Reaction of α-amido sulfones with functionalized nitrocompounds: a new two-step synthesis of *N*-alkoxycarbonyl-2,5-disubstituted pyrroles

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Supporting Information

Contents

General Experimental Methods

^{1}H NMR were recorded at 400 MHz. ^{13}C NMR were recorded at 100 MHz. IR spectra were recorded with a PerkineElmer Paragon 500 FT-IR. Mass spectra were performed on a GC/MS system by means of the EI technique (70 eV). Microanalyses were performed with a CHNS-O analyzer Model EA 1108 from Fisons Instruments. All chemicals used are commercial. KF on alumina was purchased from Sigma-Aldrich (5.5 mmol/g). α-amido sulfones **1**[1-2] and protected β-nitro ketone **2**[3] were prepared using previously reported procedures**.**

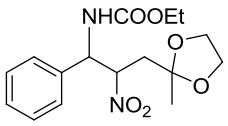
General Procedure for the Preparation of Nitro Carbamates 3.

To a stirred solution of α-amido sulfone **1** (2.0 mmol) and nitro ketal **2** (4.0 mmol) in EtOAc (20 mL), potassium fluoride on alumina (6.0 mmol, 1.1 g) was added at rt. After stirring for 18 h, the mixture was filtered over a short pad of Florisil and rinsed with EtOAc (10 mL). Removal of the solvent at reduced pressure, gave crude nitro carbamate **3** that was purified by column chromatography (hexanes/AcOEt 7:3).

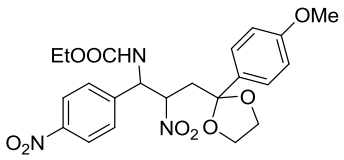
General Procedure for the Preparation of Pyrroles 4.

To a stirred solution of nitro carbamate **3** (1.0 mmol) in $CHCl_3$-MeOH (2:1, 9 mL), *p*-toluenesulfonic acid monohydrate (0.5 mmol, 0.096 g) was added at room temperature and then heated at 60 °C for 24 h. After cooling at room temperature, the solvent was removed at reduced pressure and the residue was dissolved in EtOAc (25 mL). After washing with satd. $NaHCO_3$ (3×3 mL) and brine (3×2 mL), the solution was dried over Na_2SO_4. Removal of the solvent at reduced pressure, gave crude pyrrole **4** that was purified by column chromatography (hexanes/AcOEt 95:5)

Spectroscopic Data for Compounds 3:



3a. *Ethyl (3-(2-methyl-1,3-dioxolan-2-yl)-2-nitro-1-phenylpropyl)carbamate*. Yield 86%. Yellow waxy solid. FTIR (neat) ν: 3342, 3297, 2920, 1688, 1551, 1526, 1373, 1247, 1140, 774 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.19-1.31 (m, 6H), 2.06 (d, 0.5H, *J* = 14.5 Hz), 2.22 (dd, 0.5H, *J* = 2.6, 15.8 Hz), 2.60-2.74 (m, 1H), 3.76-4.00 (m, 4H), 4.10 (q, 2H, *J* = 7.3, 14.5 Hz), 4.93-5.07 (m, 1H), 5.10-5.22 (m, 1H), 5.45 (d, 0.5H, *J* = 7.3 Hz), 5.80 (d, 0.5H, J = 10.3 Hz), 7.20-7.27 (m, 2H), 7.29-7.38 (m, 2H), 7.53 (t, 0.5H, *J* = 7.3Hz), 7.63 (t, 0.5H, *J* = 7.3 Hz). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.6, 14.7, 24.3, 24.4, 27.1, 30.0, 40.0, 57.5, 57.7, 61.3, 61.7, 61.8, 64.9, 65.0, 65.1, 86.7, 87.1, 107.9, 108.1, 126.6, 127.2, 128.8, 129.0, 129.1, 129.2, 129.3, 130.0, 134.7, 136.6, 156.0. Anal. Calcd. for $C_{16}H_{22}N_2O_6$ (338.36): C, 56.80; H, 6.55; N, 8.28. Found: C, 56.67; H, 6.61; N, 8.37.



3b. *Ethyl (3-(2-(4-methoxyphenyl)-1,3-dioxolan-2-yl)-2-nitro-1-(4-nitrophenyl)propyl)carbamate.* Yield 65%. Colorless oil. FTIR (neat) ν: 3325, 2930, 1705, 1611, 1557, 1367, 1060, 735 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.05-1.28 (m, 3H), 2.25-2.37 (m, 1H), 2.77 (dd, 0.4H, *J* = 8.5, 15.8 Hz), 2.88 (dd, 0.6H, *J* = 9.5, 15.8 Hz), 3.65-3.82 (m, 5H), 3.84-3.98 (m, 2H), 4.00-4.13 (m, 2H), 4.99-5.36 (m, 2H), 5.64-6.02 (m, 1H), 6.84-6.89 (m, 2H), 7.28-7.33 (m, 2H), 7.40-7.46 (m, 2H), 8.20 (t, 2H, *J* = 8.5 Hz). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.6, 14.7, 39.8, 41.5, 55.6, 56.8, 57.0, 612.1, 64.8, 64.8, 64.9, 86.0, 86.4, 108.0, 108.2, 114.1, 124.3, 124.5, 126.9, 127.0, 127.4, 127.5, 127.9, 128.3, 133.0, 144.5, 148.1, 148.2, 156.0, 160.1. Anal. Calcd. for $C_{22}H_{25}N_3O_9$ (475.45): C, 55.58; H, 5.30; N, 8.84. Found: C, 55.67; H, 5.22; N, 9.01.

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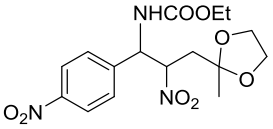
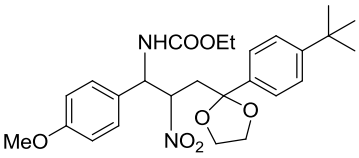
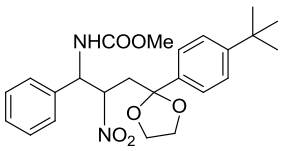
[1] A. Palmieri, S. Gabrielli, R. Ballini, *Chem. Commun.* **2010**, *46*, 6165–6167.
[2] G. Rosini, R. Ballini, P. Sorrenti, *Tetrahedron* **1983**, *39*, 4127–4132.
[3] T. Mecozzi, M. Petrini, *J. Org. Chem***.** **1999**, *64*, 8970-8972.



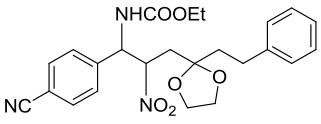
3c. *Ethyl (3-(2-methyl-1,3-dioxolan-2-yl)-2-nitro-1-(4-nitrophenyl)propyl)-carbamate.* Yield 63%. Pale yellow solid, m.p. 85-89°C. FTIR (neat) ν: 3430, 3321, 2927, 1694, 1597, 1547, 1375, 1108, 769, 698 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.36-1.41 (m, 6H), 2.08-2.17 (m, 0.6H), 2.19-2.27 (m, 0.4H), 2.61-2.80 (m, 1H), 3.78-4.03 (m, 4H), 4.06-4.17 (m, 2H), 4.89-5.31 (m, 2H), 5.69 (d, 0.4H, J = 8.5 Hz), 6.00 (d, 0.6H, J = 9.0 Hz), 7.41-7.47 (m, 2H), 8.18-8.29 (m, 2H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.7, 24.1, 24.2, 24.3, 38.6, 38.8, 40.1, 56.8, 64.9, 65.0, 65.1, 86,1, 86.5, 107.7, 107.9, 124.1, 124.3, 124.5, 127.4, 127.6, 128.0, 128.4, 144.4, 145.6, 148.2, 148.3, 156.1. Anal. Calcd. for $C_{16}H_{21}N_3O_8$ (383.35): C, 50.13; H, 5.52; N, 10.96. Found: C, 50.01; H, 5.64; N, 11.07.



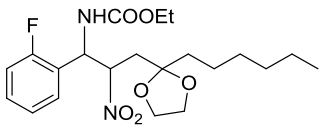
3d. *Ethyl 1-(4-tert-butylphenyl)-3-(2-(4-methoxyphenyl)-1,3-dioxolan-2-yl)-2-nitropropyl- carbamate* Yield 80%. Pale yellow oil. FTIR (neat) ν: 3433, 3341, 2926, 1701, 1589, 1562, 1376, 1116, 777, cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.16-1.33 (m, 12H), 2.24 (d, 0.5H, *J* = 15.8 Hz), 2.33-2.41 (m, 0.5H), 2.72-2.94 (m, 1H), 3.67-3.83 (m, 4H), 3.86-3.98 (m, 1H), 4.01-4.16 (m, 4H), 4.99-5.19 (m, 2H), 5.25-5.38 (m,0.5H), 5.64-5.74 (m, 0.5H), 6.81-6.88 (m, 2H), 7.13 (t, 2H, *J* = 8.5 Hz), 7.27-7.38 (m, 4H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.4, 14.6, 14.7, 21.3, 31.5, 34.8, 39.9, 41.3, 53.7, 55.5, 56.9, 57.0, 60.6, 61.6, 61.7, 64.8, 64.9, 65.0, 86.5, 87.04, 108.3, 108.5, 114.5, 114.6, 125.3, 125.4, 127.7, 128.3, 129.4, 138.3, 138.4, 151.6, 151.7, 159.8, 159.9, 171.4. Anal. Calcd. for $C_{26}H_{34}N_2O_7$ (486,56): C, 64.18; H, 7.04; N, 5.76. Found: C, 64.26; H, 6.98; N, 5.61.



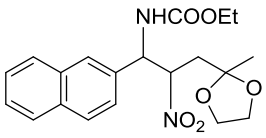
3e. *Methyl (3-(2-(4-(tert-butyl)phenyl)-1,3-dioxolan-2-yl)-2-nitro-1-phenylpropyl)carbamate.* Yield 99%. Pale yellow oil. FTIR (neat) ν: 3432, 3327, 2919, 1690, 1599, 1547, 1369, 1112, 771, 693 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.31 (s, 9H), 2.15-2.42 (m, 1H), 2.70-2.88 (m, 1H), 3.62 (s, 1.6H), 3.65 (s, 1.4H), 3.68-3.82 (m, 2H), 3.86-3.97 (m, 1H), 4.02-4.16 (m, 1H), 5.06-5.30 (m, 2H), 5.48 (d, 0.4H, *J* = 9.0 Hz), 5.83 (d, 0.6H, *J* = 8.5 Hz), 7.16-7.24 (m, 2H), 7.27-7.38 (m, 7H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.4, 21.3, 31.5, 34.8, 39.7, 41.4, 52.7, 52.8, 57.4, 57.6, 60.6, 64.8, 64.9, 65.0, 86.3, 86.9, 108.3, 108.5, 125.4, 125.5, 126.4, 127.1, 128.9, 129.2, 129.3, 137.2, 138.3, 151.8, 156.4. Anal. Calcd. for $C_{24}H_{30}N_2O_6$ (442.50): C, 65.14; H, 6.83; N, 6.33. Found: C, 65.27; H, 6.64; N, 6.41.



3f. *Ethyl (1-(4-cyanophenyl)-2-nitro-3-(2-phenethyl-1,3-dioxolan-2-yl)propyl)carbamate.* Yield 97%. Colorless oil. FTIR (neat) ν: 3427, 3327, 2919, 2227, 1688, 1604, 1555, 1377, 1112, 776, 695 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.22-1.28 (m, 3H), 1.82-1.94 (m, 2H), 2.03-2.21 (m, 2H), 2.57-2.76 (m, 2H), 3.83-4.02 (m, 4H), 4.11 (q, 2H, *J* = 7.3, 14.5 Hz), 4.89-5.05 (m, 1H), 5.12-5.20 (m, 1H), 5.79 (d, 0.4H, *J* = 7.7 Hz), 6.02 (d, 0.6H, *J* = 9.8 Hz), 7.11-7.22 (m, 3H), 7.24-7.30 (m, 2H), 7.49 (d, 2H, *J* = 8.1 Hz), 7.61-7.68 (m, 2H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.4, 14.7, 21.3, 30.2, 36.9, 38.3, 39.3, 57.1, 60.7, 62.0, 65.3, 65.4, 65.5, 86.2, 86.5, 109.3, 109.4, 112.8, 113.0, 118.4, 126.3, 127.4, 128.2, 128.4, 128.5, 128.7, 128.8, 132.9, 133.1, 141.3, 141.4, 142.6, 156.0, 171.4. Anal. Calcd. for $C_{24}H_{27}N_3O_6$ (453.49): C, 63.56; H, 6.00; N, 9.27. Found: C, 63.47; H, 6.13; N, 9.40.

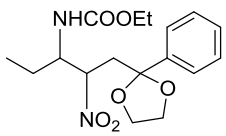


3g. *Ethyl (1-(2-fluorophenyl)-3-(2-hexyl-1,3-dioxolan-2-yl)-2-nitropropyl)carbamate.* Yield 99%. Pale yellow oil. FTIR (neat) ν: 3433, 3317, 2930, 1686, 1604, 1555, 1373, 1108, 776, 694 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 0.84-0.91 (m, 3H), 1.17-1.32 (m, 11H), 1.50-1.65 (m, 2H), 1.96-2.29 (m, 1H), 2.62-2.71 (m, 1H), 3.82-3.90 (m, 2H), 3.91-3.99 (m, 2H), 4.06-4.16 (m, 2H), 4.97-5.12 (m, 1H), 5.19-5.42 (m, 1H), 5.49 (d, 0.4H, *J* = 9.4 Hz), 5.79 (d, 0.6H, *J* = 9.8 Hz), 7.05-7.23 (m, 3H), 7.29-7.36 (m, 1H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.3, 14.7, 22.8, 23.9, 24.0, 27.2, 29.5, 29.6, 29.9, 31.9, 37.2, 37.6, 37.8, 38.1, 53.4, 55.2, 61.8, 61.9, 65.3, 85.9, 86.1, 109.7, 116.1, 116.2, 116.3, 116.4, 124.9, 125.0, 125.1, 128.5, 130.6, 130.7, 130.9, 131.0, 156.0, 159.2, 161.6. Anal. Calcd. for $C_{21}H_{31}FN_2O_6$ (426.48): C, 59.14; H, 7.33; N, 6.57. Found: C, 59.27; H, 7.21; N, 6.45.

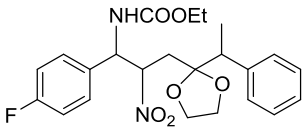


3h. *Ethyl (3-(2-methyl-1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)-2-nitropropyl)carbamate.* Yield 67%. Pale yellow oil. FTIR (neat) ν: 3437, 3333, 2927, 1699, 1586, 1532, 1377, 1101, 779 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.18-1.32 (m, 6H), 2.18 (d, 0.6H, *J* = 14.9 Hz), 2.28

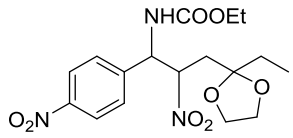
(d, 0.4H, *J* = 15.8 Hz), 2.75-2.85 (m, 1H), 3.77-4.00 (m, 4H), 4.06-4.16 (m, 2H), 5.24 (s, 1H), 5.88-6.20 (m, 2H), 7.28-7.66 (m, 4H), 7.79-7.93 (m, 2H), 8.06-8.23 (m, 1H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.4, 14.7, 21.3, 24.3, 24.4, 29.9, 38.2, 40.2, 53.2, 53.4, 53.7, 60.6, 61.8, 64.9, 65.0, 65.1, 85.6, 86.8, 108.0, 108.1, 122.2, 122.7, 123.5, 124.0, 125.3, 125.6, 126.3, 126.4, 127.4, 127.5, 129.4, 129.5, 129.6, 129.8, 130.6, 132.9, 133,3, 134.2, 134.3, 156.1. Anal. Calcd. for $C_{20}H_{24}N_2O_6$ (388.41): C, 61.84; H, 6.23; N, 7.21. Found: C, 61.97; H, 6.41; N, 7.09.



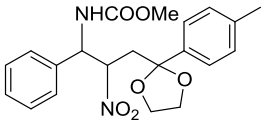
3i. *Ethyl (2-nitro-1-(2-phenyl-1,3-dioxolan-2-yl)pentan-3-yl)carbamate.* Yield 90%. White solid, m.p. 114-116°C. FTIR (neat) ν: 3437, 3318, 2924, 1676, 1602, 1538, 1373, 1019, 772, 697 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 0.90-1.02 (m, 3H), 1.16-1.30 (m, 3H), 1.29-1.43 (m, 1H), 1.50-1.67 (m, 1H), 2.25 (t, 1H, *J* = 17.0 Hz), 2.79-2.90 (m, 1H), 3.66-3.83 (m, 2H), 3.86-4.00 (m, 2H), 4.01-4.18 (m, 3H), 4.59 (d, 0.5H, *J* = 9.0 Hz), 4.88-4.94 (m, 0.5H), 4.97-5.05 (m, 1H), 7.30-7.39 (m, 3H), 7.40-7.47 (m, 2H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 10.6, 10.7, 14.6, 14.7, 23.6, 26.1, 39.8, 41.3, 54.8, 55.2, 61.4, 61.5, 64.8, 64.9, 65.0, 85.3, 85.8, 108.4, 125.7, 125.8, 128.6, 128.7, 141.5, 156.7. Anal. Calcd. for $C_{17}H_{24}N_2O_6$ (352.28): C, 57.94; H, 6.86; N, 7.95. Found: C, 58.09; H, 6.95; N, 7.76.



3j. *Ethyl (1-(4-fluorophenyl)-2-nitro-3-(2-(1-phenylethyl)-1,3-dioxolan-2-yl)propyl)carbamate.* Yield 95%. Colorless oil. FTIR (neat) ν: 3423, 3329, 2925, 1698, 1607, 1556, 1120, 778 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.17-1.26 (m, 3H), 1.28 (d, 1.8H, *J* = 6.8 Hz), 1.31 (d, 1.2H, *J* = 6.8 Hz), 1.87-2.21 (m, 1H), 2.46-2.65 (m, 1H), 2.92-3.10 (m, 1H), 3.55-3.97 (m, 4H), 4.01-4.14 (m, 2H), 4.55-4.74 (m, 0.4H), 4.75-4.87 (m, 0.6H), 4.91-5.72 (m, 2H), 6.94-7.02 (m, 2H), 7.04-7.11 (m, 2H), 7.19-7.33 (m, 5H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 14.7, 15.5, 15.6, 15.8, 16.0, 35.0, 37.0, 37.2, 38.4, 46.5, 46.9, 47.9, 48.2, 56.8, 56.9, 61.8, 65.8, 65.9, 66.0, 66.1, 66.5, 86.9, 87.1, 87.3, 87.4, 111.3, 111.4, 111.5, 111.6, 116.0, 116.1, 116.2, 116.3, 116.4, 127.2, 127.3, 128.1, 128.2, 128.4, 128.5, 128.8, 128.9, 129.1, 129.2, 129.3, 133.1, 141.4, 141.5, 141.6, 161.5, 161.7, 164.0, 164.2. Anal. Calcd. for $C_{23}H_{27}FN_2O_6$ (446.47): C, 61.87; H, 6.10; N, 6.27. Found: C, 61.99; H, 6.00; N, 6.39.

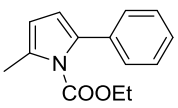


3k. *Ethyl (3-(2-ethyl-1,3-dioxolan-2-yl)-2-nitro-1-(4-nitrophenyl)propyl)carbamate.* Yield 88. Pale yellow waxy. FTIR (neat) ν: 3442, 3322, 2928, 1698, 1553, 1379, 1243, 1062, 775 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 0.79-0.91 (m, 3H), 1.17-1.30 (m, 2H), 1.46-1.61 (m, 2H), 1.62-1.84 (m, 1H), 2.04-2.23 (m, 1H), 2.57-2.65 (m, 0.4H), 2.67-2.76 (m, 0.6H), 3.78-4.03 (m, 4H), 4.06-4.17 (m, 2H), 4.89-5.00 (m, 0.4H), 5.00-5.12 (m, 06H), 5.20-5.33 (m, 1H), 5.64 (d, 0.4H, *J* = 8.5 Hz), 5.98 (d, 0.6H, *J* = 9.4 Hz), 7.40-7.47 (m, 2H), 8.18-8.28 (m, 2H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 8.3, 8.4, 14.7, 30.2, 30.4, 34.2, 36.1, 36.5, 37.7, 56.9, 62.1, 65.2, 65.3, 65.4, 74.2, 74.9, 86.2, 86.6, 88.1, 109.9, 124.1, 124.3, 124.5, 127.4, 127.6, 127.9, 128.4, 144.5, 148.1, 156.1. Anal. Calcd. for $C_{17}H_{23}N_3O_8$ (397.38): C, 51.38; H, 5.83; N, 10.57. Found: C, 51.31; H, 5.98; N, 10.45.

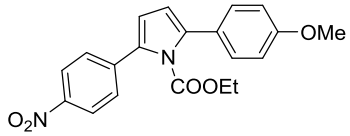


3l. *Methyl (2-nitro-1-phenyl-3-(2-(p-tolyl)-1,3-dioxolan-2-yl)propyl)carbamate.* Yield 72%. White waxy. FTIR (neat) ν: 3432, 3327, 2919, 1690, 1599, 1547, 1369, 1112, 771, 693 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 2.14-2.41 (m, 4H), 2-69-2.92 (m, 1H), 3.52-3.81 (m, 6H), 3.82-4.00 (m, 1H), 4.02-4.17 (m, 1H), 5.00-5.31 (m, 1H), 5.45 (d, 0.5H, *J* = 6.0 Hz), 5.45 (d, 0.5H, *J* = 7.7 Hz), 7.12-7.39 (m, 9H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 21.3, 40.0, 41.4, 52.8, 57.4, 57.6, 64.8, 64.9, 86.3, 86.9, 108.3, 108.5, 125.6, 126.4, 127.1, 128.8, 129.0, 129.1, 129.2, 129.3, 136.4, 137.2, 138.3, 138.4, 138.5, 138.6, 156.2, 156.4. Anal. Calcd. for $C_{21}H_{24}N_2O_6$ (400.43): C, 62.99; H, 6.04; N, 7.00. Found: C, 63.21; H, 5.85; N, 7.15.

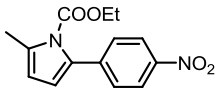
Spectroscopic Data for Compounds 4:



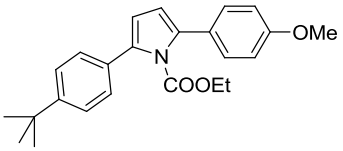
4a. *Ethyl 2-methyl-5-phenyl-1H-pyrrole-1-carboxylate*. Yield 70%. Yellow waxy solid. FTIR (neat) ν: 2921, 1699, 1556, 1372, 1239, 1029, 907, 733 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.05 (t, 3H, *J* = 7.3 Hz), 2.54 (s, 3H), 4.15 (q, 2H, *J* = 7.3, 14.5 Hz), 6.03 (d, 1H, *J* = 3.0 Hz), 6.08 (d, 1H, *J* = 3.0 Hz), 7.23-7.27 (m, 5H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 13.8, 15.6, 30.0, 53.0, 63.2, 103.4, 111.0, 112.9,127.0, 127.9, 128.5, 133.4, 135.2, 152.1. GC-MS (70eV): *m/z*: 229 [M^+], 184, 170, 156 (100), 141, 128, 104, 77, 51, 29. Anal. Calcd. for $C_{14}H_{15}NO_2$ (229.28): C, 73.34; H, 6.59; N, 6.11. Found: C, 73.49; H, 6.51; N, 5.99.



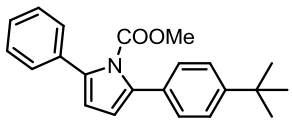
4b. *2-(4-methoxyphenyl)-5-(4-nitrophenyl)-1H-pyrrole-1carboxylate*. Yield 55%, Yellow waxy solid. FT-IR (neat) ν: 830, 1027, 1172, 1337, 1510, 1593, 1740, 2981. ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 0.97 (t, 3H, *J* = 7.3 Hz), 3.83 (s, 3H), 4.13 (q, 2H, *J* = 7.3, 14.5 Hz), 6.35 (d, 1H, *J* = 3.8 Hz), 6.45 (d, 1H, *J* = 3.8 Hz), 6.97-7.03 (m, 2H), 7.37 (d, 2H, *J* = 8.5 Hz), 7.56 (d, 2H, *J* = 8.5 Hz), 8.24 (d, 2H, *J* = 8.9 Hz). ^{13}C-NMR ($CDCl_3$, 100MHz) 13.6, 55.5, 64.1, 113.1, 113.5, 114.6, 115.4, 123.5, 123.7, 124.6, 125.8, 125.9, 128.7, 130.5, 134.1, 139.0, 140.5, 146.6, 151.6, 159.7. GC-MS (70eV): *m/z*: 366 [M^+], 336, 293 (100), 263, 247, 232, 204, 176, 117, 77, 44, 29. Anal. Calc. per $C_{20}H_{18}N_2O_5$ (366.37): C, 65.57; H, 4.95; N, 7.65. Found: C, 65.76; H, 5.05; N, 7.44.



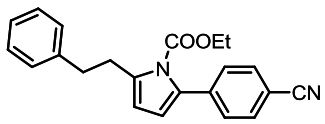
4c. *Ethyl 2-methyl-5-(4-nitrophenyl)-1H-pyrrole-1-carboxylate*. Yield 84%. Yellow solid, m.p. 61-63°C. FT-IR (neat) ν: 848, 1021, 1163, 1340, 1508, 1593, 1736, 2931. ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 1.12 (t, 3H, *J* = 7.3 Hz), 2.53 (s, 3H), 4.23 (q, 2H, *J* = 7.3, 14.5 Hz), 6.02-6.04 (m, 1H), 6.27 (d, 1H, *J* = 3.4 Hz), 7.30-3.39 (m, 2H), 8.12-8.24 (m, 2H). ^{13}C-NMR ($CDCl_3$, 100MHz) 13.9, 15.8, 63.8, 111.9, 115.6, 123.4, 124.6, 128.6, 133.1, 135.7, 141.5, 146.4, 151.6. GC-MS (70eV): *m/z*: 274 [M^+, (100)], 229, 202, 185, 155, 127, 77, 29. Anal. Calc. per $C_{14}H_{14}N_2O_4$ (274.28): C, 61.31; H, 5.15; N, 10.21. Found: C, 61.20; H, 4.98; N, 10.33.



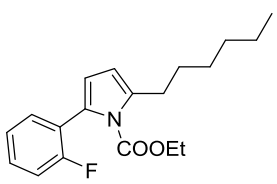
4d. *Ethyl 2-(4-tert-butylphenyl)-5-(4-methoxyphenyl)-1H-pyrrole-1-carboxylate.* Yield 55%. Yellow oil. FT-IR (neat) ν: 2967, 1756, 1555, 1376, 1382, 1149, 761. ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 0.85 (t, 3H, *J* = 7.3 Hz), 1.36 (s, 9H), 3.85 (s, 3H), 4.05 (q, 2H, *J* = 7.3, 14.5 Hz), 6.21-6.29 (m, 2H), 6.89-6.97 (m, 2H), 7.30-7.45 (m, 6H). ^{13}C-NMR ($CDCl_3$, 100MHz) 13.3, 31.5, 34.7, 55.5, 63.5, 112.3, 112.4, 113.5, 124.9, 126.6, 128.4, 130.2, 131.3, 136.5, 150.4, 152.1, 159.3. GC-MS (70eV): *m/z*: 377 [M^+], 318, 304(100), 289, 274, 246, 204, 181, 130, 102, 77, 57, 29. Anal. Calc. per $C_{24}H_{27}NO_3$ (377.48): C, 76.36; H, 7.21; N, 3.71. Found: C, 76.45; H, 7.33; N, 3.83.



4e.*Methyl 2-(4-tert-butylphenyl)-5-phenyl-1H-pyrrole-1-carboxylate*. Yield 75%. Pale yellow solid, m.p. 87-90°C. FT-IR (neat) ν: 2960, 1744, 1557, 1365, 1302, 1149, 755. ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 1.43 (s, 9H), 3.64 (s, 3H), 6.24-6.33 (m, 2H), 7.31-7.45 (m, 9H). ^{13}C-NMR ($CDCl_3$, 100MHz) 31.6, 34.9, 54.1, 112.9, 113.1, 125.1, 127.5, 128.2, 128.4, 128.5, 130.7, 134.0, 136.5, 137.0, 150.5. GC-MS (70eV): *m/z*: 333 [M^+, (100)], 318, 274, 259, 244, 217, 159, 128, 115, 77, 51, 41. Anal. Calc. per $C_{22}H_{23}NO_2$ (333.43): C, 79.25; H, 6.95; N, 4.20. Found: C, 79.31; H, 6.78; N, 4.33.

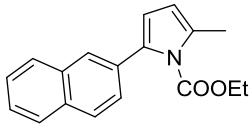


4f.*Ethyl 2-(4-cyanophenyl)-5-phenethyl-1H-pyrrole-1-carboxylate.* Yield 79%. White solid, m.p. 90-92°C. FT-IR (neat) ν: 2922, 2224, 1737, 1603, 1523, 1372, 1143, 1070, 802. ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 1.13 (t, 3H, *J* = 7.3 Hz), 2.91-3.00 (m, 2H), 3.12-3.23 (m, 2H), 4.23 (q, 2H, *J* = 7.3, 14.5 Hz), 6.11 (d, 1H, *J* = 3.4 Hz), 6.27 (d, 1H, *J* = 3.8 Hz), 7.20-7.31 (m, 5H), 7.45 (d, 2H, *J* = 8.1 Hz), 7.62 (d, 2H, *J* = 8.1 Hz). ^{13}C-NMR ($CDCl_3$, 100MHz) 13.8, 31.0, 35.7, 63.8, 110.2, 111.1, 115, 0, 119.3, 126.3, 128.5, 128.6, 131.8, 133.5, 139.1, 139.6, 141.6, 151.5. GC-MS (70eV): *m/z*: 344 [M^+], 269, 253, 209, 181 (100), 140, 91, 65, 29. Anal. Calc. per $C_{22}H_{20}N_2O_2$ (344.41): C, 76.72; H, 5.85; N, 8.13. Found: C, 76.79; H, 5.88; N, 8.01.

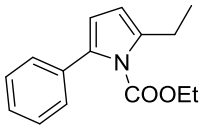


4g.*Ethyl 2-(2-fluorophenyl)-5-hexyl-1H-pyrrole-1-carboxylate.* Yield 53%. Yellow oil. FT-IR (neat) ν: 2930. 1735, 1599, 1517, 1360, 1126, 1067, 774. ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 0.89-0.94 (m, 3H), 1.03 (t, 3H, *J* = 7.3 Hz), 1.31-1.37 (m, 4H), 1.37-1.46 (m, 2H), 1.62-1.71 (m,

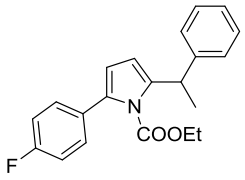
2H), 2.87 (t, 2H, *J* = 8.1 Hz), 4.18 (q, 2H, *J* = 6.8, 14.5 Hz), 6.04-6.08 (m, 1H), 6.18 (d, 1H, *J* = 3.4 Hz), 7.00-7.06 (m, 1H), 7.11-7.17 (m, 1H), 7.24-7.31 (m, 1H), 7.32-7.36 (m, 1H). ^{13}C-NMR ($CDCl_3$, 100MHz) 13.6, 14.4, 22.9, 29.2, 29.5, 30.0, 31.9, 63.3, 110.0, 114.0, 115.1, 124.1, 128.8, 128.9, 130.4, 139.0, 151.7, 158.7, 161.2. GC-MS (70eV): *m/z*: 317 [M^+], 246, 202, 174(100), 133, 102, 78, 29. Anal. Calc. per $C_{19}H_{24}FNO_2$ (317.40): C, 71.90; H, 7.62; N, 4.41. Found: C, 72.01; H, 7.58; N, 4.21.



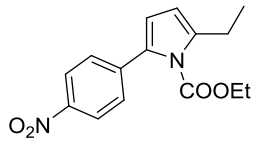
4h.*Ethyl 2-methyl-5-(naphthalen-2-yl)-1H-pyrrole-1-carboxylate*. Yield 28%. Yellow oil. FTIR (neat) ν: 2937, 1707, 1567, 1390, 1243, 1068, 913, 767 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 0.40 (t, 3H, *J* = 7.3 Hz), 2.58 (s, 3H), 3.75 (bs, 2H), 6.10-6.13 (m, 1H), 6.21 (d, 1H, *J* = 3.4 Hz), 7.36-7.50 (m, 4H), 7.63-7.69 (m, 1H), 7.78-7.89 (m, 2H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 12.9, 16.0, 62.8, 111.3, 113.9, 125.3, 125.8, 126.4, 127.4, 127.9, 128.3, 132.8, 133.2, 133.3, 133.7, 133.9, 151.8. GC-MS (70eV): *m/z*: 279 [M^+], 234, 206(100), 191, 165, 127, 102, 77, 51, 29. Anal. Calcd. for $C_{18}H_{17}NO_2$ (279.34): C, 77.40; H, 6.13; N, 5.01. Found: C, 77.56; H, 6.0; N, 4.89.



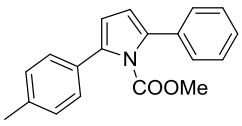
4i.*Ethyl 2-ethyl-5-phenyl-1H-pyrrole-1-carboxylate*. Yield 28%. Yellow oil. FTIR (neat) ν: 2925, 1704, 1565, 1367, 1243, 1030, 912, 737 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 0.98 (t, 3H, *J* = 7.3 Hz), 1.28 (t, 3H, *J* = 7.3 Hz), 2.88 (q, 2H, *J* = 7.3, 14.5 Hz), 4.11 (q, 2H, *J* = 6.8, 14.1 Hz), 6.01-6.04 (m, 1H), 6.15 (d, 1H, *J* = 3.4 Hz), 7.23-7.38 (m, 5H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 13.4. 13.7, 22.3, 63.3, 109.1, 112.8, 126.9, 128.0, 128.2, 128.3, 135.2, 139.7, 152.1. GC-MS (70eV): *m/z*: 243 [M^+], 228, 184, 170(100), 156, 143, 128, 115, 77, 51, 29. Anal. Calcd. for $C_{15}H_{17}NO_2$ (243.31): C, 74.05; H, 7.04; N, 5.76. Found: C, 74.16; H, 6.93; N, 5.91.



4j.*Ethyl 2-(4-fluorophenyl)-5-(1-phenylethyl)-1H-pyrrole-1-carboxylate.* Yield 57%. Pale yellow oil. FT-IR (neat) ν: 2967. 1740, 1593, 1512, 1363, 1292, 1115, 757. ^{1}H-NMR ($CDCl_3$, 400MHz) δ: 0.87 (t, 3H, *J* = 7.3 Hz), 1.63 (d, 3H, *J* = 6.6 Hz), 3.71-4.06 (m, 2H), 4.71 (q, 1H, *J* = 6.9, 13.9 Hz), 6.20-6.29 (m, 2H), 6.96-7.37 (m, 9H). ^{13}C-NMR ($CDCl_3$, 100MHz); 13.5, 23.0, 38.6, 63.4, 110.2, 112.3, 114.7, 115.2, 126.3, 127.4, 128.5, 129.8, 129.9, 130.9, 131.0, 134.8, 140.4, 146.1, 151.8, 159.7, 164.6. GC-MS (70eV): *m/z*: 337 [M^+], 322, 278, 264, 250(100), 220, 187, 133, 103, 77, 51, 29. Anal. Calc. per $C_{21}H_{20}FNO_2$ (337.39): C, 74.76; H, 5.98; N, 4.15. Found: C, 74.57; H, 6.16; N, 4.21.

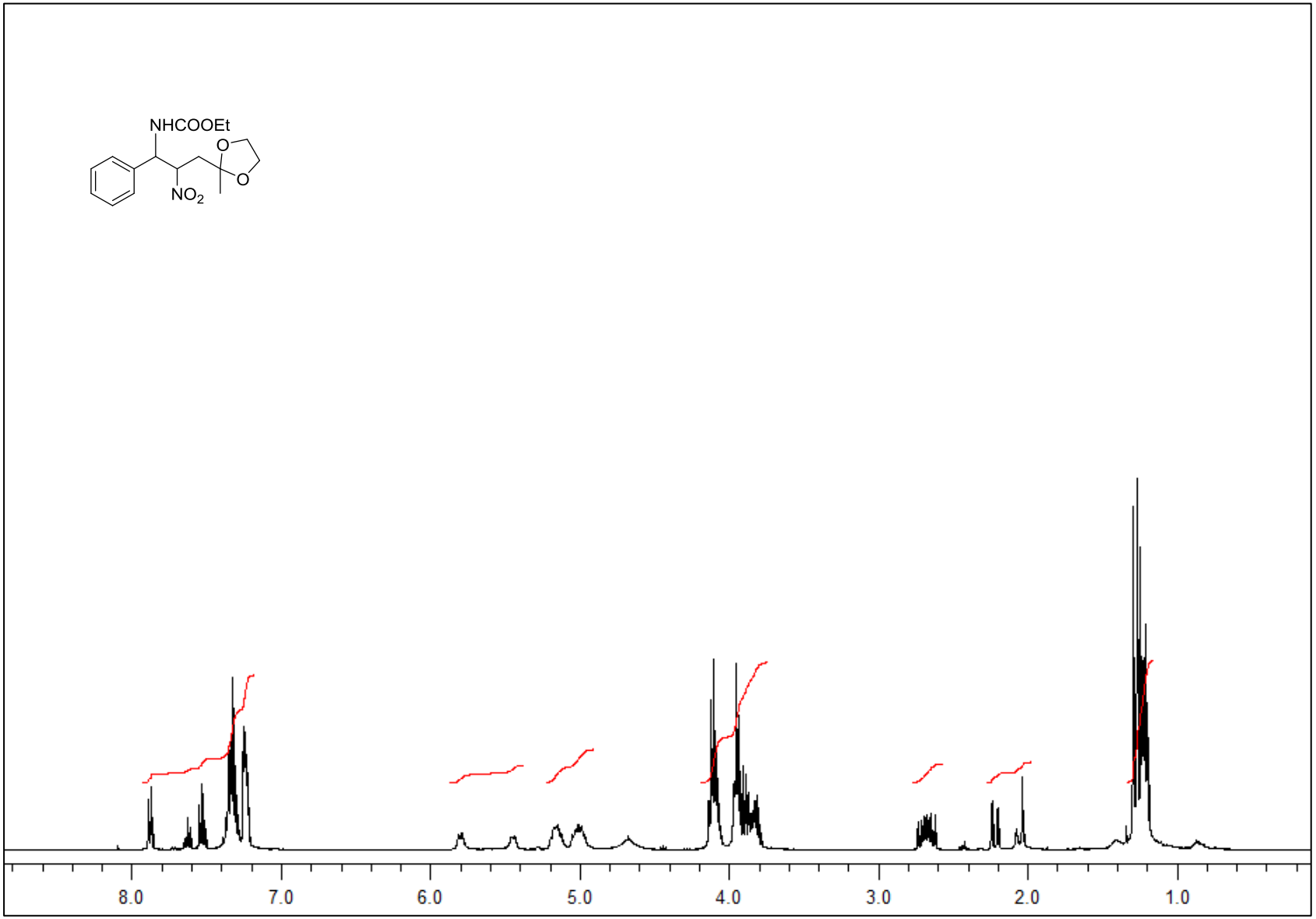


4k.*Ethyl 2-ethyl-5-(4-nitrophenyl)-1H-pyrrole-1-carboxylate*. Yield 73%. Orange solid, m.p. 48-50°C. FTIR (neat) ν: 2990, 1691, 1593, 1552, 1336, 1292, 1115, 753 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 1.10 (t, 3H, *J* = 7.3 Hz), 1.29 (t, 3H, *J* = 7.3 Hz), 2.89 (q, 2H, *J* = 7.3, 15.0 Hz), 4.21 (q, 2H, *J* = 6.8, 14.5 Hz), 6.05-6.09 (m, 1H), 6.30 (d, 1H, *J* = 3.0 Hz), 7.42 (d, 2H, *J* = 9.4 Hz), 8.20 (d, 2H, *J* = 8.9 Hz). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 13.4, 13.9, 22.4, 63.8, 109.9, 115.6, 123.4, 128.4, 133.1, 141.5, 142.0, 146.3, 151.6. GC-MS (70eV): *m/z*: 288 [M^+], 229, 215, 201, 183, 169(100), 154, 115, 77, 29. Anal. Calcd. for $C_{15}H_{16}N_2O_4$ (288.30): C, 62.49; H, 5.59; N, 9.72. Found: C, 62.56; H, 5.40; N, 10.09.

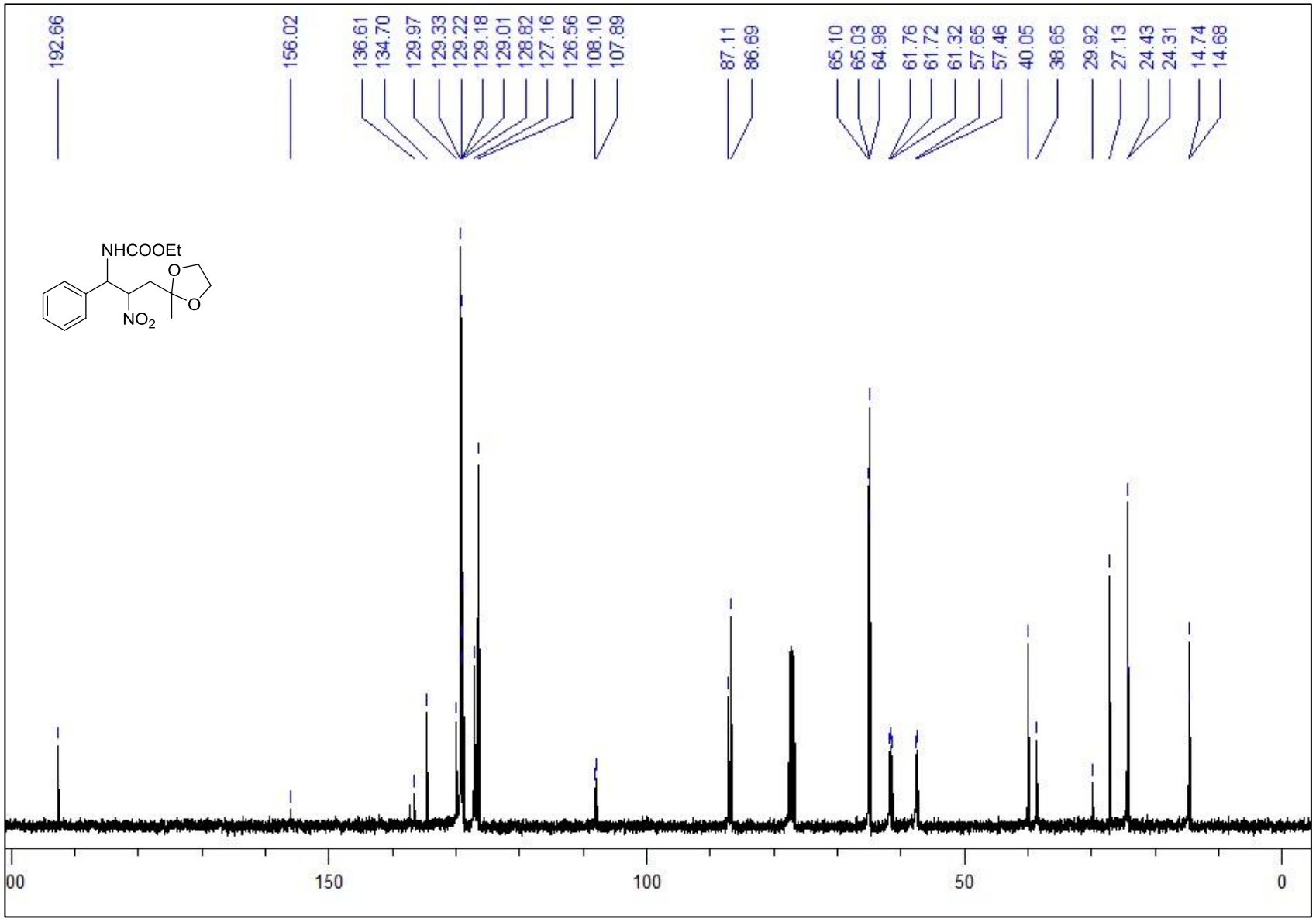


4l.*Methyl 2-phenyl-5-(p-tolyl)-1H-pyrrole-1-carboxylate.* Yield 54%. Orange oil. FTIR (neat) ν: 2937, 1704, 1553, 1376, 1220, 1062, 916, 765 cm^{-1}, ^{1}H-NMR (400MHz, $CDCl_3$) δ: 2.41 (s, 3H), 3.60 (s, 3H), 6.28-6.33 (m, 2H), 7.21 (d, 2H, *J* = 8.1 Hz), 7.30-7.36 (m, 3H), 7.39-7.43 (m, 4H). ^{13}C-NMR (100MHz, $CDCl_3$) δ: 21.5, 54.1, 112.8, 133.0, 127.5, 128.2, 128.5, 128.6, 128.9, 130.9, 133.9, 136.6, 137.0, 137.4, 152.7. GC-MS (70eV): *m/z*: 291 [M^+, 100], 259, 232, 216, 189, 154, 115, 89, 59. Anal. Calcd. for $C_{19}H_{17}NO_2$ (291.35): C, 78.33; H, 5.88; N, 4.81. Found: C, 78.39; H, 6.01; N, 4.77.

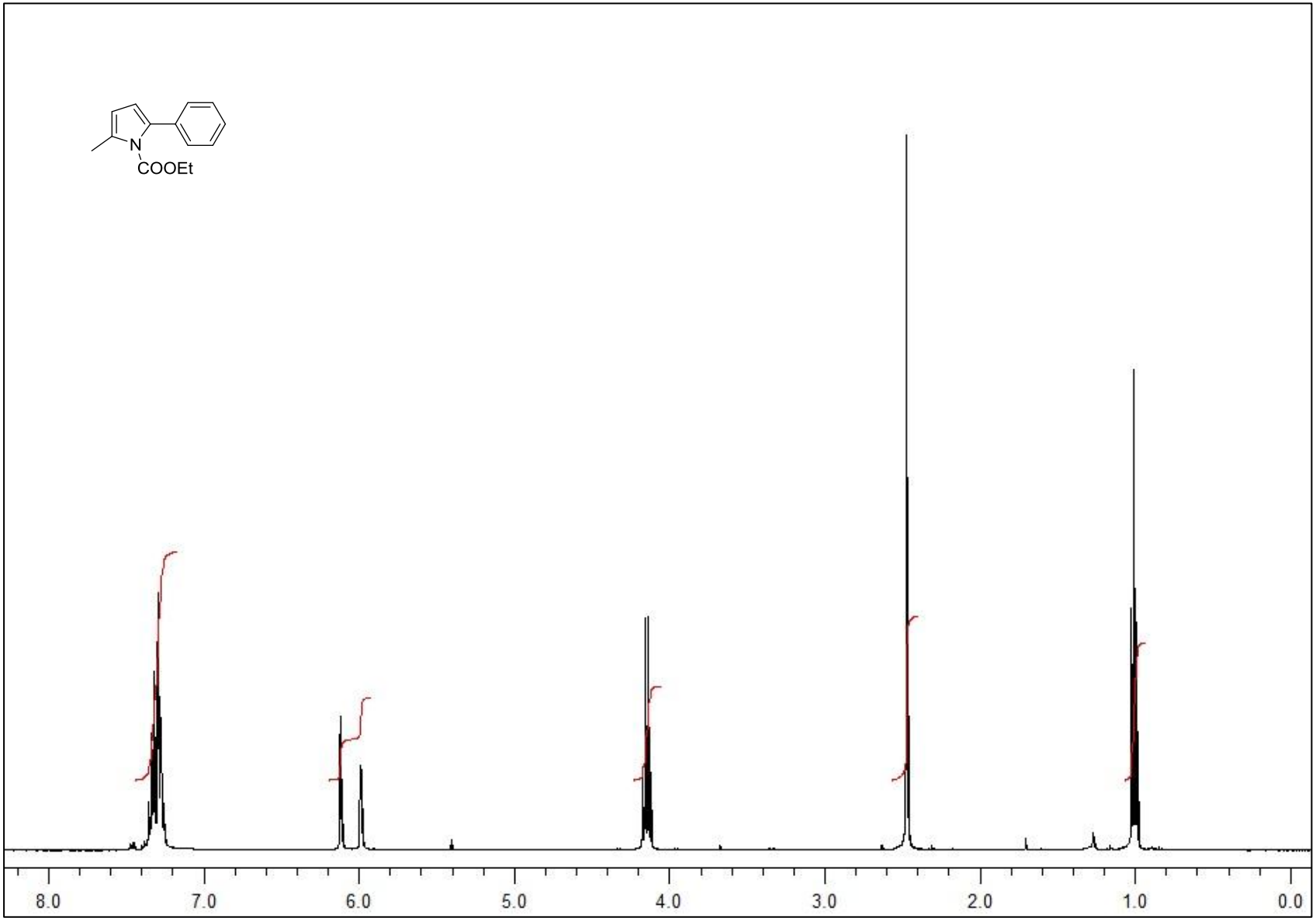
^{1}H NMR (400MHz. $CHCl_3$), **3a**



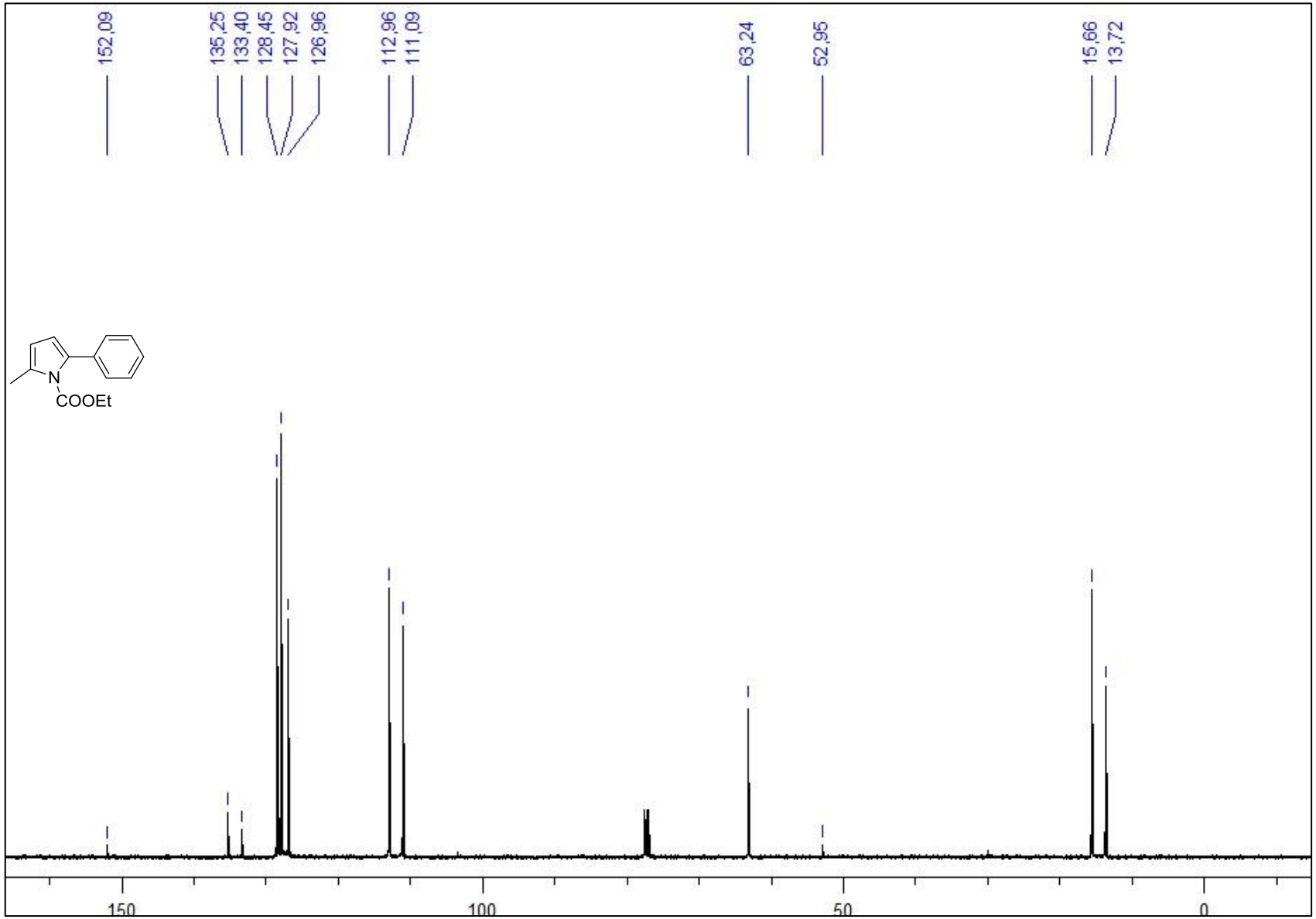
^{13}C NMR (400MHz. $CHCl_3$), **3a**



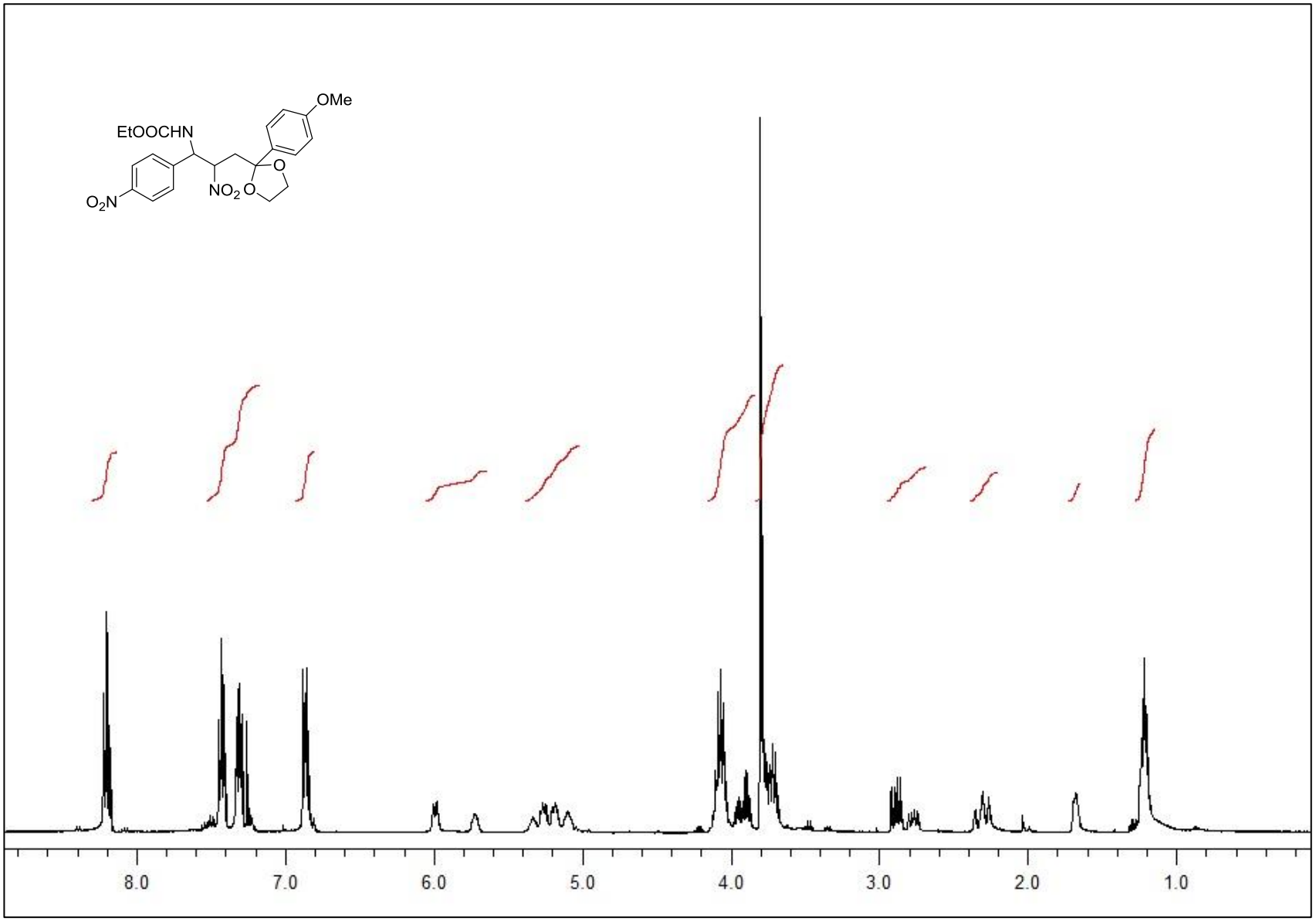
^{1}H NMR (400MHz. $CHCl_3$), **4a**



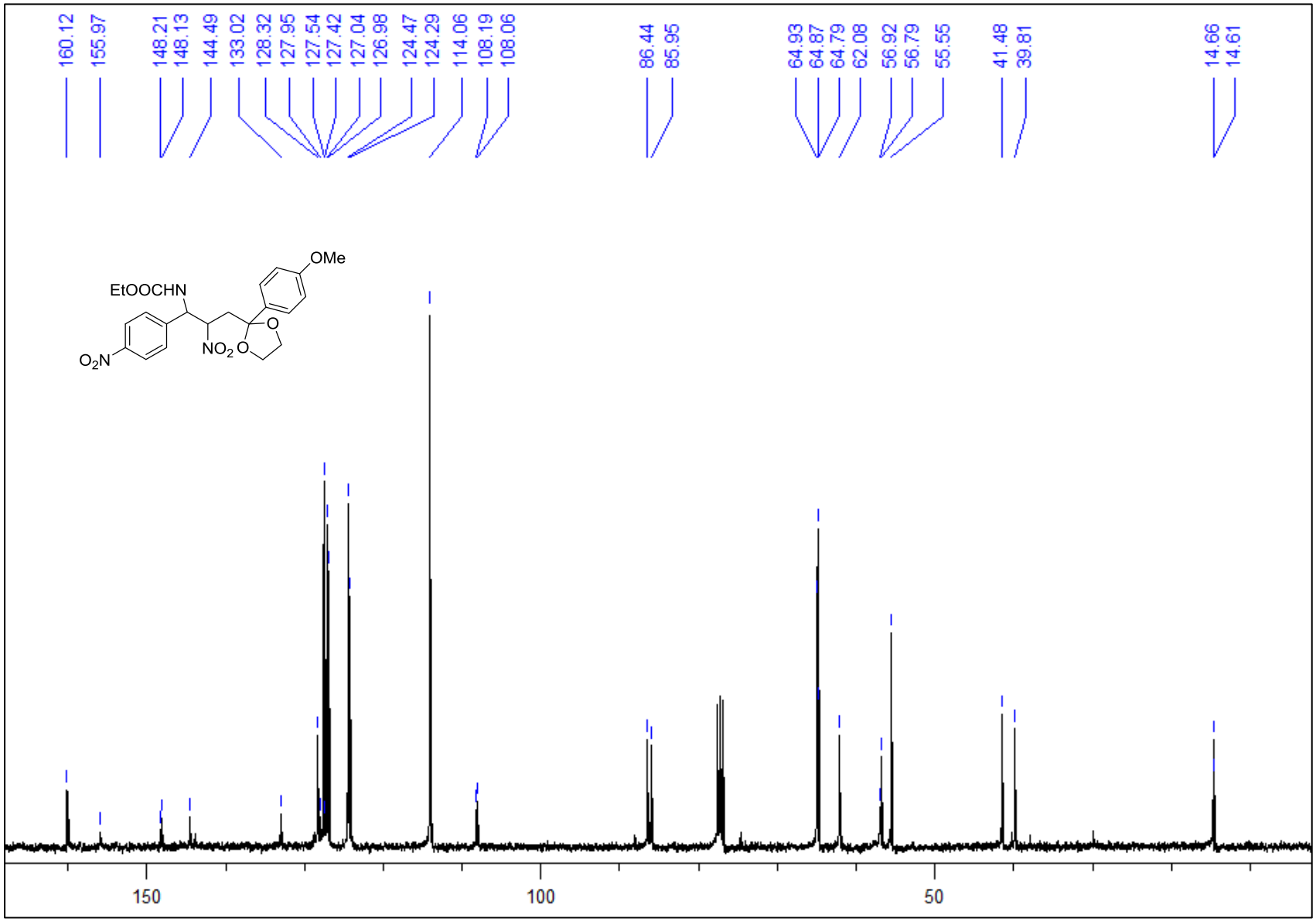
^{13}C NMR (400MHz. $CHCl_3$), **4a**



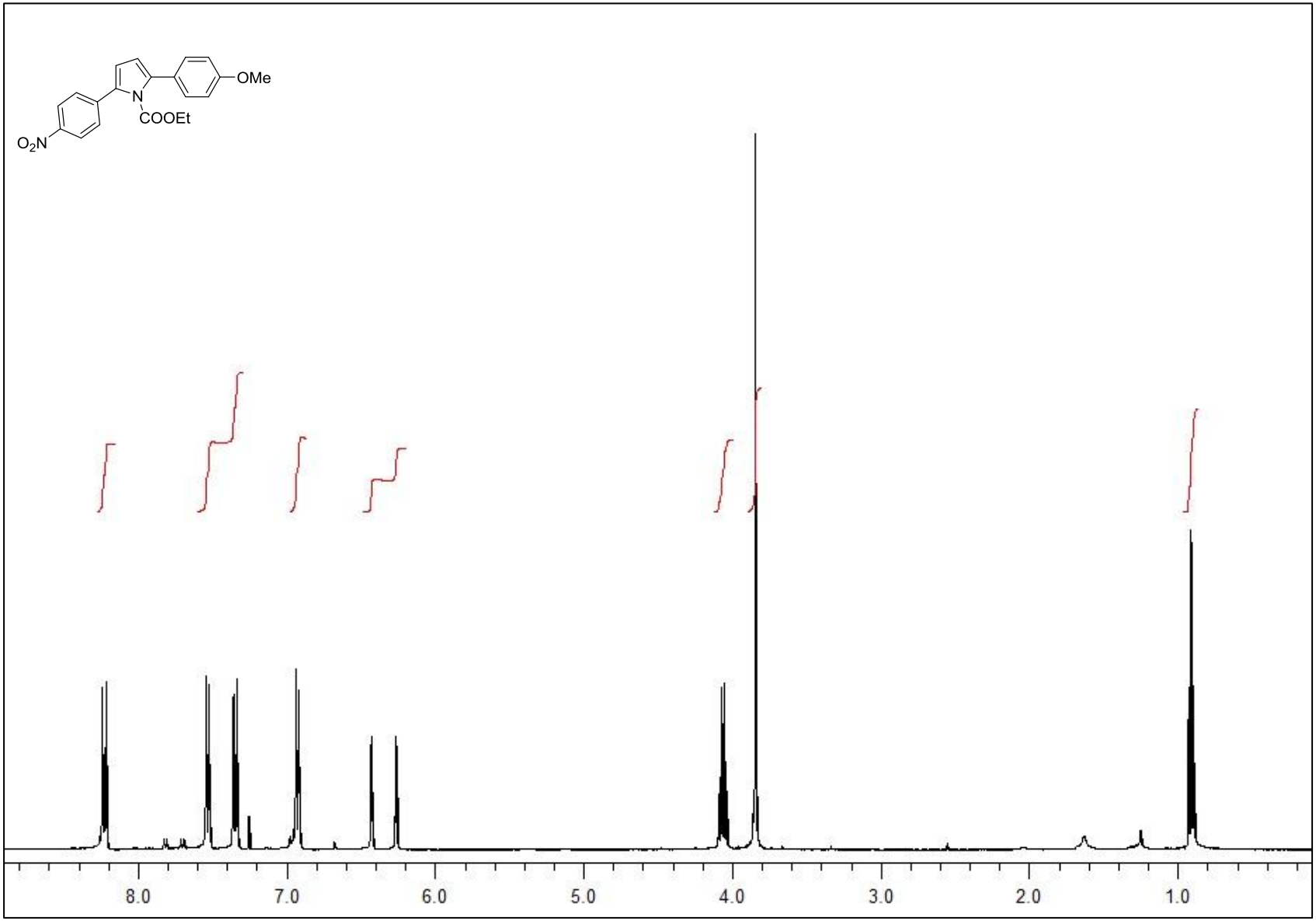
^{1}H NMR (400MHz. $CHCl_3$), **3b**



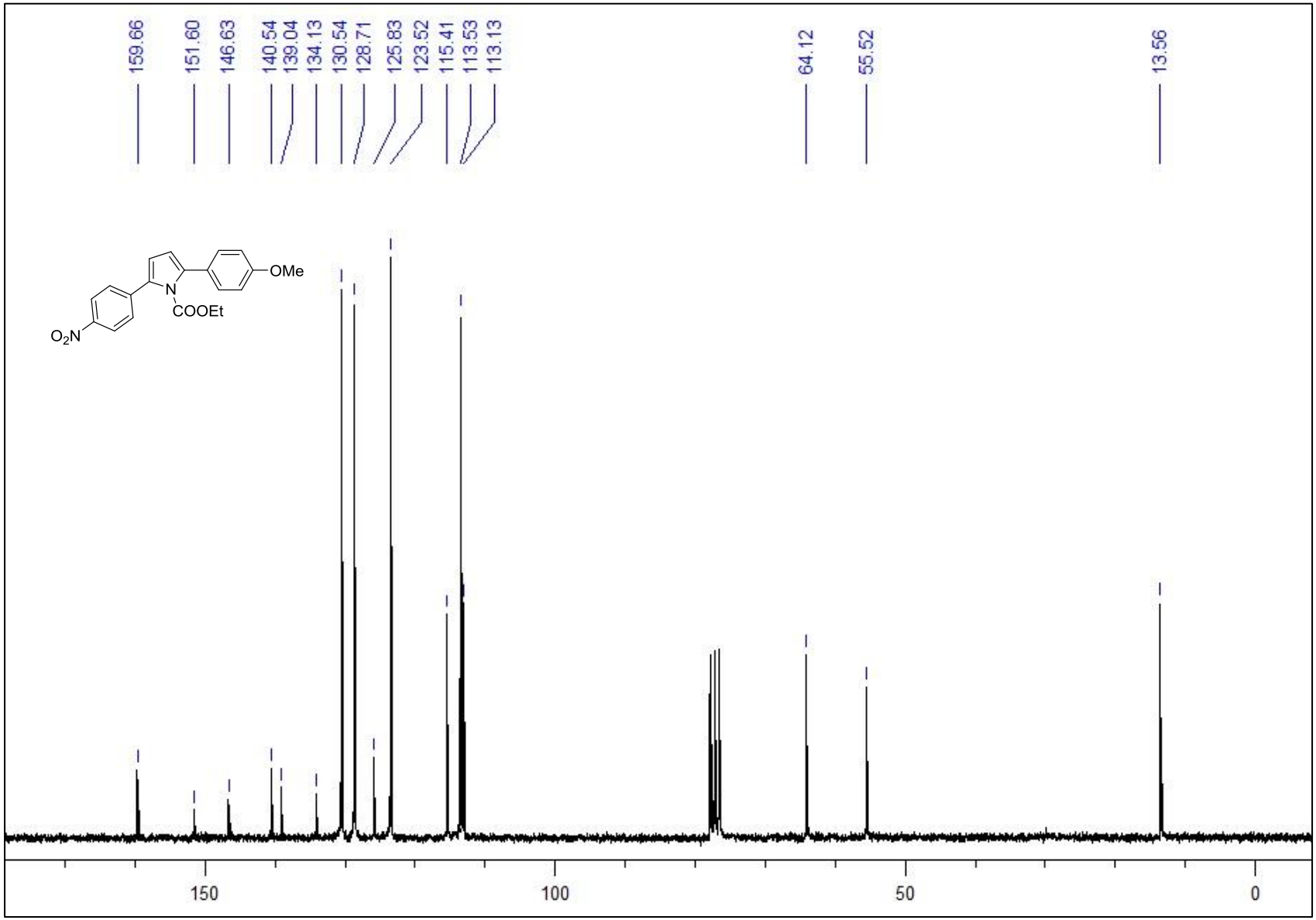
^{13}C NMR (400MHz. $CHCl_3$), **3b**



^{1}H NMR (400MHz. $CHCl_3$), **4b**



^{13}C NMR (400MHz. $CHCl_3$), **4b**



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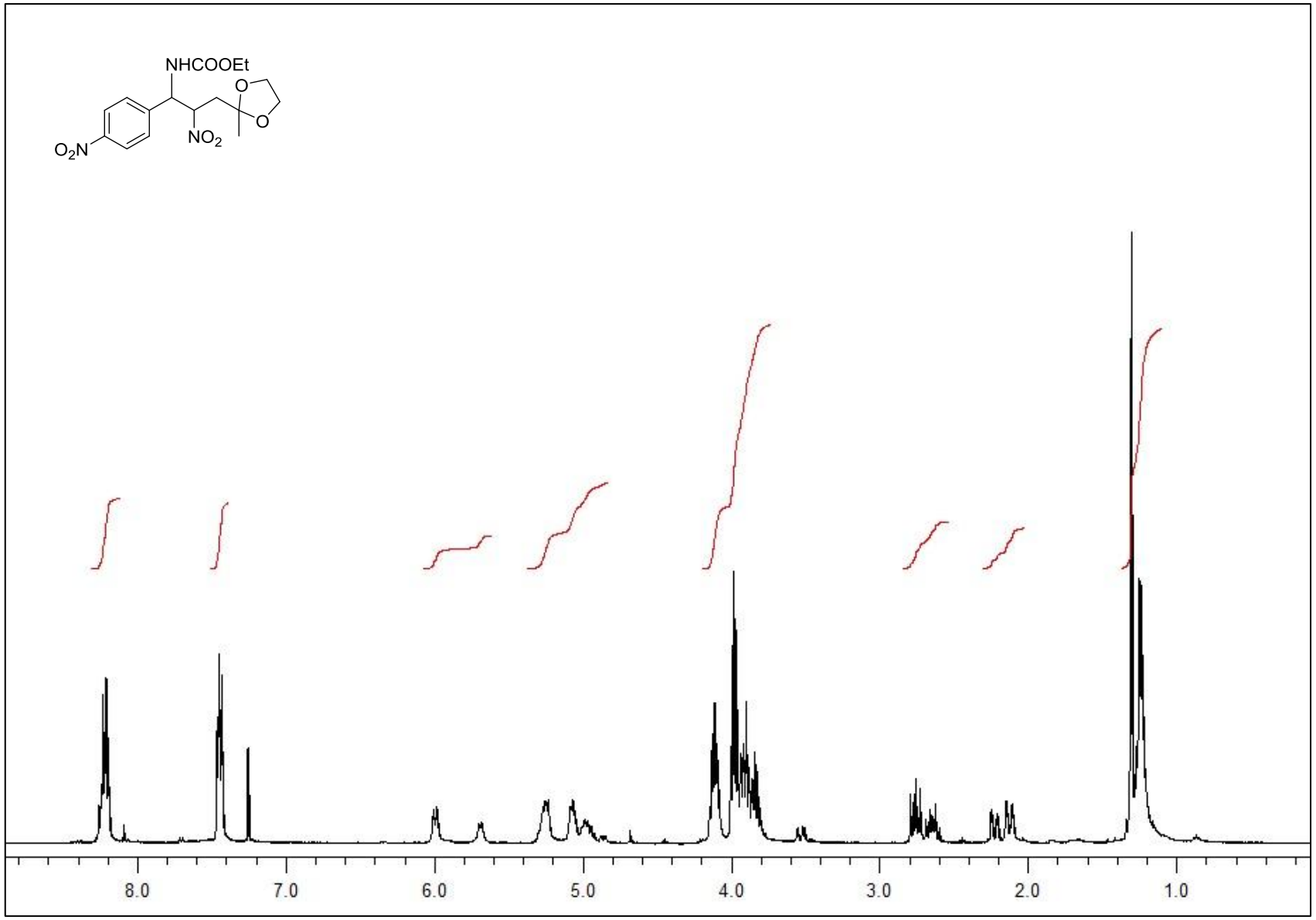
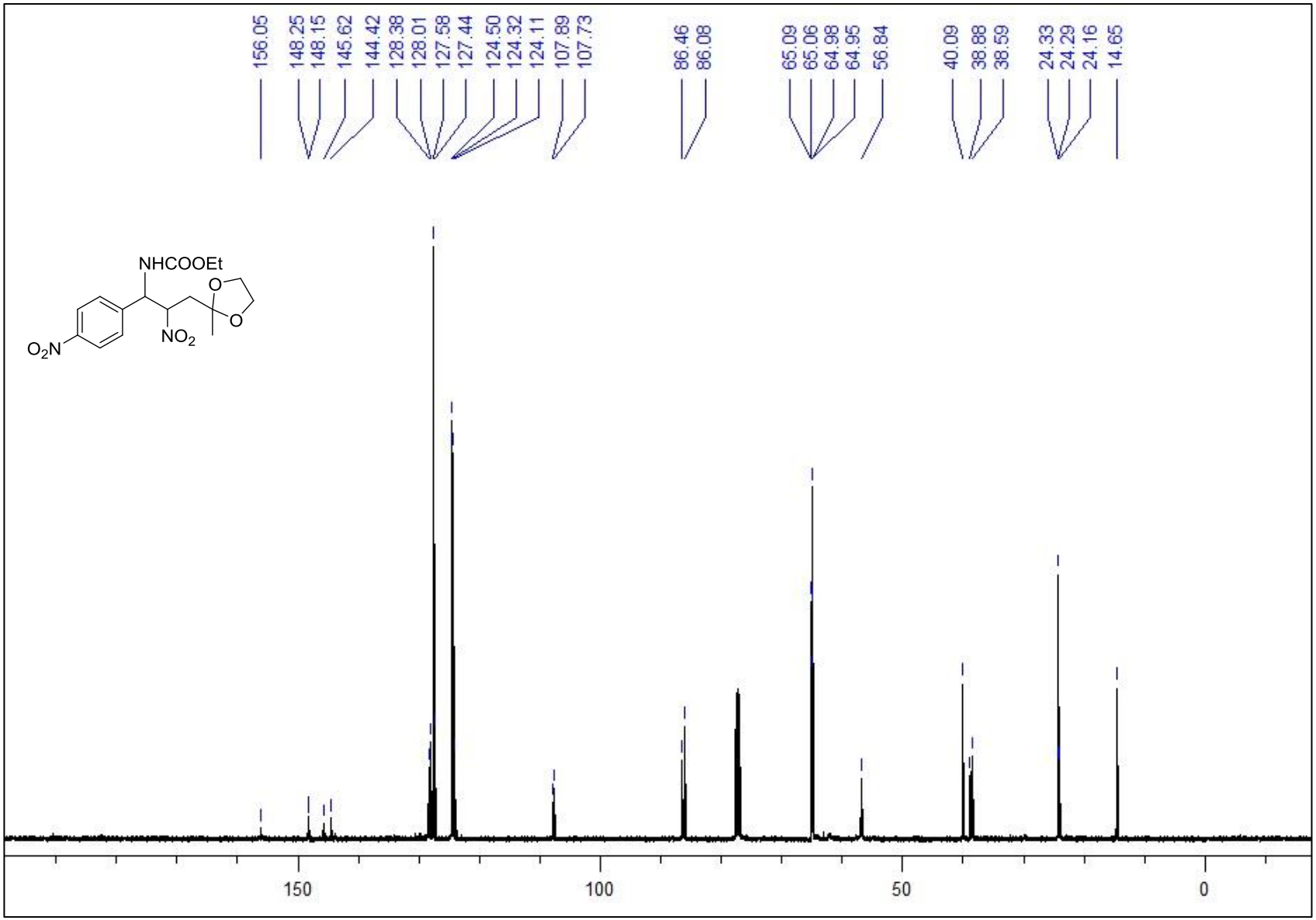


^{13}C NMR (400MHz. $CHCl_3$), **3c**



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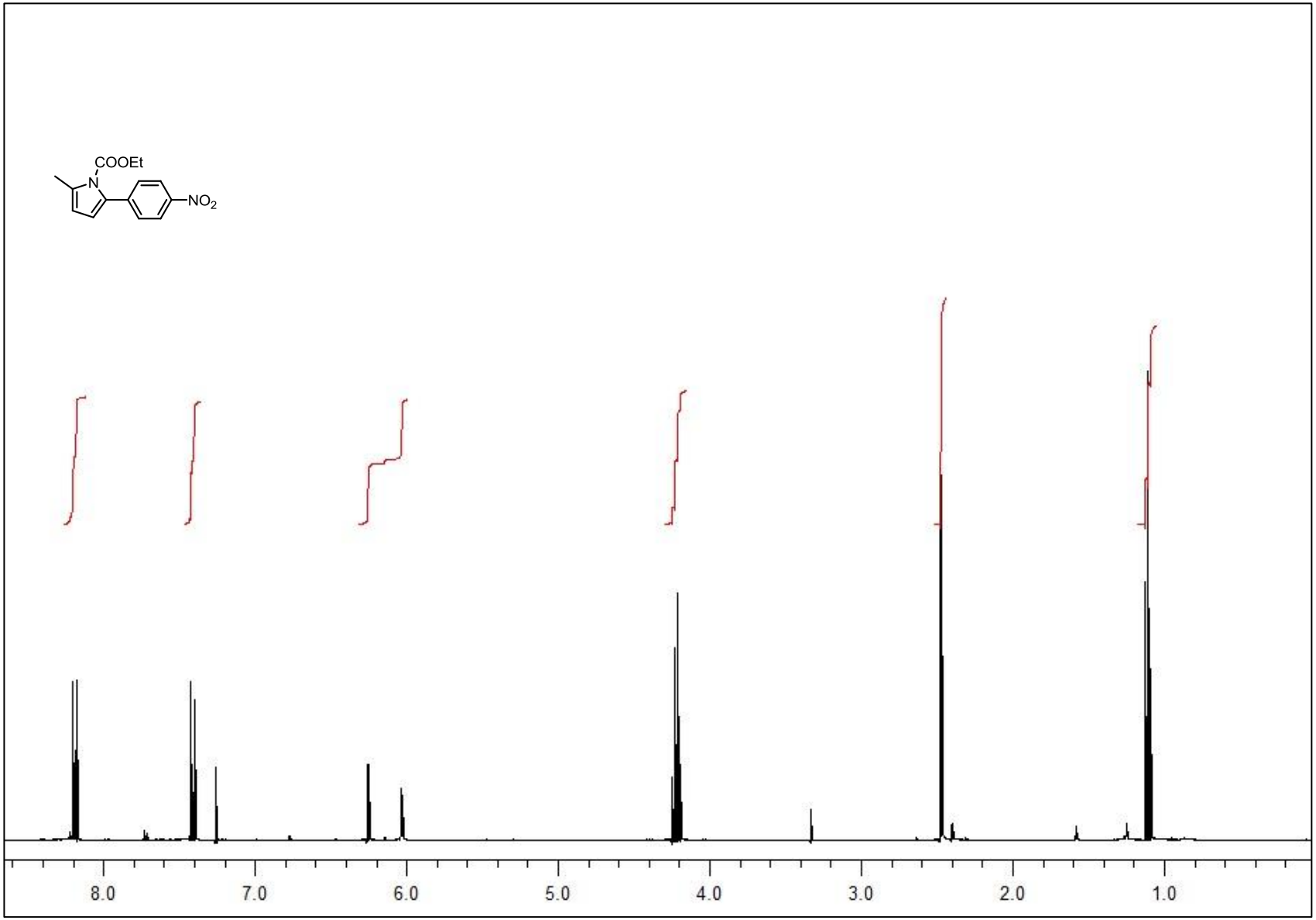

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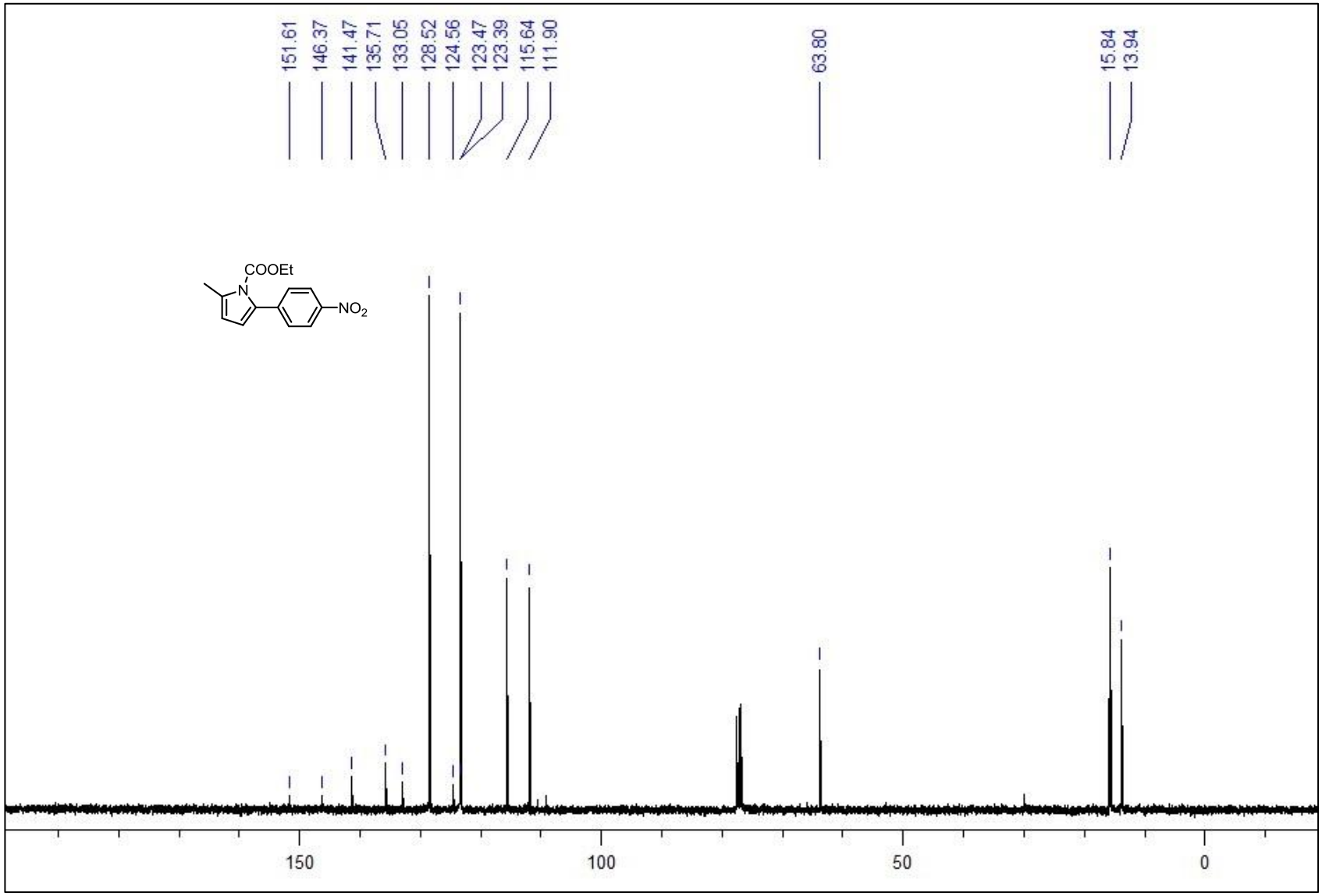

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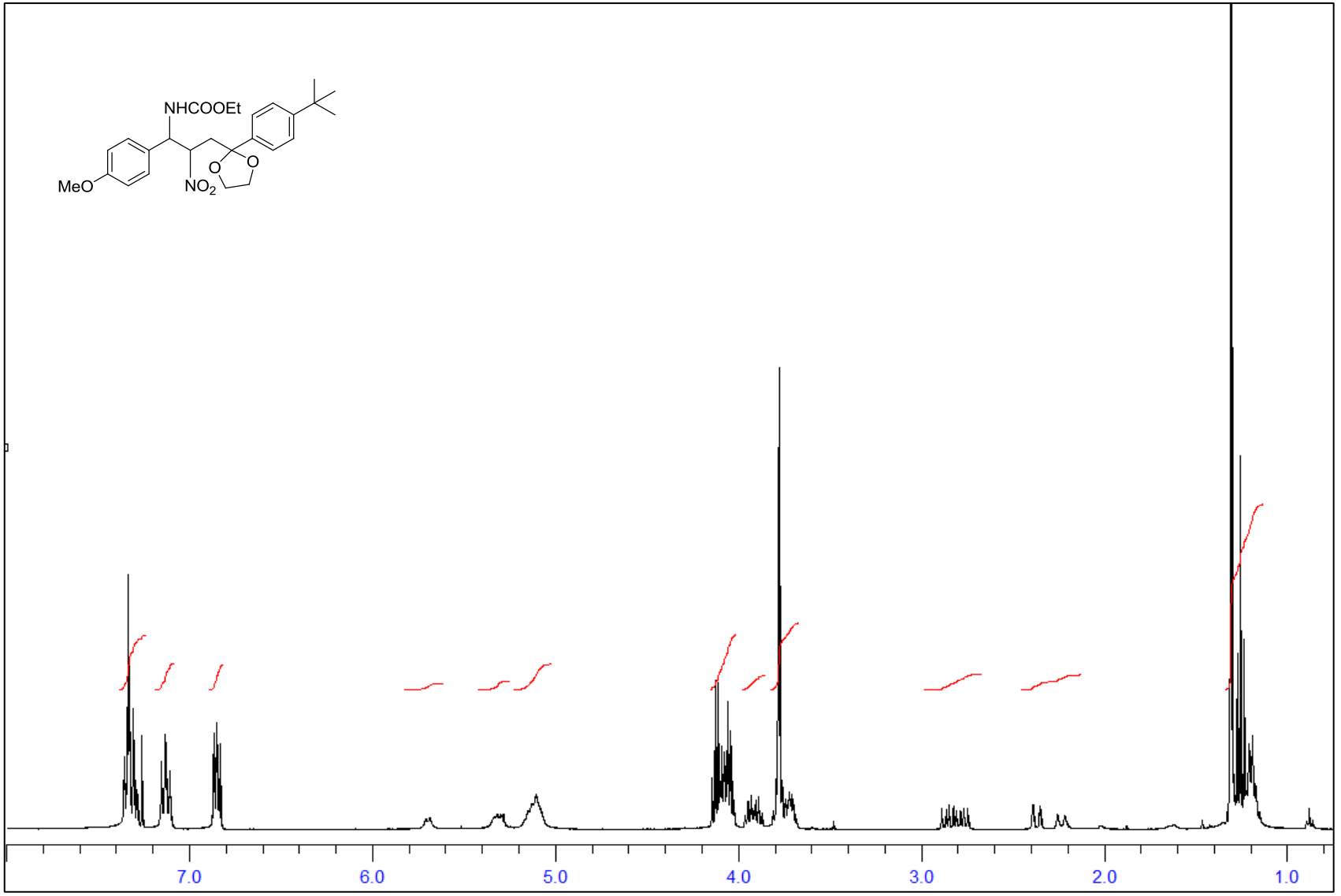

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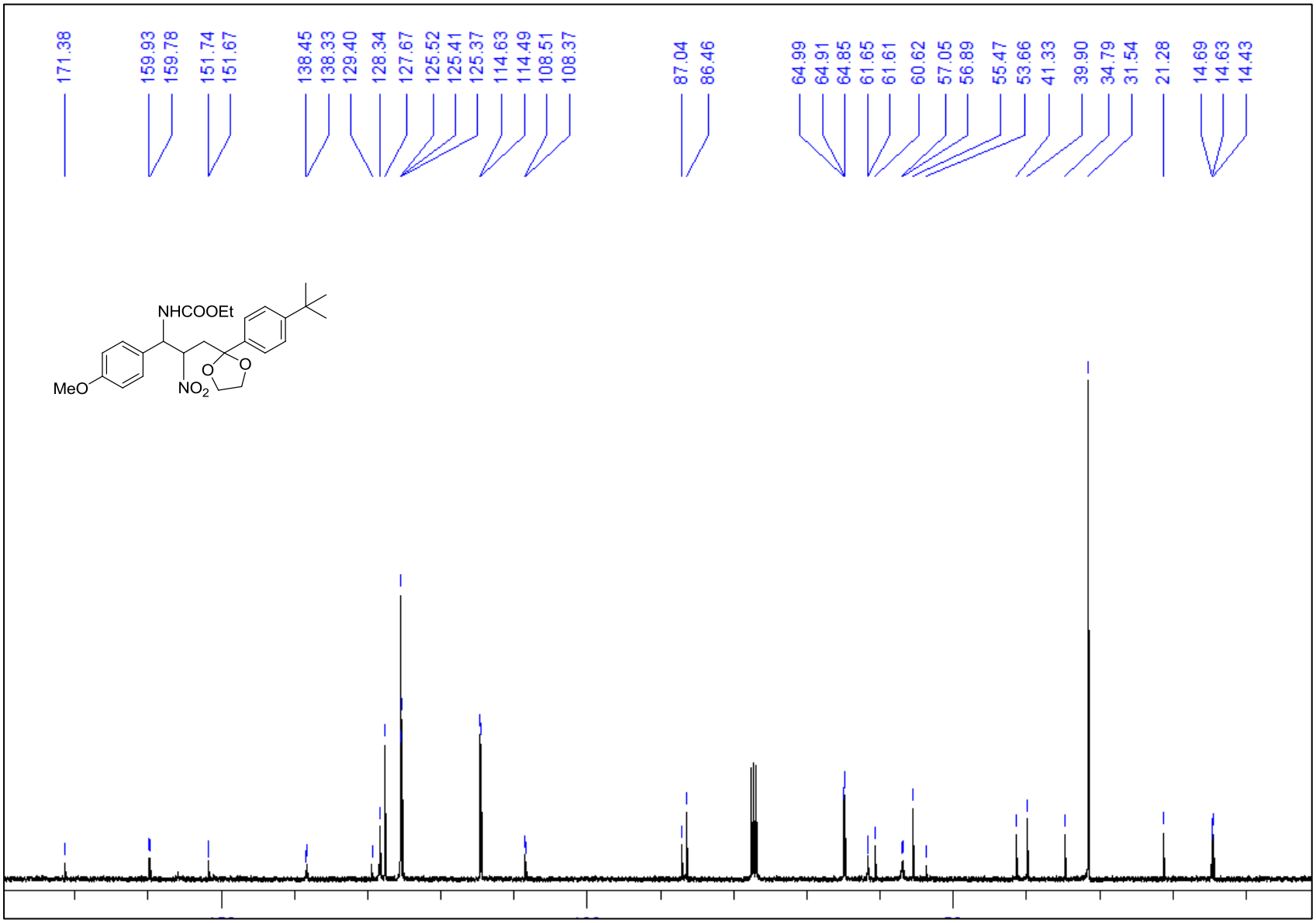

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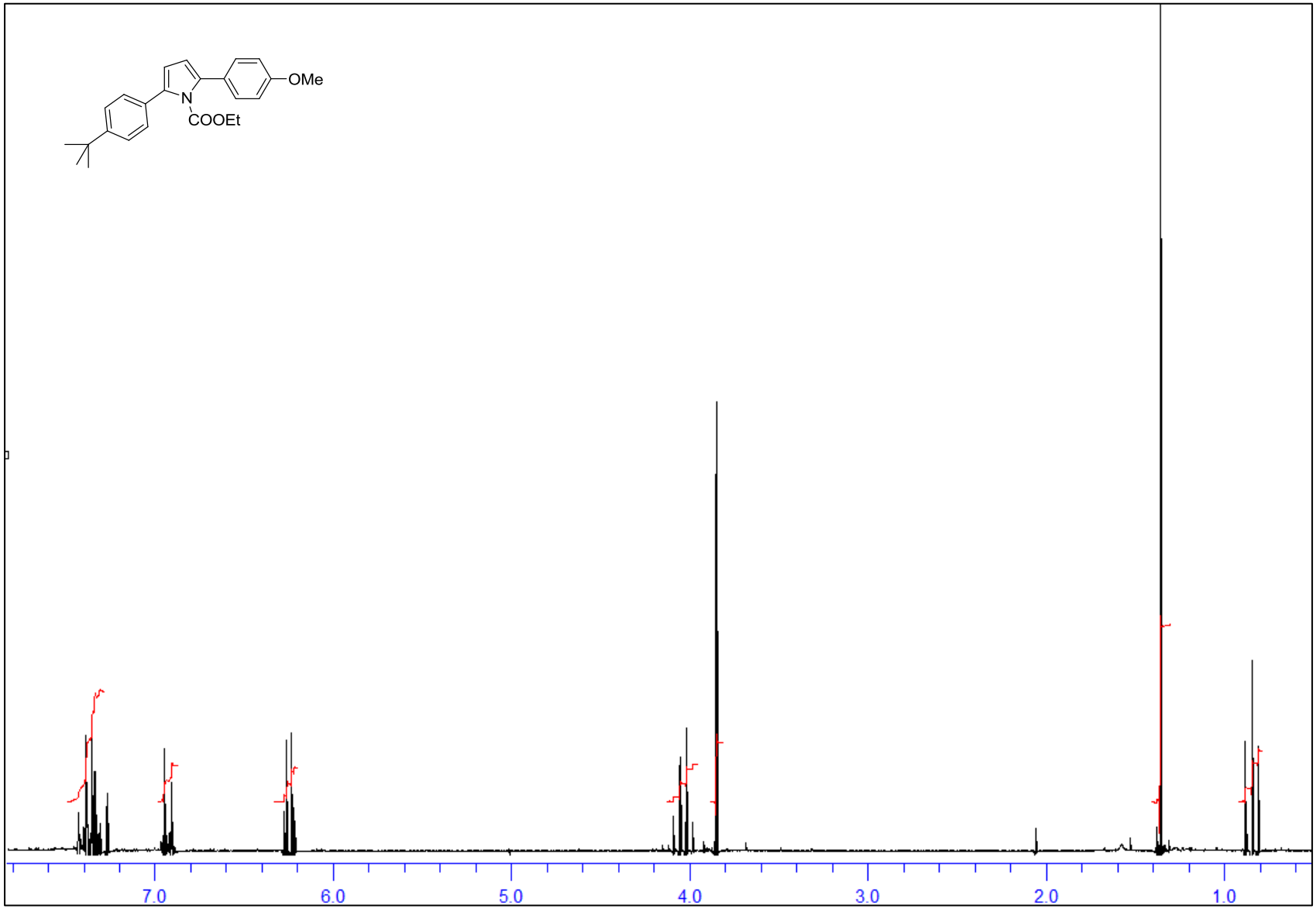

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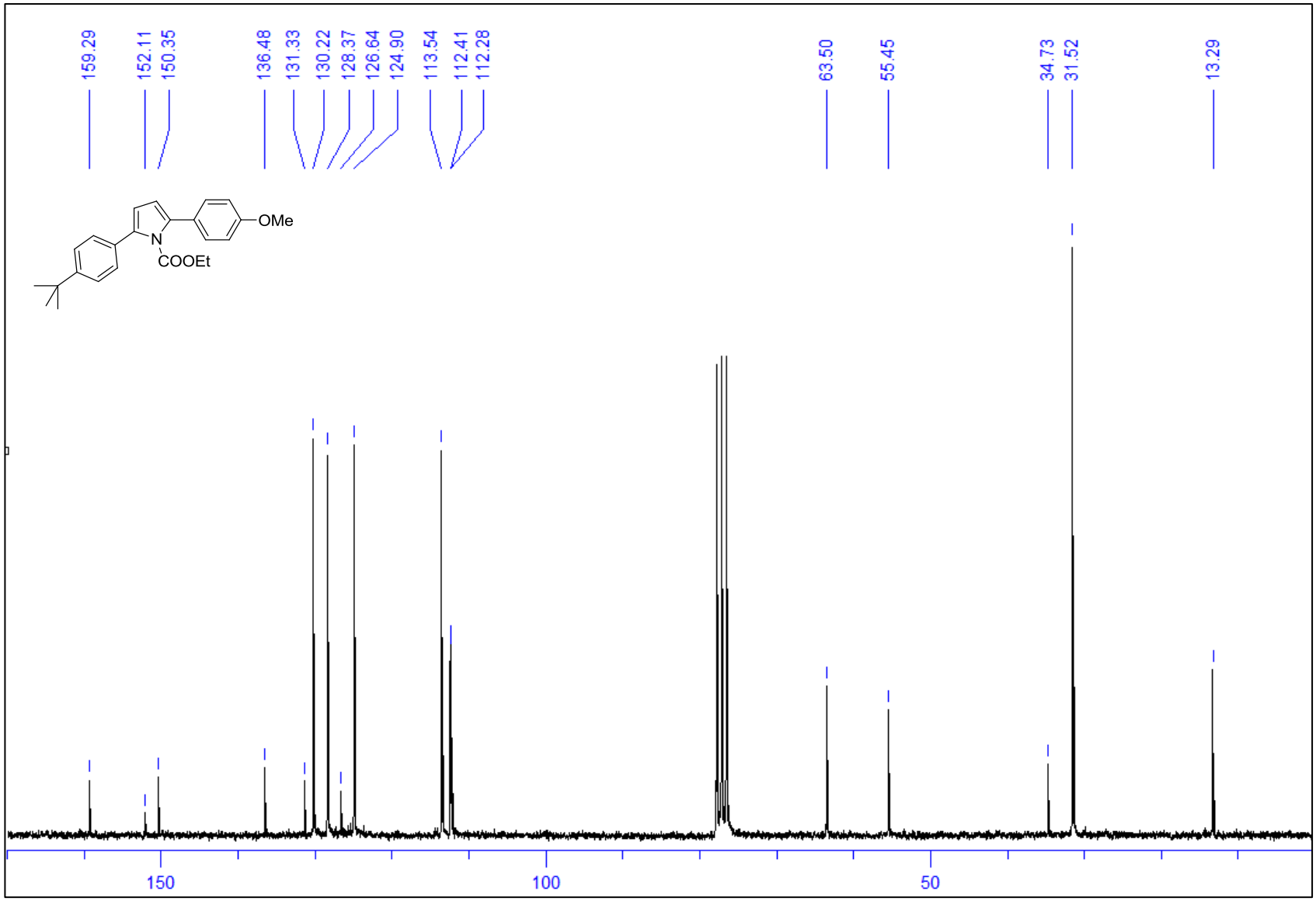

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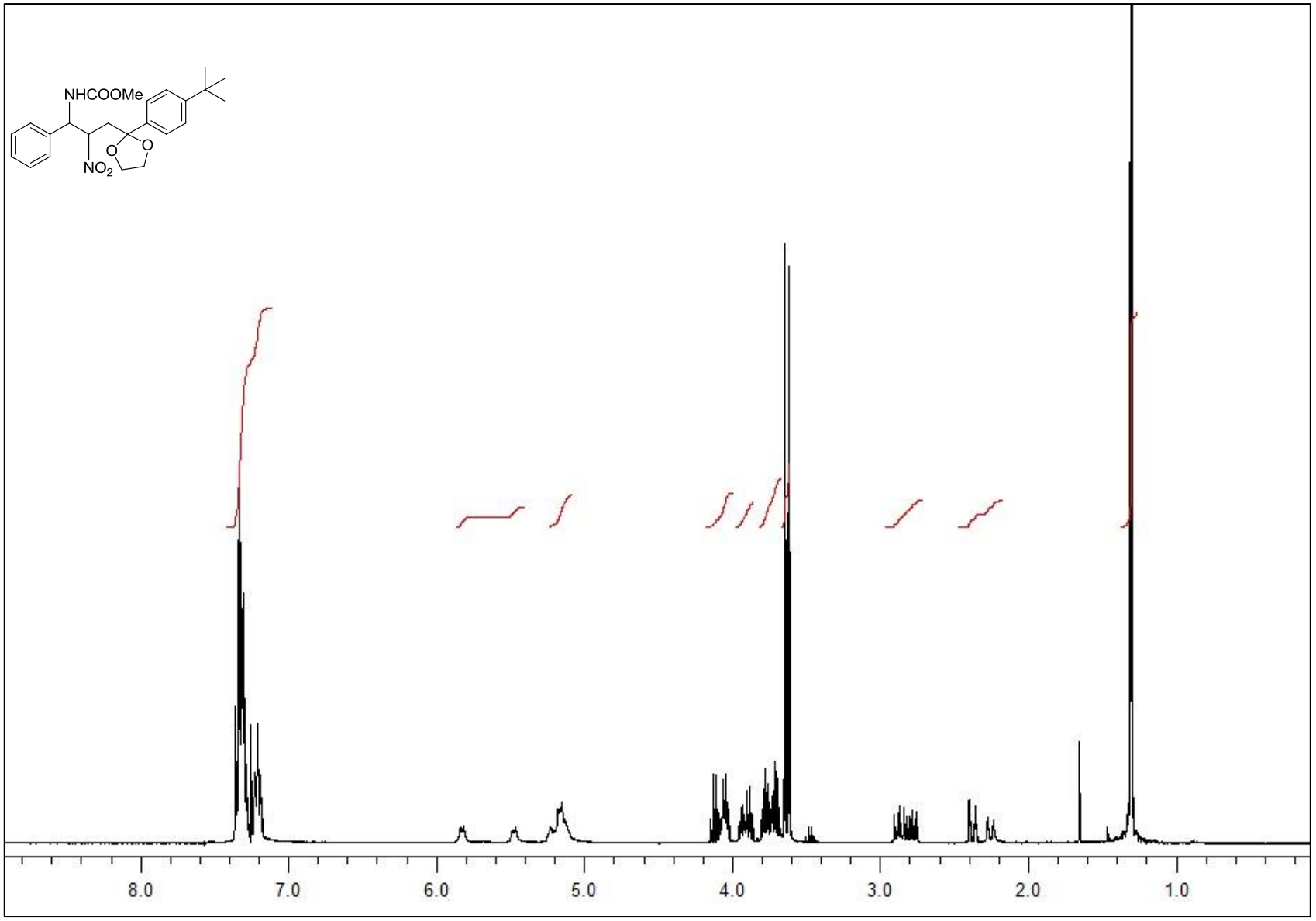

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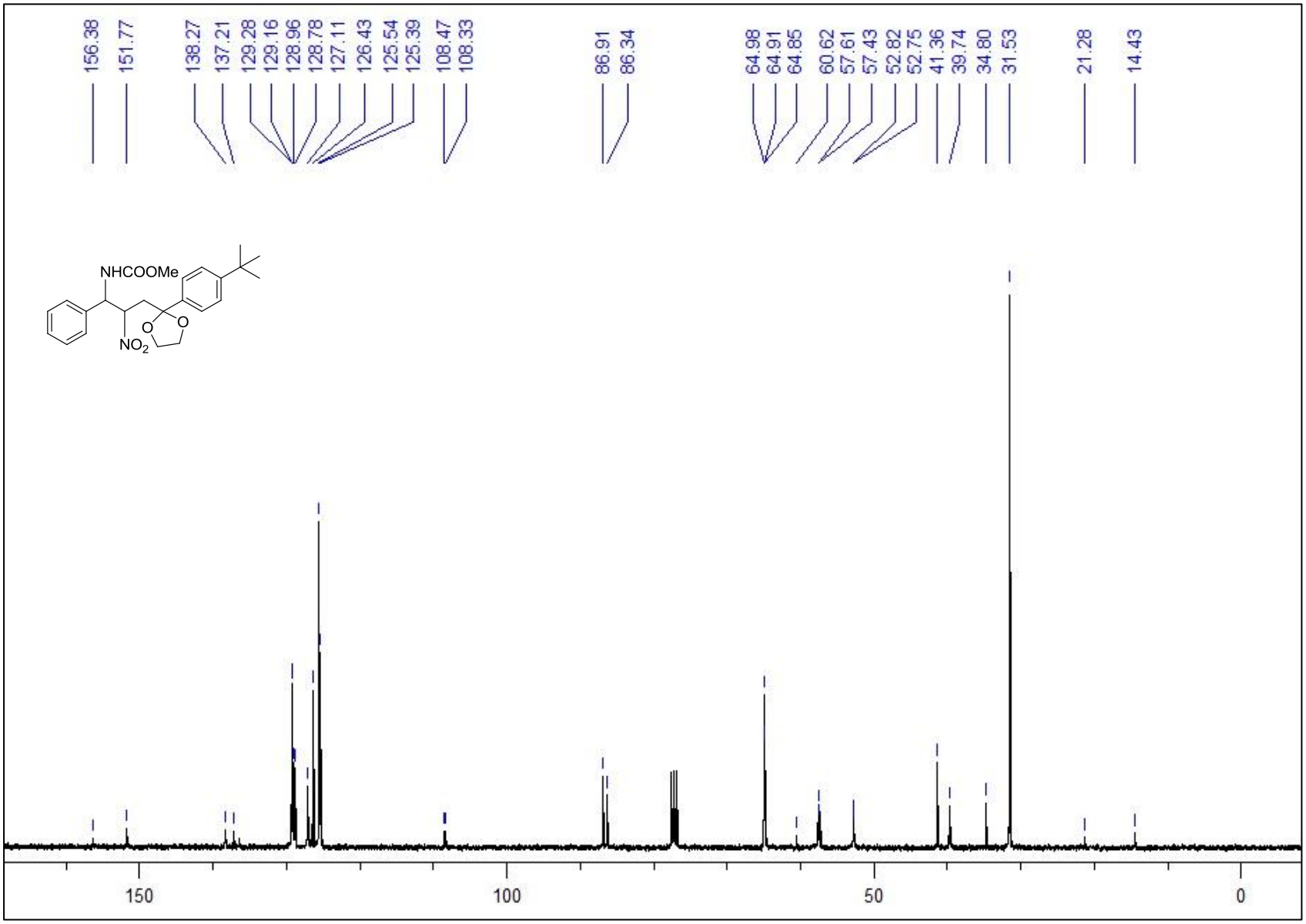

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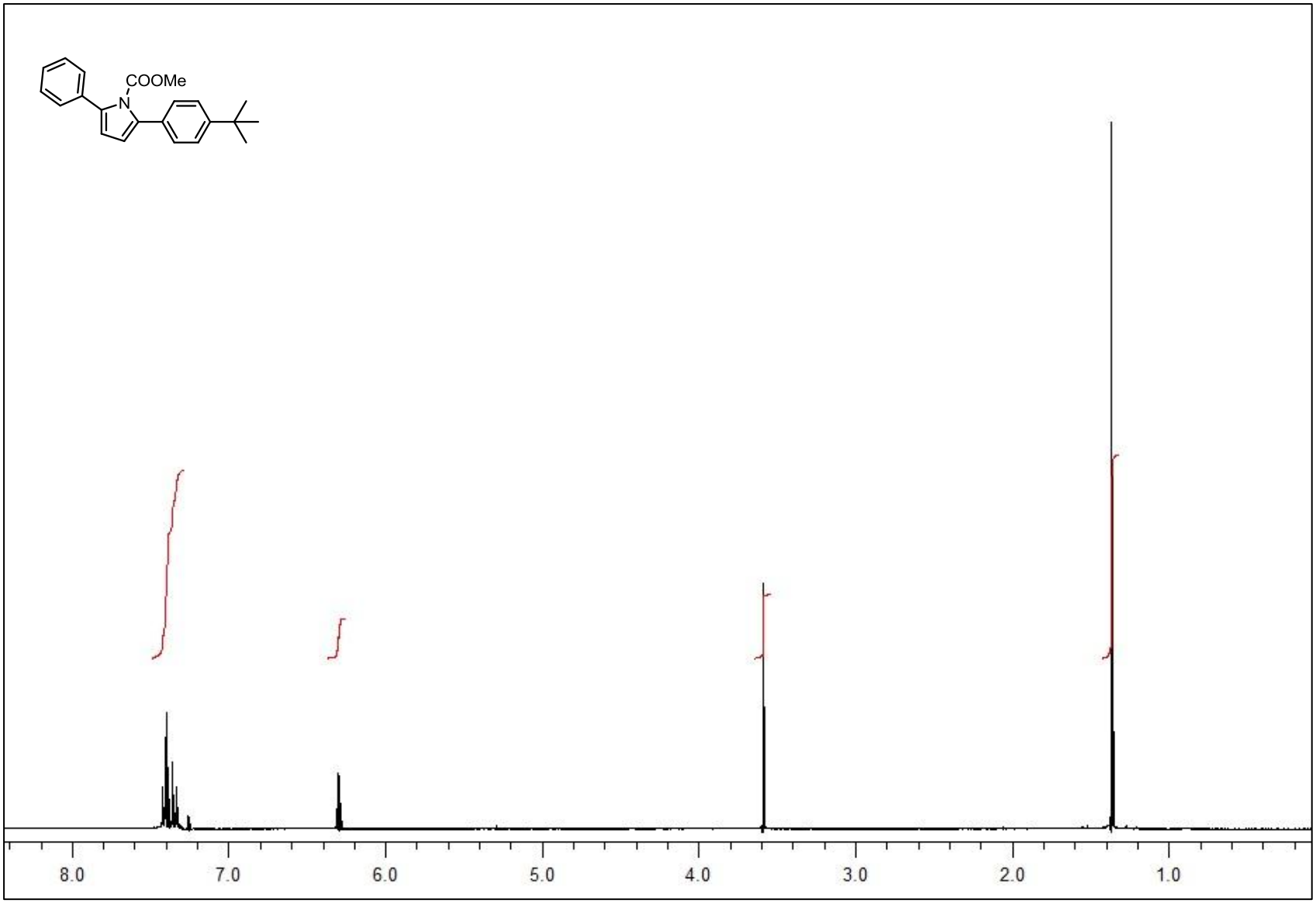

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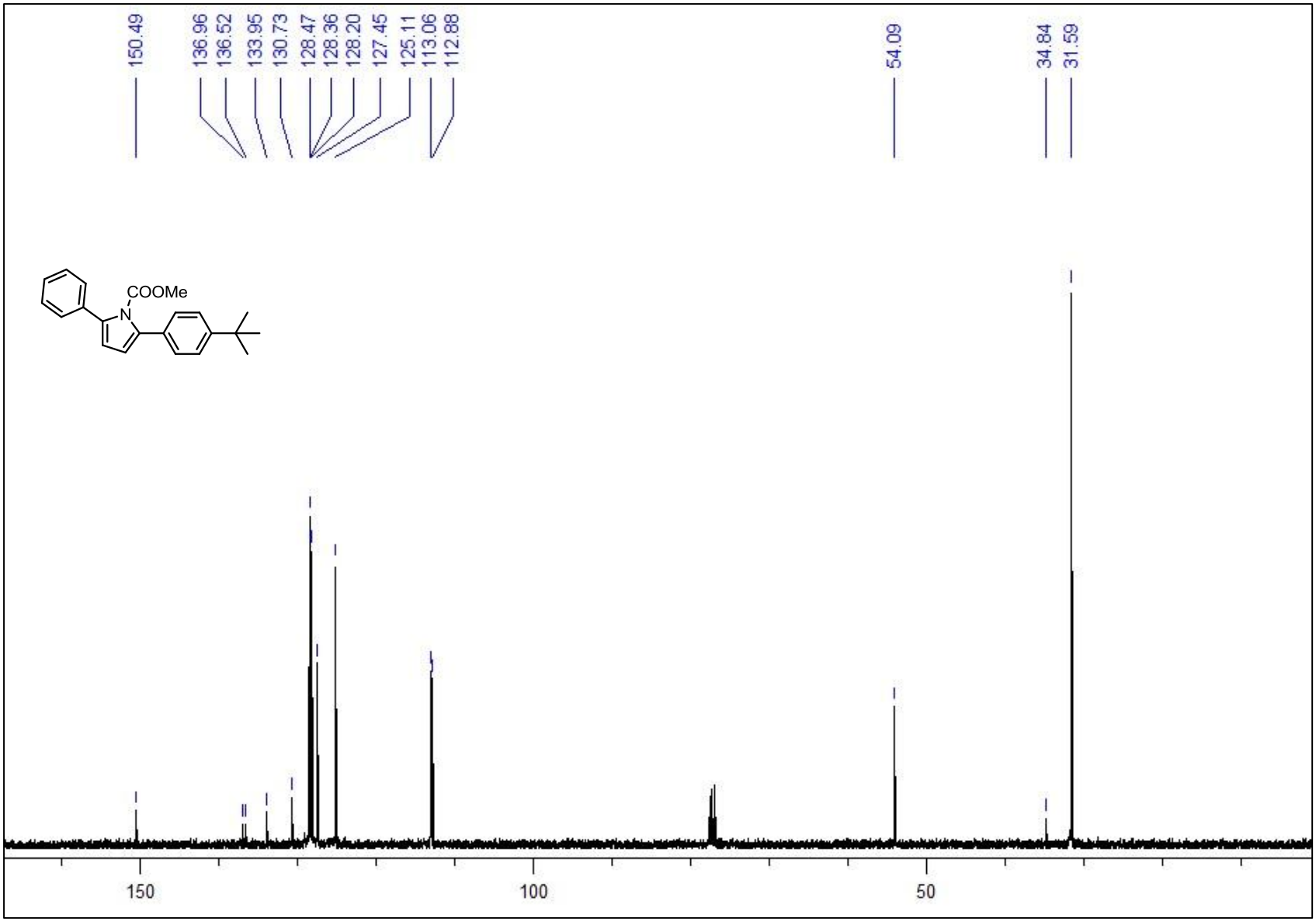

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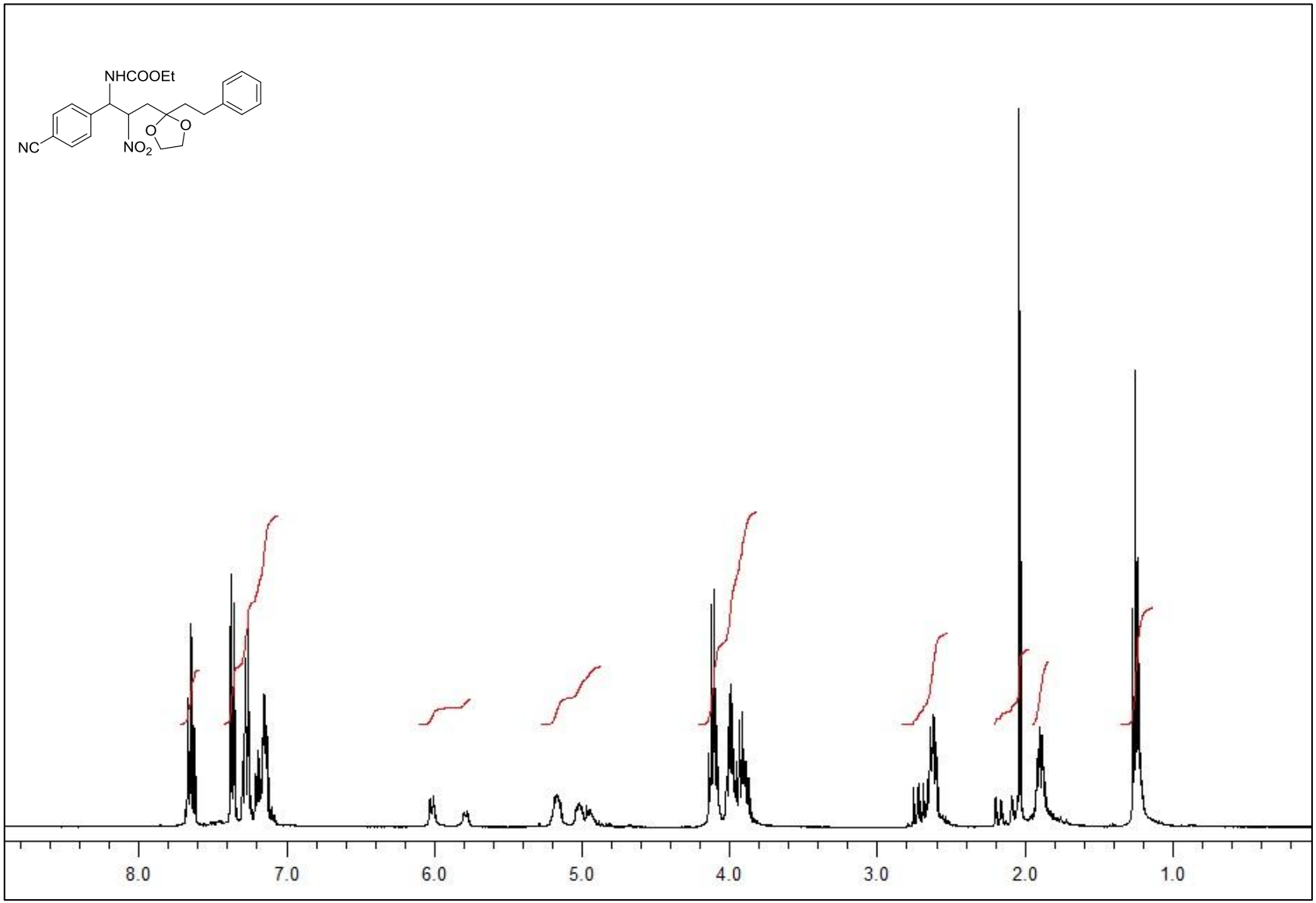

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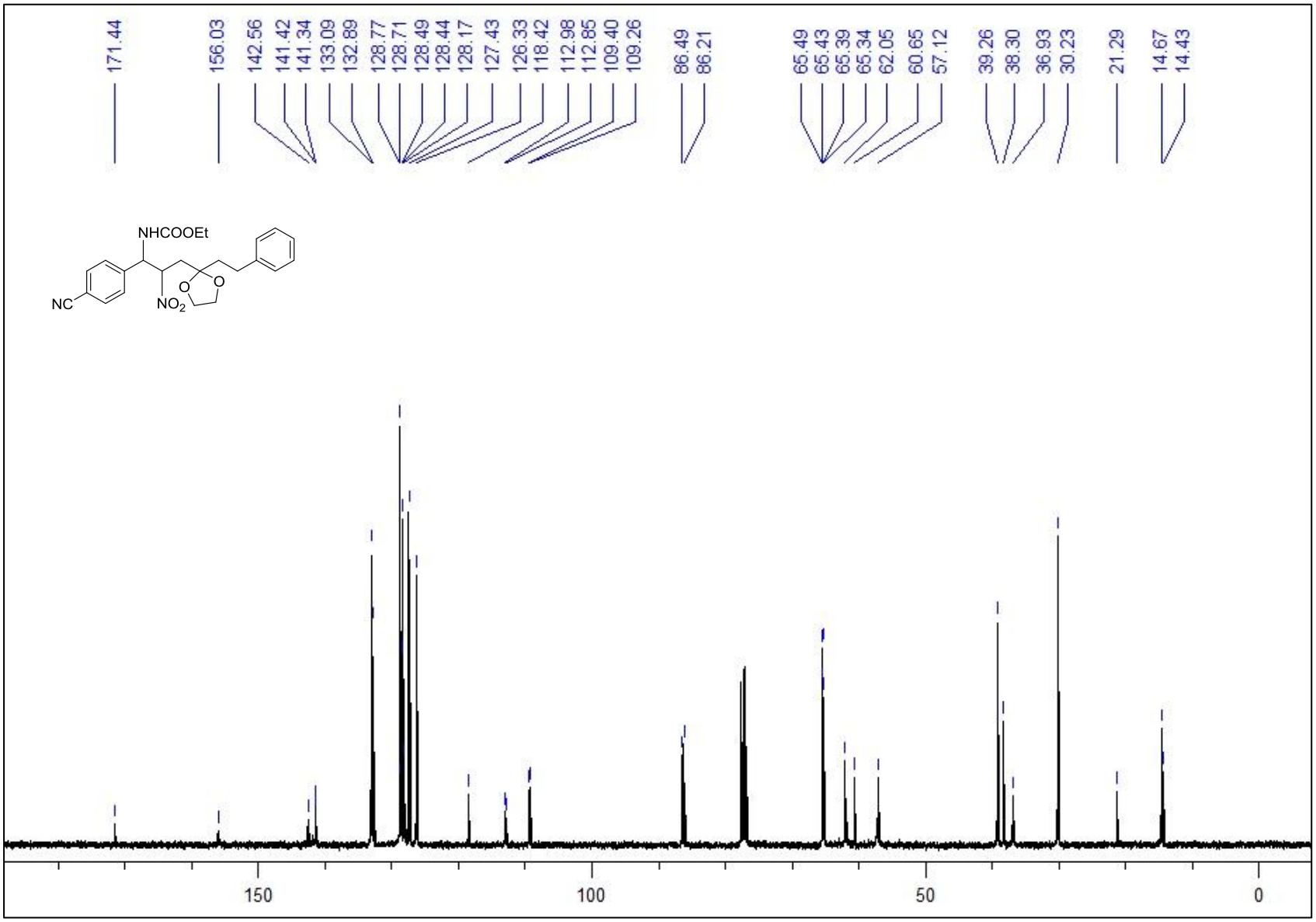

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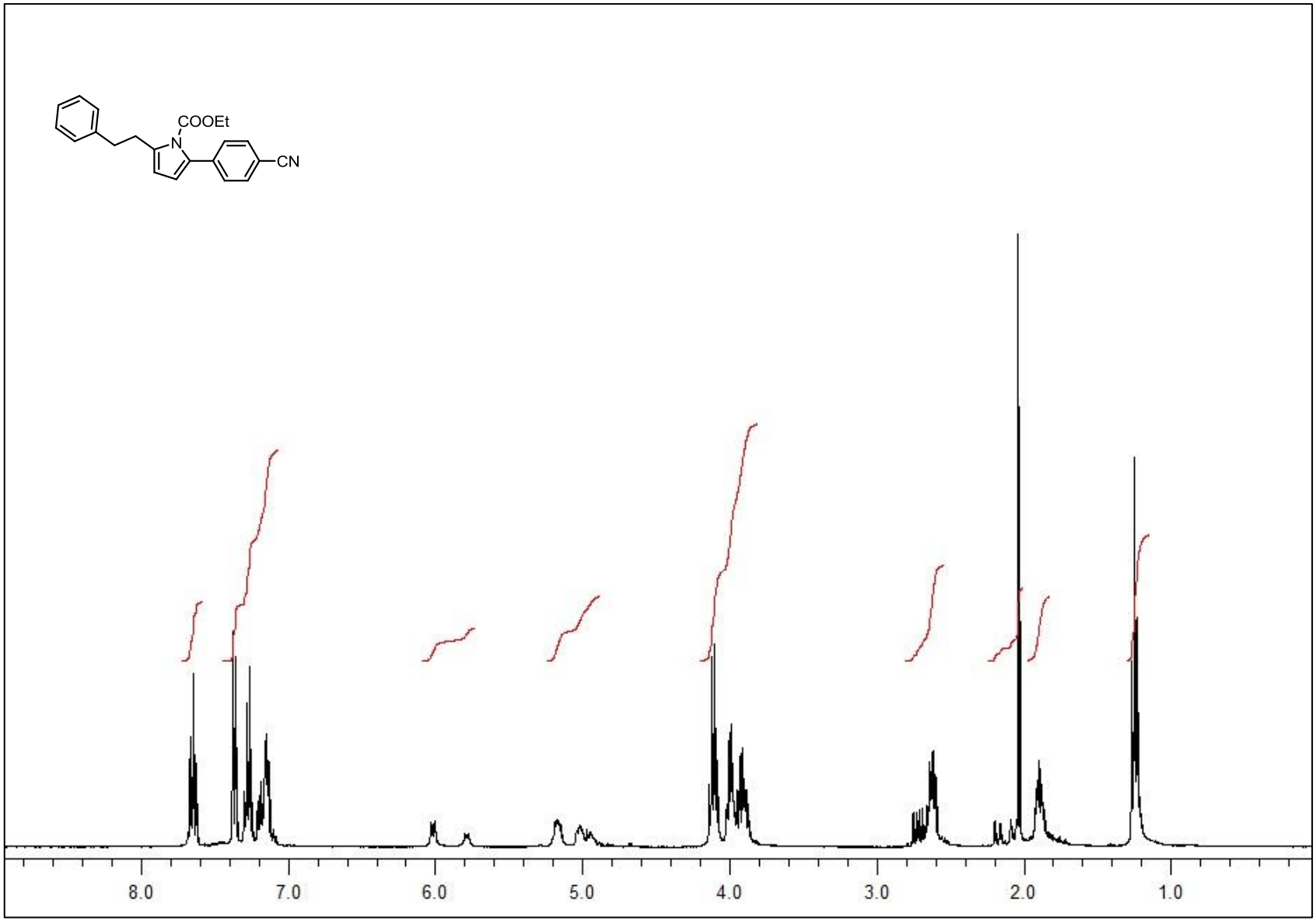

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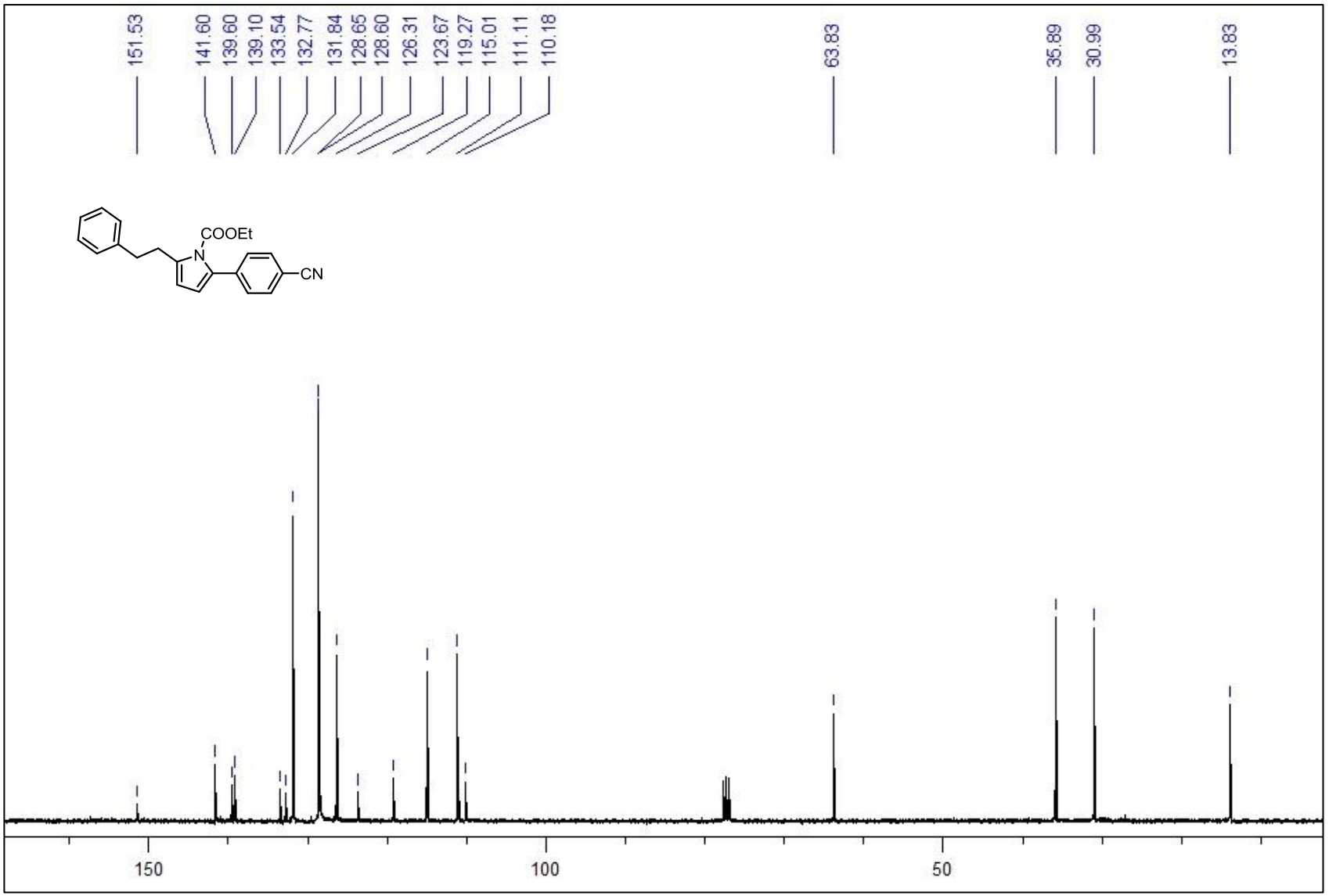

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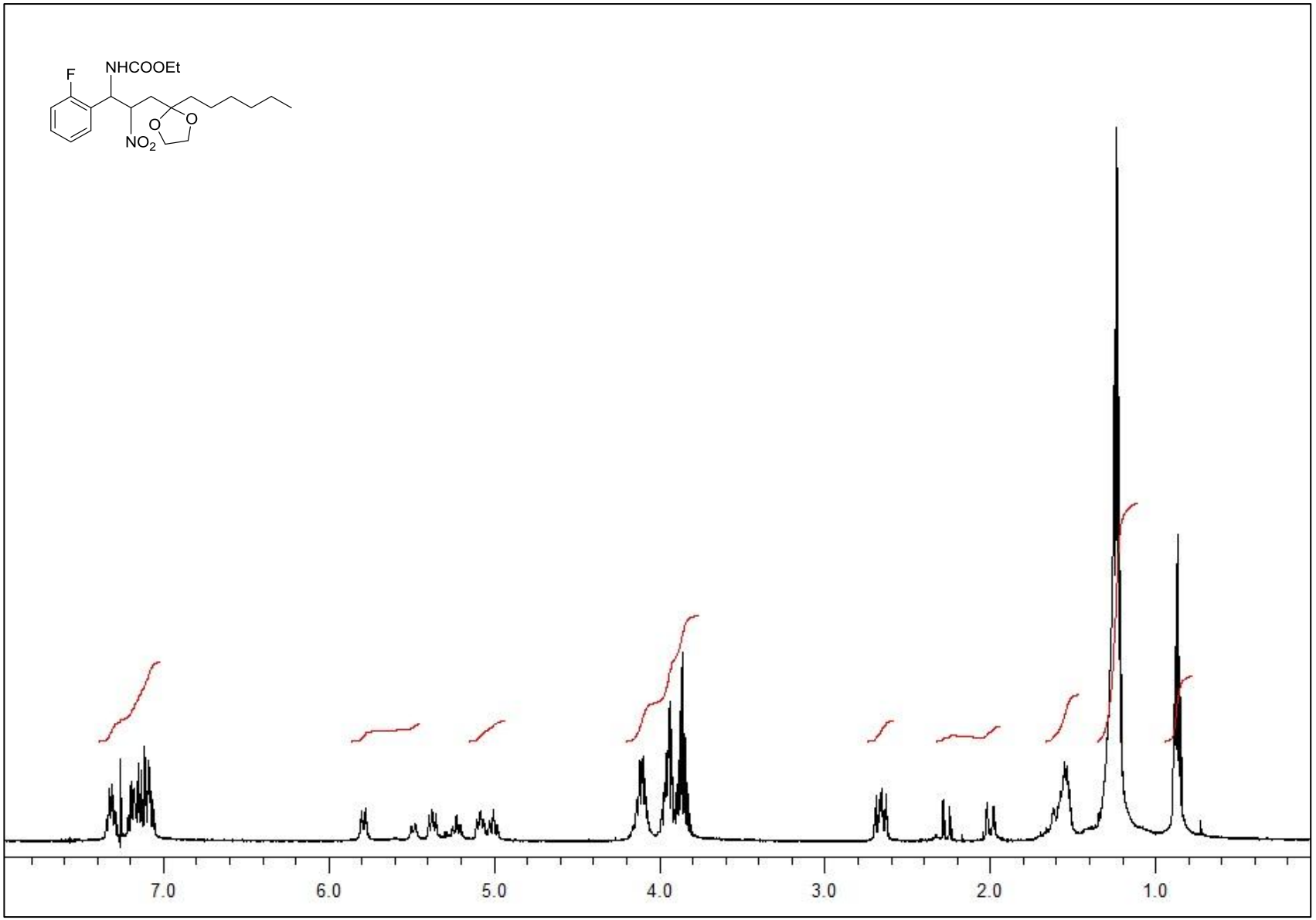

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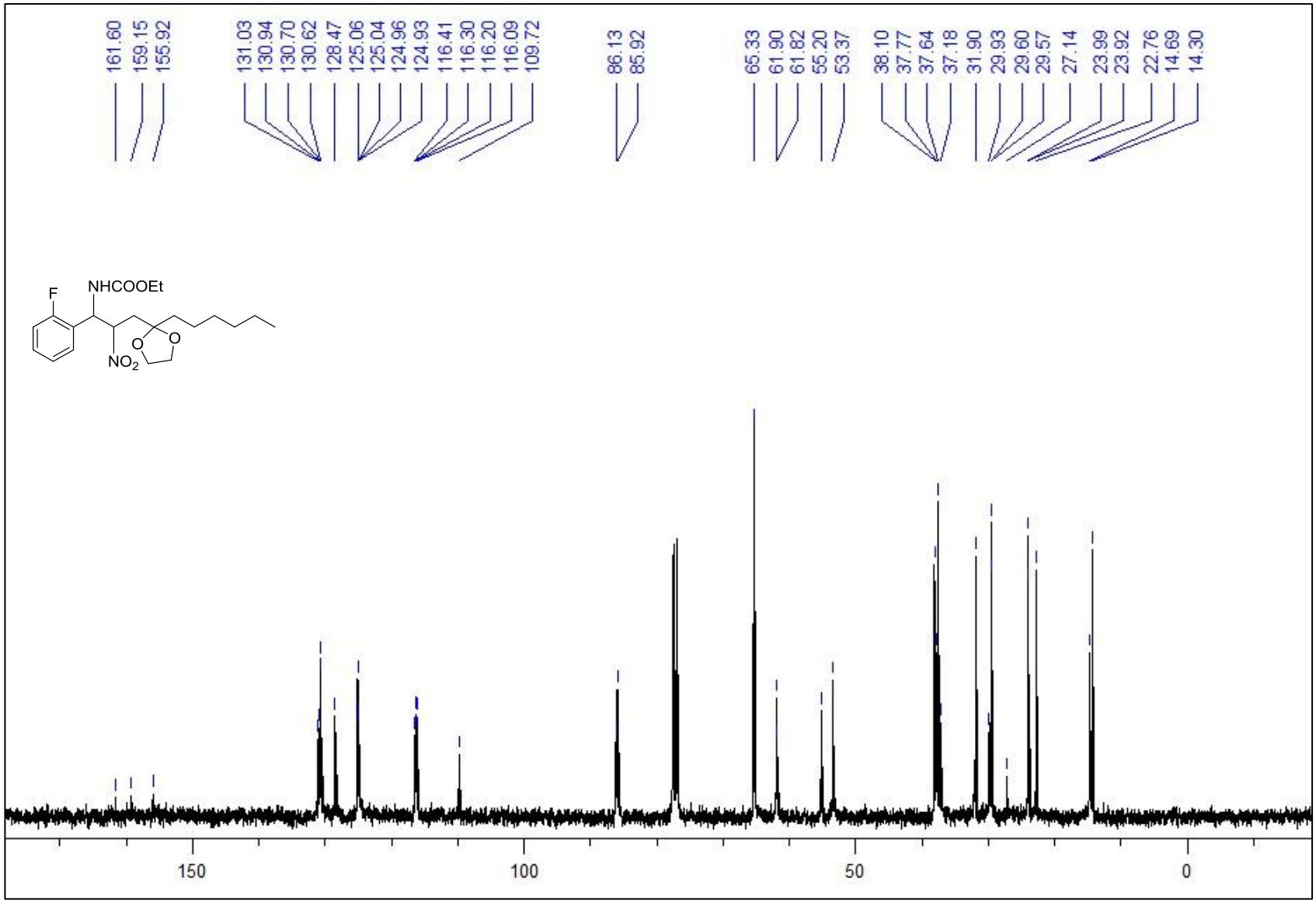

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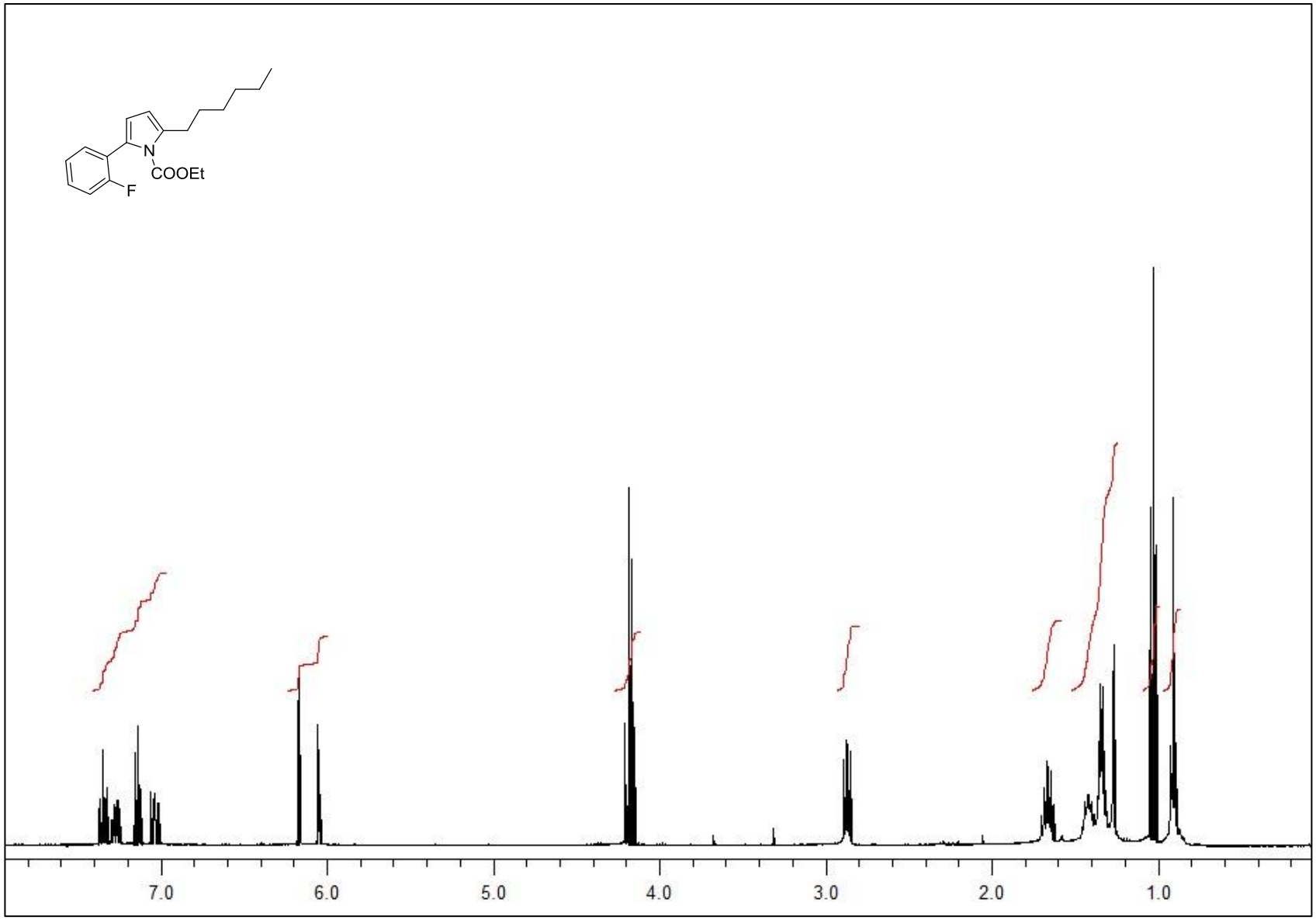

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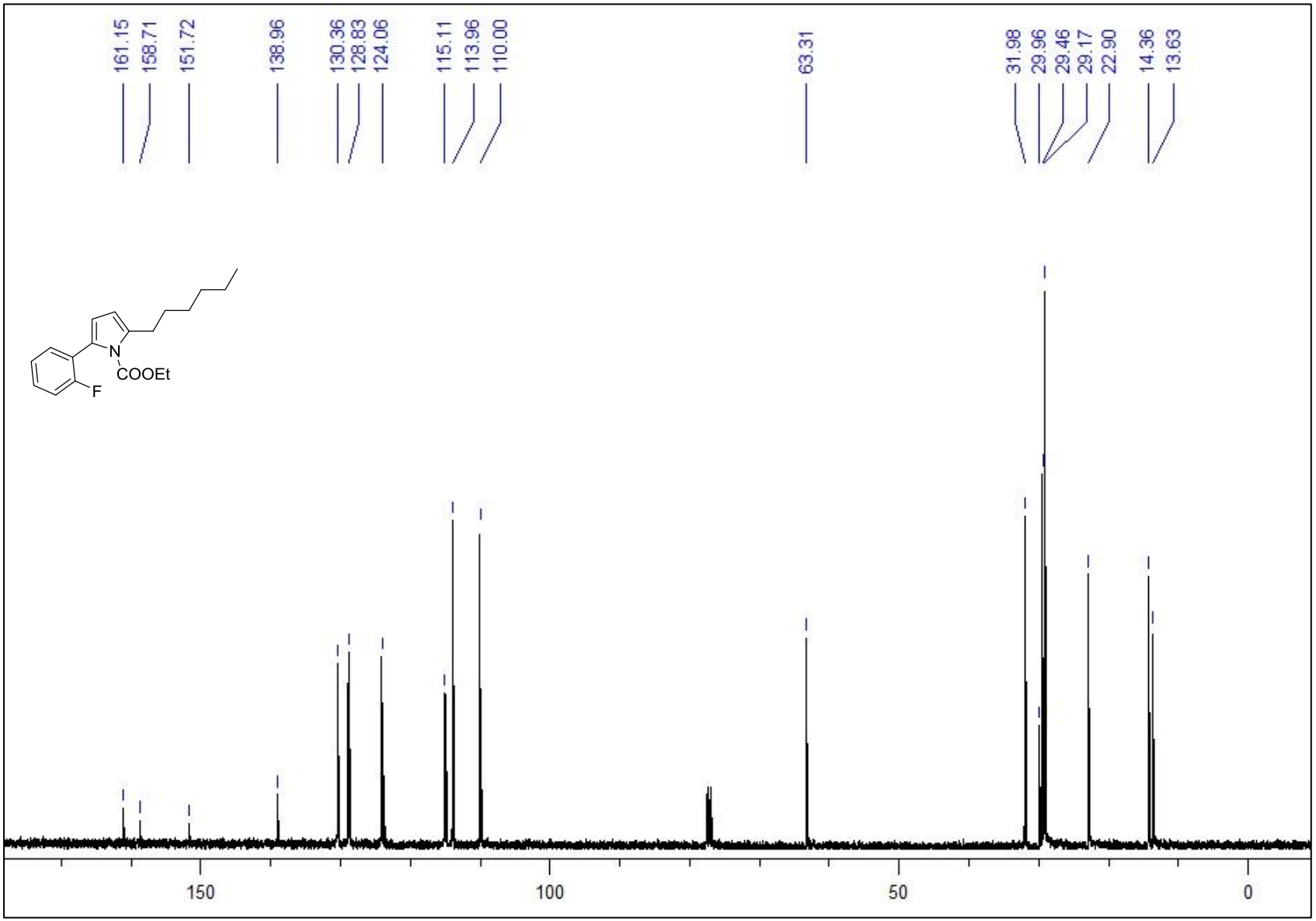

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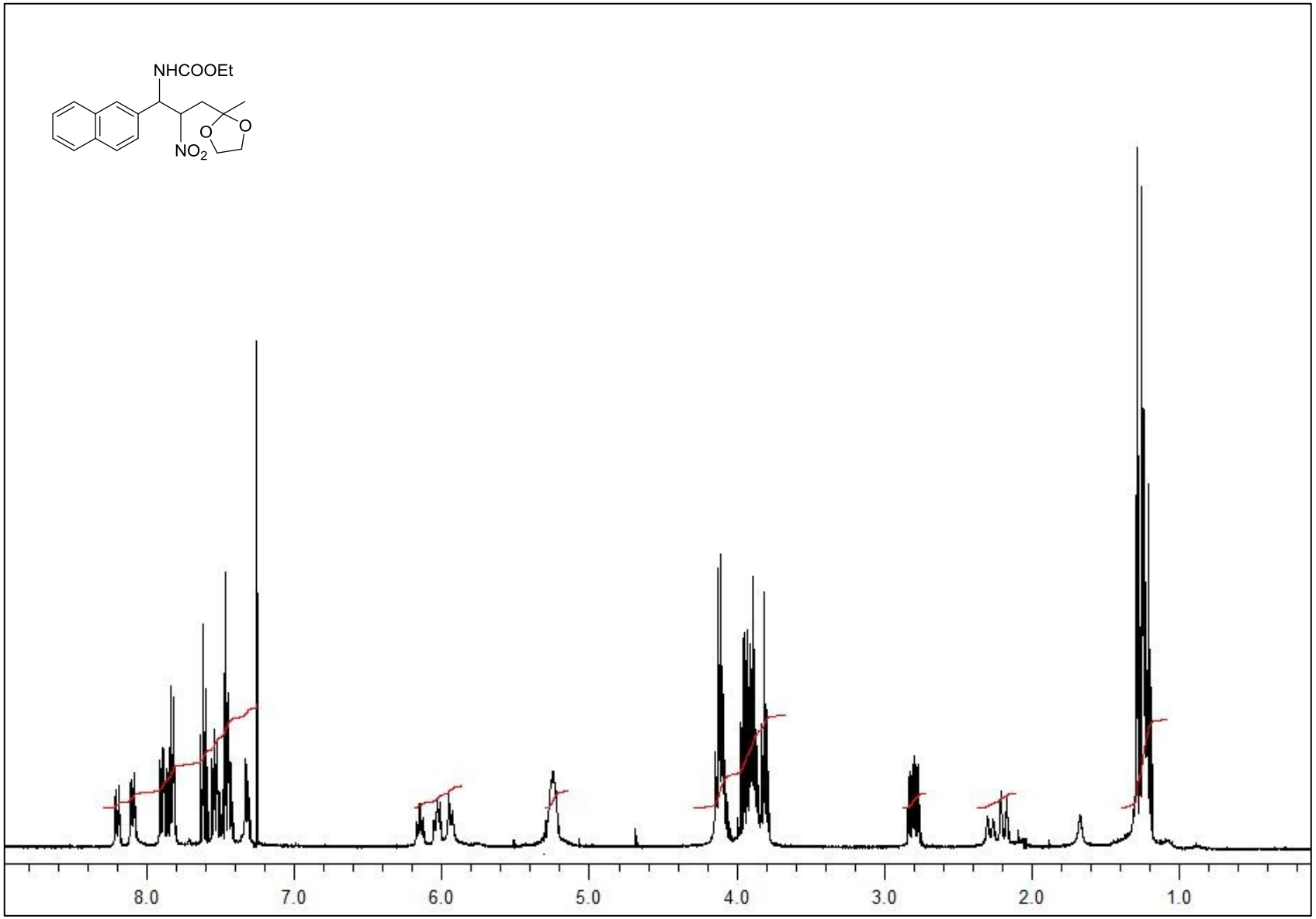

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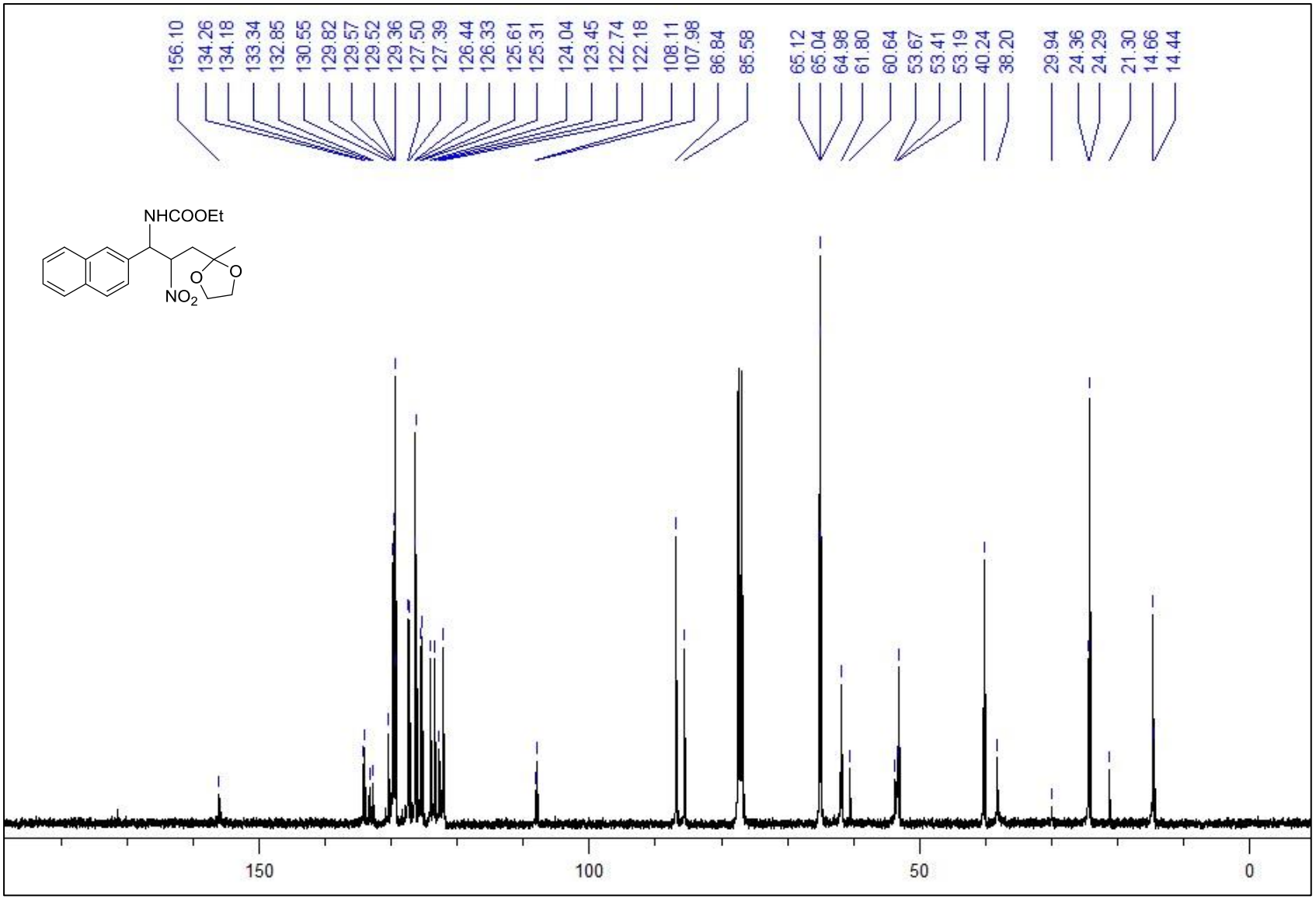

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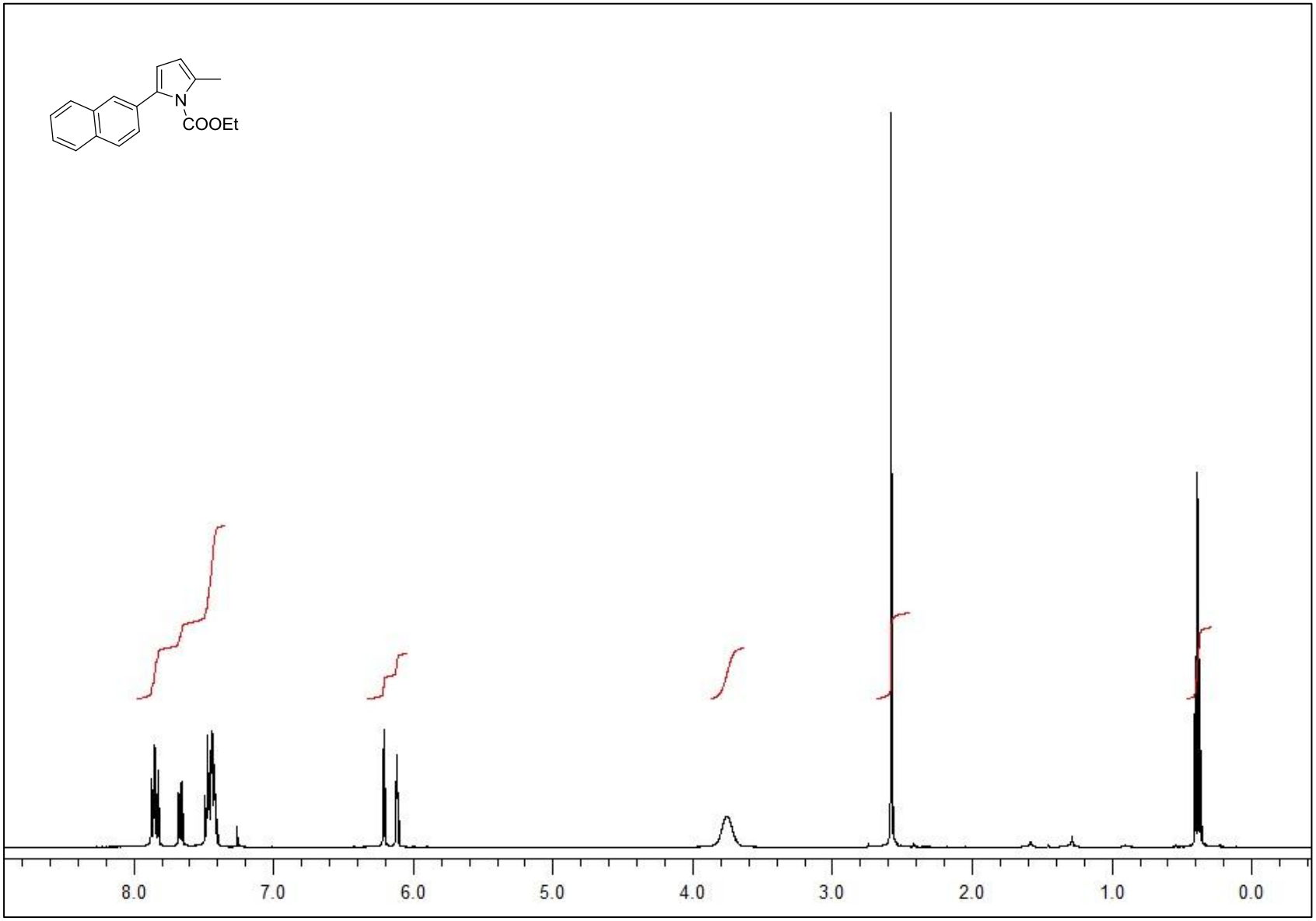

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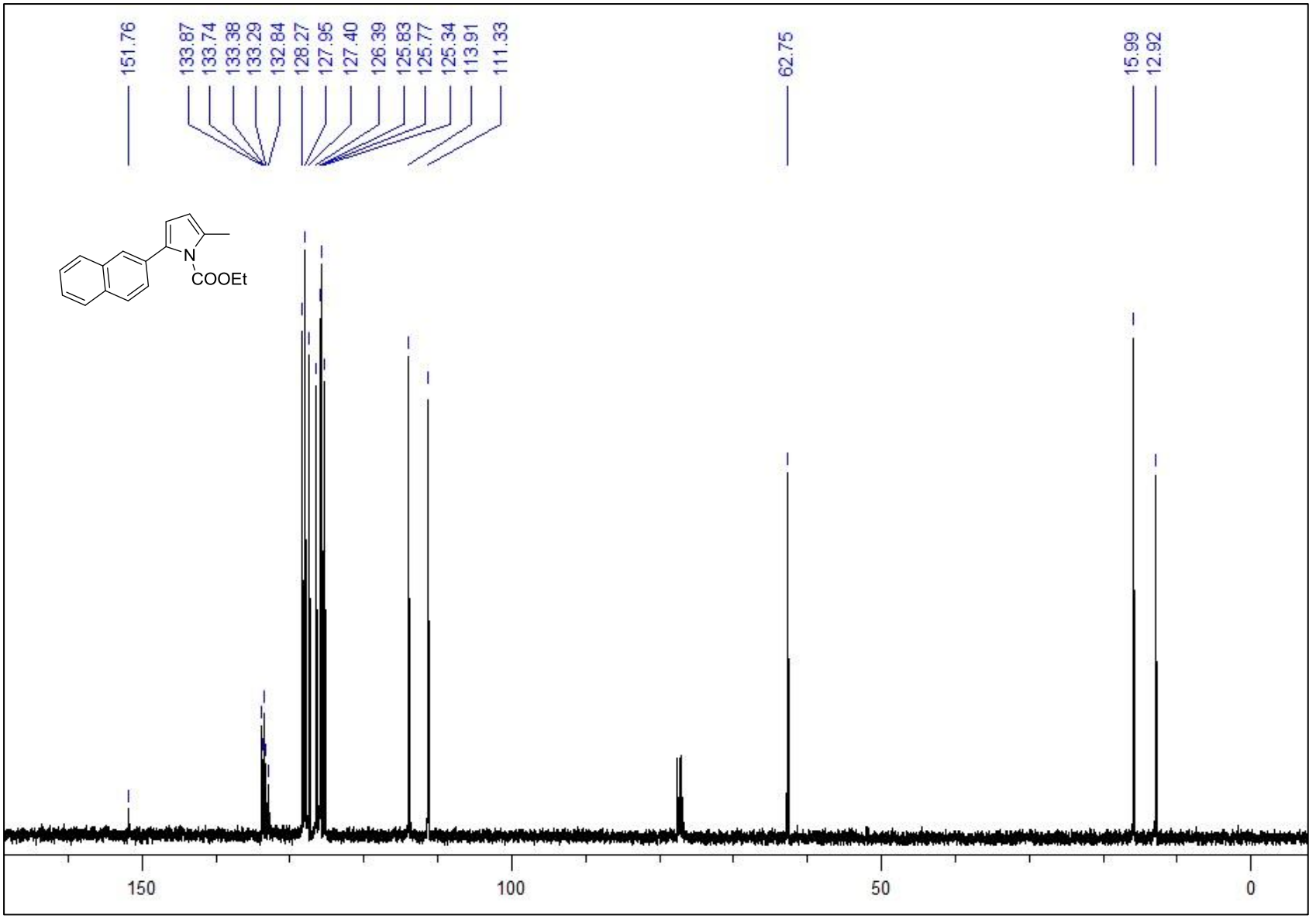

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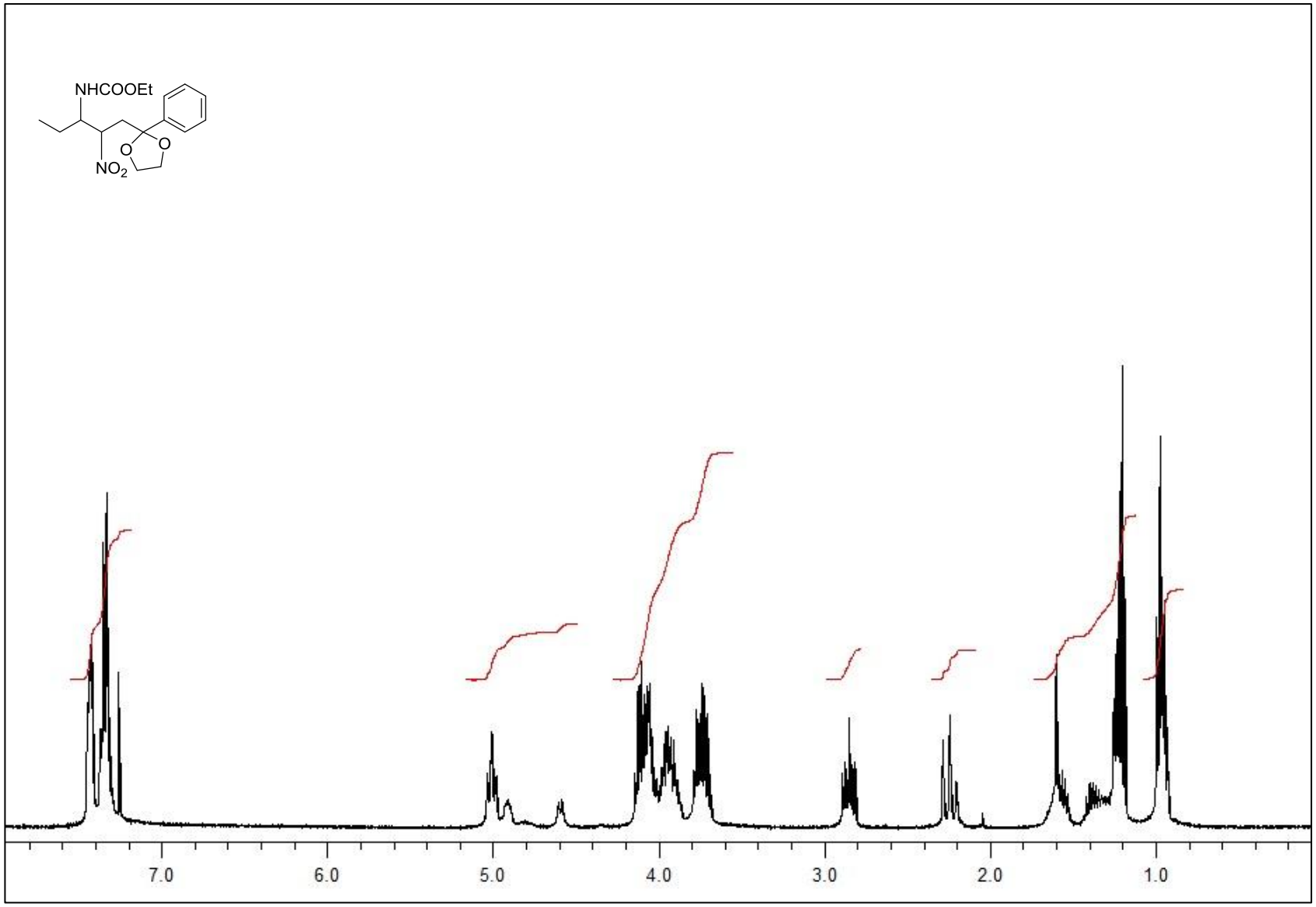
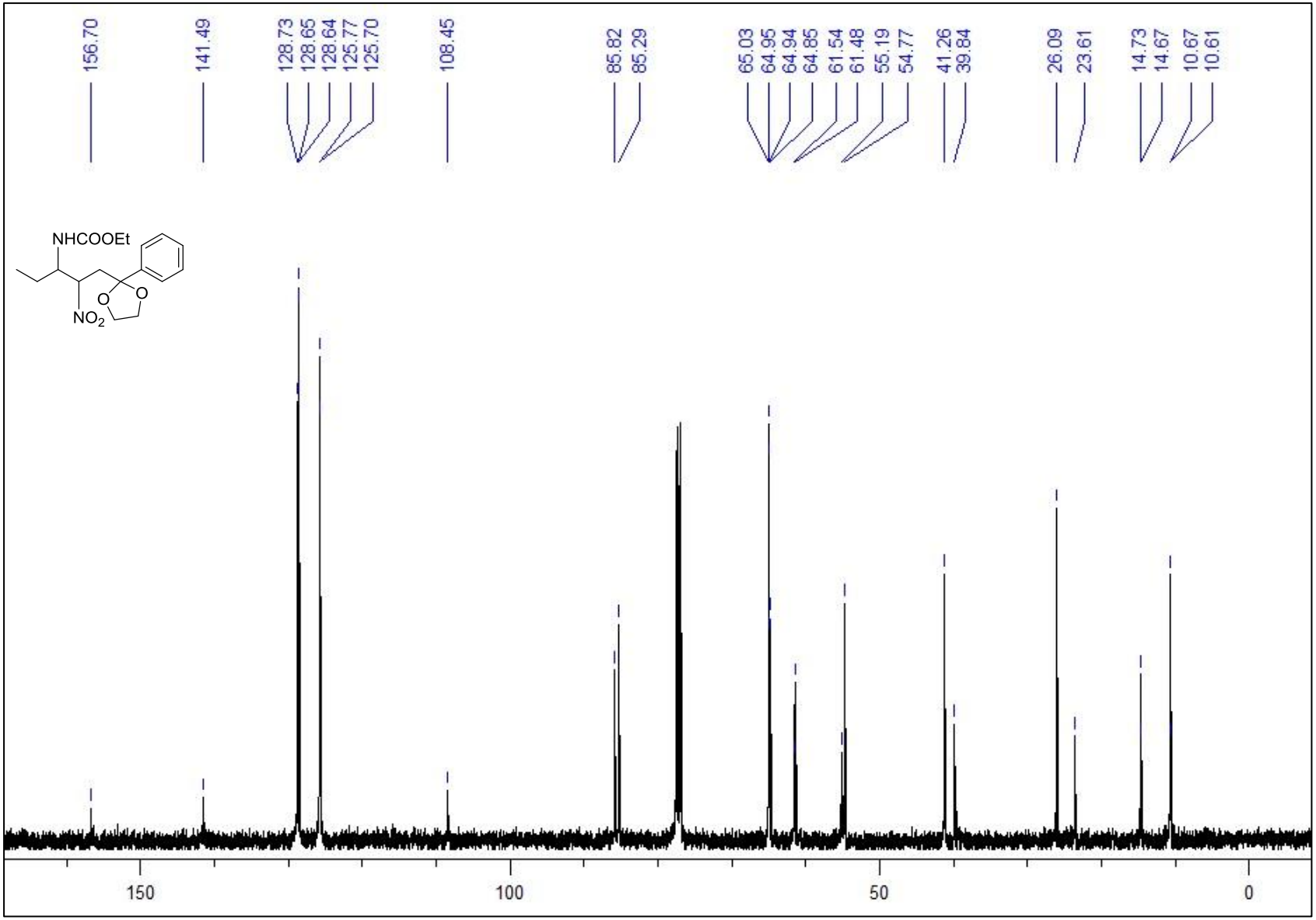


^{13}C NMR (400MHz. $CHCl_3$), **3i**



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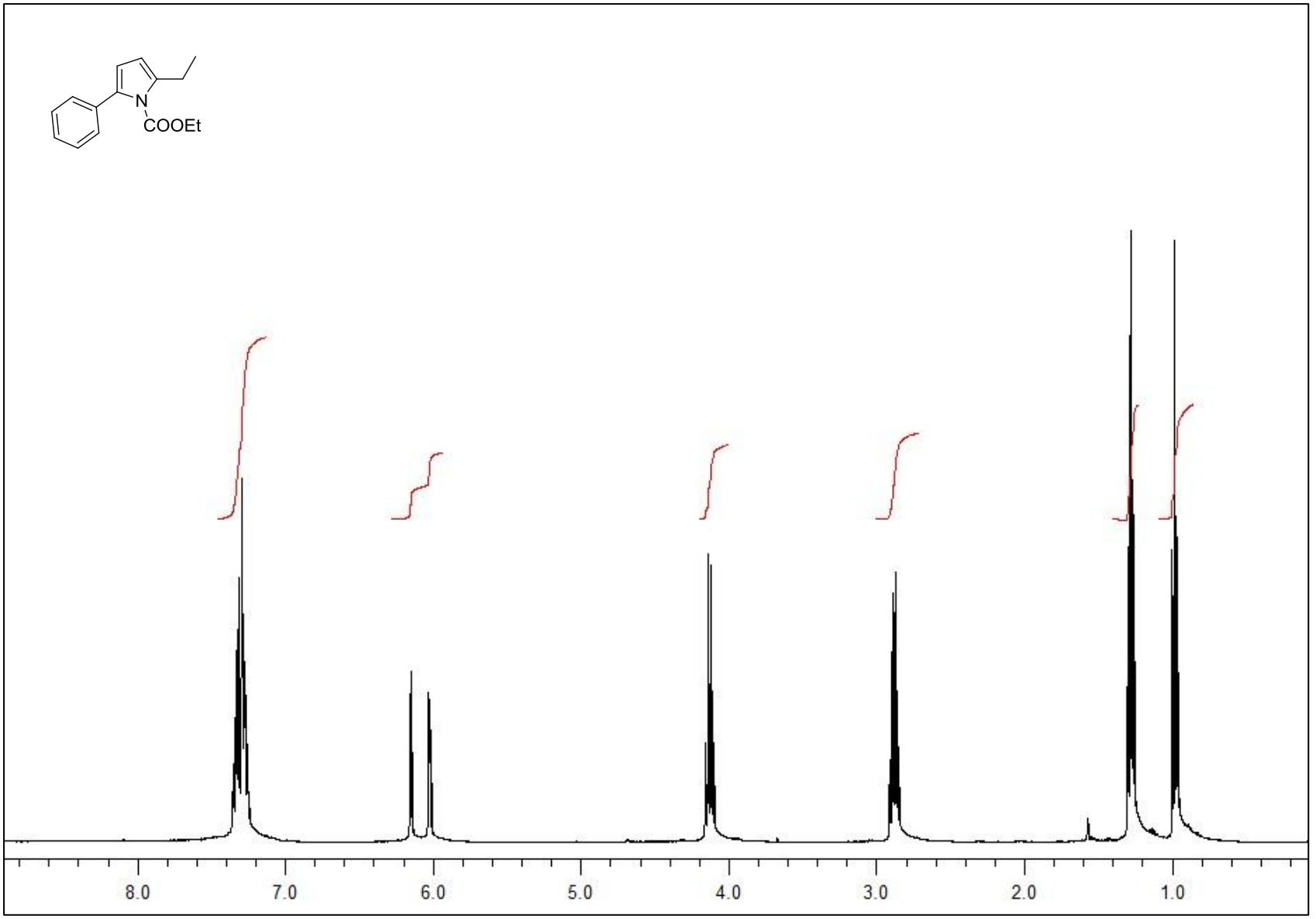

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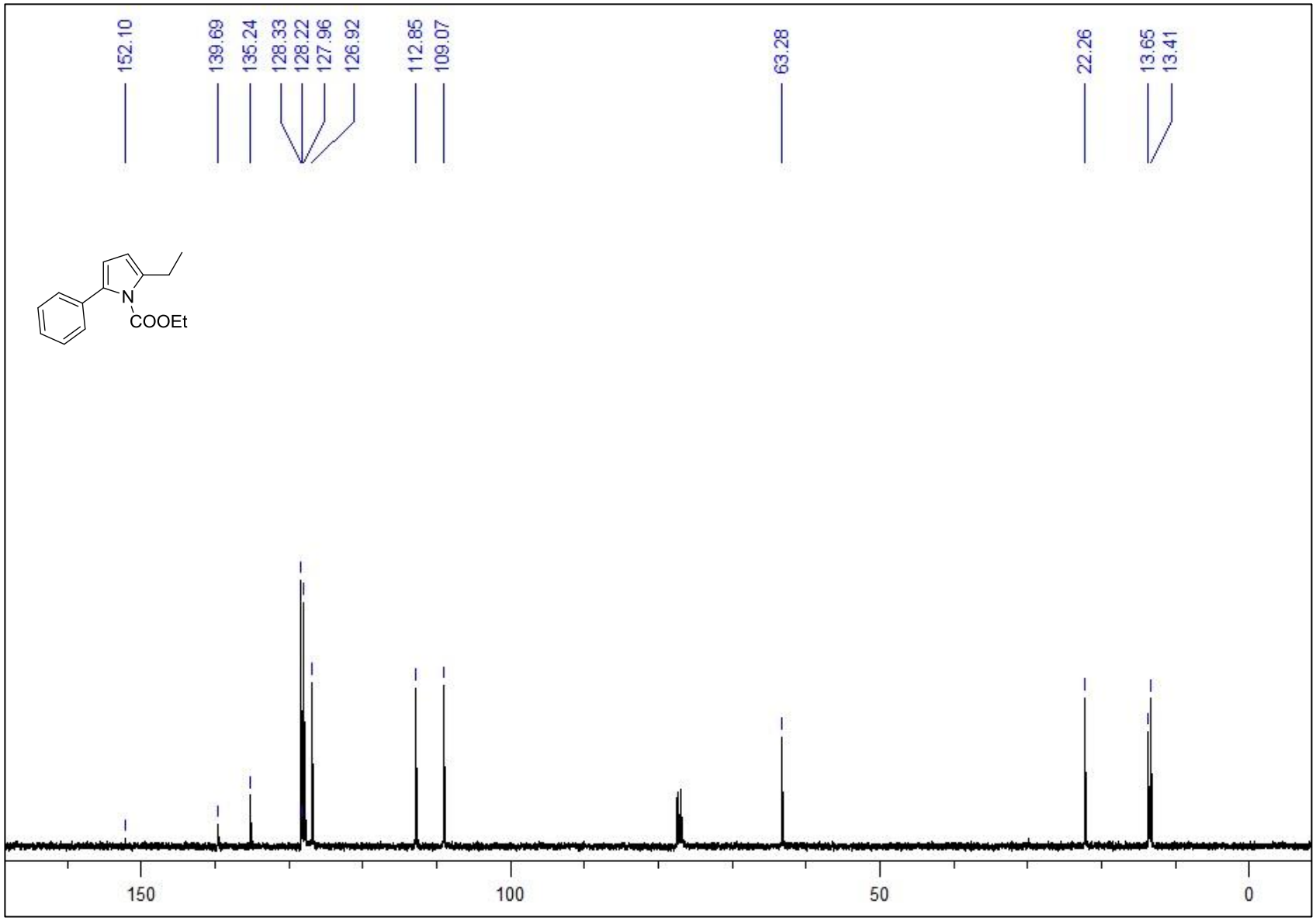

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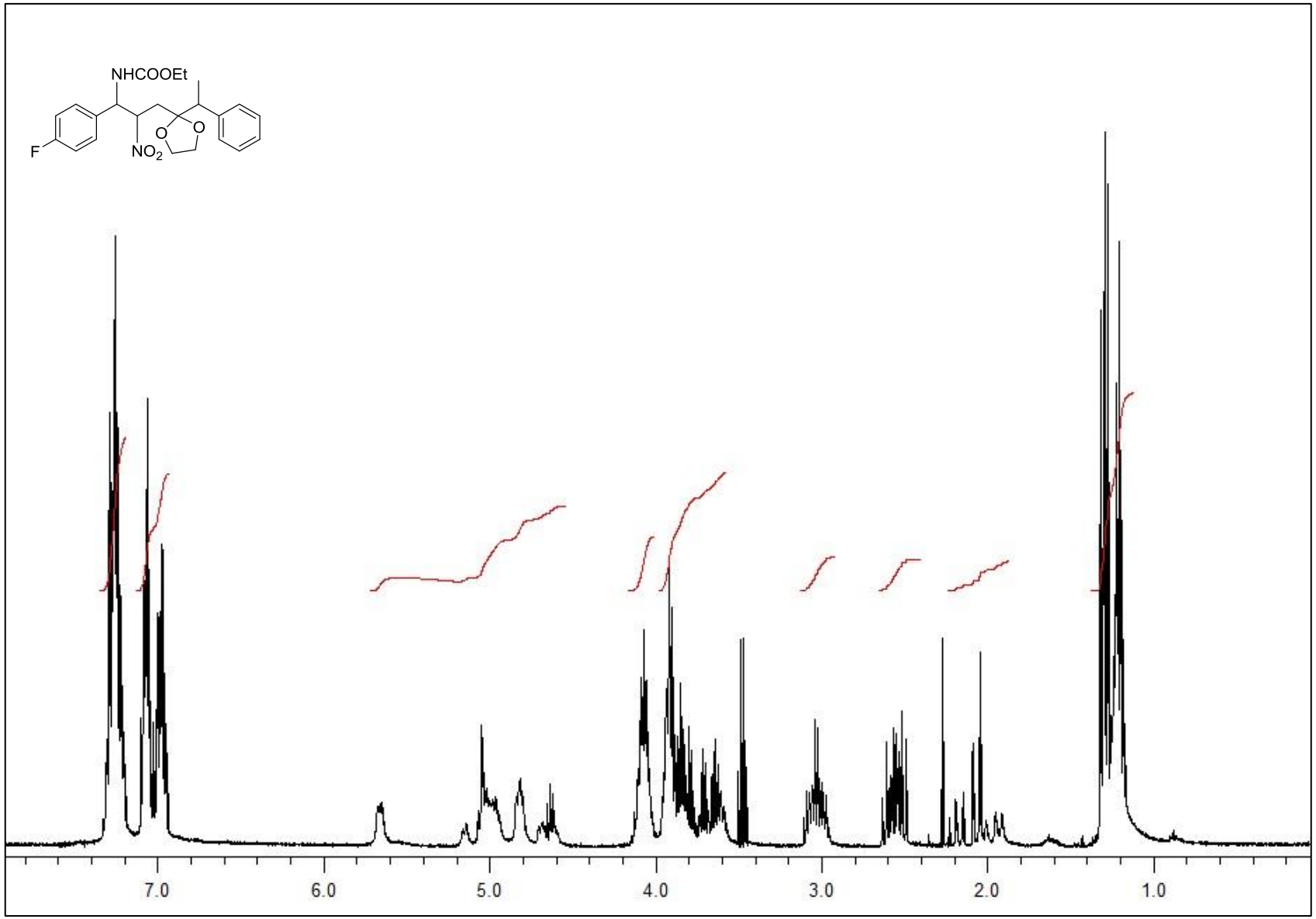

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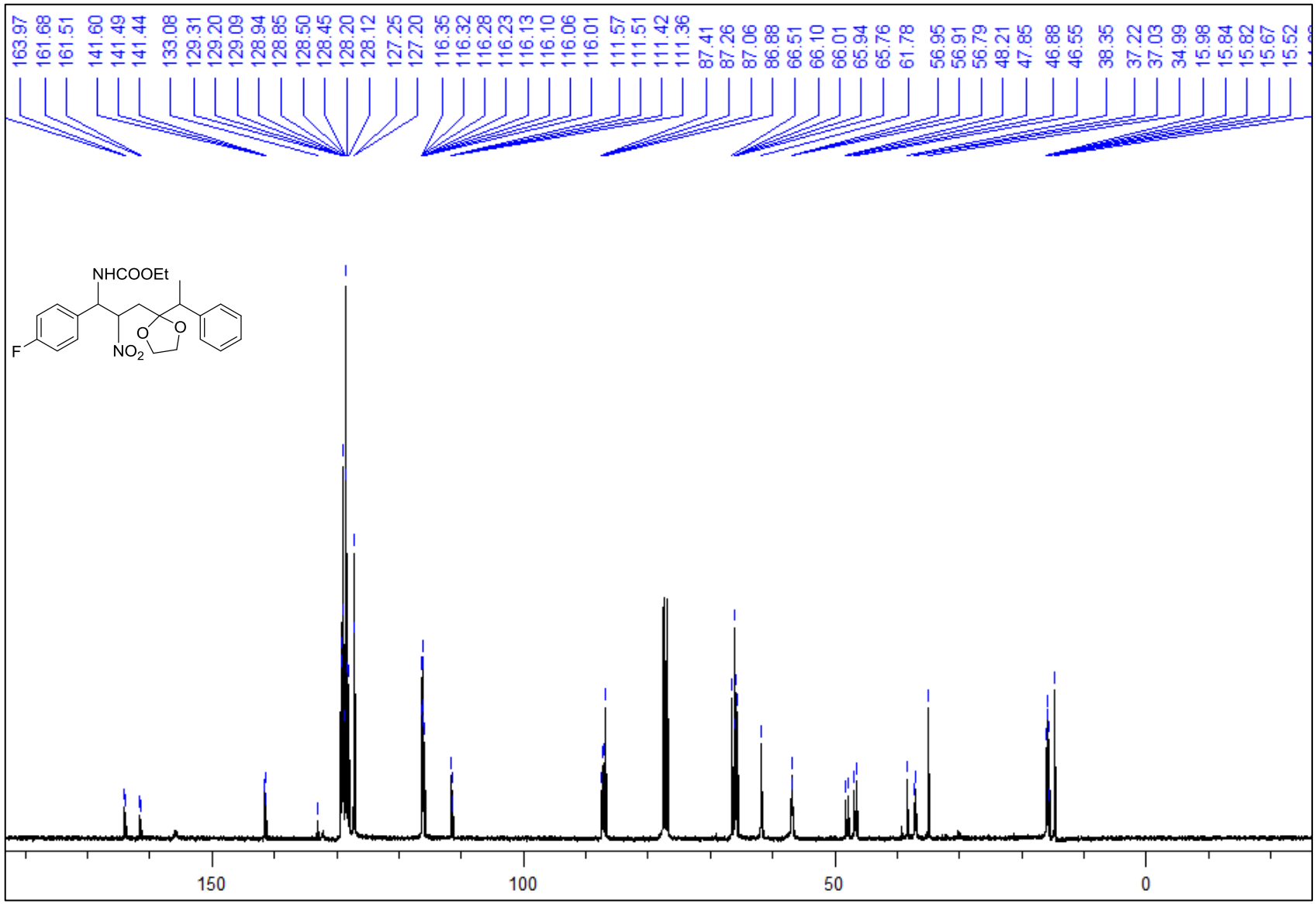

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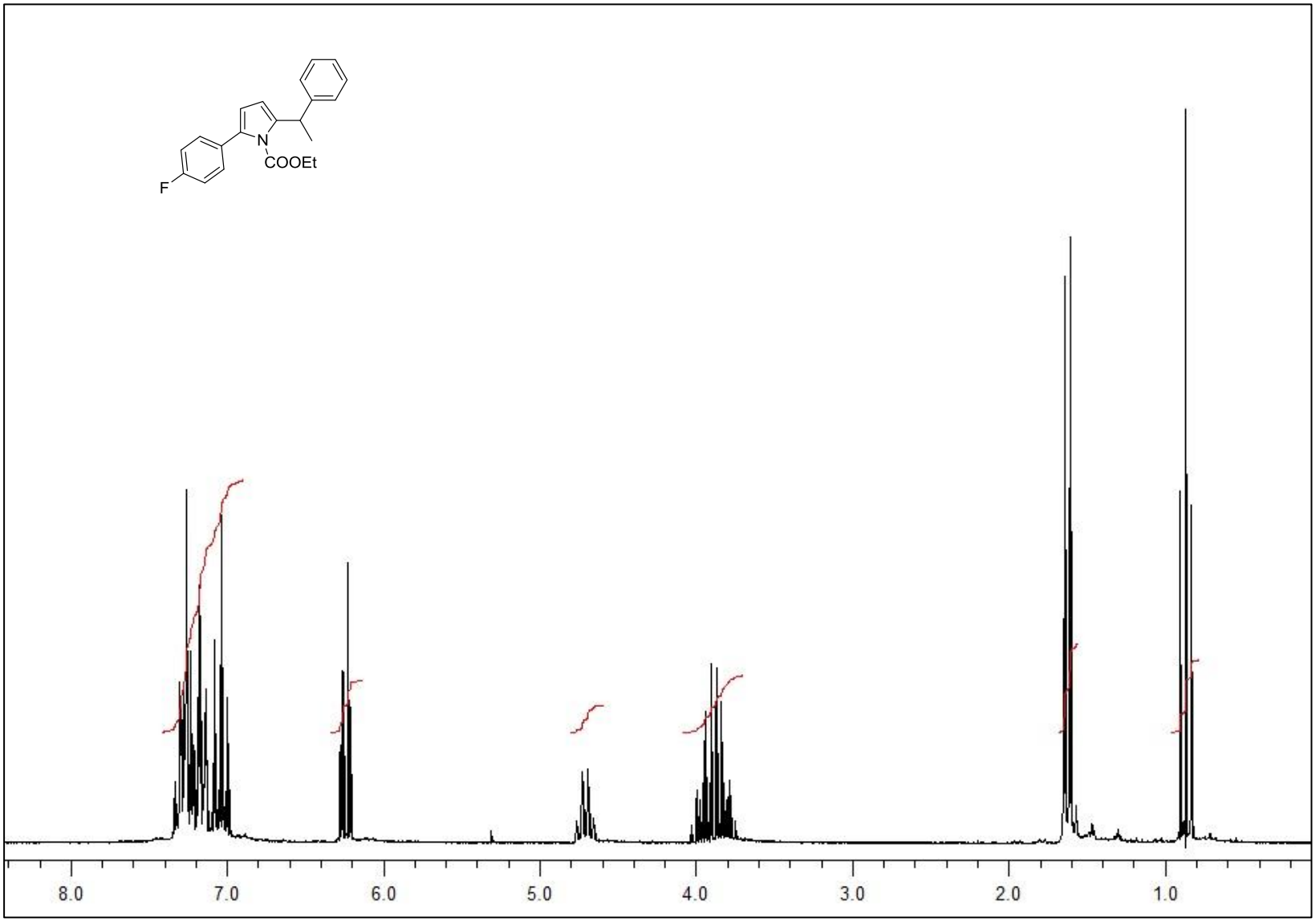

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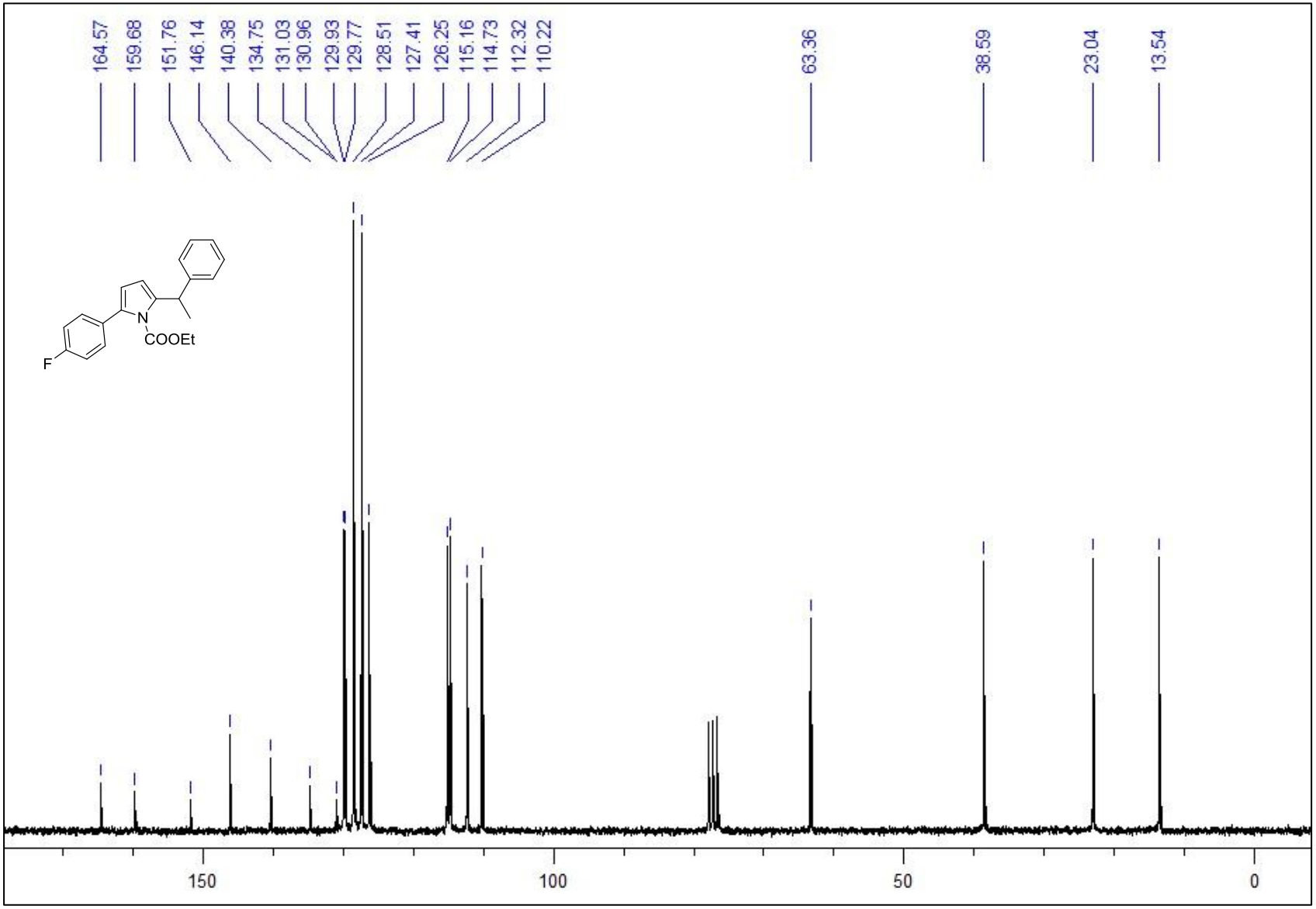

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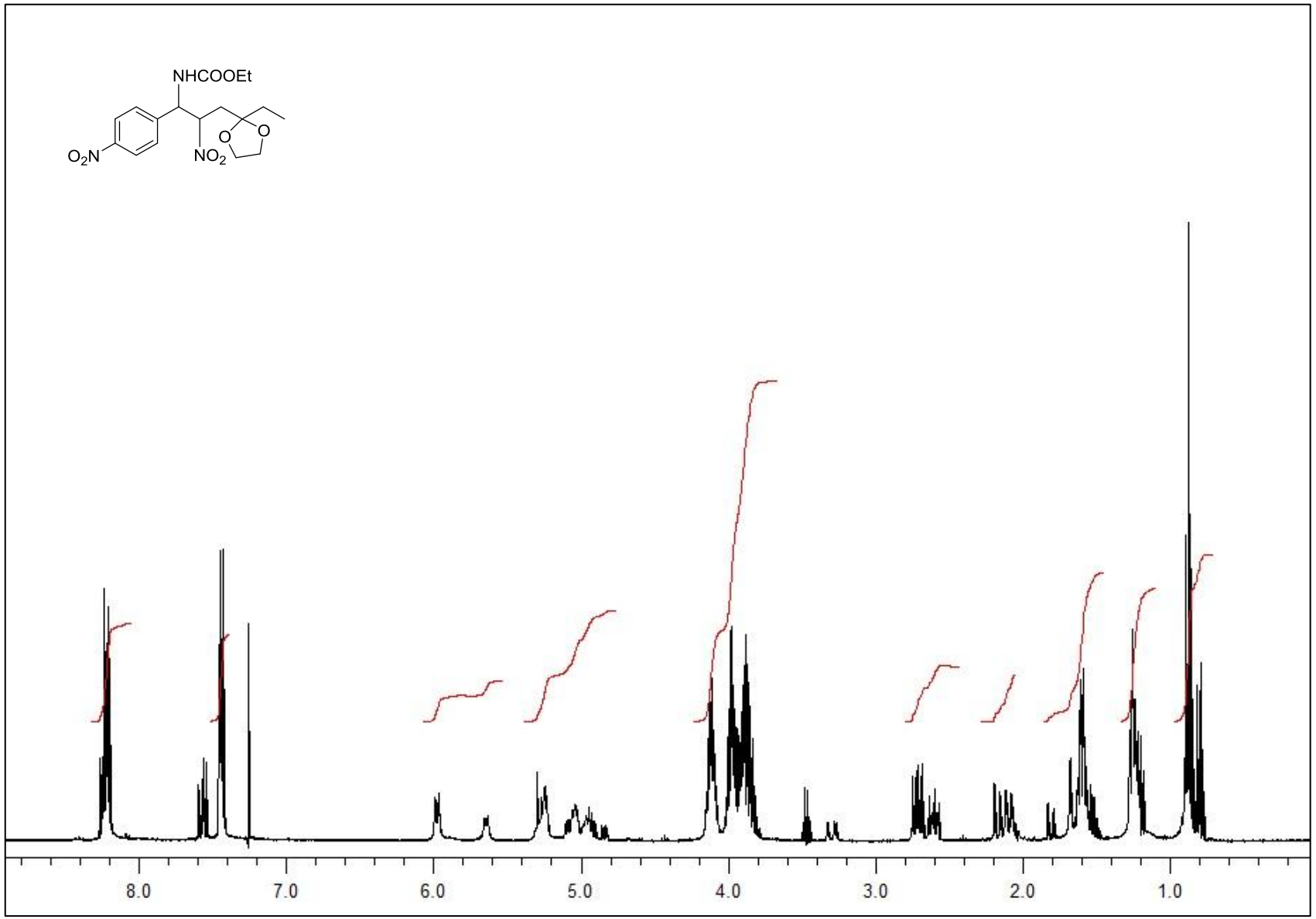

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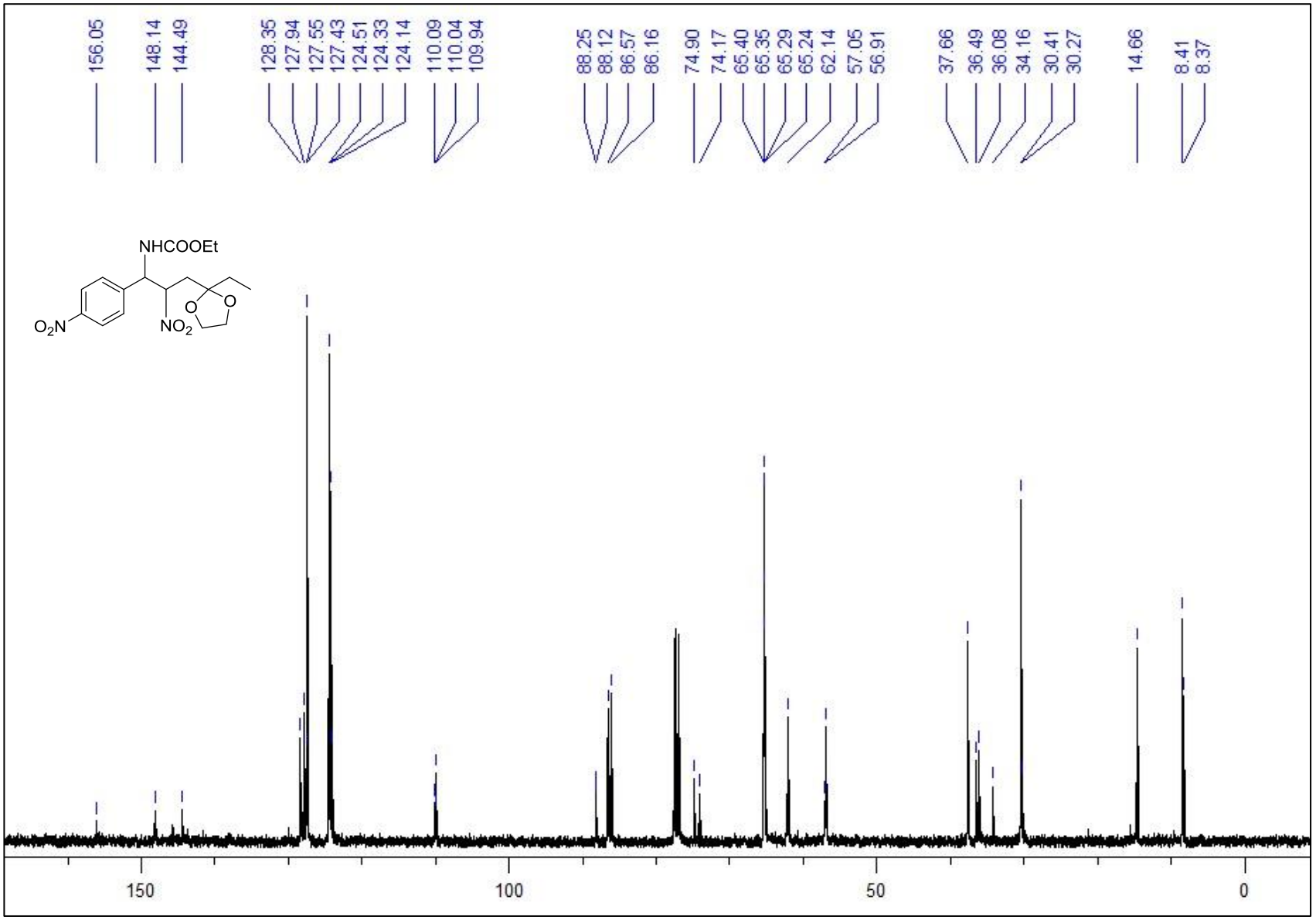

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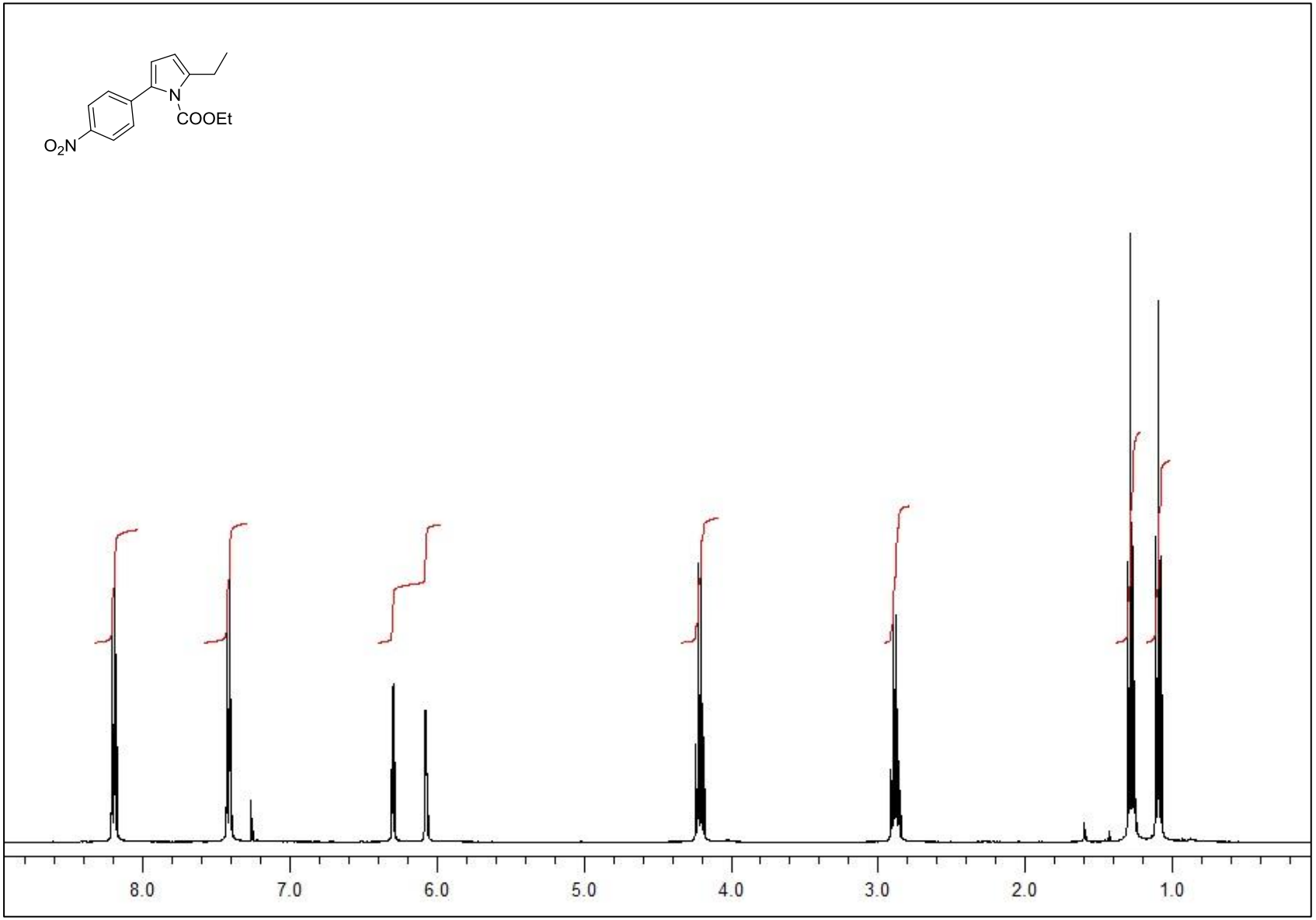

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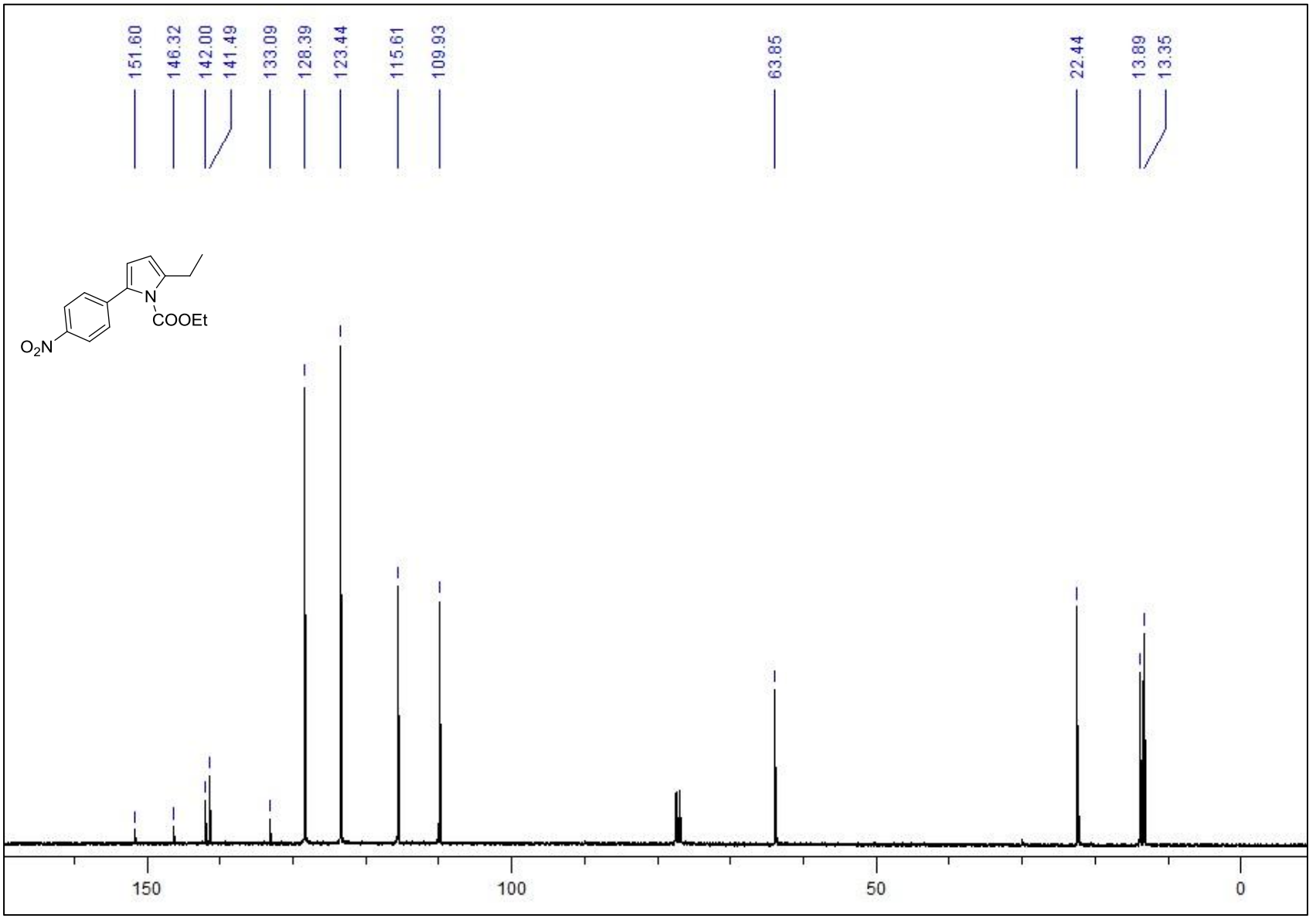

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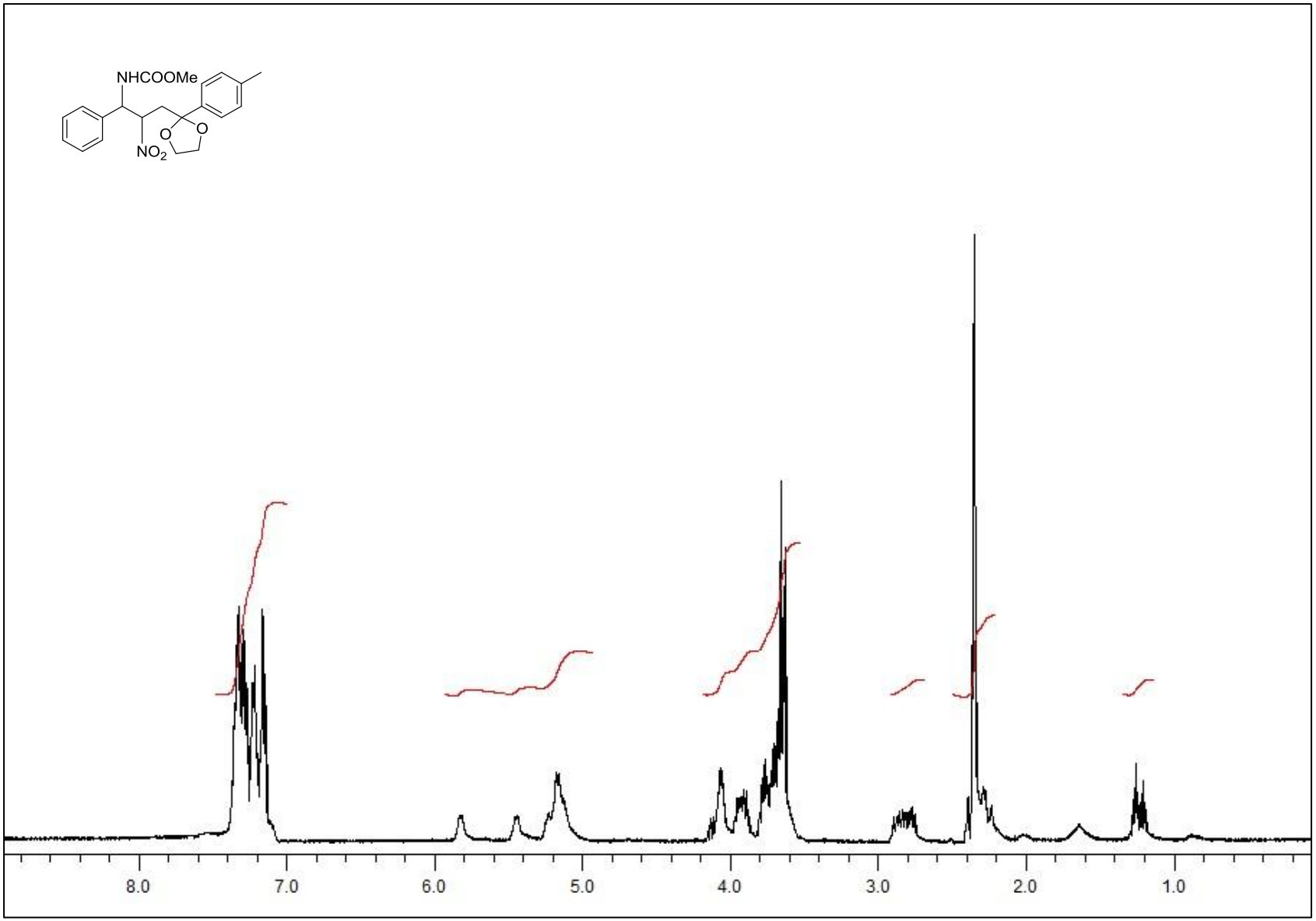

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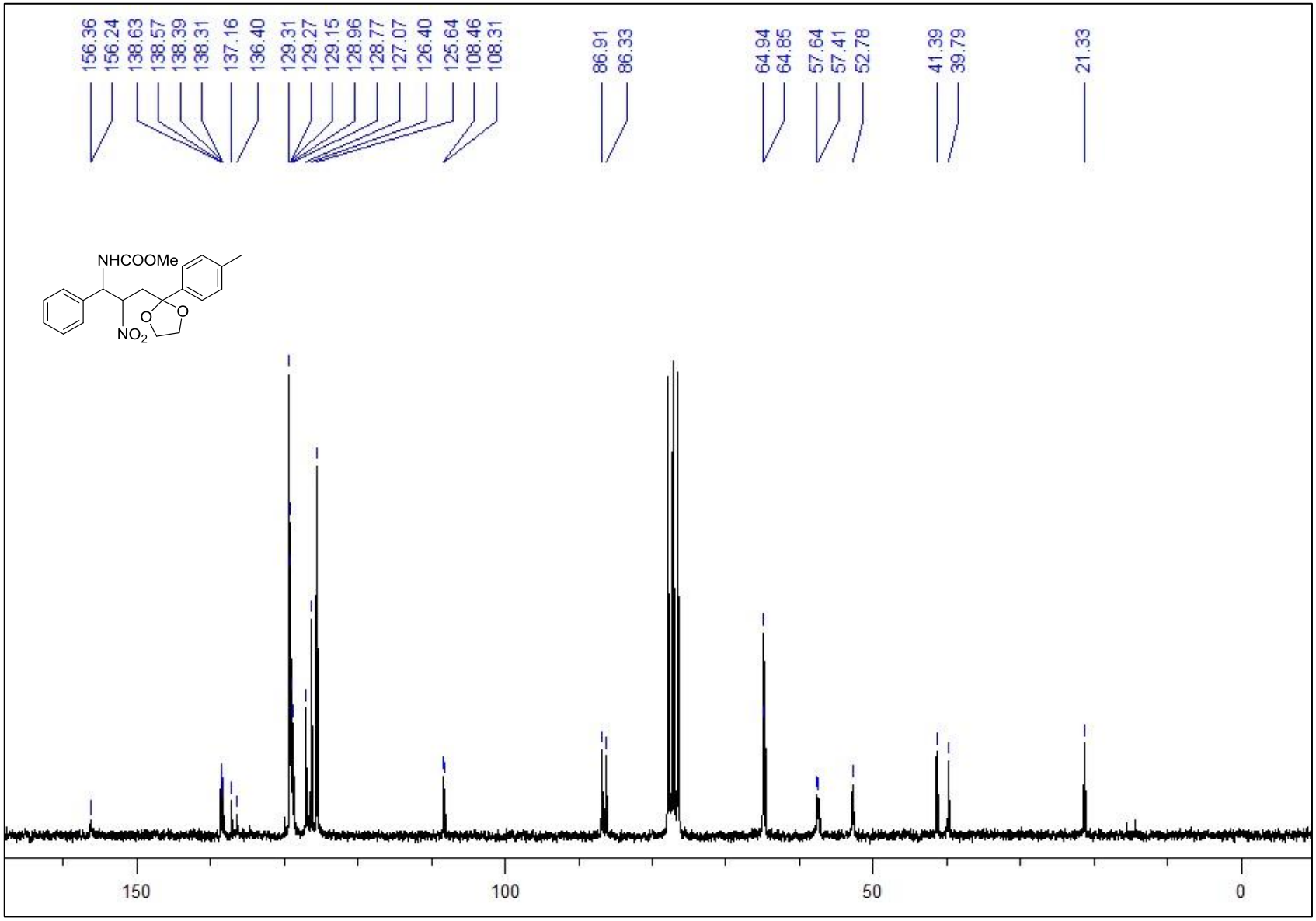

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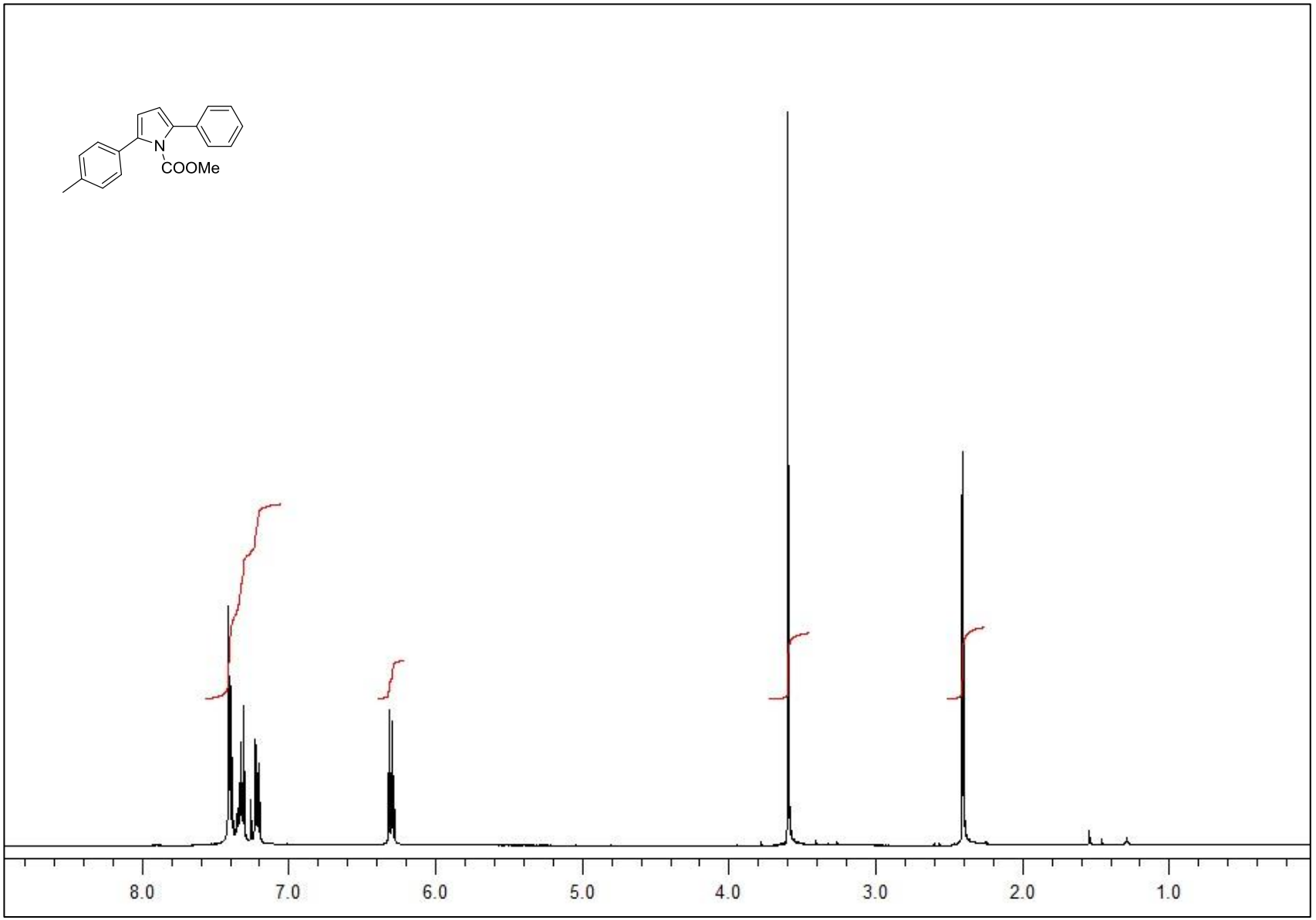

^{13}C NMR (400MHz. $CHCl_3$), **4l**