Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

A highly active organocatalyst for the asymmetric α-aminoxylation of aldehydes and α-hydroxylation of ketones

Xinyuan Fan, Esther Alza, Miquel A. Pericàs*

Institute of Chemical Research of Catalonia (ICIQ), Avda Països Catalans, 16, 43007, Tarragona, Spain, and Departament de Química Orgànica, Universitat de Barcelona (UB), 080208, Barcelona, Spain.

mapericas@iciq.es

1. General information

Unless otherwise stated, all commercial reagents were used as received and all reactions were carried out directly under open air except the aldehydes that were distilled before using. All flash chromatography was carried out using 60-mesh silica gel and dry-packed columns. NMR spectra were registered in a Bruker Advance 400 Ultrashield spectrometer in $CDCl_3$ at room temperature, operating at 400.13 MHz (1H) and 100.63 MHz (13C{1H}). TMS was used as internal standard for ^{1}H-NMR and $CDCl_3$ for ^{13}C-NMR. Chemical shifts are reported in ppm referred to TMS. Chemical shifts are given in δ and coupling constants in Hz. Optical rotations were measured at room temperature on a Jasco P-1030 polarimeter. Racemic standard products were prepared using DL-proline as catalyst according to reported procedures in order to establish HPLC conditions. The absolute configuration of the reaction products was confirmed by HPLC and optical rotations, by comparison with reported data.

2. General procedure of α-aminoxylation of aldehydes

Catalyst **3** (2 mol%, 0.005mmol) and nitrosobenzene (1 eq., 0.25 mmol, 27.6 mg) were dissolved in 0.25 mL acetonitrile in a 1 mL vial. The mixture was cooled to 0 ^{o}C in an ice-water bath and the corresponding aldehyde (3 eq., 0.75 mmol) was added with stirring. When the limiting reactant had been completely consumed, 0.5 mL of EtOH and 1 eq. of $NaBH_4$ were added respectively at 0 ^{o}C. After 20 minutes, the reaction mixture was treated with saturated aqueous NH_4Cl solution (5 mL) and extracted with dichloromethane (3 x 5 mL). The organic fraction was dried over $MgSO_4$ and concentrated under reduced pressure at room temperature. The crude alcohol was then purified by flash chromatography on silicagel, with hexane/ethyl acetate mixtures as eluent to give the pure product.

All the spectroscopic data of the products matched those reported in the literature.[1-2]

3. General procedure of α-aminoxylation of ketones

Catalyst **3** (5 mol%, 0.0125mmol) and the corresponding ketone (1 eq., 0.25 mmol) were dissolved in 0.25 mL acetonitrile in a 1 mL vial. The nitrosobenzene (3 eq., 0.75mmol, 83 mg) was dissolved in 0.25 mL of acetonitrile and was added by a syringe pump during 30 minutes. The mixture was stirred during the corresponding time (0.5h for **6a**, 1h for **6b**, 3h for **6c** and 1h for **6d**). When the reaction is completed, the solvent is evaporated and the crude of the reaction was dissolved in CH_2Cl_2 (1.0 mL/0.3 mmols) and was treated with 3,5-dinitrobenzoyl chloride (2.0 eq., benzoyl chloride was used in the case of **2l**) and DMAP (2.0 eq.). After reaction completion, the solution mixture was treated with saturated aqueous NH_4Cl solution (10 mL) and extracted with dichloromethane (3 x 5 mL). The organic fraction was dried over $MgSO_4$ and concentrated under reduced pressure at room temperature. The crude ester was then purified by flash chromatography on silica gel with hexane/ethyl acetate mixtures as eluent to give the pure product, which was analyzed by NMR and HPLC.

All the spectroscopic data of the products matched those reported in the literature.[3-4]

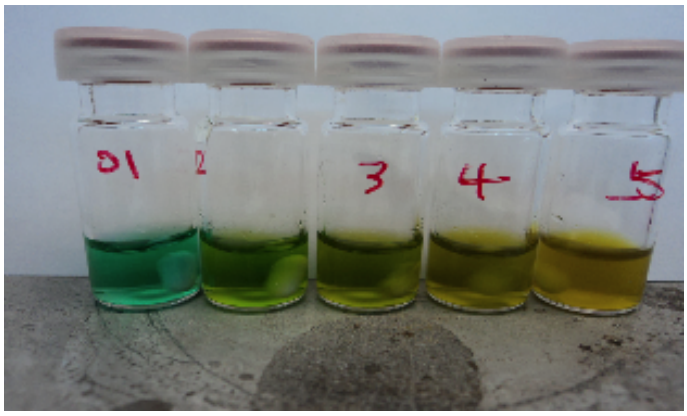
4. Competition experiments between 3 and L-proline in the α-aminoxylation of propanal

a) Experiments performed with catalyst mixtures. Five experiments were carried out in parallel, with the catalyst compositions shown in Table 1. All the reactions were carried out with 1 eq. PhNO, 3eq. propanal and the corresponding catalyst mixture (10 mol% with respect to PhNO) at room temperature in MeCN as solvent. The enantiomeric composition of the reaction product was measured by HPLC with a Chiralpak AD-H column after reduction with $NaBH_4$.

Table 1.

Vial	L-Proline [mol%]	**3** [mol%]	Time for total conv.	*S* prod [%]	*R* prod [%]
1	10%	0	61 min	2	98
2	7.50%	2.50%	21 min	57	43
3	5%	5%	14 min	75	25
4	2.50%	7.50%	9 min	86	14
5	0	10%	4 min	99	1

In a qualitative (albeit rather precise) manner, complete consumption of nitrosobenzene in α-aminoxylation reactions can be visually appreciated through a colour change from green to yellow. A picture taken at a reaction time of 3 min. shows that the reaction catalysed by **3** is essentially complete at this reaction time, while no colour change can be appreciated in the reaction catalysed by L-proline.

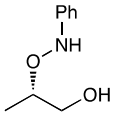


b) Experiments performed in CH_3CN-d_3 for NMR monitoring. Two parallel processes (one with L-proline and one with **3**) were run in NMR tubes with the following amounts of reagents and solvent: 0,16 mmol PhNO, 0,48 mmol propanal and 0,016 mmol catalyst in 0,48mL acetonitrile-d_3 at room temperature. In both cases, the progress of the α-aminoxylation reaction was periodically checked by 300MHz ^{1}H NMR. Results of this monitoring have been summarized in Table 2, and fully confirm the results obtained with catalyst mixtures (see above).

Table 2.

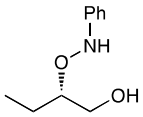
Time [min]	**3**	L-Proline
0	0	0
5	100%	0
17	-	9%
27	-	34%
37	-	75%
60	-	100%

4. Physical and spectroscopic data of the products



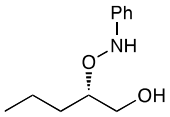
(*S*)-2-(phenylaminooxy)propan-1-ol (2a)[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 2H, ArH), 7.23-6.96 (m, 4H, NH and ArH), 4.12 (dp, 1H, J = 3.2, 6.4 Hz, CHON), 3.82-3.71 (m, 2H, CH_2O), 2.43 (s, br, 1H, OH), 1.26 (d, 3H, J = 6.4 Hz, CH_3); HPLC (Chiralpak AD-H, Hexane/ i-Propanol = 95:5 , flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 21.9 min, t_{minor} = 25.7 min, ee 98%; $[\alpha]^{25}D$ + 5.2 (c 1.02, $CHCl_3$)



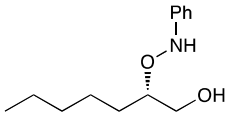
(*S*)-2-(phenylaminooxy)butan-1-ol (2b)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 2H, ArH), 7.07 (s, 1H, NH), 7.05-6.75 (m, 3H, ArH), 3.95-3.70 (m, 3H, CHON and CH_2O), 2.64 (s, br, 1H, OH), 1.76-1.50 (m, 2H), 1.01 (t, 3H, J = 7.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 129.1, 122.6, 114.9, 85.4, 65.0, 23.0, 10.3; HPLC (Chiralpak AD-H, Hexane/ i-Propanol = 95:5 , flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 21.3 min, t_{minor} = 25.3 min, ee 98%; $[\alpha]^{25}D$ - 22.2 (c 1.21, $CHCl_3$); (R)-configuration from literature(Hayashi, Yamaguchi et al. 2004): $[\alpha]^{16}D$ + 24.6 (c 0.74, $CHCl_3$), ee99%.



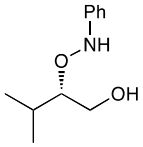
(*S*)-2-(phenylaminooxy)pentan-1-ol (2c)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 2H, ArH), 7.06 (s, 1H, NH), 7.01-6.85 (m, 3H, ArH), 4.05-3.90 (m, 1H, CHON), 3.89-3.71 (m, 2H, CH_2O), 2.50 (s, br, 1H, OH), 1.72-1.37 (m, 4H, CH_2CH_2), 0.96 (t, 3H, J = 5.7 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 129.2, 122.6, 115.0, 83.9, 65.6, 32.2, 19.2, 14.4; HPLC (Chiralpak AD-H, Hexane/ i-Propanol = 95:5 , flow rate 1.0 mL/min, λ = 215 nm): t_{major} = 19.2 min, t_{minor} = 22.7 min, ee 99%; $[\alpha]^{25}D$ – 16.9 (c 0.93, $CHCl_3$); (R)-configuration from literature(Hayashi, Yamaguchi et al. 2004): $[\alpha]^{16}D$ + 24.2 (c 0.34, $CHCl_3$), ee98%.



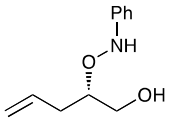
(*S*)-2-(phenylaminooxy)heptan-1-ol (2d)[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 2H, ArH), 7.20-6.85 (m, 4H, ArH and NH), 3.99-3.90 (m, 1H, CHON), 3.89-3.71 (m, 2H, CH_2O), 1.75-1.21 (m, 8H), 0.90 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 129.2, 122.9, 122.6, 115.0, 84.1, 65.5, 32.1, 30.0, 25.5, 22.7, 14.1; HPLC (Chiralpak AD-H, Hexane/ i-Propanol = 95:5 , flow rate 1.0 mL/min, λ = 240 nm): t_{major} = 17.6 min, t_{minor} = 22.5 min, ee 96%; $[\alpha]^{25}D$ – 15.7 (c 1.06, $CHCl_3$)



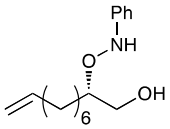
(*S*)-3-methyl-2-(phenylaminooxy)butan-1-ol (2e)[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 2H, ArH), 7.20-6.85 (m, 4H, ArH and NH), 3.90-3.80 (m, 2H, CH_2O), 3.79-3.69 (m, 1H, CHON), 2.10-1.94 (m, 1H), 1.05 (d, 3H, J = 6.8 Hz, CH_3), 1.01 (d, 3H, J = 6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 129.2, 122.8, 115.3, 88.8, 64.0, 28.9, 18.9, 18.8; HPLC (Chiralpak AD-H, Hexane/ i-Propanol = 95:5 , flow rate 1.0 mL/min, λ = 240 nm): t_{major} = 17.8 min, t_{minor} = 21.0 min, ee 97%; $[\alpha]^{25}$D – 19.7 (c 0.60, $CHCl_3$)



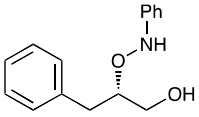
(*S*)-2-(phenylaminooxy)pent-4-en-1-ol (2f)[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.25 (m, 2H, ArH), 7.05 (s, 1H, NH), 7.02-6.85 (m, 3H, ArH), 6.00-5.70 (m, 1H), 5.74-4.86 (m, 2H), 4.11-3.95 (m, 1H, CHON), 3.90-3.74 (m, 2H, CH_2O), 2.59-2.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 134.1, 129.2, 122.7, 117.9, 114.9, 83.5, 64.8, 34.8; HPLC (Chiralpak AD-H, Hexane/ i-Propanol = 95:5 , flow rate 1.0 mL/min, λ = 230 nm): t_{major} = 20.4 min, t_{minor} = 25.3 min, ee 96%; $[\alpha]^{25}$D – 3.5 (c 1.51, $CHCl_3$)



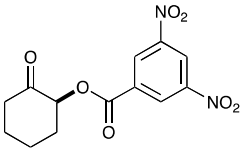
(*S*)-2-(phenylaminooxy)undec-10-en-1-ol (2g)[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.25 (m, 2H, ArH), 7.24-6.85 (m, 4H, ArH and NH), 5.87-5.75 (m, 1H), 5.03-4.89 (m, 2H), 3.98-3.92 (m, 1H, CHON), 3.87-3.72 (m, 2H, CH_2O), 2.07-2.00 (m, 2H), 1.73-1.25 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 139.3, 129.2, 122.6, 115.0, 114.3, 84.1, 65.6, 33.9, 30.1, 29.8, 29.5, 29.2, 29.0, 25.9; HPLC (Chiralpak AD-H, Hexane/ i-Propanol = 95:5 , flow rate 1.0 mL/min, λ = 240 nm): t_{major} = 15.2 min, t_{minor} = 18.6 min, ee 98%; $[\alpha]^{25}$D – 8.9 (c 1.24, $CHCl_3$)



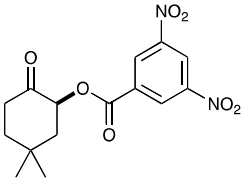
(*S*)-3-phenyl-2-(phenylaminooxy)propan-1-ol (2h)[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.18 (m, 7H, ArH), 7.06 (s, 1H, NH), 6.97-6.81 (m, 3H, ArH), 4.16-4.12 (m, 1H, CHON), 3.85 (dd, 1H, J = 12.0, 2.8 Hz, CH_2O), 3.72 (dd, 1H, J = 12.0, 5.9 Hz, CH_2O), 3.05 (dd, 1H, J = 13.8, 6.8 Hz, CH_2Ar), 2.85 (dd, 1H, J = 13.7, 7.0 Hz, CH_2Ar);; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 138.0, 129.6, 129.1, 128.6, 126.6, 122.5, 114.8, 85.2, 64.3, 36.6; HPLC (Chiralpak AD-H, Hexane/ i-Propanol = 95:5 , flow rate 1.0 mL/min, λ = 240 nm): t_{major} = 36.2 min, t_{minor} = 48.4 min, ee 98%; $[\alpha]^{25}$D – 35.3 (c 0.58, $CHCl_3$)



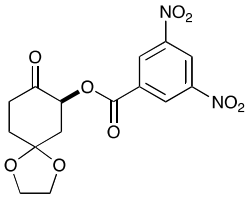
(*S*)-2-oxocyclohexyl 3,5-dinitrobenzoate (2i-derivative)[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (1H, m), 9.20 (2H, br s) (Ar-H); 5.49 (dd, 1H, J = 12.5, 7.1 Hz), 2.64 (pd, 1H), 2.49 (m, 2H), 2.22 (m, 1H), 2.13 (1H, m), 2.07 (dt, 1H, J = 12.7, 3.8 Hz), 1.68 (m, 2H). (Chiracel AD-H, Hexane/ i-Propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm): t_{minor} = 21.5 min, t_{major} = 32.1 min, ee 85%.



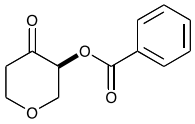
(*S*)-5,5-dimethyl-2-oxocyclohexyl 3,5-dinitrobenzoate (2j-derivative)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (1H, m), 9.18 (2H, br s) (Ar-H); 5.61 (dd, 1H, J = 12.3, 6.9 Hz), 2.73-2.62 (br td, 1H), 2.52-2.45 (m, 1H), 2.22-2.15 (m, 1H), 1.88-1.70 (3H, m), 1.36 (br s, 3H), 1.17 (br s, 3H). (Chiracel IC, Hexane/ i-Propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 47.5 min, t_{minor} = 55.4 min, ee 90%.



(*S*)-8-oxo-1,4-dioxaspiro[4.5]decan-7-yl 3,5-dinitrobenzoate (2k-derivative)[3]

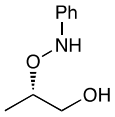
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (t, 1H, J = 2.0 Hz), 9.18 (br s, 2H), (Ar-H); 5.74 (dd, 1H, J = 12.8, 6.6 Hz), 4.16-4.06 (m, 4H), 2.84 (dt, 1H, J = 14.0, 6.5 Hz), 2.57-2.49 (m, 2H), 2.37 (t, 1H, J = 13.0 Hz), 2.17-2.06 (m, 2H). (Chiracel AD-H, Hexane/ i-Propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 23.7 min, t_{minor} = 31.5 min, ee 91%.



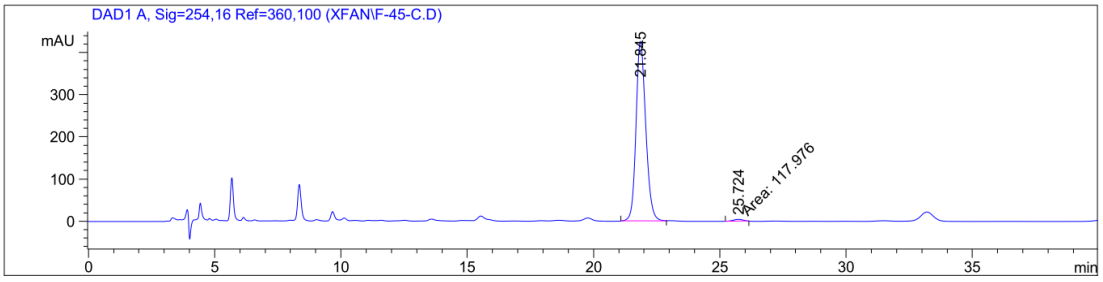
(S)-4-oxotetrahydro-2H-pyran-3-yl benzoate (2l-derivative)[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.08 (m, 2H), 7.57-7.54 (m, 1H), 7.39-7.32 (m, 2H) (Ar-H); 5.53 (ddd, J = 10.6, 7.0, 1.2 Hz, 1H), 4.46 (ddd, J = 10.8, 7.0, 1.6 Hz, 1H), 4.32 (ddt, J = 11.4, 7.1, 1.7 Hz, 1H), 3.79 – 3.68 (m, 2H), 2.88 - 2.81 (m, 1H), 2.61 (ddd, J = 14.2, 2.7, 1.8 Hz, 1H). (Chiracel OD-H, Hexane/ i-Propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm): 10.4 min, 14.7 min, ee 81%.

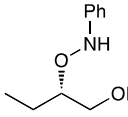
5. Compilation of HPLC chromatograms.



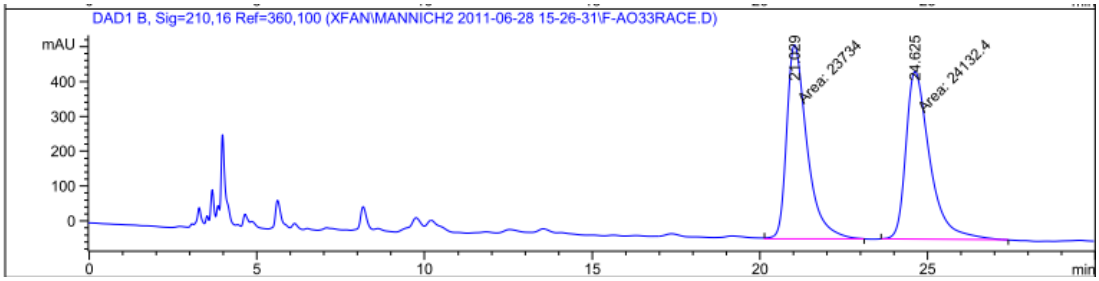
(*S*)-2-(phenylaminooxy)propan-1-ol



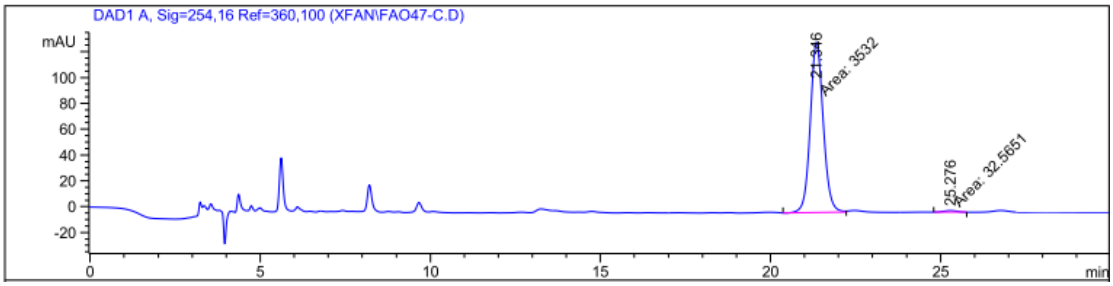
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.845	BB	0.4108	1.14180e4	425.80240	98.9773
2	25.724	MM	0.4579	117.97615	4.29421	1.0227
Totals :				1.15360e4	430.09661	



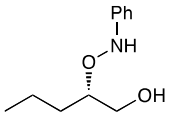
(*S*)-2-(phenylaminooxy)butan-1-ol



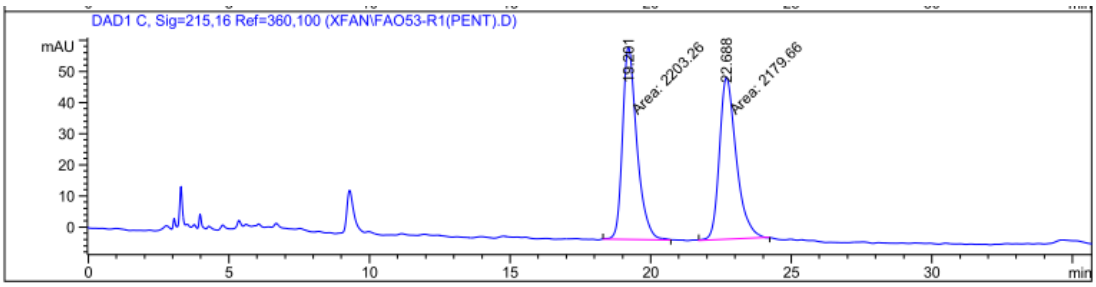
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.029	MM	0.7101	2.37340e4	557.06134	49.5838
2	24.625	MM	0.8348	2.41324e4	481.80292	50.4162
Totals :				4.78664e4	1038.86426	



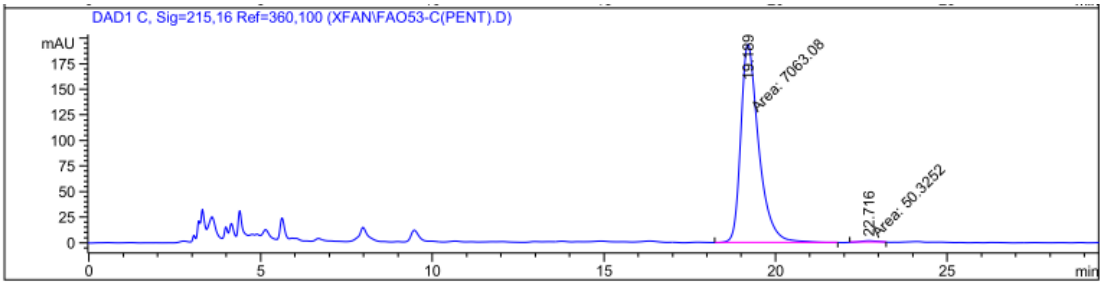
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.346	MM	0.4461	3532.00488	131.95395	99.0864
2	25.276	MM	0.4489	32.56511	1.20897	0.9136
Totals :				3564.57000	133.16291	



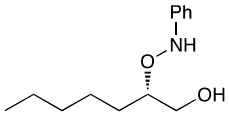
(*S*)-2-(phenylaminooxy)pentan-1-ol



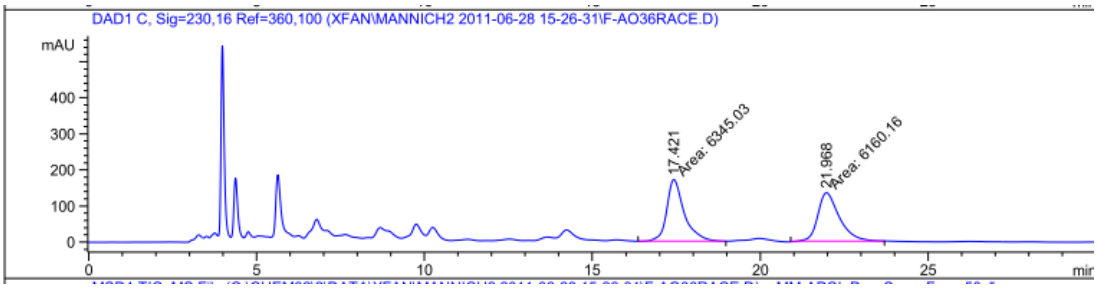
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.201	MM	0.5950	2203.26343	61.71285	50.2692
2	22.688	MM	0.6979	2179.66162	52.05249	49.7308
Totals :				4382.92505	113.76534	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.189	MM	0.6070	7063.08350	193.94524	99.2925
2	22.716	MM	0.5735	50.32521	1.46240	0.7075
Totals :				7113.40871	195.40764	

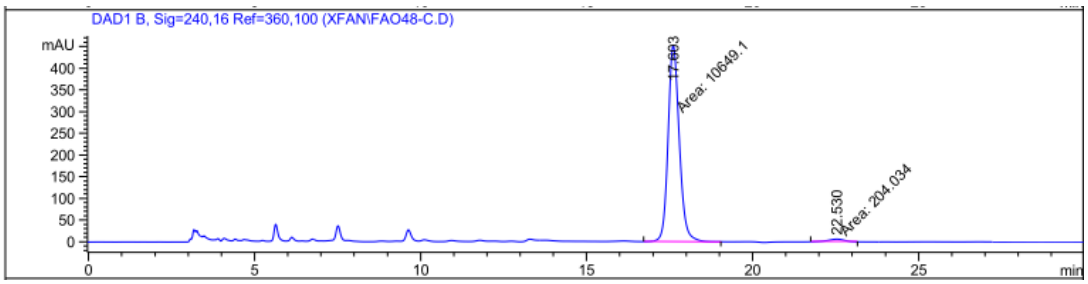


(*S*)-2-(phenylaminooxy)heptan-1-ol

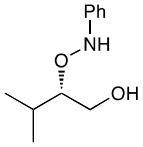


Signal 3: DAD1 C, Sig=230,16 Ref=360,100

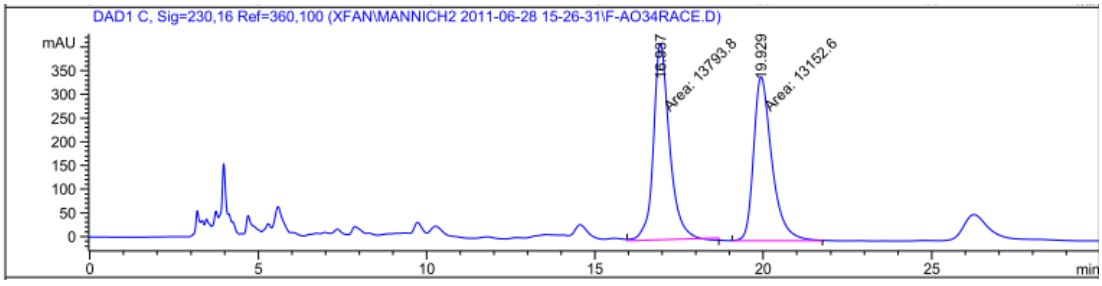
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.421	MM	0.6153	6345.02881	171.87598	50.7392
2	21.968	MM	0.7589	6160.15918	135.28281	49.2608
Totals :				1.25052e4	307.15878	



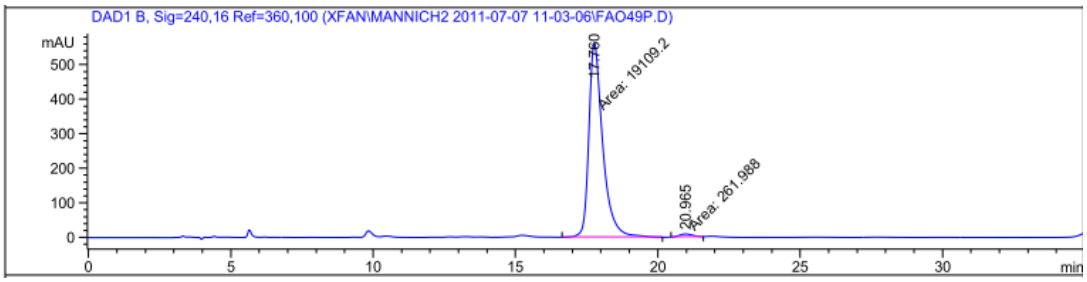
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.603	MM	0.3927	1.06491e4	451.94052	98.1200
2	22.530	MM	0.5659	204.03430	6.00919	1.8800
Totals :				1.08531e4	457.94971	



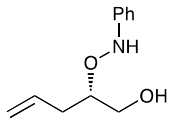
(*S*)-3-methyl-2-(phenylaminooxy)butan-1-ol



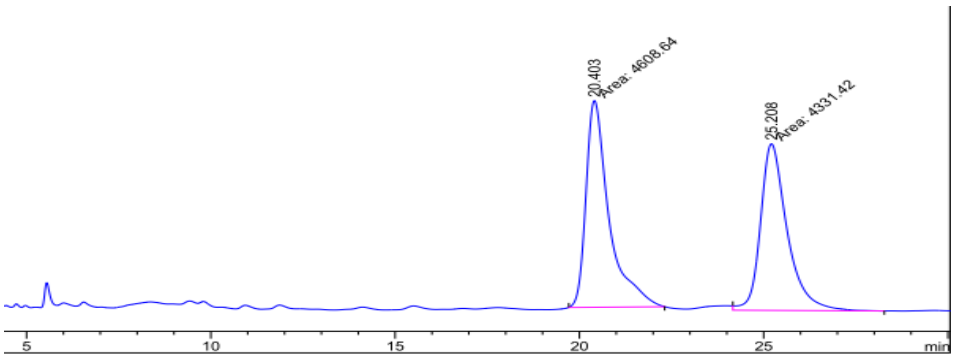
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.937	MM	0.5548	1.37938e4	414.36511	51.1898
2	19.929	MM	0.6333	1.31526e4	346.12195	48.8102
Totals :				2.69465e4	760.48706	



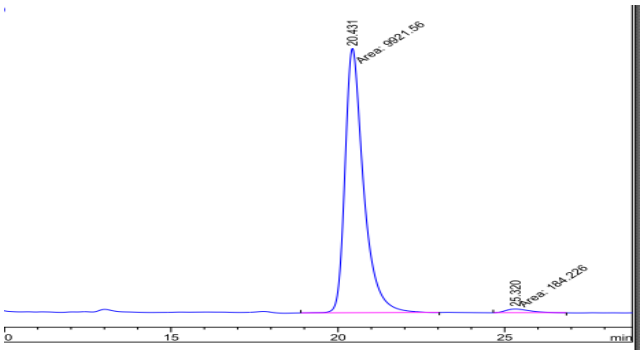
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.760	MM	0.5673	1.91092e4	561.36102	98.6475
2	20.965	MM	0.5189	261.98807	8.41557	1.3525
Totals :				1.93712e4	569.77659	



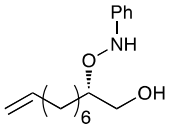
(*S*)-2-(phenylaminooxy)pent-4-en-1-ol



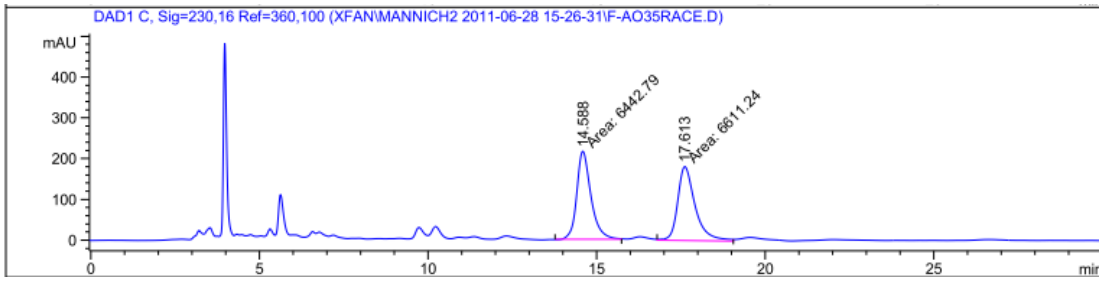
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.403	MM	0.7281	4608.63965	105.48788	51.5505
2	25.208	MM	0.8478	4331.41504	85.15261	48.4495



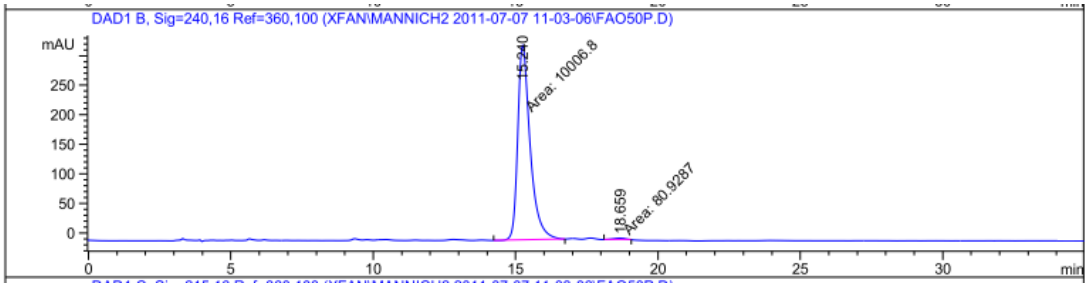
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.431	MM	0.6466	9921.56152	255.73863	98.1770
2	25.320	MM	0.8637	184.22574	3.55512	1.8230



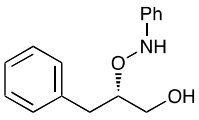
(*S*)-2-(phenylaminooxy)undec-10-en-1-ol



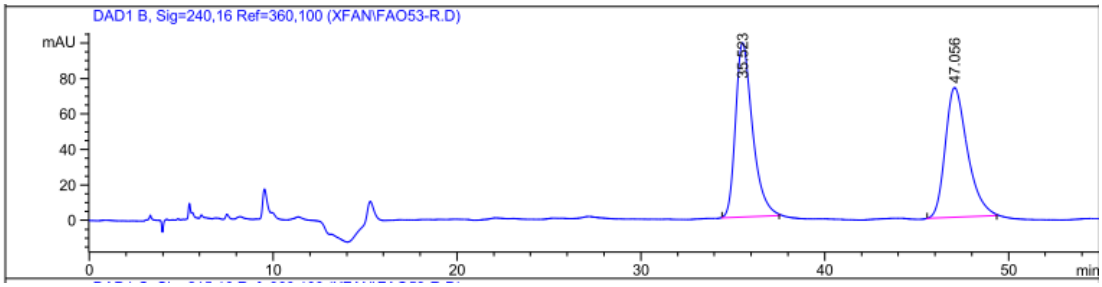
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.588	MM	0.4957	6442.78564	216.62923	49.3548
2	17.613	MM	0.6067	6611.24463	181.61951	50.6452
Totals :				1.30540e4	398.24873	



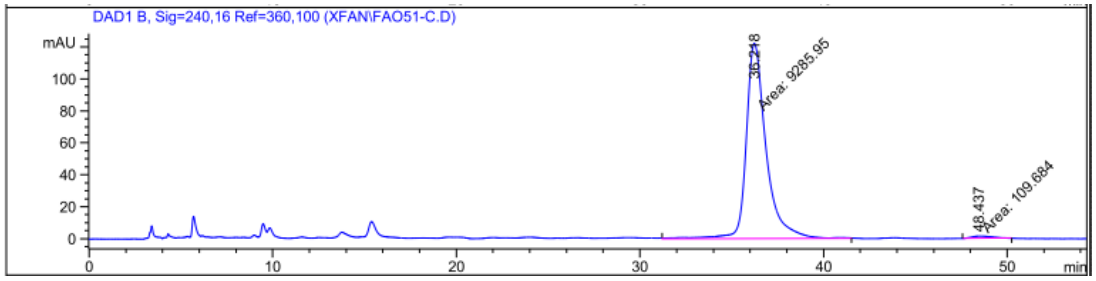
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.240	MM	0.5058	1.00068e4	329.70685	99.1977
2	18.659	MM	0.5070	80.92875	2.66064	0.8023
Totals :				1.00877e4	332.36749	



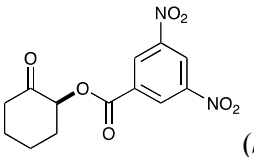
(*S*)-3-phenyl-2-(phenylaminooxy)propan-1-ol



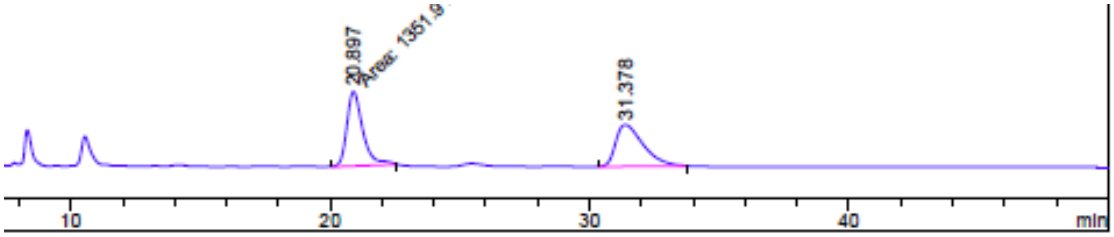
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.523	BB	0.9787	6344.84424	98.34499	50.6249
2	47.056	BB	1.2762	6188.20605	73.35532	49.3751
Totals :				1.25331e4	171.70032	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.218	MM	1.2663	9285.94727	122.22017	98.8326
2	48.437	MM	1.3217	109.68401	1.38312	1.1674
Totals :				9395.63127	123.60329	

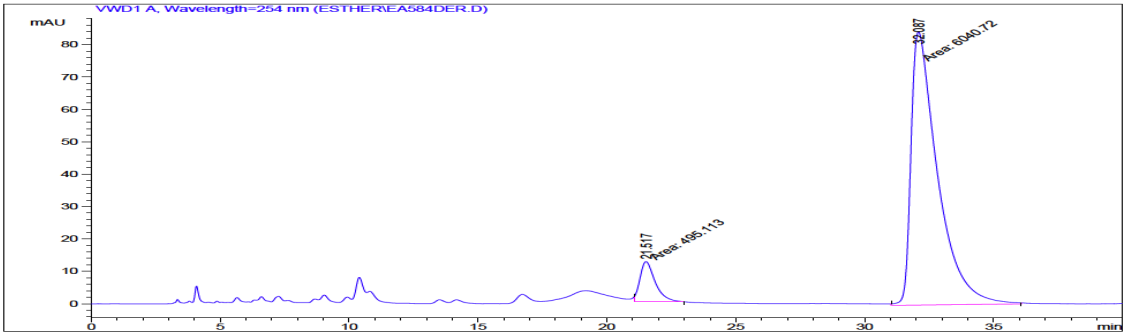


(*S*)-2-oxocyclohexyl 3,5-dinitrobenzoate

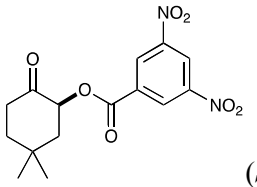


Signal 1: VWD1 A, Wavelength=254 nm

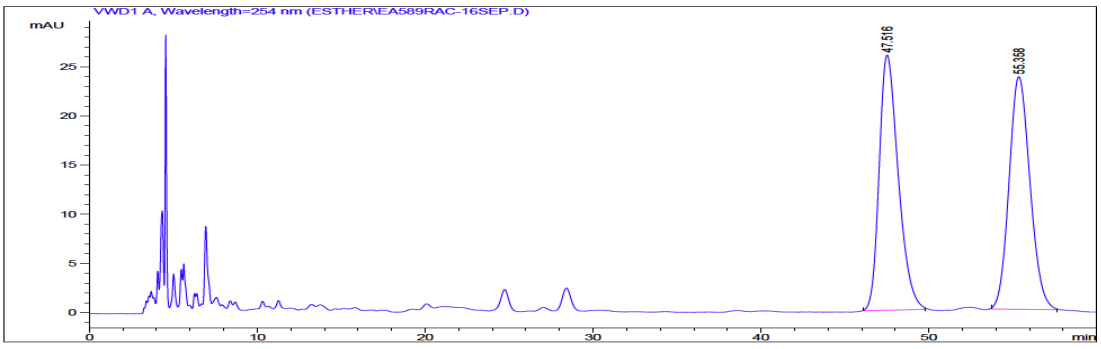
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.897	MM	0.7147	1351.90967	31.52655	50.6797
2	31.378	BB	1.1056	1315.64880	17.67840	49.3203



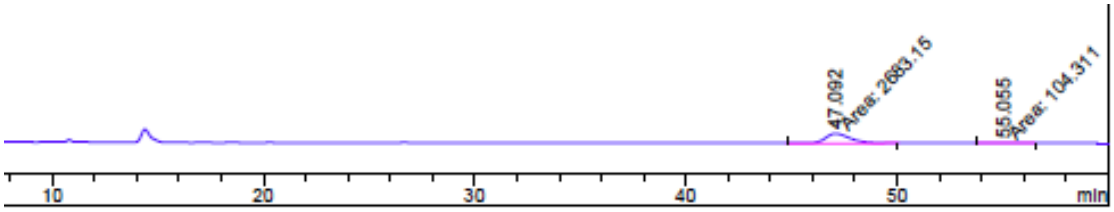
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.517	MM	0.6733	495.11264	12.25575	7.5754
2	32.087	MM	1.1934	6040.72168	84.36640	92.4246
Totals :				6535.83432	96.62215	



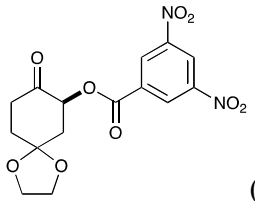
(*S*)-5,5-dimethyl-2-oxocyclohexyl 3,5-dinitrobenzoate



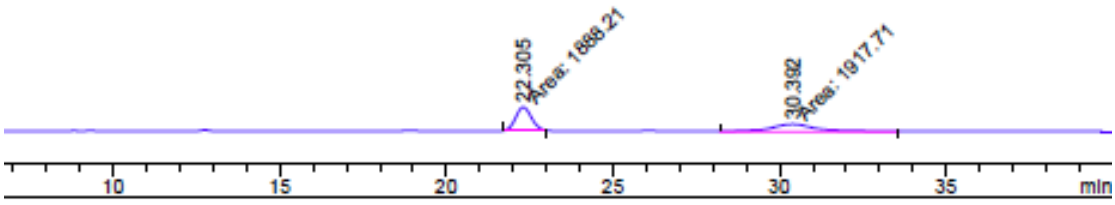
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	47.516	BB	1.2004	2048.49976	25.95410	50.0125
2	55.358	BB	1.3035	2047.47656	23.66451	49.9875
Totals :				4095.97632	49.61860	



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	47.092	MM	1.3895	2683.15454	32.18462	96.2579
2	55.055	MM	1.3768	104.31109	1.26272	3.7421
Totals :				2787.46563	33.44734	

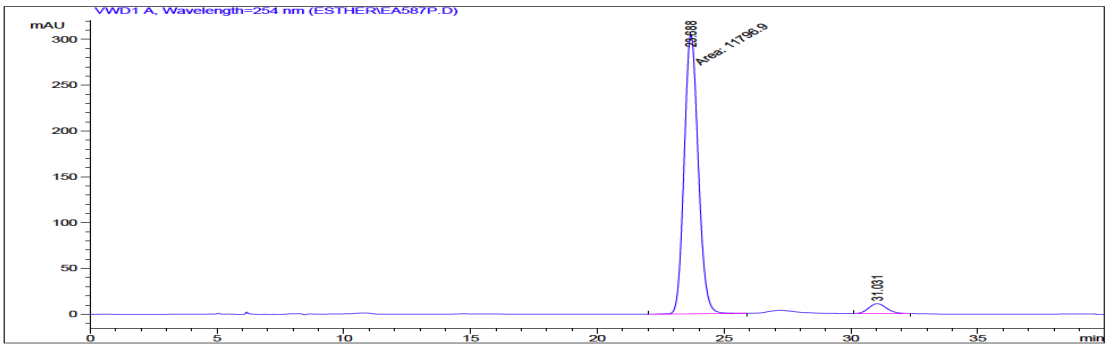


(*S*)-8-oxo-1,4-dioxaspiro[4.5]decan-7-yl 3,5-dinitrobenzoate

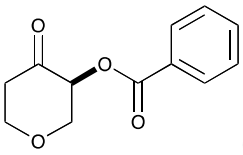


Signal 1: VWD1 A, Wavelength=254 nm

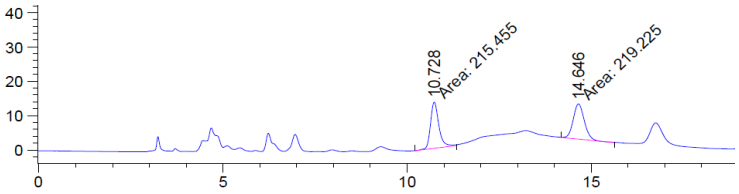
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.305	MM	0.5429	1888.20801	57.96161	49.6124
2	30.392	MM	1.7328	1917.71497	18.44547	50.3876



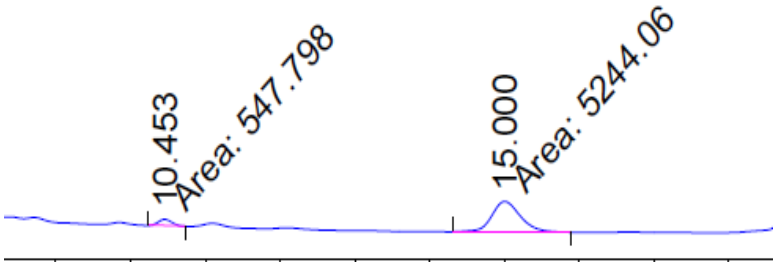
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.688	MM	0.6453	1.17969e4	304.69315	95.6013
2	31.031	BB	0.7465	542.78601	10.93604	4.3987
Totals :				1.23397e4	315.62919	



(*S*)-4-oxotetrahydro-2*H*-pyran-3-yl benzoate



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.728	MM	0.2655	215.45470	13.52358	49.5663
2	14.646	MM	0.3542	219.22549	10.31504	50.4337
Totals :				434.68019	23.83861	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.453	MM	0.2220	547.79828	41.11796	9.4581
2	15.000	MM	0.4664	5244.06299	187.39412	90.5419
Totals :				5791.86127	228.51208	

5. References for the Supporting Information

1) T. Kano, Y. Yamaguchi and K. Maruoka, *Chem. Eur. J.* **2009,** 15, 6678-6687.

2) Y. Hayashi, J. Yamaguchi, T. Sumiya, K. Hibino and M. Shoji, *J. Org. Chem.* **2004**, 69, 5966-5973.

3) D. B. Ramachary, C. F. Barbas III, *Org. Lett.* **2005**, *7*, 1577-1580

4) C. S. Beshara, A. Hall, R. L. Jenkins, K. L. Jones, T. C. Jones, N. M. Killeen, P. H. Taylor, S. P. Thomas and N. C. O. Tomkinson, *Org. Lett.* **2005**, 7, 5729-5732.