Supporting Information for

Intramolecular Michael Addition Reaction for the Synthesis of Benzylbutyrolactones

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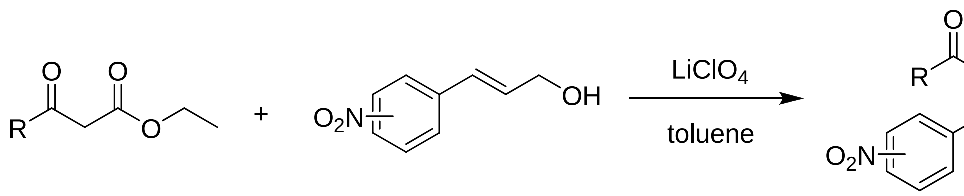
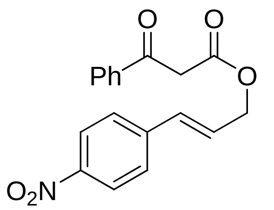
General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. The peaks with * indicate those of the enol isomer. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

General Procedures for the Synthesis of β-Ketoesters 3:

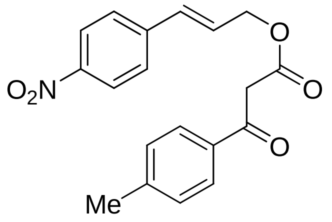


3a is used as an example: Ethyl benzoylacetate (960 mg, 5 mmol), (*E*)-3-(4-nitrophenyl)prop-2-en-1-ol (895 mg, 5 mmol) and lithium perchlorate (160 mg, 1 mmol) in toluene (20 mL) was heated to 100 °C in a round bottom flask with distillation condenser to remove ethanol. After the reaction was complete (monitored by TLC), the reaction mixture was cooled, filtered. The filtrate was concentrated and the residue was purified by silica gel column chromatography (PE / EtOAc = 30 / 1) to afford the pure compound **3a**.



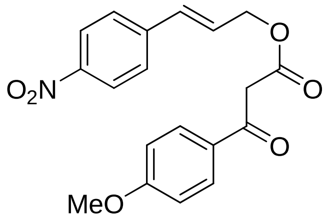
3a

Yellow solid, yield 51% (ketone : enol = 4.0:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.09 (s, 2 H), 4.87 (d, *J* = 6.6 Hz, 2 H), 4.92* (d, *J* = 6.0 Hz, 2 H), 5.74* (s, 1 H), 6.42 (dt, *J* = 15.6, 6.0 Hz, 1 H), 6.51* (dt, *J* = 16.2, 5.7 Hz, 1 H), 6.69 (d, *J* = 16.2 Hz, 1 H), 6.76* (d, *J* = 15.9 Hz, 1 H), 7.46-7.63 (m, 5 H), 7.42-7.81* (m, 9 H), 7.96 (d, *J* = 7.5 Hz, 2 H), 8.16 (d, *J* = 8.7 Hz, 2 H), 12.46* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.7, 63.9, 64.9, 86.7, 123.8, 126.0, 127.0, 127.5, 128.0, 128.4, 128.5, 128.7, 131.1, 131.2, 131.4, 133.8, 135.7, 142.4, 147.0, 167.1, 192.2; IR (thin film): ν_{max} (cm^{-1}) = 2978, 1723, 1683, 1338, 1280, 1155, 1113, 979, 952, 685; MS (EI, *m/z*, rel. intensity) 325 (M^+, 1), 105 (100); Anal. calcd for $C_{18}H_{15}NO_5$: C, 66.46; N, 4.31; H, 4.65; Found: C, 66.60; N, 4.11; H, 4.71; m.p. 54-56 ^{o}C.



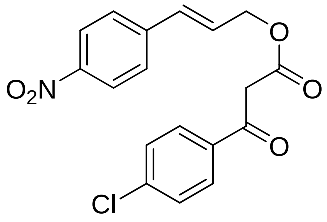
3b

Yellow oil, yield 51% (ketone : enol = 4.2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40* (s, 3 H), 2.42 (s, 3 H), 4.06 (s, 2 H), 4.87 (d, *J* = 6.0 Hz, 2 H), 4.91* (d, *J* = 6.0 Hz, 2 H), 5.71* (s, 1 H), 6.42 (dt, *J* = 15.6, 6.0 Hz, 1 H), 6.52* (dt, *J* = 16.2, 5.7 Hz, 1 H), 6.68 (d, *J* = 16.2 Hz, 1 H), 6.76* (d, *J* = 15.9 Hz, 1 H), 7.23* (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.7 Hz, 2 H), 7.54* (d, *J* = 8.7 Hz, 2 H), 7.69* (d, *J* = 8.1 Hz, 2 H), 7.86 (d, *J* = 8.1 Hz, 2 H), 8.17 (d, *J* = 9.0 Hz, 2 H), 8.33* (d, *J* = 8.4 Hz, 2 H), 12.45* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 45.7, 63.8, 64.9, 86.0, 123.9, 126.0, 127.1, 127.6, 128.5, 129.2, 129.4, 130.4, 131.2, 133.3, 142.5, 144.9, 147.1, 167.2, 191.8; IR (thin film): ν_{max} (cm^{-1}) = 2959, 2922, 2852, 1744, 1681, 1606, 1517, 1459, 1343, 1265, 1181, 1146, 739; MS (EI, *m/z*, rel. intensity) 339 (M^+, 3), 119 (100); HRMS (EI) calcd for $C_{19}H_{17}NO_5$ (M^+): 339.1107. Found: 339.1103.



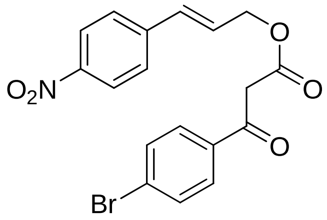
3c

Yellow solid, yield 42%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3 H), 4.04 (s, 2 H), 4.87 (t, *J* = 6.0 Hz, 2 H), 6.42 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.69 (d, *J* = 15.9 Hz, 1 H), 6.96 (d, *J* = 9.0 Hz, 2 H), 7.49 (d, *J* = 9.0 Hz, 2 H), 7.95 (d, *J* = 8.7 Hz, 2 H), 8.18 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.3, 55.3, 64.7, 113.7, 123.6, 126.9, 127.5, 128.6, 130.6, 130.8, 142.3, 146.8, 163.8, 167.2, 190.6; IR (thin film): ν_{max} (cm^{-1}) = 2974, 1728, 1675, 1600, 1500, 1329, 1267, 1168, 1153, 1108, 1070, 994, 827, 737; MS (EI, *m/z*, rel. intensity) 355 (M^+, 1), 135 (100); Anal. calcd for $C_{19}H_{17}NO_6$: C, 64.22; N, 3.94; H, 4.82; Found: C, 64.12; N, 3.82; H, 4.90; m.p. 93-95 ^{o}C.



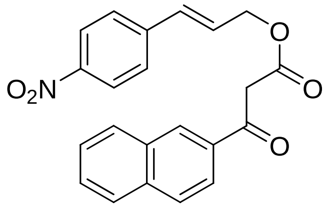
3d

Yellow solid, yield 75% (ketone : enol = 2.8:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07 (s, 2 H), 4.87 (dd, *J* = 6.0, 1.2 Hz, 2 H), 4.92* (dd, *J* = 6.0, 1.2 Hz, 2 H), 5.72* (s, 1 H), 6.42 (dt, *J* = 15.6, 6.0 Hz, 1 H), 6.51* (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.69 (d, *J* = 16.2 Hz, 1 H), 6.76* (d, *J* = 15.9 Hz, 1 H), 7.38-7.55 (m, 4 H), 7.71-7.74* (m, 4 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.89* (d, *J* = 8.9 Hz, 2 H), 8.17 (d, *J* = 9.0 Hz, 2 H), 8.18* (d, *J* = 8.7 Hz, 2 H), 12.45* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.6, 64.0, 65.0, 87.0, 123.8, 127.0, 127.3, 127.9, 128.7, 129.0, 129.8, 131.1, 131.3, 131.4, 134.0, 137.4, 140.3, 142.3, 142.4, 147.0, 166.8, 170.6, 172.4, 191.0; IR (thin film): ν_{max} (cm^{-1}) = 2959, 2922, 2852, 1744, 1681, 1606, 1517, 1459, 1343, 1265, 1181, 1146, 739; MS (EI, *m/z*, rel. intensity) 359 (M^+, 3), 119 (100); Anal. calcd for $C_{18}H_{14}NO_5Cl$: C, 60.09; N, 3.89; H, 3.92; Found: C, 60.04; N, 3.72; H, 3.99; m.p. 68-70 ^{o}C.



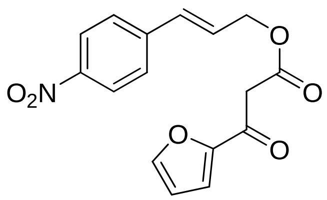
3e

Yellow solid, yield 31% (ketone : enol = 2.9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07 (s, 2 H), 4.87 (d, *J* = 6.0 Hz, 2 H), 4.92* (d, *J* = 5.7 Hz, 2 H), 5.72* (s, 1 H), 6.41 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.51* (dt, *J* = 16.2, 5.7 Hz, 1 H), 6.68 (d, *J* = 15.6 Hz, 1 H), 6.75* (d, *J* = 15.9 Hz, 1 H), 7.47 (d, *J* = 8.7 Hz, 2 H), 7.52* (d, *J* = 3.6 Hz, 2 H), 7.55* (d, *J* = 2.4 Hz, 2 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.63* (d, *J* = 14.7 Hz, 2 H), 7.82 (d, *J* = 8.7 Hz, 2 H), 8.15 (d, *J* = 8.7 Hz, 2 H), 8.17* (d, *J* = 8.4 Hz, 2 H), 12.44* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.6, 64.0, 65.0, 87.0, 123.8, 125.9, 127.0, 127.3, 127.4, 127.9, 129.1, 129.8, 131.1, 131.3, 131.7, 132.0, 134.4, 142.3, 142.4, 147.0, 166.7, 170.6, 172.4, 191.2; IR (thin film): ν_{max} (cm^{-1}) = 3057, 1735, 1675, 1584, 1508, 1349, 1318, 1147, 992, 808; MS (EI, *m/z*, rel. intensity) 403 (M^+, 1), 183 (100); Anal. calcd for $C_{18}H_{14}NO_5Br$: C, 53.49; N, 3.47; H, 3.49; Found: C, 53.60; N, 3.16; H, 3.81; m.p. 45-47 °C.



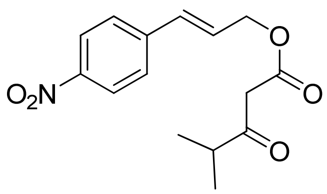
3f

Yellow oil, yield 71% (ketone : enol = 4.2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.22 (s, 2 H), 4.88 (d, *J* = 6.0 Hz, 2 H), 4.95* (d, *J* = 6.0 Hz, 2 H), 5.89* (s, 1 H), 6.38 (dt, *J* = 16.2, 6.0 Hz, 1 H), 6.54* (dt, *J* = 15.9, 5.7 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.56 (t, *J* = 7.5 Hz, 2 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.78-8.05* (m, 9 H), 7.87-8.05 (m, 4 H), 8.13 (d, *J* = 9.0 Hz, 2 H), 8.20* (d, *J* = 8.7 Hz, 2 H), 8.39* (s, 1 H), 8.47 (s, 1 H), 12.54* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.9, 64.0, 65.0, 87.2, 122.4, 123.7, 123.8, 123.9, 126.7, 126.8, 127.0, 127.4, 127.6, 127.8, 128.1, 128.3, 128.7, 129.0, 129.6, 130.6, 131.2, 131.3, 132.3, 133.1, 135.8, 142.4, 147.0, 167.2, 192.1; IR (thin film): ν_{max} (cm^{-1}) = 3062, 1761, 1615, 1516, 1339, 1228, 1177, 1155, 1067, 798, 742; MS (EI, *m/z*, rel. intensity) 375 (M^+, 1), 155 (100); HRMS (EI) calcd for $C_{22}H_{17}NO_5$ (M^+): 375.1107. Found: 375.1094.



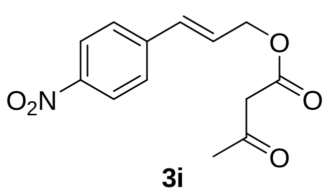
3g

Yellow solid, yield 42% (ketone : enol = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97 (s, 2 H), 4.87 (dd, *J* = 5.7, 1.2 Hz, 2 H), 6.45 (dt, *J* = 16.2, 6.0 Hz, 1 H), 6.60 (dd, *J* = 3.3, 1.5 Hz, 1 H), 6.71 (d, *J* = 15.9 Hz, 1 H), 7.32 (d, *J* = 3.9 Hz, 1 H), 7.51 (d, *J* = 8.7 Hz, 2 H), 7.65 (s, 1 H), 8.16 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.0, 64.8, 112.6, 118.4, 123.7, 126.9, 127.4, 131.0, 142.4, 146.9, 147.1, 151.5, 166.4, 180.6; IR (thin film): ν_{max} (cm^{-1}) = 1712, 1668, 1597, 1514, 1506, 1338, 1215, 1166, 1108, 1019, 778 745; MS (EI, *m/z*, rel. intensity) 95 (100); Anal. calcd for $C_{16}H_{13}NO_6$: C, 60.95; N, 4.44; H, 4.16; Found: C, 60.72; N, 4.41; H, 4.44; m.p. 67-70 ^{o}C.



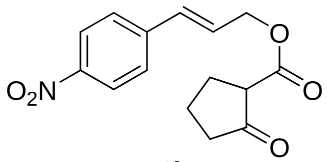
3h

Yellow oil, yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, *J* = 6.6 Hz, 6 H), 2.67-2.81 (m, 1 H), 3.60 (s, 2 H), 4.85 (d, *J* = 5.7 Hz, 2 H), 6.45 (dt, *J* = 16.2, 6.0 Hz, 1 H), 6.75 (d, *J* = 15.9 Hz, 1 H), 7.53 (d, *J* = 9.0 Hz, 2 H), 8.19 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 41.3, 46.8, 64.8, 123.9, 127.1, 127.6, 131.4, 142.5, 147.1, 167.0, 206.3; IR (thin film): ν_{max} (cm^{-1}) = 2974, 1749, 1714, 1519, 1345, 1155, 975, 862, 740; MS (EI, *m/z*, rel. intensity) 116 (100); Anal. calcd for $C_{15}H_{17}NO_5$: C, 61.85; N, 4.81; H, 5.88; Found: C, 61.68; N, 4.69; H, 6.03.



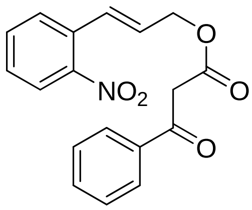
3i

Yellow oil, yield 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3 H), 3.57 (s, 2 H), 4.86 (d, *J* = 4.8 Hz, 2 H), 6.46 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.75 (d, *J* = 16.2 Hz, 1 H), 7.53 (d, *J* = 9.0 Hz, 2 H), 8.19 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.2, 49.8, 64.9, 123.9, 127.1, 127.4, 131.5, 142.4, 147.1, 166.6, 200.3; IR (thin film): ν_{max} (cm^{-1}) = 2939, 1745, 1718, 1598, 1518, 1345, 1320, 1263, 1151, 1110, 971, 862, 742; MS (EI, *m/z*, rel. intensity) 263 (M^+, 1), 179 (100); Anal. calcd for $C_{13}H_{13}NO_5$: C, 59.31; N, 5.32; H, 4.98; Found: C, 59.42; N, 5.01; H, 5.29.



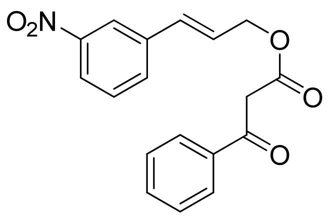
3j

Yellow oil, yield 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86-1.98 (m, 1 H), 2.11-2.23 (m, 1 H), 2.32-2.44 (m, 4 H), 3.25 (t, *J* = 9.0 Hz, 1 H), 4.79-4.94 (m, 2 H), 6.45 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.77 (d, *J* = 15.9 Hz, 1 H), 7.53 (d, *J* = 9.0 Hz, 2 H), 8.19 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 27.2, 38.0, 54.7, 64.9, 123.9, 127.1, 127.7, 131.1, 142.5, 147.0, 168.9, 212.1; IR (thin film): ν_{max} (cm^{-1}) = 2970, 1755, 1728, 1598, 1518, 1344, 1181, 1110, 977, 861, 740; MS (EI, *m/z*, rel. intensity) 289 (M^{+}, 1), 116 (100); Anal. calcd for $C_{15}H_{15}NO_5$: C, 62.28; N, 4.84; H, 5.23; Found: C, 62.19; N, 4.67; H, 5.41.



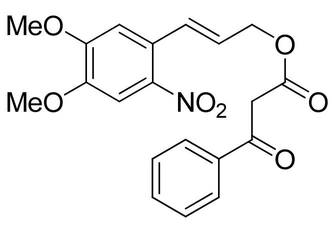
3k

Red oil, yield 72% (ketone : enol = 3.7:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.08 (s, 2 H), 4.84 (d, *J* = 6.0 Hz, 2 H), 4.88* (d, *J* = 6.3 Hz, 2 H), 5.73* (s, 1 H), 6.22 (dt, *J* = 15.6, 6.0 Hz, 1 H), 6.31* (dt, *J* = 15.9, 5.7 Hz, 1 H), 7.08 (d, *J* = 15.9 Hz, 1 H), 7.15* (d, *J* = 15.9 Hz, 1 H), 7.36-7.58 (m, 6 H), 7.31-7.58* (m, 7 H), 7.76* (d, *J* = 6.6 Hz, 2 H), 7.89 (d, *J* = 8.1 Hz, 1 H), 7.94 (d, *J* = 7.8 Hz, 2 H), 12.46* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.4, 63.9, 64.8, 86.6, 124.2, 125.7, 127.8, 128.1, 128.3, 128.5, 128.6, 131.2, 131.5, 132.7, 133.0, 133.5, 135.5, 147.3, 166.9, 171.5, 172.4, 192.1; IR (thin film): ν_{max} (cm^{-1}) = 3068, 2935, 1744, 1687, 1525, 1450, 1346, 1265, 1211, 1185, 1145, 969, 859, 690; MS (EI, *m/z*, rel. intensity) 325 (M^{+}, 1), 105 (100); Anal. calcd for $C_{18}H_{15}NO_5$: C, 66.46; N, 4.31; H, 4.65; Found: C, 66.40; N, 4.10; H, 4.76.



3l

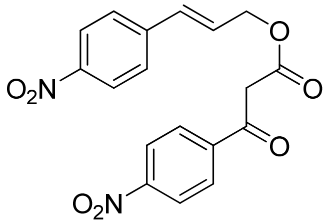
Yellow oil, yield 69% (ketone : enol = 4.1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.10 (s, 2 H), 4.86 (d, *J* = 5.7 Hz, 2 H), 4.90* (d, *J* = 5.7 Hz, 2 H), 5.75* (s, 1 H), 6.37 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.47* (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.64 (d, *J* = 16.2 Hz, 1 H), 6.74* (d, *J* = 16.2 Hz, 1 H), 7.41-7.51 (m, 3 H), 7.41-7.71* (m, 6 H), 7.58-7.68 (m, 2 H), 7.78* (d, *J* = 7.2 Hz, 2 H), 7.96 (d, *J* = 7.5 Hz, 2 H), 8.06 (d, *J* = 8.1 Hz, 1 H), 8.13 (s, 1 H), 8.22* (s, 1 H), 12.46* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.6, 63.9, 64.8, 86.7, 120.9, 122.3, 125.8, 125.9, 126.4, 128.3, 128.4, 128.6, 129.3, 131.0, 131.3, 132.2, 132.9, 133.7, 135.6, 137.6, 137.7, 148.2, 167.0, 171.8, 172.5, 192.2, ; IR (thin film): ν_{max} (cm^{-1}) = 2938, 1744, 1685, 1531, 1450, 1352, 1266,, 1211, 1187, 1145, 969, 733, 689; MS (EI, *m/z*, rel. intensity) 325 (M^+, 1), 105 (100); Anal. calcd for $C_{18}H_{15}NO_5$: C, 66.46; N, 4.31; H, 4.65; Found: C, 66.45; N, 4.21; H, 4.89.



3m

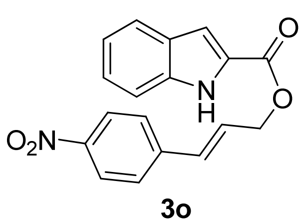
Red oil, yield 47% (ketone : enol = 4.6:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 3 H), 3.94* (s, 3 H), 3.99 (s, 3 H), 4.00* (s, 3 H), 4.09 (s, 2 H), 4.87 (dd, *J* = 6.3, 1.2 Hz, 2 H), 4.92* (dd, *J* = 6.3, 1.2 Hz, 2 H), 5.74* (s, 1 H), 6.17 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.26* (dt, *J* = 15.6, 6.0 Hz, 1 H), 6.95 (d, *J* = 10.2 Hz, 1 H), 7.24 (d, *J* = 15.6 Hz, 1 H), 7.34-7.70* (m, 6 H), 7.42-7.62 (m, 4 H), 7.78* (d, *J* = 8.1 Hz, 2 H), 7.95 (d, *J* = 7.8 Hz, 2 H), 12.48* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.6, 56.2, 56.3, 64.2, 65.3, 86.8, 107.4, 109.8, 109.9, 125.9, 126.5, 126.9, 127.0, 128.3, 128.4, 128.7, 130.1, 130.4, 131.3, 133.7, 135.6, 139.9, 148.3, 152.9, 167.2, 171.7, 192.2; IR (thin film):

ν_{max} (cm^{-1}) = 2938, 2852, 1743, 1687, 1575, 1520, 1450, 1331, 1276, 1217, 1187, 1070, 1001, 966, 796, 758, 690; MS (EI, *m/z*, rel. intensity) 385 (M^+, 4), 105 (100); HRMS (EI) calcd for $C_{20}H_{19}NO_7$ (M^+): 385.1162. Found: 385.1154.



3n

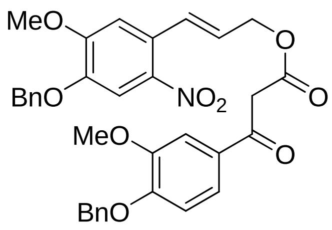
Yellow solid, yield 31% (ketone : enol = 1:1.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 2 H), 4.88 (dd, *J* = 6.0, 1.5 Hz, 2 H), 4.96* (dd, *J* = 6.0, 1.5 Hz, 2 H), 5.85* (s, 1 H), 6.43 (dt, *J* = 16.0, 6.0 Hz, 1 H), 6.52* (dt, *J* = 16.0, 6.0 Hz, 1 H), 6.29 (d, *J* = 16.0 Hz, 1 H), 6.78* (d, *J* = 16.0 Hz, 1 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 7.55* (d, *J* = 8.8 Hz, 2 H), 7.96* (d, *J* = 8.4 Hz, 2 H), 8.13 (d, *J* = 8.8 Hz, 2 H), 8.18 (d, *J* = 8.8 Hz, 2 H), 8.20* (d, *J* = 8.8 Hz, 2 H), 8.28* (d, *J* = 8.8 Hz, 2 H), 8.34 (d, *J* = 9.2 Hz, 2 H), 12.43* (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 46.0, 64.4, 65.4, 89.7, 123.8, 124.0, 127.0, 127.1, 127.2, 127.6, 129.6, 131.7, 132.0, 139.0, 140.1, 142.3, 142.4, 147.3, 149.3, 150.6, 166.4, 168.9, 172.1, 190.8; IR (thin film): ν_{max} (cm^{-1}) = 2936, 1646, 1594, 1514, 1425, 1340, 1298, 1195, 1076, 860, 834, 743; MS (EI, *m/z*, rel. intensity) 393 (M^+Na); HRMS (EI) calcd for $C_{18}H_{14}N_2O_7$ (M^+): 370.0801. Found: 370.0798; m.p. 106-109 ^{o}C.



3o

Red solid, yield 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (dd, *J* = 5.6, 1.2 Hz, 2 H), 6.58 (dt, *J* = 16.0, 6.0 Hz, 1 H), 6.81 (d, *J* = 16.4 Hz, 1 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 7.26-7.36 (m, 2 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 7.55 (d, *J* = 8.8 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 1 H), 8.20 (d, *J* = 8.4 Hz, 2 H), 8.97 (br, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

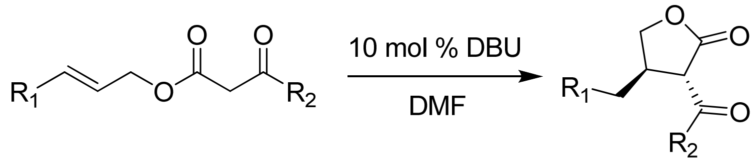
64.6, 109.3, 111.9, 121.0, 122.7, 124.0, 125.7, 126.7, 127.2, 127.4, 128.0, 131.6, 137.0, 142.5, 147.3, 161.6; IR (thin film): ν_{max} (cm^{-1}) = 3321, 1689, 1517, 1342, 1248, 1199, 1145, 1109, 970, 773, 747; MS (EI, *m/z*, rel. intensity) 322 (M^+, 24), 116 (100); Anal. calcd for $C_{18}H_{14}N_2O_4$: C, 67.07; N, 8.69; H, 4.38; Found: C, 66.87; N, 8.55; H, 4.40; m.p. 180-183 °C.



3p

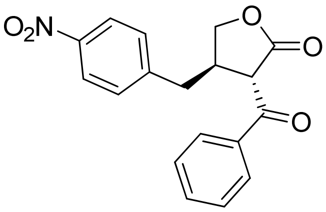
Red solid, yield 32% (ketone : enol = 13.3:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.89 (s, 3 H), 3.95 (s, 3 H), 4.00 (s, 2 H), 4.83 (d, *J* = 5.4 Hz, 2 H), 5.14 (s, 2 H), 5.18 (s, 2 H), 6.14 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.88 (d, *J* = 7.8 Hz, 1 H), 6.91 (s, 1 H), 7.19-7.52 (m, 13 H), 7.63 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.3, 55.8, 56.2, 65.2, 70.5, 70.9, 109.4, 110.1, 110.4, 111.8, 123.2, 126.5, 127.1, 127.3, 127.4, 128.0, 128.2, 128.5, 128.6, 129.1, 130.2, 135.4, 135.8, 140.0, 147.3, 149.4, 152.8, 153.5, 167.3, 190.7; IR (thin film): ν_{max} (cm^{-1}) = 2939, 1741, 1675, 1519, 1330, 1276, 1210, 1148, 1068, 1023, 870, 802, 740, 697; MS (EI, *m/z*, rel. intensity) 597 (M^+, 1), 91 (100); HRMS (EI) calcd for $C_{34}H_{31}NO_9$ (M^+): 597.1999. Found: 597.2003; m.p. 43-46 °C.

General Procedure for the Synthesis of Benzylbutyrolactones Derivatives:



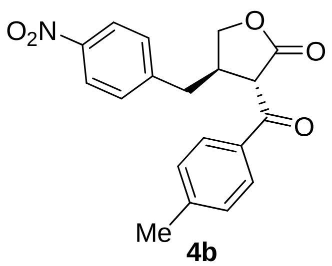
3 (±) **4**

A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this flask, β-keto esters **3** (0.2 mmol), DBU (0.02 mmol, 3 mg), and DMF (2 mL) were added. The reaction mixture was stirred at room temperature or 60 °C. After the reaction was complete (monitored by TLC), the reaction mixture was diluted with Et_2O and saturated NH_4Cl. The organic layer was separated, and the aqueous layer was extracted three times with Et_2O. The combined organic layers were dried over Na_2SO_4, and concentrated to afford the crude product. The residue was purified by silica gel column chromatography to afford the desired product **4**.



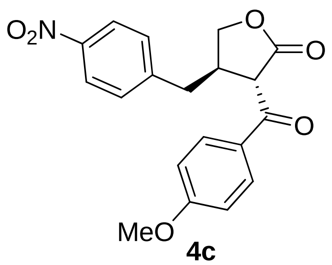
4a

Colorless solid, yield 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.97 (dd, *J* = 7.8, 2.4 Hz, 2 H), 3.51-3.63 (m, 1 H), 4.13 (dd, *J* = 8.7, 6.9 Hz, 1 H), 4.36 (d, *J* = 7.2 Hz, 1 H), 4.54 (dd, *J* = 8.7, 7.2 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.88 (d, *J* = 7.5 Hz, 2 H), 8.10 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.9, 40.5, 53.7, 71.4, 124.0, 128.7, 129.2, 129.7, 134.2, 135.2, 145.1, 146.9, 171.8, 192.3; IR (thin film): ν_{max} (cm^{-1}) = 2922, 1770, 1681, 1598, 1518, 1347, 1151, 1020, 860; MS (EI, *m/z*, rel. intensity) 325 (M^+, 7). 105 (100); HRMS (EI) calcd for $C_{18}H_{15}NO_5$ (M^+): 325.0950, Found: 325.0949; Anal. calcd for $C_{18}H_{15}NO_5$: C, 66.46; N, 4.31; H, 4.65; Found: C, 66.31; N, 4.23; H, 4.66; m.p. 109-111 °C.



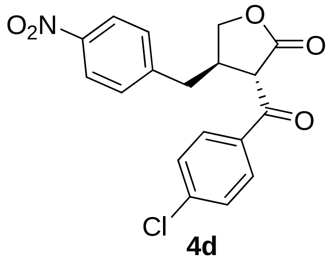
4b

Yellow oil, yield 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3 H), 2.97 (dd, *J* = 7.5, 1.8 Hz, 2 H), 3.49-3.61 (m, 1 H), 4.12 (dd, *J* = 9.0, 6.3 Hz, 1 H), 4.31 (d, *J* = 6.6 Hz, 1 H), 4.54 (dd, *J* = 9.0, 7.2 Hz, 1 H), 7.25 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.7 Hz, 2 H), 7.77 (d, *J* = 8.4 Hz, 2 H), 8.11 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 38.0, 40.4, 53.6, 71.5, 124.0, 129.3, 129.4, 129.7, 132.7, 145.1, 145.5, 147.0, 172.0, 191.8; IR (thin film): ν_{max} (cm^{-1}) = 2923, 2854, 1768, 1679, 1606, 1517, 1346, 1152, 1019, 861, 819, 736, 701; MS (EI, *m/z*, rel. intensity) 339 (M^+, 5), 119 (100); HRMS (EI) calcd for $C_{19}H_{17}NO_5$ (M^+): 339.1107, Found: 339.1098; Anal. calcd for $C_{19}H_{17}NO_5$: C, 67.25; N, 4.13; H, 5.05; Found: C, 67.25; N, 3.83; H, 5.29.



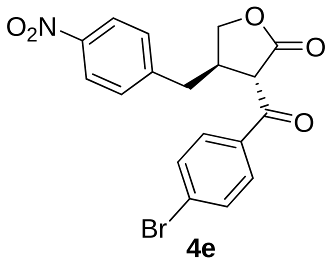
4c

Yellow solid, yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.97 (d, *J* = 7.8 Hz, 2 H), 3.56 (m, 1 H), 3.88 (s, 3 H), 4.12 (dd, *J* = 9.0, 6.3 Hz, 1 H), 4.26 (d, *J* = 6.6 Hz, 1 H), 4.54 (dd, *J* = 9.0, 7.2 Hz, 1 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.87 (d, *J* = 9.0 Hz, 2 H), 8.13 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.0, 40.2, 53.5, 55.6, 71.5, 114.0, 124.0, 128.2, 129.7, 131.7, 145.2, 147.0, 164.4, 172.1, 190.3; IR (thin film): ν_{max} (cm^{-1}) = 2902, 1768, 1655, 1597, 1509, 1349, 1256, 1168, 1023, 831, 697, 599; MS (EI, *m/z*, rel. intensity) 355 (M^+, 3), 135 (100); HRMS (EI) calcd for $C_{19}H_{17}NO_6$ (M^+): 355.1056, Found: 355.1067; Anal. calcd for $C_{19}H_{17}NO_6$: C, 64.22; N, 3.94; H, 4.82; Found: C, 64.12; N, 3.87; H, 4.78; m.p. 138-141 ^{o}C.



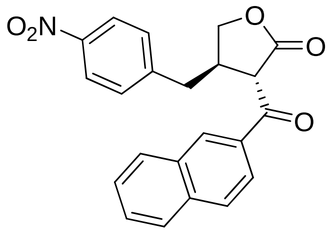
4d

Yellow solid, yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.97 (d, *J* = 7.8 Hz, 2 H), 3.54-3.66 (m, 1 H), 4.13 (dd, *J* = 9.0, 6.9 Hz, 1 H), 4.27 (d, *J* = 7.2 Hz, 1 H), 4.53 (dd, *J* = 9.0, 7.5 Hz, 1 H), 7.34 (d, *J* = 8.7 Hz, 2 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 7.86 (d, *J* = 8.7 Hz, 2 H), 8.14 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.9, 40.0, 53.9, 71.5, 124.1, 129.1, 129.6, 130.7, 133.5, 141.0, 145.0, 147.0, 171.5, 190.8; IR (thin film): ν_{max} (cm^{-1}) = 2897, 1771, 1683, 1518, 1345, 1272, 1150, 1091, 1025, 858, 798; MS (EI, *m/z*, rel. intensity) 359 (M^+, 1), 139 (100); Anal. calcd for $C_{18}H_{14}ClNO_5$: C, 60.09; N, 3.89; H, 3.92; Found: C, 59.85; N, 3.74; H, 4.13; m.p. 142-144 ^{o}C.



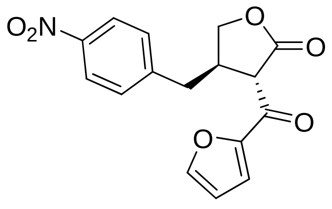
4e

Yellow solid, yield 93%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.97 (d, *J* = 7.8 Hz, 2 H), 3.54-3.66 (m, 1 H), 4.13 (dd, *J* = 9.0, 6.9 Hz, 1 H), 4.27 (d, *J* = 6.9 Hz, 1 H), 4.53 (dd, *J* = 9.0, 7.5 Hz, 1 H), 7.34 (d, *J* = 8.7 Hz, 2 H), 7.61 (d, *J* = 8.7 Hz, 2 H), 7.78 (d, *J* = 8.7 Hz, 2 H), 8.14 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.9, 40.0, 53.9, 71.5, 124.1, 129.6, 129.8, 130.7, 132.1, 133.9, 144.9, 147.0, 171.4, 191.0; IR (thin film): ν_{max} (cm^{-1}) = 2897, 1770, 1683, 1585, 1517, 1344, 1272, 1149, 1025, 858; MS (EI, *m/z*, rel. intensity) 403 (M^+, 3), 183 (100); Anal. calcd for $C_{18}H_{14}BrNO_5$: C, 53.49; N, 3.47; H, 3.49; Found: C, 53.73; N, 3.47; H, 3.63; m.p. 150-153 ^{o}C.



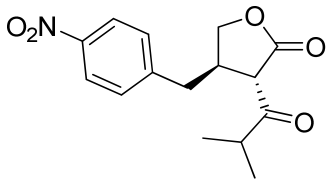
4f

Yellow solid, yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.96 (d, *J* = 7.8 Hz, 2 H), 3.53-3.60 (m, 1 H), 4.13 (dd, *J* = 8.7, 6.9 Hz, 1 H), 4.51-4.56 (m, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.52 (dd, *J* = 8.1, 6.9 Hz, 1 H), 7.61 (dd, *J* = 8.1, 6.9 Hz, 1 H), 7.81-7.90 (m, 4 H), 8.03 (d, *J* = 8.4 Hz, 2 H), 8.36 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.8, 40.6, 53.7, 71.5, 123.8, 123.9, 127.0, 127.7, 128.6, 129.2, 129.6, 129.7, 131.8, 132.1, 132.6, 135.8, 145.1, 146.8, 172.1, 192.4; IR (thin film): ν_{max} (cm^{-1}) = 2918, 1771, 1677, 1518, 1347, 1152, 1019, 860, 753, 702; MS (EI, *m/z*, rel. intensity) 375 (M^+, 7), 155 (100); Anal. calcd for $C_{22}H_{17}NO_5$: C, 70.39; N, 3.73; H, 4.56; Found: C, 70.41; N, 3.63; H, 4.42; m.p. 47-50 ^{o}C.



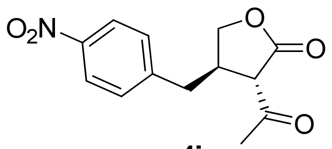
4g

Yellow solid, yield 93%. ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 2.92 (dd, *J* = 13.5, 8.7 Hz, 1 H), 3.05 (dd, *J* = 13.5, 6.6 Hz, 1 H), 3.33-3.44 (m, 1 H), 4.11 (t, *J* = 8.7 Hz, 1 H), 4.52 (t, *J* = 8.4 Hz, 1 H), 4.64 (d, *J* = 9.9 Hz, 1 H), 6.73 (dd, *J* = 3.6, 1.8 Hz, 1 H), 7.42-7.48 (m, 3 H), 7.99-8.03 (m, 3 H); ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ 36.4, 41.0, 53.1, 71.3, 113.0, 121.5, 123.3, 130.2, 146.1, 146.7, 149.3, 151.3, 173.1, 181.8; IR (thin film): ν_{max} (cm^{-1}) = 2908, 1766, 1666, 1513, 1467, 1357, 1162, 1014, 830, 784, 703; MS (EI, *m/z*, rel. intensity) 315 (M^+, 7), 95 (100); Anal. calcd for $C_{16}H_{13}NO_6$: C, 60.95; N, 4.44; H, 4.16; Found: C, 60.93; N, 4.26; H, 4.28; m.p. 144-147 ^{o}C.



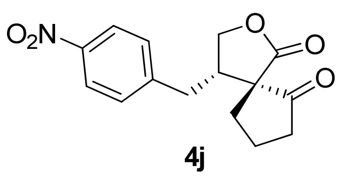
4h

Yellow solid, yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (d, *J* = 7.2 Hz, 3 H), 1.08 (d, *J* = 6.9 Hz, 3 H), 2.92 (d, *J* = 7.8 Hz, 2 H), 3.00-3.10 (m, 1 H), 3.38-3.51 (m, 1 H), 3.63 (d, *J* = 7.5 Hz, 1 H), 4.03 (dd, *J* = 8.7, 6.6 Hz, 1 H), 4.43 (dd, *J* = 9.0, 7.8 Hz, 1 H), 7.37 (d, *J* = 8.1 Hz, 2 H), 8.19 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.0, 18.3, 38.0, 38.3, 40.2, 55.7, 71.2, 124.0, 129.6, 145.1, 147.0, 171.7, 206.0; IR (thin film): ν_{max} (cm^{-1}) = 2976, 1771, 1714, 1516, 1342, 1156, 1068, 1019, 864; MS (EI, *m/z*, rel. intensity) 291 (M^+, 2), 43 (100); Anal. calcd for $C_{15}H_{17}NO_5$: C, 61.85; N, 4.81; H, 5.88; Found: C, 61.60; N, 4.74; H, 5.99; m.p. 77-79 ^oC.



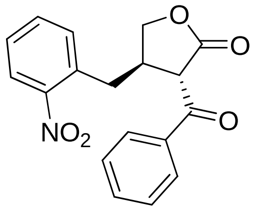
4i

Yellow solid, yield 71%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3 H), 2.89 (dd, *J* = 13.5, 8.4 Hz, 1 H), 2.98 (dd, *J* = 13.5, 6.6 Hz, 1 H), 3.40-3.51 (m, 2 H), 4.02 (dd, *J* = 6.9, 6.9 Hz, 1 H), 4.37 (dd, *J* = 7.2 7.2 Hz, 1 H), 7.38 (d, *J* = 8.7 Hz, 2 H), 8.19 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.6, 37.7, 37.9, 58.4, 71.0, 124.0, 129.5, 145.2, 146.9, 171.5, 199.5; IR (thin film): ν_{max} (cm^{-1}) = 2920, 1755, 1716, 1511, 1346, 1240, 1177, 1151, 1006, 863; MS (EI, *m/z*, rel. intensity) 263 (M^+, 1), 43 (100); Anal. calcd for $C_{13}H_{13}NO_5$: C, 59.31; N, 5.32; H, 4.98; Found: C, 59.63; N, 5.19; H, 5.28, m.p. 107-109 ^oC.



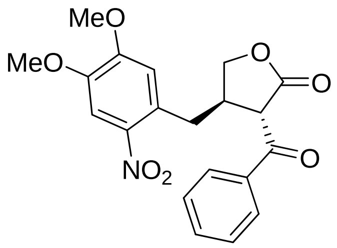
4j

Yellow solid, yield 83% (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.87-1.95 (m, 2 H), 2.31-2.34 (m, 2 H), 2.47-2.59 (m, 2 H), 2.84-3.02 (m, 3 H), 4.13-4.19 (m, 1 H), 4.33-4.39 (m, 1 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 8.20 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 32.6, 32.8, 39.5, 46.5, 59.4, 70.3, 124.0, 129.4, 145.2, 146.9, 174.7, 213.5; IR (thin film): ν_{max} (cm^{-1}) = 1770, 1732, 1522, 1350, 1091, 1010, 853; MS (EI, *m/z*, rel. intensity) 289 (M^+, 1), 153 (100); Anal. calcd for $C_{15}H_{15}NO_5$: C, 62.28; N, 4.84; H, 5.23; Found: C, 62.12; N, 4.76; H, 5.44; m.p. 129-131 ^{o}C.



4k

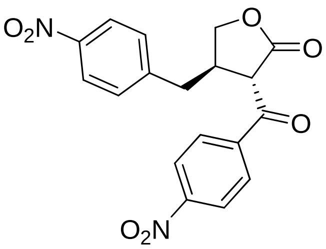
Yellow oil, yield 92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.09 (dd, *J* = 13.5, 7.8 Hz, 1 H), 3.26 (dd, *J* = 13.5, 7.2 Hz, 1 H), 3.57-3.69 (m, 1 H), 4.19 (dd, *J* = 9.0, 6.6 Hz, 1 H), 4.49 (d, *J* = 7.2 Hz, 1 H), 4.56 (dd, *J* = 9.3, 7.5 Hz, 1 H), 7.30-7.60 (m, 6 H), 7.83 (d, *J* = 7.5 Hz, 2 H), 7.92 (dd, *J* = 8.4, 0.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.9, 40.2, 53.8, 71.4, 125.3, 128.3, 128.6, 129.0, 132.3, 132.7, 133.4, 133.9, 135.3, 148.9, 172.2, 192.5; IR (thin film): ν_{max} (cm^{-1}) = 3067, 1772, 1682, 1525, 1346, 1155, 1019, 859, 690; MS (EI, *m/z*, rel. intensity) 105 (100); Anal. calcd for $C_{18}H_{15}NO_5$: C, 66.46; N, 4.31; H, 4.65; Found: C, 66.78; N, 4.17; H, 4.50.



4m

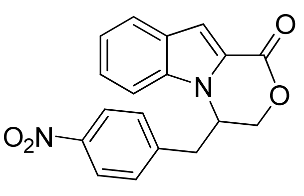
Yellow solid, yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10 (dd, *J* = 13.5, 8.4 Hz, 1 H), 3.31 (dd, *J* = 13.5, 6.6 Hz, 1 H), 3.64-3.75 (m, 1 H), 3.77 (s, 3 H), 3.91 (s, 3 H), 4.21 (dd, *J* = 7.5, 6.9 Hz, 1 H), 4.46 (d, *J* = 7.5 Hz, 1 H), 4.63 (dd, *J* = 7.5, 7.2 Hz, 1

H), 6.57 (s, 1 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 7.55-7.63 (m, 2 H), 7.85 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.4, 40.6, 54.0, 56.3, 71.4, 108.5, 113.3, 127.8, 128.8, 129.0, 134.1, 135.5, 141.0, 147.9, 153.1, 172.3, 192.6; IR (thin film): ν_{max} (cm^{-1}) = 2926, 1758, 1681, 1580, 1523, 1332, 1271, 1170, 1062, 1004, 892, 801; MS (EI, *m/z*, rel. intensity) 385 (M^+, 3), 105 (100); HRMS (EI) calcd for $C_{20}H_{19}NO_7$ (M^+): 385.1162. Found: 385.1174; m.p. 194-196 ^oC.



4n

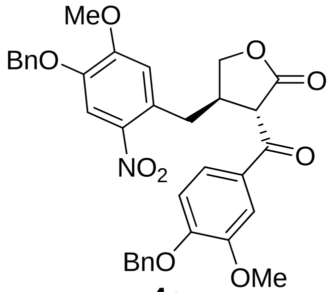
Light yellow solid, yield 76%. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 2.94 (dd, *J* = 13.6, 8.4 Hz, 1 H), 3.04 (dd, *J* = 13.6, 7.2 Hz, 1 H), 3.46-3.53 (m, 1 H), 4.15 (t, *J* = 8.8 Hz, 1 H), 4.54 (t, *J* = 8.4 Hz, 1 H), 5.14 (d, *J* = 9.6 Hz, 1 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.97 (d, *J* = 8.8 Hz, 2 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 8.31 (d, *J* = 9.2 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ 36.3, 41.1, 53.2, 71.3, 123.5, 123.7, 130.1, 130.2, 140.0, 146.2, 146.8, 150.2, 172.6, 193.6; IR (thin film): ν_{max} (cm^{-1}) = 3429, 3108, 2929, 1769, 1689, 1604, 1515, 1477, 1348, 1290, 1281, 1154, 1111, 1019; MS (EI, *m/z*, rel. intensity) 393 (M^+Na); HRMS (EI) calcd for $C_{18}H_{14}N_2O_7$ (M^+): 370.0801. Found: 370.0805; m.p. 210-212 ^oC.



4o

Yellow solid, yield 71% . ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28-3.30 (m, 2 H), 4.58(d, *J* = 10.8 Hz, 1H), 4.69-4.74 (m, 2 H), 7.02 (d, *J* = 8.7 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1 H), 7.24-7.31 (m, 3 H), 7.50 (s, 1 H), 7.75 (d, *J* = 8.1 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 2 H);

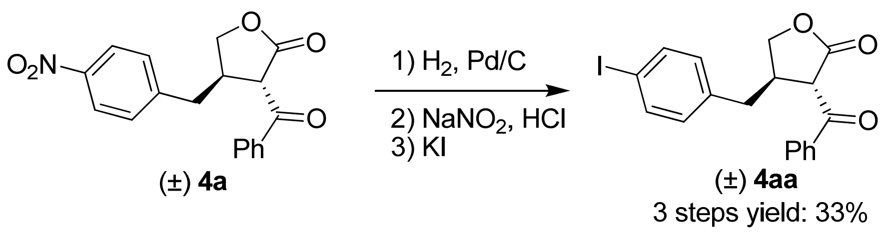
^{13}C NMR (75 MHz, $CDCl_3$) δ 38.1, 51.8, 68.8, 109.5, 111.2, 121.7, 122.4, 123.5, 124.8, 126.3, 126.7, 130.3, 136.1, 143.6, 147.3, 159.1; IR (thin film): ν_{max} (cm^{-1}) = 2929, 1720, 1519, 1342, 1320, 1179, 1089, 765; MS (EI, *m/z*, rel. intensity) 322 (M^+, 15), 186 (100); HRMS (EI) calcd for $C_{18}H_{14}N_2O_4$ (M^+): 322.0954. Found: 322.0964; m.p. 211-214 °C.



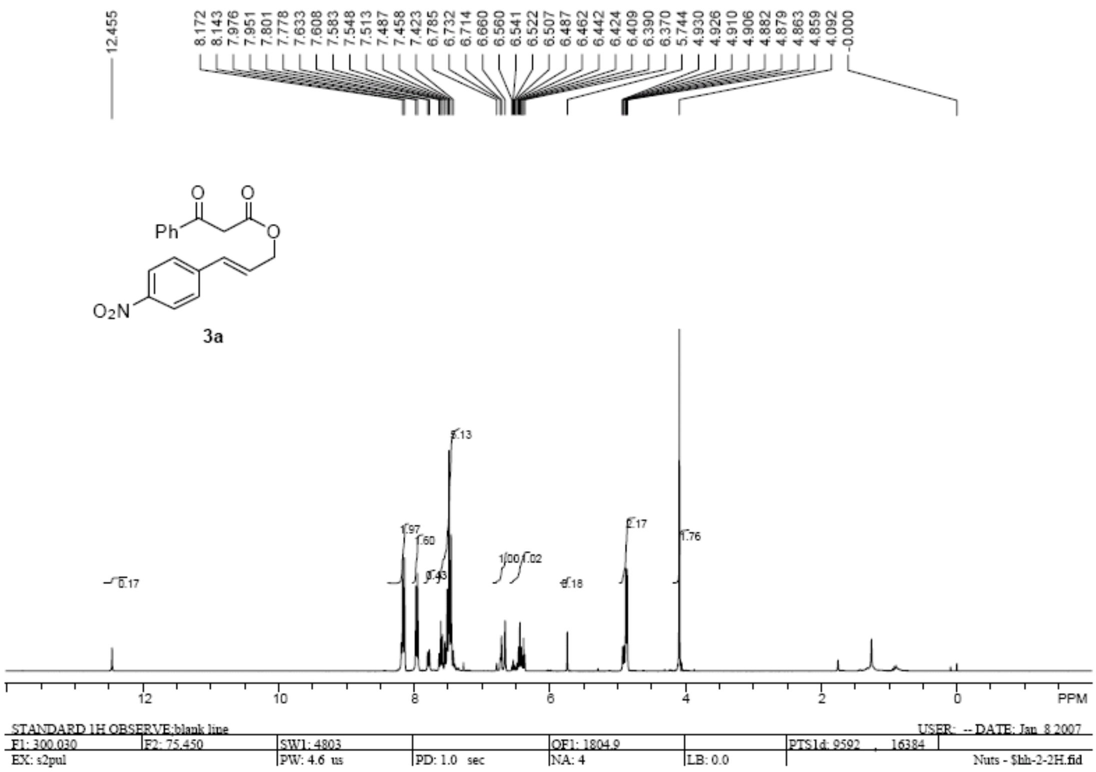
4p

Yellow solid, yield 78%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.09-3.26 (m, 2 H), 3.59-3.68 (m, 1 H), 3.78 (s, 3 H), 3.90 (s, 3 H), 4.18 (dd, *J* = 8.7, 7.5 Hz, 1 H), 4.39 (d, *J* = 7.2 Hz, 1 H), 4.59 (t, *J* = 7.8 Hz, 1 H), 5.09 (s, 2 H), 5.23 (s, 2 H), 6.58 (s, 1 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 7.32-7.44 (m, 12 H), 7.59 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.3, 40.8, 53.7, 56.0, 56.3, 70.8, 71.2, 71.5, 110.5, 111.1, 112.1, 113.7, 124.1, 127.2, 127.6, 128.1, 128.2, 128.5, 128.7, 128.8, 129.0, 135.5, 136.0, 141.0, 147.0, 149.6, 153.3, 153.7, 172.6, 191.0; IR (thin film): ν_{max} (cm^{-1}) = 1761, 1677, 1580, 1524, 1421, 1271, 1226, 1140, 1008; MS (EI, *m/z*, rel. intensity) 597 (M^+, 1), 91 (100); HRMS (EI) calcd for $C_{34}H_{31}NO_9$ (M^+): 597.1999. Found: 597.2004; m.p. 203-205 °C.

Procedure for the Synthesis of 4aa:



To a solution of **4a** (135.5 mg, 0.42 mmol) in EtOAc (5 mL) was added 10% Pd/C (27.8 mg) under Ar atmosphere. Then the reactor was charged with 1 atm of H_2 and the reaction mixture was stirred at room temperature. After **4a** was fully consumed (monitored by TLC), the reaction mixture was filtrated through a celite pad. After removal of the solvent, the residue was purified by silica gel column chromatography (*n*-Hexane/EtOAc = 100/1) to afford the amine. To a solution of the amine in dioxane (2 mL) and H_2O (1 mL) was added $NaNO_2$ (21.4 mg, 0.31 mmol) and H_2O (2 mL). This mixture was stirred at 0 ^oC. After 30 min, a solution of KI (83.3 mg, 0.50 mmol) in water (5 mL) was added slowly. Then the reactor was heated at 80 ^oC for 2h. The reaction mixture was extracted with CH_2Cl_2 and the combined organic layers were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-Hexane/EtOAc = 3/1) to afford 56.1 mg of **4aa** (3 steps, 33% yield) as yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 2.74-2.88 (m, 2H), 3.36-3.43 (m, 1H), 4.13 (dd, *J* = 9.0, 5.4 Hz, 1H), 4.28 (d, *J* = 6.3 Hz, 1H), 4.52 (dd, *J* = 9.0, 7.2 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 8.1 Hz, 2H), 7.58-7.61 (m, 3H), 7.80 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.8, 41.0, 53.8, 71.7, 92.4, 128.7, 129.2, 130.9, 134.1, 135.2, 137.0, 137.9, 172.3, 192.7. IR (thin film): ν_{max} (cm^{-1}) = 2920, 1770, 1680, 1596, 1484, 1447, 1382, 1247, 1152, 1006, 737; MS (EI, *m/z*, rel. intensity) 406 (M^+, 7), 105 (100); HRMS (EI) calcd for $C_{18}H_{15}IO_3$ (M^+): 406.0066. Found: 406.0068.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8.172 8.143 7.976 7.951 7.801 7.778 7.633 7.608 7.583 7.548 7.513 7.487 7.458 7.423 6.785 6.732 6.714 6.660 6.560 6.541 6.522 6.507 6.487 6.462 6.442 6.424 6.409 6.390 6.370 5.744 4.930 4.926 4.910 4.906 4.882 4.879 4.863 4.859 4.092 -0.000
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3a
PPM
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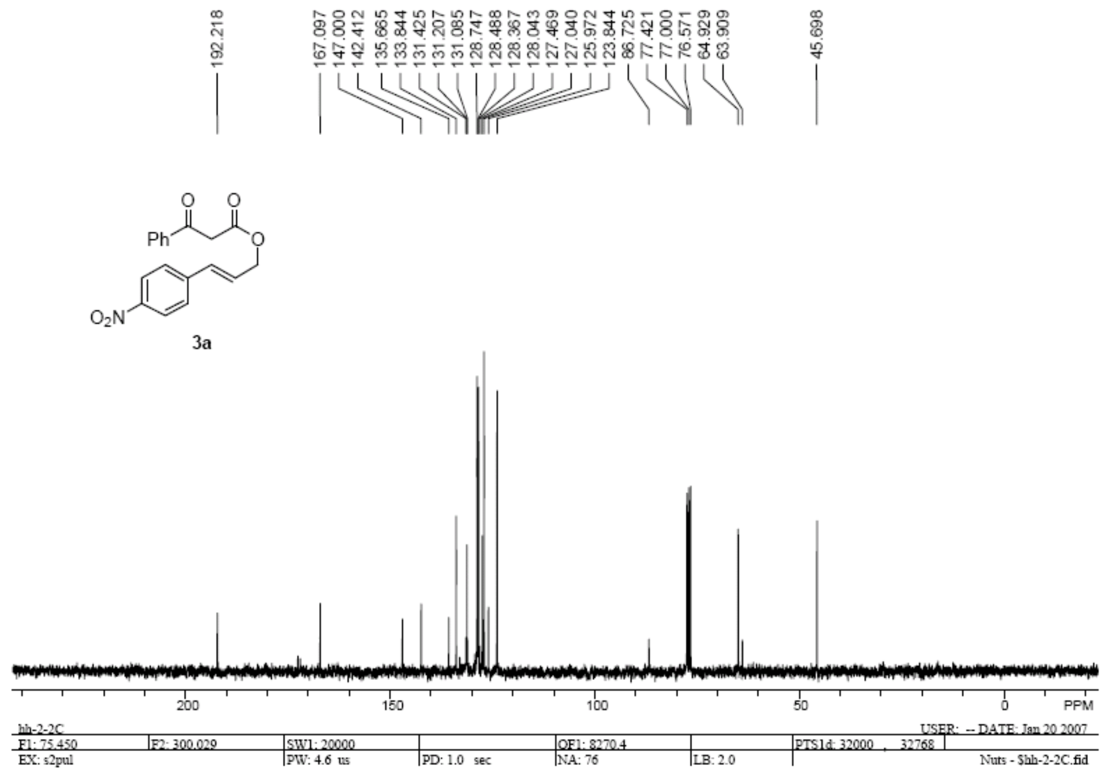
NA: 4
LB: 0.0
Nuts - $hh-2-2H.fid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167.097 147.000 142.412 135.665 133.844 131.425 131.207 131.085 128.747 128.488 128.367 128.043 127.469 127.040 125.972 123.844 86.725 77.421 77.000 76.571 64.929 63.909
45.698
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PPM
hh-2-2C
USER: -- DATE: Jan 20 2007
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SW1: 20000
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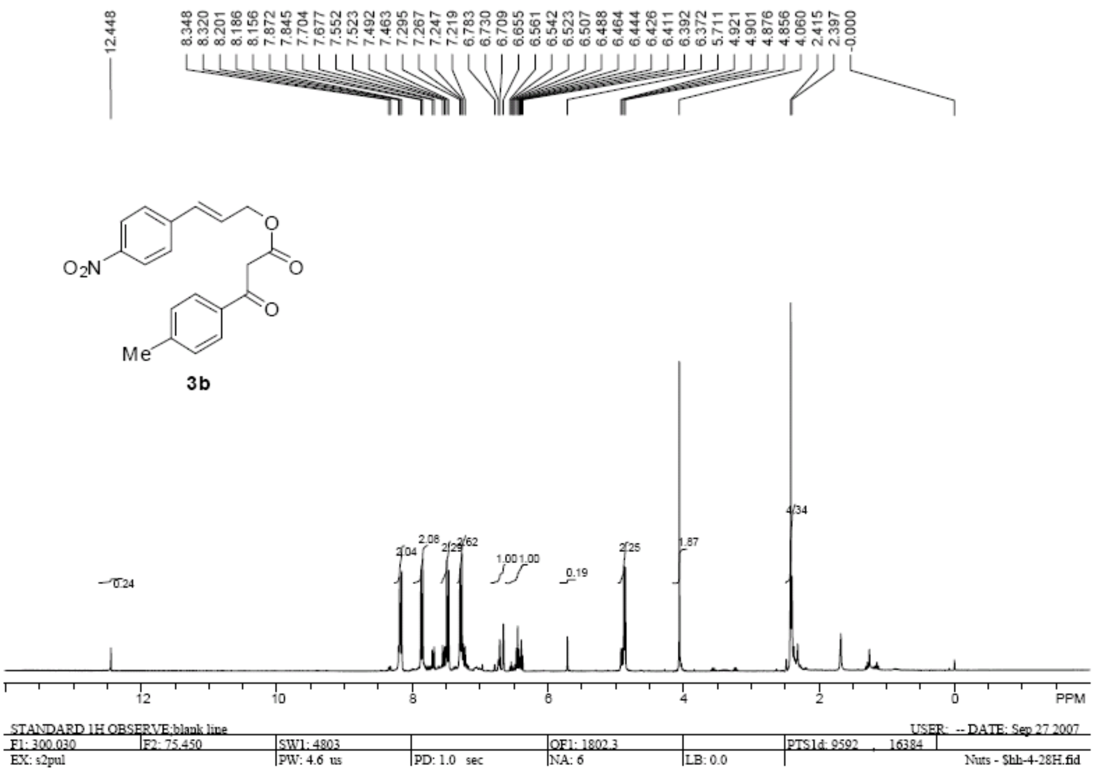
Nuts - $hh-2-2C.fid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8.156
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7.845
7.704
7.677
7.552
7.523
7.492
7.463
7.295
7.267
7.247
7.219
6.783
6.730
6.709
6.655
6.561
6.542
6.523
6.507
6.488
6.464
6.444
6.426
6.411
6.392
6.372
5.711
4.921
4.901
4.876
4.856
4.060
2.415
2.397
-0.000
0.24
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2.08
2.29
2.62
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1.00
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2.25
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PD: 1.0 sec
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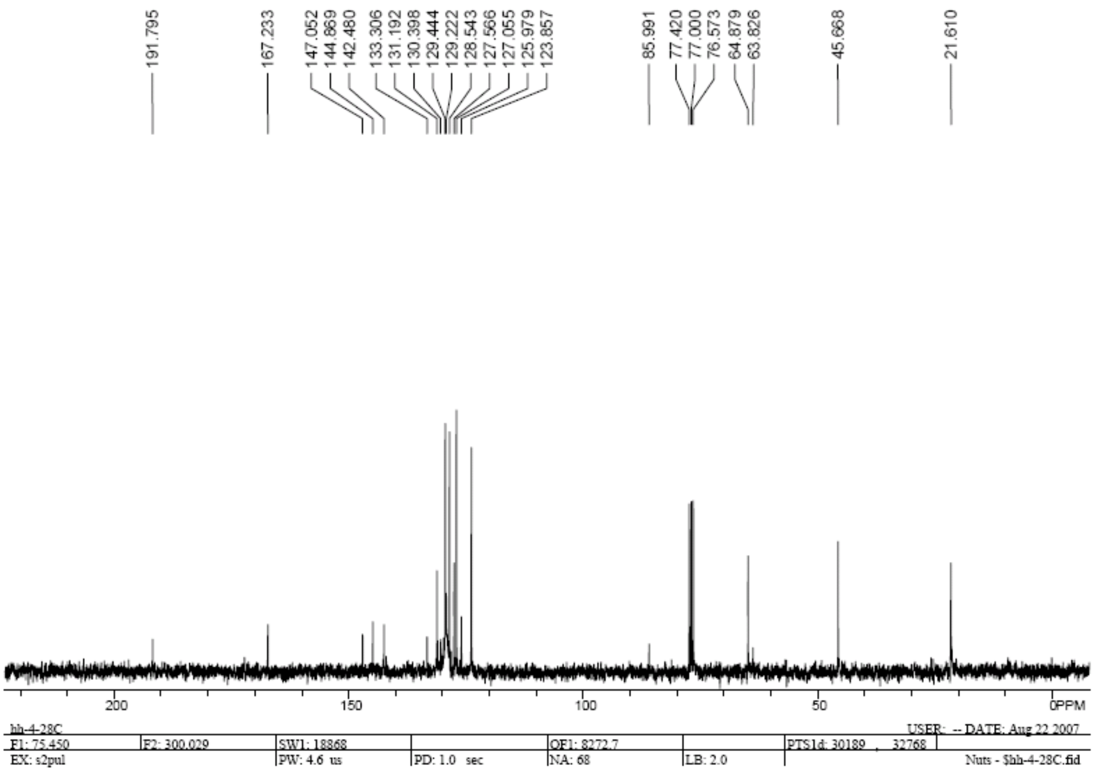
LB: 0.0
Nuts - $hh-4-28H.fid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127.055
125.979
123.857
85.991
77.420
77.000
76.573
64.879
63.826
45.668
21.610
200
150
100
50
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USER: -- DATE: Aug 22 2007
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F2: 300.029
SW1: 18868
OF1: 8272.7
PTS1d: 30189 , 32768
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PW: 4.6 us
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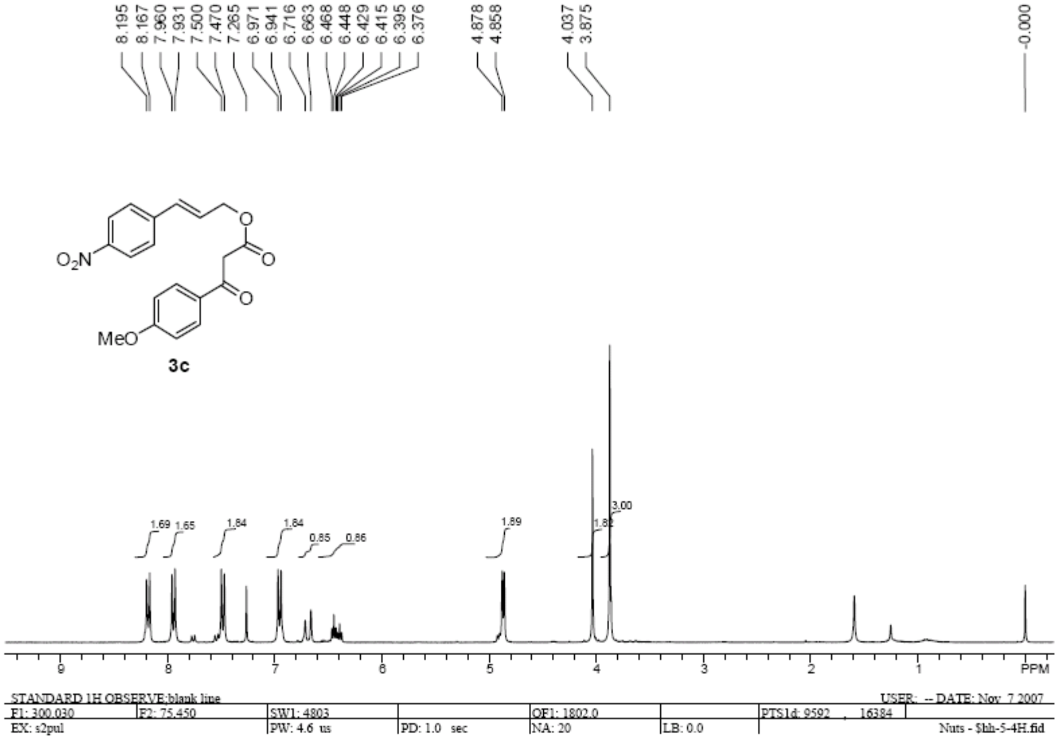
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7.265
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6.448
6.429
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6.395
6.376
4.878
4.858
4.037
3.875
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MeO
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0.86
1.89
1.82
3.00
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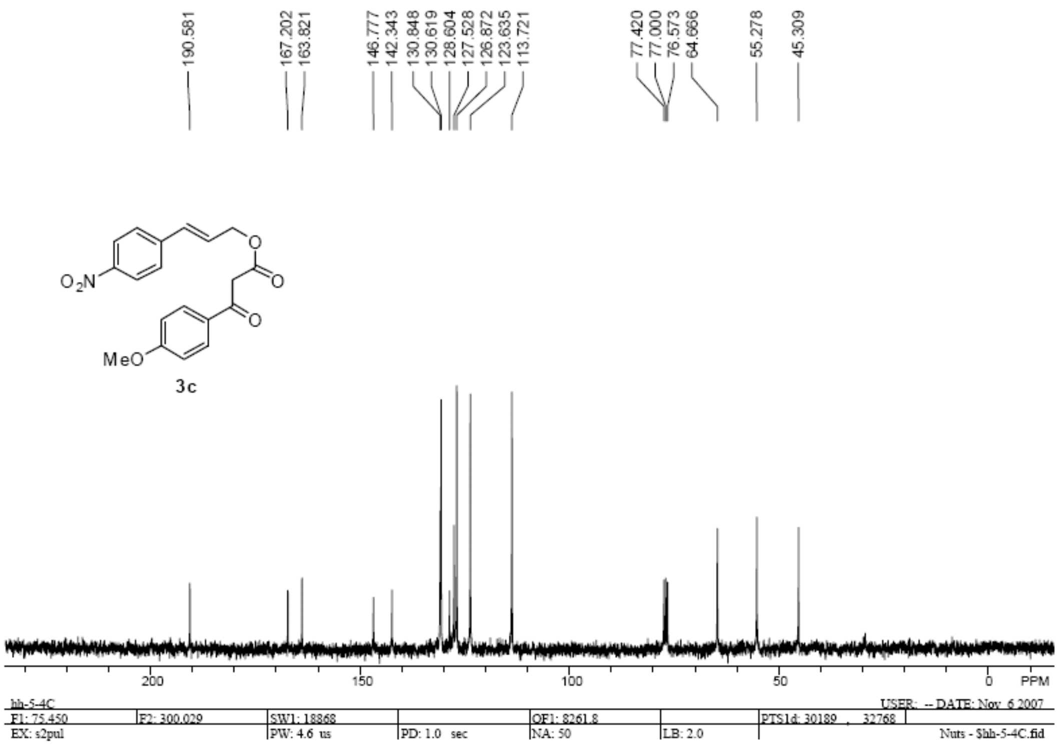
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127.528
126.872
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113.721
77.420
77.000
76.573
64.666
55.278
45.309
O_2N
MeO
3c
PPM
hh-5-4C
USER: -- DATE: Nov 6 2007
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F2: 300.029
SW1: 18868
OF1: 8261.8
PTS1d: 30189 , 32768
EX: s2pul
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PD: 1.0 sec
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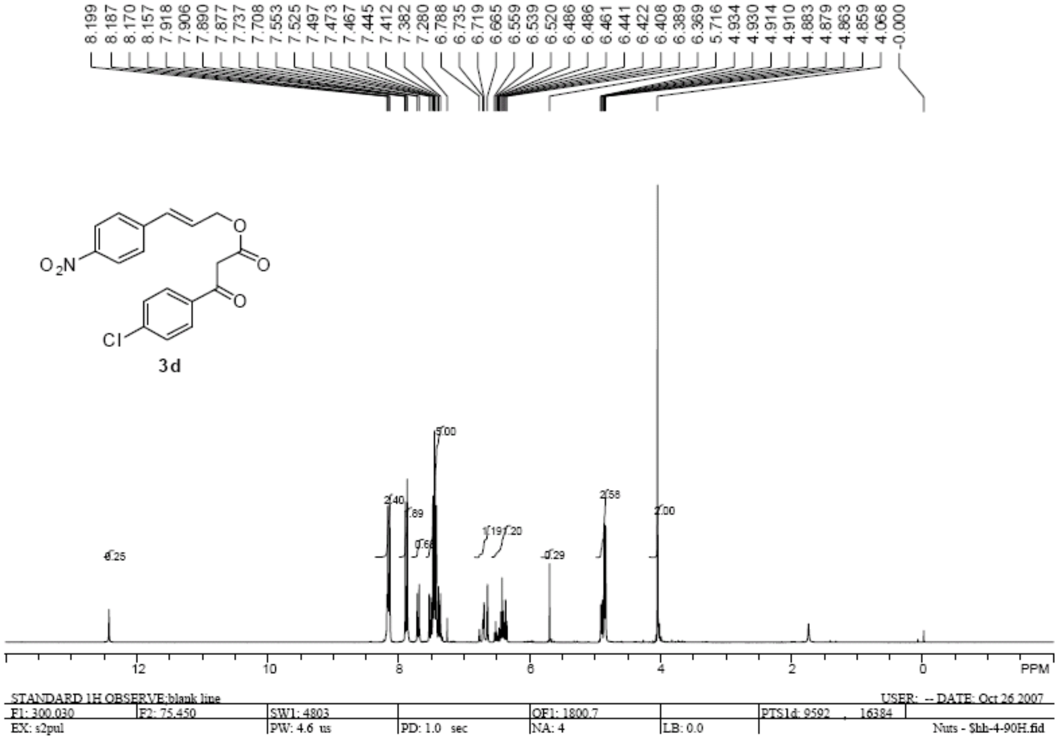
LB: 2.0
Nuts - $hh-5-4C.fid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O_2N
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10
8
6
4
2
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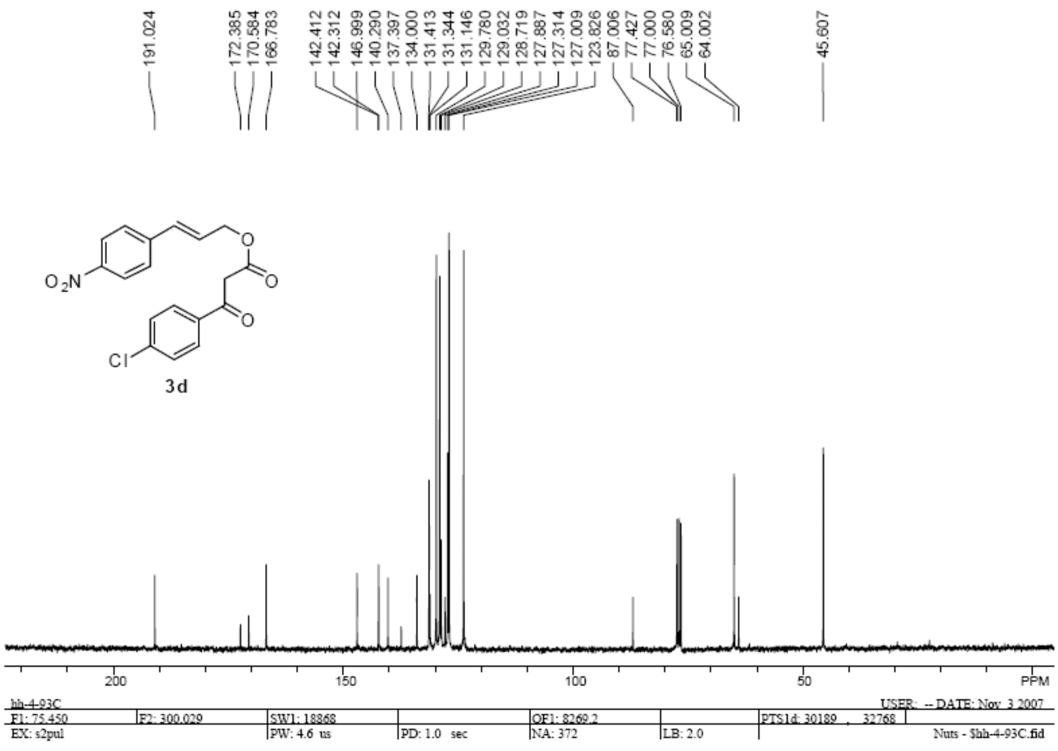
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45.607
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50
PPM
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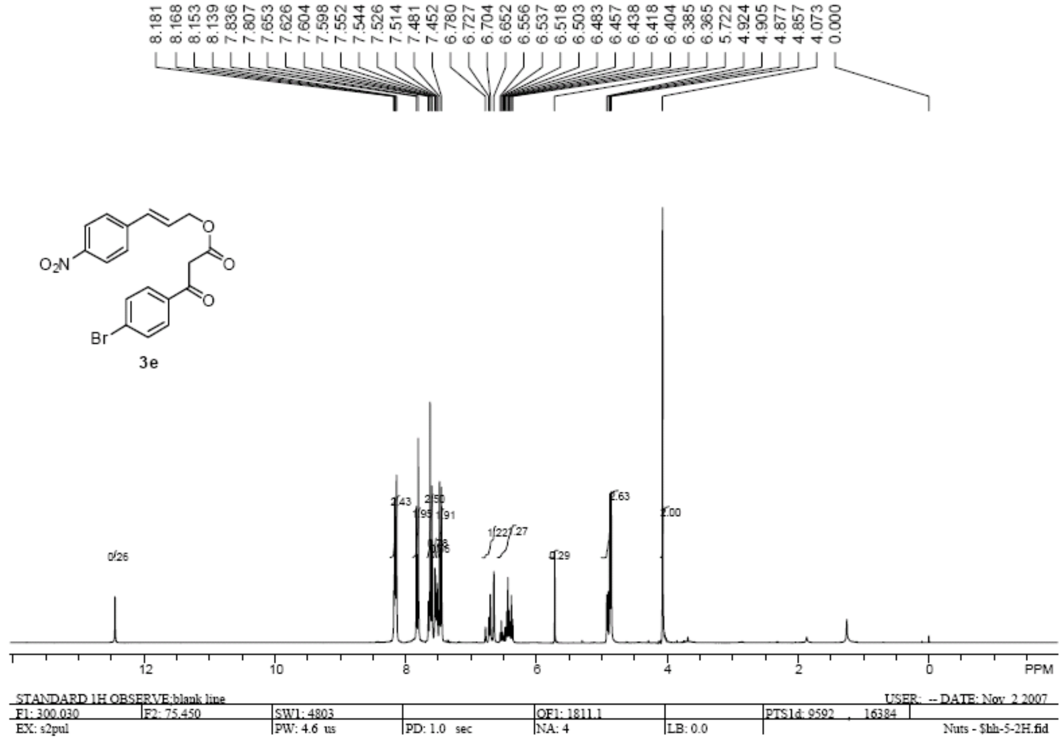
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6.457
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O
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10
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PW: 4.6 us
PD: 1.0 sec
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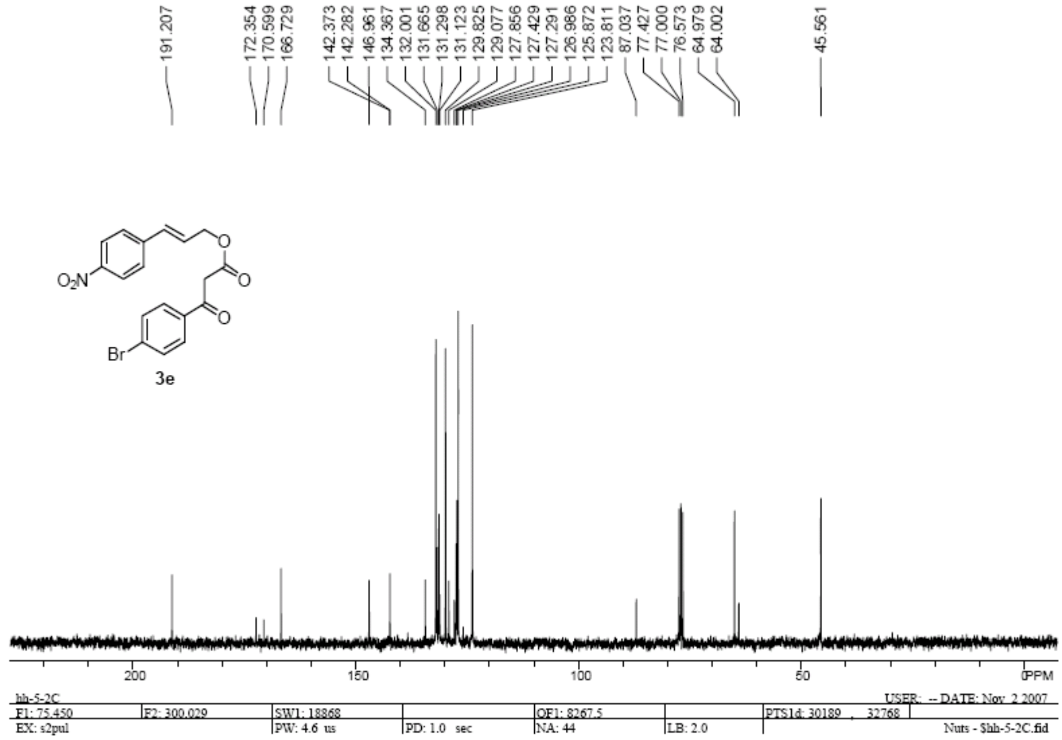
LB: 0.0
Nuts - $hh-5-2H.fid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hh-5-2C
USER: -- DATE: Nov 2 2007
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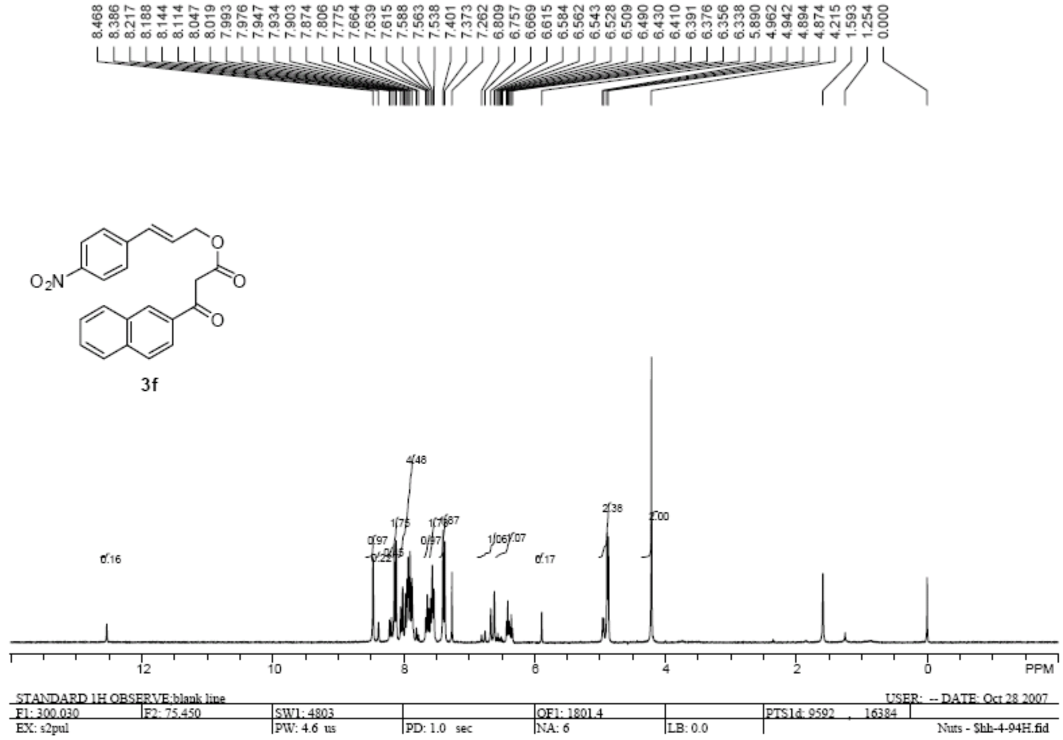
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F2: 75.450
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OF1: 1801.4
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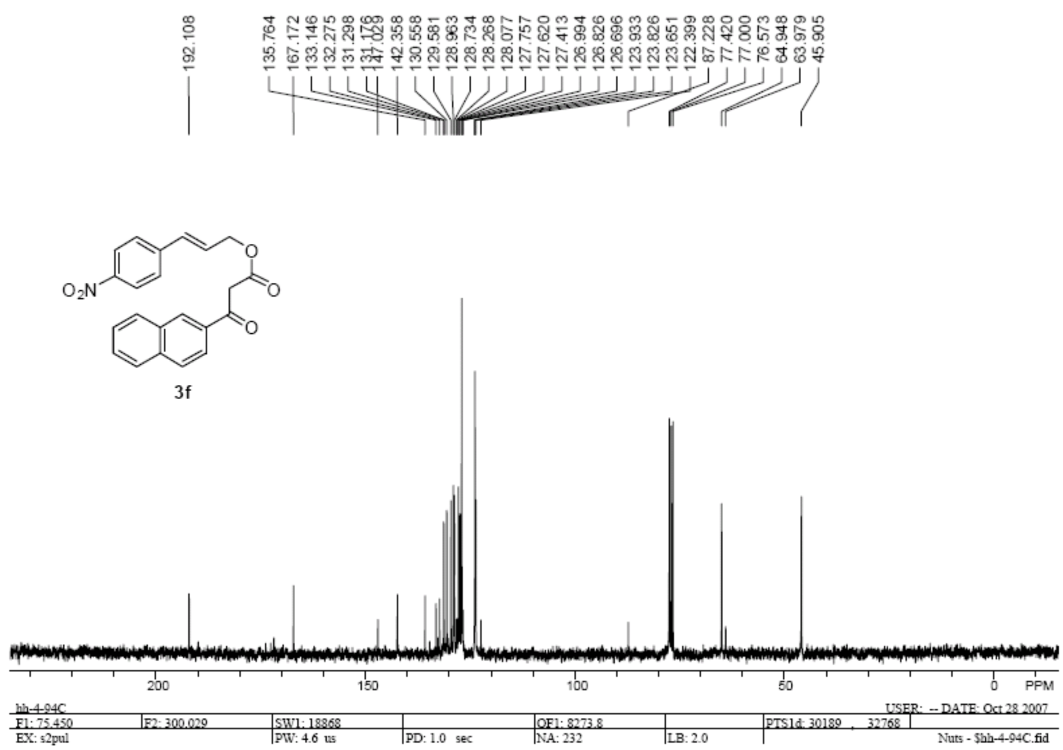
USER: -- DATE: Oct 28 2007
Nuts - $hh-4-94H.fid
PPM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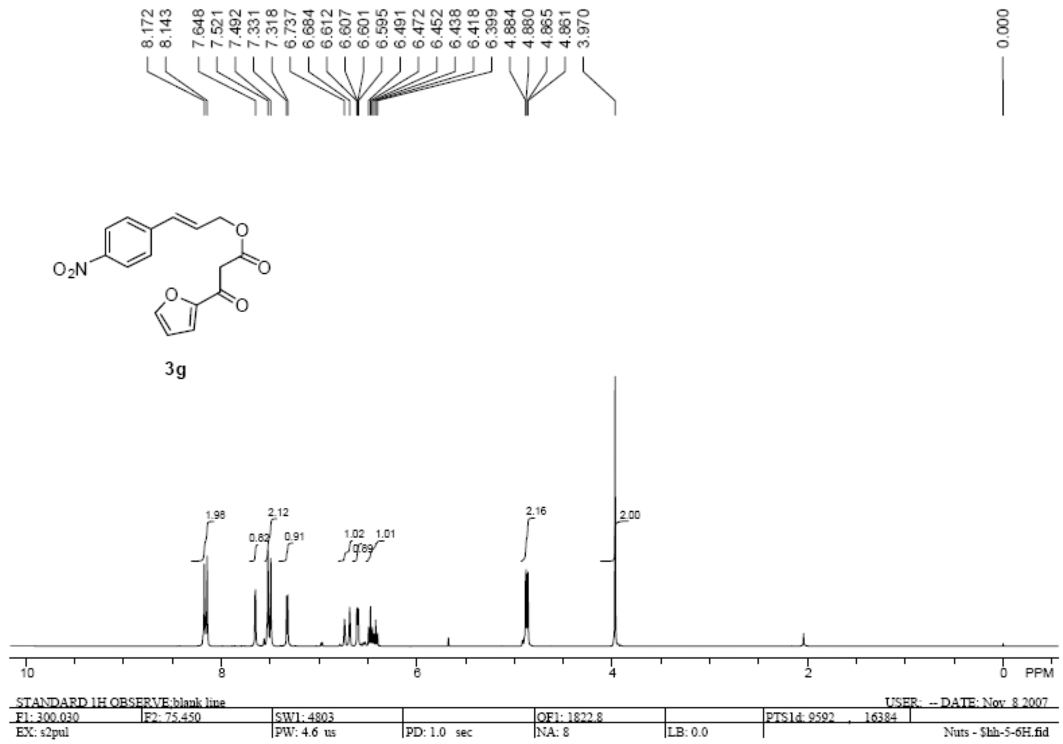
USER: -- DATE: Oct 28 2007
Nuts - $hh-4-94C.fid
PPM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4.880
4.865
4.861
3.970
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1.02
0.89
1.01
2.16
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8
6
4
2
0
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USER: -- DATE: Nov 8 2007
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PTS1d: 9592 , 16384
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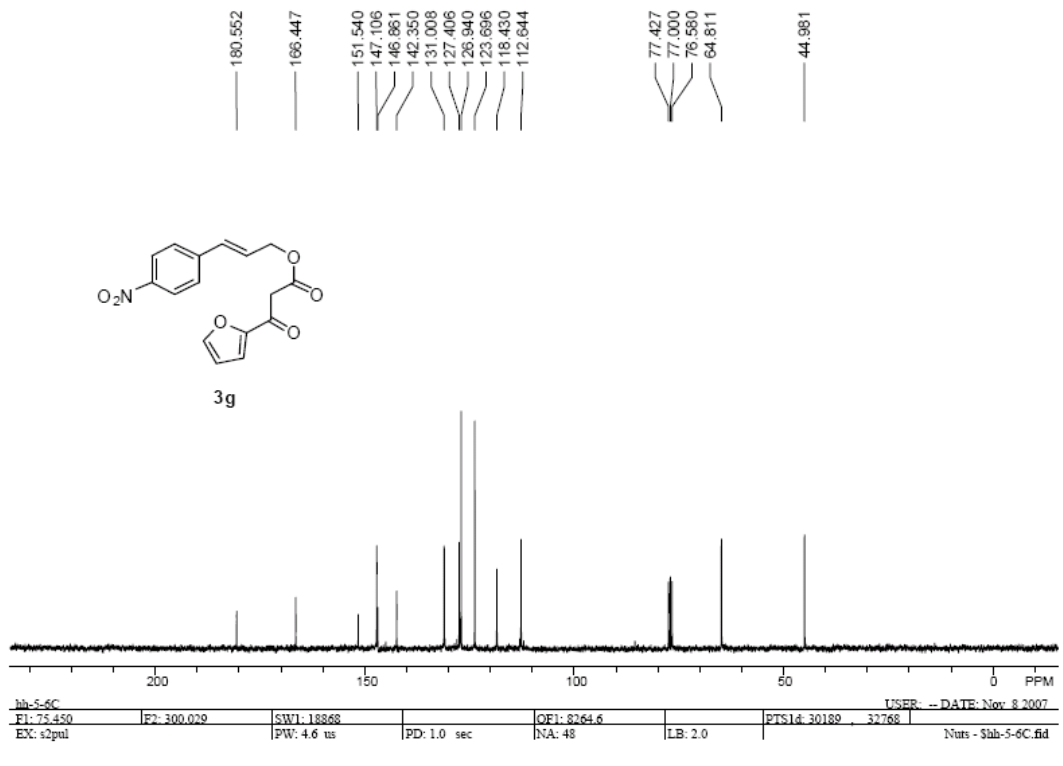
PW: 4.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $hh-5-6H.fid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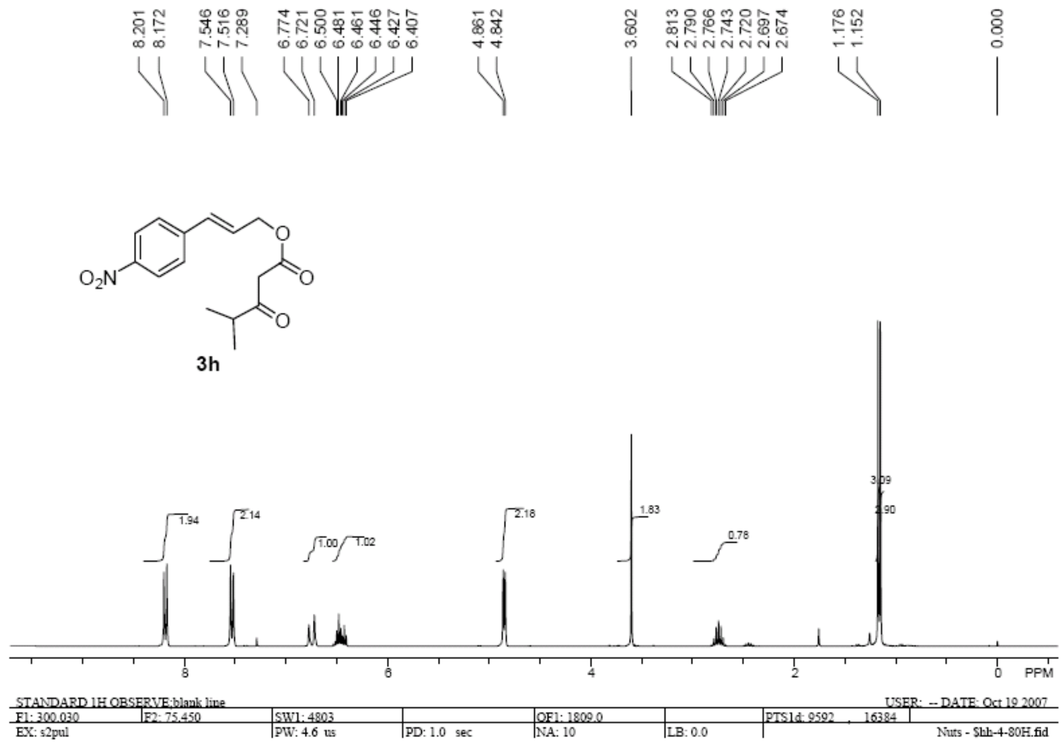
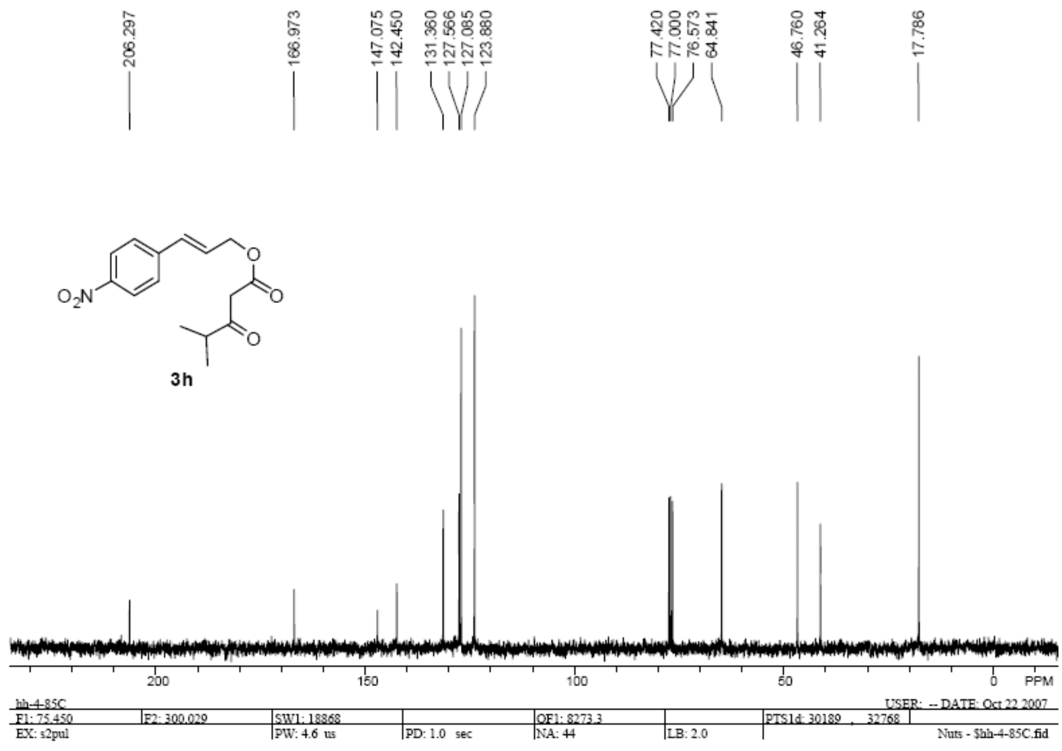
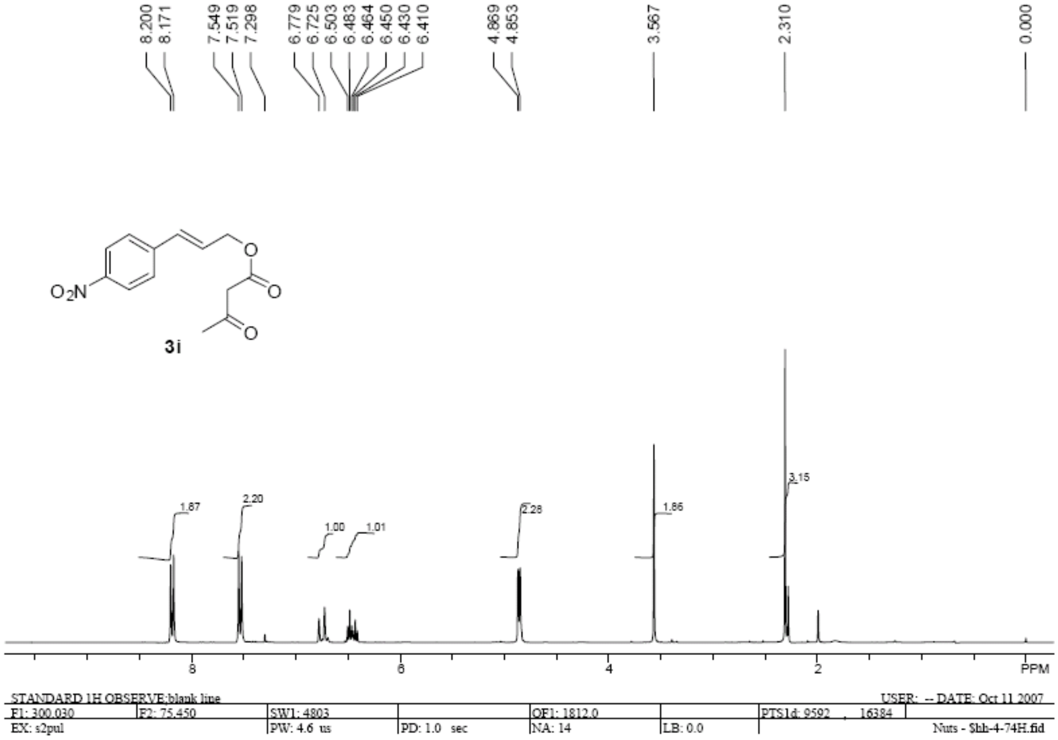
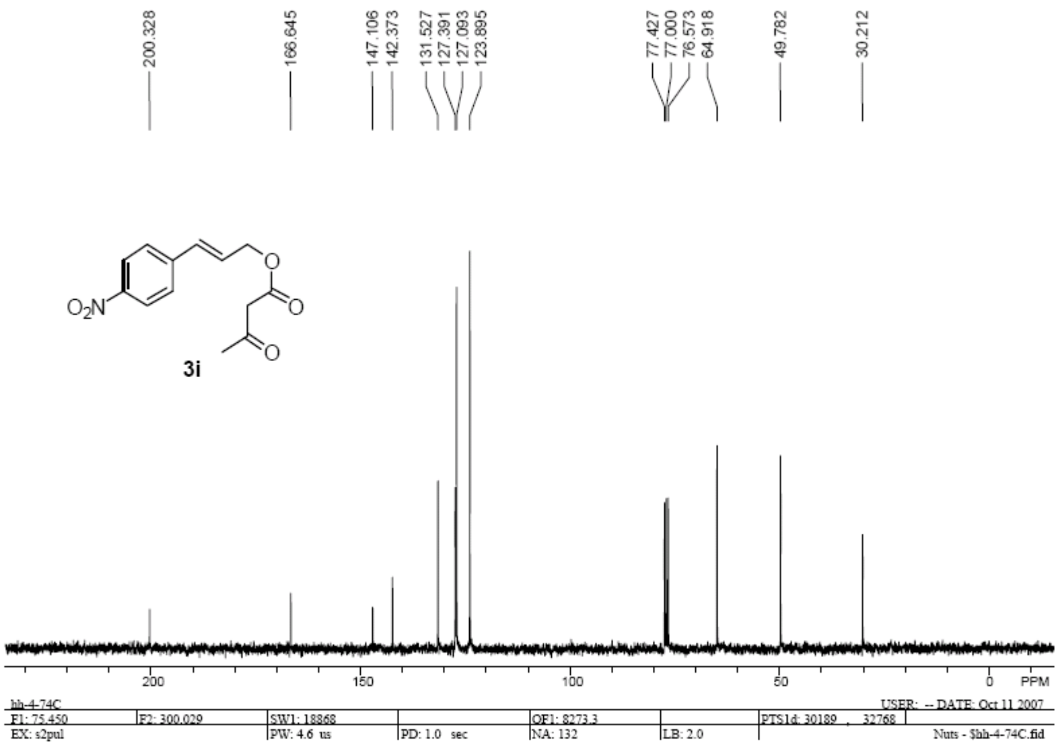
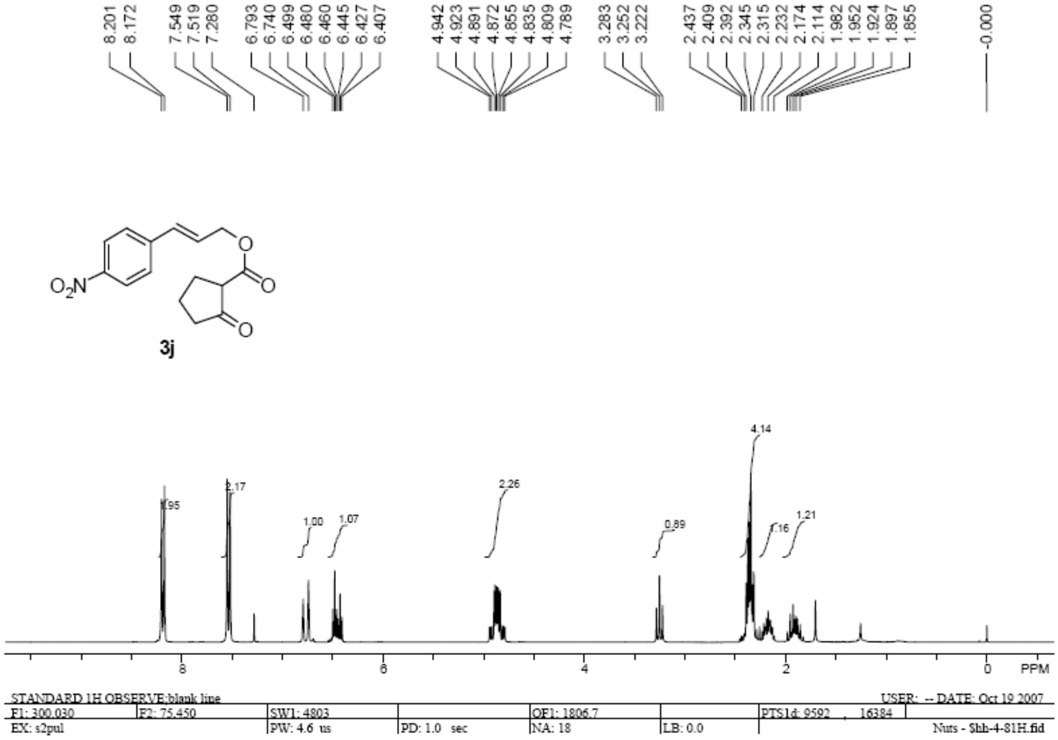
166.447
151.540
147.106
146.861
142.350
131.008
127.406
126.940
123.696
118.430
112.644
77.427
77.000
76.580
64.811
44.981
O_2N
O
O
O
O
3g
200
150
100
50
0
PPM
hh-5-6C
USER: -- DATE: Nov 8 2007
F1: 75.450
F2: 300.029
SW1: 18868
OF1: 8264.6
PTS1d: 30189 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 48
LB: 2.0
Nuts - $hh-5-6C.fid

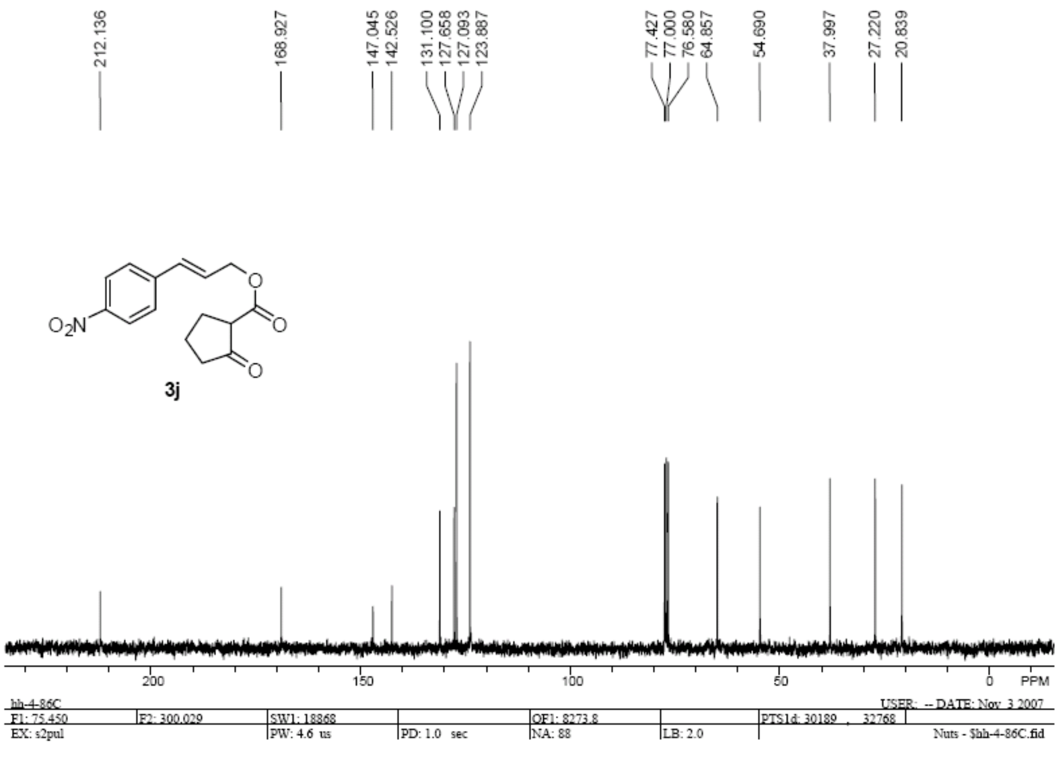

8.201
8.172
7.546
7.516
7.289
6.774
6.721
6.500
6.481
6.461
6.446
6.427
6.407
4.861
4.842
3.602
2.813
2.790
2.766
2.743
2.720
2.697
2.674
1.176
1.152
0.000
O2N
O
O
O
3h
1.94
2.14
1.00
1.02
2.16
1.83
0.78
3.09
2.90
8
6
4
2
0
PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Oct 19 2007
F1: 300.030
F2: 75.450
SW1: 4803
OF1: 1809.0
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 10
LB: 0.0
Nuts - $hh-4-80H.fid

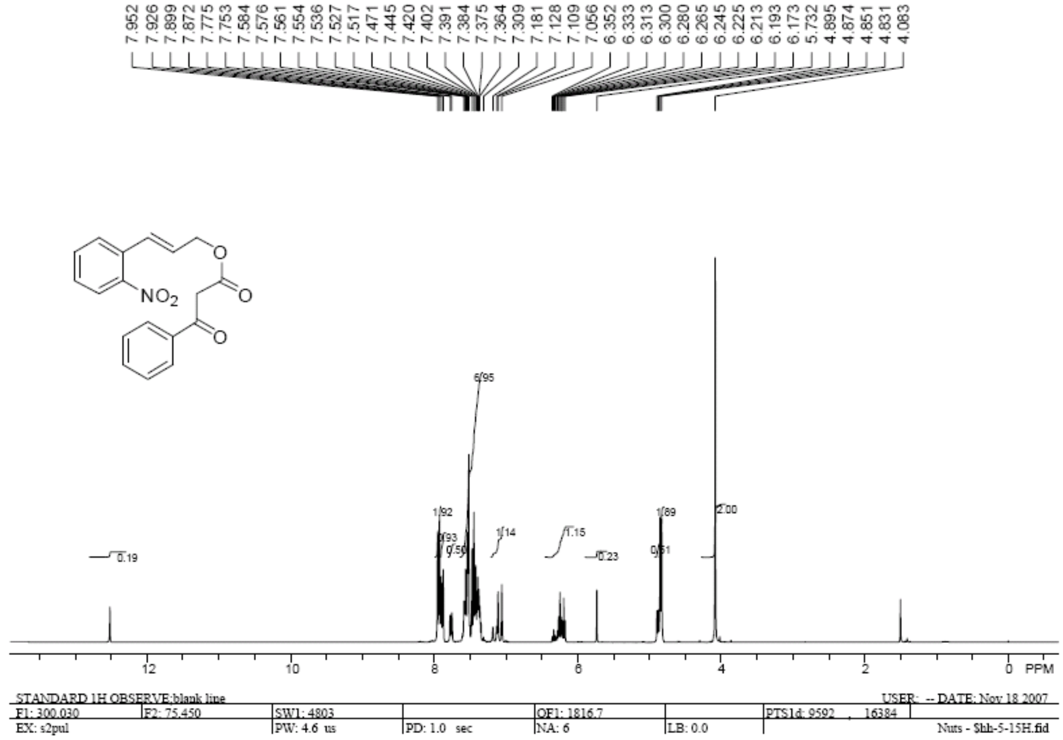

206.297
166.973
147.075
142.450
131.360
127.566
127.085
123.880
77.420
77.000
76.573
64.841
46.760
41.264
17.786
O2N
O
O
O
3h
200
150
100
50
0
PPM
hh-4-85C
USER: -- DATE: Oct 22 2007
F1: 75.450
F2: 300.029
SW1: 18868
OF1: 8273.3
PTS1d: 30189 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 44
LB: 2.0
Nuts - $hh-4-85C.fid

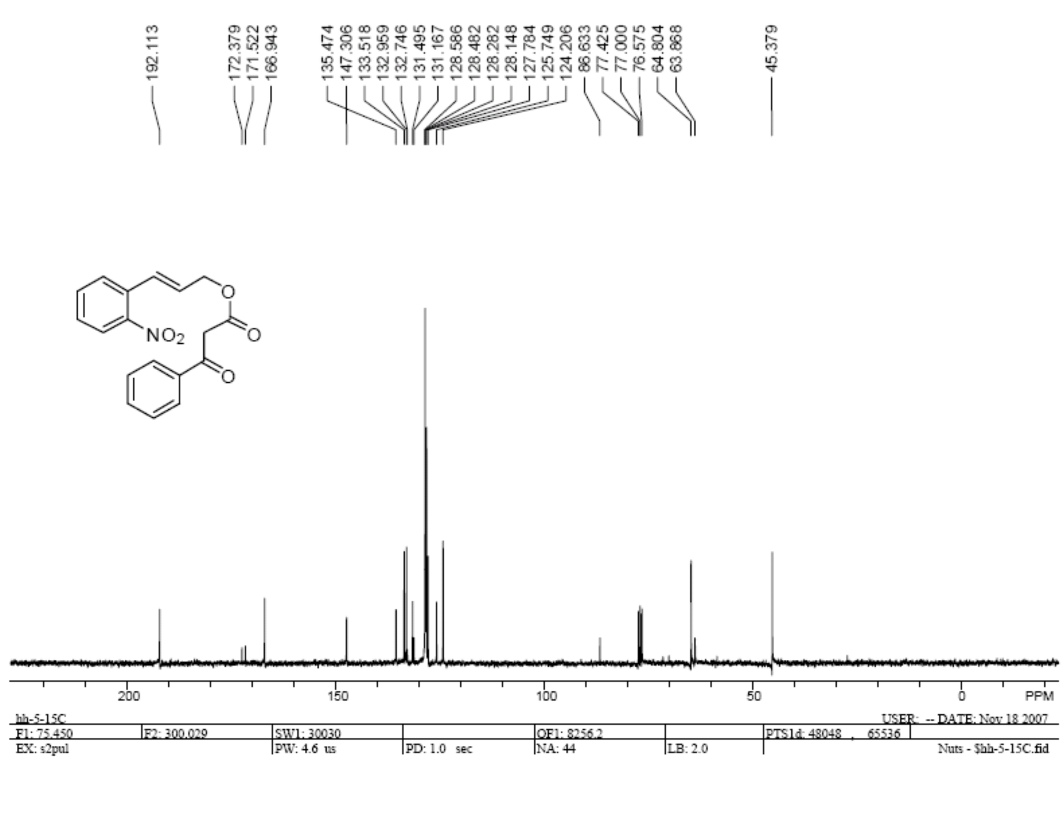

8.200
8.171
7.549
7.519
7.298
6.779
6.725
6.503
6.483
6.464
6.450
6.430
6.410
4.869
4.853
3.567
2.310
0.000
O2N
O
O
O
3i
1.87
2.20
1.00
1.01
2.28
1.86
3.15
8
6
4
2
PPM
STANDARD 1H OBSERVE;blank line
F1: 300.030
F2: 75.450
SW1: 4803
OF1: 1812.0
PTS1d: 9592 , 16384
USER: -- DATE: Oct 11 2007
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 14
LB: 0.0
Nuts - $hh-4-74H.fid

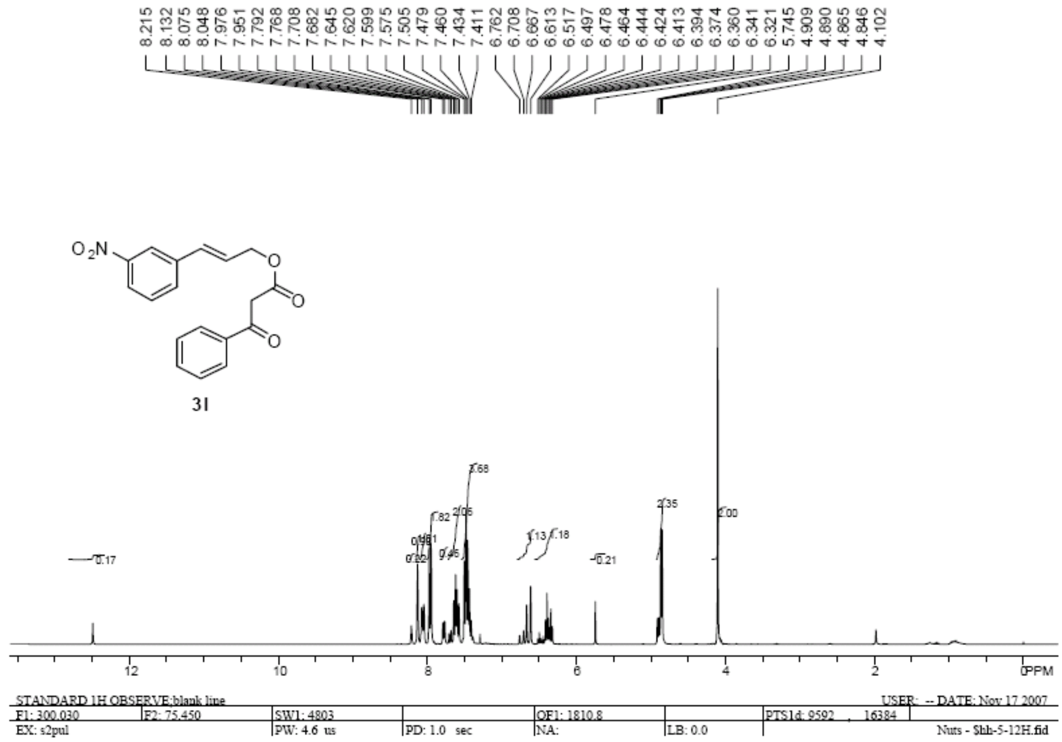

200.328
166.645
147.106
142.373
131.527
127.391
127.093
123.895
77.427
77.000
76.573
64.918
49.782
30.212
O2N
O
O
O
3i
200
150
100
50
0
PPM
hh-4-74C
F1: 75.450
F2: 300.029
SW1: 18868
OF1: 8273.3
PTS1d: 30189 , 32768
USER: -- DATE: Oct 11 2007
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 132
LB: 2.0
Nuts - $hh-4-74C.fid

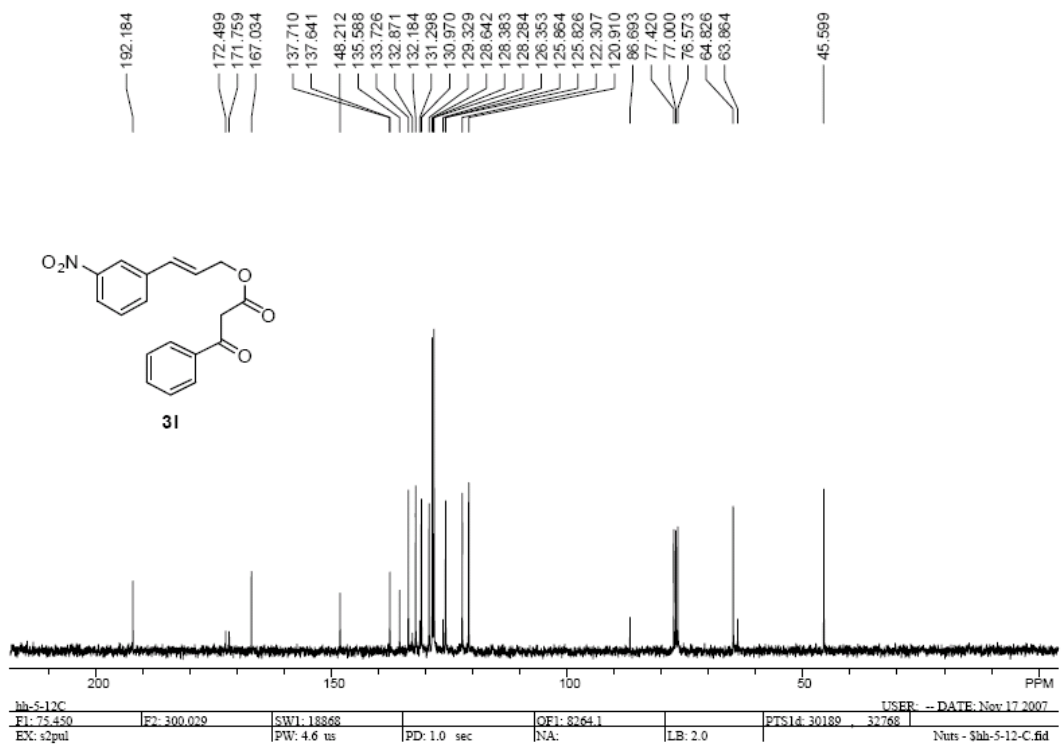

8.201
8.172
7.549
7.519
7.280
6.793
6.740
6.499
6.480
6.460
6.445
6.427
6.407
4.942
4.923
4.891
4.872
4.855
4.835
4.809
4.789
3.283
3.252
3.222
2.437
2.409
2.392
2.345
2.315
2.232
2.174
2.114
1.982
1.952
1.924
1.897
1.855
-0.000
3j
1.95
2.17
1.00
1.07
2.26
0.89
4.14
1.16
1.21
PPM
STANDARD 1H OBSERVE;blank line
USER: -- DATE: Oct 19 2007
F1: 300.030
F2: 75.450
SW1: 4803
OF1: 1806.7
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 18
LB: 0.0
Nuts - $hh-4-81H.fid

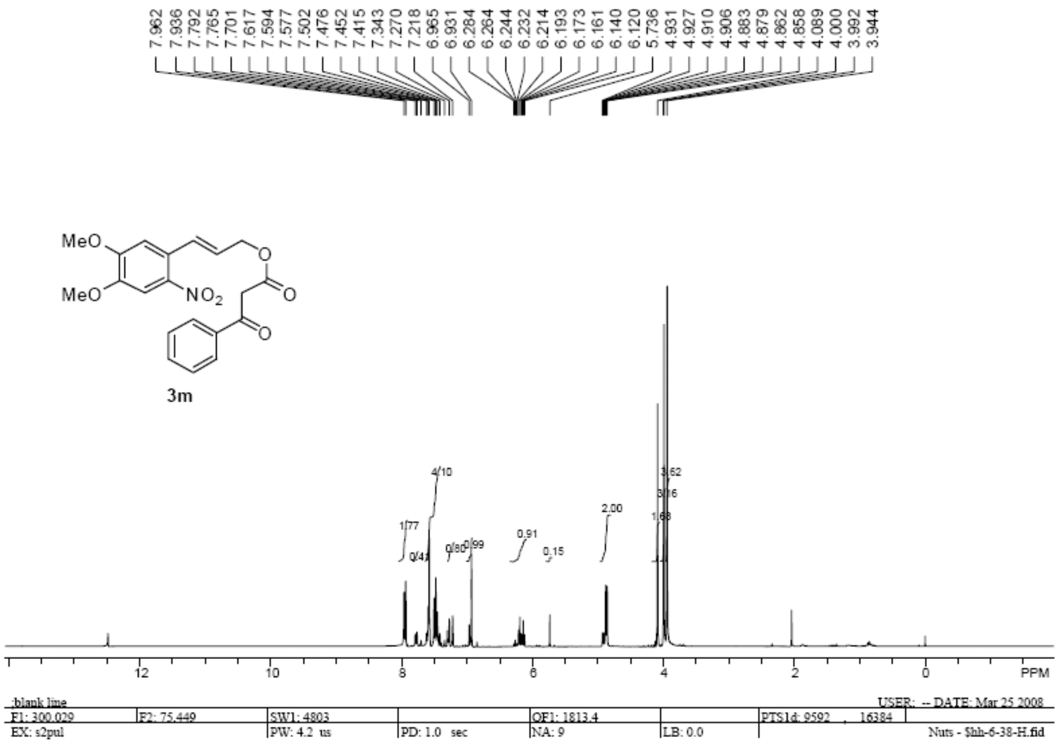

212.136
168.927
147.045
142.526
131.100
127.658
127.093
123.887
77.427
77.000
76.580
64.857
54.690
37.997
27.220
20.839
3j
PPM
hh-4-86C
USER: -- DATE: Nov 3 2007
F1: 75.450
F2: 300.029
SW1: 18868
OF1: 8273.8
PTS1d: 30189 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 88
LB: 2.0
Nuts - $hh-4-86C.fid


7.952 7.926 7.899 7.872 7.775 7.753 7.584 7.576 7.561 7.554 7.536 7.527 7.517 7.471 7.445 7.420 7.402 7.391 7.384 7.375 7.364 7.309 7.181 7.128 7.109 7.056 6.352 6.333 6.313 6.300 6.280 6.265 6.245 6.225 6.213 6.193 6.173 5.732 4.895 4.874 4.851 4.831 4.083
NO2
O
0.19
1.92
0.93
0.56
6.95
1.14
1.15
0.23
0.61
1.89
2.00
12
10
8
6
4
2
0 PPM
STANDARD 1H OBSERVE;blank line
USER: -- DATE: Nov 18 2007
F1: 300.030
F2: 75.450
SW1: 4803
OF1: 1816.7
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 6
LB: 0.0
Nuts - $hh-5-15H.fid


192.113
172.379 171.522 166.943
135.474 147.306 133.518 132.959 132.746 131.495 131.167 128.586 128.482 128.282 128.148 127.784 125.749 124.206 86.633 77.425 77.000 76.575 64.804 63.868
45.379
NO2
O
200
150
100
50
0
PPM
hh-5-15C
USER: -- DATE: Nov 18 2007
F1: 75.450
F2: 300.029
SW1: 30030
OF1: 8256.2
PTS1d: 48048 , 65536
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 44
LB: 2.0
Nuts - $hh-5-15C.fid


8.215 8.132 8.075 8.048 7.976 7.951 7.792 7.768 7.708 7.682 7.645 7.620 7.599 7.575 7.505 7.479 7.460 7.434 7.411 6.762 6.708 6.667 6.613 6.517 6.497 6.478 6.464 6.444 6.424 6.413 6.394 6.374 6.360 6.341 6.321 5.745 4.909 4.890 4.865 4.846 4.102
O_2N
O
O
O
3l
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Nov 17 2007
F1: 300.030 F2: 75.450 SW1: 4803 OF1: 1810.8 PTS1d: 9592 , 16384
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: LB: 0.0 Nuts - $hh-5-12H.fid


192.184 172.499 171.759 167.034 137.710 137.641 148.212 135.588 133.726 132.871 132.184 131.298 130.970 129.329 128.642 128.383 128.284 126.353 125.864 125.826 122.307 120.910 86.693 77.420 77.000 76.573 64.826 63.864 45.599
O_2N
O
O
O
3l
hh-5-12C
USER: -- DATE: Nov 17 2007
F1: 75.450 F2: 300.029 SW1: 18868 OF1: 8264.1 PTS1d: 30189 , 32768
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: LB: 2.0 Nuts - $hh-5-12-C.fid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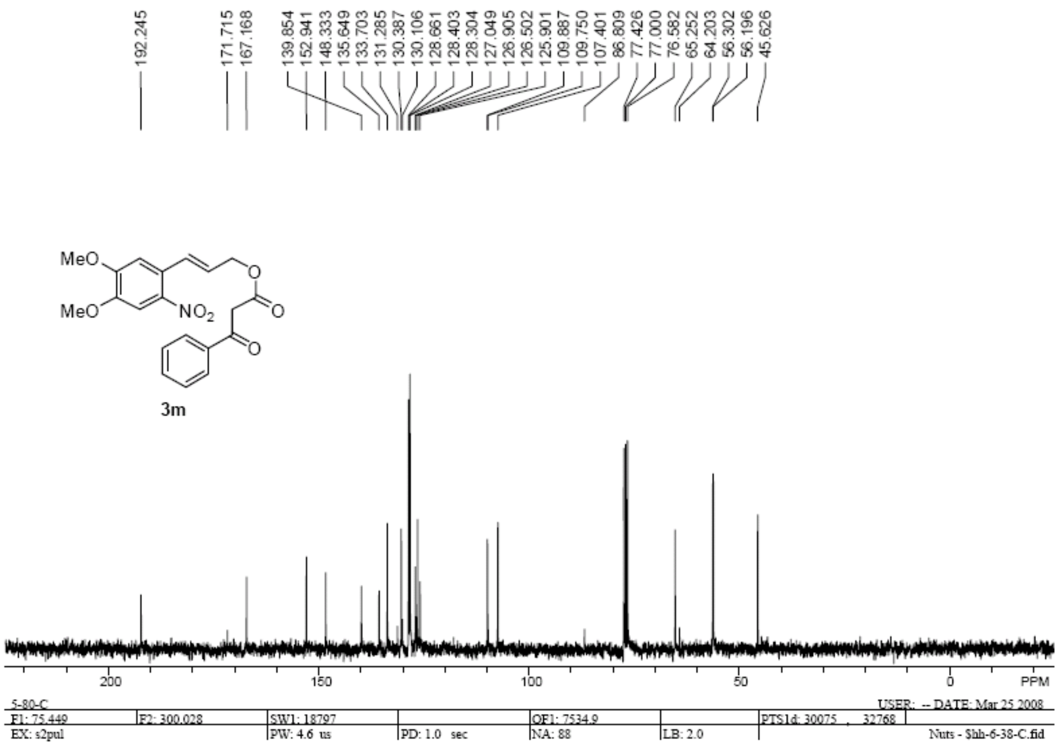
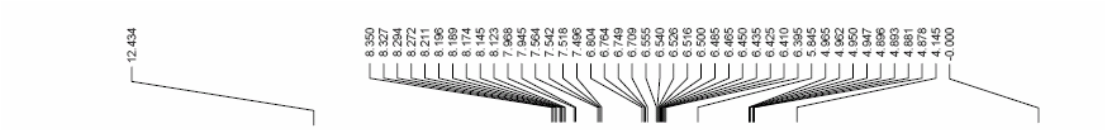
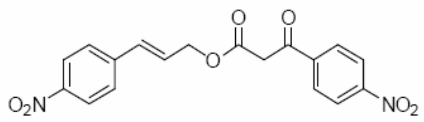
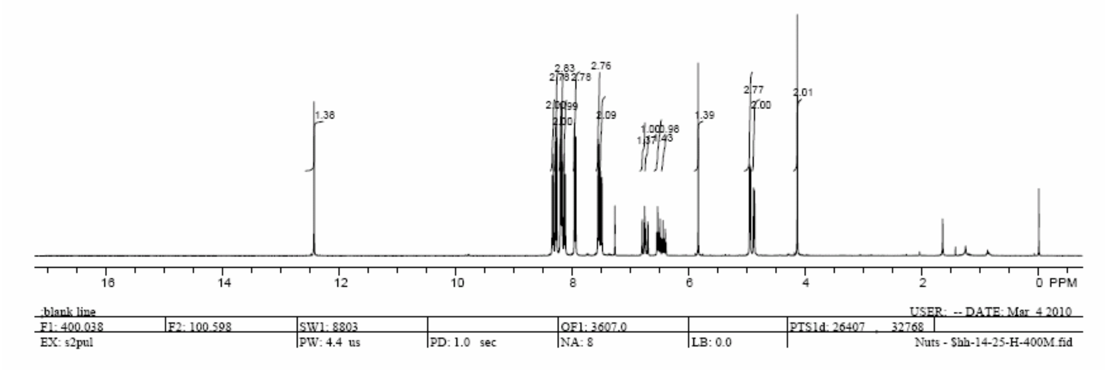
7.936
7.792
7.765
7.701
7.617
7.594
7.577
7.502
7.476
7.452
7.415
7.343
7.270
7.218
6.965
6.931
6.284
6.264
6.244
6.232
6.214
6.193
6.173
6.161
6.140
6.120
5.736
4.931
4.927
4.910
4.906
4.883
4.879
4.862
4.858
4.089
4.000
3.992
3.944
MeO
MeO
NO2
O
O
O
3m
PPM
USER: -- DATE: Mar 25 2008
F1: 300.029
F2: 75.449
SW1: 4803
OF1: 1813.4
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 9
LB: 0.0
Nuts - $hh-6-38-H.fid

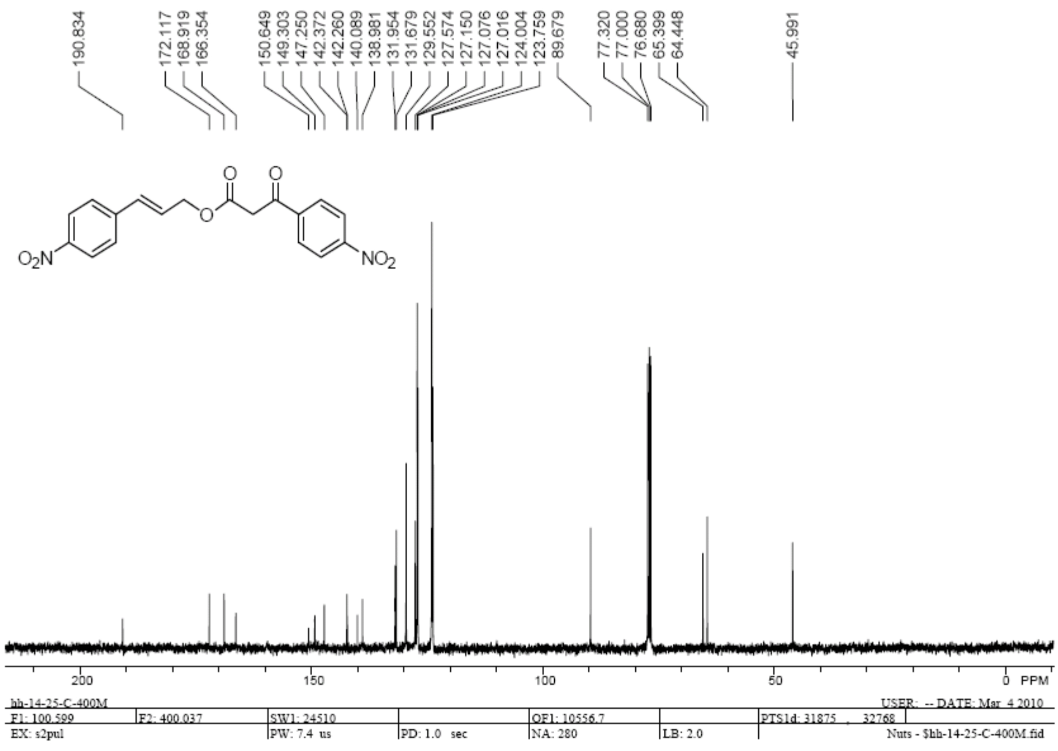

192.245
171.715
167.168
139.854
152.941
148.333
135.649
133.703
131.285
130.387
130.106
128.661
128.403
128.304
127.049
126.905
126.502
125.901
109.887
109.750
107.401
86.809
77.426
77.000
76.582
65.252
64.203
56.302
56.196
45.626
MeO
MeO
NO2
O
O
O
3m
PPM
5-80-C
USER: -- DATE: Mar 25 2008
F1: 75.449
F2: 300.028
SW1: 18797
OF1: 7534.9
PTS1d: 30075 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 88
LB: 2.0
Nuts - $hh-6-38-C.fid

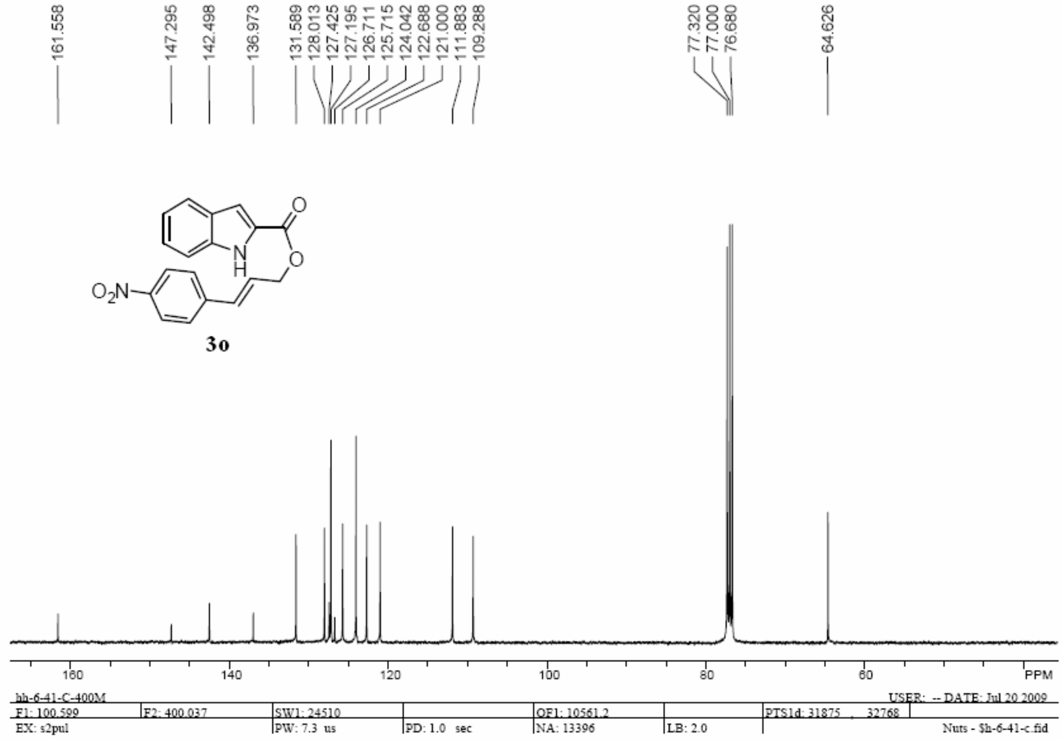


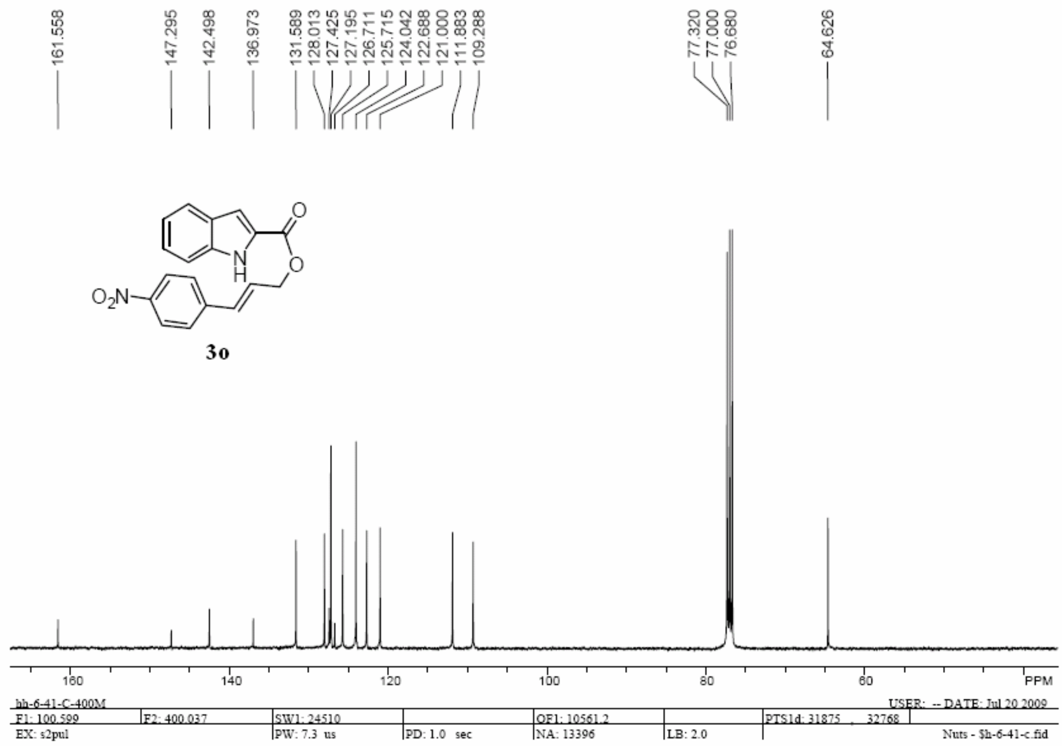


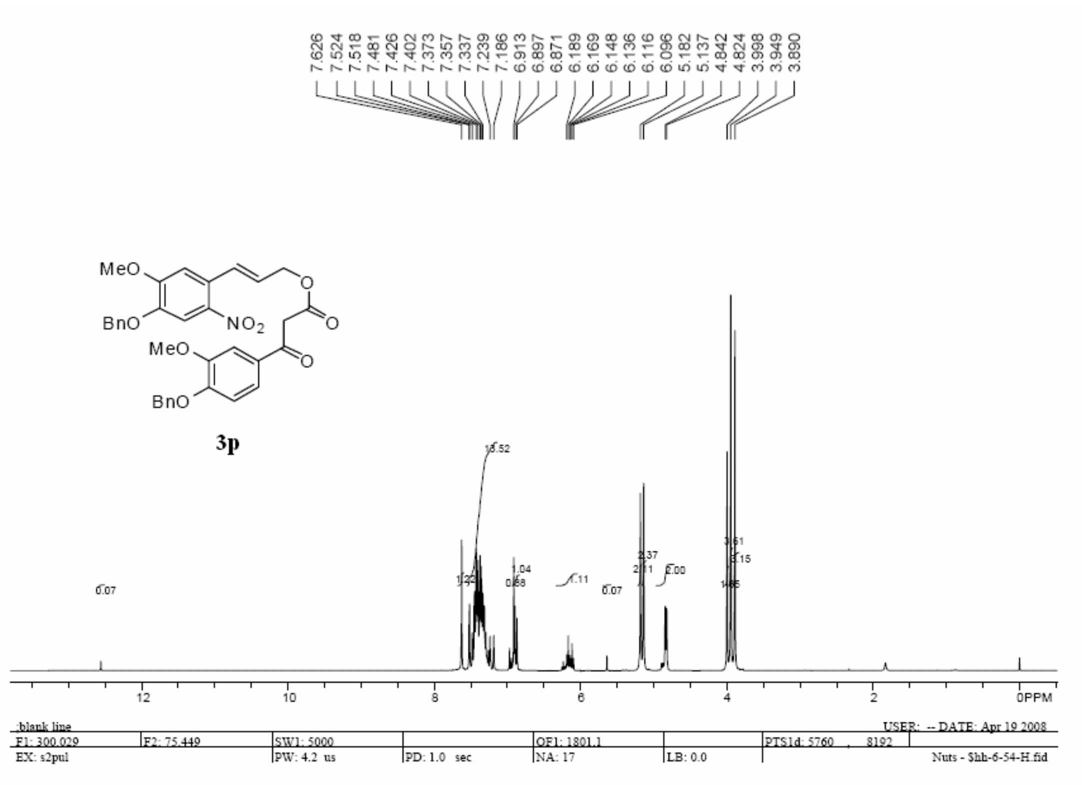
3n

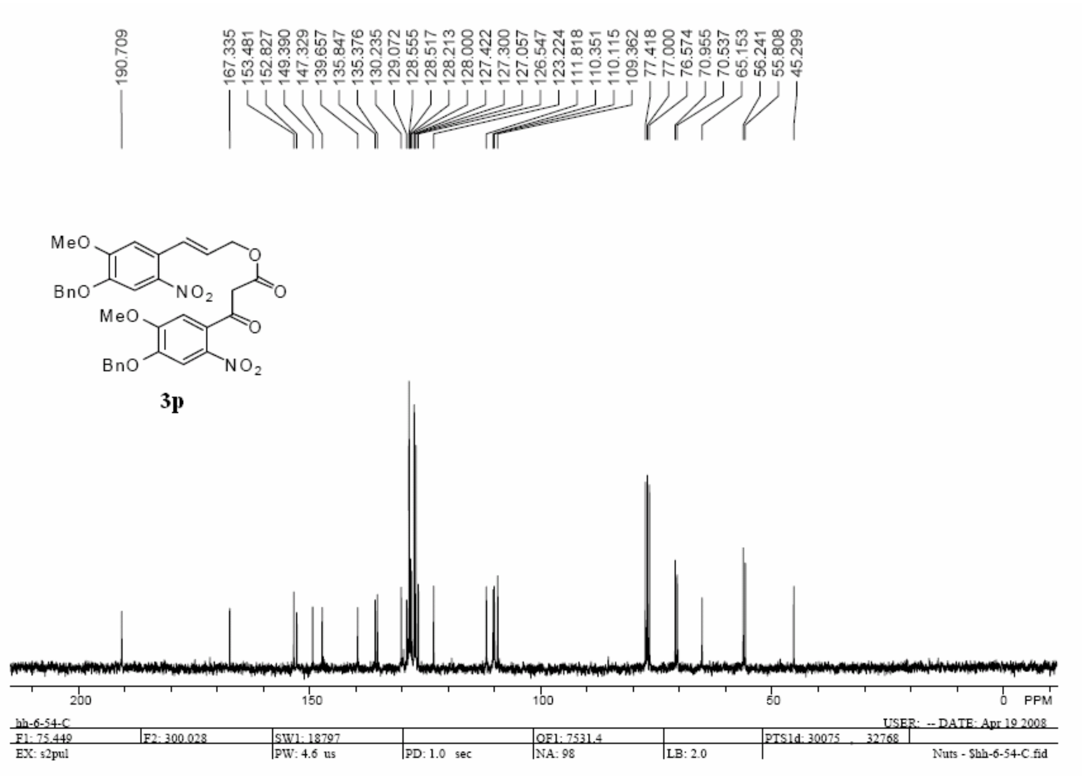


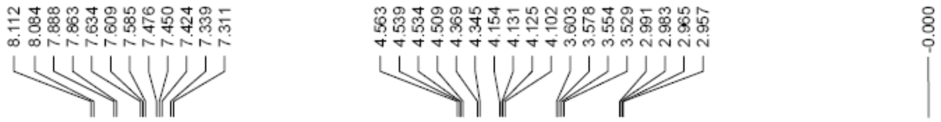


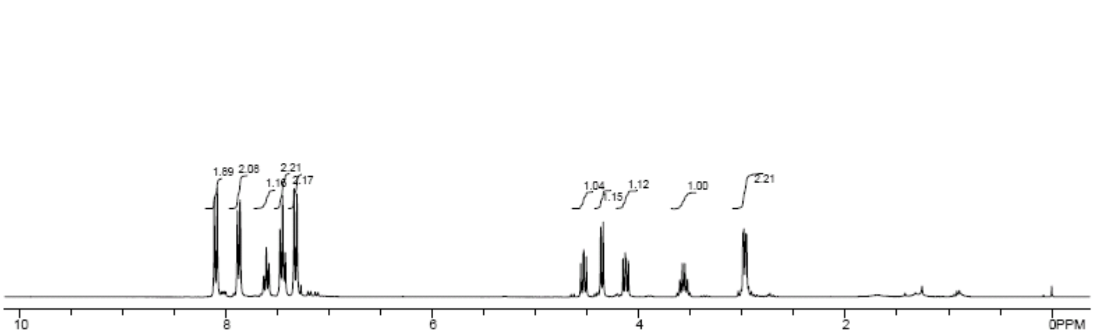

161.558
147.295
142.498
136.973
131.589
128.013
127.425
127.195
126.711
125.715
124.042
122.688
121.000
111.883
109.288
77.320
77.000
76.680
64.626
3o
160
140
120
100
80
60
PPM
hh-6-41-C-400M
USER: -- DATE: Jul 20 2009
F1: 100.599
F2: 400.037
SW1: 24510
OF1: 10561.2
PTS1d: 31875 , 32768
EX: s2pul
PW: 7.3 us
PD: 1.0 sec
NA: 13396
LB: 2.0
Nuts - $h-6-41-c.fid

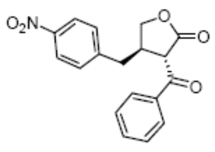

161.558
147.295
142.498
136.973
131.589
128.013
127.425
127.195
126.711
125.715
124.042
122.688
121.000
111.883
109.288
77.320
77.000
76.680
64.626
3o
160
140
120
100
80
60
PPM
hh-6-41-C-400M
USER: -- DATE: Jul 20 2009
F1: 100.599
F2: 400.037
SW1: 24510
OF1: 10561.2
PTS1d: 31875 , 32768
EX: s2pul
PW: 7.3 us
PD: 1.0 sec
NA: 13396
LB: 2.0
Nuts - $h-6-41-c.fid


MeO
BnO
NO2
MeO
BnO
3p
:blank line
F1: 300.029
F2: 75.449
SW1: 5000
OF1: 1801.1
PTS1d: 5760 , 8192
USER: -- DATE: Apr 19 2008
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 17
LB: 0.0
Nuts - $hh-6-54-H.fid


MeO
BnO
NO2
MeO
BnO
NO2
3p
hh-6-54-C
F1: 75.449
F2: 300.028
SW1: 18797
OF1: 7531.4
PTS1d: 30075 , 32768
USER: -- DATE: Apr 19 2008
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 98
LB: 2.0
Nuts - $hh-6-54-C.fid

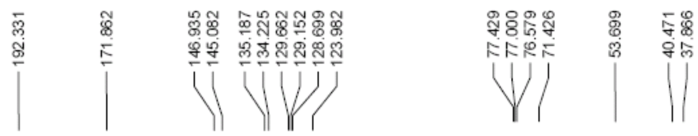


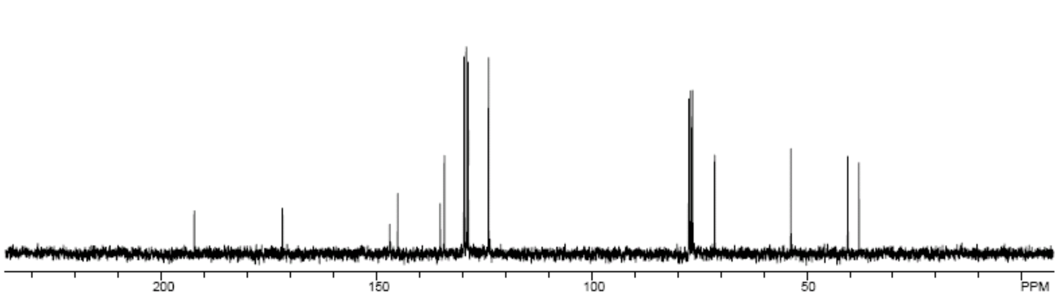


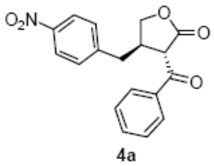


4a

STANDARD 1H OBSERVE:blank line USER: -- DATE: Jan 9 2007
F1: 300.030 F2: 75.450 SW1: 4803 OF1: 1804.6 PTS1d: 9592 , 16384
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 16 LB: 0.0 Nuts - $hh-2-42H.fid

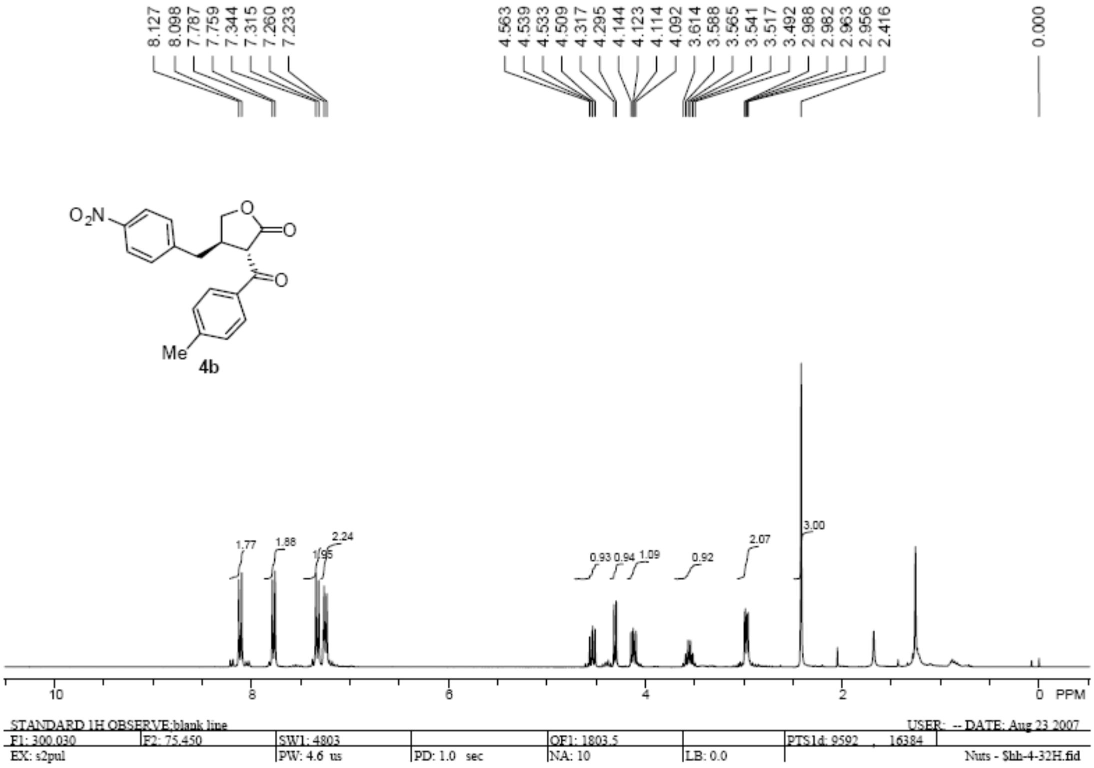


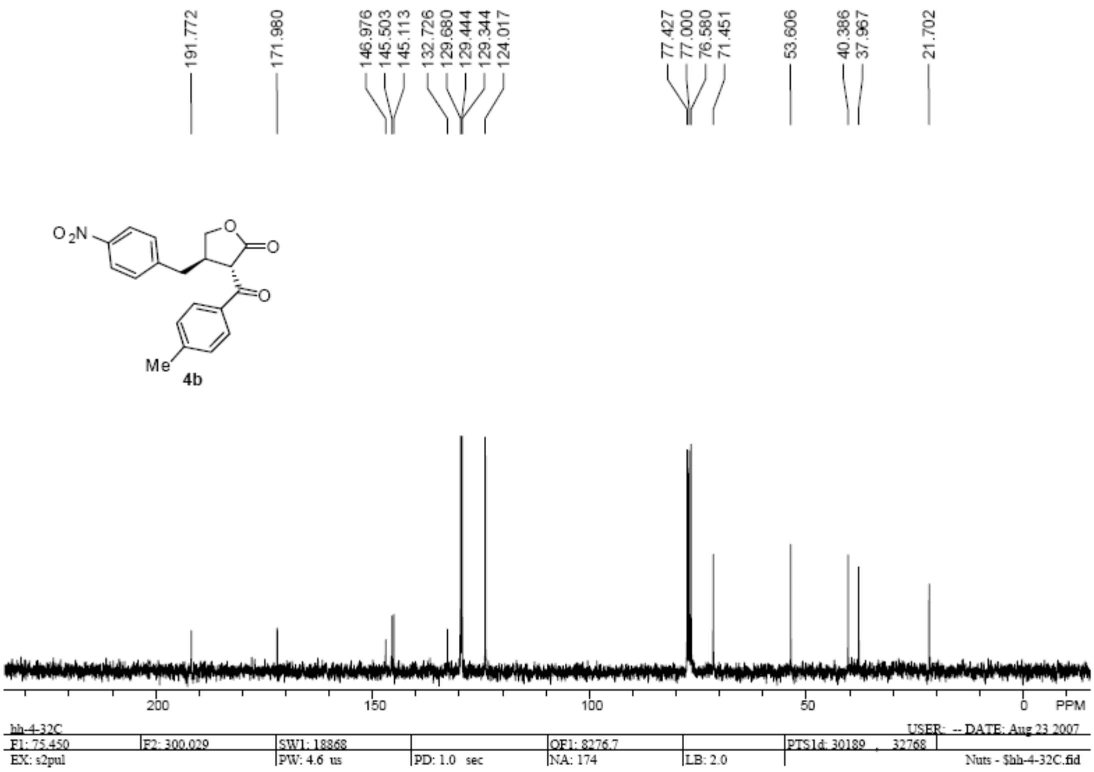


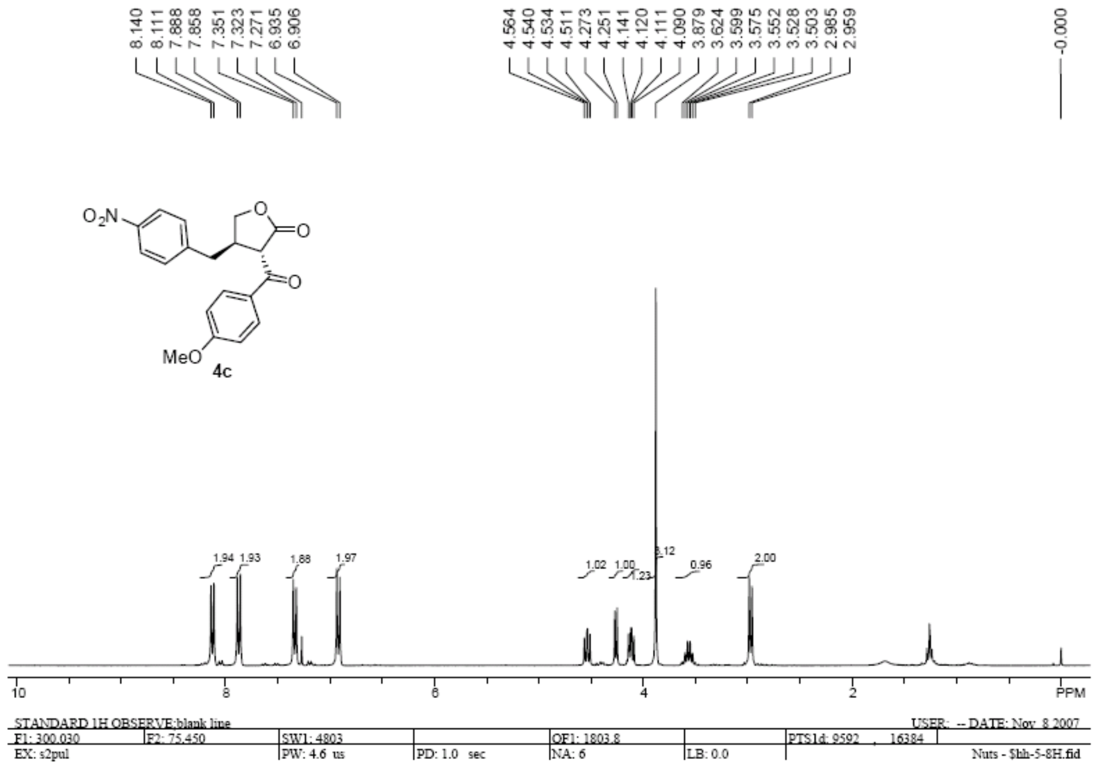


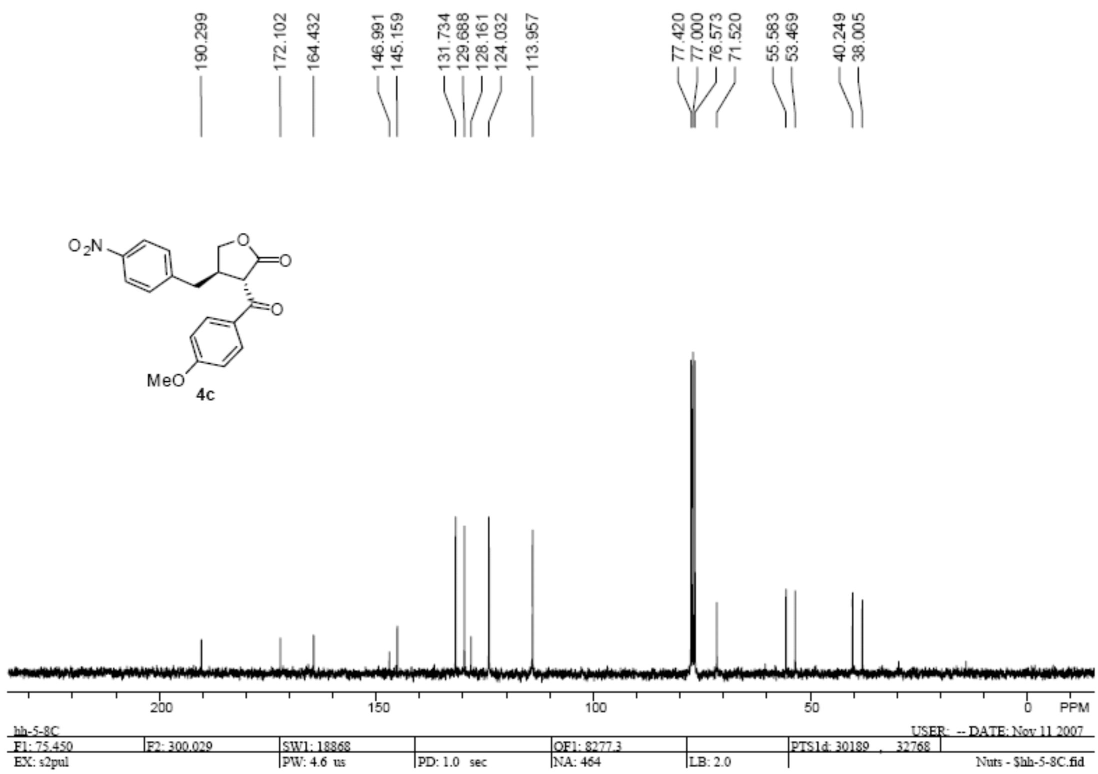
4a

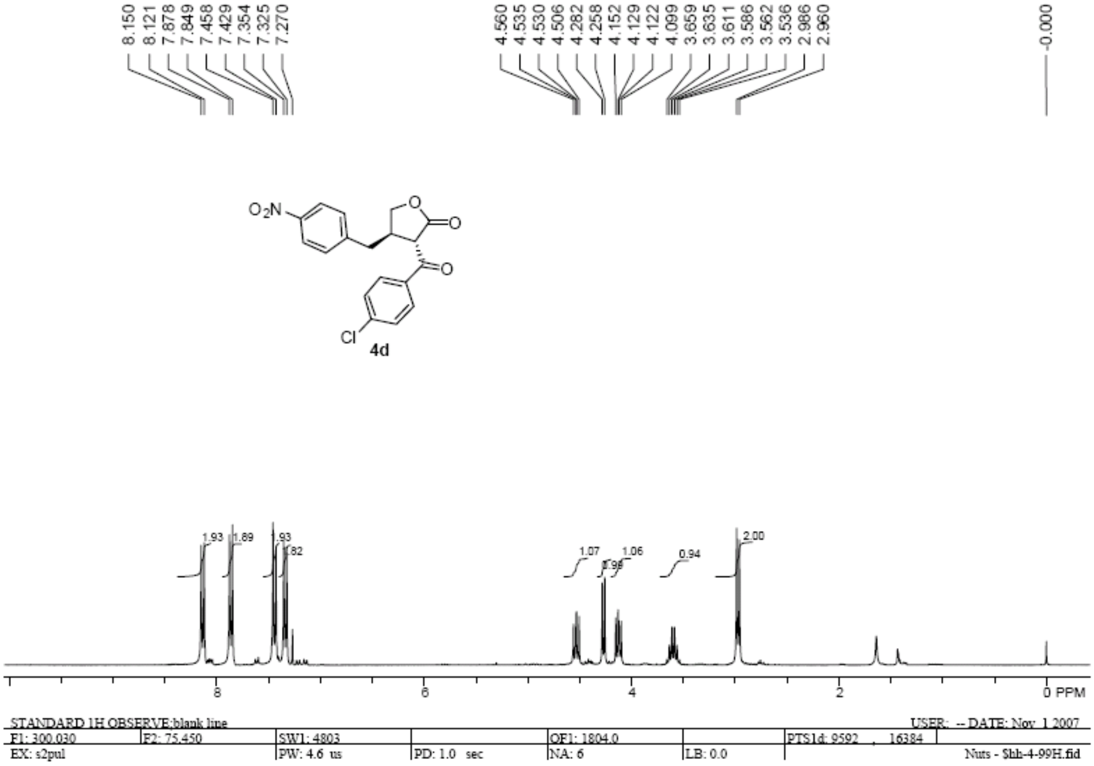
hh-2-42C USER: -- DATE: Jan 12 2007
F1: 75.450 F2: 300.029 SW1: 20000 OF1: 8274.6 PTS1d: 32000 , 32768
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 54 LB: 2.0 Nuts - $hh-2-42C.fid

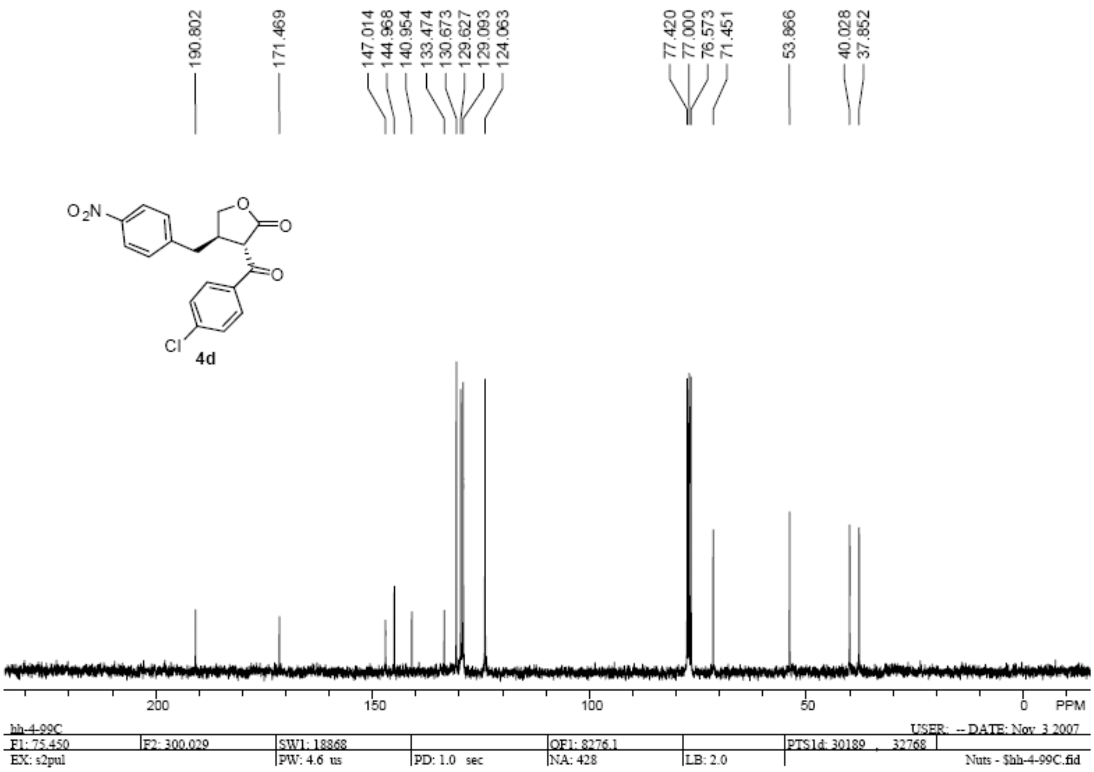

8.127 8.098 7.787 7.759 7.344 7.315 7.260 7.233
4.563 4.539 4.533 4.509 4.317 4.295 4.144 4.123 4.114 4.092 3.614 3.588 3.565 3.541 3.517 3.492 2.988 2.982 2.963 2.956 2.416
0.000
O_2N
O
Me
4b
1.77 1.88 1.95 2.24 0.93 0.94 1.09 0.92 2.07 3.00
10 8 6 4 2 0 PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Aug 23 2007
F1: 300.030 F2: 75.450 SW1: 4803 OF1: 1803.5 PTS1d: 9592 , 16384
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 10 LB: 0.0
Nuts - $hh-4-32H.fid

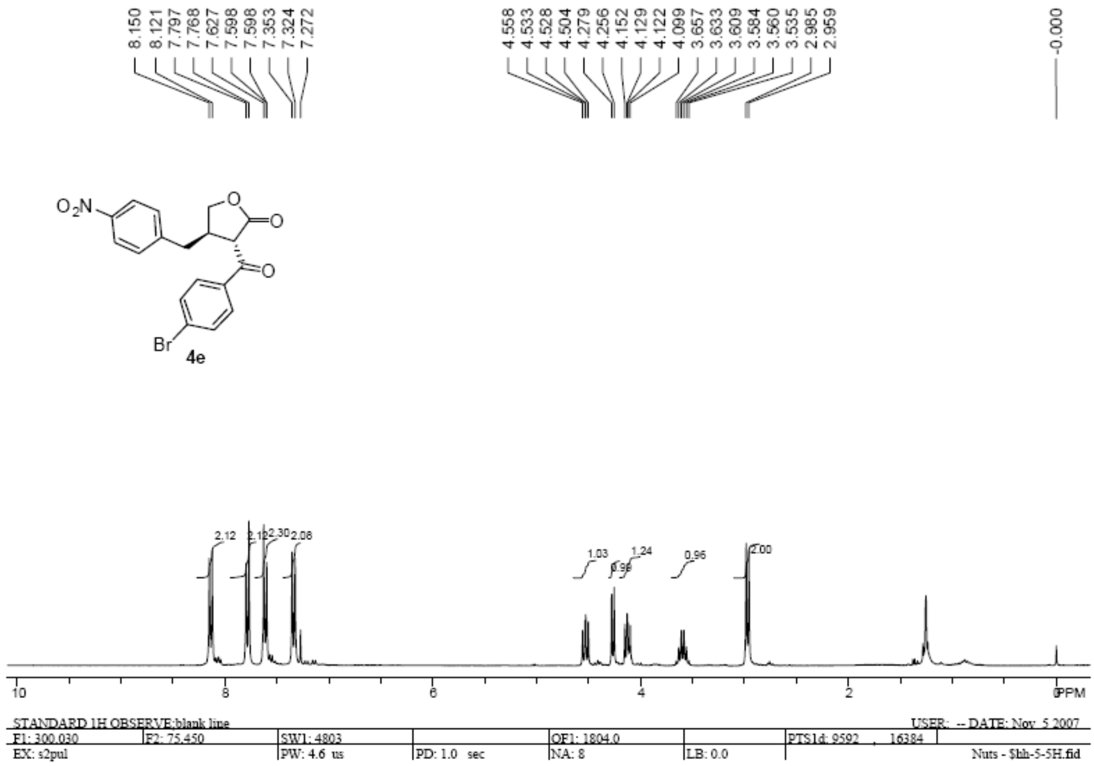

191.772 171.980 146.976 145.503 145.113 132.726 129.680 129.444 129.344 124.017 77.427 77.000 76.580 71.451 53.606 40.386 37.967 21.702
O_2N
O
Me
4b
200 150 100 50 0 PPM
hh-4-32C
USER: -- DATE: Aug 23 2007
F1: 75.450 F2: 300.029 SW1: 18868 OF1: 8276.7 PTS1d: 30189 , 32768
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 174 LB: 2.0
Nuts - $hh-4-32C.fid

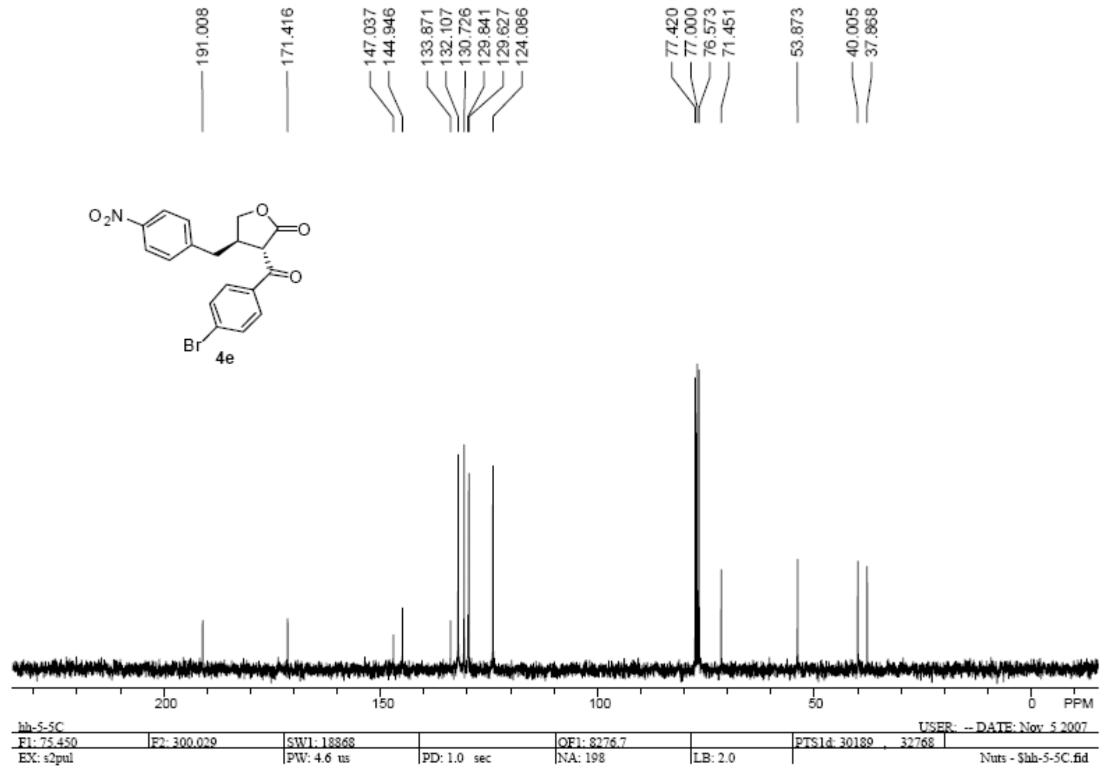


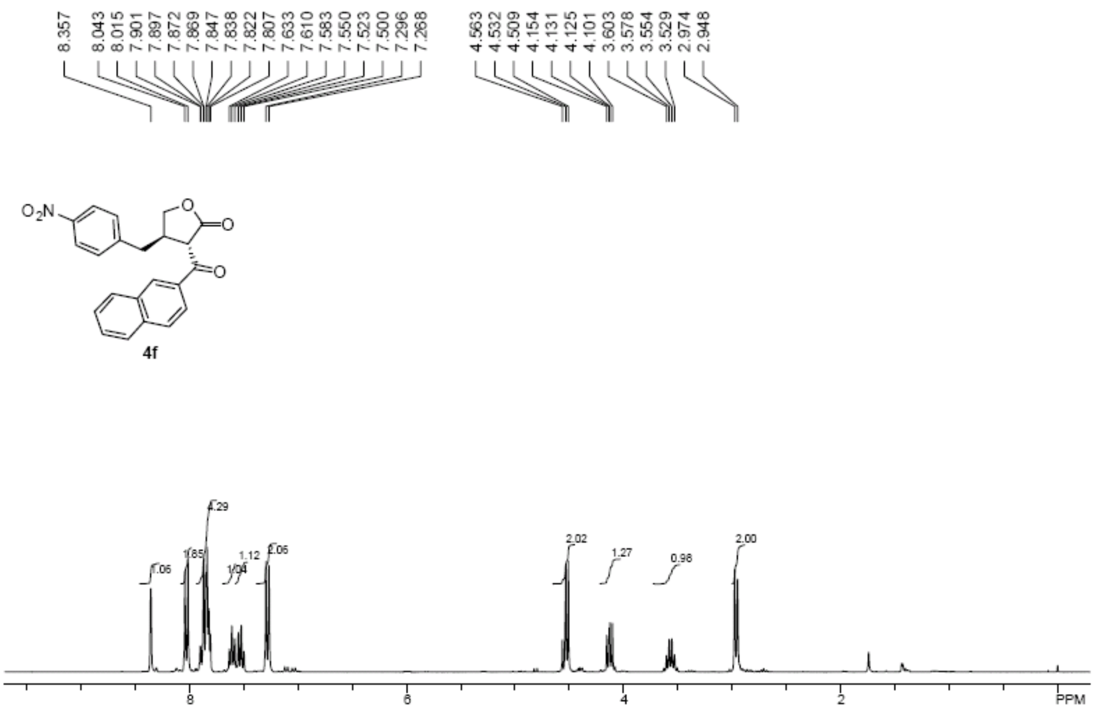



8.150 8.121 7.878 7.849 7.458 7.429 7.354 7.325 7.270
4.560 4.535 4.530 4.506 4.282 4.258 4.152 4.129 4.122 4.099 3.659 3.635 3.611 3.586 3.562 3.536 2.986 2.960
-0.000
4d
1.93 1.89 1.93 1.82 1.07 0.99 1.06 0.94 2.00
8 6 4 2 0 PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Nov 1 2007
F1: 300.030 F2: 75.450 SW1: 4803 OF1: 1804.0 PTS1d: 9592 , 16384
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 6 LB: 0.0 Nuts - $hh-4-99H.fid

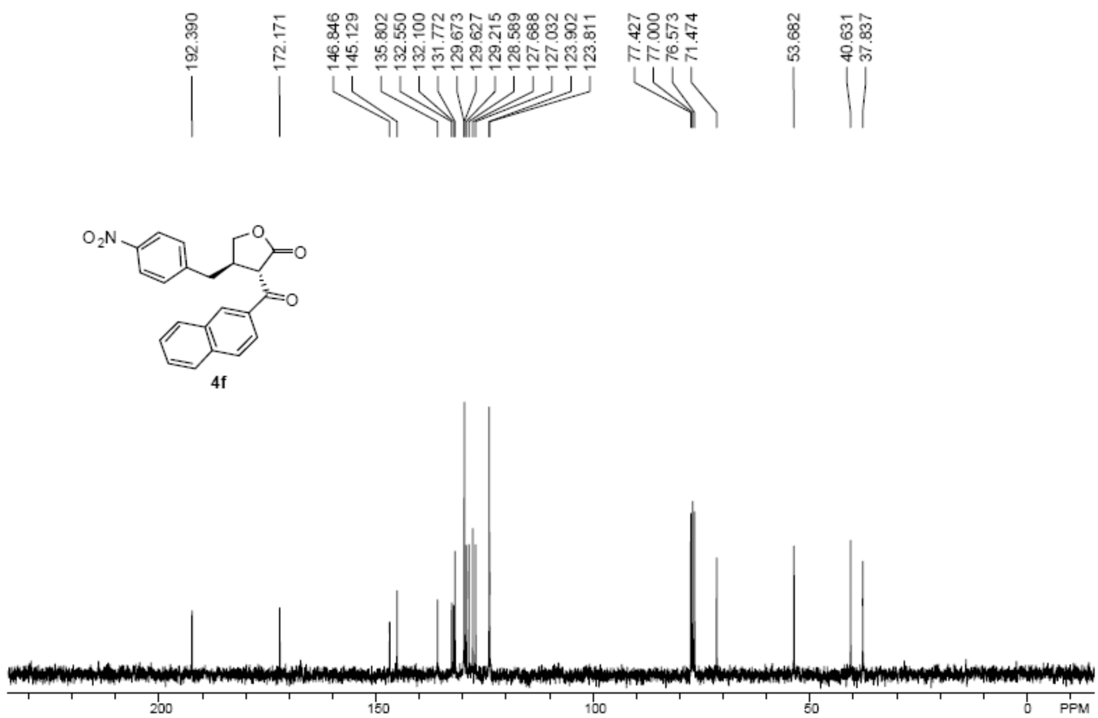

190.802 171.469 147.014 144.968 140.954 133.474 130.673 129.627 129.093 124.063 77.420 77.000 76.573 71.451 53.866 40.028 37.852
4d
200 150 100 50 0 PPM
hh-4-99C
USER: -- DATE: Nov 3 2007
F1: 75.450 F2: 300.029 SW1: 18868 OF1: 8276.1 PTS1d: 30189 , 32768
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 428 LB: 2.0 Nuts - $hh-4-99C.fid


8.150
8.121
7.797
7.768
7.627
7.598
7.598
7.353
7.324
7.272
4.558
4.533
4.528
4.504
4.279
4.256
4.152
4.129
4.122
4.099
3.657
3.633
3.609
3.584
3.560
3.535
2.985
2.959
-0.000
O_2N
O
O
O
Br
4e
2.12
2.12
2.30
2.08
1.03
0.96
1.24
0.96
2.00
10
8
6
4
2
0
PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Nov 5 2007
F1: 300.030
F2: 75.450
SW1: 4803
OF1: 1804.0
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $hh-5-5H.fid

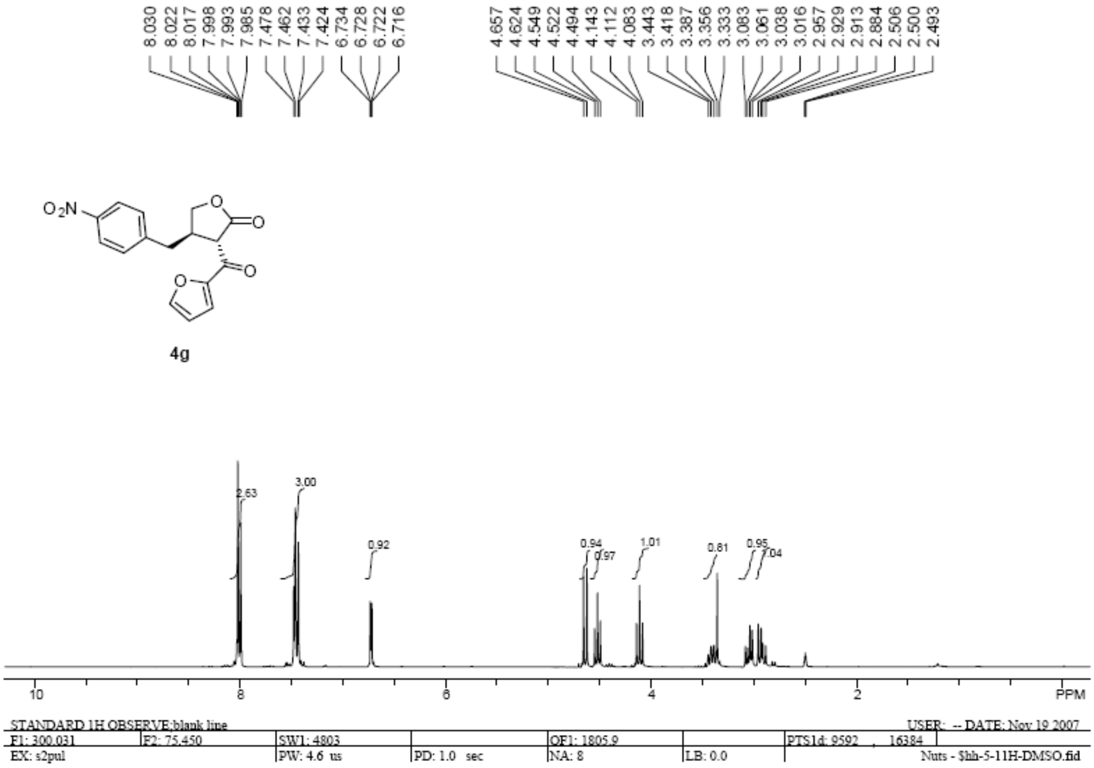

191.008
171.416
147.037
144.946
133.871
132.107
130.726
129.841
129.627
124.086
77.420
77.000
76.573
71.451
53.873
40.005
37.868
O_2N
O
O
O
Br
4e
200
150
100
50
0
PPM
hh-5-5C
USER: -- DATE: Nov 5 2007
F1: 75.450
F2: 300.029
SW1: 18868
OF1: 8276.7
PTS1d: 30189 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 198
LB: 2.0
Nuts - $hh-5-5C.fid



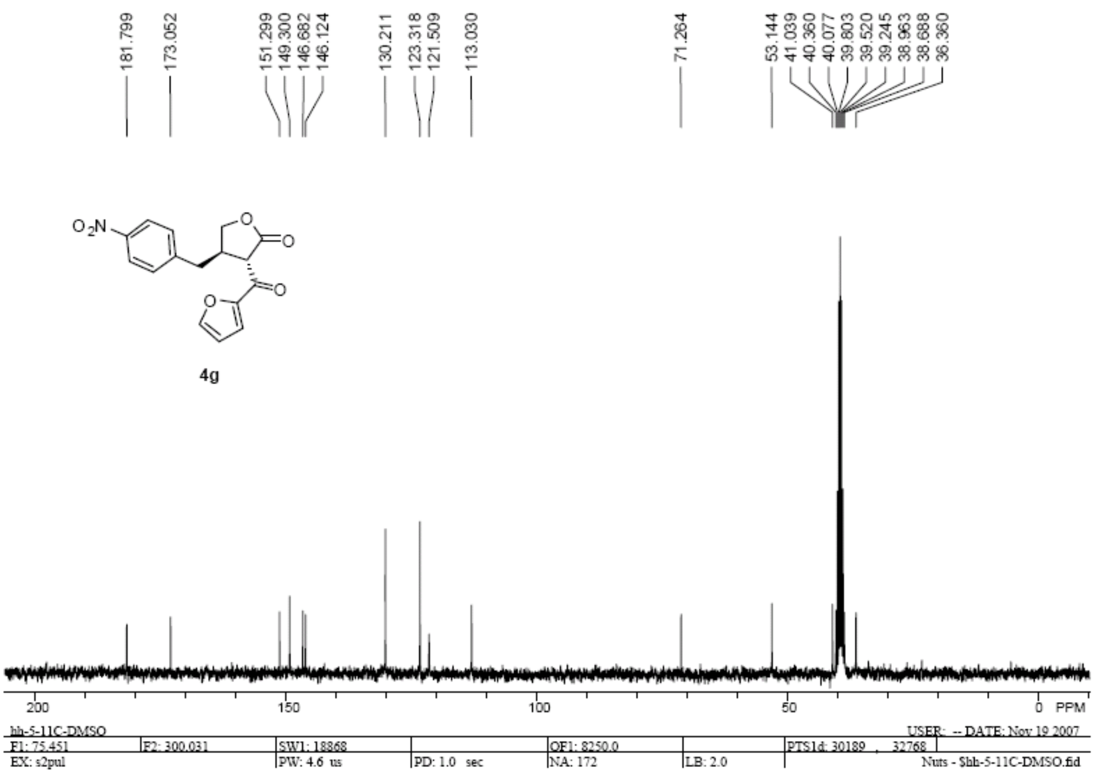
STANDARD 1H OBSERVE:blank line USER: -- DATE: Nov 1 2007
F1: 300.030 | F2: 75.450 | SW1: 4803 | OF1: 1802.0 | PTS1d: 9592 , 16384
EX: s2pul | PW: 4.6 us | PD: 1.0 sec | NA: 4 | LB: 0.0 | Nuts - $hh-4-100H.fid



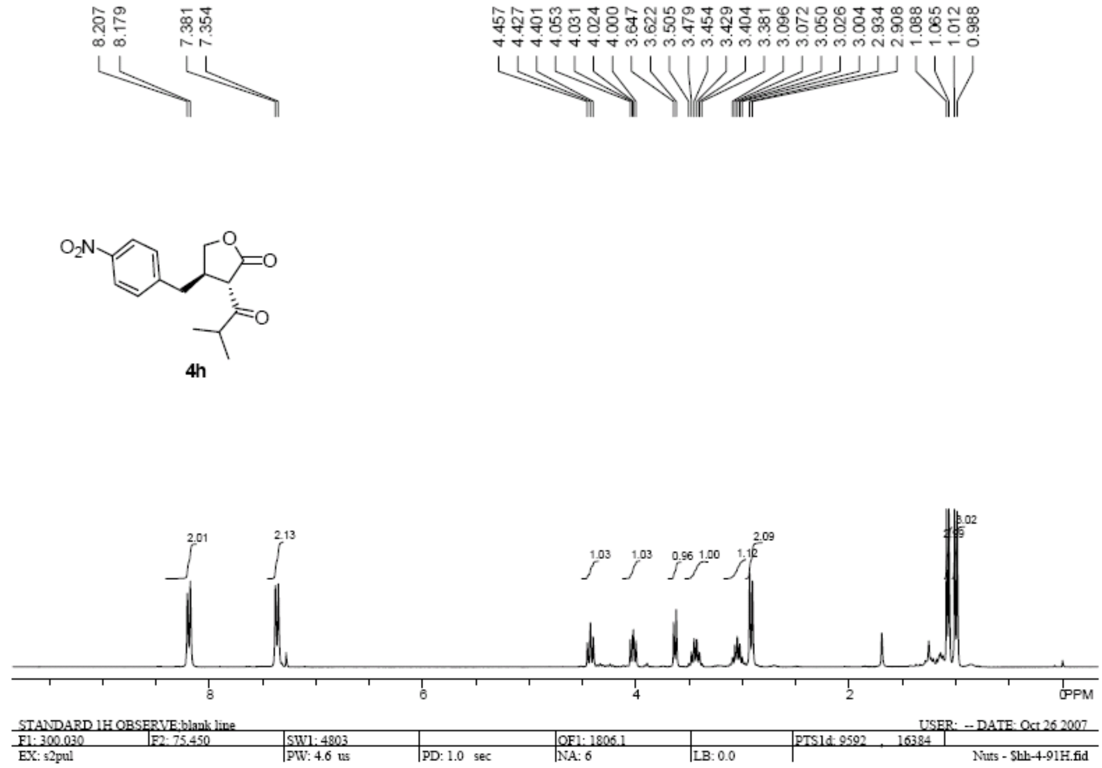
hh-4-100C USER: -- DATE: Nov 1 2007
F1: 75.450 | F2: 300.029 | SW1: 18868 | OF1: 8272.1 | PTS1d: 30189 , 32768
EX: s2pul | PW: 4.6 us | PD: 1.0 sec | NA: 42 | LB: 2.0 | Nuts - $hh-4-100C.fid

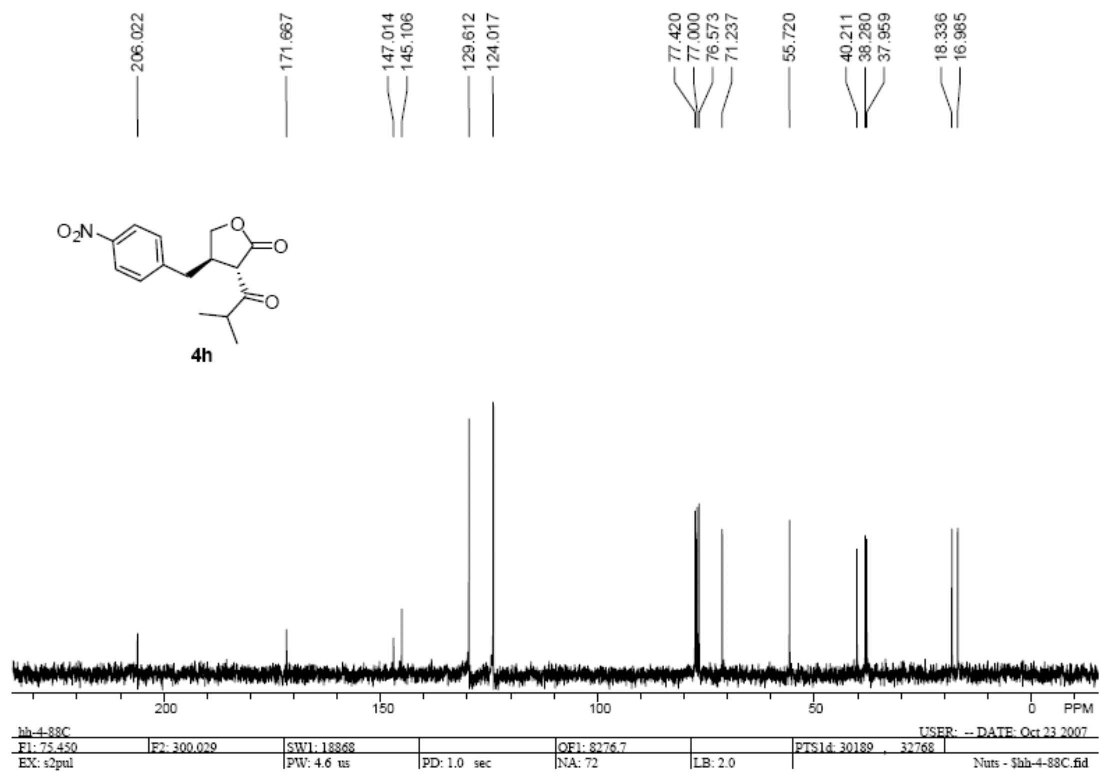

8.030
8.022
8.017
7.998
7.993
7.985
7.478
7.462
7.433
7.424
6.734
6.728
6.722
6.716
4.657
4.624
4.549
4.522
4.494
4.143
4.112
4.083
3.443
3.418
3.387
3.356
3.333
3.083
3.061
3.038
3.016
2.957
2.929
2.913
2.884
2.506
2.500
2.493
2.63
3.00
0.92
0.94
0.97
1.01
0.81
0.95
1.04
PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Nov 19 2007
F1: 300.031
F2: 75.450
SW1: 4803
OF1: 1805.9
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $hh-5-11H-DMSO.fid

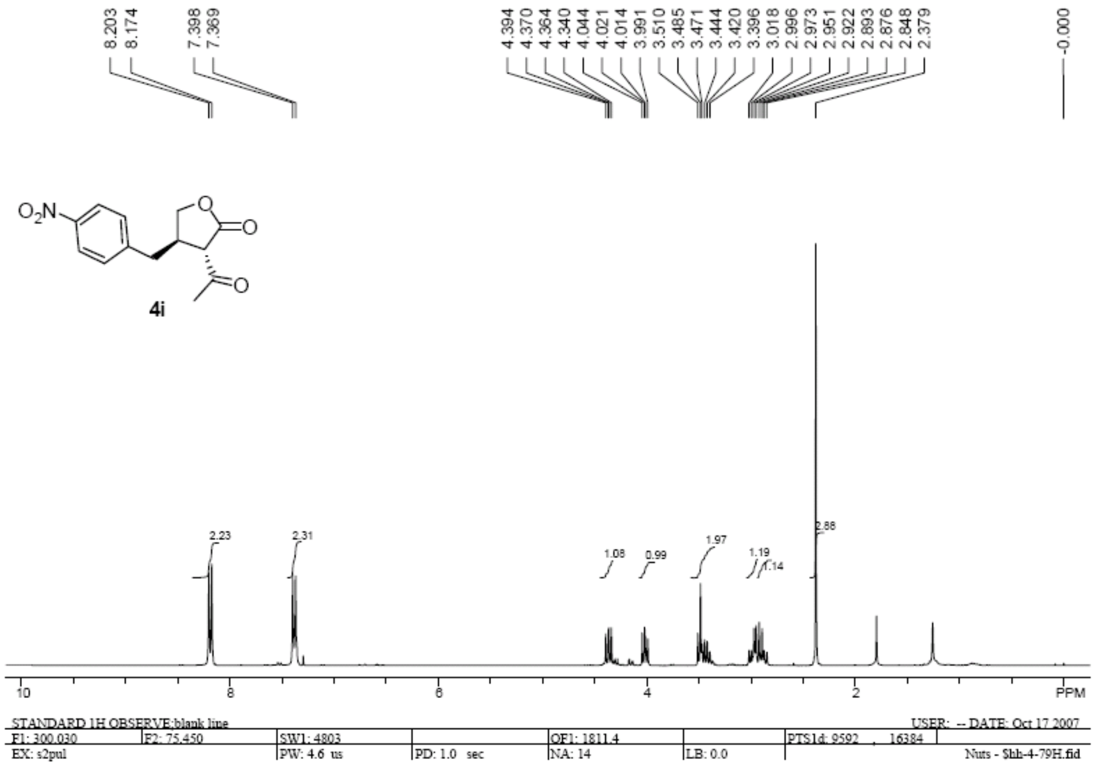
4g

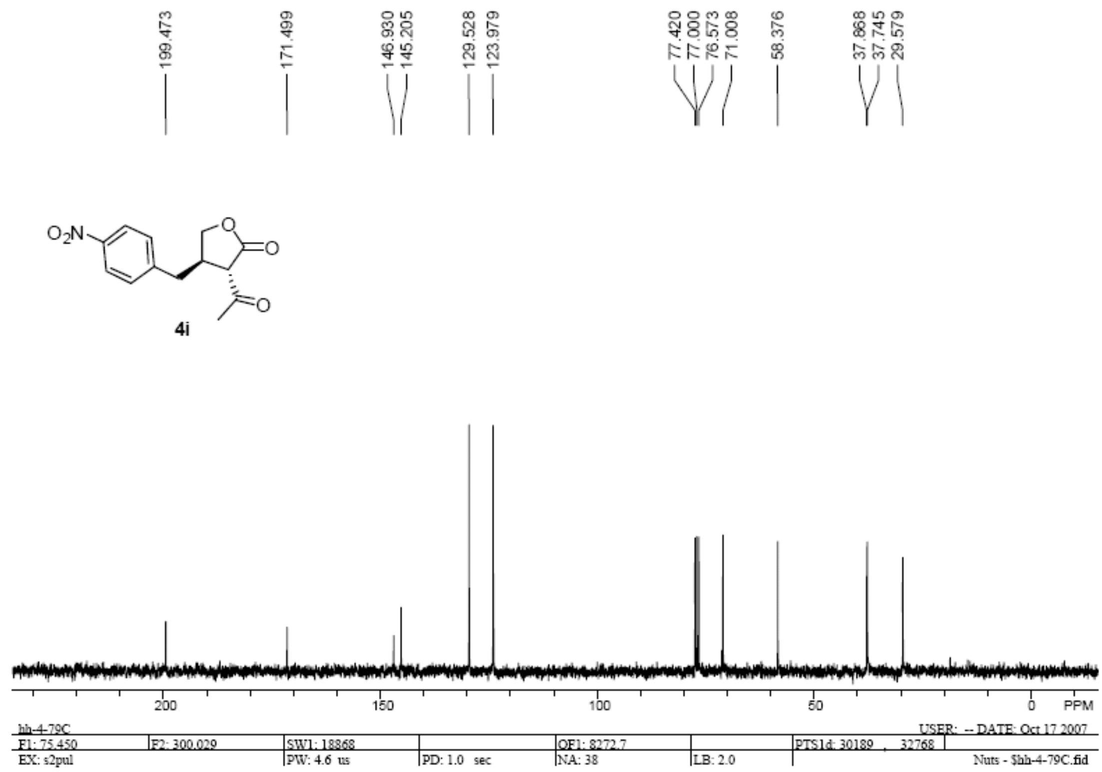

181.799
173.052
151.299
149.300
146.682
146.124
130.211
123.318
121.509
113.030
71.264
53.144
41.039
40.360
40.077
39.803
39.520
39.245
38.963
38.688
36.360
PPM
hh-5-11C-DMSO
USER: -- DATE: Nov 19 2007
F1: 75.451
F2: 300.031
SW1: 18868
OF1: 8250.0
PTS1d: 30189 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 172
LB: 2.0
Nuts - $hh-5-11C-DMSO.fid

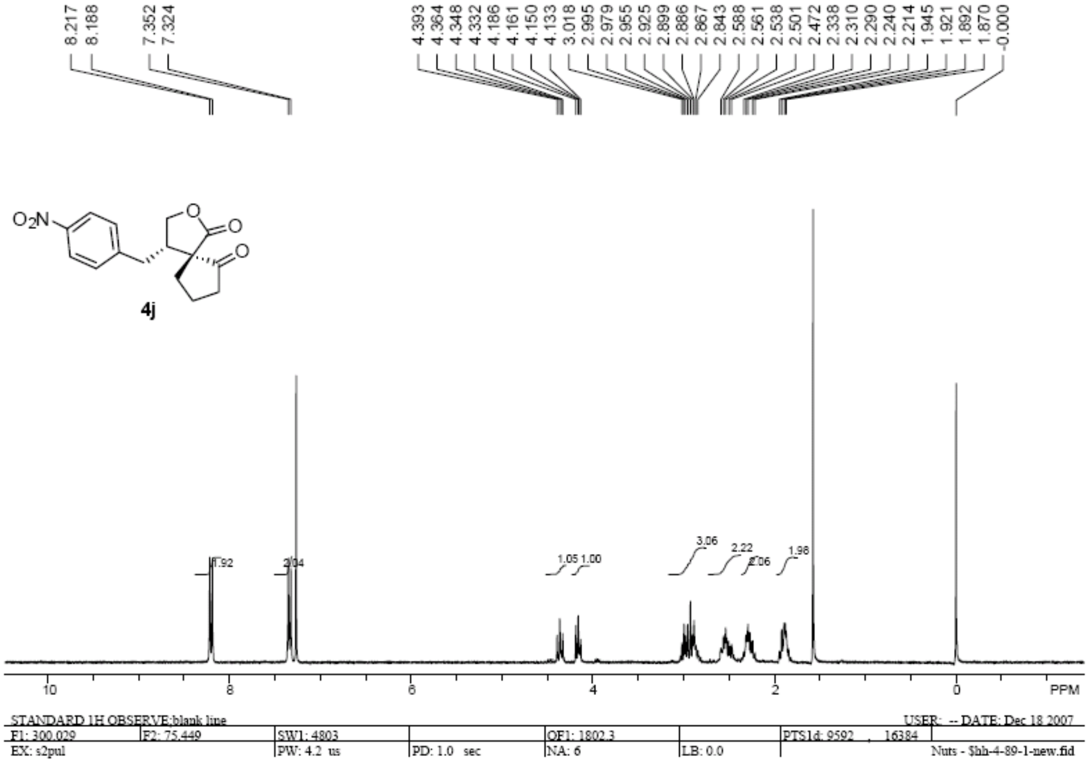
4g

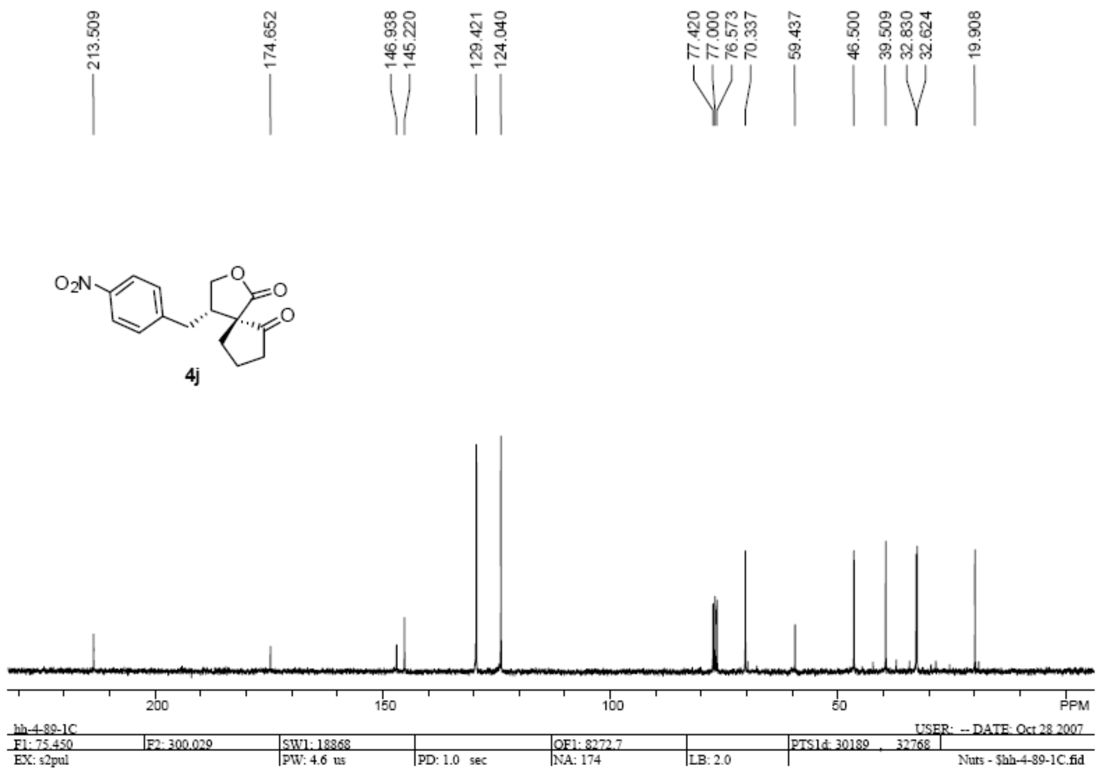

8.207
8.179
7.381
7.354
4.457
4.427
4.401
4.053
4.031
4.024
4.000
3.647
3.622
3.505
3.479
3.454
3.429
3.404
3.381
3.096
3.072
3.050
3.026
3.004
2.934
2.908
1.088
1.065
1.012
0.988
O_2N
O
O
O
4h
2.01
2.13
1.03
1.03
0.96
1.00
1.12
2.09
3.02
PPM
STANDARD 1H OBSERVE:blank line
F1: 300.030
F2: 75.450
SW1: 4803
OF1: 1806.1
PTS1d: 9592 , 16384
USER: -- DATE: Oct 26 2007
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 6
LB: 0.0
Nuts - $hh-4-91H.fid

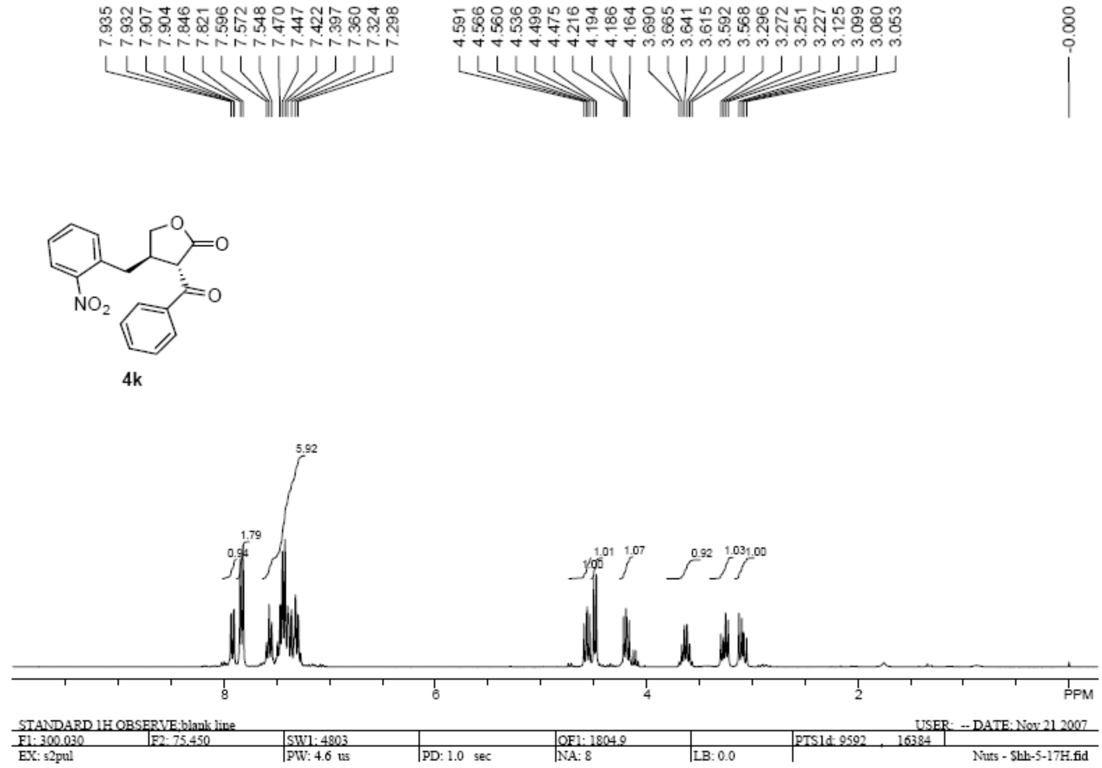

206.022
171.667
147.014
145.106
129.612
124.017
77.420
77.000
76.573
71.237
55.720
40.211
38.280
37.959
18.336
16.985
O_2N
O
O
O
4h
200
150
100
50
0
PPM
hh-4-88C
F1: 75.450
F2: 300.029
SW1: 18868
OF1: 8276.7
PTS1d: 30189 , 32768
USER: -- DATE: Oct 23 2007
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 72
LB: 2.0
Nuts - $hh-4-88C.fid

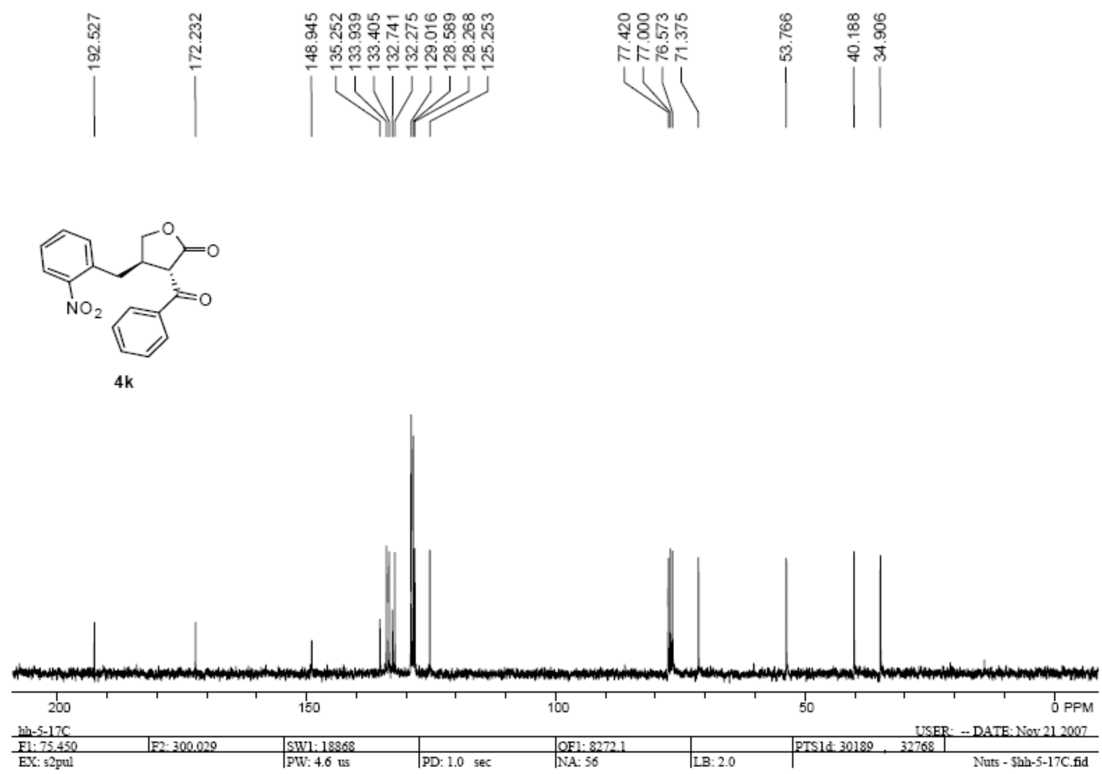

8.203
8.174
7.398
7.369
4.394
4.370
4.364
4.340
4.044
4.021
4.014
3.991
3.510
3.485
3.471
3.444
3.420
3.396
3.018
2.996
2.973
2.951
2.922
2.893
2.876
2.848
2.379
-0.000
4i
2.23
2.31
1.08
0.99
1.97
1.19
1.14
2.88
PPM
STANDARD 1H OBSERVE;blank line
USER: -- DATE: Oct 17 2007
F1: 300.030
F2: 75.450
SW1: 4803
OF1: 1811.4
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 14
LB: 0.0
Nuts - $hh-4-79H.fid

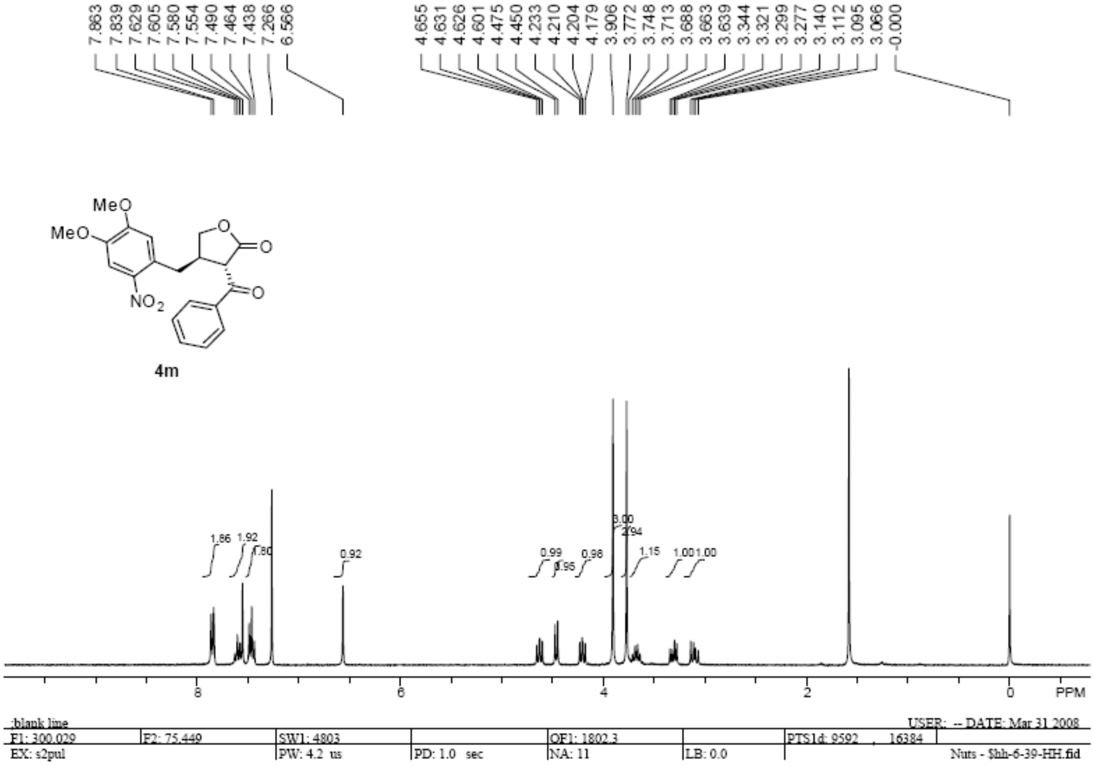

199.473
171.499
146.930
145.205
129.528
123.979
77.420
77.000
76.573
71.008
58.376
37.868
37.745
29.579
4i
PPM
hh-4-79C
USER: -- DATE: Oct 17 2007
F1: 75.450
F2: 300.029
SW1: 18868
OF1: 8272.7
PTS1d: 30189 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 38
LB: 2.0
Nuts - $hh-4-79C.fid

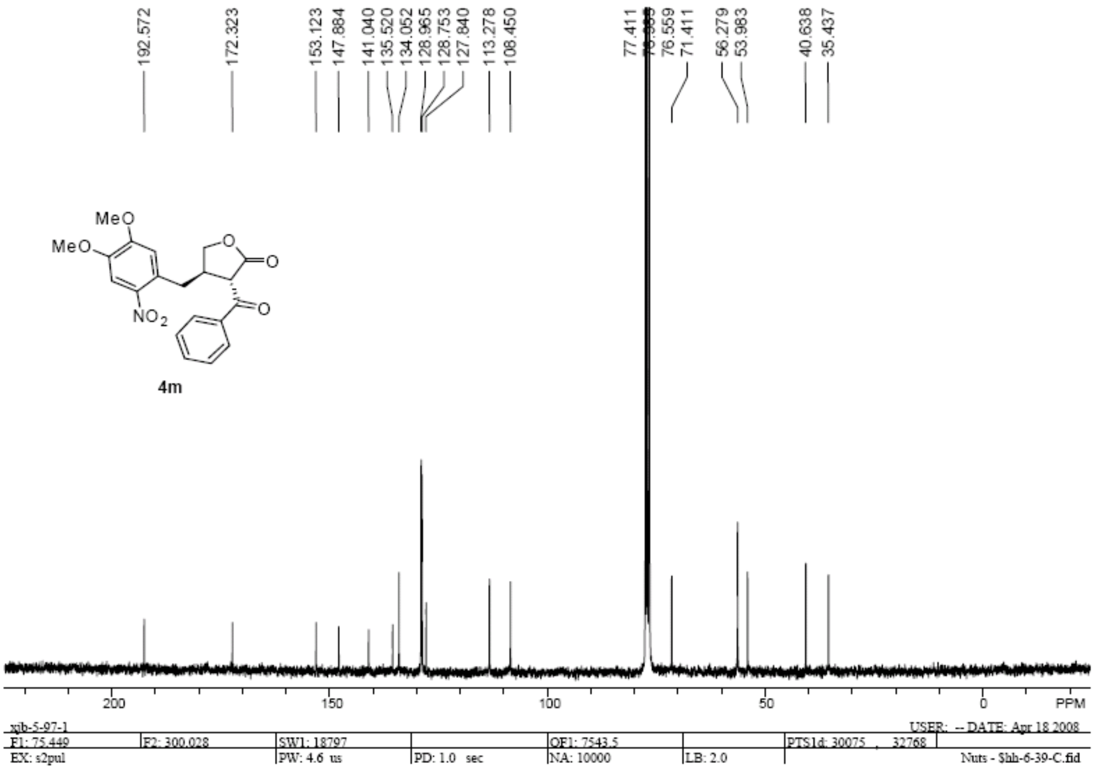

8.217
8.188
7.352
7.324
4.393
4.364
4.348
4.332
4.186
4.161
4.150
4.133
3.018
2.995
2.979
2.955
2.925
2.899
2.886
2.867
2.843
2.588
2.561
2.538
2.501
2.472
2.338
2.310
2.290
2.240
2.214
1.945
1.921
1.892
1.870
-0.000
O_2N
O
O
O
4j
1.92
2.04
1.05
1.00
3.06
2.22
2.06
1.98
10
8
6
4
2
0
PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Dec 18 2007
F1: 300.029
F2: 75.449
SW1: 4803
OF1: 1802.3
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 6
LB: 0.0
Nuts - $hh-4-89-1-new.fid

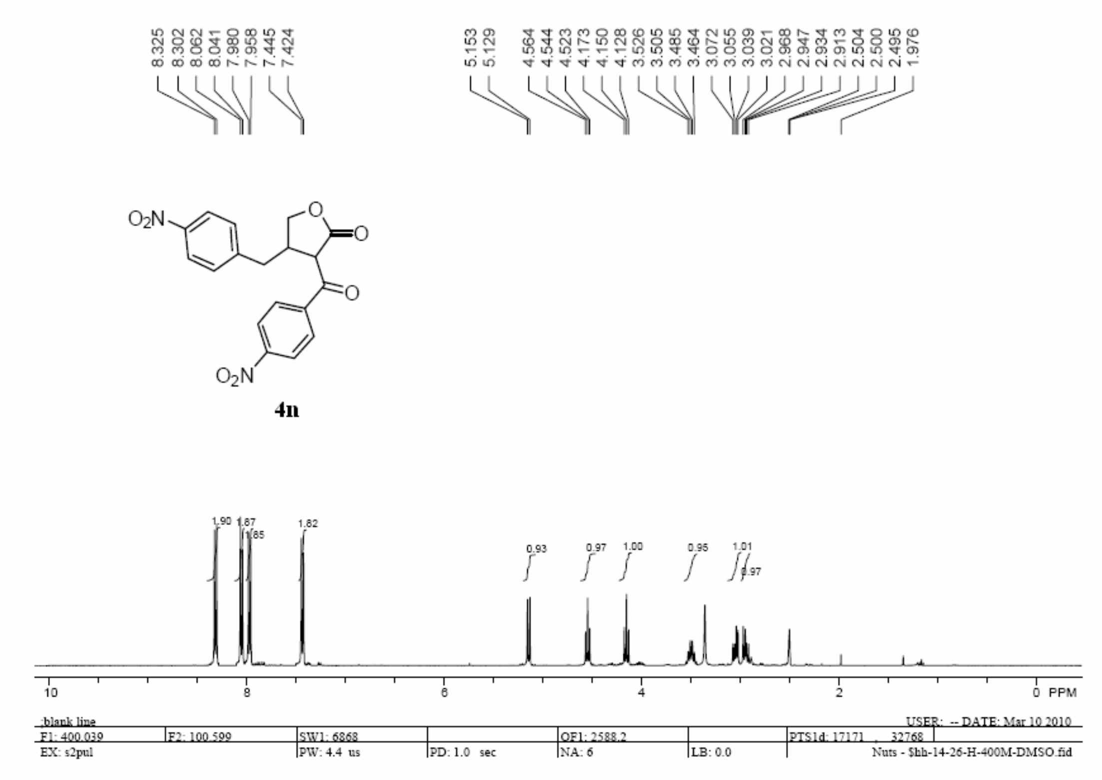

213.509
174.652
146.938
145.220
129.421
124.040
77.420
77.000
76.573
70.337
59.437
46.500
39.509
32.830
32.624
19.908
O_2N
O
O
O
4j
200
150
100
50
PPM
hh-4-89-1C
USER: -- DATE: Oct 28 2007
F1: 75.450
F2: 300.029
SW1: 18868
OF1: 8272.7
PTS1d: 30189 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 174
LB: 2.0
Nuts - $hh-4-89-1C.fid

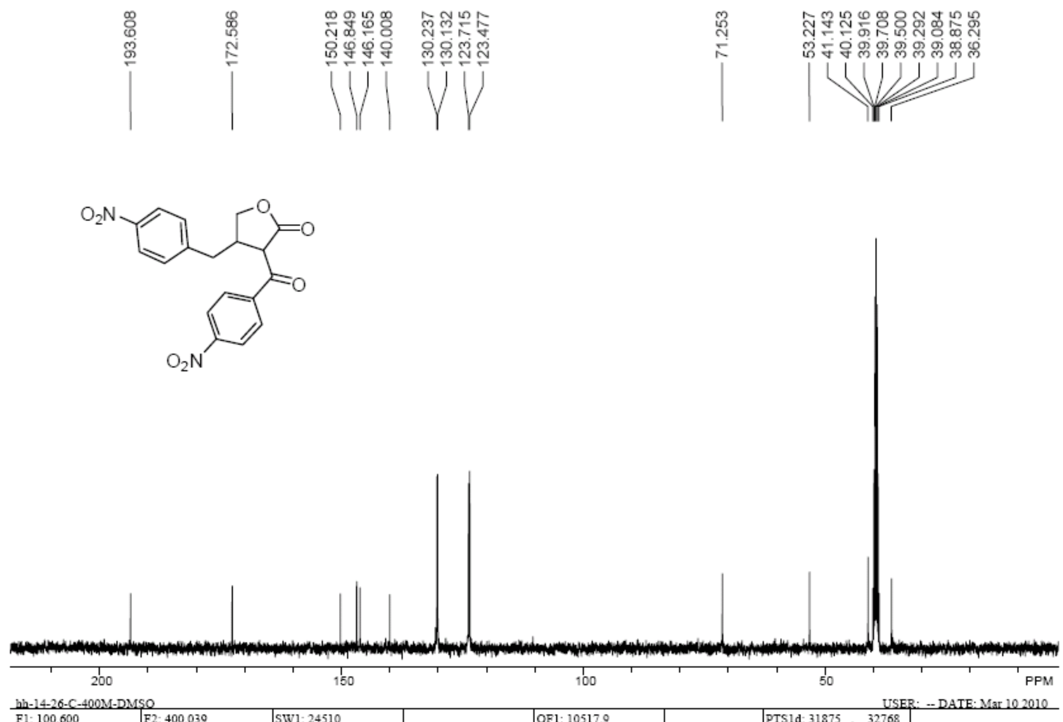

7.935 7.932 7.907 7.904 7.846 7.821 7.596 7.572 7.548 7.470 7.447 7.422 7.397 7.360 7.324 7.298
4.591 4.566 4.560 4.536 4.499 4.475 4.216 4.194 4.186 4.164 3.690 3.665 3.641 3.615 3.592 3.568 3.296 3.272 3.251 3.227 3.125 3.099 3.080 3.053
-0.000
NO_2
4k
5.92 1.79 0.94 1.00 1.01 1.07 0.92 1.03 1.00
8 6 4 2 PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Nov 21 2007
F1: 300.030 F2: 75.450 SW1: 4803 OF1: 1804.9 PTS1d: 9592 , 16384
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 8 LB: 0.0
Nuts - $hh-5-17H.fid

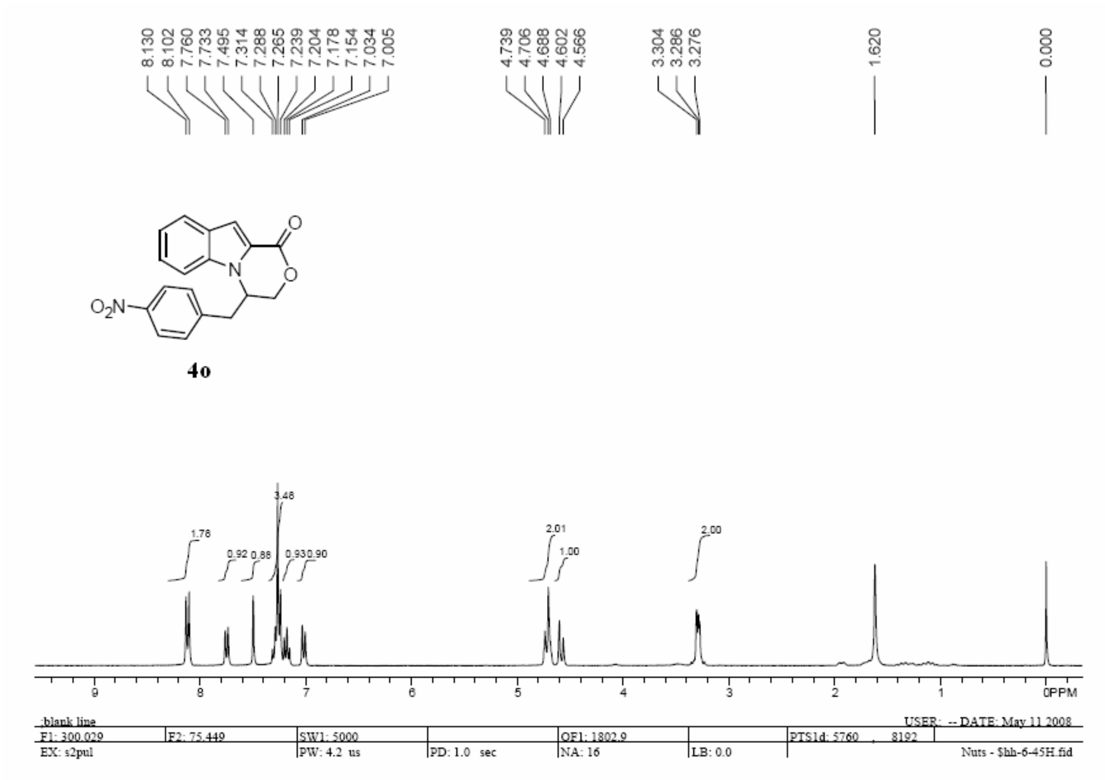

192.527
172.232
148.945 135.252 133.939 133.405 132.741 132.275 129.016 128.589 128.268 125.253
77.420 77.000 76.573 71.375
53.766
40.188 34.906
NO_2
4k
200 150 100 50 0 PPM
hh-5-17C
USER: -- DATE: Nov 21 2007
F1: 75.450 F2: 300.029 SW1: 18868 OF1: 8272.1 PTS1d: 30189 , 32768
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 56 LB: 2.0
Nuts - $hh-5-17C.fid

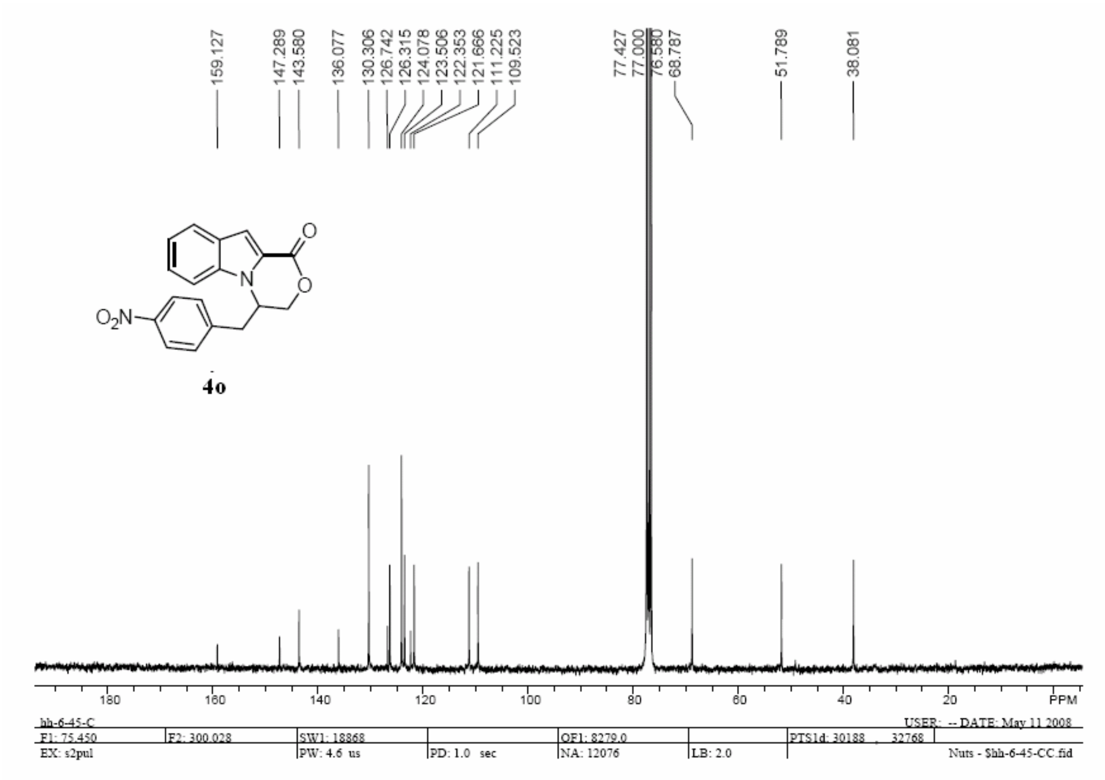

7.863
7.839
7.629
7.605
7.580
7.554
7.490
7.464
7.438
7.266
6.566
4.655
4.631
4.626
4.601
4.475
4.450
4.233
4.210
4.204
4.179
3.906
3.772
3.748
3.713
3.688
3.663
3.639
3.344
3.321
3.299
3.277
3.140
3.112
3.095
3.066
-0.000
MeO
MeO
O
O
NO2
O
4m
1.86
1.92
1.80
0.92
0.99
0.95
0.96
3.00
2.94
1.15
1.00
1.00
8
6
4
2
0
PPM
;blank line
USER: -- DATE: Mar 31 2008
F1: 300.029
F2: 75.449
SW1: 4803
OF1: 1802.3
PTS1d: 9592 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 11
LB: 0.0
Nuts - $hh-6-39-HH.fid

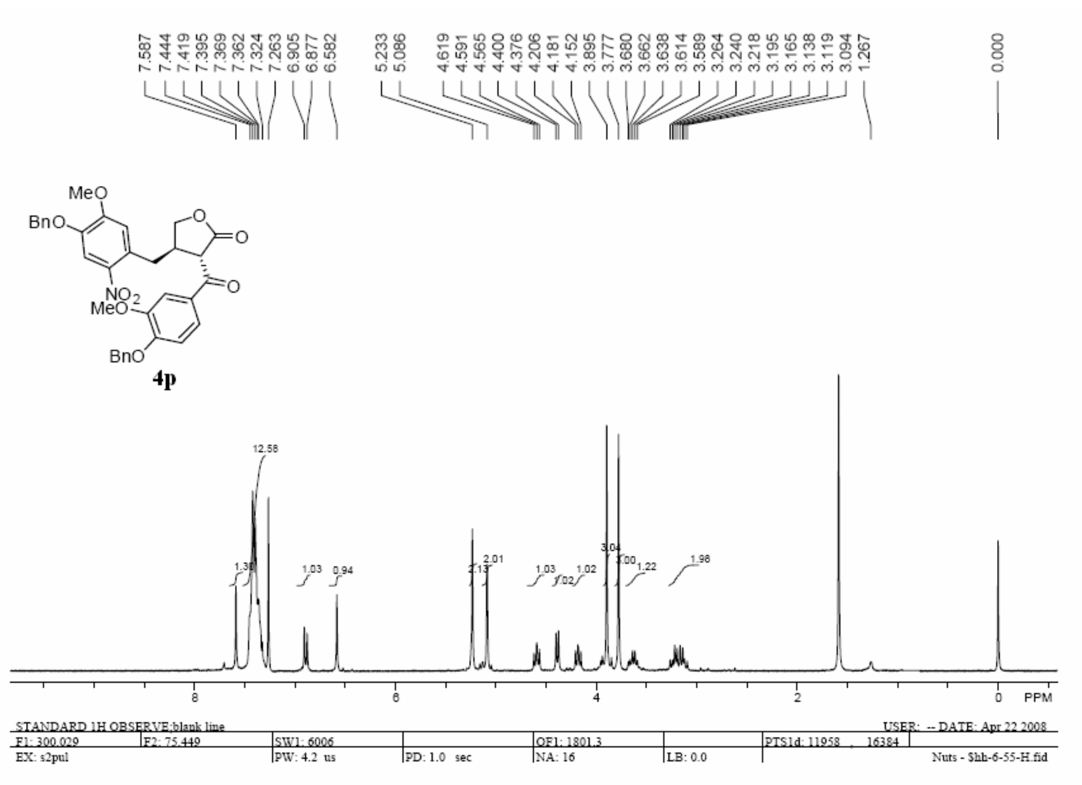

192.572
172.323
153.123
147.884
141.040
135.520
134.052
128.965
128.753
127.840
113.278
108.450
77.411
76.559
71.411
56.279
53.983
40.638
35.437
MeO
MeO
O
O
NO2
O
4m
200
150
100
50
0
PPM
xjb-5-97-1
USER: -- DATE: Apr 18 2008
F1: 75.449
F2: 300.028
SW1: 18797
OF1: 7543.5
PTS1d: 30075 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 10000
LB: 2.0
Nuts - $hh-6-39-C.fid

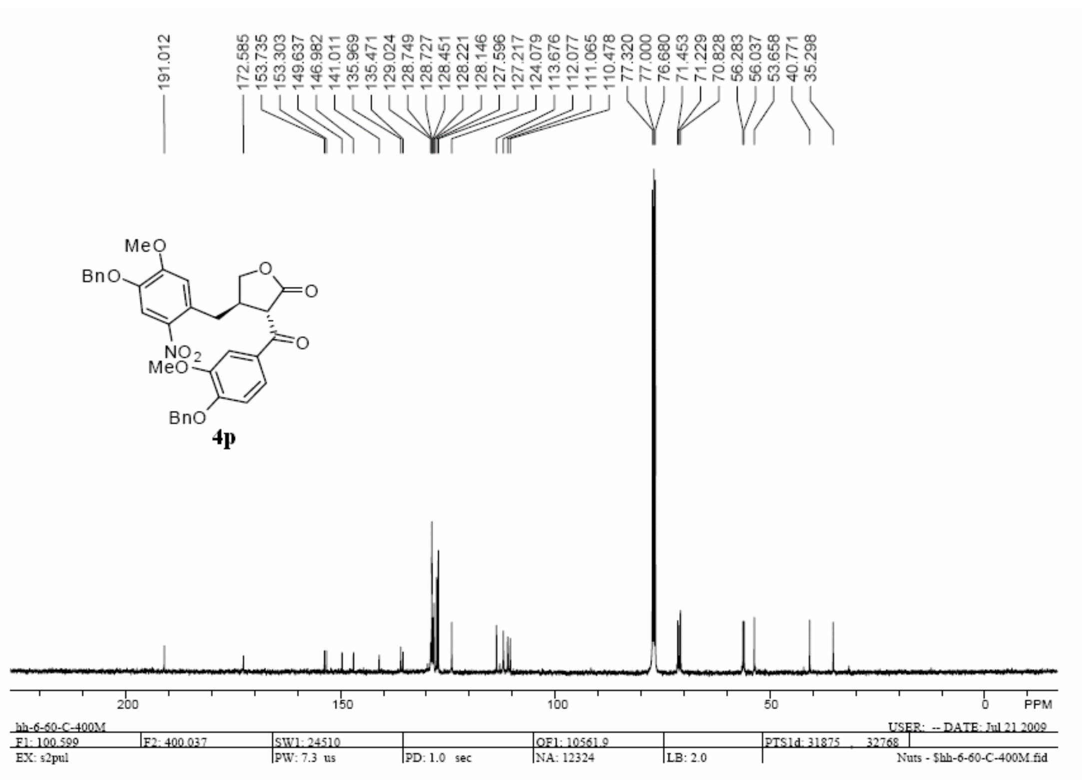

4n
:blank line
F1: 400.039
F2: 100.599
SW1: 6868
OF1: 2588.2
PTS1d: 17171 , 32768
USER: -- DATE: Mar 10 2010
EX: s2pul
PW: 4.4 us
PD: 1.0 sec
NA: 6
LB: 0.0
Nuts - $hh-14-26-H-400M-DMSO.fid


hh-14-26-C-400M-DMSO
F1: 100.600
F2: 400.039
SW1: 24510
OF1: 10517.9
PTS1d: 31875 , 32768
USER: -- DATE: Mar 10 2010
EX: s2pul
PW: 7.3 us
PD: 1.0 sec
NA: 108
LB: 2.0
Nuts - $hh-14-26-C-400M-DMSO.fid


8.130
8.102
7.760
7.733
7.495
7.314
7.288
7.265
7.239
7.204
7.178
7.154
7.034
7.005
4.739
4.706
4.688
4.602
4.566
3.304
3.286
3.276
1.620
0.000
O2N
N
O
O
4o
1.78
0.92
0.88
3.46
0.93
0.90
2.01
1.00
2.00
PPM
:blank line
F1: 300.029
F2: 75.449
SW1: 5000
OF1: 1802.9
PTS1d: 5760 , 8192
USER: -- DATE: May 11 2008
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $hh-6-45H.fid


159.127
147.289
143.580
136.077
130.306
126.742
126.315
124.078
123.506
122.353
121.666
111.225
109.523
77.427
77.000
76.580
68.787
51.789
38.081
O2N
N
O
O
4o
PPM
hh-6-45-C
F1: 75.450
F2: 300.028
SW1: 18868
OF1: 8279.0
PTS1d: 30188 , 32768
USER: -- DATE: May 11 2008
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 12076
LB: 2.0
Nuts - $hh-6-45-CC.fid





X-ray Crystallography of 4a

Single Crystal X-Ray Analysis. A representative crystal was surveyed on a Bruker APEX diffractometer. All crystallographic calculations were facilitated by the SHELXL-97 system.

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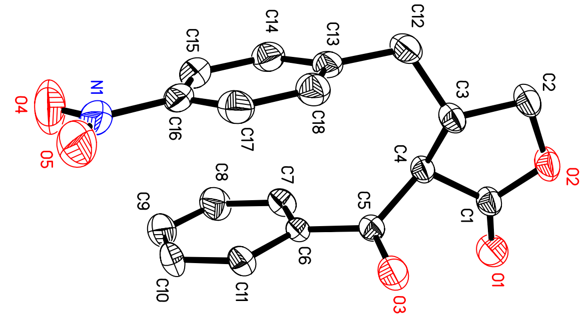
computing_cell_refinement 'Bruker SMART'
computing_data_reduction 'Bruker SHELXTL'
computing_structure_solution 'Bruker SHELXTL'
computing_structure_refinement 'Bruker SHELXTL'
computing_molecular_graphics 'Bruker SHELXTL'
computing_publication_material 'Bruker SHELXTL'



(Thermal ellipsoids are set at 30% probability)

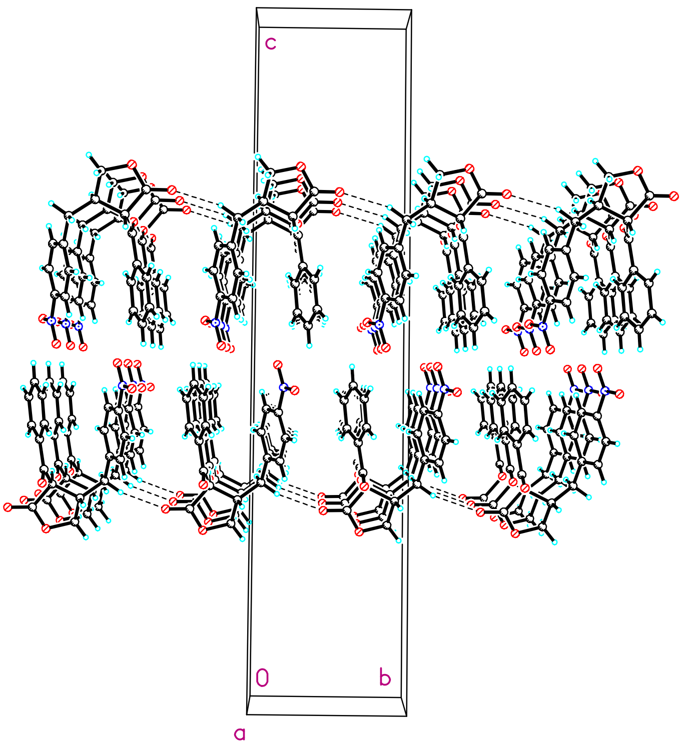


Table 1. Crystal data and structure refinement for cd27310.

Identification code	cd27310
Empirical formula	C18 H15 N O5
Formula weight	325.31
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 5.8692(11) A alpha = 90 deg.
	b = 7.6984(14) A beta = 94.634(3) deg.
	c = 34.643(7) A gamma = 90 deg.
Volume	1560.2(5) A^3
Z, Calculated density	4, 1.385 Mg/m^3
Absorption coefficient	0.102 mm^-1
F(000)	680
Crystal size	0.496 x 0.267 x 0.215 mm
Theta range for data collection	2.36 to 27.00 deg.
Limiting indices	-7<=h<=6, -9<=k<=7, -41<=l<=44
Reflections collected / unique	8662 / 3360 [R(int) = 0.1004]
Completeness to theta = 27.00	98.6 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.75534
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3360 / 0 / 218
Goodness-of-fit on F^2	0.944
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1486
R indices (all data)	R1 = 0.0919, wR2 = 0.1601
Extinction coefficient	0.006(2)
Largest diff. peak and hole	0.249 and -0.209 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd27310. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	-1406(3)	4655(2)	2821(1)	72(1)
O(2)	-2782(3)	6978(2)	2510(1)	60(1)
O(3)	2560(3)	7169(3)	3206(1)	69(1)
O(4)	2597(4)	11699(4)	4877(1)	108(1)
O(5)	5104(4)	12779(3)	4527(1)	113(1)
N(1)	3281(4)	12096(3)	4564(1)	84(1)
C(1)	-1834(4)	6168(3)	2823(1)	49(1)
C(2)	-3261(4)	8757(3)	2603(1)	57(1)
C(3)	-1670(4)	9191(3)	2960(1)	48(1)
C(4)	-1454(3)	7424(3)	3156(1)	42(1)
C(5)	846(3)	7106(3)	3378(1)	43(1)
C(6)	964(3)	6796(2)	3799(1)	40(1)
C(7)	-811(4)	6100(3)	3985(1)	52(1)
C(8)	-614(5)	5902(4)	4386(1)	72(1)
C(9)	1342(5)	6442(4)	4596(1)	75(1)
C(10)	3106(5)	7101(4)	4417(1)	71(1)
C(11)	2966(4)	7264(3)	4020(1)	53(1)
C(12)	-2572(4)	10659(3)	3197(1)	60(1)
C(13)	-1051(4)	11075(3)	3556(1)	51(1)
C(14)	-1687(4)	10641(3)	3920(1)	59(1)
C(15)	-279(4)	10979(3)	4251(1)	64(1)
C(16)	1758(4)	11763(3)	4212(1)	58(1)
C(17)	2442(4)	12235(3)	3858(1)	62(1)

C(18)	1030(4)	11886(3)	3530(1)	58(1)

Table 3. Bond lengths [A] and angles [deg] for cd27310.

O(1)-C(1)	1.192(2)
O(2)-C(1)	1.333(2)
O(2)-C(2)	1.440(3)
O(3)-C(5)	1.211(2)
O(4)-N(1)	1.224(4)
O(5)-N(1)	1.208(3)
N(1)-C(16)	1.476(3)
C(1)-C(4)	1.507(3)
C(2)-C(3)	1.525(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(12)	1.517(3)
C(3)-C(4)	1.520(3)
C(3)-H(3)	0.9800
C(4)-C(5)	1.519(3)
C(4)-H(4A)	0.9800
C(5)-C(6)	1.475(3)
C(6)-C(7)	1.377(3)
C(6)-C(11)	1.396(3)
C(7)-C(8)	1.391(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.372(4)
C(8)-H(8)	0.9300
C(9)-C(10)	1.348(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.376(3)
C(10)-H(10)	0.9300

C(11)-H(11)	0.9300
C(12)-C(13)	1.504(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(18)	1.381(3)
C(13)-C(14)	1.385(3)
C(14)-C(15)	1.383(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.356(4)
C(15)-H(15)	0.9300
C(16)-C(17)	1.369(4)
C(17)-C(18)	1.378(3)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(1)-O(2)-C(2)	109.78(16)
O(5)-N(1)-O(4)	124.0(3)
O(5)-N(1)-C(16)	118.1(3)
O(4)-N(1)-C(16)	117.9(3)
O(1)-C(1)-O(2)	121.81(19)
O(1)-C(1)-C(4)	127.80(19)
O(2)-C(1)-C(4)	110.39(18)
O(2)-C(2)-C(3)	105.81(16)
O(2)-C(2)-H(2A)	110.6
C(3)-C(2)-H(2A)	110.6
O(2)-C(2)-H(2B)	110.6
C(3)-C(2)-H(2B)	110.6
H(2A)-C(2)-H(2B)	108.7
C(12)-C(3)-C(4)	116.45(19)
C(12)-C(3)-C(2)	112.61(17)
C(4)-C(3)-C(2)	100.87(16)

C(12)-C(3)-H(3)	108.8
C(4)-C(3)-H(3)	108.8
C(2)-C(3)-H(3)	108.8
C(1)-C(4)-C(5)	110.76(17)
C(1)-C(4)-C(3)	103.39(16)
C(5)-C(4)-C(3)	114.12(17)
C(1)-C(4)-H(4A)	109.5
C(5)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4A)	109.5
O(3)-C(5)-C(6)	121.33(17)
O(3)-C(5)-C(4)	118.87(19)
C(6)-C(5)-C(4)	119.76(18)
C(7)-C(6)-C(11)	118.62(19)
C(7)-C(6)-C(5)	123.33(18)
C(11)-C(6)-C(5)	118.04(19)
C(6)-C(7)-C(8)	120.3(2)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	119.5(2)
C(9)-C(8)-H(8)	120.2
C(7)-C(8)-H(8)	120.2
C(10)-C(9)-C(8)	120.8(2)
C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6
C(9)-C(10)-C(11)	120.5(2)
C(9)-C(10)-H(10)	119.8
C(11)-C(10)-H(10)	119.8
C(10)-C(11)-C(6)	120.2(2)
C(10)-C(11)-H(11)	119.9
C(6)-C(11)-H(11)	119.9

C(13)-C(12)-C(3)	113.29(17)
C(13)-C(12)-H(12A)	108.9
C(3)-C(12)-H(12A)	108.9
C(13)-C(12)-H(12B)	108.9
C(3)-C(12)-H(12B)	108.9
H(12A)-C(12)-H(12B)	107.7
C(18)-C(13)-C(14)	118.2(2)
C(18)-C(13)-C(12)	120.9(2)
C(14)-C(13)-C(12)	121.0(2)
C(15)-C(14)-C(13)	121.5(2)
C(15)-C(14)-H(14)	119.2
C(13)-C(14)-H(14)	119.2
C(16)-C(15)-C(14)	118.2(3)
C(16)-C(15)-H(15)	120.9
C(14)-C(15)-H(15)	120.9
C(15)-C(16)-C(17)	122.2(2)
C(15)-C(16)-N(1)	118.3(3)
C(17)-C(16)-N(1)	119.5(3)
C(16)-C(17)-C(18)	119.1(2)
C(16)-C(17)-H(17)	120.5
C(18)-C(17)-H(17)	120.5
C(17)-C(18)-C(13)	120.8(2)
C(17)-C(18)-H(18)	119.6
C(13)-C(18)-H(18)	119.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd27310. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	86(1)	54(1)	72(1)	-11(1)	-15(1)	8(1)
O(2)	72(1)	63(1)	43(1)	-5(1)	-15(1)	-2(1)
O(3)	46(1)	114(2)	48(1)	10(1)	7(1)	8(1)
O(4)	103(2)	153(3)	62(2)	-36(2)	-14(1)	1(2)
O(5)	66(1)	155(2)	116(2)	-54(2)	-22(1)	0(1)
N(1)	66(2)	102(2)	81(2)	-41(2)	-14(1)	19(1)
C(1)	51(1)	50(1)	43(1)	-1(1)	-7(1)	-2(1)
C(2)	64(1)	58(1)	46(1)	5(1)	-14(1)	1(1)
C(3)	47(1)	49(1)	45(1)	2(1)	-10(1)	-1(1)
C(4)	40(1)	50(1)	36(1)	1(1)	-3(1)	1(1)
C(5)	37(1)	51(1)	40(1)	-1(1)	0(1)	3(1)
C(6)	42(1)	40(1)	37(1)	0(1)	-4(1)	7(1)
C(7)	48(1)	53(1)	52(1)	9(1)	0(1)	1(1)
C(8)	78(2)	88(2)	51(2)	24(1)	13(1)	11(1)
C(9)	90(2)	94(2)	41(2)	13(1)	2(2)	23(2)
C(10)	74(2)	86(2)	48(2)	-5(1)	-24(1)	13(2)
C(11)	46(1)	60(1)	51(1)	0(1)	-7(1)	2(1)
C(12)	60(1)	50(1)	67(2)	-3(1)	-18(1)	7(1)
C(13)	52(1)	40(1)	60(2)	-11(1)	-9(1)	8(1)
C(14)	52(1)	55(1)	71(2)	-12(1)	0(1)	3(1)
C(15)	66(2)	66(2)	60(2)	-14(1)	1(1)	13(1)
C(16)	53(1)	58(1)	61(2)	-22(1)	-7(1)	13(1)

C(17)	50(1)	54(1)	80(2)	-12(1)	-9(1)	-1(1)
C(18)	59(1)	52(1)	63(2)	-2(1)	-2(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd27310.

	x	y	z	U(eq)
H(2A)	-4846	8889	2658	68
H(2B)	-2965	9516	2390	68
H(3)	-175	9527	2877	57
H(4A)	-2674	7287	3330	51
H(7)	-2148	5761	3843	62
H(8)	-1800	5408	4511	86
H(9)	1452	6351	4864	90
H(10)	4426	7449	4563	85
H(11)	4209	7687	3898	63
H(12A)	-2741	11691	3037	72
H(12B)	-4075	10345	3272	72
H(14)	-3094	10111	3942	71
H(15)	-717	10676	4494	77
H(17)	3841	12783	3840	74
H(18)	1484	12201	3289	70

Table 6. Torsion angles [deg] for cd27310.

C(2)-O(2)-C(1)-O(1)	175.7(2)
C(2)-O(2)-C(1)-C(4)	-3.7(2)
C(1)-O(2)-C(2)-C(3)	22.3(2)
O(2)-C(2)-C(3)-C(12)	-155.45(19)
O(2)-C(2)-C(3)-C(4)	-30.6(2)
O(1)-C(1)-C(4)-C(5)	41.7(3)
O(2)-C(1)-C(4)-C(5)	-138.84(18)
O(1)-C(1)-C(4)-C(3)	164.4(2)
O(2)-C(1)-C(4)-C(3)	-16.2(2)
C(12)-C(3)-C(4)-C(1)	149.72(18)
C(2)-C(3)-C(4)-C(1)	27.5(2)
C(12)-C(3)-C(4)-C(5)	-89.9(2)
C(2)-C(3)-C(4)-C(5)	147.92(19)
C(1)-C(4)-C(5)-O(3)	57.1(3)
C(3)-C(4)-C(5)-O(3)	-59.1(3)
C(1)-C(4)-C(5)-C(6)	-125.3(2)
C(3)-C(4)-C(5)-C(6)	118.5(2)
O(3)-C(5)-C(6)-C(7)	-155.7(2)
C(4)-C(5)-C(6)-C(7)	26.8(3)
O(3)-C(5)-C(6)-C(11)	25.5(3)
C(4)-C(5)-C(6)-C(11)	-152.03(19)
C(11)-C(6)-C(7)-C(8)	1.2(3)
C(5)-C(6)-C(7)-C(8)	-177.6(2)
C(6)-C(7)-C(8)-C(9)	1.5(4)
C(7)-C(8)-C(9)-C(10)	-2.5(4)
C(8)-C(9)-C(10)-C(11)	0.7(4)
C(9)-C(10)-C(11)-C(6)	2.0(4)

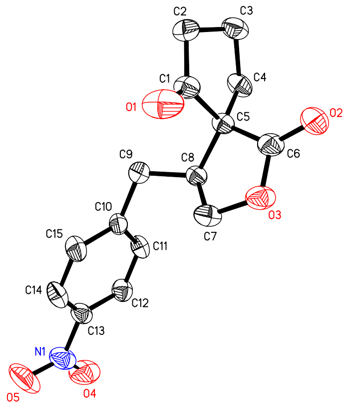
C(7)-C(6)-C(11)-C(10)	-2.9(3)
C(5)-C(6)-C(11)-C(10)	175.9(2)
C(4)-C(3)-C(12)-C(13)	62.8(3)
C(2)-C(3)-C(12)-C(13)	178.6(2)
C(3)-C(12)-C(13)-C(18)	71.5(3)
C(3)-C(12)-C(13)-C(14)	-107.9(2)
C(18)-C(13)-C(14)-C(15)	-1.0(3)
C(12)-C(13)-C(14)-C(15)	178.4(2)
C(13)-C(14)-C(15)-C(16)	0.4(3)
C(14)-C(15)-C(16)-C(17)	0.5(4)
C(14)-C(15)-C(16)-N(1)	-178.9(2)
O(5)-N(1)-C(16)-C(15)	179.3(2)
O(4)-N(1)-C(16)-C(15)	-2.4(4)
O(5)-N(1)-C(16)-C(17)	-0.1(4)
O(4)-N(1)-C(16)-C(17)	178.2(3)
C(15)-C(16)-C(17)-C(18)	-0.7(4)
N(1)-C(16)-C(17)-C(18)	178.6(2)
C(16)-C(17)-C(18)-C(13)	0.1(3)
C(14)-C(13)-C(18)-C(17)	0.7(3)
C(12)-C(13)-C(18)-C(17)	-178.7(2)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystallography of 4j

Single Crystal X-Ray Analysis. A representative crystal was surveyed on a Bruker APEX diffractometer. All crystallographic calculations were facilitated by the SHELXL-97 system.

computing_data_collection	'Bruker SMART'
computing_cell_refinement	'Bruker SMART'
computing_data_reduction	'Bruker SHELXTL'
computing_structure_solution	'Bruker SHELXTL'
computing_structure_refinement	'Bruker SHELXTL'
computing_molecular_graphics	'Bruker SHELXTL'
computing_publication_material	'Bruker SHELXTL'



(Thermal ellipsoids are set at 30% probability)

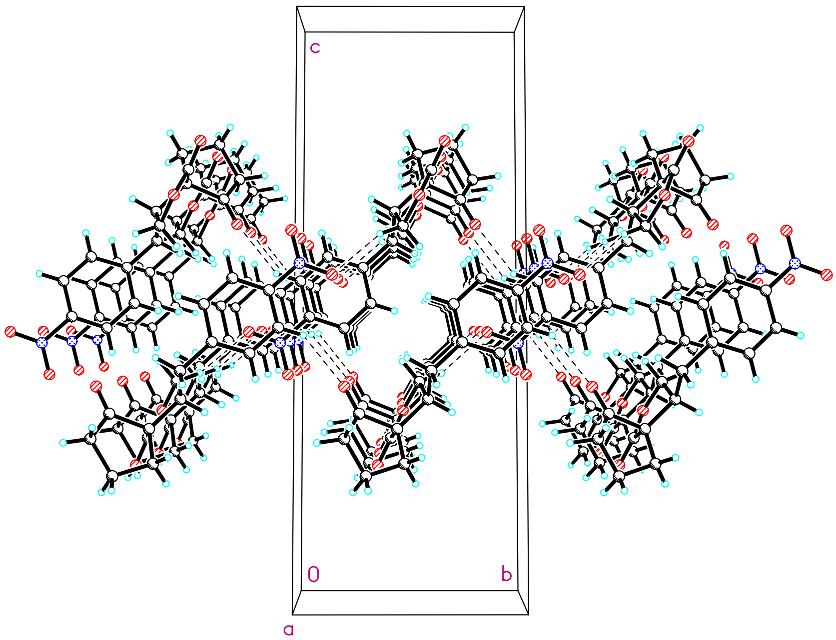


Table 1. Crystal data and structure refinement for cd28519.

Identification code	cd28519
Empirical formula	C15 H15 N O5
Formula weight	289.28
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 6.8274(9) A alpha = 90 deg.
	b = 8.8266(11) A beta = 96.661(2) deg.
	c = 23.345(3) A gamma = 90 deg.
Volume	1397.3(3) A^3
Z, Calculated density	4, 1.375 Mg/m^3
Absorption coefficient	0.104 mm^-1
F(000)	608
Crystal size	0.304 x 0.168 x 0.155 mm
Theta range for data collection	1.76 to 25.48 deg.
Limiting indices	-8<=h<=8, -5<=k<=10, -28<=l<=28
Reflections collected / unique	7130 / 2597 [R(int) = 0.0997]
Completeness to theta = 25.48	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.7612
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2597 / 0 / 190
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0632, wR2 = 0.1538
R indices (all data)	R1 = 0.0808, wR2 = 0.1656
Largest diff. peak and hole	0.180 and -0.202 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd28519. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	2540(3)	5493(4)	-620(1)	84(1)
O(1)	3367(4)	-2699(2)	1280(1)	112(1)
O(2)	6605(3)	-1371(2)	2540(1)	88(1)
O(3)	6869(3)	-332(2)	1687(1)	75(1)
O(4)	2725(3)	6793(3)	-443(1)	108(1)
O(5)	2415(5)	5160(4)	-1124(1)	131(1)
C(1)	2818(4)	-2092(3)	1687(1)	58(1)
C(2)	1311(4)	-2650(3)	2042(1)	67(1)
C(3)	1712(4)	-1803(3)	2607(1)	69(1)
C(4)	2466(4)	-278(3)	2435(1)	60(1)
C(5)	3639(3)	-570(2)	1931(1)	46(1)
C(6)	5821(4)	-827(2)	2102(1)	61(1)
C(7)	5569(4)	343(3)	1223(1)	65(1)
C(8)	3668(3)	676(2)	1475(1)	46(1)
C(9)	1884(4)	793(3)	1029(1)	60(1)
C(10)	2077(3)	2026(2)	594(1)	48(1)
C(11)	2277(3)	3525(3)	764(1)	55(1)
C(12)	2450(3)	4653(3)	371(1)	58(1)
C(13)	2410(3)	4276(3)	-201(1)	59(1)
C(14)	2247(4)	2811(3)	-383(1)	68(1)
C(15)	2078(4)	1691(3)	16(1)	63(1)

Table 3. Bond lengths [A] and angles [deg] for cd28519.

N(1)-O(5)	1.207(4)
N(1)-O(4)	1.220(3)
N(1)-C(13)	1.463(3)
O(1)-C(1)	1.189(3)
O(2)-C(6)	1.198(3)
O(3)-C(6)	1.343(3)
O(3)-C(7)	1.447(3)
C(1)-C(2)	1.479(3)
C(1)-C(5)	1.539(3)
C(2)-C(3)	1.513(4)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.512(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.521(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.514(3)
C(5)-C(8)	1.531(3)
C(7)-C(8)	1.515(3)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.511(3)
C(8)-H(8)	0.9800
C(9)-C(10)	1.506(3)
C(9)-H(9A)	0.9700

C(9)-H(9B)	0.9700
C(10)-C(15)	1.381(3)
C(10)-C(11)	1.383(3)
C(11)-C(12)	1.367(3)
C(11)-H(11)	0.9300
C(12)-C(13)	1.373(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.362(4)
C(14)-C(15)	1.373(3)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300

O(5)-N(1)-O(4)	123.4(3)
O(5)-N(1)-C(13)	118.1(3)
O(4)-N(1)-C(13)	118.5(3)
C(6)-O(3)-C(7)	110.05(19)
O(1)-C(1)-C(2)	127.1(2)
O(1)-C(1)-C(5)	123.7(2)
C(2)-C(1)-C(5)	109.3(2)
C(1)-C(2)-C(3)	104.9(2)
C(1)-C(2)-H(2A)	110.8
C(3)-C(2)-H(2A)	110.8
C(1)-C(2)-H(2B)	110.8
C(3)-C(2)-H(2B)	110.8
H(2A)-C(2)-H(2B)	108.8
C(4)-C(3)-C(2)	103.95(19)
C(4)-C(3)-H(3A)	111.0
C(2)-C(3)-H(3A)	111.0
C(4)-C(3)-H(3B)	111.0
C(2)-C(3)-H(3B)	111.0

H(3A)-C(3)-H(3B)	109.0
C(3)-C(4)-C(5)	106.31(18)
C(3)-C(4)-H(4A)	110.5
C(5)-C(4)-H(4A)	110.5
C(3)-C(4)-H(4B)	110.5
C(5)-C(4)-H(4B)	110.5
H(4A)-C(4)-H(4B)	108.7
C(6)-C(5)-C(4)	114.2(2)
C(6)-C(5)-C(8)	101.52(17)
C(4)-C(5)-C(8)	117.76(17)
C(6)-C(5)-C(1)	105.83(17)
C(4)-C(5)-C(1)	103.46(18)
C(8)-C(5)-C(1)	113.79(18)
O(2)-C(6)-O(3)	121.6(2)
O(2)-C(6)-C(5)	127.9(2)
O(3)-C(6)-C(5)	110.5(2)
O(3)-C(7)-C(8)	105.47(19)
O(3)-C(7)-H(7A)	110.6
C(8)-C(7)-H(7A)	110.6
O(3)-C(7)-H(7B)	110.6
C(8)-C(7)-H(7B)	110.6
H(7A)-C(7)-H(7B)	108.8
C(9)-C(8)-C(7)	113.8(2)
C(9)-C(8)-C(5)	116.95(18)
C(7)-C(8)-C(5)	102.21(17)
C(9)-C(8)-H(8)	107.8
C(7)-C(8)-H(8)	107.8
C(5)-C(8)-H(8)	107.8
C(10)-C(9)-C(8)	112.84(19)
C(10)-C(9)-H(9A)	109.0

C(8)-C(9)-H(9A)	109.0
C(10)-C(9)-H(9B)	109.0
C(8)-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
C(15)-C(10)-C(11)	118.3(2)
C(15)-C(10)-C(9)	121.0(2)
C(11)-C(10)-C(9)	120.8(2)
C(12)-C(11)-C(10)	121.2(2)
C(12)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4
C(11)-C(12)-C(13)	118.7(2)
C(11)-C(12)-H(12)	120.6
C(13)-C(12)-H(12)	120.6
C(14)-C(13)-C(12)	121.8(2)
C(14)-C(13)-N(1)	119.8(3)
C(12)-C(13)-N(1)	118.4(3)
C(13)-C(14)-C(15)	118.8(2)
C(13)-C(14)-H(14)	120.6
C(15)-C(14)-H(14)	120.6
C(14)-C(15)-C(10)	121.2(2)
C(14)-C(15)-H(15)	119.4
C(10)-C(15)-H(15)	119.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd28519. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	65(2)	112(2)	76(2)	43(2)	11(1)	15(1)
O(1)	178(2)	63(1)	108(2)	-41(1)	72(2)	-33(1)
O(2)	85(1)	77(1)	99(2)	40(1)	-8(1)	5(1)
O(3)	59(1)	69(1)	98(1)	29(1)	16(1)	7(1)
O(4)	97(2)	95(2)	132(2)	53(2)	12(1)	1(1)
O(5)	160(3)	170(3)	62(2)	50(2)	18(2)	16(2)
C(1)	80(2)	38(1)	58(2)	-6(1)	16(1)	-5(1)
C(2)	70(2)	56(2)	76(2)	6(1)	11(1)	-13(1)
C(3)	73(2)	76(2)	61(2)	14(1)	21(1)	-2(1)
C(4)	85(2)	53(1)	46(1)	-1(1)	17(1)	10(1)
C(5)	61(1)	34(1)	44(1)	-2(1)	10(1)	2(1)
C(6)	71(2)	39(1)	74(2)	11(1)	8(1)	0(1)
C(7)	69(2)	62(2)	68(2)	14(1)	20(1)	0(1)
C(8)	58(1)	38(1)	43(1)	-1(1)	8(1)	-2(1)
C(9)	63(1)	62(2)	53(1)	2(1)	2(1)	-11(1)
C(10)	48(1)	56(1)	40(1)	-1(1)	0(1)	-1(1)
C(11)	65(1)	62(2)	37(1)	-2(1)	3(1)	7(1)
C(12)	61(1)	53(1)	58(2)	4(1)	0(1)	6(1)
C(13)	48(1)	78(2)	51(1)	19(1)	5(1)	9(1)
C(14)	80(2)	85(2)	38(1)	-1(1)	5(1)	11(1)
C(15)	77(2)	64(2)	47(1)	-6(1)	0(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd28519.

	x	y	z	U(eq)
H(2A)	1440	-3734	2104	80
H(2B)	-6	-2434	1858	80
H(3A)	516	-1692	2790	83
H(3B)	2694	-2324	2869	83
H(4A)	3301	174	2754	73
H(4B)	1375	403	2321	73
H(7A)	5334	-352	900	78
H(7B)	6136	1268	1090	78
H(8)	3825	1649	1677	56
H(9A)	1690	-169	830	72
H(9B)	727	987	1223	72
H(11)	2295	3769	1152	66
H(12)	2591	5657	490	69
H(14)	2249	2574	-771	81
H(15)	1962	688	-105	76

Table 6. Torsion angles [deg] for cd28519.

O(1)-C(1)-C(2)-C(3)	159.5(3)
C(5)-C(1)-C(2)-C(3)	-19.4(3)
C(1)-C(2)-C(3)-C(4)	32.8(3)
C(2)-C(3)-C(4)-C(5)	-34.4(3)
C(3)-C(4)-C(5)-C(6)	-92.4(2)
C(3)-C(4)-C(5)-C(8)	148.6(2)
C(3)-C(4)-C(5)-C(1)	22.2(2)
O(1)-C(1)-C(5)-C(6)	-60.1(3)
C(2)-C(1)-C(5)-C(6)	118.9(2)
O(1)-C(1)-C(5)-C(4)	179.4(3)
C(2)-C(1)-C(5)-C(4)	-1.6(3)
O(1)-C(1)-C(5)-C(8)	50.5(3)
C(2)-C(1)-C(5)-C(8)	-130.5(2)
C(7)-O(3)-C(6)-O(2)	-176.9(2)
C(7)-O(3)-C(6)-C(5)	2.5(3)
C(4)-C(5)-C(6)-O(2)	30.2(3)
C(8)-C(5)-C(6)-O(2)	158.1(3)
C(1)-C(5)-C(6)-O(2)	-82.9(3)
C(4)-C(5)-C(6)-O(3)	-149.05(19)
C(8)-C(5)-C(6)-O(3)	-21.2(2)
C(1)-C(5)-C(6)-O(3)	97.8(2)
C(6)-O(3)-C(7)-C(8)	17.9(3)
O(3)-C(7)-C(8)-C(9)	-157.00(19)
O(3)-C(7)-C(8)-C(5)	-30.0(2)
C(6)-C(5)-C(8)-C(9)	155.0(2)
C(4)-C(5)-C(8)-C(9)	-79.5(3)
C(1)-C(5)-C(8)-C(9)	41.8(3)
C(6)-C(5)-C(8)-C(7)	30.1(2)

C(4)-C(5)-C(8)-C(7)	155.6(2)
C(1)-C(5)-C(8)-C(7)	-83.1(2)
C(7)-C(8)-C(9)-C(10)	-59.7(3)
C(5)-C(8)-C(9)-C(10)	-178.64(19)
C(8)-C(9)-C(10)-C(15)	117.7(2)
C(8)-C(9)-C(10)-C(11)	-61.7(3)
C(15)-C(10)-C(11)-C(12)	0.8(3)
C(9)-C(10)-C(11)-C(12)	-179.9(2)
C(10)-C(11)-C(12)-C(13)	0.4(3)
C(11)-C(12)-C(13)-C(14)	-1.4(4)
C(11)-C(12)-C(13)-N(1)	178.3(2)
O(5)-N(1)-C(13)-C(14)	3.0(4)
O(4)-N(1)-C(13)-C(14)	-178.6(3)
O(5)-N(1)-C(13)-C(12)	-176.7(3)
O(4)-N(1)-C(13)-C(12)	1.7(4)
C(12)-C(13)-C(14)-C(15)	1.3(4)
N(1)-C(13)-C(14)-C(15)	-178.4(2)
C(13)-C(14)-C(15)-C(10)	-0.2(4)
C(11)-C(10)-C(15)-C(14)	-0.9(4)
C(9)-C(10)-C(15)-C(14)	179.8(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd28519 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(12)-H(12)...O(1)#1	0.93	2.36	3.169(3)	145.6
C(8)-H(8)...O(2)#2	0.98	2.57	3.494(3)	157.4
C(7)-H(&B)...O(4)#3	0.97	2.47	3.398(4)	161

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 -x+1,y+1/2,-z+1/2 #3 1-x, 1-y, -z