

Supporting Information

Sc(OTf)₃-Catalyzed Three-Component Cyclization of Arylamines, β , γ -unsaturated α -ketoesters and 1, 3-Dicarbonyl Compounds for the Synthesis of Highly Substituted 1,4-Dihydropyridines and Tetrahydropyridines

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5-Ethyl 2-methyl 1-(4-methoxyphenyl)-6-methyl-4-phenyl-1,4-dihydropyridine-2,5-dicarboxylate (4a). Yield 74.7 mg, 92%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.09 (t, $J = 7.0$ Hz, 3H), 2.15 (s, 3H), 3.48 (s, 3H), 3.81 (s, 3H), 4.01 (q, $J = 7.0$ Hz, 2H), 4.75 (d, $J = 6.0$ Hz, 1H), 6.00 (d, $J = 6.0$ Hz, 1H), 6.87 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.5$ Hz, 2H), 7.20-7.26 (m, 1H), 7.32-7.40 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.0, 18.2, 40.2, 51.8, 55.3, 59.6, 102.4, 113.8, 118.3, 126.5, 127.6, 128.5, 130.9, 132.8, 134.6, 146.4, 150.4, 158.8, 163.9, 168.2; HRMS (TOF) calculated for ($\text{C}_{24}\text{H}_{25}\text{NO}_5+\text{Na}$) 430.1630, found 430.1616.

2-Benzyl 5-ethyl 1-(4-methoxyphenyl)-6-methyl-4-phenyl-1,4-dihydropyridine-2,5-dicarboxylate (4b). Yield 86.8 mg, 90%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.10 (t, $J = 7.0$ Hz, 3H), 2.16 (s, 3H), 3.81 (s, 3H), 4.02 (q, $J = 7.0$ Hz, 2H), 4.75 (d, $J = 6.0$ Hz, 1H), 4.87 (d, $J = 12.0$ Hz, 1H), 4.97 (d, $J = 12.0$ Hz, 1H), 6.03 (d, $J = 6.0$ Hz, 1H), 6.81 (d, $J = 9.0$ Hz, 2H), 7.08-7.12 (m, 2H), 7.16 (d, $J = 9.0$ Hz, 2H), 7.20-7.25 (m, 1H), 7.27-7.31 (m, 3H), 7.33-7.40 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.0, 18.2, 40.3, 55.3, 59.6, 66.6, 102.4, 113.8, 118.5, 126.5, 127.6, 128.2, 128.3, 128.4, 128.5, 130.8, 133.0, 134.5, 135.2, 146.3, 150.4, 158.8, 163.4, 168.2; HRMS (TOF) calculated for ($\text{C}_{30}\text{H}_{29}\text{NO}_5+\text{Na}$) 506.1943, found 506.1938.

5-Ethyl 2-(4-nitrobenzyl) 1-(4-methoxyphenyl)-6-methyl-4-phenyl-1,4-dihydropyridine-2,5-dicarboxylate (4c). Yield 95.1 mg, 90%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.09 (t, $J = 7.0$ Hz, 3H), 2.14 (s, 3H), 3.78 (s, 3H), 4.01 (q, $J = 7.0$ Hz, 2H), 4.76 (d, $J = 6.0$ Hz, 1H), 4.96 (d, $J = 13.0$ Hz, 1H), 5.05 (d, $J = 13.0$ Hz, 1H), 6.03 (d, $J = 6.0$ Hz, 1H), 6.79 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.18-7.26 (m, 1H), 7.30-7.38 (m, 4H), 8.10 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR

(125 MHz, CDCl₃): δ 14.0, 18.2, 40.3, 55.3, 59.7, 65.1, 102.6, 113.8, 119.0, 123.6, 126.6, 127.6, 128.5, 128.6, 130.8, 132.7, 134.5, 142.5, 146.1, 147.6, 150.2, 158.9, 163.2, 168.1; HRMS (TOF) calculated for (C₃₀H₂₈N₂O₇+Na) 551.1794, found 551.1801.

5-Ethyl 2-methyl 1-(4-methoxyphenyl)-6-methyl-4-(p-tolyl)-1,4-dihydropyridine-2,5-dicarboxylate (4d). Yield 66.7 mg, 79%; Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 1.14 (t, *J* = 7.0 Hz, 3H), 2.16 (s, 3H), 2.36 (s, 3H), 3.50 (s, 3H), 3.83 (s, 3H), 4.04 (q, *J* = 7.0 Hz, 2H), 4.72 (d, *J* = 6.0 Hz, 1H), 6.02 (d, *J* = 6.0 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 7.16-7.24 (m, 4H), 7.27 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 14.1, 18.3, 21.0, 39.7, 51.8, 55.3, 59.6, 102.5, 113.8, 118.6, 127.4, 129.2, 130.8, 132.7, 134.6, 136.0, 143.4, 150.3, 158.8, 163.9, 168.3; HRMS (TOF) calculated for (C₂₅H₂₇NO₅+Na) 444.1787, found 444.1771.

2-Benzyl 5-ethyl 4-(4-chlorophenyl)-1-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4e). Yield 90.0 mg, 87%; Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 1.11 (t, *J* = 7.0 Hz, 3H), 2.14 (s, 3H), 3.81 (s, 3H), 4.03 (q, *J* = 7.0 Hz, 2H), 4.72 (d, *J* = 6.0 Hz, 1H), 4.87 (d, *J* = 12.5 Hz, 1H), 4.96 (d, *J* = 12.5 Hz, 1H), 5.95 (d, *J* = 6.0 Hz, 1H), 6.78-6.82 (m, 2H), 7.08-7.14 (m, 4H), 7.26-7.34 (m, 7H). ¹³C NMR (125 MHz, CDCl₃): δ 14.1, 18.2, 39.6, 55.3, 59.7, 66.7, 102.0, 113.8, 117.5, 128.2, 128.3, 128.4, 128.6, 128.9, 130.7, 132.2, 133.3, 134.2, 135.2, 144.9, 150.6, 158.9, 163.3, 168.0; HRMS (TOF) calculated for (C₃₀H₂₈ClNO₅+Na) 540.1554, found 540.1566.

5-Ethyl 2-methyl 4-(4-bromophenyl)-1-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4f). Yield 80.6 mg, 83%; Yellow oil; HPLC analysis chiralpak AD-H, *i*-PrOH/hexanes = 5/95, 1.0 mL/min; 214 nm, t_r (major) = 23.57, t_r (minor) = 28.01 min; ¹H NMR (500 MHz, CDCl₃) δ 1.11 (t, *J* = 7.0 Hz, 3H),

2.14 (s, 3H), 3.48 (s, 3H), 3.81 (s, 3H), 4.02 (q, $J = 7.0$ Hz, 2H), 4.70 (d, $J = 6.0$ Hz, 1H), 5.92 (d, $J = 6.0$ Hz, 1H), 6.87 (d, $J = 9.0$ Hz, 2H), 7.14 (d, $J = 9.0$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.1, 18.3, 39.7, 51.9, 55.3, 59.7, 101.8, 113.8, 117.3, 120.3, 129.2, 130.8, 131.6, 133.2, 134.3, 145.4, 150.8, 158.9, 163.7, 168.0; HRMS (TOF) calculated for ($\text{C}_{24}\text{H}_{24}\text{BrNO}_5+\text{Na}$) 508.0736, found 508.0745.

2-Benzyl 5-ethyl 4-(4-bromophenyl)-1-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4g). Yield 104.4 mg, 93%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.14 (t, $J = 6.5$ Hz, 3H), 2.17 (s, 3H), 3.82 (s, 3H), 4.04 (q, $J = 6.5$ Hz, 2H), 4.73 (d, $J = 6.0$ Hz, 1H), 4.89 (d, $J = 12.0$ Hz, 1H), 4.98 (d, $J = 12.0$ Hz, 1H), 5.97 (d, $J = 6.0$ Hz, 1H), 6.82 (d, $J = 8.5$ Hz, 2H), 7.12-7.18 (m, 4H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.28-7.36 (m, 3H), 7.49 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.1, 18.2, 39.7, 55.3, 59.7, 66.7, 101.8, 113.8, 117.4, 120.3, 128.2, 128.3, 128.3, 129.3, 130.7, 131.6, 133.3, 134.2, 135.1, 145.4, 150.6, 158.8, 163.2, 168.0; HRMS (TOF) calculated for ($\text{C}_{30}\text{H}_{28}\text{BrNO}_5+\text{Na}$) 584.1049, found 584.1056.

5-Ethyl 2-methyl 1,4-bis(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4h). Yield 80.4 mg, 92%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.12 (t, $J = 7.0$ Hz, 3H), 2.13 (s, 3H), 3.48 (s, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 4.02 (q, $J = 7.0$ Hz, 2H), 4.68 (d, $J = 6.5$ Hz, 1H), 5.98 (d, $J = 6.5$ Hz, 1H), 6.87 (d, $J = 9.0$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 9.0$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.1, 18.3, 39.3, 51.8, 55.2, 55.3, 59.6, 102.7, 113.8, 113.9, 118.5, 128.6, 130.8, 132.7, 134.6, 138.8, 150.0, 158.3, 158.8, 163.9, 168.3; HRMS (TOF) calculated for ($\text{C}_{25}\text{H}_{27}\text{NO}_6+\text{Na}$) 460.1736, found 460.1752.

5-Ethyl 2-methyl 4-(2,6-dichlorophenyl)-1-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4i). Yield 89.3 mg, 94%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 0.97 (t, $J = 7.0$ Hz, 3H), 2.07 (s, 3H), 3.43 (s, 3H), 3.81 (s, 3H), 3.91 (q, $J = 7.0$ Hz, 2H), 5.53 (d, $J = 4.5$ Hz, 1H), 5.83 (d, $J = 4.5$ Hz, 1H), 6.86 (d, $J = 9.0$ Hz, 2H), 7.07 (t, $J = 8.0$ Hz, 1H), 7.19 (d, $J = 9.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 13.8, 18.1, 38.3, 51.8, 55.3, 59.4, 98.7, 112.0, 113.8, 127.8, 130.9, 134.6, 135.1, 139.0, 152.2, 158.8, 163.8, 167.8; HRMS (TOF) calculated for ($\text{C}_{24}\text{H}_{23}\text{Cl}_2\text{NO}_5+\text{Na}$) 498.0851, found 498.0841.

(E)-diethyl 1-(4-methoxyphenyl)-6-methyl-4-styryl-1,4-dihydropyridine-2,5-dicarboxylate (4j). Yield 67.9 mg, 76%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.11 (t, $J = 7.0$ Hz, 3H), 1.28 (t, $J = 7.0$ Hz, 3H), 2.12 (s, 3H), 3.80 (s, 3H), 3.92-4.04 (m, 2H), 4.12-4.22 (m, 2H), 4.27 (t, $J = 6.5$ Hz, 1H), 6.01 (d, $J = 6.5$ Hz, 1H), 6.29 (dd, $J = 16.0$, 6.5 Hz, 1H), 6.43 (d, $J = 16.0$ Hz, 1H), 6.84 (d, $J = 9.0$ Hz, 2H), 7.17 (d, $J = 9.0$ Hz, 2H), 7.18-7.24 (m, 1H), 7.28-7.34 (m, 2H), 7.38-7.44 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 13.9, 14.4, 18.2, 36.7, 55.4, 59.8, 61.0, 101.7, 113.7, 116.9, 126.3, 127.2, 128.5, 129.3, 131.2, 132.6, 134.4, 134.6, 137.5, 151.3, 158.9, 163.4, 168.1; HRMS (TOF) calculated for ($\text{C}_{27}\text{H}_{29}\text{NO}_5+\text{Na}$) 470.1943, found 470.1960.

5-Ethyl 2-methyl 4-(4-methoxyphenyl)-6-methyl-1-phenyl-1,4-dihydropyridine-2,5-dicarboxylate (4k). Yield 67.7 mg, 83%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.15 (t, $J = 7.0$ Hz, 3H), 2.17 (s, 3H), 3.47 (s, 3H), 3.83 (s, 3H), 4.05 (q, $J = 7.0$ Hz, 2H), 4.72 (d, $J = 6.0$ Hz, 1H), 6.05 (d, $J = 6.0$ Hz, 1H), 6.92 (d, $J = 8.5$ Hz, 2H), 7.24-7.42 (m, 7H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.1, 18.4, 39.4, 51.8, 55.2, 59.7, 102.8, 113.9, 119.0,

127.8, 128.6, 128.7, 129.7, 132.4, 138.6, 142.1, 149.4, 158.3, 163.8, 168.3; HRMS (TOF) calculated for ($C_{24}H_{25}NO_5+Na$) 430.1630, found 430.1615.

5-Ethyl 2-methyl 1-(4-chlorophenyl)-4-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylat (4l). Yield 70.7 mg, 80%; Yellow oil; 1H NMR (500 MHz, $CDCl_3$) δ 1.14 (t, $J = 7.0$ Hz, 3H), 2.15 (s, 3H), 3.51 (s, 3H), 3.83 (s, 3H), 4.05 (q, $J = 7.0$ Hz, 2H), 4.71 (d, $J = 6.0$ Hz, 1H), 6.10 (d, $J = 6.0$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 18.3, 39.4, 51.9, 55.2, 59.8, 103.6, 114.0, 119.8, 128.6, 128.9, 131.1, 132.1, 133.6, 138.3, 140.8, 148.9, 158.4, 163.6, 168.2; HRMS (TOF) calculated for ($C_{24}H_{24}ClNO_5+Na$) 464.1241, found 464.1226.

5-Ethyl 2-methyl 1-(4-bromophenyl)-4-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4m). Yield 71.8 mg, 74%; Yellow oil; 1H NMR (500 MHz, $CDCl_3$) δ 1.14 (t, $J = 7.0$ Hz, 3H), 2.15 (s, 3H), 3.51 (s, 3H), 3.82 (s, 3H), 4.05 (q, $J = 7.0$ Hz, 2H), 4.71 (d, $J = 6.0$ Hz, 1H), 6.11 (d, $J = 6.0$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 7.17 (d, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 18.3, 39.3, 51.9, 55.2, 59.8, 103.6, 113.9, 119.9, 121.7, 128.6, 131.5, 131.9, 132.0, 138.2, 141.3, 148.8, 158.4, 163.5, 168.1; HRMS (TOF) calculated for ($C_{24}H_{24}BrNO_5+Na$) 508.0736, found 508.0734.

5-Ethyl 2-methyl 1-(3-chlorophenyl)-4-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4n). Yield 55.6 mg, 63%; Yellow oil; 1H NMR (500 MHz, $CDCl_3$) δ 1.14 (t, $J = 7.0$ Hz, 3H), 2.16 (s, 3H), 3.52 (s, 3H), 3.83 (s, 3H), 4.05 (q, $J = 7.0$ Hz, 2H), 4.72 (d, $J = 6.0$ Hz, 1H), 6.12 (d, $J = 6.0$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 7.18-7.24 (m, 1H), 7.25-7.31 (m, 3H), 7.32-7.38 (m, 2H). ^{13}C NMR (125

MHz, CDCl₃): δ 14.1, 18.3, 39.4, 51.9, 55.2, 59.8, 103.8, 114.0, 120.0, 128.1, 128.3, 128.6, 129.5, 130.0, 132.0, 134.2, 138.2, 143.5, 148.6, 158.4, 163.5, 168.1; HRMS (TOF) calculated for (C₂₄H₂₄ClNO₅+Na) 464.1241, found 464.1226.

5-Ethyl 2-methyl 1-(2-chlorophenyl)-4-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4o). Yield 74.9 mg, 85%; Yellow oil; **Major:** ¹H NMR (500 MHz, CDCl₃) δ 1.13 (t, *J* = 7.0 Hz, 3H), 2.11 (s, 3H), 3.51 (s, 3H), 3.82 (s, 3H), 4.03 (q, *J* = 7.0 Hz, 2H), 4.75 (d, *J* = 5.5 Hz, 1H), 6.11 (d, *J* = 5.5 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.26-7.38 (m, 4H), 7.46-7.51 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 14.0, 17.1, 39.6, 51.9, 55.2, 59.6, 102.4, 113.9, 117.5, 118.8, 127.4, 128.7, 129.9, 130.7, 131.4, 135.6, 139.0, 139.3, 147.8, 158.3, 162.9, 168.3; **Minor:** ¹H NMR (500 MHz, CDCl₃) δ 1.12 (t, *J* = 7.0 Hz, 3H), 2.09 (s, 3H), 3.47 (s, 3H), 3.82 (s, 3H), 4.03 (q, *J* = 7.0 Hz, 2H), 4.75 (d, *J* = 4.5 Hz, 1H), 5.98 (d, *J* = 4.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 7.26-7.38 (m, 4H), 7.46-7.51 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 14.0, 17.5, 40.0, 51.9, 55.2, 59.6, 101.9, 113.7, 117.5, 118.8, 127.0, 129.1, 129.4, 130.8, 131.6, 135.2, 139.3, 139.5, 148.3, 158.3, 163.2, 168.4; HRMS (TOF) calculated for (C₂₄H₂₄ClNO₅+Na) 464.1241, found 464.1253.

5-Ethyl 2-methyl 1-(2-iodophenyl)-4-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4p). Yield 88.4 mg, 83%; Yellow oil; **Major:** ¹H NMR (500 MHz, CDCl₃) δ 1.11 (t, *J* = 7.0 Hz, 3H), 2.08 (s, 3H), 3.46 (s, 3H), 3.81 (s, 3H), 4.01 (q, *J* = 7.0 Hz, 2H), 4.77 (d, *J* = 5.5 Hz, 1H), 5.96 (d, *J* = 5.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 7.06-7.12 (m, 1H), 7.24-7.26 (m, 1H), 7.37-7.40 (m, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.92-7.95 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 14.0, 17.9, 40.0, 51.8, 55.2, 59.6, 102.3, 103.5, 113.7, 117.1, 128.8, 129.4, 129.4, 129.9, 130.9, 139.2, 139.4,

144.6, 147.5, 158.3, 163.0, 168.3; **Minor:** ^1H NMR (500 MHz, CDCl_3) δ 1.11 (t, $J = 7.0$ Hz, 3H), 2.09 (s, 3H), 3.51 (s, 3H), 3.82 (s, 3H), 4.03 (q, $J = 7.0$ Hz, 2H), 4.78 (d, $J = 5.5$ Hz, 1H), 6.08 (d, $J = 5.5$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 7.06-7.12 (m, 1H), 7.30 (d, $J = 8.5$ Hz, 2H), 7.37-7.43 (m, 2H), 7.89-7.91 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 14.0, 18.0, 39.9, 51.9, 55.2, 59.6, 101.8, 102.4, 113.8, 118.6, 128.9, 129.3, 129.5, 130.3, 131.2, 139.2, 139.3, 144.2, 147.5, 158.3, 162.9, 168.4; HRMS (TOF) calculated for $(\text{C}_{24}\text{H}_{24}\text{INO}_5+\text{Na})$ 556.0597, found 556.0617.

5-Ethyl 2-methyl 1-(3,4-dimethoxyphenyl)-4-(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4q). Yield 60.7 mg, 65%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.12 (t, $J = 7.0$ Hz, 3H), 2.15 (s, 3H), 3.49 (s, 3H), 3.79 (s, 3H), 3.84 (s, 3H), 3.88 (s, 3H), 4.03 (q, $J = 7.0$ Hz, 2H), 4.68 (d, $J = 6.0$ Hz, 1H), 5.98 (d, $J = 6.0$ Hz, 1H), 6.76 (s, 1H), 6.78-6.84 (m, 2H), 6.87 (d, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.1, 18.2, 39.2, 51.9, 55.3, 55.9, 56.0, 59.7, 76.8, 77.0, 77.2, 110.4, 112.4, 113.4, 113.9, 118.5, 122.0, 128.6, 132.9, 134.9, 138.8, 148.5, 148.7, 150.0, 158.3, 164.0, 168.3; HRMS (TOF) calculated for $(\text{C}_{26}\text{H}_{29}\text{NO}_7+\text{Na})$ 490.1842, found 490.1858.

Dimethyl 1,4-bis(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4r). Yield 74.4 mg, 88%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 2.16 (s, 3H), 3.50 (s, 3H), 3.60 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 4.69 (d, $J = 6.5$ Hz, 1H), 6.03 (d, $J = 6.5$ Hz, 1H), 6.89 (d, $J = 8.5$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 18.3, 39.1, 50.9, 51.8, 55.2, 55.3, 102.3, 113.8, 114.0, 118.6, 128.4, 130.8, 132.7, 134.5, 138.6, 150.4, 158.3, 158.8, 163.8, 168.8; HRMS (TOF) calculated for $(\text{C}_{24}\text{H}_{25}\text{NO}_6+\text{Na})$ 446.1580, found 446.1595.

5-*tert*-Butyl 2-methyl 1,4-bis(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2,5-dicarboxylate (4s). Yield 88.4 mg, 95%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.30 (s, 9H), 2.09 (s, 3H), 3.49 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 4.67 (d, $J = 6.0$ Hz, 1H), 5.95 (d, $J = 6.0$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 18.1, 28.0, 40.0, 51.7, 55.2, 55.3, 79.5, 104.4, 113.7, 113.8, 118.4, 128.6, 130.9, 132.6, 135.0, 139.0, 148.6, 158.2, 158.7, 164.0, 167.8; HRMS (TOF) calculated for ($\text{C}_{27}\text{H}_{31}\text{NO}_6+\text{Na}$) 488.2049, found 488.2051.

Methyl 5-acetyl-1,4-bis(4-methoxyphenyl)-6-methyl-1,4-dihydropyridine-2-carboxylate (4t). Yield 63.5 mg, 78%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 2.07 (s, 3H), 2.10 (s, 3H), 3.47 (s, 3H), 3.80 (s, 6H), 4.62 (d, $J = 6.5$ Hz, 1H), 6.08 (d, $J = 6.5$ Hz, 1H), 6.85 (d, $J = 8.5$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 7.12 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 18.8, 29.8, 39.9, 51.8, 55.3, 55.4, 110.9, 113.8, 114.4, 119.2, 128.3, 130.7, 132.3, 134.2, 137.8, 149.6, 158.6, 158.9, 163.7, 199.7; HRMS (TOF) calculated for ($\text{C}_{24}\text{H}_{25}\text{NO}_5+\text{Na}$) 430.1630, found 430.1612.

5-Ethyl 2-methyl 1,4-bis(4-methoxyphenyl)-6-phenyl-1,4-dihydropyridine-2,5-dicarboxylate (4u). Yield 73.8 mg, 74%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 0.69 (t, $J = 7.0$ Hz, 3H), 3.52 (s, 3H), 3.67 (s, 3H), 3.69 (q, $J = 7.0$ Hz, 2H), 3.83 (s, 3H), 4.82 (d, $J = 6.0$ Hz, 1H), 6.19 (d, $J = 6.0$ Hz, 1H), 6.55 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 2H), 7.04-7.18 (m, 5H), 7.43 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 13.4, 39.5, 51.9, 55.1, 55.3, 59.5, 105.4, 113.1, 114.1, 120.0, 127.3, 127.7, 128.7, 129.6, 130.7, 133.4, 135.2, 136.6, 138.2, 152.2, 157.9, 158.4, 163.9, 167.6; HRMS (TOF) calculated for ($\text{C}_{30}\text{H}_{29}\text{NO}_6+\text{Na}$) 522.1893, found 522.1878.

Dimethyl 1-(4-methoxyphenyl)-4-phenyl-1,4,4a,5,6,7-hexahydroquinoline-2,4a-dicarboxylate (5a). Yield 57.2 mg, 66%; Yellow solid, mp 53-55 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.34-1.46 (m, 2H), 1.64-1.72 (m, 1H), 2.01-2.12 (m, 2H), 2.24-2.32 (m, 1H), 3.49 (s, 3H), 3.58 (s, 3H), 3.73 (d, *J* = 3.0 Hz, 1H), 3.81 (s, 3H), 4.66-4.72 (m, 1H), 5.63 (d, *J* = 3.0 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 7.14-7.22 (m, 4H), 7.26-7.34 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 19.8, 24.8, 33.3, 49.0, 49.9, 51.5, 51.8, 55.3, 105.9, 109.3, 114.1, 127.3, 127.8, 129.5, 129.6, 135.7, 136.4, 139.7, 140.0, 157.8, 165.0, 171.5; HRMS (TOF) calculated for (C₂₆H₂₇NO₅+Na) 456.1787, found 456.1776.

Dimethyl 1,4-bis(4-methoxyphenyl)-1,4,4a,5,6,7-hexahydroquinoline-2,4a-dicarboxylate (5b). Yield 53.7 mg, 58%; Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 1.34-1.46 (m, 2H), 1.64-1.72 (m, 1H), 2.02-2.12 (m, 2H), 2.24-2.30 (m, 1H), 3.48 (s, 3H), 3.59 (s, 3H), 3.68 (d, *J* = 3.0 Hz, 1H), 3.81 (s, 6H), 4.64-4.68 (m, 1H), 5.60 (d, *J* = 3.0 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 19.9, 24.8, 33.4, 49.1, 49.1, 51.5, 51.8, 55.2, 55.3, 105.8, 109.8, 113.2, 114.1, 129.6, 130.4, 131.7, 135.6, 136.5, 140.1, 157.8, 158.8, 165.0, 171.6; HRMS (TOF) calculated for (C₂₇H₂₉NO₆+Na) 486.1893, found 486.1903.

Dimethyl 1,4-diphenyl-1,4,4a,5,6,7-hexahydroquinoline-2,4a-dicarboxylate (5c). Yield 45.1 mg, 56%; Yellow solid, mp 63-66 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.32-1.44 (m, 2H), 1.66-1.74 (m, 1H), 2.04-2.12 (m, 2H), 2.26-2.32 (m, 1H), 3.46 (s, 3H), 3.58 (s, 3H), 3.75 (d, *J* = 3.0 Hz, 1H), 4.76-4.81 (m, 1H), 5.69 (d, *J* = 3.0 Hz, 1H), 7.14-7.38 (m, 10H). ¹³C NMR (125 MHz, CDCl₃): δ 19.8, 24.8, 33.4, 48.7, 50.0, 51.5, 51.8, 107.0,

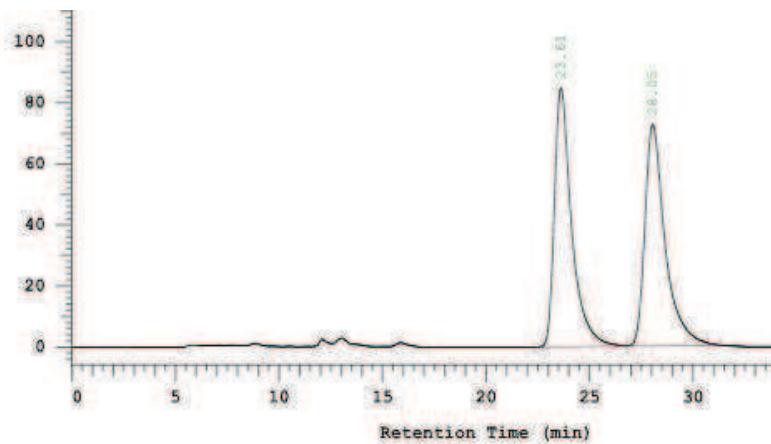
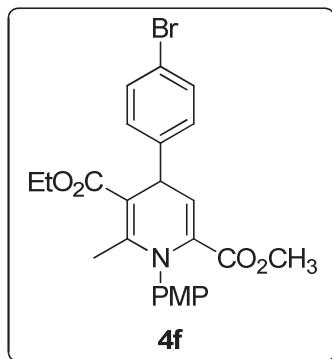
110.3, 126.1, 127.3, 127.8, 128.1, 128.9, 129.5, 135.6, 139.6, 144.0, 165.0, 171.4; HRMS (TOF) calculated for ($C_{25}H_{25}NO_4+Na$) 426.1681, found 426.1665.

Dimethyl 1-(4-methoxyphenyl)-4-phenyl-4,4a,5,6-tetrahydro-1H-cyclopenta[b]pyridine-2,4a-dicarboxylate (5d). Yield 46.9 mg, 56%; Yellow solid, mp 59-61 °C; 1H NMR (500 MHz, $CDCl_3$) δ 1.92-1.99 (m, 1H), 2.17-2.23 (m, 1H), 2.35-2.42 (m, 1H), 2.70-2.76 (m, 1H), 3.53 (s, 3H), 3.54 (s, 3H), 3.81 (s, 3H), 3.83 (d, $J = 3.0$ Hz, 1H), 4.54-4.57 (m, 1H), 5.92 (d, $J = 3.0$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 7.15 (d, $J = 8.5$ Hz, 2H), 7.18-7.24 (m, 2H), 7.27-7.36 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.9, 37.1, 50.4, 51.6, 51.9, 55.4, 59.1, 104.7, 113.5, 114.1, 127.3, 127.7, 128.3, 128.3, 134.9, 136.9, 139.7, 144.0, 157.7, 164.6, 171.3; HRMS (TOF) calculated for ($C_{25}H_{25}NO_5+Na$) 442.1630, found 442.1611.

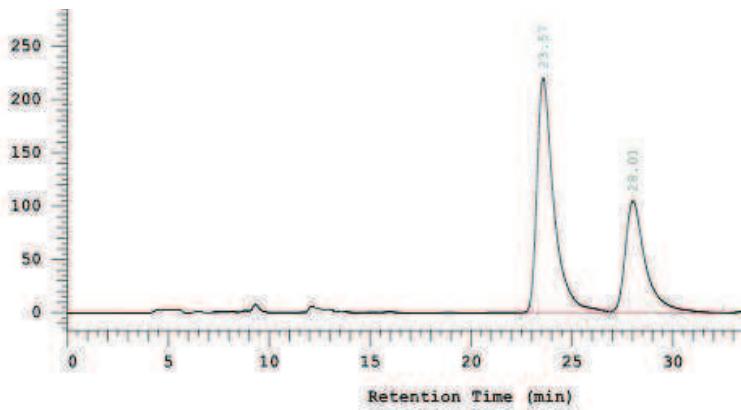
Dimethyl 1,4-bis(4-methoxyphenyl)-4,4a,5,6-tetrahydro-1H-cyclopenta[b]pyridine-2,4a-dicarboxylate (5e). Yield 45.8 mg, 51%; Yellow oil; 1H NMR (500 MHz, $CDCl_3$) δ 1.88-1.96 (m, 1H), 2.14-2.22 (m, 1H), 2.34-2.39 (m, 1H), 2.68-2.74 (m, 1H), 3.53 (s, 3H), 3.54 (s, 3H), 3.78 (d, $J = 2.5$ Hz, 1H), 3.80 (s, 3H), 3.81 (s, 3H), 4.54-4.58 (m, 1H), 5.89 (d, $J = 2.5$ Hz, 1H), 6.85 (d, $J = 8.5$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 7.12-7.18 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.9, 37.0, 49.7, 51.6, 51.9, 55.2, 55.3, 60.0, 104.6, 113.7, 114.0, 114.1, 127.7, 129.3, 131.8, 134.7, 137.0, 144.1, 157.7, 158.8, 164.6, 171.4; HRMS (TOF) calculated for ($C_{26}H_{27}NO_6+Na$) 472.1736, found 472.1733.

Dimethyl 1,4-diphenyl-4,4a,5,6-tetrahydro-1H-cyclopenta[b]pyridine-2,4a-dicarboxylate (5f). Yield 39.7 mg, 51%; Yellow oil; 1H NMR (500 MHz, $CDCl_3$) δ 1.94-2.02 (m, 1H), 2.16-2.24 (m, 1H), 2.36-2.44 (m, 1H), 2.72-2.77 (m, 1H), 3.52 (s, 3H), 3.54 (s, 3H), 3.85 (d, $J = 2.5$ Hz, 1H), 4.66-4.69 (m, 1H), 5.98 (d, $J = 2.5$ Hz, 1H), 7.18-7.25

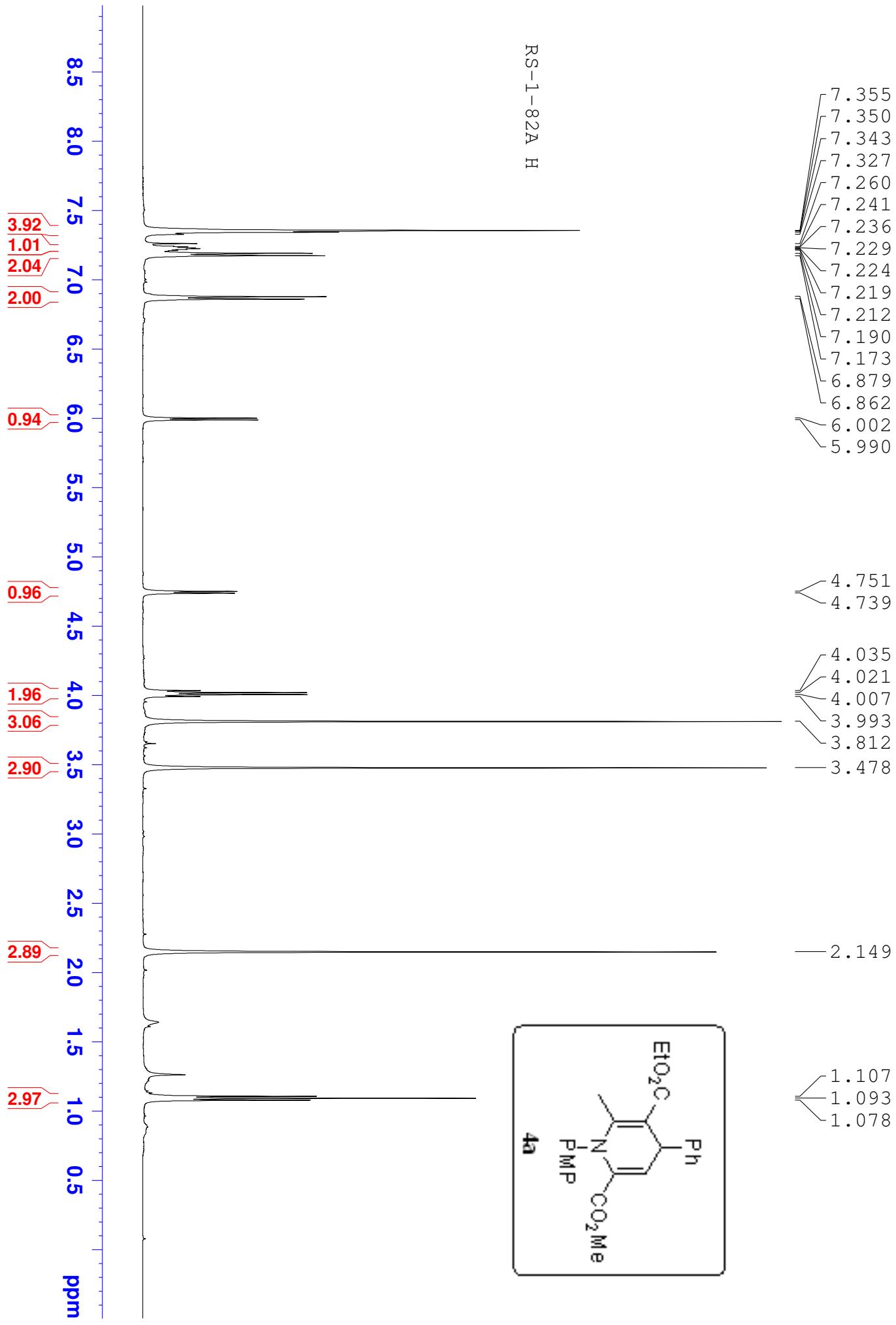
(m, 5H), 7.27-7.38 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3): δ 45.7, 48.7, 55.9, 73.6, 78.7, 111.2, 111.4, 115.0, 126.0, 128.2, 128.6, 130.1, 133.5, 140.5, 156.5, 176.6, 203.6; HRMS (TOF) calculated for ($\text{C}_{24}\text{H}_{23}\text{NO}_4\text{Na}$) 412.1525, found 412.1521.

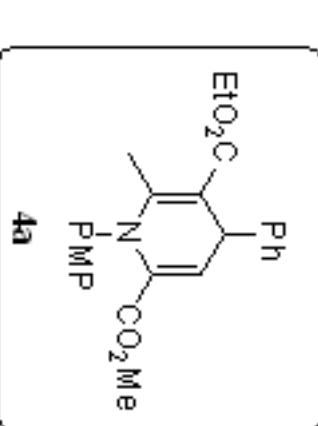
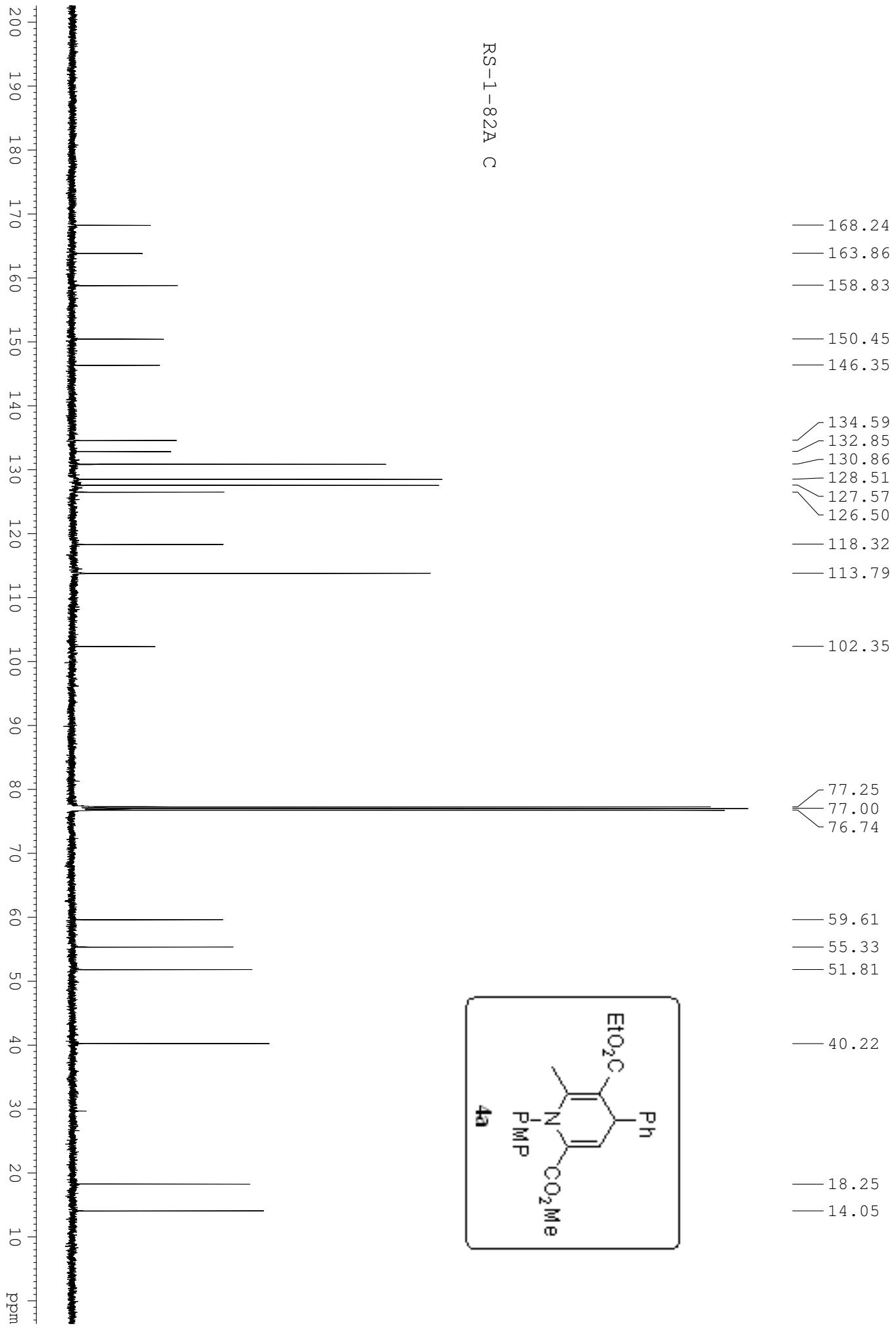


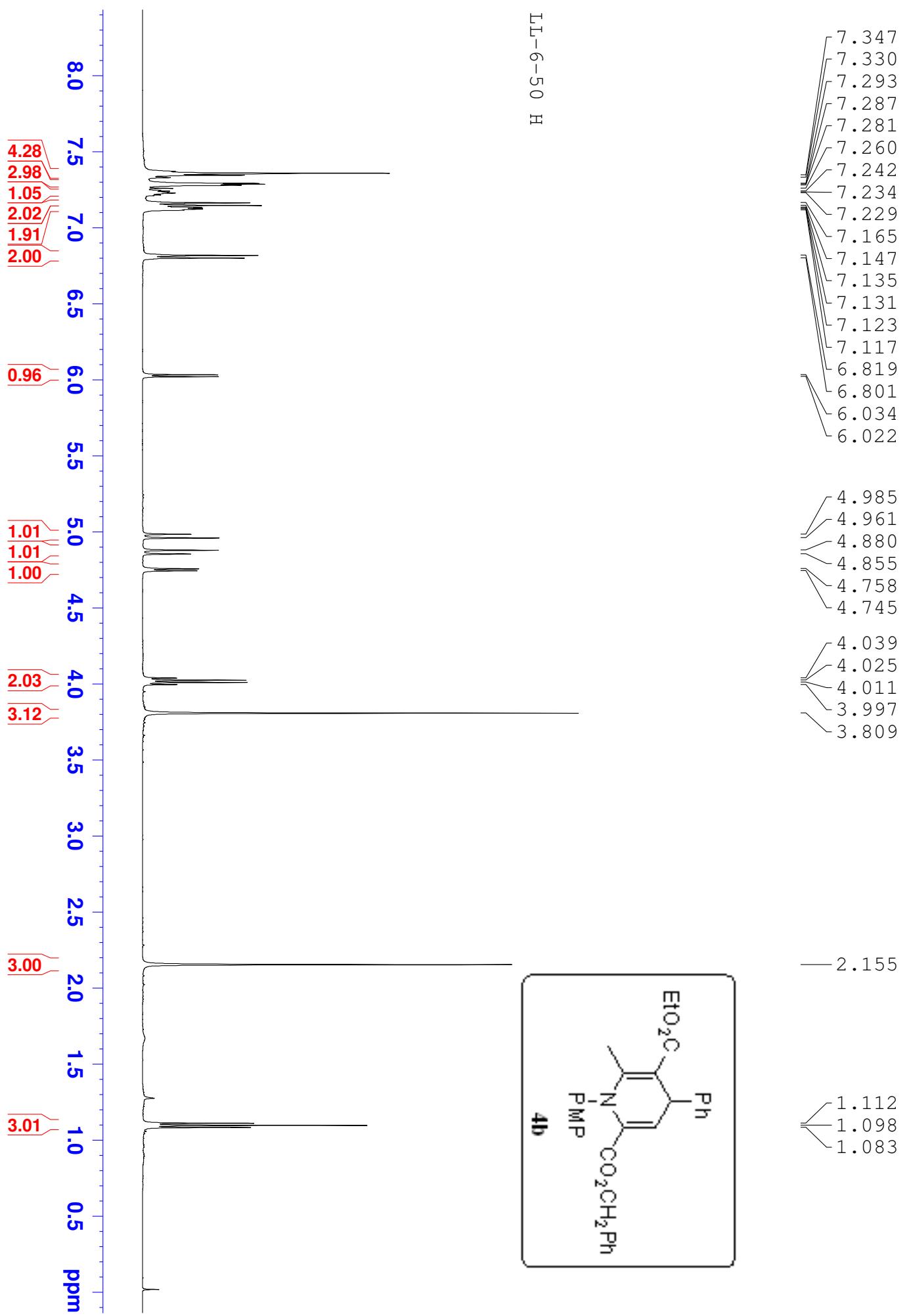
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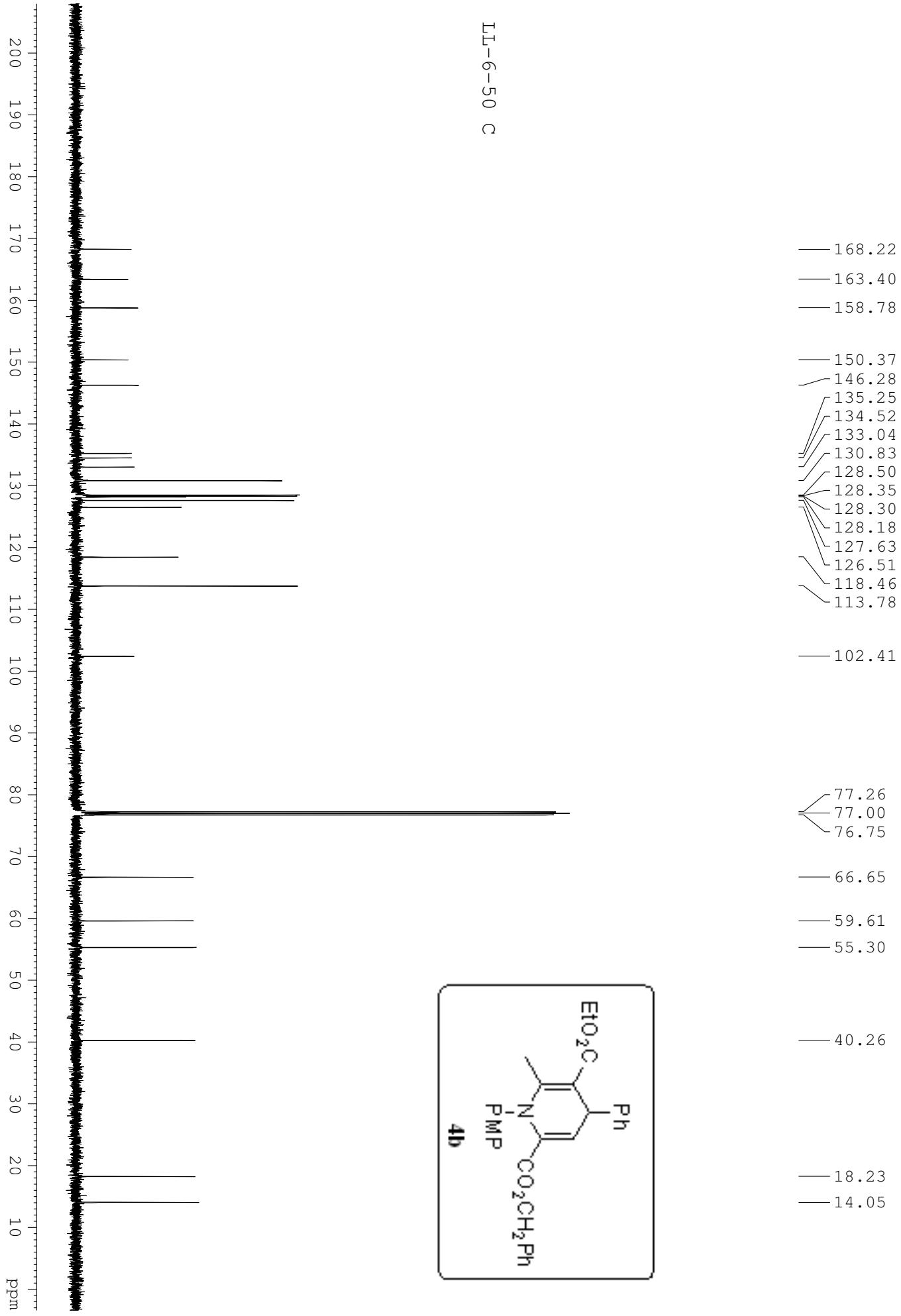


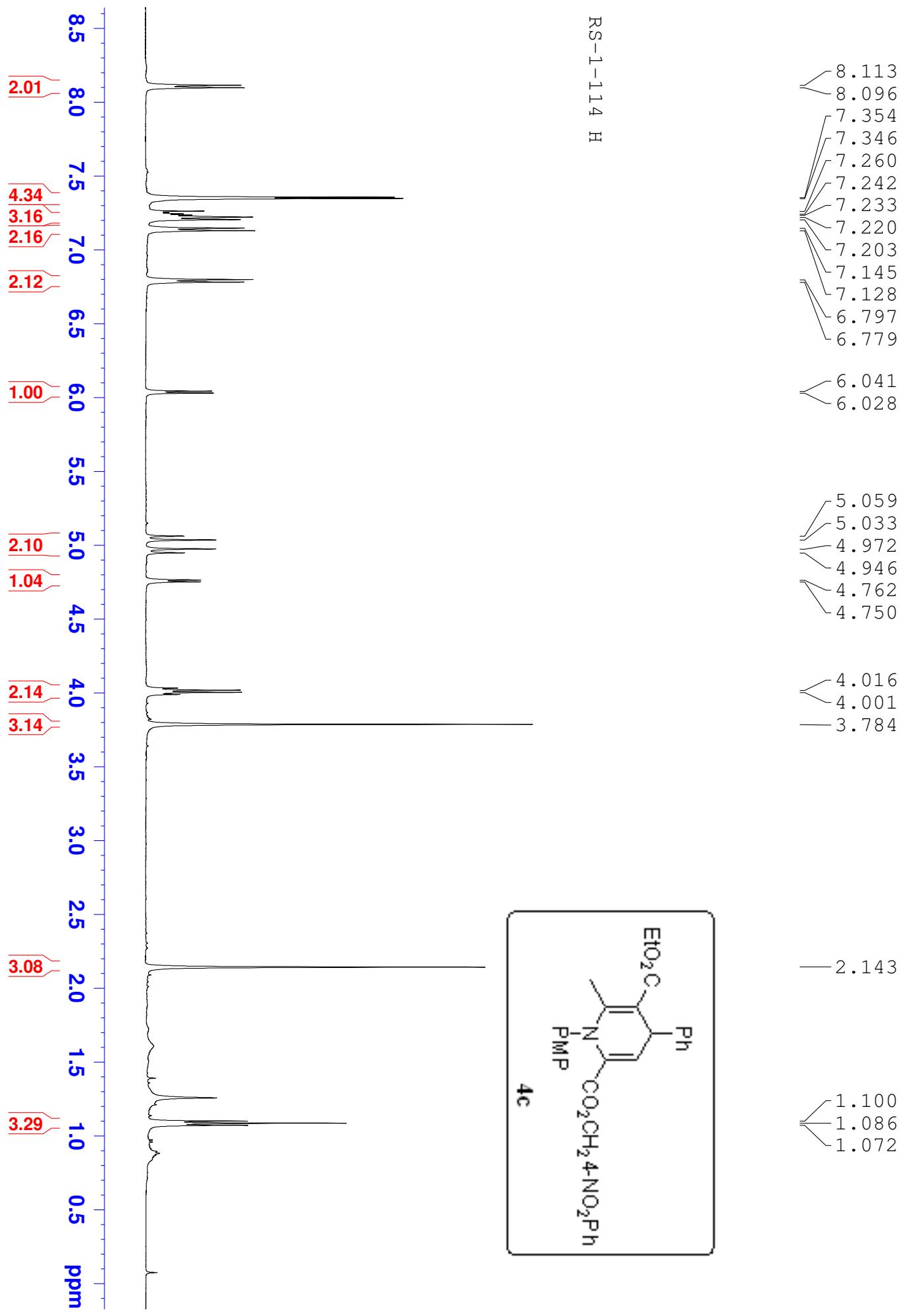
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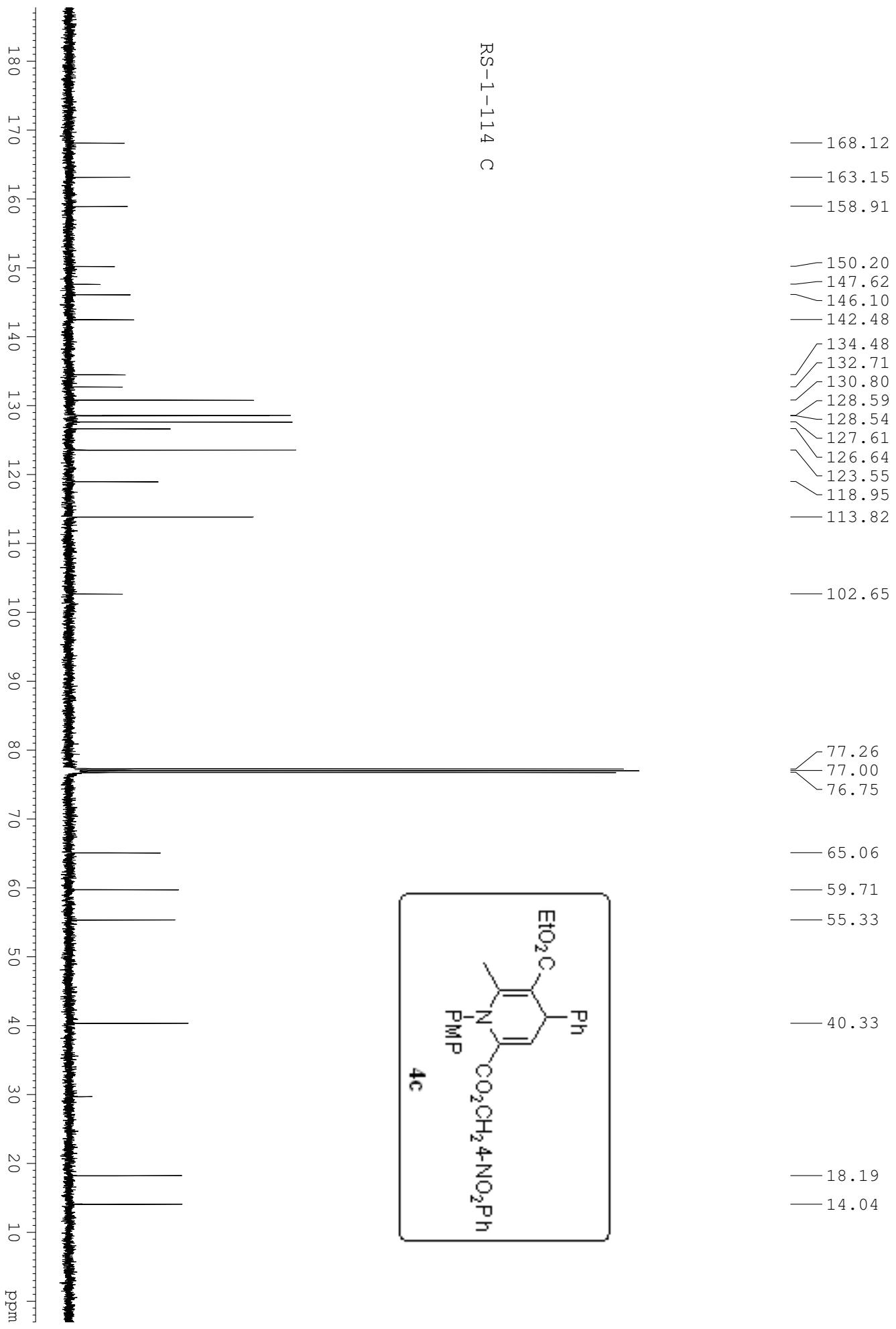


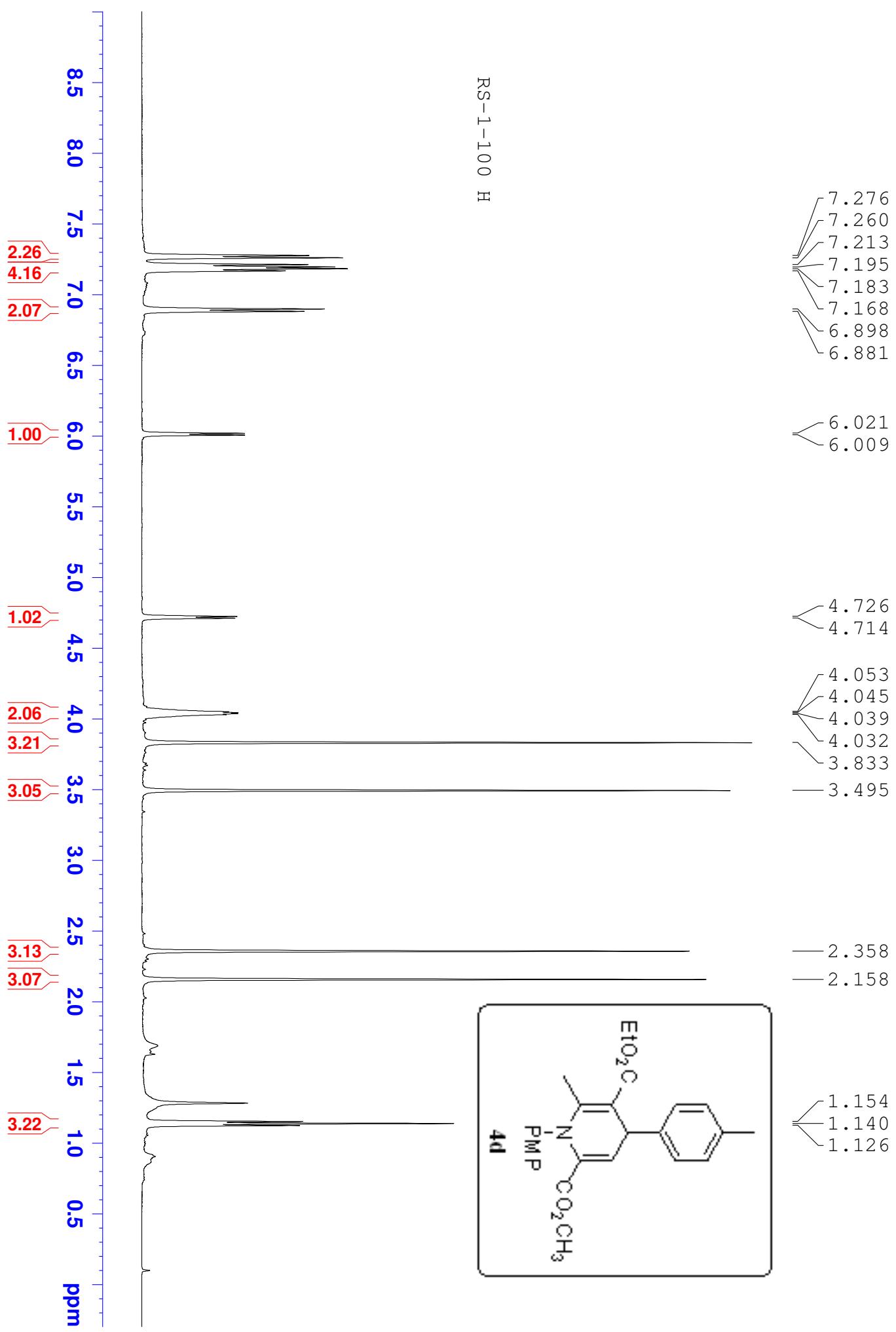












RS-1-100 C

