Electronic Supplementary Material (ESI) for Chemical Communications

Palladium-Catalyzed Reaction of 2-Alkynylhalobenzene with 2-Alkynylbenzamide: An Efficient Approach to Indeno[1,2-*c*]azepin-3(2*H*)-ones

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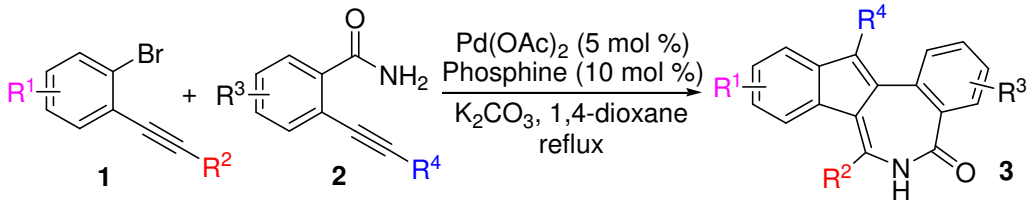
Supporting Information

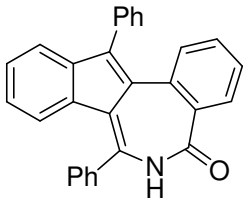
General experimental methods:

All reactions were performed in reaction tubes under nitrogen atmosphere. 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 on rotary evaporators at ~20 Torr (house vacuum) at 25–35°C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

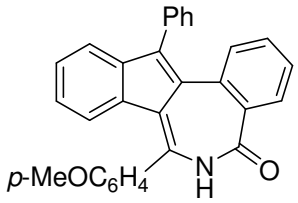
General procedure for the synthesis of indeno[1,2-*c*]azepin-3(2*H*)-ones via a Pd-catalyzed reaction of 2-alkynylbromobenzene **1** with 2-alkynylbenzamide **2**.



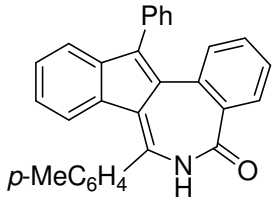
2-Alkynylhalobenzene (0.24 mmol) was added to a mixture of $Pd(OAc)_2$ (0.01 mmol, 5 mol %), PCy_3 or PPh_3 (0.02 mmol, 10 mol %), K_2CO_3 (0.4 mmol), and 2-alkynylbenzamide (0.20 mmol) in 1,4-dioxane (2.0 mL). The reaction was stirred under reflux conditions. After completion of the reaction as indicated by TLC (usually 3-6 hours), the reaction was cooled and the mixture was purified immediately by flash chromatography on silica gel to give products **3**.



7,12-Diphenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.0 Hz, 1H), 7.94 (br, 1H), 7.63-7.59 (m, 5H), 7.47-7.33 (m, 7H), 7.27 (t, J = 7.8 Hz, 1H), 7.19-7.14 (m, 2H), 6.89 (t, J = 8.0 Hz, 1H), 6.08 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz) δ 168.0, 140.9, 140.2, 138.9, 137.6, 136.4, 135.2, 134.8, 132.7, 132.3, 131.9, 130.2, 129.8, 129.7, 129.0, 128.5, 127.6, 127.1, 125.9, 124.8, 122.2, 121.4, 120.1. HRMS (ESI) calculated for $C_{29}H_{19}NO$ $[M+Na]^+$ requires 420.1364, found 420.1369.

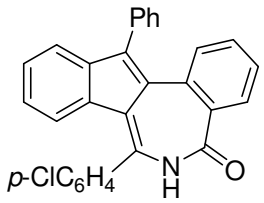


7-(4-Methoxyphenyl)-12-phenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 7.6 Hz, 1H), 7.88(br, 1H), 7.51-7.49 (m, 2H), 7.46-7.35 (m, 7H), 7.9-7.25 (m, 1H), 7.20-7.16 (m, 2H), 7.12-7.09 (m, 2H), 6.93 (t, J = 7.6 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz) δ 168.0, 160.9, 147.3, 140.8, 139.9, 139.1, 136.5, 135.4, 134.8, 132.7, 132.2, 131.8, 130.0, 129.9, 129.8, 129.7, 129.0, 127.6, 127.1, 125.8, 124.9, 122.3, 121.4, 120.1, 114.9, 55.5. HRMS (ESI) calculated for $C_{30}H_{21}NO_2$ $[M+H]^+$ requires 428.1651, found 428.1648.

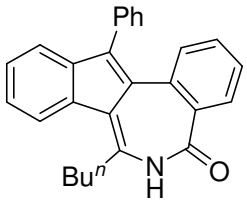


12-Phenyl-7-(*p*-tolyl)benzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3c**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 7.2 Hz, 1H), 7.77(br, 1H), 7.47-7.27 (m, 11H), 7.28 (t, J = 7.2Hz, 1H), 7.20-7.16 (m, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.19 (d, J = 8.0 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz) δ 168.0, 147.3, 140.9, 140.4, 140.0, 139.2, 136.5, 135.3, 134.9,

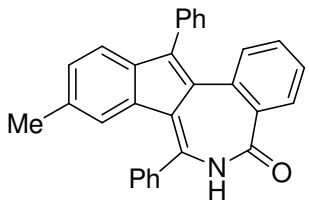
134.7, 132.8, 132.3, 131.9, 130.4, 129.9, 129.0, 128.4, 127.6, 127.1, 125.8, 124.8, 121.4, 120.1, 21.6. HRMS (ESI) calculated for $C_{30}H_{21}NO$ $[M+H]^+$ requires 412.1701, found 412.1703.



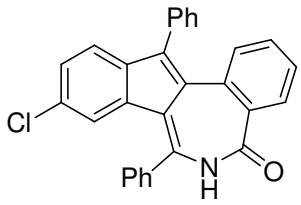
7-(4-Chlorophenyl)-12-phenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3d**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.0 Hz, 1H), 7.78(br, 1H), 7.61-7.51 (m, 4H), 7.45-7.40 (m, 6H), 7.35-7.27 (m, 2H), 7.23-7.17 (m, 2H), 6.95 (t, J = 7.2 Hz, 1H), 6.16 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz) δ 168.0, 141.1, 140.6, 137.4, 136.4, 136.2, 135.9, 135.0, 134.7, 132.7, 132.3, 132.0, 131.8, 130.2, 130.1, 130.0, 129.8, 129.7, 129.1, 127.8, 127.2, 126.2, 125.0, 121.3, 120.3. HRMS (ESI) calculated for $C_{29}H_{18}ClNO$ $[M+Na]^+$ requires 454.0975, found 454.0983.



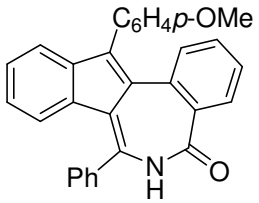
7-Butyl-12-phenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3e**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (br, 1H), 8.25-8.23 (m, 1H), 7.72-7.70 (m, 1H), 7.53-7.51 (m, 1H), 7.46-7.40 (m, 4H), 7.37-7.31 (m, 3H), 7.27-7.24 (m, 2H), 7.14-7.10 (m, 1H), 3.02 (t, J = 8.4 Hz, 2H), 1.94-1.90 (m, 2H), 1.66-1.60 (m, 2H), 1.07-1.03 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz) δ 169.0, 147.4, 141.2, 141.0, 136.4, 135.2, 134.9, 132.9, 132.6, 131.9, 131.8, 130.0, 129.4, 128.9, 127.5, 126.9, 125.7, 125.2, 121.7, 121.5, 120.6, 35.9, 30.7, 22.8, 13.9. HRMS (ESI) calculated for $C_{27}H_{23}NO$ $[M+H]^+$ requires 378.1858, found 378.1865.



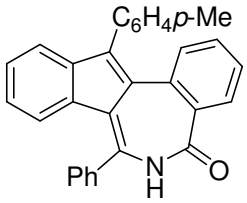
9-Methyl-7,12-diphenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3f**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.0 Hz, 1H), 7.70(br, 1H), 7.64-7.55 (m, 5H), 7.47-7.41 (m, 4H), 7.39-7.32 (m, 2H), 7.29-7.27 (m, 2H), 7.17-7.15 (m, 1H), 7.00 (d, J = 8.0 Hz, 1H), 5.83 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz) δ 168.0, 138.7, 138.4 137.7, 136.6, 134.5, 132.7, 132.3, 131.9, 130.1, 129.8, 129.6, 129.0, 128.6, 127.6, 126.9, 126.8, 122.2, 119.8, 21.8. HRMS (ESI) calculated for $C_{30}H_{21}NO$ $[M+Na]^+$ requires 434.1521, found 434.1527.



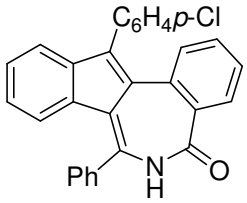
9-Chloro-7,12-diphenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3g**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 7.6 Hz, 1H), 7.75 (br, 1H), 7.68-7.62 (m, 3H), 7.58-7.56 (m, 2H), 7.45-7.43 (m, 5H), 7.35-7.29 (m, 3H), 7.20-7.12 (m, 2H), 5,95 (s, 1H). ^{13}C NMR (100 MHz) δ 132.7, 132.5, 132.1, 130.6, 129.9, 129.8, 129.2, 128.4, 128.9, 127.4, 125.8, 121.6, 120.9. HRMS (ESI) calculated for $C_{28}H_{18}ClNO$ $[M+H]^+$ requires 432.1155, found 432.1178.



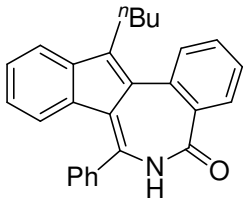
12-(4-Methoxyphenyl)-7-phenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3h**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25(dd, J = 7.6, 1.2 Hz, 1H), 7.69 (br, 1H), 7.63-7.55 (m, 5H), 7.43-7.39 (m, 4H), 7.31-7.29 (m, 1H), 7.22-7.17 (m, 2H), 6.99-6.90 (m, 2H), 6.88 (t, J = 7.6 Hz, 1H), 6.08 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz) δ 168.1, 137.7, 132.6, 132.3, 131.9, 131.0, 130.2, 129.7, 128.5, 127.0, 125.9, 124.8, 121.4, 120.2, 114.5. HRMS (ESI) calculated for $C_{30}H_{21}NO_2$ $[M+Na]^+$ requires 450.1470, found 450.1485.



7-Phenyl-12-(*p*-tolyl)benzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3i**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 7.6 Hz, 1H), 7.72(br, 1H), 7.63-7.55 (m, 5H), 7.42-7.34 (m, 4H), 7.31-7.23 (m, 3H), 7.20-7.16 (m, 2H), 6.88 (t, J = 7.6 Hz, 1H), 6.08 (d, J = 7.6 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz) δ 168.0, 141.1, 140.3, 138.5, 137.6, 137.4, 135.2, 135.0, 133.3, 132.7, 132.3, 131.9, 130.2, 129.8, 129.73, 129.70, 128.5, 127.0, 125.9, 124.8, 121.3, 120.2, 21.4. HRMS (ESI) calculated for $C_{30}H_{21}NO$ $[M+H]^+$ requires 412.1701, found 412.1715.

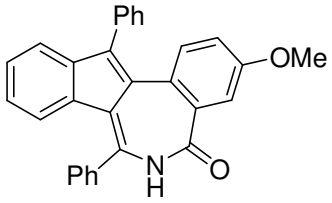


12-(4-Chlorophenyl)-7-phenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3j**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 7.6 Hz, 1H), 7.78(br, 1H),7.63-7.56 (m, 4H), 7.46-7.41 (m, 5H), 7.37-7.31 (m, 4H), 7.25-7.17 (m, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.09 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz) δ 167.9, 140.5, 139.3, 138.7, 137.5, 135.2, 134.9, 134.5, 133.6, 133.4, 132.7, 132.4, 132.1, 131.2, 130.3, 129.9, 129.8, 129.4, 128.9, 128.5, 127.4, 126.0, 125.0, 121.4, 119.9. HRMS (ESI) calculated for $C_{29}H_{18}ClNO$ $[M+H]^+$ requires 432.1155, found 432.1138.

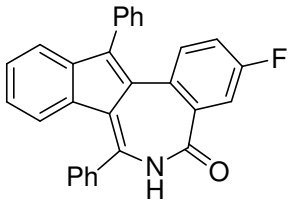


12-butyl-7-phenylbenzo[c]indeno[2,1-e]azepin-5(6H)-one **3k**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 8.0 Hz, 1H), 7.73-7.71(m, 1H), 7.66-7.62 (m, 2H), 7.60-7.51 (m, 5H), 7.48-7.44 (m, 2H), 7.24-7.20 (m, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.02 (d, J = 8.0 Hz,

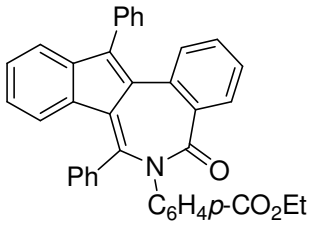
1H), 2.99 (t, J = 8.0 Hz, 2H), 1.84-1.80 (m, 2H), 1.54-1.48 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz) δ 167.9, 147.3, 141.4, 140.6, 137.7, 136.8, 135.3, 135.2, 132.5, 132.46, 132.43, 132.1, 130.7, 130.0, 129.6, 128.7, 127.1, 124.4, 125.6, 121.1, 119.2, 31.5, 27.3, 23.3, 13.9. HRMS (ESI) calculated for $C_{27}H_{23}NO$ $[M+H]^+$ requires 378.1858, found 378.1827.



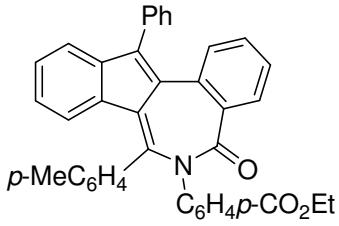
3-Methoxy-7,12-diphenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3l**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.74 (br, 1H), 7.61-7.58 (m, 5H), 7.45-7.37 (m, 6H), 7.30-7.25 (m, 1H), 7.17 (d, J = 7.6 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 6.75 (dd, J = 8.8, 2.4 Hz, 1H), 6.07 (d, J = 7.6 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz) δ 167.6, 158.3, 147.3, 141.2, 138.6, 138.3, 137.6, 136.6, 134.9, 134.4, 131.7, 130.8, 130.2, 129.8, 129.7, 129.0, 128.6, 127.5, 125.9, 124.5, 122.5, 121.4,120.2,119.8,114.2, 55.5. HRMS (ESI) calculated for $C_{30}H_{21}NO_2$ $[M+H]^+$ requires 428.1651, found 428.1623.



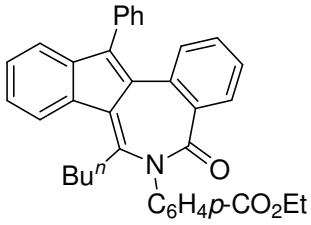
3-Fluoro-7,12-diphenylbenzo[*c*]indeno[2,1-*e*]azepin-5(6*H*)-one **3m**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (br, 1H), 7.87 (dd, J = 10, 2.8 Hz, 1H), 7.65-7.57 (m, 5H), 7.45-7.44 (m, 4H), 7.40-7.38 (m, 2H), 7.37-7.32 (m, 1H), 7.18 (t, J = 7.2 Hz, 1H), 6.91-6.87 (m, 2H), 6.09 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz) δ 166.6, 161.1 (d, $J_{(C,F)}$ = 247.3 Hz), 140.9, 140.1, 138.6, 137.3, 136.1, 135.0, 134.9 (d, $J_{(C,F)}$ = 7.2 Hz), 131.6 (d, $J_{(C,F)}$ = 7.1 Hz), 131.2, 130.8, 130.3, 129.8, 129.7, 129.2, 128.5, 127.8, 126.1, 125.0, 122.5, 121.5, 120.1, 119.6, (d, $J_{(C,F)}$ = 21.4 Hz), 118.0 (d, $J_{(C,F)}$ = 23.8 Hz). HRMS (ESI) calculated for $C_{29}H_{18}FNO$ $[M+H]^+$ requires 416.1451, found 416.1434.



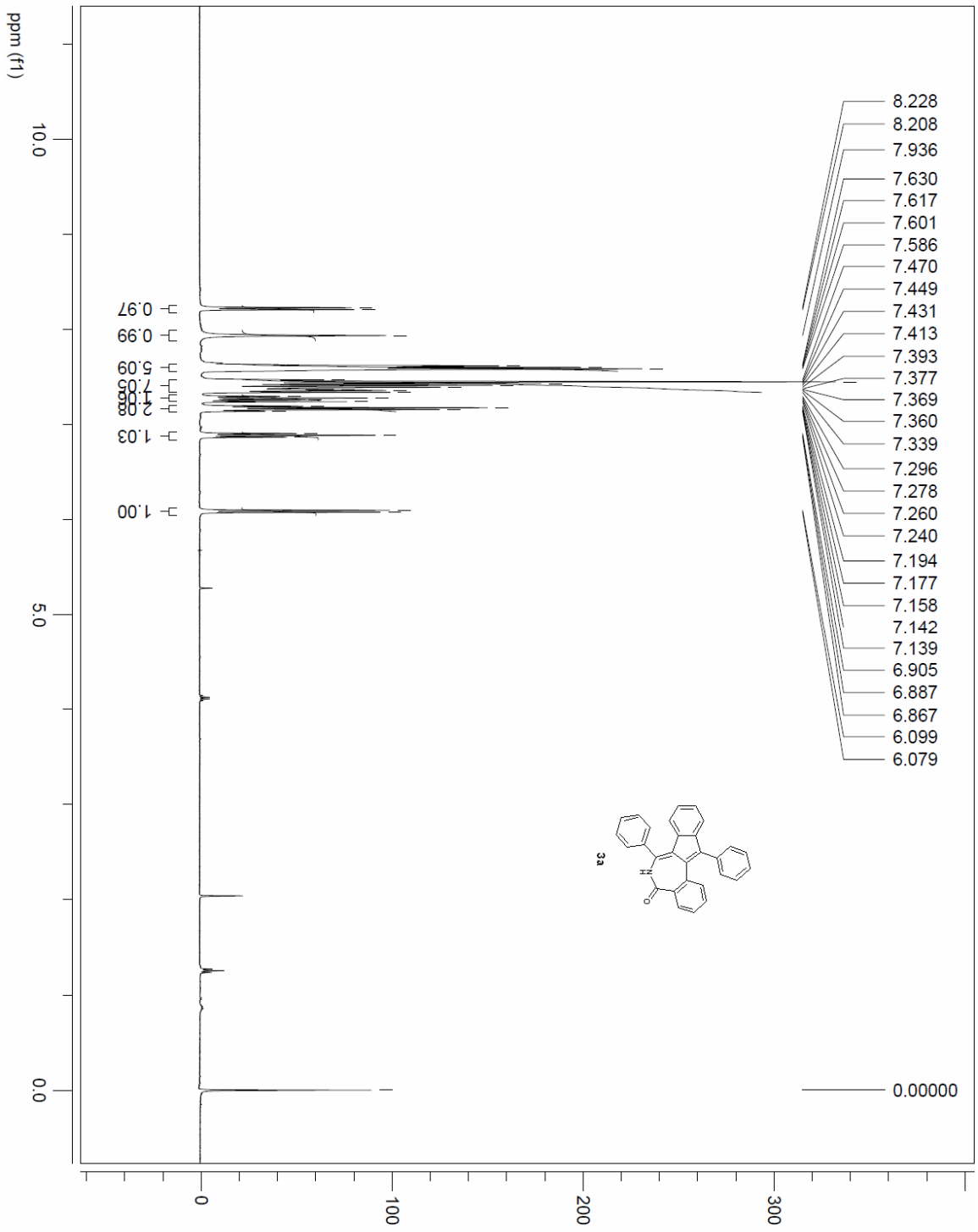
Ethyl 4-(5-oxo-7,12-diphenylbenzo[*c*]indeno[2,1-*e*]azepin-6(5*H*)-yl)benzoate **3n**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.58 (m, 2H), 7.48-7.40 (m, 4H), 7.27-7.20 (m, 5H), 7.17-7.12 (m, 4H), 7.05-7.03 (m, 2H), 6.77 (t, J = 8.0 Hz, 1H), 5.47 (t, J = 8.0 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz) δ 170.2, 165.8, 145.2, 141.4, 141.1, 140.8,137.1, 136.4, 135.8, 134.7, 132.5, 132.3, 131.9, 131.5, 131.2, 130.34, 130.30, 130.0, 129.9, 129.4, 129.0, 128.6, 128.5, 128.0, 127.1, 127.0, 126.1, 124.9, 122.1, 120.3, 61.1, 14.2. HRMS (ESI) calculated for $C_{38}H_{27}NO_3$ $[M+H]^+$ requires 546.2069, found 546.2054.



Ethyl 4-(5-oxo-12-phenyl-7-(*p*-tolyl)benzo[*c*]indeno[2,1-*e*]azepin-6(5*H*)-yl)benzoate **3o**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.59-7.57 (m, 2H), 7.47-7.39 (m, 4H), 7.26-7.12 (m, 6H), 7.03-7.01 (m, 2H), 6.92-6.90 (m, 2H), 6.80 (t, J = 7.6 Hz, 1H), 5.53 (d, J = 8.0 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 2.32 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz) δ 170.3, 165.9, 147.2, 145.2, 141.7, 141.0, 140.6, 138.5, 137.3, 135.9, 134.7, 133.4, 132.4, 132.2, 132.0, 131.4, 131.2, 130.3, 130.1, 129.98, 129.93, 129.3, 129.2, 129.0, 127.9, 127.0, 126.0, 124.9, 122.1, 120.3, 21.4, 14.2. HRMS (ESI) calculated for $C_{39}H_{29}NO_3$ $[M+H]^+$ requires 560.2226, found 560.2189.



Ethyl 4-(7-butyl-5-oxo-12-phenylbenzo[*c*]indeno[2,1-*e*]azepin-6(5*H*)-yl)benzoate **3p**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 6.8 Hz, 1H), 7.58-7.55 (m, 3H), 7.46-7.39 (m, 5H), 7.35-7.32 (m, 2H), 7.25-7.22 (m, 1H), 7.11 (t, J = 8.0 Hz, 1H), 7.04-7.02 (m, 1H), 4.41 (q, J = 7.6 Hz, 2H), 2.69 (t, J = 8.0 Hz, 2H), 1.65-1.62 (m, 2H), 1.42 (t, J = 6.8 Hz, 3H), 0.88-0.84 (m, 2H), 0.79 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz) δ 169.9, 165.8, 147.3, 146.4, 145.4, 141.6, 140.9, 136.6, 135.5, 134.9, 133.2, 131.9, 131.8, 131.7, 131.1, 130.7, 130.1, 130.0, 129.0, 128.9, 128.1, 127.0, 126.4, 125.9, 121.9, 121.4, 61.2, 34.3, 32.5, 22.4, 14.3, 13.8. HRMS (ESI) calculated for $C_{36}H_{31}NO_3$ $[M+H]^+$ requires 526.2382, found 526.2368.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7.601
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7.449
7.431
7.413
7.393
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7.339
7.296
7.278
7.260
7.240
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7.158
7.142
7.139
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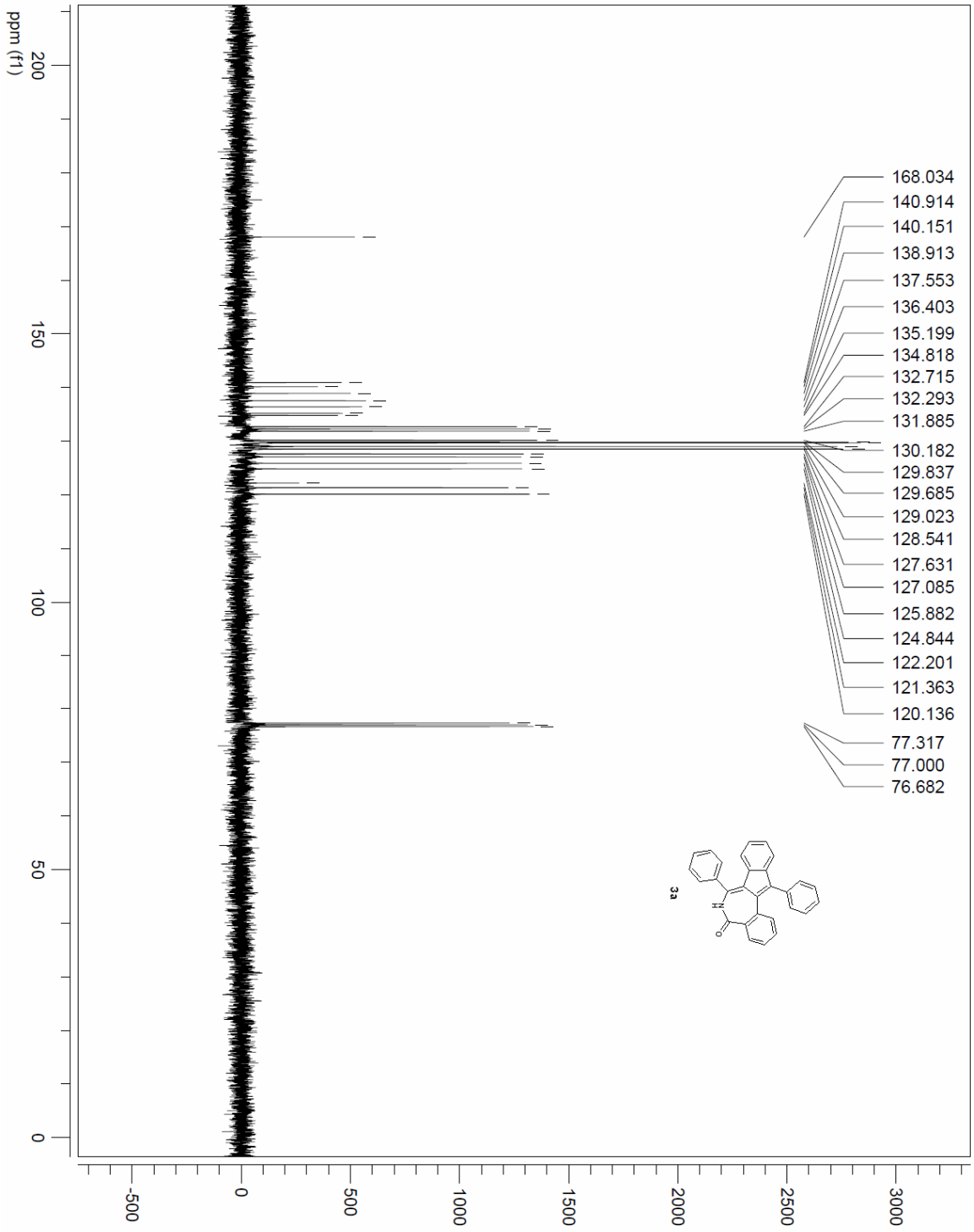

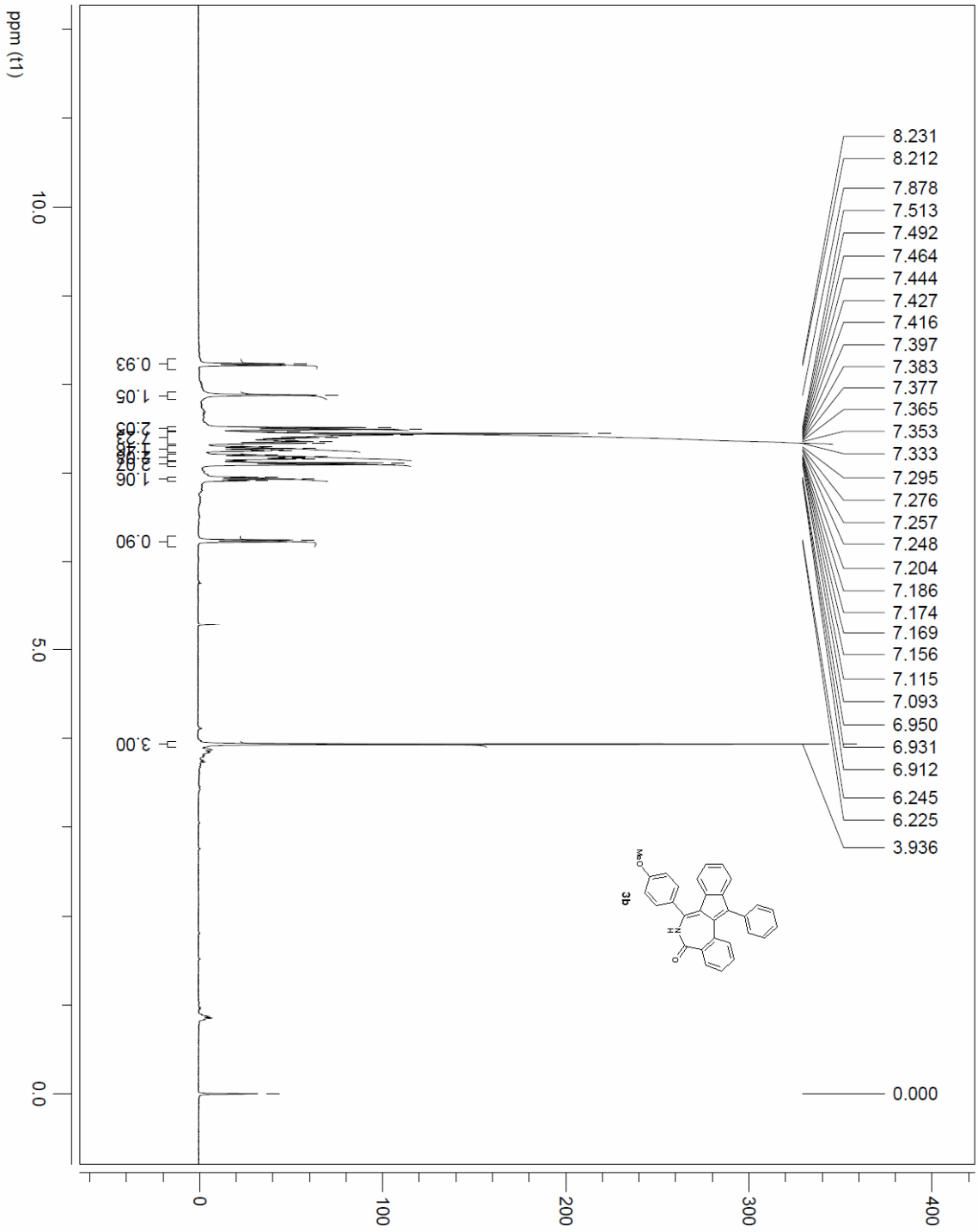
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N
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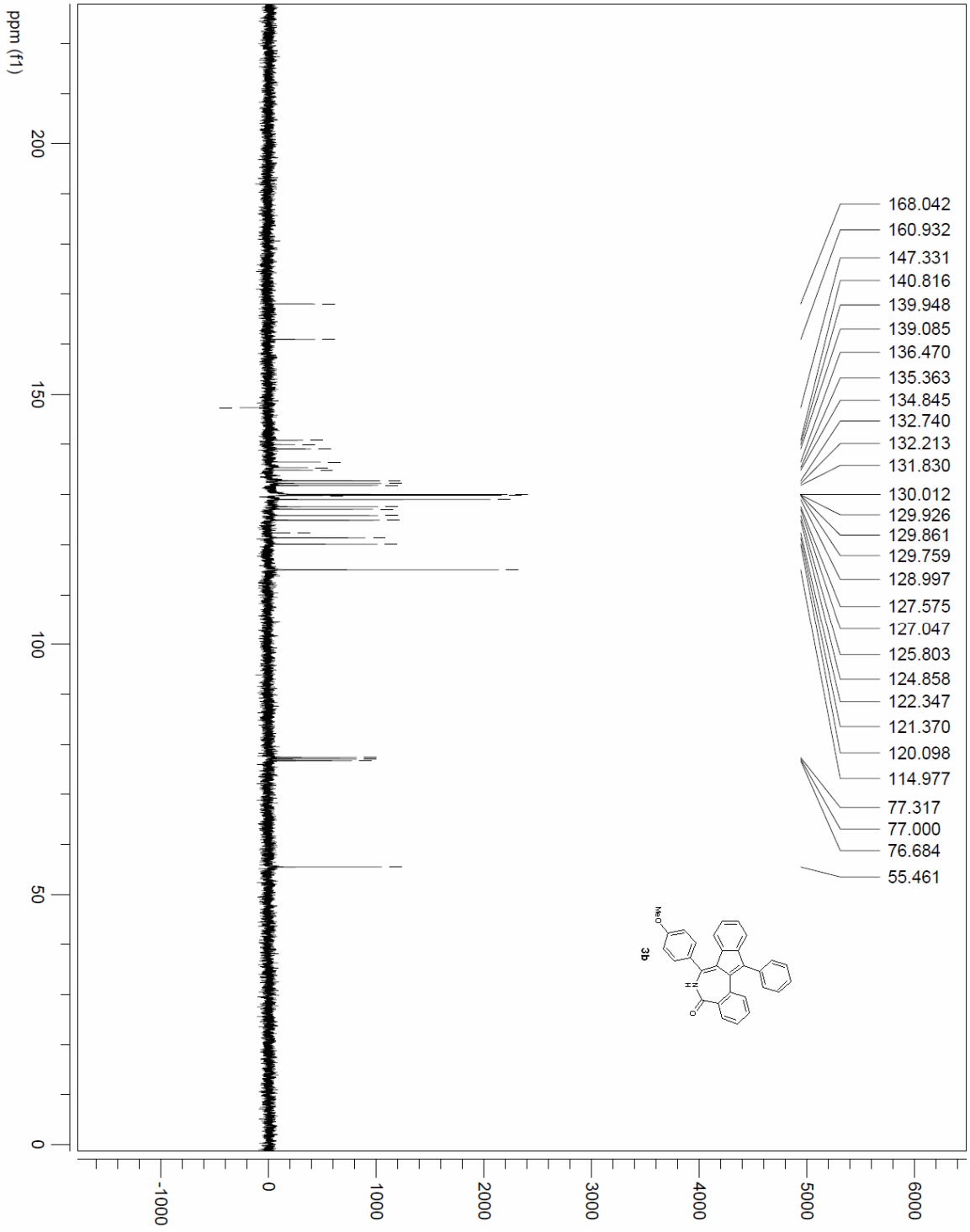

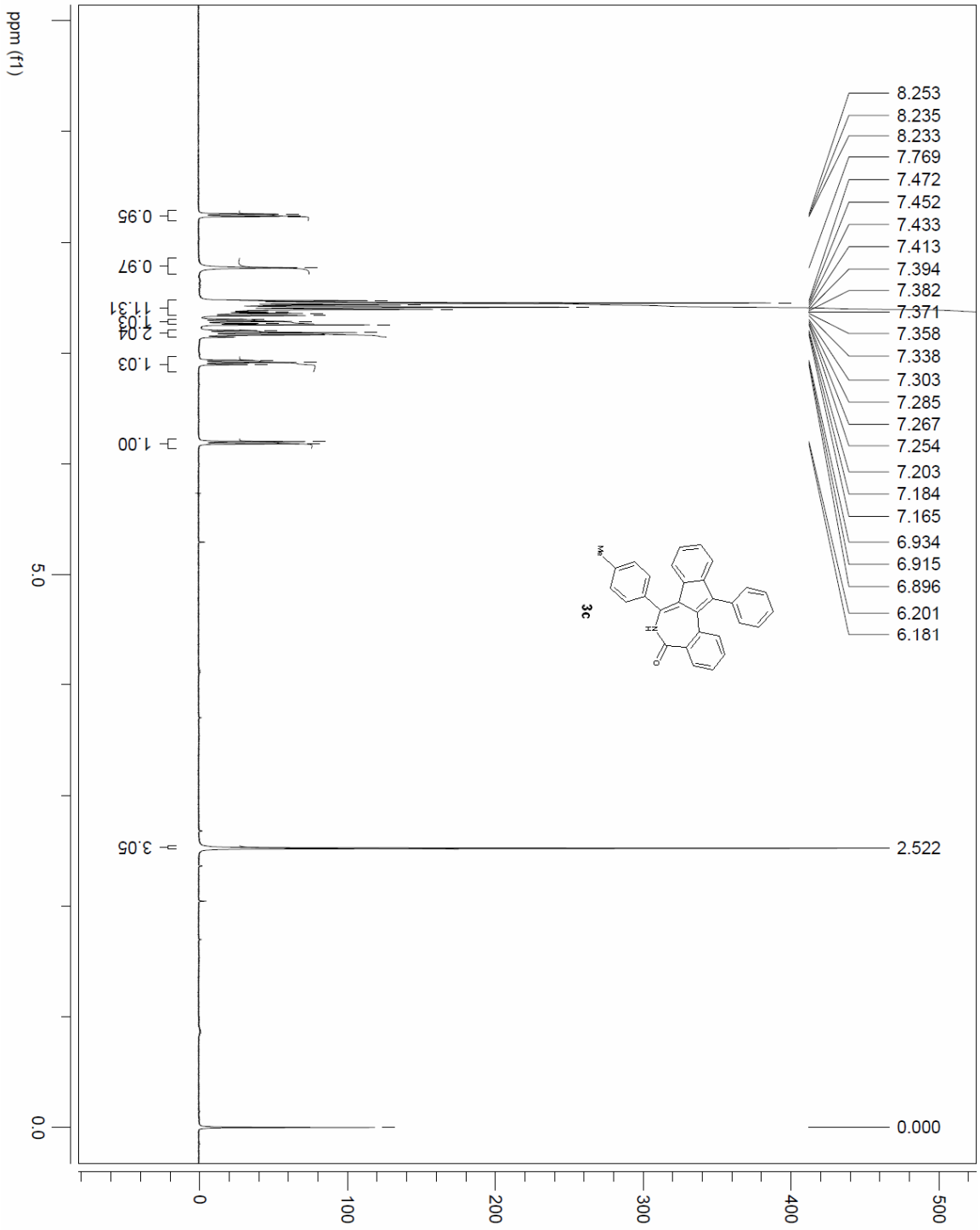
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7.203
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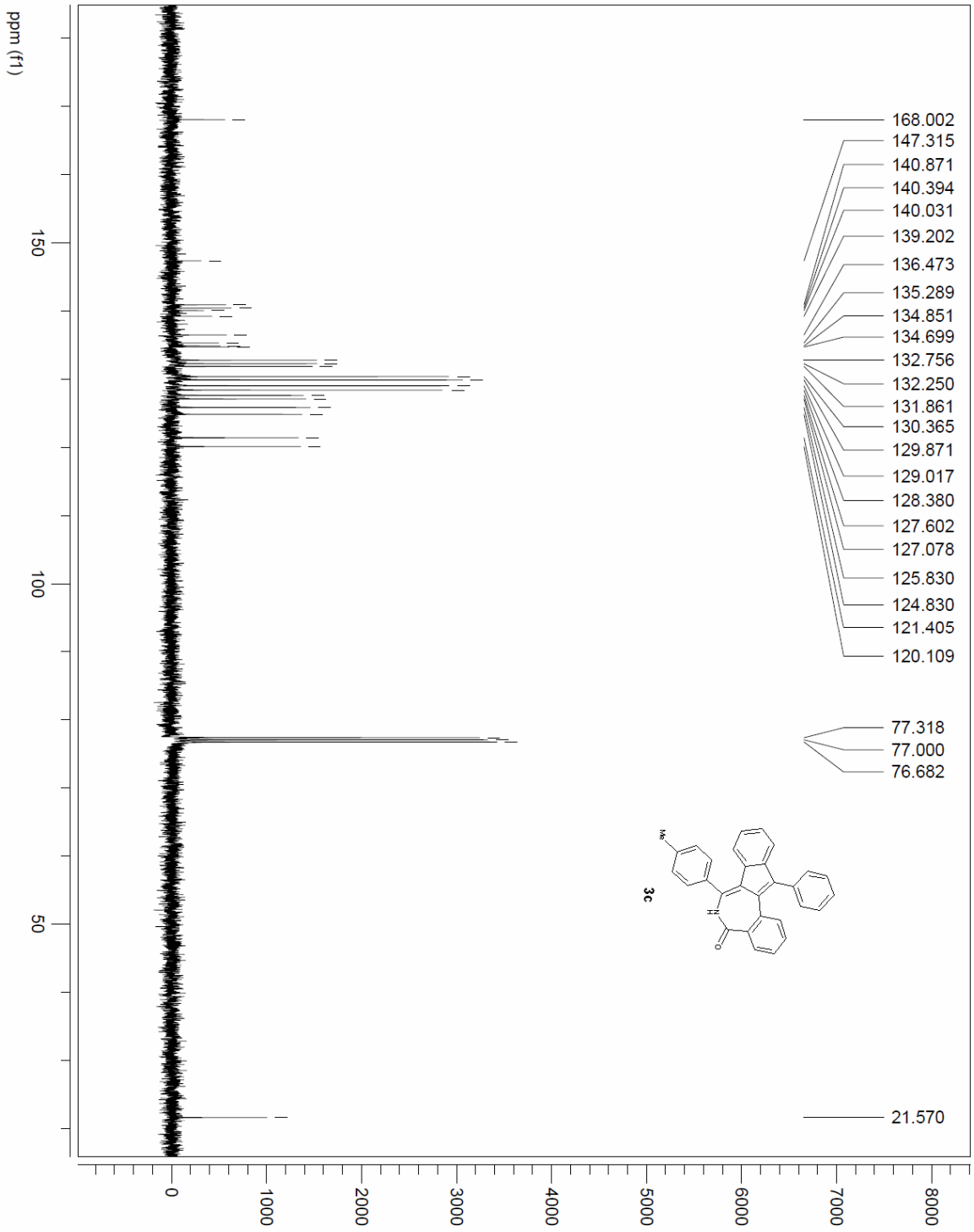

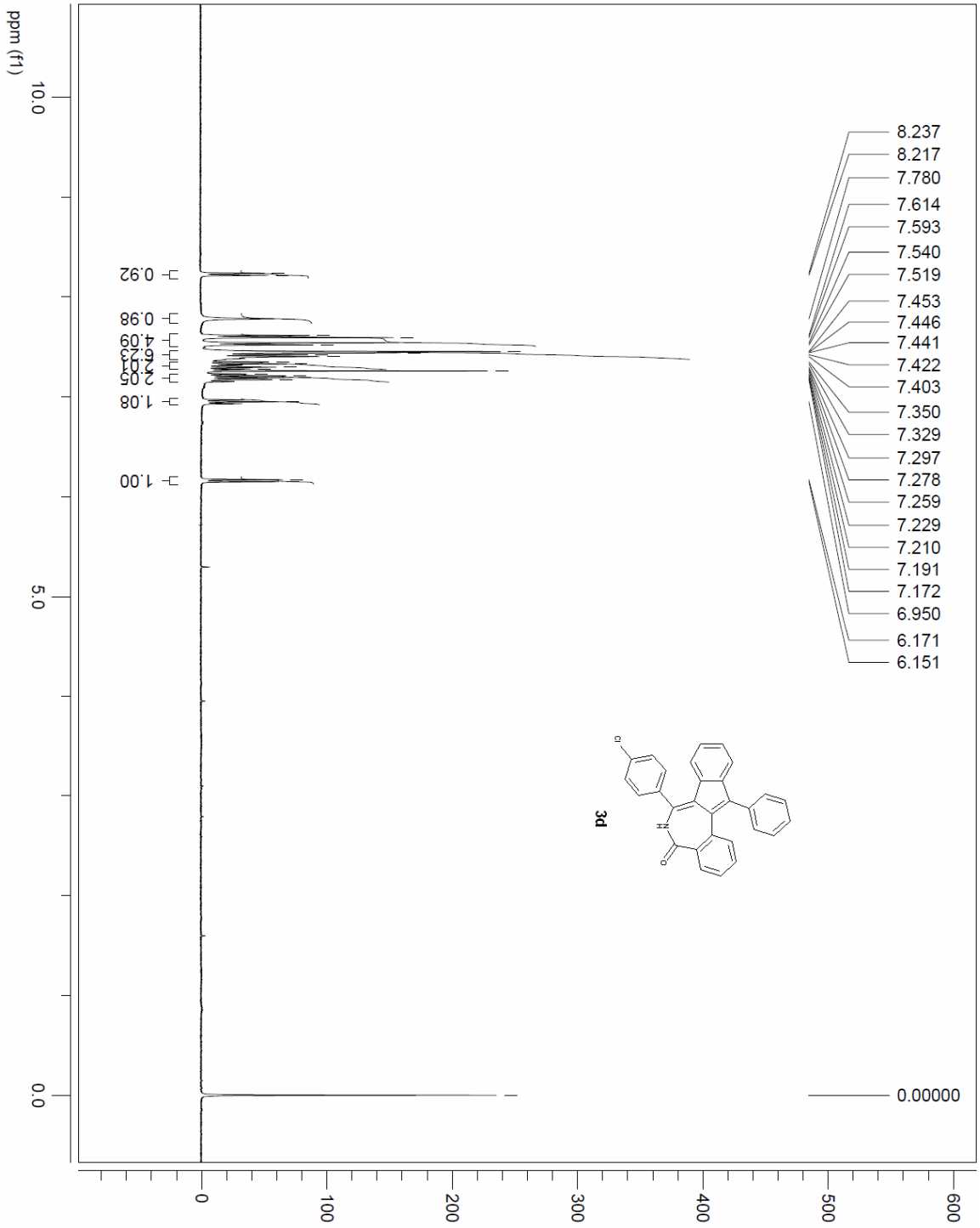
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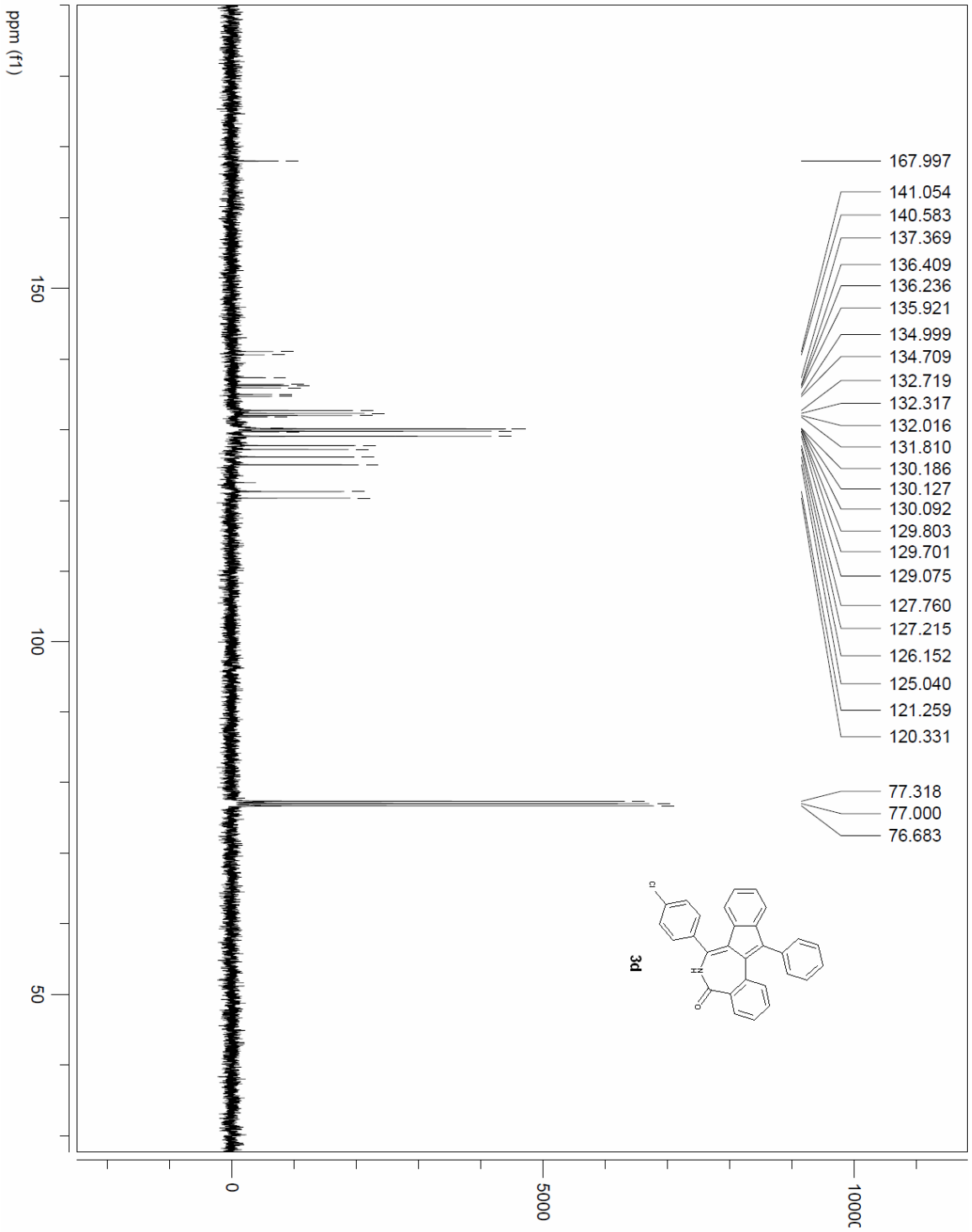

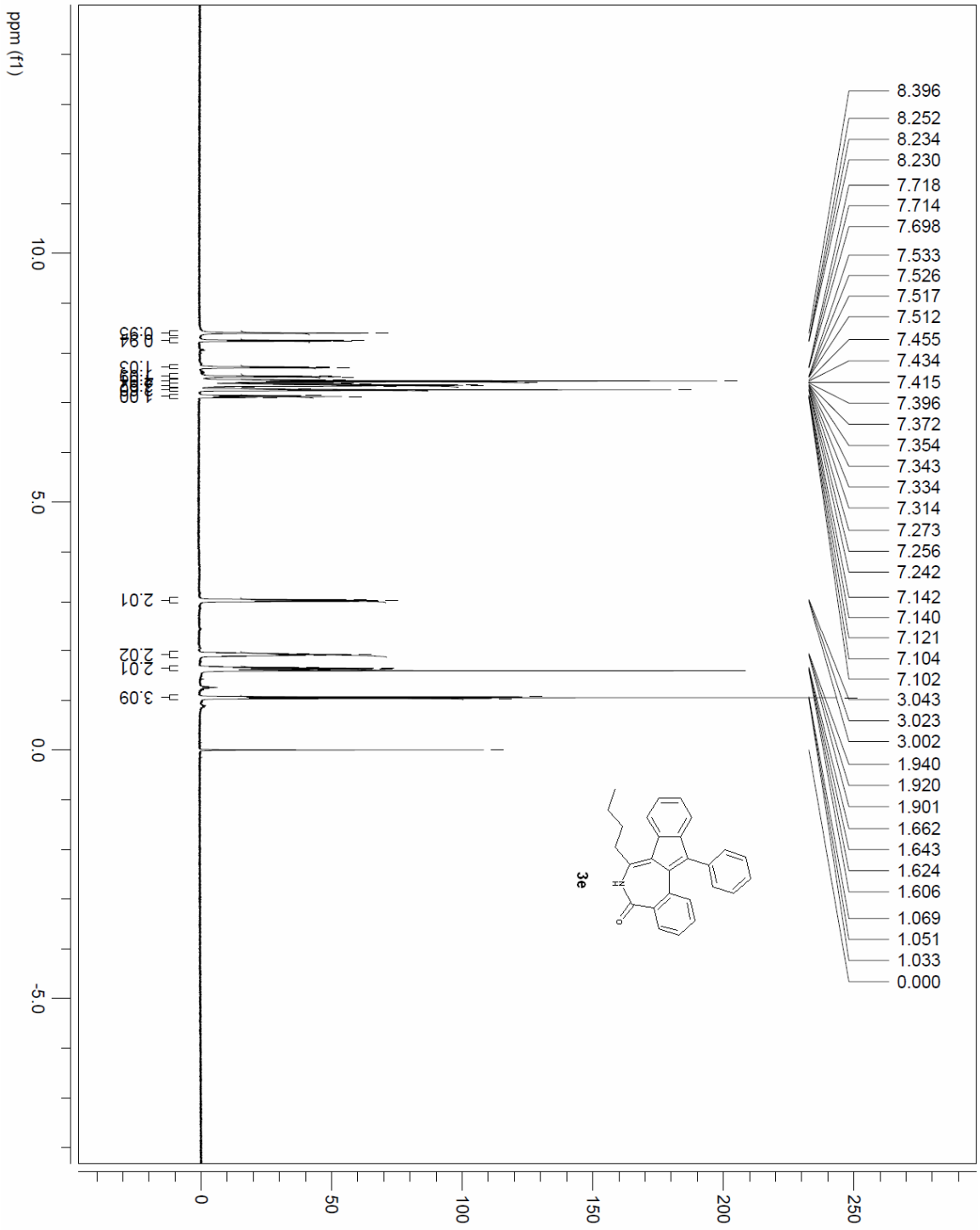

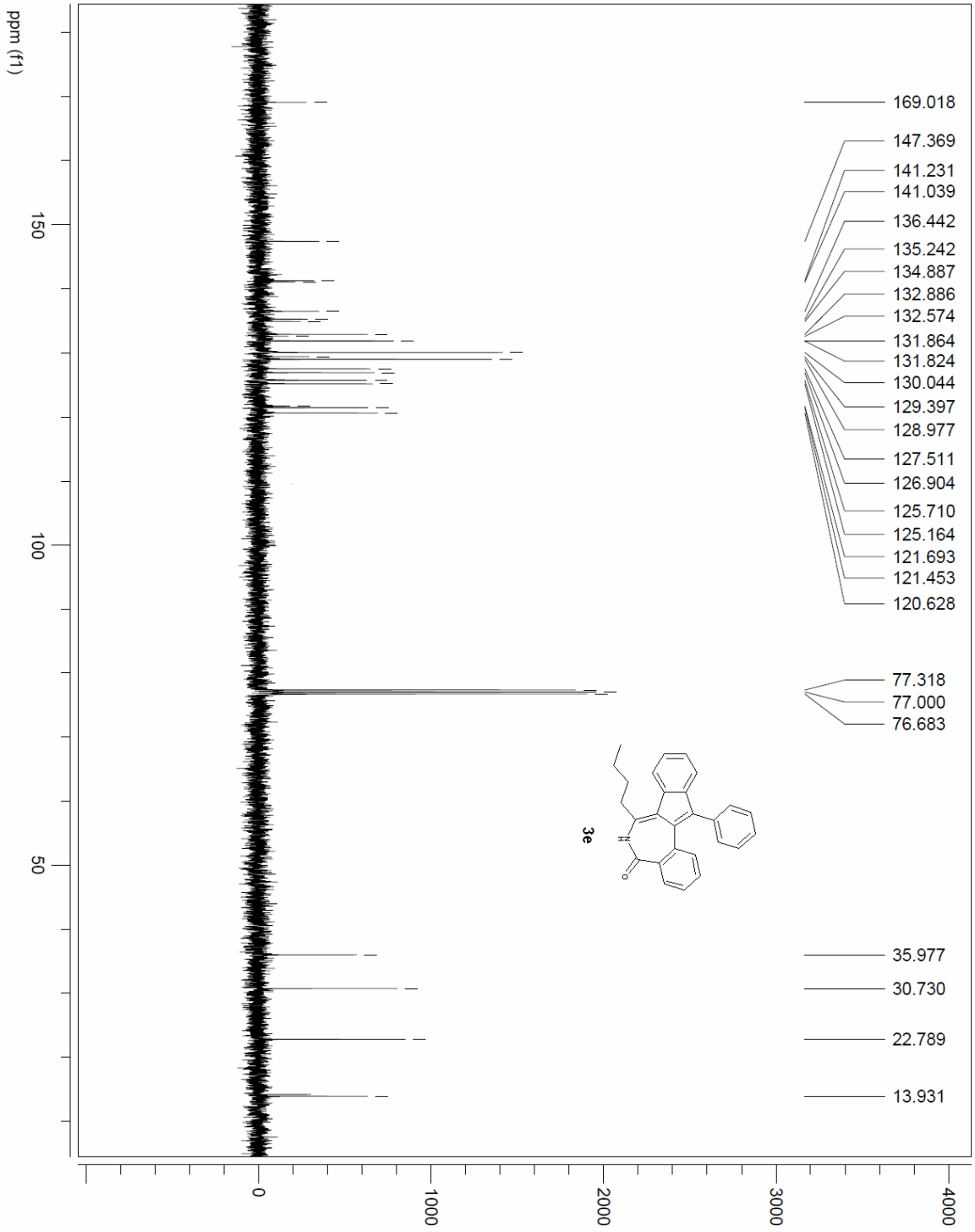

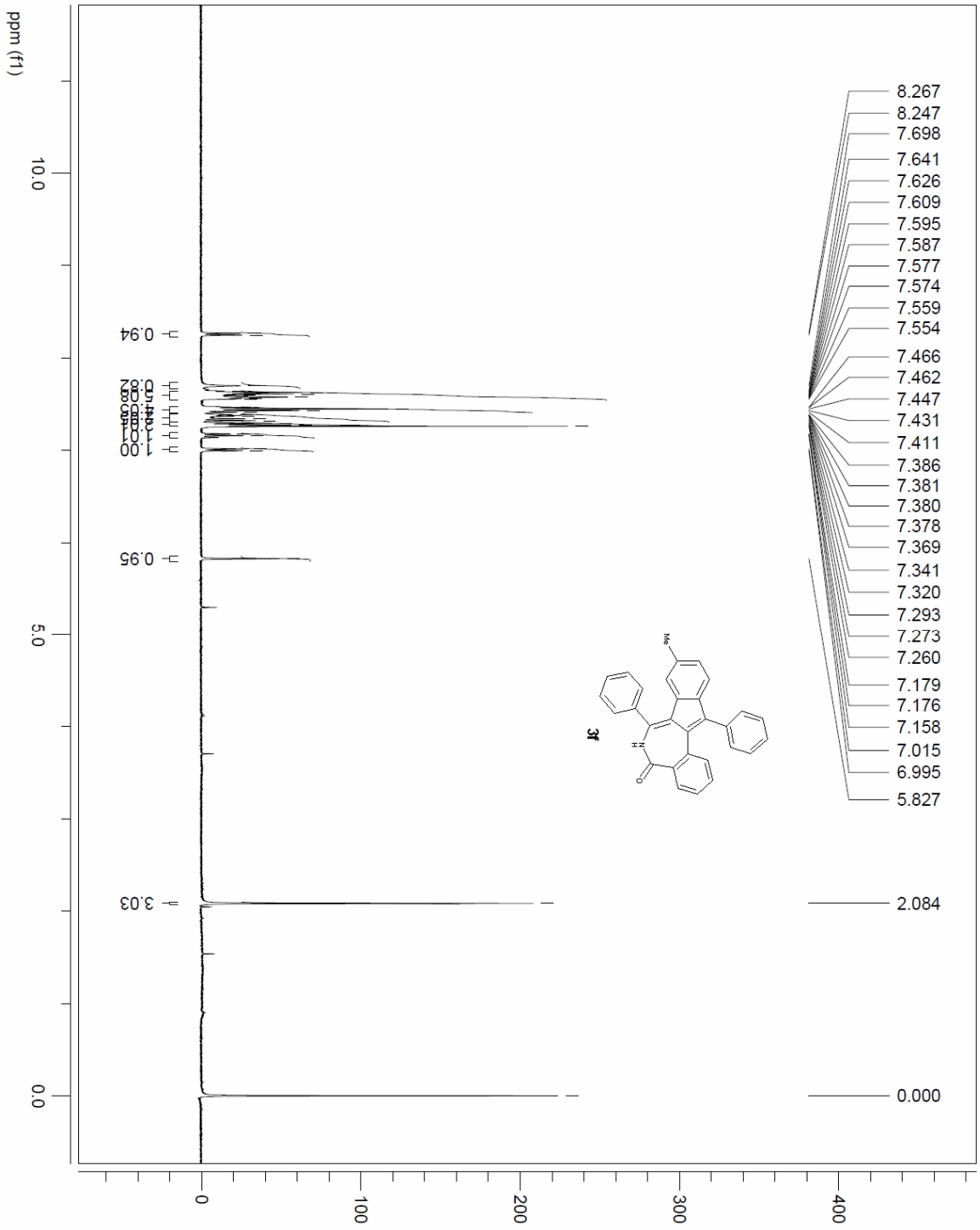
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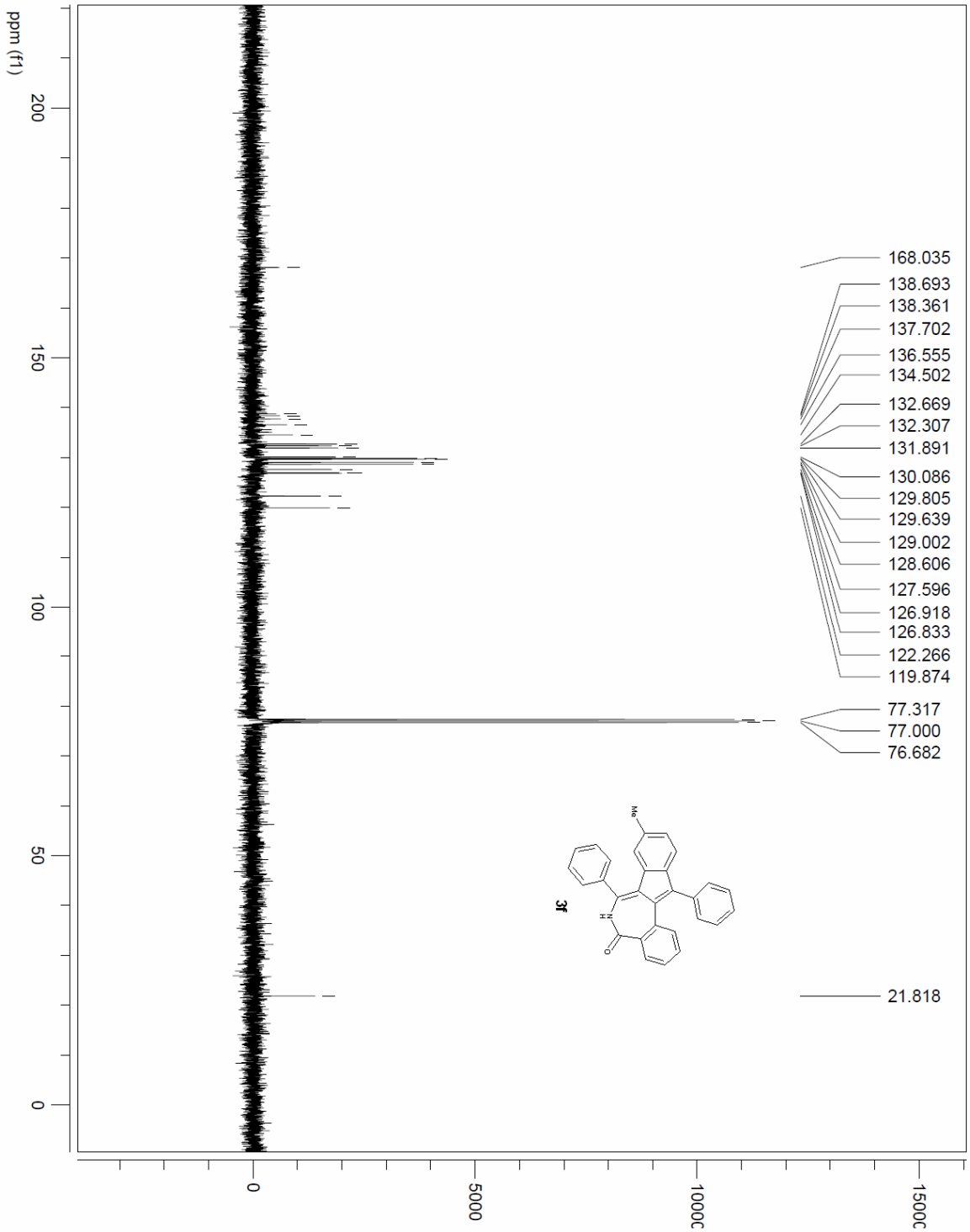

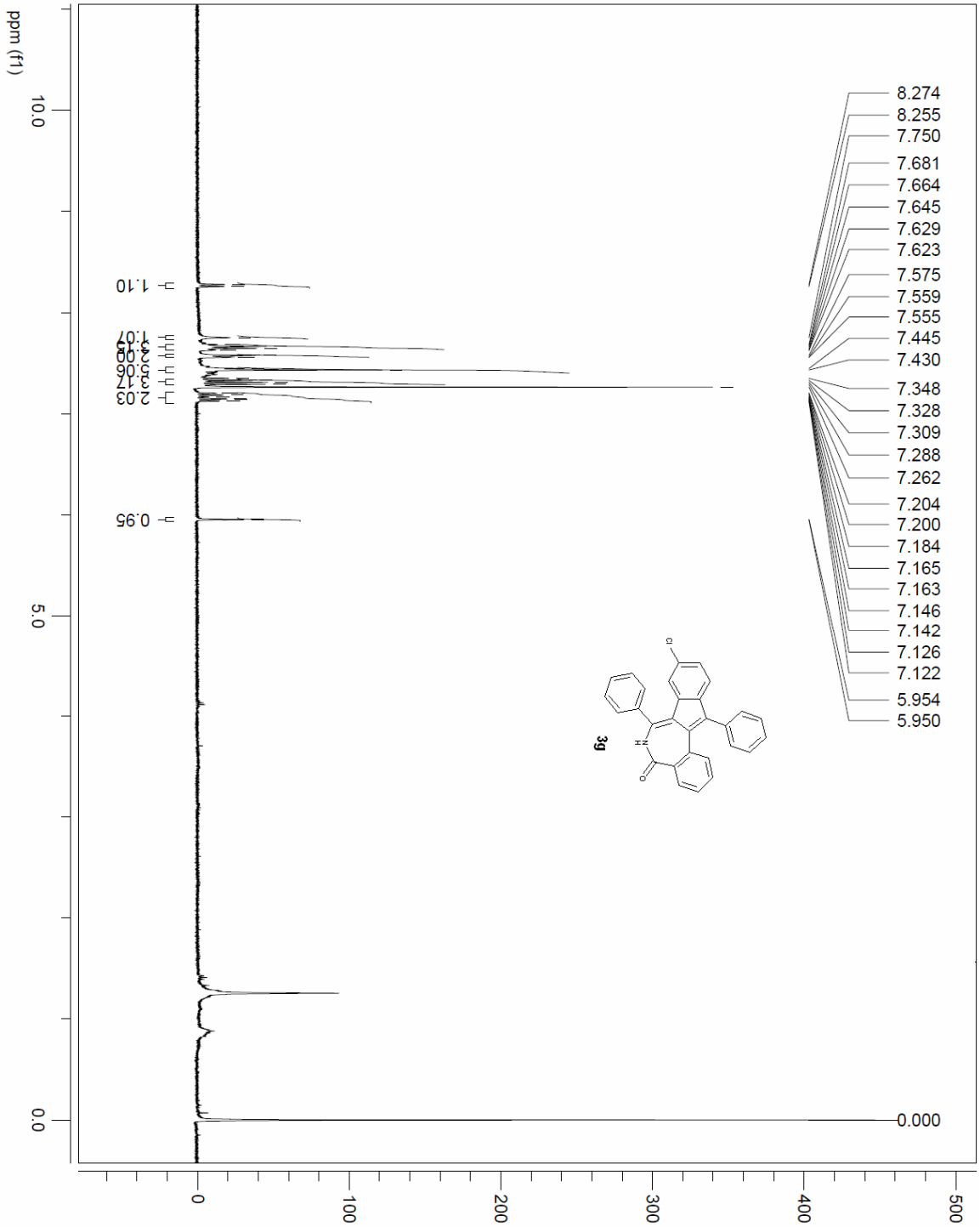
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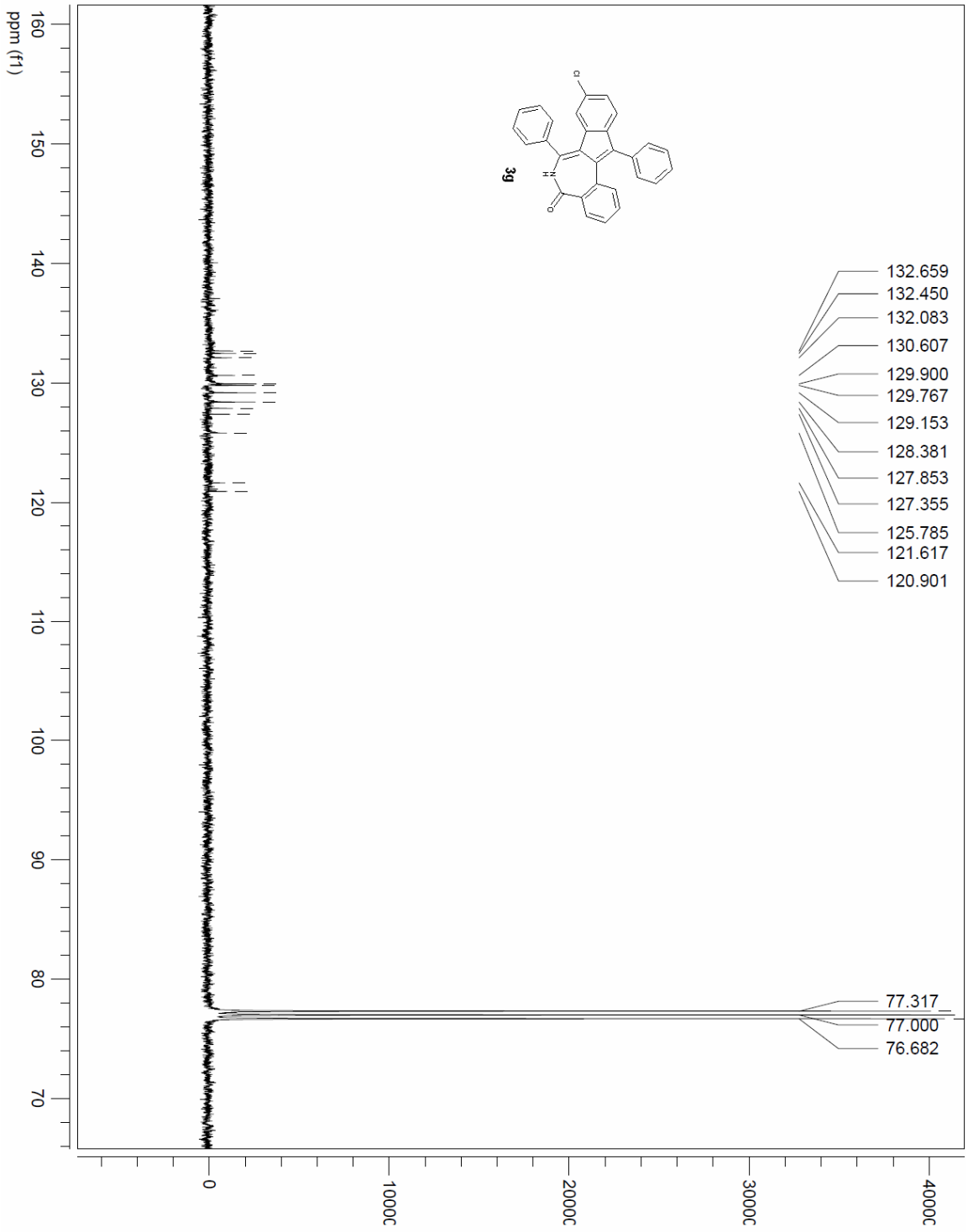

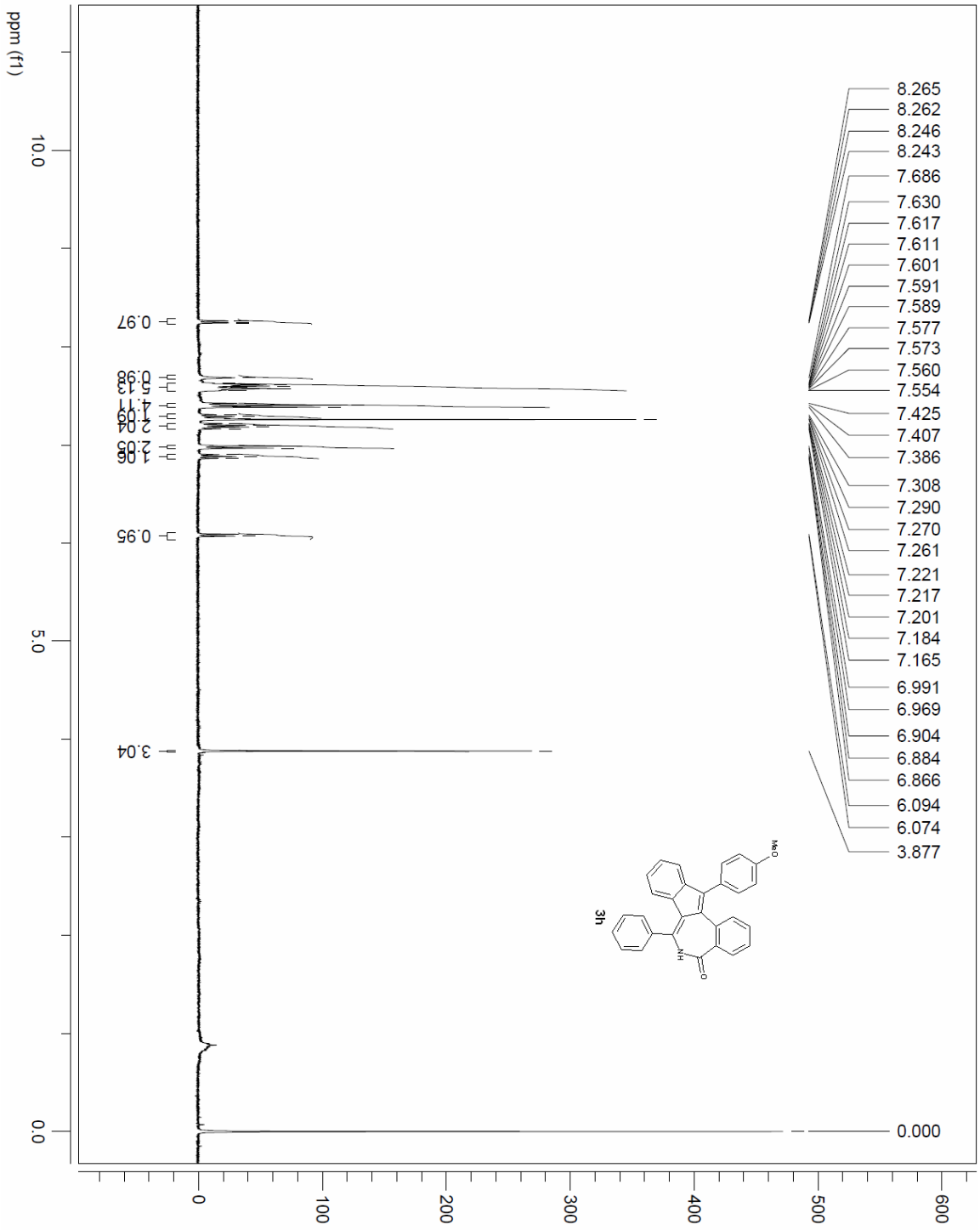
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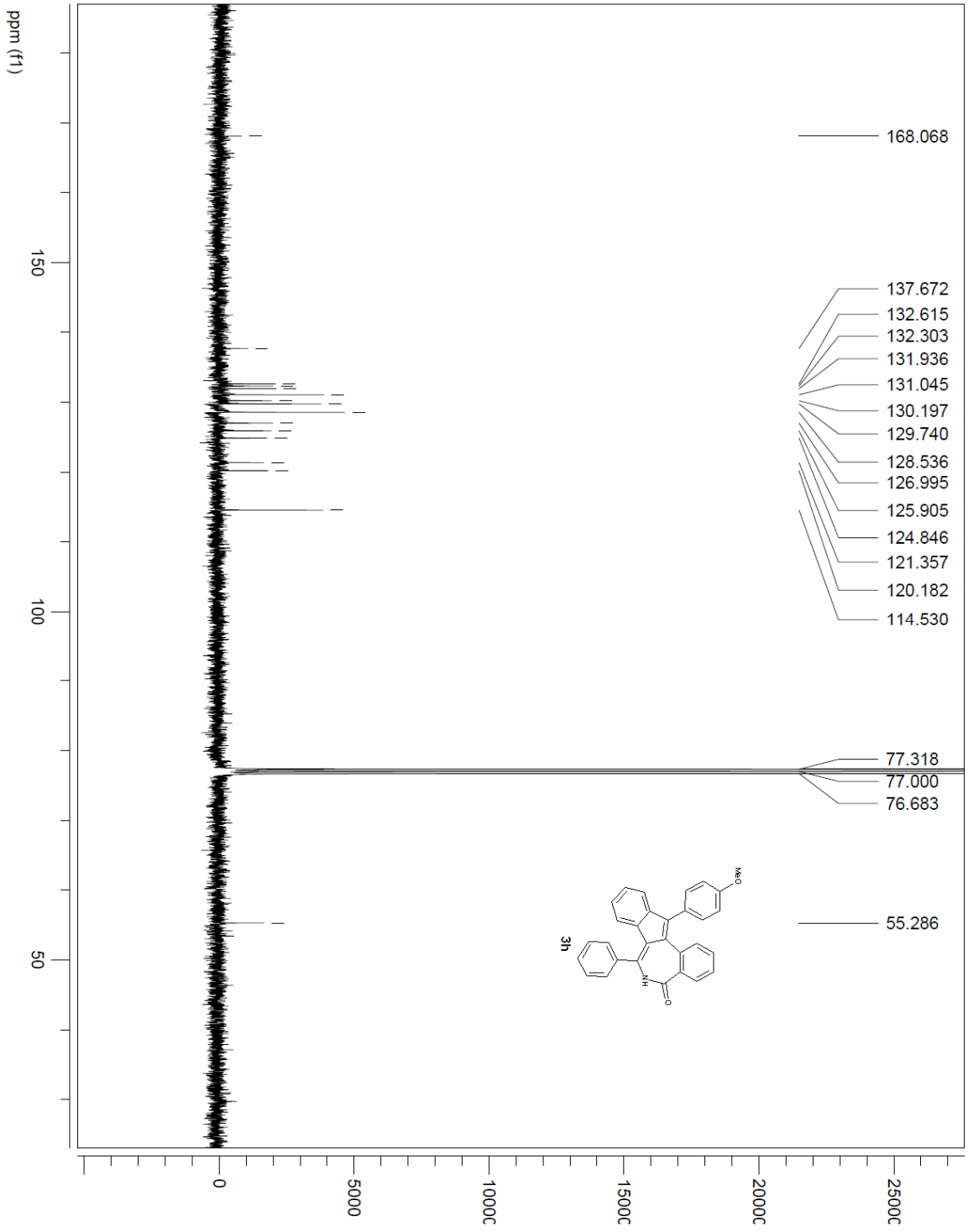
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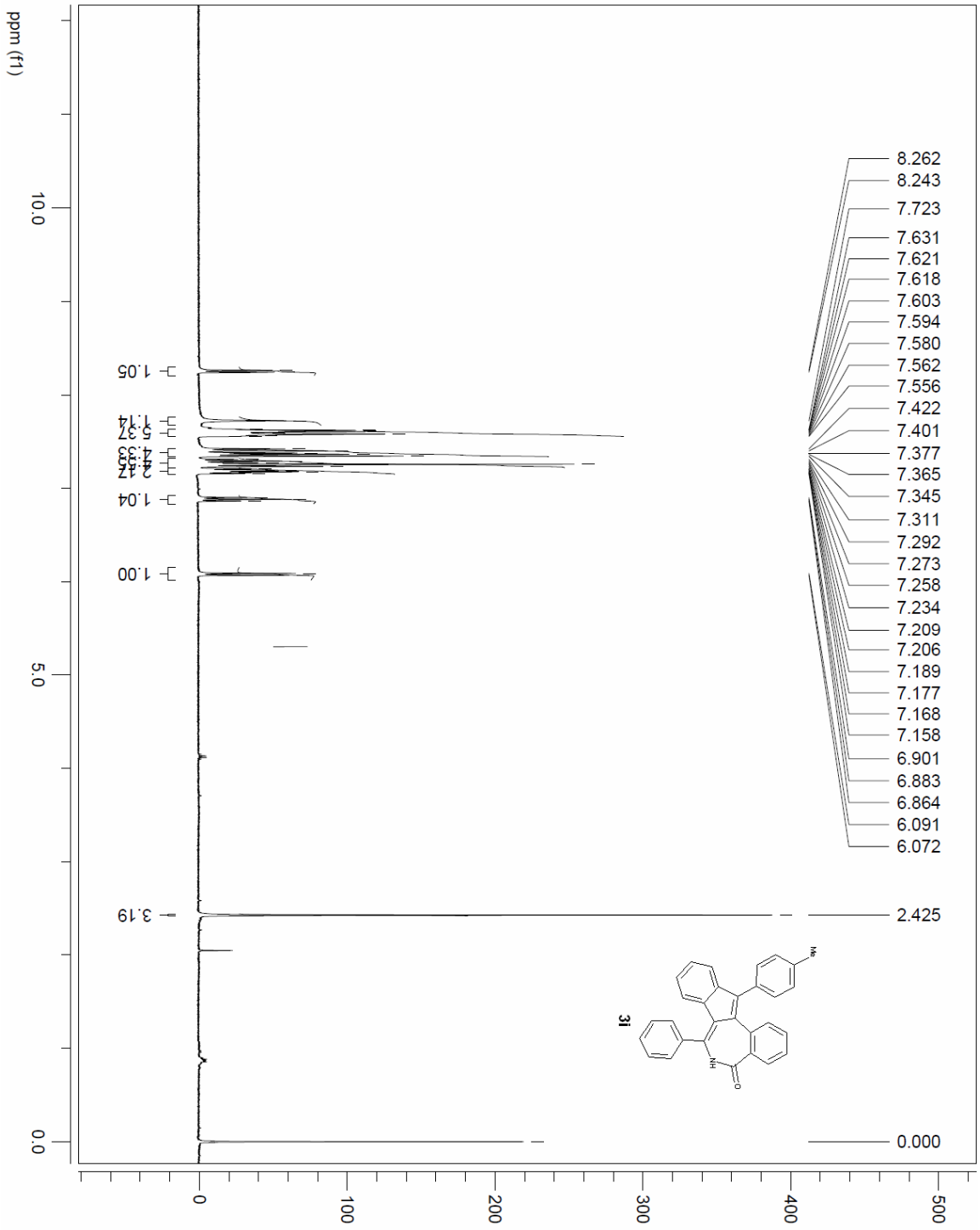
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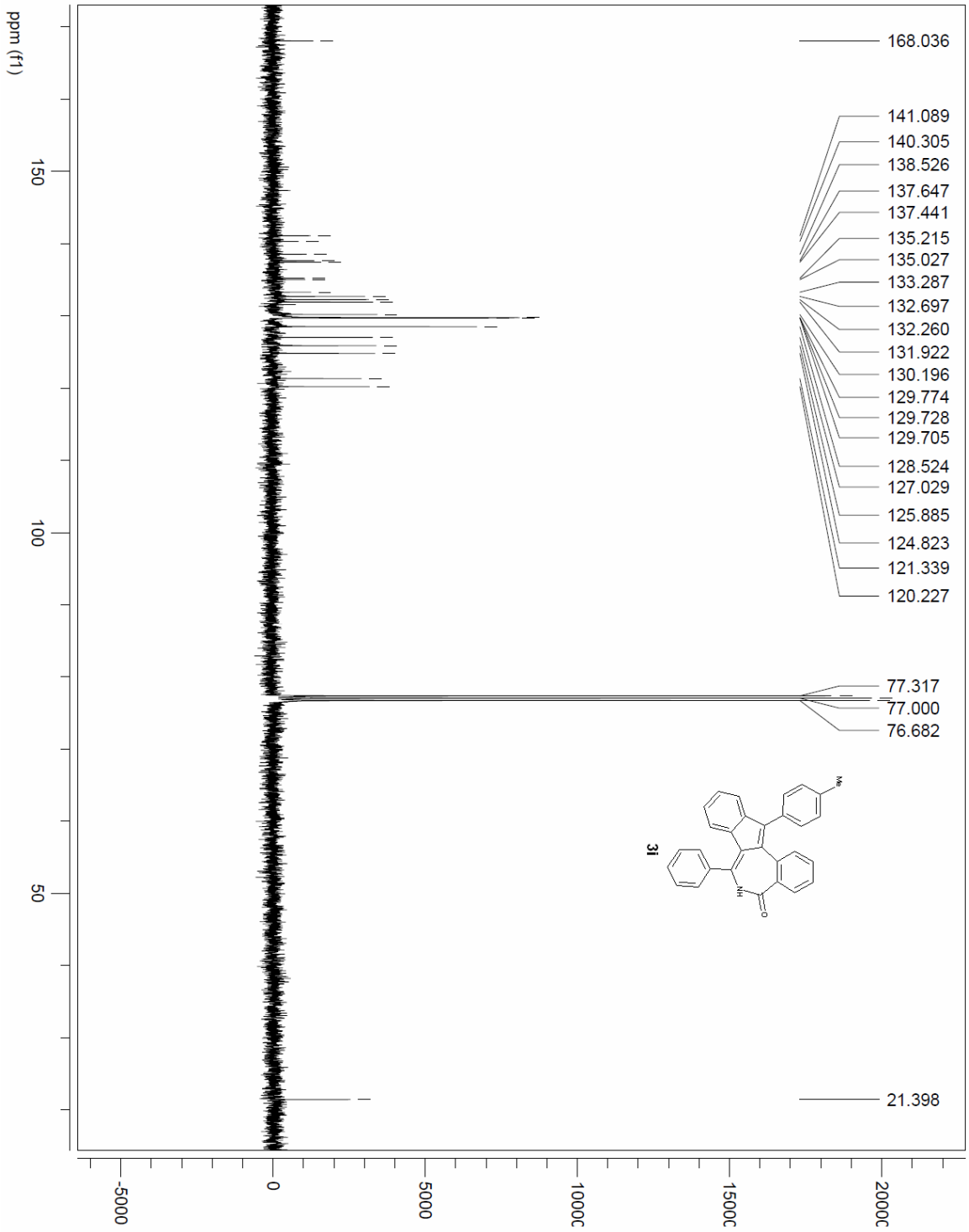

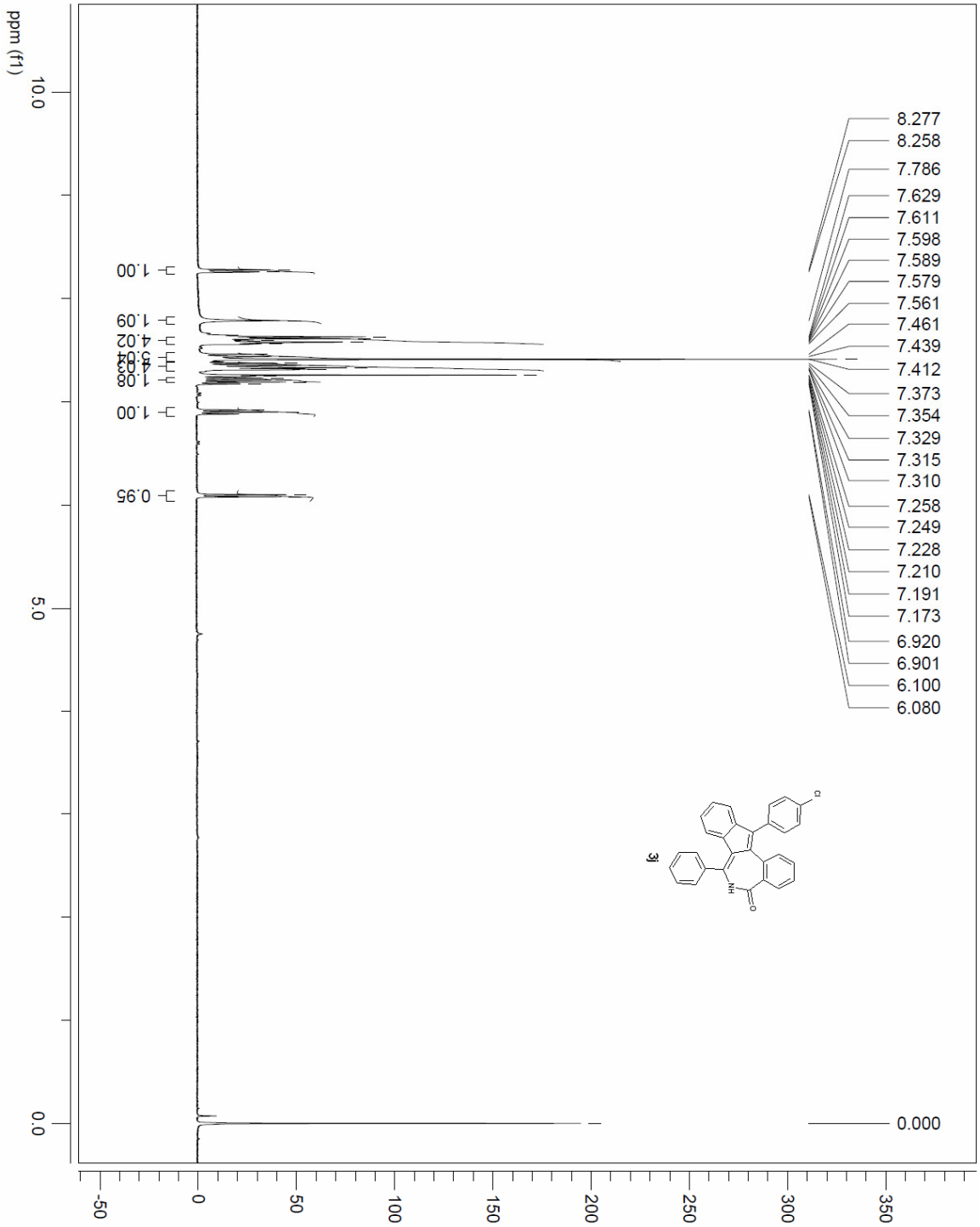
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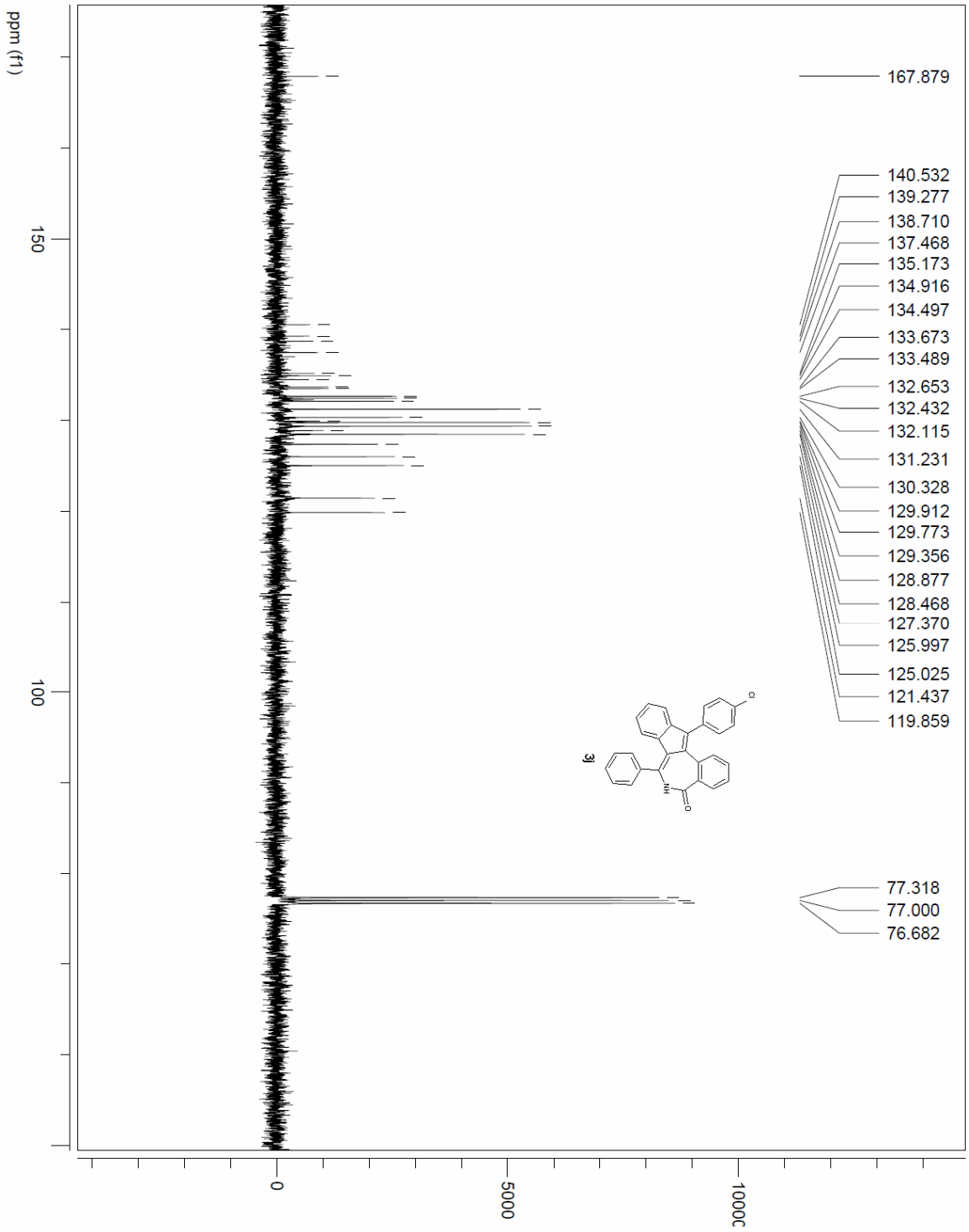
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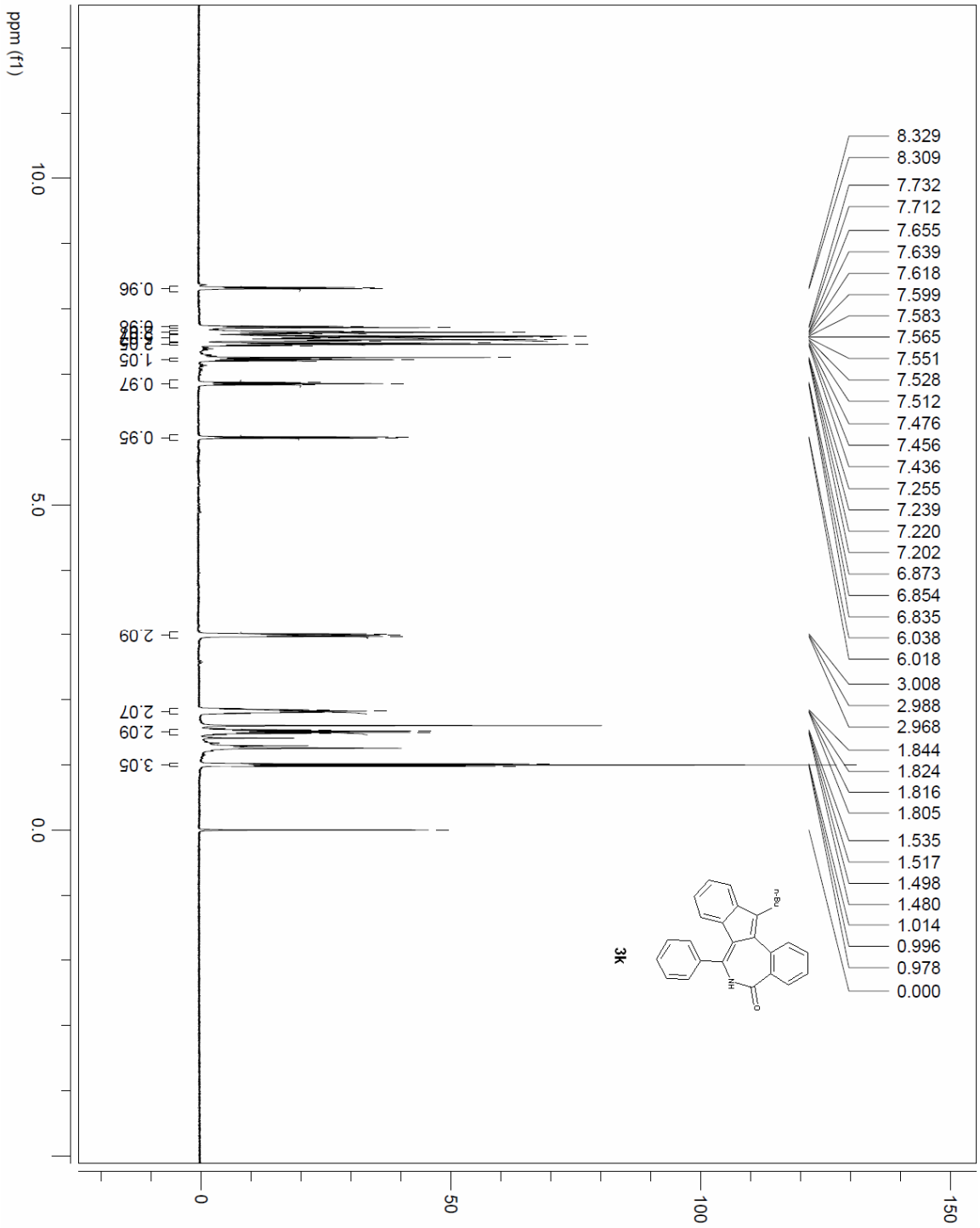
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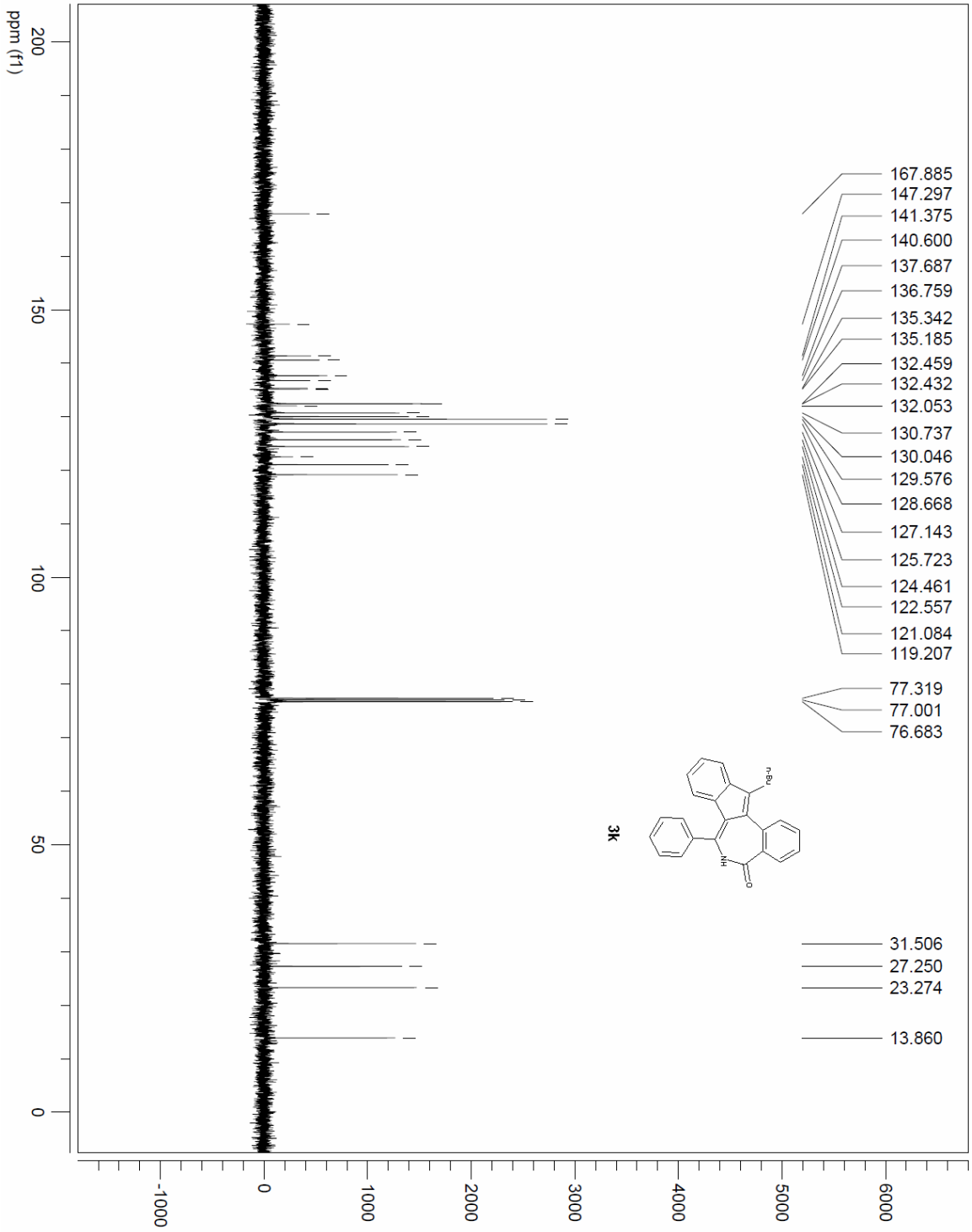
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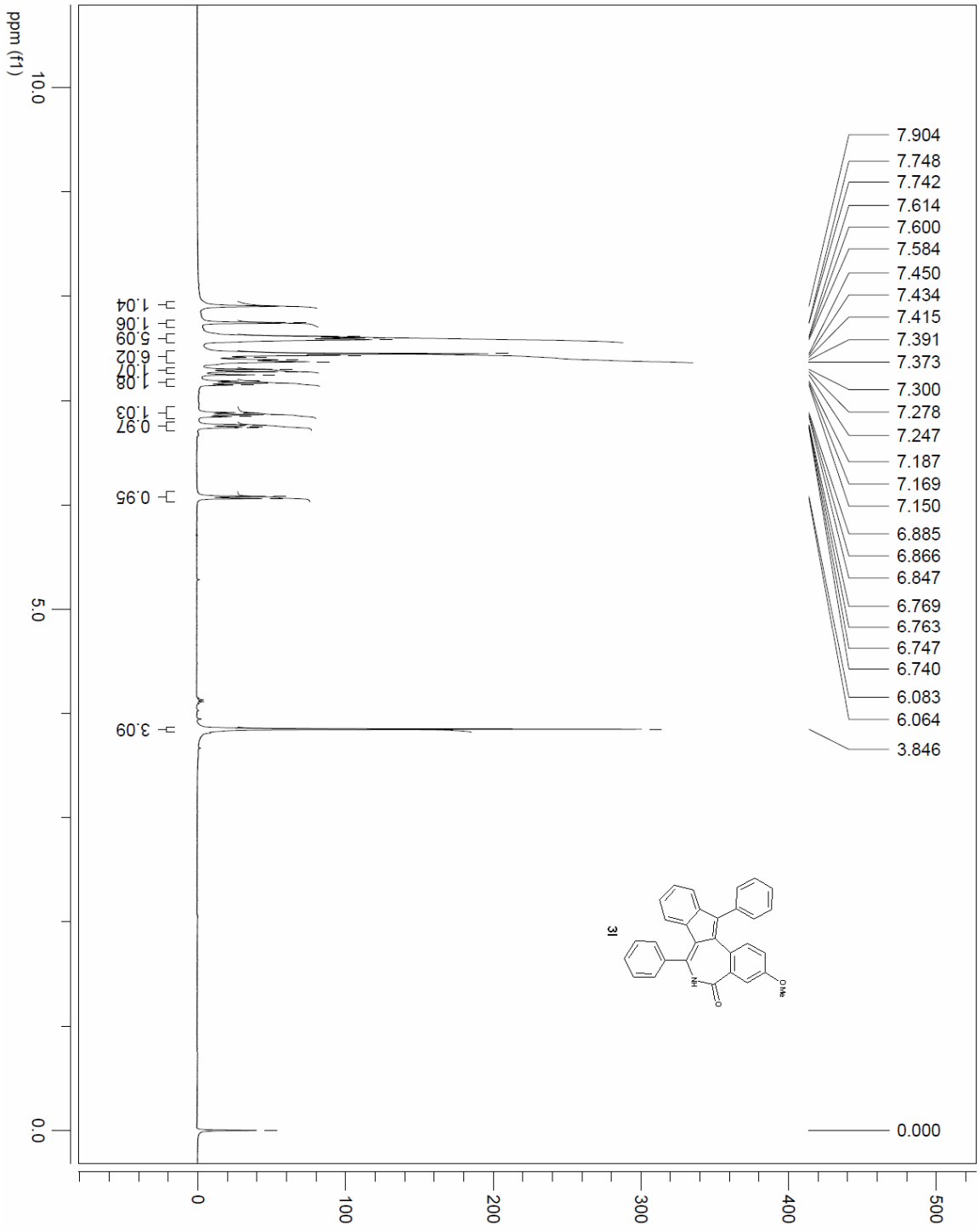
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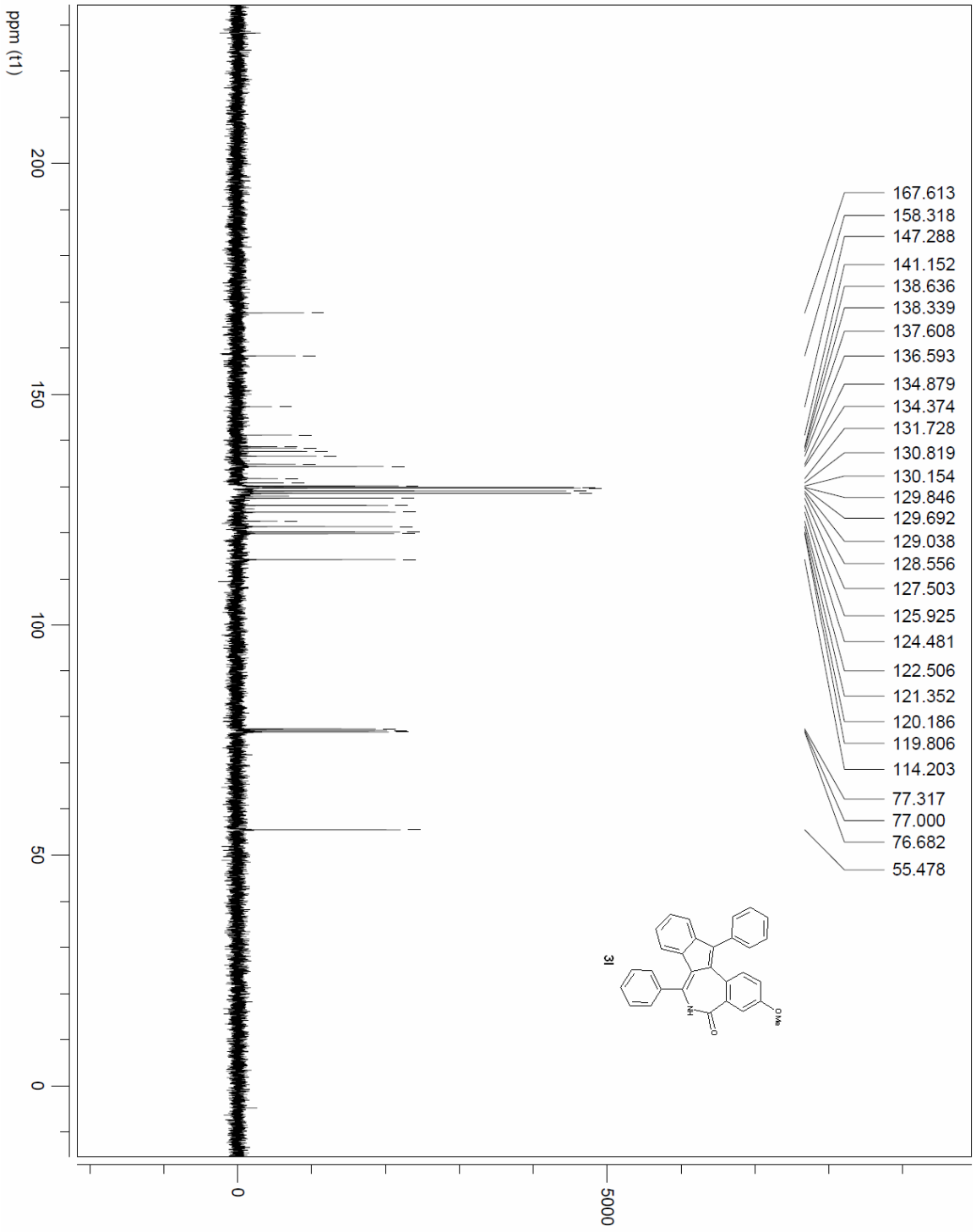

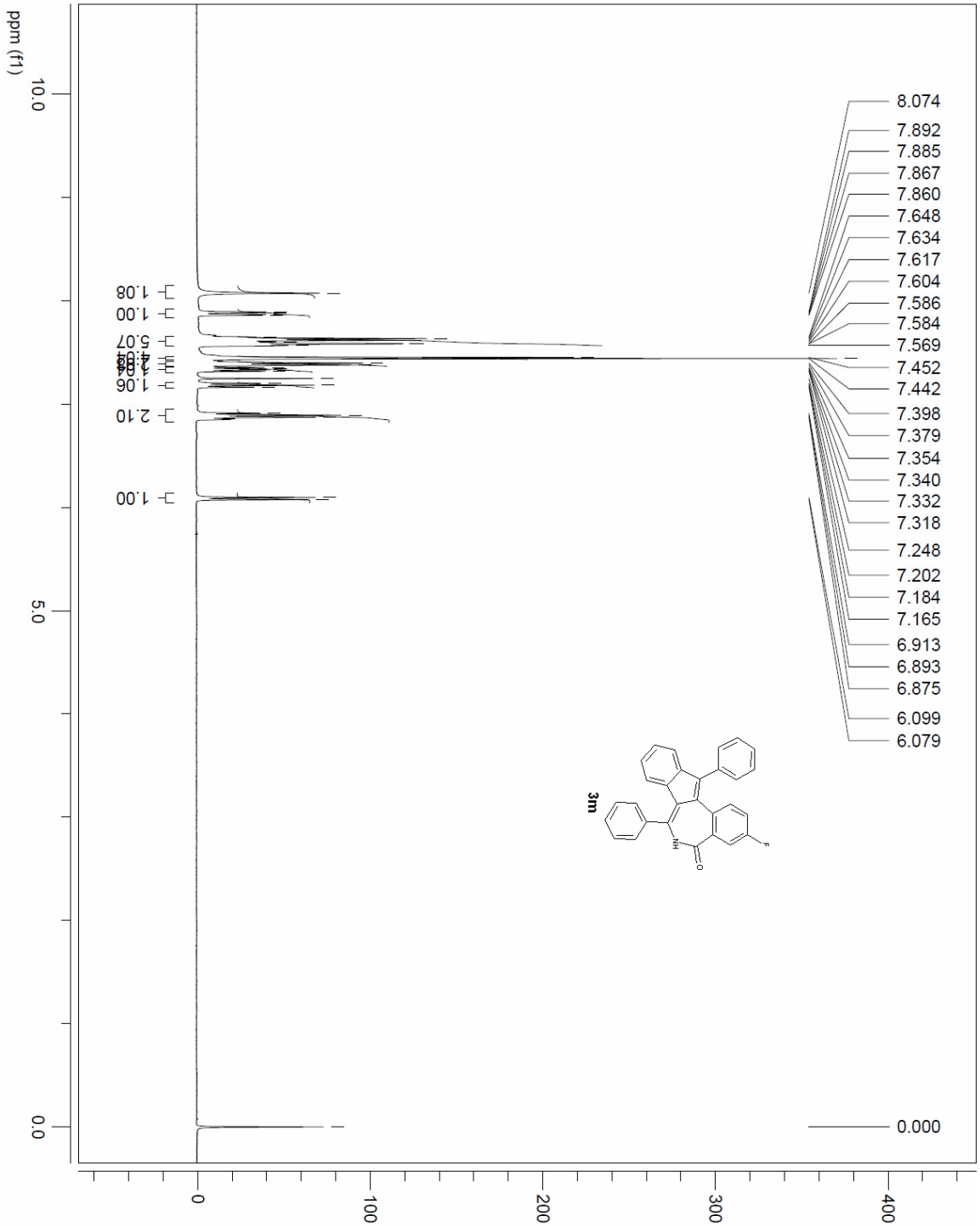
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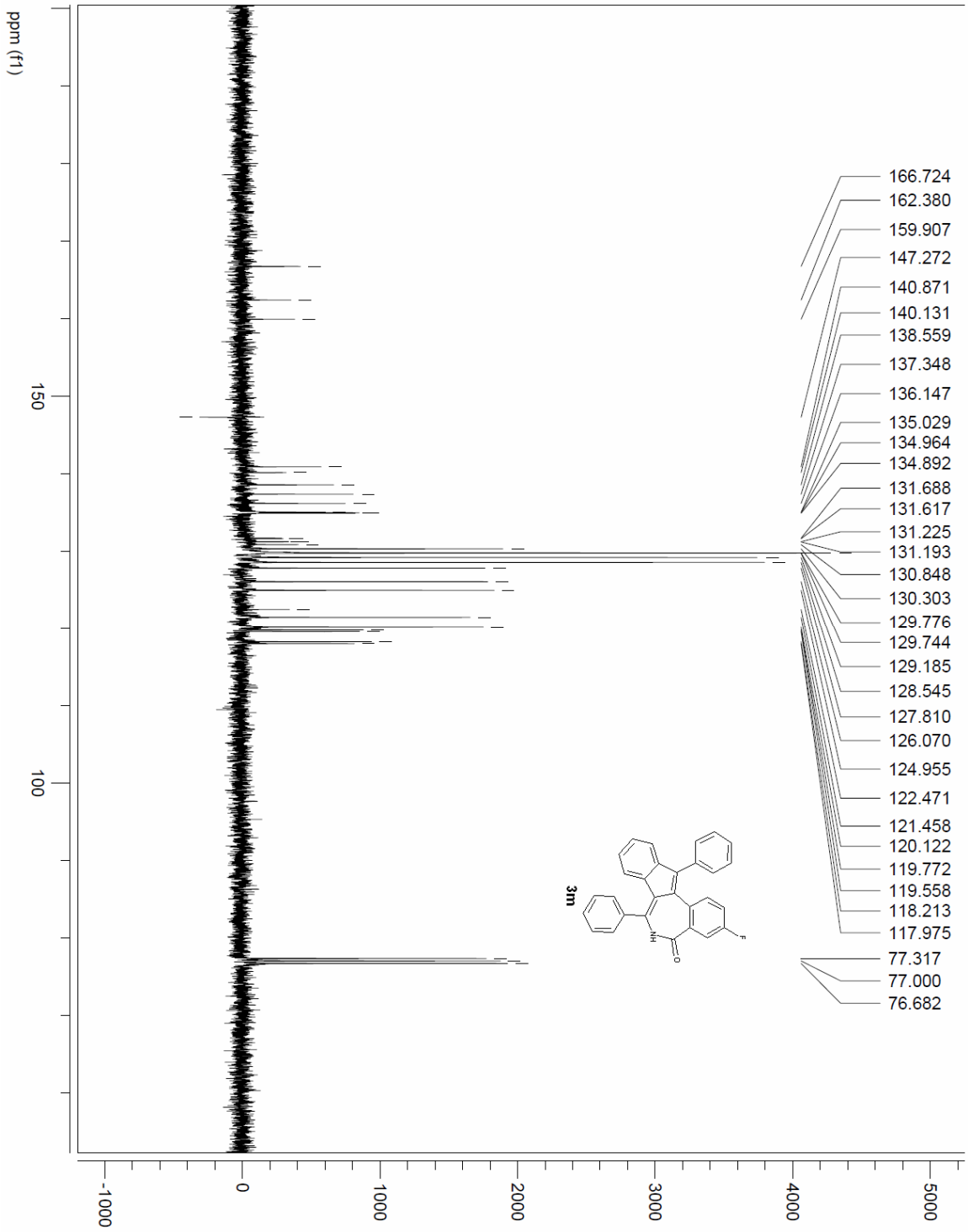

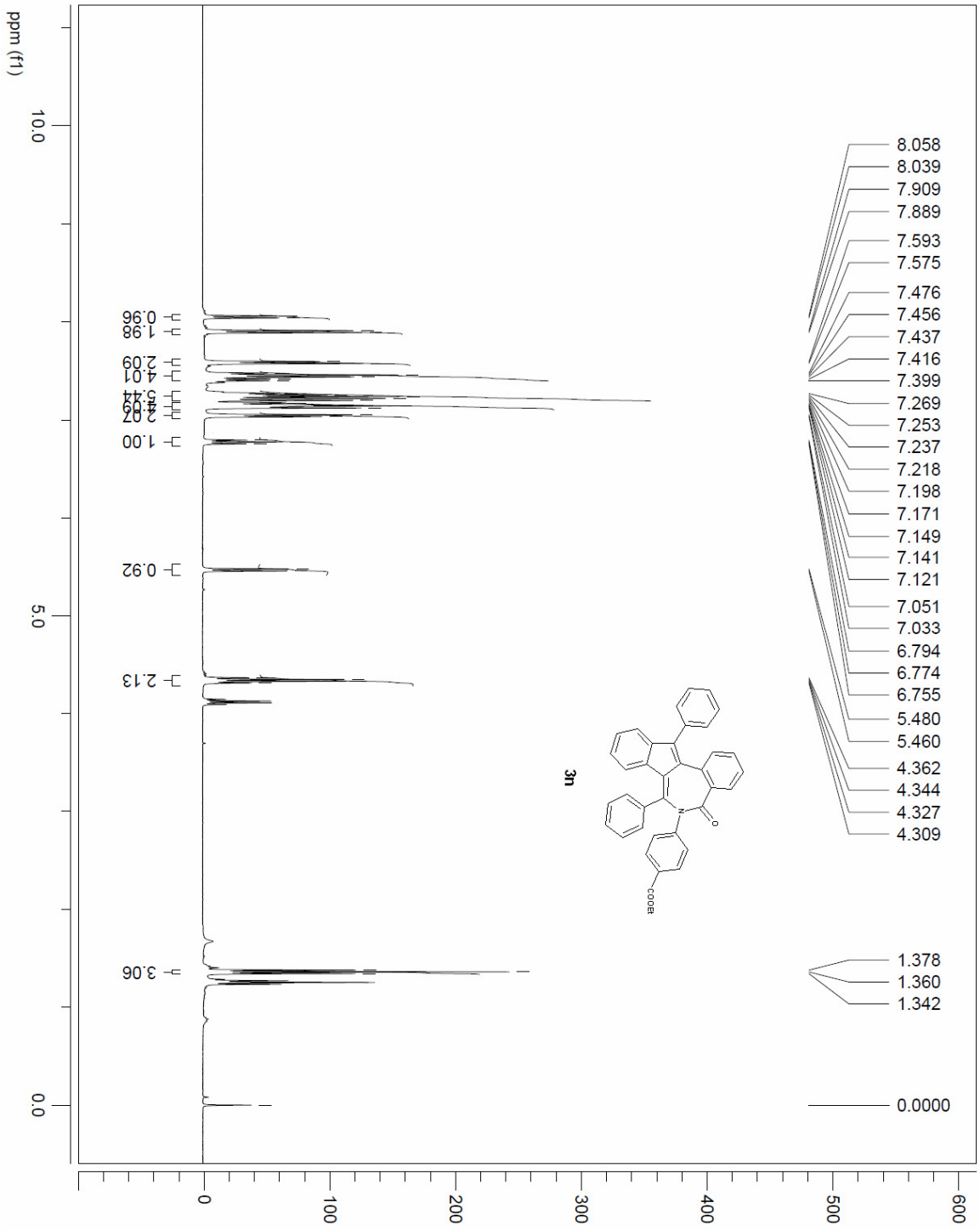
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1.342
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3n
COOEt
0
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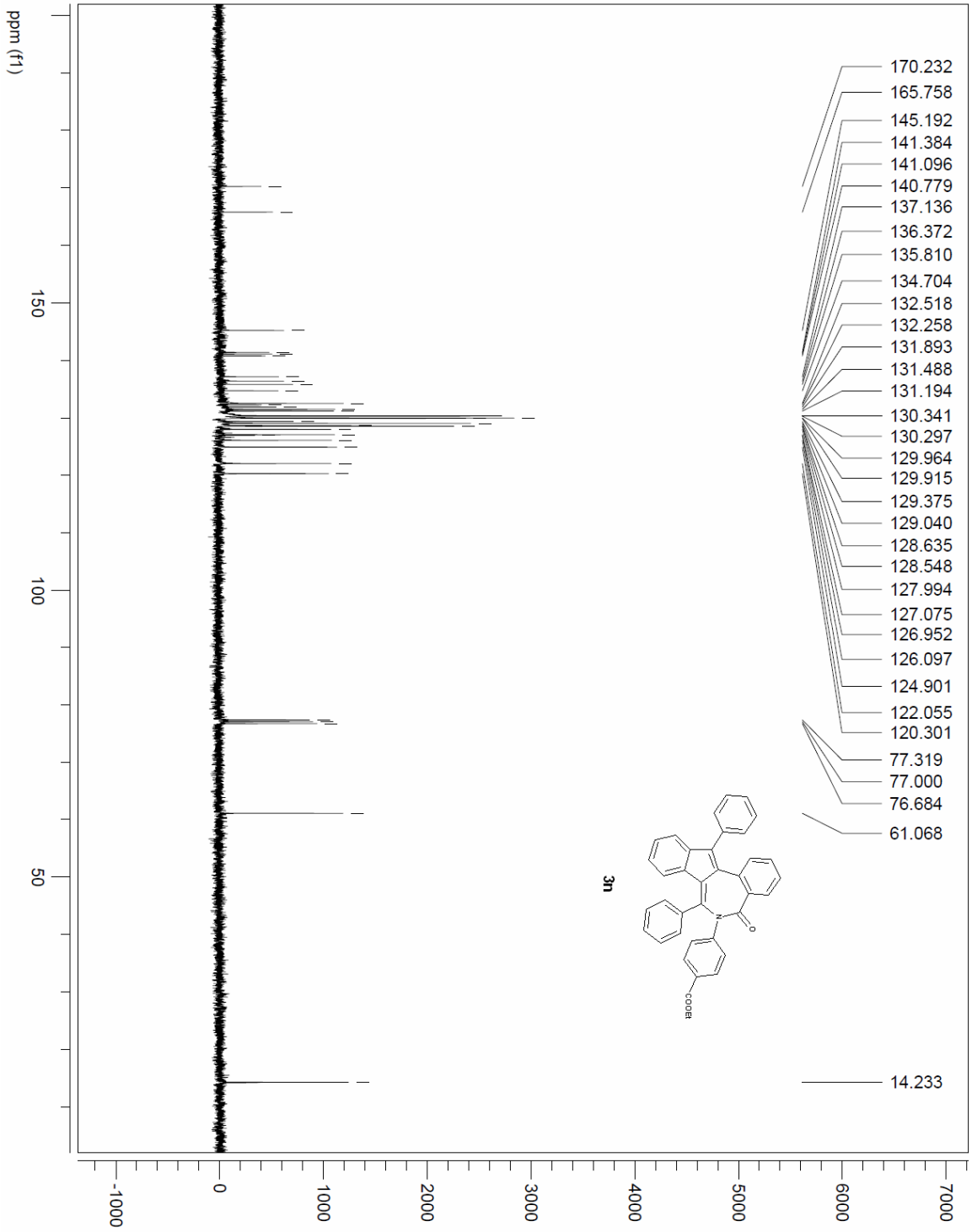
200
300
400
500
600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100
50
-1000
0
1000
2000
3000
4000
5000
6000
7000
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165.758
145.192
141.384
141.096
140.779
137.136
136.372
135.810
134.704
132.518
132.258
131.893
131.488
131.194
130.341
130.297
129.964
129.915
129.375
129.040
128.635
128.548
127.994
127.075
126.952
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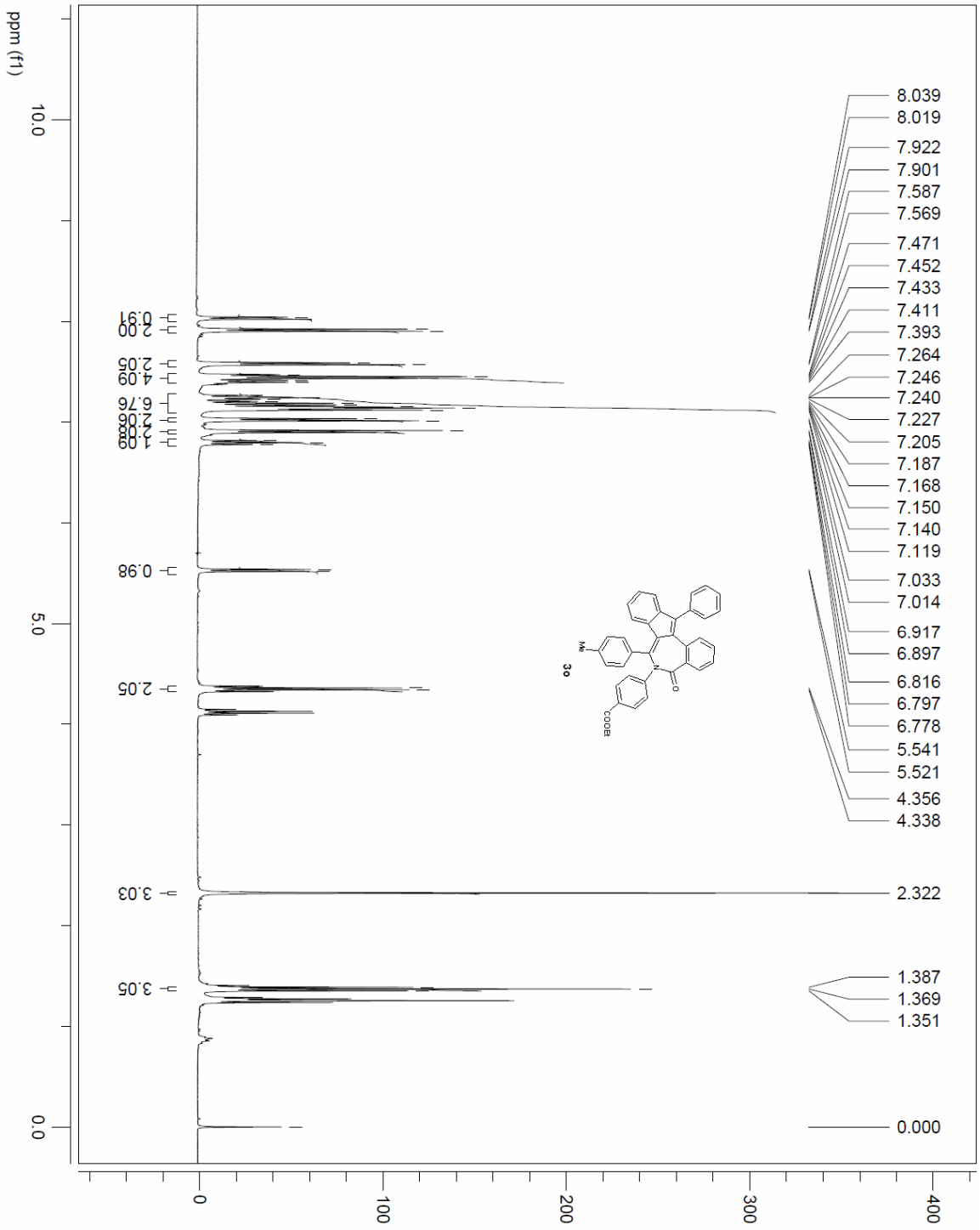
124.901
122.055
120.301
77.319
77.000
76.684
61.068
14.233
3n
COOEt


ppm (f1)
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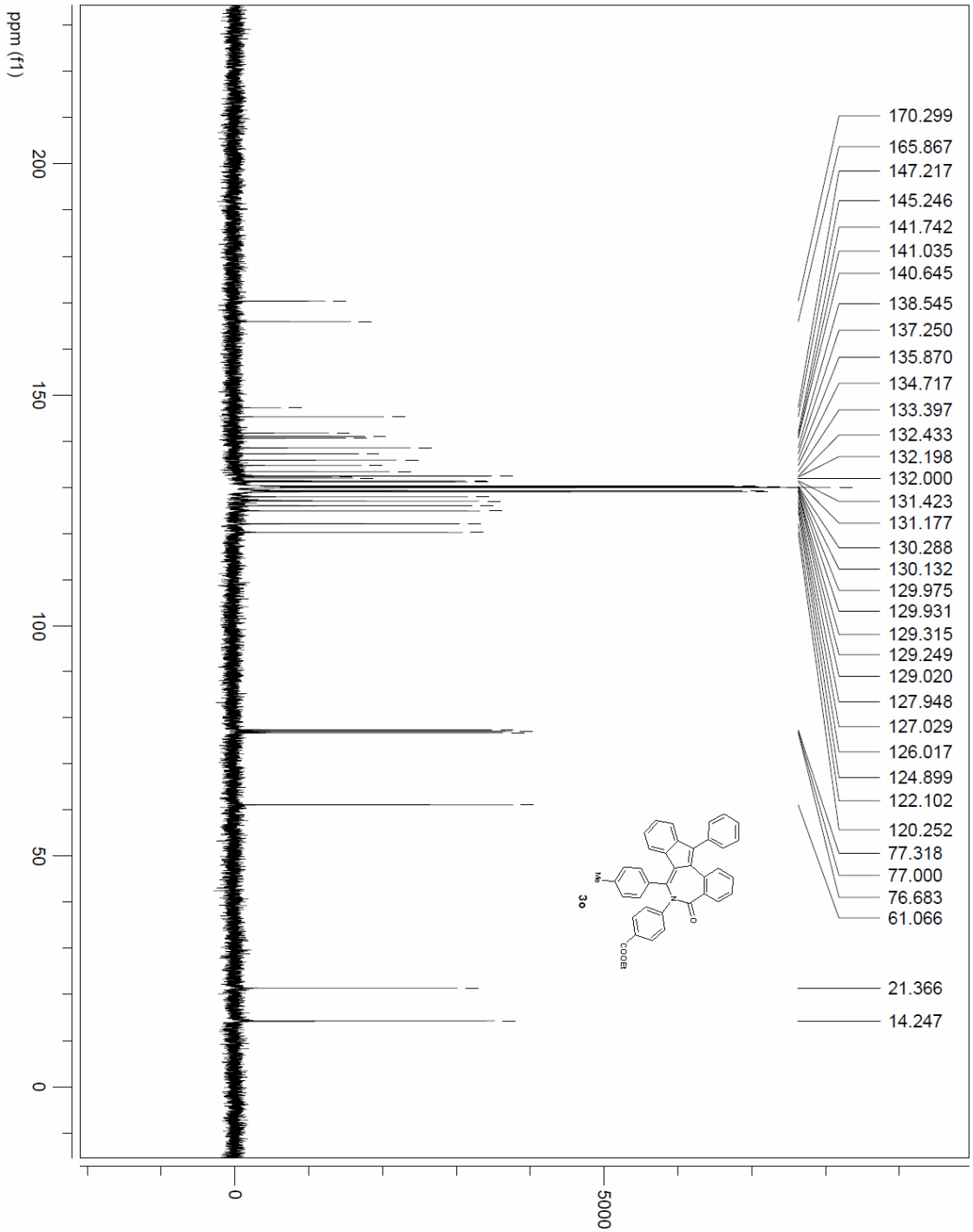
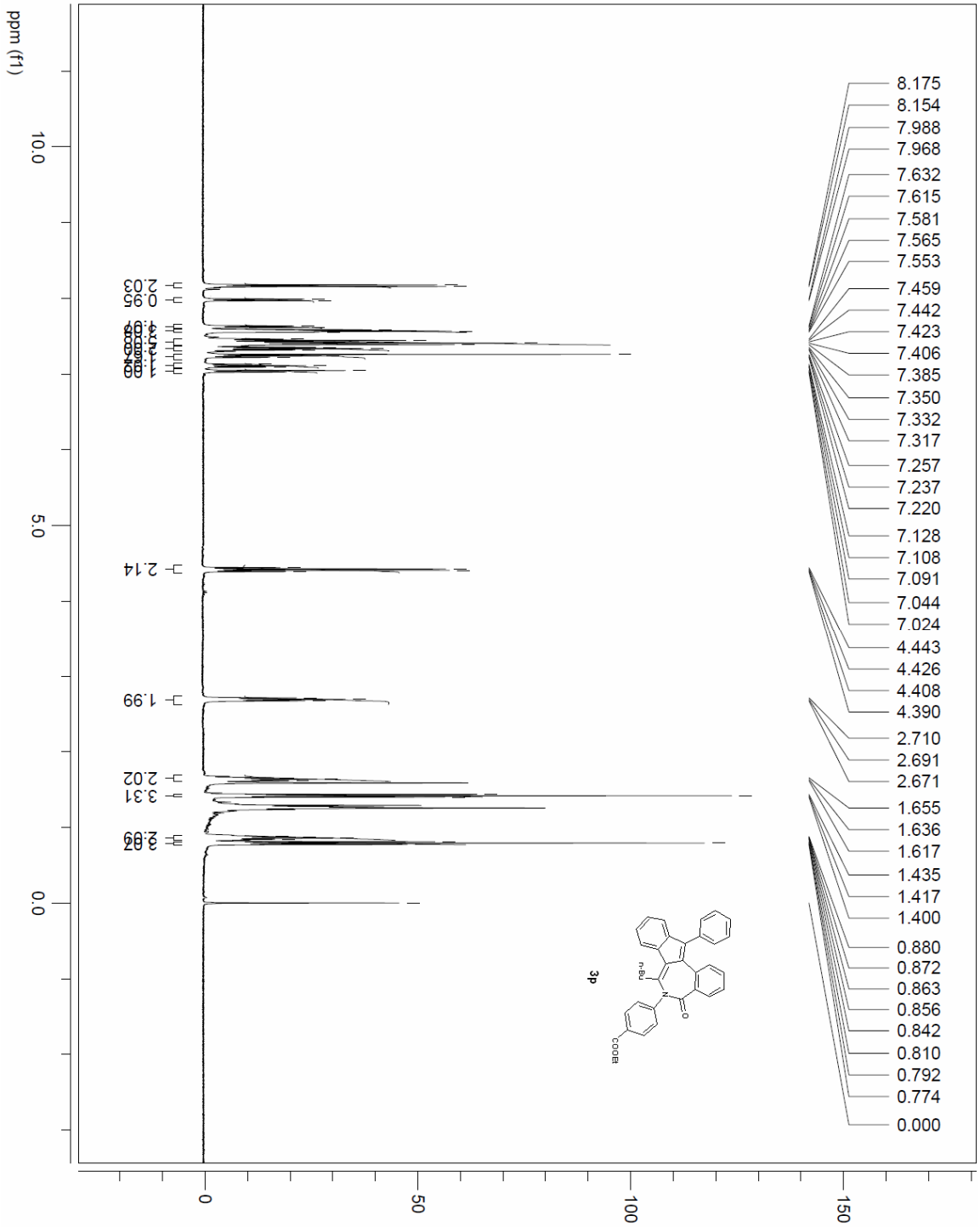
5.0
0.0
0
100
200
300
400
8.039
8.019
7.922
7.901
7.587
7.569
7.471
7.452
7.433
7.411
7.393
7.264
7.246
7.240
7.227
7.205
7.187
7.168
7.150
7.140
7.119
7.033
7.014
6.917
6.897
6.816
6.797
6.778
5.541
5.521
4.356
4.338
2.322
1.387
1.369
1.351
0.000
0.91
2.00
2.05
4.09
6.76
2.06
2.08
1.09
0.98
2.05
3.03
3.05
3o
Me
O
COOEt




ppm (f1)
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5.0
0.0
0
50
100
150
2.03
0.95
2.14
1.99
2.02
3.31
2.09
3.02
8.175
8.154
7.988
7.968
7.632
7.615
7.581
7.565
7.553
7.459
7.442
7.423
7.406
7.385
7.350
7.332
7.317
7.257
7.237
7.220
7.128
7.108
7.091
7.044
7.024
4.443
4.426
4.408
4.390
2.710
2.691
2.671
1.655
1.636
1.617
1.435
1.417
1.400
0.880
0.872
0.863
0.856
0.842
0.810
0.792
0.774
0.000
3p
n-Bu
COOEt