*Supporting Information for*

# SYNTHESIS OF ENANTIOENRICHED INDOLOPIPERAZINONES *VIA* IRIDIUM(I) *N*-HETEROCYCLIC CARBENE COMPLEX CATALYZED ASYMMETRIC INTRAMOLECULAR ALLYLIC AMINATION REACTION

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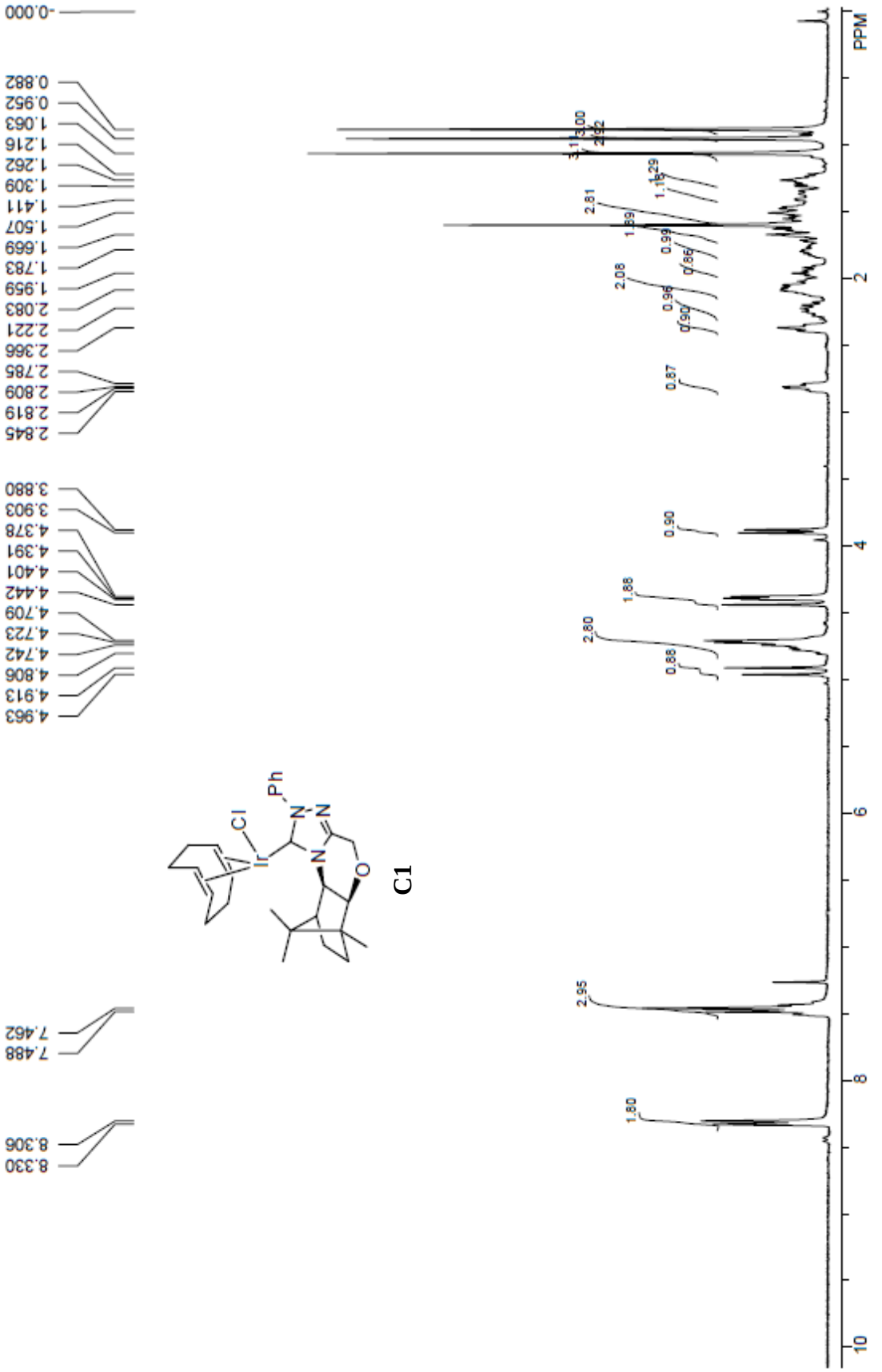
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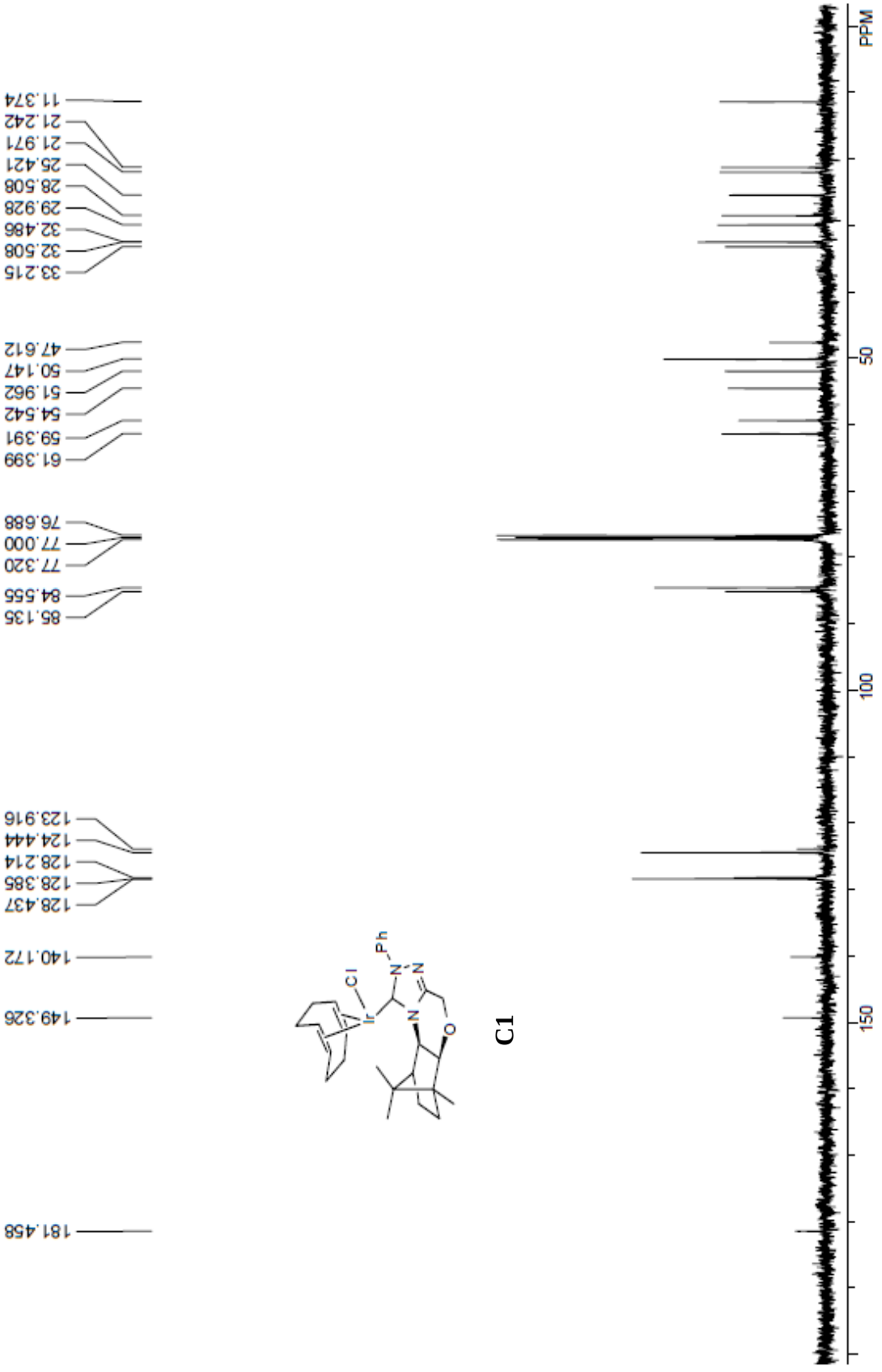
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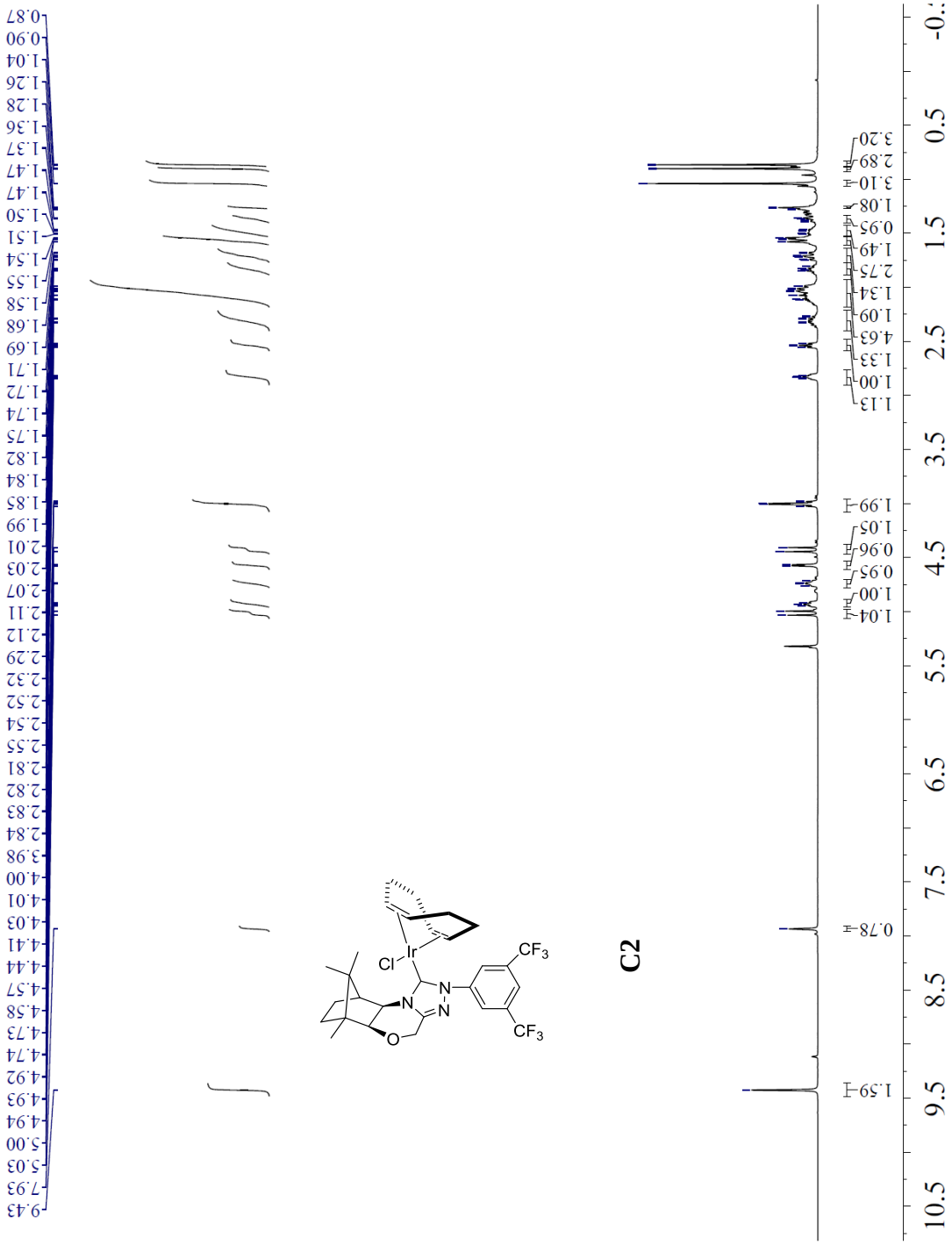
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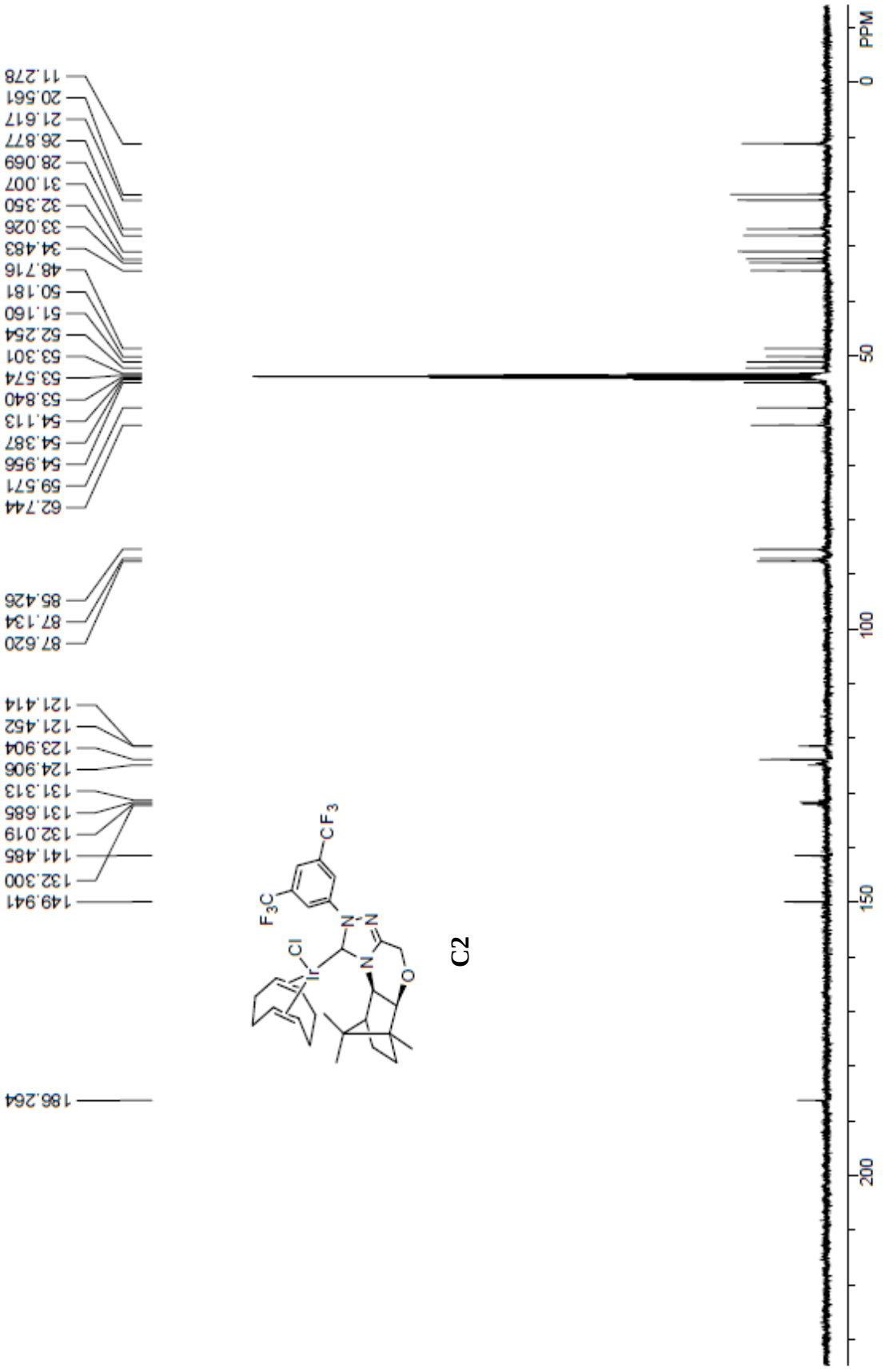
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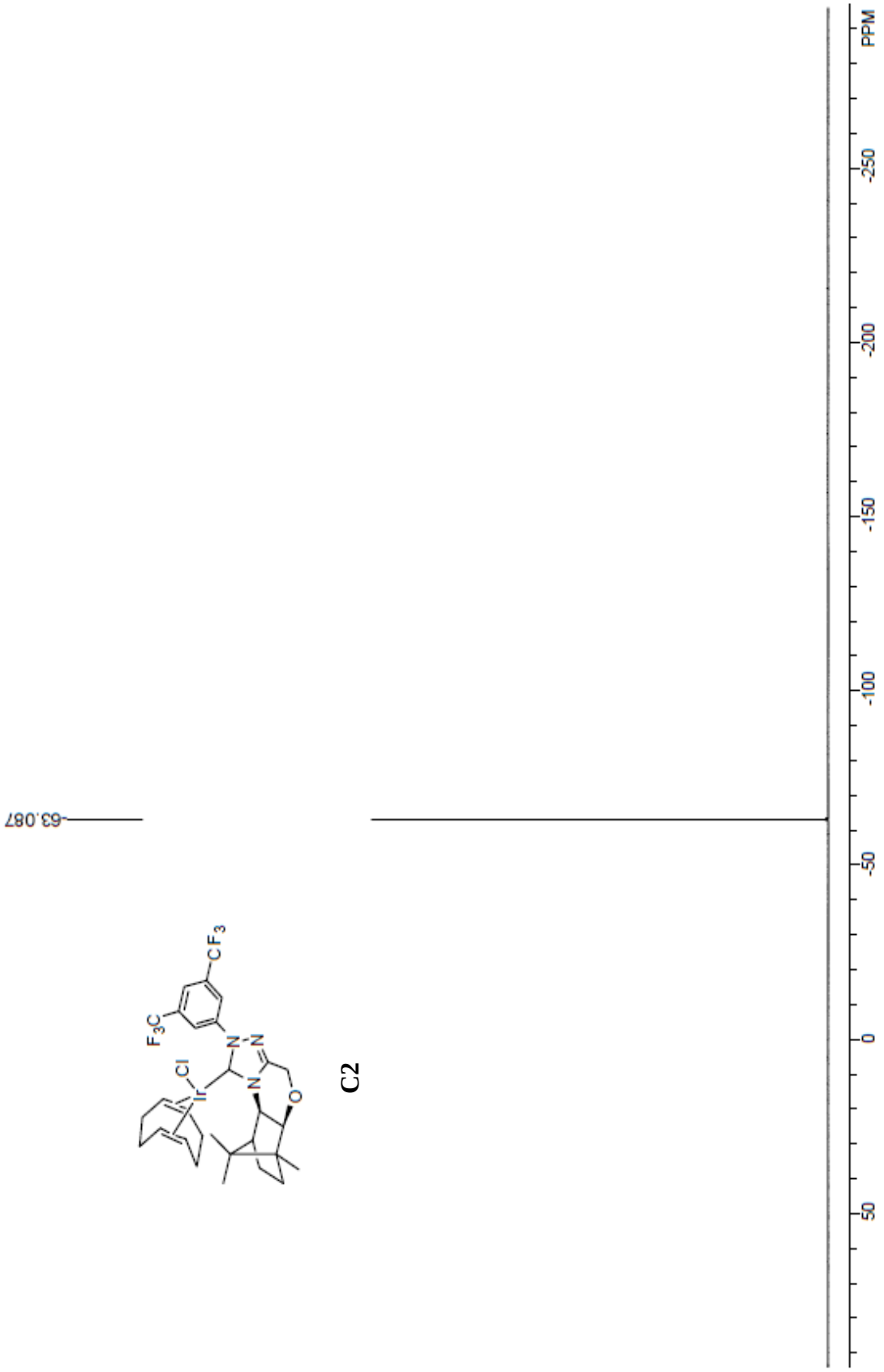
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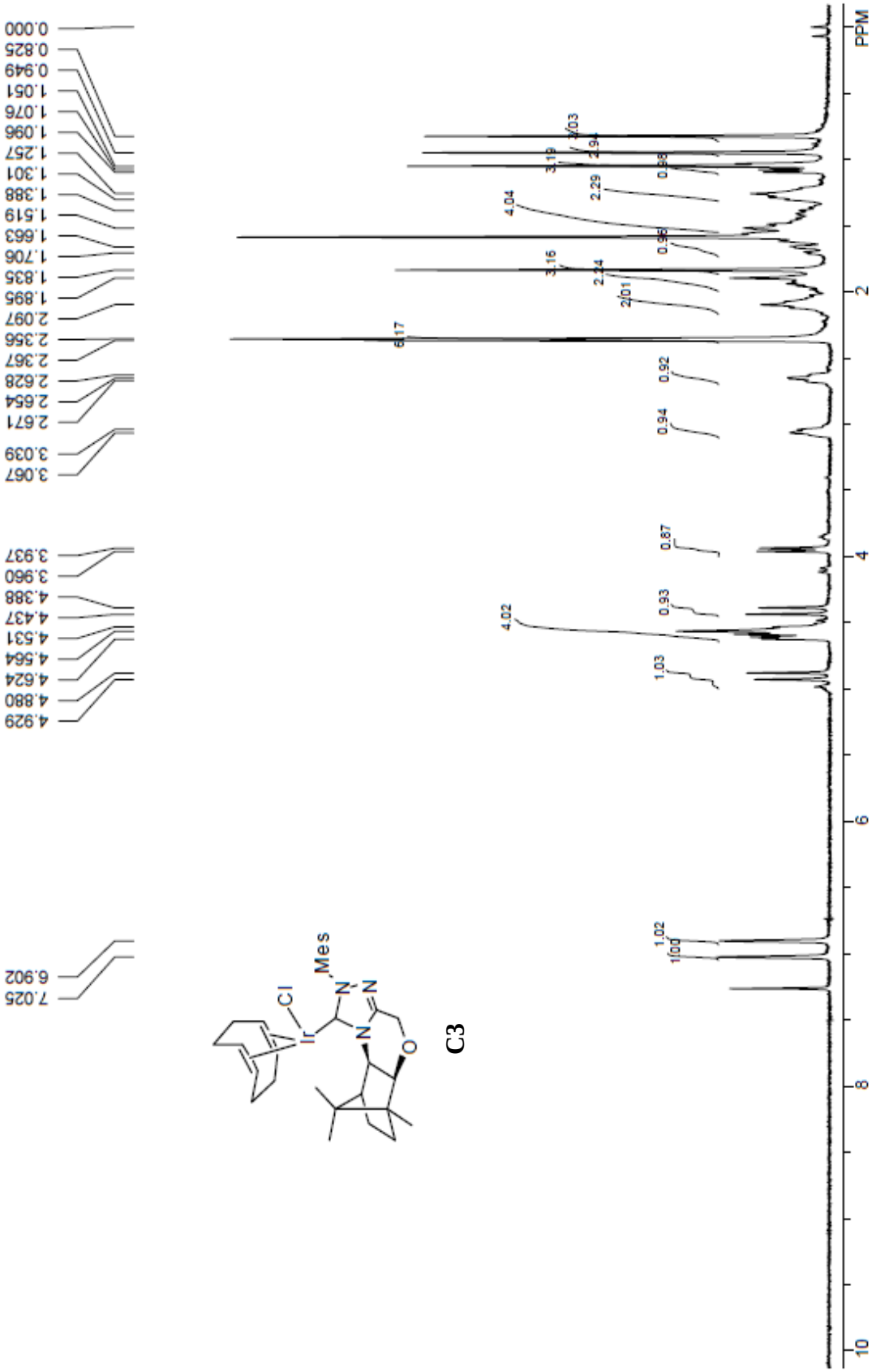
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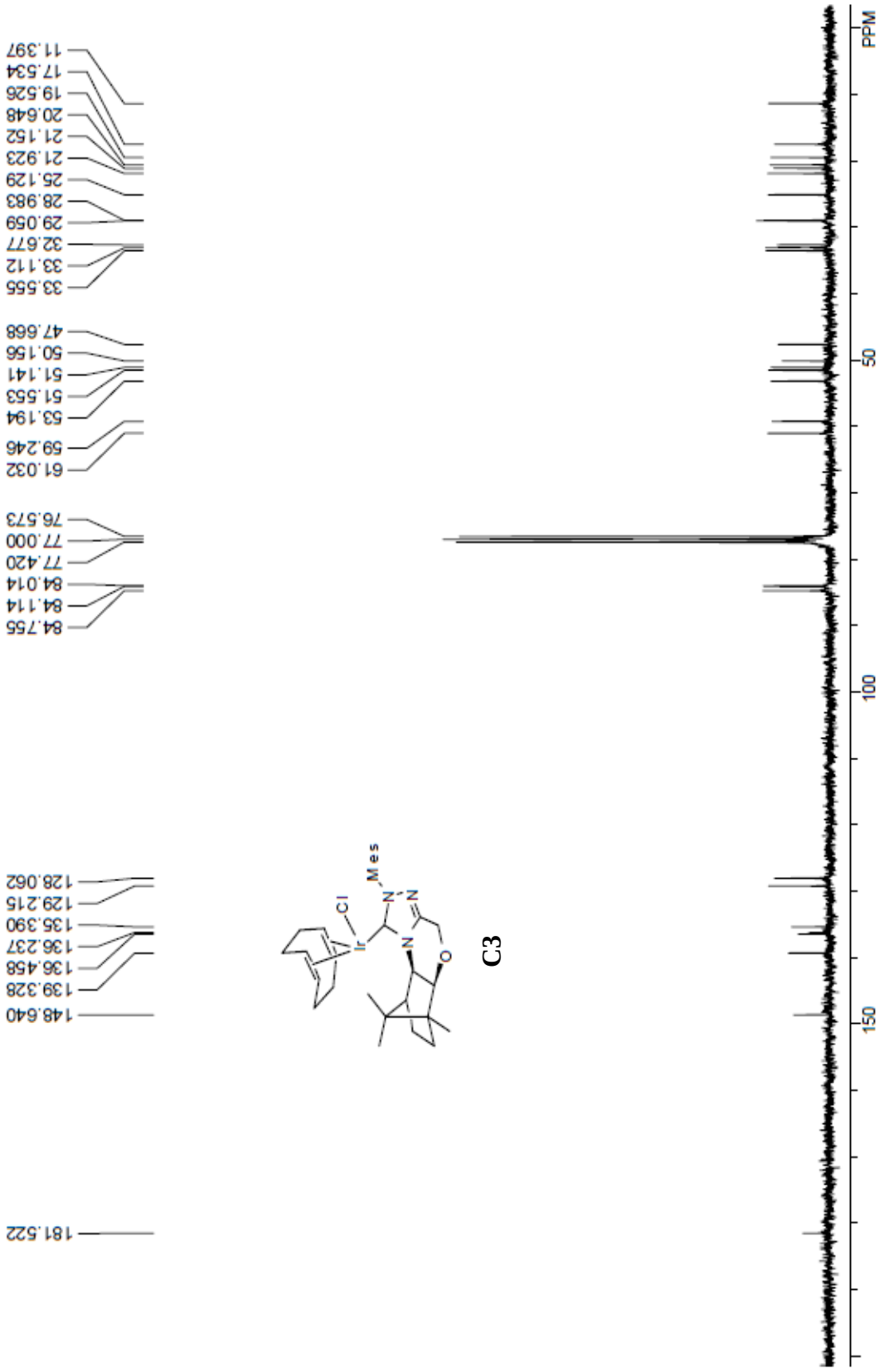
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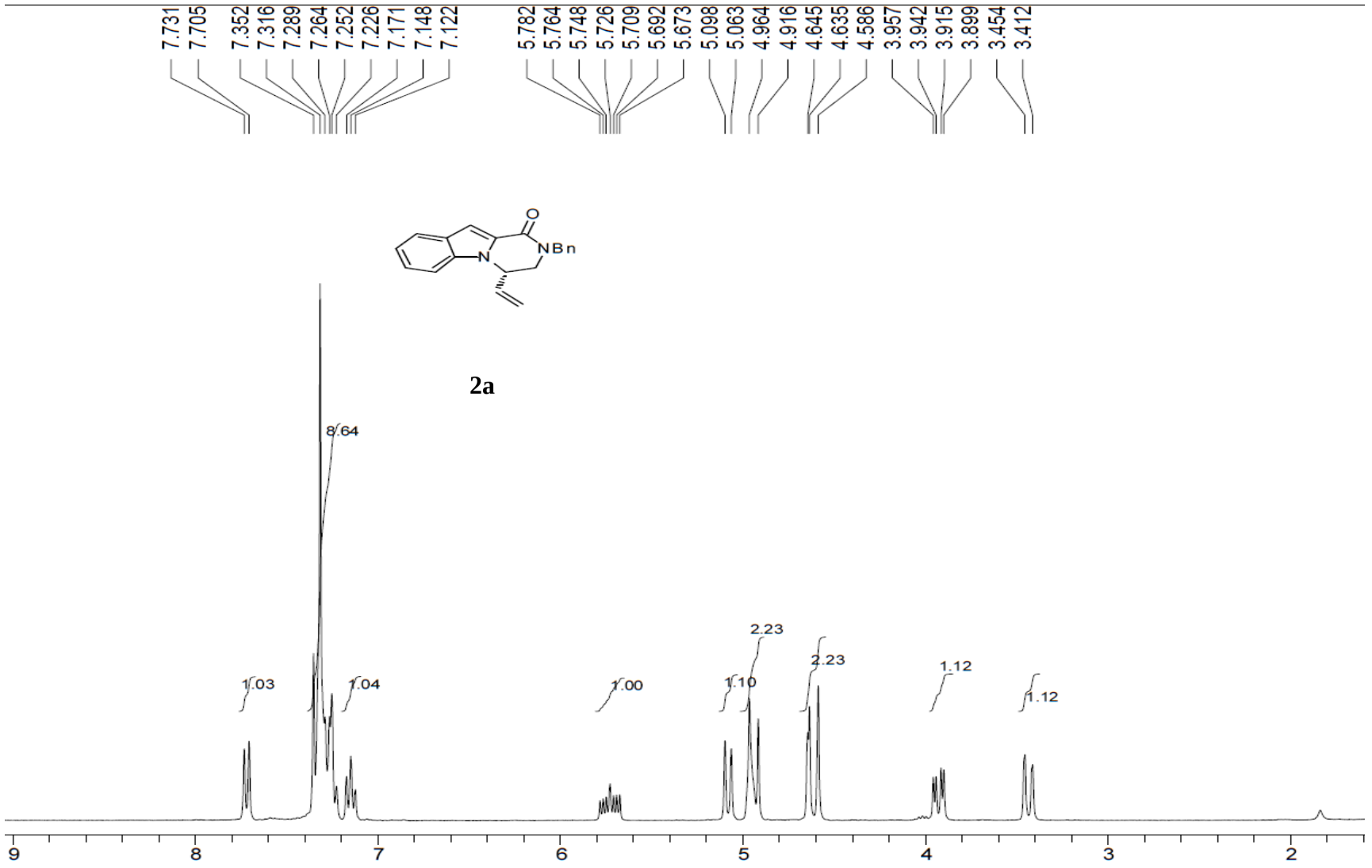
C3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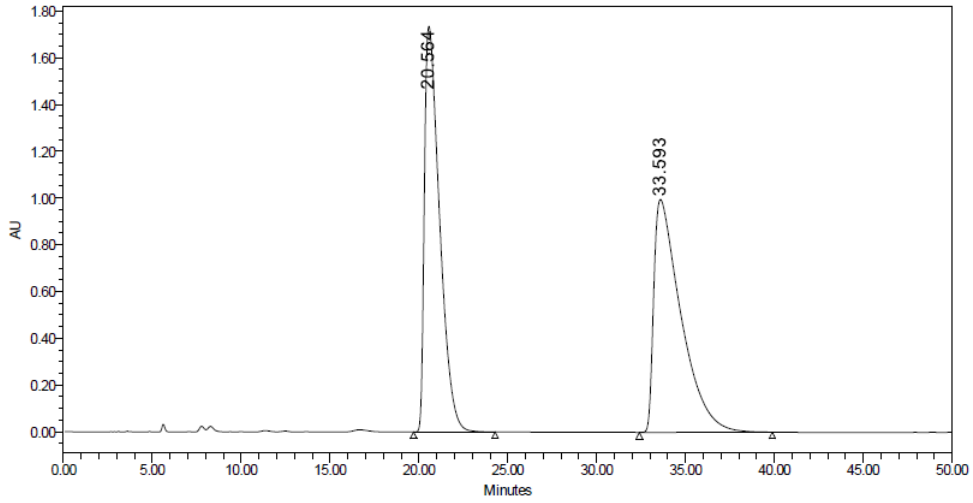
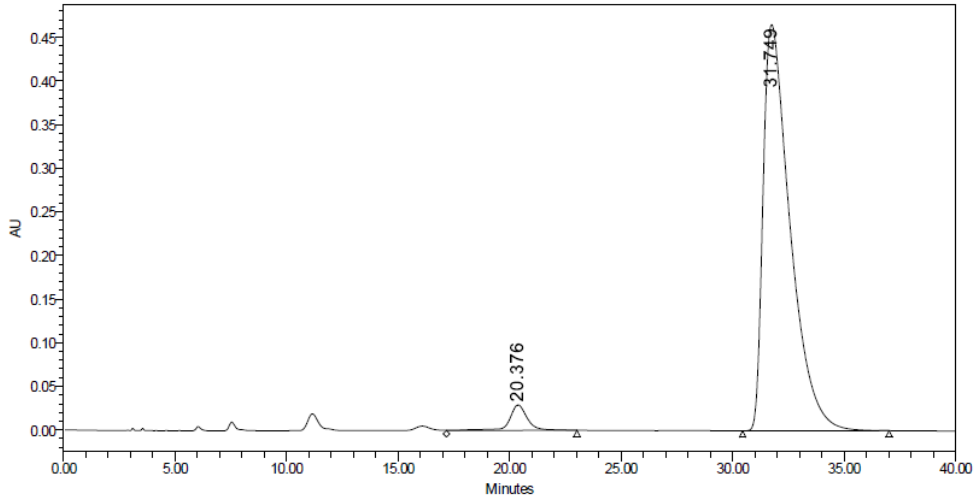



| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 20.564 | 102859724 | 49.27 | 1735412 | 63.52 |
| 2 | 33.593 | 105924785 | 50.73 | 996502 | 36.48 |

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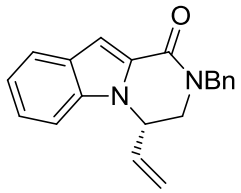
|---|---|---|---|---|---|
| 1 | 20.376 | 1613778 | 3.95 | 29125 | 5.89 |
| 2 | 31.749 | 39198903 | 96.05 | 465569 | 94.11 |

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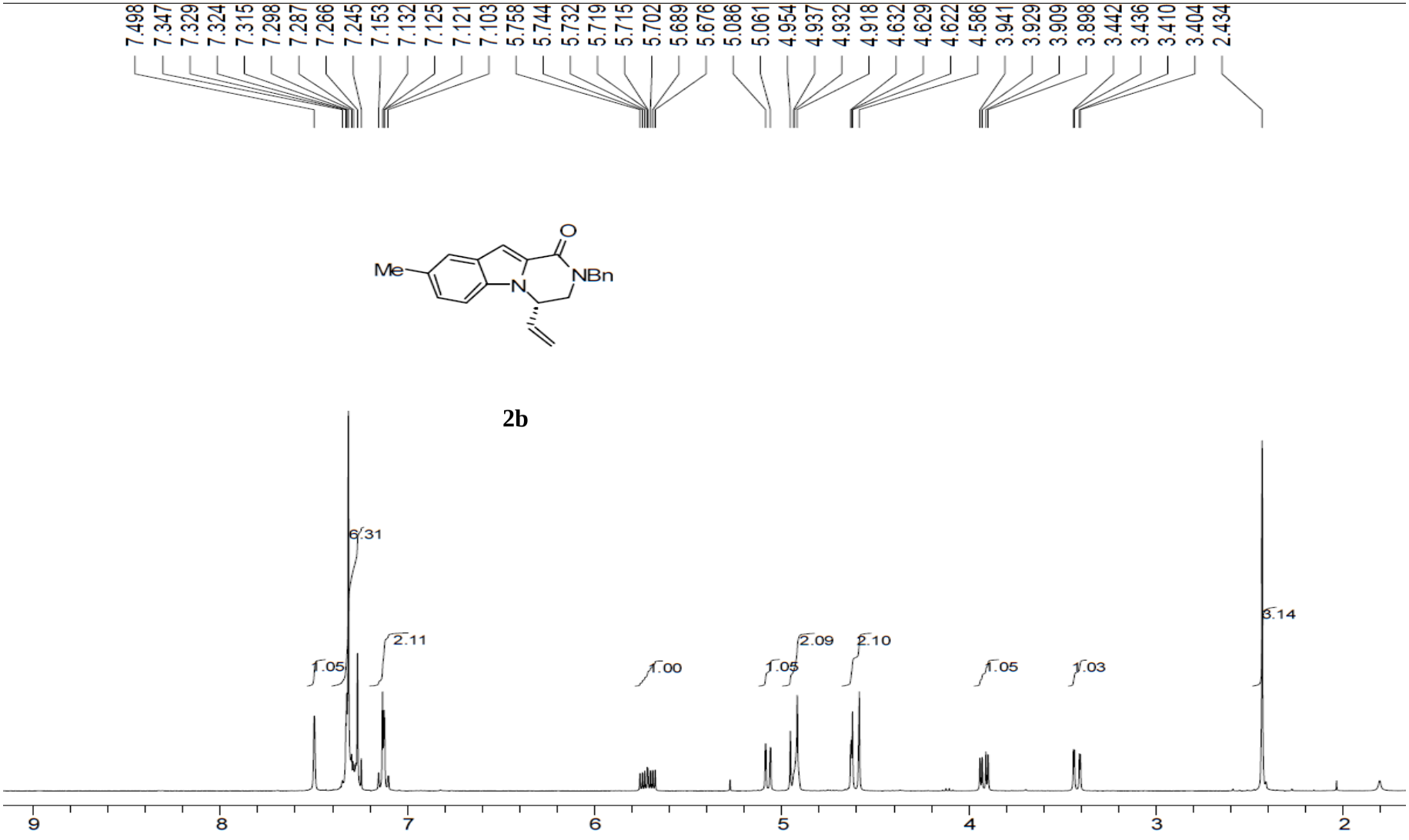
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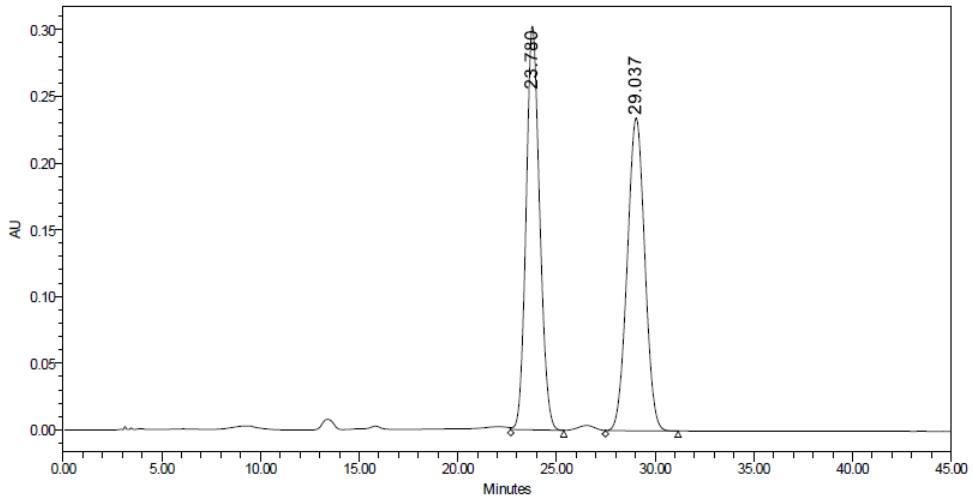


| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
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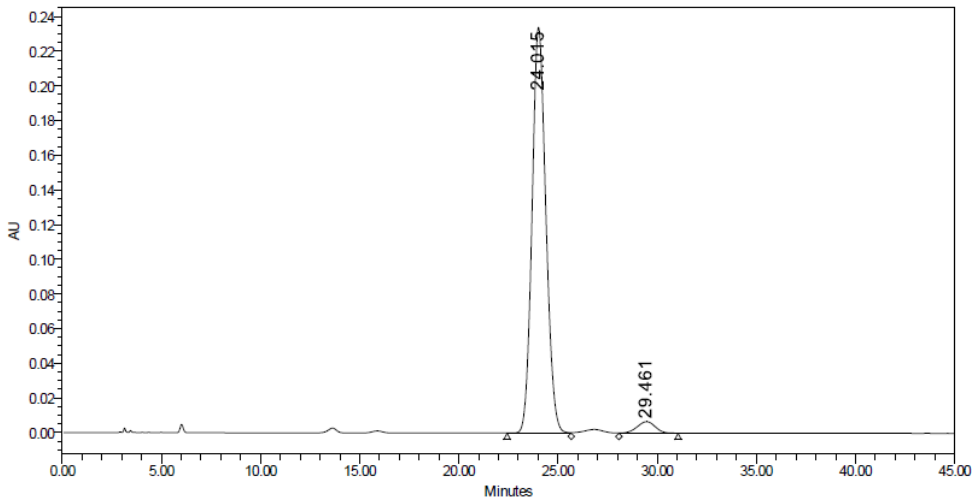


| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
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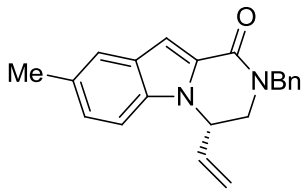
| 2 | 29.461 | 421652 | 3.58 | 6647 | 2.76 |

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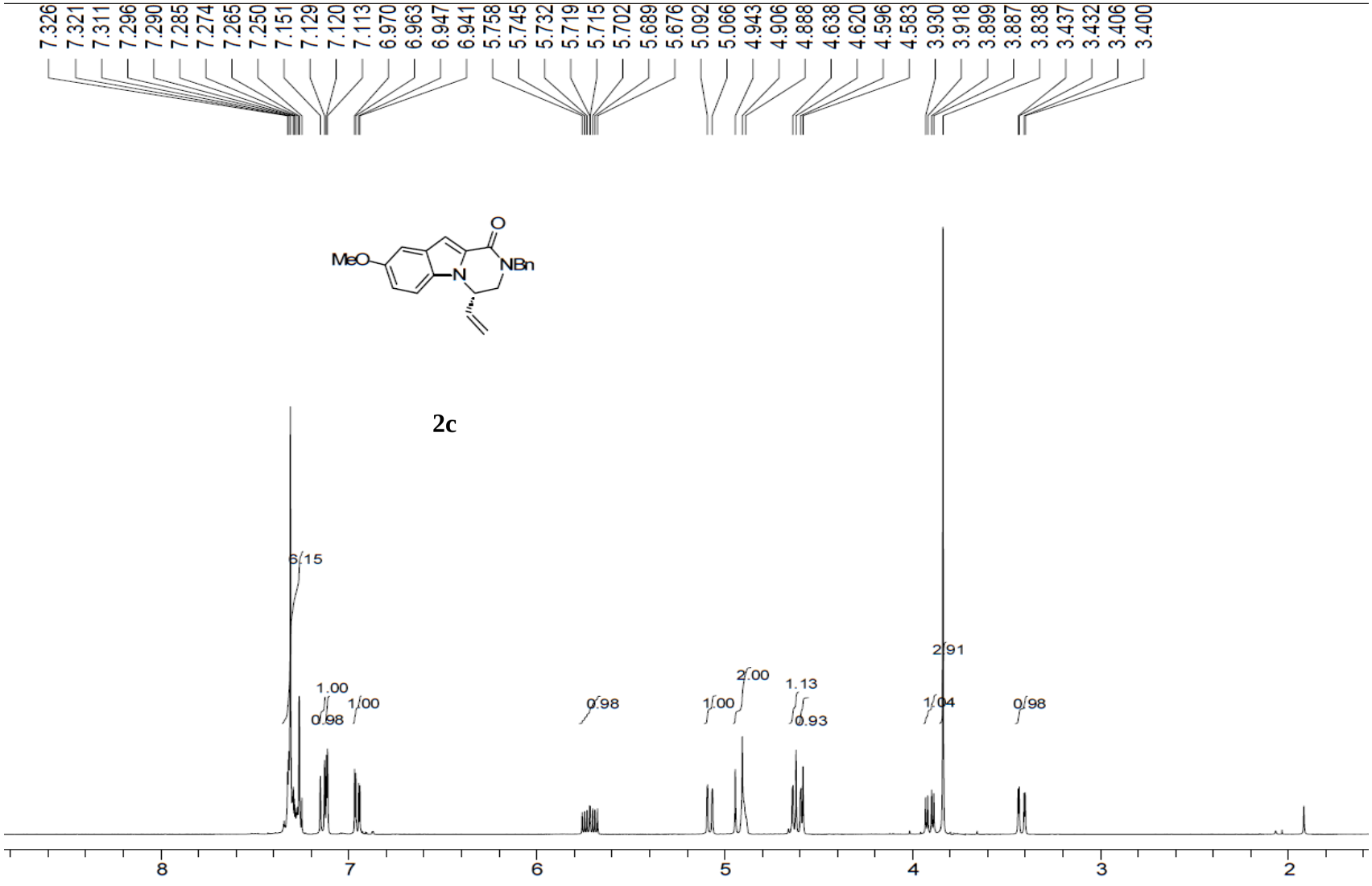
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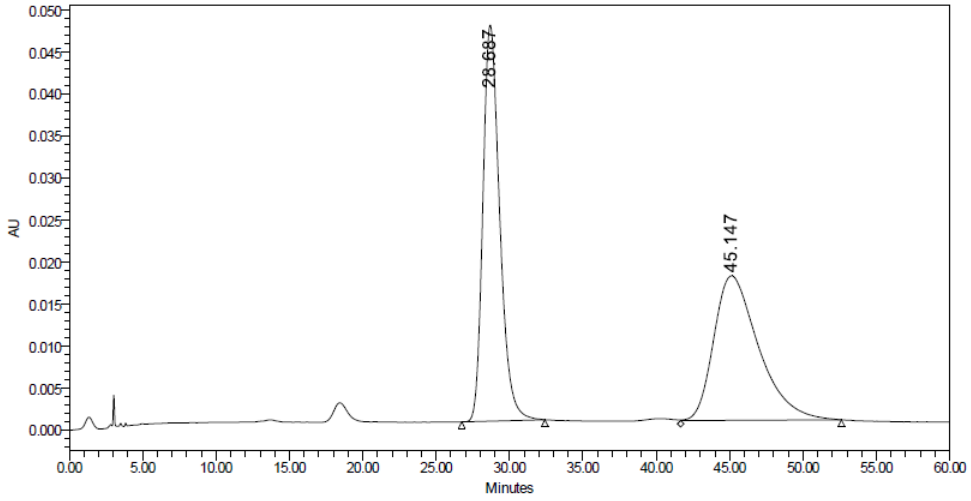


| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
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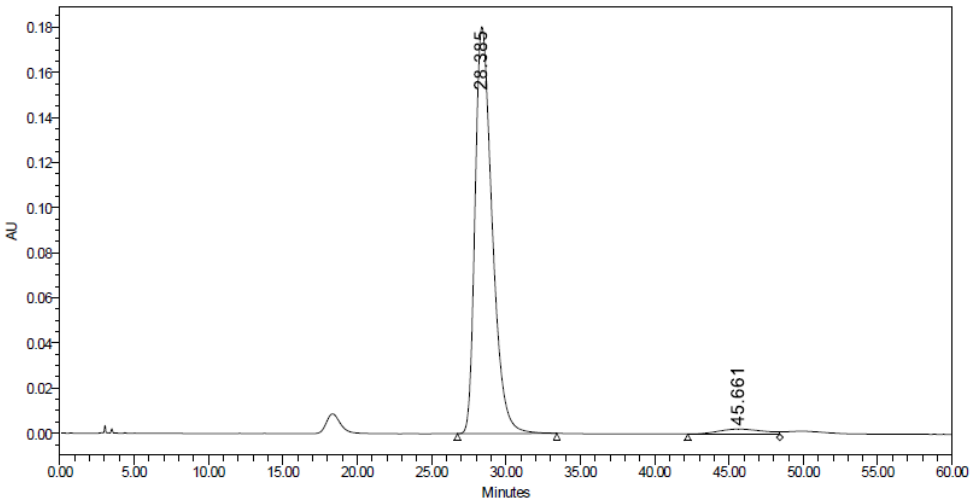
| 1 | 28.687 | 3750784 | 50.71 | 47128 | 73.26 |
| 2 | 45.147 | 3646093 | 49.29 | 17203 | 26.74 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
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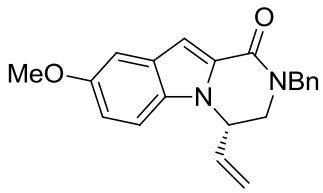
| 2 | 45.661 | 449718 | 3.03 | 2182 | 1.20 |

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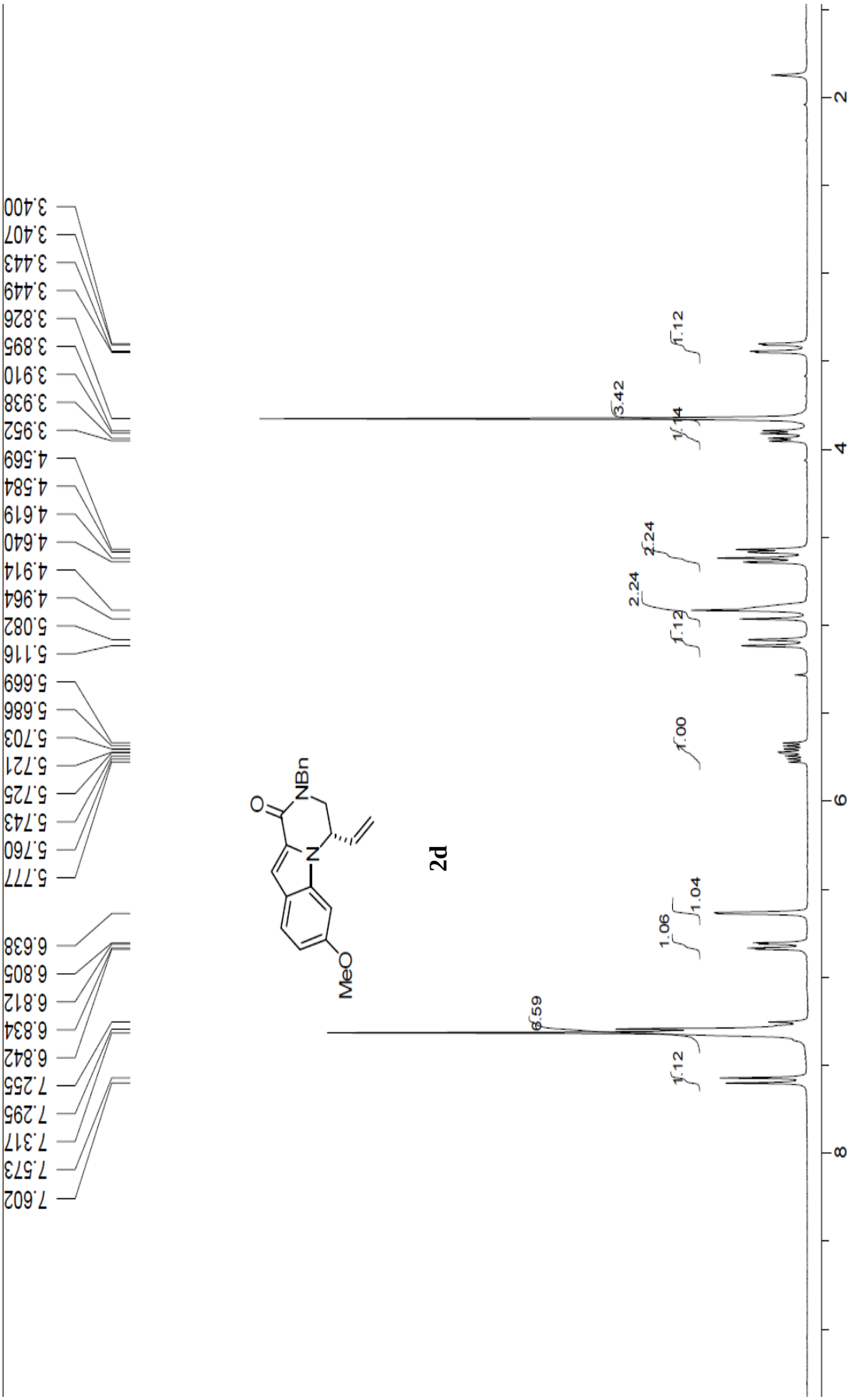
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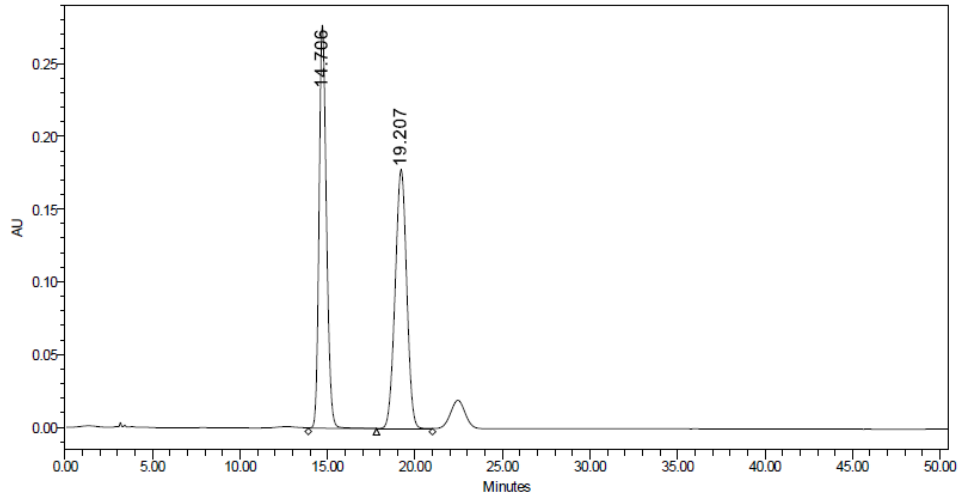
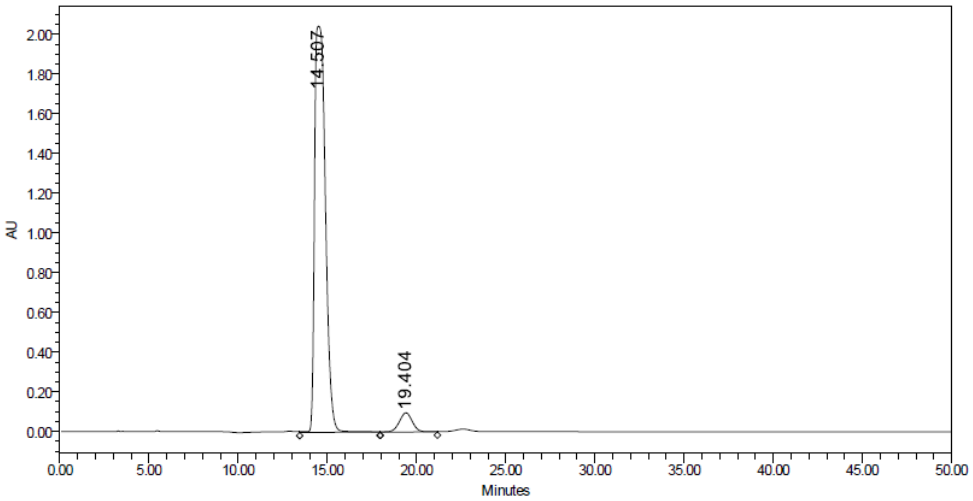
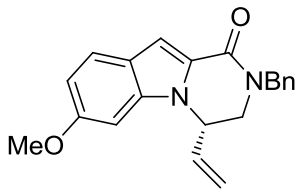



| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 14.706 | 8083285 | 49.78 | 277075 | 60.91 |
| 2 | 19.207 | 8155493 | 50.22 | 177817 | 39.09 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 14.507 | 86246515 | 94.56 | 2045435 | 95.48 |
| 2 | 19.404 | 4964616 | 5.44 | 96872 | 4.52 |

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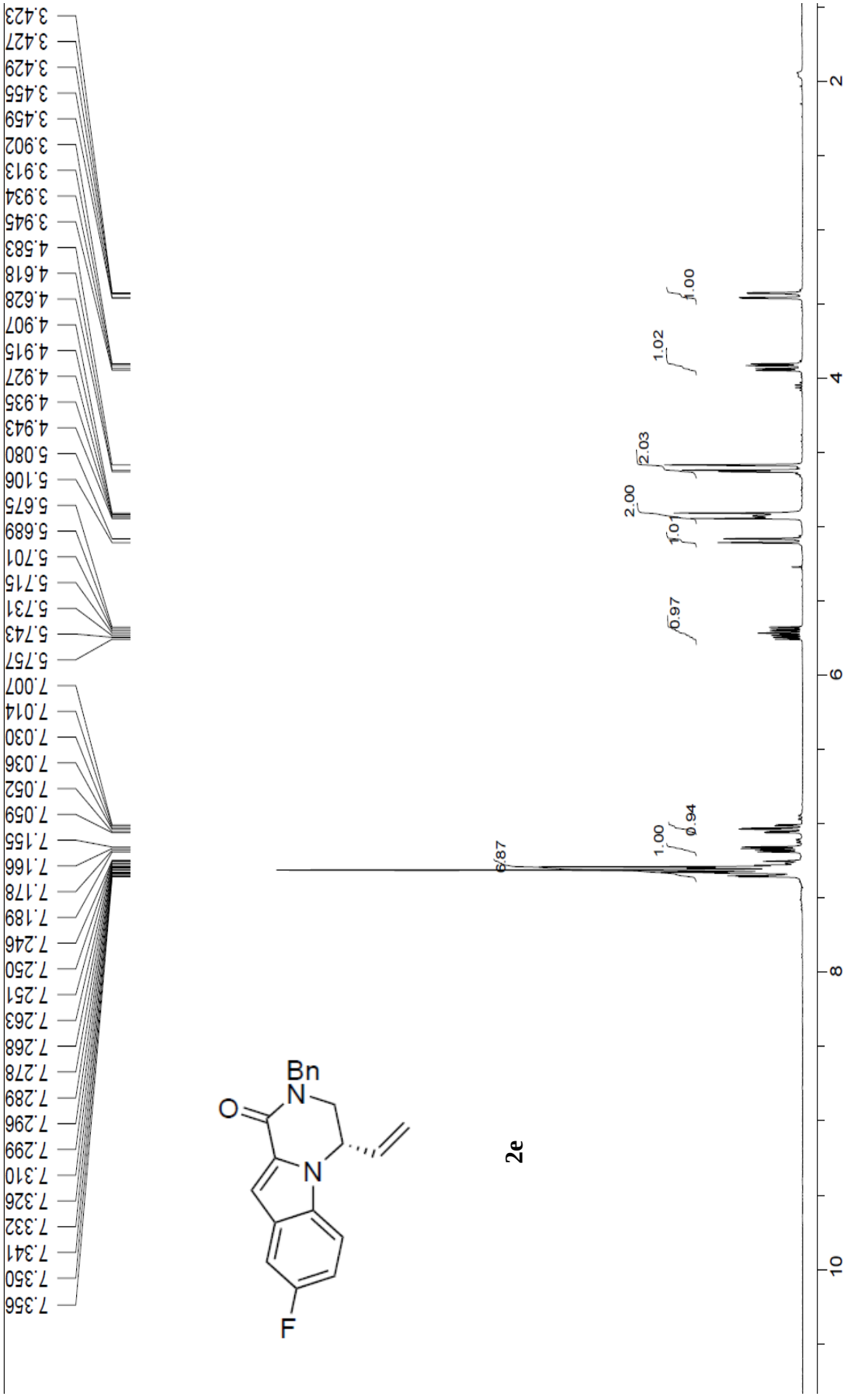
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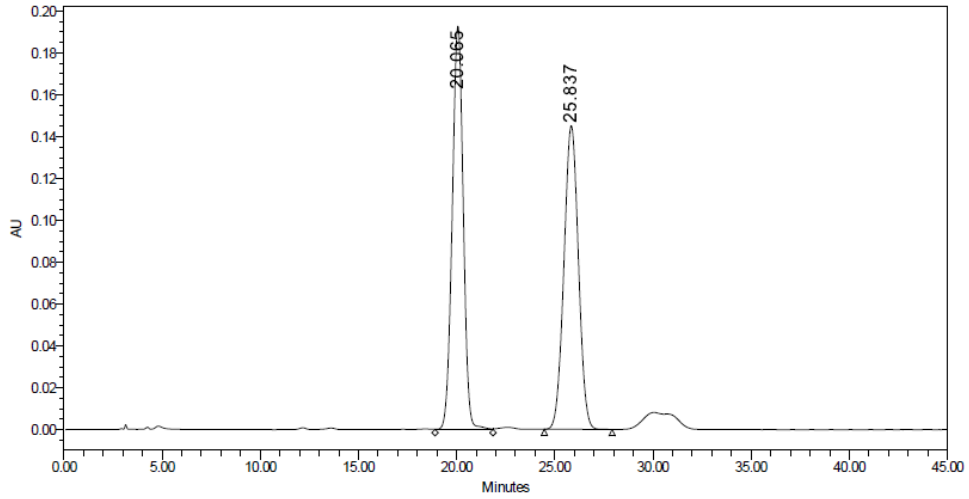
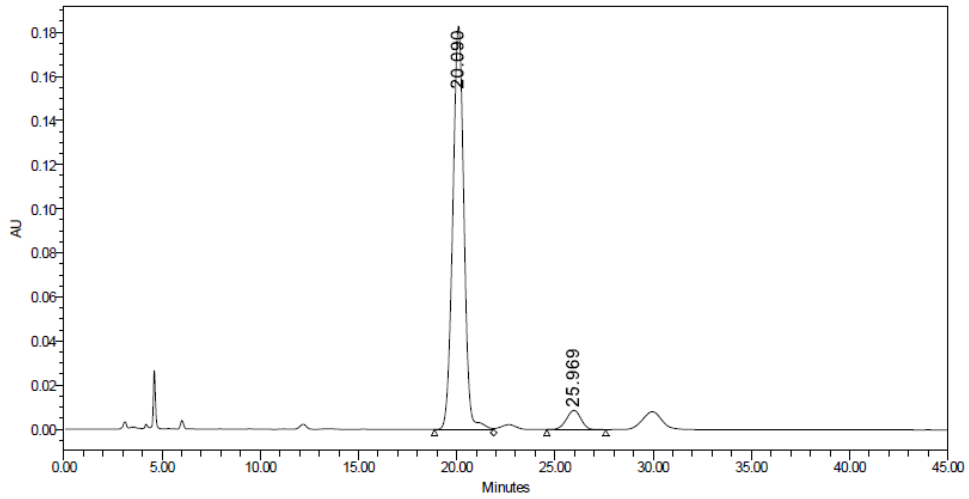
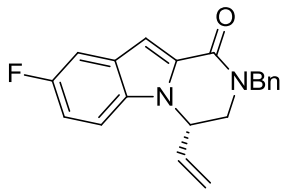



| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 20.065 | 7507516 | 50.25 | 192664 | 57.05 |
| 2 | 25.837 | 7432657 | 49.75 | 145024 | 42.95 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 20.090 | 7203891 | 94.13 | 182903 | 95.45 |
| 2 | 25.969 | 449292 | 5.87 | 8727 | 4.55 |

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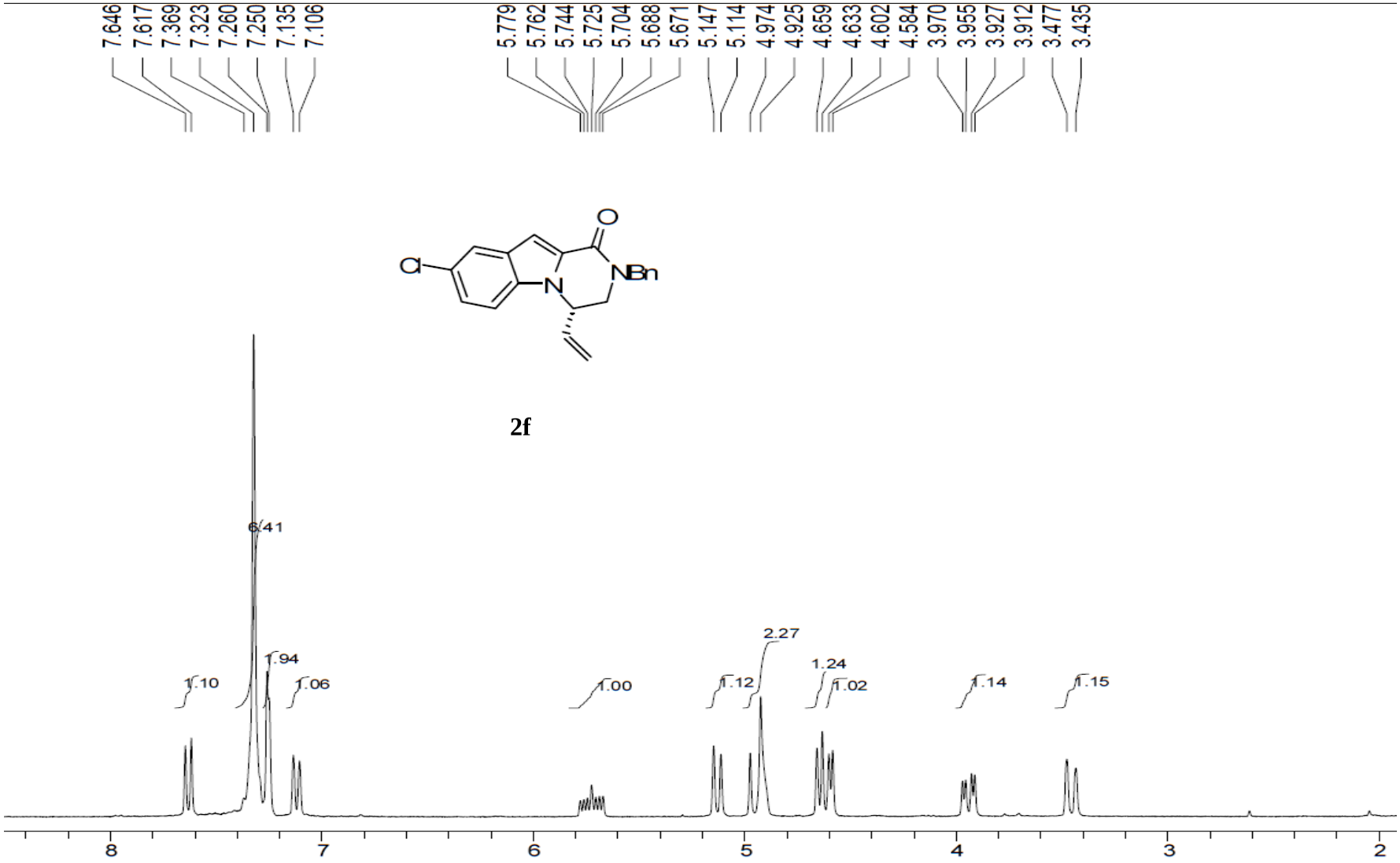
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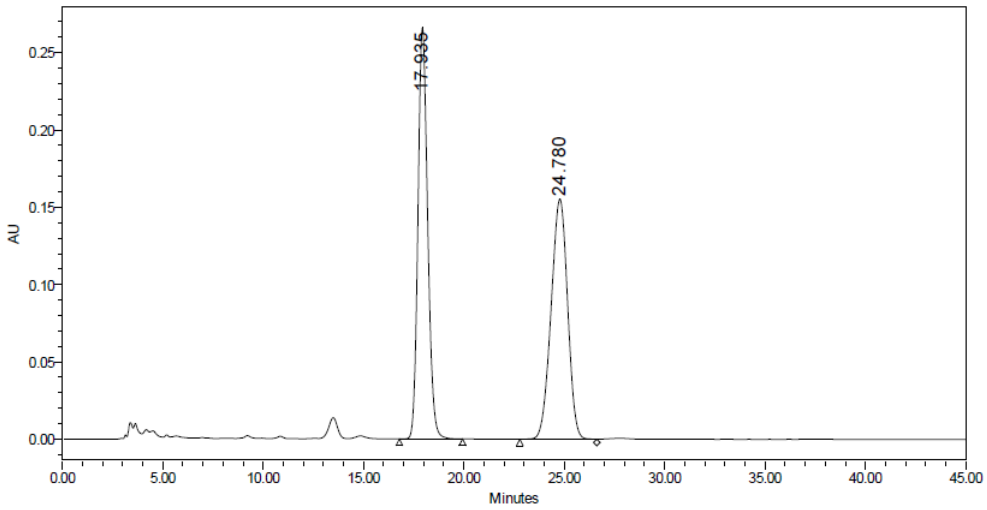
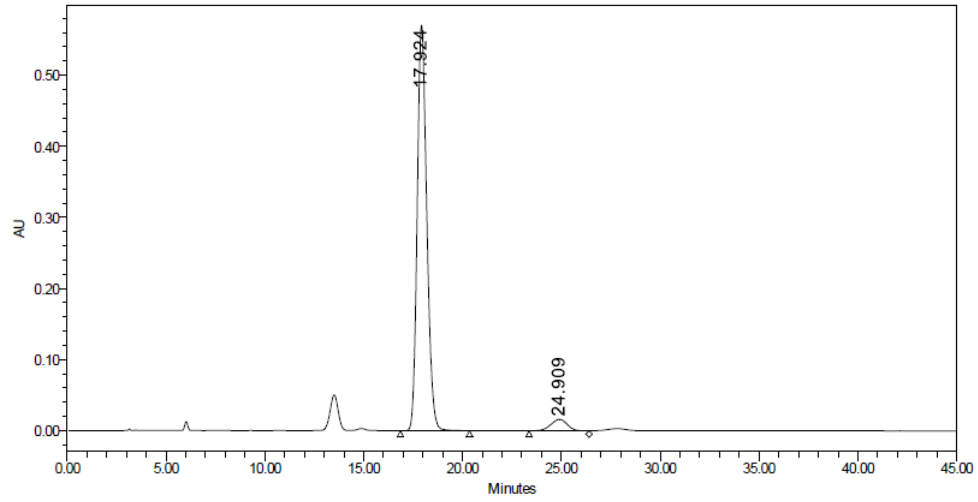
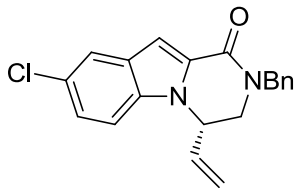


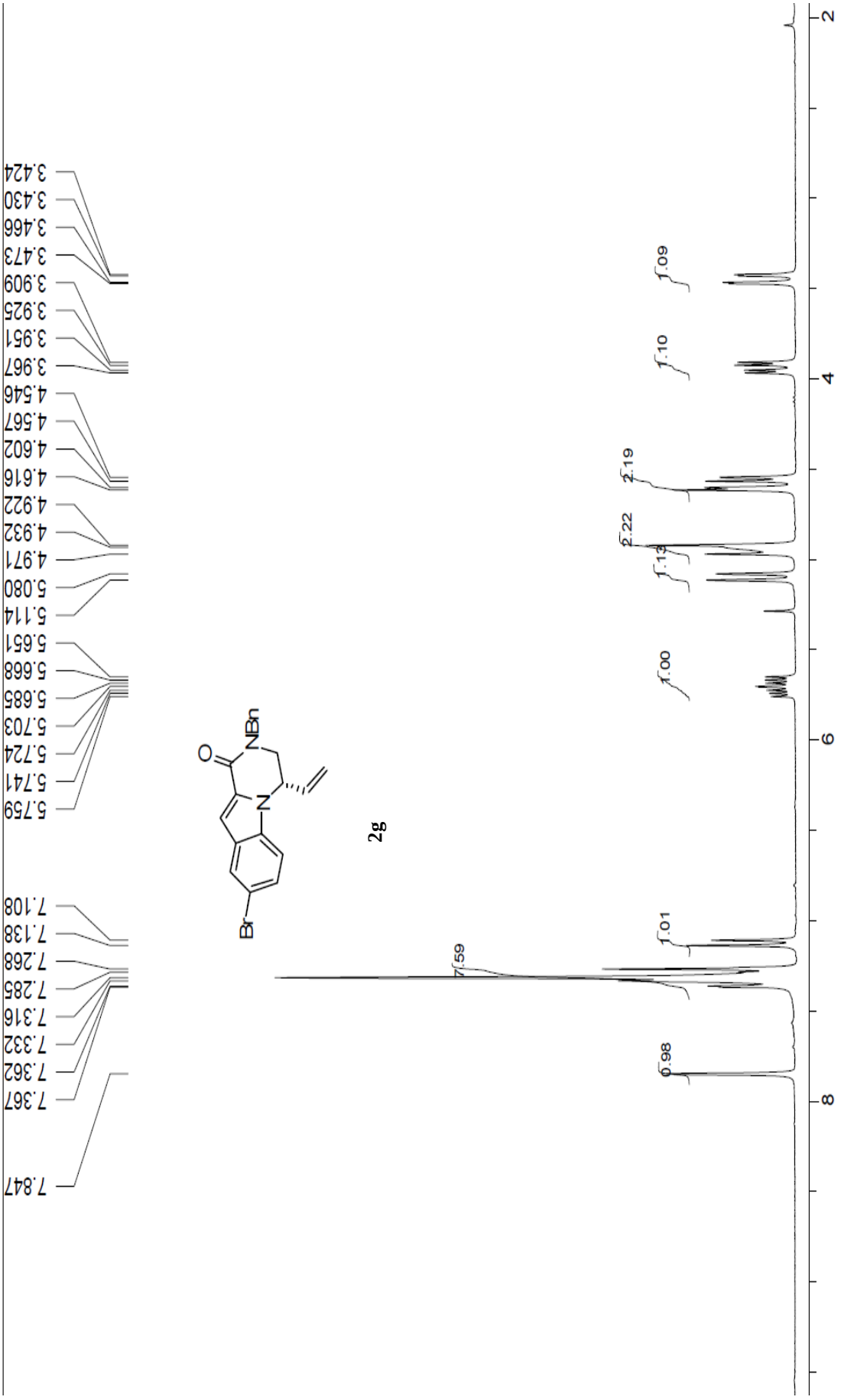

| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 17.935 | 8913385 | 50.18 | 265994 | 63.15 |
| 2 | 24.780 | 8849674 | 49.82 | 155236 | 36.85 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 17.924 | 19170978 | 95.46 | 570405 | 97.27 |
| 2 | 24.909 | 910924 | 4.54 | 15991 | 2.73 |




**2f**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4.616
4.922
4.932
4.971
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5.651
5.668
5.685
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7.138
7.268
7.285
7.316
7.332
7.362
7.367
7.847
O
NBn
N
Br
2g
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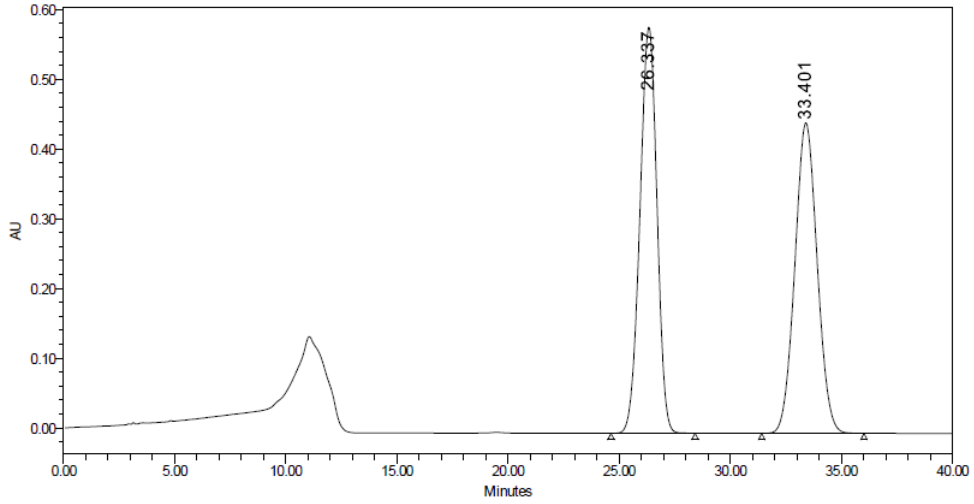
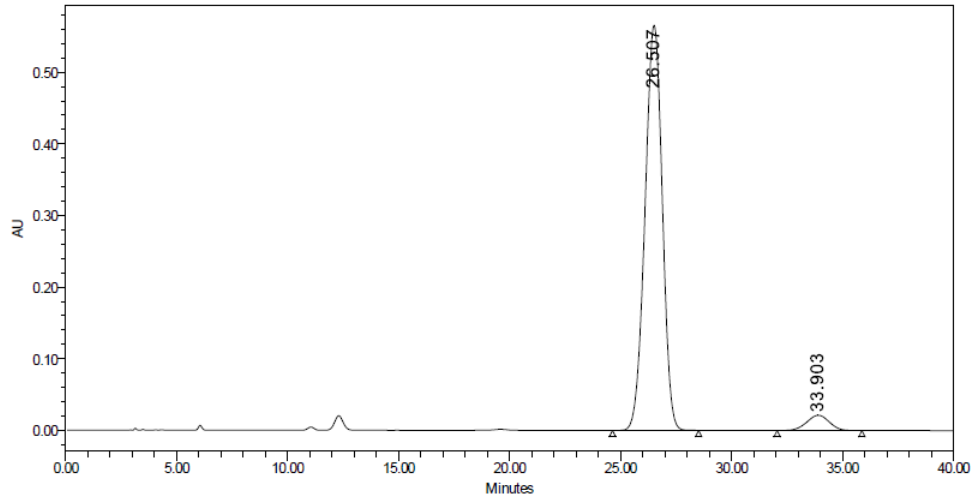
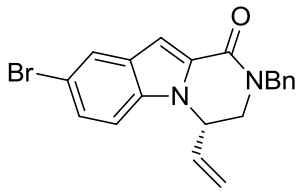
0.98
1.00
2.22
1.13
2.19
1.10
1.09
8
6
4
2



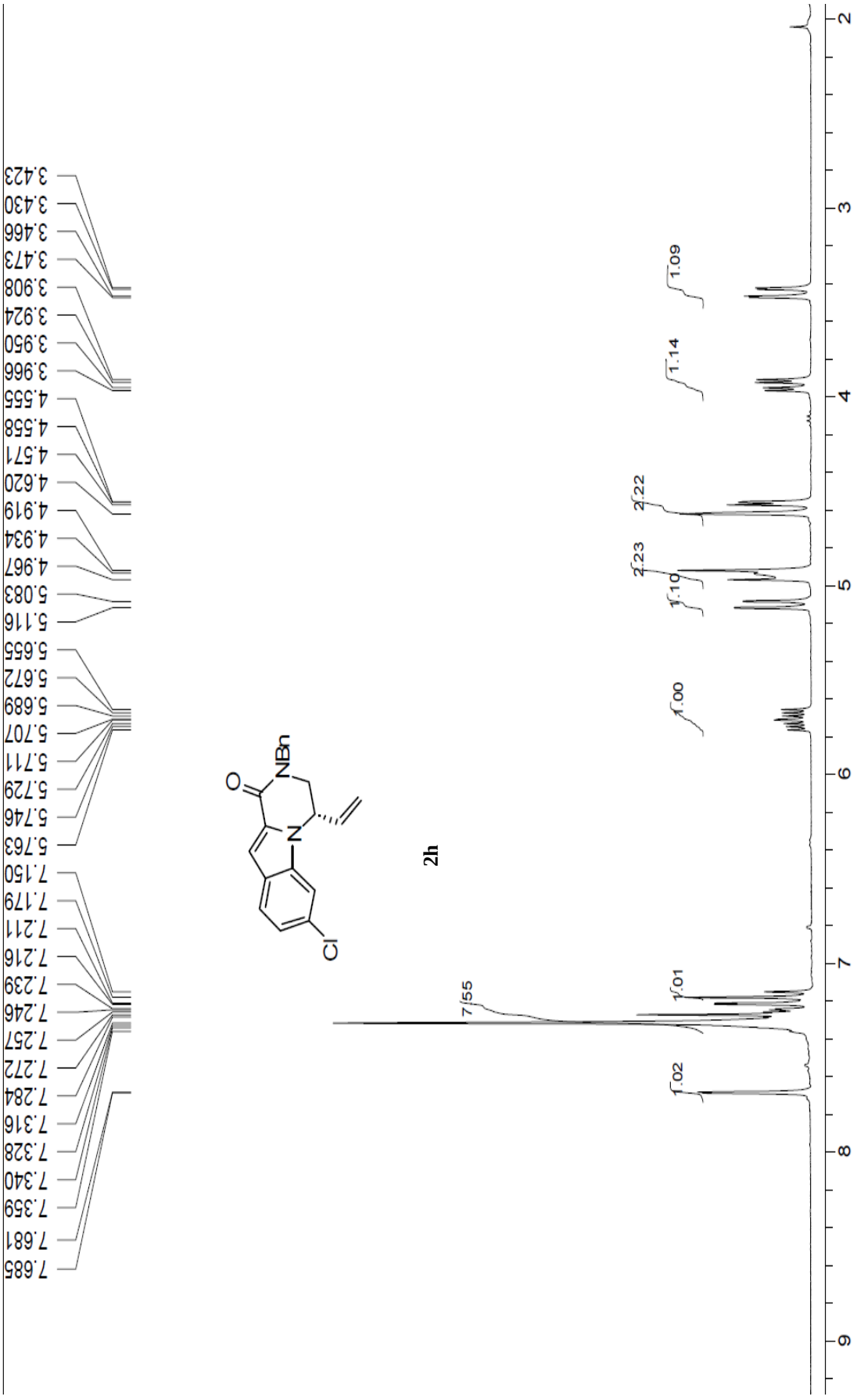

| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 26.337 | 31081743 | 49.97 | 582419 | 56.67 |
| 2 | 33.401 | 31119685 | 50.03 | 445352 | 43.33 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 26.507 | 30690204 | 95.32 | 565866 | 96.37 |
| 2 | 33.903 | 1506001 | 4.68 | 21336 | 3.63 |




**2g**


7.685
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7.359
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7.239
7.216
7.211
7.179
7.150
5.763
5.746
5.729
5.711
5.707
5.689
5.672
5.655
5.116
5.083
4.967
4.934
4.919
4.620
4.571
4.558
4.555
3.966
3.950
3.924
3.908
3.473
3.466
3.430
3.423
O
NBn
N
Cl
2h
7.55
1.01
1.02
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1.10
2.23
2.22
1.14
1.09
9
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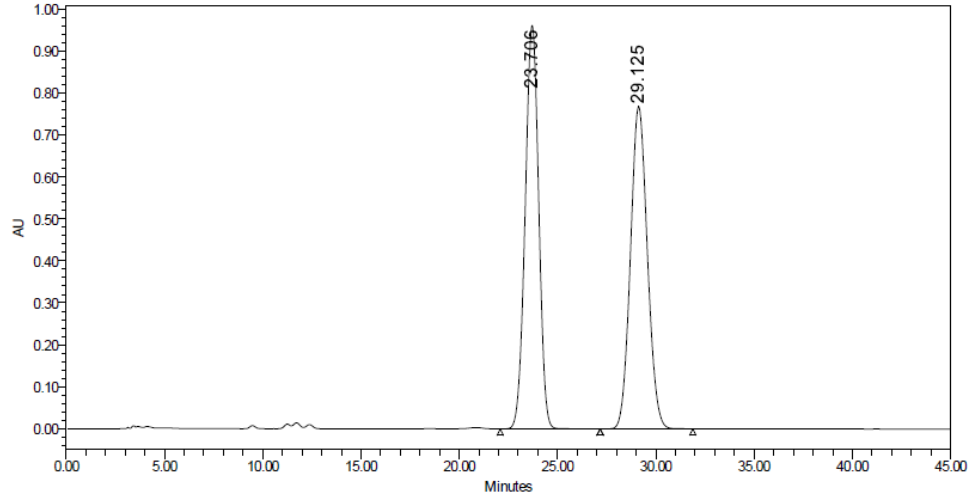
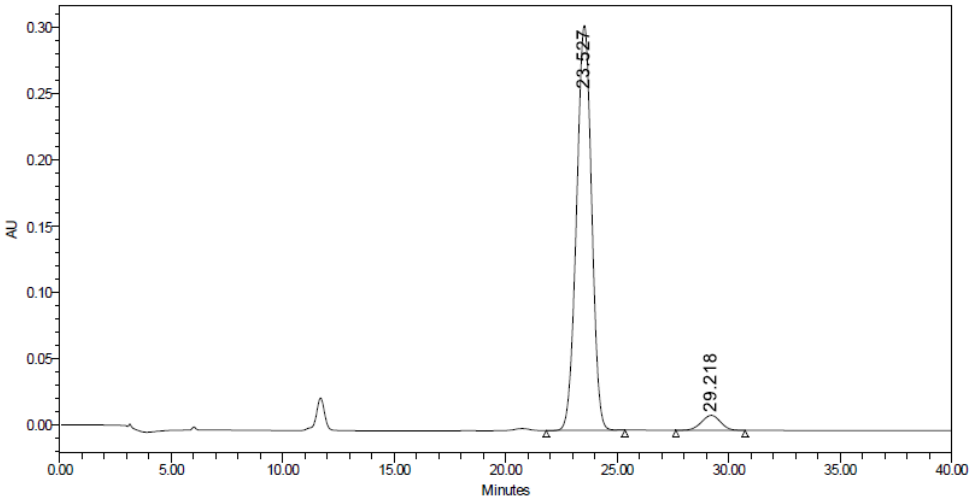
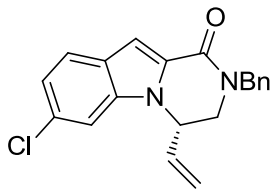
5
4
3
2



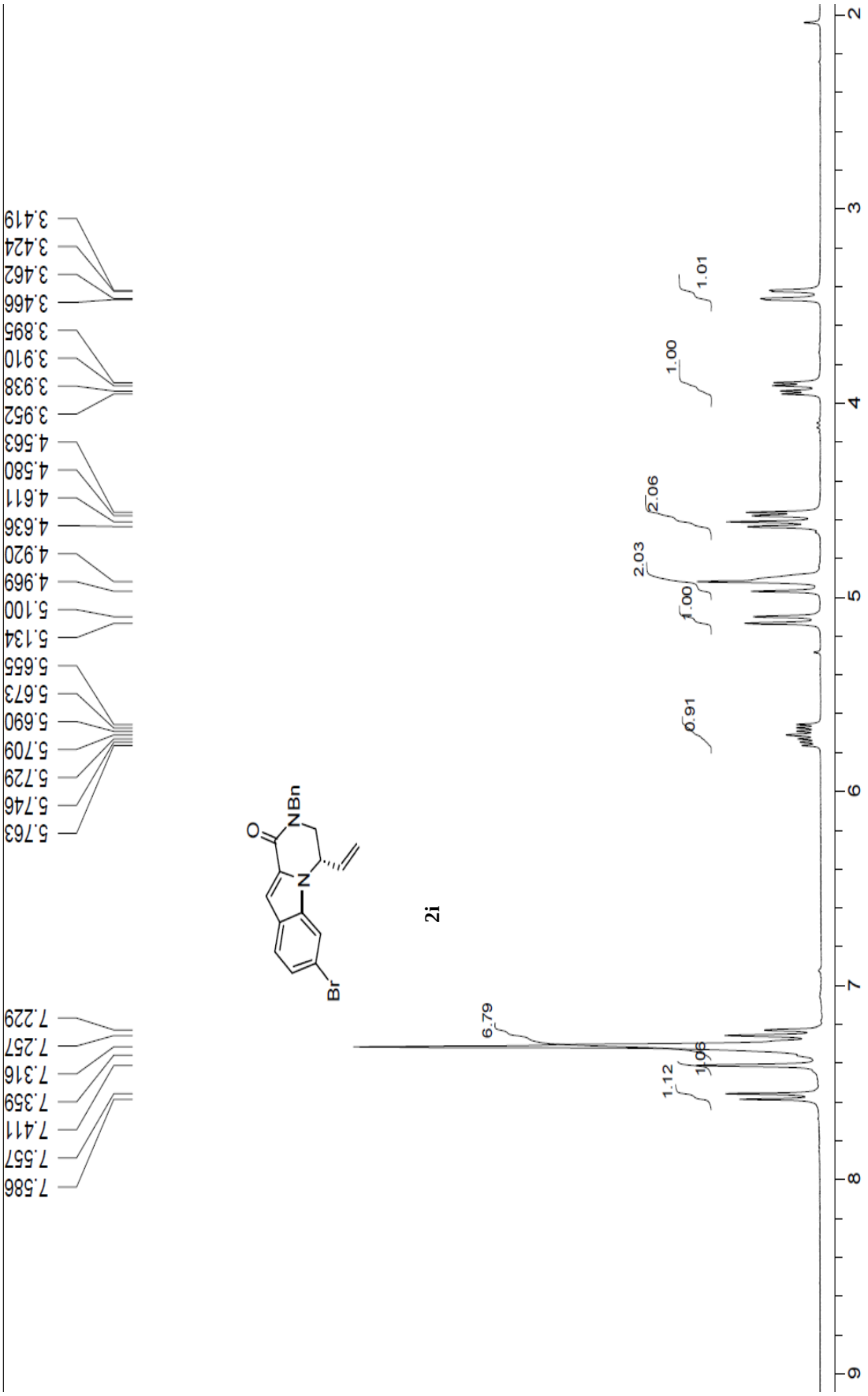

| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 23.706 | 45968855 | 49.97 | 960645 | 55.59 |
| 2 | 29.125 | 46016363 | 50.03 | 767366 | 44.41 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 23.527 | 14361677 | 95.56 | 305552 | 96.45 |
| 2 | 29.218 | 666771 | 4.44 | 11254 | 3.55 |




**2h**


7.586
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5.655
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4.611
4.580
4.563
3.952
3.938
3.910
3.895
3.466
3.462
3.424
3.419
O
NBn
N
Br
2i
6.79
1.12
1.06
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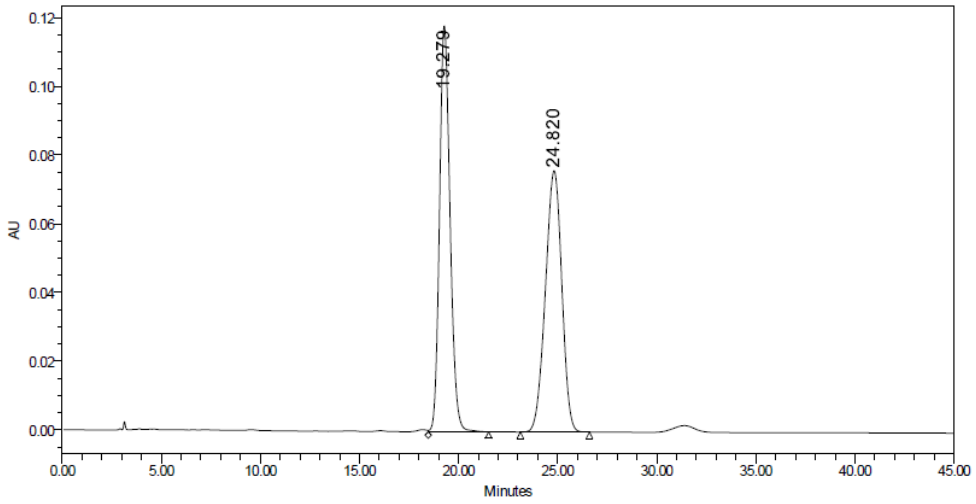
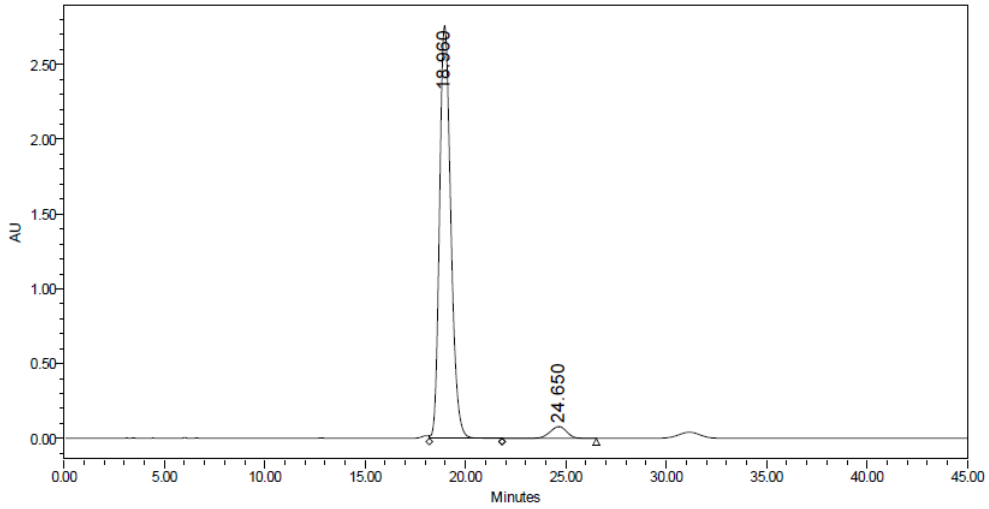
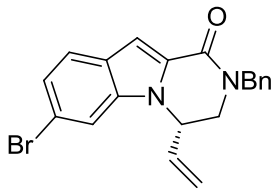
1.00
2.03
2.06
1.00
1.01
9
8
7
6
5
4
3
2



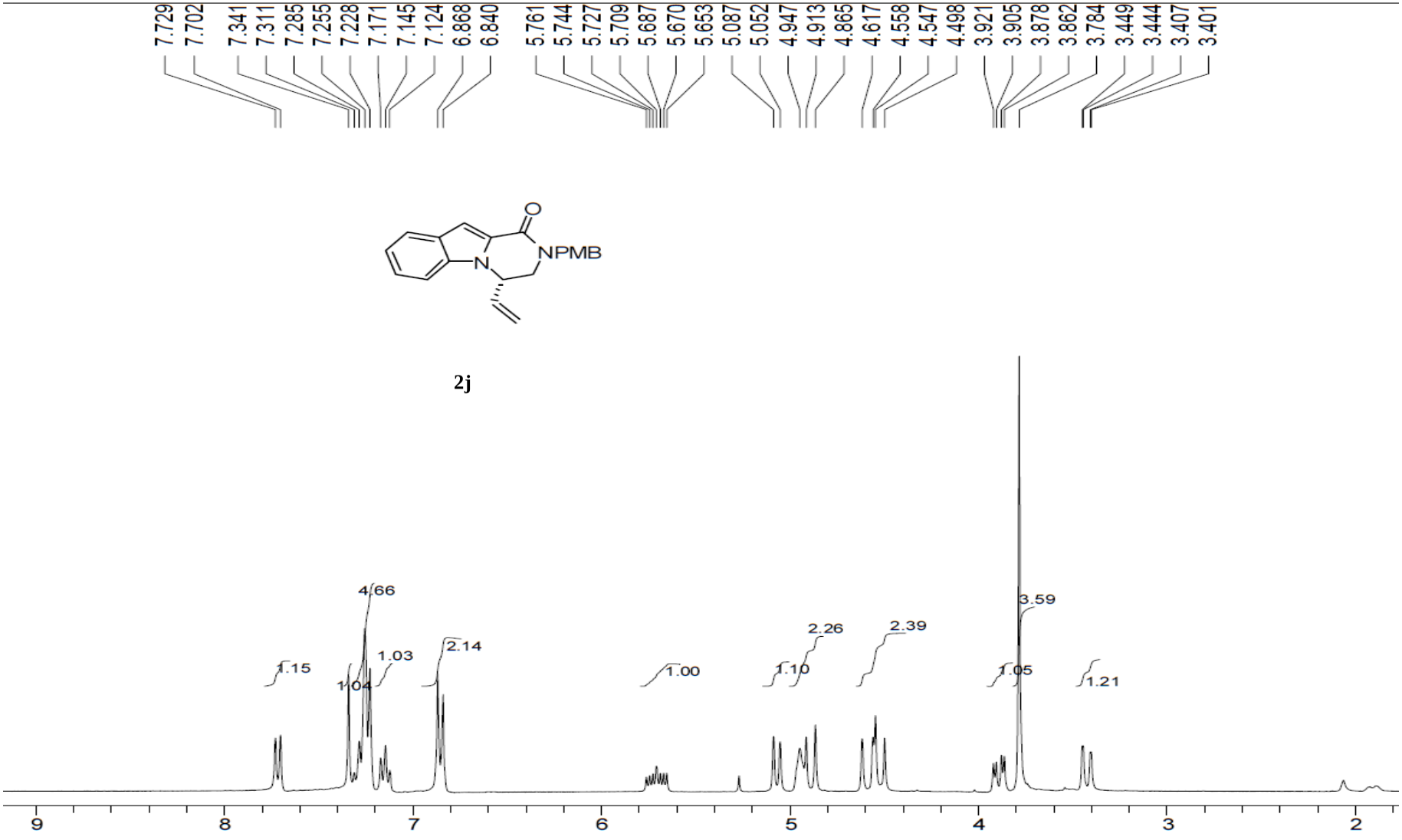

| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 19.279 | 4358724 | 49.90 | 118132 | 60.83 |
| 2 | 24.820 | 4375694 | 50.10 | 76061 | 39.17 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 18.960 | 107385909 | 95.95 | 2757890 | 97.22 |
| 2 | 24.650 | 4535875 | 4.05 | 78808 | 2.78 |




**2i**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7.171
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5.727
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5.670
5.653
5.087
5.052
4.947
4.913
4.865
4.617
4.558
4.547
4.498
3.921
3.905
3.878
3.862
3.784
3.449
3.444
3.407
3.401
O
NPMB
N
4.66
1.15
1.04
1.03
2.14
1.00
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3.59
1.05
1.21
9
8
7
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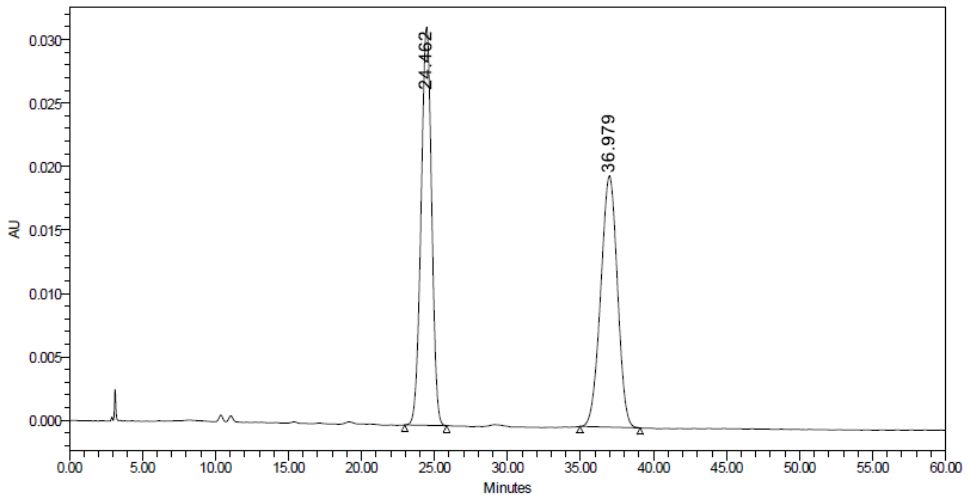
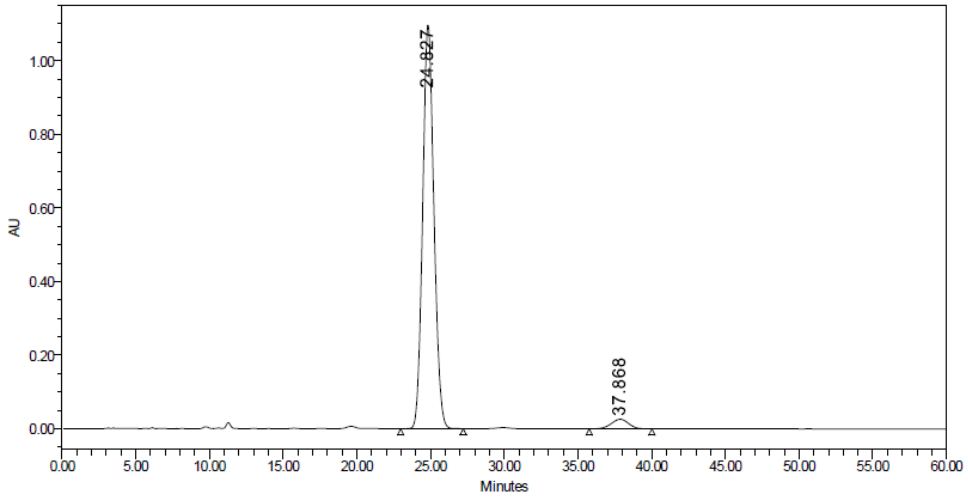
5
4
3
2

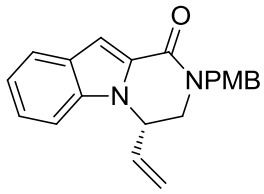
**2j**



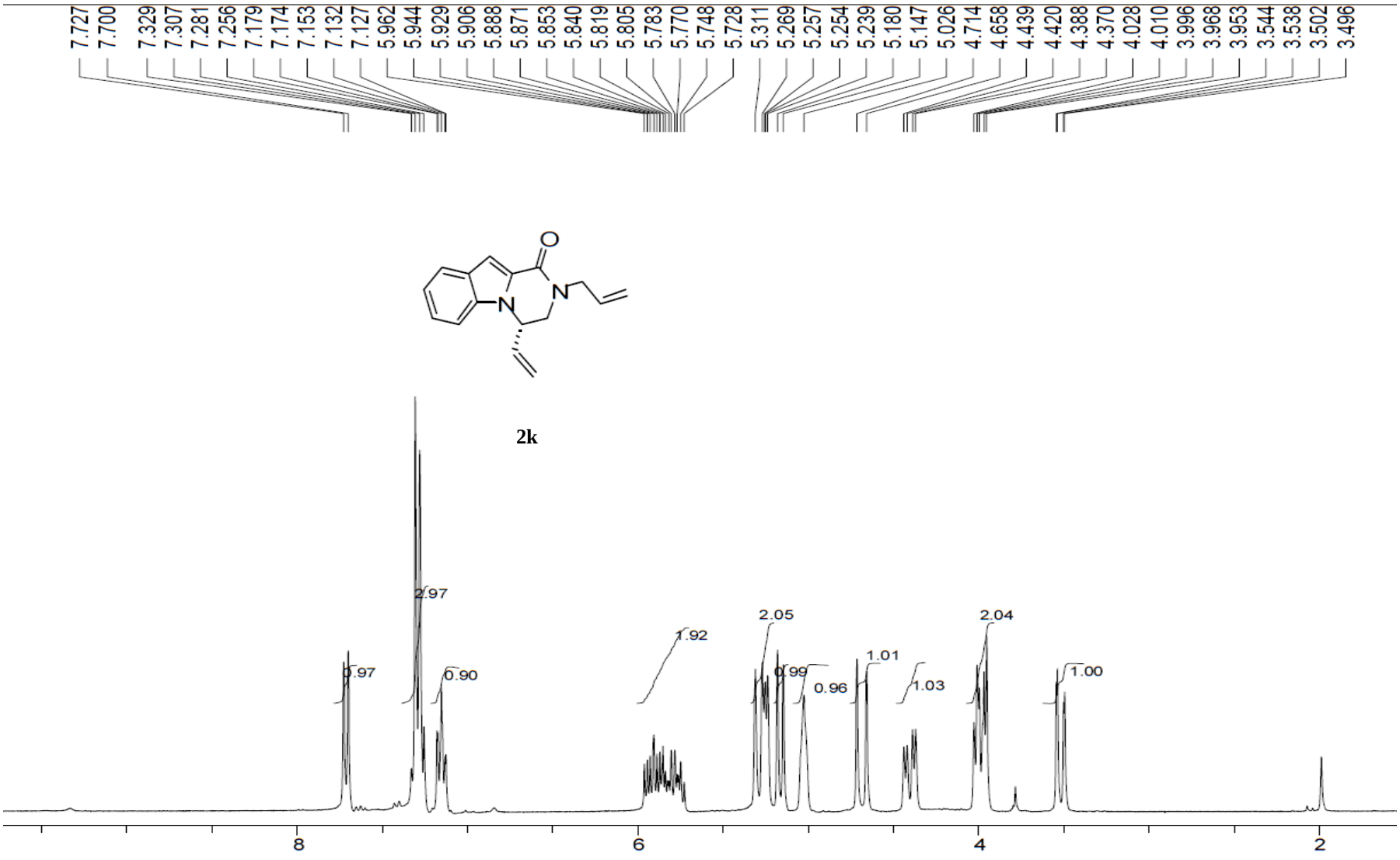

| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 24.462 | 1578087 | 50.10 | 31374 | 61.34 |
| 2 | 36.979 | 1571860 | 49.90 | 19774 | 38.66 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 24.827 | 58102921 | 96.48 | 1096620 | 97.68 |
| 2 | 37.868 | 2120020 | 3.52 | 26101 | 2.32 |




**2j**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7.174
7.153
7.132
7.127
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5.944
5.929
5.906
5.888
5.871
5.853
5.840
5.819
5.805
5.783
5.770
5.748
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5.311
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5.257
5.254
5.239
5.180
5.147
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4.370
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3.538
3.502
3.496
O
N
N
2k
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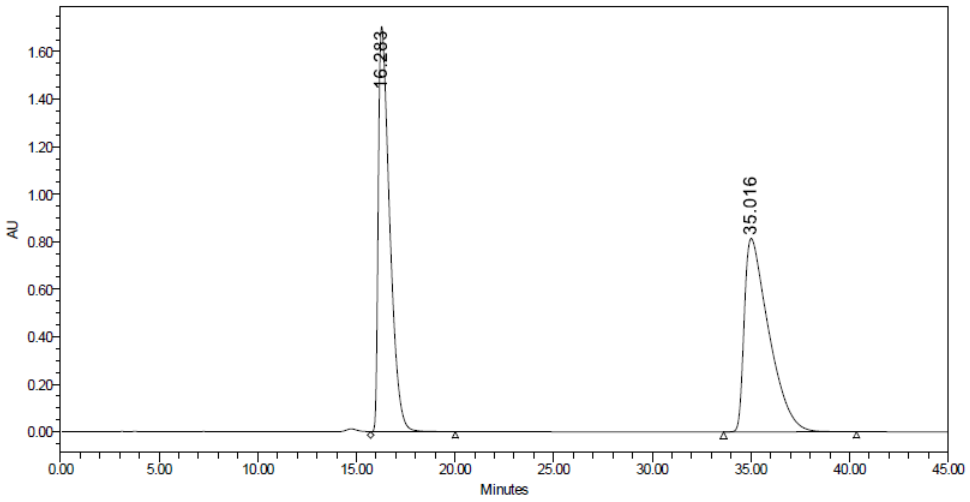
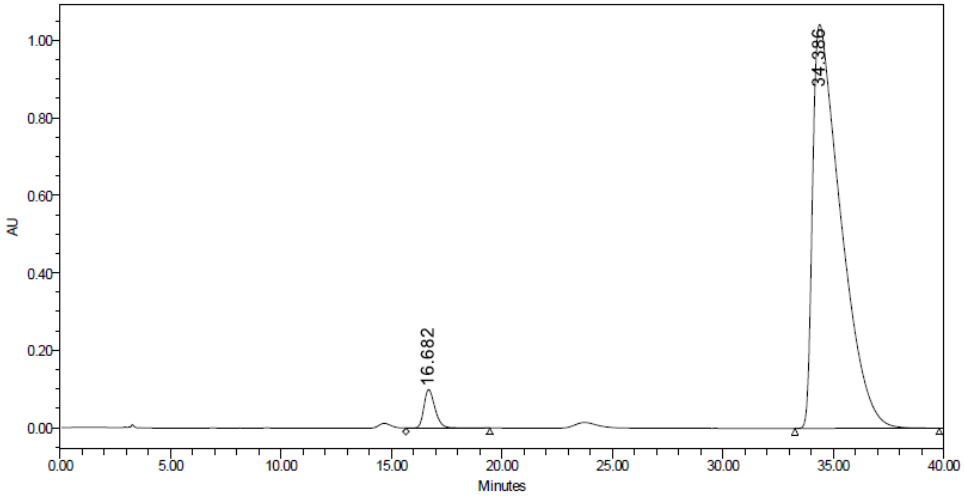
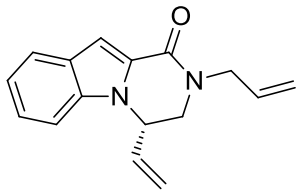
1.03
2.04
1.00
8
6
4
2



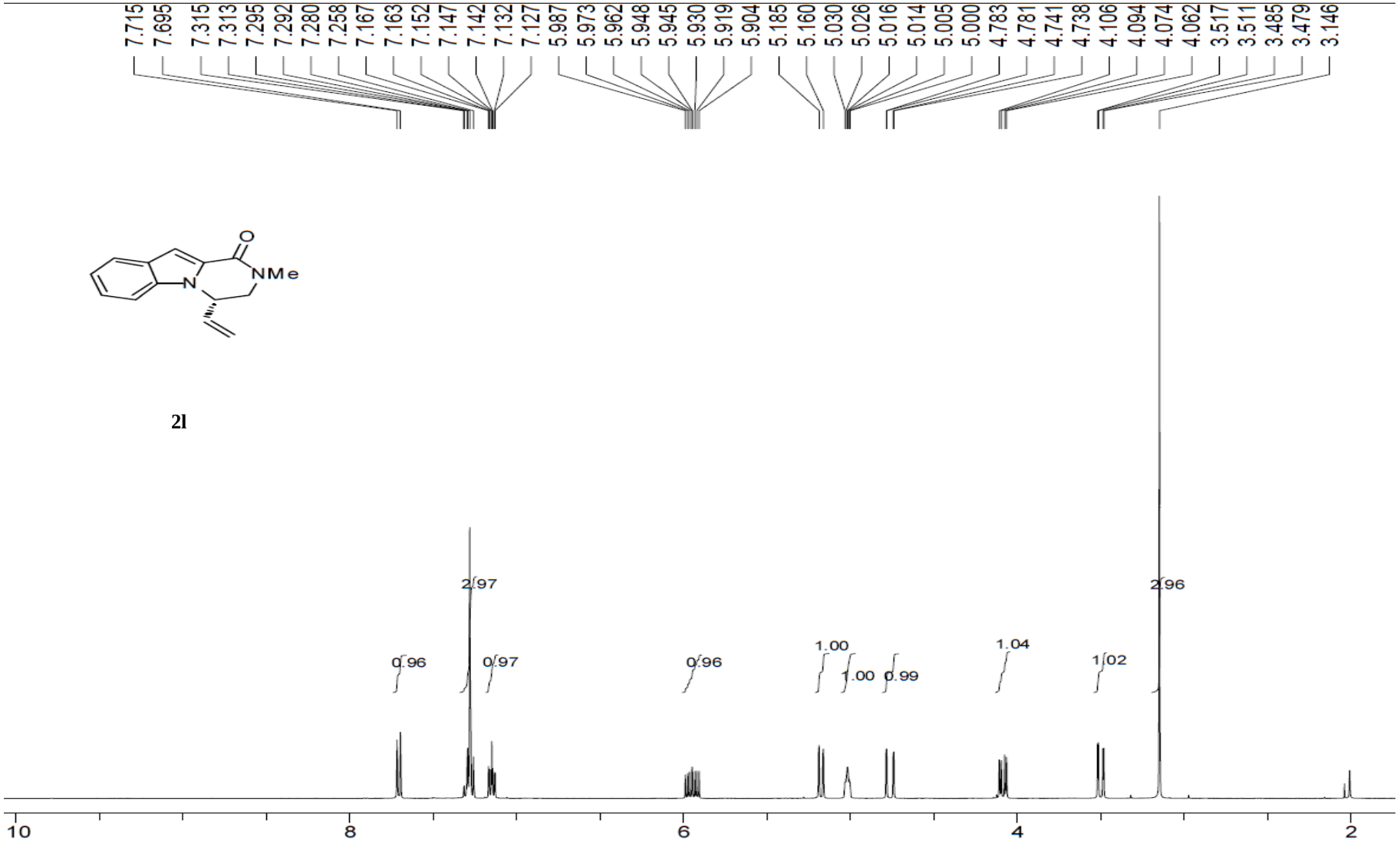

| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 16.283 | 68258544 | 49.26 | 1705396 | 67.71 |
| 2 | 35.016 | 70310043 | 50.74 | 813352 | 32.29 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 16.682 | 3549435 | 3.70 | 99905 | 8.74 |
| 2 | 34.386 | 92480309 | 96.30 | 1042807 | 91.26 |




**2k**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7.132
7.127
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5.948
5.945
5.930
5.919
5.904
5.185
5.160
5.030
5.026
5.016
5.014
5.005
5.000
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4.781
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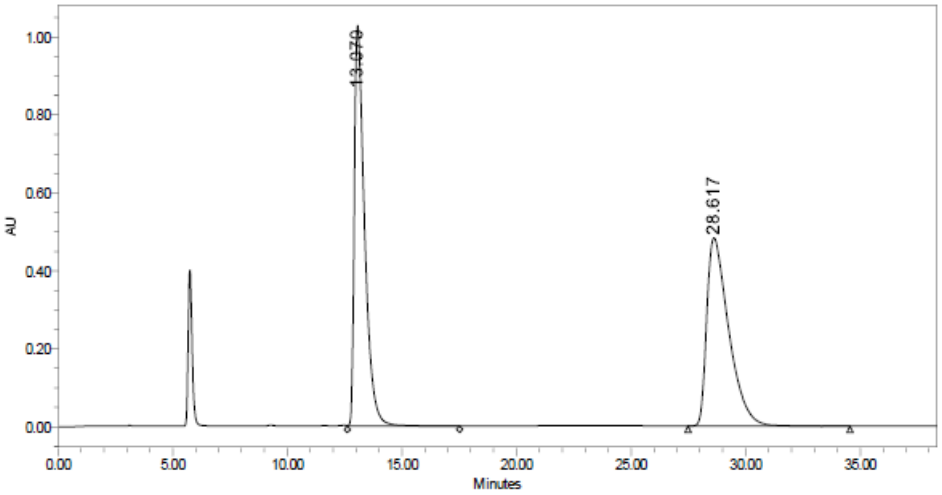
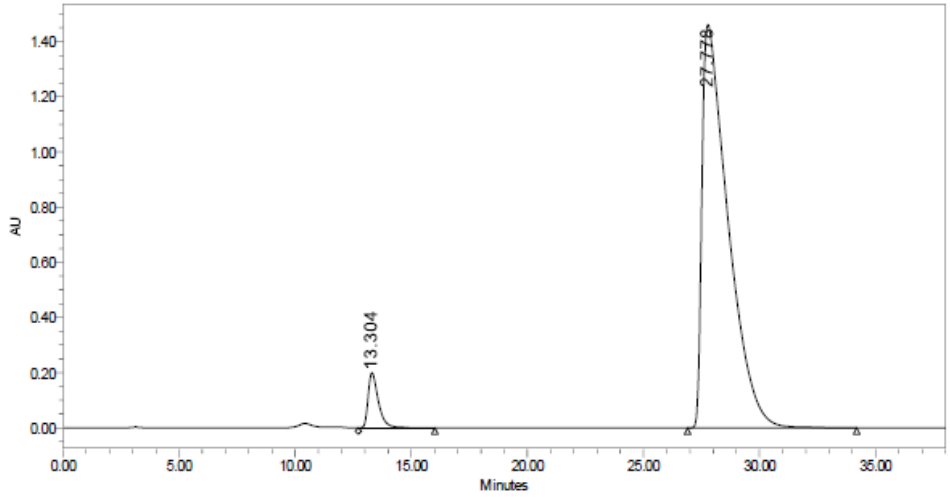
2

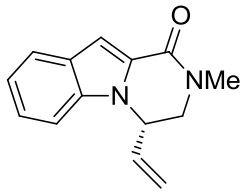
**2l**




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 13.070 | 31891952 | 49.81 | 1028007 | 68.06 |
| 2 | 28.617 | 32140362 | 50.19 | 482503 | 31.94 |




| | RT (min) | Area (μV*sec) | % Area | Height (μV) | % Height |
|---|---|---|---|---|---|
| 1 | 13.304 | 6087754 | 5.08 | 199463 | 12.01 |
| 2 | 27.778 | 11381110( | 94.92 | 1460993 | 87.99 |




**2l**

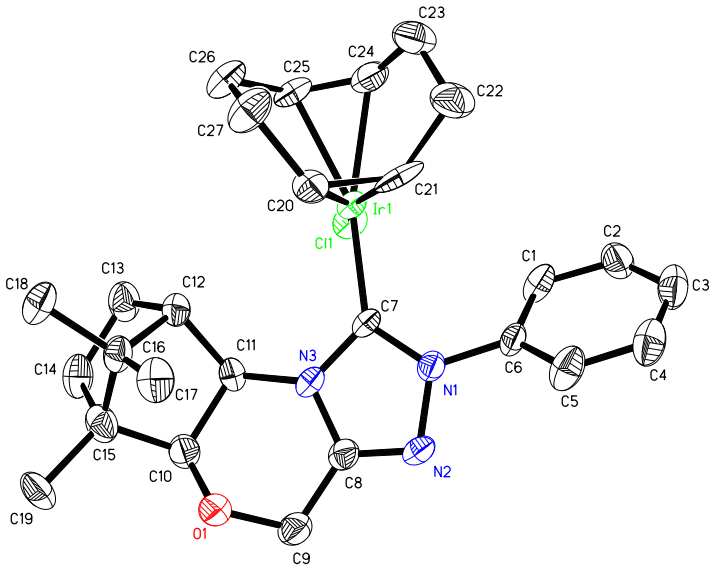



Table 1. Crystal data and structure refinement for **C1**.

| | | |
|---|---|---|
| Identification code | cd211346 | |
| Empirical formula | C27 H35 Cl Ir N3 O | |
| Formula weight | 645.23 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | Triclinic, P1 | |
| Unit cell dimensions | a = 9.9910(8) Å | alpha = 114.5730(10) deg. |
| | b = 11.2165(9) Å | beta = 101.430(2) deg. |
| | c = 12.8912(10) Å | gamma = 91.1840(10) deg. |
| Volume | 1279.11(18) Å^3 | |
| Z, Calculated density | 2, 1.675 Mg/m^3 | |
| Absorption coefficient | 5.348 mm^-1 | |
| F(000) | 640 | |
| Crystal size | 0.203 x 0.127 x 0.085 mm | |
| Theta range for data collection | 1.78 to 26.00 deg. | |

| | |
|---|---|
| Limiting indices | -12<=h<=12, -13<=k<=13, -11<=l<=15 |
| Reflections collected / unique | 6959 / 5874 [R(int) = 0.0203] |
| Completeness to theta = 26.00 | 97.9 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 1.00000 and 0.52252 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 5874 / 3 / 601 |
| Goodness-of-fit on F^2 | 1.005 |
| Final R indices [I>2sigma(I)] | R1 = 0.0266, wR2 = 0.0635 |
| R indices (all data) | R1 = 0.0289, wR2 = 0.0644 |
| Absolute structure parameter | 0.015(8) |
| Largest diff. peak and hole | 1.247 and -0.711 e. Å^-3 |

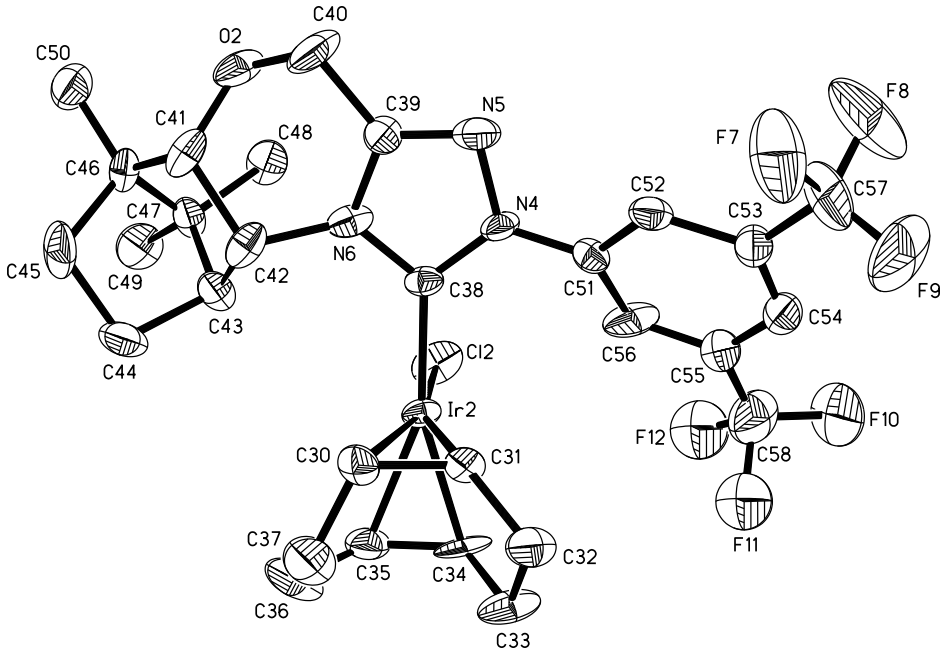



Table 2. Crystal data and structure refinement for **C2**.

| | |
|---|---|
| Identification code | cd201144 |

| | |
|---|---|
| Empirical formula | C58 H66 Cl2 F12 Ir2 N6 O2 |
| Formula weight | 1562.47 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, C2 |
| Unit cell dimensions | a = 33.024(3) Å alpha = 90 deg.<br>b = 7.1824(7) Å beta = 93.428(2) deg.<br>c = 25.055(3) Å gamma = 90 deg. |
| Volume | 5932.1(10) Å^3 |
| Z, Calculated density | 4, 1.749 Mg/m^3 |
| Absorption coefficient | 4.657 mm^-1 |
| F(000) | 3072 |
| Crystal size | 0.312 x 0.061 x 0.045 mm |
| Theta range for data collection | 1.52 to 25.50 deg. |
| Limiting indices | -40<=h<=34, -8<=k<=8, -30<=l<=27 |
| Reflections collected / unique | 15816 / 10408 [R(int) = 0.0429] |
| Completeness to theta = 25.50 | 99.5 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 1.00000 and 0.82246 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 10408 / 5 / 770 |
| Goodness-of-fit on F^2 | 1.022 |
| Final R indices [I>2sigma(I)] | R1 = 0.0505, wR2 = 0.1111 |
| R indices (all data) | R1 = 0.0622, wR2 = 0.1366 |
| Absolute structure parameter | -0.001(13) |
| Largest diff. peak and hole | 1.281 and -0.889 e. Å^-3 |

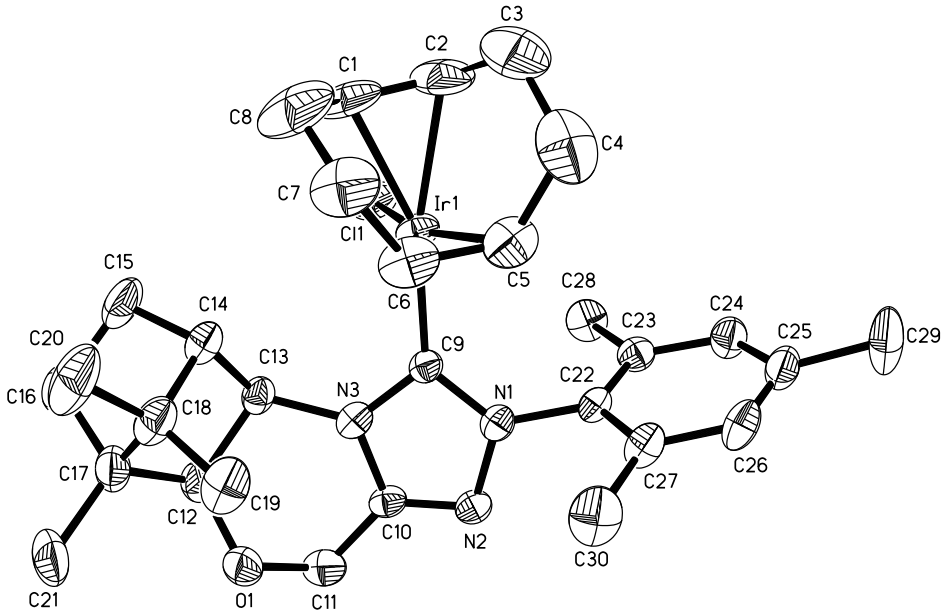



Table 3. Crystal data and structure refinement for **C3**.

| | |
|---|---|
| Identification code | cd201254 |
| Empirical formula | C30 H41 Cl Ir N3 O |
| Formula weight | 687.31 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Orthorhombic, P2(1)2(1)2(1) |
| Unit cell dimensions | a = 9.7893(8) Å alpha = 90 deg.<br>b = 12.0920(10) Å beta = 90 deg.<br>c = 24.571(2) Å gamma = 90 deg. |
| Volume | 2908.5(4) Å ^3 |
| Z, Calculated density | 4, 1.570 Mg/m^3 |
| Absorption coefficient | 4.709 mm^-1 |
| F(000) | 1376 |
| Crystal size | 0.341 x 0.307 x 0.231 mm |
| Theta range for data collection | 1.66 to 27.00 deg. |
| Limiting indices | -12<=h<=11, -14<=k<=15, -31<=l<=16 |
| Reflections collected / unique | 17244 / 6337 [R(int) = 0.0595] |
| Completeness to theta = 27.00 | 99.9 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 1.0000 and 0.3330 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 6337 / 0 / 331 |
| Goodness-of-fit on F^2 | 0.942 |

| | |
|---|---|
| Final R indices [I>2sigma(I)] | R1 = 0.0456, wR2 = 0.0769 |
| R indices (all data) | R1 = 0.0609, wR2 = 0.0809 |
| Absolute structure parameter | 0.000(9) |
| Largest diff. peak and hole | 1.841 and -1.162 e. Å ^-3 |