

Supporting Information

γ -Sultam-cored N,N-ligands in ruthenium(II)-catalyzed asymmetric transfer hydrogenation of aryl ketones

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1. Determination of X-ray structures

Data for crystals of [*syn*-(3*S*,1'*R*)-6]·(*S*)-CSA, [*anti*-(3*R*,1'*R*)-6]·(*S*)-CSA, and racemic *trans*-5 were collected using monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and for crystals of **S7-reduced** (**S7** ATH major reduction product) using Cu-K α radiation ($\lambda = 1.54184$ Å). The coordinates of some or all of the non-hydrogen atoms were found *via* direct methods using the structure solution SHELXS-97 program.¹ Positions of the remaining non-hydrogen atoms were located by using a combination of least-squares refinement and difference Fourier maps in the SHELXL-97 program.¹ Except hydrogen atoms, all atoms were refined anisotropically. The absolute configuration of [*syn*-(3*S*,1'*R*)-6]·(*S*)-CSA and [*anti*-(3*R*,1'*R*)-6]·(*S*)-CSA were determined by refinement of the completed model together with the Flack *x* parameter² which refined to value of 0.00(8) and -0.06(5), respectively, and as such confirmed that the refined coordinates represent in both cases the true enantiomorph. For **S7-reduced**, the value of the Flack *x* parameter refined to 0.1(3). In this case, the absolute configuration of one chiral center, *i.e.* C(1), was known prior to the analysis. Figures depicting the structures were prepared by Ortep3³ and Mercury⁴. The supplementary crystallographic data (atomic coordinates, anisotropic displacement parameters, and extended lists of interatomic distances and angles) are contained in cif files.

1 G. M. Sheldrick, *SHELX-97. Programs for Crystal Structure Analysis*; University of Göttingen: Göttingen, Germany, 1998.

2 H. D. Flack, *Acta Crystallogr.*, 1983, **A39**, 876–881.

3 L. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.

4 C.F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453.

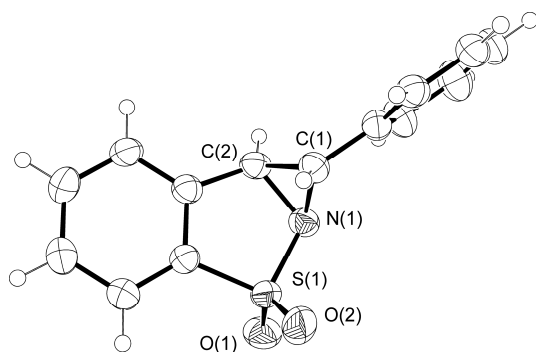


Fig. S1 ORTEP drawing of racemic *trans*-5 at the 50% probability level (only one enantiomorph is shown). $C_{14}H_{11}NO_2S$, F_w 257.30, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.1388(2)$, $b = 9.6226(2)$, $c = 9.7540(2)$ Å, $\alpha = 117.1972(15)$, $\beta = 112.3062(17)$, $\gamma = 92.1331(15)^\circ$, $V = 607.64(2)$ Å³, $Z = 2$, $T = 293(2)$ K, $d_{\text{calcd}} = 1.406$ g cm⁻³, $\mu = 0.258$ mm⁻¹, 4740 measured reflections, 2729 unique reflections ($R_{\text{int}} = 0.0141$), 171 refined parameters, $R_1 [I > 2\sigma(I)] = 0.0347$, $wR2$ [all data] = 0.0958.

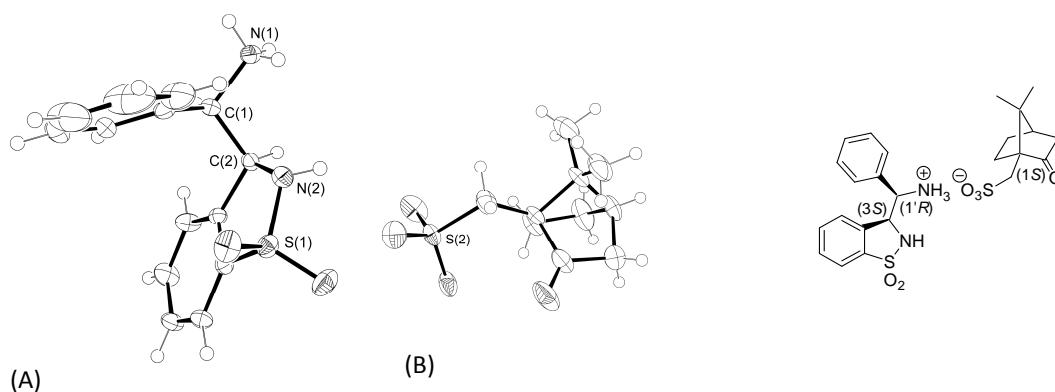


Fig. S2 ORTEP drawing of [*syn*-(3*S*,1'*R*)-6]·(*S*)-CSA at the 50% probability level; (A) cationic part, (B) anionic part.

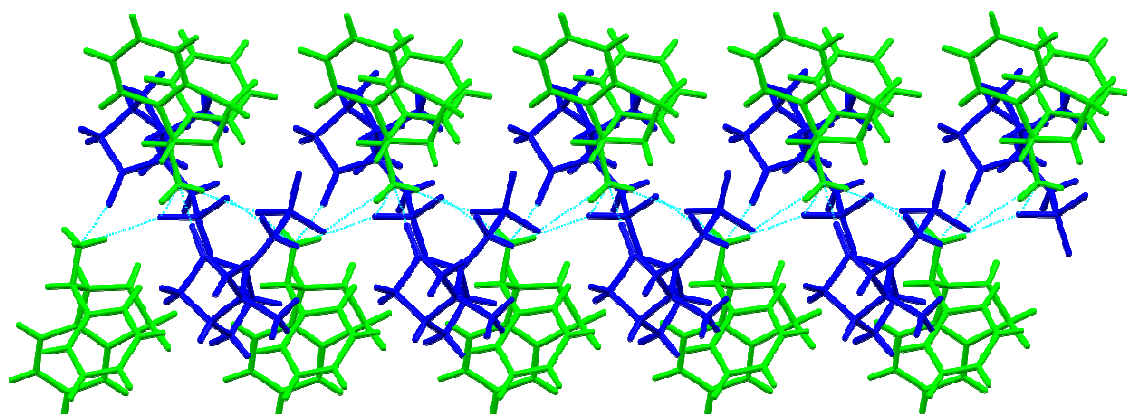


Fig. S3 Hydrogen-bonding pattern in [*syn*-(3*S*,1'*R*)-6]·(*S*)-CSA: each NH_3^+ group is engaged in H-bonds with three SO_3^- moieties with $N\cdots O$ contacts in the 2.979(3)–2.997(4) Å range.⁵ Infinite chains which run parallel to *b*-axis are thus formed. Color code: green - cations, blue - anions.

⁵ The sum of the van der Waals radii for O atoms is 3.07 Å. Data were taken from B. Douglas, D. McDaniel and J. Alexander, *Concepts and Models of Inorganic Chemistry*, 3rd Ed.; John Wiley and Sons: New York, 1994; p. 102.

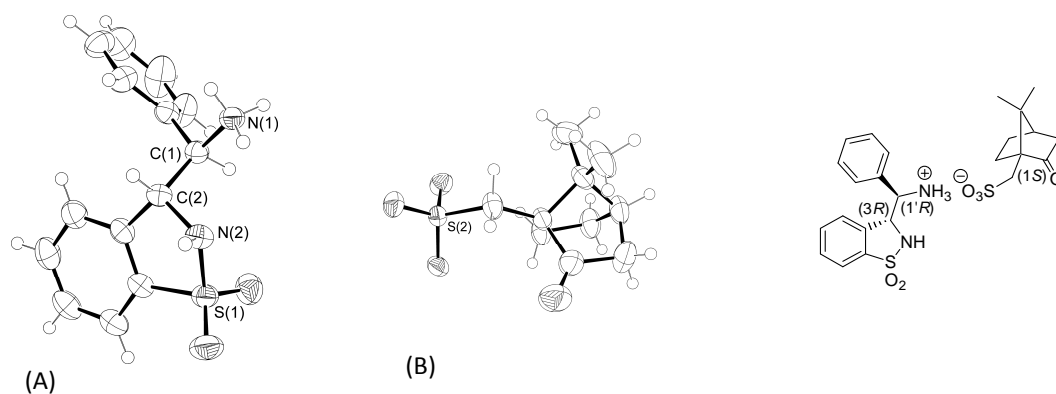


Fig. S4 ORTEP drawing of $[anti-(3R,1'R)-6] \cdot (S)\text{-CSA}$ at the 50% probability level; (A) cationic part, (B) anionic part.

Structural similarities exist between $[anti-(3R,1'R)-6] \cdot (S)\text{-CSA}$ and $[syn-(3S,1'R)-6] \cdot (S)\text{-CSA}$. Both crystallize in monoclinic space group $P 2_1$ with alike packing arrangement. Hydrogen bonds between NH_3^+ and SO_3^- groups in $[anti-(3R,1'R)-6] \cdot (S)\text{-CSA}$ also link cations and anions into infinite chains which run parallel to b -axis. The respective $\text{N} \cdots \text{O}$ contacts in $[anti-(3R,1'R)-6] \cdot (S)\text{-CSA}$, *i.e.*, 2.835(2)–2.861(2) Å, are slightly shorter than those observed for $[syn-(3S,1'R)-6] \cdot (S)\text{-CSA}$.

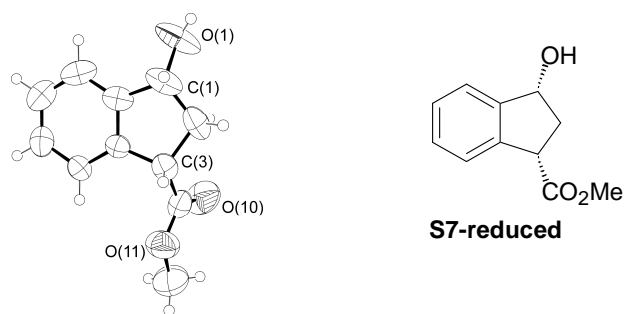


Fig. S5 ORTEP drawing of **S7** ATH major reduction product at the 50% probability level. $\text{C}_{11}\text{H}_{12}\text{O}_3$, F_w 192.21, orthorhombic, space group $P 2_12_12_1$ (No. 19), $a = 4.79020(10)$, $b = 12.6722(2)$, $c = 16.8843(3)$ Å, $V = 1024.92(3)$ Å³, $Z = 4$, $T = 293(2)$ K, $d_{\text{calcd}} = 1.246$ g cm⁻³, $\mu = 0.745$ mm⁻¹, 17698 measured reflections, 2070 unique reflections ($R_{\text{int}} = 0.0331$), 141 refined parameters, $R_1 [I > 2\sigma(I)] = 0.0418$, $wR2$ [all data] = 0.1206.

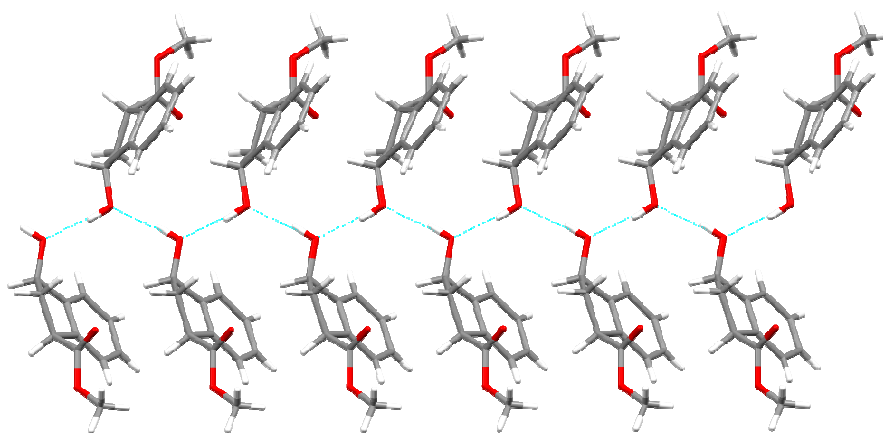
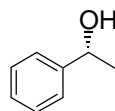


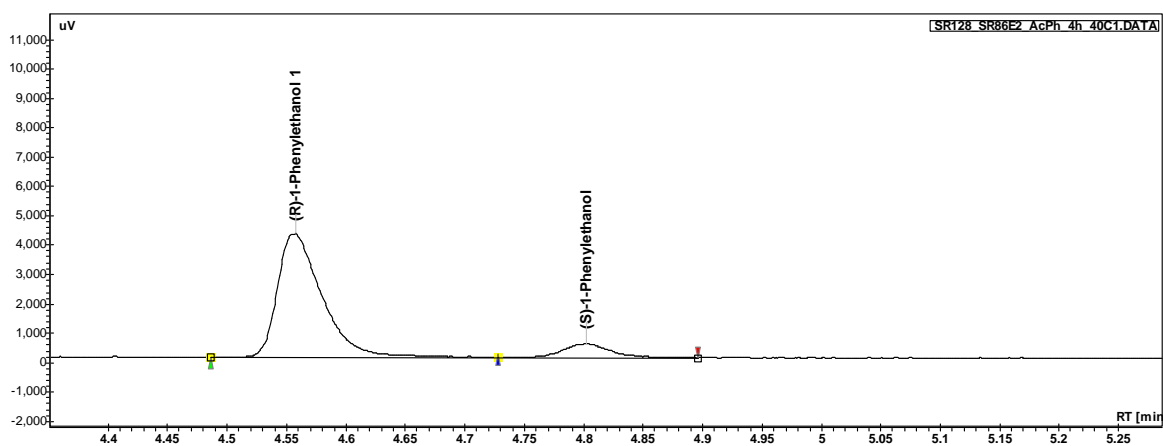
Fig. S6 In **S7-reduced**, the hydroxyl groups are engaged in H-bonds. Each molecule forms two H-bonds with two adjacent molecules. The respective $\text{O} \cdots \text{O}$ contacts are 2.6702(12) Å.⁵ Infinite chains are formed thereby. The chains propagate along a -axis.

2. GC & HPLC chromatograms

(R)-1-Phenylethanol. Ee was determined by chiral GC analysis⁶ on ChiralSil-DEX CB column (25m×0.25mm), 120 °C (isothermal), t_R : 4.6 min (R), 4.8 min (S).

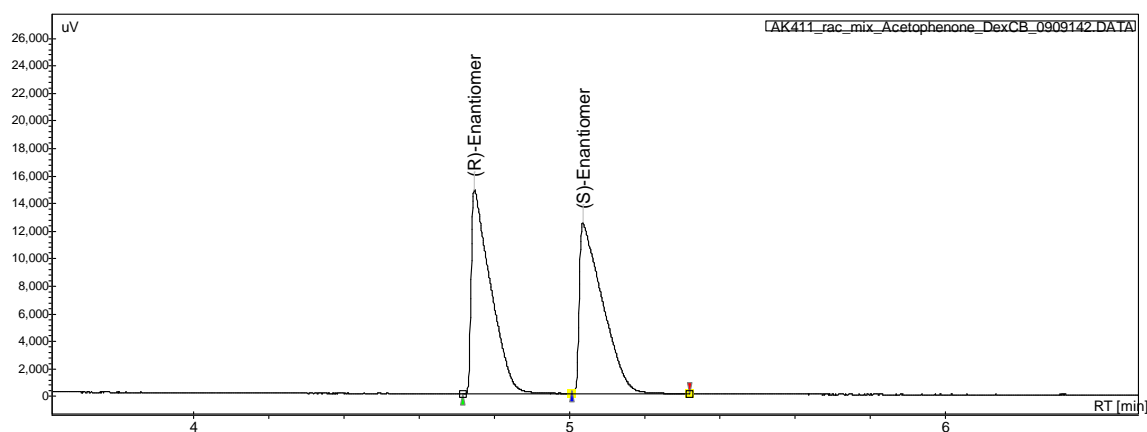


77.8% ee:



Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	(R)-1-Phenylethanol	4.56	4222.1	185.5	88.903
2	(S)-1-Phenylethanol	4.8	479.4	23.2	11.097
Total			4701.5	208.7	100

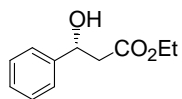
Racemate:



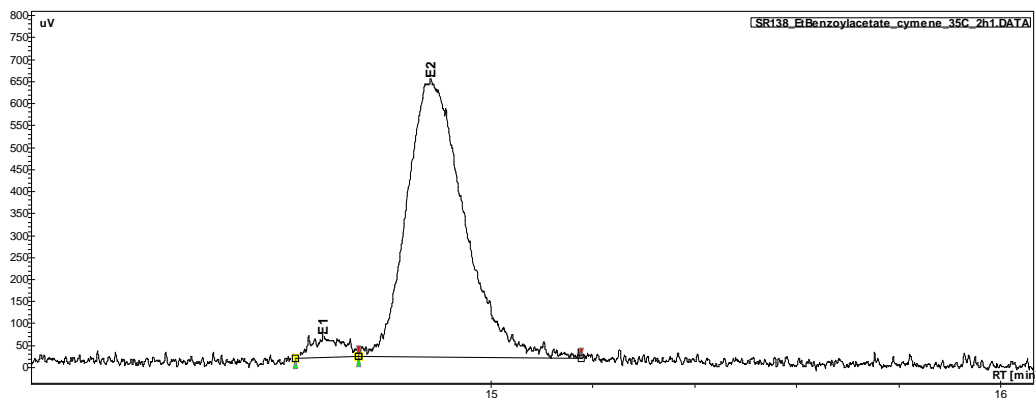
Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area %
1	(R)-Enantiomer	4.75	14823.3	888.1	50.007
2	(S)-Enantiomer	5.04	12434.6	887.9	49.993
Total			27257.8	1776	100

6 For chiral GC analysis, see: A. Kišić, M. Stephan and B. Mohar, *Adv. Synth. Catal.*, 2015, **357**, 2540–2546.

Ethyl (R)-3-hydroxy-3-phenylpropionate. Ee was determined by chiral GC analysis⁷ on Chiralsil-DEX CB (25m×0.25mm), 140 °C (isothermal); racemate, t_R : 14.6 min (S), 14.9 min (R).

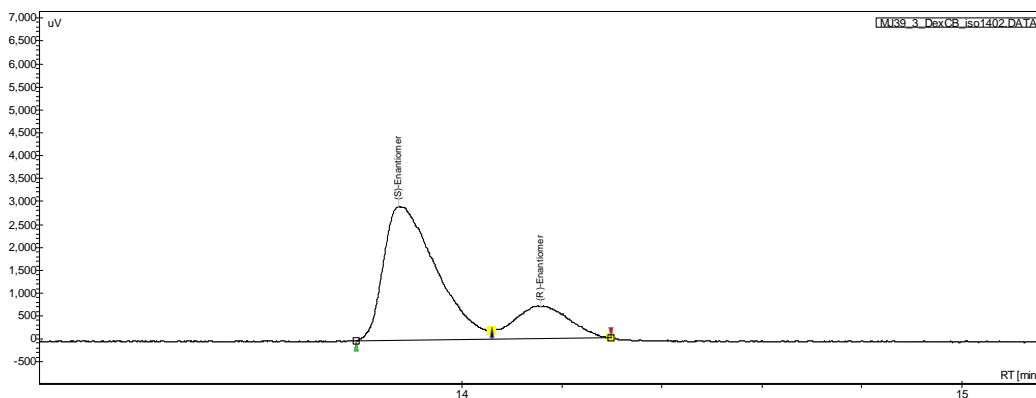


92.2% ee:



Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	(S)	14.67	46	3.3	3.897
2	(R)	14.88	632.8	82.3	96.103
Total			678.9	85.7	100

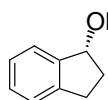
59% ee (S):



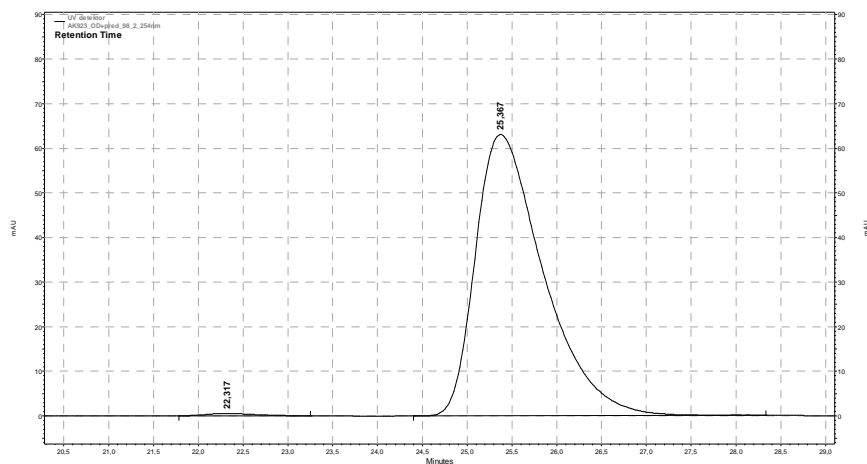
Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	(S)-Enantiomer	13.88	2920.7	355.4	79.466
2	(R)-Enantiomer	14.16	711.8	91.8	20.534
Total			3632.5	447.3	100

⁷ For chiral GC analysis, see: D. Šterk, M.S. Stephan and B. Mohar, *Tetrahedron: Asymmetry*, 2002, **13**, 2605–2608.

(R)-1-Indanol. Ee was determined by chiral HPLC analysis on Chiralcel OD column (25 cm). Eluent hexane/2-ProOH = 98:2, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_R : 22.6 min (S), 26.2 min (R).⁶

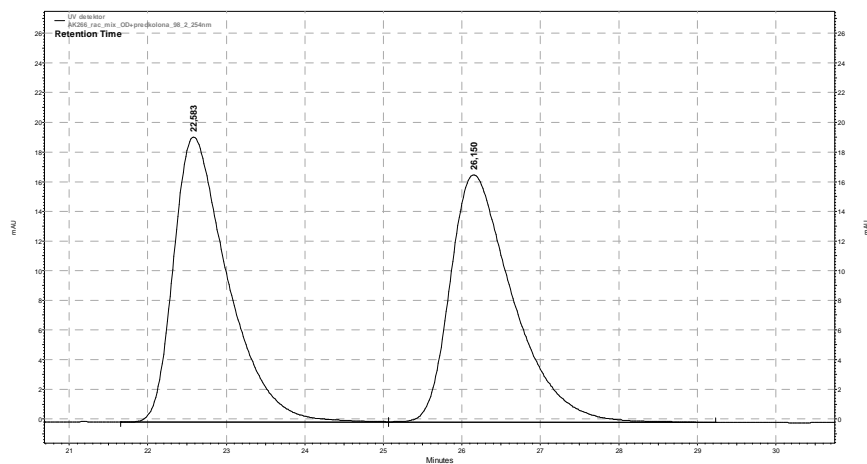


98.8% ee:



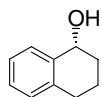
Peak	Retention [min]	Area	Area %	Height	Height %
E1	22,317	20364	0,61	514	0,81
E2	25,367	3329183	99,39	63074	99,19
Totals		3349547	100	63588	100

Racemate:

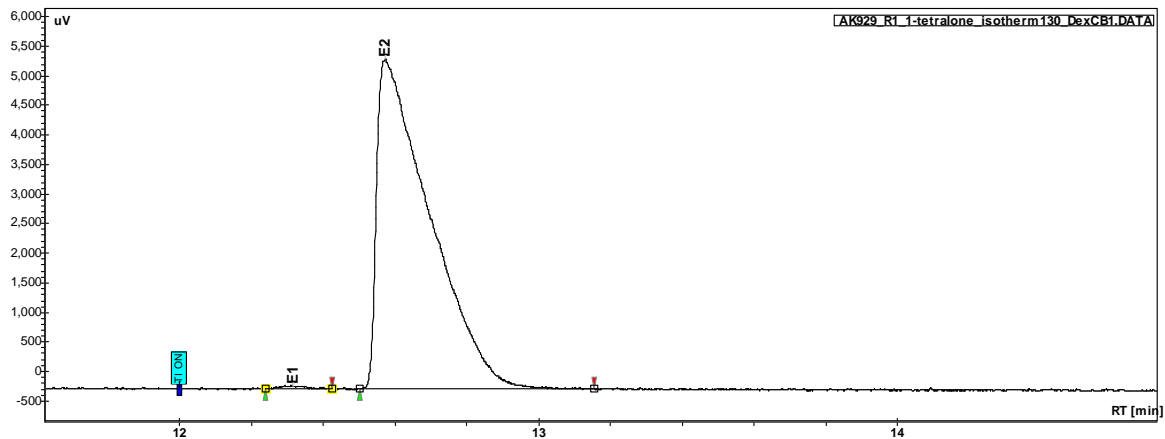


Peak	Retention [min]	Area	Area %	Height	Height %
E1	22,583	922630	49,84	19218	53,52
E2	26,15	928369	50,16	16689	46,48
Totals		1850999	100	35907	100

(R)-1-Tetralol. Ee was determined by chiral GC analysis on Chiralsil-DEX CB column (25m×0.25mm), 130 °C (isothermal), t_R : 13.3 min (S), 13.8 min (R).⁶

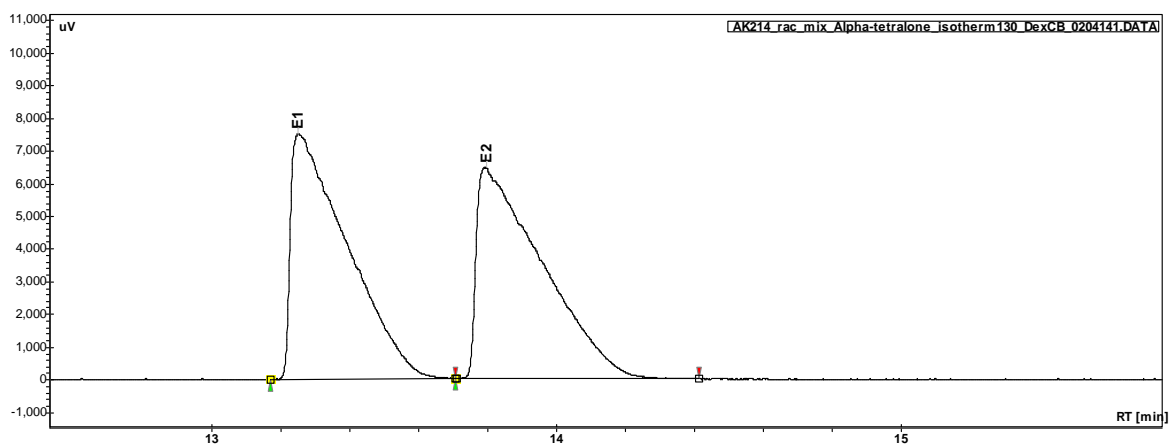


99.1% ee:



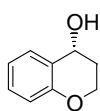
Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	E1	12.31	48.3	4.3	0.446
2	E2	12.57	5579	953	99.554
Total			5627.3	957.2	100

Racemate:

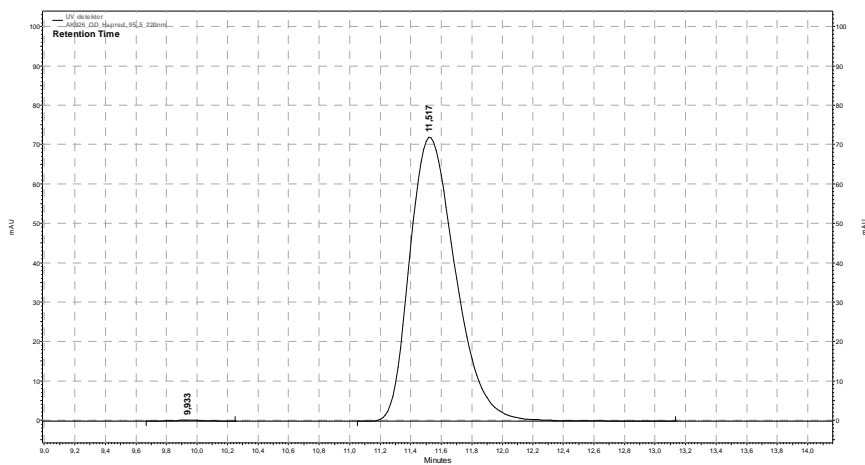


Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	E1	13.25	7499.5	1421.7	50.023
2	E2	13.8	6458.2	1420.4	49.977
Total			13957.7	2842.2	100

(R)-4-Chromanol. Ee was determined by chiral HPLC analysis on Chiralcel OD-H column (25 cm). Eluent hexane/2-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 220$ nm, t_R : 10.0 min (S), 11.7 min (R).⁶

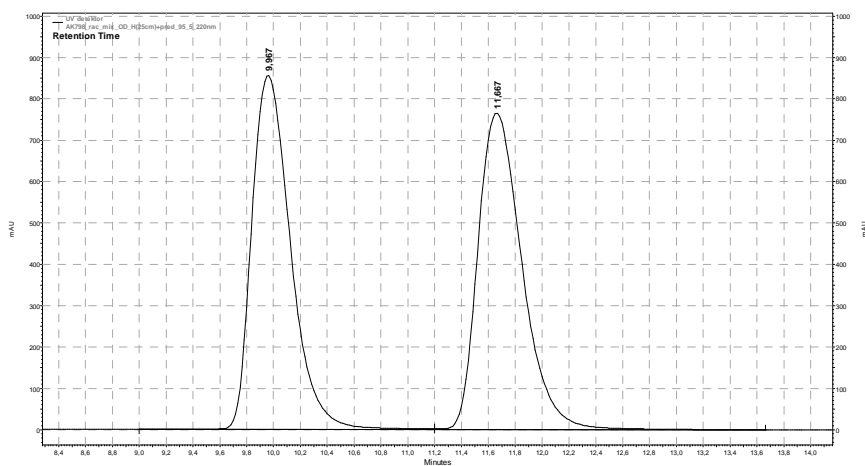


99.4% ee:



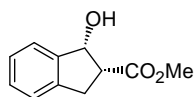
Peak	Retention [min]	Area	Area %	Height	Height %
E1	9,933	3852	0,26	226	0,31
E2	11,517	1503073	99,74	72088	99,69
Totals		1506925	100	72314	100

Racemate:



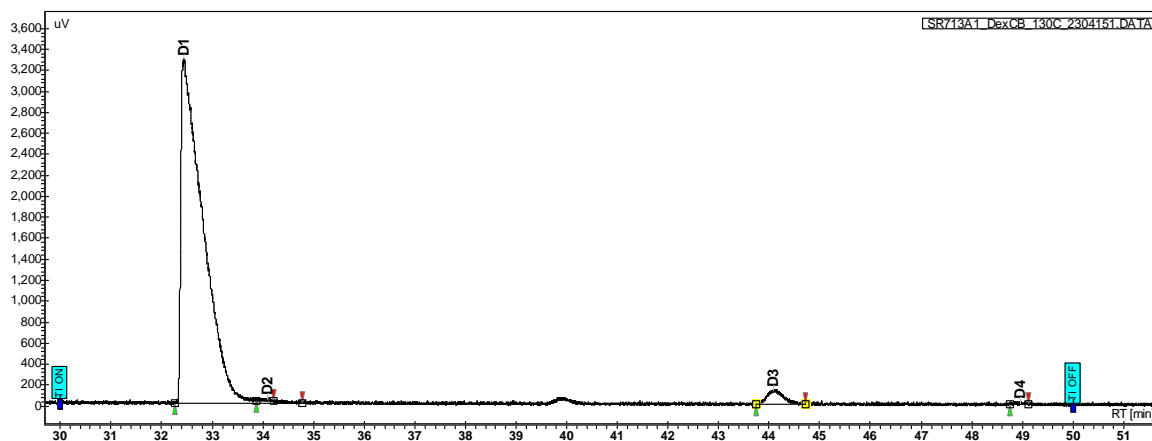
Peak	Retention [min]	Area	Area %	Height	Height %
E1	9,967	17102626	49,52	854922	52,79
E2	11,667	17433312	50,48	764598	47,21
Totals		34535938	100	1619520	100

(1*R*,2*R*)-2-Methoxycarbonyl-1-indanol. Ee was determined by chiral GC analysis on Chiralasil-DEX CB column (25m×0.25mm), 130 °C (isothermal); racemates (*cis/trans* = 55:45), *t_R*: 33.7 min [*cis* (*R,R*)], 34.8 min [*cis* (*S,S*)], 45.0 min (*trans*-1), 50.0 min (*trans*-2).⁶



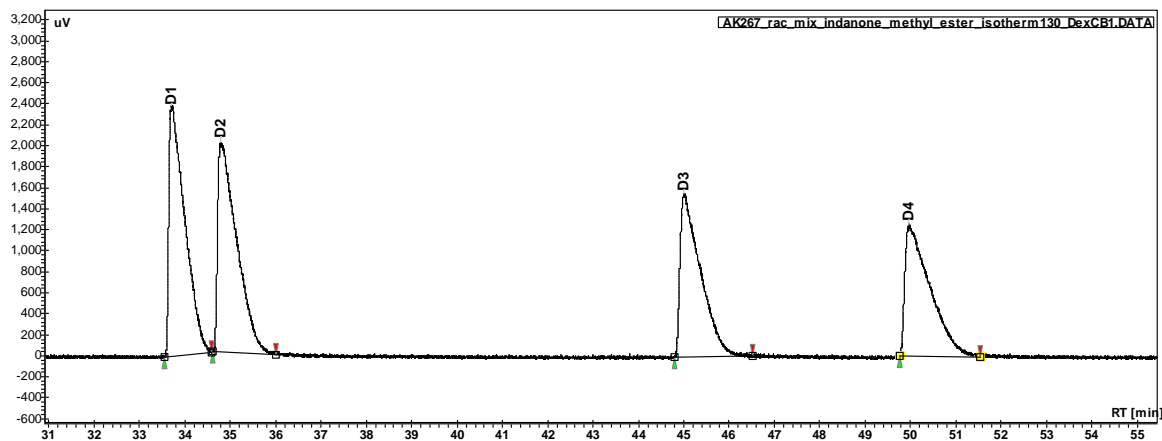
99.5% ee, *cis:trans*

97:3



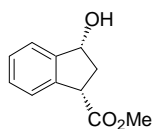
Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	(<i>R,R</i>)	32.45	3277.9	1649.6	96.466
2	(<i>S,S</i>)	34.09	16.6	4.3	0.253
3	<i>trans</i> -1	44.09	134.2	52.1	3.047
4	<i>trans</i> -2	48.95	15.8	4	0.234
Total			3444.6	1710	100

Racemates:

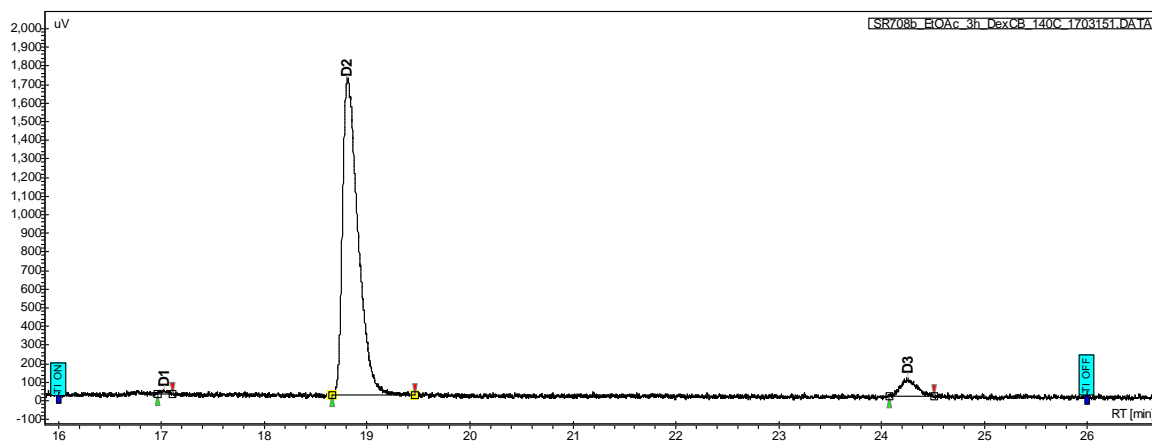


Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	(<i>R,R</i>)	33.71	2385.5	977.2	27.468
2	(<i>S,S</i>)	34.79	1991	972	27.323
3	<i>trans</i> -1	45	1550.7	807.9	22.71
4	<i>trans</i> -2	49.96	1253.2	800.4	22.499
Total			7180.4	3557.6	100

(1*R*,3*S*)-3-Methoxycarbonyl-1-indanol. Ee was determined by chiral GC analysis on Chiralsil-DEX CB column (25m×0.25mm), 130 °C (isothermal); racemates (*cis/trans* = 97:3), *t_R*: 16.8 min [*cis* (1*S*,3*R*)], 18.6 min [*cis* (1*R*,3*S*)], 24.1 min (*trans*-1), 25.2 min (*trans*-2).

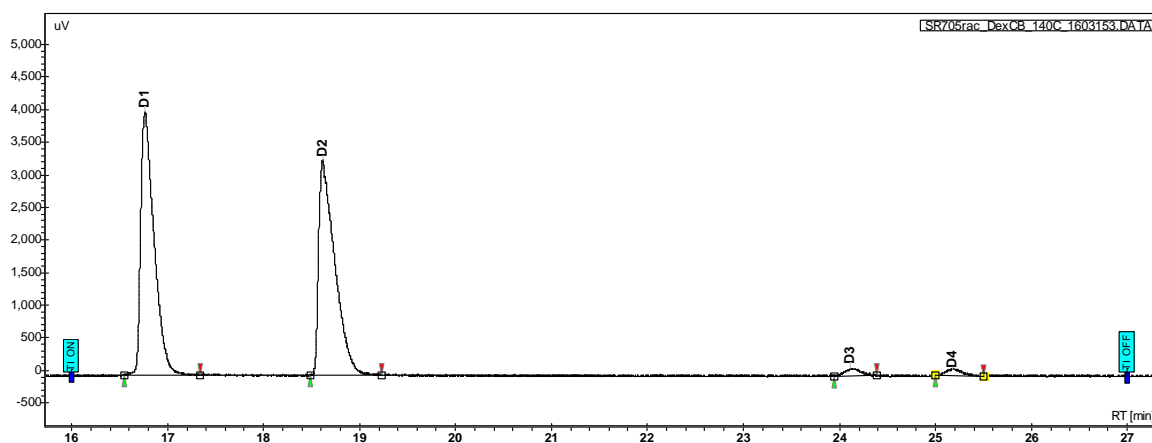


98.8% ee (*cis*), >99% ee (*trans*):



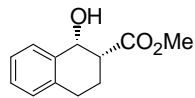
Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	(S,R)	17.03	24	1.8	0.566
2	(R,S)	18.81	1704.4	299.5	94.123
3	trans	24.25	95.9	16.9	5.311
Total			1824.3	318.2	100

Racemates:

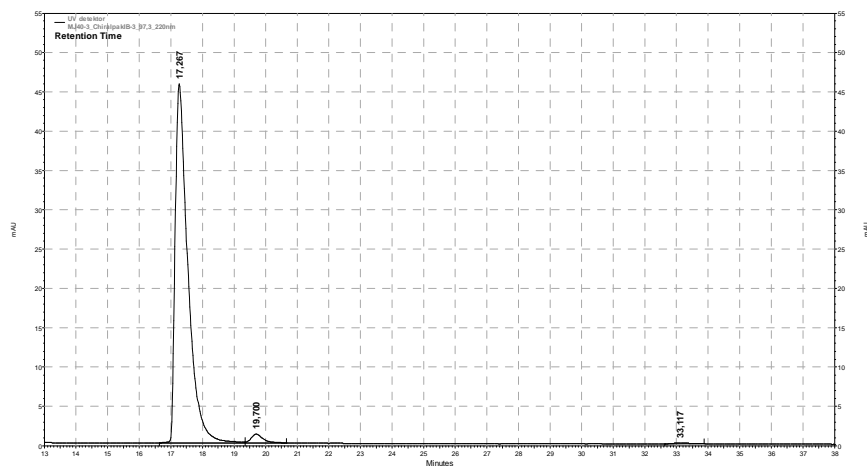


Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area [%]
1	(S,R)	16.76	4029.6	648	48.569
2	(R,S)	18.62	3304.1	641.9	48.109
3	trans-1	24.11	114.1	22.7	1.699
4	trans-2	25.18	104.7	21.7	1.623
Total			7552.5	1334.2	100

(1*R*,2*R*)-2-Methoxycarbonyl-1-tetralol. Dr (*cis/trans* = 97.6:2.4) was determined by ¹H NMR; ee (*cis* 99.4%) was determined by chiral HPLC analysis on Chiralpak IB-3 column (25 cm). Eluent hexane/2-PrOH = 97/3, flow rate 1.0 mL/min, λ = 220 nm; racemates: *t_R*: 15.4 min (*trans*-1), 17.4 min [*cis* (*R,R*)], 19.7 min (*trans*-2), 32.7 min [*cis* (*S,S*)].

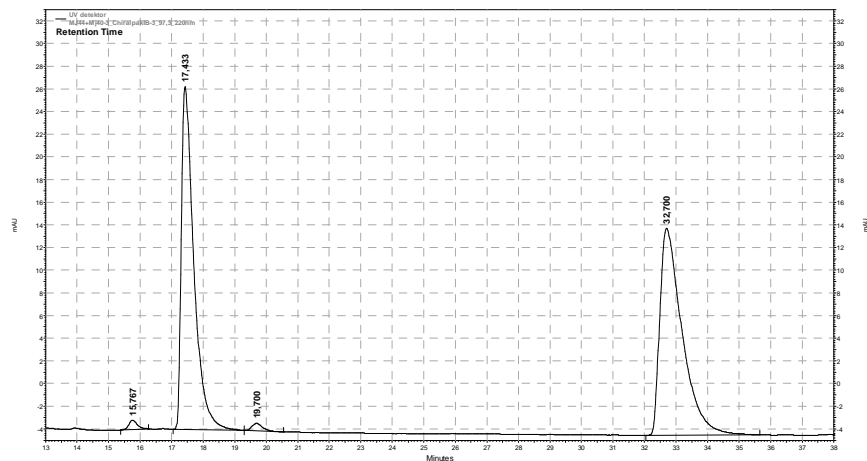


cis/trans = 98:2, >99% ee (*cis*)



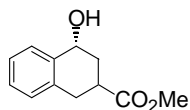
Retention Time	Area	Area %	Height	Height %
17,267	1273876	97,49	45633	97,35
19,700	28950	2,22	1120	2,39
33,117	3868	0,30	124	0,26
Totals	1306694	100,00	46877	100,00

Mixture prepared by weighing both corresponding ATH products derived from enantiomeric catalysts:



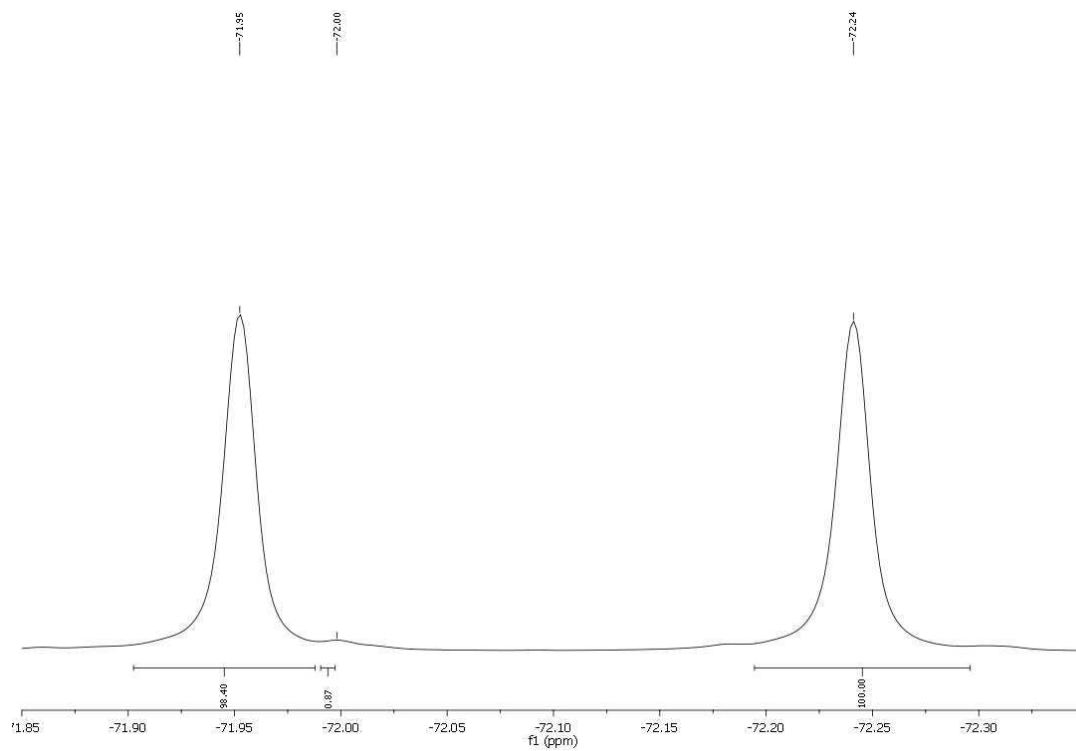
Retention Time	Area	Area %	Height	Height %
15,767	15468	0,88	820	1,64
17,433	836859	47,35	30256	60,51
19,700	15787	0,89	662	1,32
32,700	899355	50,88	18265	36,53
Totals	1767469	100,00	50003	100,00

(1*R*,3*RS*)-3-Methoxycarbonyl-1-tetralol. Dr (*cis/trans* = 50:50) was determined by ^1H NMR; ee (99% for *cis*) was determined by ^{19}F NMR (CDCl_3) of the (*R*)-Mosher ester (prepared from (*S*)-Mosher's acid chloride): δ 71.95 [*cis* (1*R*,3*R*)], 72.00 [*cis* (1*S*,3*S*)], 72.24 (*trans*; stereoisomers not separated).

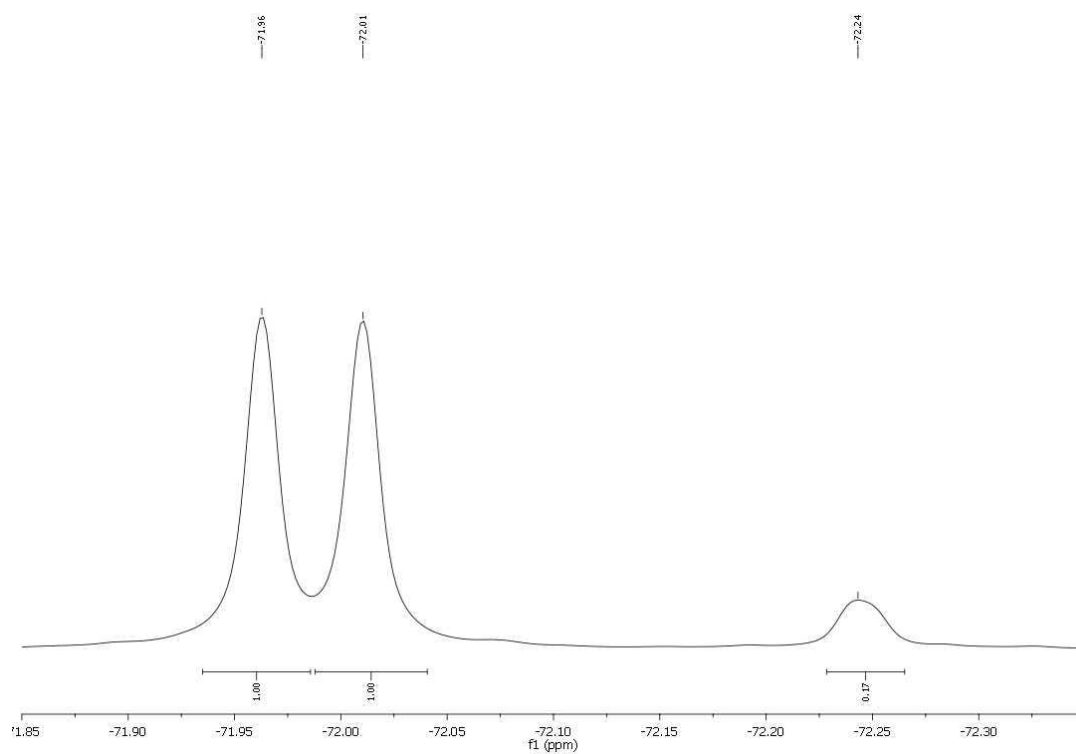


cis/trans = 50:50, 99% ee (*cis*)

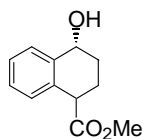
^{19}F NMR (CDCl_3) of the (*R*)-Mosher ester



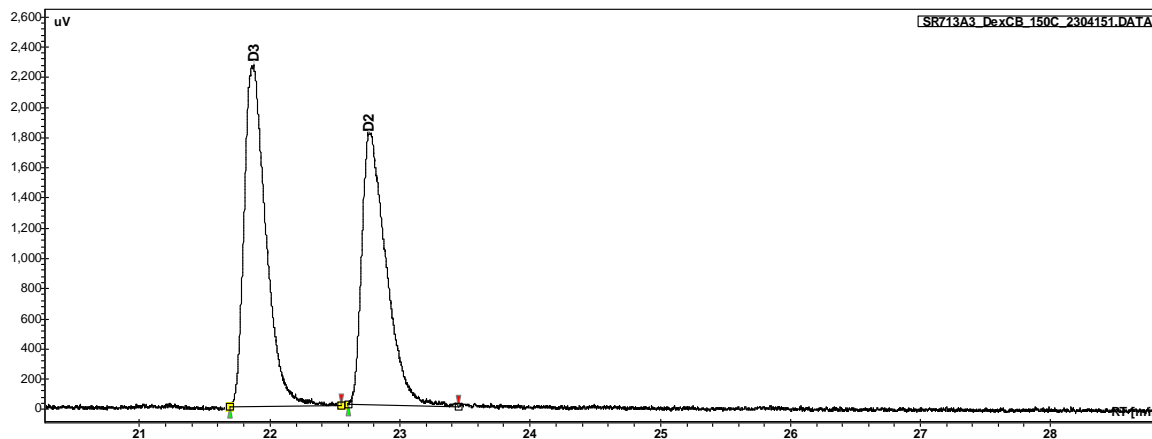
Racemates:



(1*R*,4*R*S)-4-Methoxycarbonyl-1-tetralol. Dr (*cis/trans* = 50:50) was determined by ¹H NMR; ee was determined by chiral GC analysis on Chiralsil-DEX CB column (25m×0.25mm), 150 °C (isothermal); racemates (*cis/trans* = 72:28), *t_R*: 21.1 min (*cis* 1*R*,4*S*), 21.9 min (*trans* 1*R*,4*R*), 22.7 min (*cis* 1*S*,4*R*), 24.4 min (*trans* 1*S*,4*S*).

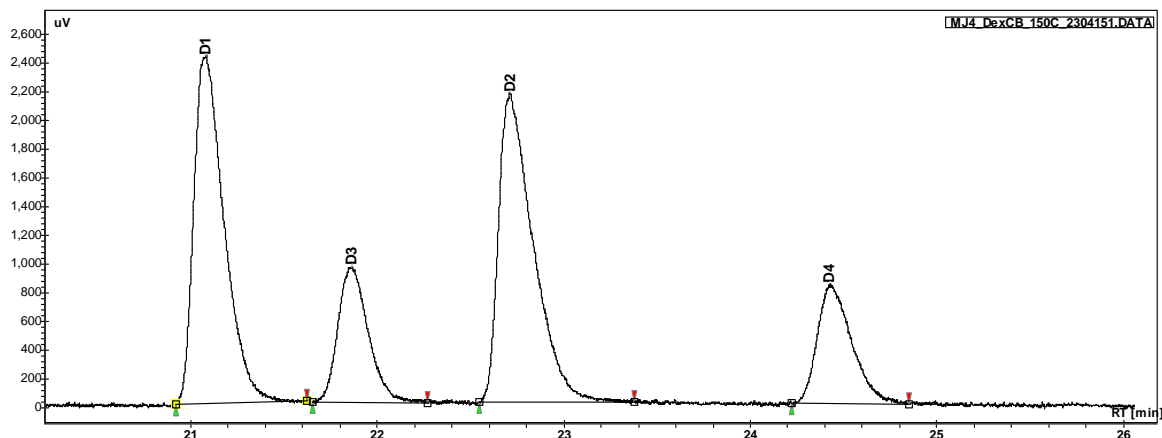


>99% ee (*cis*), >99% ee (*trans*):



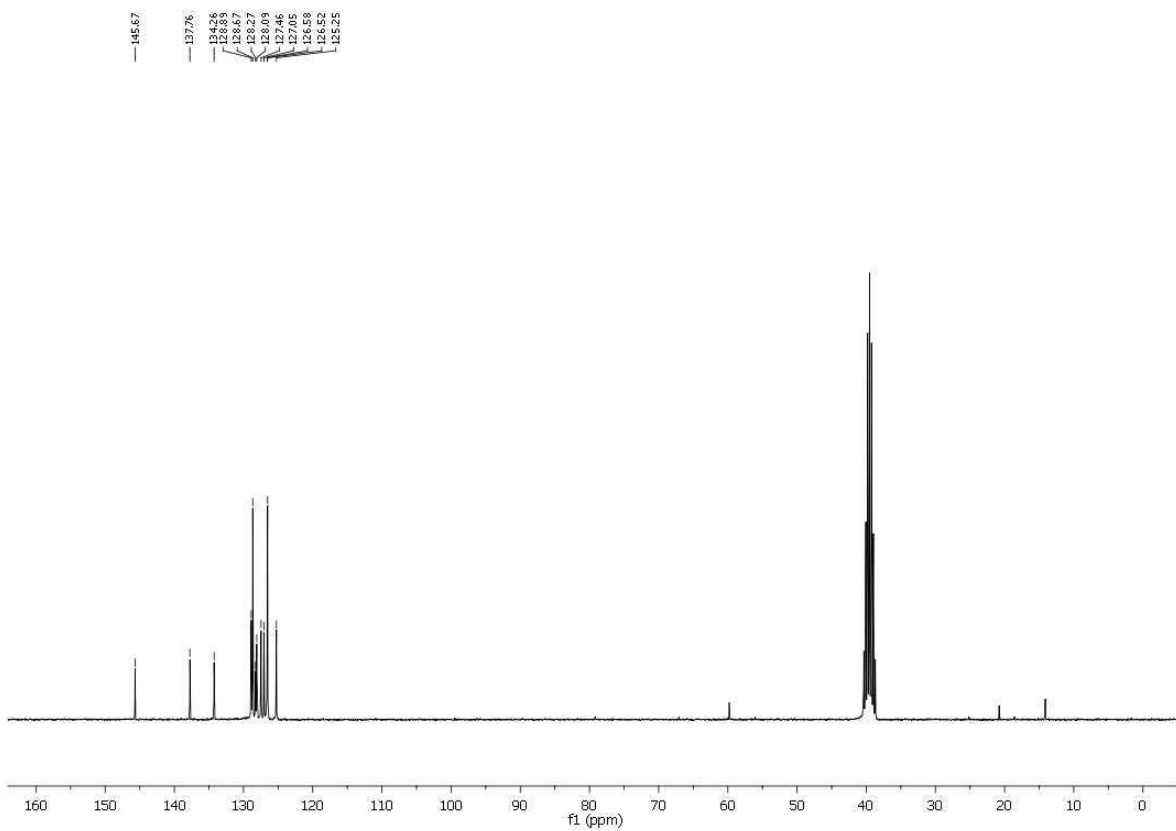
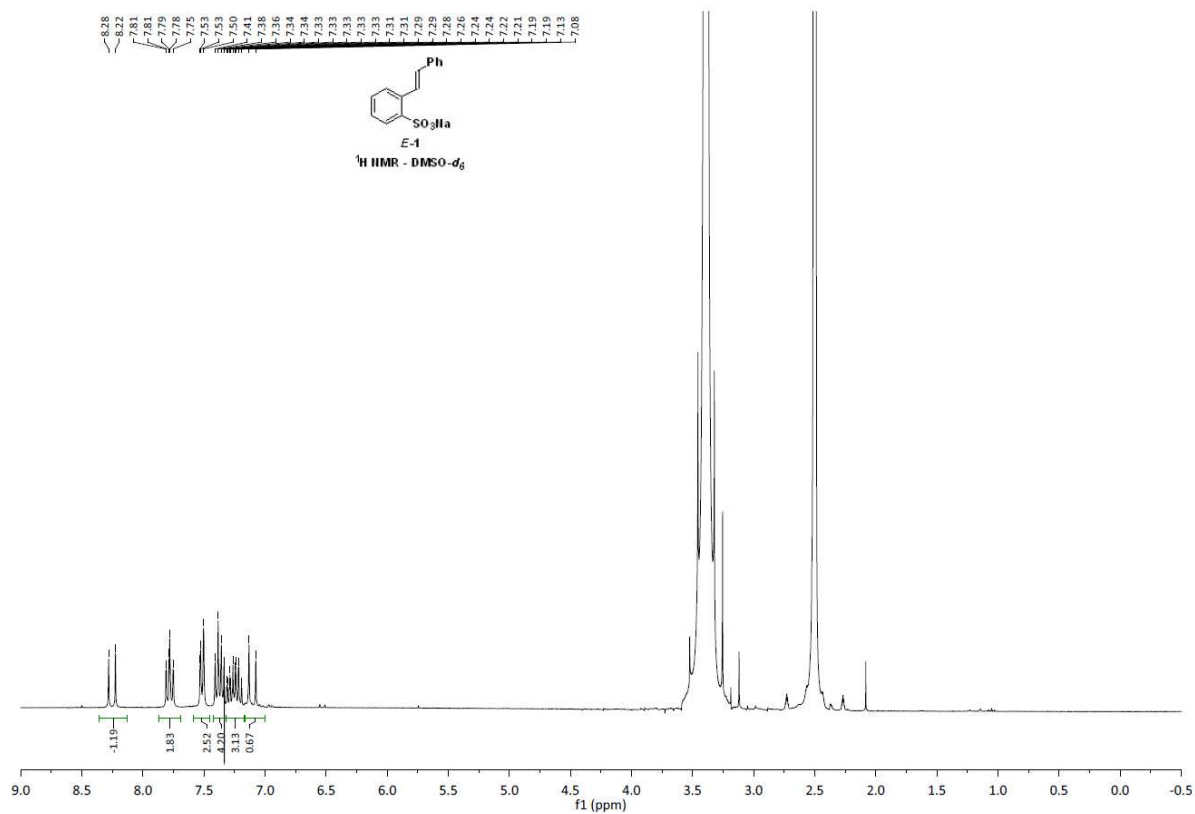
Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	D3	21.88	2268.4	438.8	52.845
2	D2	22.76	1803.8	391.6	47.155
Total			4072.2	830.4	100

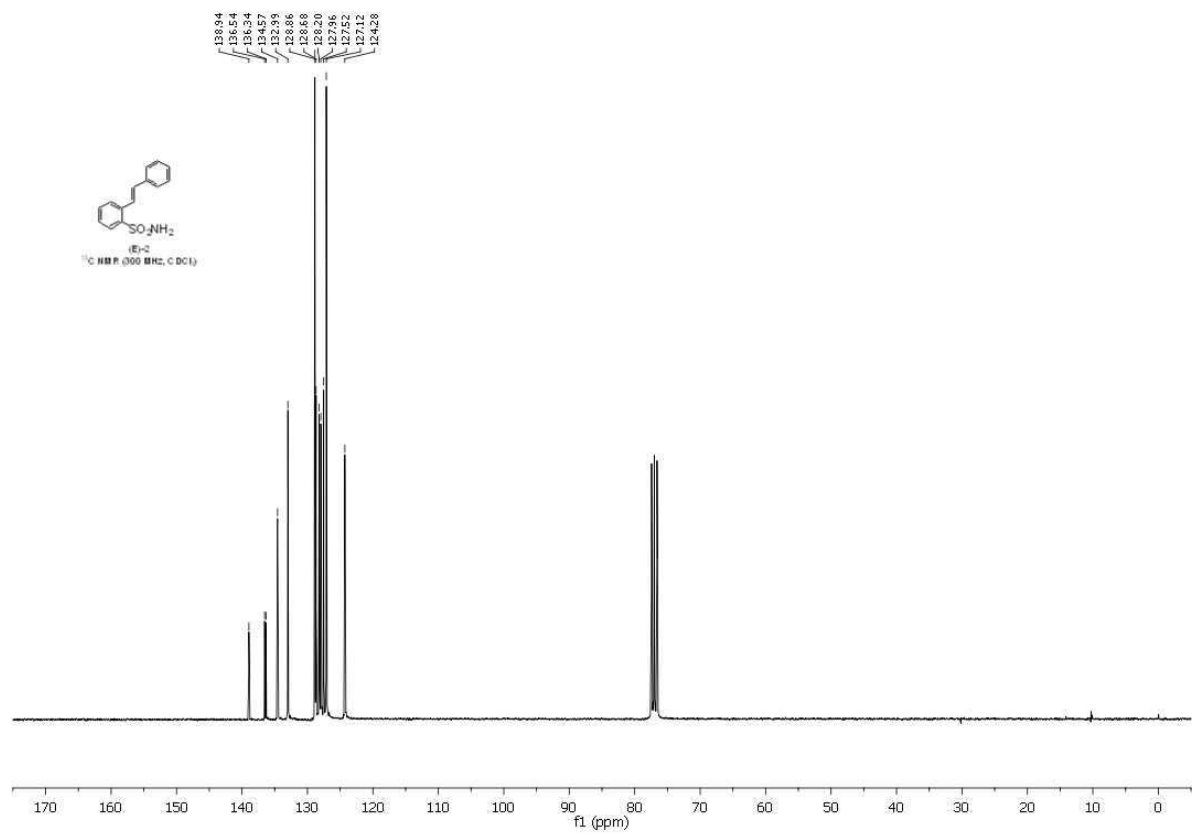
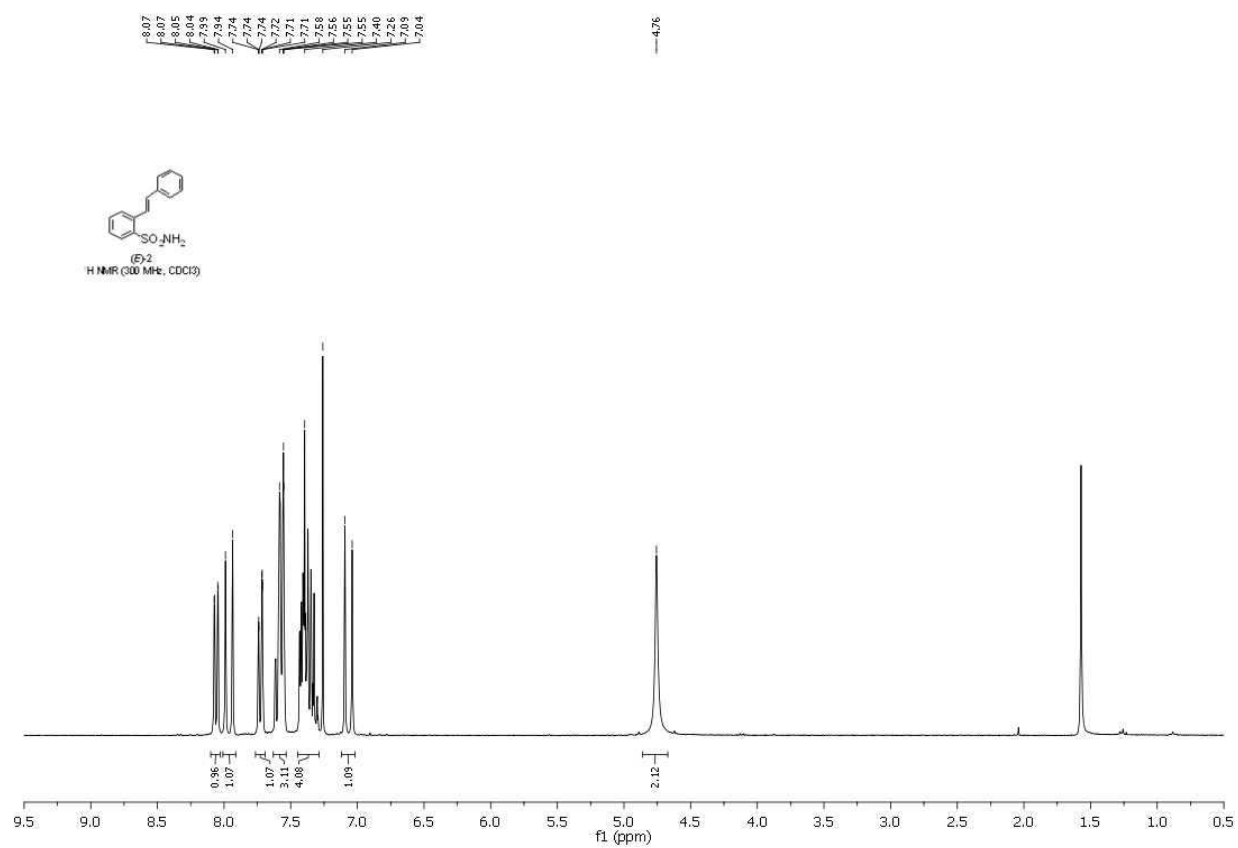
Racemates (*cis/trans* 72:28):

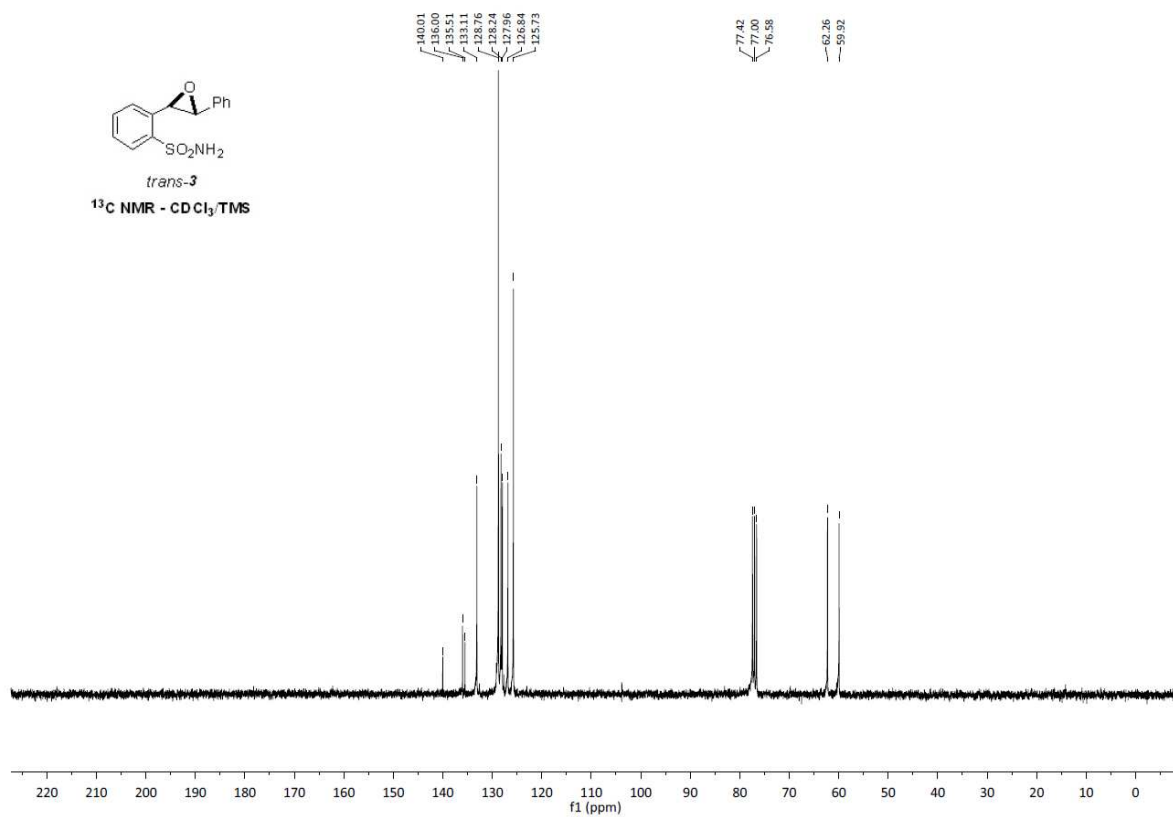
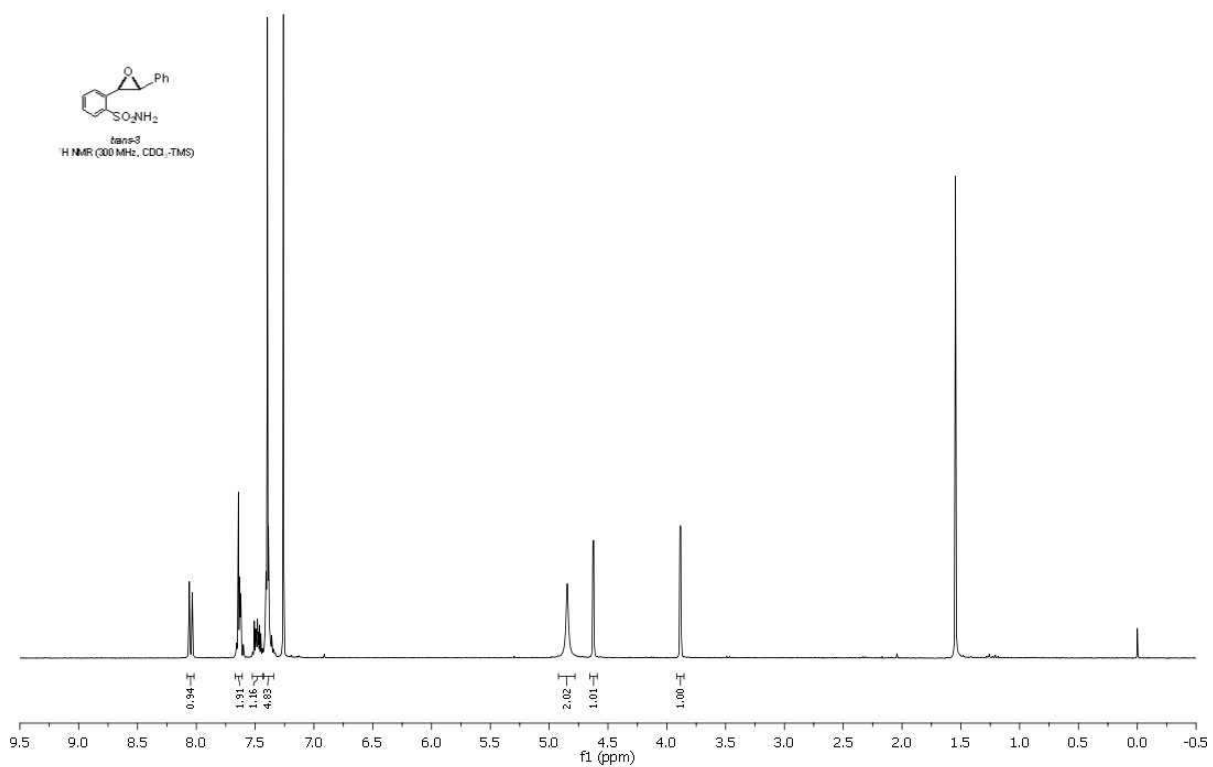


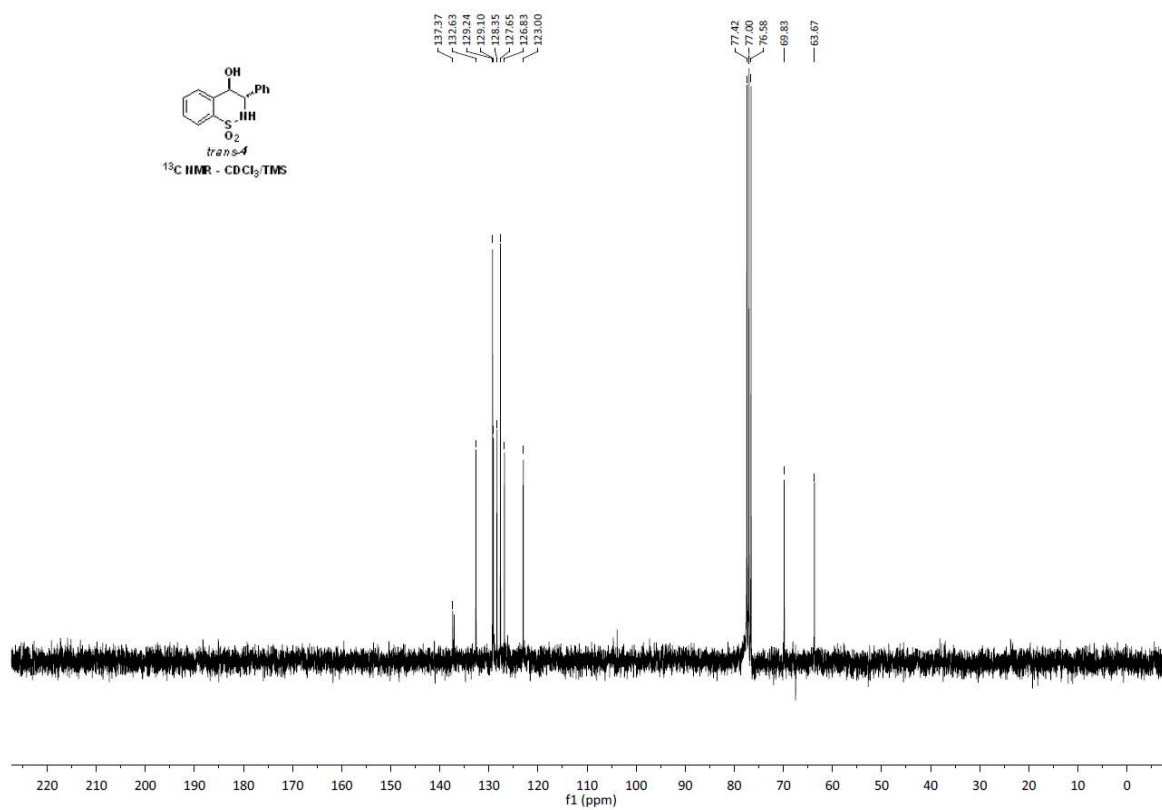
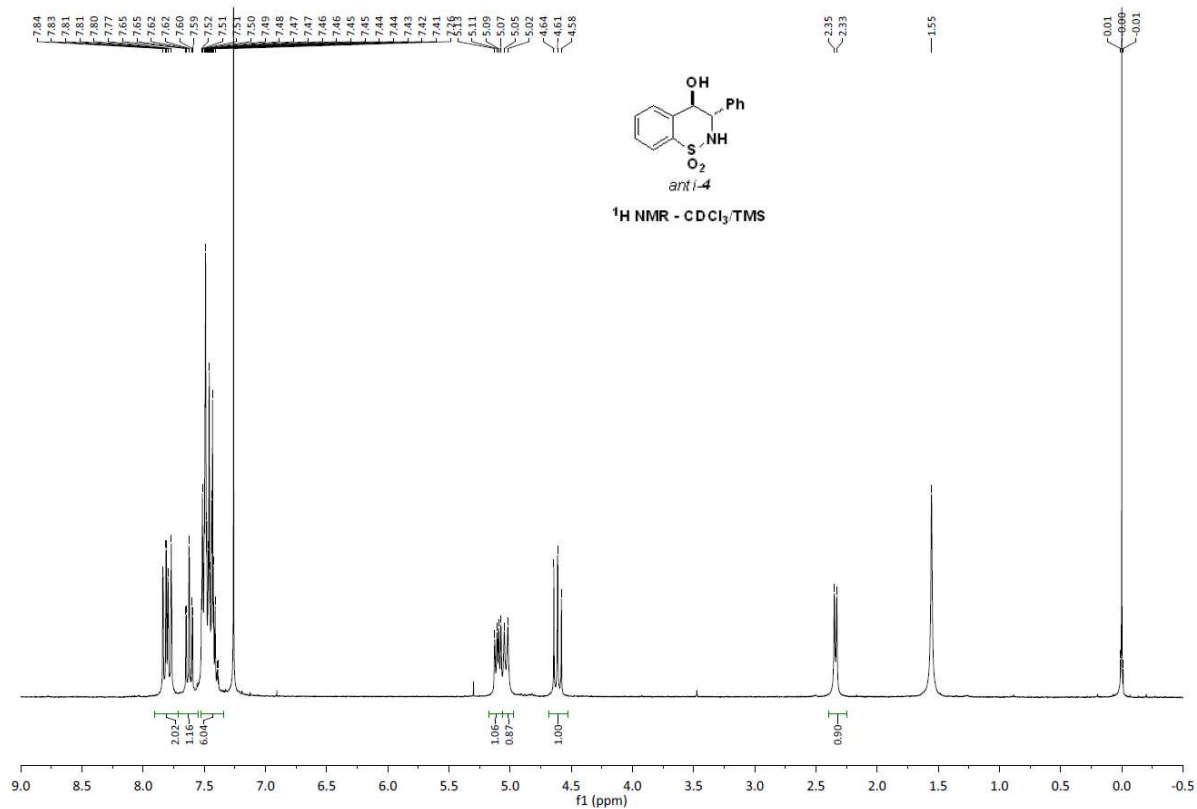
Peak	Name	Time [Min]	Height [uV]	Area [uV.Min]	Area % [%]
1	D1	21.08	2418.5	453.4	35.934
3	D3	21.86	942.9	178.2	14.126
2	D2	22.71	2150	453.5	35.939
4	D4	24.43	833.6	176.7	14.001
Total			6345	1261.8	100

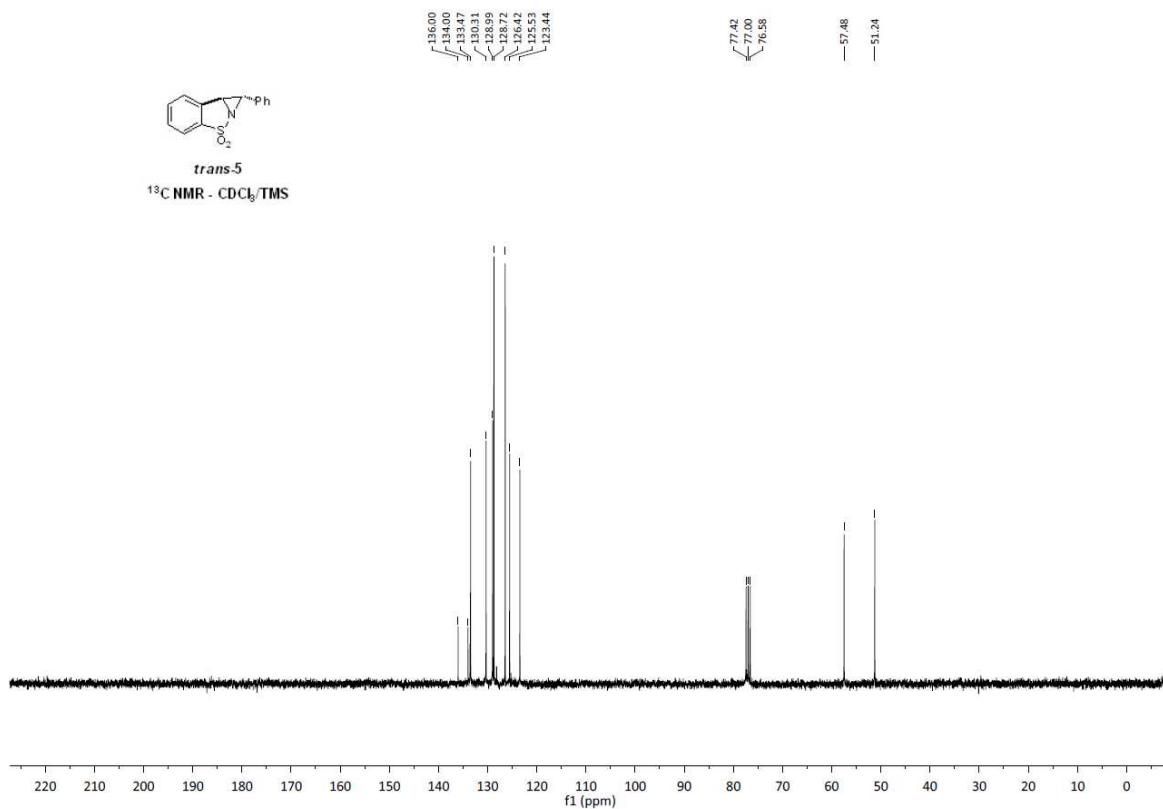
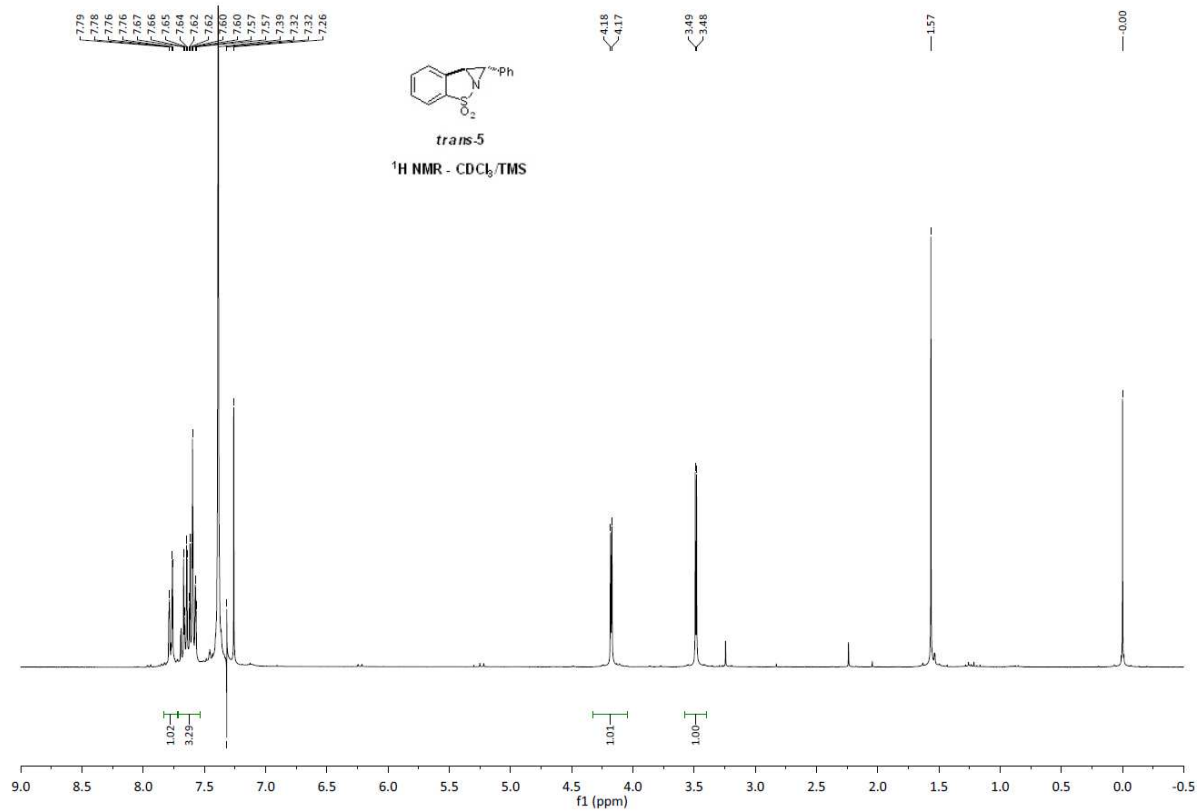
3. ^1H NMR and ^{13}C NMR spectra

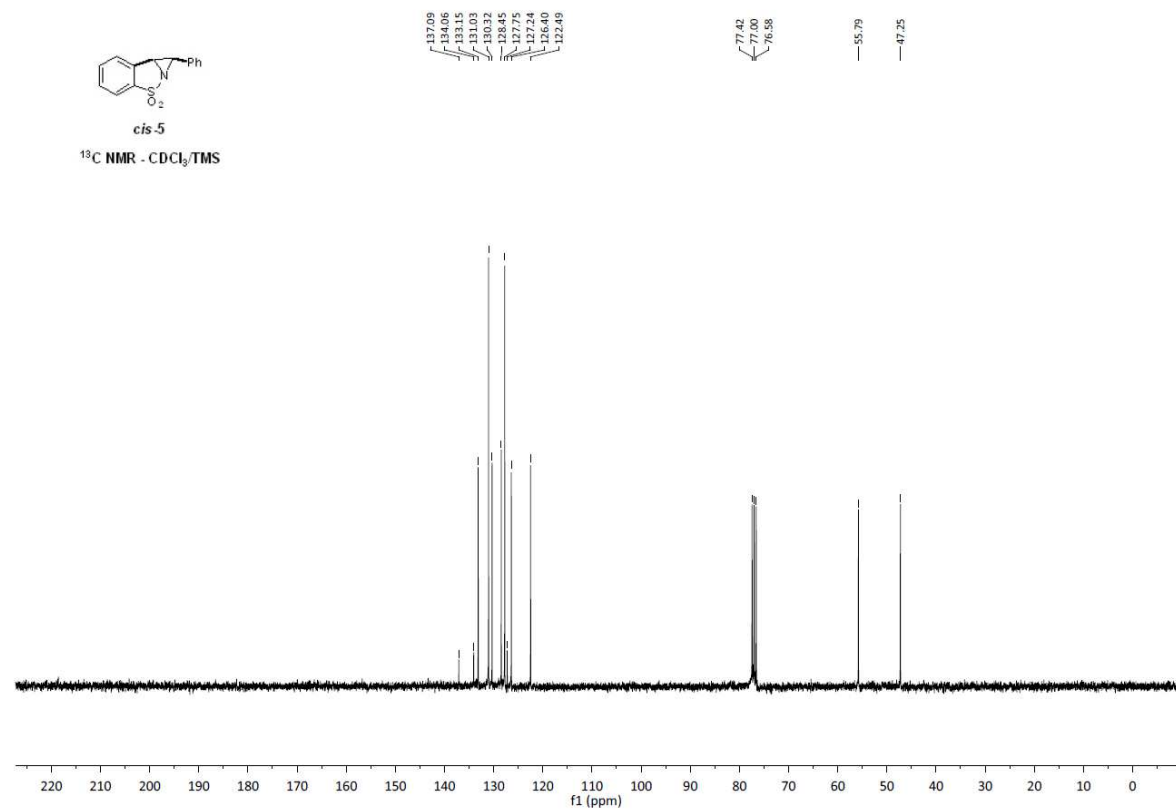
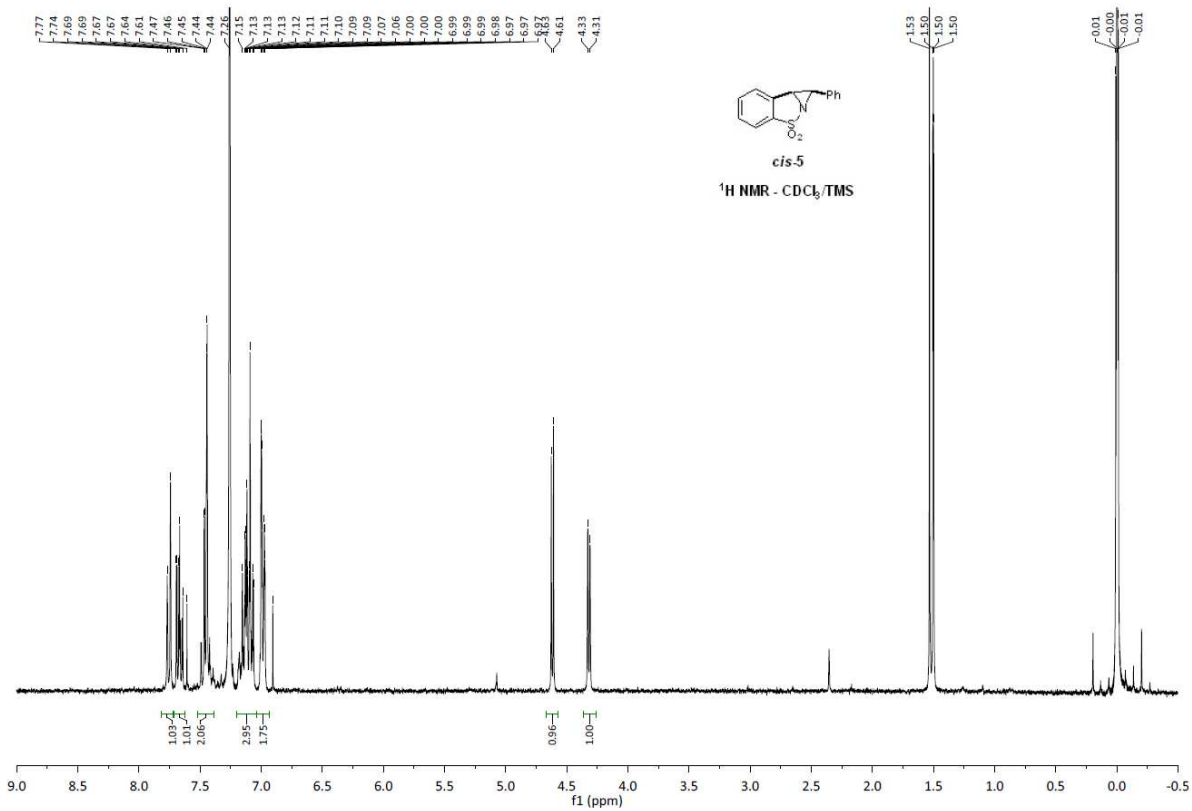


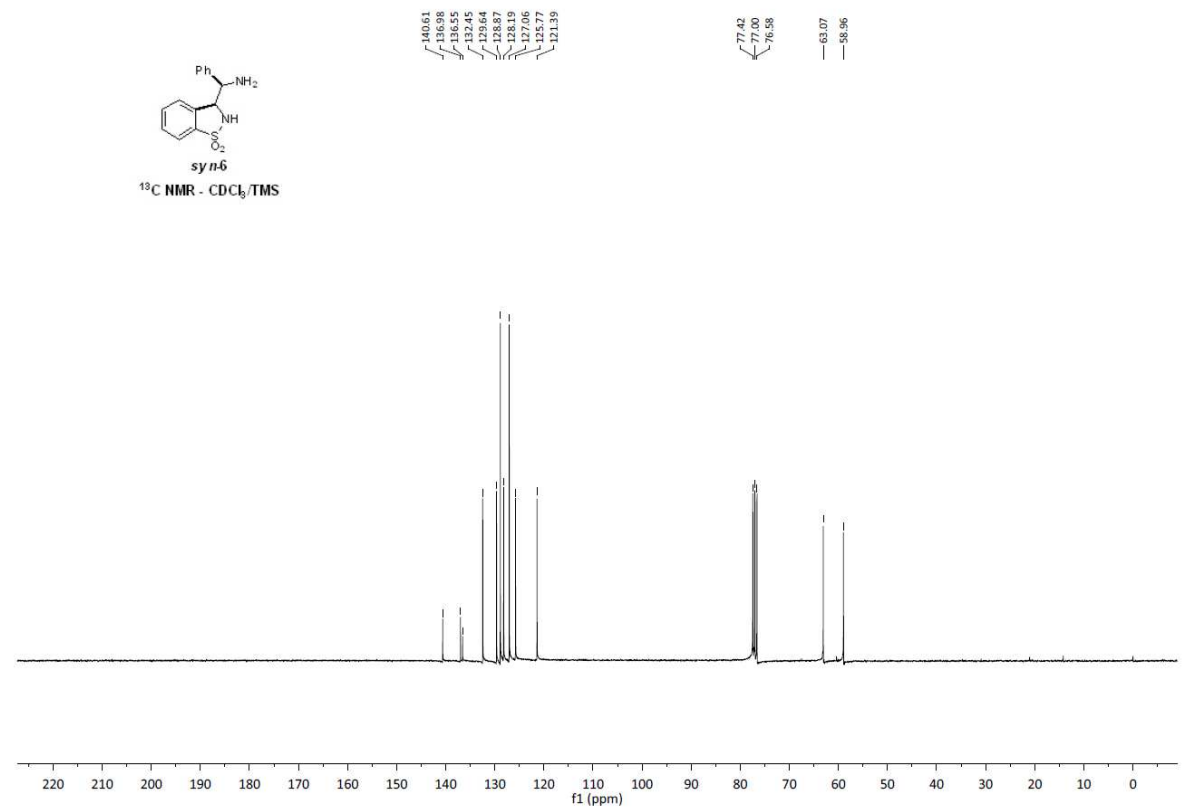
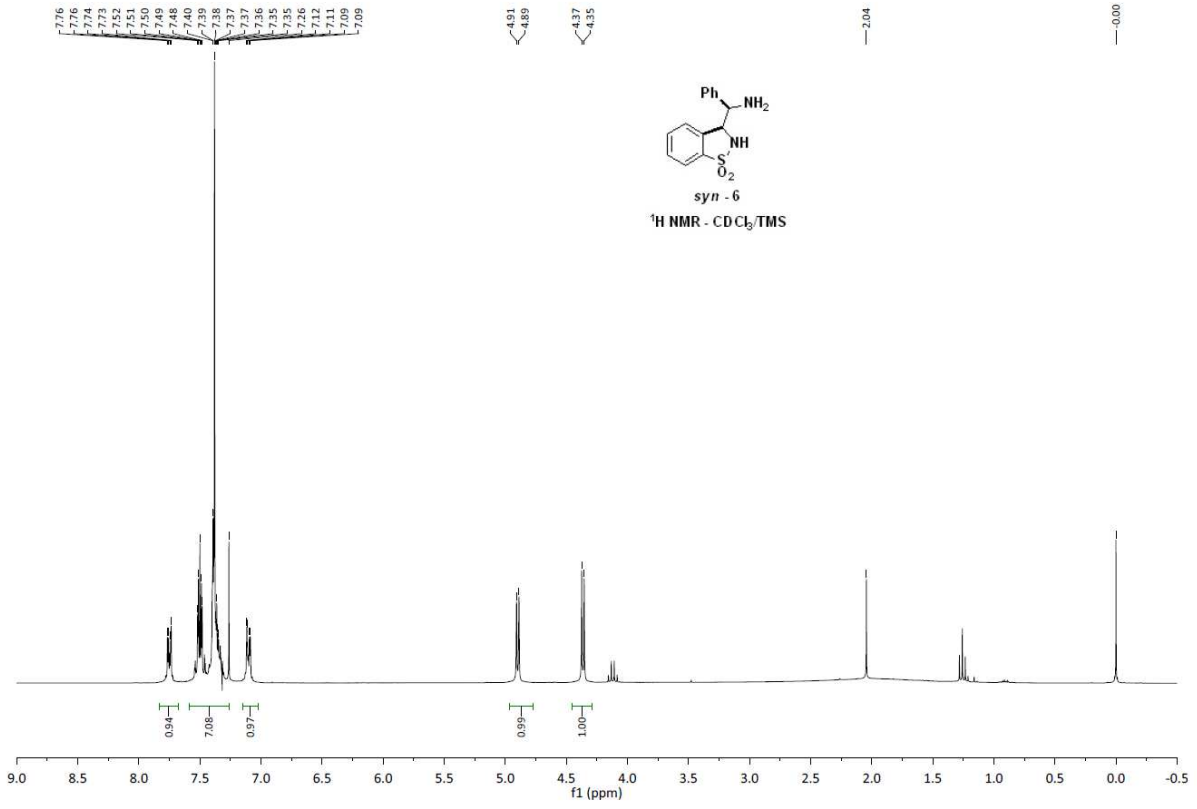


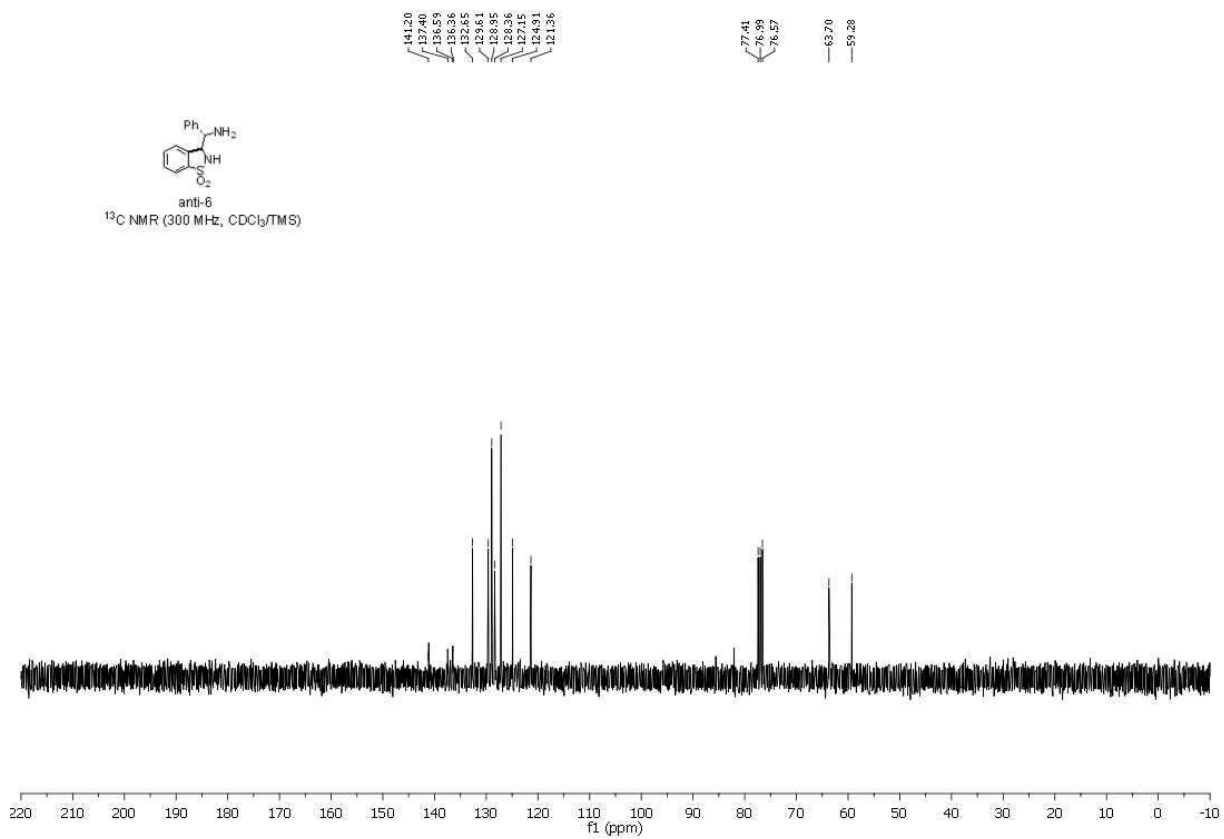
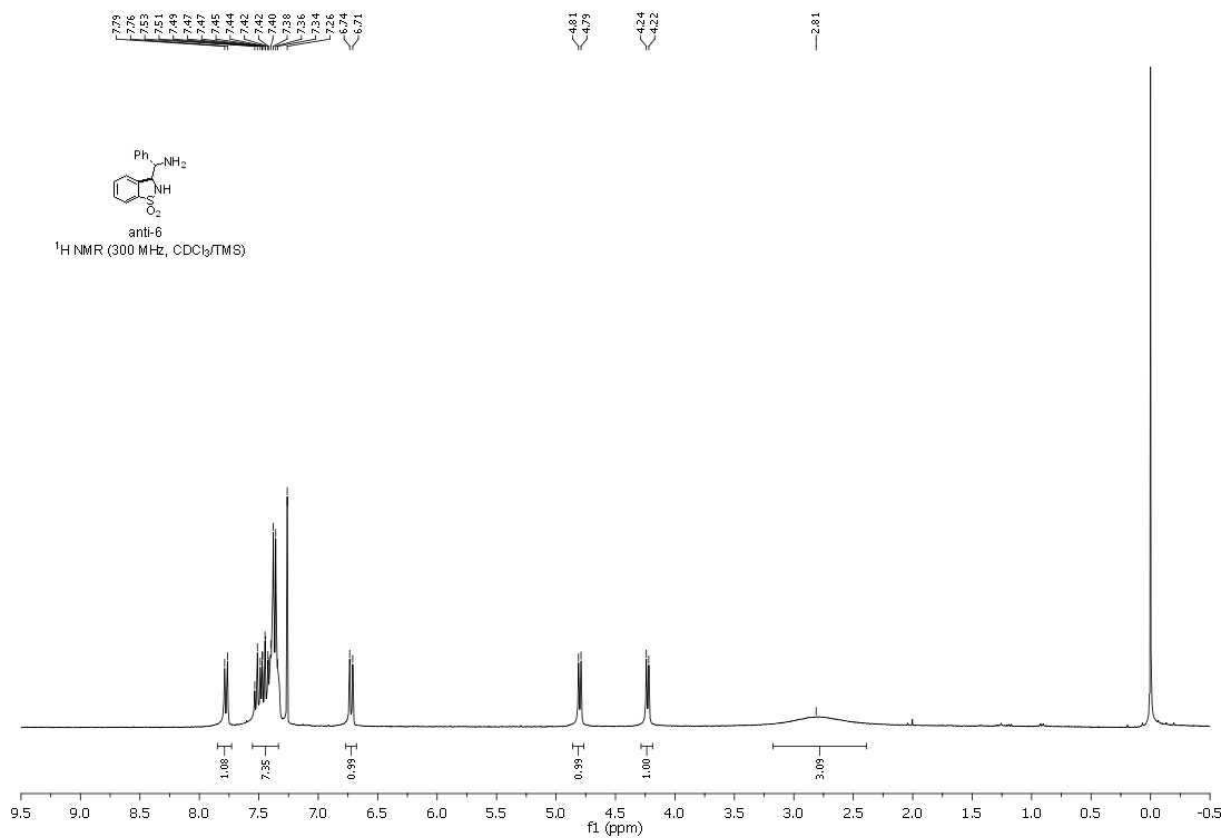


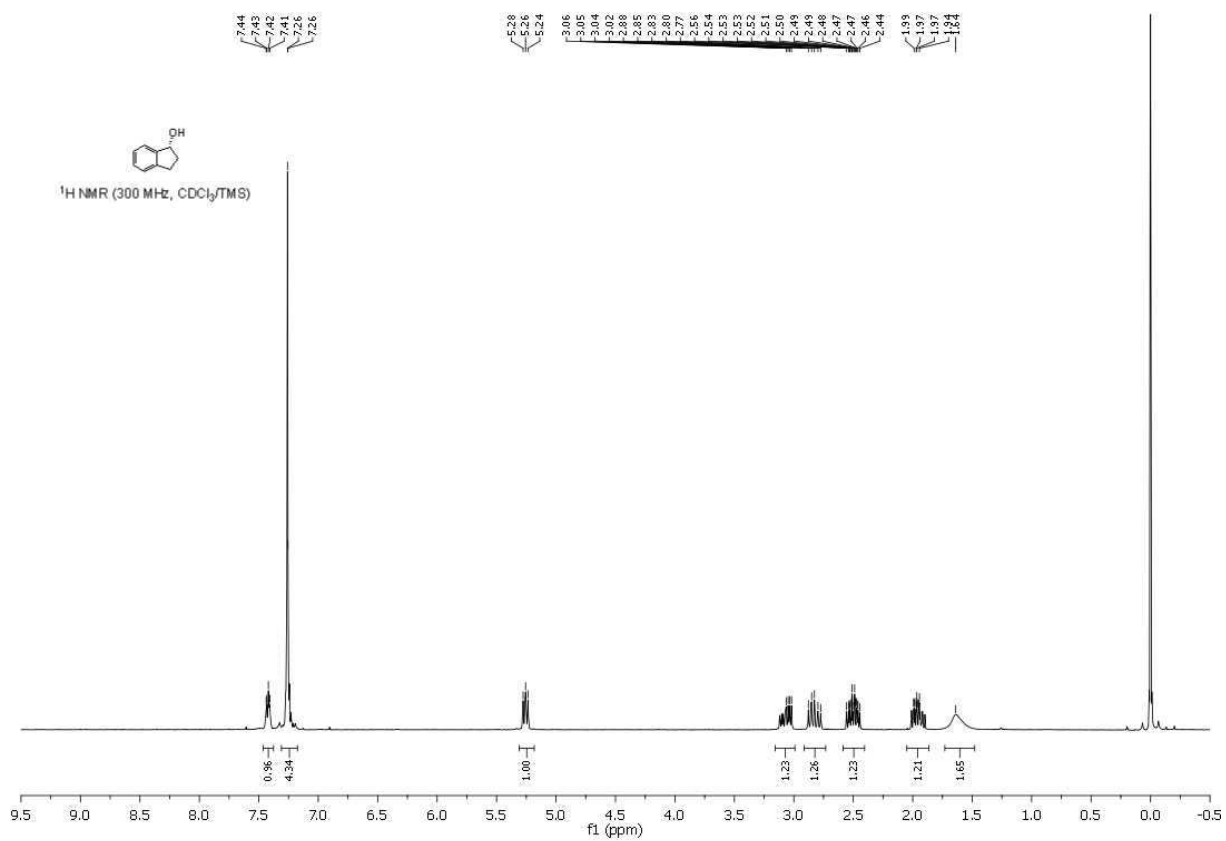
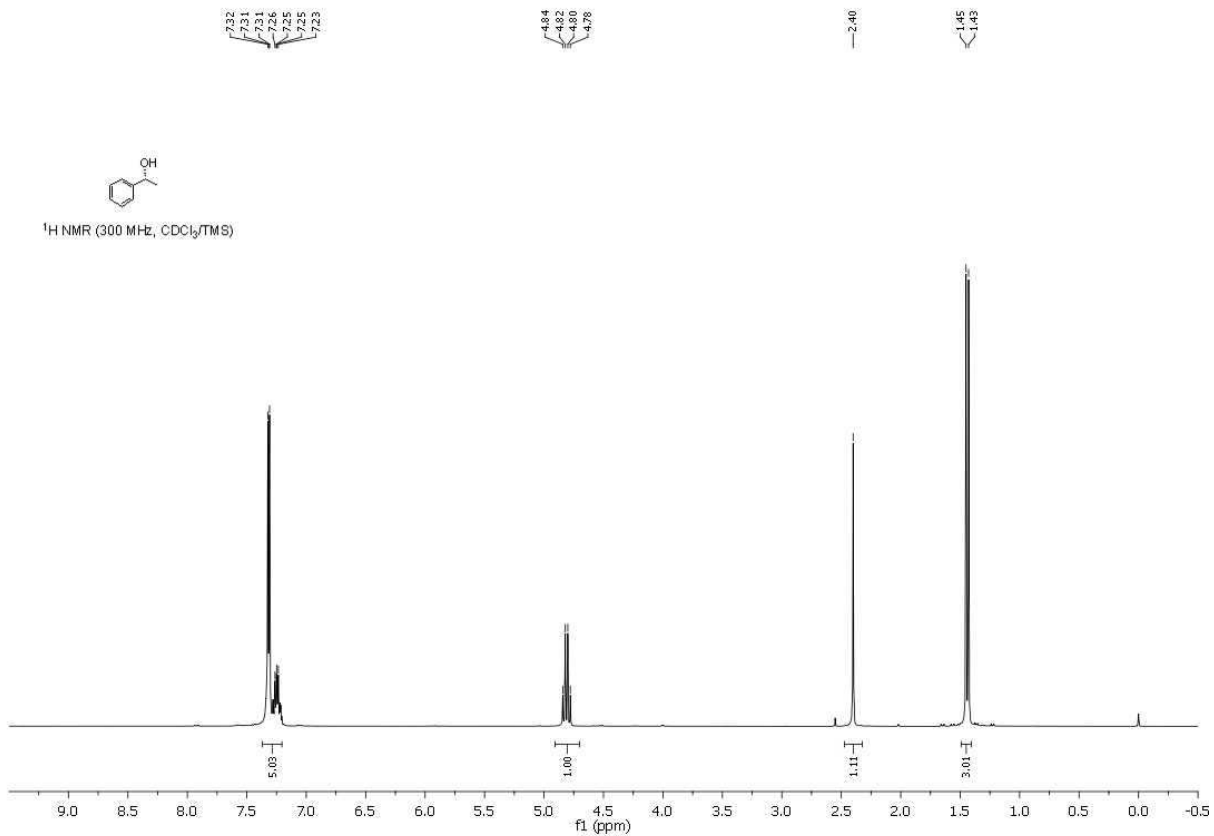


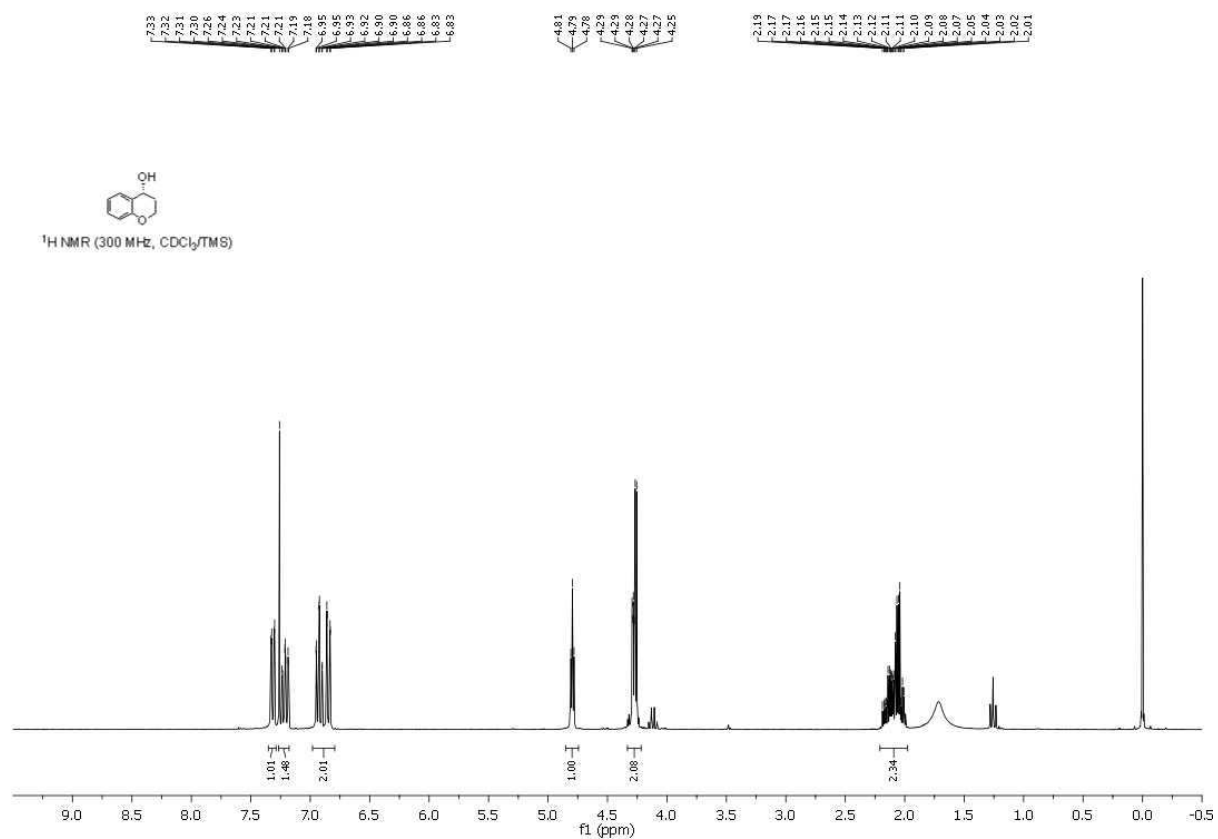
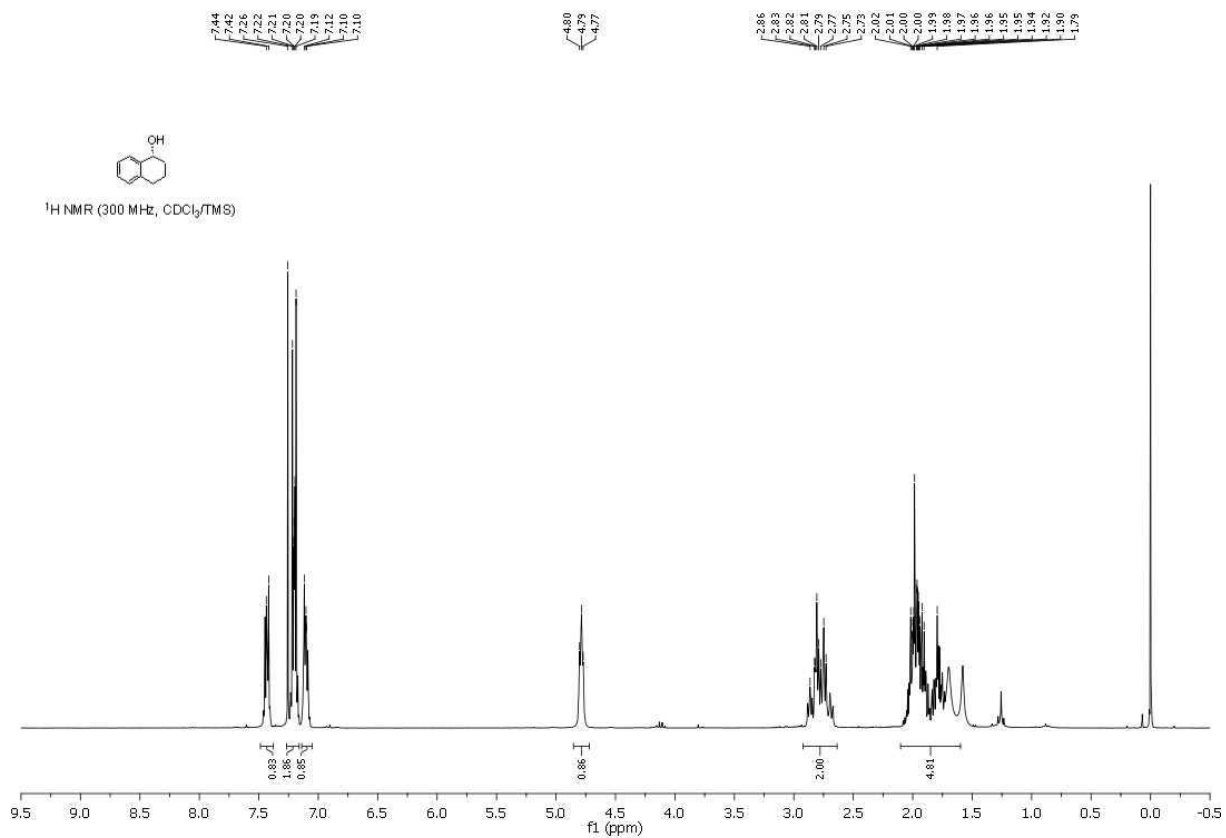


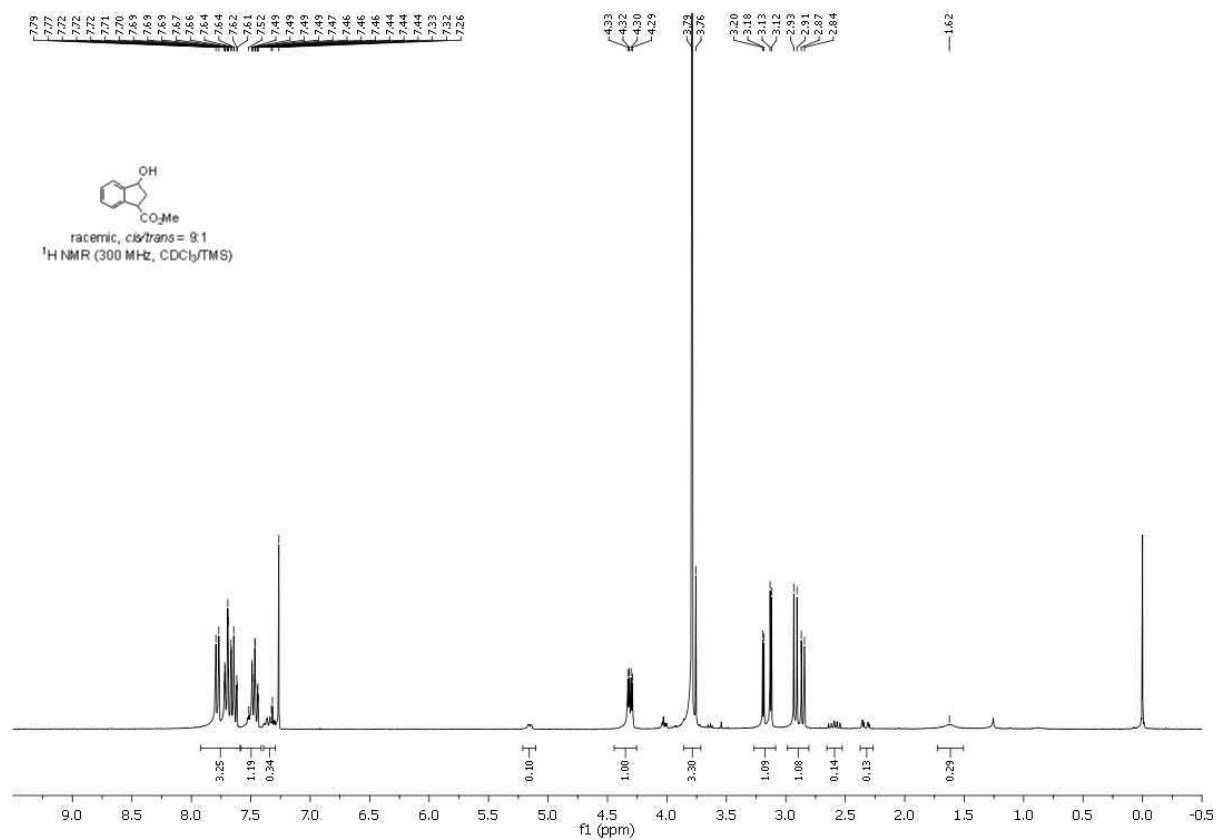
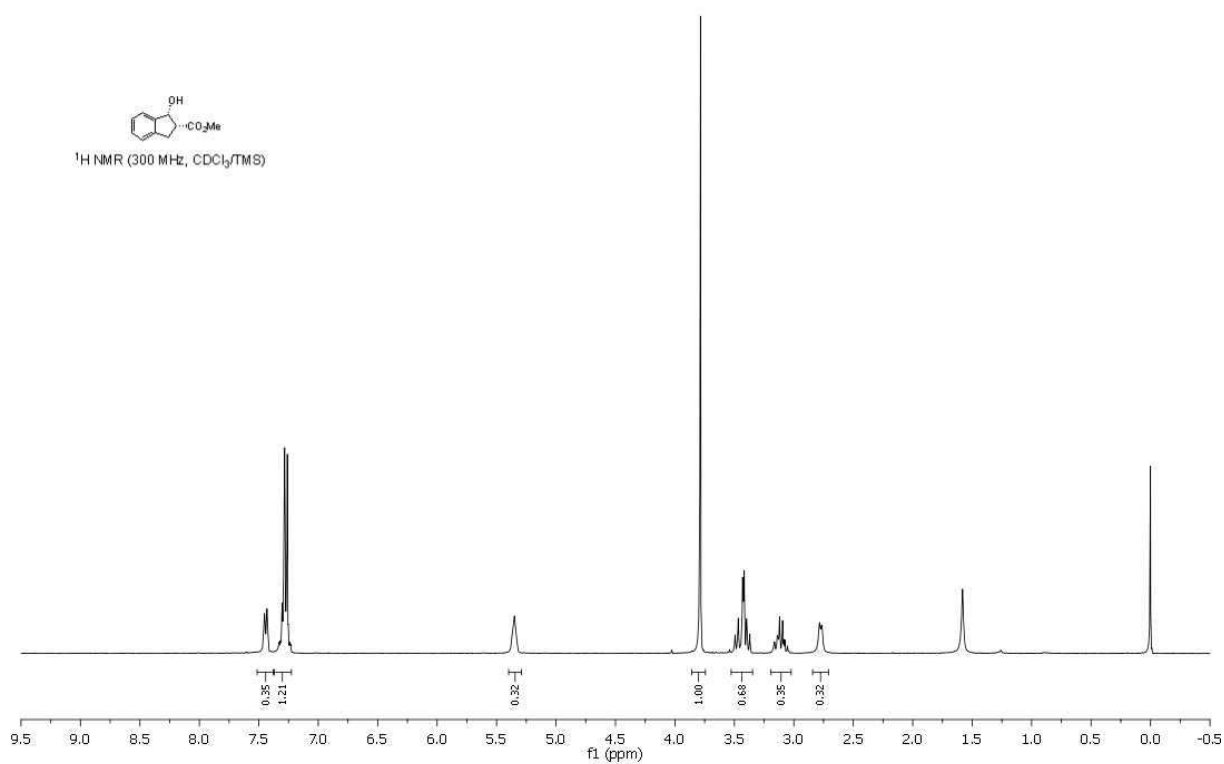


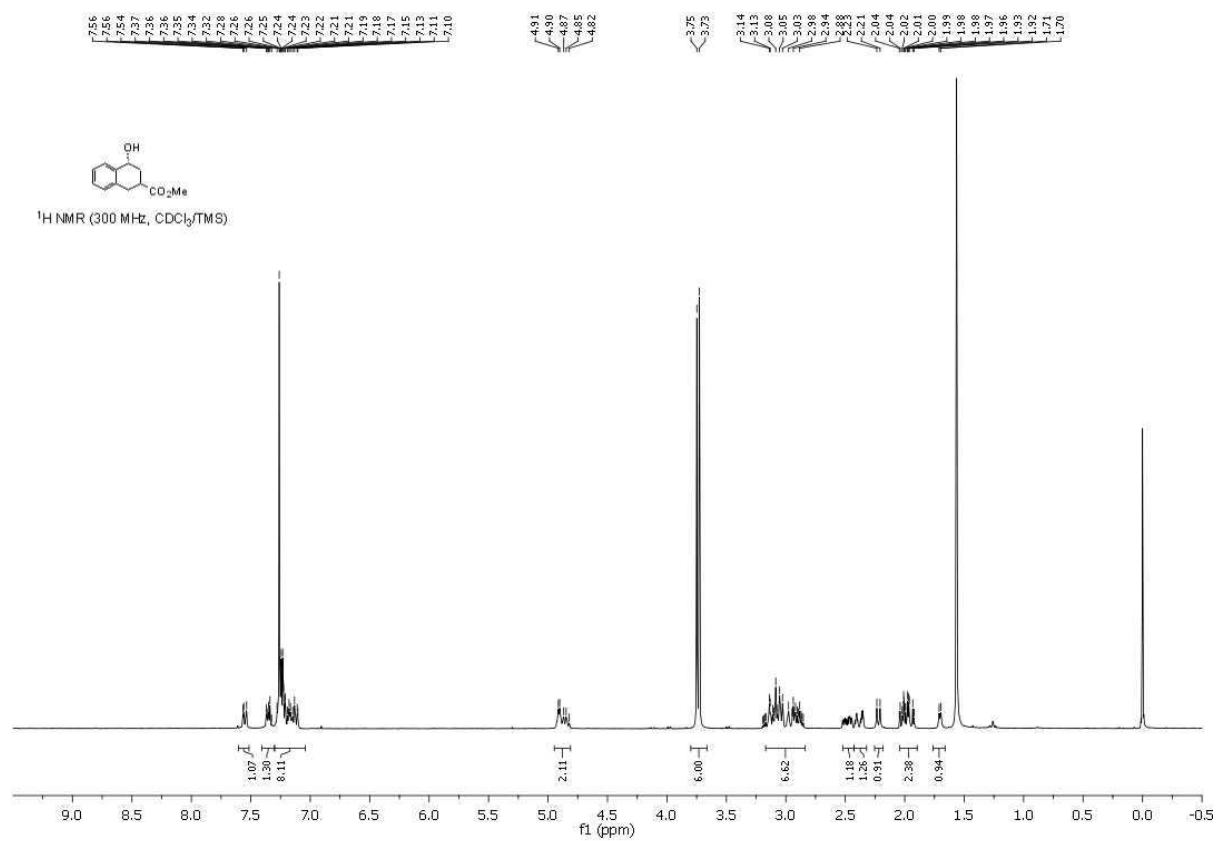
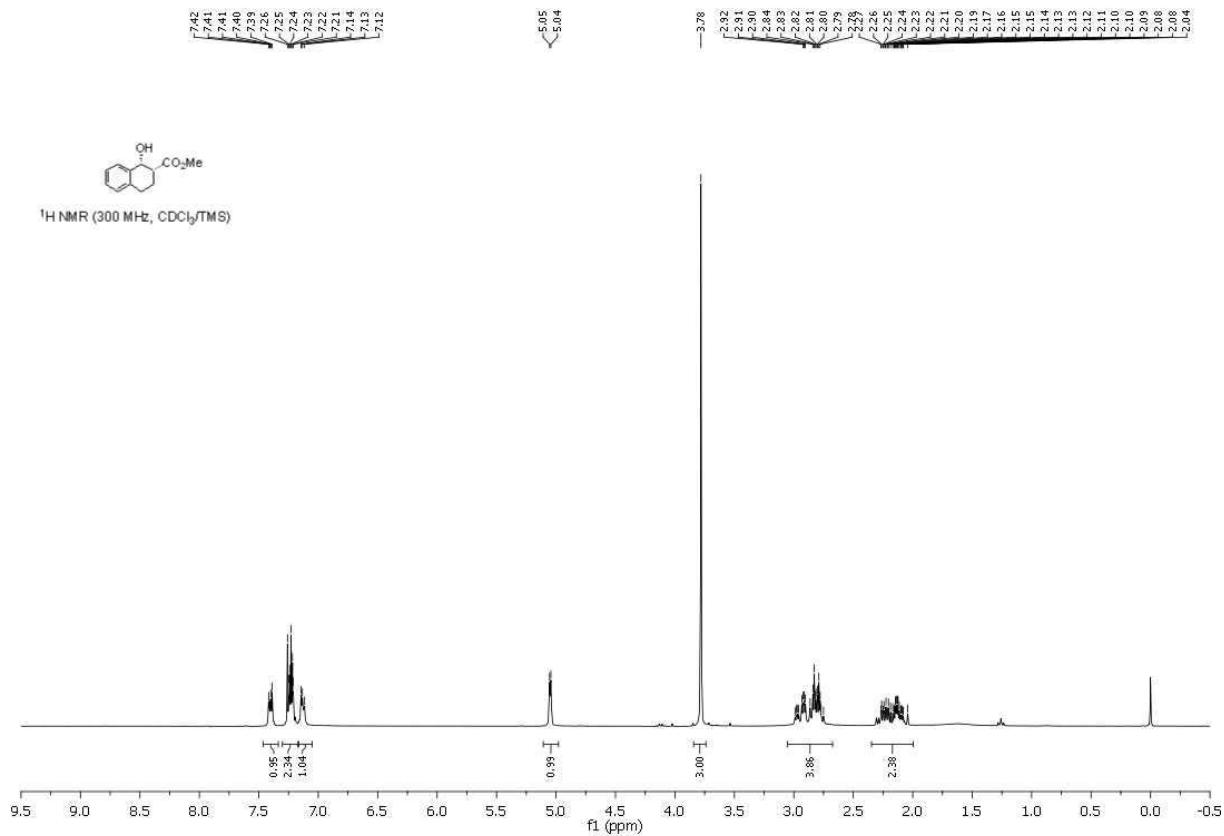


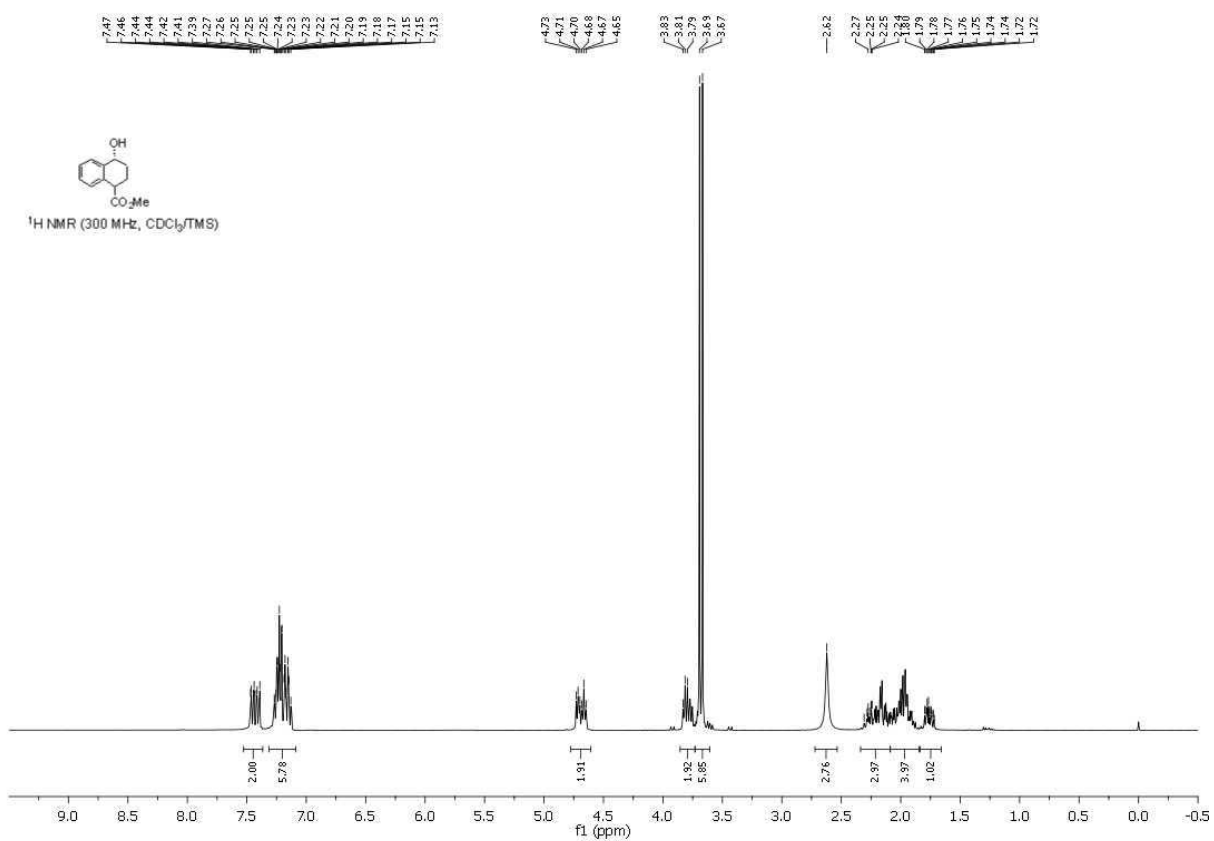












4. ^1H , ^{13}C -HMBC analysis of *trans*-4

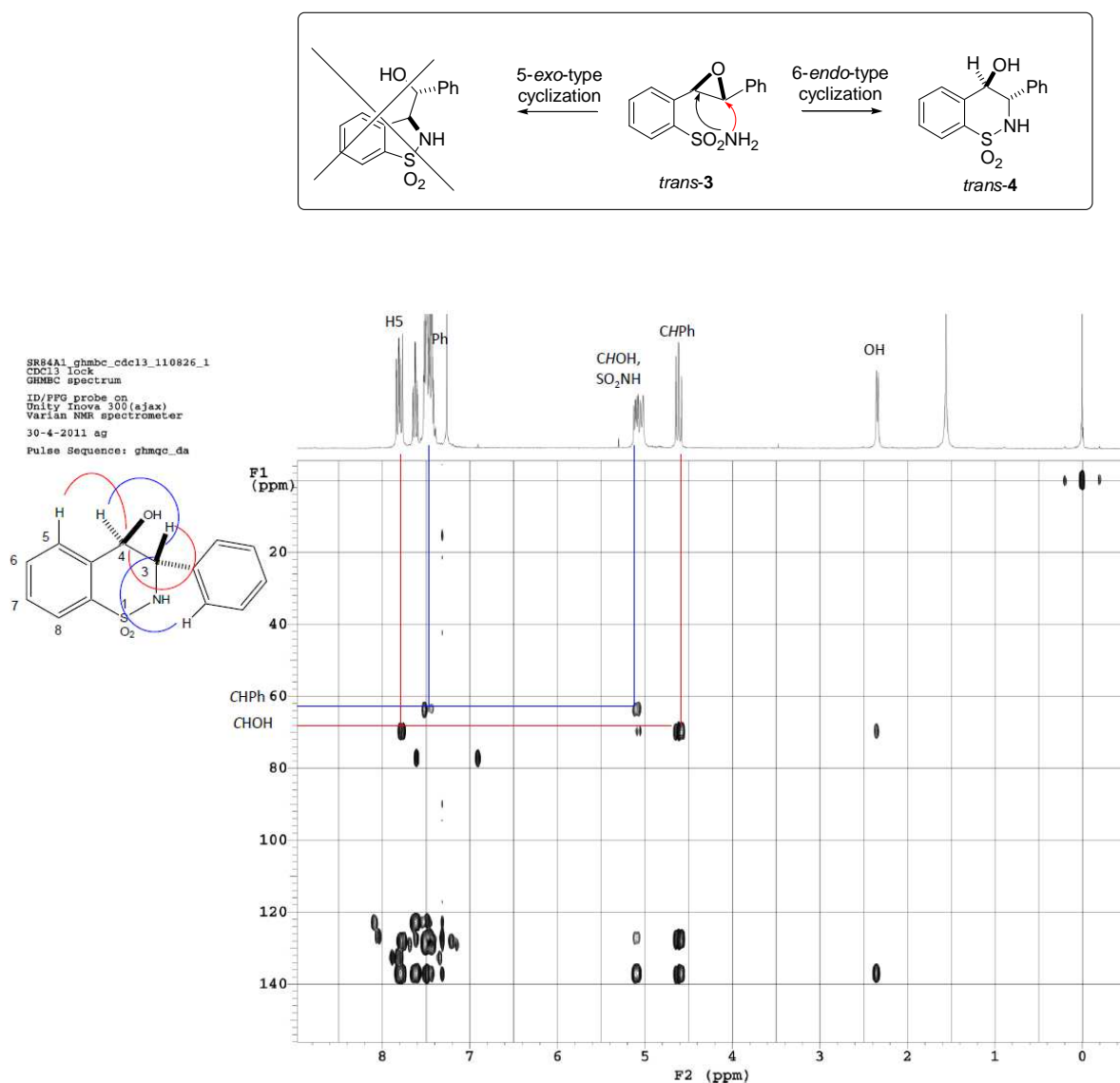


Fig. S7 6-endo-*tet*- vs. 5-exo-*tet*-type cyclization of *trans*-3; ^1H , ^{13}C -HMBC analysis revealing chemical shift correlation between the marked proximal aromatic hydrogen of the 1,1-dioxo-2-phenyl-2,3-dihydro-1,2-thiazinane core and the carbon atom bearing the hydroxyl group.

5. ^1H , ^{13}C -HMBC analysis of *syn*-6

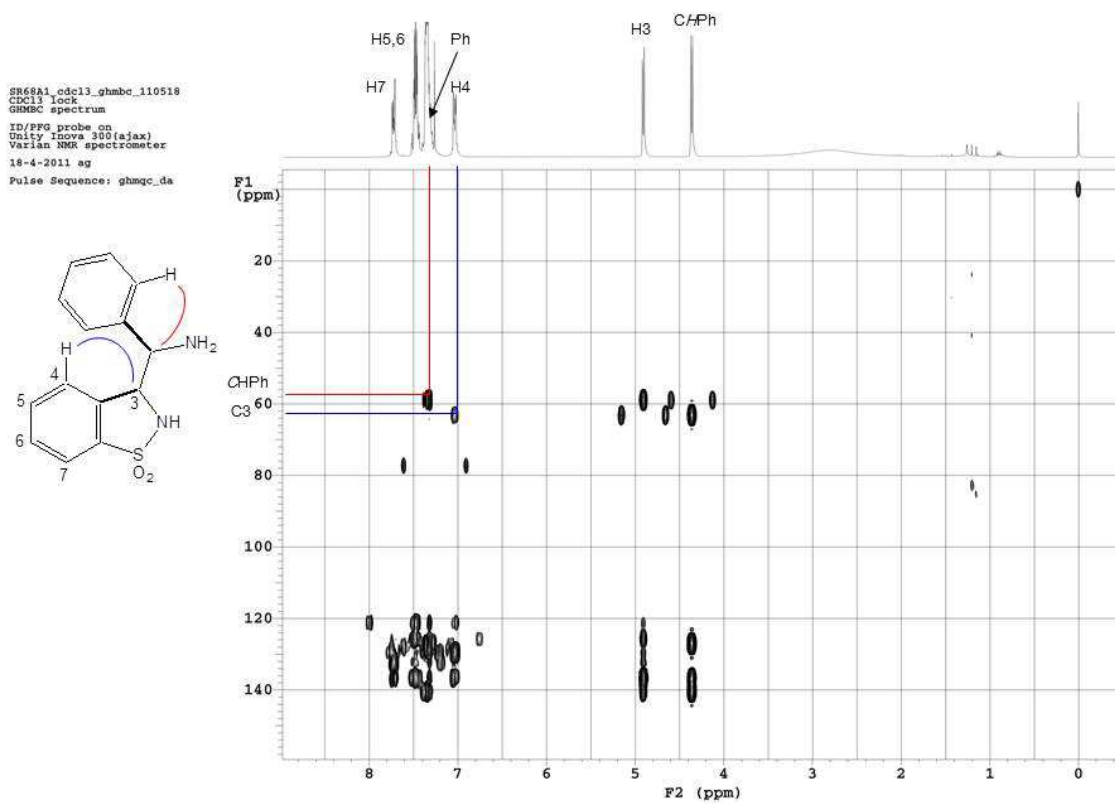
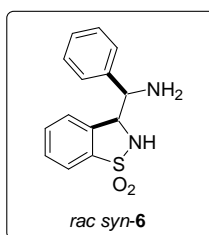


Fig. S8 ^1H , ^{13}C -HMBC analysis of *syn*-6 revealing chemical shift correlation between the marked proximal aromatic hydrogen of the 1,1-dioxo-benzo-1,2-thiazolidine core and the carbon atom bearing the α -aminobenzyl group.