

## Supporting Information

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## ***Supporting Information***

### **Organocatalytic, Enantioselective Conjugate Addition of Nitroalkanes to Nitroolefins**

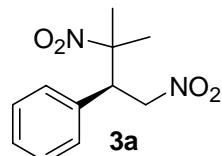
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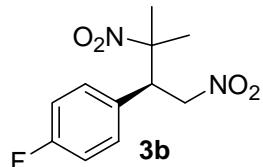
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**General Information:** Commercial reagents were used as received, unless otherwise stated. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with fluorescence F<sub>254</sub> indicator were used for thin-layer chromatography (TLC) analysis. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Advance 500, and tetramethylsilane (TMS) was used as a reference. Data for <sup>1</sup>H are reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

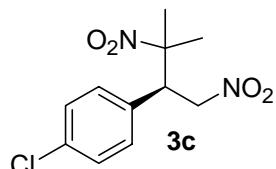
**Typical Procedure for Michael-type Addition Reaction of nitroalkanes:** Catalyst **I** (7 mg, 0.02 mmol) was added to a vial containing 2-nitro-propane (1 mL, 11.2 mmol) and *trans*- $\beta$ -nitrostyrene (30 mg, 0.20 mmol) at 0 °C. After 6d of stirring, TLC analysis indicated completion of the reaction. The reaction mixture was concentrated *in vacuo*. The residue was purified by flash silica gel chromatography (ethyl acetate/hexane=1:20 to 1:10) to afford 38 mg (79% yield) of the adduct as a clear oil.



**(2-Methyl-2-nitro-1-nitromethyl-propyl)-benzene (3a)**<sup>[1]</sup> (Table 2, entry 1): The title compound was prepared according the typical procedure, as described above in 79% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.32-7.24 (m, 3H; Ar), 7.17-7.07 (m, 2H; Ar), 4.91 (dd, <sup>3</sup>J(H,H) = 13.0 Hz, <sup>3</sup>J(H,H) = 11.5 Hz, 1H; CH), 4.72 (dd, <sup>3</sup>J(H,H) = 13.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 4.07 (dd, <sup>3</sup>J(H,H) = 11.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 1.52 (s, 3H; CH<sub>3</sub>), 1.51 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 133.6, 129.1, 129.0, 128.9, 89.4, 75.9, 51.6, 26.2, 23.0; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 18.5 min, t<sub>major</sub> = 19.2 min, ee = 78%;  $[\alpha]^{25}_D$  (major) = +15.7 (c = 1.2 in CHCl<sub>3</sub>).

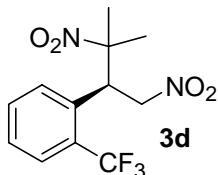


**1-Fluoro-4-(2-methyl-2-nitro-1-nitromethyl-propyl)-benzene (3b)** (Table 2, entry 2): The title compound was prepared according the typical procedure, as described above in 76% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.24-7.12 (m, 2H; Ar), 7.11-7.02 (m, 2H; Ar), 4.92 (dd, <sup>3</sup>J(H,H) = 13.5 Hz, <sup>3</sup>J(H,H) = 11.5 Hz, 1H; CH), 4.80 (dd, <sup>3</sup>J(H,H) = 13.5 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 4.11 (dd, <sup>3</sup>J(H,H) = 11.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 1.62 (s, 3H; CH<sub>3</sub>), 1.58 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 130.6, 130.5, 129.4, 116.3, 116.1, 89.6, 75.9, 50.9, 25.9, 23.2; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 18.5 min, t<sub>major</sub> = 19.8 min, ee = 73%;  $[\alpha]^{25}_D$  (major) = +9.5 (c = 0.8 in CHCl<sub>3</sub>).

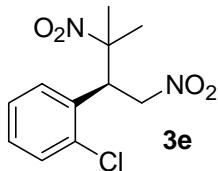


**1-Chloro-4-(2-methyl-2-nitro-1-nitromethyl-propyl)-benzene (3c)** (Table 2, entry 3): The title compound was prepared according the typical procedure, as described above in 70% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.27 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; Ar), 7.06 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; Ar), 4.86 (dd, <sup>3</sup>J(H,H) = 13.5 Hz, <sup>3</sup>J(H,H) = 11.5 Hz, 1H; CH), 4.74 (dd, <sup>3</sup>J(H,H) = 13.5 Hz, <sup>2</sup>J(H,H) = 4.0

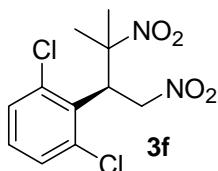
Hz, 1H; CH<sub>2</sub>), 4.01 (dd, <sup>3</sup>J(H,H) = 11.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 1.54 (s, 3H; CH<sub>3</sub>), 1.50 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS): δ = 135.2, 132.1, 130.1, 129.4, 89.3, 75.7, 51.1, 26.0, 23.2; HPLC (Chiralcel OD-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min, λ = 254 nm): t<sub>minor</sub> = 19.6 min, t<sub>major</sub> = 20.5 min, ee = 83%; [α]<sup>25</sup><sub>D</sub> (major) = +18.4 (c = 1.1 in CHCl<sub>3</sub>).



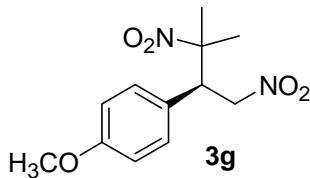
**1-(2-Methyl-2-nitro-1-nitromethyl-propyl)-2-trifluoromethyl-benzene (3d)** (Table 2, entry 4): The title compound was prepared according the typical procedure, as described above in 78% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ = 7.67 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; Ar), 7.55-7.48 (m, 1H; Ar), 7.46-7.38 (m, 1H; Ar), 7.18 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; Ar), 5.09 (dd, <sup>3</sup>J(H,H) = 12.5 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 4.74 (dd, <sup>3</sup>J(H,H) = 12.5 Hz, <sup>3</sup>J(H,H) = 9.5 Hz, 1H; CH), 4.01 (dd, <sup>3</sup>J(H,H) = 9.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 1.66 (s, 3H; CH<sub>3</sub>), 1.42 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS): δ = 133.5, 132.7, 130.3, 130.6, 129.1, 127.7, 127.3, 124.9, 122.7, 89.7, 76.7, 46.3, 27.0, 23.8; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min, λ = 254 nm): t<sub>minor</sub> = 14.0 min, t<sub>major</sub> = 12.6 min, ee = 83%; [α]<sup>25</sup><sub>D</sub> (major) = +20.3 (c = 0.8 in CHCl<sub>3</sub>).



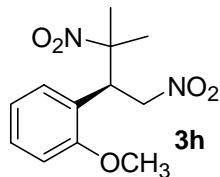
**1-Chloro-2-(2-methyl-2-nitro-1-nitromethyl-propyl)-benzene (3e)** (Table 2, entry 5): The title compound was prepared according the typical procedure, as described above in 73% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ = 7.38 (dd, <sup>3</sup>J(H,H) = 6.0 Hz, <sup>4</sup>J(H,H) = 4.0 Hz, 1H; Ar), 7.27-7.18 (m, 2H; Ar), 7.05 (dd, <sup>3</sup>J(H,H) = 6.0 Hz, <sup>4</sup>J(H,H) = 3.5 Hz, 1H; Ar), 4.94-4.86 (m, 2H; CH<sub>2</sub>, CH), 4.86-4.78 (m, 1H; CH<sub>2</sub>), 1.66 (s, 3H; CH<sub>3</sub>), 1.49 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS): δ = 136.1, 132.2, 130.5, 130.0, 127.7, 127.3, 89.9, 76.1, 45.8, 26.3, 22.8; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 40/60, flow rate 0.5 mL/min, λ = 254 nm): t<sub>minor</sub> = 17.2 min, t<sub>major</sub> = 16.1 min, ee = 81%; [α]<sup>25</sup><sub>D</sub> (major) = +18.8 (c = 1.6 in CHCl<sub>3</sub>).



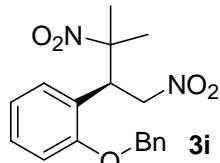
**1,3-Dichloro-2-(2-methyl-2-nitro-1-nitromethyl-propyl)-benzene (3f)** (Table 2, entry 6): The title compound was prepared according the typical procedure, as described above in 75% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ = 7.35 (dd, <sup>3</sup>J(H,H) = 9.6 Hz, <sup>4</sup>J(H,H) = 1.0 Hz, 1H; Ar), 7.25 (dd, <sup>3</sup>J(H,H) = 9.6 Hz, <sup>4</sup>J(H,H) = 1.0 Hz, 1H; Ar), 7.18-7.12 (m, 1H; Ar), 5.41 (dd, <sup>3</sup>J(H,H) = 14.0 Hz, <sup>3</sup>J(H,H) = 9.0 Hz, 1H; CH), 4.74 (dd, <sup>3</sup>J(H,H) = 9.0 Hz, <sup>2</sup>J(H,H) = 4.5 Hz, 1H; CH<sub>2</sub>), 4.01 (dd, <sup>3</sup>J(H,H) = 14.0 Hz, <sup>2</sup>J(H,H) = 4.5 Hz, 1H; CH<sub>2</sub>), 1.66 (s, 3H; CH<sub>3</sub>), 1.60 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS): δ = 138.6, 134.9, 130.9, 130.8, 130.3, 129.4, 88.8, 74.0, 47.2, 27.2, 24.5; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min, λ = 254 nm): t<sub>minor</sub> = 15.3 min, t<sub>major</sub> = 16.6 min, ee = 80%; [α]<sup>25</sup><sub>D</sub> (major) = +15.9 (c = 1.2 in CHCl<sub>3</sub>).



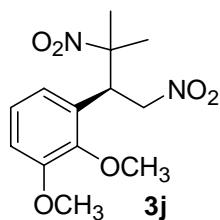
**1-Methoxy-4-(2-methyl-2-nitro-1-nitromethyl-propyl)-benzene (3g)** (Table 2, entry 7): The title compound was prepared according the typical procedure, as described above in 78% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.09 (d, <sup>3</sup>J(H,H) = 9.0 Hz, 2H; Ar), 6.86 (d, <sup>3</sup>J(H,H) = 8.5 Hz, 2H; Ar), 4.93 (dd, <sup>3</sup>J(H,H) = 13.0 Hz, <sup>3</sup>J(H,H) = 11.5 Hz, 1H; CH), 4.70 (dd, <sup>3</sup>J(H,H) = 13.5 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 4.02 (dd, <sup>3</sup>J(H,H) = 11.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 3.78 (s, 3H; OCH<sub>3</sub>), 1.62 (s, 3H; CH<sub>3</sub>), 1.59 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 159.9, 129.9, 125.3, 114.4, 89.7, 76.0, 55.2, 51.0, 26.0, 23.0; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 27.6 min, t<sub>major</sub> = 25.5 min, ee = 67%;  $[\alpha]^{25}_D$  (major) = +13.3 ( $c$  = 1.6 in CHCl<sub>3</sub>).



**1-Methoxy-2-(2-methyl-2-nitro-1-nitromethyl-propyl)-benzene (3h)** (Table 2, entry 8): The title compound was prepared according the typical procedure, as described above in 73% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.27-7.18 (m, 1H; Ar), 7.02-6.97 (m, 1H; Ar), 6.90-6.81 (m, 2H; Ar), 5.01-4.90 (m, 1H; CH), 4.81 (dd, <sup>3</sup>J(H,H) = 13.5 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 4.70-4.50 (m, 1H; CH<sub>2</sub>), 3.76 (s, 3H; OCH<sub>3</sub>), 1.57 (s, 3H; CH<sub>3</sub>), 1.45 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 157.8, 130.0, 122.5, 121.0, 111.5, 89.9, 75.7, 55.5, 26.3, 23.1; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 17.0 min, t<sub>major</sub> = 15.9 min, ee = 84%;  $[\alpha]^{25}_D$  (major) = +19.2 ( $c$  = 1.5 in CHCl<sub>3</sub>).

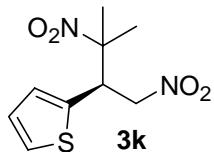


**1-Benzylxy-2-(2-methyl-2-nitro-1-nitromethyl-propyl)-benzene (3i)** (Table 2, entry 9): The title compound was prepared according the typical procedure, as described above in 80% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.40-7.25 (m, 4H; Ar), 7.22-7.05 (m, 1H; Ar), 7.02-6.96 (m, 1H; Ar), 6.91-6.80 (m, 2H; Ar), 5.08-4.88 (m, 1H; CH), 5.00 (s, 2H; OCH<sub>2</sub>), 4.77-4.70 (m, 2H; CH<sub>2</sub>), 1.52 (s, 3H; CH<sub>3</sub>), 1.42 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 159.2, 136.5, 129.9, 128.6, 128.1, 127.5, 125.6, 115.3, 89.7, 76.0, 70.1, 51.0, 26.1, 23.0; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 16.8 min, t<sub>major</sub> = 16.1 min, ee = 77 %;  $[\alpha]^{25}_D$  (major) = +17.5 ( $c$  = 1.5 in CHCl<sub>3</sub>).

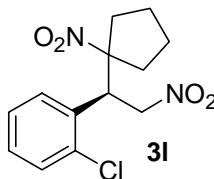


**1,2-Dimethoxy-3-(2-methyl-2-nitro-1-nitromethyl-propyl)-benzene (3j)** (Table 2, entry 10): The title compound was prepared according the typical procedure, as described above in 78% yield. <sup>1</sup>H

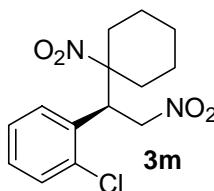
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.01-6.92 (m, 1H; Ar), 6.95 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 1H; Ar), 6.59 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 1H; Ar), 4.91 (dd, <sup>3</sup>J(H,H) = 13.0 Hz, <sup>3</sup>J(H,H) = 11.5 Hz, 1H; CH), 4.77 (dd, <sup>3</sup>J(H,H) = 13.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 4.72-4.61 (m, 1H; CH<sub>2</sub>), 1.56 (s, 3H; CH<sub>3</sub>), 1.43 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 152.8, 148.0, 127.6, 124.3, 118.4, 112.6, 76.1, 60.8, 55.6, 26.5, 22.5; HPLC (Chiralcel OD-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 16.3 min, t<sub>major</sub> = 15.3 min, ee = 85%;  $[\alpha]^{25}_D$  (major) = +22.1 (c = 1.1 in CHCl<sub>3</sub>).



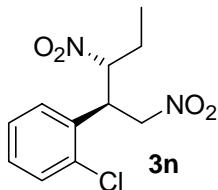
**2-(2-Methyl-2-nitro-1-nitromethyl-propyl)-thiophene (3k)** (Table 2, entry 11): The title compound was prepared according the typical procedure, as described above in 78% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.27-7.22 (m, 1H; Ar), 6.94-6.89 (m, 2H; Ar), 4.80 (dd, <sup>3</sup>J(H,H) = 13.0 Hz, <sup>3</sup>J(H,H) = 11.0 Hz, 1H; CH), 4.69 (dd, <sup>3</sup>J(H,H) = 13.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 4.46 (dd, <sup>3</sup>J(H,H) = 11.0 Hz, <sup>2</sup>J(H,H) = 3.5 Hz, 1H; CH<sub>2</sub>), 1.61 (s, 3H; CH<sub>3</sub>), 1.57 (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 135.5, 128.4, 127.2, 126.4, 89.6, 76.7, 47.2, 26.1, 23.0; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 19.7 min, t<sub>major</sub> = 20.6 min, ee = 70%;  $[\alpha]^{25}_D$  (major) = +11.8 (c = 1.7 in CHCl<sub>3</sub>).



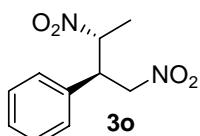
**1-Chloro-2-[2-nitro-1-(1-nitro-cyclopentyl)-ethyl]-benzene (3l)** (Scheme 1): The title compound was prepared according the typical procedure, as described above in 61% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.40-7.34 (m, 1H; Ar), 7.25-7.15 (m, 2H; Ar), 7.02-6.95 (m, 1H; Ar), 5.02-4.87 (m, 1H; CH<sub>2</sub>, CH), 4.72 (dd, <sup>3</sup>J(H,H) = 10.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 2.70-2.57 (m, 1H; CH<sub>2</sub>), 2.42-2.30 (m, 1H; CH<sub>2</sub>), 2.08-1.87 (m, 2H; CH<sub>2</sub>), 1.85-1.53 (m, 4H; CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 135.3, 132.6, 130.4, 130.0, 127.7, 127.0, 102.2, 76.7, 45.3, 38.1, 33.5, 23.1, 22.8; HPLC (Chiralpak AS-H, ethanol/hexane = 40/60, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 37.1 min, t<sub>major</sub> = 17.2 min, ee = 84%;  $[\alpha]^{25}_D$  (major) = +33.5 (c = 1.3 in CHCl<sub>3</sub>).



**1-Chloro-2-[2-nitro-1-(1-nitro-cyclohexyl)-ethyl]-benzene (3m)** (Scheme 1): The title compound was prepared according the typical procedure, as described above in 80% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.42-7.34 (m, 1H; Ar), 7.28-7.17 (m, 2H; Ar), 7.00-6.91 (m, 1H; Ar), 4.96 (dd, <sup>3</sup>J(H,H) = 13.5 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 4.74 (dd, <sup>3</sup>J(H,H) = 13.5 Hz, <sup>3</sup>J(H,H) = 11.0 Hz, 1H; CH), 4.62 (dd, <sup>3</sup>J(H,H) = 11.0 Hz, <sup>2</sup>J(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 2.77-2.67 (m, 1H; CH<sub>2</sub>), 2.15-2.03 (m, 1H; CH<sub>2</sub>), 1.75-1.50 (m, 5H; CH<sub>2</sub>), 1.35-1.05 (m, 3H; CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 136.0, 131.9, 130.3, 129.9, 127.5, 127.4, 93.0, 75.6, 46.6, 34.2, 31.1, 24.1, 22.1, 21.8; HPLC (Chiralpak AS-H, ethanol/hexane = 40/60, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): t<sub>minor</sub> = 41.6 min, t<sub>major</sub> = 18.2 min, ee = 87%;  $[\alpha]^{25}_D$  (major) = +27.3 (c = 0.6 in CHCl<sub>3</sub>).



**1-Chloro-2-(2-nitro-1-nitromethyl-butyl)-benzene (3n)** (Scheme 1): The title compound was prepared according to the typical procedure, as described above in 85% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS) (major isomer):  $\delta$  = 7.49-7.42 (m, 1H; Ar), 7.34-7.25 (m, 2H; Ar), 7.22-7.14 (m, 1H; Ar), 5.08-4.95 (m, 1H;  $\text{CH}_2$ ), 4.94-4.83 (m, 1H;  $\text{CH}_2$ ), 4.78-4.55 (m, 2H; CH), 2.07-1.93 (m, 2H;  $\text{CH}_2$ ), 0.96 (t,  $^3J(\text{H},\text{H})$  = 7.5 Hz, 3H;  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 134.2, 131.9, 130.9, 130.1, 127.9, 127.6, 89.8, 75.0, 25.4, 10.1; HPLC (Chiralcel OJ-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm): (major isomer)  $t_{\text{minor}}$  = 40.1 min,  $t_{\text{major}}$  = 29.3 min, ee = 81%; (minor isomer)  $t_{\text{minor}}$  = 61.2 min,  $t_{\text{major}}$  = 41.23 min, ee = 74%; dr = 2:1.



**(2-Nitro-1-nitromethyl-propyl)-benzene (3o)** (Scheme 1): The title compound was prepared according to the typical procedure, as described above in 84% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS) (major isomer):  $\delta$  = 7.40-7.25 (m, 3H; Ar), 7.22-7.10 (m 2H; Ar), 5.10-4.86 (m, 2H; CH,  $\text{CH}_2$ ), 4.85-4.76 (m, 1H; CH), 4.10-3.97 (m, 1H;  $\text{CH}_2$ ), 1.58 (d,  $^3J(\text{H},\text{H})$  = 6.5 Hz, 3H;  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS) (major isomer):  $\delta$  = 133.4, 129.2, 129.0, 127.9, 84.0, 76.0, 47.3, 16.7; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm):  $t_{\text{minor}}$  = 24.1 min,  $t_{\text{major}}$  = 15.1 min, ee = 74%;  $[\alpha]^{25}_D$  (major) = +15.3 ( $c$  = 1.6 in  $\text{CH}_2\text{Cl}_2$ ) (lit.<sup>[2]</sup>:  $[\alpha]^{25}_D$  = +21.6 ( $c$  = 1.12 in  $\text{CH}_2\text{Cl}_2$ )).

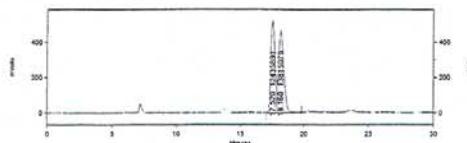
Data for Minor isomer:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS) (minor isomer):  $\delta$  = 7.45-7.27 (m, 3H; Ar), 7.22-7.15 (m 2H; Ar), 4.91-4.70 (m, 2H; CH,  $\text{CH}_2$ ), 4.70-4.60 (m, 1H; CH), 4.10-3.97 (m, 1H;  $\text{CH}_2$ ), 1.40 (d,  $^3J(\text{H},\text{H})$  = 7.0 Hz, 3H;  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS) (minor isomer):  $\delta$  = 133.7, 129.5, 129.1, 129.1, 128.0, 84.6, 76.7, 47.8, 17.9; HPLC (Chiralcel OJ-H, *i*-propanol/hexane = 30/70, flow rate 0.5 mL/min,  $\lambda$  = 254 nm):  $t_{\text{minor}}$  = 39.5 min,  $t_{\text{major}}$  = 31.4 min, ee = 65%;  $[\alpha]^{25}_D$  (major) = +10.1 ( $c$  = 1.0 in  $\text{CH}_2\text{Cl}_2$ ).

## References

- [1] C. Michael, H. Roland, J. Michael, T. Andre *J. Chem. Res. (S)*, **1986**, 5, 184.
- [2] S.-F. Lu, D.-M. Du, J. Xu, S.-W. Zhang, *J. Am. Chem. Soc.*, **2006**, 128, 7418.

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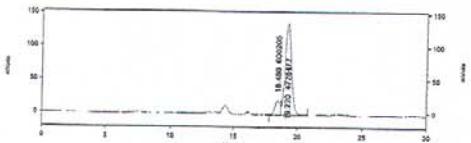
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SPO-10Avp Chi-242nm Results				
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1	18.120	12433893	47.371	
2	18.160	13815973	52.629	
Totals		26251870	100.000	

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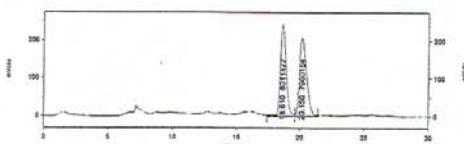
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SPO-10Avp Chi-242nm Results				
Pk #	RT	Area	Area %	
1	19.480	600205	11.264	
2	19.220	4728477	88.736	
Totals		5328682	100.000	

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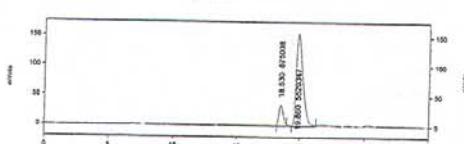
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SPO-10Avp Chi-242nm Results				
Pk #	RT	Area	Area %	
1	18.610	8011477	50.181	
2	20.150	7960154	49.839	
Totals		15971641	100.000	

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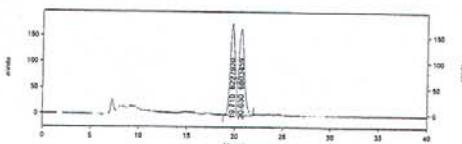
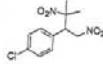
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SPO-10Avp Chi-242nm Results				
Pk #	RT	Area	Area %	
1	18.530	875038	13.482	
2	19.860	5520347	86.518	
Totals		6395385	100.000	

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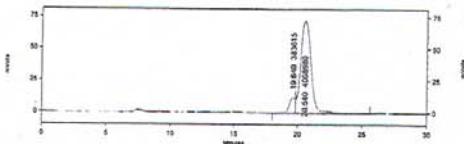
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SPO-10Avp Chi-242nm Results				
Pk #	RT	Area	Area %	
1	19.710	6227920	47.792	
2	20.150	6803159	52.208	
Totals		13031179	100.000	

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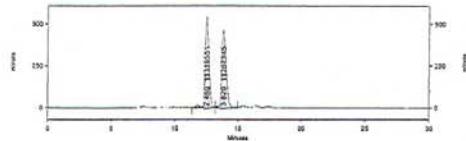
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SPO-10Avp Chi-242nm Results				
Pk #	RT	Area	Area %	
1	19.640	383615	8.814	
2	20.340	4069980	91.186	
Totals		4452595	100.000	

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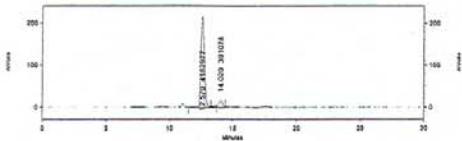
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SFD-10Avp Ch1-242nm Results			
Pk #	RT	Area	Area %
1	12.60	11319351	50.11
2	13.020	11267945	49.88
<b>Totals</b>		<b>22587496</b>	<b>100.000</b>

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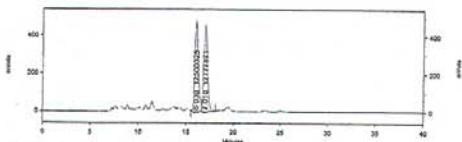
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SFD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
1	12.570	4182977	91.450
2	14.020	391078	8.550
<b>Totals</b>		<b>4574055</b>	<b>100.000</b>

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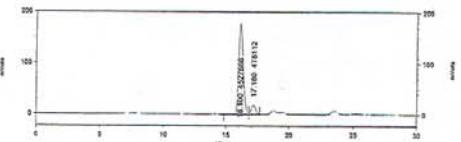
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SFD-10Avp Ch1-242nm Results			
Pk #	RT	Area	Area %
1	16.030	12500325	49.43
2	17.010	12777871	50.56
<b>Totals</b>		<b>25278196</b>	<b>100.000</b>

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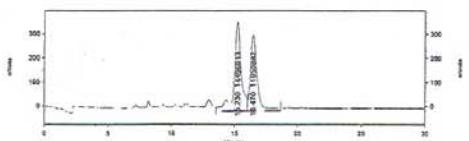
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SFD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
1	18.100	4527866	90.44
2	17.180	478112	9.55
<b>Totals</b>		<b>5005778</b>	<b>100.000</b>

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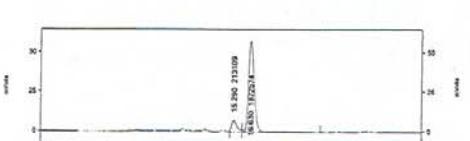
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SFD-10Avp Ch1-242nm Results			
Pk #	RT	Area	Area %
1	15.230	14498013	34.11
2	16.470	11959862	45.18
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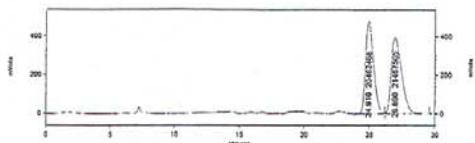
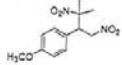
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SFD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
1	15.230	2113109	10.218
2	16.630	1872574	89.782
<b>Totals</b>		<b>2085683</b>	<b>100.000</b>

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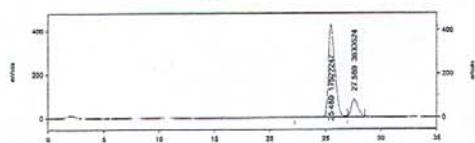
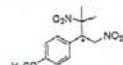
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SPD-10Avp Ch1-242nm Results			
Pk #	RT	Area	Area %
1	21.910	20462468	48.801
2	26.090	21467565	51.199
Totals		41930033	100.000

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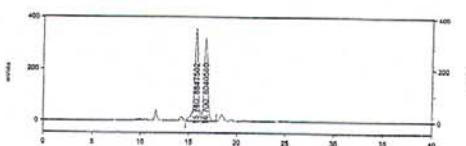
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SPD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
1	25.480	17522247	82.825
2	27.580	1633524	17.175
Totals		21155771	100.000

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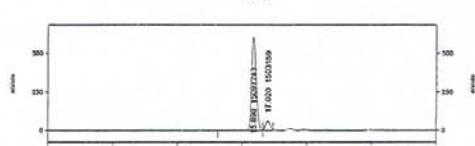
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SPD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
1	15.740	8847502	52.389
2	16.700	8040560	47.611
Totals		16888062	100.000

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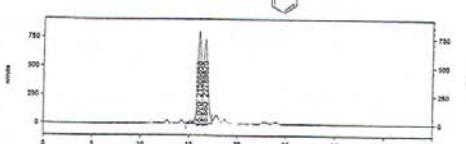
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SPD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
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2	17.020	15031158	9.055
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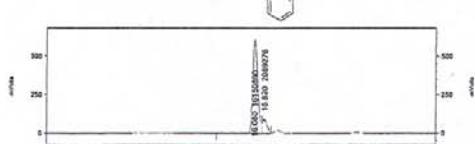
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SPD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
1	16.030	21569358	48.921
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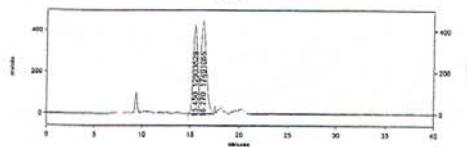
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SPD-10Avp Ch1-254nm Results			
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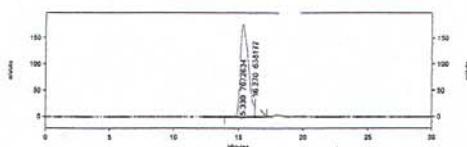
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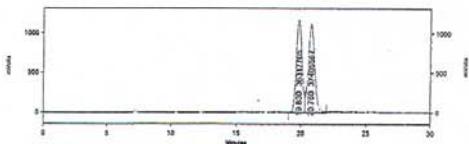
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SPD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
1	15.330	7672934	92.321
2	16.270	638177	7.679
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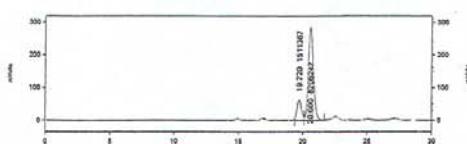
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Data File: C:\EZStart\Projects\WeiWang\jwp58el.dat  
Date Acquired: 3/22/2006 8:22:19 PM Date Printed: 04/20/2006 11:14:41 AM  
Sample ID: jwp58el



SPD-10Avp Ch1-242nm Results			
Pk #	RT	Area	Area %
1	19.430	36317705	49.252
2	20.760	37405567	50.738
Totals		73723272	100.000

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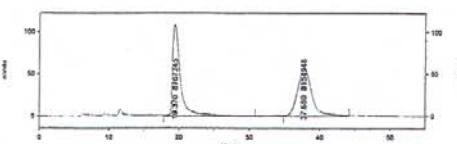
Method Name: C:\EZStart\Projects\Default\Method\Nacl11.net  
Data File: C:\EZStart\Projects\WeiWang\jwp75el.dat  
Date Acquired: 3/27/2006 5:56:14 PM Date Printed: 04/20/2006 11:18:20 AM  
Sample ID: jwp75el



SPD-10Avp Ch1-254nm Results			
Pk #	RT	Area	Area %
1	19.720	1511367	15.353
2	20.600	8206242	84.447
Totals		9717609	100.000

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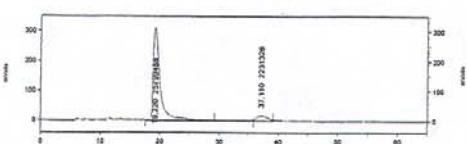
Method Name: C:\EZStart\Projects\Default\Method\Nacl11.net  
Data File: C:\EZStart\Projects\WeiWang\jwq21el.dat  
Date Acquired: 4/4/2006 3:57:32 PM Date Printed: 04/20/2006 11:20:06 AM  
Sample ID: jwq21el



SPD-10Avp Ch1-242nm Results			
Pk #	RT	Area	Area %
1	19.370	8757245	51.889
2	37.680	8154948	48.191
Totals		16922193	100.000

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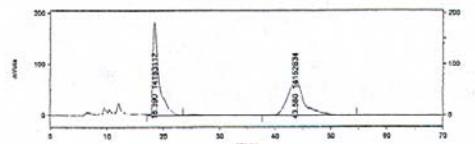
Method Name: C:\EZStart\Projects\Default\Method\Nacl11.net  
Data File: C:\EZStart\Projects\WeiWang\jwq21el.dat  
Date Acquired: 4/4/2006 3:57:32 PM Date Printed: 04/20/2006 11:22:30 AM  
Sample ID: jwq21el



SPD-10Avp Ch1-242nm Results			
Pk #	RT	Area	Area %
1	19.220	25799488	92.040
2	37.110	2211326	7.960
Totals		28030814	100.000

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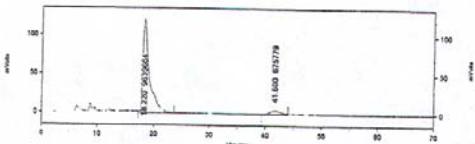
Method Name: C:\EZstart\Projects\Default\Method\HaoLili.net  
Data File: C:\EZstart\Projects\WeiXiang\jqwl487.dat  
Date Acquired: 4/4/2006 11:42:10 AM Date Printed: 04/20/2006 11:23:49 AM  
Sample ID: jqwl487



SPD-10Avp Chi-242nd Results			
Pk #	RT	Area	Area 1
1	18.390	14153112	50.054
2	43.580	14152634	49.316
<b>Totals</b>		28335746	100.000

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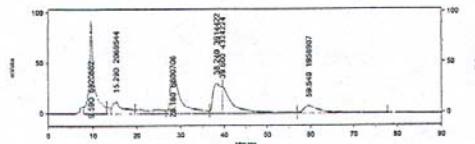
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Data File: C:\EZStart\Projects\WeiWang\jwg20e.dat  
Date Acquired: 4/4/2006 10:24:37 AM Date Printed: 04/20/2006 11:24:57 AM  
Sample ID: jwg20e



SPD-10Avp Ch1-254nm Results		RT	Area	Area %
Pk #				
1		18.220	9629644	93.449
2		41.600	675779	6.551
TOTALS			10315443	100.000

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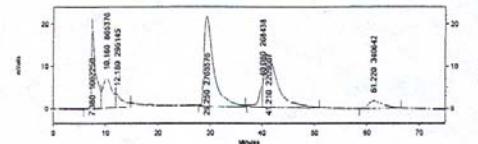
Method Name: C:\EZStart\Projects\Default\Method\HaoLii.net  
Data File: C:\EZStart\Projects\WeiWang\jwql7e.dat  
Date Acquired: 4/13/2006 2:13:56 PM Run Date: 04/20/2006 11:33:11 AM  
Sample ID: jwql7e



SPO-10Avp Chi-254nm Results		PPM	PPM	PPM
3	28,170	4602705	25,595	
4	38,240	3914122	15,179	
5	39,600	3226224	16,768	
6	39,340	1955907	7,596	
<b>Total</b>		<b>16798259</b>	<b>65,138</b>	

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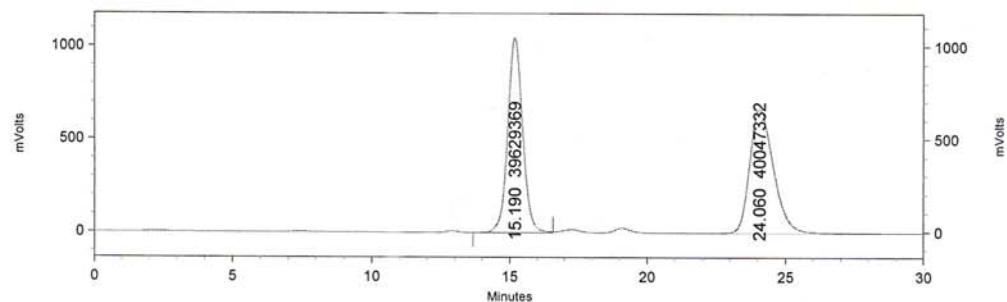
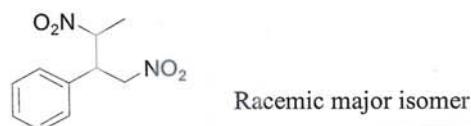
Method Name: C:\EZStart\Projects\Default\Method\KaoLil.net  
Data File: C:\EZStart\Projects\WeiMang\jwq23el.dat  
Date Acquired: 4/13/2006 4:33:41 PM Date Printed: 04/20/2006 11:29:57 AM  
Sample ID: jwq23e



SPD-10Avp Ch1-254nm Results			
px #	RT	Area	Area %
4	29.150	2765575	35.424
5	40.080	284838	3.438
6	41.210	1209467	28.303
7	61.220	1304842	4.363
Totals		594323	71.529

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Method Name: C:\EZStart\Projects\WeiWang\zls0450.met  
Data File: C:\EZStart\Projects\WeiWang\jws7e1.dat  
Date Acquired: 7/5/2006 1:08:08 PM Date Printed: 07/11/2006 06:03:41 PM  
Sample ID:



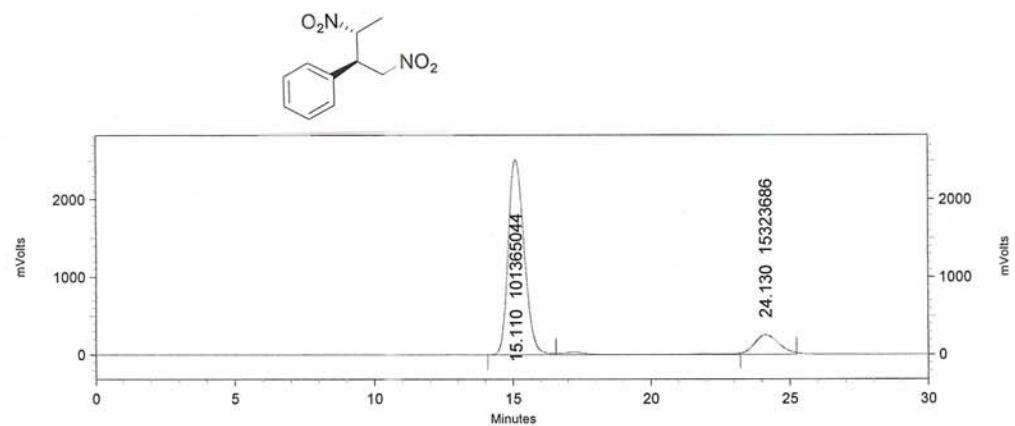
SPD-10Avp

Ch1-254nm Results

Pk #	RT	Area	Area %
1	15.190	39629369	49.738
2	24.060	40047332	50.262
Totals		79676701	100.000

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Method Name: C:\EZStart\Methods\1.met  
Data File: C:\EZStart\Projects\WeiWang\jws11el.dat  
Date Acquired: 7/5/2006 6:33:00 PM Date Printed: 07/11/2006 06:04:24 PM  
Sample ID:

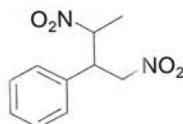


SPD-10Avp  
Ch1-254nm Results

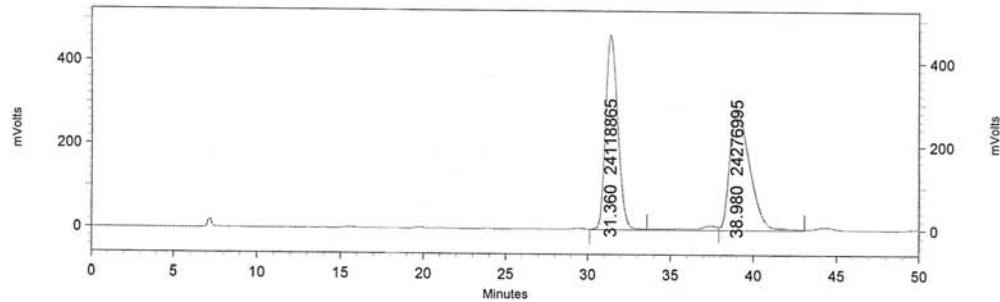
Pk #	RT	Area	Area %
1	15.110	101365044	86.868
2	24.130	15323686	13.132
Totals		116688730	100.000

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Method Name: C:\EZStart\Projects\Default\Method\HaoLi1.met  
Data File: C:\EZStart\Projects\WeiWang\jwp53e1.dat  
Date Acquired: 3/22/2006 10:13:24 PM Date Printed: 07/11/2006 06:22:57  
PM  
Sample ID:



Racemic minor isomer

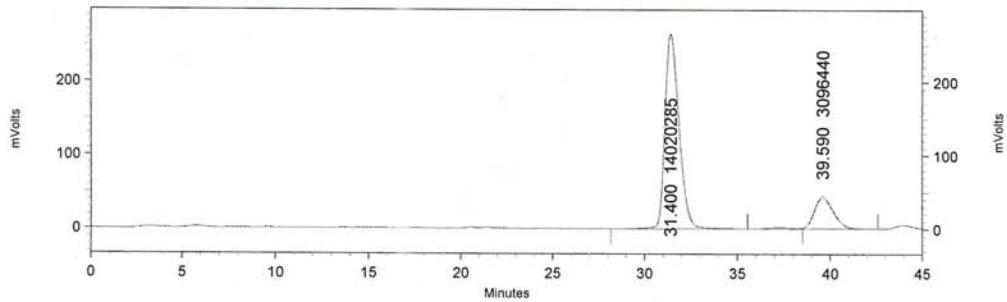
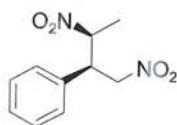


SPD-10Avp  
Ch1-242nm Results

Pk #	RT	Area	Area %
1	31.360	24118865	49.837
2	38.980	24276995	50.163
Totals		48395860	100.000

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Method Name: C:\EZStart\Projects\Default\Method\HaoLi1.met  
Data File: C:\EZStart\Projects\WeiWang\jwp70e1.dat  
Date Acquired: 4/3/2006 11:23:46 PM Date Printed: 07/11/2006 06:22:05 PM  
Sample ID:



SPD-10Avp

Ch1-254nm Results

Pk #	RT	Area	Area %
1	31.400	14020285	81.910
2	39.590	3096440	18.090
Totals		17116725	100.000

