Supporting Information

Pd-catalyzed stereospecific allyl-aryl coupling of allylic alcohols with arylboronic acids

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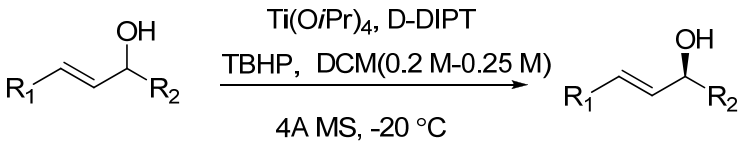
General Experimental Details

Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shenghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still.[1] Toluene, cyclohexane, dichloromethane, ether and pentane were distilled from CaH_2, THF was distilled from sodium/benzophenone. Methanol was treated with a small amount of sodium before distillation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Mercuryplus 400 NMR spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. And the following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High performance liquid chromatography (HPLC) was performed on Thermo Fisher Scientific Dionex Ultimate 3000 HPLC by using Daicel Chiracel OD-H or OJ-H columns with *i*-PrOH/hexane as the eluent. Optical rotations were measured on a SGW-1 polarimeter. The melting points were measured by Netzsch DSC-200 F3 differential scanning calorimeter.

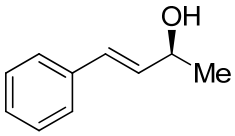
$Pd_2(dba)_3$•$CHCl_3$ and all ligands were purchased from Sinocompound Co. and used as received. The arylboronic acids were purchased from Accela ChemBio Inc. and used after recrystallization with water. Racemic allylic alcohols were prepared by available methods: *rac*–**1a**,[2] *rac*–**1b**,[3] *rac*–**1c**,[4] *rac*–**1f** [5]; for *rac*–**1d** and *rac*–**1e**: the first step is to synthesis the corresponding unsaturated ketones,[6] then reduce the ketones by using $NaBH_4$ and $CeCl_3{\cdot}7H_2O$ (MeOH as solvent, ice bath) under the monitoring of TLC. All other chemicals were used as received from commercial resources.

General Procedure for Synthesis of Chiral Allylic Alcohols[7]



To a cooled (-20 °C) suspension of 4Å Molecular Sieves in dry DCM (0.2 M–0.25M), $Ti(OiPr)_4$ (0.3 eq) and D-DIPT (0.3 eq) were added under N_2 atmosphere. After stirred for half an hour, allylic alcohol (1.0 eq) in DCM and TBHP (0.6–0.8 eq, approx 5.5 M solution in decane) was added subsequently. After keeping stirred for another 12 hours at the same temperature, the reaction was quenched by adding an aqueous solution of $FeSO_4 \cdot 7H_2O$ (2.0 eq) and tartaric acid (1.3 eq). Then the mixture was continued to be stirred for 30 min at -20 °C and more than 3 hours in addtion at room temperature. The mixture was extracted with DCM three times, dried over Na_2SO_4 and concentrated under reduced pressure. The crude compound was purified by flash column chromatography (EA:PE = 1:100–1:20, *v/v*) to afford enantioenriched allylic alcohols in 25–37% yields.

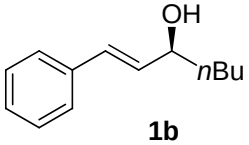
(*S*,*E*)-4-phenylbut-3-en-2-ol (1a)[8]



1a

White solid; m.p. 54 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.22 (m, 5H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.26 (dd, *J* = 15.8, 6.4 Hz, 1H), 4.53–4.46 (m, 1H), 1.75 (br s, 1H), 1.38 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 133.5, 129.3, 128.5, 127.6, 126.4, 68.9, 23.4; $[\alpha]^{25}_D$ = -26.0 (*c* = 0.32, $CHCl_3$); 96% ee; [lit.[8] $[\alpha]^{20}_D$ = -27.0 (*c* = 1.0, $CHCl_3$), 98% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 10/90, t_{major} = 13.2 min, t_{minor} = 8.7 min.

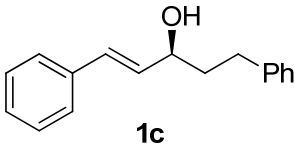
(*S*,*E*)-1-phenylhept-1-en-3-ol (1b)[9]



1b

Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.22 (m, 5H), 6.57 (d, *J* = 16.4 Hz, 1H), 6.23 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.28 (m, 1H), 1.71–1.56 (m, 3H), 1.46–1.32 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 132.6, 130.2, 128.6, 127.6, 126.4, 73.1, 37.1, 27.6, 22.6, 14.1; $[\alpha]^{22}_D$ = +1.3 (*c* = 0.72, $CHCl_3$); 96% ee; [lit.[9] $[\alpha]^{20}_D$ = +1.5 (*c* = 0.68, $CHCl_3$), 98% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 10/90, t_{major} = 12.2 min, t_{minor} = 7.9 min.

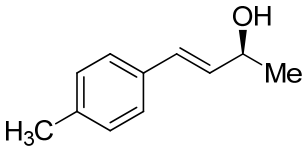
(*S*,*E*)-1,5-diphenylpent-1-en-3-ol (1c)[10]



1c

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.18 (m, 10H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.25 (dd, *J* = 16.0, 7.2 Hz, 1H), 4.34–4.28 (m, 1H), 2.83–2.70 (m, 2H), 2.04–1.89 (m, 2H), 1.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 136.6, 132.1, 130.6, 128.6, 128.45, 128.38, 127.7, 126.4, 125.9, 72.3, 38.7, 31.7; $[\alpha]^{22}_D$ = +13.2 (*c* = 0.68, $CHCl_3$); 98% ee; [lit.[10] $[\alpha]^{20}_D$ = +20 (*c* = 0.6, EtOH), 79% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 15/85, t_{major} = 16.0 min, t_{minor} = 14.1 min.

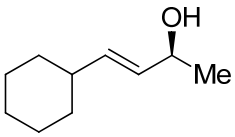
(*S*,*E*)-4-(p-tolyl)but-3-en-2-ol (1d)[8,11]



1d

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 15.2, 1H), 6.21 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.51–4.45 (m, 1H), 1.59 (bs, 1H), 2.34 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 133.8, 132.5, 129.3, 129.2, 126.3, 69.0, 23.4, 21.2; $[\alpha]^{25}_D$ = -20.9 (*c* = 0.67, $CHCl_3$); 98% ee; [lit.[8] $[\alpha]^{20}_D$ = -22.8 (*c* = 1.0, $CHCl_3$), >99% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 10/90, t_{major} = 9.9 min, t_{minor} = 8.5 min.

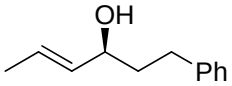
(*S*,*E*)-4-cyclohexylbut-3-en-2-ol (1e)[12]



1e

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.58 (dd, *J* = 15.2, 6.4 Hz, 1H), 5.46 (ddd, *J* = 15.2, 6.4, 0.8 Hz, 1H), 4.25 (m, 1H), 1.97–1.89 (m, 1H), 1.75–1.62 (m, 4H), 1.46 (d, *J* = 2.8 Hz, 1H, OH), 1.32–1.00 (m, 6H), 1.25 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 131.5, 68.8, 40.0, 32.71, 32.69, 26.0, 25.9, 23.3; $[\alpha]^{22}_D$ = -16.4 (*c* = 0.56, $CHCl_3$); 95% ee; [The *ee* value was determined after converted to *p*-nitrobenzoate. HPLC conditions: Chiralcel OJ-H column, 254 nm, flow rate: 0.8 ml/min, *i*-PrOH/hexane = 3/97, t_{major} = 7.32 min, t_{minor} = 8.76 min].

(*S*,*E*)-1-phenylhex-4-en-3-ol (1f)[13]



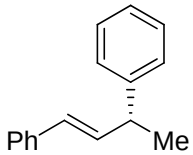
1f

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.21–7.16 (m, 3H), 5.68 (dq, *J* = 21.6, 6.8 Hz, 1H), 5.52 (ddd, *J* = 15.2, 6.8, 1.6 Hz, 1H), 4.09–4.04 (m, 1H), 2.75–2.62 (m, 2H), 1.71 (d, *J* = 6.4 Hz, 3H), 1.46 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 134.0, 128.4, 128.3, 127.1, 125.7, 72.3, 38.7, 31.7, 17.7; $[\alpha]^{22}_D$ = -21.1 (*c* = 0.56, $CHCl_3$); 98% ee; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 10/90, t_{major} = 6.8 min, t_{minor} = 8.9 min.

General Procedure for Pd-Catalyzed Allyl-Aryl Coupling of Allyl Alcohols with Arylboronic Acids

To a 10 mL Schlenck flask equipped with a stir bar, was added $Pd_2(dba)_3{\cdot}CHCl_3$ (0.004 mmol), *rac*-BINAP (0.008 mmol), Allyl alcohol **1** (0.4 mmol), and Arylboronic acid **2** (0.6 mmol), after the system was degassed and recharged with N_2 three times, Toluene (0.8 mL) was injected *via* syringe. The mixture was stirred at 50 ºC for 18 or 24 h, and then the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate: petroleum ether, 1:200–1000) to furnish corresponding allyl–aryl coupling products.

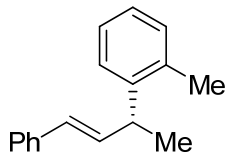
(*R, E*)-But-1-ene-1,3-diyldibenzene (3a)[12]



3a

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.17 (m, 10H), 6.44–6.35 (m, 2H), 3.64 (dq, *J* = 6.8, 6.8 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 137.5, 135.2, 128.5, 127.3, 127.0, 126.2, 126.1, 42.5, 21.2; $[\alpha]^{25}_D$ = +34.7 (*c* = 0.41, $CHCl_3$); 96% ee; [lit.[12] $[\alpha]^{20}_D$ = +37.4 (*c* = 0.59, $CHCl_3$), 97% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexanes = 0.1/99.9, t_{minor}=10.8 min, t_{major} = 11.3 min. The absolute configurations were determined by comparing the sign of the optical rotation with that reported.[12]

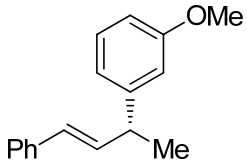
(*R, E*)-1-methyl-2-(4-phenylbut-3-en-2-yl)benzene (3b)[12]



3b

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.10 (m, 9H), 6.37–6.35 (m, 2H), 3.89–3.82 (m, 1H), 2.37 (s, 3H), 1.44 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 137.6, 135.6, 134.8, 130.4, 128.5, 128.4, 127.0, 126.3, 126.2, 126.1, 126.0, 38.0, 20.4, 19.5; $[\alpha]^{25}_D$ = +32.7 (*c* = 1.47, $CHCl_3$); 94% ee; [lit.[12] $[\alpha]^{20}_D$ = +38.9 (*c* = 0.55, $CHCl_3$), 96% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 0.1/99.9, t_{major} = 8.9 min, t_{minor} = 7.9 min.

(*R, E*)-1-methoxy-3-(4-phenylbut-3-en-2-yl)benzene (3c)[12]

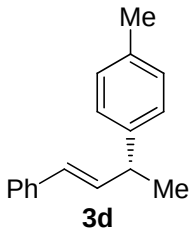


3c

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.17 (m, 6H), 6.88–6.74 (m, 3H), 6.44–6.34 (m, 2H), 3.80 (s, 3H), 3.61 (dq, *J* = 7.2, 6.8 Hz, 1H), 1.45 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 147.3, 137.5, 135.0, 129.4, 128.5, 128.4, 127.0, 126.1, 119.7, 113.3, 111.2, 55.1, 42.6, 21.1; $[\alpha]^{25}_D$ = +8.5 (*c* = 0.45, $CHCl_3$);

95% ee; [lit.[12] $[\alpha]^{20}_D$ = +10 (*c* = 0.28, $CHCl_3$), 92% ee]; HPLC conditions: Chralcel OJ-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexane = 10/90, t_{major} = 8.2 min, t_{minor} = 9.5 min.

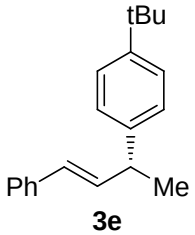
(*R*,*E*)-1-methyl-4-(4-phenylbut-3-en-2-yl)benzene (3d)[14]



3d

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.15 (m, 9H), 6.43–6.34 (m, 2H), 3.61 (dq, *J* = 6.8, 6.8 Hz, 1H), 2.33 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 137.6, 135.7, 135.4, 129.1, 128.4, 128.3, 127.2, 127.0, 126.1, 42.1, 21.25, 21.0; $[\alpha]^{20}_D$ = +39.8 (*c* = 0.42, $CHCl_3$); 95% ee; HPLC conditions: Chralcel OJ-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexane = 15/85, t_{major} = 6.4 min, t_{minor} = 5.9 min.

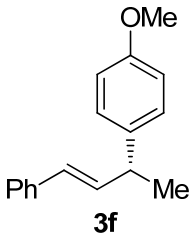
(*R*,*E*)-1-(tert-butyl)-4-(4-phenylbut-3-en-2-yl)benzene (3e)



3e

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.17 (m, 9H), 6.45–6.34 (m, 2H), 3.62 (dq, *J* = 6.8, 6.8 Hz, 1H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 142.5, 137.6, 135.4, 128.4, 128.2, 126.9, 126.8, 126.1, 125.3, 42.1, 34.4, 31.4, 21.1; $[\alpha]^{15}_D$ = +20.2 (*c* = 0.92, $CHCl_3$); 95% ee; HPLC conditions: Chralcel OD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexane = 0.1/99.9, t_{major} = 7.4 min, t_{minor} = 6.7 min.

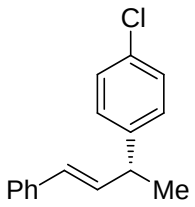
(*R*,*E*)-1-methoxy-4-(4-phenylbut-3-en-2-yl)benzene(3f)[12]



3f

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.16 (m, 7H), 6.88–6.84 (m, 2H), 6.41–6.32 (m, 2H), 3.79 (s, 3H), 3.60 (dq, *J* = 7.2, 6.8 Hz, 1H), 1.44 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 137.6, 135.6, 128.5, 128.2, 127.0, 126.1, 113.8, 55.3, 41.7, 21.3; $[\alpha]^{20}_D$ = +11.3 (*c* = 0.51, $CHCl_3$); 94% ee; [lit.[12] $[\alpha]^{20}_D$ = +36.1 (*c* = 0.29, $CHCl_3$), 94% ee]; HPLC conditions: Chralcel OJ-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexane = 10/90, t_{major} = 10.0 min, t_{minor} = 9.4 min.

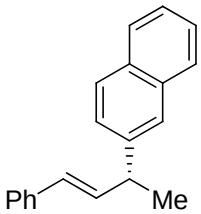
(*R, E*)-1-chloro-4-(4-phenylbut-3-en-2-yl)benzene (3g)[12]



3g

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.19 (m, 9H), 6.42–6.30 (m, 2H), 3.62 (dq, *J* = 6.8, 6.8 Hz, 1H), 1.44 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 137.3, 134.5, 131.8, 128.8, 128.7, 128.5, 128.5, 127.2, 126.1, 41.9, 21.1; $[\alpha]^{25}_{D}$ = +23.4 (*c* = 0.60, $CHCl_3$); 89% ee; [lit.[12] $[\alpha]^{20}_{D}$ = +14.2 (*c* = 0.75, $CHCl_3$), 93% ee]; HPLC conditions: Chralcel OJ-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexane = 1/99, t_{major} = 12.5 min, t_{minor} = 11.3 min.

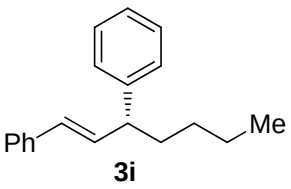
(*R, E*)-2-(4-phenylbut-3-en-2-yl)naphthalene (3h)[12]



3h

Off-white solid, m.p. 72 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.87 (m, 1H), 7.81–7.78 (m, 3H), 7.69 (s, 1H), 7.45–7.17 (m, 7H), 6.46–6.45 (m, 2H), 3.83–3.70 (m, 1H), 1.55 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 137.5, 135.1, 133.6, 132.2, 128.8, 128.5, 128.0, 127.6, 127.6, 127.1, 126.3, 126.2, 125.9, 125.3, 125.2, 42.6, 21.1; $[\alpha]^{25}_{D}$ = +21.0 (*c* = 0.40, $CHCl_3$); 94% ee; [lit.[12] $[\alpha]^{20}_{D}$ = +13.1 (*c* = 0.17, $CHCl_3$), 93% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 0.1/99.9, t_{major} = 24.2 min, t_{minor} = 23.1 min.

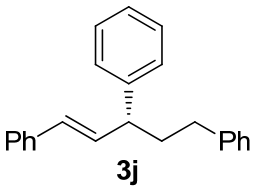
(*R, E*)-hept-1-ene-1,3-diyldibenzene (3i)[12]



3i

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.16 (m, 10H), 6.41–6.30 (m, 2H), 3.39 (dt, *J* = 7.2, 7.2 Hz), 1.83–1.76 (m, 2H), 1.37–1.20 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 129.2, 128.4, 128.4, 127.6, 127.0, 126.1, 126.1, 49.2, 35.6, 29.8, 22.7, 14.0; $[\alpha]^{16}_{D}$ = +15.3 (*c* = 0.76, $CHCl_3$); 94% ee; [lit.[12] $[\alpha]^{20}_{D}$ = +17.4 (*c* = 0.46, $CHCl_3$), 95% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 0.1/99.9, t_{major} = 8.1 min, t_{minor} = 7.7 min.

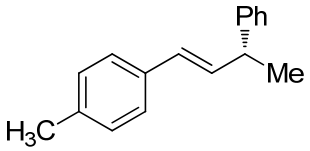
(*R, E*)-pent-1-ene-1,3,5-triyltribenzene (3j)[12]



3j

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.15 (m, 15H), 6.43–6.31 (m, 2H), 3.45 (dt, *J* = 7.2, 7.6 Hz, 1H), 2.69–2.55 (m, 2H), 2.15 (dt, *J* = 8.4, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 129.7, 128.6, 128.4, 128.3, 127.7, 127.1, 126.3, 126.1, 125.8, 48.5, 37.3, 33.7; $[\alpha]^{20}_D$ = -9.0 (c = 1.06, $CHCl_3$); 91% ee; [lit.[12] $[\alpha]^{20}_D$ = -4.5 (*c* = 0.45, $CHCl_3$), 97% ee]; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1.0 ml/min, *i*-PrOH/hexane = 0.5/99.5, t_{major} = 11.4 min, t_{minor} = 10.5 min.

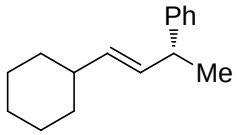
(*R*,*E*)-1-methyl-4-(3-phenylbut-1-en-1-yl)benzene(3k)[15]



3k

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.19 (m, 7H), 7.10–7.08 (m, 2H), 6.41–6.30 (m, 2H), 3.63 (dq, *J* = 7.2, 6.4 Hz, 1H), 2.32 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 136.7, 134.7, 134.2, 129.2, 128.4, 128.3, 127.3, 126.1, 126.0, 42.5, 21.3, 21.1; $[\alpha]^{20}_D$ = +38.4 (*c* = 0.98, $CHCl_3$); 91% ee; HPLC conditions: Chralcel OJ-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexane = 10/90, t_{major} = 11.6 min, t_{minor} = 14.3 min.

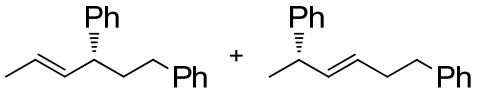
(*R*,*E*)-(4-cyclohexylbut-3-en-2-yl)benzene(3l)[12]



3l

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.12 (m, 5H), 5.55 (ddd, *J* = 15.6, 6.8, 0.8 Hz, 1H), 5.41 (dd, *J* = 15.6, 6.0 Hz, 1H), 3.40 (dq, *J* = 7.2, 6.8 Hz, 1H), 1.96–1.89 (m, 1H), 1.74–1.67 (m, 4H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.27–1.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.2, 132.3, 128.3, 127.9, 127.1, 125.8, 42.2, 40.6, 33.18, 33.17, 26.2, 26.1, 21.6; $[\alpha]^{22}_D$ = +8.0 (*c* = 0.50, $CHCl_3$); 93% ee; [lit.[12] $[\alpha]^{20}_D$ = +10.1 (*c* = 0.45, $CHCl_3$), 95% ee]; HPLC conditions: Chiralcel OJ-H column, 254 nm, flow rate: 0.4 ml/min, *i*-PrOH/hexane = 0/100, t_{major} = 11.7 min, t_{minor} = 12.8 min.

(*R*,*E*)-hex-4-ene-1,3-diyldibenzene(3m) + (*S*,*E*)-hex-3-ene-1,5-diyldibenzene(3n)[12,16]



3m **3n**

Compouds **3m** and **3n** are inseparable mixture isolated in 91% yield with a ratio **3m**:**3n** = 42:58 by ^{1}H NMR analysis. Pure racemic **3m** and **3n** can be synthesized by the method described in the literature.[16]

For **3m**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.14 (m, 10H), 5.63–5.59 (m, 1H), 5.47–5.40 (m, 1H), 3.22 (dt, *J* = 8.0, 7.2 Hz, 1H), 2.61–2.47 (m, 2H), 2.00 (dt, *J* = 8.4, 7.2, 2H), 1.68–1.66 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 142.4, 134.9, 128.43, 128.41, 128.2, 127.5, 126.0, 125.6, 125.0, 48.4, 37.6, 33.8, 18.0.

For **3n**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.13 (m, 10H), 5.60 –5.56 (m, 1H), 5.52–5.49 (m, 1H), 3.40 (dq, *J* = 7.2, 7.2 Hz, 1H), 2.70–2.63 (m, 2H), 2.36–2.31 (m, 2H), 1.31 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 142.0, 135.7, 128.5, 128.3, 128.2, 127.1, 125.9, 125.7, 42.2, 36.0, 34.4, 21.4.

HPLC conditions for **3m** and **3n**: Chiralcel OJ-H column, 220 nm, flow rate: 0.75 ml/min, *i*-PrOH/hexane = 0.3/99.7. t_{major} (**3m**) = 13.9 min, t_{minor} (**3m**) = 15.3 min, 96%ee; t_{major} (**3n**) = 19.3 min, t_{minor} (**3n**) = 18.0 min, 97% ee.

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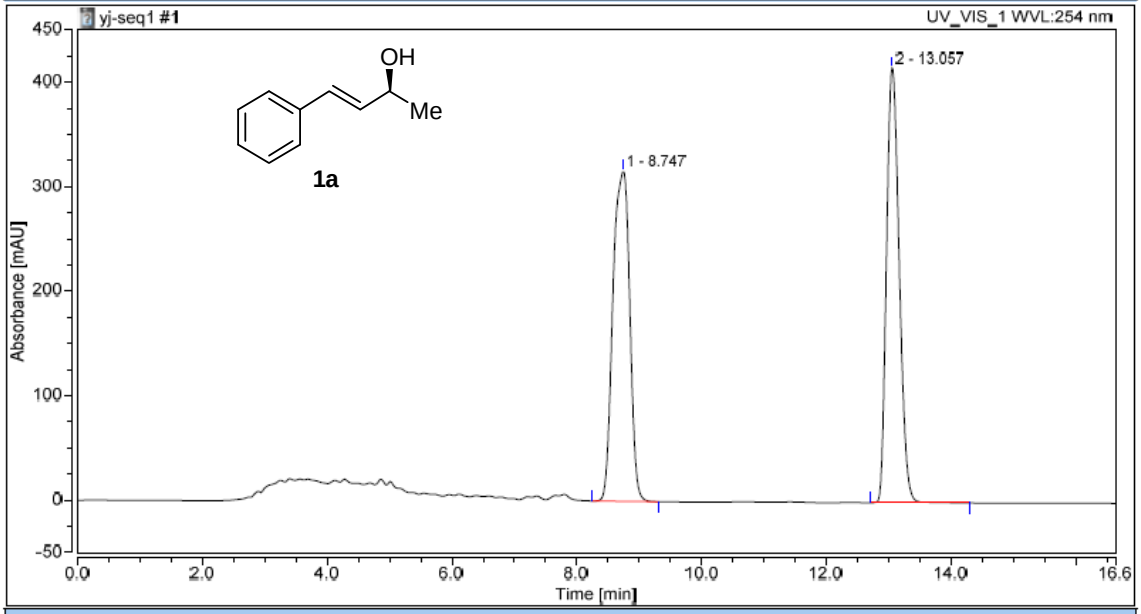
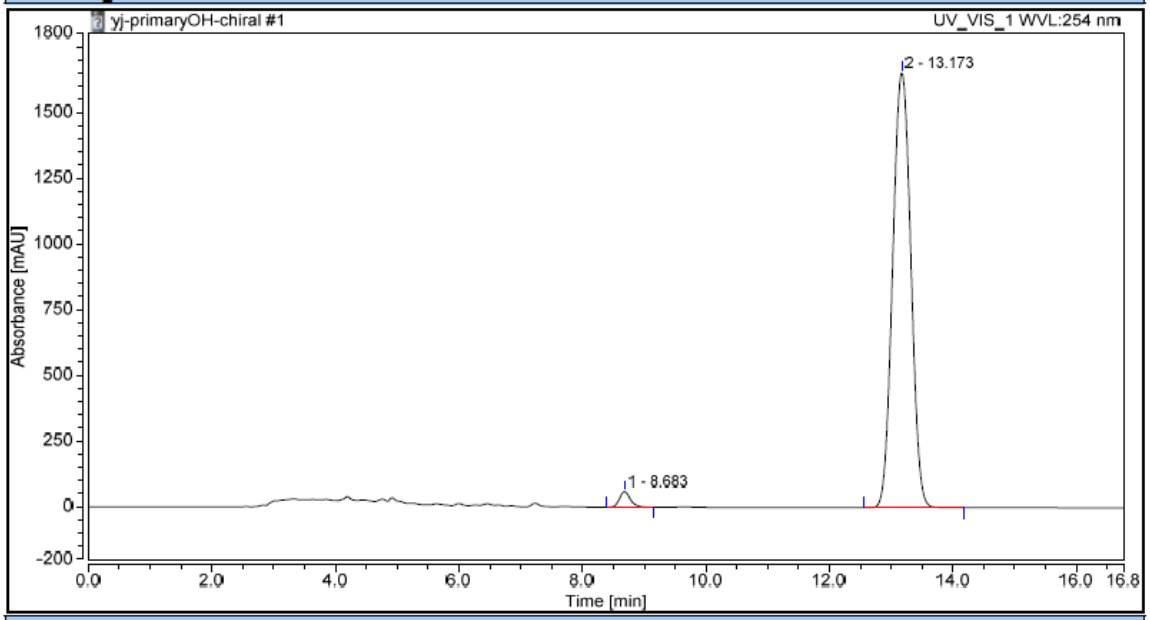
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.747	98.139	316.000	49.99	43.17	n.a.
2		13.057	98.179	416.069	50.01	56.83	n.a.
Total:			**196.318**	**732.069**	**100.00**	**100.00**	

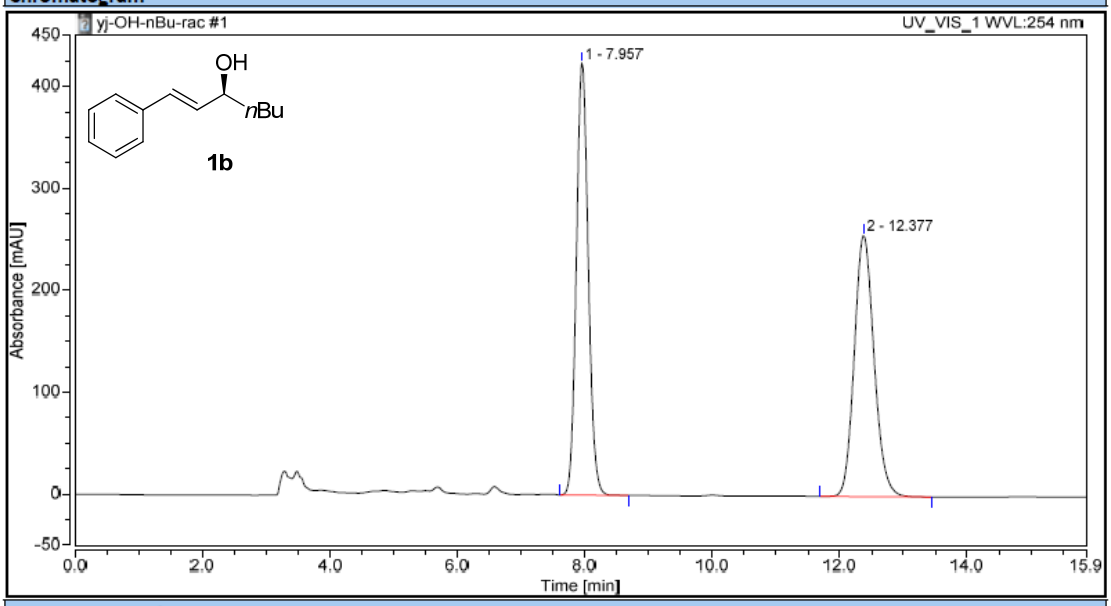
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.683	12.058	59.430	2.10	3.47	n.a.
2		13.173	561.490	1654.529	97.90	96.53	n.a.
Total:			**573.548**	**1713.959**	**100.00**	**100.00**	

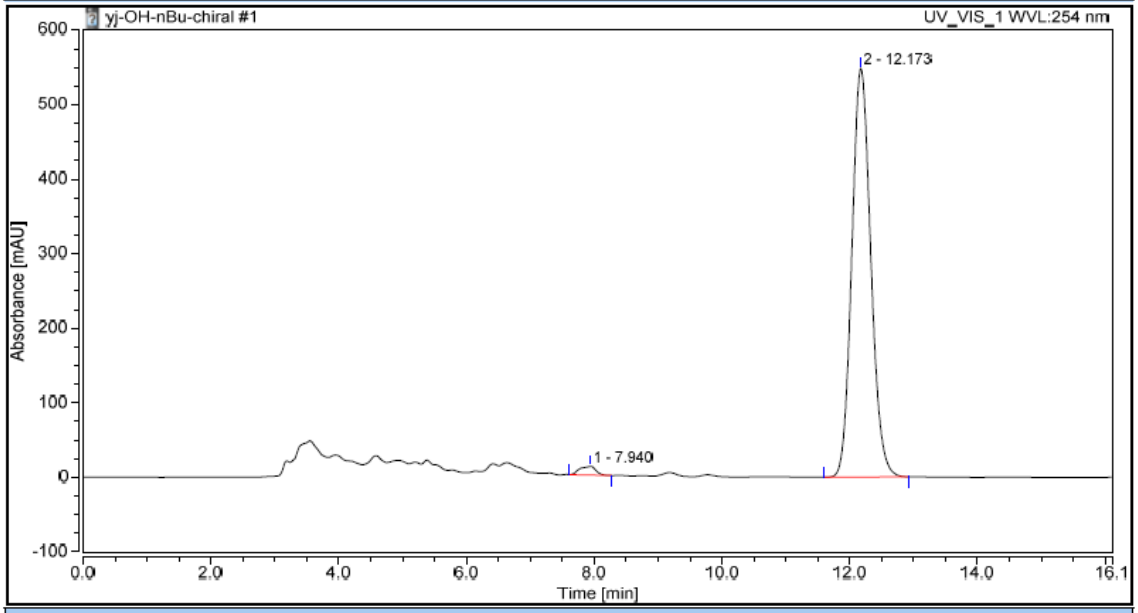
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.957	91.760	424.030	49.94	62.35	n.a.
2		12.377	91.997	256.058	50.06	37.65	n.a.
Total:			**183.758**	**680.088**	**100.00**	**100.00**	

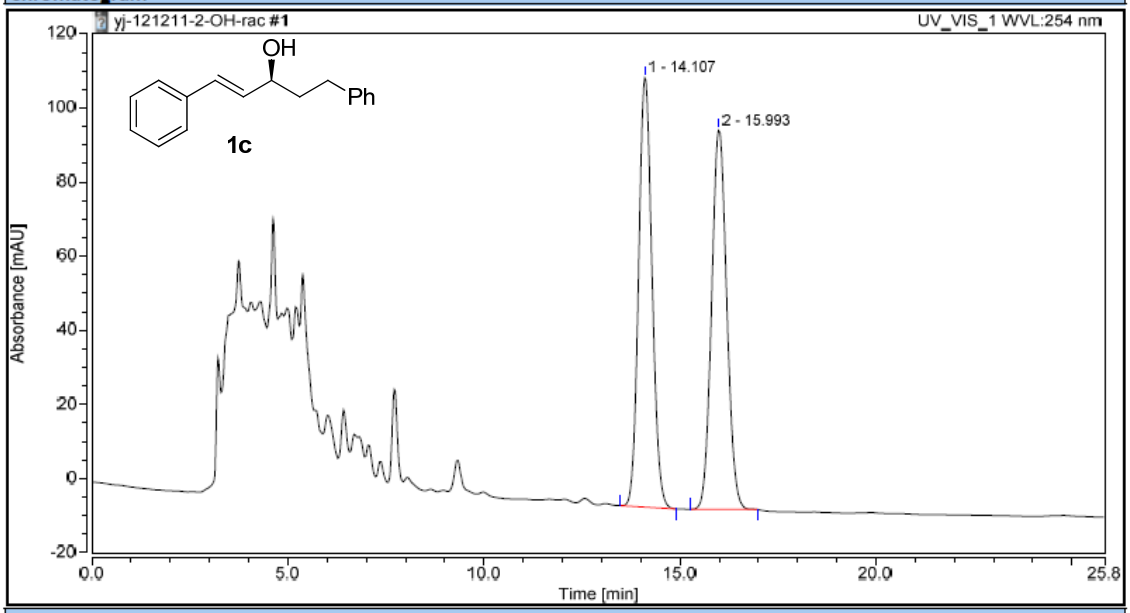
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.940	3.430	11.887	1.79	2.12	n.a.
2		12.173	188.503	547.960	98.21	97.88	n.a.
Total:			**191.933**	**559.848**	**100.00**	**100.00**	

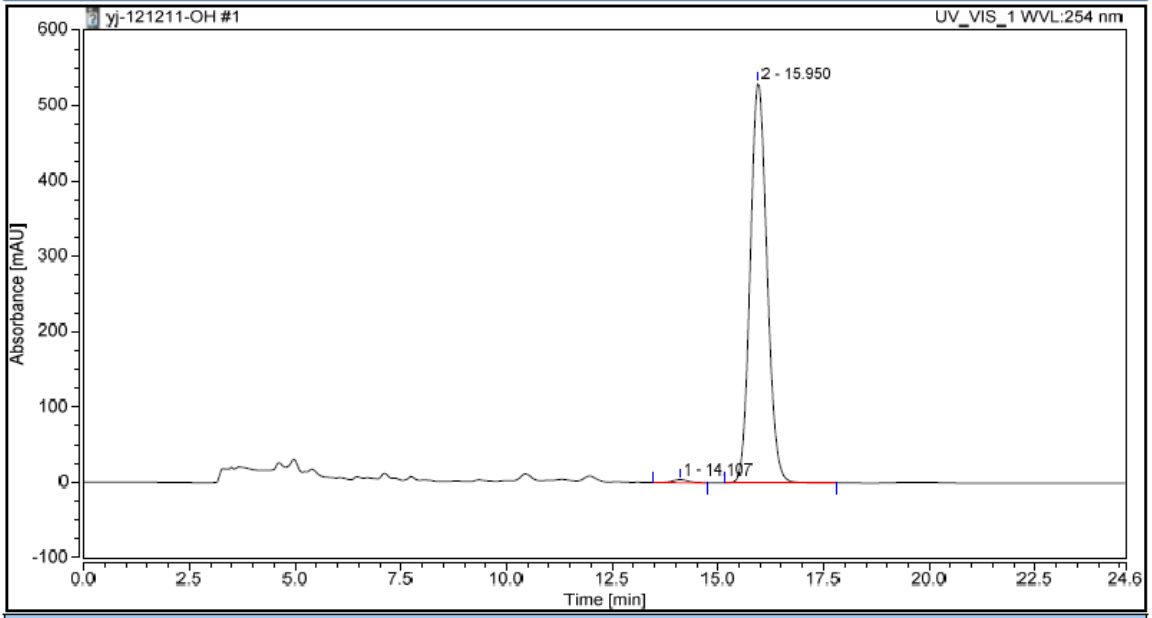
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.107	45.919	116.032	50.00	53.09	n.a.
2		15.993	45.914	102.509	50.00	46.91	n.a.
Total:			**91.833**	**218.541**	**100.00**	**100.00**	

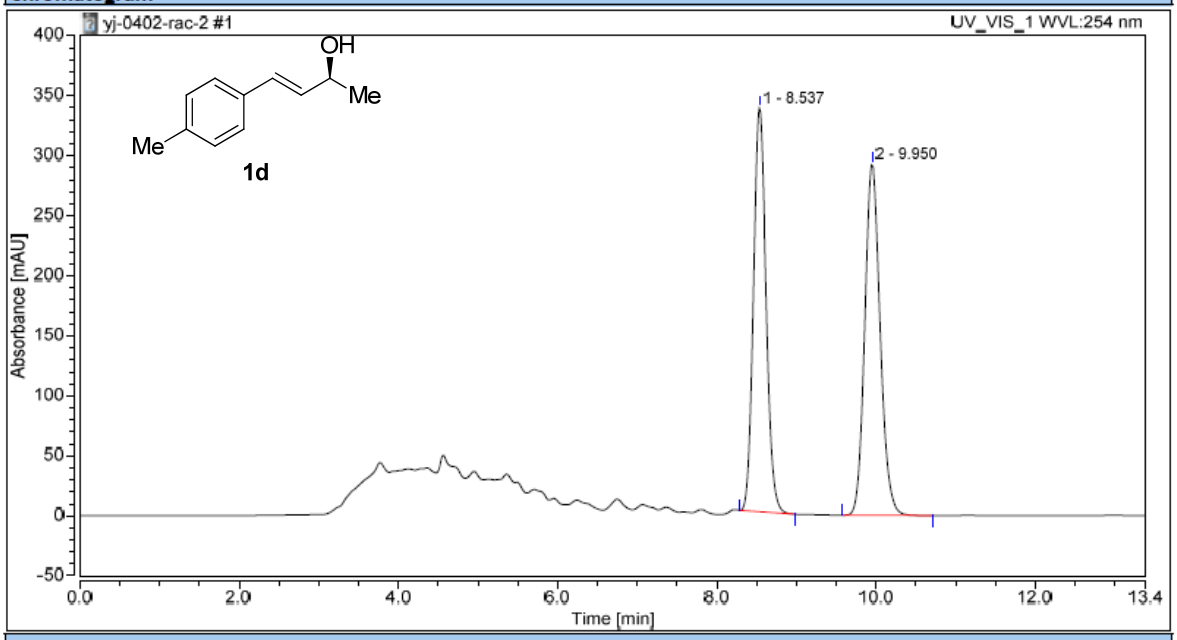
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.107	1.703	4.120	0.69	0.77	n.a.
2		15.950	244.483	530.599	99.31	99.23	n.a.
Total:			**246.186**	**534.719**	**100.00**	**100.00**	

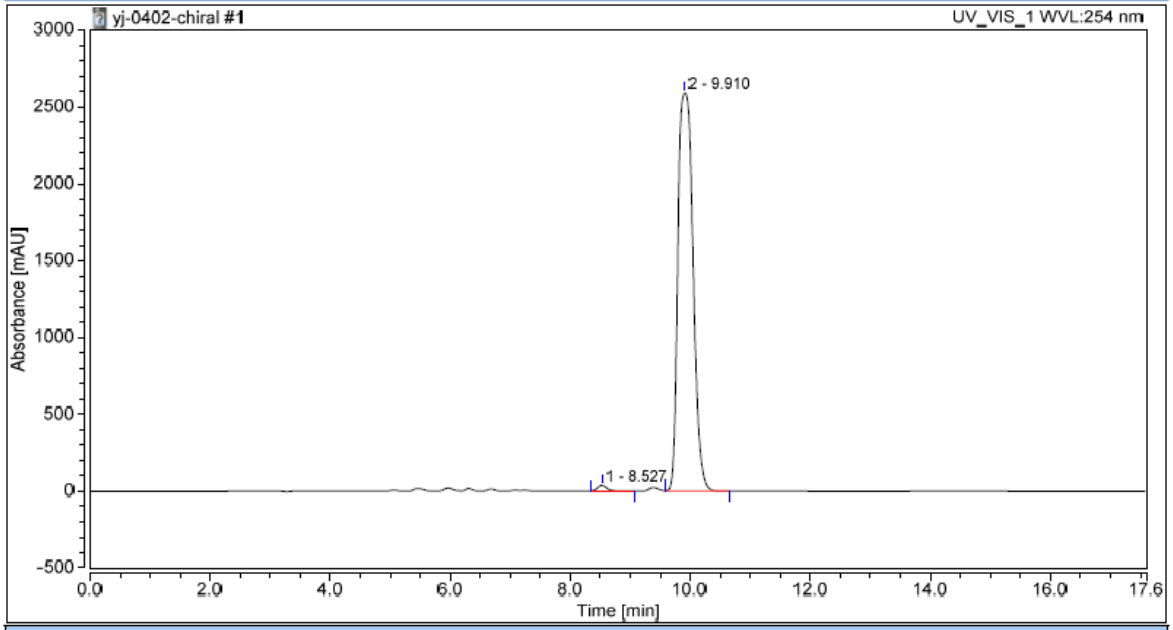
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.537	61.527	336.705	48.35	53.45	n.a.
2		9.950	65.729	293.234	51.65	46.55	n.a.
Total:			**127.256**	**629.938**	**100.00**	**100.00**	

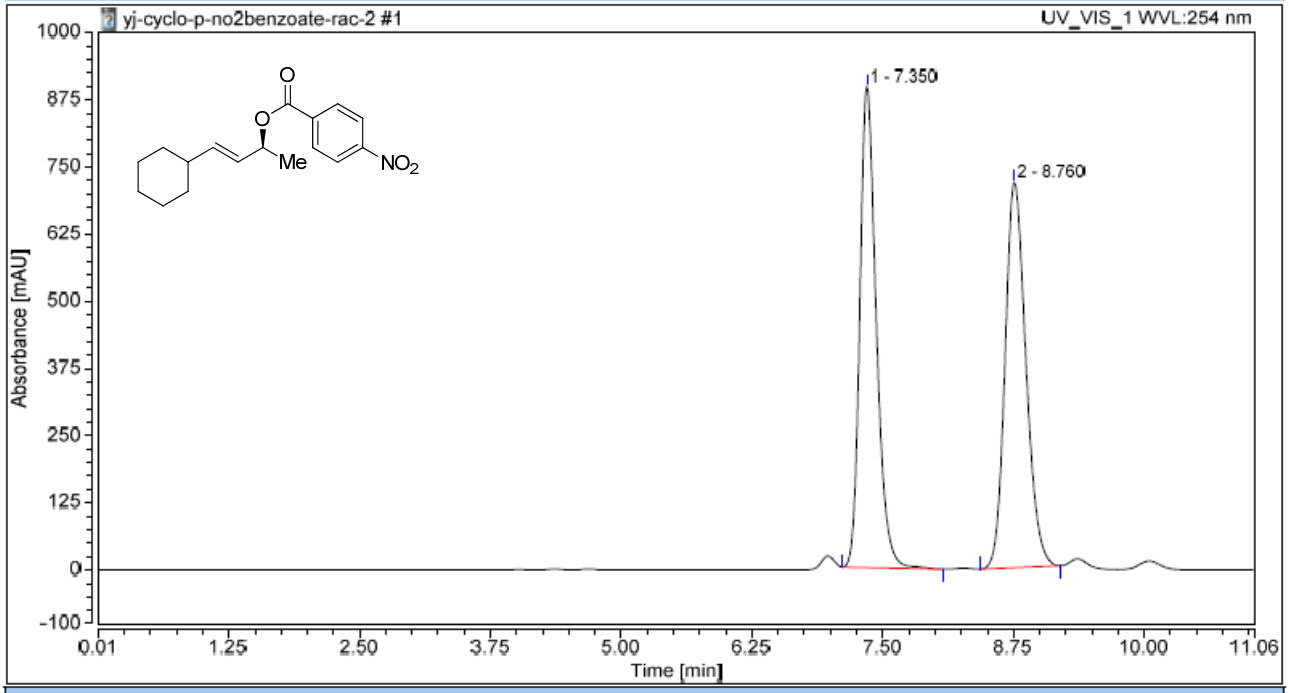
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.527	6.823	35.987	0.90	1.37	n.a.
2		9.910	752.637	2590.263	99.10	98.63	n.a.
Total:			**759.459**	**2626.250**	**100.00**	**100.00**	

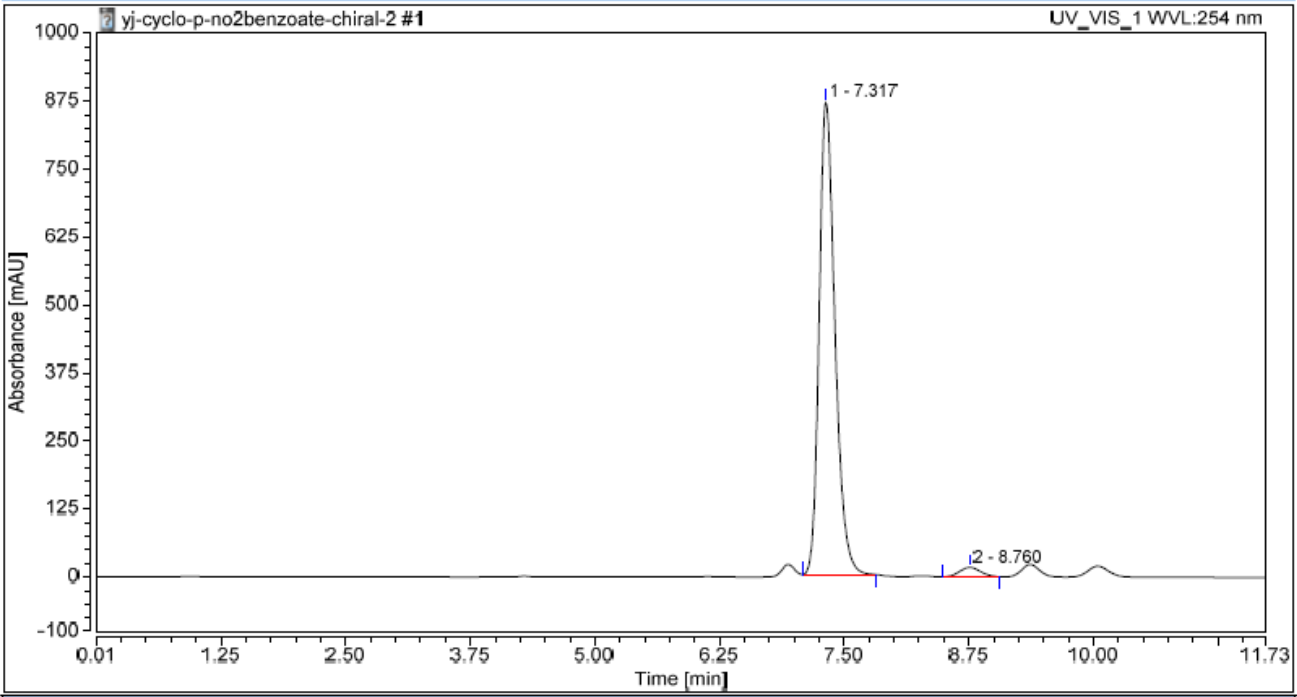
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.350	162.617	894.766	49.59	55.49	n.a.
2		8.760	165.330	717.618	50.41	44.51	n.a.
Total:			**327.948**	**1612.384**	**100.00**	**100.00**	

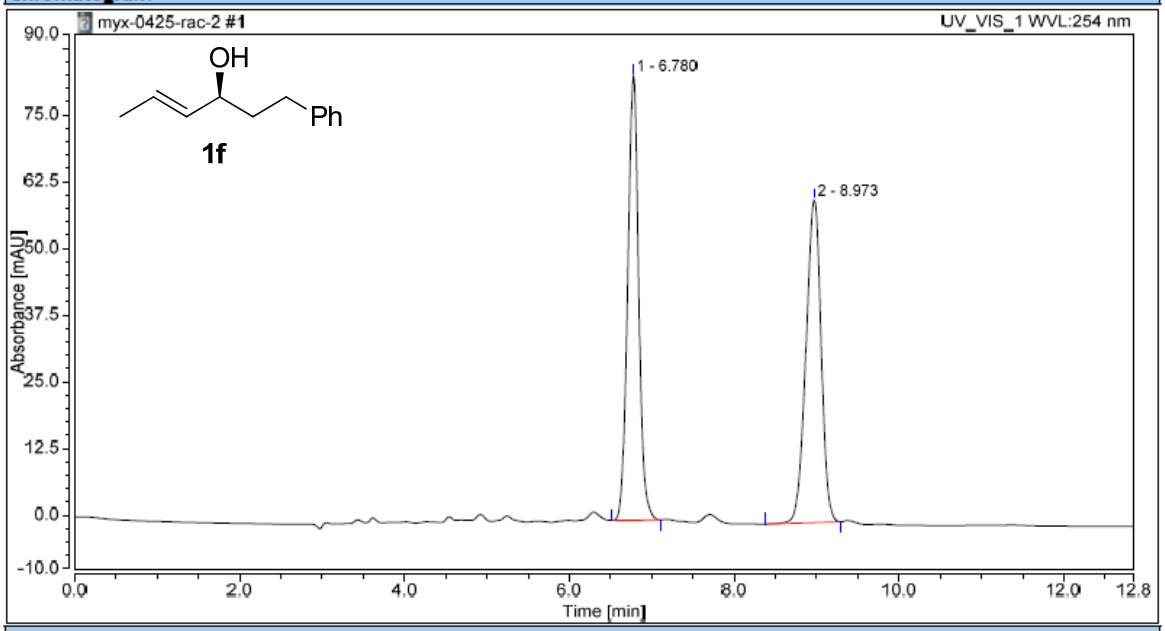
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.317	159.903	869.579	97.46	98.05	n.a.
2		8.760	4.172	17.271	2.54	1.95	n.a.
Total:			**164.076**	**886.851**	**100.00**	**100.00**	

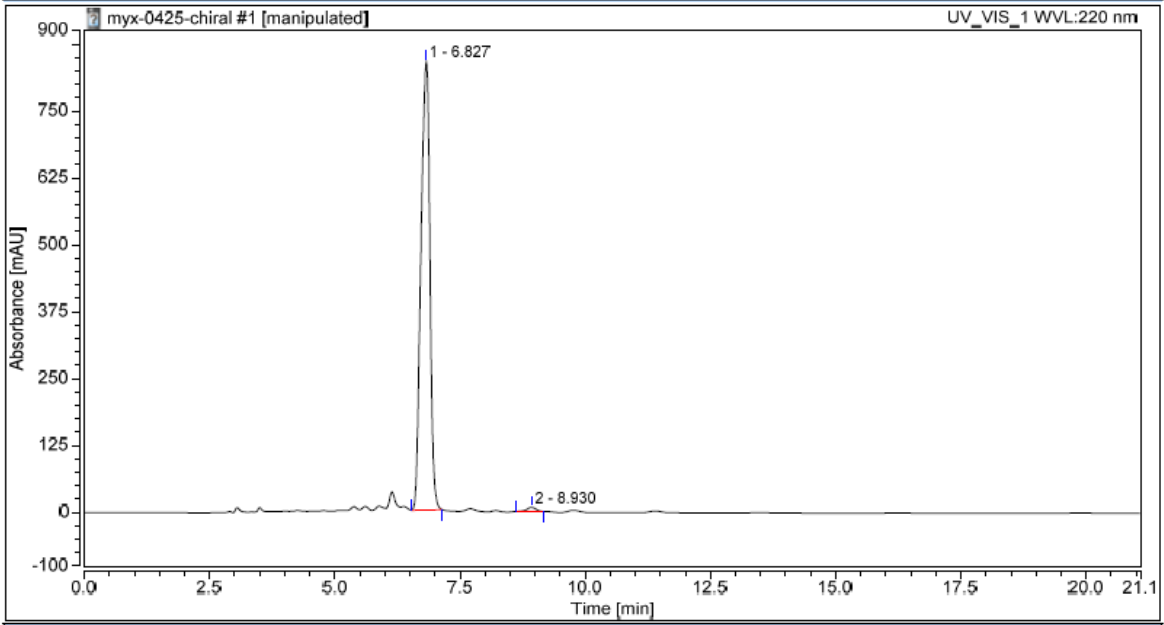
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.780	12.874	83.234	50.00	57.96	n.a.
2		8.973	12.875	60.380	50.00	42.04	n.a.
Total:			**25.749**	**143.614**	**100.00**	**100.00**	

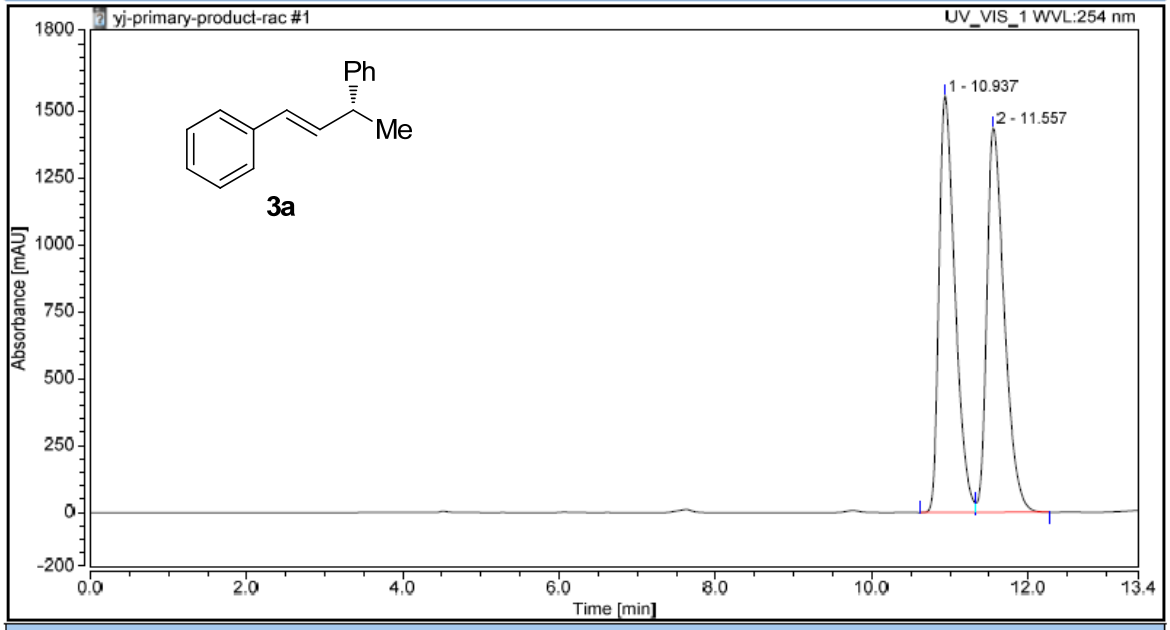
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.827	173.803	836.900	99.08	99.08	n.a.
2		8.930	1.619	7.761	0.92	0.92	n.a.
Total:			**175.422**	**844.661**	**100.00**	**100.00**	

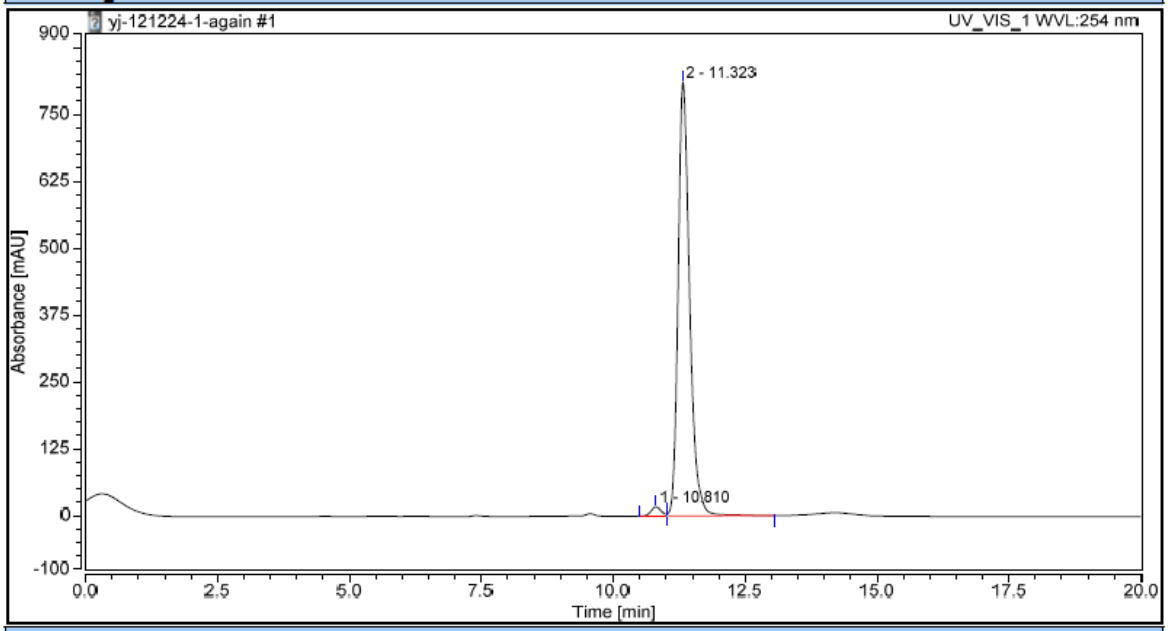
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.937	368.749	1552.931	49.82	51.99	n.a.
2		11.557	371.474	1433.867	50.18	48.01	n.a.
Total:			**740.222**	**2986.798**	**100.00**	**100.00**	

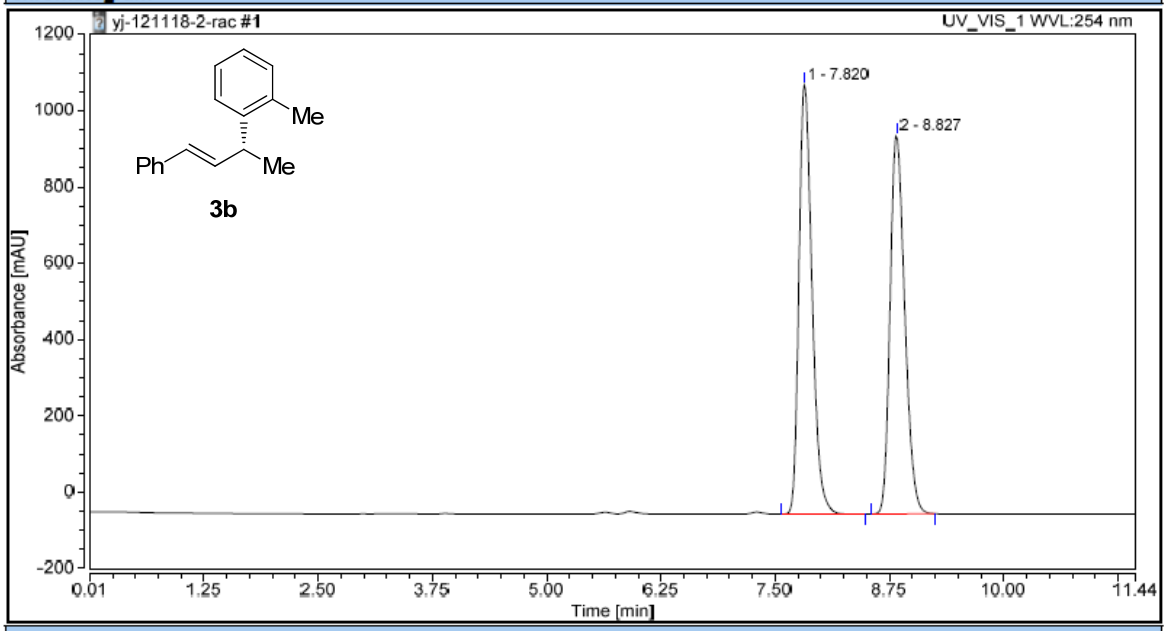
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.810	3.829	17.297	1.83	2.09	n.a.
2		11.323	205.093	809.165	98.17	97.91	n.a.
Total:			**208.923**	**826.461**	**100.00**	**100.00**	

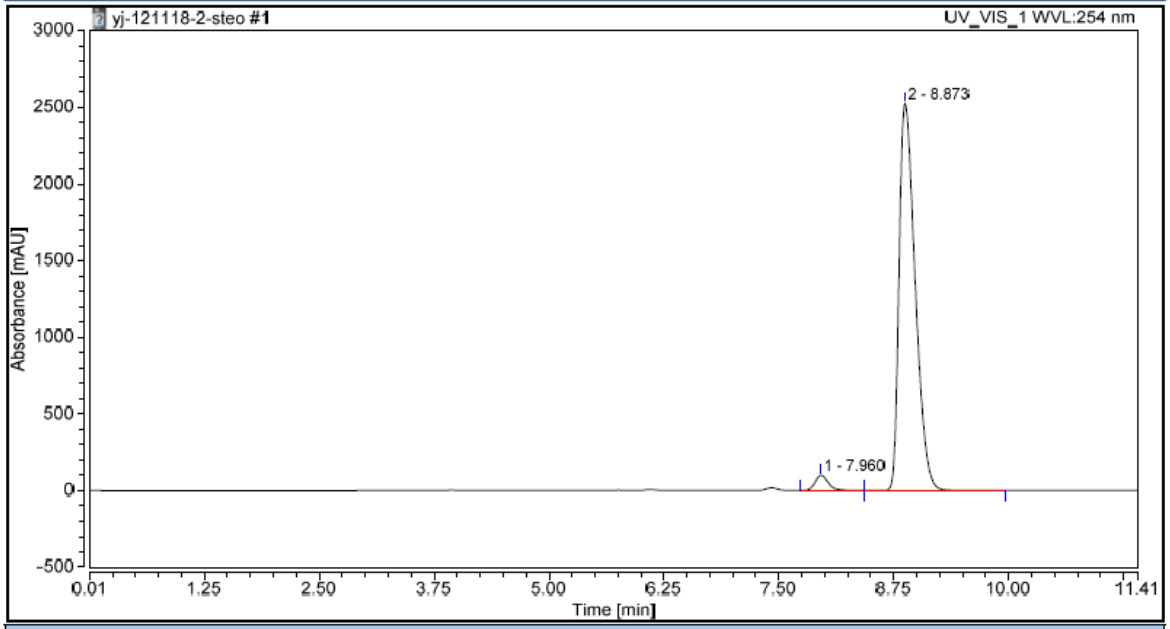
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.820	187.022	1126.276	50.30	53.14	n.a.
2		8.827	184.775	993.023	49.70	46.86	n.a.
Total:			**371.796**	**2119.299**	**100.00**	**100.00**	

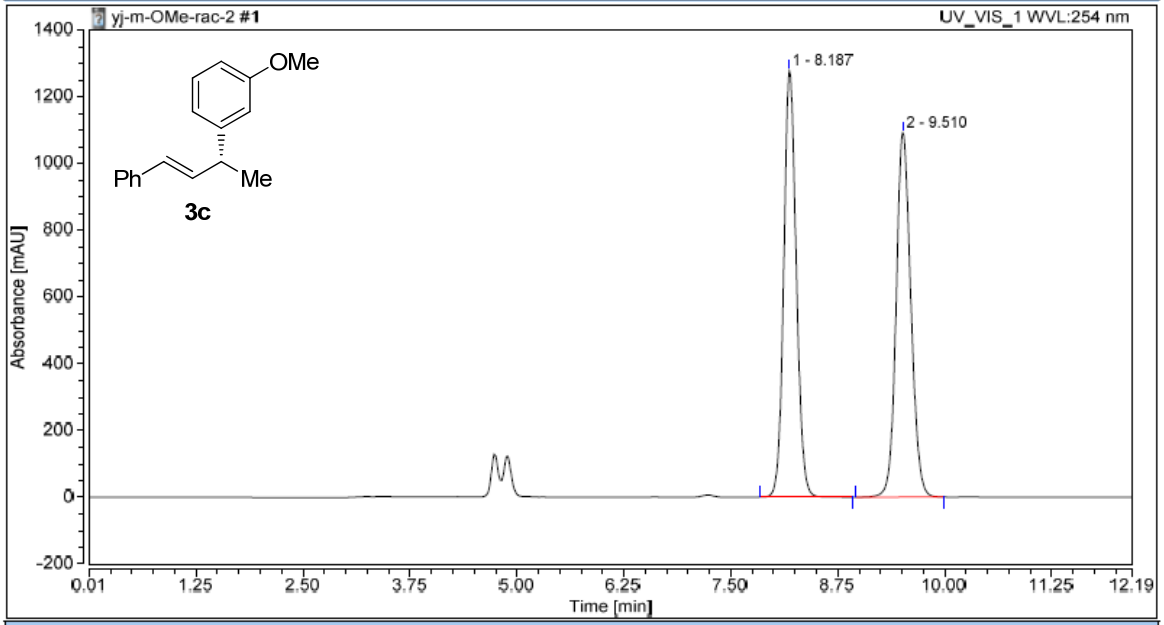
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.960	16.339	99.421	3.09	3.79	n.a.
2		8.873	511.645	2524.316	96.91	96.21	n.a.
Total:			**527.985**	**2623.737**	**100.00**	**100.00**	

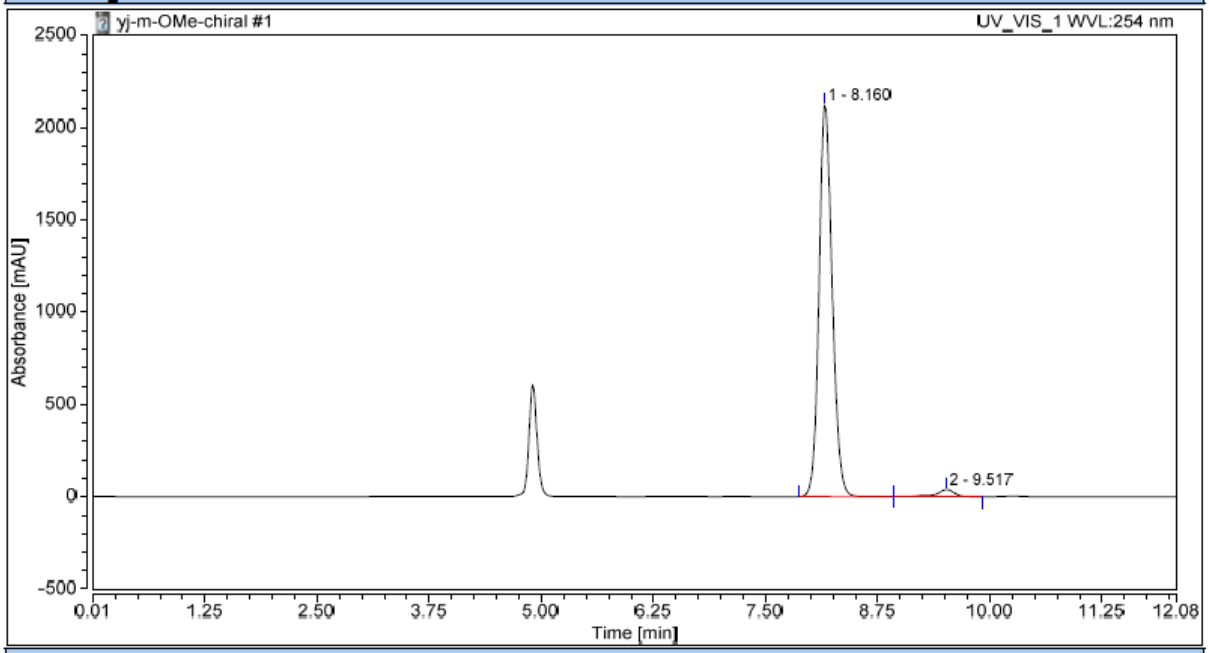
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.187	216.960	1280.120	49.87	53.95	n.a.
2		9.510	218.073	1092.717	50.13	46.05	n.a.
Total:			**435.033**	**2372.837**	**100.00**	**100.00**	

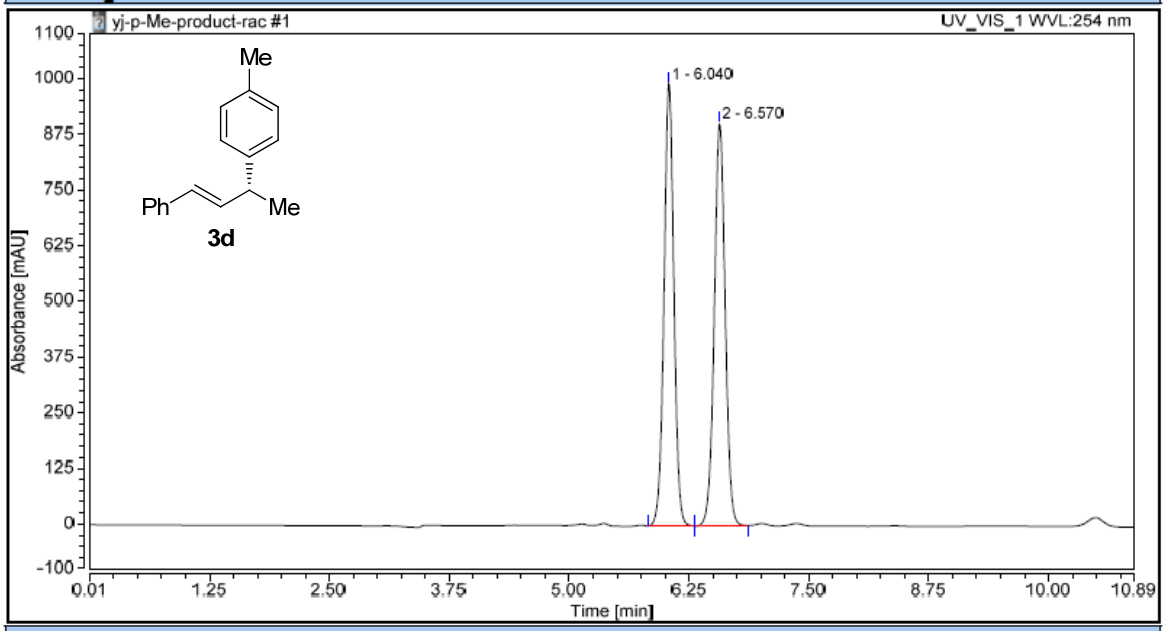
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.160	361.553	2121.539	97.49	98.19	n.a.
2		9.517	9.297	39.002	2.51	1.81	n.a.
Total:			**370.850**	**2160.541**	**100.00**	**100.00**	

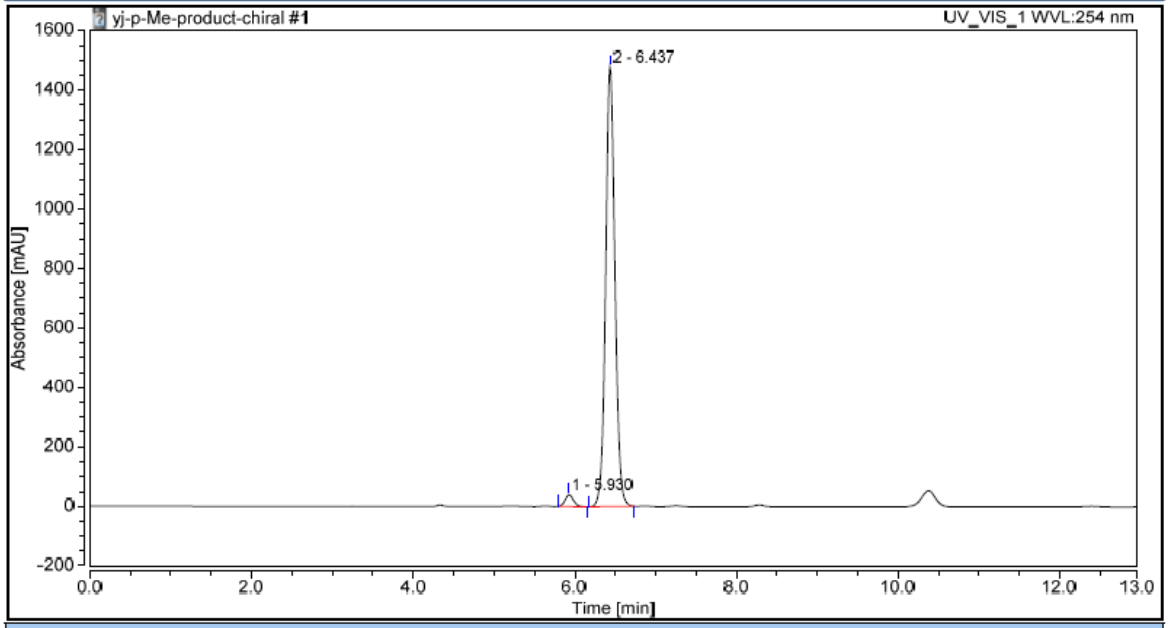
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.040	118.731	992.652	49.89	52.34	n.a.
2		6.570	119.240	903.736	50.11	47.66	n.a.
Total:			**237.971**	**1896.388**	**100.00**	**100.00**	

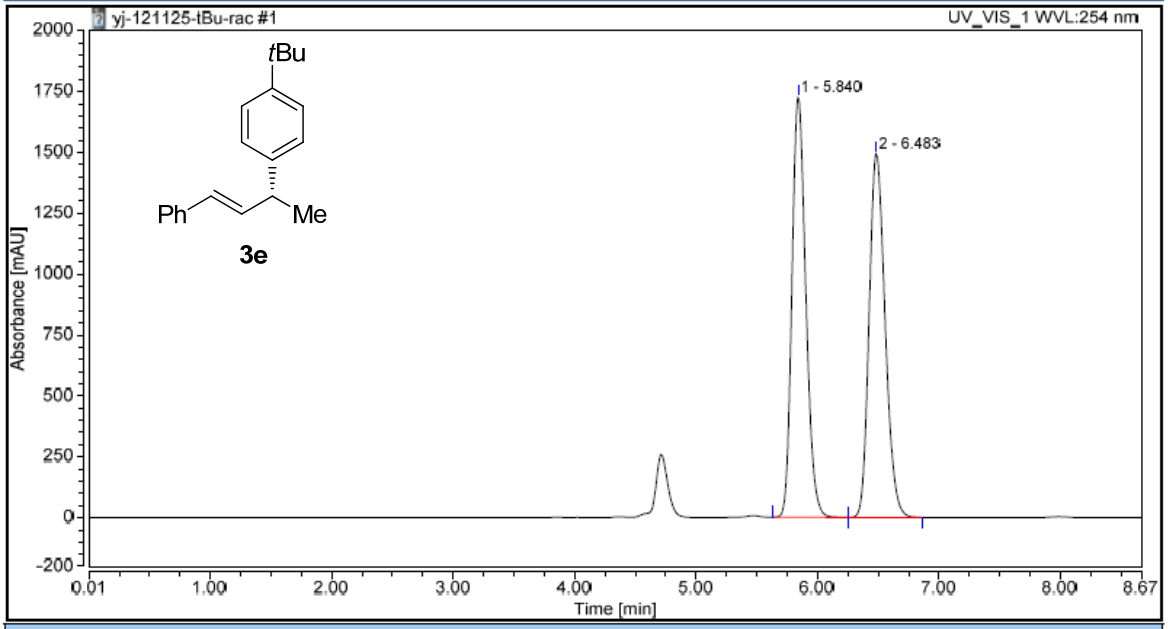
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.930	4.691	40.307	2.32	2.65	n.a.
2		6.437	197.738	1479.610	97.68	97.35	n.a.
Total:			**202.429**	**1519.917**	**100.00**	**100.00**	

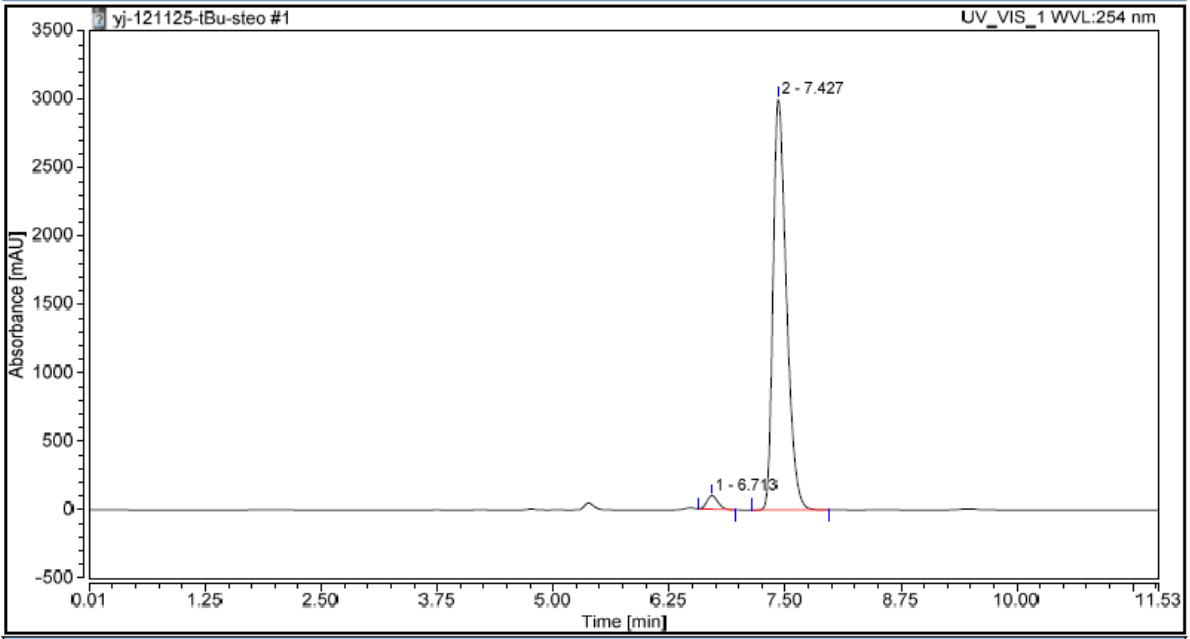
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.840	228.115	1727.738	50.03	53.61	n.a.
2		6.483	227.863	1495.060	49.97	46.39	n.a.
Total:			**455.978**	**3222.798**	**100.00**	**100.00**	

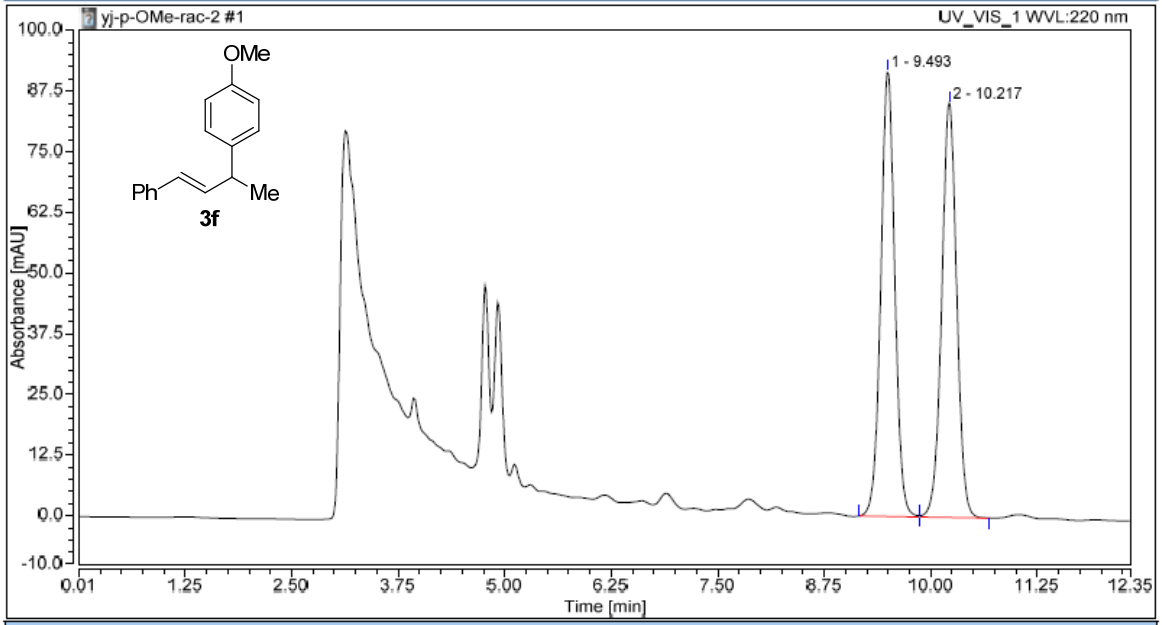
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.713	13.824	101.389	2.69	3.26	n.a.
2		7.427	500.496	3006.268	97.31	96.74	n.a.
Total:			**514.320**	**3107.657**	**100.00**	**100.00**	

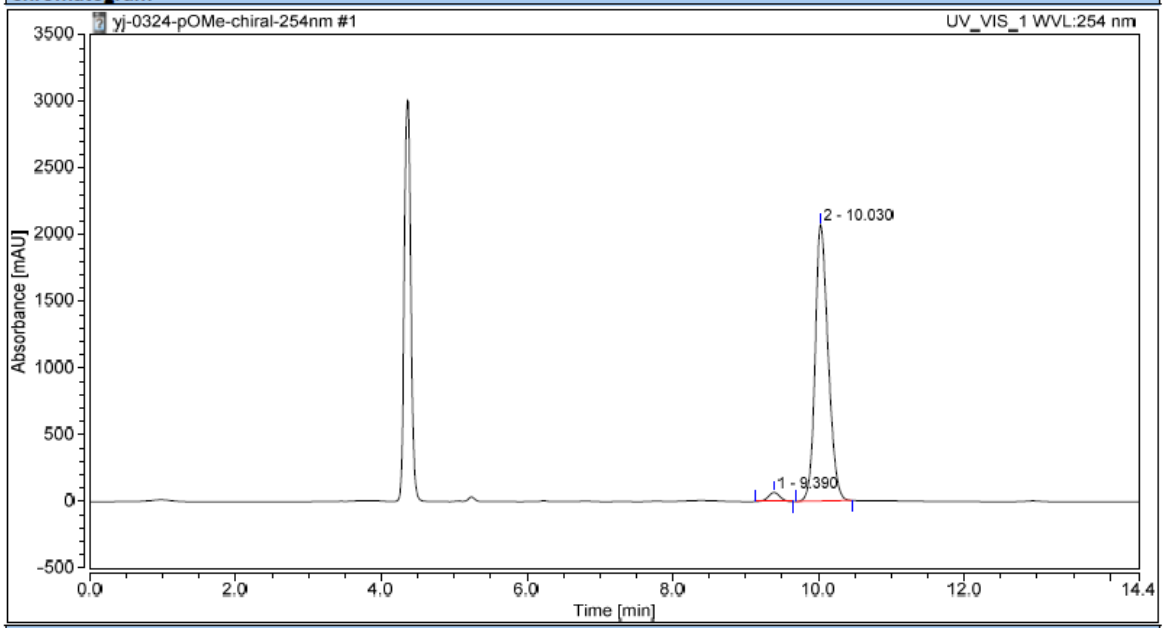
Chromatogram



Integration Results

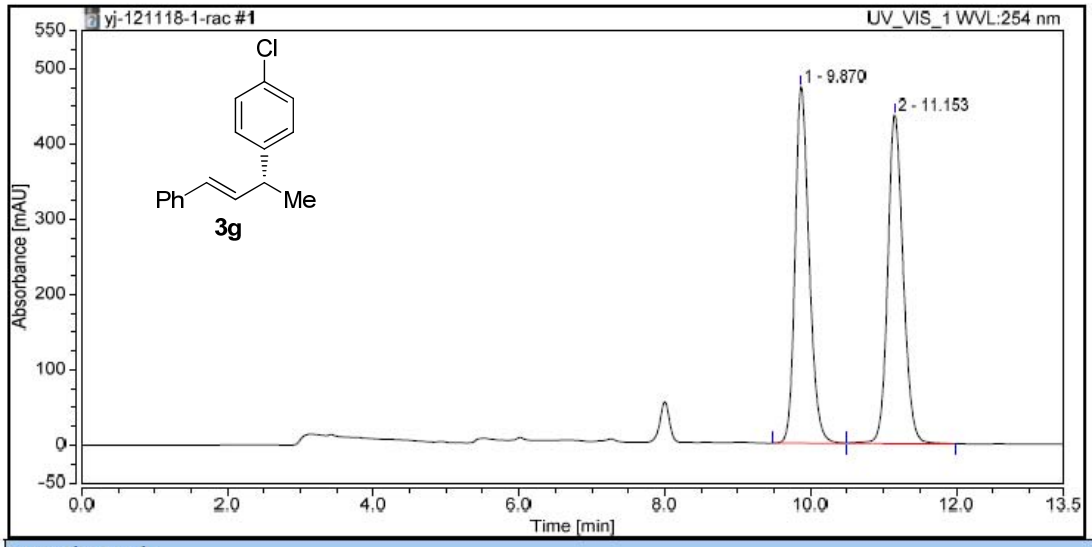
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.493	17.488	91.710	50.09	51.78	n.a.
2		10.217	17.424	85.418	49.91	48.22	n.a.
Total:			**34.911**	**177.128**	**100.00**	**100.00**	

Chromatogram



Integration Results

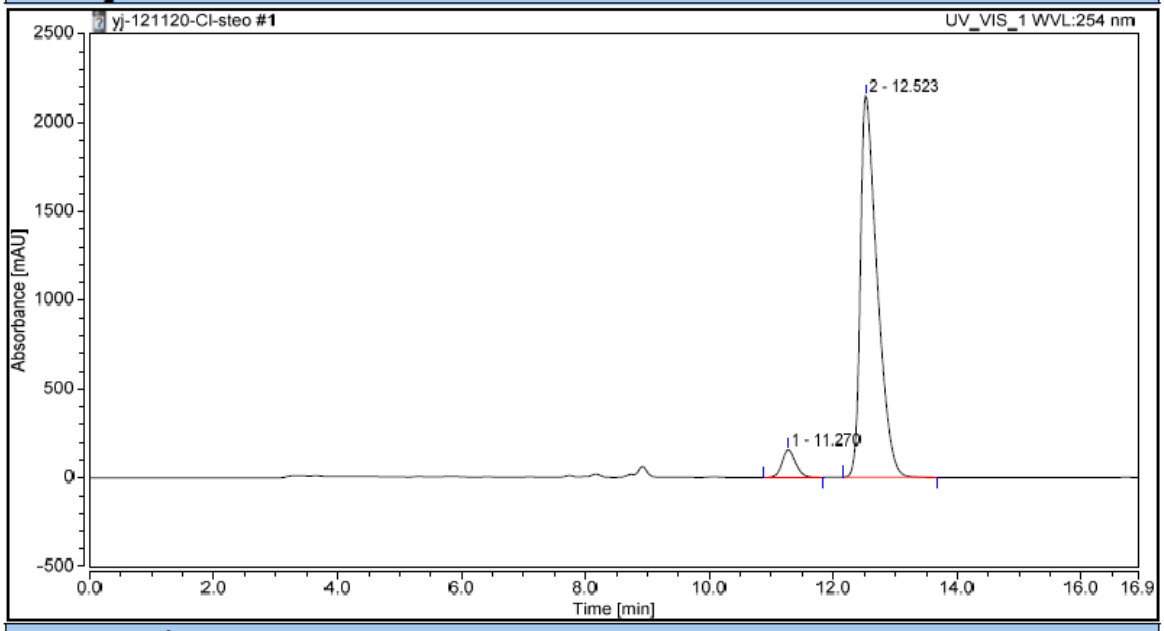
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.390	12.762	69.411	2.90	3.24	n.a.
2		10.030	428.002	2070.940	97.10	96.76	n.a.
Total:			**440.764**	**2140.351**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Peak Start min
1		9.870	105.899	473.732	49.70	52.02	9.48
2		11.153	107.195	436.959	50.30	47.98	10.48
Total:			213.094	910.692	100.00	100.00	

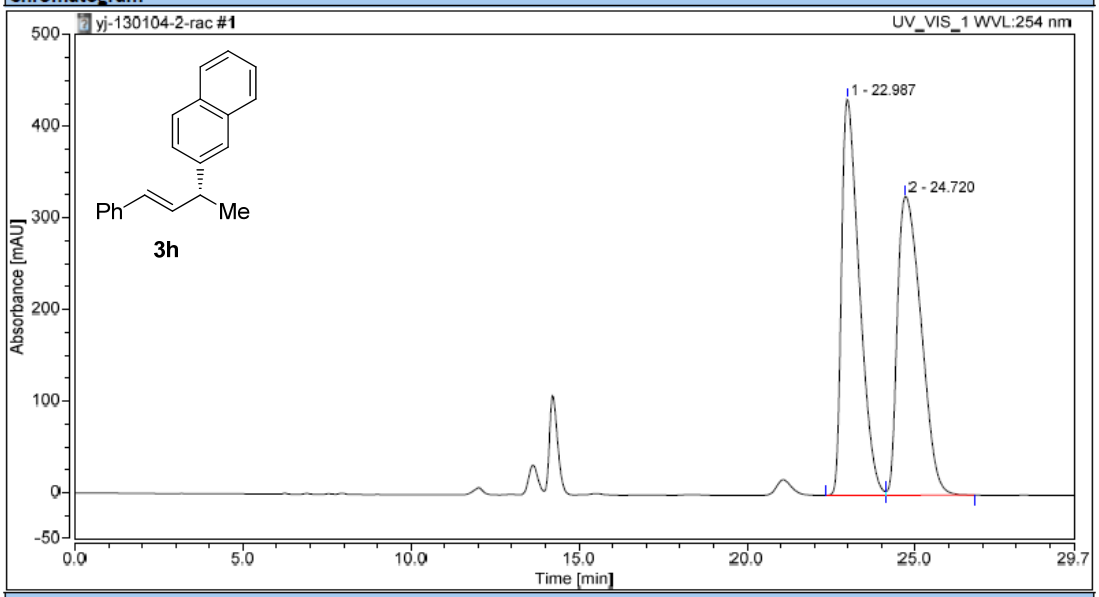
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.270	39.199	155.048	5.50	6.73	n.a.
2		12.523	674.036	2148.927	94.50	93.27	n.a.
Total:			713.235	2303.975	100.00	100.00	

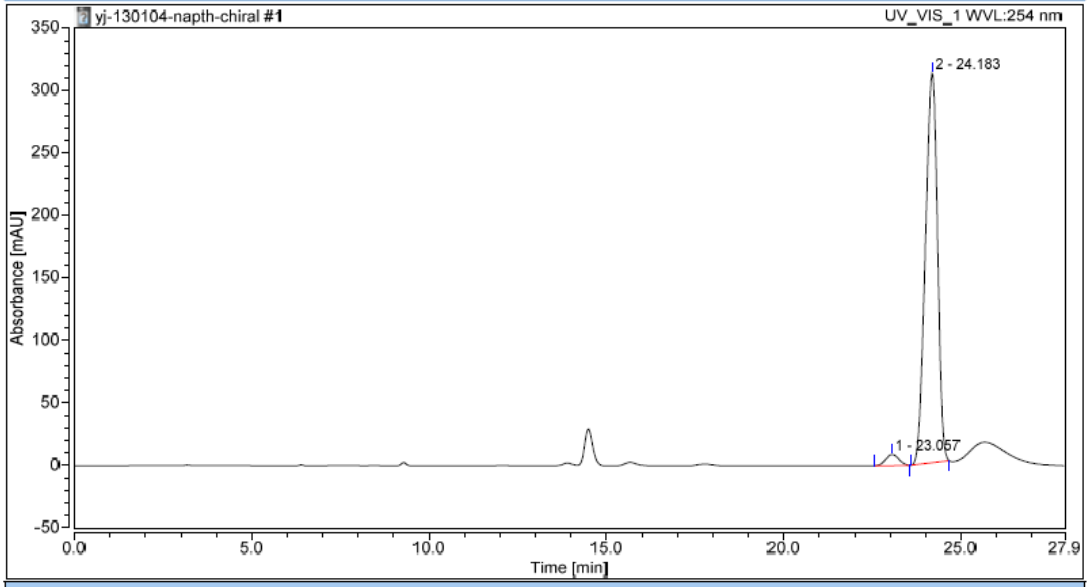
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.987	265.298	432.611	49.93	57.00	n.a.
2		24.720	266.068	326.310	50.07	43.00	n.a.
Total:			**531.365**	**758.922**	**100.00**	**100.00**	

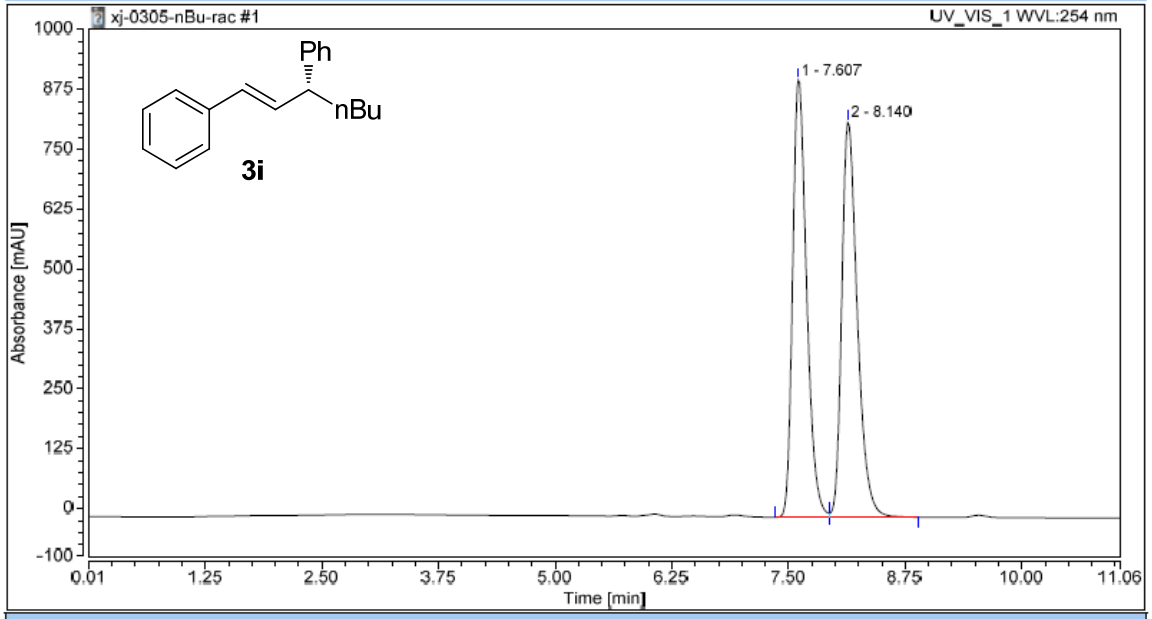
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.057	3.786	8.881	2.97	2.77	n.a.
2		24.183	123.477	311.720	97.03	97.23	n.a.
Total:			**127.263**	**320.601**	**100.00**	**100.00**	

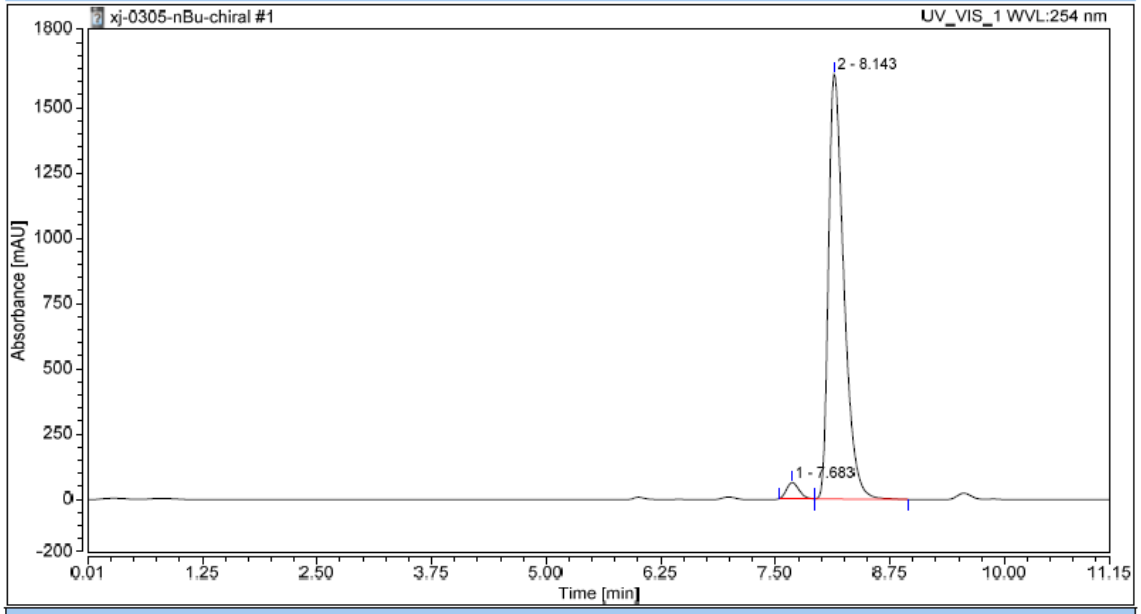
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.607	158.563	914.545	49.83	52.53	n.a.
2		8.140	159.677	826.453	50.17	47.47	n.a.
Total:			**318.240**	**1740.998**	**100.00**	**100.00**	

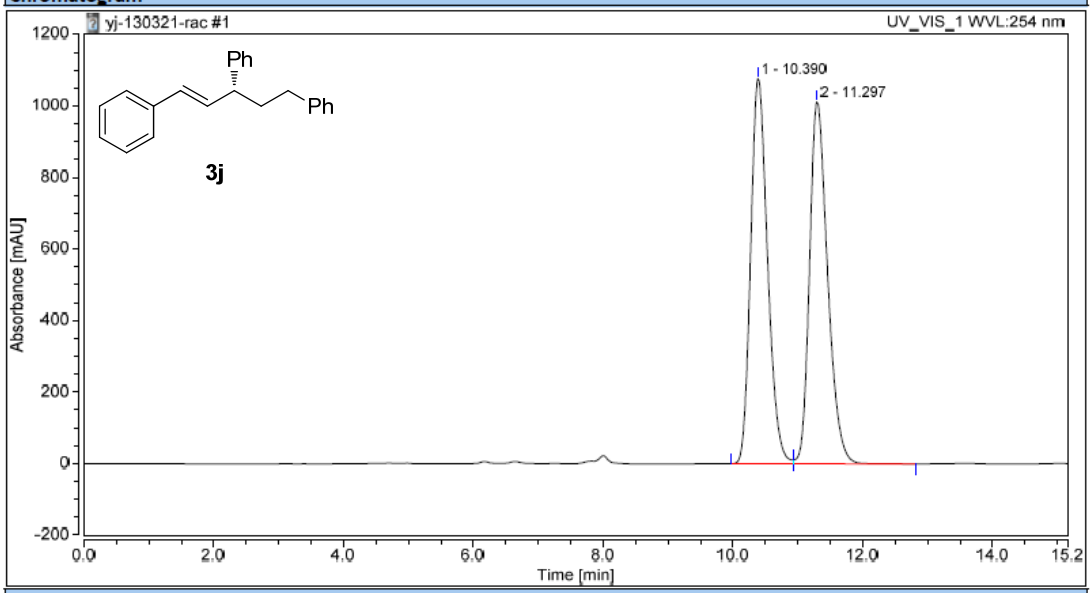
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.683	10.069	63.088	3.08	3.73	n.a.
2		8.143	317.005	1627.870	96.92	96.27	n.a.
Total:			**327.074**	**1690.958**	**100.00**	**100.00**	

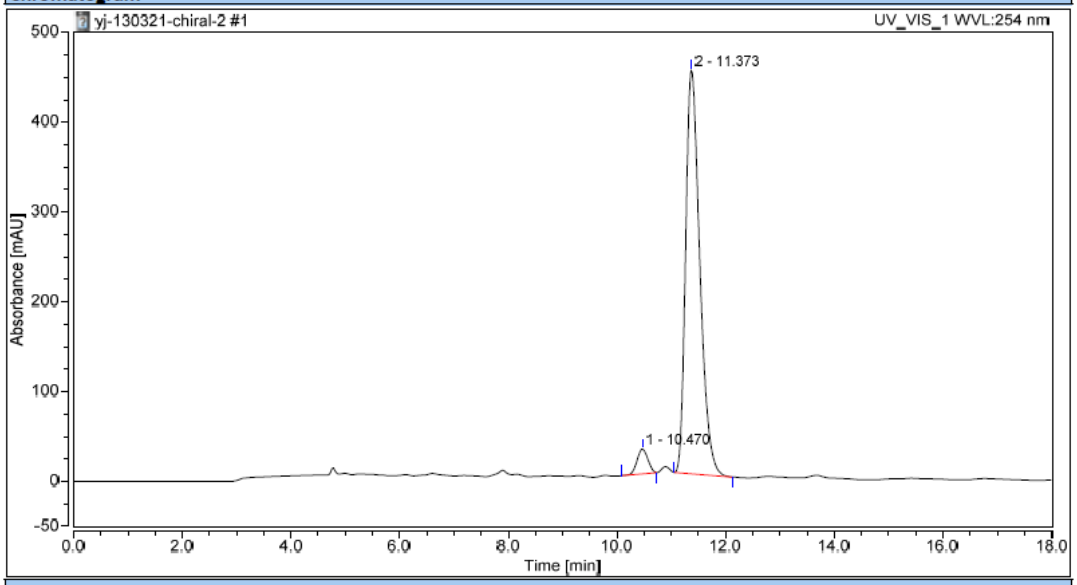
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.390	324.796	1077.973	49.87	51.54	n.a.
2		11.297	326.449	1013.442	50.13	48.46	n.a.
Total:			**651.244**	**2091.415**	**100.00**	**100.00**	

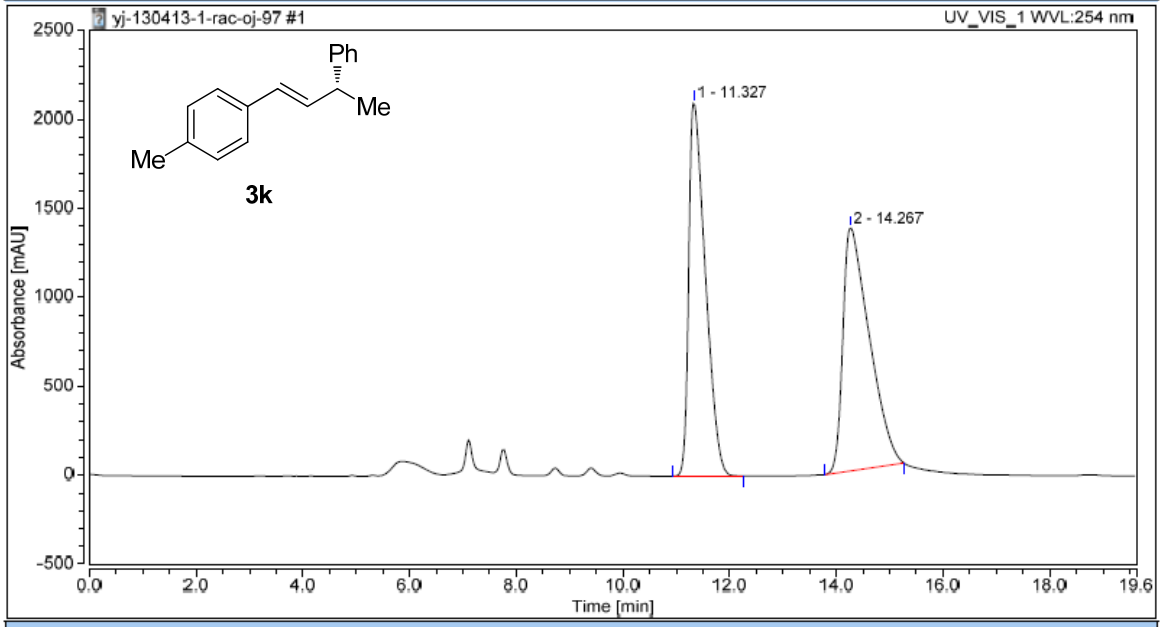
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.470	6.377	27.681	4.49	5.80	n.a.
2		11.373	135.667	449.507	95.51	94.20	n.a.
Total:			**142.043**	**477.188**	**100.00**	**100.00**	

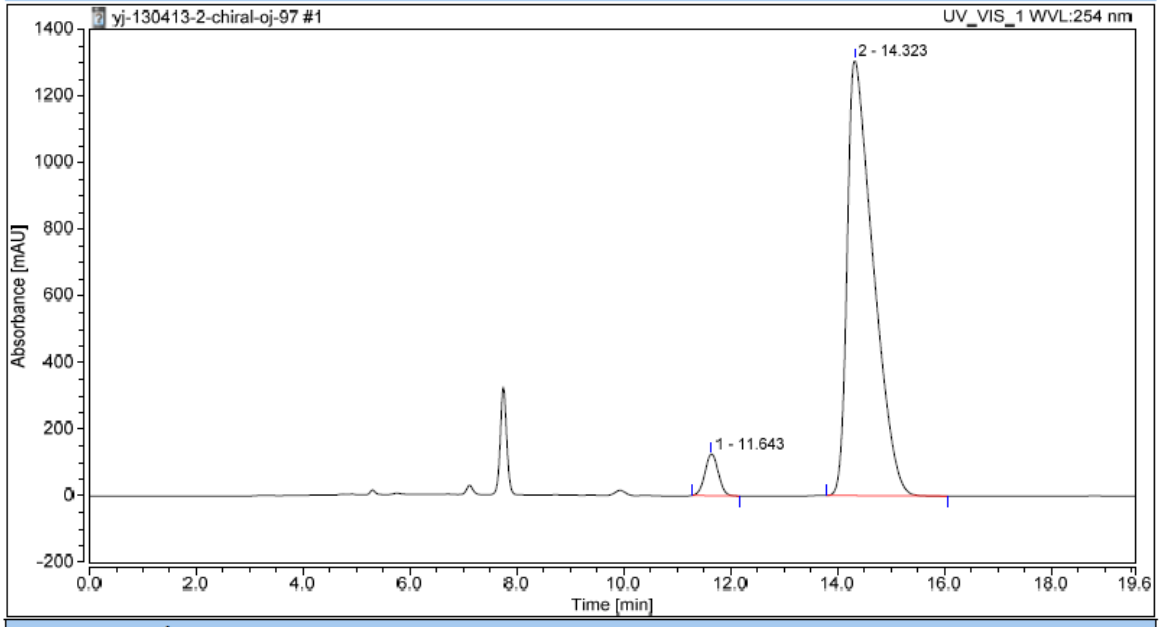
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.327	755.296	2103.646	49.11	60.59	n.a.
2		14.267	782.582	1368.177	50.89	39.41	n.a.
Total:			**1537.878**	**3471.823**	**100.00**	**100.00**	

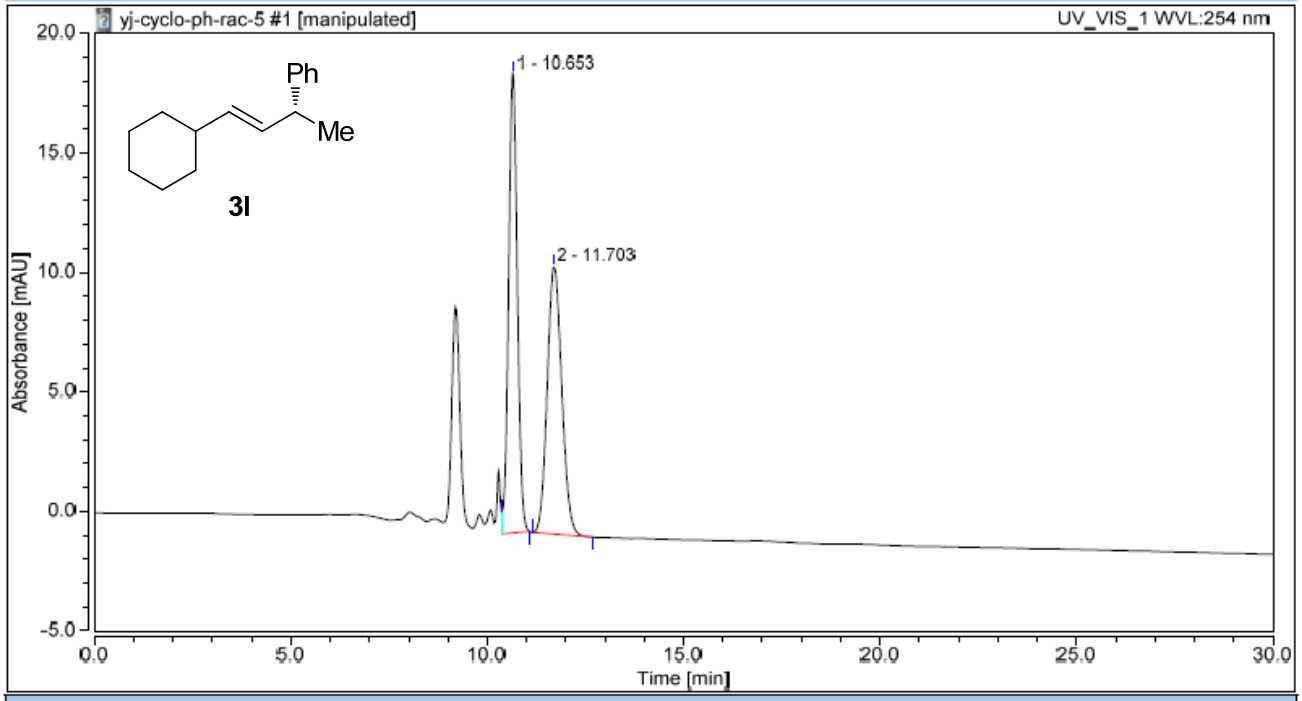
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.643	36.258	125.955	4.70	8.78	n.a.
2		14.323	734.629	1308.281	95.30	91.22	n.a.
Total:			**770.886**	**1434.236**	**100.00**	**100.00**	

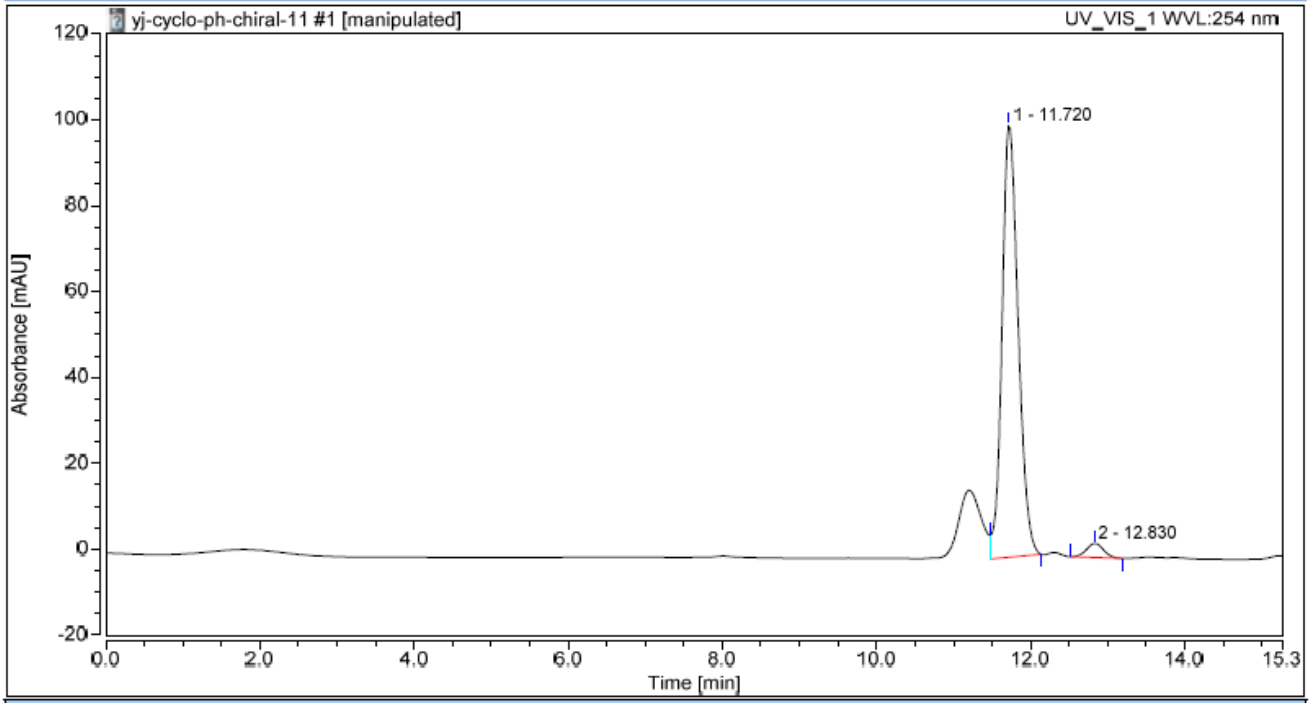
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.653	4.932	19.225	50.67	63.18	n.a.
2		11.703	4.801	11.204	49.33	36.82	n.a.
Total:			**9.732**	**30.429**	**100.00**	**100.00**	

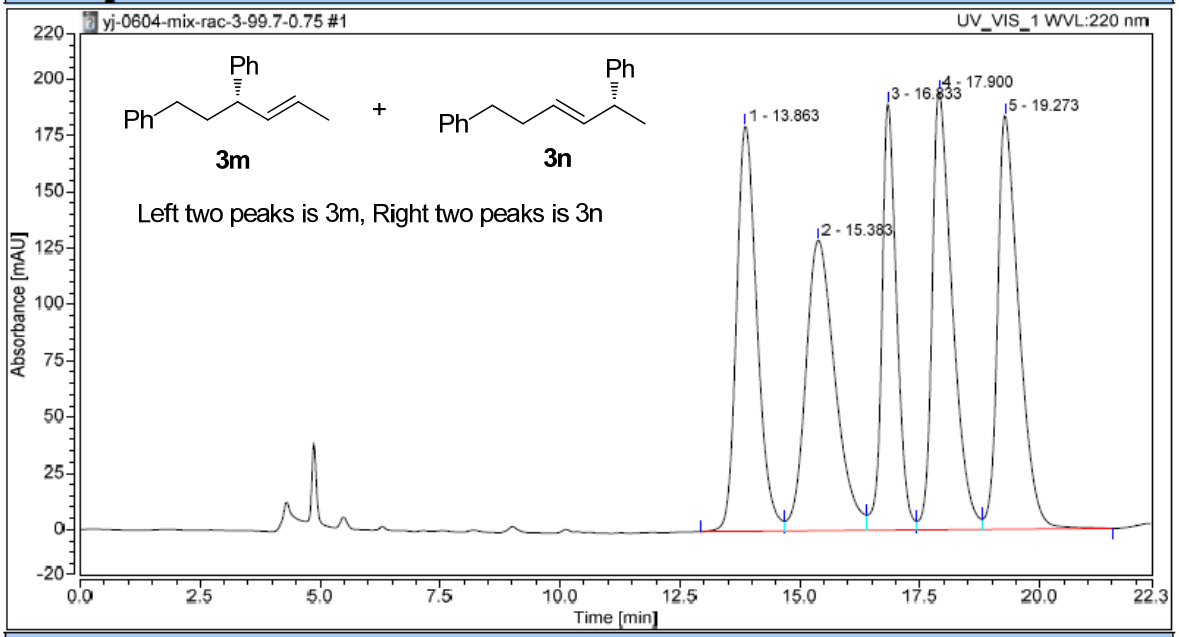
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.720	24.474	100.606	96.66	96.83	n.a.
2		12.830	0.845	3.294	3.34	3.17	n.a.
Total:			**25.319**	**103.900**	**100.00**	**100.00**	

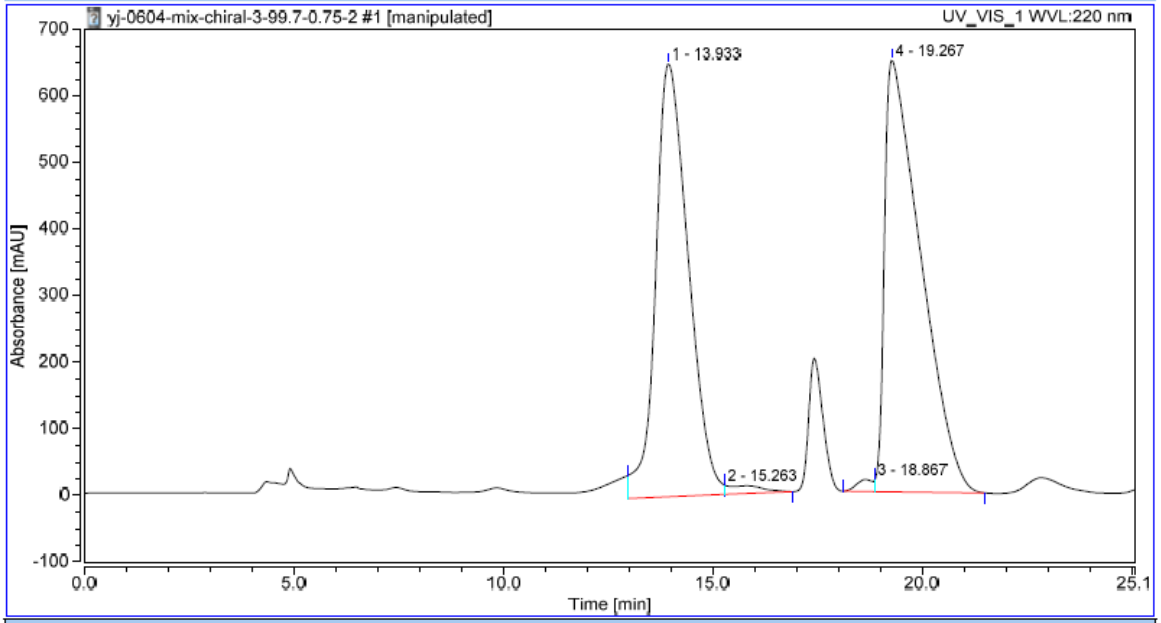
Chromatogram



Integration Results

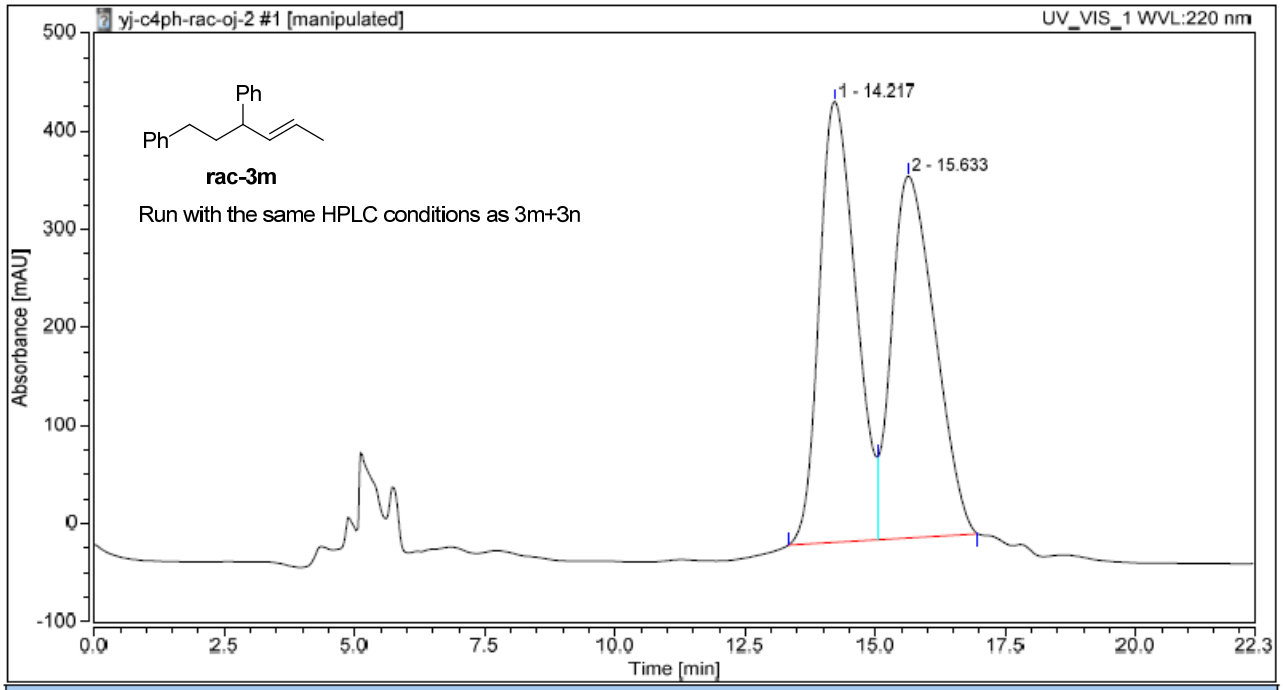
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.863	89.096	180.182	20.37	20.55	n.a.
2		15.383	91.229	128.971	20.86	14.71	n.a.
3		16.833	67.521	189.516	15.44	21.61	n.a.
4		17.900	94.772	194.674	21.67	22.20	n.a.
5		19.273	94.688	183.617	21.65	20.94	n.a.
Total:			**437.306**	**876.959**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.933	587.338	650.697	46.71	48.84	n.a.
2		15.263	11.748	14.087	0.93	1.06	n.a.
3		18.867	8.330	18.678	0.66	1.40	n.a.
4		19.267	649.975	648.827	51.69	48.70	n.a.
Total:			**1257.391**	**1332.289**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.217	365.058	449.078	50.63	54.92	n.a.
2		15.633	355.985	368.648	49.37	45.08	n.a.
Total:			**721.043**	**817.726**	**100.00**	**100.00**	