An efficient approach to *H*-pyrazolo[5,1-*a*]isoquinolin-2-amines via a silver(I)-catalyzed three-component reaction of 2-alkynylbenzaldehyde, sulfonohydrazide, and nitrile

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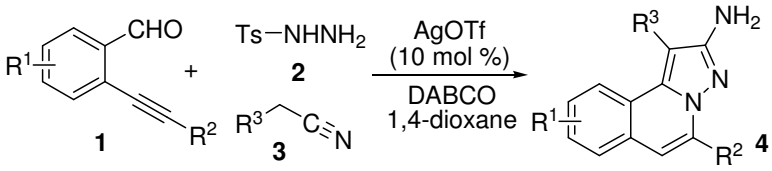
Supporting Information

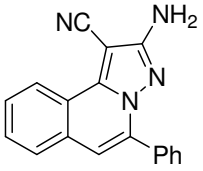
General Experimental Method:

All reactions were performed in test tubes in the air. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated at ~20 Torr (house vacuum) at 25–35 °C. Solvents were re-distilled prior to use in the reactions. Other commercial reagents were used as received. 2-Alkynylbenzaldehyde **1** was synthesized via Sonogashira coupling according to the literature report. Chemical shifts (δ) are reported in parts per million (ppm) relative solvent signals.

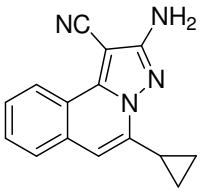
Experimental procedure for the synthesis of H-pyrazolo[5,1-a]isoquinolin-2-amines via AgOTf-catalyzed three-component reaction of 2-alkynylbenzaldehyde, sulfonohydrazide, and nitrile.



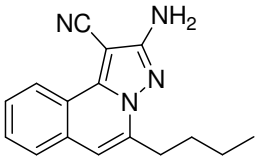
A mixture of 2-alkynylbenzaldehyde **1** (0.3 mmol, 1.0 equiv), AgOTf (7.7 mg, 10 mol %), and sulfonohydrazide **2** (0.3 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL) was stirred at 70 °C vigorously for 1 hour. Then nitrile **3** (0.6 mmol, 2.0 equiv) and DABCO (0.6 mmol, 2.0 equiv) were added. After completion of the reaction as indicated by TLC, the reaction mixture was quenched with water (5.0 mL) and diluted with ethyl acetate (5.0 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the desired product **4**.



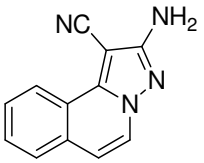
2-Amino-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4a**). ^{1}H NMR (400 MHz, DMSO-d_6): 6.32 (s, 2H), 7.29 (s, 1H), 7.47-7.53 (m, 3H), 7.65-7.70 (m, 2H), 7.77-7.79 (m, 2H), 7.91-7.93 (m, 1H), 8.46-8.48 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 69.7, 112.6, 115.9, 120.7, 122.1, 127.7, 127.9, 128.1, 129.2, 129.4, 129.5, 130.1, 133.0, 137.2, 140.4, 159.2; HRMS calcd for $C_{18}H_{12}N_4$ (M^++H): 285.1140, found: 285.1147.



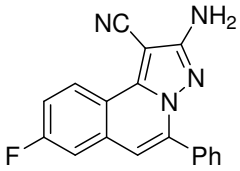
2-Amino-5-cyclopropyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4b**). ^{1}H NMR (400 MHz, DMSO-d_6): 0.90-0.91 (m, 2H), 1.07-1.09 (m, 2H), 2.45-2.50 (m, 1H), 6.34 (s, 2H), 6.93 (s, 1H), 7.59-7.61 (m, 2H), 7.77-7.78 (m, 1H), 8.39-8.40 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 7.4, 11.1, 69.4, 106.5, 116.0, 119.8, 122.0, 127.0, 127.1, 129.2, 130.2, 139.7, 140.2, 159.3; HRMS calcd for $C_{15}H_{12}N_4$ (M^++Na): 271.0960, found: 271.0977.



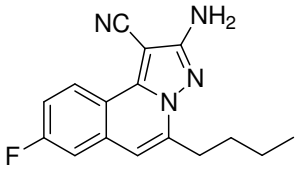
2-Amino-5-butyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4c**). ^{1}H NMR (400 MHz, DMSO-d_6): 0.89 (t, J = 7.2 Hz, 3H), 1.33-1.38 (m, 2H), 1.67-1.71 (m, 2H), 2.91-2.94 (m, 2H), 6.31 (s, 2H), 7.03 (s, 1H), 7.61-7.62 (m, 2H), 7.79-7.80 (m, 1H), 8.38-8.40 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.7, 21.9, 28.3, 30.1, 69.2, 109.7, 116.0, 120.1, 122.0, 127.0, 127.1, 129.3, 130.0, 138.5, 139.7, 159.2; HRMS calcd for $C_{16}H_{16}N_4$ (M^++H): 265.1453, found: 265.1464.



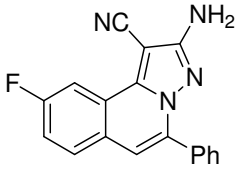
2-Amino*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4d**). ^{1}H NMR (400 MHz, DMSO-d_6): 6.29 (s, 2H), 7.24 (d, J = 6.4 Hz, 1H), 7.65-7.73 (m, 2H), 7.89-7.91 (m, 1H), 8.26 (d, J = 6.4 Hz, 1H), 8.40 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 69.0, 112.2, 115.9, 121.2, 122.2, 126.1, 127.7, 128.1, 129.4, 129.8, 139.3, 159.7; HRMS calcd for $C_{12}H_8N_4$ (M^++Na): 231.0647, found: 231.0660.



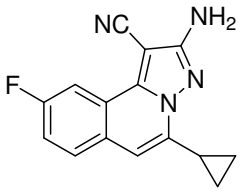
2-Amino-8-fluoro-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4e**). ^{1}H NMR (400 MHz, DMSO-d_6): 6.34 (s, 2H), 7.28 (s, 1H), 7.50-7.59 (m, 4H), 7.71-7.76 (m, 3H), 8.46 (dd, J = 8.4, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 69.7, 111.9, 112.1 (d, $^{2}J_{CF}$ = 22 Hz), 115.8, 116.9 (d, $^{2}J_{CF}$ = 24 Hz), 117.7, 125.1 (d, $^{3}J_{CF}$ = 10 Hz), 128.1, 129.4, 132.2 (d, $^{3}J_{CF}$ = 10 Hz), 132.7, 138.1, 140.2, 159.1, 161.9 (d, $^{1}J_{CF}$ = 246 Hz); HRMS calcd for $C_{18}H_{11}FN_4$ (M^++Na): 325.0865, found: 325.0861.



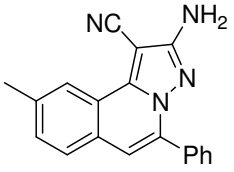
2-Amino-5-butyl-8-fluoro*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4f**). ^{1}H NMR (400 MHz, DMSO-d_6): 0.92 (t, J = 7.2 Hz, 3H), 1.34-1.43 (m, 2H), 1.69-1.72 (m, 2H), 2.92-2.96 (m, 2H), 6.35 (s, 2H), 7.07 (s, 1H), 7.51-7.55 (m, 1H), 7.65 (d, J = 9.6 Hz, 1H), 8.39-8.42 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.7, 21.9, 28.2, 30.1, 69.2, 109.0, 111.4 (d, $^{2}J_{CF}$ = 22 Hz), 115.8, 116.1 (d, $^{2}J_{CF}$ = 24 Hz), 117.0, 124.9 (d, $^{3}J_{CF}$ = 10 Hz), 132.2 (d, $^{3}J_{CF}$ = 10 Hz), 139.5, 139.6, 159.1, 161.9 (d, $^{1}J_{CF}$ = 246 Hz); HRMS calcd for $C_{16}H_{15}FN_4$ (M^++Na): 305.1178, found: 305.1189.



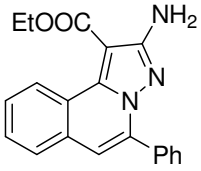
2-Amino-9-fluoro-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4g**). ^{1}H NMR (400 MHz, DMSO-d_6): 6.34 (s, 2H), 7.30 (s, 1H), 7.49-7.55 (m, 4H), 7.75-7.76 (m, 2H), 7.98-8.00 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 69.9, 106.6 (d, $^{2}J_{CF}$ = 24 Hz), 112.2, 115.6, 118.5 (d, $^{2}J_{CF}$ = 24 Hz), 121.5 (d, $^{3}J_{CF}$ = 10 Hz), 127.0, 128.1, 129.2, 129.4, 130.8 (d, $^{3}J_{CF}$ = 9 Hz), 132.8, 136.6, 139.5, 159.1, 160.6 (d, $^{1}J_{CF}$ = 245 Hz); HRMS calcd for $C_{18}H_{11}FN_4$ (M^++H): 303.1046, found: 303.1057.



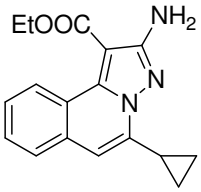
2-Amino-5-cyclopropyl-9-fluoro*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4h**). ^{1}H NMR (400 MHz, DMSO-d_6): 0.90-0.91 (m, 2H), 1.08-1.10 (m, 2H), 2.45-2.50 (m, 1H), 6.42 (s, 2H), 7.02 (s, 1H), 7.53-7.57 (m, 1H), 7.88-7.91 (m, 1H), 7.98 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 7.4, 11.1, 69.5, 106.3, 106.5(d, $^{2}J_{CF}$ = 24 Hz), 115.8, 118.4(d, $^{2}J_{CF}$ = 24 Hz), 120.6 (d, $^{3}J_{CF}$ = 10 Hz), 127.3, 130.2 (d, $^{3}J_{CF}$ = 9 Hz), 138.9, 139.8, 159.3, 160.1 (d, $^{1}J_{CF}$ = 243 Hz); HRMS calcd for $C_{15}H_{11}FN_4$ (M^++Na): 289.0865, found: 289.0879.



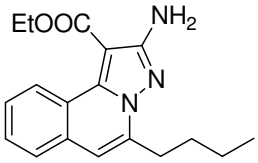
2-Amino-9-methyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carbonitrile (**4i**). ^{1}H NMR (400 MHz, DMSO-d_6): 2.47 (s, 3H), 6.26 (s, 2H), 7.20 (s, 1H), 7.44-7.49 (m, 4H), 7.75-7.76 (m, 3H), 8.18 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.5, 69.4, 112.5, 116.0, 120.7, 121.2, 127.5, 127.9, 128.1, 129.1, 129.4, 131.0, 133.0, 136.3, 137.4, 139.9, 159.0; HRMS calcd for $C_{19}H_{14}N_4$ (M^++H): 299.1297, found: 299.1321.



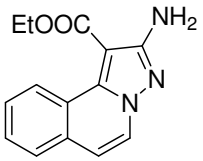
Ethyl 2-amino-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4j**). ^{1}H NMR (400 MHz, $CDCl_3$): 1.48 (t, *J* = 7.2 Hz, 3H), 4.44-4.50 (m, 2H), 5.16 (s, 2H), 7.07 (s, 1H), 7.48-7.51 (m, 3H), 7.56-7.59 (m, 2H), 7.69-7.71 (m, 1H), 7.77-7.79 (m, 2H), 9.67-9.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 60.6, 93.4, 114.3, 123.2, 127.1, 127.2, 127.7, 128.5, 129.2, 129.6, 129.9, 131.5, 134.1, 137.8, 140.5, 158.5, 164.9; HRMS calcd for $C_{20}H_{17}N_3O_2$ (M^++H): 332.1399, found: 332.1396.



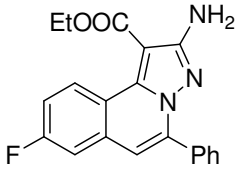
Ethyl 2-amino-5-cyclopropyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4k**). ^{1}H NMR (400 MHz, $CDCl_3$): 0.86-0.90 (m, 2H), 1.14-1.19 (m, 2H), 1.48 (t, *J* = 7.2 Hz, 3H), 2.56-2.63 (m, 1H), 4.44-4.50 (m, 2H), 5.29 (s, 2H), 6.17 (s, 1H), 7.50-7.62 (m, 3H), 9.62-9.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.3, 11.5, 14.5, 60.2, 92.9, 108.0, 122.1, 126.0, 126.2, 127.2, 128.6, 131.2, 139.9, 158.3, 164.6; HRMS calcd for $C_{17}H_{17}N_3O_2$ (M^++H): 296.1399, found: 296.1397.



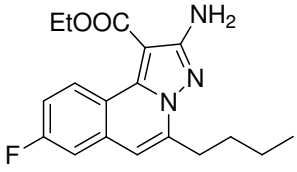
Ethyl 2-amino-5-butyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4l**). ^{1}H NMR (400 MHz, $CDCl_3$): 0.99 (t, *J* = 7.2 Hz, 3H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.43-1.53 (m, 2H), 1.78-1.85 (m, 2H), 3.03-3.07 (m, 2H), 4.44-4.49 (m, 2H), 5.22 (s, 2H), 6.89 (s, 1H), 7.50-7.57 (m, 2H), 7.63-7.65 (m, 1H), 9.62-9.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 14.9, 22.8, 29.2, 31.2, 60.5, 93.1, 111.2, 122.7, 126.3, 126.6, 127.6, 128.9, 131.5, 139.0, 140.0, 158.5, 165.0; HRMS calcd for $C_{18}H_{21}N_3O_2$ (M^++H): 312.1712, found: 312.1721.



Ethyl 2-amino*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4m**). ^{1}H NMR (400 MHz, $CDCl_3$): 1.48 (t, *J* = 7.2 Hz, 3H), 4.44-4.49 (m, 2H), 5.23 (s, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.56-7.61 (m, 2H), 7.67-7.70 (m, 1H), 8.01 (d, *J* = 7.2 Hz, 1H), 9.65-9.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 60.7, 93.2, 113.5, 123.9, 125.9, 127.3, 127.5, 128.0, 129.2, 131.3, 139.6, 159.2, 164.8; HRMS calcd for $C_{14}H_{13}N_3O_2$ (M^++H): 256.1086, found: 256.1101.

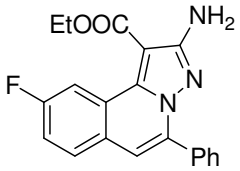


Ethyl 2-amino-8-fluoro-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4n**) ^{1}H NMR (400 MHz, DMSO-d_6): 1.37 (t, *J* = 6.8 Hz, 3H), 4.35-4.40 (m, 2H), 6.05 (s, 2H), 7.33 (s, 1H), 7.45-7.55 (m, 4H), 7.70-7.76 (m, 3H), 9.68-9.72 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.3, 59.9, 92.0, 111.4 (d, $^{2}J_{CF}$ = 20 Hz), 112.7, 115.5 (d, $^{2}J_{CF}$ = 24 Hz), 118.9, 128.1, 129.2, 129.5, 129.8 (d, $^{3}J_{CF}$ = 9 Hz), 133.0 (d, $^{3}J_{CF}$ = 10 Hz), 133.4, 137.9, 138.9, 158.3, 161.6 (d, $^{1}J_{CF}$ = 246 Hz), 163.9; HRMS calcd for $C_{20}H_{16}FN_3O_2$ (M^++H): 350.1305, found: 350.1321.

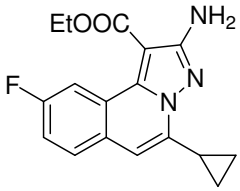


Ethyl 2-amino-5-butyl-8-fluoro*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4o**). ^{1}H NMR (400 MHz, $CDCl_3$): 0.99 (t, *J* = 7.2 Hz, 3H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.43-1.52 (m, 2H), 1.75-1.83 (m, 2H), 3.01-3.04 (m, 2H), 4.43-4.48 (m, 2H), 5.21 (s, 2H), 6.80 (s, 1H), 7.21-7.25 (m, 2H), 9.70-9.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.8, 22.8, 29.1, 31.1, 60.6, 93.0, 110.4, 110.7 (d, $^{2}J_{CF}$ = 22 Hz), 115.1 (d, $^{2}J_{CF}$ = 23 Hz), 119.4, 130.6 (d, $^{3}J_{CF}$ = 9 Hz), 133.5 (d, $^{3}J_{CF}$ = 9 Hz), 139.9, 140.0, 158.4, 162.6 (d, $^{1}J_{CF}$ = 248 Hz), 164.8; HRMS calcd for $C_{18}H_{20}FN_3O_2$ (M^++H): 330.1618, found:

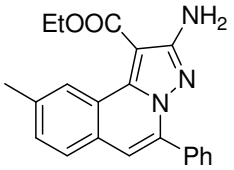
330.1592.



Ethyl 2-amino-9-fluoro-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4p**). ^{1}H NMR (400 MHz, DMSO-d_6): 1.38 (t, J = 6.8 Hz, 3H), 4.35-4.41 (m, 2H), 6.09 (s, 2H), 7.39 (s, 1H), 7.48-7.58 (m, 4H), 7.75-7.77 (m, 2H), 7.98 (t, J = 6.8 Hz, 1H), 9.45-9.48 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.2, 60.0, 92.1, 111.3 (d, $^{2}J_{CF}$ = 25 Hz), 113.0, 118.9 (d, $^{2}J_{CF}$ = 24 Hz), 119.0, 123.1, 127.7, 128.1, 129.0, 129.6, 130.0, 133.5, 136.4, 158.3, 160.2 (d, $^{1}J_{CF}$ = 232 Hz), 163.9; HRMS calcd for $C_{20}H_{16}FN_3O_2$ (M^++H): 350.1305, found: 350.1305.

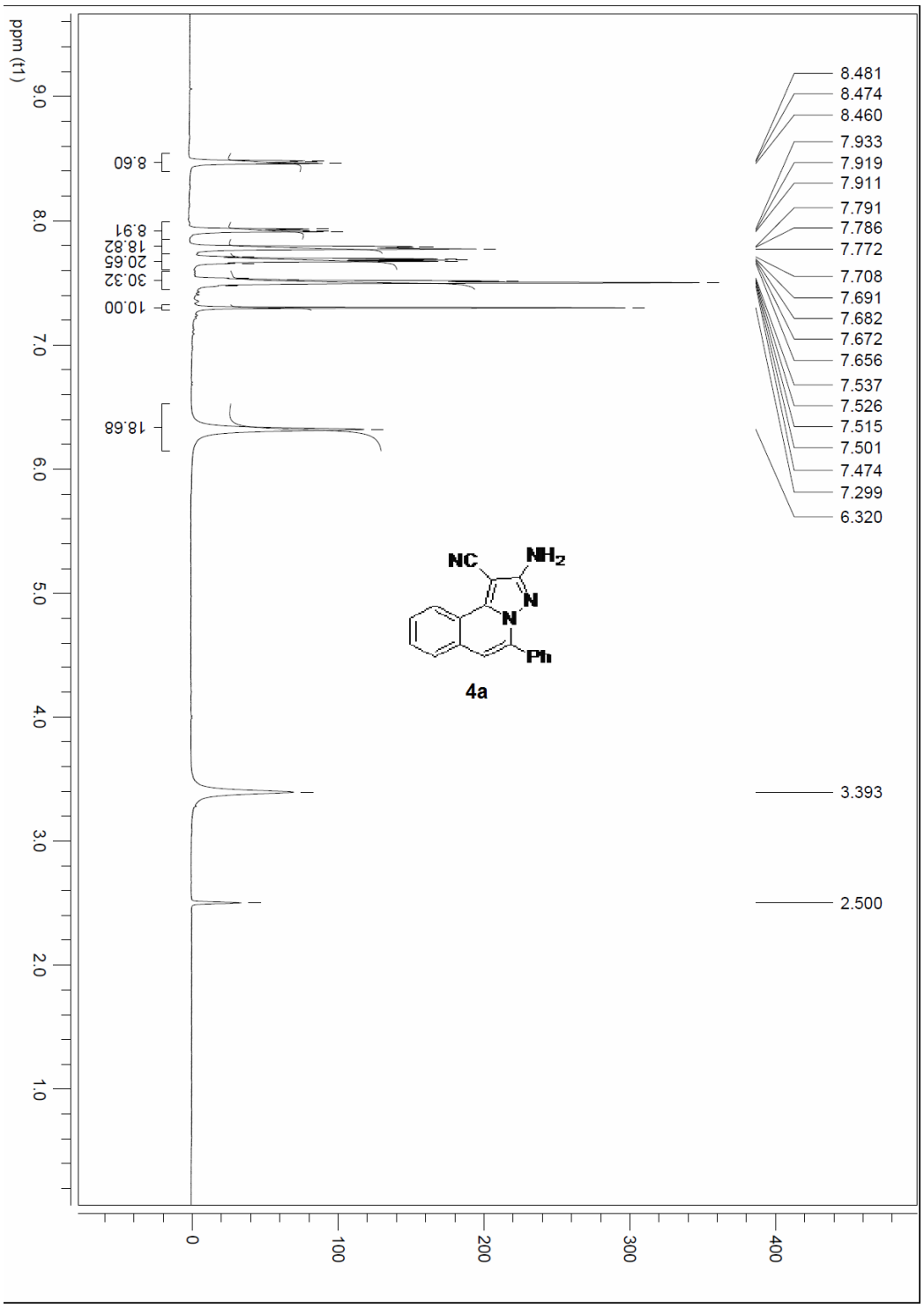


Ethyl 2-amino-5-cyclopropyl-9-fluoro*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4q**). ^{1}H NMR (400 MHz, $CDCl_3$): 0.84-0.85 (m, 2H), 1.03-1.05 (m, 2H), 1.35 (t, J = 6.8 Hz, 3H), 2.45-2.50 (m, 1H), 4.32-4.34 (m, 2H), 6.09 (s, 2H), 6.94 (s, 1H), 7.38-7.42 (m, 1H), 7.72-7.75 (m, 1H), 9.30-9.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.3, 11.3, 14.2, 59.9, 91.9, 107.0, 111.1 (d, $^{2}J_{CF}$ = 26 Hz), 117.4 (d, $^{2}J_{CF}$ = 24 Hz), 122.1 (d, $^{3}J_{CF}$ = 11 Hz), 127.7, 129.1 (d, $^{3}J_{CF}$ = 9 Hz), 137.8, 139.2, 158.4, 159.6 (d, $^{1}J_{CF}$ = 240 Hz), 163.9; HRMS calcd for $C_{17}H_{16}FN_3O_2$ (M^++Na): 336.1124, found: 336.1143.

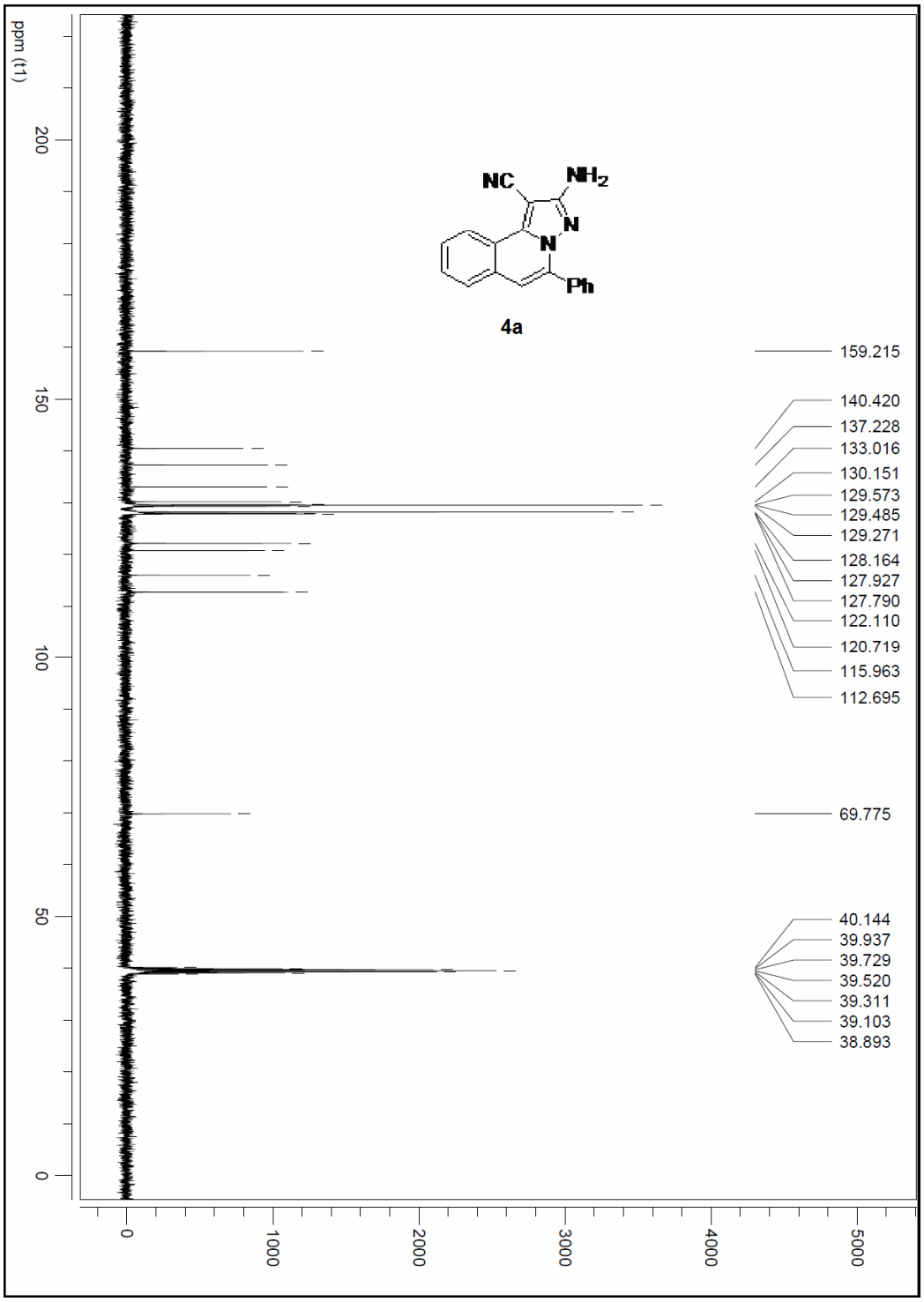


Ethyl 2-amino-9-methyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline-1-carboxylate (**4r**). ^{1}H NMR (400 MHz, $CDCl_3$): 1.50 (t, J = 7.2 Hz, 3H), 2.58 (s, 3H), 4.46-4.51 (m, 2H), 5.18 (s, 2H), 7.05 (s, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.46-7.52 (m, 3H), 7.61 (d, J = 8.0 Hz, 1H), 7.77-7.79 (m, 2H), 9.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 22.0,

60.2, 92.7, 113.9, 122.9, 126.7, 126.8, 128.1, 129.0, 129.1, 129.5, 130.5, 133.9, 136.7, 139.7, 147.0, 158.3, 164.6; HRMS calcd for $C_{21}H_{19}N_3O_2$ (M^++H): 346.1556, found: 346.1558.



4a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NH2
N
N
Ph
4a
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140.420
137.228
133.016
130.151
129.573
129.485
129.271
128.164
127.927
127.790
122.110
120.719
115.963
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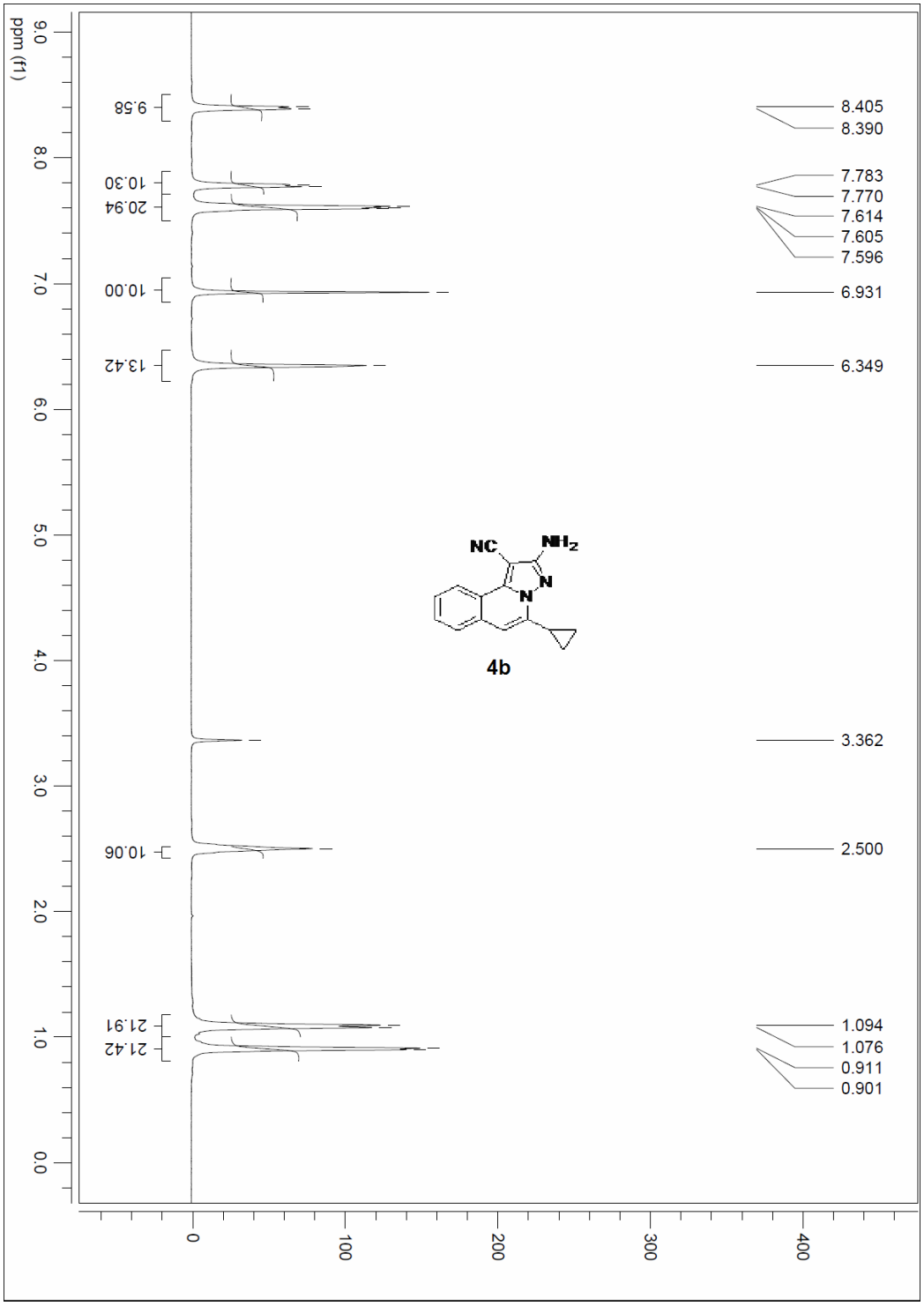
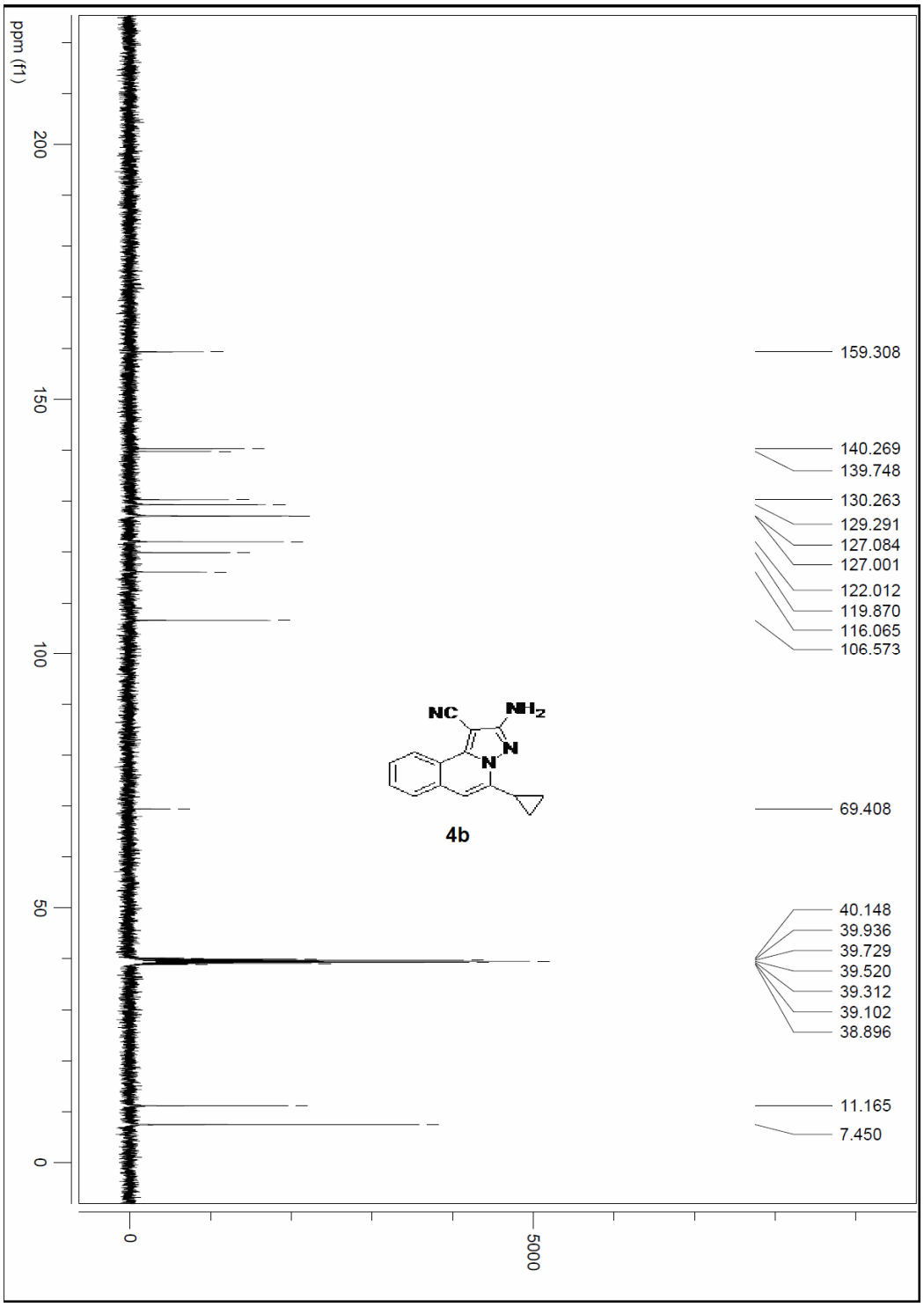
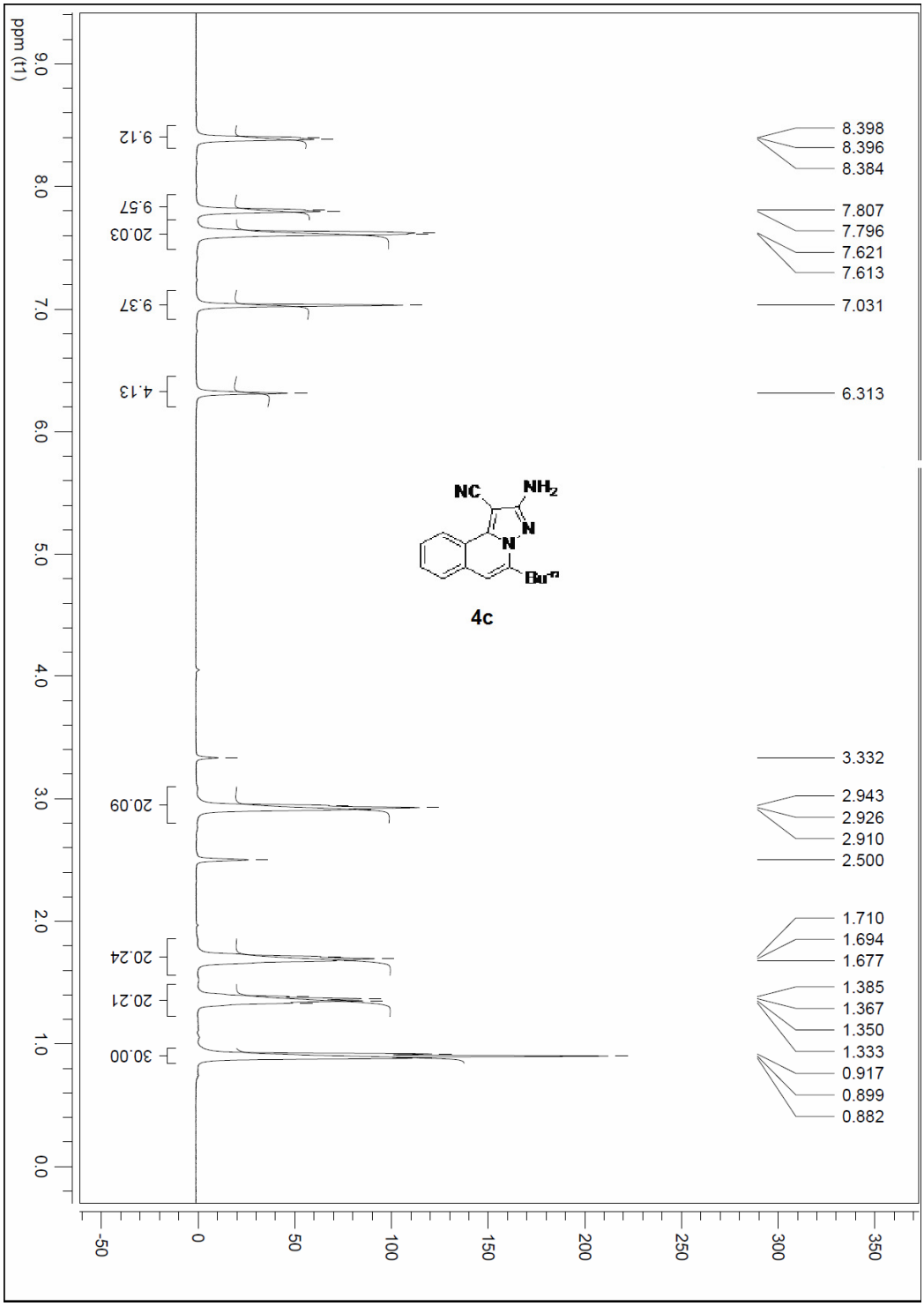
39.937
39.729
39.520
39.311
39.103
38.893



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0
50
100
150
200
250
300
350
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9.57
20.03
9.37
4.13
20.09
20.24
20.21
30.00
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8.396
8.384
7.807
7.796
7.621
7.613
7.031
6.313
3.332
2.943
2.926
2.910
2.500
1.710
1.694
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NH2
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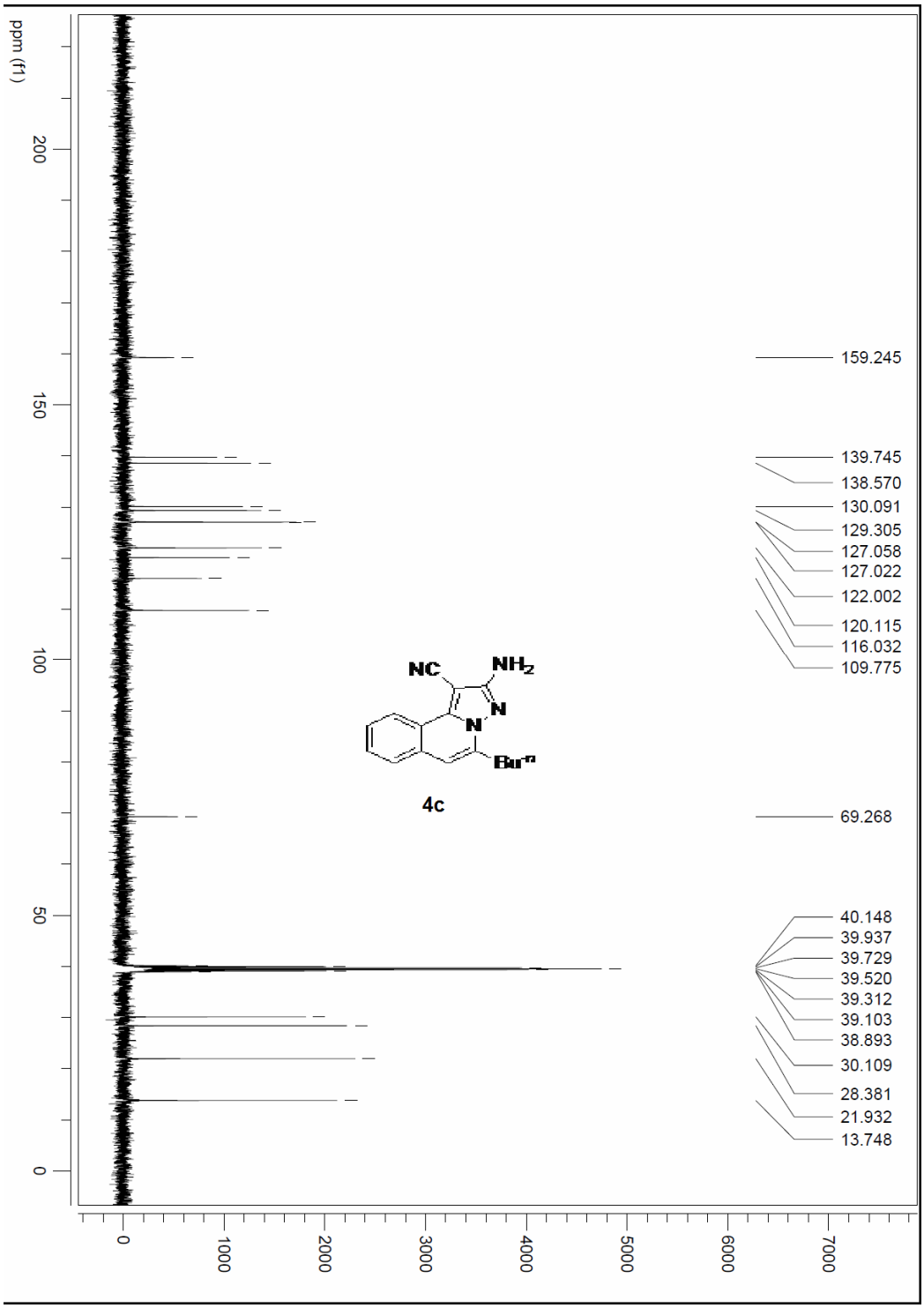
N
Bu
4c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130.091
129.305
127.058
127.022
122.002
120.115
116.032
109.775
69.268
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39.937
39.729
39.520
39.312
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30.109
28.381
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13.748
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NH2
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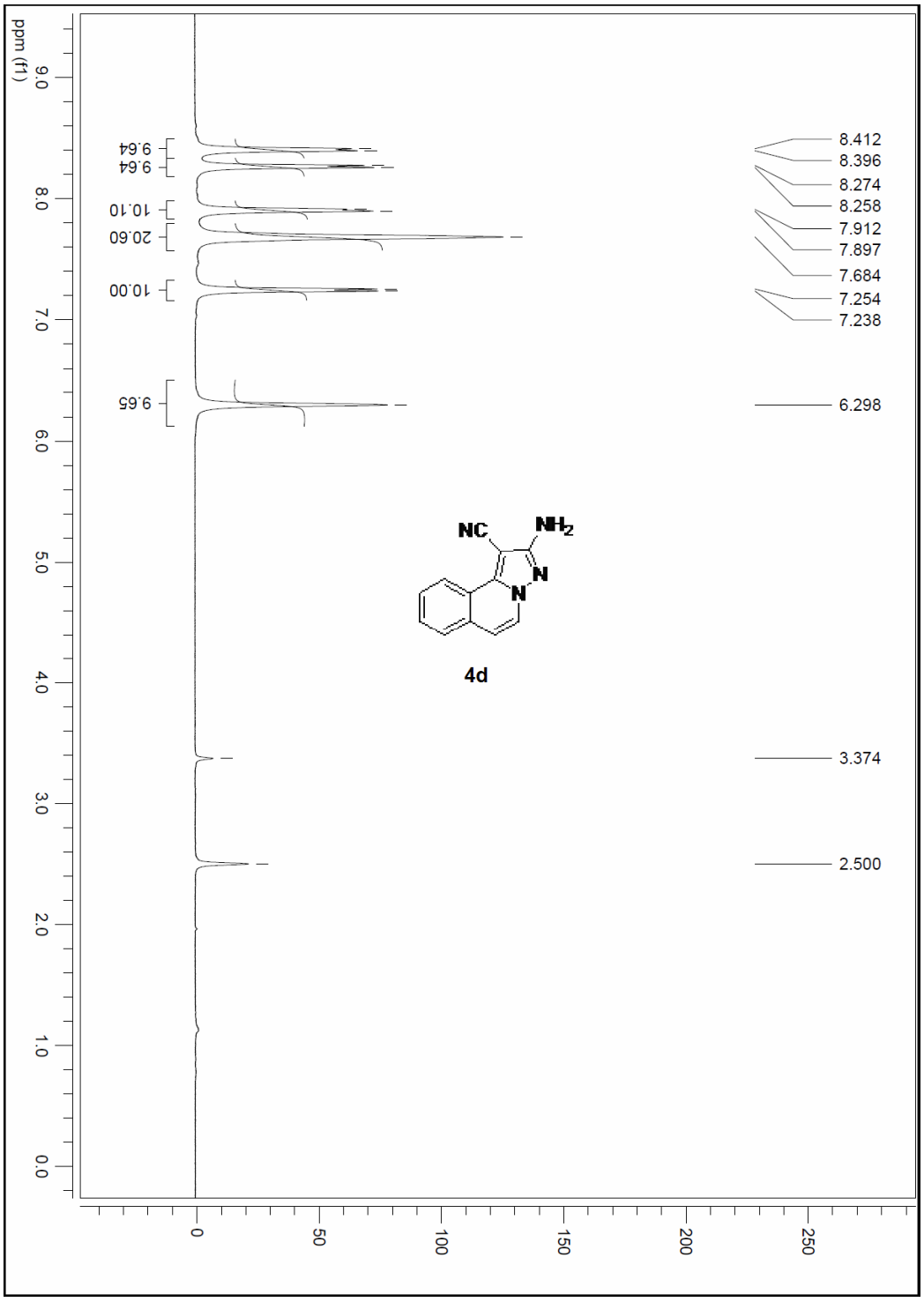
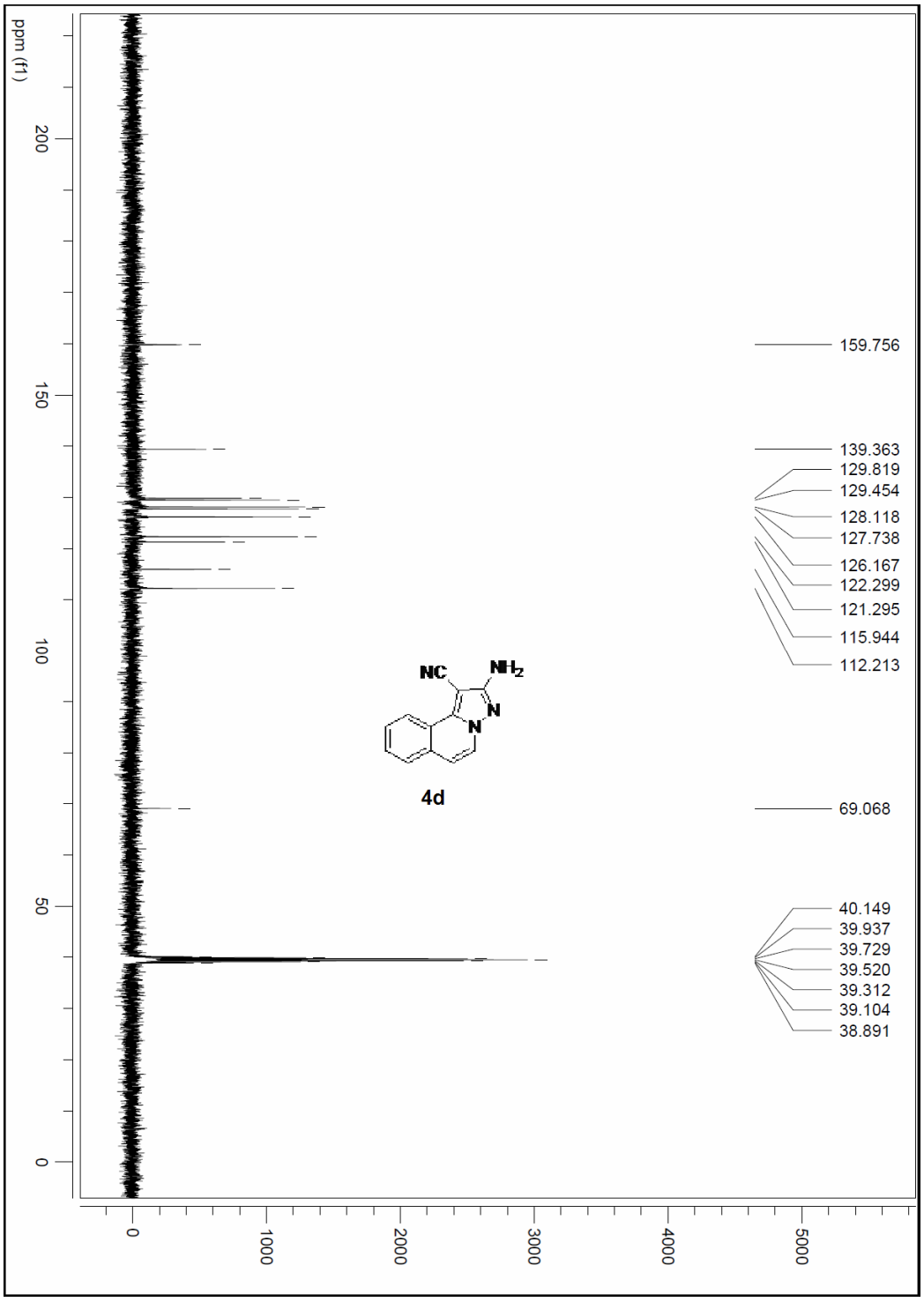
Br
4c



4d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115.944
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39.729
39.520
39.312
39.104
38.891
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NH2
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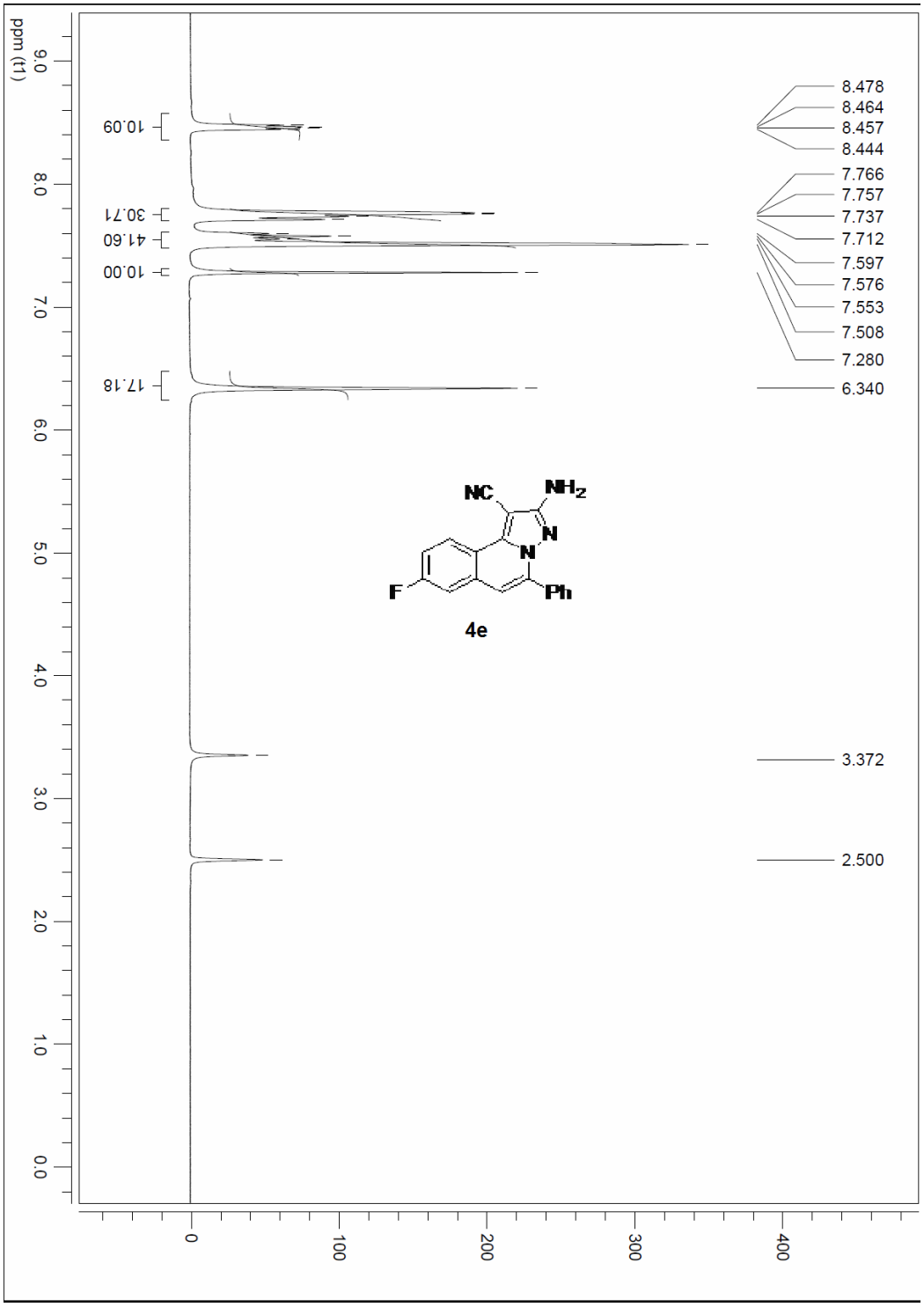
N
4d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1.0
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0
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200
300
400
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41.60
10.00
17.18
8.478
8.464
8.457
8.444
7.766
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7.712
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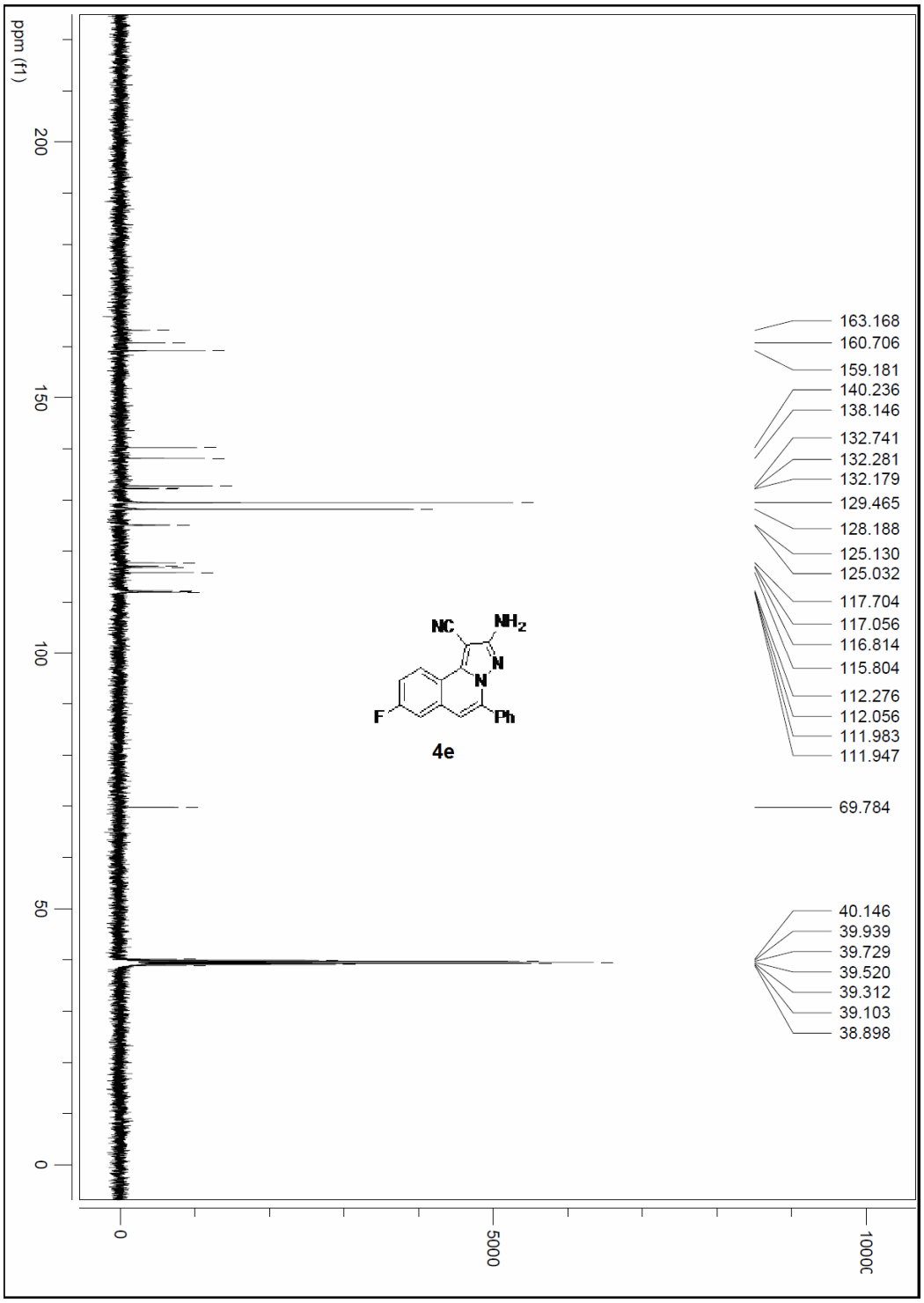
N
F
Ph

4e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10000
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NH2
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N
F
Ph
4e
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138.146
132.741
132.281
132.179
129.465
128.188
125.130
125.032
117.704
117.056
116.814
115.804
112.276
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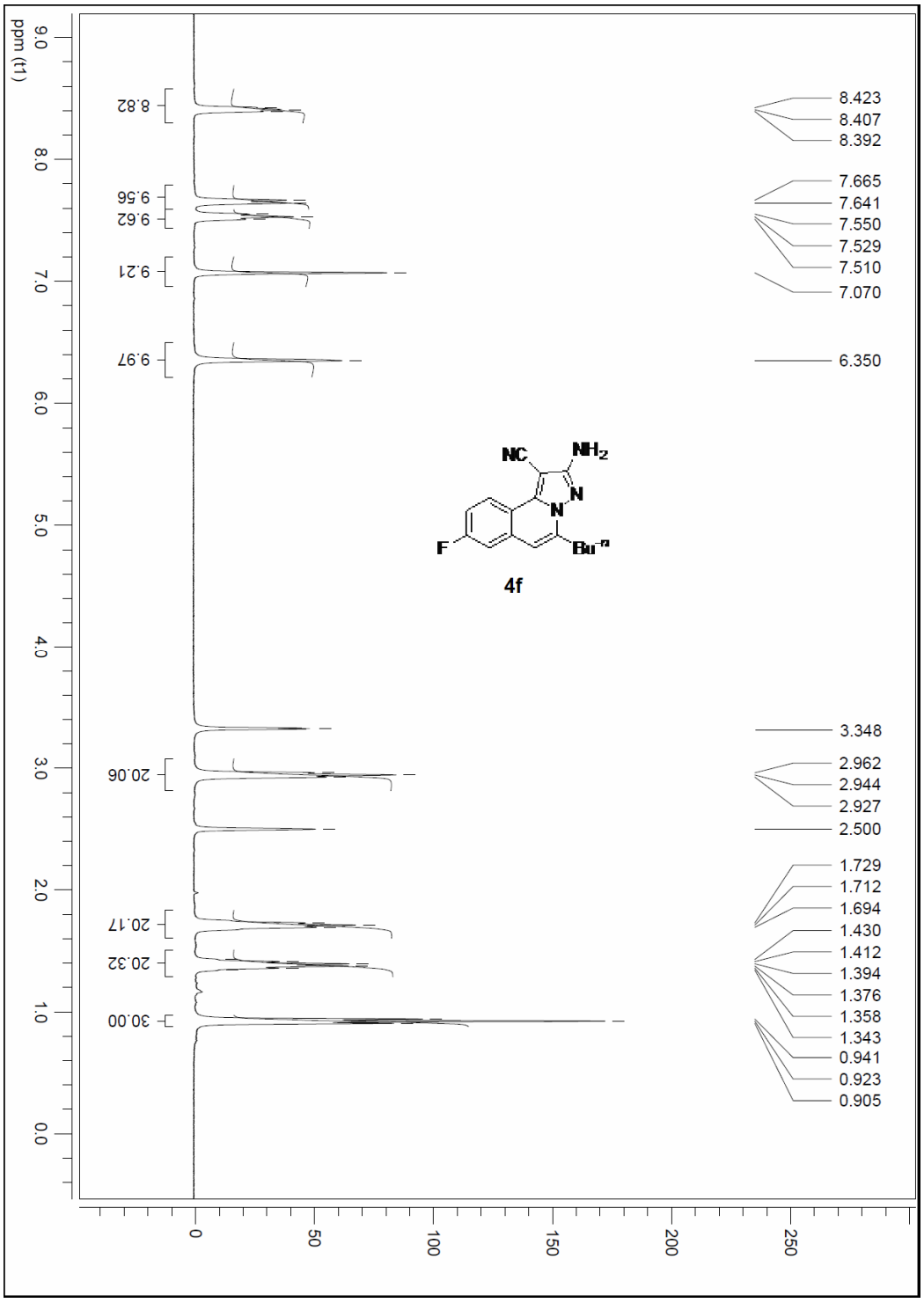
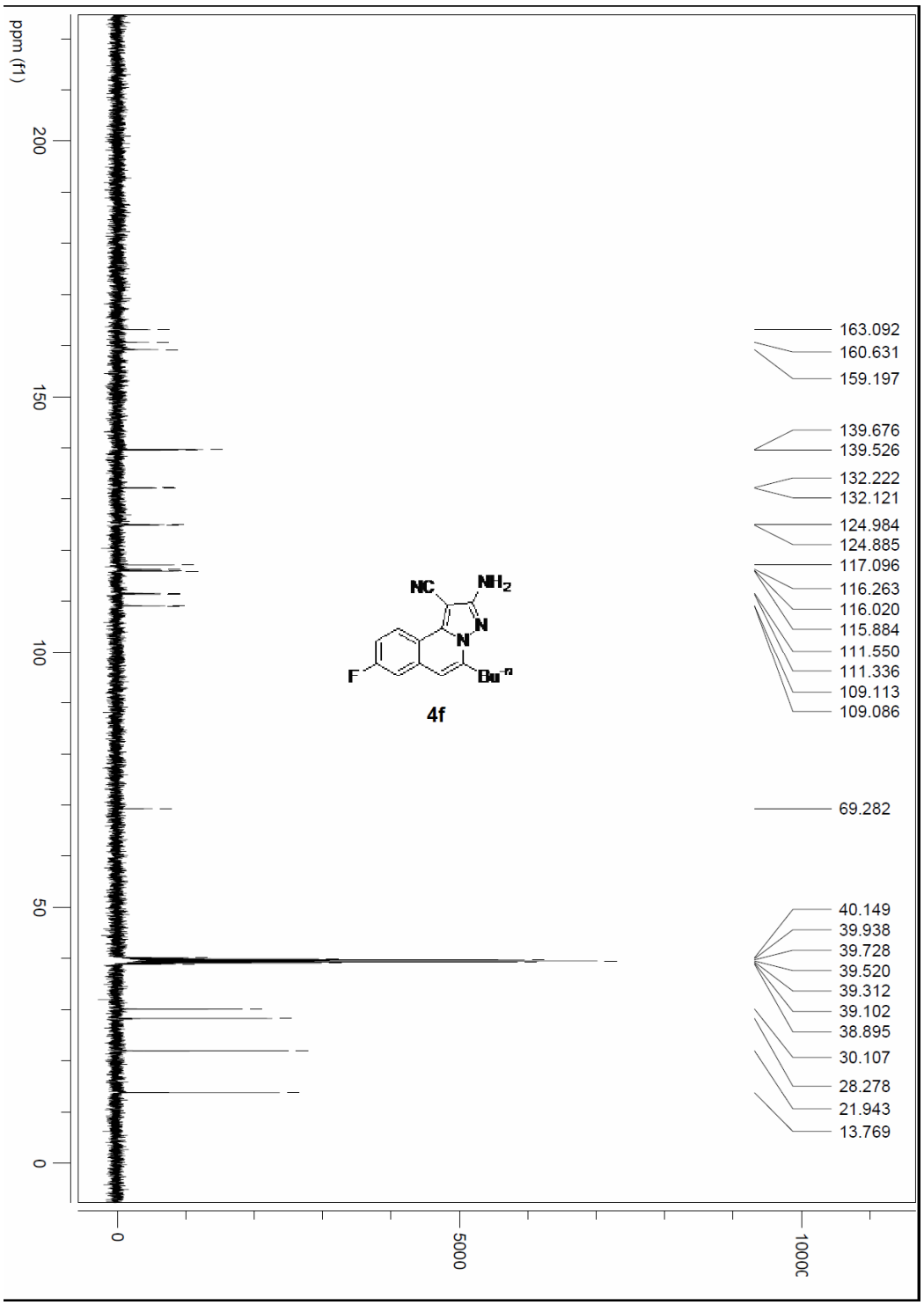
39.729
39.520
39.312
39.103
38.898

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10000
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NH2
N
N
F
Bu-n
4f
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139.526
132.222
132.121
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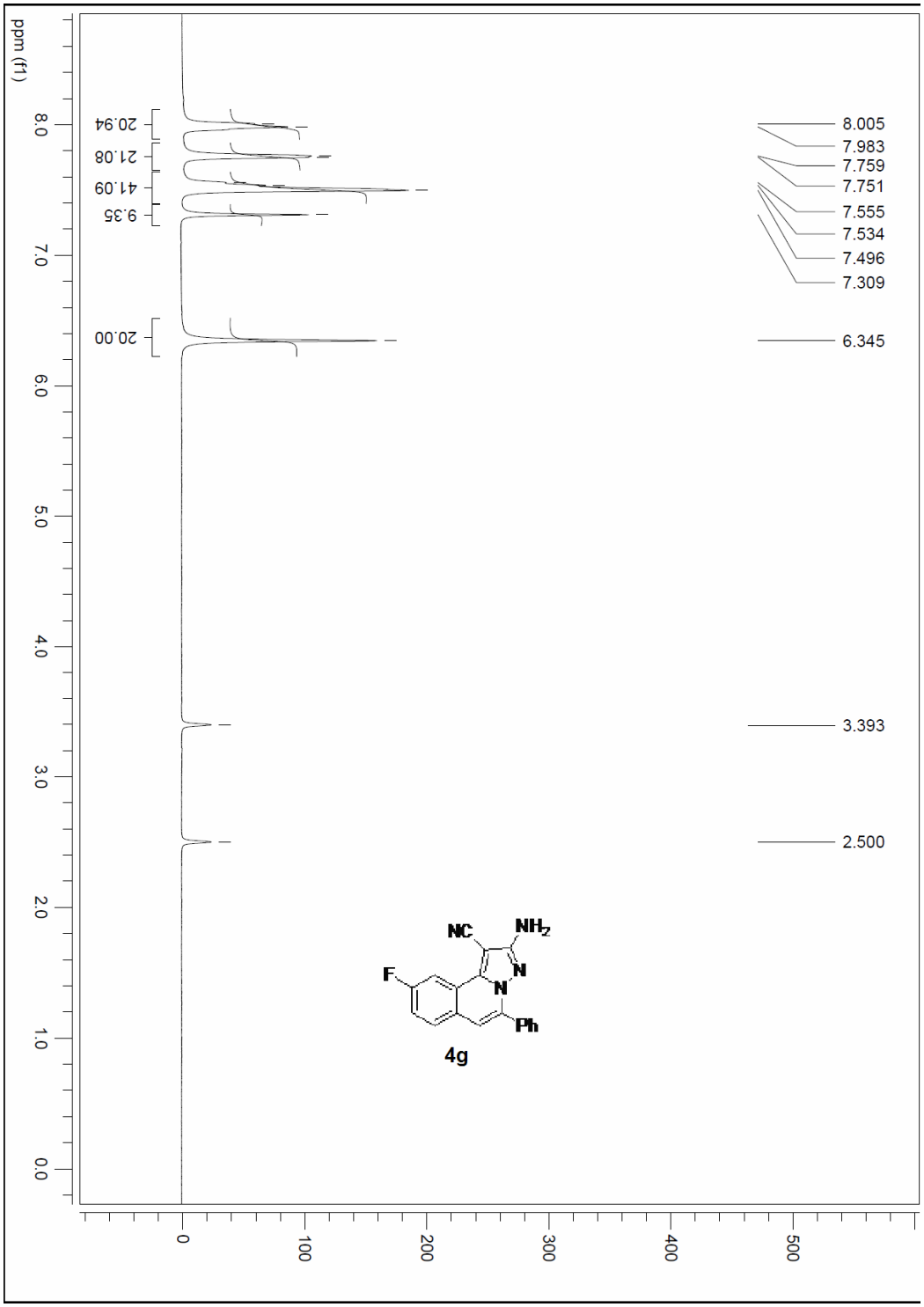
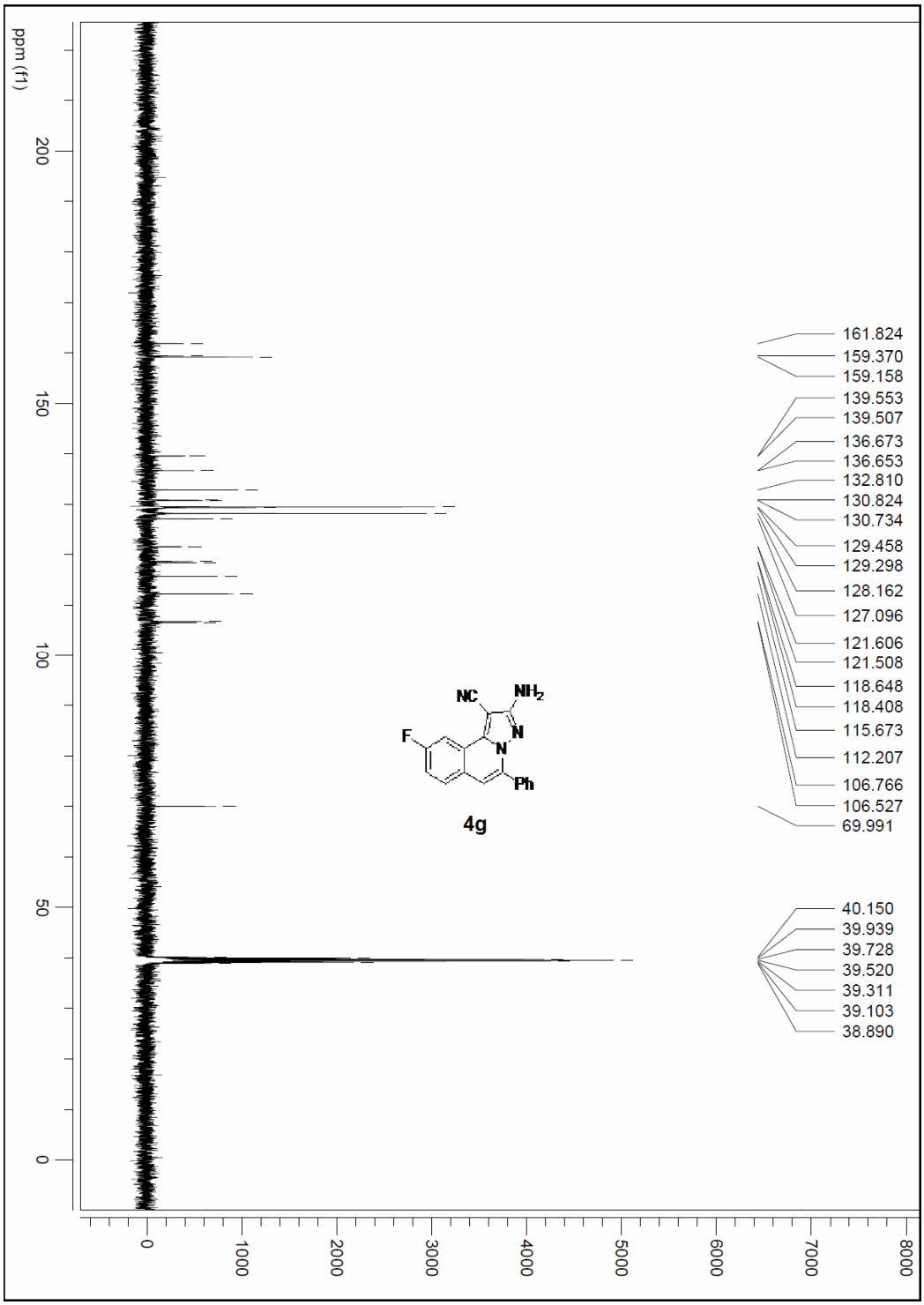


4g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7000
8000
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127.096
121.606
121.508
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115.673
112.207
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106.527
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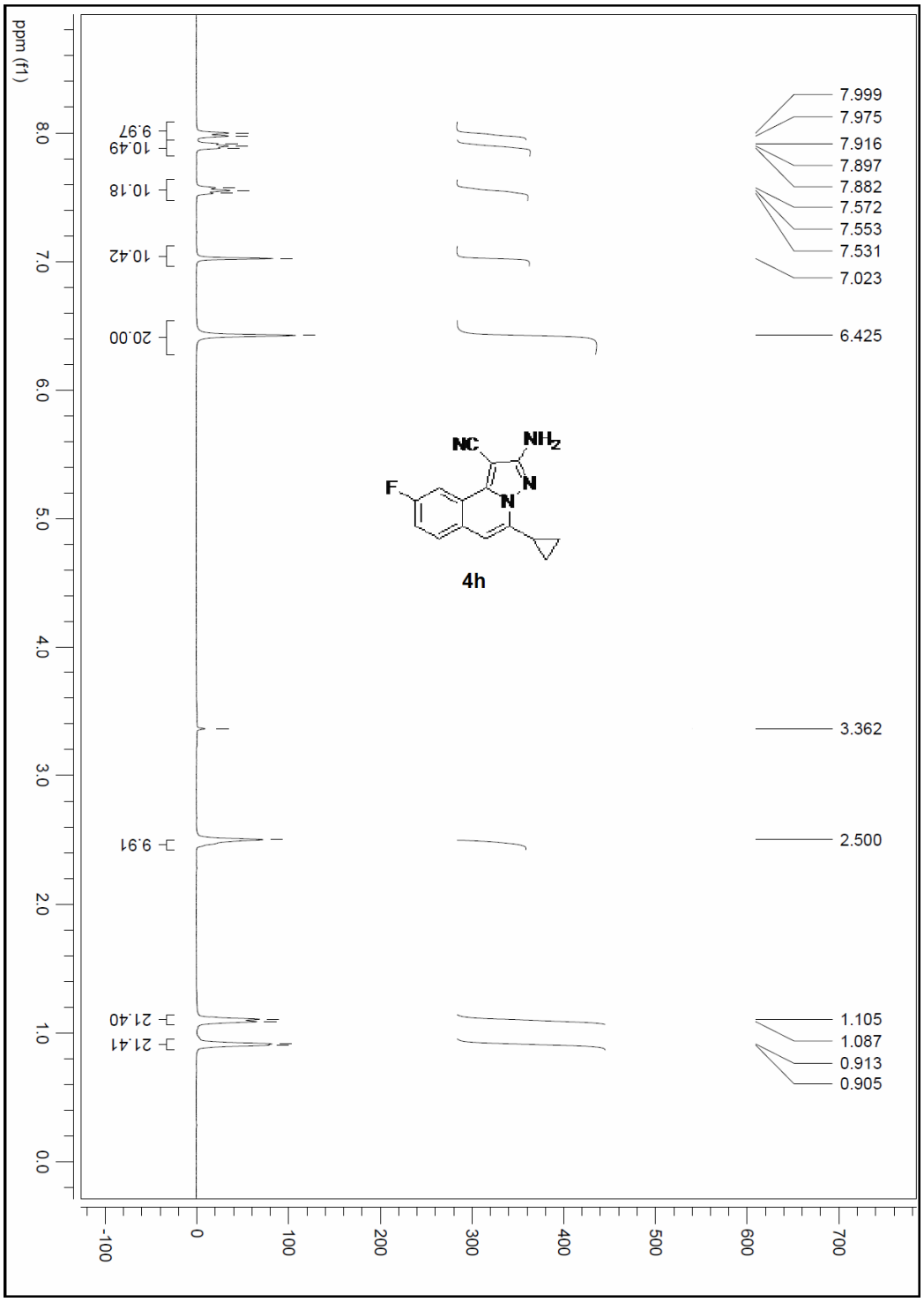
N
Ph
4g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300
400
500
600
700
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20.00
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21.40
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7.897
7.882
7.572
7.553
7.531
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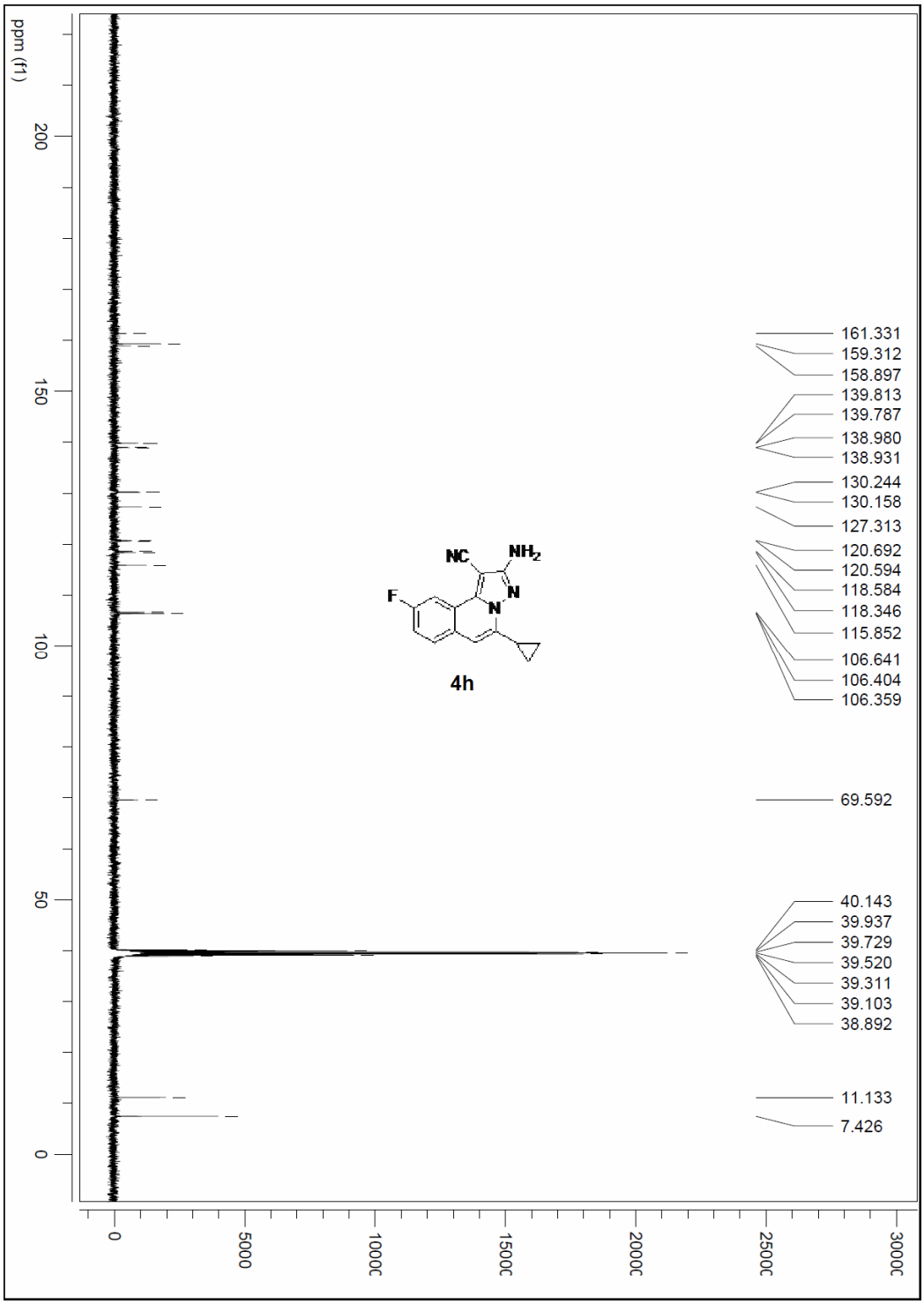
F
N
N
4h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NC
NH2
F
N
N
4h
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159.312
158.897
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138.931
130.244
130.158
127.313
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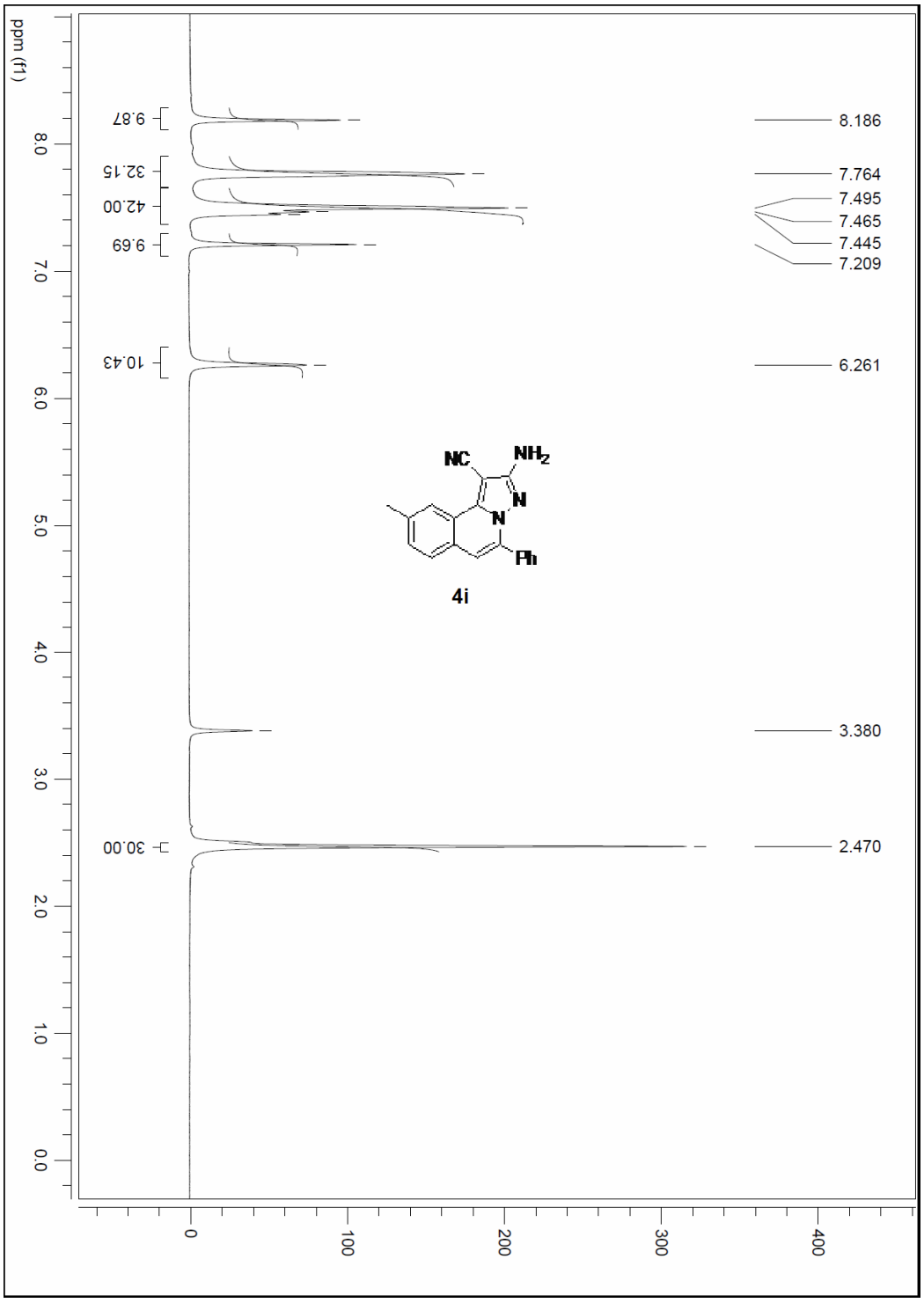
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300
400
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30.00
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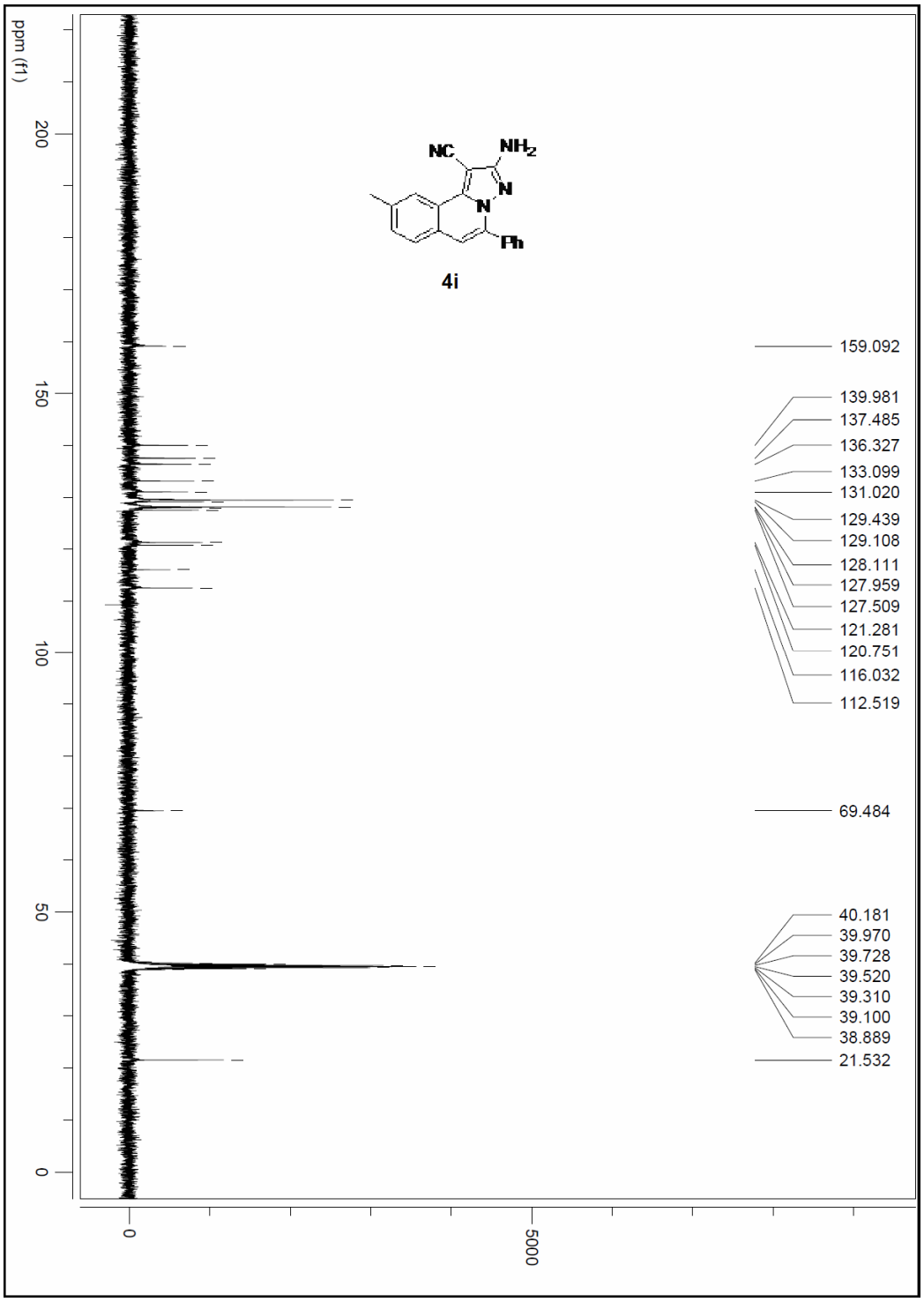
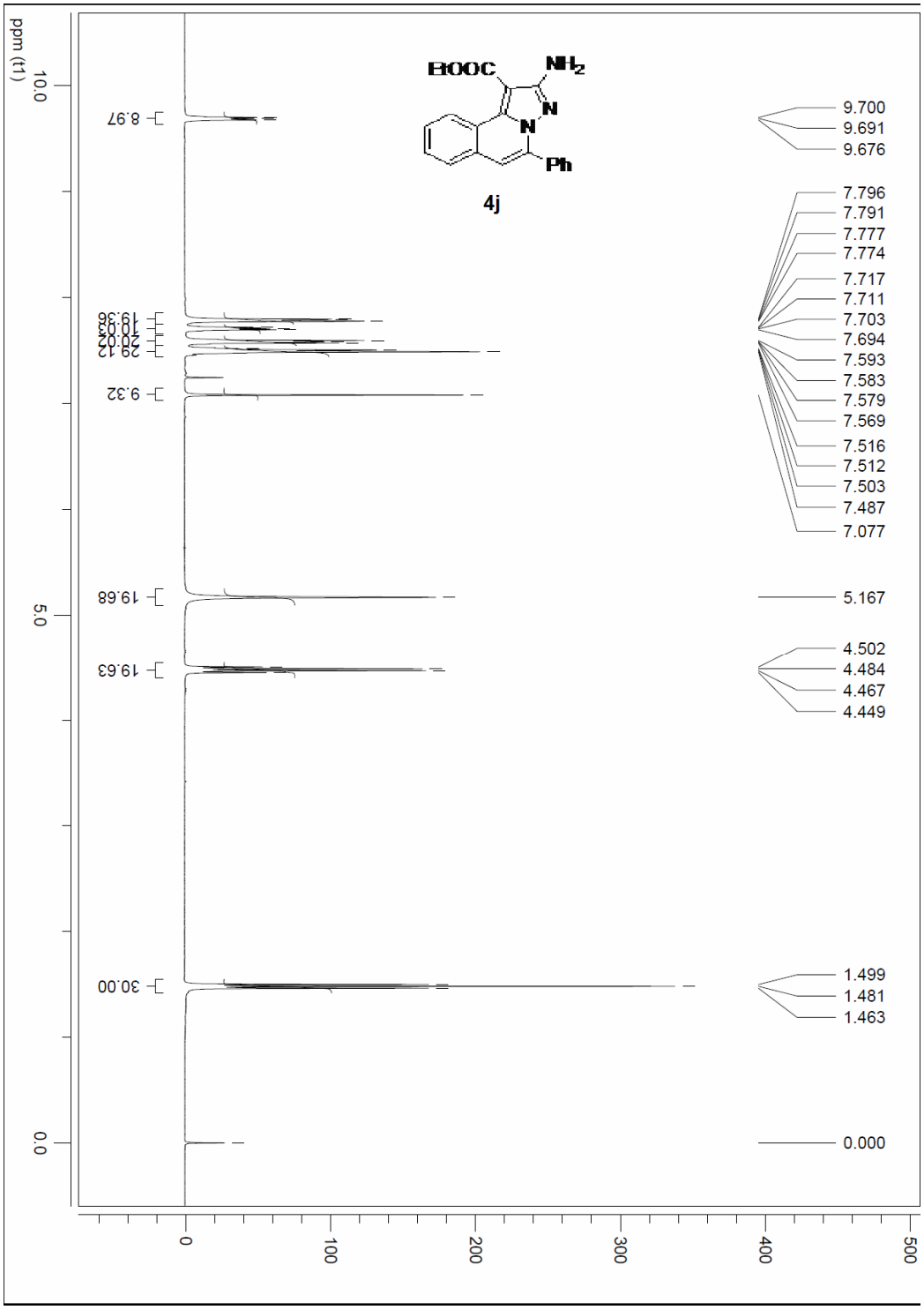
NH2
N
N
Ph

4i

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30.00
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NH2
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N
Ph
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7.717
7.711
7.703
7.694
7.593
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7.569
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7.512
7.503
7.487
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4.467
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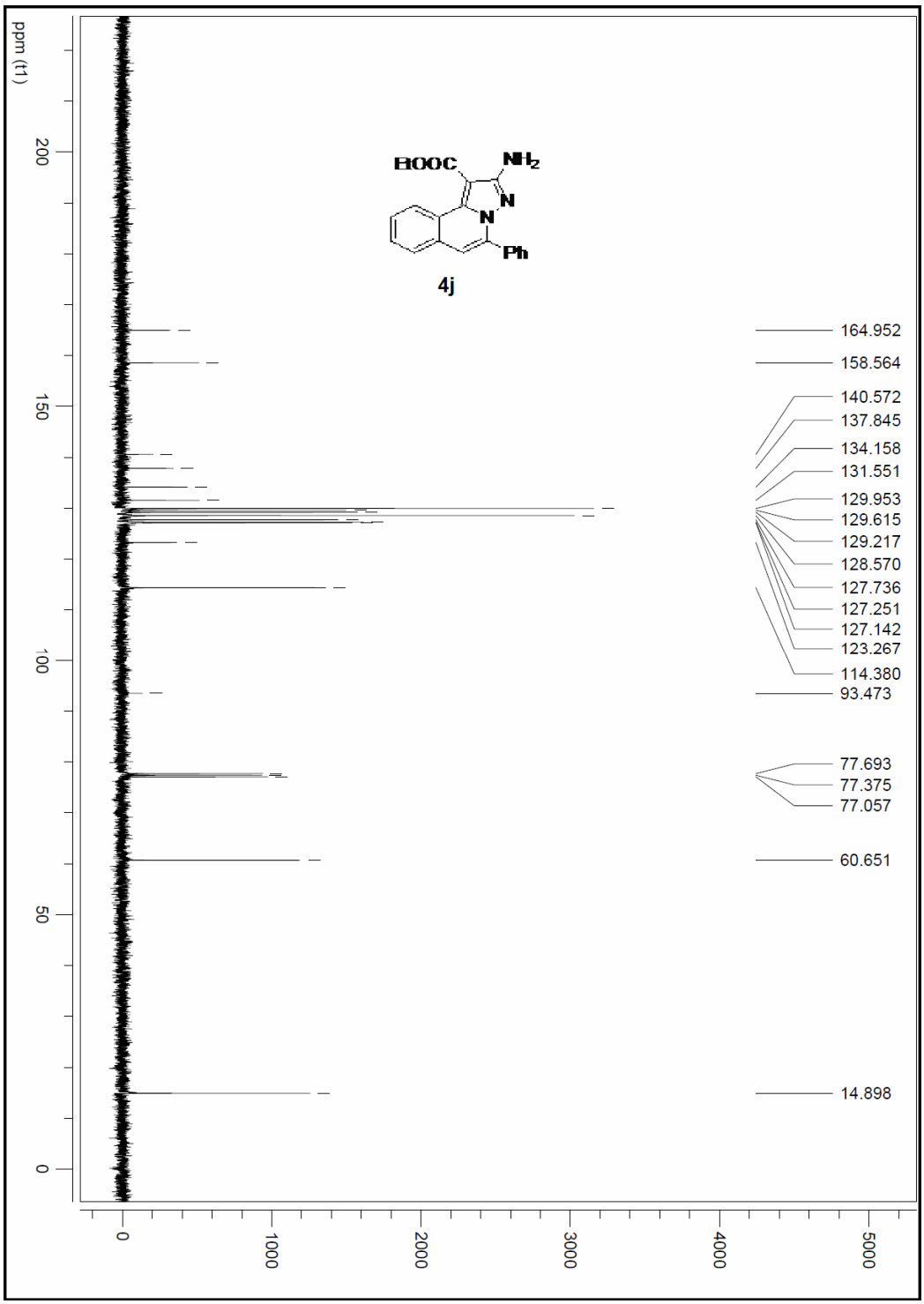
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NH2
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N
Ph
4j
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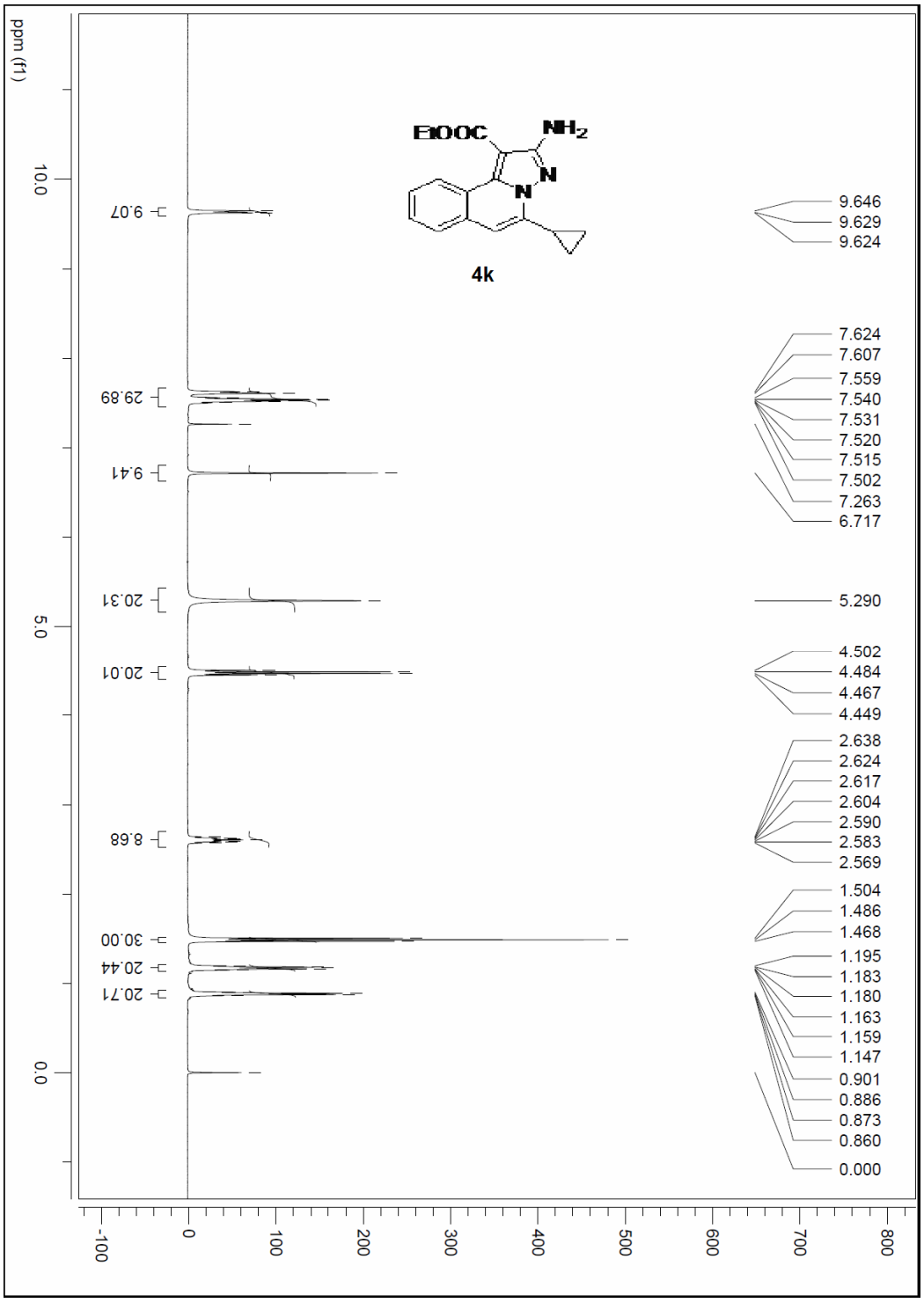
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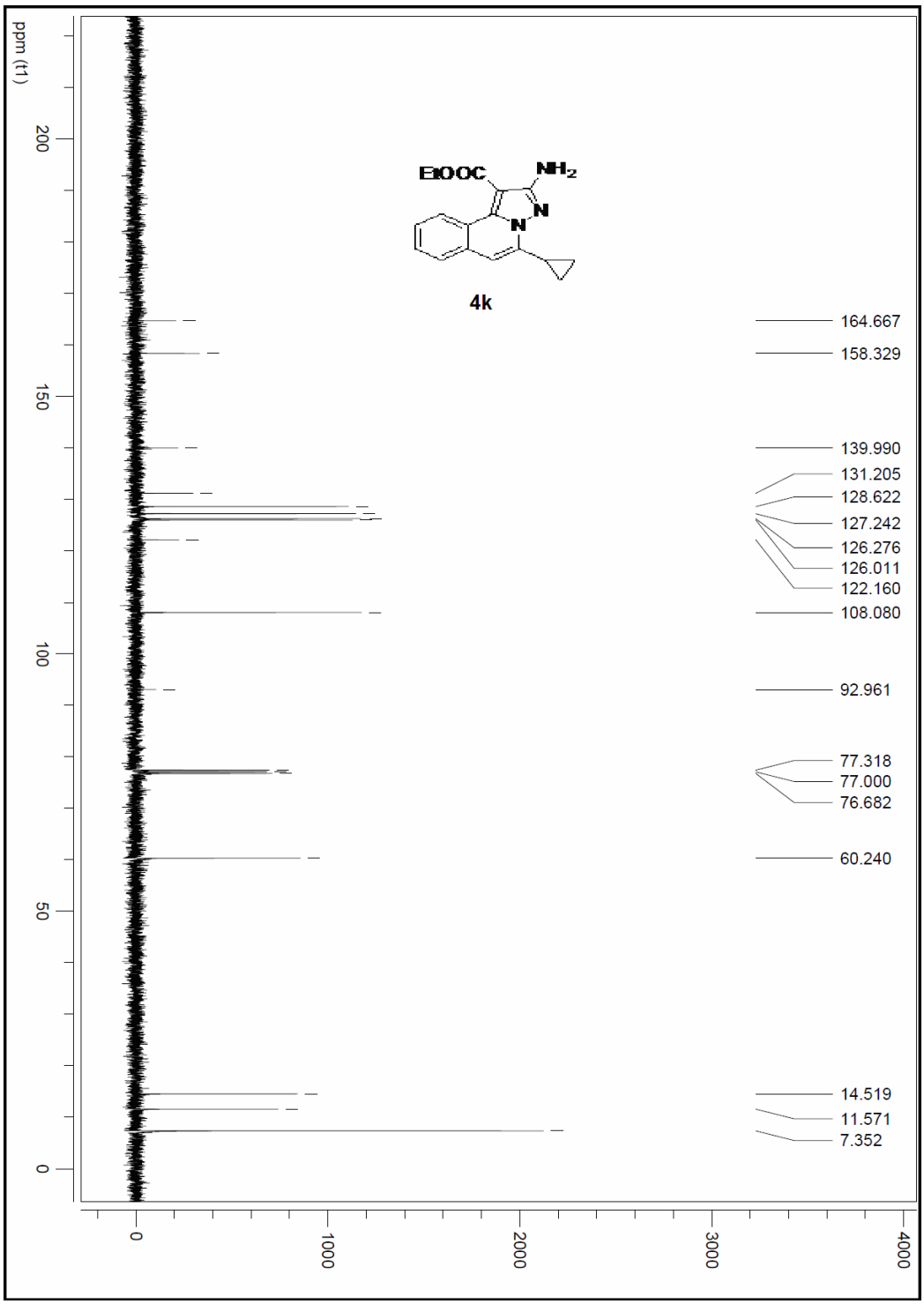
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122.160
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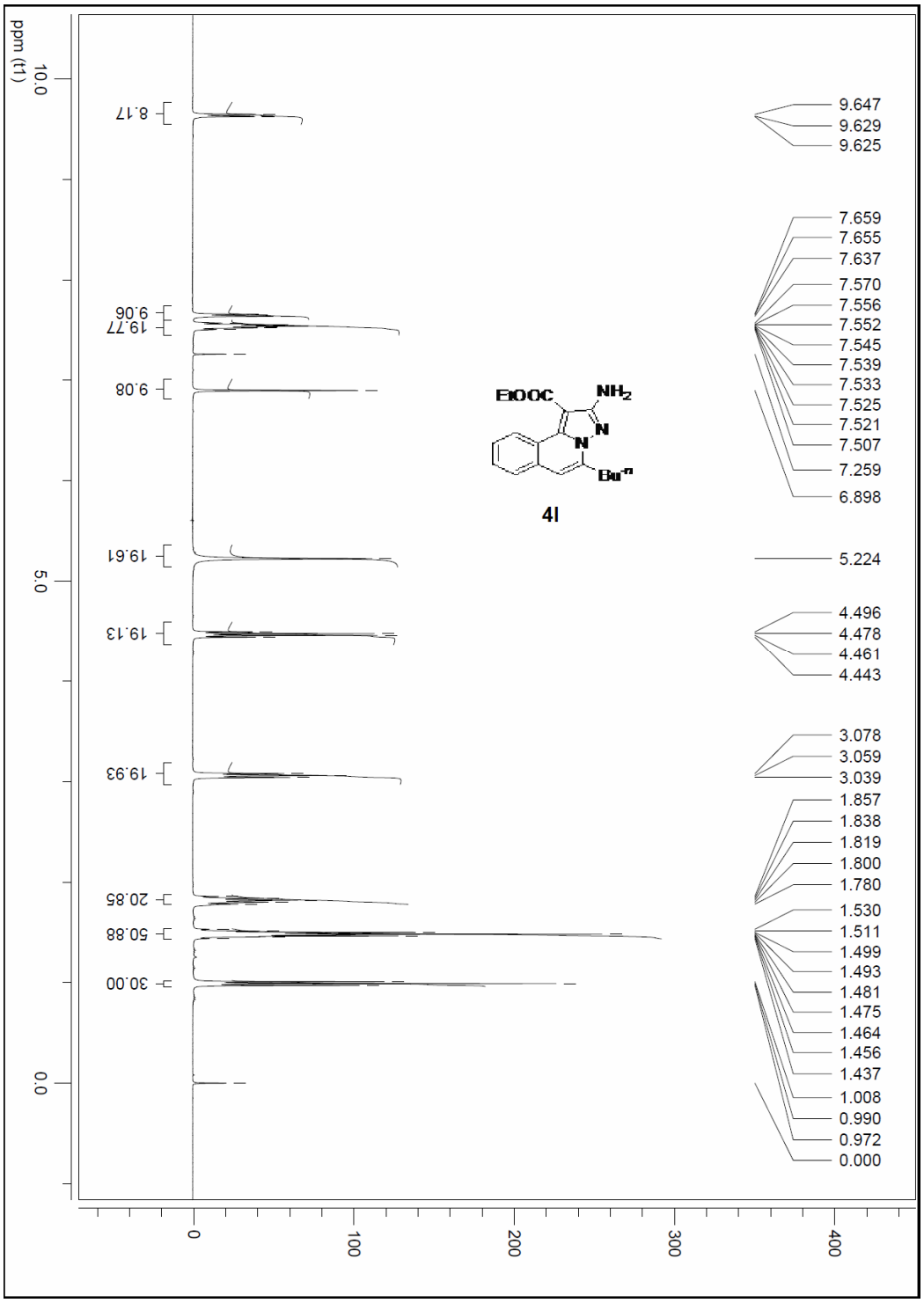
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50.88
30.00
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N
Bun
4l
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9.625
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7.637
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7.507
7.259
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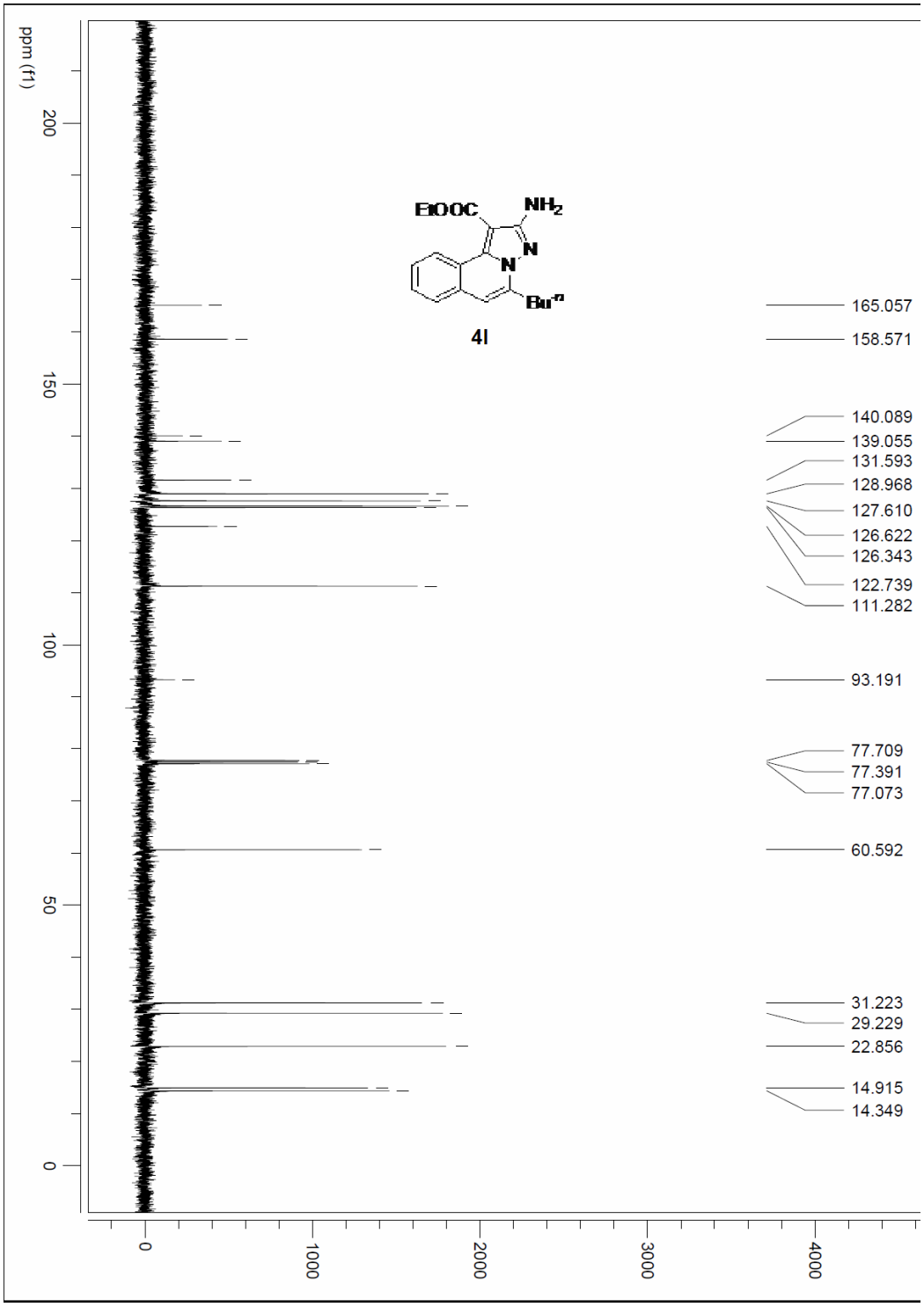
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EtOOC
NH2
N
N
Bun
4l
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31.223
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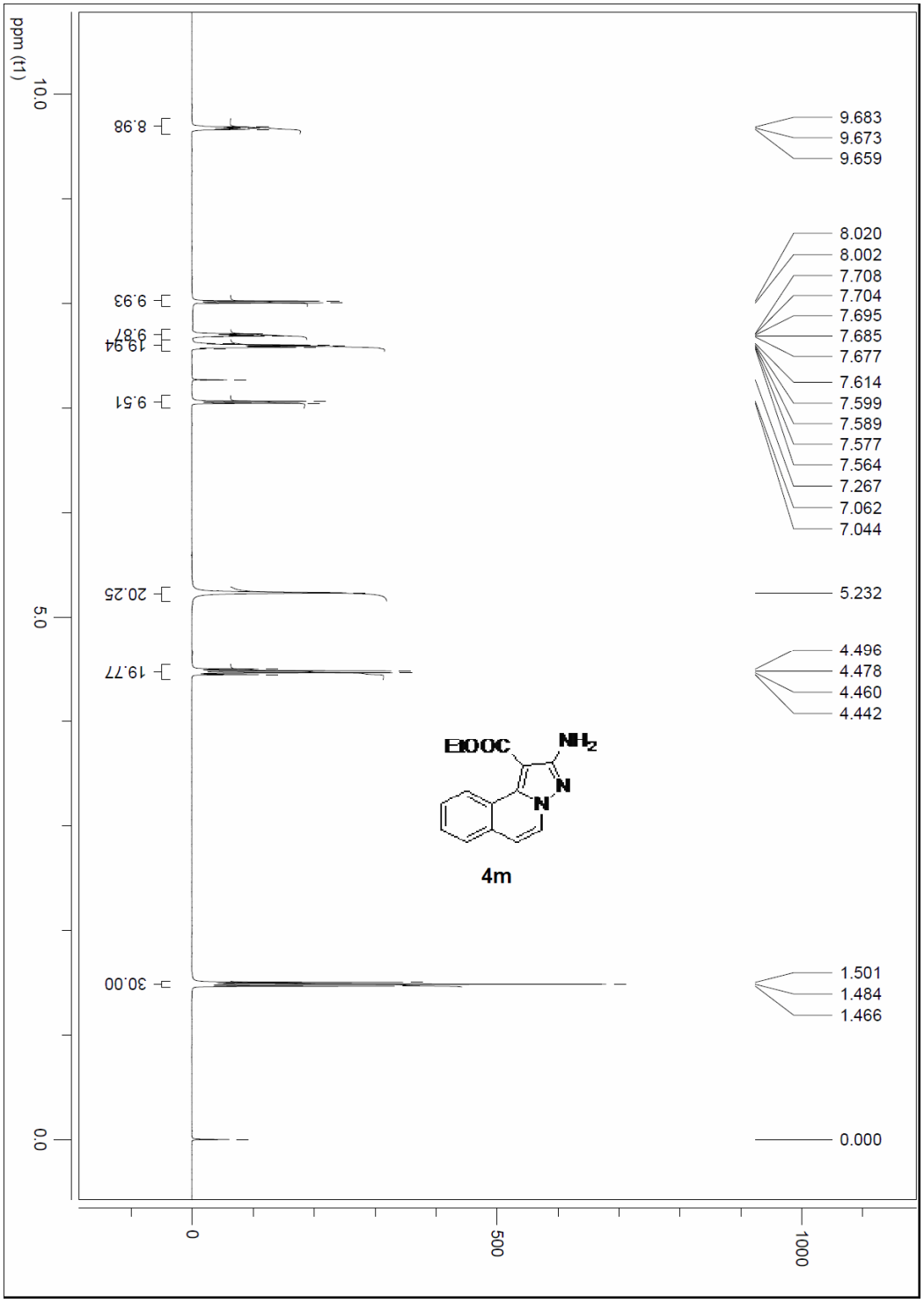
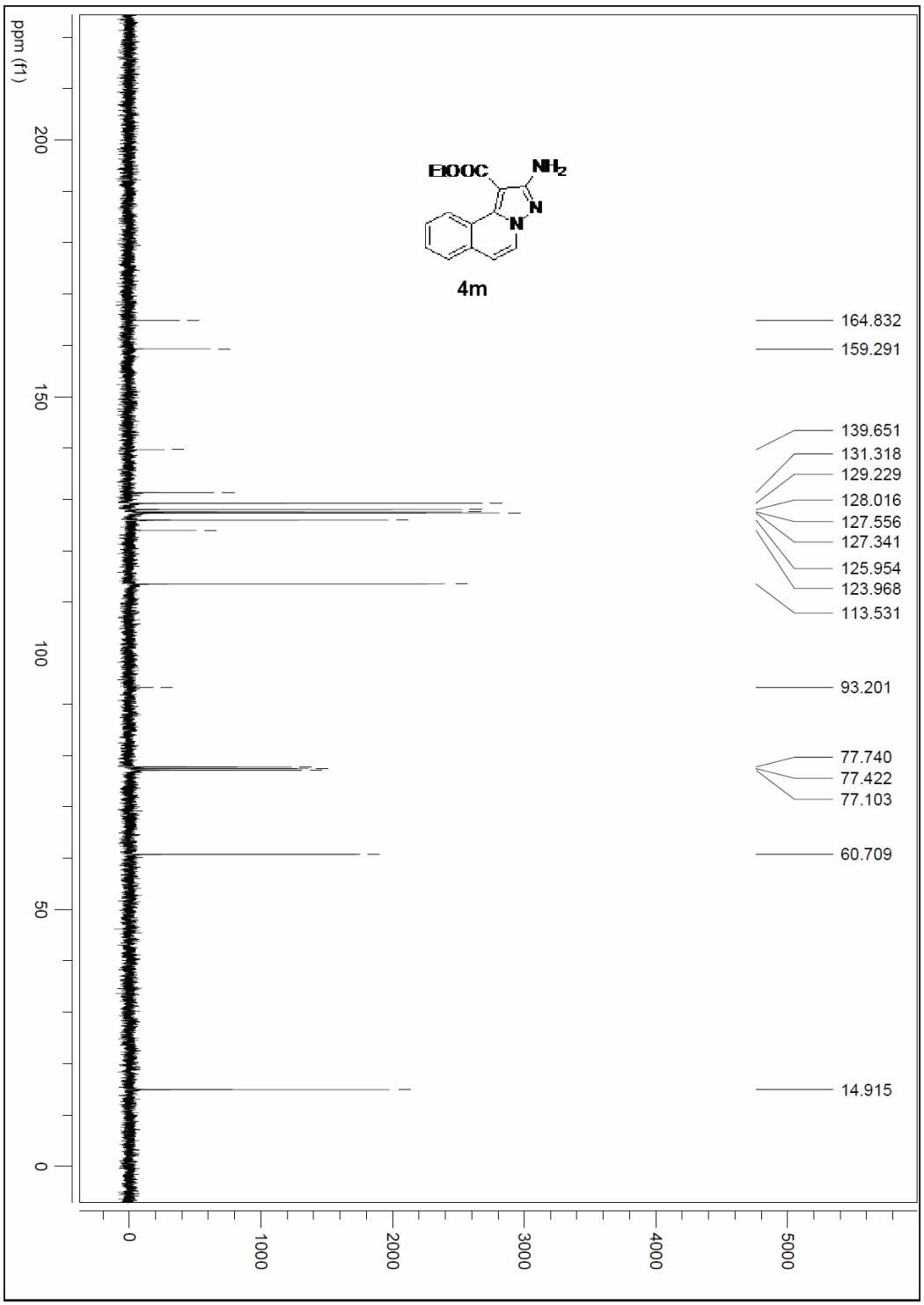
14.349



4m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4m
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127.341
125.954
123.968
113.531
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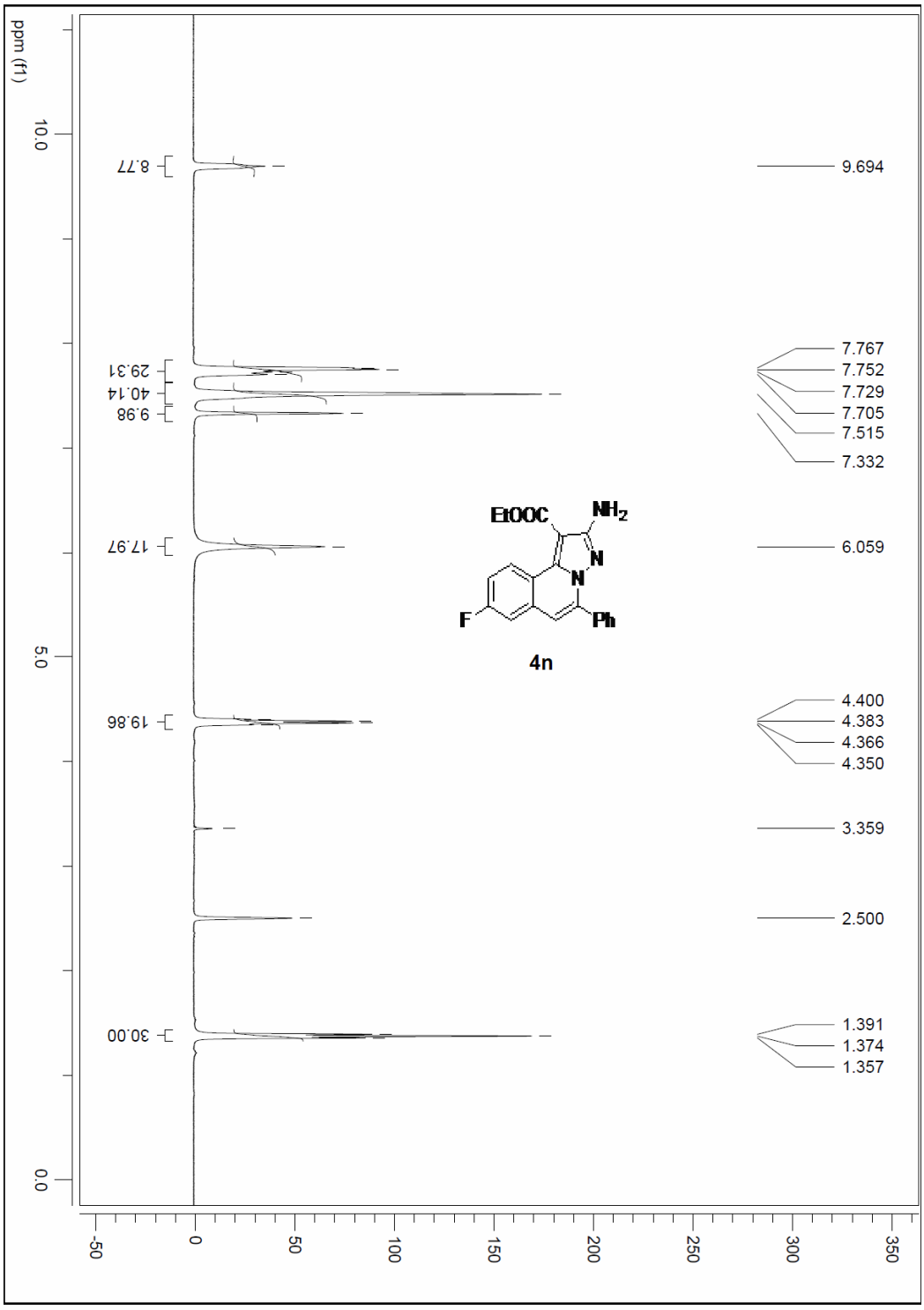
77.422
77.103
60.709
14.915
0
1000
2000
3000
4000
5000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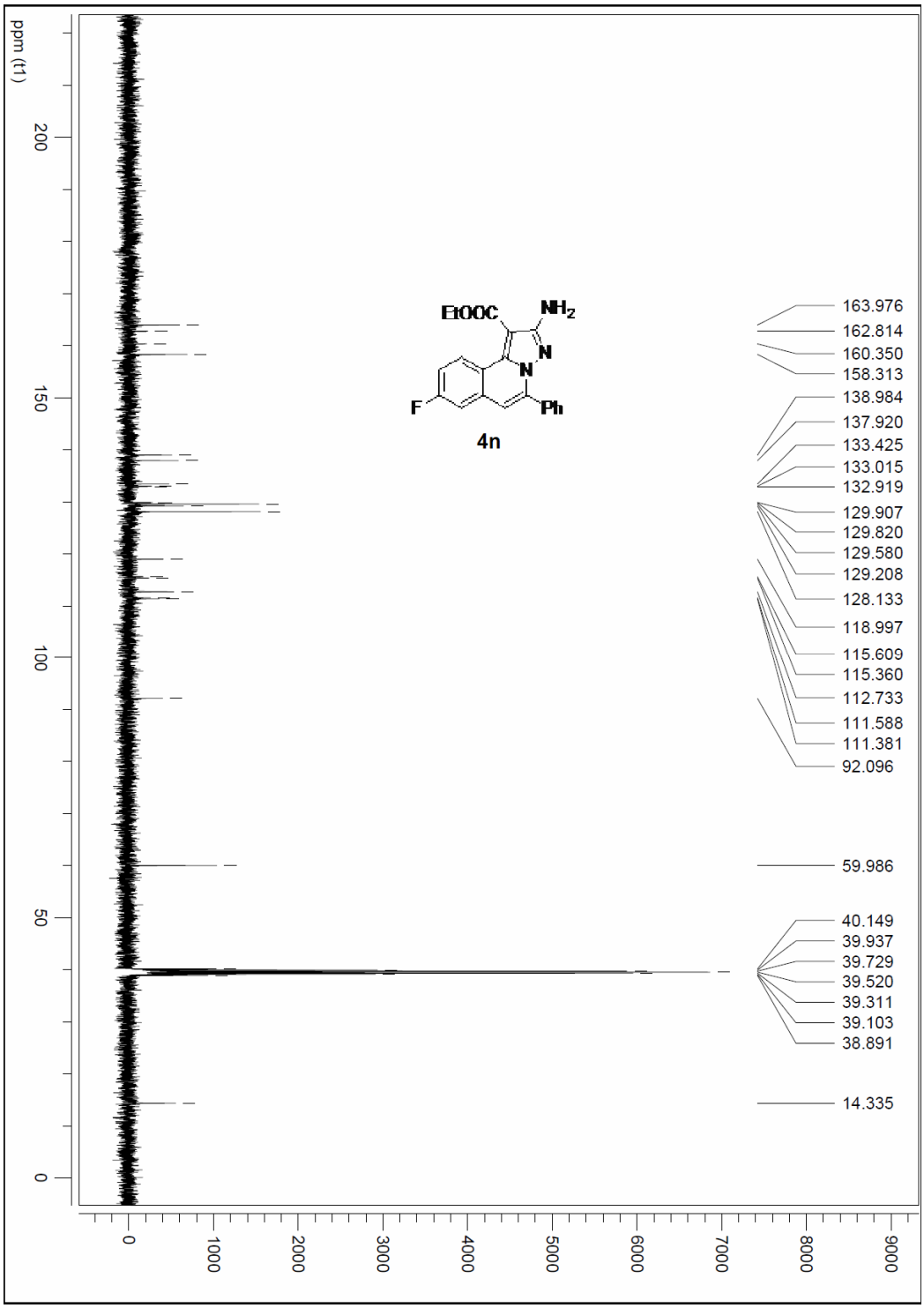
5.0
0.0
8.77
29.31
40.14
9.98
17.97
19.86
30.00
9.694
7.767
7.752
7.729
7.705
7.515
7.332
6.059
4.400
4.383
4.366
4.350
3.359
2.500
1.391
1.374
1.357
EtOOC
NH2
N
N
F
Ph
4n
-50
0
50
100
150
200
250
300
350


ppm (t1)
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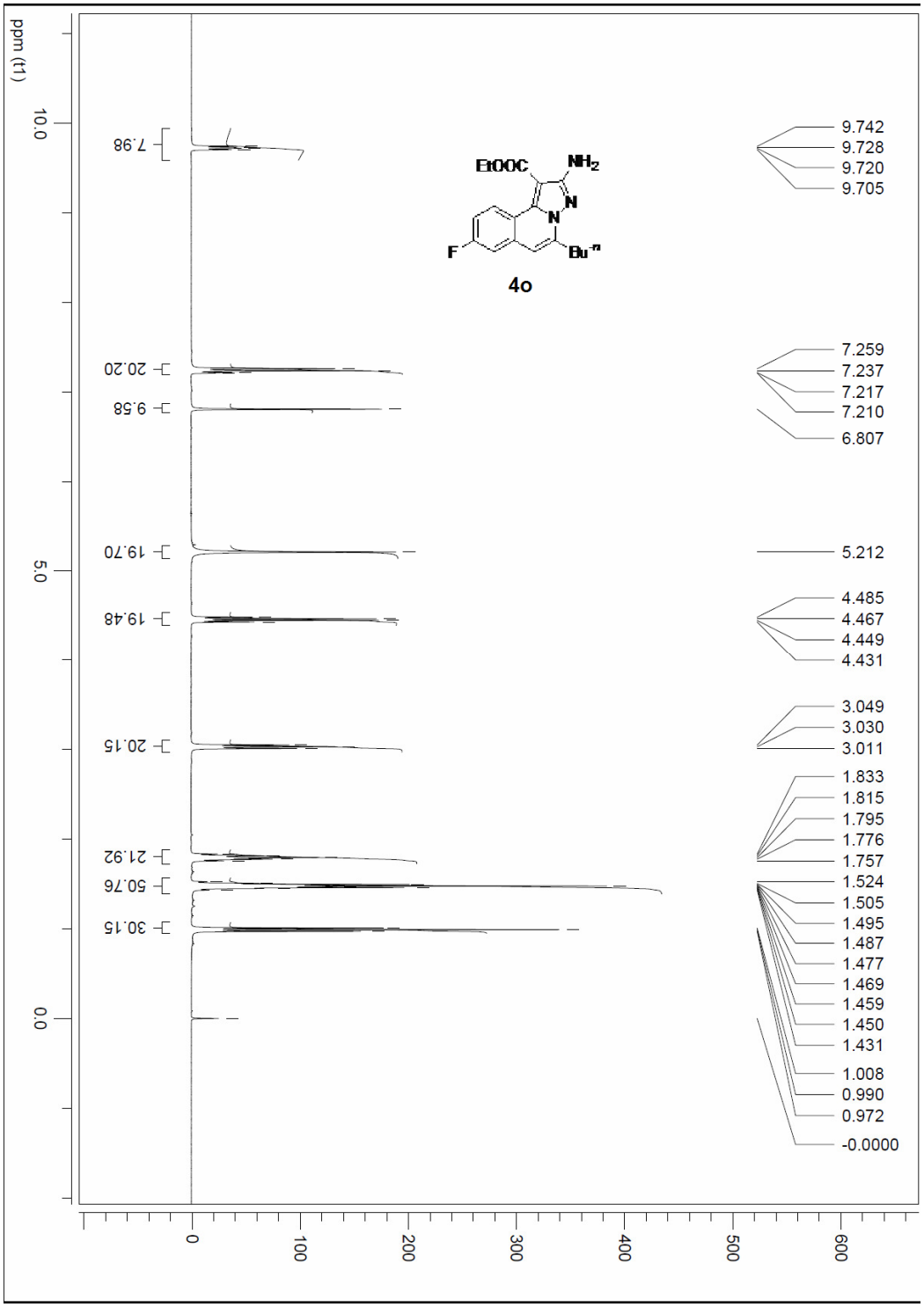
NH2
N
N
F
Ph
4n
163.976
162.814
160.350
158.313
138.984
137.920
133.425
133.015
132.919
129.907
129.820
129.580
129.208
128.133
118.997
115.609
115.360
112.733
111.588
111.381
92.096
59.986
40.149
39.937
39.729
39.520
39.311
39.103
38.891
14.335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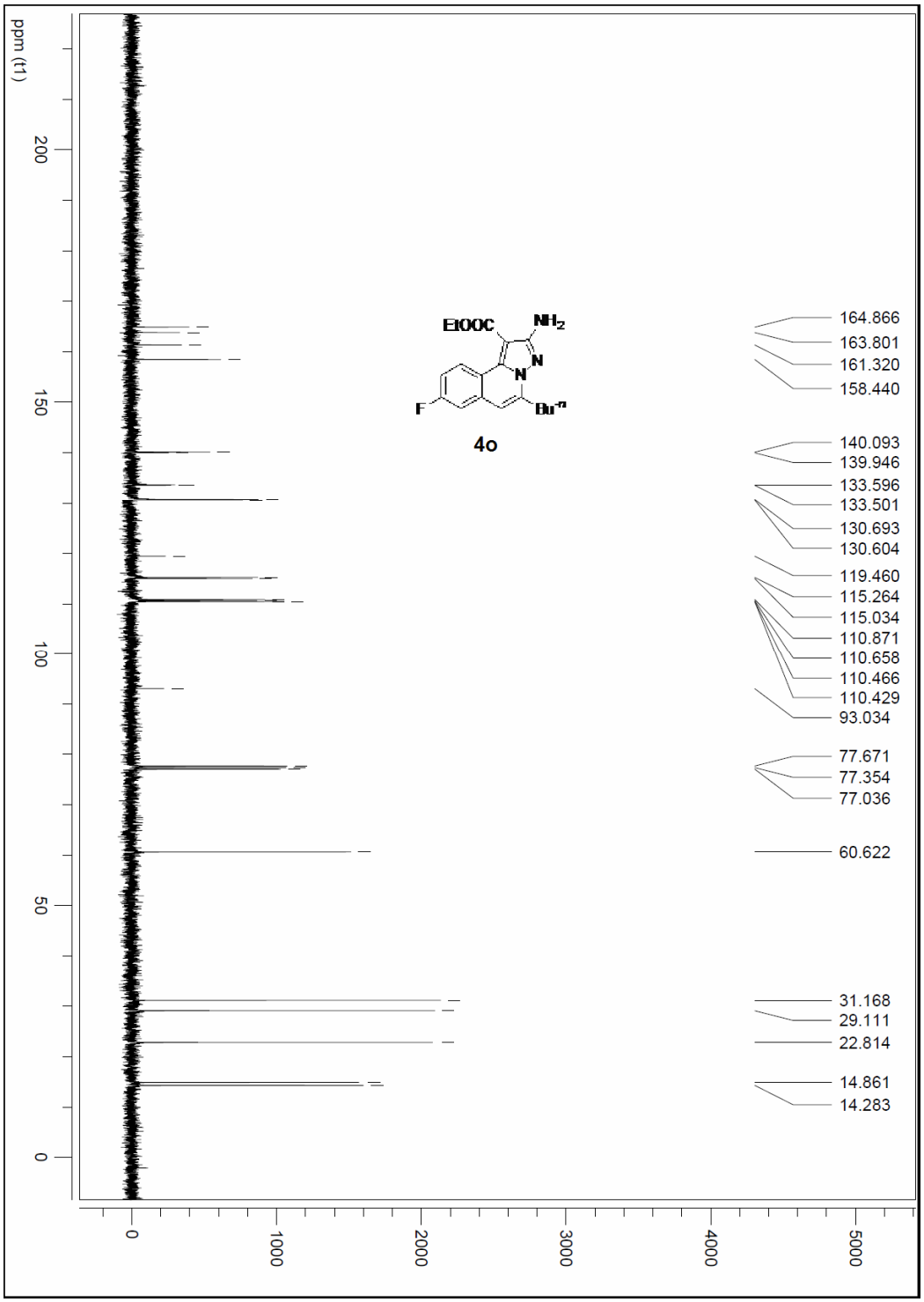
0.0
7.98
20.20
9.58
19.70
19.48
20.15
21.92
50.76
30.15
EtOOC
NH2
N
N
F
Bu
4o
9.742
9.728
9.720
9.705
7.259
7.237
7.217
7.210
6.807
5.212
4.485
4.467
4.449
4.431
3.049
3.030
3.011
1.833
1.815
1.795
1.776
1.757
1.524
1.505
1.495
1.487
1.477
1.469
1.459
1.450
1.431
1.008
0.990
0.972
-0.0000
0
100
200
300
400
500
600


ppm (t1)
200
150
100
50
0
0
1000
2000
3000
4000
5000
EtOOC
NH2
N
N
F
Bu-n
4o
164.866
163.801
161.320
158.440
140.093
139.946
133.596
133.501
130.693
130.604
119.460
115.264
115.034
110.871
110.658
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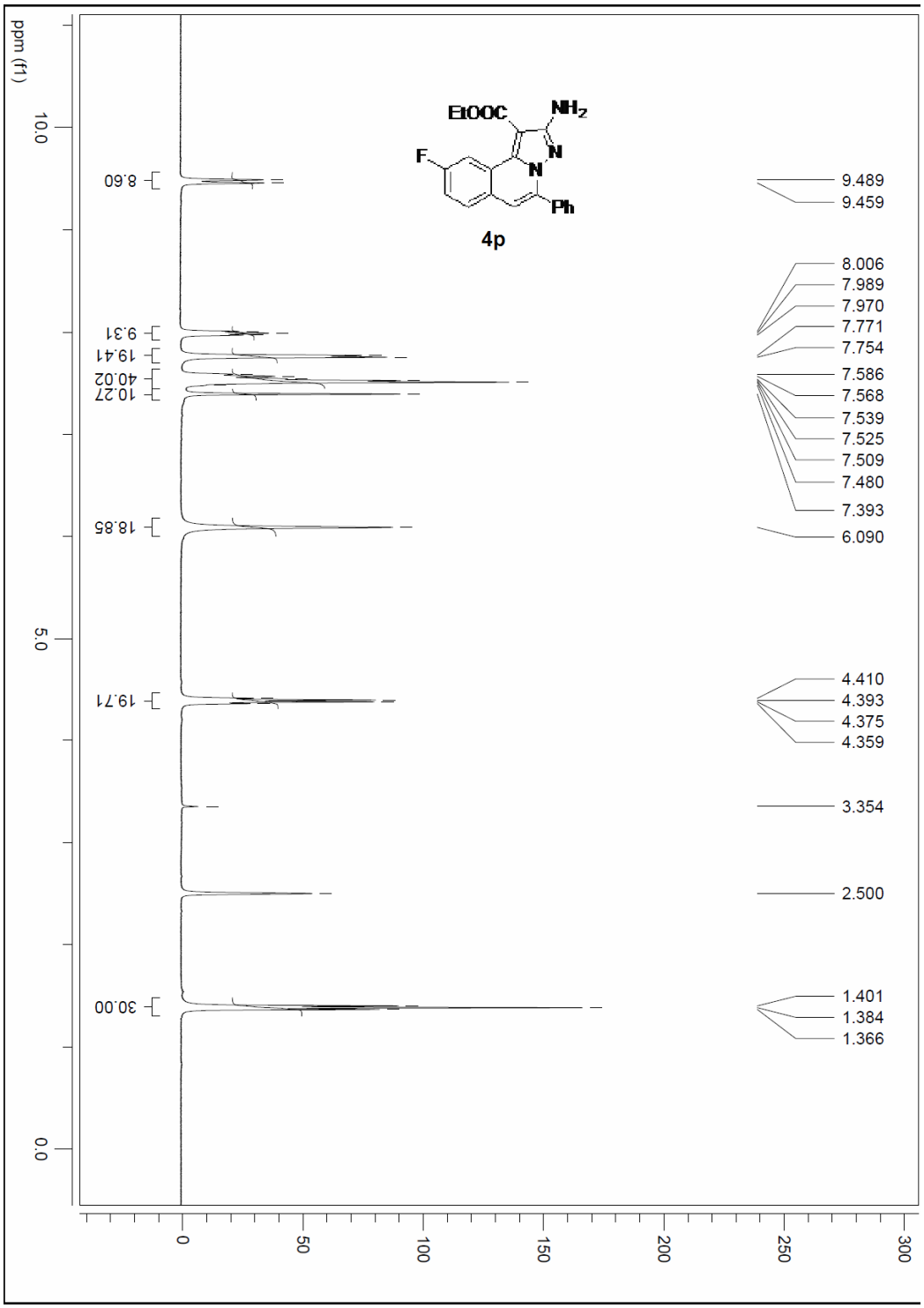
77.671
77.354
77.036
60.622
31.168
29.111
22.814
14.861
14.283


ppm (f1)
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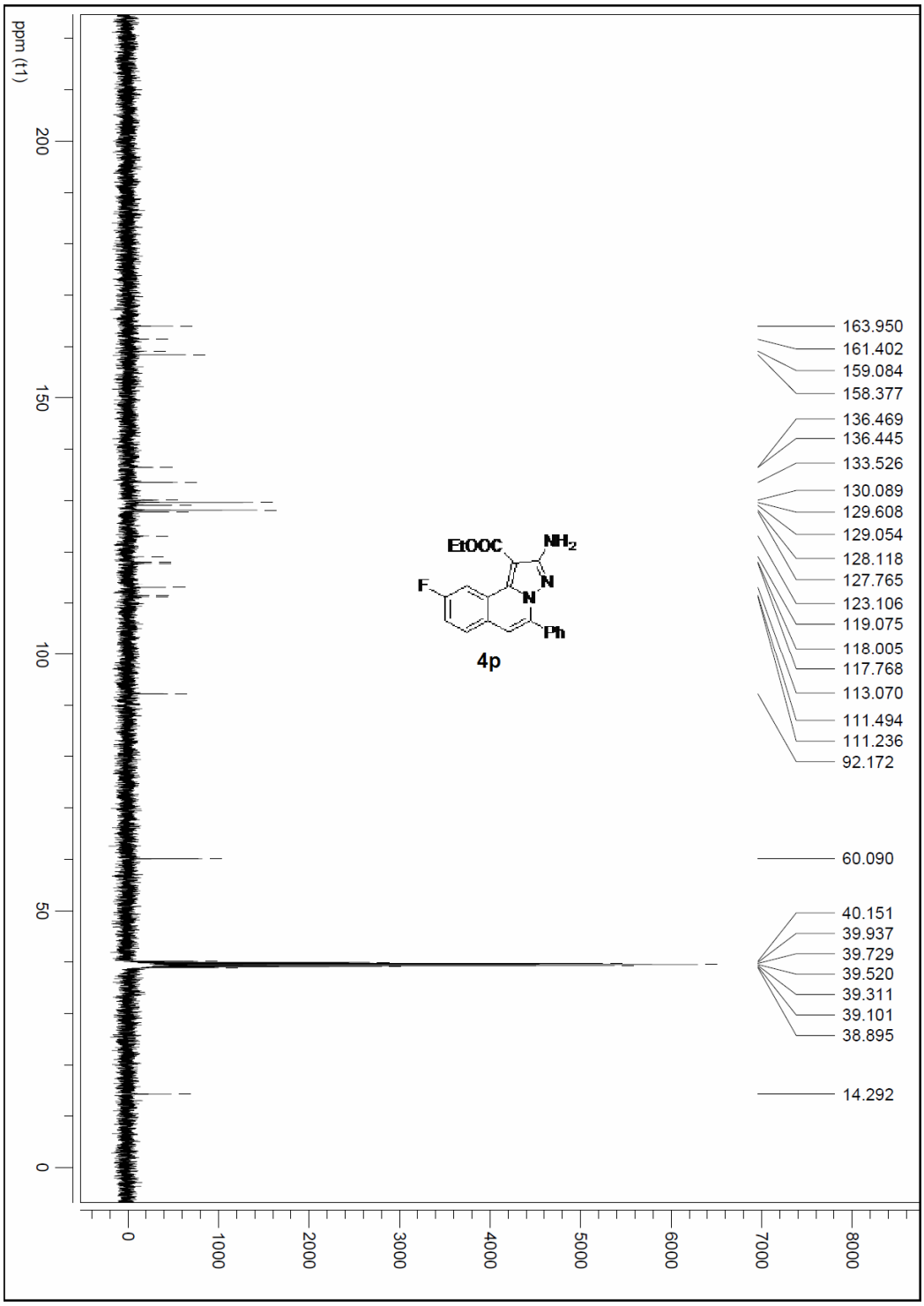
0
50
100
150
200
250
300
EtOOC
NH2
F
N
N
Ph
4p
8.60
9.31
19.41
40.02
10.27
18.85
19.71
30.00
9.489
9.459
8.006
7.989
7.970
7.771
7.754
7.586
7.568
7.539
7.525
7.509
7.480
7.393
6.090
4.410
4.393
4.375
4.359
3.354
2.500
1.401
1.384
1.366


ppm (t1)
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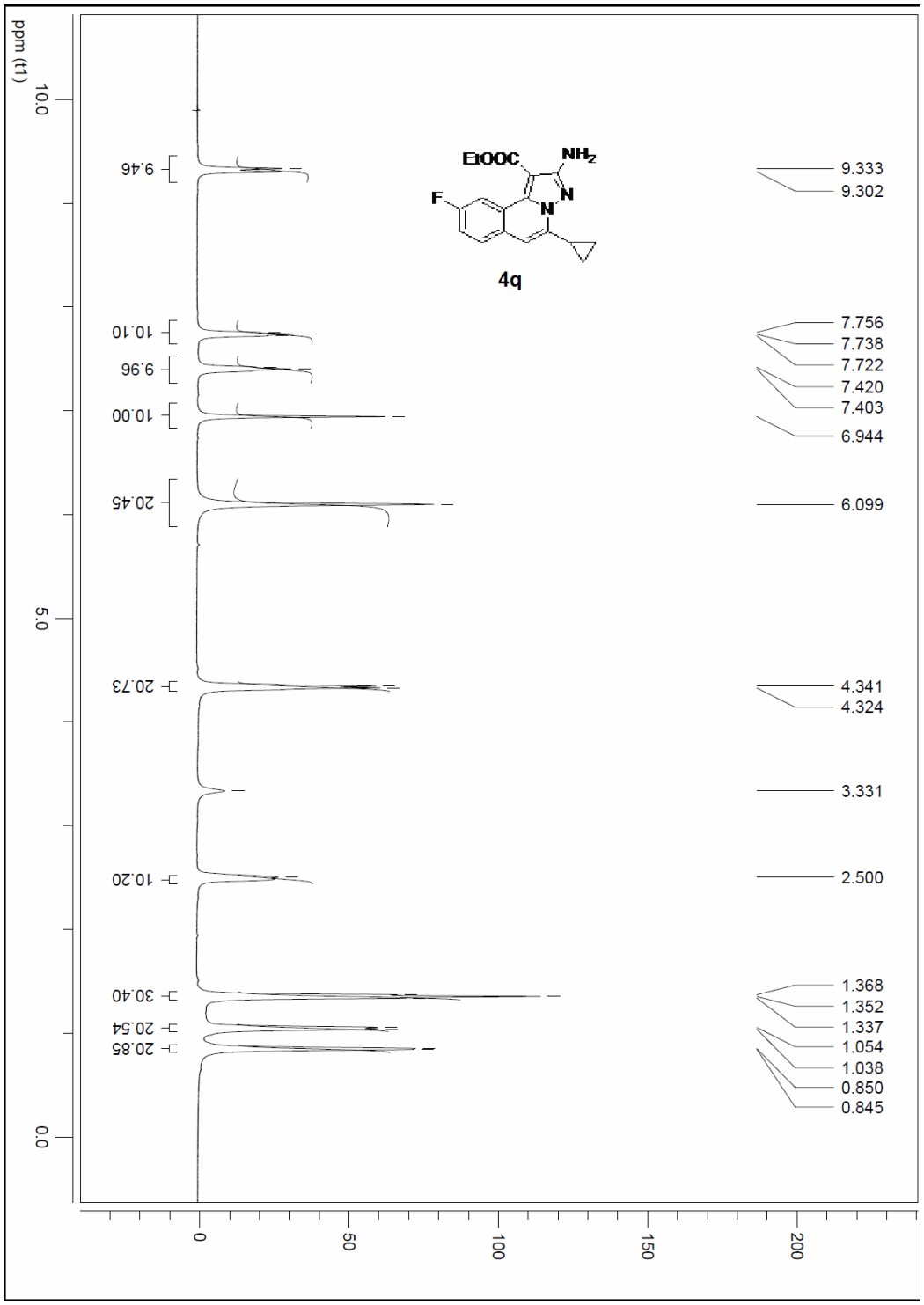
150
100
50
0
0
1000
2000
3000
4000
5000
6000
7000
8000
EtOOC
NH2
F
N
N
Ph
4p
163.950
161.402
159.084
158.377
136.469
136.445
133.526
130.089
129.608
129.054
128.118
127.765
123.106
119.075
118.005
117.768
113.070
111.494
111.236
92.172
60.090
40.151
39.937
39.729
39.520
39.311
39.101
38.895
14.292


ppm (t1)
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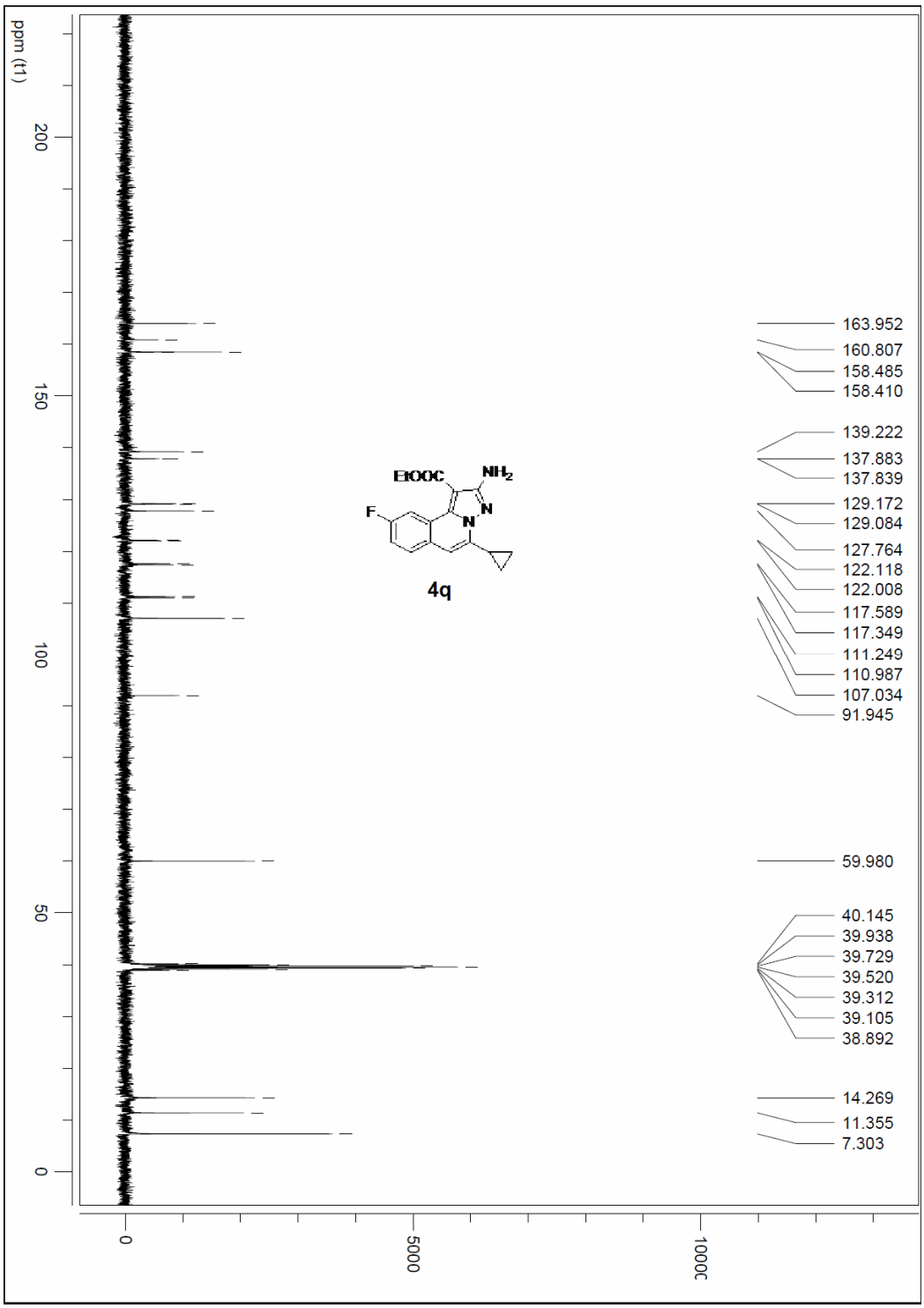
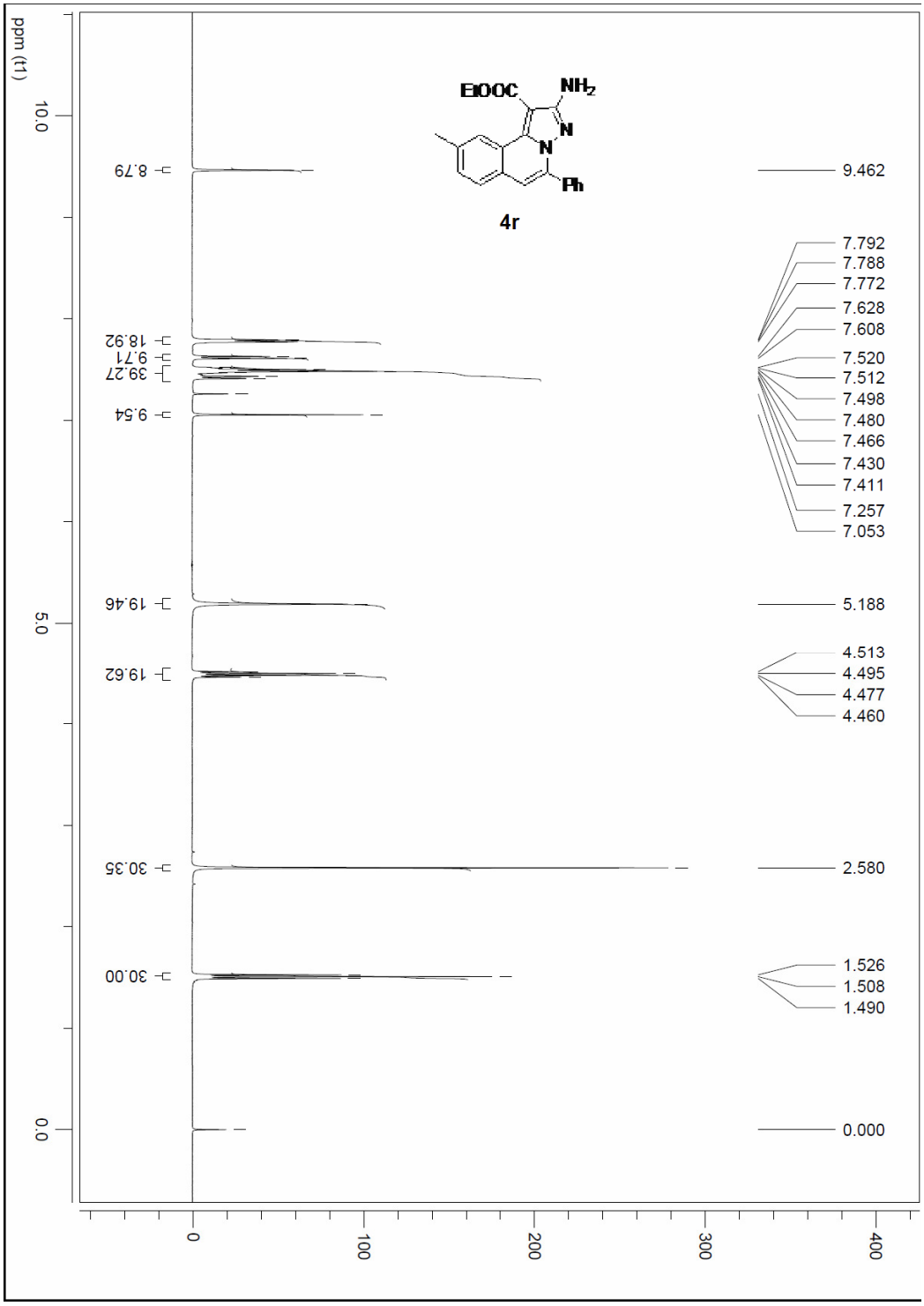
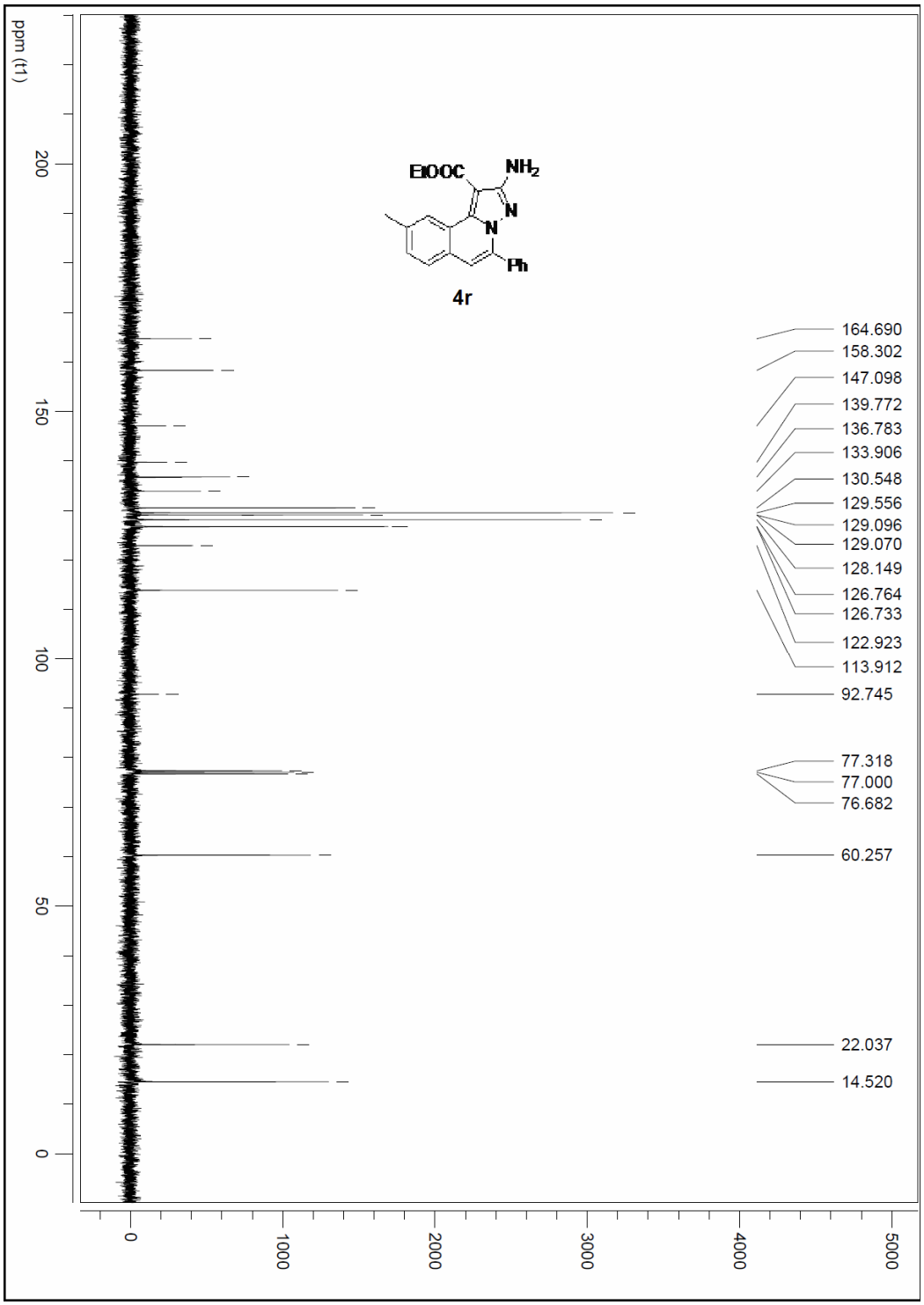
0
50
100
150
200
9.46
10.10
9.96
10.00
20.45
20.73
10.20
30.40
20.54
20.85
EtOOC
NH2
F
N
N
4q
9.333
9.302
7.756
7.738
7.722
7.420
7.403
6.944
6.099
4.341
4.324
3.331
2.500
1.368
1.352
1.337
1.054
1.038
0.850
0.845


ppm (t1)
200
150
100
50
0
0
5000
10000
EtOOC
NH2
F
N
N
4q
163.952
160.807
158.485
158.410
139.222
137.883
137.839
129.172
129.084
127.764
122.118
122.008
117.589
117.349
111.249
110.987
107.034
91.945
59.980
40.145
39.938
39.729
39.520
39.312
39.105
38.892
14.269
11.355
7.303


ppm (t1)
10.0
5.0
0.0
0
100
200
300
400
8.79
18.92
9.71
39.27
9.54
19.46
19.62
30.35
30.00
EtOOC
NH2
N
N
Ph
4r
9.462
7.792
7.788
7.772
7.628
7.608
7.520
7.512
7.498
7.480
7.466
7.430
7.411
7.257
7.053
5.188
4.513
4.495
4.477
4.460
2.580
1.526
1.508
1.490
0.000


ppm (t1)
200
150
100
50
0
0
1000
2000
3000
4000
5000
EtOOC
NH2
N
N
Ph
4r
164.690
158.302
147.098
139.772
136.783
133.906
130.548
129.556
129.096
129.070
128.149
126.764
126.733
122.923
113.912
92.745
77.318
77.000
76.682
60.257
22.037
14.520