SUPPORTING INFORMATION

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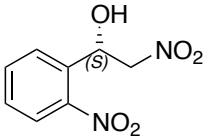
General considerations

All manipulations (except catalytic runs) were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line techniques. Valinol and phenylglycinol were obtained by reduction of Valine and Phenylglycine, respectively.[1] All other reagents were commercially available and used as received. Solvents were purified and degassed by standard procedures. Metal complexes were obtained using methanol as solvent (ACS reagent grade). ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 300 spectrometer using the residual solvent peak as reference ($CDCl_3$: δ_H = 7.26 ppm; δ_C = 77.16 ppm) at 298K. Chemical shifts are given in ppm (δ) compared to TMS (tetramethylsilane). Infrared (IR) spectra were recorded on a Nicolet 380 FT-IR spectrometer. KBr discs were made for all samples. Elemental analyses were recorded by the 'Institut de Chimie' laboratory, Université de Strasbourg. HRMS ESI analyses were recorded on microTOF, Bruker Daltonics by the 'Institut de Chimie' laboratory, Université de Strasbourg. Specific rotations were recorded at the 'Laboratoire de Stéréochimie', ECPM, Strasbourg. HPLC analyses were performed on a Gilson apparatus (UV-VIS156/321 PUMP) with Chiralcel Daicel columns (AD, OD-H, AS, 0.46 X 25 cm) using *n*-Hexane/*i*-PrOH eluents. A dual wavelength UV detector was used. To confirm the retention times of both enantiomers, all racemic derivatives were prepared and injected on chiral HPLC.

*i*Pr-DiBox (1), Ph-DiBox (2), *i*Pr-TriBox (3) and *i*Pr-TetraBox (4) have been prepared as previously reported.[2]

Methods Used to Assay Enantiomeric Excess

Conversions and ee determinations of the nitroaldolisation product

Product	ee assay	Conditions	Retention time of enantiomer 1 (min)	Retention time of enantiomer 2 (min)	[α] Solvent
	HPLC Chiracel OD-H column	Hexane/*i*PrOH 90/10 flow: 0.9 mL/min	21.5	25.0 (major enantiomer)	(-) CH_2Cl_2

For other ee assays, see :

a) D. A. Evans, D. Seidel, M. Rueping, H. W. Lam, J. T. Shaw, C. W. Downeys, *J. Am. Chem. Soc*. **2003**, *125*, 12692.

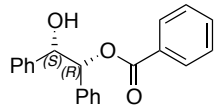
b) Y. Xiong, F. Wang, X. Huang, Y. Wen, X. Feng, *Chem. Eur: J.* **2007**, *13*, 829.

c) M. Bandini, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, C. Ventrici, *Chem. Commun.* **2007**, 616.

d) I. Panov, P. Drabina, Z. Padelkova, P. Simunek, M. Sedlàk, *J. Org. Chem.* **2011**, *76*, 4787.

e) G. Lai, F. Guo, Y. Zheng, Y. Fang, H. Song, K. Xu, S. Wang, Z. Zha, Z. Wang, *Chem. Eur: J.* **2011**, *17*, 1114.

Conversions and ee determinations of the benzoylation product

Product	ee assay	Conditions	Retention time of enantiomer 1 (min)	Retention time of enantiomer 2 (min)	[α] Solvent
 1*(R),2(S)*	HPLC Chiracel AD column	Hexane/*i*PrOH 80/20 flow: 1 mL/min	11.2	19.0 (major enantiomer)	(+) CH_2Cl_2

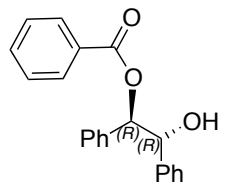
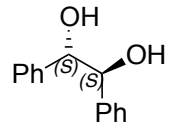
For other ee assays, see :

a) Y. Matsumura, T. Maki, S. Murakami, O. Onomura, *J. Am. Chem. Soc.* **2003**, *125*, 2052

b) D. Nakamura, K. Kakiuchi, K. Koga, R. Shirai, *Org. Lett.* **2006**, *8*, 6139.

c) E. P. Kündig, A. E. Garcia, T. Lomberget, P. Perez Garcia, P. Romanens, *Chem. Commun.* **2008**, 3519

Conversions and ee determinations of the benzoylation product and diol

Product	ee assay	Conditions	Retention time of enantiomer 1 (min)	Retention time of enantiomer 2 (min)	[α] Solvent
 (1*R*,2*R*)	HPLC Chiracel AS column	Hexane/*i*PrOH 85/15 flow: 0.9 mL/min	11.1	14.5	(+) $CHCl_3$
 (*S*,*S*)	HPLC Chiracel AS column	Hexane/*i*PrOH 85/15 flow: 0.9 mL/min	9.6	12.5	(+) $CHCl_3$

For other ee assays, see :

a) Y. Matsumura, T. Maki, S. Murakami, O. Onomura, *J. Am. Chem. Soc.* **2003**, *125*, 2052

b) A. Gissibl, M. G. Finn, O. Reiser, *Org. Lett.* **2005**, *7*, 2325.

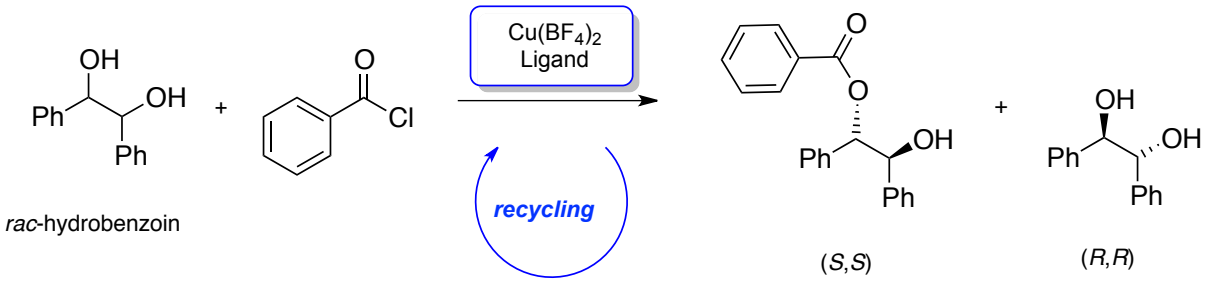
c) C. Mazet, S. Roseblade, V. Köhler, A. Pfaltz, *Org. Lett.* **2006**, *8*, 1879.

d) A. Schätz, R. N. Grass, Q. Kainz, W. J. Stark, O. Reiser, *Chem. Mater.* **2010**, *22*, 305.

Kinetic resolution of *rac*-hydrobenzoin

Equations used to calculate the selectivity factor:

- (ee of starting material)/(ee of product) = (conversion)/(1-conversion)
- s = (ln[1-conversion(1+ee of product)])/(ln[1-conversion(1-ee of product)])



rac-hydrobenzoin

(*S*,*S*)

ee'

(*R*,*R*)

ee

	RUN	1	2	3	4	5	6
(*S*)-*i*Pr-DiBox	$conv_{(exp)}$	49	50	48	50	45	16
	ee	92	86	79	85	59	<10
	ee'	93	94	90	82	68	17
	$conv_{(th)}$	50	48	47	51	46	10
	S	**91**	**89**	**46**	**27**	**9.4**	**1.4**
(*R*)-Ph-DiBox	$conv_{(exp)}$	49	54	51	53	50	-
	ee	84	66	76	82	77	-
	ee'	83	88	88	90	88	-
	$conv_{(th)}$	50	43	46	48	47	-
	S	**28**	**31**	**36**	**48**	**36**	**-**
(*S*)-*i*Pr-TriBox	$conv_{(exp)}$	47	54	50	50	-	-
	ee	85	84	82	80	-	-
	ee'	94	67	84	93	-	-
	$conv_{(th)}$	47	45	49	46	-	-
	S	**88**	**37**	**29**	**49**	**-**	**-**
(*S*)-*i*Pr-TetraBox	$conv_{(exp)}$	45	57	50	44	-	-
	ee	72	81	71	80	-	-
	ee'	94	92	89	88	-	-
	$conv_{(th)}$	43	47	44	48	-	-
	S	**70**	**60**	**36**	**38**	**-**	**-**

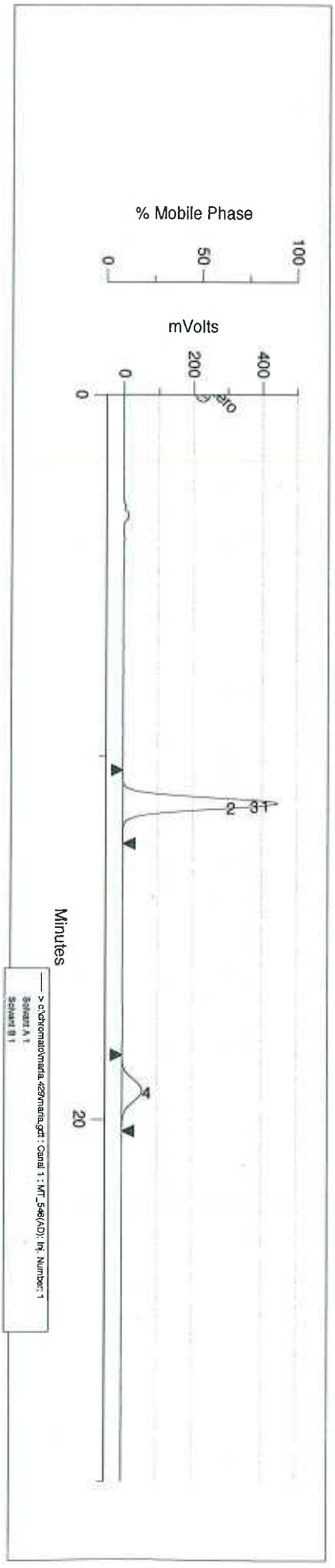
$conv_{(exp)}$ = conversion determined by ^1H NMR in the crude.
$conv_{(th)}$ = conversion determined from the enantiomeric excess of starting material and the enantiomeric excess of product.

[1] A. Abiko, S. Masamune, *Tetrahedron Lett*. **1992**, *33*, 5517.

[2] M. Torres, A. Maisse-Françoi, S. Bellemin-Laponnaz, *ChemCatChem* **2013**, *5*, 3078.

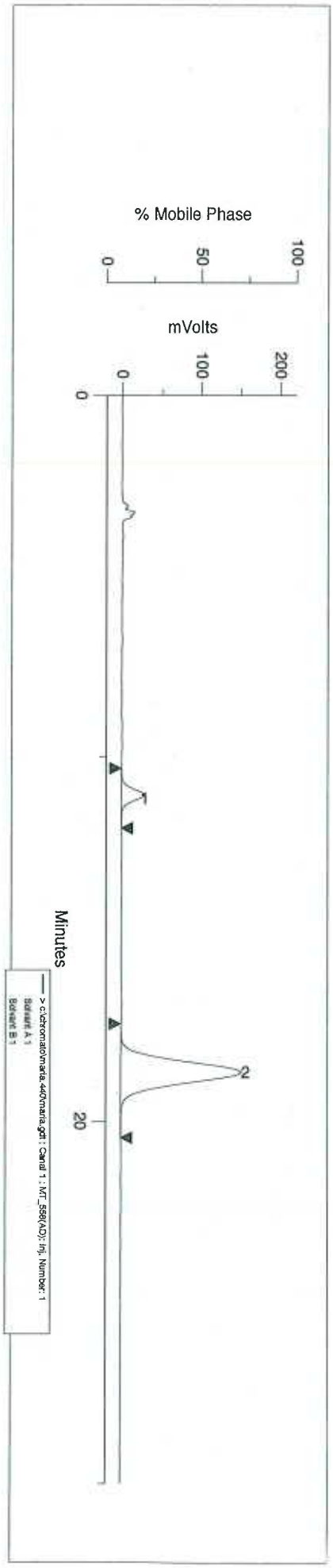
	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	11.31	29139932.00	87.72	MT_546	*3
2	1	19.21	4083272.25	12.28	MT_546	*4

Benzoylation of meso-hydrobenzoin
Table 1, Entry 2
Ligand (R,R) Ph-DiBox



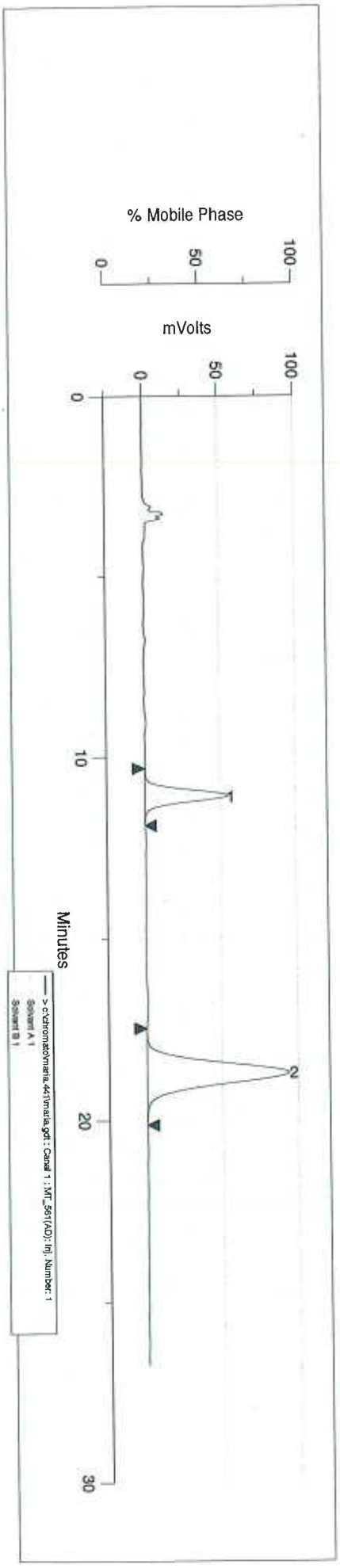
	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	11.24	1180766.25	10.06	MT_558	*1
2	1	19.00	10556045.00	89.94	MT_558	*2

Benzoylation of meso-hydrobenzoin
Table 1, Entry 3
Ligand (S,S) iPr-DiBox



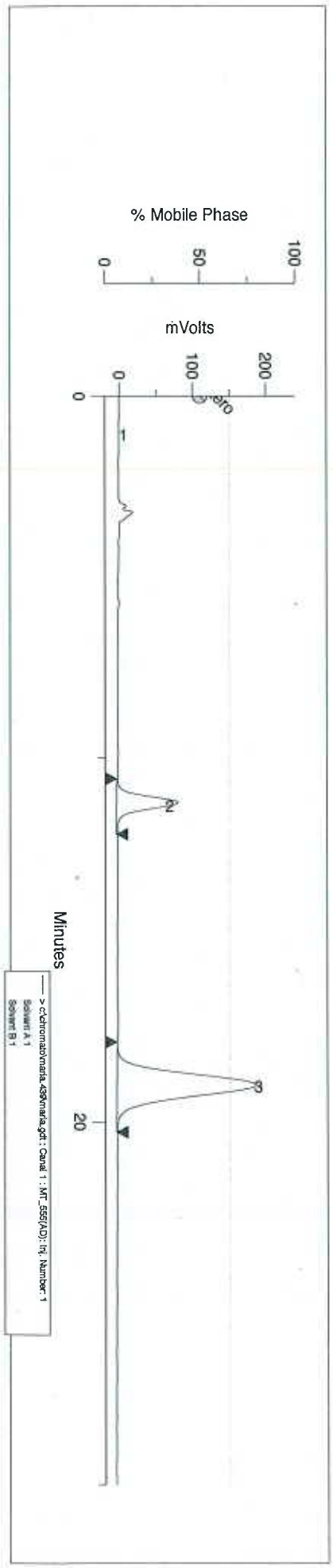
	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	11.07	2195412.25	25.32	MT_561	*1
2	1	18.70	6473653.00	74.68	MT_561	*2

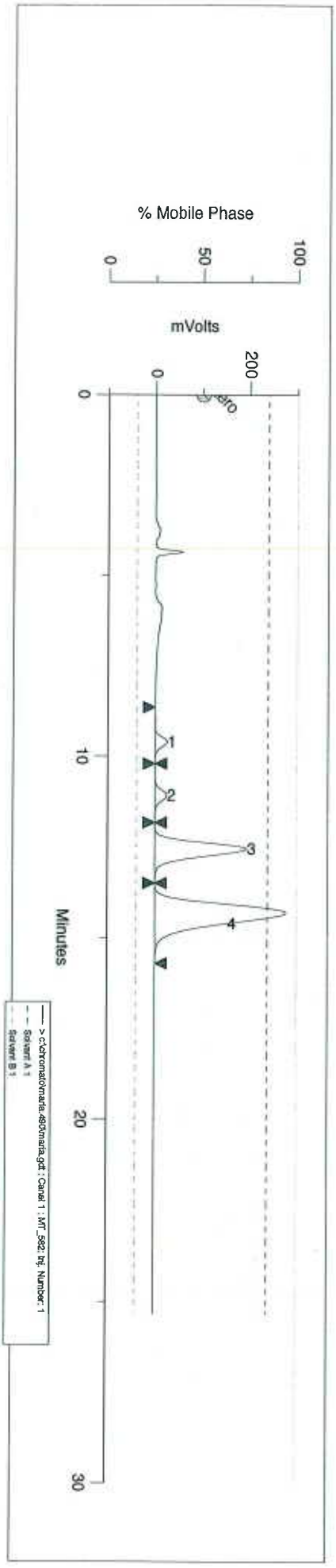
Benzoylation of meso-hydrobenzoin
Table 2, Entry 1, Run 4
Ligand (S,S) iPr-DiBox



	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	11.24	3465864.00	20.37	MT_555	*2
2	1	19.00	13546493.00	79.63	MT_555	*3

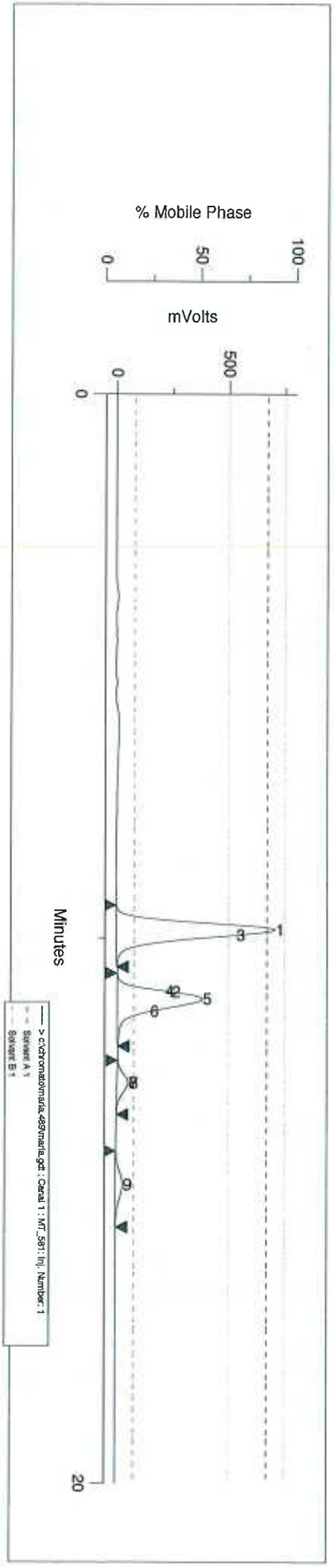
Benzoylation of meso-hydrobenzoin
Table 2, Entry 4, Run 4
Ligand (S,S) iPr-TetraBox





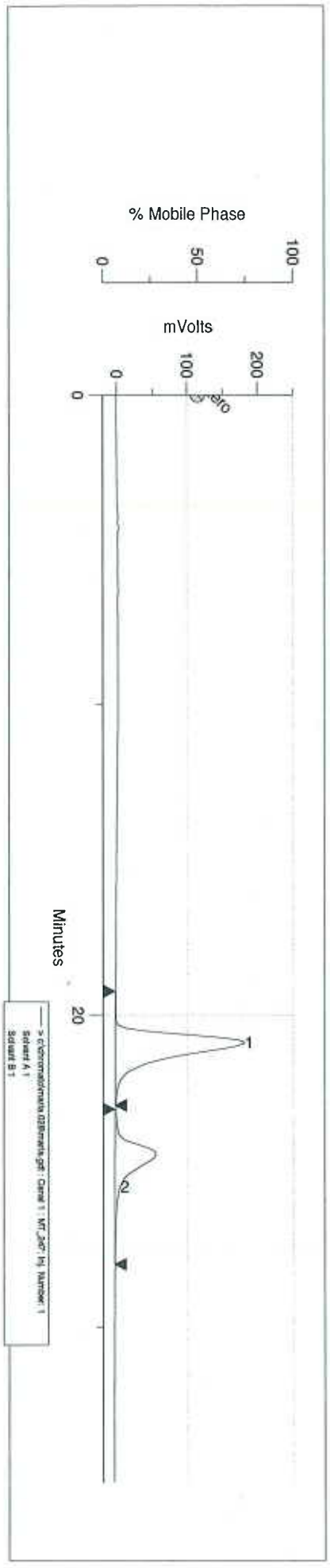
	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	9.60	971901.81	3.47	MT_582	*1
2	1	11.08	995889.38	3.55	MT_582	*2
3	1	12.55	8640794.00	30.84	MT_582	*3
4	1	14.31	17411008.00	62.14	MT_582	*4

Kinetic Resolution of rac-hydrobenzoin
Peak 1 and 3: hydrobenzoin
Peak 2 and 4: product
Table 3, ligand (S,S) iPr-DiBox, run 3



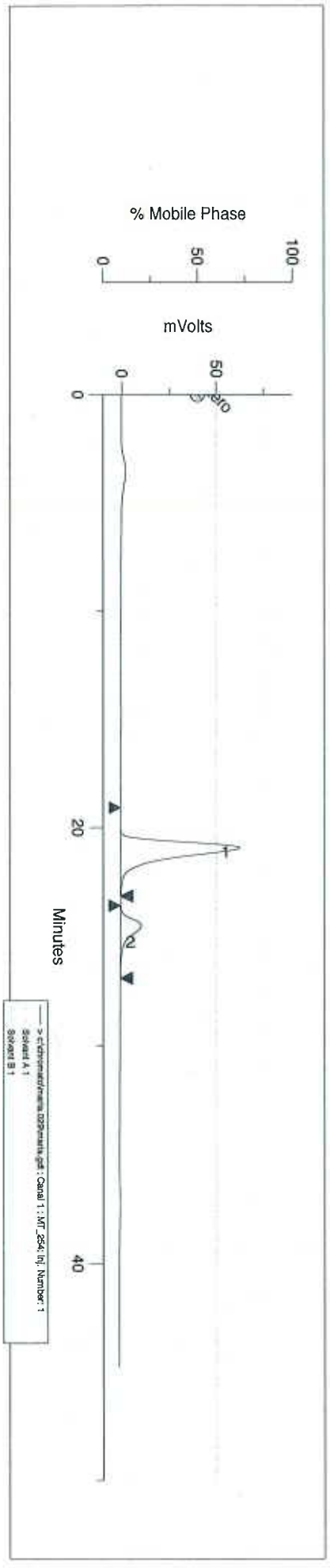
	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	9.85	23364804.00	47.66	MT_581	*1
2	1	11.12	21458248.00	43.77	MT_581	*5
3	1	12.66	2152407.25	4.39	MT_581	*7
4	1	14.52	2046736.12	4.18	MT_581	*9

Kinetic Resolution of rac-hydrobenzoin
Peak 1 and 3: hydrobenzoin
Peak 2 and 4: product
Table 3, ligand (R,R) Ph-DiBox, run 1



	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	20.88	14759151.00	68.15	MT_247	*1
2	1	24.45	6898212.50	31.85	MT_247	*2

Henry reaction
Table 4, Entry 4
Ligand (R,R) Ph-Dibox

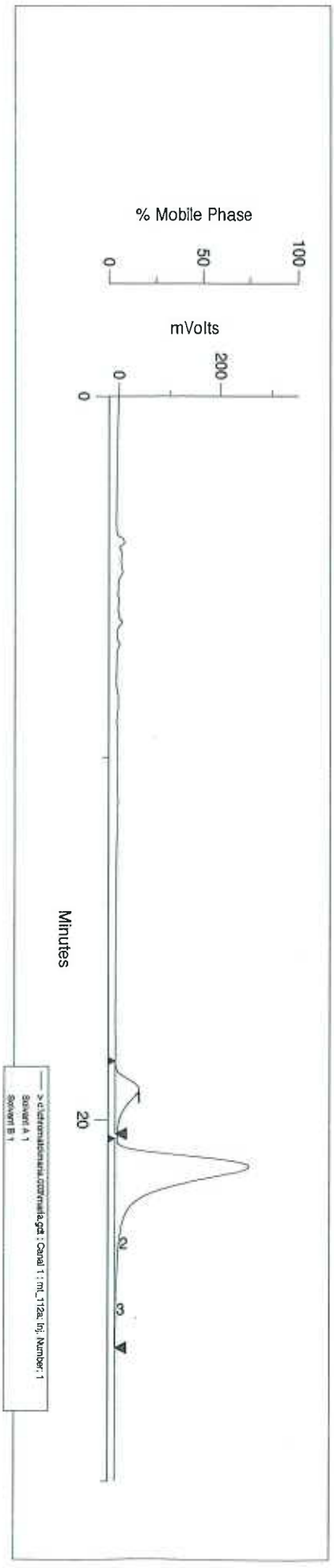


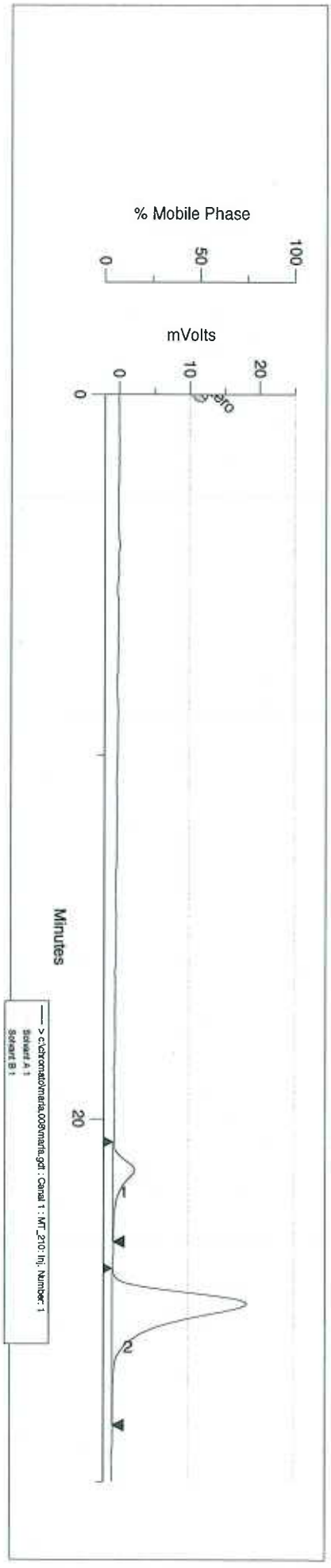
	Inj. Number	R. Time	Area	Area %	Sample Descrip	Peak Name
1	1	20.93	4997235.00	82.89	MT_254	*1
2	1	24.51	1031672.56	17.11	MT_254	*2

Henry reaction
Table 4, Entry 5
Ligand (R,R) iPrBox

	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	19.15	3943539.75	10.50	MT_112a	*1
2	1	21.27	33613981.00	89.50	MT_112a	*2

Henry reaction
Table 6, Run 1
Ligand (S,S) iPr-TetraBox





	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	21.41	261480.28	12.92	MT_210	*1
2	1	25.08	1763111.00	87.08	MT_210	*2

Henry reaction
Table 6, Run 3
Ligand (S,S) iPr-TetraBox

	Inj. Number	R. Time	Area	Area %	Sample Descrip.	Peak Name
1	1	21.77	865356.31	16.67	MT_217	*1
2	1	25.50	4328085.00	83.33	MT_217	*2

Henry reaction
Table 6, Run 5