

Supporting Information-I

**“On Water” Organocatalyzed [4+2] Cycloaddition of Enones and Nitrodiienes
for the Enantioselective Synthesis of Densely Substituted Cyclohexanones**

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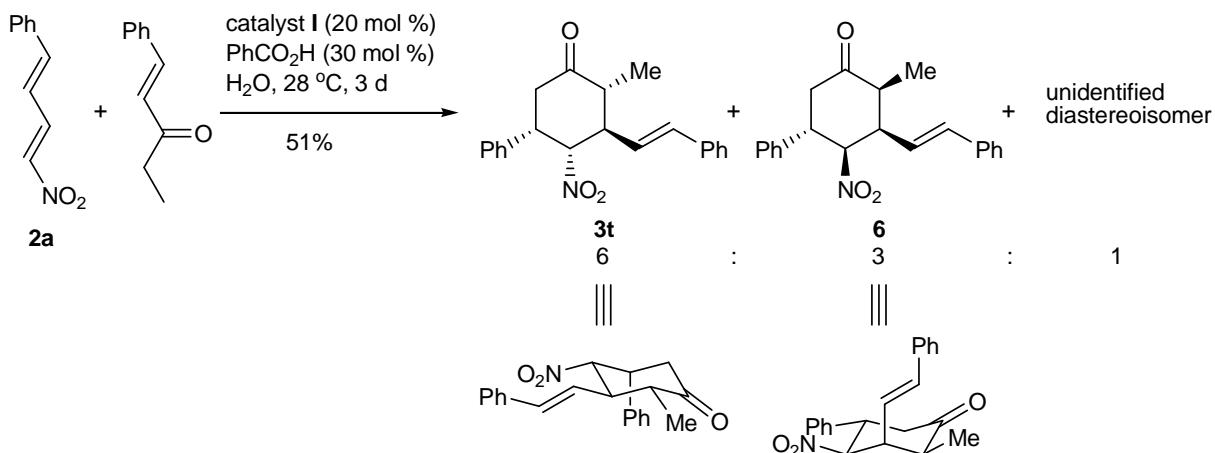
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1. Discussion about the reaction of (*E*)-1-phenylpent-1-en-3-one and 4-phenyl-1-nitro-1,3-butadiene in the presence of catalyst I under optimized conditions.

It is worth mentioning that the reaction between 4-phenyl-1-nitro-1,3-butadiene and (*E*)-1-phenylpent-1-en-3-one as enone under optimized reaction conditions with catalyst **I** worked well providing two diastereoisomeric products **3t** and **6** along with an unidentified minor diastereoisomer in a ratio of 6:3:1 in a combined yield of 51% (Scheme 1). The diastereoisomer **3t** could be obtained in pure form after careful chromatographic separation while diastereoisomer **6** was contaminated with about 12% of the unidentified minor diastereoisomer.

Scheme 1 Synthesis of tetrasubstituted cyclohexanone



The relative stereochemistry of product **3t** and **6** were assigned on the basis of NOE interactions obtained from 2D-ROESY experiments (Figs. 1 and 2). The absolute stereochemistry of each of these products is assigned by analogy to adducts **3g/ 3l/ 3m/ 3s**.

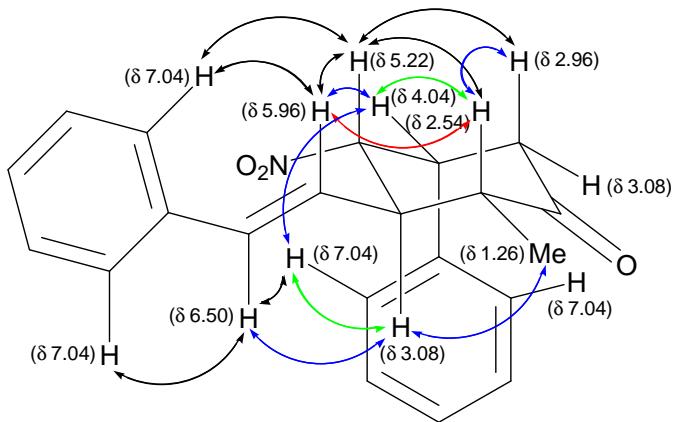


Figure 1 Important ^1H - ^1H ROESY interactions to ascertain the relative stereochemistry of major diastereoisomer **3t**

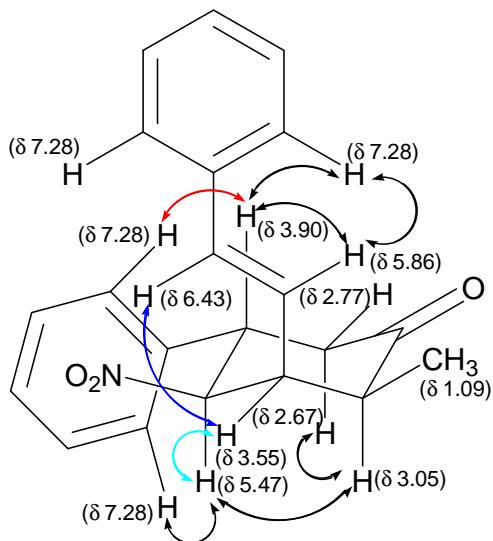
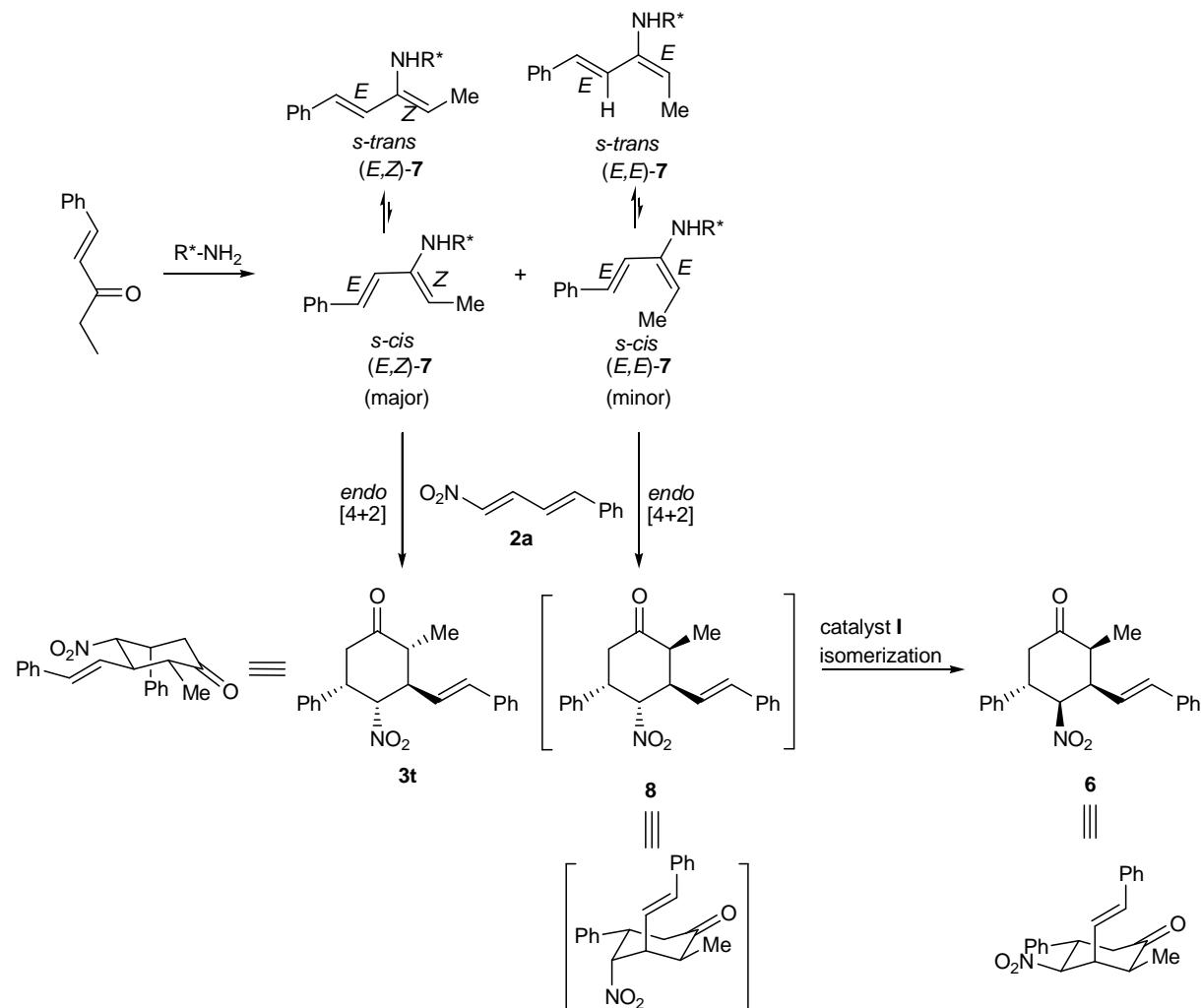


Figure 2 Important ^1H - ^1H ROESY interactions to ascertain the relative stereochemistry of minor diastereoisomer **6**

The formation of diastereoisomeric products **3t** and **6** can be explained by an *endo* selective [4+2] cycloaddition of the dienophile 4-phenyl-1-nitro-1,3-butadiene **2a** with two geometrical isomeric enamines (*E,Z*)-**7** and (*E,E*)-**7**, generated *in situ* from the chiral primary amine catalyst **I** (R^*NH_2) and (*E*)-1-phenylpent-1-en-3-one (Scheme 2). The formation of the enamine (*E,Z*)-**7** would be favoured^{1,2} over enamine (*E,E*)-**7**. As shown in Scheme 2, major

enamine (*E,Z*)-**7** leads to major diastereoisomer **3t** while minor enamine (*E,E*)-**7** leads to diastereoisomer **8** but could not be isolated due to its high energy configuration. Like the favourable isomerisation of axial nitro substituted **4a** to equatorial nitro substituted **3a**, this diastereoisomer **8** presumably underwent epimerization of the nitro-bearing centre from axial nitro substituted **8** to equatorial nitro substituted **6** where three substituent became equatorial.

Scheme 2 Plausible pathways for diastereoisomers **3t and **6****



2. General methods

Solvent removal was performed with a rotary evaporator that was connected to a dry ice condenser. TLC (0.5 mm) was carried out using homemade silica gel plates with fluorescence indicator. Column chromatography was performed on silica gel (230-400 mesh). The ¹H and ¹³C NMR spectroscopic data were recorded with 200 MHz (¹H NMR: 200 MHz, ¹³C NMR: 50 MHz), 500 MHz (¹H NMR: 500 MHz, ¹³C NMR: 125 MHz) and 800 MHz (¹H NMR: 800 MHz, ¹³C NMR: 200 MHz) Bruker spectrometers, and 500 MHz (¹H NMR: 500 MHz, ¹³C NMR: 125 MHz), 600 MHz (¹H NMR: 600 MHz, ¹³C NMR: 150 MHz) Varian spectrometers. The ¹H and ¹³C chemical shifts are given in ppm (δ scale) and are measured relative to CHCl₃ (7.27 ppm) and CDCl₃ (77.0 ppm), respectively, as internal standards. High resolution mass spectra were recorded at 60-70 eV with a Waters Micromass Q-TOF spectrometer (ESI, Ar). Enantiomeric excess (*ee*) values were determined by HPLC analysis with a JASCO (JASCOPU-2080) instrument fitted with a Daicel Chiralpak AD-H column/ Daicel Chiralcel OD-H and UV-2075 detector (λ fixed at 254 nm). Optical rotations were measured with a JASCO DIP polarimeter. Melting points (mp) were measured in a Büchi B-540 apparatus. Elemental analyses (C, H, N) were carried out by Elementar, varioMICRO CHNS instrument.

Materials

Benzylidene acetone **1a** was purchased from Spectrochem Private Limited, India. Other arylidene acetones **1** were synthesized from respective aryl aldehydes and acetone following the literature procedures.³ Nitrodienes **2** were prepared from substituted cinnamaldehydes and nitromethane following the procedures reported in the literatures.^{4,5} Organocatalysts **I-IV** were prepared according to literature.⁶

3 General Procedures

(a) General Procedure A for the preparation of trisubstituted *rac*-cyclohexanone derivatives

All the reactions were carried out in normal toluene and no special precautions were taken to exclude water or air from the reaction flask. Pyrrolidine (0.1 mmol) and benzoic acid (6.0 mg, 0.05 mmol) were added to a stirred solution of the nitrodiene **2** (0.2 mmol) and enones **1** (0.4 mmol) in toluene (1 mL). Then the reaction mixture was stirred at 50 °C for 2 d. After that, the solvent was removed under reduced pressure and the resulting residue was directly subjected to column chromatography on silica gel to afford the corresponding products *rac*-**3a-3s**.

(b) General Procedure B for the preparation of trisubstituted chiral cyclohexanone derivatives

All the reactions were carried out in double distilled water and no special precautions were taken to exclude air from the reaction flask. Benzoic acid (7.5 mg, 0.06 mmol, 30 mol %) was added to a heterogeneous mixture of the catalyst **I** (13 mg, 0.04 mmol, 20 mol %) and water (0.5 mL). The resulting heterogeneous mixture was stirred at 40 °C for 10 min in a pre-heated oil bath. After that, the mixture was brought to room temperature and enone **1** (0.4 mmol, 2 equiv) was added, followed by the addition of nitrodiene **2** (0.2 mmol, 1 equiv). The heterogeneous mixture was stirred at 28 °C for 2 d. The reaction mixture was extracted with dichloromethane (3×10 mL) and the combined extract was washed with brine, dried (MgSO_4) and evaporated. The residue was purified by column chromatography on silica using hexane/EtOAc as eluent to give **3a-3s**. Except mentioned, each solid product was recrystallized from hexane/EtOAc combined solvent systems to give the corresponding enantiomerically pure cyclohexanone.

(c) General Procedure C for the preparation of trisubstituted *rac*-cyclohexanone **4a and **rac-5****

The reaction was carried out in double distilled water and no special precautions were taken to exclude air from the reaction flask. Benzoic acid (7.5 mg, 0.06 mmol, 30 mol %) was added to a heterogeneous mixture of the catalyst **I** (6.5 mg, 0.02 mmol, 10 mol %) and catalyst **II** (6.5 mg, 0.02 mmol, 10 mol %) in water (0.5 mL). The resulting heterogeneous mixture was stirred at 40 °C for 10 min in a pre-heated oil bath. After that, the mixture was brought to room temperature and then benzylidene acetone **1a** (58 mg, 0.4 mmol, 2 equiv) was added, followed by the addition of nitrodiene **2a** (35 mg, 0.2 mmol, 1 equiv). The heterogeneous mixture was stirred at 28 °C for 2 d and extracted with dichloromethane (3×10 mL). The combined organic extract was washed with brine, dried (MgSO_4) and evaporated. The residue was purified by column chromatography on silica using hexane/EtOAc as eluent to give *rac*-**4a** and *rac*-**5**

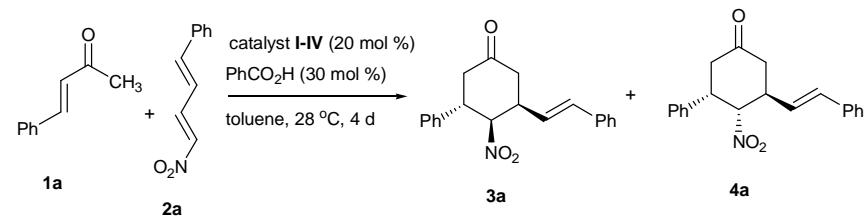
(d) General Procedure D for the preparation of tetrasubstituted *rac*-cyclohexanones **3t and **6****

The reaction was carried out in double distilled water and no special precautions were taken to exclude air from the reaction flask. Benzoic acid (7.5 mg, 0.06 mmol, 30 mol %) was added to a heterogeneous mixture of the catalyst **I** (6.5 mg, 0.02 mmol, 10 mol %) and catalyst **II** (6.5 mg, 0.02 mmol, 10 mol %) in water (0.5 mL). The resulting heterogeneous mixture was stirred at 40 °C for 10 min in a pre-heated oil bath. After that, the mixture was brought to room temperature and then (*E*)-1-phenylpent-1-en-3-one (64 mg, 0.4 mmol, 2 equiv) was added, followed by the addition of nitrodiene **2a** (35 mg, 0.2 mmol, 1 equiv). The heterogeneous mixture was stirred at 28 °C for 3 d and extracted with dichloromethane (3×10 mL). The combined organic extract was washed with brine, dried (MgSO_4) and evaporated. The residue was purified by column

chromatography on silica using hexane/EtOAc as eluent to give *rac*-**3t** and *rac*-**6**. The diastereoisomer *rac*-**6** was contaminated with about 18% of an unidentified diastereoisomer.

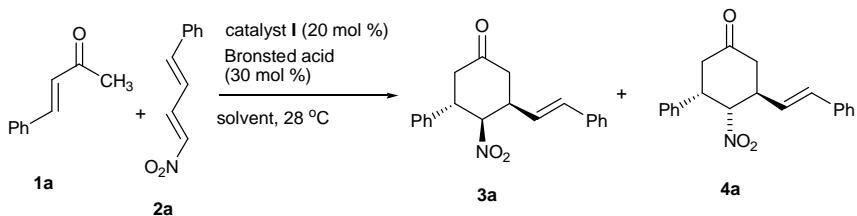
4. Optimization Table

Table 1. Catalyst screening using benzoic acid as an additive in toluene^a



entry	catalyst	3a/4a ^b	yield (%) of 3a ^c	ee (%) of 3a ^d
1	I	65:35	52	99
2	II	64:36	46	96 ^e
3	III	44:56	35	98
4	IV	40:60	22 ^f	96

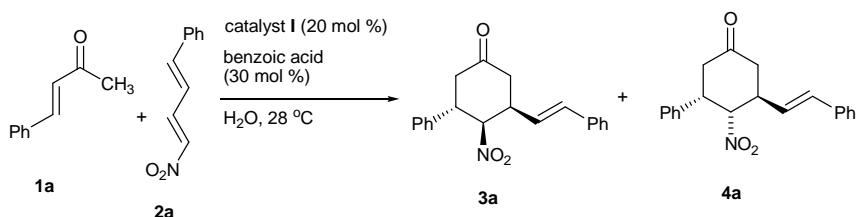
^a Unless noted otherwise, all reactions were performed using **1a** (0.4 mmol), **2a** (0.2 mmol), catalyst (0.04 mmol) and benzoic acid (0.06 mmol) in toluene (0.5 mL). ^b Determined by ¹H NMR of the crude reaction mixture. ^c Isolated yield of diastereoisomer **3a** after chromatographic purification. ^d Enantiomeric excess of **3a** as determined by HPLC on chiral stationary phase. ^e Product formed with opposite enantioselectivity. ^f Incomplete reaction.

Table 2. Additive and solvent screening using catalysts I (20 mol%)^a

entry	additive	solvent	time	3a/4a^b	yield (%)	ee (%)
				of 3a^c		
1	benzoic acid	toluene	4 d	65:35	52	99
2	3,5-dinitrobenzoic acid	toluene	5 d	55:45	16 ^e	93
3	4-nitrobenzoic acid	toluene	5 d	50:50	21 ^e	93
4	2-fluorobenzoic acid	toluene	5 d	60:40	35	96
5	acetic acid	toluene	5 d	60:40	20 ^e	95
6	benzoic acid	xylene	5 d	50:50	38	95
7	benzoic acid	CHCl ₃	5 d	67:33	42	96
8	benzoic acid	MTBE	5 d	83:17	39	>99
9	benzoic acid	THF	5 d	50:50	41	92
10	benzoic acid	MeOH	5 d	50:50	32	94
11	benzoic acid	H ₂ O	2 d	80:20	75	>98

^a Unless noted otherwise, all reactions were performed using **1a** (0.4 mmol), **2a** (0.2 mmol), catalyst (0.04 mmol) and additive (0.06 mmol) in solvent (0.5 mL). ^b Determined by ¹H NMR of the crude reaction mixture. ^c Isolated yield of diastereoisomer **3a** after chromatographic purification. ^d Enantiomeric excess of **3a** as determined by HPLC on chiral stationary phase. ^e Incomplete reaction.

Table 3. Effect of the ratio of the enone **1a to nitrodiene **2a** on the [4+2] cycloaddition reaction^a**



entry	1a/2a	3a/4a^b	yield (%) of 3a^c	ee (%) of 3a^d
1	1.0/1.0	87/13	45	95
2	1.2/1.0	83/17	50	96
3	1.5/1.0	81/19	62	96
4	2.0/1.0	80:20	75	>98

^a Unless noted otherwise, all reactions were performed using nitrodiene **2a** (0.2 mmol), catalyst (0.04 mmol) and benzoic acid (0.06 mmol) in H₂O (0.5 mL). ^b Determined by ¹H NMR of the crude reaction mixture. ^c Isolated yield of diastereoisomer **3a** after chromatographic purification.

^d Determined by HPLC on chiral stationary phase.

5. X-ray Crystallographic Studies

Single crystal X-ray diffraction data were collected on Agilent Supernova system equipped with a microfocus Cu-source ($\lambda = 1.5418 \text{ \AA}$) and a Titan CCD detector. The crystals were separated, coated with paraffin oil and mounted on a loop for X-ray diffraction data collection at specified temperatures. The data reduction and analysis were carried out with CrysAlisPro software suit. Analytical absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid⁷ and as implemented in the CrysAlisPro software suit was carried out for all the crystals. The structures were solved by direct method using Shelxs and refined using Shelxl

softwares⁸ using Olex2 interface.⁹ All the non-hydrogen atoms were refined anisotropically and hydrogens were generated at their idealized positions and refined isotropically according to riding model.

6. Table of X-ray Crystallographic Data

Compounds	3g	3l	3m	3s
Formula	C ₂₁ H ₁₈ F ₃ NO ₃	C ₂₀ H ₁₈ ClNO ₃	C ₂₀ H ₁₈ BrNO ₃	C ₂₀ H ₁₇ Br ₂ NO ₃
Formula Wt	389.36	355.80	400.26	479.17
Crystal System	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space Group	P 21 21 21	P 1 21 1	P 1 21 1	P 21 21 21
T,K	293(2)	293(2)	293(2)	293(2)
Z	4	2	2	4
a, Å	6.0481(3)	5.9375(5)	5.9479(5)	6.04125(16)
b, Å	15.9843(8)	12.3627(14)	12.3464(13)	9.8526(4)
c, Å	19.4099(10)	12.7571(11)	12.9363(12)	31.9892(11)
α, deg	90	90	90	90
β, deg	90	99.297(8)	99.635(8)	90
γ, deg	90	90	90	90
V, Å ³	1876.44(16)	924.12(15)	936.59(15)	1904.07(12)
ρ _{calc} , mg/mm ³	1.378	1.279	1.419	1.671
μ, m/mm ⁻¹	0.955	1.977	3.138	5.566
θ range, deg	3.571-68.719	3.532-69.987	3.451-60.870	4.686-72.914
GOF (F ²)	1.049	1.003	0.981	1.073
R ₁ ^a (wR ₂ ^b), %	0.0857 (0.2589)	0.0601 (0.1741)	0.0619 (0.1960)	0.0629 (0.1745)

7. X-ray Crystal Structures (50% ellipsoid contour percent probability):

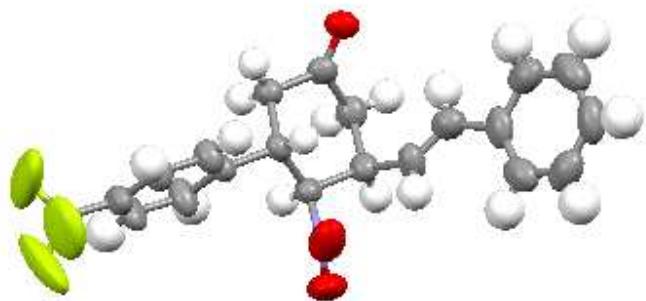


Figure 1: X-ray structure of **3g**, CCDC No. 1450559

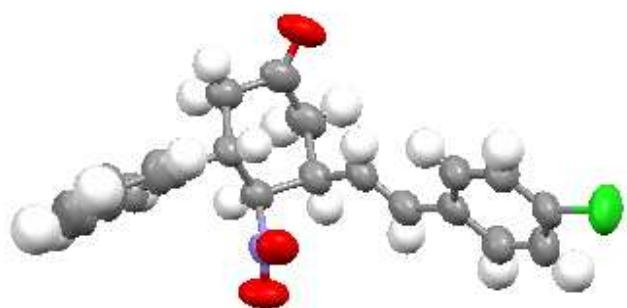


Figure 2: X-ray structure of **3l**, CCDC No. 1450560

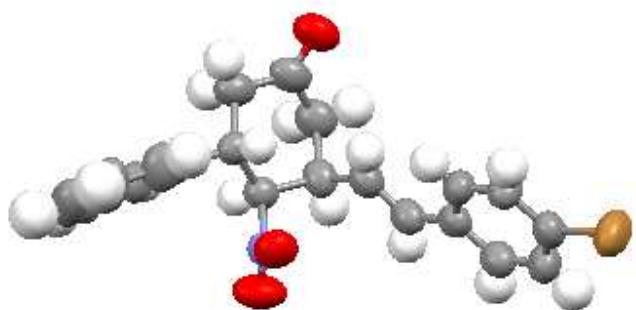


Figure 3: X-ray structure of **3m**, CCDC No. 1450561

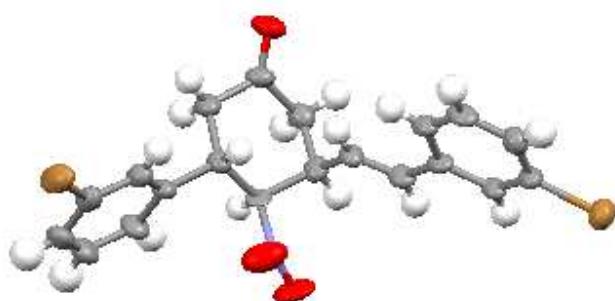
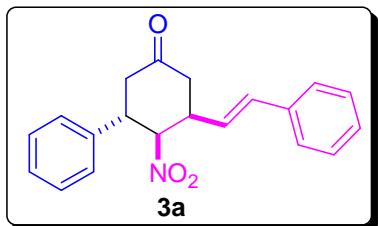


Figure 4: X-ray structure of **3s**, CCDC No. 1450562

8. Characterization data of products

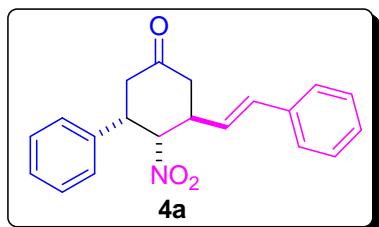


(3*S*,4*R*,5*S*)-4-Nitro-3-phenyl-5-styrylcyclohexanone 3a

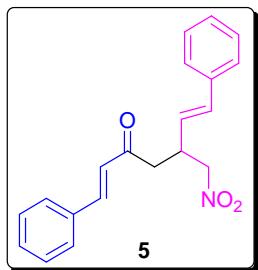
The reactions were carried out in double distilled water and no special precautions were taken to exclude air from the reaction flask. Benzoic acid (7.5 mg, 0.06 mmol, 30 mol %) was added to a heterogeneous mixture of the catalyst **I** (13 mg, 0.04 mmol, 20 mol %) and water (0.5 mL). The resulting heterogeneous mixture was stirred at 40 °C for 10 min in a pre-heated oil bath. After that the mixture was brought to room temperature and enone **1a** (58 mg, 0.4 mmol, 2 equiv) was added, followed by the addition of nitrodiene **2a** (35 mg, 0.2 mmol, 1 equiv). The heterogeneous mixture was stirred at 28 °C for 2 d. The reaction mixture was extracted with dichloromethane (3 × 10 mL) and the combined extract was washed with brine, dried (MgSO_4) and evaporated. The residue was purified by column chromatography on silica using hexane/EtOAc as eluent to give **3a** (48 mg, 75%), **4a** (6 mg, 9%) and **5** (2 mg, 3%).

Data for 3a: White solid. mp: 209-210 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 14.05$ min, $\tau_{\text{minor}} = 18.73$ min, >98% ee; $[\alpha]_D^{25} = -69.9$ (*c* 2.00, CHCl_3 , ee >99.99%); ^1H NMR (CDCl_3 , 200 MHz): δ 7.40-7.25 (m, 10 H), 6.46 (dd, *J* = 0.6, 15.8 Hz, 1 H), 6.10 (dd, *J* = 7.7, 15.9 Hz, 1 H), 5.30 (dd, *J* = 4.4, 9.4 Hz, 1 H), 3.99-3.86 (m, 1 H), 3.58-3.47 (m, 1 H), 2.90-2.86 (m, 2 H), 2.83-2.61 (m, 2 H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 205.97, 139.0, 135.8, 134.7, 129.2 (2 C), 128.6 (2 C), 128.3, 128.0, 127.1 (2 C), 126.6 (2 C), 123.6, 90.4, 45.0, 43.2, 42.3, 41.5; IR (film): ν 1715, 1542, 1493,

1370, 1210, 1027, 968, 907, 757, 695 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_3$: C, 74.75; H, 5.96; N, 4.36; Found: C, 74.76; H, 6.14; N, 4.22.

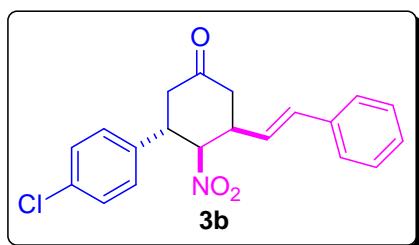


Data for (3S,4S,5S)-4-nitro-3-phenyl-5-styrylcyclohexanone 4a: Yellow liquid. The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 17.74$ min, $\tau_{\text{minor}} = 24.00$ min, >97% ee; $[\alpha]_D^{25} = -93.0$ (*c* 0.91, CHCl_3 , ee >97.0%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.38-7.29 (m, 8 H), 7.15 (d, *J* = 7.5 Hz, 2 H), 6.61 (d, *J* = 16 Hz, 1 H), 6.10 (dd, *J* = 7.3, 15.8 Hz, 1 H), 5.07 (t, *J* = 5.0 Hz, 1 H), 3.79 (quin, *J* = 5.0 Hz, 1 H), 3.60 (quin, *J* = 6.0 Hz, 1 H), 3.40 (dd, *J* = 10.8, 15.3 Hz, 1 H), 3.08 (dd, *J* = 6.0, 15.5 Hz, 1 H), 2.75 (dd, *J* = 5.5, 15.5 Hz, 1 H), 2.69 (dd, *J* = 6.0, 16.0 Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 207.3, 136.9, 135.8, 134.3, 129.1 (2 C), 128.7 (2 C), 128.4, 128.4, 127.4 (2 C), 126.6 (2 C), 126.2, 90.3, 42.3, 41.7, 41.5, 41.0; IR (film): ν 1711, 1541, 1492, 1372, 1210, 1027, 968, 907, 759, 697 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_3$: C, 74.75; H, 5.96; N, 4.36; Found: C, 74.71; H, 6.11; N, 4.31.



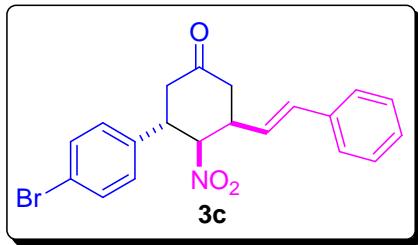
Data for 5: The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 24.98$ min, $\tau_{\text{minor}} = 32.9$ min, 60% ee; ^1H NMR (CDCl_3 ,

500 MHz): δ 7.60 (d, J = 16.5 Hz, 1 H), 7.57-7.55 (m, 2 H), 7.42-7.40 (m, 3 H), 7.35-7.34 (m, 2 H), 7.32-7.29 (m, 2 H), 7.26-7.15 (m, 1 H), 6.76 (d, J = 16.0 Hz, 1 H), 6.58 (d, J = 15.5 Hz, 1 H), 6.15 (dd, J = 8.5, 16.0 Hz, 1 H), 4.69 (dd, J = 6.0, 12.5 Hz, 1 H), 4.59 (dd, J = 7.5, 12.5 Hz, 1 H), 3.71-3.64 (m, 1 H), 3.00 (d, J = 6.5 Hz, 2H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 196.8, 143.7, 136.2, 134.1, 133.4, 130.9, 129.0 (2 C), 128.6 (2 C), 128.4 (3 C), 128.0, 126.5 (2 C), 125.7, 78.8, 42.4, 37.4.



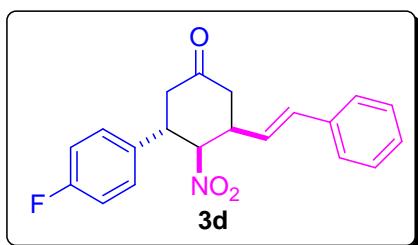
(3*S*,4*R*,5*S*)-3-(4-Chlorophenyl)-4-nitro-5-styrylcyclohexanone 3b

Following the general procedure B, the product was obtained in 70% yield (50 mg) as a white solid. mp: 201-202 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 19.10$ min, $\tau_{\text{minor}} = 25.36$ min, >94% ee; $[\alpha]_D^{25} = -217.9$ (c 1.54, CHCl_3 , ee >99.99%); ^1H NMR (CDCl_3 , 200 MHz): δ 7.35-7.18 (m, 9 H), 6.47 (d, J = 15.8 Hz, 1 H), 6.07 (dd, J = 7.8, 15.8 Hz, 1 H), 5.24 (dd, J = 4.6, 9.8 Hz, 1 H), 3.96-3.83 (m, 1 H), 3.57-3.49 (m, 1 H), 2.89-2.85 (m, 2 H), 2.79-2.56 (m, 2 H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 205.3, 137.4, 135.8, 135.0, 134.0, 129.4 (2 C), 128.6 (2 C), 128.5 (2 C), 128.4, 126.7 (2 C), 123.2, 90.3, 45.1, 43.3, 41.6 (2 C); IR (film): ν 1715, 1545, 1493, 1377, 1092, 1015, 969, 837, 750, 694 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{18}\text{ClNO}_3$: C, 67.51; H, 5.10; N, 3.94; Found: C, 67.46; H, 4.84; N, 3.66.



(3*S*,4*R*,5*S*)-3-(4-Bromophenyl)-4-nitro-5-styrylcyclohexanone 3c

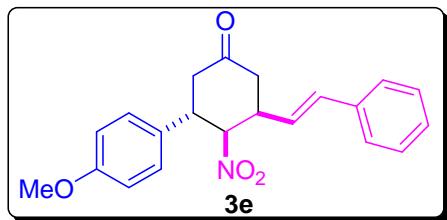
Following the general procedure B, the product was obtained in 62% yield (50 mg) as a white solid. mp: 169-170 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 19.36$ min, $\tau_{\text{minor}} = 25.80$ min, >94% ee; $[\alpha]_D^{25} = -187.9$ (*c* 1.30, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 500 MHz): δ 7.48 (d, *J* = 8.5 Hz, 2 H), 7.35-7.27 (m, 5 H), 7.15 (d, *J* = 8.5 Hz, 2 H), 6.47 (d, *J* = 15.5 Hz, 1 H), 6.08 (dd, *J* = 7.5, 15.5 Hz, 1 H), 5.25 (dd, *J* = 4.5, 9.5 Hz, 1 H), 3.91-3.86 (m, 1 H), 3.58-3.53 (m, 1 H), 2.90-2.84 (m, 2 H), 2.83-2.79 (m, 1 H), 2.64 (dd, *J* = 11.0, 15.5 Hz, 1 H); ¹³C NMR (CDCl₃, 50 MHz): δ 205.3, 138.0, 135.8, 135.1, 132.4 (2 C), 128.8 (2 C), 128.6 (2 C), 128.4, 126.7 (2 C), 123.2, 122.1, 90.2, 45.0, 43.3, 41.7, 41.66; IR (film): ν 1715, 1546, 1485, 1373, 1289, 1011, 968, 836, 749, 694 cm⁻¹; Anal. calcd for C₂₀H₁₈BrNO₃: C, 60.01; H, 4.53; N, 3.50; Found: C, 60.35; H, 4.24; N, 3.36.



(3*S*,4*R*,5*S*)-3-(4-Fluorophenyl)-4-nitro-5-styrylcyclohexanone 3d

Following the general procedure B, the product was obtained in 80% yield (54 mg) as a white solid. mp: 216-218 °C; The *ee* was determined by HPLC using a Daicel

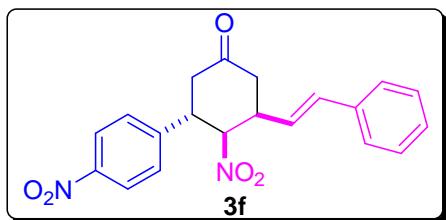
Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 18.11$ min, $\tau_{\text{minor}} = 23.46$ min, >94% ee; $[\alpha]_D^{25} = -192.8$ (*c* 1.34, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 200 MHz): δ 7.34-7.21 (m, 7 H), 7.08-6.99 (m, 2 H), 6.46 (d, *J* = 15.8 Hz, 1 H), 6.08 (dd, *J* = 7.8, 16.0 Hz, 1 H), 5.24 (dd, *J* = 4.5, 9.7 Hz, 1 H), 3.97-3.84 (m, 1 H), 3.59-3.48 (m, 1 H), 2.89-2.77 (m, 3 H), 2.63 (dd, *J* = 10.7, 15.5 Hz, 1 H); ¹³C NMR (CDCl₃, 125 MHz): δ 205.6, 162.2 (d, *J*_{C-F} = 248 Hz), 135.8, 134.9, 134.7 (d, *J*_{C-F} = 4 Hz), 128.8 (d, *J*_{C-F} = 8 Hz), 128.6 (2 C), 128.4, 126.7 (2 C), 123.3, 116.2 (d, *J*_{C-F} = 22 Hz), 90.6, 45.2, 43.3, 41.6; IR (film): ν 1715, 1544, 1509, 1373, 1224, 1160, 969, 842, 750, 695 cm⁻¹; Anal. calcd for C₂₀H₁₈FNO₃: C, 70.78; H, 5.35; N, 4.13; Found: C, 70.67; H, 5.01; N, 3.95.



(3*S*,4*R*,5*S*)-3-(4-Methoxyphenyl)-4-nitro-5-styrylcyclohexanone 3e

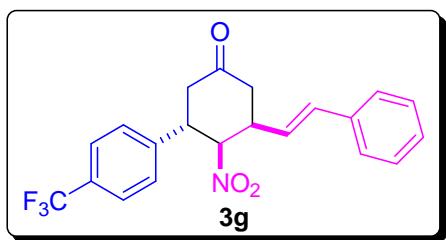
Following the general procedure B, the product was obtained in 45% yield (32 mg) as a white solid. mp: 138-140 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 18.51$ min, $\tau_{\text{minor}} = 33.03$ min, >95% ee; $[\alpha]_D^{25} = -192.0$ (*c* 1.28, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 200 MHz): δ 7.35-7.24 (m, 5 H), 7.22-7.14 (m, 2 H), 6.90-6.82 (m, 2 H), 6.45 (dd, *J* = 0.8, 15.8 Hz, 1 H), 6.09 (dd, *J* = 7.7, 15.7 Hz, 1 H), 5.22 (dd, *J* = 4.4, 9.2 Hz, 1 H), 3.93-3.81 (m, 1 H), 3.76 (s, 3 H), 3.54-3.42 (m, 1 H), 2.89-2.78 (m, 3 H), 2.66 (dd, *J* = 10.2, 15.6 Hz, 1 H); ¹³C NMR (CDCl₃, 50 MHz): δ 206.2, 159.2, 135.9, 134.6, 130.9, 128.6 (2 C), 128.2 (3 C), 126.6 (2 C), 123.8, 114.6 (2 C), 90.8, 55.3, 45.0, 43.2, 41.7, 41.3; IR (film): ν 1715, 1550, 1514, 1368, 1252, 1180, 1032,

964, 748, 695 cm^{-1} ; Anal. calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_4$: C, 71.78; H, 6.02; N, 3.99; Found: C, 71.61; H, 5.71; N, 3.88.



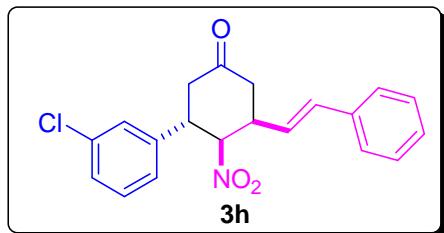
(3*S*,4*R*,5*S*)-3-(4-Nitrophenyl)-4-nitro-5-styrylcyclohexanone 3f

Following the general procedure B, the product was obtained in 65% yield (48 mg) as a yellow solid. mp: 172-174 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (80:20)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 53.09$ min, $\tau_{\text{minor}} = 68.35$ min, >95% ee; $[\alpha]_D^{25} = -158.0$ (*c* 0.92, CHCl_3 , ee >95%); ^1H NMR (CDCl_3 , 600 MHz): δ 8.22 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 9.0 Hz, 2 H), 7.35-7.26 (m, 5 H), 6.50 (d, *J* = 16.2 Hz, 1 H), 6.07 (dd, *J* = 7.8, 15.6 Hz, 1 H), 5.36 (dd, *J* = 4.2, 10.2 Hz, 1 H), 4.06-4.01 (m, 1 H), 3.67-3.65 (m, 1 H), 2.96-2.89 (m, 2 H), 2.80 (dd, *J* = 4.8, 15.6 Hz, 1 H), 2.65 (dd, *J* = 12.0, 15.6 Hz, 1 H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 204.2, 147.5, 146.0, 135.5, 128.6 (3 C), 128.5, 128.1 (2 C), 126.6 (2 C), 124.4 (2 C), 122.4, 89.7, 45.1, 43.4, 42.0, 41.7; IR (film): ν 1719, 1596, 1550, 1520, 1347, 1252, 1016, 855, 748, 695 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_5$: C, 65.57; H, 4.95; N, 7.65; Found: C, 65.55; H, 5.11; N, 7.74.



(3*S*,4*R*,5*S*)-3-(4-Trifluoromethylphenyl)-4-nitro-5-styrylcyclohexanone 3g

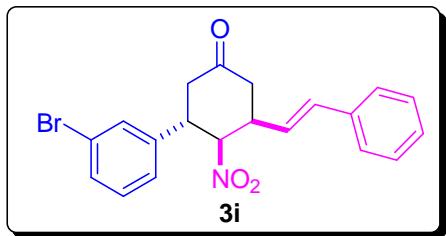
Following the general procedure B, the product was obtained in 70% yield (55 mg) as a colorless solid. mp: 162-164 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 14.50$ min, $\tau_{\text{minor}} = 18.66$ min, >94% ee; $[\alpha]_D^{25} = -194.0$ (*c* 1.07, CHCl₃, ee >99.99%) ¹H NMR (CDCl₃, 600 MHz): δ 7.62 (d, *J* = 7.2 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 7.35-7.27 (m, 5 H), 6.49 (d, *J* = 16.2 Hz, 1 H), 6.09 (dd, *J* = 7.8, 15.6 Hz, 1 H), 5.33 (dd, *J* = 4.2, 10.2 Hz, 1 H), 4.00-3.96 (m, 1 H), 3.62-3.59 (m, 1 H), 2.94-2.88 (m, 2 H), 2.82 (dd, *J* = 5.4, 15.6 Hz, 1 H), 2.67 (dd, *J* = 11.4, 15.6 Hz, 1 H); ¹³C NMR (CDCl₃, 125 MHz): δ 204.9, 142.9, 135.7, 135.3, 130.3 (q, *J*_{C-F} = 32.6 Hz), 128.7 (2 C), 128.5, 127.6 (2 C), 126.7 (3 C), 126.3 (q, *J*_{C-F} = 3.5 Hz), 122.9, 122.7 (q, *J*_{C-F} = 270 Hz), 90.0, 45.1, 43.4, 41.92, 41.85; IR (film): ν 1717, 1544, 1373, 1327, 1252, 1168, 1131, 1069, 1018, 969, 846, 758, 694 cm⁻¹; HRMS (ESI): *m/z* calcd. for C₂₁H₁₈F₃NNaO₃ [M + Na]⁺ 412.1131, found 412.1126.



(3*S*,4*R*,5*S*)-3-(3-Chlorophenyl)-4-nitro-5-styrylcyclohexanone 3h

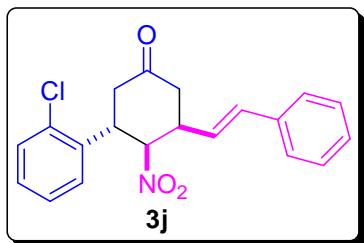
Following the general procedure B, the product was obtained in 65% yield (46 mg) as a white solid. mp: 170-172 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 14.54$ min, $\tau_{\text{minor}} = 16.74$ min, 87% ee; $[\alpha]_D^{25} = -218$ (*c* 1.07, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 600 MHz): δ 7.36-7.31 (m, 4 H), 7.29-7.26 (m, 4 H), 7.16-7.15 (m, 1 H), 6.48 (d, *J* = 16.2 Hz, 1 H), 6.07 (dd, *J* = 8.4, 16.2 Hz, 1 H), 5.28 (dd, *J* = 4.5, 9.9 Hz, 1 H), 3.92-3.87 (m, 1 H), 3.59-3.57 (m, 1 H), 2.92-2.86 (m, 2 H), 2.82 (dd, *J* = 5.4, 15.6 Hz, 1 H), 2.65 (dd, *J* = 11.4, 15.6 Hz, 1 H); ¹³C NMR

(CDCl₃, 150 MHz): δ 205.2, 140.9, 135.7, 135.1, 135.0, 130.5, 128.7 (2 C), 128.4, 128.3, 127.3, 126.7 (2 C), 125.3, 123.1, 90.1, 45.2, 43.3, 41.8 (2 C); IR (film): ν 1718, 1574, 1544, 1373, 1207, 1081, 969, 789, 749, 692 cm⁻¹; HRMS (ESI): *m/z* calcd. for C₂₀H₁₈ClNNaO₃ [M + Na]⁺ 378.0867, found. 378.0886.



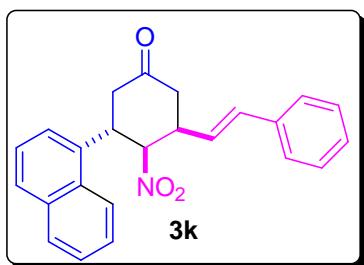
(3*S*,4*R*,5*S*)-3-(3-Bromophenyl)-4-nitro-5-styrylcyclohexanone 3i

Following the general procedure B, the product was obtained in 75% yield (60 mg) as a white solid. mp: 177-179 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 15.34$ min, $\tau_{\text{minor}} = 17.27$ min, 93% ee; $[\alpha]_D^{25} = -183$ (*c* 1.09, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 600 MHz): δ 7.42-7.23 (m, 7 H), 7.22-7.18 (m, 2 H), 6.47 (d, *J* = 15.6 Hz, 1 H), 6.07 (dd, *J* = 7.8, 15.6 Hz, 1 H), 5.27 (dd, *J* = 4.2, 9.9 Hz, 1 H), 3.90-3.85 (m, 1 H), 3.59-3.56 (m, 1 H), 2.91-2.84 (m, 2 H), 2.80 (dd, *J* = 5.4, 16.2 Hz, 1 H), 2.63 (dd, *J* = 11.4, 15.6 Hz, 1 H); ¹³C NMR (CDCl₃, 150 MHz): δ 205.1, 141.2, 135.8, 135.2, 131.3, 130.8, 130.3, 128.7 (2 C), 128.4, 126.7 (2 C), 125.8, 132.3, 123.1, 90.1, 45.2, 43.4, 41.8 (2 C); IR (film): ν 1717, 1543, 1371, 1208, 1070, 968, 785, 771, 696 cm⁻¹; Anal. calcd for C₂₀H₁₈BrNO₃: C, 60.01; H, 4.53; N, 3.50; Found: C, 60.32; H, 4.26; N, 3.36.



(3*S*,4*R*,5*S*)-3-(2-Chlorophenyl)-4-nitro-5-styrylcyclohexanone 3j

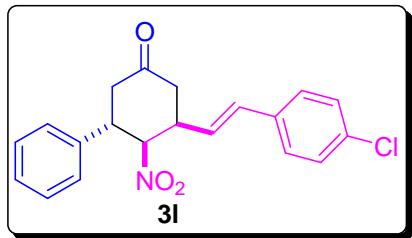
Following the general procedure B, the product was obtained in 70% yield (50 mg) as a white solid. mp: 156-158 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 12.54$ min, $\tau_{\text{minor}} = 16.37$ min, >94% ee; $[\alpha]_D^{27} = -92.0$ (*c* 1.00, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 600 MHz): δ 7.44-7.42 (m, 1 H), 7.32-7.26 (m, 8 H), 6.46 (d, *J* = 15.6 Hz, 1 H), 6.09 (dd, *J* = 7.5, 15.9 Hz, 1 H), 5.41 (m, 1 H), 4.46-4.427 (m, 1 H), 3.47-3.43 (m, 1 H), 3.02-2.94 (m, 2 H), 2.82 (dd, *J* = 5.4, 15.6 Hz, 1 H), 2.69 (dd, *J* = 9.0, 15.0 Hz, 1 H); ¹³C NMR (CDCl₃, 150 MHz): δ 206.2, 136.5, 135.9, 134.6 (2 C), 133.8, 130.7, 129.3, 128.6 (2 C), 128.3, 127.8, 126.6 (2 C), 123.7, 88.0, 42.9, 42.7, 40.9, 39.5; IR (film): ν 1718, 1574, 1544, 1438, 1372, 1207, 1082, 969, 789, 749, 692 cm⁻¹; HRMS (ESI): *m/z* calcd. for C₂₀H₁₈ClNNaO₃ [M + Na]⁺ 378.0867, found. 378.0890.



(3*S*,4*R*,5*S*)-3-(Naphthalene-1-yl)-4-nitro-5-styrylcyclohexanone 3k

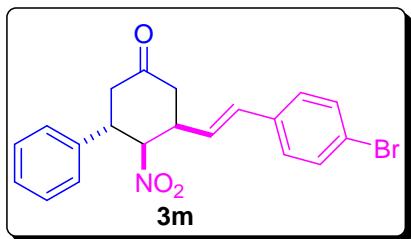
Following the general procedure B, the product was obtained in 65% yield (48 mg) as a white solid. mp: 150-152 °C; The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 13.17$ min, $\tau_{\text{minor}} =$

14.47 min, >89% ee; $[\alpha]_D^{27} = -46.0$ (*c* 0.75, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 600 MHz): δ 8.15 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 7.8 Hz, 1 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 7.66-7.63 (m, 1 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 1 H), 7.36-7.34 (m, 1 H), 7.30-7.27 (m, 4 H), 7.26-7.23 (m, 1 H), 6.40 (d, *J* = 16.2 Hz, 1 H), 6.11 (dd, *J* = 7.2, 15.6 Hz, 1 H), 5.40 (t, *J* = 7.5 Hz, 1 H), 4.86 (q, *J* = 6.0 Hz, 1 H), 3.34-3.30 (m, 1 H), 3.16-3.12 (m, 2 H), 2.84-2.81 (m, 2 H); ¹³C NMR (CDCl₃, 150 MHz): δ 207.1, 135.8, 135.3, 134.1 (2 C), 130.5, 129.4, 129.9, 128.5 (2 C), 128.2, 127.3, 126.5 (2 C), 126.2, 125.3, 124.4, 123.9, 122.1, 88.6, 43.1, 42.2, 40.0, 38.6; IR (film): ν 1714, 1549, 1367, 1210, 1019, 969, 776, 751, 694 cm⁻¹; HRMS (ESI): *m/z* calcd. for C₂₄H₂₁NNaO₃ [M + Na]⁺ 394.1414, found. 394.1414.



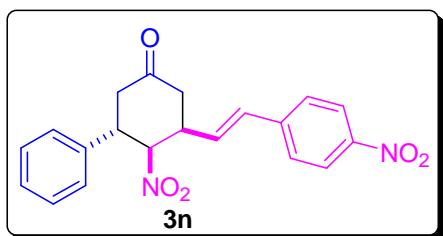
(3*S*,4*R*,5*S*)-3-(4-Chlorostyryl)-4-nitro-5-phenylcyclohexanone 3l

Following the general procedure B, the product was obtained in 70% yield (50 mg) as a colorless solid. mp: 180-182 °C; The *ee* was determined by HPLC using a Daicel Chiralcel OD-H [hexane/i-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{minor}} = 33.95$ min, $\tau_{\text{major}} = 52.47$ min, 94% ee; $[\alpha]_D^{26} = -247.0$ (*c* 0.88, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 500 MHz): δ 7.38-7.35 (m, 2 H), 7.31-7.26 (m, 7 H), 6.42 (d, *J* = 16.2 Hz, 1 H), 6.09 (dd, *J* = 7.7, 15.7 Hz, 1 H), 5.30 (dd, *J* = 4.5, 9.0 Hz, 1 H), 3.95-3.90 (m, 1 H), 3.54-3.50 (m, 1 H), 2.93-2.84 (m, 3 H), 2.71 (dd, *J* = 10.7, 15.2 Hz, 1 H); ¹³C NMR (CDCl₃, 125 MHz): δ 205.8, 138.9, 134.3, 134.1, 133.5, 129.3, 128.8 (2 C), 128.1, 127.9 (2 C), 127.1 (3 C), 124.3, 90.4, 44.9, 43.2, 42.3, 41.5; IR (film): ν 1719, 1547, 1492, 1371, 1303, 1209, 1090, 1011, 970, 816, 773, 699 cm⁻¹; Anal. calcd for C₂₀H₁₈CINO₃: C, 67.51; H, 5.10; N, 3.94; Found: C, 67.62; H, 4.74; N, 3.73.



(3*S*,4*R*,5*S*)-3-(4-Bromostyryl)-4-nitro-5-phenylcyclohexanone 3m

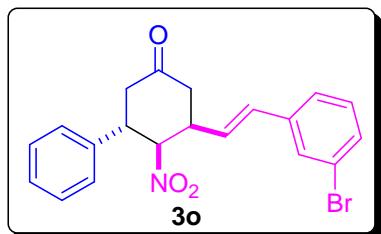
Following the general procedure B, the product was obtained in 62% yield (50 mg) as a colorless solid. mp: 197-198 °C; The *ee* was determined by HPLC using a Chiralcel OD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{minor}} = 34.48$ min, $\tau_{\text{major}} = 52.01$ min, 90% ee; $[\alpha]_D^{26} = -211.0$ (*c* 0.86, CHCl₃, ee >97%); ¹H NMR (CDCl₃, 500 MHz): δ 7.44 (d, *J* = 8.0 Hz, 2 H), 7.38-7.35 (m, 2 H), 7.32-7.27 (m, 3 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 6.40 (d, *J* = 16.5 Hz, 1 H), 6.10 (dd, *J* = 7.75, 16.2 Hz, 1 H), 5.30 (dd, *J* = 4.5, 9.0 Hz, 1 H), 3.95-3.90 (m, 1 H), 3.54-3.50 (m, 1 H), 2.93-2.84 (m, 3 H), 2.71 (dd, *J* = 10.5, 15.2 Hz, 1 H); ¹³C NMR (CDCl₃, 125 MHz): δ 205.8, 138.9, 134.8, 133.8, 131.8, 129.3 (3 C), 128.2 (2 C), 128.1, 127.1 (2 C), 124.5, 122.2, 90.3, 44.9, 43.2, 42.3, 41.5; IR (film): ν 1720, 1546, 1487, 1370, 1303, 1210, 1070, 1008, 973, 699 cm⁻¹; Anal. calcd for C₂₀H₁₈BrNO₃: C, 60.01; H, 4.53; N, 3.50; Found: C, 60.34; H, 4.19; N, 3.18.



(3*S*,4*R*,5*S*)-3-(4-nitrostyryl)-4-nitro-5-phenylcyclohexanone 3n

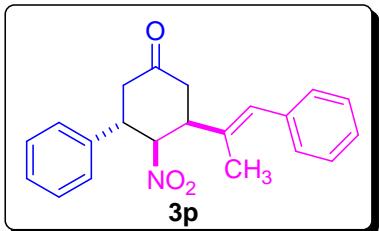
Following the general procedure B, the product was obtained in 60% yield (44 mg) as a white solid. mp: 146-148 °C; The *ee* was determined by HPLC using a Daicel Chiralcel OD-H [hexane/*i*-PrOH (80:20)]; flow rate 0.75 mL/min; $\tau_{\text{minor}} = 75.35$ min, $\tau_{\text{major}} = 99.22$ min, >94%

ee; $[\alpha]_D^{25} = -200.0$ (c 0.70, CHCl_3 , ee >94%); ^1H NMR (CDCl_3 , 500 MHz): δ 8.19 (d, $J = 9.0$ Hz, 2 H), 7.49 (d, $J = 9.0$ Hz, 2 H), 7.39-7.36 (m, 2 H), 7.33-7.27 (m, 3 H), 6.54 (d, $J = 16.5$ Hz, 1 H), 6.31 (dd, $J = 8.0, 16.5$ Hz, 1 H), 5.31 (dd, $J = 4.0, 8.8$ Hz, 1 H), 3.97-3.92 (m, 1 H), 3.60-3.55 (m, 1 H), 2.94-2.87 (m, 3 H), 2.75 (dd, $J = 10.5, 15.5$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 205.4, 147.5, 142.1, 138.7, 132.7, 129.3 (2 C), 128.7, 128.2, 127.3 (2 C), 127.1 (3 C), 124.1, 90.2, 44.8, 42.9, 42.5, 41.4; IR (film): ν 1719, 1597, 1550, 1516, 1343, 1218, 1109, 864, 826, 745, 700, 637 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_5$: C, 65.57; H, 4.95; N, 7.65; Found: C, 65.77; H, 4.93; N, 7.29.



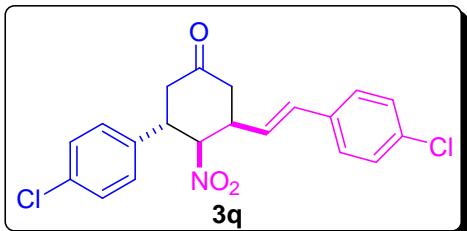
(3S,4R,5S)-3-(3-Bromostyryl)-4-nitro-5-phenylcyclohexanone 3o

Following the general procedure B, the product was obtained in 64% yield (51 mg) as a white solid. mp: 205-206 °C; The *ee* was determined by HPLC using a Daicel Chiralcel OD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{minor}} = 39.80$ min, $\tau_{\text{major}} = 61.56$ min, >95% ee; $[\alpha]_D^{26} = -212.0$ (c 0.83, CHCl_3 , ee >99.99%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.50 (br s, 1 H), 7.40-7.35 (m, 3 H), 7.31-7.24 (m, 4 H), 7.20-7.15 (m, 1 H), 6.40 (d, $J = 15.5$ Hz, 1 H), 6.12 (dd, $J = 8.0, 15.5$ Hz, 1 H), 5.30 (dd, $J = 4.2, 9.3$ Hz, 1 H), 3.96-3.91 (m, 1 H), 3.54-3.52 (m, 1 H), 2.93-2.85 (m, 3 H), 2.71 (dd, $J = 10.5, 16.0$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 205.7, 138.8, 137.9, 133.4, 131.7, 130.1, 129.4, 129.3 (2 C), 128.1, 127.1 (2 C), 125.4, 125.3, 122.8, 90.4, 44.9, 43.1, 42.3, 41.5; IR (film): ν 1720, 1546, 1487, 1370, 1303, 1210, 1070, 1008, 973, 699 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{18}\text{BrNO}_3$: C, 60.01; H, 4.53; N, 3.50; Found: C, 60.30; H, 4.29; N, 3.38.



(3S,4R,5S)-4-Nitro-3-phenyl-5-[(E)-1-phenylprop-1-en-2yl]-cyclohexanone 3p

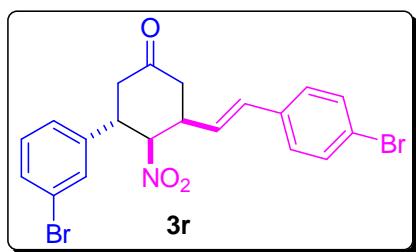
Following the general procedure B, the product was obtained in 74% yield (50 mg) as a gummy liquid (47 mg, 74%). The *ee* was determined by HPLC using a Daicel Chiralcel OD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.00 mL/min; $\tau_{\text{minor}} = 26.81$ min, $\tau_{\text{major}} = 30.51$ min, 96% ee; $[\alpha]_D^{25} = -17.0$ (*c* 1.11, CHCl₃, mixture of diastereoisomers); ¹H NMR (CDCl₃, 500 MHz): δ 7.36-7.33 (m, 5 H), 7.26-7.24 (m, 3 H), 7.14-7.13 (m, 2 H), 6.43 (br s, 1 H), 5.26 (dd, *J* = 4.5, 7.5 Hz, 1 H), 3.87-3.83 (m, 1 H), 3.45-3.41 (m, 1 H), 3.30 (dd, *J* = 9.0, 16.0 Hz, 1 H), 2.94-2.90 (m, 1 H), 2.82-2.73 (m, 2 H), 1.95 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz): δ 207.6, 136.8, 136.6, 135.1, 129.3, 129.0 (2 C), 128.9 (2 C), 128.4, 128.2 (2 C), 127.6 (2 C), 127.1, 88.9, 45.8, 42.3, 41.9, 41.5, 16.5; HRMS (ESI): *m/z* calcd. for C₂₁H₂₁NNaO₃ [M + Na]⁺ 358.1414, found. 358.1391.



(3S,4R,5S)-3-(4-Chlorostyryl)-5-(4-chlorophenyl)-4-nitrocyclohexanone 3q

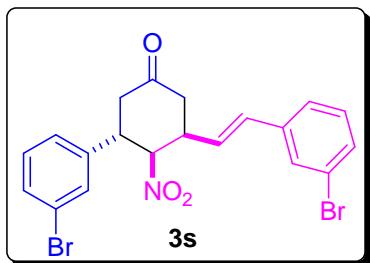
Following the general procedure B, the product was obtained in 65% yield (51 mg) as a white solid. mp: 183-185 °C; The *ee* was determined by HPLC using a Daicel Chiralcel OD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{minor}} = 37.16$ min, $\tau_{\text{major}} = 60.82$ min, 94% ee; $[\alpha]_D^{27} = -254.0$ (*c* 0.87, CHCl₃, ee >98%); ¹H NMR (CDCl₃, 500 MHz): δ 7.35-7.33 (m, 2 H), 7.30-7.25 (m, 4 H), 7.22-7.20 (m, 2 H), 6.42 (d, *J* = 15.5 Hz, 1 H), 6.07 (dd, *J* = 8.0, 15.5 Hz, 1

H), 5.29 (dd, $J = 4.25, 9.75$ Hz, 1 H), 3.92-3.87 (m, 1 H), 3.55-3.53 (m, 1 H), 2.88 (br s, 2 H), 2.82 (dd, $J = 5.0, 16.0$ Hz, 1 H), 2.65 (dd, $J = 11.5, 15.5$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 205.2, 137.3, 134.2, 134.1, 134.0, 133.8, 129.5 (2 C), 128.8 (2 C), 128.5 (2 C), 127.8 (2 C), 123.9, 90.2, 45.0, 43.2, 41.7, 41.6; IR (film): ν 1717, 1592, 1545, 1491, 1407, 1372, 1213, 1093, 1013, 970, 835, 814, 757 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{NO}_3$: C, 61.55; H, 4.39; N, 3.59; Found: C, 61.45; H, 4.38; N, 3.52.



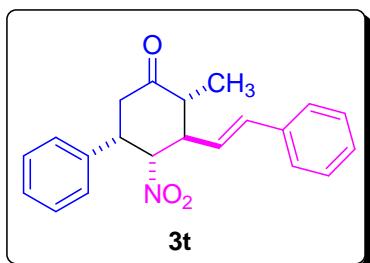
(3*S*,4*R*,5*S*)-3-(4-Bromostyryl)-5-(3-bromophenyl)-4-nitrocyclohexanone **3r**

Following the general procedure B, the product was obtained in 70% yield (67 mg) as a white solid. mp: 210-212 °C; The *ee* was determined by HPLC using a Daicel Chiralcel OD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{minor}} = 47.62$ min, $\tau_{\text{major}} = 68.53$ min, 92% ee; $[\alpha]_D^{27} = -211.0$ (*c* 0.97, CHCl_3 , ee >99.99%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.45-7.43 (m, 4 H), 7.25-7.20 (m, 4 H), 6.42 (d, $J = 16.0$ Hz, 1 H), 6.07 (dd, $J = 8.0, 16.0$ Hz, 1 H), 5.29 (dd, $J = 4.5, 10.0$ Hz, 1 H), 3.90-3.85 (m, 1 H), 3.57-3.55 (m, 1 H), 2.88 (d, $J = 5.0$ Hz, 2 H), 2.81 (dd, $J = 5.2, 15.8$ Hz, 1 H), 2.65 (dd, $J = 11.5, 15.5$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 205.0, 141.1, 134.7, 133.9, 131.8 (2 C), 131.4, 130.8, 130.2, 128.2 (2 C), 125.8, 123.9, 123.3, 122.3, 90.0, 45.1, 43.2, 41.8, 41.8; IR (film): ν 1717, 1592, 1548, 1497, 1373, 1207, 1071, 1009, 968, 784, 691 cm^{-1} ; Anal. calcd for $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{NO}_3$: C, 50.13; H, 3.58; N, 2.92; Found: C, 50.43; H, 3.40; N, 2.91.



(3*S*,4*R*,5*S*)-3-(3-Bromostyryl)-5-(3-bromophenyl)-4-nitrocyclohexanone 3s

Following the general procedure B, the product was obtained in 58% yield (56 mg) as a colorless solid. mp: 184-186 °C; The *ee* was determined by HPLC using a Daicel Chiralcel OD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{minor}} = 46.24$ min, $\tau_{\text{major}} = 70.03$ min, >96% ee; $[\alpha]_D^{25} = -187.0$ (*c* 0.87, CHCl₃, ee >99.99%); ¹H NMR (CDCl₃, 500 MHz): δ 7.50 (s, 1 H), 7.44-7.40 (m, 3 H), 7.27-7.17 (m, 4 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 6.10 (dd, *J* = 7.75, 15.8 Hz, 1 H), 5.29 (dd, *J* = 4.5, 9.5 Hz, 1 H), 3.91-3.86 (m, 1 H), 3.60-3.56 (m, 1 H), 2.88 (d, *J* = 5.0 Hz, 2 H), 2.83 (dd, *J* = 5.5, 15.5 Hz, 1 H), 2.65 (dd, *J* = 11.5, 15.5 Hz, 1 H); ¹³C NMR (CDCl₃, 125 MHz): δ 204.9, 141.1, 137.8, 133.8, 131.4, 131.2, 130.8, 130.2, 130.15, 129.4, 125.8, 125.4, 124.7, 123.3, 122.8, 90.0, 45.2, 43.3, 41.8 (2 C); IR (film): ν 1718, 1592, 1547, 1476, 1372, 1208, 1072, 1013, 970, 758, 692 cm⁻¹; Anal. calcd for C₂₀H₁₇Br₂NO₃: C, 50.13; H, 3.58; N, 2.92; Found: C, 50.26; H, 3.30; N, 2.79.

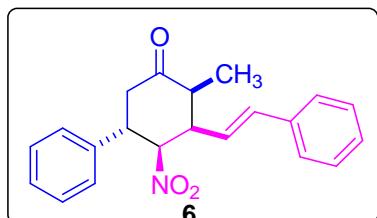


(2*R*,3*R*,4*S*,5*S*)-2-Methyl-4-nitro-5-phenyl-3-styrylcyclohexanone 3t

The reactions were carried out in double distilled water and no special precautions were taken to exclude air from the reaction flask. Benzoic acid (7.5 mg, 0.06 mmol, 30 mol %) was added to a

heterogeneous mixture of the catalyst **I** (13 mg, 0.04 mmol, 20 mol %) and water (0.5 mL). The resulting heterogeneous mixture was stirred at 40 °C for 10 min in a pre-heated oil bath. After that the mixture was brought to room temperature and enone (*E*)-1-phenylpent-1-en-3-one (64 mg, 0.4 mmol, 2 equiv) was added, followed by the addition of nitrodiene **2a** (35 mg, 0.2 mmol, 1 equiv). The heterogeneous mixture was stirred at 28 °C for 3 d. The reaction mixture was extracted with dichloromethane (3 × 10 mL) and the combined extract was washed with brine, dried (MgSO_4) and evaporated. The residue was purified by column chromatography on silica using hexane/EtOAc as eluent to give a mixture of diastereoisomeric products (34 mg, 51%). Careful chromatographic separation provided pure **3t**. The diastereoisomer **6** was contaminated with about 12% of the unidentified diastereoisomer.

Data for 3t: Yellow gum. The *ee* was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 21.01$ min, >99.9% ee; $[\alpha]_D^{26} = -63.0$ (*c* 0.59, CHCl_3 , ee >99.9%); ^1H NMR (CDCl_3 , 800 MHz): δ 7.36-7.35 (m, 3H), 7.33-7.28 (m, 4H), 7.27-7.25 (m, 1H), 7.05 (t, $J = 4.0$ Hz, 1 H), 6.50 (d, $J = 16.0$ Hz, 2 H), 5.96 (dd, $J = 8.8, 15.2$ Hz, 1 H), 5.22 (dd, $J = 5.6, 10.4$ Hz, 1 H), 4.03 (q, $J = 5.6$ Hz, 1 H), 3.11-3.07 (m, 2 H), 2.96 (dd, $J = 6.4, 16.0$ Hz, 1 H), 2.54 (sex, 1 H), 1.26 (d, $J = 6.4$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 208.0, 136.8, 136.0, 135.3, 128.9 (2 C), 128.6 (2 C), 128.4, 128.1, 128.0 (2 C), 126.4 (2 C), 126.0, 91.1, 46.1, 46.0, 43.8, 42.5, 12.4; IR (film): ν 1714, 1551, 1495, 1453, 1368, 969, 746, 697 cm^{-1} ; HRMS (ESI): m/z calcd. for $\text{C}_{21}\text{H}_{21}\text{NNaO}_3$ [$\text{M} + \text{Na}$]⁺ 358.1413, found. 358.1371.

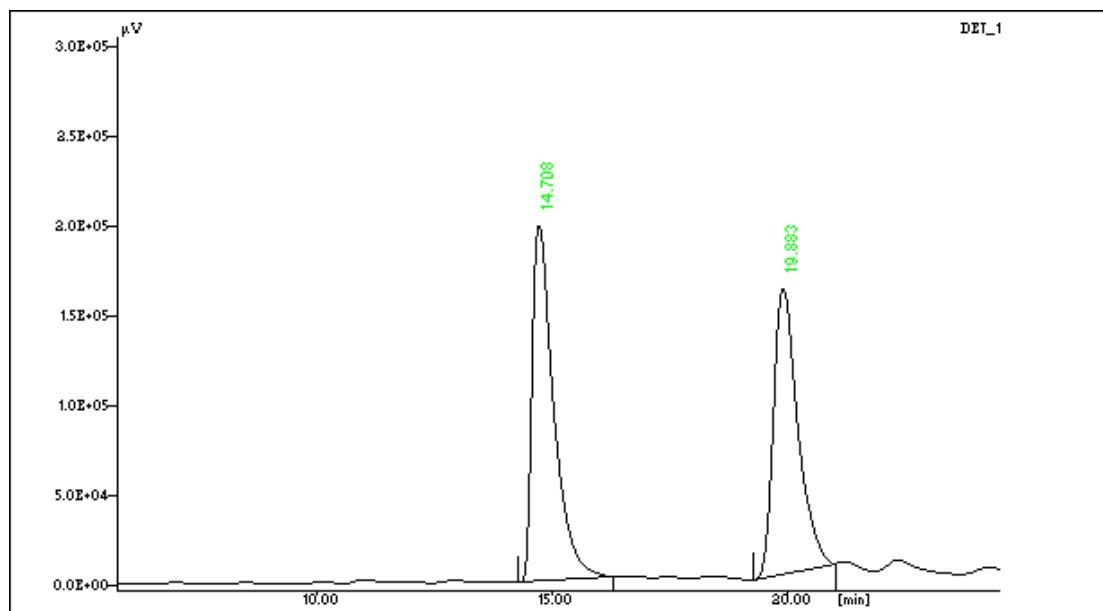
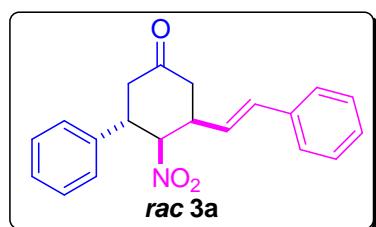


Data for 6: Thick yellow gum. The ee was determined by HPLC using a Daicel Chiralpak AD-H [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 12.86$ min, $\tau_{\text{minor}} = 14.65$ min, 97.6% ee; $[\alpha]_D^{25} = -265.8$ (*c* 0.26, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 7.36-7.26 (m, 10 H), 6.44 (d, *J* = 15.0 Hz, 1 H), 5.87 (dd, *J* = 11.0, 16.0 Hz, 1 H), 5.47 (dd, *J* = 4.5, 11.5 Hz, 1 H), 3.95-3.89 (m, 1 H), 3.57-3.53 (m, 1 H), 3.08-3.03 (m, 1 H), 2.78 (dd, *J* = 5.5, 15.0 Hz, 1 H), 2.70-2.65 (m, 1 H), 1.10 (d, *J* = 7.0 Hz, 1 H); ¹³C NMR (CDCl₃, 125 MHz): δ 206.8, 138.8, 137.5, 135.8, 129.1 (2 C), 128.6 (2 C), 128.3, 128.0, 127.0 (2 C), 126.8 (2 C), 120.1, 91.2, 51.5, 46.9, 46.6, 42.3, 12.4; IR (film): ν 1716, 1553, 1494, 1452, 1368, 968, 747, 697 cm⁻¹; HRMS (ESI): *m/z* calcd. for C₂₁H₂₁NNaO₃ [M + Na]⁺ 358.1413, found. 358.1369.

9. References

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- 2 Huang, H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2006**, 128, 7170.
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10. HPLC traces



File name : 1325.CH1

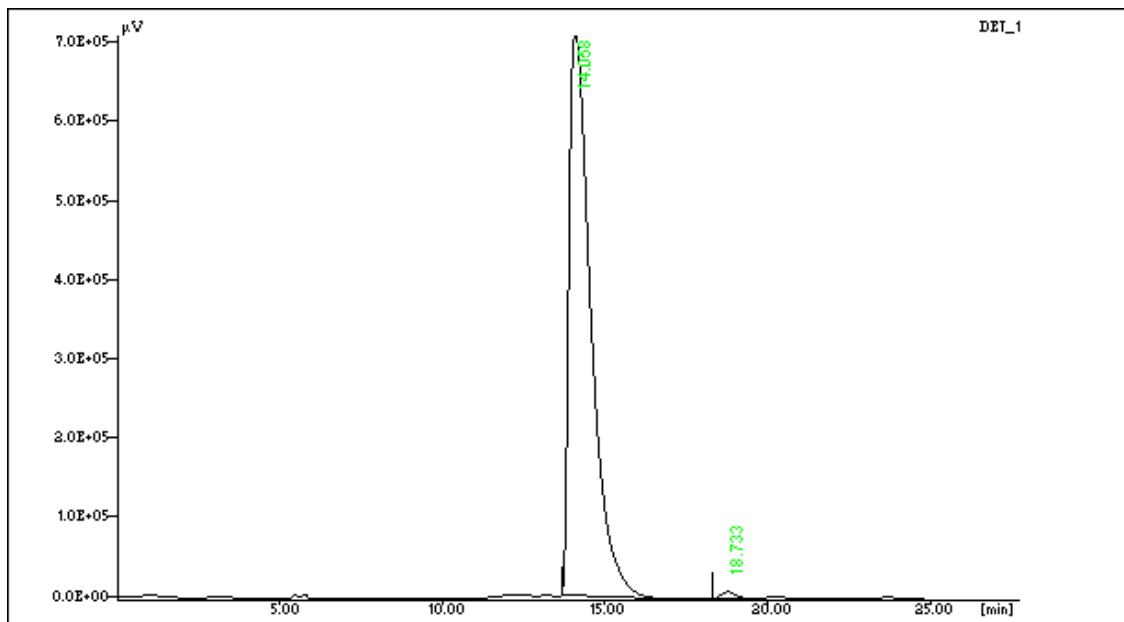
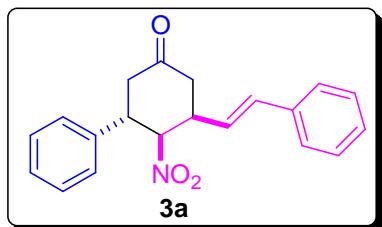
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Curr. Date : 17-Mar-2015 17:11:26

Control Method : RC

Name	RT	%Area	Area[$\mu\text{V}.\text{Sec}$]
1	14.70	52.268	5863230.204
2	19.88	47.732	5354353.471

Total Area of Peak = = 11217583.675 [$\mu\text{V}.\text{Sec}$]



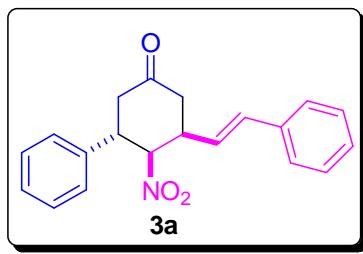
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Injection Date : 18-Mar-2015 15:20:16

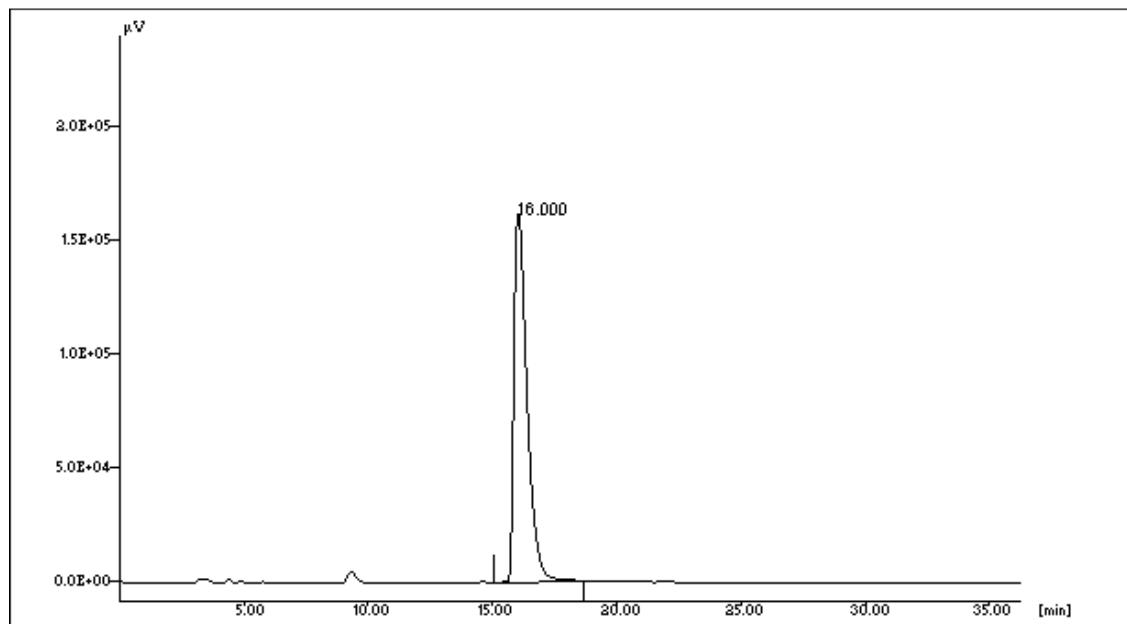
Curr. Date : 18-Mar-2015 18:25:12

Control Method : RC

Name	RT	% Area	Area [$\mu\text{V} \cdot \text{Sec}$]
1	14.05	99.222	30909469.500
2	18.73	0.778	242292.500



After single recrystallization



File name : 1248.CH1

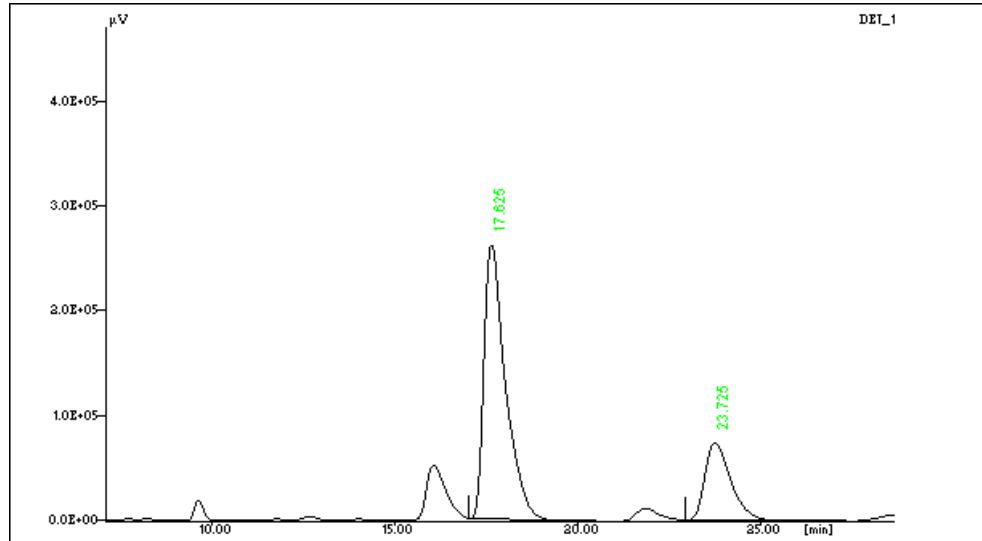
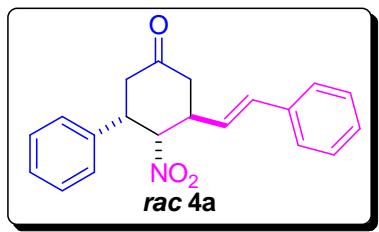
Injection Date : 13-Jan-2004 10:32:10

Curr. Date : 13-Jan-2004 11:58:10

Control Method : RC

Name	RT	%Area	Area[μV.Sec]
1	16.02	100.000	5260316.690

Total Area of Peak = 5260316.690 [μV.Sec]



File name : vgb-414-minor-rac204.CH1

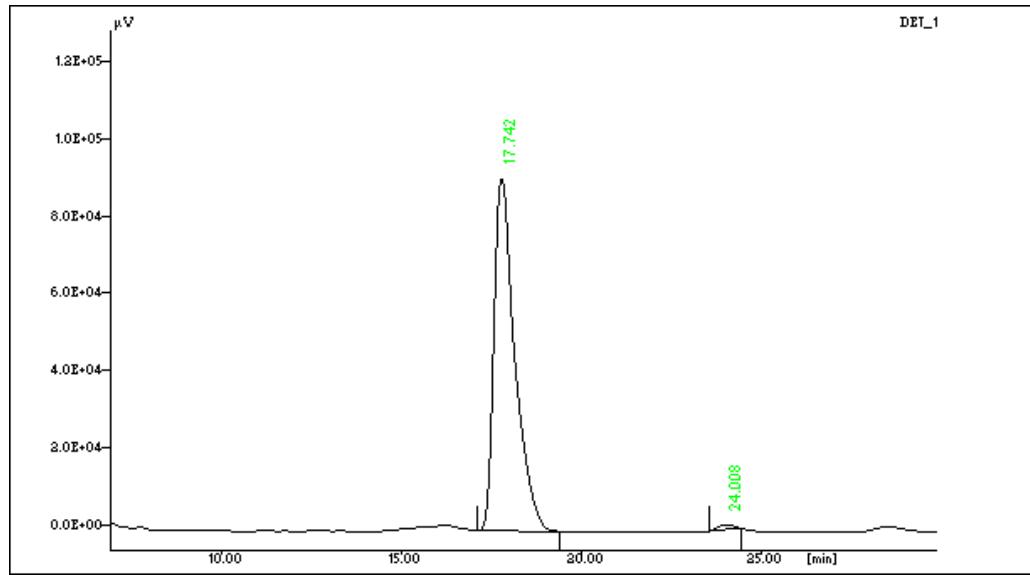
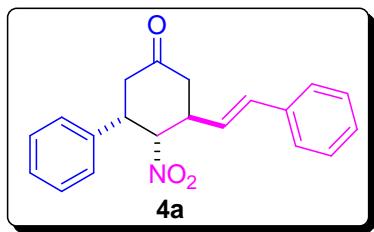
Injection Date : 6-Jan-2016 14:01:42

Curr. Date : 6-Jan-2016 16:16:16

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V}.\text{Sec}$]
1	17.62	74.891	10062386.687
2	23.72	25.109	3373592.648

Total Area of Peak = 13435979.334 [$\mu\text{V}.\text{Sec}$]



File name : VGB-415-MINOR 205.CH1

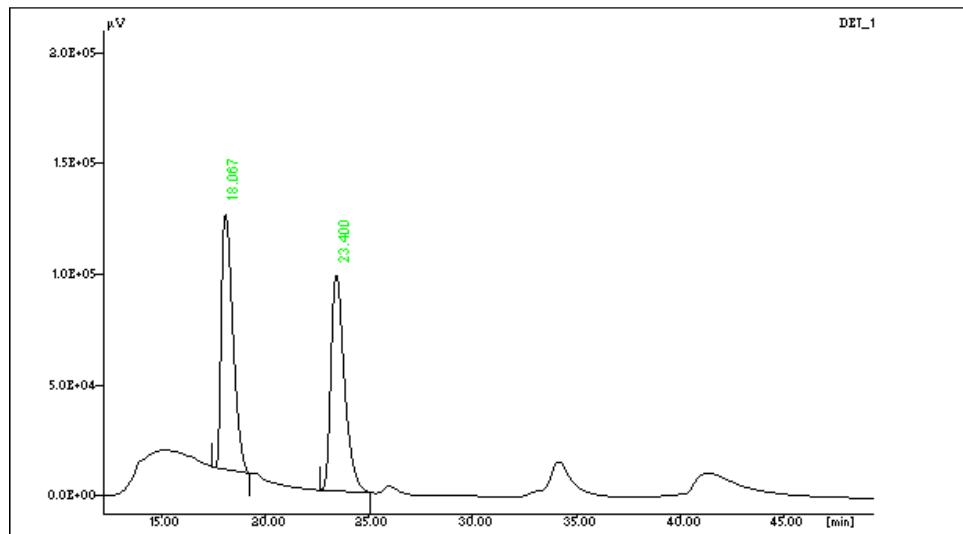
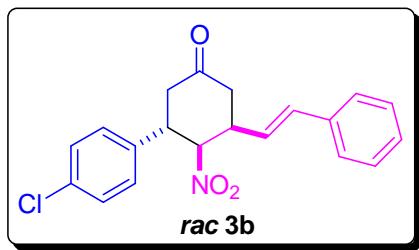
Injection Date : 6-Jan-2016 14:31:54

Curr. Date : 6-Jan-2016 16:20:10

Control Method :RC

Name	RT	%Area	Area[µV.Sec]
1	17.74	98.860	3420060.000
2	24.00	1.140	39436.500

Total Area of Peak = 3459496.500 [µV.Sec]



File name : VGB 269-Major-(4-chloro)-rac422.CH1

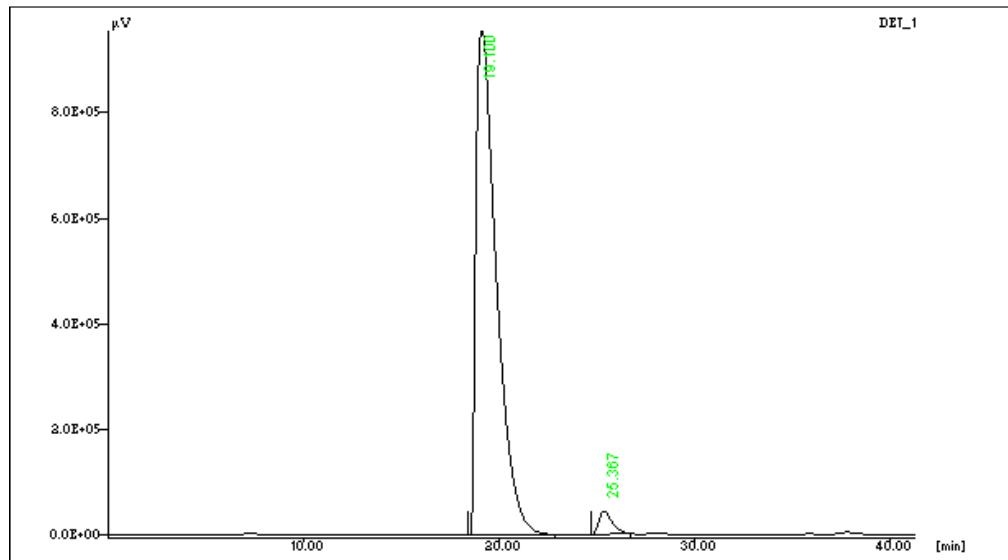
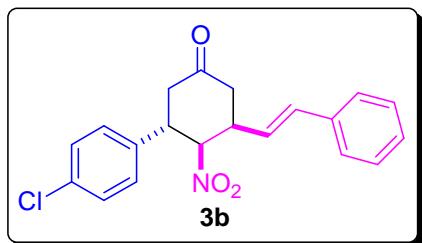
Injection Date : 5-Jun-2015 17:53:50

Curr. Date : 5-Jun-2015 18:47:06

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V.Sec}$]
1	18.06	49.452	3918398.33
2	23.40	50.548	4005310.50

Total Area of Peak = 7923708.83 [$\mu\text{V.Sec}$]



File name : vgb 291(4-chloro)-major hplc portion451.CH1

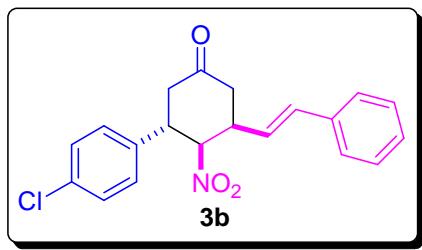
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Curr. Date : 5-Jun-2015 18:42:20

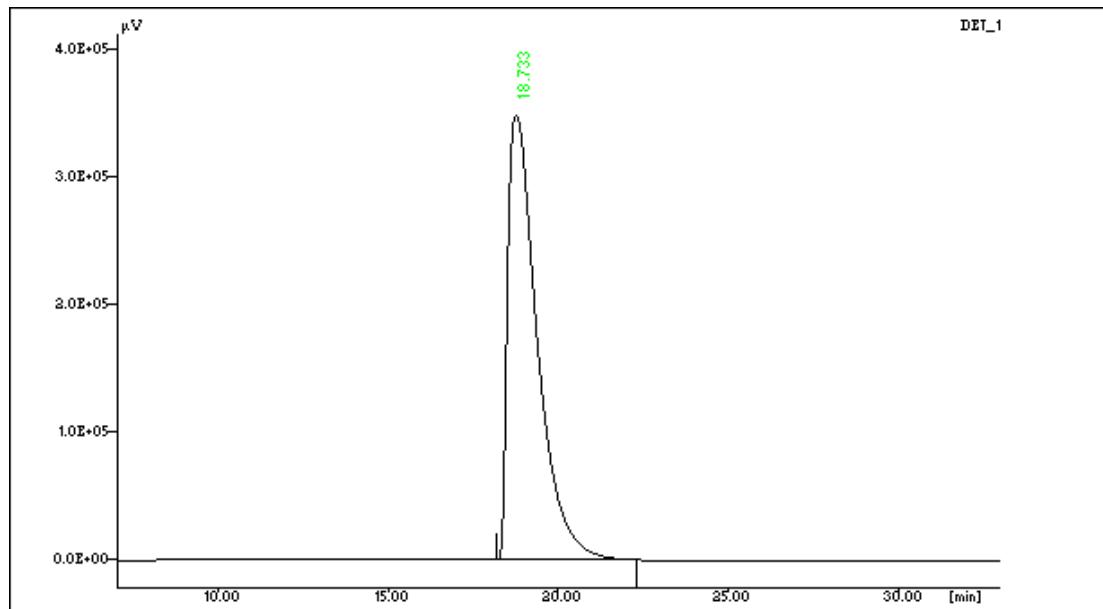
Control Method :RC

Name	RT	% Area	Area[μ V.Sec]
1	19.10	97.144	64859178.50
2	25.36	2.856	1907173.00

Total Area of Peak = 66766351.50 [μ V.Sec]



After single recrystallization



File name : vgb 291

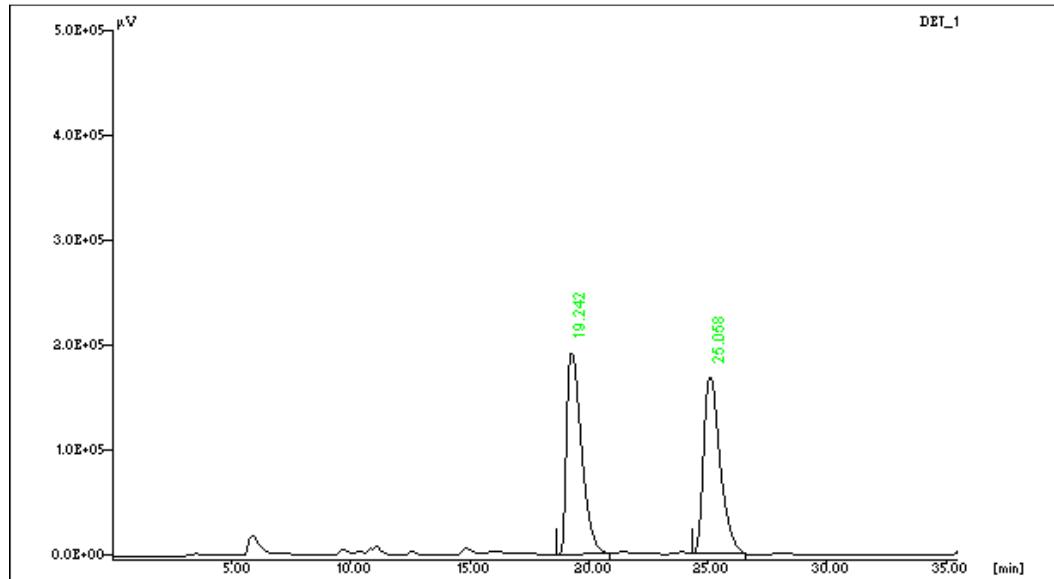
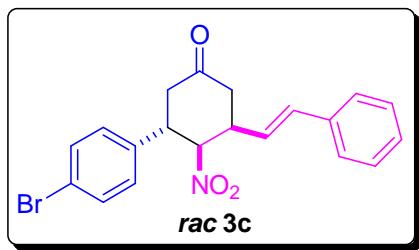
Injection Date : 10-Jun-2015 17:33:08

Curr. Date : 10-Jun-2015 19:01:58

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	18.71	100.000	19978552.75

Total Area of Peak = 19978552.75 [μV.Sec]



File name : VGB 268-Major-(4-bromo) -rac421.CH1

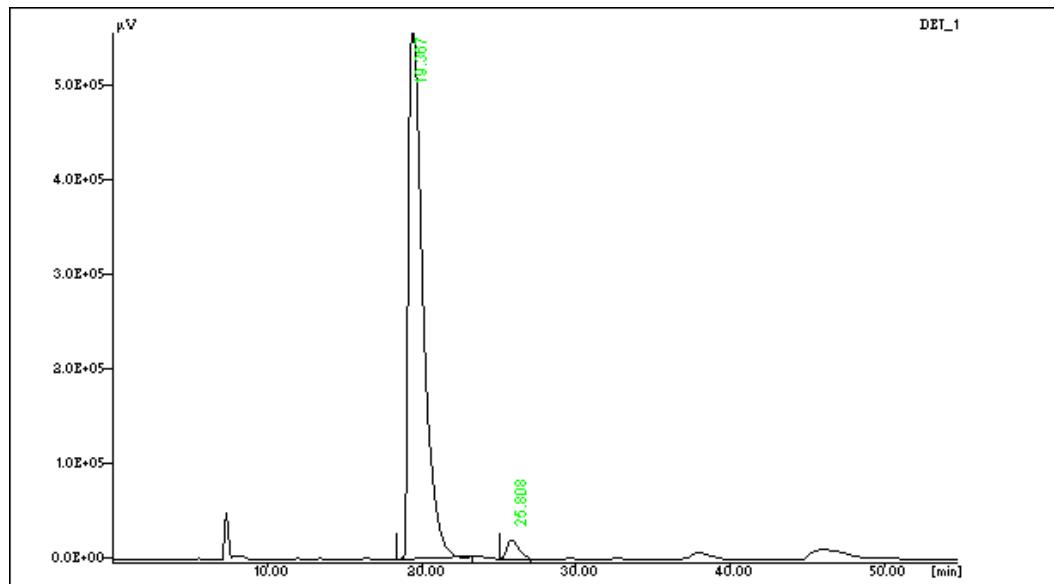
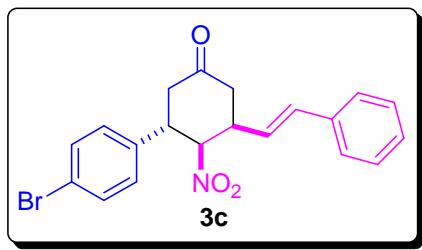
Injection Date :12-May-2015 17:10:44

Curr. Date : 10-Jun-2015 19:00:04

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V.Sec}$]
1	19.24	50.228	7517237.72
2	25.05	49.772	7448844.50

Total Area of Peak = 14966082.22 [$\mu\text{V.Sec}$]



File name : vgb 294

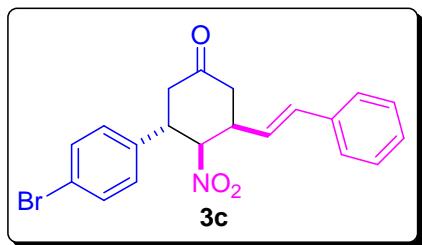
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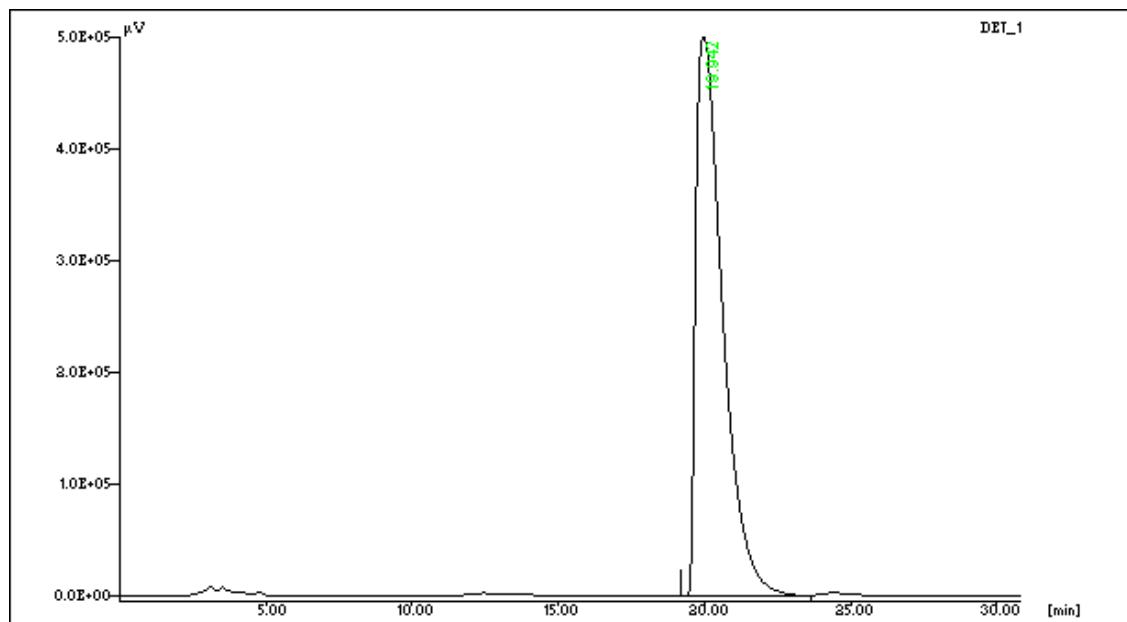
Control Method :RC

Name	RT	% Area	Area [$\mu\text{V}.\text{Sec}$]
1	19.36	97.226	32892553.55
2	25.80	2.774	938354.50

Total Area of Peak = 33830908.05 [$\mu\text{V}.\text{Sec}$]



After single recrystallization



File name : vgb 294

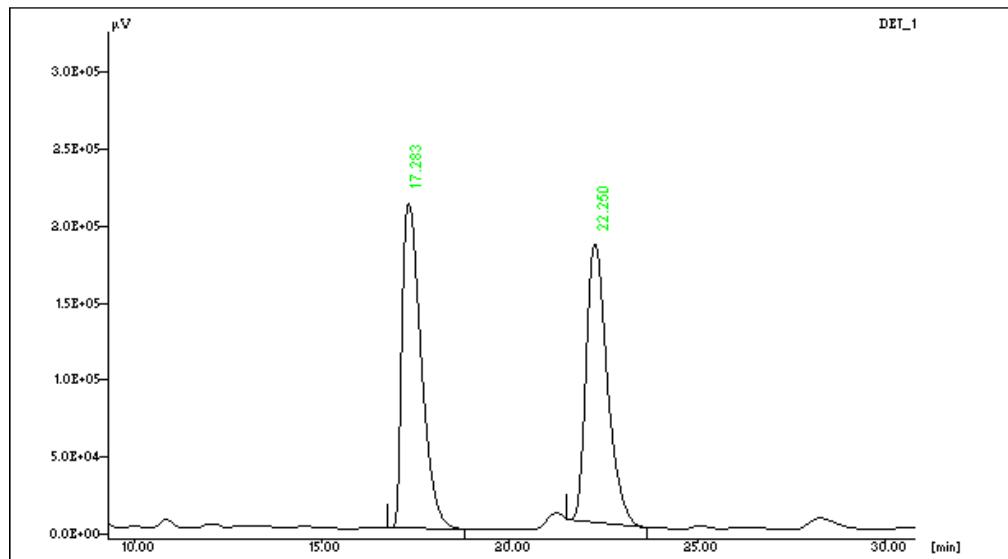
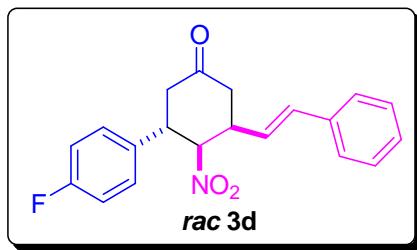
Injection Date :11-Jun-2015 14:05:12

Curr. Date : 11-Jun-2015 14:53:14

Control Method :RC

Name	RT	%Area	Area[µV.Sec]
1	19.90	100.000	30125239.44

Total Area of Peak = 30125239.44 [µV.Sec]



File name : vgb-304 (4-Fluoro)-rac023.CH1

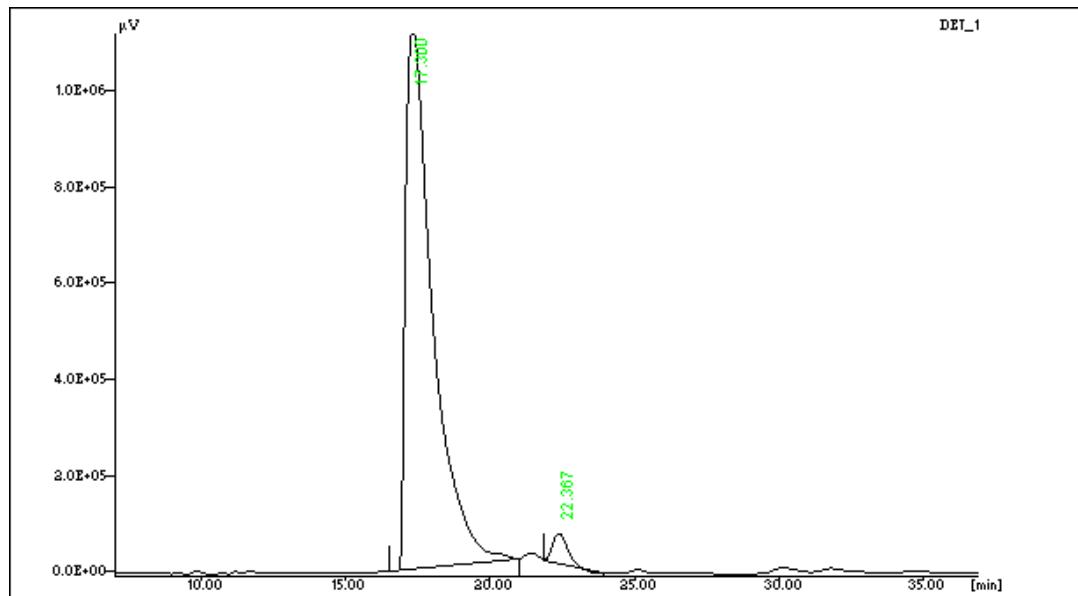
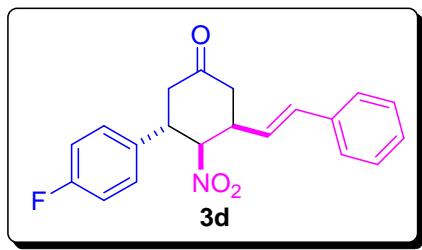
Injection Date :30-Jun-2015 12:24:46

Curr. Date : 30-Jun-2015 16:57:58

Control Method :RC

Name	RT	% Area	Area [$\mu\text{V}.\text{Sec}$]
1	17.28	51.202	6919653.07
2	22.25	48.798	6594804.27

Total Area of Peak = 13514457.34 [$\mu\text{V}.\text{Sec}$]



File name : vgb-301- (4-fluoro) hplc-022.CH1

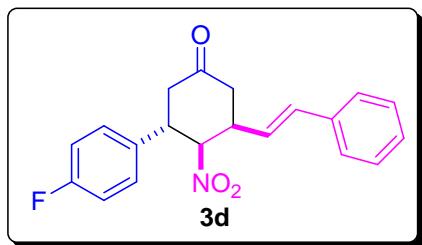
Injection Date :30-Jun-2015 11:17:42

Curr. Date : 30-Jun-2015 17:05:36

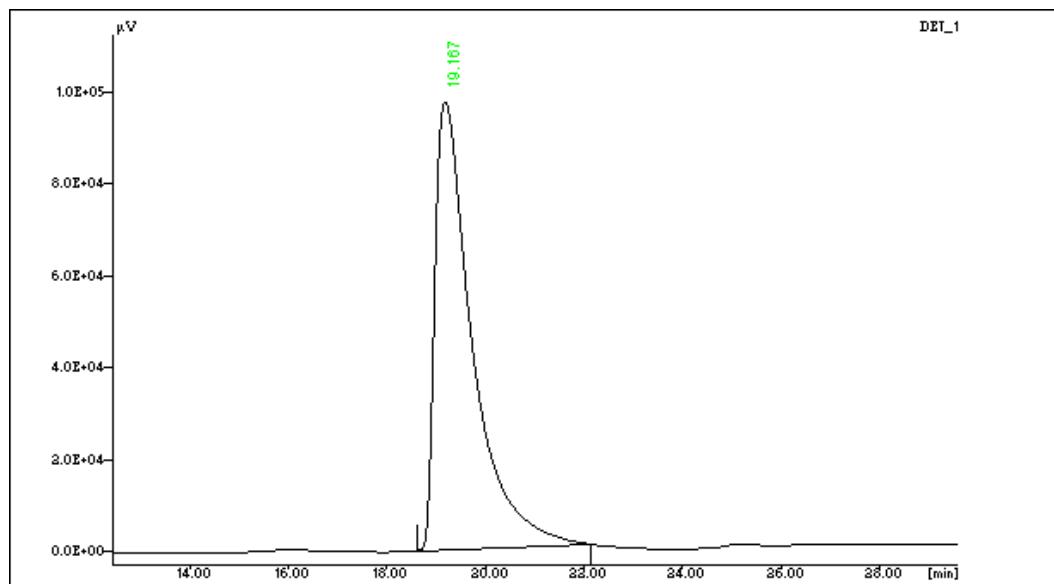
Control Method :RC

Name	RT	% Area	Area [$\mu\text{V.Sec}$]
1	17.30	97.232	69703445.62
2	22.36	2.768	1984534.91

Total Area of Peak = 71687980.53 [$\mu\text{V.Sec}$]



After single recrystallization



File name : RC-301 (4-fluoro)-crystal036.CH1

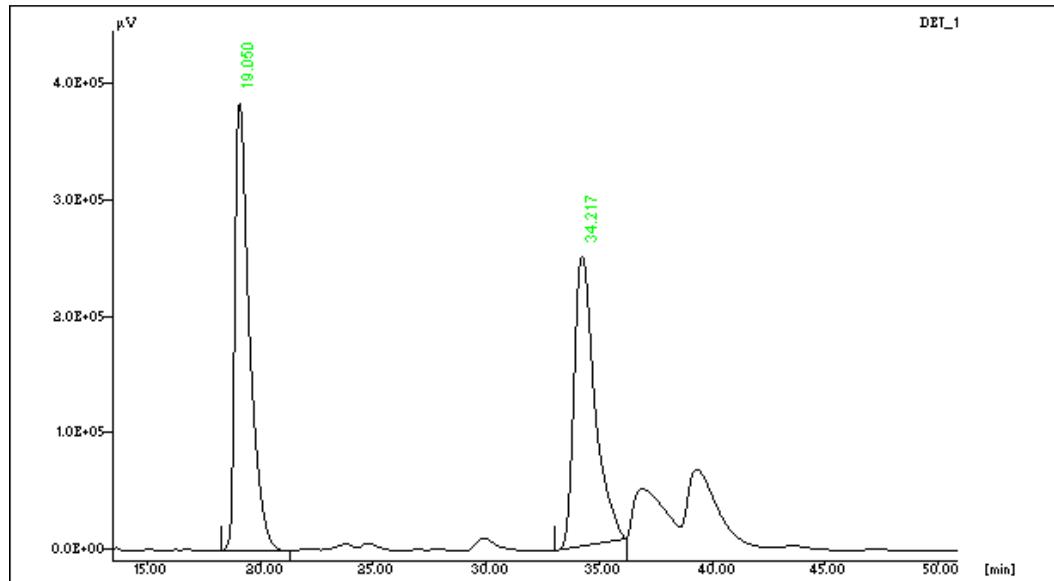
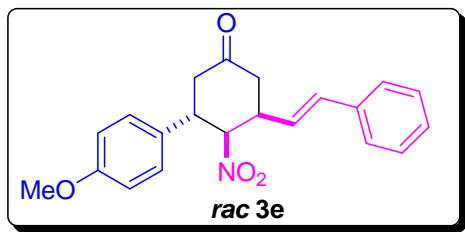
Injection Date : 1-Jul-2015 16:14:28

Curr. Date : 1-Jul-2015 16:52:40

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V.Sec}$]
1	19.11	100.000	4933468.25

Total Area of Peak = 4933468.25 [$\mu\text{V.Sec}$]



File name : vgb 295 - 4-OMe Racemic469.CH1

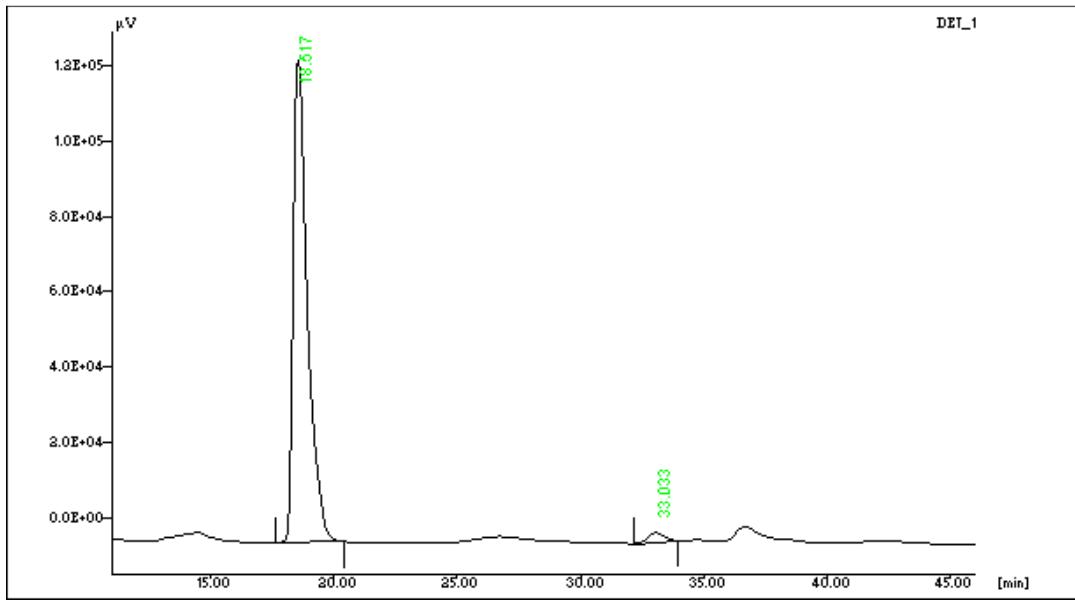
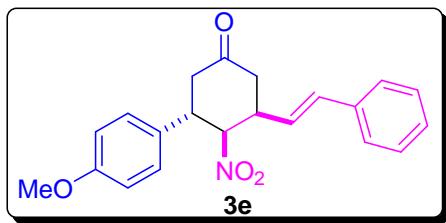
Injection Date : 10-Jun-2015 18:08:00

Curr. Date : 10-Jun-2015 19:06:36

Control Method :RC

Name	RT	% Area	Area [$\mu\text{V}.\text{Sec}$]
1	19.05	51.176	15505495.50
2	34.21	48.824	14793102.91

Total Area of Peak = 30298598.41 [$\mu\text{V}.\text{Sec}$]



File name : vgb297

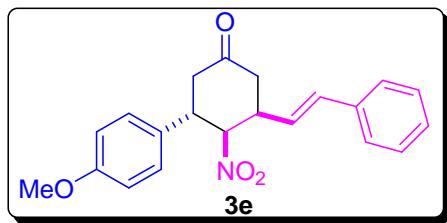
Injection Date : 12-Jun-2015 19:07:06

Curr. Date : 13-Jun-2015 11:56:52

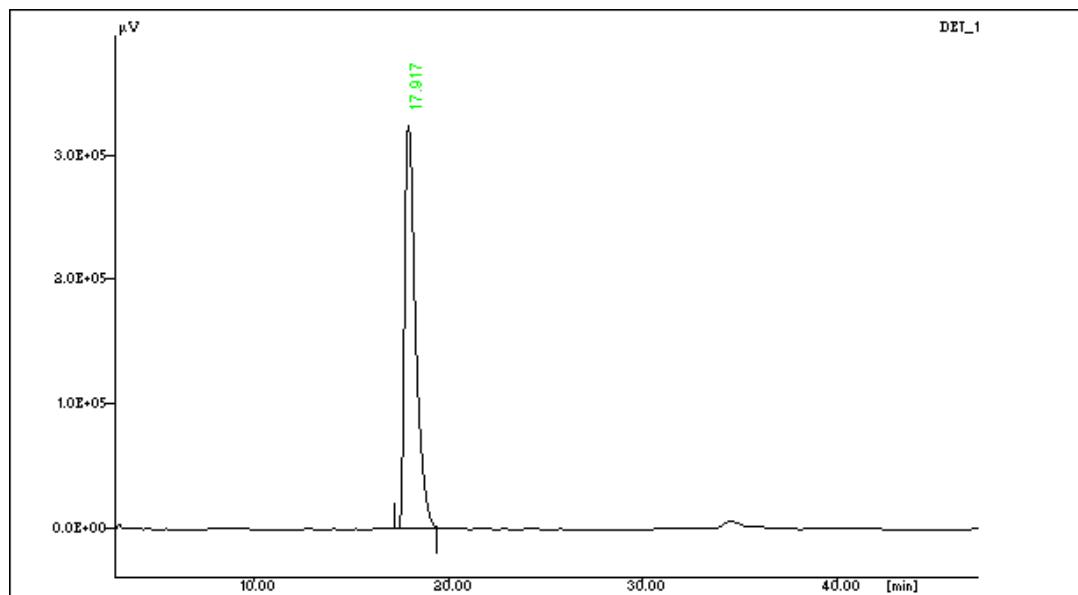
Control Method :RC

Name	RT	%Area	Area[μV.Sec]
1	18.51	97.604	4605985.30
2	33.03	2.396	113070.89

Total Area of Peak = 4719056.20 [μV.Sec]



After single recrystallization



File name : vgb297-(4-methoxy)crystal483.CH1

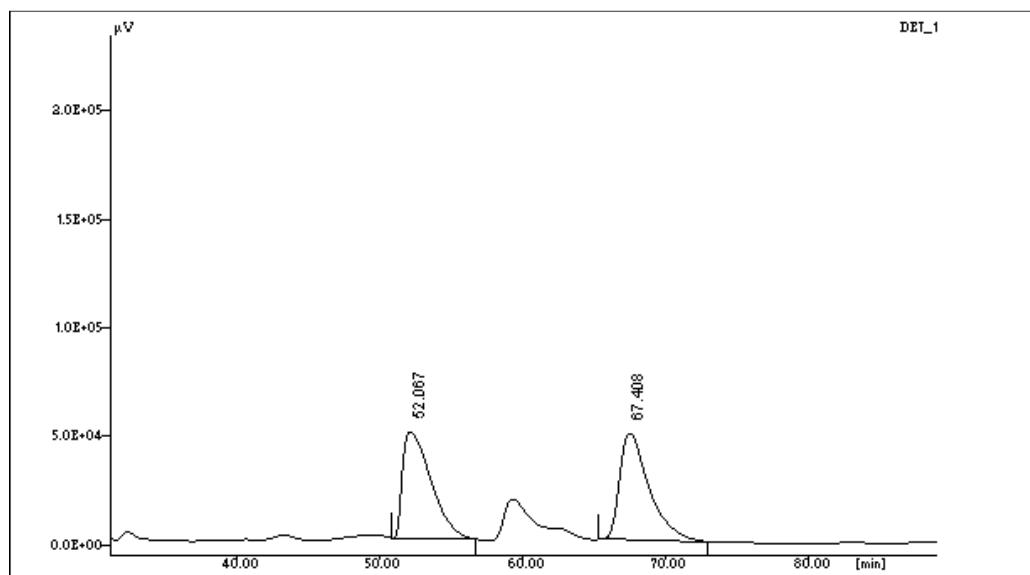
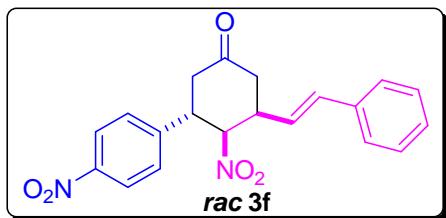
Injection Date :13-Jun-2015 12:59:26

Curr. Date : 13-Jun-2015 14:27:40

Control Method :RC

Name	RT	% Area	Area[μ V.Sec]
1	17.91	100.000	11077704.47

Total Area of Peak = 11077704.47 [μ V.Sec]



File name : vgb-337-rac108.CH1

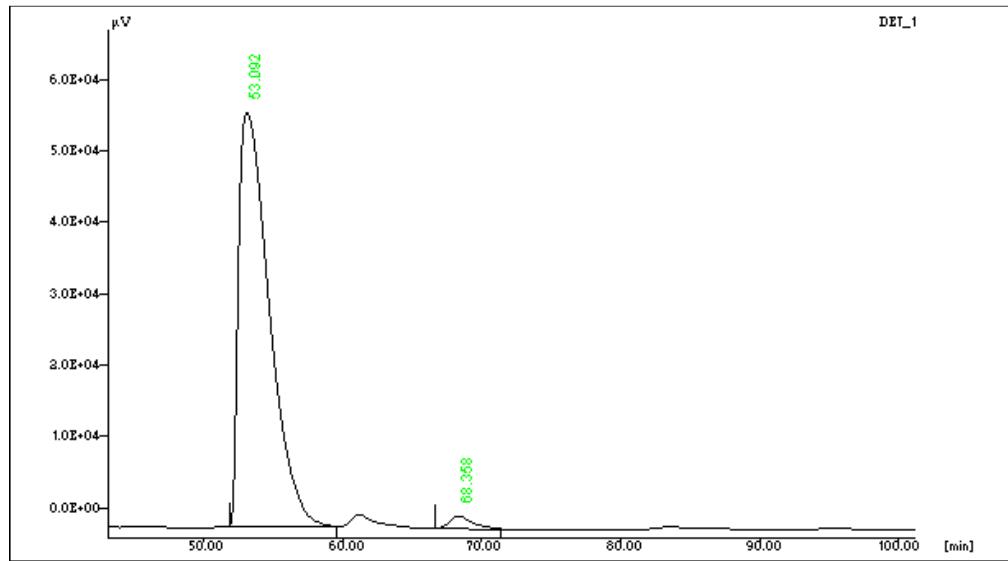
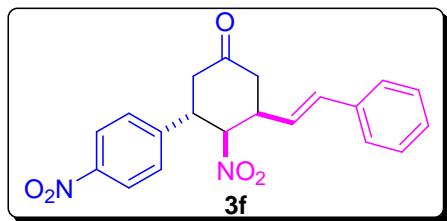
Injection Date :25-Jul-2015 14:44:40

Curr. Date : 25-Jul-2015 16:21:30

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	52.06	49.110	6501692.64
2	67.40	50.890	6737383.50

Total Area of Peak = 13239076.14 [μV.Sec]



File name : vgb-323-(4-nitrochalcone)-317092.CH1

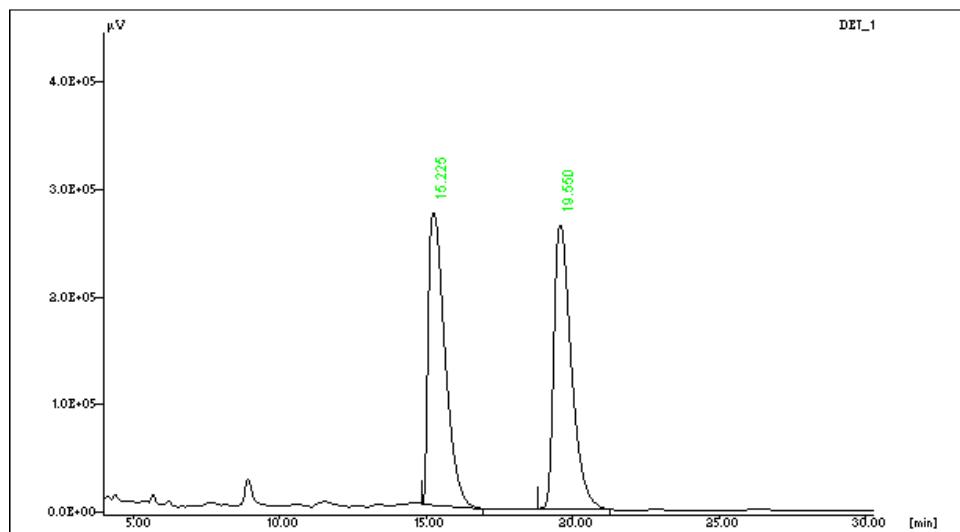
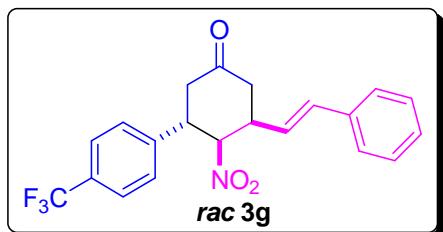
Injection Date :20-Jul-2015 17:51:06

Curr. Date :27-Jul-2015 17:08:10

Control Method :RC

Name	RT	% Area	Area[μ V.Sec]
1	53.09	97.690	8493572.00
2	68.35	2.310	200827.50

Total Area of Peak = 8694399.50 [μ V.Sec]



File name : VGB-321-(4-CF₃)-RAC077.CH1

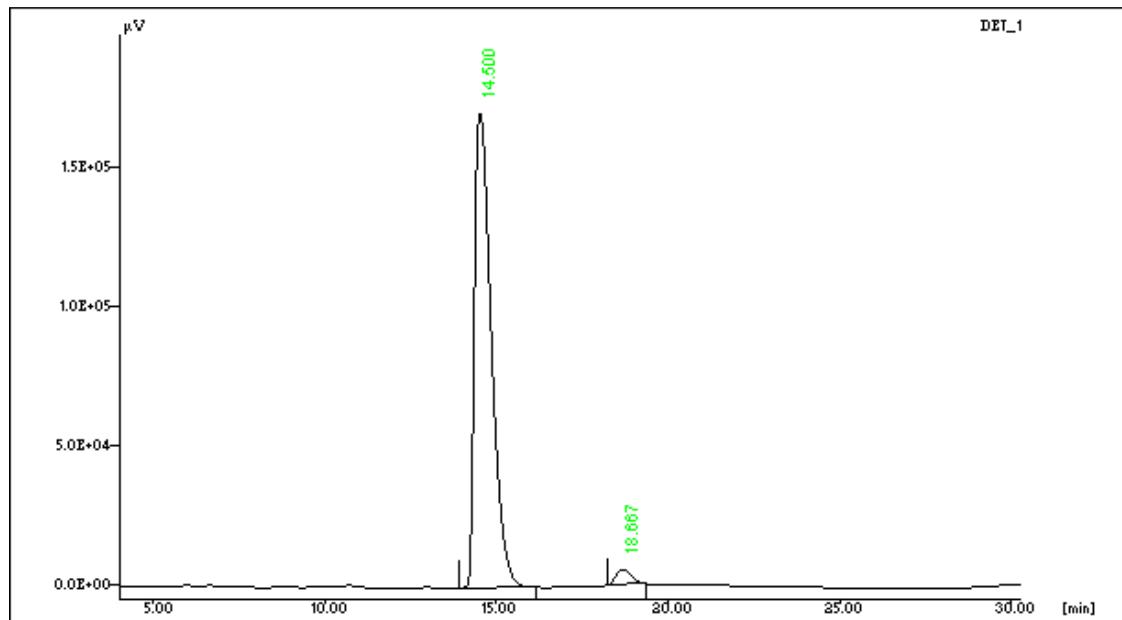
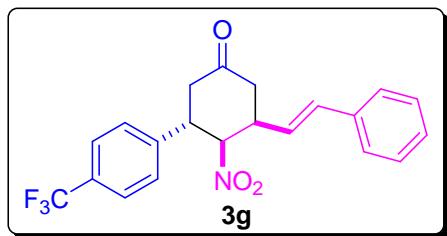
Injection Date : 16-Jul-2015 18:19:16

Curr. Date : 16-Jul-2015 18:54:24

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	15.22	49.319	9853843.50
2	19.55	50.681	10125781.75

Total Area of Peak = 19979625.25 [μV.Sec]



File name : VGB-322-(4-CF₃)-hplc078.CH1

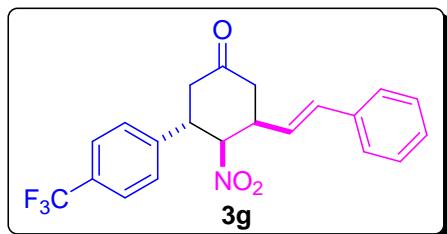
Injection Date : 16-Jul-2015 19:05:08

Curr. Date : 16-Jul-2015 19:43:04

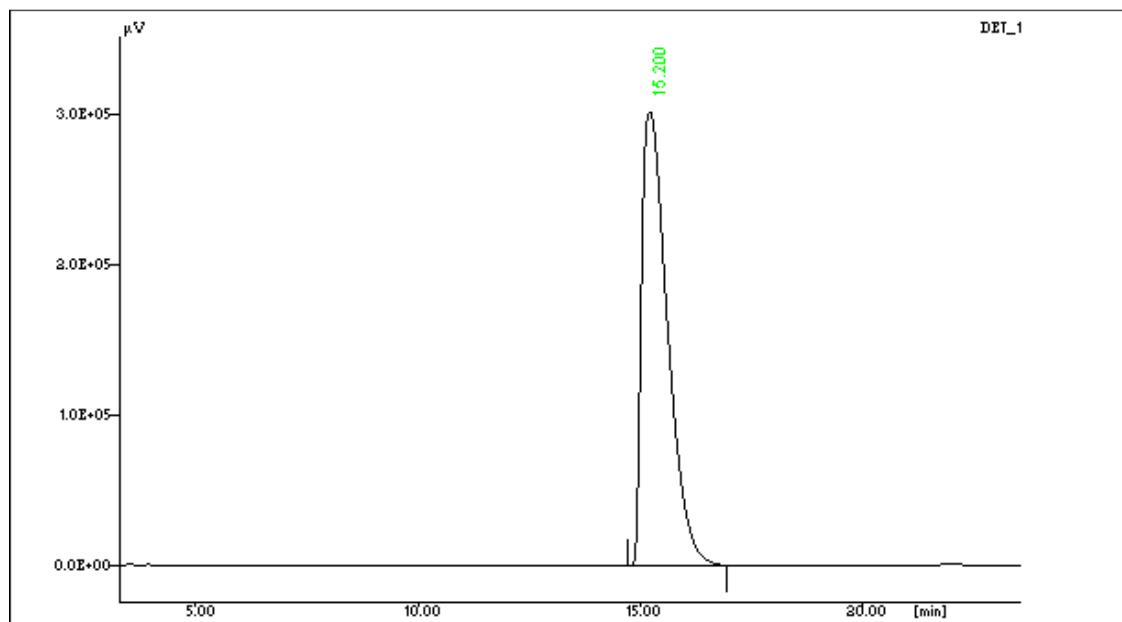
Control Method :RC

Name	RT	% Area	Area[µV.Sec]
1	14.50	97.115	5283025.00
2	18.66	2.885	156946.50

Total Area of Peak = 5439971.50 [µV.Sec]



After single recrystallization



File name : vgb-322-(4-CF₃-crystal)089.CH1

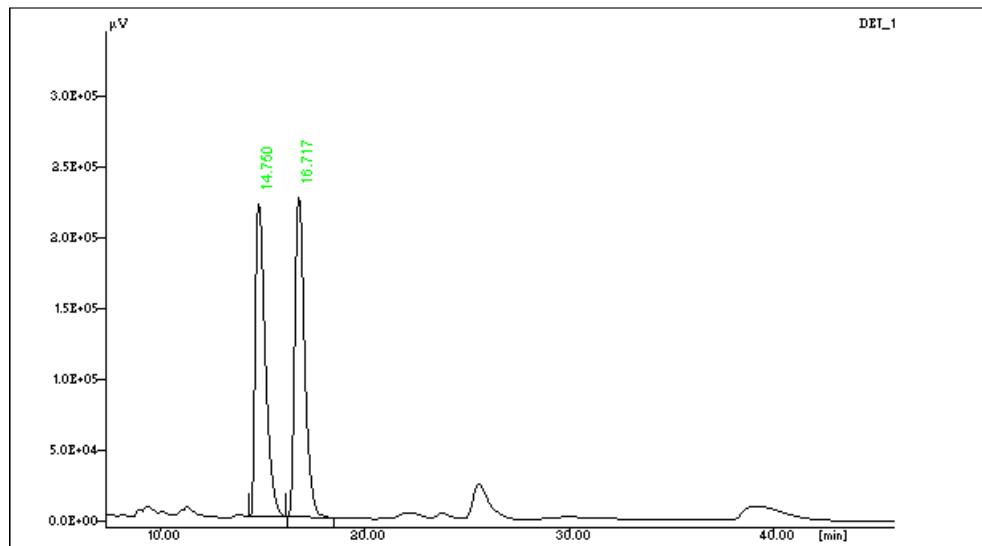
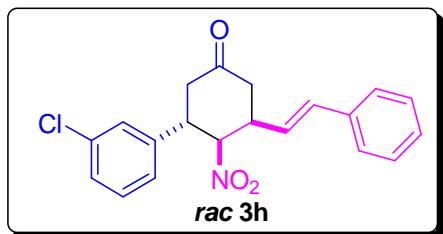
Injection Date :20-Jul-2015 15:22:12

Curr. Date : 20-Jul-2015 16:07:18

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V.Sec}$]
1	15.23	100.000	11611182.75

Total Area of Peak = 11611182.75 [$\mu\text{V.Sec}$]



File name : vgb 319- (3-chloro)-rac065.CH1

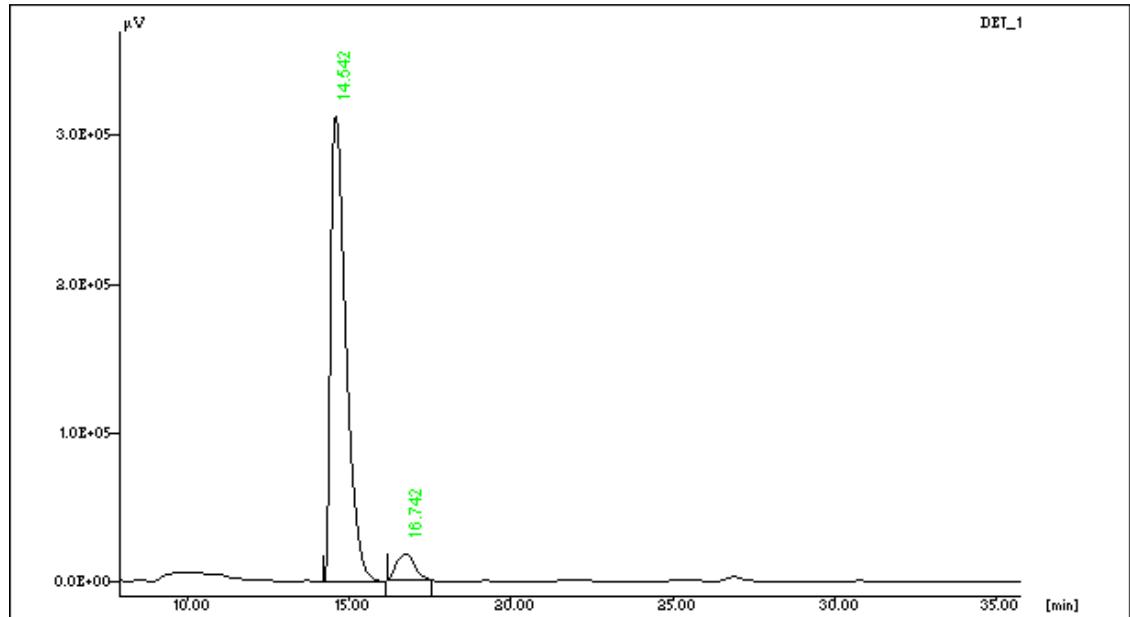
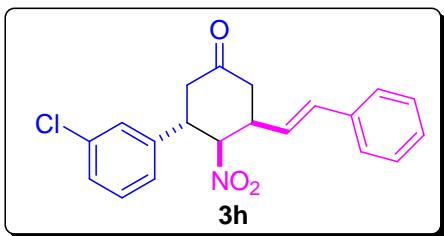
Injection Date : 16-Jul-2015 10:26:50

Curr. Date : 16-Jul-2015 13:16:50

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	14.75	49.969	6567042.26
2	16.71	50.031	6575192.34

Total Area of Peak = 13142234.61 [μV.Sec]



File name : vgb 318-hplc (3-chloro)068.CH1

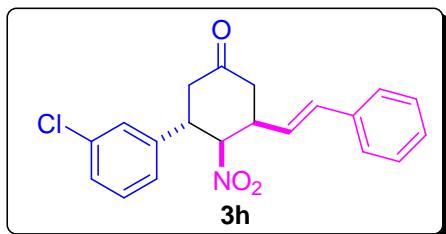
Injection Date : 16-Jul-2015 12:22:12

Curr. Date : 16-Jul-2015 13:00:46

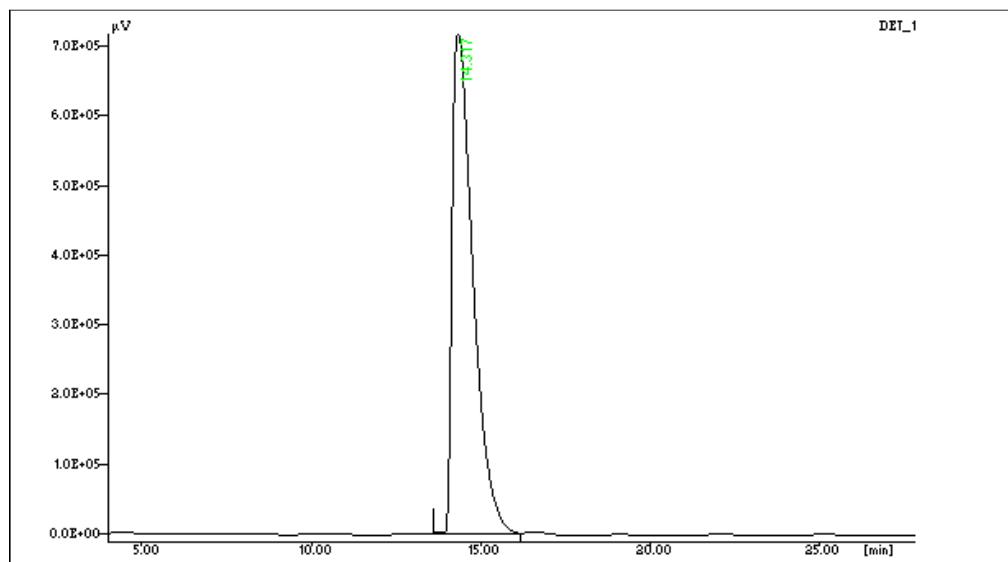
Control Method :RC

Name	RT	% Area	Area[µV.Sec]
1	14.54	93.528	9230346.50
2	16.74	6.472	638696.75

Total Area of Peak = 9869043.25 [µV.Sec]



After single recrystallization



File name : VGB-318-(3-chloro)-crystal081.CH1

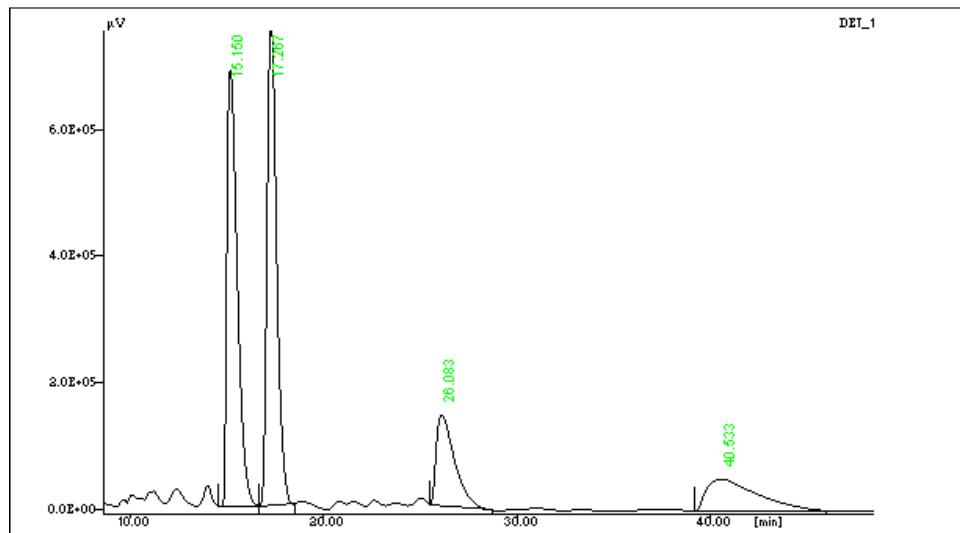
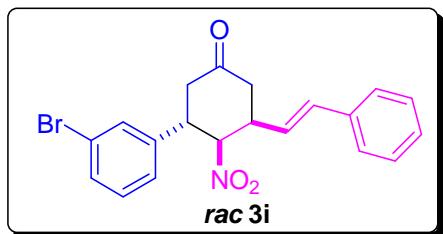
Injection Date :17-Jul-2015 12:02:14

Curr. Date : 17-Jul-2015 12:51:10

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V}.\text{Sec}$]
1	14.31	100.000	28739350.60

Total Area of Peak = 28739350.60 [$\mu\text{V}.\text{Sec}$]



File name : vgb 312-(3-bromo) racemic

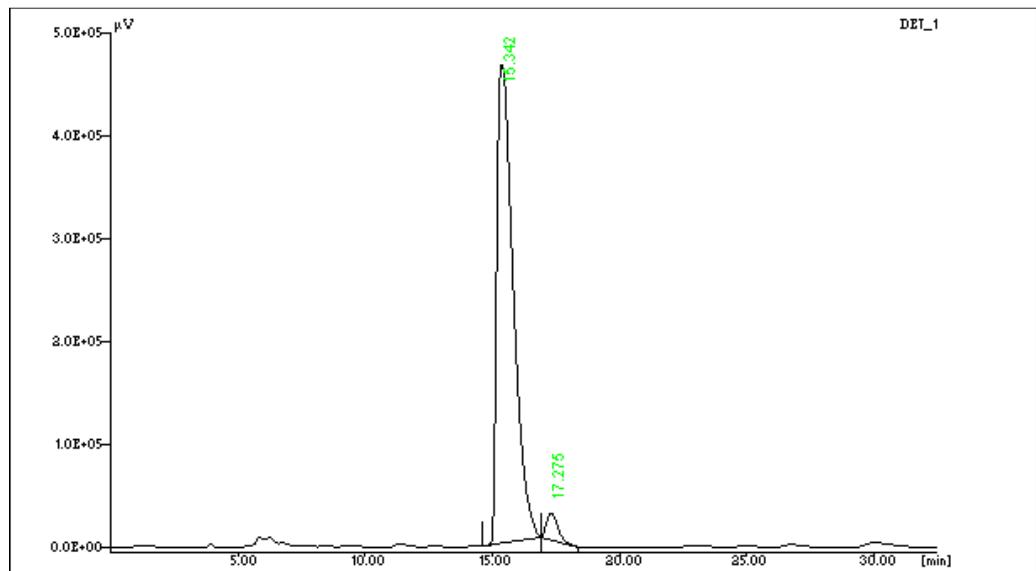
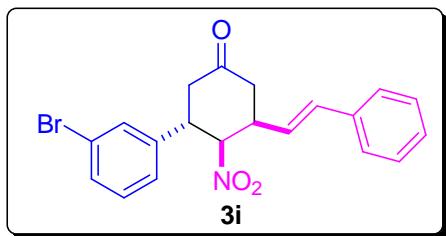
Injection Date : 15-Jul-2015 13:12:26

Curr. Date : 15-Jul-2015 16:22:48

Control Method :RC

Name	RT	% Area	Area[µV.Sec]
1	15.15	35.951	22479240.14
2	17.26	36.276	22682691.65
3	26.08	13.936	8713607.50
4	40.53	13.837	8651957.13

Total Area of Peak = 62527496.42 [µV.Sec]



File name : vgb 311-bulk(3-bromo)057.CH1

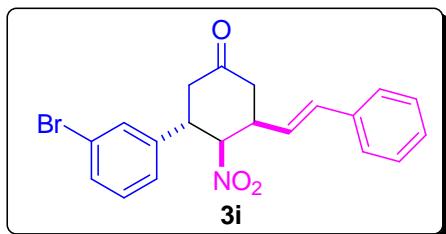
Injection Date : 15-Jul-2015 14:03:06

Curr. Date : 15-Jul-2015 16:20:34

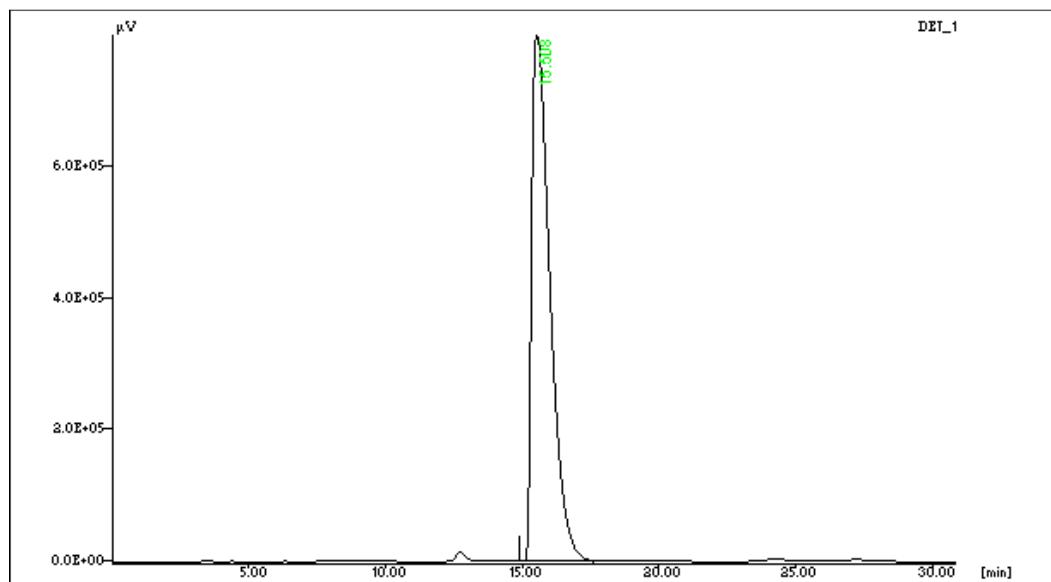
Control Method :RC

Name	RT	% Area	Area [$\mu\text{V.Sec}$]
1	15.34	96.459	18976071.91
2	17.27	3.541	696630.57

Total Area of Peak = 19672702.48 [$\mu\text{V.Sec}$]



After single recrystallization



File name : VGB-311-(3-bromo)-CRYSTAL071.CH1

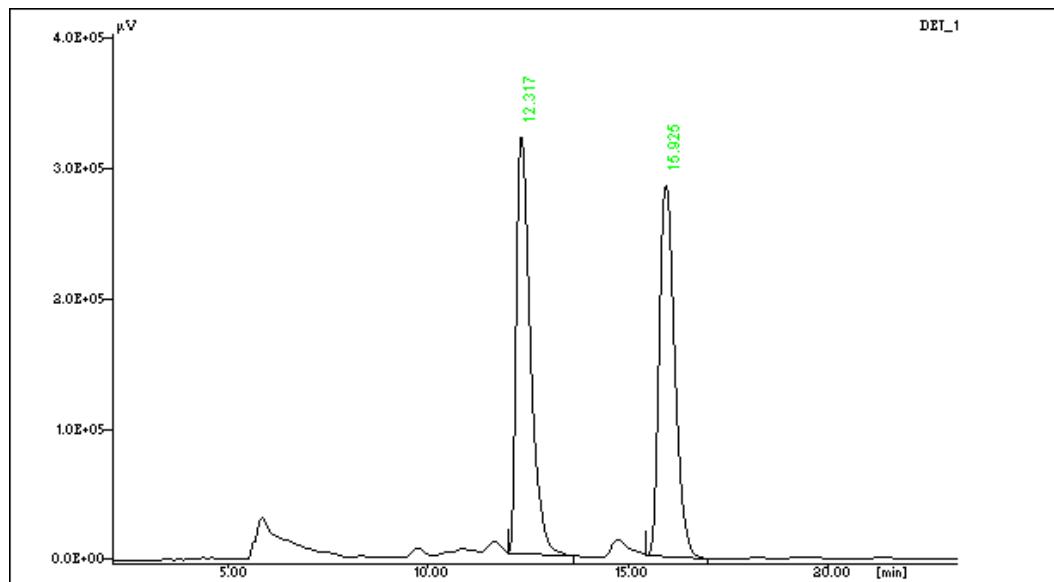
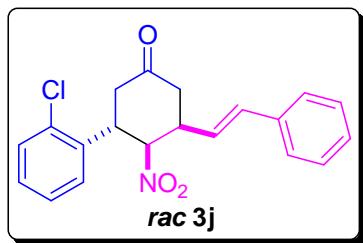
Injection Date : 16-Jul-2015 14:19:36

Curr. Date : 16-Jul-2015 18:26:40

Control Method :RC

Name	RT	%Area	Area[μV.Sec]
1	15.5	100.000	34245042.00

Total Area of Peak = 34245042.00 [μV.Sec]



File name : vgb 314- 2-chloro -rac069.CH1

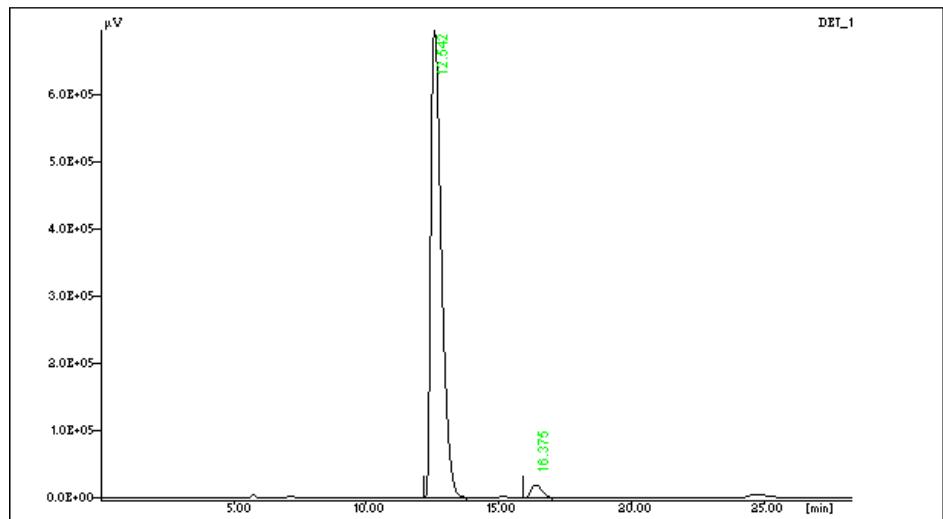
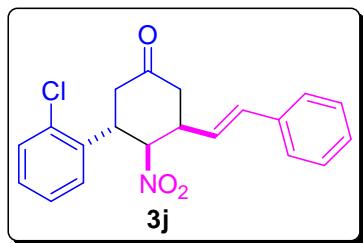
Injection Date :16-Jul-2015 13:08:22

Curr. Date : 16-Jul-2015 14:49:06

Control Method :RC

Name	RT	% Area	Area [$\mu\text{V.Sec}$]
1	12.31	50.505	7079668.75
2	15.92	49.495	6938020.50

Total Area of Peak = 14017689.25 [$\mu\text{V.Sec}$]



File name : vgb 314- 2-chloro -313070.CH1

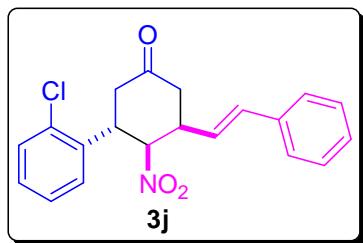
Injection Date :16-Jul-2015 13:50:10

Curr. Date : 16-Jul-2015 14:50:16

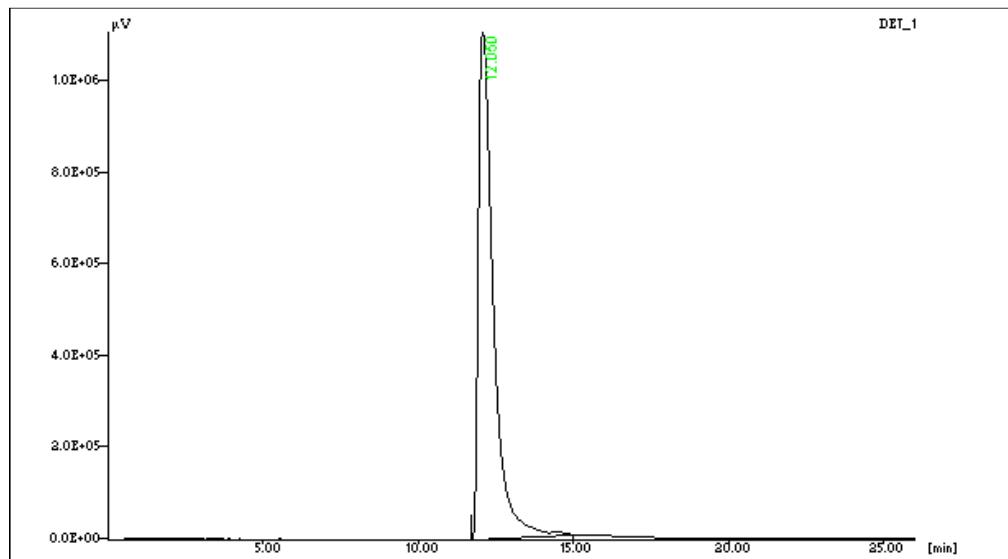
Control Method :RC

Name	RT	% Area	Area [$\mu\text{V.Sec}$]
1	12.54	97.363	17123974.03
2	16.37	2.637	463726.00

Total Area of Peak = 17587700.03 [$\mu\text{V.Sec}$]



After single recrystallization



File name : VGB-2-chloro-crystal082.CH1

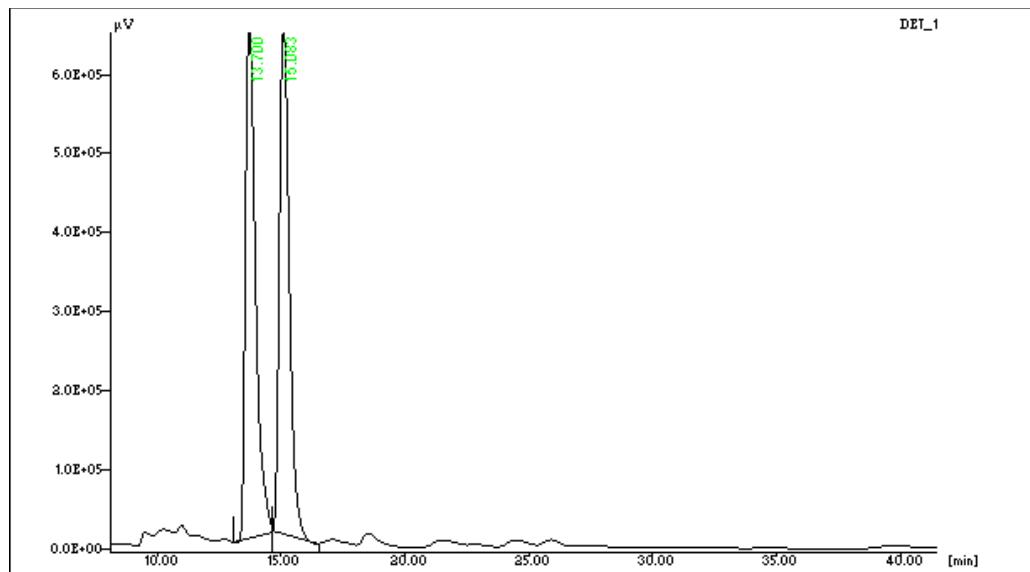
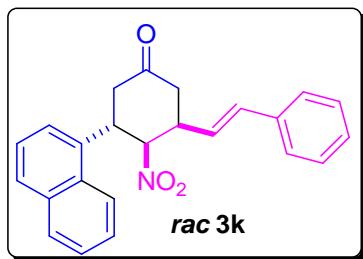
Injection Date :17-Jul-2015 12:40:14

Curr. Date : 17-Jul-2015 13:07:26

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V.Sec}$]
1	12.01	100.000	33723490.50

Total Area of Peak = 33723490.50 [$\mu\text{V.Sec}$]



File name : vgb 309-rac (naphthalene)060.CH1

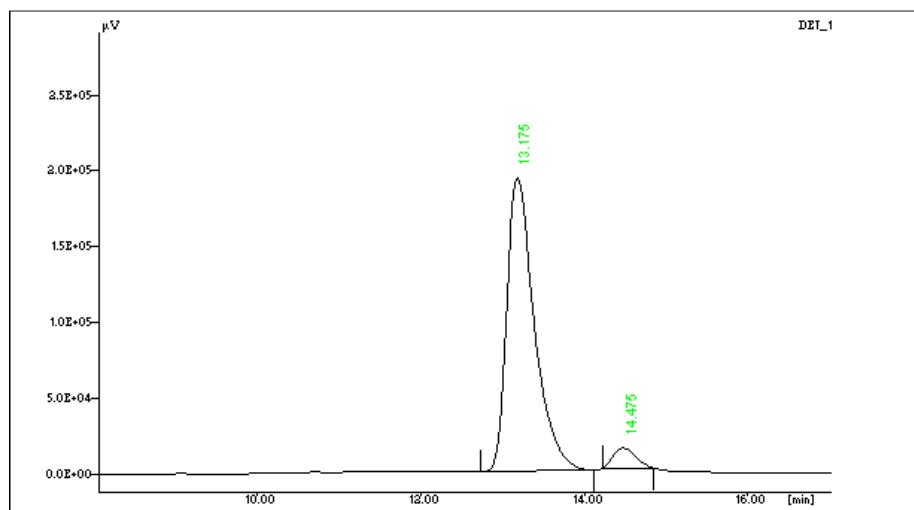
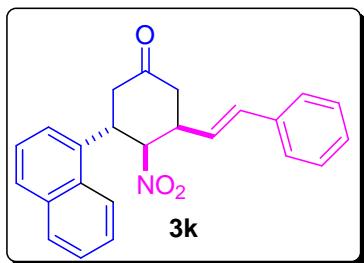
Injection Date :15-Jul-2015 16:24:28

Curr. Date : 15-Jul-2015 19:14:48

Control Method :RC

Name	RT	% Area	Area[µV.Sec]
1	13.70	50.837	15919428.10
2	15.08	49.163	15395268.92

Total Area of Peak = 31314697.03 [µV.Sec]



File name : vgb 308-hplc (naphthalene)063.CH1

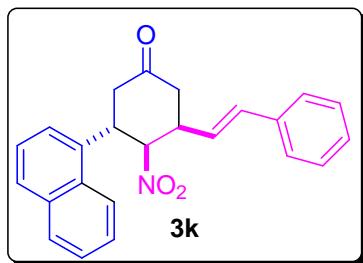
Injection Date : 15-Jul-2015 18:51:44

Curr. Date : 15-Jul-2015 19:12:36

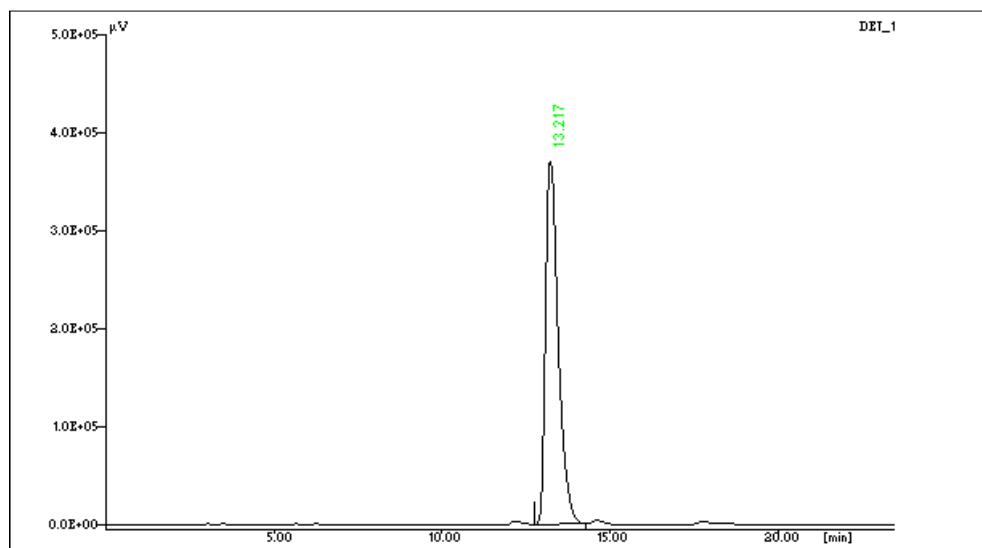
Control Method :RC

Name	RT	% Area	Area[μ V.Sec]
1	13.17	94.656	4310369.80
2	14.47	5.344	243351.50

Total Area of Peak = 4553721.30 [μ V.Sec]



After single recrystallization



File name : VGB-naphthal-crystal083.CH1

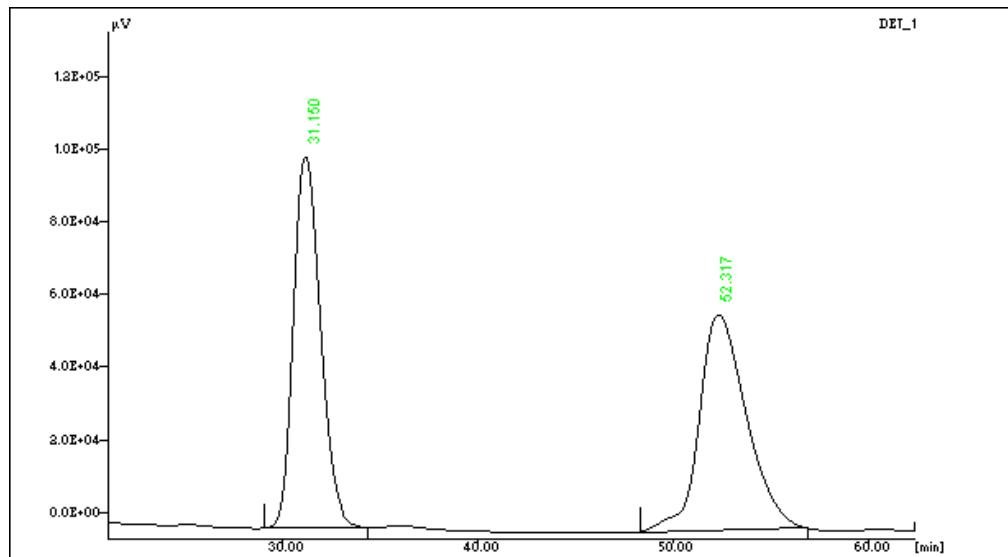
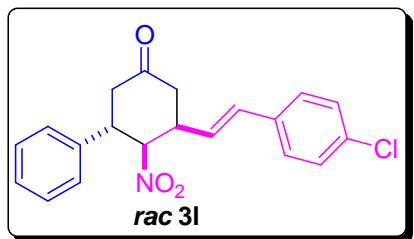
Injection Date : 17-Jul-2015 13:09:40

Curr. Date : 17-Jul-2015 13:44:36

Control Method :RC

Name	RT	%Area	Area[μ V.Sec]
1	13.23	100.000	8745033.74

Total Area of Peak = 8745033.74 [μ V.Sec]



File name : vgb346063.CH1

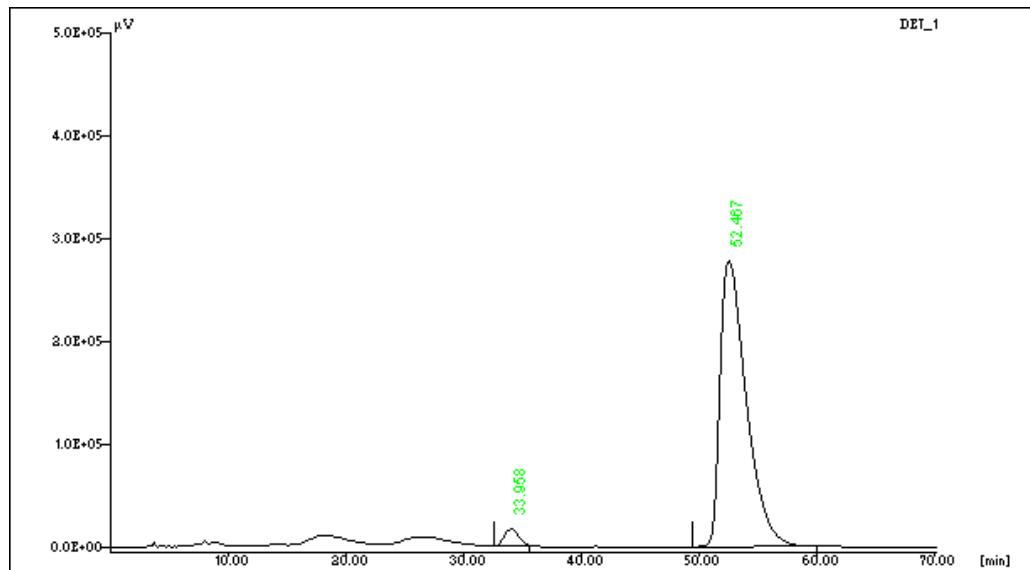
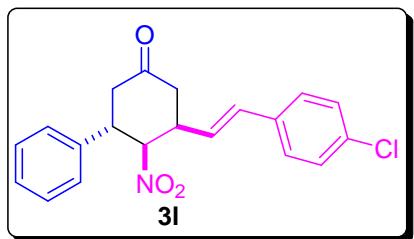
Injection Date : 3-Sep-2015 12:37:12

Curr. Date : 3-Sep-2015 15:56:06

Control Method :RC

Name	RT	% Area	Area [$\mu\text{V}.\text{Sec}$]
1	31.15	49.251	9406829.00
2	52.31	50.749	9692934.00

Total Area of Peak = 19099763.00 [$\mu\text{V}.\text{Sec}$]



File name : vgb348065.CH1

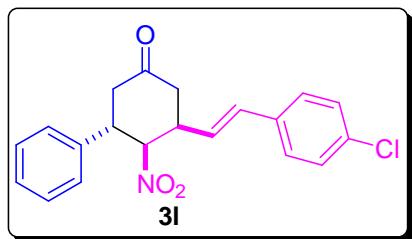
Injection Date : 3-Sep-2015 14:47:40

Curr. Date : 3-Sep-2015 16:00:54

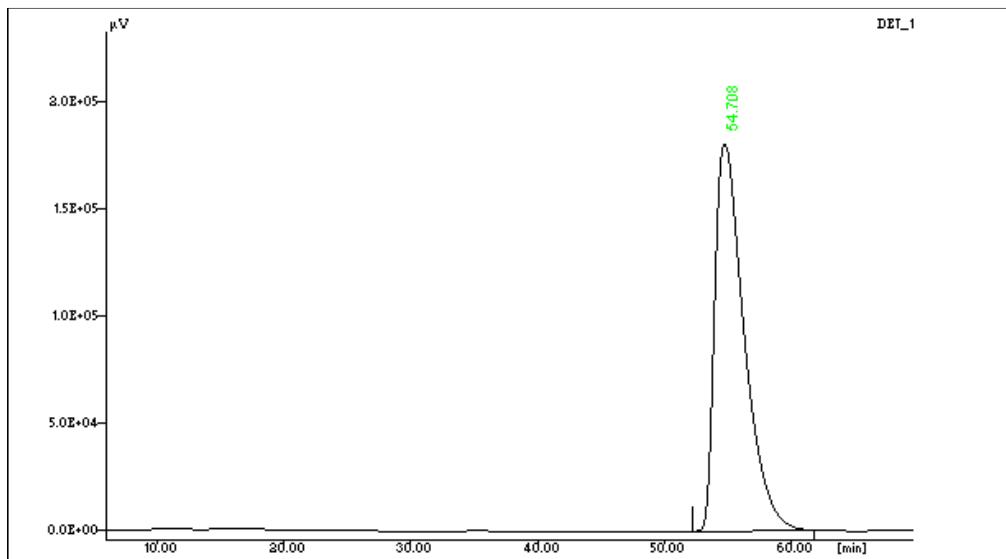
Control Method :RC

Name	RT	% Area	Area[μ V.Sec]
1	33.95	2.999	1261510.00
2	52.46	97.001	40795939.00

Total Area of Peak = 42057449.00 [μ V.Sec]



After single recrystallization



File name : vgb348-crystal082.CH1

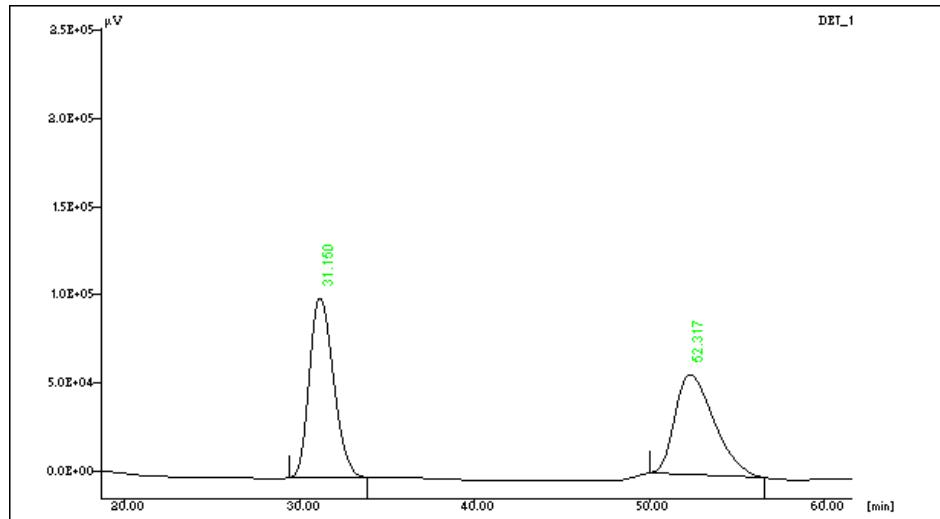
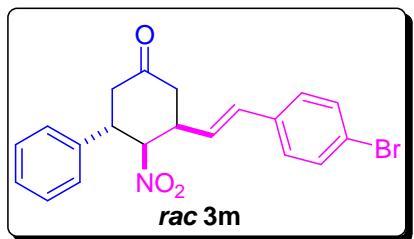
Injection Date :10-Sep-2015 14:53:20

Curr. Date : 10-Sep-2015 18:38:00

Control Method :RC

Name	RT	%Area	Area[μ V.Sec]
1	54.71	100.000	27749478.50

Total Area of Peak = 27749478.50 [μ V.Sec]



File name : vgb351063.CH1

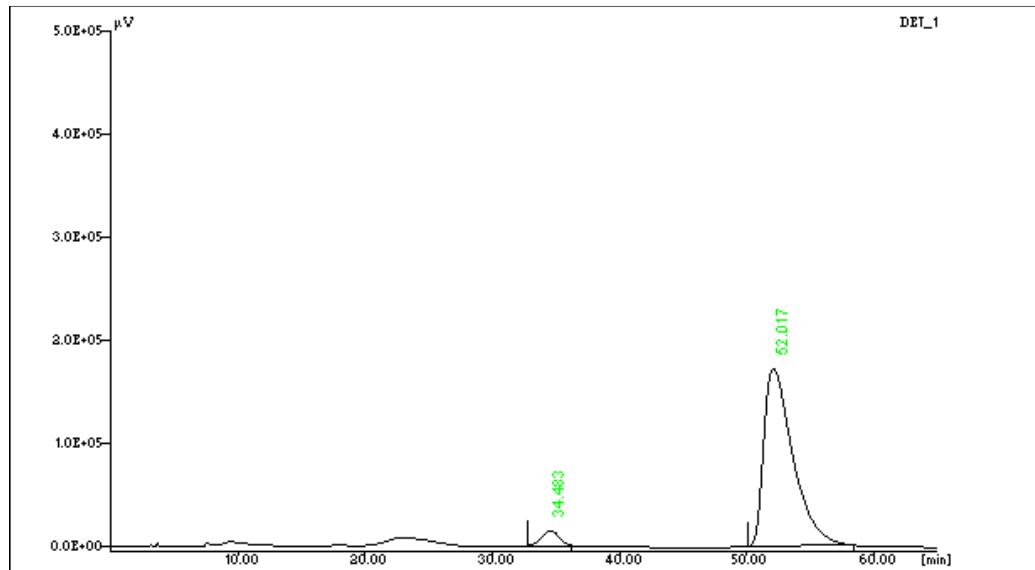
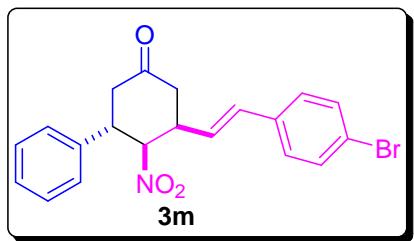
Injection Date : 3-Sep-2015 12:37:12

Curr. Date : 7-Sep-2015 16:53:48

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V.Sec}$]
1	31.15	51.834	9287164.25
2	52.31	48.166	8630087.25

Total Area of Peak = 17917251.50 [$\mu\text{V.Sec}$]



File name : vgb350068.CH1

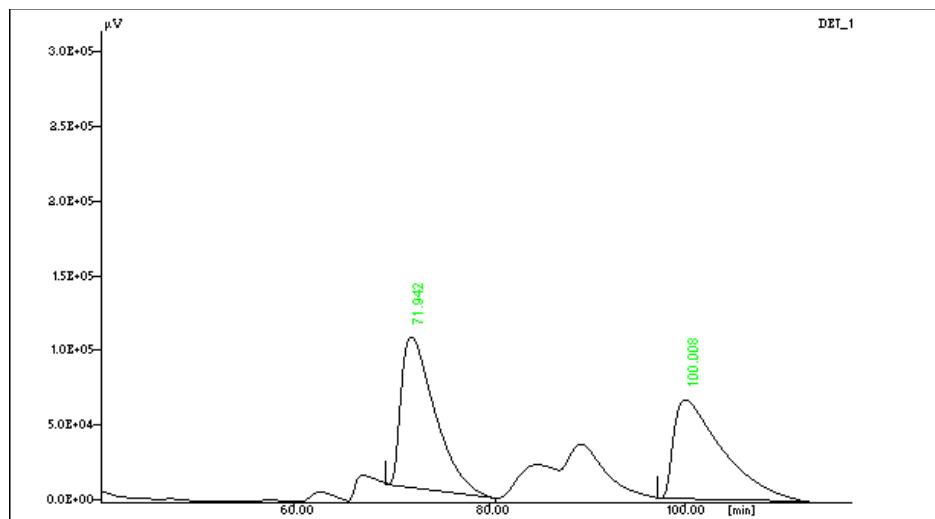
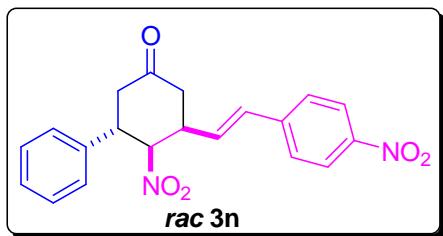
Injection Date : 5-Sep-2015 12:23:20

Curr. Date : 7-Sep-2015 16:48:50

Control Method :RC

Name	RT	%Area	Area[µV.Sec]
1	34.48	4.789	1318367.00
2	52.01	95.211	26207951.50

Total Area of Peak = 27526318.50 [µV.Sec]



File name : vgb330035.CH1

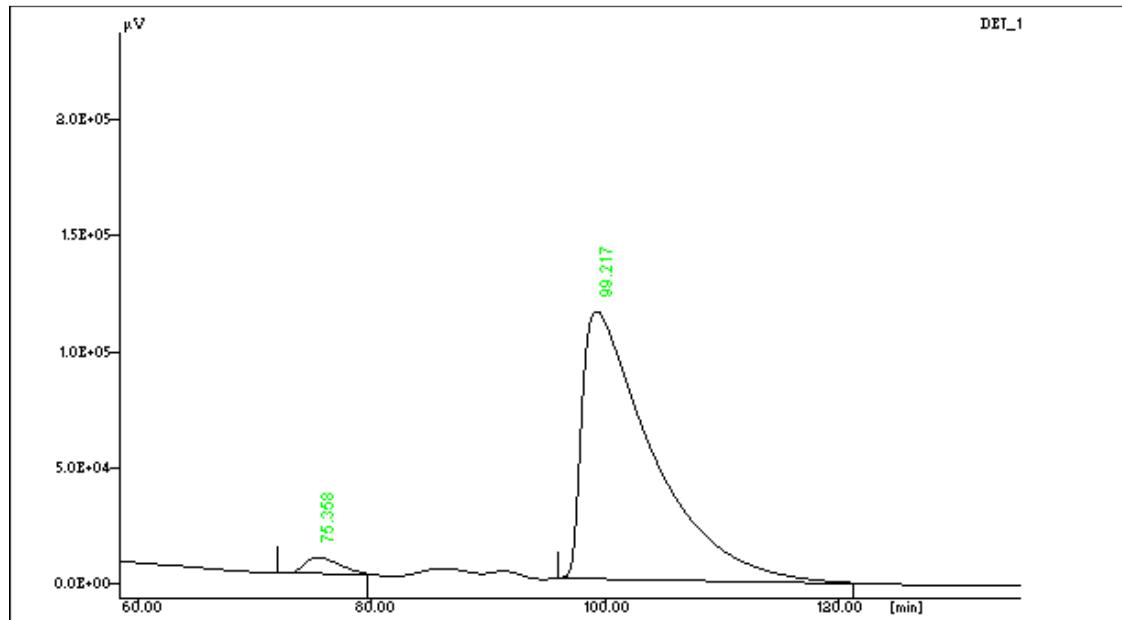
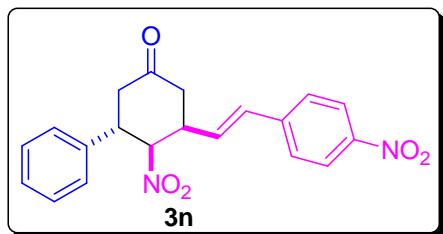
Injection Date :19-Aug-2015 9:25:04

Curr. Date : 19-Aug-2015 11:23:54

Control Method :RC1

Name	RT	% Area	Area [$\mu\text{V}.\text{Sec}$]
1	71.94	50.852	23235251.81
2	100.00	49.148	22456259.79

Total Area of Peak = 45691511.60 [$\mu\text{V}.\text{Sec}$]



File name : vgb329033.CH1

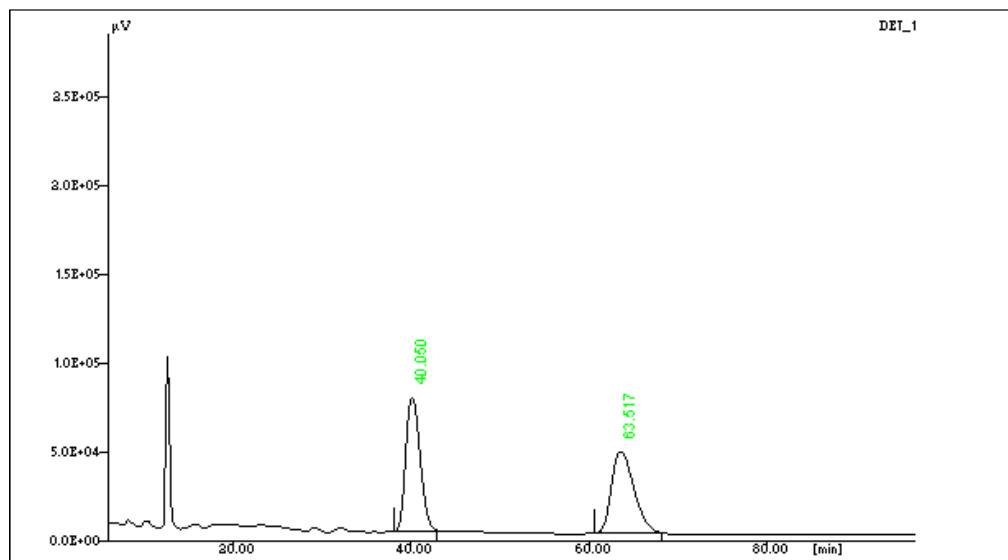
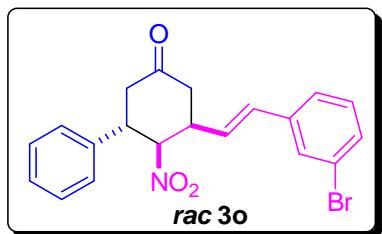
Injection Date : 18-Aug-2015 15:14:58

Curr. Date : 19-Aug-2015 11:44:22

Control Method :RC1

Name	RT	% Area	Area[μV.Sec]
1	75.35	2.820	1364743.70
2	99.21	97.180	47022036.50

Total Area of Peak = 48386780.20 [μV.Sec]



File name : vgb347061.CH1

Info : OD-H, ipa/hexane 10/90, flow rate 1.0 ml/min

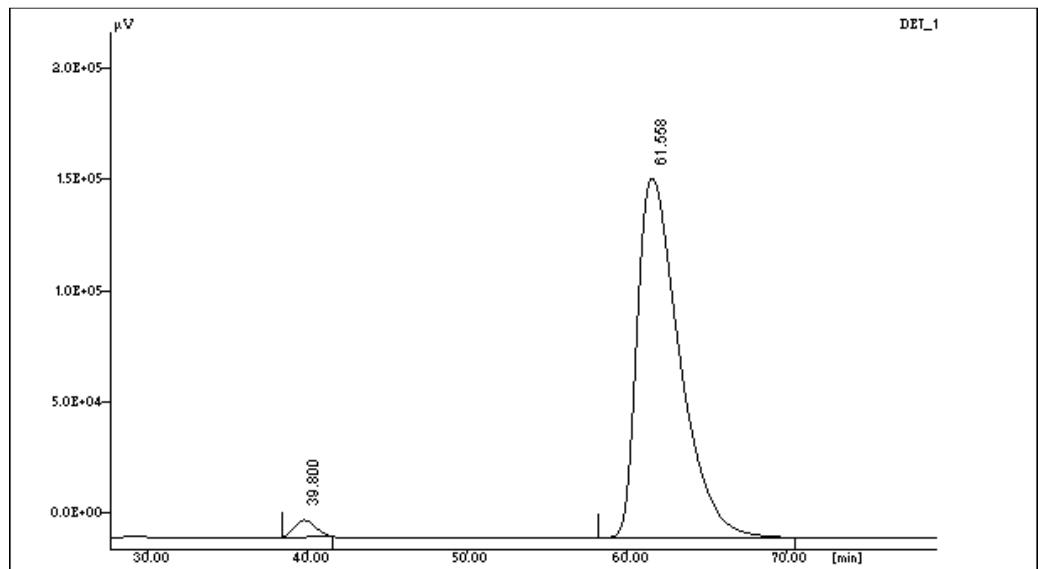
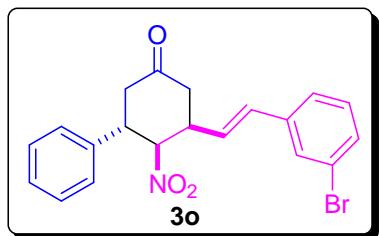
Injection Date : 2-Sep-2015 15:26:44

Curr. Date : 2-Sep-2015 18:49:28

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	40.05	50.110	7660441.00
2	63.51	49.890	7626867.00

Total Area of Peak = 15287308.00 [μV.Sec]



File name : vgb349062.CH1

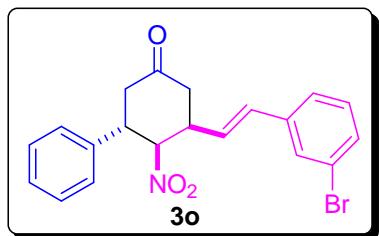
Injection Date : 2-Sep-2015 17:36:28

Curr. Date : 3-Sep-2015 14:28:48

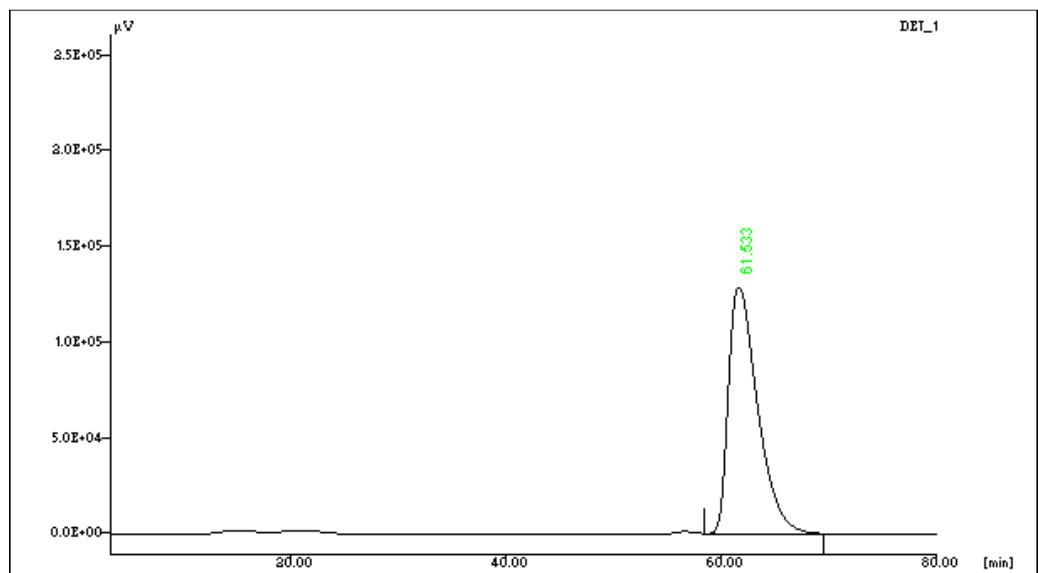
Control Method :RC

Name	RT	% Area	Area [$\mu\text{V.Sec}$]
1	39.80	2.335	691239.00
2	61.55	97.665	28914044.50

Total Area of Peak = 29605283.50 [$\mu\text{V.Sec}$]



After single recrystallization



File name : vgb349-crystal083.CH1

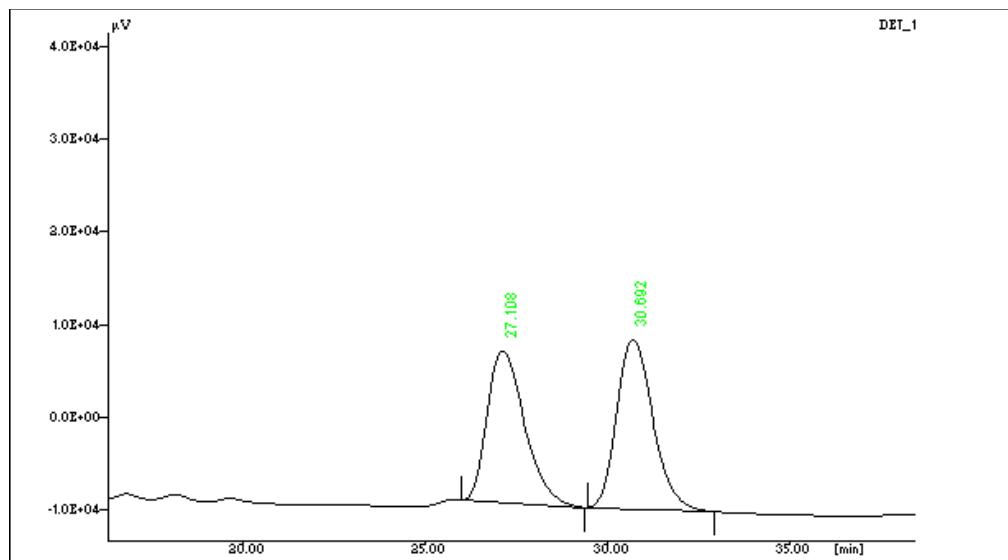
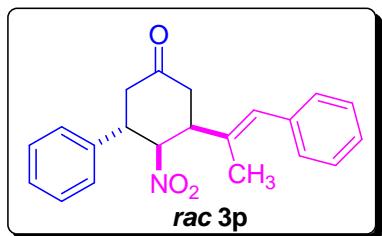
Injection Date : 10-Sep-2015 16:15:44

Curr. Date : 10-Sep-2015 18:41:12

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	61.53	100.000	23136671.05

Total Area of Peak = 23136671.05 [μV.Sec]



File name : vgb-324-Racemic96.CH1 Alpha methyl diene

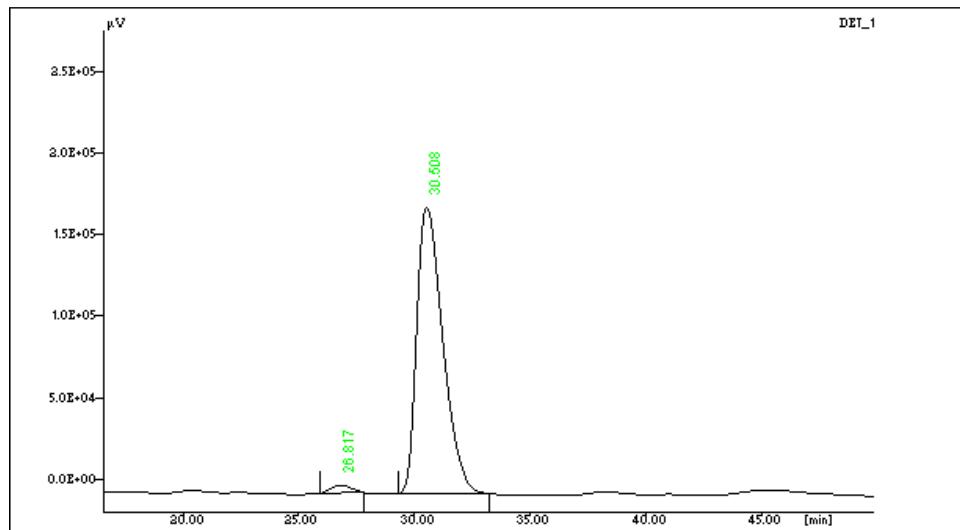
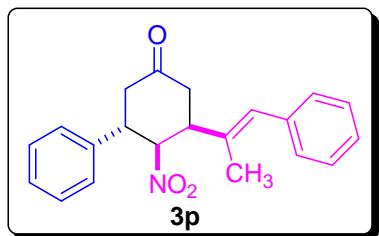
Injection Date :22-Jul-2015 18:00:28

Curr. Date : 23-Jul-2015 11:50:26

Control Method :RC

Name	RT	% Area	Area [$\mu\text{V}.\text{Sec}$]
1	27.10	48.221	1160101.25
2	30.69	51.779	1245705.50

Total Area of Peak = 2405806.75 [$\mu\text{V}.\text{Sec}$]



File name : vgb-324-bulk097.CH1

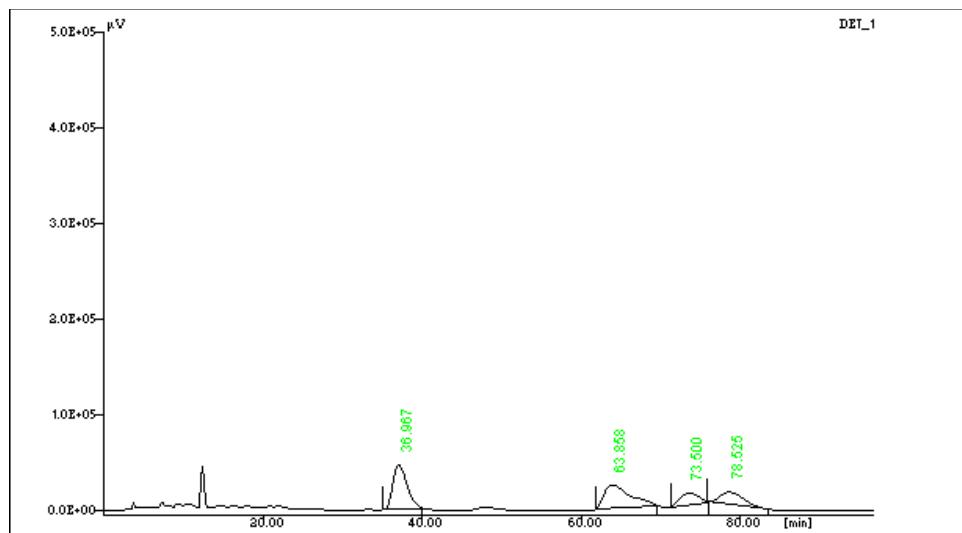
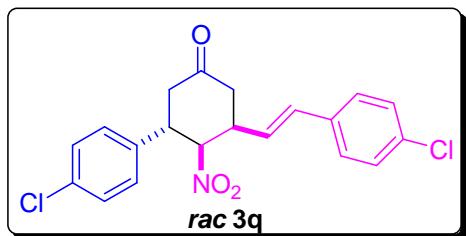
Injection Date :23-Jul-2015 10:07:48

Curr. Date : 23-Jul-2015 17:54:46

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V}.\text{Sec}$]
1	26.81	2.073	277442.25
2	30.50	97.927	13106343.50

Total Area of Peak = 13383785.75 [$\mu\text{V}.\text{Sec}$]



File name : vgb356079.CH1

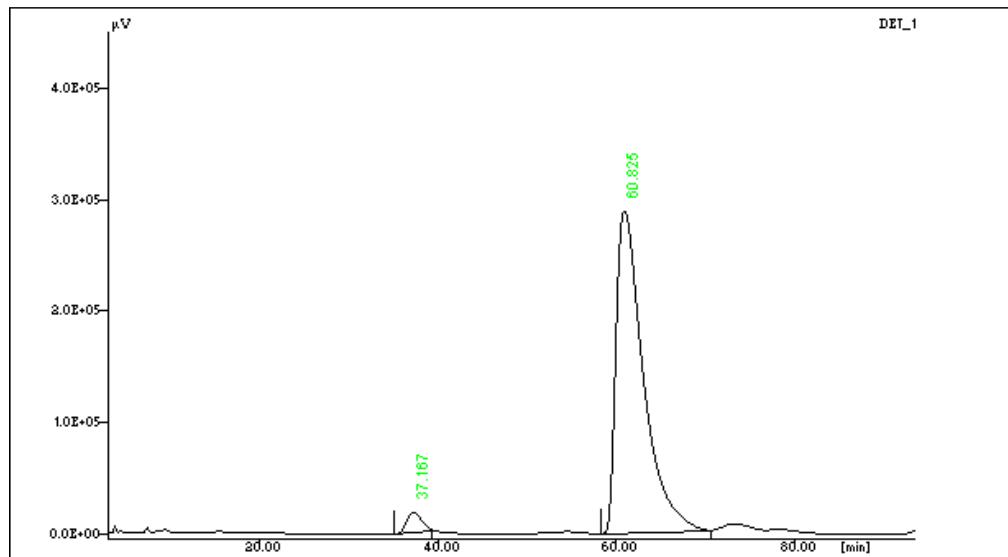
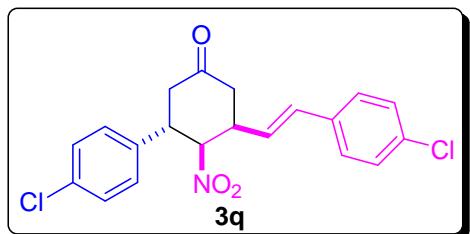
Injection Date : 9-Sep-2015 12:03:14

Curr. Date : 9-Sep-2015 14:59:54

Control Method :RC

Name	RT	%Area	Area[μV.Sec]
1	36.96	35.127	5224066.50
2	63.85	36.462	5422503.75
3	73.50	11.895	1768977.50
4	78.52	16.516	2456269.42

Total Area of Peak = 14871817.17 [μV.Sec]



File name : vgb354080.CH1

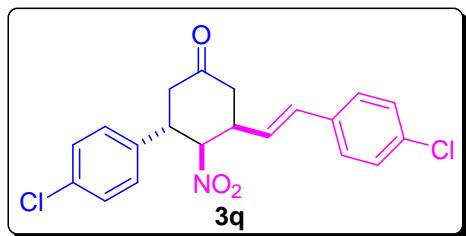
Injection Date : 9-Sep-2015 13:40:30

Curr. Date : 9-Sep-2015 15:21:42

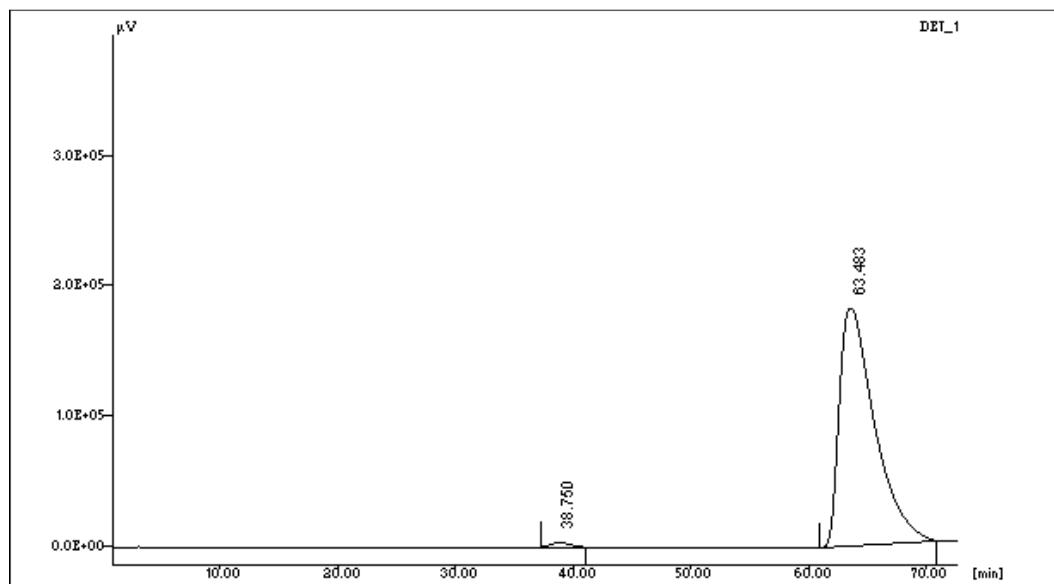
Control Method :RC

Name	RT	% Area	Area[µV.Sec]
1	37.16	3.078	1862940.21
2	60.82	96.922	58663000.79

Total Area of Peak = 60525941.00 [µV.Sec]



After single recrystallization



File name : vgb354-crystal088.CH1

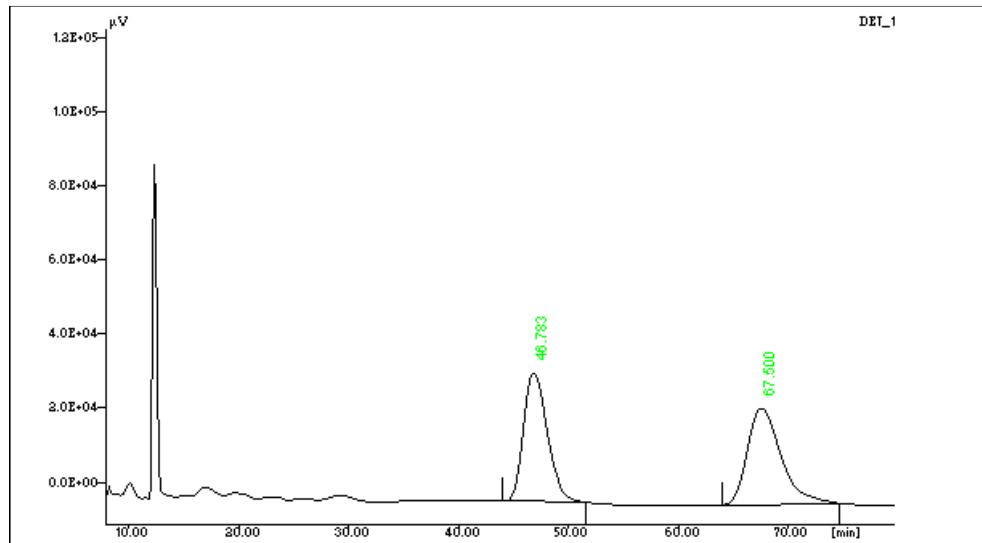
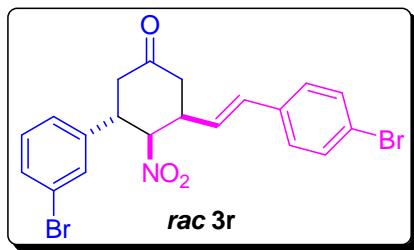
Injection Date : 11-Sep-2015 15:06:42

Curr. Date : 11-Sep-2015 16:22:08

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	38.75	0.998	368566.50
2	63.48	99.002	36549202.92

Total Area of Peak = 36917769.42 [μV.Sec]



File name : vgb357075.CH1

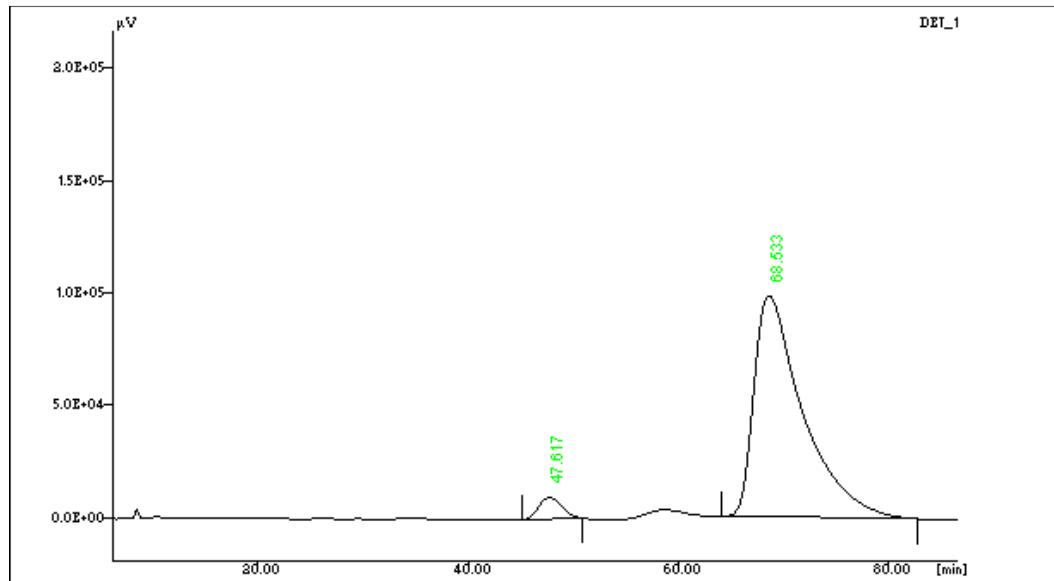
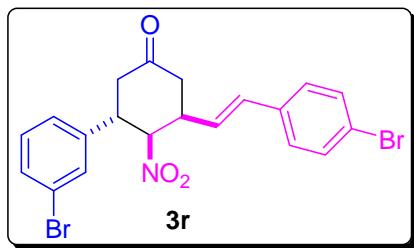
Injection Date : 8-Sep-2015 14:47:20

Curr. Date : 8-Sep-2015 19:32:20

Control Method :RC

Name	RT	% Area	Area [$\mu\text{V}.\text{Sec}$]
1	46.78	48.297	4999168.28
2	67.50	51.703	5351625.00

Total Area of Peak = 10350793.28 [$\mu\text{V}.\text{Sec}$]



File name : vgb355077.CH1

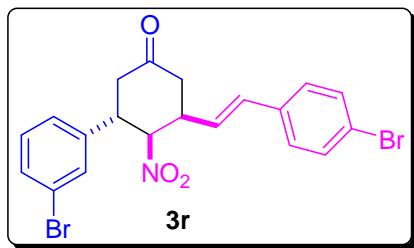
Injection Date : 8-Sep-2015 17:54:40

Curr. Date : 8-Sep-2015 19:31:04

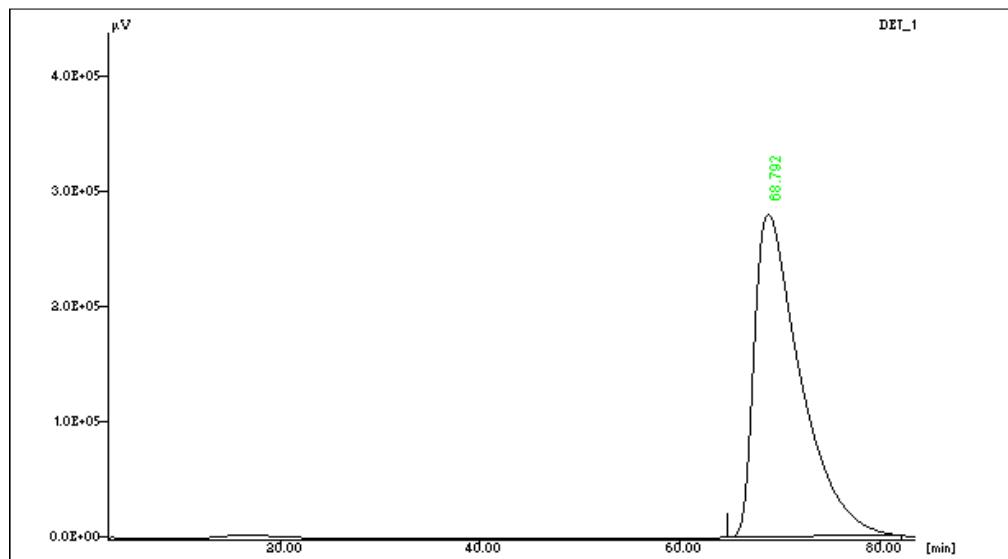
Control Method :RC

Name	RT	%Area	Area[µV.Sec]
1	47.61	4.195	1352370.00
2	68.53	95.805	30885096.50

Total Area of Peak = 32237466.50 [µV.Sec]



After single recrystallization



File name : vgb355-crystal089.CH1

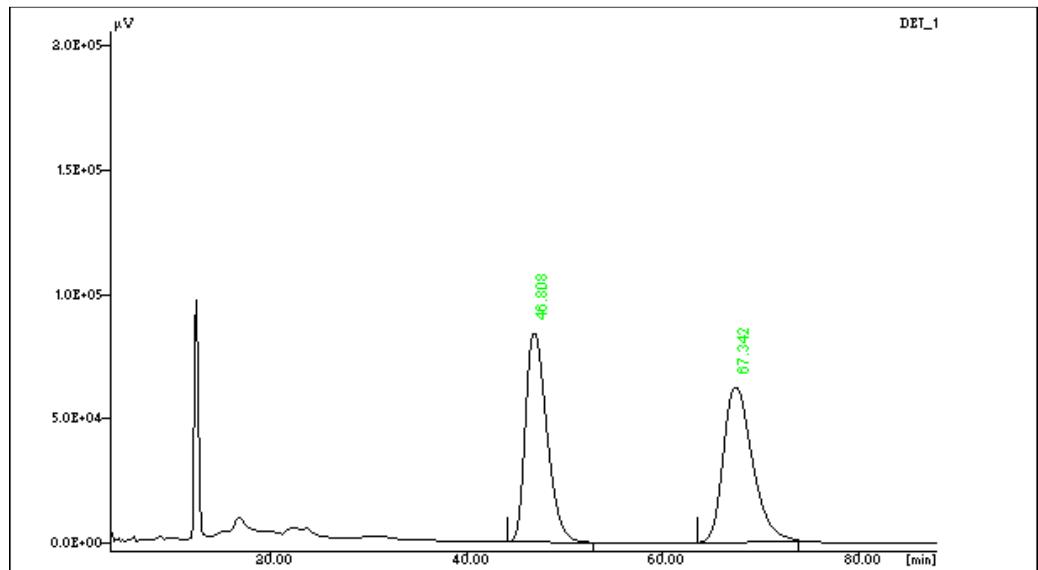
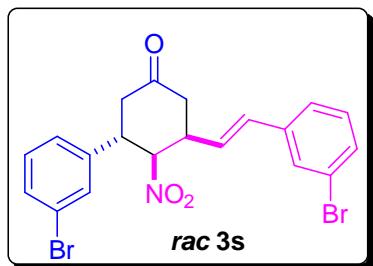
Injection Date : 11-Sep-2015 16:31:56

Curr. Date : 19-Sep-2015 13:20:30

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V}.\text{Sec}$]
1	68.79	100.000	87481429.75

Total Area of Peak = 87481429.75 [$\mu\text{V}.\text{Sec}$]



File name : vgb353074.CH1

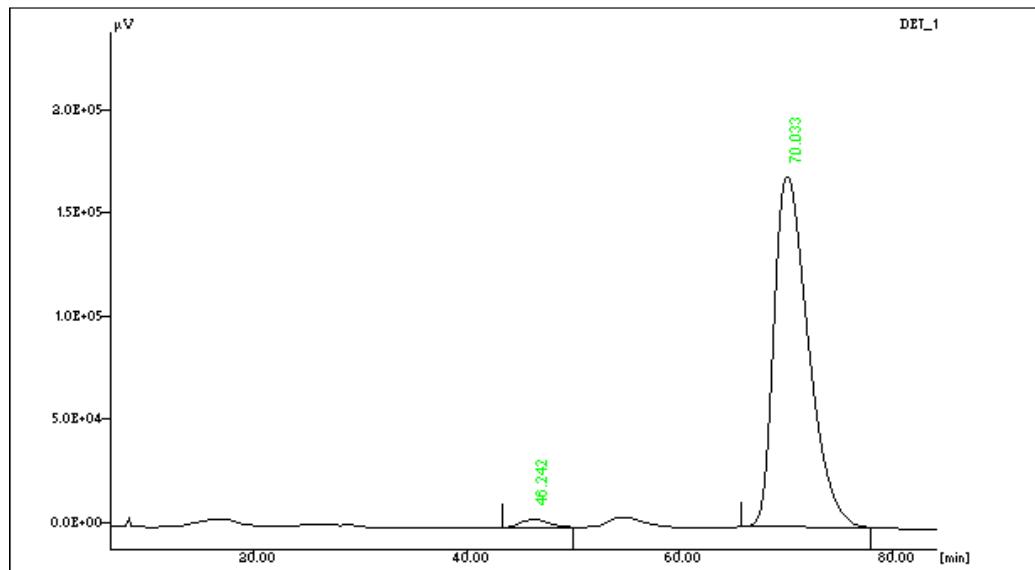
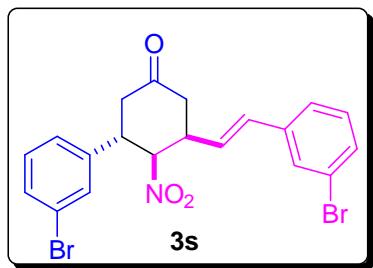
Injection Date : 7-Sep-2015 15:08:26

Curr. Date : 7-Sep-2015 16:38:40

Control Method :RC

Name	RT	%Area	Area[μV.Sec]
1	46.80	49.497	11941348.50
2	67.34	50.503	12184085.75

Total Area of Peak = 24125434.25 [μV.Sec]



File name : vgb351073.CH1

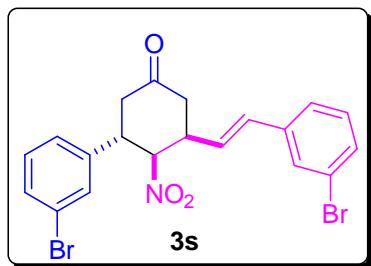
Injection Date : 7-Sep-2015 13:41:00

Curr. Date : 7-Sep-2015 16:43:44

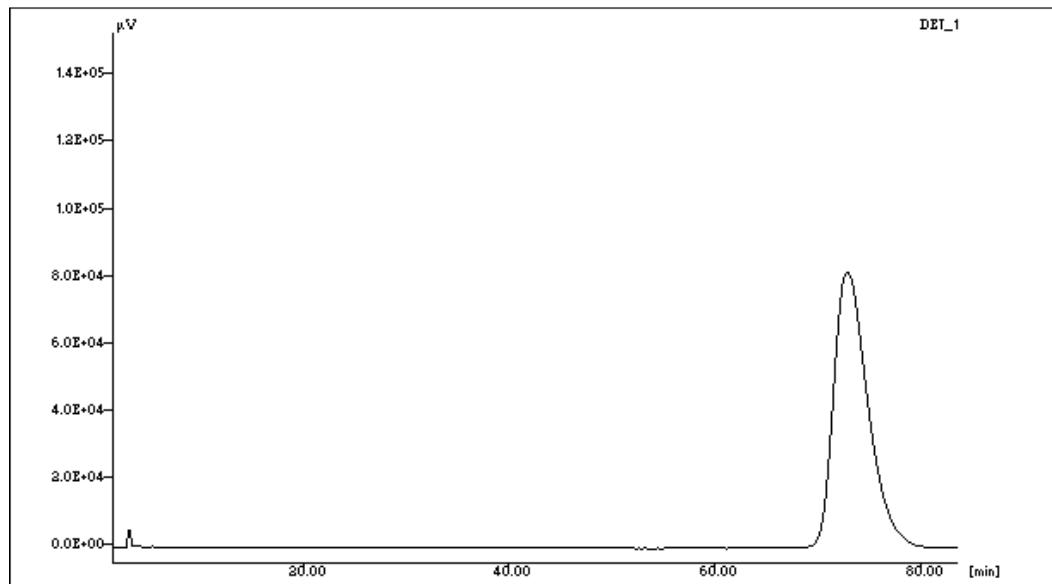
Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	46.24	1.826	678818.25
2	70.03	98.174	36488559.50

Total Area of Peak = 37167377.75 [μV.Sec]



After single recrystallization



File name : vgb351-crystal087.CH1

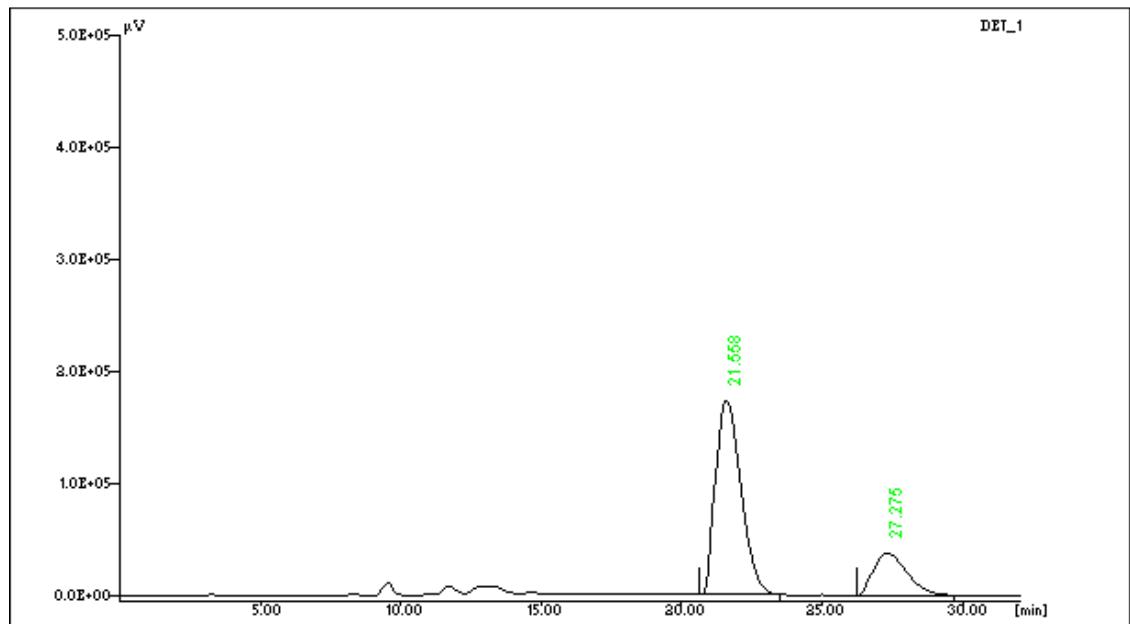
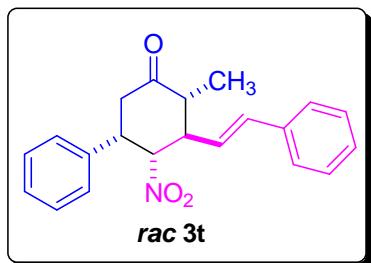
Injection Date : 11-Sep-2015 13:42:16

Curr. Date : 19-Sep-2015 13:14:24

Control Method :RC

Name	RT	%Area	Area[$\mu\text{V}.\text{Sec}$]
1	71.11	100.000	18058443.25

Total Area of Peak = 18058443.25 [$\mu\text{V}.\text{Sec}$]



File name : vgb-474-4th spot428.CH1

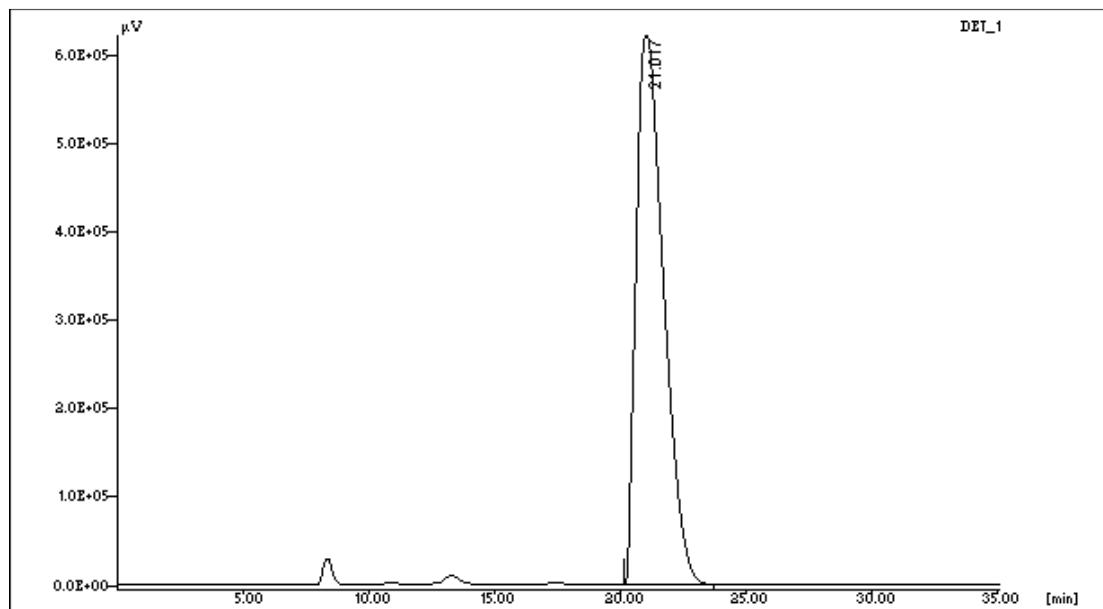
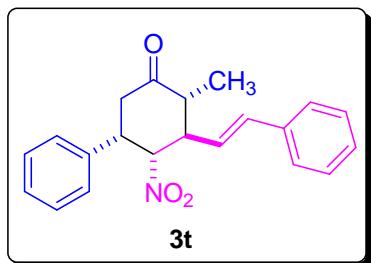
Injection Date :12-Apr-2016 11:31:48

Curr. Date : 12-Apr-2016 12:05:04

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	21.55	78.074	10309142.00
2	27.27	21.926	2895186.50

Total Area of Peak = 13204328.50 [μV.Sec]



File name : vgb-473-4th spot429.CH1

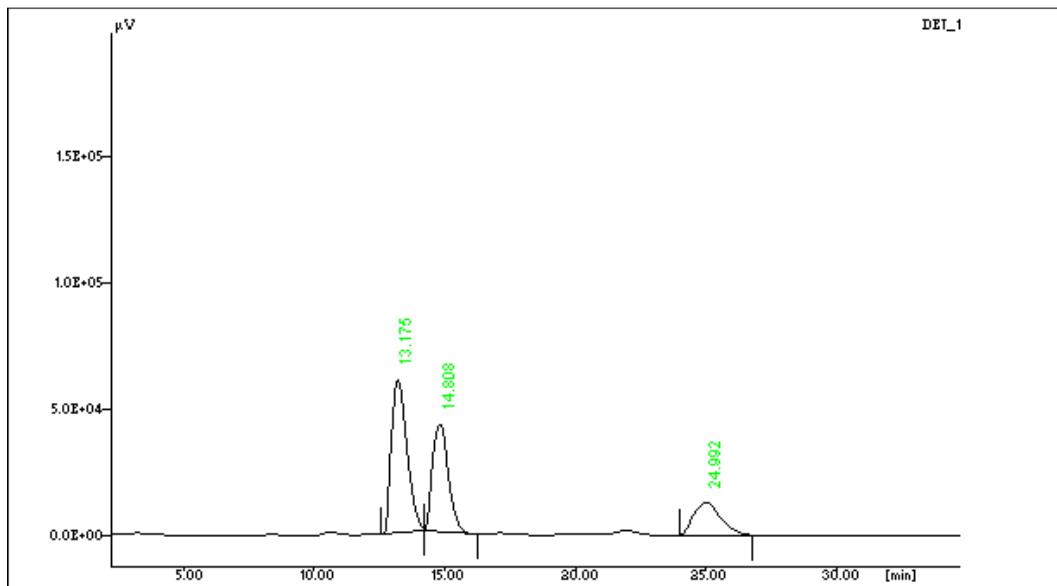
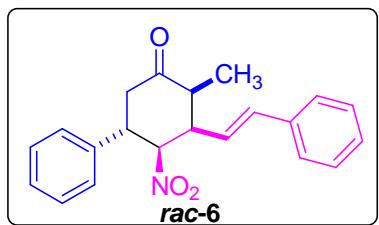
Injection Date :12-Apr-2016 12:05:58

Curr. Date : 12-Apr-2016 12:42:06

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	21.01	100.000	44500176.00

Total Area of Peak = 44500176.00 [μV.Sec]



File name : vgb-474-3rd spot430.CH1

Injection Date :12-Apr-2016 12:44:38

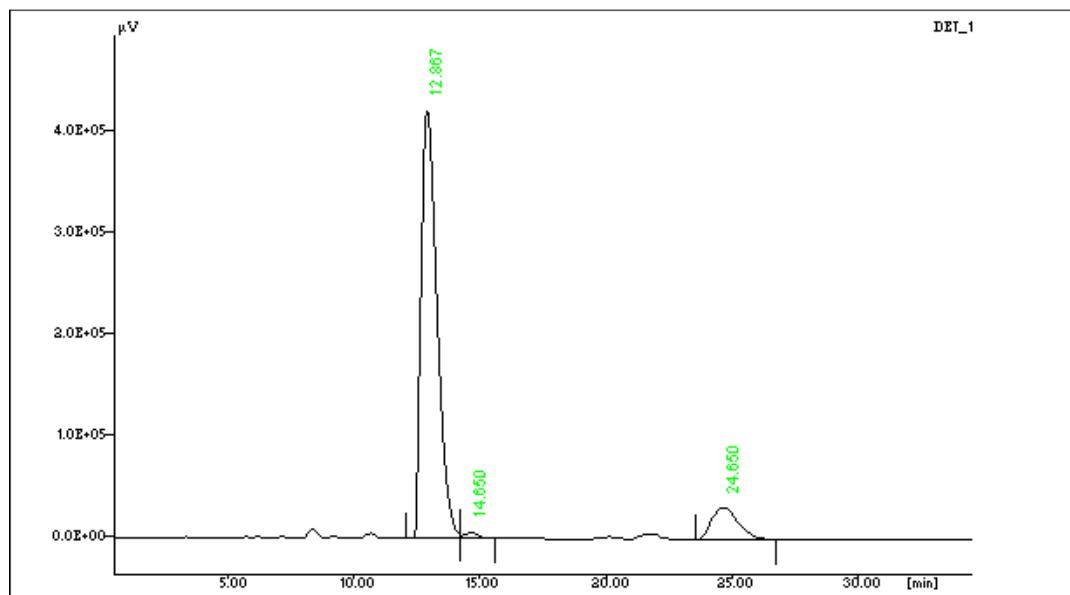
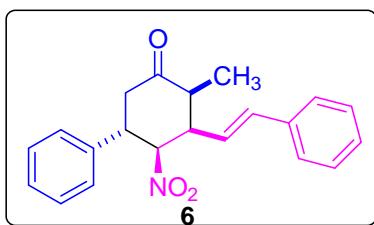
Curr. Date : 12-Apr-2016 15:11:26

Control Method :RC

Name	RT	% Area	Area[μV.Sec]
1	13.17	47.518	22479240.14
2	14.80	34.164	22682691.65
3*	24.99	18.318	8713607.50

Total Area of Peak = 4752049.92 [μV.Sec]

* Peak with RT 24.99 is due to unidentified diastereoisomer.



File name : vgb-473-3rd spot431.CH1

Injection Date :12-Apr-2016 14:39:10

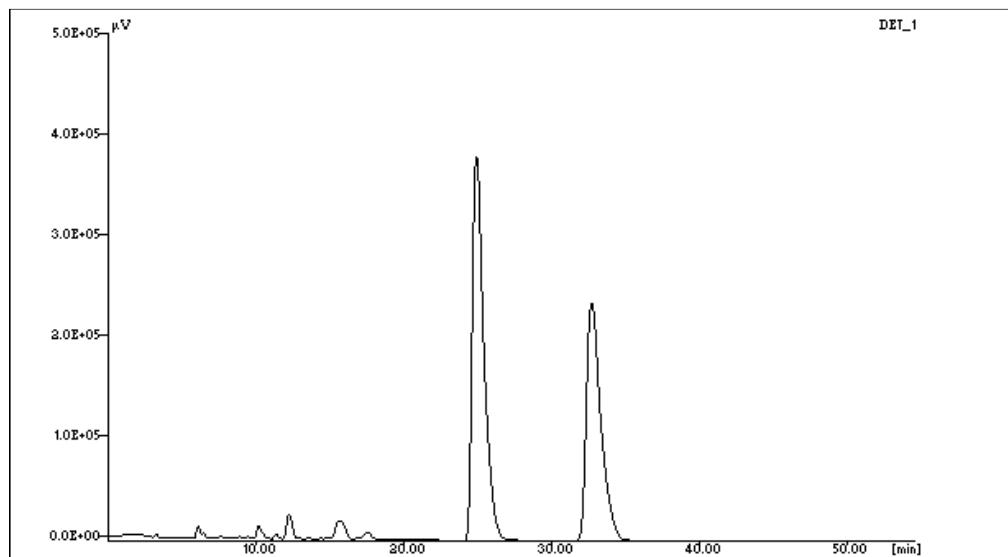
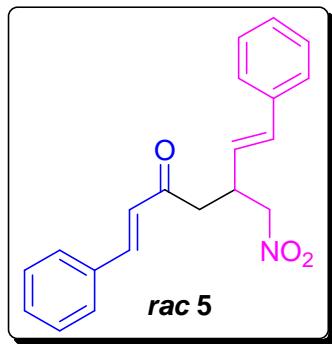
Curr. Date : 12-Apr-2016 15:13:14

Control Method :RC

Name	RT	% Area	Area[µV.Sec]
1	12.86	87.627	16817696.31
2	14.65	1.039	199369.69
3*	24.65	11.334	2175305.00

Total Area of Peak = 19192371.00 [µV.Sec]

* Peak with RT 24.65 is due to unidentified diastereoisomer.



File name : vgb-415-*rac*-linear product238.CH1

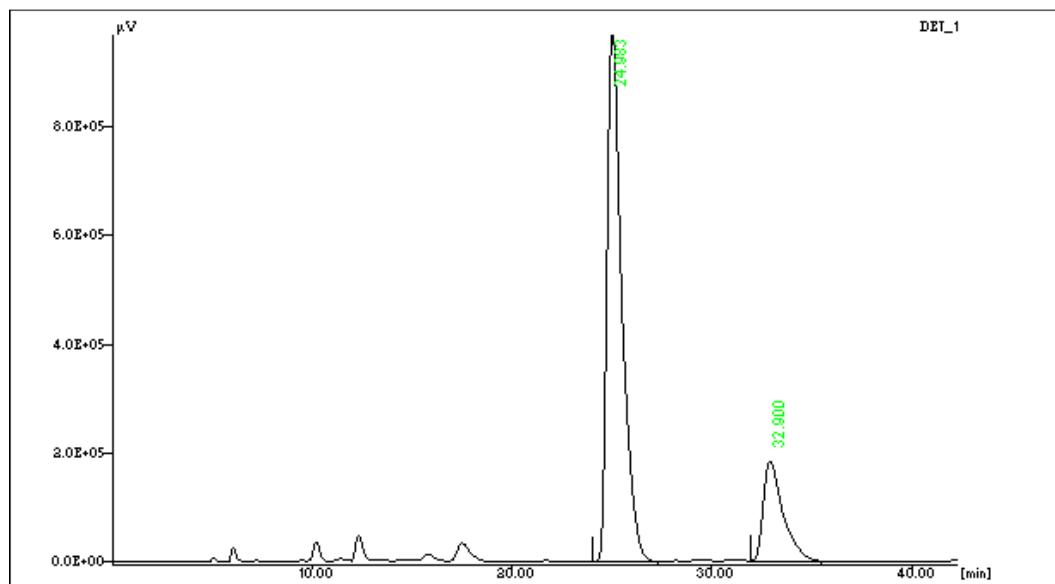
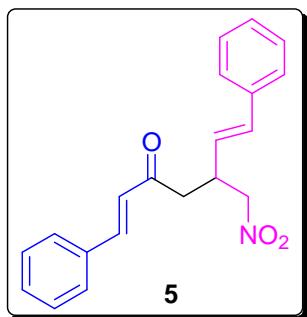
Injection Date : 15-Jan-2016 13:44:50

Curr. Date : 1-Feb-2016 14:39:30

Control Method :RC

Name	RT	% Area	Area[$\mu\text{V}.\text{Sec}$]
1	24.85	55.864	18345720.114
2	32.65	44.136	14494032.507

Total Area of Peak = 32839752.621 [$\mu\text{V}.\text{Sec}$]



File name : RC-546-linear product239.CH1

Injection Date :15-Jan-2016 14:42:24

Curr. Date : 1-Feb-2016 14:40:32

Control Method :RC

Name	RT	%Area	Area[μ V.Sec]
1	24.98	79.648	45557076.195
2	32.90	20.352	11641050.000

Total Area of Peak = 57198126.195 [μ V.Sec]