Supporting Information

for

Supported bifunctional thioureas as recoverable and reusable catalysts for enantioselective nitro-Michael reactions

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Physical and spectral data for all the compounds. Copies of ^{1}H, ^{13}C NMR spectra, and HPLC traces for all compounds synthesized

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1. Compound characterization data

(S)-Diethyl 2-(2-nitro-1-phenylethyl)malonate (4aa).[1] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.1 Hz, 3H, $C\underline{H}_3$), 1.27 (t, *J* = 7.1 Hz, 3H, $C\underline{H}_3$), 3.82 (d, *J* = 9.3 Hz, 1H, $C\underline{H}CO_2Et$), 4.01 (q, *J* = 7.1 Hz, 2H, $C\underline{H}_2O$), 4.23 (m, 3H, $C\underline{H}_2O$ and $C\underline{H}$), 4.86 (dd, *J* = 13.1, 9.2 Hz, 1H, $C\underline{H}HNO_2$), 4.92 (dd, *J* = 13.1, 4.8 Hz, 1H, $CH\underline{H}NO_2$), 7.23-7.33 (m, 5H, $\underline{H}$ar). **HPLC** (Chiralpak AD-H, *n*-hexane/2-propanol = 80/20, 1.0 mL/min, λ = 220 nm); t_R = 10.0 min (minor, *R*), 24.6 min (major, *S*).

(*R*)-Dimethyl 2-methyl-2-(2-nitro-1-phenylethyl)malonate (4ab).[1] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.36 (s, 3H, $C\underline{H}_3$), 3.74 (s, 3H, $C\underline{H}_3O$), 3.79 (s, 3H, $C\underline{H}_3O$), 4.19 (dd, *J* = 9.9, 4.4 Hz, 1H, $C\underline{H}$), 5.05 (m, 2H, $C\underline{HH}NO_2$), 7.15-7.18 (m, 2H, $\underline{H}$ar), 7.27–7.32 (m, 3H, $\underline{H}$ar). **HPLC** (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 0.8 mL/min, λ = 220 nm); t_R = 15.0 min (major, *R*), 16.3 min (minor, *S*).

(*R*)-Diethyl 2-methyl-2-(2-nitro-1-phenylethyl)malonate (4ac).[2] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H, $C\underline{H}_3CH_2$); 1.29 (t, *J* = 7.2 Hz, 3H, $C\underline{H}_3CH_2$), 1.34 (s, 3H, $C\underline{H}_3$), 4.18 (m, 3H, CH_2 and $C\underline{H}$), 4.26 (q, *J* = 7.1 Hz, 2H, $C\underline{H}_2$), 5.05 (m, 2H, $C\underline{H}_2NO_2$), 7.17-7.21 (m, 2H, $\underline{H}$ar), 7.28-7.34 (m, 3H, $\underline{H}$ar). **HPLC** (Chiralpak AD-H, *n*-hexane/2-propanol = 98/2, 0.5 mL/min, λ = 220 nm); t_R = 18.9 min (minor, *S*), 20.8 min (major, *R*).

(*S*)-Dimethyl 2-chloro-2-(2-nitro-1-phenylethyl)malonate (4ad).[1] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.60 (s, 3H, $C\underline{H}_3$), 3.86 (s, 3H, $C\underline{H}_3$), 4.64 (dd, *J* = 10.3, 3.5 Hz, 1H, $C\underline{H}$), 5.01 (dd, *J* = 13.6, 10.3 Hz, 1H, $C\underline{H}HNO_2$), 5.22 (dd, *J* = 13.6, 3.5 Hz, 1H, $CH\underline{H}NO_2$), 7.22–7.41 (m, 5H, $\underline{H}$ar). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 90/10, 1.0 mL/min, λ = 220 nm); t_R = 11.3 min (major, *S*), 18.1 min (minor, *R*).

(*S*)-3-(2-Nitro-1-phenylethyl)pentane-2,4-dione (4ae).[3] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.92 (s, 3H, $C\underline{H}_3$), 2.27 (s, 3H, $C\underline{H}_3$), 4.22 (m, 1H, $C\underline{H}$), 4.37 (d, *J* = 10.8 Hz, 1H, $C\underline{H}COMe$), 4.59 (dd, *J* = 11.3, 3.9 Hz, 1H, $C\underline{H}HNO_2$), 4.63 (dd, *J* = 11.3, 6.8 Hz, 1H, $CH\underline{H}NO_2$), 7.15–7.17 (m, 2H, $\underline{H}$ar), 7.24–7.33 (m, 3H, $\underline{H}$ar). **HPLC** (Chiralpak AD–H, *n*-hexane/2-propanol = 85/15, 1.0 mL/min, λ = 220 nm); t_R = 9.5 min (major, *S*), 12.2 min (minor, *R*).

(*R*)-3-Methyl-3-(2-nitro-1-phenylethyl)pentane-2,4-dione (4af). Colorless solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 1.39 (s, 3H, CH$_3$), 2.00 (s, 3H, CH$_3$CO), 2.06 (s, 3H, CH$_3$CO), 4.19 (dd, *J* = 11.0, 3.5 Hz, 1H, CH), 4.75 (dd, *J* = 13.4, 3.6 Hz, 1H, CHHNO$_2$), 4.85 (dd, *J* = 13.4, 11.1 Hz, 1H, CHHNO$_2$), 7.14-7.16 (m, 2H, Har), 7.24-7.30 (m, 3H, Har). **^{13}C NMR** (75 MHz, CDCl$_3$) δ 18.3 (CH$_3$), 27.1, 28.8 (CH$_3$CO), 47.4 (CH), 67.7 (C), 76.8 (CH$_2$), 128.4, 128.8, 129.2 (CHar), 135.0 (Car), 205.6, 208.0 (CO). IR (ATR): 2987, 1714, 1698, 1551, 1358, 1207, 1087, 962, 705 cm^{-1}. **HRMS** calcd. for $C_{14}H_{17}NO_4$ + Na: 286.1050; found: 286.1053. $[\alpha]_D^{23}$ = +29.0 (c = 0.6, CHCl$_3$) for er 93:7. **HPLC** (Chiralpak AD–H, *n*-hexane/2-propanol = 95/5, 1.0 mL/min, λ = 210 nm); t$_R$ = 17.0 min (minor, *S*), 18.6 min (major, *R*).

(2*R*,3*R*)-Ethyl 2-acetyl-2-methyl-4-nitro-3-phenylbutanoate (4ag).[4] Colorless solid. Major diastereoisomer. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 1.20 (t, *J* = 7.2 Hz, 3H, CH$_3$CH$_2$), 1.44 (s, 3H, CH$_3$), 2.12 (s, 3H, CH$_3$CO), 3.98–4.17 (m, 2H, CH$_2$CH$_3$), 4.23 (m, 1H, CHPh), 4.94–4.97 (m, 2H, CHHNO$_2$), 7.20–7.24 (m, 2H, Har), 7.26–7.31 (m, 3H, Har). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 90/10, 0.8 mL/min, λ = 220 nm): t$_R$ (major diastereoisomer) =13.6 min (major, 2*R*,3*R*), 19.6 min (minor, 2*S*,3*S*).

(*S*)-Diethyl 2-(1-(4-chlorophenyl)-2-nitroethyl)malonate (4ba).[1] Colorless solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 1.06 (t, *J* = 7.2 Hz, 3H, CH$_3$), 1.24 (t, *J* = 7.1 Hz, 3H, CH$_3$), 3.76 (d, *J* = 9.2 Hz, 1H, CHCO$_2$Et), 4.01 (q, *J* = 7.1 Hz, 2H, CH$_2$O), 4.20 (m, 3H, CH$_2$O and CH), 4.81 (dd, *J* = 13.2, 9.3 Hz, 1H, CHHNO$_2$), 4.89 (dd, *J* = 13.2, 4.8 Hz, 1H, CHHNO$_2$), 7.17 (d, *J* = 8.5 Hz, 2H, Har), 7.28 (d, *J* = 8.5 Hz, 2H, Har). **HPLC** (Chiralpak AD–H, *n*-hexane/2-propanol = 70/30, 1.0 mL/min, λ = 220 nm); t$_R$ = 9.4 min (minor, *R*), 25.0 min (major, *S*).

(*S*)-Diethyl 2-(1-(4-fluorophenyl)-2-nitroethyl)malonate (4ca).[2] Colorless solid. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 1.09 (t, *J* = 7.2 Hz, 3H, CH$_3$), 1.28 (t, *J* = 7.2 Hz, 3H, CH$_3$), 3.79 (d, *J* = 9.3 Hz, 1H, CHCO$_2$Et), 4.04 (q, *J* = 7.1 Hz, 2H, CH$_2$O), 4.24 (m, 3H, CH$_2$O and CH), 4.83 (dd, *J* = 13.1, 9.4 Hz, 1H, CHHNO$_2$), 4.92 (dd, *J* = 13.1, 4.7 Hz, 1H, CHHNO$_2$), 7.02 (m, 2H, Har), 7.24 (m, 2H, Har). **HPLC** (Chiralpak AD–H, *n*-hexane/2-propanol = 80/20, 1.0 mL/min, λ = 220 nm); t$_R$ = 12.5 min (minor, *R*), 51.6 min (major, *S*).

(*S*)-Diethyl 2-(1-(4-methoxyphenyl)-2-nitroethyl)malonate (4da).[1] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.08 (t, *J* = 7.1 Hz, 3H, C$\underline{H}_3$), 1.27 (t, *J* = 7.1 Hz, 3H, C$\underline{H}_3$), 3.78 (s, 3H, C$\underline{H}_3$O), 3.79 (d, *J* = 10.0 Hz, 1H, C$\underline{H}$$CO_2$Et), 4.02 (q, *J* = 7.1 Hz, 2H, C$\underline{H}_2$O), 4.22 (m, 3H, C$\underline{H}_2$O and C$\underline{H}$), 4.82 (dd, *J* = 12.9, 9.3 Hz, 1H, C$\underline{H}$HNO_2), 4.89 (dd, *J* = 12.9, 4.8 Hz, 1H, C$\underline{H}$HNO_2), 6.84 (d, *J* = 8.7 Hz, 2H, $\underline{H}$ar), 7.16 (d, *J* = 8.7 Hz, 2H, $\underline{H}$ar). **HPLC** (Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, 1.0 mL/min, λ = 254 nm); t_R = 11.5 min (minor, *R*), 41.8 min (major, *S*).

(*S*)-Ethyl 1-((*R*)-2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (5aa).[5] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H, C$\underline{H}_3$), 1.80–2.09 (m, 4H, C$\underline{H}_2$), 2.36 (m, 2H, C$\underline{H}_2$CO), 4.07 (dd, *J* = 10.9, 3.8 Hz, 1H, C$\underline{H}$Ph), 4.21 (q, *J* = 7.1 Hz, 1H, C$\underline{H}$HCH_3), 4.22 (q, *J* = 7.1 Hz, 1H, CH$\underline{H}$$CH_3$), 5.01 (dd, *J* = 13.5, 11.0 Hz, 1H, C$\underline{H}$HNO_2), 5.17 (dd, *J* = 13.5, 3.7 Hz, 1H, CH$\underline{H}$$NO_2$), 7.20–7.35 (m, 5H, Har). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 80/20, 1.0 mL/min, λ = 220 nm); t_R (major diastereoisomer) = 9.2 min (major), 12.4 min (minor).

(*S*)-Ethyl 1-((*R*)-2-nitro-1-phenylethyl)-2-oxocyclohexanecarboxylate (5ab).[5] Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H, C$\underline{H}_3$), 1.44–1.74 (m, 4H, C$\underline{H}_2$), 2.00–2.12 (m, 2H, C$\underline{H}_2$), 2.42–2.54 (m, 2H, C$\underline{H}_2$CO), 4.00 (dd, *J* = 11.3, 3.2 Hz, 1H, C$\underline{H}$), 4.20 (m, 2H, OC$\underline{H}_2$), 4.79 (dd, *J* = 13.5, 11.4 Hz, 1H, C$\underline{H}$HNO_2), 5.06 (dd, *J* = 13.5, 3.3 Hz, 1H, CH$\underline{H}$$NO_2$), 7.14–7.17 (m, 2H, $\underline{H}$ar), 7.25–7.30 (m, 3H, $\underline{H}$ar). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 95/5, 1.0 mL/min, λ = 220 nm); t_R (major diastereoisomer) = 121.8 min (major), 15.4 min (minor).

(*S*)-Methyl 1-((*R*)-2-nitro-1-phenylethyl)-2-oxocycloheptanecarboxylate (5ac).[4] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.40–1.94 (m, 8H, C$\underline{H}_2$), 2.50–2.63 (m, 2H, C$\underline{H}_2$CO), 3.77 (s, 3H, C$\underline{H}_3$O), 4.06 (dd, *J* = 10.0, 4.2 Hz, 1H, C$\underline{H}$), 4.92 (dd, *J* = 13.6, 10.0 Hz, 1H, C$\underline{H}$HNO_2), 4.96 (dd, *J* = 13.6, 4.2 Hz, 1H, CH$\underline{H}$$NO_2$), 7.14–7.21 (m, 2H, $\underline{H}$ar), 7.28–7.34 (m, 3H, $\underline{H}$ar). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 95/5, 1.0 mL/min, λ = 220 nm); t_R (major diastereoisomer) = 14.6 min (major), 30.5 min (minor).

(*R*)-2-Acetyl-2-((*R*)-2-nitro-1-phenylethyl)cyclopentanone (5ad).[5] Colorless solid. Major diastereoisomer. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.72 (m, 3H), 1.98 (m, 1H), 2.19 (m, 1H), 2.32 (s, 3H, C$\underline{H}_3$), 2.57 (m, 1H, CH), 4.39 (dd, *J* = 11.5, 3.9 Hz, 1H, C$\underline{H}$Ph), 4.51 (dd, *J* = 13.6, 3.9 Hz, 1H, C$\underline{\mathrm{H}}$HNO$_2$), 4.86 (dd, *J* = 13.6, 11.5 Hz, 1H, CH$\underline{\mathrm{H}}$NO$_2$), 7.24-7.33 (m, 5H, $\underline{\mathrm{H}}$ar). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 70/30, 1.0 mL/min, λ= 220 nm); t$_R$ (major diastereoisomer) = 14.3 min (major), 44.9 min (minor).

(*R*)-3-acetyl-3-((*R*)-2-nitro-1-phenylethyl)dihydrofuran-2(3H)-one (5ae).[5] Colorless solid. Major diastereoisomer. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 2.23–2.32 (m, 1H), 2.49 (s, 3H, C$\underline{\mathrm{H}}_3$), 2.84 (ddd, *J* = 13.2, 7.8, 4.2 Hz, 1H), 3.85 (td, *J* = 8.9, 4.2 Hz, 1H, C$\underline{\mathrm{H}}$HO), 4.03 (dt, *J* = 8.9, 7.8 Hz, 1H, CH$\underline{\mathrm{H}}$O), 4.49–4.56 (m, 2H, C$\underline{\mathrm{H}}$HNO$_2$ and C$\underline{\mathrm{H}}$Ph), 4.85 (dd, *J* = 12.6, 10.3 Hz, 1H, CH$\underline{\mathrm{H}}$NO$_2$), 7.32–7.39 (m, 5H). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 70/30, 1.0 mL/min, λ = 220 nm); t$_R$ (major diastereoisomer) = 25.1 min (major), 54.5 min (minor).

(*S*)-Ethyl 1-((*R*)1-(4-chlorophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (5ba).[6] Colorless oil. **^{1}H NMR** (500 MHz, CDCl$_3$) 1.26 (t, 3H, *J* = 7.1 Hz, C$\underline{\mathrm{H}}_3$), 2.11-1.82 (m, 4H, C$\underline{\mathrm{H}}_2$), 2.38 (m, 2H, C$\underline{\mathrm{H}}_2$CO), 4.03 (dd, *J* = 11.1, 3.7 Hz, 1H, C$\underline{\mathrm{H}}$), 4.20 (q, 1H, *J* = 7.1 Hz, OC$\underline{\mathrm{H}}$H), 4.21 (q, 1H, *J* = 7.1 Hz, OCH$\underline{\mathrm{H}}$), 4.97 (dd, *J* = 13.7, 11.1 Hz, 1H, C$\underline{\mathrm{H}}$HNO$_2$), 5.15 (dd, 1H, *J* = 13.7, 3.7 Hz, CH$\underline{\mathrm{H}}$NO$_2$), 7.22 (d, 2H, *J* = 8.6 Hz, Har), 7.28 (d, 2H, *J* = 8.6 Hz, Har). **HPLC** (Chiralcel OD column, *n*-hexane/2-propanol = 90/10, 1.0 mL/min, λ = 220 nm); t$_R$ (major diastereoisomer) = 15.1 min (major), 24.0 min (minor).

(*S*)-Ethyl 1-((*R*)1-(4-fluorophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (5ca).[6] Colorless oil. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H, C$\underline{\mathrm{H}}_3$), 1.81-2.11 (m, 4H, C$\underline{\mathrm{H}}_2$), 2.38 (m, 2H, C$\underline{\mathrm{H}}_2$CO), 4.04 (dd, *J* = 11.2, 3.7 Hz, 1H, C$\underline{\mathrm{H}}$), 4.19 (q, *J* =7.2 Hz, 1H, OC$\underline{\mathrm{H}}_2$), 4.20 (q, *J* =7.2 Hz, 1H, OC$\underline{\mathrm{H}}_2$), 4.96 (dd, *J* = 13,5, 11.1 Hz, 1H, CH$\underline{\mathrm{H}}$NO$_2$), 5.14 (dd, *J* = 13.5, 3.8 Hz, 1H, C$\underline{\mathrm{H}}$HNO$_2$), 7.00 (m, 2H, $\underline{\mathrm{H}}$ar), 7.26 (m, 2H, $\underline{\mathrm{H}}$ar). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 90/10, 0.5 mL/min, λ = 220 nm); t$_R$ (major diastereoisomer) = 24.2 min (major), 40.6 min (minor).

(*S*)-Ethyl 1-((*R*)1-(4-methoxyphenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (5da).[6] Colorless oil. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 1.27 (t, *J* = 7.1 Hz, 3H, C$\underline{\mathrm{H}}_3$), 1.78-2.05 (m, 4H, C$\underline{\mathrm{H}}_2$), 2.35 (m, 2H, C$\underline{\mathrm{H}}_2$CO), 3.77 (s, 3H, OC$\underline{\mathrm{H}}_3$), 4.05 (dd, *J* =11.1, 3.8 Hz, 1H, C$\underline{\mathrm{H}}$), 4.20 (q, *J* = 7.2 Hz, 2H, OCH$_2$), 4.96 (dd, *J* =13.4, 11.1 Hz, 1H, C$\underline{\mathrm{H}}$HNO$_2$), 5.12 (dd, *J* = 13.4, 3.8 Hz, 1H, CH$\underline{\mathrm{H}}$NO$_2$), 6.82 (d, *J* = 8.8 Hz, 2H, $\underline{\mathrm{H}}$ar), 7.18 (d, *J* = 8.8 Hz, 2H, $\underline{\mathrm{H}}$ar). **HPLC** (Chiralpak AD-H column, *n*-hexane/2-propanol =

97/3, 1.0 mL/min, λ = 210 nm); t_R (major diastereoisomer) = 27.5 min (minor), 33.1 min (major).

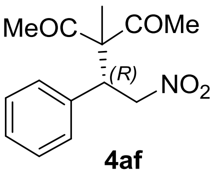
(*S*)-2-Nitro-2-((*S*)-2-nitro-1-phenylethyl)cyclohexanone (7aa).[7] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.53-1.80 (m, 4H, C<u>H</u>$_2$), 2.05 (m, 1H, C<u>H</u>HCO), 2.30 (ddd, *J* = 14.9, 6.3, 3.4 Hz, 1H, CH<u>H</u>CO), 2.58 (m, 1H, C<u>H</u>HCNO$_2$), 2.66 (dtd, *J* = 13.4, 4.2, 1.5 Hz, 1H, CH<u>H</u>CNO$_2$), 4.30 (dd, *J* = 11.1, 3.1 Hz, 1H, C<u>H</u>Ph), 4.70 (dd, *J* = 13.8, 11.1 Hz, 1H, C<u>H</u>HNO$_2$), 5.14 (dd, *J* = 13.7, 3.2 Hz, 1H, CH<u>H</u>NO$_2$), 7.06-7.09 (m, 2H, <u>H</u>ar), 7.32-7.37 (m, 3H, <u>H</u>ar). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, λ= 220 nm); t_R = 22.4 min (major), 38.8 min (minor).

(*S*)-2-((*S*)-1-(4-Chlorophenyl)-2-nitroethyl)-2-nitrocyclohexanone (7ba). [7] Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.57 (m, 1H), 1.64-1.81 (m, 3H), 2.05 (m, 1H), 2.31 (dq, *J* = 15.0, 3.5 Hz, 1H), 2.57 (m, 1H), 2.65 (m, 1H), 4.27 (dd, *J* = 11.1, 3.2 Hz, 1H, C<u>H</u>Ar), 4.63 (dd, *J* = 13.8, 11.1 Hz, 1H, C<u>H</u>HNO$_2$), 5.10 (dd, *J* = 13.8, 3.2 Hz, 1H, CH<u>H</u>NO$_2$), 7.04 (d, *J* = 8.5 Hz, 2H, Har), 7.31 (d, *J* = 8.5 Hz, 2H, <u>H</u>ar**). HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, λ = 220 nm); t_R = 22.9 min (major), 48.8 min (minor).

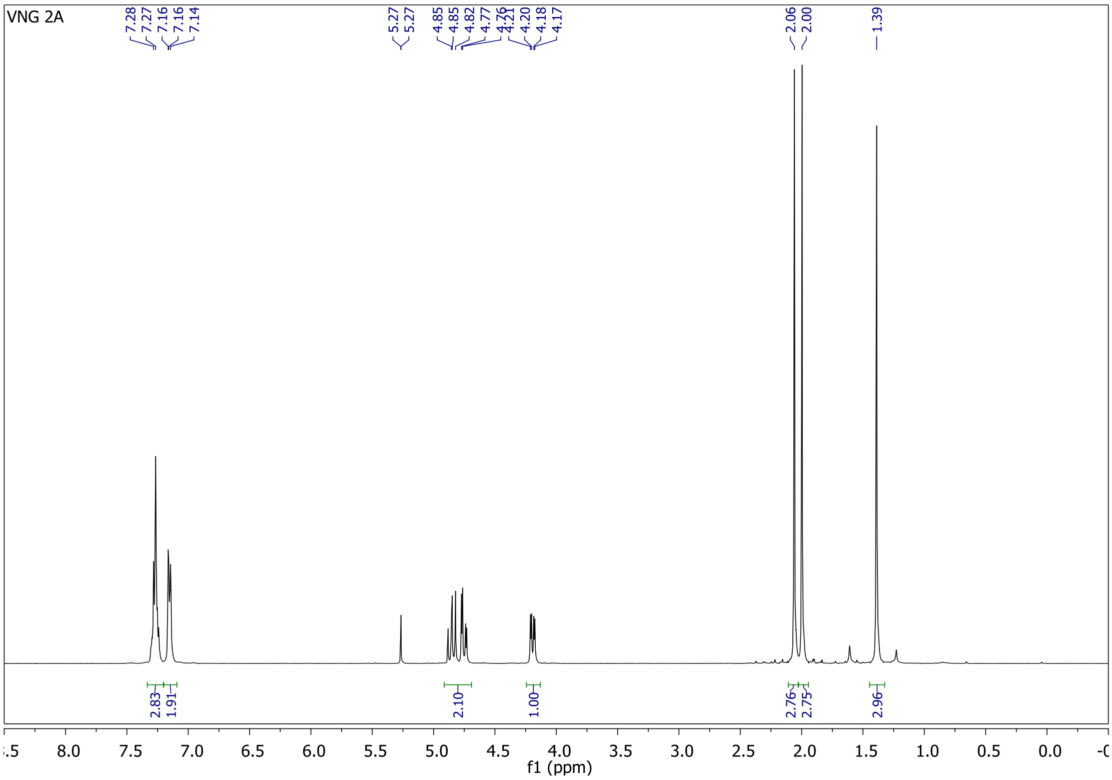
(*S*)-2-[(*S*)-1-(4-Methoxyphenyl)-2-nitroethyl)-2-nitrocyclohexanone (7da). [7] Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.58 (m, 1H), 1.64-1.81 (m, 4H, C<u>H</u>$_2$), 2.04 (m, 1H), 2.33 (dq, *J* = 14.8, 3.5 Hz, 1H), 2.57 (ddd, *J* = 13.5, 12.1, 5.8 Hz, 1H), 2.64 (dtd, *J* = 13.5, 4.3, 1.5 Hz, 1H), 3.78 (s, 3H, C<u>H</u>$_3$), 4.24 (dd, *J* = 11.1, 3.2 Hz, 1H, CHAr), 4.66 (dd, *J* = 13.5, 11.1 Hz, 1H, C<u>H</u>HNO$_2$), 5.09 (dd, *J* = 13.6, 3.2 Hz, 1H, CH<u>H</u>NO$_2$), 6.84 (d, *J* = 8.8 Hz, 2H, <u>H</u>ar), 7.00 (d, *J* = 8.8 Hz, 2H, <u>H</u>ar). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, λ = 220 nm); t_R = 18.1 min (major), 30.3 min (minor).

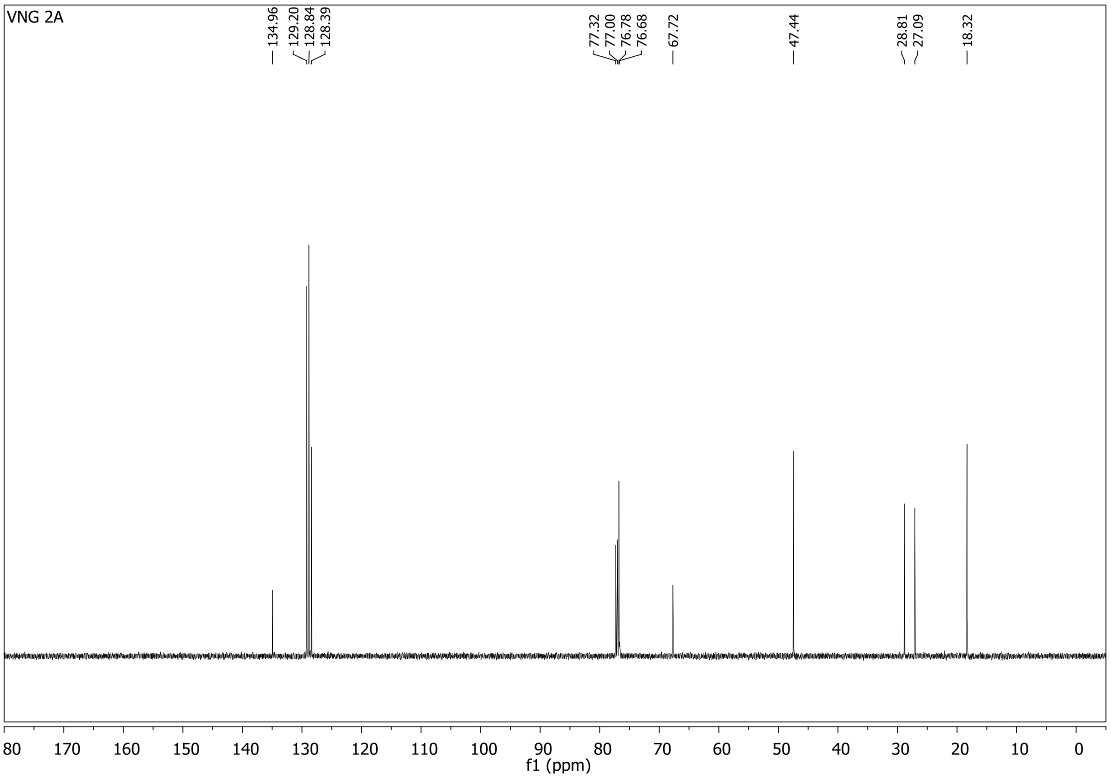
(2*S*,3*S*)-Ethyl 2-Methyl-2,4-dinitro-3-phenylbutanoate (7ab).[8] Colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H, C<u>H</u>$_3$CH$_2$); 1.64 (s, 3H, C<u>H</u>$_3$); 4.32 (q, *J* = 7.2 Hz, 3H, C<u>H</u>$_2$CH$_3$); 4.40 (dd, *J* = 10.4, 3.1 Hz, 1H, C<u>H</u>Ph); 5.06 (dd, *J* = 14.0, 10.4 Hz, 1H, C<u>H</u>HNO$_2$); 5.12 (dd, *J* = 14.0, 3.2 Hz, 1H, CH<u>H</u>NO$_2$); 7.12–7.14 (m, 2H, Har); 7.34-7.36 (m, 3H, <u>H</u>ar). **HPLC** (Chiralcel OD, *n*-hexane/2-propanol = 80:20, 1.0 mL/min, λ = 220 nm); *anti*-adduct: t_R = 12.3 min (major), 28.8 min (major) (er 74:26); *syn*-adduct: t_R = 14.1 min (major), 16.6 min (minor) (er 60:40).

2. NMR spectra for new compounds

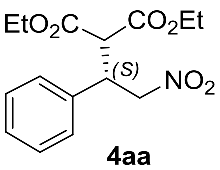


4af



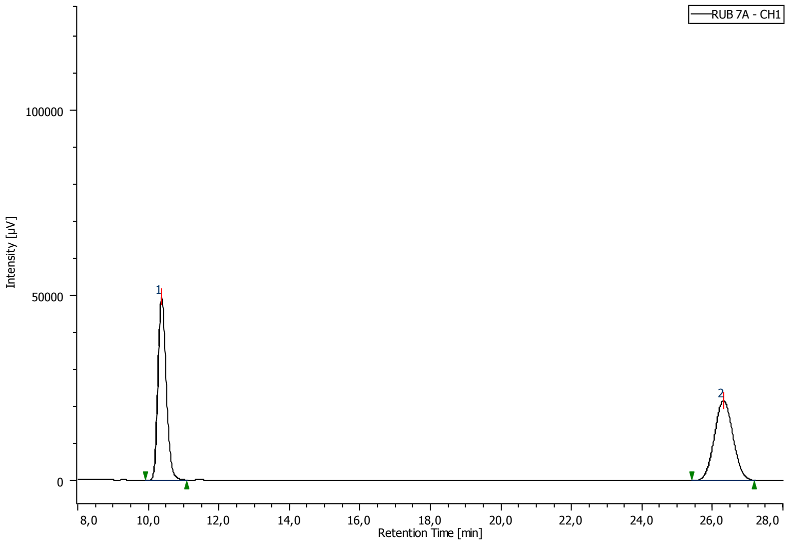


3. HPLC Profiles of the Nitro-Michael Products.



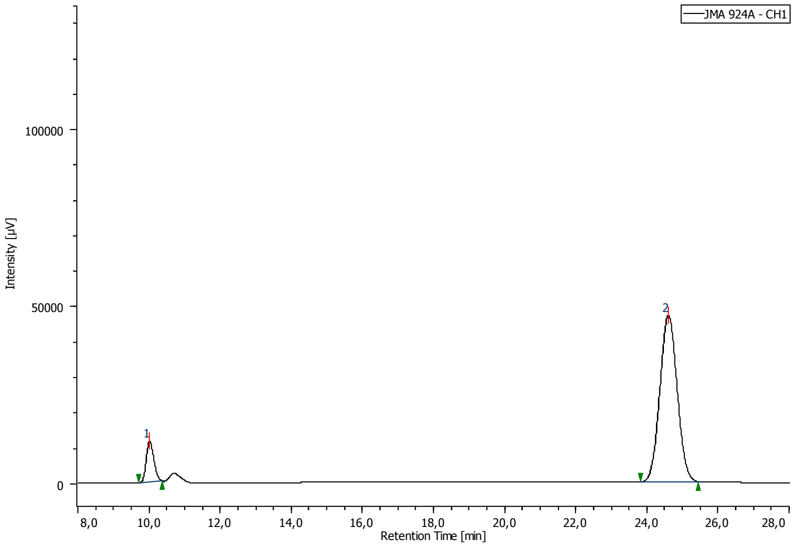
4aa

Racemic molecule:

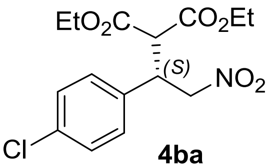


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,375	799837	49174	50,348	69,552	1,237
2	26,292	788792	21527	49,652	30,448	1,034

HPLC profile for entry 5, table 1. 90:10 er.

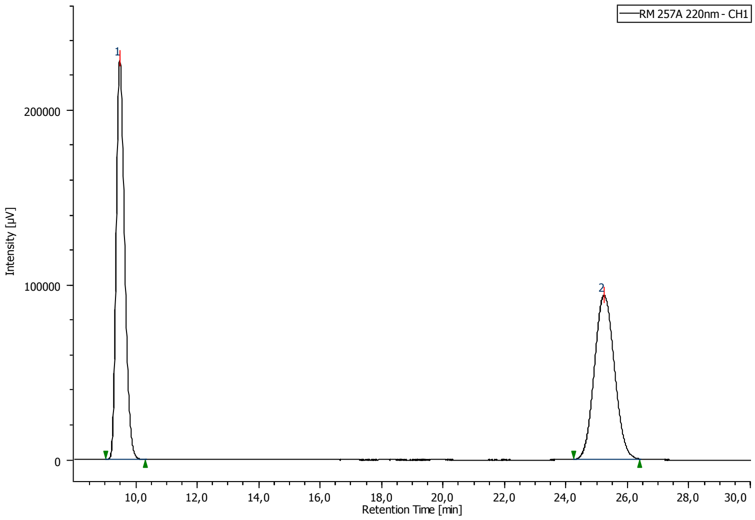


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	10,017	172995	11618	9,844	19,852	1,189
2	24,583	1584300	46904	90,156	80,148	1,044



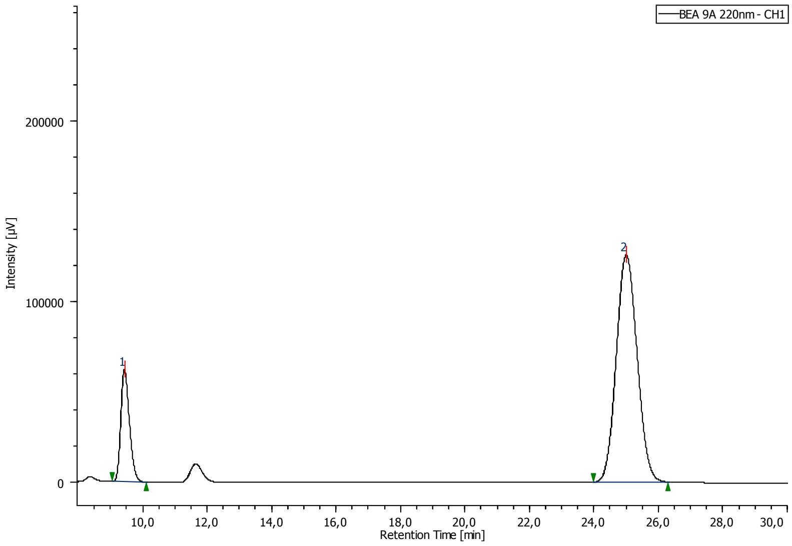
4ba

Racemic molecule:

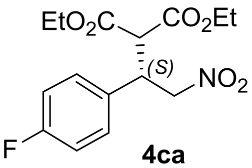


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	9,483	4269299	228674	50,230	70,937	1,279
2	25,217	4230130	93688	49,770	29,063	1,073

HPLC profile for entry 1, table 2. 83:17 er.

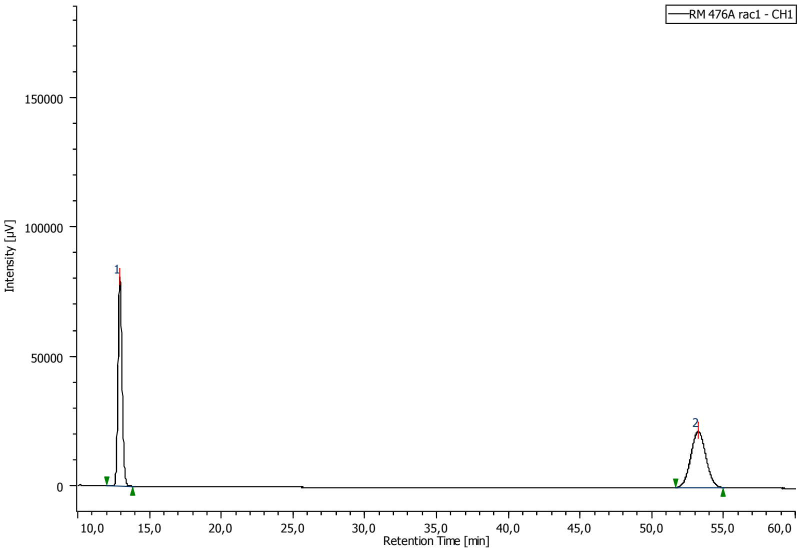


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	9,442	1148279	62097	16,903	33,086	1,254
2	24,983	5645227	125586	83,097	66,914	1,081



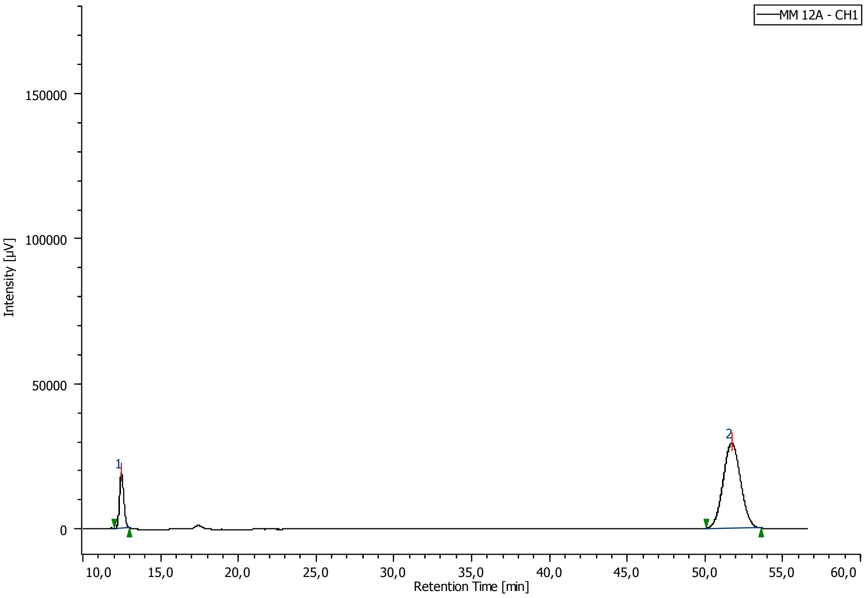
4ca

Racemic molecule:

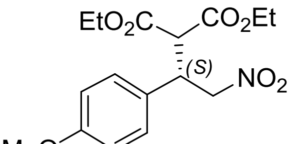


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	12,933	1590400	80477	50,138	78,766	1,163
2	53,175	1581672	21695	49,862	21,234	1,037

HPLC profile for entry 2, table 2. 86:14 er.

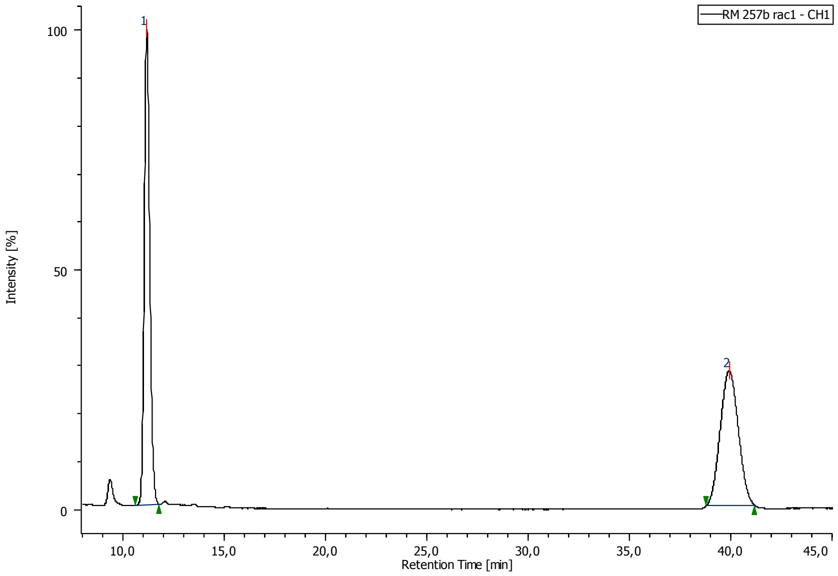


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	12,483	367409	18932	13,921	39,276	1,174
2	51,658	2271851	29271	86,079	60,724	1,056



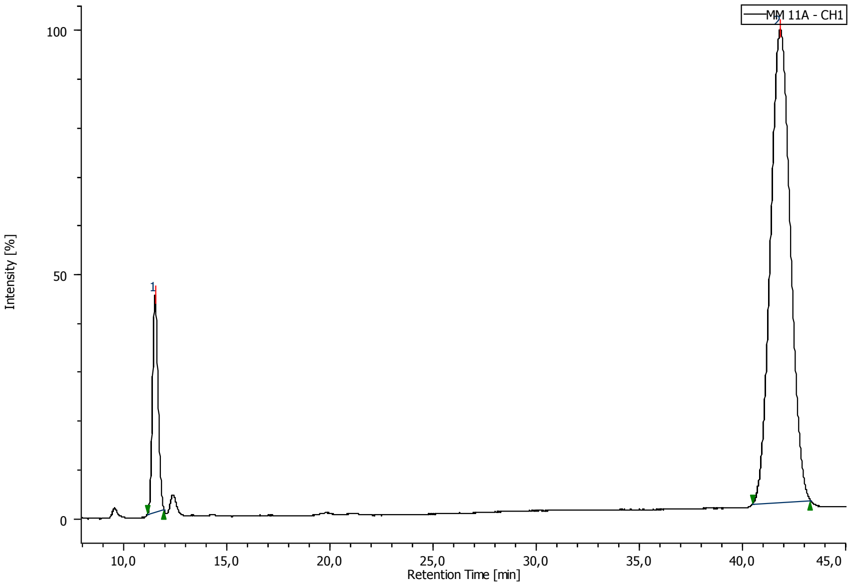
4da

Racemic molecule:

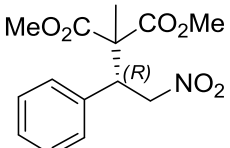


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	11,175	214500	11405	51,758	77,903	1,182
2	39,875	199931	3235	48,242	22,097	1,048

HPLC profile for entry 3, table 2. 89:11 er.

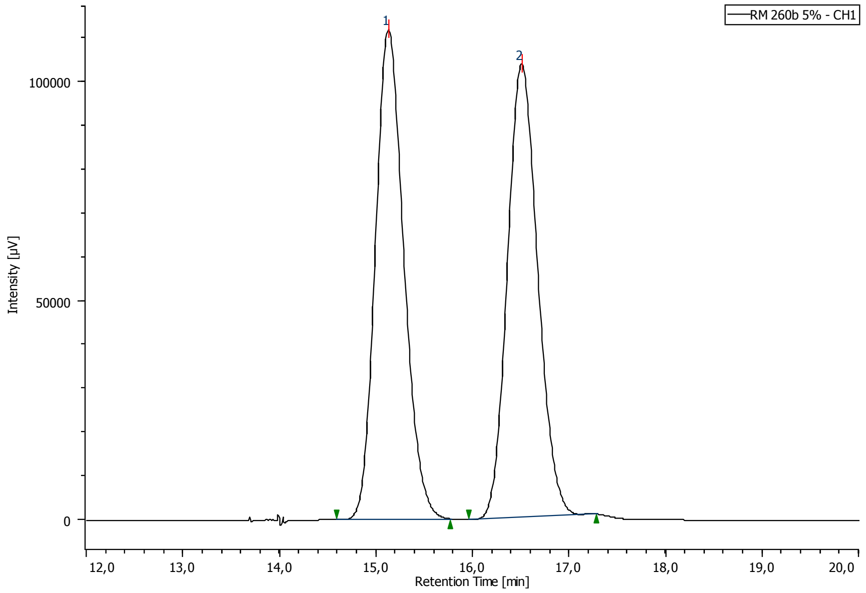


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	11,525	65493	3471	11,457	31,464	1,120
2	41,783	506173	7560	88,543	68,536	1,051



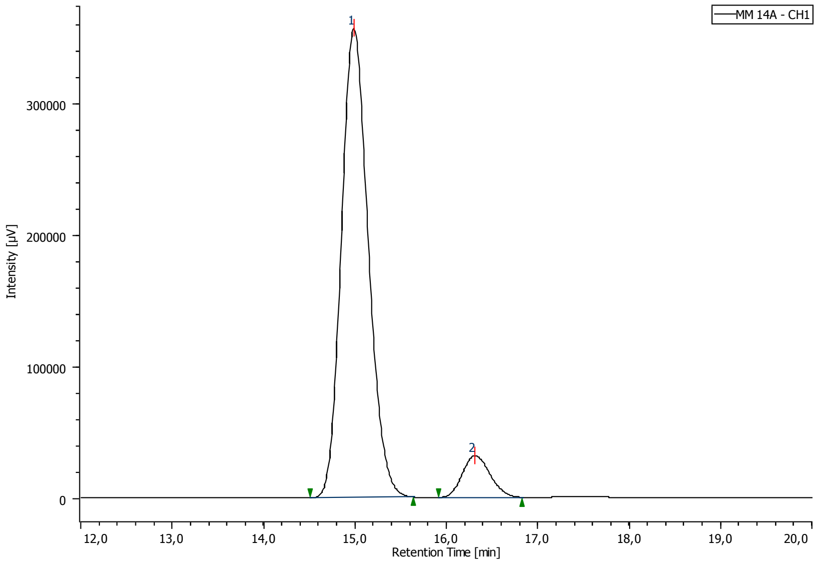
4ab

Racemic molecule:

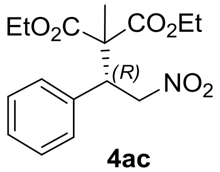


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	15,125	2283252	111593	50,339	51,938	1,178
2	16,508	2252481	103267	49,661	48,062	1,115

HPLC profile for entry 4, table 2. 92:8 er.

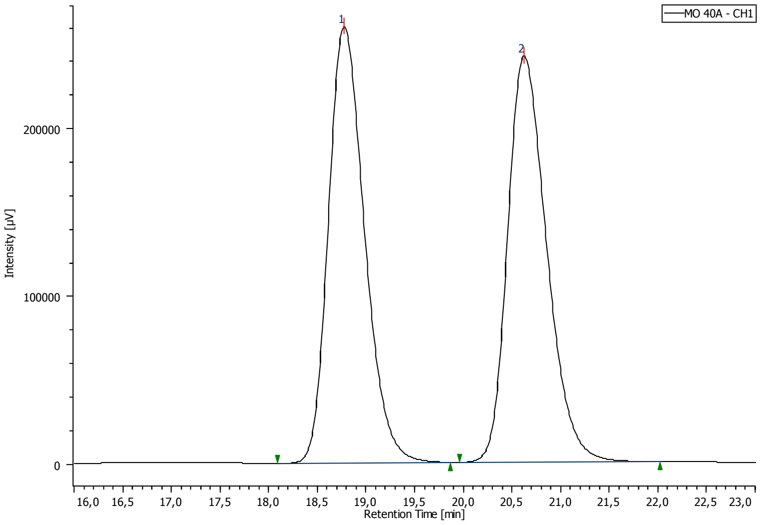


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	14,983	7273303	355446	91,545	91,786	1,165
2	16,308	671768	31807	8,455	8,214	1,152



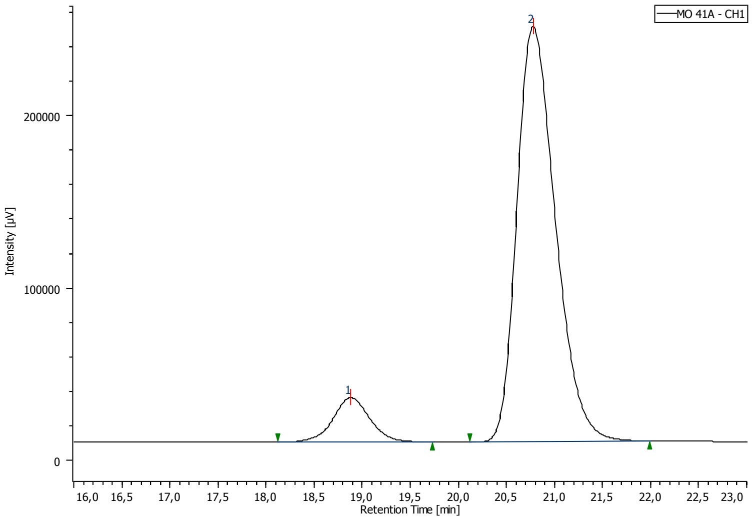
4ac

Racemic molecule:

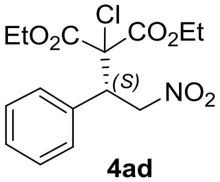


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	18,775	6686021	259376	49,801	51,761	1,245
2	20,617	6739497	241725	50,199	48,239	1,305

HPLC profile for entry 10, table 2. 91:9 er.

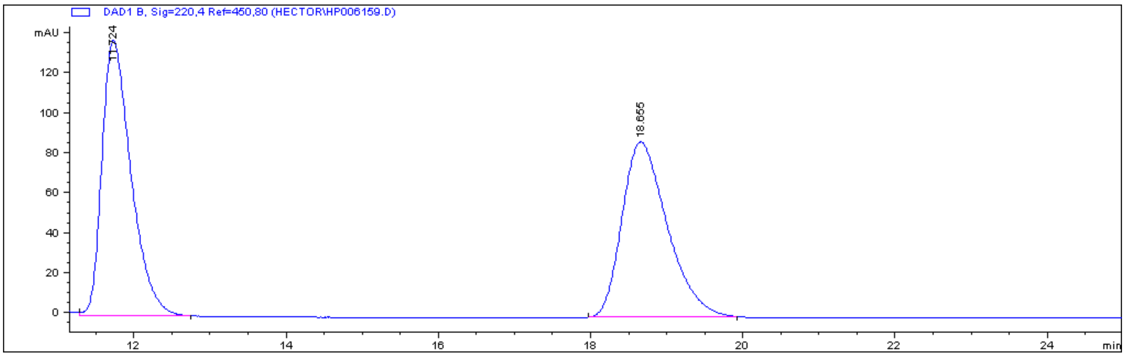


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	18,875	690331	25772	9,335	9,670	1,027
2	20,775	6704599	240753	90,665	90,330	1,300



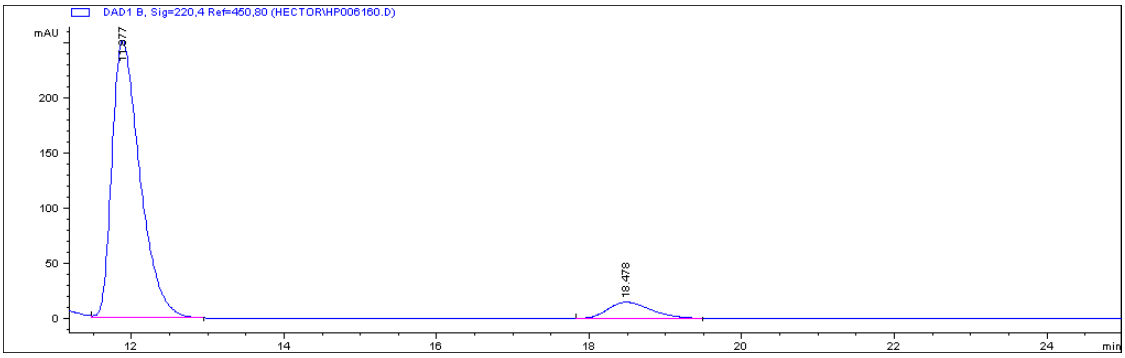
4ad

Racemic molecule:

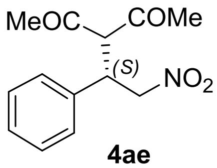


#	Time	Area	Height	Width	Area%	Symmetry
1	11.724	3679.4	138.3	0.4	50.253	0.604
2	18.655	3642.3	87.8	0.6025	49.747	0.676

HPLC profile for entry 5, table 2. 92:8 er.

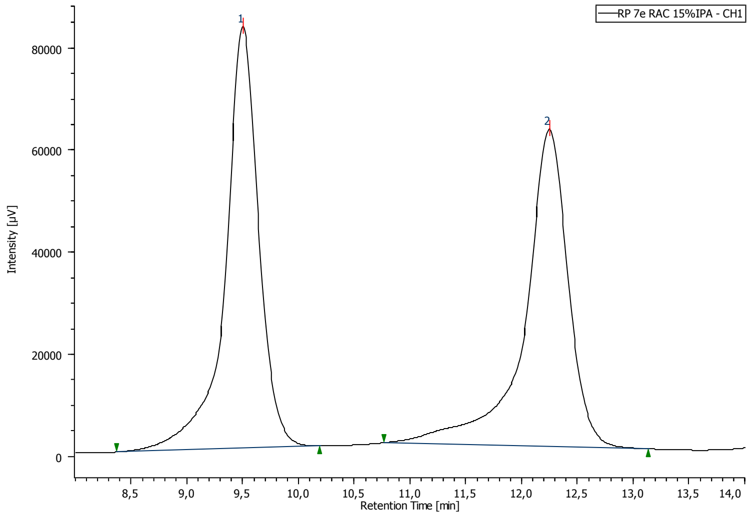


#	Time	Area	Height	Width	Area%	Symmetry
1	11.877	6450.4	252.6	0.3875	91.717	0.563
2	18.478	582.5	14.8	0.5039	8.283	0.674



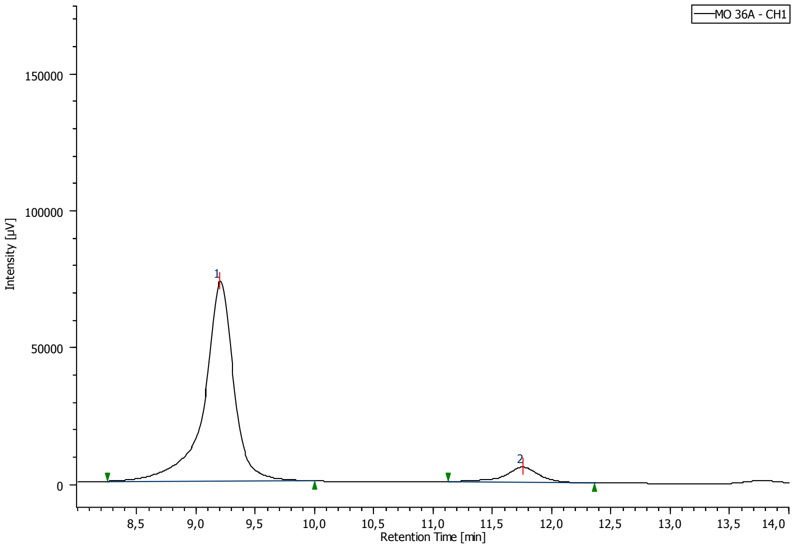
4ae

Racemic molecule:

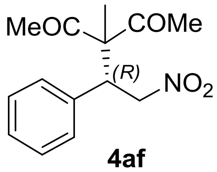


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	9,500	1719557	82405	50,406	57,039	0,826
2	12,242	1691837	62066	49,594	42,961	0,724

HPLC profile for entry 12, table 2. 92:8 er.

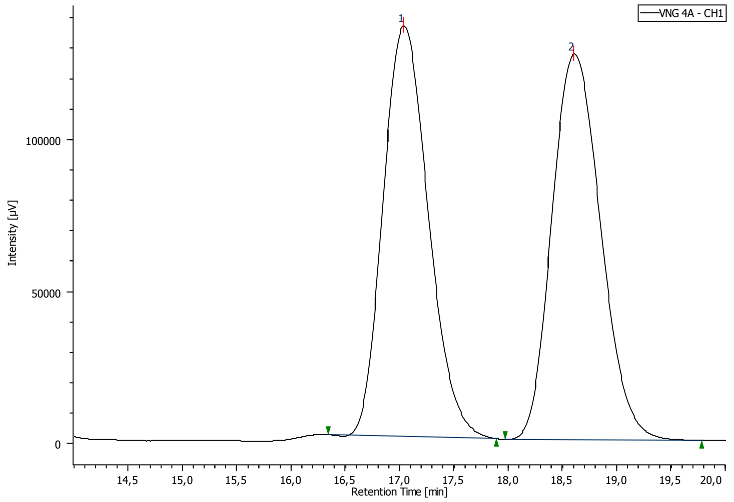


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	9,200	1262224	72827	91,684	92,909	0,817
2	11,750	114483	5559	8,316	7,091	0,875



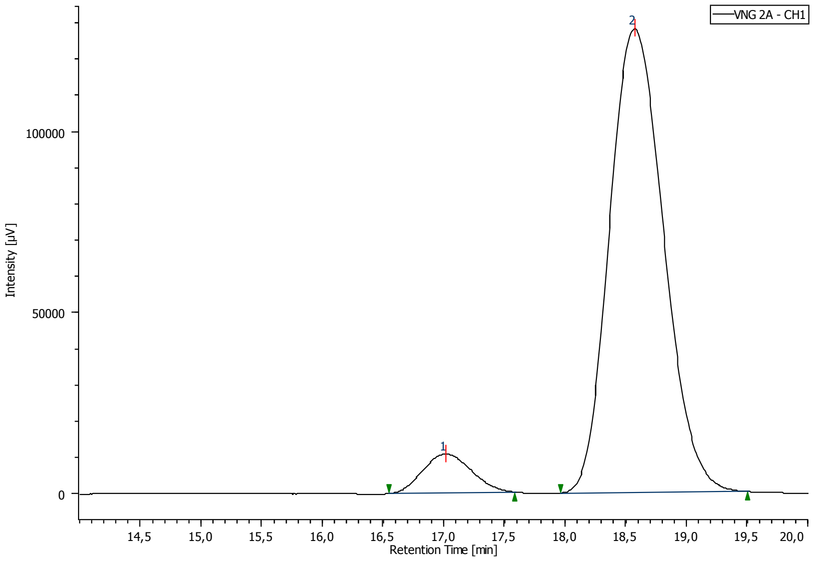
4af

Racemic molecule:

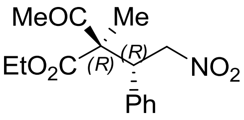


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	17,033	3902459	134727	49,656	51,545	1,196
2	18,600	3956485	126651	50,344	48,455	1,180

HPLC profile for entry 13, table 2. 93:7 er.

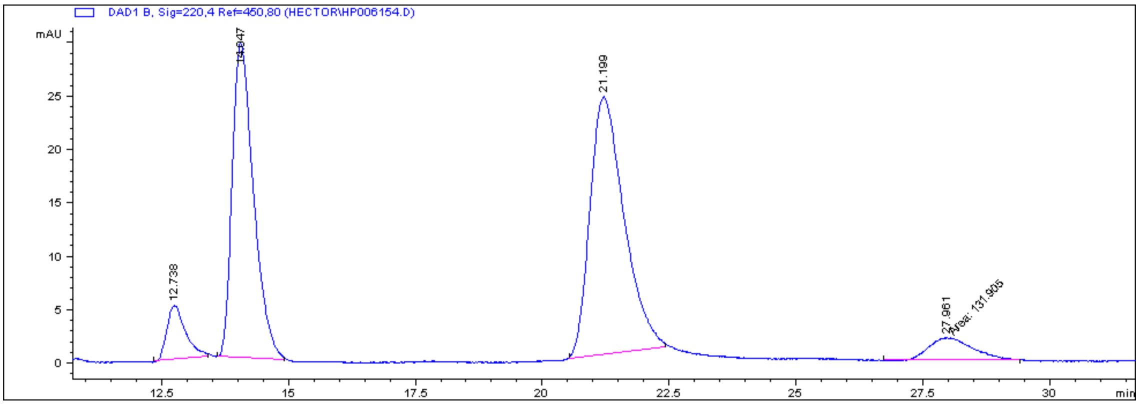


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	17,017	299487	10738	7,024	7,754	1,104
2	18,567	3964206	127736	92,976	92,246	1,161



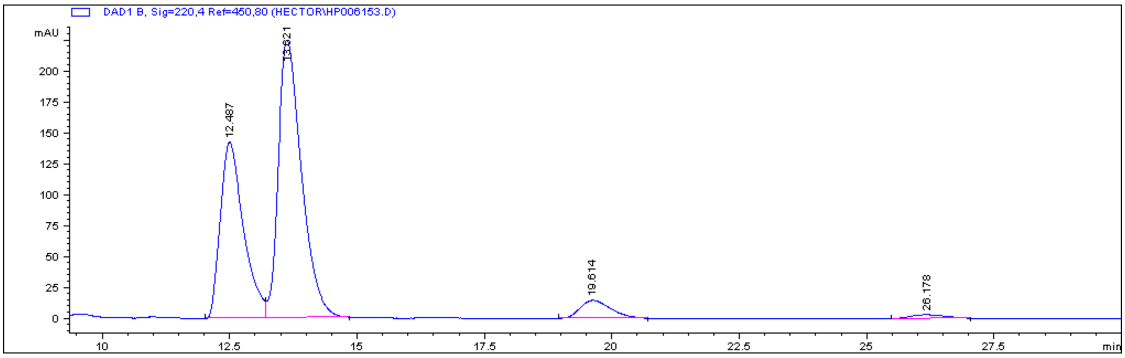
4ag

Racemic molecule:

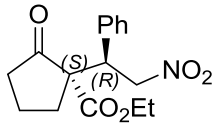


#	Time	Area	Height	Width	Area%	Symmetry
1	12.738	131.2	5.1	0.3114	5.804	0.606
2	14.047	985.1	29.5	0.4216	43.582	0.597
3	21.199	1012.1	24.2	0.5858	44.777	0.63
4	27.961	131.9	2.1	1.0383	5.836	0.532

HPLC profile for entry 8, table 2. 75/25 dr; 92:8 er.

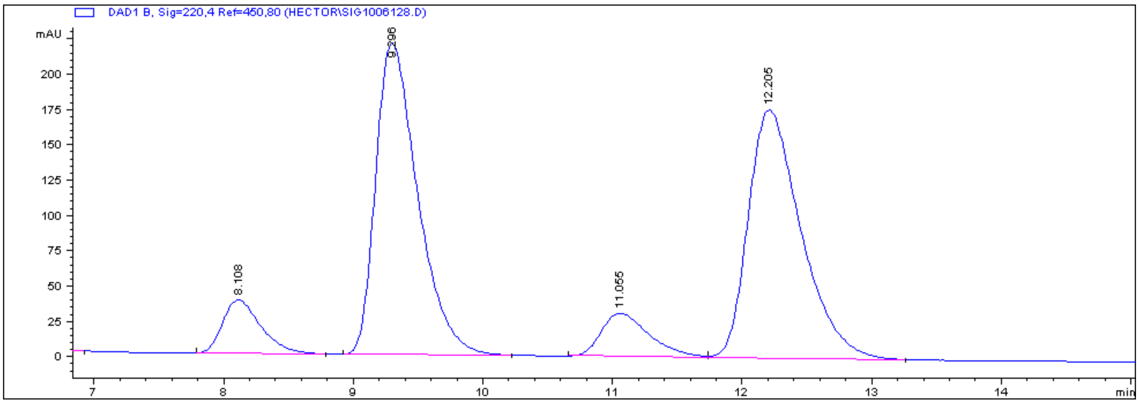


#	Time	Area	Height	Width	Area%	Symmetry
1	12.487	4519.2	142.4	0.4663	36.346	0.605
2	13.621	7140.1	224.7	0.4827	57.425	0.584
3	19.614	622.2	14.7	0.5191	5.004	0.679
4	26.178	152.4	3.2	0.5748	1.226	0.832



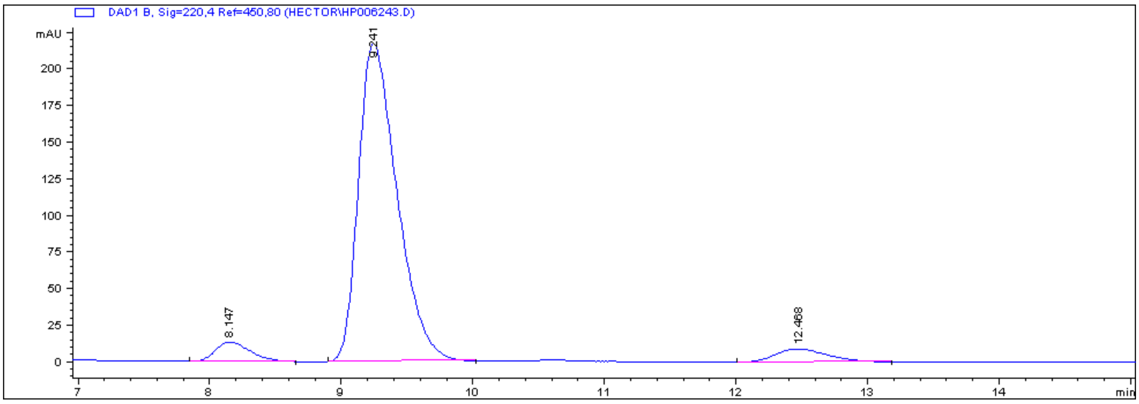
5aa

Racemic molecule:

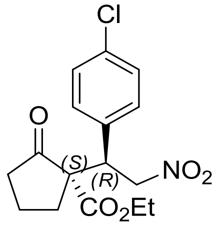


#	Time	Area	Height	Width	Area%	Symmetry
1	8.108	772.2	37.9	0.3146	6.702	0.642
2	9.296	4974.2	220.7	0.3462	43.173	0.604
3	11.055	790.4	30.6	0.3652	6.860	0.613
4	12.205	4984.9	175.9	0.433	43.265	0.625

HPLC profile for entry 15, table 1. 89/11 dr; 95:5 er.

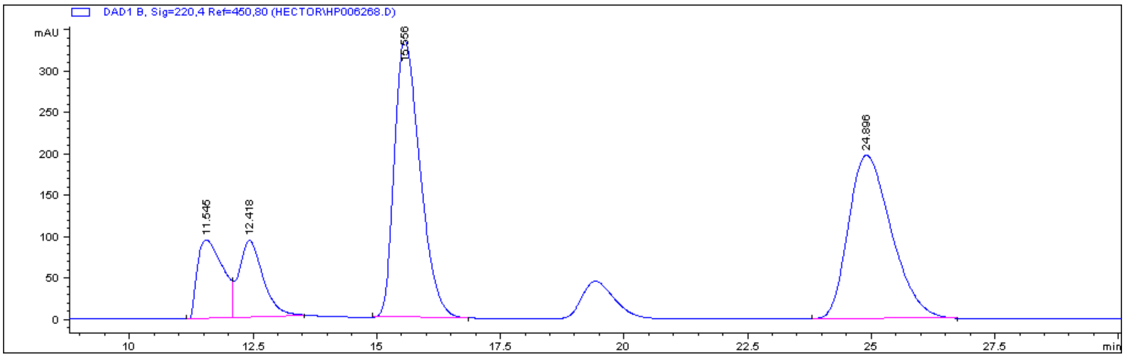


#	Time	Area	Height	Width	Area%	Symmetry
1	8.147	243.5	13.3	0.2655	4.950	0.659
2	9.241	4427.6	217.5	0.3111	90.025	0.597
3	12.468	247.1	9.1	0.3345	5.025	0.719



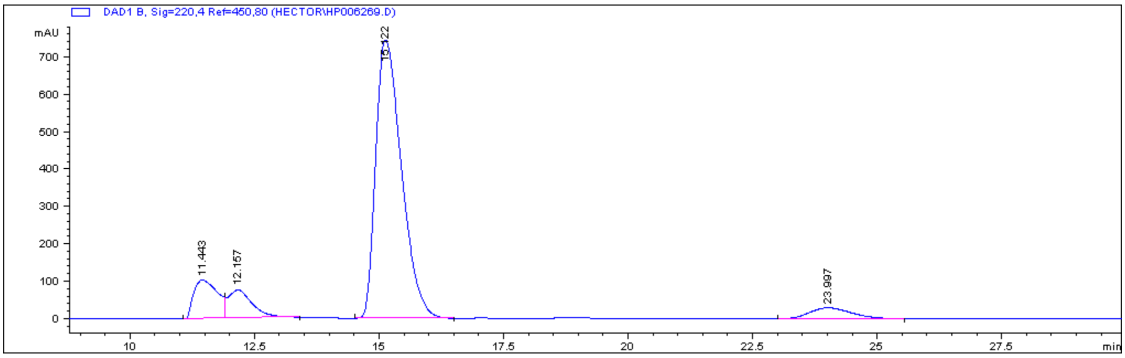
5ba

Racemic molecule:

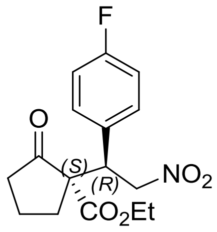


#	Time	Area	Height	Width	Area%	Symmetry
1	11.545	3443.7	94.7	0.5297	11.224	0.501
2	12.418	3123.4	93.1	0.4843	10.180	0.691
3	15.556	12156.1	335.4	0.554	39.620	0.637
4	24.896	11958.1	197.6	0.8563	38.975	0.698

HPLC profile for entry 2, table 3. 90/10 dr; 94:6 er.

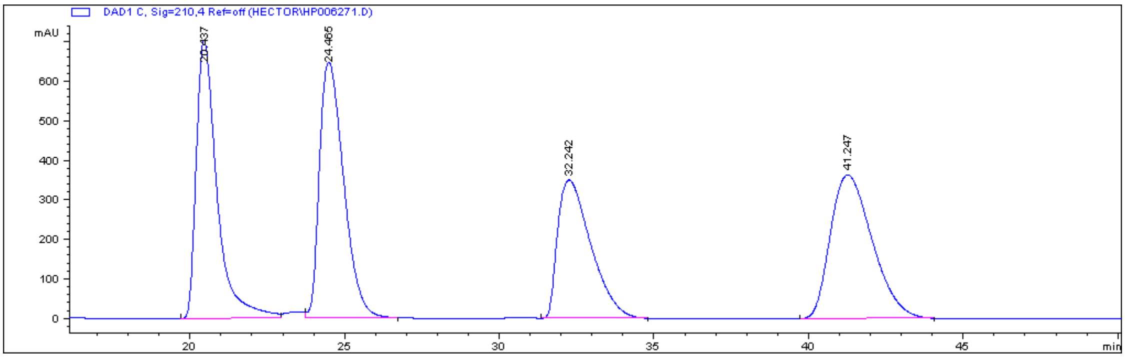


#	Time	Area	Height	Width	Area%	Symmetry
1	11.443	3506.3	103.3	0.5048	10.143	0.554
2	12.157	2560.8	76.1	0.4598	7.407	0.565
3	15.122	26758.7	744.1	0.554	77.404	0.592
4	23.997	1744.6	29.4	0.7112	5.046	0.741



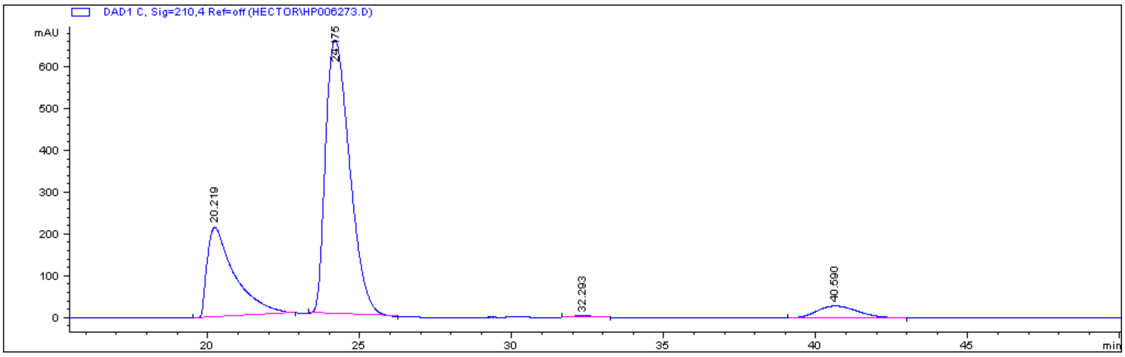
5ca

Racemic molecule:

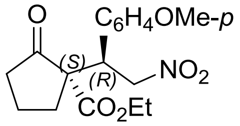


#	Time	Area	Height	Width	Area%	Symmetry
1	20.437	33057.3	704.9	0.6911	25.662	0.542
2	24.465	35332.8	648	0.7513	27.429	0.566
3	32.242	26142.1	349.7	0.8977	20.294	0.509
4	41.247	34284.6	364	1.1117	26.615	0.679

HPLC profile for entry 3, table 3. 89/11 dr; 93:7 er.

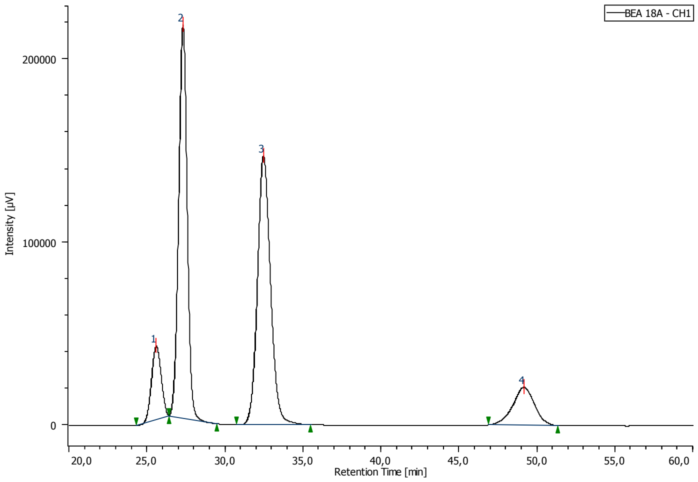


#	Time	Area	Height	Width	Area%	Symmetry
1	20.219	13530.1	215.3	0.8741	25.665	0.353
2	24.175	36262.5	656.3	0.7758	68.785	0.607
3	32.293	229.1	3.9	0.6973	0.435	0.777
4	40.59	2696.6	28.8	1.1065	5.115	0.705



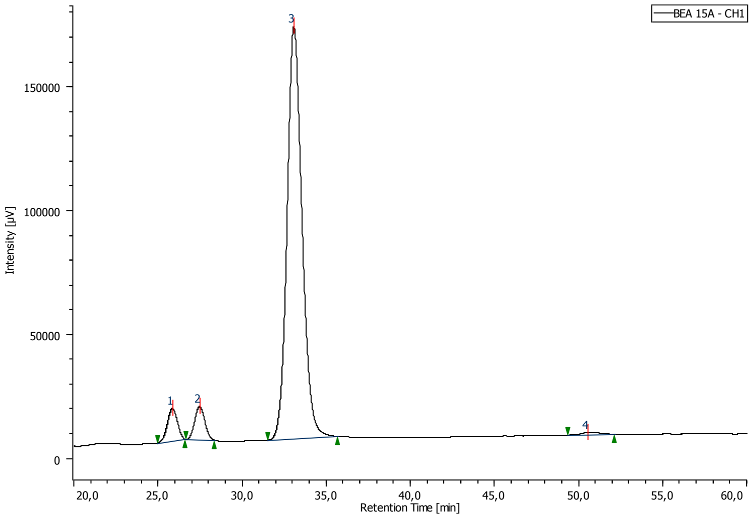
5da

Racemic molecule:

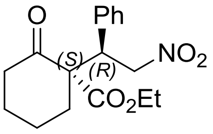


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	25,600	1708176	40011	8,412	9,501	1,010
2	27,317	8088582	214091	39,833	50,838	0,987
3	32,467	8517863	146421	41,947	34,769	1,114
4	49,117	1991760	20604	9,809	4,892	0,950

HPLC profile for entry 4, table 3. 89/11 dr; 95:5 er.

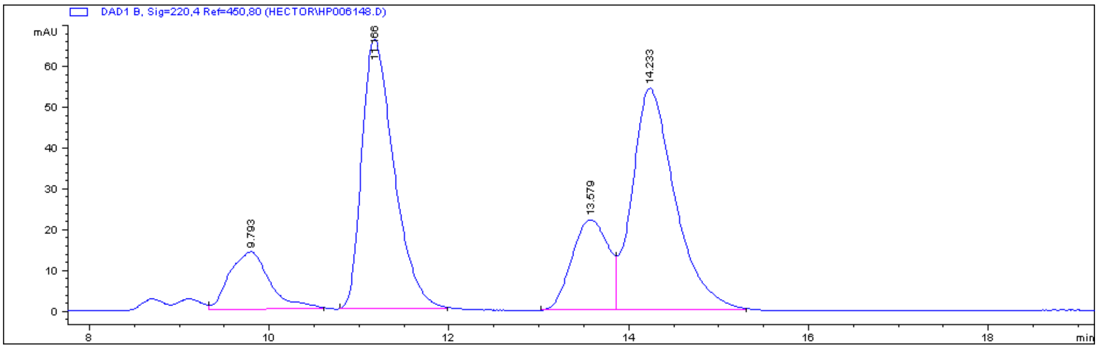


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	25,867	543032	13106	4,763	6,770	0,966
2	27,475	564460	13554	4,951	7,001	1,044
3	33,067	10218843	166097	89,634	85,794	1,146
4	50,517	74353	842	0,652	0,435	1,160



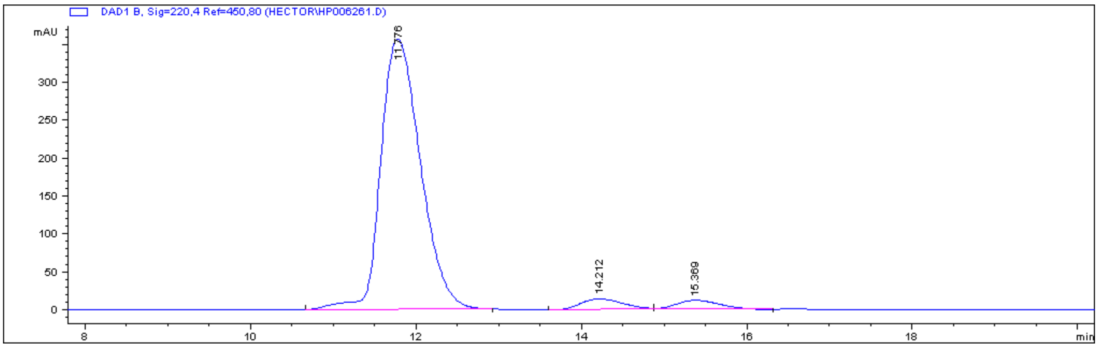
5ab

Racemic molecule:

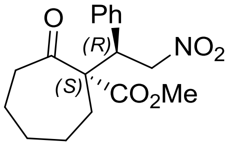


#	Time	Area	Height	Width	Area%	Symmetry
1	9.793	445.9	14.1	0.4162	9.876	1.033
2	11.166	1639.9	66	0.3794	36.317	0.607
3	13.579	629.4	22.2	0.3856	13.939	1.094
4	14.233	1800.2	54.3	0.47	39.868	0.675

HPLC profile for entry 6, table 3. 88/12 dr; 96:4 er.

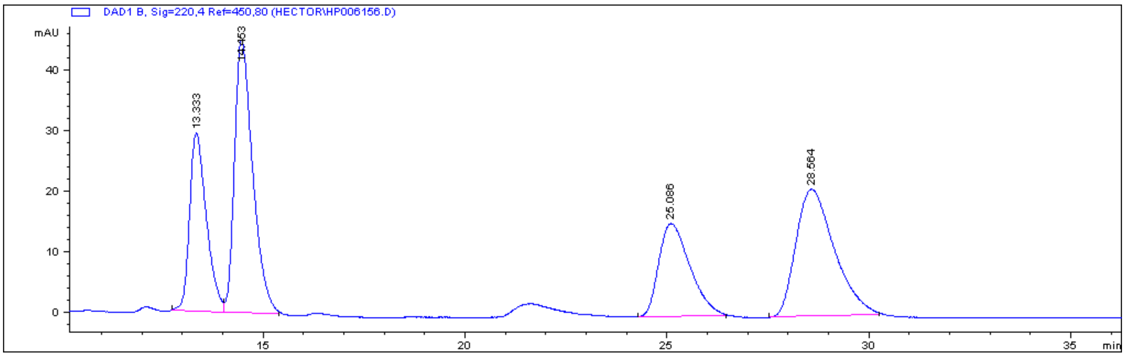


#	Time	Area	Height	Width	Area%	Symmetry
1	11.776	11928.8	357.3	0.5143	92.510	0.731
2	14.212	518	14.3	0.4324	4.017	0.742
3	15.369	447.8	12.1	0.4617	3.473	0.75



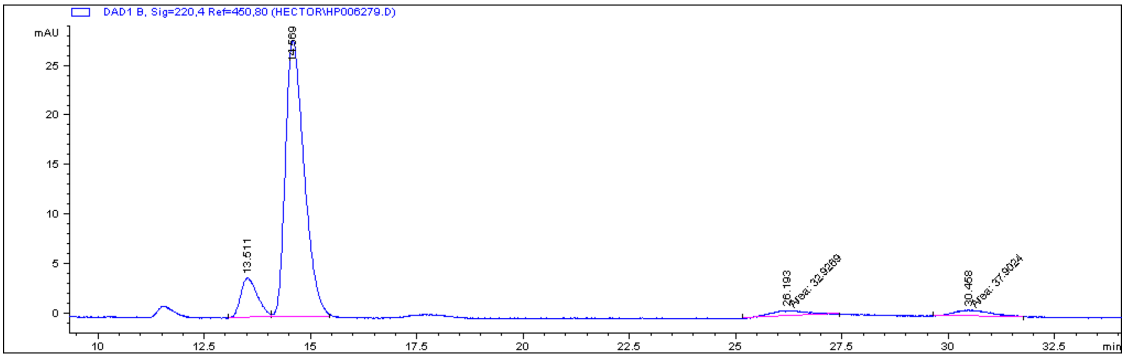
5ac

Racemic molecule:

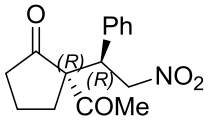


#	Time	Area	Height	Width	Area%	Symmetry
1	13.333	863.8	29.5	0.4183	19.187	0.638
2	14.453	1422.2	45.2	0.4537	31.589	0.603
3	25.086	827.2	15.4	0.6457	18.374	0.61
4	28.564	1388.9	21	0.7883	30.850	0.658

HPLC profile for entry 8, table 3. 82/18 dr; 96:4 er.

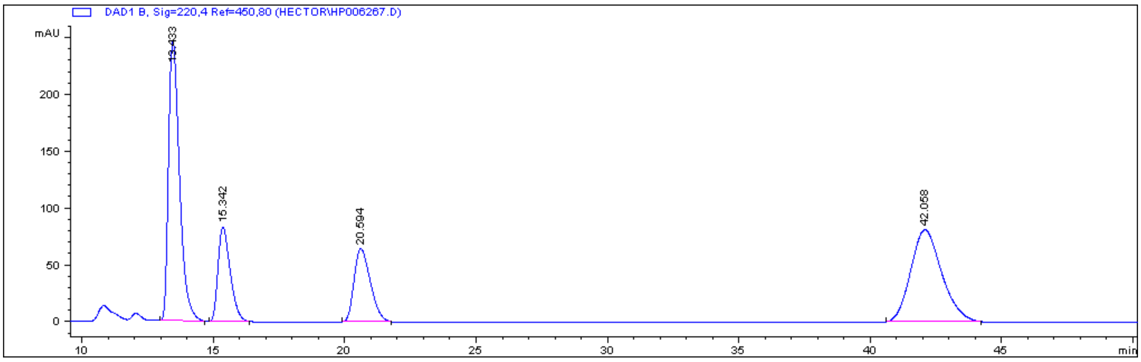


#	Time	Area	Height	Width	Area%	Symmetry
1	13.511	110.3	4	0.3349	10.591	0.675
2	14.569	860.3	28	0.4224	82.608	0.608
3	26.193	32.9	5.2E-1	1.0484	3.162	0.798
4	30.458	37.9	6.4E-1	0.9883	3.639	0.631



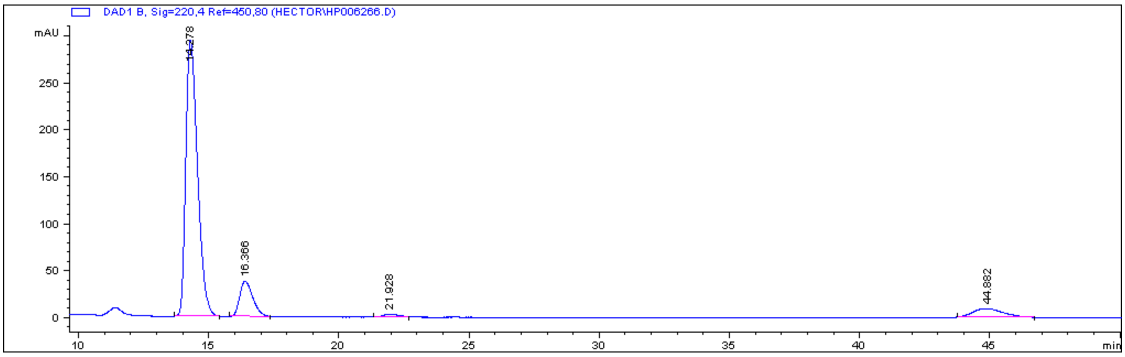
5ad

Racemic molecule:

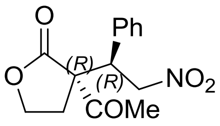


#	Time	Area	Height	Width	Area%	Symmetry
1	13.433	7077.5	246.8	0.437	36.660	0.586
2	15.342	2698.7	83.2	0.4841	13.979	0.634
3	20.594	2800.2	64.5	0.5928	14.505	0.682
4	42.058	6729.3	81.3	1.0067	34.856	0.793

HPLC profile for entry 9, table 3. 83/17 dr; 93:7 er.

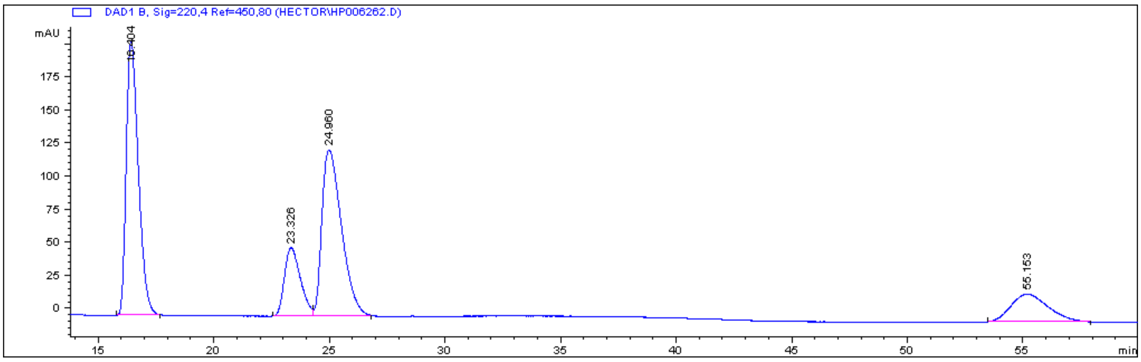


#	Time	Area	Height	Width	Area%	Symmetry
1	14.278	9284.7	294.3	0.4737	80.921	0.633
2	16.366	1320.2	37.8	0.4941	11.506	0.626
3	21.928	129.7	3.3	0.48	1.130	0.656
4	44.882	739.1	9.3	0.9665	6.442	0.806



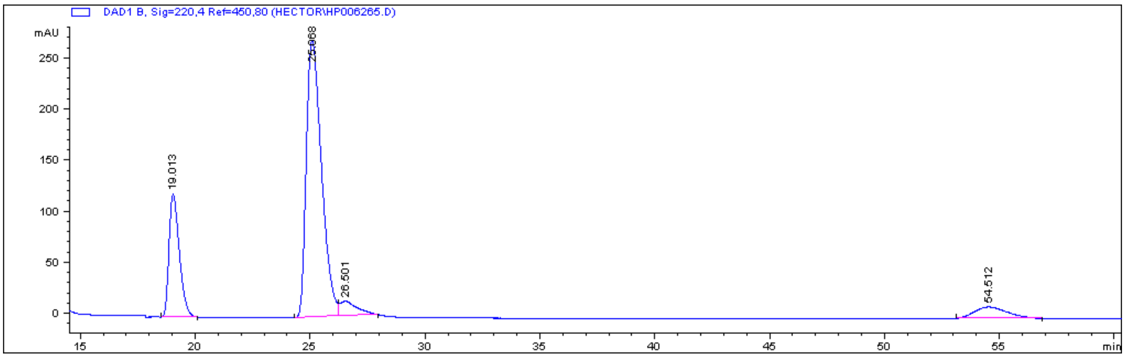
5ae

Racemic molecule:

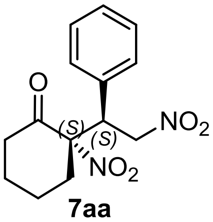


#	Time	Area	Height	Width	Area%	Symmetry
1	16.404	7547.3	207.8	0.5614	38.164	0.633
2	23.326	2482.5	51.6	0.5836	12.553	0.708
3	24.96	7411.7	125.6	0.8293	37.478	0.527
4	55.153	2334.5	20.8	1.3132	11.805	0.728

HPLC profile for entry 10, table 3. 70/30 dr; 92:8 er.

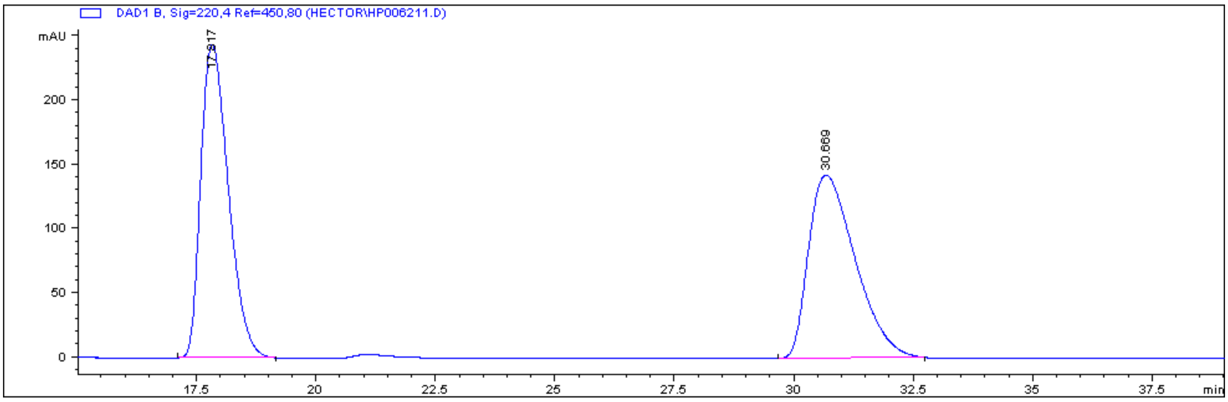


#	Time	Area	Height	Width	Area%	Symmetry
1	19.013	3765.9	120.4	0.4642	20.692	0.616
2	25.068	12527.7	271.3	0.6731	68.832	0.582
3	26.501	789.9	14.6	0.6471	4.340	0.37
4	54.512	1116.8	11.1	1.1891	6.136	0.721



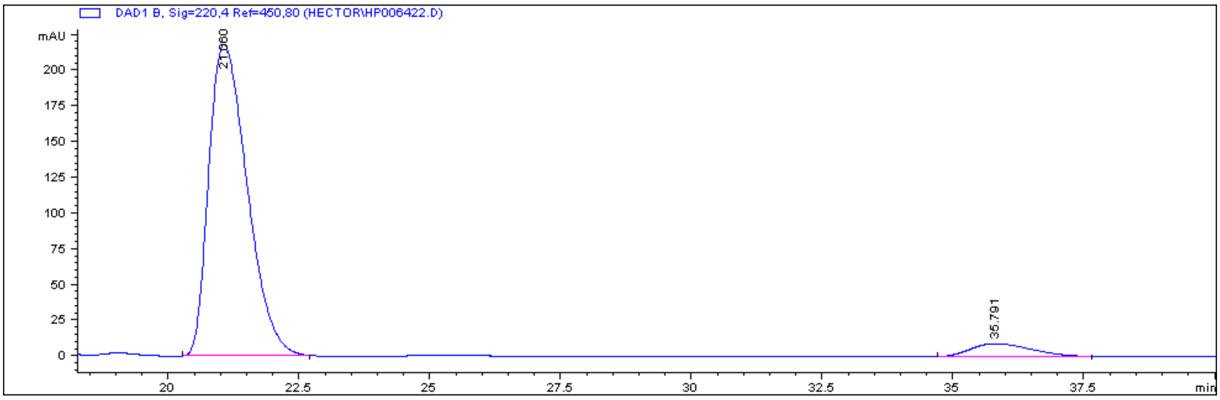
7aa

Racemic molecule:

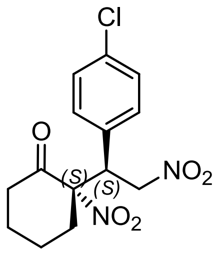


Peak Name	Time	Area	Height	Area%	Symmetry
1	17.817	9794.4	243.9	50.250	0.665
2	30.669	9697.1	142.6	49.750	0.57

HPLC profile for entry 6, table 4. 100:0 rd, 94:6 er.

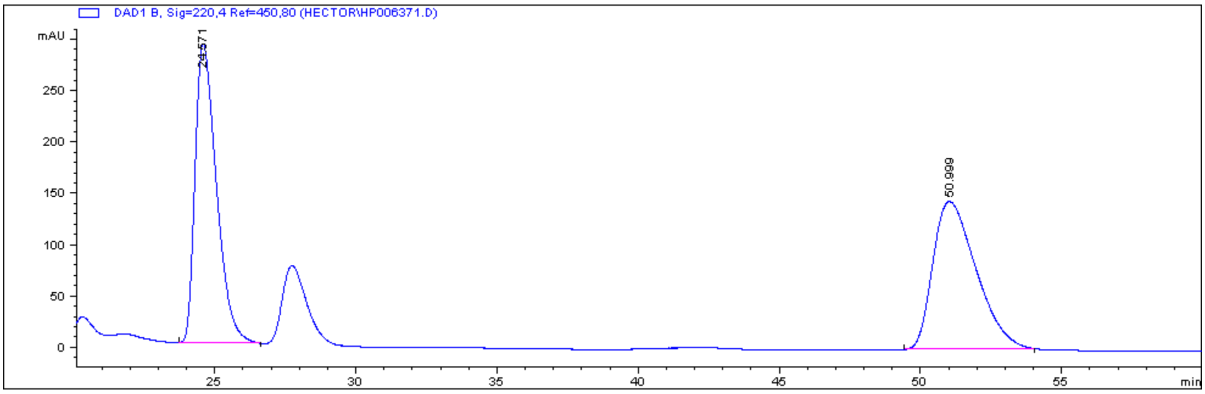


Peak Name	Time	Area	Height	Area%	Symmetry
1	21.06	11152.6	218.3	93.859	0.631
2	35.791	729.7	9.1	6.141	0.638



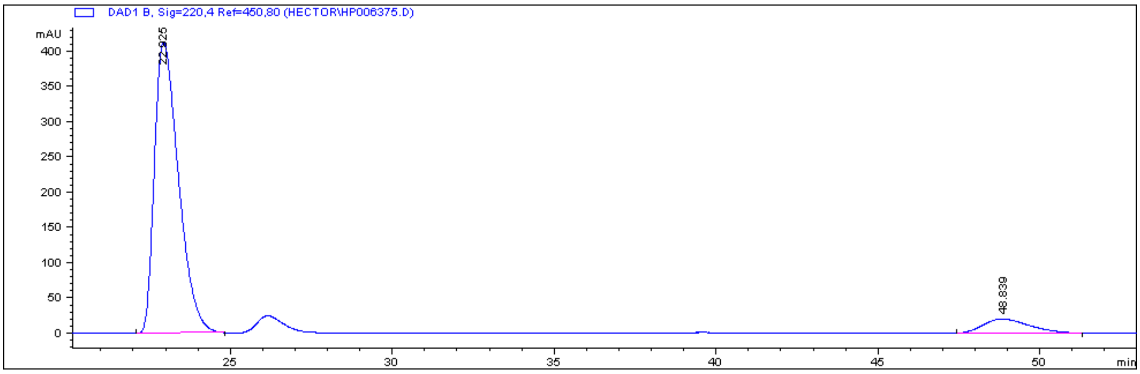
7ba

Racemic molecule:

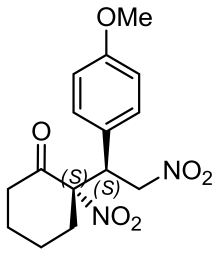


Peak Name	Time	Area	Height	Area%	Symmetry
1	24.571	15376.7	291.4	50.073	0.581
2	50.999	15332.1	144	49.927	0.593

HPLC profile for entry 9, table 4. 100:0 rd, 91:9 er.

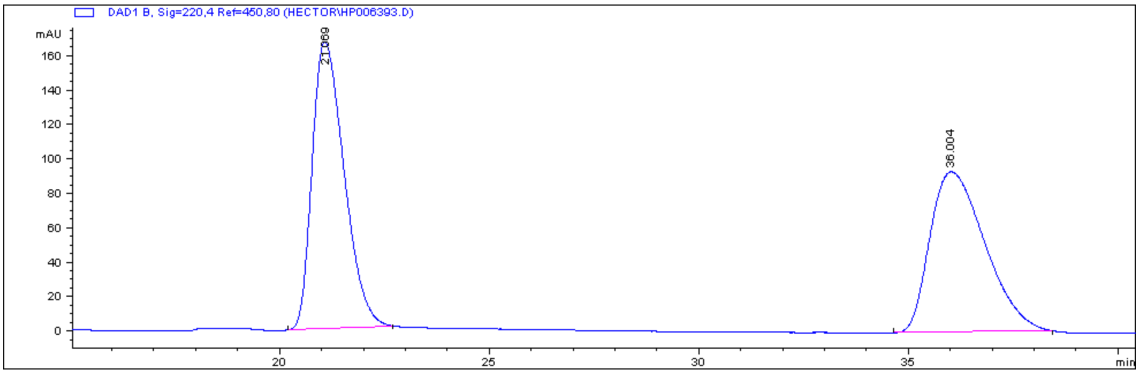


Peak Name	Time	Area	Height	Area%	Symmetry
1	22.925	21353	413.7	91.382	0.571
2	48.839	2013.6	20.2	8.618	0.704



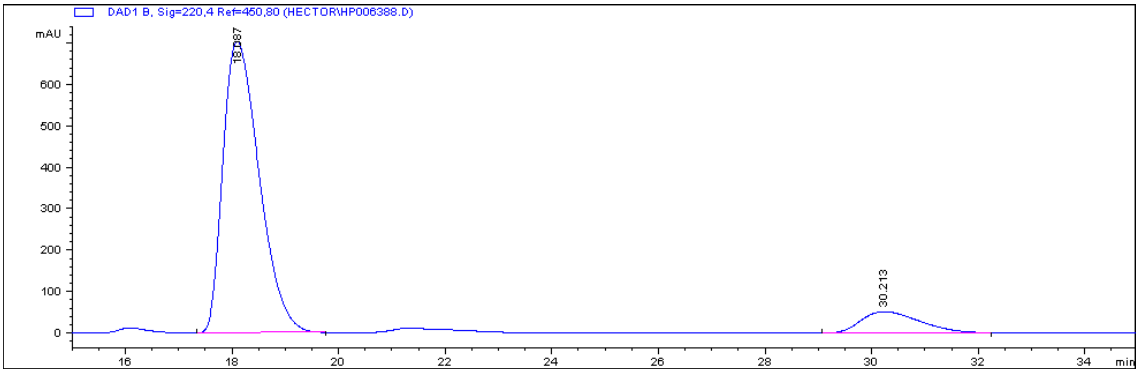
7da

Racemic molecule:

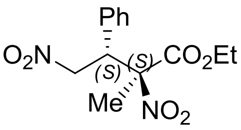


Peak Name	Time	Area	Height	Area%	Symmetry
1	21.069	8883.6	167.1	50.950	0.625
2	36.004	8552.3	93.4	49.050	0.593

HPLC profile for entry 11, table 4. 100:0 rd, 89:11 er.

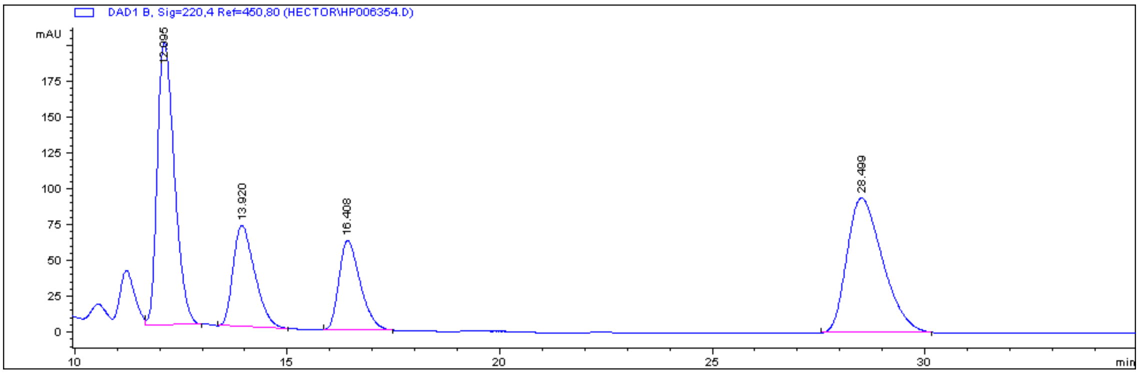


Peak Name	Time	Area	Height	Area%	Symmetry
1	18.087	33190	703.8	89.299	0.601
2	30.213	3977.2	51.7	10.701	0.609



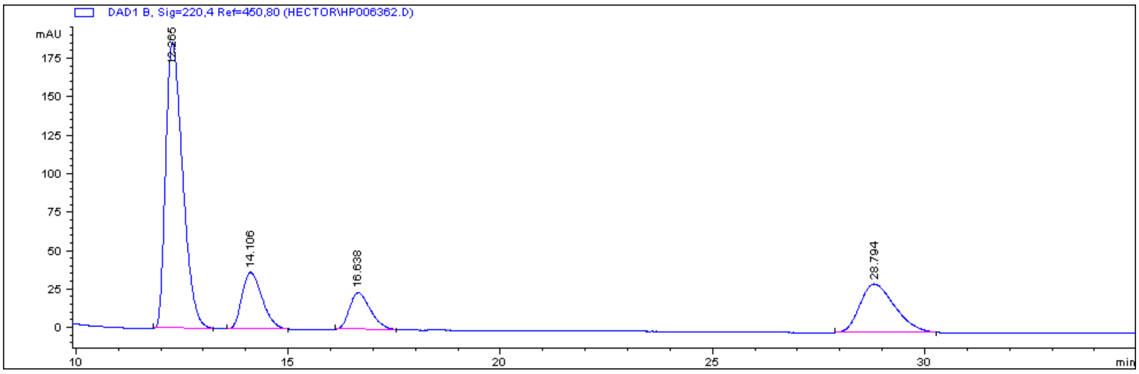
7ab

Racemic molecule:



Peak Name	Time	Area	Height	Area%	Symmetry
1	12.095	5540.7	197.7	35.181	0.662
2	13.92	2507	70.6	15.918	0.649
3	16.408	2174.6	62.4	13.808	0.652
4	28.499	5527	94.2	35.094	0.676

HPLC profile for entry 15, table 4. 76:24 rd, 74:26 er.



Peak Name	Time	Area	Height	Area%	Symmetry
1	12.265	5182.3	186.5	57.326	0.625
2	14.106	1220.8	37	13.504	0.705
3	16.638	829.1	24.1	9.172	0.659
4	28.794	1807.9	31.6	19.999	0.65

4. REFERENCES

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