

Supporting Information

Highly Regioselective Lewis Acid-Catalyzed [3+2] Cycloadditions of Alkynes with Donor-acceptor Oxiranes by Selective Carbon-Carbon Bond Cleavage of Epoxides.

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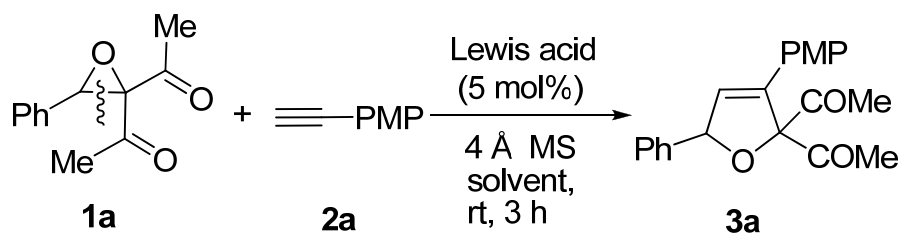
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General Information. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ^1H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform- d_3 . All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. $\text{ClCH}_2\text{CH}_2\text{Cl}$ (DCE), was freshly distilled from CaH_2 ; toluene was freshly distilled from sodium metal prior to use. Lewis-acid purchased from Alfa or Aldrich were used directly. Commercially available reagents were used without further purification. 4 Å molecular sieves purchased from Sinopharm Chemical Reagent Co.,Ltd were powdered and dried at 300 °C in muffle furnace for 8-10 hours prior to use.

Table 1. Screening Reaction Conditions.^a



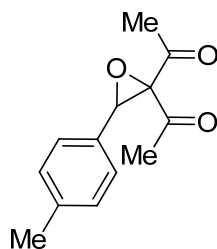
Entry	Catalyst	Solvent	Yield 3a (%) ^b
1	Sc(OTf) ₃	DCE	98
2	Yb(OTf) ₃	DCE	73
3	Y(OTf) ₃	DCE	67
4	In(OTf) ₃	DCE	92
5	Sn(OTf) ₂	DCE	78
6	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	67
7	Sc(OTf) ₃	DCM	95
8	Sc(OTf) ₃	toluene	82
9	----- ^c	DCE	0
10	----- ^d	DCE	9
11	----- ^e	PhCl	5

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), 5 mol % of catalyst, and 80 mg of activated 4 Å MS in 2 mL of solvent at room temperature. ^b Isolated yield and no other stereoisomer is detected. PMP = 4-MeOC₆H₄. ^c No Lewis acid was added. ^d No Lewis acid was added, 100°C in sealed tube, 12 hours. ^e No Lewis acid was added, 160°C, 10 hours.

Synthesis of Oxiranyl diketones

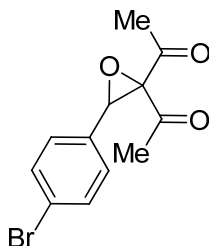
The substrate **1a-1m**, **5**, **6** were synthesized according to the procedure of references.^{[1],[2]} The spectral data of **1a-1b**,^[4] **1h-1j**,^[2] **1l**,^[3] **1m**^[1] are consisted with the literature.

1. 1,1'-(3-*p*-Tolyloxirane-2,2-diyl)diethanone (**1c**)



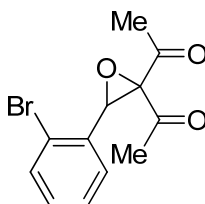
Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.16 (s, 4 H), 4.37 (s, 1 H), 2.33 (s, 3 H), 2.28 (s, 3 H), 1.64 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 201.8, 199.5, 139.2, 129.4, 128.7, 126.0, 72.7, 62.1, 29.8, 25.2, 21.2 ppm; IR (neat) ν (cm^{-1}) 3664, 2987, 2902, 1700, 1407, 1252, 1066, 1055, 870, 812; MS (70 eV): m/z (%): 218 (0.49) [M^+], 43 (100); HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$: 218.0943, found: 218.0944.

2. 1,1'-(3-(4-Bromophenyl)oxirane-2,2-diyl)diethanone (1d)



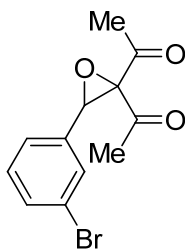
White solid, m.p. 121-122°C. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.49 (d, 2 H, $J = 8.0$ Hz), 7.17 (d, 2 H, $J = 8.0$ Hz), 4.37 (s, 1 H), 2.28 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 201.3, 198.8, 131.9, 130.7, 127.8, 123.4, 72.4, 61.3, 29.7, 25.2 ppm; IR (neat) ν (cm^{-1}) 3089, 2989, 1718, 1699, 1490, 1413, 1360, 1255, 1169, 1086, 1071, 1011, 890, 807, 642; MS (70 eV): m/z (%): 282 (0.18) [M^+], 284 (0.21) [$\text{M}^+ + 2$], 43 (100); HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{O}_3\text{Br}$: 281.9892, found: 281.9894.

3. 1,1'-(3-(2-Bromophenyl)oxirane-2,2-diyl)diethanone (1e)



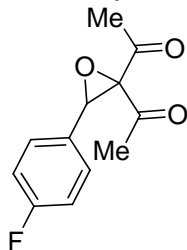
White solid, m.p. 71-73 °C. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.55 (d, 1 H, $J = 8.0$ Hz), 7.30-7.34 (m, 2 H), 7.23-7.26 (m, 1 H), 4.50 (s, 1 H), 2.35 (s, 3 H), 2.06 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 201.1, 198.7, 132.4, 131.3, 130.6, 127.9, 127.6, 122.2, 71.7, 62.4, 29.6, 25.5 ppm; IR (neat) ν (cm^{-1}) 3005, 1712, 1519, 1391, 1353, 1247, 1175, 1104, 1029; MS (70 eV): m/z (%): 282 (3.53) [M^+], 284 (3.41) [$\text{M}^+ + 2$], 43 (100); HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{O}_3\text{Br}$ (M^+): 281.9892, found: 281.9892.

4. 1,1'-(3-(3-Bromophenyl)oxirane-2,2-diyl)diethanone (1f)



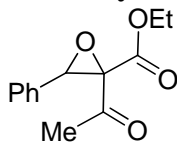
Yellow oil, ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.46-7.50 (m, 2 H), 7.19-7.28 (m, 2 H), 4.36 (s, 1 H), 2.28 (s, 3 H), 2.05 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 201.1, 198.8, 134.0, 132.4, 130.3, 129.3, 124.7, 122.8, 72.3, 61.1, 29.8, 25.3 ppm; IR (neat) ν (cm^{-1}) 3066, 2926, 1706, 1570, 1421, 1360, 1250, 1170, 1100, 1071; MS (70 eV): m/z (%): 282 (18.0) [M^+], 282 (16.0) [M^++2], 126.9 (100); HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{O}_3\text{Br}$ (M^+): 281.9892, found: 281.9895.

5. 1,1'-(3-(4-Fluorophenyl)oxirane-2,2-diyl)diethanone (1g)



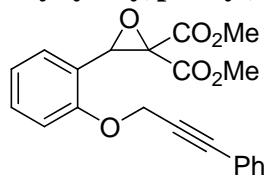
Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.27 (s, 2 H), 7.06 (t, 2 H, $J = 8.4$ Hz), 4.38 (s, 1 H), 2.28 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 201.5, 199.1, 163.1 (d, $^1J_{\text{C},\text{F}} = 248$ Hz), 128.1, (d, $^3J_{\text{C},\text{F}} = 9$ Hz), 127.5, 115.9 (d, $^2J_{\text{C},\text{F}} = 22$ Hz), 72.6, 61.4, 29.8, 25.3 ppm; IR (neat) ν (cm^{-1}) 1725, 1708, 1608, 1513, 1421, 1361, 1289, 1228, 1158, 1101; MS (70 eV): m/z (%): 222 (9.51) [M^+], 43 (100); HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{O}_3\text{F}$: 222.0692, found: 222.0694.

6. Ethyl 2-acetyl-3-phenyloxirane-2-carboxylate (1k)



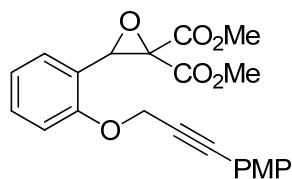
Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.33 (s, 5 H), 4.43 (s, 1 H), 3.97-4.07 (m, 2 H), 2.32 (s, 3 H), 0.95 (t, 3 H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 199.4, 163.9, 132.0, 129.0, 128.3, 126.0, 68.2, 61.9, 61.7, 25.2, 13.6 ppm; IR (neat) ν (cm^{-1}) 2984, 1748, 1714, 1457, 1372, 1314, 1257, 1221, 1200, 1109, 1031; MS (70 eV): m/z (%): 234 (9.07) [M^+], 43 (100); HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{O}_4$: 234.0892, found: 234.0893.

7. Dimethyl 3-(2-(3-phenylprop-2-ynoxy)phenyl)oxirane-2,2-dicarboxylate (5)



Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.41 (d, 2 H, $J = 7.6$ Hz), 7.25-7.32 (m, 4 H), 7.23 (d, 1 H, $J = 7.2$ Hz), 7.11 (d, 1 H, $J = 8.0$ Hz), 6.96 (t, 1 H, $J = 7.2$ Hz), 5.00 (d, 1 H, $J = 17.6$ Hz), 4.96 (d, 1 H, $J = 17.6$ Hz), 4.83 (s, 1 H), 3.87 (s, 3 H), 3.52 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 166.0, 164.1, 156.5, 131.7, 130.0, 128.7, 128.3, 126.2, 122.1, 121.2, 121.1, 112.2, 87.5, 83.6, 62.6, 59.2, 57.0, 53.4, 52.5 ppm; IR (neat) ν (cm^{-1}) 3658, 2955, 1750, 1604, 1492, 1439, 1372, 1335, 1274, 1238, 1219, 1190, 1163, 1121, 1047, 1016; ESI-MS: m/z : 367.0 $[\text{M}+\text{H}]^+$; HR-ESI-MS calcd for $\text{C}_{21}\text{H}_{19}\text{O}_6$ $[\text{M}+\text{H}]^+$: 367.11739, found: 367.11761.

8. Dimethyl 3-(2-(3-(4-methoxyphenyl)prop-2-ynoxy)phenyl)oxirane-2,2-dicarboxylate (6)



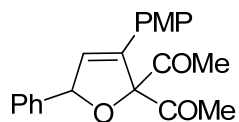
White solid, m.p. 118-120 °C. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.29-7.37 (m, 3 H), 7.22 (d, 1 H, $J = 7.6$ Hz), 7.11 (d, 1 H, $J = 8.0$ Hz), 6.95 (t, 1 H, $J = 7.2$ Hz), 6.82 (d, 2 H, $J = 8.0$ Hz), 4.98 (d, 1 H, $J = 14.0$ Hz), 4.94 (d, 1 H, $J = 14.0$ Hz), 4.83 (s, 1 H), 3.86 (s, 3 H), 3.79 (s, 3 H), 3.52 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 166.0, 164.1, 159.9, 156.5, 133.2, 129.9, 126.2, 121.2, 121.0, 114.1, 113.9, 112.2, 87.4, 82.3, 62.6, 59.2, 57.1, 55.2, 53.4, 52.5 ppm; IR (neat) ν (cm^{-1}) 3652, 2955, 1751, 1605, 1510, 1493, 1457, 1439, 1335, 1290, 1244, 1219, 1174, 1121, 1108, 1030; MS (70 eV): m/z (%): 396 (0.23) $[\text{M}^+]$, 145 (100); HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{O}_7$ (M) $^+$: 396.1209, found: 396.1209.

Typical procedure for $\text{Sc}(\text{OTf})_3$ catalyzed [3+2] cycloaddition reaction.

In an inert atmosphere glovebox, a flame-dried vial was charged with 80 mg of activated 4Å molecular sieves powder (MS), and a magnetic stir bar. Outside of the glovebox, the vial was placed under an N_2 atmosphere and added the alkyl 2 (0.4 mmol), oxirane 1 (0.2 mmol) and 2 mL of DCE were added followed by 5 mol %

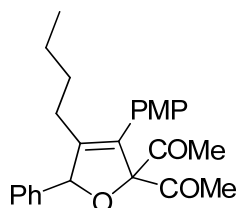
Sc(OTf)₃, The reaction was stirred at room temperature and detected by TLC, the reaction mixture was then passed over a plug of silica with 30 mL of EtOAc. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, eluting with (hexanes: EtOAc = 5:1) to afford the desired product.

9. 1,1'-(3-(4-Methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2,2-diyl)diethanone (3a)



The reaction of **1a** (40.8 mg, 0.2 mmol), **2a** (55 μL, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 65.6 mg (89%) of **3a**, white solid, m.p. 118-120 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 7.32-7.39 (m, 7 H), 6.83 (d, 2 H, *J* = 8.0 Hz), 6.43 (s, 1 H), 6.08 (s, 1 H), 3.78 (s, 3 H), 2.32 (s, 3 H), 2.17 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 206.4, 205.1, 159.9, 139.4, 139.2, 129.2, 128.9, 127.5, 127.4, 123.8, 113.9, 101.0, 88.8, 55.3, 26.7, 26.0; MS (70 eV): IR (neat) ν (cm⁻¹) 3072, 3013, 2935, 2839, 1721, 1707, 1606, 1574, 1518, 1490, 1355, 1302, 1282, 1262, 1221, 1117, 1085, 1026; MS (70 eV): *m/z* (%): 336 (0.65) [M⁺], 43 (100); HRMS calcd for C₂₁H₂₀O₄ (M)⁺: 336.1362, found: 336.1367.

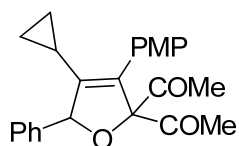
10. 1,1'-(4-Butyl-3-(4-methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2,2-diyl)diethanone (3b)



The reaction of **1a** (40.8 mg, 0.2 mmol), **2b** (76.2 mg, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 69.3 mg (88%) of **3b**, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ_H 7.37-7.44 (m, 3 H), 7.34 (d, 2 H, *J* = 7.2 Hz), 7.15 (d, 2 H, *J* = 8.4 Hz), 6.87 (d, 2 H, *J* = 8.4 Hz), 5.93 (s, 1 H), 3.80 (s, 3 H), 2.34 (s, 3 H), 2.13-2.22 (m, 1 H), 2.13 (s, 3 H), 1.70-1.75 (m, 1 H), 1.09-1.26 (m, 4 H), 0.73 (t, 3 H, *J* = 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ_C 206.0, 204.9, 159.1, 143.8, 139.0, 133.0, 130.9, 128.9, 128.8, 127.9, 124.6,

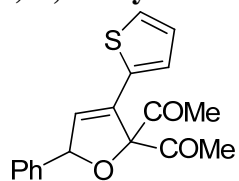
113.6, 102.6, 90.9, 55.1, 29.6, 27.0, 26.0, 25.8, 22.3, 13.6 ppm; IR (neat) ν (cm^{-1}) 2956, 2933, 2861, 1711, 1608, 1511, 1457, 1352, 1248, 1179, 1125, 1061, 1032; MS (70 eV): m/z (%): 392 (0.28) [M^+], 43 (100); HRMS calcd for $\text{C}_{25}\text{H}_{28}\text{O}_4(\text{M})^+$: 392.1988, found: 392.1989.

11. 1,1'-(4-Cyclopropyl-3-(4-methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2,2-diyl) diethanone (3c)



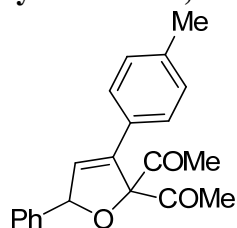
The reaction of **1a** (40.8 mg, 0.2 mmol), **2c** (69 mg, 0.4 mmol), 80 mg of 4Å MS and 5 mol % $\text{Sc}(\text{OTf})_3$ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 69 mg (92%) of **3c**, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.30-7.42 (m, 7 H), 6.88 (d, 2 H, $J = 7.6$ Hz), 5.73 (s, 1 H), 3.80 (s, 3 H), 2.32 (s, 3 H), 2.08 (s, 3 H), 1.40-1.45 (m, 1 H), 0.54-0.60 (m, 1 H), 0.40-0.50 (m, 2 H), 0.01-0.06 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 206.2, 205.2, 159.0, 142.6, 139.4, 133.3, 131.1, 128.9, 128.7, 128.0, 124.5, 113.5, 102.2, 90.1, 55.1, 26.9, 25.8, 9.3, 6.6, 5.9 ppm; IR (neat) ν (cm^{-1}) 3006, 2960, 2837, 1753, 1710, 1669, 1607, 1572, 1543, 1458, 1418, 1352, 1290, 1247, 1177, 1077, 1029; MS (70 eV): m/z (%): 376 (0.01) [M^+], 43 (100); HRMS calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4(\text{M})^+$: 376.1675, found: 376.1676.

12. 1,1'-(5-Phenyl-3-(thiophen-2-yl)-2,5-dihydrofuran-2,2-diyl)diethanone (3d)



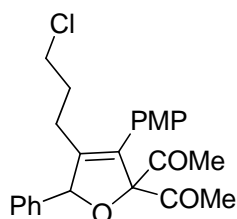
The reaction of **1a** (40.8 mg, 0.2 mmol), **2d** (44 mg, 0.4 mmol), 80 mg of 4Å MS and 5 mol % $\text{Sc}(\text{OTf})_3$ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 55.8 mg (90%) of **3d**, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.30-7.39 (m, 5 H), 7.21-7.23 (m, 1 H), 7.06 (s, 1 H), 6.95 (d, 1 H, $J = 3.2$ Hz), 6.40 (s, 1 H), 6.10 (s, 1 H), 2.32 (s, 3 H), 2.17 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 205.8, 204.2, 138.9, 133.7, 133.3, 128.83, 128.78, 128.6, 128.0, 127.8, 127.2, 125.9, 100.8, 88.8, 26.4, 25.6 ppm; IR (neat) ν (cm^{-1}) 3105, 3070, 3030, 2924, 2856, 1726, 1710, 1624, 1493, 1454, 1301, 1211, 1080, 1038, 1001; MS (70 eV): m/z (%): 312 (0.12) [M^+], 105 (100); HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{O}_3\text{S}(\text{M})^+$: 310.0820, found: 310.0817.

13. 1,1'-(5-Phenyl-3-p-tolyl-2,5-dihydrofuran-2,2-diyl)diethanone (3e).



The reaction of **1a** (40.8 mg, 0.2 mmol), **2e** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 43.5 mg (68%) of **3e**, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ_H 7.30-7.39 (m, 7 H), 7.11 (d, 2 H, *J* = 8.0 Hz), 6.50 (s, 1 H), 6.08 (s, 1 H), 2.32 (s, 6 H), 2.17 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 206.1, 204.8, 139.5, 139.2, 138.6, 129.1, 128.8, 128.6, 128.3, 127.6, 127.3, 126.4, 100.9, 88.7, 26.6, 25.9, 21.2 ppm; IR (neat) ν (cm⁻¹) 3031, 2921, 2861, 1710, 1672, 1605, 1512, 1475, 1451, 1415, 1352, 1251, 1071, 1028, 1002; MS (70 eV): *m/z* (%): 320 (0.90) [M⁺], 43 (100); HRMS calcd for C₂₁H₂₀O₃ (M)⁺: 320.1412, found: 320.1411.

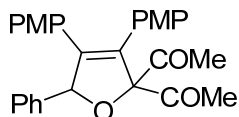
14. 1,1'-(4-(3-Chloropropyl)-3-(4-methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2,2-diyl)diethanone (3f)



The reaction of **1a** (40.8 mg, 0.2 mmol), **2f** (84 mg, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 79 mg (96%) of **3f**, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ_H 7.38-7.45 (m, 3 H), 7.35 (d, 2 H, *J* = 7.6 Hz), 7.15 (d, 2 H, *J* = 8.4 Hz), 6.87 (d, 2 H, *J* = 8.4 Hz), 5.90 (s, 1 H), 3.79 (s, 3 H), 3.26-3.36 (m, 2 H), 2.30-2.40 (m, 1 H), 2.33 (s, 3 H), 2.15 (s, 3 H), 1.89-1.99 (m, 1 H), 1.59-1.76 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 205.5, 204.7, 159.3, 141.8, 138.6, 134.4, 130.7, 129.1, 128.9, 127.9, 124.1, 113.7, 102.5, 90.8, 55.1, 43.9, 30.2, 26.9, 26.1, 23.6 ppm; IR (neat) ν (cm⁻¹) 3004, 2956, 2837, 1711, 1670, 1608, 1572, 1510, 1444, 1353, 1247, 1177, 1109, 1071, 1029; MS (70 eV): *m/z* (%): 412 (0.09) [M⁺], 43 (100); HRMS calcd for C₂₄H₂₅O₄Cl (M)⁺: 412.1441, found: 412.1439.

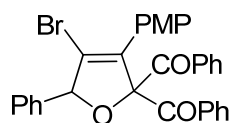
15. 1,1'-(3,4-Bis(4-methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2,2-diyl)diethanon

e (**3g**).



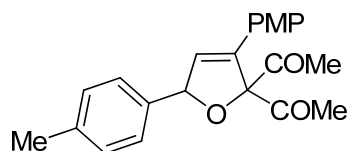
The reaction of **1a** (40.8 mg, 0.2 mmol), **2g** (96 mg, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 61 mg (69%) of **3g**, including 9% product with double bond migration. colorless oil. ¹H NMR (400 MHz, CDCl₃) δ_H 7.29-7.33 (m, 5 H), 7.20 (d, 2 H, $J = 8.4$ Hz), 6.93 (d, 2 H, $J = 8.0$ Hz), 6.78 (d, 2 H, $J = 8.4$ Hz), 6.59 (d, 2 H, $J = 8.4$ Hz), 6.36 (s, 1 H), 3.76 (s, 3 H), 3.65 (s, 3 H), 2.31 (s, 3 H), 2.11 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 206.0, 205.3, 159.2, 159.1, 140.1, 138.9, 133.1, 131.5, 130.2, 128.7, 128.3, 124.7, 113.8, 113.6, 102.9, 91.2, 55.0, 55.0, 27.0, 25.8 ppm; IR (neat) ν (cm⁻¹) 3063, 3004, 2837, 1710, 1671, 1606, 1572, 1509, 1458, 1417, 1352, 1291, 1247, 1178, 1107, 1080, 1029; MS (70 eV): m/z (%): 442 (0.23) [M⁺], 43 (100); HRMS calcd for C₂₈H₂₆O₅ (M)⁺: 442.1780, found: 442.1783.

16. (4-Bromo-3-(4-methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2,2-diyl)bis(phenylmethanone) (3h)



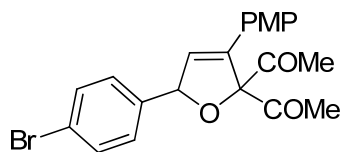
The reaction of **1b** (81.2 mg, 0.2 mmol), **2h** (84 mg, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Ni(ClO₄)₂·6H₂O (0.01 mmol, 3.6 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 100 mg (82%) of **3h**. ¹H NMR (400 MHz, CDCl₃) δ_H 7.96-7.99 (m, 2 H), 7.85-7.88 (m, 2 H), 7.57 (t, 1 H, $J = 7.6$ Hz), 7.46 (t, 2 H, $J = 7.2$ Hz), 7.21-7.41 (m, 10 H), 6.85 (d, 2 H, $J = 8.0$ Hz), 6.05 (s, 1 H), 3.74 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 196.8, 195.2, 159.7, 138.7, 136.7, 135.5, 134.4, 133.4, 132.8, 131.2, 129.8, 129.2, 129.1, 128.7, 128.6, 128.4, 128.2, 123.3, 122.5, 113.6, 101.7, 91.7, 55.1 ppm; IR (neat) ν (cm⁻¹) 3064, 2953, 2836, 1690, 1597, 1509, 1446, 1248, 1178, 1125, 1052, 1029; MS (70 eV): m/z (%): 538 (0.40) [M⁺], 540 (0.43) [M⁺+2], 77 (100); HRMS calcd for C₃₁H₂₃O₄Br (M)⁺: 538.0780, found: 538.0783.

17. 1,1'-(3-(4-Methoxyphenyl)-5-p-tolyl-2,5-dihydrofuran-2,2-diyl)diethanone (3i)



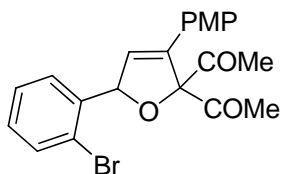
The reaction of **1c** (43.6 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 67.4 mg (97%) of **3i**, yellow solid, m.p. 43-45 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 7.37 (d, 2 H, *J* = 7.6 Hz), 7.17-7.24 (m, 4 H), 6.83 (d, 2 H, *J* = 7.2 Hz), 6.41 (s, 1 H), 6.04 (s, 1 H), 3.78 (s, 3 H), 2.35 (s, 3 H), 2.31 (s, 3 H), 2.16 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 206.4, 205.1, 159.7, 138.9, 138.6, 136.3, 129.4, 129.0, 127.5, 127.3, 123.7, 113.7, 100.8, 88.6, 55.2, 26.6, 25.8, 21.1 ppm; IR (neat) ν (cm⁻¹) 3006, 2936, 2839, 1753, 1710, 1667, 1607, 1573, 1482, 1420, 1382, 1292, 1181, 1075, 1030; MS (70 eV): *m/z* (%): 350 (0.75) [M⁺], 43 (100); HRMS calcd for C₂₂H₂₂O₄(M)⁺: 350.1518, found: 350.1516.

18. 1,1'-(5-(4-bromophenyl))-3-(4-methoxyphenyl)-2,5-dihydrofuran-2,2-diyl)diet hanone (3j)



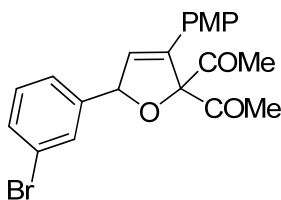
The reaction of **1d** (56.4 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 81.4 mg (98%) of **3j**, white solid, m.p. 104-106 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 7.51 (d, 2 H, *J* = 6.8 Hz), 7.36 (d, 2 H, *J* = 7.2 Hz), 7.21 (d, 2 H, *J* = 7.2 Hz), 6.83 (d, 2 H, *J* = 7.6 Hz), 6.40 (s, 1 H), 6.04 (s, 1 H), 3.78 (s, 3 H), 2.31 (s, 3 H), 2.16 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 206.1, 204.6, 159.9, 139.4, 138.3, 131.9, 129.1, 128.9, 126.7, 123.3, 122.7, 113.7, 100.9, 87.9, 55.2, 26.6, 25.8 ppm; IR (neat) ν (cm⁻¹) 3397, 3083, 2945, 2844, 1727, 1706, 1605, 1571, 1511, 1489, 1417, 1352, 1223, 1184, 1072, 1026, 1010; MS (70 eV): *m/z* (%): 414 (0.29) [M⁺], 416 (0.27) [M⁺+2], 43 (100); HRMS calcd for C₂₁H₁₉O₄Br (M)⁺: 414.0467, found: 414.0463.

19. 1,1'-(5-(2-Bromophenyl))-3-(4-methoxyphenyl)-2,5-dihydrofuran-2,2-diyl)diet hanone (3k).



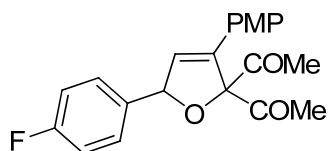
The reaction of **1e** (56.4 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 10 mol % Sc(OTf)₃ (0.02 mmol, 9.8 mg) in DCE (2 mL) was carried out at r.t. for 12 hours to afford 78 mg (95%) of **3k**, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ_H 7.60 (d, 1 H, *J* = 8.0 Hz), 7.29-7.38 (m, 4 H), 7.19 (t, 1 H, *J* = 7.2 Hz), 6.82 (d, 2 H, *J* = 8.4 Hz), 6.52 (s, 1 H), 6.48 (s, 1 H), 3.78 (s, 3 H), 2.36 (s, 3 H), 2.22 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 206.4, 204.2, 159.8, 139.1, 138.3, 133.0, 129.9, 129.1, 128.1, 127.9, 126.5, 123.5, 122.6, 113.7, 101.0, 87.3, 55.2, 26.7, 25.9 ppm; IR (neat) ν (cm⁻¹) 3068, 3005, 2934, 2837, 1711, 1607, 1571, 1512, 1465, 1439, 1352, 1255, 1217, 1183, 1118, 1077, 1027; MS (70 eV): *m/z* (%): 414 (0.18) [M⁺], 416 (0.17) [M⁺+2], 43 (100); HRMS calcd for C₂₁H₁₉O₄Br (M)⁺: 414.0467, found: 414.0466.

**20. 1,1'-(5-(3-Bromophenyl)-3-(4-methoxyphenyl)-2,5-dihydrofuran-2,2-diyl)diet
hanone (3l)**



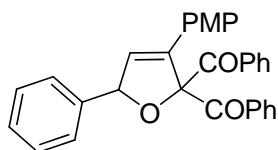
The reaction of **1f** (56.4 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 69.9 mg (85%) of **3l**, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ_H 7.47-7.50 (m, 2 H), 7.36 (d, 2 H, *J* = 7.2 Hz), 7.26 (s, 2 H), 6.83 (d, 2 H, *J* = 7.6 Hz), 6.40 (s, 1 H), 6.03 (s, 1 H), 3.78 (s, 3 H), 2.31 (s, 3 H), 2.18 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 205.9, 204.5, 159.9, 141.6, 139.5, 131.7, 130.4, 130.3, 129.1, 126.5, 125.6, 123.3, 122.8, 113.8, 101.0, 87.8, 55.2, 26.6, 25.9 ppm; IR (neat) ν (cm⁻¹) 3066, 3006, 2932, 1710, 1607, 1569, 1513, 1471, 1439, 1357, 1254, 1183, 1096, 1078, 1026; MS (70 eV): *m/z* (%): 414 (0.15) [M⁺], 416 (0.14) [M⁺+2], 43 (100); HRMS calcd for C₂₁H₁₉O₄Br (M)⁺: 414.0467, found: 414.0468.

**21. 1,1'-(5-(4-Fluorophenyl)-3-(4-methoxyphenyl)-2,5-dihydrofuran-2,2-diyl)diet
hanone (3m)**



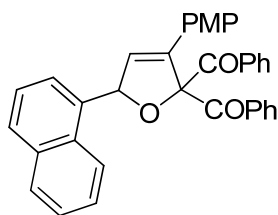
The reaction of **1a** (44.4 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 3 hours to afford 63.7 mg (90%) of **3m**, white solid, m.p. 76-78 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 7.37 (d, 2 H J = 7.6 Hz), 7.29-7.33 (m, 2 H), 7.07 (t, 2 H, J = 7.6 Hz), 6.84 (d, 2 H, J = 8.0 Hz), 6.41 (s, 1 H), 6.07 (s, 1 H), 3.80 (s, 3 H), 2.31 (s, 3 H), 2.16 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 206.3, 204.8, 162.9 (d, ¹ J_{C-F} = 246 Hz), 159.9, 139.3, 135.2, 129.2 (d, ² J_{C-F} = 9 Hz), 127.0, 123.5, 115.7 (d, ³ J_{C-F} = 21 Hz), 113.8, 100.9, 88.0, 55.2, 26.6, 25.8 ppm; IR (neat) ν (cm⁻¹) 2839, 1712, 1607, 1510, 1421, 1353, 1257, 1221, 1184, 1158, 1075, 1033; MS (70 eV): m/z (%): 354 (0.65) [M⁺], 43 (100); HRMS calcd for C₂₁H₁₉O₄F (M)⁺: 354.1267, found: 354.1268.

22. (3-(4-Methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2,2-diyl)bis(phenylmethanone) (**3n**)



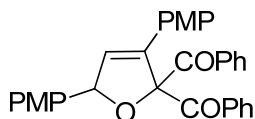
The reaction of **1b** (81.2 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 2 hours to afford 85.5 mg (93%) of **3n**, white solid, m.p. 68-70 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 8.01 (d, 2 H, J = 7.6 Hz), 7.92 (d, 2 H, J = 8.0 Hz), 7.54 (t, 1 H, J = 7.6 Hz), 7.39-7.48 (m, 5 H), 7.20-7.30 (m, 7 H), 6.80 (d, 2 H, J = 8.0 Hz), 6.53 (s, 1 H), 6.17 (s, 1 H), 3.71 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 198.5, 196.4, 159.7, 141.4, 138.8, 135.9, 134.7, 133.0, 132.6, 130.0, 129.7, 129.2, 128.49, 128.45, 128.3, 128.0, 127.1, 124.3, 113.6, 101.6, 88.9, 55.1 ppm; IR (neat) ν (cm⁻¹) 3058, 3029, 2936, 2836, 1782, 1728, 1689, 1598, 1577, 1511, 1448, 1419, 1254, 1180, 1118, 1066, 1028; MS (70 eV): m/z (%): 460 (1.20) [M⁺], 105 (100); HRMS calcd for C₃₁H₂₄O₄ (M)⁺: 460.1675, found: 460.1676.

23. (3-(4-Methoxyphenyl)-5-(naphthalen-1-yl)-2,5-dihydrofuran-2,2-diyl)bis(phenylmethanone) (**3o**)



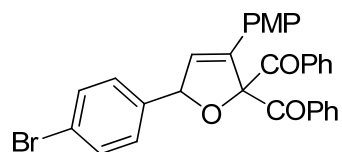
The reaction of **1h** (75.6 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 2 hours to afford 91.8 mg (90%) of **3o**, white solid, m.p. 190-192 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 8.10 (d, 2 H, J = 7.6 Hz), 8.05 (d, 1 H, J = 7.2 Hz), 7.87 (d, 2 H, J = 7.2 Hz), 7.82 (d, 1 H, J = 6.8 Hz), 7.76 (d, 1 H, J = 7.6 Hz), 7.58 (t, 1 H, J = 7.2 Hz), 7.43-7.51 (m, 7 H), 7.32-7.38 (m, 2 H), 7.18 (t, 2 H, J = 7.6 Hz), 6.87 (s, 1 H), 6.82 (d, 3 H, J = 4.8 Hz), 3.75 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 197.7, 196.9, 159.7, 142.6, 135.7, 134.9, 134.2, 133.7, 133.0, 132.6, 130.9, 129.9, 129.7, 129.6, 128.9, 128.7, 128.4, 127.9, 127.2, 126.3, 125.7, 125.2, 124.6, 124.1, 123.3, 113.7, 101.3, 85.0, 55.2 ppm; IR (neat) ν (cm⁻¹) 3390, 2934, 2361, 1749, 1684, 1602, 1510, 1446, 1366, 1285, 1255, 1182, 1111, 1074, 1028; MS (70 eV): m/z (%): 510 (1.10) [M⁺], 105 (100); HRMS calcd for C₃₅H₂₆O₄ (M)⁺: 530.1831, found: 530.1823.

24. (3,5-Bis(4-methoxyphenyl)-2,5-dihydrofuran-2,2-diyl)bis(phenylmethanone) (**3p**)



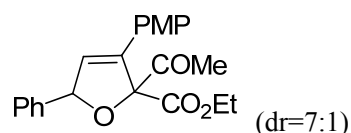
The reaction of **1i** (40.8 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 2 hours to afford 91.6 mg (94%) of **3p**, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ_H 8.01 (d, 2 H, J = 7.6 Hz), 7.91 (d, 2 H, J = 7.6 Hz), 7.55 (t, 1 H, J = 7.2 Hz), 7.39-7.48 (m, 5 H), 7.28 (t, 2 H, J = 7.2 Hz), 7.18 (d, 2 H, J = 8.0 Hz), 6.76-6.83 (m, 4 H), 6.50 (s, 1 H), 6.12 (s, 1 H), 3.74 (s, 3 H), 3.71 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 198.6, 196.6, 159.7, 141.4, 136.0, 134.8, 133.0, 132.6, 130.9, 130.0, 129.8, 129.2, 128.8, 128.5, 128.0, 124.4, 113.9, 113.6, 101.4, 88.7, 55.2, 55.1 ppm; IR (neat) ν (cm⁻¹) 3067, 3003, 2933, 2836, 1771, 1688, 1607, 1510, 1446, 1249, 1176, 1116, 1065, 1029; MS (70 eV): m/z (%): 490 (1.40) [M⁺], 105 (100); HRMS calcd for C₃₂H₂₆O₅ (M)⁺: 490.1780, found: 490.1783.

25. (5-(4-Bromophenyl)-3-(4-methoxyphenyl)-2,5-dihydrofuran-2,2-diyl)bis(phenylmethanone) (3q)



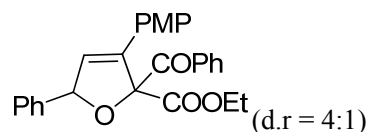
The reaction of **1j** (40.8 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 2 hours to afford 101 mg (94%) of **3q**, white solid, m.p. 72-74 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 7.99 (d, 2 H, $J = 7.6$ Hz), 7.88 (d, 2 H, $J = 7.6$ Hz), 7.56 (t, 1 H, $J = 7.2$ Hz), 7.42-7.47 (m, 5 H), 7.36 (d, 2 H, $J = 7.6$ Hz), 7.30 (t, 2 H, $J = 7.6$ Hz), 7.10 (d, 2 H, $J = 8.0$ Hz), 6.81 (d, 2 H, $J = 8.0$ Hz), 6.49 (s, 1 H), 6.12 (s, 1 H), 3.74 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ_C 198.3, 196.4, 159.8, 141.9, 137.9, 135.9, 134.6, 133.1, 132.8, 131.7, 129.9, 129.8, 129.1, 128.8, 128.5, 128.1, 127.5, 124.1, 122.4, 113.7, 101.5, 88.2, 55.2 ppm; IR (neat) ν (cm⁻¹) 3063, 2958, 2837, 1781, 1689, 1598, 1511, 1488, 1447, 1409, 1253, 1180, 1117, 1067, 1028, 1010; MS (70 eV): m/z (%): 538 (0.07) [M⁺], 540 (0.09) [M⁺+2], 105 (100); HRMS calcd for C₃₁H₂₃O₄Br (M)⁺: 538.0780, found: 538.0778.

26. Ethyl 2-acetyl-3-(4-methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2-carboxylate (3r)



The reaction of **1k** (46.8 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 4 hours to afford 68 mg (93%) of **3r** (dr=7:1), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ_H 7.44 (d, 2 H, $J = 7.6$ Hz), 7.30-7.40 (m, 5 H), 6.84 (d, 2 H, $J = 7.2$ Hz), 6.40 (s, 1 H), 6.11 (s, 1 H), 4.26 (q, 2 H, $J_1 = 7.2$ Hz, $J_2 = 7.2$ Hz), 3.79 (s, 3 H), 2.25 (s, 3 H), 1.24 (t, 3 H, $J = 6.8$ Hz); ¹³C NMR (100 MHz, CDCl₃) δ_C 203.0, 169.3, 159.7, 139.2, 129.2, 129.1, 128.6, 128.44, 128.38, 127.2, 123.9, 113.6, 96.9, 88.5, 61.9, 55.2, 26.1, 13.9 ppm; IR (neat) ν (cm⁻¹) 3064, 3033, 2936, 2838, 1721, 1608, 1576, 1541, 1454, 1420, 1353, 1253, 1182, 1097, 1030; MS (70 eV): m/z (%): 366 (0.61) [M⁺], 43 (100); HRMS calcd for C₂₂H₂₂O₅ (M)⁺: 366.1467, found: 366.1470.

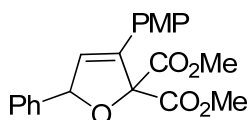
27. Ethyl 2-benzoyl-3-(4-methoxyphenyl)-5-phenyl-2,5-dihydrofuran-2-carboxylate (3s)



The reaction of **11** (59.2 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 4 hours to afford 72.7 mg (85%) of **3s** (d r = 4:1), Major isomer: yellow solid, m.p. 58-60 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 8.04 (d, 2 H, $J = 8.0$ Hz), 7.50 (t, 3 H, $J = 8.4$ Hz), 7.37 (t, 2 H, $J = 7.6$ Hz), 7.19-7.24 (m, 5 H), 6.84 (d, 2 H, $J = 8.4$ Hz), 6.38 (s, 1 H), 6.26 (s, 1 H), 4.10 (q, 2 H, $J_1 = 6.8$ Hz, $J_2 = 6.0$ Hz), 3.78 (s, 3 H), 0.99 (t, 3 H, $J = 7.6$ Hz); ¹³C NMR (100 MHz, CDCl₃) δ_C 193.4, 170.3, 159.6, 139.5, 138.8, 134.9, 132.9, 129.8, 129.6, 129.5, 128.5, 128.2, 127.0, 124.4, 113.4, 96.3, 89.6, 61.8, 55.2, 13.7 ppm; IR (neat) ν (cm⁻¹) 3063, 2981, 2935, 2838, 1748, 1728, 1690, 1606, 1512, 1450, 1367, 1254, 1224, 1183, 1118, 1075, 1029, 1002; MS (70 eV): m/z (%): 428 (1.99) [M⁺], 77 (100);

Minor isomer: white solid, m.p. 145-147 °C. HRMS calcd for C₂₇H₂₄O₅ (M)⁺: 428.1624, found: 428.1619. ¹H NMR (400 MHz, CDCl₃) δ_H 8.08 (d, 2 H, $J = 7.6$ Hz), 7.61 (d, 2 H, $J = 7.6$ Hz), 7.53 (t, 1 H, $J = 7.6$ Hz), 7.40-7.46 (m, 6 H), 7.33-7.38 (m, 1 H), 6.84 (d, 2 H, $J = 8.0$ Hz), 6.30 (s, 1 H), 5.97 (s, 1 H), 4.08 (q, 2 H, $J_1 = 7.2$ Hz, $J_2 = 7.2$ Hz), 3.80 (s, 3 H), 0.98 (t, 3 H, $J = 7.2$ Hz); ¹³C NMR (100 MHz, CDCl₃) δ_C 194.1, 169.6, 159.7, 139.9, 139.5, 135.1, 133.0, 130.0, 129.8, 129.5, 128.6, 128.5, 128.3, 127.5, 124.5, 113.4, 97.0, 88.8, 61.8, 55.2, 13.6 ppm; IR (neat) ν (cm⁻¹) 3057, 3028, 2873, 1749, 1682, 1602, 1509, 1447, 1418, 1391, 1366, 1284, 1255, 1225, 1111, 1074, 1029; MS (70 eV): m/z (%): 428 (1.89) [M⁺], 105 (100); HRMS calcd for C₂₇H₂₄O₅ (M)⁺: 428.1624, found: 428.1629.

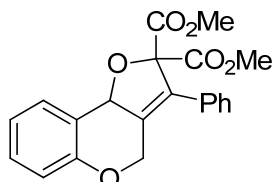
28. Dimethyl 3-(4-methoxyphenyl)-5-phenylfuran-2,2(5H)-dicarboxylate (3t)



The reaction of **1m** (47.2 mg, 0.2 mmol), **2a** (55 μ L, 0.4 mmol), 80 mg of 4Å MS and 5 mol % Sc(OTf)₃ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 2 hours to afford 39 mg (53%) of **3t**, white solid, m.p. 100-102 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 7.42-7.44 (m, 4 H), 7.31-7.39 (m, 3 H), 6.85 (d, 2 H, $J = 7.8$ Hz),

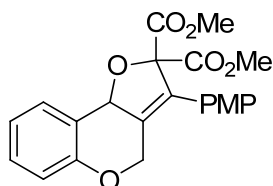
6.31 (s, 1 H), 6.10 (s, 1 H), 3.80 (s, 6 H), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 169.0, 168.4, 159.7, 139.3, 137.9, 129.6, 129.1, 128.5, 127.2, 123.7, 113.6, 93.4, 89.0, 55.2, 52.9 ppm; IR (neat) ν (cm^{-1}) 3081, 3037, 3011, 2988, 2962, 2842, 2565, 1744, 1730, 1605, 1511, 1361, 1259, 1105, 1053, 1024; MS (70 eV): m/z (%): 368 (3.55) [M^+], 105 (100); HRMS calcd for $\text{C}_{21}\text{H}_{20}\text{O}_6(\text{M})^+$: 368.1260, found: 368.1272.

29. Dimethyl 3-phenyl-2H-furo[3,2-c]chromene-2,2(4H,9bH)-dicarboxylate (7).



The reaction of **5** (73.2 mg, 0.2 mmol), 80 mg of 4Å MS and 5 mol % $\text{Sc}(\text{OTf})_3$ (0.01 mmol, 4.9 mg) in DCE (2 mL) was carried out at r.t. for 12 hours to afford 31.5 mg (43%) of **7**, white solid, m.p. 55-57 °C. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.48 (d, 1 H, $J = 7.2$ Hz), 7.36 (s, 3 H), 7.21-7.23 (m, 3 H), 6.99-7.03 (m, 1 H), 6.85 (d, 1 H, $J = 8.0$ Hz), 6.13 (s, 1 H), 4.87 (d, 1 H, $J = 13.2$ Hz), 4.80 (d, 1 H, $J = 13.2$ Hz), 3.80 (s, 3 H), 3.64 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 168.3, 167.3, 152.7, 136.2, 132.5, 131.0, 129.13, 129.06, 128.6, 128.3, 126.4, 124.8, 121.5, 116.7, 96.3, 81.6, 62.8, 52.9, 52.8 ppm; IR (neat) ν (cm^{-1}) 2954, 1739, 1609, 1580, 1484, 1461, 1435, 1258, 1220, 1198, 1129, 1111, 1075, 1036; MS (70 eV): m/z (%): 366 (4.01) [M^+], 115 (100); HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{O}_6(\text{M})^+$: 366.1103, found: 366.1105.

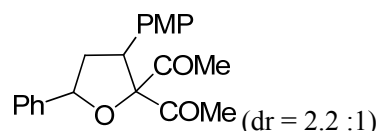
30. Dimethyl 3-(4-methoxyphenyl)-2H-furo[3,2-c]chromene-2,2(4H,9bH)-dicarboxylate (8).



The reaction of **6** (79.2 mg, 0.2 mmol), 80 mg of 4Å MS and 5 mol % $\text{Sc}(\text{OTf})_3$ (0.01 mmol, 4.9 mg) in DCM (2 mL) was carried out at r.t. for 12 hours to afford 60 mg (76%) of **7**, white solid, m.p. 69-71 °C. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.47 (d, 1 H, $J = 7.6$ Hz), 7.14-7.22 (m, 3 H), 7.00 (d, 1 H, $J = 7.2$ Hz), 6.83-6.90 (m, 3 H), 6.10 (s, 1 H), 4.88 (d, 1 H, $J = 13.2$ Hz), 4.82 (d, 1 H, $J = 13.2$ Hz), 3.82 (s, 3 H), 3.80 (s, 3 H), 3.65 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 168.5, 167.5, 159.8, 152.8, 135.2,

132.2, 130.8, 130.5, 129.1, 126.4, 125.0, 123.2, 121.5, 116.7, 113.8, 96.2, 81.5, 63.0, 55.2, 52.9 ppm; IR (neat) ν (cm^{-1}) 2954, 1740, 1608, 1579, 1512, 1484, 1459, 1249, 1221, 1181, 1153, 1130, 1110, 1074, 1033; MS (70 eV): m/z (%): 396 (23.15) [M^+], 249 (100); HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{O}_7$ (M) $^+$: 396.1209, found: 396.1211.

31. 1,1'-(3-(4-Methoxyphenyl)-5-phenyltetrahydrofuran-2,2-diyl)diethanone (**9**)

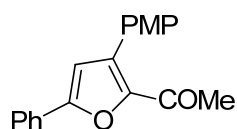


The reaction of **3a** (50.4 mg, 0.15 mmol), Pd/C(2.4 mg) in EtOAc (3 mL) was carried out in the presence of H_2 (balloon) at r.t. for 12 hours to afford 48 mg (95%) of **9** (dr = 2.2 :1), colorless oil. The major isomer: ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.30-7.40 (m, 5 H), 7.22 (d, 2 H, $J = 8.0$ Hz), 6.86 (d, 2 H, $J = 8.0$ Hz), 5.71 (t, 1 H, $J = 7.2$ Hz), 4.40-4.50 (m, 1 H), 3.79 (s, 3 H), 2.55-2.61 (m, 1 H), 2.30-2.40 (m, 1 H), 2.37 (s, 3 H), 1.79 (s, 3 H).

The minor isomer: ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.57 (d, 2 H, $J = 7.2$ Hz), 7.44 (t, 2 H, $J = 7.2$ Hz), 7.30-7.40 (m, 1 H), 7.17 (d, 2 H, $J = 8.0$ Hz), 6.80 (d, 2 H, $J = 8.0$ Hz), 4.92-4.97 (m, 1 H), 4.40-4.50 (m, 1 H), 3.76 (s, 3 H), 2.65-2.75 (m, 1 H), 2.30-2.40 (m, 1 H), 2.40 (s, 3 H), 1.91 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ_{C} 206.2, 204.1, 158.7, 141.1, 140.0, 130.7, 129.6, 129.5, 128.62, 128.55, 128.1, 127.9, 126.0, 125.9, 114.1, 113.8, 101.6, 98.9, 83.3, 81.2, 55.2, 55.1, 47.9, 47.8, 41.3, 40.6, 28.0, 27.1, 26.2, 26.1 ppm; IR (neat) ν (cm^{-1}) 2956, 2933, 2833, 1727, 1708, 1610, 1582, 1513, 1457, 1420, 1353, 1291, 1249, 1181, 1115, 1068, 1031; MS (70 eV): m/z (%): 338 (0.79) [M^+], 43 (100); HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4$ (M) $^+$: 338.1518, found: 338.1513.

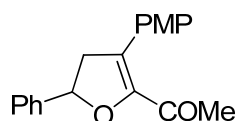
32. 1-(3-(4-Methoxyphenyl)-5-phenylfuran-2-yl)ethanone (**10**)



Method A: The reaction of **3a** (50.4 mg, 0.15 mmol), DDQ (1.5eq., 51 mg) in THF (1.5 mL) was carried out at r.t. for 20 hours to afford 37.2 mg (85%) of **10**. Method B: The reaction of **3a** (50.4 mg, 0.15 mmol), Cs_2CO_3 (1.0eq., 49 mg) in CH_3OH (3 mL) was refluxed for 12 hours to afford 36.8 mg (84%) of **10**. white solid, m.p. 115-117 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.81 (d, 2 H, $J = 7.2$ Hz), 7.69 (d, 2

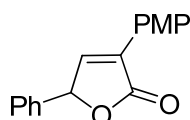
H, $J = 7.6$ Hz), 7.46 (t, 2 H, $J = 7.2$ Hz), 7.40 (t, 1 H, $J = 7.2$ Hz), 6.96 (d, 2 H, $J = 7.6$ Hz), 6.89 (s, 1 H), 3.85 (s, 3 H), 2.56 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 187.6, 159.9, 155.3, 146.0, 135.4, 130.6, 129.3, 128.9, 124.8, 124.1, 113.6, 109.8, 55.3, 27.6 ppm; IR (neat) ν (cm^{-1}) 2921, 2849, 1752, 1664, 1610, 1575, 1532, 1502, 1451, 1420, 1387, 1353, 1294, 1256, 1211, 1183, 1153, 1071, 1025; MS (70 eV): m/z (%): 292 (4.82) [M^+], 43 (100); HRMS calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3(\text{M})^+$: 292.1099, found: 292.1101.

33. 1-(3-(4-Methoxyphenyl)-5-phenyl-4,5-dihydrofuran-2-yl)ethanone (11)

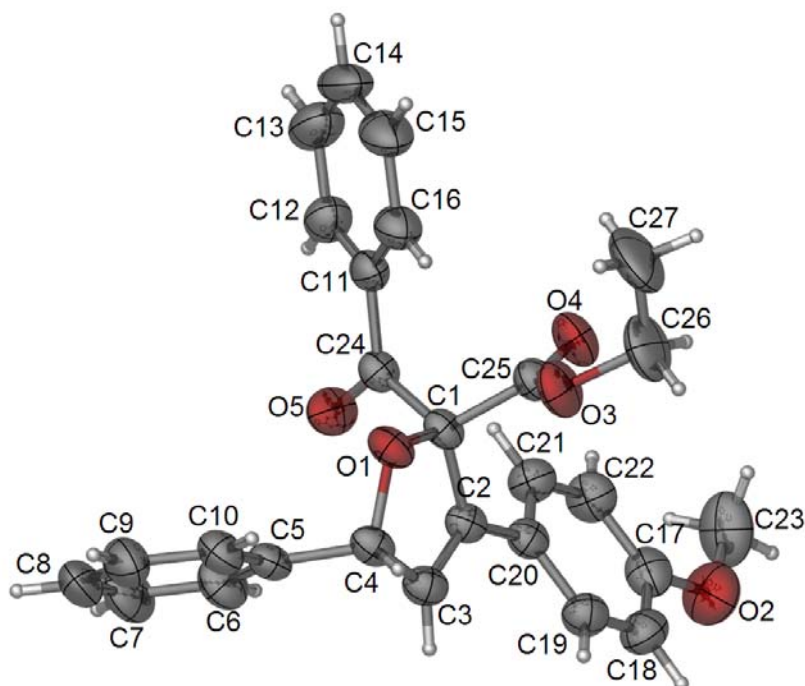


The reaction of **3a** (50.4 mg, 0.15 mmol), KOH (1.0 eq, 8.4mg) in CH_3OH (3 mL) was carried out at r.t. for 13 hours to afford 40 mg (90%) of **11**, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.54 (d, 2 H, $J = 7.6$ Hz), 7.39-7.50 (m, 4 H), 7.35 (d, 1 H, $J = 6.0$ Hz), 6.89 (d, 2 H, $J = 7.2$ Hz), 5.64 (t, 1 H, $J = 9.6$ Hz), 3.82 (s, 3 H), 3.54-3.62 (m, 1 H), 3.19-3.26 (m, 1 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 192.5, 159.4, 146.6, 141.9, 129.8, 128.6, 128.0, 125.6, 125.2, 122.7, 113.4, 80.1, 55.2, 44.9, 29.1 ppm; IR (neat) ν (cm^{-1}) 2960, 2934, 2838, 1720, 1688, 1604, 1511, 1455, 1420, 1356, 1295, 1253, 1221, 1179, 1133, 1111, 1028; MS (70 eV): m/z (%): 294 (0.73) [M^+], 43 (100); HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3(\text{M})^+$: 294.1256, found: 294.1248.

34. 3-(4-Methoxyphenyl)-5-phenylfuran-2(5H)-one (12)



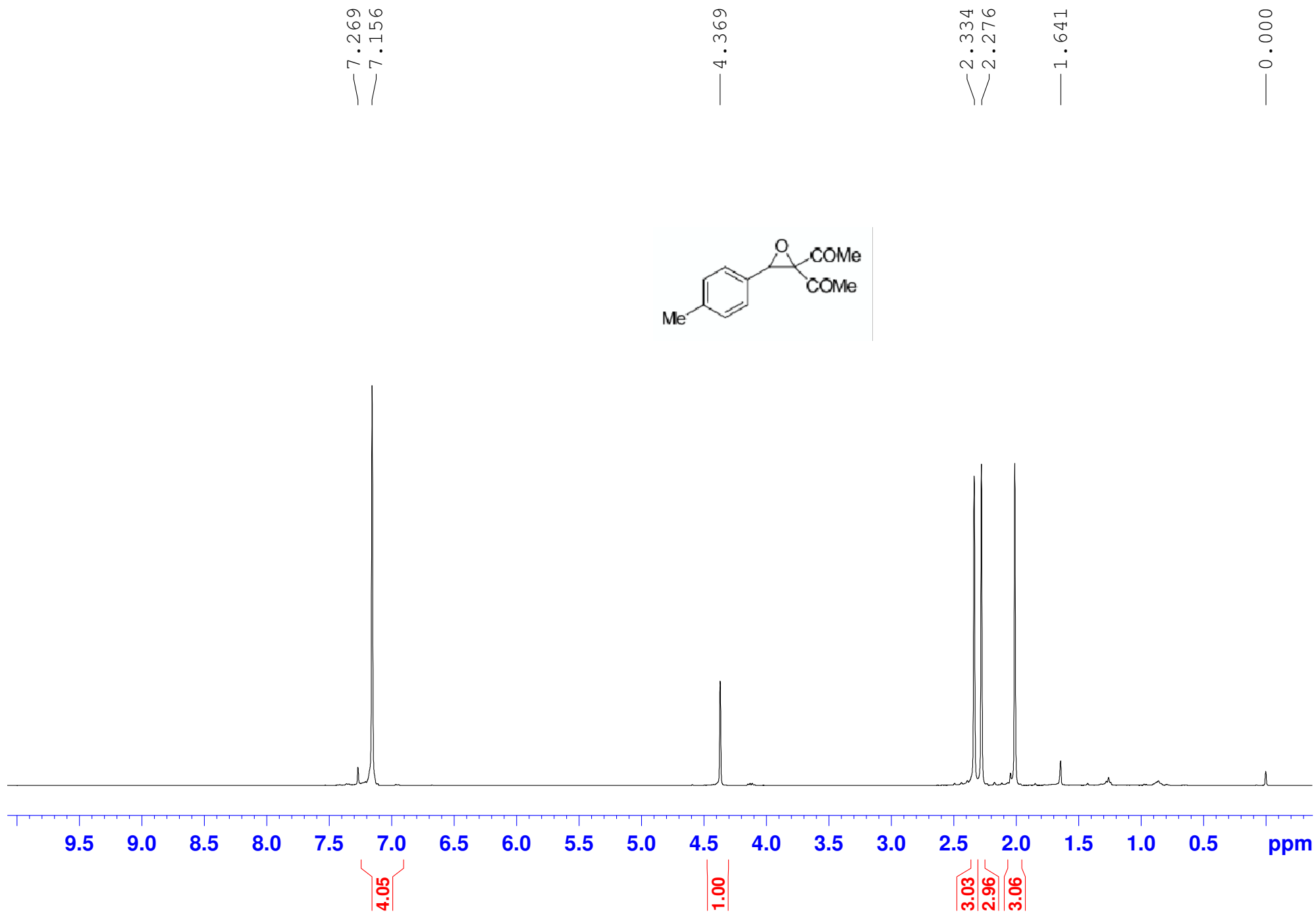
The reaction of **3a** (67.2 mg, 0.2 mmol), *m*-CPBA (0.6 mmol, 122 mg), NaHCO_3 (0.6 mmol, 52 mg) in DCM (2 mL) was carried out at r.t. for 8 hours to afford 23 mg (38%) of **12**, (PE:DCM:Et₂O = 3:2:0.1), white solid, m.p. 85-87 °C. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.87 (d, 2 H, $J = 8.4$ Hz), 7.50 (s, 1 H), 7.33-7.39 (m, 3 H), 7.32 (d, 2 H, $J = 5.2$ Hz), 6.94 (d, 2 H, $J = 8.4$ Hz), 6.00 (s, 1 H), 3.84 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 172.0, 160.5, 145.0, 135.1, 130.2, 129.2, 129.0, 128.5, 126.6, 121.8, 114.1, 81.5, 55.3 ppm; IR (neat) ν (cm^{-1}) 3095, 2953, 2833, 1737, 1608, 1574, 1511, 1438, 1333, 1308, 1267, 1236, 1182, 1127, 1058, 1039; MS (70 eV): m/z (%): 266 (3.64) [M^+], 43 (100); HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3(\text{M})^+$: 266.0493, found: 266.0491.

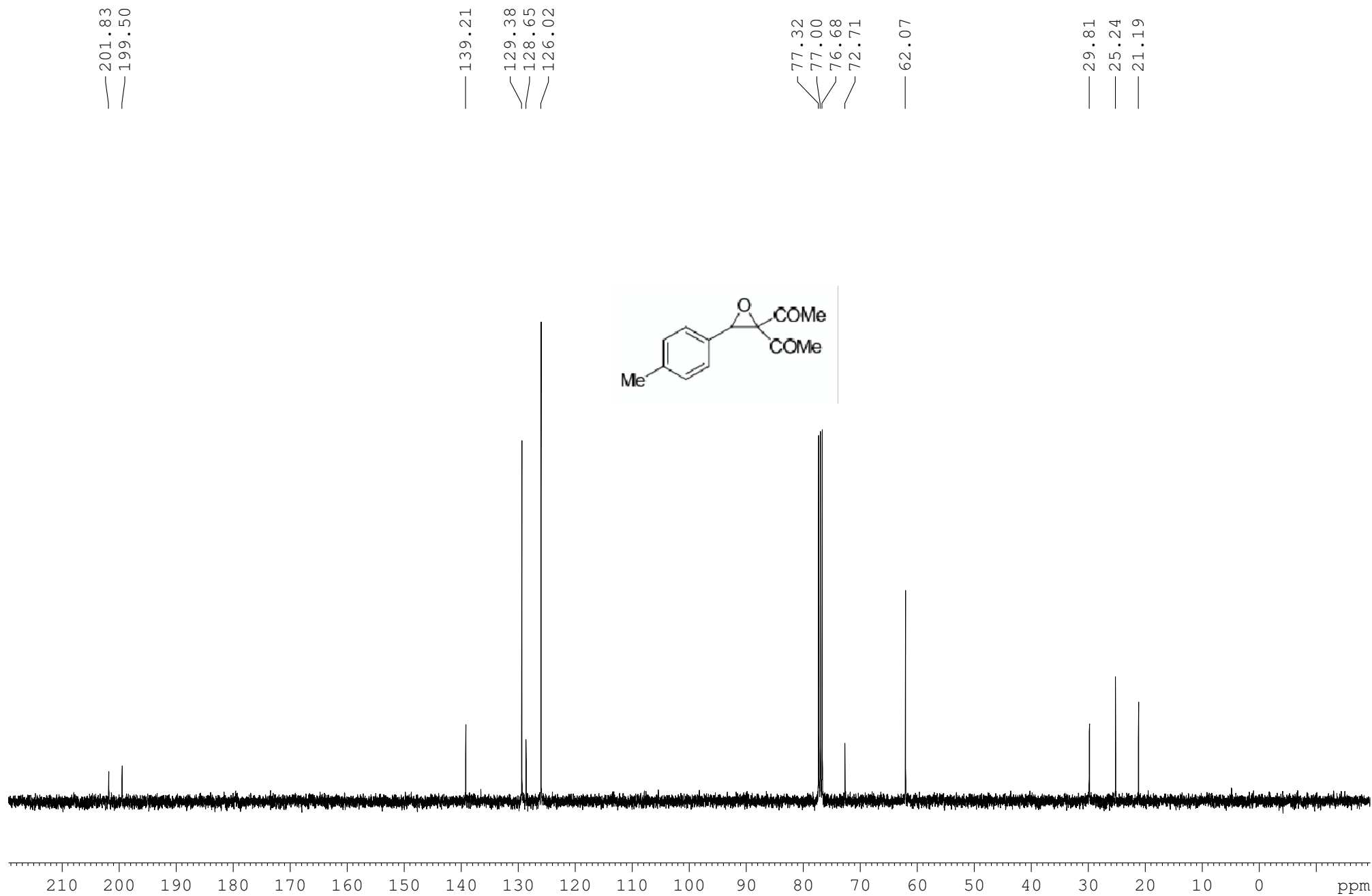


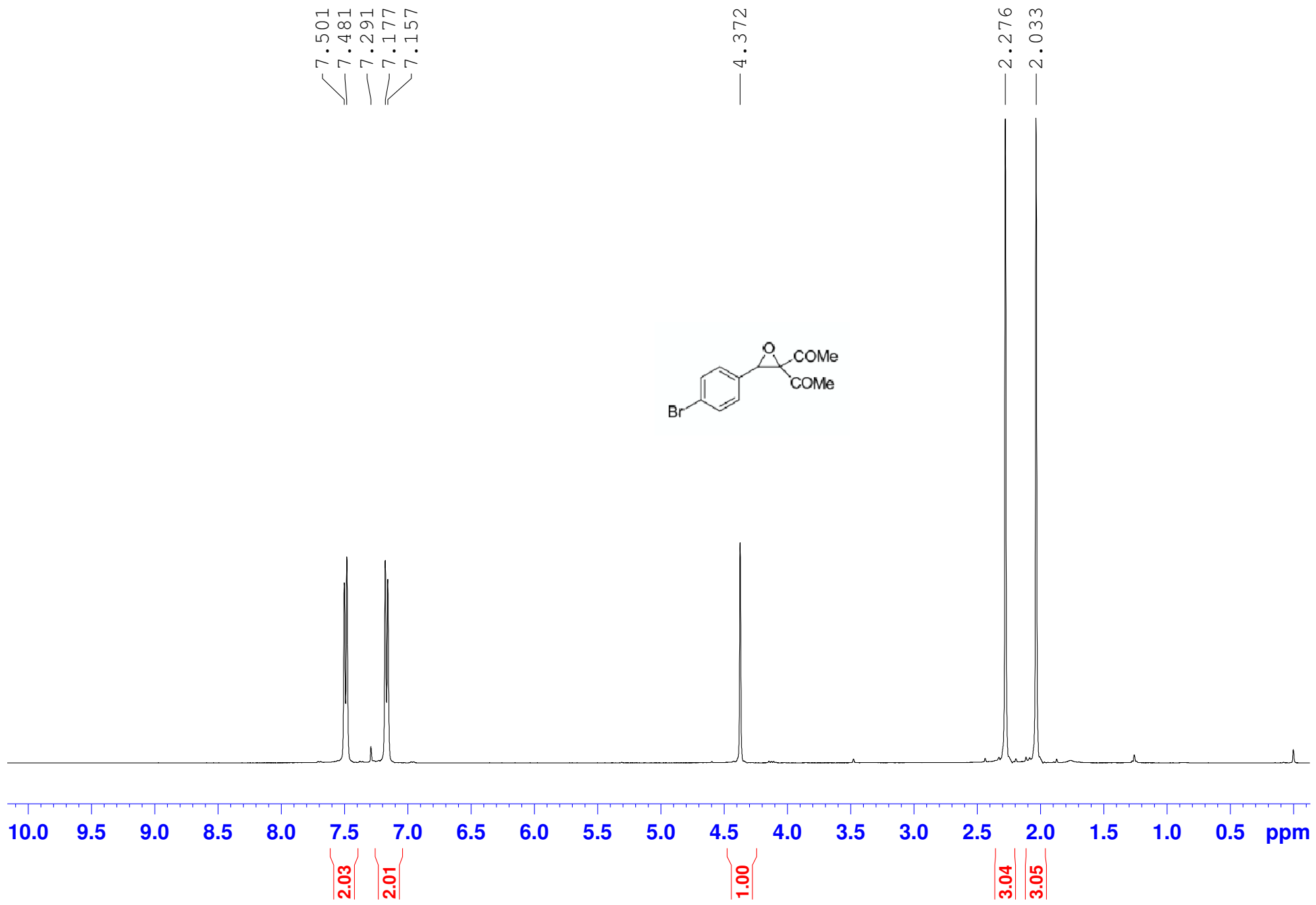
SI- Fig. 1. X-ray structure of the major product of **3s**.

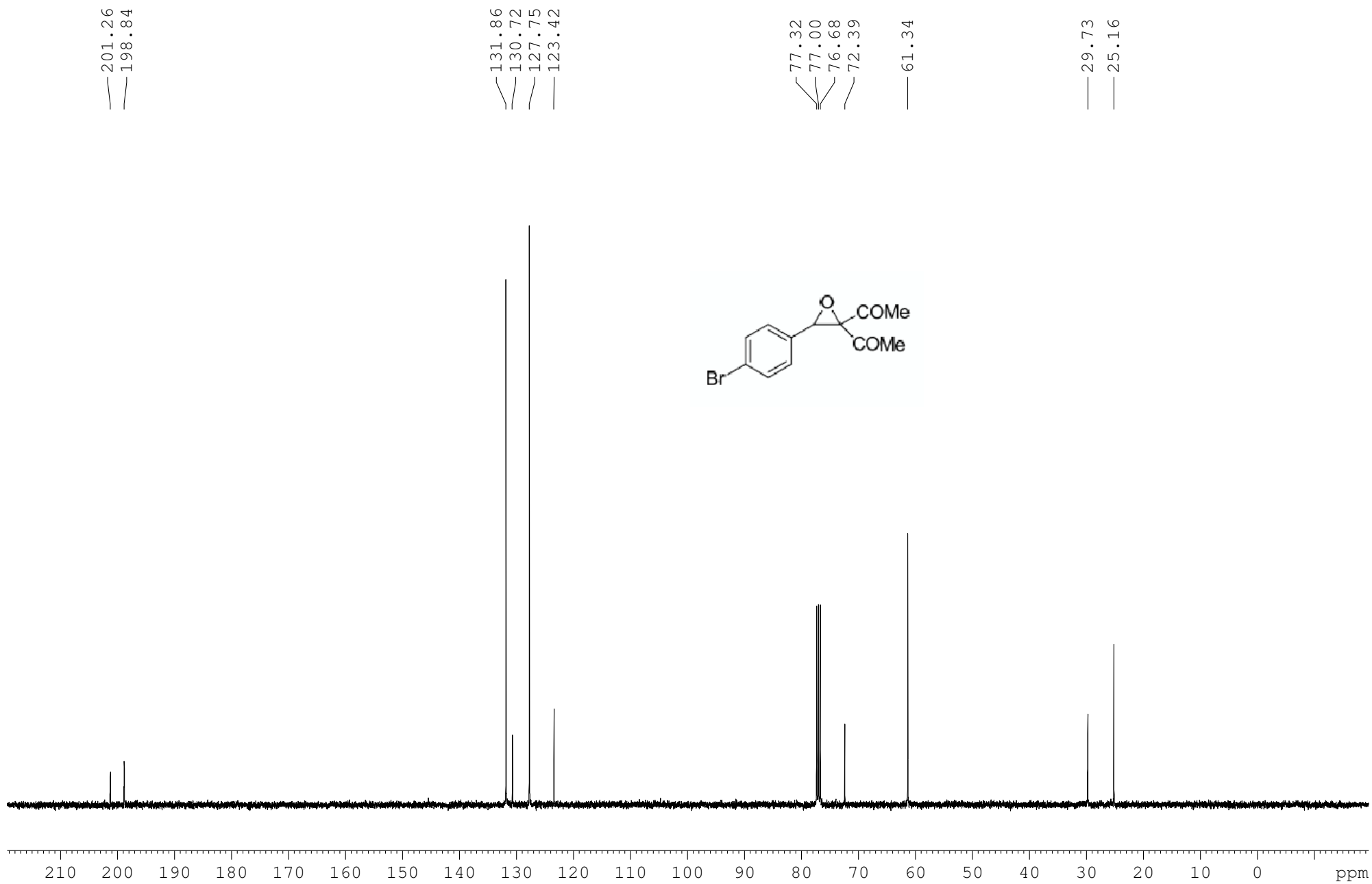
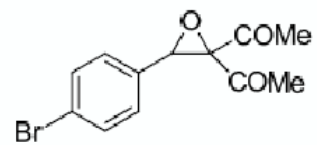
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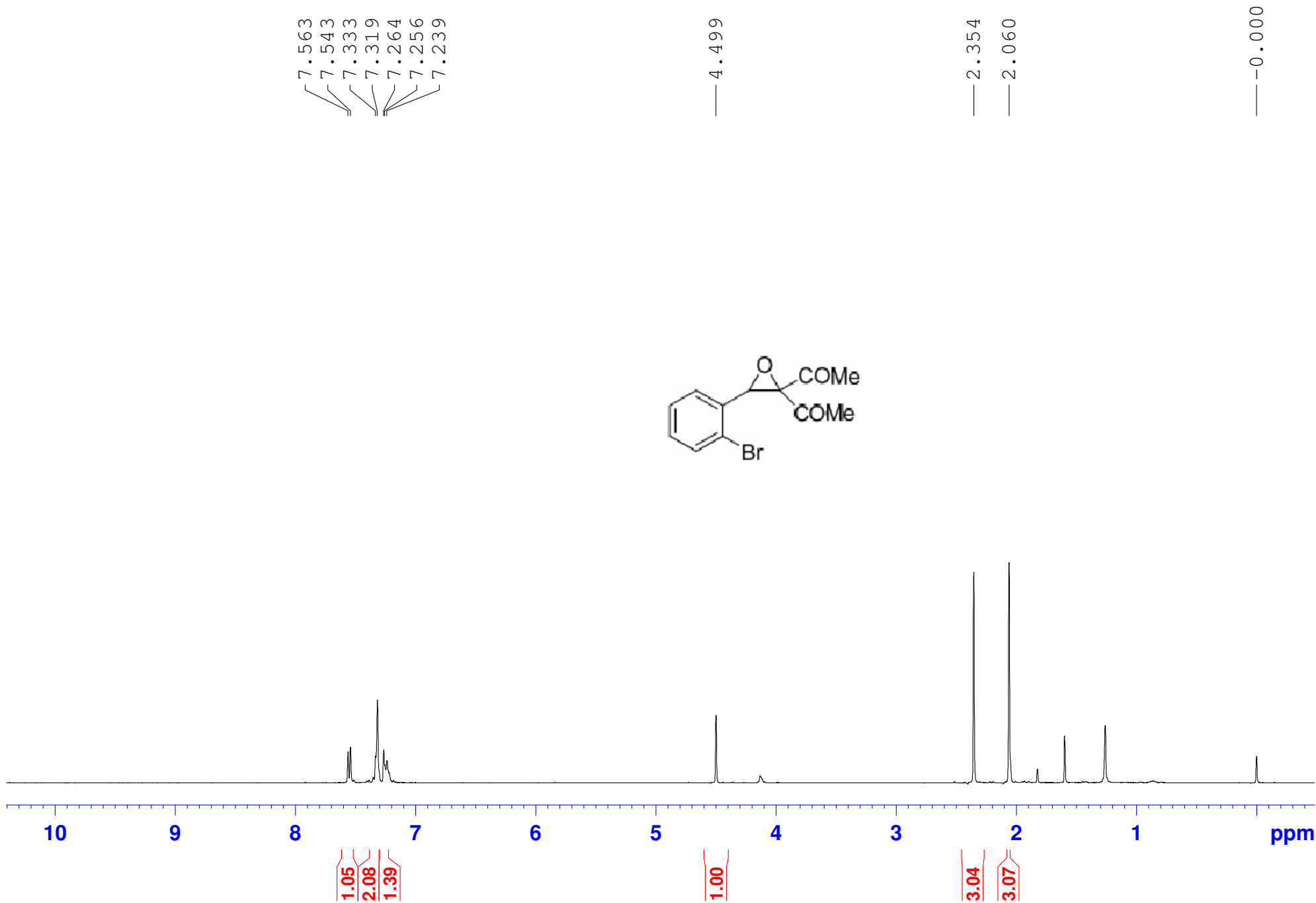
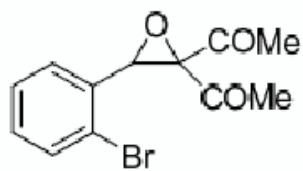
1. V.K. Yadav, K. K. Kapoor, *Tetrahedron* **1995**, *51*, 8573.
2. Z. Chen, L. Wei, J. Zhang, *Org. Lett.* **2011**, *13*, 1170.
3. B.-F. Sun, R. Hong, Y.-B. Kang, L.Deng, *J. Am. Chem. Soc* **2009**, *131*, 10384.
4. M. Ochiai, A. Nakanishi, T. Suefuji, *Org. Lett.* **2000**, *2*, 2923.

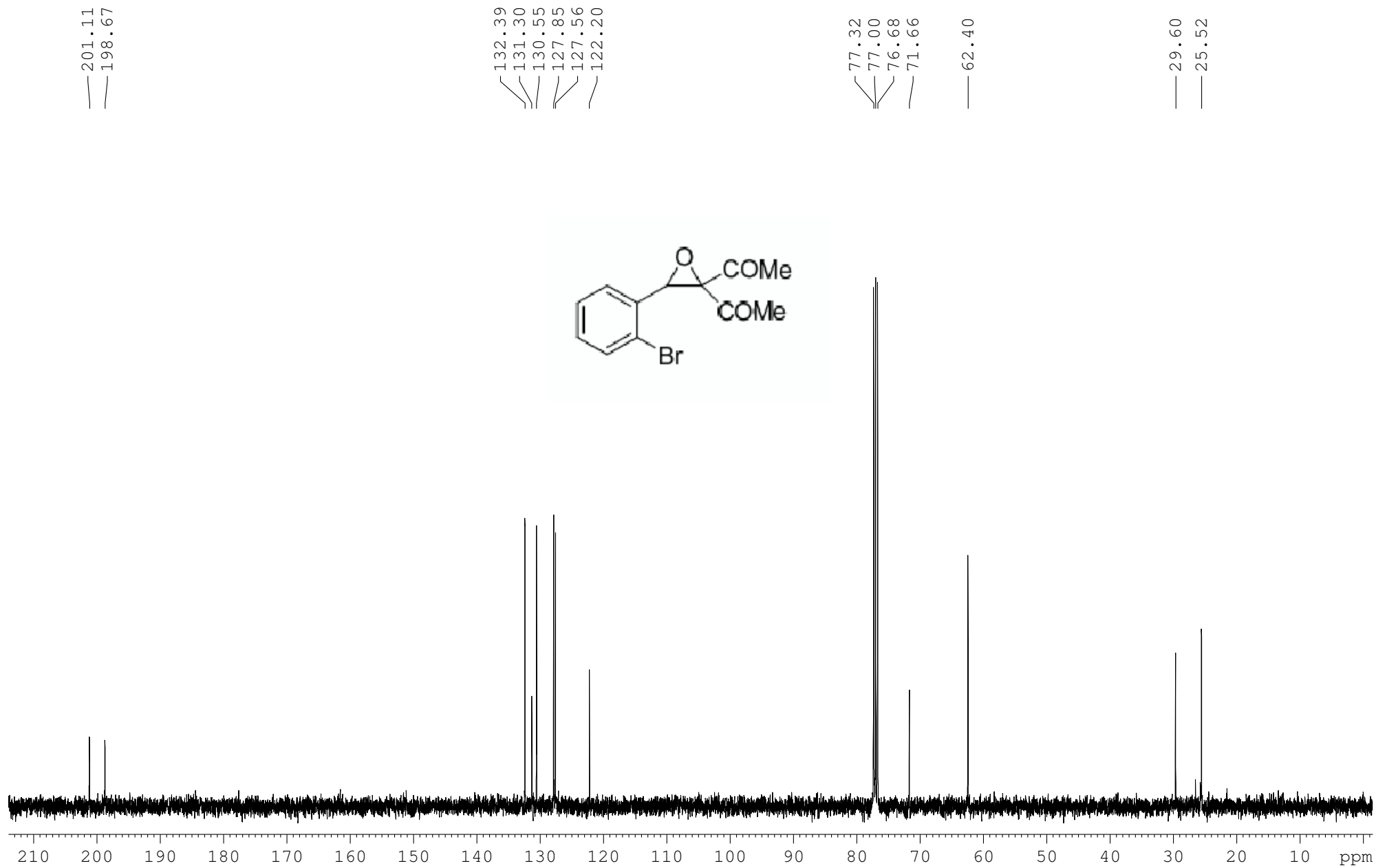










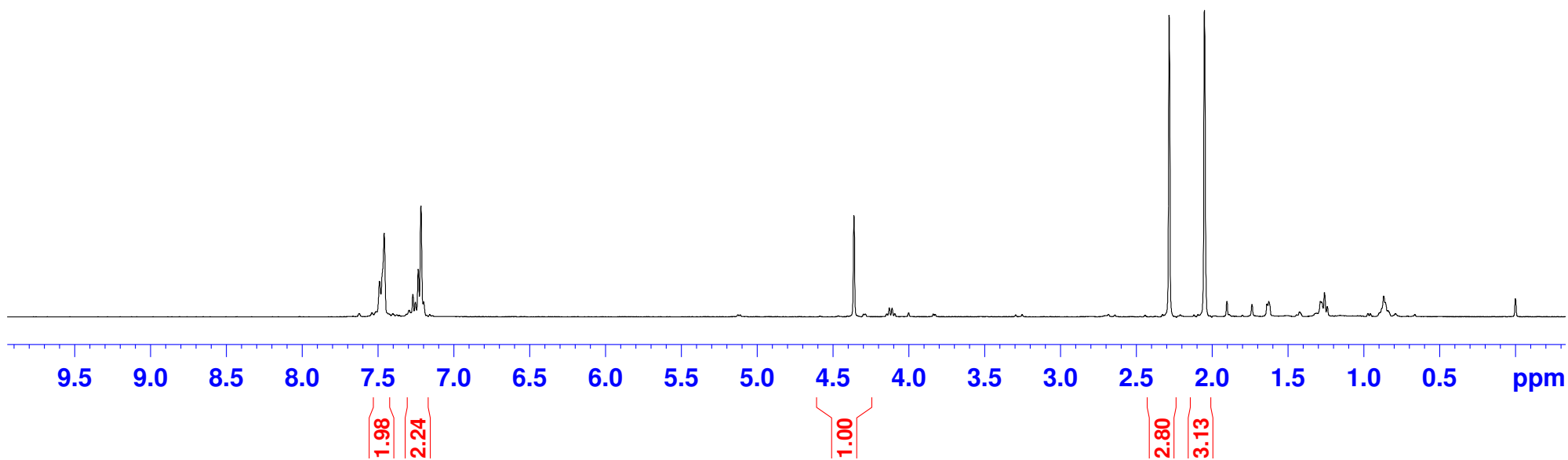
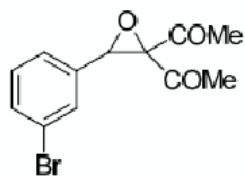


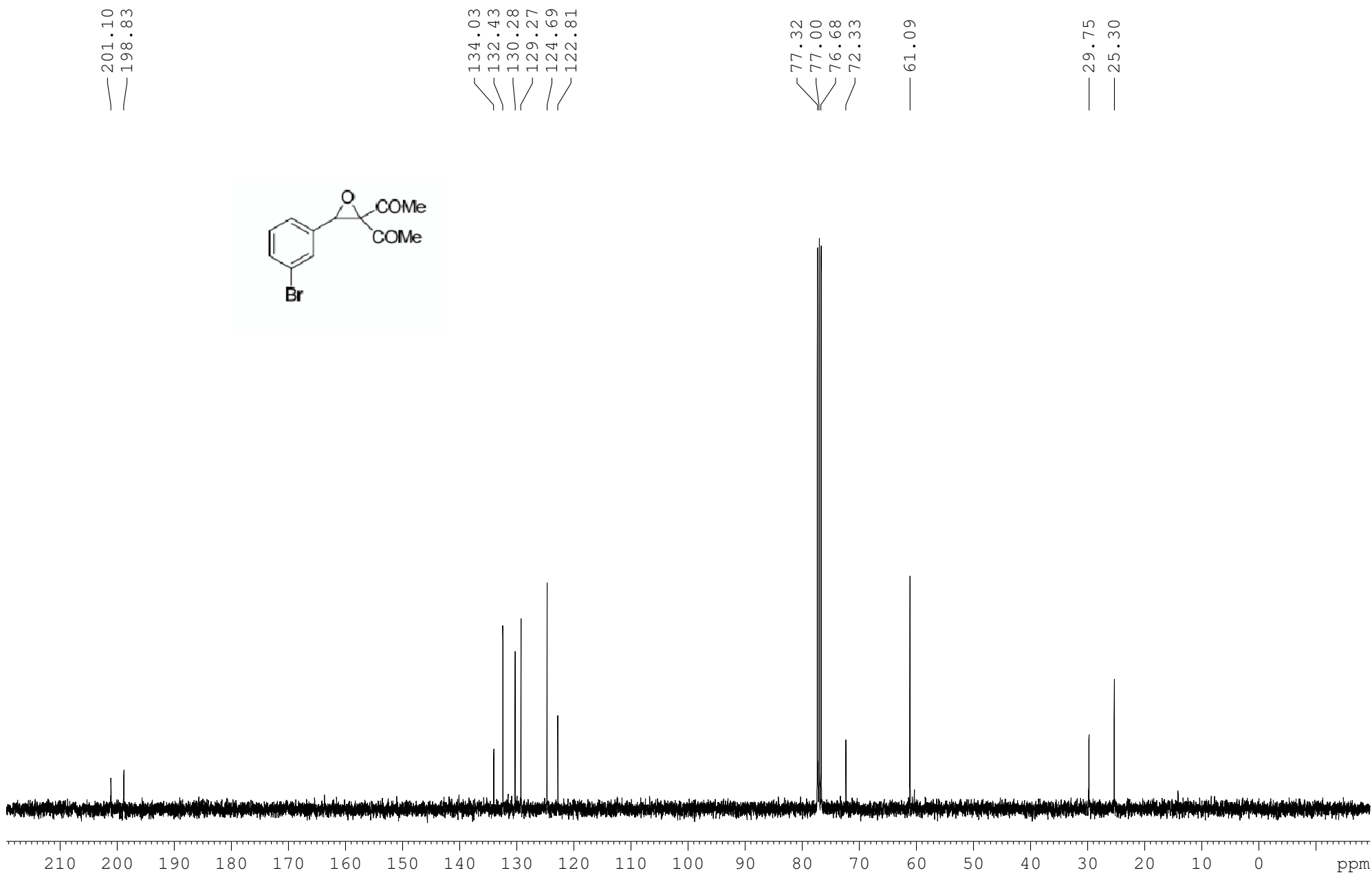
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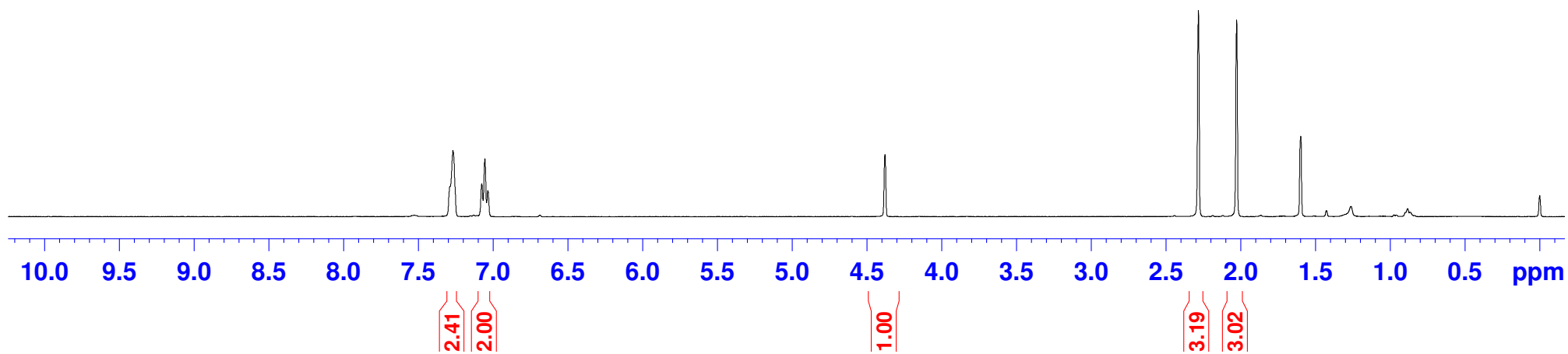
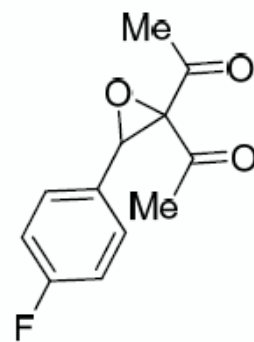
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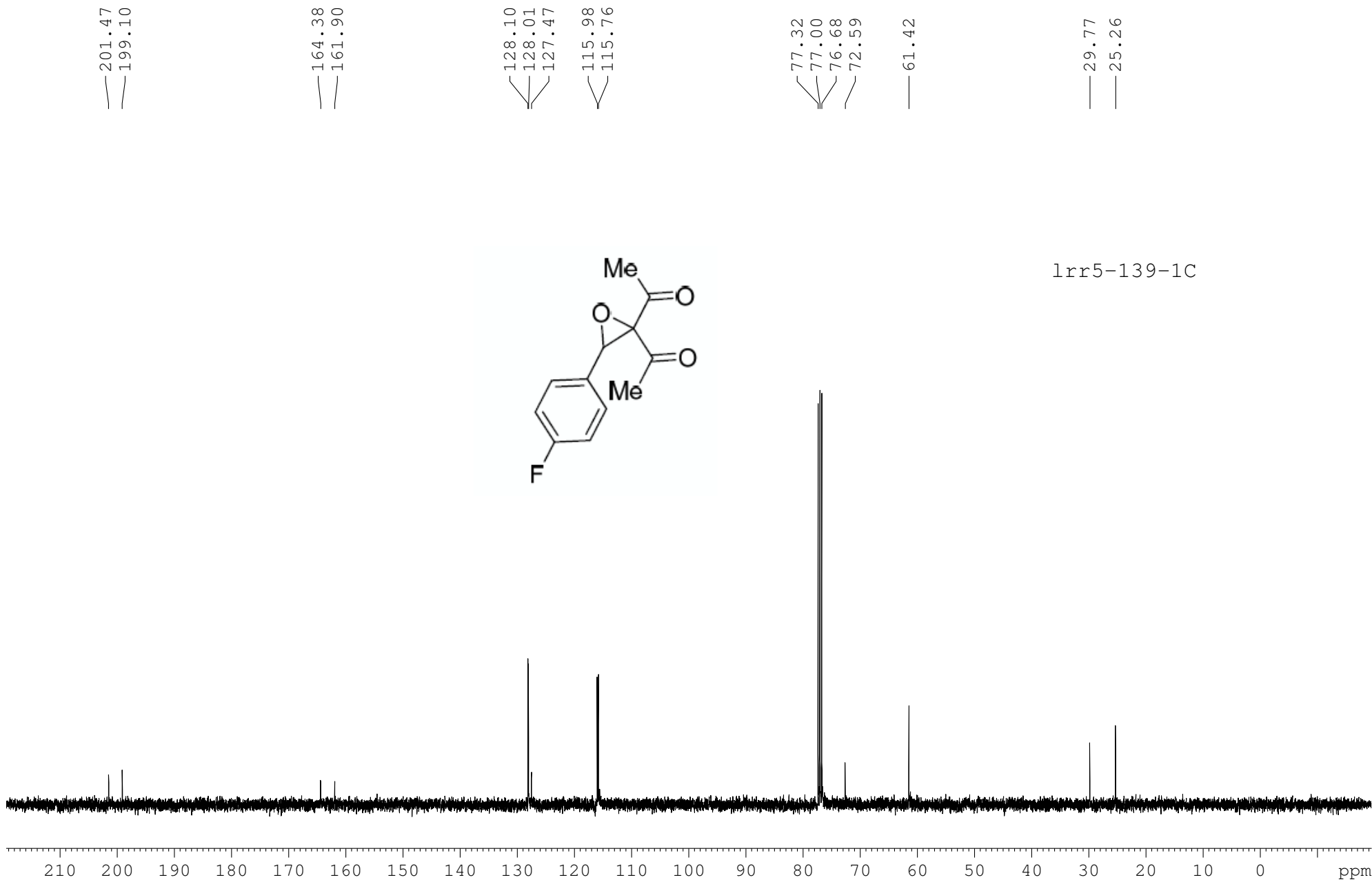
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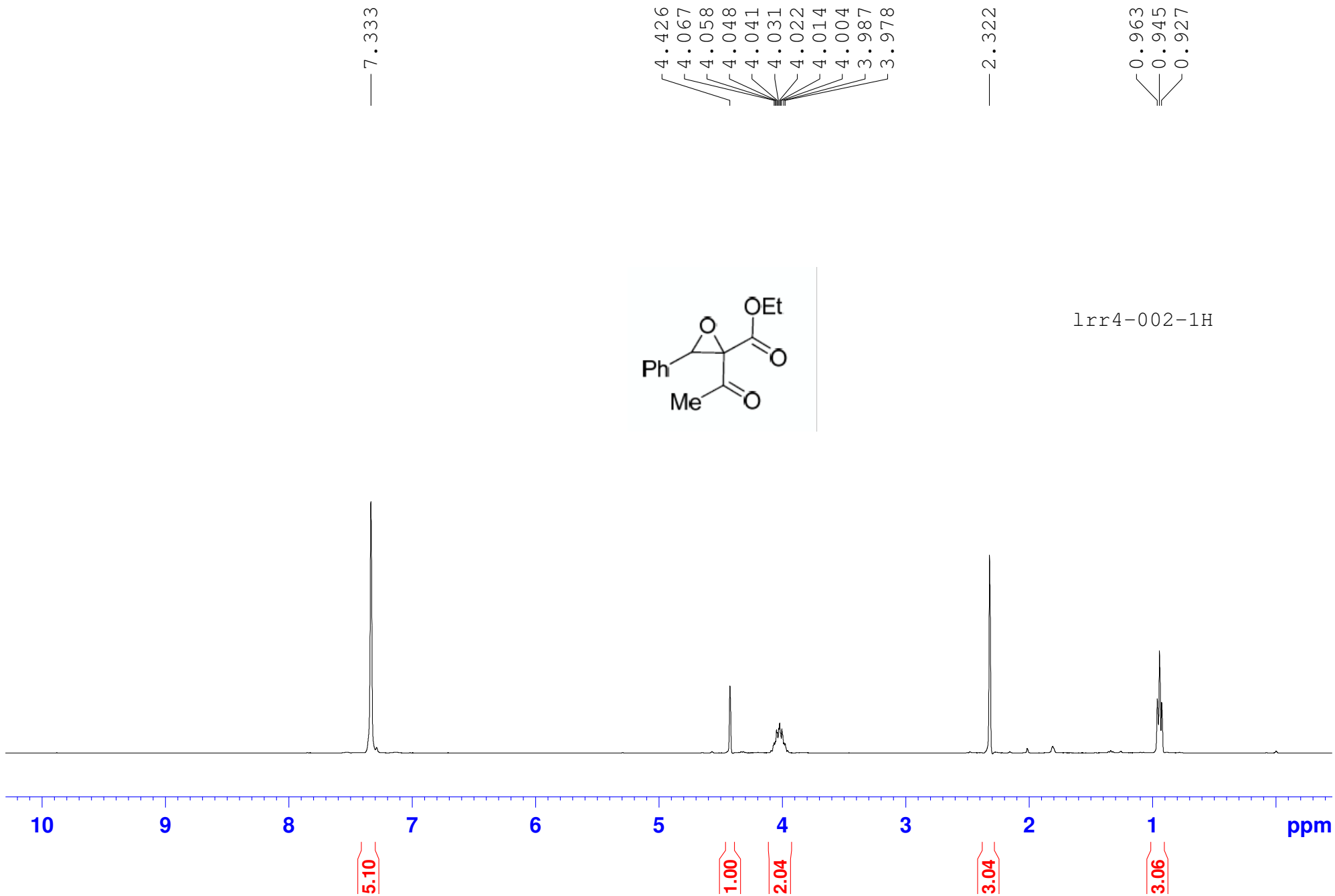
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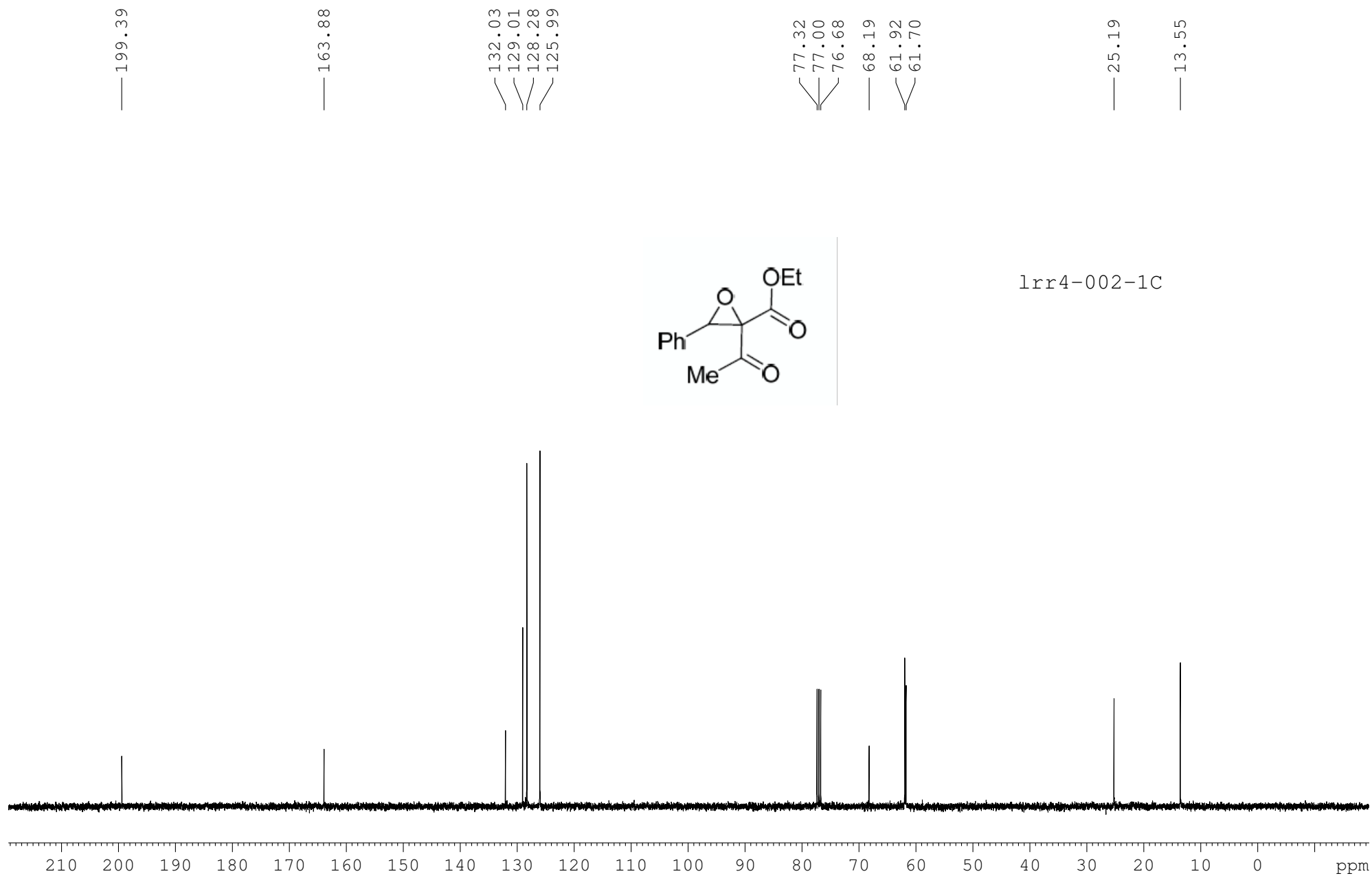
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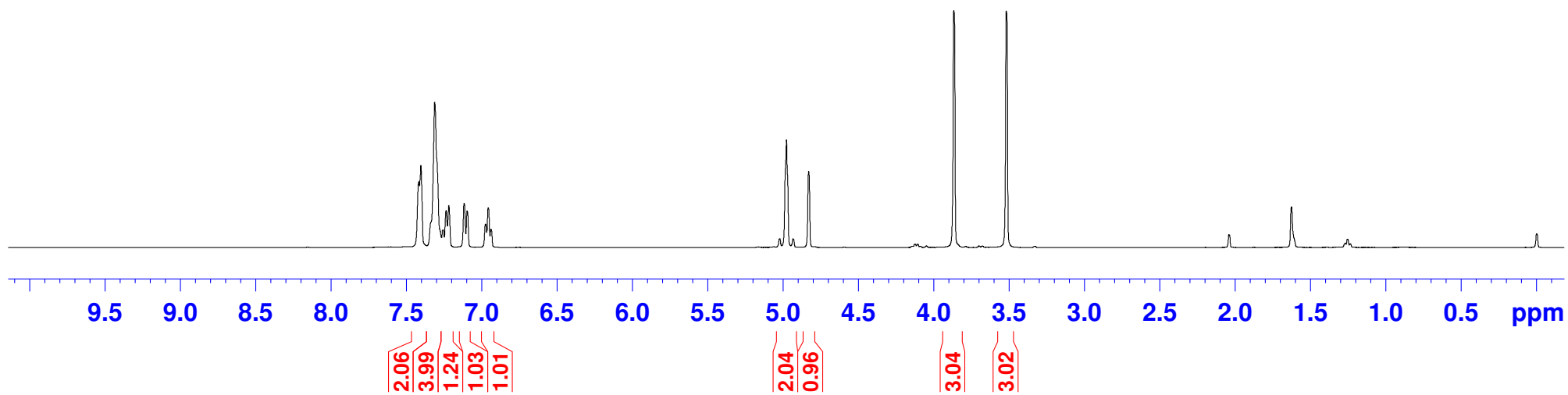
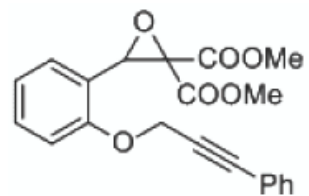








lrr4-002-1C



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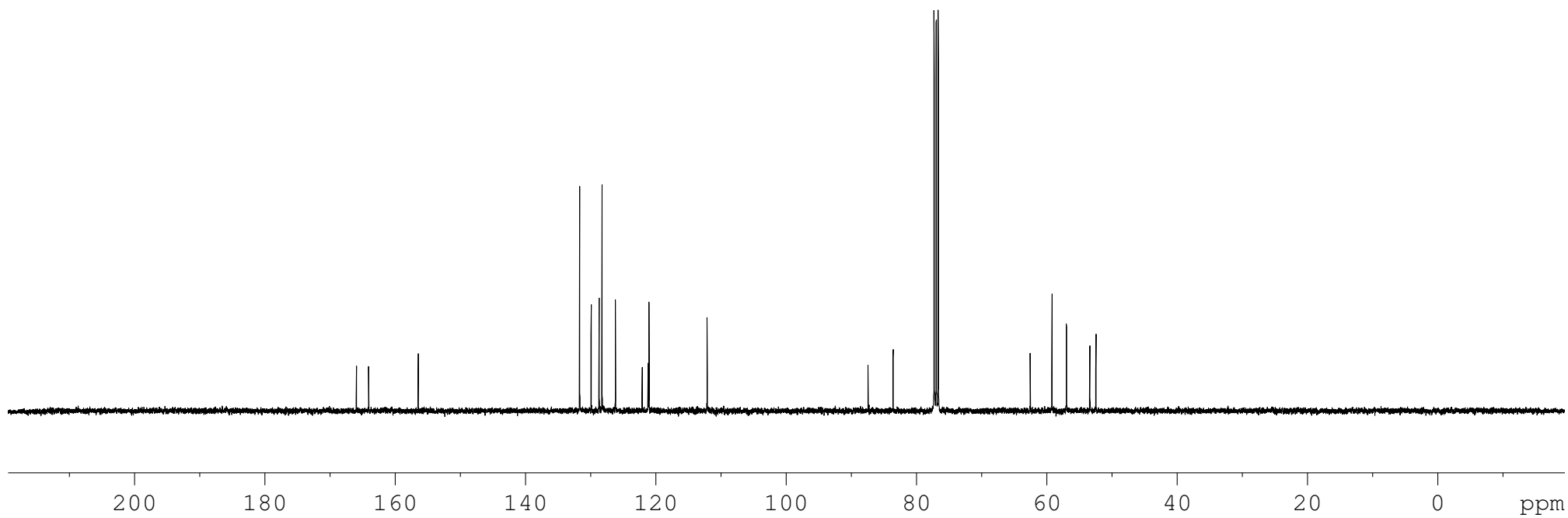
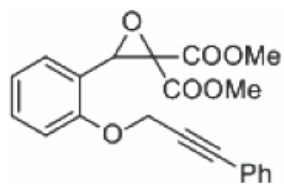
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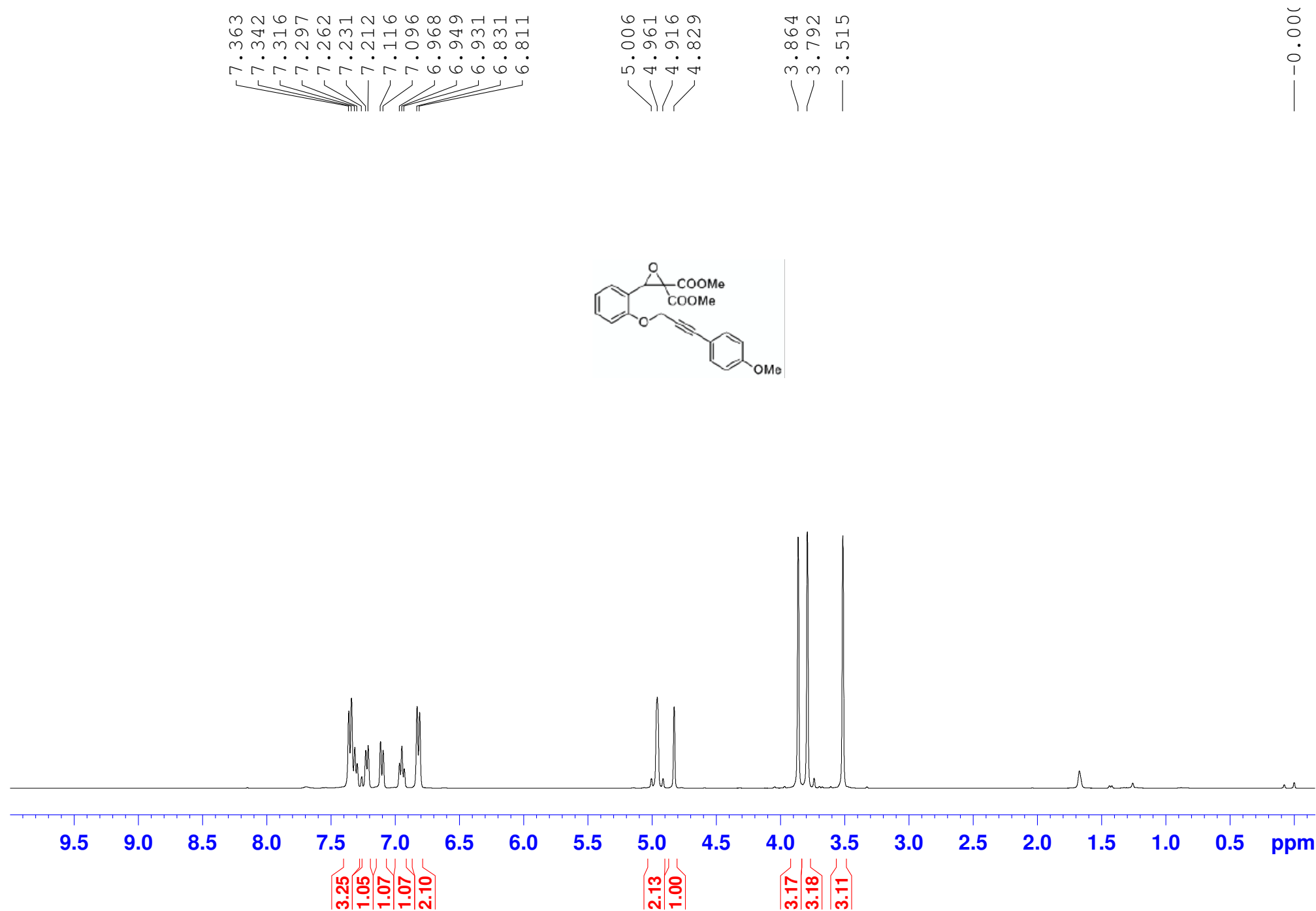
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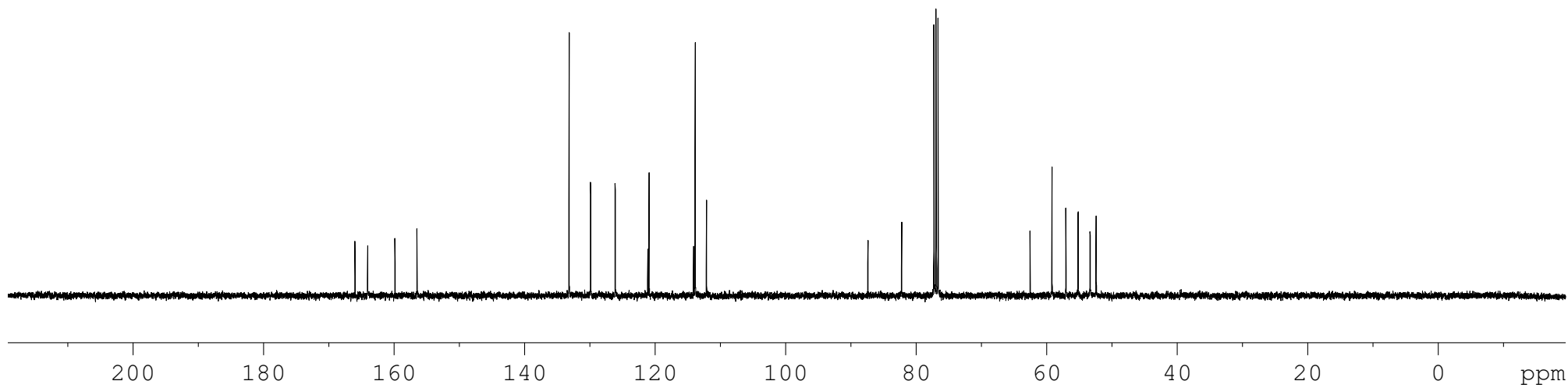
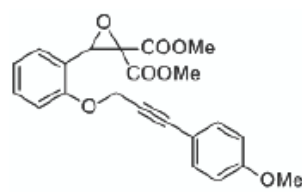


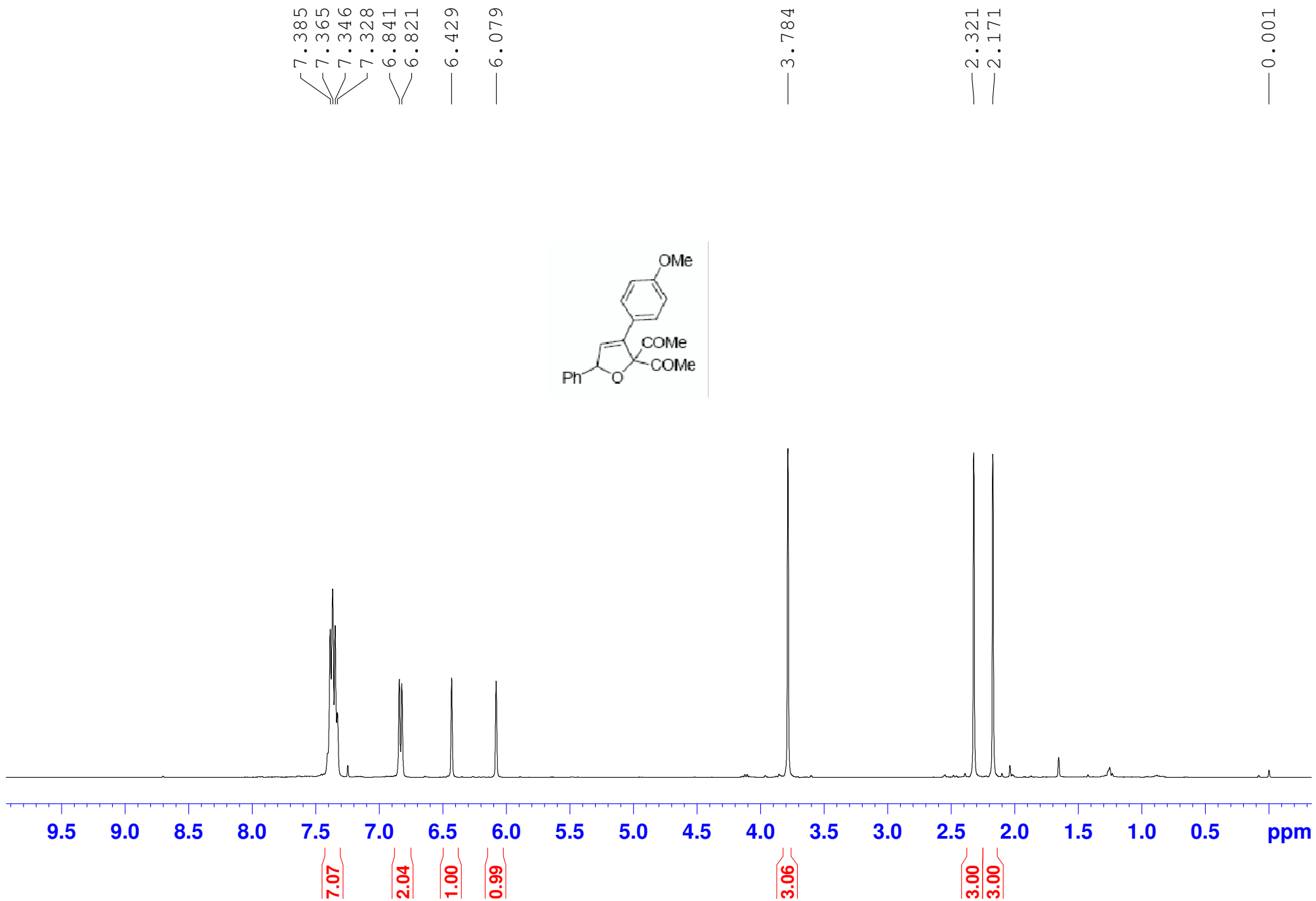


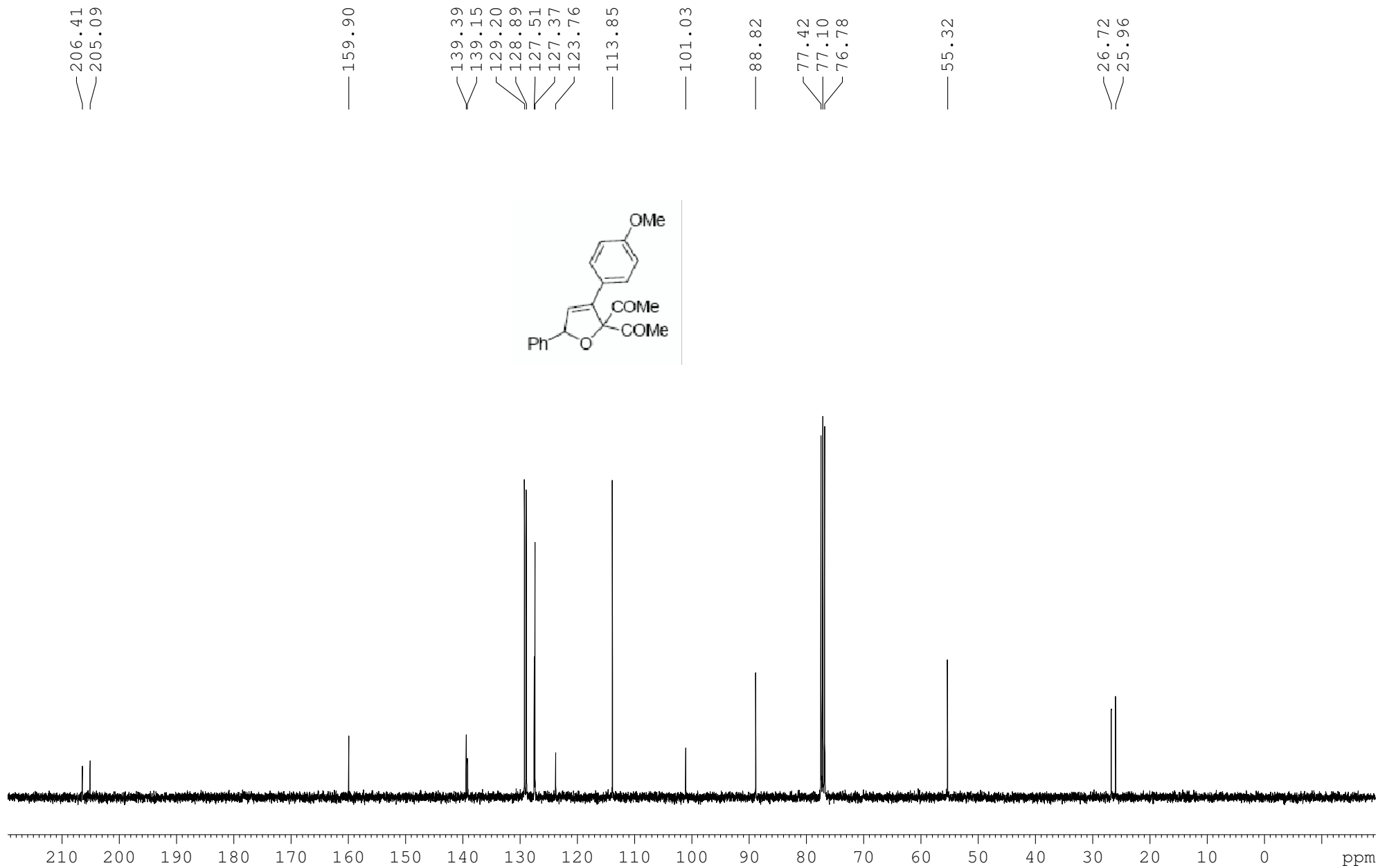
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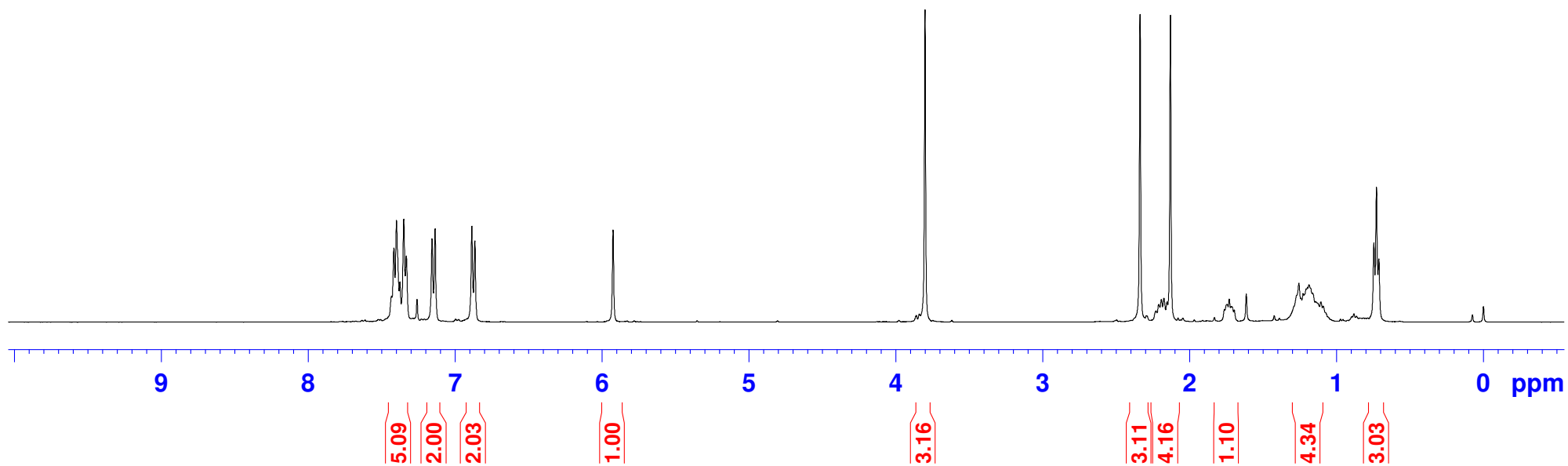
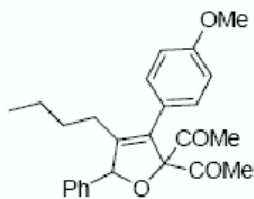


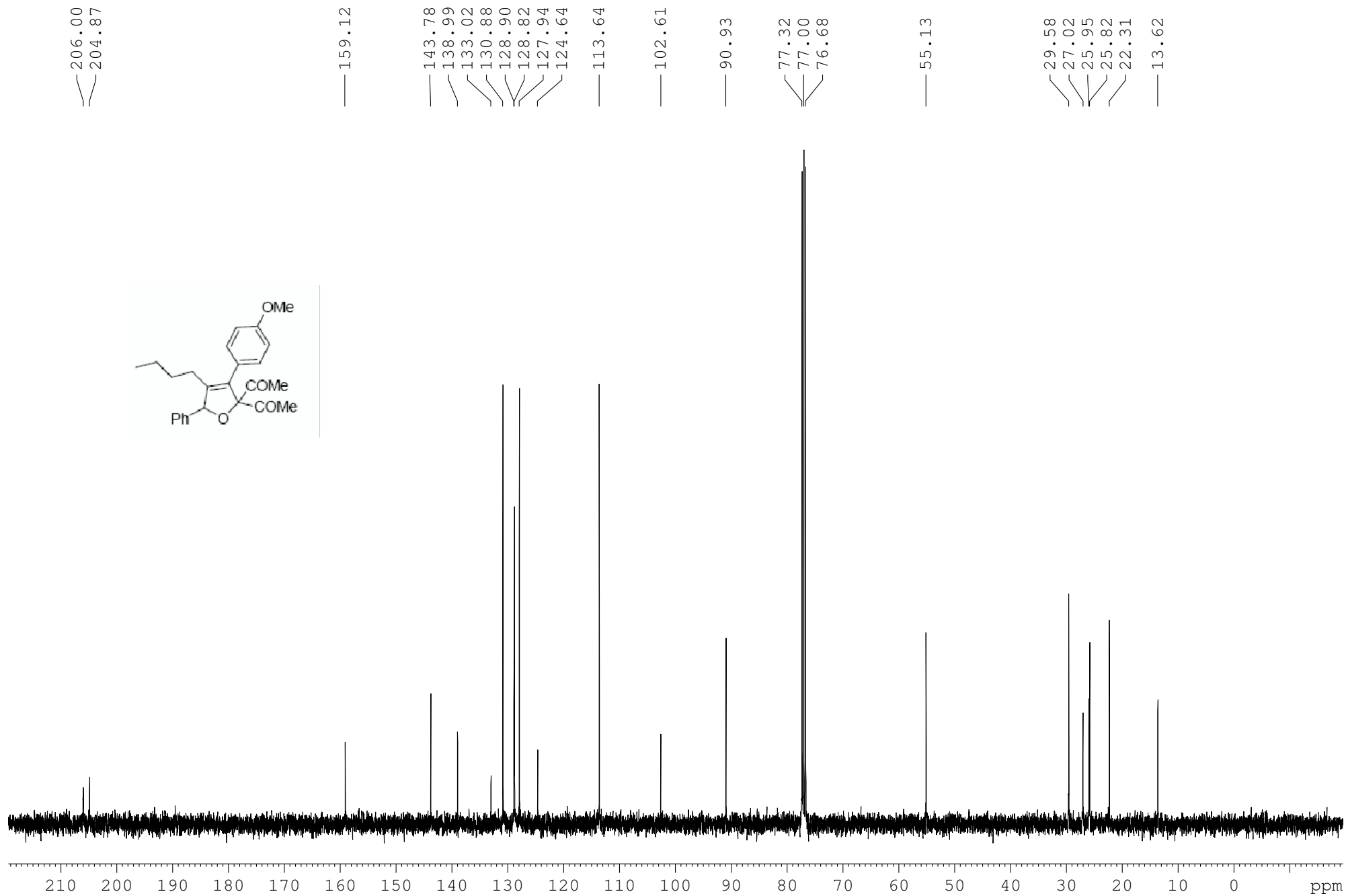


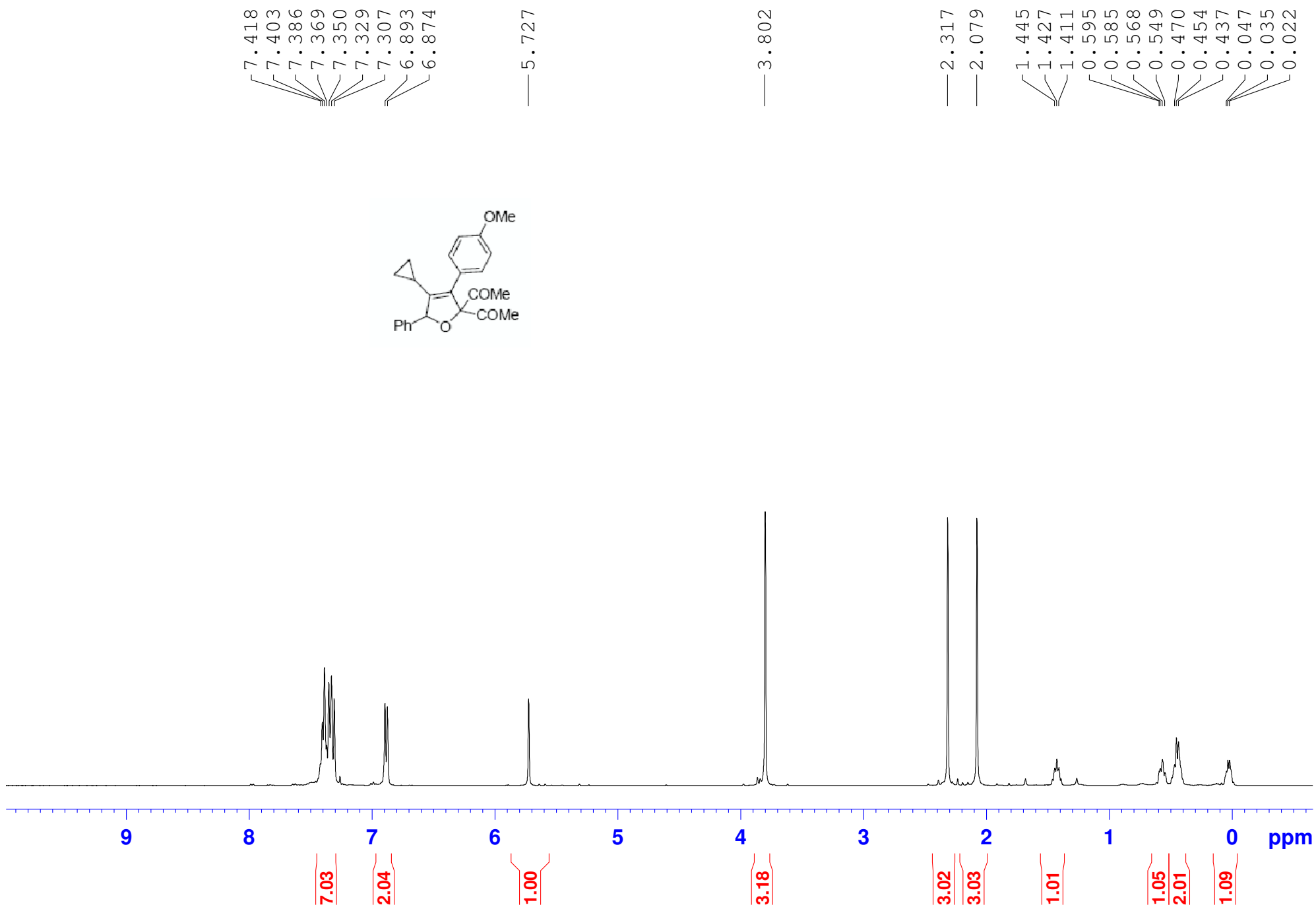


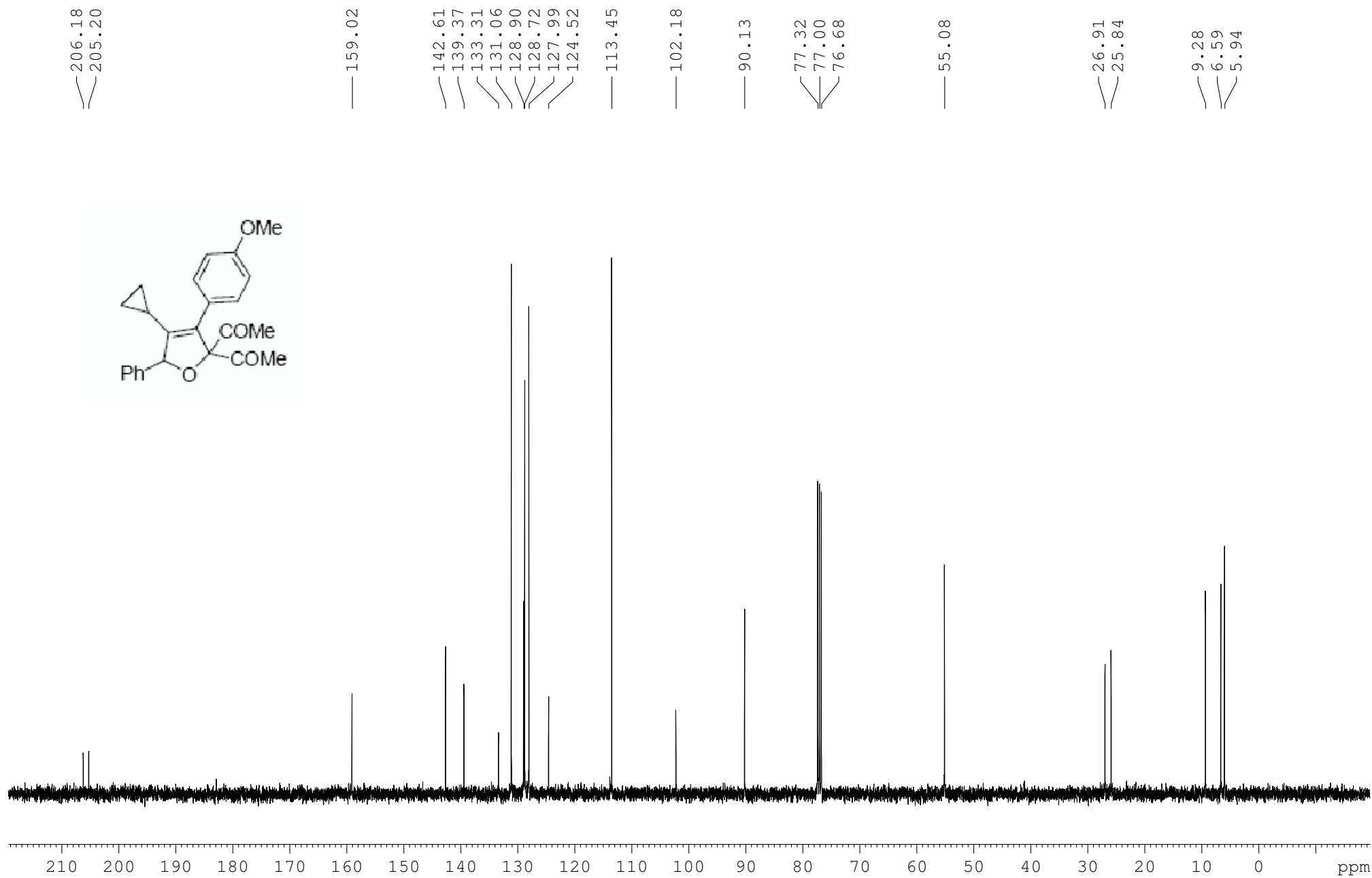
7.431
7.415
7.398
7.374
7.348
7.330
7.258
7.156
7.135
6.885
6.864
— 5.926

3.802
2.338
2.211
2.193
2.175
2.155
2.131
1.745
1.730
1.717
1.256
1.227
1.207
1.198
1.188
1.164
1.143
1.107
1.091
0.746
0.728
0.712



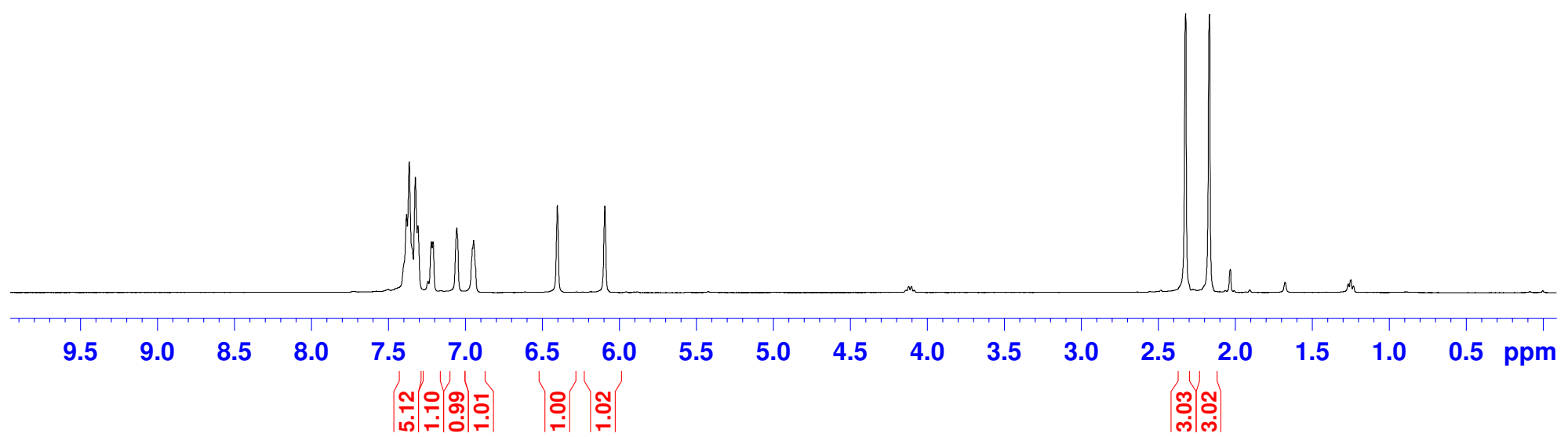
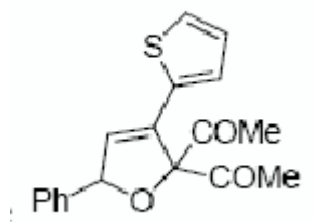


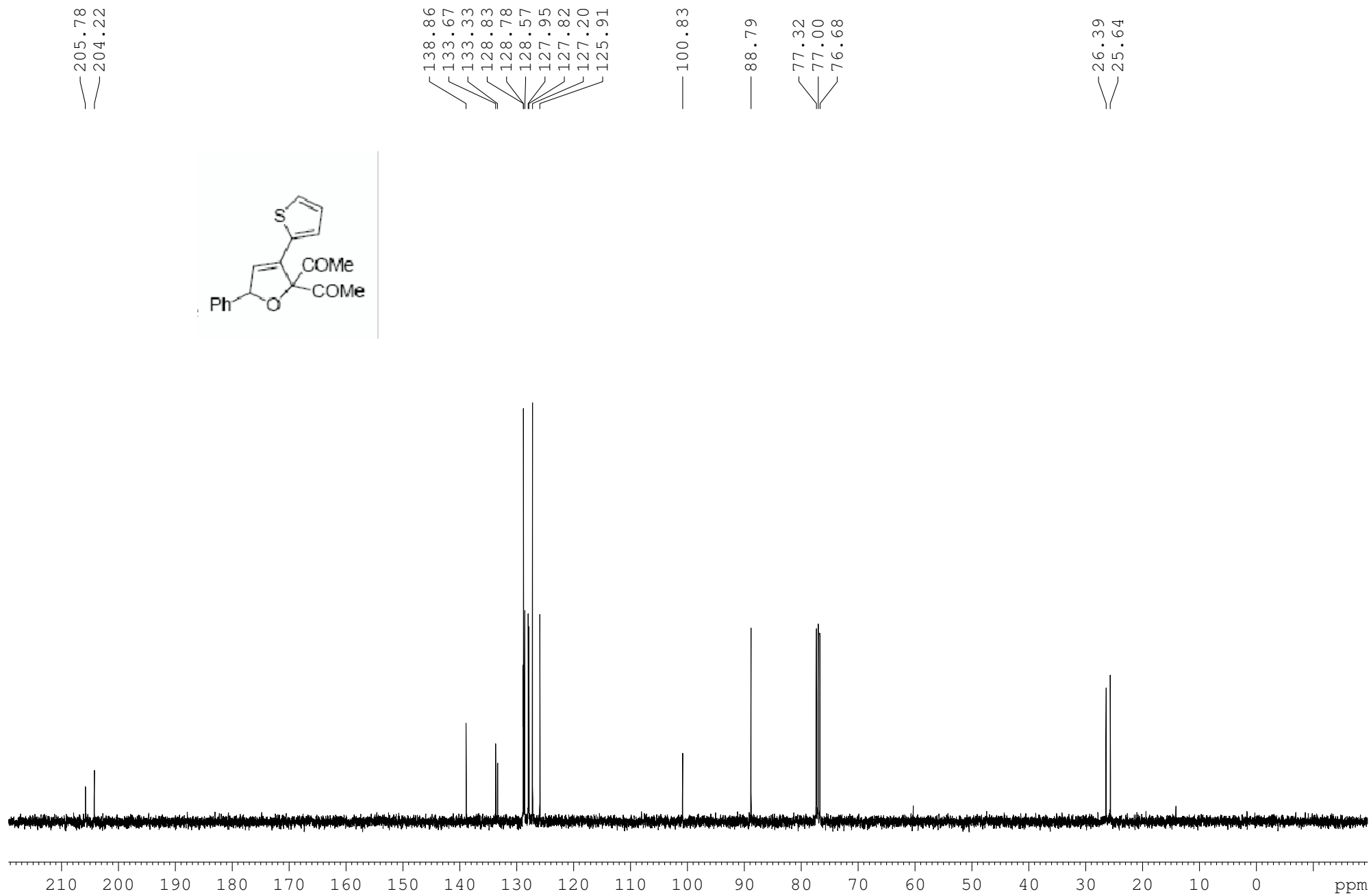


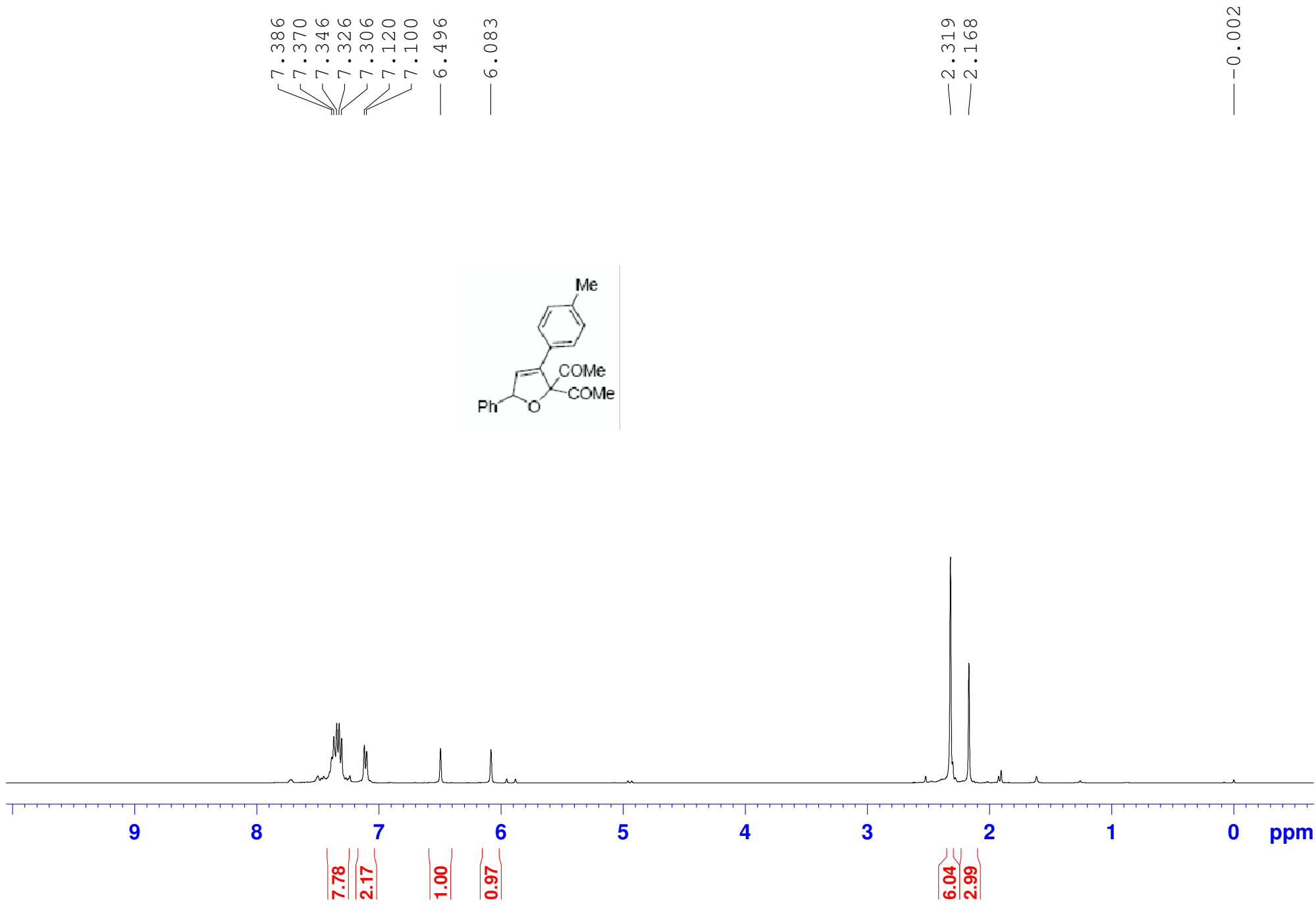


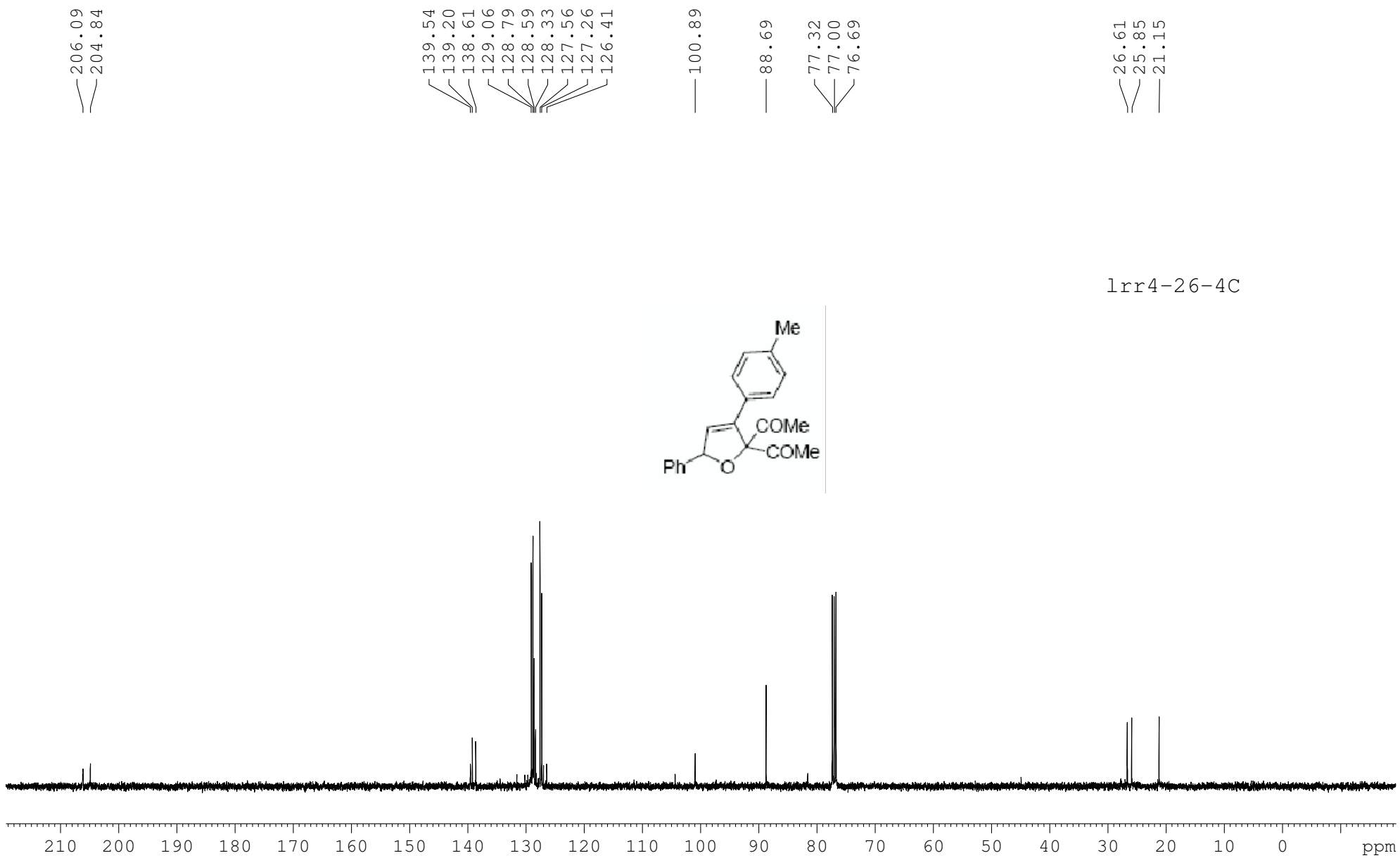
7.382
7.365
7.325
7.308
7.221
7.211
7.056
6.954
6.946
6.403
6.095

2.322
2.167





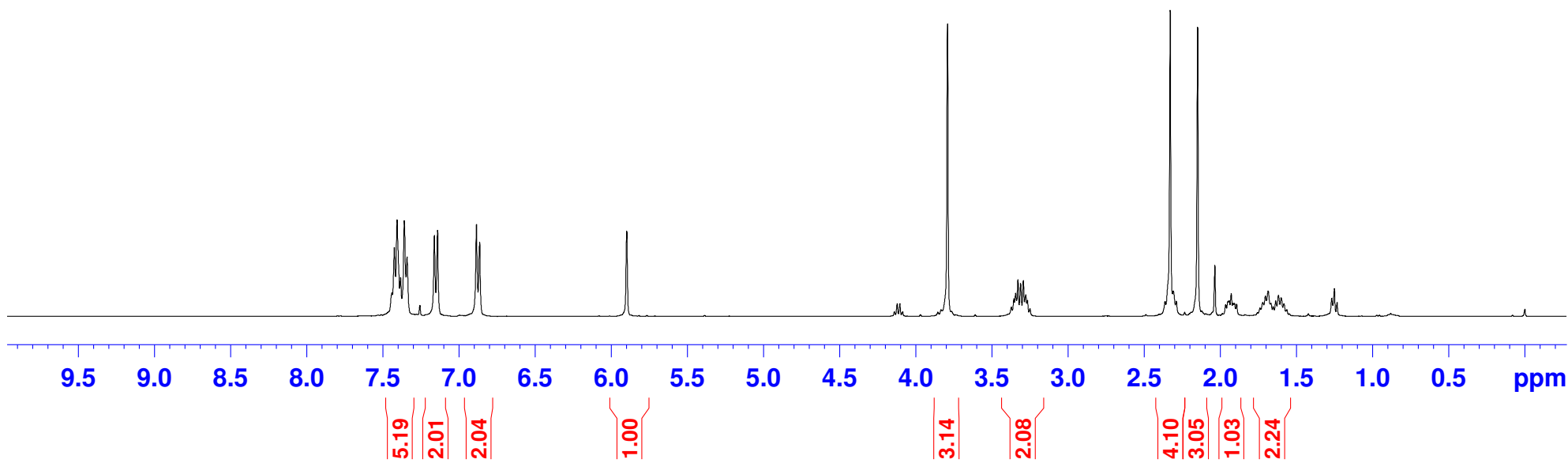
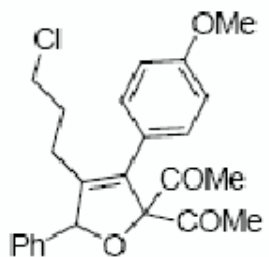


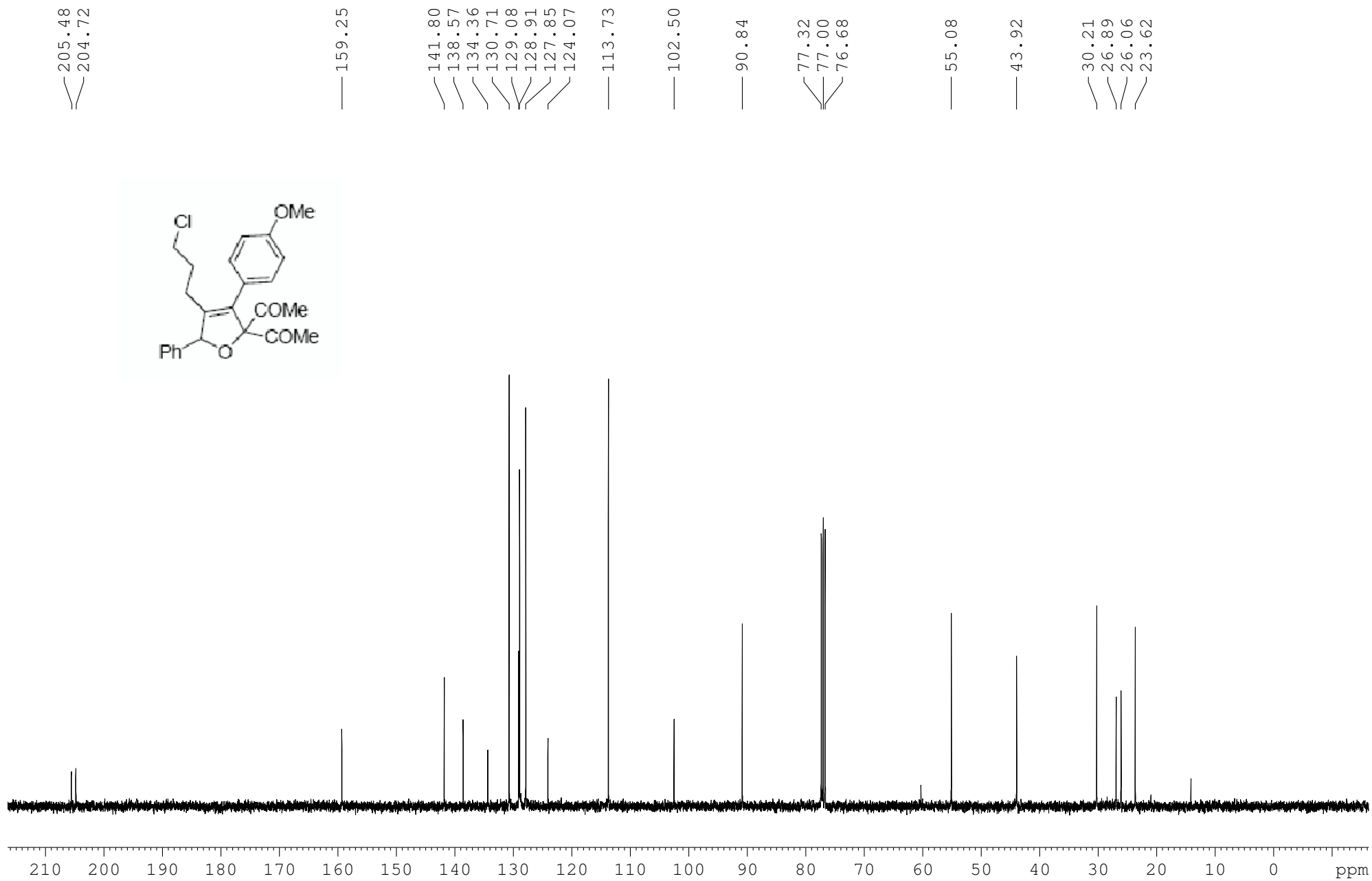


7.441
7.425
7.407
7.384
7.360
7.341
7.162
7.141
6.885
6.864

— 5.898

3.791
3.355
3.344
3.328
3.311
3.293
3.276
3.266
2.328
2.148
1.985
1.964
1.949
1.941
1.928
1.914
1.906
1.892
1.754
1.739
1.720
1.703
1.685
1.667
1.651
1.635
1.617
1.599



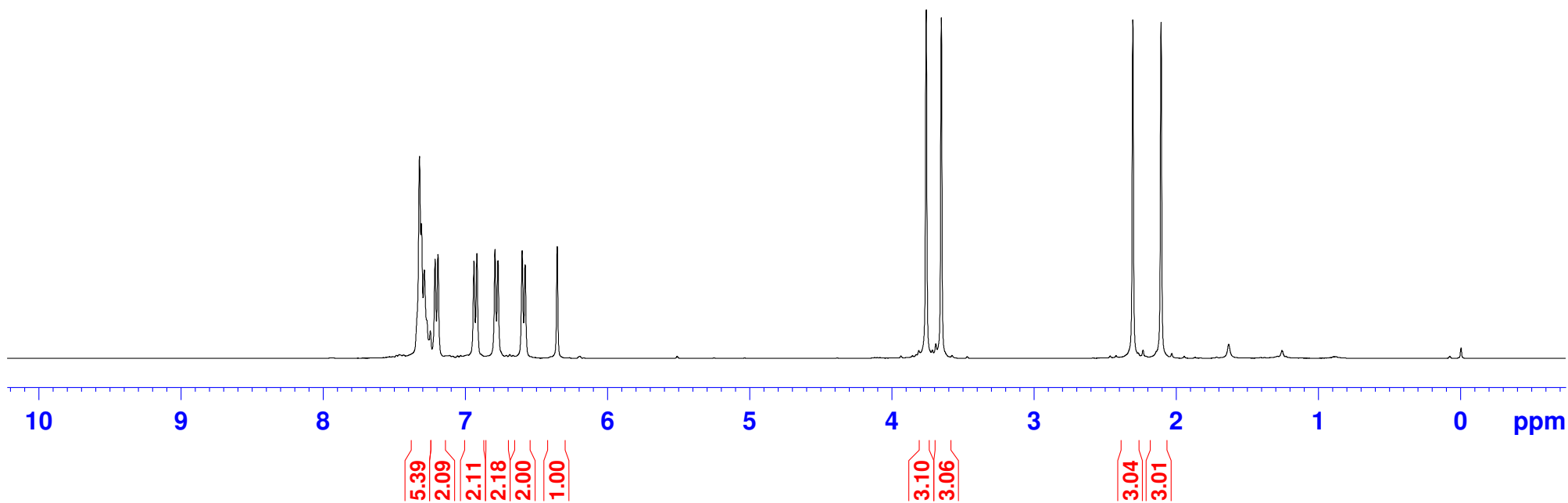
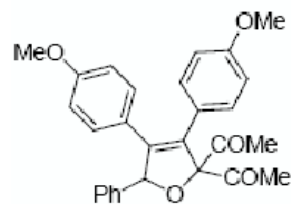


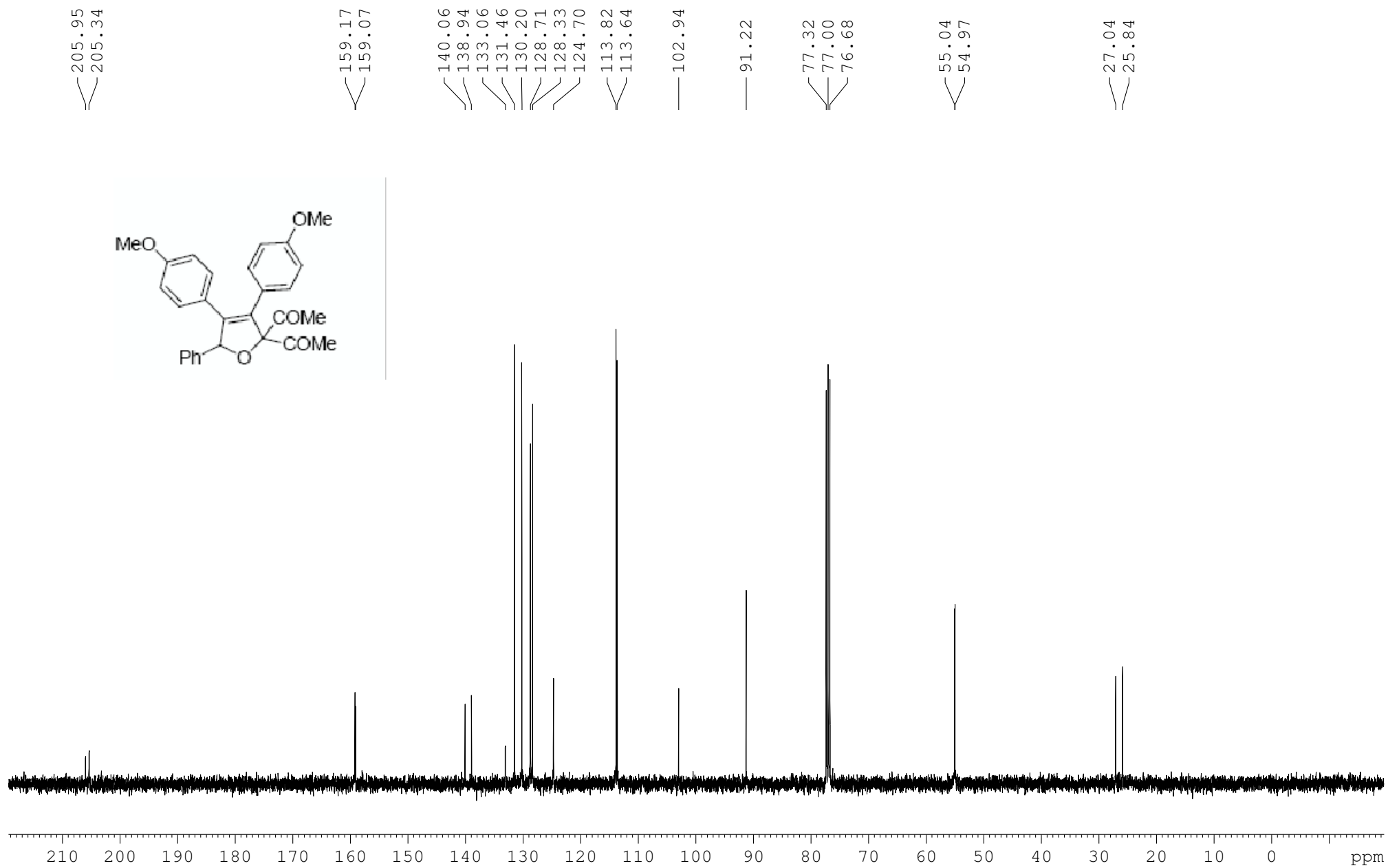
7.324
7.310
7.290
7.214
7.193
6.940
6.920
6.792
6.771
6.601
6.580
6.355

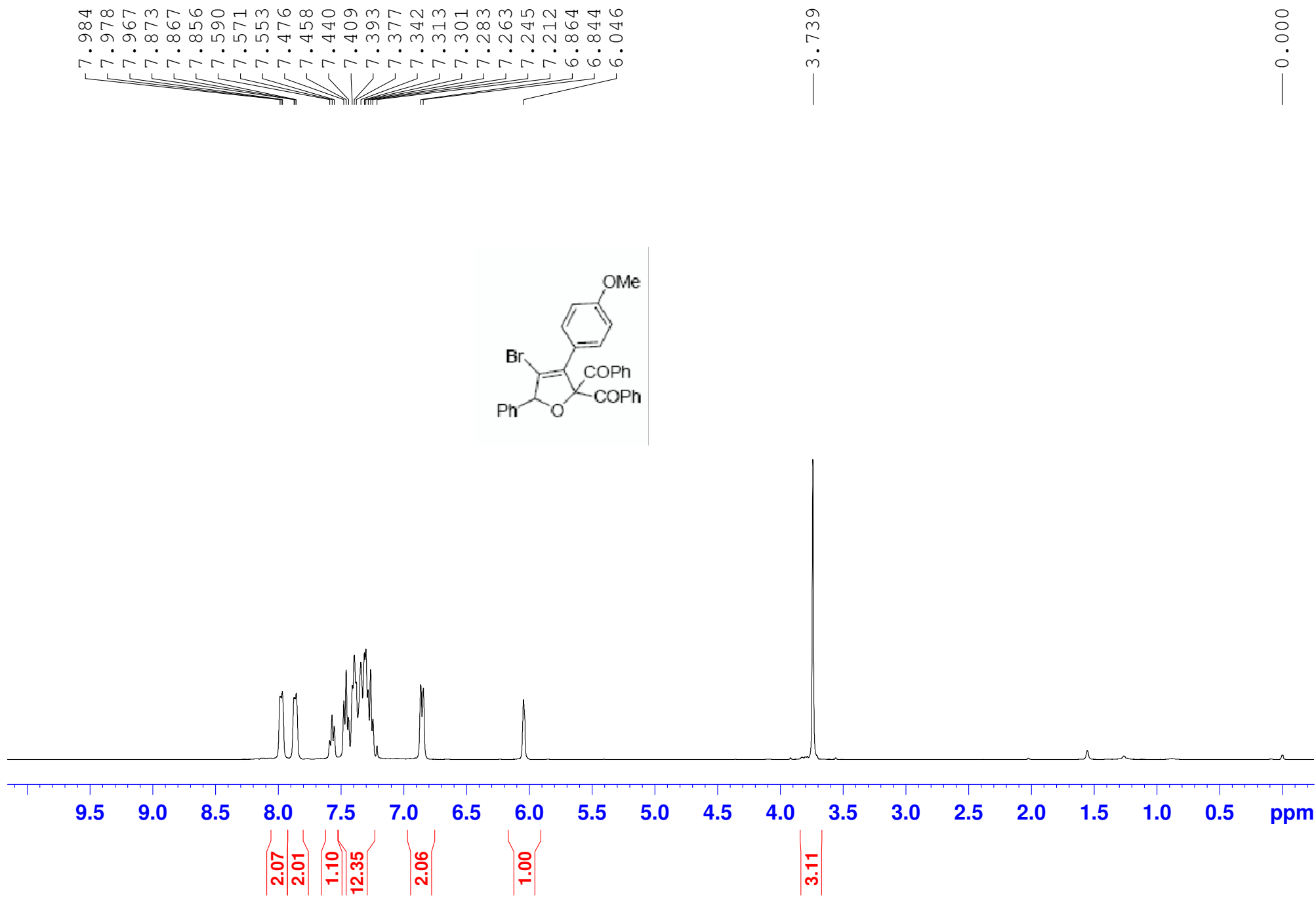
3.759
3.653

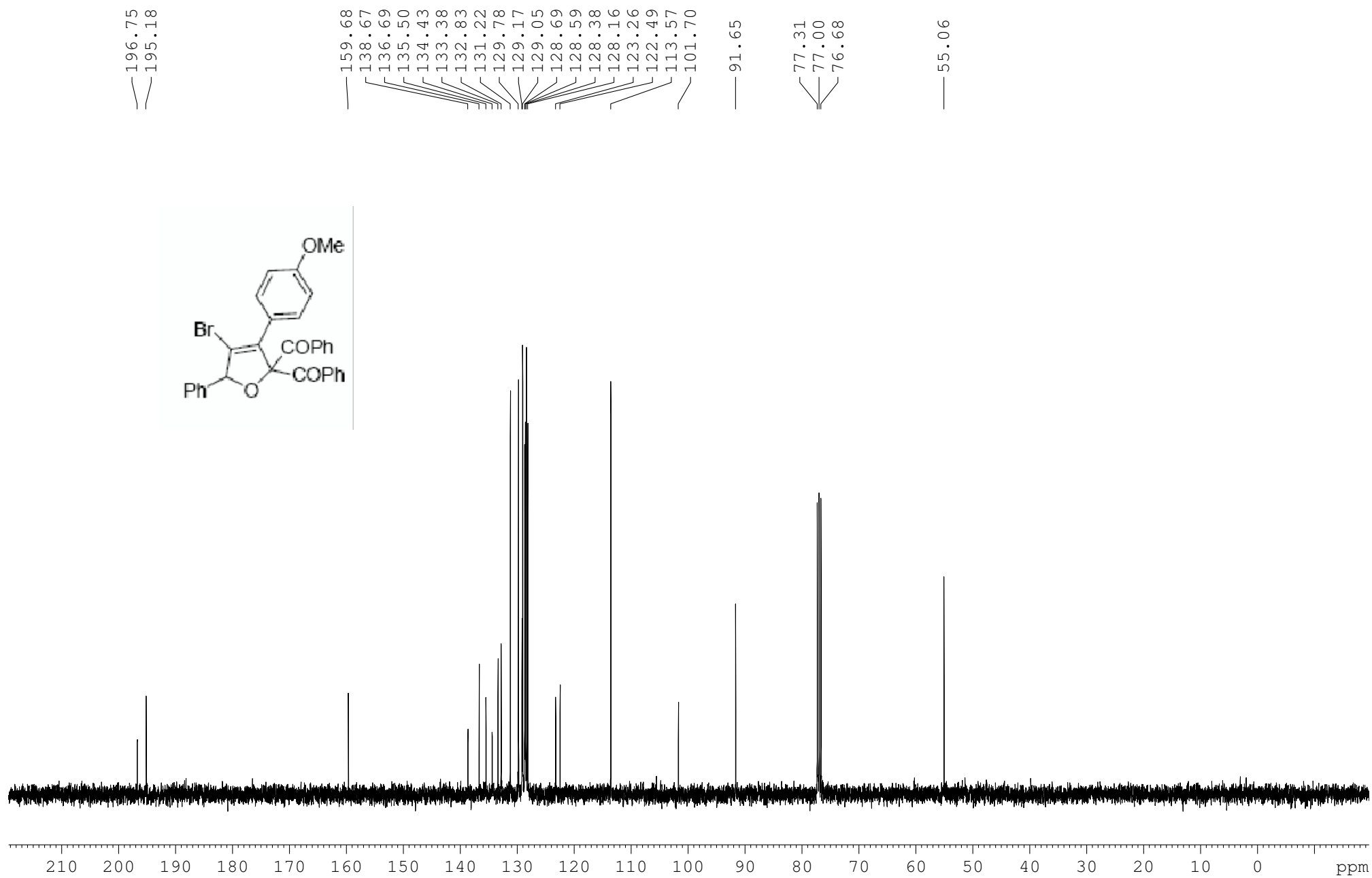
2.306
2.107

-0.003





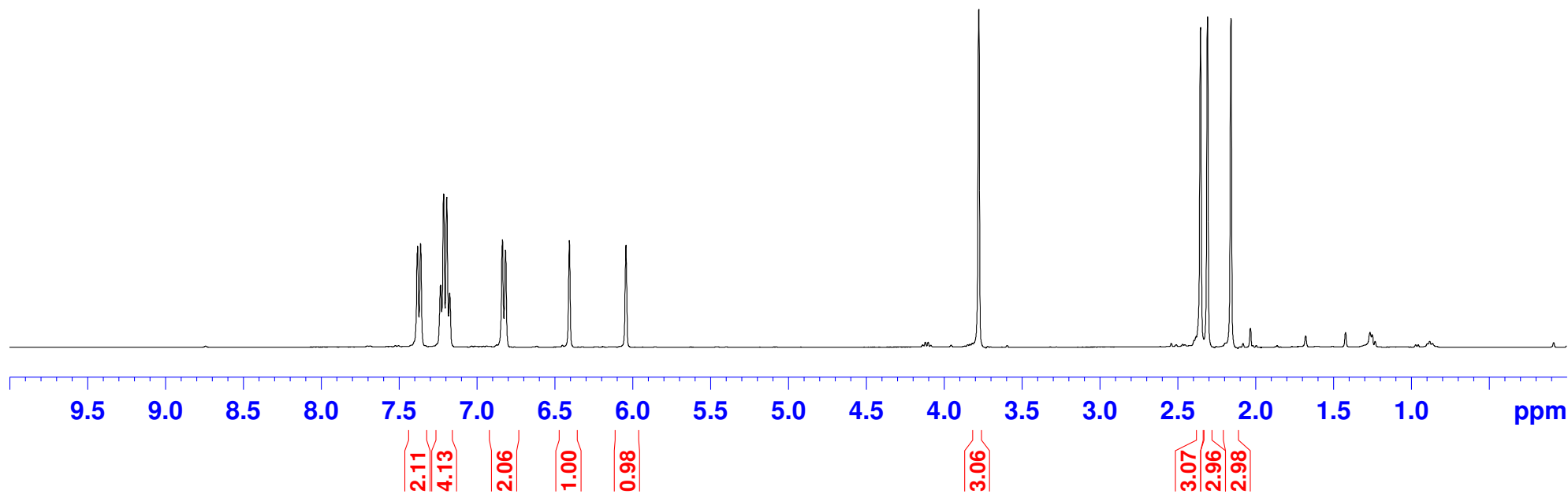
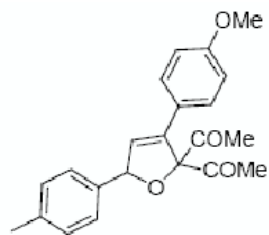


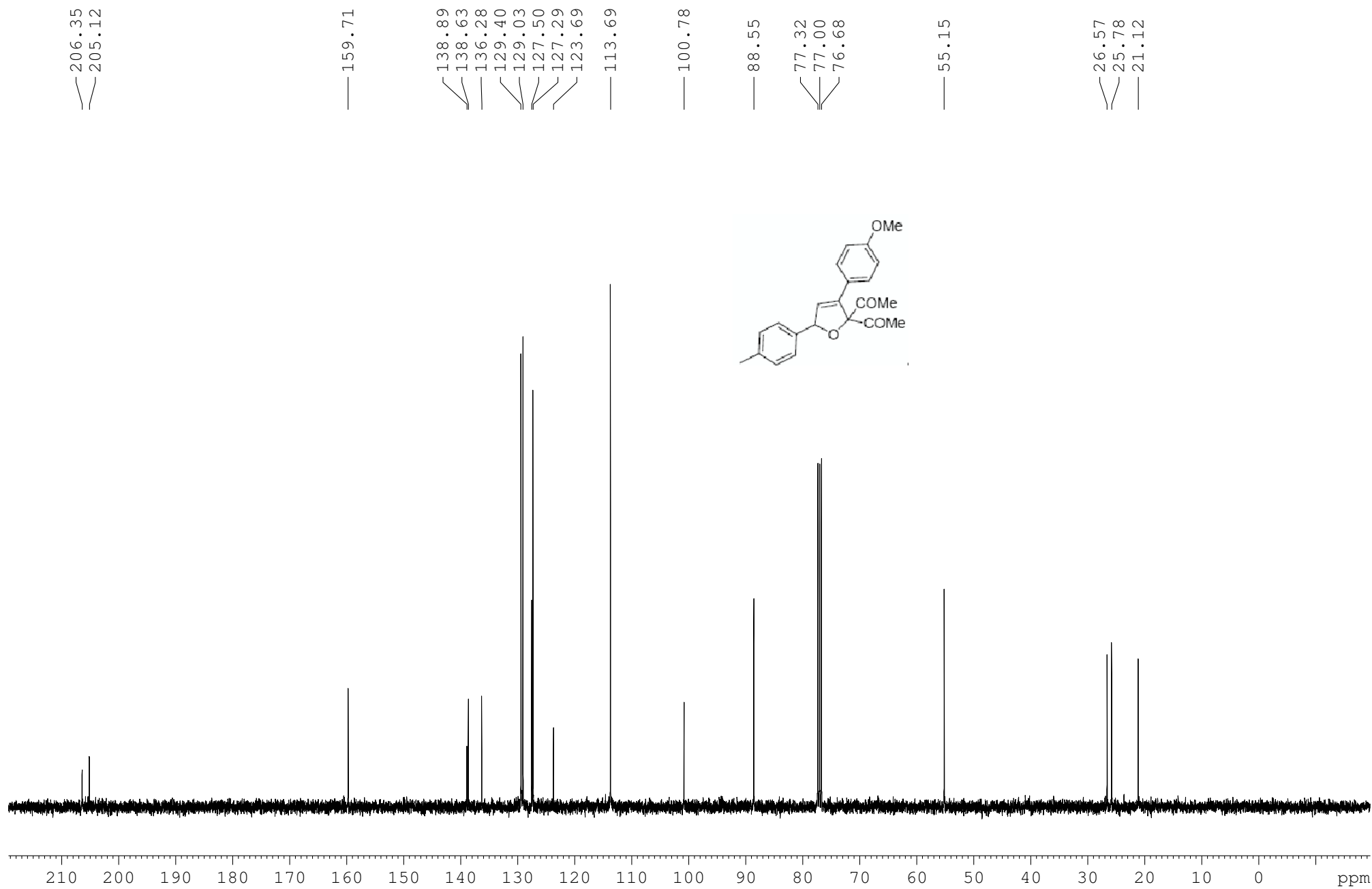


7.381
7.362
7.233
7.213
7.193
7.174
6.835
6.817
6.406
— 6.043

— 3.776

2.352
2.307
2.157

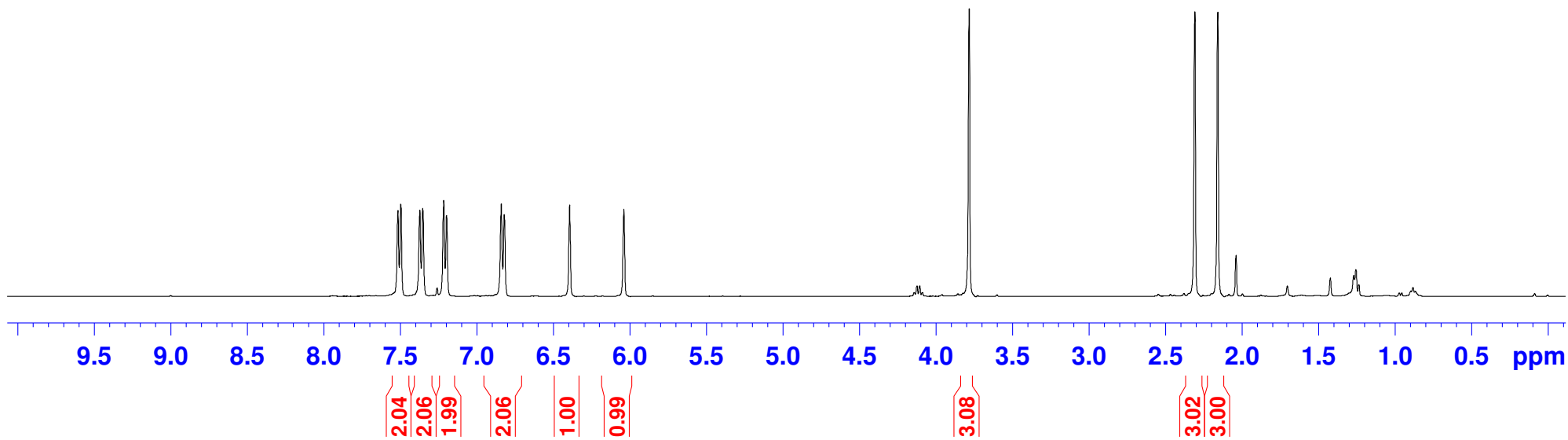
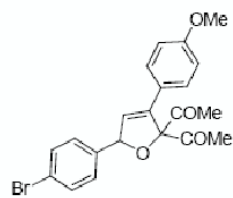


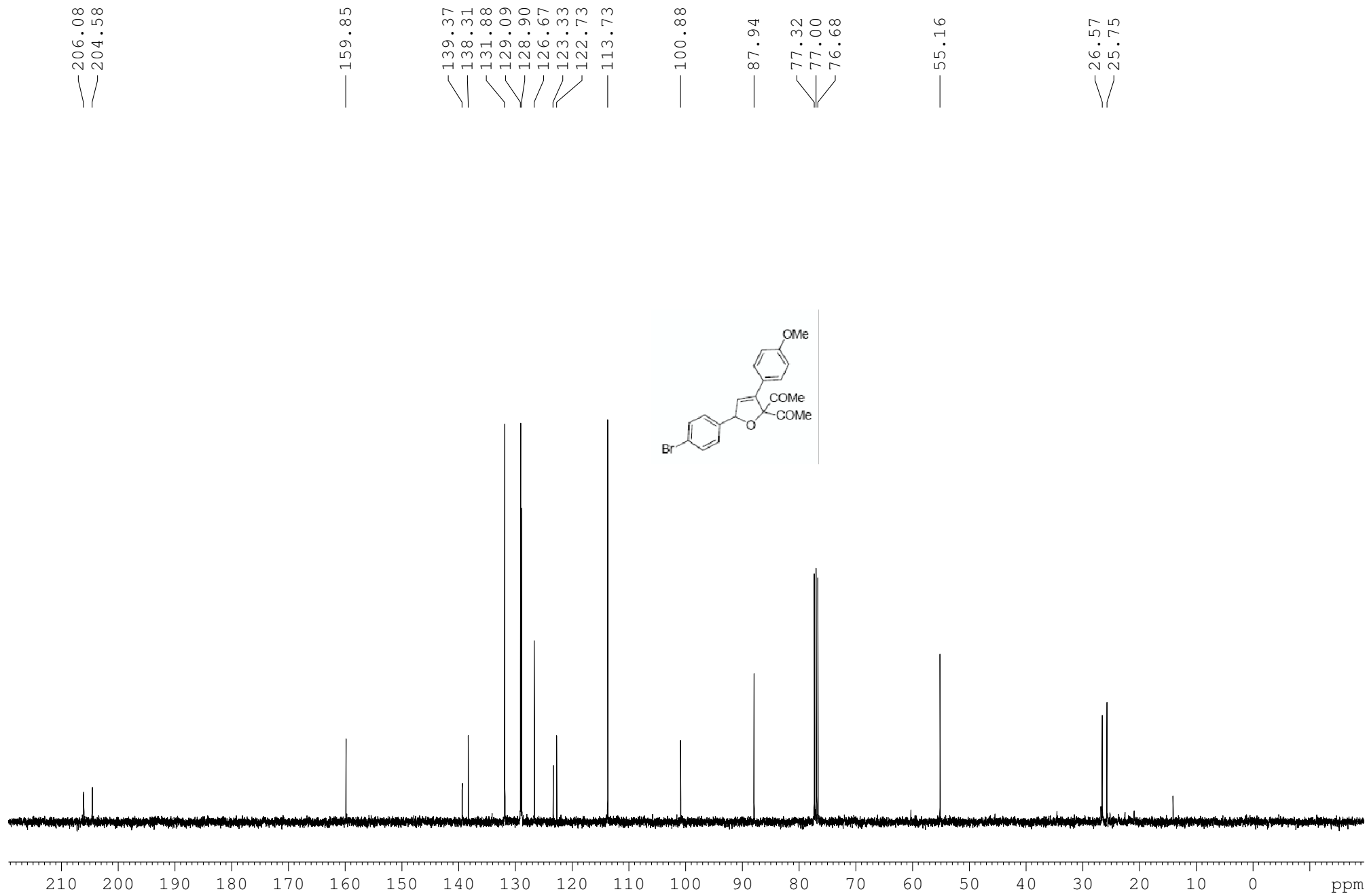


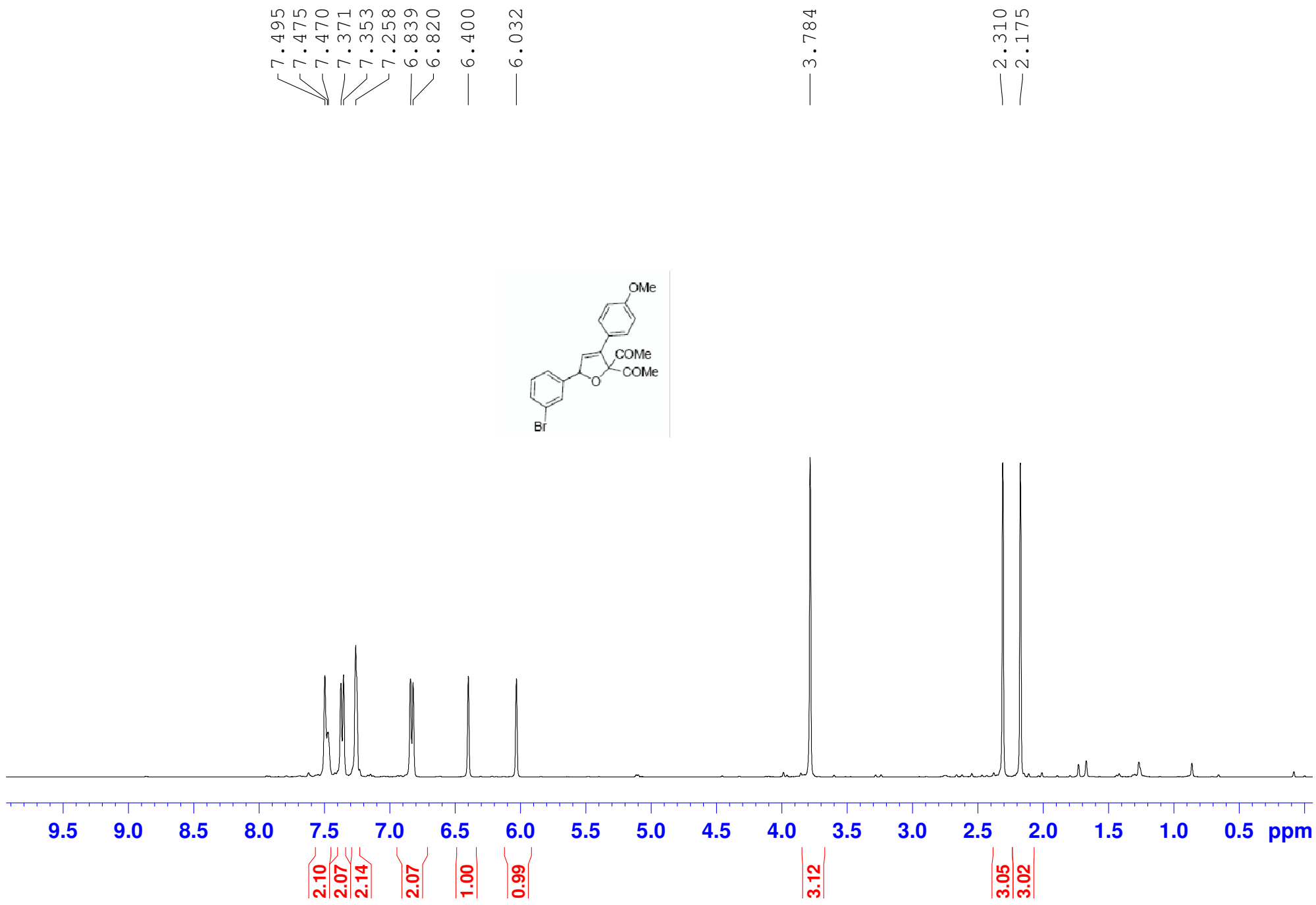
7.516
7.499
7.373
7.355
7.217
7.199
6.841
6.822
— 6.395
— 6.040

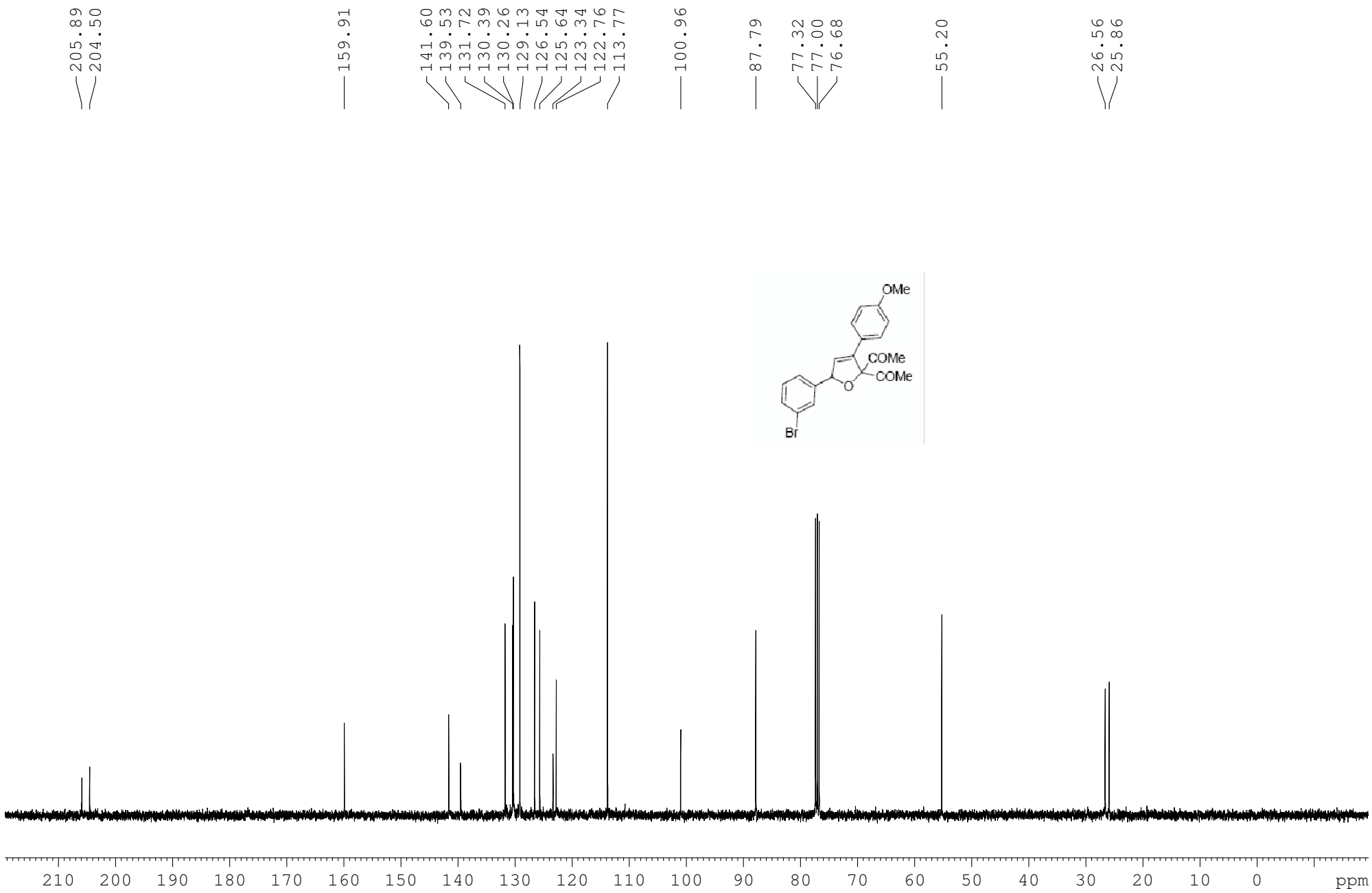
— 3.783

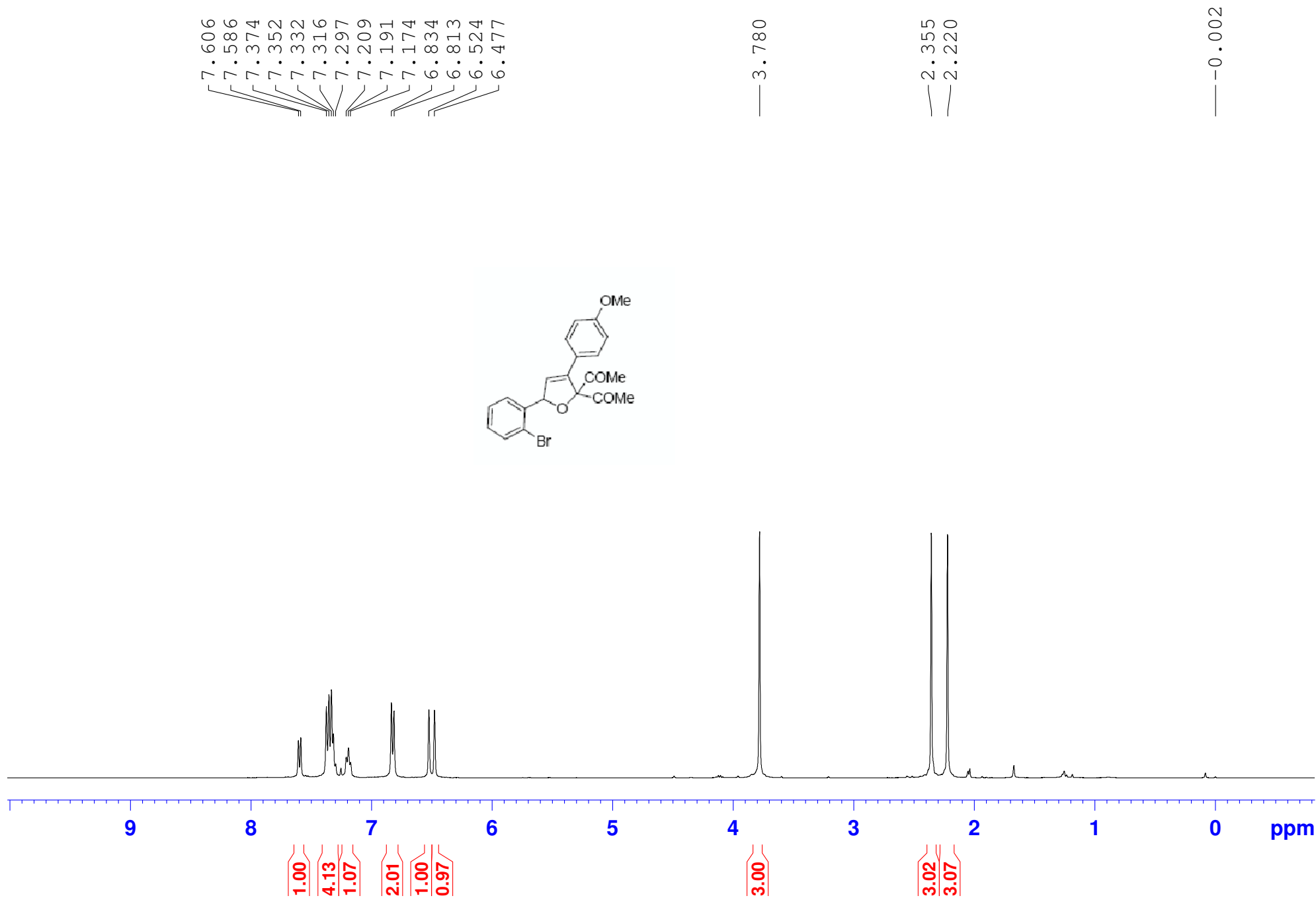
— 2.308
— 2.158

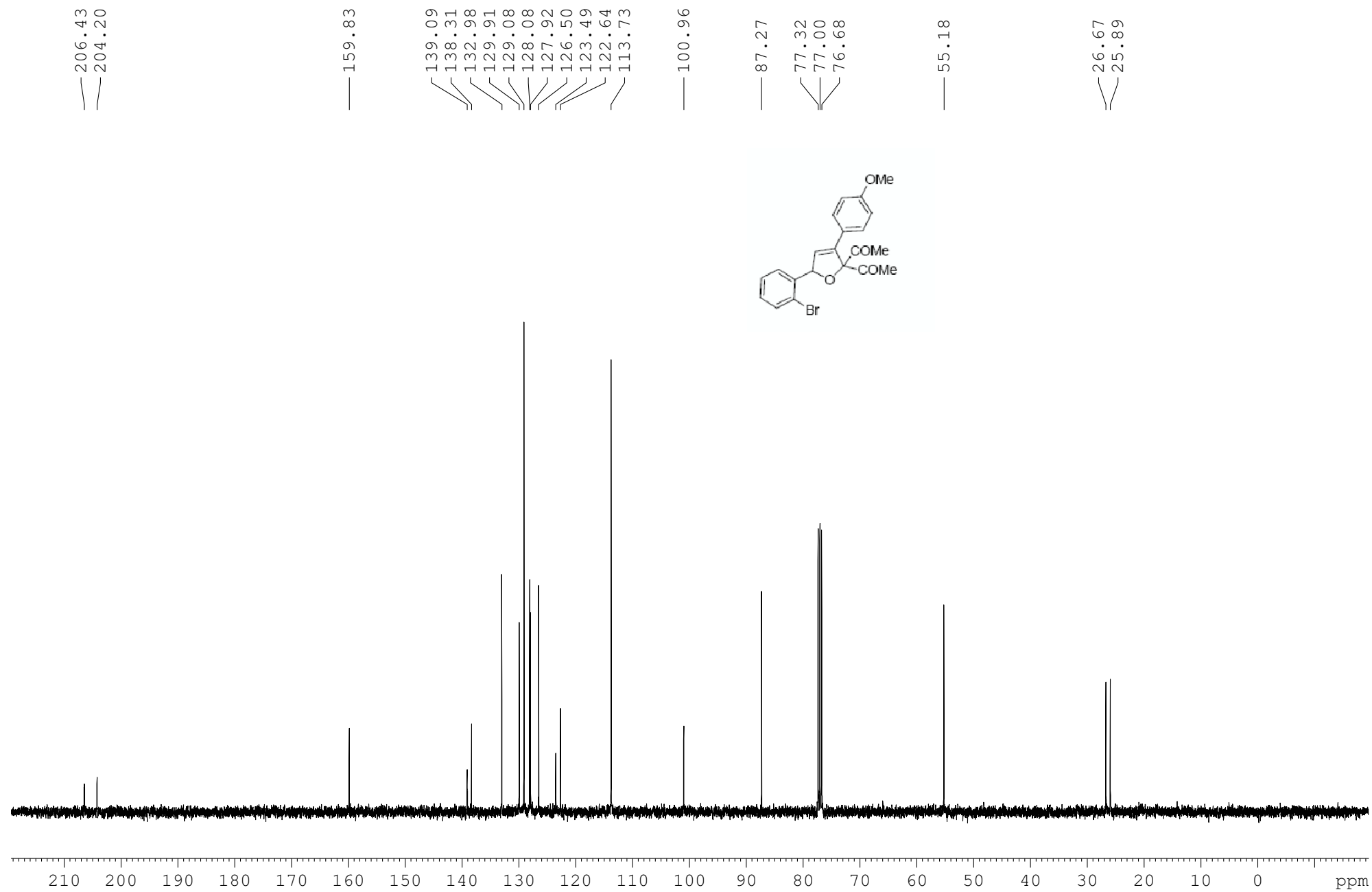


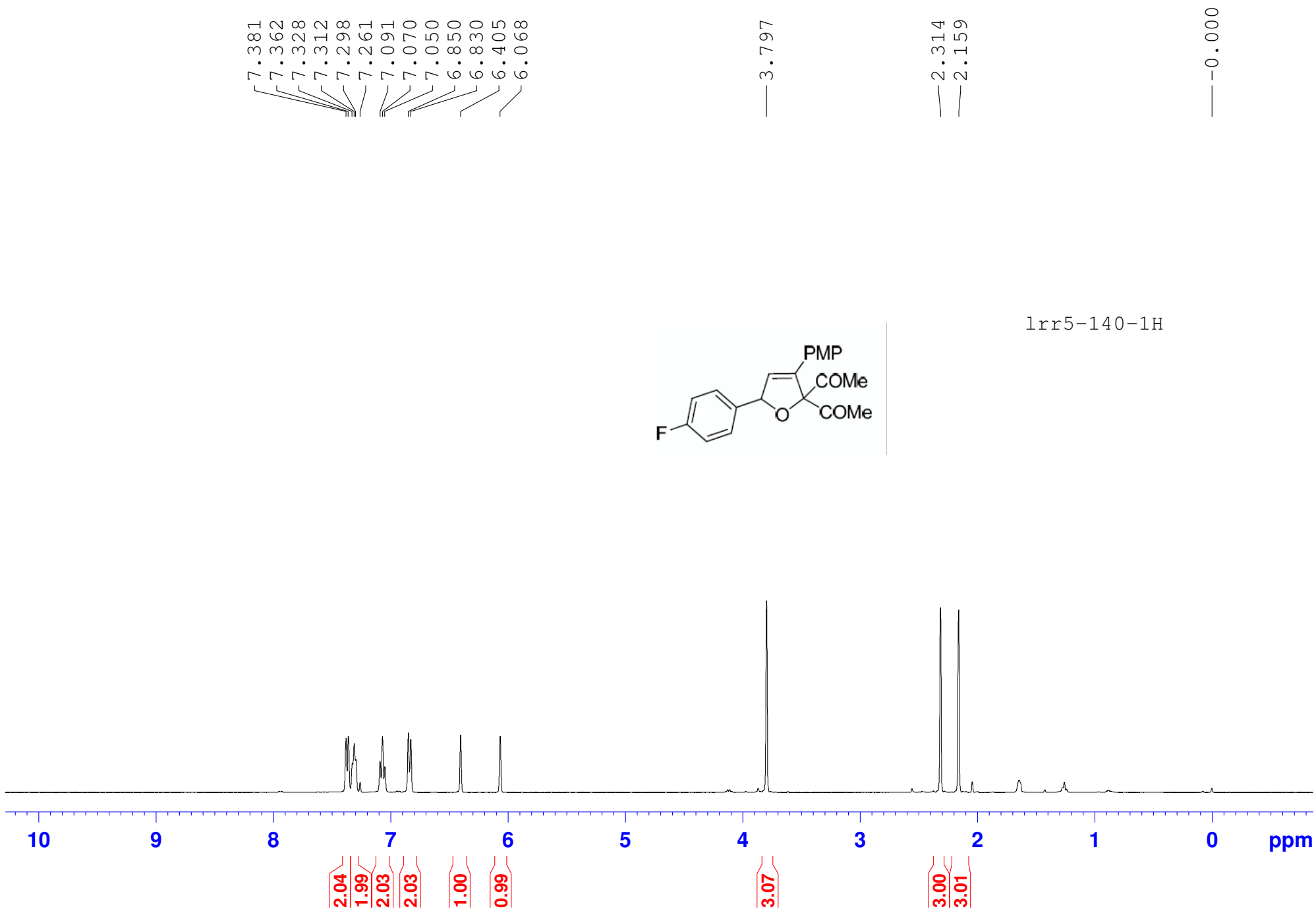


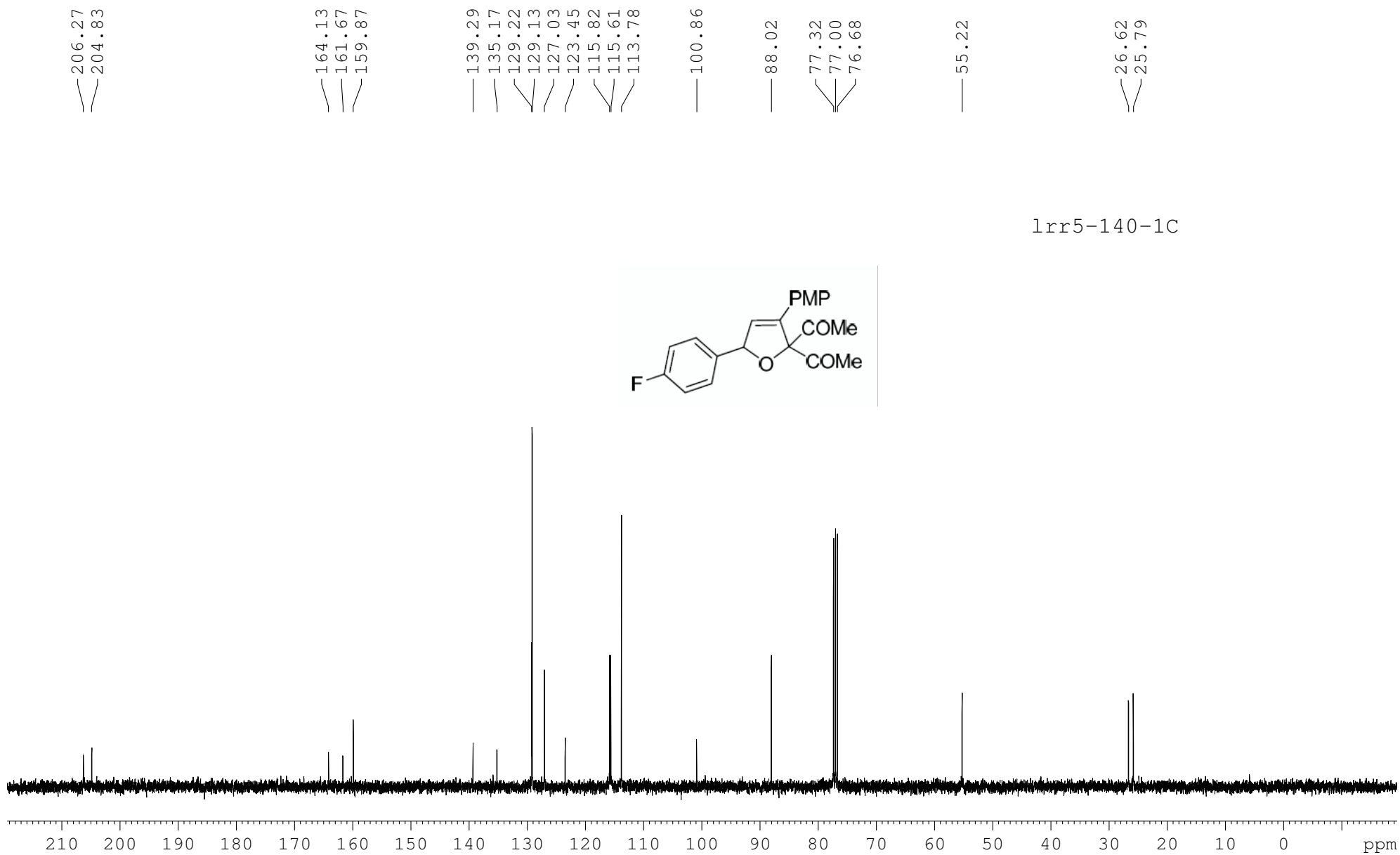




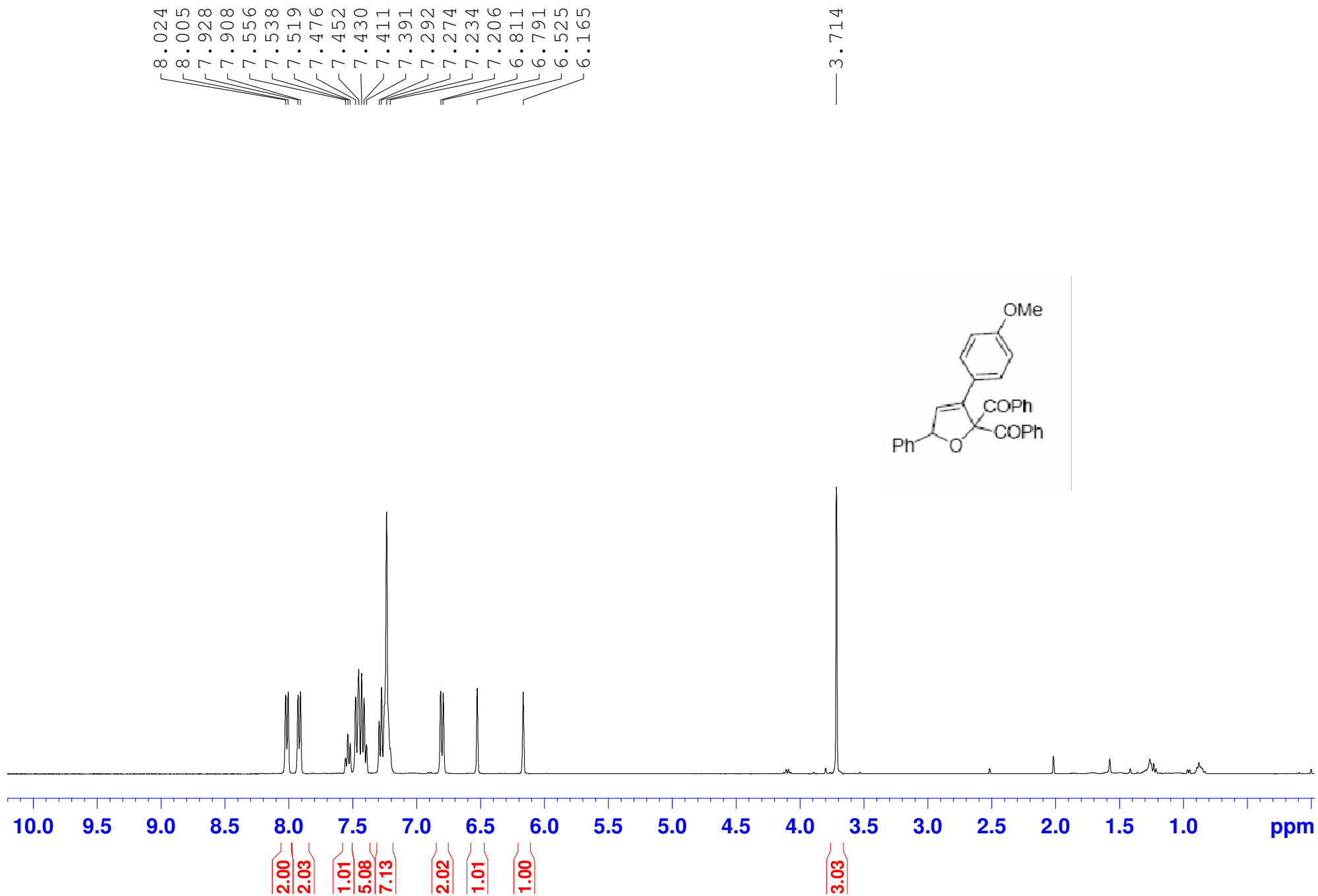


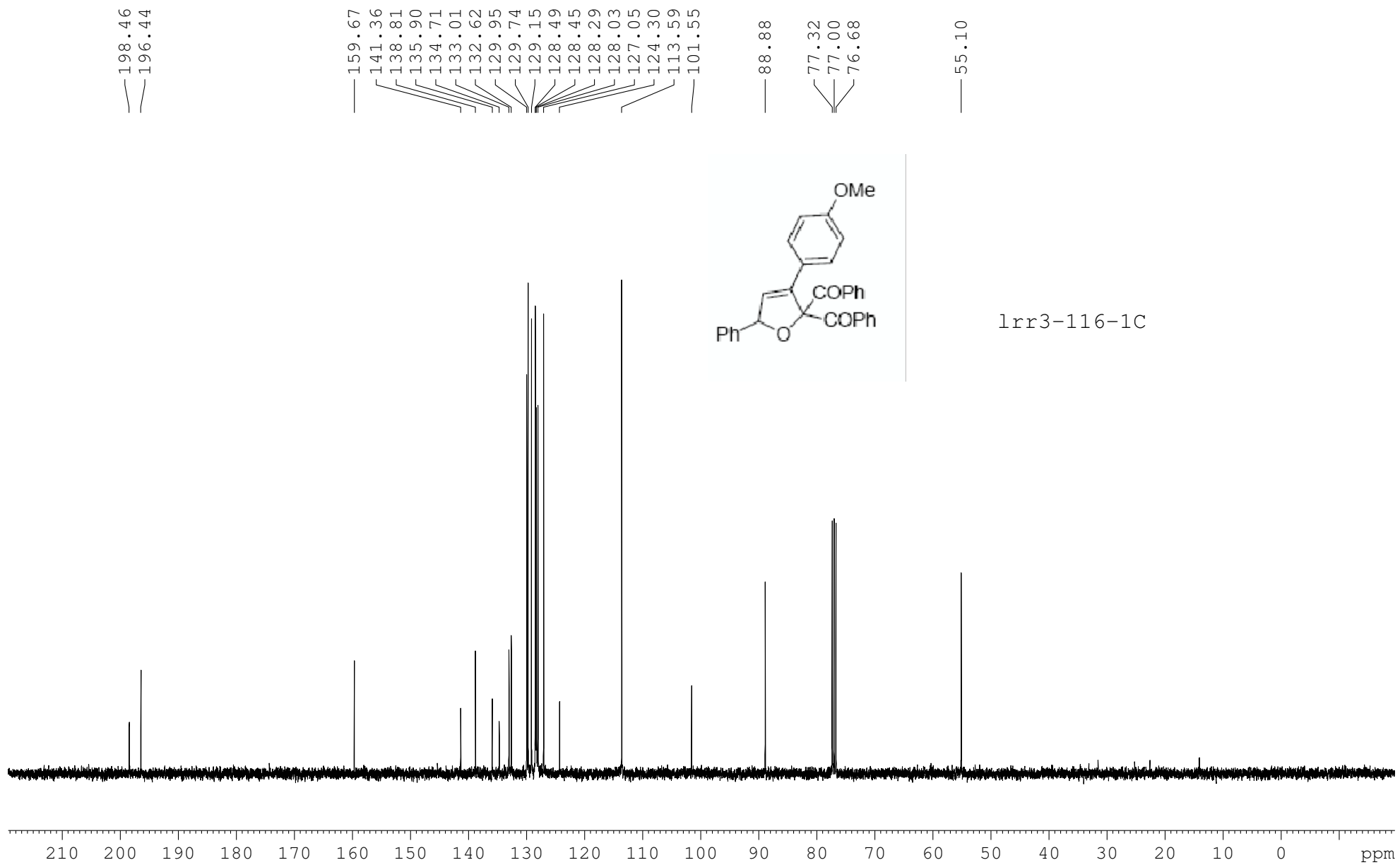


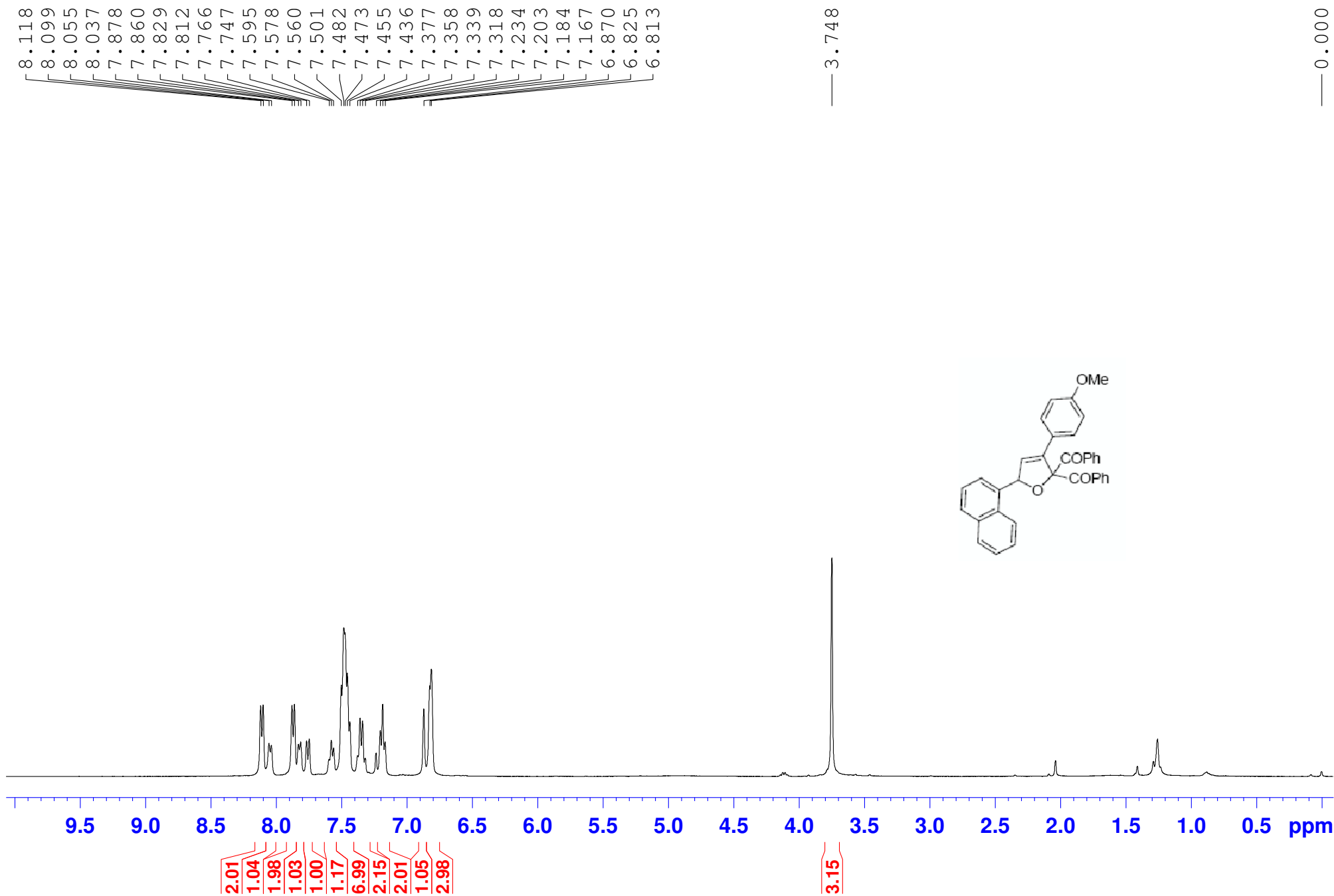


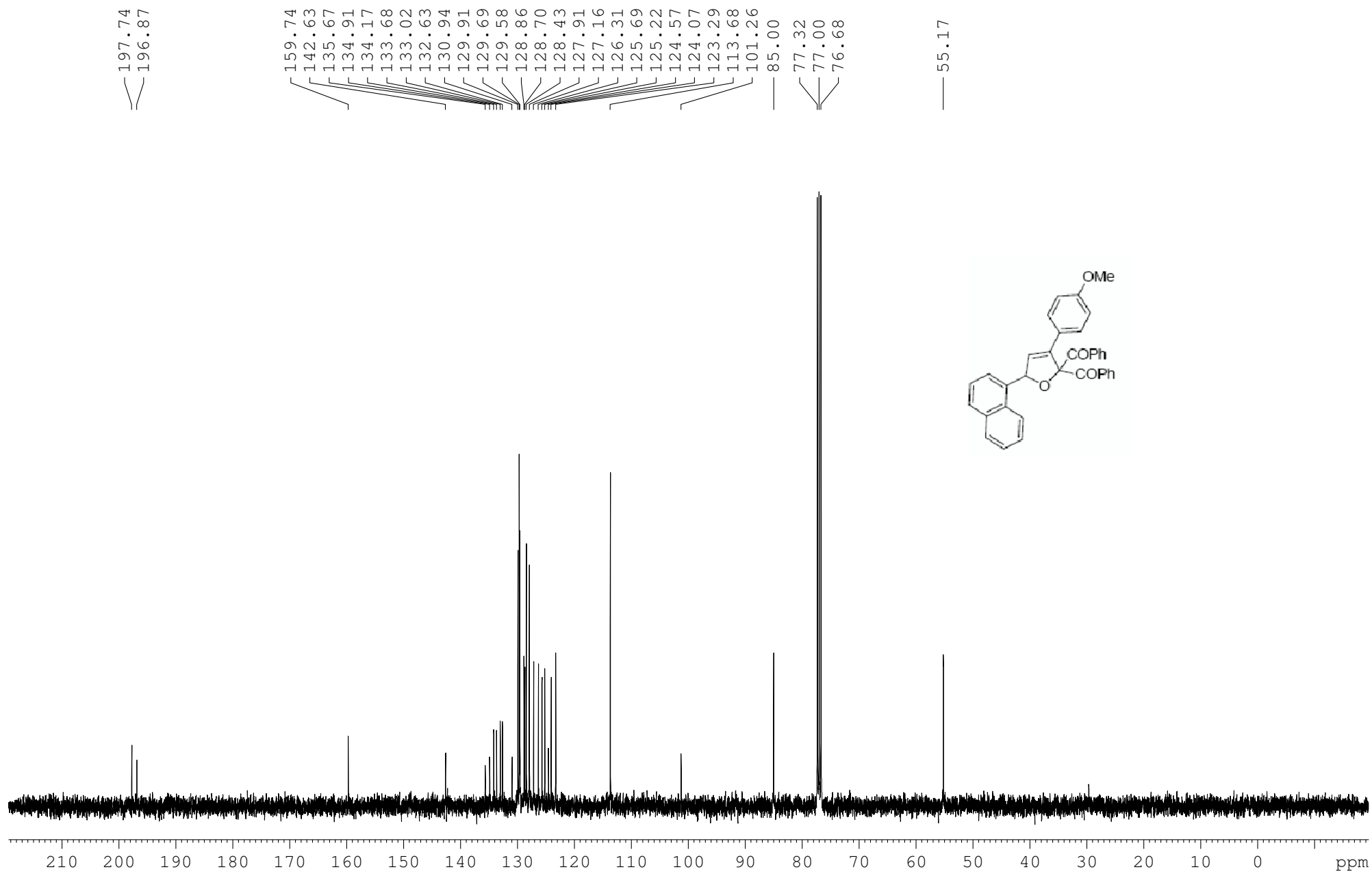


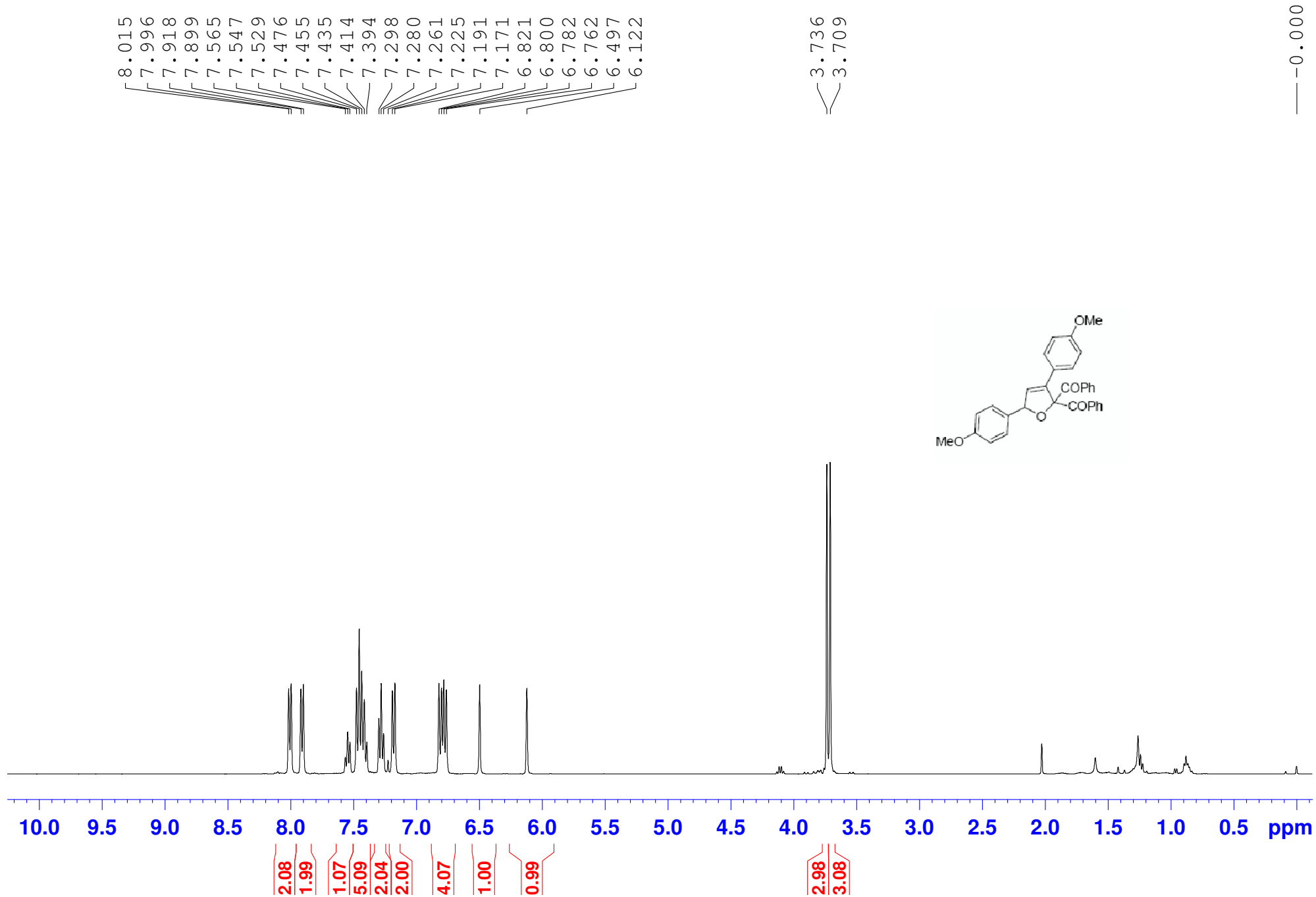
lrr5-140-1C

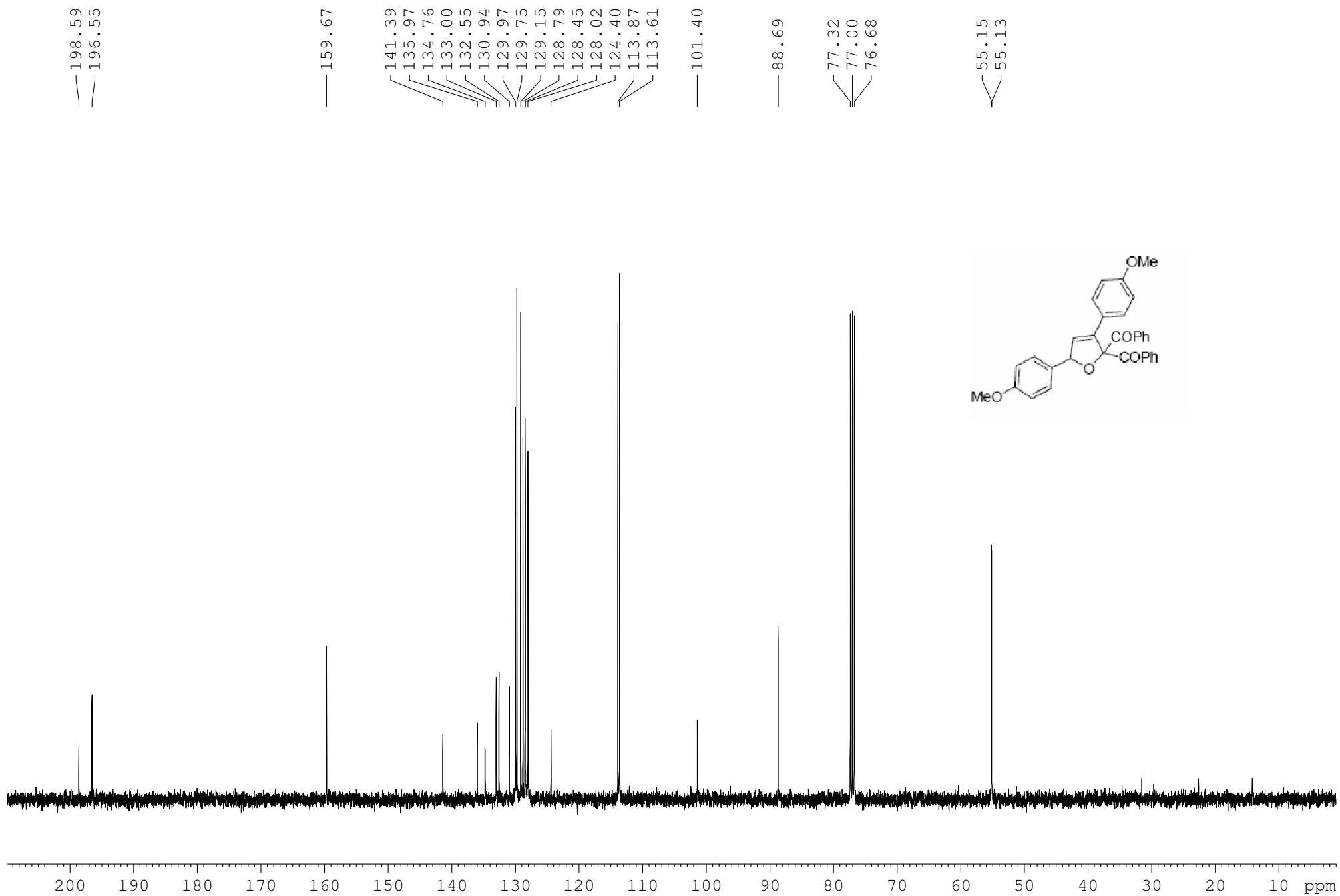


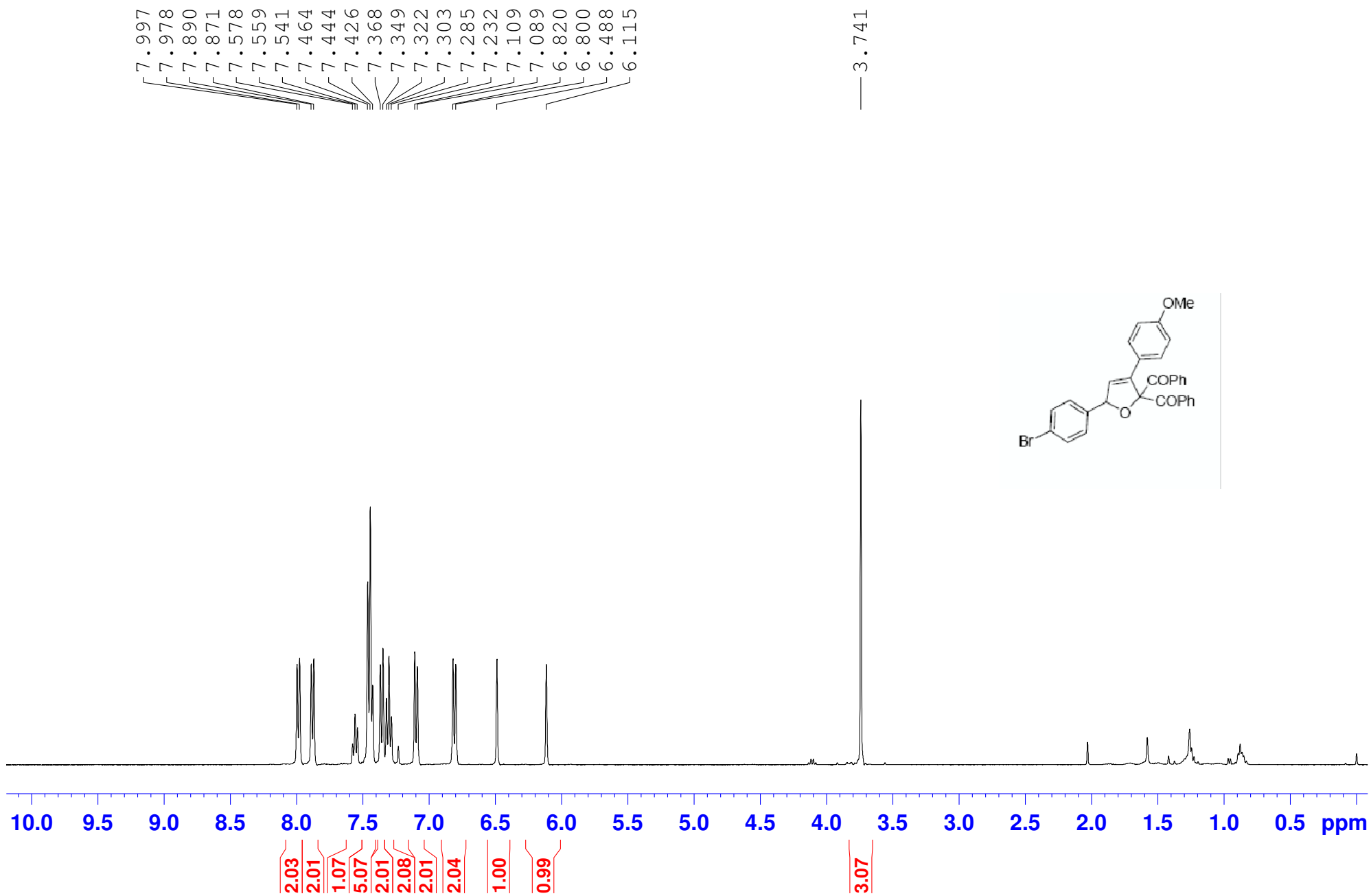


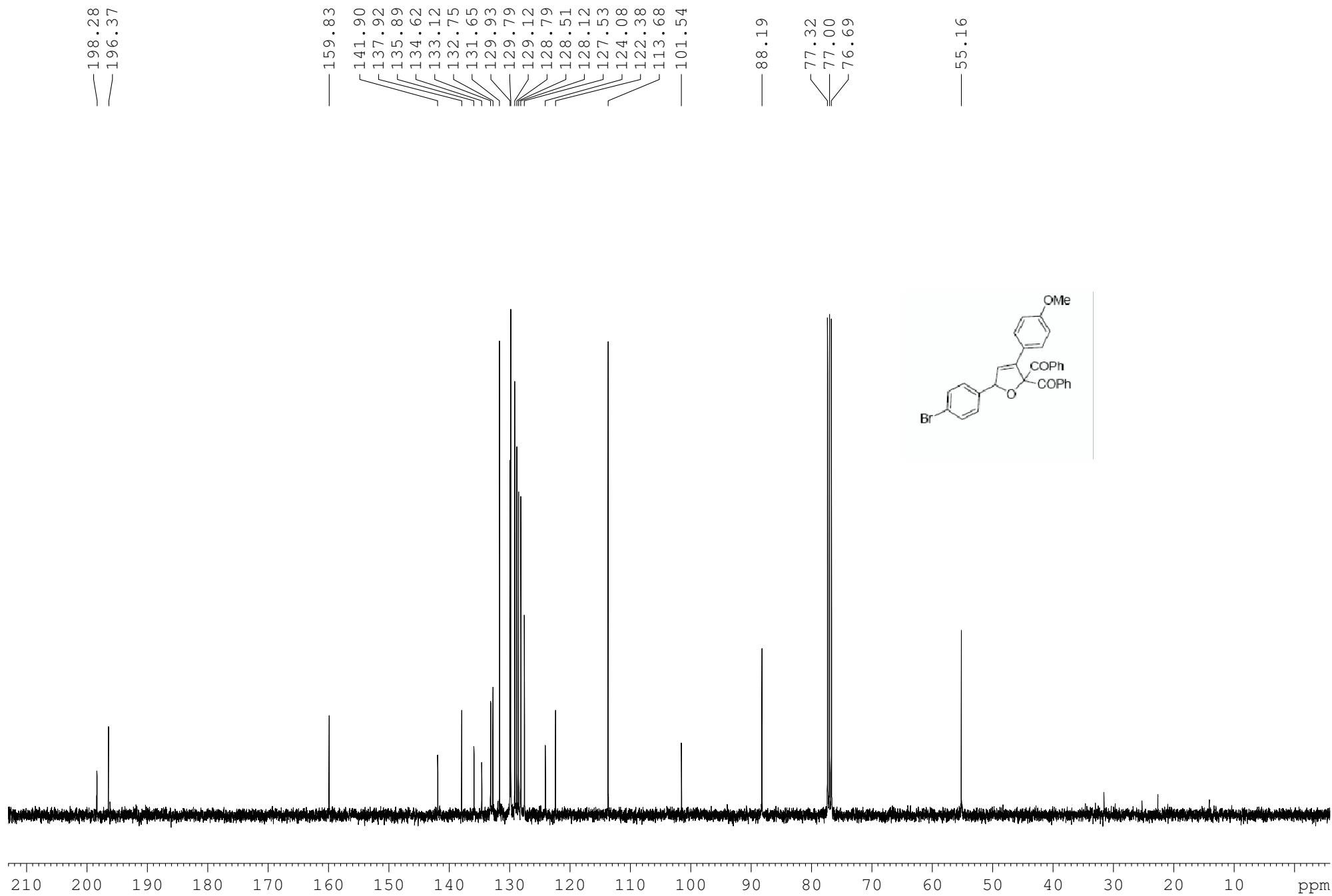










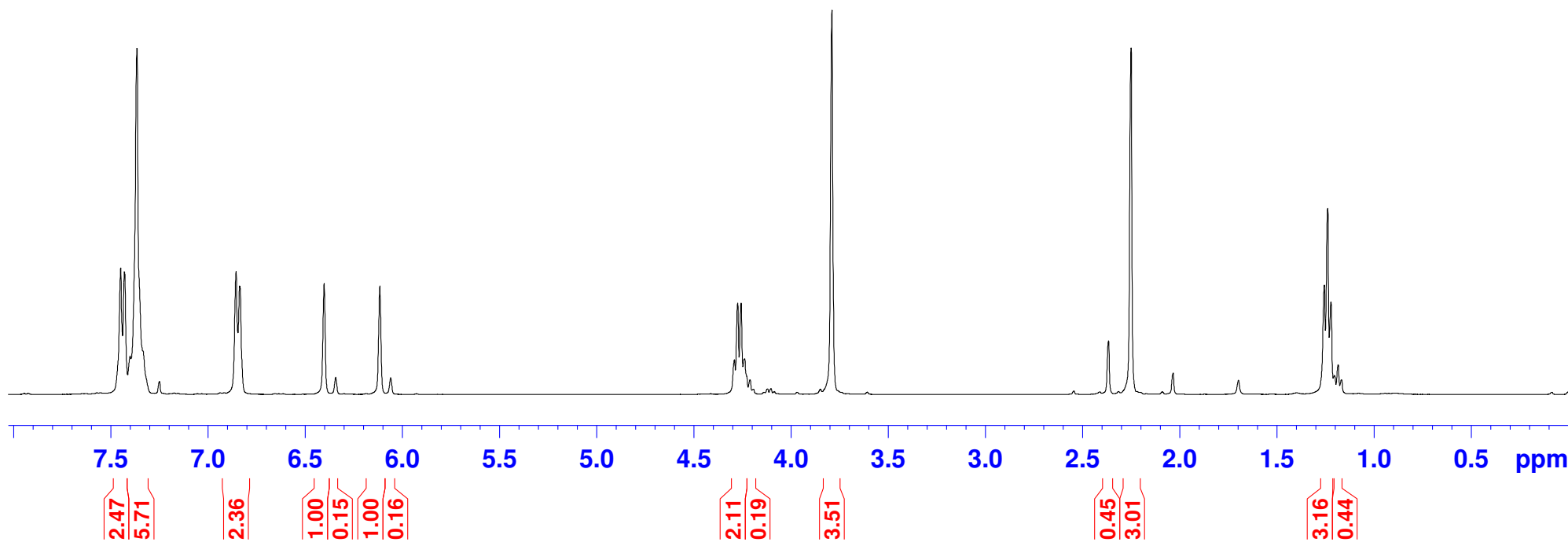
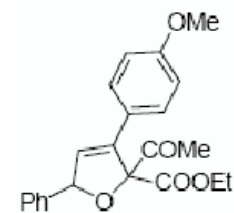


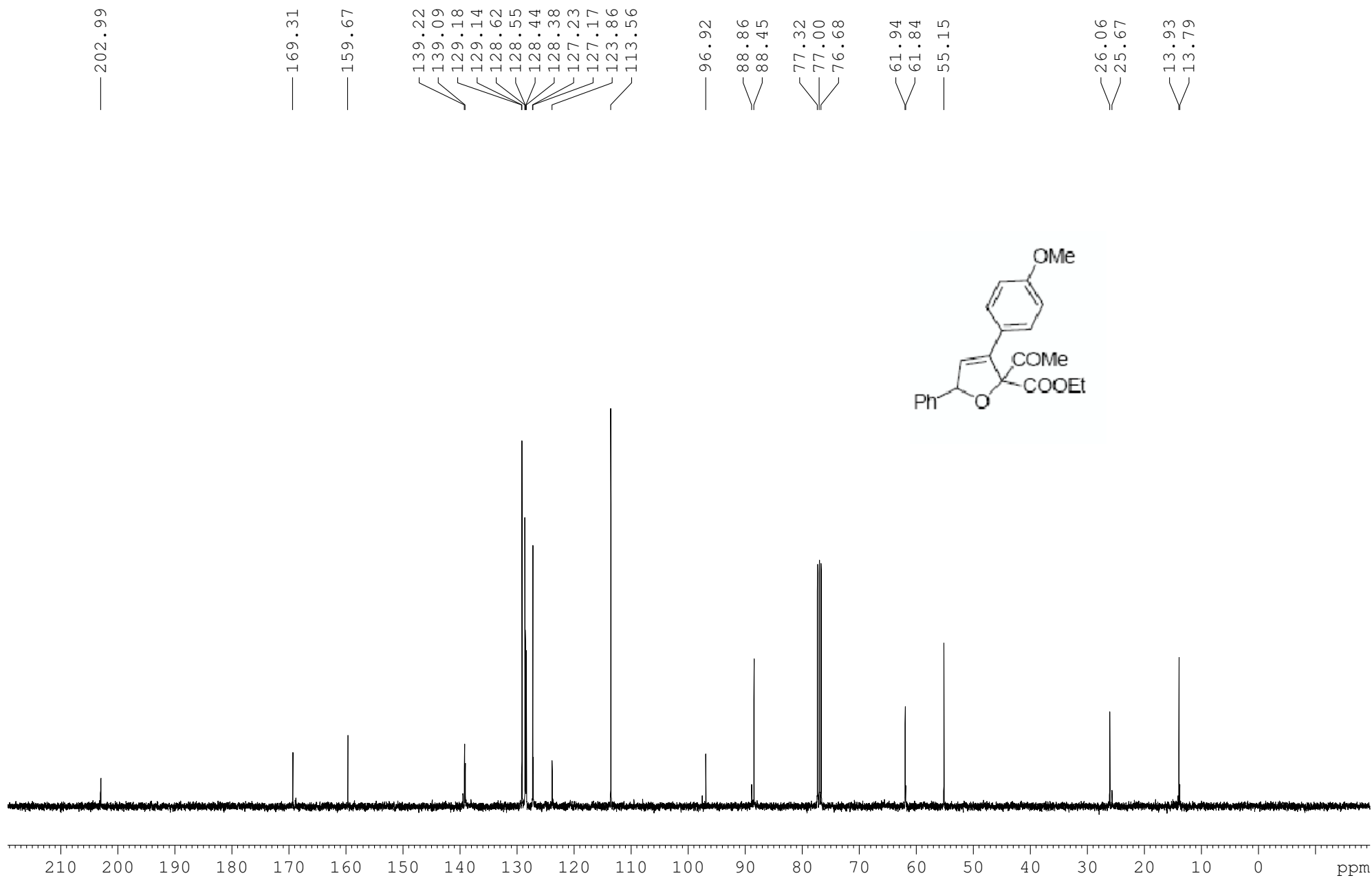
7.447
7.428
7.399
7.364
7.247
6.853
6.835
6.400
6.340
6.114
6.058

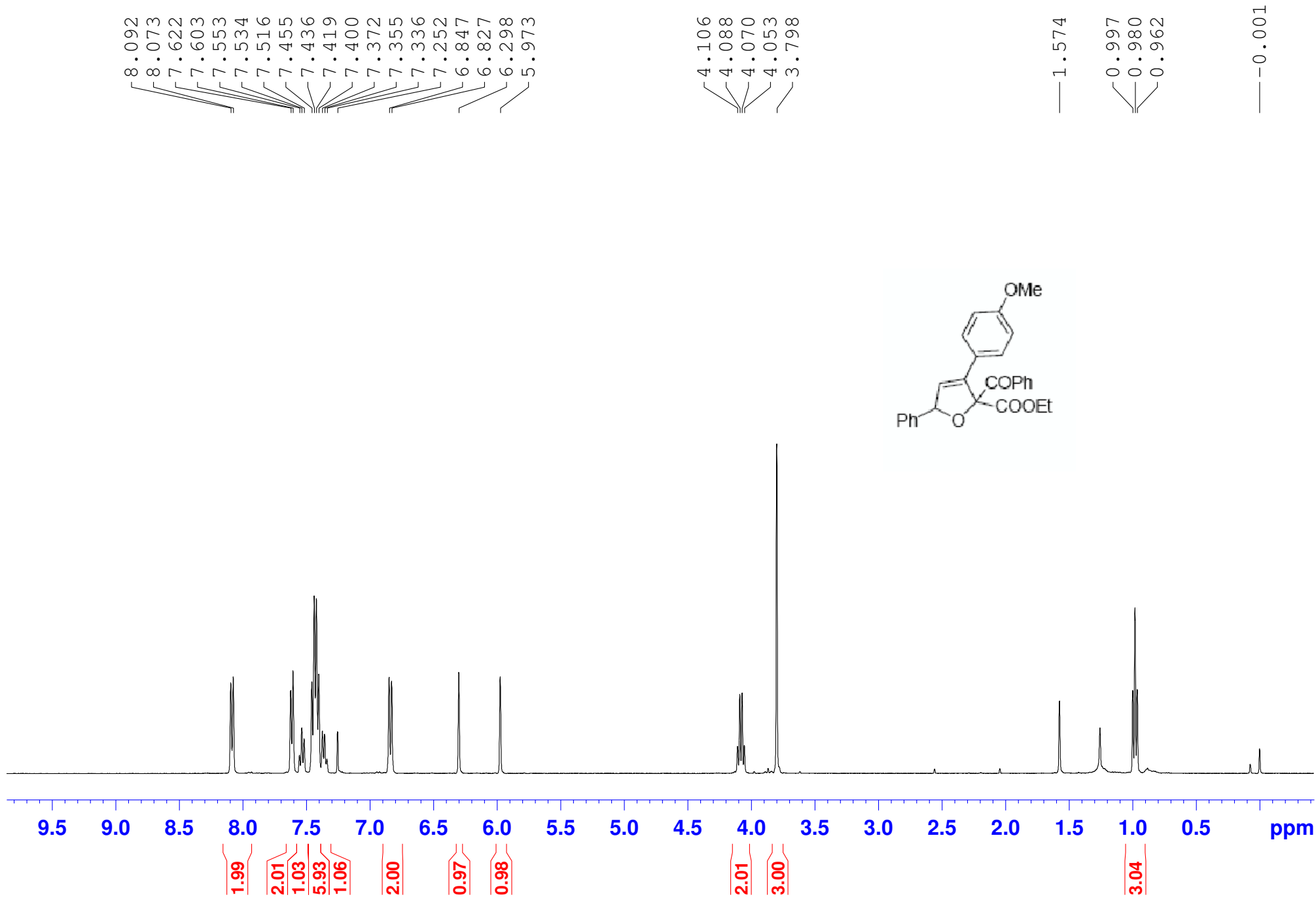
4.291
4.274
4.256
4.238
3.789

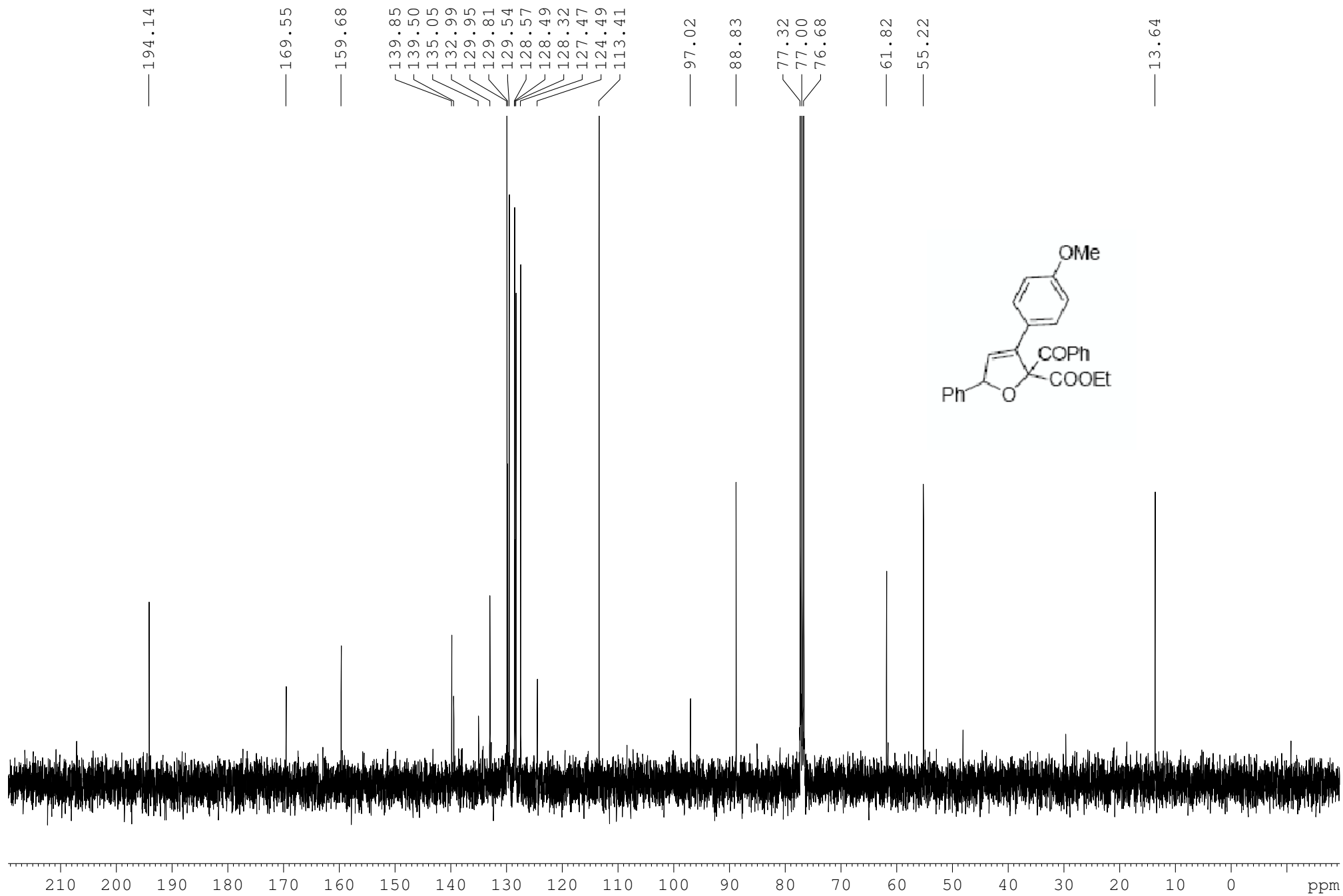
2.365
2.249

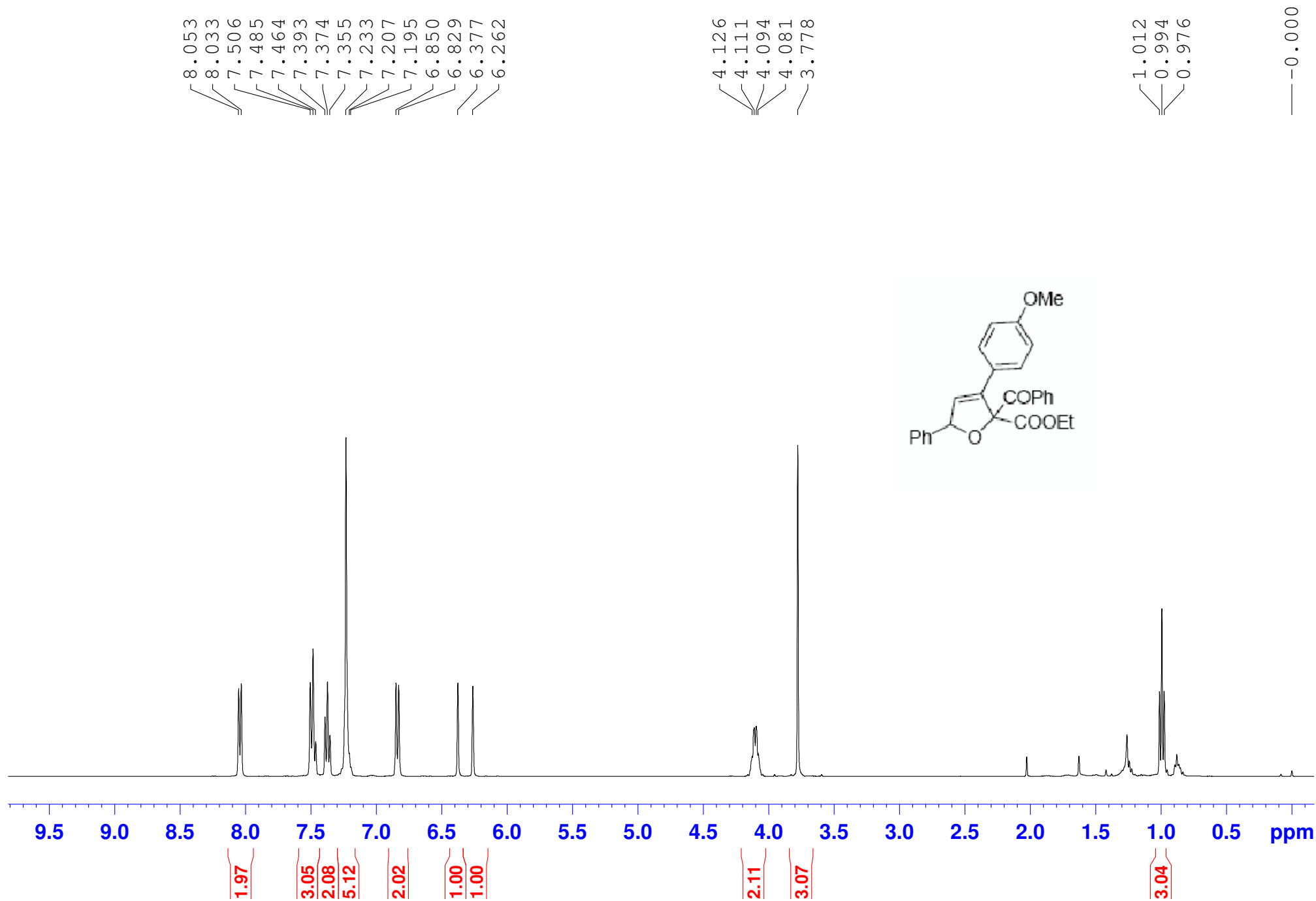
1.255
1.238
1.221
1.202
1.184
1.167

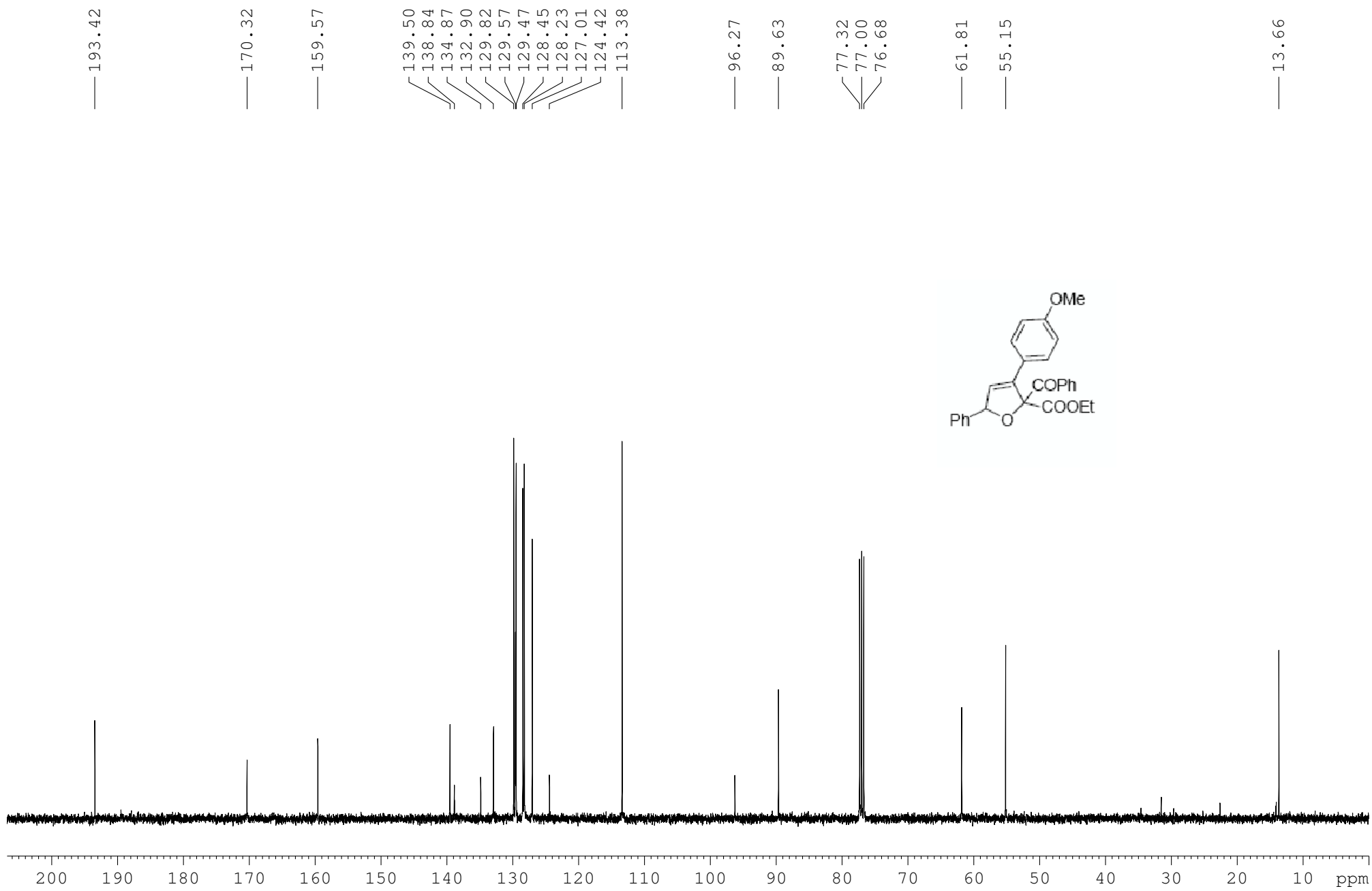


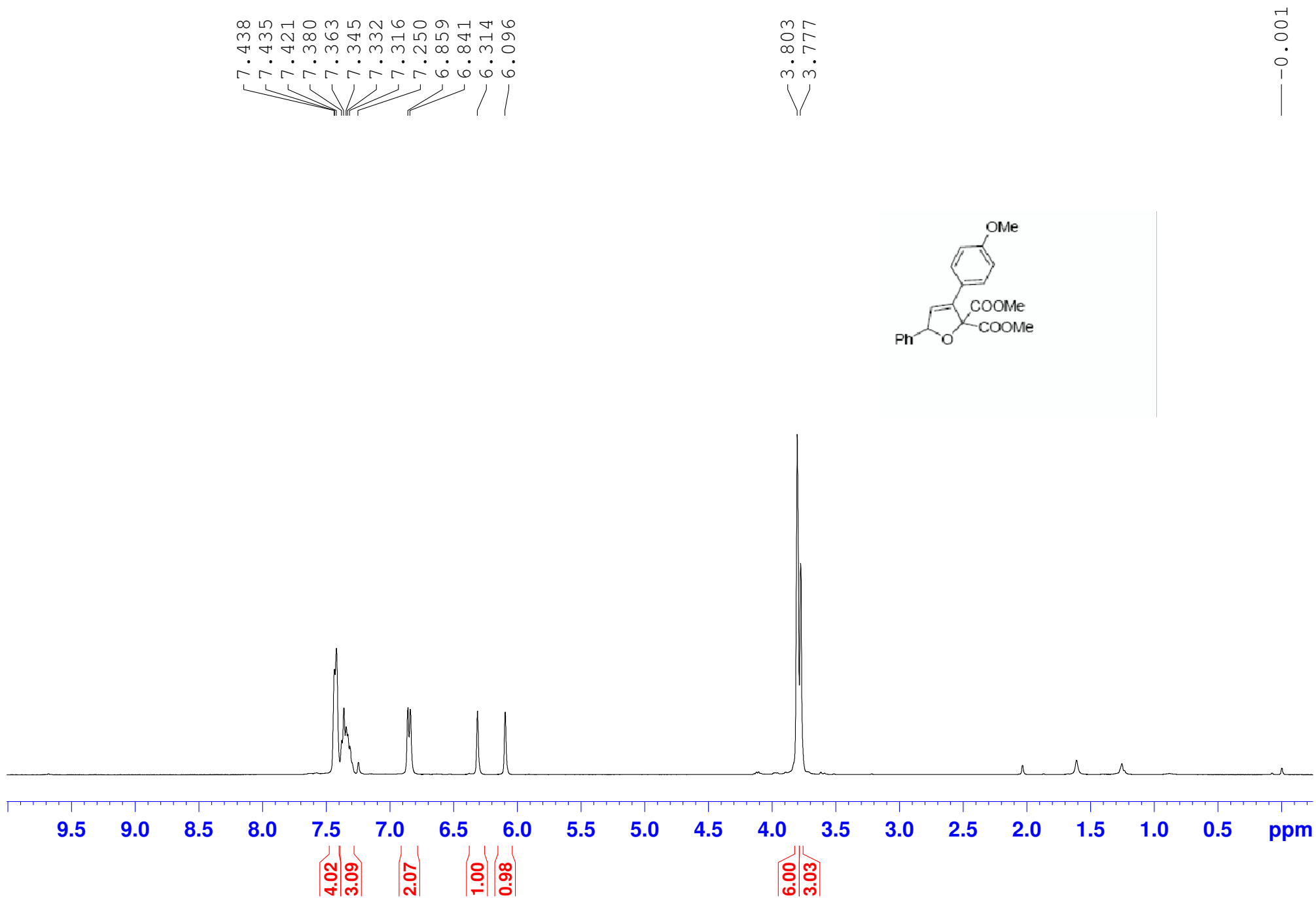


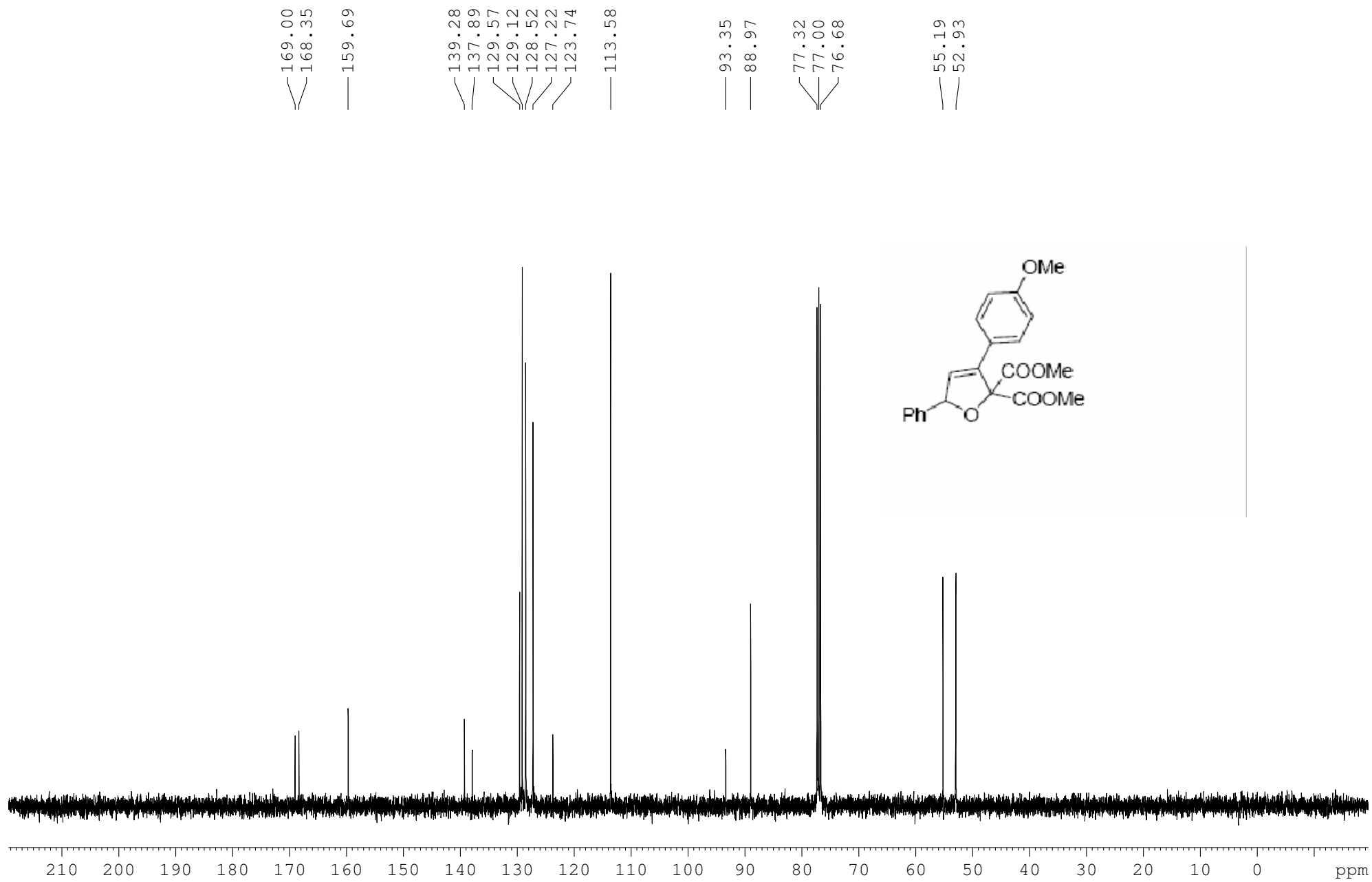












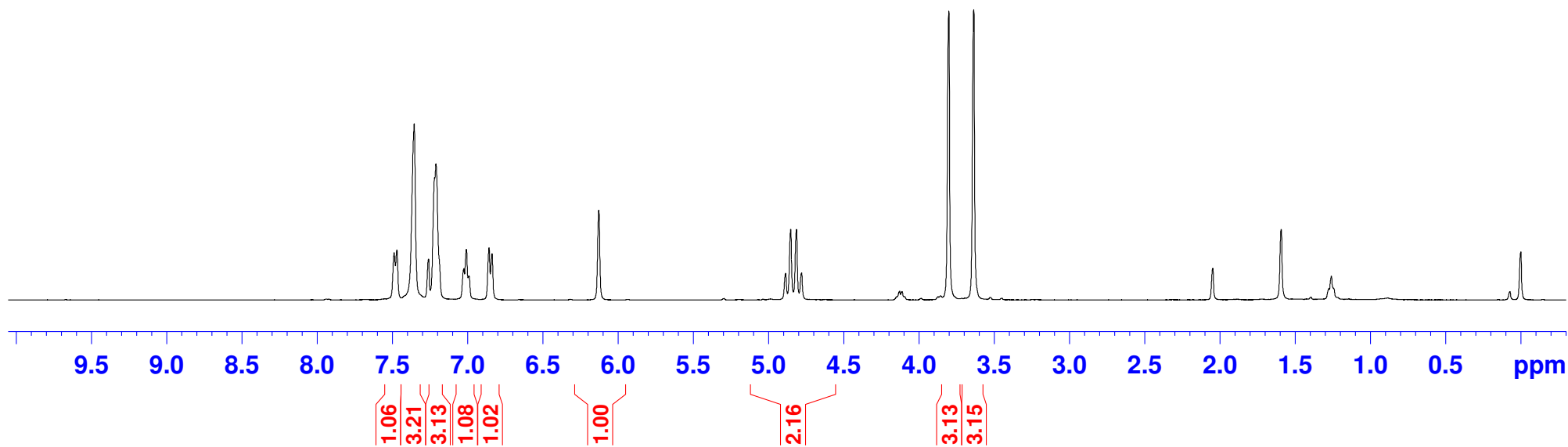
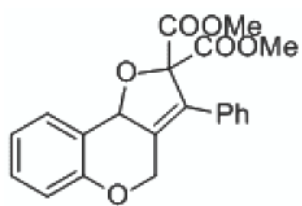
7.490
7.472
7.356
7.260
7.222
7.212
7.027
7.009
6.993
6.859
6.839
6.129

4.887
4.854
4.815
4.781

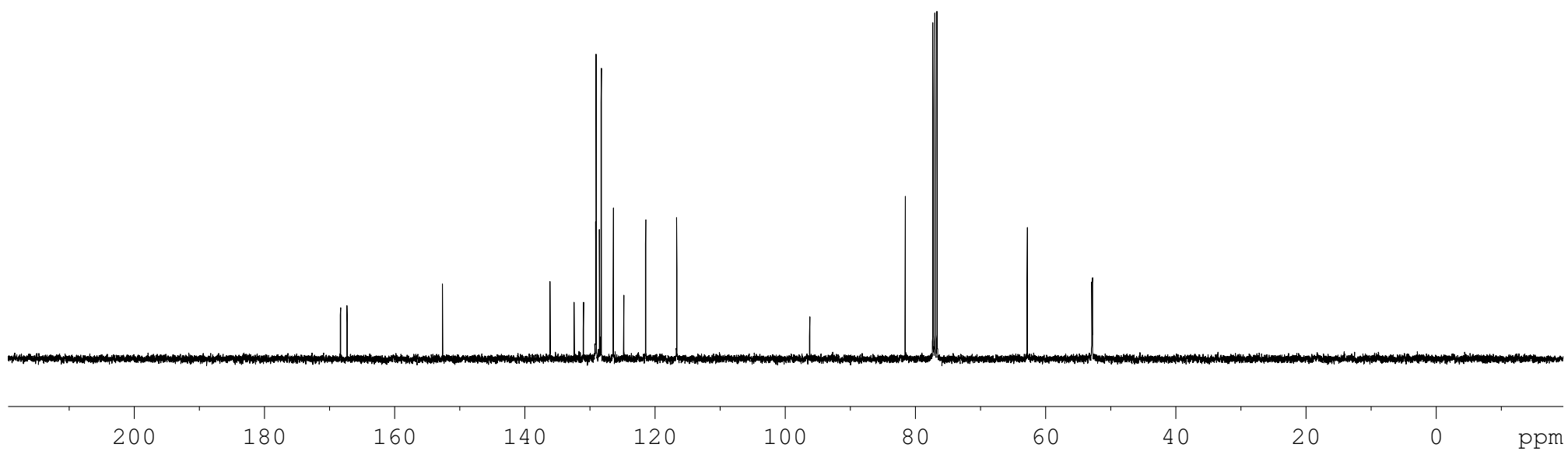
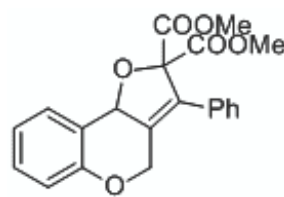
3.803
3.638

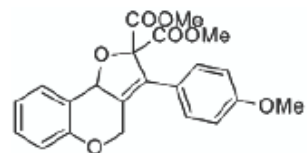
1.594

0.000



168.34
167.33
152.67
136.15
132.45
131.01
129.13
129.06
128.56
128.28
126.42
124.80
121.45
116.67
96.25
81.56
77.32
77.00
76.68
62.82
52.89
52.81



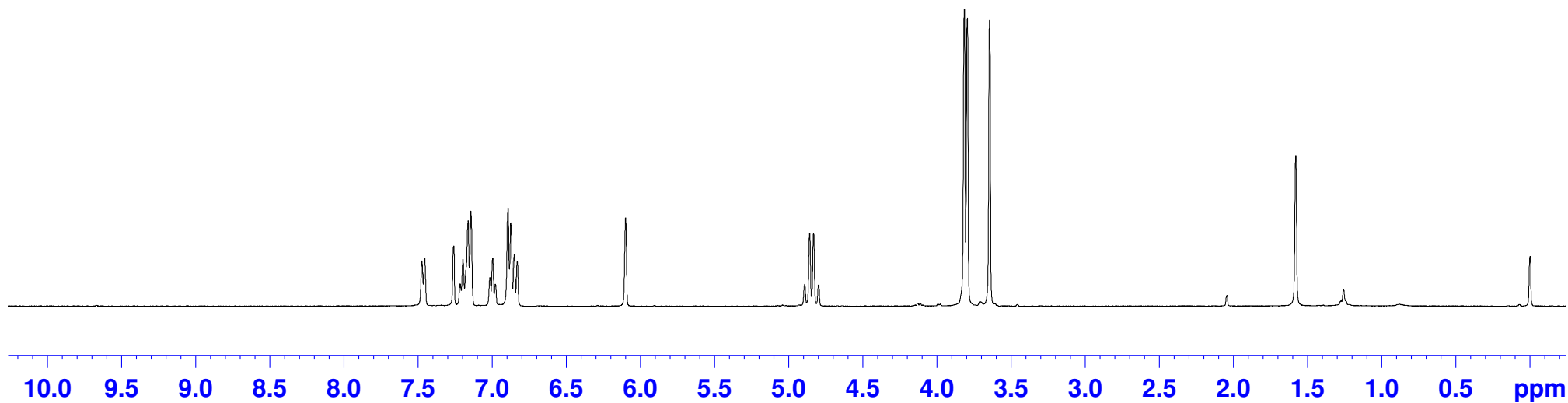


7.476
7.457
7.261
7.218
7.199
7.164
7.146
7.016
6.998
6.980
6.895
6.877
6.853
6.832
6.102

4.894
4.860
4.833
4.800

3.816
3.796
3.646

— -0.000



1.05

3.15

1.05

3.12

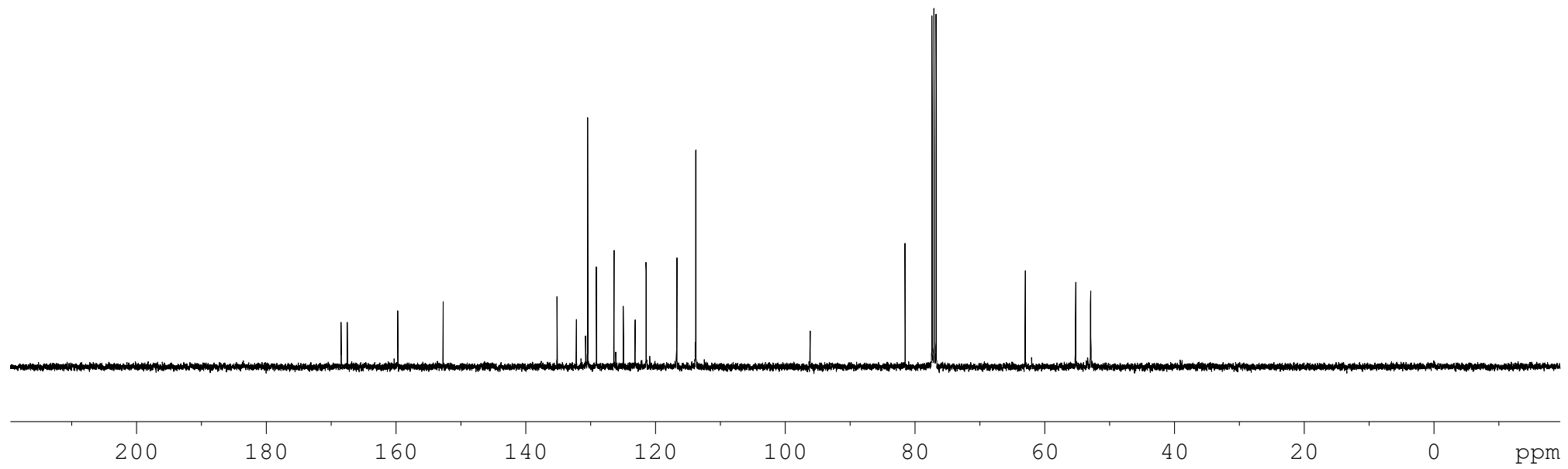
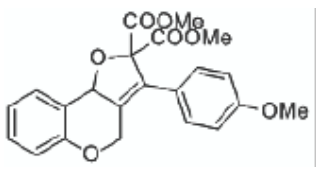
1.00

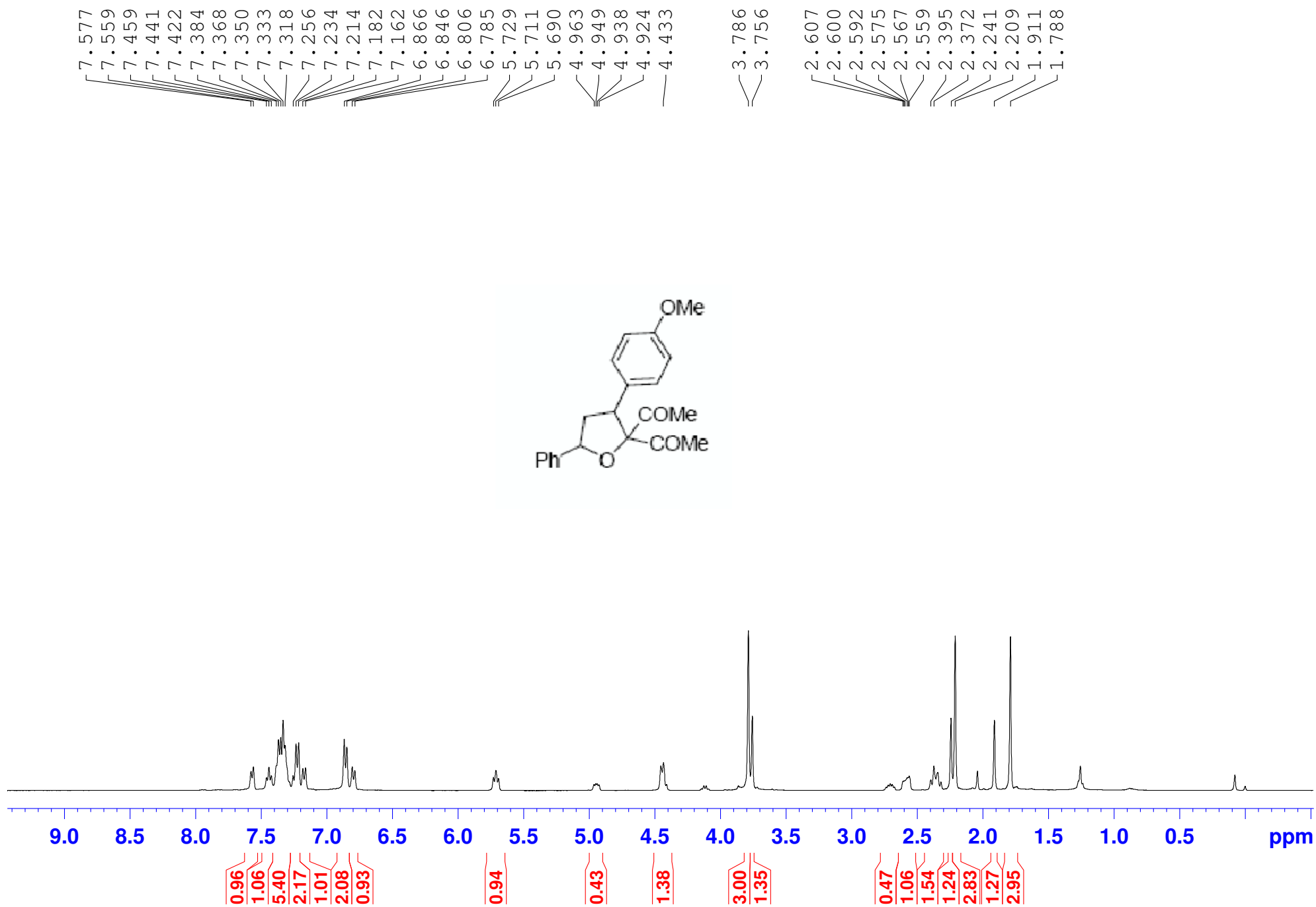
2.09

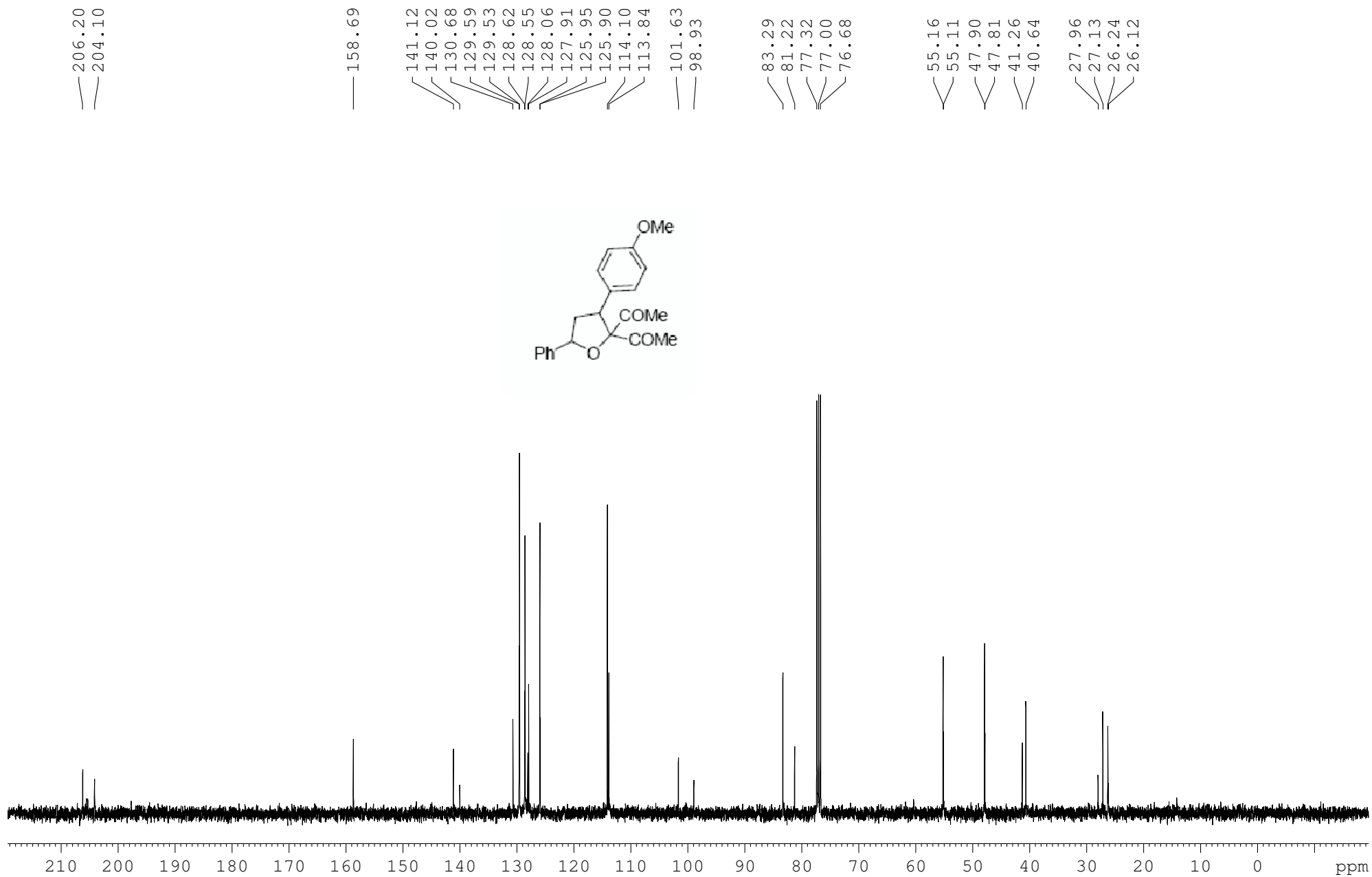
6.32

3.10

168.49
167.54
159.75
152.75
135.20
132.20
130.80
130.47
129.13
126.42
124.98
123.17
121.46
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113.80
96.18
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77.38
77.06
76.74
63.00
55.23
52.93







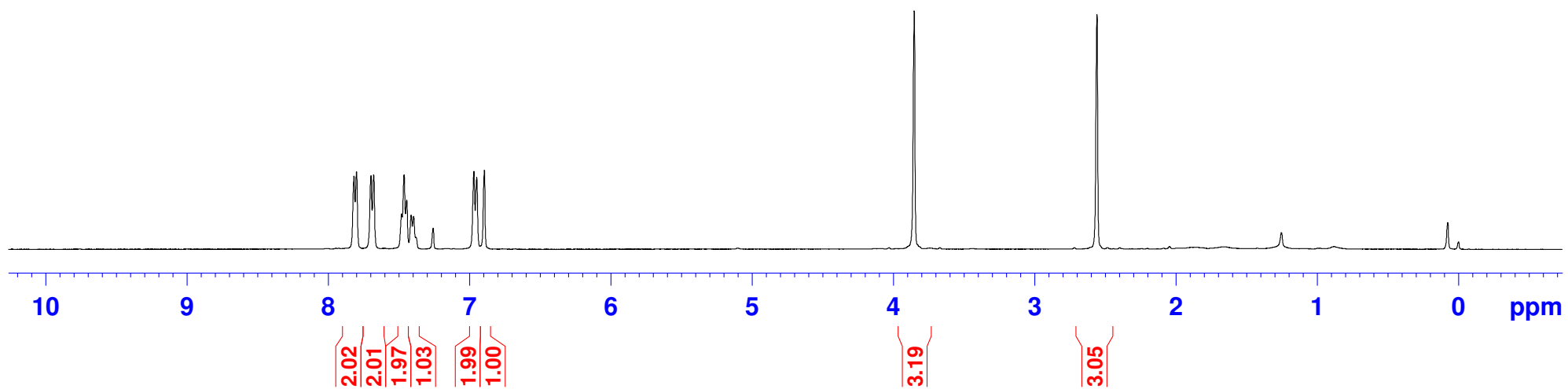
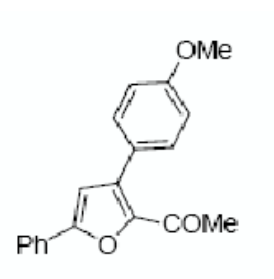
7.816
7.798
7.695
7.676
7.479
7.461
7.443
7.411
7.394
7.376
7.256
6.966
6.947
6.893

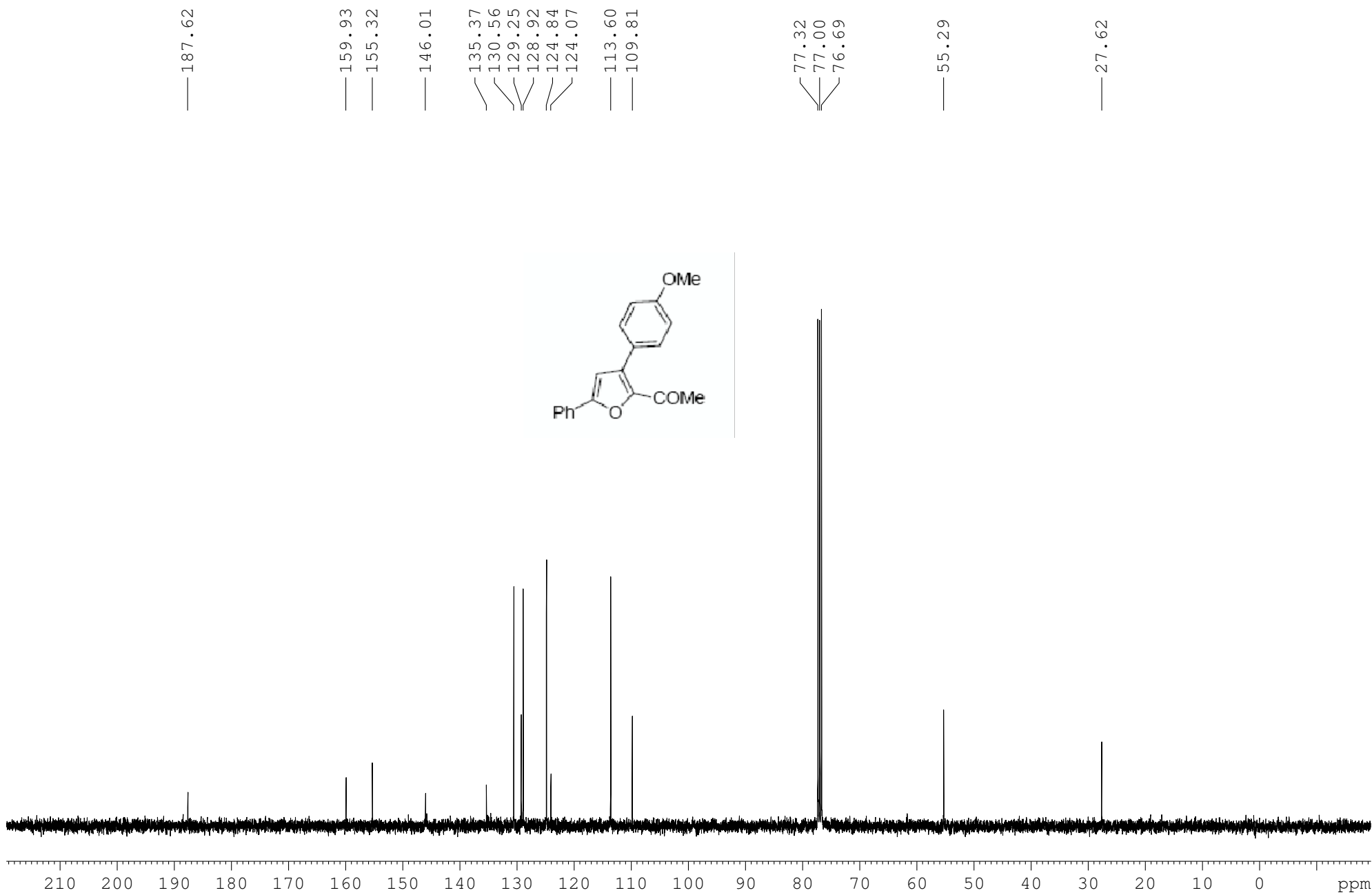
3.853

2.559

1.253

0.000

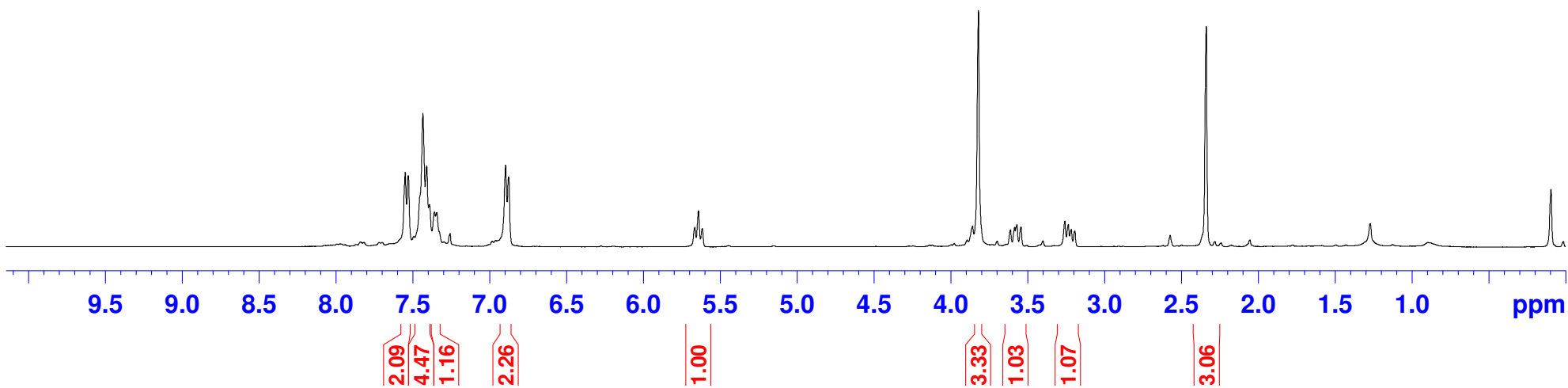
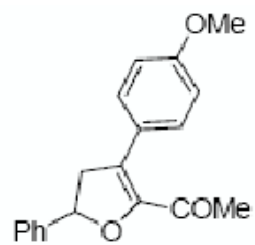


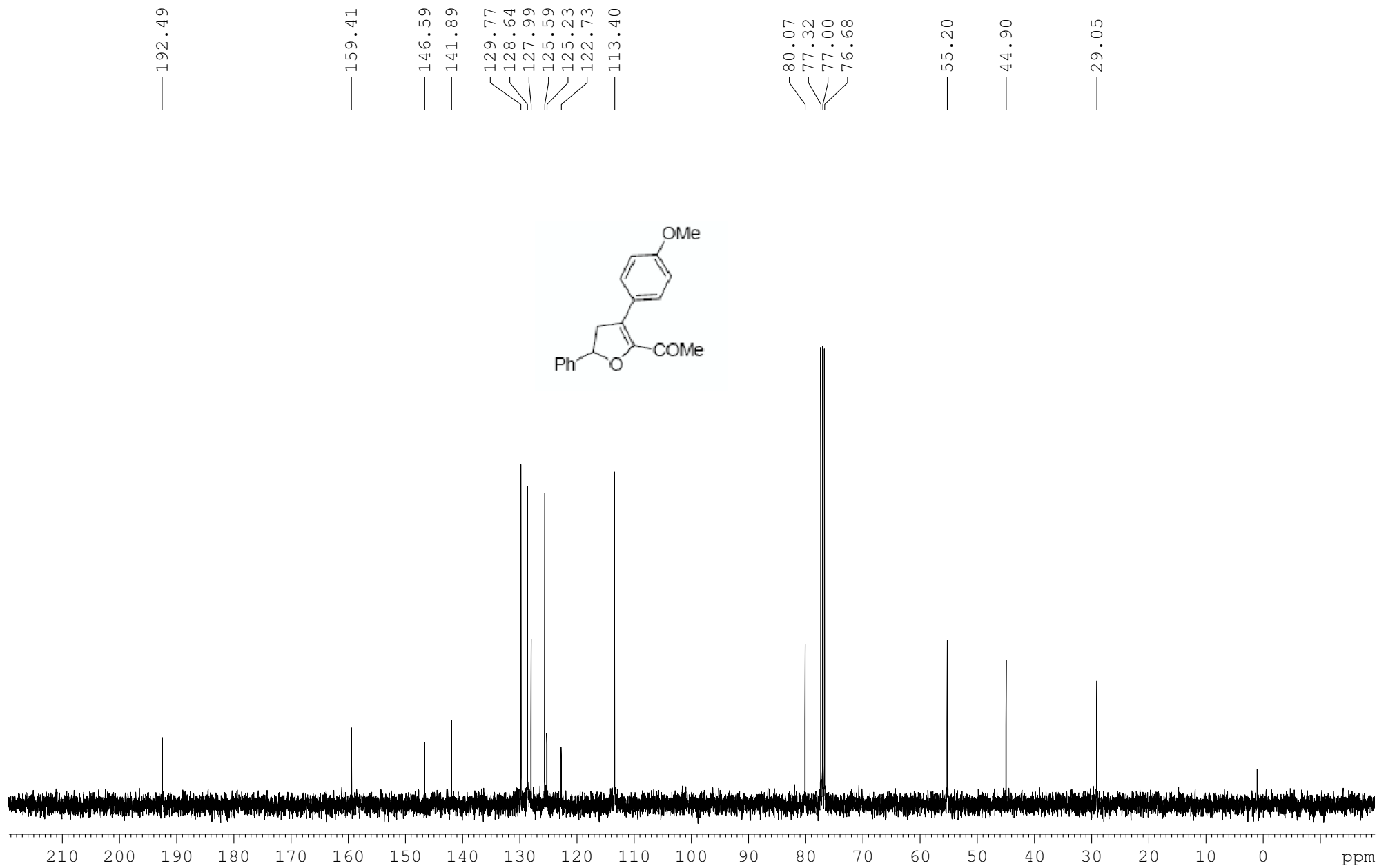


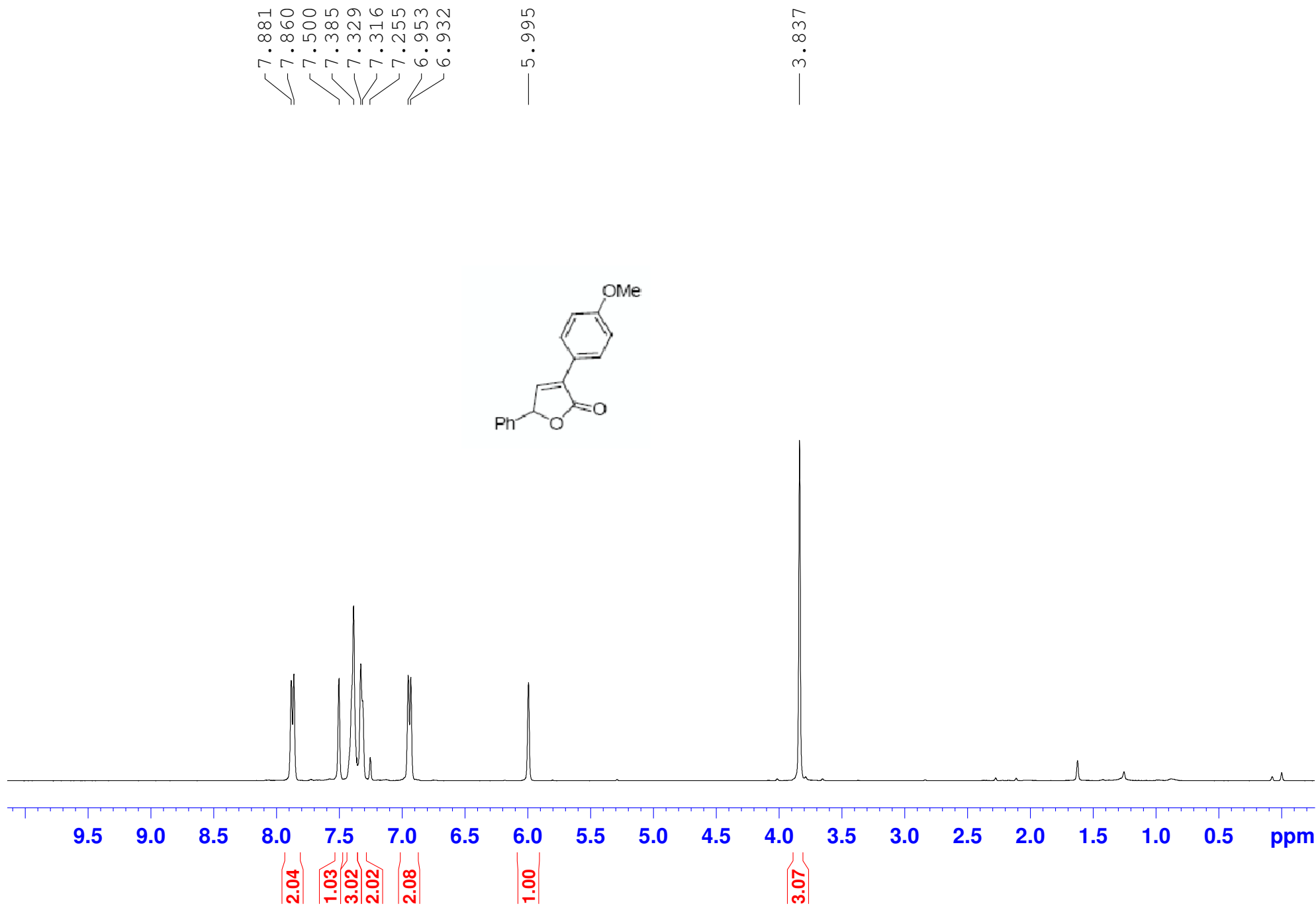
7.550
7.531
7.493
7.435
7.410
7.392
7.361
7.346
7.258
6.896
6.878

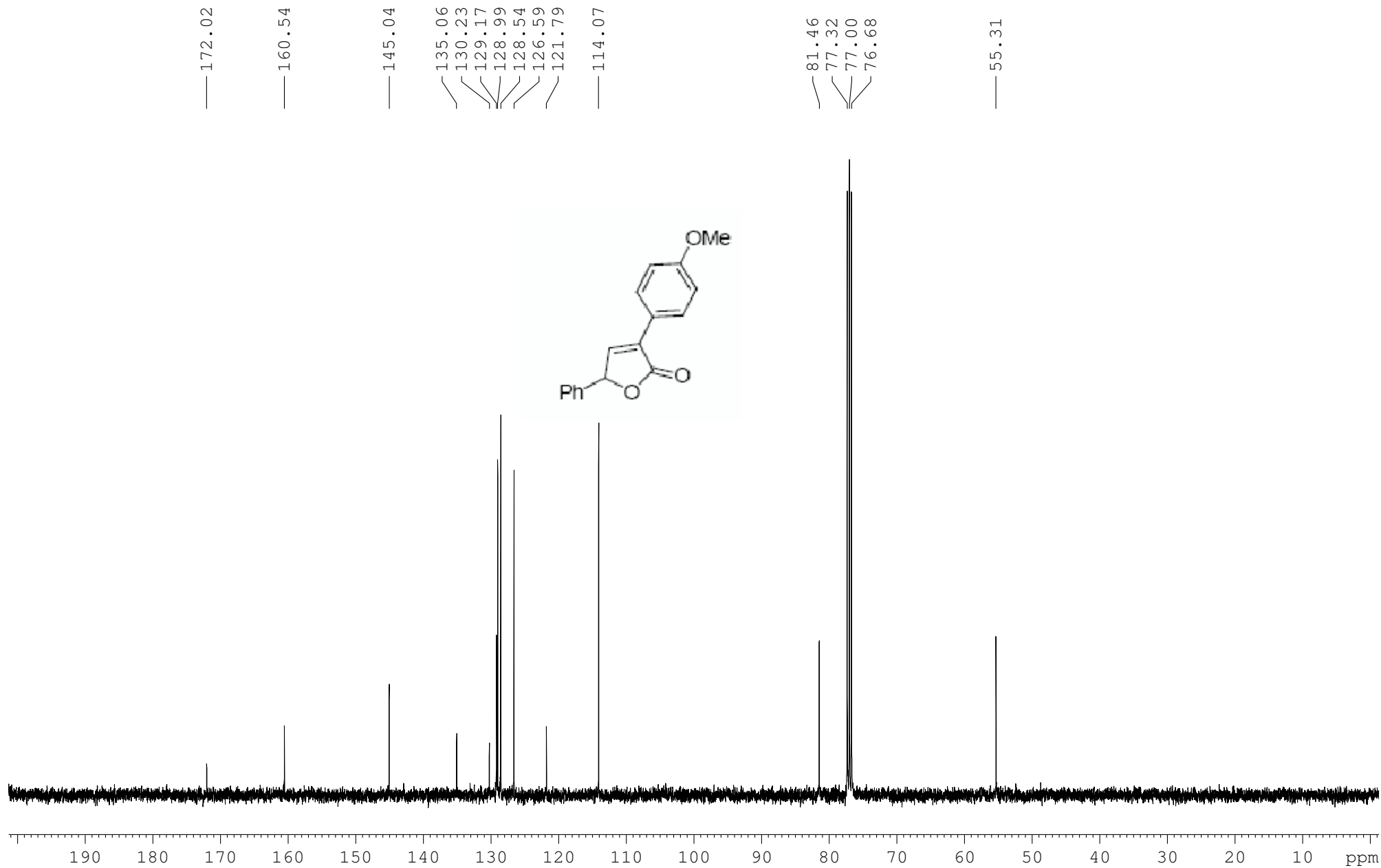
5.666
5.642
5.617

3.858
3.820
3.612
3.584
3.570
3.543
3.258
3.235
3.216
3.193
2.572
2.338

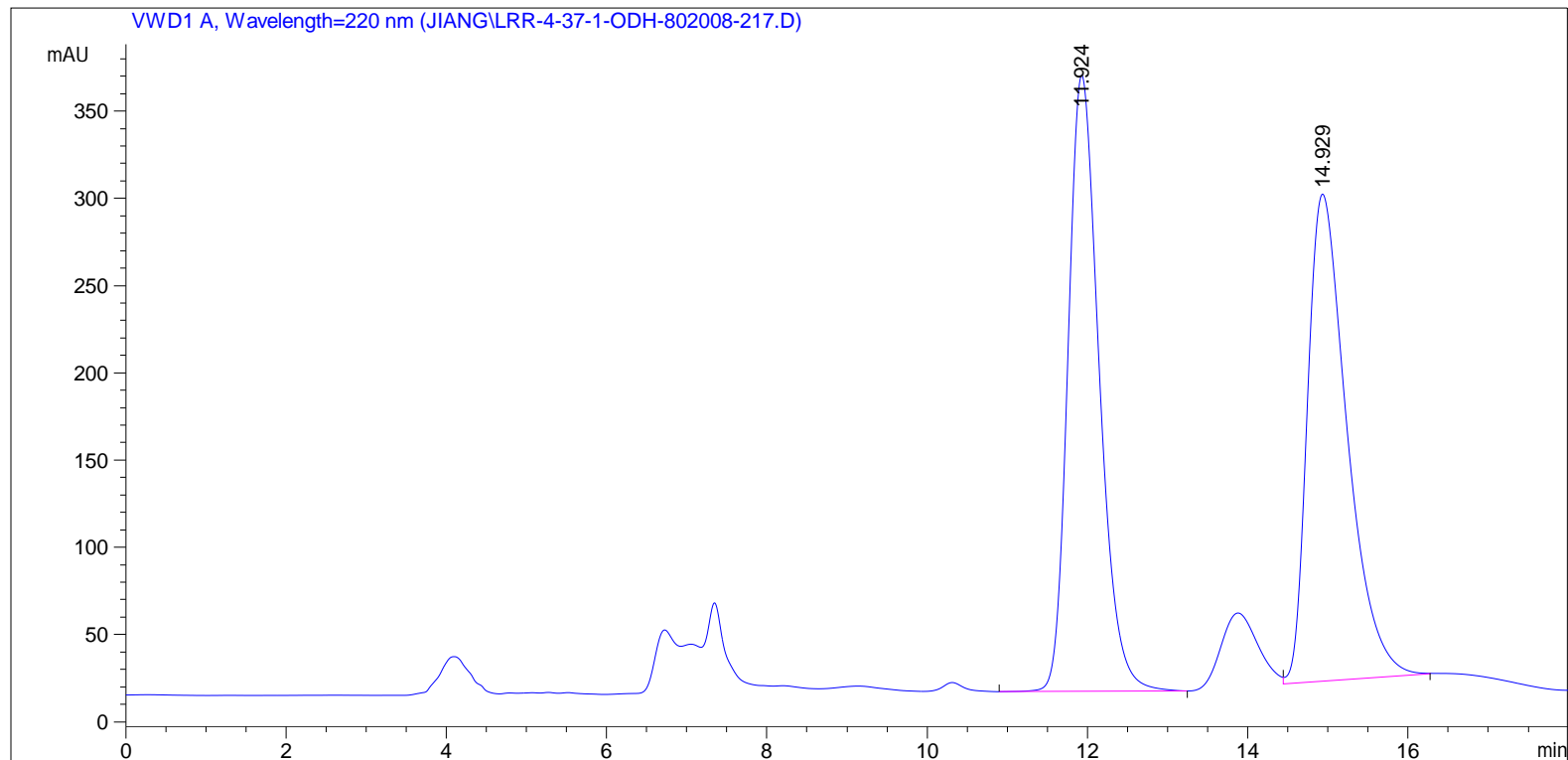








=====
Acq. Operator :
Acq. Instrument : HPLC1200LC Location : Vial 1
Injection Date : 2010-12-2 5:30:33 下午
Acq. Method : C:\CHEM32\1\METHODS\JWHTTEST.M
Last changed : 2010-12-2 5:31:46 下午
(modified after loading)
Analysis Method : C:\CHEM32\1\DATA\JIANG\LRR-4-37-1-ODH-802008-217.D\DA.M (JWHTTEST.M)
Last changed : 2011-6-27 11:25:02 上午



=====
Area Percent Report
=====

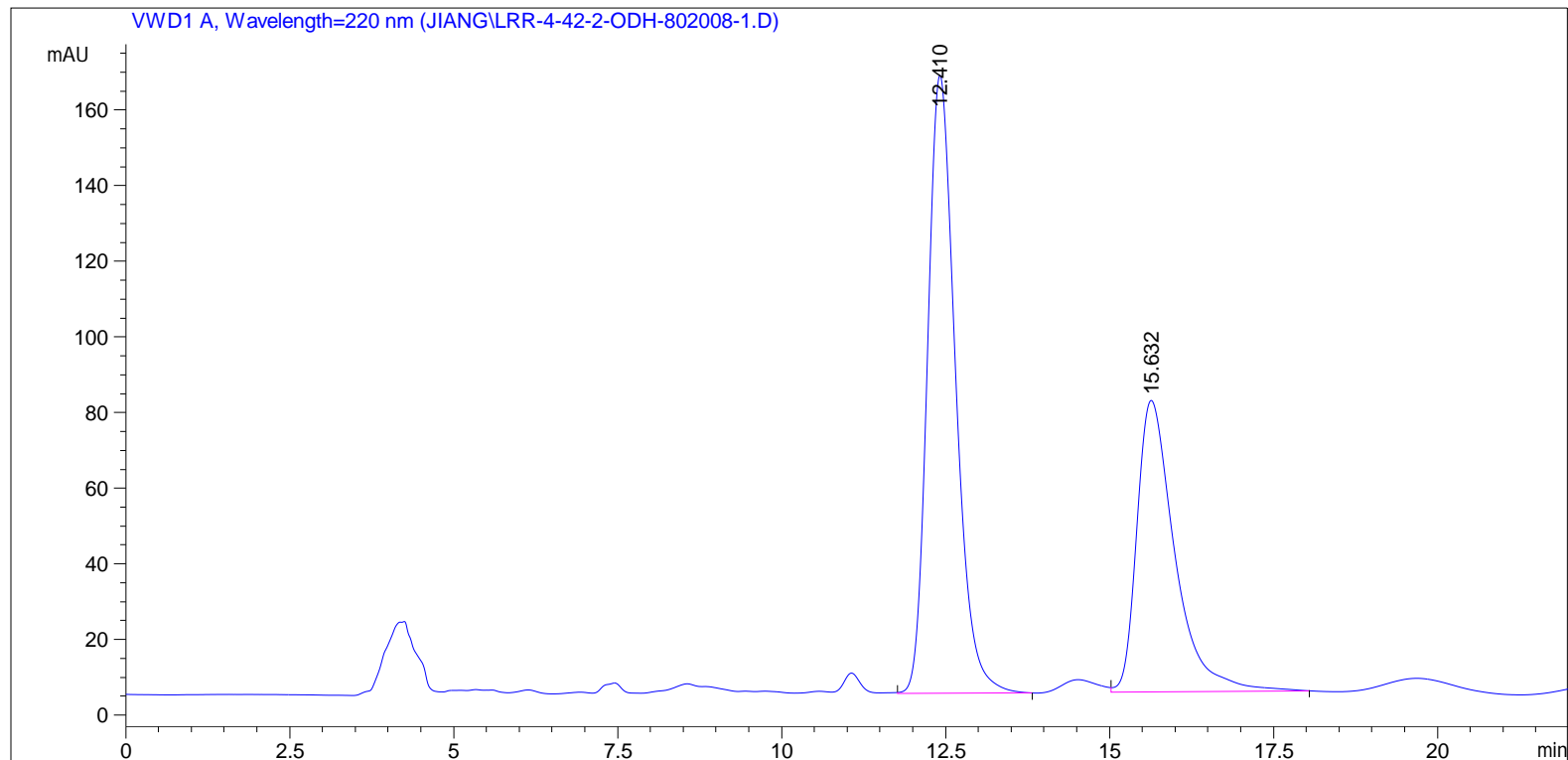
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.924	VV	0.4171	9544.48145	353.24939	49.8994
2	14.929	VB	0.5239	9582.97363	279.37442	50.1006

Totals : 1.91275e4 632.62381

=====
Acq. Operator :
Acq. Instrument : HPLC1200LC Location : -
Injection Date : 2010-12-8 2:50:22 下午
Acq. Method : C:\CHEM32\1\METHODS\JWHTTEST.M
Last changed : 2010-12-8 2:48:28 下午
(modified after loading)
Analysis Method : C:\CHEM32\1\DATA\JIANG\LRR-4-42-2-ODH-802008-1.D\DA.M (JWHTTEST.M)
Last changed : 2011-6-27 11:21:13 上午



=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.410	BB	0.4550	4844.50146	163.45033	60.8920
2	15.632	VB	0.6058	3111.39355	77.16866	39.1080

Totals : 7955.89502 240.61900