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Novel synthetic methodology for the assembly of a-carbolines and 7-azaindoles

Henning, Hendrik

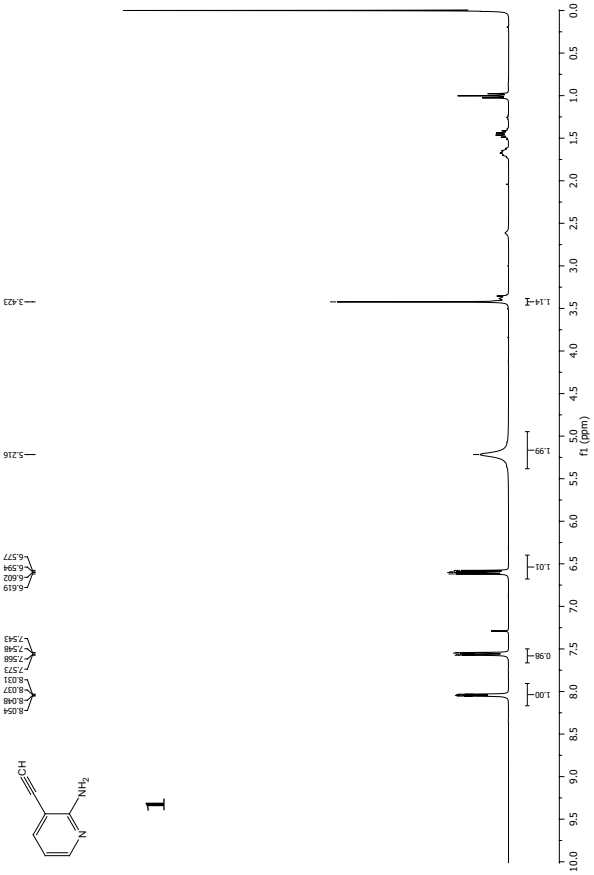
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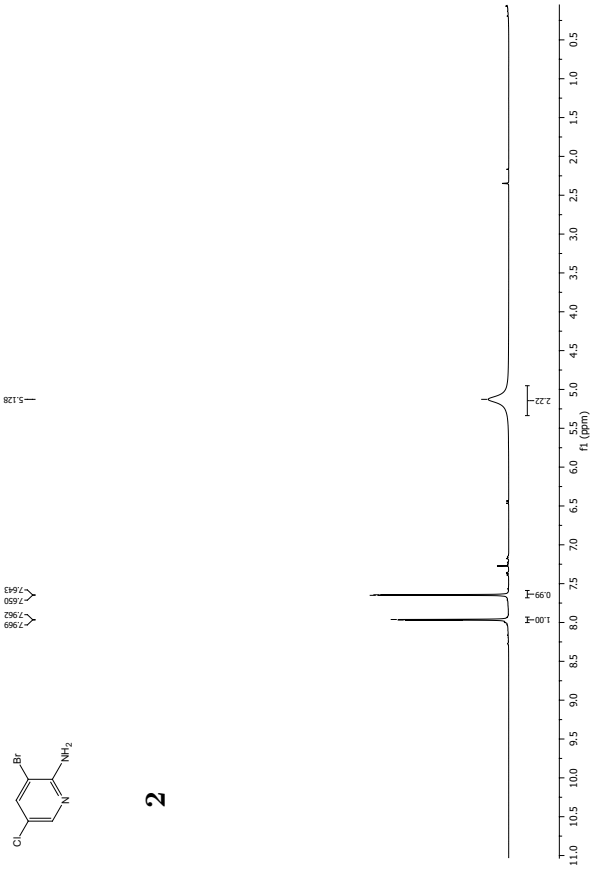
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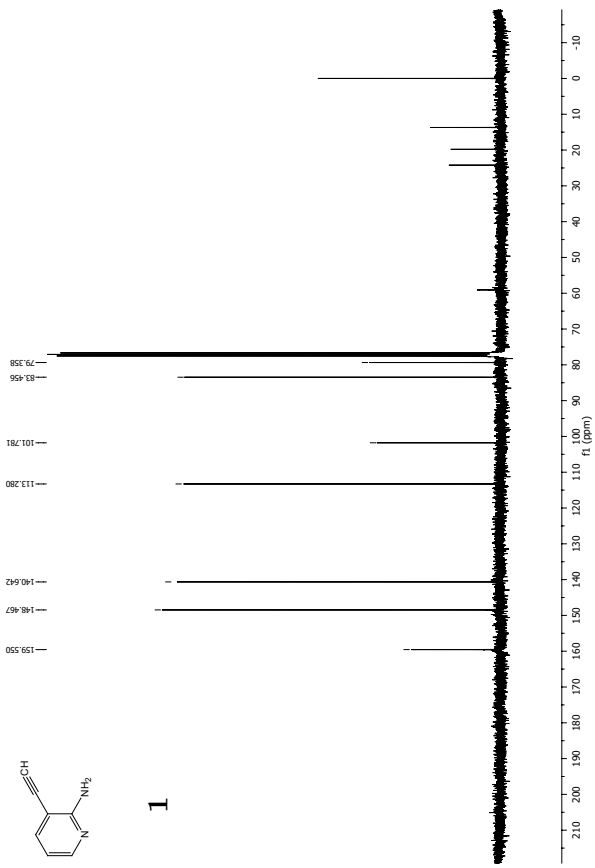
Henning, Hendrik (2018) Novel synthetic methodology for the assembly of a -carbolines and 7-azaindoles, University of the Witwatersrand, Johannesburg, <http://hdl.handle.net/10539/25742>

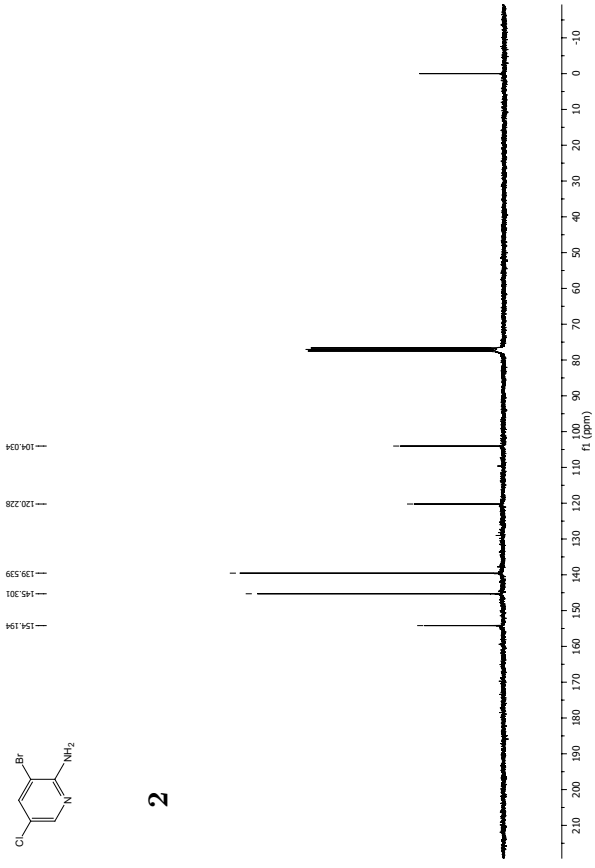
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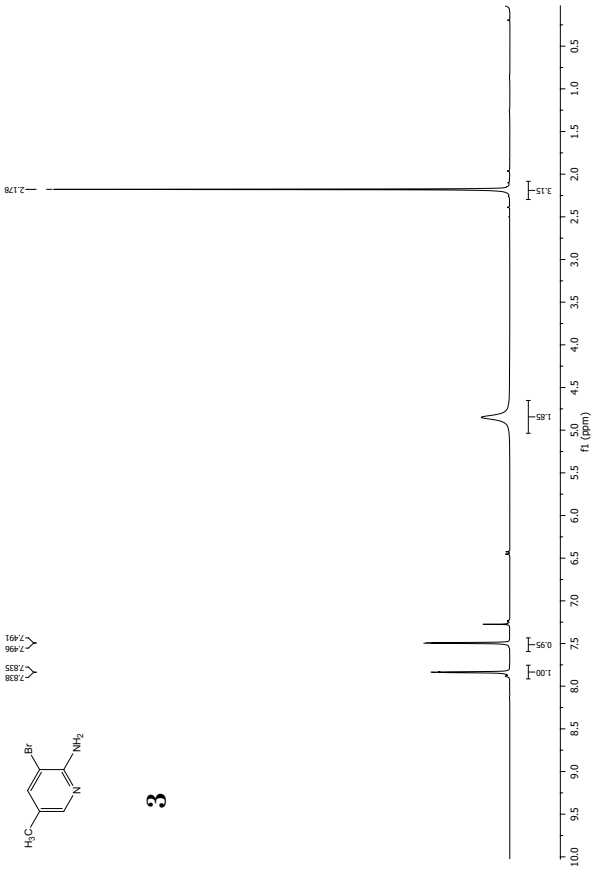
Appendix: NMR spectra

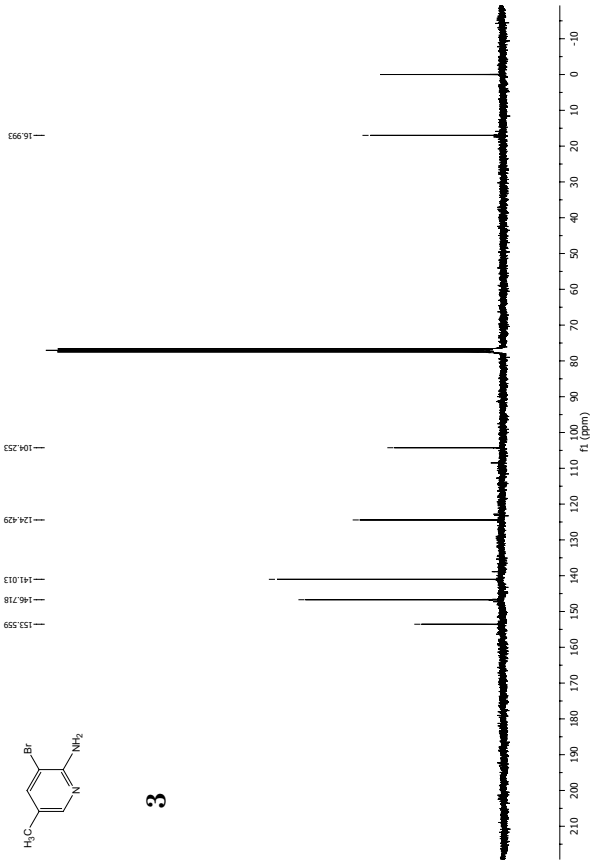

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8.037
8.031
7.573
7.568
7.548
7.543
6.619
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6.577
5.216
3.423
1.00
0.98
1.01
1.99
1.14
f1 (ppm)
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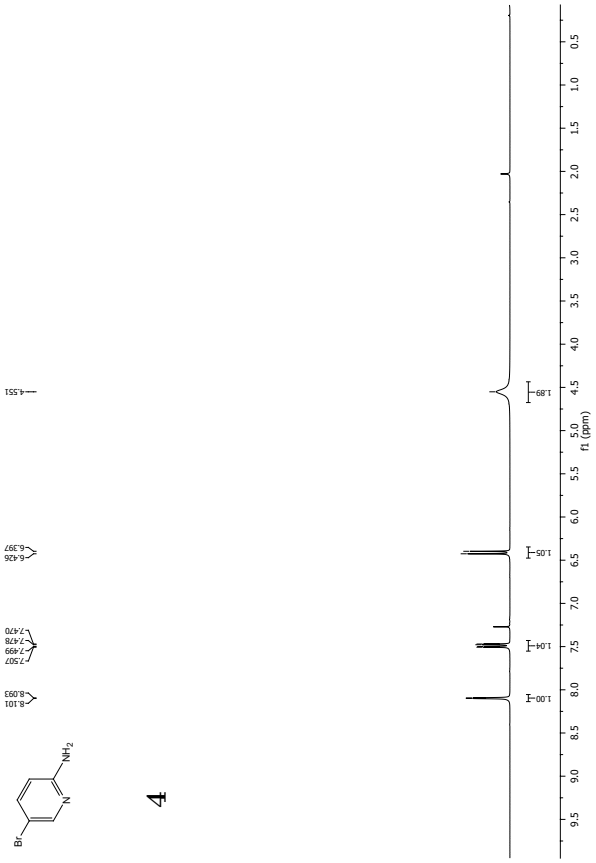

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7.650
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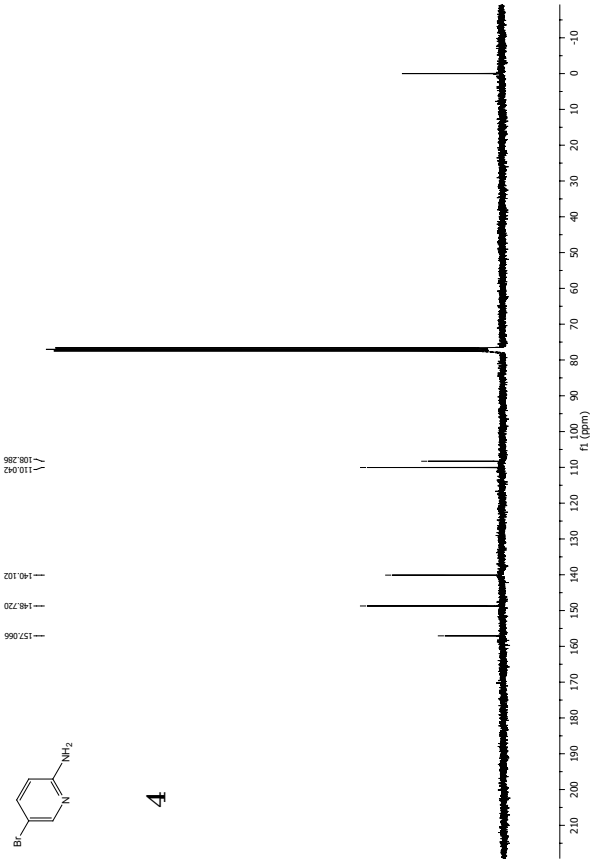

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113.280
101.781
83.456
79.358
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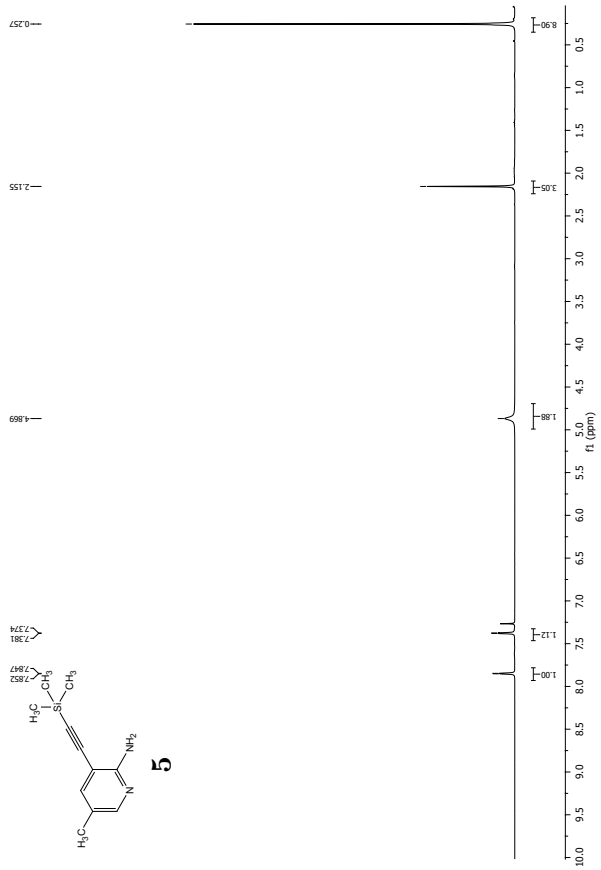

154.194
145.301
139.539
120.228
104.034
f1 (ppm)
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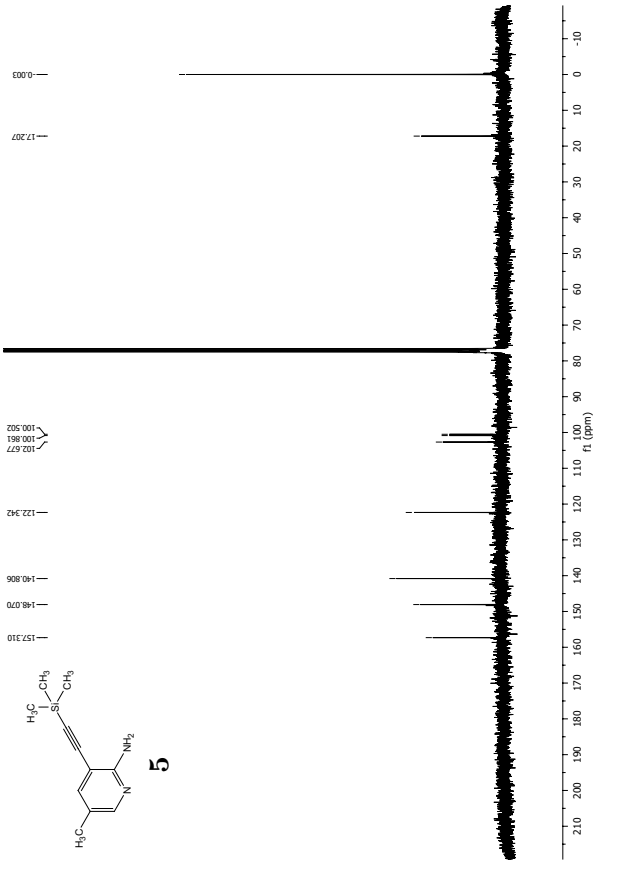

2.178
7.838
7.835
7.496
7.491
3.15
1.85
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NH2
H3C
N
3
f1 (ppm)

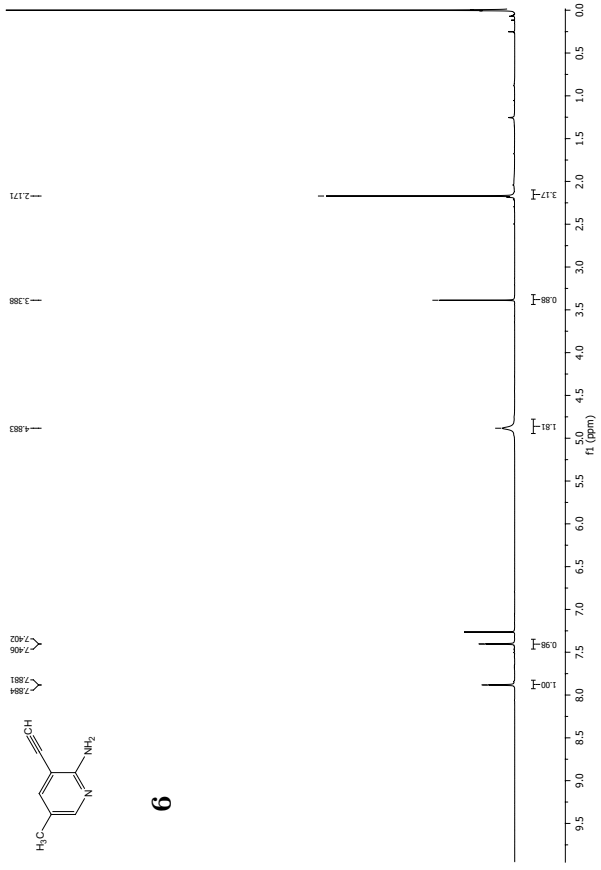

16.993
104.253
124.429
141.013
146.718
153.559
Br
NH2
H3C
N
3
f1 (ppm)

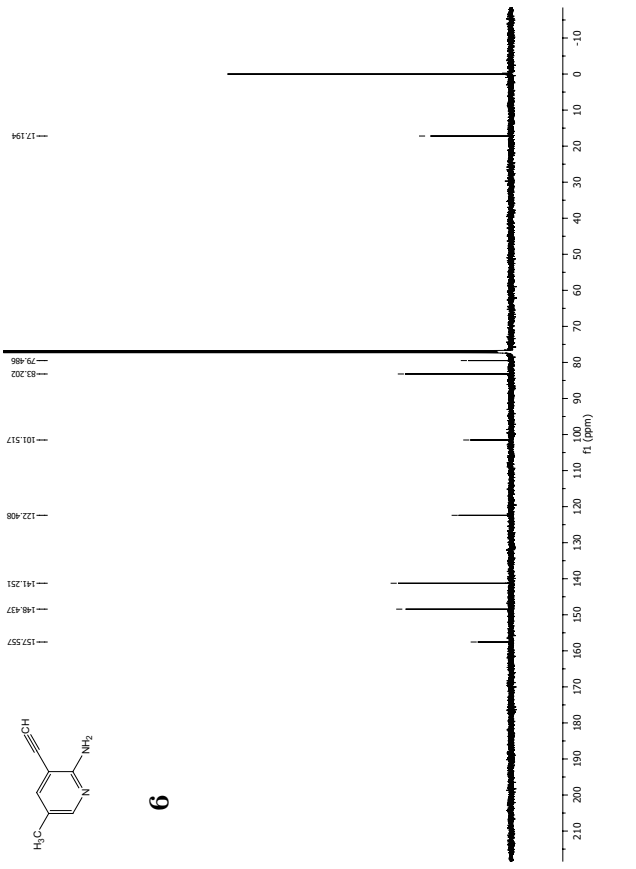

8.101
8.093
7.507
7.499
7.428
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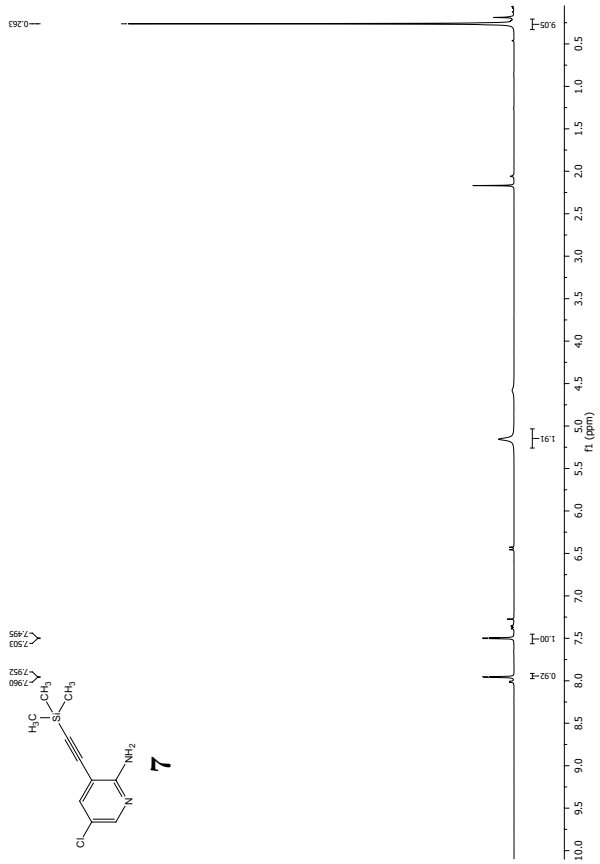

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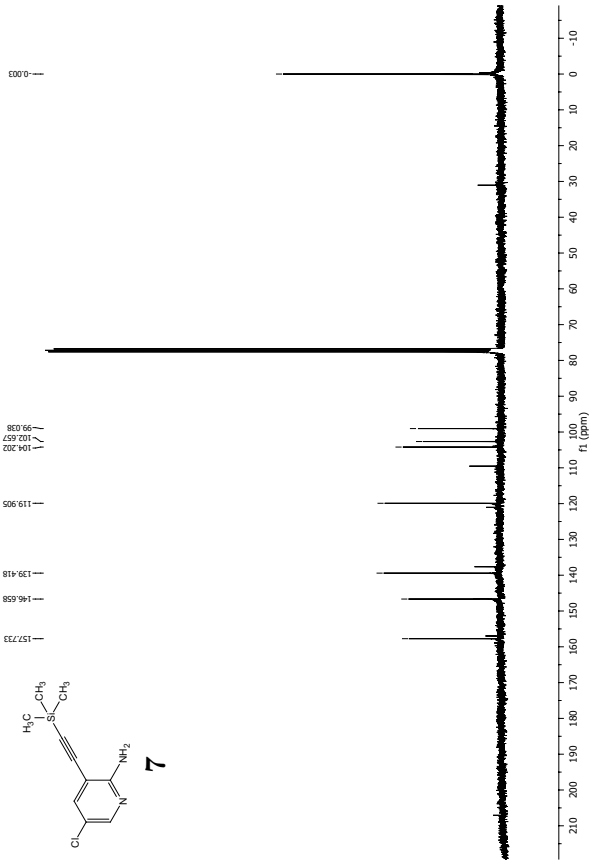

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7.381
7.324
7.852
7.847
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H_3C
Si
CH_3
CH_3
NH_2
N

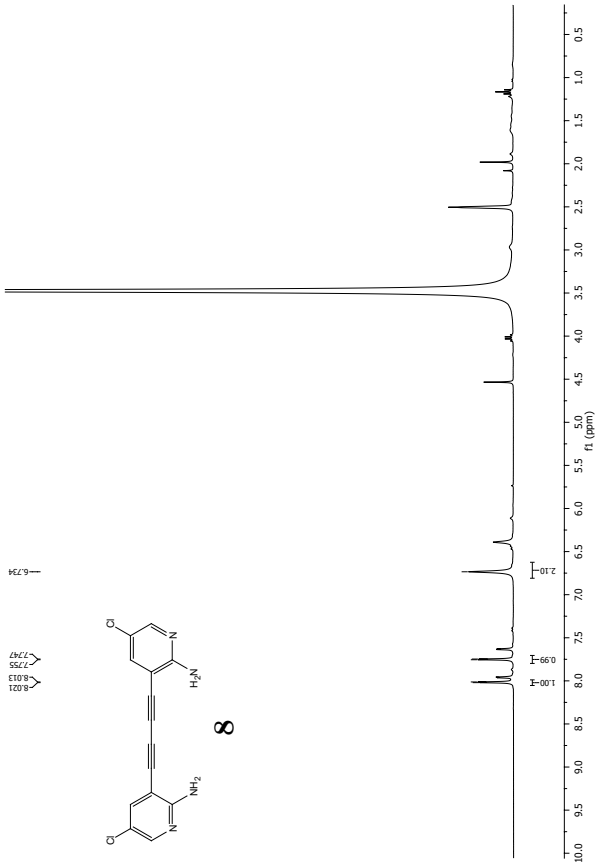

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148.070
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CH_3
CH_3
NH_2
N

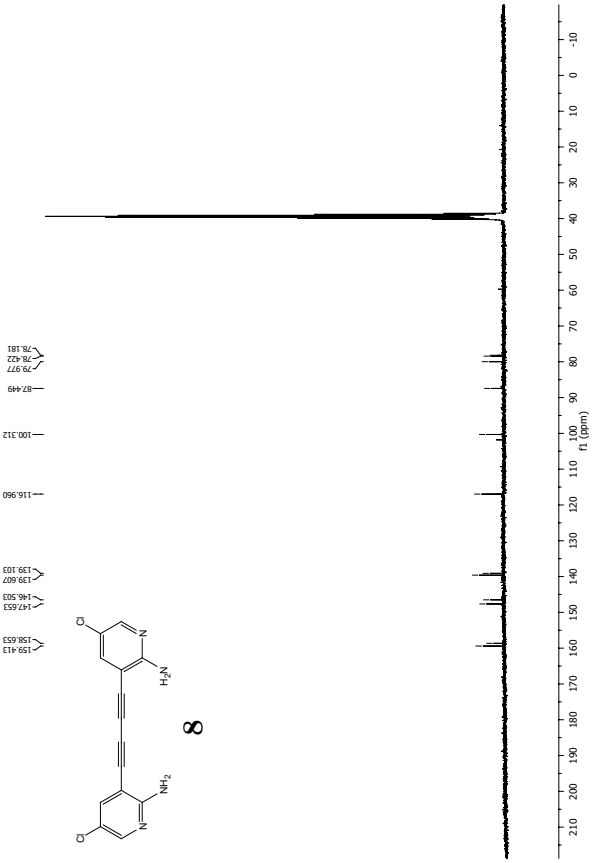

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CH
NH_2
N
H_3C

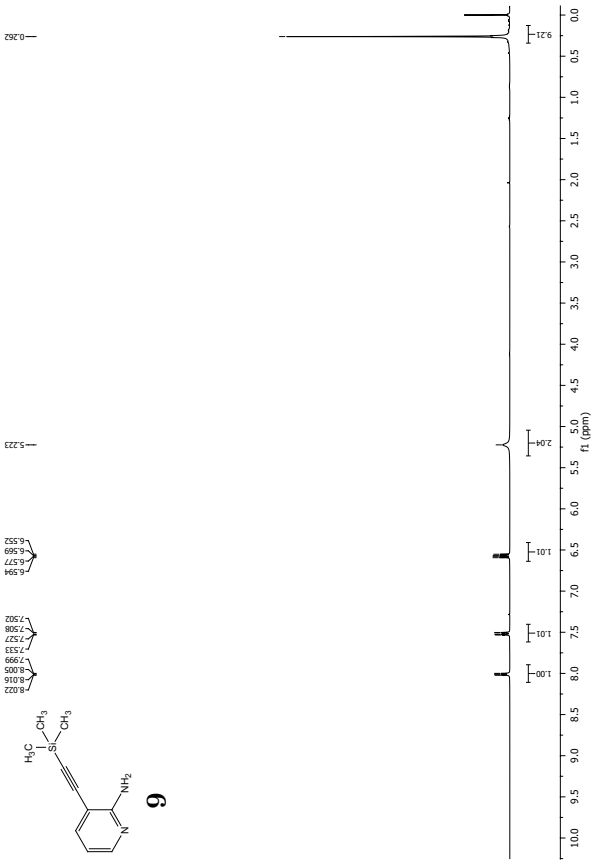

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H_3C

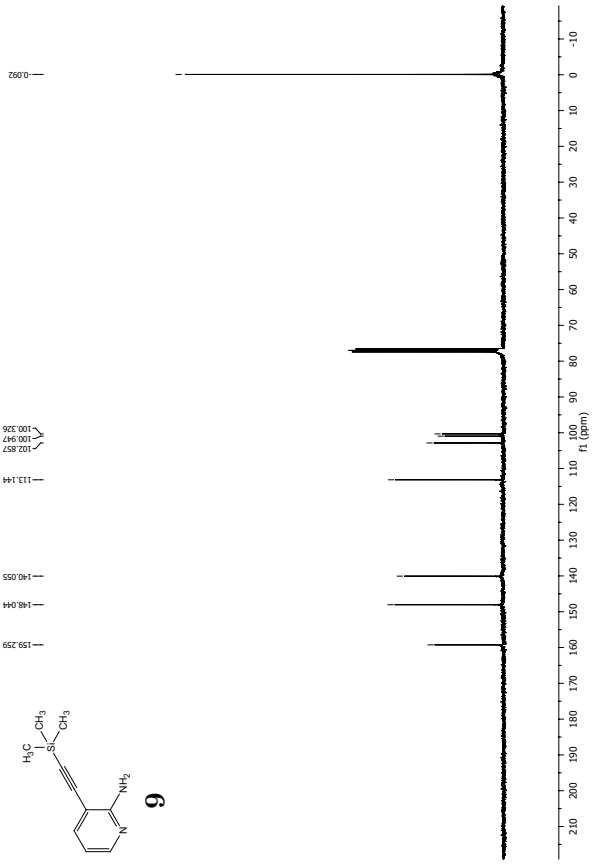

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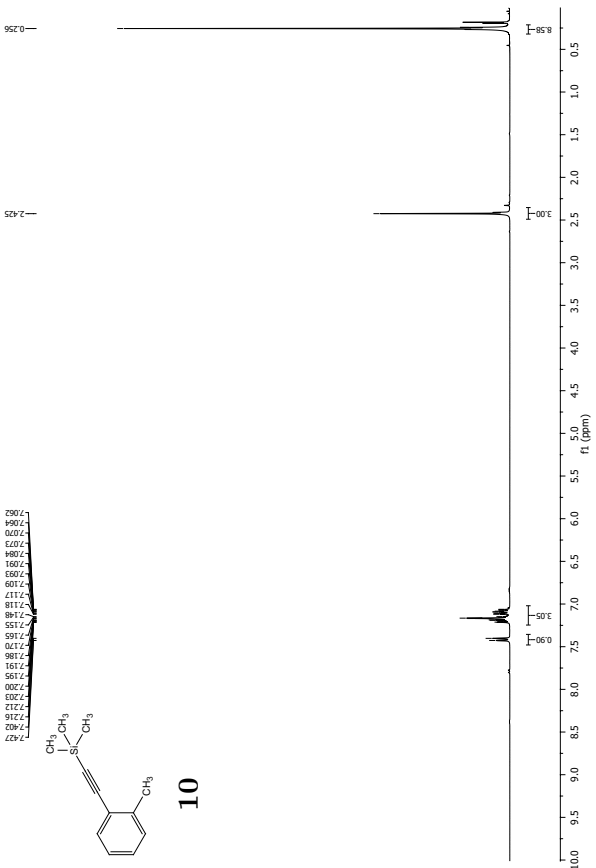

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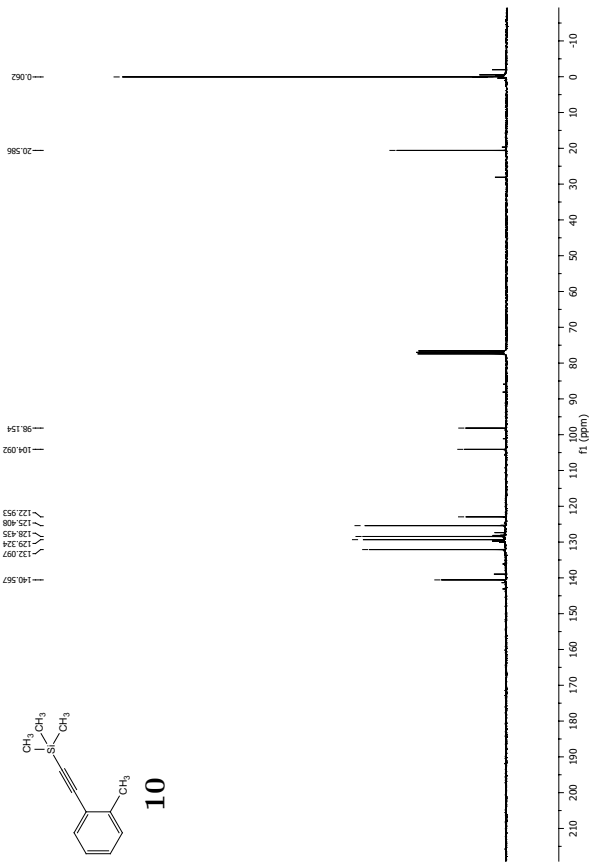

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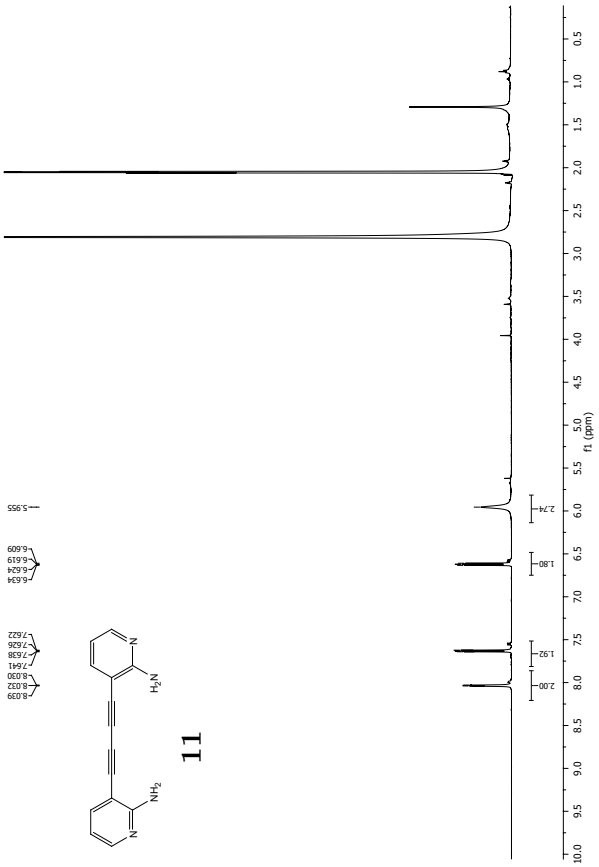

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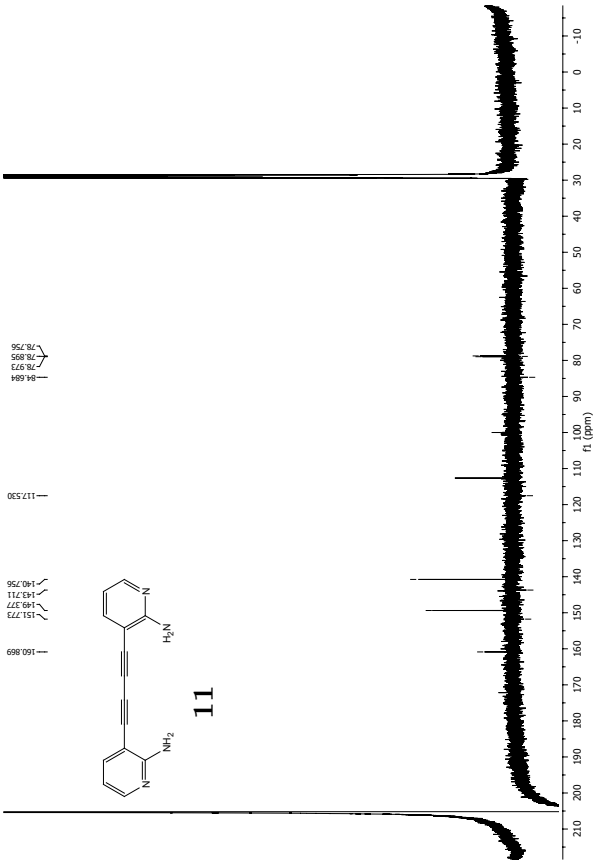

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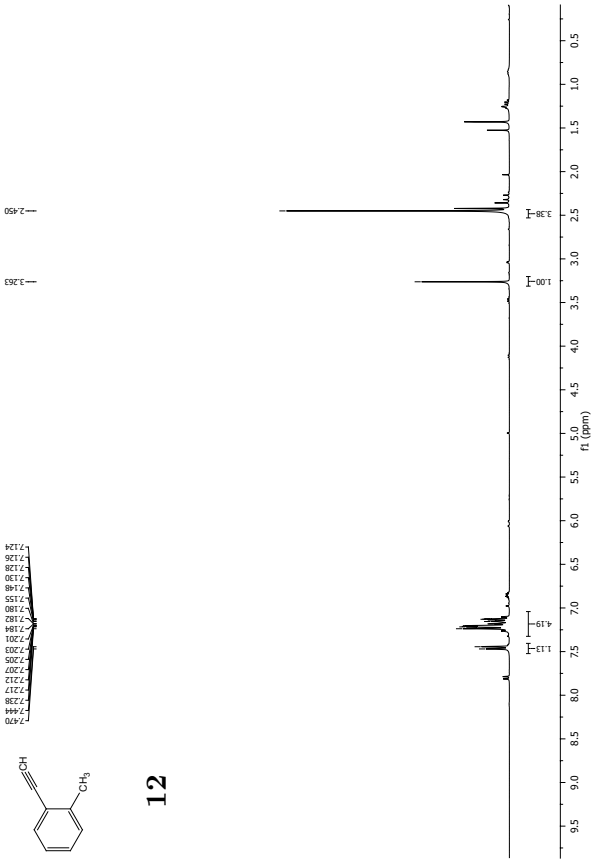

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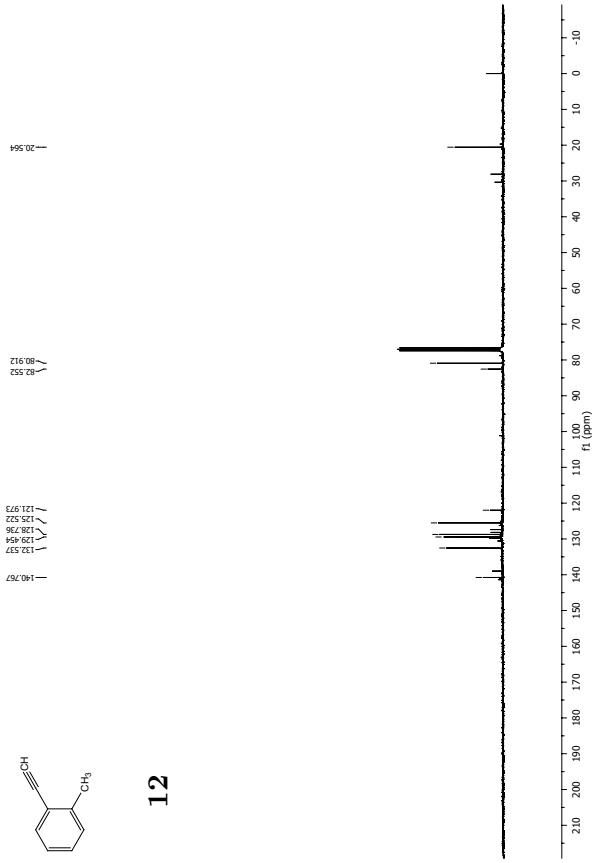

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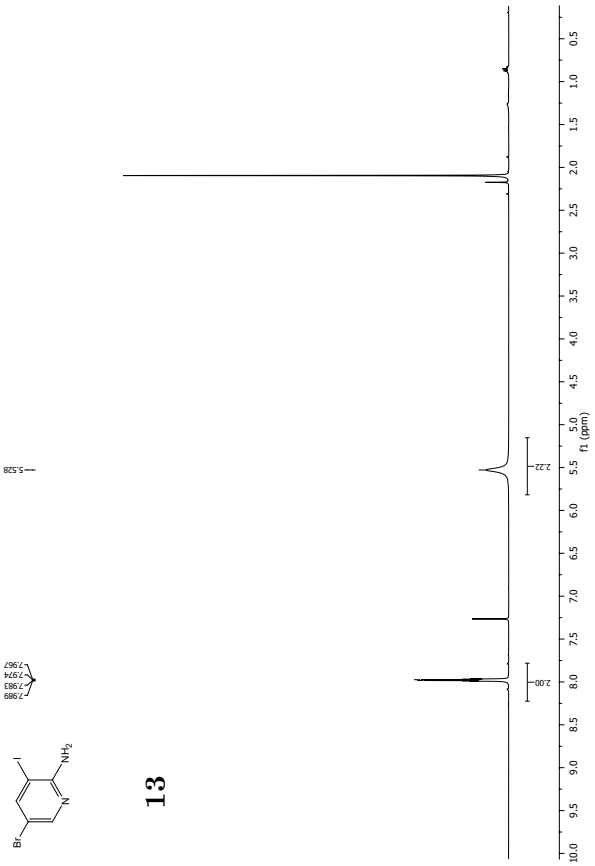

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140.567
f1 (ppm)
10


11
f1 (ppm)

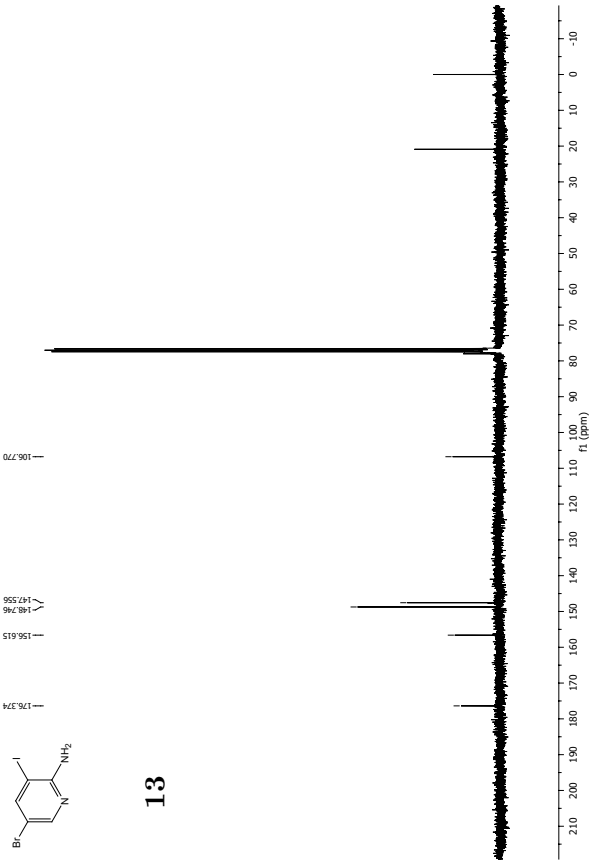

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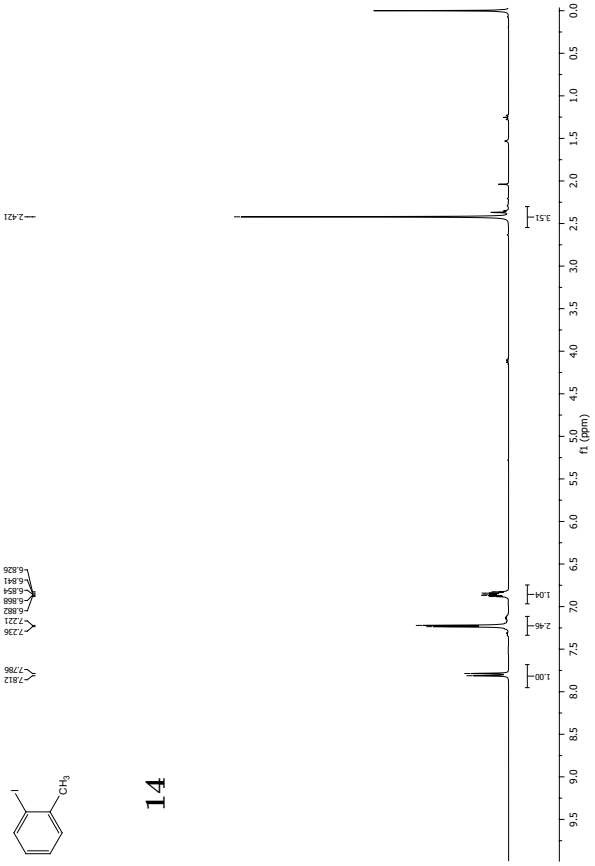

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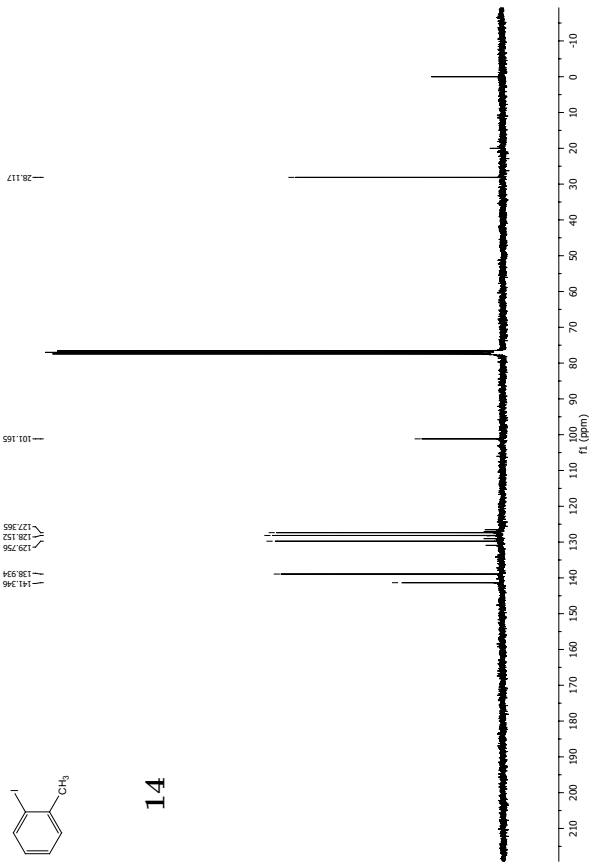
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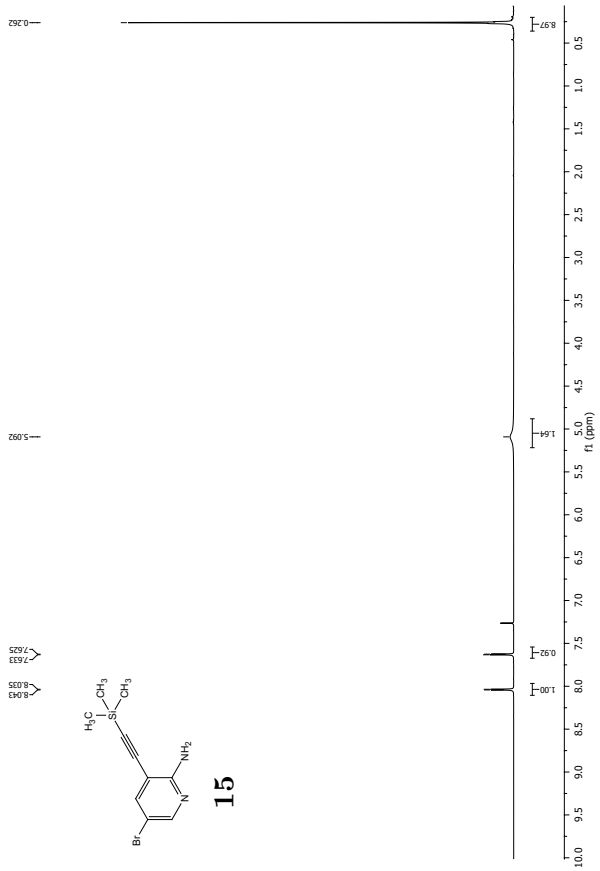
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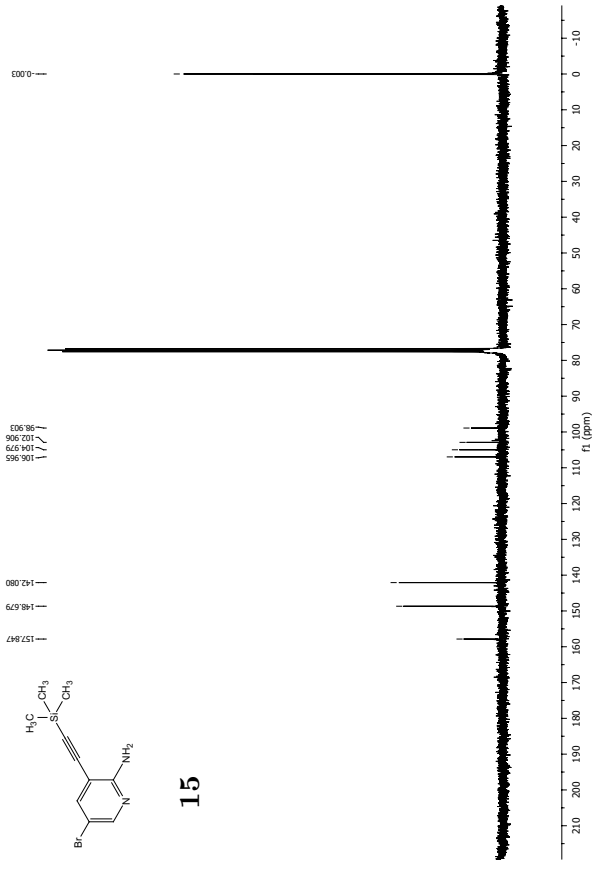

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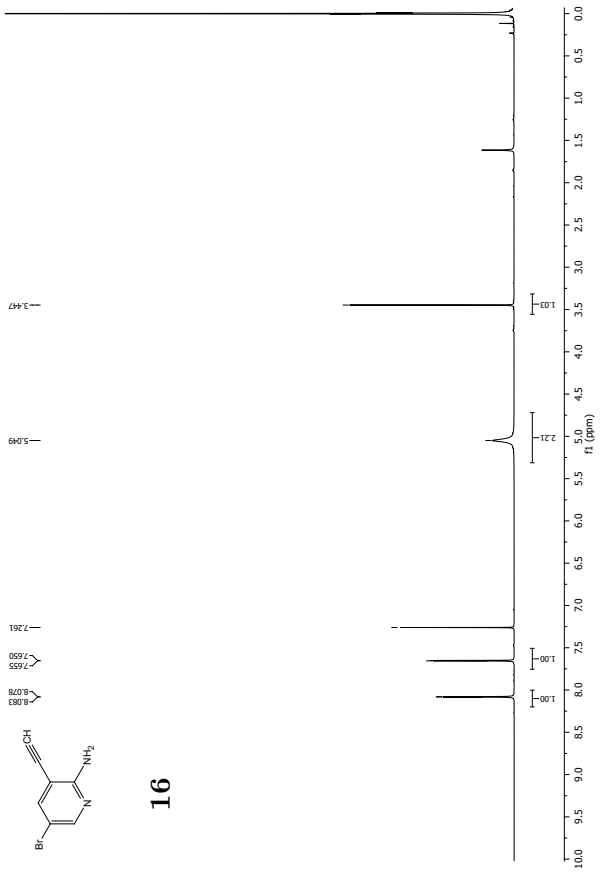
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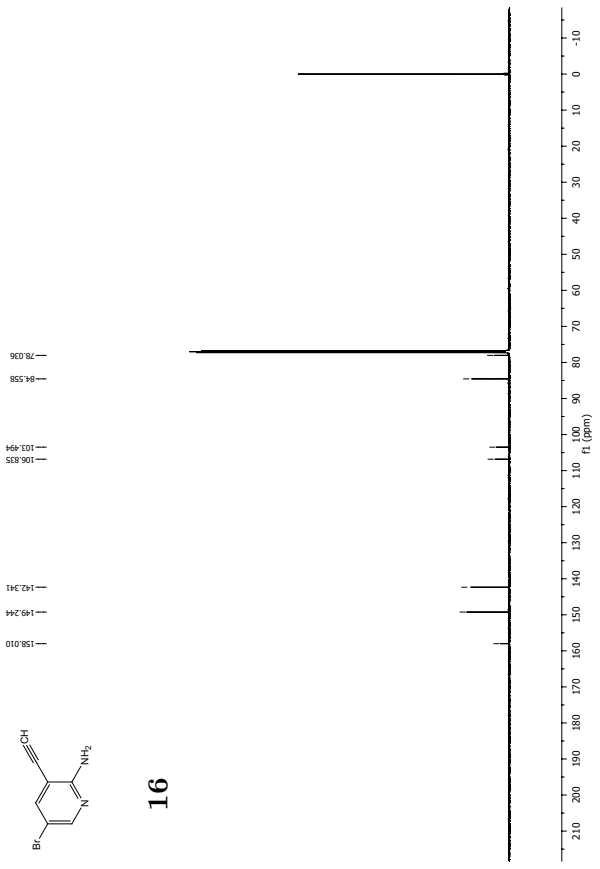

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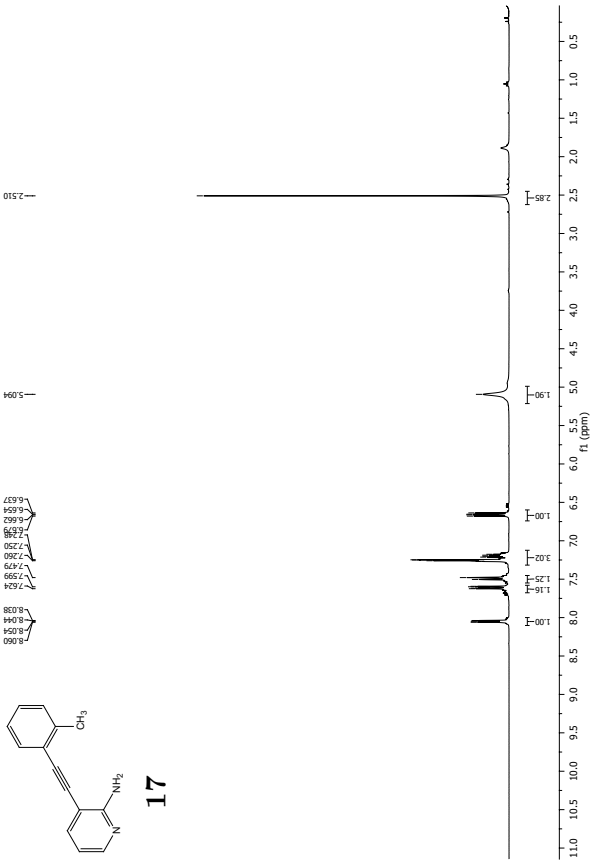
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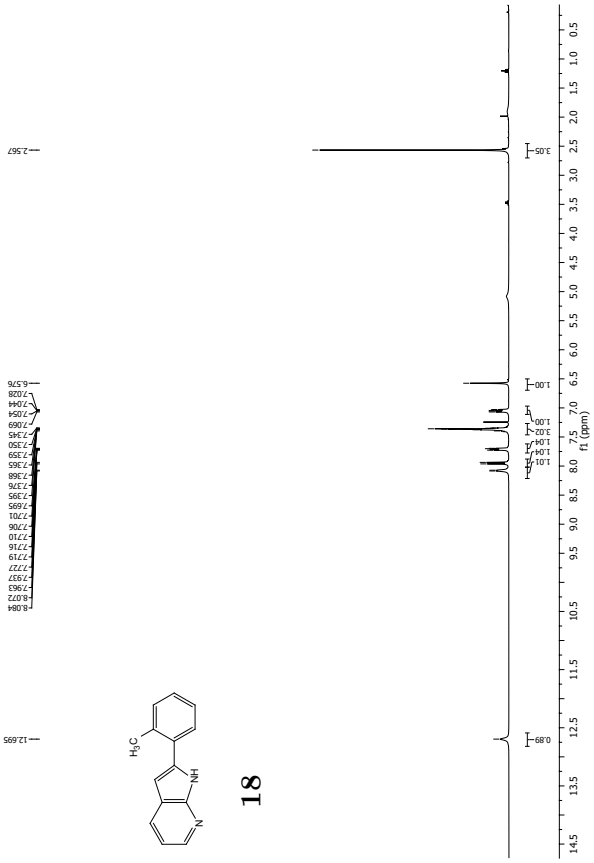

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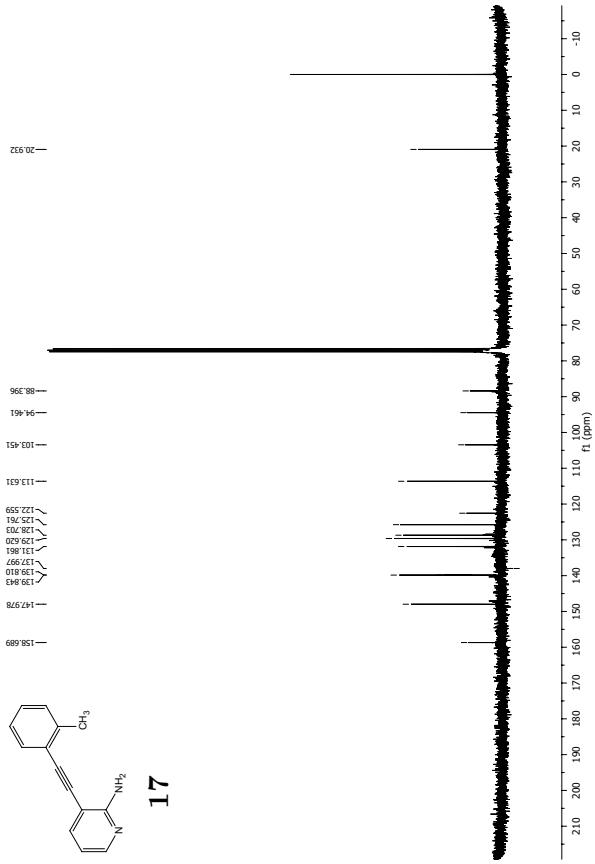

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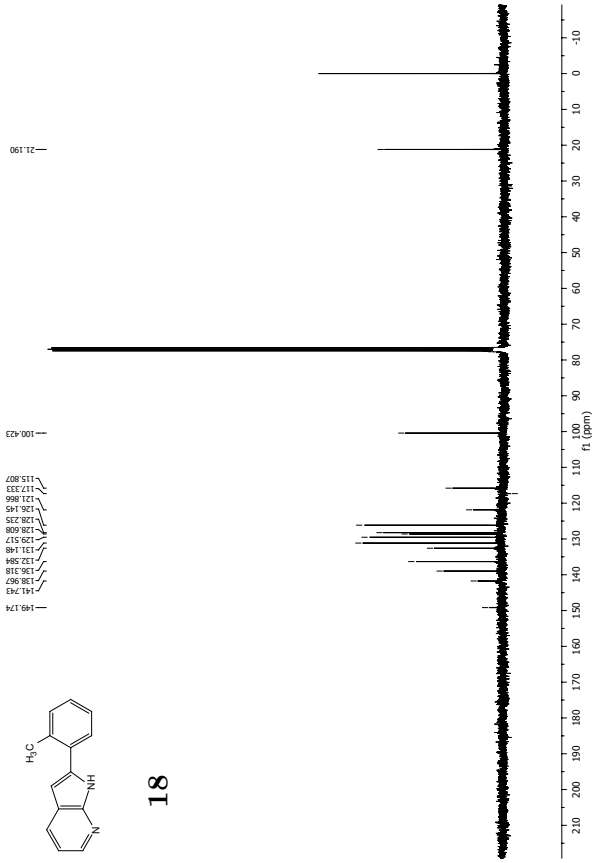
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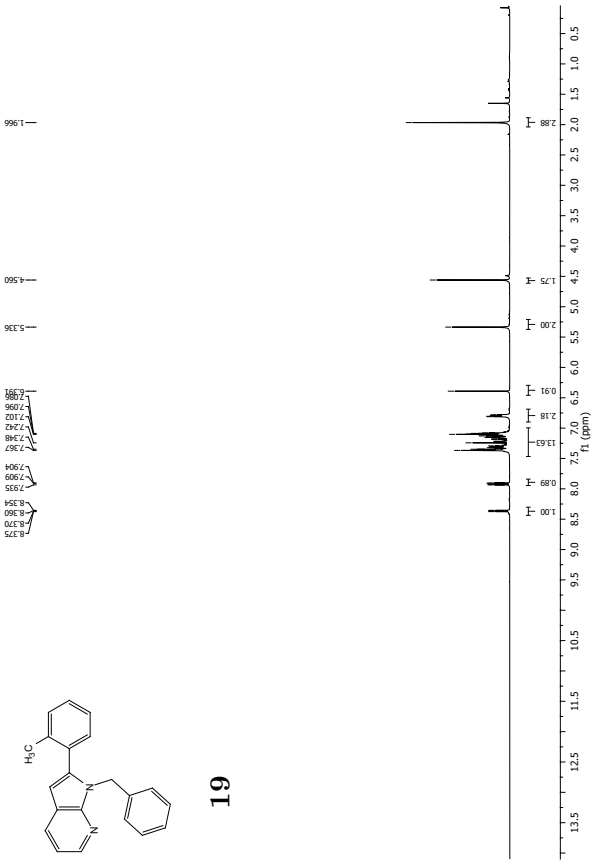
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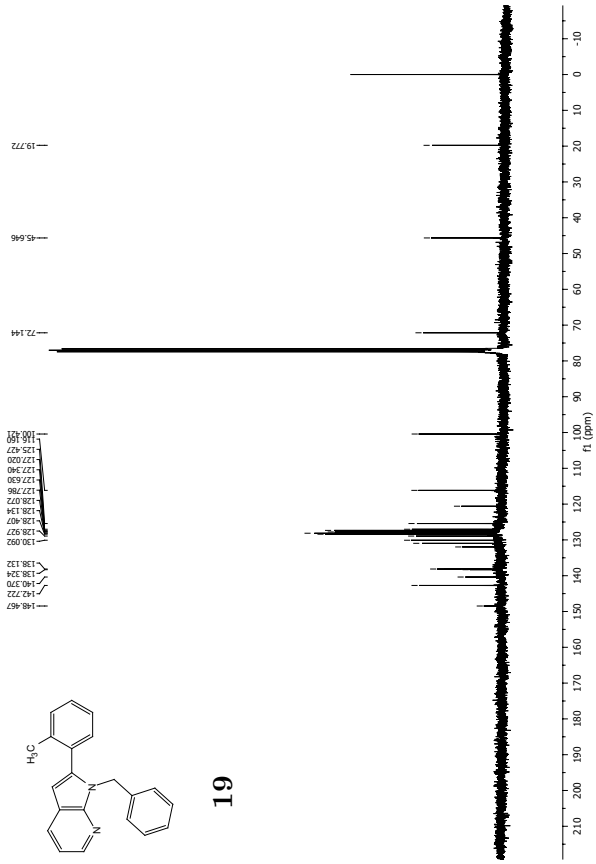
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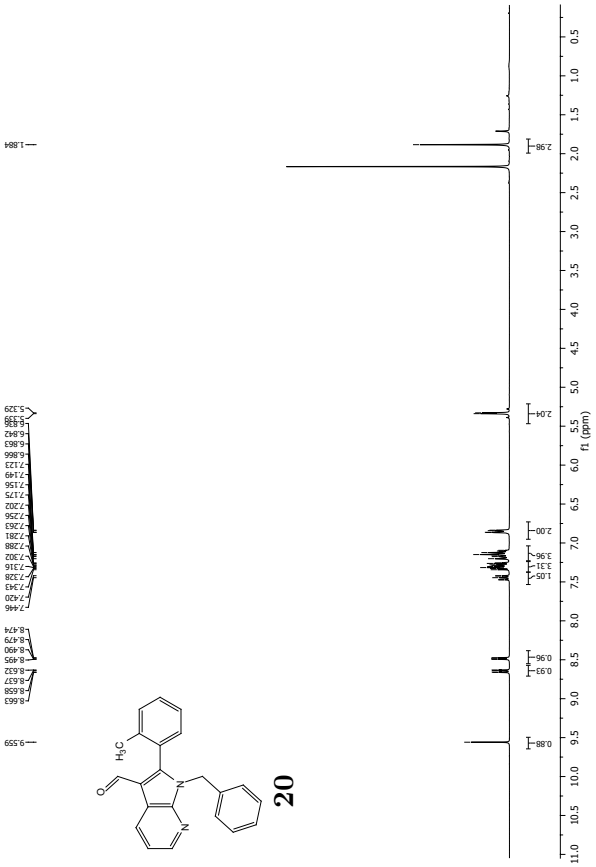
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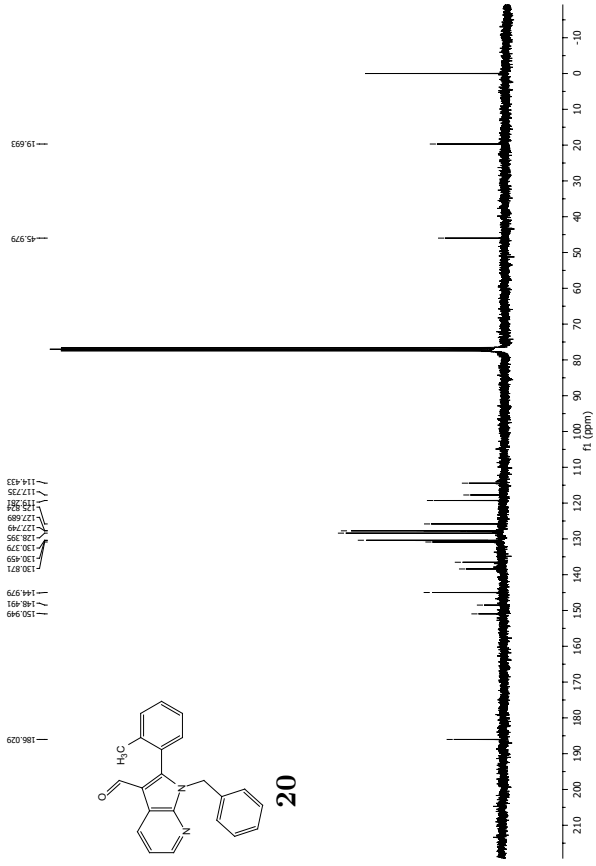
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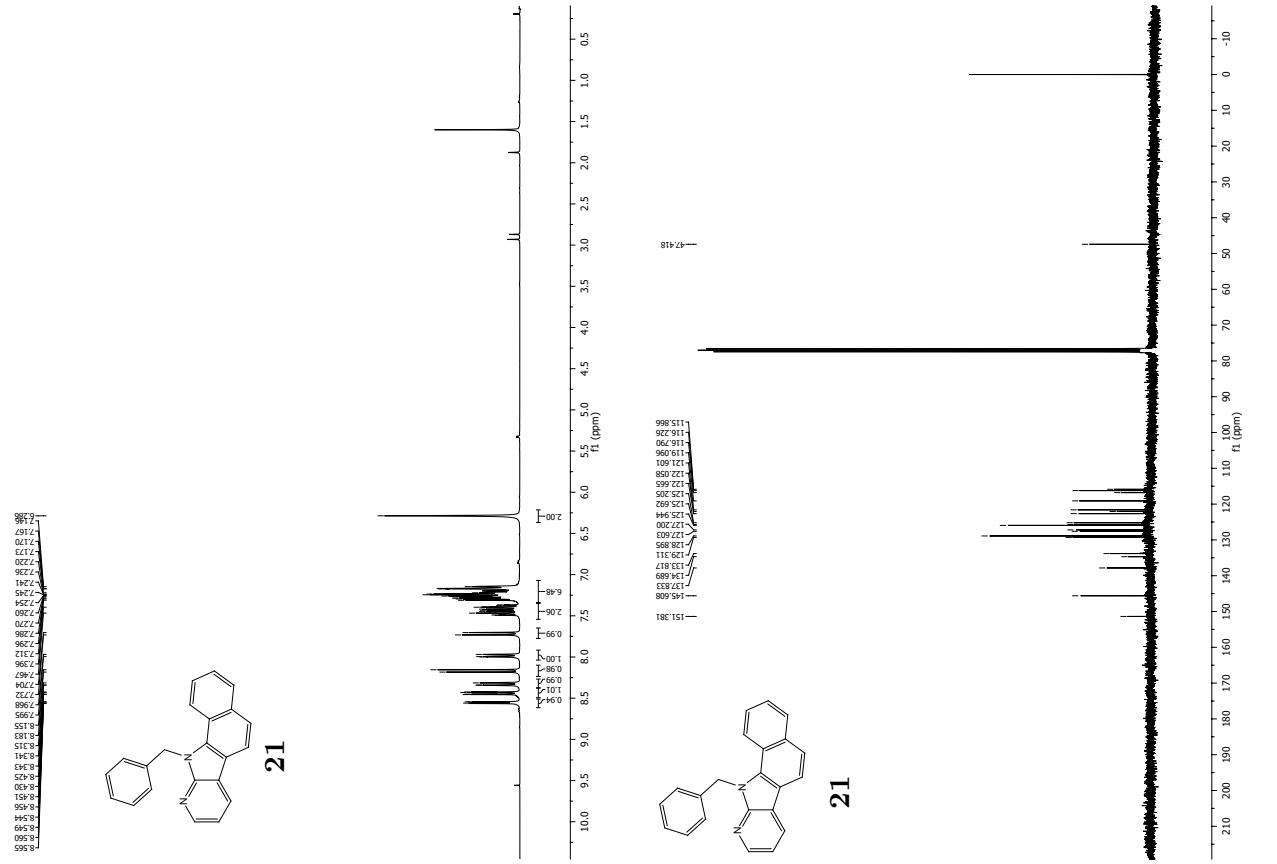
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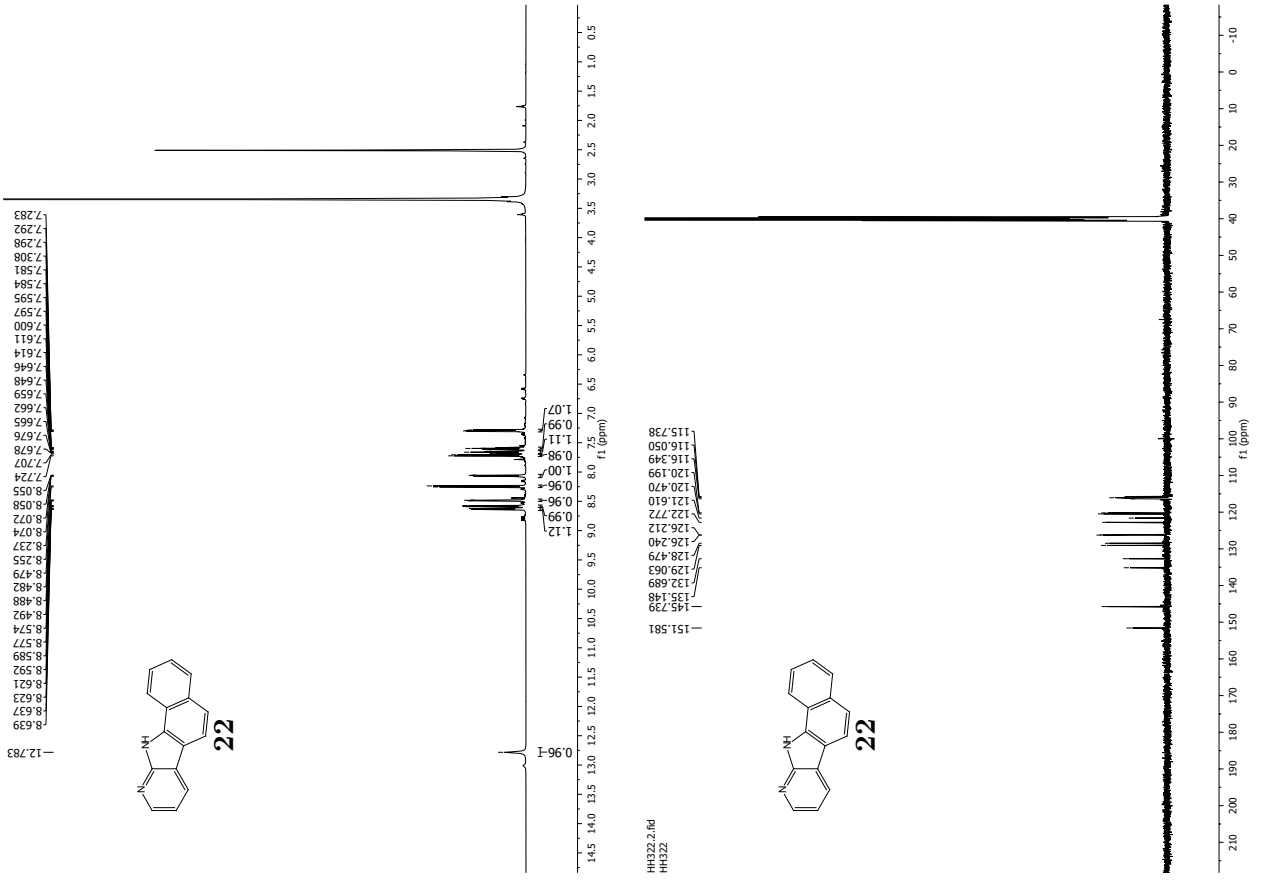


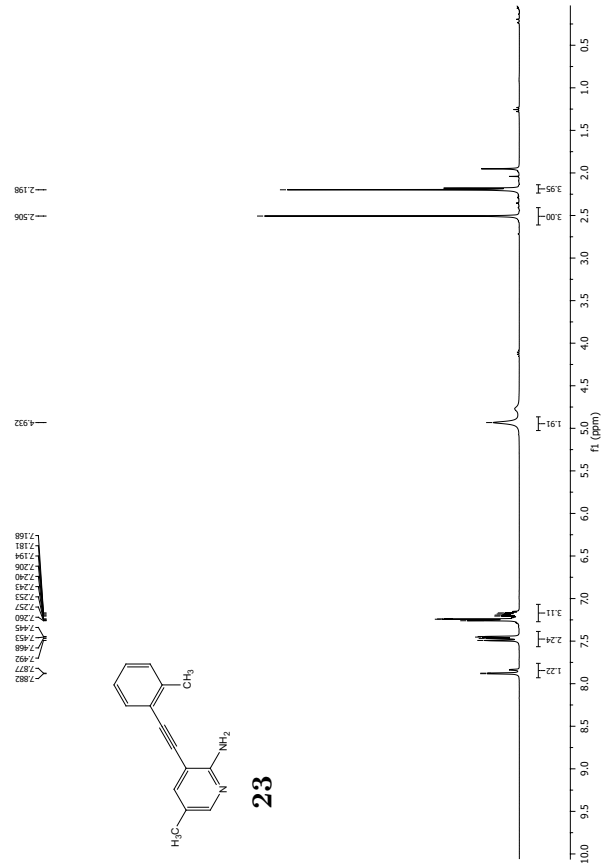
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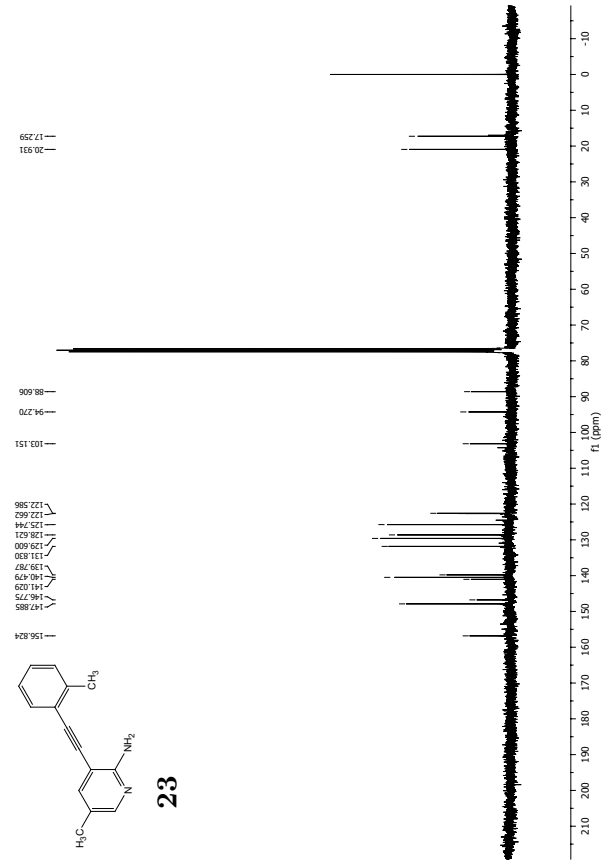


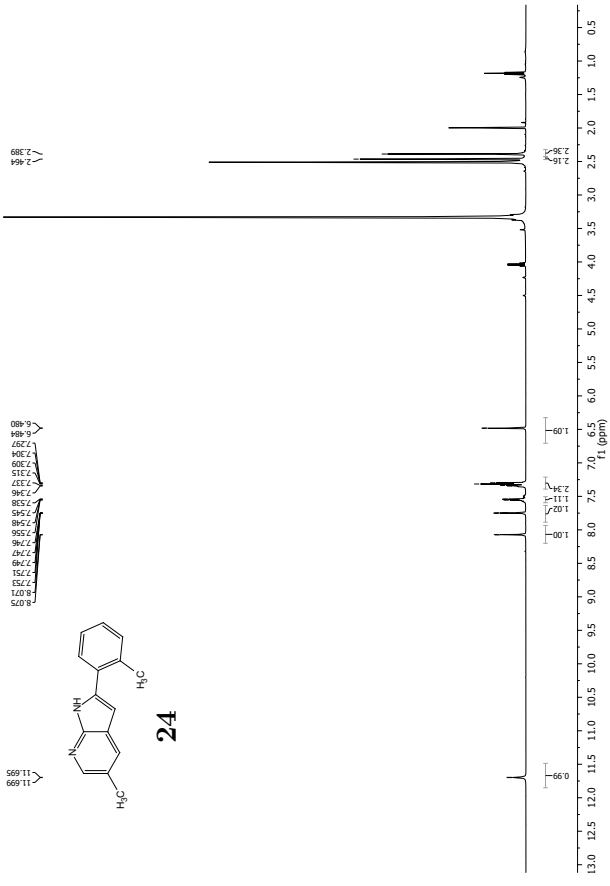
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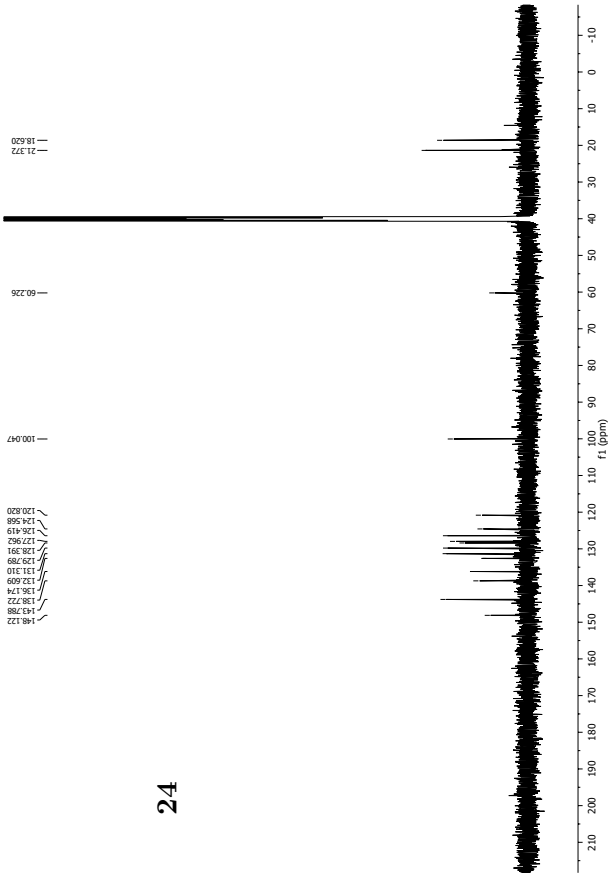

21
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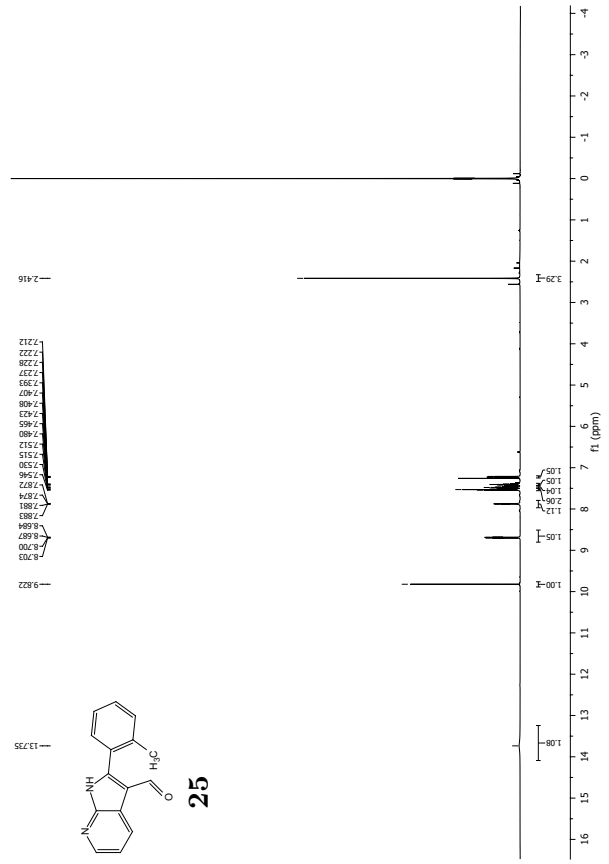

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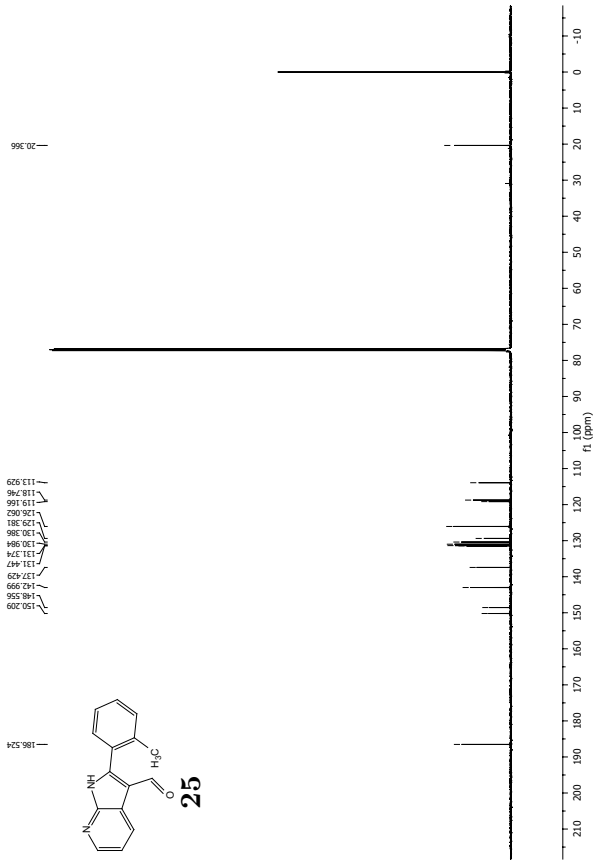

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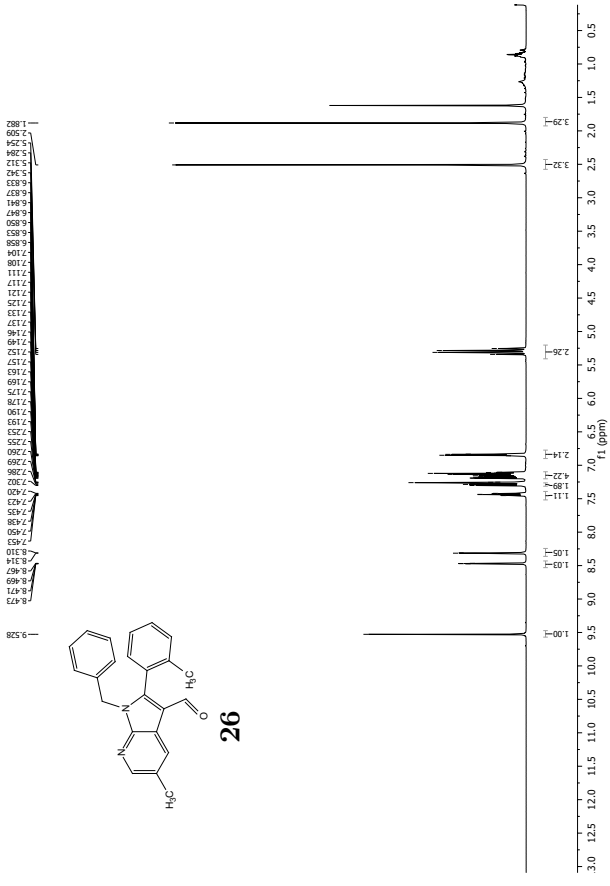

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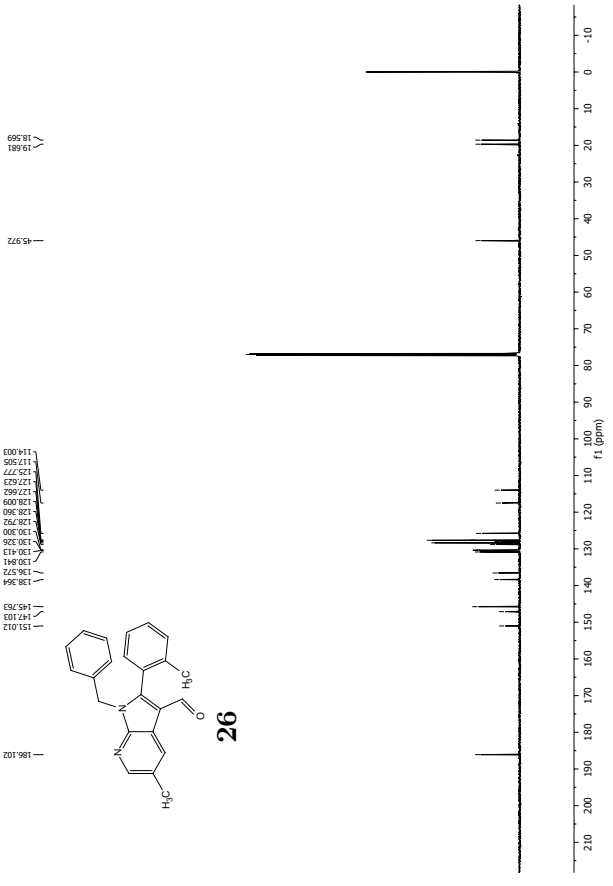

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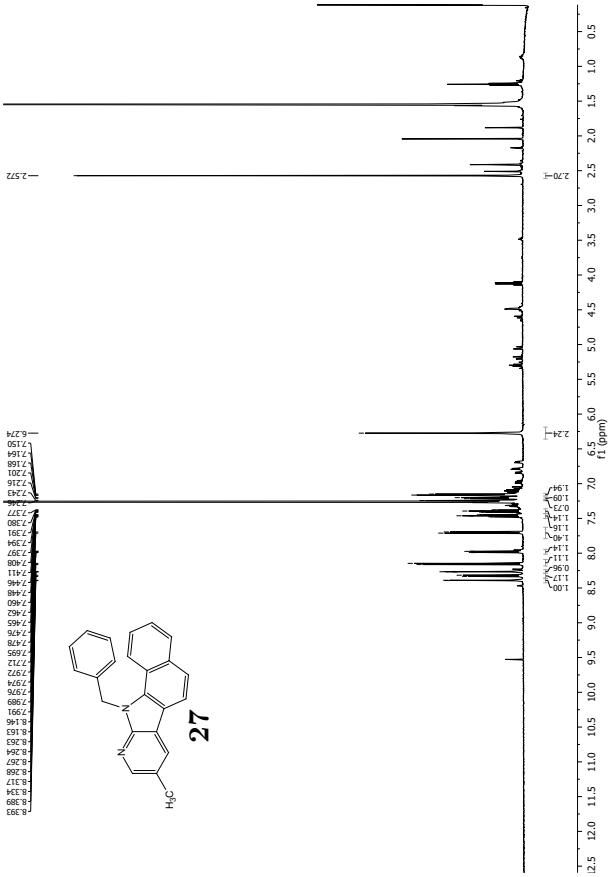

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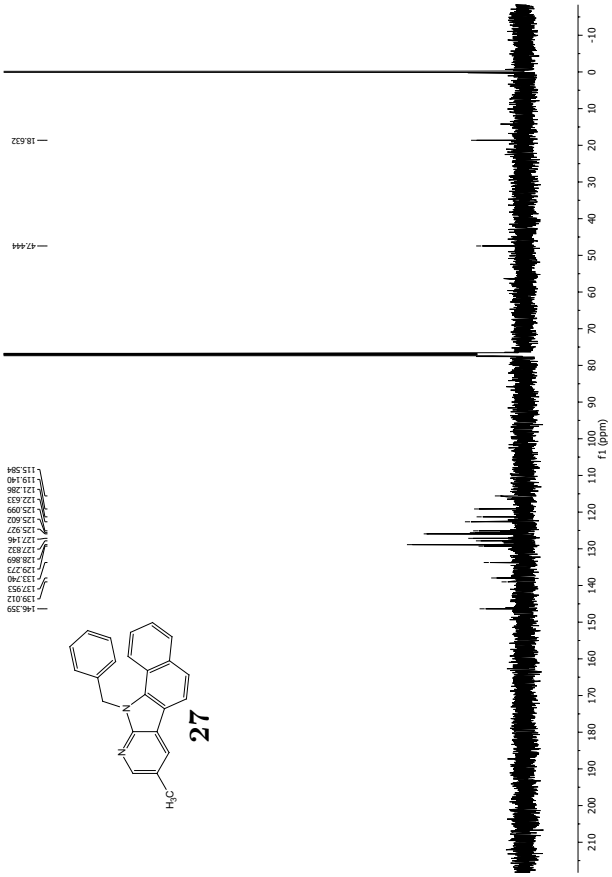

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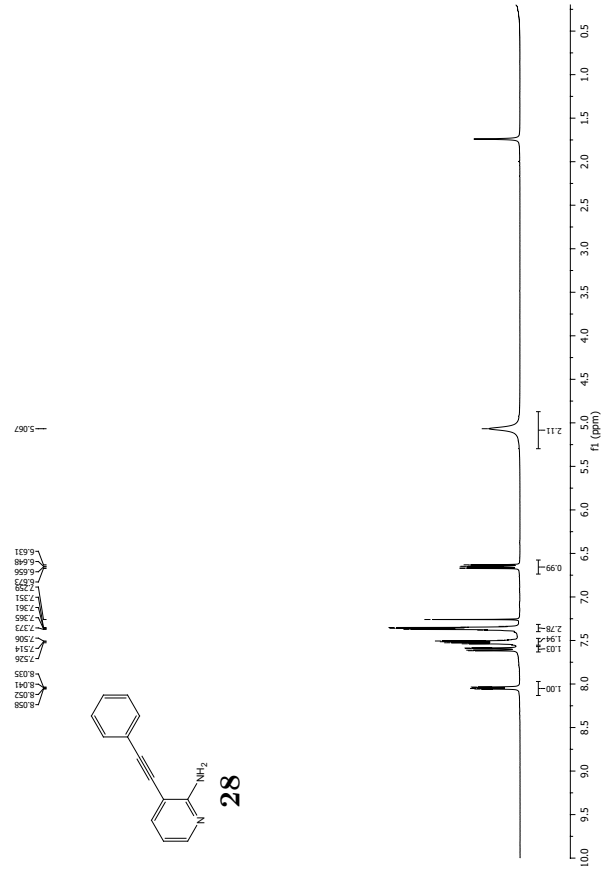

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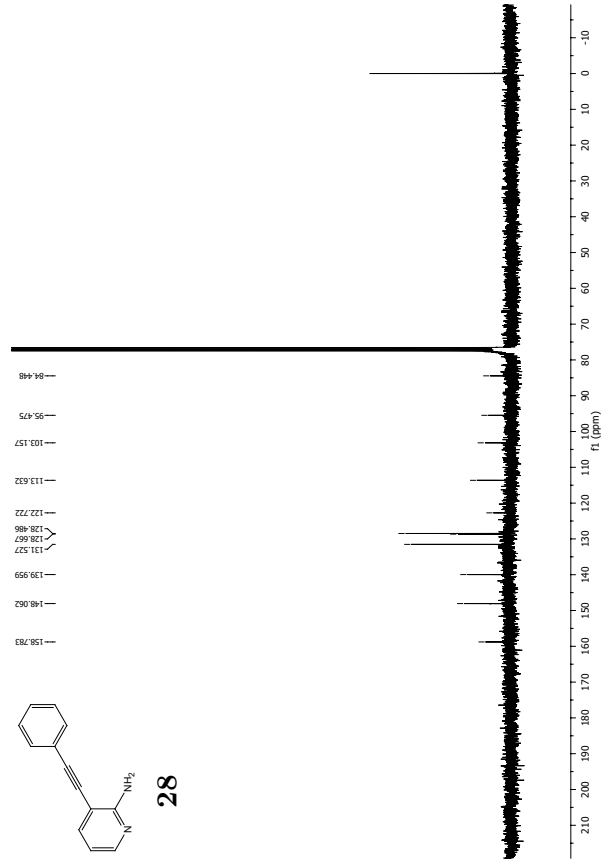

26
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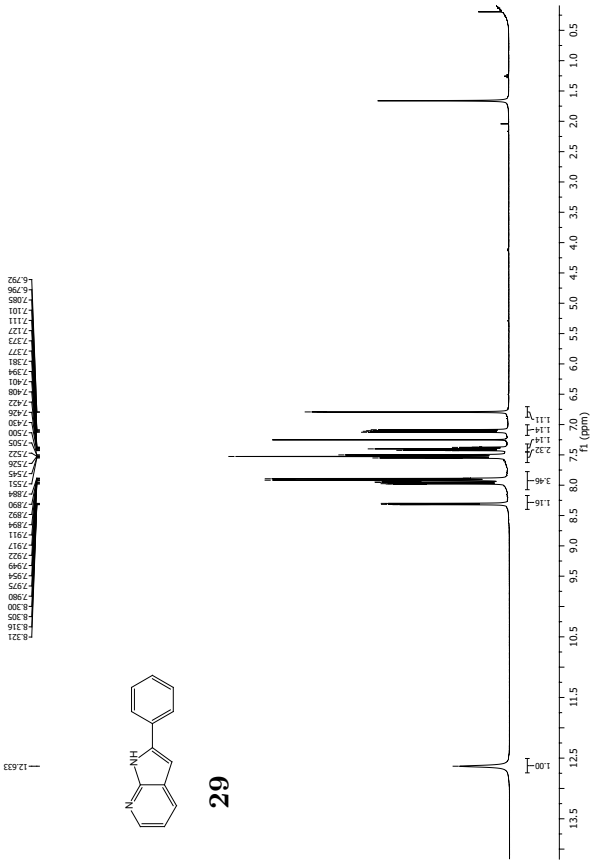

26
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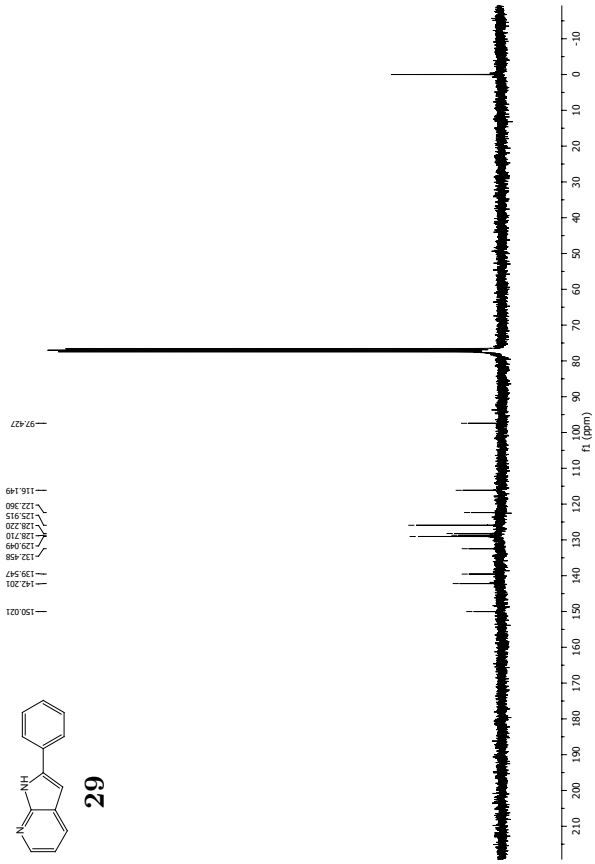

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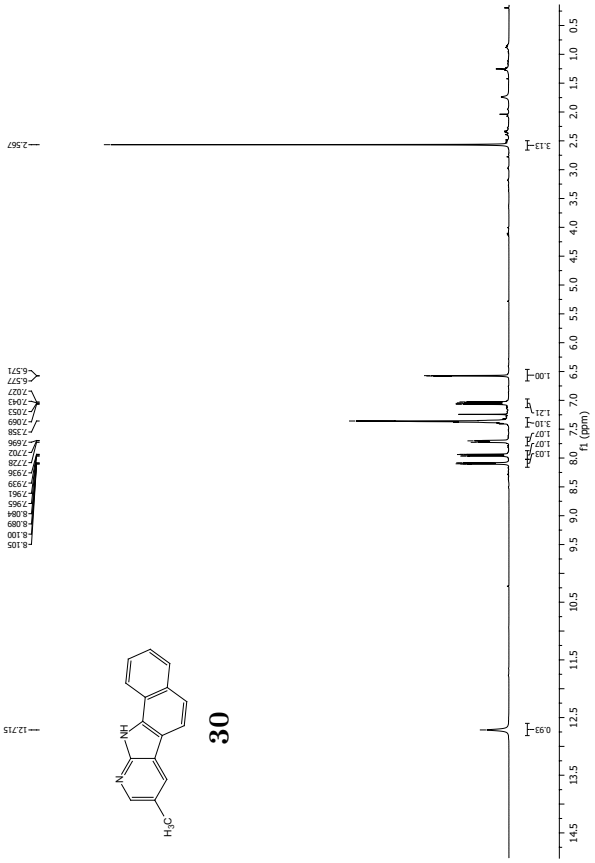

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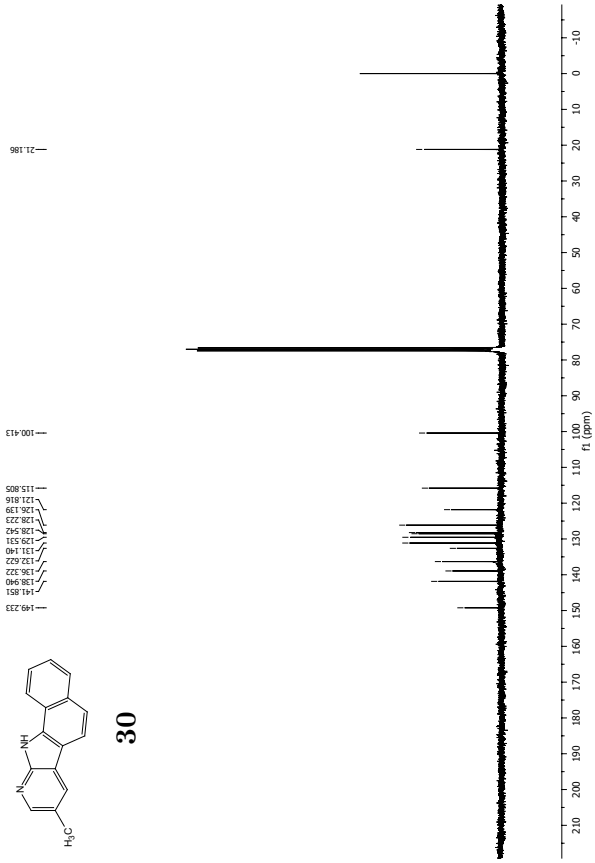

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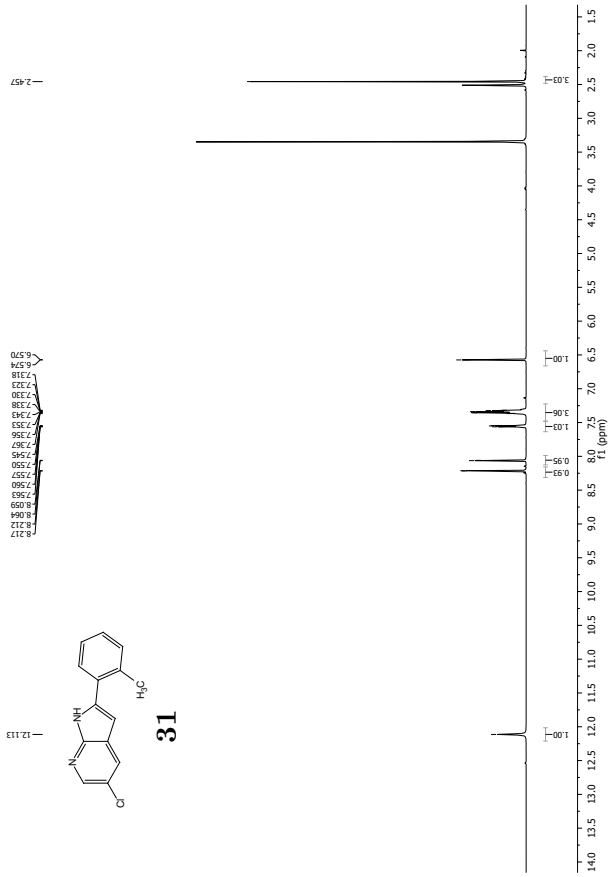

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f1 (ppm)

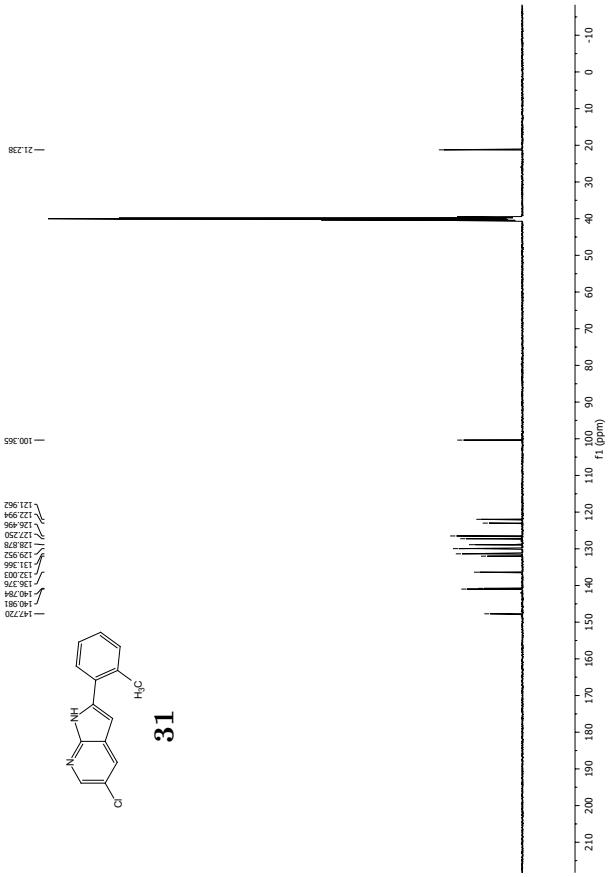

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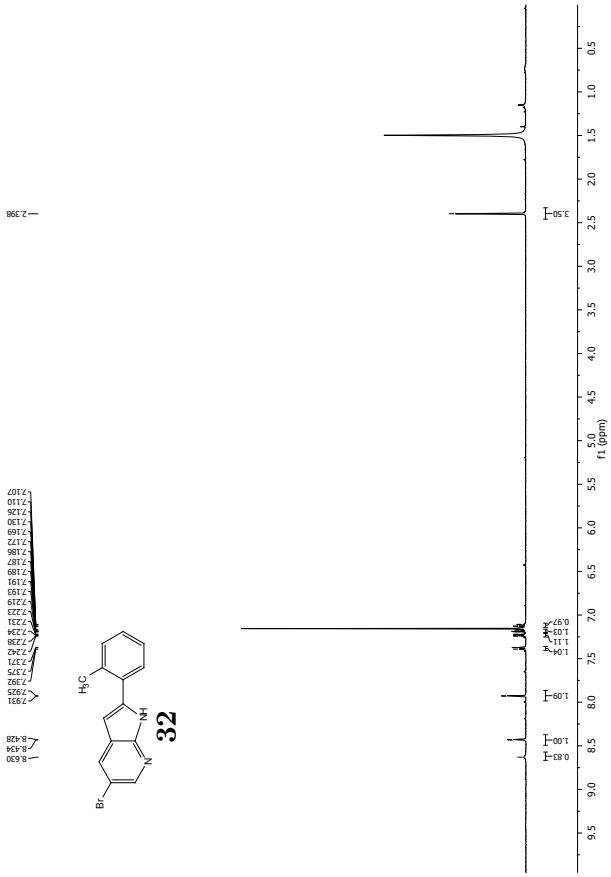

29
f1 (ppm)

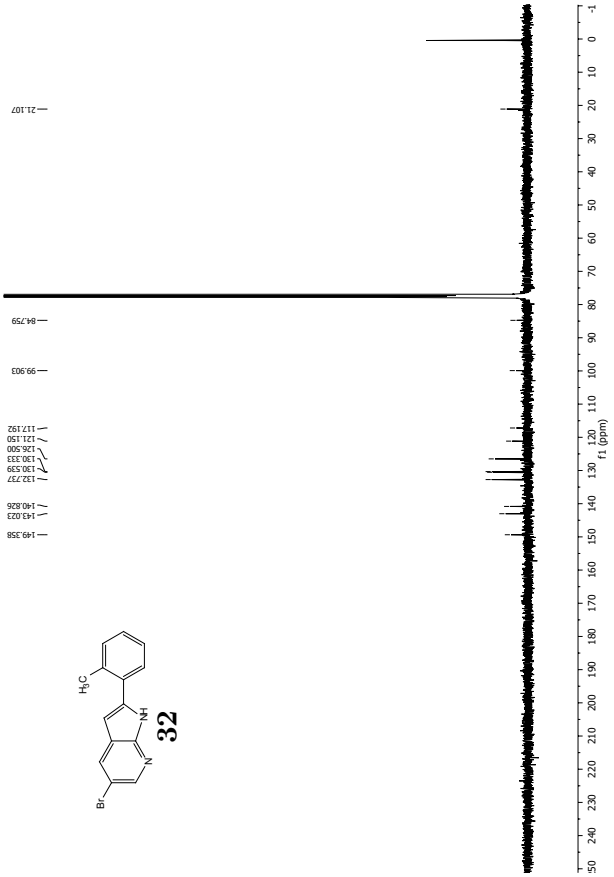

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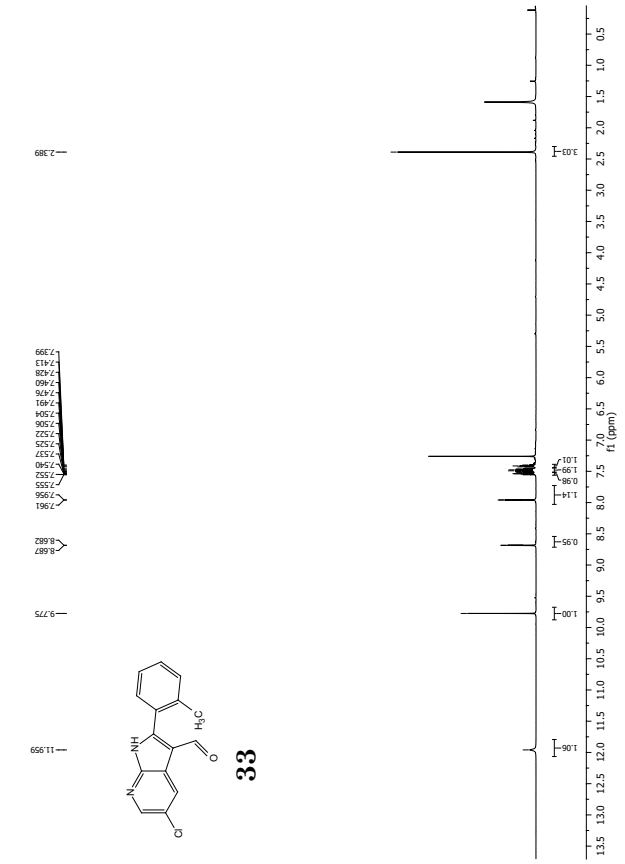

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f1 (ppm)

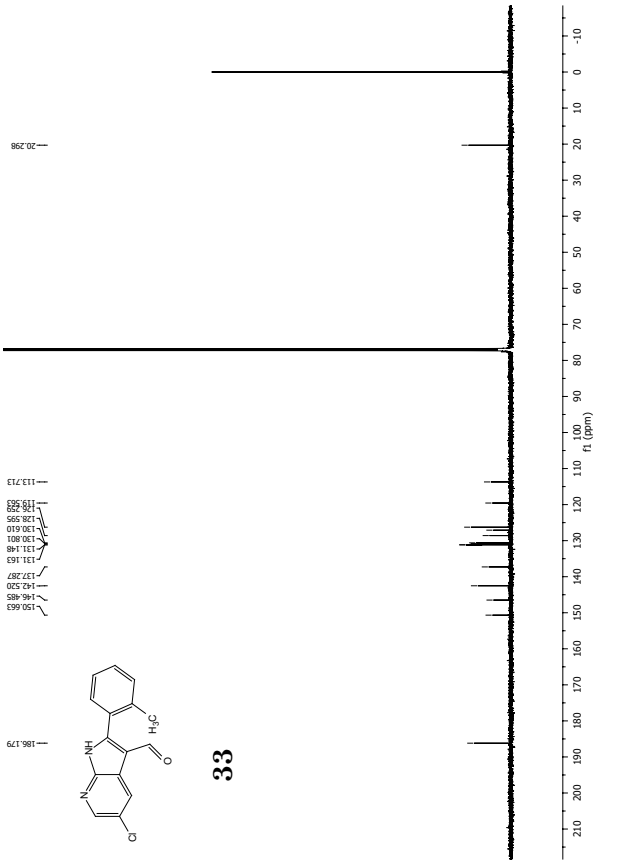

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8.059
8.064
7.563
7.560
7.557
7.550
7.367
7.346
7.356
7.353
7.343
7.338
7.323
7.330
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0.93
1.00
f1 (ppm)

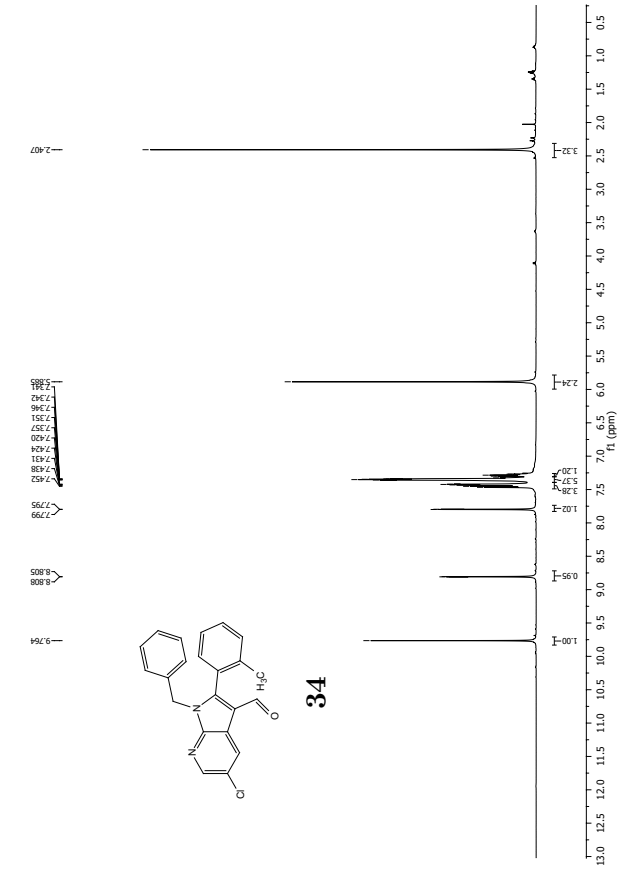

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147.720
140.981
140.784
136.376
132.003
131.366
129.952
128.828
127.250
126.496
122.994
121.962
31
f1 (ppm)

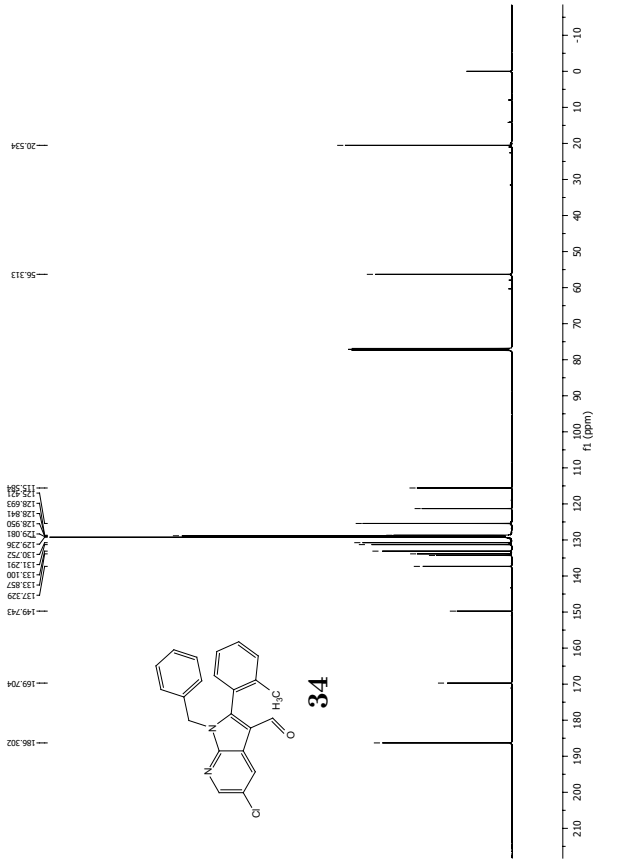

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8.494
8.428
7.931
7.925
7.392
7.375
7.321
7.242
7.238
7.234
7.231
7.223
7.219
7.193
7.191
7.189
7.187
7.186
7.172
7.169
7.130
7.126
7.110
7.107
32
3.50
1.09
1.00
0.83
1.04
1.11
1.03
0.97
f1 (ppm)

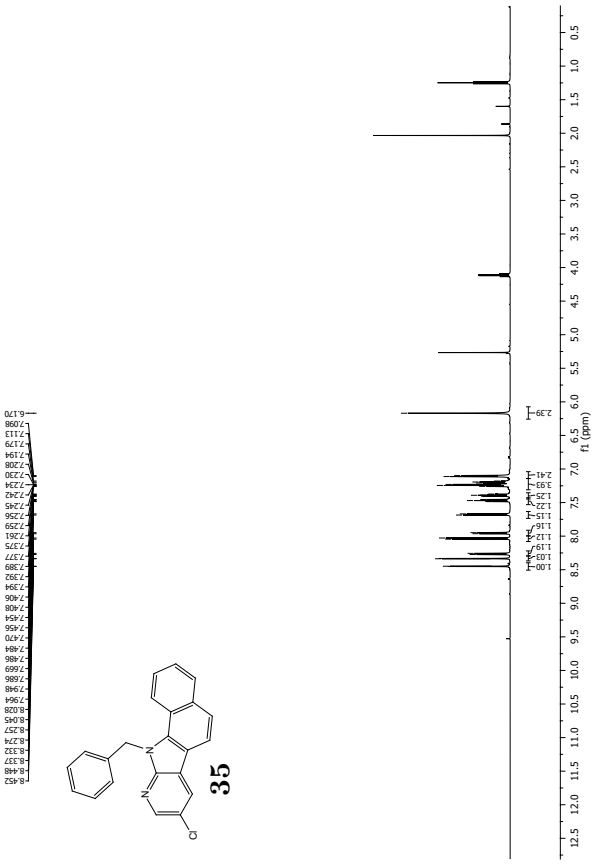

21.107
84.759
99.903
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143.023
140.826
132.737
130.539
130.333
126.500
121.150
117.192
32
f1 (ppm)

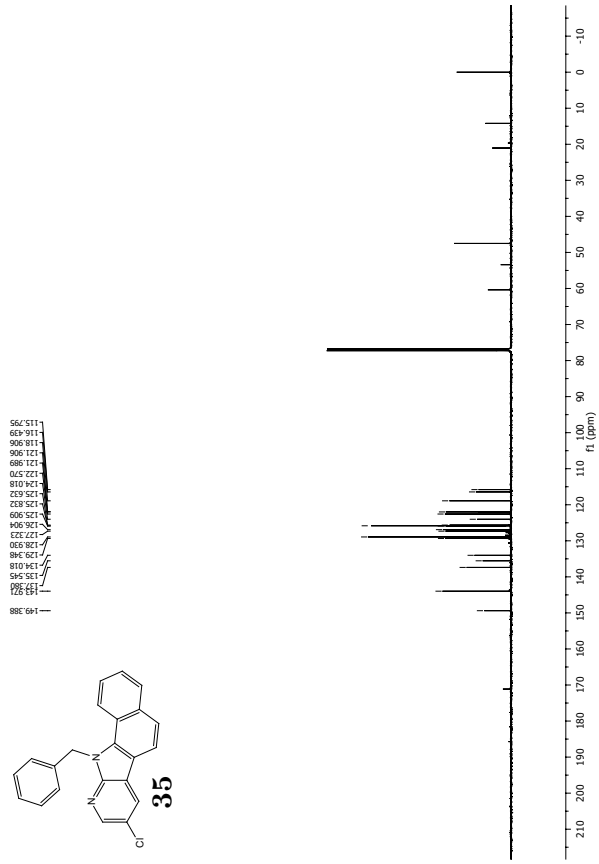

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11.959
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7.956
8.687
8.682
7.552
7.555
7.540
7.537
7.525
7.504
7.506
7.491
7.475
7.460
7.428
7.413
7.399
3.03
1.00
1.06
1.14
1.99
0.98
1.01
0.95
f1 (ppm)
33

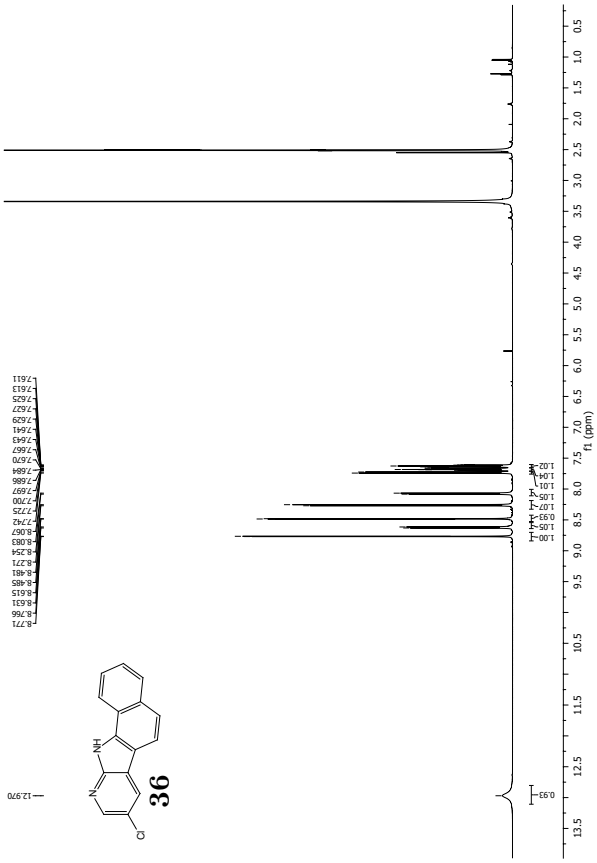

20.298
186.179
113.713
150.663
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142.520
137.287
131.163
131.148
130.801
130.610
128.595
126.829
119.563
f1 (ppm)
33

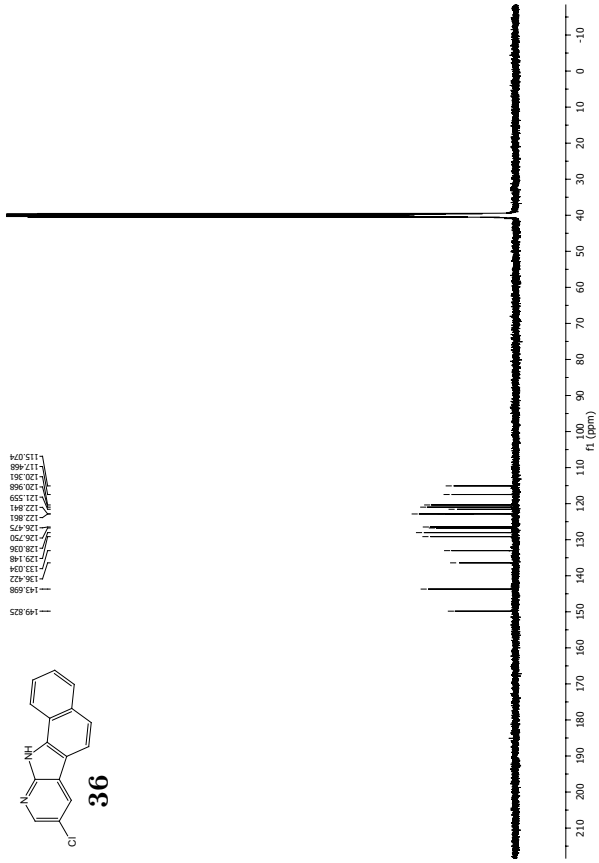

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8.805
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7.795
7.452
7.441
7.431
7.424
7.420
7.357
7.351
7.346
7.342
7.341
5.885
3.32
2.24
1.20
3.28
5.37
1.02
0.95
1.00
f1 (ppm)
34

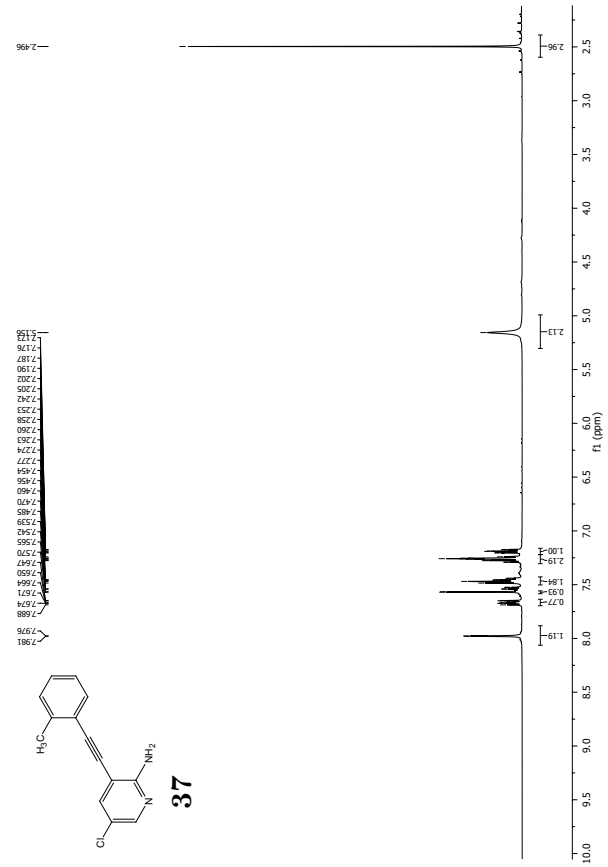

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56.313
186.302
169.704
149.743
137.329
133.857
133.100
131.291
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129.236
129.081
128.950
128.841
126.693
125.921
115.584
f1 (ppm)
34

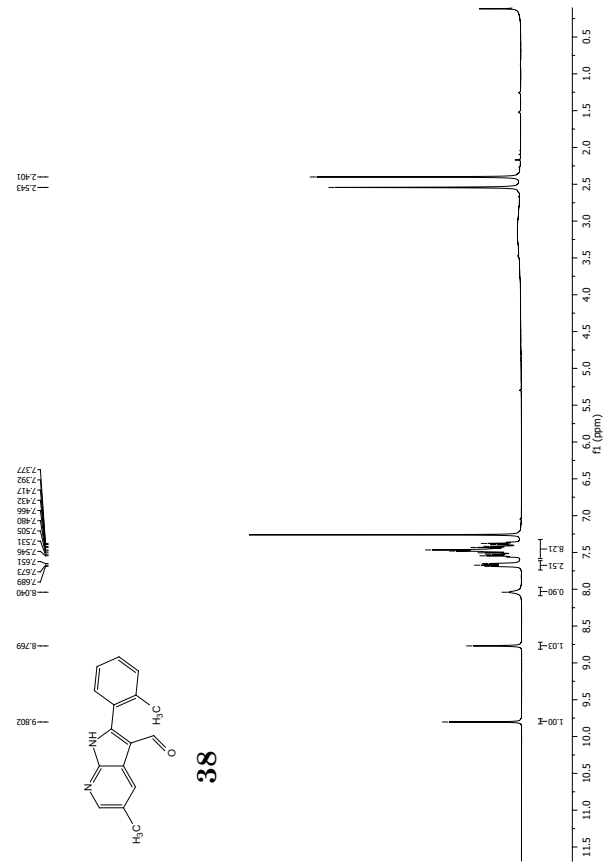

35
f1 (ppm)

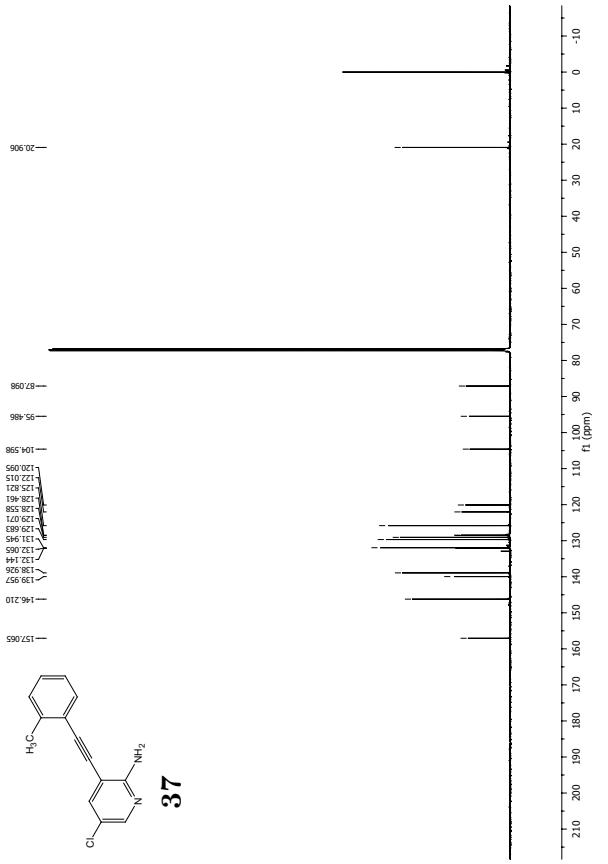

35
f1 (ppm)

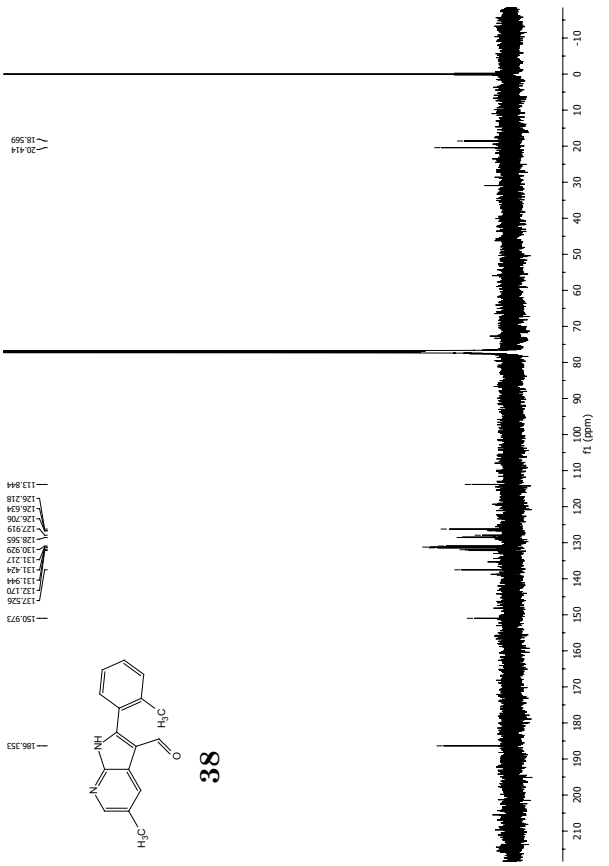

36
f1 (ppm)

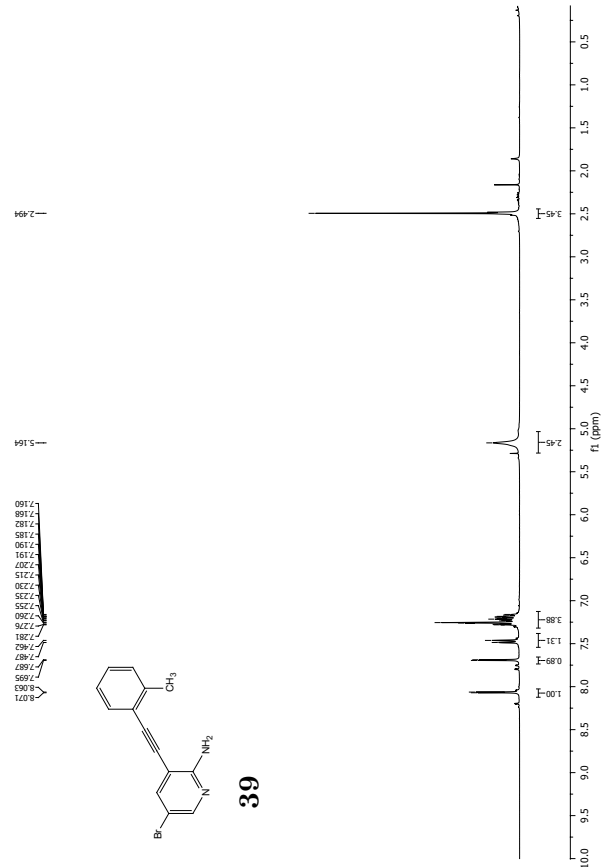

36
f1 (ppm)

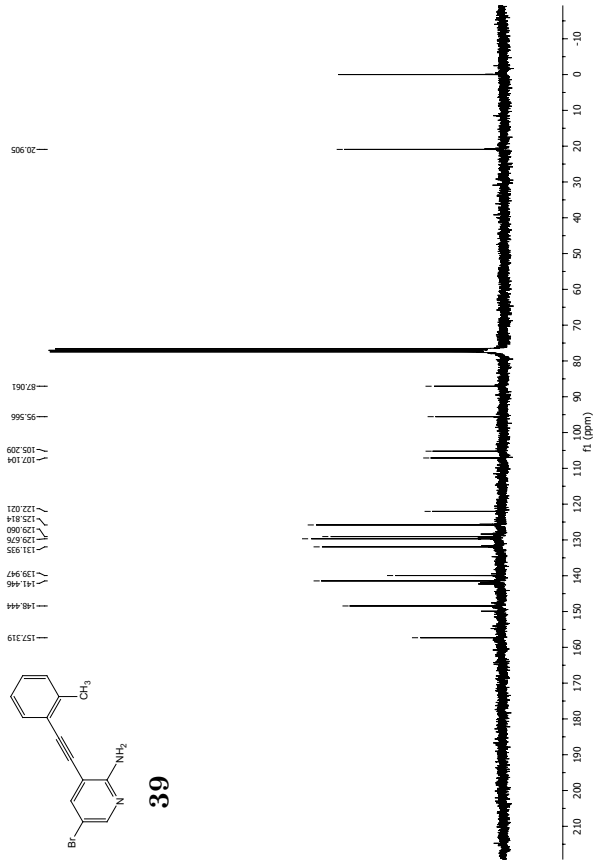

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2.19
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0.93
0.77
1.19
2.496
7.981
7.976
7.688
7.624
7.571
7.564
7.547
7.520
7.497
7.485
7.470
7.460
7.456
7.454
7.277
7.274
7.263
7.260
7.258
7.253
7.242
7.205
7.202
7.190
7.187
7.176
7.173
7.168
f1 (ppm)
37

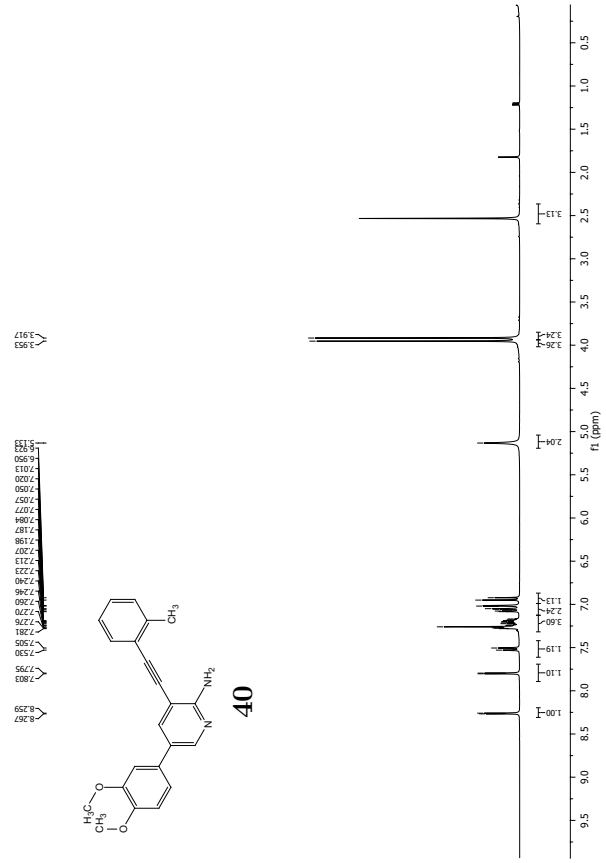

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2.543
2.401
9.802
8.769
8.040
7.689
7.673
7.651
7.546
7.531
7.505
7.480
7.466
7.432
7.417
7.392
7.377
f1 (ppm)
38

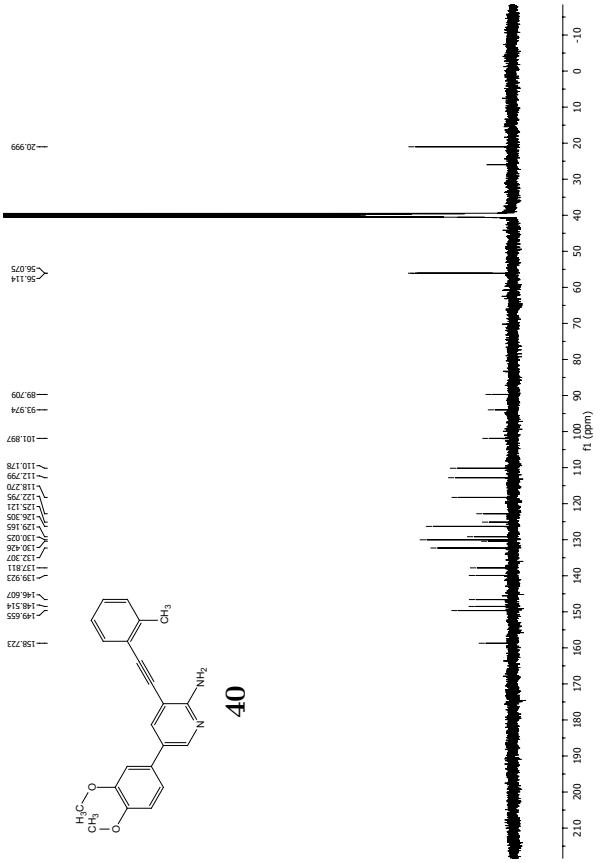

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122.015
125.821
128.461
128.558
129.071
129.683
131.945
132.065
132.144
138.926
139.957
146.210
157.065
f1 (ppm)
37

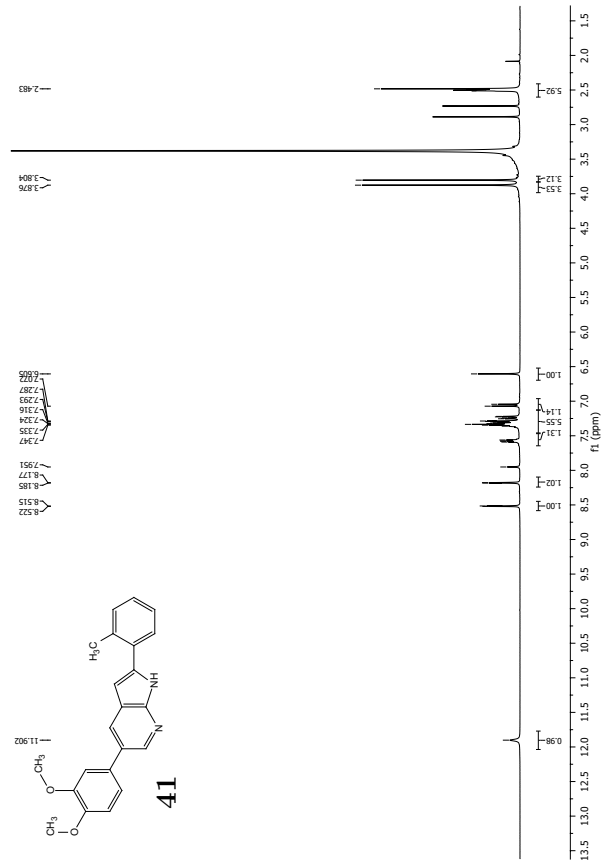

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113.844
126.218
126.634
126.786
127.919
128.565
130.929
131.177
131.424
131.944
132.170
132.526
150.973
186.353
f1 (ppm)
38

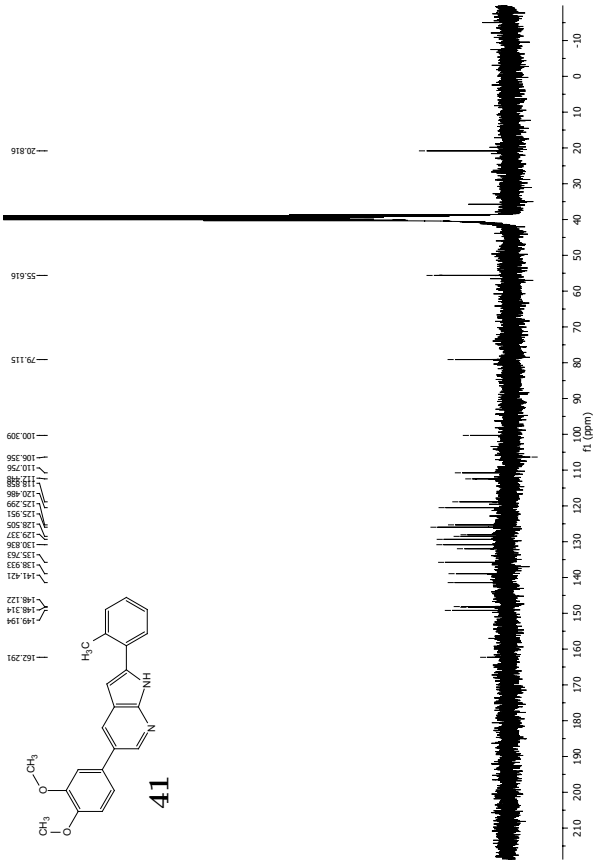

39
f1 (ppm)

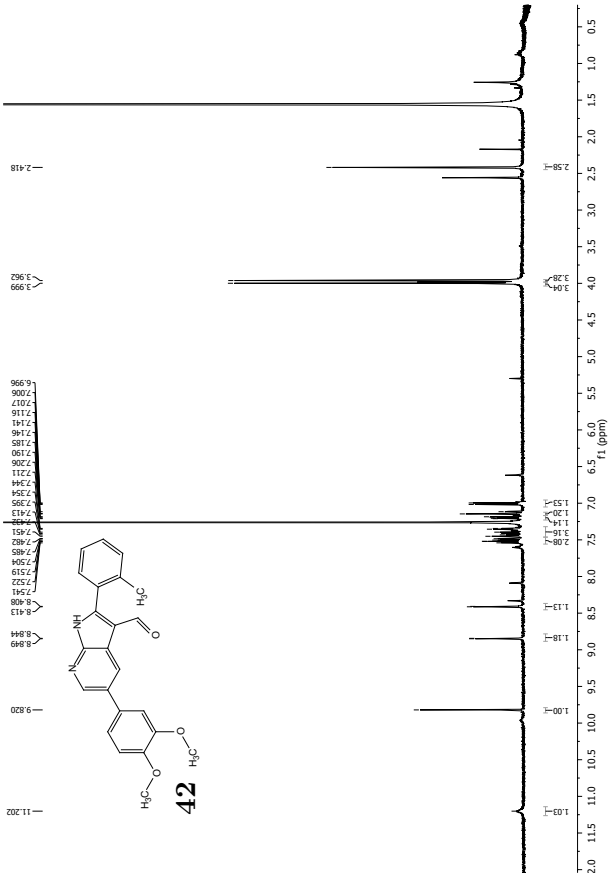

39
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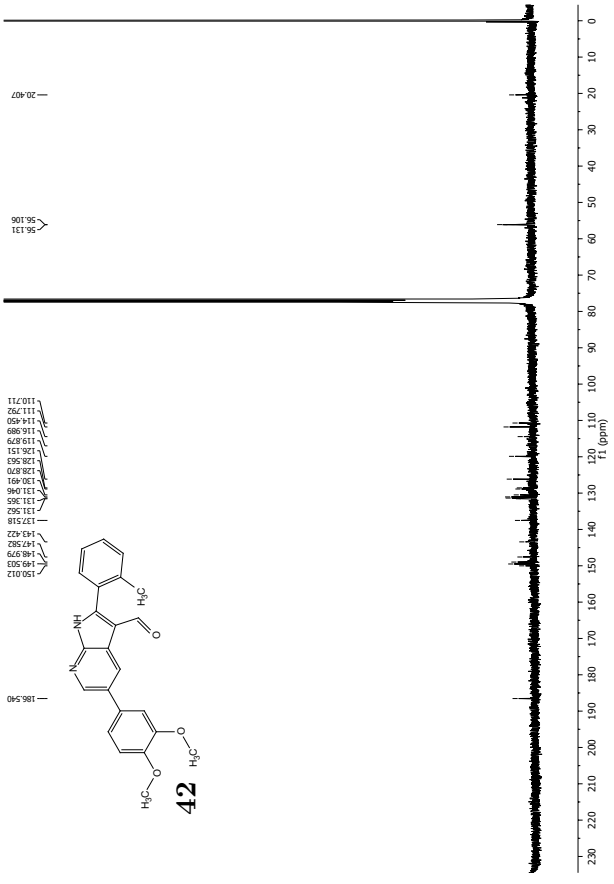

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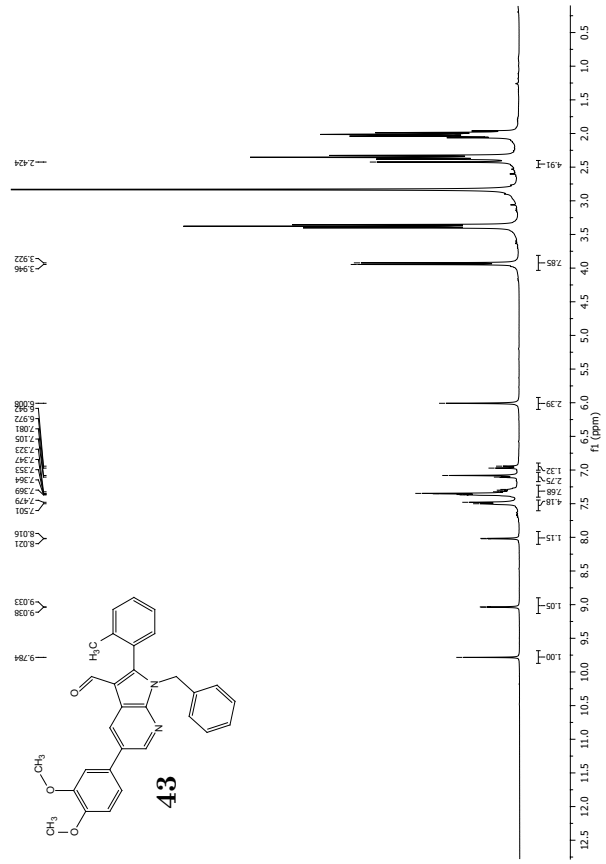

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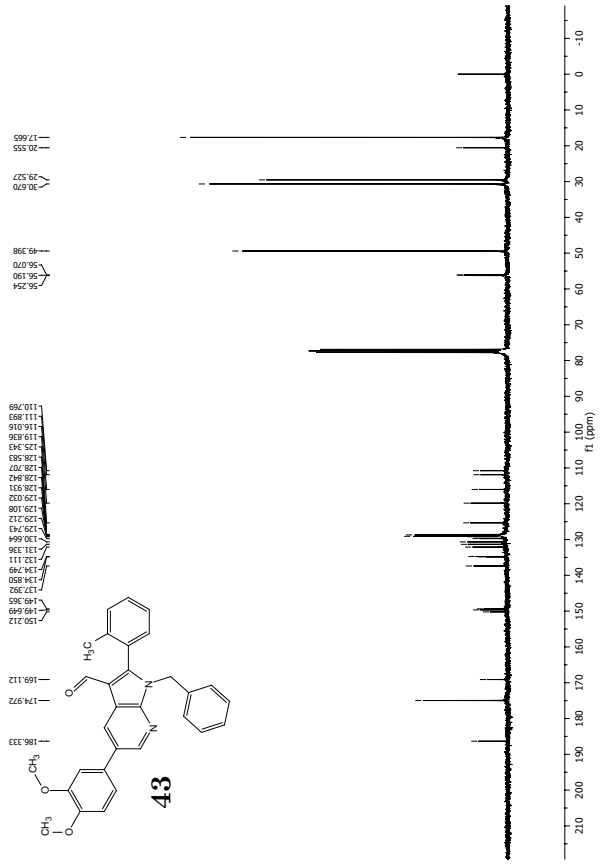

41
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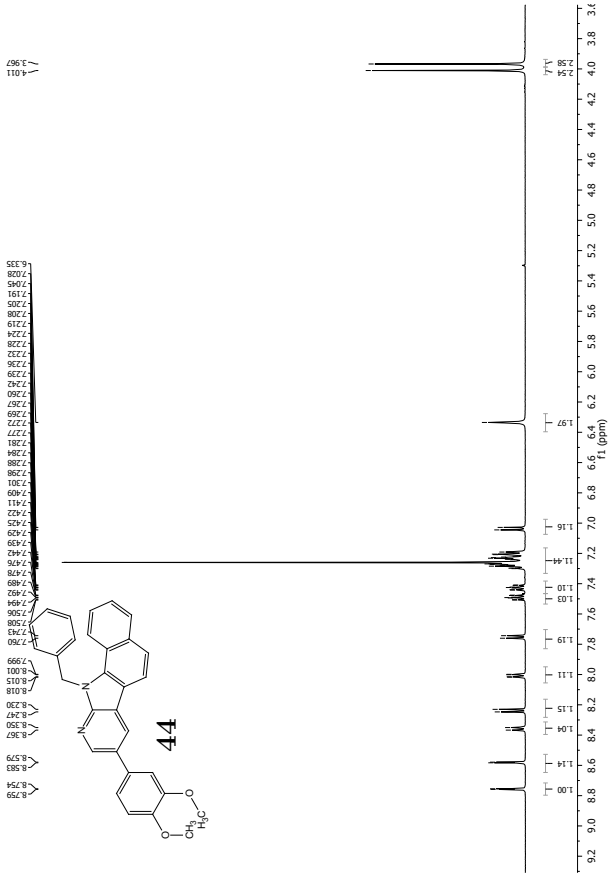

41
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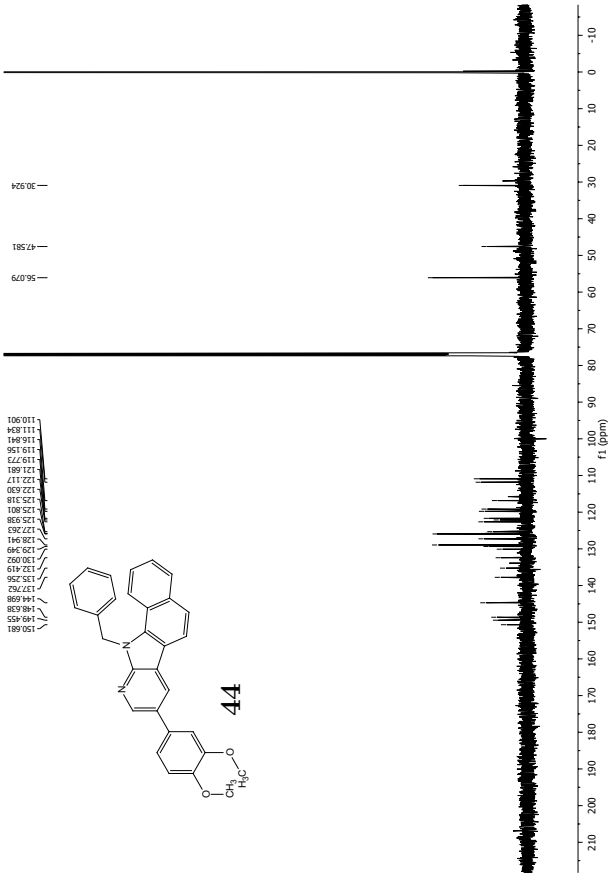

42
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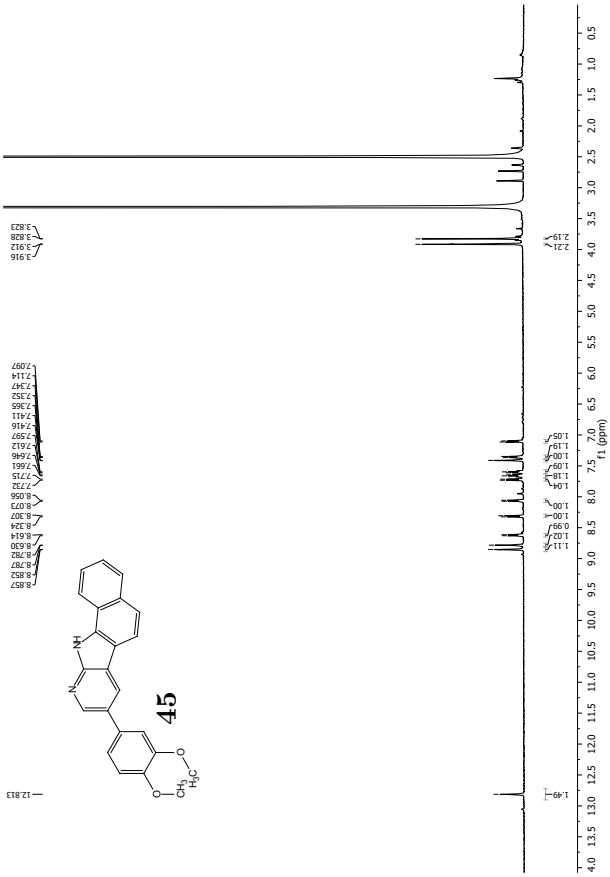

42
f1 (ppm)

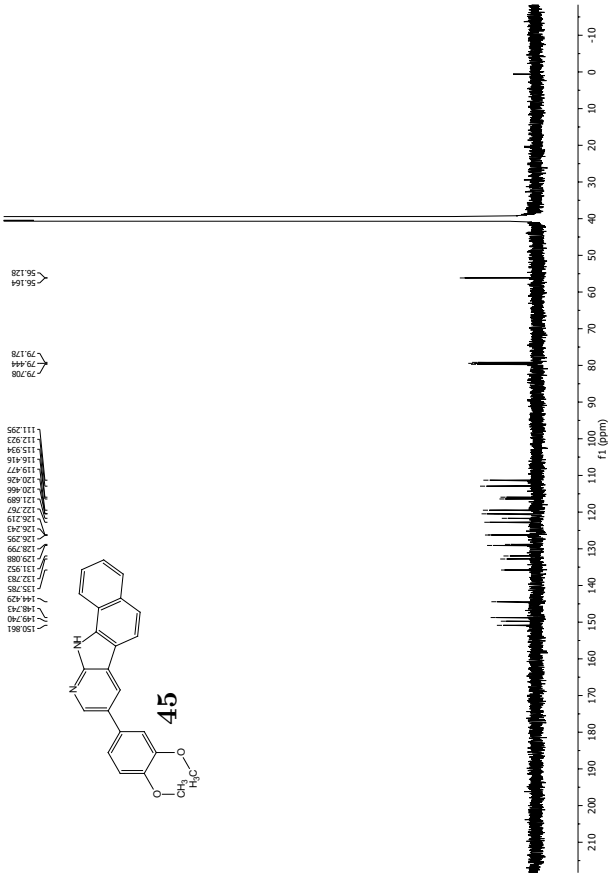

43
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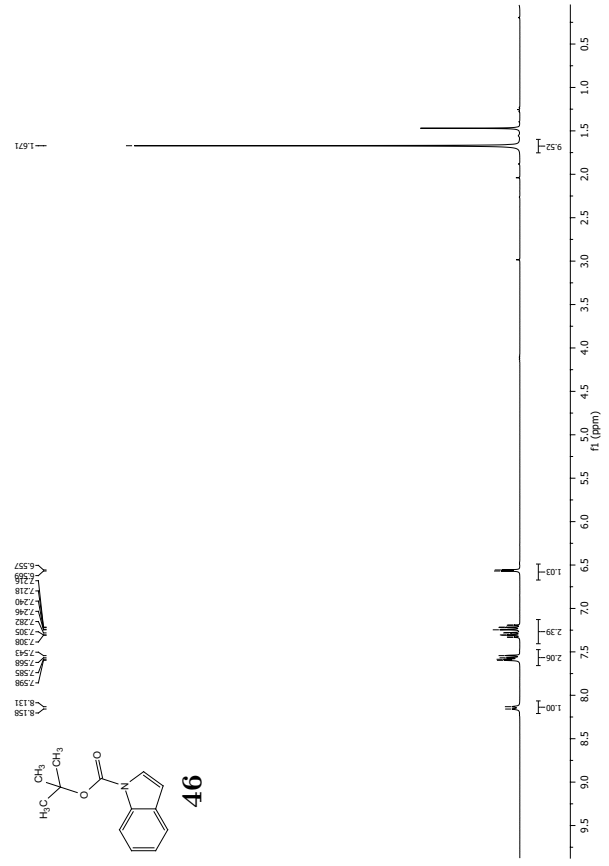

43
f1 (ppm)

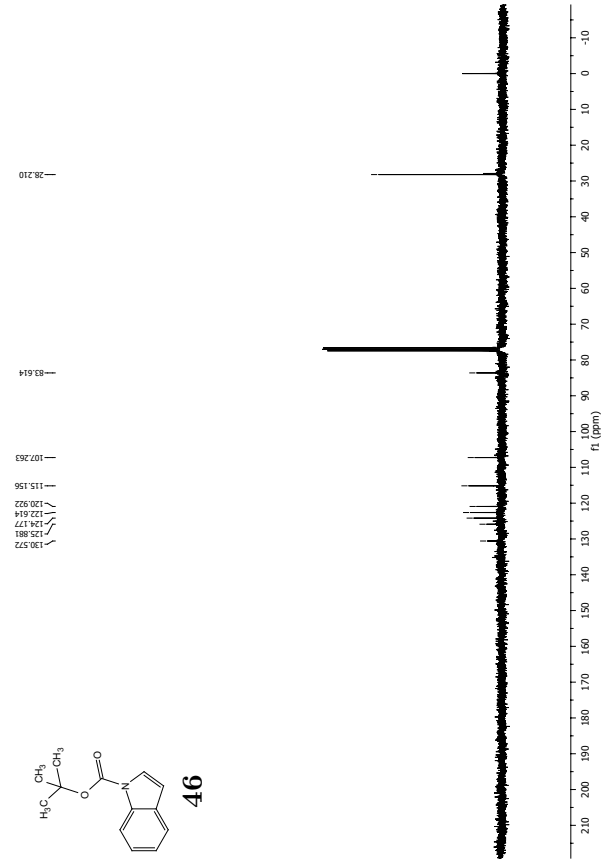

44
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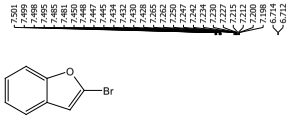

44
f1 (ppm)


45
f1 (ppm)

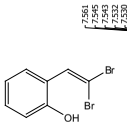

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46
f1 (ppm)

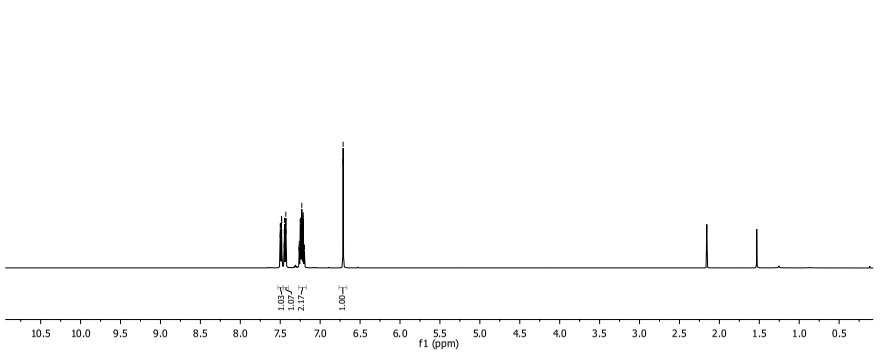

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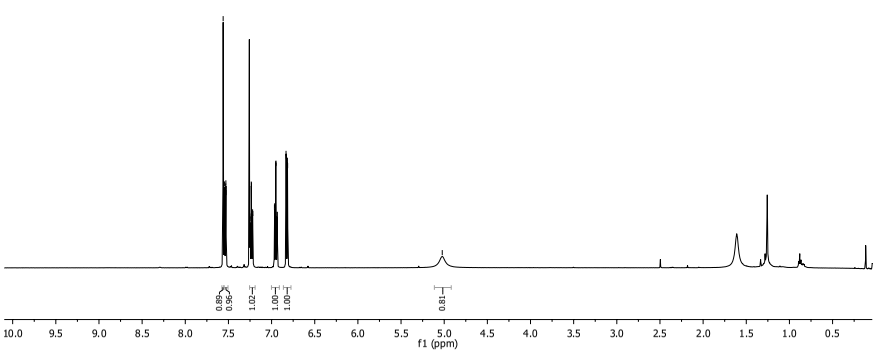

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7.498
7.495
7.495
7.481
7.450
7.448
7.447
7.445
7.434
7.432
7.430
7.428
7.265
7.262
7.250
7.247
7.242
7.234
7.230
7.227
7.215
7.212
7.200
7.198
6.714
6.712
O
Br

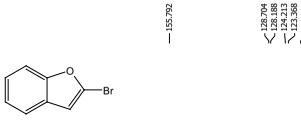
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7.561
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7.543
7.532
7.530
7.268
7.251
7.248
7.235
7.233
7.220
7.217
6.967
6.965
6.952
6.949
6.937
6.934
6.833
6.830
6.816
6.814
5.023
Br
Br
OH

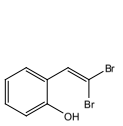
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1.03
1.07
2.17
1.00
f1 (ppm)

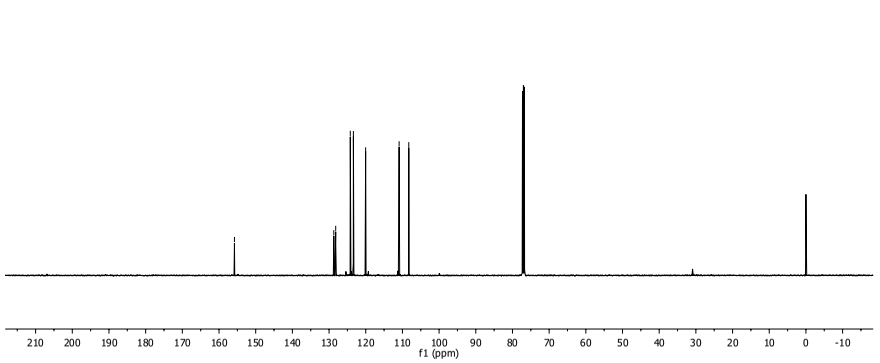

0.89
0.96
1.02
1.00
1.00
0.81
f1 (ppm)

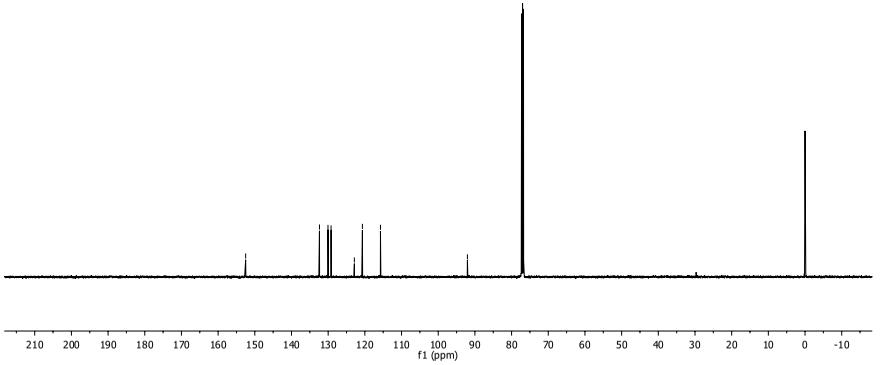

155.792
128.704
128.188
124.213
113.368
120.027
110.900
108.264
O
Br

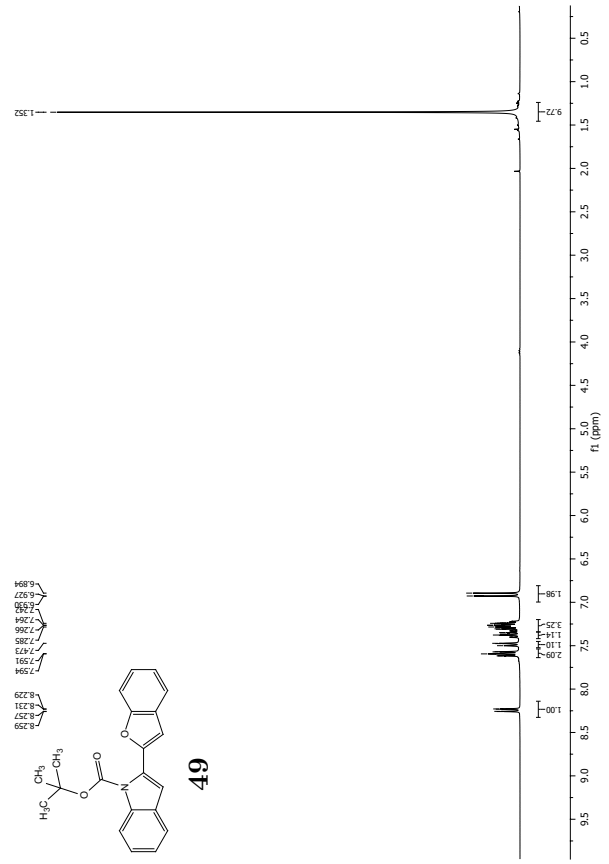
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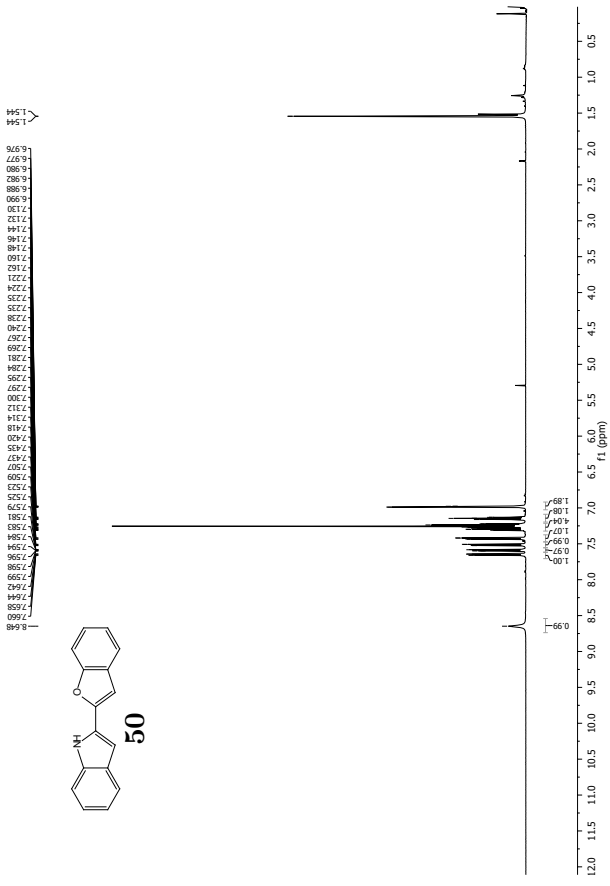

152.495
132.376
130.951
129.210
122.863
120.668
115.744
92.040
Br
Br
OH

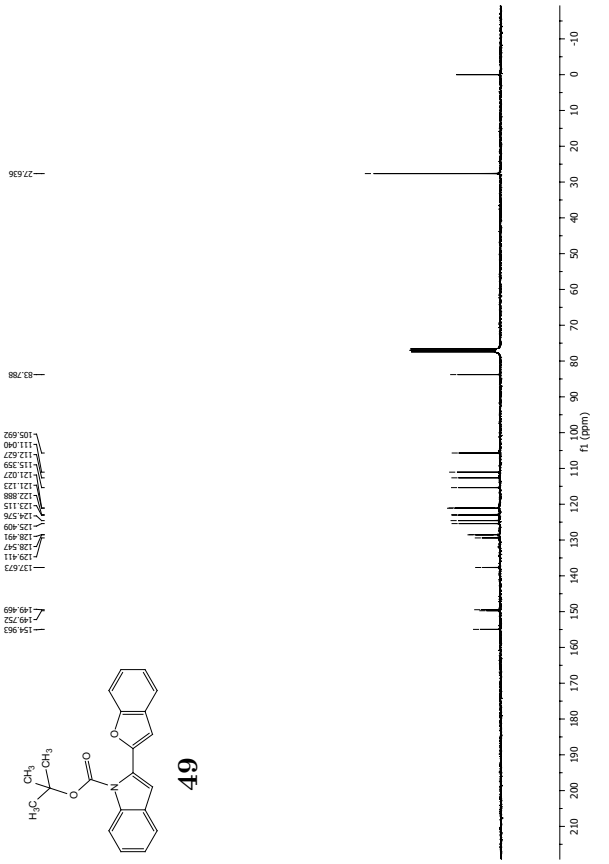
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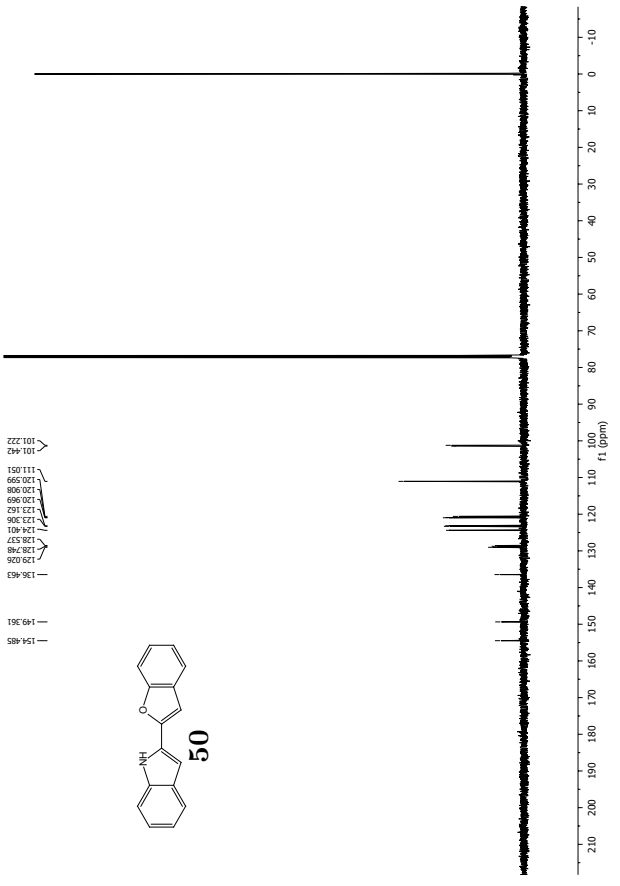

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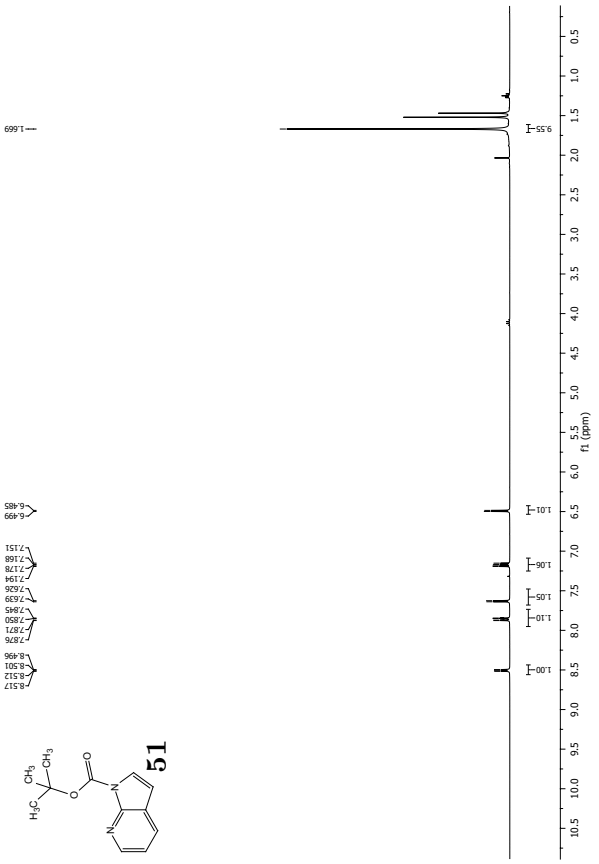

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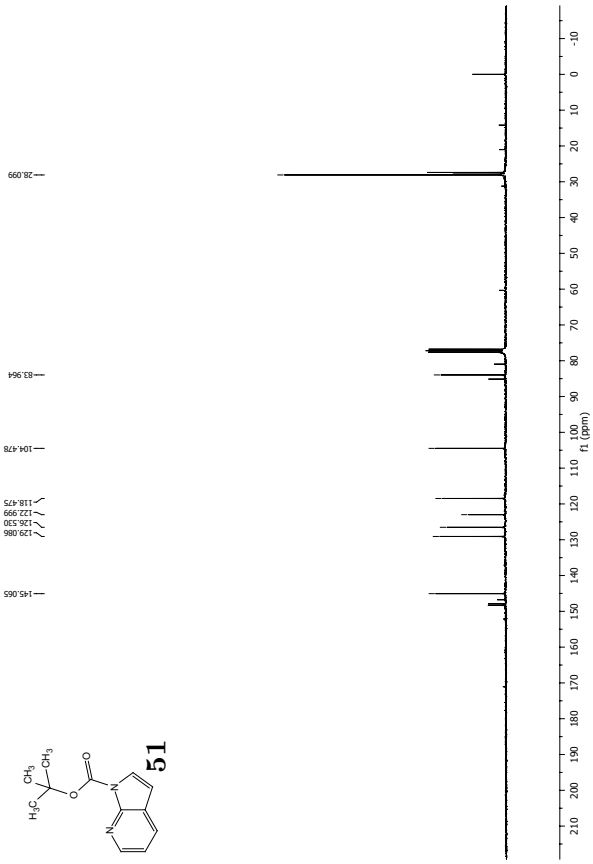

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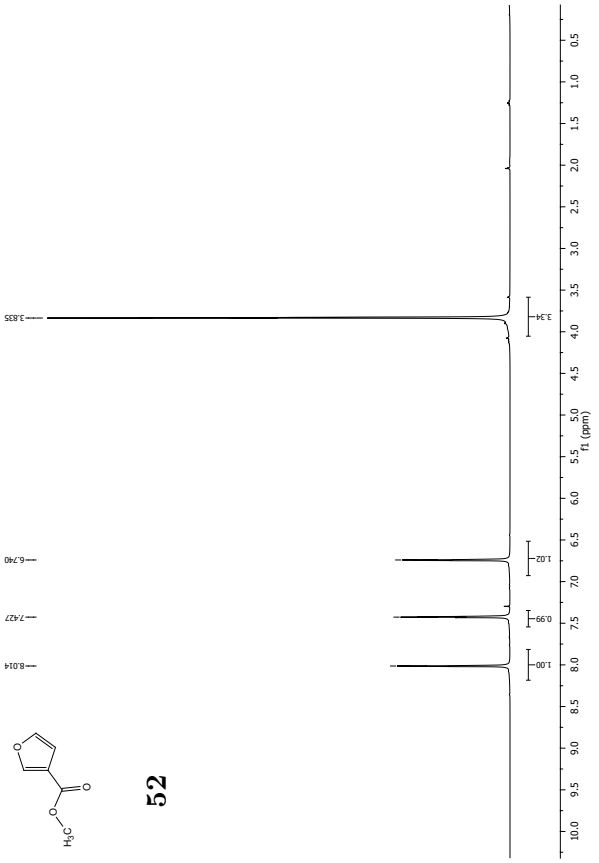

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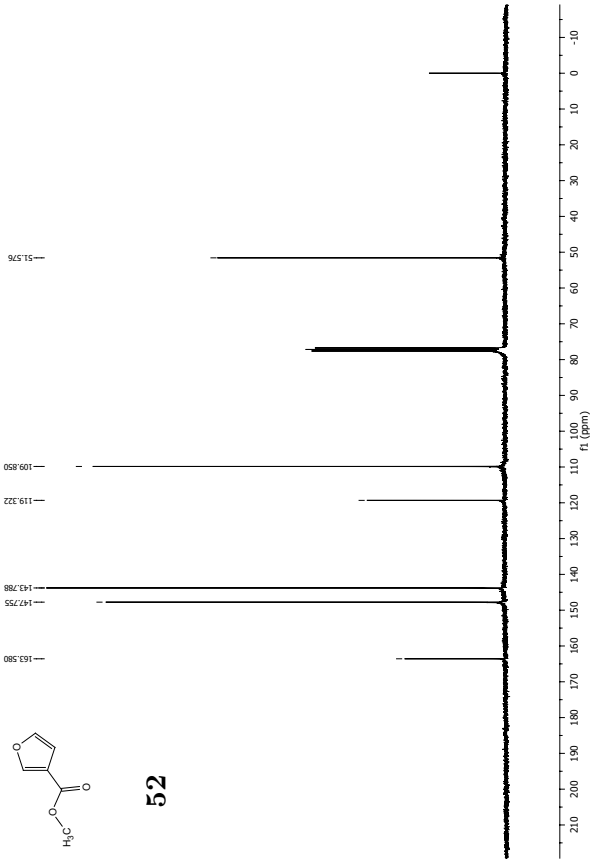

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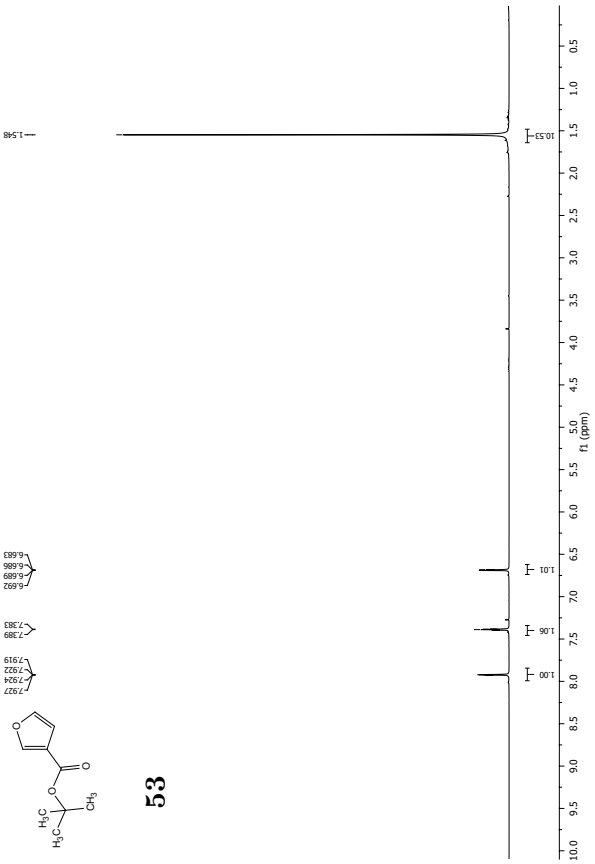

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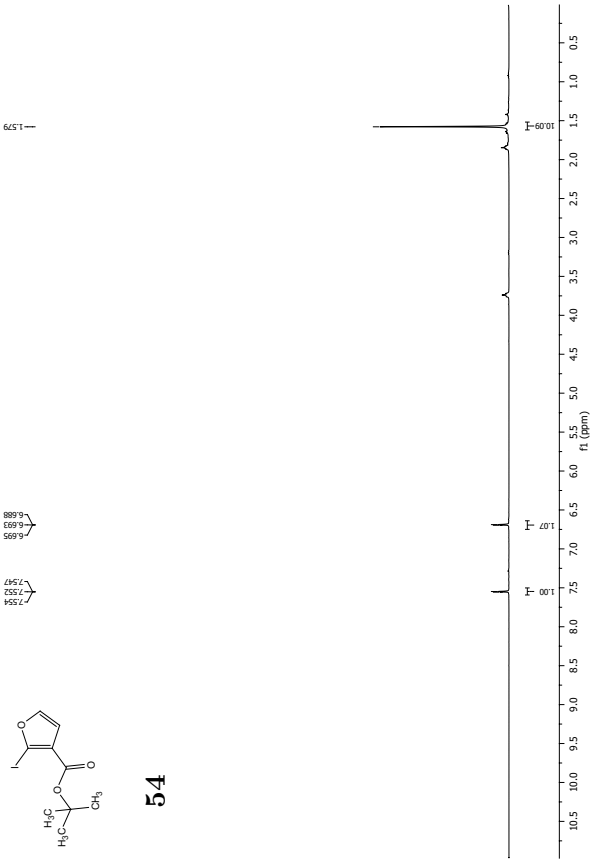

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6.485
1.01
1.06
1.05
1.10
1.00
8.517
8.512
8.501
8.496
7.876
7.871
7.850
7.845
7.639
7.636
7.194
7.178
7.168
7.151
f1 (ppm)
51

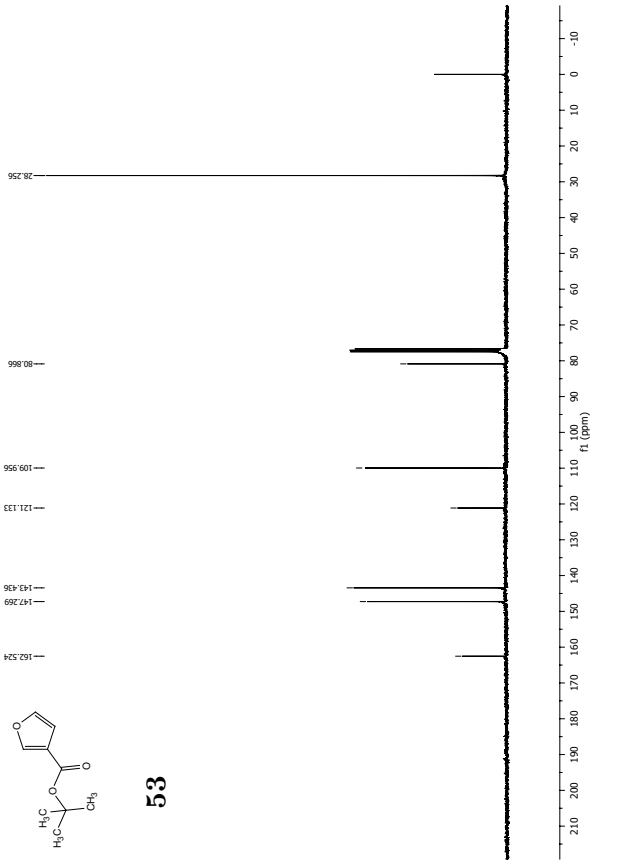

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83.364
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118.475
122.999
125.530
129.086
145.065
f1 (ppm)
51

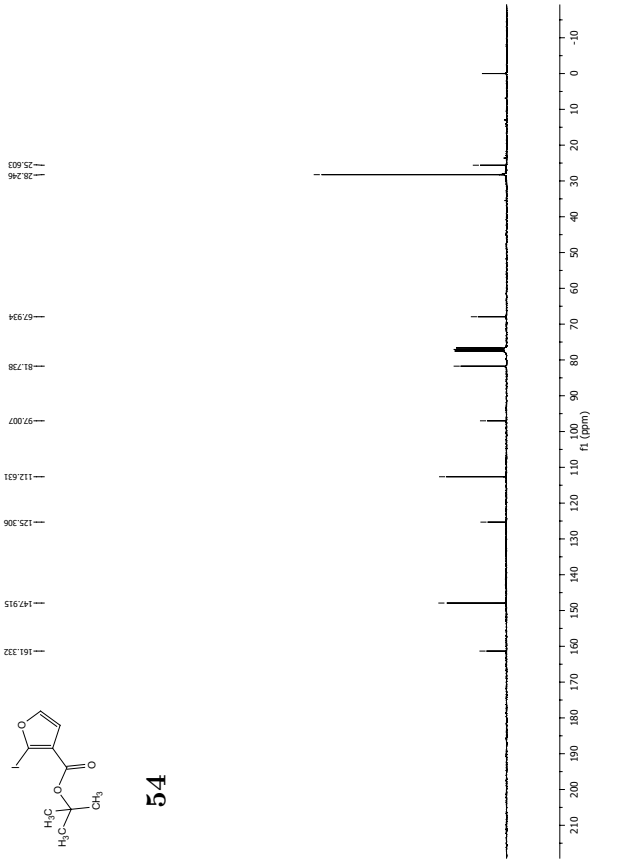

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6.740
3.835
1.00
0.99
1.02
3.34
f1 (ppm)
52

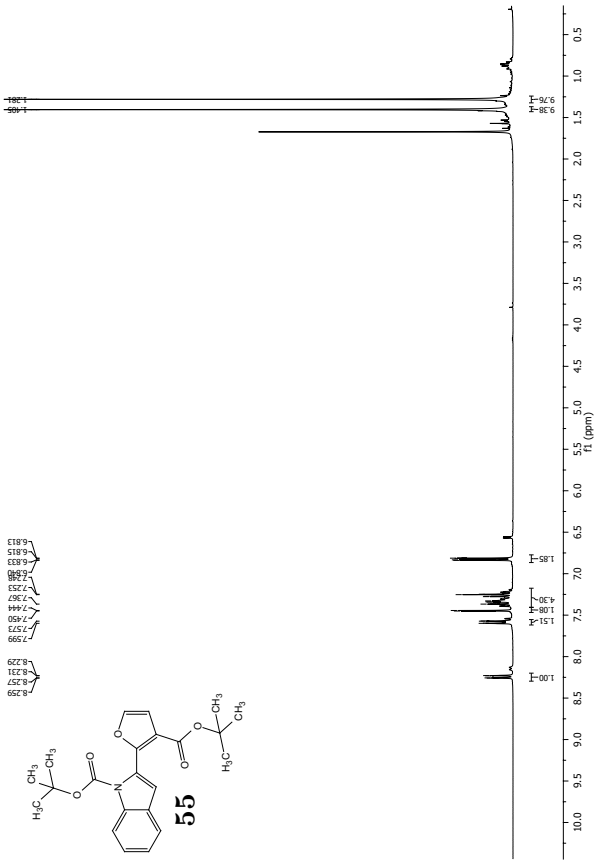

163.580
147.755
143.788
119.322
109.850
51.576
f1 (ppm)
52

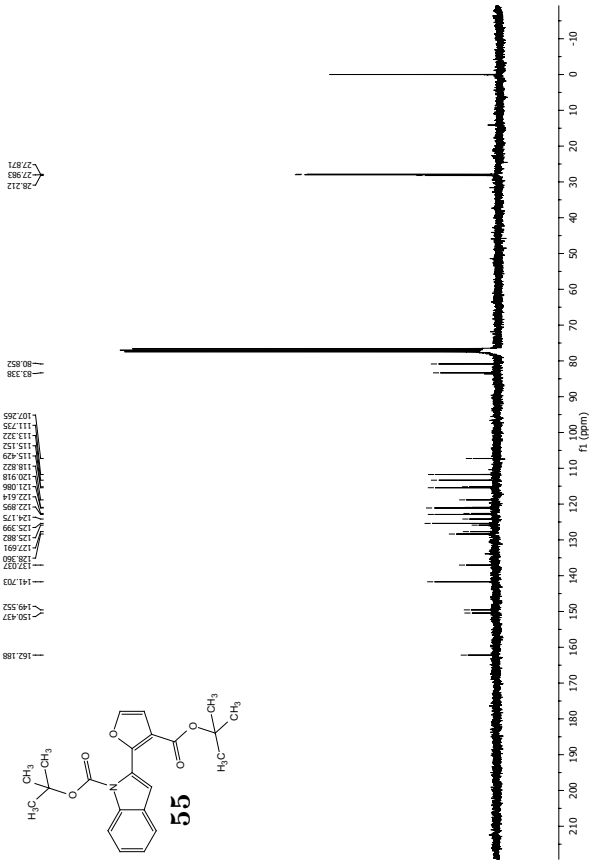

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7.924
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7.919
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6.692
6.689
6.686
6.683
10.53
1.01
1.06
1.00
f1 (ppm)
53

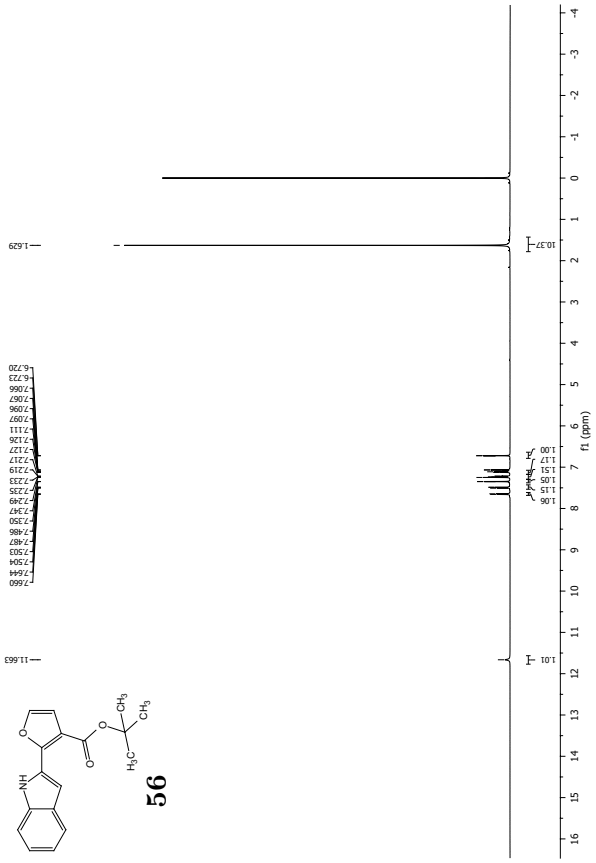

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6.688
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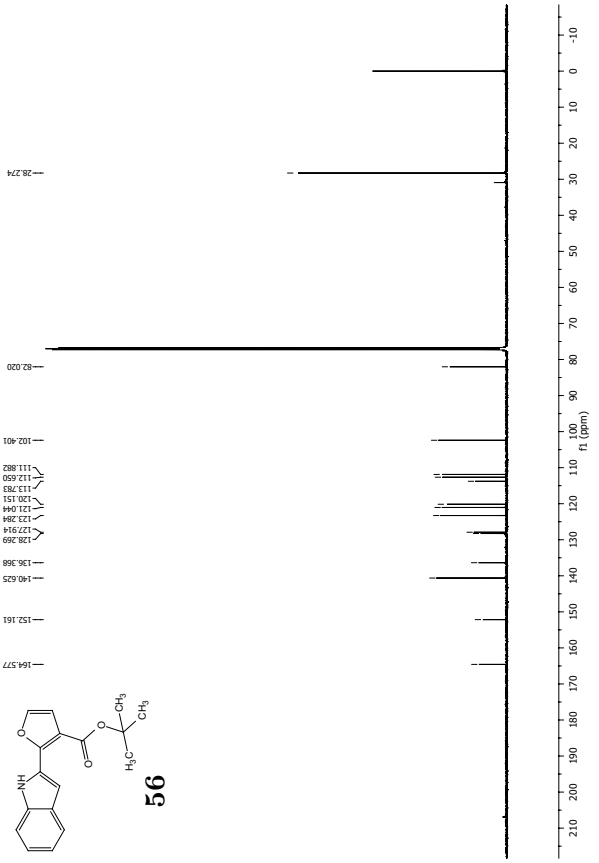

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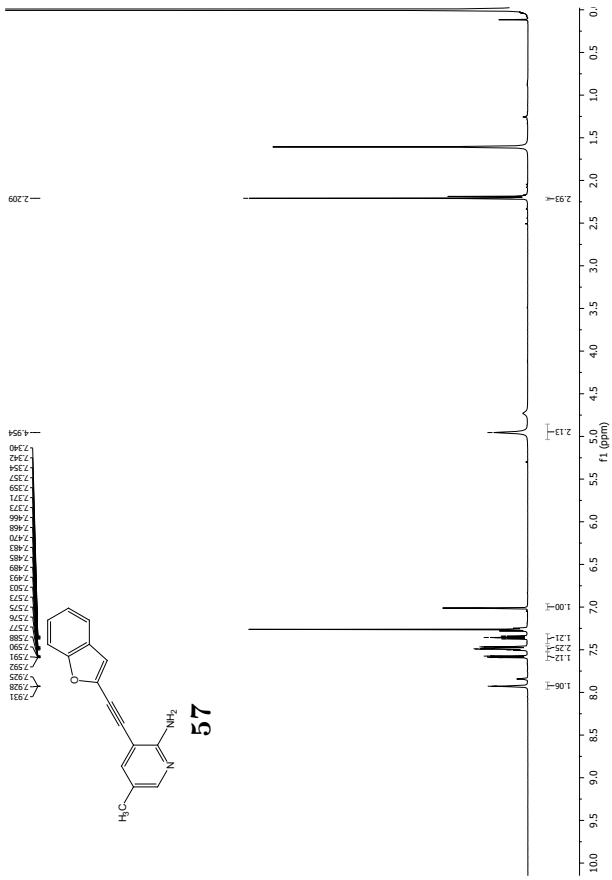

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f1 (ppm)
54

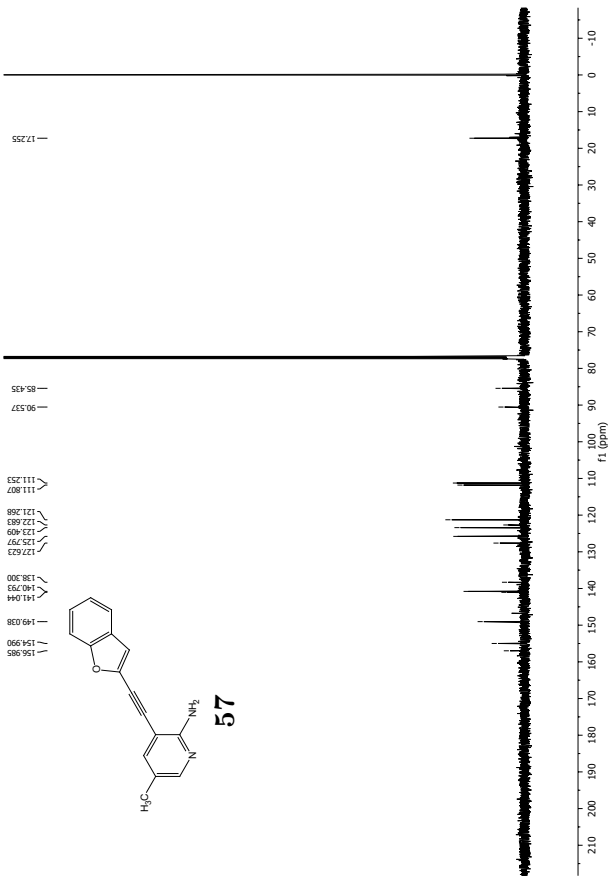

55
f1 (ppm)

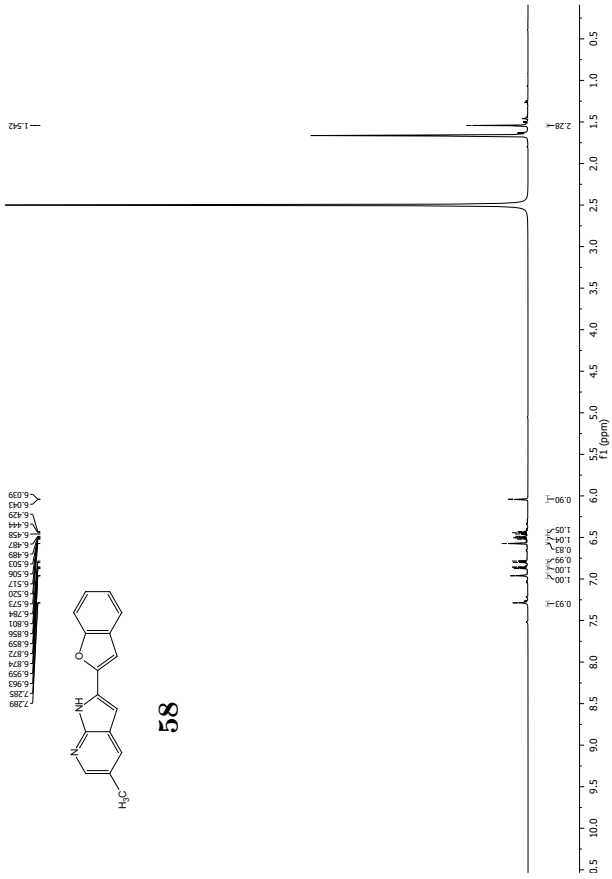

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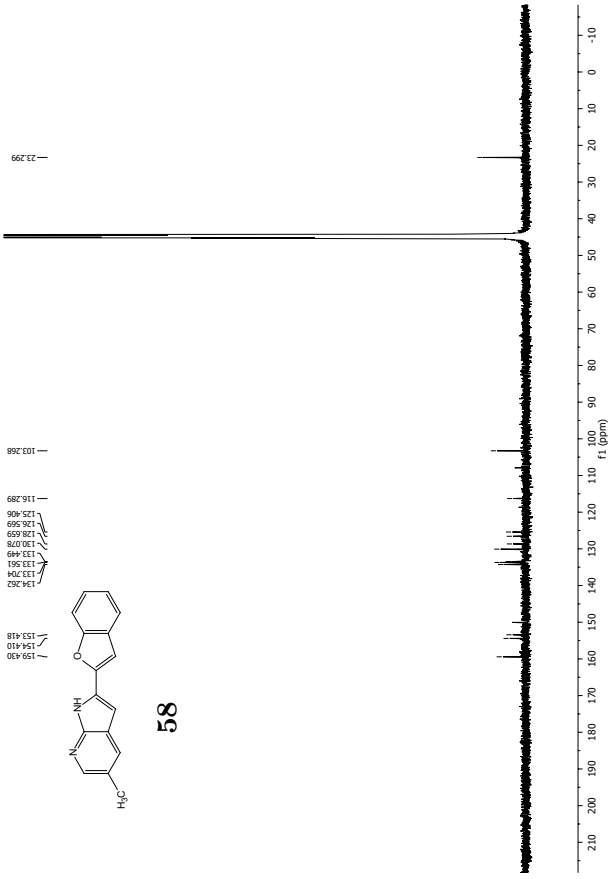

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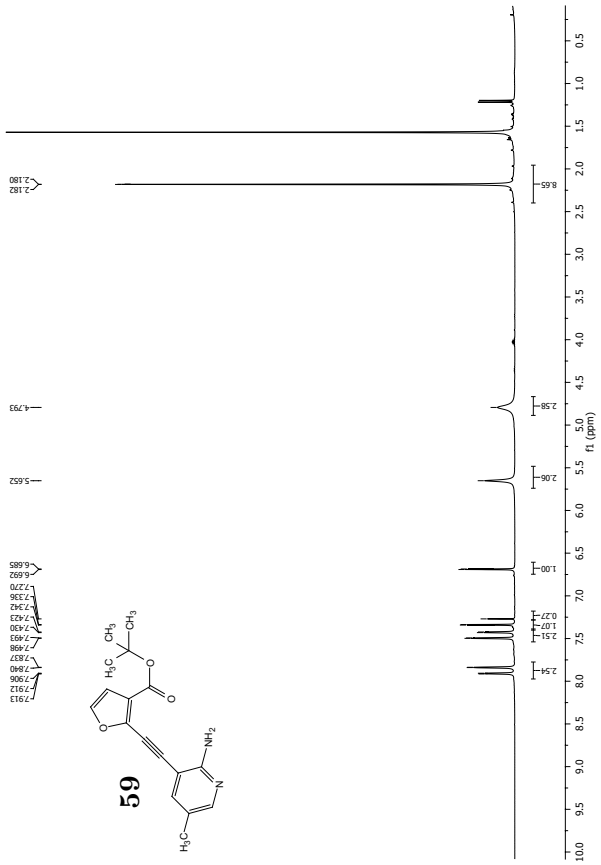

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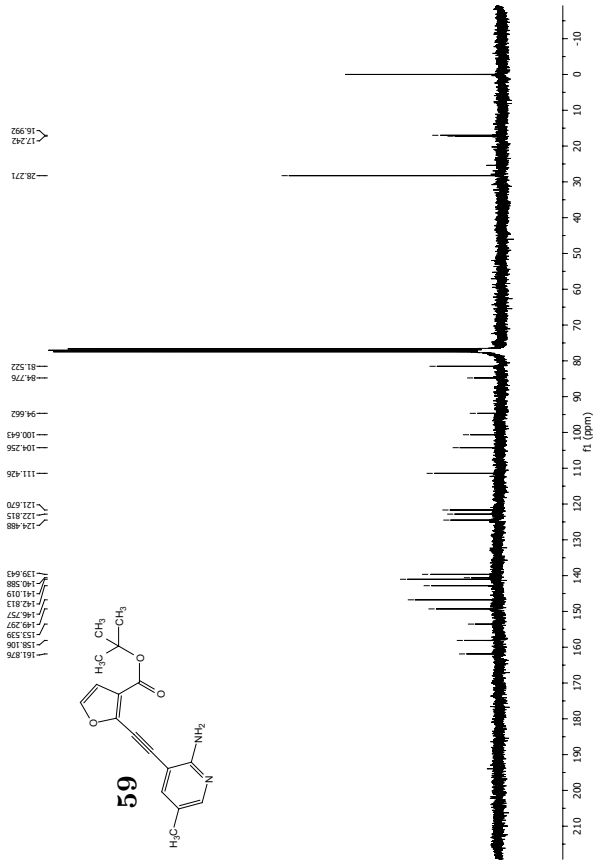

57
f1 (ppm)


57
f1 (ppm)


58
f1 (ppm)

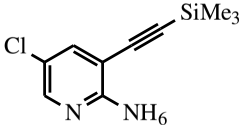
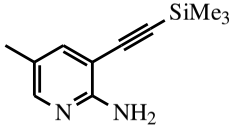
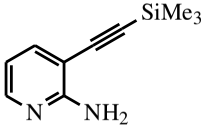
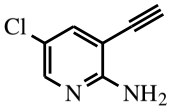
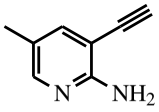
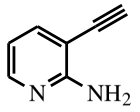

58
f1 (ppm)


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4.793
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6.685
6.682
1.00
7.270
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7.342
7.423
7.430
7.493
7.498
7.837
7.840
7.906
7.912
7.913
2.51
1.07
0.27
2.54
59
f1 (ppm)


17.242
16.992
28.271
81.522
84.776
94.662
100.643
104.256
111.426
121.670
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59
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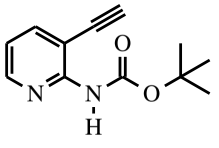
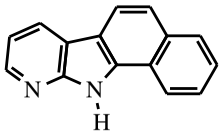
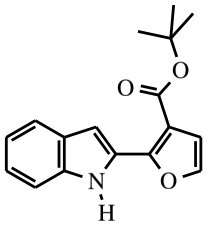
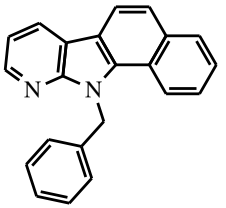
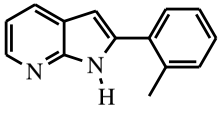
Appendix: Crystallography data

TABLE 1: Collection data of elucidated structures

Compound	 **7**	 **5**	 **9**	 **60**	 **6**	 **1**
Empirical formula	$C_{10}H_{13}Cl_1N_2Si_1$	$C_{11}H_{16}N_2Si_1$	$C_{10}H_{14}N_2Si_1$	$C_7H_6N_2$	$C_8H_8N_2$	$C_7H_6N_2$
Formula weight	224.76	204.35	190.32	118.14	132.16	118.14
Temperature	173.0(2) K	173.0(10) K	173.0(2) K	173.0(2) K	173.0(2) K	173.0(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/n	P 21/n	C 2/c	P 21/n	P 21/c	P 21/n
Unit cell dimensions						
a	6.1555(2) Å	5.7804(2) Å		8.1199(2) Å	15.4791(4) Å	8.1199(2) Å
b	20.9072(6) Å	19.1377(6) Å	7.8254(2) Å	6.3376(2) Å	8.8958(2) Å	6.3376(2) Å
c	9.4985(3) Å	10.7436(3) Å	14.5560(4) Å	12.4126(3) Å	11.1615(3) Å	12.4126(3) Å
α	90°	90°	90°	90°	90°	90°
β	95.4480(10)°	92.805(2)°	108.7830(10)°	102.9350(10)°	111.007(2)°	102.9350(10)°
γ	90°	90°	90°	90°	90°	90°
Volume	1216.88(7) $Å^3$	1187.07(6) $Å^3$	2241.08(10) $Å^3$	622.55(3) $Å^3$	1434.78(7) $Å^3$	622.55(3) $Å^3$
Z	4	4	8	4	8	4
Density (calculated)	1.227 Mg/m^3	1.143 Mg/m^3		1.260 Mg/m^3		
Absorption coefficient	0.378 mm^{-1}	0.164 mm^{-1}		0.079 mm^{-1}		
F(000)	472	440	816	248	560	248

Crystal size (mm^3)	0.557 x 0.341	0.433 x 0.213	0.637 x 0.369	0.28 x 0.246	0.308 x 0.229	0.28 x 0.246
	x 0.196	x 0.164	x 0.326	0.16 mm^3	x 0.209	x 0.16
	$1.95°to28.29°$	$2.13°to28°$	$2.07°to28.27°$	$2.742°to27.997°$	$1.41°to28°$	$2.74°to28.00°$
Index ranges						
	$-8 \preceq h \preceq 8$	$-7 \preceq h \preceq 7$	$-26 \preceq h \preceq 27$		$-20 \preceq h \preceq 20$	$-10 \preceq h \preceq 9$
	$-27 \preceq k \preceq 27$	$-24 \preceq k \preceq 25$	$-10 \preceq k \preceq 10$		$-11 \preceq k \preceq 11$	$-7 \preceq k \preceq 8$
	$-11 \preceq l \preceq 12$	$-14 \preceq l \preceq 11$	$-16 \preceq l \preceq 19$		$-14 \preceq l \preceq 13$	$-16 \preceq l \preceq 15$
Reflections collected	29454	11039	10023	11264	17343	11264
Independent reflections	3014	2859	2783	1507	3476	1507
R(int)	0.0442	0.0371	0.0306	0.0348	0.0254	0.0348
Completeness	99.70%	99.40%	99.90%	100.00%	100.00%	100.00%
Refinement method	Full-matrix least-squares on F^2					
Data / restraints / parameters	3014 / 0 / 138	2859 / 0 / 139	2783 / 0 / 129	1507 / 0 / 90	3476 / 0 / 199	1507 / 0 / 90
Goodness-of-fit on F^2	1.064	1	1.038	1.038	1.058	1.05
	$R1 = 0.0299$	$R1 = 0.0381$	$R1 = 0.0463$	$R1 = 0.0400$	$R1 = 0.0412$	$R1 = 0.0402$
	$wR2 = 0.0814$	$wR2 = 0.0859$	$wR2 = 0.1256$	$wR2 = 0.1010$	$wR2 = 0.0989$	$wR2 = 0.1022$
R indices (all data)	$R1 = 0.0339$	$R1 = 0.0536$	$R1 = 0.0524$	$R1 = 0.0493$	$R1 = 0.0642$	$R1 = 0.0496$
	$wR2 = 0.0841$	$wR2 = 0.0939$	$wR2 = 0.1303$	$wR2 = 0.1086$	$wR2 = 0.1132$	$wR2 = 0.1098$
Largest diff. peak and hole($e.Å^{-3}$)	0.316 / -0.334	0.313 / -0.251	0.688 / -0.229	0.274 / -0.226	0.247 / -0.217	0.275 / -0.225

Table 2: Collection data of elucidated structures 2

Compound					
	61	**22**	**56**	**21**	**18**
Empirical formula	$C_{12}H_{14}N_2O_2$	$C_{15}H_{10}N_2$	$C_{17}H_{17}NO_3$	$C_{22}H_{17}N_2$	$C_{14}H_{12}N_2$
Formula weight	218.25	218.32	283.32	309.38	208.26
Temperature	173.0(2) K	173.0(2) K	173.0(2) K	173.0(2) K	173.0(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P b c a	P2(1)/c	P2(1)/n	P2(1)/c	P2(1)/c
Unit cell dimensions					
a	9.2470(3) Å	11.477(6) Å	10.4765(4) Å	5.5833(2) Å	3.8759(2) Å
b	14.5102(4) Å	4.886(3) Å	7.7837(3) Å	18.2498(6) Å	23.5592(8) Å
c	17.4380(6) Å	19.046(11) Å	18.1482(7) Å	15.3217(5) Å	11.4047(5) Å
α	90°	90°	90°	90°	90°
β	90°	96.09(2)°	101.666(2)°	93.940(2)°	91.651(2)°
γ	90°	90°	90°	90°	90°
Volume	2339.76(13) $Å^3$	1061.9(11) $Å^3$	1449.34(10) $Å^3$		

Z	8	4	4	4	4
Density (calculated)		1.365 Mg/m^3	1.298 Mg/m^3	1.319 Mg/m^3	1.329 Mg/m^3
Absorption coefficient		0.082 mm^{-1}	0.089 mm^{-1}	0.078 mm^{-1}	0.080 mm^{-1}
F(000)	928	456	600	652	440
Crystal size (mm^3)	0.355 x 0.165	0.24 x 0.11	0.46 x 0.28	0.374 x 0.263	
	x 0.09	x 0.02	x 0.11	x 0.116	
	$2.86°to27.99°$	1.78ĉirc to 26.00ĉirc	$2.08°to28.00°$	$1.74°to28.35°$	$1.73°to28.00°$
Index ranges					
	-12⪯h⪯11	-13⪯h⪯14	-13⪯h⪯13	-7⪯h⪯7	-5⪯h⪯4
	-19⪯k⪯19	-6⪯k⪯6	-10⪯k⪯10	-21⪯k⪯24	-31⪯k⪯31
	-23⪯l⪯22	-23 ⪯l⪯23	-23⪯l⪯23	-20⪯l⪯20	-14⪯l⪯50
Reflections collected	19630	8638	12764	23975	10479
Independent reflections	2811	2065	3501	3902	2495
R(int)	0.0325	0.0988	0.0412	0.0408	0.0586
Completeness	99.70%	99.50%	100.00%	99.90%	99.90%
Refinement method			Full-matrix least-squares on F^2		
Data / restraints / parameters	2811 / 0 / 152	2065 / 0 / 154	3501 / 0 / 193	3902 / 0 / 217	2495 / 0 / 150
Goodness-of-fit on F^2	1.26	0.99	0.578	1.003	1.037
	R1 = 0.0428	R1 = 0.0676	R1 = 0.0392	R1 = 0.0403	R1 = 0.0533
	wR2 = 0.1089	wR2 = 0.1723	wR2 = 0.1200	wR2 = 0.0922	wR2 = 0.1144
R indices (all data)	R1 = 0.0697	R1 = 0.1576	R1 = 0.0558	R1 = 0.0530	R1 = 0.0916
	wR2 = 0.1469	wR2 = 0.2259	wR2 = 0.1454	wR2 = 0.1008	wR2 = 0.1285
Largest diff. peak and hole($e.Å^{-3}$)	0.590 / -0.881	0.335 / -0.292	0.272 / -0.261	0.319 / -0.193	0.473 / -0.206