Supporting information

A BINOL-based Ratiometric Fluorescent Sensor for Zn^{2+} and In Situ Generated Ensemble for Selective Recognition of Histidine in Aqueous Solution

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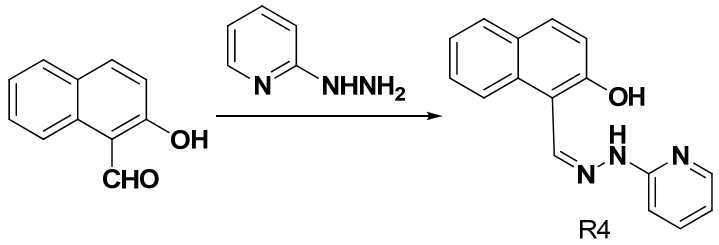


Scheme S1 Synthesis route for **R4**

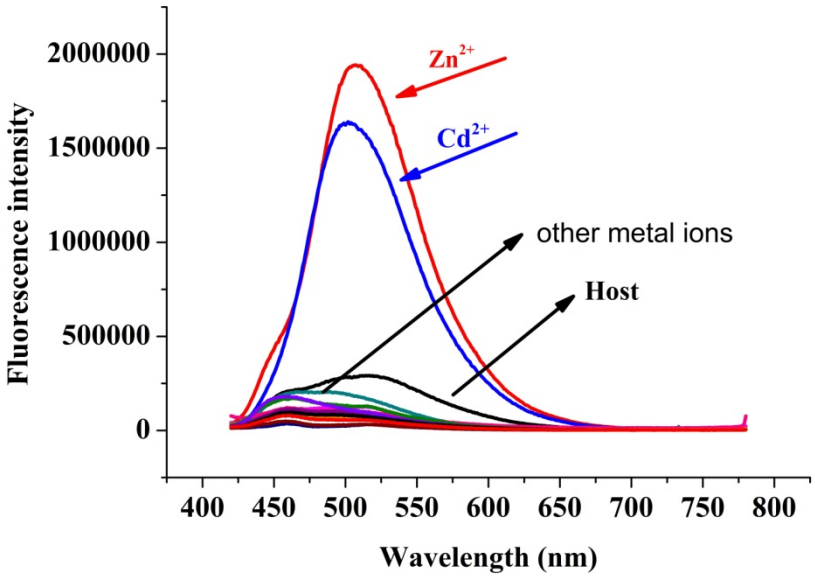


Fig.S1 Fluorescence responses of **R4** with different test metals.

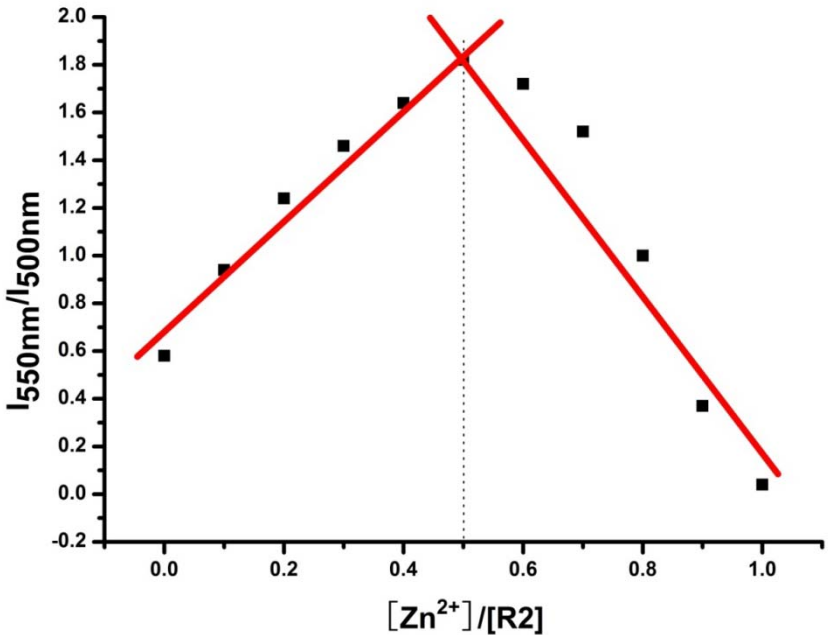


Fig.S2 The Job plot using ratio of emissions (I_{550nm}/I_{500nm}) of **R2** and Zn^{2+} in CH_3CN/HEPES=1:1(v/v), total

concentration of [**R2**] and [Zn^{2+}] was 10 μM.

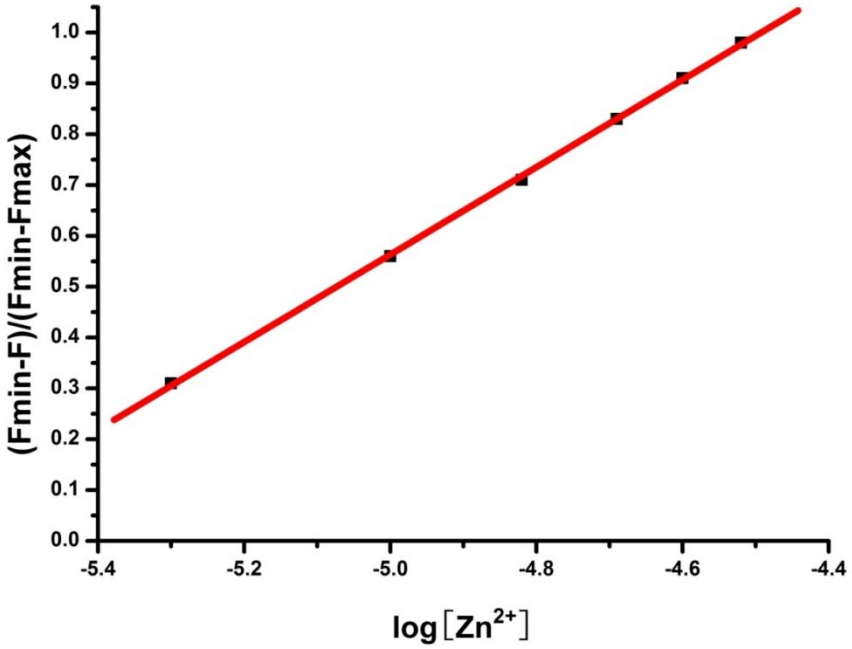


Fig.S3 The determination **R2** of the detection limit (LOD) for Zn^{2+} in HEPES buffer (10 mM, pH =7.4 CH_3CN:HEPES = 1:1,v/v) F = $I_{550\ nm}/I_{500\ nm}$

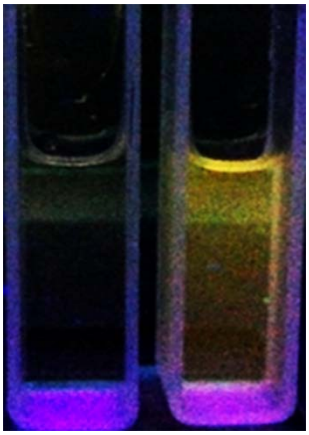


Figure S4. The color change of **R2** (20 μM) in HEPES (10 mM, pH = 7.4) under a UV lamp (365 nm) by addition of 2 equiv. Zn^{2+} .From left to right：**R2**, **R2**+2 equiv Zn^{2+}

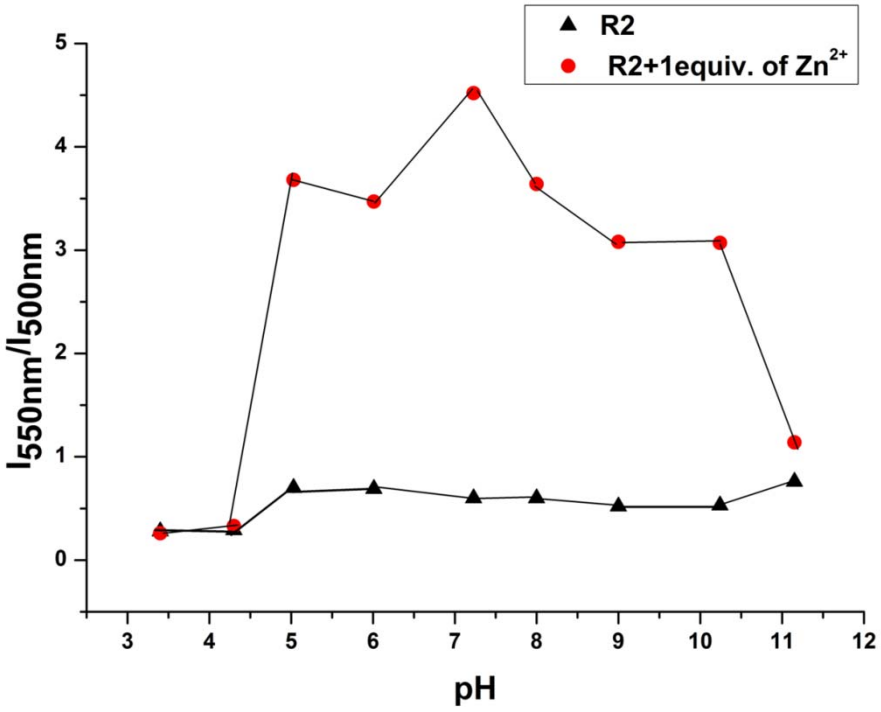


Fig.S5 Ratio of emissions (I_{550nm}/I_{500nm}) of **R2** in CH_3CN/HEPES (v/v=1:1 PH=7.4) with (red) and without (black) of Zn^{2+} (1 equiv) as a function of pH

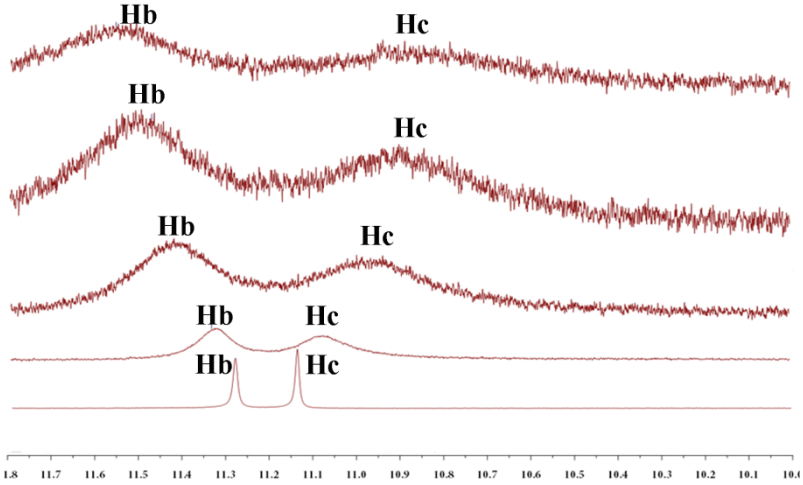


Fig.S6 ^{1}H NMR spectra changes of Hb and Hc (400 MHz) of **R2** in d_6-DMSO with titration of various equiv of Zn^{2+}

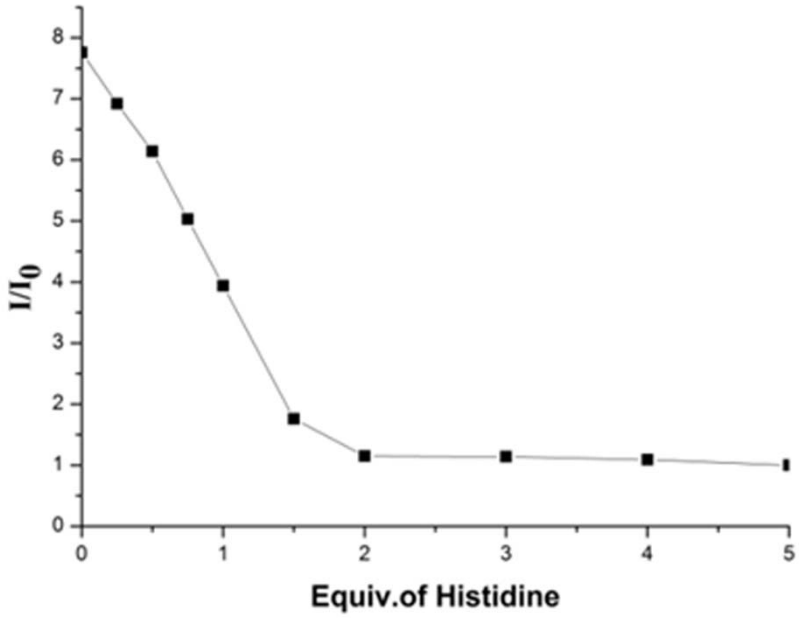


Fig.S7 Plot of relative fluorescence intensity of **R2**-Zn2+ complex versus the mole ratio of added Histidine in CH_3CN/HEPES (v/v=1:1 pH=7.4) I_0 is the fluorescence intensity of **R2**, I is intensity of **R2** with 1 equiv of Zn^{2+} and various equiv of histidine

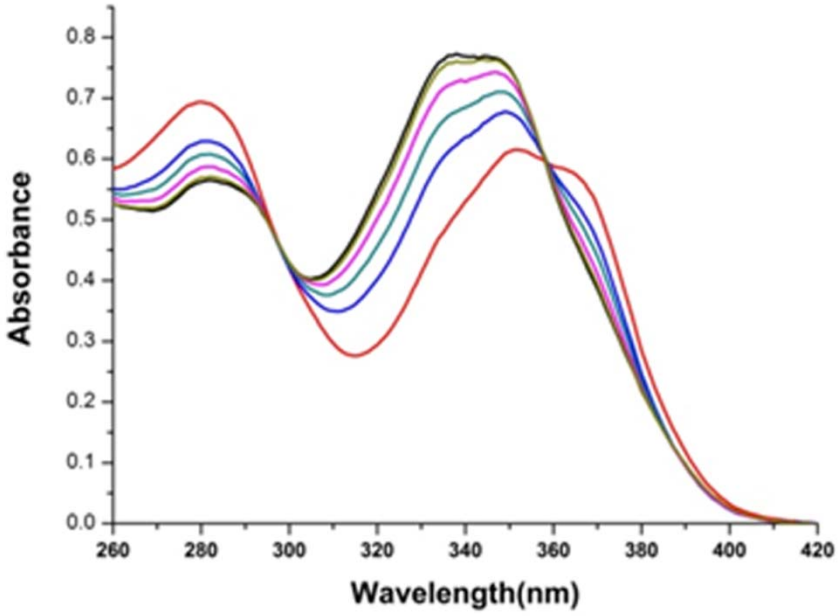


Fig.S8 Absorption spectra of **R2** during the titration of **R2**-Zn2+ complex with Histidine (0, 0.5, 1.0, 1.5, 2.0 equiv) in CH_3CN/HEPES (v/v = 1:1 pH = 7.4)

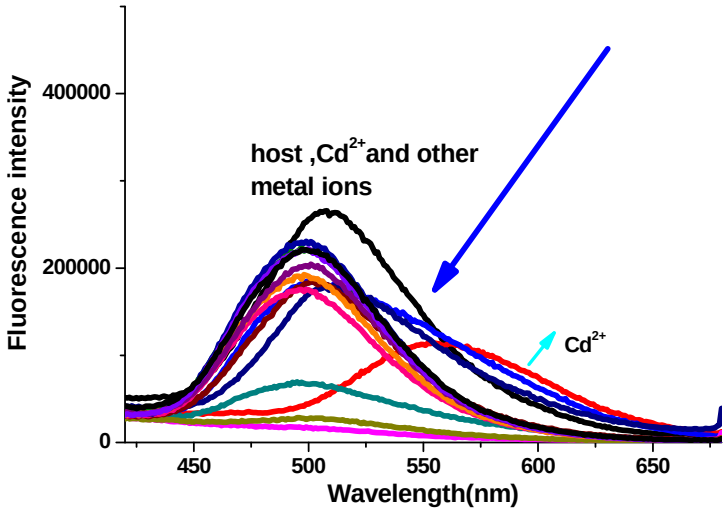
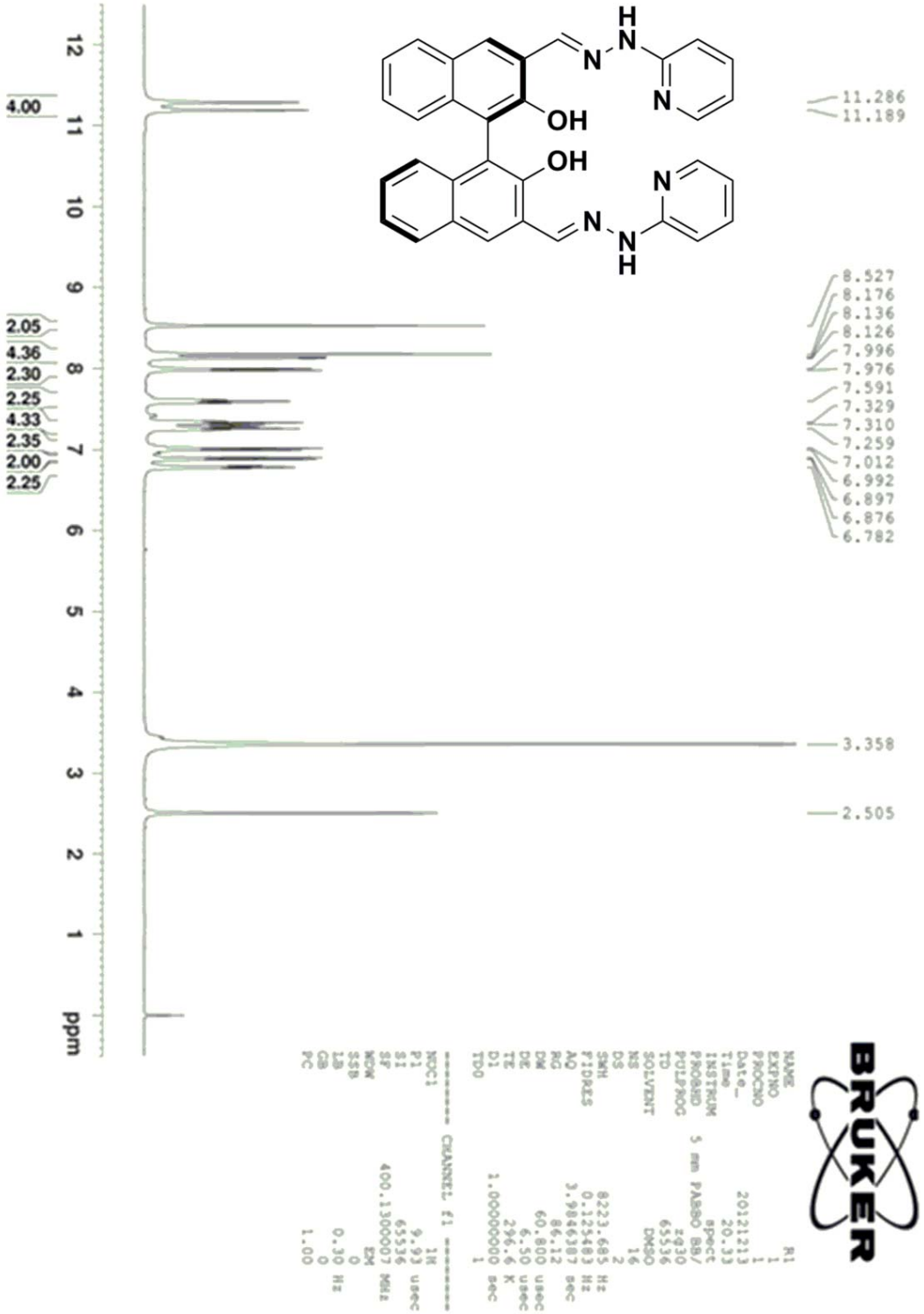


Fig.S9 Fluorescence spectra of **R2** (10 μM) in CH_3CN/HEPES (10 mM, pH=7.4) = 1:1 (V/V).Upon addition of (30 μM) various metal ions. λex=350 nm

^{1}H-NMR, ^{13}C-NMR and HRMS spectra of R1/R2/R3/R4 and intermediates.

^{1}H-NMR of R1



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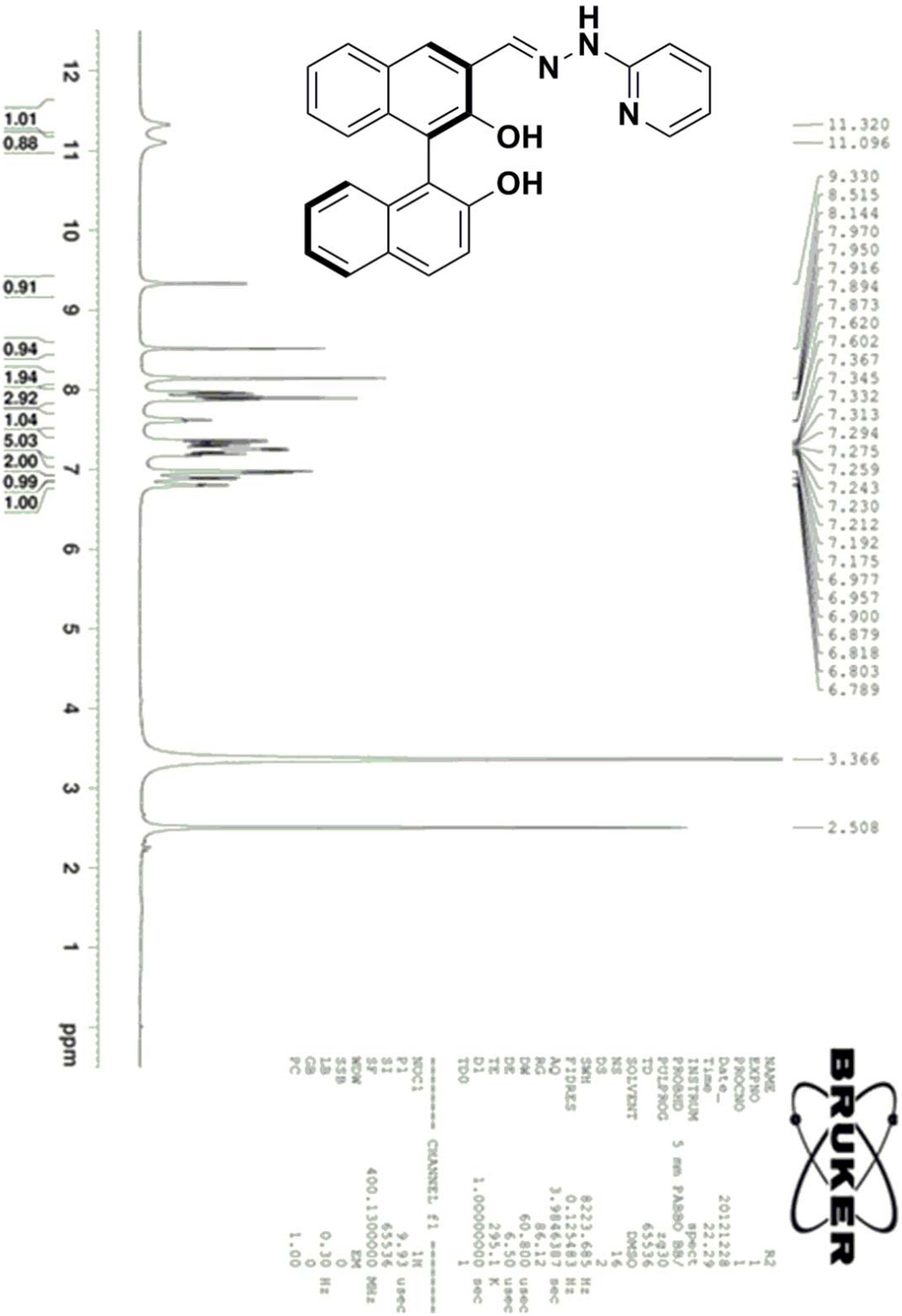
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2.92
1.04
5.03
2.00
0.99
1.00
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11.096
9.330
8.515
8.144
7.970
7.950
7.916
7.894
7.873
7.620
7.602
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7.192
7.175
6.977
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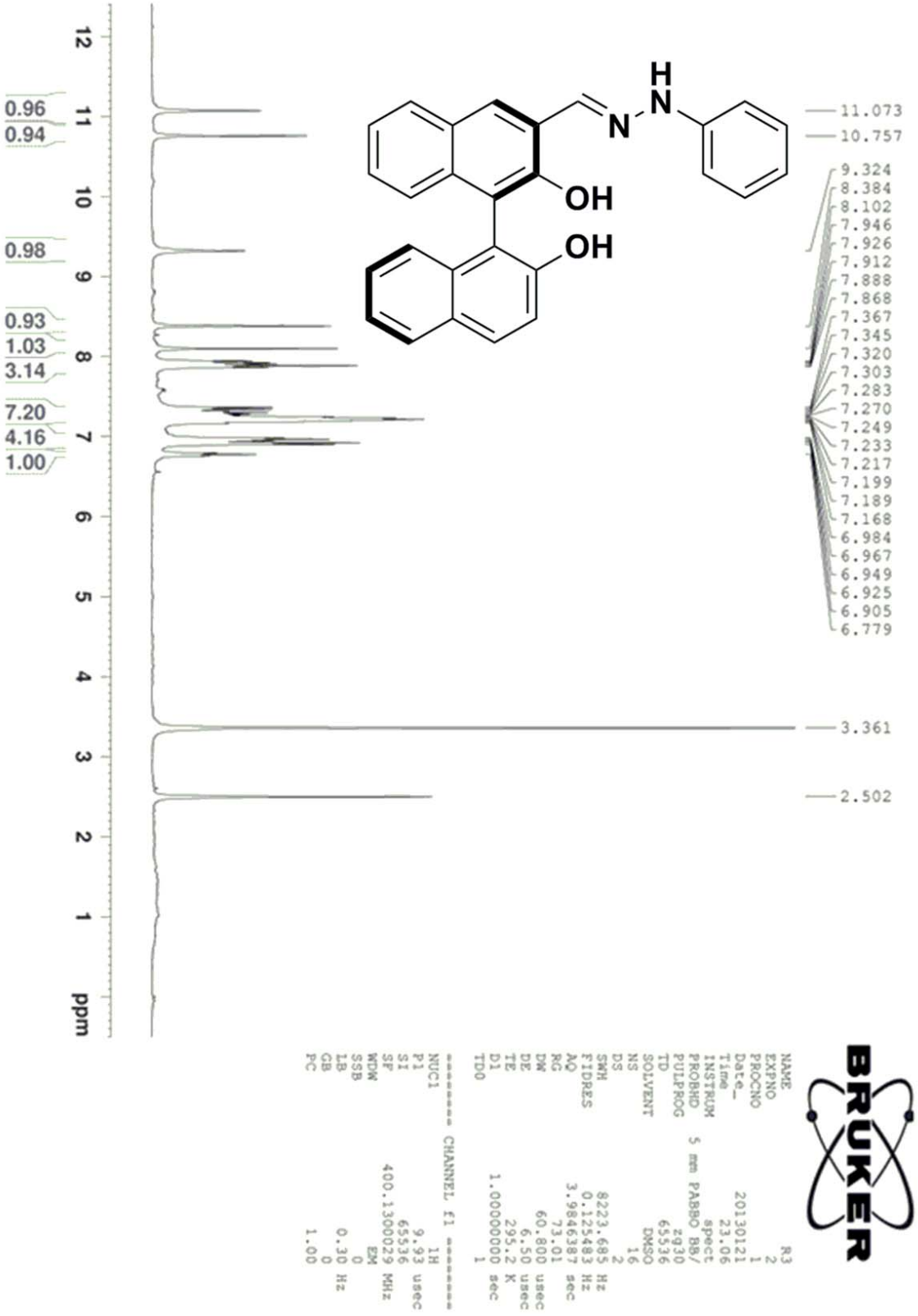
^{1}H-NMR of R3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7.946
7.926
7.912
7.888
7.868
7.367
7.345
7.320
7.303
7.283
7.270
7.249
7.233
7.217
7.199
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6.925
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DE 6.50 usec
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TD0 1
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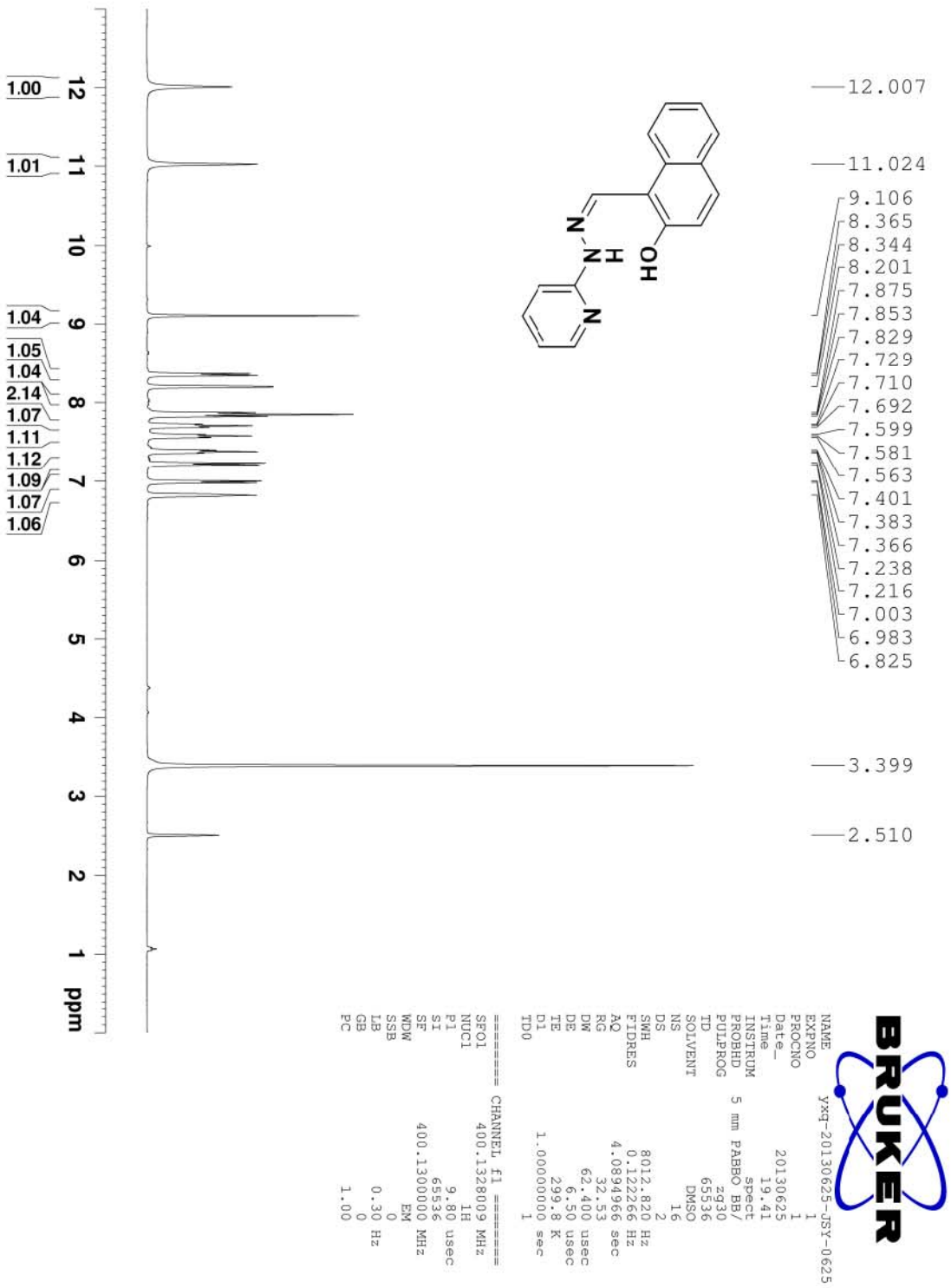
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7.729
7.710
7.692
7.599
7.581
7.563
7.401
7.383
7.366
7.238
7.216
7.003
6.983
6.825
3.399
2.510
1.00
1.01
1.04
1.05
1.04
2.14
1.07
1.11
1.12
1.09
1.07
1.06
12 11 10 9 8 7 6 5 4 3 2 1 ppm
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H
N
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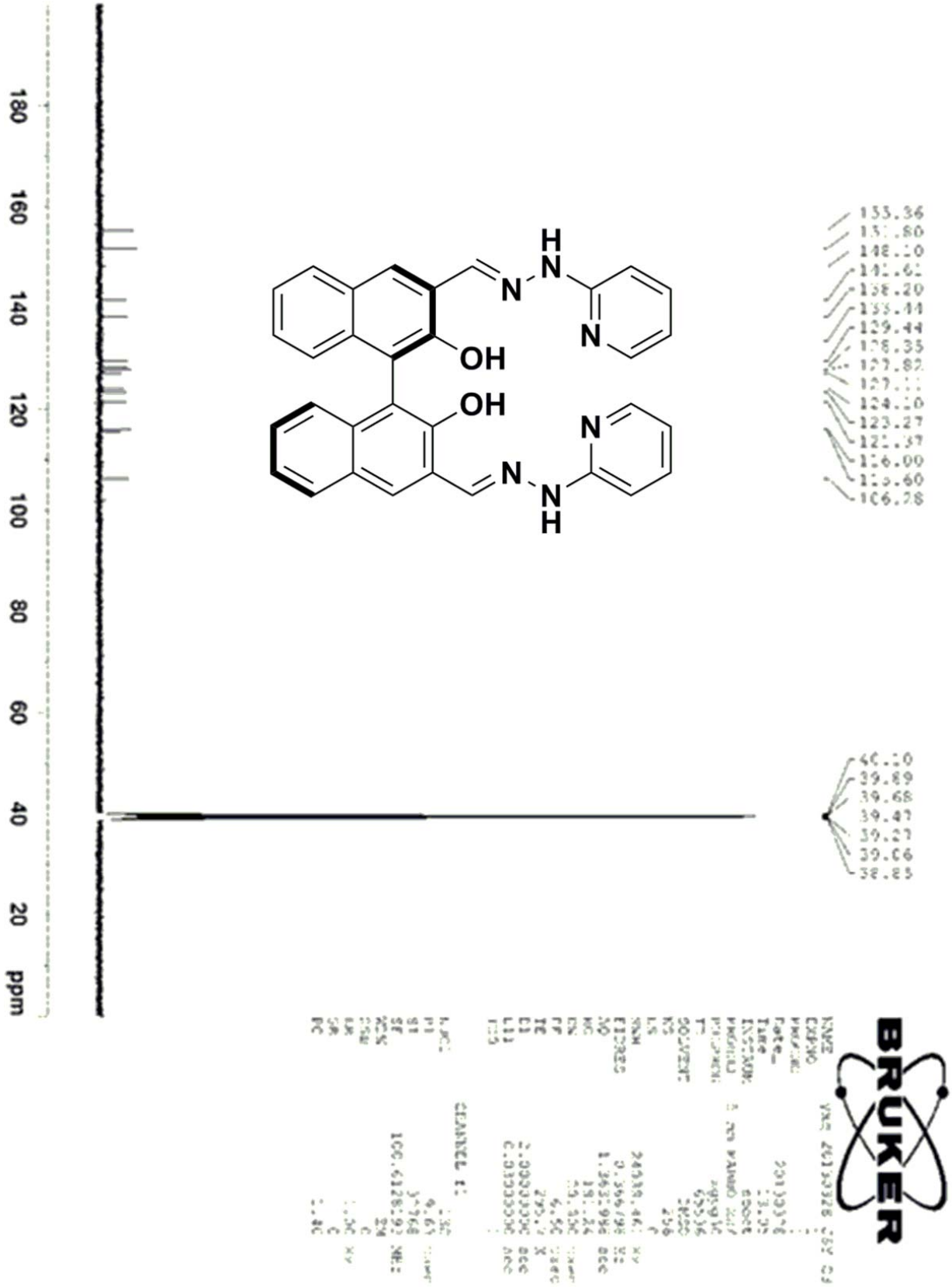
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OH
OH
N
N
NH
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139.44
129.44
123.27
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39.89
39.68
39.47
39.27
39.06
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160
140
120
100
80
60
40
20
ppm
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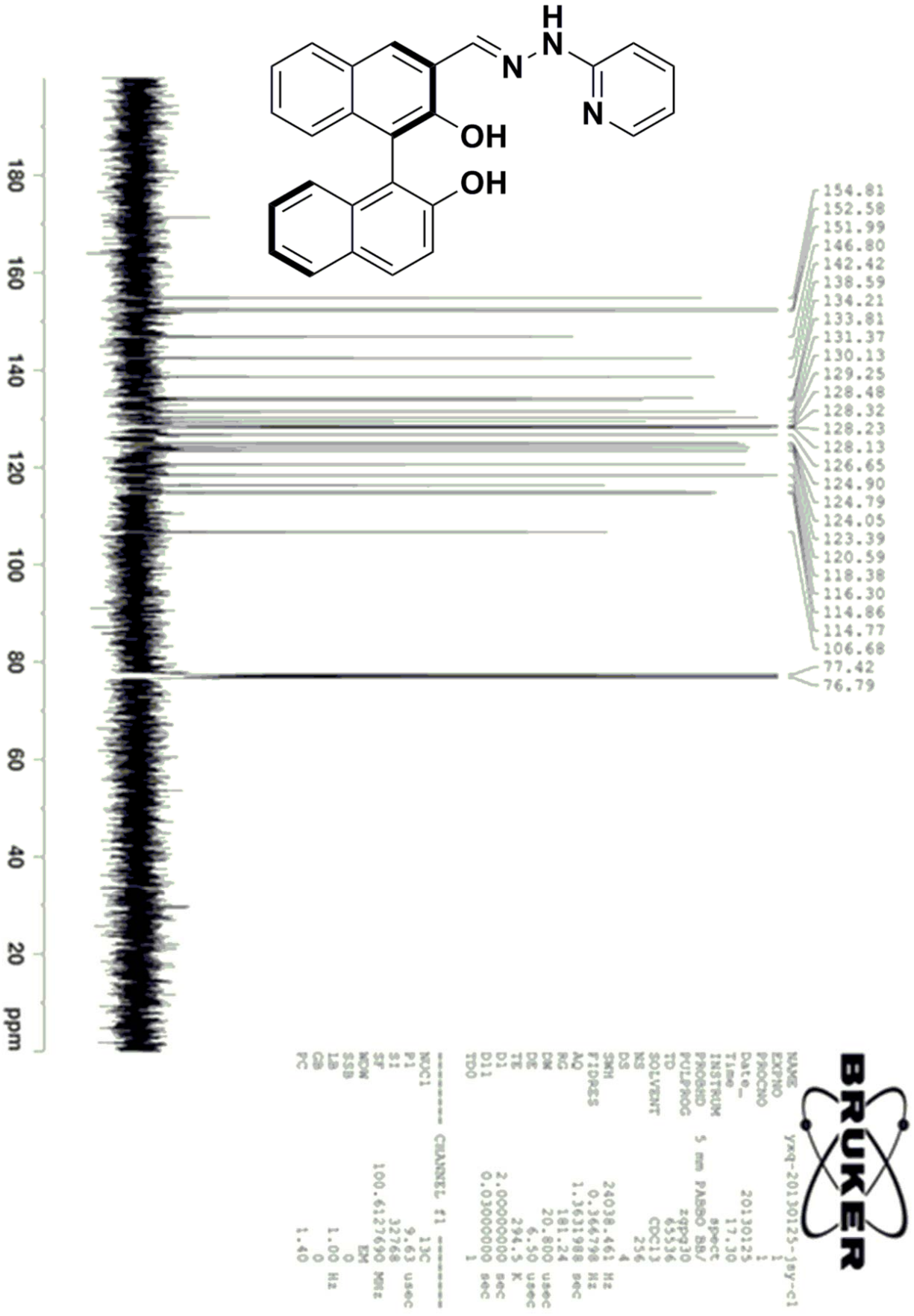
^{13}C-NMR of R2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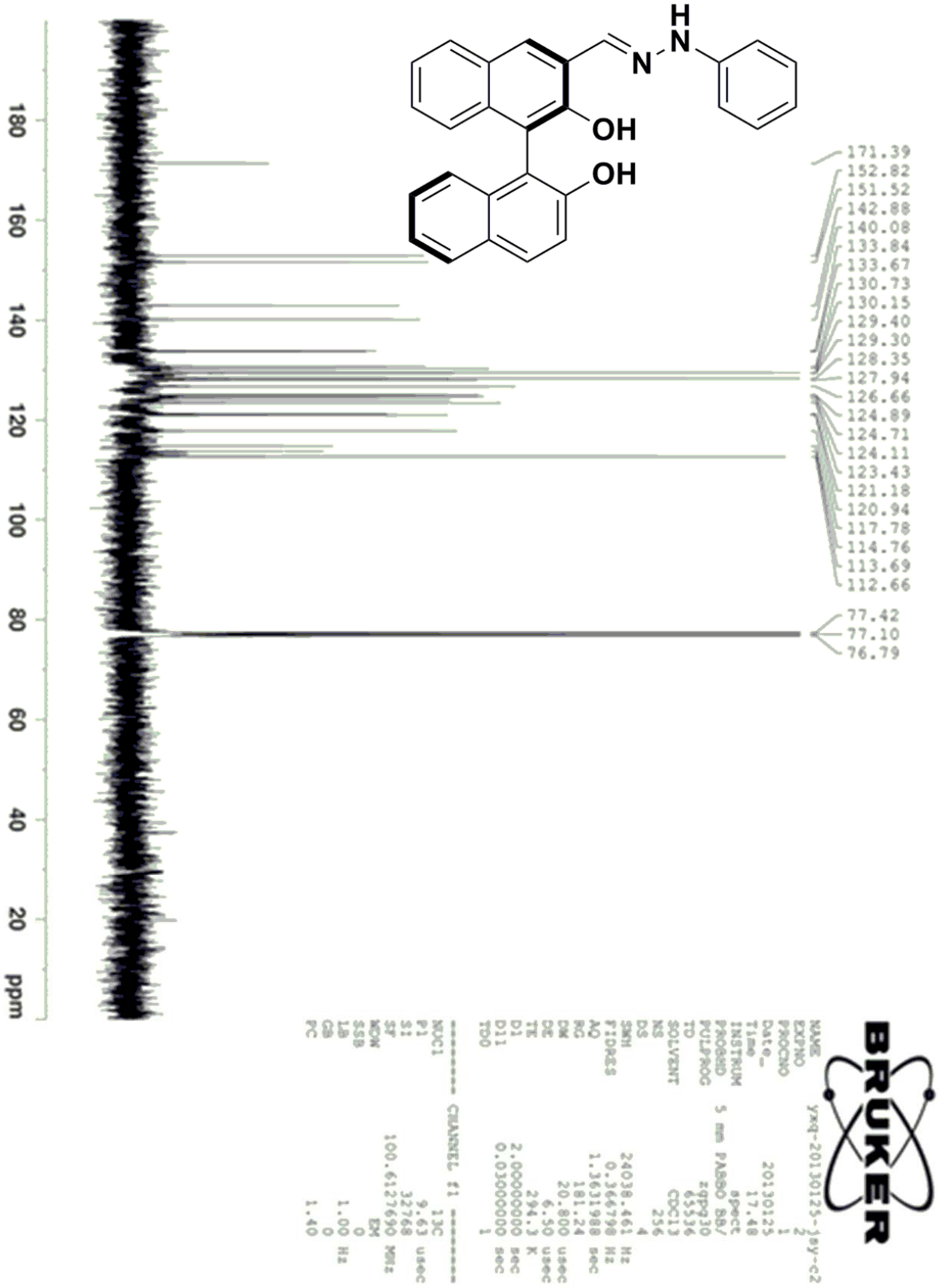
BRUKER

^{13}C-NMR of R3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OH
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129.40
129.30
128.35
127.94
126.66
124.89
124.71
124.11
123.43
121.18
120.94
117.78
114.76
113.69
112.66
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140
120
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80
60
40
20
ppm
BRUKER

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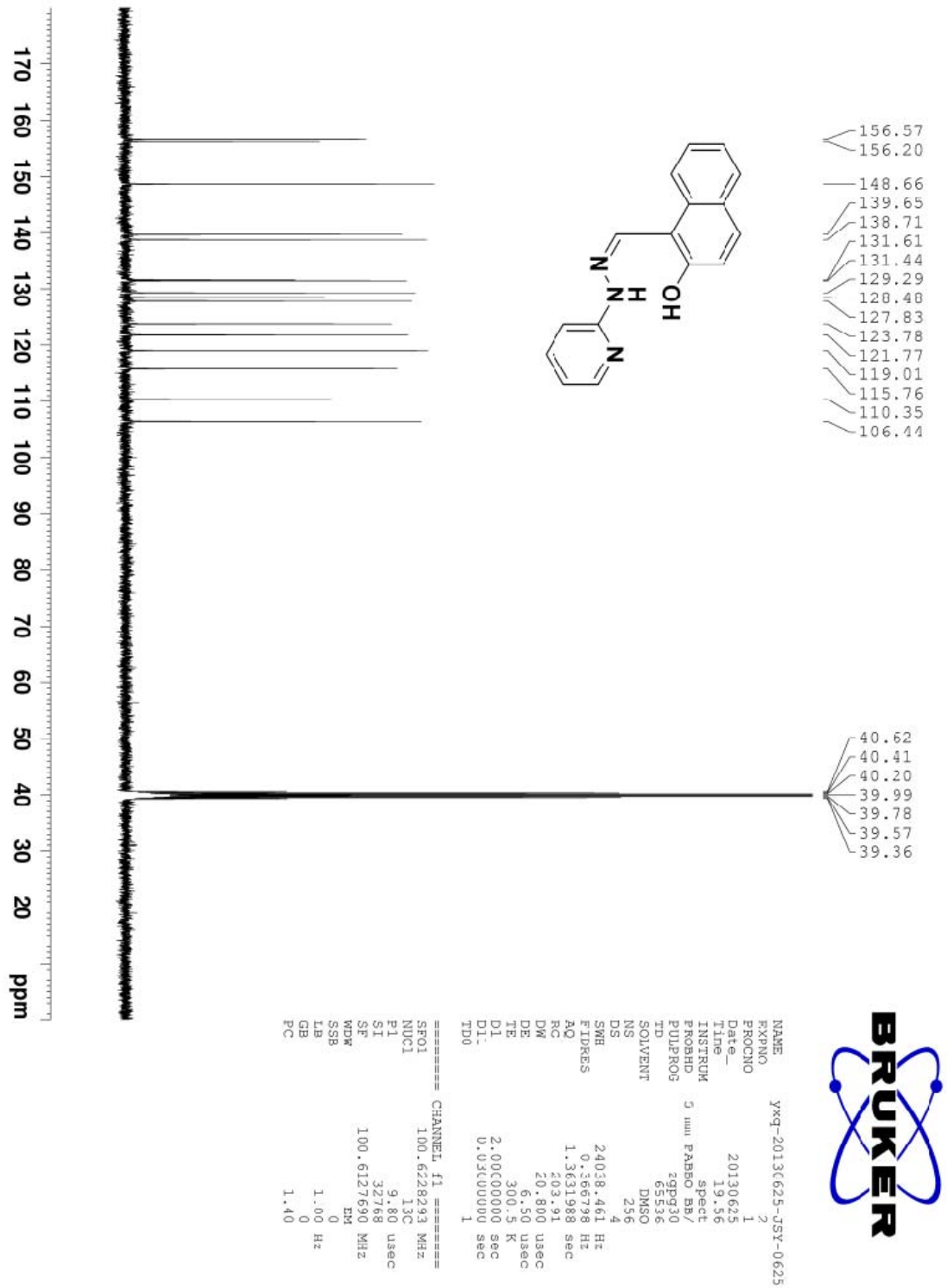
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131.44
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128.48
127.83
123.78
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119.01
115.76
110.35
106.44
40.62
40.41
40.20
39.99
39.78
39.57
39.36
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N
H
N
N
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SOLVENT DMSO
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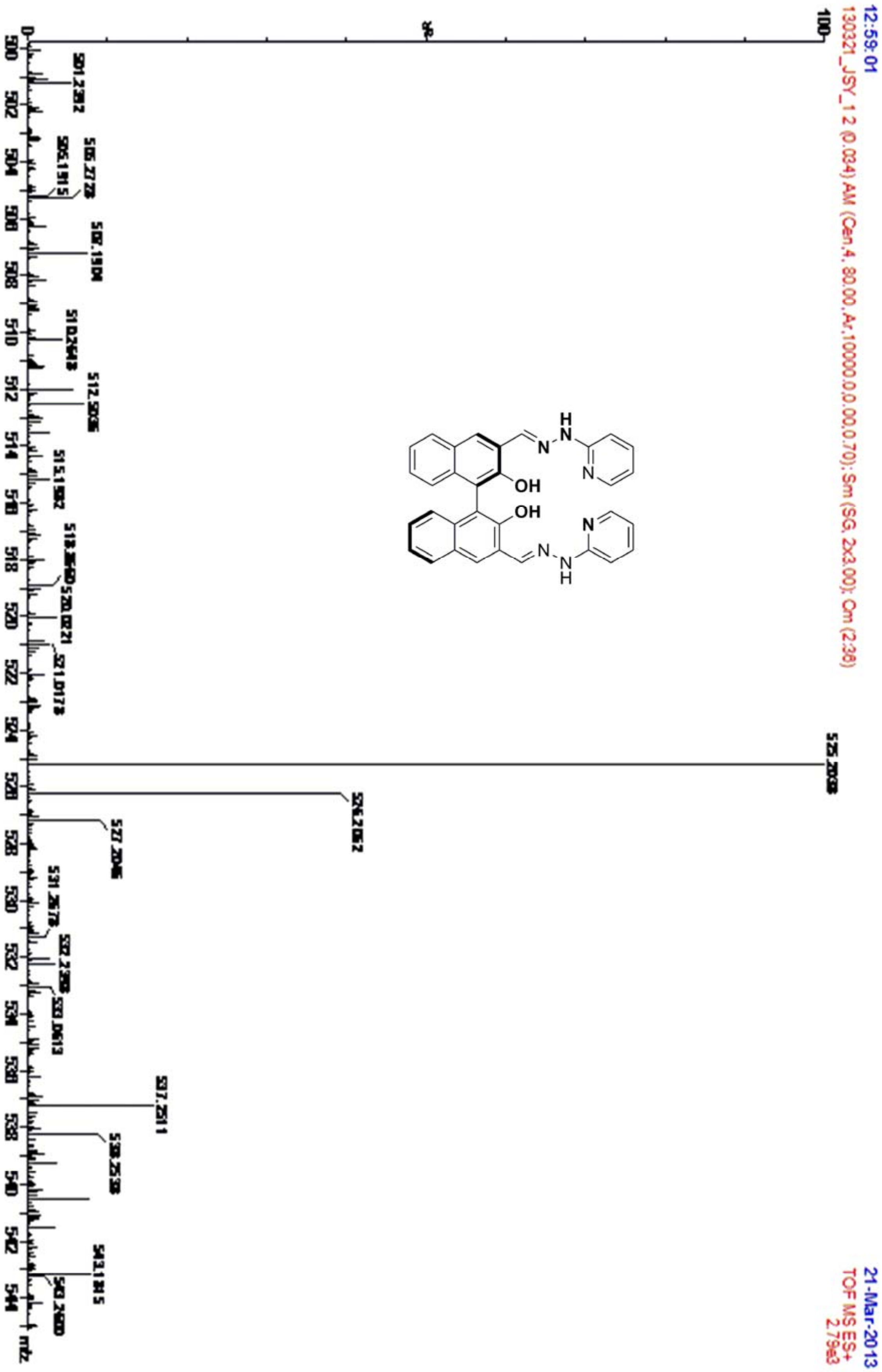

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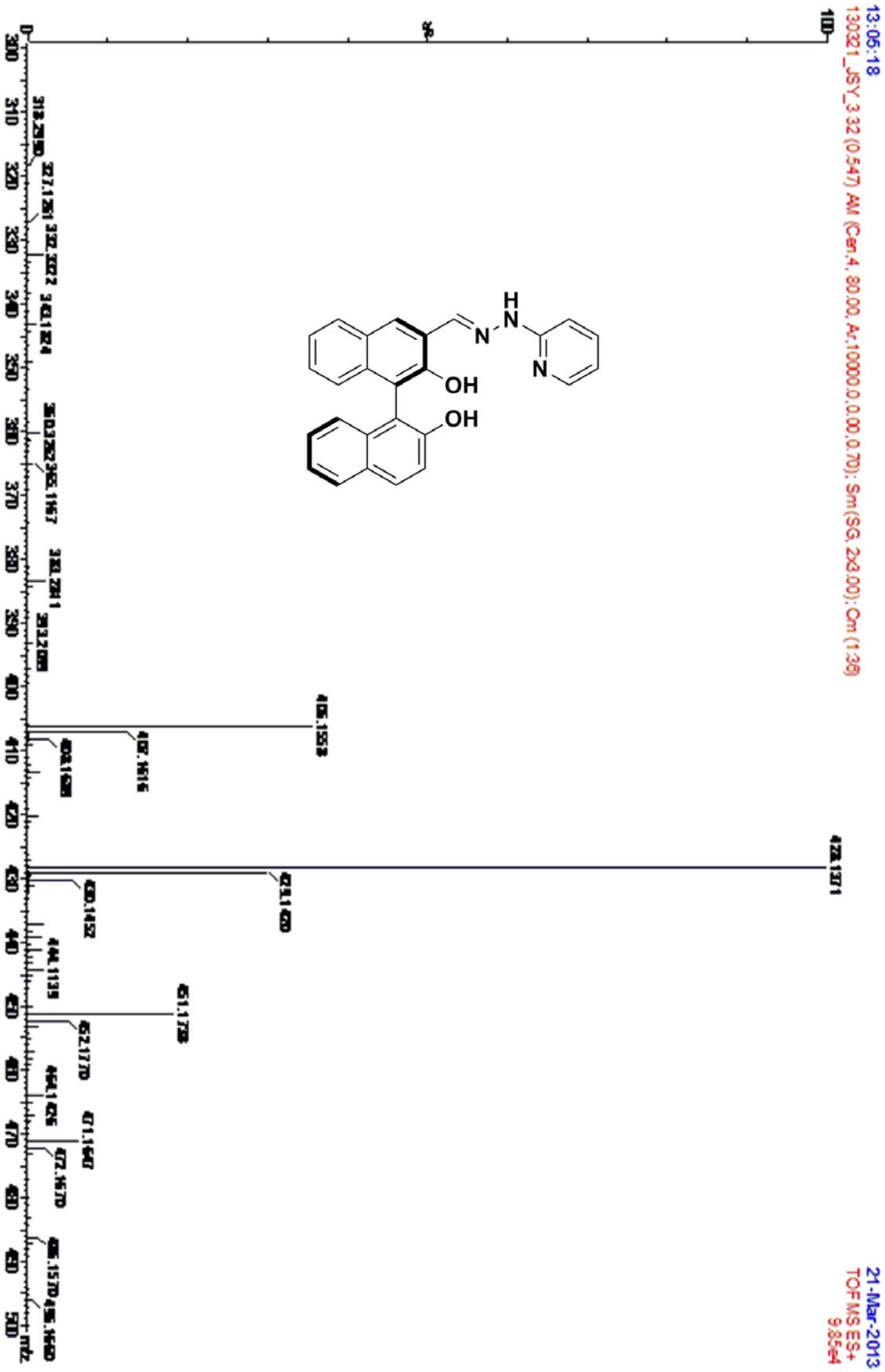
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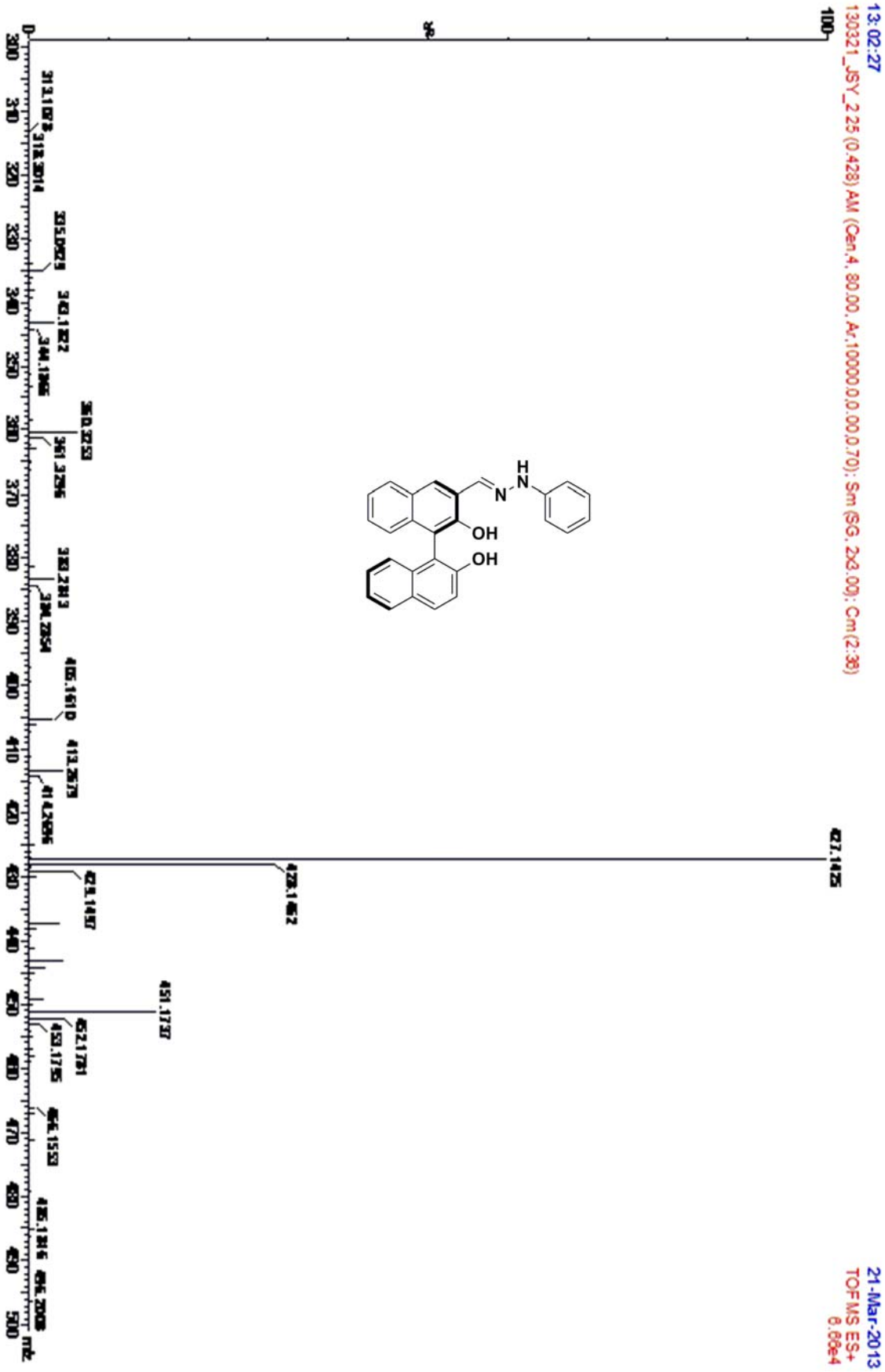
N
H
N
21-Mar-2013
TOF MS ES+
9.85e4
m/z

HRMS of 3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21-Mar-2013
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m/z

HRMS of 2-Zn^{2+} complex