

Supporting Information

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Supporting Information

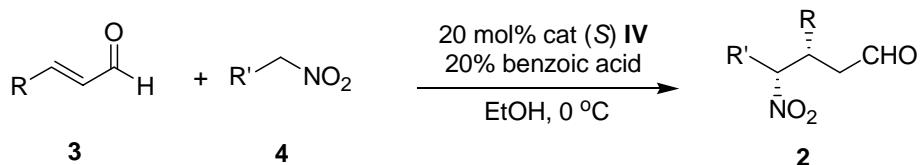
**Highly Enantioselective Organocatalytic Conjugate Addition of Nitromethane to
 α , β -Unsaturated Aldehydes: Three Step Synthesis of Optically Active Baclofen**

*Liansuo Zu, Hexin Xie, Hao Li, Jian Wang, and Wei Wang**

Department of Chemistry and Chemical Biology University of New Mexico, Albuquerque, NM 87131-0001

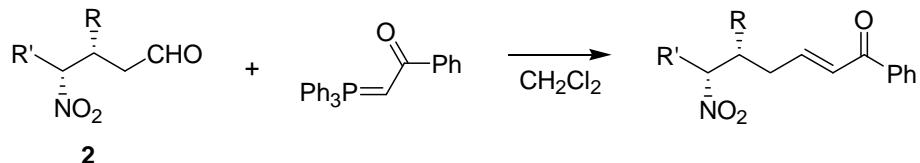
General Information: Commercial reagents were used as received, unless otherwise stated. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with fluorescence F₂₅₄ were used for thin-layer chromatography (TLC) analysis. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 500, and tetramethylsilane (TMS) was used as a reference. Data for ¹H are reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Data for ¹³C NMR are reported as ppm. Mass Spectra were obtained from University of New Mexico mass spectral facility.

General procedure for conjugate reaction of nitroalkanes to α , β -unsaturated aldehydes (Table 2)

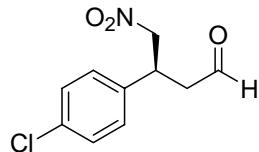


A mixture of **3** (0.10 mmol), **4** (0.3 mmol), benzoic acid (0.02 mmol), and catalyst (S)-IV (0.02 mmol) in EtOH (0.2 mL) was stirred at 0 °C. The crude product was purified by column chromatography on silica gel to give the desired product **2**.

Method of conversion of **2 to α , β -unsaturated ketones for HPLC analysis.**

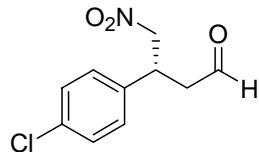


A mixture of **2** (1 eq.) and the Wittig reagent (1.5 eq.) in CH₂Cl₂ was stirred at rt for 5 h. The crude product was purified by column chromatography on silica gel to give the α , β -unsaturated ketones.



(S)-3-(4-Chlorophenyl)-4-nitrobutyraldehyde (2a) (Table 2, entry 1)

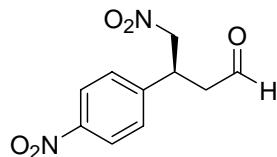
The title compound was prepared according to the general procedure, as described above in 75% yield. ¹H NMR (500 MHz, CDCl₃): 9.71 (s, 1H), 7.32 (d, 2H; *J* = 8.5 Hz), 7.18 (d, 2H; *J* = 8.0 Hz), 4.57-4.69 (m, 2H), 4.05-4.08 (m, 1H), 2.94 (d, 2H; *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 198.2, 136.7, 129.4, 128.8, 79.1, 46.3, 37.3; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): *t*_{major} = 31.64 min, *t*_{minor} = 43.79 min, ee = 97%; $[\alpha]_D^{25}$ = -11.7 (*c* = 1.0 in CHCl₃).



(R)-3-(4-Chlorophenyl)-4-nitrobutyraldehyde (2b) (Table 2, entry 2)

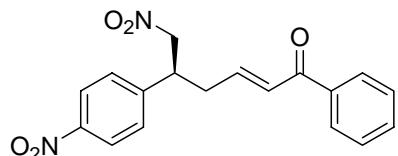
The title compound was prepared according to the general procedure, using (R)-IV as the catalyst, as described above in 73% yield. ¹H NMR (500 MHz, CDCl₃): 9.70 (s, 1H), 7.32 (d, 2H; *J* = 8.5 Hz), 7.18 (d, 2H; *J* = 8.0 Hz), 4.57-4.69 (m, 2H), 4.05-4.07 (m, 1H), 2.94 (d, 2H; *J* = 6.5 Hz); HPLC (Chiralpak

AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): $t_{\text{major}} = 40.09$ min, $t_{\text{minor}} = 32.08$ min, ee = 96%; $[\alpha]_D^{25} = +11.5$ ($c = 1.0$ in CHCl_3).

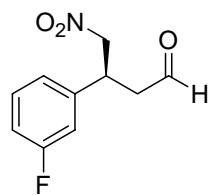


3-(4-Nitro-phenyl)-4-nitro-butyraldehyde (2c) (Table 2, entry 3)

The title compound was prepared according to the general procedure, as described above in 72% yield. ^1H NMR (500 MHz, CDCl_3): 9.74 (s, 1H), 8.22 (d, 2H; $J = 8.5$ Hz), 7.45 (d, 2H; $J = 8.5$ Hz), 4.65-4.79 (m, 2H), 4.21-4.23 (m, 1H), 3.04 (d, 2H; $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 197.5, 147.6, 145.7, 128.6, 124.3, 78.4, 46.1, 37.5; $[\alpha]_D^{25} = +7.2$ ($c = 1.0$ in CHCl_3).

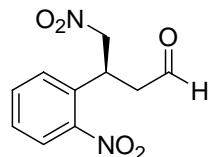


HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 254 nm): $t_{\text{major}} = 83.68$ min, $t_{\text{minor}} = \text{not observed}$, ee = 99%.



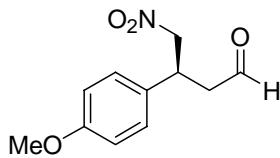
3-(3-Fluoro-phenyl)-4-nitro-butyraldehyde (2d) (Table 2, entry 4)

The title compound was prepared according to the general procedure, as described above in 80% yield. ^1H NMR (500 MHz, CDCl_3): 9.72 (d, 1H; $J = 5.5$ Hz), 7.26-7.34 (m, 1H), 6.94-7.03 (m, 3H), 4.60-4.70 (m, 2H), 4.07-4.11 (m, 1H), 2.95 (d, 2H; $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 198.3, 164.0, 162.0, 140.8, 140.7, 130.8, 130.7, 123.1, 115.2, 115.0, 114.6, 114.4, 79.0, 46.2, 37.5; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): $t_{\text{major}} = 39.05$ min, $t_{\text{minor}} = 60.55$ min, ee = 95%; $[\alpha]_D^{25} = -11.8$ ($c = 2.0$ in CHCl_3).



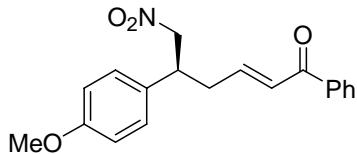
3-(2-Nitro-phenyl)-4-nitro-butyraldehyde (2e) (Table 2, entry 5)

The title compound was prepared according to the general procedure, as described above in 65% yield. ^1H NMR (500 MHz, CDCl_3): 9.73 (s, 1H), 7.92 (d, 1H; $J = 8.0$ Hz), 7.61 (t, 1H; $J = 7.5$ Hz), 7.48 (t, 1H; $J = 7.5$ Hz), 7.40 (d, 1H; $J = 8.0$ Hz), 4.83 (d, 2H; $J = 6.5$ Hz), 4.61-4.64 (m, 1H), 3.11 (d, 2H; $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 198.0, 133.4, 129.0, 128.6, 125.4, 77.8, 45.8, 32.7; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): $t_{\text{major}} = 61.93$ min, $t_{\text{minor}} = 81.56$ min, ee = 97%; $[\alpha]_D^{25} = -1.8$ ($c = 1.0$ in CHCl_3).

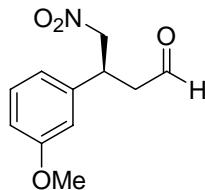


3-(4-Methoxy-phenyl)-4-nitro-butyraldehyde (2f) (Table 2, entry 6)

The title compound was prepared according to the general procedure, as described above in 70% yield. ^1H NMR (500 MHz, CDCl_3): 9.69 (s, 1H), 7.14 (d, 2H; J = 8.5 Hz), 6.87 (d, 2H; J = 8.5 Hz), 4.57-4.66 (m, 2H), 4.01-4.04 (m, 1H), 3.78 (s, 3H), 2.91 (d, 2H; J = 7.0 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 198.9, 159.3, 130.0, 128.4, 114.6, 79.7, 55.2, 46.5, 37.3; $[\alpha]_D^{25}$ = -11.2 (c = 1.0 in CHCl_3).

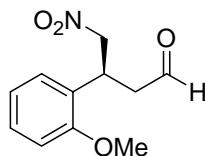


HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 254 nm): t_{major} = 115.34 min, t_{minor} = not observed, ee = 99%.



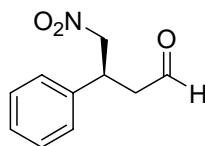
3-(3-Methoxy-phenyl)-4-nitro-butyraldehyde (2g) (Table 2, entry 7)

The title compound was prepared according to the general procedure, as described above in 76% yield. ^1H NMR (500 MHz, CDCl_3): 9.70 (d, 1H), 7.24-7.31 (m, 1H), 6.76-6.82 (m, 3H), 4.61-4.68 (m, 2H), 4.04-4.06 (m, 1H), 3.83 (s, 3H), 2.91-2.98 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 198.7, 160.1, 139.7, 130.3, 119.4, 113.6, 113.0, 79.3, 55.2, 46.4, 38.0; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): t_{major} = 51.50 min, t_{minor} = 64.45 min, ee = 96%; $[\alpha]_D^{25}$ = -5.9 (c = 2.0 in CHCl_3).



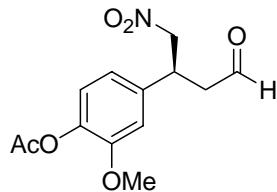
3-(2-Methoxy-phenyl)-4-nitro-butyraldehyde (2h) (Table 2, entry 8)

The title compound was prepared according to the general procedure, as described above in 70% yield. ^1H NMR (500 MHz, CDCl_3): 9.69 (s, 1H), 7.25-7.28 (m, 1H), 7.15 (d, 1H; J = 6.5 Hz), 6.88-6.93 (m, 2H), 4.70-4.76 (m, 2H), 4.28-4.30 (m, 1H), 3.86 (s, 3H), 3.00 (dd, 2H; J = 4.0 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 199.6, 157.1, 129.3, 121.0, 111.1, 77.8, 55.3, 45.0, 34.7; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): t_{major} = 43.61 min, t_{minor} = 58.15 min, ee = 97%; $[\alpha]_D^{25}$ = -3.9 (c = 1.0 in CHCl_3).



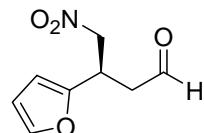
3-Phenyl-4-nitro-butyraldehyde (2i) (Table 2, entry 9)¹

The title compound was prepared according to the general procedure, as described above in 82% yield. ^1H NMR (500 MHz, CDCl_3): 9.69 (s, 1H), 7.22-7.35 (m, 5H), 4.60-4.69 (m, 2H), 4.06-4.08 (m, 1H), 2.94 (d, 2H; J = 3.5 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 198.8, 138.2, 129.2, 128.1, 127.4, 79.4, 46.4, 37.9; HPLC (Chiraldak AS-H, *i*-PrOH/hexanes = 20/80, flow rate = 0.5 mL/min, λ = 210 nm): $t_{\text{major}} = 58.96$ min, $t_{\text{minor}} = 64.05$ min, ee = 97%; $[\alpha]_D^{25} = -7.8$ ($c = 2.0$ in CHCl_3).



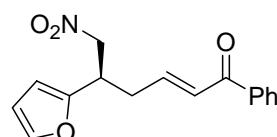
3-(4-Acetoxy-3-methoxy-phenyl)-4-nitro-butyraldehyde (2j) (Table 2, entry 10)

The title compound was prepared according to the general procedure, as described above in 65% yield. ^1H NMR (500 MHz, CDCl_3): 9.70 (s, 1H), 6.99 (d, 1H; J = 8.0 Hz), 6.78-6.82 (m, 2H), 4.60-4.68 (m, 2H), 4.05-4.08 (m, 1H), 3.82 (s, 3H), 2.94 (dd, 2H; J = 5.0 Hz), 2.29 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 198.6, 168.8, 151.5, 139.5, 137.1, 123.4, 119.1, 112.0, 79.1, 56.0, 46.5, 37.7, 20.6; HPLC (Chiraldak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): $t_{\text{major}} = 57.99$ min, $t_{\text{minor}} = \text{not observed}$, ee = 99%; $[\alpha]_D^{25} = +1.0$ ($c = 2.0$ in CHCl_3).

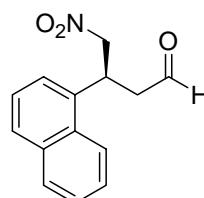


3-Furan-2-yl-4-nitro-butyraldehyde (2k) (Table 2, entry 11)

The title compound was prepared according to the general procedure, as described above in 68% yield. ^1H NMR (500 MHz, CDCl_3): 9.97 (s, 1H), 7.57 (m, 1H), 6.52 (m, 1H), 6.39 (m, 1H), 4.89-4.91 (m, 2H), 4.38-4.41 (m, 1H), 3.11-3.23 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 198.4, 151.0, 142.5, 110.5, 107.4, 43.9, 31.8; $[\alpha]_D^{25} = -6.2$ ($c = 2.0$ in CHCl_3).

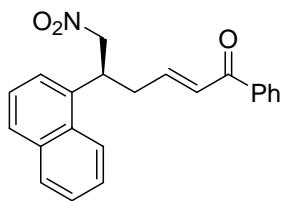


HPLC (Chiraldak AS-H, *i*-PrOH/hexanes = 20/80, flow rate = 0.5 mL/min, λ = 254 nm): $t_{\text{major}} = 42.71$ min, $t_{\text{minor}} = 39.33$ min, ee = 96%.

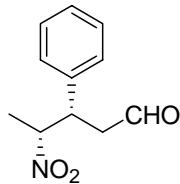


3-Naphthalen-1-yl-4-nitro-butyraldehyde (2l) (Table 2, entry 12)

The title compound was prepared according to the general procedure, as described above in 70% yield. ^1H NMR (500 MHz, CDCl_3): 9.71 (s, 1H), 8.15 (d, 1H; J = 8.5 Hz), 7.89 (d, 1H; J = 8.5 Hz), 7.80 (d, 1H; J = 8.0 Hz), 7.62 (t, 1H; J = 7.0 Hz), 7.54 (t, 1H; J = 7.5 Hz), 7.42 (t, 1H; J = 8.0 Hz), 7.33 (d, 1H; J = 7.0 Hz), 4.98-5.00 (m, 1H), 4.72-4.82 (m, 2H), 3.12 (d, 2H; J = 6.5 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 198.8, 134.2, 133.9, 130.8, 129.4, 128.8, 127.1, 126.2, 125.3, 123.9, 122.0, 78.9, 46.3, 32.5; $[\alpha]_D^{25} = +22.1$ ($c = 2.0$ in CHCl_3).

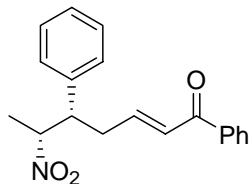


HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 254 nm): $t_{\text{major}} = 45.27$ min, $t_{\text{minor}} = 53.56$ min, ee = 96%.

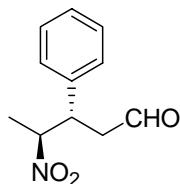


***syn*-4-Nitro-3-phenyl-pentanal (2m) (Table 2, entry 13)**

The title compound was prepared according to the general procedure, at RT instead of 0 °C, as described above in 92% yield (total yield with *syn* and *anti*). Spectroscopic data are in agreement with the literature reported data.^{2,3} ^1H NMR (500 MHz, CDCl_3): 9.57 (s, 1H), 7.20-7.37 (m, 5H), 4.76-4.79 (m, 1H), 3.73-3.78 (m, 1H), 2.94-2.99 (m, 1H), 2.74-2.78 (m, 1H), 1.34 (d, 3H; J = 6.5 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 198.6, 137.5, 129.2, 128.1, 128.0, 87.0, 46.3, 44.2, 17.7; $[\alpha]_D^{25} = -4.2$ (c = 2.0 in CHCl_3).

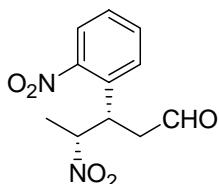


HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 20/80, flow rate = 0.5 mL/min, λ = 254 nm): $t_{\text{major}} = 20.29$ min, $t_{\text{minor}} = 21.69$ min, ee = 87%.



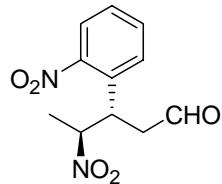
***anti*-4-Nitro-3-phenyl-pentanal (2m') (Table 2, entry 13)**

The title compound was prepared according to the general procedure, at rt instead of 0 °C, as described above in 92% yield (total yield with *syn* and *anti*). Spectroscopic data are in agreement with the literature reported data.^{2,3} ^1H NMR (500 MHz, CDCl_3): 9.67 (s, 1H), 7.17-7.34 (m, 5H), 4.85-4.88 (m, 1H), 3.81-3.83 (m, 1H), 2.95-3.00 (m, 2H), 1.52 (d, 3H; J = 7.0 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 199.1, 137.5, 128.9, 128.7, 128.2, 128.1, 128.0, 86.3, 44.7, 43.5, 16.6; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): $t_{\text{major}} = 25.65$ min, $t_{\text{minor}} = \text{not observed}$, ee = 99%; $[\alpha]_D^{25} = -30.0$ (c = 2.0 in CHCl_3).



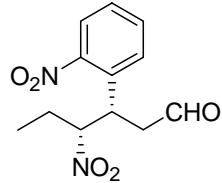
syn-4-Nitro-3-(2-nitro-phenyl)pentanal (2n) (Table 2, entry 14)

The title compound was prepared according to the general procedure, at RT instead of 0 °C, as described above in 87% yield (total yield with syn and anti). ¹H NMR (500 MHz, CDCl₃): 9.59 (s, 1H), 7.89 (d, 1H; *J* = 8.0 Hz), 7.61 (t, 1H; *J* = 7.0 Hz), 7.47 (t, 1H; *J* = 7.0 Hz), 7.32 (d, 1H; *J* = 7.5 Hz), 5.00-5.03 (m, 1H), 4.39-4.42 (m, 1H), 2.97-3.08 (m, 2H), 1.51 (d, 3H; *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 197.8, 150.5, 133.3, 132.8, 128.9, 128.6, 125.1, 86.5, 45.4, 37.7, 17.9; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): t_{major} = 31.12 min, t_{minor} = 44.59 min, ee = 92%; [α]_D²⁵ = -250.6 (c = 2.0 in CHCl₃).



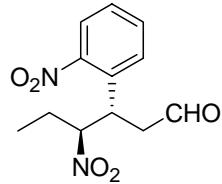
anti-4-Nitro-3-(2-nitro-phenyl)pentanal (2n') (Table 2, entry 14)

The title compound was prepared according to the general procedure, at RT instead of 0 °C, as described above in 87% yield (total yield with syn and anti). ¹H NMR (500 MHz, CDCl₃): 9.71 (s, 1H), 7.86 (d, 1H; *J* = 8.0 Hz), 7.58 (t, 1H; *J* = 8.0 Hz), 7.45 (t, 1H; *J* = 8.0 Hz), 7.39 (d, 1H; *J* = 8.0 Hz), 5.14-5.16 (m, 1H), 4.49-4.52 (m, 1H), 3.12-3.16 (m, 1H), 2.96-3.01 (m, 1H), 1.58 (d, 3H; *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 198.3, 133.2, 129.0, 128.9, 125.2, 85.1, 45.0, 37.8, 17.1; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): t_{major} = 45.62 min, t_{minor} = 52.21 min, ee = 94%; [α]_D²⁵ = +99.4 (c = 2.0 in CHCl₃).



syn-4-Nitro-3-(2-nitro-phenyl)hexanal (2o) (Table 2, entry 15)

The title compound was prepared according to the general procedure, at RT instead of 0 °C, as described above in 90% yield (total yield with syn and anti). Spectroscopic data are in agreement with the literature reported data. ³¹H NMR (500 MHz, CDCl₃): 9.58 (s, 1H), 7.88 (d, 1H; *J* = 7.0 Hz), 7.60 (t, 1H; *J* = 7.0 Hz), 7.46 (t, 1H; *J* = 7.0 Hz), 7.31 (d, 1H; *J* = 7.5 Hz), 4.81-4.85 (m, 1H), 4.40-4.44 (m, 1H), 2.95-3.10 (m, 2H), 2.04-2.09 (m, 1H), 1.60-1.64 (m, 1H), 0.93 (t, 3H; *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 197.9, 150.4, 133.3, 132.9, 128.8, 128.5, 125.1, 93.5, 45.3, 36.8, 25.4, 10.3; HPLC (Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): t_{major} = 24.10 min, t_{minor} = 30.31 min, ee = 92%; [α]_D²⁵ = -191.5 (c = 3.0 in CHCl₃).

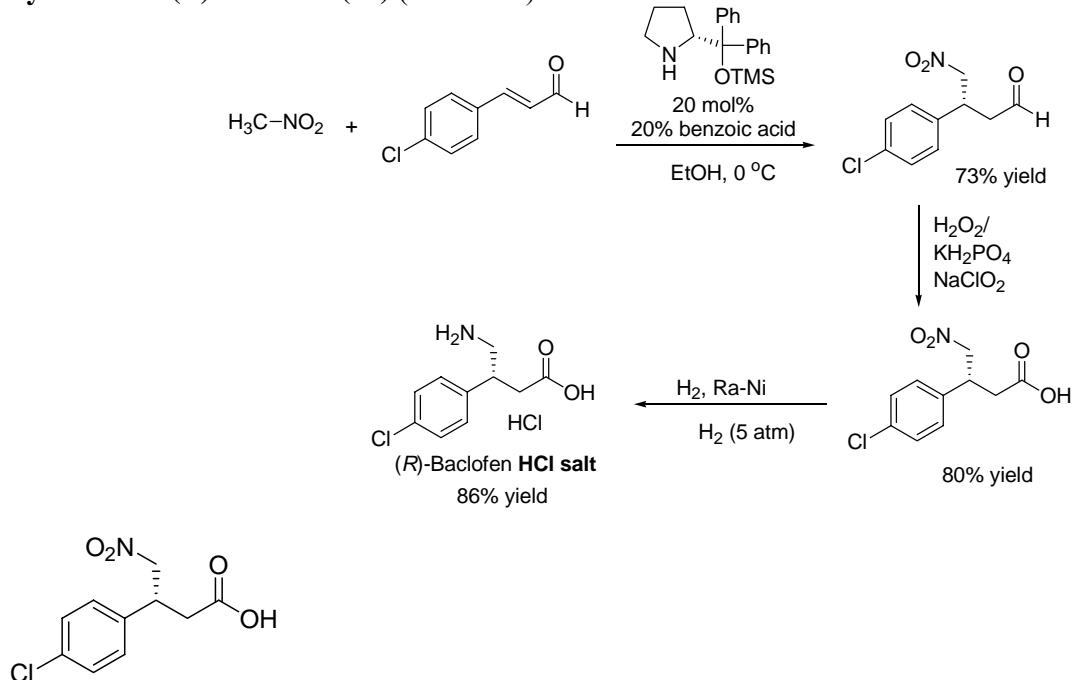


anti-4-Nitro-3-(2-nitro-phenyl)hexanal (2o') (Table 2, entry 15)

The title compound was prepared according to the general procedure, at RT instead of 0 °C, as described above in 90% yield (total yield with syn and anti). Spectroscopic data are in agreement with the literature reported data. ³¹H NMR (500 MHz, CDCl₃): 9.71 (s, 1H), 7.44-7.85 (m, 4H), 4.97 (m, 1H), 4.48 (m, 1H), 3.11-3.15 (m, 1H), 2.92-2.96 (m, 1H), 1.91 (m, 2H), 0.96 (t, 3H; *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 198.4, 150.1, 133.1, 132.5, 129.3, 128.9, 125.1, 92.2, 45.5, 37.3, 24.8, 10.2; HPLC

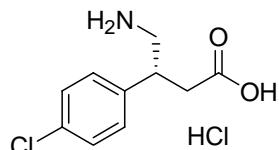
(Chiralpak AS-H, *i*-PrOH/hexanes = 30/70, flow rate = 0.5 mL/min, λ = 210 nm): $t_{\text{major}} = 73.7$ min, $t_{\text{minor}} =$ not observed, ee = 99%; $[\alpha]_D^{25} = +197.4$ ($c = 2.0$ in CHCl_3).

Synthesis of (*R*)-Baclofen (1a) (Scheme 2).



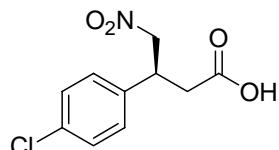
(*R*)-3-(4-Chloro-phenyl)-4-nitro-butyric acid (5b)

The title compound was prepared according to the similar procedure⁴ in 80% yield. A solution of (*R*)-3-(4-chloro-phenyl)-4-nitro-butyraldehyde (1.1 g, 4.83 mmol) in CH_3CN (25 mL) was cooled to 0 °C, then KH_2PO_4 (500 mg) in H_2O (12.5 mL) and H_2O_2 (30%, 650 μL) were added with rigorous stirring. After addition of a solution of NaClO_2 (1.25 g) in H_2O (25 mL), the resulting mixture was stirred from 0 °C to RT for 2 h. The reaction was quenched with aqueous $\text{Na}_2\text{S}_2\text{O}_3$, acidified with aqueous KHSO_4 , extracted with CH_2Cl_2 , dried over MgSO_4 . ^1H NMR (500 MHz, CDCl_3): 7.32 (d, 2H; $J = 8.0$ Hz), 7.17 (d, 2H; $J = 8.5$ Hz), 4.58-4.72 (m, 2H), 3.94-3.97 (m, 1H), 2.79-2.82 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 175.8, 136.4, 134.2, 129.4, 128.7, 79.0, 39.2, 37.1; $[\alpha]_D^{25} = +10.4$ ($c = 1.0$ in CHCl_3), and this value is in agreement with the literature reported data.⁵



(*R*)-3-(4-chlorophenyl)-4-amino-butyric acid hydrochloride

The title compound was prepared according to the literature procedure⁵ in 86% yield. ^1H NMR (500 MHz, DMSO): 8.13 (m, 3H), 7.33-7.38 (m, 4H), 3.38 (m, 1H), 3.09 (m, 1H), 2.94 (m, 1H), 2.86 (dd, 1H; $J = 4.5$ Hz), 2.55 (dd, 1H; $J = 9.5$ Hz); ^{13}C NMR (125 MHz, DMSO): δ 172.1, 139.2, 131.7, 129.8, 128.4, 43.0, 39.0, 37.7; HRMS: calculated for $[\text{M}+\text{H}]^+$ of $\text{C}_{10}\text{H}_{12}\text{ClNO}_2$ 214.0635, found 214.0640; $[\alpha]_D^{27} = -3.6$ ($c = 1.0$ in H_2O). The spectra data and optical rotation data are in agreement with the literature reported data.⁵

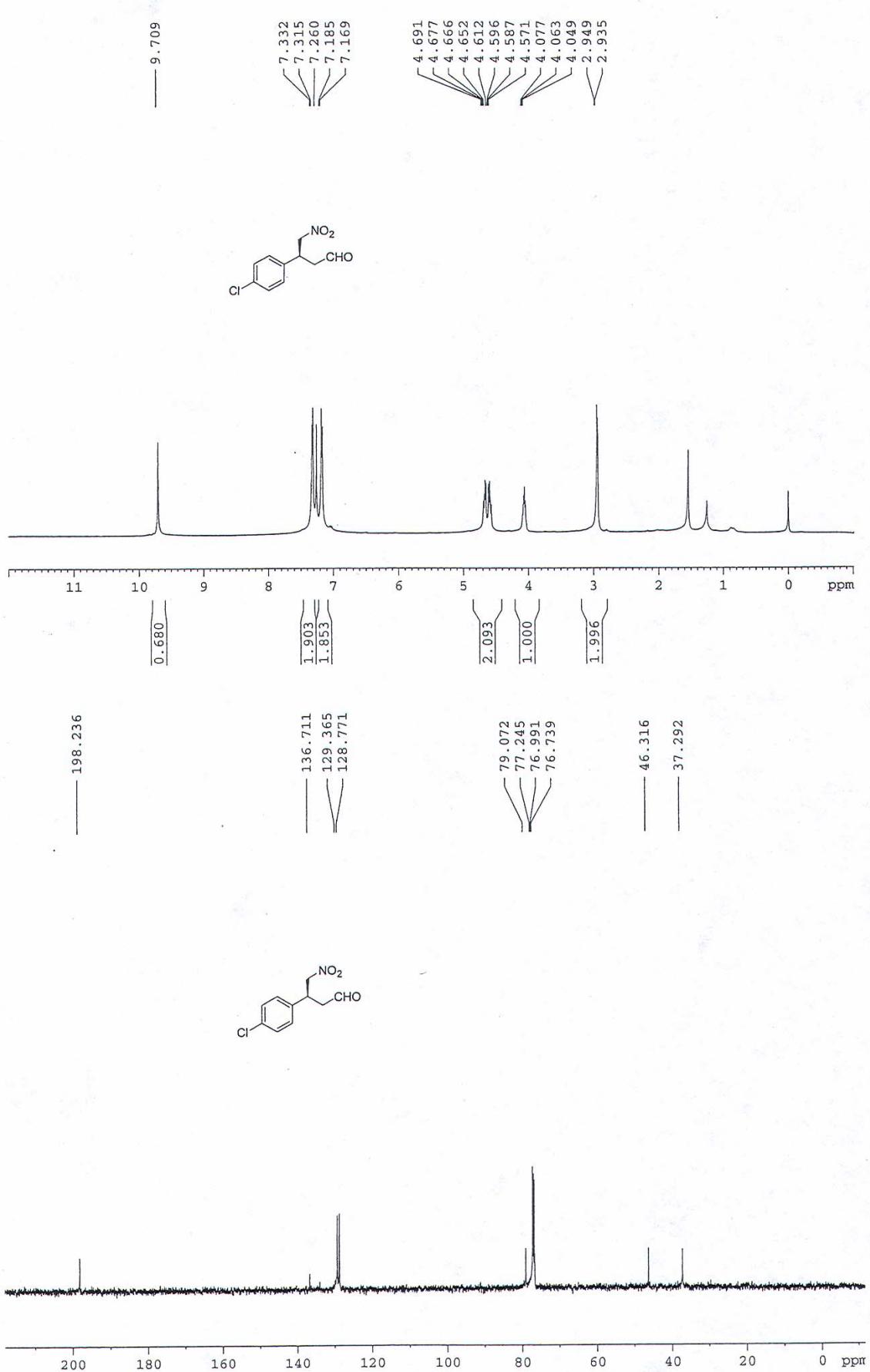


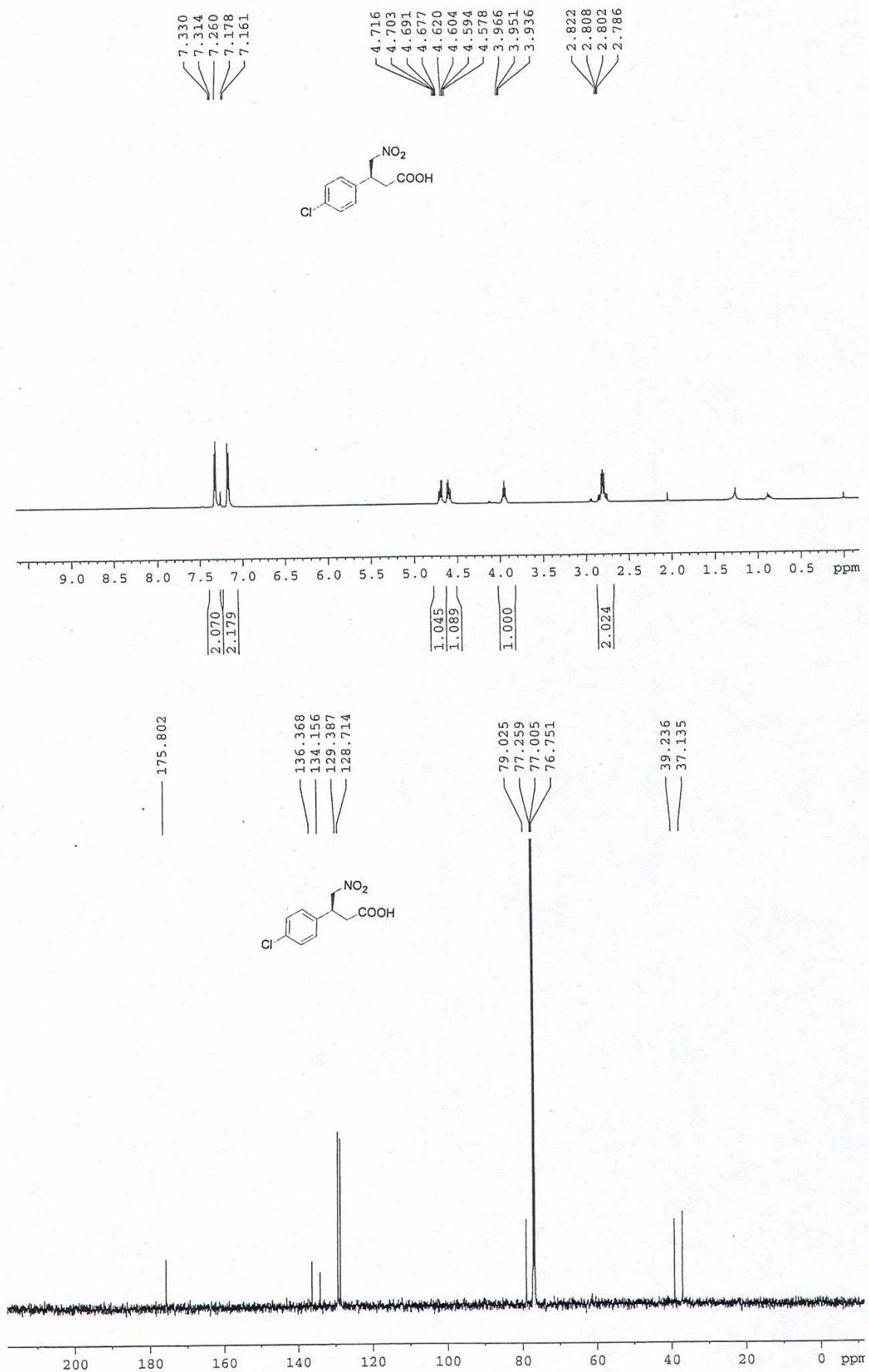
(S)-3-(4-Chloro-phenyl)-4-nitro-butrylic acid (5a)

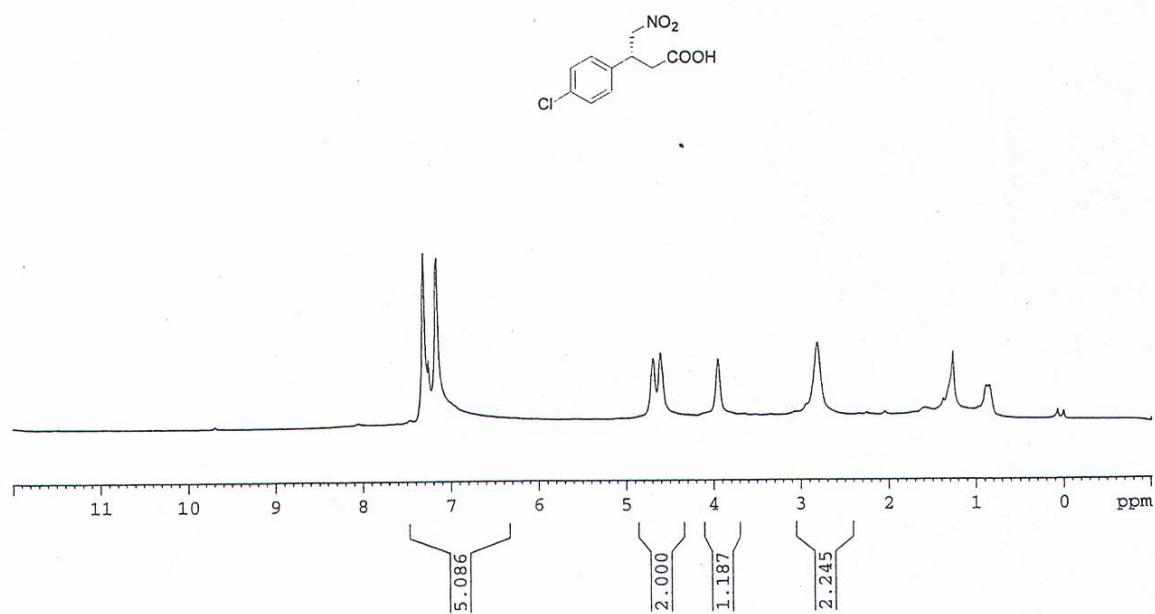
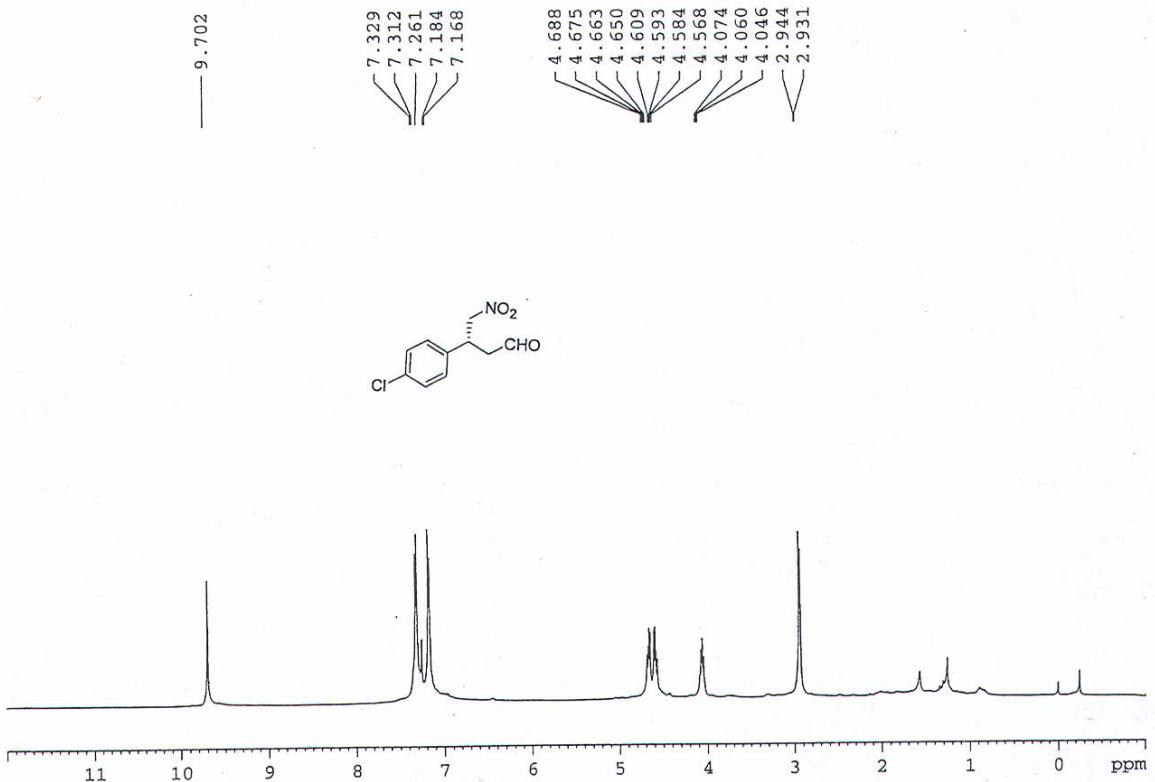
The title compound was prepared according to the same procedure in 90% yield. The optical value is in agreement with the that of its *R* enantiomer; $[\alpha]_D^{25} = -11.1$ ($c = 1.0$ in CHCl_3), and this value and sign is in agreement with the literature reported data.

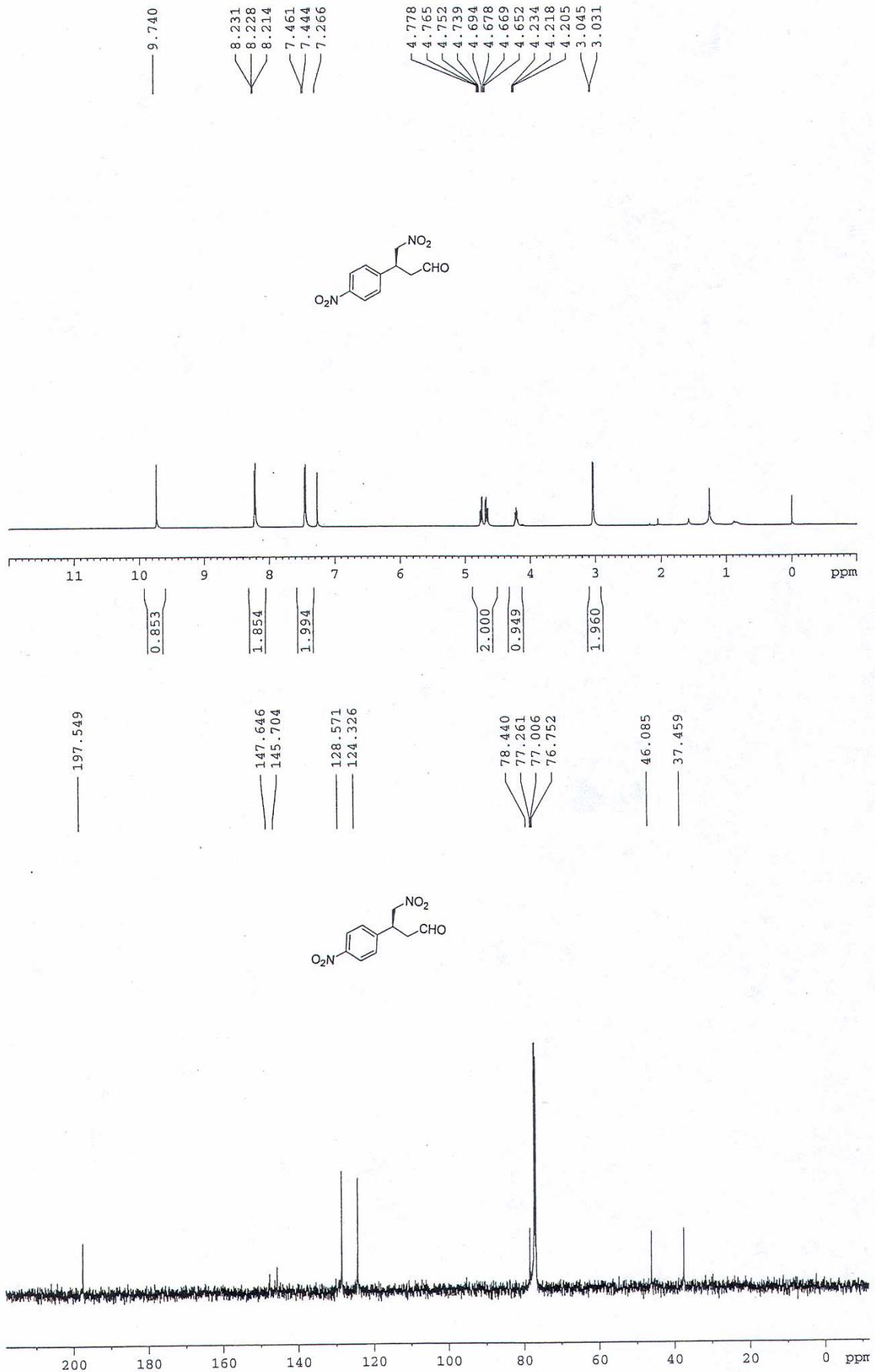
References

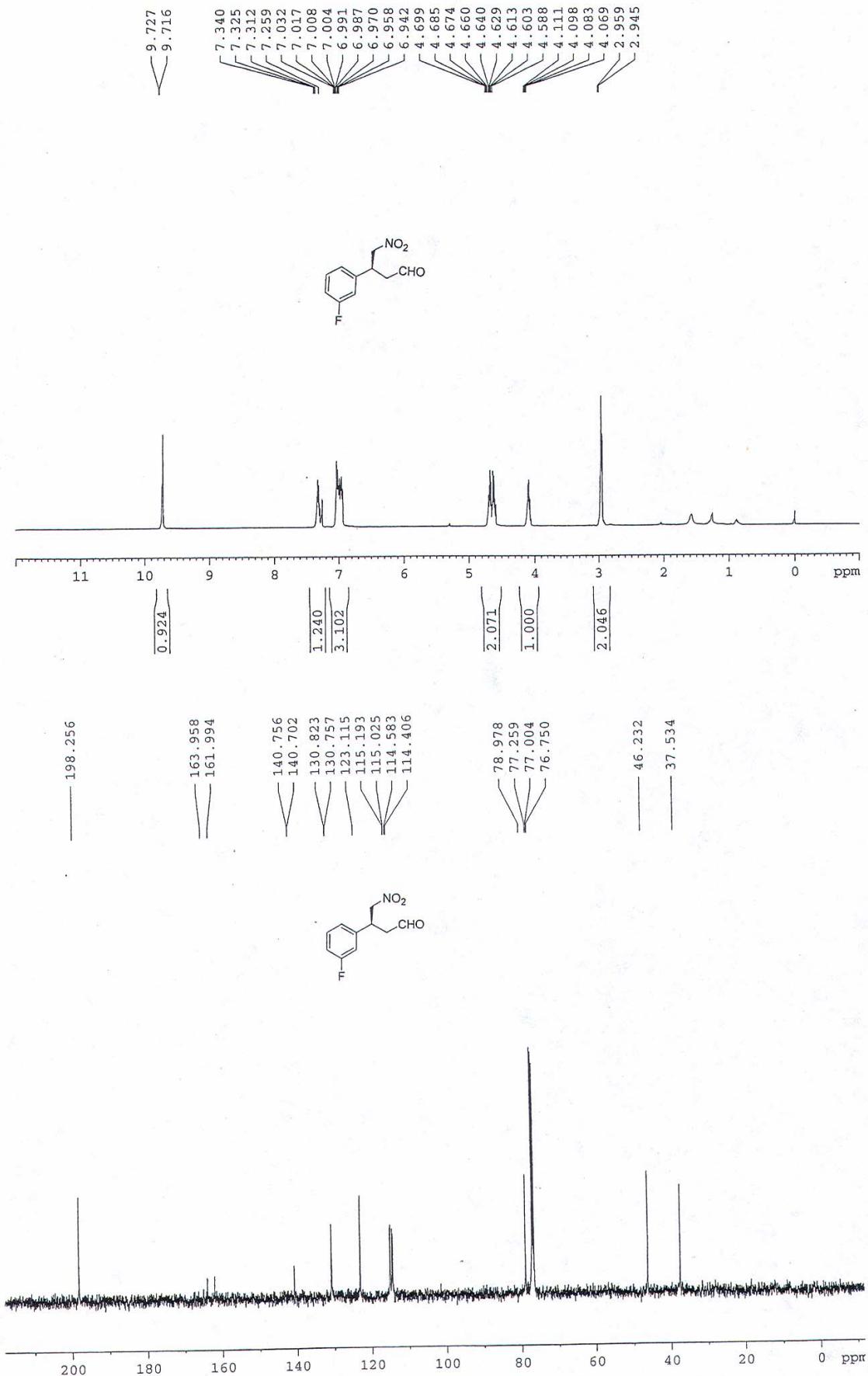
- (1) Palomo, C.; Pazos, R.; Oiarbide, M.; Garcia, J. M. *Adv. Synth. Catal.* **2006**, *348*, 1161.
- (2) Ooi, T.; Doda, K.; Maruoka, K. *J. Am. Chem. Soc.* **2003**, *125*, 9022.
- (3) Hojabri, L.; Hartikka, A.; Moghaddam, F.; Arvidsson, M. P. I. *Adv. Synth. Catal.* **2007**, *349*, 740.
- (4) Beumer, R.; Bubert, C.; Cabrele, C.; Vielhauer, O.; Pietzsch, M.; Reiser, O. *J. Org. Chem.* **2000**, *65*, 8960.
- (5) Camps, P.; Munoz-Torrero, D.; Sanchez, L. *Tetrahedron: Asymmetry* **2004**, *15*, 2039.

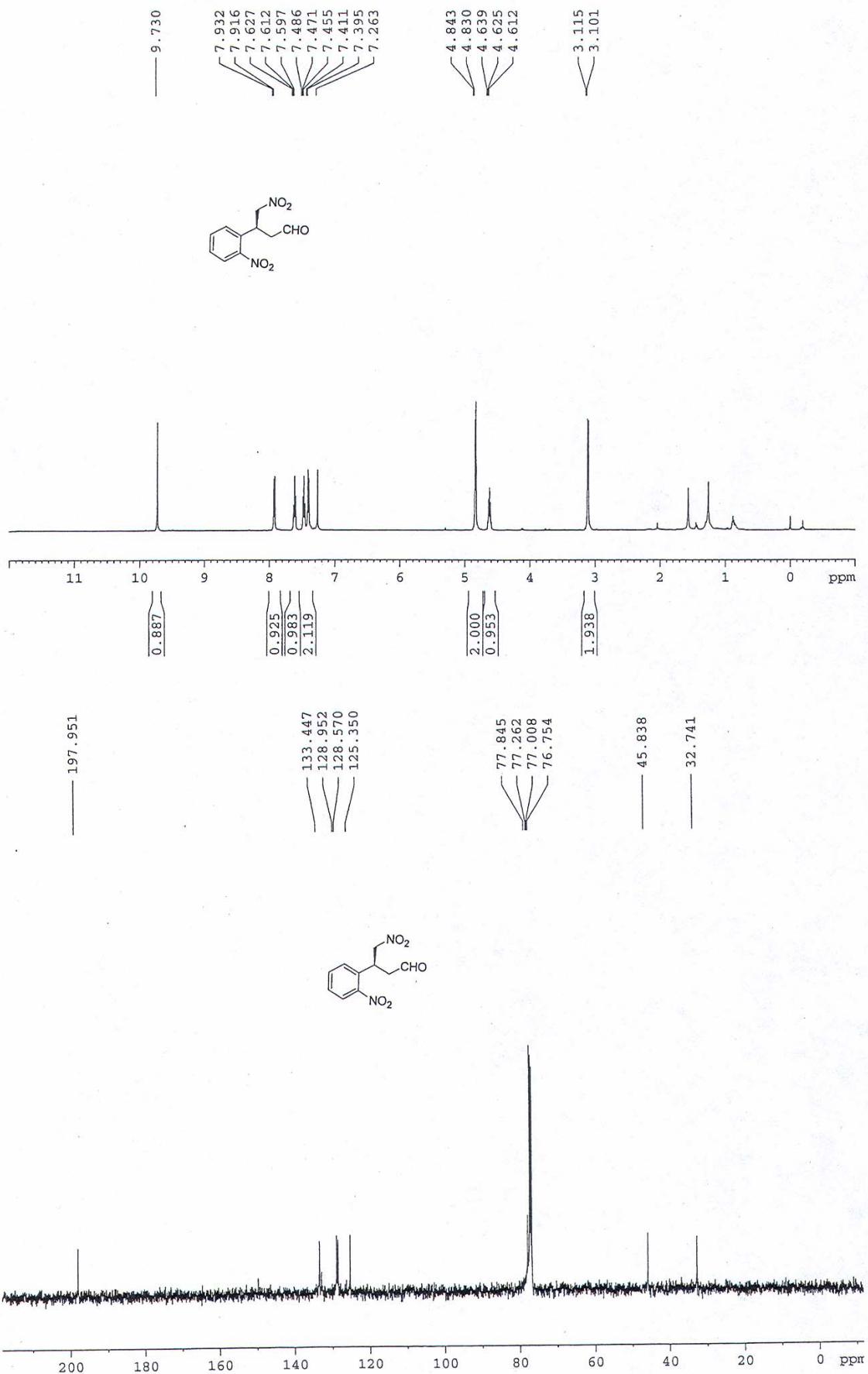


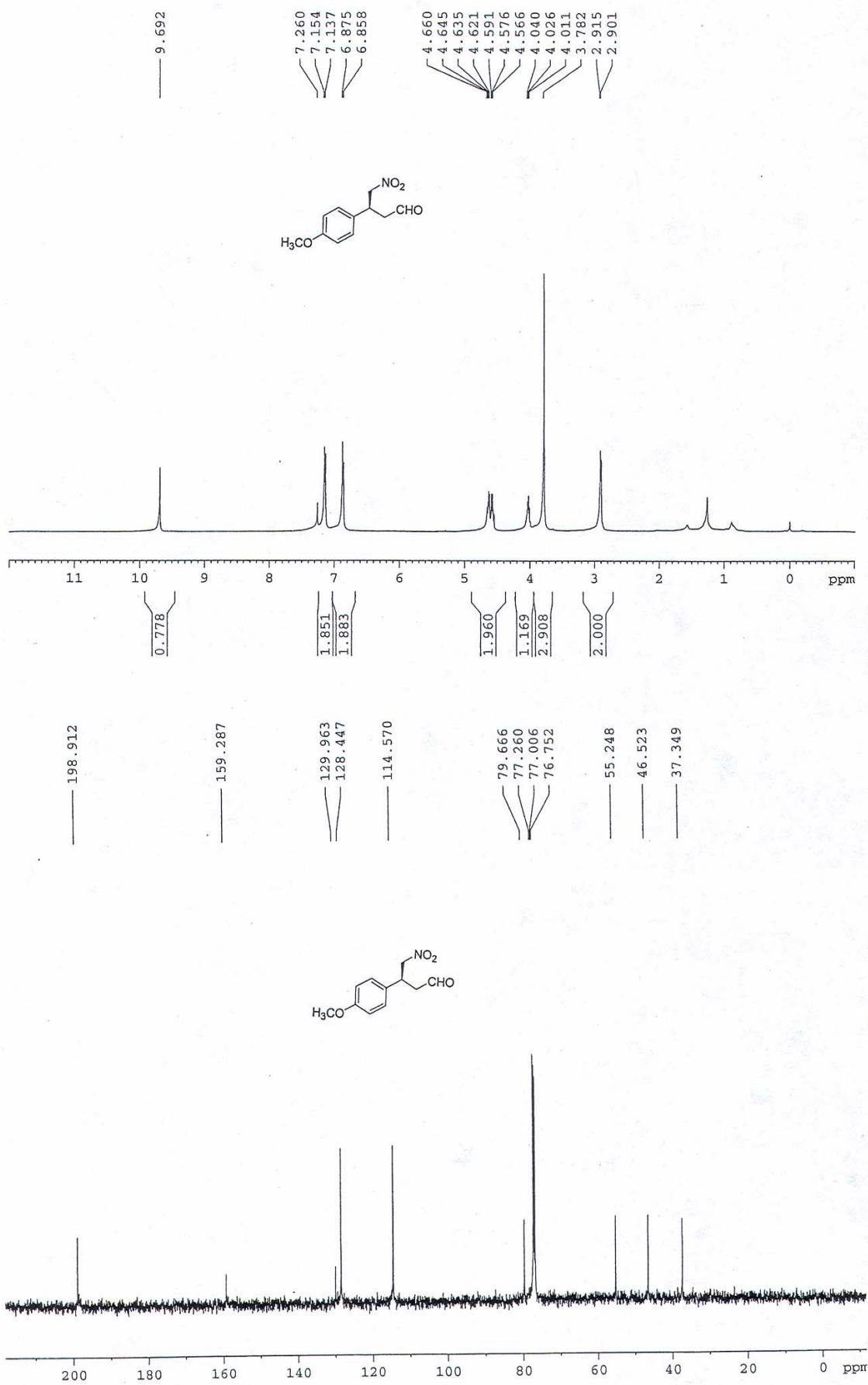


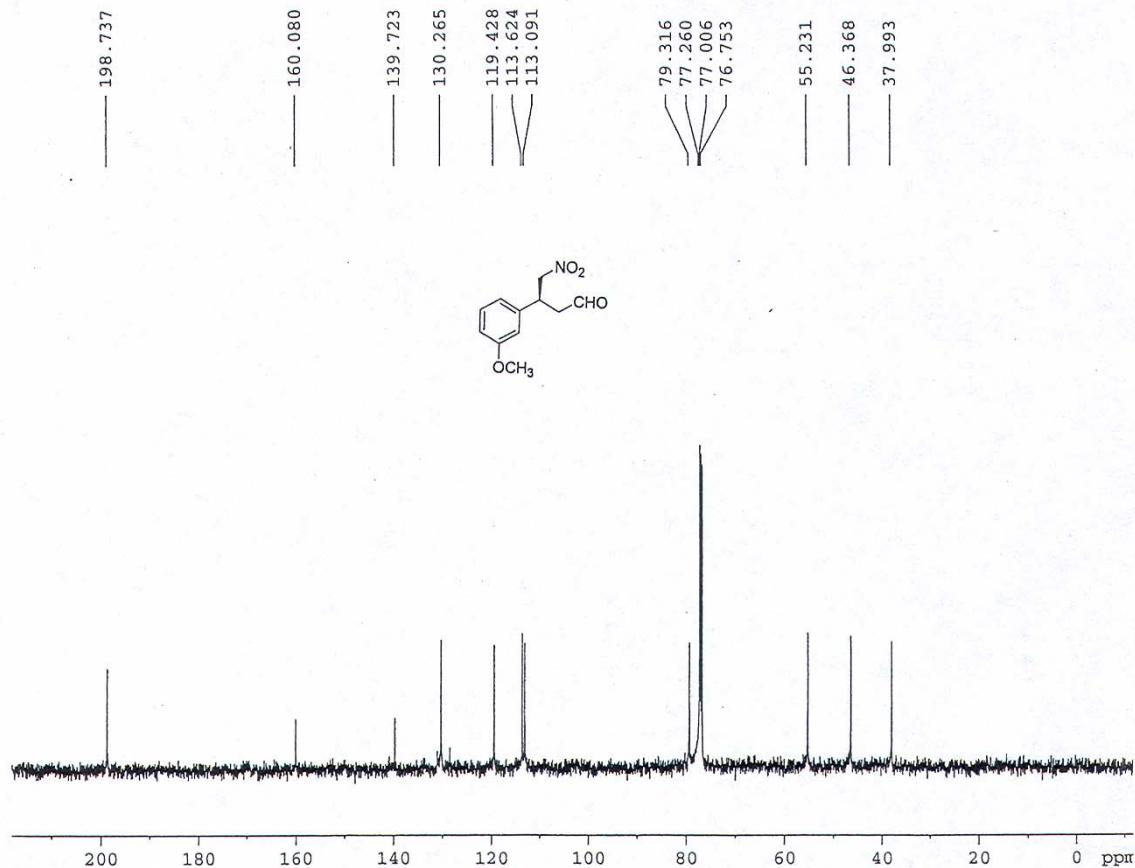
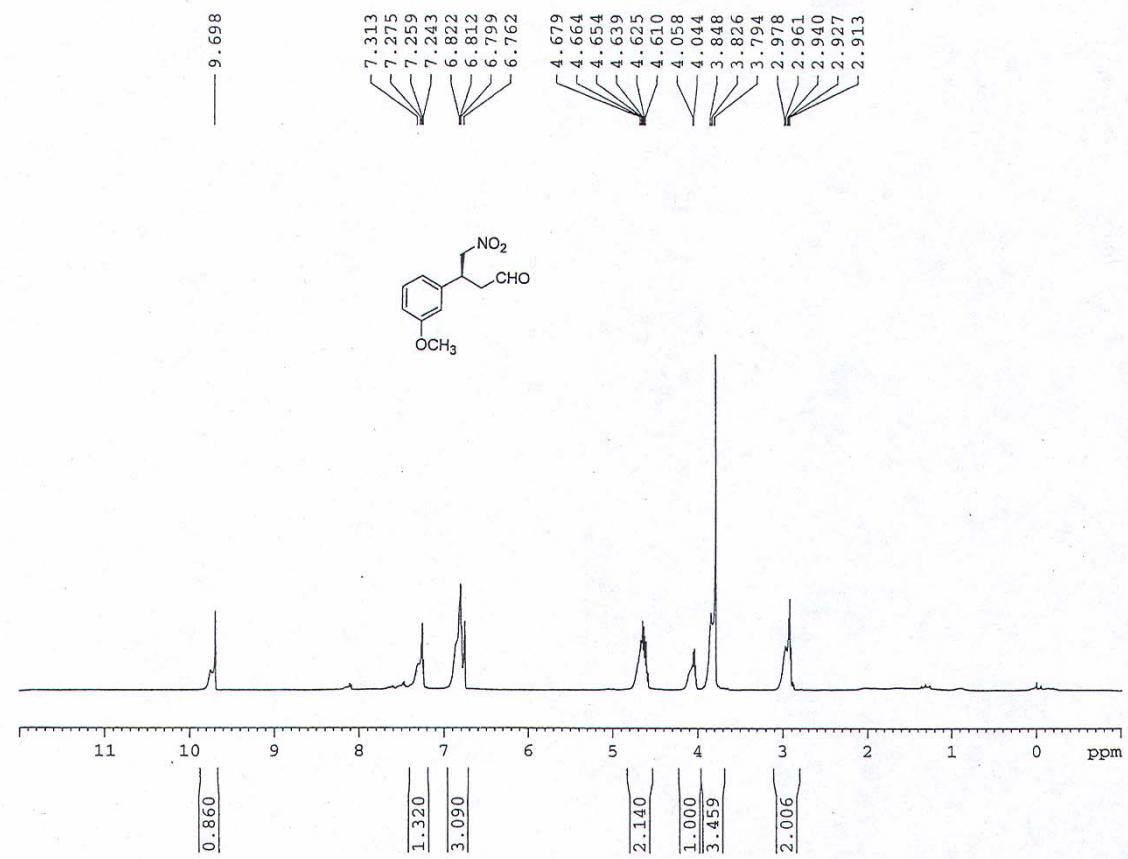


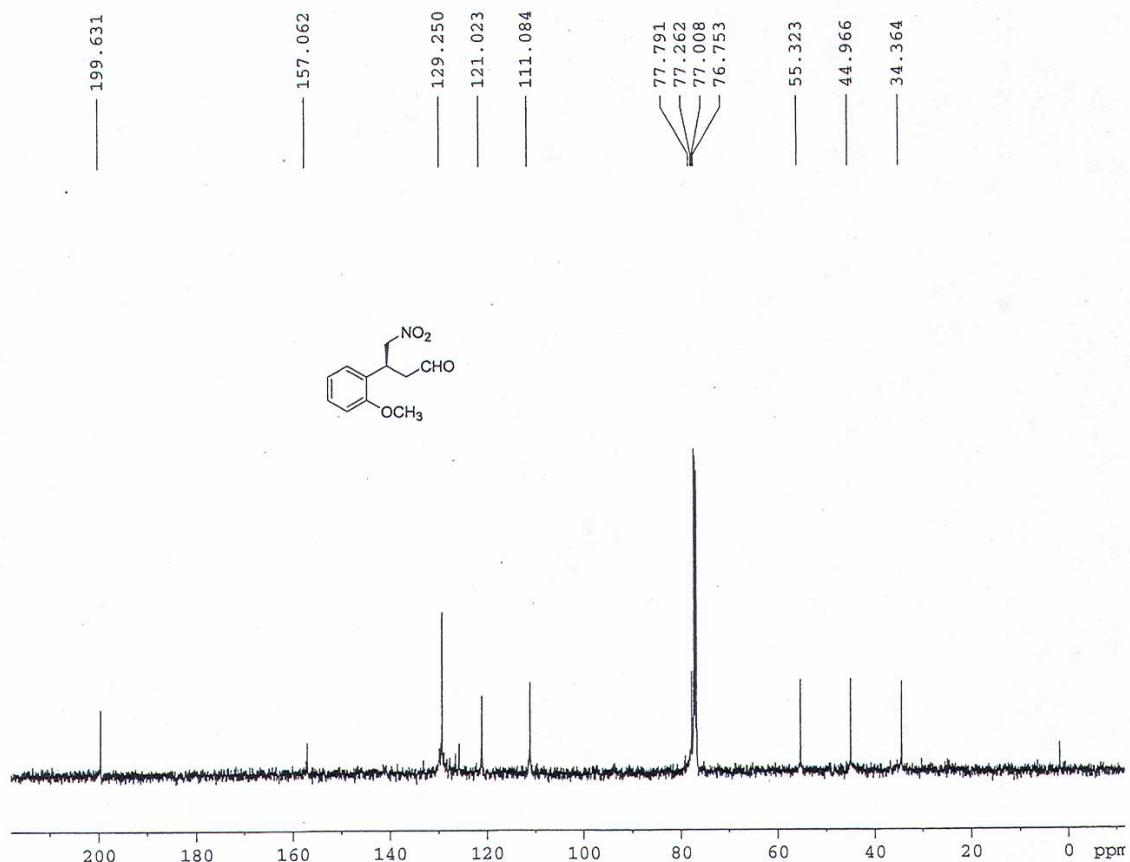
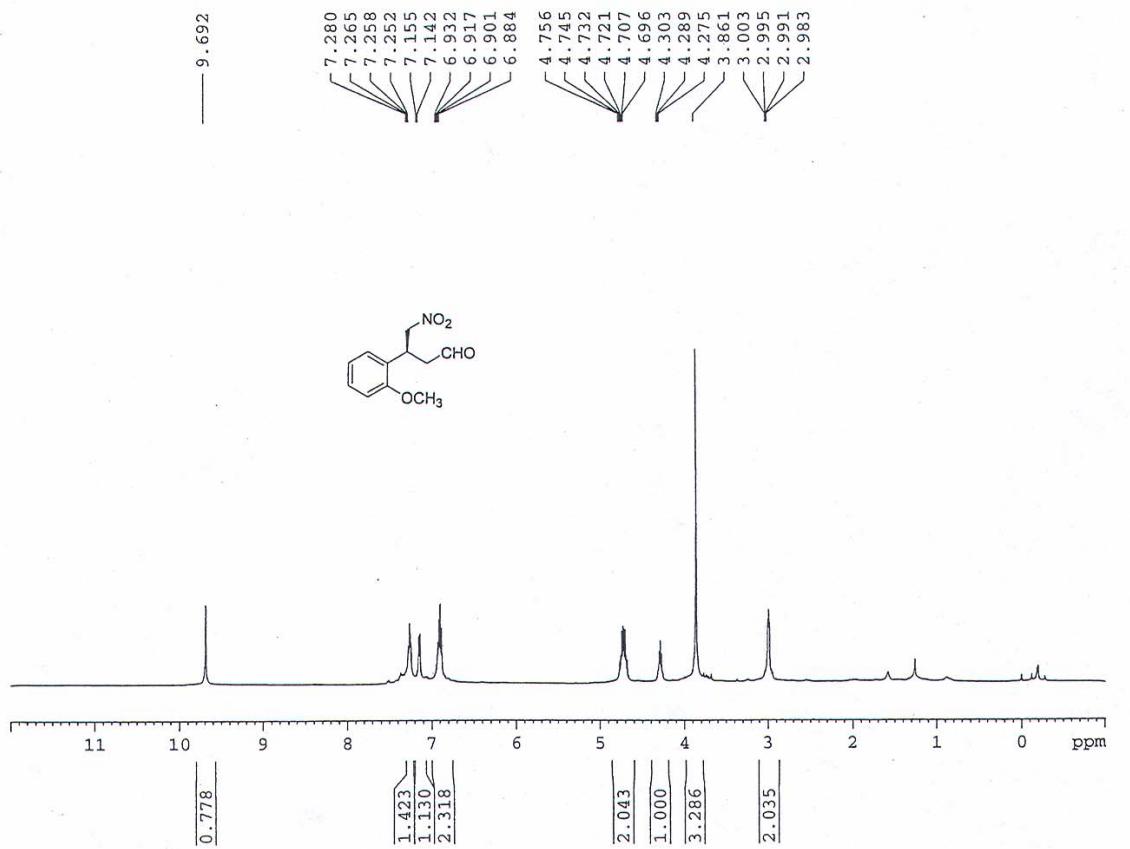


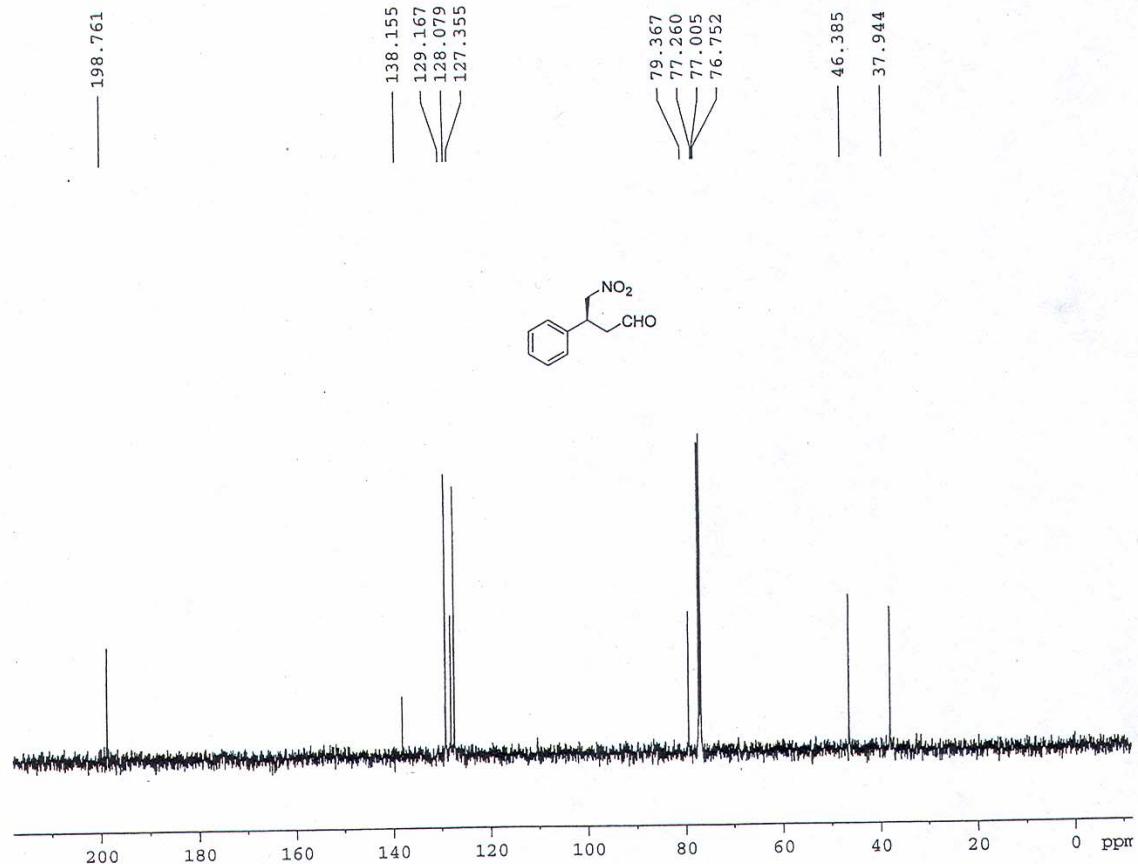
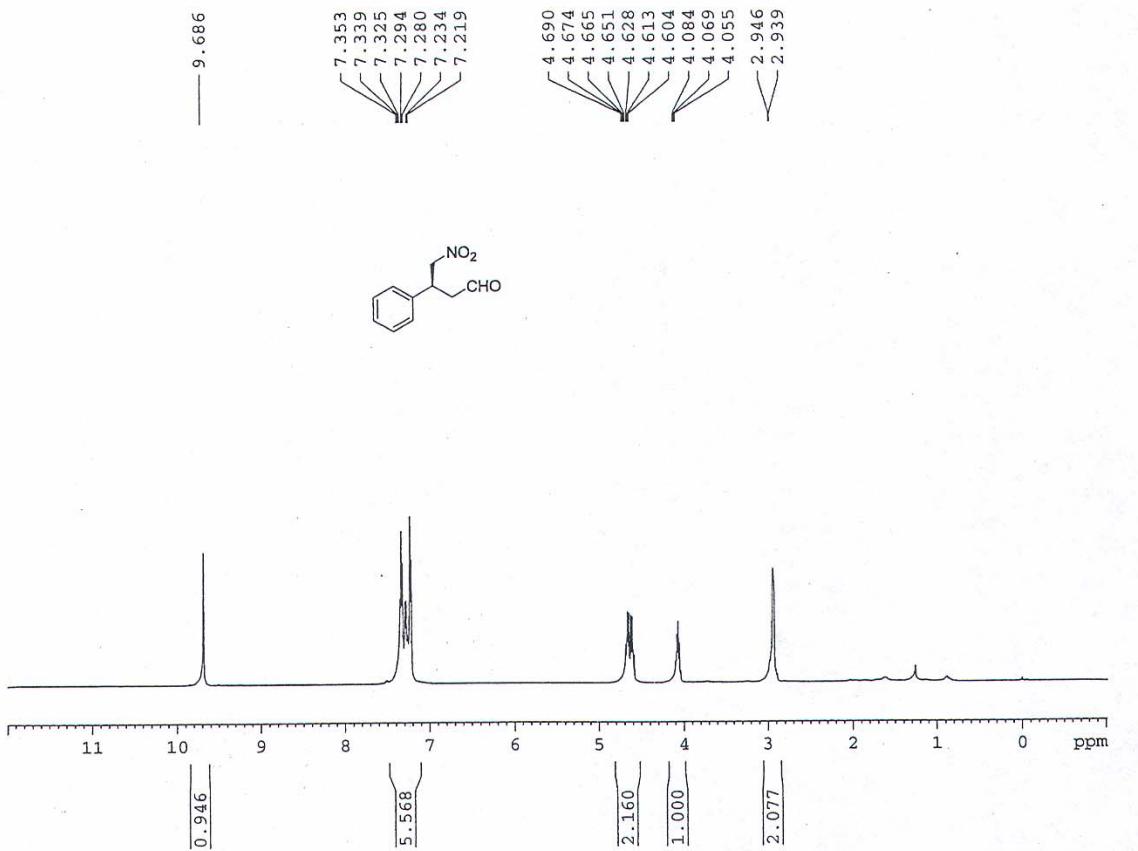


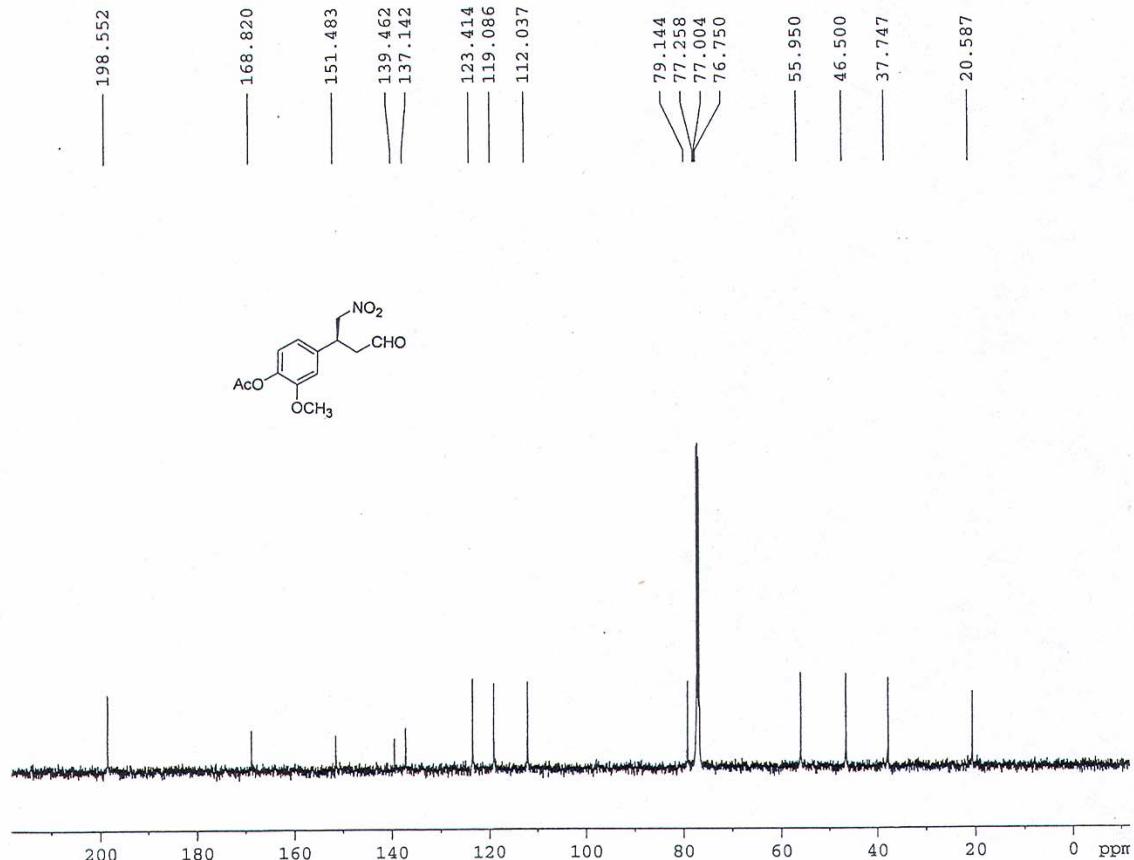
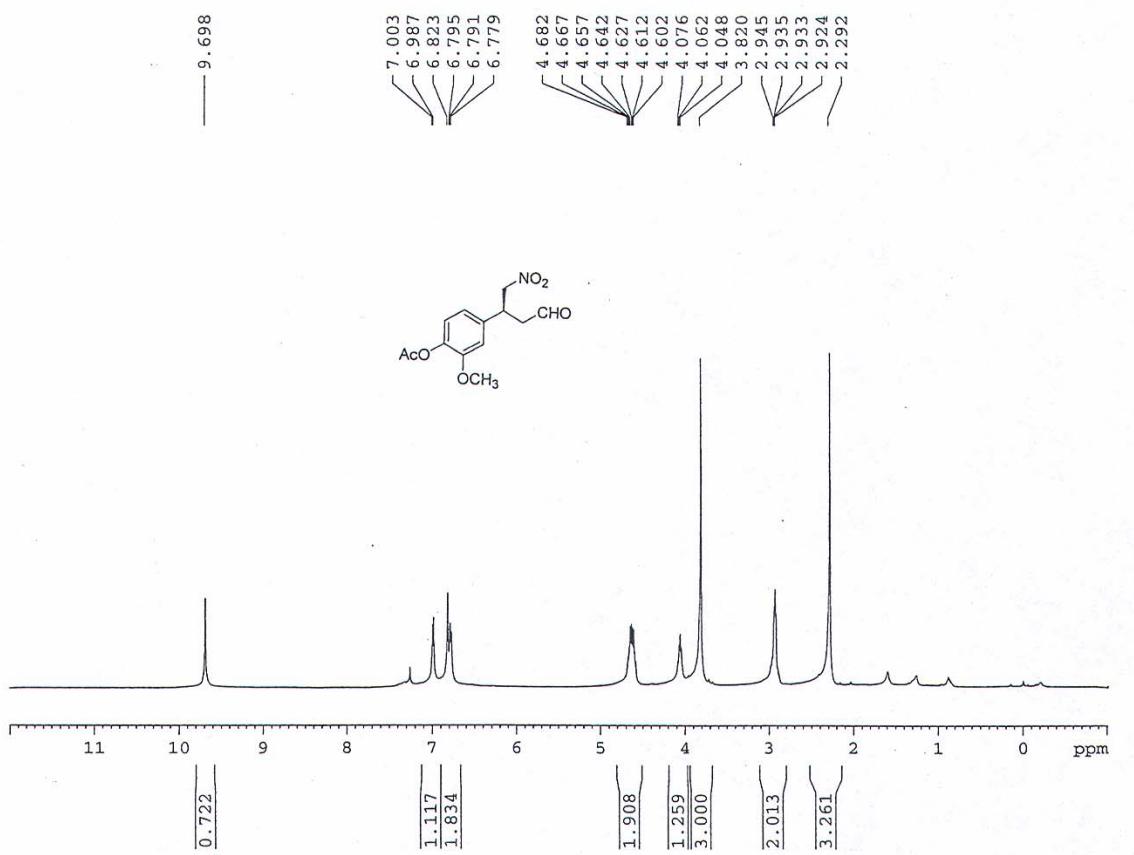


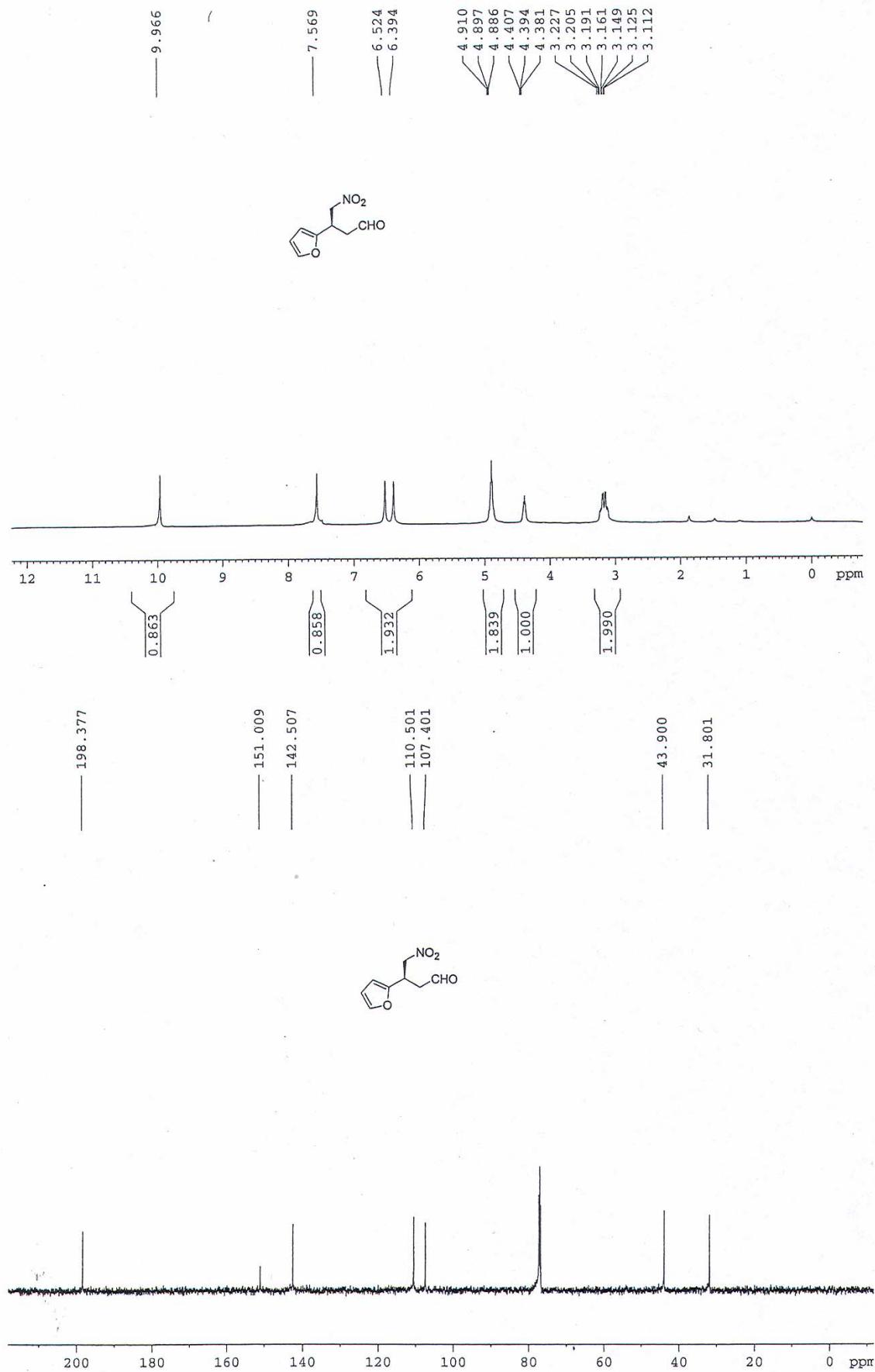


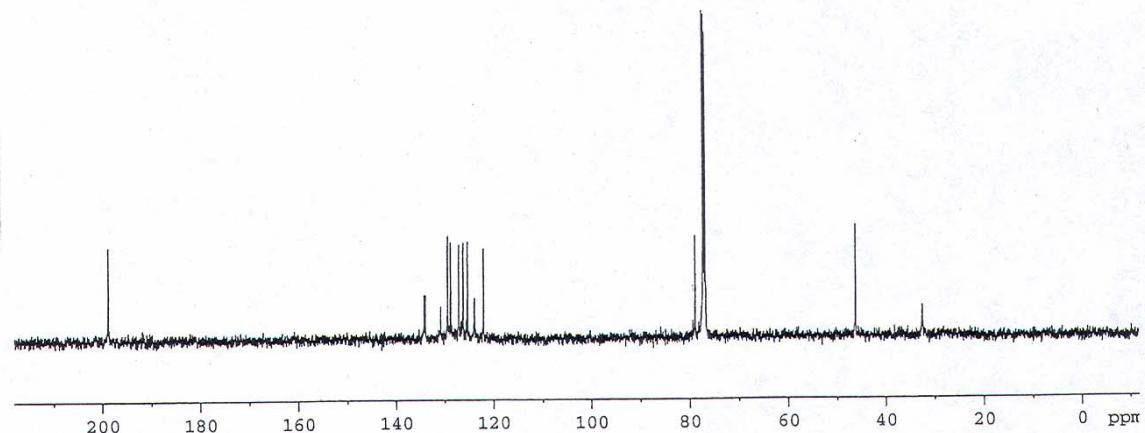
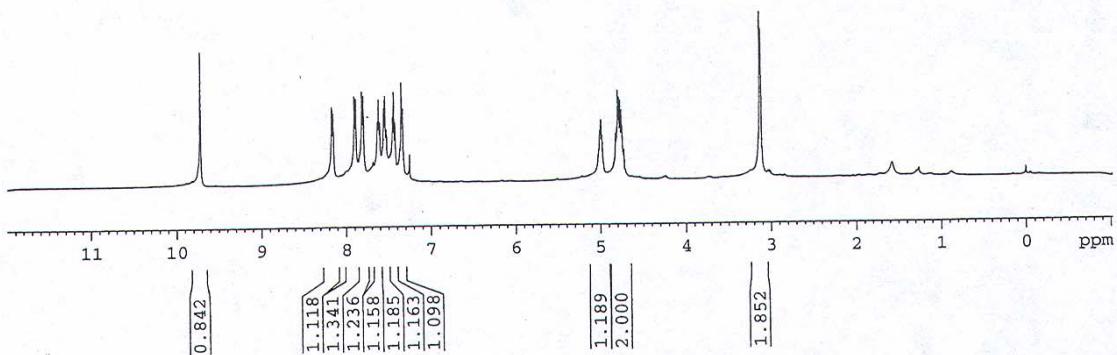
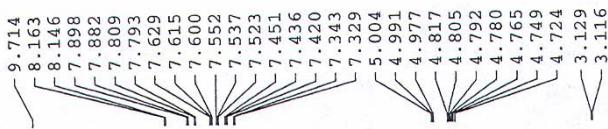


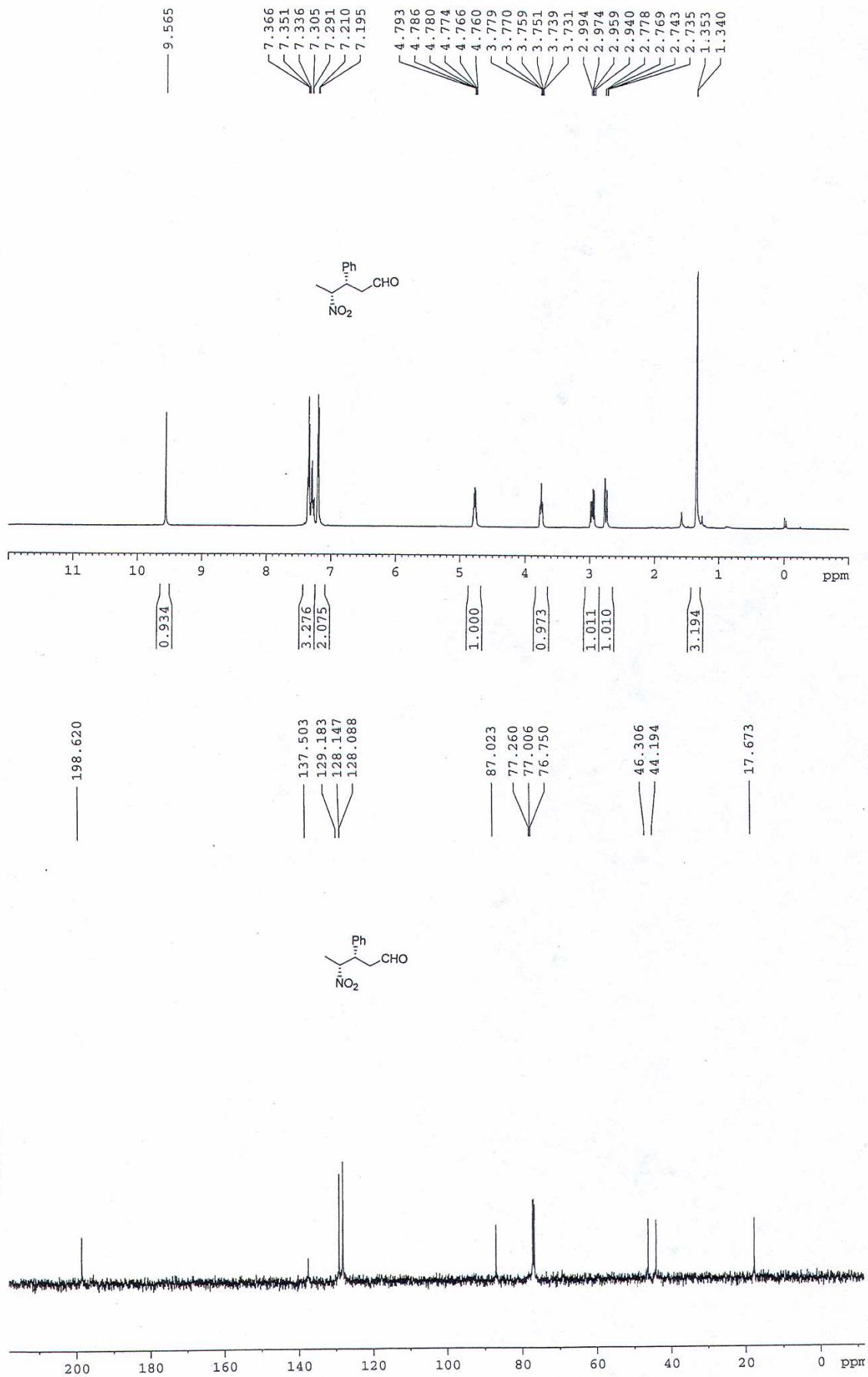


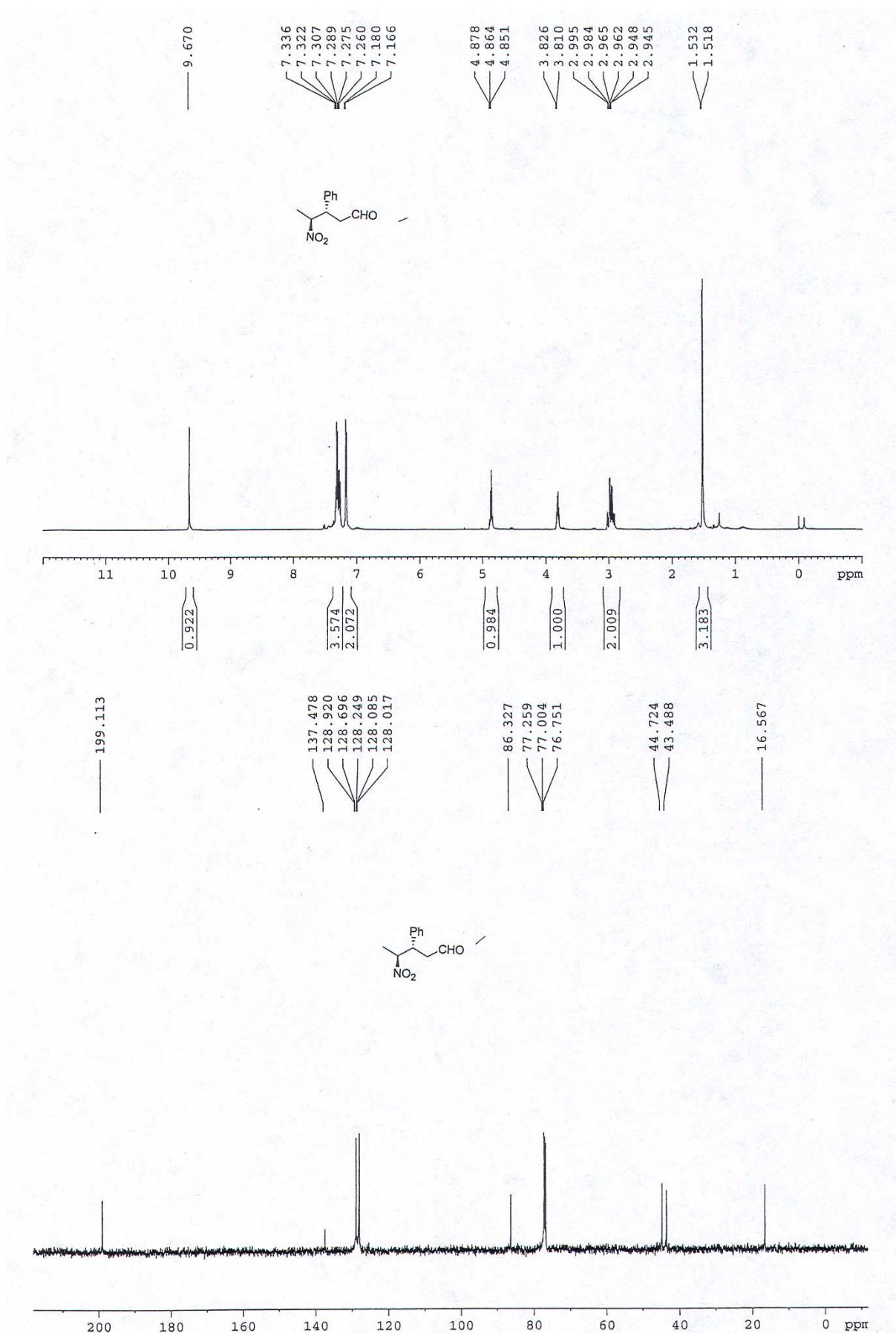


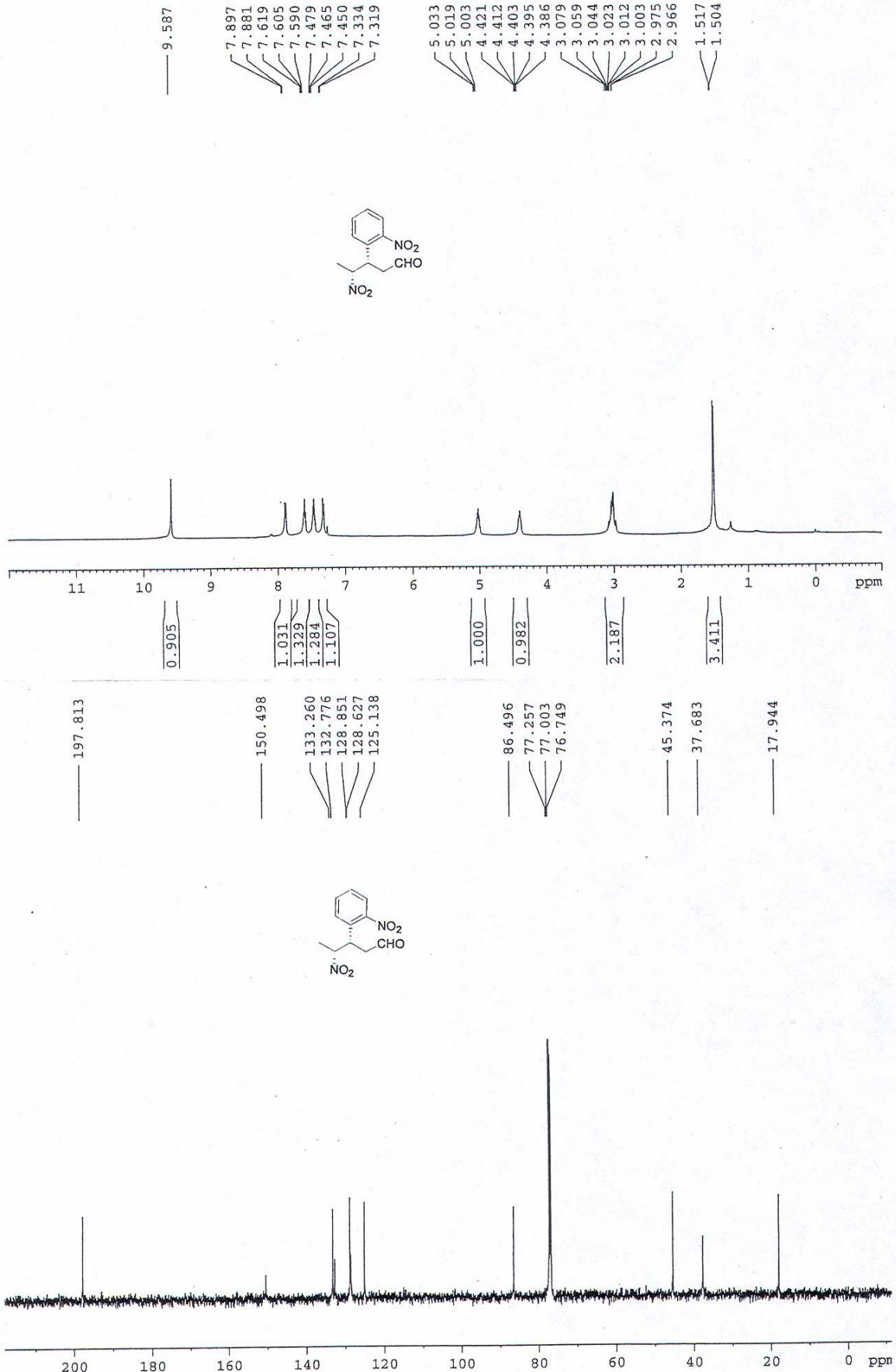


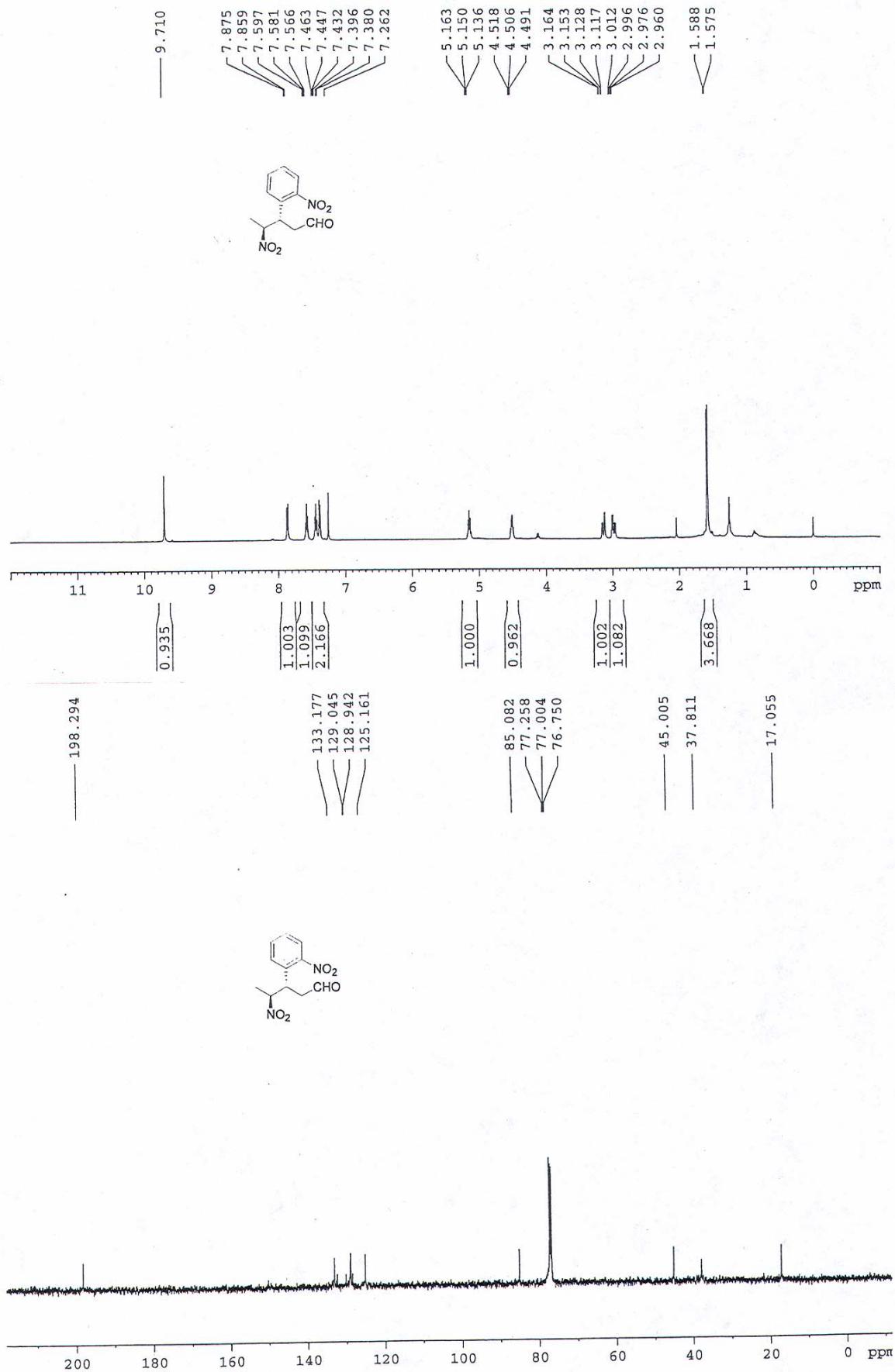


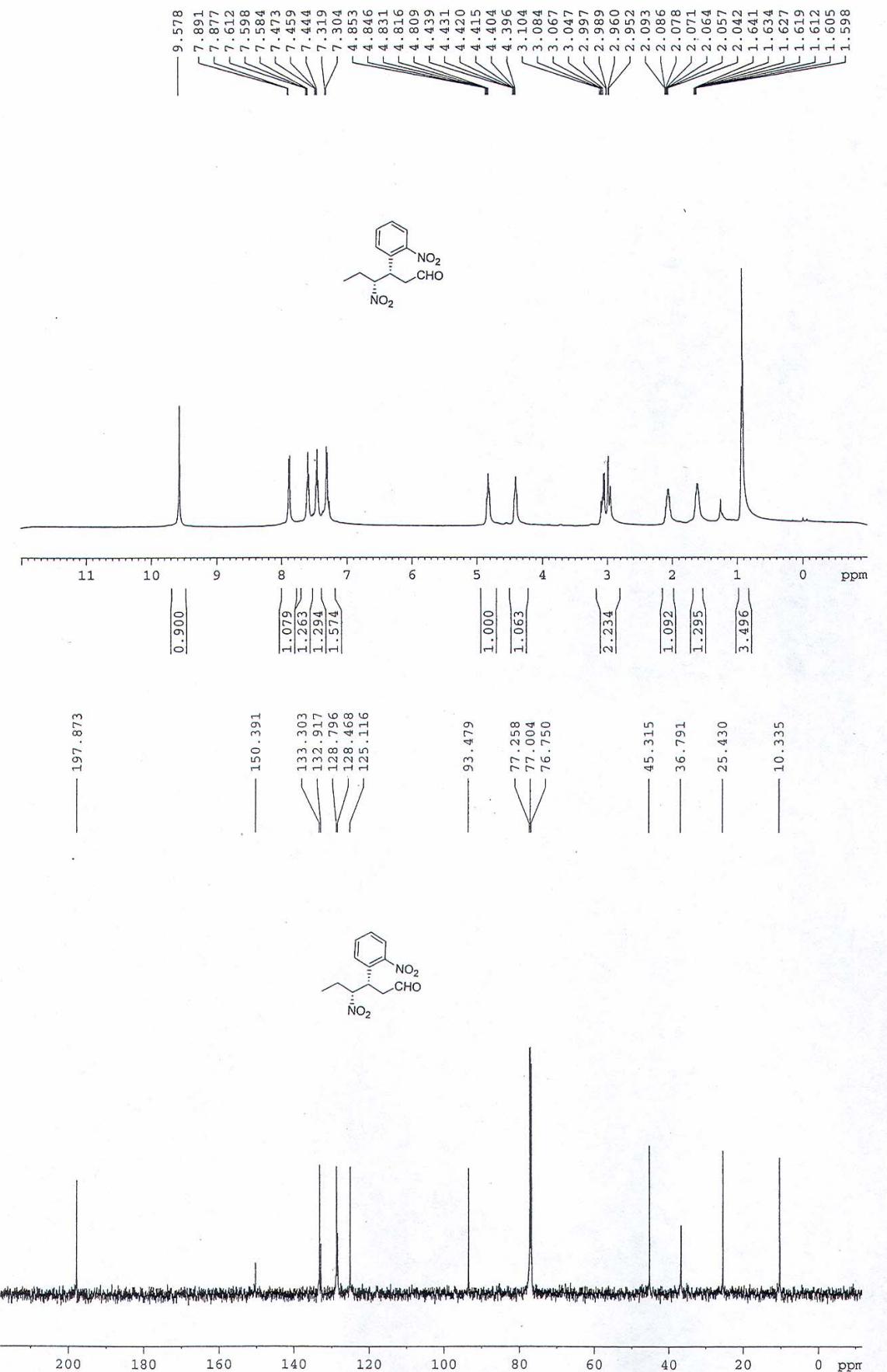


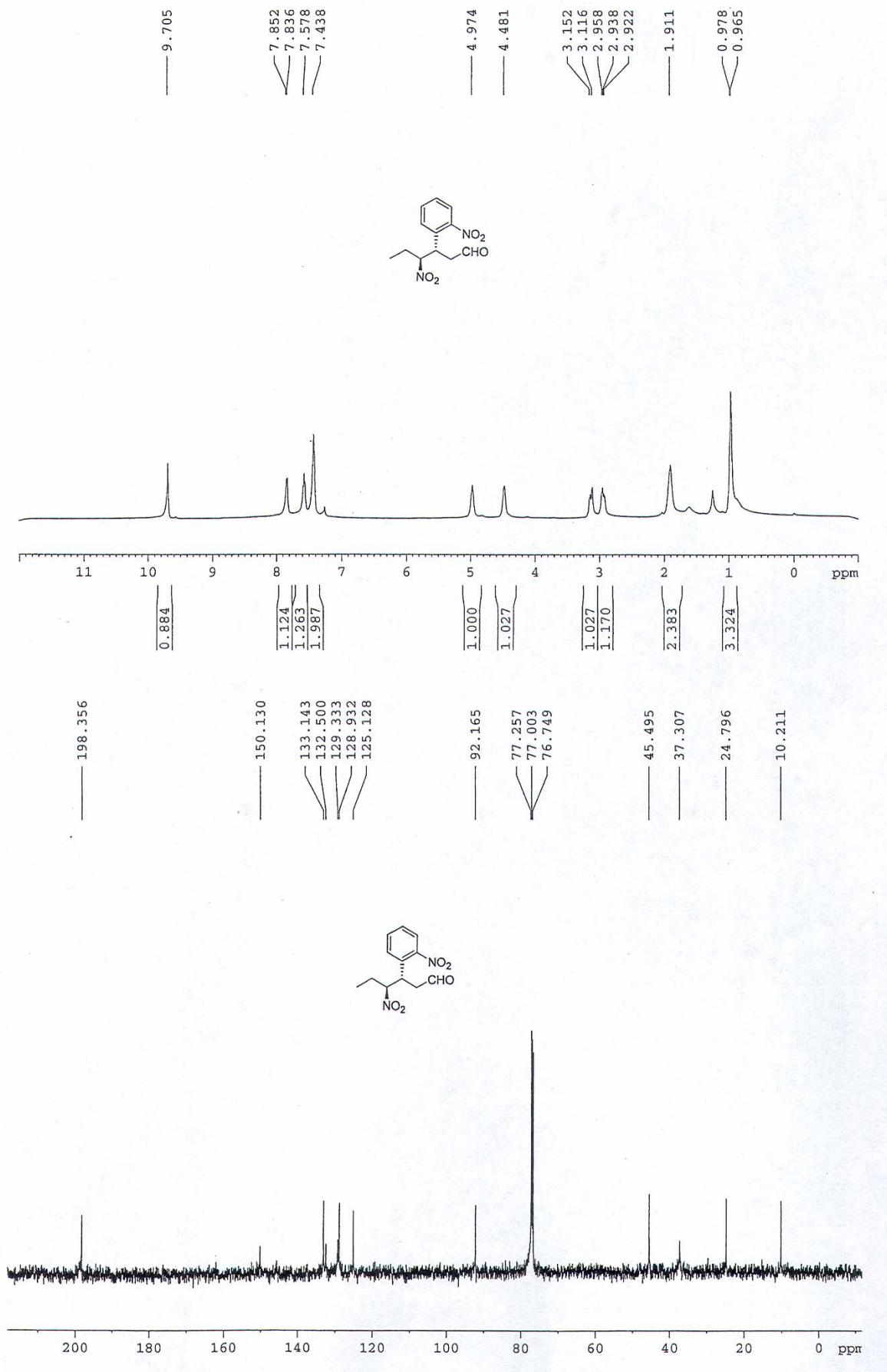






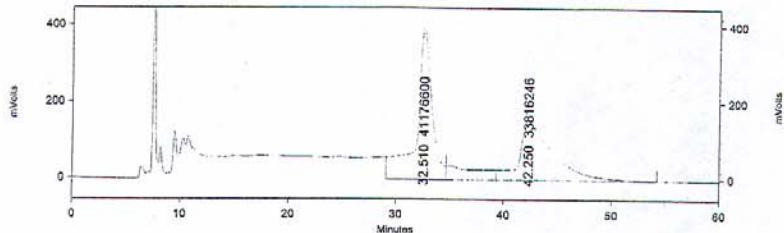
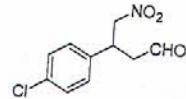






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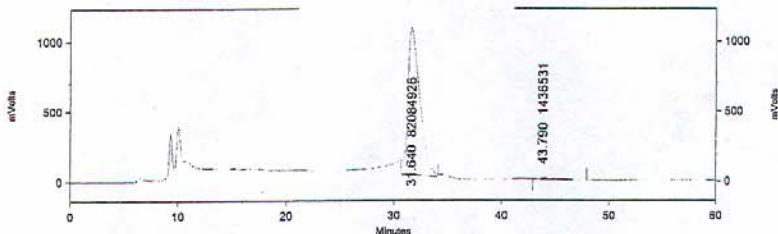
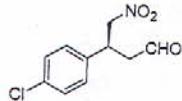


SPD-10Avp
Ch1-210nm Results

Pk #	RT	Area	Area %
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Totals		74992846	100.000

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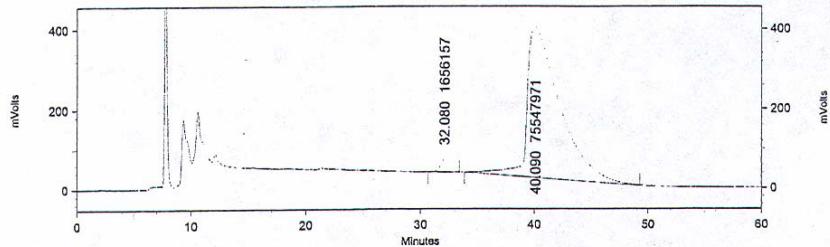
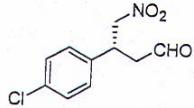


SPD-10Avp
Ch1-210nm Results

Pk #	RT	Area	Area %
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2	43.790	1436531	1.720
Totals		83521457	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls10100.net
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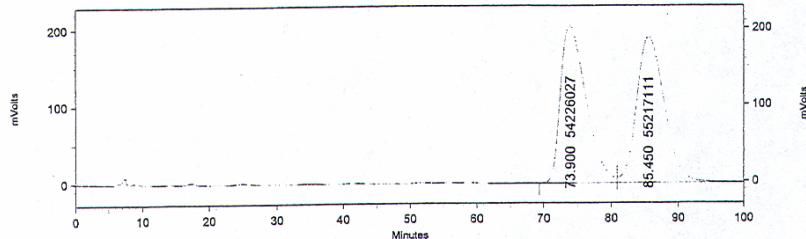
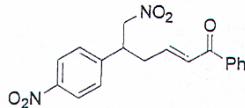


SPD-10Avp
Ch1-210nm Results

Pk #	RT	Area	Area %
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Totals		77204128	100.000

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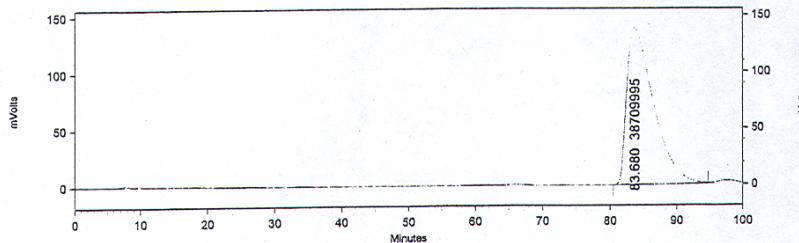
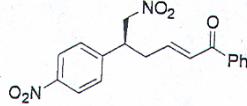
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SPD-10Avp Ch1-254nm Results Pk #	RT	Area	Area %
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Totals		109443138	100.000

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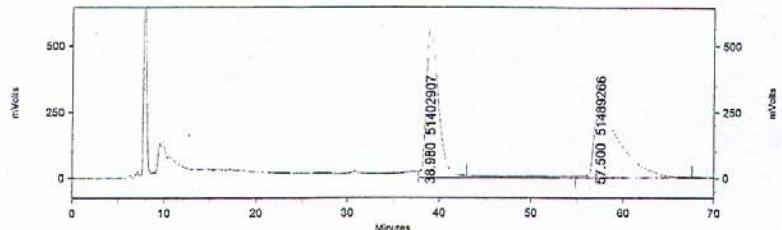
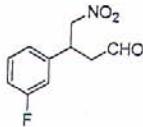
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SPD-10Avp Ch1-254nm Results Pk #	RT	Area	Area %
1	83.680	38709995	100.000
Totals		38709995	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1140-1.met
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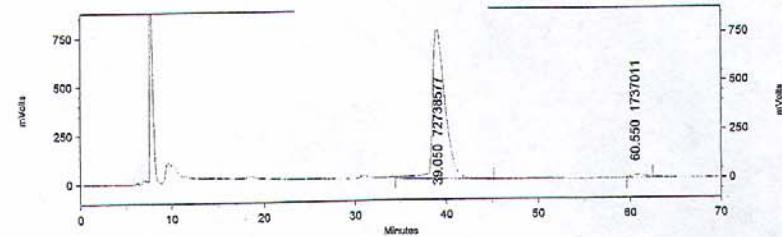
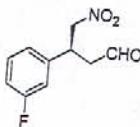


SPD-10Avp		Ch1-210nm Results	
Pk #	RT	Area	Area %

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2	57.500	51489266	50.042
Totals		102892173	100.000

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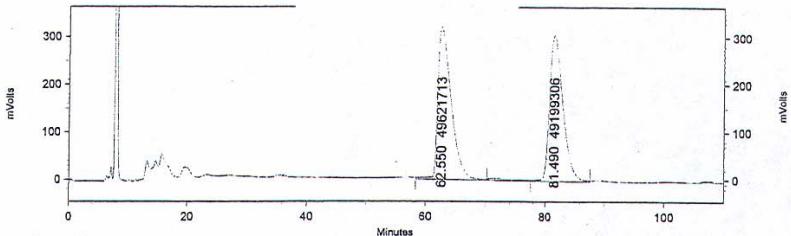
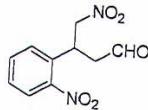


SPD-10Avp		Ch1-210nm Results	
Pk #	RT	Area	Area %

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2	60.550	1737011	2.332
Totals		74475588	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1119-1.met
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SPD-10Avp
Ch1-210nm Results
Pk #

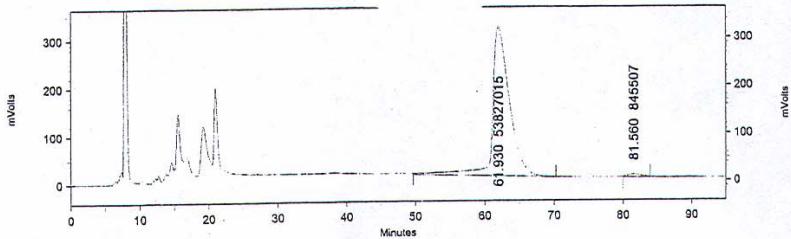
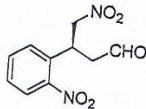
RT Area Area %

1	62.550	49621713	50.214
2	81.490	49199306	49.786

Totals		98821019	100.000
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Method Name: C:\EZStart\Projects\WeiWang\zls1133.met
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SPD-10Avp
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Pk #

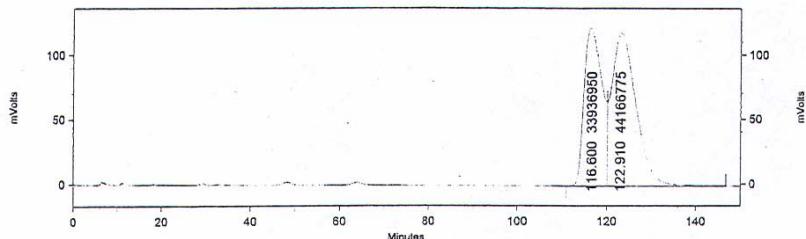
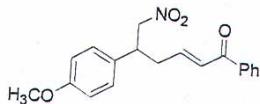
RT Area Area %

1	61.930	53827015	98.454
2	81.560	845507	1.546

Totals		54672522	100.000
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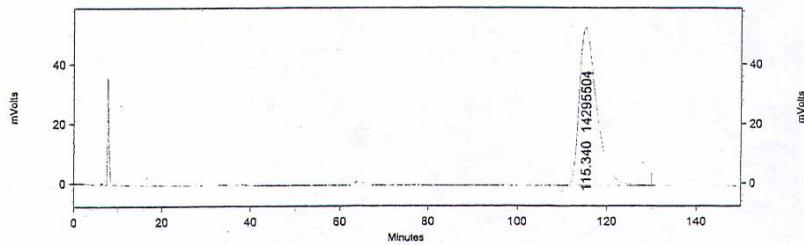
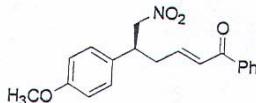
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Sample ID: zls1081



SPD-10Avp Ch1-254nm Results	Pk #	RT	Area	Area %
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	2	122.910	44166775	56.549
Totals			78103725	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1132.met
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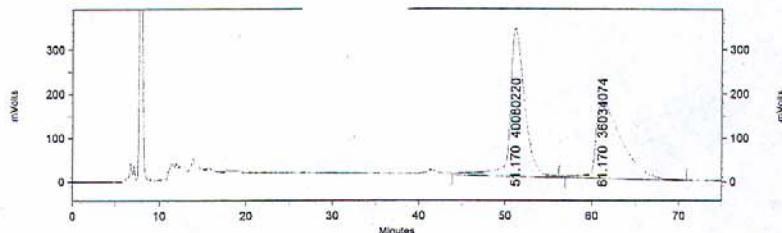
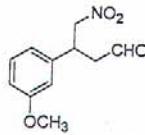


SPD-10Avp Ch1-254nm Results	Pk #	RT	Area	Area %
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Totals			14295504	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1147-2.met
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Date Acquired: 5/24/2007 10:19:52 PM Date Printed: 05/25/2007 02:26:59
AM

Sample ID: zls1147



SPD-10Avp
Ch1-210nm Results
Pk #

RT

Area

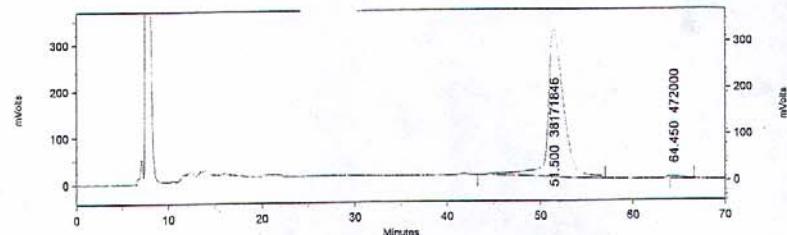
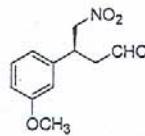
Area %

Pk #	RT	Area	Area %
1	51.170	40080220	52.658
2	61.170	36034074	47.342

Totals		76114294	100.000
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Method Name: C:\EZStart\Projects\WeiWang\zls1150.met
Data File: C:\EZStart\Projects\WeiWang\zls1150-1.dat
Date Acquired: 5/24/2007 9:08:13 PM Date Printed: 05/25/2007 02:27:49 AM
Sample ID: zls1150



SPD-10Avp
Ch1-210nm Results
Pk #

RT

Area

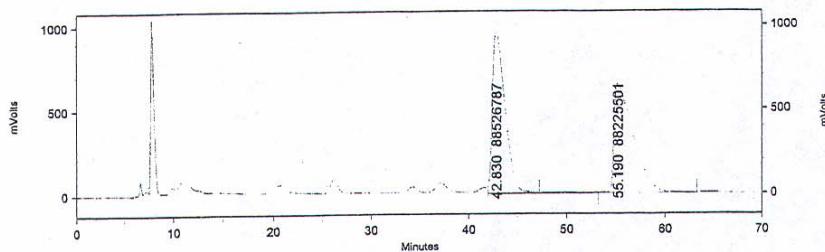
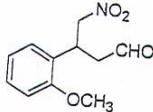
Area %

1	51.500	38171846	98.779
2	64.450	472000	1.221

Totals		38643846	100.000
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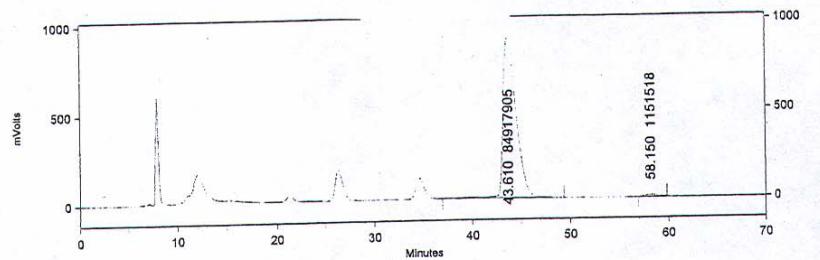
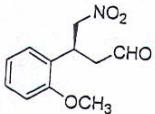
Method Name: C:\EZStart\Projects\WeiWang\zls1120.met
Data File: C:\EZStart\Projects\WeiWang\zls1120-2.dat
Date Acquired: 5/12/2007 10:55:13 PM Date Printed: 05/25/2007 01:52:23
AM
Sample ID: zls1120



SPD-10Avp Ch1-210nm Results			
Pk #	RT	Area	Area %
1	42.830	88526787	50.085
2	55.190	88225501	49.915
Totals		176752288	100.000

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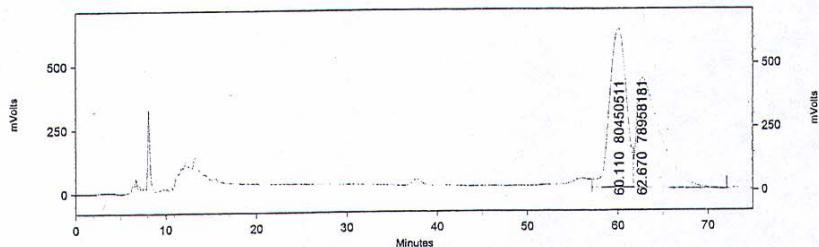
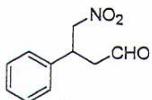
Method Name: C:\EZStart\Projects\WeiWang\zls1134-1.met
Data File: C:\EZStart\Projects\WeiWang\zls1134-2.dat
Date Acquired: 5/15/2007 4:25:57 PM Date Printed: 05/25/2007 01:53:01 AM
Sample ID: zls1134



SPD-10Avp Ch1-210nm Results			
Pk #	RT	Area	Area %
1	43.610	84917905	98.662
2	58.150	1151518	1.338
Totals		86069423	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1142-1.met
Data File: C:\EZStart\Projects\WeiWang\zls1142-3.dat
Date Acquired: 5/22/2007 9:57:13 PM Date Printed: 05/25/2007 02:17:07 AM
Sample ID: zls1142



SPD-10Avp
Ch1-210nm Results

Pk #

RT

Area

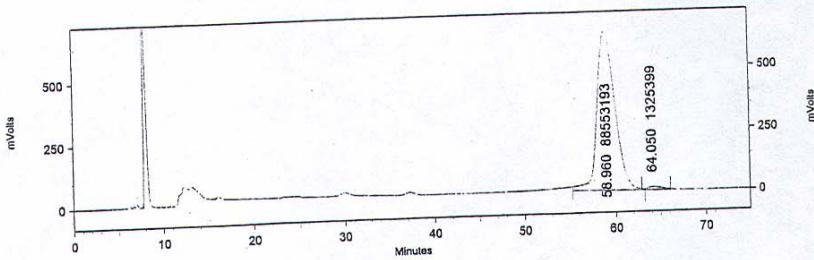
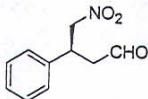
Area %

1	60.110	80450511	50.468
2	62.670	78958181	49.532

Totals		159408692	100.000
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Method Name: C:\EZStart\Projects\WeiWang\zls1143-1.met
Data File: C:\EZStart\Projects\WeiWang\zls1143-2.dat
Date Acquired: 5/22/2007 11:21:37 PM Date Printed: 05/25/2007 02:22:35
AM
Sample ID: zls1143



SPD-10Avp
Ch1-210nm Results

Pk #

RT

Area

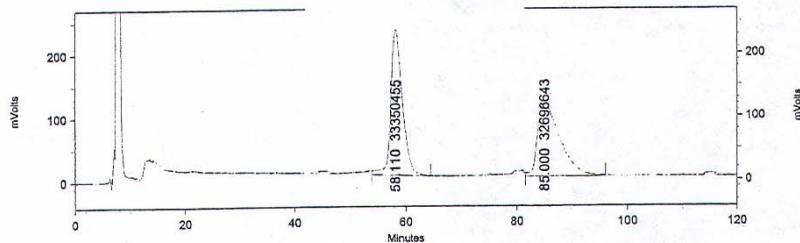
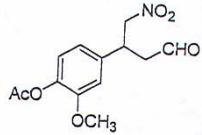
Area %

1	58.960	88553193	98.525
2	64.050	1325399	1.475

Totals		89878592	100.000
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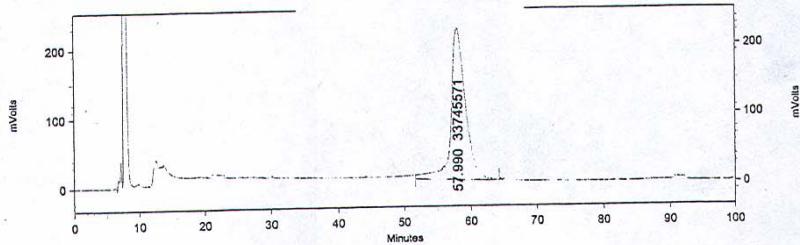
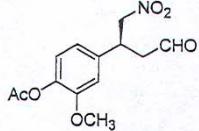
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Data File: C:\EZStart\Projects\WeiWang\zls1146-1.dat
Date Acquired: 5/23/2007 3:55:19 PM Date Printed: 05/25/2007 02:24:08 AM
Sample ID: zls1146



SPD-10Avp		Ch1-210nm Results	RT	Area	Area %
Pk #					
1		58.110	33350455	50.495	
2		85.000	32696643	49.505	
Totals			66047098	100.000	

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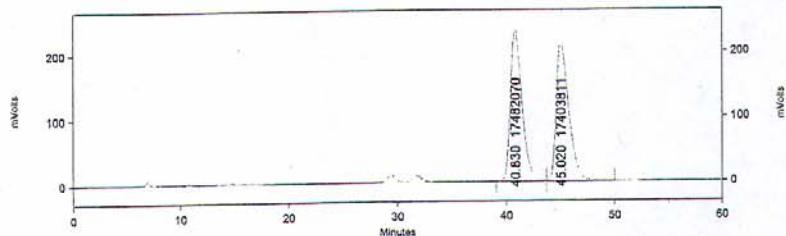
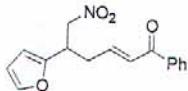
Method Name: C:\EZStart\Projects\WeiWang\zls1149.met
Data File: C:\EZStart\Projects\WeiWang\zls1149-1.dat
Date Acquired: 5/24/2007 7:23:14 PM Date Printed: 05/25/2007 02:25:05 AM
Sample ID: zls1149



SPD-10Avp		Ch1-210nm Results	RT	Area	Area %
Pk #					
1		57.990	33745571	100.000	
Totals			33745571	100.000	

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Method Name: C:\EZStart\Projects\WeiWang\zls1130.met
Data File: C:\EZStart\Projects\WeiWang\zls1130-1.dat
Date Acquired: 5/13/2007 9:27:50 PM Date Printed: 05/25/2007 01:54:40 AM
Sample ID: zls1130

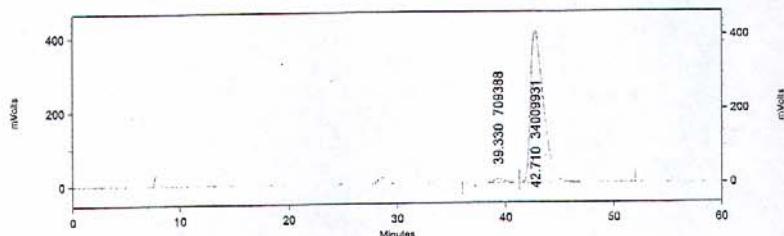
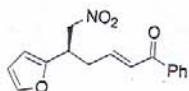


SPD-10Avp Ch1-254nm Results	Pk #	RT	Area	Area %
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1	40.830	17482070	50.112
2	45.020	17403811	49.888
Totals		34885881	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1135.met
Data File: C:\EZStart\Projects\WeiWang\zls1135-1.dat
Date Acquired: 5/16/2007 12:22:15 AM Date Printed: 05/25/2007 01:56:03
AM
Sample ID: zls1135



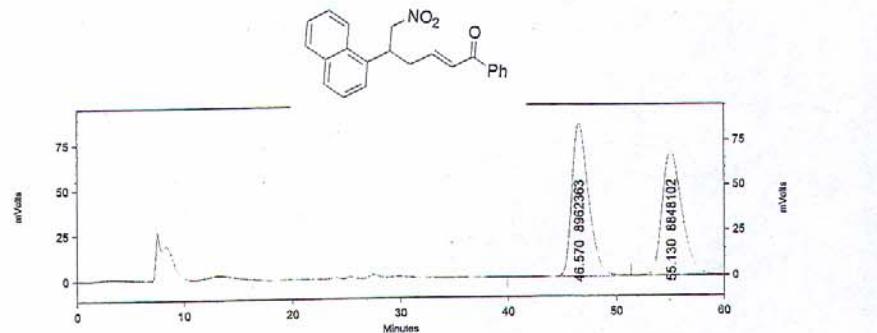
SPD-10Avp Ch1-254nm Results	Pk #	RT	Area	Area %
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1	39.330	709388	2.043
2	42.710	34009931	97.957

Totals		34719319	100.000
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Method Name: C:\EZStart\Projects\WeiWang\zls1148.met
Data File: C:\EZStart\Projects\WeiWang\zls1148-3.dat
Date Acquired: 5/24/2007 6:00:26 PM Date Printed: 05/25/2007 02:29:17 AM
Sample ID: zls1148

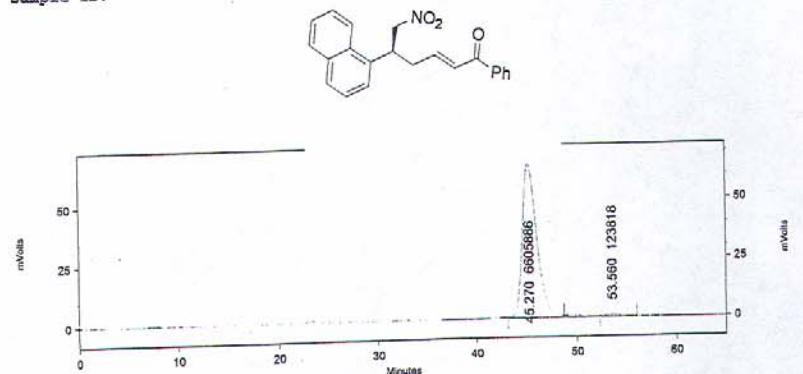


SPD-10Avp		Ch1-254nm Results	
Pk #	RT	Area	Area %

1	46.570	8962363	50.321
2	55.130	8848102	49.679
Totals		17810465	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1151.met
Data File: C:\EZStart\Projects\WeiWang\zls1151-1.dat
Date Acquired: 5/24/2007 11:38:11 PM Date Printed: 05/25/2007 02:29:54
AM
Sample ID: zls1151

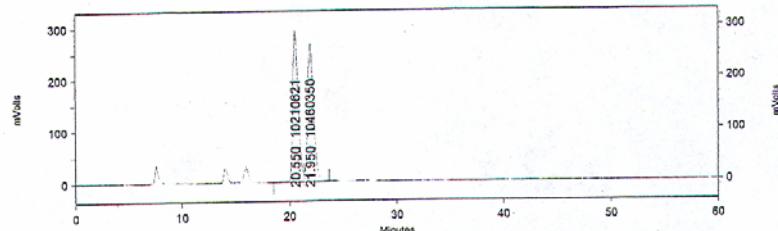
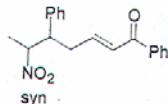


SPD-10Avp		Ch1-254nm Results	
Pk #	RT	Area	Area %

1	45.270	6605886	98.160
2	53.560	123818	1.840
Totals		6729704	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1143.met
Data File: C:\EZStart\Projects\WeiWang\zls1141-1-7.dat
Date Acquired: 5/20/2007 9:45:23 AM Date Printed: 05/25/2007 02:13:00 AM
Sample ID: zls1141

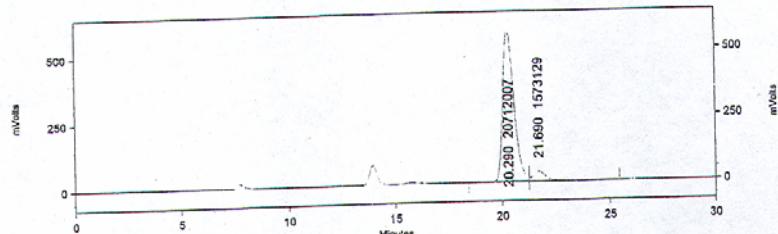
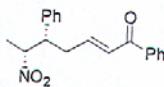


SPD-10Avp	Ch1-254nm Results	RT	Area	Area %
Pk #				
1	20.550	10210621	49.396	
2	21.950	10460350	50.604	

Totals		20670971	100.000
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Method Name: C:\EZstart\Projects\WeiWang\zls1143.met
Data File: C:\EZstart\Projects\WeiWang\zls1145-1.dat
Date Acquired: 5/20/2007 10:47:11 AM Date Printed: 05/25/2007 02:15:25
AM
Sample ID: zls1145

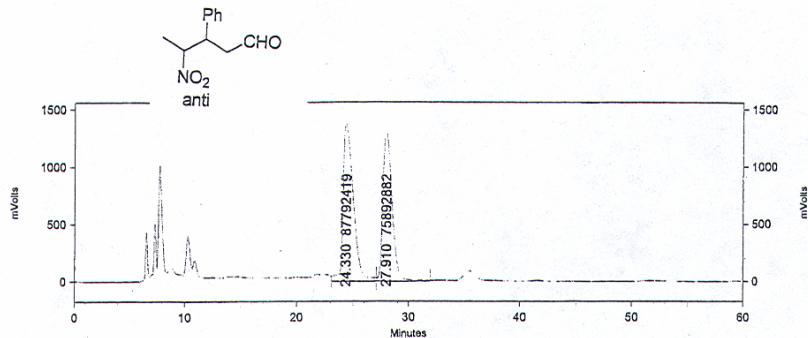


SPD-10Avp	Ch1-254nm Results	RT	Area	Area %
Pk #				
1	20.290	20712007	92.941	
2	21.690	1573129	7.059	

Totals		22285136	100.000
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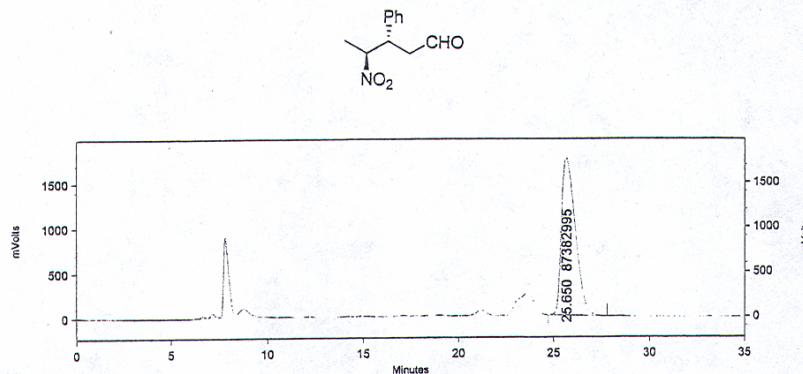
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Data File: C:\EZStart\Projects\WeiWang\zls1141-2.dat
Date Acquired: 5/19/2007 8:37:11 AM Date Printed: 05/25/2007 02:13:59 AM
Sample ID: zls1141



SPD-10Avp Ch1-210nm Results	Pk #	RT	Area	Area %
	1	24.330	87792419	53.635
	2	27.910	75892882	46.365
	Totals		163685301	100.000

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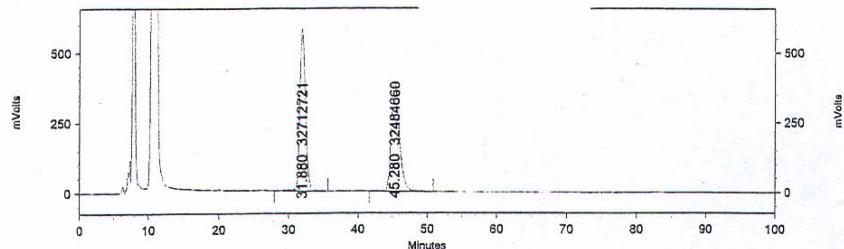
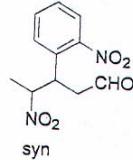
Method Name: C:\EZStart\Projects\WeiWang\zls1145.met
Data File: C:\EZStart\Projects\WeiWang\zls1145-2.dat
Date Acquired: 5/20/2007 12:58:38 AM Date Printed: 05/25/2007 02:15:58
AM
Sample ID: zls1145



SPD-10Avp Ch1-210nm Results	Pk #	RT	Area	Area %
	1	25.650	87382995	100.000
	Totals		87382995	100.000

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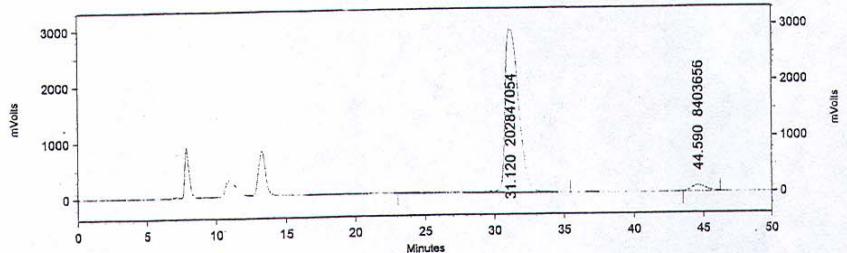
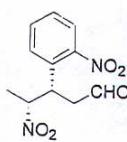
Method Name: C:\EZStart\Projects\WeiWang\zls1126.met
Data File: C:\EZStart\Projects\WeiWang\zls1126-1.dat
Date Acquired: 5/13/2007 5:59:06 PM Date Printed: 05/25/2007 04:15:33 PM
Sample ID: zls1126



SPD-10Avp Ch1-210nm Results Pk #	RT	Area	Area %
1	31.880	32712721	50.175
2	45.280	32484660	49.825
Totals		65197381	100.000

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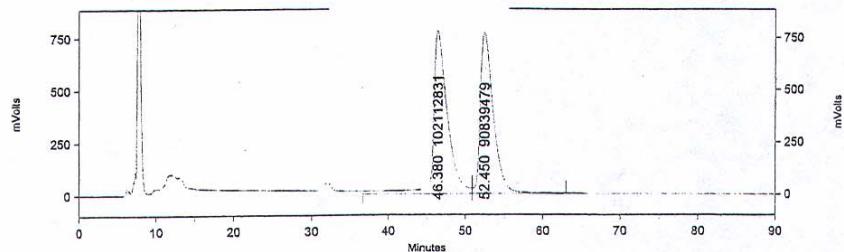
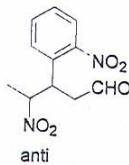
Method Name: C:\EZStart\Projects\WeiWang\zls1137.met
Data File: C:\EZStart\Projects\WeiWang\zls1137-1.dat
Date Acquired: 5/16/2007 12:47:19 PM Date Printed: 05/25/2007 04:17:54
PM
Sample ID: zls1137



SPD-10Avp Ch1-210nm Results Pk #	RT	Area	Area %
1	31.120	202847054	96.022
2	44.590	8403656	3.978
Totals		211250710	100.000

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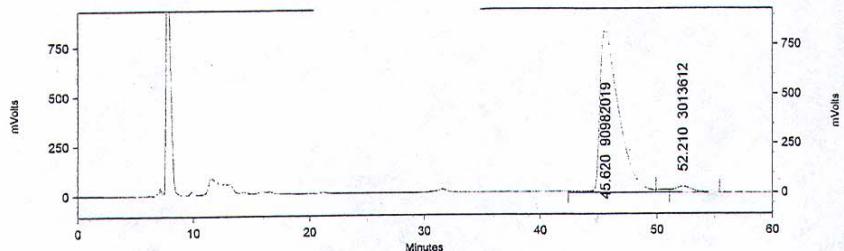
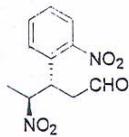
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Date Acquired: 5/13/2007 7:40:53 PM Date Printed: 05/25/2007 04:17:15 PM
Sample ID: zls1126



SPD-10Avp Ch1-210nm Results			
Pk #	RT	Area	Area %
1	46.380	102112831	52.921
2	52.450	90839479	47.079
Totals		192952310	100.000

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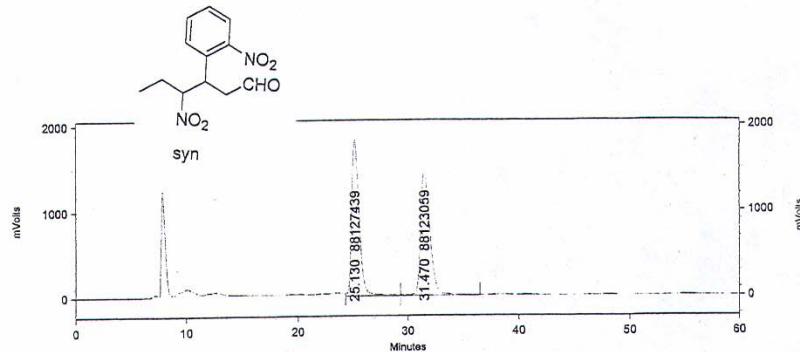
Method Name: C:\EZStart\Projects\WeiWang\zls1137-2.met
Data File: C:\EZStart\Projects\WeiWang\zls1137-2.dat
Date Acquired: 5/16/2007 1:42:05 PM Date Printed: 05/25/2007 04:19:10 PM
Sample ID: zls1137



SPD-10Avp Ch1-210nm Results			
Pk #	RT	Area	Area %
1	45.620	90982019	96.794
2	52.210	3013612	3.206
Totals		93995631	100.000

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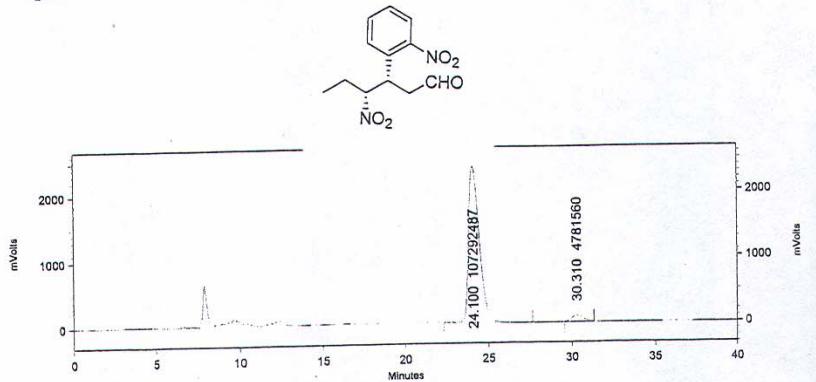
Method Name: C:\EZStart\Projects\WeiWang\zls1127.met
Data File: C:\EZStart\Projects\WeiWang\zls1127-1.dat
Date Acquired: 5/14/2007 2:25:23 PM Date Printed: 05/25/2007 02:03:19 AM
Sample ID: zls1127



SPD-10Avp Ch1-210nm Results Pk #	RT	Area	Area %
1	25.130	88127439	50.001
2	31.470	88123059	49.999
Totals		176250498	100.000

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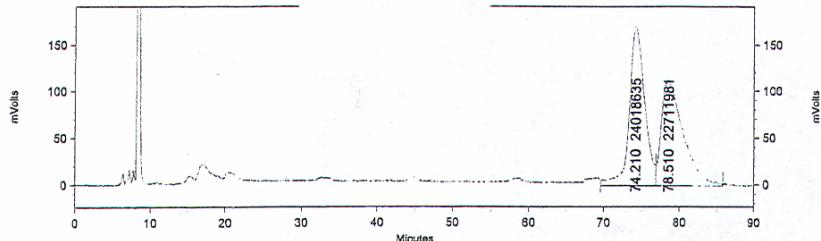
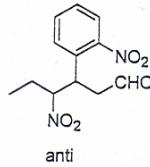
Method Name: C:\EZStart\Projects\WeiWang\zls1138.met
Data File: C:\EZStart\Projects\WeiWang\zls1138-2.dat
Date Acquired: 5/17/2007 10:32:54 AM Date Printed: 05/25/2007 02:08:24
AM
Sample ID: zls1138



SPD-10Avp Ch1-210nm Results Pk #	RT	Area	Area %
1	24.100	107292487	95.734
2	30.310	4781560	4.266
Totals		112074047	100.000

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Method Name: C:\EZStart\Projects\WeiWang\zls1127.met
Data File: C:\EZStart\Projects\WeiWang\zls1127-3.dat
Date Acquired: 5/14/2007 4:23:31 PM Date Printed: 05/25/2007 02:06:31 AM
Sample ID: zls1127



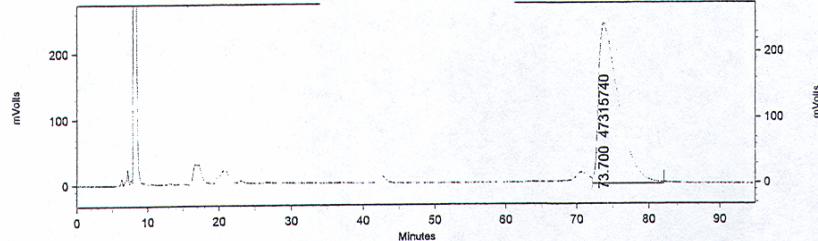
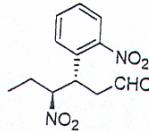
SPD-10Avp
Ch1-210nm Results

Pk #	RT	Area	Area %
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Totals			
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Method Name: C:\EZStart\Projects\WeiWang\zls1138-3.met
Data File: C:\EZStart\Projects\WeiWang\zls1138-3.dat
Date Acquired: 5/17/2007 11:31:15 AM Date Printed: 05/25/2007 02:09:31 AM
Sample ID: zls1138



SPD-10Avp
Ch1-210nm Results

Pk #	RT	Area	Area %
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1	73.700	47315740	100.000
Totals		47315740	100.000