



Supporting Information

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Supporting Information for

Organocatalytic Asymmetric Three-Component Cyclization Reactions of Cinnamaldehydes and a Primary Amine with β -Dicarbonyls. A Straightforward Pathway to Access Enantioenriched Dihydropyridines

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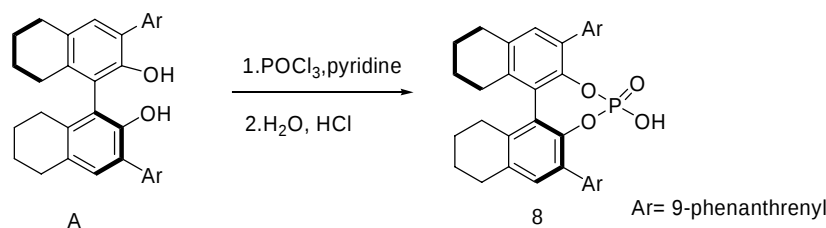
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General: NMR spectra were recorded on a Bruker-400 MHz spectrometer. HRMS (Micromass GCT-MS) spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak AS and AD columns were purchased from Daicel Chemical Industries, LTD. Solvents for the column chromatography were distilled before use.

Experimental Section:

The synthesis of chiral catalysts **8**



To a solution of **A** (2 mmol) in pyridine (5 mL) was added phosphorus oxychloride (4.0 mmol) at room temperature under N_2 and the reaction mixture was stirred at 70 °C for 3 h. Then water (3 mL) was added and the resulting suspension was stirred for the additional 2 h. Dichloromethane was added and pyridine was removed by the reverse extraction with aqueous HCl (6.0 M). The organic phase was dried over Na_2SO_4 and purified by column chromatography on silica gel (2% MeOH in CH_2Cl_2) to yield **8** as a white solid (yield: 80%)

(S)-2,6-Bis-(9-phenanthrenyl)-4-oxo-3,5-dioxo-4 λ 5-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-ol (8**):** yield: 80%; 1H NMR (DMSO, 400 MHz) δ (ppm) 1.74-1.76 (m, 2H), 1.83-1.93 (m, 6H), 2.49-2.52 (m, 2H); 2.88-2.94 (m, 6H), 7.25-7.26 (m, 2H), 7.56-7.69 (m, 10H), 7.81 (m, 2H),

7.90-7.92 (m, 2H), 8.83-8.89 (m, 4H); ^{13}C NMR (DMSO, 100 MHz) δ (ppm) 23.174, 28.523, 29.574, 123.716, 124.083, 127.172, 127.490, 127.755, 127.872, 129.535, 129.711, 130.526, 131.151, 131.988, 132.802, 134.700, 135.688, 138.199.

General Procedure for the Organocatalytic Asymmetric Three-Component Cyclization Reactions of Cinnamaldehydes and a Primary Amine with β -Dicarbonyls: After a solution of aldehyde (0.3 mmol), primary amine (0.2 mmol) and a chiral phosphoric acid (0.02 mmol) in PhCN (1.5ml) was stirred at 25 °C for 15min, a β -Dicarbonyls (0.4 mmol) was added. The resulting reaction mixture was stirred at 50 °C for 1 day (monitored by TLC). The reaction mixture was purified through flash column chromatography on a silica gel (eluent: petroleum ether: ethyl acetate = 50:1) to yield pure products

Ethyl 1-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4a): yield: 82%; $[\alpha]_{\text{D}}^{29} = +329.2^{\circ}$ ($c = 0.315$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.12 (t, $J = 7.1$ Hz, 3H), 2.15 (s, 3H), 3.83 (s, 3H); 3.99-4.05 (q, 2H), 4.81(d, $J = 5.4$ Hz, 1H); 4.93 (dd, $J_1 = 5.4$ Hz, $J_2 = 7.6$ Hz, 1H), 6.13 (d, $J = 7.6$ Hz, 1H); 6.92-6.95 (m, 2H), 7.08-7.12 (m, 2H), 7.49-7.52 (m, 2H), 8.16-8.19 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.305, 18.549, 40.561, 55.609, 59.638, 99.751, 105.741, 114.883, 123.820, 128.274, 128.827, 130.666, 136.152, 146.433, 149.688, 155.909, 158.996, 168.320; IR (KBr) γ 2925, 1691, 1564, 1513, 1341, 1220, 1112, 1074, 826 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_5)^+$ requires m/z 394.1529, found m/z 394.1522; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol= 70/ 30, flow rate 1.0 mL/min): $t_{\text{R}} = 5.68$ min (minor), $t_{\text{R}} = 11.80$ min (major).

Ethyl 1-(3-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4b): yield: 53%; $[\alpha]_{\text{D}}^{25} = +358^{\circ}$ ($c = 0.133$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.13 (t, $J = 7.1$ Hz, 3H), 2.19 (s, 3H), 3.83 (s, 3H); 4.00-4.06 (q, 2H), 4.82(d, $J = 5.4$ Hz, 1H); 4.94 (dd, $J_1 = 5.4$ Hz, $J_2 = 7.6$ Hz, 1H), 6.18 (d, $J = 7.6$ Hz, 1H); 6.67 (m, 1H), 6.77-6.79 (m, 1H), 6.88-6.90 (m, 1H), 7.31-7.35 (m, 1H), 7.49-7.51 (m, 2H), 8.16-8.19 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.318, 18.687, 40.566, 55.573, 59.719, 100.477, 105.959, 113.196, 113.558, 119.800, 123.850, 128.320, 130.319, 130.464, 144.422, 146.492, 149.051, 155.686, 160.698, 168.267; IR (KBr) γ , 2965, 1695, 1595, 1570, 1348, 1198, 1109, 824, 699 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_5)^+$ requires m/z 394.1529, found m/z 394.1525; Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol= 85/ 15, flow rate 1.0 mL/min): $t_{\text{R}} = 6.88$ min (minor), $t_{\text{R}} = 13.18$ min (major).

Ethyl 1-(4-methylphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4c): yield: 57%; $[\alpha]_{\text{D}}^{25} = +392^{\circ}$ ($c = 0.2$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.12 (t, $J = 7.1$ Hz, 3H), 2.16 (s, 3H), 3.38 (s, 3H); 4.00-4.05 (q, 2H), 4.81(d, $J = 5.4$ Hz, 1H); 4.94 (dd, $J_1 = 5.4$ Hz, $J_2 = 7.6$ Hz, 1H), 6.16 (d, $J = 7.6$ Hz, 1H); 7.06-7.08 (m, 2H), 7.22-7.24 (m, 2H), 7.49-7.52 (m, 2H), 8.15-8.18 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.311, 18.647, 21.116, 40.567, 59.644, 100.028, 105.835, 123.820, 127.386, 128.286, 130.368, 130.545, 137.800, 140.758, 146.453, 149.409, 155.843, 168.298; IR (KBr) γ , 2927, 1690, 1513, 1348, 1223, 1109, 1064, 824, 730 cm^{-1} ; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4)^+$ requires m/z 378.1580, found m/z 378.1576. Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol= 85/ 15, flow rate 1.0 mL/min): $t_{\text{R}} = 6.08$ min (minor), $t_{\text{R}} = 11.25$ min (major).

Ethyl 1-(3-methylphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4d): yield: 53%; $[\alpha]_{\text{D}}^{25} = +401^{\circ}$ ($c = 0.2$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.12 (t, $J = 7.2$ Hz, 3H), 2.17 (s, 3H), 2.39 (s, 3H); 4.00-4.05 (q, 2H), 4.82(d, $J = 5.4$ Hz, 1H); 4.94 (dd, $J_1 = 5.4$ Hz, $J_2 = 7.6$ Hz, 1H), 6.18 (d, $J = 7.6$ Hz, 1H); 6.97-6.99 (m, 2H), 7.14-7.16 (m, 1H), 7.26-7.33 (m, 1H), 7.49-7.52 (m, 2H), 8.16-8.19 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.315, 18.741, 21.362, 40.577, 59.644, 100.181, 105.848, 123.831, 124.562, 128.156, 128.303, 128.551, 129.535, 130.464, 139.942, 143.255, 146.467, 149.244, 155.805, 168.292; IR (KBr) γ , 2984, 2927, 1695, 1570, 1519, 1228, 1109, 837, 704 cm^{-1} ; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4)^+$ requires m/z 378.1580, found m/z 378.1576. Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol= 85/ 15, flow rate 1.0 mL/min): $t_{\text{R}} = 5.22$ min (minor), $t_{\text{R}} = 7.30$ min (major).

Ethyl 1-(4-chlorophenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4e): yield: 60%; $[\alpha]_{\text{D}}^{25} = +370^{\circ}$ ($c = 0.215$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.12 (t, $J = 7.1$ Hz, 3H), 2.16 (s, 3H), 4.00-4.06 (q, 2H), 4.82(d, $J = 5.4$ Hz, 1H); 4.97 (dd, $J_1 = 5.4$ Hz, $J_2 = 7.6$ Hz, 1H), 6.15 (d, $J = 7.6$ Hz, 1H); 7.12-7.15 (m, 2H), 7.39-7.42 (m, 2H), 7.43-7.49 (m, 2H), 8.16-8.18 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.283, 18.713, 40.541, 59.816, 101.147, 106.369, 123.871, 128.292, 128.917, 130.012, 130.053, 133.608, 141.814, 146.528, 148.467, 155.396, 168.111; IR (KBr) γ 2984, 2933, 1695, 1570, 1513, 1488, 1348, 1216, 1115, 837, 749 cm^{-1} ; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{21}\text{H}_{19}\text{ClN}_2\text{O}_4)^+$ requires m/z 398.1033, found m/z 398.1031. Enantiomeric excess: 89%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol= 94.9: 5.1, flow rate 1.0 mL/min): $t_{\text{R}} = 13.81$ min (major), $t_{\text{R}} = 16.88$ min (minor).

Isopropyl 1-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4f): yield: 81%; $[\alpha]_{\text{D}}^{29} = +372.6^{\circ}$ ($c = 0.388$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.96 (d, $J = 6.2$ Hz, 3H), 1.18 (d, $J = 6.2$ Hz, 3H), 2.15 (s, 3H), 3.83 (s, 3H), 4.81 (d, $J = 5.4$ Hz, 1H), 4.87-4.93 (m, 2H), 6.11 (d, $J = 7.5$ Hz, 1H), 6.92-6.95 (m, 2H), 7.08-7.11 (m, 2H), 7.49-7.52 (m, 2H), 8.16-8.19 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 17.443, 20.634, 21.139, 39.633, 54.527, 65.720, 98.988, 104.617, 113.790, 122.693, 127.246, 127.771, 129.514, 135.131, 145.319, 148.376, 155.015, 157.896, 166.715; IR (KBr) γ , 2970, 2925, 1691, 1570, 1507, 1348, 1227, 1099, 832 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_5)^+$ requires m/z 408.1685, found m/z 408.1678; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol = 70: 30, flow rate 1.0 mL/min): $t_{\text{R}} = 4.95$ min (minor), $t_{\text{R}} = 10.36$ min (major).

Allyl-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4g): yield: 75%; $[\alpha]_{\text{D}}^{29} = +355.9^{\circ}$ ($c = 0.33$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 2.17 (s, 3H), 3.83 (s, 3H), 4.47-4.49 (m, 2H), 4.83 (d, $J = 5.5$ Hz, 1H), 4.95 (dd, $J_1 = 5.5$ Hz, $J_2 = 7.6$ Hz, 1H), 5.10-5.16 (m, 2H), 5.74-5.82 (m, 1H), 6.13 (d, $J = 7.6$ Hz, 1H), 6.93-6.95 (m, 2H), 7.09-7.11 (m, 2H), 7.49-7.51 (m, 2H), 8.16-8.18 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 17.557, 39.347, 54.534, 63.410, 98.261, 104.829, 113.831, 116.415, 122.779, 127.184, 127.728, 129.574, 131.766, 135.000, 145.386, 149.152, 154.637, 157.964, 166.807; IR (KBr) γ , 2938, 1697, 1564, 1513, 1348, 1212, 1067, 832, 737 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_5)^+$ requires m/z 406.1529, found m/z 406.1523; Enantiomeric excess: 82%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol = 70/ 30, flow rate 1.0 mL/min): $t_{\text{R}} = 5.86$ min (minor), $t_{\text{R}} = 10.28$ min (major).

Methyl 1-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4h): yield: 93%; $[\alpha]_{\text{D}}^{29} = +350^{\circ}$ ($c = 0.25$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 2.15 (s, 3H), 3.57 (s, 3H), 3.84 (s, 3H), 4.79 (d, $J = 5.5$ Hz, 1H), 4.94 (dd, $J_1 = 5.5$ Hz, $J_2 = 7.6$ Hz, 1H), 6.14 (d, $J = 7.6$ Hz, 1H), 6.92-6.95 (m, 2H), 7.09-7.11 (m, 2H), 7.48-7.51 (m, 2H), 8.16-8.19 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 17.504, 39.311, 49.844, 54.533, 98.428, 104.699, 113.823, 122.807, 127.083, 127.731, 129.655, 135.018, 145.390, 148.830, 154.634, 157.949, 167.708; IR (KBr) γ , 2932, 1691, 1564, 1507, 1348, 1220, 1067, 934, 826 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_5)^+$ requires m/z 380.1372, found m/z 380.1369; Enantiomeric

excess: 81%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 70/ 30, flow rate 1.0 mL/min): t_R = 5.89 min (minor), t_R = 10.36 min (major).

Isopropyl 1-(3-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4i): yield: 48%; $[\alpha]_D^{25} = +249^\circ$ ($c = 0.2$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.97 (d, $J = 6.2$ Hz, 3H), 1.19 (d, $J = 6.2$ Hz, 3H), 2.19 (s, 3H), 3.83 (s, 3H), 4.82 (d, $J = 5.4$ Hz, 1H), 4.89-4.94 (m, 2H), 6.18 (d, $J = 7.6$ Hz, 1H), 6.71-6.72 (m, 1H), 6.77-6.79 (m, 1H), 6.89-6.90 (m, 1H), 7.31-7.35 (m, 1H), 7.49-7.51 (m, 2H), 8.16-8.18 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 18.650, 21.716, 22.209, 30.218, 40.694, 55.544, 66.885, 100.766, 105.893, 113.153, 113.539, 119.793, 123.777, 128.350, 130.228, 130.421, 144.451, 146.428, 148.791, 155.842, 160.666, 167.715; IR (KBr) γ , 2982, 2925, 1684, 1570, 1517, 1347, 1201, 822, 698 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_5)^+$ requires m/z 408.1685, found m/z 408.1678; Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 10.37 min (minor), t_R = 23.46 min (major).

Allyl 1-(3-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4j): yield: 52%; $[\alpha]_D^{25} = +300^\circ$ ($c = 0.22$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 2.20 (s, 3H), 3.83 (s, 3H), 4.48-4.50 (m, 2H), 4.84 (d, $J = 5.5$ Hz, 1H), 4.97 (dd, $J_1 = 5.5$ Hz, $J_2 = 7.6$ Hz, 1H), 5.11-5.16 (m, 2H), 5.75-5.84 (m, 1H), 6.19-6.21 (m, 1H), 6.20 (d, $J = 7.6$ Hz, 1H), 6.71-6.72 (m, 1H), 6.76-6.79 (m, 1H), 6.79 (m, 1H), 7.32-7.36 (m, 1H), 7.48-7.50 (m, 2H), 8.16-8.18 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 18.760, 40.428, 55.569, 64.556, 100.037, 106.104, 113.247, 113.546, 117.582, 119.772, 123.877, 128.302, 130.292, 130.486, 132.802, 144.340, 146.510, 149.580, 155.494, 160.706, 167.826; IR (KBr) γ , 2935, 1601, 1564, 1486, 1341, 1108, 1067, 827, 698 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_5)^+$ requires m/z 406.1529, found m/z 406.1516; Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 85/ 15, flow rate 1.0 mL/min): t_R = 7.62 min (minor), t_R = 16.98 min (major).

Methyl 1-(3-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4k): yield: 47%; $[\alpha]_D^{25} = +195^\circ$ ($c = 0.146$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 2.19 (s, 3H), 3.57 (s, 3H), 3.84 (s, 3H), 4.80 (d, $J = 5.5$ Hz, 1H), 4.97 (dd, $J_1 = 5.5$ Hz, $J_2 = 7.6$ Hz, 1H), 6.21 (d, $J = 7.6$ Hz, 1H), 6.70-6.71 (m, 1H), 6.76-6.79 (m, 1H), 6.90-6.91 (m, 1H), 7.31-7.36 (m, 1H), 7.48-7.50 (m, 2H), 8.16-8.18 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 18.701, 40.392, 50.972, 55.565, 100.214, 105.978, 113.213, 113.543, 119.769, 123.901, 128.197, 130.370, 130.474,

144.354, 146.509, 149.256, 155.488, 160.697, 168.714; IR (KBr) γ , 2925, 1689, 1601, 1564, 1347, 1191, 1113, 827, 703 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_5)^+$ requires m/z 380.1372, found m/z 380.1377; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 85/ 15, flow rate 1.0 mL/min): t_R = 7.92 min (minor), t_R = 14.24 min (major).

Methyl 2-ethyl-1-(4-methoxyphenyl) -4-(4-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4l): yield: 38%; $[\alpha]_D^{29} = +406.9^\circ$ ($c = 0.137$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.99 (t, $J = 7.3$ Hz, 3H), 2.61-2.67 (m, 2H), 3.57 (s, 3H), 3.84 (s, 3H), 4.78 (d, $J = 5.7$ Hz, 1H), 4.95 (dd, $J_1 = 5.7$ Hz, $J_2 = 7.5$ Hz, 1H), 6.10 (d, $J = 7.5$ Hz, 1H), 6.93-6.96 (m, 2H), 7.13-7.16 (m, 2H), 7.48-7.50 (m, 2H), 8.16-8.20 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 12.463, 22.143, 39.085, 49.844, 54.526, 97.211, 104.790, 113.749, 122.825, 126.951, 128.114, 130.102, 134.699, 145.370, 154.765, 154.962, 158.032, 167.041; IR (KBr) γ , 2925, 1691, 1557, 1507, 1341, 1220, 1112, 832 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_5)^+$ requires m/z 394.1529, found m/z 394.1526; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 85/ 15, flow rate 1.0 mL/min): t_R = 7.03 min (minor), t_R = 13.29 min (major).

Isopropyl 1-(4-methoxyphenyl)-2-methyl-4-phenyl-1,4-dihydropyridine-3-carboxylate (4m): yield: 40%; $[\alpha]_D^{29} = +260.4^\circ$ ($c = 0.225$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.95 (d, $J = 6.2$ Hz, 3H), 1.18 (d, $J = 6.2$ Hz, 3H), 2.12 (s, 3H), 3.82 (s, 3H), 4.67 (d, $J = 5.4$ Hz, 1H), 4.86-4.92 (m, 1H), 4.95 (dd, $J_1 = 5.4$ Hz, $J_2 = 7.6$ Hz, 1H), 6.07 (d, $J = 7.6$ Hz, 1H), 6.90-6.92 (m, 2H), 7.10-7.12 (m, 2H), 7.16 (m, 1H), 7.25-7.31 (m, 2H), 7.33-7.36 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 17.400, 20.515, 21.154, 39.365, 54.491, 65.351, 100.356, 106.116, 113.627, 124.986, 126.568, 127.197, 127.813, 128.573, 135.637, 147.203, 147.839, 157.616, 167.340; IR (KBr) γ , 2976, 2925, 1685, 1570, 1513, 1220, 1106, 838 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{23}\text{H}_{25}\text{NO}_3)^+$ requires m/z 363.1834, found m/z 363.1829; Enantiomeric excess: 81%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 6.73 min (minor), t_R = 12.99 min (major).

Ethyl 4-(2,3dichlorophenyl)-1-(4-methoxyphenyl)-2-methyl-1,4-dihydropyridine-3-carboxylate (4n): yield: 72%; $[\alpha]_D^{29} = +357.3^\circ$ ($c = 0.614$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.00 (t, $J = 7.1$ Hz, 3H), 2.21 (s, 3H), 3.82 (s, 3H); 3.92-3.97 (q, 2H), 5.02 (dd, $J_1 = 5.2$ Hz, $J_2 = 7.7$ Hz, 1H), 5.24 (d, $J = 5.2$ Hz, 1H), 5.98 (d, $J = 7.7$ Hz, 1H), 6.90-6.92 (m, 2H), 7.08-7.10 (m, 2H), 7.20-7.22 (m, 1H), 7.27-7.30 (m, 1H), 7.32-7.35 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm)

12.980, 17.273, 37.451, 54.487, 58.339, 98.080, 103.949, 113.689, 126.612, 126.779, 127.848, 128.583, 129.040, 131.689, 135.245, 147.286, 149.254, 157.815, 167.325, IR (KBr) γ , 2925, 2849, 1691, 1570, 1513, 1227, 845, 788, 750 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{21}\text{Cl}_2\text{NO}_3)^+$ requires m/z 417.0898, found m/z 417.0894; Enantiomeric excess: 87%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 7.85 min (minor), t_R = 18.29 min (major).

Ethyl 4-(2,3dichlorophenyl)-1-(3-methoxyphenyl)-2-methyl--1,4-dihydropyridine-3-carboxylate (4o): yield: 72%; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.93 (t, J =7.1 Hz, 3H), 2.17 (s, 3H), 3.74 (s, 3H); 3.85-3.90 (q, 2H), 4.97 (dd, J_1 = 5.1 Hz, J_2 = 7.8 Hz, 1H), 5.17(d, J = 5.1 Hz, 1H), 5.96 (d, J = 7.8 Hz, 1H), 6.62-6.63 (m, 1H), 6.68-6.70 (m, 1H), 6.77-6.80 (m, 1H), 7.12-7.14 (m, 1H), 7.18-7.27 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.057, 18.487, 38.543, 55.515, 59.478, 99.823, 105.251, 113.112, 113.629, 119.930, 127.700, 127.913, 129.729, 130.310, 132.798, 144.565, 148.173, 149.694, 160.594, 168.331; IR (KBr) γ , 2984, 2933, 1695, 1576, 1203, 1103, , 787, 699 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{21}\text{Cl}_2\text{NO}_3)^+$ requires m/z 417.0898, found m/z 417.0894; Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol= 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 6.35 min (minor), t_R = 10.22 min (major).

Ethyl 1-(4-methoxyphenyl)-2-methyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4p): yield: 70%; $[\alpha]_D^{29} = +247.9^\circ$ (c = 0.503, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.16 (t, J = 7.1 Hz, 3H), 2.16 (s, 3H), 3.83 (s, 3H), 4.01-4.07 (q, 2H), 4.79 (d, J = 5.6 Hz, 1H), 4.98 (dd, J_1 = 5.6 Hz, J_2 = 7.5 Hz, 1H), 6.18 (d, J = 7.5 Hz, 1H), 6.94-6.96 (m, 2H), 7.13-7.16 (m, 2H), 7.43-7.47 (m, 1H), 7.67-7.70 (m, 1H), 8.03-8.05 (m, 1H), 8.25-8.26 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.295, 18.476, 40.074, 55.571, 59.616, 100.115, 105.957, 114.895, 121.263, 122.744, 128.854, 129.020, 130.812, 133.708, 136.106, 148.588, 149.641, 150.747, 158.986, 168.270; IR (KBr) γ , 2925, 1691, 1564, 1513, 1348, 1220, 1074, 832 ,743 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_5)^+$ requires m/z 394.1529, found m/z 394.1525; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 7.13 min (minor), t_R = 10.98 min (major).

Ethyl 1-(4-methoxyphenyl)-2-methyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4q): yield: 72%; $[\alpha]_D^{29} = +40.2^\circ$ (c = 0.375, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.93 (t, J = 7.1 Hz, 3H), 2.19 (s, 3H), 3.83 (s, 3H), 3.84-3.90 (m, 2H), 5.14-5.18 (m, 2H), 6.04-6.06 (m, 1H);

6.92-6.95 (m, 2H), 7.12-7.14 (m, 2H), 7.26-7.29 (m, 1H), 7.60-7.61 (m, 1H), 7.70-7.74 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 12.827, 17.266, 35.255, 54.525, 58.355, 98.685, 104.963, 113.767, 122.136, 125.536, 127.772, 129.207, 130.133, 132.112, 135.214, 142.575, 146.829, 149.407, 157.888, 166.904; IR (KBr) γ 2925, 1691, 1570, 1513, 1354, 1220, 1074, 838, 750 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_5)^+$ requires m/z 394.1529, found m/z 394.1522; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol= 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 15.79 min (minor), t_R = 22.85 min (major).

Ethyl 1-(3-methoxyphenyl)-2-methyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4r): yield: 37%; $[\alpha]_D^{25} = +37^\circ$ ($c = 0.114$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.93 (t, $J = 7.1$ Hz, 3H), 2.23 (s, 3H), 3.84 (s, 3H), 3.85-3.91 (m, 2H), 5.18-5.20 (m, 2H), 6.11-6.14 (m, 1H), 6.73-6.75 (m, 1H), 6.79-6.81 (m, 1H), 6.87-6.90 (m, 1H), 7.29-7.35 (m, 2H), 7.59-7.60 (m, 1H), 7.69-7.74 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 13.919, 18.500, 36.340, 55.573, 59.515, 100.403, 106.276, 113.193, 113.689, 119.951, 123.267, 126.681, 129.912, 130.407, 131.222, 133.224, 143.465, 144.552, 149.884, 160.673, 167.928; IR (KBr) γ 2925, 1694, 1564, 1523, 1486, 1357, 1196, 780, 749, 698 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_5)^+$ requires m/z 394.1529, found m/z 394.1526; Enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol= 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 11.20 min (minor), t_R = 13.65 min (major).

Methyl 1-(4-methoxyphenyl)-2-methyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4s): yield: 85%; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 2.18 (s, 3H), 3.42 (s, 3H), 3.83 (s, 3H), 5.12-5.18 (m, 2H), 6.10 (d, $J = 7.3$ Hz, 1H), 6.93-6.95 (m, 2H), 7.12-7.14 (m, 2H), 7.26-7.29 (m, 1H), 7.59 (m, 1H), 7.69-7.72 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 17.292, 34.796, 49.755, 54.527, 98.699, 104.923, 113.788, 122.042, 125.637, 127.814, 129.466, 130.196, 131.972, 135.141, 142.118, 146.879, 149.424, 157.916, 167.352; IR (KBr) γ , 2951, 1691, 1570, 1500, 1354, 1220, 1074, 838, 750 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_5)^+$ requires m/z 380.1377, found m/z 380.1372; Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol= 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 17.44 min (minor), t_R = 20.23 min (major).

Methyl 1-(3-methoxyphenyl)-2-methyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (4t): yield: 53%; $[\alpha]_D^{25} = +37^\circ$ ($c = 0.155$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 2.22 (s, 3H), 3.43 (s, 3H), 3.84 (s, 3H), 5.14-5.19 (m, 2H), 6.16 (d, $J = 6.6$ Hz, 1H), 6.74-6.75 (m, 1H),

6.79-6.81 (m, 1H), 6.88-6.91 (m, 1H), 7.26-7.36 (m, 2H), 7.59 (m, 1H), 7.69-7.72 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 18.493, 35.858, 50.867, 55.554, 100.388, 106.201, 113.178, 113.651, 119.871, 123.143, 126.767, 130.163, 130.423, 131.262, 133.076, 142.975, 144.450, 148.002, 149.892, 160.671, 168.343; IR (KBr) γ , 2948, 1694, 1523, 1500, 1355, 701 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_5)^+$ requires m/z 380.1372, found m/z 380.1382; Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 12.29 min (minor), t_R = 13.65 min (major)

Isopropyl 4-(2-methoxyphenyl)-1-(4-methoxyphenyl)-2-methyl-1,4-dihydropyridine-3-

-carboxylate (4u): yield: 50%; $[\alpha]_D^{29} = +235.4^\circ$ ($c = 0.155$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.79 (d, $J = 6.2$ Hz, 3H), 1.13 (d, $J = 6.2$ Hz, 3H), 2.18 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 4.81-4.84 (m, 1H), 5.00 (dd, $J_1 = 5.2$ Hz, $J_2 = 7.6$ Hz, 1H), 5.10 (d, $J = 5.2$ Hz, 1H), 5.93 (d, $J = 7.6$ Hz, 1H), 6.82-6.84 (m, 1H), 6.88-6.90 (m, 2H), 6.95 (m, 1H), 7.08-7.10 (m, 2H), 7.14 (m, 1H), 7.30-7.32 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 17.328, 20.263, 21.015, 32.459, 54.400, 54.472, 64.996, 98.863, 105.778, 109.109, 113.529, 119.932, 125.686, 127.574, 127.904, 128.278, 135.803, 136.362, 148.188, 154.588, 157.521, 167.484; IR (KBr) γ , 2932, 2856, 1685, 1570, 1507, 1227, 1106, 832, 756 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{24}\text{H}_{27}\text{NO}_4)^+$ requires m/z 393.1940, found m/z 393.1939; Enantiomeric excess: 82%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 12.25 min (minor), t_R = 24.33 min (major).

Ethyl 4-(2-chlorophenyl)-1-(4-methoxyphenyl)-2-methyl-1,4-dihydropyridine-3-carboxylate

(4v): yield: 74%; $[\alpha]_D^{29} = +366.2^\circ$ ($c = 0.31$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.99 (t, $J = 7.1$ Hz, 3H), 2.21 (s, 3H), 3.81 (s, 3H), 3.91-3.96 (t, 2H), 5.03 (dd, $J_1 = 5.2$ Hz, $J_2 = 7.7$ Hz, 1H), 5.19 (d, $J = 5.2$ Hz, 1H), 5.96 (d, $J = 7.7$ Hz, 1H), 6.89-6.92 (m, 2H), 7.08-7.12 (m, 3H), 7.26-7.32 (m, 2H), 7.41-7.44 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.019, 18.345, 37.427, 55.550, 59.329, 99.287, 105.578, 114.725, 127.072, 127.395, 128.950, 129.147, 129.589, 129.785, 131.392, 136.495, 145.965, 150.113, 158.814, 168.592; IR (KBr) γ , 2925, 1691, 1564, 1507, 1220, 838, 750 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{NO}_3\text{Cl})^+$ requires m/z 383.1288, found m/z 383.1284; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 9.28 min (minor), t_R = 16.57 min (major).

Ethyl 4-(2-chlorophenyl)-1-(3-methoxyphenyl)-2-methyl-1,4-dihydropyridine-3-carboxylate

(4w): yield: 69%; $[\alpha]_D^{25} = +467^\circ$ ($c = 0.263$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.00 (t, $J = 7.1$ Hz, 3H), 2.25 (s, 3H), 3.81 (s, 3H), 3.92-3.97 (t, 2H), 5.05 (dd, $J_1 = 5.2$ Hz, $J_2 = 7.7$ Hz, 1H),

5.20 (d, J = 5.2 Hz, 1H), 6.03 (d, J = 7.7 Hz, 1H), 6.71 (m, 1H), 6.77-6.79 (m, 1H), 6.76-6.77 (m, 1H), 7.10 (m, 1H), 7.25-7.32 (m, 3H), 7.41-7.43 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.033, 18.507, 37.456, 55.515, 59.408, 99.996, 105.819, 113.058, 113.603, 119.977, 127.140, 127.426, 129.183, 129.417, 129.608, 130.262, 131.466, 144.740, 145.776, 149.487, 160.574, 168.536; IR (KBr) γ , 2978, 2933, 1695, 1570, 494, 1203, 749, 699 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{NO}_3\text{Cl})^+$ requires m/z 383.1288, found m/z 383.1293; Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 11.73 min (minor), t_R = 16.9 min (major).

Ethyl 1-(4-methoxyphenyl)-2-methyl-4-(2-(trifluoromethyl)phenyl)-1,4-dihydropyridine-

3-carboxylate (4x): yield: 75%; $[\alpha]_D^{29} = +327.8^\circ$ (c = 0.593, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.91 (t, J = 7.1 Hz, 3H), 2.22 (s, 3H); 3.83 (s, 3H), 3.87-3.92 (m, 2H), 4.95 (dd, J_1 = 4.9 Hz, J_2 = 7.7 Hz, 1H), 5.12 (d, J = 4.9 Hz, 1H), 5.92 (d, J = 7.8 Hz, 1H), 6.91-6.93 (m, 2H), 7.10-7.13 (m, 2H), 7.26-7.28 (m, 1H), 7.54-7.61 (m, 2H), 7.66-7.68 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 12.763, 17.335, 35.923, 54.478, 58.231, 98.689, 105.822, 113.688, 124.255, 124.315, 127.904, 128.106, 129.157, 131.510, 135.386, 143.034, 147.221, 149.064, 157.801, 167.443; IR (KBr) γ , 2925, 1691, 1564, 1507, 1310, 1220, 1125, 838, 762 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{23}\text{H}_{22}\text{NO}_3\text{F}_3)^+$ requires m/z 417.1552, found m/z 417.1544; Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 8.93 min (minor), t_R = 13.74 min (major).

Ethyl 4-(2-bromophenyl)-1-(4-methoxyphenyl)-2-methyl-1,4-dihydropyridine-3-carboxylate

(4y): yield: 70%; $[\alpha]_D^{29} = +322.2^\circ$ (c = 0.467, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 0.99 (t, J = 6.7 Hz, 3H), 2.21 (s, 3H), 3.81 (s, 3H), 3.91-3.96 (m, 2H), 5.04 (dd, J_1 = 5.1 Hz, J_2 = 7.7 Hz, 1H), 5.16 (d, J = 5.1 Hz, 1H), 5.95 (d, J = 7.7 Hz, 1H), 6.89-6.92 (m, 2H), 7.00-7.04 (m, 1H), 7.08-7.11 (m, 2H), 7.31 (m, 1H), 7.41-7.44 (m, 1H), 7.48-7.50 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.060, 18.317, 40.142, 55.555, 59.332, 99.605, 105.542, 114.726, 121.761, 127.422, 128.096, 128.944, 129.645, 129.737, 132.433, 136.473, 147.640, 150.073, 158.818, 168.582; IR (KBr) γ , 2932, 1691, 1570, 1507, 1220, 1074, 832, 750 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{22}\text{NO}_3\text{Br})^+$ requires m/z 427.0783, found m/z 427.0767; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 10.32 min (minor), t_R = 17.76 min (major).

Ethyl 1-(4-methoxyphenyl)-2-methyl-propyl -1,4-dihydropyridine-3-carboxylate (4z) 31%; ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 0.91 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.33-1.42 (m, 4H), 2.04 (s, 3H), 3.47-3.48 (m, 1H), 3.81 (s, 3H), 4.10-4.18 (m, 2H), 4.90 (dd, *J*₁ = 5.9 Hz, *J*₂ = 7.5 Hz, 1H), 6.06 (d, *J* = 7.5 Hz, 1H), 6.87-6.90 (m, 2H), 7.02-7.05 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 14.288, 14.444, 18.000, 18.313, 32.968, 41.291, 55.459, 59.200, 101.053, 106.712, 114.549, 128.651, 130.687, 136.784, 148.882, 158.472, 169.271; IR (KBr) γ, 2959, 2933, 1690, 1563, 1507, 1223, 1115, 1071, 831, 730 cm⁻¹; HRMS (Micromass GCT-MS EI) exact mass calcd for (C₁₉H₂₅NO₃)⁺ requires *m/z* 315.1834, found *m/z* 315.1838; Enantiomeric excess: 66%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 94.9: 5.1, flow rate 1.0 mL/min): *t*_R = 6.43 min (minor), *t*_R = 12.04 min (major).

1-(1-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3-yl)ethanone (9a): yield: 60%; ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 2.12 (s, 3H), 2.13 (s, 3H); 3.83 (s, 3H), 4.81 (d, *J* = 5.8 Hz, 1H), 5.05 (dd, *J*₁ = 5.8 Hz, *J*₂ = 7.5 Hz, 1H), 6.11 (d, *J* = 7.5 Hz, 1H), 6.92-6.95 (m, 2H), 7.07-7.11 (m, 2H), 7.46-7.49 (m, 2H), 8.18-8.21 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 19.423, 30.364, 40.974, 55.630, 106.356, 109.327, 114.959, 124.237, 127.970, 128.762, 130.534, 135.888, 146.622, 149.028, 154.809, 159.138, 198.457; IR (KBr) γ, 2965, 2920, 1675, 838, 730 cm⁻¹; HRMS (Micromass GCT-MS EI) exact mass calcd for (C₂₁H₂₀N₂O₄)⁺ requires *m/z* 364.1423, found *m/z* 364.1422, Enantiomeric excess: 81%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 70/ 30, flow rate 1.0 mL/min): *t*_R = 7.22 min (minor), *t*_R = 9.58 min (major).

1-(1-(4-methoxyphenyl)-2-methyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3-yl)ethanone (9b): yield: 69 %; ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 1.97 (s, 3H), 2.17 (s, 3H); 3.83 (s, 3H), 5.23 (dd, *J*₁ = 5.5 Hz, *J*₂ = 7.5 Hz, 1H), 5.30 (d, *J* = 5.5 Hz, 1H), 6.04 (d, *J* = 7.5 Hz, 1H), 6.91-6.94 (m, 2H), 7.09-7.10 (m, 2H), 7.32-7.36 (m, 1H), 7.61-7.63 (m, 2H), 7.82-7.84 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 19.272, 29.626, 37.167, 55.601, 106.055, 108.216, 114.882, 124.135, 127.225, 128.790, 130.422, 130.901, 133.744, 136.001, 141.728, 147.502, 149.719, 159.061, 198.821; IR (KBr) γ, 2964, 2925, 1670, 1507, 1348, 1233, 838, 730 cm⁻¹; HRMS (Micromass GCT-MS EI) exact mass calcd for (C₂₁H₂₀N₂O₄)⁺ requires *m/z* 364.1423, found *m/z* 364.1422 Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak AS-H, hexane/ *iso*-propanol = 90/ 10, flow rate 1.0 mL/min): *t*_R = 15.77 min (major), *t*_R = 23.58 min (minor).

1-(4-(2-bromophenyl)-1-(4-methoxyphenyl)-2-methyl-1,4-dihydropyridine-3-yl)ethanone (9c): yield: 63%; ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 1.96 (s, 3H), 2.18 (s, 3H); 3.81 (s, 3H), 5.10 (d,

$J = 5.5$ Hz, 1H), 5.20 (dd, $J_1 = 5.5$ Hz, $J_2 = 7.6$ Hz, 1H), 5.96 (d, $J = 7.6$ Hz, 1H), 6.90-6.92 (m, 2H), 7.06-7.09 (m, 3H), 7.34-7.38 (m, 2H), 7.52-7.54 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 19.121, 29.339, 40.929, 55.573, 105.657, 107.914, 114.794, 121.535, 128.069, 128.614, 128.814, 129.795, 130.080, 132.836, 136.217, 146.134, 149.496, 158.930, 199.672; IR (KBr) γ , 2927, 2925, 1677, 1645, 1513, 1228, 1109, 1026, 837, 749 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{21}\text{H}_{20}\text{BrNO}_2)^+$ requires m/z 397.0677, found m/z 397.0670, Enantiomeric excess: 73%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol = 85/ 15, flow rate 1.0 mL/min): $t_R = 8.12$ min (major), $t_R = 10.07$ min (minor).

1-(4-(2,3-dichlorophenyl)-1-(4-methoxyphenyl)-2-methyl-1,4-dihydropyridine-3-yl)-ethanone

(9d): yield: 72%; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.97 (s, 3H), 2.18 (s, 3H); 3.82 (s, 3H), 5.18-5.19 (m, 2H), 5.97-5.99 (m, 1H), 6.90-6.92 (m, 2H), 7.06-7.08 (m, 2H), 7.24-7.29 (m, 2H), 7.32-7.35 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 19.157, 29.344, 39.337, 55.595, 105.148, 107.593, 114.843, 127.854, 128.192, 128.489, 128.801, 129.439, 130.302, 133.254, 136.074, 146.803, 149.727, 159.014, 199.305; IR (KBr) γ , 2927, 2833, 1665, 1639, 1507, 1228, 1109, 1039, 957, 837, 736 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{NO}_2)^+$ requires m/z 387.0789, found m/z 387.0793 Enantiomeric excess: 77%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol = 85/ 15, flow rate 1.0 mL/min): $t_R = 6.40$ min (minor), $t_R = 8.95$ min (major).

1-(1-(4-methoxyphenyl)-2-methyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3-yl)ethanone (9e):

yield: 64%; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 2.14 (s, 3H), 2.16 (s, 3H); 3.84 (s, 3H), 4.78 (d, $J = 5.9$ Hz, 1H), 5.09 (dd, $J_1 = 5.9$ Hz, $J_2 = 7.4$ Hz, 1H), 6.14 (d, $J = 7.4$ Hz, 1H), 6.94-6.96 (m, 2H), 7.12-7.15 (m, 2H), 7.46-7.50 (m, 1H), 7.65-7.67 (m, 1H), 8.05-8.07 (m, 1H), 8.21-8.22 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 19.424, 30.490, 40.548, 55.639, 106.783, 109.742, 115.018, 121.576, 122.303, 128.823, 129.538, 130.591, 133.311, 135.898, 148.959, 149.111, 149.927, 159.169, 198.275; 2933, 1677, 1513, 1355, 1235, 1109, 1033, 837, 730; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4)^+$ requires m/z 364.1423, found m/z 364.1415 Enantiomeric excess: 79%, determined by HPLC (Daicel Chirapak AD-H, hexane/ iso-propanol = 85/ 15, flow rate 1.0 mL/min): $t_R = 10.84$ min (minor), $t_R = 13.13$ min (major).

1-(1-(3-methoxyphenyl)-2-methyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3-yl)ethanone (9f):

yield: 52%; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 2.17 (s, 3H), 2.18 (s, 3H); 3.84 (s, 3H), 4.79 (d, $J = 5.9$ Hz, 1H), 5.12 (dd, $J_1 = 5.9$ Hz, $J_2 = 7.4$ Hz, 1H), 6.21 (d, $J = 7.4$ Hz, 1H), 6.75-6.77 (m, 1H),

6.80-6.83 (m, 1H), 6.91-6.92 (m, 1H), 7.32-7.37 (m, 1H), 7.46-7.50 (m, 1H), 7.65 (m, 1H), 8.05-8.07 (m, 1H), 8.21-8.22 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 19.479, 30.477, 40.525, 55.585, 106.916, 110.225, 113.203, 113.815, 119.714, 121.599, 122.310, 129.535, 130.198, 130.567, 133.288, 144.148, 148.420, 148.942, 149.738, 160.762, 198.370; IR (KBr) γ , 2933, 1670, 1645, 1525, 1343, 730 699 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4)^+$ requires m/z 364.1423, found m/z 364.1417; Enantiomeric excess: 87%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 85/ 15, flow rate 1.0 mL/min): t_R = 15.72 min (minor), t_R = 27.16 min (major).

1-(1-(3-methoxyphenyl)-2-methyl-4-(2-(trifluoromethyl)phenyl)1,4-dihydropyridine-3-yl)ethanone (9g): yield: 48%; $[\alpha]_D^{25} = +375^\circ$ ($c = 0.12$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.96 (s, 3H), 2.19 (s, 3H); 3.82 (s, 3H), 5.08-5.10 (m, 2H), 6.00 (d, $J = 6.6$ Hz, 1H), 6.71-6.72 (m, 1H), 6.77-6.79 (m, 1H), 6.88-6.89 (m, 1H), 7.29-7.33 (m, 2H), 7.59-7.65 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 19.379, 29.784, 37.806, 55.548, 107.171, 109.134, 113.226, 113.604, 119.892, 126.049, 126.522, 129.062, 130.374, 130.754, 133.129, 144.515, 146.219, 148.288, 160.638, 200.117; IR (KBr) γ , 2927, 1677, 1652, 1602, 1532, 1311, 1121, 1033, 768 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{22}\text{H}_{20}\text{NO}_2\text{F}_3)^+$ requires m/z 387.1446, found m/z 387.1444 Enantiomeric excess: 86%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol= 94.9/ 5.1, flow rate 1.0 mL/min): t_R = 7.46 min (major), t_R = 9.74 min (minor).

Procedure for the synthesis of Diethyl7-(4-methoxyphenyl)-6-methyl-4-(4-nitrophenyl)-3a,4,7,7a-tetrahydroisoxazolo[5,4-*b*]pyridine-3,5-dicarboxylate (11): **4a** (140 mg, 0.355 mmol) and ethyl chlorooximidoacetate **10** (80 mg, 0.533 mmol) were dissolved in ether (2 mL). Under a nitrogen atmosphere, triethylamine (74 μL , 0.533 mmol) was added to the reaction mixture over 1 h with syringe pump. The mixture was concentrated and purified through flash chromatography to give pure product **11** in 67% yield; $[\alpha]_D^{25} = +410$ ($c = 0.16$, CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.22 (t, $J = 7.1$ Hz, 3H), 1.41 (t, $J = 7.1$ Hz, 3H), 2.19 (s, 3H), 3.80 (s, 3H), 4.08-4.19 (m, 2H), 4.38-4.43 (m, 2H), 4.30-4.63 (m, 1H), 5.10 (s, 1H), 5.90 (d, $J = 10.2$ Hz, 1H), 6.85-6.87 (m, 2H), 6.99-7.01 (m, 2H), 7.55-7.57 (m, 2H), 8.18-8.20 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 14.140, 14.376, 19.918, 37.215, 55.553, 55.700, 60.235, 62.362, 94.441, 107.622, 114.701, 123.881, 127.021, 128.027, 135.812, 146.922, 149.882, 152.302, 156.628, 158.446, 159.802, 166.715; IR (KBr) γ , 2972, 1715, 1607, 1513, 1348, 1241, 1064, 837, 749 cm^{-1} ; HRMS (Micromass GCT-MS EI) exact mass calcd for $(\text{C}_{26}\text{H}_{27}\text{N}_3\text{O}_8)^+$ requires m/z 509.1798, found m/z 509.1791; Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol= 70/ 30, flow rate 1.0 mL/min): t_R = 20.07 min (minor), t_R = 21.9 min(major).

Procedure for synthesis of Ethyl 1-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1,4,5,6-tetrahydropyridine-3-carboxylate **12:** To a solution of **4a** (119 mg, 0.3 mmol) and trifluoroacetic acid (1.0 mL) in CH₂Cl₂ (2.0 mL) was added triethylsilane (348 mg, 3 mmol) in one portion. After being stirred for 2 h, saturated aqueous sodium hydrogen carbonate (20 mL) was added. The mixture was extracted with ethyl acetate, and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the residue is purified through flash chromatography to give pure product **12** in 85% yield; $[\alpha]_D^{25} = -101^\circ$ ($c = 0.06$, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 0.98 (t, $J = 7.1$ Hz, 3H), 1.86-1.90 (m, 1H), 2.27 (s, 3H); 3.19-3.25 (m, 1H), 3.31-3.35 (m, 1H), 3.82 (s, 3H), 3.91-3.96 (m, 2H), 4.33 (s, 1H), 6.89-6.92 (m, 2H), 7.02-7.05 (m, 2H), 7.41-7.44 (m, 2H), 8.15-8.18 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 14.348, 19.785, 29.458, 39.207, 48.325, 55.581, 58.968, 96.596, 114.815, 123.526, 128.491, 128.579, 139.097, 146.365, 155.694, 155.963, 158.407, 168.497; IR (KBr) γ 2933, 1677, 1563, 1343, 1235, 831, 749 cm⁻¹; HRMS (Micromass GCT-MS EI) exact mass calcd for (C₂₂H₂₄N₂O₅)⁺ requires m/z 396.1685, found m/z 396.1681.

Procedure for synthesis of Ethyl 1-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)piperidine-3-carboxylate (13**):** A solution of NaBH(OAc)₃, which was prepared by adding NaBH₄ (49mg, 1.29 mmol) to glacial acid (1 mL) while the temperature was kept between 15-20 °C. After the H₂ evolution ceased, the **12** was added in one portion and the reaction was stirred for 2 hours at room temperature. Then saturated aqueous sodium hydrogen carbonate was added to this solution. The mixture was extracted with ethyl acetate, and the organic layer was dried over anhydrous sodium sulfate. After removal of solvent, the residue is purified through flash chromatography to give pure product **13** in 76% yield, $[\alpha]_D^{25} = -15^\circ$ ($c = 0.1$, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 0.90 (d, $J = 6.5$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H), 1.77-1.80 ((m, 1H), 2.93-2.97 (m, 3H), 3.15-3.17 (m, 2H), 3.30-3.33 (m, 1H), 3.79 (s, 3H), 3.85-3.96 (m, 2H), 6.82-6.86 (m, 2H), 7.09-7.13 (m, 2H), 7.44-7.46 (m, 2H), 8.15-8.18 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 14.251, 19.397, 26.341, 44.604, 53.195, 55.450, 56.463, 58.748, 59.752, 114.048, 123.515, 127.074, 128.464, 144.759, 146.769, 150.730, 157.139, 170.629; IR (KBr) γ 2959, 1727, 1602, 1513, 1343, 1241, 1171, 863, 837, 749, 699 cm⁻¹; HRMS (Micromass GCT-MS EI) exact mass calcd for (C₂₂H₂₆N₂O₅)⁺ requires m/z 398.1842, found m/z 398.1837, Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak AD-H, hexane/ *iso*-propanol = 70/ 30, flow rate 1.0 mL/min): $t_R = 10.18$ min (major), $t_R = 12.59$ min (minor).

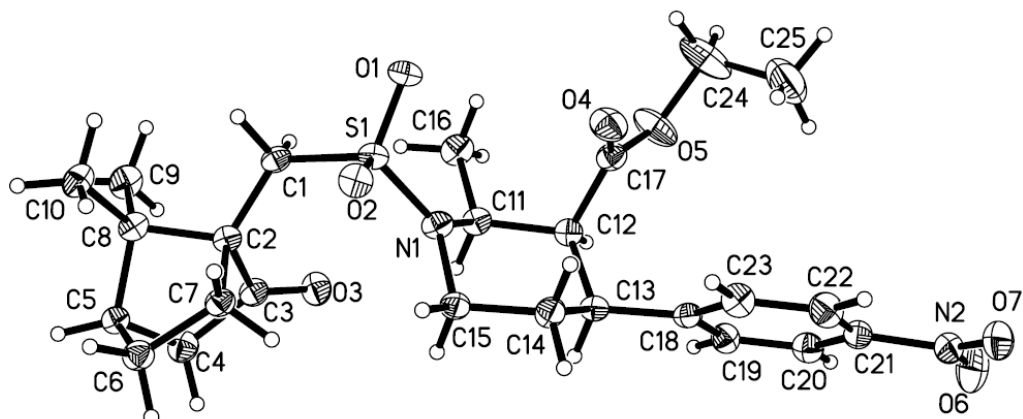
Procedure for synthesis **14:** CAN (411 mmg, 0.75 mmol) was added to a solution of **13** (100 mg, 0.25 mmol) in a 5/1 mixture of MeCN/H₂O (5 mL) at ambient temperature. After 30 min, NaOH

(1.0 M) was added and the mixture was extracted four times with CH₂Cl₂. The combined organic layers were washed with brine, filtered through cotton, and dried over anhydrous sodium sulfate. After removal of solvent, the residue was mixed with DMAP (97.6 mg, 0.8 mmol) and (1S)-(+)-camphor-10-sulfonyl chloride (188 mg, 0.75 mmol) in anhydrous CH₂Cl₂ at 0 °C. The reaction mixture was stirred at room temperature until reaction was complete. The crude product was purified through flash chromatography to give pure product **14** in 47% yield. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 0.89 (s, 3H), 1.07 (t, *J*= 7.1 Hz, 3H), 1.12 (s, 3H), 1.44 (m, 1H), 1.58 (d, *J*= 7 Hz, 1H), 1.65-1.67 (m, 1H), 1.88-1.90 (m, 1H), 1.91-1.96 ((m, 1H), 2.10-2.12 (m, 1H), 2.35-2.40 (m, 1H), 2.55 (m, 1H), 2.75 (m, 1H), 2.89 (m, *J*= 14.7 Hz, 1H), 2.95-2.97 (m, 1H), 3.11 (m, 1H), 3.17-3.20 (m, 1H), 3.40 (d, *J*= 14.7 Hz, 1H), 3.86-3.89 (m, 1H), 3.91-4.01 (m, 2H), 4.17-4.21 (m, 1H), 7.26-7.42 (m, 2H), 8.14-8.17 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 14.125, 18.560, 19.884, 20.044, 25.277, 25.820, 27.052, 42.707, 42.892, 43.224, 46.820, 48.130, 50.437, 52.383, 55.794, 58.714, 60.591, 123.651, 128.502, 146.945, 149.279, 169.977, 215.610; IR (KBr) γ 2965, 1740, 1595, 1519, 1140, 894 cm⁻¹.

References and notes:

- (1) Taylor M. D.; Himmelsbach R. J.; Kornberg B. E.; Quin J., III; Lunney, E.; Michel, A. *J. Org. Chem.* **1989**, *54*, 5585.

X-ray data of 14



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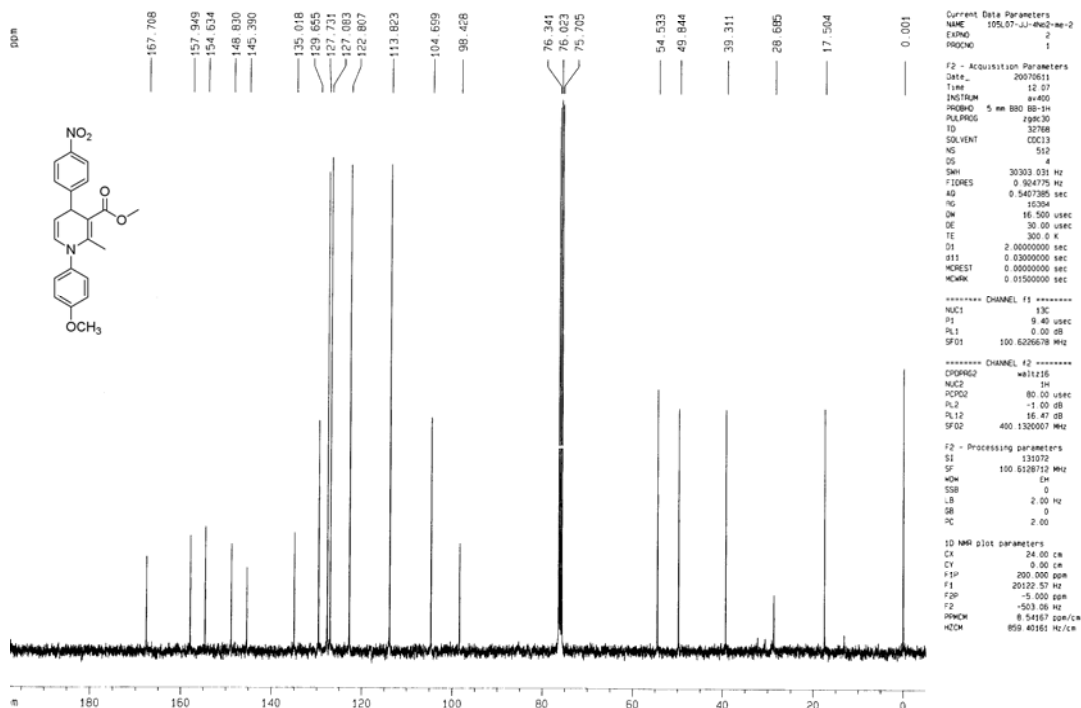
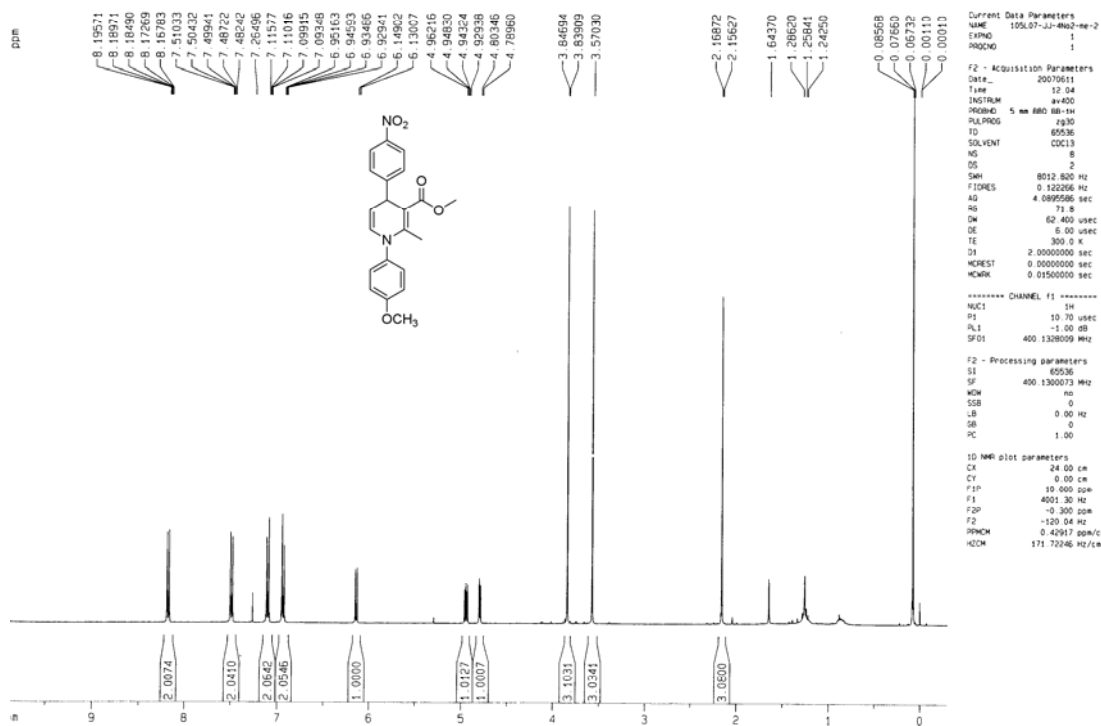
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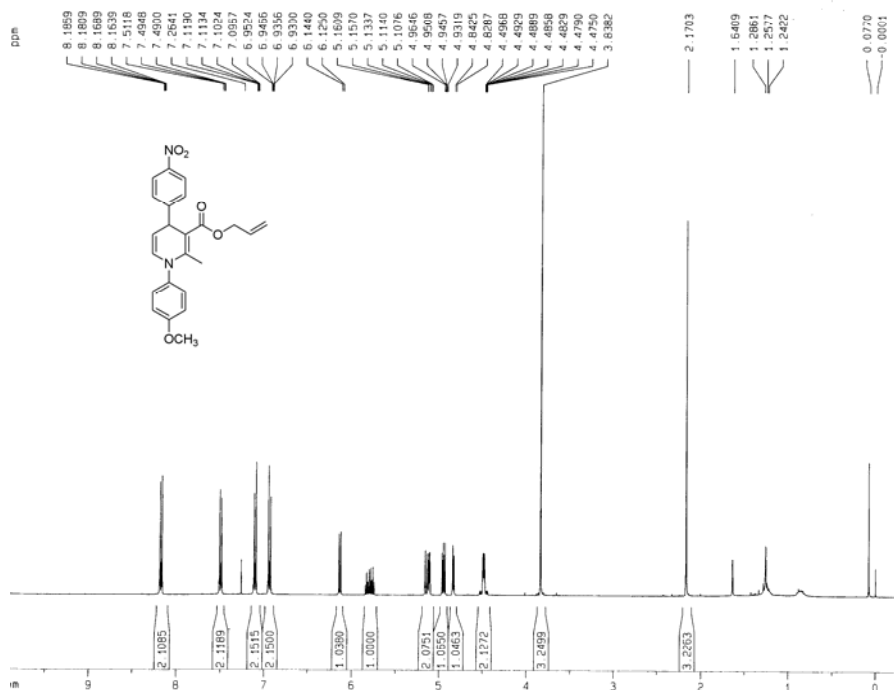
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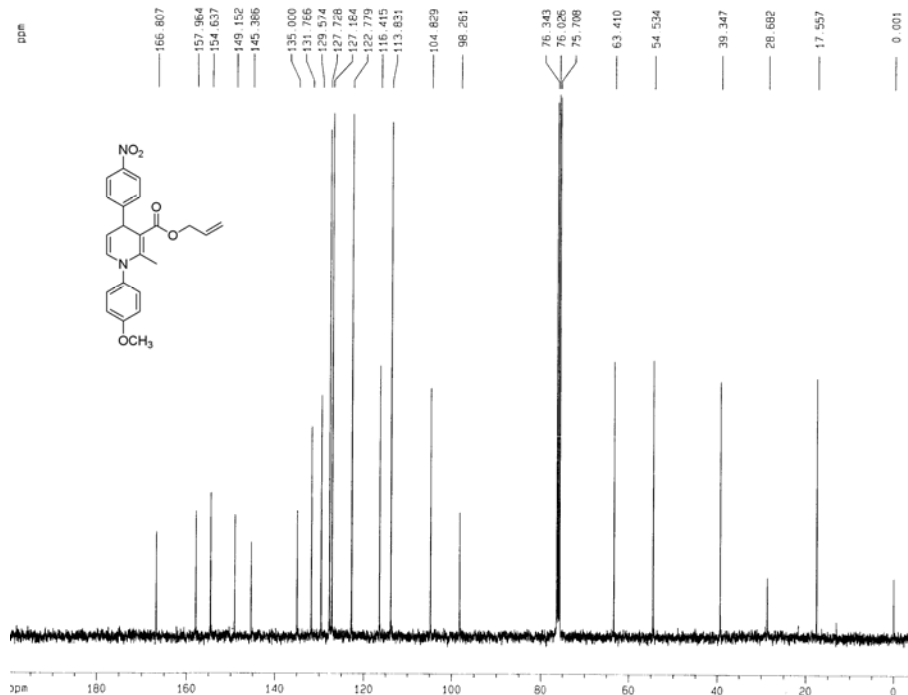
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EXPNO 2
PROCNO 1

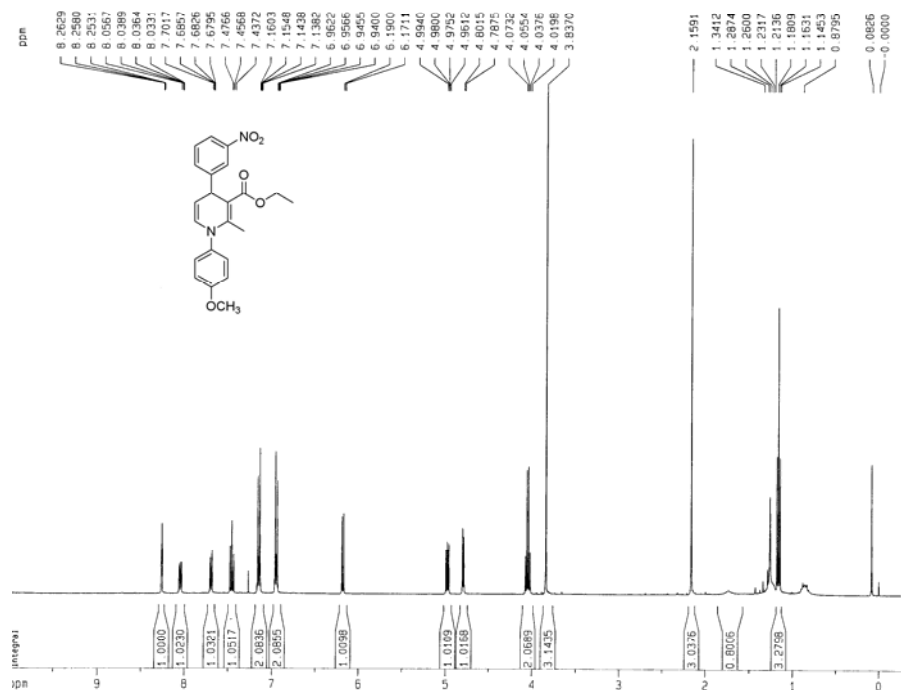
F2 - Acquisition Parameters
Date_ 20070611
Time 10.49
INSTRUM svt400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 512
DS 4
SWH 30303.031 Hz
FIDRES 0.024775 Hz
AQ 0.5407305 sec
RG 16384
DM 16.500 usec
DE 30.00 usec
TE 300.0 K
D1 2.0000000 sec
D11 0.0300000 sec
MCREST 0.0000000 sec
MCWIR 0.0150000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 9.40 usec
PL1 0.00 dB
SFO1 100.622678 MHz

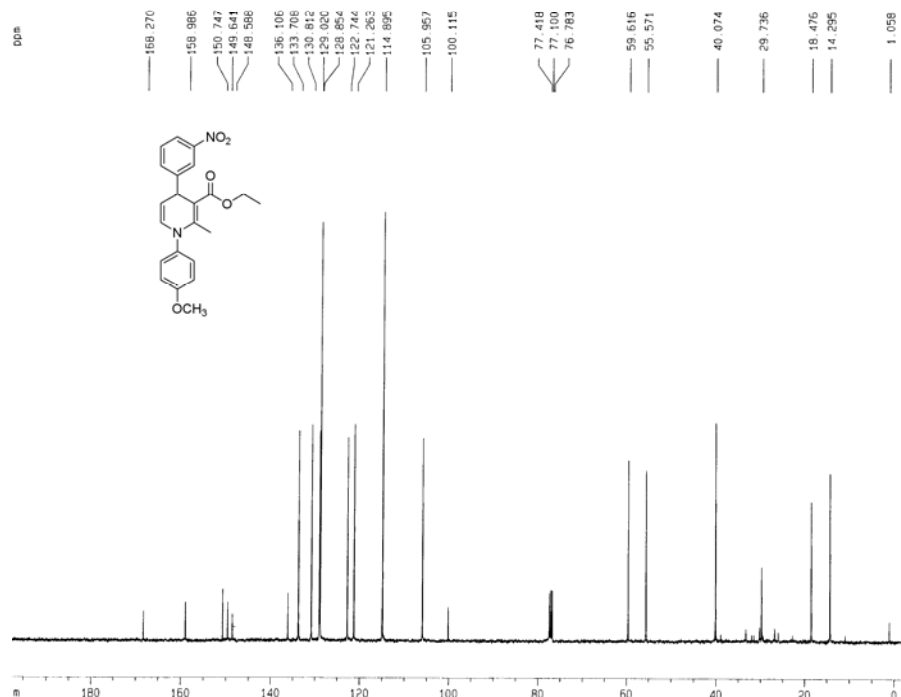
***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 16.47 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 131072
SF 100.6128714 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 2.00

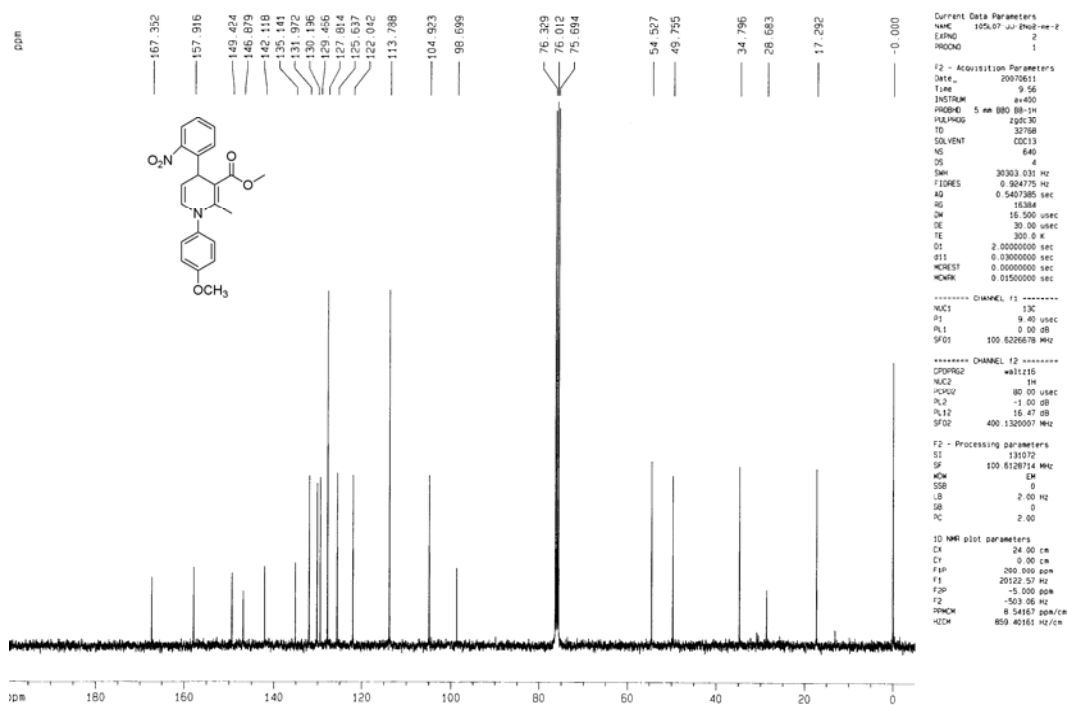
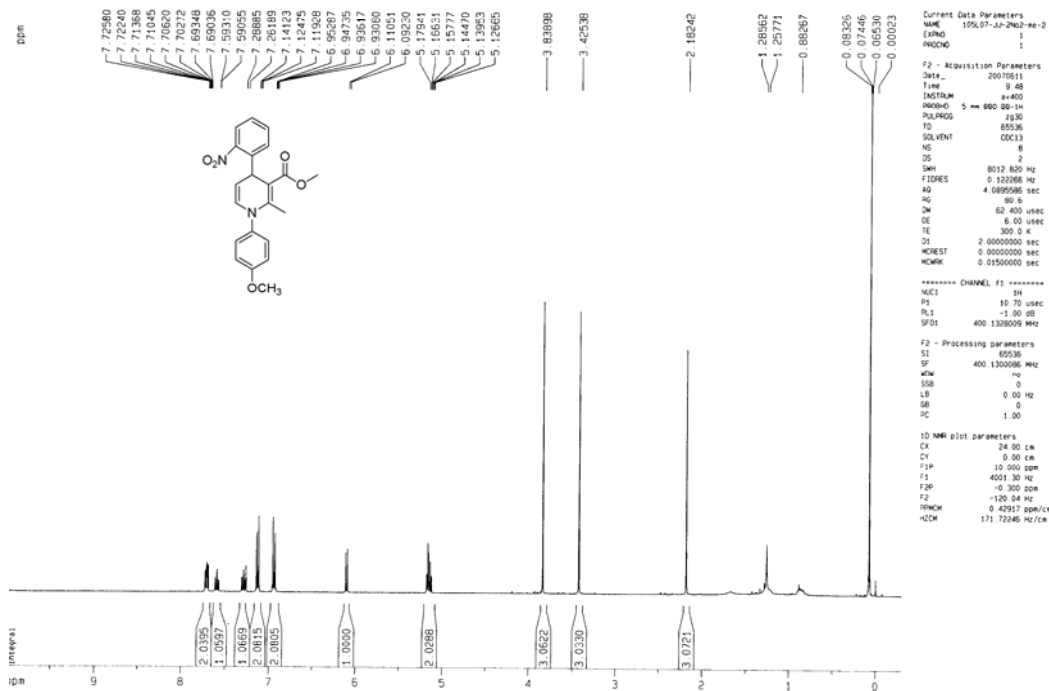
1D NMR plot parameters
CX 24.00 cm
CY 0.00 cm
FIP 200.000 ppm
F1 20122.57 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PWHW 8.54167 ppm/cm
H2CM 859.40161 Hz/cm

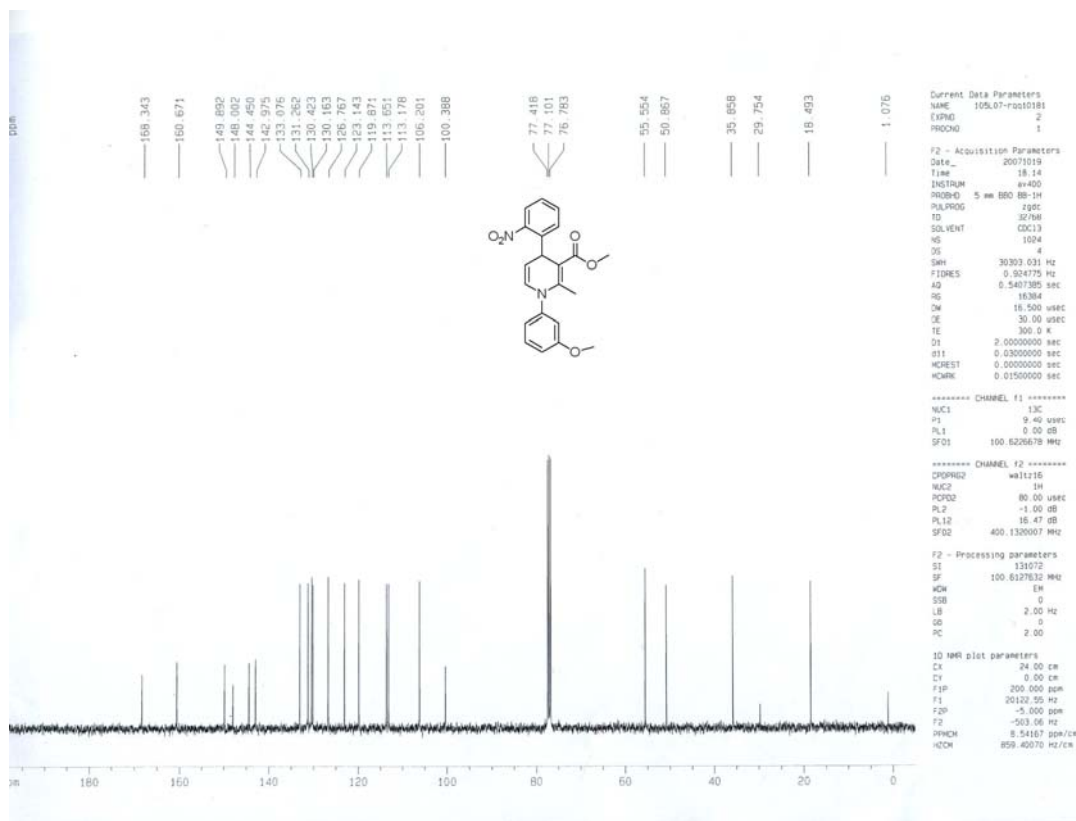
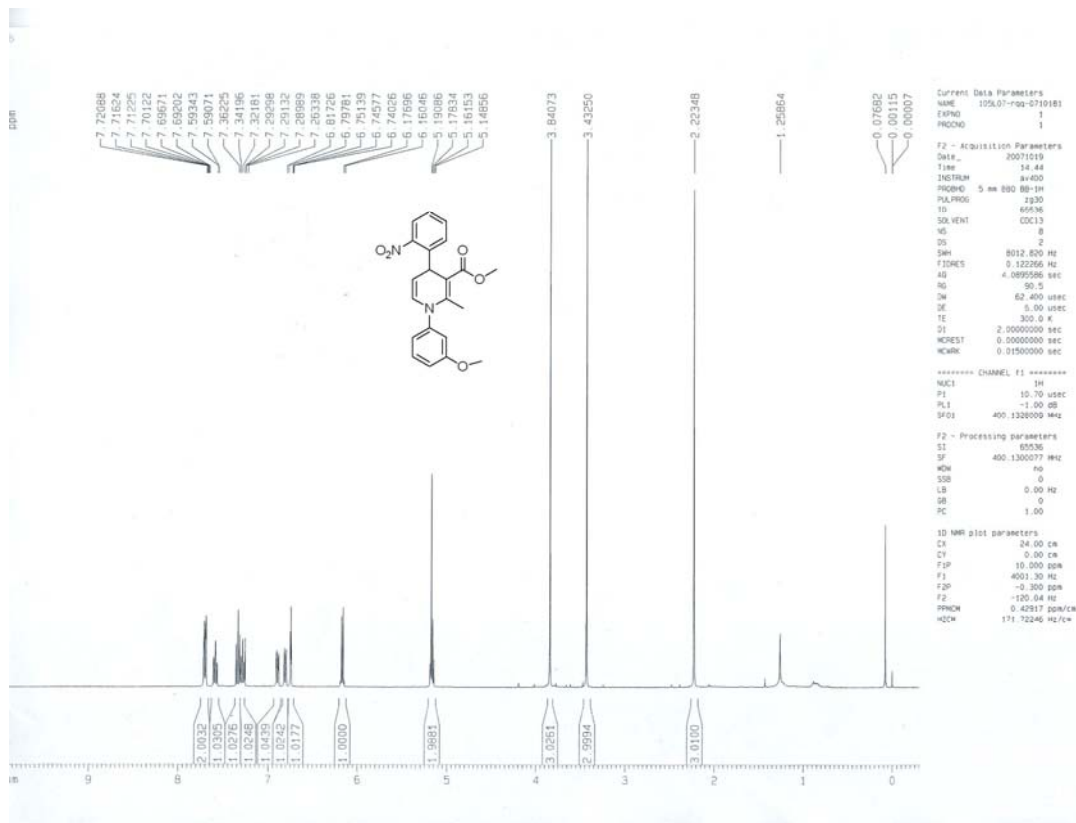


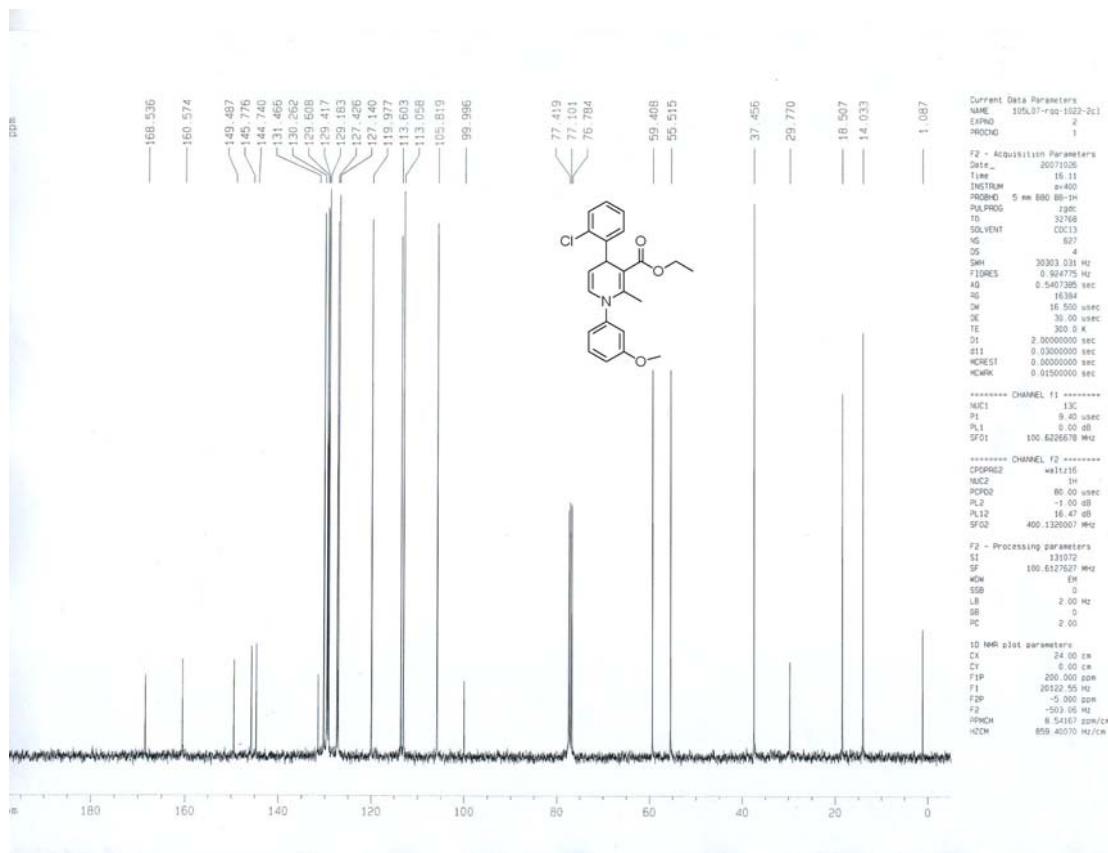
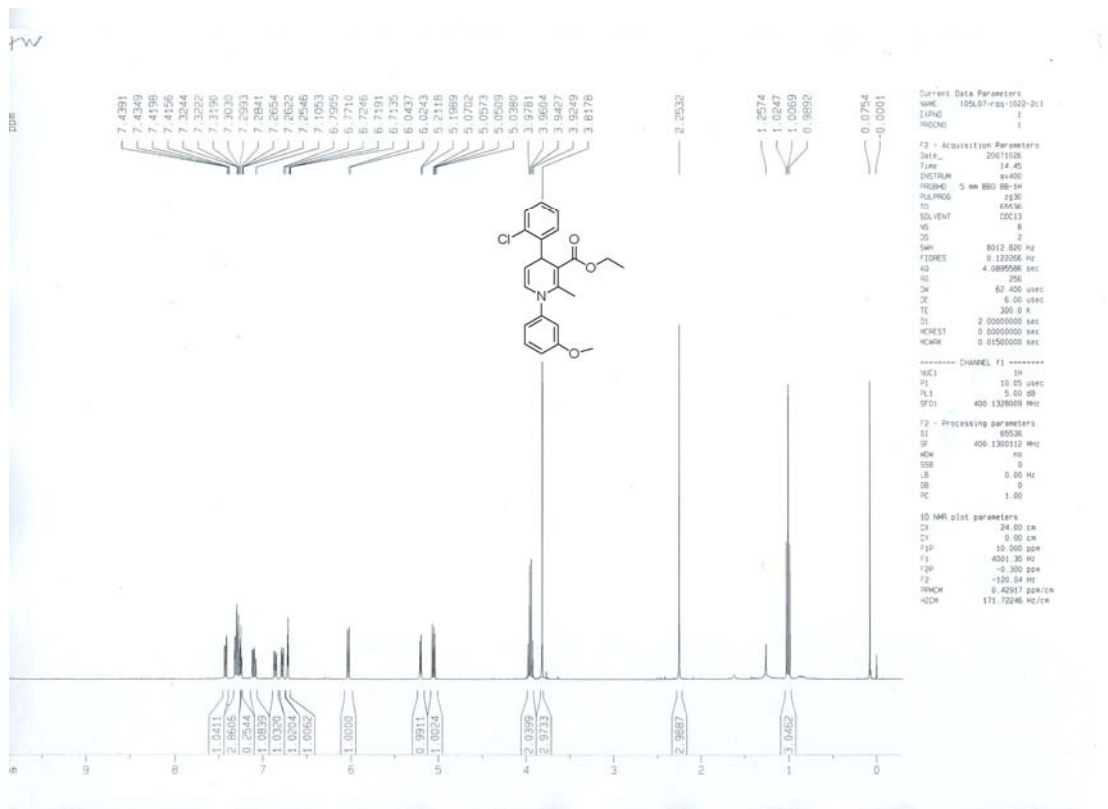
Current Data Parameters
 NAME 105L07-11-3m2-rt
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20070618
 Time 17.39
 INSTRUM av400
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TO 65536
 SOLVENT CDCl₃
 NS 8
 DS 2
 SWH 8032.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0895586 sec
 RG 64
 DW 62.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 MCREST 0.00000000 sec
 MCWIR 0.01500000 sec
 CHANNEL f1
 NUC1 1H
 P1 10.70 usec
 PL1 -1.00 dB
 SFO1 400.132609 MHz
 F2 - Processing parameters
 SI 65536
 SF 400.132609 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00
 1D NMR plot parameters
 CX 24.00 cm
 CY 0.00 cm
 FAP 10.000 ppm
 F1 4001.30 Hz
 F2 -0.300 ppm
 FZ -120.04 Hz
 HPCW 0.42917 ppm/cm
 HZCM 171.72246 Hz/cm

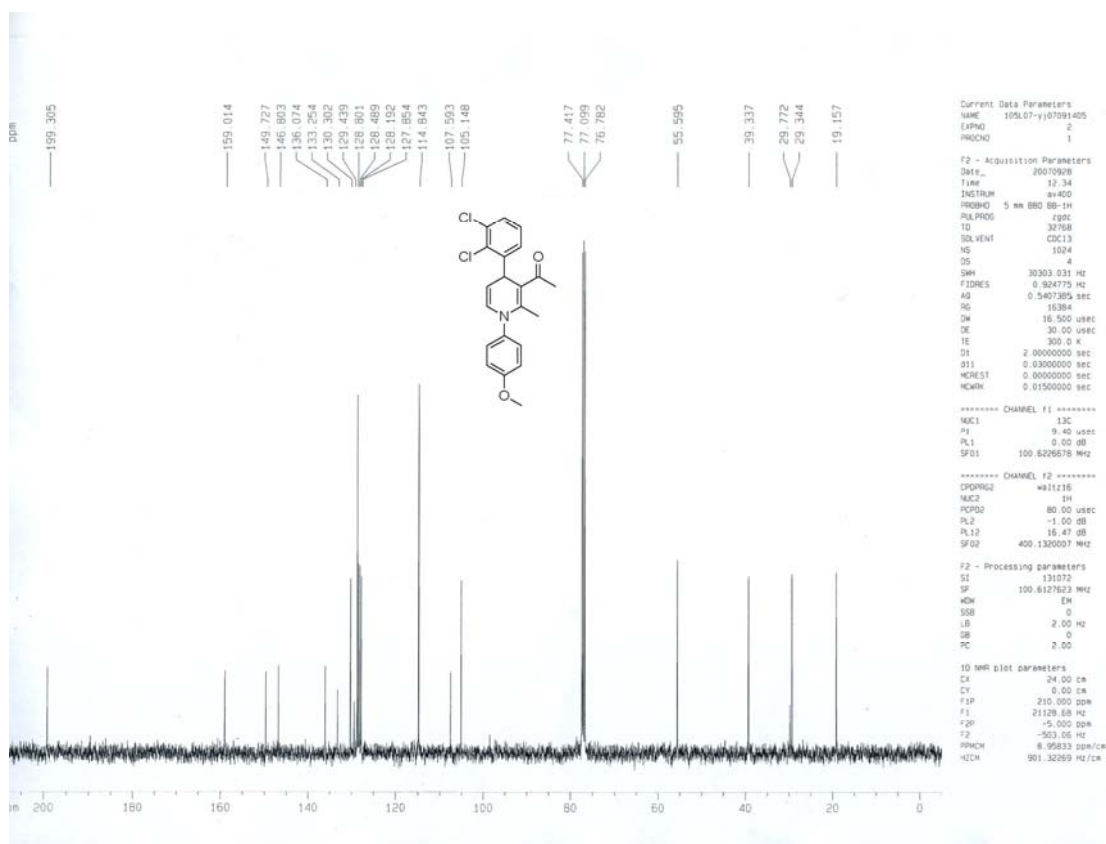
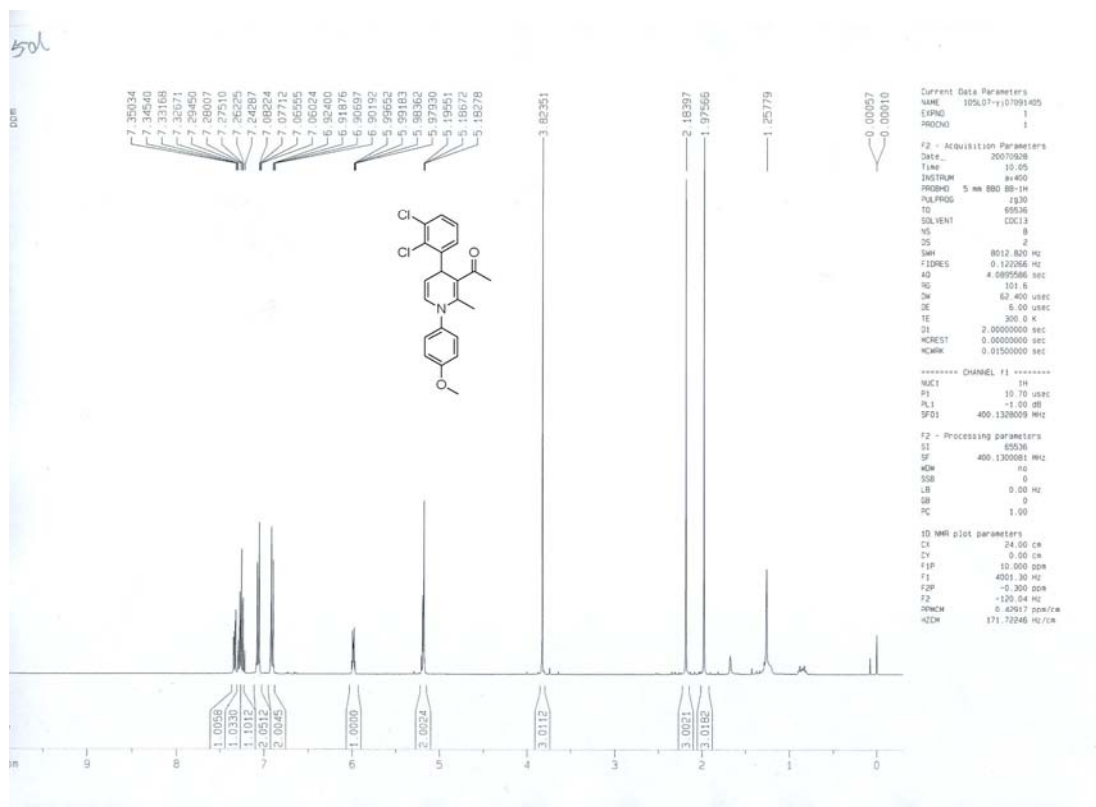


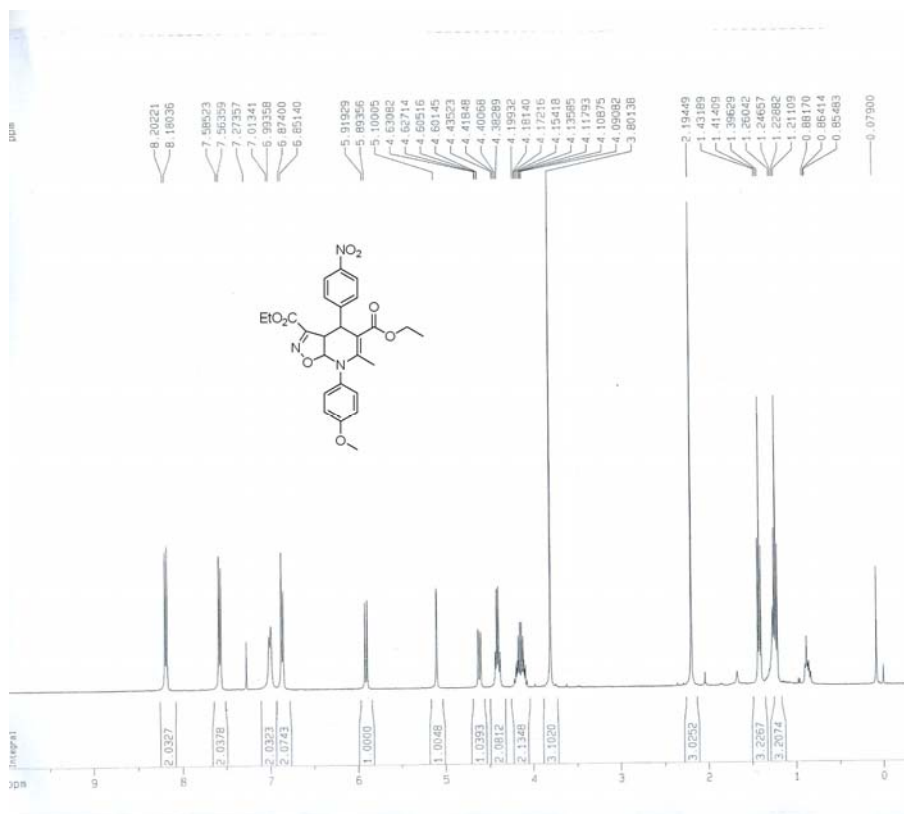
Current Data Parameters
 NAME 105L07-11-3m2-rt
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20070618
 Time 17.44
 INSTRUM av400
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TO 32768
 SOLVENT CDCl₃
 NS 536
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.924775 Hz
 AQ 0.5407385 sec
 RG 16384
 DW 16.500 usec
 DE 30.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWIR 0.01500000 sec
 CHANNEL f1
 NUC1 13C
 P1 9.40 usec
 PL1 0.00 dB
 SFO1 100.6226678 MHz
 CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -1.00 dB
 PL12 16.47 dB
 SFO2 400.132609 MHz
 F2 - Processing parameters
 SI 131072
 SF 100.6127653 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 2.00
 1D NMR plot parameters
 CX 24.00 cm
 CY 0.00 cm
 FAP 200.000 ppm
 F1 20122.55 Hz
 F2P -5.000 ppm
 FZ -503.06 Hz
 HPCW 8.54167 ppm/cm
 HZCM 859.40070 Hz/cm









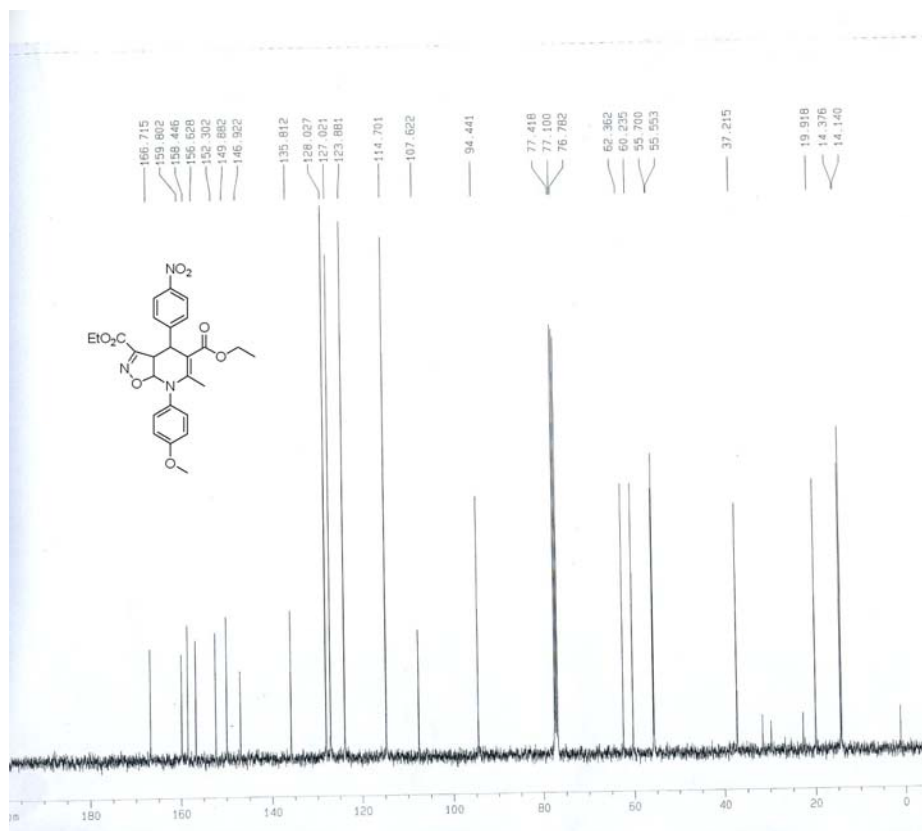


Current Data Parameters
 NAME 105b-07-JJ-131p2
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20071112
 Time 15.27
 INSTRUM av400
 PROBHD 5 mm BBO 1H
 PULPROG zg30
 TO 300.0 K
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 8012.800 Hz
 FIDRES 0.122266 Hz
 AQ 4.0892586 sec
 RG 60.6
 DW 62.400 usec
 DE 5.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 NUC1 1H
 P1 10.70 usec
 PL1 -1.00 dB
 SFO1 400.132609 MHz

F2 - Processing parameters
 SI 65536
 SF 400.132609 MHz
 WDW EM
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 24.00 cm
 CY 0.00 cm
 FXP 10.000 ppm
 FI 4001.30 Hz
 F2P -0.300 ppm
 F2 -120.24 Hz
 DNM 0.45917 ppm/cm
 HZDM 171.72248 Hz/cm



Current Data Parameters
 NAME 105b-07-JJ-131p2
 EXPNO 2
 PROCNO 1

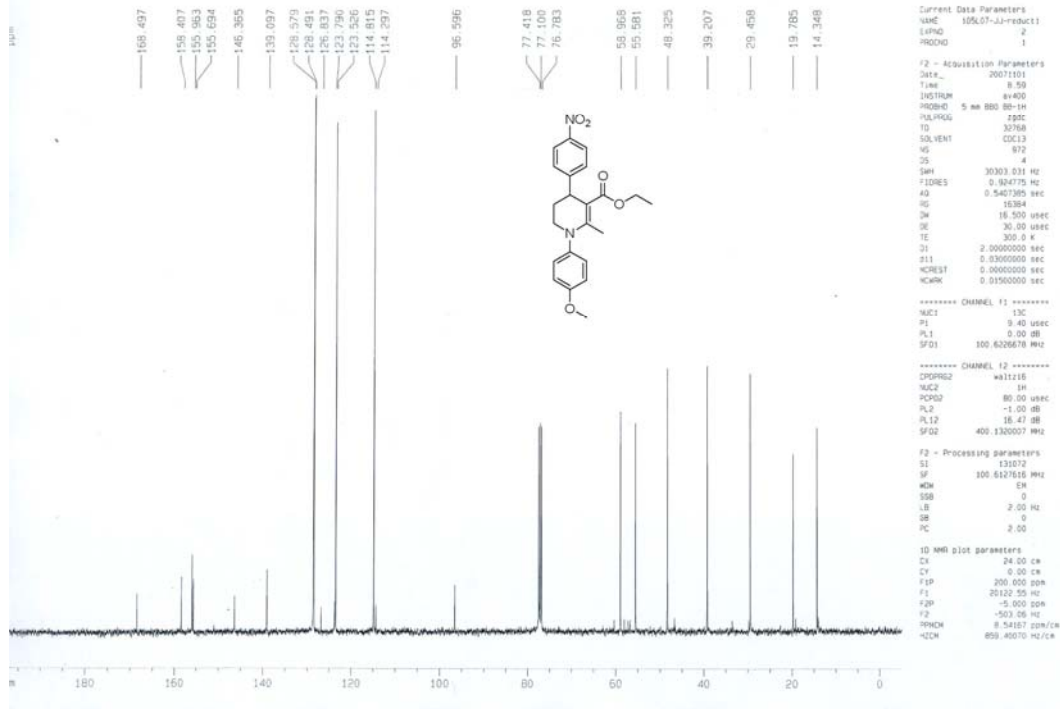
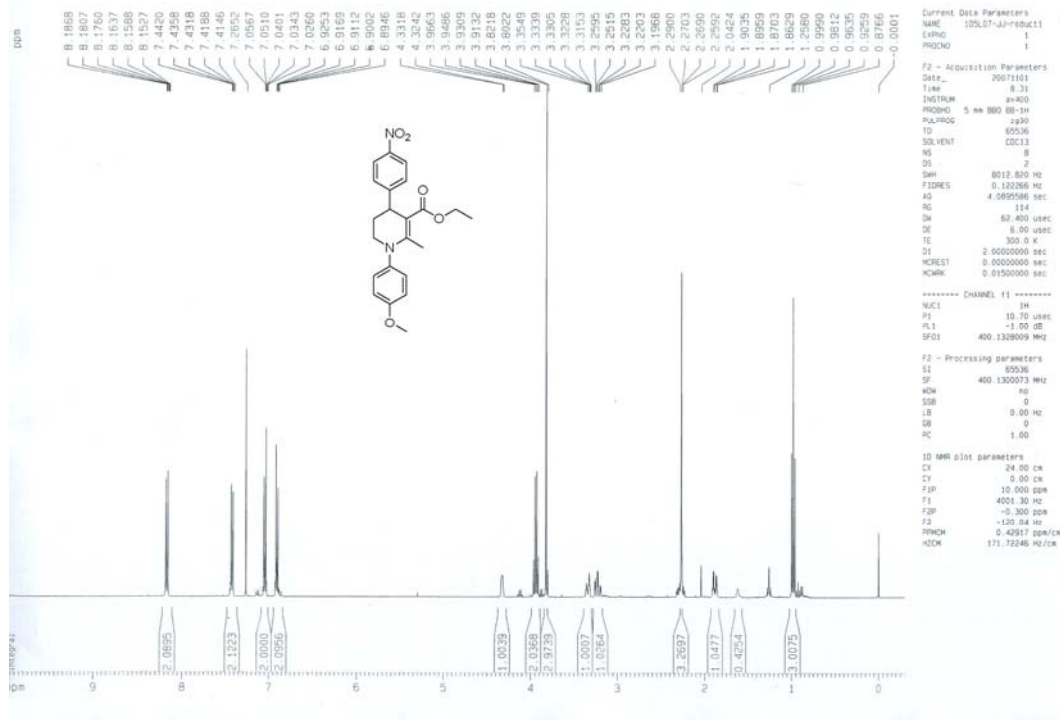
F2 - Acquisition Parameters
 Date_ 20071112
 Time 15.33
 INSTRUM av400
 PROBHD 5 mm BBO 1H
 PULPROG zgpg30
 TO 32768
 SOLVENT CDCl3
 NS 4
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.924775 Hz
 AQ 0.5407385 sec
 RG 16384
 DW 16.500 usec
 DE 35.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 NUC1 13C
 P1 9.40 usec
 PL1 0.00 dB
 SFO1 100.626678 MHz

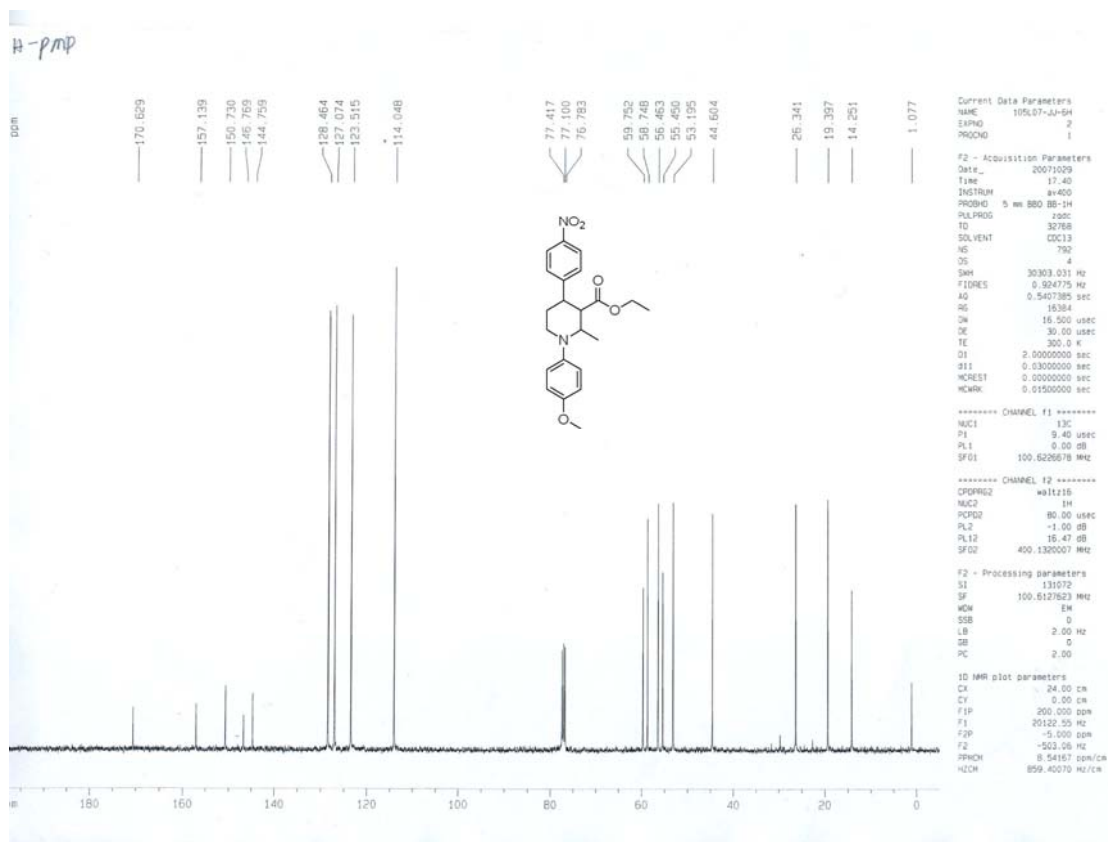
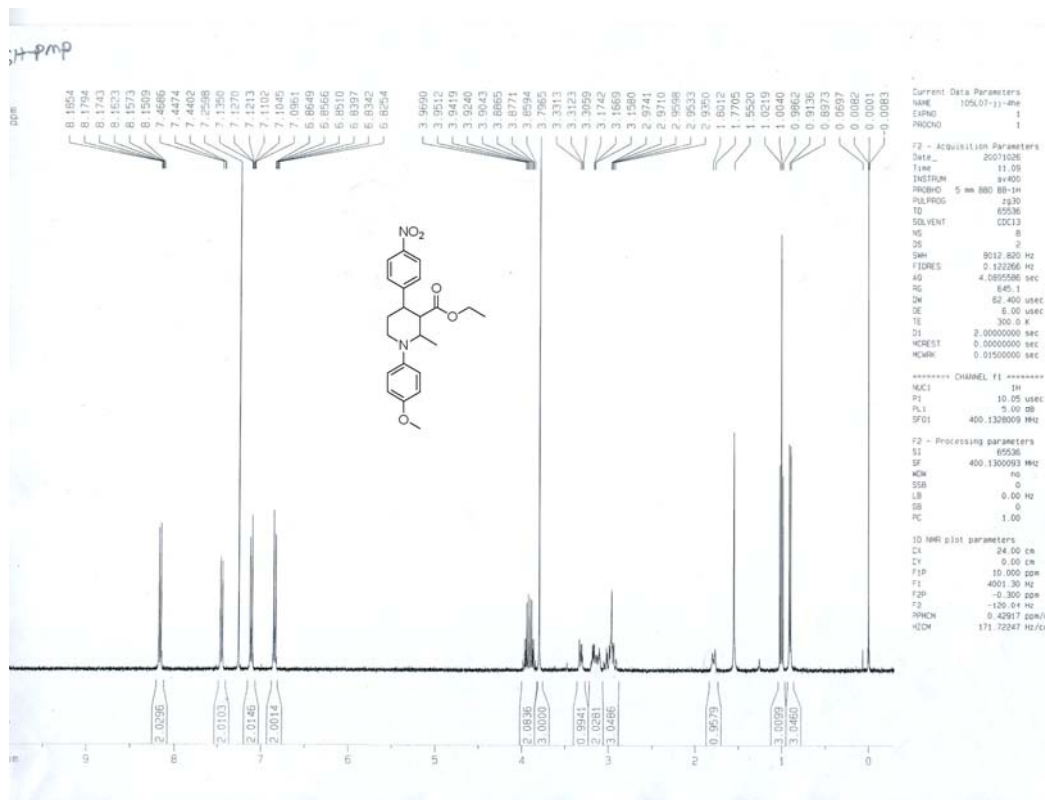
Channel f1
 NUC1 13C
 P1 9.40 usec
 PL1 0.00 dB
 SFO1 100.626678 MHz

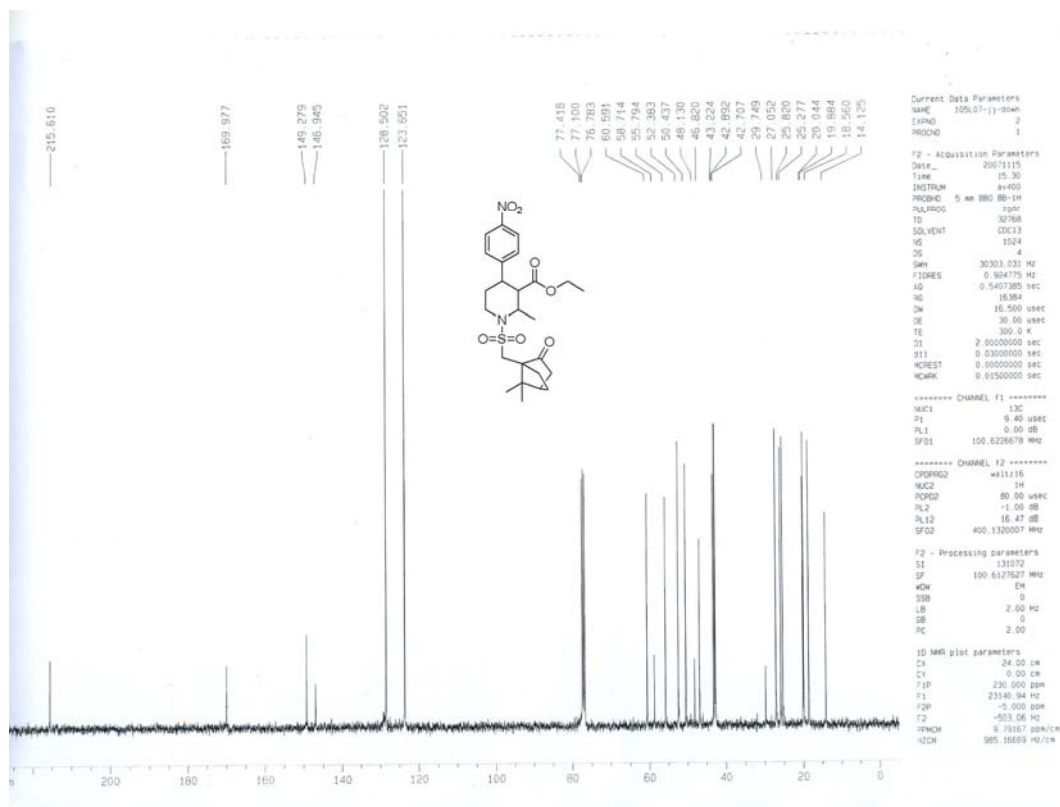
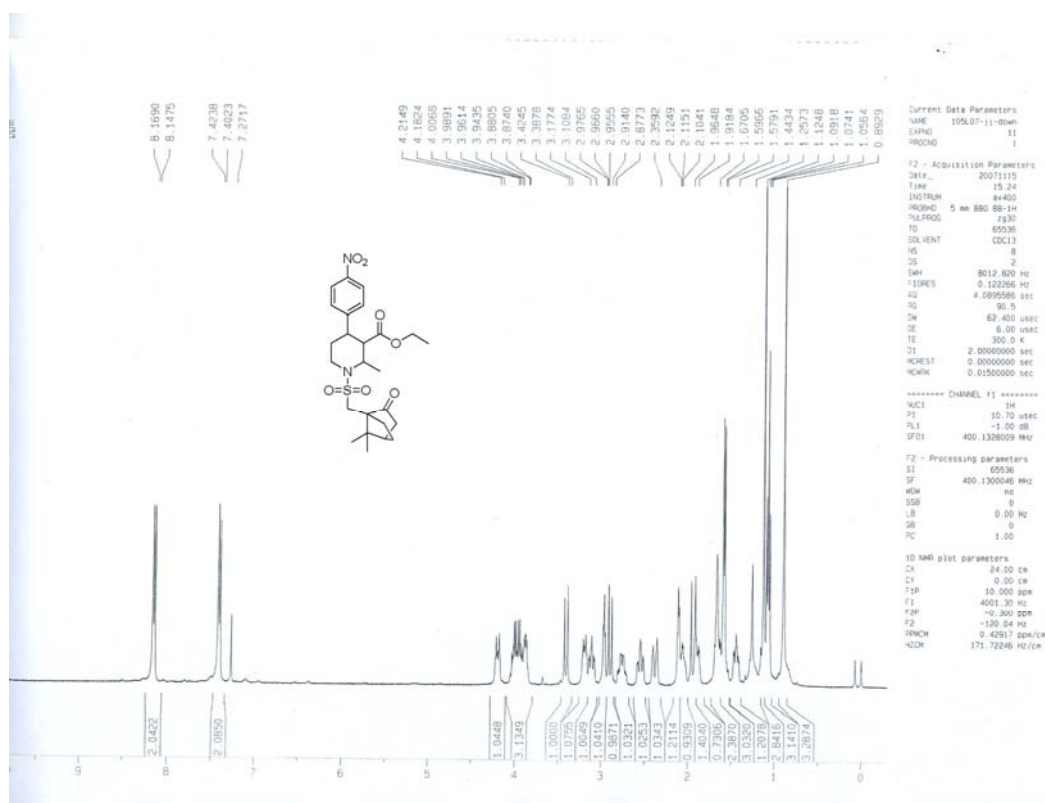
Channel f2
 NUC2 1H
 P2 80.00 usec
 PL2 -1.00 dB
 PL12 16.47 dB
 SFO2 400.132007 MHz

F2 - Processing parameters
 SI 131072
 SF 100.627644 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 2.00

1D NMR plot parameters
 CX 24.00 cm
 CY 0.00 cm
 FXP 200.000 ppm
 FI 20122.55 Hz
 F2P -5.000 ppm
 F2 -503.06 Hz
 DNM 8.54167 ppm/cm
 HZDM 859.40070 Hz/cm



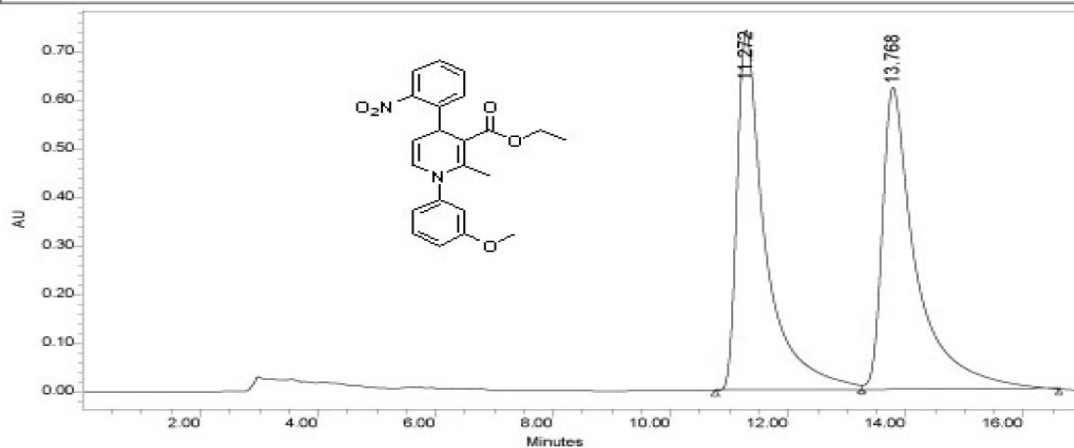




SAMPLE INFORMATION

Sample Name: 2-NO2-3-OMe-yixianEtzhi-DL
 Sample Type: Unknown
 Vial: 1
 Injection #: 2
 Injection Volume: 20.00 ul
 Run Time: 60.00 Minutes

Acquired By: System
 Date Acquired: 10/21/2007 4:37:27 PM
 Acq. Method: yj005
 Date Processed: 10/21/2007 4:55:10 PM
 Channel Name: 2487Channel 1
 Sample Set Name:

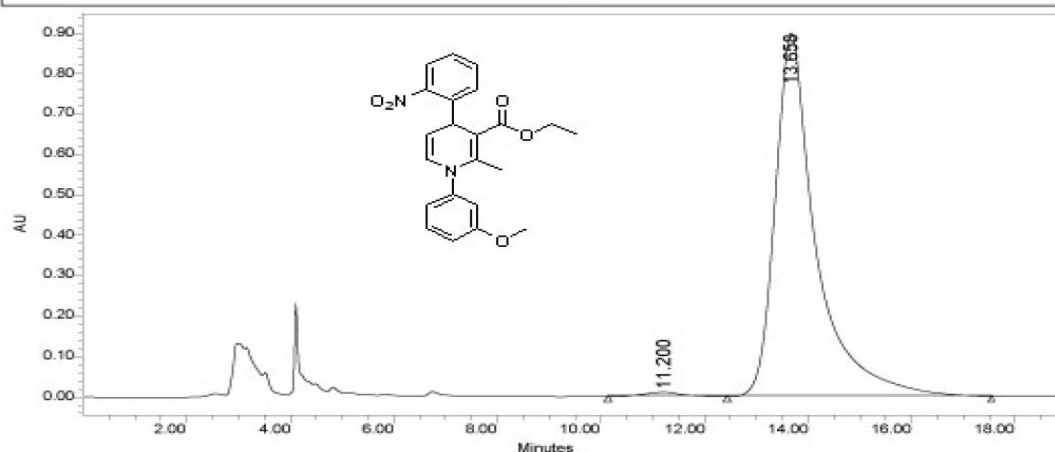


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.272	24930675	49.98	744734	54.39
2	13.768	24948588	50.02	624491	45.61

SAMPLE INFORMATION

Sample Name: 2-NO2-3-OMe-yixianEtzhi-ee5%
 Sample Type: Unknown
 Vial: 1
 Injection #: 3
 Injection Volume: 20.00 ul
 Run Time: 60.00 Minutes

Acquired By: System
 Date Acquired: 10/21/2007 5:02:19 PM
 Acq. Method: yj005
 Date Processed: 10/21/2007 5:21:30 PM
 Channel Name: 2487Channel 1
 Sample Set Name:

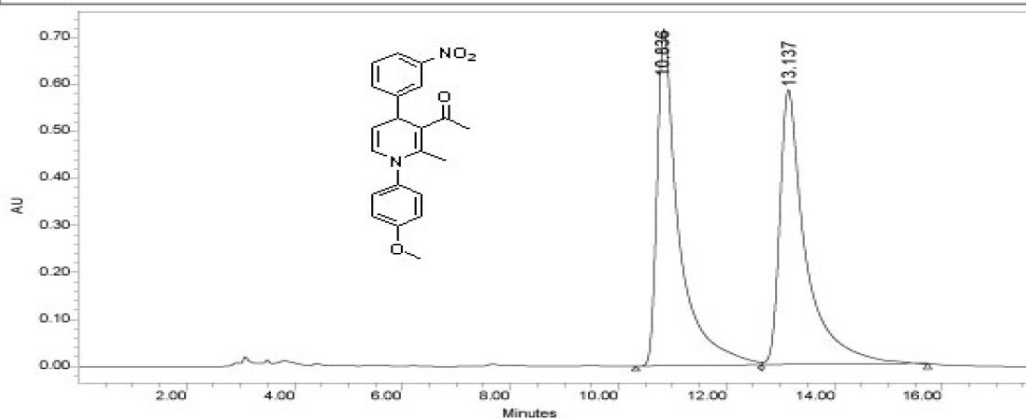


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.200	581113	1.17	11555	1.27
2	13.658	49255959	98.83	899158	98.73

SAMPLE INFORMATION

Sample Name: yj-3no2-yixianbingtong-rac
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 9/15/2007 4:12:35 PM
Acq. Method: jj15
Date Processed: 9/15/2007 4:30:51 PM
Channel Name: 2487Channel 1
Sample Set Name:

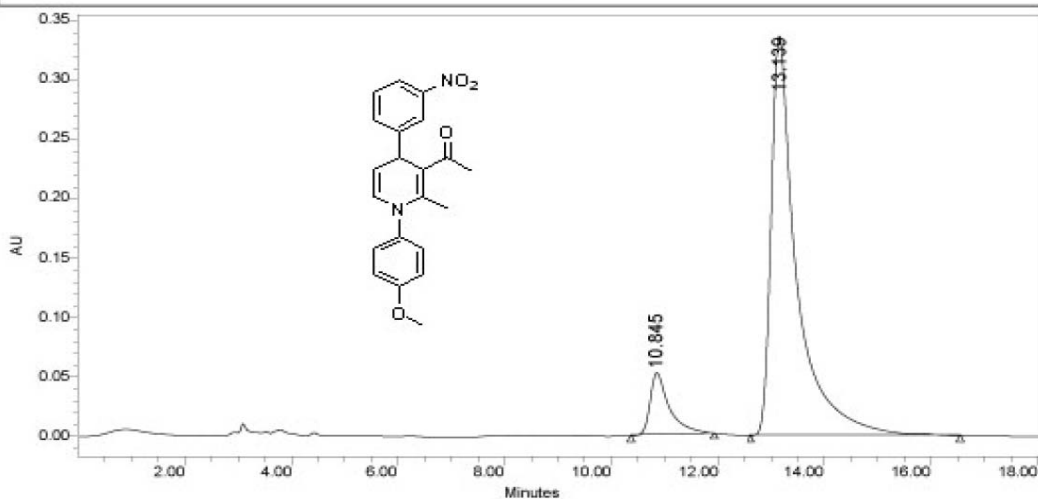


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.836	20137756	50.70	717261	55.02
2	13.137	19584546	49.30	586302	44.98

SAMPLE INFORMATION

Sample Name: yj-3no2-yixianbingtong
Sample Type: Unknown
Vial: 1
Injection #: 2
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 9/15/2007 4:33:54 PM
Acq. Method: jj15
Date Processed: 9/15/2007 4:52:51 PM
Channel Name: 2487Channel 1
Sample Set Name:

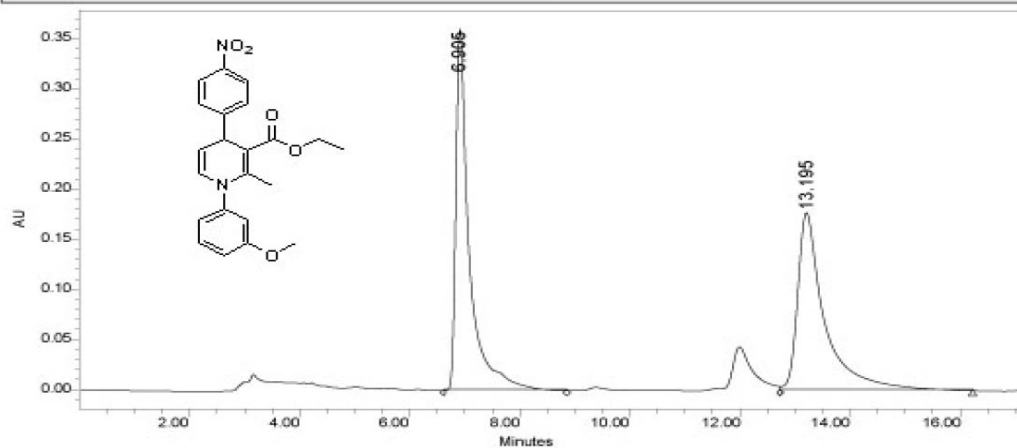


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.845	1331919	10.58	52590	13.51
2	13.139	11257408	89.42	336628	86.49

SAMPLE INFORMATION

Sample Name: rqq-3-CH3O-rac
Sample Type: Unknown
Vial: 1
Injection #: 4
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 9/22/2007 1:21:54 PM
Acq. Method: jj15
Date Processed: 9/22/2007 1:40:18 PM
Channel Name: 2487Channel 1
Sample Set Name:

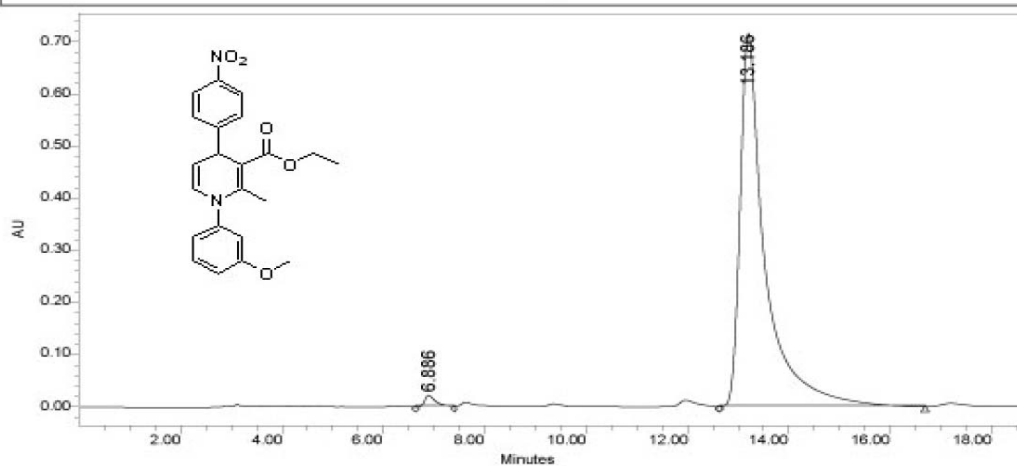


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.905	6141426	50.10	360655	67.00
2	13.195	6115970	49.90	177614	33.00

SAMPLE INFORMATION

Sample Name: rqq-3-CH3O-ee
Sample Type: Unknown
Vial: 1
Injection #: 5
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 9/22/2007 1:40:03 PM
Acq. Method: jj15
Date Processed: 9/22/2007 2:01:44 PM
Channel Name: 2487Channel 1
Sample Set Name:

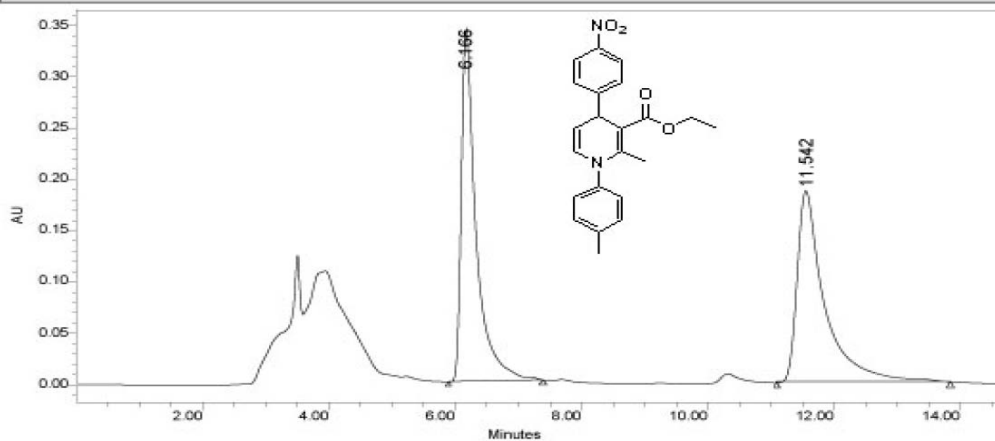


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.886	346470	1.39	22174	3.01
2	13.186	24541790	98.61	715375	96.99

SAMPLE INFORMATION

Sample Name: rqq-3ch3N-rac
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 9/16/2007 4:04:16 PM
Acq. Method: jj15
Date Processed: 9/16/2007 4:19:42 PM
Channel Name: 2487Channel 1
Sample Set Name:

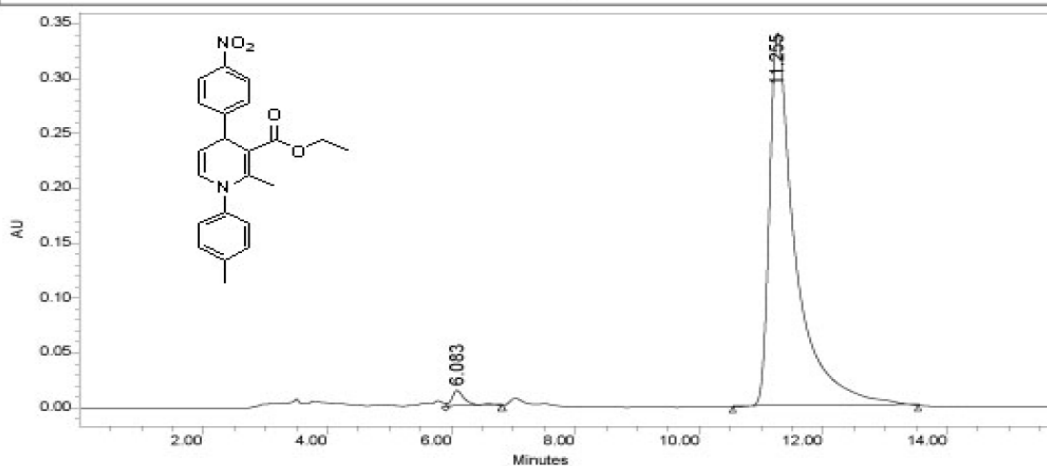


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.166	5586163	49.52	343514	64.74
2	11.542	5693995	50.48	187092	35.26

SAMPLE INFORMATION

Sample Name: rqq-3ch3N2
Sample Type: Unknown
Vial: 1
Injection #: 3
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 9/16/2007 4:51:39 PM
Acq. Method: jj15
Date Processed: 9/16/2007 5:08:22 PM
Channel Name: 2487Channel 1
Sample Set Name:

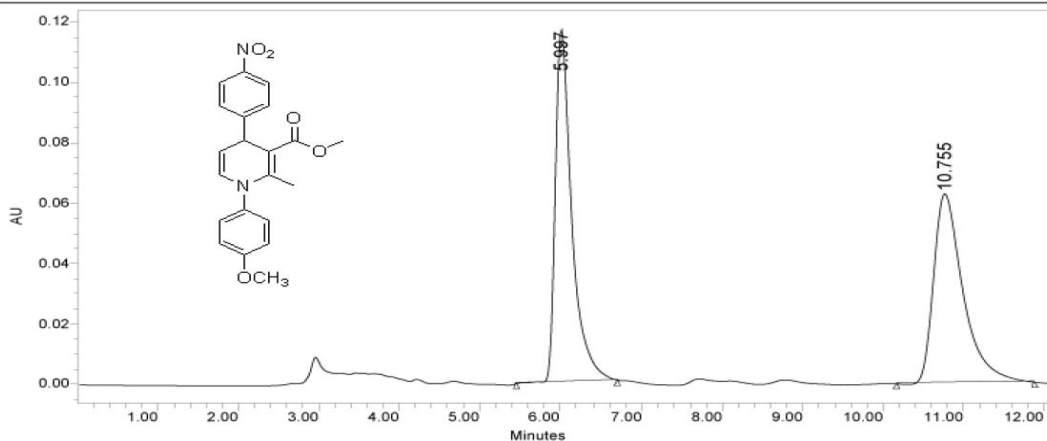


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.083	214735	2.10	14175	3.99
2	11.255	10021595	97.90	341277	96.01

SAMPLE INFORMATION

Sample Name: jj051104-rac
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 5/14/2007 12:49:54 PM
Acq. Method: jiangjun2
Date Processed: 5/14/2007 1:03:27 PM
Channel Name: 2487Channel 1
Sample Set Name:

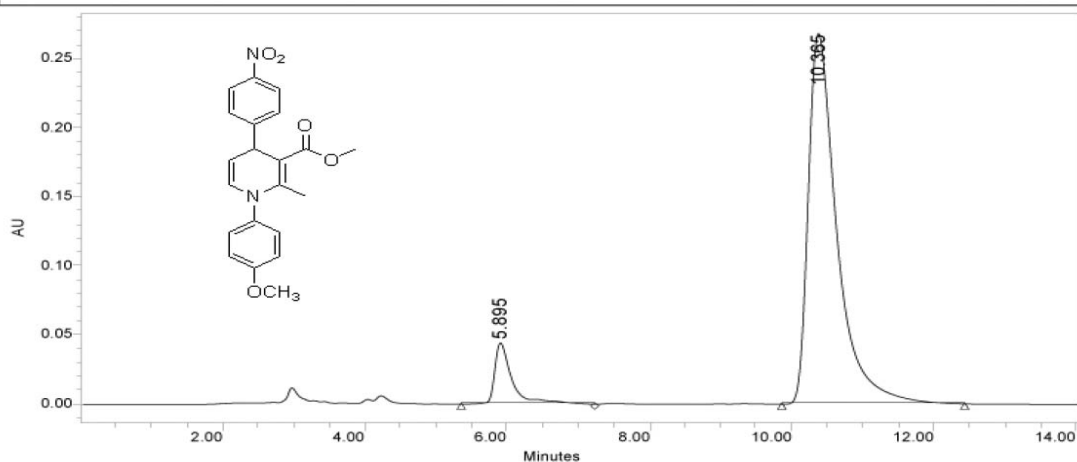


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.997	1661997	50.92	116747	64.98
2	10.755	1601708	49.08	62910	35.02

SAMPLE INFORMATION

Sample Name: 07052401-1
Sample Type: Unknown
Vial: 1
Injection #: 5
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 5/25/2007 11:42:47 PM
Acq. Method: jiangjun2
Date Processed: 5/25/2007 11:57:07 PM
Channel Name: 2487Channel 1
Sample Set Name:

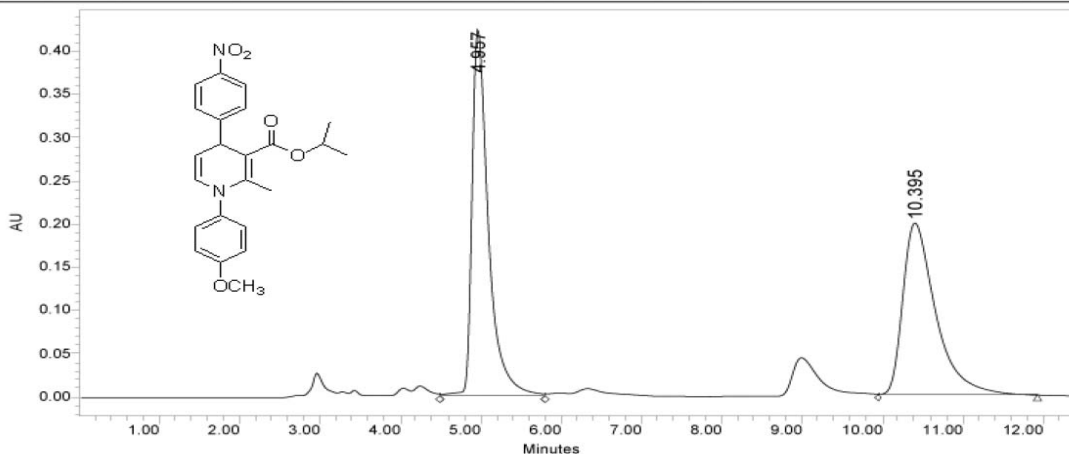


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.895	774115	9.31	44424	14.20
2	10.365	7541015	90.69	268519	85.80

SAMPLE INFORMATION

Sample Name: 07051102-rac
Sample Type: Unknown
Vial: 1
Injection #: 6
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 5/25/2007 11:26:33 AM
Acq. Method: jiangjun2
Date Processed: 5/25/2007 11:39:30 AM
Channel Name: 2487Channel 1
Sample Set Name:

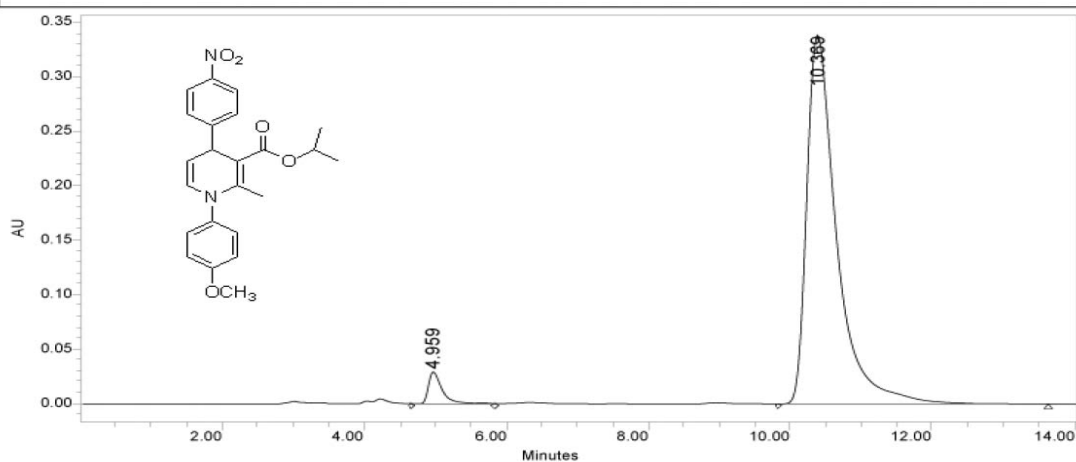


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.957	6065870	51.34	426337	68.08
2	10.395	5749850	48.66	199852	31.92

SAMPLE INFORMATION

Sample Name: 07052402-3
Sample Type: Unknown
Vial: 1
Injection #: 4
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 5/25/2007 11:25:05 PM
Acq. Method: jiangjun2
Date Processed: 5/25/2007 11:39:23 PM
Channel Name: 2487Channel 1
Sample Set Name:

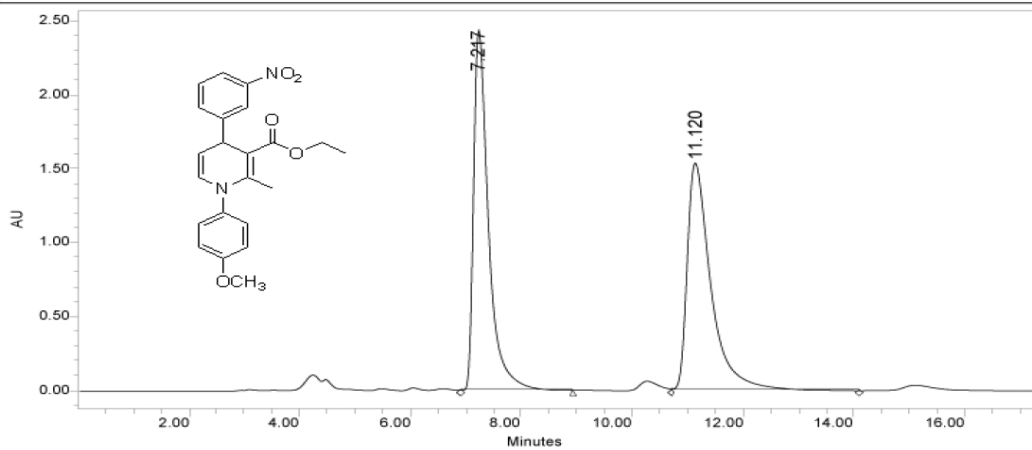


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.959	410413	3.99	29467	8.00
2	10.369	9864057	96.01	338646	92.00

SAMPLE INFORMATION

Sample Name: 3-NO₂-yizhi-rac
 Sample Type: Unknown
 Vial: 1
 Injection #: 1
 Injection Volume: 20.00 ul
 Run Time: 60.00 Minutes

Acquired By: System
 Date Acquired: 6/16/2007 3:33:33 PM
 Acq. Method: jj15
 Date Processed: 6/16/2007 3:51:25 PM
 Channel Name: 2487Channel 1
 Sample Set Name:

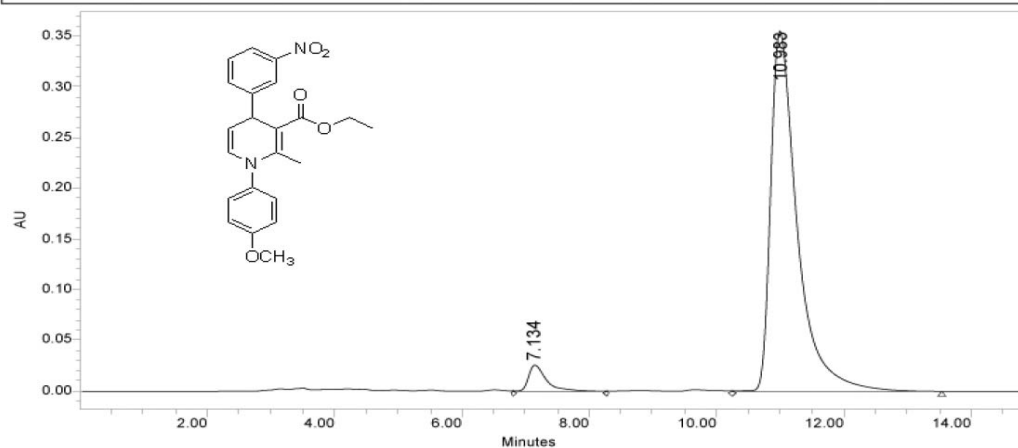


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.217	45390754	49.58	2434098	61.26
2	11.120	46151114	50.42	1539117	38.74

SAMPLE INFORMATION

Sample Name: 3-NO₂-yizhi
 Sample Type: Unknown
 Vial: 1
 Injection #: 1
 Injection Volume: 20.00 ul
 Run Time: 60.00 Minutes

Acquired By: System
 Date Acquired: 6/16/2007 5:19:15 PM
 Acq. Method: jj15
 Date Processed: 6/16/2007 5:34:39 PM
 Channel Name: 2487Channel 1
 Sample Set Name:

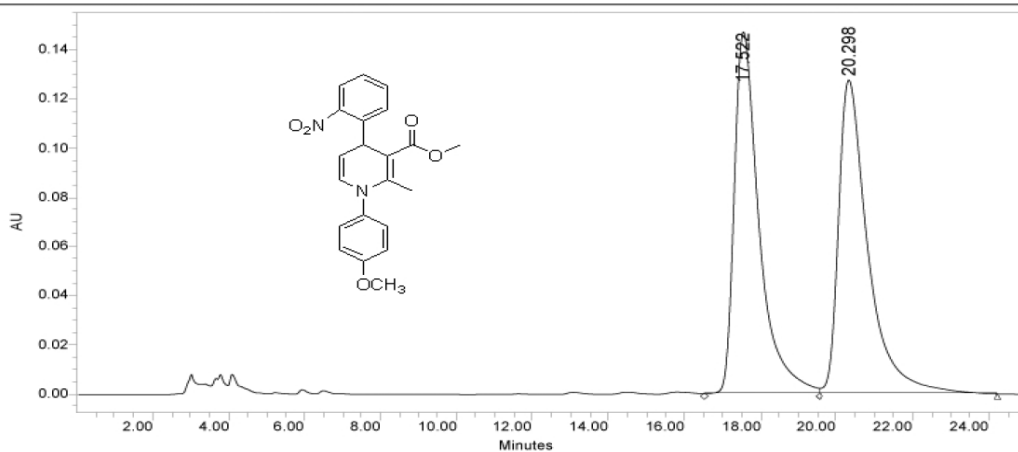


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.134	512886	4.73	25900	6.79
2	10.983	10325579	95.27	355576	93.21

USTC

Project Name: jiangjun
Reported by User: System*Breeze*

SAMPLE INFORMATION

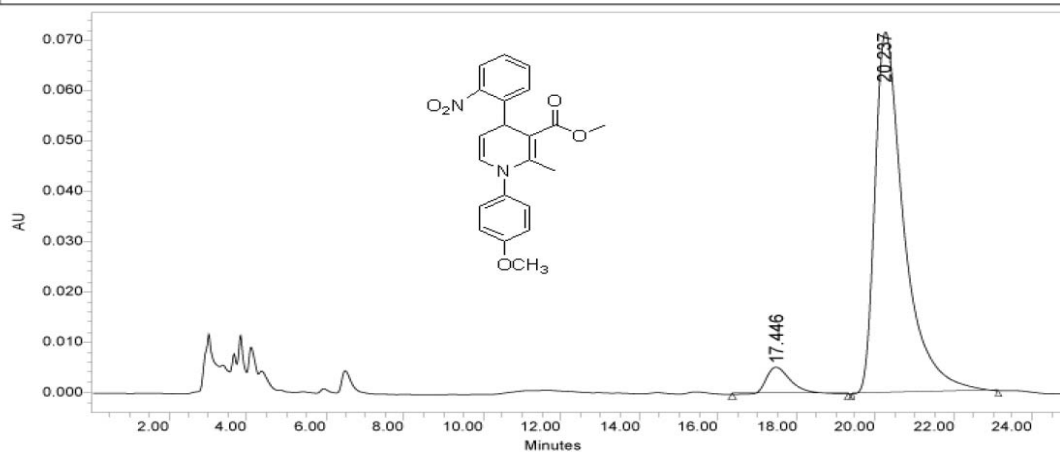
Sample Name: 07052505-rac01
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 60.00 MinutesAcquired By: System
Date Acquired: 5/26/2007 4:36:00 PM
Acq. Method: yj005
Date Processed: 5/26/2007 5:01:21 PM
Channel Name: 2487Channel 1
Sample Set Name:

	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	17.522	6760859	49.39	147431	53.56
2	20.298	6929088	50.61	127826	46.44

USTC

Project Name: jiangjun
Reported by User: System*Breeze*

SAMPLE INFORMATION

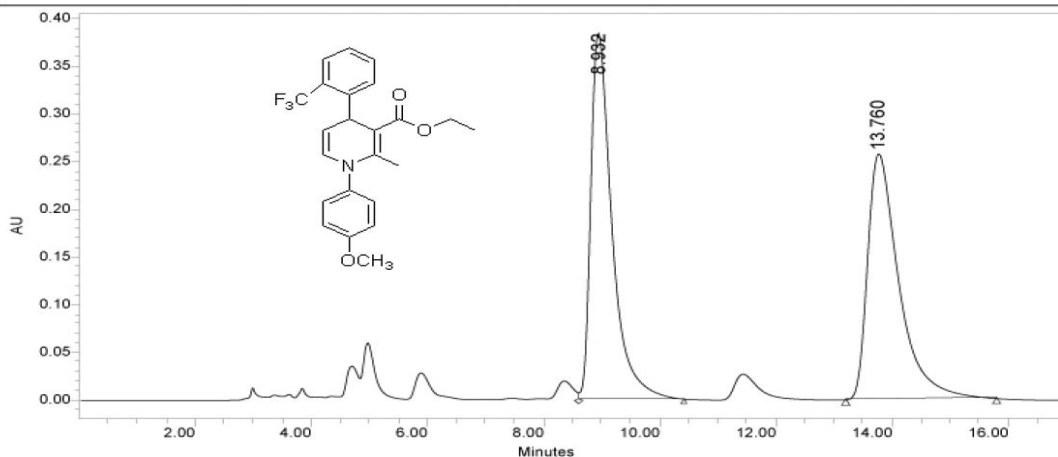
Sample Name: 07052505
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 60.00 MinutesAcquired By: System
Date Acquired: 5/26/2007 8:59:55 PM
Acq. Method: yj005
Date Processed: 5/26/2007 9:25:33 PM
Channel Name: 2487Channel 1
Sample Set Name:

	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	17.446	242257	6.14	5390	6.98
2	20.237	3703031	93.86	71885	93.02

SAMPLE INFORMATION

Sample Name: 2,CF3-yizhi-rac2
Sample Type: Unknown
Vial: 1
Injection #: 2
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 6/21/2007 9:48:39 PM
Acq. Method: yj005
Date Processed: 6/21/2007 10:06:23 PM
Channel Name: 2487Channel 1
Sample Set Name:

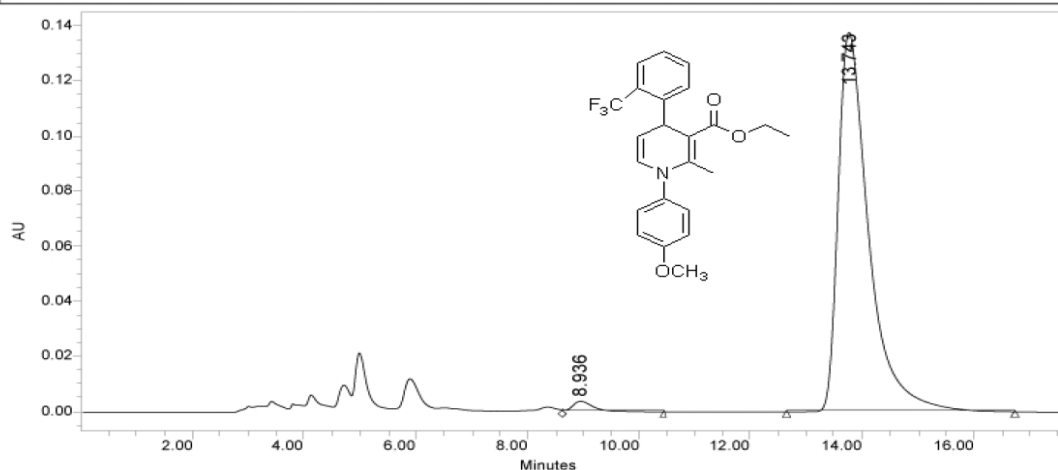


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.932	9699765	50.13	383259	59.81
2	13.760	9647997	49.87	257506	40.19

SAMPLE INFORMATION

Sample Name: 2,CF3-yizhi-2
Sample Type: Unknown
Vial: 1
Injection #: 3
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

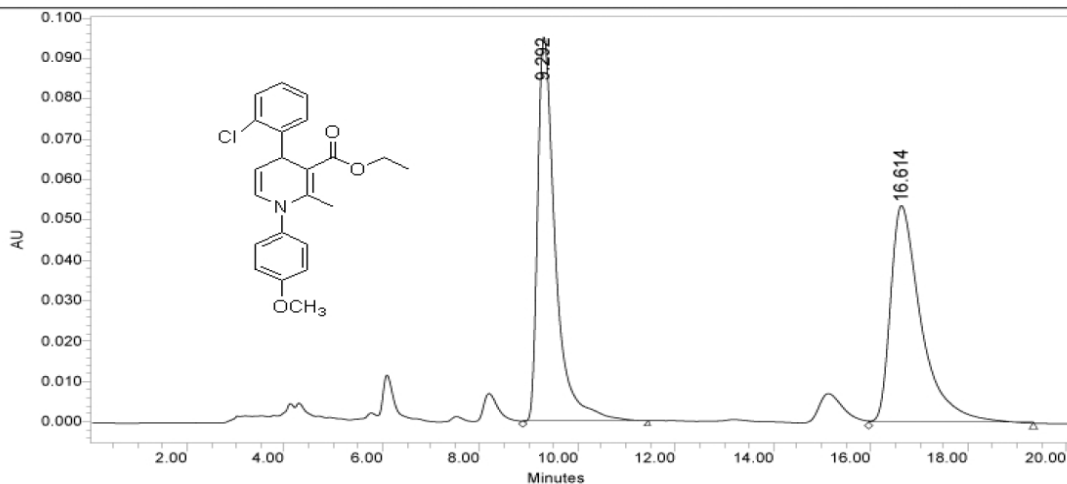
Acquired By: System
Date Acquired: 6/21/2007 10:25:54 PM
Acq. Method: yj005
Date Processed: 6/21/2007 10:44:00 PM
Channel Name: 2487Channel 1
Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.936	106919	1.99	3903	2.75
2	13.743	5257859	98.01	137767	97.25

SAMPLE INFORMATION

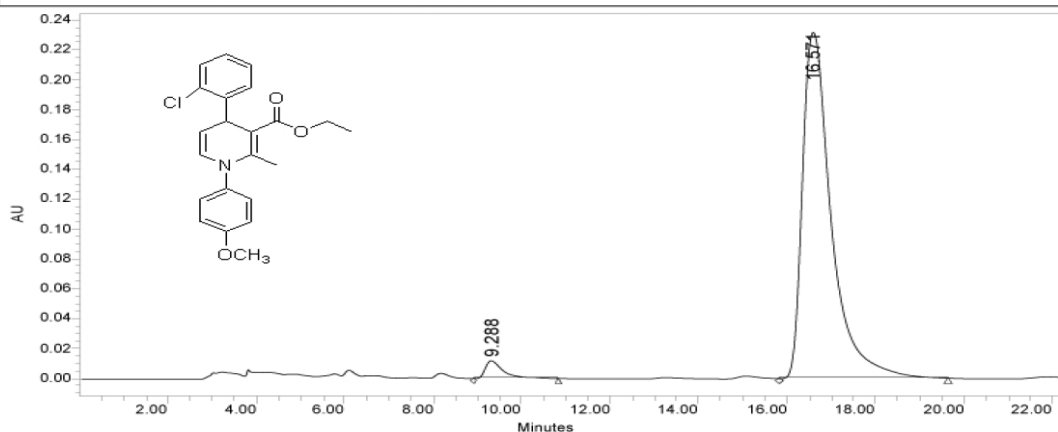
Sample Name:	2cl-yizhi-rac3	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	6/23/2007 1:36:41 PM
Vial:	1	Acq. Method:	yj005
Injection #:	2	Date Processed:	6/23/2007 1:57:24 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	60.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.292	2391426	50.17	95097	63.88
2	16.614	2375325	49.83	53764	36.12

SAMPLE INFORMATION

Sample Name:	2cl-yizhi2	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	6/23/2007 2:01:37 PM
Vial:	1	Acq. Method:	yj005
Injection #:	3	Date Processed:	6/23/2007 2:24:25 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	60.00 Minutes	Sample Set Name:	

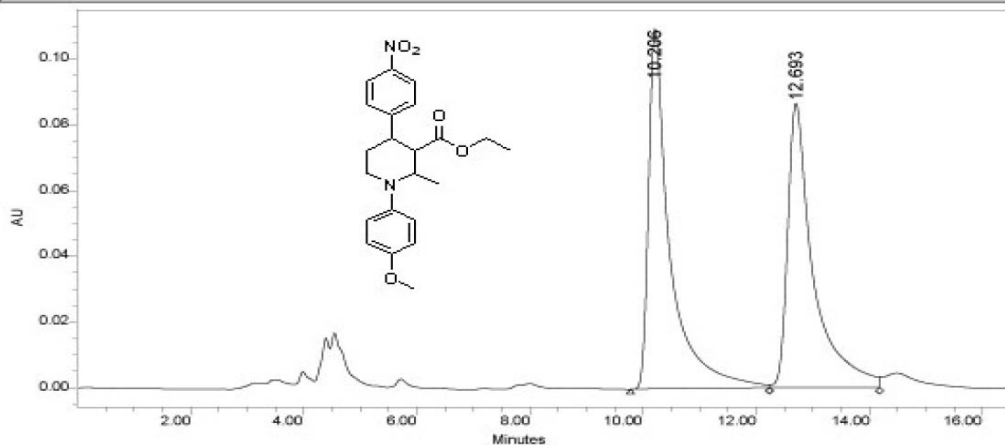


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.288	346247	3.19	11931	4.89
2	16.571	10501702	96.81	231899	95.11

SAMPLE INFORMATION

Sample Name: 6H-pyridine-rac
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 10/27/2007 9:17:59 PM
Acq. Method: jj15
Date Processed: 10/27/2007 9:35:02 PM
Channel Name: 2487Channel 1
Sample Set Name:

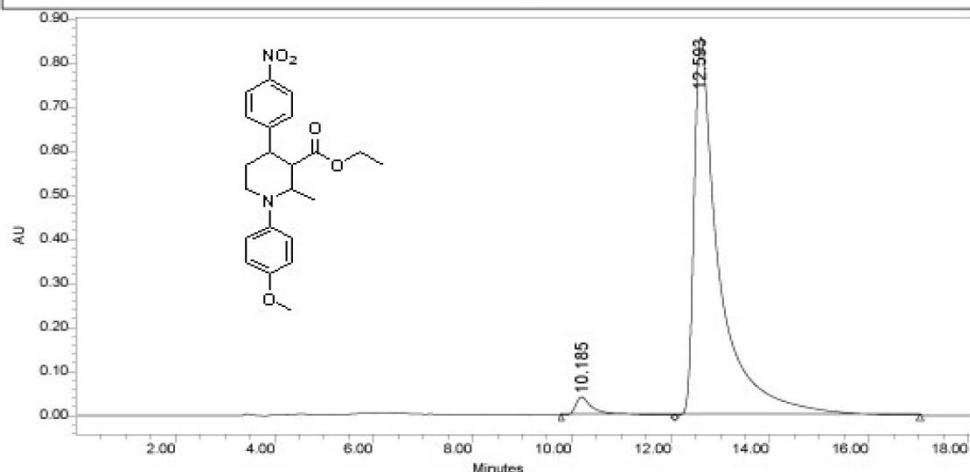


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.206	2898256	51.37	109710	55.82
2	12.693	2744136	48.63	86827	44.18

SAMPLE INFORMATION

Sample Name: 6H-pyridine
Sample Type: Unknown
Vial: 1
Injection #: 2
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

Acquired By: System
Date Acquired: 10/27/2007 9:36:42 PM
Acq. Method: jj15
Date Processed: 10/27/2007 9:55:07 PM
Channel Name: 2487Channel 1
Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.185	1088532	3.45	41291	4.58
2	12.593	30470386	96.55	859663	95.42