	ok

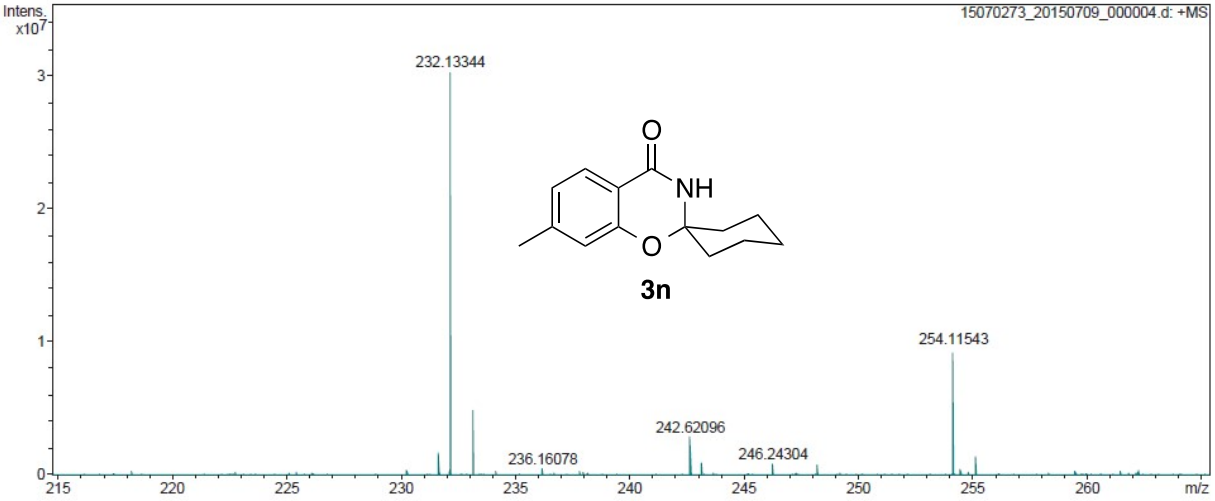


3l

Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
222.09243	3628703	C 12 H 13 F N O 2	100.00	222.09248	0.1	0.2	8.4	6.5	even	ok
244.07445	1915499	C 12 H 12 F N Na O 2	100.00	244.07443	-0.0	-0.1	15.5	6.5	even	ok

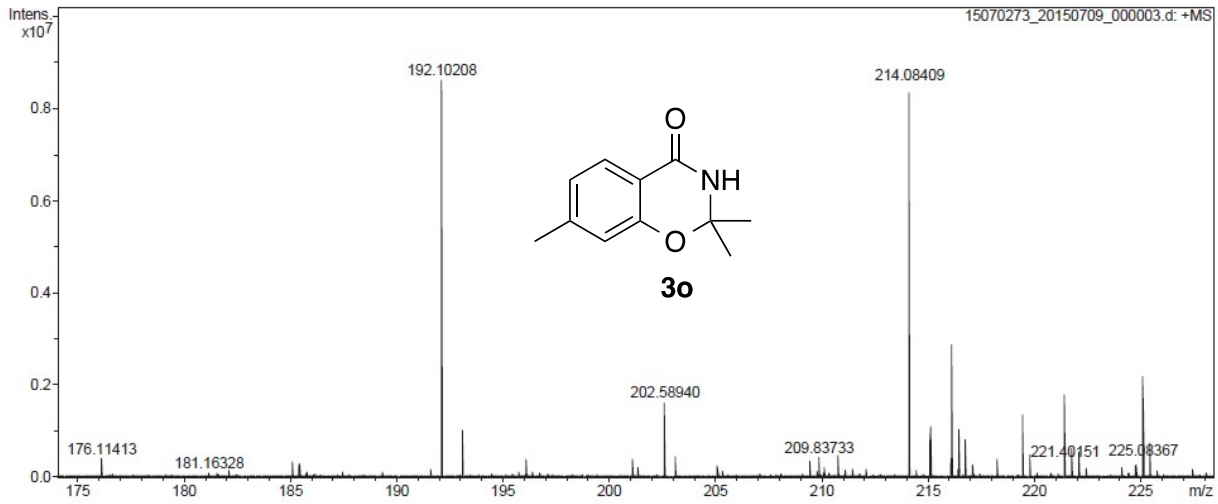


Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
196.07671	705643	C 10 H 11 F N O 2	100.00	196.07683	0.1	0.6	9.1	5.5	even	ok
218.05880	744723	C 10 H 10 F N Na O 2	100.00	218.05878	-0.0	-0.1	26.9	5.5	even	ok



3n

Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
232.13344	30388600	C 14 H 18 N O 2	100.00	232.13321	-0.2	-1.0	4.9	6.5	even	ok
254.11543	9541691	C 14 H 17 N Na O 2	100.00	254.11515	-0.3	-1.1	9.0	6.5	even	ok



3o

Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
192.10208	8661366	C 11 H 14 N O 2	100.00	192.10191	-0.2	-0.9	6.4	5.5	even	ok
214.08409	8548627	C 11 H 13 N Na O 2	100.00	214.08385	-0.2	-1.1	6.2	5.5	even	ok