Supporting Information

Synthetic Approach to Polysubstituted Furans: An Efficient Addition/Oxidative Cyclization of Alkynoates and 1,3-Dicarbonyl Compounds

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Content

General method

All the reactions were carried out at 100 ^{o}C in a round bottom flask equipped with magnetic stir bar. Solvents and all reagents were used as received. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz. The chemical shifts (d) were referenced to TMS. GC–MS was obtained using electron ionization (EI). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. The other materials and solvents were purchased from common commercial sources and used without additional purification.

General procedure

To a stirring mixture of diethyl but-2-ynedioate (**1a**, 85 mg, 0.50 mmol) and 1-phenylbutane-1,3-dione (**2a**, 81 mg, 0.5 mmol), 2 mL toluene, $SnCl_2$ (9.5 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and DDQ (135.6 mg, 0.6 mmol) were added successively. The mixture was stirred at 100 ^{o}C for 4 h in a round bottom flask. After cooling, the solvent was diluted with water and extracted with diethyl ether. The ether layer was washed with saturated salt water, and dried with anhydrous $MgSO_4$. The resulting mixture was then analyzed by GC and GC–MS. Volatiles were removed under a reduced pressure and the crude product was subjected to isolation by PTLC (GF_{254}), eluted with a 10:2 petroleum ether–diethyl ether mixture to afford the desired product **3aa**.[1]

Characterization data for all prepared compounds

Diethyl 4-acetyl-5-phenylfuran-2,3-dicarboxylate (3aa)[1]: pale yellow viscous oil, IR ν_{max} (KBr): 3065, 2996, 2938, 1724, 1659, 1597, 1410, 1252, 1171, 1060, 942, 910, 864, 772, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.70 (m, 2H), 7.57–7.53 (m, 1H), 7.45–7.41 (m, 2H), 4.36 (q, 2H, *J* = 7.2 Hz), 3.94 (q, 2H, *J* = 7.2 Hz), 2.41 (s, 3H), 1.34 (t, 3H, *J* = 7.2 Hz), 1.05 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 262.2, 159.3, 157.4, 140.4, 137.8, 133.2, 128.8, 128.5, 125.5, 122.1, 67.8, 61.7, 14.0, 13.9, 13.5; GC–MS m/z (% rel inten.): 330.07 (M^+, 69.67), 240.92 (100).

Diethyl 4-benzoyl-5-phenylfuran-2,3-dicarboxylate (3ab)[1]: pale yellow viscous oil, IR ν_{max} (KBr): 3053, 2964, 2935, 1725, 1667, 1596, 1234, 1078, 1038, 903, 860, 812, 771, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.79 (m, 2H), 7.61–7.59 (m, 2H), 7.50–7.48 (m, 1H), 7.38–7.24 (m, 5H), 4.41 (q, 2H, *J* = 7.2 Hz), 4.06 (q, 2H, *J* = 7.2 Hz), 1.38 (t, 3H, *J* = 7.2 Hz), 1.07 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 161.6, 157.5, 155.2, 141,4, 136.9, 133.7, 130.2, 129.0, 128.8, 128.6, 127.8, 127.4, 126.2, 121.5, 61.8, 14.1, 13.6; GC–MS m/z (% rel inten.): 392.08 (M^+, 100).

Triethyl 5-phenylfuran-2,3,4-tricarboxlate (3ac): yellow viscous oil, IR ν_{max} (KBr): 3066, 2964,

1937, 1723, 1606, 1548, 1388, 1371, 1283, 1164, 1071, 938, 847, 771, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93–7.90 (m, 2H), 7.46–7.43 (m, 3H), 4.43–4.34 (m, 4H), 4.26 (q, 2H, *J* = 7.2 Hz), 1.41–1.33 (m, 3H), 1.25 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 163.1, 161.4, 159.5, 157.3, 139.7, 130.8, 129.2, 128.2, 128.0, 127.7, 127.4, 62.2, 61.8, 61.4, 14.1, 14.0, 13.9; GC–MS m/z (% rel inten.): 359.95 (M^+, 100); Anal. Calcd for $C_{19}H_{20}O_7$: C, 63.33; H, 5.59; Found: C, 63.58; H, 5.40.

Diethyl 4-acetyl-5-methylfuran-2,3-dicarboxylate (3ad) [1, 2]**:** pale yellow viscous oil, IR ν_{max} (KBr): 2965, 2936, 1709, 1675, 1547, 1411, 1295, 1207, 1156, 1055, 1020, 958, 896, 860, 774, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.40 (q, 2H, *J* = 7.2 Hz), 4.33 (q, 2H, *J* = 7.2 Hz), 2.64 (s, 3H), 2.38 (s, 3H), 1.37 (t, 3H, *J* = 7.2 Hz), 1.33 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 163.8, 160.9, 157.3, 139.2, 125.5, 122.3, 62.3, 61.7, 29.4, 15.0, 14.1, 13.9; GC–MS m/z (% rel inten.): 368.04 (M^+, 18.14), 221.96 (100).

Triethyl 5-methylfuran-2,3,4-tricarboxylate (3ae) [1]**:** yellow viscous oil, IR ν_{max} (KBr): 2985, 2938, 1722, 1609, 1566, 1373, 1251, 1175, 1058, 1022, 982, 908, 860, 786, 705, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.39–4.23 (m, 6H), 2.62 (s, 3H), 1.37–1.27 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 162.2, 161.6, 157.2, 139.0, 126.1, 114.0, 62.0, 61.6, 60.9, 14.1, 14.0; GC–MS m/z (% rel inten.): 297.98 (M^+, 21.74), 251.84 (100).

Ethyl 4-benzoyl-3,5-diphenylfuran-2-carboxylate (3bb): yellow solid, mp: 109–110°C; IR ν_{max} (KBr): 2961, 2896, 1815, 1710, 1659, 1401, 1270, 1236, 1173, 1029, 973, 900, 863, 765, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74–7.72 (m, 1H), 7.66–7.65 (m, 1H), 7.30–7.28 (m, 1H), 7.24–7.18 (m, 7H), 4.27 (q, 2H, *J* = 7.2 Hz), 1.23 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 158.7, 154.1, 138.6, 136.9, 135.3, 133.6, 130.2, 129.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 127.0, 123.4, 61.0, 14.0; GC–MS m/z (% rel inten.): 396.14 (M^+, 73.45), 104.98 (100); Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09; Found: C, 78.60.; H, 4.89.

Ethyl 4-acetyl-5-methyl-3-phenylfuran-2-carboxylate (3bd): yellow viscous oil; IR ν_{max} (KBr): 3061, 2983, 2931, 1725, 1674, 1366, 1355, 1292, 1228, 1095, 1040, 976, 918, 867, 804, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.67 (m, 2H), 7.40–7.35 (m, 3H), 4.32 (q, 2H, *J* = 7.2 Hz), 2.54 (s, 3H), 2.42 (s, 3H), 1.29 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 164.8, 155.6, 152.0, 129.5, 128.9, 128.4, 126.9, 123.8, 113.9, 61.6, 30.1, 14.0, 13.9; GC–MS m/z (% rel inten.): 271.95 (M^+, 35.64), 225.68 (100); Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92; Found: C,

70.69; H, 5.98.

Methyl 4-acetyl-5-phenylfuran-2-carboxylate (3ca): yellow solid; mp: 68–70°C; IR ν_{max} (KBr): 1710, 1682, 1585, 1265, 1173, 1080, 996, 884, 840, 798, 710, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95–7.93 (m, 2H), 7.52 (s, 1H), 7.45–7.44 (m, 3H), 3.91 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 163.0, 158.7, 141.8, 138.1, 132.6, 128.7, 128.3, 122.0, 119.4, 52.0, 14.4; GC–MS m/z (% rel inten.): 244.03 (M^+, 62.76), 228.86 (100); Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95; Found: C, 69.10; H, 4.90.

Methyl 4-benzoyl-5-phenylfuran-2-carboxylate (3cb): yellow solid; mp: 87–89°C; IR ν_{max} (KBr): 1722, 1650, 1441, 1385, 1023, 921, 885, 770, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82–7.76 (m, 4H), 7.55–7.53 (m, 1H), 7.41–7.32 (m, 6H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 158.8, 158.5, 142.3, 137.3, 133.3, 130.2, 129.7, 128.5, 128.0, 122.2, 121.0, 52.2; GC–MS m/z (% rel inten.): 306.07 (M^+, 100); Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61; Found: C, 74.68; H, 4.72.

4-Ethyl 2-methyl 5-phenylfuran-2,4-dicarboxylate (3cc): colorless solid; mp: 72–73°C; IR ν_{max} (KBr): 2983, 2930, 1732, 1660, 1428, 1327, 1191, 1084, 997, 865, 765, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.04–8.02 (m, 2H), 7.56 (s, 1H), 7.44–7.42 (m, 3H), 4.29 (q, 2H, J = 7.2 Hz), 3.90 (s, 3H), 1.32 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 160.1, 158.7, 142.4, 130.4, 128.9, 128.5, 120.6, 115.5, 60.9, 52.1, 14.1; GC–MS m/z (% rel inten.): 273.90 (M^+, 100); Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15; Found: C, 65.60; H, 5.31.

Methyl 4-acetyl-5-methylfuran-2-carboxylate (3cd): yellow solid; mp: 86–88°C; IR ν_{max} (KBr): 1726, 1647, 1540, 1362, 1172, 1121, 1020, 995, 764, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 3.88 (s, 3H), 2.64 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 162.1, 158.6, 142.0, 122.8, 118.2, 52.1, 29.0, 14.7; GC–MS m/z (% rel inten.): 181.97 (M^+, 38.35), 166.95 (100); Anal. Calcd for $C_9H_{10}O_4$: C, 59.34; H, 5.53; Found: C, 59.55; H, 5.62.

4-Ethyl 2-methyl 5-methylfuran-2,4-dicarboxylate (3ce): pale yellow viscous oil; IR ν_{max} (KBr): 2987, 2958, 1727, 1637, 1442, 1095, 1032, 963, 896, 805, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 4.29 (q, 2H, J = 7.2 Hz), 3.80 (s, 3H), 2.48 (s, 3H), 1.32 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 162.7, 159.1, 145.3, 118.8, 113.5, 60.7, 51.8, 14.1, 13.4; GC–MS m/z (% rel inten.): 212.02 (M^+, 17.62), 165.99 (100); Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70; Found: C, 56.61; H, 5.77.

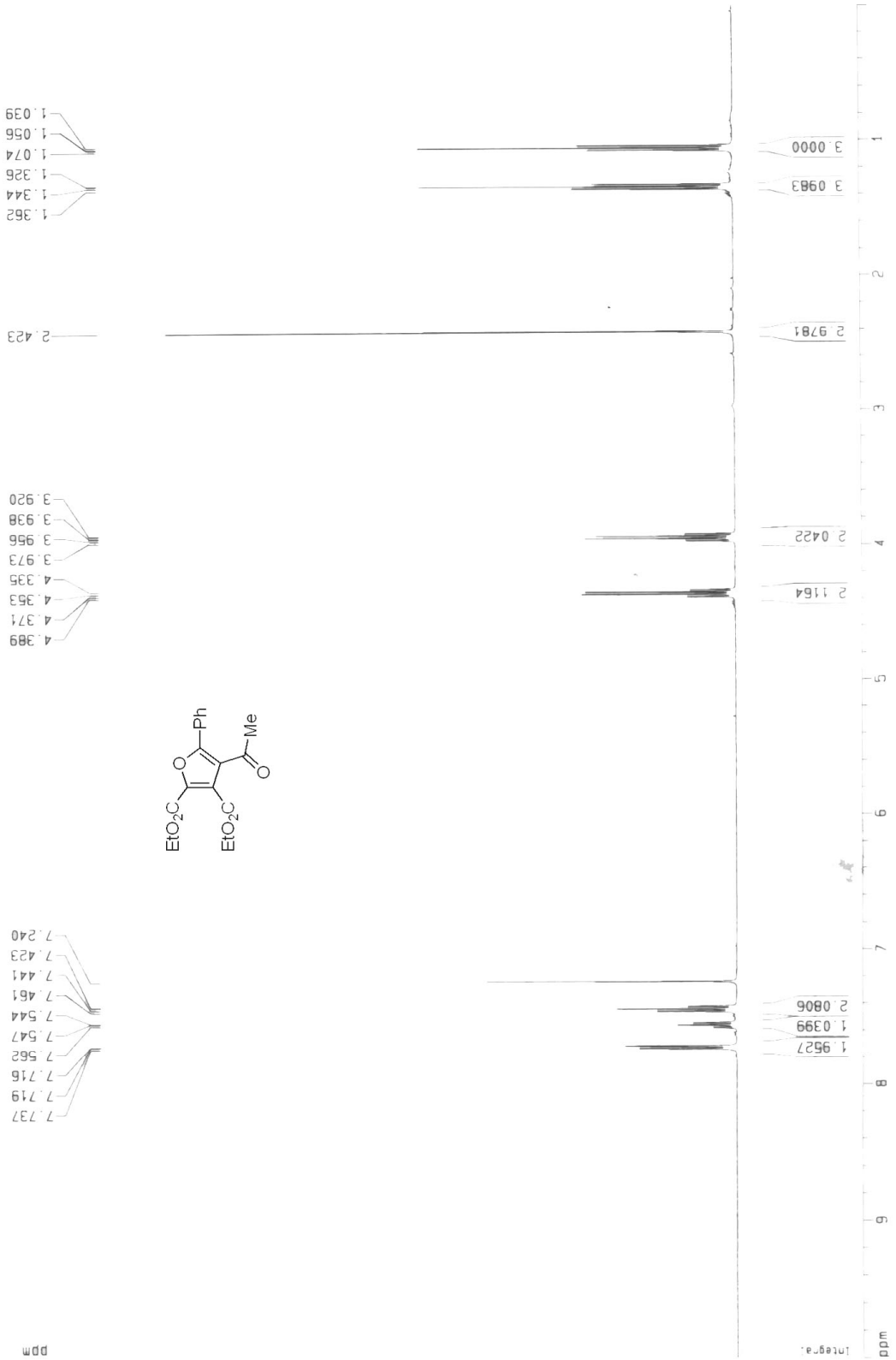
References

(1) (a) Yoshiyuki, H.; Kobayasi, M.; Hitosi, N. *Tetrahedron* **1970**, *26*, 4353–4360; (b) Masaaki, T.; Yoshiyuki; H.; Hitosi. N. *Tetrahedron Lett.* **1969**, *25*, 2053–2056.

(2) Aggarwal, V.; Richardson, J. *Science of Synthesis* **2004**, *27*, 21–104.

NMR spectra

Diethyl 4-acetyl-5-phenylfuran-2,3-dicarboxylate (3aa)



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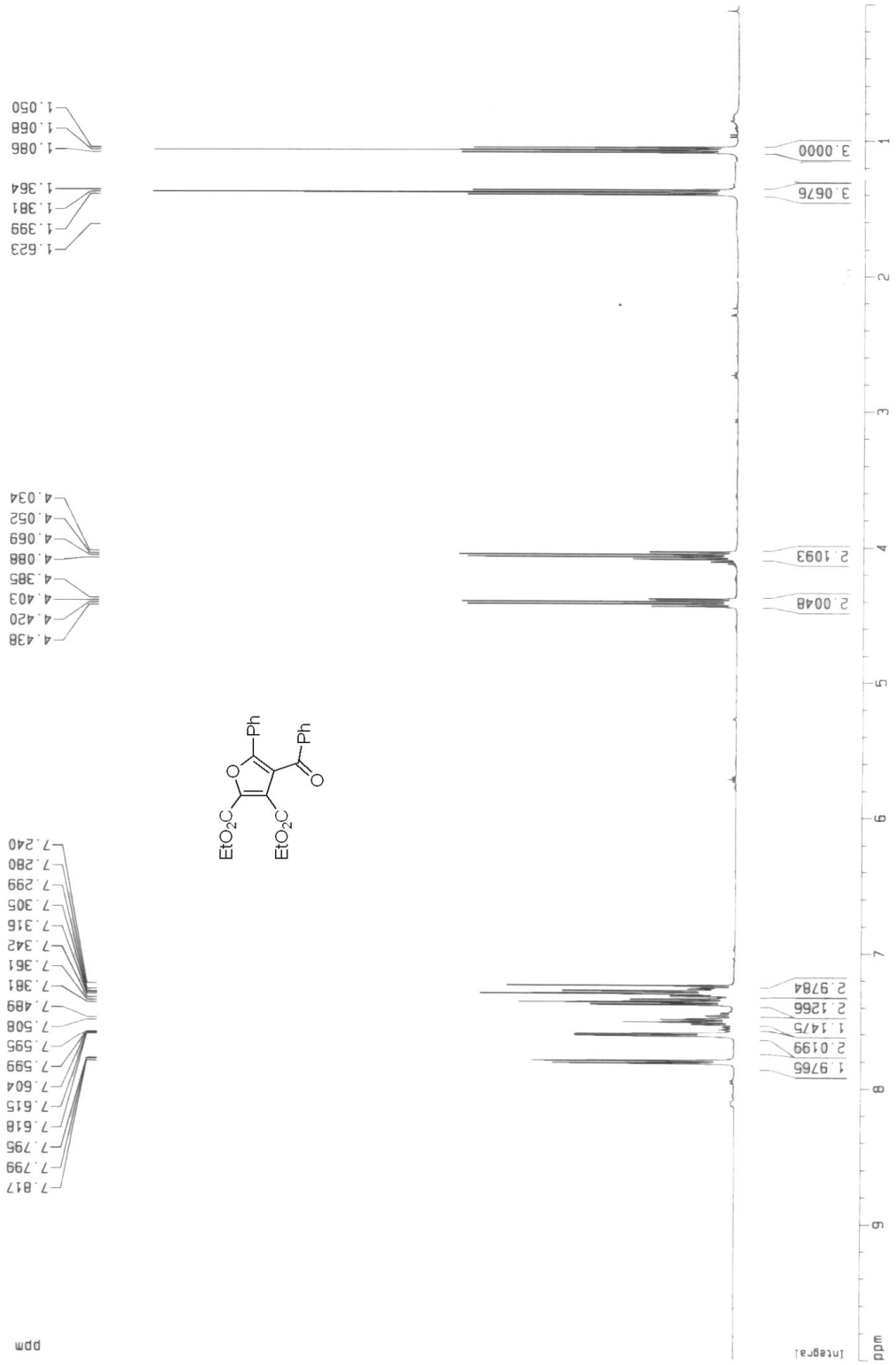
Diethyl 4-benzoyl-5-phenylfuran-2,3-dicarboxylate (3ab)



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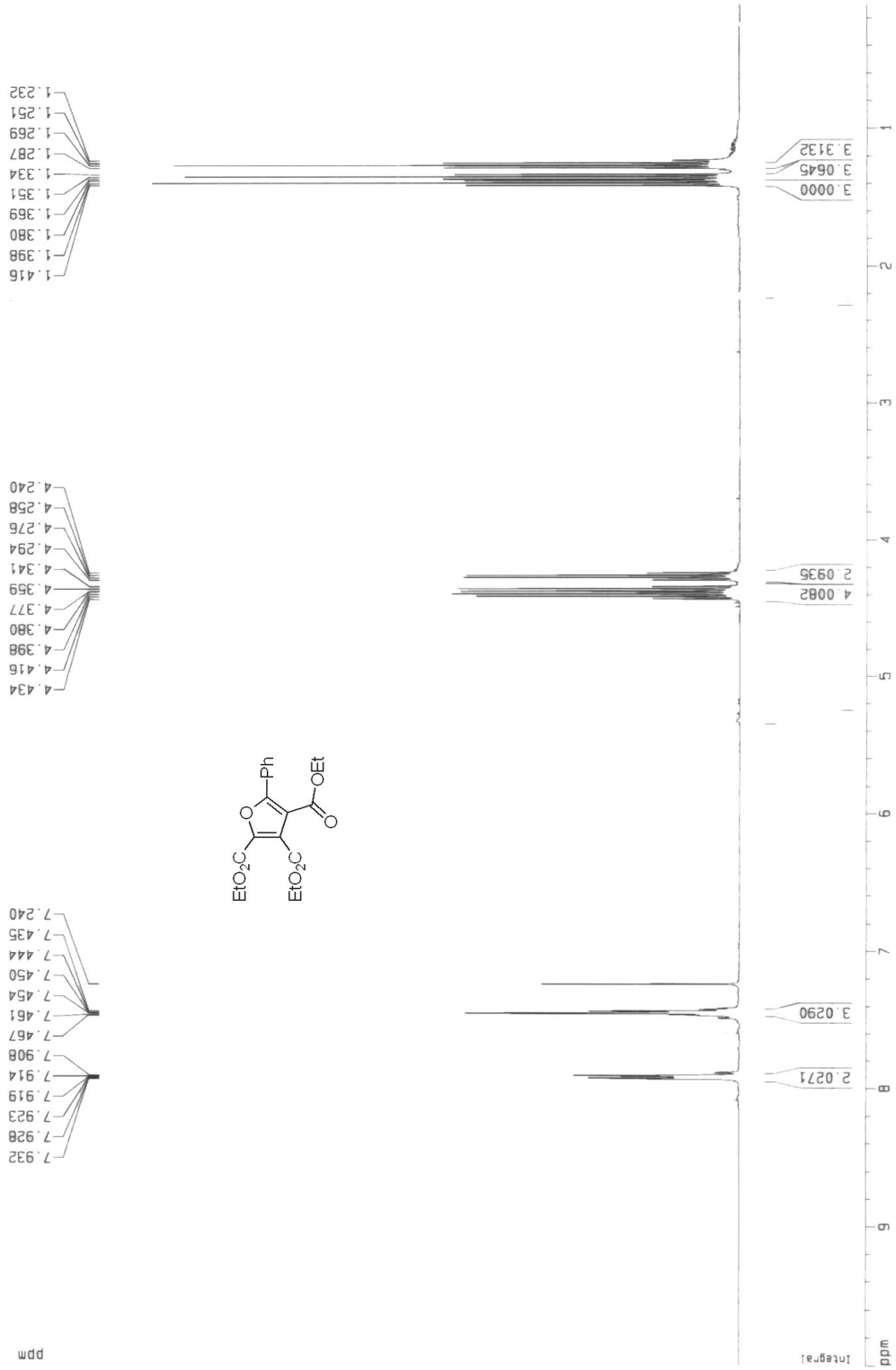
Triethyl 5-phenylfuran-2,3,4-tricarboxlate (3ac)



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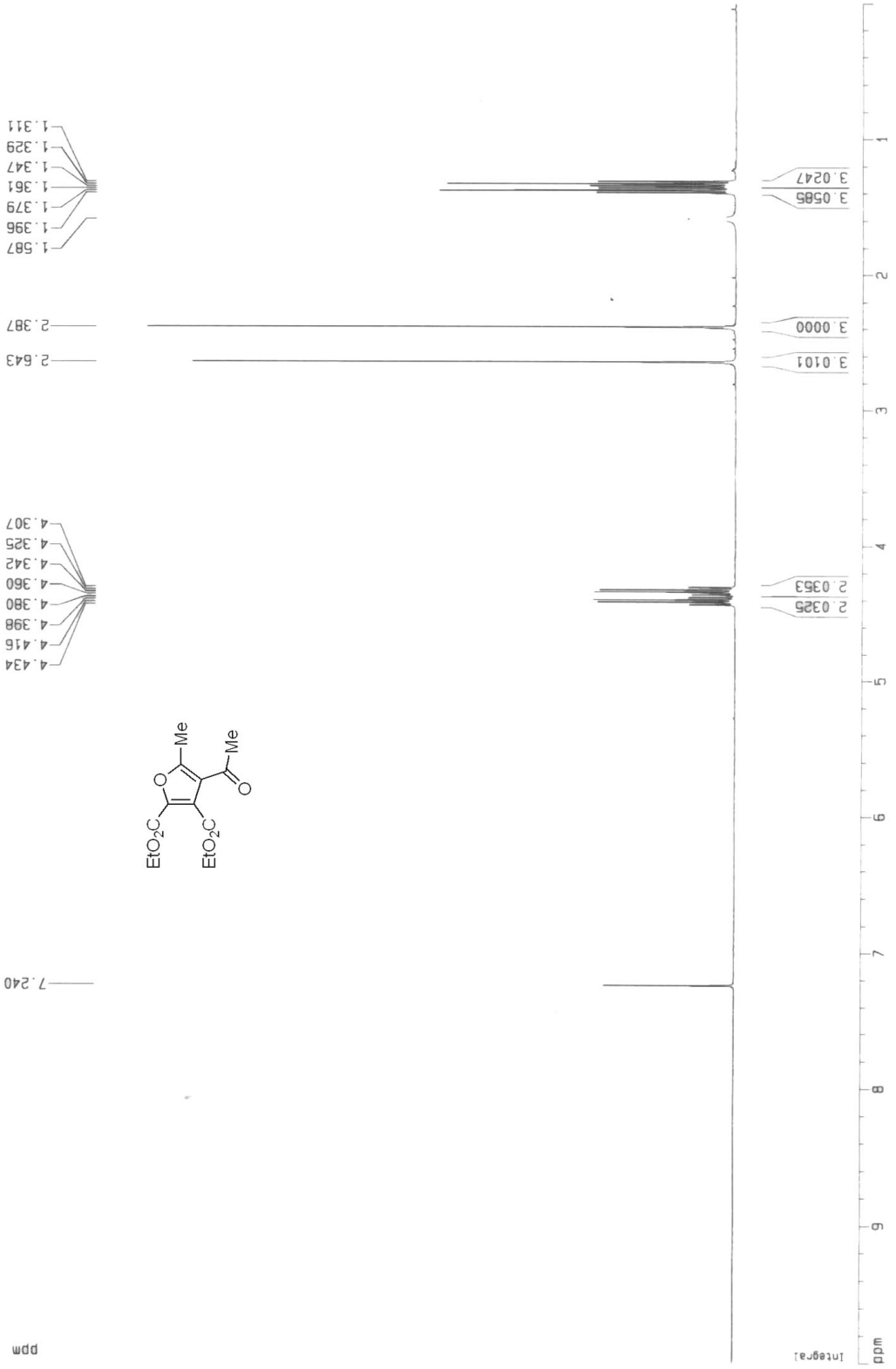

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Triethyl 5-methylfuran-2,3,4-tricarboxylate (3ae)

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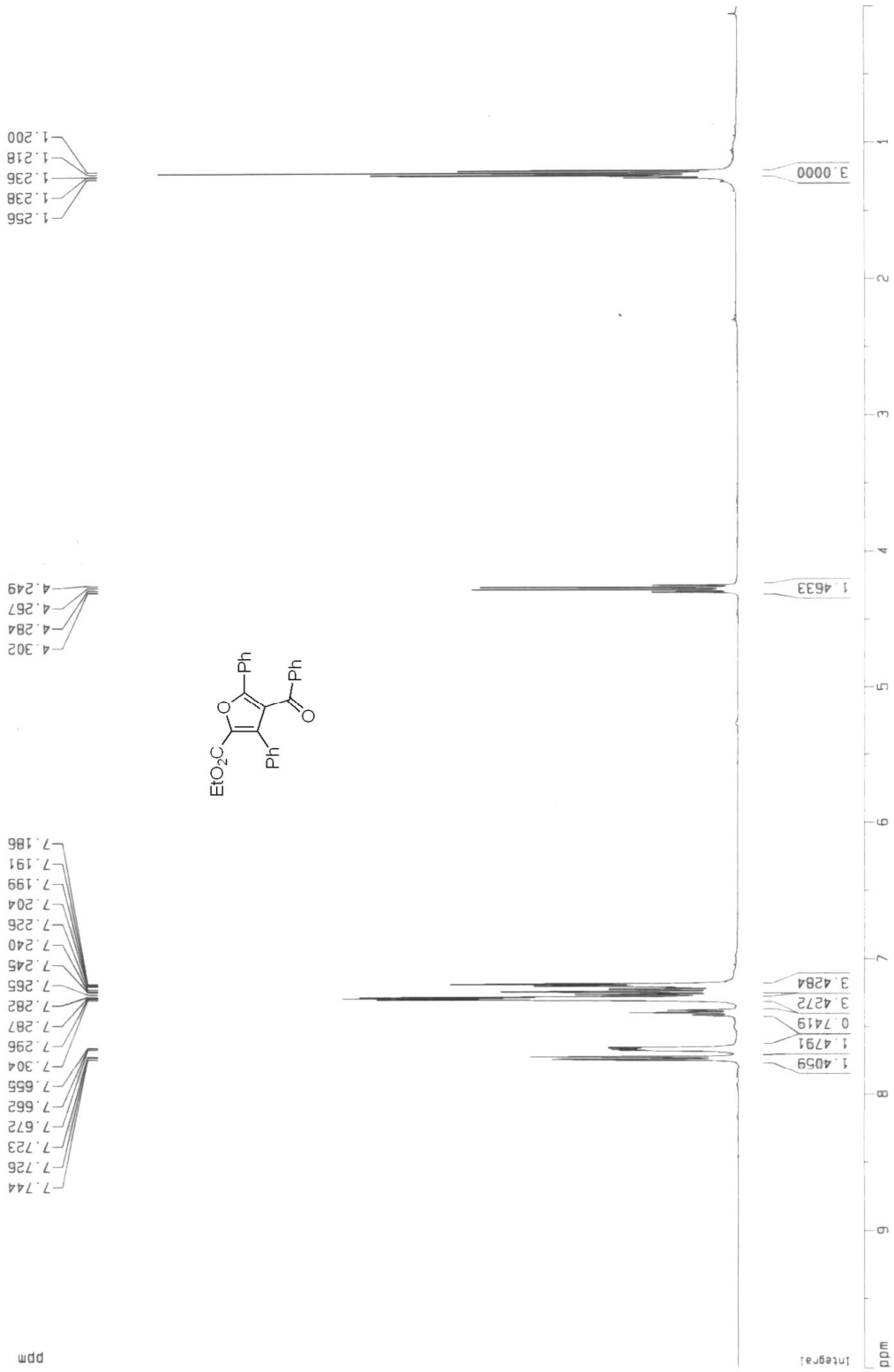

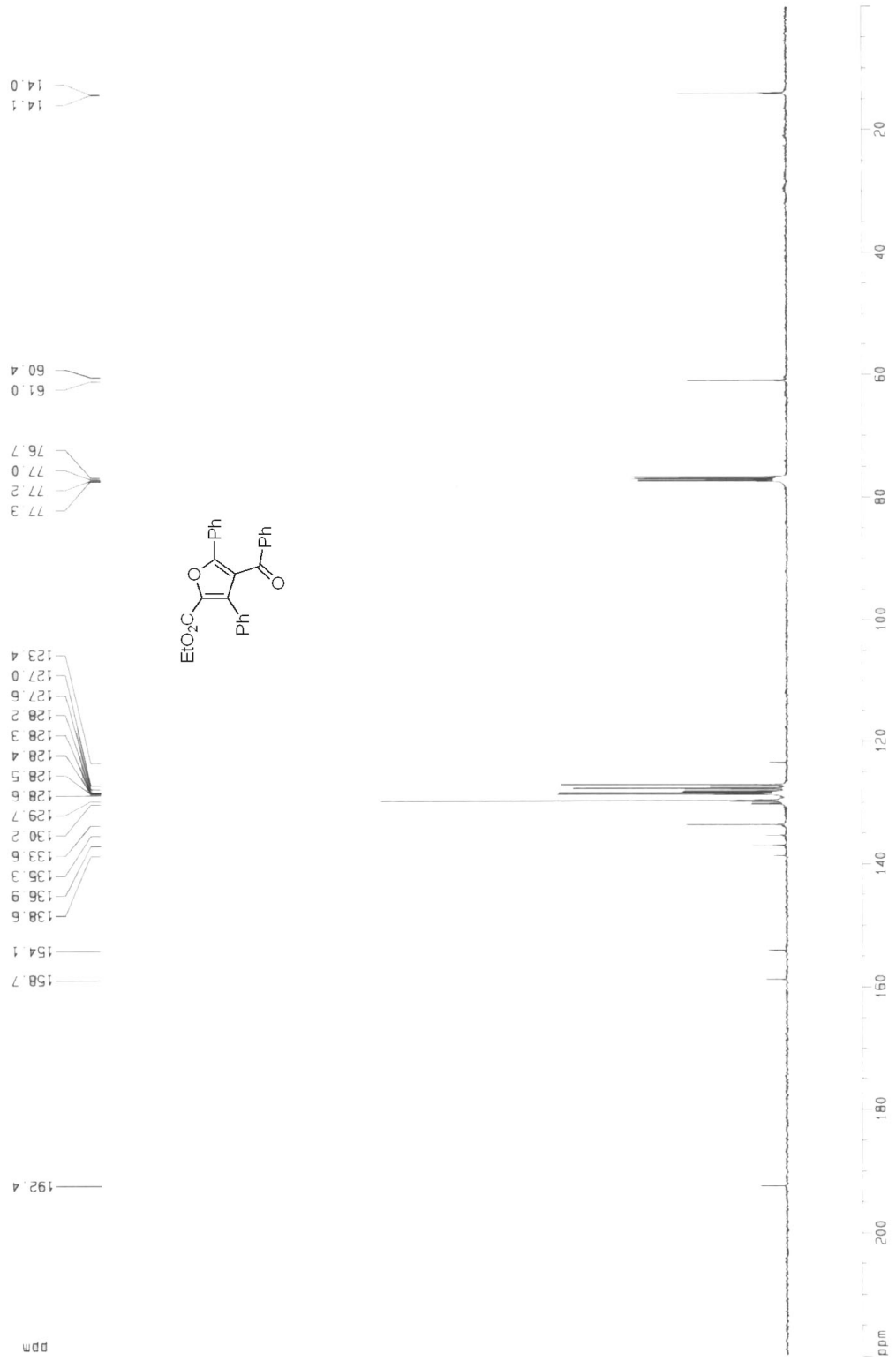
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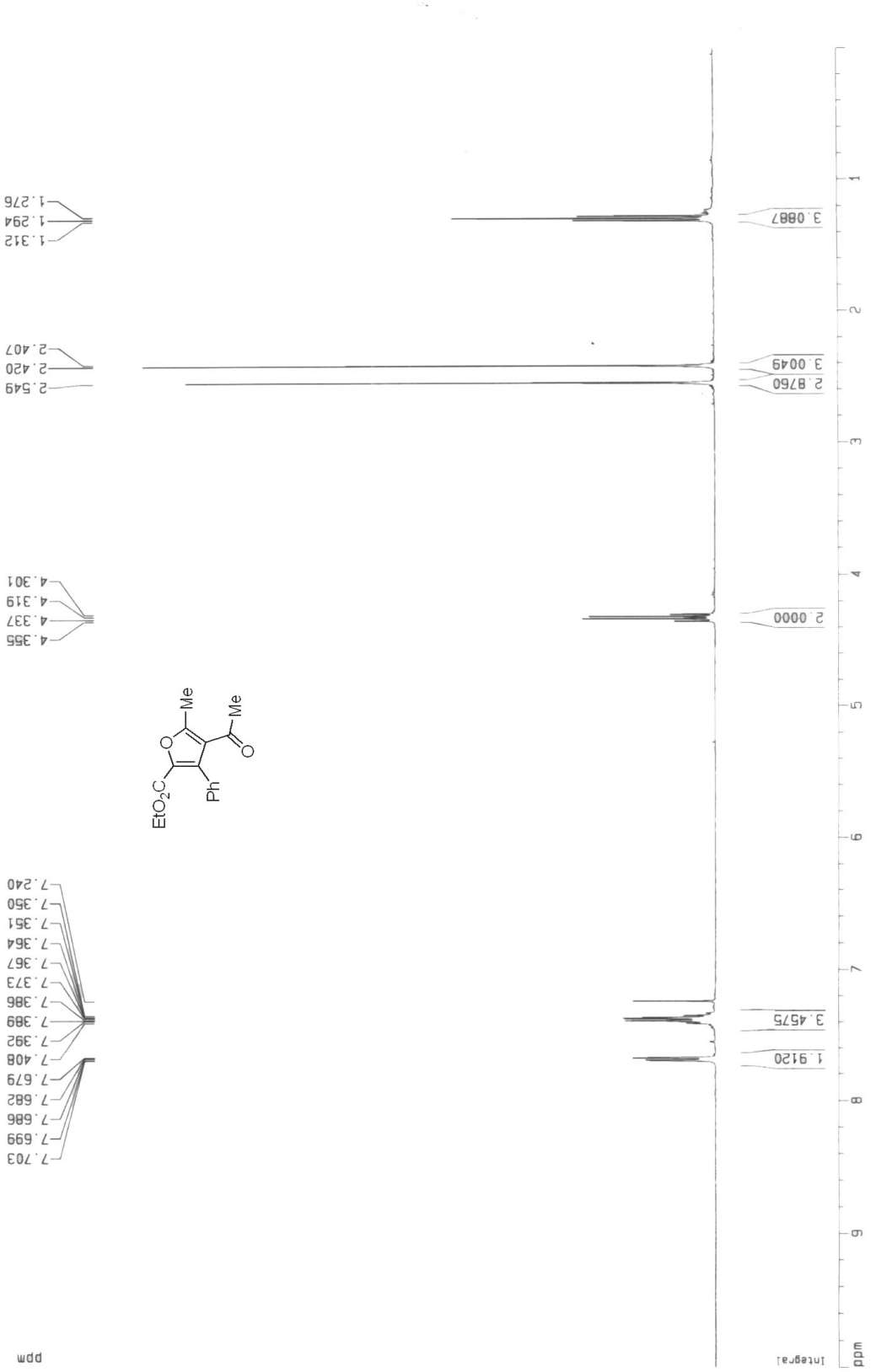

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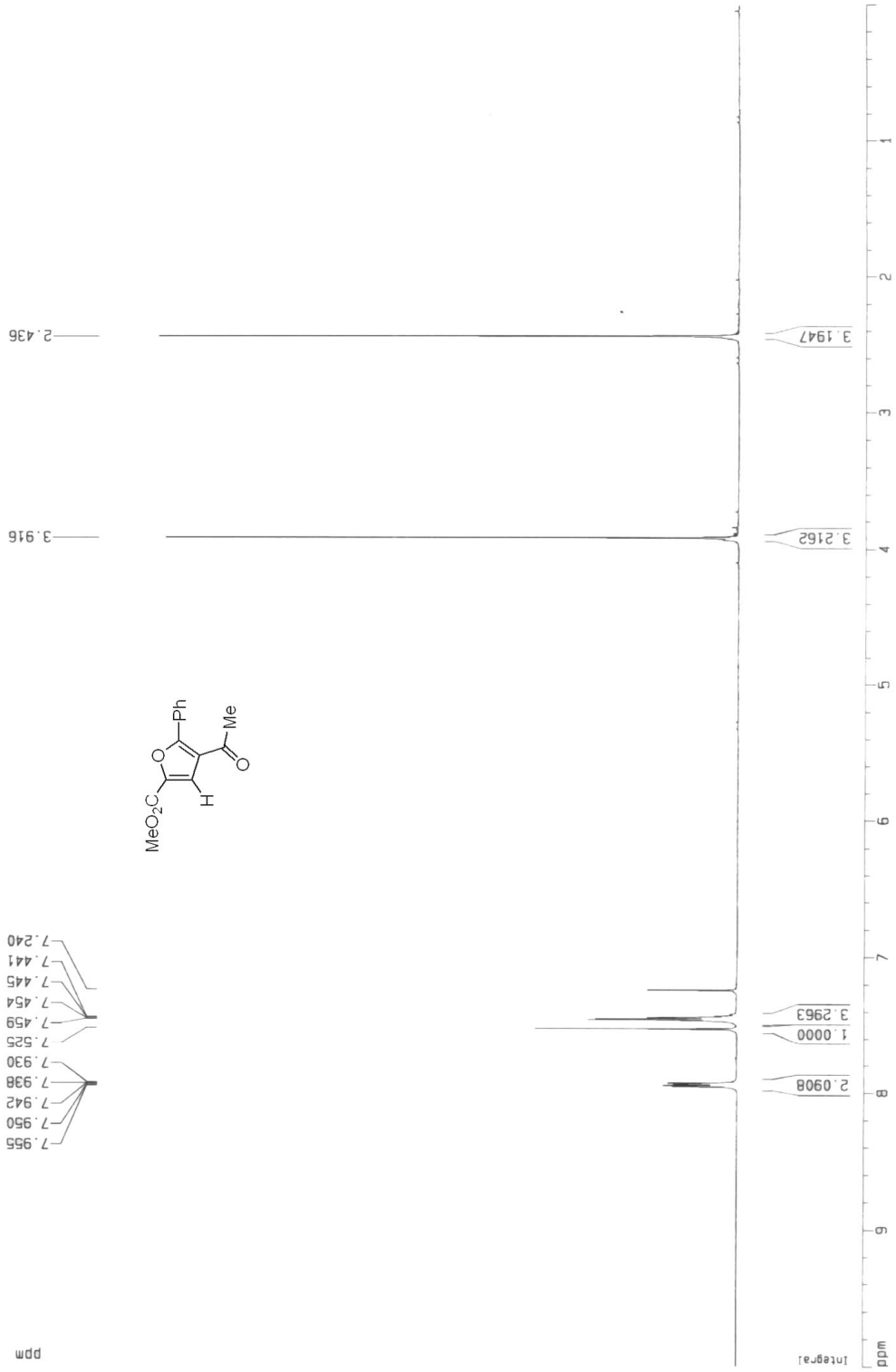

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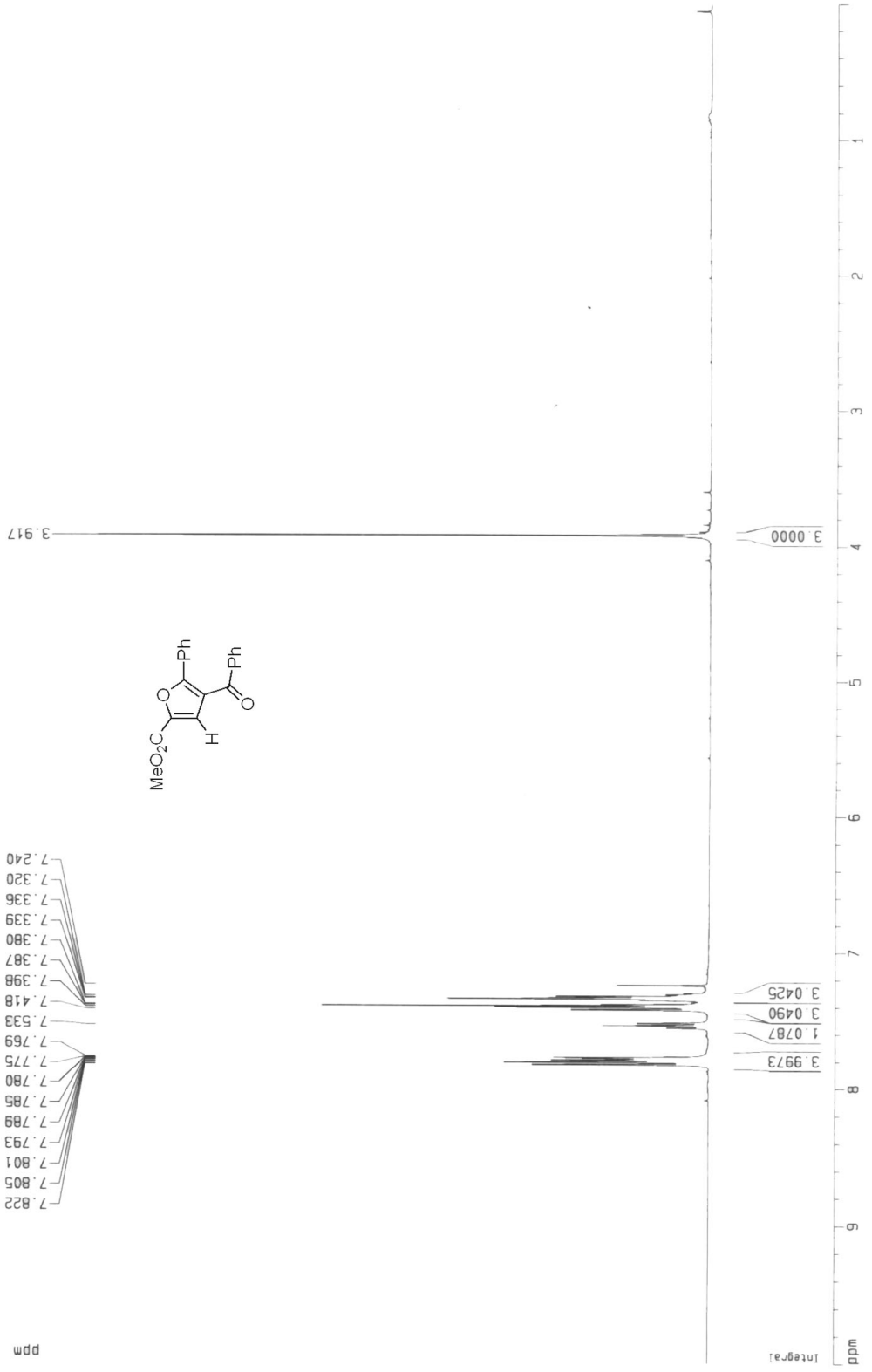

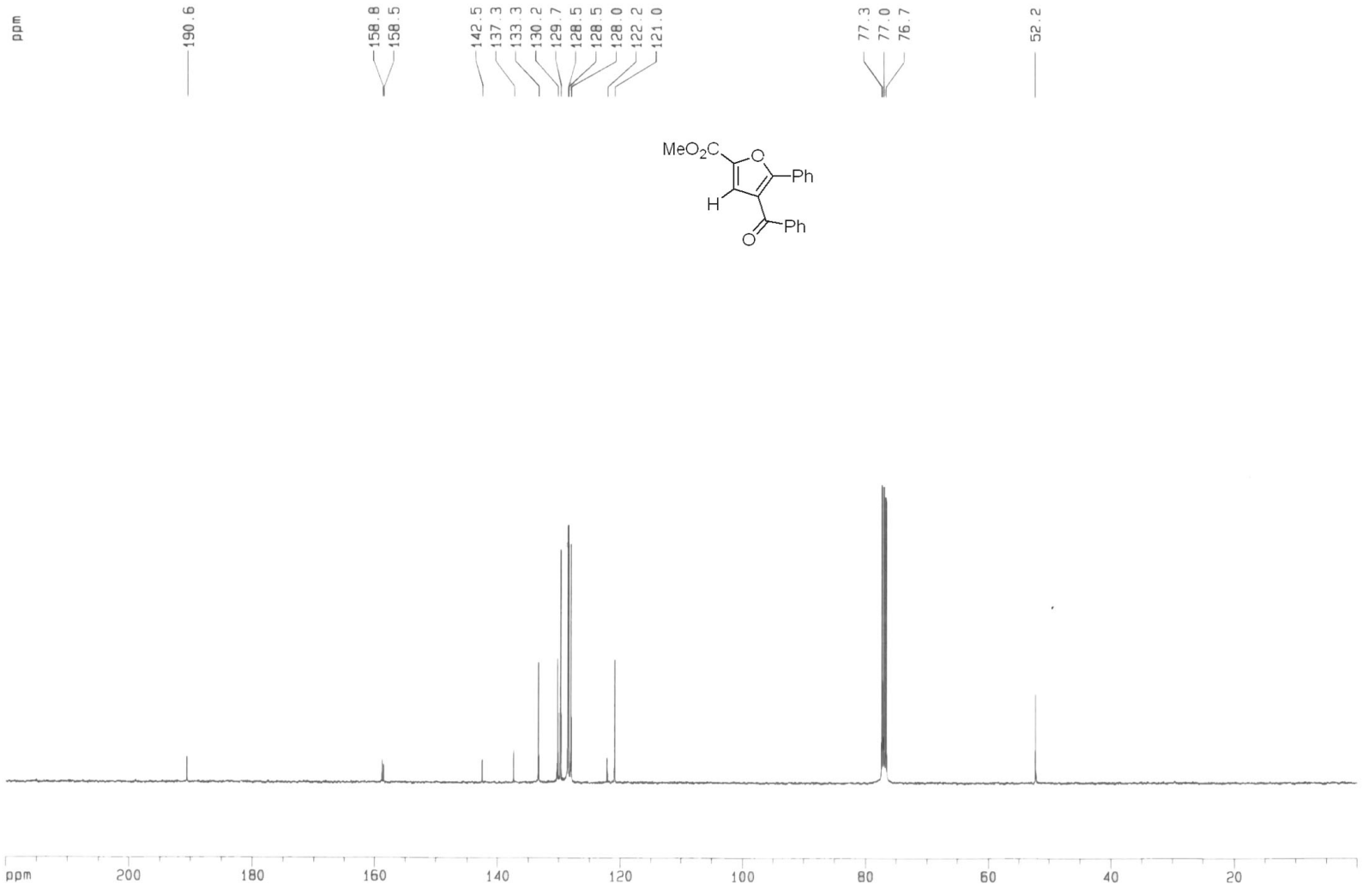
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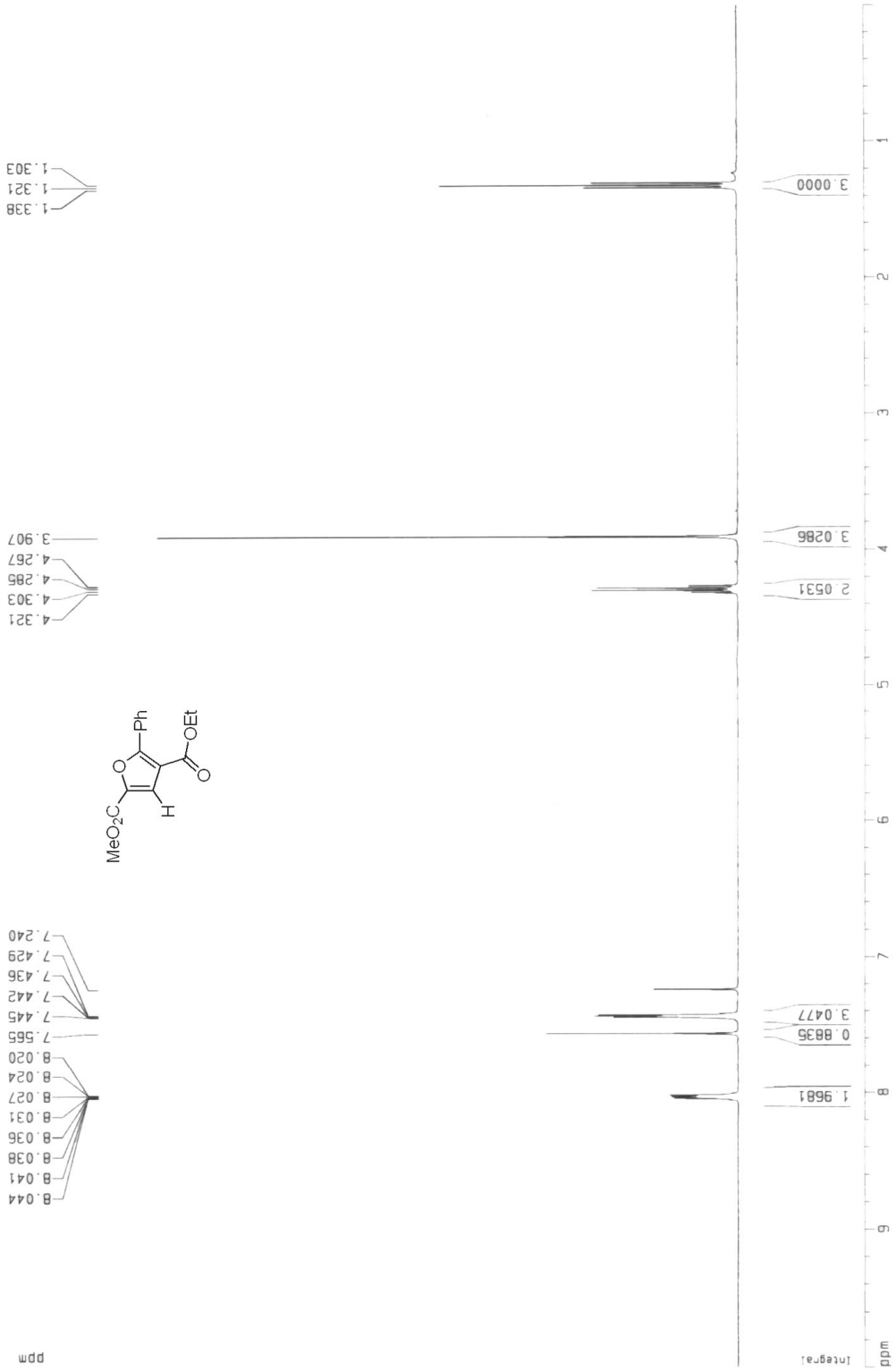
4-ethyl 2-methyl 5-phenylfuran-2,4-dicarboxylate (3cc)



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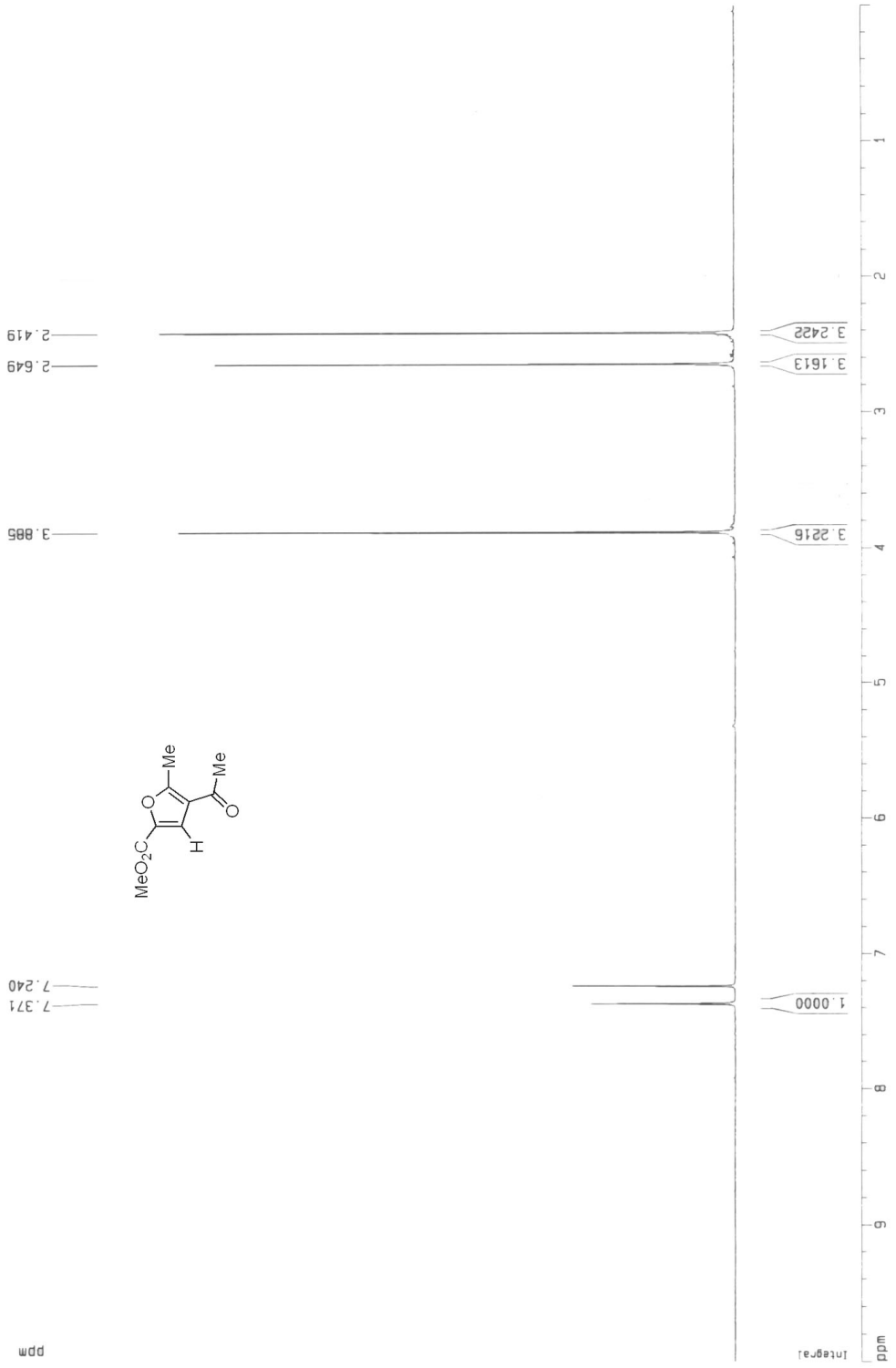

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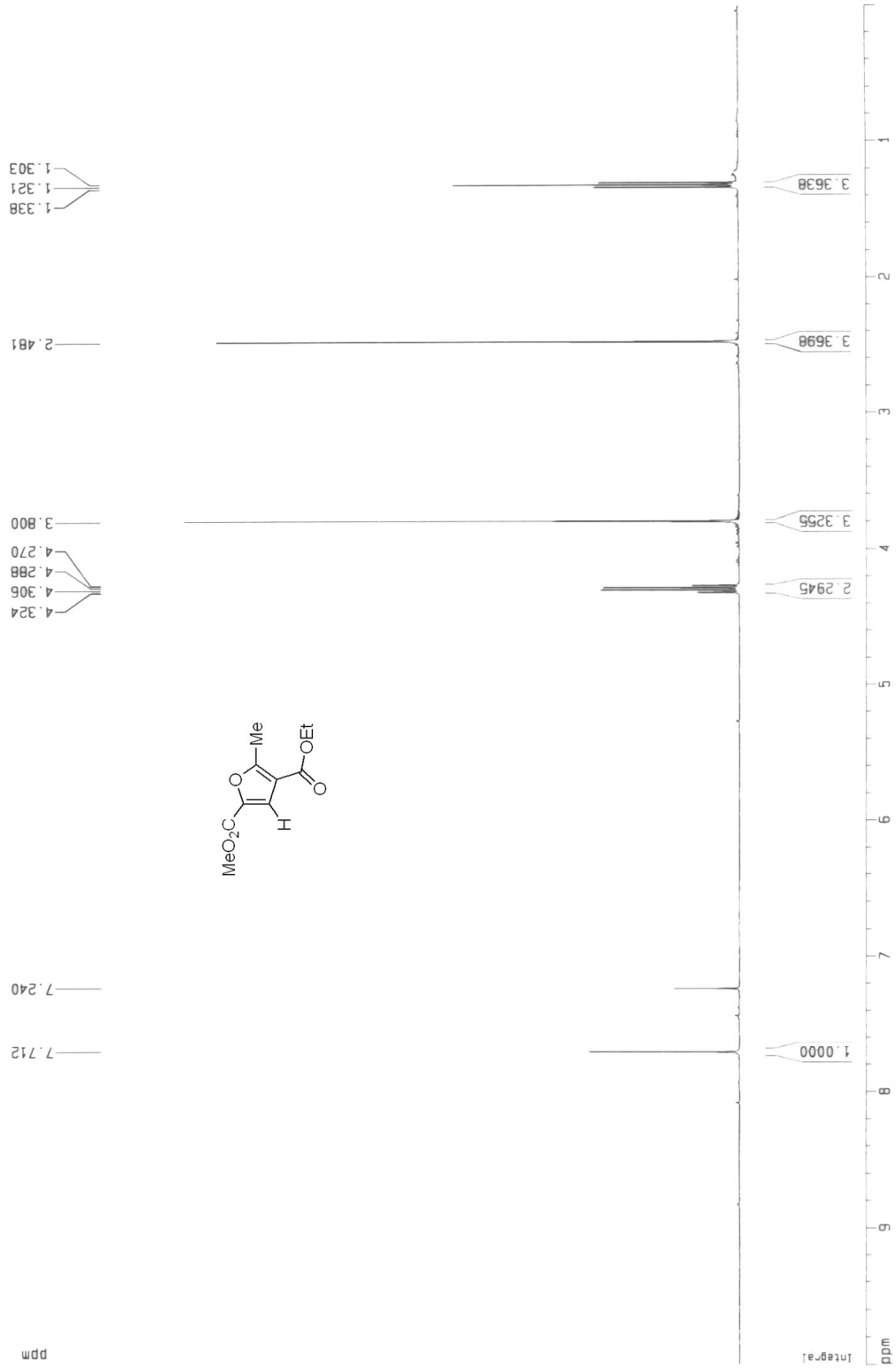
4-ethyl 2-methyl 5-methylfuran-2,4-dicarboxylate (3ce)



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40
60
80
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ppm