Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information:

A heterotrimetallic Pd/Sm/Pd complex for asymmetric Friedel-Crafts alkylations of pyrroles with nitroalkenes

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Experimental Section

General aspects. Reagents were purchased from Fluka AG or Aldrich (Buchs, Switzerland). All reactions were performed at ambient conditions without protection of inert atmosphere. Pyrrole was distilled prior to use. The nitroalkenes **5a-5g** were purchased from Sigma-Aldrich. nitroalkene **5h** was prepared according to a literature procedure.[1] Racemic samples of the Friedel-Crafts products described below were prepared using $InCl_3$ as a catalyst following a literature procedure.[2] Flash chromatography was performed on silica gel (Fluka, Kieselgel 60, 230-400 mesh) using compressed air. ^1H NMR and ^{13}C NMR spectra were obtained with a Bruker DPX-NMR (400 MHz) spectrometer using tetramethylsilane as the internal reference. Electron spray ionization mass spectra (ESI-MS) were recorded on a Bruker Esquire 3000^{plus}. IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer with solid (or liquid) samples in a Golden Gate diamond ATR accessory. Optical rotations were measured in a Perkin Elmer Polarimeter 341, sodium lamp, 1 dm cuvette lengths, c in g/100 mL, at ambient temperature in the solvent and concentration indicated. HPLC was carried out using an intelligent pump, detector, integrator on Hewlett Packard S1100 with Chiralcel ODH or ADH columns.

X-ray crystallography. Crystallographic data for **1a**: orthorhombic, space group $P2_12_12_1$, a = 13.4805(4), b = 20.3239(6), c = 24.9820(7) Å, α = β = γ = 90º, V = 6844.5(3) Å^3. Z = 2, ρ_{calcd} = 1.682 gcm^{-1}, μ(Mo Kα) = 1.555 mm^{-1}. Least-squares refinements based on 3874 reflections with $I > 2\sigma(I)$ and 947 parameters led to convergence, with a final R1 = 0.0553, wR_2 = 0.0739, and GOF = 1.0093. Determination of the cell parameters and collection of the reflection intensities were performed on an Enraf-Nonius Kappa CCD diffractometer (graphite monochromated MoKa radiation, λ = 0.71073 N) at 203 K. The structure was solved by direct methods using the program SIR92. Anisotropic least-squares refinement was carried out on all non-hydrogen atoms using the program CRYSTALS. Hydrogen atoms are added in calculated positions. The final refinement was, unfortunately, not great due to the poor crystal quality. CCDC 842060 contains the supplementary crystallographic data for this paper.

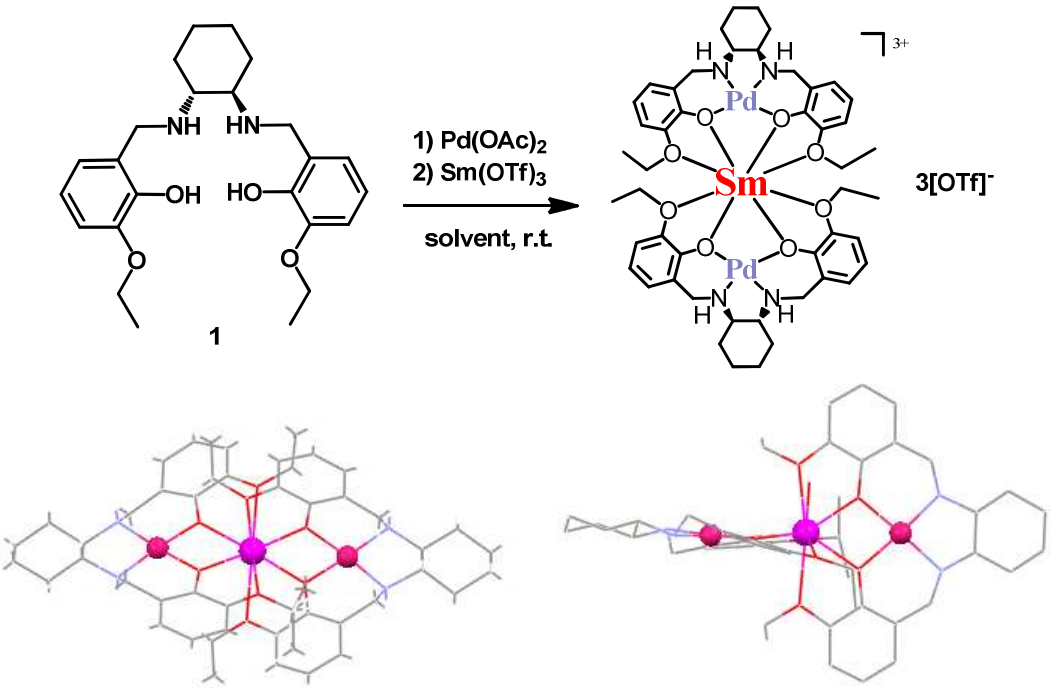
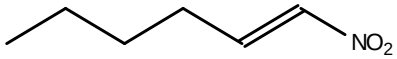


Fig. S1. The preparation and crystal structures of **1a**.

Synthesis of 1/Pd/Sm (2: 2: 1) complex 1a

To a stirred solution of **1** (41.5 mg, 0.1 mmol) in THF (10 mL) was added solid $Pd(OAc)_2$ (22.4 mg, 0.1 mmol) in one portion at room temperature, the resulting mixture was stirred for 15 min, resulting in the formation of a yellow suspension, to which $Sm(OTf)_3$ (29.9 mg, 0.05 mmol) was added in one portion, upon addition the suspension turned into a clear yellow solution immediately. The solution was allowed to stir at room temperature for another 15 min, the solvent was removed by evaporation, the resulting solid was washed with Et_2O, then dried in vacuo. Yield: 83%. The complex for catalytic reactions, however, was prepared in situ. Yellow pellets suitable X-ray structural analysis were obtained by slow diffusion of Et_2O into a $CHCl_3$-C_7H_8 solution of **1a** over a period of two weeks. FT-IR (solid, cm^{-1}): 3136w, 2933w, 1468s, 1386w, 1246s, 1221s, 1156s, 1136w, 1026s, 945w, 870m, 839w, 773w, 736m, 717m, 636s. ESI-MS (MeOH) m/z 541.1 $[Pd\mathbf{L} + Na]^+$ (base peak, calc. 541.1), 1039.6 $[(Pd\mathbf{L})_2 + H]^+$ (calc. 1039.3), 1061.5 $[(Pd\mathbf{L})_2 + Na]^+$ (calc. 1061.5), 1227.4 $[Sm(Pd\mathbf{L})_2 + 2F^-]^+$ (calc. 1227.2).

Synthesis of (*E*)-1-nitrohex-1-ene 5h

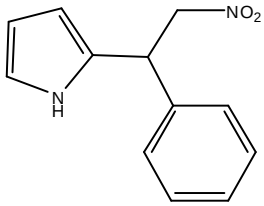


To a mixture of pentaldehyde (1.72 g, 20 mmol) and nitromethane (1.22 g, 20 mmol) in methanol (5 cm^{-3}) at 0 °C was added dropwise a solution of NaOH in H_2O (1.00 g, 25 mmol in 2 cm^{-3}) Further methanol (2 cm^{-3}) was added and the resulting yellow slurry stirred at that temperature for ca. 1 h. Water (15 cm^{-3}) was added and the clear yellow solution was poured into hydrochloric acid (10 cm^{-3} conc. HCl in 15 cm^{-3} H_2O) and stirred for 10 min. The resulting mixture was extracted with CH_2Cl_2 (20 cm^{-3} x 3), the combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc, 25:1, v/v) to yield the title product as a pale-yellow liquid (0.723 g, 28%). IR (liquid, cm^{-1}): 2958m, 2930m, 2860m, 1646m, 1517s, 1464m, 1349s, 1040w, 967s, 913s, 832m, 730s. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (dt, *J* = 4.7, 14.7 Hz, 1H, $H^{CH2CH=CH}$), 6.96 (d, *J* = 13.4 Hz, 1H, $H^{CH=CHNO2}$), 2.25 (m, 2H, H^{CH2}), 1.47 (m, 2H, H^{CH2}), 1.35 (m, 2H, H^{CH2}), 0.90 (m, 3H, H^{CH3}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 139.6, 29.8, 28.1, 22.2, 13.7. Anal. Calc. for $C_6H_{11}NO_2$: C 55.80, H 8.58, N 10.84; Found: 56.22, 8.54, N 10.45%.

General procedure for catalytically asymmetric Friedel-Crafts reaction

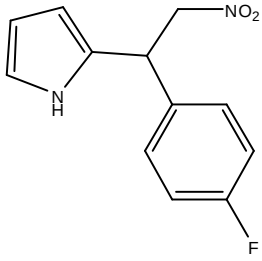
The catalyst was prepared in situ and all reactions were performed in the air without any protection of inert atmosphere. To a stirred solution of **1** (4.15 mg, 0.01 mmol) in THF (0.4 mL) was added solid $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) in one portion at r.t., the resulting mixture was stirred for 15 min, to which $Sm(OTf)_3$ (2.99 mg, 0.005 mmol) was added in one portion, giving a clear yellow solution. The solution was allowed to stir at r.t. for another 15 min to give a solution of catalyst **1a**. To this solution was added the pyrrole substrate (0.60 mmol) and the nitroalkene substrate (0.20 mmol) sequentially. The reaction mixture was stirred for 65 h at room temperature. After the reaction, the Friedel-Crafts product was isolated by flash column chromatography on silica gel with hexane/ethyl acetate as eluents.

2-(2-nitro-1-phenylethyl)-1*H*-pyrrole 6aa



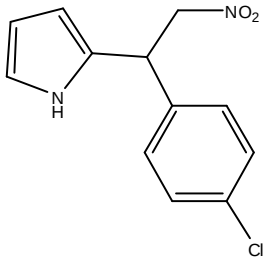
Yellow solid (37.2 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (bs, 1H), 7.38-7.29 (m, 3H), 7.25-7.23 (m, 2H), 6.70-6.68 (m, 1H), 6.18-6.16 (m, 1H), 6.10-6.08 (m, 1H), 4.99 (dd, *J* = 12.0, 7.2 Hz, 1H), 4.92-4.89 (m, 1H), 4.81 (dd, *J* = 12.0, 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.4, 129.6, 129.3, 128.6, 128.3, 118.6, 109.1, 106.2, 79.6, 43.3. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 heptane: isopropanol, 0.8 mL/min, 250 nm); major enantiomer t_r = 28.0 min, minor enantiomer t_r = 34.7 min; 85% ee; $[\alpha]_D^{20}$ +58.8 (c = 1.1, CH_2Cl_2).

2-[1-(4-fluorophenyl)-2-nitroethyl]-1*H*-pyrrole 6ab



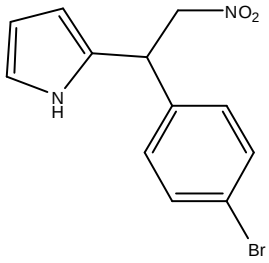
Pale-yellow crystals (43.1 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (bs, 1H), 7.23-7.19 (m, 2H), 7.07-7.03 (m, 2H), 6.72-6.70 (m, 1H), 6.19-6.17 (m, 1H), 6.09-6.07 (m, 1H), 4.97 (dd, *J* = 12.0, 7.2 Hz, 1H), 4.89 (t, *J* = 8.0 Hz, 1H), 4.77 (dd, *J* = 12.4, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.2, 130.1, 130.0, 129.1, 118.8, 116.7, 109.2, 106.3, 79.6, 42.6. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 heptane: isopropanol, 0.6 mL/min, 230 nm); major enantiomer t_r = 70.8 min, minor enantiomer t_r = 74.7 min; 91% ee; $[\alpha]_D^{20}$ +60.6 (c = 1.0 , CH_2Cl_2).

2-[1-(4-chlorophenyl)-2-nitroethyl]-1*H*-pyrrole 6ac



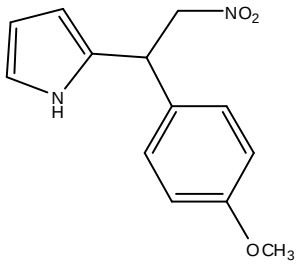
White crystals (47.0 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (bs, 1H), 7.34-7.31 (m, 2H), 7.19-7.15 (m, 2H), 6.72-6.70 (m, 1H), 6.19-6.16 (m, 1H), 6.08-6.07 (m, 1H), 4.97 (dd, *J* = 12.4, 7.2 Hz, 1H), 4.88 (t, *J* = 7.6 Hz, 1H), 4.77 (dd, *J* = 12.0, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.9, 134.5, 129.8, 129.7, 128.7, 118.9, 109.2, 106.4, 79.4, 42.7. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (85:15 heptane: isopropanol, 0.8 mL/min, 250 nm); major enantiomer t_r = 19.8 min, minor enantiomer t_r = 21.7 min; 71% ee; $[\alpha]_D^{20}$ +56.2 (c = 1.1, CH_2Cl_2).

2-[1-(4-bromophenyl)-2-nitroethyl]-1*H*-pyrrole 6ad



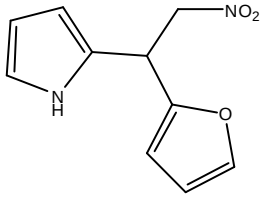
White crystals (54.7 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (bs, 1H), 7.50-7.46 (m, 2H), 7.13-7.09 (m, 2H), 6.72-6.70 (m, 1H), 6.19-6.16 (m, 1H), 6.07-6.06 (m, 1H), 4.97 (dd, *J* = 12.0, 6.8 Hz, 1H), 4.86 (t, *J* = 7.6 Hz, 1H), 4.77 (dd, *J* = 12.0, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.5, 132.8, 130.0, 128.6, 122.6, 118.9, 109.2, 106.4, 79.3, 42.8. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (85:15 heptane: isopropanol, 0.8 mL/min, 250 nm); major enantiomer t_r = 22.8 min, minor enantiomer t_r = 25.1 min; 80% ee; $[\alpha]_D^{20}$ +37.4 (c = 1.5 , CH_2Cl_2).

2-[1-(4-methoxyphenyl)-2-nitroethyl]-1*H*-pyrrole 6ae



Yellow oil (43.1 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (bs, 1H), 7.17-7.13 (m, 2H), 6.90-6.86 (m, 2H), 6.70-6.68 (m, 1H), 6.18-6.16 (m, 1H), 6.07-6.06 (m, 1H), 4.96 (dd, *J* = 12.0, 7.2 Hz, 1H), 4.85 (t, *J* = 8.0 Hz, 1H), 4.76 (dd, *J* = 12.0, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 130.2, 129.7, 129.5, 118.5, 115.0, 109.1, 106.0, 79.8, 55.7, 42.6. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 heptane: isopropanol, 0.6 mL/min, 230 nm); major enantiomer t_r = 70.8 min, minor enantiomer t_r = 74.7 min; 89% ee; $[\alpha]_D^{20}$ +77.2 (c = 0.9 , CH_2Cl_2).

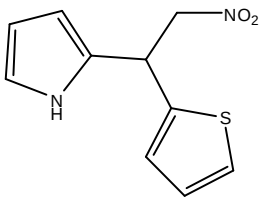
2-(2-nitro-1-furylethyl)-1*H*-pyrrole 6af



Brownish solid (39.1 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (bs, 1H), 7.41-7.40 (m, 1H), 7.19-7.15 (m, 1H), 6.74-6.73 (m, 1H), 6.35-6.34 (m, 1H), 6.21-6.20 (m, 1H), 6.18-6.16 (m, 1H), 6.10 (bs, 1H), 5.02 (t, *J* = 7.6 Hz, 1H), 4.90 (dd, *J* = 12.8, 7.6 Hz, 1H), 4.82 (dd, *J* = 12.8, 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 143.2, 126.7, 118.7, 111.0, 109.3, 108.6, 108.3, 107.1, 78.2, 37.4.Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (85:15 heptane:

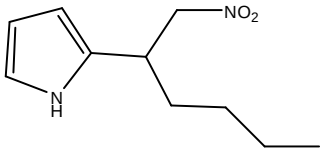
isopropanol, 0.8 mL/min, 250 nm); minor enantiomer t_r = 12.5 min, major enantiomer t_r = 14.5 min; 85% ee; $[\alpha]_D^{20}$ -26.4 (c = 0.8 , CH_2Cl_2).

2-(2-nitro-1-thiophenylethyl)-1*H*-pyrrole 6ag



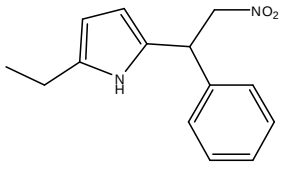
Brownish solid (38.2 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (bs, 1H), 7.27-7.25 (m, 1H), 6.99-6.97 (m, 1H), 6.96-6.94 (m, 1H), 6.73-6.71 (m, 1H), 6.19-6.17 (m, 1H), 6.12 (bs, 1H), 5.22 (t, *J* = 8.0 Hz, 1H), 4.95 (dd, *J* = 12.8, 7.6 Hz, 1H), 4.84 (dd, *J* = 13.2, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.4, 128.7, 127.6, 126.4, 126.0, 118.7, 109.3, 106.4, 80.1, 38.7. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (85:15 heptane: isopropanol, 0.8 mL/min, 250 nm); minor enantiomer t_r = 17.8 min, major enantiomer t_r = 21.3 min; 93% ee; $[\alpha]_D^{20}$ +47.9 (c = 0.5 , CH_2Cl_2).

2-(1-butyl-2-nitroethyl)-1*H*-pyrrole 6ah



Colourless oil (21.6 mg, 55%). IR (liquid, cm^{-1}): 3392m, 2926s, 2858m, 1541s, 1429w, 1177s, 1331w, 1121w, 1028w, 716s. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (bs, 1H), 6.70-6.68 (m, 1H), 6.17-6.15 (m, 1H), 6.01-6.99 (m, 1H), 4.56-4.46 (m, 2H), 1.70-1.62 (m, 2H), 1.35-1.21 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 130.5, 117.7, 109.1, 106.2, 105.8, 80.9, 37.9, 32.5, 29.6, 22.9, 14.3. ESI-MS (MeOH): m/z 219.1 $[M + Na]^+$ (base peak, calc. 219.1). Anal. Calc. C 61.20, H 8.22, N 14.27 for $C_{10}H_{16}N_2O_2$; Found: 61.52, 8.35, N 13.96%. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 heptane: isopropanol, 0.5 mL/min, 230 nm); minor enantiomer t_r = 29.9 min, major enantiomer t_r = 32.4 min; 59% ee; $[\alpha]_D^{20}$ -15.7 (c = 0.6 , CH_2Cl_2).

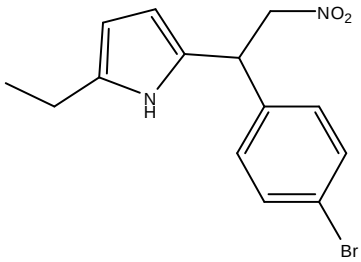
2-(2-nitro-1-phenylethyl)-5-ethyl-1*H*-pyrrole 6ba



Brownish oil (42.0 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (bs, 1H), 7.40-7.35 (m, 3H), 7.32 (m, 2H), 5.98 (t, *J* = 4.0 Hz, 1H), 5.86 (t, *J* = 3.8 Hz, 1H), 5.00 (dd, *J* = 12.0, 8.0 Hz, 1H), 4.88 (t, *J*

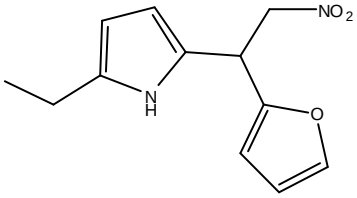
= 8.0 Hz, 1H), 4.80 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.55 (q, *J* = 8.0 Hz, 2H), 1.20 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.7, 135.2, 129.6, 128.5, 128.3, 127.7, 106.1, 104.8, 79.7, 43.4, 21.1, 13.8. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 heptane: isopropanol, 0.8 mL/min, 250 nm); major enantiomer t_r = 19.3 min, minor enantiomer t_r = 22.9 min; 66% ee; $[\alpha]_D^{20}$ +31.0 (c = 0.7, CH_2Cl_2).

2-[1-(4-bromophenyl)-2-nitroethyl]-5-ethyl-1*H*-pyrrole 6bd



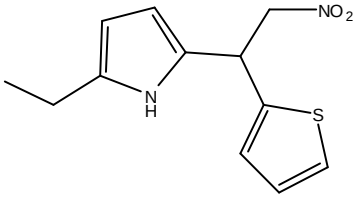
Brownish oil (58.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (bs, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.96 (t, *J* = 4.0 Hz, 1H), 5.86 (t, *J* = 4.0 Hz, 1H), 4.97 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.83 (t, *J* = 8.0 Hz, 1H), 4.76 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.55 (q, *J* = 8.0 Hz, 2H), 1.21 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.8, 135.6, 132.7, 130.0, 127.0, 122.5, 106.3, 104.9, 79.4, 42.9, 25.8, 21.1, 13.8. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 heptane: isopropanol, 0.8 mL/min, 250 nm); major enantiomer t_r = 23.6 min, minor enantiomer t_r = 26.6 min; 50% ee; $[\alpha]_D^{20}$ +11.6 (c = 0.6, CH_2Cl_2).

2-(2-nitro-1-furylethyl)-5-ethyl-1*H*-pyrrole 6bf



Brownish oil (43.0 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (bs, 1H), 7.43 (m, 1H), 6.36 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 5.99 (t, *J* = 4.0 Hz, 1H), 5.86 (t, *J* = 4.0 Hz, 1H), 4.99 (t, *J* = 8.0 Hz, 1H), 4.91 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.83 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.60 (q, *J* = 8.0 Hz, 2H), 1.24 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 147.8, 143.1, 138.7, 135.3, 125.0, 111.0, 108.1, 107.0, 105.1, 78.3, 37.5, 25.9, 21.2, 13.7. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 heptane: isopropanol, 0.8 mL/min, 250 nm); minor enantiomer t_r = 12.4 min, major enantiomer t_r = 15.3 min; 85% ee; $[\alpha]_D^{20}$ -24.2 (c = 0.5, CH_2Cl_2).

2-(2-nitro-1-thiophenylethyl)-5-ethyl-1*H*-pyrrole 6bg



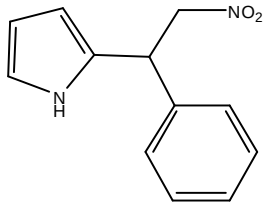
Brownish oil (47.0 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (bs, 1H), 7.43 (m, 1H), 7.29 (m, 1H), 7.01-6.96 (m, 2H), 6.01 (t, *J* = 4.0 Hz, 1H), 5.87 (t, *J* = 4.0 Hz, 1H), 5.18 (t, *J* = 8.0 Hz, 1H), 4.96 (dd, *J* = 12.0, 8.0 Hz, 1H), 4.84 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.58 (q, *J* = 8.0 Hz, 2H), 1.23 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.5, 134.9, 127.2, 126.7, 125.8, 125.5, 105.8, 104.6, 79.8, 38.3, 20.8, 13.4. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 heptane: isopropanol, 0.8 mL/min, 250 nm); minor enantiomer t_r = 18.0 min, major enantiomer t_r = 21.8 min; 87% ee; $[\alpha]_D^{20}$ +20.7 (c = 1.2, CH_2Cl_2).

References:

(1) J. T. Liu, C. F. Yao, *Tetrahedron Lett.* 2001, **42**, 6147-6150.
(2) B. M. Trost, C. Müller, *J. Am. Chem. Soc.*, 2008, **130**, 2438-2439.

HPLC profiles:

Racemates and products



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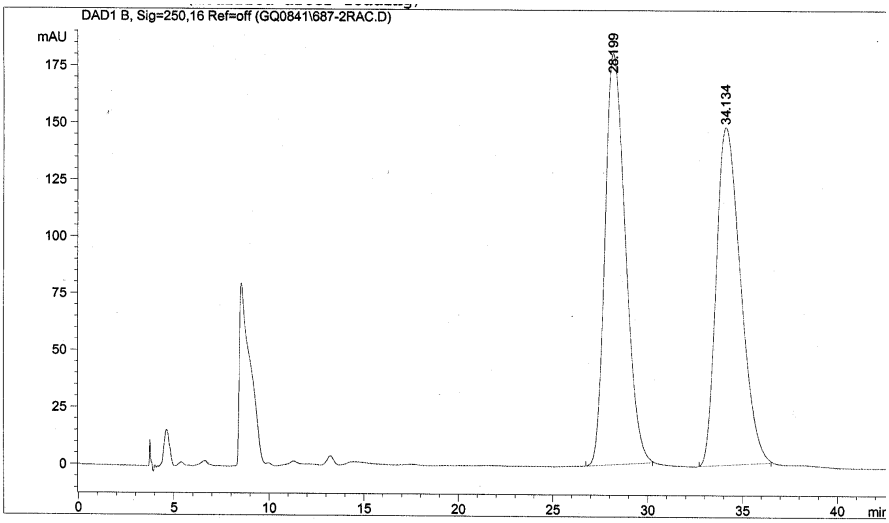
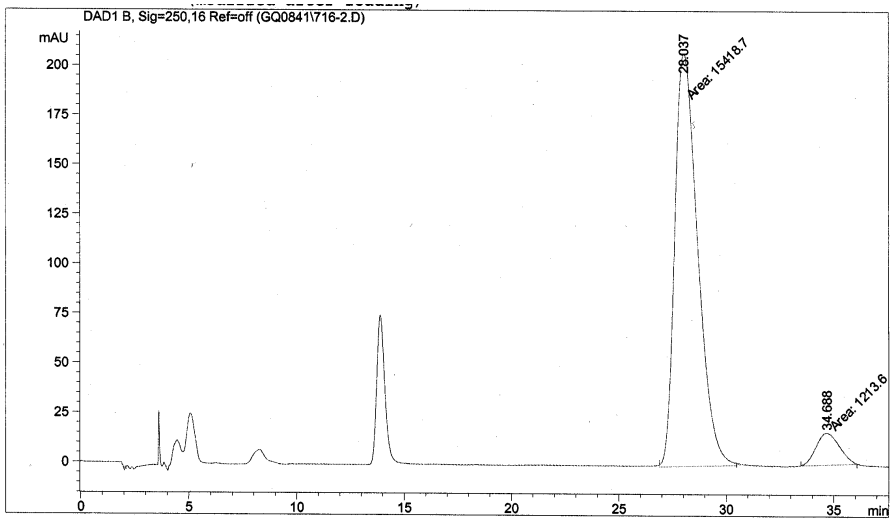
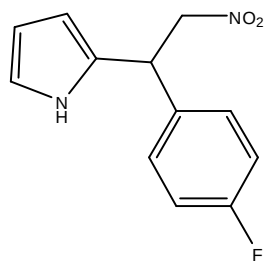


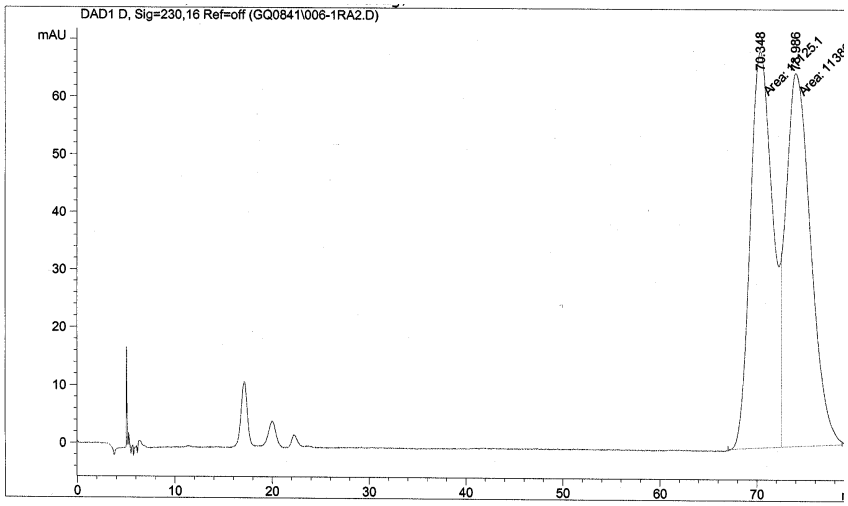


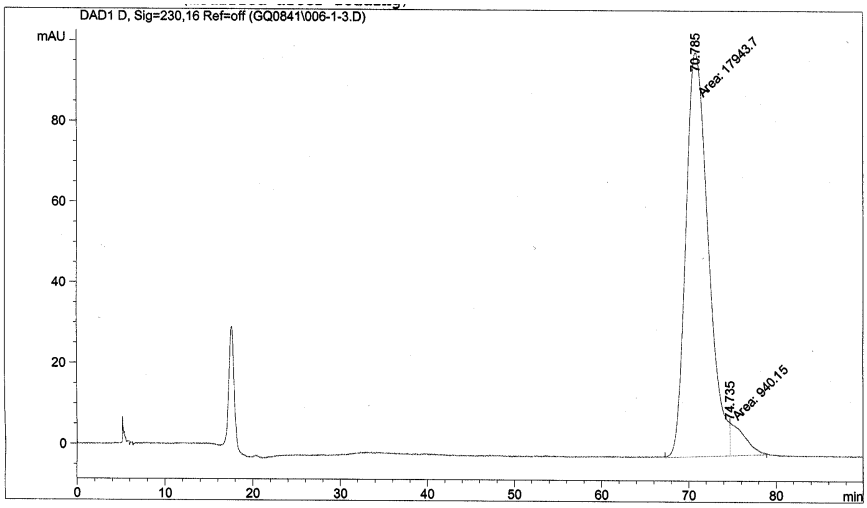
Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.037	MM	1.2365	1.54187e4	207.82443	92.7034
2	34.688	MM	1.2549	1213.59900	16.11799	7.2966



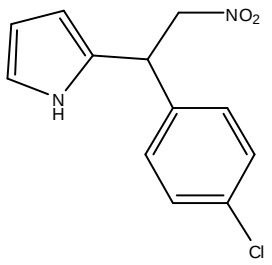
6ab



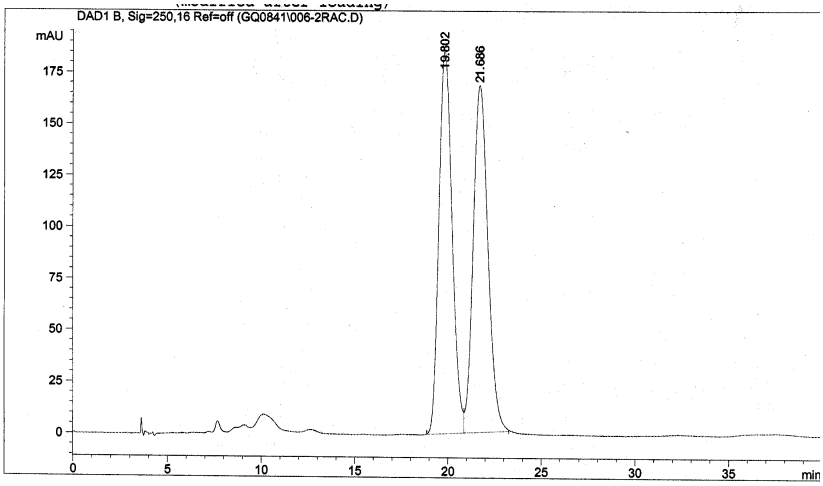


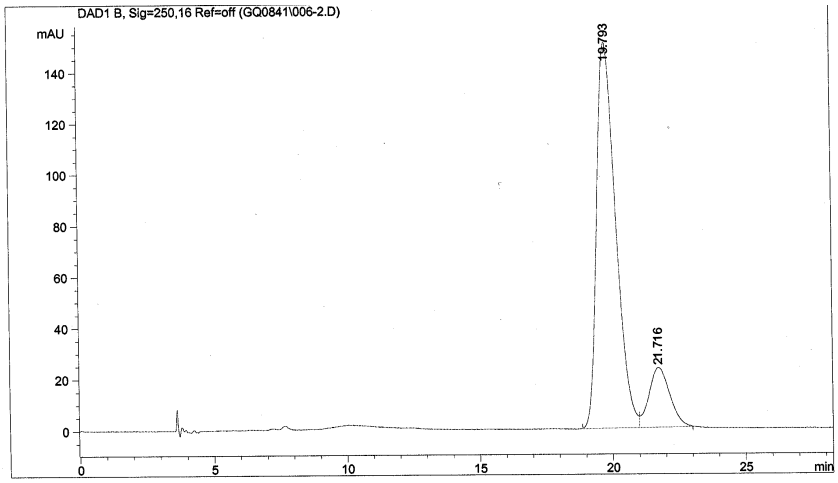
Signal 1: DAD1 D, Sig=230,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	70.785	MF	2.9850	1.79437e4	100.18740	95.0214
2	74.735	FM	1.9168	940.15045	8.17478	4.9786



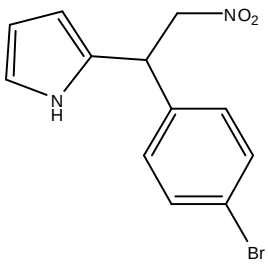
6ac





Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.793	BV	0.7642	7458.44629	150.50403	85.5280
2	21.716	VB	0.6844	1262.03137	23.06211	14.4720



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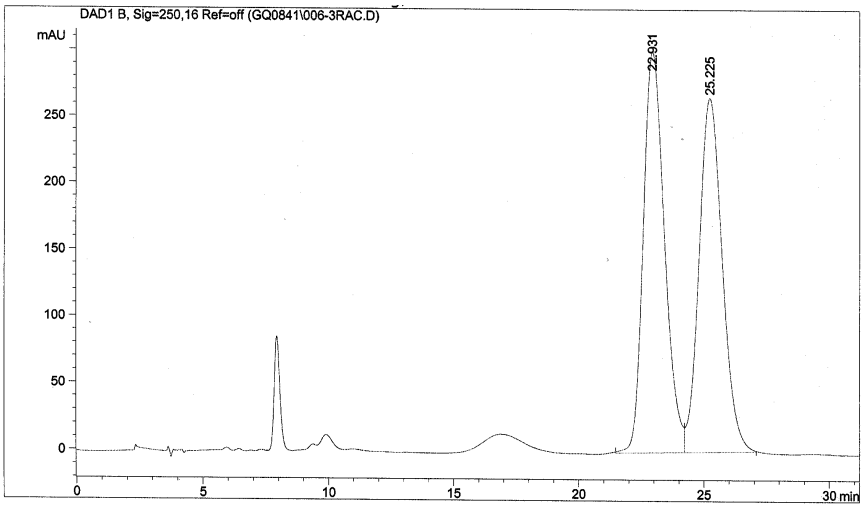
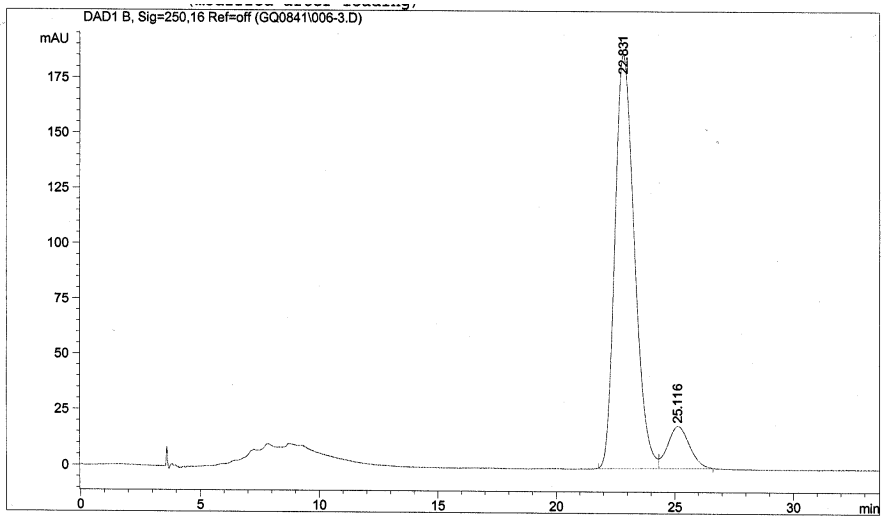
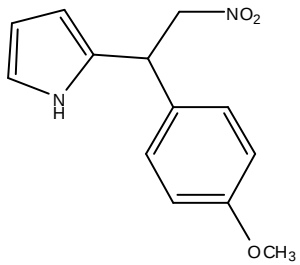


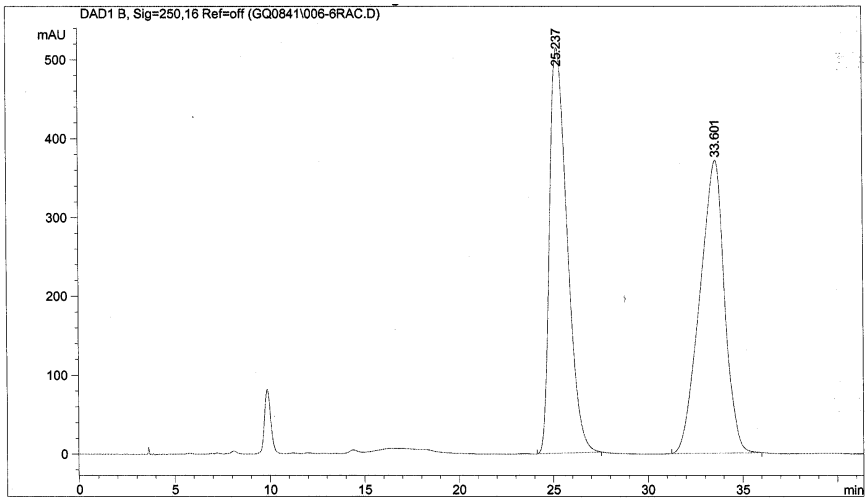


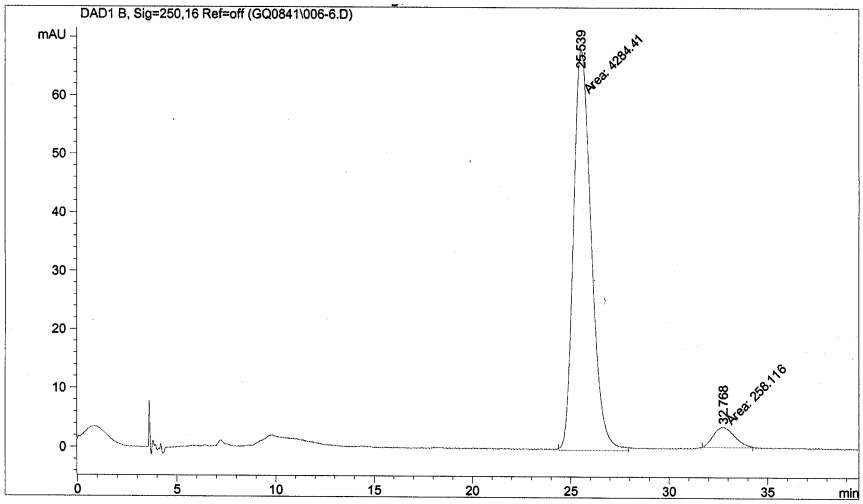
Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.831	BB	0.8675	1.06772e4	186.62993	89.8100
2	25.116	BB	0.7768	1211.45251	18.87497	10.1900



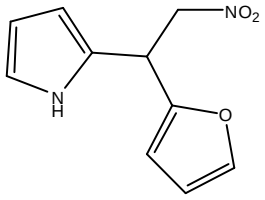
6ae





Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.539	MM	1.0448	4284.41260	68.34254	94.3178
2	32.768	MM	1.2609	258.11563	3.41170	5.6822



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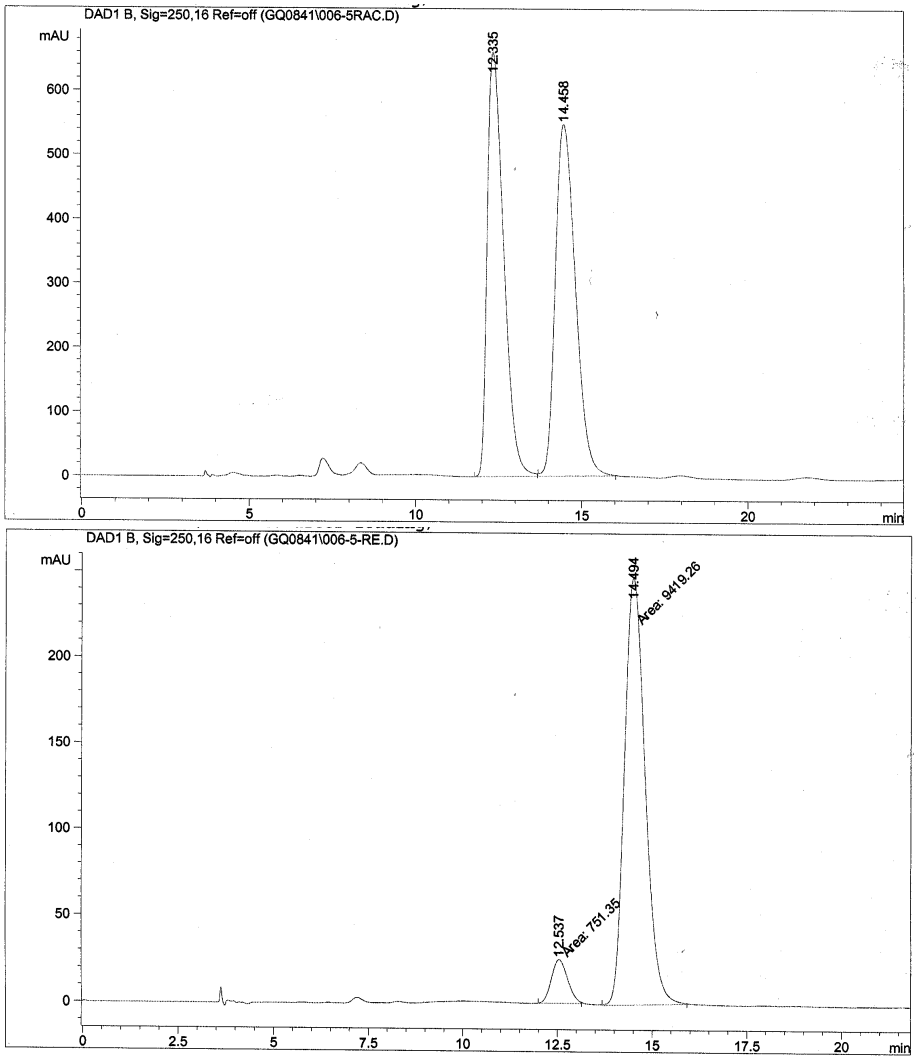
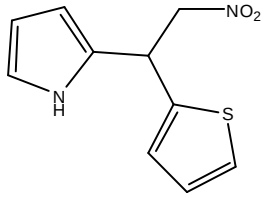


Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.537	MM	0.4973	751.34973	25.18150	7.3875
2	14.494	MM	0.6337	9419.25781	247.73141	92.6125



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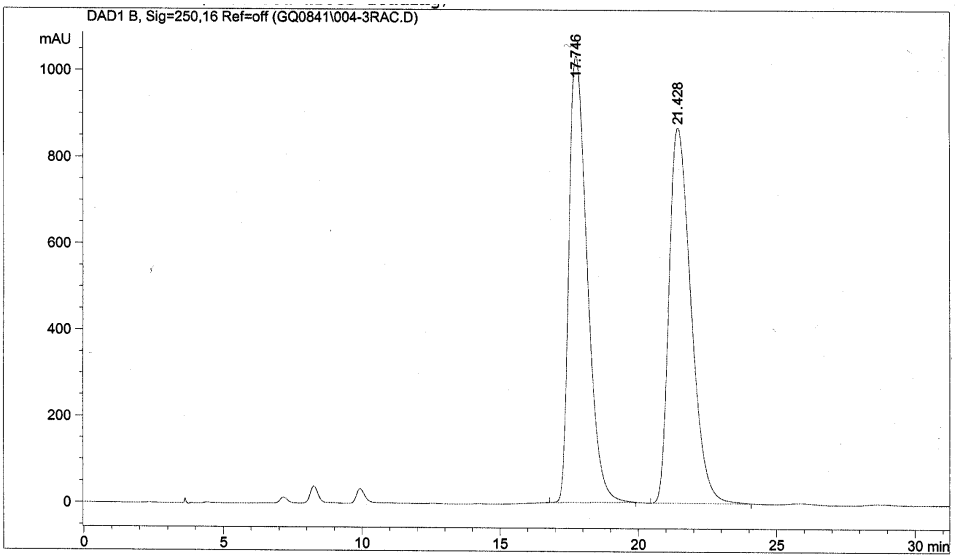
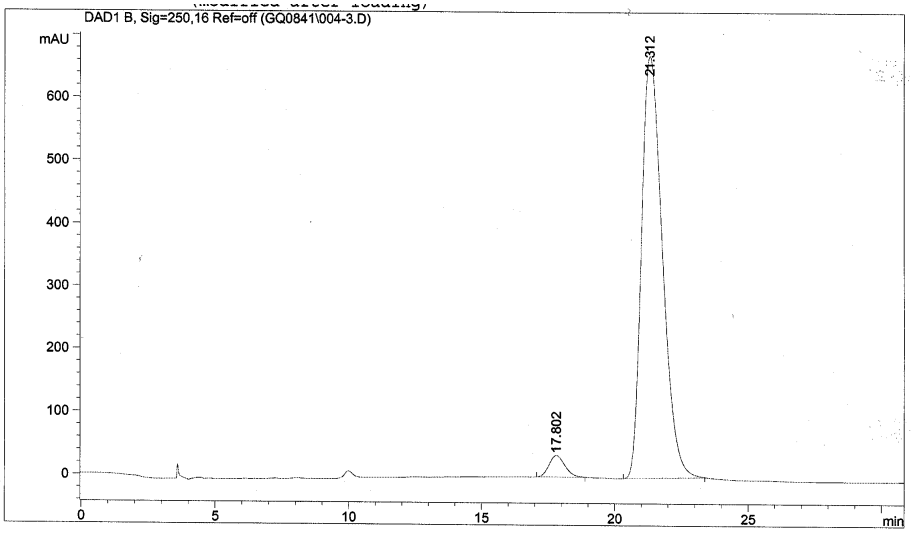
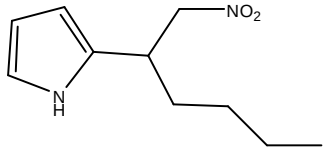




Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.802	BB	0.6249	1429.00464	34.37843	3.7527
2	21.312	BB	0.8410	3.66504e4	671.21082	96.2473



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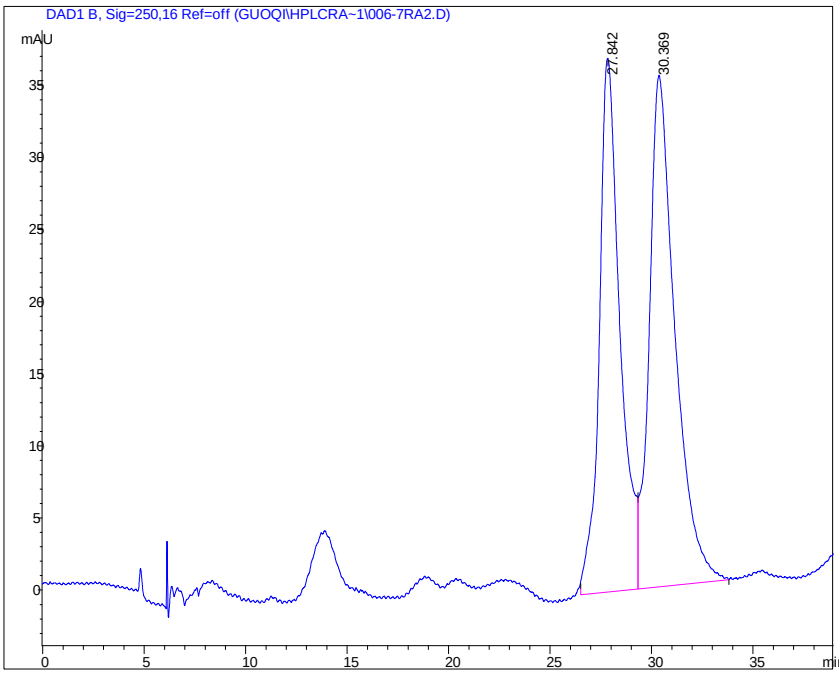
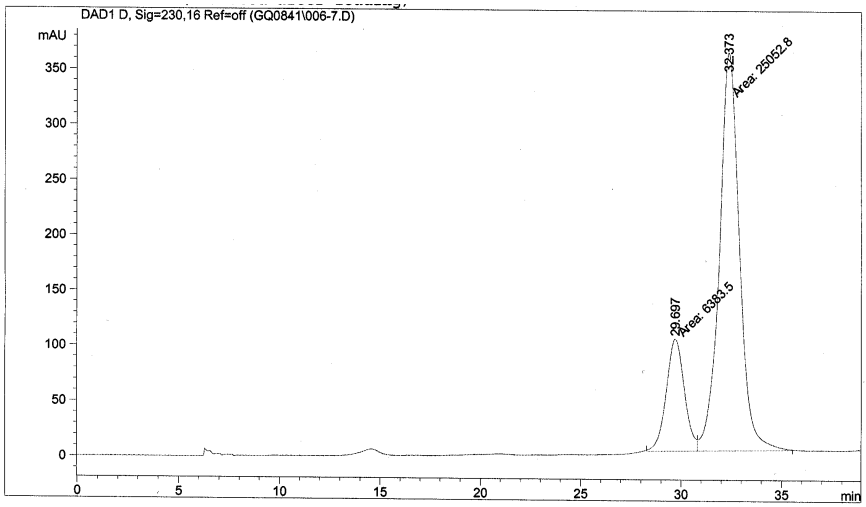
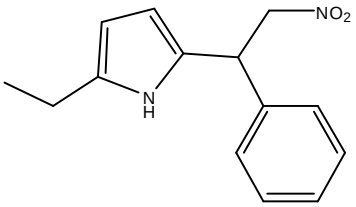




Signal 1: DAD1 D, Sig=230,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.697	MF	1.0504	6383.49512	101.28540	20.3061
2	32.373	FM	1.1623	2.50528e4	359.23685	79.6939



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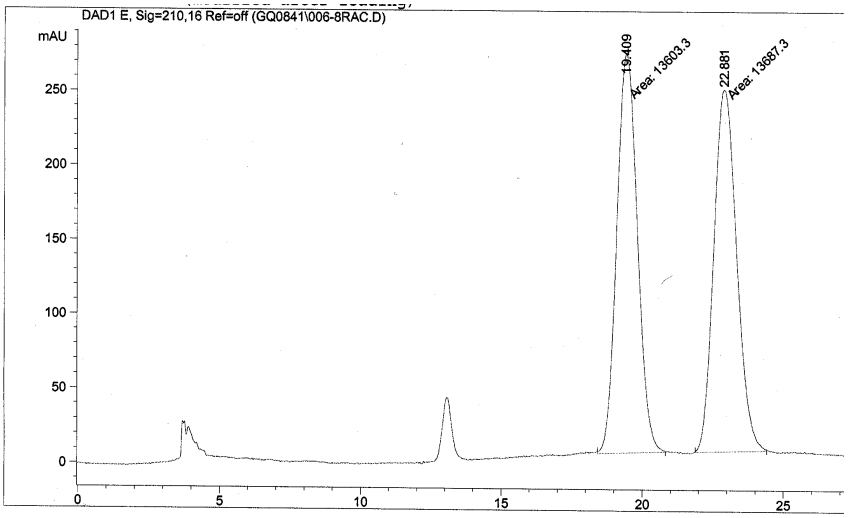
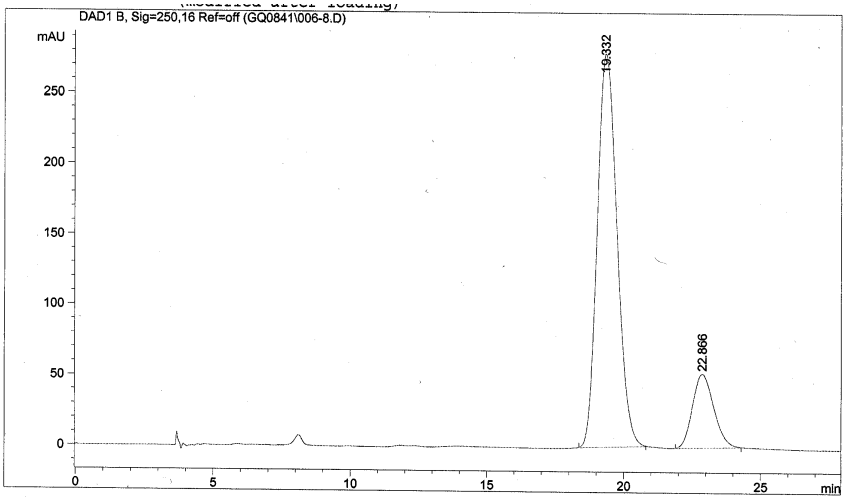
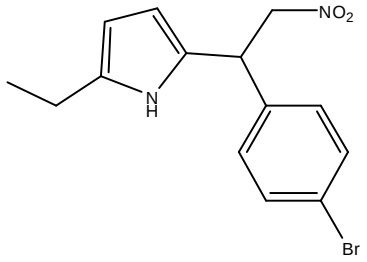




Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.332	BB	0.7661	1.39924e4	278.50830	83.1151
2	22.866	BB	0.7945	2842.55713	52.26468	16.8849



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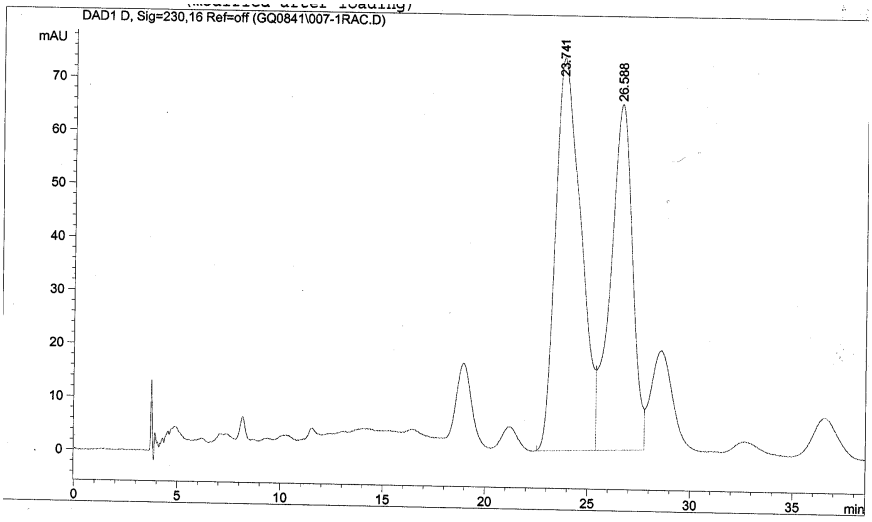
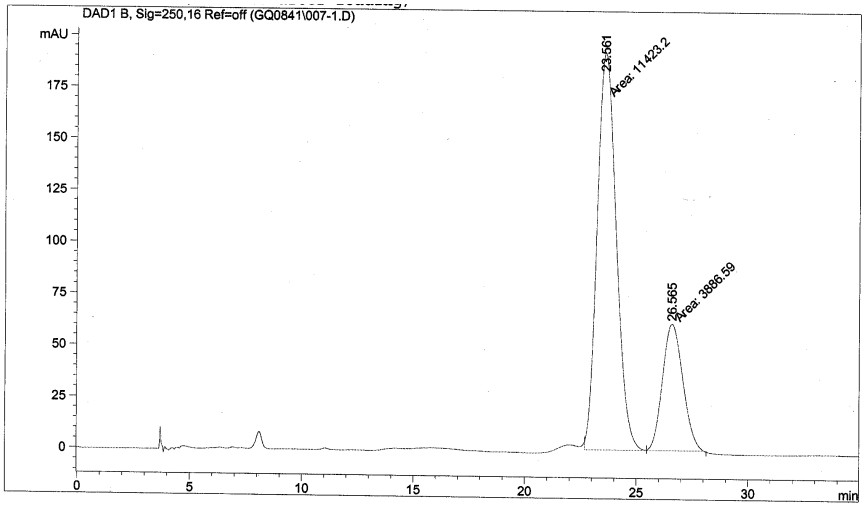
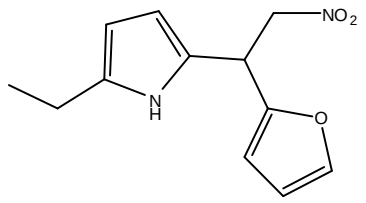




Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.561	MF	0.9926	1.14232e4	191.80528	74.6137
2	26.565	FM	1.0594	3886.59009	61.14575	25.3863



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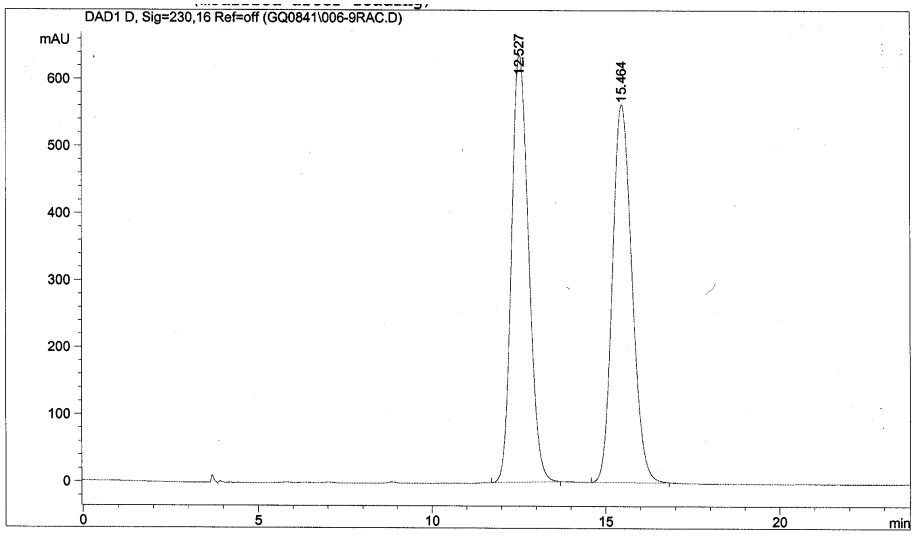
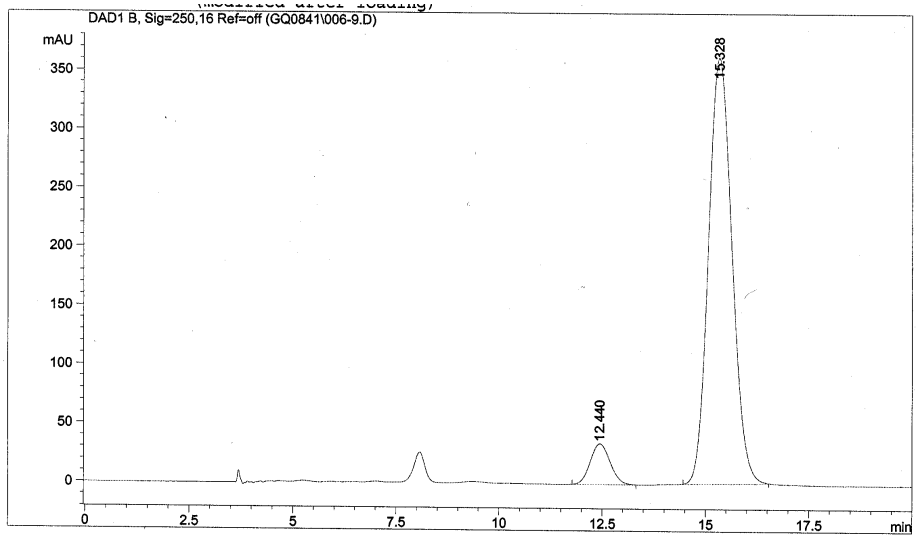
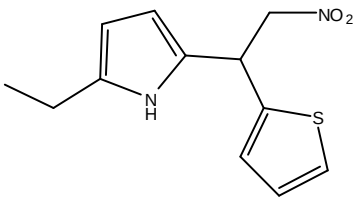


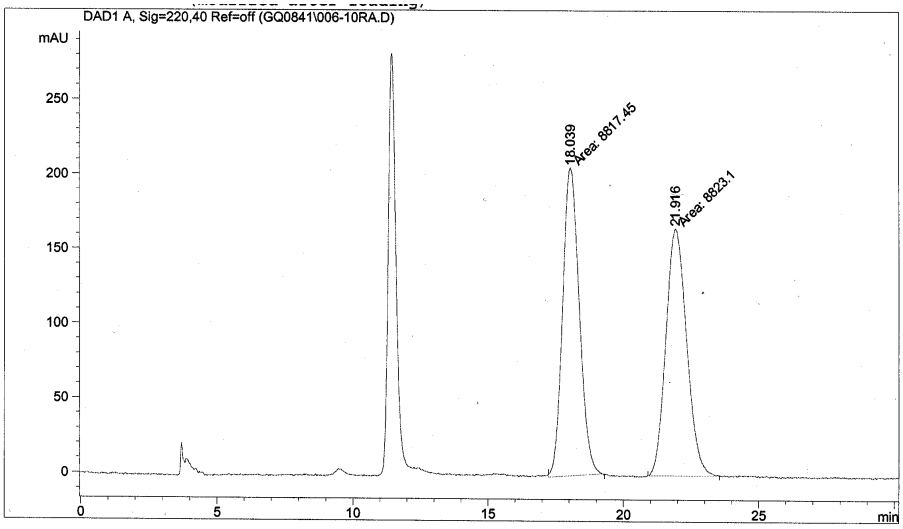


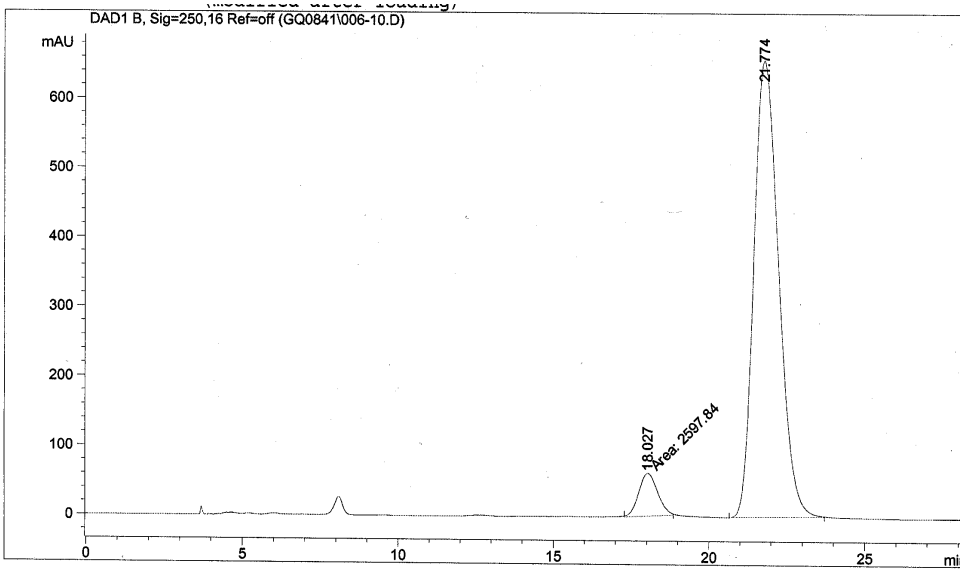
Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.440	BB	0.5154	1162.87952	34.48457	7.5026
2	15.328	BB	0.6187	1.43369e4	361.51810	92.4974



6bg





Signal 1: DAD1 B, Sig=250,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.027	MM	0.7039	2597.84399	61.51017	6.6668
2	21.774	BB	0.8683	3.63693e4	656.54767	93.3332