Supporting Information

Chiral squaramide-catalyzed highly diastereo- and enantioselective direct Michael addition of nitroalkanes to nitroalkenes

Wen Yang and Da-Ming Du*
School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China
dudm@bit.edu.cn

Contents

Generel Methods

Column chromatography was carried out with silica gel (200–300 mesh). Melting points were measured with a XT-4 melting point apparatus without correction. ^{1}H NMR spectra were recorded with a Varian Mercury-plus 400 MHz spectrometer. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad singlet), coupling constant(s) in Hz, and integration. ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Infrared spectra were obtained with a Perkin Elmer Spectrum One spectrometer. The ESI-MS spectra were obtained with a Bruker APEX IV mass spectrometer. Optical rotations were measured with Krüss P8000 or WZZ-3 polarimeter at the indicated concentration with unit g/100 mL. The diastereomeric ratios and enantiomeric excesses of the products were determined by chiral HPLC using an Agilent 1200 LC instrument with Daicel Chiralcel column (OD-H, OF) or Daicel Chiralpak columns (AS-H, IB, IA). The absolute configurations of the known adducts were assigned by HPLC and optical rotation comparisons with the reported data[1], and those of other adducts were assigned by analogy.

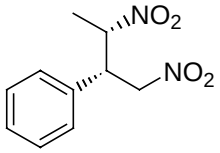
Materials

Commercially available compounds were used without further purification, unless otherwise stated. Nitroalkanes were obtained from commercial sources and used with distillation. Nitroalkenes were prepared according to the literature procedures.[2] Racemic samples of **3a**–**3r** and **6a**–**6b** were prepared with 10 mol% Et_3N as the catalyst. The squaramide organocatalysts **I**–**IV**[3], **V**–**VIII**[4], and **IX**–**X**[5] were prepared following the reported procedures.

General procedure for the direct asymmetric addition of nitroalkanes to nitroalkenes

The mixture of nitroalkene **1** (0.2 mmol, 1.0 equiv) and catalyst **IX** (2 mol%) in dichloromethane (0.5 mL) was stirred at –20 ^{o}C for 30 min. Then nitroalkene **2** (1.0 mmol, 5.0 equiv) was added. After stirring at –20 ^{o}C for 48–96 h, the reaction mixture was concentrated and directly purified by silica gel column chromatography to afford the mixture of the *syn* and *anti* diastereomer of chiral 1,3-dinitro compounds **3**. The mixture was analyzed

to determine the diastereoselectivity and enantioselectivity of the reaction by chiral HPLC. Then the *syn* diastereoisomer was obtained by another column chromatography separation on silica gel, and used for characterization.

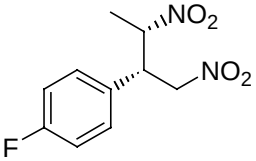


3a

[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3a) (Table 3, entry 1)

The compound **3a** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (42.2 mg, 94% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (95:5 dr, 97% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak AS-H column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 29.6 min, t_{major} = 31.3 min; *anti* diastereomer: t_R = 20.2, 21.8 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 78–80 °C. $[\alpha]_D^{30}$ = –6.7 (*c* 0.42, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.32 (m, 3H), 7.16–7.15 (m, 2H), 4.97–4.90 (m, 2H), 4.82 (dd, J_1 = 13.6 Hz, J_2 = 8.4 Hz, 1H), 4.05–4.00 (m, 1H), 1.58 (d, J = 6.8 Hz, 3H).



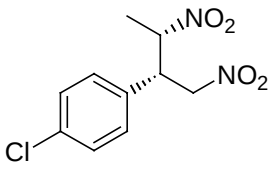
3b

1-Fluoro-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3b) (Table 3, entry 2)

The compound **3b** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (47.2 mg, 98% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (94:6 dr, 96% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 20.5 min, t_{major} = 23.4 min; *anti* diastereomer: t_R = 15.4, 16.2 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p.

125–127 °C. $[\alpha]_D^{30} = -8.0$ (*c* 0.40, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.14 (m, 2H), 7.07–7.03 (m, 2H), 4.95–4.87 (m, 2H), 4.79 (dd, J_1 = 13.6 Hz, J_2 = 8.8 Hz, 1H), 4.03–4.00 (m, 1H), 1.58 (d, *J* = 6.4 Hz, 3H).

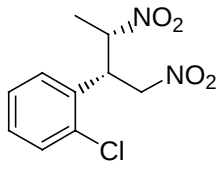


3c

1-Chloro-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3c) (Table 3, entry 3)

The compound **3c** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (48.9 mg, 95% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (92:8 dr, 96% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 23.3 min, t_{major} = 33.3 min; *anti* diastereomer: t_R = 18.2 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 96–98 °C. $[\alpha]_D^{30} = -7.2$ (*c* 0.64, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 6.4 Hz, 2H), 7.10 (d, *J* = 6.8 Hz, 2H), 4.94–4.88 (m, 2H), 4.79 (dd, J_1 = 12.4 Hz, J_2 = 8.4 Hz, 1H), 4.02–3.99 (m, 1H), 1.59 (d, *J* = 4.8 Hz, 3H).



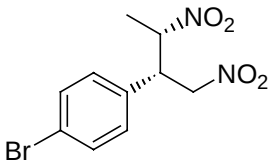
3d

1-Chloro-2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3d) (Table 3, entry 4)

The compound **3d** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (42.8 mg, 83% yield). It was analysed to determine the diastereoselectivity and enantioselectivity of the reaction (88:12 dr, 95% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 16.2 min, t_{major} = 27.4 min; *anti* diastereomer: t_R = 12.7 min.

The *syn* distereomer was purified by flash chromatography to afford a pale yellow oil. $[\alpha]_D^{30}$ =

+10.1 (*c* 0.73, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.44 (m, 1H), 7.29–7.27 (m, 2H), 7.21–7.13 (m, 1H), 5.18–5.14 (m, 1H), 4.95–4.85 (m, 2H), 4.76–4.70 (m, 1H), 1.62 (d, *J* = 6.4 Hz, 3H).

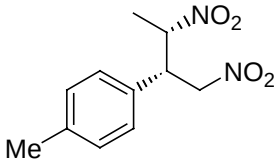


3e

1-Bromo-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3e) (Table 3, entry 5)

The compound **3e** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (55.0 mg, 91% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (94:6 dr, 96% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 18.4 min, t_{major} = 29.0 min; *anti* diastereomer: t_R = 14.8, 16.0 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 77–79 °C. $[\alpha]_D^{30}$ = –5.2 (*c* 0.85, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.48 (m, 2H), 7.09–7.03 (m, 2H), 4.94–4.87 (m, 2H), 4.78 (dd, J_1 = 13.6 Hz, J_2 = 8.4 Hz, 1H), 4.01–3.96 (m, 1H), 1.58 (d, *J* = 6.4 Hz, 3H).



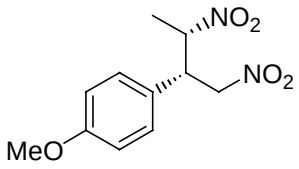
3f

1-Methyl-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3f) (Table 3, entry 6)

The compound **3f** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (43.5 mg, 91% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (91:9 dr, 96% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 17.2 min, t_{major} = 40.7 min; *anti* diastereomer: t_R = 12.9, 14.3 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 50–52

°C. $[\alpha]_D^{30} = -11.2$ (*c* 0.86, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 7.2 Hz, 2H), 4.94–4.87 (m, 2H), 4.79 (dd, J_1 = 13.6 Hz, J_2 = 8.4 Hz, 1H), 3.99–3.94 (m, 1H), 2.31 (s, 3H), 1.56 (d, *J* = 6.0 Hz, 3H).

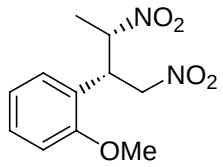


3g

1-Methoxy-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3g) (Table 3, entry 7)

The compound **3g** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (46.0 mg, 90% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (94:6 dr, 97% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 23.1 min, t_{major} = 37.6 min; *anti* diastereomer: t_R = 17.4, 18.9 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 80–82 °C. $[\alpha]_D^{30} = -12.0$ (*c* 0.98, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.93–4.86 (m, 2H), 4.78 (dd, J_1 = 13.6 Hz, J_2 = 8.4 Hz, 1H), 3.97–3.92 (m, 1H), 3.77 (s, 3H), 1.56 (d, *J* = 6.8 Hz, 3H).



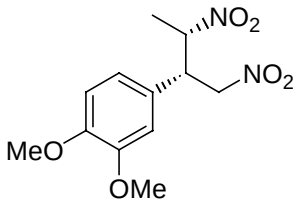
3h

1-Methoxy-2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3h) (Table 3, entry 8)

The compound **3h** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (44.7 mg, 88% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (94:6 dr, 97% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 12.5 min, t_{major} = 16.6 min;

anti diastereomer: t_R = 9.0, 9.6 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 64–66 °C. $[\alpha]_D^{30}$ = +4.5 (*c* 0.98, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.92–6.89 (m, 2H), 5.16 (dd, J_1 = 14.0 Hz, J_2 = 6.8 Hz, 1H), 4.88–4.86 (m, 2H), 4.30 (dd, J_1 = 14.0 Hz, J_2 = 6.8 Hz, 1H), 3.85 (s, 3H), 1.58 (d, *J* = 6.8 Hz, 3H).

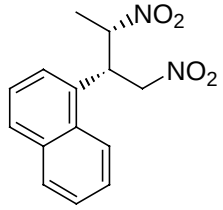


3i

1,2-Dimethoxy-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3i) (Table 3, entry 9)

The compound **3i** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (40.5 mg, 71% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (88:12 dr, 96% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 43.5 min, t_{major} = 46.6 min; *anti* diastereomer: t_R = 30.6 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 85–86 °C. $[\alpha]_D^{30}$ = –15.0 (*c* 0.96, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82 (d, *J* = 8.4 Hz, 1H), 6.71–6.69 (m, 1H), 6.62 (s, 1H), 4.96–4.88 (m, 2H), 4.80 (dd, J_1 = 13.2 Hz, J_2 = 8.4 Hz, 1H), 3.96–3.92 (m, 1H), 3.85 (s, 6H), 1.58 (d, *J* = 6.4 Hz, 3H).



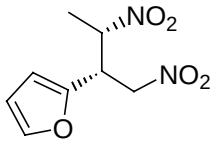
3j

1-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]naphthalene (3j) (Table 3, entry 10)

The compound **3j** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (43.3 mg, 79% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (92:8 dr, 95% ee for the major

syn-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 21.2 min, t_{major} = 78.8 min; *anti* diastereomer: t_R = 14.1, 17.1 min.

The *syn* distereomer was purified by flash chromatography to afford pale yellow oil. $[\alpha]_D^{30}$ = +40.5 (*c* 0.82, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.65–7.62 (m, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 5.15 (dd, J_1 = 12.4 Hz, J_2 = 6.4 Hz, 2H), 4.97 (d, *J* = 6.8 Hz, 2H), 1.56 (d, *J* = 6.4 Hz, 3H).

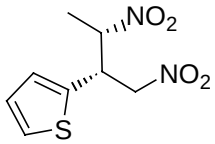


3k

2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]furan (3k) (Table 3, entry 11)

The compound **3k** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (27.4 mg, 64% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (89:11 *dr*, 96% *ee* for the major *syn*-distereomer) by HPLC (Daicel Chiralcel OD H column, *n*-hexane/2-propanol = 95:5 flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 29.3 min, t_{major} = 30.6 min; *anti* diastereomer: t_R = 21.6, 23.5 min.

The *syn* distereomer was purified by flash chromatography to afford yellow oil. $[\alpha]_D^{30}$ = –27.0 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 1.2 Hz, 1H), 6.34 (d, *J* = 1.2 Hz, 1H), 6.27 (d, *J* = 2.0 Hz, 1H), 4.93–4.81 (m, 3H), 4.31–4.24 (m, 1H), 1.61 (d, *J* = 6.8 Hz, 3H).



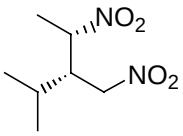
3l

2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]thiophene (3l) (Table 3, entry 12)

The compound **3l** (the mixture of the *syn* and *anti* diastereomer) was obtained according to

the general procedure (29.0 mg, 63% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (79:21 dr, 95% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 19.6 min, t_{major} = 29.7 min; *anti* diastereomer: t_R = 16.5 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 66–68 °C. $[\alpha]_D^{30}$ = –54.7 (*c* 0.34, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (s, 1H), 6.89 (d, *J* = 1.6 Hz, 1H), 6.92 (d, *J* = 1.6 Hz, 1H), 4.97–4.94 (m, 2H), 4.85–4.80 (m, 1H), 4.34–4.32 (m, 1H), 1.62 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.8, 127.4, 127.2, 126.2, 83.9, 76.7, 42.6, 16.6. IR (KBr): ν 3110, 2918, 1551, 1432, 1377, 1361, 852, 708 cm^{-1}. HRMS (ESI): m/z calcd. for $C_8H_{10}N_2NaO_4S$ $[M+Na]^+$ 253.02535, found 253.02543.

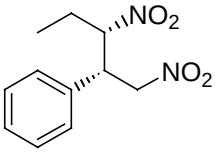


3m

(3*S*,4*S*)-2-Methyl-4-nitro-3-(nitromethyl)pentane (3m) (Table 3, entry 13)

The compound **3m** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (6.1 mg, 16% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (67:33 dr, 80% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralcel OD H column, *n*-hexane/2-propanol = 95:5, flow rate 0.5 mL/min, detection at 210 nm), *syn* diastereomer: t_{major} = 27.1 min, t_{minor} = 28.8 min; *anti* diastereomer: t_R = 22.3 min.

The *syn* distereomer was purified by flash chromatography to afford colorless oil. $[\alpha]_D^{30}$ = +4.0 (*c* 0.20, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.81–4.78 (m, 1H), 4.51–4.42 (m, 2H), 2.98–2.87 (m, 1H), 1.89–1.86 (m, 1H), 1.56 (d, *J* = 5.2 Hz, 3H), 1.05 (d, *J* = 4.8 Hz, 3H), 0.92 (d, *J* = 5.2 Hz, 3H).

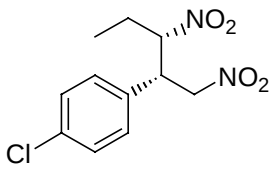


3n

[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3n) (Table 3, entry 14)

The compound **3n** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (37.8 mg, 79% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (88:12 dr, 92% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 16.0 min, t_{major} = 57.8 min; *anti* diastereomer: t_R = 12.0 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 51–53 °C. $[\alpha]_D^{30}$ = –9.8 (*c* 0.92, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (s, 3H), 7.16 (s, 2H), 4.90–4.86 (m, 1H), 4.79–4.74 (m, 2H), 4.06–4.03 (m, 1H), 2.03–1.99 (m, 1H), 1.89–1.87 (m, 1H), 1.01 (t, *J* = 6.8 Hz, 3H).

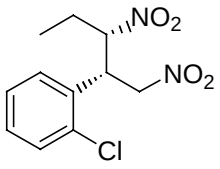


3o

1-Chloro-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3o) (Table 3, entry15)

The compound **3o** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (48.0 mg, 88% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (89:11 dr, 96% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 0.5 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 38.5 min, t_{major} = 63.8 min; *anti* diastereomer: t_R = 25.5, 27.4 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 97–98 °C. $[\alpha]_D^{30}$ = –4.4 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 4.85 (dd, J_1 = 13.2 Hz, J_2 = 5.2 Hz, 1H), 4.76–4.70 (m, 2H), 4.04–3.99 (m, 1H), 2.04–1.97 (m, 1H), 1.89–1.84 (m, 1H), 1.02 (t, *J* = 6.4 Hz, 3H).

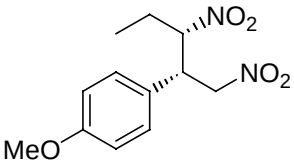


3p

1-Chloro-2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3p) (Table 3, entry16)

The compound **3p** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (39.4 mg, 72% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (81:19 dr, 96% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 12.5 min, t_{major} = 26.2 min; *anti* diastereomer: t_R = 9.4, 9.9 min.

The *syn* distereomer was purified by flash chromatography to afford a pale yellow oil. $[\alpha]_D^{30}$ = +11.6 (*c* 0.91, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 6.4 Hz, 1H), 7.28–7.25 (m, 2H), 7.16 (d, *J* = 6.4 Hz, 1H), 5.15–4.95 (m, 1H), 4.92–4.82 (m, 2H), 4.67–4.63 (m, 1H), 2.02–1.95 (m, 2H), 1.02 (t, *J* = 6.4 Hz, 3H).



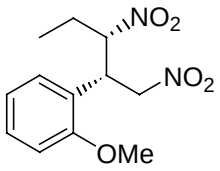
3q

1-Methoxy-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3q) (Table 3, entry17)

The compound **3q** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (34.6 mg, 64% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (92:8 dr, 97% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 19.0 min, t_{major} = 34.5 min; *anti* diastereomer: t_R = 12.8 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 69–71 ^{o}C. $[\alpha]_D^{30}$ = –11.2 (*c* 0.64, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.84 (dd, J_1 = 13.2 Hz, J_2 = 6.0 Hz, 1H), 4.75–4.70 (m, 2H),

4.00–3.94 (m, 1H), 3.78 (s, 3H), 2.04–1.96 (m, 1H), 1.88–1.83 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).



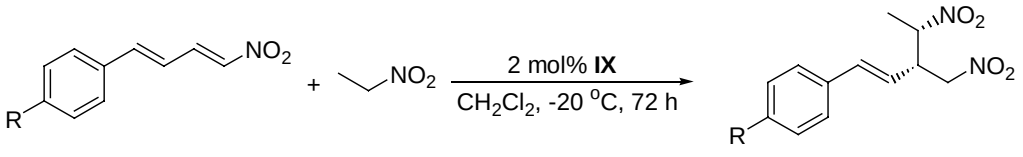
3r

1-Methoxy-2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3r) (Table 3, entry18)

The compound **3r** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (31.4 mg, 58% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (90:10 dr, 96% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 210 nm), *syn* diastereomer: t_{minor} = 10.4 min, t_{major} = 14.7 min; *anti* diastereomer: t_R = 7.7, 8.3 min.

The *syn* distereomer was purified by flash chromatography to afford colorless oil. $[\alpha]_D^{30}$ = +9.2 (*c* 1.30, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 6.4 Hz, 1H), 6.91–6.89 (m, 2H), 5.03–4.98 (m, 1H), 4.90–4.82 (m, 2H), 4.28–4.23 (m, 1H), 3.86 (s, 3H), 2.03–1.96 (m, 1H), 1.90–1.85 (m, 1H), 0.99 (t, *J* = 6.4 Hz, 3H).

Further investigation of substrate scope

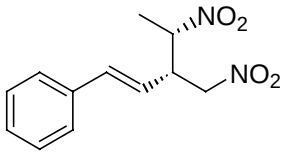


5 **2a** **6**

6a: R = H 46% yield, 81:19 dr, 87% ee
6b: R = OMe 53% yield, 76:24 dr, 90% ee

The mixture of nitrodiene **5** (0.4 mmol, 1.0 equiv) and catalyst **IX** (2 mol%) in dichloromethane (1.0 mL) was stirred for 30 min. Then nitroethane **2a** (72 μL, 2.0 mmol, 5.0 equiv) was added. After stirring at –20 °C for 72 h, the reaction mixture was concentrated and directly purified by silica gel column chromatography to afford the mixture of the *syn* and *anti* diastereomer of chiral 1,3-dinitro compounds **6**. The mixture was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction by chiral HPLC. Then the *syn*

diastereoisomer was obtained by another column chromatography separation on silica gel, and used for characterization.

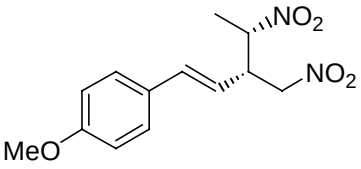


6a

[(1*E*,3*S*,4*S*)-4-nitro-3-(nitromethyl)-1-penten-1-yl]benzene (6a)

The compound **6a** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (46.4 mg, 46% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (81:19 dr, 87% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IB column, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 254 nm), *syn* diastereomer: t_{minor} = 22.2 min, t_{major} = 29.2 min; *anti* diastereomer: t_R = 19.2, 26.1 min.

The *syn* distereomer was purified by flash chromatography to afford a white solid, m.p. 57–59 °C. $[\alpha]_D^{30}$ = –42.5 (*c* 0.71, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.30 (m, 5H), 6.62 (d, *J* = 15.6 Hz, 1H), 5.90 (dd, J_1 = 15.6 Hz, J_2 = 10.0 Hz, 1H), 4.82–4.79 (m, 1H), 4.75–4.70 (m, 1H), 4.60–4.55 (m, 1H), 3.52–3.45 (m, 1H), 1.62 (d, *J* = 4.8 Hz, 3H).



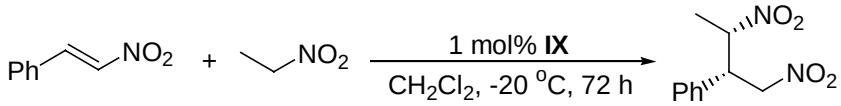
6b

1-Methoxy-4-[(1*E*,3*S*,4*S*)-4-nitro-3-(nitromethyl)-1-penten-1-yl]benzene (6b)

The compound **6b** (the mixture of the *syn* and *anti* diastereomer) was obtained according to the general procedure (59.3 mg, 53% yield). It was analyzed to determine the diastereoselectivity and enantioselectivity of the reaction (76:24 dr, 90% ee for the major *syn*-distereomer) by HPLC (Daicel Chiralpak IA column, *n*-hexane/2-propanol = 97:3, flow rate 1.0 mL/min, detection at 254 nm), *syn* diastereomer: t_{minor} = 31.8 min, t_{major} = 33.0 min; *anti* diastereomer: t_R = 35.3, 37.6 min.

The *syn* distereomer was purified by flash chromatography to afford pale yellow oil. $[\alpha]_D^{30}$ = –62.1 (*c* 0.82, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ =7.27 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 6.8 Hz, 2H), 6.54 (d, *J* = 15.2 Hz, 1H), 5.74 (dd, J_1 = 15.2 Hz, J_2 = 9.6 Hz, 1H), 4.80–4.77 (m, 1H), 4.73–4.96 (m, 1H), 4.58–4.53 (m, 1H), 3.80 (s, 3H), 3.47–3.42 (m, 1H), 1.59 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 137.1, 128.0, 117.3, 114.0, 83.2, 76.4, 55.3, 45.7, 16.6. IR (KBr): ν 2956, 2924, 2846, 1722, 1651, 1606, 1554, 1511, 1463, 1378, 1250, 1176, 1029, 970, 814, 761 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{13}H_{17}N_2O_5$ $[M + H]^+$ 281.11320, found 281.11331.

The gram-scale preparation and transformation of 3a

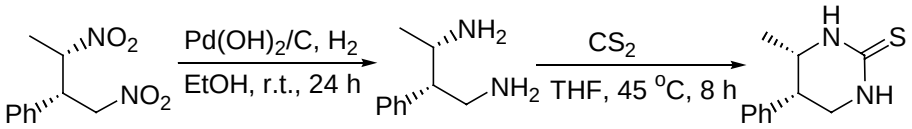


1a 1.49 g, 10.0 mmol

2a

3a 1.84 g, 8.2 mmol
82% yield, 94% ee and 92:8 dr
99% ee after a simple recrystallization

The mixture of nitroalkene **1a** (1.49 g, 10.0 mmol) and catalyst **IX** (72.5 mg, 0.1 mmol, 1 mol%) in dichloromethane (25 mL) was stirred at –20 °C for 30 min. Then nitroalkene **2a** (3.6 mL, 50.0 mmol) was added. After stirring at –20 °C for 72 h, the reaction mixture was concentrated and directly purified by silica gel column chromatography to afford 183 mg of the *anti*-adduct (8% yield) and 1.654 g of the *syn*-adduct (74% yield) , respectively. Enantiomeric excess of the *syn*-adduct (94% ee, 99% ee after a simple recrystallization with ethyl acetate/petroleum ether) was determined by HPLC with Chiralpak AS-H column.



3a 2.35 g, 10.5 mmol
99% ee

7

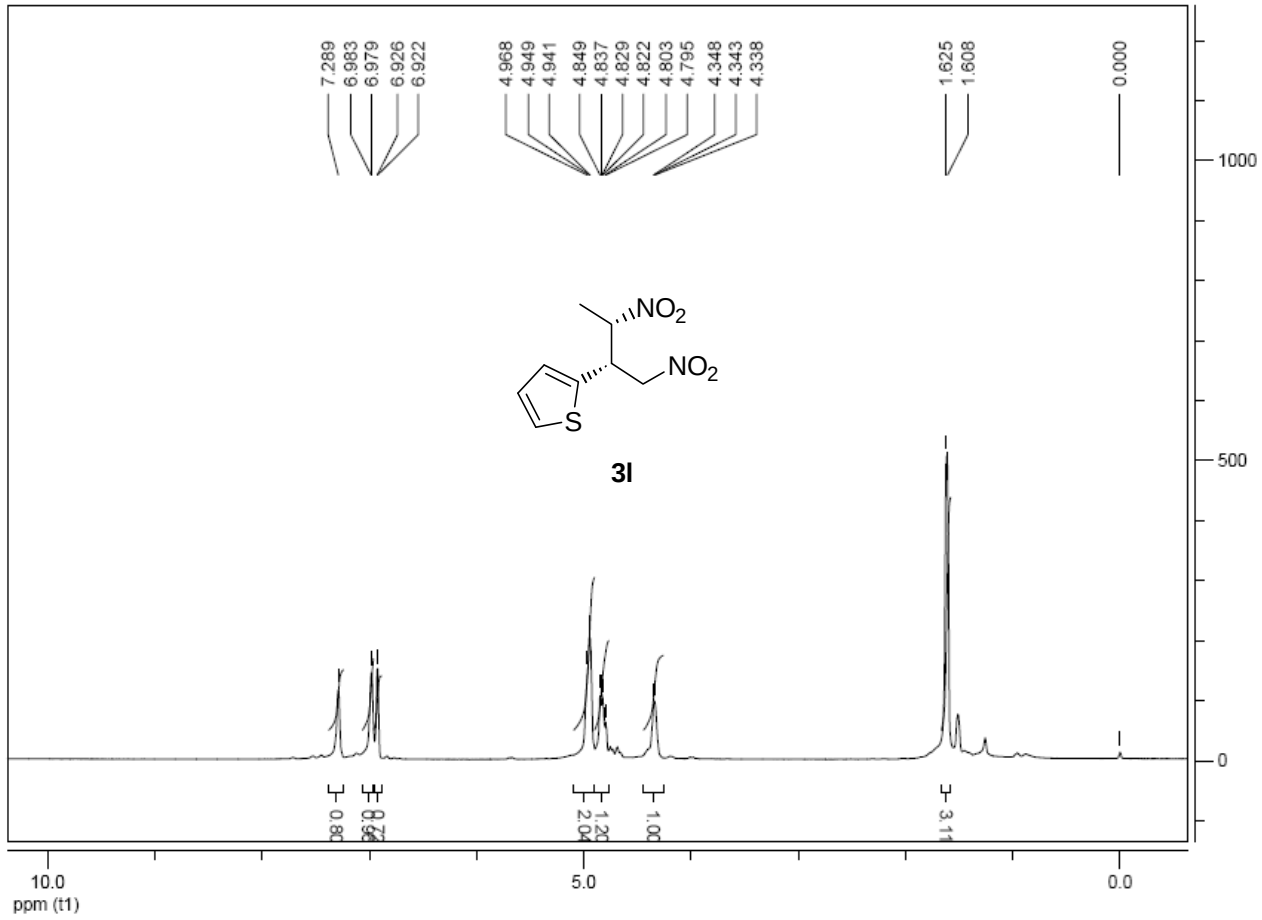
8 1.13 g, 5.5 mmol
52% yield for two steps, 99% ee

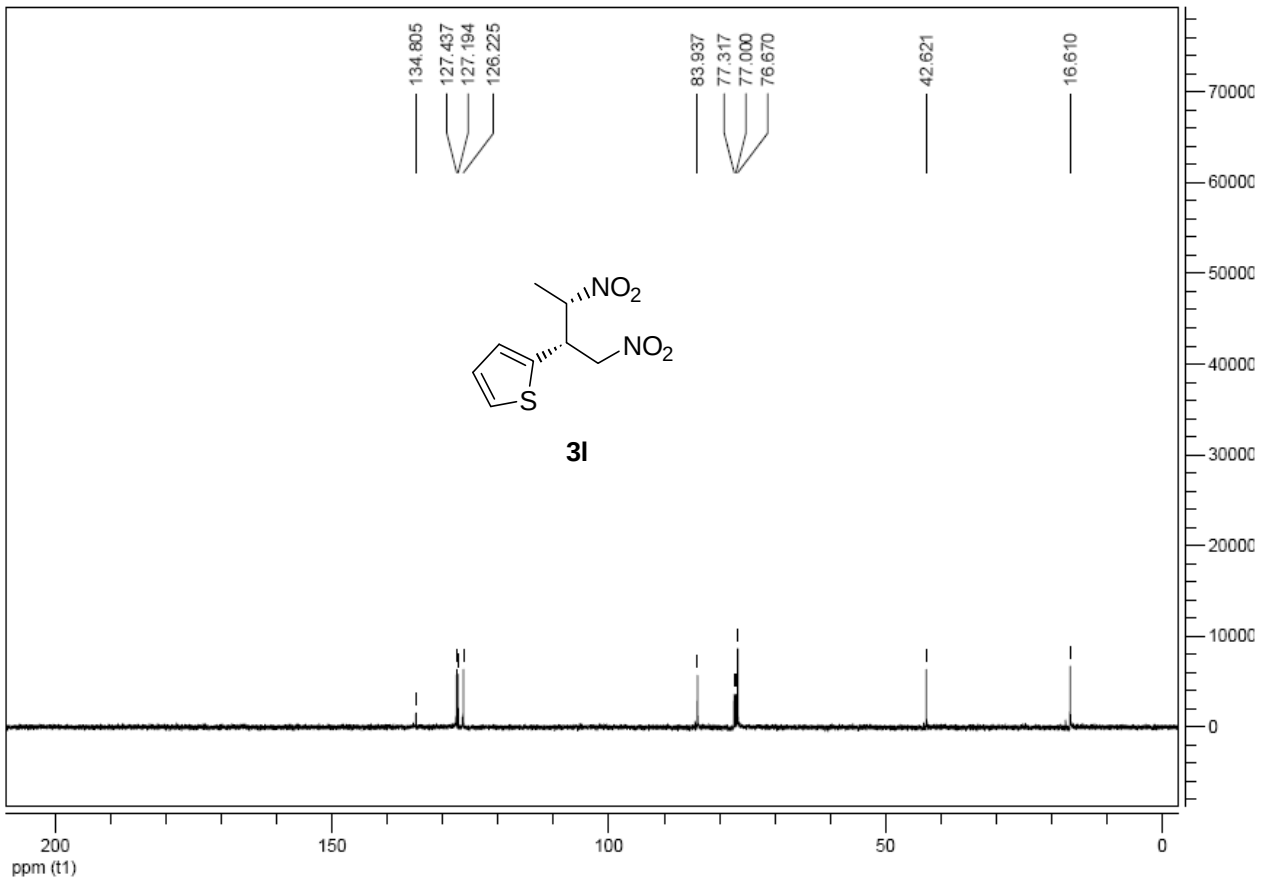
To a solution of the *syn*-adduct **3a** (2.35 g, 10.5 mmol, 99% ee) in EtOH (100 mL) was added 10 wt % $Pd(OH)_2/C$ (1.47 g, 10 mol%). The mixture was placed under an atmosphere of H_2 in a rubber balloon and stirred for 24 h at room temperature. After filtration, the filtrate was concentrated in vacuo to afford the crude product (1,3-diamine compound **7**) as colorless oil. The colorless oil was dissolved in THF (50 mL), and CS_2 (1.60 g, 21.0 mmol) was added.

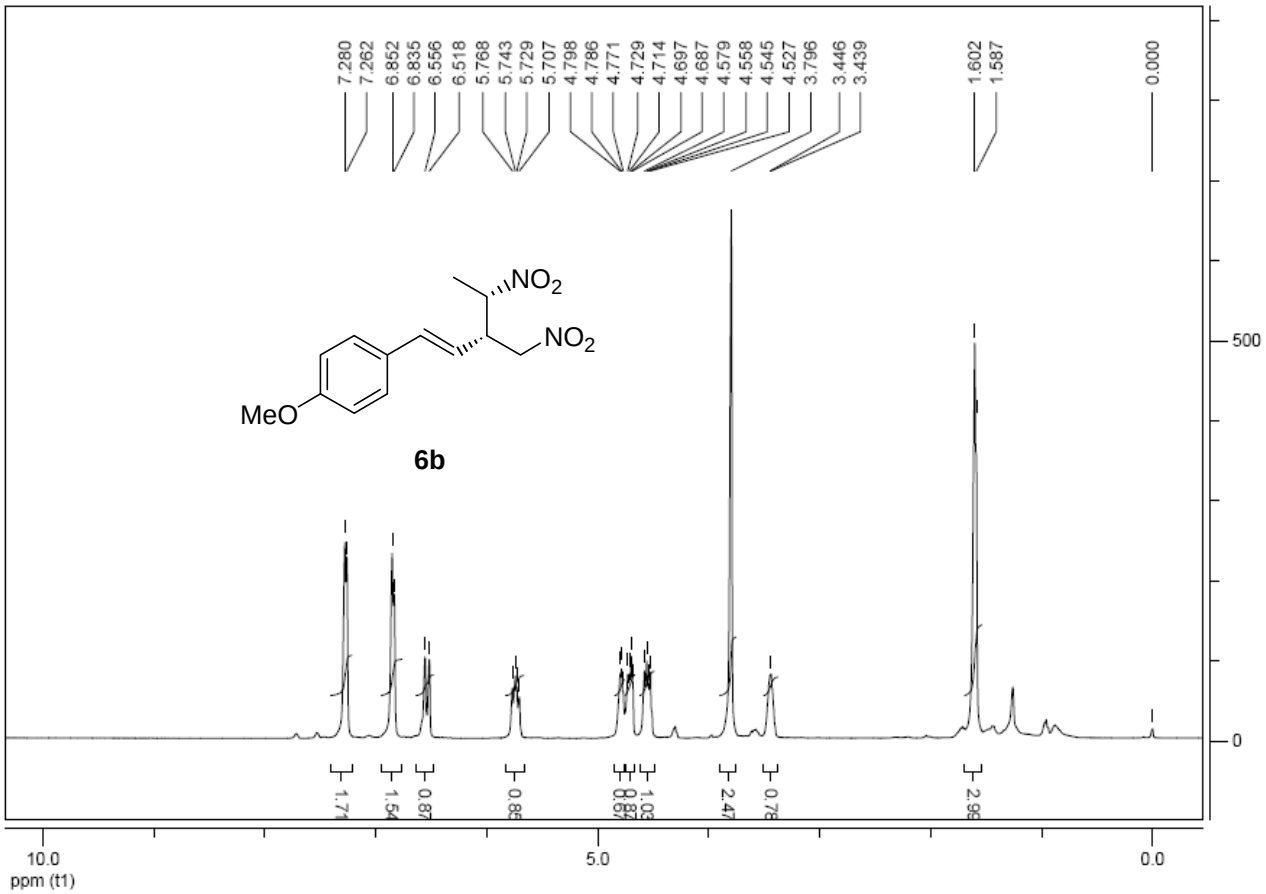
After stirring at 45 ^{o}C for 8 h, the reaction mixture was concentrated and directly purified by silica gel column chromatography to afford 1.13 g of the thiourea **8** (52% yield) as a white solid. m.p. 223–225 ^{o}C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel OF column, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm); major enantiomer t_R = 29.8 min, minor enantiomer t_R = 38.6 min; 99% ee; $[\alpha]_D^{25}$ = – 127.8 (*c* 0.52, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.84 (br s, 1H), 6.72 (br s, 1H), 3.85–3.82 (m, 1H), 3.62 (dd, J_1 = 6.0 Hz, J_2 = 2.4 Hz, 2H), 3.24 (dd, J_1 = 10.8 Hz, J_2 = 6.0 Hz, 1H), 1.00 (d, *J* = 6.4 Hz, 3H).

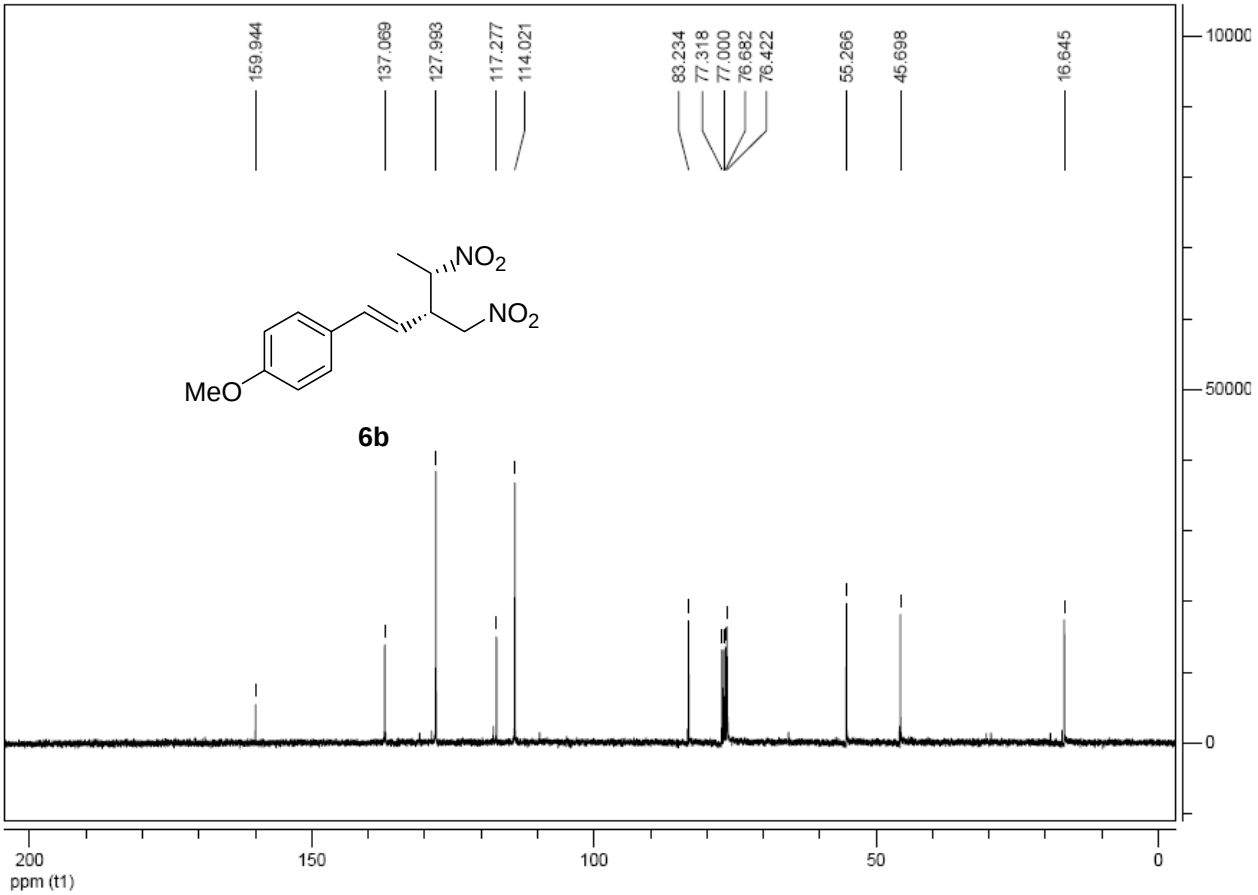
References

1. (*a*) S. F. Lu, D. M. Du, J. X. Xu and S. W. Zhang, *J. Am. Chem. Soc.*, 2006, **128**, 7418; (*b*) X. Yang, X. Zhou, L. L. Lin, L. Chang, X. H. Liu and X. M. Feng, *Angew. Chem., Int. Ed.*, 2008, **47**, 7049; (*c*) C. Rabalakos and W. D. Wulff, *J. Am. Chem. Soc.*, 2008, **130**, 13524; (*d*) X. Q. Dong, H. L. Teng and C. J. Wang, *Org. Lett.*, 2009, **11**, 1265; (*e*) T. Ooi, S. Takada, K. Doda and K. Maruoka, *Angew. Chem., Int. Ed.*, 2006, **45**, 7606.
2. (*a*) C. Dockendorff, S. Sahli, M. Olsen, L. Milhau and M. Lautens, *J. Am. Chem. Soc.*, 2005, **127**, 15028; (*b*) A. Côté, V. N. G. Lindsay and A. B. Charette, *Org. Lett.*, 2007, **9**, 85; (*c*) B. M. Trost and M. Müller, *J. Am. Chem. Soc.*, 2008, **130**, 2438;
3. W. Yang and D. M. Du, *Adv. Synth. Catal.*, 2011, **353**, 1241.
4. W. Yang and D. M. Du, *Org. Lett.*, 2010, **12**, 5450.
5. J. W. Lee, T. H. Ryu, J. S. Oh, H. Y. Bae, H. B. Jang and C. E. Song, *Chem. Commun.*, 2009, 7224.


7.289
6.983
6.979
6.926
6.922
4.968
4.949
4.941
4.849
4.837
4.829
4.822
4.803
4.795
4.348
4.343
4.338
1.625
1.608
0.000
NO2
NO2
S
3I
1000
500
0
10.0
ppm (t1)
5.0
0.0

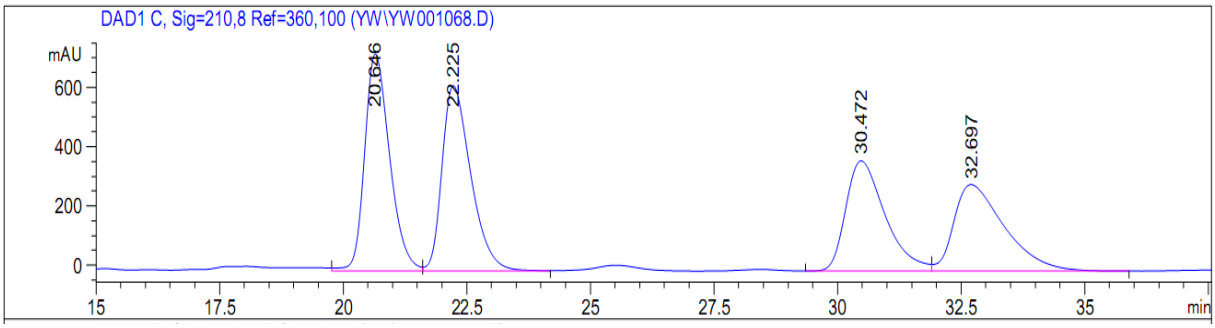

134.805
127.437
127.194
126.225
83.937
77.317
77.000
76.670
42.621
16.610
NO2
NO2
S
3I
70000
60000
50000
40000
30000
20000
10000
0
200
ppm (t1)
150
100
50
0


7.280
7.262
6.852
6.835
6.556
6.518
5.768
5.743
5.729
5.707
4.798
4.786
4.771
4.729
4.714
4.697
4.687
4.579
4.558
4.545
4.527
3.796
3.446
3.439
1.602
1.587
0.000
NO2
NO2
MeO
6b
500
0
10.0
ppm (t1)
5.0
0.0


159.944
137.069
127.993
117.277
114.021
83.234
77.318
77.000
76.682
76.422
55.266
45.698
16.645
NO2
NO2
MeO
6b
10000
50000
0
200
ppm (t1)
150
100
50
0

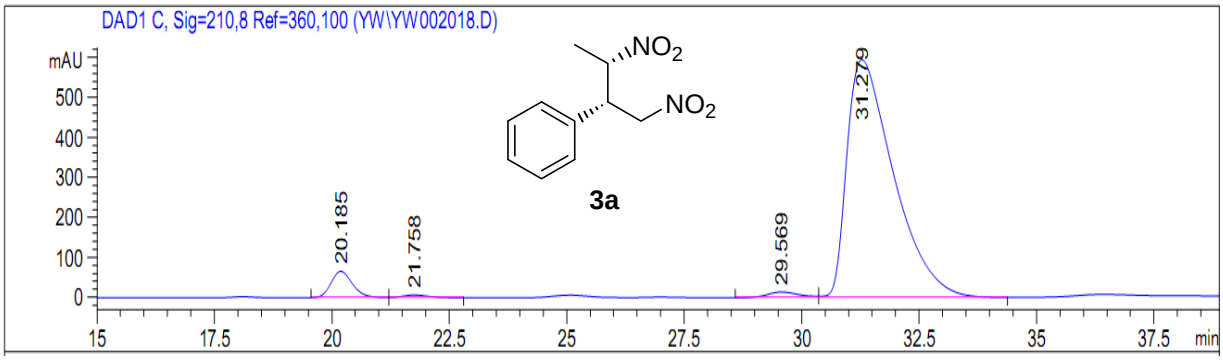
Copies of HPLC profiles of Michael addition products

[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3a) (Table 3, entry 1)



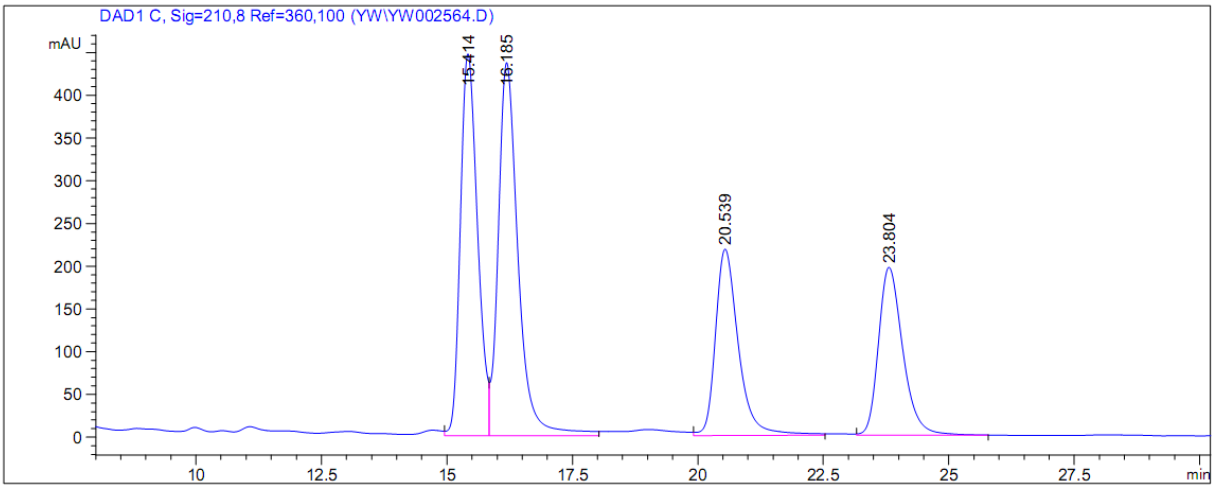
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.646	VV	0.5432	2.57959e4	731.90820	27.8685
2	22.225	VB	0.6210	2.53574e4	625.38293	27.3948
3	30.472	VV	0.8474	2.06440e4	372.00656	22.3027
4	32.697	VB	1.0695	2.07655e4	292.04581	22.4340



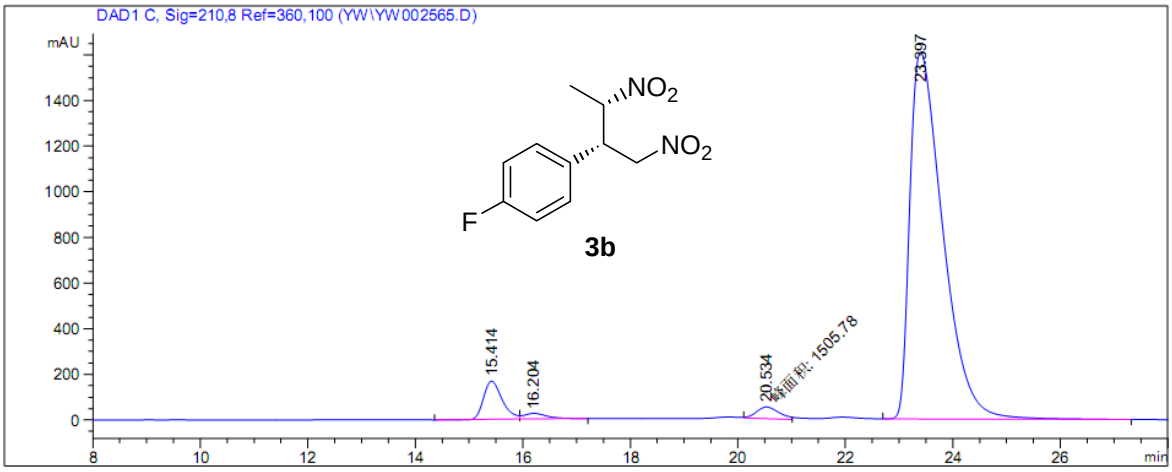
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.185	BV	0.4864	2091.91064	65.88589	4.7268
2	21.758	VB	0.5411	239.63422	6.83388	0.5415
3	29.569	BV	0.7418	696.17700	14.45639	1.5731
4	31.279	VB	1.0643	4.12286e4	595.07794	93.1587

1-Fluoro-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3b) (Table 3, entry 2)



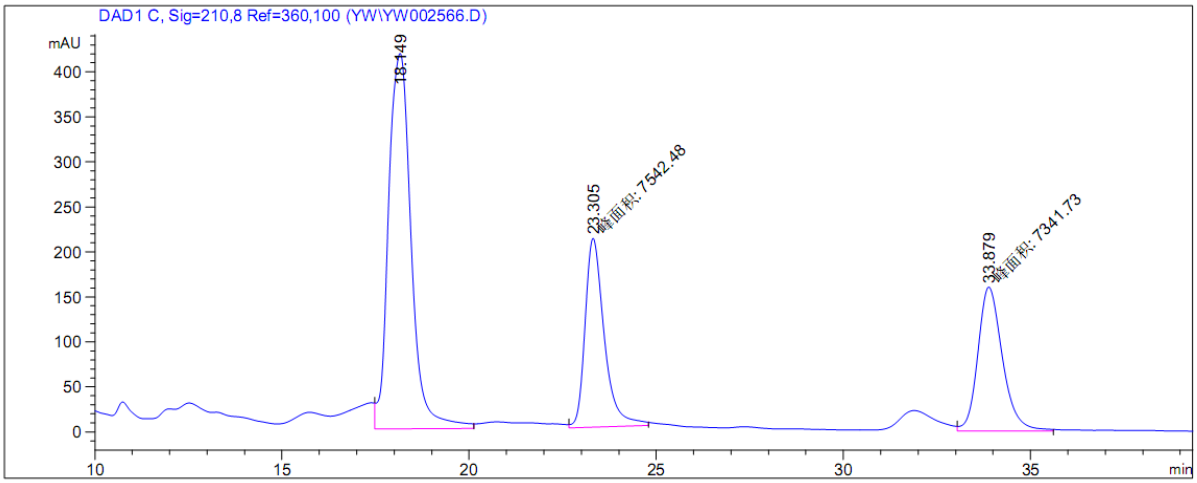
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.414	VV	0.3691	1.06109e4	446.78024	29.2202
2	16.185	VB	0.4131	1.20139e4	436.54669	33.0838
3	20.539	VB	0.4865	7004.39062	218.21170	19.2886
4	23.804	BB	0.5203	6684.43115	196.80370	18.4075



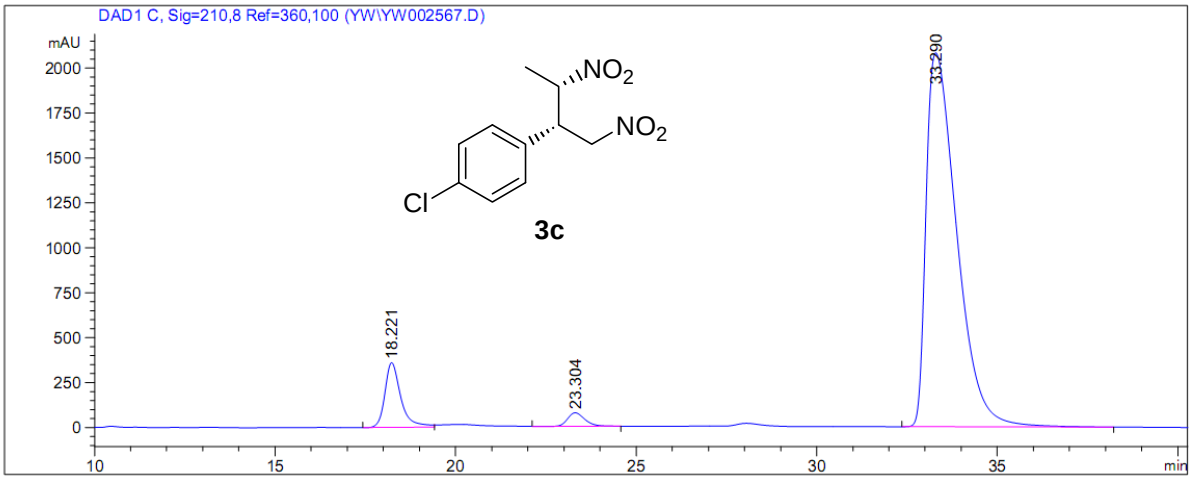
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.414	VV	0.3729	4046.06641	168.04848	5.3996
2	16.204	VB	0.4552	815.51361	25.90995	1.0883
3	20.534	MM	0.4895	1505.77625	51.27092	2.0095
4	23.397	VB	0.6534	6.85651e4	1608.10059	91.5025

1-Chloro-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3c) (Table 3, entry 3)



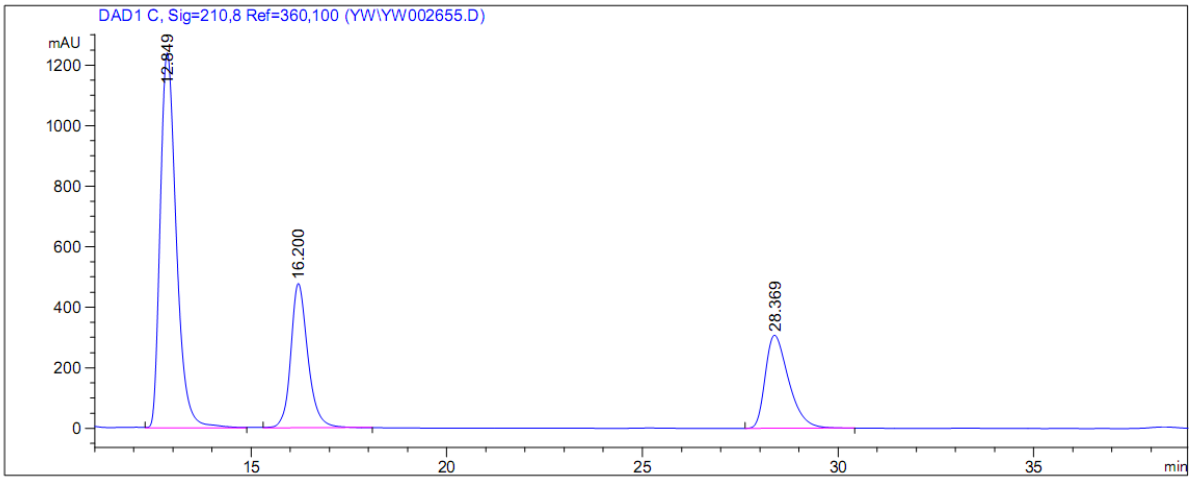
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.149	VV	0.6643	1.76241e4	417.62024	54.2142
2	23.305	MM	0.5978	7542.48047	210.29138	23.2017
3	33.879	MM	0.7643	7341.72949	160.09258	22.5841



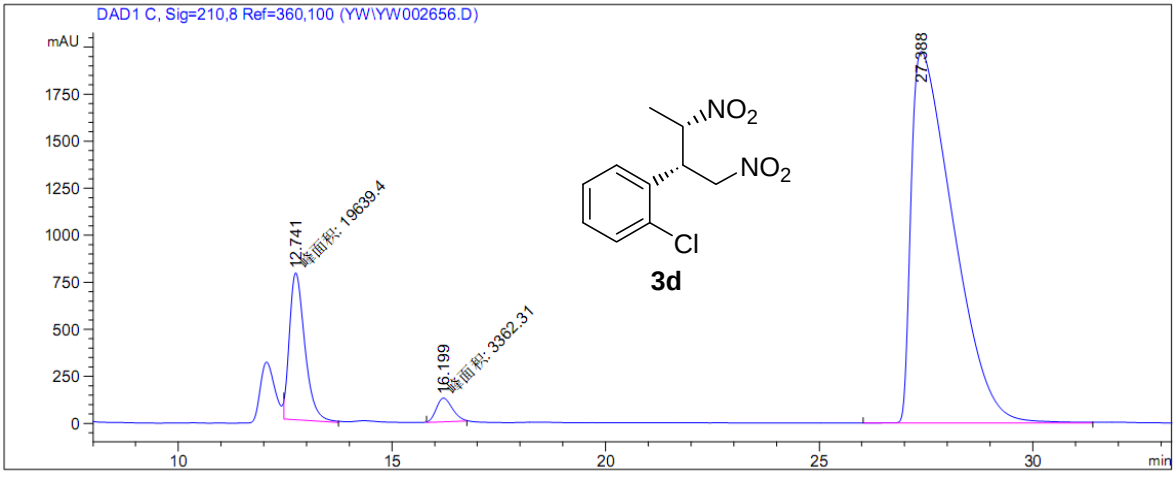
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.221	VV	0.4648	1.11553e4	360.71475	8.1774
2	23.304	VB	0.5328	2719.52051	76.85118	1.9935
3	33.290	BB	0.9111	1.22542e5	2080.75537	89.8291

1-Chloro-2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3d) (Table 3, entry 4)



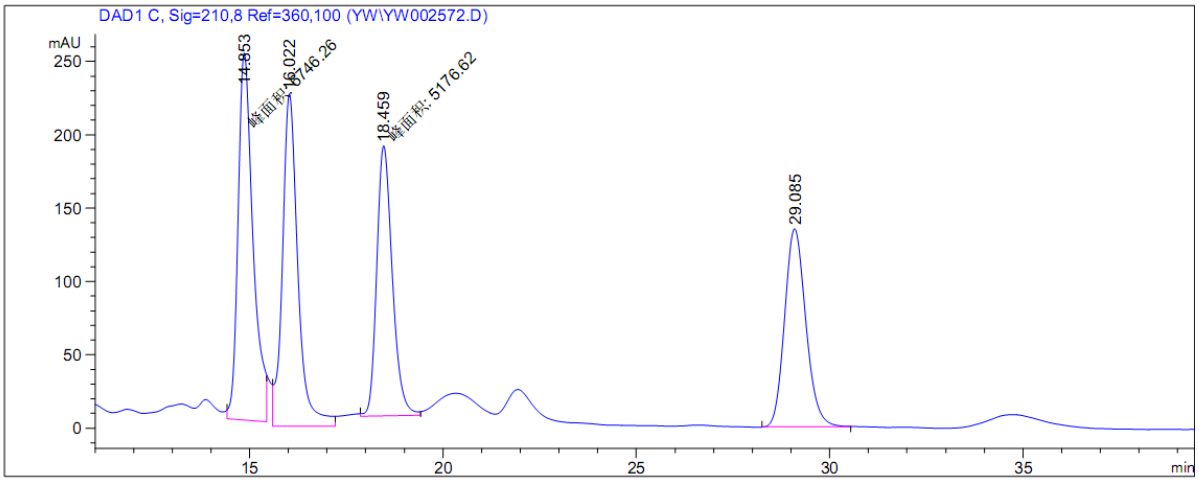
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.849	VB	0.4464	3.55272e4	1239.37842	56.5099
2	16.200	BB	0.4593	1.45279e4	477.07352	23.1083
3	28.369	BB	0.6378	1.28138e4	307.69827	20.3818



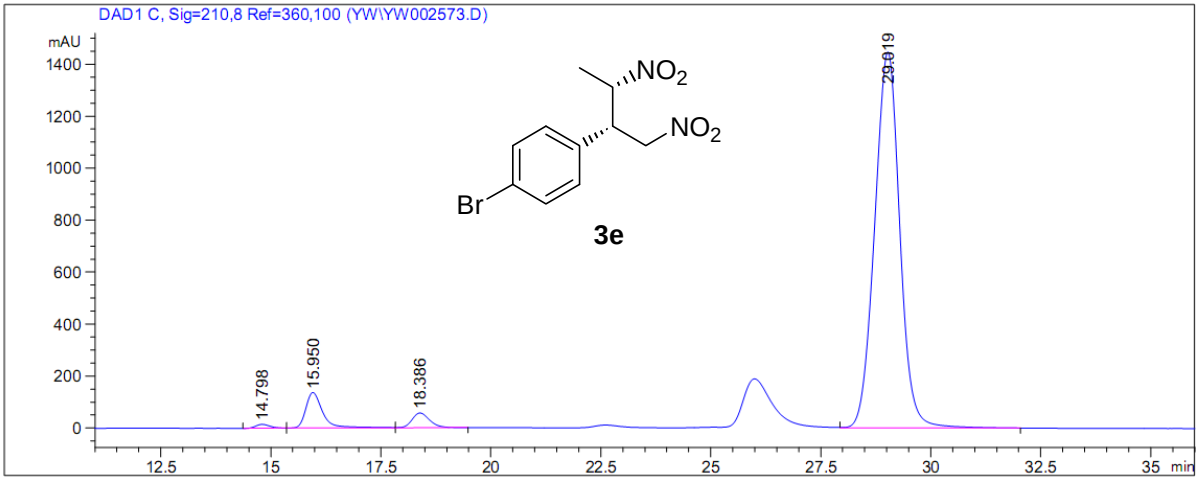
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.741	MM	0.4182	1.96394e4	782.66382	12.4378
2	16.199	MM	0.4402	3362.31030	127.29000	2.1294
3	27.388	BV	1.0645	1.34900e5	1975.93774	85.4329

1-Bromo-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3e) (Table 3, entry 5)



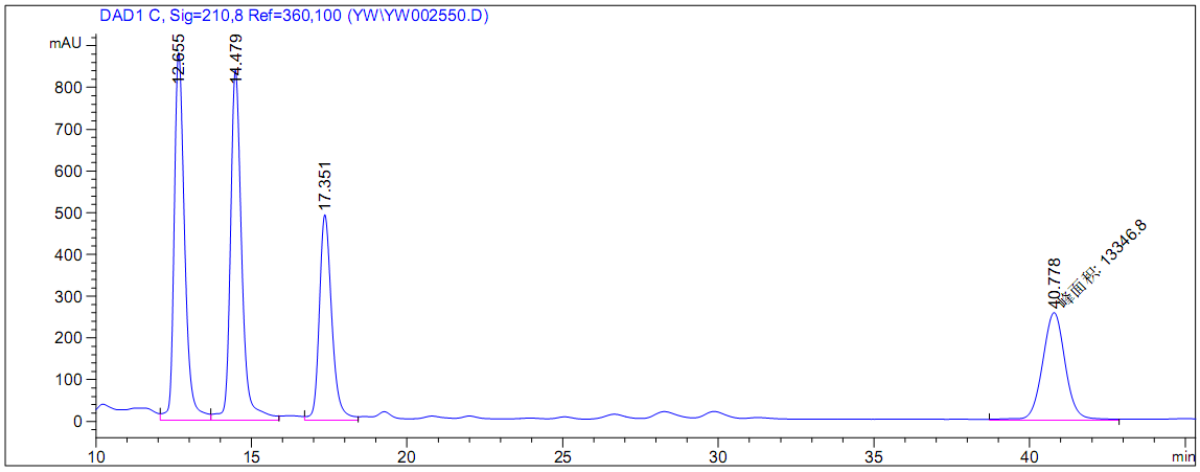
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.853	MM	0.4486	6746.26318	250.61475	28.8065
2	16.022	VB	0.4167	6314.20898	226.87080	26.9617
3	18.459	MM	0.4681	5176.62305	184.31537	22.1042
4	29.085	BB	0.5911	5182.10986	135.23743	22.1276



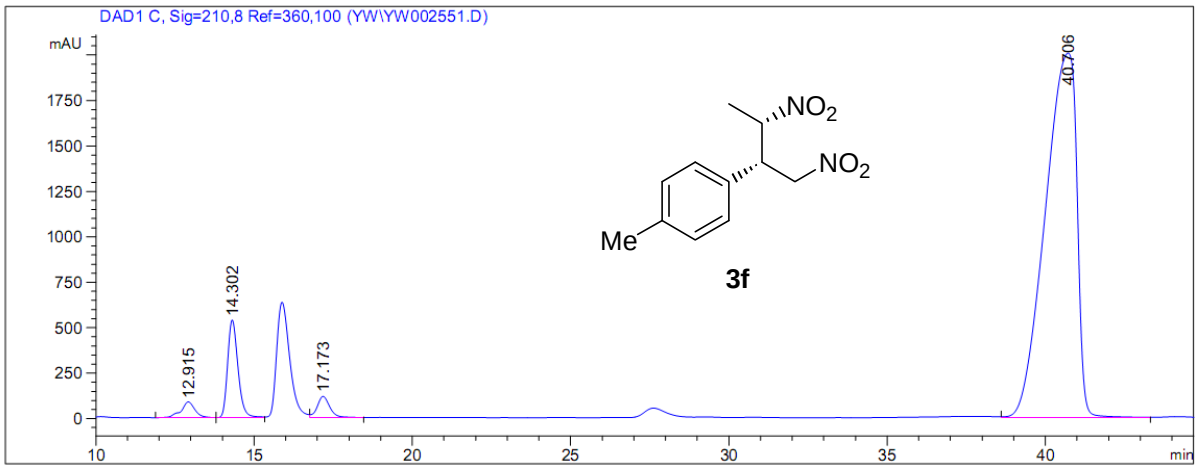
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.798	BV	0.3575	350.94824	15.19030	0.5559
2	15.950	VV	0.4091	3730.29224	137.24399	5.9084
3	18.386	VB	0.4323	1614.28442	57.37154	2.5569
4	29.019	VB	0.6110	5.74397e4	1447.40149	90.9789

1-Methyl-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3f) (Table 3, entry 6)



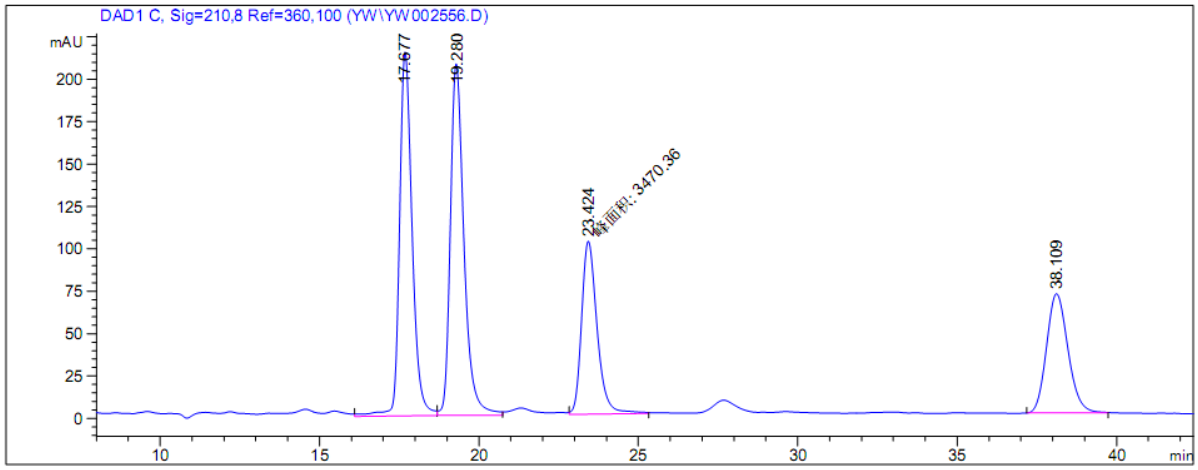
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.655	VV	0.3623	2.07270e4	881.71478	30.0401
2	14.479	VV	0.3869	2.12093e4	838.93195	30.7392
3	17.351	VV	0.4291	1.37146e4	492.12997	19.8769
4	40.778	MM	0.8615	1.33468e4	258.19855	19.3439



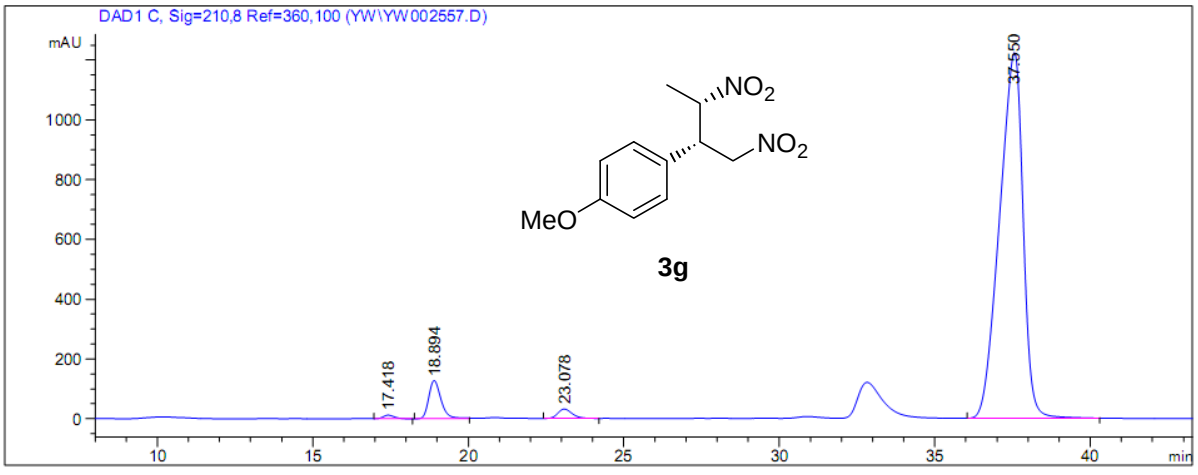
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.915	VV	0.4502	2665.20020	86.81057	1.6901
2	14.302	VV	0.3539	1.22419e4	537.14301	7.7630
3	17.173	VB	0.4235	3241.14380	116.87358	2.0553
4	40.706	VV	1.0958	1.39548e5	2005.44519	88.4917

1-Methoxy-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3g) (Table 3, entry 7)



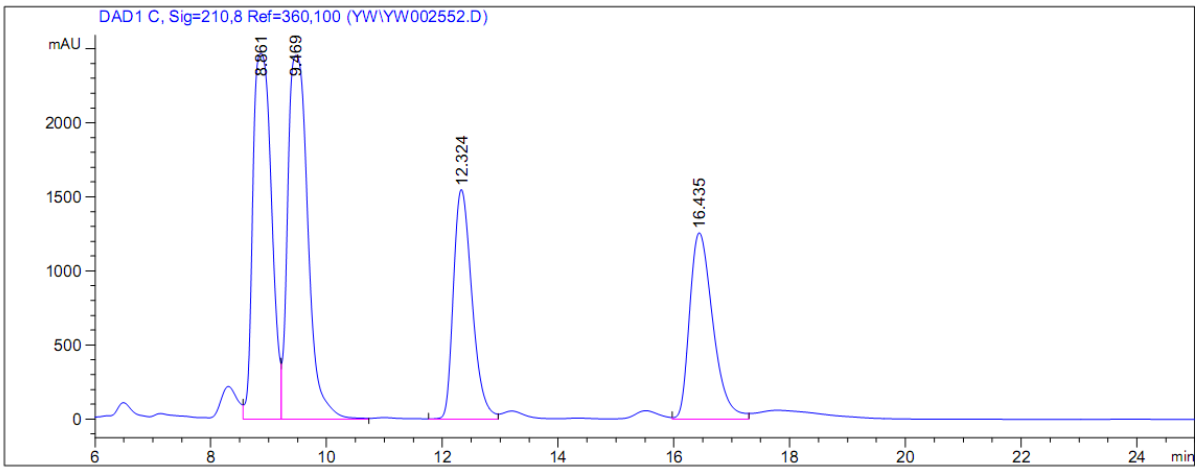
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.677	VV	0.4172	5907.56934	214.59361	31.3220
2	19.280	VV	0.4509	6167.34766	207.43471	32.6993
3	23.424	MM	0.5661	3470.36206	102.16521	18.3999
4	38.109	BB	0.7290	3315.50098	70.45744	17.5788



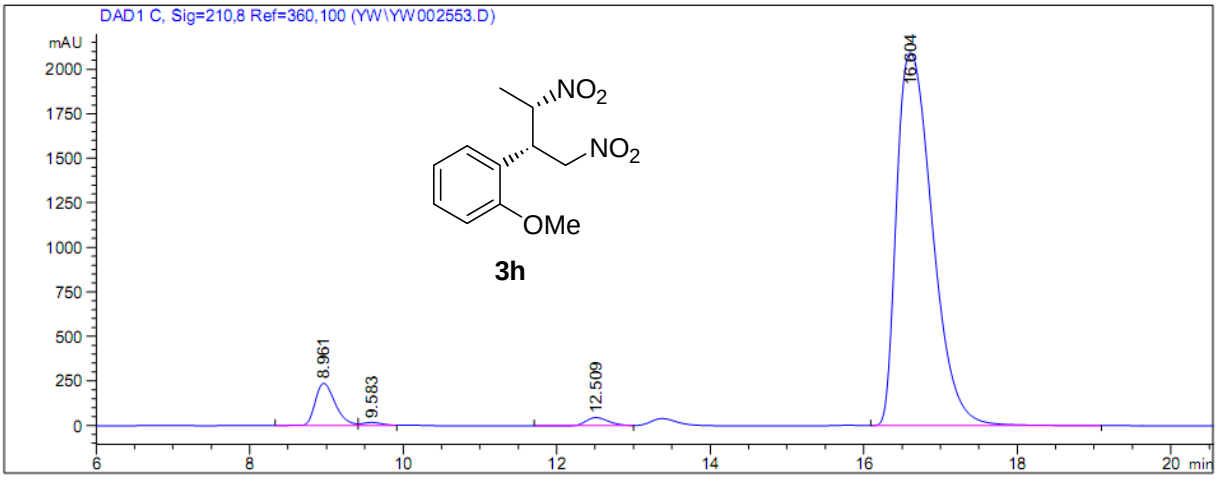
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.418	VB	0.3939	311.10349	12.18189	0.4500
2	18.894	BB	0.4223	3529.77222	127.77267	5.1061
3	23.078	BB	0.4969	1028.53662	31.83606	1.4879
4	37.550	BB	0.8166	6.42589e4	1223.69336	92.9560

1-Methoxy-2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3h) (Table 3, entry 8)



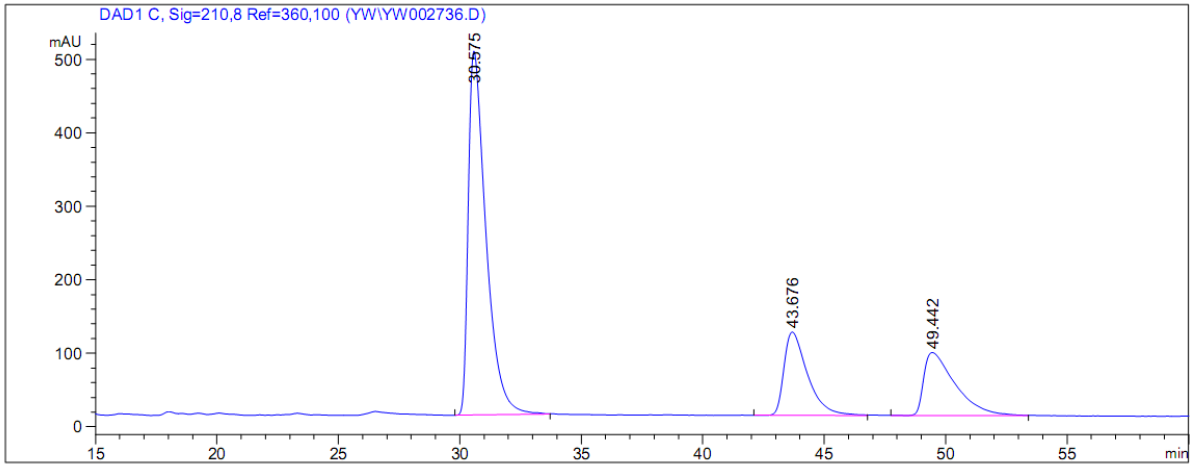
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.861	VV	0.3612	5.53107e4	2470.89795	29.8567
2	9.469	VV	0.3840	5.98385e4	2458.26416	32.3008
3	12.324	VV	0.3492	3.47356e4	1551.63721	18.7502
4	16.435	VV	0.4356	3.53693e4	1259.58252	19.0923



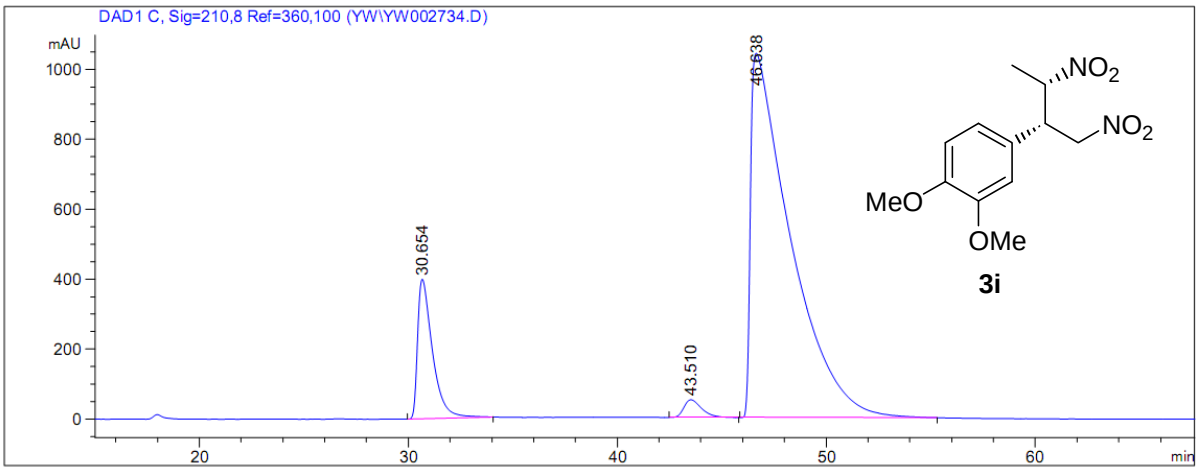
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.961	VV	0.2822	4382.54248	238.68210	5.9615
2	9.583	VV	0.2894	363.52969	19.15360	0.4945
3	12.509	VV	0.3241	969.98822	46.35315	1.3195
4	16.604	VB	0.5097	6.77976e4	2094.43115	92.2245

1,2-Dimethoxy-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]benzene (3i) (Table 3, entry 9)



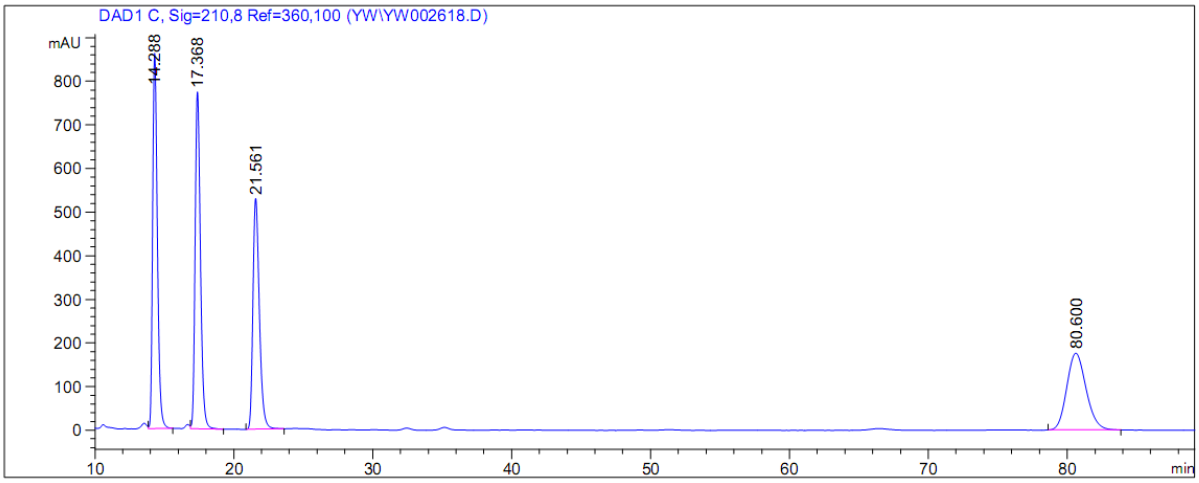
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.575	BB	0.7574	2.51719e4	494.92450	61.7300
2	43.676	VB	1.0256	7724.61572	113.56469	18.9434
3	49.442	BB	1.3645	7880.88770	86.05252	19.3266



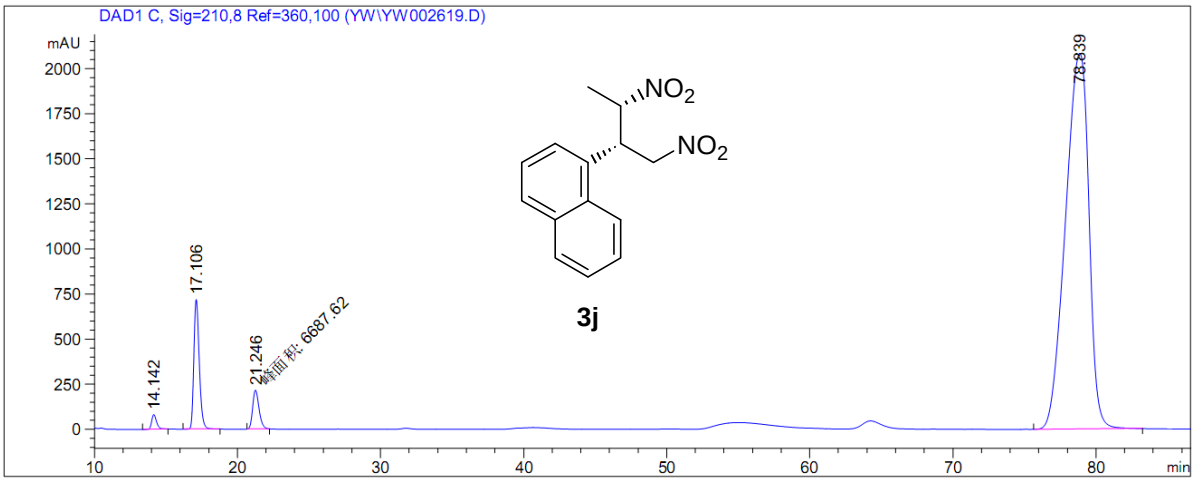
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.654	BB	0.7359	1.98411e4	399.16238	12.3003
2	43.510	BB	0.9117	2994.83789	50.51318	1.8566
3	46.638	BB	1.7829	1.38470e5	1041.65942	85.8430

1-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]naphthalene (3j) (Table 3, entry 10)



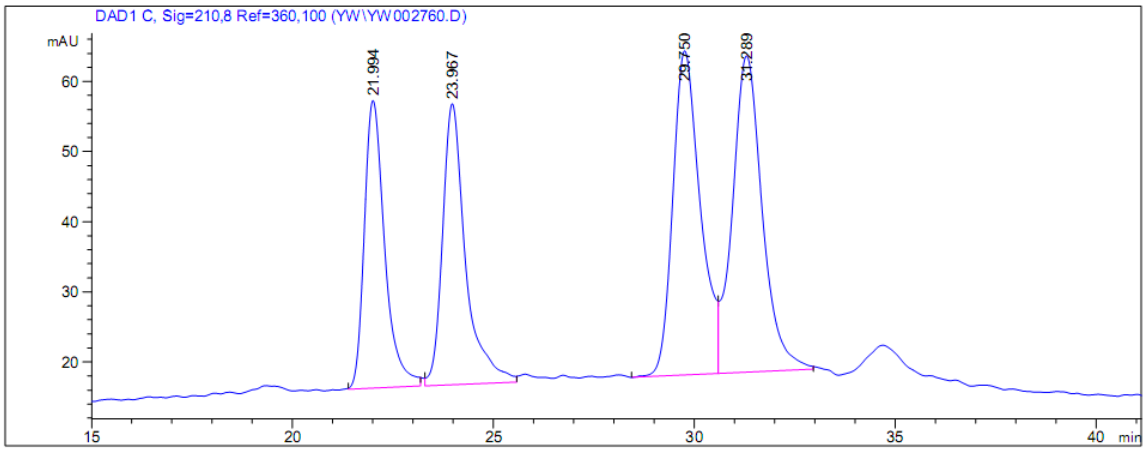
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.288	VB	0.3650	2.04378e4	860.79376	27.2197
2	17.368	VB	0.4105	2.05530e4	772.23706	27.3732
3	21.561	BB	0.4949	1.70013e4	529.02228	22.6428
4	80.600	BB	1.5063	1.70924e4	176.42952	22.7643



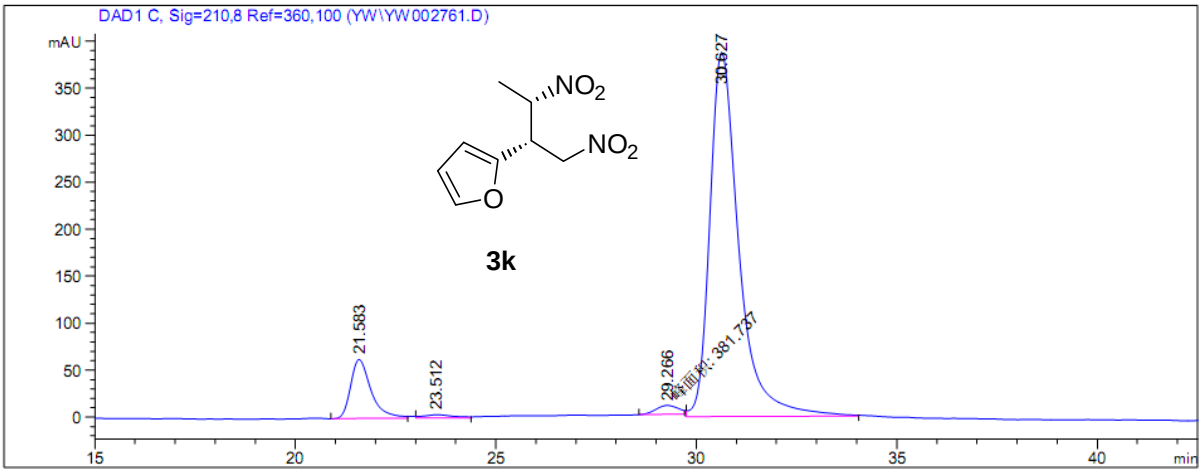
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.142	BB	0.3669	1947.73486	81.47685	0.7364
2	17.106	BB	0.4038	1.89646e4	718.87689	7.1703
3	21.246	MM	0.5164	6687.62451	215.84418	2.5285
4	78.839	BB	1.7989	2.36888e5	2082.81982	89.5648

2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]furan (3k) (Table 3, entry 11)



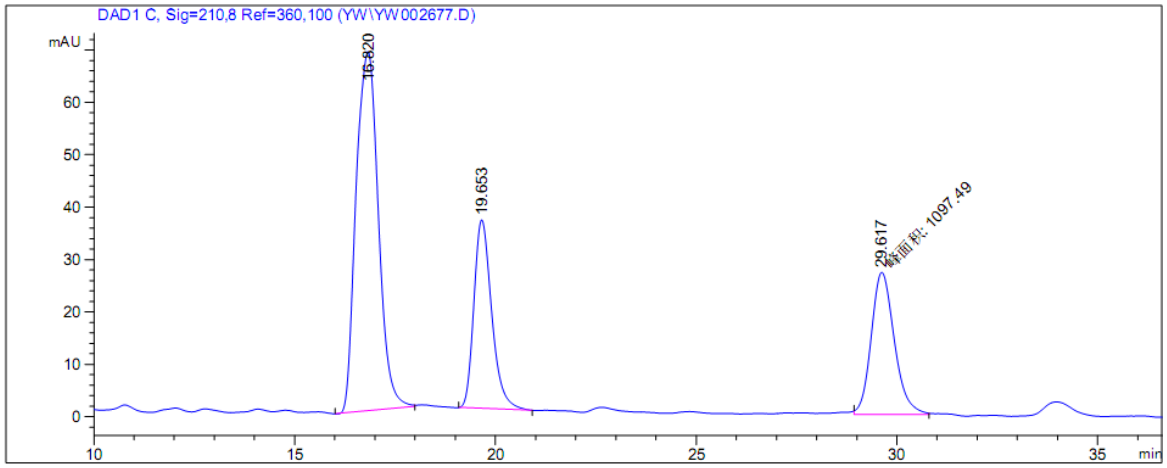
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.994	BB	0.5378	1448.26074	41.02683	19.0850
2	23.967	BB	0.5964	1603.10693	40.09898	21.1255
3	29.750	VV	0.7161	2204.09546	46.23941	29.0453
4	31.289	VB	0.7790	2333.01123	45.14212	30.7441



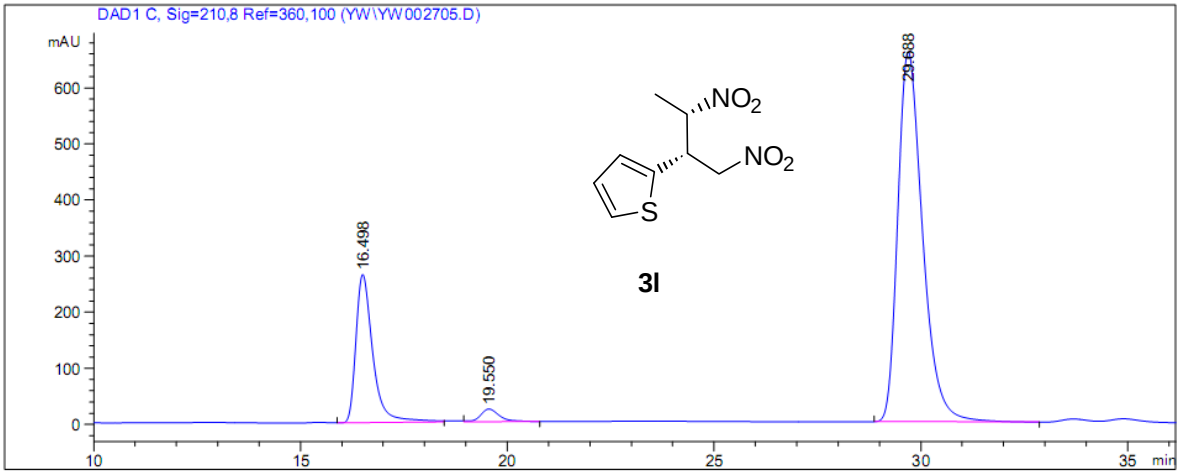
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.583	VB	0.5391	2252.11865	62.99090	10.0345
2	23.512	BV	0.7255	211.84442	3.77070	0.9439
3	29.266	MM	0.6572	381.73734	9.68079	1.7009
4	30.627	VB	0.7597	1.95980e4	387.70859	87.3207

2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)propyl]thiophene (3l) (Table 3, entry 12)



(*racemic*)

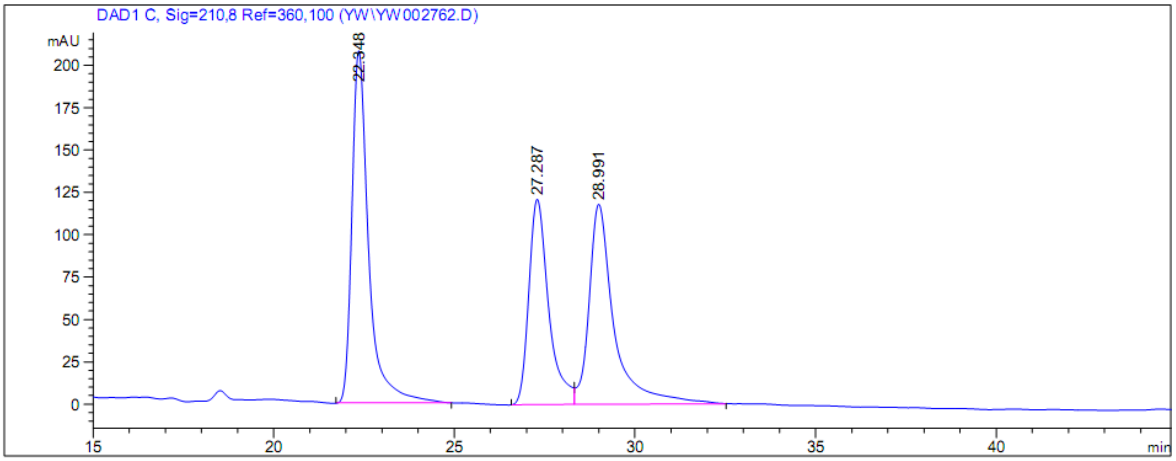
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.820	BB	0.6262	2646.73291	68.58443	54.5435
2	19.653	BB	0.4753	1108.28845	35.98270	22.8395
3	29.617	MM	0.6718	1097.49280	27.22573	22.6170



3l

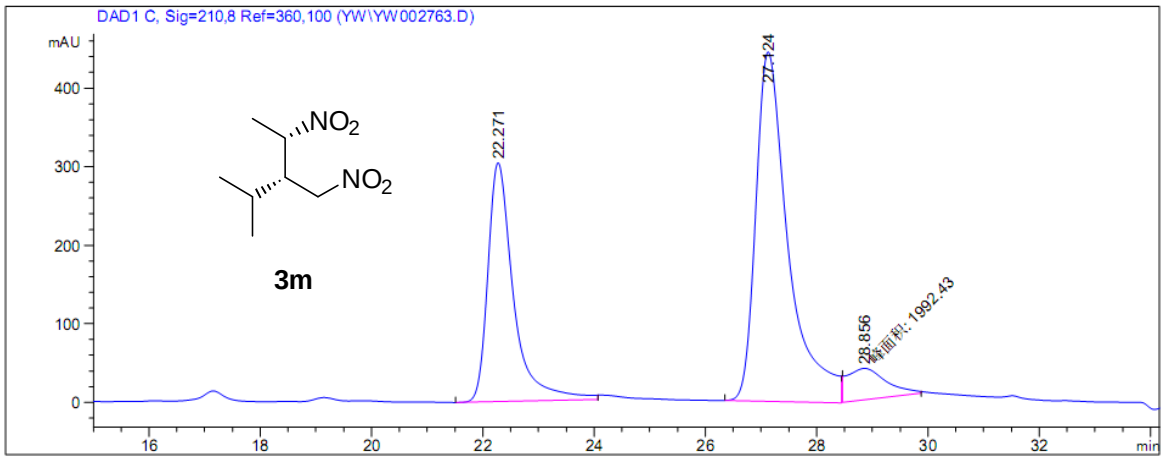
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.498	VB	0.4338	7555.92871	264.05371	21.0850
2	19.550	BB	0.4867	745.31531	22.96297	2.0798
3	29.688	BB	0.6429	2.75343e4	659.78186	76.8352

(3*S*,4*S*)-2-Methyl-4-nitro-3-(nitromethyl)pentane (3m) (Table 3, entry 13)



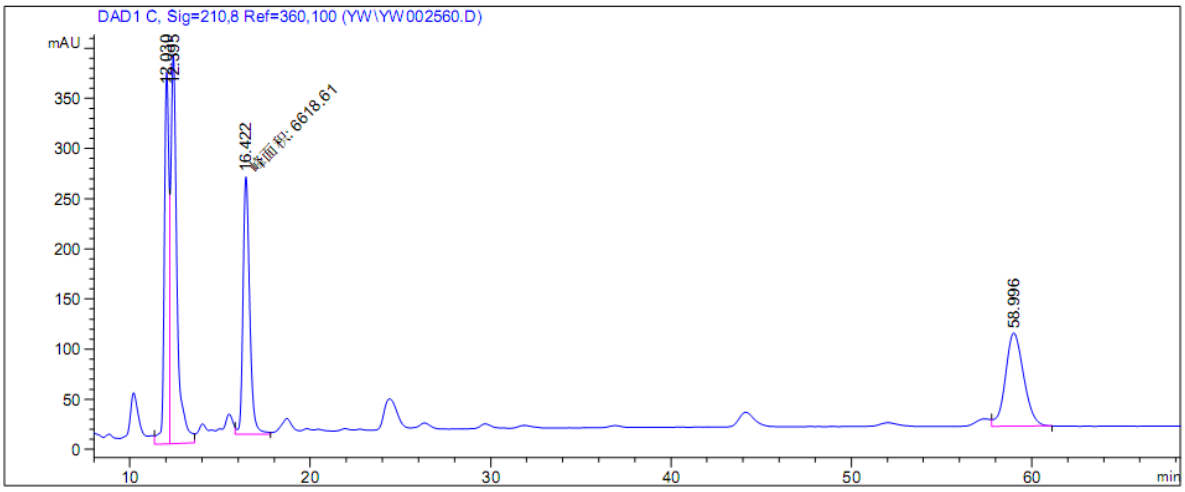
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.348	BB	0.4807	6715.84912	208.01157	39.3922
2	27.287	BV	0.5743	4639.11328	121.26227	27.2110
3	28.991	VB	0.6981	5693.70801	118.18575	33.3968



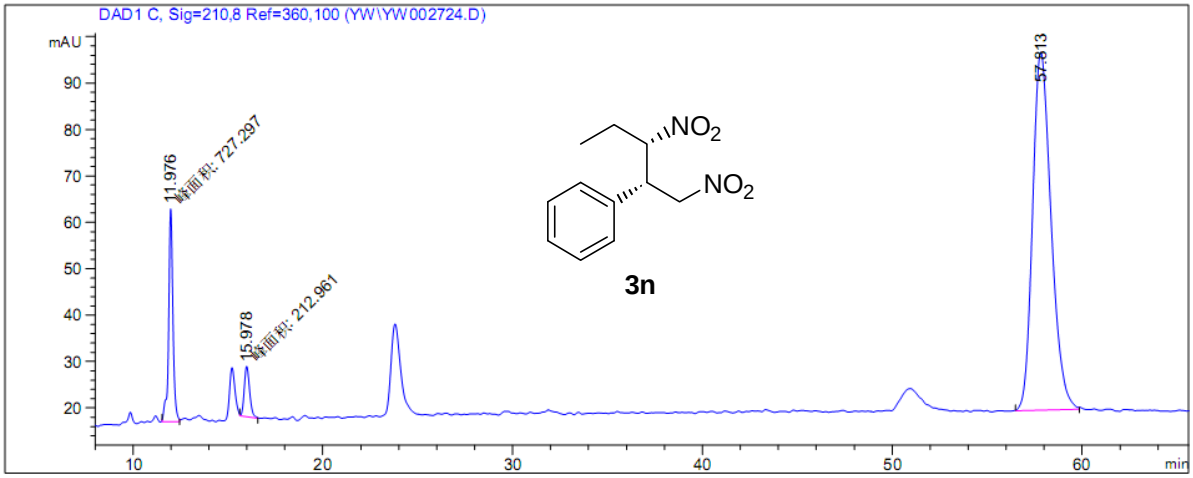
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.271	VB	0.4791	9780.90137	304.17566	32.7688
2	27.124	BV	0.6056	1.80749e4	445.25870	60.5560
3	28.856	MM	0.8197	1992.42896	40.50911	6.6752

[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3n) (Table 3, entry 14)



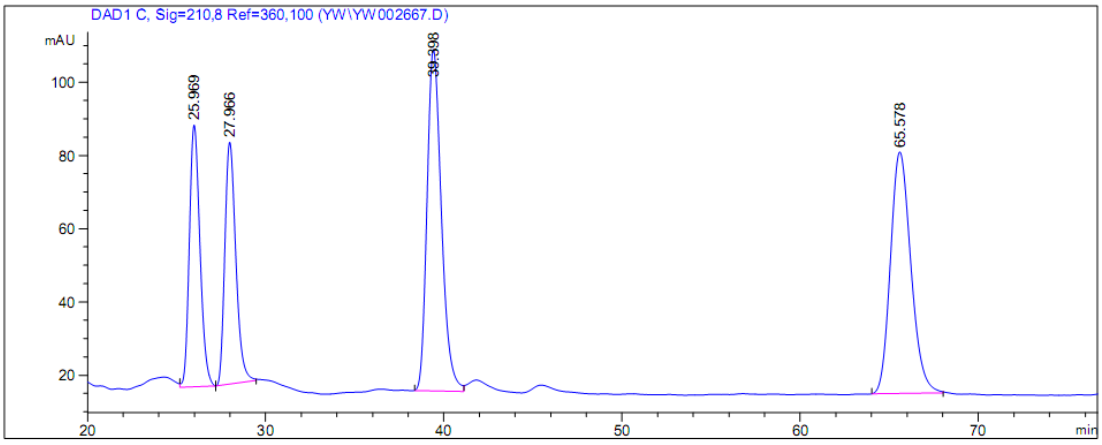
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.030	VV	0.2760	6742.04639	371.06805	23.1018
2	12.395	VV	0.3501	9260.43066	388.42801	31.7311
3	16.422	MM	0.4296	6618.60645	256.76227	22.6788
4	58.996	VB	1.0869	6562.96582	93.04486	22.4882



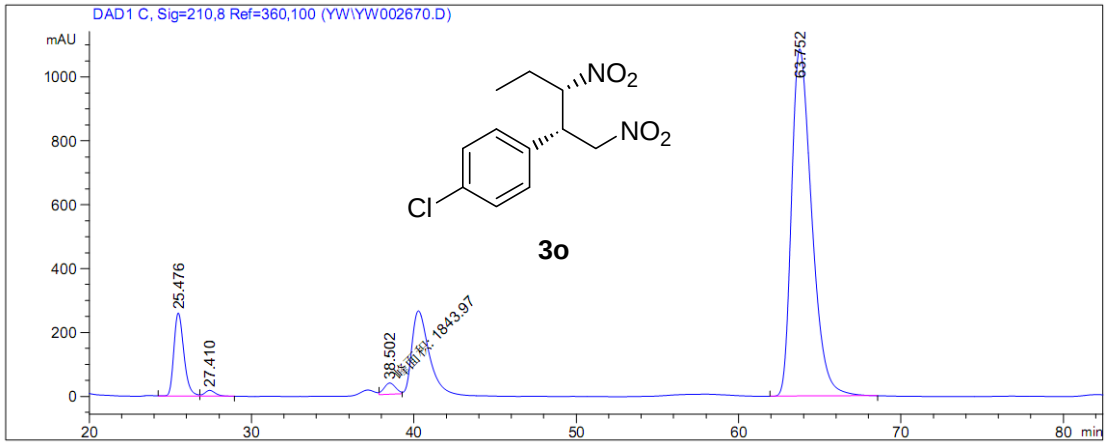
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.976	MM	0.2640	727.29706	45.91275	11.7671
2	15.978	MM	0.3265	212.96124	10.87026	3.4455
3	57.813	BB	1.0442	5240.51660	77.17812	84.7874

1-Chloro-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3o) (Table 3, entry15)



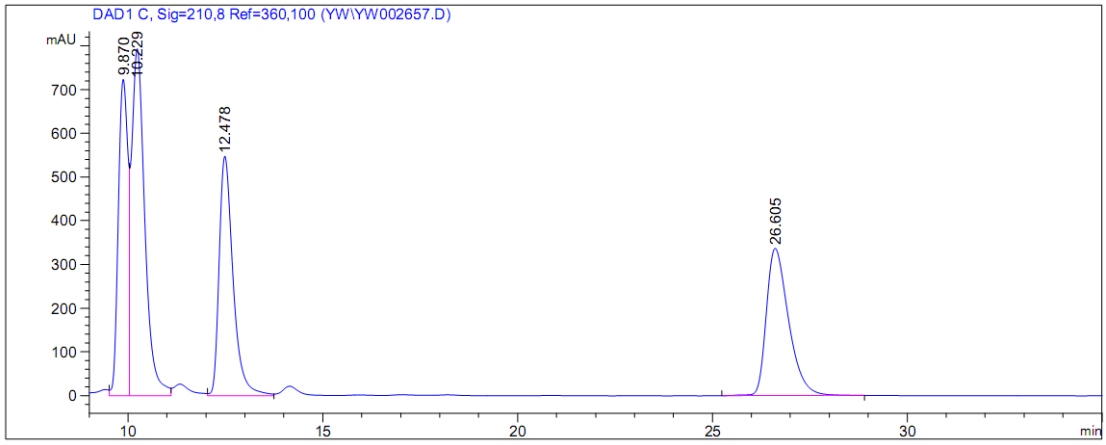
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.969	VV	0.6430	2961.60278	71.53230	18.1758
2	27.966	VB	0.6696	2841.75049	66.09180	17.4402
3	39.398	BB	0.8574	5222.30859	93.25040	32.0500
4	65.578	BB	1.2269	5268.57275	66.02775	32.3340



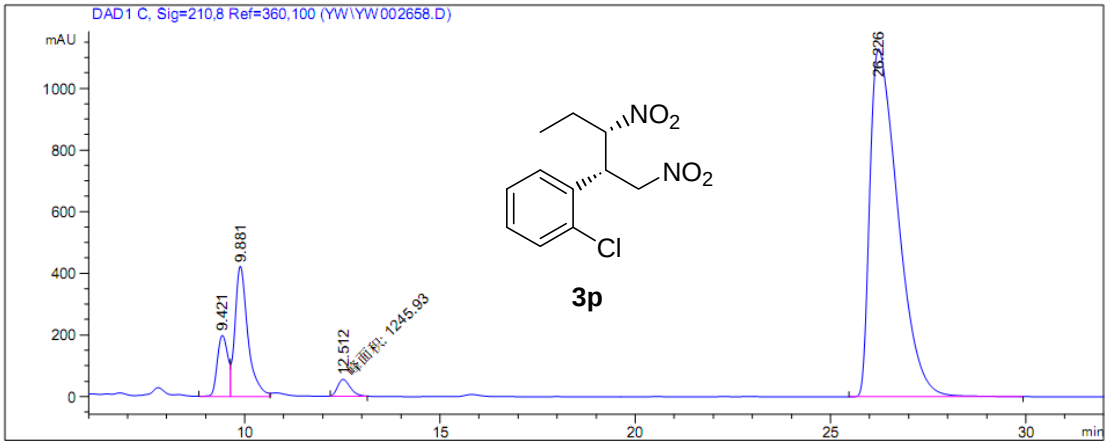
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.476	VV	0.6628	1.12448e4	260.92331	10.3888
2	27.410	VB	0.7102	879.22180	18.64414	0.8123
3	38.502	MM	0.8506	1843.97168	36.13269	1.7036
4	63.752	VB	1.3309	9.42718e4	1087.99536	87.0953

1-Chloro-2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3p) (Table 3, entry16)



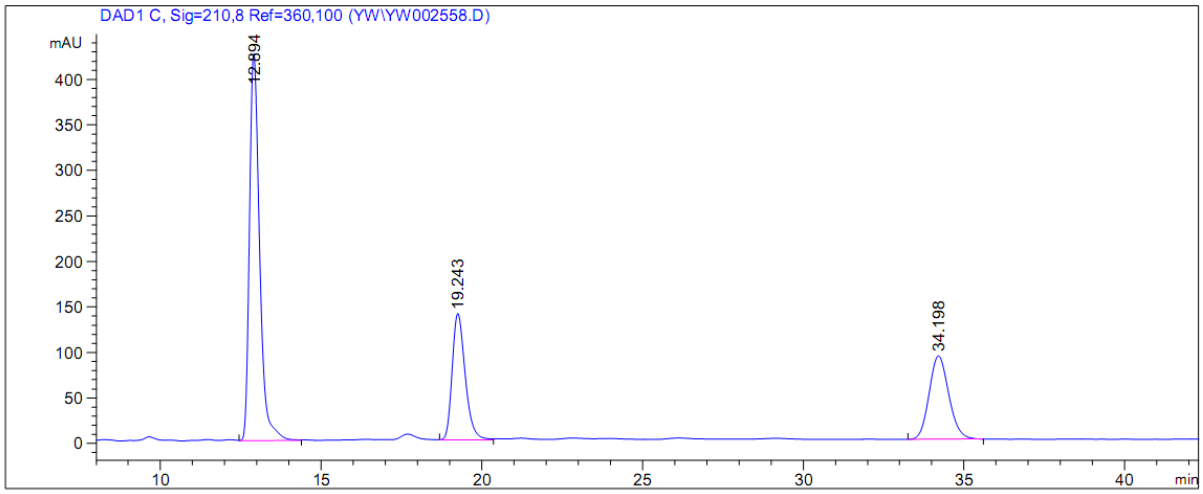
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.554	VV	0.2262	1.61008e4	1090.54004	21.0127
2	8.841	VV	0.3035	2.46118e4	1209.01758	32.1200
3	10.378	VV	0.3211	1.77539e4	845.22968	23.1700
4	20.349	MM	0.5328	1.81580e4	568.01459	23.6974



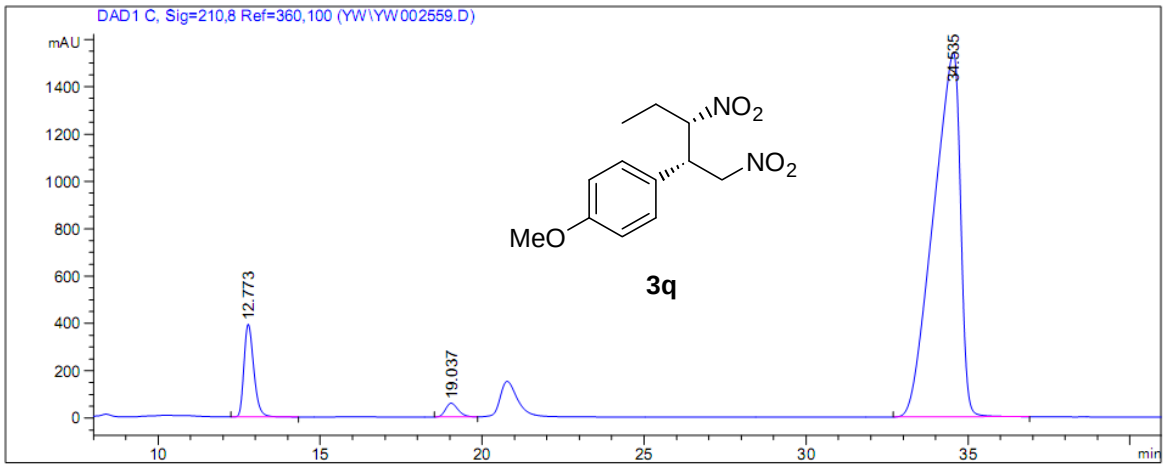
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.421	VV	0.2949	3736.90186	199.17834	5.2556
2	9.881	VV	0.3451	9760.63379	423.24365	13.7274
3	12.512	MM	0.3775	1245.93091	55.01082	1.7523
4	26.226	BB	0.7905	5.63600e4	1128.75293	79.2648

1-Methoxy-4-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3q) (Table 3, entry17)



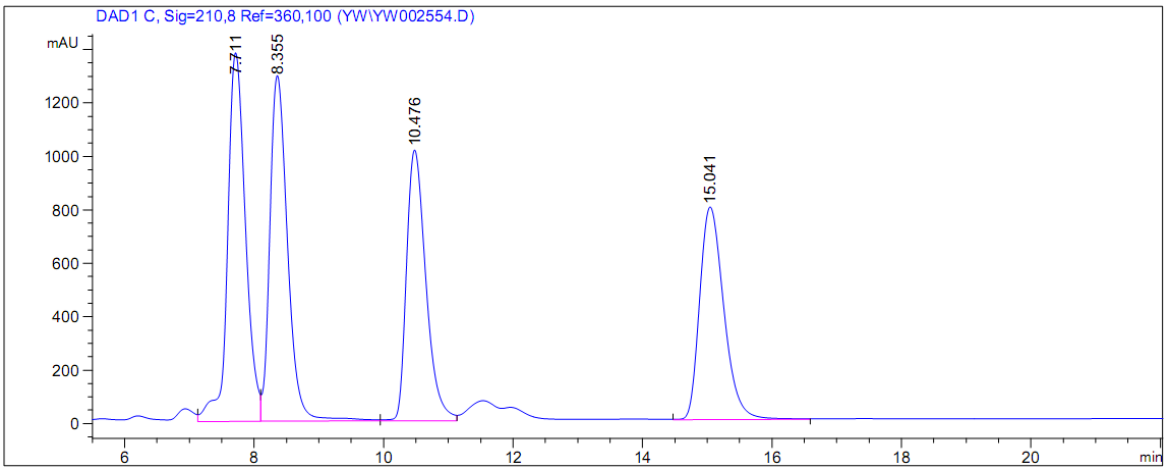
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.894	VB	0.3366	9360.00195	425.55746	54.5418
2	19.243	BB	0.4329	3910.50049	138.72722	22.7869
3	34.198	BB	0.6601	3890.64697	91.50182	22.6712



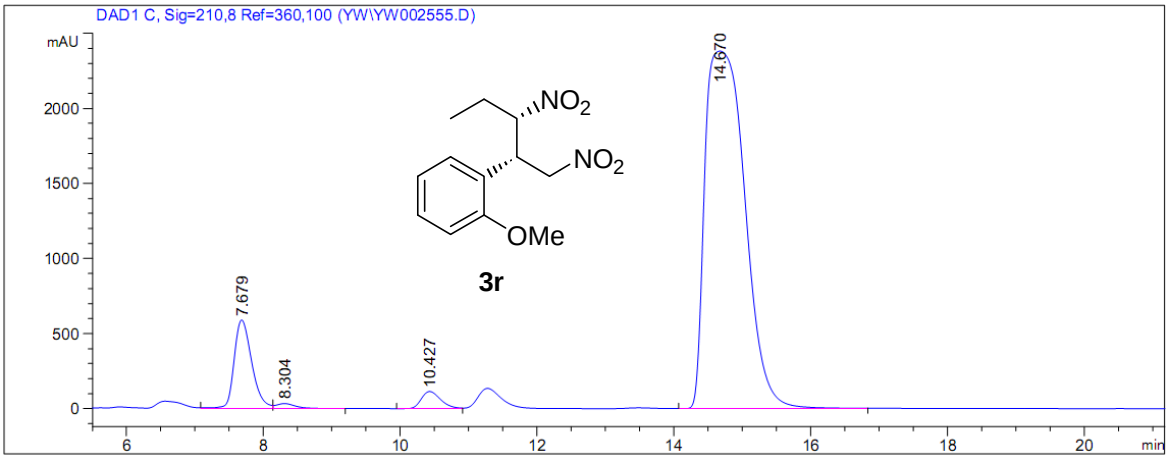
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.773	VB	0.3272	8305.14258	391.93497	8.3810
2	19.037	BV	0.4245	1612.53796	58.70742	1.6273
3	34.535	BB	0.9154	8.91771e4	1540.39868	89.9917

1-Methoxy-2-[(1*S*,2*S*)-2-nitro-1-(nitromethyl)butyl]benzene (3r) (Table 3, entry18)



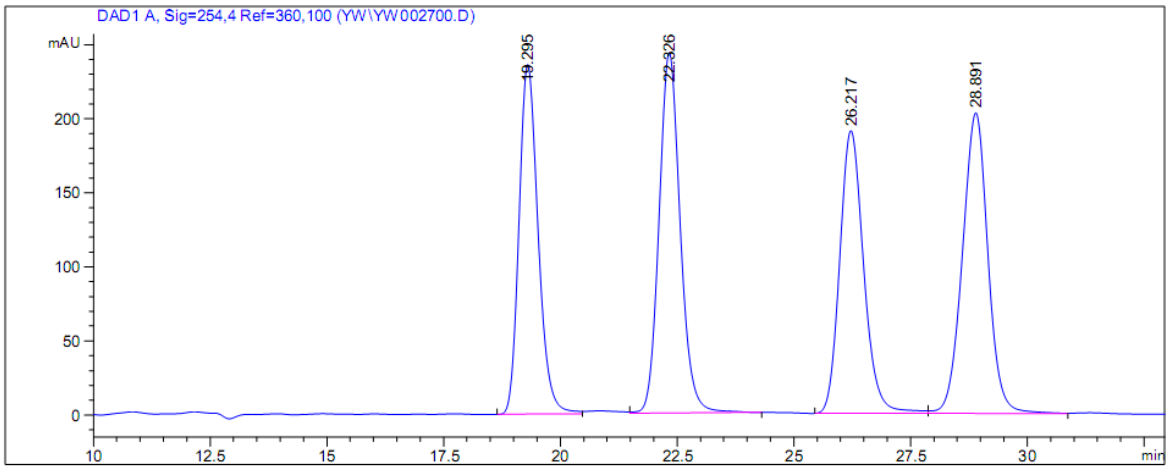
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.711	VV	0.2973	2.66671e4	1380.98596	28.5507
2	8.355	VV	0.2951	2.47724e4	1295.15588	26.5222
3	10.476	VV	0.3237	2.11907e4	1014.38397	22.6875
4	15.041	VB	0.4082	2.07725e4	796.74072	22.2397



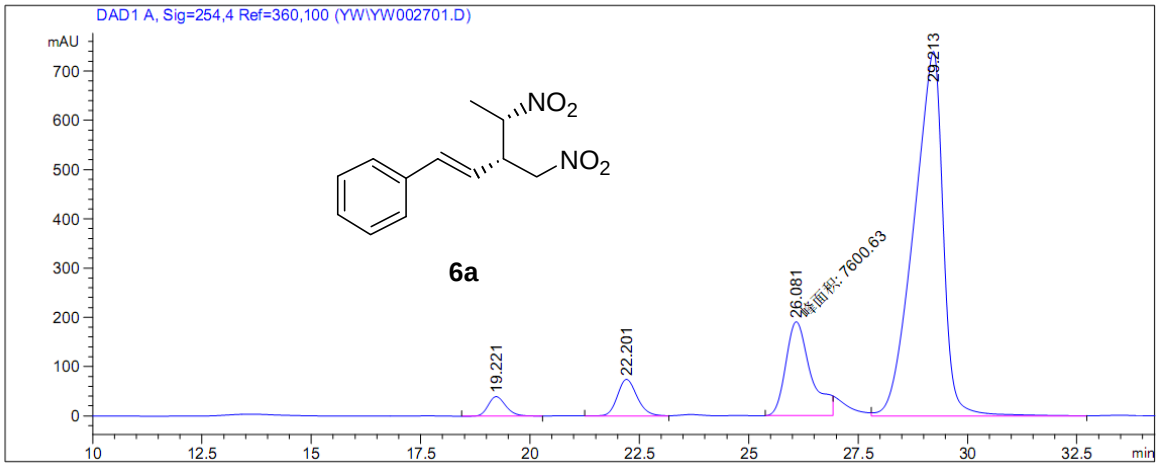
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.679	VV	0.2797	1.06288e4	591.22729	9.6402
2	8.304	VB	0.3080	720.74457	34.46310	0.6537
3	10.427	VV	0.3065	2266.71606	114.74529	2.0559
4	14.670	VV	0.6574	9.66387e4	2381.38428	87.6502

[(1*E*,3*S*,4*S*)-4-nitro-3-(nitromethyl)-1-penten-1-yl]benzene (6a)



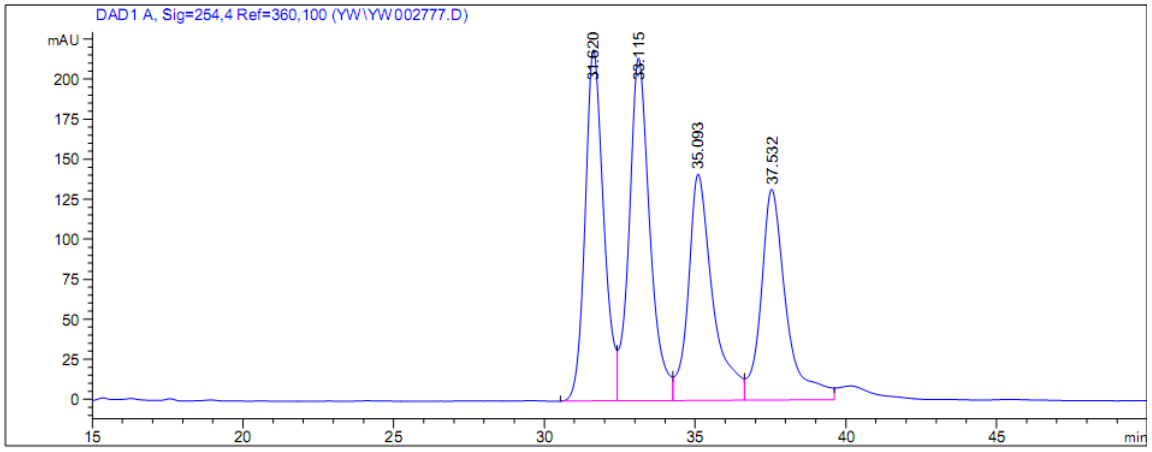
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.295	BV	0.4358	6718.58887	236.21274	23.1913
2	22.326	VB	0.4842	7688.96924	243.63316	26.5409
3	26.217	BV	0.5487	6819.81299	190.95496	23.5407
4	28.891	VV	0.5846	7742.93506	203.19475	26.7271



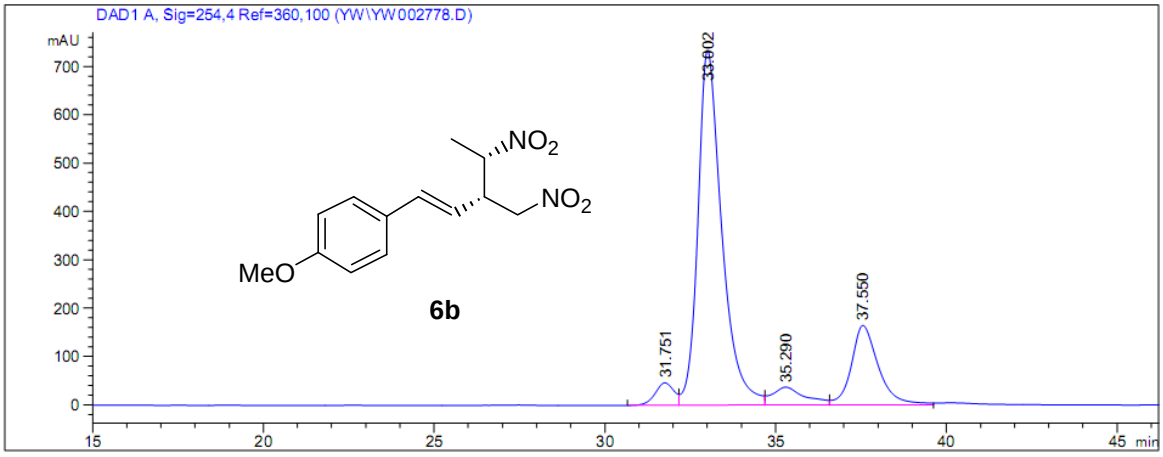
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.221	VB	0.4390	1127.67395	39.75204	2.4694
2	22.201	VV	0.4931	2388.38354	74.69344	5.2301
3	26.081	MM	0.6630	7600.62988	191.05316	16.6438
4	29.213	VB	0.6723	3.45497e4	740.48212	75.6567

1-Methoxy-4-[(1*E*,3*S*,4*S*)-4-nitro-3-(nitromethyl)-1-penten-1-yl]benzene (6b)



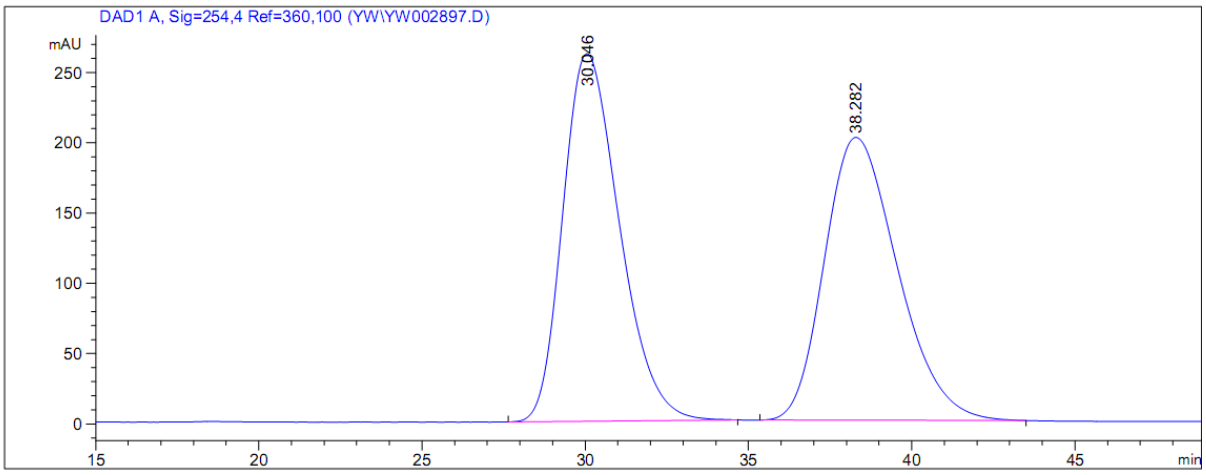
(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.620	BV	0.6440	9403.88770	219.43159	26.5964
2	33.115	VV	0.7102	1.02483e4	214.19907	28.9845
3	35.093	VV	0.8217	8024.64893	141.48724	22.6956
4	37.532	VV	0.8475	7680.95801	131.87622	21.7235



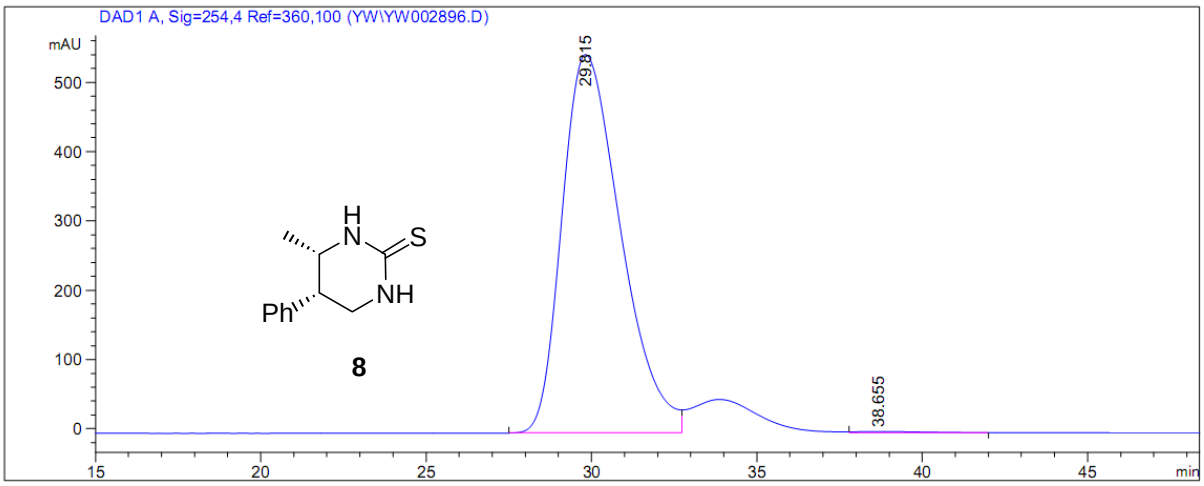
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.751	BV	0.5854	1795.97449	46.62074	3.6453
2	33.002	VV	0.7172	3.58262e4	734.34698	72.7158
3	35.290	VV	0.9353	2515.74365	37.47216	5.1062
4	37.550	VV	0.8146	9130.84668	164.75151	18.5327

(4*R*,5*R*)-tetrahydro-4-methyl-5-phenyl-2(1*H*)-pyrimidinethione (8)



(*racemic*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.046	BB	1.8559	3.15755e4	261.65881	50.1567
2	38.282	BB	2.4094	3.13782e4	201.43040	49.8433



8

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.815	BV	1.9526	6.74441e4	546.18695	99.6260
2	38.655	BB	1.7122	253.20485	1.74981	0.3740