Supporting Information for

Microwave-assisted catalytic allyation of aldehydes promoted by a mesoporous silica-supported BINOL ligand in solid media

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Experimental

1. General Methods.

1.1. Materials and general methods.

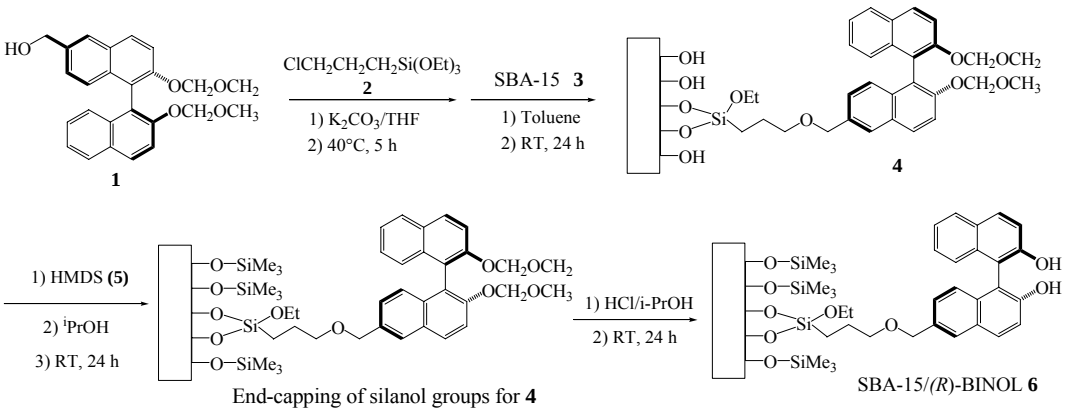
All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using standard Schlenk techniques. THF were distilled from sodium benzophenone ketyl, and dichloromethane from calcium hydride. Aldehydes and i-PrOH was distilled before use. Commercial reagents were used without further purification unless otherwise noted. Triblock PEO-PPO-PEO copolymer **P123** [$HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2\text{-}CH_2O)_{20}H$], 3-(chloropropyl)triethoxysilane, BINOL, Titanium(IV) isopropoxide, HMDS [$N(SiMe_3)_2$] and aldehydes were purchased from Sigma-Aldrich Company Ltd. and used as received. SBA-15 (pore size 7.6 nm) and was synthesized and characterized as described in our previous reports (a) Li, H. X.; Zhang, F.; Wan, Y.; Lu, Y. F. *J. Phys. Chem. B:* **2006**, *110*, 22942. b) Wan, Y.; Zhang, F.; Lu, Y. F.; Li, H. X. *J. Mol. Catal. A: Chem.* **2007**, *267*, 165. c) Wan, Y.; Chen, J.; Zhang, D. Q.; Li, H. X. *J. Mol. Catal. A: Chem.* **2006**, *258*, 89). 6-Hydroxymethyl-2,2'-bis(methoxymethyl)-1,1'-binaphthol **1** was readily prepared following our previous procedure from commercially available BINOL (Liu, G. H.; Tang, W. J.; Fan, Q. H. *Tetrahedron,* **2003**, *59*, 8603). The representative aromatic aldehydes were chosen as model substrates to test the heterogeneous ligand. The retention times was determined by comparing the retention times with those of commercially available substituted phenyl homoallylic alcohols and ketones. HPLC was performed on a

Shimadzu SPD-10AVP with a UV-Vis detector and chiral separations were performed using Kromasil 100-5-TBB chiralcel columns (Φ0.46 x 25 cm).

1.2. Characterization

The X-ray powder diffraction (XRD) experiments were carried out on a Rigaku D/Max-RB diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM2010 electron microscope, operated at an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectra were collected with a Nicolet Magna 550 spectrometer by using the KBr method. N2 adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas (S_{BET}) of samples were determined from the linear parts of BET plots (p/p_0 = 0.05-0.95). TG–DTA curves were recorded on a Perkin Elmer 7-series thermogravimetric analyzer. The ^{29}Si CP/MAS NMR and ^{13}C CP/MAS NMR spectra were recorded at 79.5 and 100.6 MHz, respectively, using a Bruker AV-400 spectrometer.

2. Synthetic procedures.



2.1. Preparations of the mesoporous silica-supported chiral ligand.

2.1.1. Immobilization of modified BINOL on mesoporous silicas **4**: The typical procedures as follows: Under argon atmosphere, to a stirred suspension of **1** (0.20 g, 0.50 mmol) and K_2CO_3 (0.21 g, 1.50 mmol) in 10 mL dry THF was added dropwise a solution of 3-chloropropyltriethoxysilane (0.12 g, 0.50 mmol) in 2 mL of dry THF at room temperature. The resulting mixture was stirred at 40 ºC for 5h. The reaction was

completed by TLC. After filtration and evaporation of most of the solvent, the residues were used directly in following reaction. Then pure siliceous support [SBA-15 (poresize of 7.6), 1.0 g] was dehydrated at 125 ºC under 0.01 Torr for 4 h before the addition of the fresh above-products in dry toluene (25 mL). The resulting mixture was stirred and refluxed for 24 h under Argon atmosphere, during which time the BINOL derivatives were grafted onto the supports. After being cooled, filtrated, and washed thoroughly with toluene and C_2H_5OH : CH_2Cl_2 (v:v = 1:1), the solid was dried at 60 ºC under reduced pressure overnight to afford the mesoporous ligand **4** (1.18 g, 56.3% relative to **1**) in the form of a white powder (Scheme 1). IR (KBr) cm^{-1}: 3449 (m), 2983 (w), 2915 (w), 1642 (w), 1458 (w), 1078 (s), 961 (w), 806 (w), 573 (w), 456 (s). Anal. Found: C, 10.62; H, 1.77%.

2.1.2. End-capping of silanol groups (trimethylsilylation) of **4:** Under argon atmosphere, a suspension of **4** (1.15 g) and HMDS [$(CH_3)_3Si)_2N$] (5 mL, 0.025 mol) in 25 mL dry toluene were stirred overnight. The volatiles were stripped on a rotary evaporator and the dry powder was washed three times with 10 mL of dry acetone by centrifugation and finally dried under vacuum at 60 °C for 6 h to afford **5** (1.63 g, 96.0% relative to **4**) in the form of a white powder (Scheme 1). IR (KBr) cm^{-1}: 3480 (w), 2964 (w), 1663 (m), 1635 (b), 1563 (w), 1455 (w), 1078 (s), 857 (b), 805 (w), 710 (w), 657 (w), 582 (w), 462 (m). Anal. Found: C, 26.69; H, 3.63%.

2.1.3. Removal of the MOM-protected groups **6**: Under argon atmosphere, to a stirred suspension of **5** (0.80 g) in 5 mL CH_2Cl_2 was added a solution of ^{i}PrOH/HCl (6.0 N, 5 mL). After stirring overnight at room temperatrue and evaporation most of the solvent, the residue was diluted with CH_2Cl_2 and washed with an aqueous saturated solution of $NaHCO_3$. The resulting solid was filtered off, washed successively with water, acetone, and CH_2Cl_2, and finally dried at 60°C under vacuum for 10 h. The mesoporous ligand **6** is in the form of a white powder (0.69 g). IR (KBr) cm^{-1}: 3431 (s), 3076 (w), 2964 (w), 2924 (w), 1657 (m), 1510 (w), 1444 (w), 1388 (w), 1320 (w), 1088 (s), 952 (w), 848 (m), 804 (w), 756 (w), 694 (w), 565 (w), 461 (m) cm^{-1}. (IR spectrum was shown in Fig.S1); Anal. Found:: C 23.42, H 2.91; S_{BET}: 214 m^2/g, V_{pore}: 0.41 cm^2/g, d_{pore}: 3.5 nm; ^{29}Si MAS/NMR (300 MHz): Q^4 (δ = -113 ppm), T^2 (δ = -63 ppm) and T^3 (δ = -71 ppm); ^{13}C CP/MAS (161.9 MHz): 128.7, 50.5, 45.6, 26.3, 10.0 and 0.1 ppm; Nitrogen

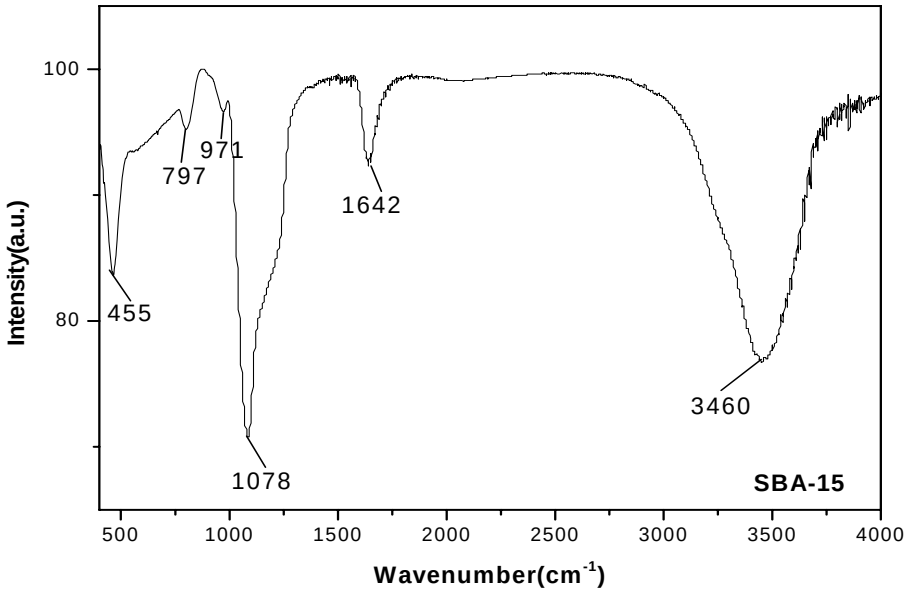
adsorption-desorption isotherms of SBA-15 (**3**) and SBA-15/BINOL (**6**), the TEM images of **6**, the powder XRD patterns of SBA-15 (**3**) and SBA-15/BINOL (**6**) and the TG and DTA of SBA-15/BINOL (**6**) were shown in Fig.S2-S5.

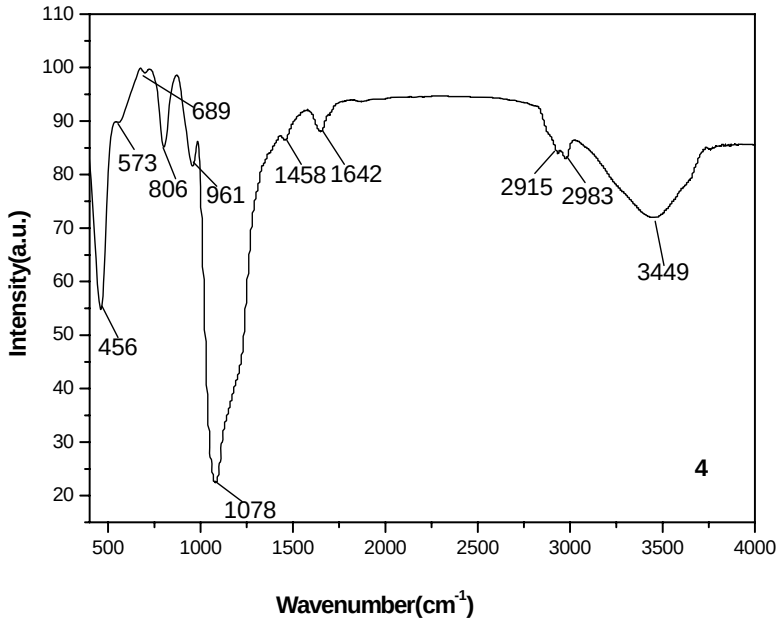
3. General Procedure for Catalytic Allyation of Aldehydes

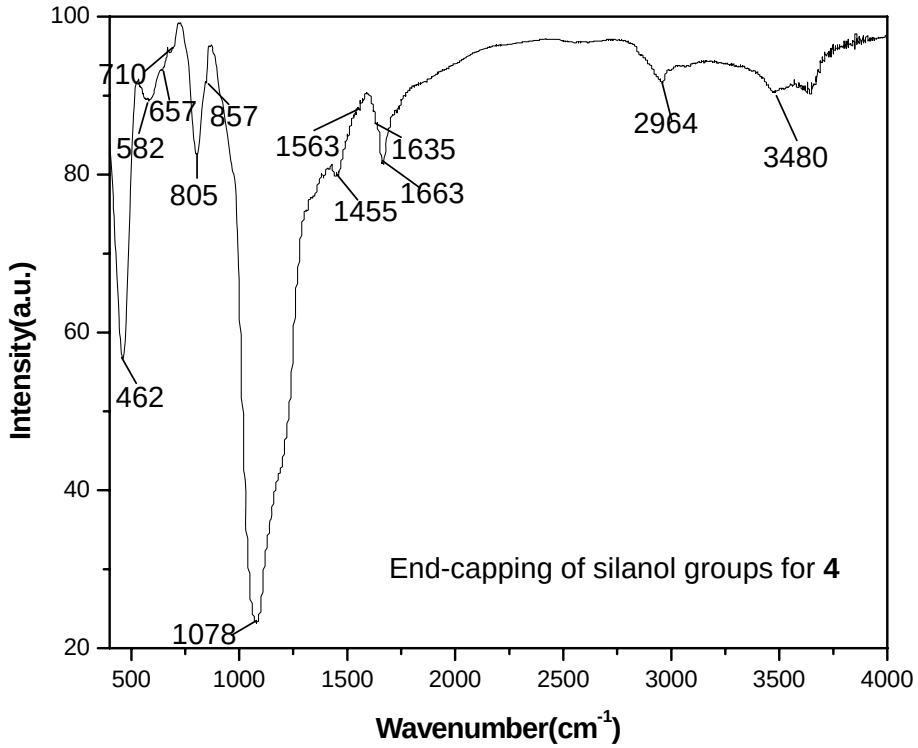
3.1 General Procedure for Catalytic Allyation of Aldehydes under microwave irradiation in solid media. Under argon atmosphere, $Ti(OiPr)_4$ (4.47 μL, 0.015 mmol) was added to a suspension of SBA-15/BINOL (**6**) [17 mg, 0.015 mmol BINOL, 10 mol% (ligand to benzaldehyde)] in 2 mL of ^{i}PrOH at room temperature and the mixture was stirred at ambient temperature for 10 min. After being filtrated, the solids were transferred to a thick walled Pyrex tube followed by the addition of tetraallyltin (9.52 μL, 0.041 mmol) and benzaldehyde (15.22 μL, 0.15 mmol). The tube was positioned in a MAS-1 single mode cavity microwave from Sineo Microwave Chemistry Technology (China) Co., LTD, Shanghai, producing continuous irradiation at 2.45 GHz, and the mixture was irradiated with 700W for 15 minutes. Then 2 mL of ethyl acetate was added. After being filtrated, the solid was washed several times with ethyl acetate, which were employed directly for recycling-experiments. The mother liquid was were dried over Na_2SO_4 and concentrated. The residue was further purified by flash column chromatography on silica gel (eluent: Et_2O) to afford 1-phenyl-3-buten-l-ol as a colorless liquid.

3.2 General Procedure for Catalytic Allyation of Aldehydes in Solvent Conditions. Under argon atmosphere, $Ti(OiPr)_4$ (4.47 μL, 0.015 mmol) was added to a suspension of SBA-15/BINOL (**6**) [17 mg, 0.015 mmol BINOL, 10 mol% (ligand to benzaldehyde)] in 2 mL of ^{i}PrOH (or water) at room temperature and the mixture was stirred at ambient temperature for 10 min followed by the addition of tetraallyltin (9.52 μL, 0.041 mmol) under stirring., After 10 min, benzaldehyde (15.22 μL, 0.15 mmol) was added with a microsyringe at ambient temperature. The reaction mixture was allowed to stir for 12h. The reaction mixture was quenched with 2.0 mL of 1.0N hydrochloric acid solution. After being filtrated, the mother liquid was extracted with 1.0 mL of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was further purified by flash column chromatography on silica gel (eluent: Et_2O) to afford 1-phenyl-3-buten-l-ol as a colorless liquid.

Figure S1. FTIR spectra of SBA-15 and **4-6**.






710
657
857
582
805
1563
1635
1663
1455
2964
3480
462
1078
End-capping of silanol groups for 4
Intensity(a.u.)
Wavenumber(cm-1)

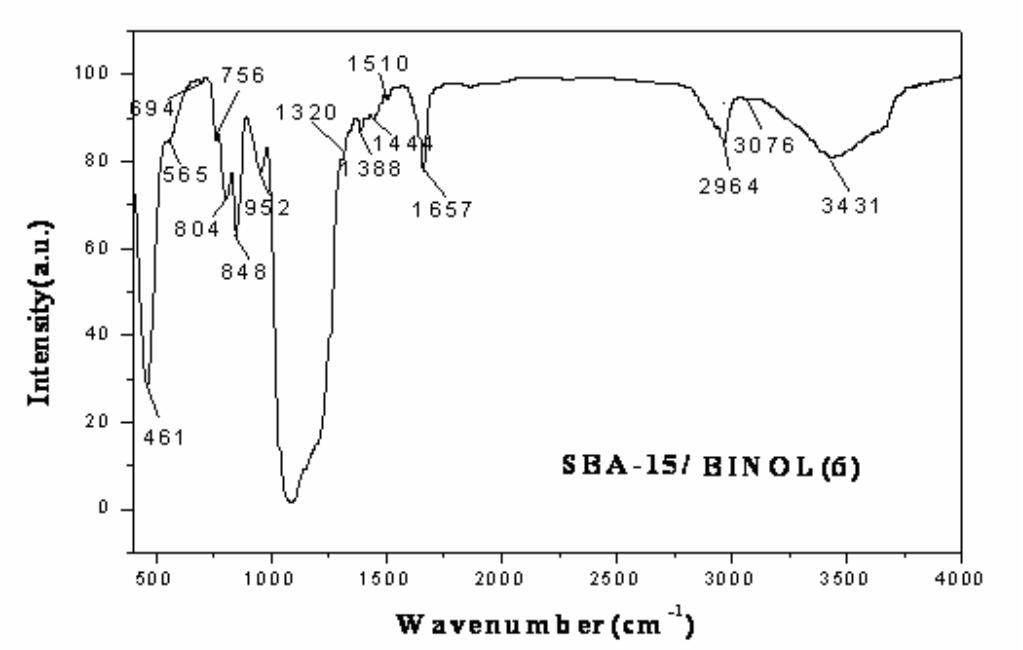

756
694
1510
1320
1444
1388
565
804
952
848
1657
2964
3076
3431
461
SBA-15/ BINOL (6)
Intensity(a.u.)
Wavenumber (cm-1)

Figure S2a. Nitrogen adsorption-desorption isotherms of SBA-15 (**3**) and SBA-15/BINOL (**6**).

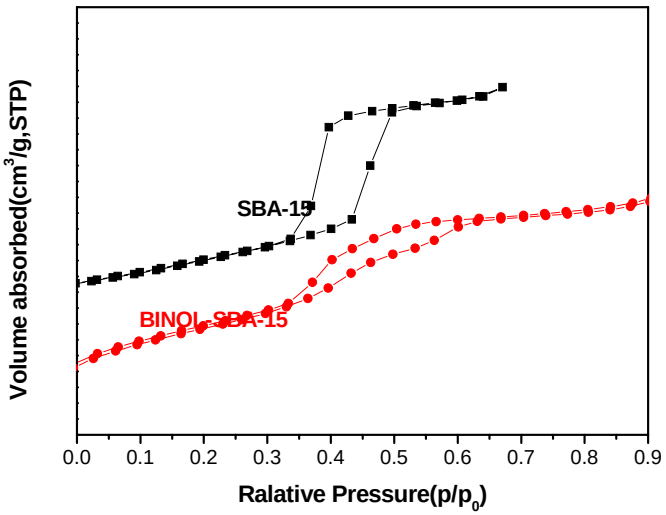
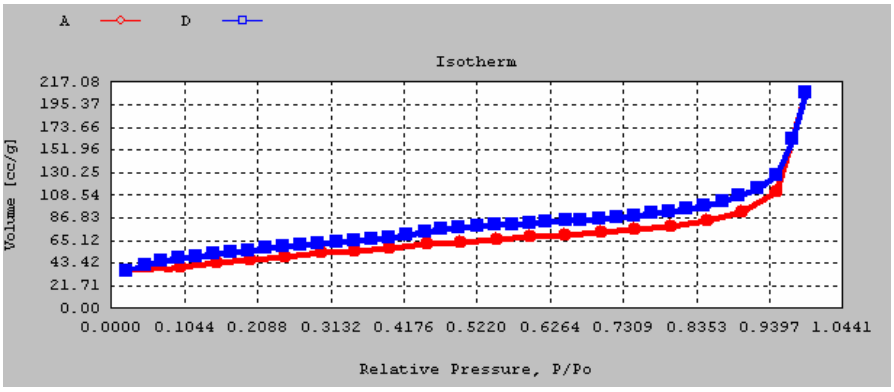


Figure S2b. Nitrogen adsorption-desorption isotherms and pore size distributions of SBA-15/BINOL (**6**) after recycling-experiments.



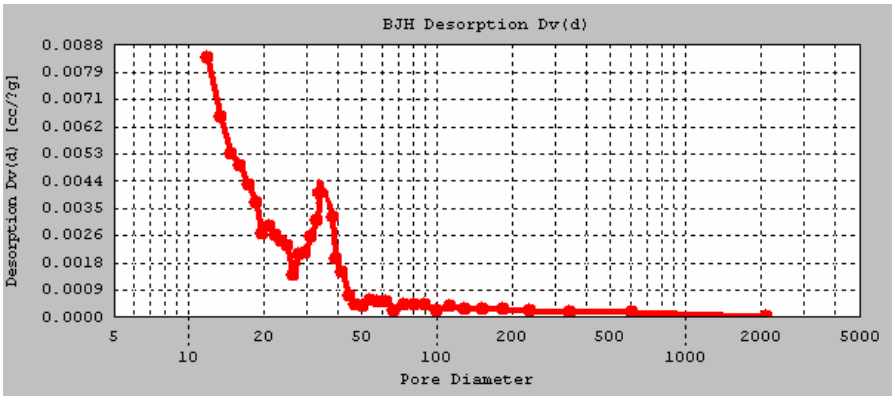
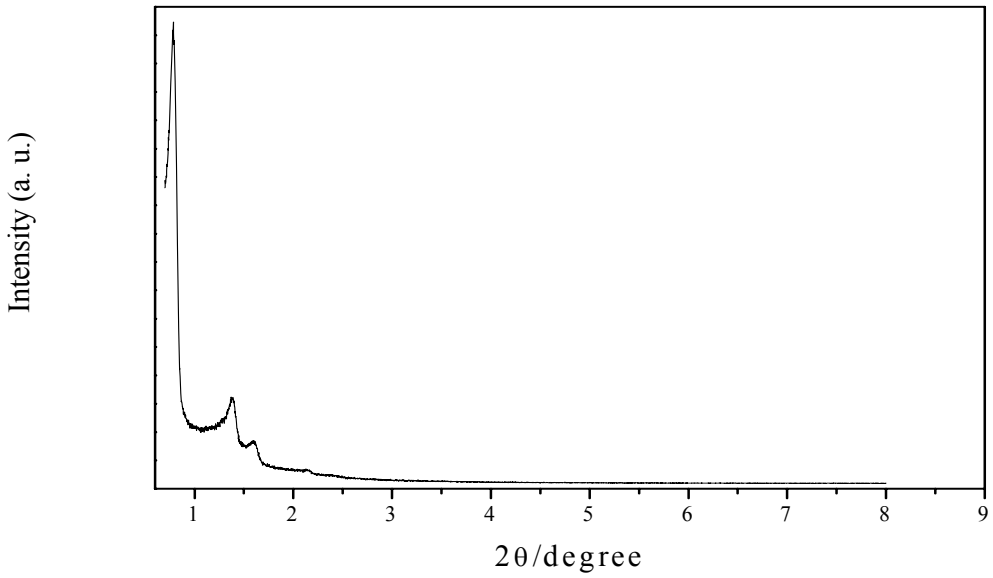


Figure S3. The powder XRD patterns of SBA-15 (**3**) and SBA-15/BINOL (**6**).

SBA-15 (**3**)



SBA-15/BINOL (**6**).

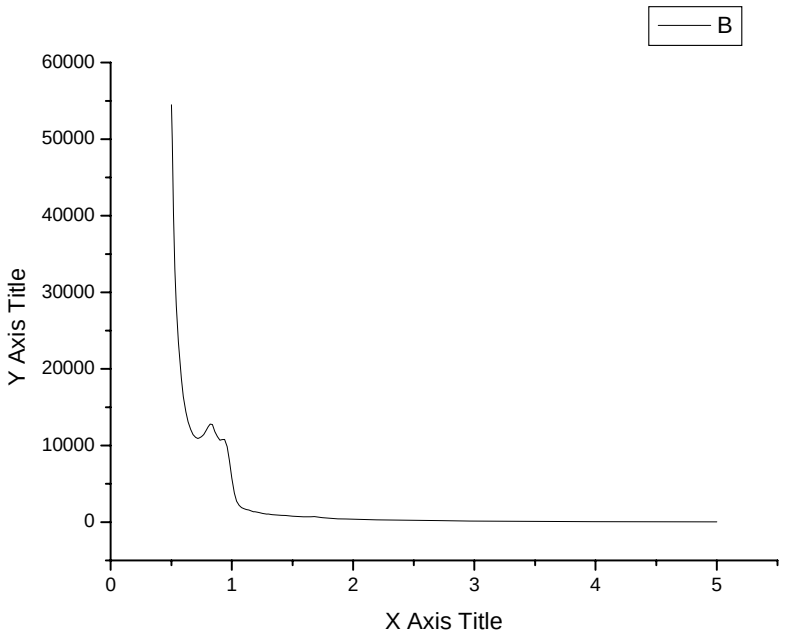


Figure S4. The TEM images of SBA-15/BINOL (**6**) viewed along [100] and [001] directions.

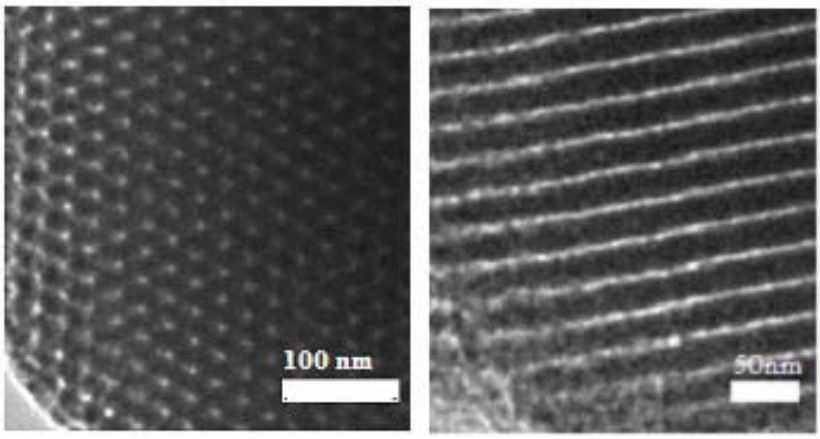


Figure S5. The TG and DTA of SBA-15/BINOL (**6**).

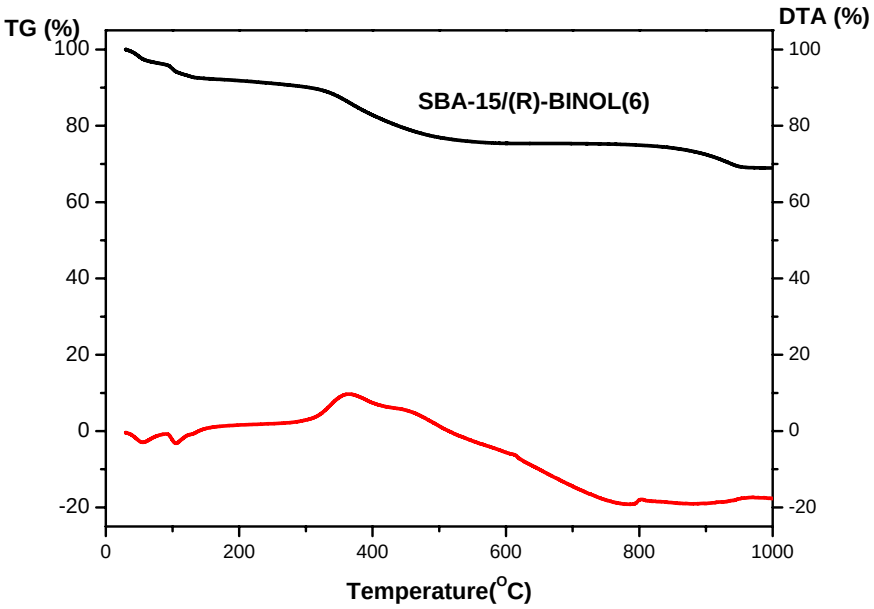
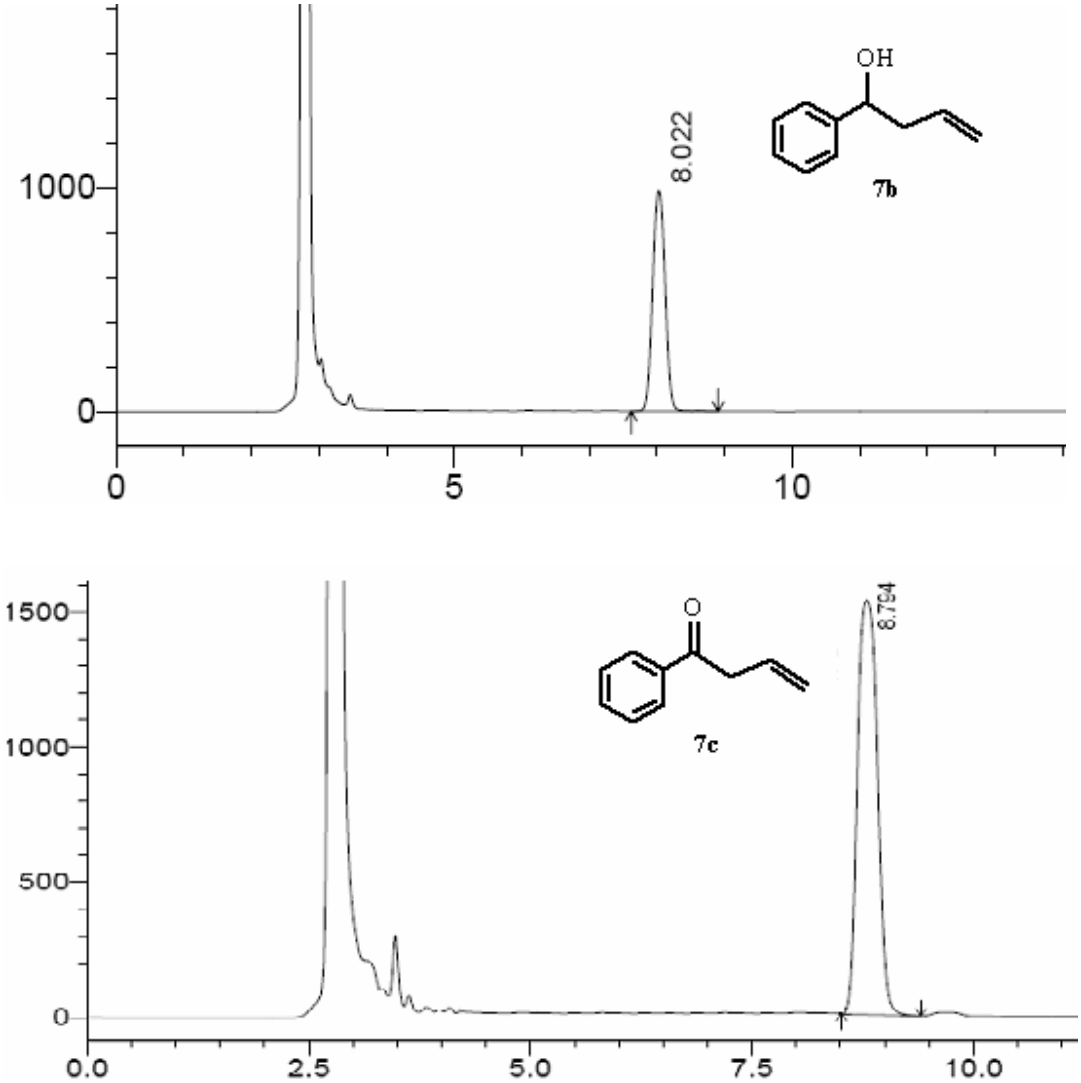
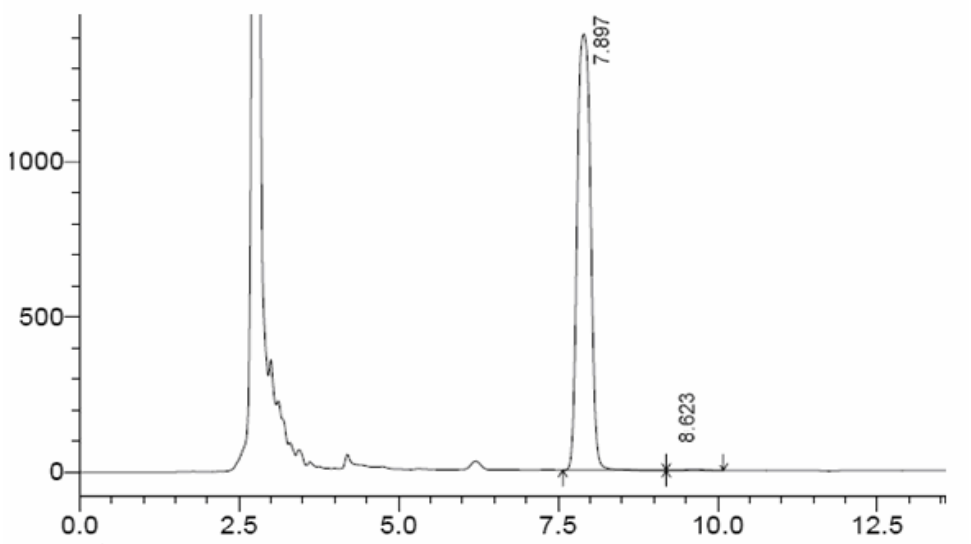


Figure S6 The Conversion of products on the basis of start material (aldehydes) and selectivity determined by HPLC peak area integration at 210 nm using a Shimadzu SPD-10AVP with a UV-Vis detector and the separations were performed using Kromasil 100-5-TBB chiralcel columns (Φ0.46 x 25 cm).

Compound 7a: (Kromasil 100-5-TBB: 1.0 mL/min, hex/IPA=99:1). Benzaldehyde: *t*: 4.3 min.



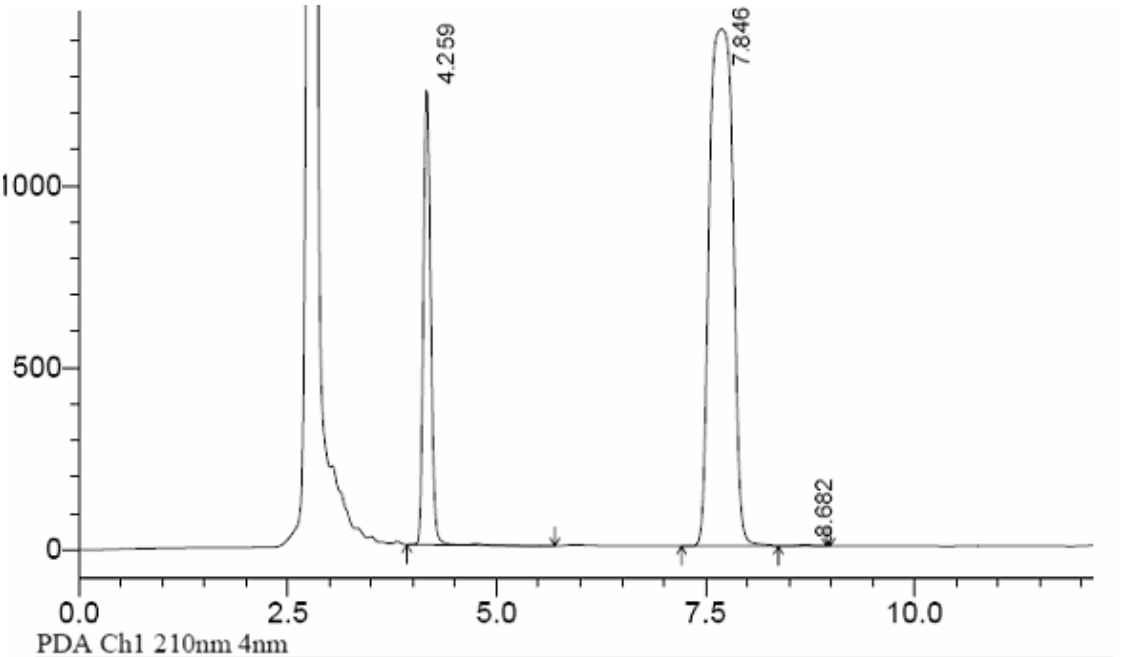
Data were obtained using **6** as catalyst and **7a** as a substrate.



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.897	20430951	1404885	99.718	99.770
2	8.623	57811	3234	0.282	0.230
Total		20488762	1408119	100.000	100.000

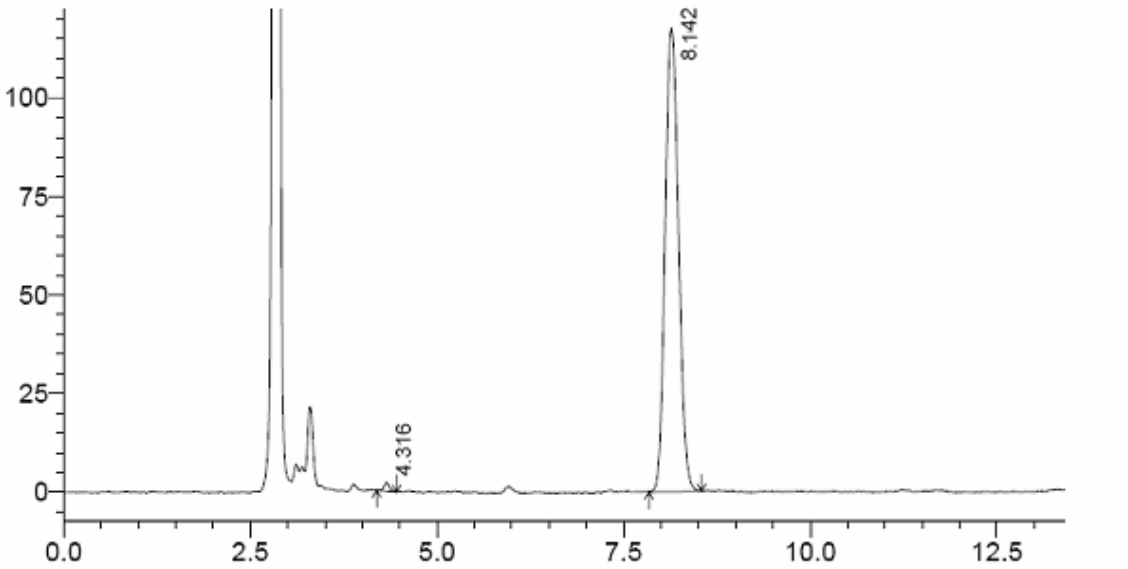
Data were obtained with 5% mol of **6** using **7a** as a substrate.



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.259	7563442	1249212	21.315	46.741
2	7.346	27890390	1420808	78.600	53.162
3	8.682	30164	2582	0.085	0.097
Total		35483996	2672602	100.000	100.000

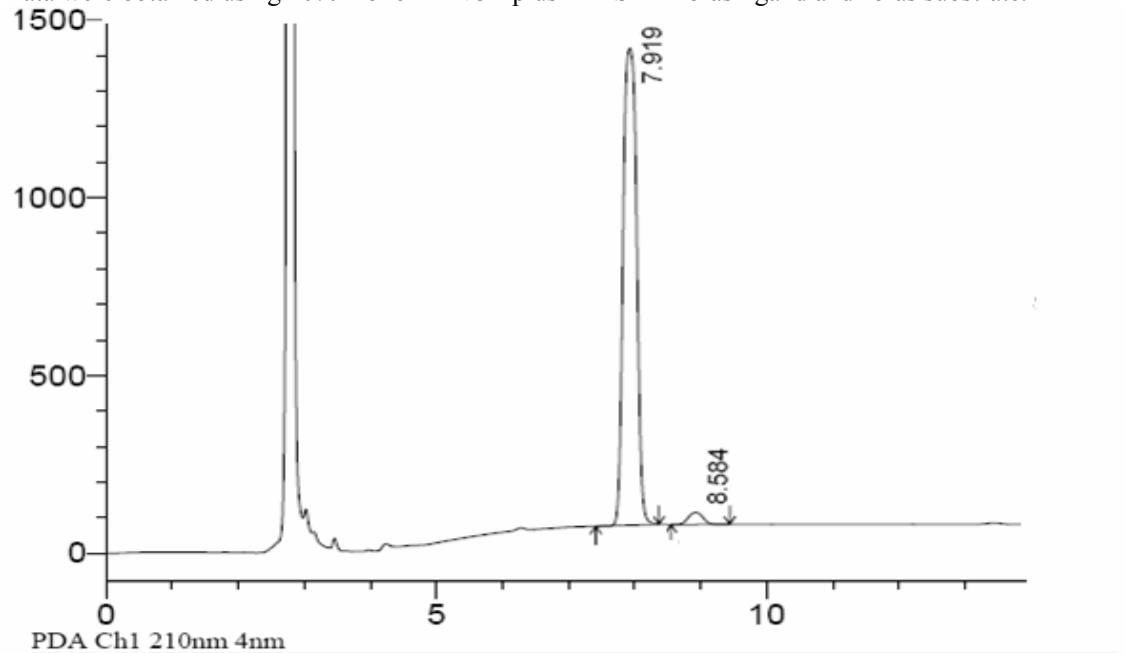
Data were obtained using 10% mol of BINOL as ligand and **7a** as a substrate.



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.316	10923	2235	0.738	1.864
2	8.142	1469006	117718	99.262	98.136
Total		1479930	119954	100.000	100.000

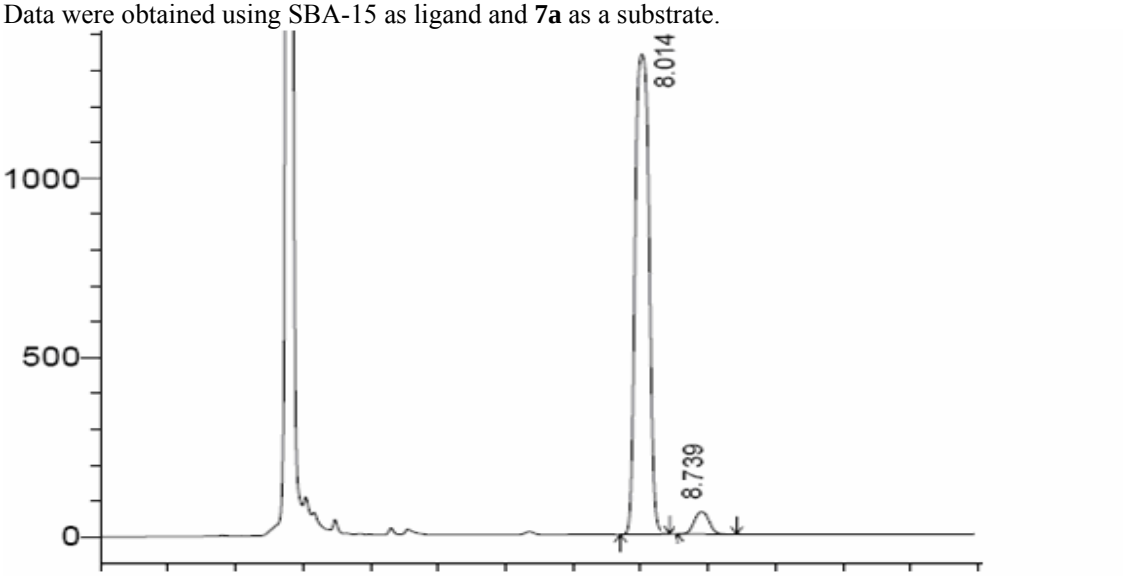
Data were obtained using 10% mol of BINOL plus TM-SBA-15 as ligand and **7a** as substrate.



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.919	18953168	1341362	97.282	97.546
2	8.584	529476	33743	2.718	2.454
Total		19482644	1375105	100.000	100.000

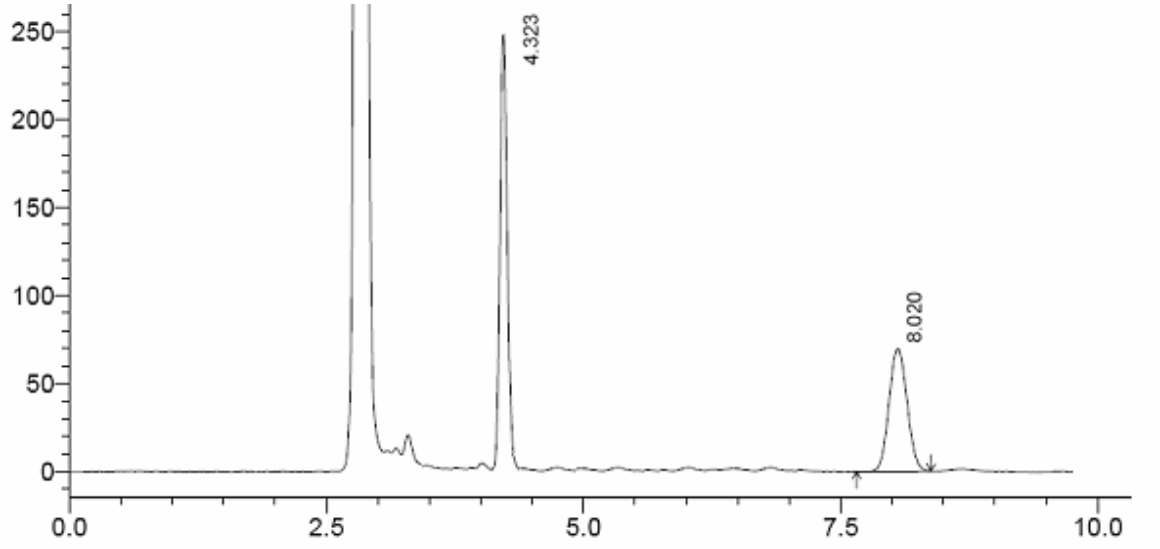
Data were obtained using SBA-15 as ligand and **7a** as a substrate.



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.014	19153067	1338900	95.315	95.579
2	8.739	941473	61933	4.685	4.421
Total		20094539	1400833	100.000	100.000

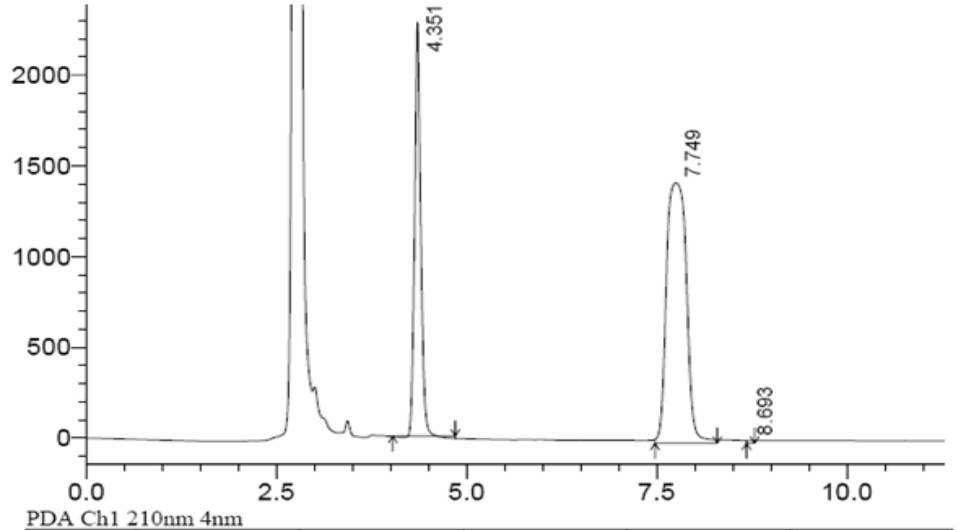
Data were obtained without titanium(IV) isopropoxide using **7a** as a substrate.



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.323	1184586	236693	58.180	77.267
2	8.020	851491	69638	41.820	22.733
Total		2036077	306331	100.000	100.000

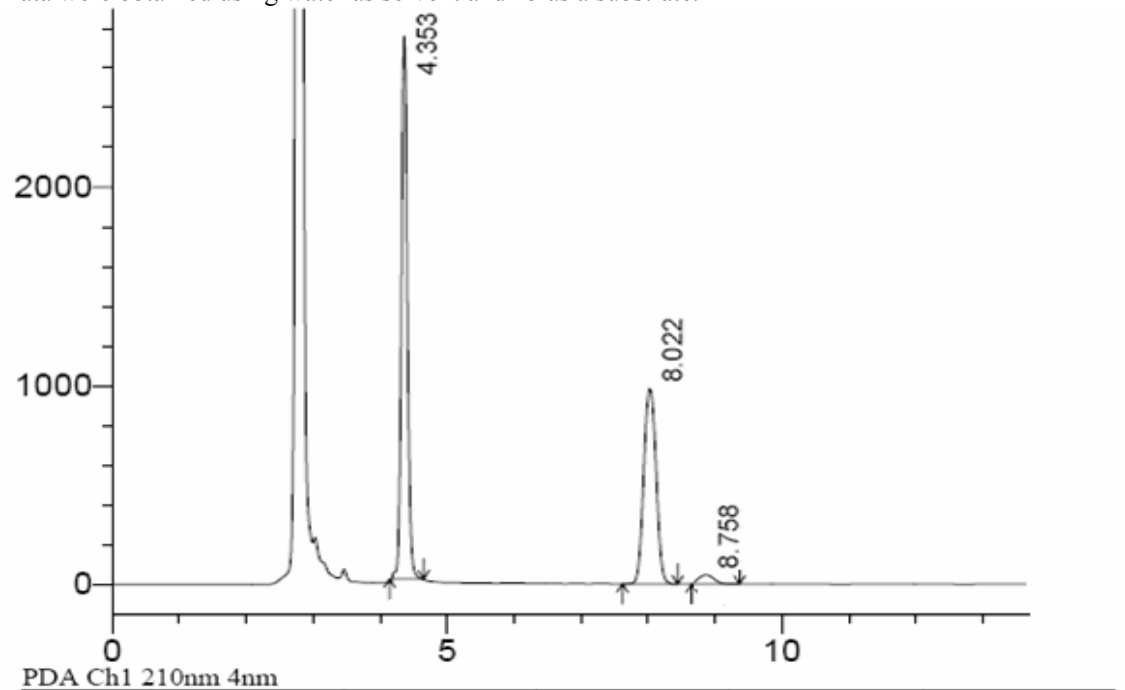
Data were obtained using isopropoxide as solvent and **7a** as a substrate.



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.351	12461706	2280188	32.202	61.137
2	7.749	26142379	1434656	67.555	38.467
3	8.693	94111	14774	0.243	0.396
Total		38698197	3729618	100.000	100.000

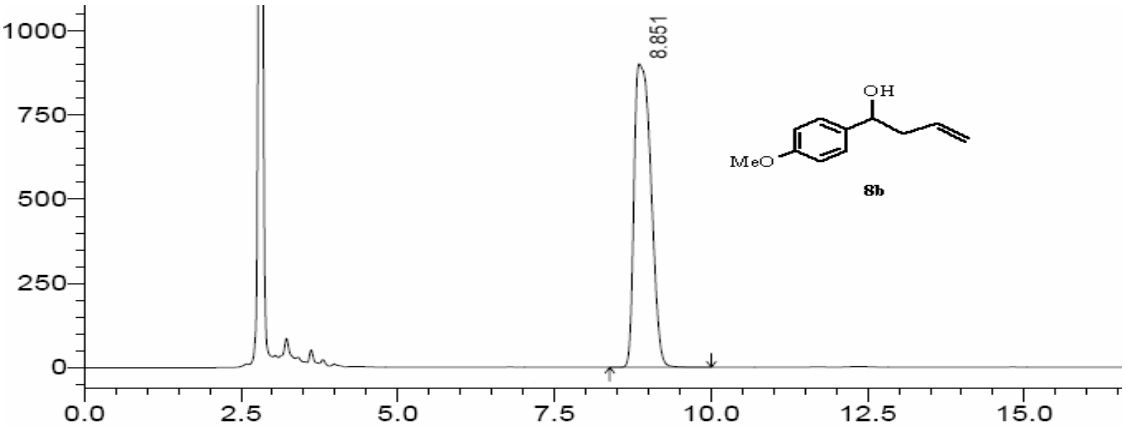
Data were obtained using water as solvent and **7a** as a substrate.

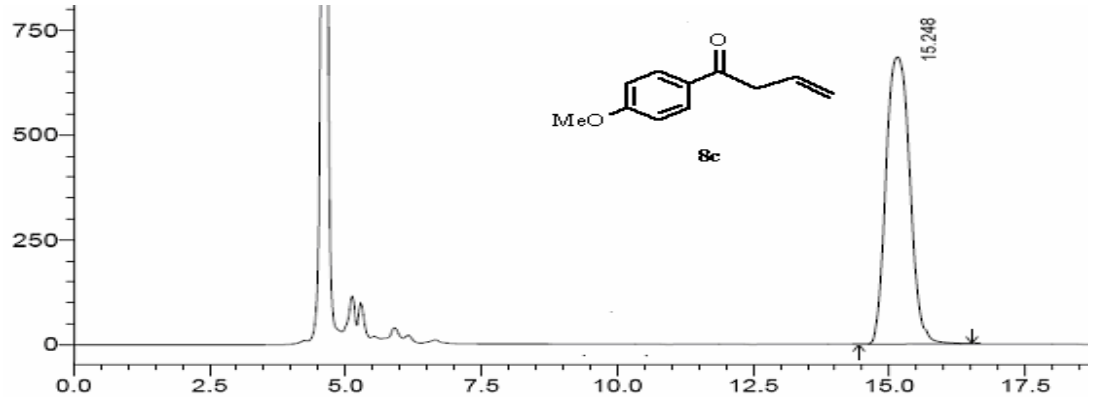


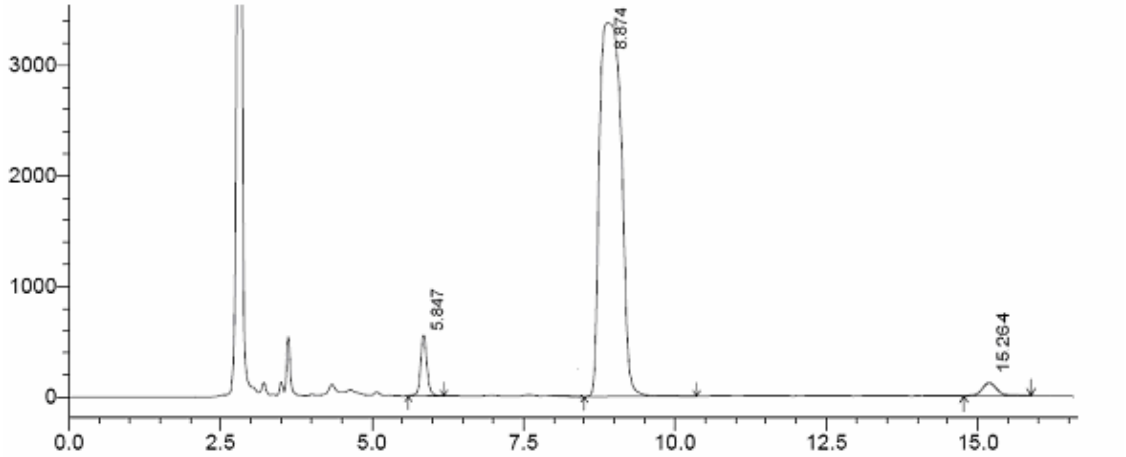
PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.353	16904661	2731795	55.795	72.643
2	8.022	12635261	982671	41.704	26.131
3	8.758	757670	46085	2.501	1.225
Total		30297592	3760552	100.000	100.000

Compound 8a: (Kromasil 100-5-TBB: 1.0 mL/min, hex/IPA=97:3). 4-methoxybenzaldehyde: *t*: 5.8 min.



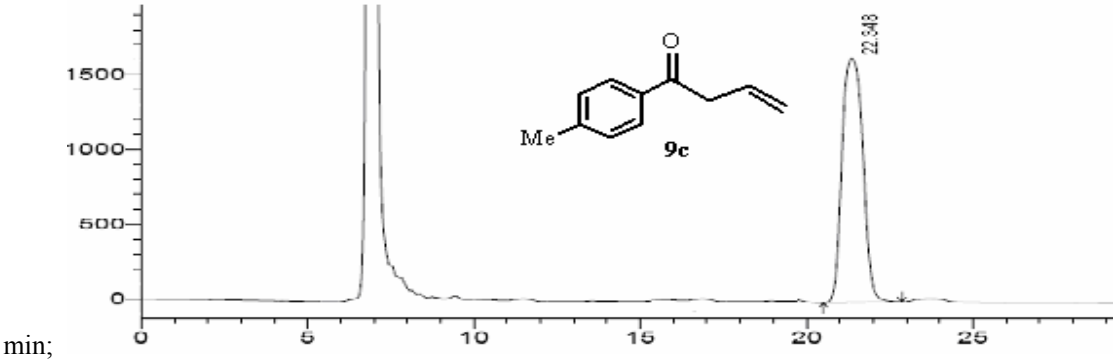


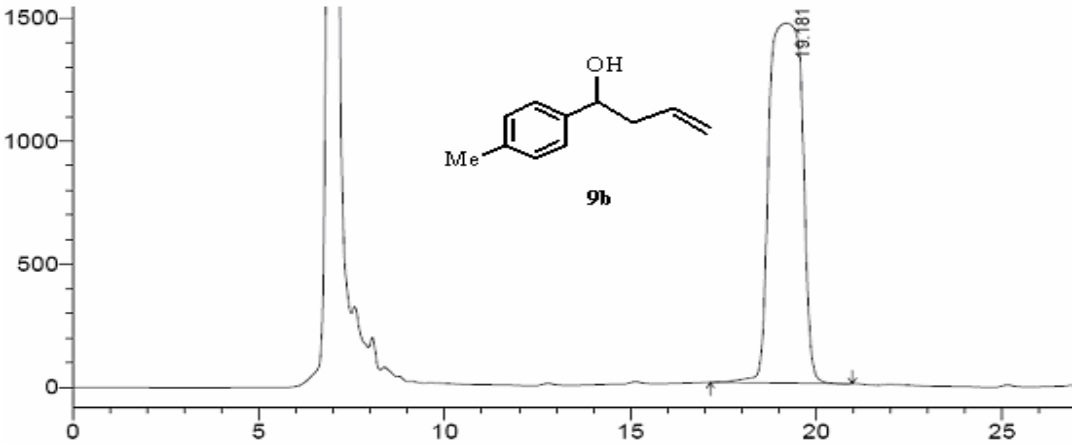


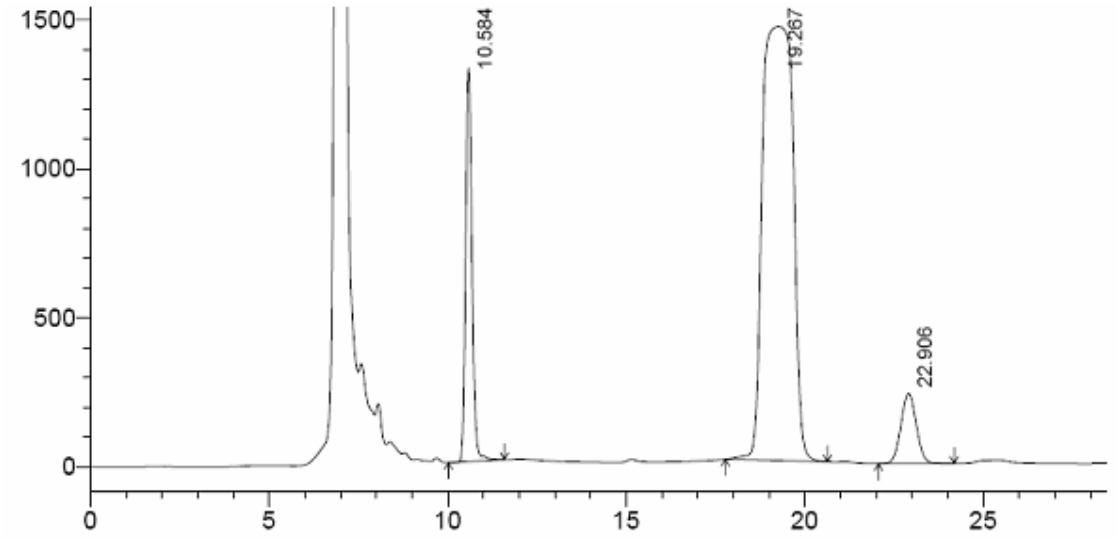
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.847	2954102	511021	3.343	10.008
2	8.874	84167561	3377805	95.344	85.871
3	15.264	1155915	44760	1.312	4.121
Total		88277578	3933587	100.000	100.000

Compound 9a: (Kromasil 100-5-TBB: 0.4mL/min, hex/IPA=99:1). 4-methyl-benzaldehyde: *t*: 10.6 min;



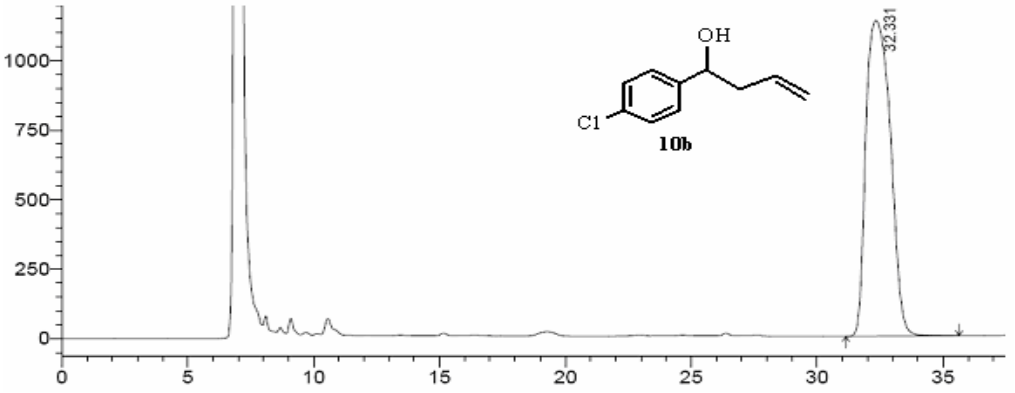


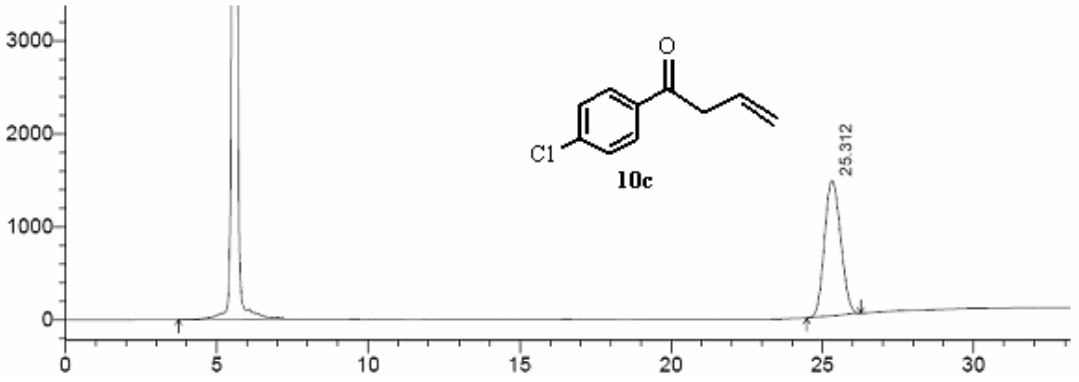


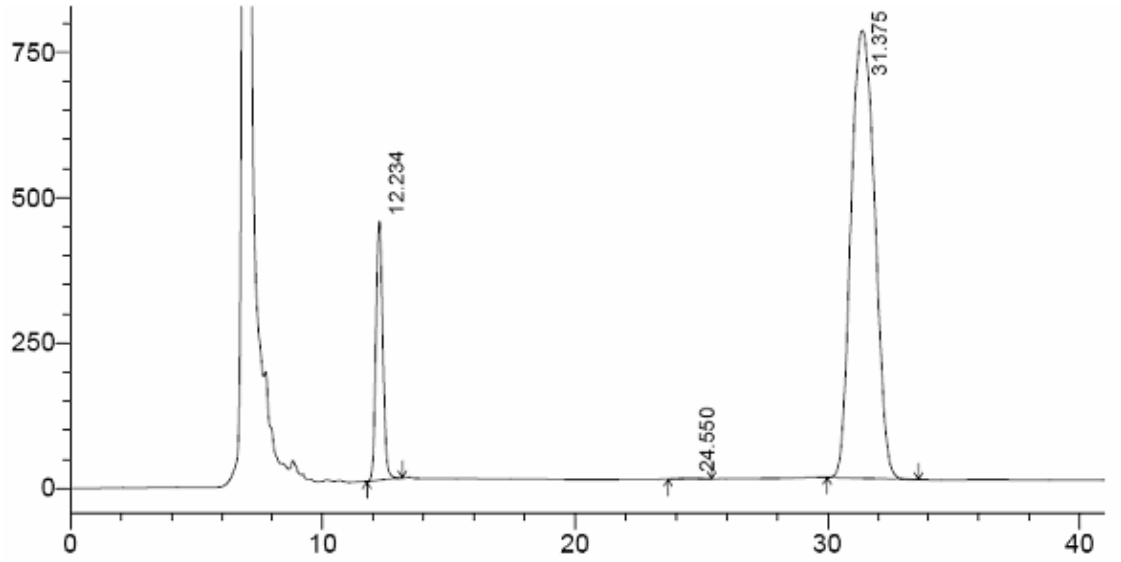
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.584	16337560	1318539	14.885	43.828
2	19.267	86384924	1455222	78.703	48.372
3	22.906	7038187	234656	6.412	7.800
Total		109760670	3008417	100.000	100.000

Compound 10a: (Kromasil 100-5-TBB: 0.4 mL/min, hex/IPA=99:1). 4-chloro-benzaldehyde: *t*: 12.2 min.



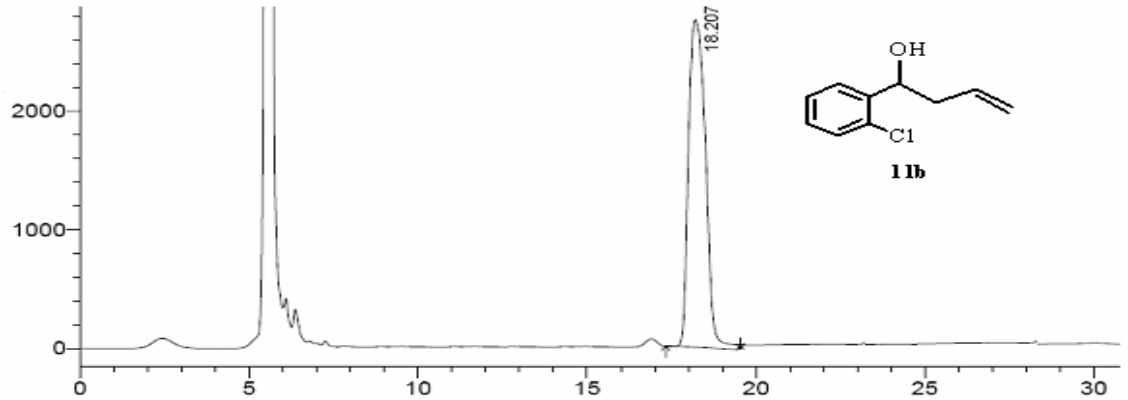


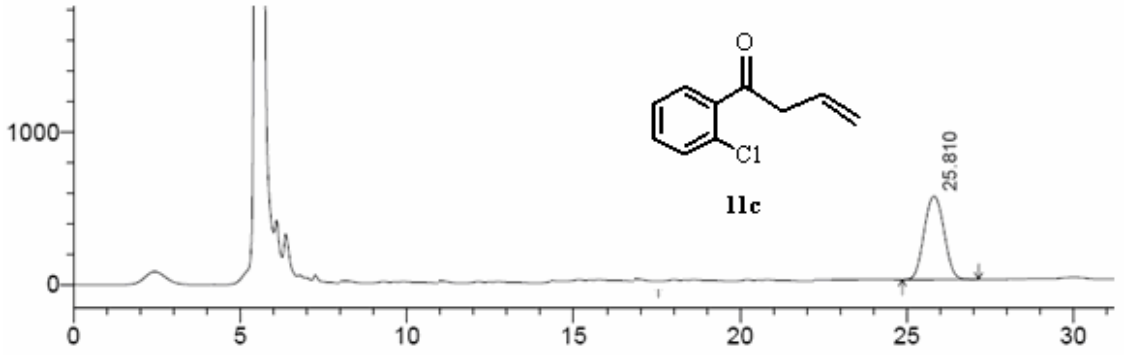


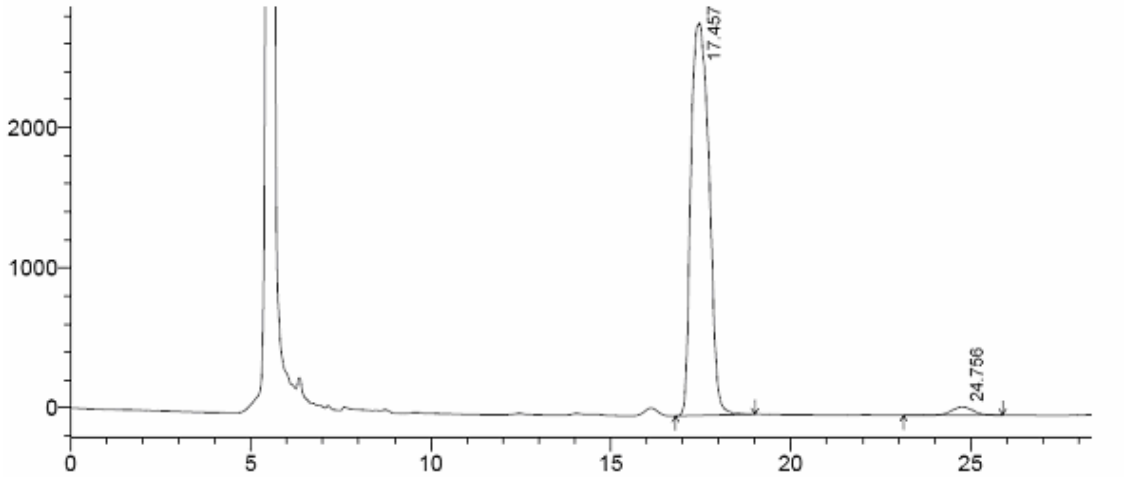
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.234	8411930	445938	14.276	36.639
2	24.550	102632	1878	0.174	0.154
3	31.375	50407448	769300	85.549	63.207
Total		58922009	1217116	100.000	100.000

Compound 11a: (Kromasil 100-5-TBB: 0.5 mL/min, hex/IPA=99:1). 2-chloro-benzaldehyde: *t*: 8.6 min.



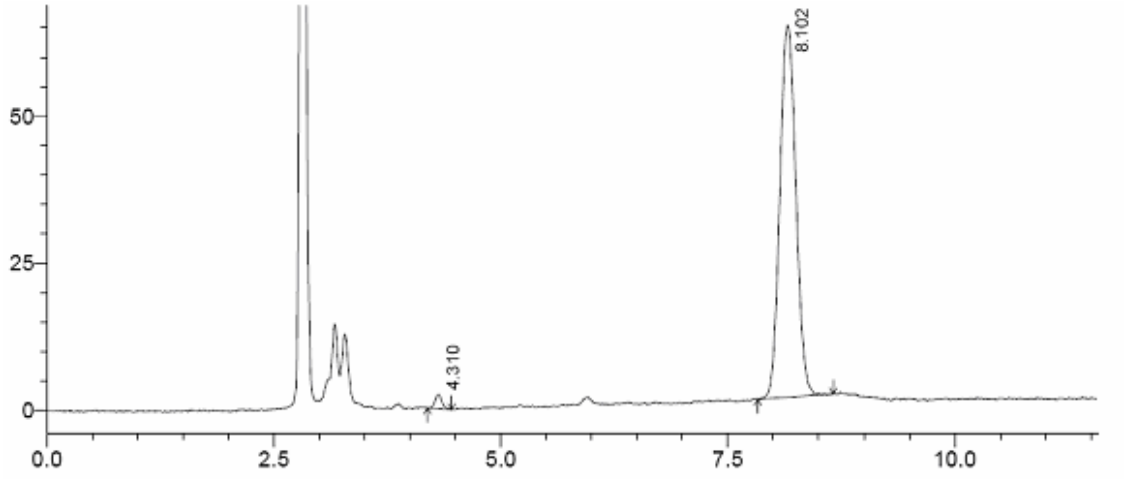




PDA Ch1 207nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.457	97731208	2803988	97.652	98.012
2	24.756	2350279	56879	2.348	1.988
Total		100081487	2860866	100.000	100.000

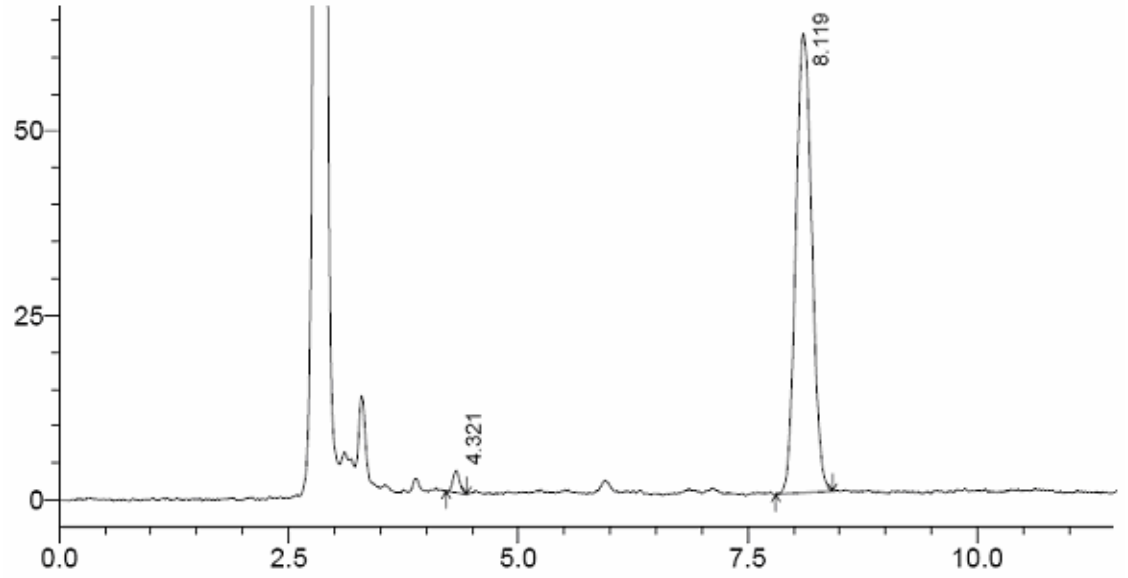
Recycling-experiment 2：



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.310	12975	2428	1.640	3.700
2	8.102	778184	63184	98.360	96.300
Total		791159	65612	100.000	100.000

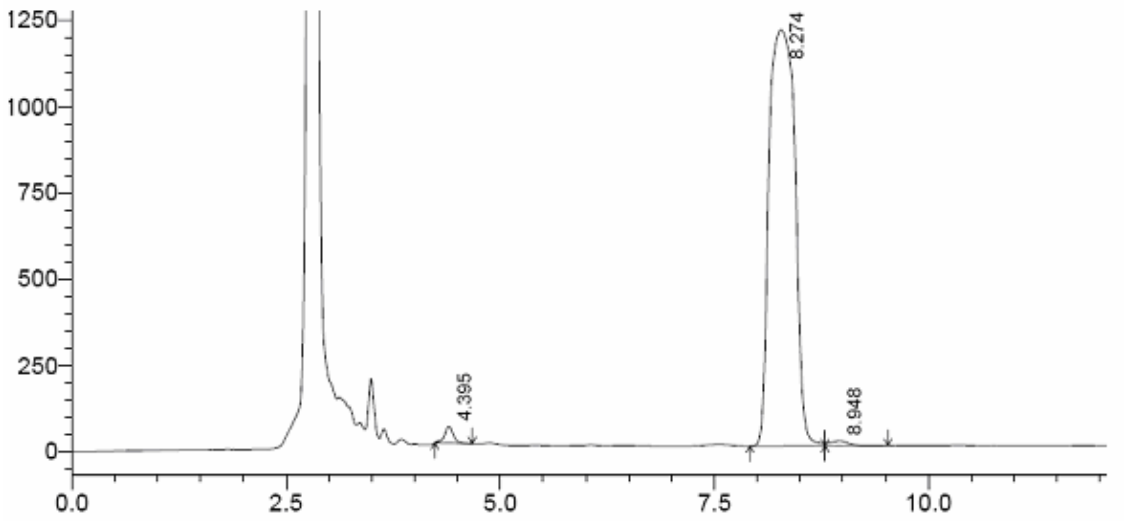
Recycling-experiment 3：



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.321	15224	2968	1.970	4.549
2	8.119	757633	62281	98.030	95.451
Total		772857	65249	100.000	100.000

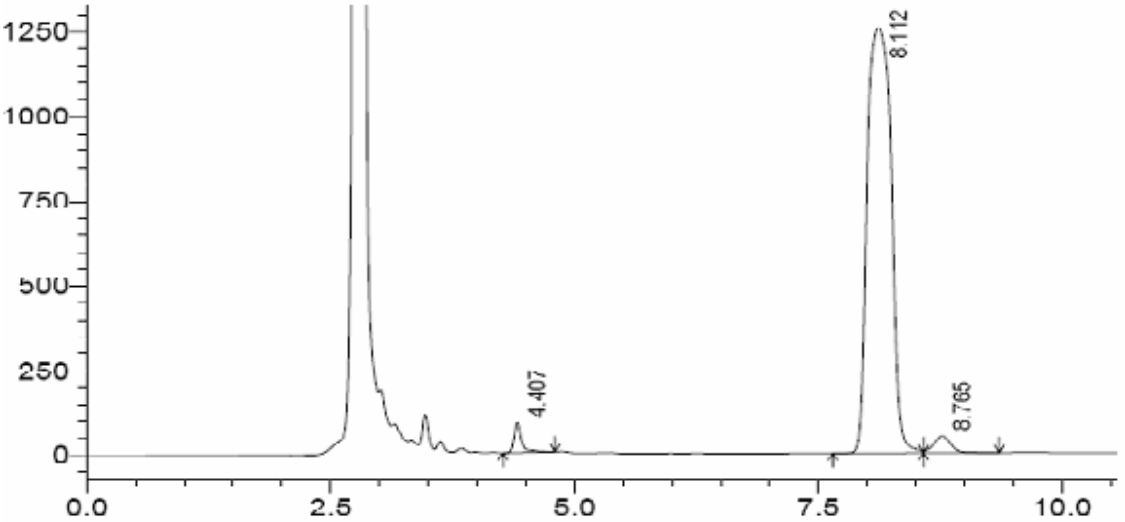
Recycling-experiment 4：



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.395	342025	47873	1.328	3.778
2	8.274	25198741	1205140	97.850	95.103
3	8.948	211546	14177	0.821	1.119
Total		25752312	1267191	100.000	100.000

Recycling-experiment 5：



PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.407	464805	86316	2.075	6.218
2	8.112	21356679	1252271	95.343	90.206
3	8.765	578392	49654	2.582	3.577
Total		22399876	1388241	100.000	100.000