Supporting information

DBU-catalyzed cyclization of electron-deficient 1,3-conjugated enynes with 2-aminomalonates: a facile access to highly substituted 2,3-dihydro-1*H*-pyrroles

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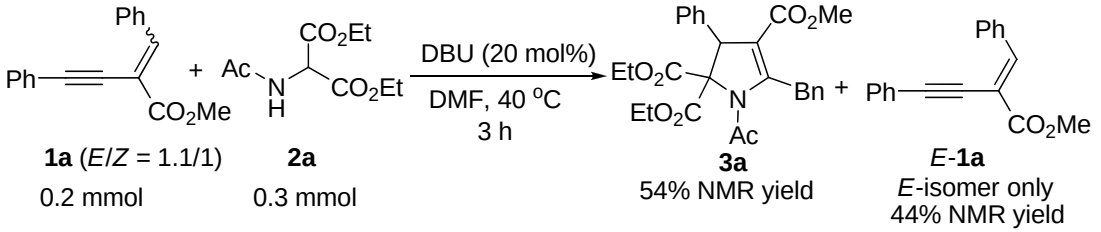
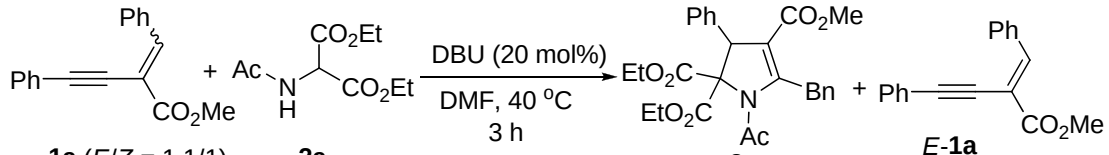
The control experiments about the reactivity of *E*- and *Z*-isomers:



1a (*E*/*Z* = 1.1/1) 0.2 mmol; **2a** 0.3 mmol; **3a** 54% NMR yield; *E*-**1a** *E*-isomer only 44% NMR yield

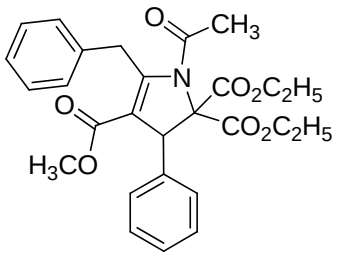


1a (*E*/*Z* = 1.1/1) 0.3 mmol; **2a** 0.15 mmol; **3a** 76% NMR yield; *E*-**1a** *E*-isomer only 70% NMR yield based on **1a**

The control experiment indicated *Z*-isomer is more reactive than the *E*-isomer.

Typical procedure for the synthesis of 2-pyrroline 3a (Table 1, entry 3):

1. **2,2-Diethyl 4-methyl 1-acetyl-5-benzyl-3-phenyl-1*H*-pyrrole-2,2,4(3*H*)-tricarboxylate.**

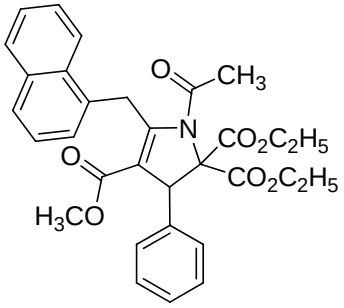


3a

Under Ar, DBU (15.2 mg, 0.1 mmol) was added to a mixture of enyne **1a** (*E*/*Z* = 1.1/1, 131.0 mg, 0.5 mmol) and 2-acetamidomalonate **2a** (163.0 mg, 0.75 mmol) in dry DMF (2.5 mL) at 40 ℃. The reaction was stirred at this temperature till the complete consumption of **2a** which was determined by TLC analysis. After cooling down to room temperature, H_2O (5 mL) was added to the reaction mixture which was then extracted by diethyl ether (3 × 10 mL). The combined organic phase was washed by water and saturated aqueous NaCl solution and dried over $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography on silica gel (PE : EA = 5 : 1) to give **3a** in 90% (215.1 mg) yield as a white solid. m.p.: 87 ~ 88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 ~ 7.15 (m, 10 H), 4.91 (d, *J* = 15.9 Hz, 1 H), 4.87

(s, 1 H), 4.70 (d, *J* = 15.9 Hz, 1 H), 4.38 ~ 4.16 (m, 2 H), 3.60 ~ 3.50 (m, 1 H), 3.45 (s, 3 H), 3.43 ~ 3.33 (m, 1 H), 2.06 (s, 3 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 0.85 (m, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 169.55, 167.49, 164.75, 164.25, 153.73, 137.21, 136.63, 128.40 (2C), 127.78(2C), 127.62, 126.34, 112.41, 78.44, 62.52, 61.67, 54.11, 51.07, 32.09, 24.62, 13.65, 13.11 ppm. IR (neat): *v* (cm^{-1}) 3444, 3029, 1759, 1687, 1625, 1307, 1232, 1047, 1012, 699. HRMS calcd for $C_{27}H_{29}NO_7$: 479.1944, found: 479.1959. MS (70 eV): m/z (%): 479 (M^+, 0.60), 91 (100).

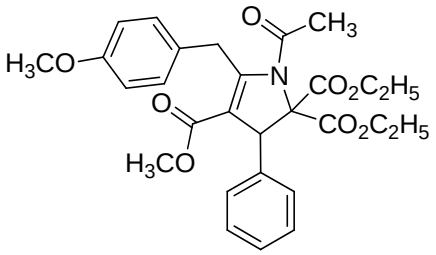
2. 2,2-Diethyl 4-methyl 1-acetyl-5-(naphthalen-1-ylmethyl)-3-phenyl-1*H*-pyrrole -2,2,4(3*H*)-tricarboxylate.



3b

A mixture of **1b** (*E*/*Z* = 1.5/1, 156.0 mg, 0.5 mmol), **2a** (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 41 h to afford **3b** in the yield of 72% (190.4 mg). Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 7.5 Hz, 1 H), 7.84 ~ 7.77 (m, 1 H), 7.64 ~ 7.51 (m, 3 H), 7.50 ~7.42 (m, 1 H), 7.36 ~ 7.26 (m, 5 H), 5.22 (d, *J* = 15.6 Hz, 1 H), 5.18 (d, *J* = 15.6 Hz, 1 H), 4.90 (s, 1 H), 4.47 ~ 4.27 (m, 2 H), 3.63 ~ 3.40 (m, 2 H), 3.44 (s, 3 H), 2.02 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H), 0.93 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 169.49, 167.77, 164.98, 164.33, 153.05, 137.67, 133.77, 132.60, 131.44, 128.87, 127.99, 127.77, 127.50, 126.48, 125.88, 125.63, 124.11, 122.72, 113.16, 78.32, 62.67, 61.73, 53.87, 51.29, 30.02, 24.11, 13.98, 13.39 ppm. IR (neat): *v* (cm^{-1}) 3488, 2993, 1749, 1706, 1664, 1630, 1390, 1335 1226, 1059, 1018, 805, 698. HRMS calcd for $C_{31}H_{31}NO_7$: 529.2101, found: 529.2094. MS (70 eV): m/z (%): 529 (M^+, 0.18), 141 (100).

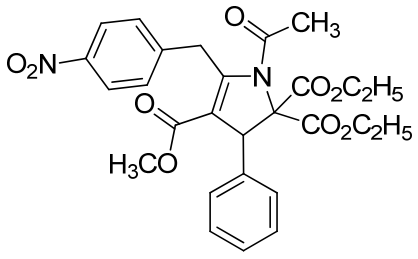
3. 2,2-Diethyl 4-methyl 5-(4-methoxybenzyl)-1-acetyl-3-phenyl-1*H*-pyrrole-2,2,4 (3*H*)-tricarboxylate



3c

A mixture of **1c** (*E*/*Z* = 1.2/1, 146.0 mg, 0.5 mmol), **2a** (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 29 h to afford **3c** in the yield of 70% (178.2 mg). Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 ~ 7.10 (m, 7 H), 6.86 (dd, *J* = 2.1, 6.6 Hz, 2 H), 4.84 (s, 1 H), 4.81 (d, *J* = 15.6 Hz, 1 H), 4.62 (d, *J* = 15.6 Hz, 1 H), 4.39 ~ 4.18 (m, 2 H), 3.78 (s, 3 H), 3.57 ~ 3.45 (m, 1 H), 3.48 (s, 3 H), 3.43 ~ 3.35 (m, 1 H), 2.09 (s, 3 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 0.86 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 169.75, 167.67, 164.94, 164.42, 158.20, 154.26, 137.36, 128.92, 128.67, 127.91, 127.73, 113.99, 112.36, 78.58, 62.67, 61.82, 55.12, 54.22, 51.22, 31.37, 24.74, 13.78, 13.25 ppm. IR (neat): *v* (cm^{-1}) 2984, 2953, 1746, 1707, 1620, 1511, 1369, 1223, 1133, 1019, 818, 700. HRMS calcd for $C_{28}H_{31}NO_8$: 509.2050, found: 509.2055. MS (70 eV): m/z (%): 509 (M^+, 0.63), 121 (100).

4. 2,2-Diethyl 4-methyl 5-(4-nitrobenzyl)-1-acetyl-3-phenyl-1*H*-pyrrole-2,2,4(3*H*) -tricarboxylate

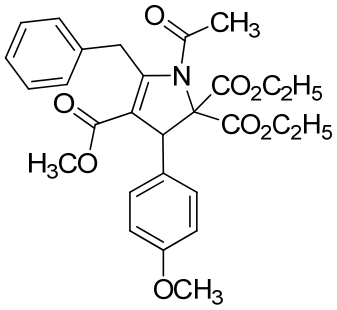


3d

A mixture of **1d** (*E*/*Z* = 1.3/1, 153.6 mg, 0.5 mmol), **2a** (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 1 h to

afford **3d** in the yield of 65% (170.3 mg). Yellow solid, m.p.: 134 ~ 135 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.7 Hz, 2 H), 7.47 (d, *J* = 8.7 Hz, 2 H), 7.30 ~ 7.10 (m, 5 H), 4.99 (d, *J* = 15.6 Hz, 1 H), 4.94 (s, 1 H), 4.83 (d, *J* = 15.6 Hz, 1 H), 4.40 ~ 4.26 (m, 2 H), 3.58 ~ 3.50 (m, 1 H), 3.48 (s, 3 H), 3.47 ~ 3.37 (m, 1 H), 1.92 (s, 3 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 0.86 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 170.20, 167.89, 164.80, 164.64, 153.87, 146.65, 145.39, 136.82, 129.11, 128.16, 123.63, 112.67, 79.09, 63.28, 62.49, 55.38, 51.51, 32.90, 25.04, 13.92, 13.32 ppm. IR (neat): *v* (cm^{-1}) 2987, 2955, 1745, 1701, 1679, 1515, 1346, 1306, 1233, 1048, 1003, 739, 698. HRMS calcd for $C_{27}H_{28}N_2O_9$: 524.1795, found: 524.1796. MS (70 eV): m/z (%): 524 (M^+, 0.79), 409 (100).

5. 2,2-Diethyl 4-methyl 1-acetyl-5-benzyl-3-(4-methoxyphenyl)-1*H*-pyrrole-2,2,4 (3*H*)-tricarboxylate.

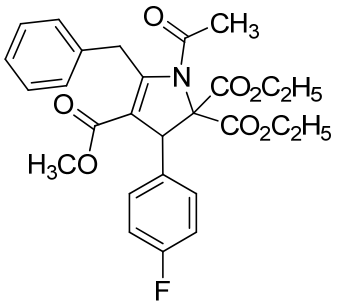


3e

A mixture of **1e** (*E*/*Z* = 1.3/1, 146.0 mg, 0.5 mmol), **2a** (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 23 h to afford **3e** in the yield of 64% (162.9 mg); White solid, m.p.:105 ~ 106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 ~ 7.13 (m, 7 H), 6.81 (dd, *J* = 1.5, 7.5 Hz, 2 H), 4.87 (d, *J* = 15.9 Hz, 1 H), 4.82 (s, 1 H), 4.69 (d, *J* = 15.9 Hz, 1 H), 4.36 ~ 4.19 (m, 2 H), 3.77 (s, 3 H), 3.64 ~ 3.55 (m, 1 H), 3.58 ~ 3.43 (m, 4 H), 2.06 (s, 3 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 0.92 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 169.86, 167.78, 165.07, 164.56, 159.18, 153.67, 136.91, 129.32, 128.59, 128.00, 126.52, 113.36, 112.92, 78.65, 62.70, 61.93, 55.17, 53.86, 51.34, 32.34, 24.86, 13.85, 13.41 ppm. IR (neat): *v* (cm^{-1}) 2957, 2846, 2043, 1758, 1686, 1514, 1368, 1284, 1232, 1052, 1013, 854, 731, 697. HRMS calcd for $C_{28}H_{31}NO_8$: 509.2050,

found: 509.2069. MS (70 eV): m/z (%): 509 (M^+, 1.29), 91 (100).

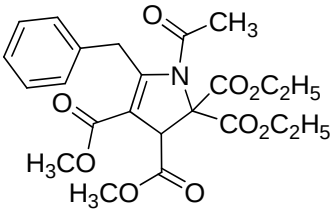
6. 2,2-Diethyl 4-methyl 1-acetyl-5-benzyl-3-(4-fluorophenyl)-1*H*-pyrrole-2,2,4 (3*H*)-tricarboxylate.



3f

A mixture of **1f** (*E*/*Z* = 1.2/1, 140.0 mg, 0.5 mmol), **2a** (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 4.5 h to afford **3f** in the yield of 89% (221.0 mg). White solid; m.p.:101 ~ 102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 ~ 7.20 (m, 7 H), 6.98 (t, *J* = 8.4 Hz, 2 H), 4.89 (d, *J* = 15.9 Hz, 1 H), 4.84 (s, 1 H), 4.65 (d, *J* = 15.9 Hz, 1 H), 4.37 ~ 4.19 (m, 2 H), 3.65 ~ 3.59 (m, 1 H), 3.58 ~ 3.44 (m, 4 H), 2.08 (s, 3 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 0.92 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 169.77, 167.59, 164.86, 164.41, 162.34 (d, $^1J_{F\text{-}C}$ = 246.9 Hz), 154.08, 136.69, 133.20 (d, $^4J_{F\text{-}C}$ = 3.0 Hz), 128.65, 127.93, 126.61, 114.91 (d, $^2J_{F\text{-}C}$ = 21.1 Hz), 112.45, 78.47, 62.82, 62.02, 53.55, 51.37, 32.29, 24.85, 13.84, 13.40 ppm. IR (neat): *v* (cm^{-1}) 3067, 2983, 1756, 1706, 1672, 1622, 1506, 1380, 1227, 1059, 1018, 1012, 861, 733, 698. HRMS calcd for $C_{27}H_{28}NO_7F$: 497.1850, found: 497.1856. MS (70 eV): m/z (%): 497 (M^+, 0.27), 91 (100).

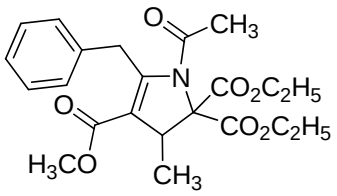
7. 2,2-Diethyl 3,4-dimethyl 1-acetyl-5-benzyl-1*H*-pyrrole-2,2,3,4(3*H*)-tetracarbo -xylate.



3g

A mixture of **1g** (*E*/*Z* = 3.2/1, 73.2 mg, 0.3 mmol), **2a** (97.7 mg, 0.45 mmol), and DBU (9.1 mg, 0.06 mmol) in 2.5 mL of DMF was stirred at 40 ^{o}C for 3 h to afford **3g** in the yield of 81% (112.0 mg). Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 ~ 7.21 (m, 5 H), 4.68 (s, 2 H), 4.44 (s, 1 H), 4.34 ~ 4.25 (m, 2 H), 4.23 ~ 4.15 (m, 2 H), 3.73 (s, 3 H), 3.68 (s, 3 H), 2.16 (s, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.27 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 169.58, 168.85, 166.93, 164.86, 164.41, 153.45, 135.74, 128.89, 127.62, 126.74, 110.04, 76.07, 63.08, 62.79, 53.07, 52.70, 51.64, 32.26, 24.46, 13.85, 13.72 ppm. IR (neat): *v* (cm^{-1}) 2955, 2850, 1751, 1685, 1625, 1438, 1223, 1199, 1017, 733, 698. HRMS calcd for $C_{23}H_{27}NO_9$: 461.1686, found: 461.1689. MS (70 eV): m/z (%): 461 (M^+, 1.96), 91 (100).

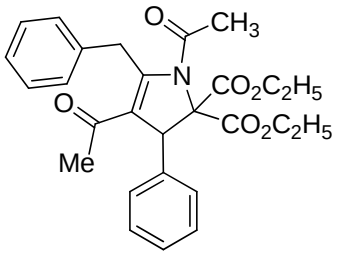
8. 2,2-Diethyl 4-methyl 1-acetyl-5-benzyl-3-methyl-1*H*-pyrrole-2,2,4(3*H*)-tricarboxylate.



3h

A mixture of **1h** (*E*, 100.0 mg, 0.5 mmol), **2a** (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 ^{o}C for 1.5 h to afford **3h** in the yield of 49% (102.2 mg). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 ~ 7.24 (m, 2 H), 7.21 ~ 7.17 (m, 3 H), 4.59 (s, 2 H), 4.28 ~ 4.16 (m, 4 H), 3.69 (s, 3 H), 3.62 (q, *J* = 6.9 Hz, 1 H), 2.09 (s, 3 H), 1.32 ~1.18 (m, 9 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 169.41, 167.70, 164.95, 164.93, 151.13, 136.39, 128.48, 127.53, 126.34, 115.23, 77.06, 62.24, 61.80, 51.13, 43.15, 31.94, 24.48, 16.68, 13.82, 13.69 ppm. IR (neat): *v* (cm^{-1}) 2983, 1745, 1707, 1679, 1619, 1371, 1222, 1097, 1031, 729, 698. HRMS calcd for $C_{22}H_{27}NO_7$: 417.1788, found: 417.1806. MS (70 eV): m/z (%): 417 (M^+, 1.05), 91 (100).

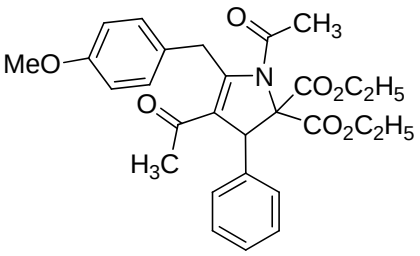
9. Diethyl 1,4-diacetyl-5-benzyl-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.



3i

A solution of **1i** (*E*, 123.0 mg, 0.5 mmol) in 1.5 mL of DMF was slowly added to a solution of **2a** (163.0 mg, 0.75 mmol) and DBU (15.2 mg, 0.10 mmol) in 1.0 mL of DMF via syringe pump over 2 h at 40 ^{o}C. After finishing addition, the mixture was then stirred for another 26 h. After the routine work-up, 2-pyrroline **3i** was obtained in the yield of 70% (163.0 mg). White solid, m.p.:111 ~ 112 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 ~ 7.12 (m, 10 H), 4.89 (s, 1 H), 4.87 (d, *J* = 15.6 Hz, 1 H), 4.64 (d, *J* = 15.6 Hz, 1 H), 4.39 ~ 4.29 (m, 1 H), 4.28 ~ 4.17 (m, 1 H), 3.62 ~ 3.50 (m, 1 H), 3.43 ~ 3.32 (m, 1 H), 2.07 (s, 3 H), 1.88 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 0.85 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 195.48, 169.93, 167.51, 164.16, 152.82, 136.70, 136.63, 128.40, 128.26, 128.19, 127.84, 126.35, 119.96, 78.67, 62.63, 61.76, 54.88, 32.20, 29.92, 24.82, 13.63, 13.13 ppm. IR (neat): *v* (cm^{-1}) 3463, 2986, 1759, 1740, 1669, 1574, 1378, 1222, 1063, 1026, 744, 700. HRMS calcd for $C_{27}H_{29}NO_6$: 463.1995, found: 463.2015. MS (70 eV): m/z (%): 463 (M^+, 3.80), 260 (100) ppm.

10. Diethyl 1,4-diacetyl-5-(4-methoxybenzyl)-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.

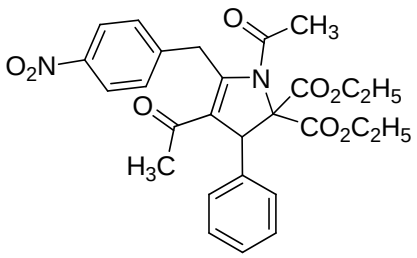


3j

According to the procedure of synthesis of **3i**, the reaction of **2a** (97.7 mg, 0.45 mmol), **1j** (*E*, 82.8 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg,

0.06 mmol) at 40 °C for 70 h affords **3j** in the yield of 61% (90.0 mg). Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (bs, 4 H), 7.21 (d, *J* = 7.6 Hz, 3 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 4.89 (s, 1 H), 4.79 (d, *J* = 15.6 Hz, 1 H), 4.59 (d, *J* = 15.6 Hz, 1 H), 4.40 ~ 4.20 (m, 2 H), 3.79 (s, 3 H), 3.61 ~ 3.53 (m, 1 H) 3.46 ~ 3.37 (m, 1 H), 2.13 (s, 3 H), 1.90 (s, 3 H), 1.29 (t, *J* = 6.8 Hz, 3 H), 0.88 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 195.64, 170.08, 167.70, 164.32, 158.20, 153.36, 136.85, 128.98, 128.64, 128.40, 128.31, 119.90, 113.98, 78.79, 62.79, 61.90, 55.14, 54.96, 31.48, 30.09, 24.96, 13.77, 13.28 ppm. IR (neat): *v* (cm^{-1}) 2983, 2836, 2253, 1747, 1672, 1579, 1512, 1343, 1222, 1053, 1030, 735, 701. HRMS calcd for $C_{28}H_{31}NO_7$: 493.2101, found: 493.2104. MS (70 eV): m/z (%): 493 (M^+, 11.87), 451 (100).

11. Diethyl 1,4-diacetyl-5-(4-nitrobenzyl)-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxy -late.

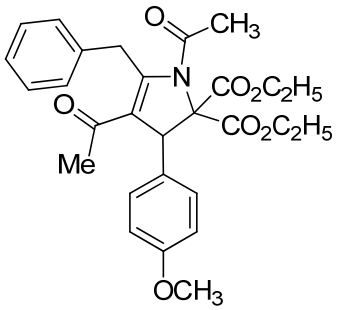


3k

According to the procedure of synthesis of **3i**, the reaction of **2a** (97.7 mg, 0.45 mmol), **1k** (*E*, 87.3 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 14 h affords **3k** in the yield of 49% (75 mg). Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.8 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.35 (bs, 4 H), 7.15 (bs, 1 H), 5.00 (d, *J* = 15.6 Hz 1 H), 5.00 (s, 1 H), 4.81 (d, *J* = 15.6 Hz, 1 H), 4.46 ~ 4.35 (m, 1 H), 4.35 ~ 4.27 (m, 1 H), 3.66 ~ 3.55 (m, 1 H), 3.50 ~ 3.41 (m, 1 H), 1.98 (s, 3 H), 1.89 (s, 3 H), 1.32 (t, *J* = 7.2 Hz, 3 H), 0.90 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 195.78, 170.42, 167.75, 164.45, 152.89, 146.57, 145.40, 136.22, 129.14, 128.74, 128.64, 123.57, 119.78, 79.26, 63.34, 62.52, 55.96, 32.92, 30.13, 25.21, 13.87, 13.31 ppm. IR (neat): *v*

(cm^{-1}) 2984, 2254, 1744, 1693, 1591, 1520, 1344, 1223, 1052, 1014, 860, 737, 701. HRMS calcd for $C_{27}H_{28}N_2O_8$: 508.1846, found: 508.1845. MS (70 eV): m/z (%): 508 (M^+, 1.15), 43 (100).

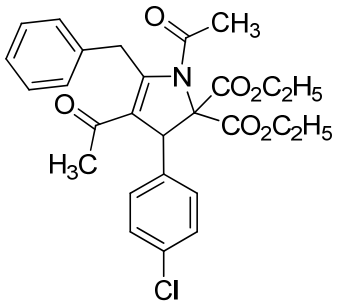
12. Diethyl 1,4-diacetyl-5-benzyl-3-(4-methoxyphenyl)-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.



3l

According to the procedure of synthesis of **3i**, the reaction of **2a** (163.0 mg, 0.75 mmol), **1l** (*E*, 136.0 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 12 h affords **3l** in the yield of 76% (187.4 mg). Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 ~ 7.00 (m, 7 H), 6.80 (d, *J* = 8.1 Hz, 2 H), 4.823 (d, *J* = 15.9 Hz, 1 H), 4.824 (s, 1 H), 4.60 (d, *J* = 15.9 Hz, 1 H), 4.32 ~ 4.13 (m, 2 H), 3.72 (s, 3 H), 3.64 ~ 3.48 (m, 2 H), 2.04 (s, 3 H), 1.85 (s, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 0.88 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 195.59, 169.95, 167.54, 164.21, 159.42, 152.56, 136.73, 128.49, 128.35, 127.85, 126.29, 120.14, 113.61, 78.64, 62.54, 61.74, 55.00, 54.40, 32.16, 29.85, 24.83, 13.62, 13.21 ppm. IR (neat): *v* (cm^{-1}) 2983, 2838, 1745, 1672, 1579, 1511, 1344, 1222, 1029, 840, 736, 700. HRMS calcd for $C_{28}H_{31}NO_7$: 493.2101, found: 493.2121. MS (70 eV): m/z (%): 493 (M^+, 5.24), 332 (100).

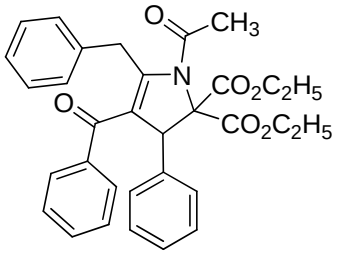
13. Diethyl 1,4-diacetyl-5-benzyl-3-(4-chlorophenyl)-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.



3m

According to the procedure of synthesis of **3i**, the reaction of **2a** (97.7 mg, 0.45 mmol) and **1m** (*E*, 84.0 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 17 h affords **3m** in the yield of 69% (103.0 mg). Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 ~ 7.21 (m, 8 H), 7.14 (bs, 1 H), 4.90 (s, 1 H), 4.87 (d, *J* = 15.6 Hz 1 H), 4.64 (d, *J* = 15.6 Hz, 1 H), 4.39 ~ 4.30 (m, 1 H), 4.28 ~ 4.19 (m, 1 H), 3.70 ~ 3.61 (m, 1 H), 3.57 ~ 3.47 (m, 1 H), 2.11 (s, 3 H), 1.92 (s, 3 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 0.93 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 195.17, 169.98, 167.42, 164.13, 153.19, 136.48, 135.41, 134.26, 128.55, 127.87, 126.56, 119.78, 78.56, 62.87, 62.04, 54.19, 32.30, 30.04, 24.93, 13.72, 13.29 ppm. IR (neat): *v* (cm^{-1}) 2983, 2253, 1747, 1673, 1583, 1492, 1345, 1222, 1054, 1014, 735, 700. HRMS calcd for $C_{27}H_{28}ClNO_6$: 497.1605, found: 497.1602. MS (70 eV): m/z (%): 497 (M^+, 2.46), 43 (100).

14. Diethyl 1-acetyl-4-benzoyl-5-benzyl-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.

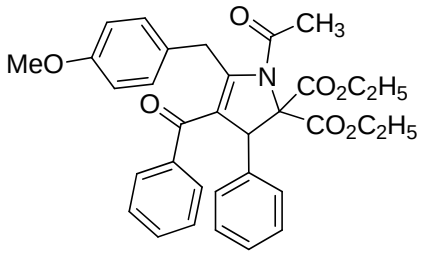


3n

According to the procedure of synthesis of **3i**, the reaction of **2a** (163.0 mg, 0.75 mmol) and **1n** (*E*, 154.0 mg, 0,5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 20 h affords **3n** in the yield of 66% (173.2 mg).

Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 ~ 7.58 (m, 2 H), 7.45 ~ 7.35 (m, 1 H), 7.31 ~ 7.24 (m, 4 H), 7.22 ~ 7.16 (m, 8 H), 5.19 (s, 1 H), 4.40 ~ 4.21 (m, 4 H), 3.53 (q, *J* = 7.2 Hz, 2 H), 2.03 (s, 3 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 192.78, 170.08, 167.59, 164.70, 150.50, 139.13, 136.75, 136.17, 132.10, 129.21, 128.39, 128.24, 128.03, 127.93, 126.50, 122.53, 78.41, 62.58, 61.96, 55.92, 33.49, 24.65, 13.75, 13.21 ppm. IR (neat): *v* (cm^{-1}) 2983, 1743, 1674, 1600, 1451, 1369, 1236, 1056, 1004, 735, 697. HRMS calcd for $C_{32}H_{31}NO_6$: 525.2151, found: 525.2145. MS (70 eV): m/z (%): 525 (M^+, 2.00), 105 (100).

15. Diethyl 1-acetyl-4-benzoyl-5-(4-methoxybenzyl)-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.

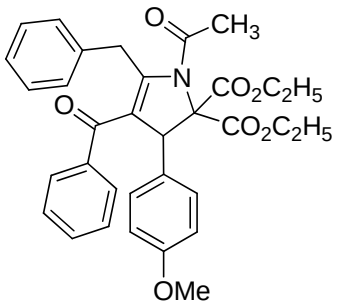


3o

According to the procedure of synthesis of **3i**, the reaction of **2a** (97.7 mg, 0.45 mmol) and **1o** (*E*, 101.4 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 16 h affords **3o** in the yield of 65% (108.3 mg). Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.6 Hz, 2 H), 7.43 (t, *J* = 7.2 Hz, 1 H), 7.31 (t, *J* = 7.2 Hz, 2 H), 7.22 ~ 7.16 (m, 5 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 6.83 (d, *J* = 8.0 Hz, 2 H), 5.10 (s, 1 H), 4.40 ~ 4.26 (m, 2 H), 4.25 (d, *J* = 16.4 Hz, 1 H), 4.15 (d, *J* = 16.4 Hz, 1 H), 3.77 (s, 3 H), 3.54 (q, *J* = 6.8 Hz, 2 H), 2.08 (s, 3 H), 1.31 (t, *J* = 6.8 Hz, 3 H), 0.88 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 192.88, 170.13, 167.69, 164.81, 158.22, 150.86, 139.21, 136.27, 132.16, 129.26, 129.00, 128.72, 128.30, 128.12, 128.01, 127.96, 122.41, 113.89, 78.45, 62.64, 62.02, 55.91, 55.13, 32.71, 24.71, 13.83, 13.29 ppm. IR (neat): *v* (cm^{-1}) 2981, 2253, 1744, 1610, 1512, 1369, 1242, 1177, 1056, 1030, 725, 698.

HRMS calcd for $C_{33}H_{33}NO_7$: 555.2257, found: 555.2266. MS (70 eV): m/z (%): 555 (M^+, 4.31), 43 (100).

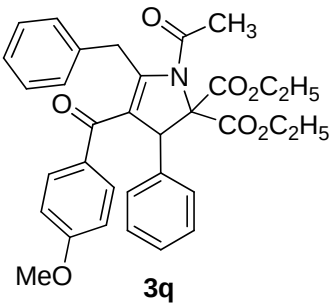
16. Diethyl 1-acetyl-4-benzoyl-5-benzyl-3-(4-methoxyphenyl)-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.



3p

According to the procedure of synthesis of **3i**, the reaction of **2a** (97.7 mg, 0.45 mmol) and **1p** (*E*, 101.4 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 28 h affords **3p** in the yield of 67% (112.0 mg). Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.2 Hz, 2 H), 7.43 (t, *J* = 7.2 Hz, 1 H), 7.34 ~ 7.25 (m, 4 H), 7.22 ~ 7.18 (m, 3 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.74 (d, *J* = 8.0 Hz, 2 H), 5.14 (s, 1 H), 4.38 ~ 4.21 (m, 4 H), 3.70 (s, 3 H), 3.61 (q, *J* = 6.8 Hz, 2 H), 2.04 (s, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 0.94 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 192.91, 170.13, 167.66, 164.78, 159.21, 150.16, 139.12, 136.83, 132.15, 130.37, 128.41, 128.27, 128.08, 128.04, 127.95, 126.51, 122.78, 113.35, 78.38, 62.57, 62.00, 55.43, 55.02, 33.50, 24.70, 13.79, 13.35 ppm. IR (neat): *v* (cm^{-1}) 2982, 2837, 2253, 1744, 1608, 1511, 1447, 1243, 1177, 1056, 1030, 732, 698. HRMS calcd for $C_{33}H_{33}NO_7$: 555.2257, found: 555.2261. MS (70 eV): m/z (%): 555 (M^+, 3.90), 105 (100).

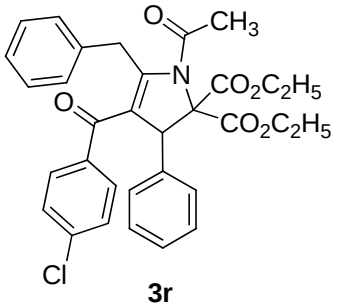
17. Diethyl 1-acetyl-5-benzyl-4-(4-methoxybenzoyl)-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.



3q

According to the procedure of synthesis of **3i**, the reaction of **2a** (97.7 mg, 0.45 mmol) and **1q** (*E*, 101.4 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 ^{o}C for 46 h affords **3q** in the yield of 61% (101.6 mg). Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 2 H), 7.34 ~ 7.14 (m, 10 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 5.24 (s, 1 H), 4.40 ~ 4.17 (m, 4 H), 3.80 (s, 3 H), 3.54 (q, *J* = 6.8 Hz, 2 H), 2.03 (s, 3 H), 1.29 (t, *J* = 6.8 Hz, 3 H), 0.88 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 191.19, 170.04, 167.72, 164.91, 163.18, 148.72, 136.90, 136.15, 131.50, 130.93, 129.31, 128.41, 128.03, 127.99, 126.53, 122.94, 113.63, 78.40, 62.61, 62.02, 56.25, 55.32, 33.79, 24.63, 13.81, 13.28 ppm. IR (neat): *v* (cm^{-1}) 2981, 2253, 1744, 1676, 1598, 1455, 1304, 1247, 1169, 1055, 1026, 847, 734, 699. HRMS calcd for $C_{33}H_{33}NO_7$: 555.2257, found: 555.2260. MS (70 eV): m/z (%): 555 (M^+, 2.83), 135 (100).

18. Diethyl 1-acetyl-5-benzyl-4-(4-chlorobenzoyl)-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxylate.

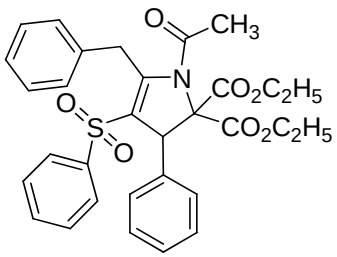


3r

According to the procedure of synthesis of **3i**, the reaction of **2a** (163.0 mg, 0.75 mmol) and **1r** (*E*, 171.5 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 ^{o}C for 16 h affords **3r** in the yield of 74% (206.8 mg). Orange oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.4 Hz, 2 H), 7.32 ~

7.18 (m, 12 H), 5.16 (s, 1 H), 4.38 ~ 4.20 (m, 4 H), 3.54 (q, *J* = 7.2 Hz, 2 H), 2.04 (s, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 191.48, 170.10, 167.56, 164.63, 151.04, 138.37, 137.47, 136.60, 136.01, 129.45, 129.17, 128.56, 128.46, 128.02, 127.91, 126.60, 122.08, 78.46, 62.67, 62.04, 55.89, 33.55, 24.69, 13.76, 13.22 ppm. IR (neat): *v* (cm^{-1}) 3267, 2995, 1755, 1720, 1641, 1611, 1386, 1258, 1219, 1061, 1014, 766, 702. HRMS calcd for $C_{32}H_{30}NO_6Cl$: 559.1762, found: 559.1757. MS (70 eV): m/z (%): 559 (M^+, 1.42), 139 (100).

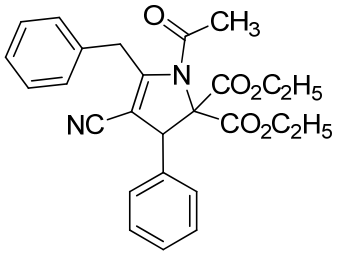
19. Diethyl 1-acetyl-5-benzyl-4-(methylsulfonyl)-3-phenyl-1*H*-pyrrole-2,2(3*H*)-di-carboxylate.



3s

The reaction of **2a** (163.0 mg, 0.75 mmol) and **1s** (*E*, 172 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 ^{o}C for 22 h affords **3s** in the yield of 51% (143.0 mg). White solid, m.p.: 90 ~91 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 ~ 7.01 (m, 13 H), 6.86 (t, *J* = 7.5 Hz, 1 H), 6.72 (d, *J* = 7.5 Hz, 1 H), 4.94 (s, 1 H), 4.85 (d, *J* = 15.6 Hz, 1 H), 4.52 (d, *J* = 15.6 Hz, 1 H), 4.21 ~ 4.03 (m, 2 H), 3.44 ~ 3.37 (m, 2 H), 1.84 (s, 3 H), 1.11 (t, *J* = 7.2 Hz, 3 H), 0.74 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 170.59, 166.70, 164.04, 153.44, 141.65, 135.76, 134.24, 132.72, 130.31, 128.81, 128.54, 128.15, 127.94, 127.83, 127.21, 126.73, 121.66, 79.19, 63.00, 62.39, 55.84, 31.81, 25.17, 13.67, 13.19 ppm. IR (neat): *v* (cm^{-1}) 3503, 2926, 1760, 1740, 1695, 1613, 1305, 1265, 1229, 1150, 1106, 1080, 1018, 725, 699. HRMS calcd for $C_{31}H_{31}NO_7S$: 561.1821, found: 561.1818. MS (70 eV): m/z (%): 561 (M^+, 0.26), 233 (100).

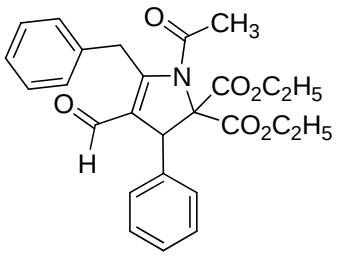
20. Diethyl 1-acetyl-5-benzyl-4-cyano-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxylat-e.



3t

The reaction of **2a** (163.0 mg, 0.75 mmol) and **1t** (*E*, 114.5 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 ^{o}C for 0.5 h affords **3t** in the yield of 80% (178.0 mg). Orange solid, m.p.:119 ~ 120 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 ~ 7.26 (m, 10 H), 4.81 (s, 1 H), 4.48 (d, *J* = 15.9 Hz, 1 H), 4.35 (d, *J* = 15.9 Hz, 1 H), 4.38 ~ 4.28 (m, 2 H), 3.60 ~ 3.40 (m, 2 H), 2.03 (s, 3 H), 1.31 (t, *J* = 6.9 Hz, 3 H), 0.87 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 168.95, 167.04, 163.75, 157.28, 135.04, 134.14, 129.26, 128.88, 128.43, 127.83, 127.24, 115.48, 94.51, 79.22, 63.11, 62.30, 54.28, 54.23, 34.47, 24.32, 13.87, 13.25 ppm. IR (neat): *v* (cm^{-1}) 3461, 2928, 2210, 1757, 1741, 1678, 1625, 1379, 1362, 1236, 1058, 1008, 737, 697. HRMS calcd for $C_{26}H_{26}N_2O_5$: 446.1842, found: 446.1863. MS (70 eV): m/z (%): 404 (M^++H^+-[CH_3CO^+]), 21.40), 43 (100).

21. Diethyl 1-acetyl-5-benzyl-4-formyl-3-phenyl-1*H*-pyrrole-2,2(3*H*)-dicarboxyl -ate.

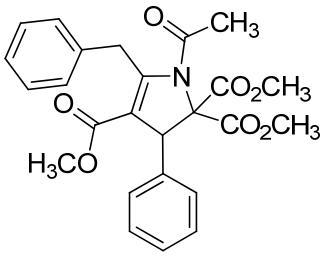


3u

According to the procedure of synthesis of **3i**, the reaction of **2a** (163.0 mg, 0.75 mmol) and **1u** (*E*, 116.0 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2

mg, 0.10 mmol) at 40 °C for 10 h affords **3u** in the yield of 55% (123.0 mg). Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.89 (s, 1 H), 7.39 ~ 7.26 (m, 10 H), 4.92 (s, 1 H), 4.66 (d, *J* = 16.2 Hz, 1 H), 4.61 (d, *J* = 16.2 Hz, 1 H), 4.37 ~ 4.20 (m, 2 H), 3.60 ~ 3.39 (m, 2 H), 2.05 (s, 3 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 0.88 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 185.05, 170.01, 167.29, 164.26, 157.87, 136.01, 135.71, 128.75, 127.94, 127.88, 127.03, 122.24, 79.22, 62.87, 62.10, 53.29, 31.44, 24.86, 13.74, 13.18 ppm. IR (neat): *v* (cm^{-1}) 2919, 2850, 1743, 1684, 1652, 1613, 1454, 1261, 1208, 1055, 1015, 803, 739, 698. HRMS calcd for $C_{26}H_{27}NO_6$: 449.1838, found: 449.1845. MS (70 eV): m/z (%): 449 (M^+, 5.06), 91 (100).

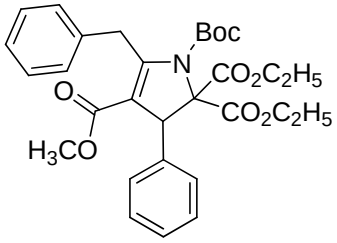
22. Trimethyl 1-acetyl-5-benzyl-3-phenyl-1*H*-pyrrole-2,2,4(3*H*)-tricarboxylate.



3v

The reaction of **1a** (*E*/*Z* = 1.1/1, 131.0 mg, 0.5 mmol) and **2b** (141.8 mg, 0.75 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 10 h affords **3v** in the yield of 93% (210.0 mg). White solid, m.p.: 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 ~ 7.20 (m, 10 H), 4.94 (d, *J* = 16.0 Hz, 1 H), 4.82 (s, 1 H), 4.67 (d, *J* = 16.0 Hz, 1 H), 3.83 (s, 3 H), 3.48 (s, 3 H), 3.05 (s, 3 H), 2.11 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.54, 168.11, 164.78, 164.65, 153.38, 137.26, 136.41, 128.60, 127.93, 127.80, 127.76, 126.53, 112.70, 78.62, 54.17, 53.38, 52.09, 51.23, 32.18, 24.54 ppm. IR (neat): *v* (cm^{-1}) 2950, 2889, 1741, 1703, 1672, 1631, 1438, 1391, 1242, 1207, 1067, 986, 740, 721, 671. HRMS calcd for $C_{25}H_{25}NO_7$: 451.1631, found: 451.1635. MS (70 eV): m/z (%): 451 (M^+, 0.80), 43 (100).

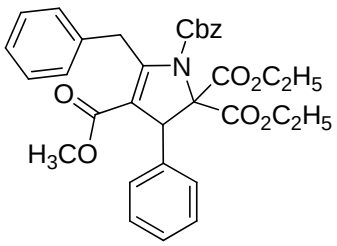
23. 1-*tert*-Butyl 2,2-diethyl 4-methyl 5-benzyl-3-phenyl-1*H*-pyrrole-1,2,2,4(3*H*)-te -tracarboxylate.



3w

The reaction of **1a** (*E*/*Z* = 1.1/1, 131.0 mg, 0.5 mmol) and **2c** (156.0 mg, 0.75 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 ^{o}C for 3.5 h affords **3w** in the yield of 80% (215.0 mg). White solid, m.p.: 87~88 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.2 Hz, 2 H), 7.34 ~ 7.18 (m, 8 H), 4.93 (d, *J* = 14.7 Hz, 1 H), 4.79 (s, 1 H), 4.78 (d, *J* = 14.7 Hz, 1 H), 4.38 ~ 4.23 (m, 2 H), 3.60 ~ 3.54 (m, 1 H) 3.48 (s, 3 H), 3.35 ~ 3.29 (m, 1 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.26 (s, 9 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 168.18, 165.11, 164.71, 155.66, 150.40, 138.10, 137.88, 128.29, 128.07, 127.85, 127.55, 125.99, 109.02, 83.11, 77.89, 62.37, 61.49, 54.66, 51.04, 31.98, 27.55, 13.98, 13.35 ppm. IR (neat): *v* (cm^{-1}) 2979, 1754, 1727, 1702, 1625, 1368, 1226, 1153, 1009, 731, 705. HRMS calcd for $C_{30}H_{35}NO_8$: 537.2363, found: 537.2358. MS (70 eV): m/z (%): 537 (M^+, 1.82), 57 (100).

24. 1-Benzyl 2,2-diethyl 4-methyl 5-benzyl-3-phenyl-1*H*-pyrrole-1,2,2,4(3*H*)-tetra -carboxylate.

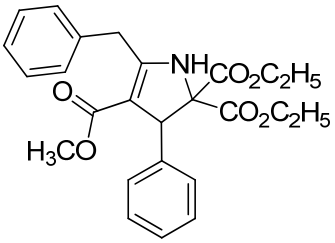


3x

The reaction of **1a** (*E*/*Z* = 1.1/1, 78.6 mg, 0.3 mmol) and **2d** (139.0 mg, 0.45 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 ^{o}C for 11 h

affords **3x** in the yield of 93% (159.0 mg). Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 ~ 7.18 (m, 13 H), 7.11 ~ 7.08 (m, 2 H), 5.00 (s, 2 H), 4.90 (d, *J* = 14.4 Hz, 1 H), 4.85 (s, 1 H), 4.78 (d, *J* = 14.4 Hz, 1 H), 4.27 ~ 4.15 (m, 2 H), 3.49 (s, 3 H), 3.34 ~ 3.25 (m, 1 H), 3.20 ~ 3.10 (m, 1 H), 1.17 (t, *J* = 7.2 Hz, 3 H), 0.68 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 168.00, 164.92, 164.30, 155.11, 151.66, 137.67, 137.42, 134.81, 128.27, 128.22, 127.89, 127.67, 126.08, 110.14, 77.85, 77.20, 67.99, 62.57, 61.59, 54.95, 51.19, 32.10, 13.77, 13.16 ppm. IR (neat): *v* (cm^{-1}) 2986, 2901, 1737, 1702, 1631, 1393, 1226, 1056, 1018, 740, 697. HRMS calcd for $C_{33}H_{33}NO_8$: 571.2206, found: 571.2205. MS (70 eV): m/z (%): 571 (M^+, 1.28), 91 (100).

25. 2,2-Diethyl 4-methyl 5-benzyl-3-phenyl-1*H*-pyrrole-2,2,4(3*H*)-tricarboxylate.



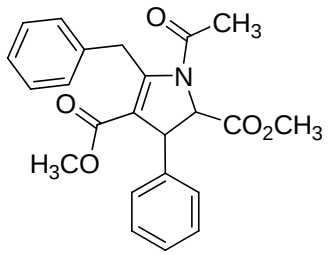
3y

The reaction of **1a** (*E*/*Z* = 1.1/1, 52.4 mg, 0.2 mmol), **2e** (50.8 mg, 0.24 mmol) and DBU (42.6 mg, 0.28 mmol) in DMF at 40 °C for 2 h affords **3y** in the yield of 87% (76.0 mg). White solid, m.p.: 97-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 ~ 7.16 (m, 10 H), 5.05 (s, 1 H), 4.85 (s, 1 H), 4.43 (d, *J* = 15.2 Hz, 1 H), 4.17 ~ 4.04 (m, 2 H), 4.00 (d, *J* = 15.2 Hz, 1 H), 3.71 ~ 3.64 (m, 1 H), 3.56 ~ 3.48 (m, 1 H), 3.51 (s, 3 H), 1.09 (t, *J* = 7.2 Hz, 3 H), 0.77 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 168.57, 167.14, 165.82, 159.23, 138.95, 136.38, 128.80, 128.75, 128.53, 127.83, 127.16, 126.97, 102.93, 76.92, 62.36, 61.80, 53.42, 50.44, 33.39, 13.72, 13.27. IR (neat): *v* (cm^{-1}) 3371, 2994, 2885, 2814, 1726, 1678, 1598, 1432, 1267, 1211, 1130, 1094, 1052, 776, 739, 702 ppm. HRMS calcd for $C_{25}H_{27}NO_6$: 437.1838, found: 437.1839. MS (70 eV): m/z (%): 437 (M^+, 44.80), 91 (100).

Synthesis of **3y** from 2-pyrroline **3w**: 2-Pyrroline **3w** (126.7 mg, 0.29 mmol) was dissolved in 4 mL of CH_2Cl_2 under 0 ^oC, CF_3CO_2H (1 mL, 14.5 mmol) was added and the mixture was stirred for 30 min, then was stirred for overnight. After the reaction was complete, 4 mL of H_2O was added and the aqueous phase was neutralized by 1 N NaOH. The reaction mixture was then extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic phase was washed successively with saturated $NaHCO_3$, NaCl and dried over anhydrous $MgSO_4$. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel to give 84% (106 mg) of **3y**.

The procedure for the synthesis of pyrrole 4

26. dimethyl 1-acetyl-5-benzyl-3-phenyl-2,3-dihydro-1*H*-pyrrole-2,4-dicarboxylat –e.

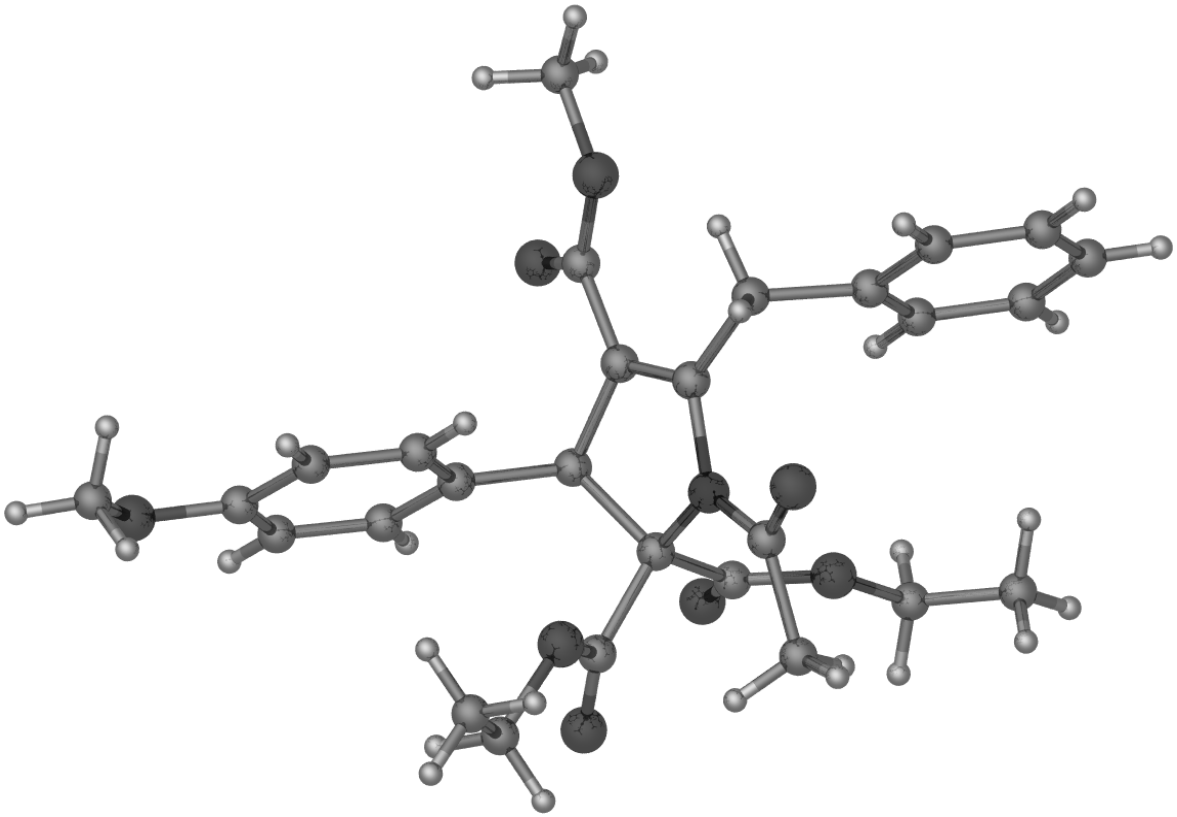


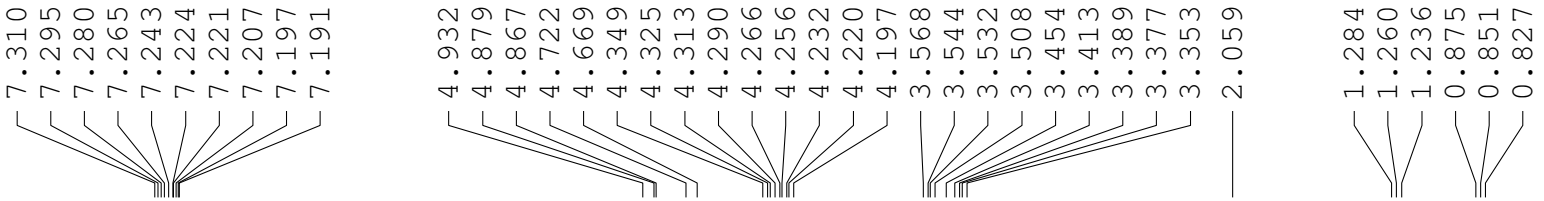
4

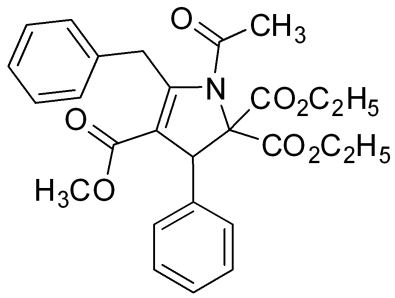
A mixture of **3v** (270.6 mg, 0.6 mmol), lithium chloride (32.5 mg, 0.75 mmol), and water (15.5 mg, 0.85 mmol) in 2.0 mL of anhydrous dimethylformamide under nitrogen was stirred at 160-165 ^oC,. The solution immediately became cloudy and began evolving CO_2. After stirring for 1h, the reaction mixture was cooling down and poured into 15 mL water with vigorous stirring. The gummy solid which formed was collected by filtration through glass wool, dissolved in dichloromethane, and dried with anhydrous $MgSO_4$. After the solution was concentrated under vacuum, the residual product was purified by column chromatography on silica gel to give white solid; yield: 54% (127.0 mg). m.p.: 134~135 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 ~ 7.20 (m, 10 H), 4.92 (d, J = 14.8 Hz, 1 H), 4.30 (d, J = 14.8 Hz, 1 H), 4.59 (bs, 1 H), 4.29 (s, 1 H), 3.76 (s, 3

H) 3.58 (s, 3 H), 2.00 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.63, 168.85, 165.24, 141.78, 137.15, 128.95, 128.51, 128.29, 127.59, 126.62, 126.32, 69.31, 52.87, 51.30, 49.90, 32.65, 24.29 ppm. IR (neat): ν (cm^{-1}) 2954, 2924, 2853, 1743, 1704, 1672, 1631, 1439, 1391, 1243, 1207, 1089, 986, 747, 721, 693. HRMS calcd for $C_{23}H_{23}NO_5$: 393.1576, found: 393.1578. MS (70 eV): m/z (%): 393 (M^+, 14.52), 91 (100).

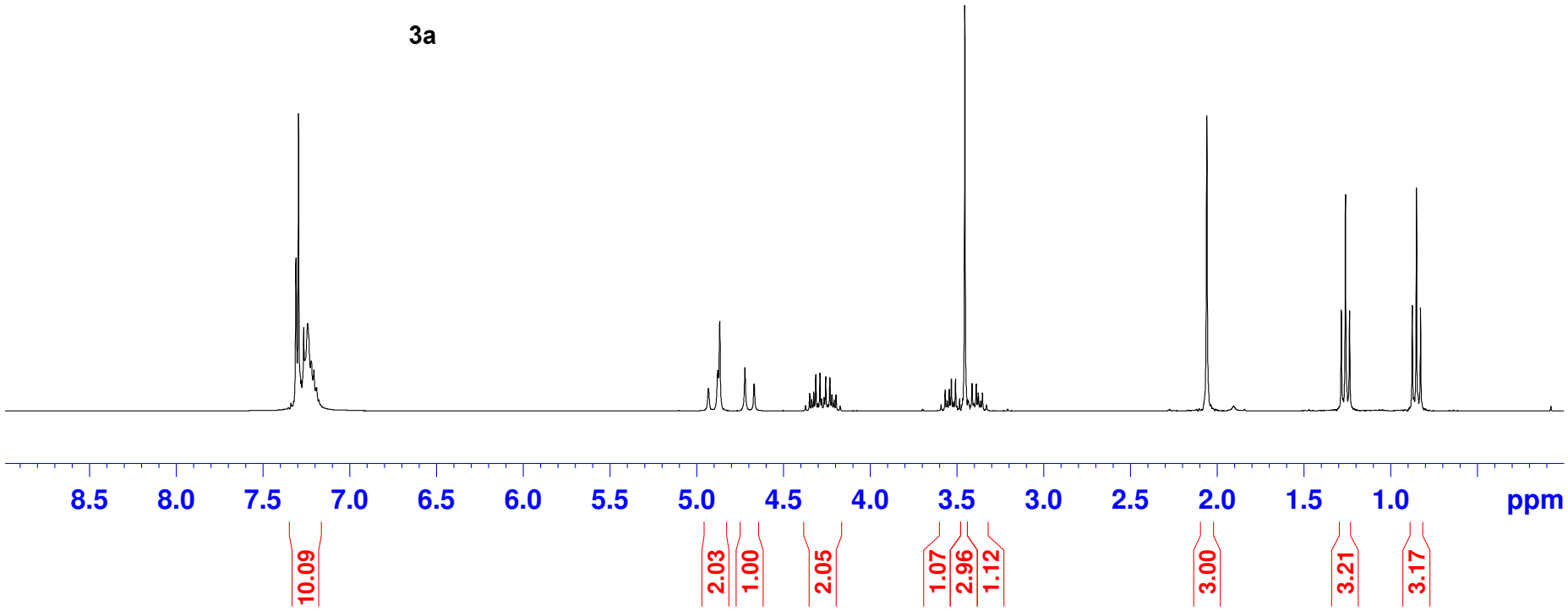
X-ray crystal structure of 3e.

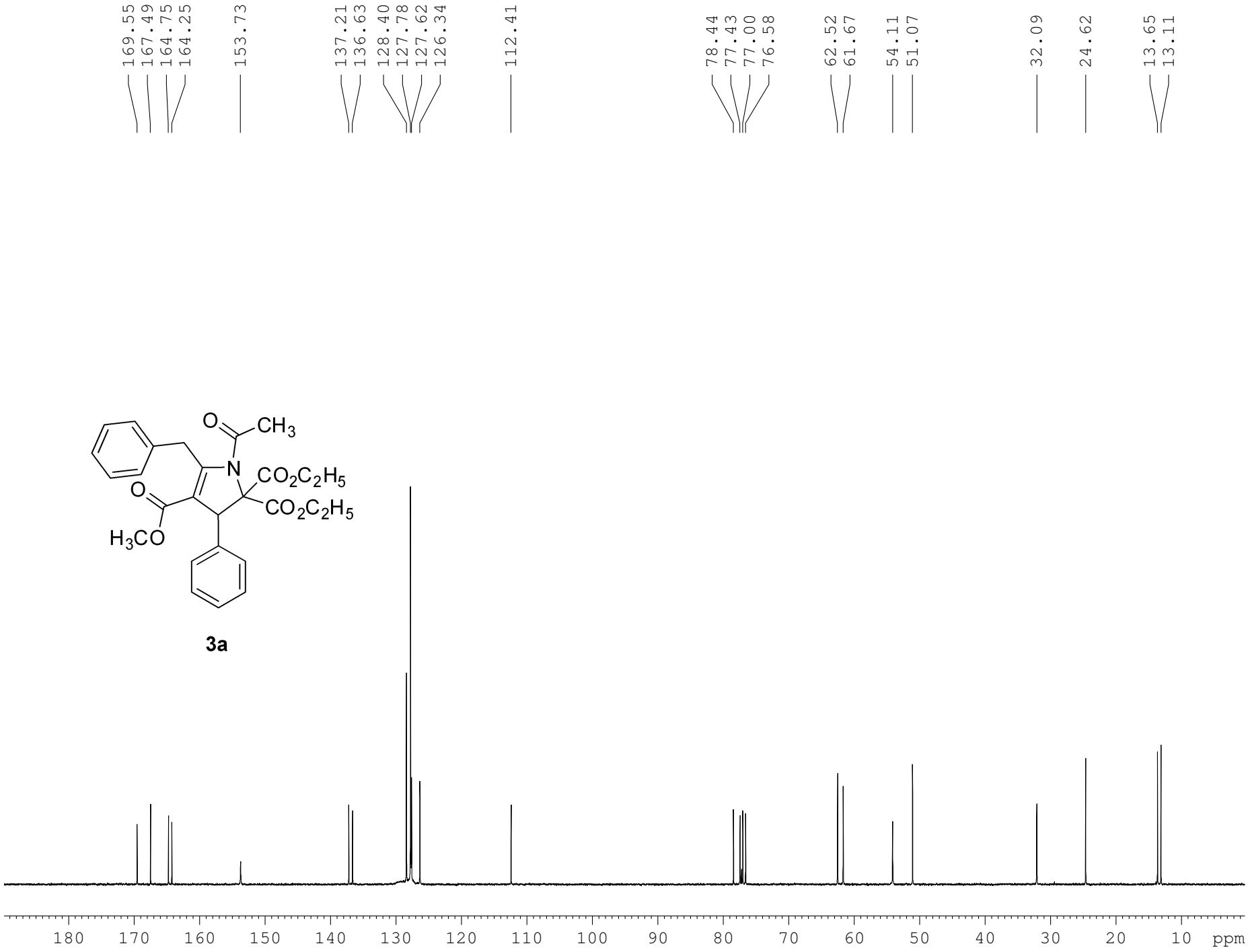


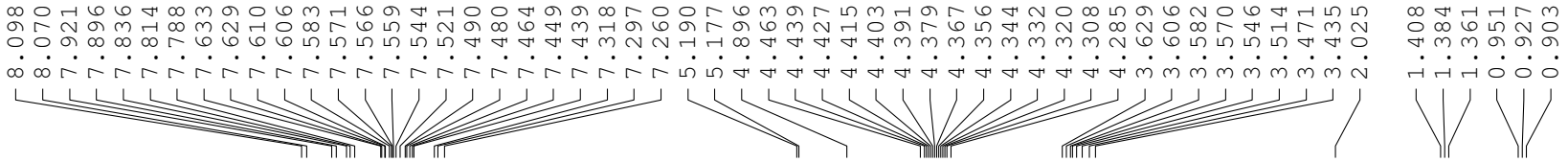


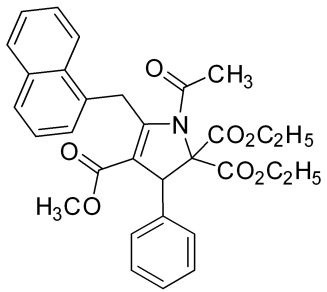


3a









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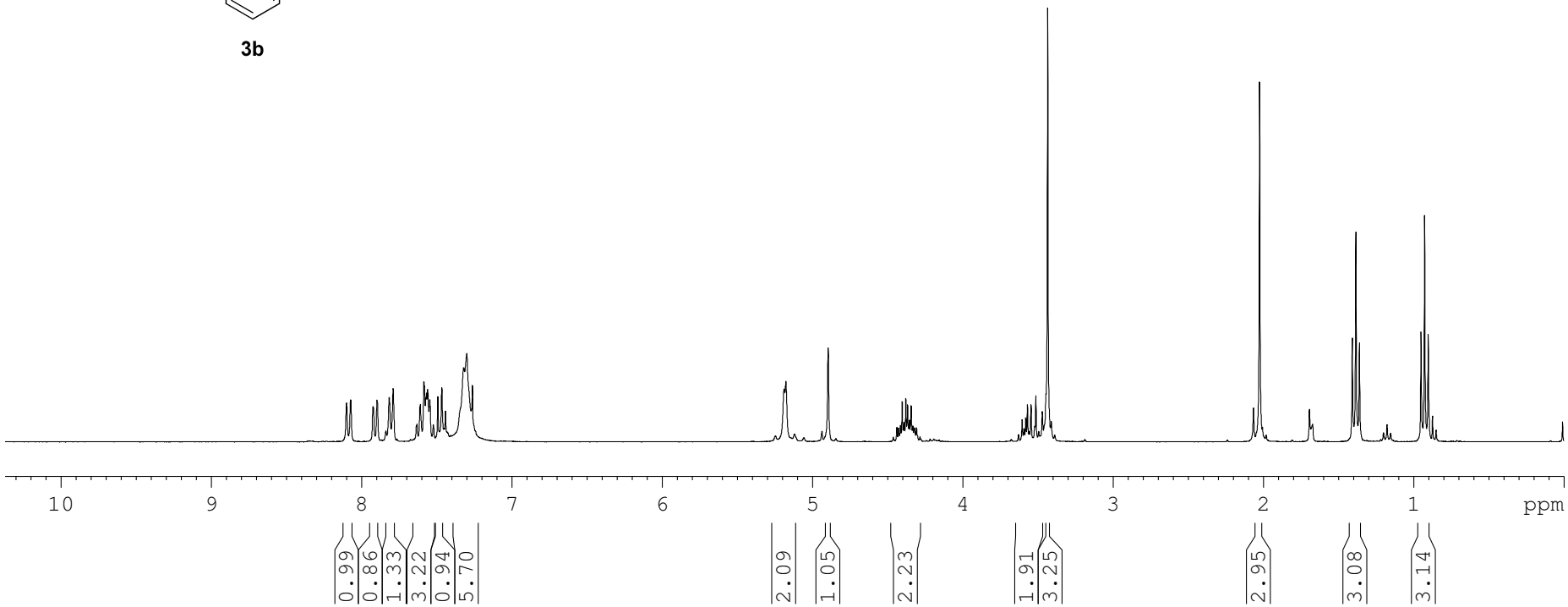

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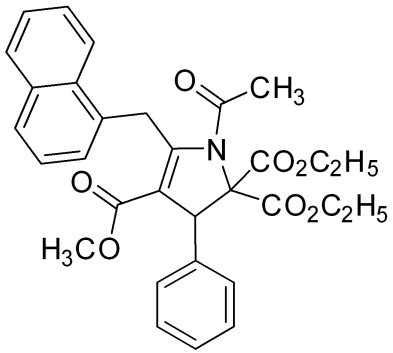

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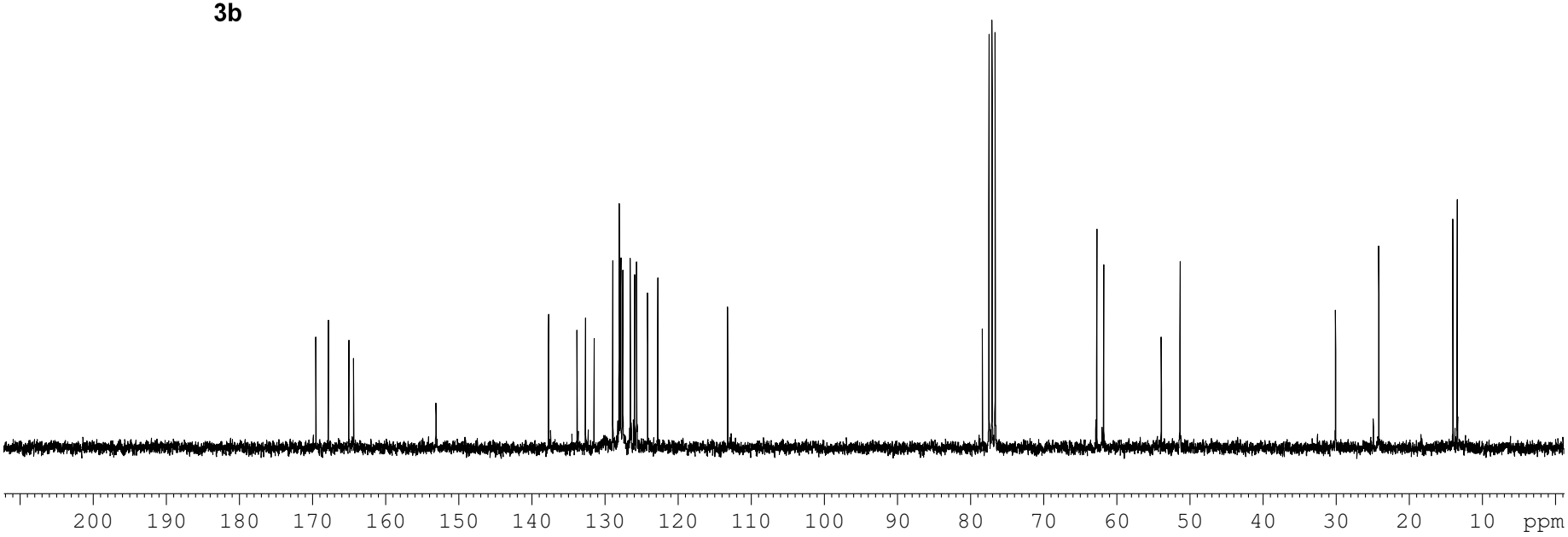

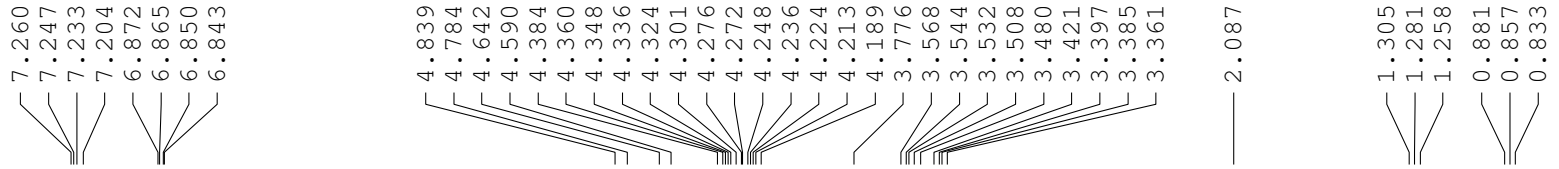

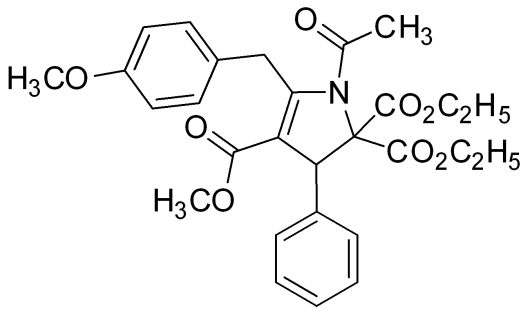

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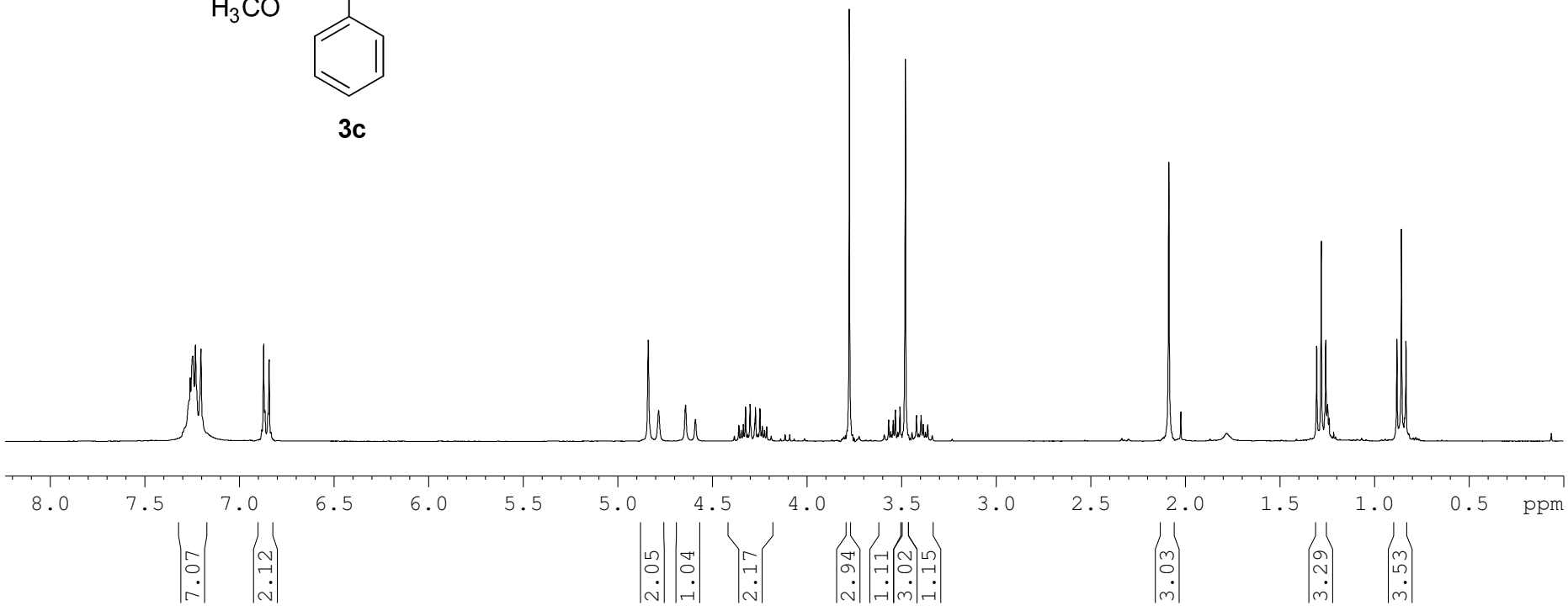

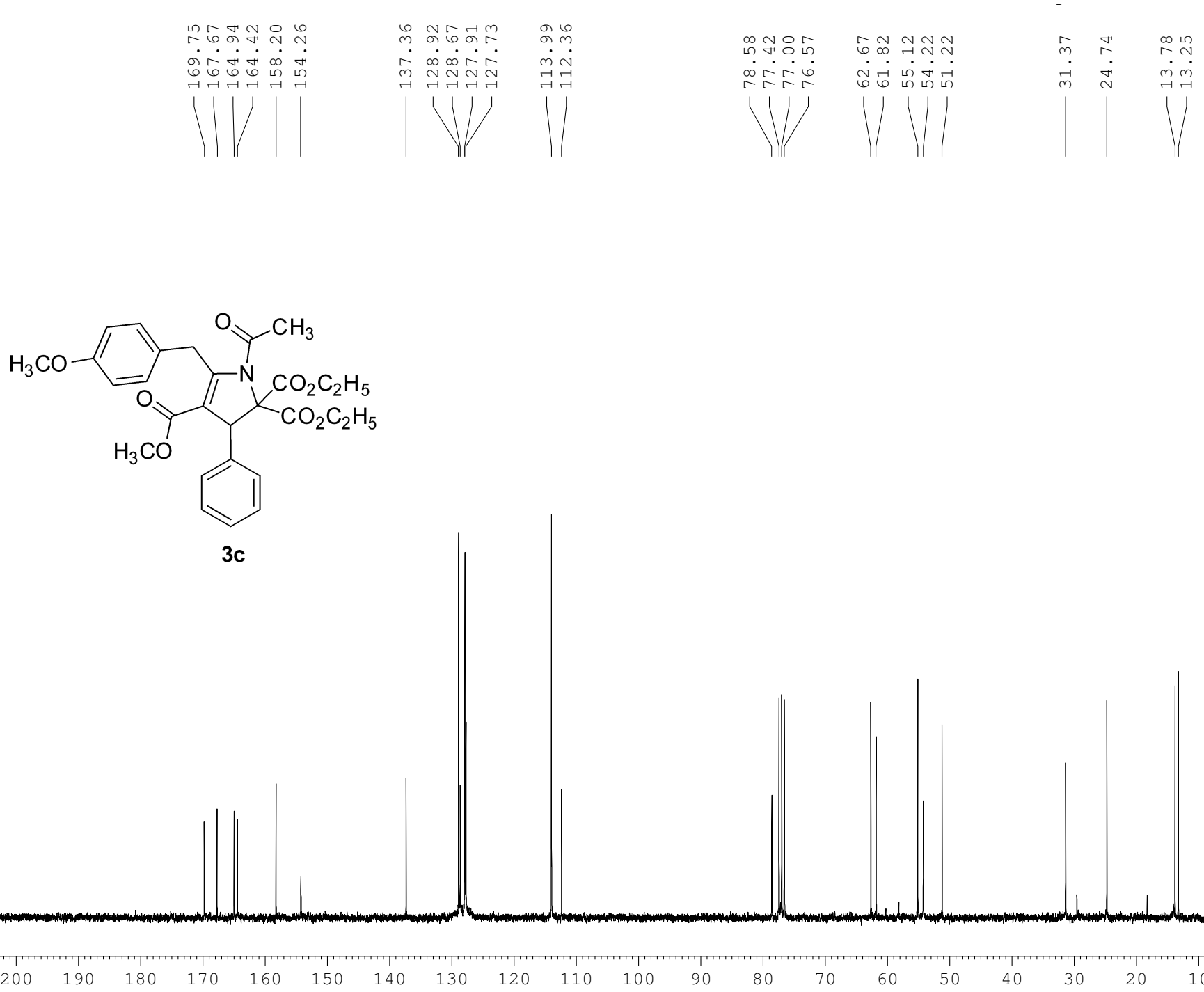

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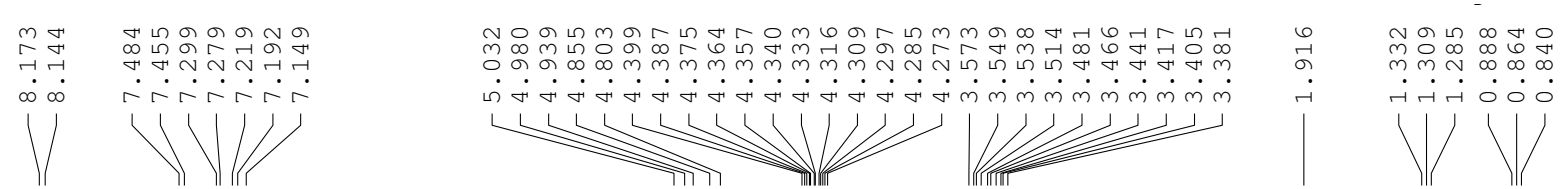

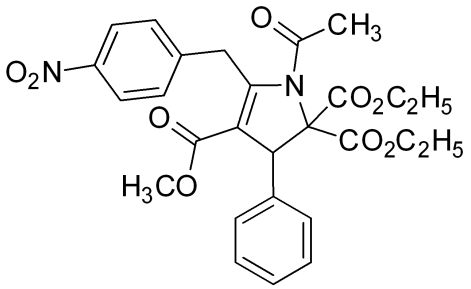

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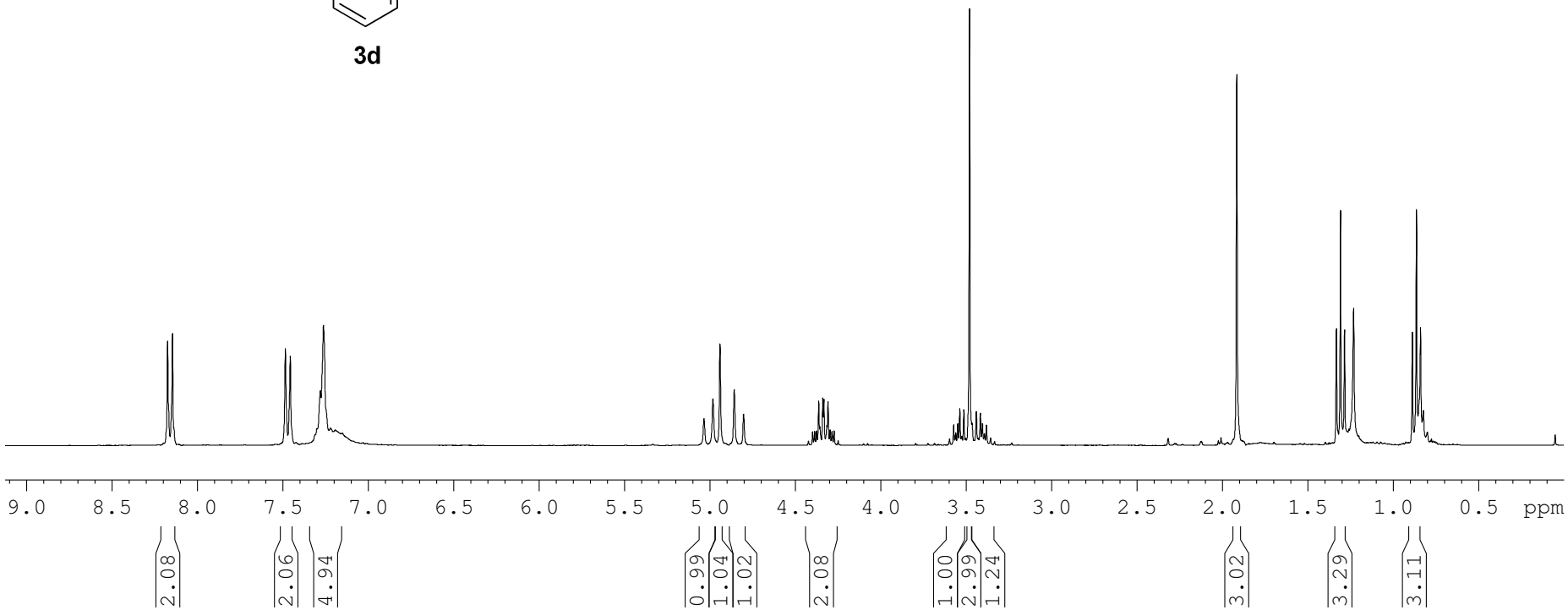

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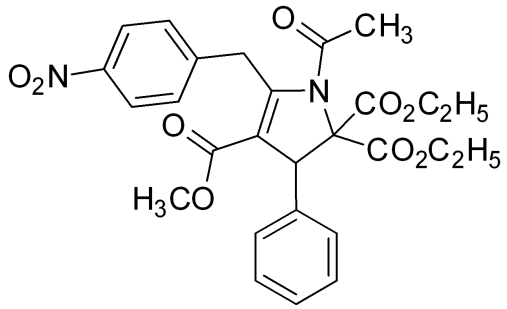

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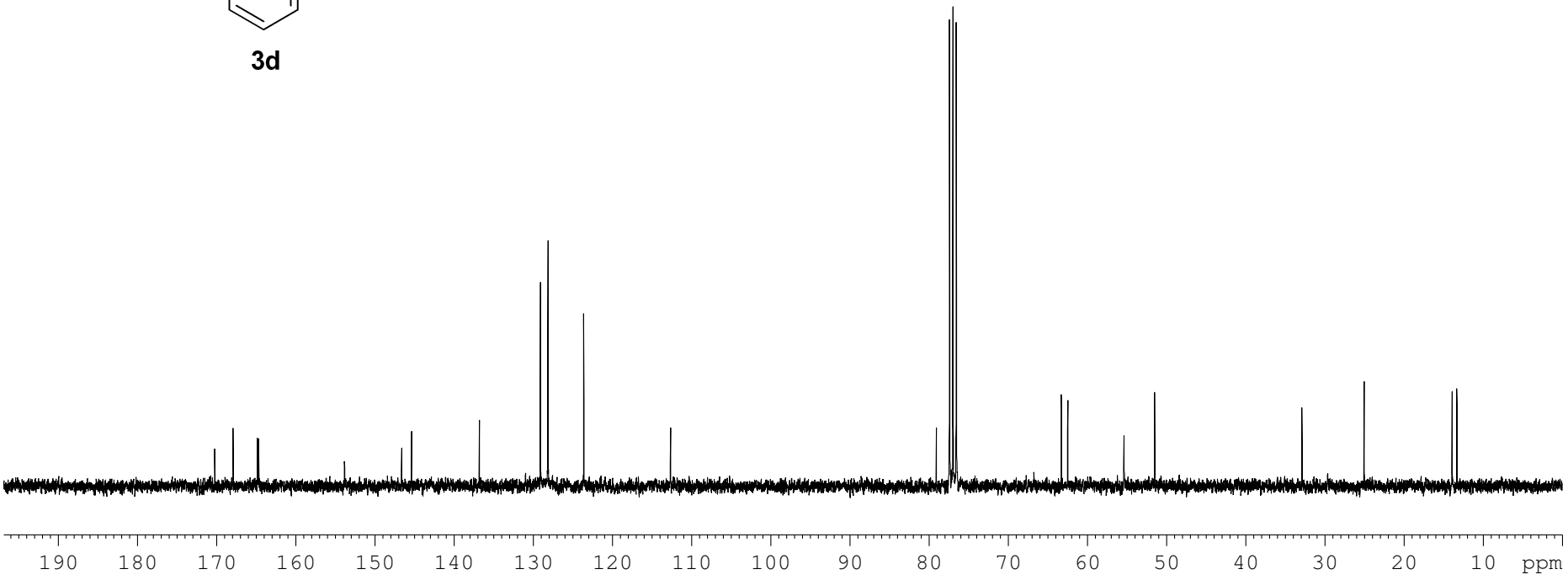

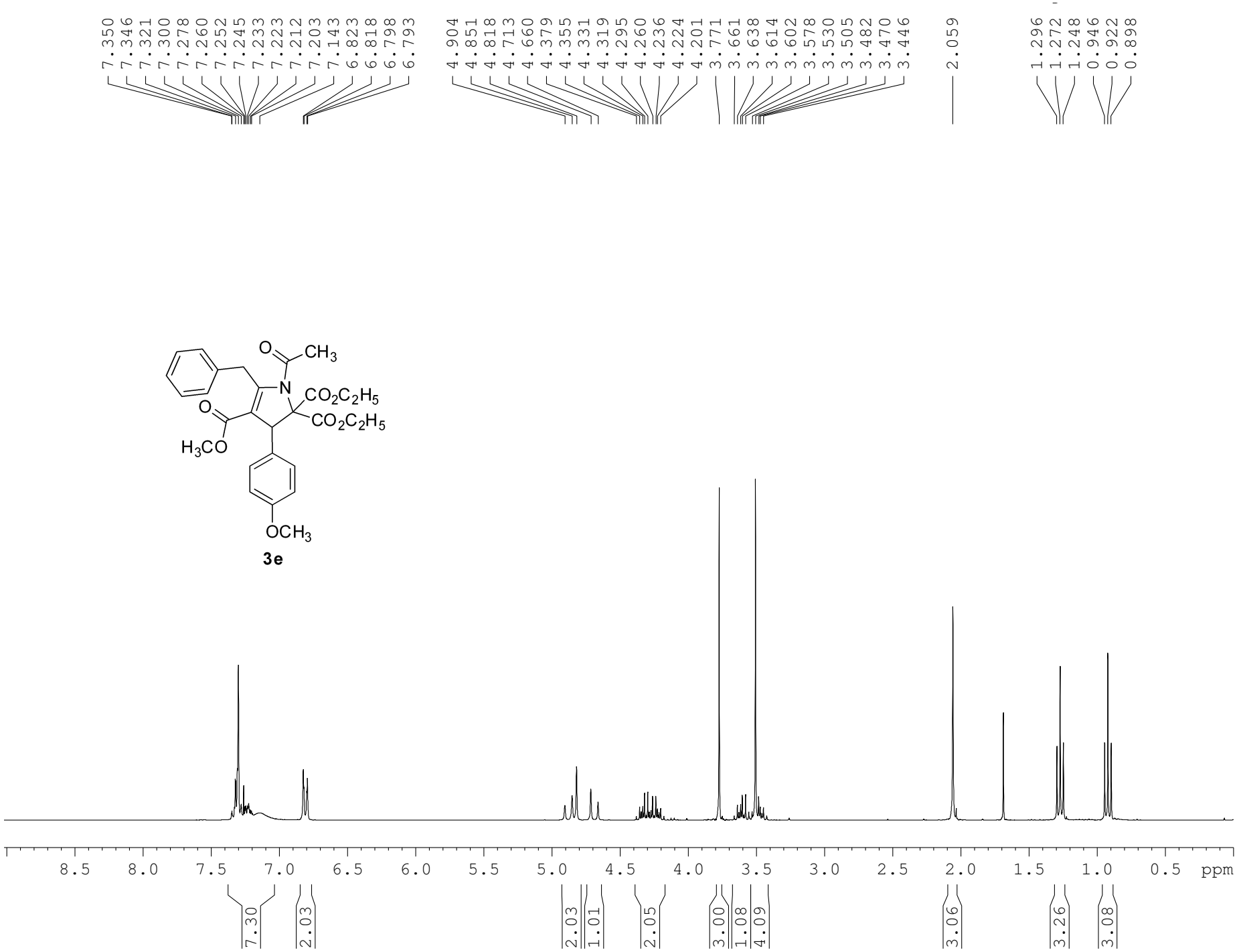

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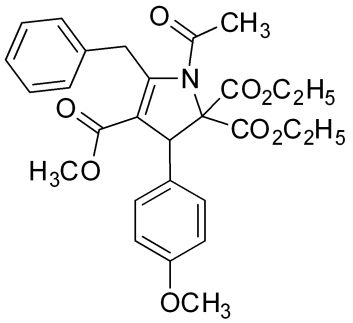

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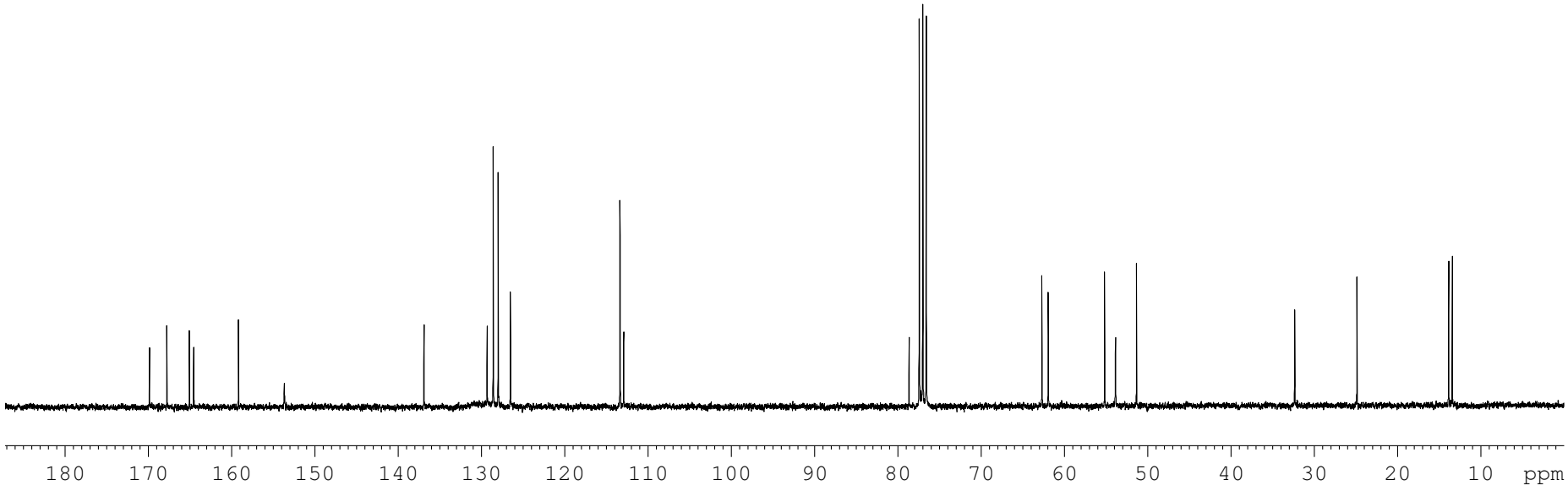

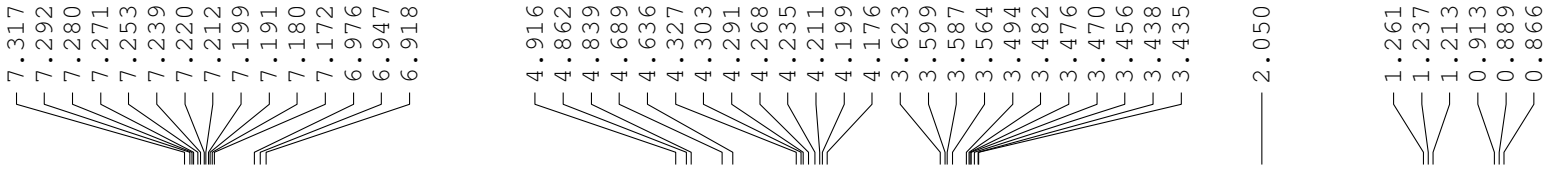

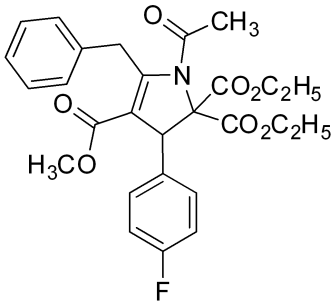

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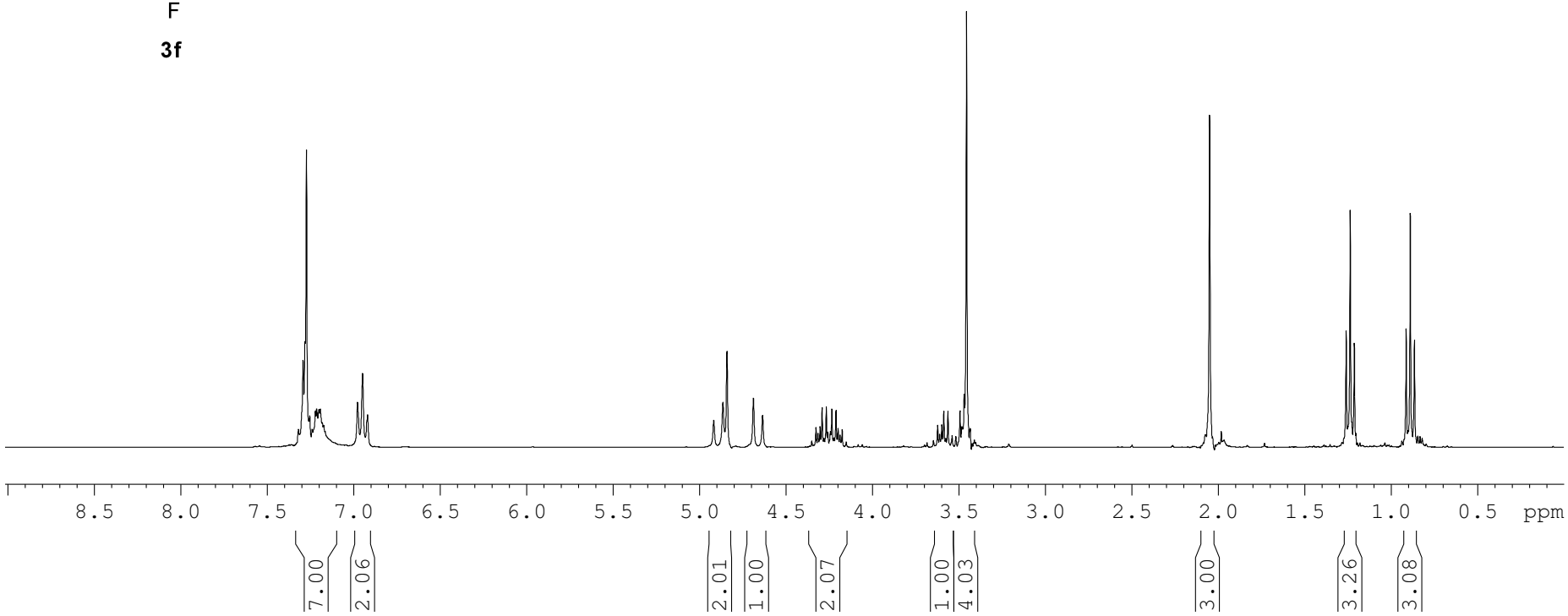

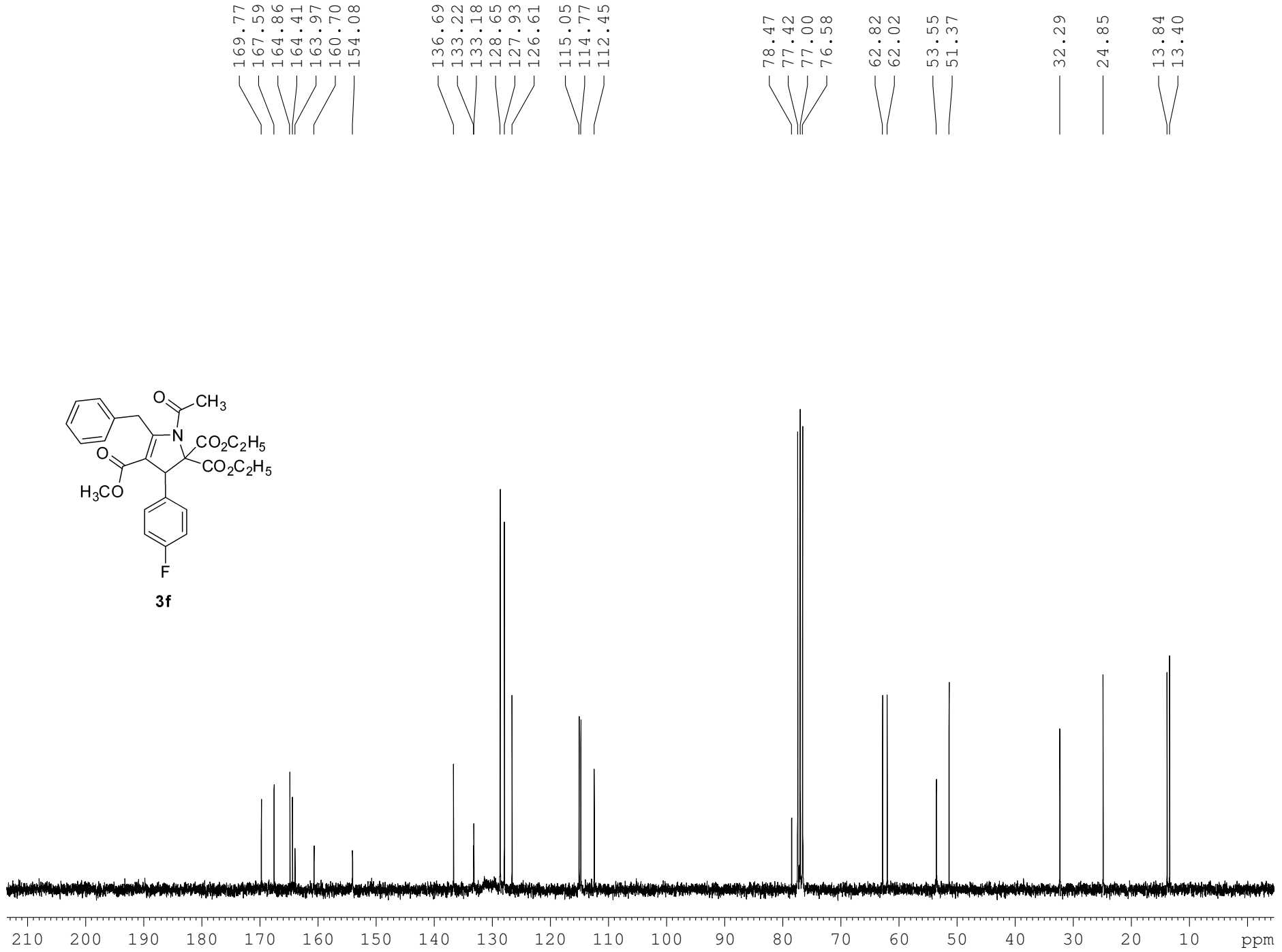

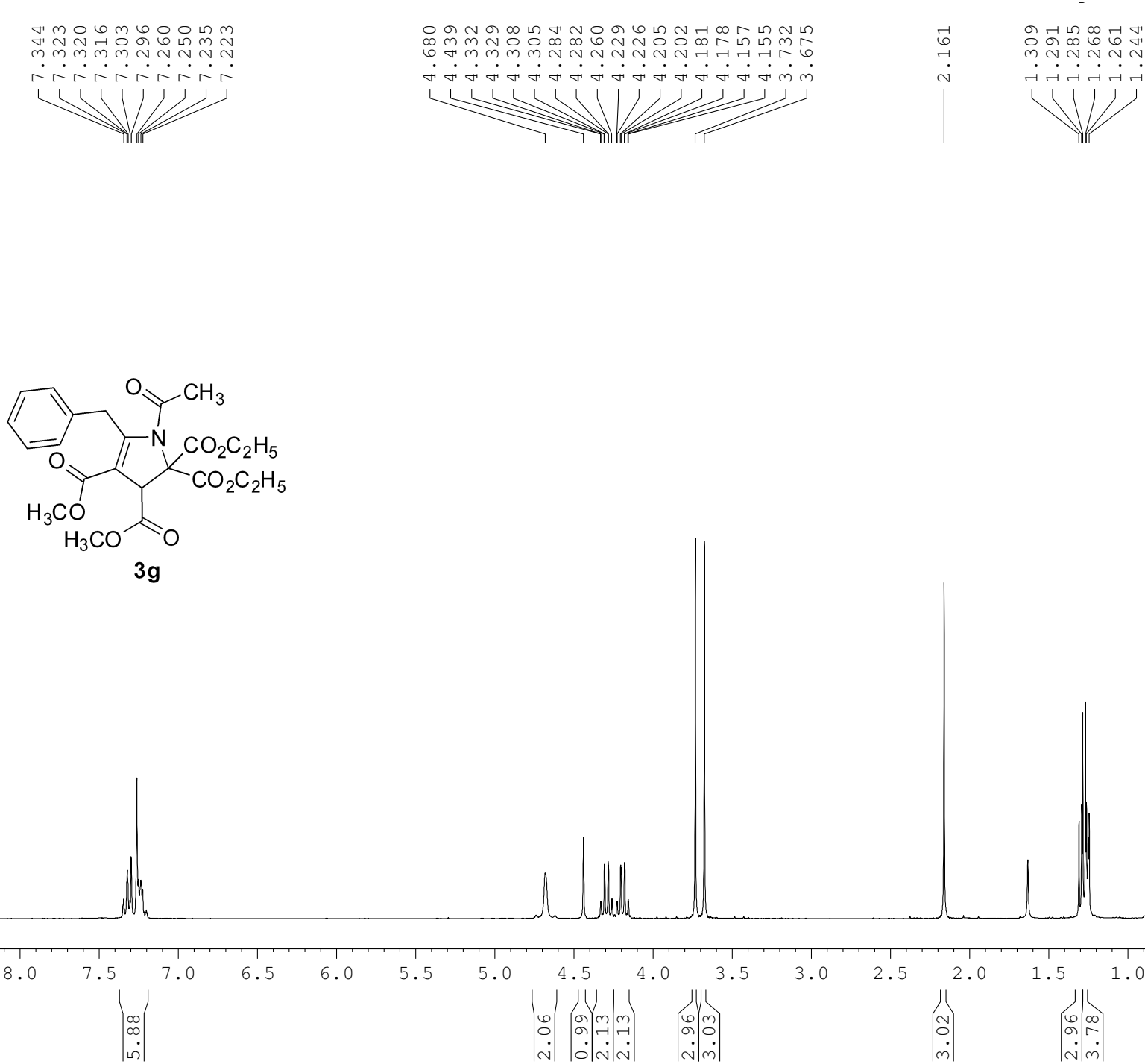

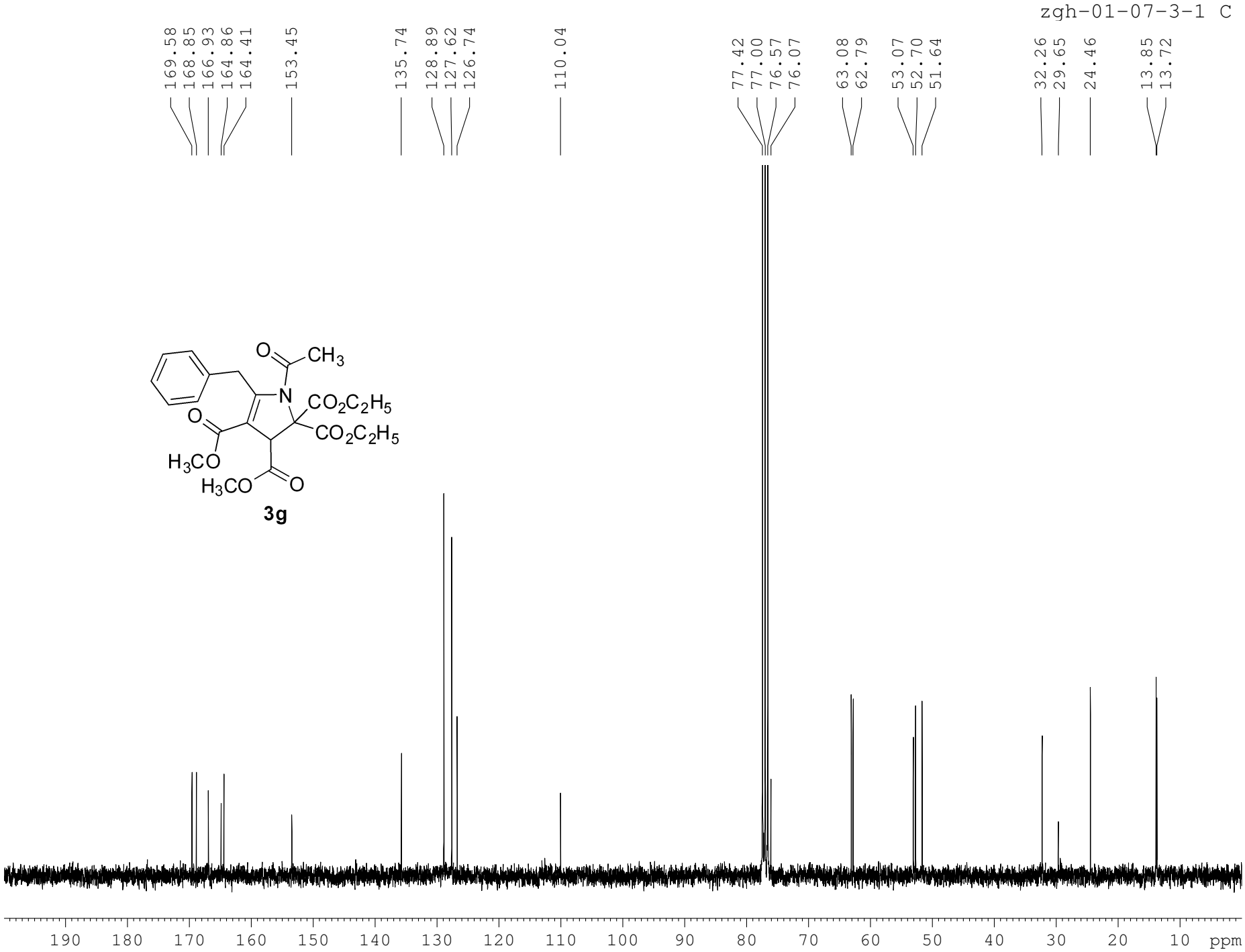

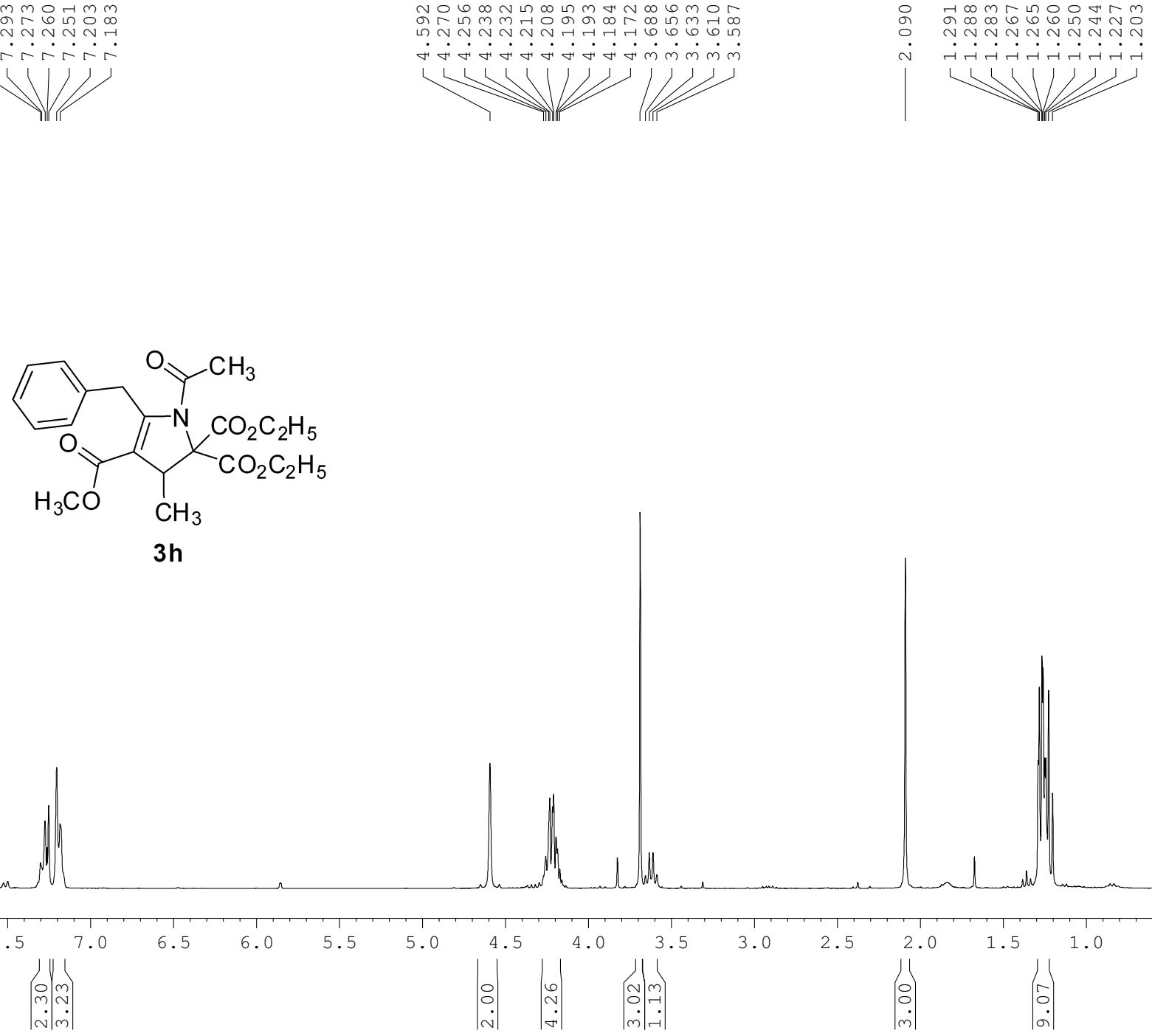

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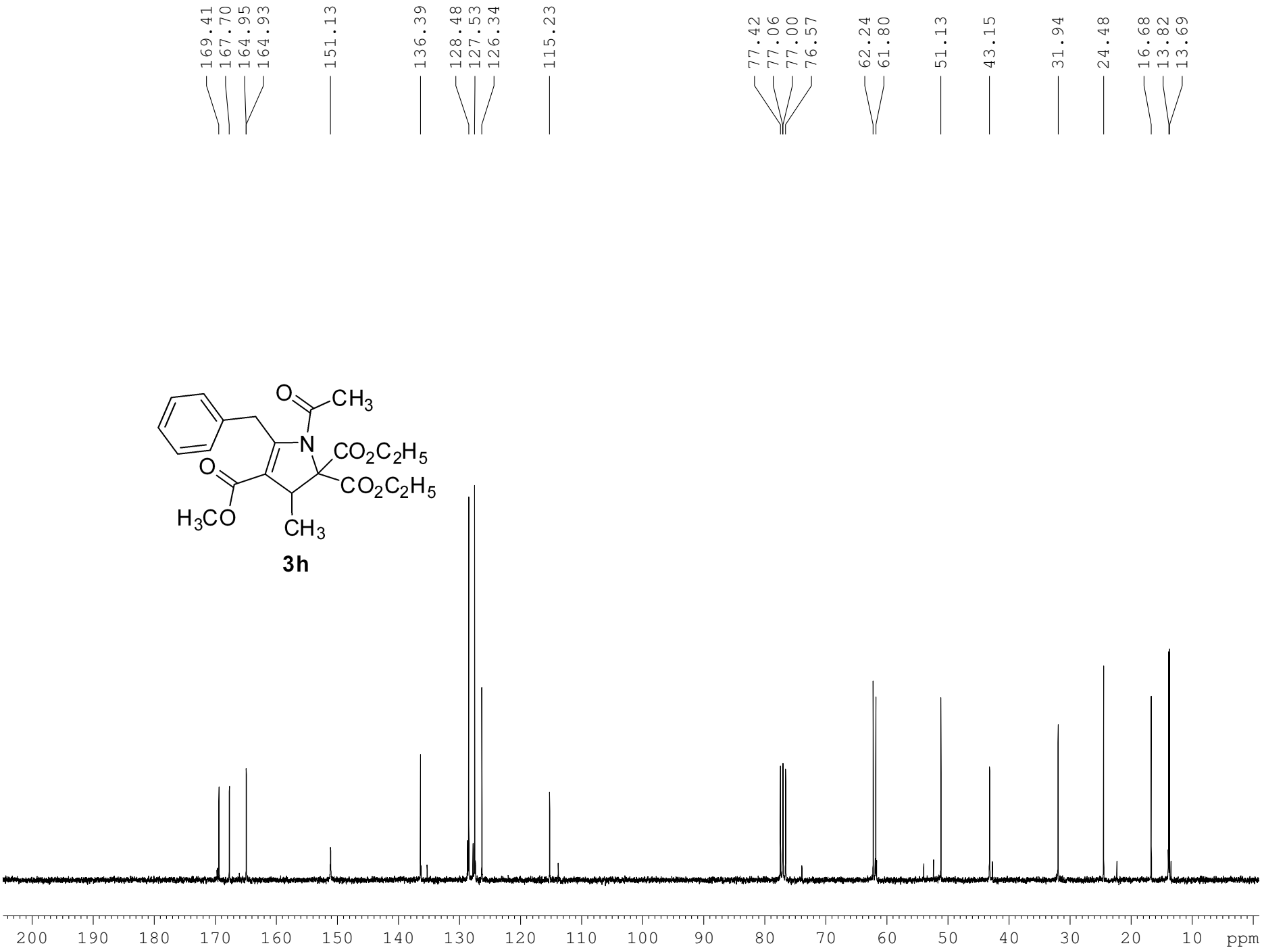

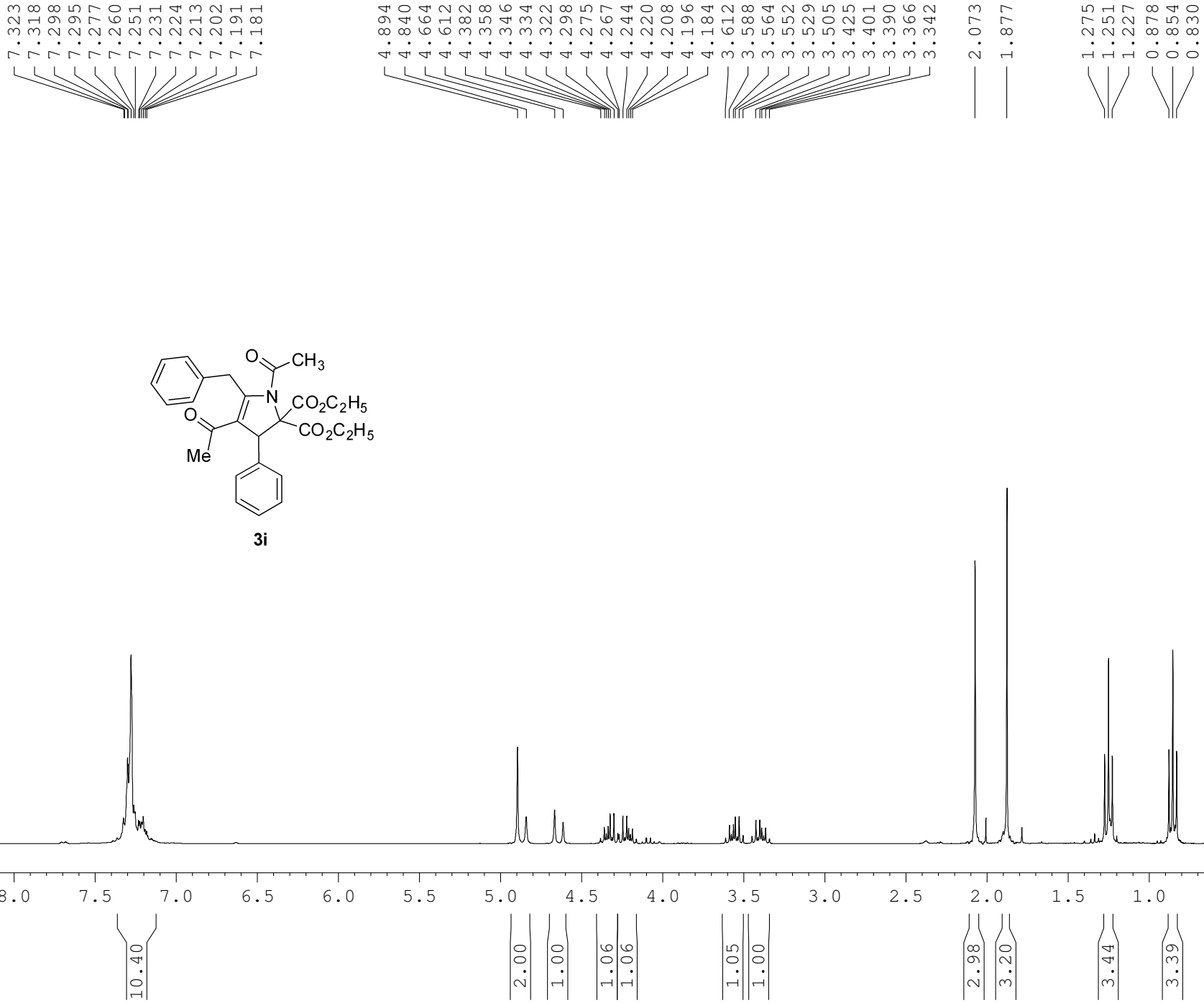

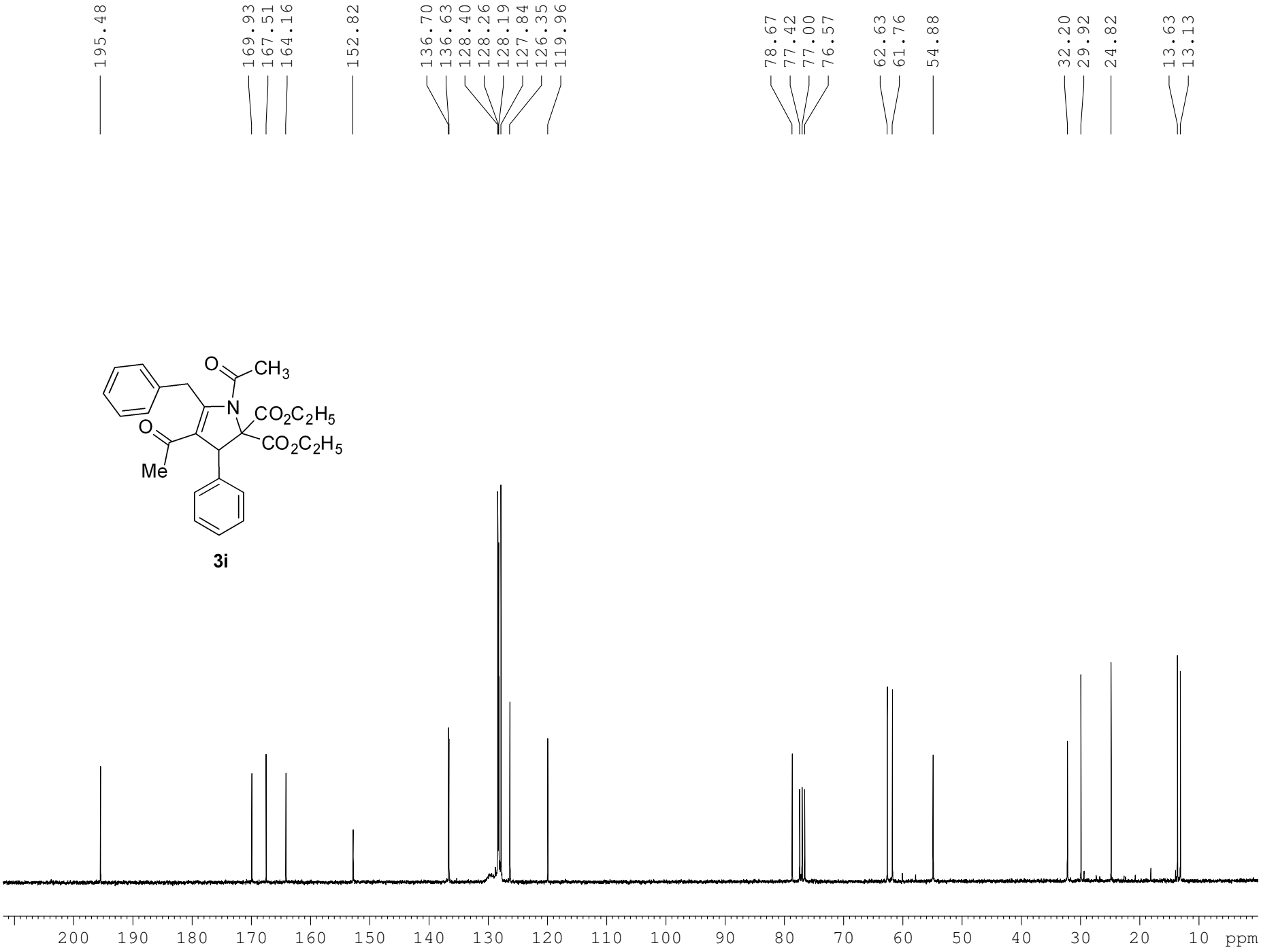

3i

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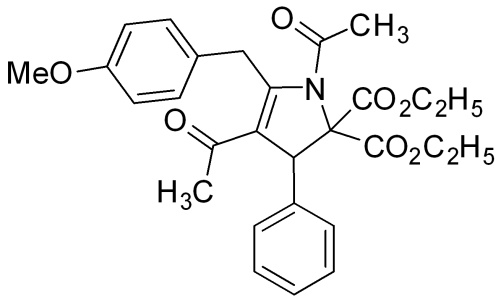
1.307 1.290 1.272 0.895 0.878 0.861



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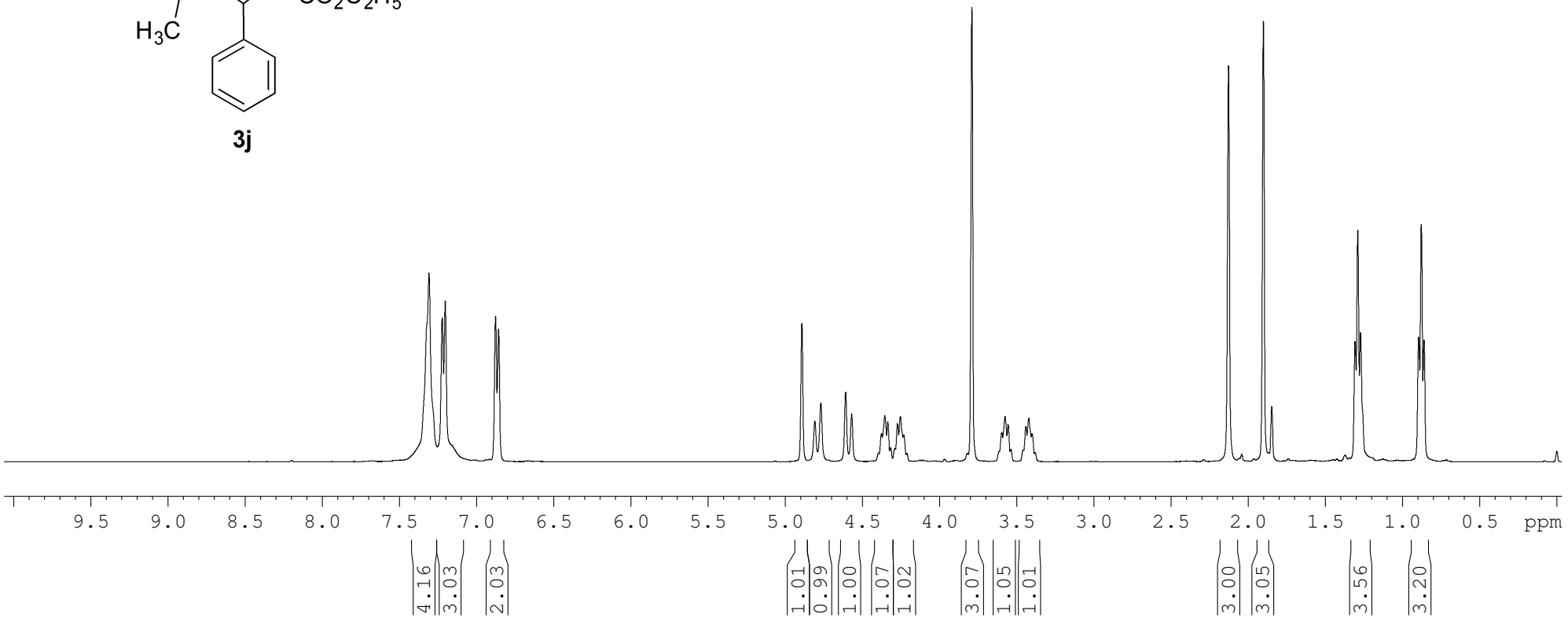

195.64
170.08
167.70
164.32
158.20
153.36
136.85
128.98
128.64
128.40
128.31
119.90
113.98
78.79
77.32
77.00
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61.90
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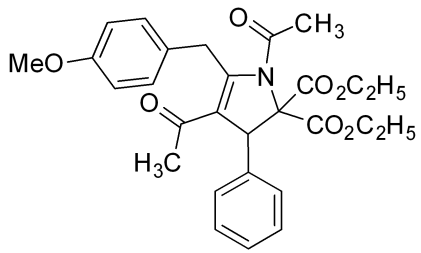
54.96
31.48
30.09
24.96
13.77
13.28

yxz-10-31 C



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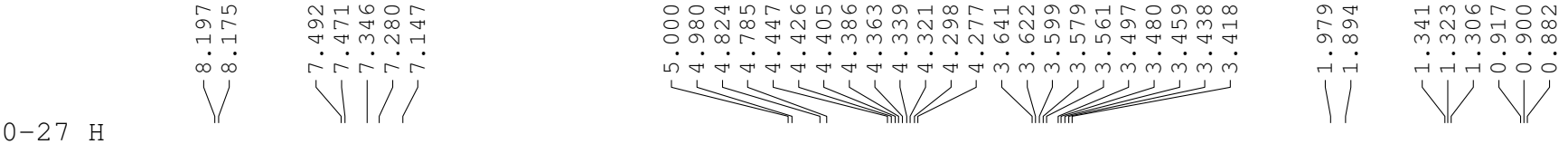
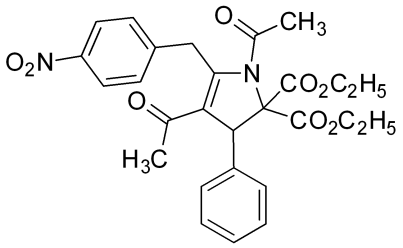
yxz-10-27 H





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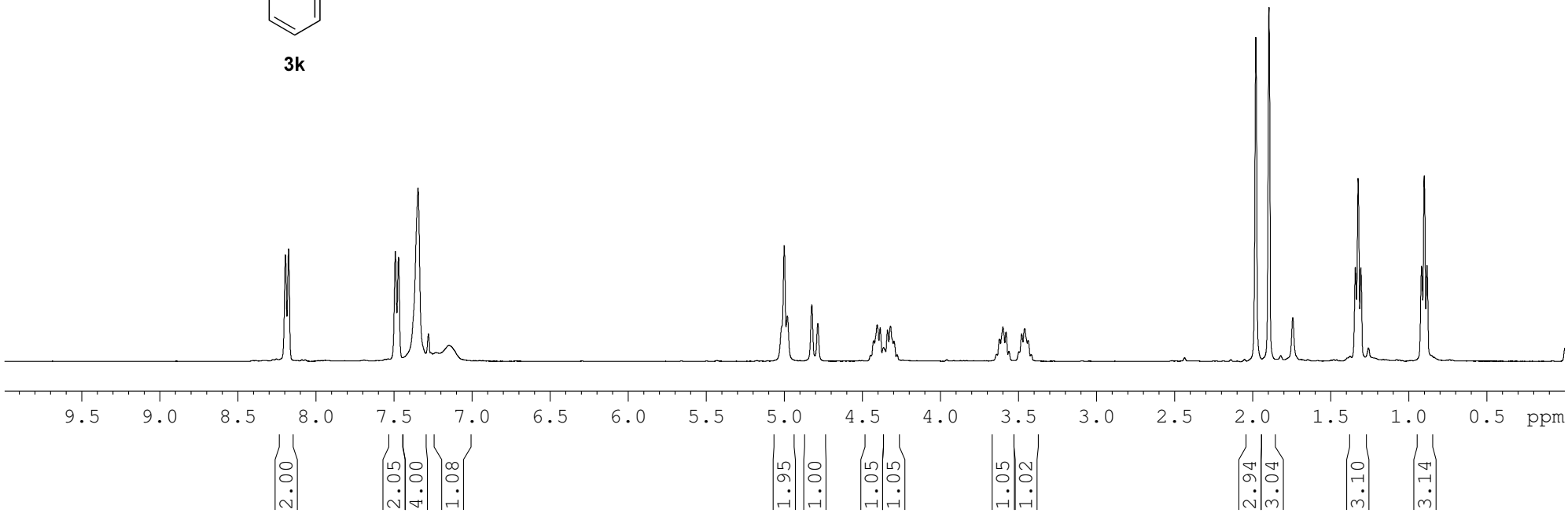

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164.45
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146.57
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136.22
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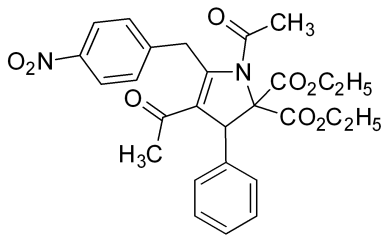
128.64
123.57
119.78
79.26
77.32
77.00
76.69
63.34
62.52
55.96
32.92
30.13
25.21
13.87
13.31

yxz-10-27 C



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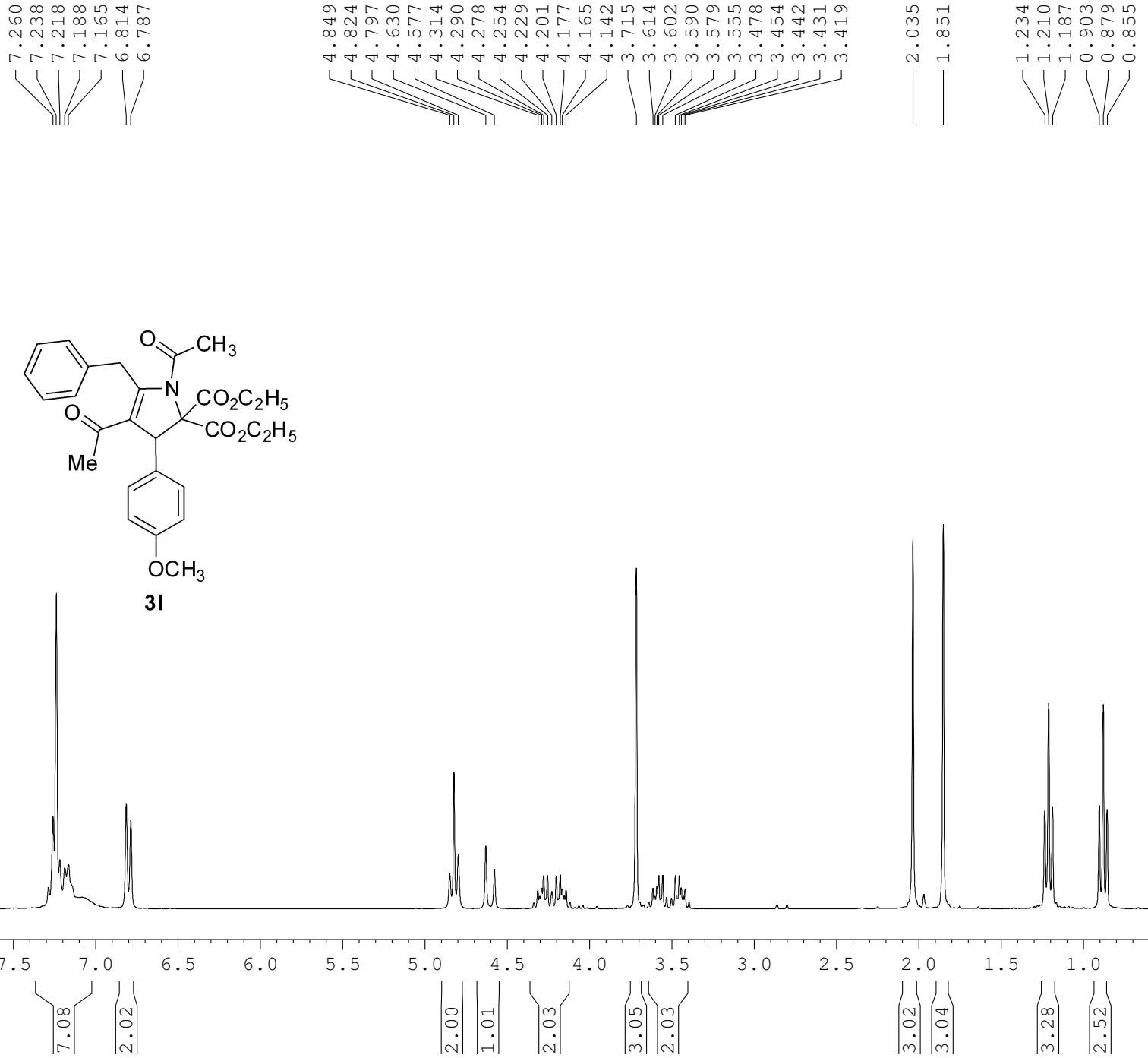

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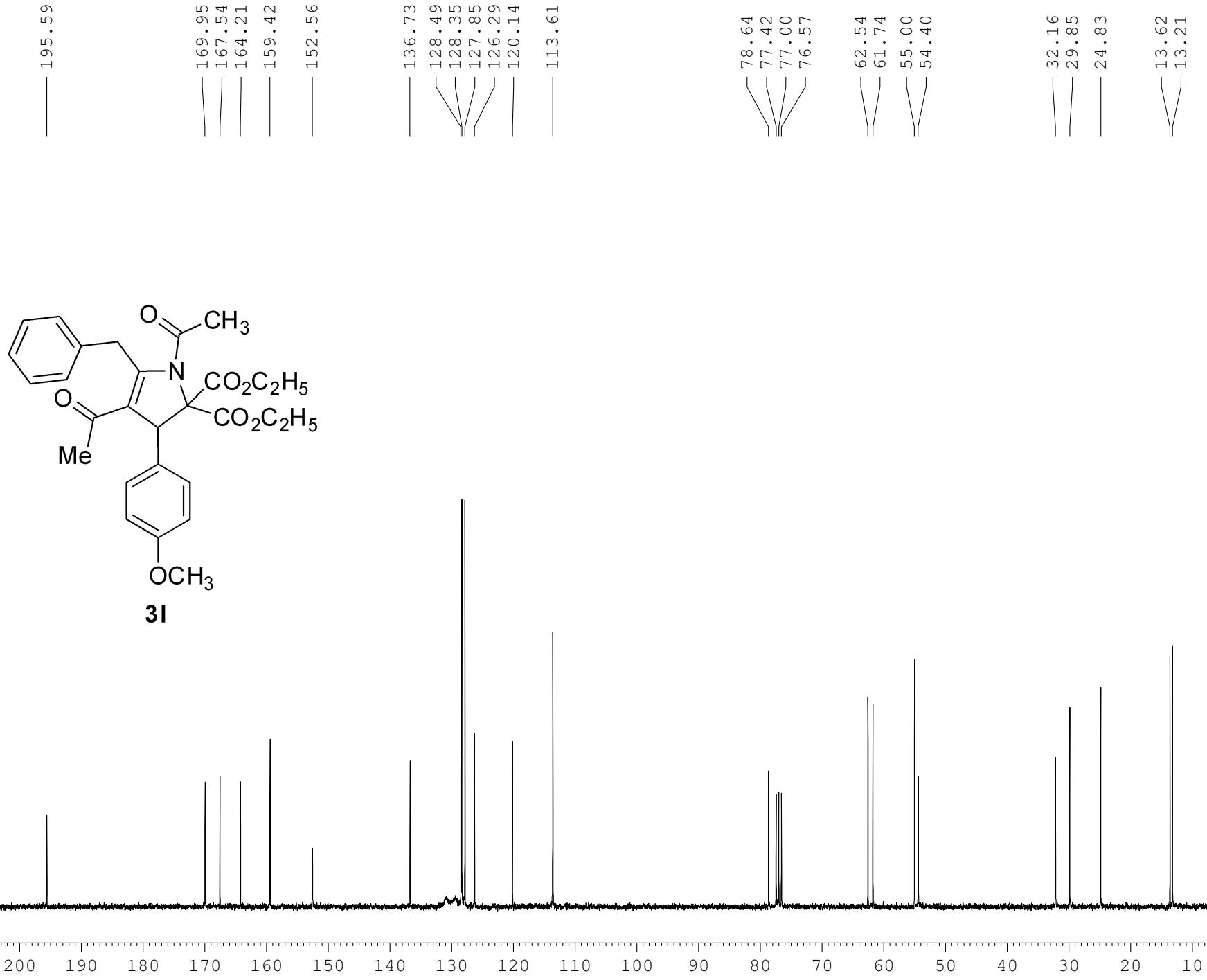


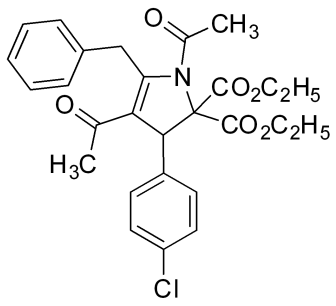
yxz-10-26 H

7.324 7.307 7.277 7.258 7.238 7.223 7.140

4.895 4.852 4.659 4.620 4.385 4.366 4.345 4.324 4.306 4.275 4.257 4.239 4.217 4.196 3.694 3.675 3.654 3.633 3.615 3.560 3.543 3.524 3.502 3.482

2.105 1.922

1.288 1.270 1.253 0.951 0.934 0.916



3m

195.17
169.98
167.42
164.13
153.19
136.48
135.41
134.26
128.55
127.87
126.56
119.78
78.56
77.32
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76.68
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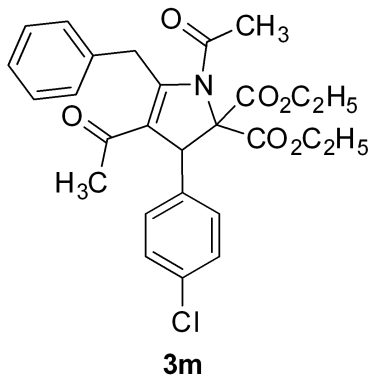
62.04
54.19
32.30
30.04
24.93
13.72
13.29

yxz-10-26 C



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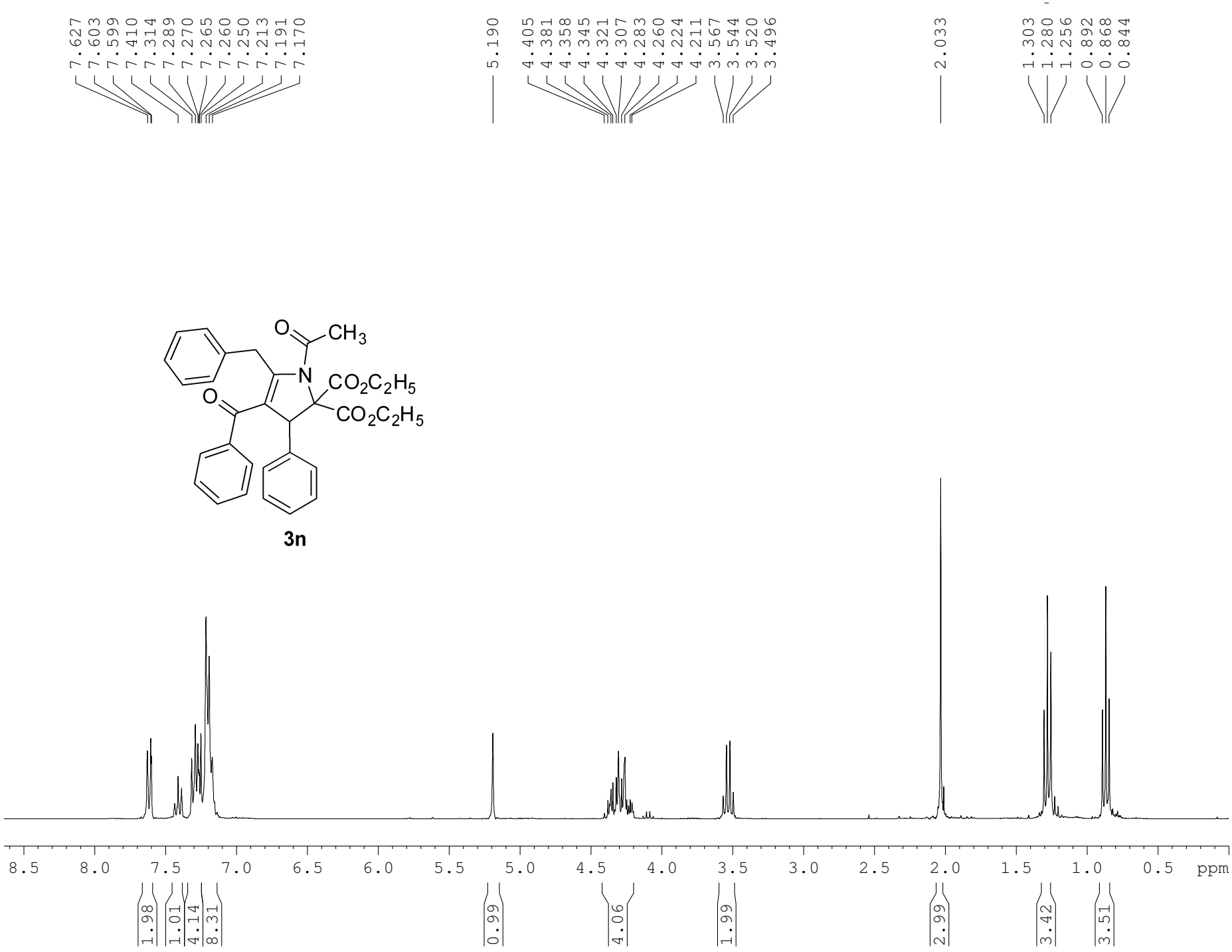

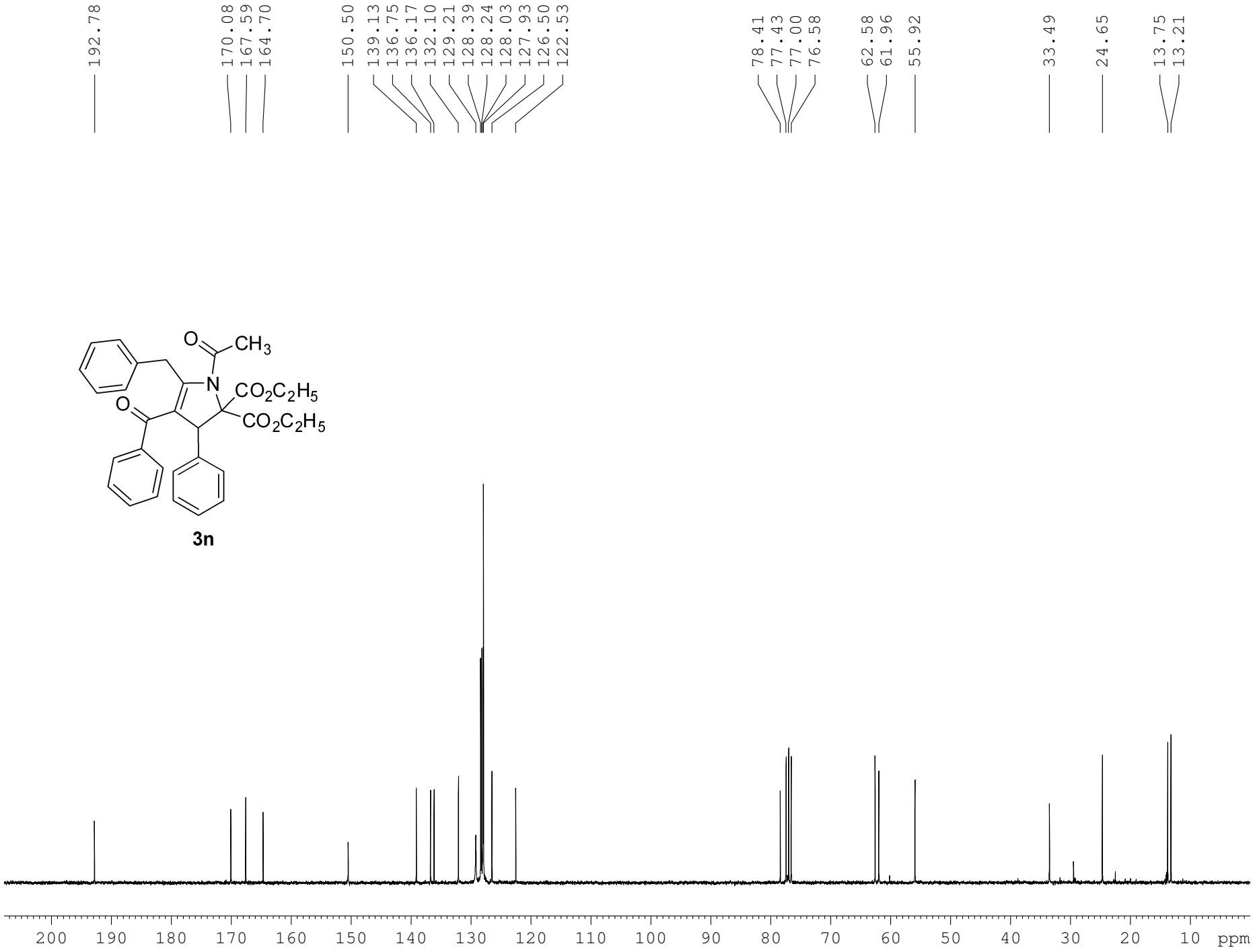

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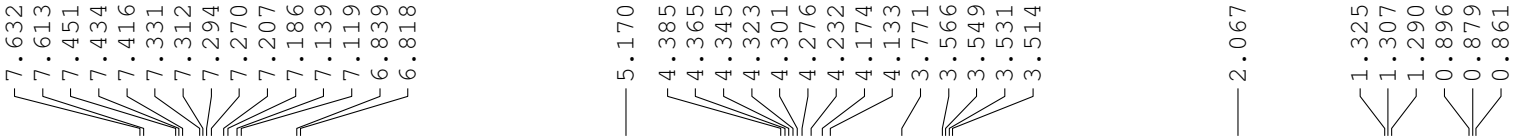
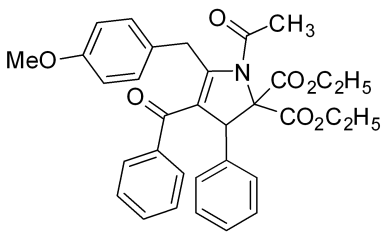


yxz-10-30 H



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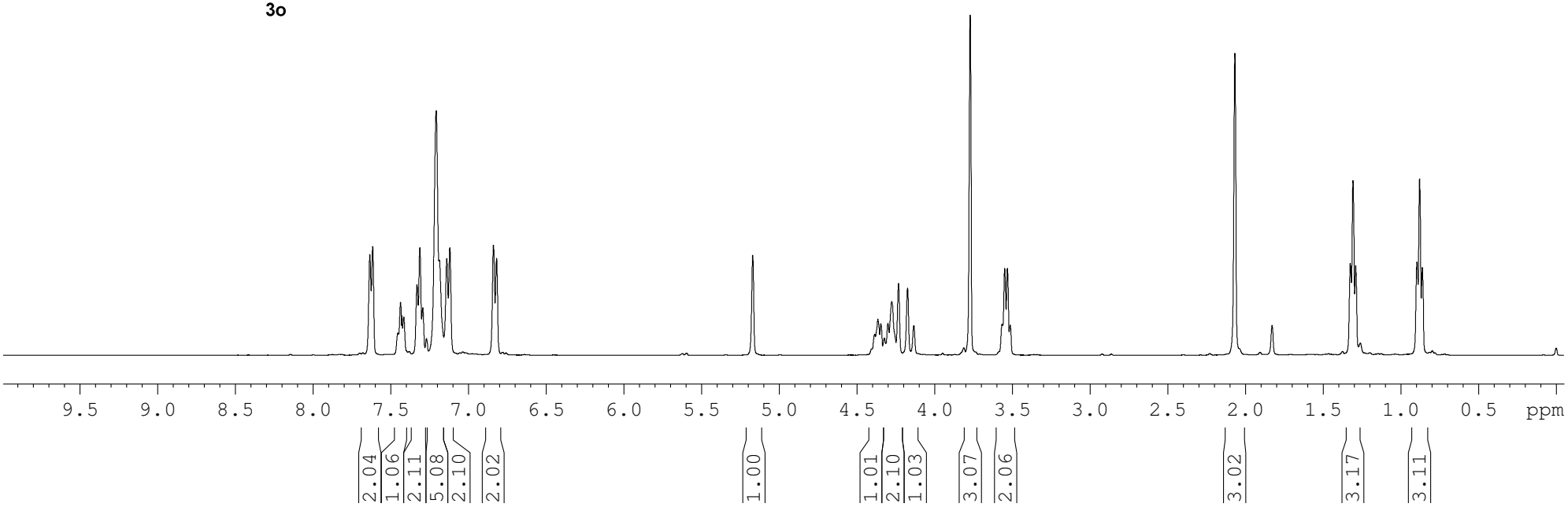

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170.13
167.69
164.81
158.22
150.86
139.21
136.27
132.16
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128.01
127.96
122.41
113.89
78.45
77.32
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55.13
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24.71
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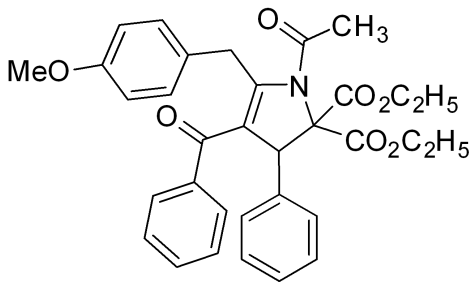
13.29

yxz-10-30 C



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yxz-10-28 H

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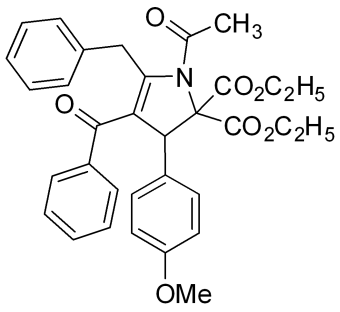
5.143

4.374 4.351 4.332 4.310 4.282 4.258 4.217

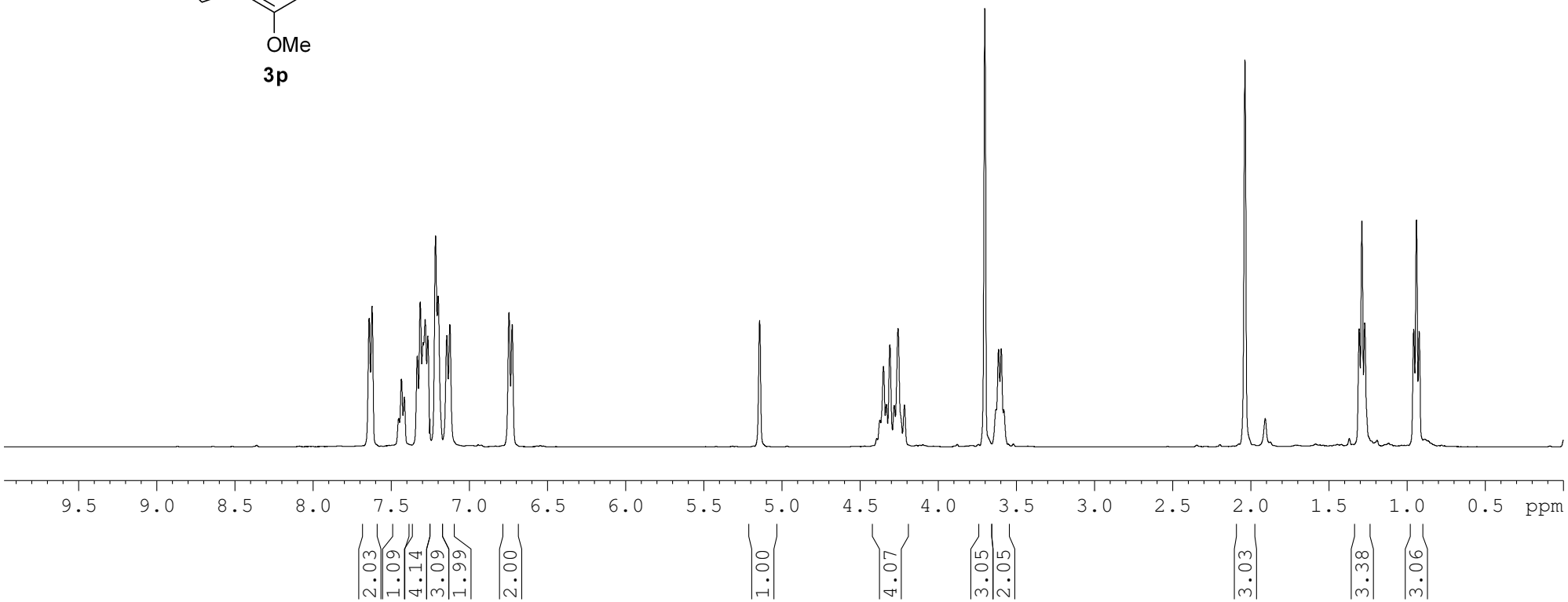
3.702 3.631 3.614 3.597 3.581

2.038

1.307 1.289 1.272 0.958 0.941 0.923



3p



192.91
170.13
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159.21
150.16
139.12
136.83
132.15
130.37
128.41
128.27
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128.04
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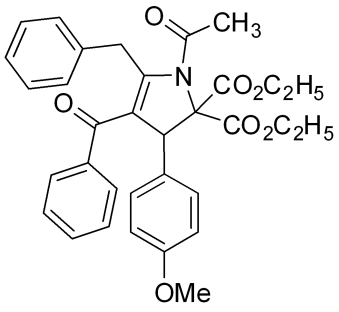
126.51
122.78
113.35
78.38
77.32
77.00
76.68
62.57
62.00
55.43
55.02
33.50
24.70
13.79
13.35

yxz-10-28 C



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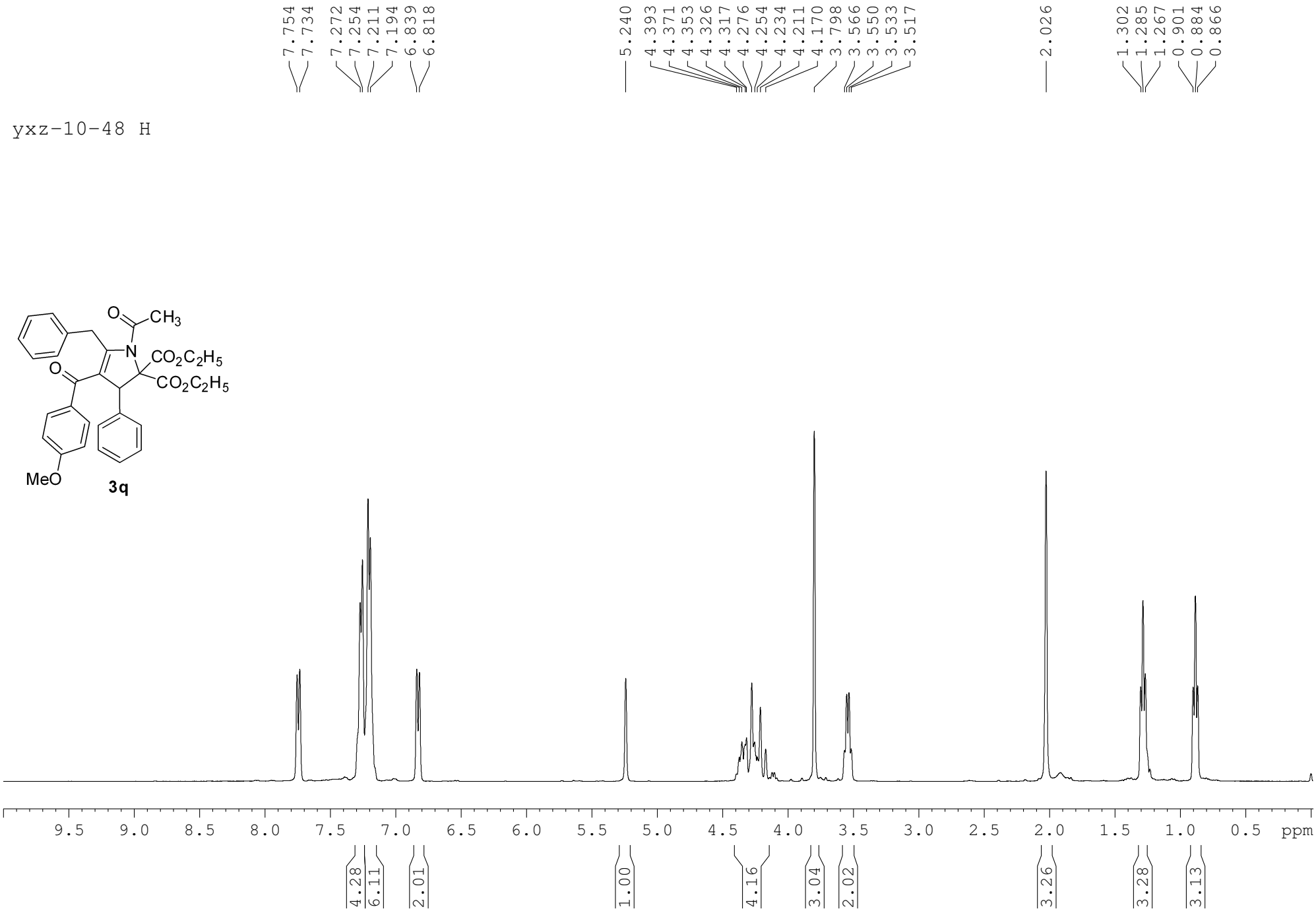

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122.94
113.63
78.40
77.32
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62.02
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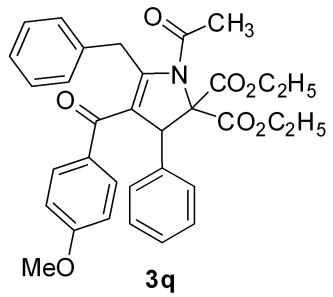
33.79
24.63
13.81
13.28

yxz-10-35 H



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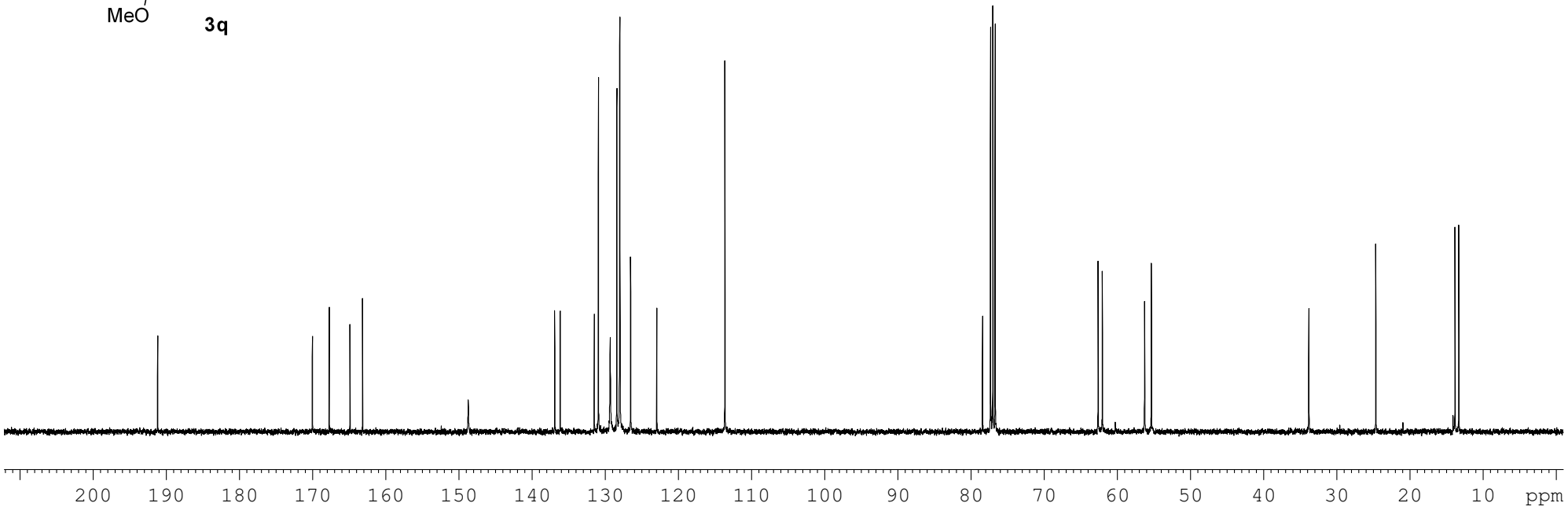

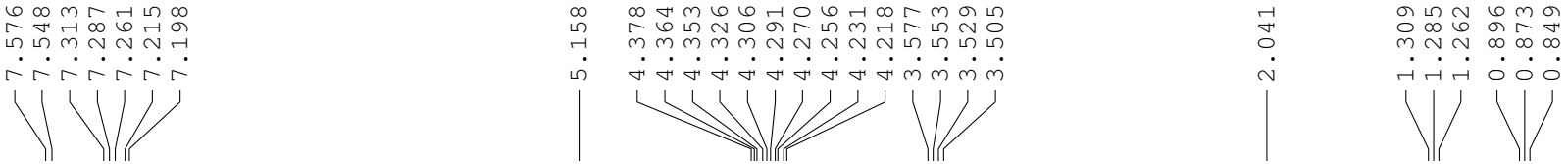

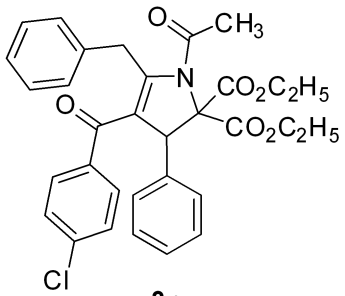

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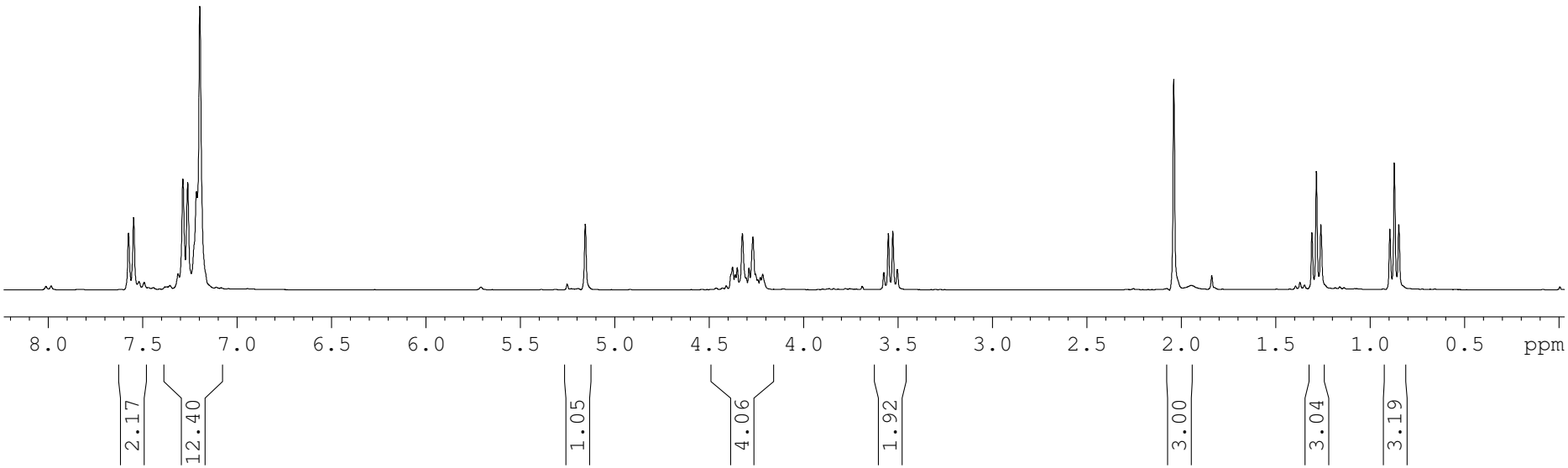

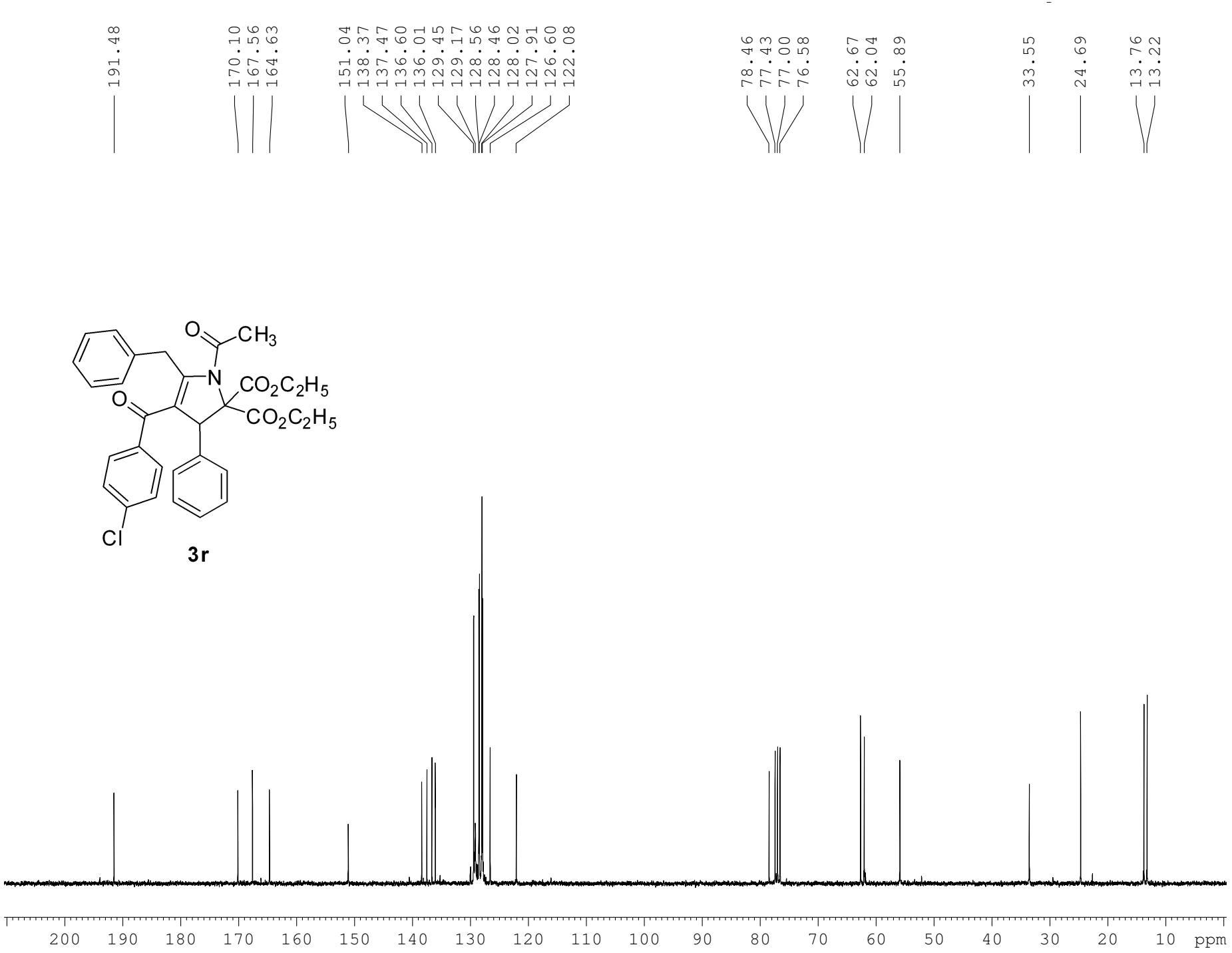

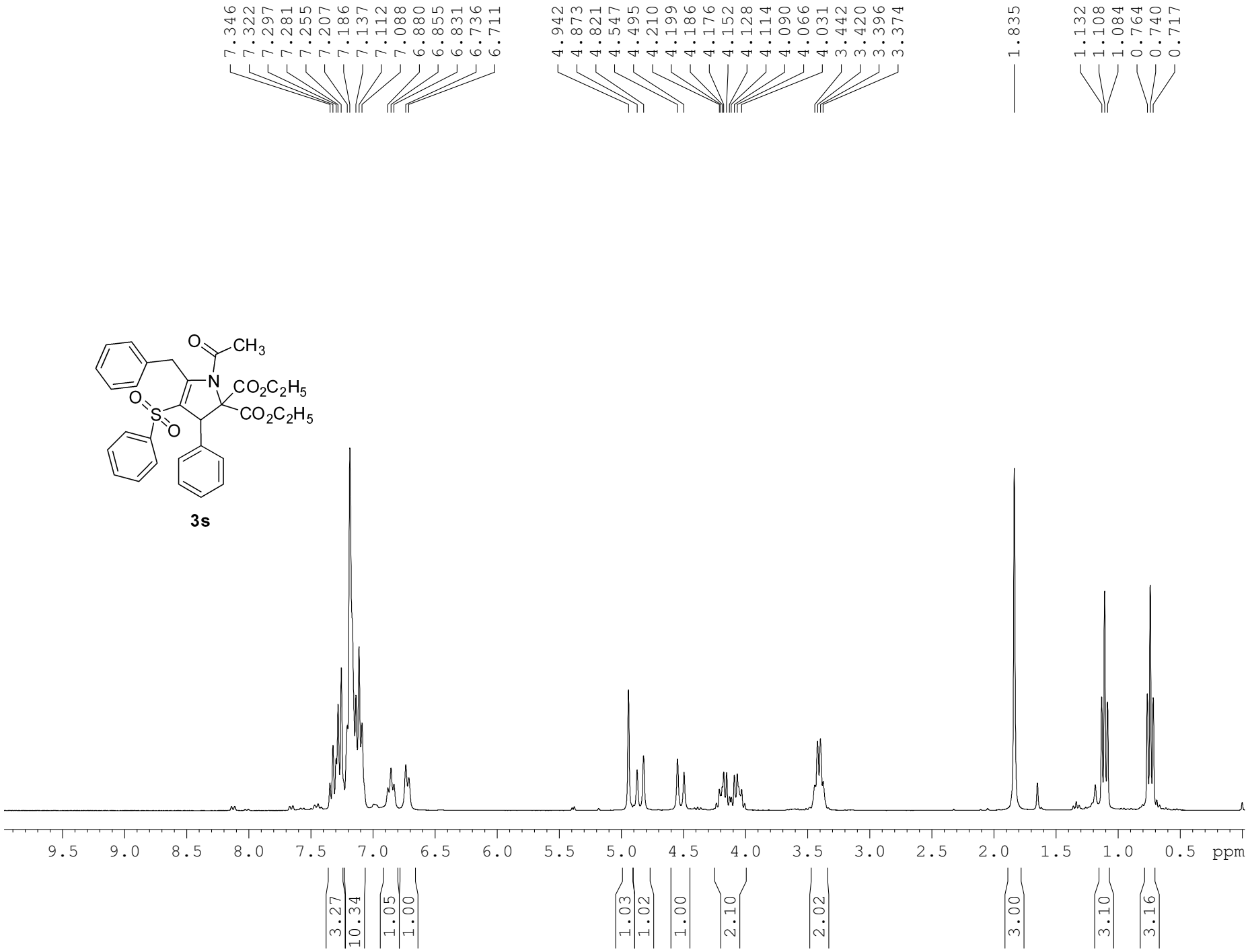

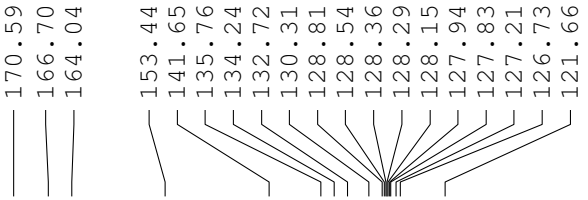

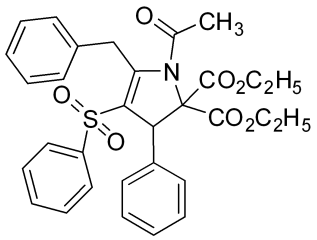

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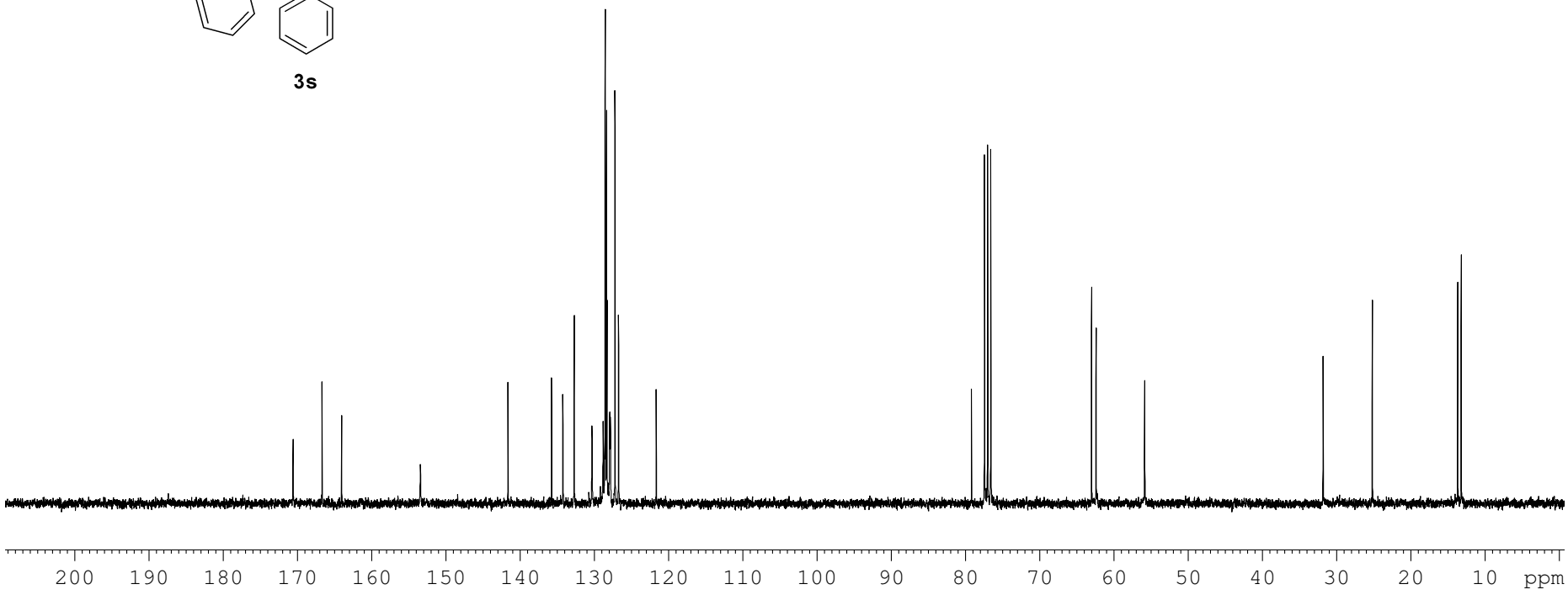

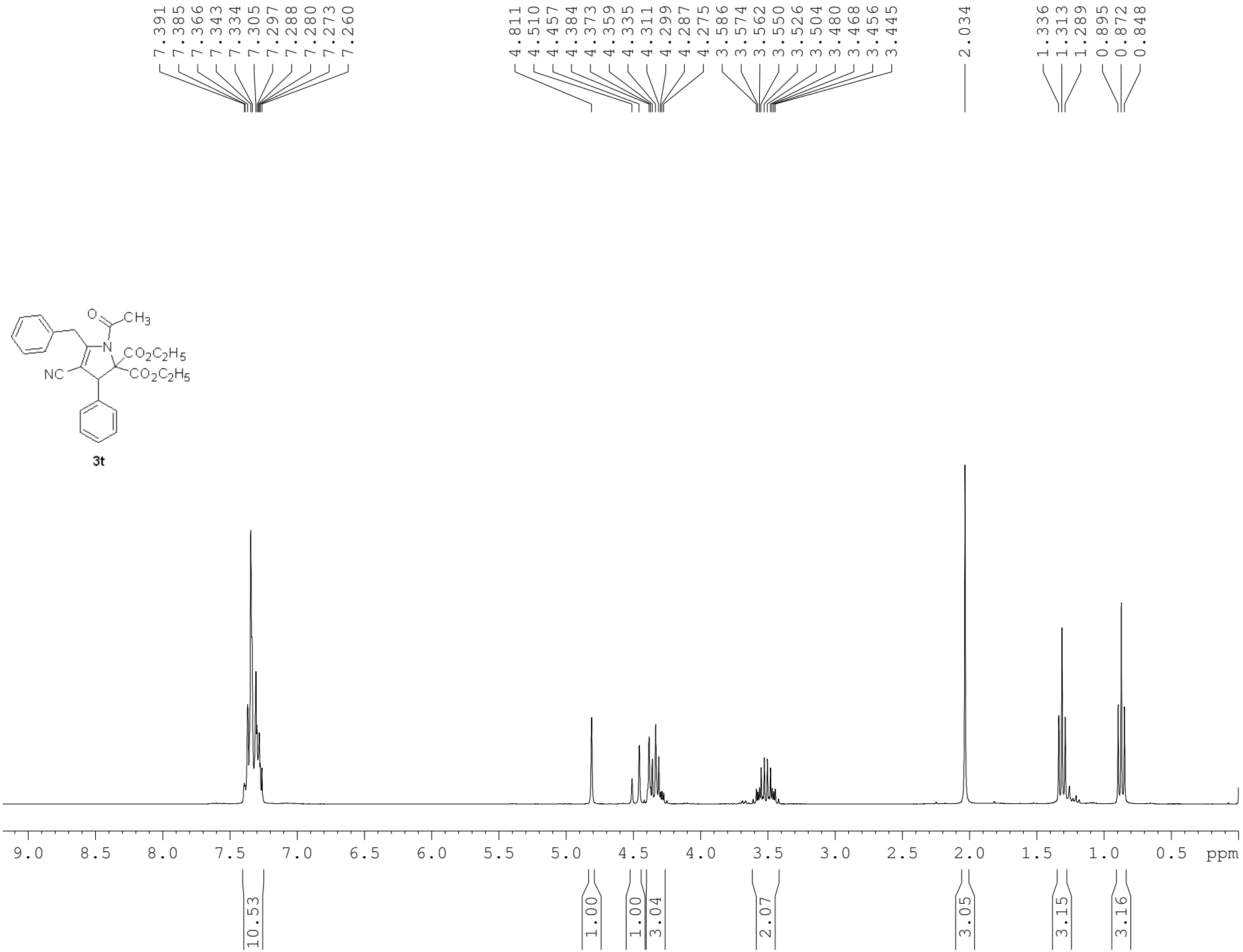

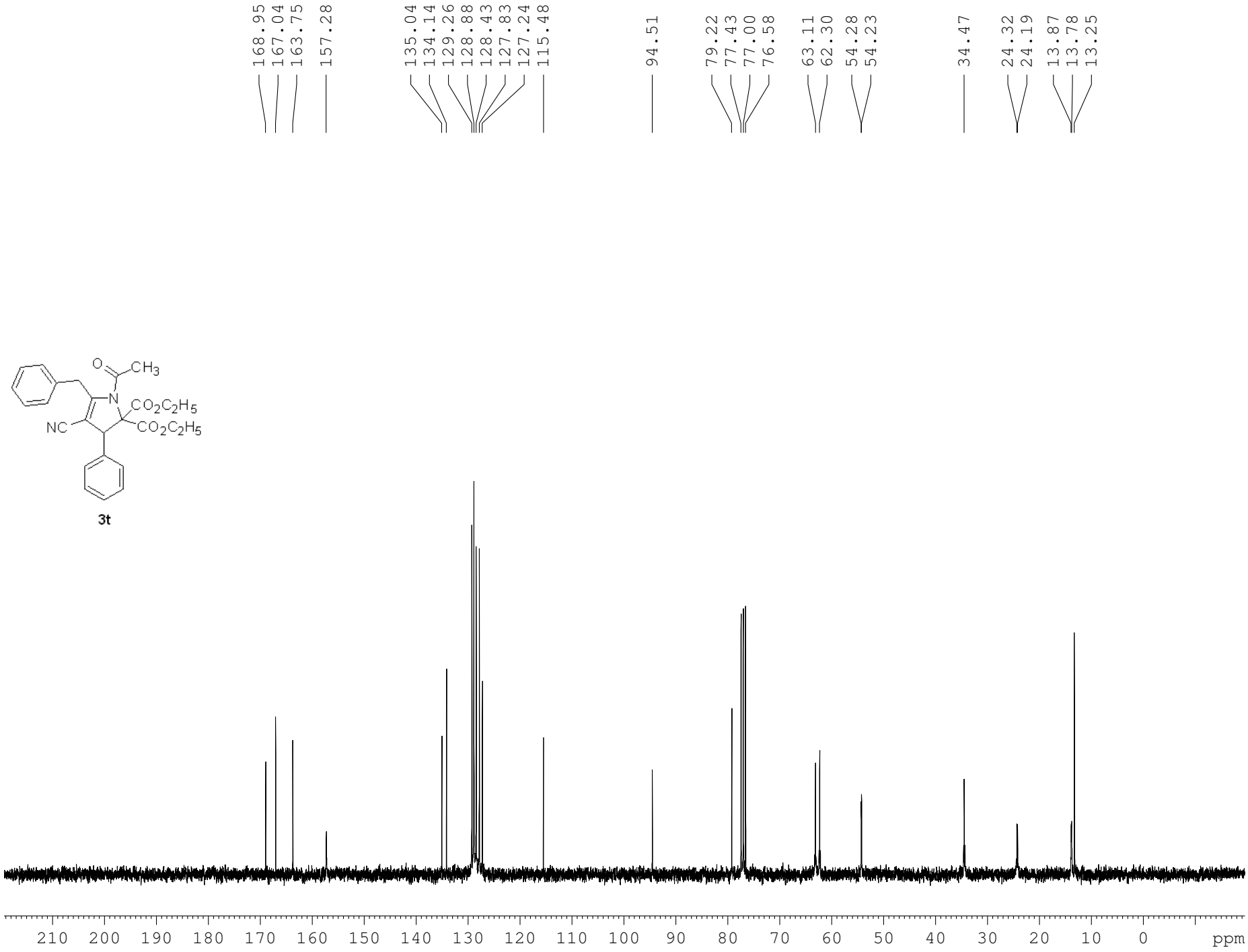

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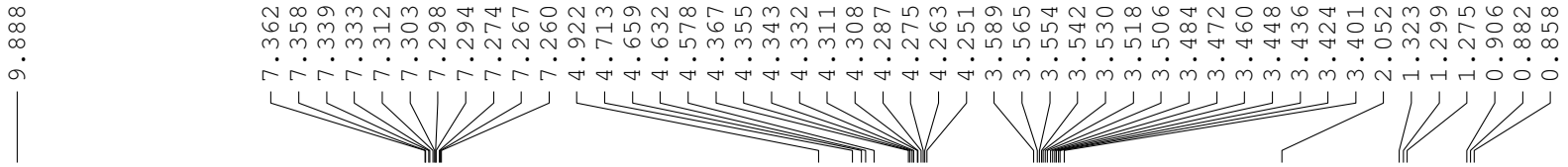

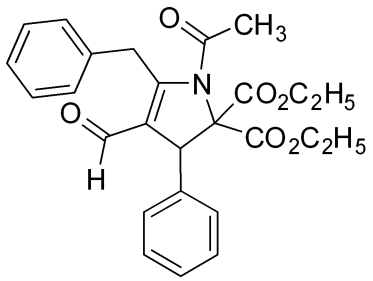

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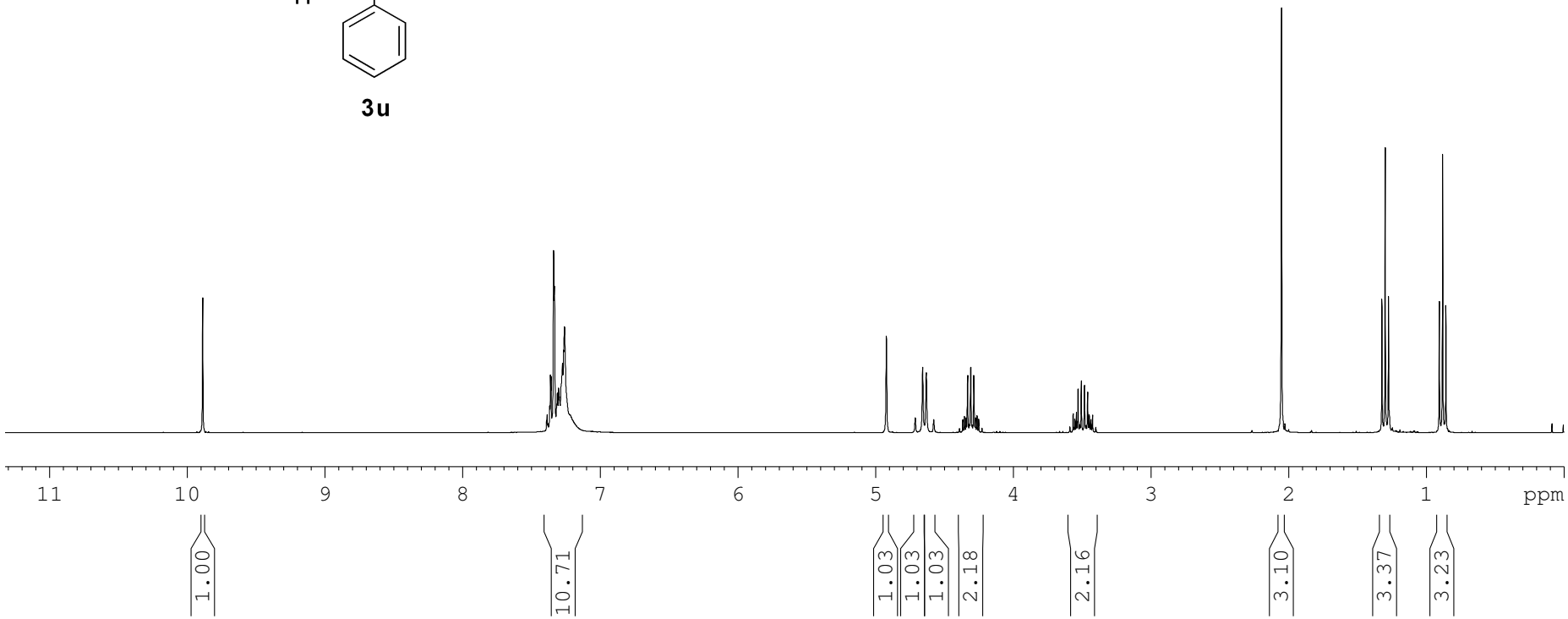

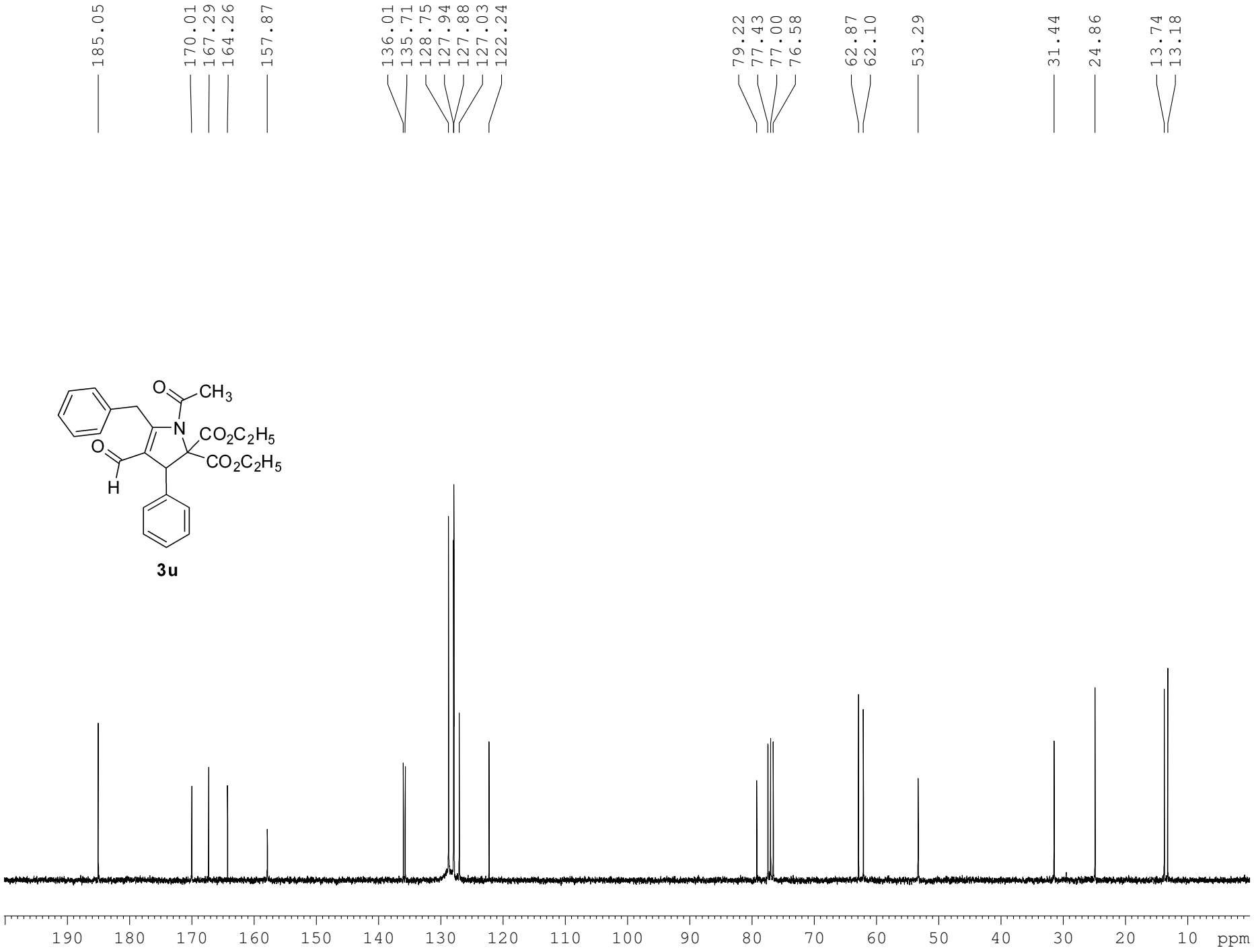

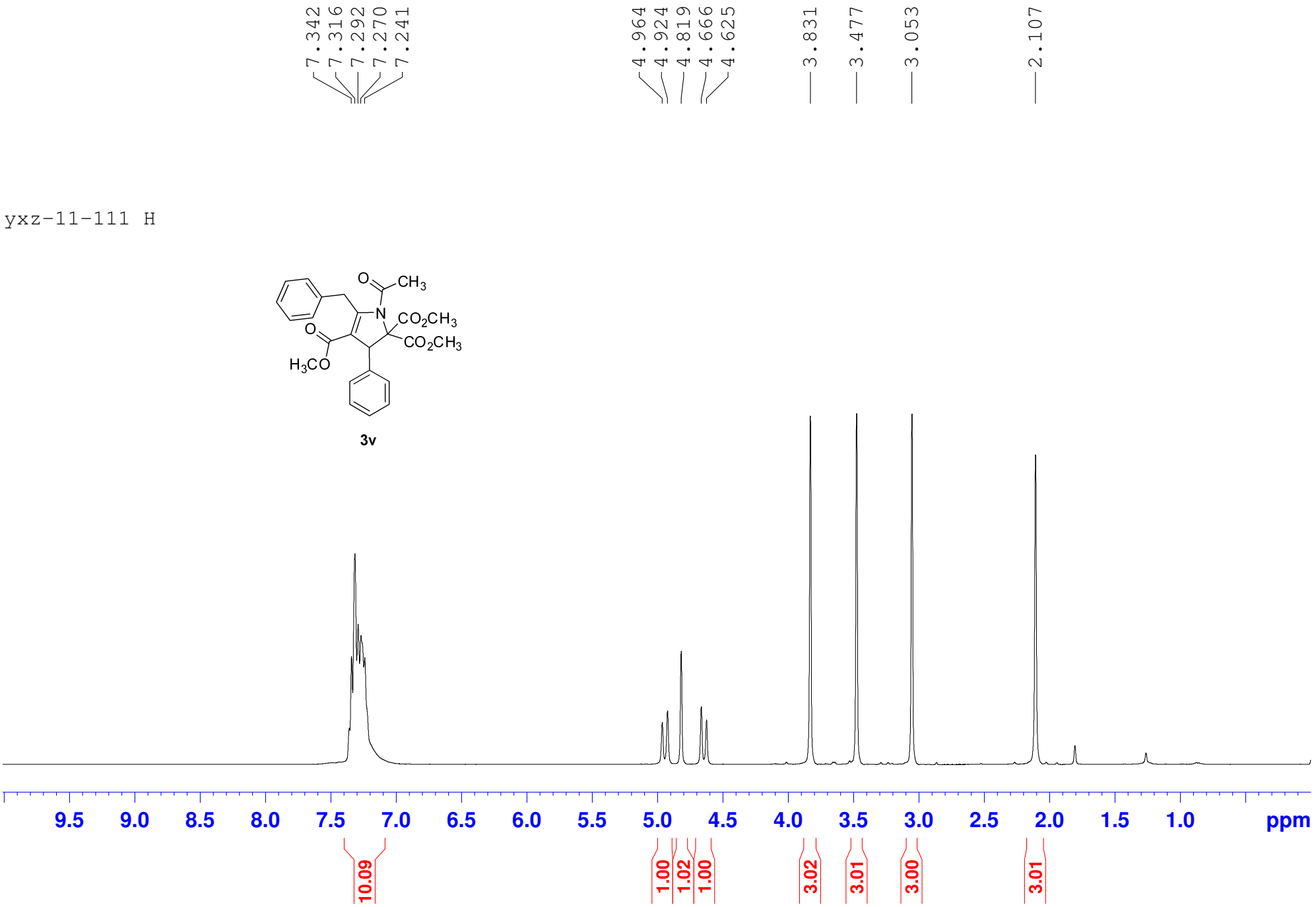

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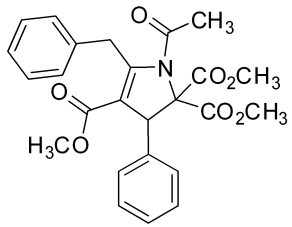
yxz-11-111 C



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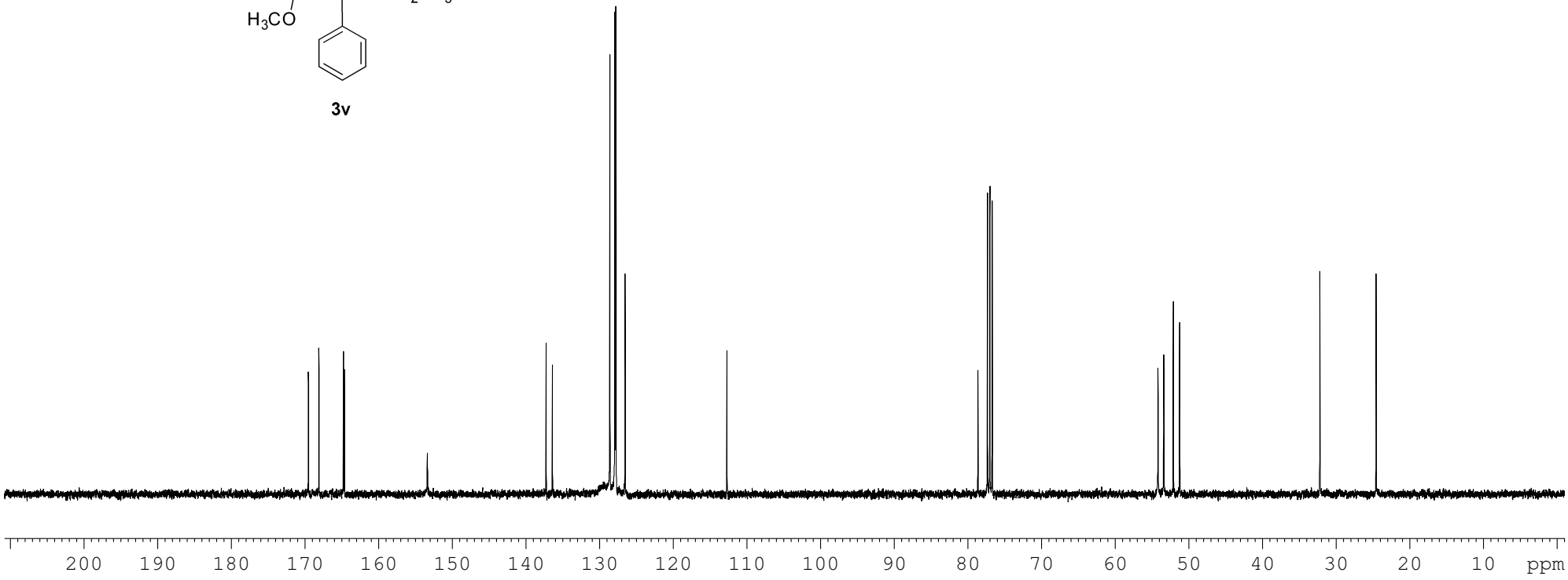

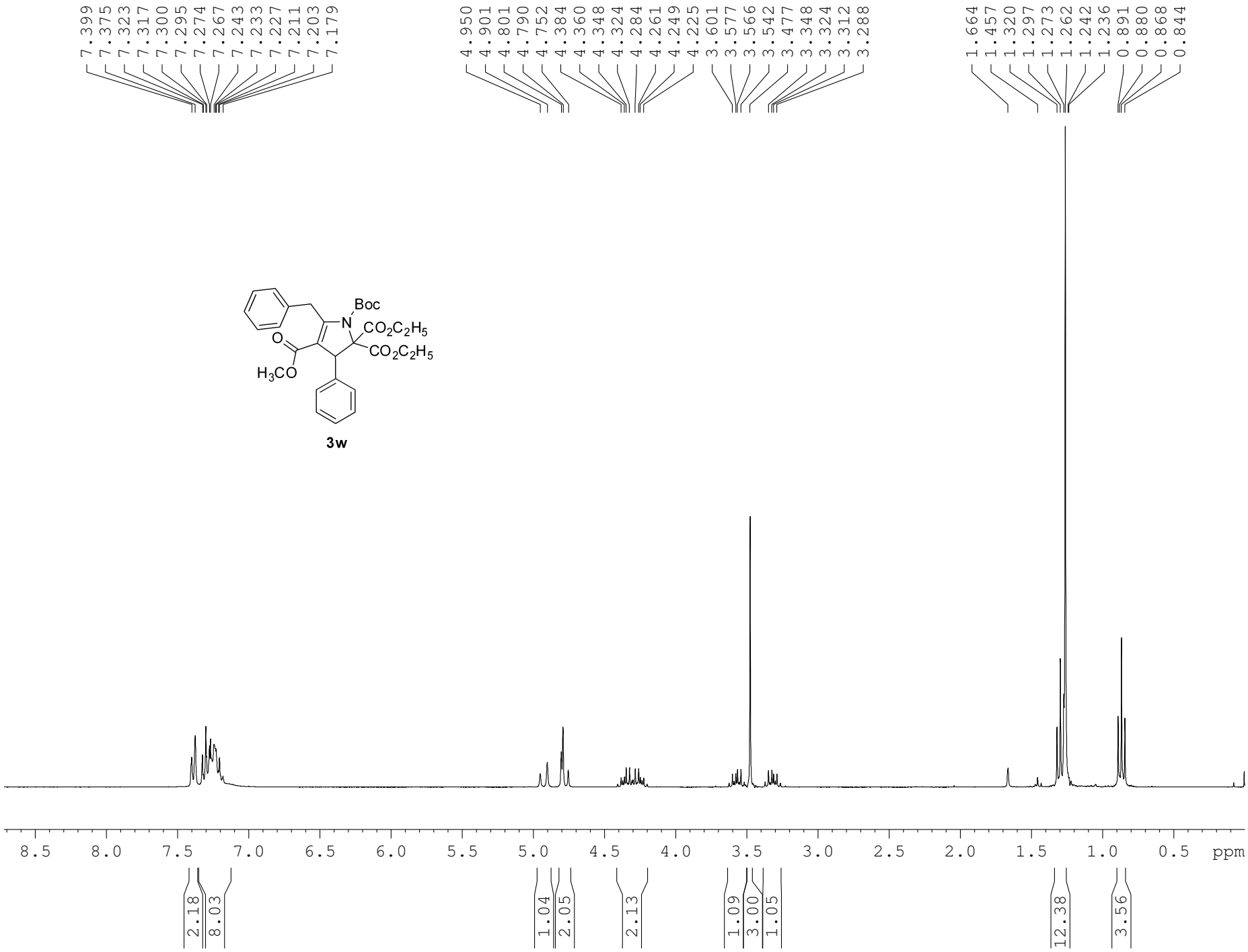

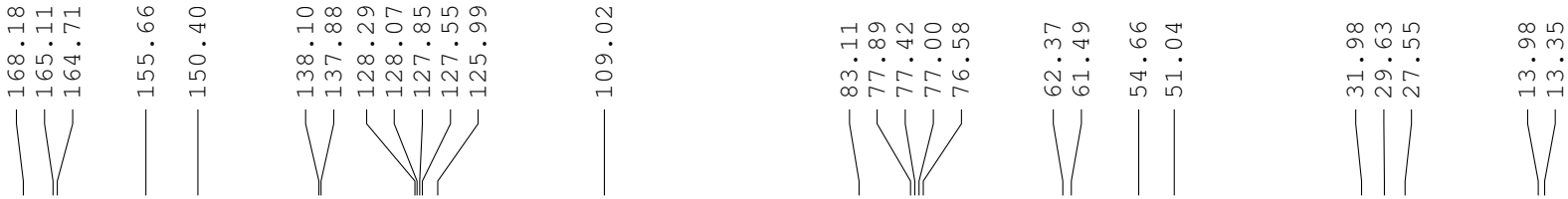

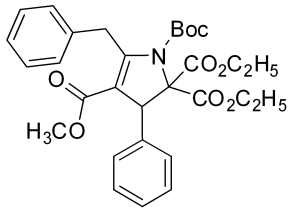

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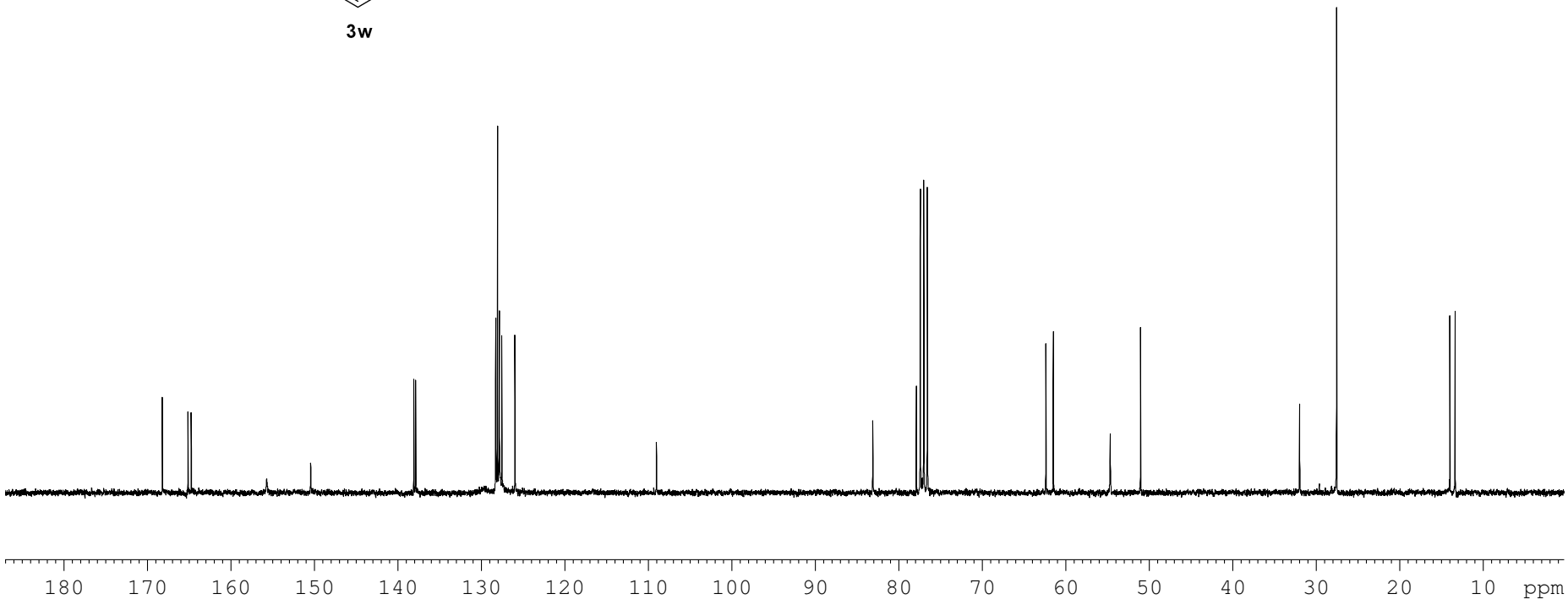
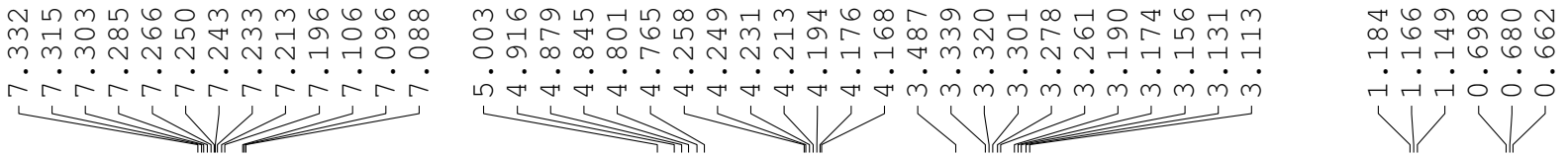
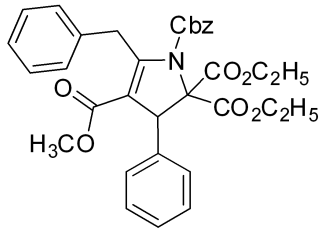




yxz-13-64 H



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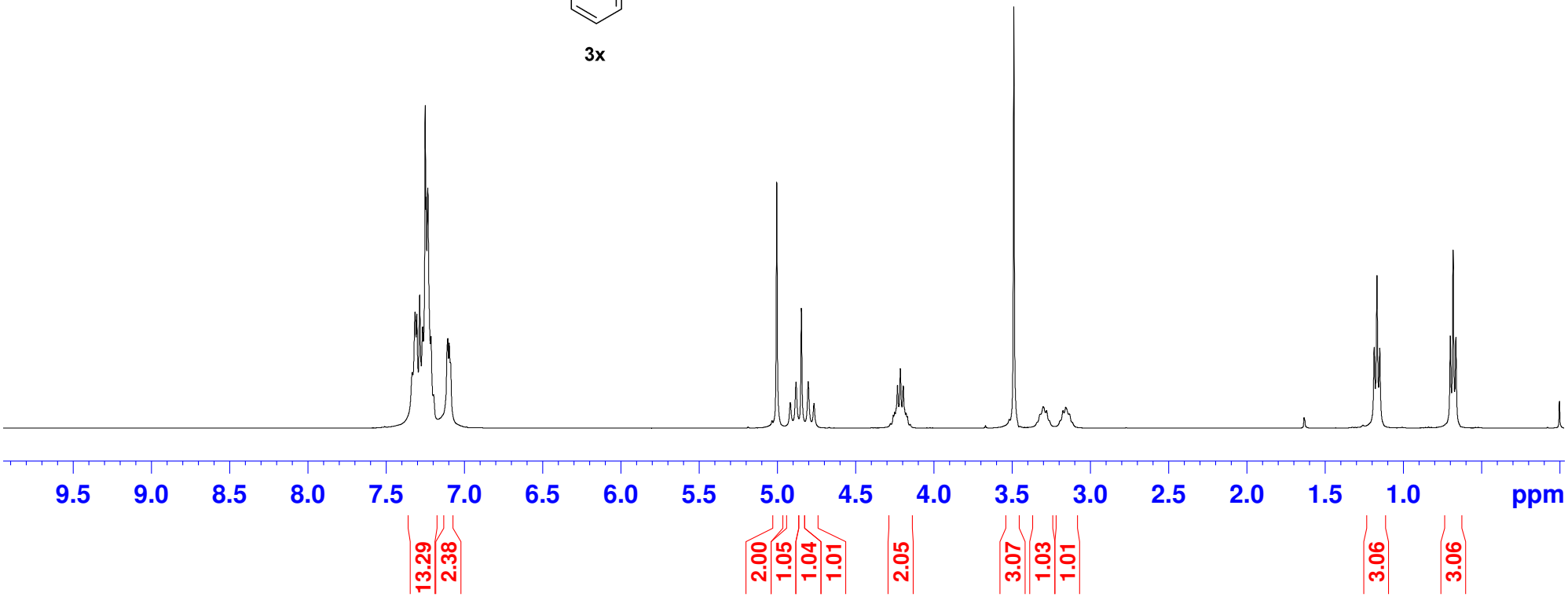

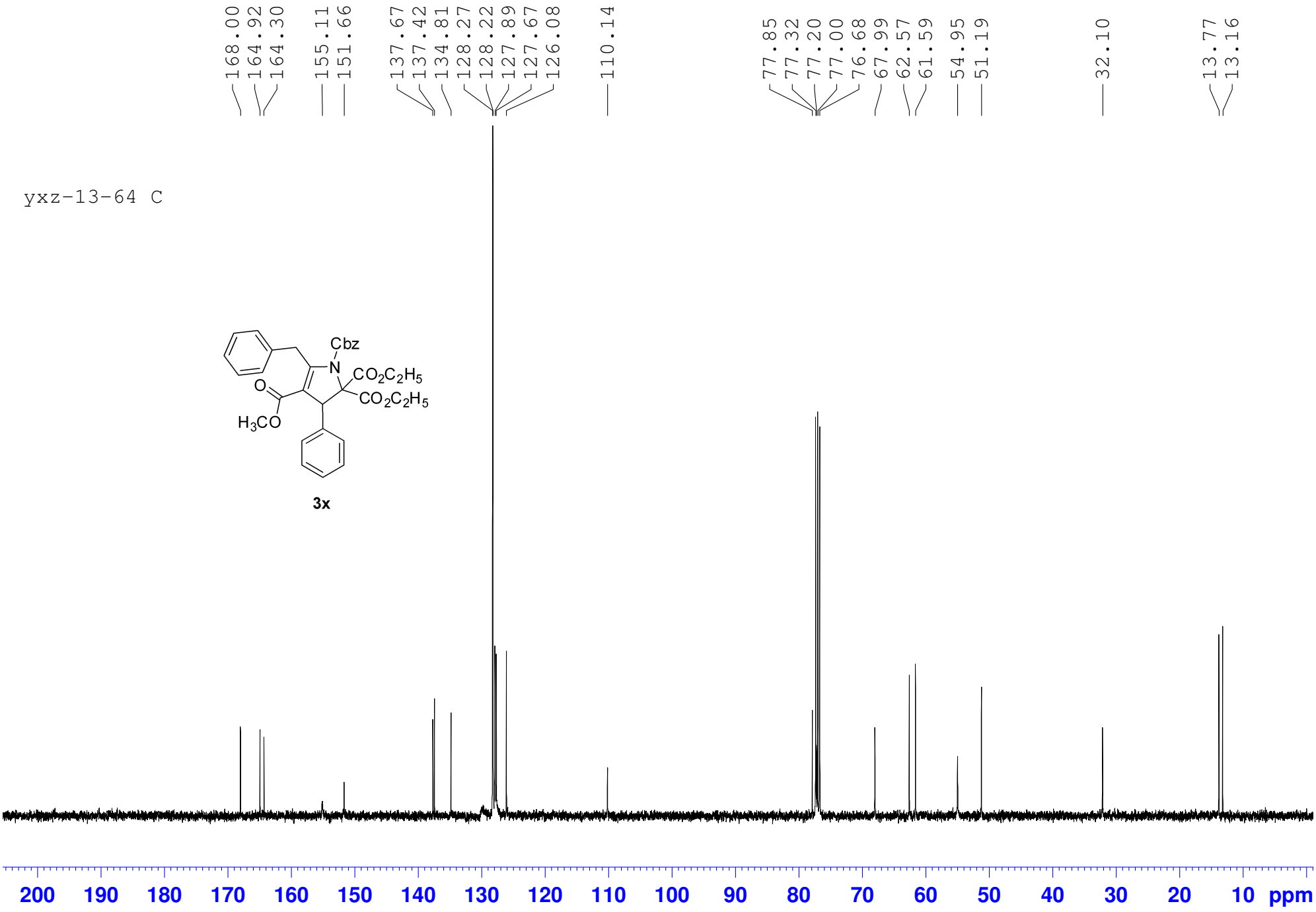

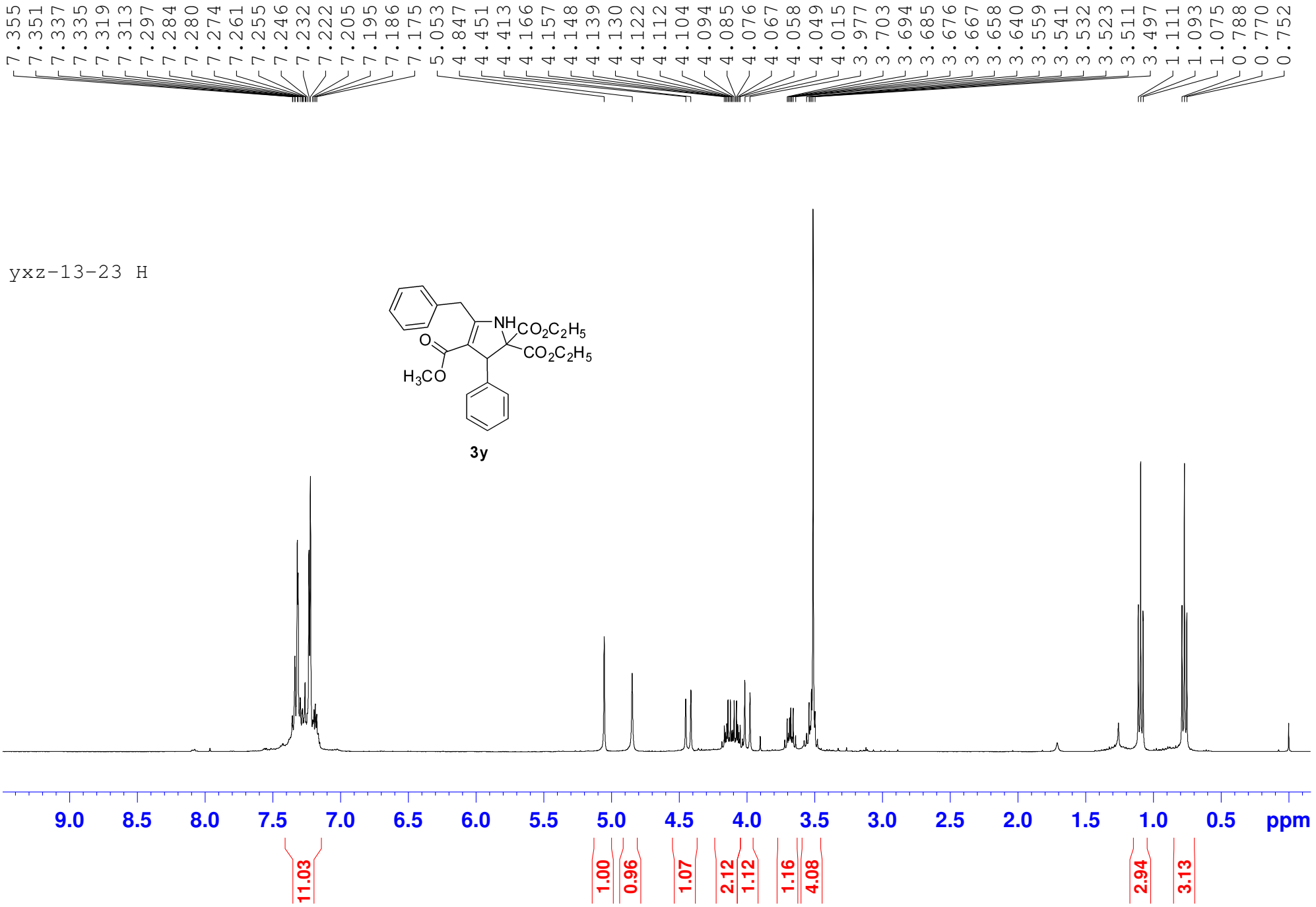

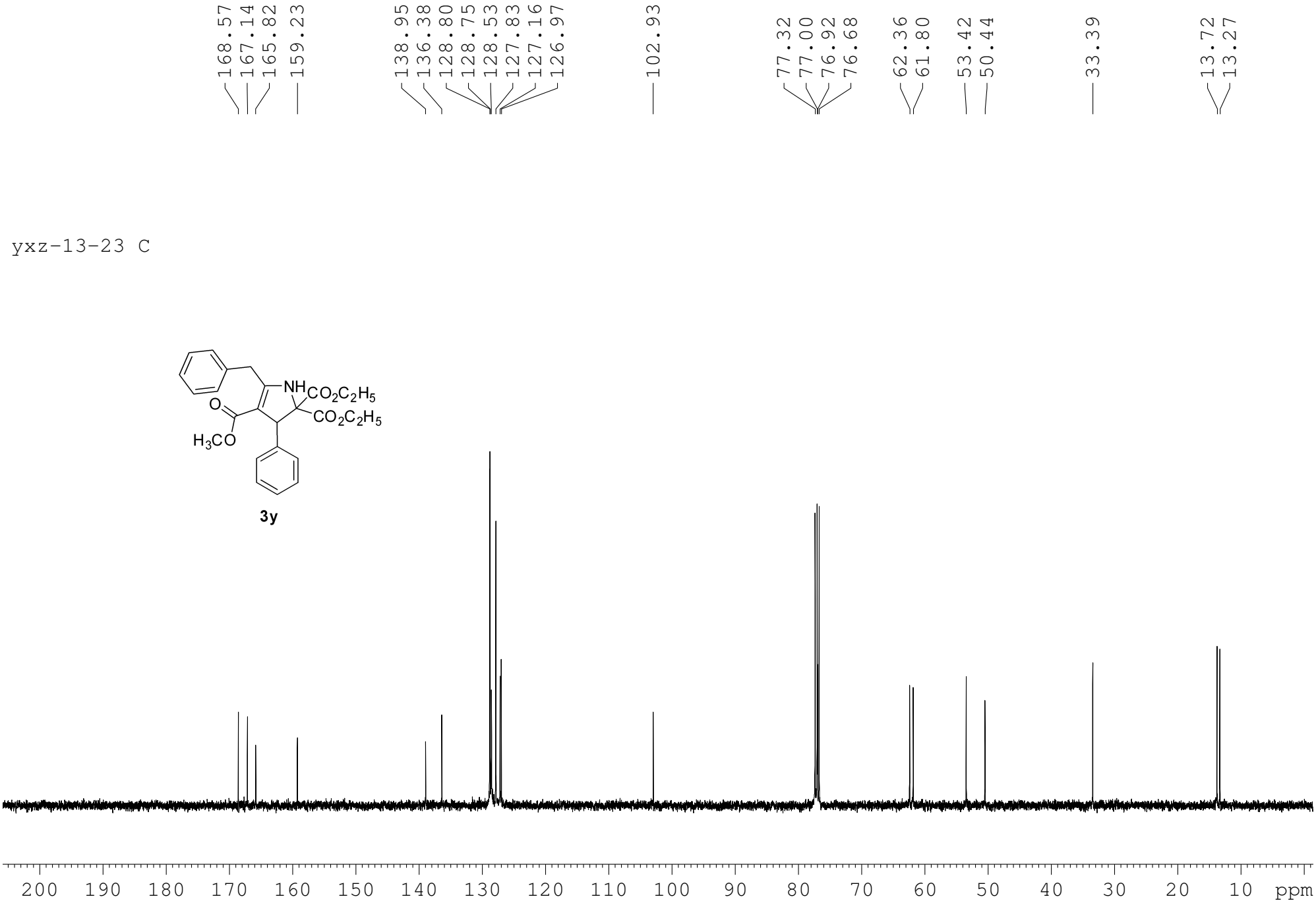

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7.297
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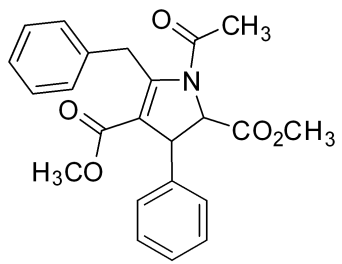
4.292

3.764
3.582

2.004

yxz-11-105 H



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