



Supporting Information

for

Green synthesis of C5–C6-unsubstituted 1,4-DHP scaffolds using an efficient Ni–chitosan nanocatalyst under ultrasonic conditions

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Characterization data and copies of spectra

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Characterization data of synthesized compounds:

Dimethyl 4-phenyl-1-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (4a, yield: 88%)

Yellowish solid; R_f : 0.40 (25% ethyl acetate in petroleum ether); M.p: 132 °C; δ_H (300 MHz, $CDCl_3$): 7.42-7.34 (m, 4H), 7.27-7.19 (m, 5H), 6.19 (d, J = 7.5 Hz, 1H), 5.06 (dd, J = 5.4 Hz, 1H), 4.60 (d, J = 5.1 Hz, 1H), 3.59 (s, 3H), 3.56 (s, 3H), 2.37 (s, 3H); δ_C (75 MHz, $CDCl_3$): 167.2, 164.8, 147.1, 143.5, 139.4, 137.8, 129.9, 128.5, 127.5, 126.5, 126.4, 108.2, 100.8, 52.3, 51.4, 38.4, 21.0; HRMS: calcd for $C_{22}H_{21}NO_4$ [$M + H$] 364.1549, found 364.1586.

Diethyl 4-phenyl-1-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (4b, yield: 87%).

Yellowish solid; R_f : 0.34 (25% ethyl acetate in petroleum ether); M.p: 136 °C; δ_H (300 MHz, $CDCl_3$): 7.21-7.10 (m, 4H), 7.04-6.96 (m, 5H), 5.95 (d, J = 7.8 Hz, 1H), 4.83-4.80 (m, 1H), 4.39 (d, J = 5.1 Hz, 1H), 3.82-3.76 (m, 4H), 2.13 (s, 3H), 0.89 (t, J = 7.2 Hz, 3H), 0.78 (t, J = 7.2 Hz, 3H); δ_C (75 MHz, $CDCl_3$): 166.6, 164.2, 147.3, 143.4, 139.5, 137.8, 129.7, 128.6, 128.4, 127.7, 126.8, 126.4, 108.0, 100.9, 61.4, 60.0, 38.6, 21.0, 13.9, 13.5; HRMS: calcd for $C_{24}H_{25}NO_4$, [$M + H$] 392.1862, found 392.1815.

Dimethyl 1-(4-methoxyphenyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (4c, yield: 89%).

Light yellowish solid; R_f : 0.36 (25% ethyl acetate in petroleum ether); M.p: 138 °C; δ_H (300 MHz, $CDCl_3$): 7.22-7.14 (m, 5H), 7.03 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 5.94 (d, J = 7.8 Hz, 1H), 4.85 (dd, J = 5.4 Hz, 1H), 4.41 (d, J = 5.4 Hz, 1H), 3.62 (s, 3H), 3.41 (s, 3H), 3.39 (s, 3H); δ_C (75 MHz, $CDCl_3$): 167.2, 164.8, 159.0, 147.2, 143.8, 134.7, 128.9, 128.3, 127.5, 126.5, 114.3, 108.9, 100.3, 55.4, 52.3, 51.3, 38.4.

Diethyl 1-(2,5-dichlorophenyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (4d, yield: 80%).

Yellowish solid; R_f : 0.37 (25% ethyl acetate in petroleum ether); M.p: 142 °C; δ_H (300 MHz, $CDCl_3$): 7.41-7.33 (m, 5H), 7.28-7.21 (m, 3H), 6.18 (d, J = 7.8 Hz, 1H), 5.07 (dd,

$J = 5.1$ Hz, 1H), 4.61 (d, $J = 5.1$ Hz, 1H), 4.06-3.99 (m, 4H), 1.12 (t, $J = 7.2$ Hz, 3H), 1.04 (t, $J = 7.2$ Hz, 3H); δ_{C} (75 MHz, CDCl_3): 166.4, 164.0, 146.9, 142.7, 140.6, 133.6, 129.4, 128.9, 128.3, 128.1, 127.4, 126.6, 125.9, 108.6, 102.1, 61.7, 60.2, 38.6, 13.9, 13.5.

Dimethyl 1-(4-nitrophenyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (4e, yield: 78%). Yellowish solid; R_{f} : 0.31 (25% ethyl acetate in petroleum ether); M.p: 146°C ; δ_{H} (300 MHz, CDCl_3): 8.05 (d, $J = 8.4$ Hz, 2H), 7.37-7.27 (m, 5H), 7.09 (d, $J = 8.1$ Hz, 2H), 6.49 (d, $J = 9.6$ Hz, 1H), 5.79-5.74 (m, 1H), 5.32 (d, $J = 5.7$ Hz, 1H), 3.65 (s, 6H); δ_{C} (75 MHz, CDCl_3): 165.4, 164.6, 150.0, 144.6, 140.9, 129.2, 128.9, 128.3, 124.9, 124.8, 122.7, 120.4, 119.5, 111.9, 100.8, 62.9, 52.9, 51.9, 38.4.

Diethyl 1-benzyl-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (4f, yield: 82%). White solid; R_{f} : 0.44 (25% ethyl acetate in petroleum ether); M.p: 134°C ; δ_{H} (300 MHz, CDCl_3): 7.30-7.27 (m, 7H), 7.19-7.18 (m, 3H), 5.81 (d, $J = 7.5$ Hz, 1H), 4.91 (dd, $J = 5.1$ Hz, 1H), 4.48 (d, $J = 5.1$ Hz, 1H), 4.35 (d, $J = 8.4$ Hz, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 3.93 (d, $J = 7.2$ Hz, 2H), 1.15 (t, $J = 7.2$ Hz, 3H), 1.02 (t, $J = 7.2$ Hz, 3H); δ_{C} (75 MHz, CDCl_3): 166.8, 165.2, 147.3, 143.9, 136.5, 128.6, 128.4, 128.2, 127.6, 127.4, 127.0, 126.2, 109.1, 99.8, 61.9, 59.9, 54.4, 38.6, 13.9, 13.6.

Dimethyl 1-benzyl-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (4g, yield: 81%). Light yellowish solid; R_{f} : 0.42 (25% ethyl acetate in petroleum ether); M.p: 136°C ; δ_{H} (300 MHz, CDCl_3): 7.41-7.34 (m, 7H), 7.31-7.26 (m, 3H), 5.92 (d, $J = 7.8$ Hz, 1H), 5.01 (dd, $J = 5.4$ Hz, 1H), 4.57 (d, $J = 5.4$ Hz, 1H), 4.43 (d, $J = 9.9$ Hz, 2H), 3.87 (s, 3H), 3.60 (s, 3H); δ_{C} (75 MHz, CDCl_3): 167.4, 165.7, 147.1, 144.0, 136.4, 128.8, 128.4, 128.0, 127.6, 127.0, 126.6, 126.4, 109.3, 99.8, 54.7, 52.8, 51.3, 38.4;

Dimethyl 1-(3-nitrophenyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (4h, yield: 84%). Yellowish solid; R_f : 0.32 (25% ethyl acetate in petroleum ether); M.p: 140 °C; δ_H (300 MHz, $CDCl_3$): 7.99-7.90(m, 2H), 7.45 (d, J = 7.8 Hz, 1H), 7.41-7.28 (m, 6H), 6.52 (d, J = 7.5Hz, 1H), 5.64 (dd, J = 6.0Hz, 1H), 5.22 (d, J = 5.1 Hz, 1H), 3.85 (s, 3H), 3.51 (s, 3H); δ_C (75 MHz, $CDCl_3$): 167.8, 165.5, 148.5, 145.2, 141.3, 139.1, 131.3, 128.7, 128.3, 127.5, 125.4, 120.9, 120.3, 119.1, 118.2, 108.2, 52.7, 51.4, 39.6.

Diethyl 1-benzyl-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (4i, yield: 86%). Yellowish solid; R_f : 0.35 (25% ethyl acetate in petroleum ether); M.p: 182-142 °C; δ_H (400 MHz, $CDCl_3$): 8.11(d, J = 7.2Hz, 2H), 7.39-7.26 (m, 7H), 5.95 (d, J = 7.6Hz, 1H), 4.91 (dd, J = 5.2Hz, 1H), 4.69 (d, J = 5.2Hz, 1H), 4.43(ABq, J = 15.6Hz, 2H), 4.32-4.28(m, 2H), 4.02-4.00 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H); δ_C (100 MHz, $CDCl_3$): 166.4, 164.9, 154.3, 146.7, 144.7, 136.4, 129.0, 128.8, 128.3, 127.7, 123.9, 123.0, 107.9, 99.0, 62.4, 60.5, 54.9, 39.0, 14.2, 13.8.

Dimethyl 1-(4-methoxyphenyl)-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (4j, yield: 87%). Yellowish solid; R_f : 0.37 (25% ethyl acetate in petroleum ether); M.p: 140 °C; δ_H (400 MHz, $CDCl_3$): 8.20 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.8Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.16(d, J = 7.6Hz, 1H), 4.97 (dd, J = 5.2Hz, 1H), 4.73 (d, J = 5.2Hz, 1H), 3.80 (s, 3H), 3.54 (s, 3H), 3.52 (s, 3H); δ_C (100 MHz, $CDCl_3$): 166.7, 164.3, 159.2, 154.0, 146.5, 144.4, 134.1, 129.1, 128.3, 123.9, 123.7, 114.4, 106.5, 98.9, 55.4, 52.9, 51.6, 38.5.

Dimethyl 1,4-bis(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (4k, yield: 82%). Light yellowish solid; R_f : 0.37 (25% ethyl acetate in petroleum ether); M.p: 138 °C; δ_H (400 MHz, $CDCl_3$): 7.30 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 6.8 Hz, 2H), 6.89-6.86 (m, 4H), 6.11(d, J = 8.0Hz, 1H), 5.01 (dd, J = 5.2 Hz, 1H), 4.52 (d, J = 5.2 Hz, 1H), 3.81 (s, 3H), 3.80

(s, 3H), 3.57 (s, 3H), 3.54 (s, 3H); δ_{C} (100 MHz, CDCl_3): 167.3, 164.9, 158.9, 158.2, 143.5, 139.7, 134.7, 128.5, 128.3, 127.9, 114.1, 113.8, 108.2, 100.5, 55.3, 55.2, 52.4, 51.4, 37.4; HRMS: calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_5$ [$\text{M} + \text{H}$] 410.1604, found 410.1658.

Dimethyl 1-benzyl-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (4l, yield: 86%). Yellowish solid; R_{f} : 0.35 (25% ethyl acetate in petroleum ether); M.p: 148 $^{\circ}\text{C}$; δ_{H} (400 MHz, CDCl_3): 8.11 (d, $J = 6.8$ Hz, 2H), 7.41-7.29 (m, 7H), 5.95 (d, $J = 7.6$ Hz, 1H), 4.93 (dd, $J = 5.2$ Hz, 1H), 4.66 (d, $J = 5.4$ Hz, 1H), 4.41 (ABq, $J = 15.6$ Hz, 2H), 3.85 (s, 3H), 3.56 (s, 3H); δ_{C} (100 MHz, CDCl_3): 159.8, 158.3, 146.9, 139.5, 137.5, 129.7, 121.8, 121.3, 121.0, 120.8, 120.8, 116.8, 100.9, 91.6, 47.9, 46.0, 44.6, 31.5.

Dimethyl 1-benzyl-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (4m, yield: 76%). Light yellowish solid; R_{f} : 0.37 (25% ethyl acetate in petroleum ether); M.p: 136 $^{\circ}\text{C}$; δ_{H} (400 MHz, CDCl_3): 7.32-7.25 (m, 4H), 7.23-7.19 (m, 3H), 6.83 (d, $J = 6.8$ Hz, 2H), 6.37 (d, $J = 8.0$ Hz, 1H), 5.02-5.00 (m, 1H), 4.83 (d, $J = 4.8$ Hz, 1H), 4.08 (ABq, $J = 15.6$ Hz, 2H), 3.82 (s, 3H), 3.73 (s, 3H), 3.65 (s, 3H); δ_{C} (100 MHz, CDCl_3): 166.1, 165.7, 159.7, 148.8, 135.2, 134.1, 128.6, 128.1, 127.9, 119.7, 115.3, 114.3, 113.7, 95.1, 55.2, 53.5, 53.0, 51.2, 38.1; HRMS: calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_5$ [$\text{M} + \text{H}$] 394.1654, found 394.1678.

Diethyl 1-benzyl-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (4n, yield: 79%). Yellowish solid; R_{f} : 0.39 (25% ethyl acetate in petroleum ether); M.p: 138 $^{\circ}\text{C}$; δ_{H} (400 MHz, CDCl_3): 7.37-7.31 (m, 5H), 7.15 (d, $J = 6.4$ Hz, 2H), 6.79 (d, $J = 6.8$ Hz, 2H), 5.88 (d, $J = 8.0$ Hz, 1H), 4.93 (dd, $J = 5.2$ Hz, 1H), 4.48 (d, $J = 5.2$ Hz, 1H), 4.41 (d, $J = 14.0$ Hz, 2H), 4.17 (q, $J = 7.2$ Hz, 2H), 4.01 (q, $J = 7.2$ Hz, 2H), 3.78 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H), 1.11 (t, $J = 7.2$ Hz, 3H); δ_{C} (100 MHz, CDCl_3): 166.9, 165.3, 158.1, 143.6, 139.9, 136.6, 128.7, 128.1, 127.9, 127.4, 126.9, 113.5, 109.3, 100.1, 62.0, 59.7, 55.2, 53.3, 37.7, 14.0, 13.7.

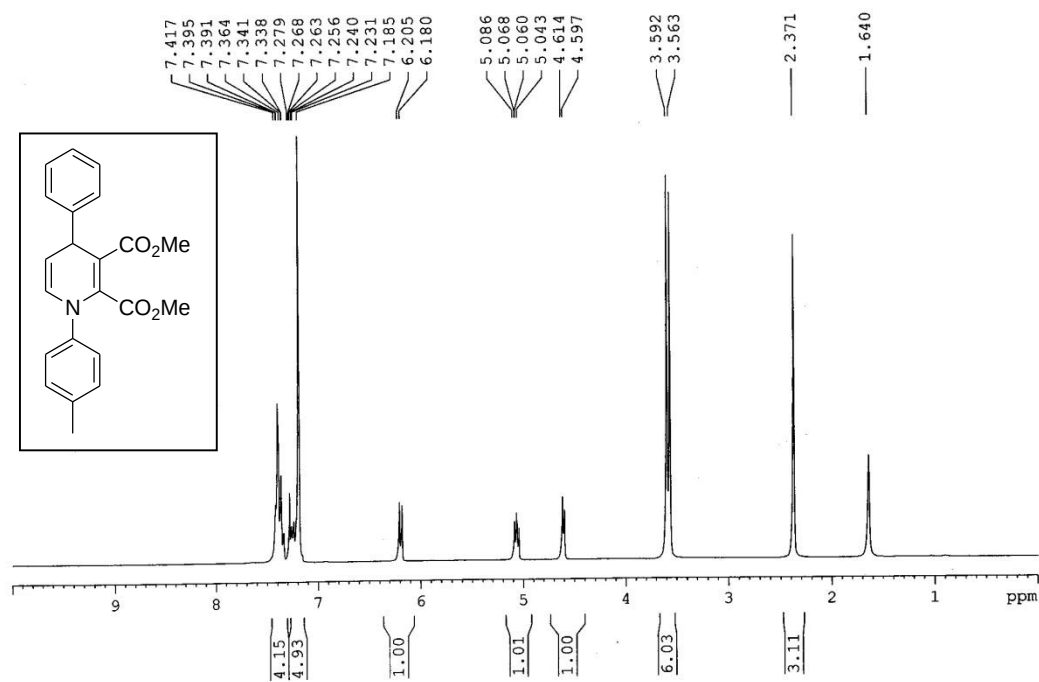
Dimethyl 1-(4-methoxybenzyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (4o, yield: 82%). Yellowish solid; R_f : 0.34 (25% ethyl acetate in petroleum ether); M.p: 130 °C; δ_H (400 MHz, $CDCl_3$): 7.45-7.29 (m, 3H), 7.23-7.19 (m, 4H), 6.89 (d, J = 6.8 Hz, 2H), 5.87 (d, J = 7.6 Hz, 1H), 4.97-4.94 (m, 1H), 4.51 (d, J = 5.2 Hz, 1H), 4.35-4.31 (m, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 3.55 (s, 3H); δ_C (100 MHz, $CDCl_3$): 167.4, 165.7, 159.2, 147.0, 143.9, 128.6, 128.3, 127.9, 127.2, 126.7, 126.3, 113.8, 109.2, 55.1, 54.1, 52.6, 51.2, 38.3.

Dimethyl 1-(4-methoxybenzyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (4p, yield: 82%). Yellowish solid; R_f : 0.37 (25% ethyl acetate in petroleum ether); M.p: 134 °C; δ_H (400 MHz, $CDCl_3$): 7.23 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 5.86 (d, J = 7.6 Hz, 1H), 5.09-5.03 (m, 1H), 4.40 (d, J = 5.2 Hz, 1H), 4.32 (ABq, J = 16 Hz, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 3.71 (s, 3H), 3.56 (s, 3H); δ_C (100 MHz, $CDCl_3$): 167.5, 165.9, 159.6, 158.3, 143.6, 139.7, 134.0, 128.9, 128.3, 126.8, 115.2, 114.2, 113.6, 109.5, 59.7, 55.2, 54.2, 52.8, 51.3, 37.4.

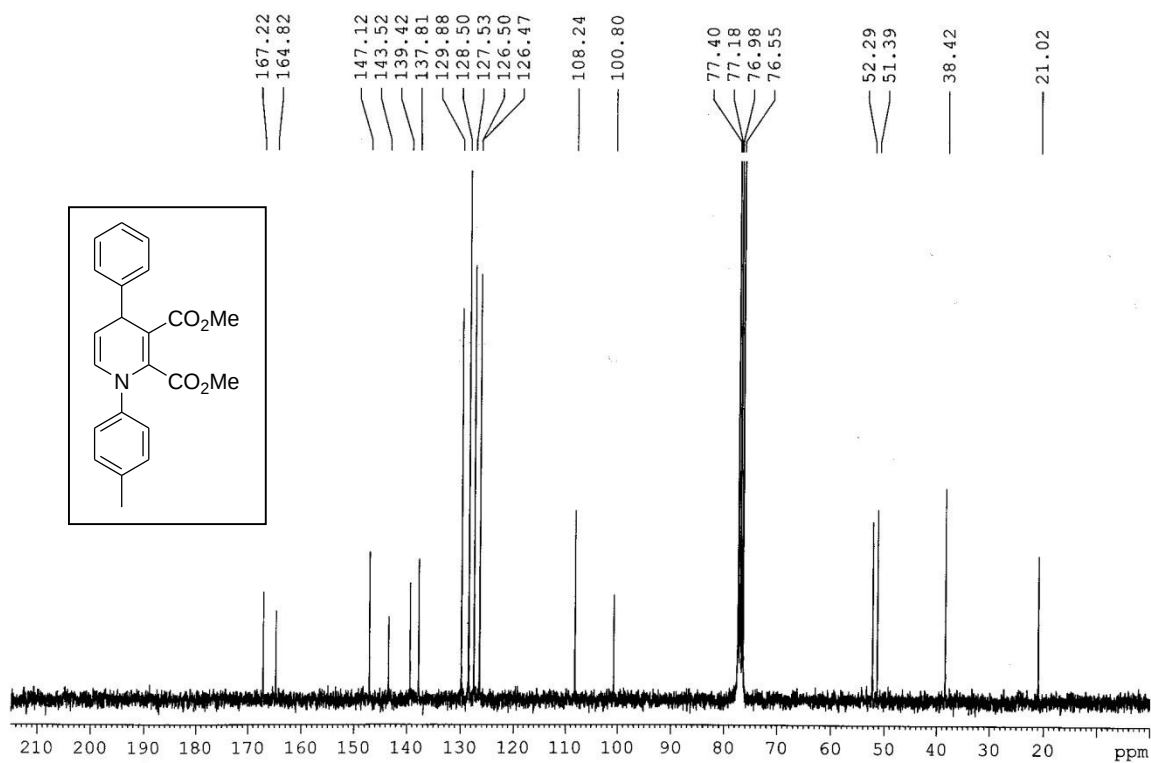
Dimethyl 1-butyl-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (4q, yield: 76%). Light yellow solid; R_f : 0.42 (25% ethyl acetate in petroleum ether); M.p: 118 °C; δ_H (400 MHz, $CDCl_3$): 7.31-7.25 (m, 5H), 5.88 (d, J = 7.6 Hz, 1H), 4.98 (dd, J = 5.2 Hz, 1H), 4.50 (d, J = 5.2 Hz, 1H), 3.90 (s, 3H), 3.53 (s, 3H), 3.17 (t, J = 6.4 Hz, 2H), 1.66-1.58 (m, 2H), 1.35-1.27 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); δ_C (100 MHz, $CDCl_3$): 167.5, 165.7, 147.5, 144.1, 128.4, 127.4, 127.1, 126.3, 108.9, 98.7, 52.8, 51.5, 51.3, 38.3, 32.1, 19.7, 13.7.

Diethyl 2-(benzylamino)maleate (intermediate 4fA) : δ_H (300 MHz, $CDCl_3$): 8.46 (s, 1H), 7.37-7.26 (m, 5H), 5.19 (s, 1H), 4.58 (d, J = 6.3 Hz, 2H), 4.26-4.11 (m, 4H), 1.29-1.23 (m, 6H); δ_C (75 MHz, $CDCl_3$): 170.0, 163.6, 151.5, 138.8, 128.5, 127.2, 127.1, 88.1, 67.7, 59.1, 48.4, 14.2, 13.7.

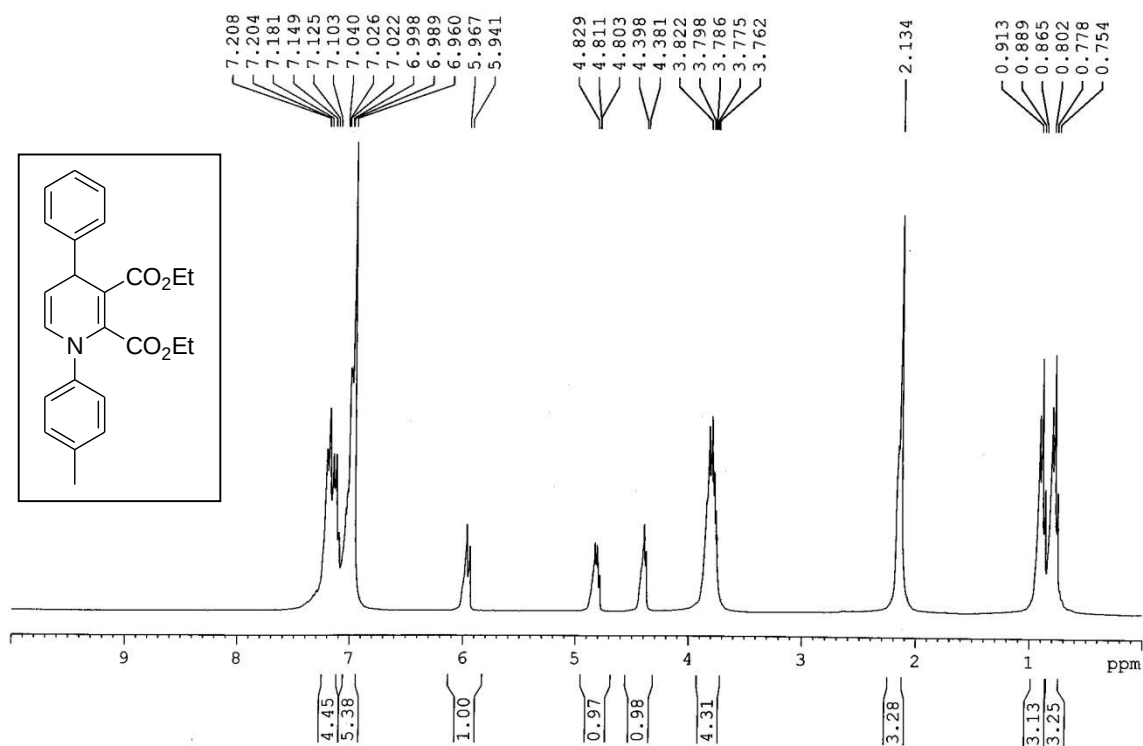
^1H NMR and ^{13}C NMR spectra for 4a–q:



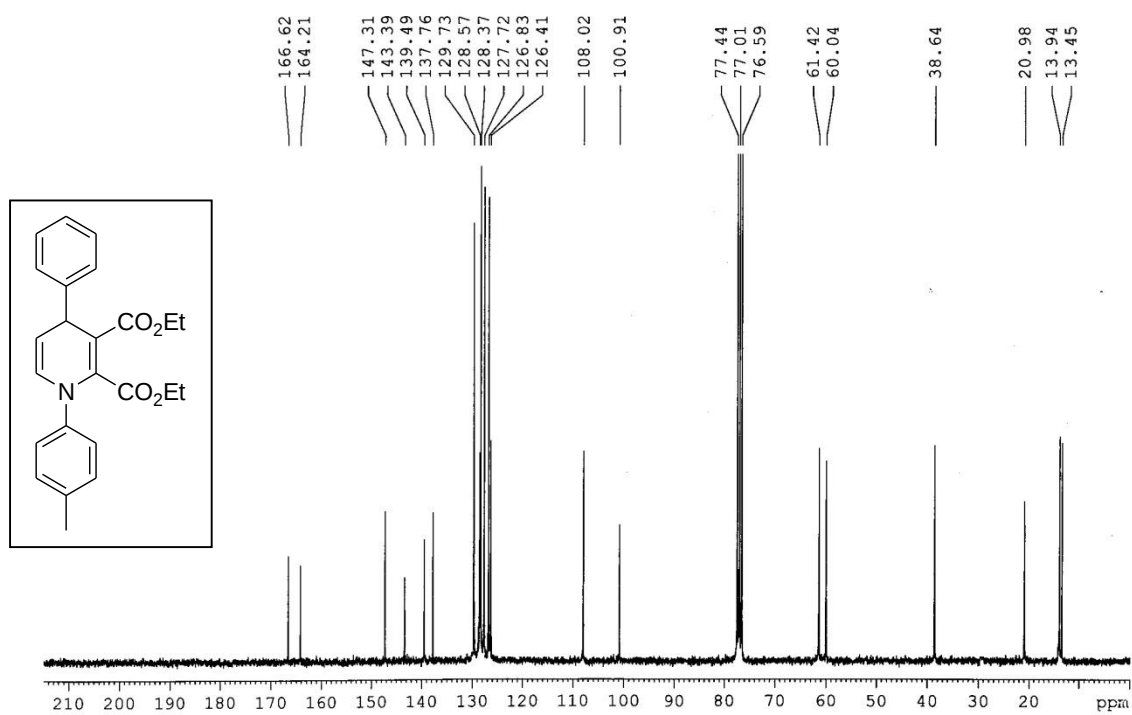
^1H NMR spectrum for 4a



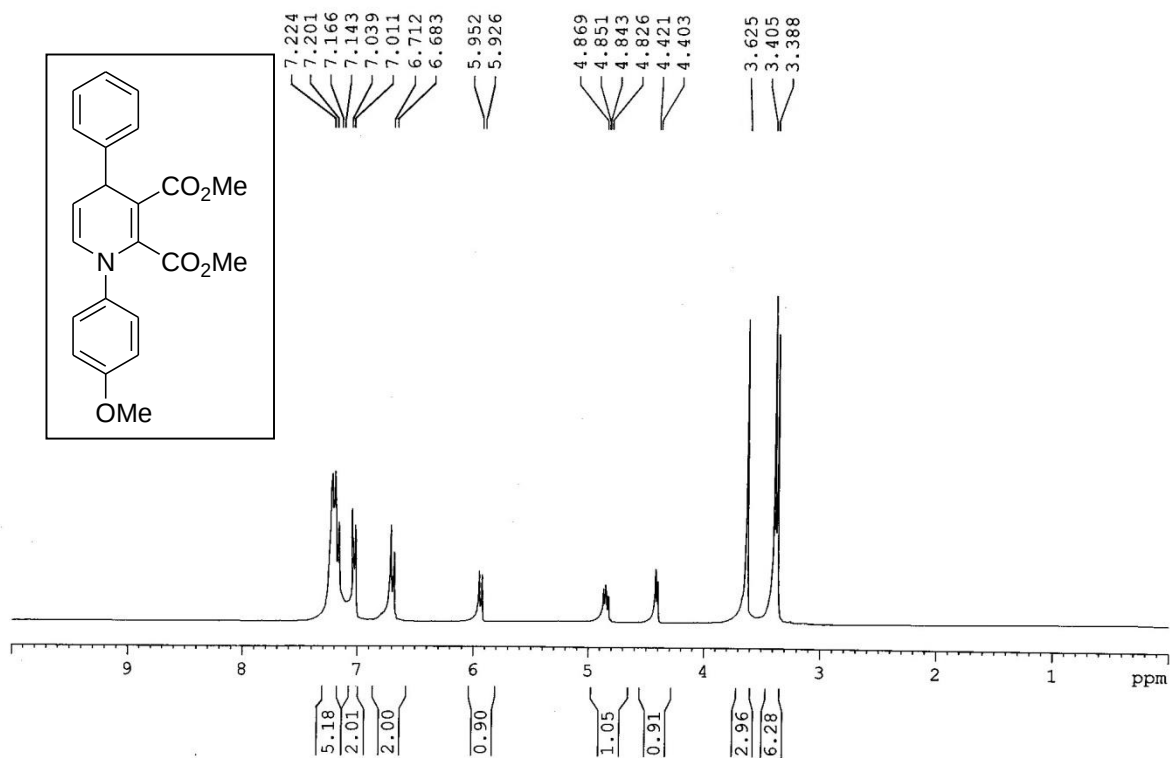
^{13}C NMR spectrum for 4a



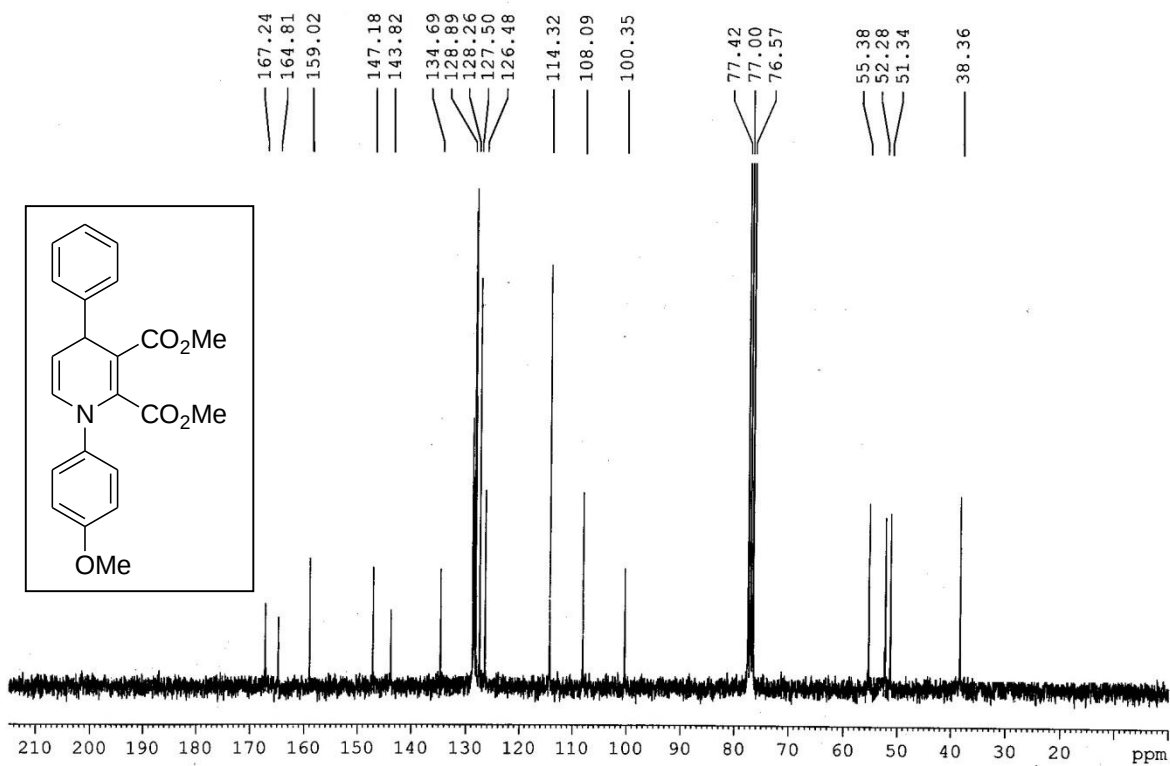
¹H NMR spectrum for 4b



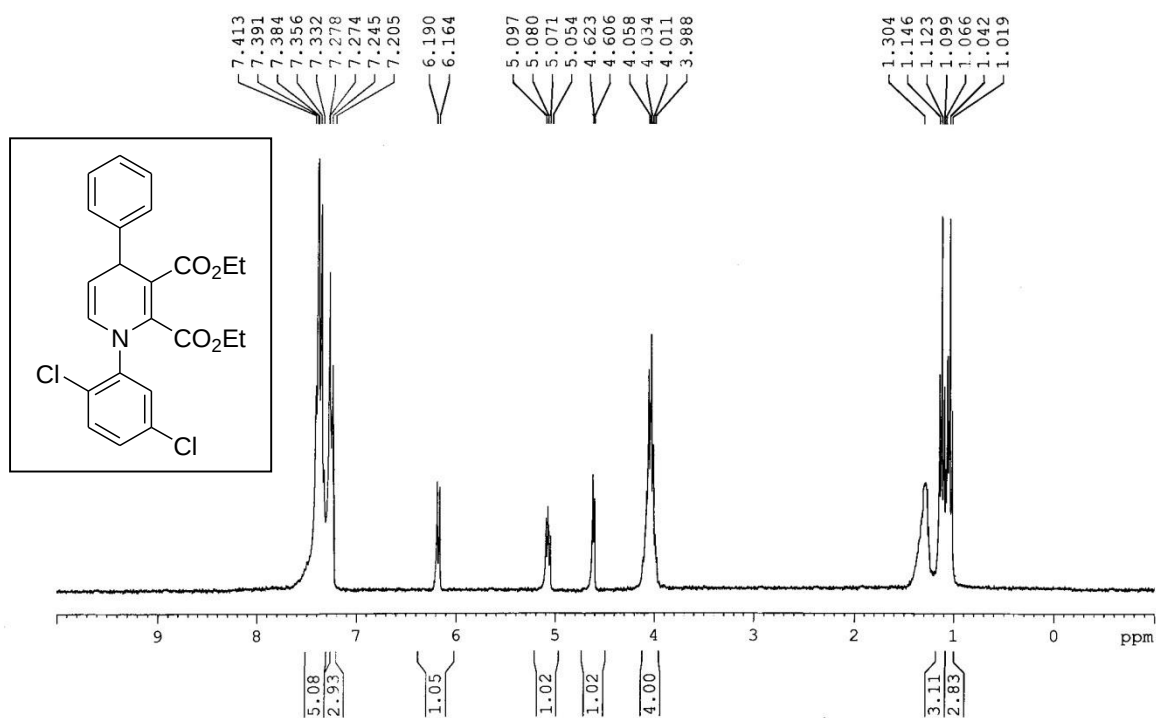
¹³C NMR spectrum for 4b



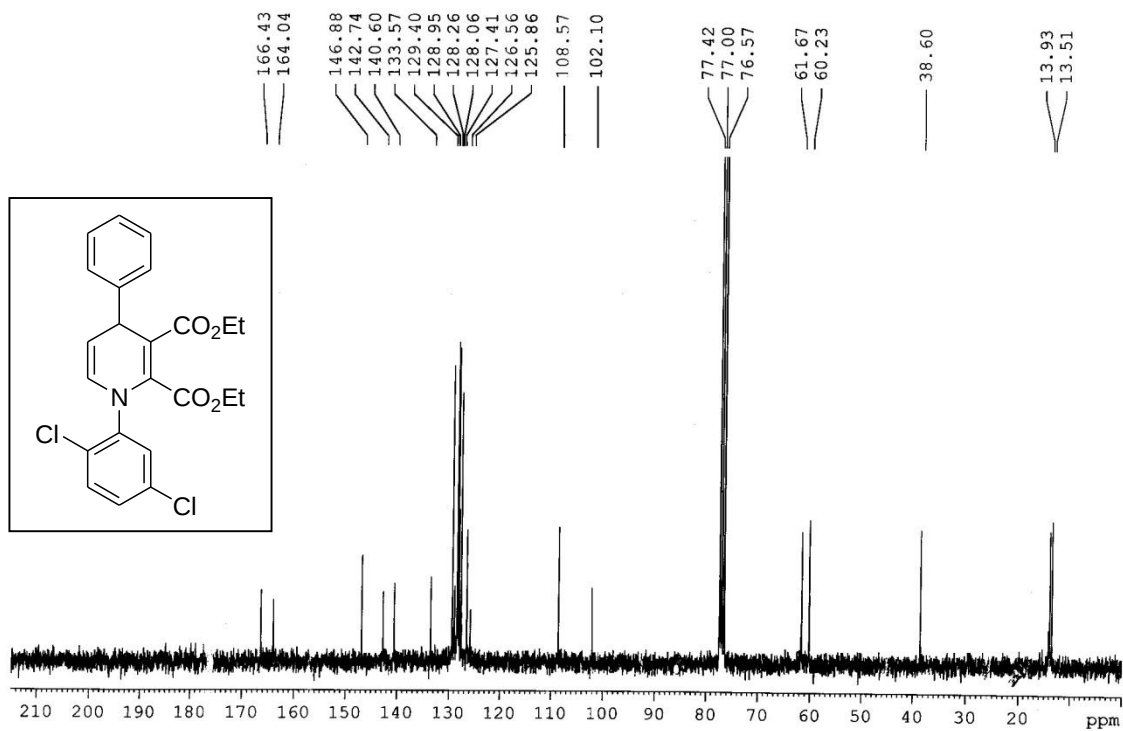
¹H NMR spectrum for 4c



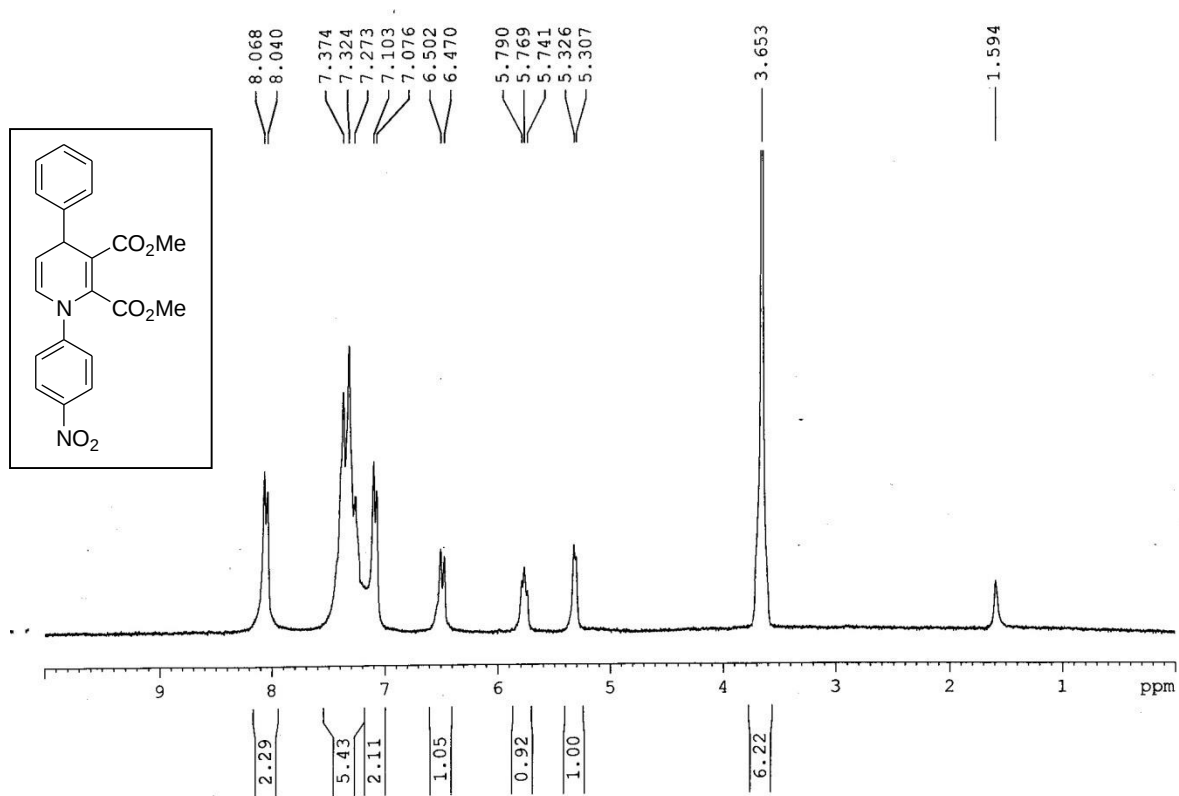
¹³C NMR spectrum for 4c



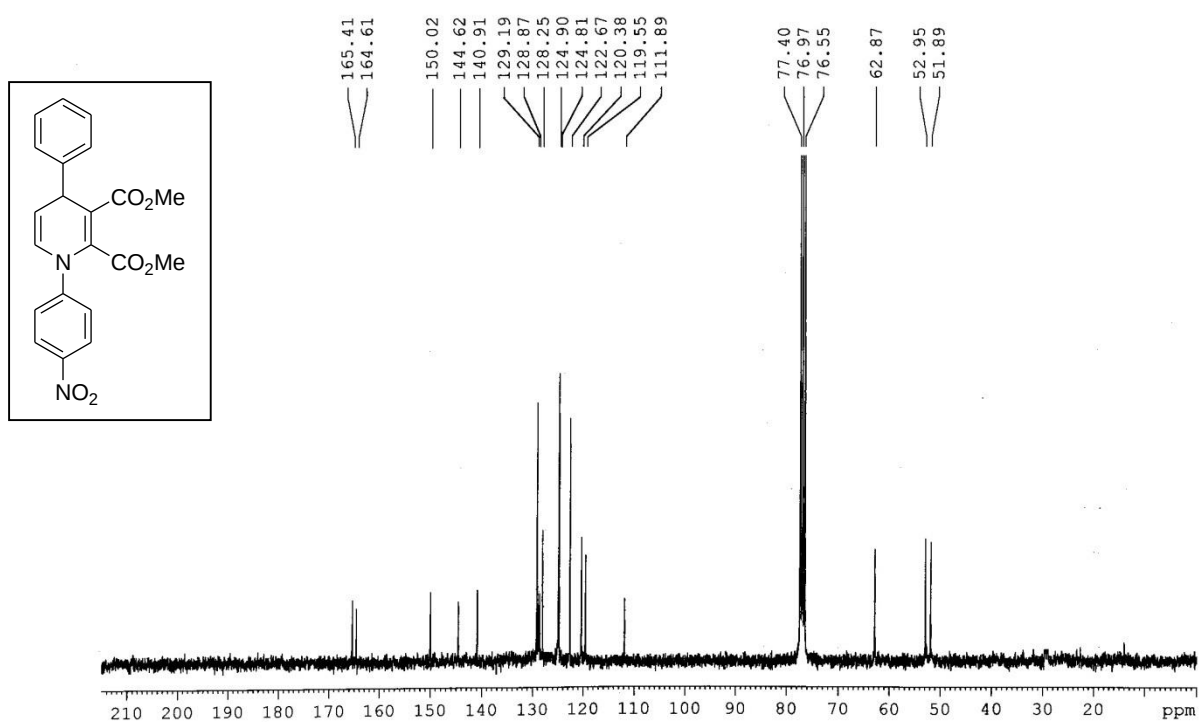
¹H NMR spectrum for 4d



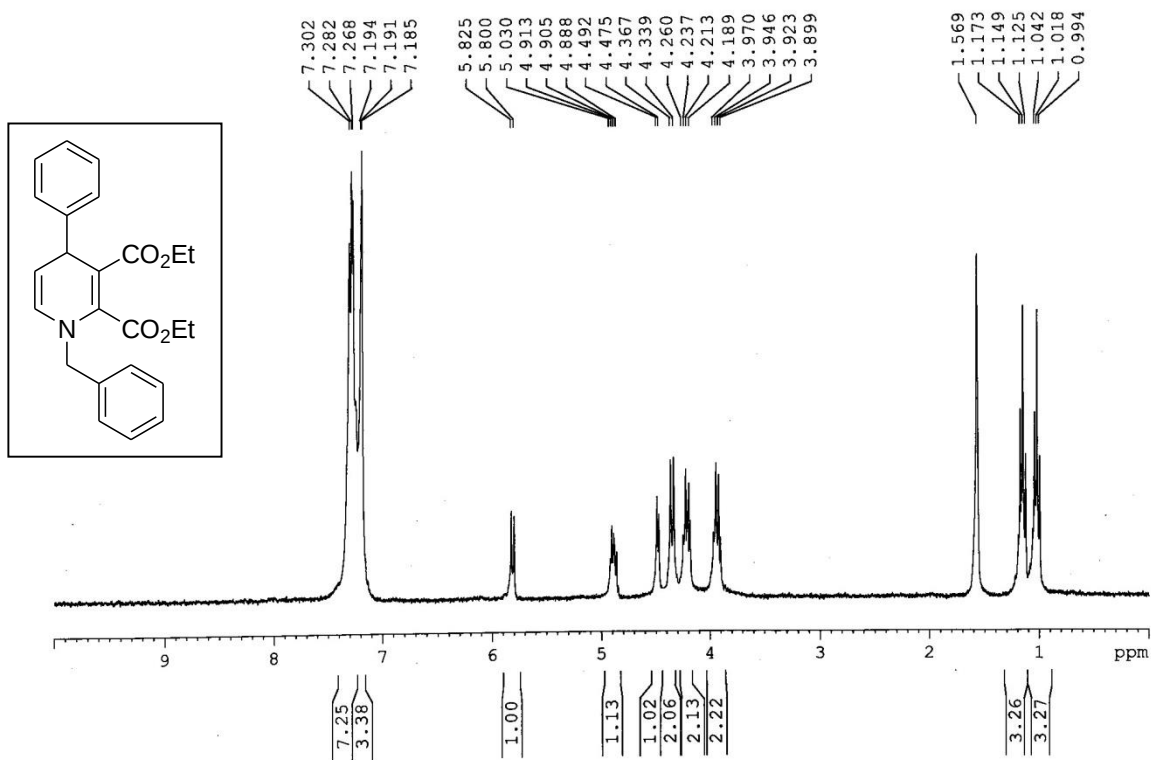
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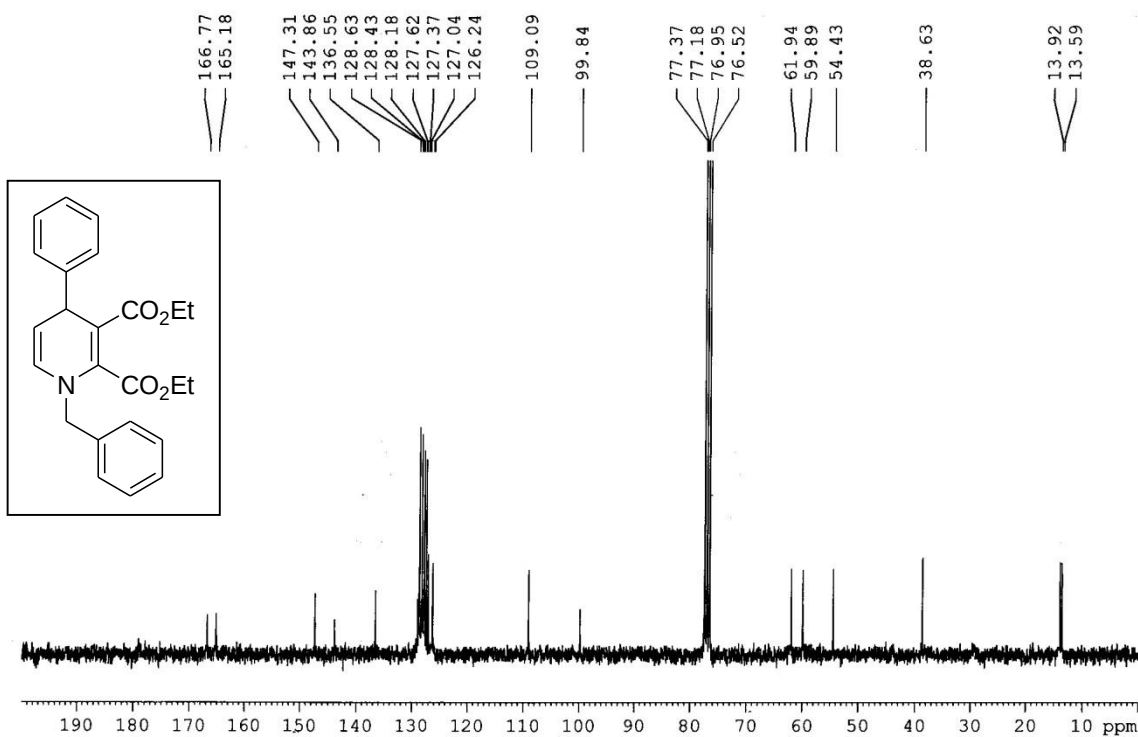
¹H NMR spectrum for 4e



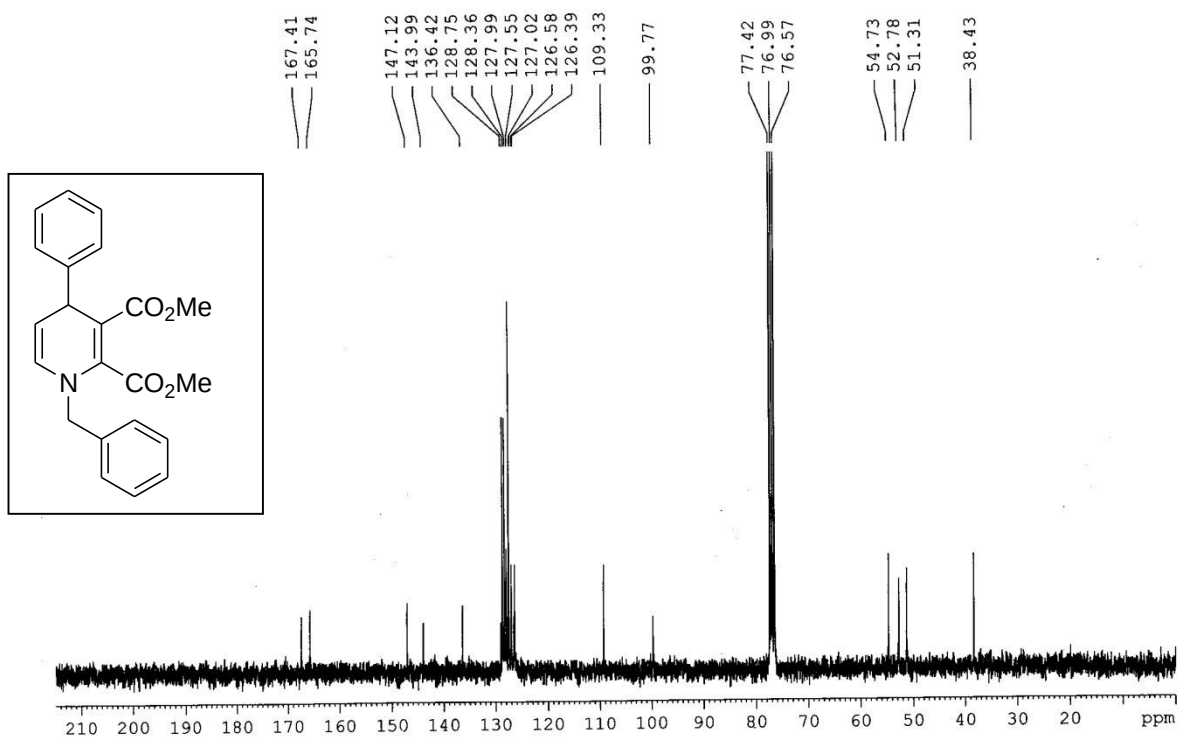
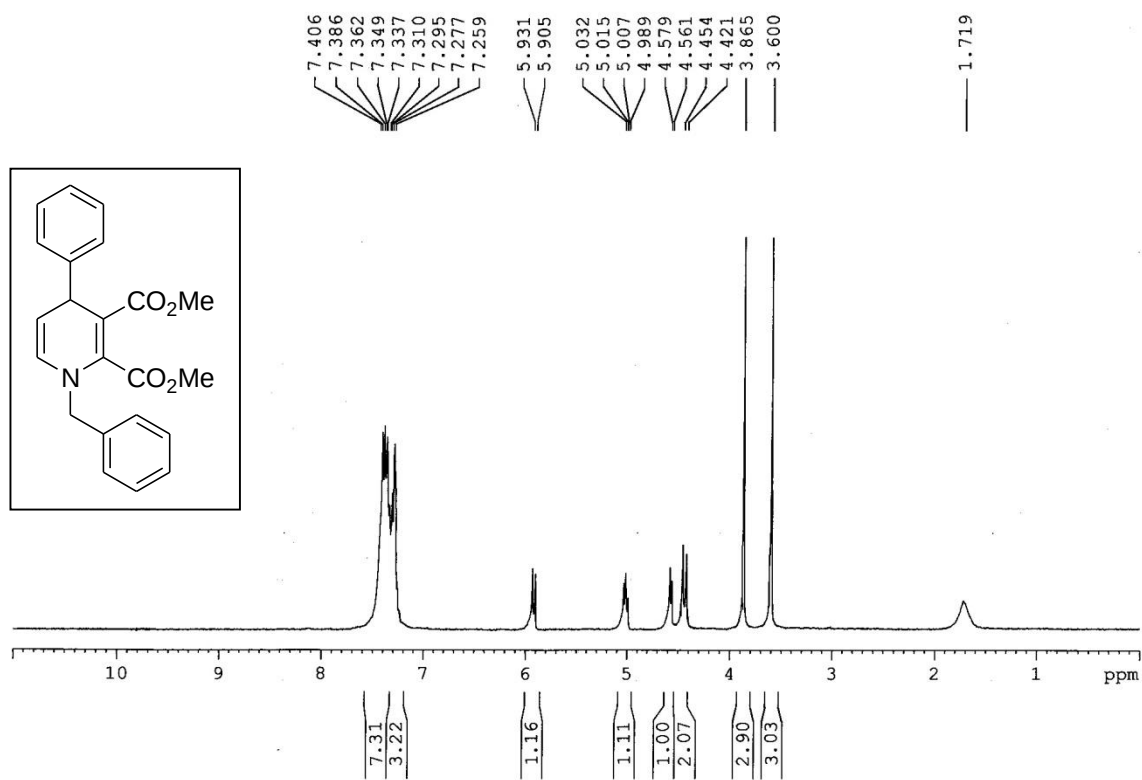
¹³C NMR spectrum for 4e

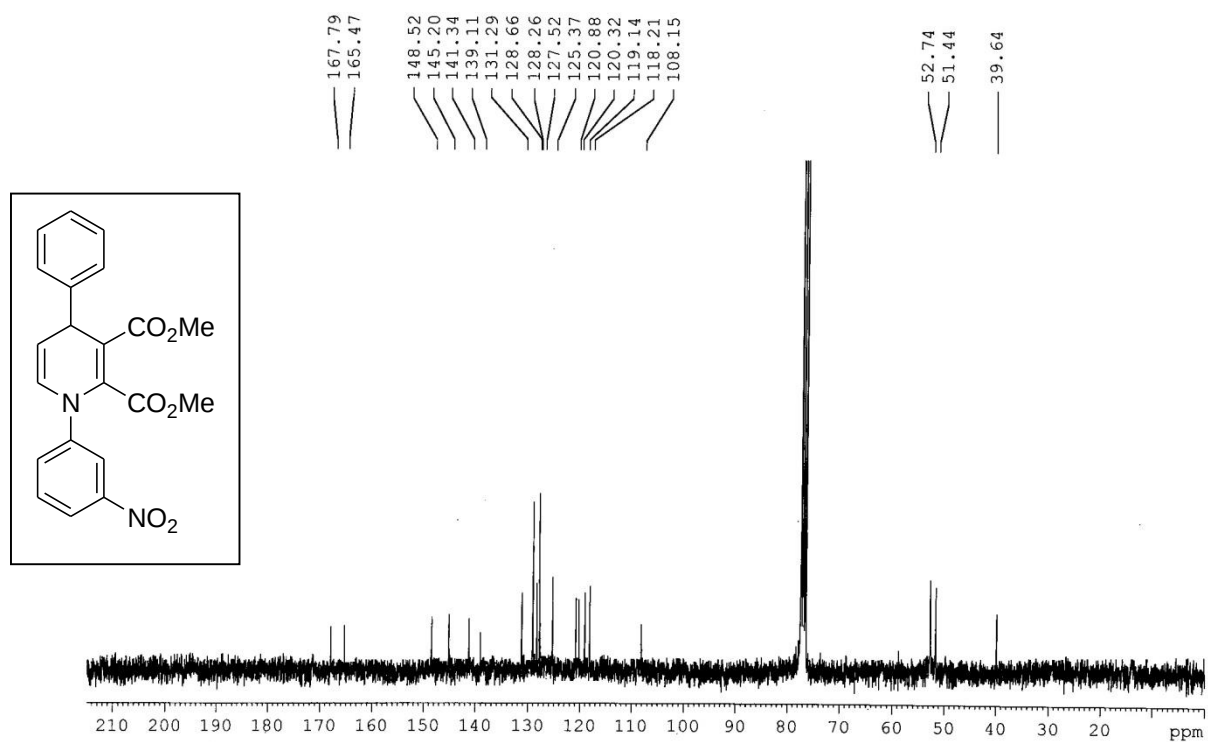
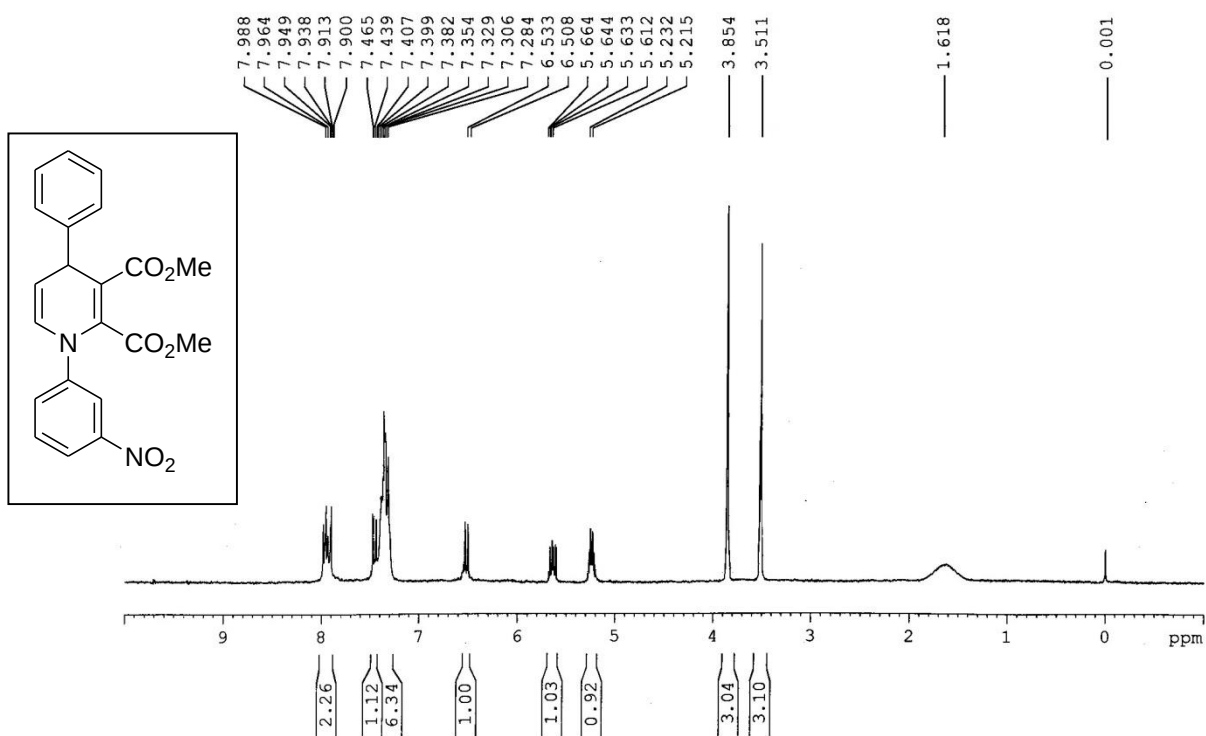


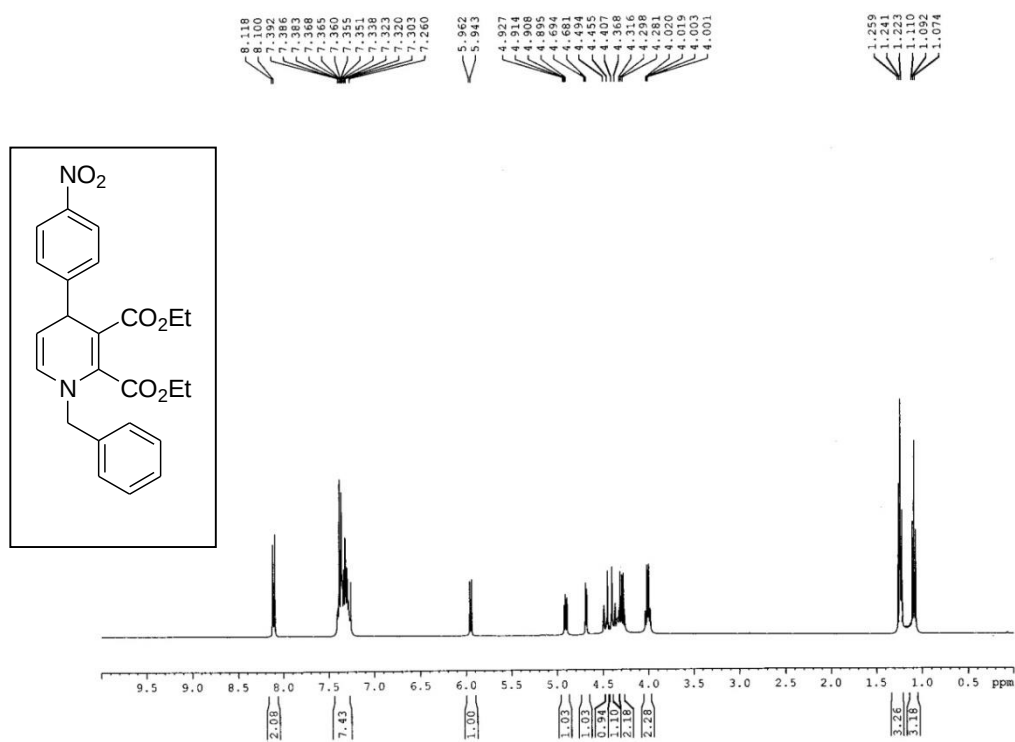
¹H NMR spectrum for 4f



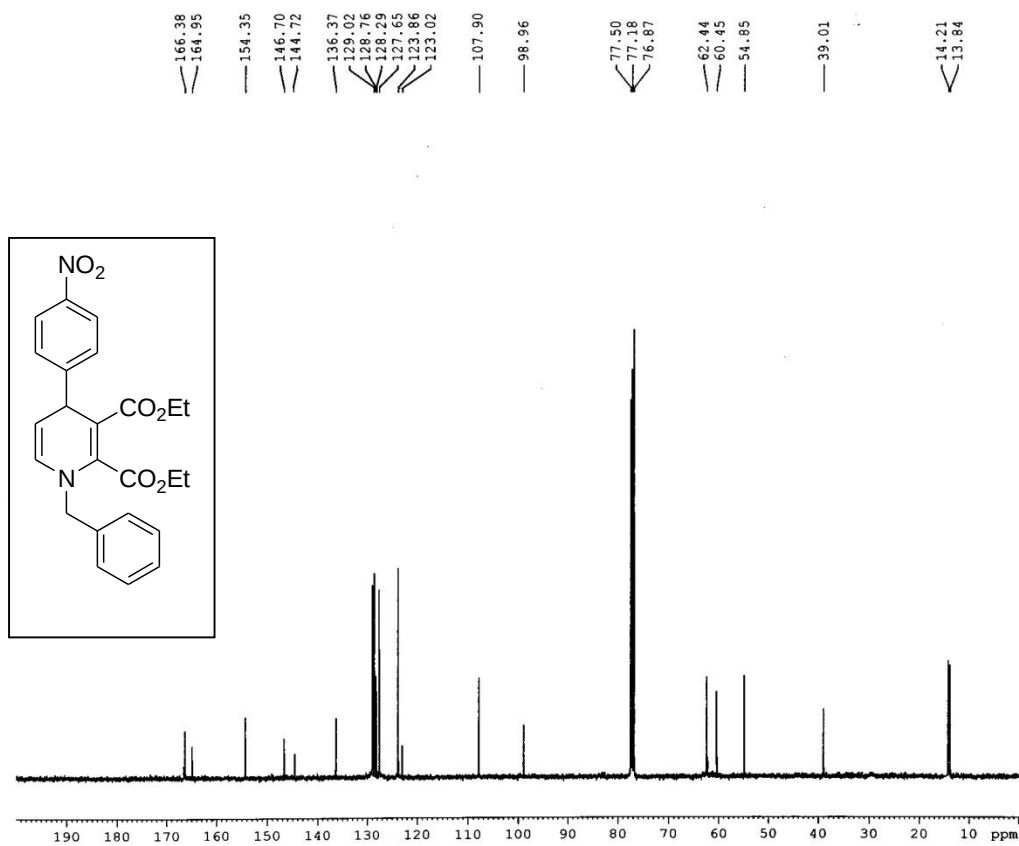
¹³C NMR spectrum for 4f



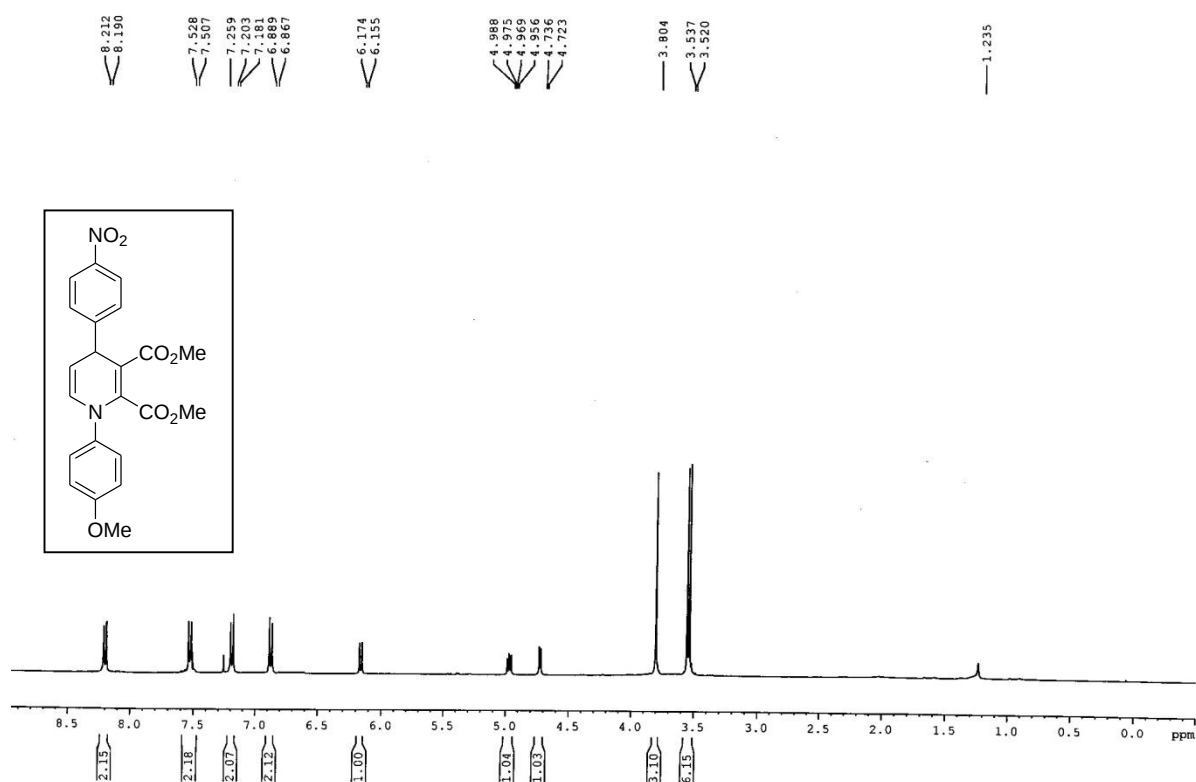




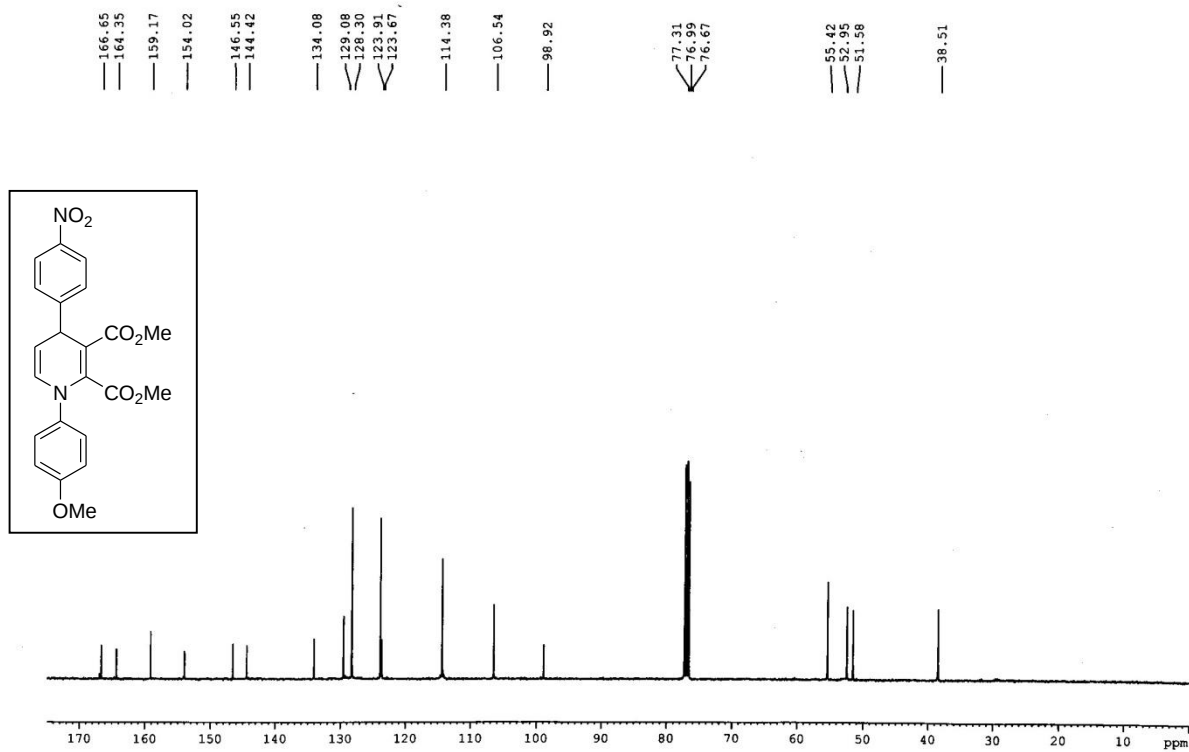
¹H NMR spectrum for 4i



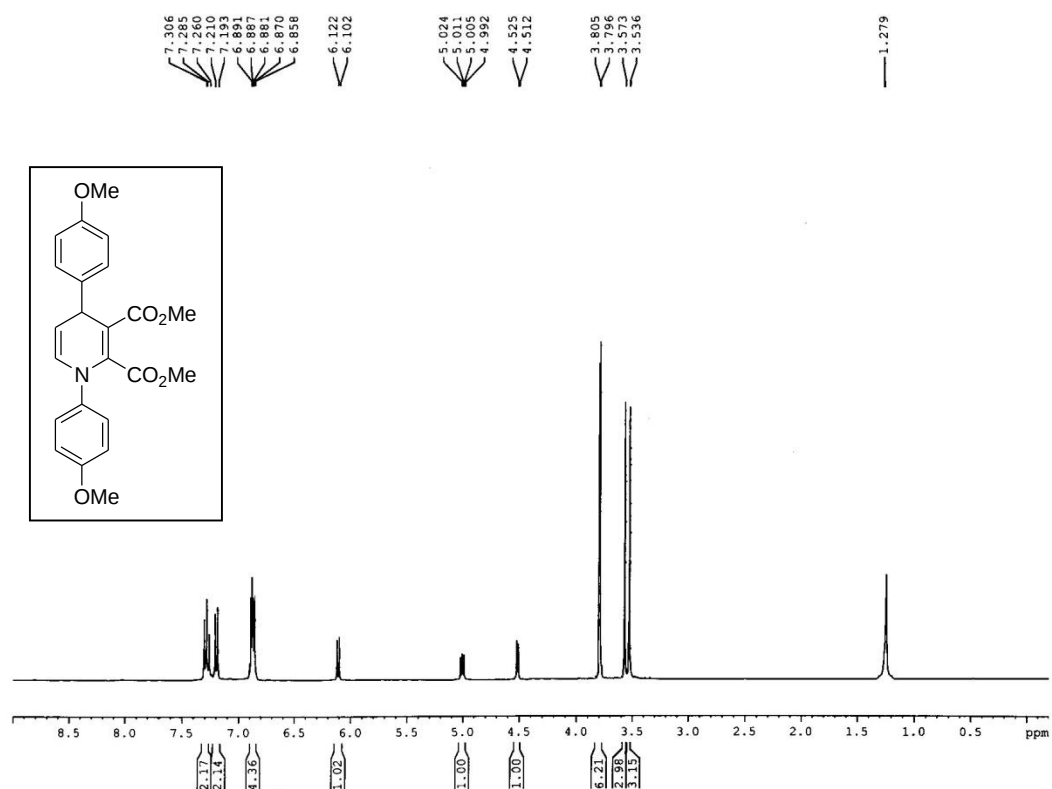
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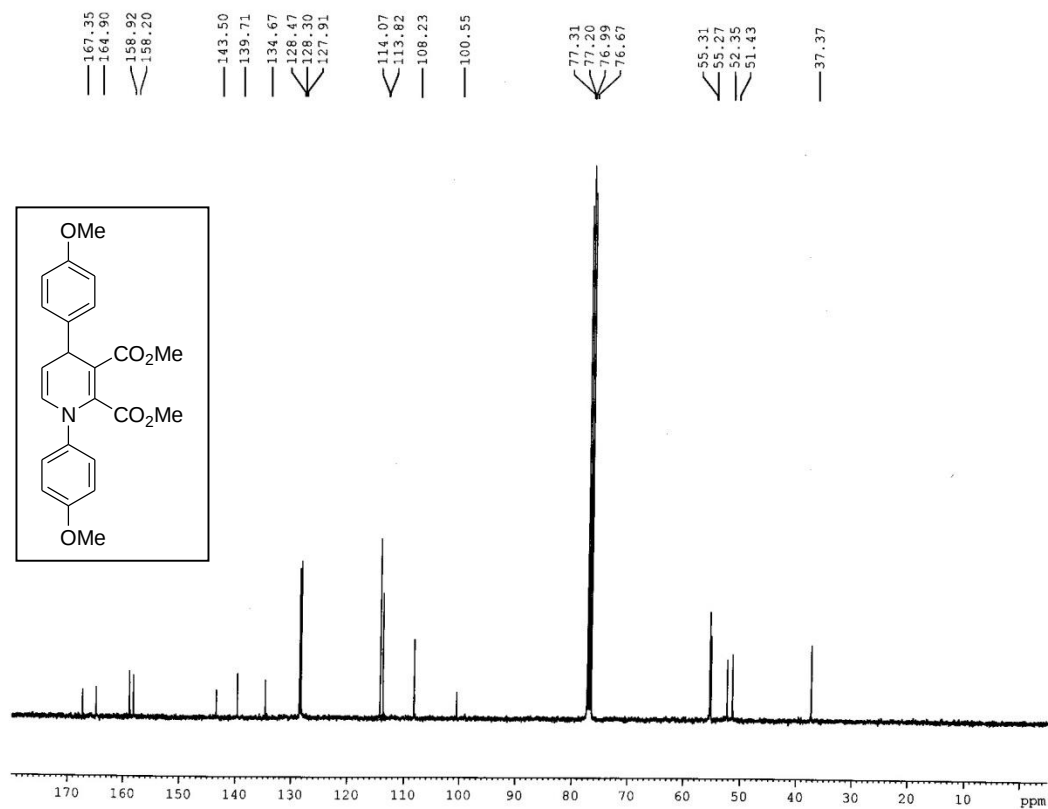
¹H NMR spectrum for 4j



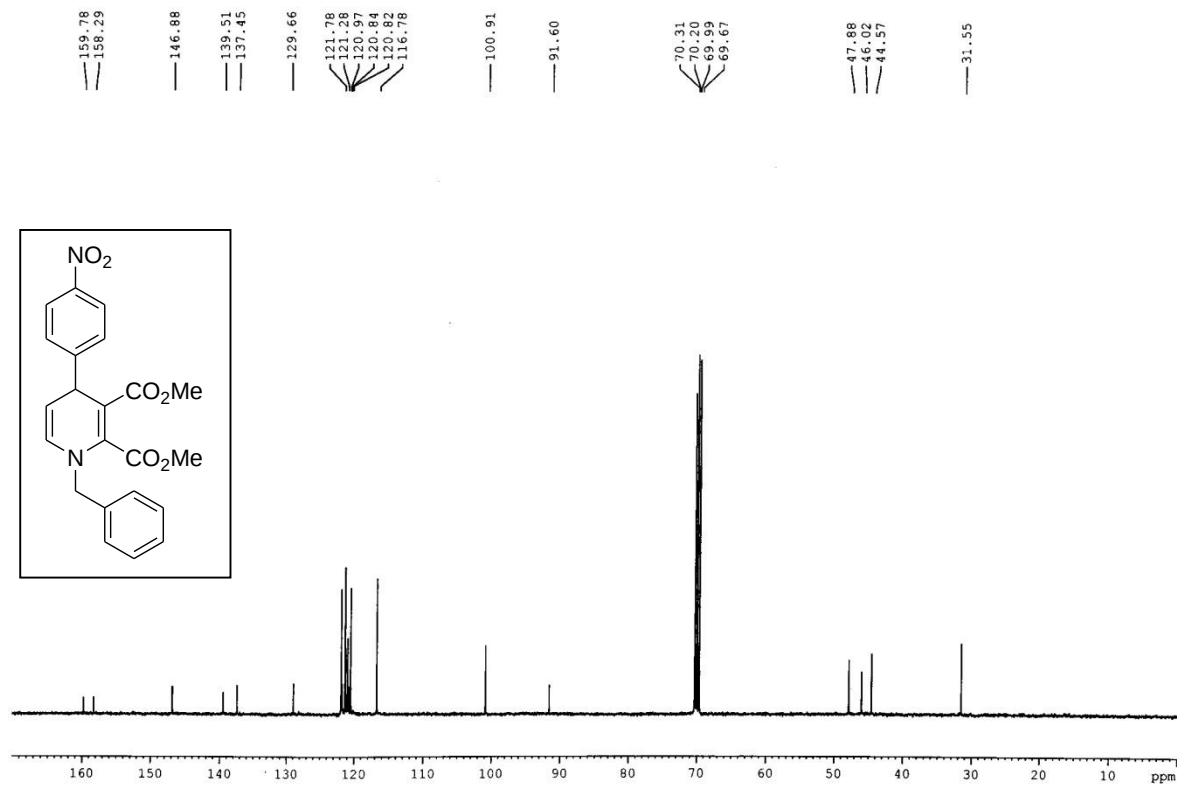
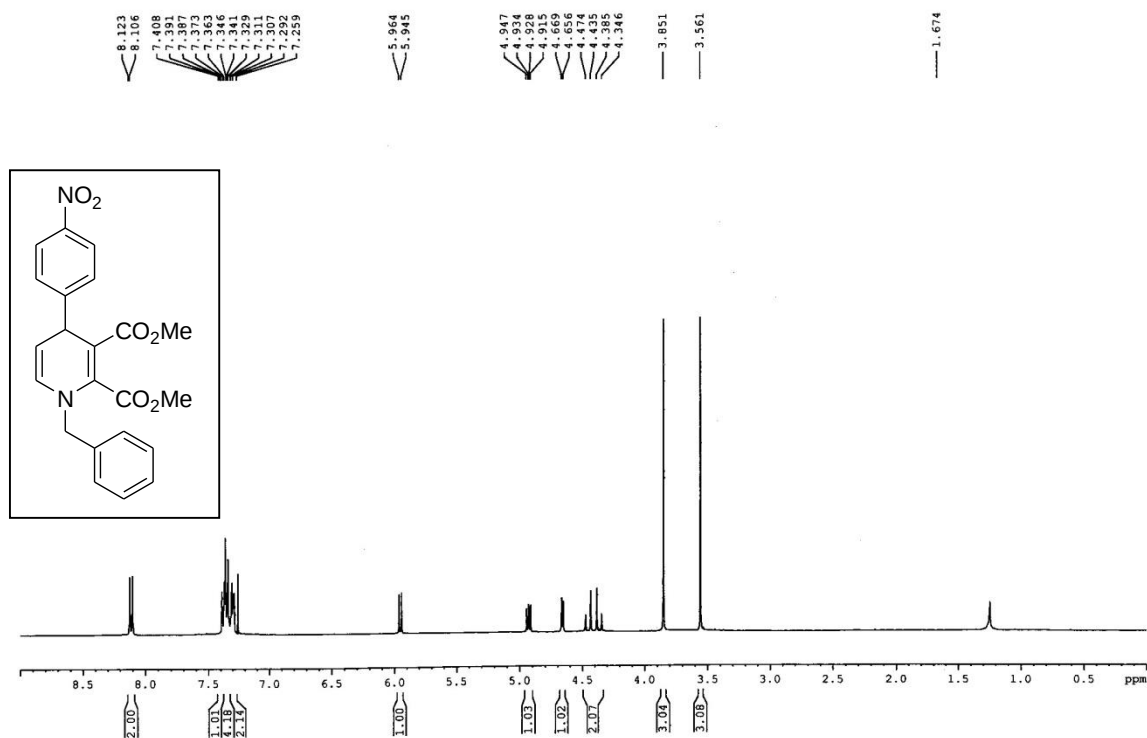
¹³C NMR spectrum for 4j

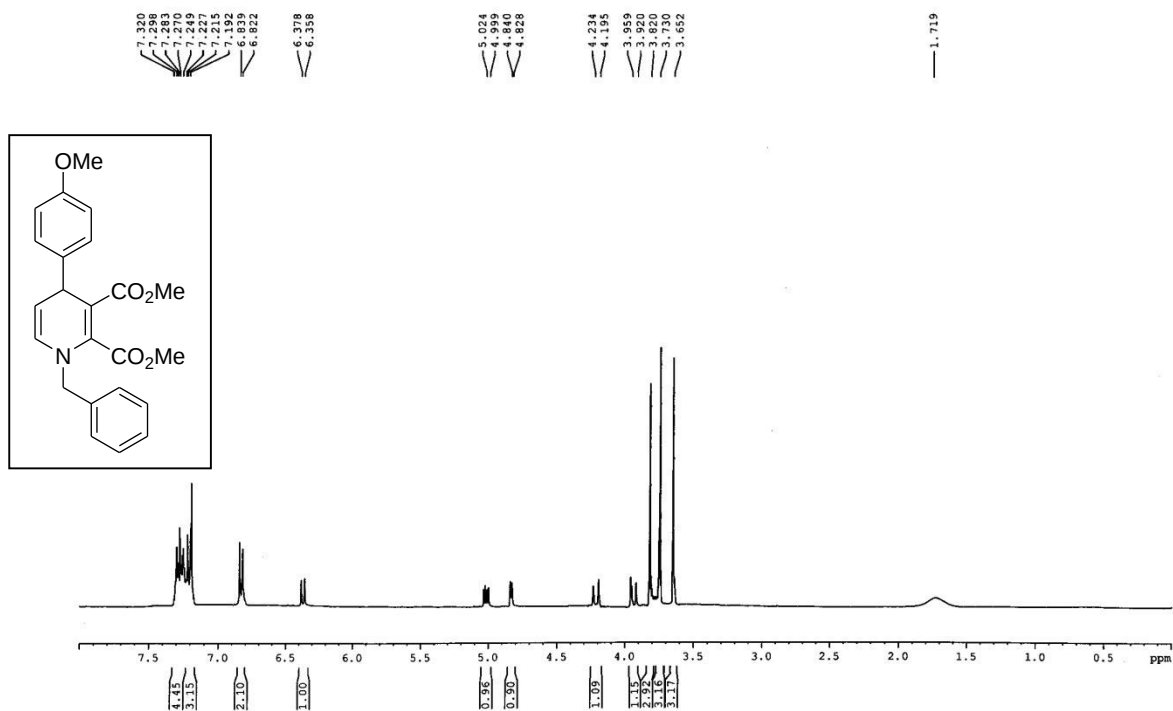


¹H NMR spectrum for 4k

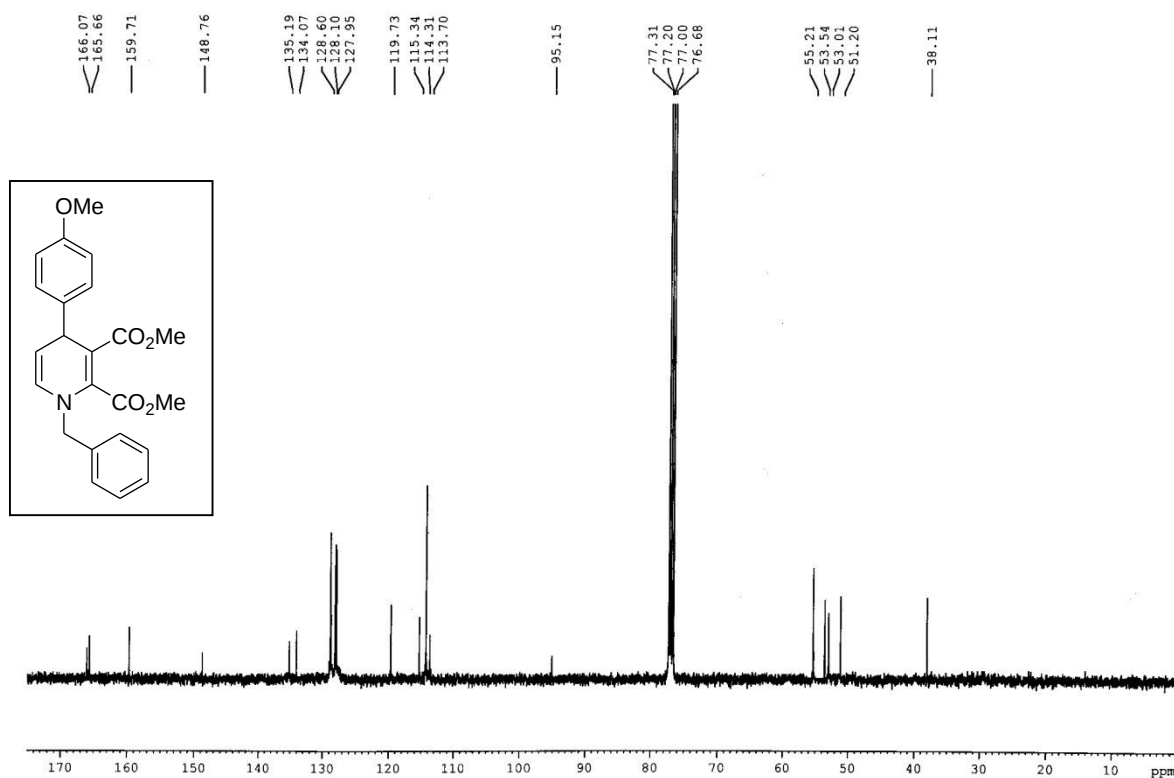


¹³C NMR spectrum for 4k

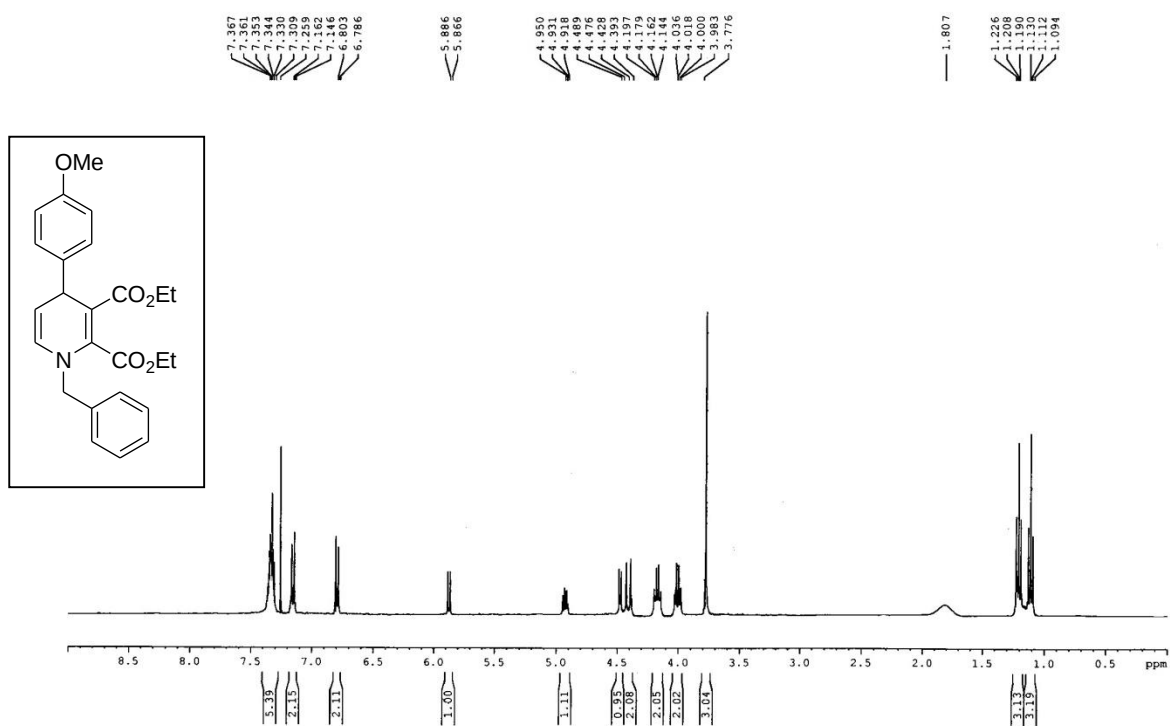




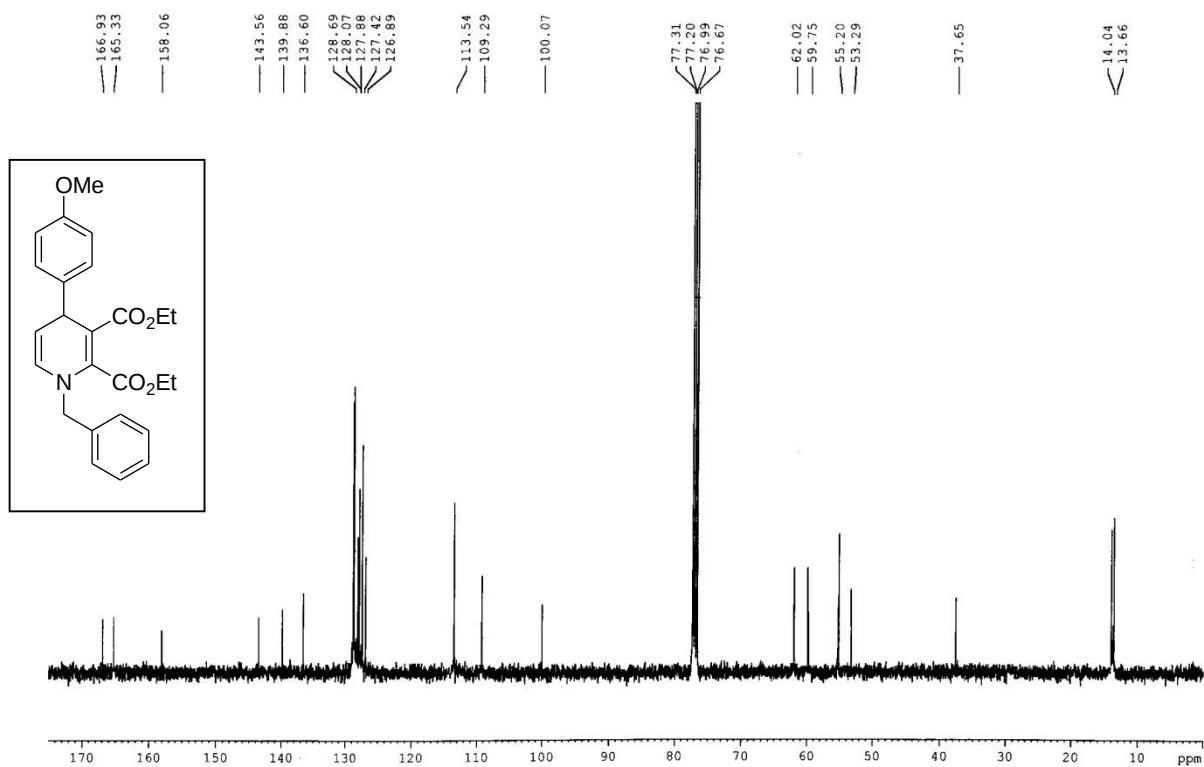
¹H NMR spectrum for 4m



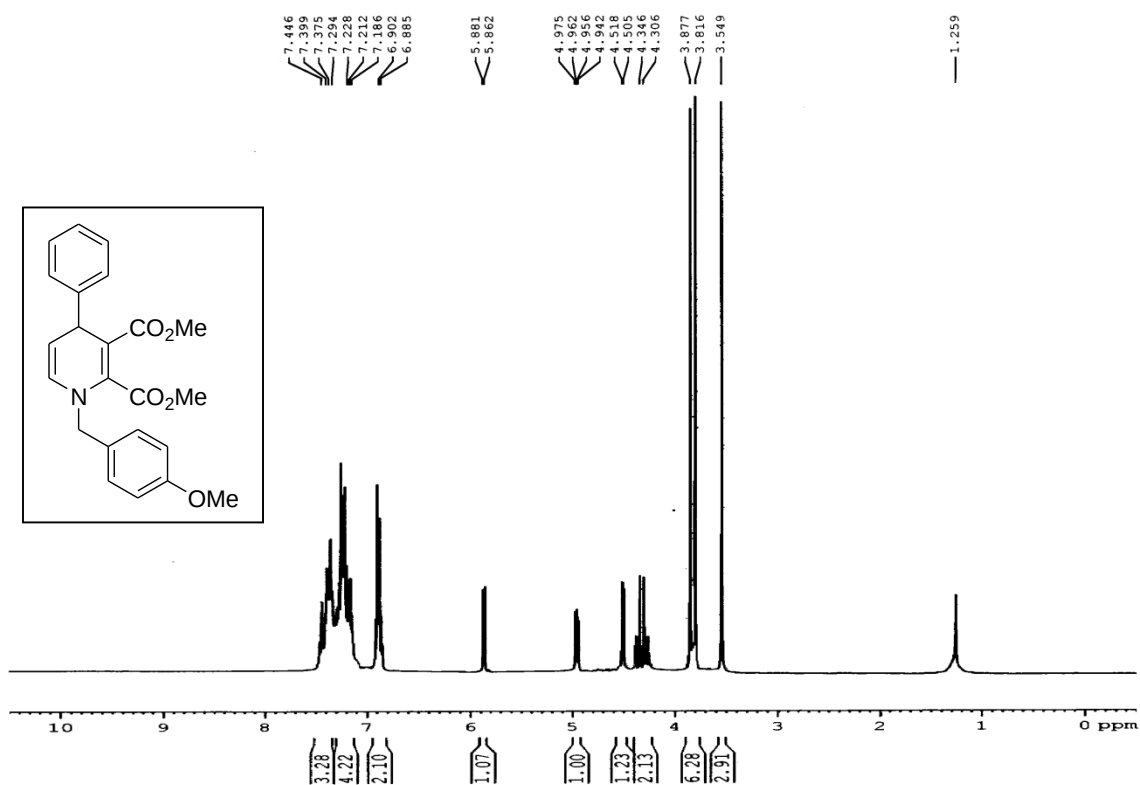
¹³C NMR spectrum for 4m



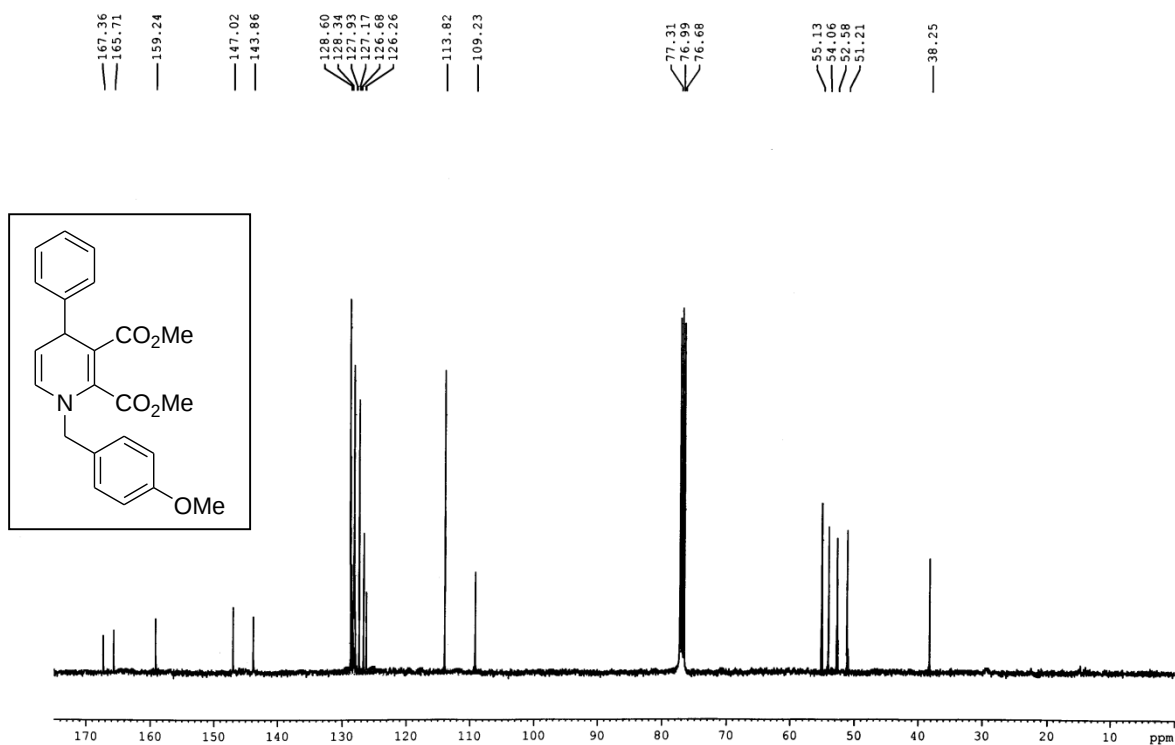
¹H NMR spectrum for 4n



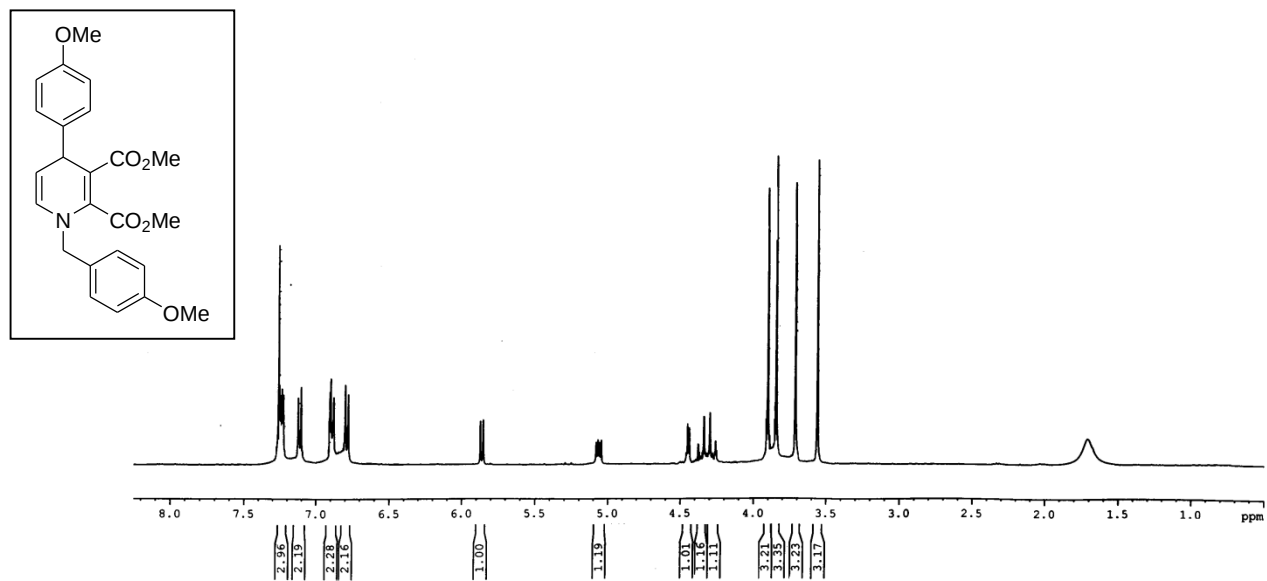
¹³C NMR spectrum for 4n



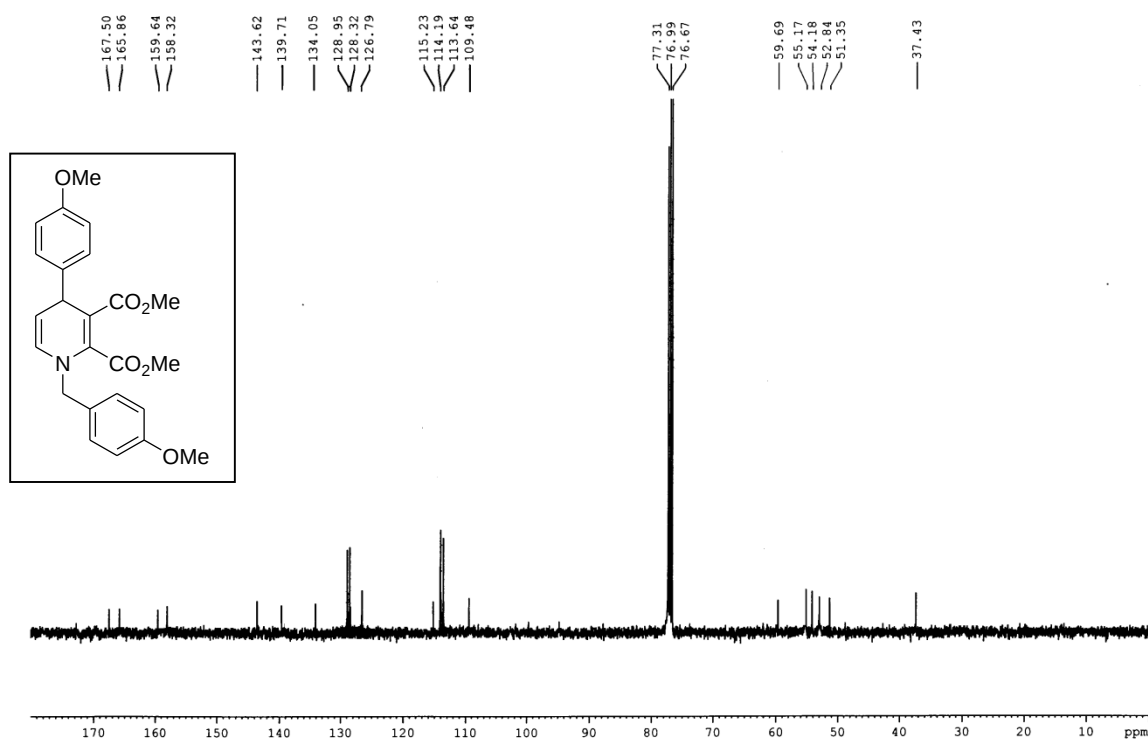
¹H NMR spectrum for 4o



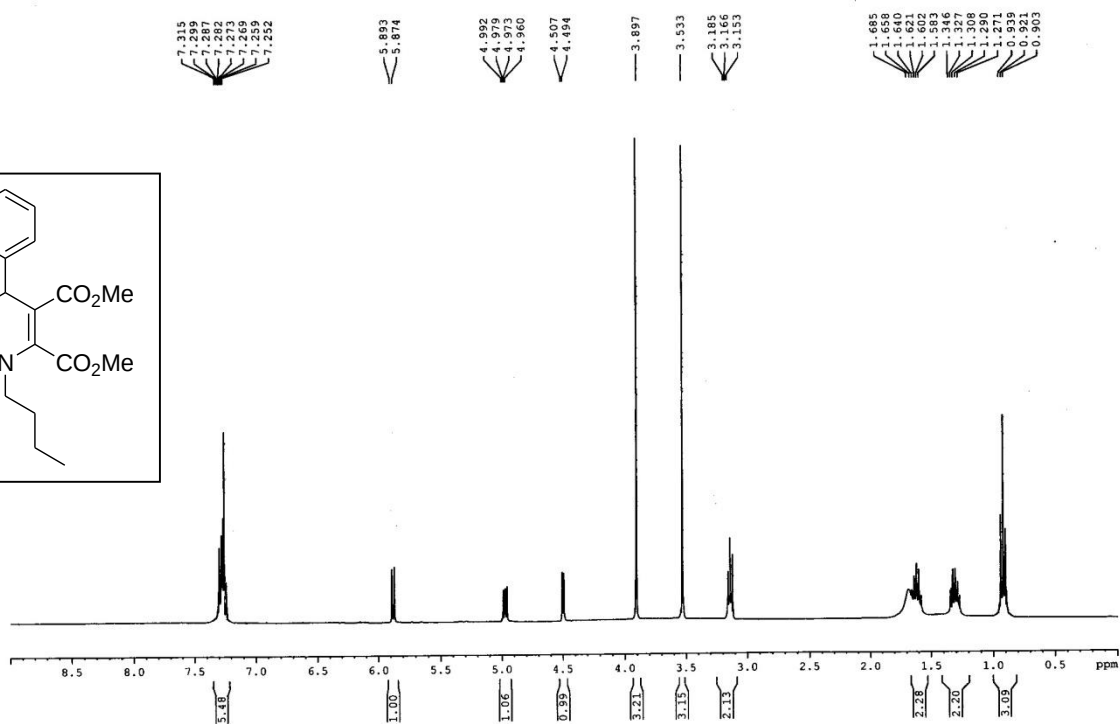
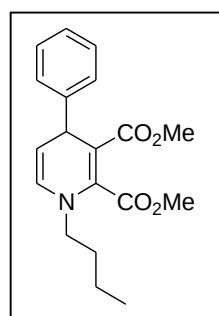
¹³C NMR spectrum for 4o



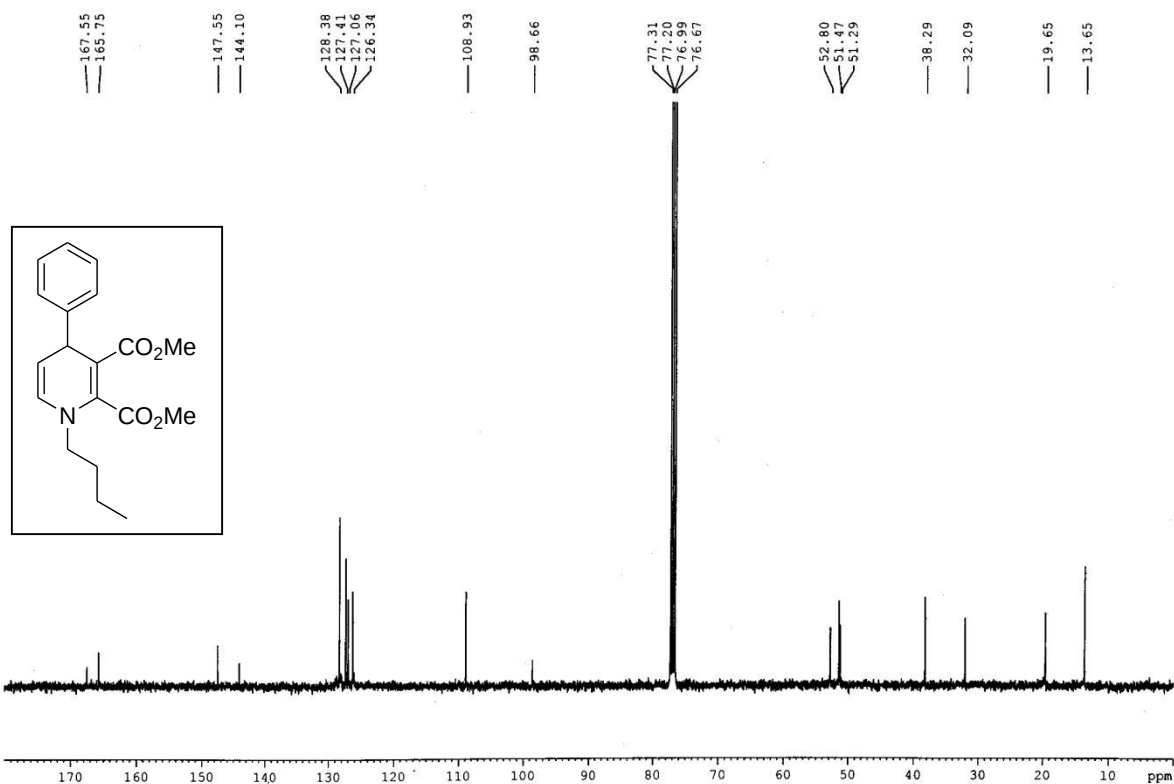
¹H NMR spectrum for 4p



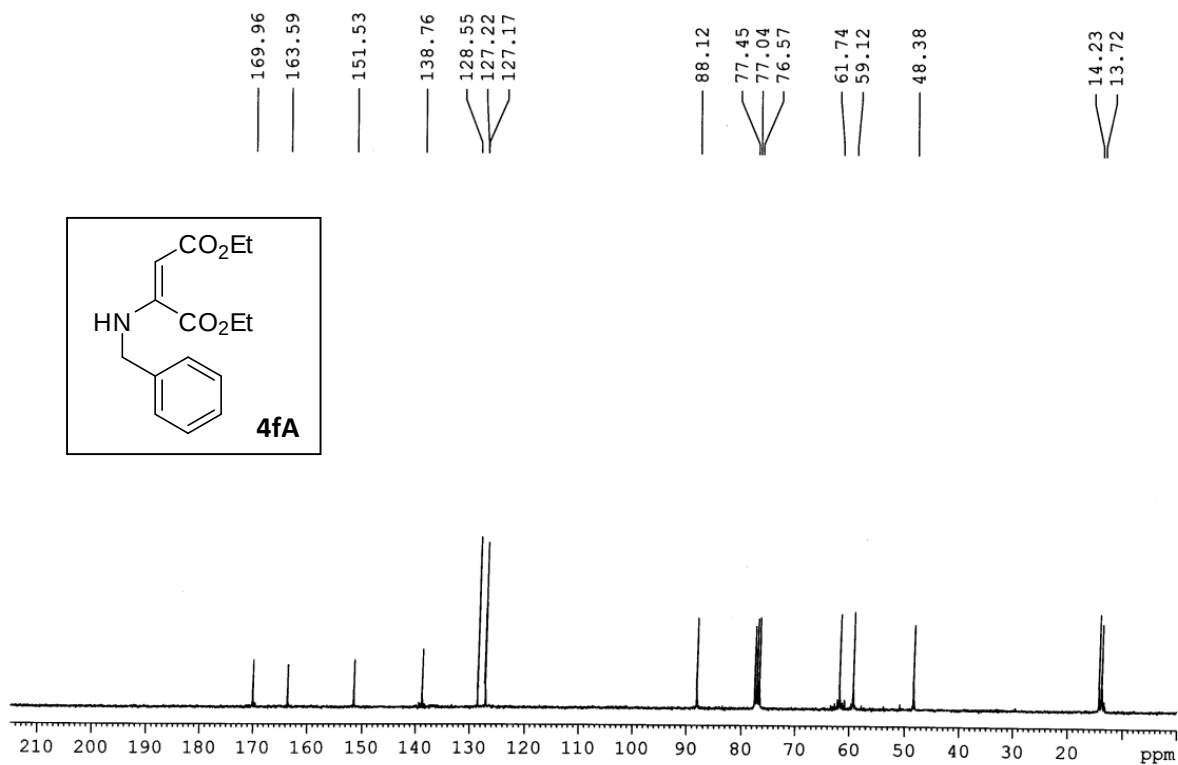
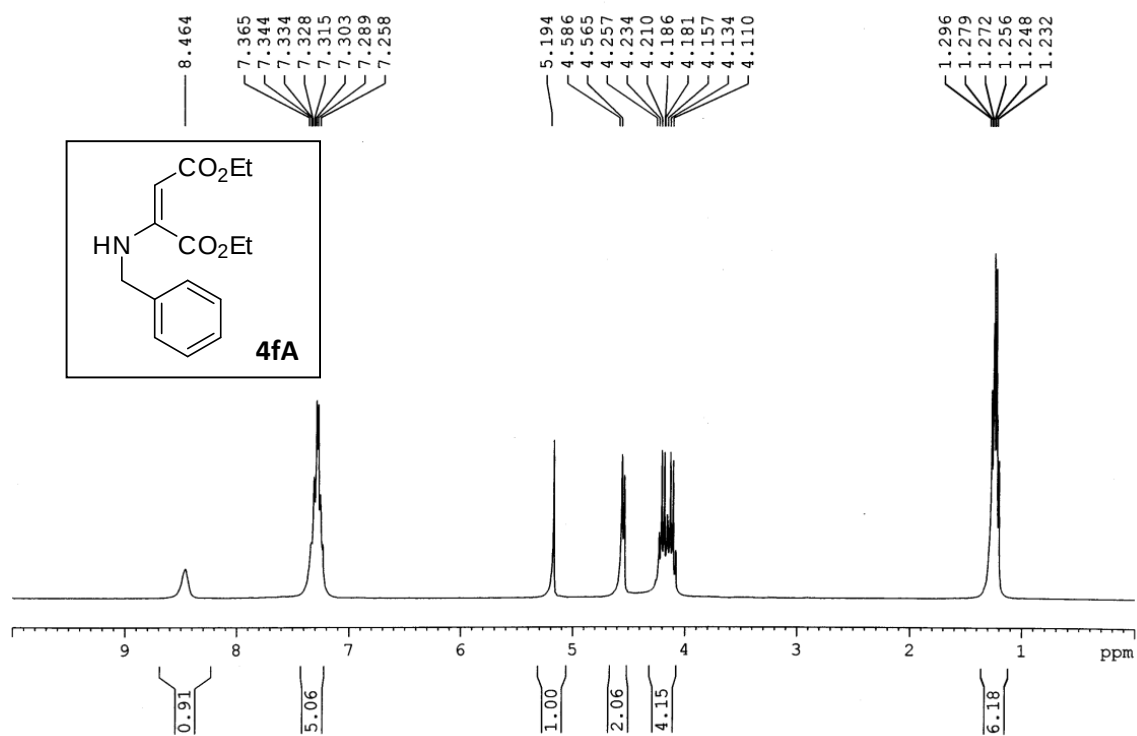
¹³C NMR spectrum for 4p



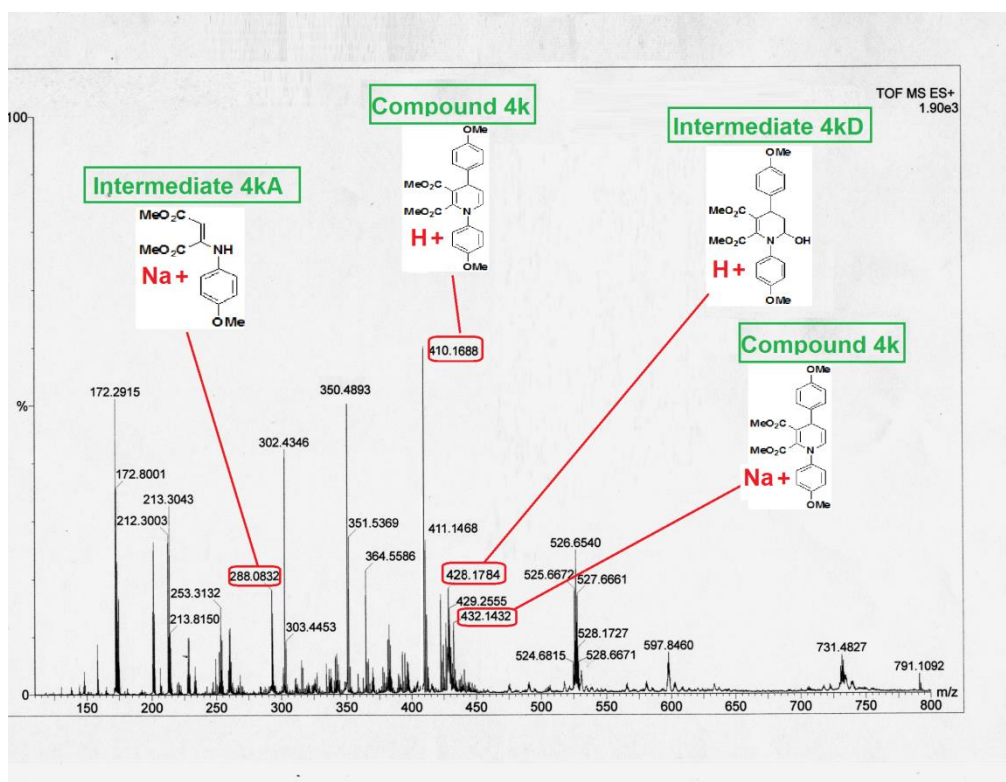
¹H NMR spectrum for 4q



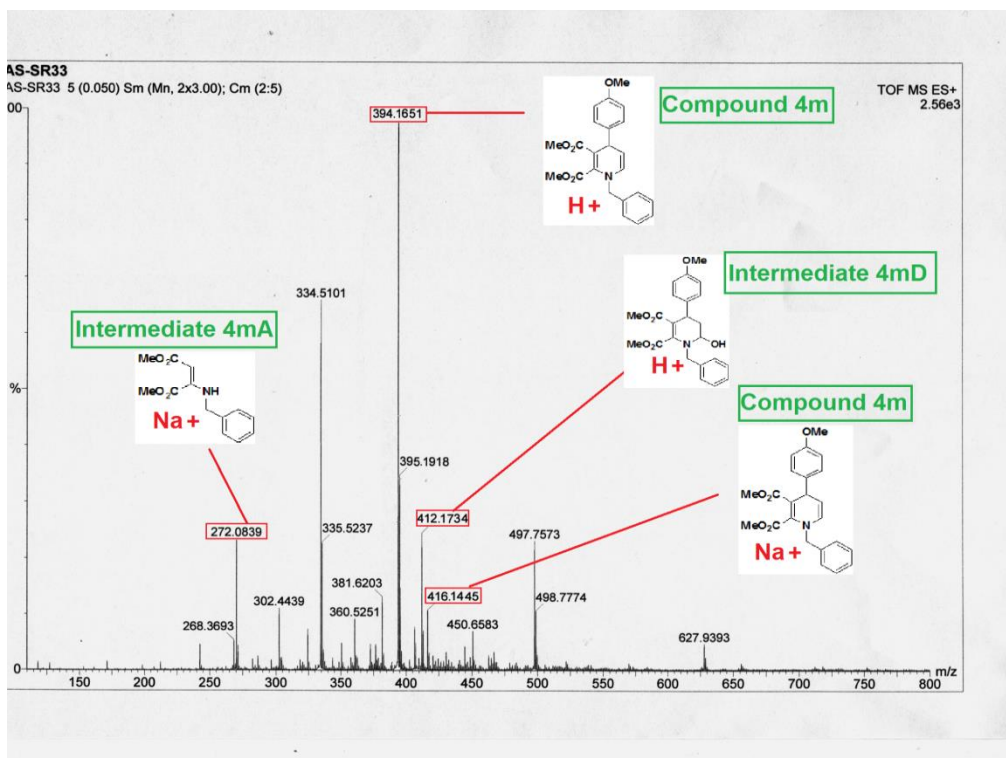
¹³C NMR spectrum for 4q



Crude mass spectra of compound 4k and 4m:



Crude mass spectrum of compound 4k



Crude mass spectrum of compound 4m