

Asymmetric transfer hydrogenation of acetophenone derivatives using 2-benzyl-tethered ruthenium (II)/TsDPEN complexes bearing η^6 -(*p*-OR) (R = H, ^{*i*}Pr, Bn, Ph) ligands

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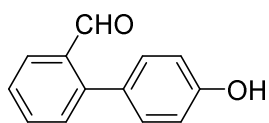
E-mail: R.C.Knighton@warwick.ac.uk ; M.Wills@warwick.ac.uk

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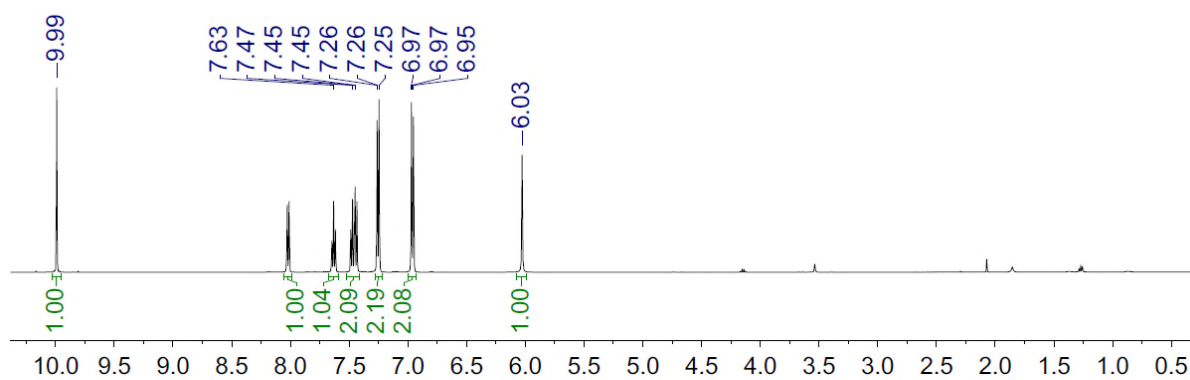
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1. ^1H and ^{13}C NMR spectra for catalyst preparation

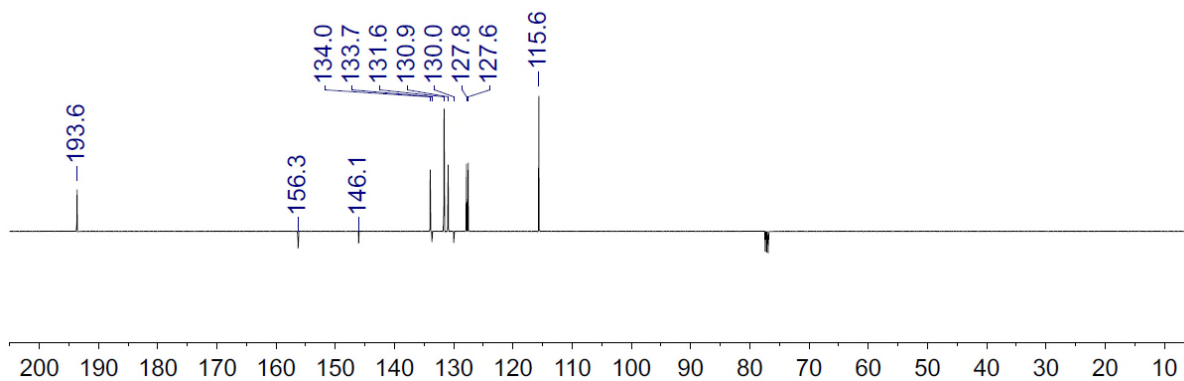
4'-Hydroxy-[1,1'-biphenyl]-2-carbaldehyde **5**



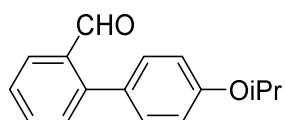
^1H NMR spectrum (500 MHz, CDCl_3)



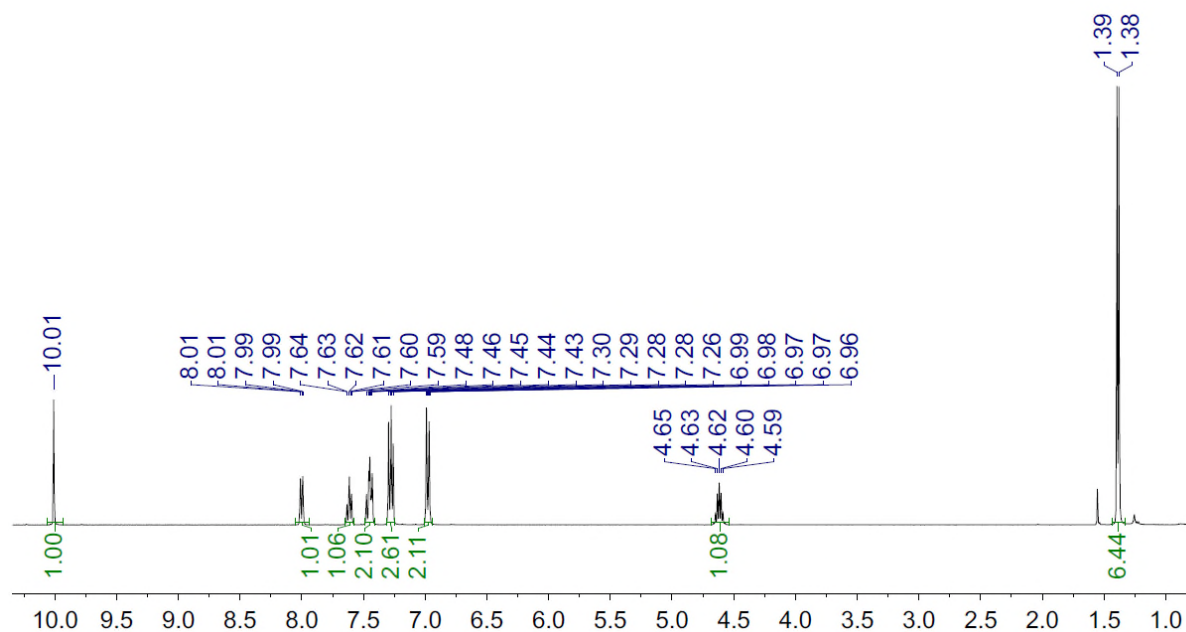
^{13}C NMR spectrum (126 MHz, CDCl_3)



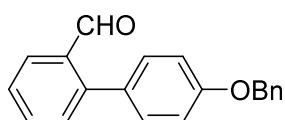
4'-Isopropoxy-[1,1'-biphenyl]-2-carbaldehyde 6



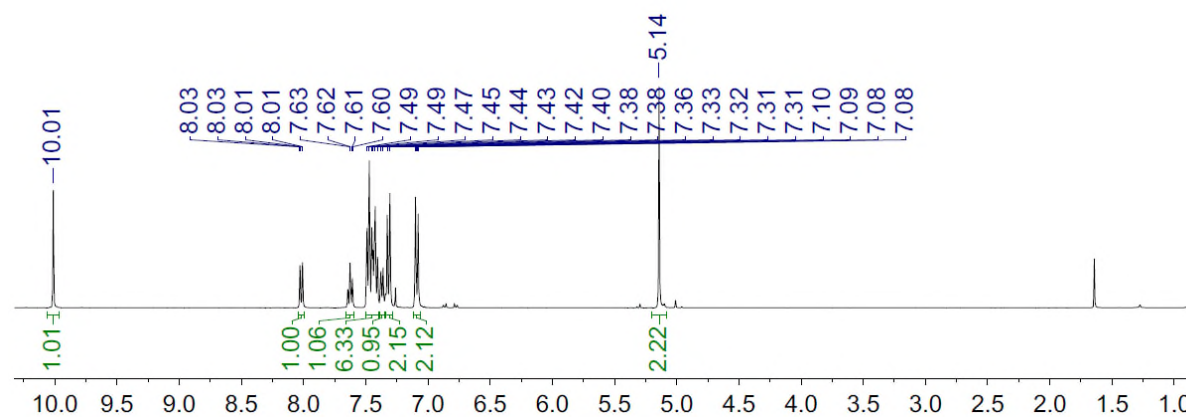
¹H NMR spectrum (400 MHz, CDCl₃)



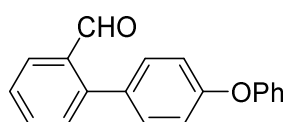
Benzyloxy)-[1,1'-biphenyl]-2-carbaldehyde 7



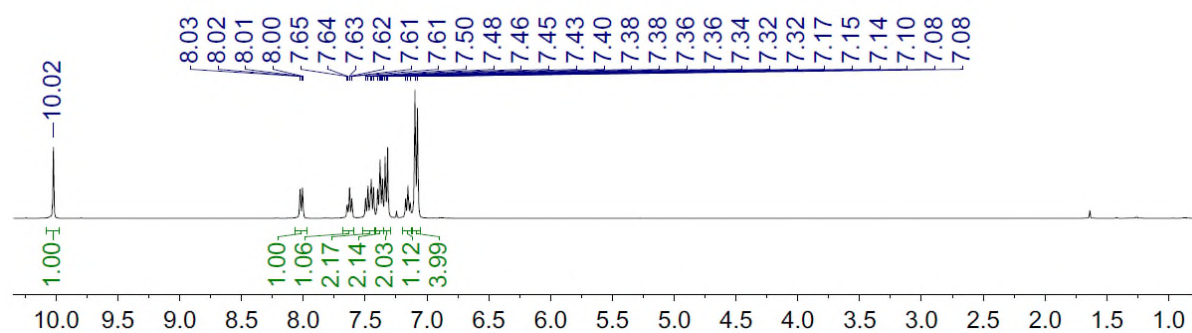
¹H NMR spectrum (400 MHz, CDCl₃)



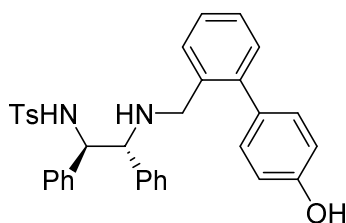
Phenoxy)-[1,1'-biphenyl]-2-carbaldehyde **8**



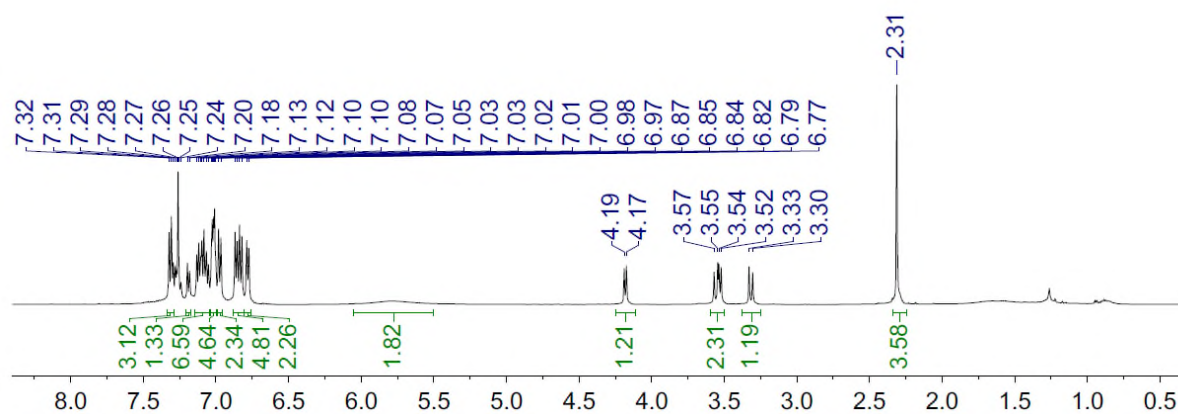
^1H NMR spectrum (400 MHz, CDCl_3)



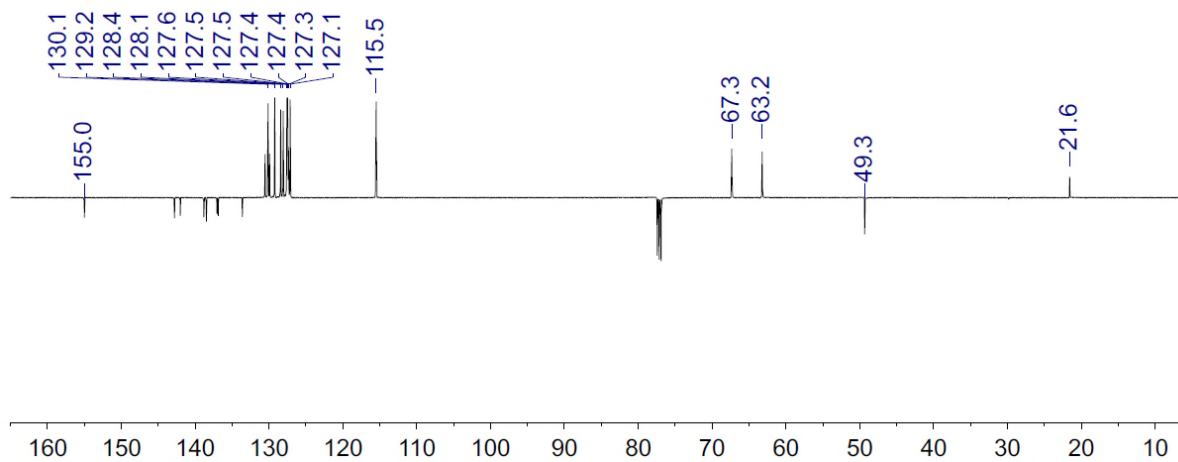
N-((*R,R*)-2-(((4'-Hydroxy-[1,1'-biphenyl]-2-yl)methyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide 9



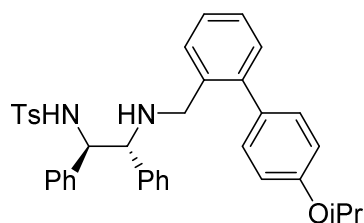
¹H NMR spectrum (500 MHz, CDCl₃)



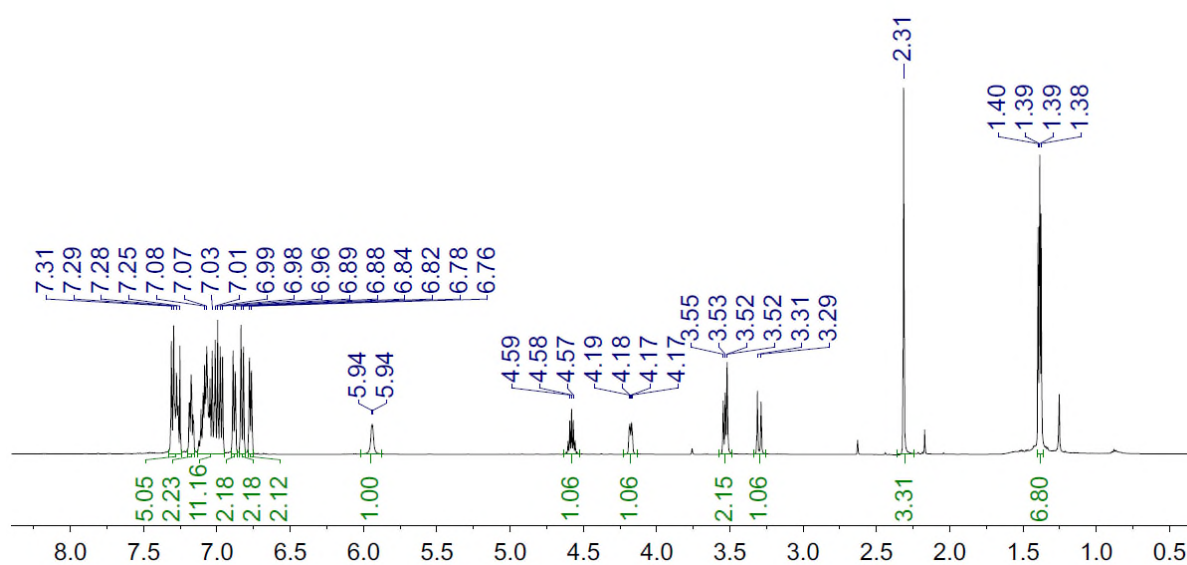
¹³C NMR spectrum (126 MHz, CDCl₃)



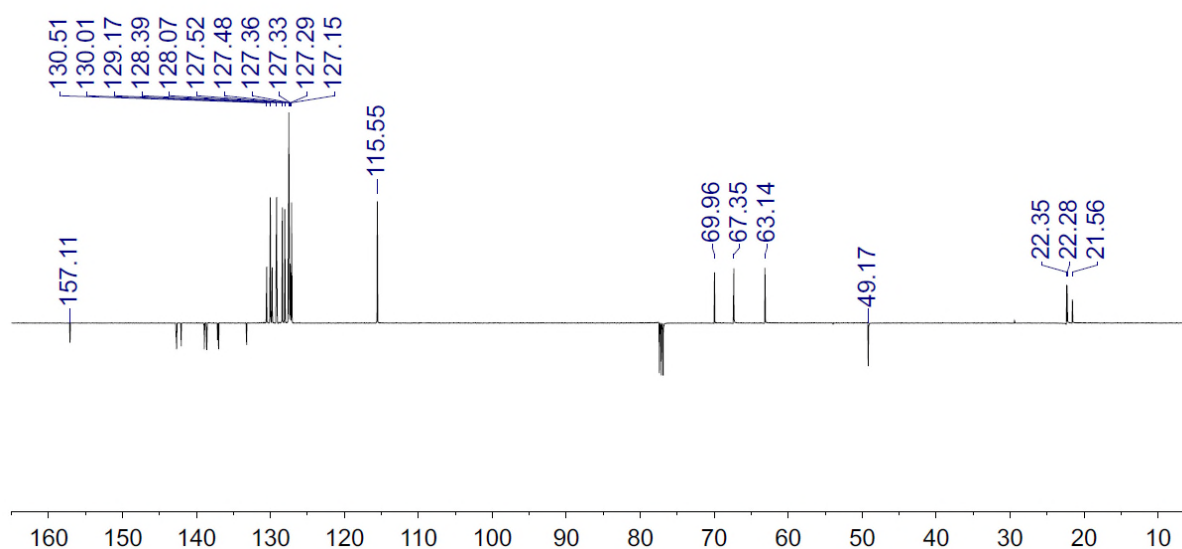
N-((*R,R*)-2-(((4'-Isopropoxy-[1,1'-biphenyl]-2-yl)methyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide 10



¹H NMR spectrum (500 MHz, CDCl₃)

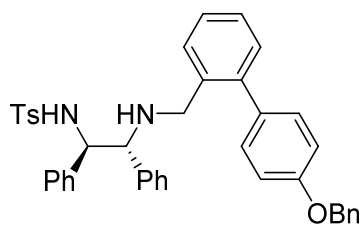


¹³C NMR spectrum (126 MHz, CDCl₃)

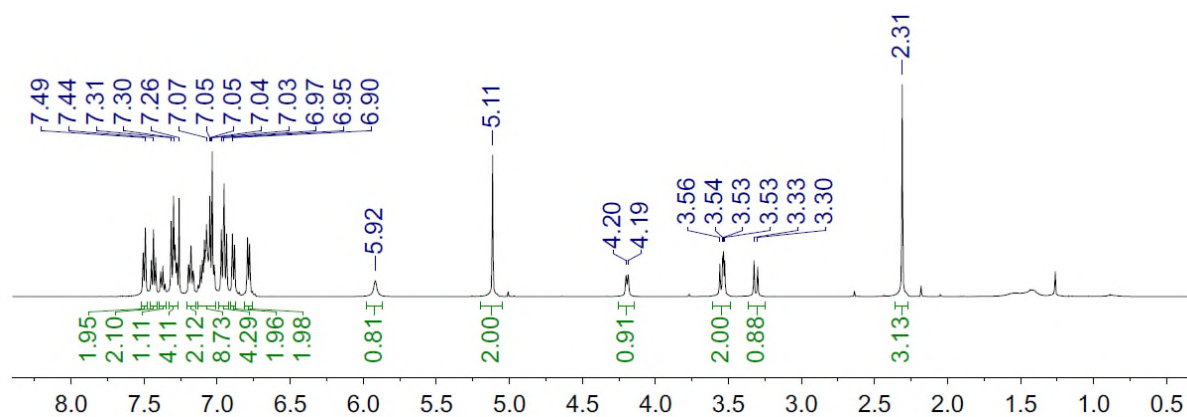


Benzyloxy)-[1,1'-biphenyl]-2-yl)methyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide

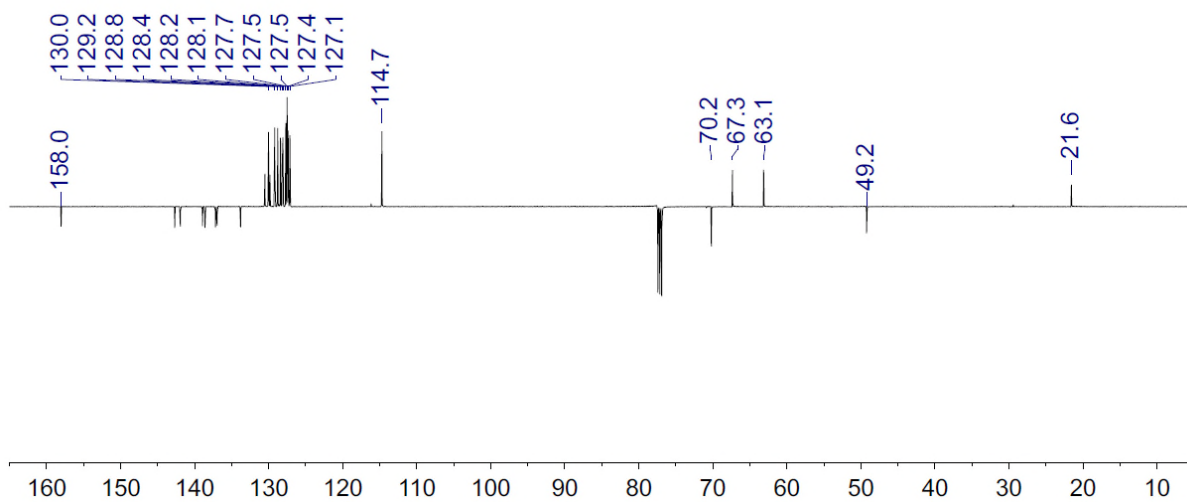
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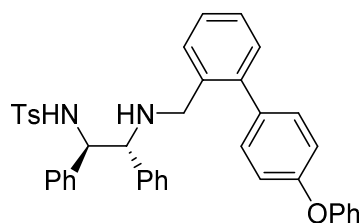
¹H NMR spectrum (500 MHz, CDCl₃)



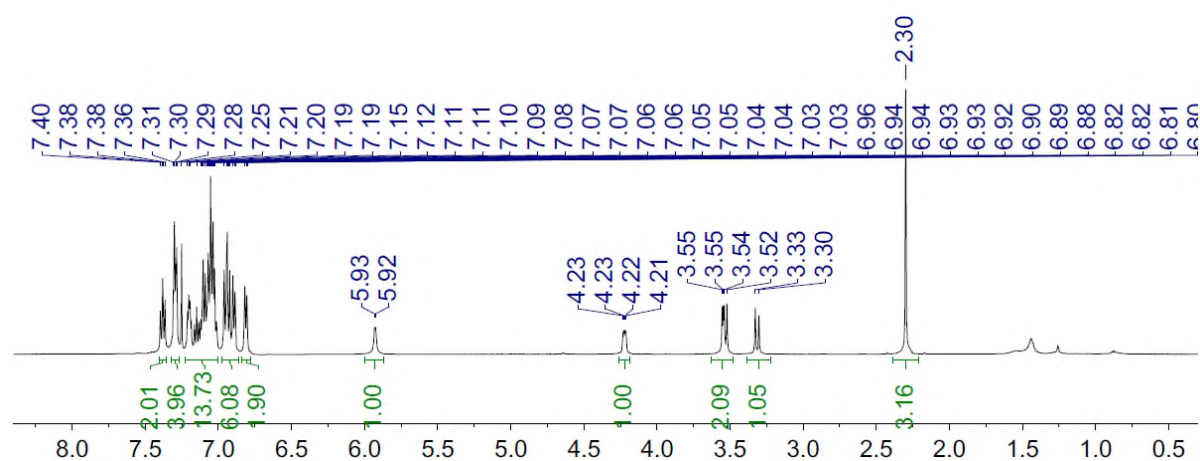
¹³C NMR spectrum (126 MHz, CDCl₃)



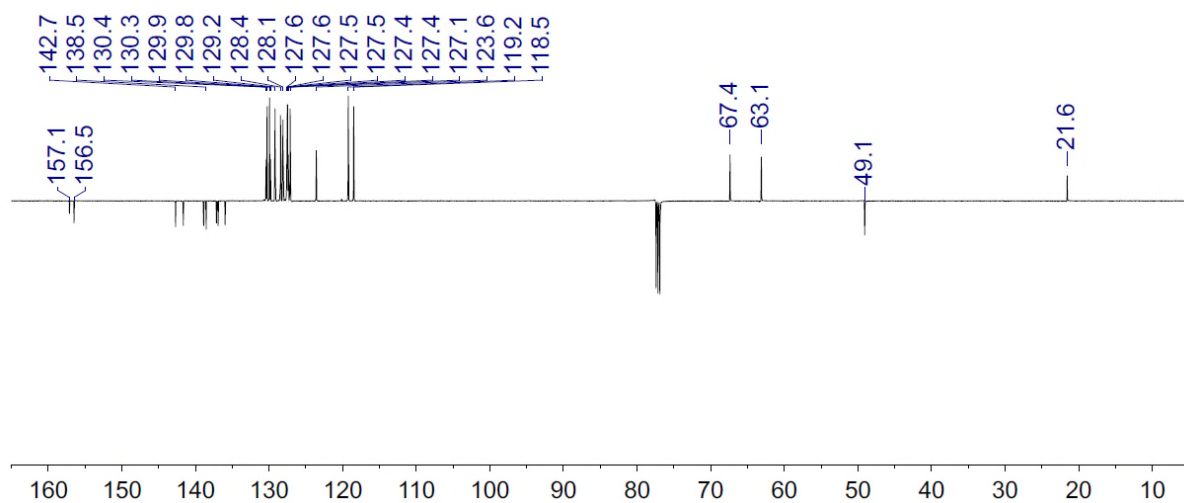
N-((*R,R*)-2-(((4'-Isopropoxy-[1,1'-biphenyl]-2-yl)methyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide 12



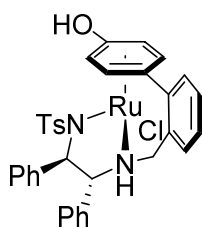
¹H NMR spectrum (500 MHz, CDCl₃)



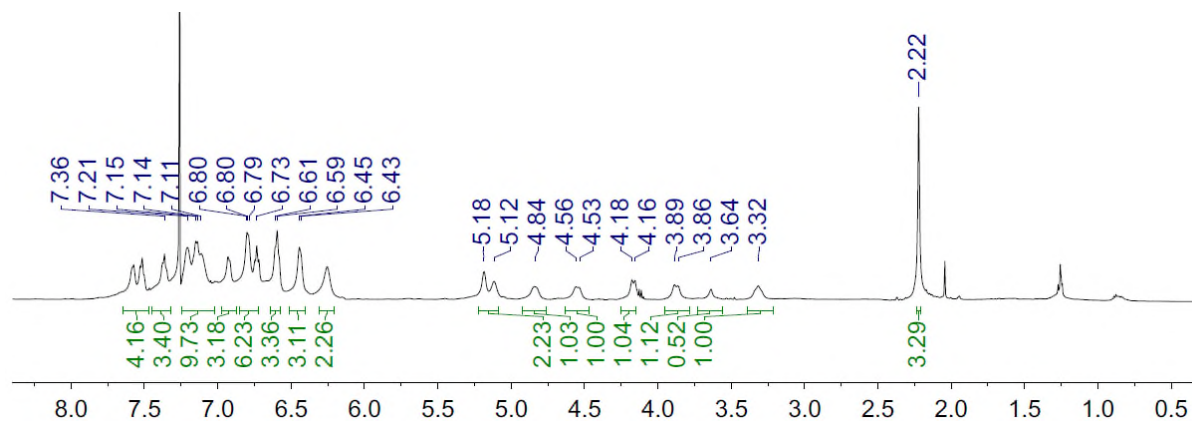
¹³C NMR spectrum (126 MHz, CDCl₃)



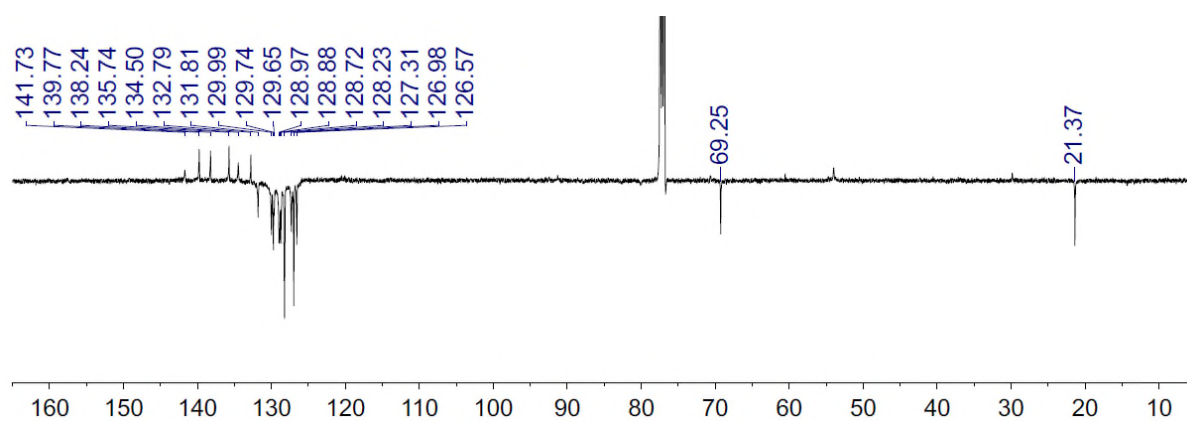
4-Hydroxy (*R,R*)-TsDPENRuCl complex 1



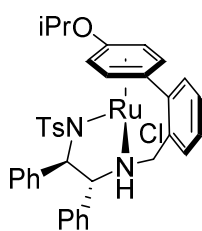
^1H NMR spectrum (500 MHz, CDCl_3)



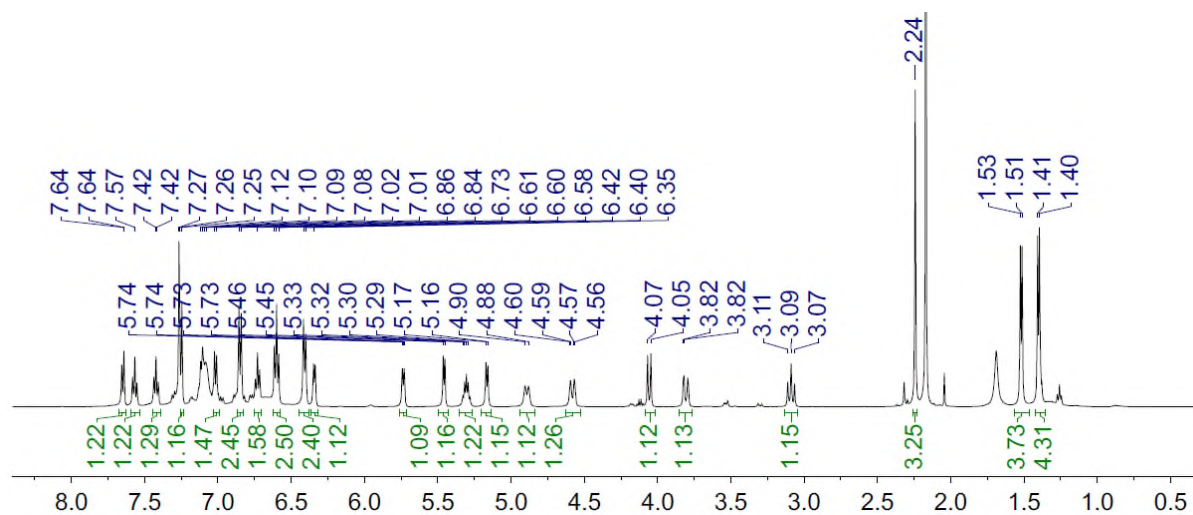
^{13}C NMR spectrum (126 MHz, CDCl_3)



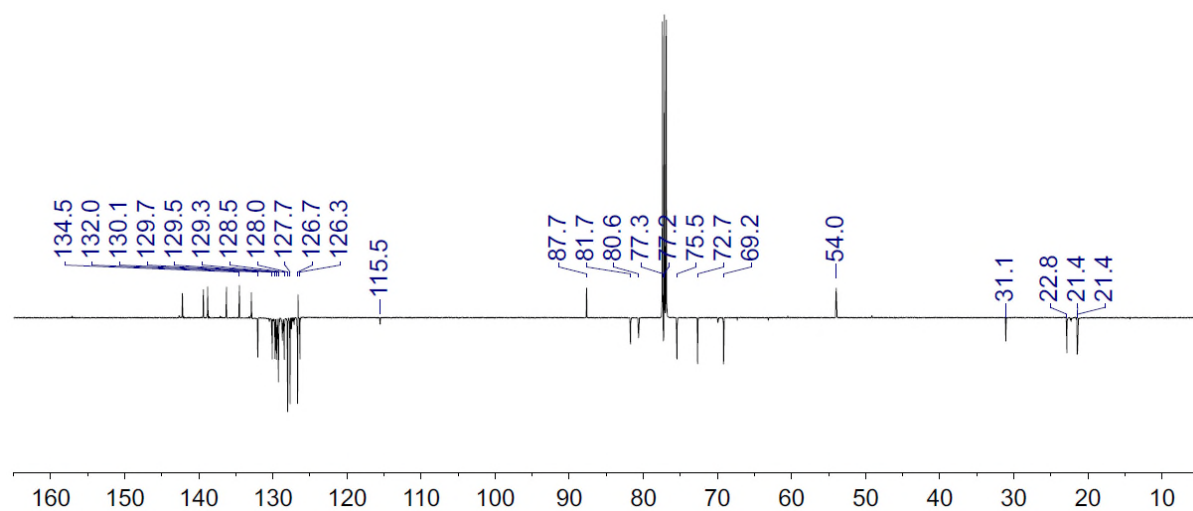
4-Isopropoxy (*R,R*)-TsDPENRuCl complex 2



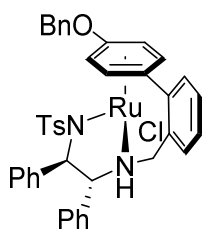
^1H NMR spectrum (500 MHz, CDCl_3)



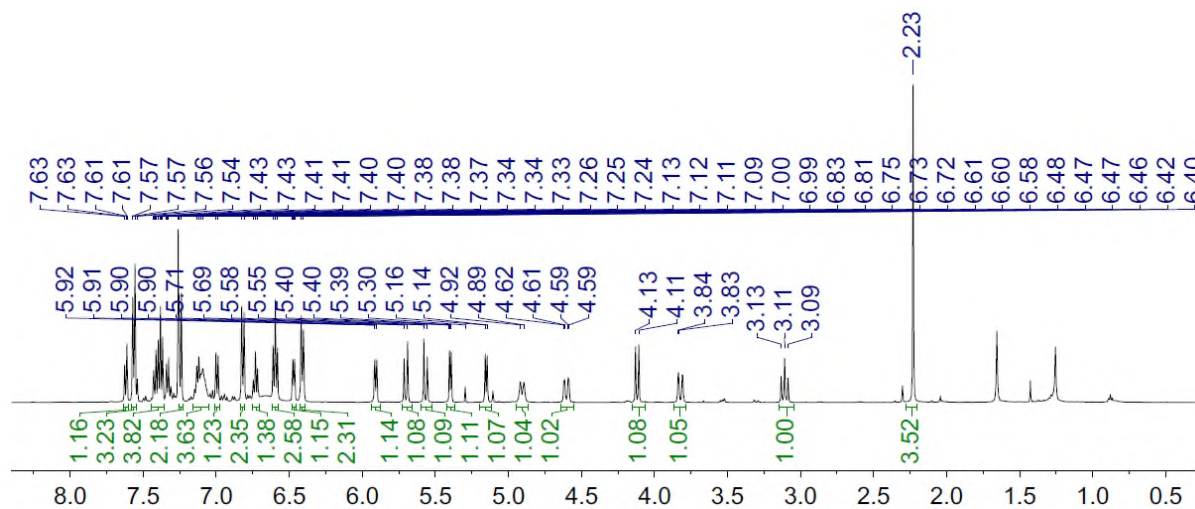
^{13}C NMR spectrum (126 MHz, CDCl_3)



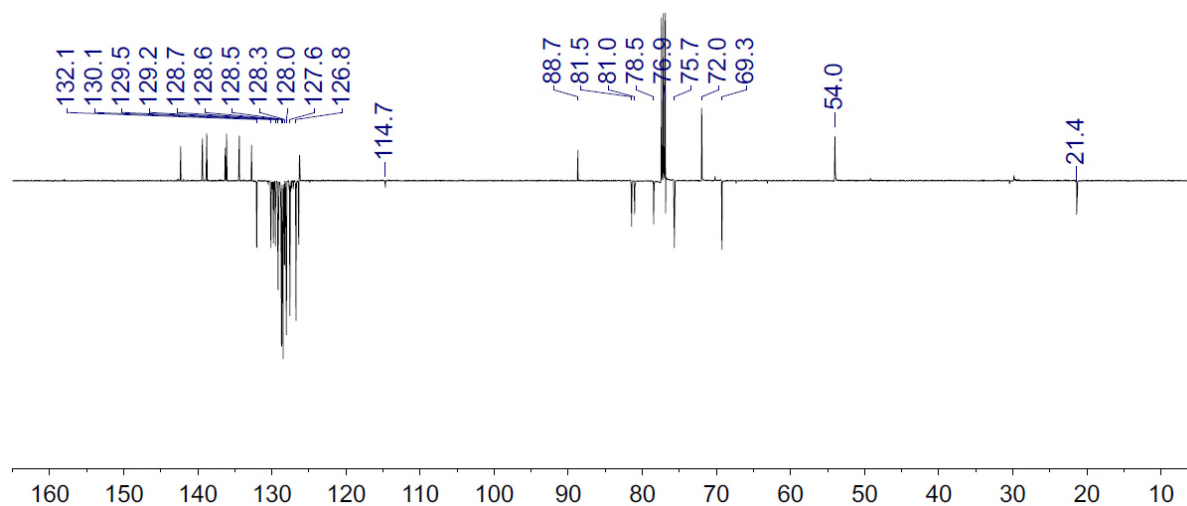
4-Benzyloxy (*R,R*)-TsDPENRuCl complex **3**



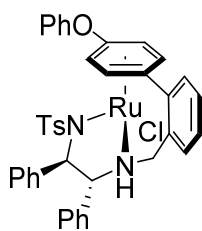
^1H NMR spectrum (500 MHz, CDCl_3)



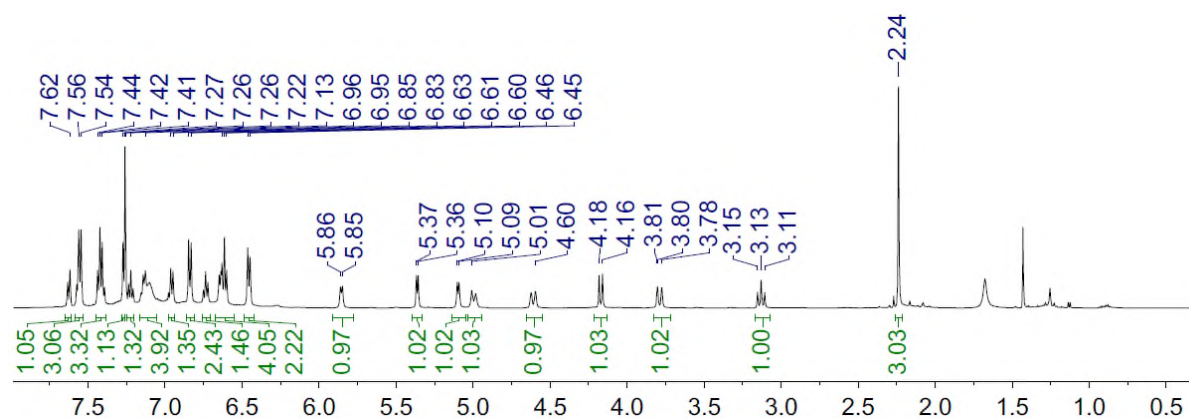
^{13}C NMR spectrum (126 MHz, CDCl_3)



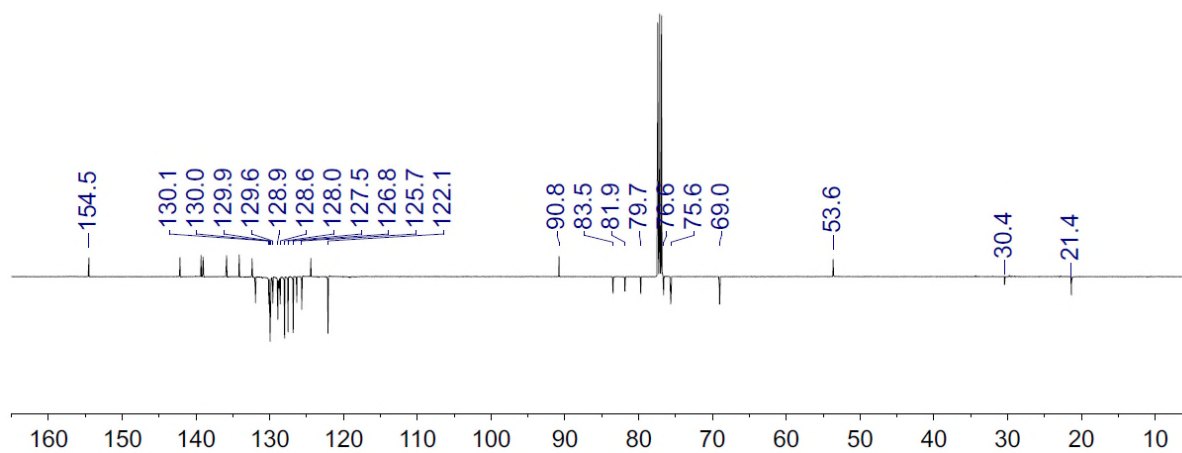
4-Phenoxy (*R,R*)-TsDPENRuCl complex 4



^1H NMR spectrum (500 MHz, CDCl_3)

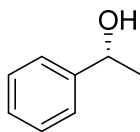


^{13}C NMR spectrum (126 MHz, CDCl_3)



2. Asymmetric Reduction Products.

(*R*)-1-Phenylethan-1-ol

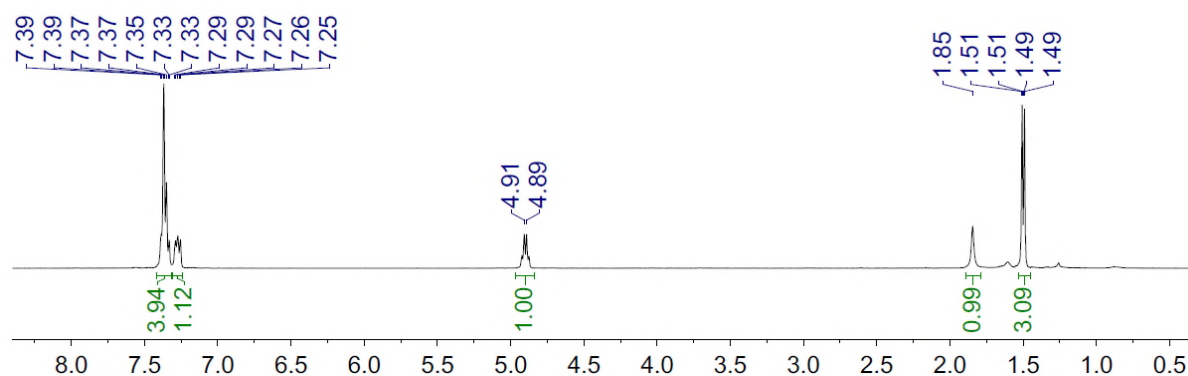


This compound was prepared by the general procedure for ATH in FA/TEA using acetophenone (0.088 mg, 0.73 mmol, 1.0 eq), catalyst (0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give 1-phenylethan-1-ol as a colourless oil (42 mg, 47%);

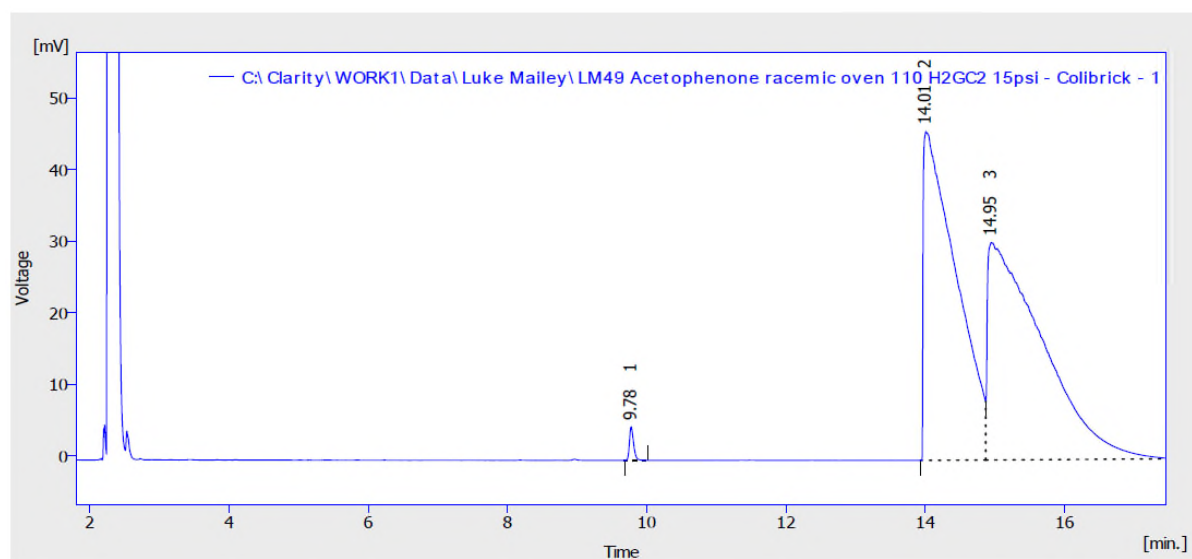
δ_{H} (400 MHz, CDCl₃) 7.38 – 7.25 (5 H, m, ArH), 4.90 (1 H, q, *J* 6.4, CHOH), 1.85 (1 H, s, OH) and 1.50 (3 H, d, *J* 6.4, CH₃).

Conversion and enantiomeric excess were determined by chiral GC analysis (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μ m, gas hydrogen, T = 110 $^{\circ}$ C, P = 15 psi, FID temp 250 $^{\circ}$ C, injector temp 220 $^{\circ}$ C): ketone 9.9 min, R isomer 15.3 min, S isomer 16.6 min.

¹H NMR spectrum (400 MHz, CDCl₃)



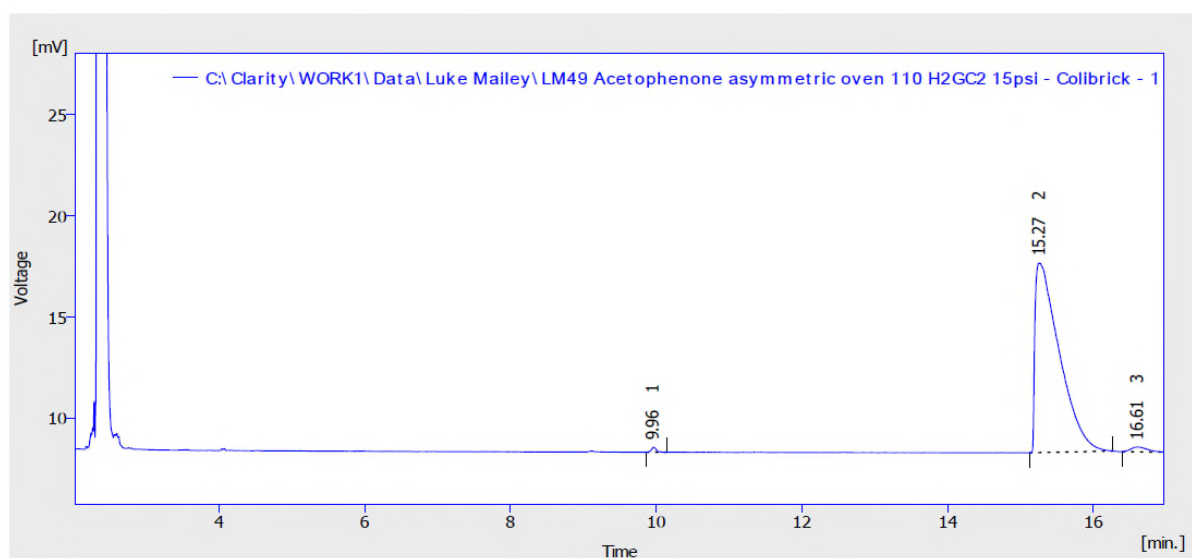
GC trace of (±)-1-Phenylethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM49 Acetophenone racemic oven 110 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	9.776	19.164	4.681	0.6	5.8	0.06	
2	14.008	1496.720	45.975	46.9	56.7	0.55	
3	14.948	1673.332	30.402	52.5	37.5	0.87	
Total		3189.216	81.057	100.0	100.0		

GC trace of (R)-1-Phenylethan-1-ol

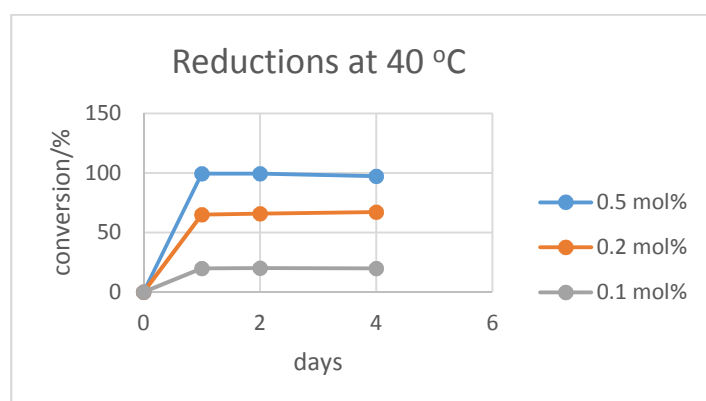


Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM49 Acetophenone asymmetric oven 110 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	9.964	1.137	0.242	0.5	2.5	0.07	
2	15.268	217.248	9.376	97.8	95.1	0.36	
3	16.612	3.670	0.242	1.7	2.5	0.24	
Total		222.054	9.861	100.0	100.0		

The reduction of acetophenone was repeated at 40 °C using lower loadings of catalyst (no DCM was added) and followed over time by GC. The results are summarised below (followed each day, conversion and ee are in %ages):

loading	0	1	2	4			ee	1	2	4
	conv									
0.5 mol%	0	99.5	99.6	97.5				97.6	97.8	97.7
0.2 mol%	0	65.2	66	67.3				97.5	97.3	97.6
0.1 mol%	0	20	20.3	20.1				97	97	97



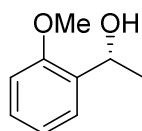
At 0.5 mol% the reaction was complete more quickly at 40 °C than it was at 25 °C (>99% within 1 day rather than 2d). However at the lower catalyst loadings the catalyst appeared to deactivate after 1 day, presumably as a result of decomposition at the higher temperature. The ees of the reactions did not deteriorate even after the reactions reached maximum% conversion and were kept running, indicating no reversal or racemisation even at the higher temperatures (the ees are within experimental measurement errors).

The reduction of acetophenone was repeated at 60 °C using lower loadings of catalyst (no DCM was added) and followed over time by GC. The results are summarised below (conversion and ee are in %ages):

loading	start	1 day	ee	1 day
	conv			
0.2 mol%	0	99.6		95.4
0.1 mol%	0	99.5		95

At 0.2 and 0.1 mol% the reactions go to >99% conversion within 24h and the ee is only slightly reduced.

(R)-1-(2-Methoxyphenyl)ethan-1-ol

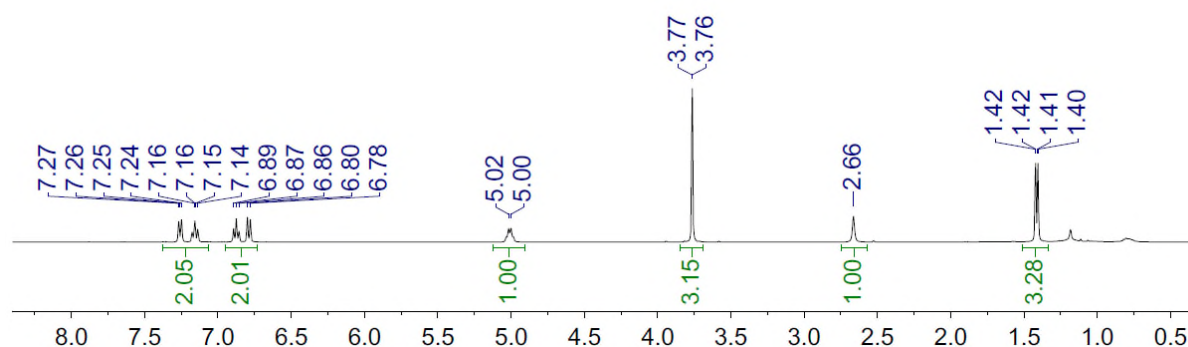


This compound was prepared by the general procedure for ATH in FA/TEA using 1-(2-methoxyphenyl)ethan-1-one (0.111g, 0.73 mmol, 1.0 eq), catalyst 0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give 1-(2-methoxyphenyl)ethan-1-ol as a colourless oil (56.5 mg, 50% yield);

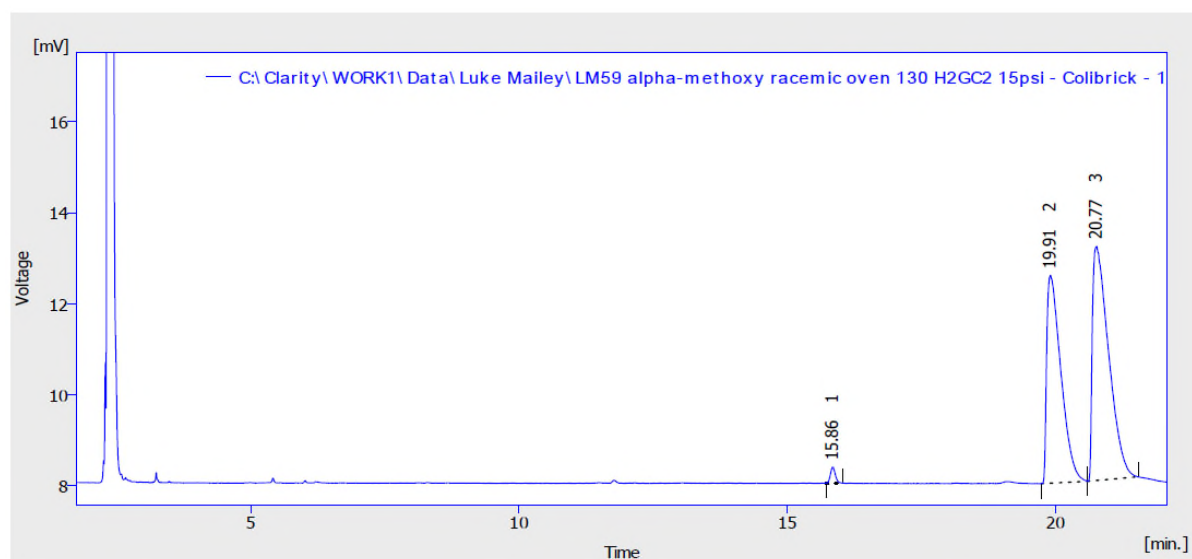
δ_{H} (400 MHz, CDCl_3) 7.26 (1 H, d, J 7.5, ArH), 7.16 (1 H, app. t, J 7.8, ArH), 6.87 (1 H, app. t, J 7.4, ArH), 6.79 (1 H, d, J 8.2, ArH), 5.01 (1 H, q, J 6.0, CHOH), 3.77 (3 H, s, OCH_3), 2.66 (1 H, s, OH) and 1.41 (3 H, d, J 6.5, CH_3).

Conversion and enantiomeric excess were determined by chiral GC analysis (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μm , gas hydrogen, $T = 130^\circ\text{C}$, $P = 15$ psi, FID temp 250°C , injector temp 220°C): ketone 11.8 min, R isomer 20.0 min, S isomer 20.5 min.

^1H NMR spectrum (400 MHz, CDCl_3)



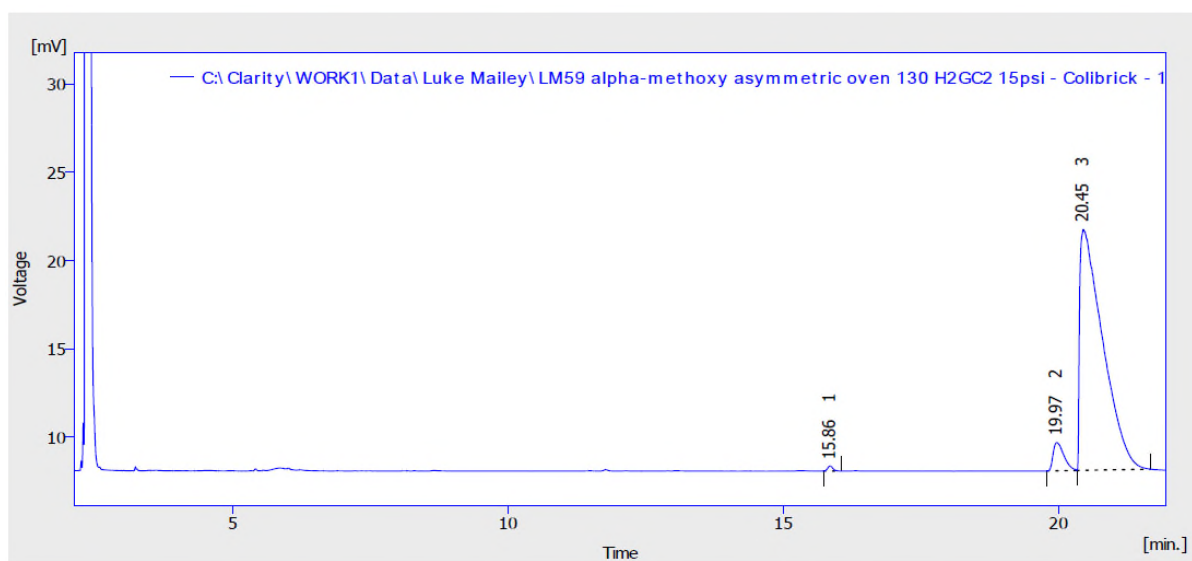
GC trace of (±)-1-(2-Methoxyphenyl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM59 alpha-methoxy racemic oven 130 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	15.856	2.258	0.352	1.2	3.5	0.10	
2	19.912	83.949	4.572	43.1	45.4	0.29	
3	20.772	108.446	5.149	55.7	51.1	0.34	
Total		194.653	10.074	100.0	100.0		

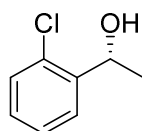
GC trace of (R)-1-(2-Methoxyphenyl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM59 alpha-methoxy asymmetric oven 130 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	15.856	1.859	0.287	0.4	1.8	0.10	
2	19.968	21.748	1.607	5.2	10.3	0.22	
3	20.452	396.361	13.647	94.4	87.8	0.46	
Total		419.967	15.540	100.0	100.0		

(R)-1-(2-Chlorophenyl)ethan-1-ol

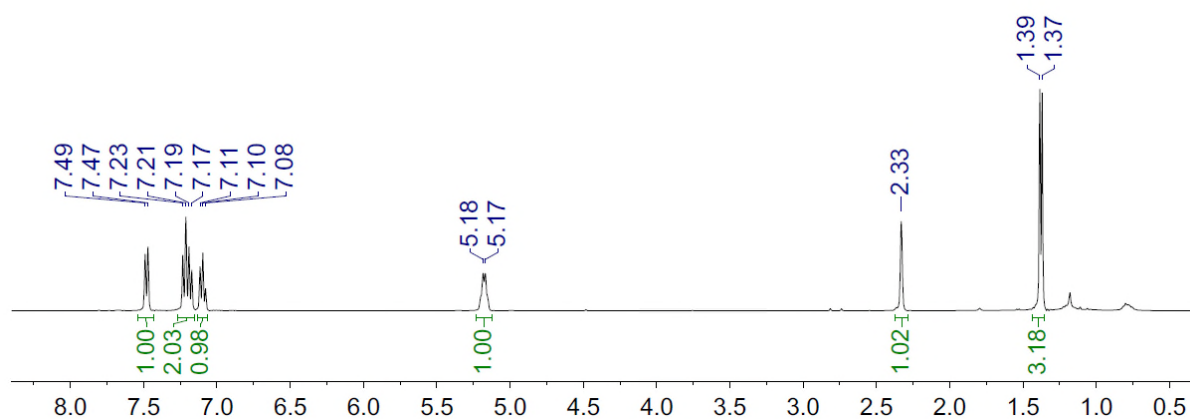


This compound was prepared by the general procedure for ATH in FA/TEA using 1-(2-chlorophenyl)ethan-1-one (0.112 g, 0.73 mmol, 1.0 eq), catalyst (0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give 1-(2-chlorophenyl)ethan-1-ol as a colourless oil (0.059 g, 52% yield);

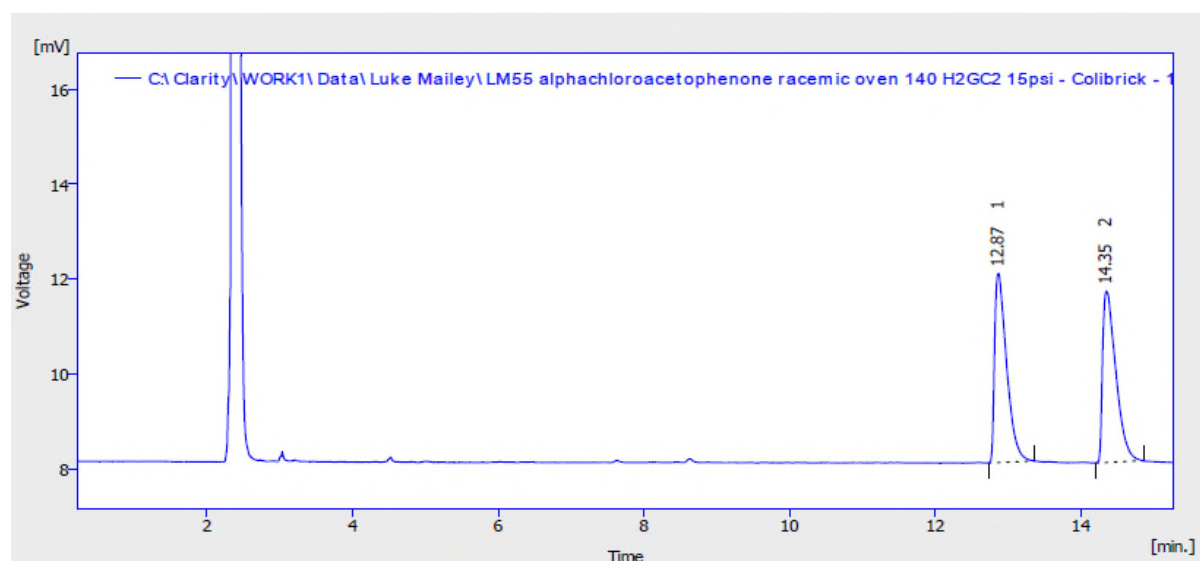
δ_{H} (400 MHz, CDCl_3) 7.48 (1 H, d, J 7.7, ArH), 7.25 – 7.15 (2 H, m, ArH), 7.13 – 7.06 (1 H, m, ArH), 5.18 (1 H, q, J 6.2, CHOH), 2.23 (1 H, s, OH) and 1.38 (1 H, d, J 6.4, CH_3).

Conversion and enantiomeric excess were determined by chiral GC analysis (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μm , gas hydrogen, $T = 140^\circ\text{C}$, $P = 18$ psi, FID temp 250°C , injector temp 220°C): ketone 7.9 min, R isomer 12.9 min, S isomer 14.4 min.

^1H NMR spectrum (400 MHz, CDCl_3)



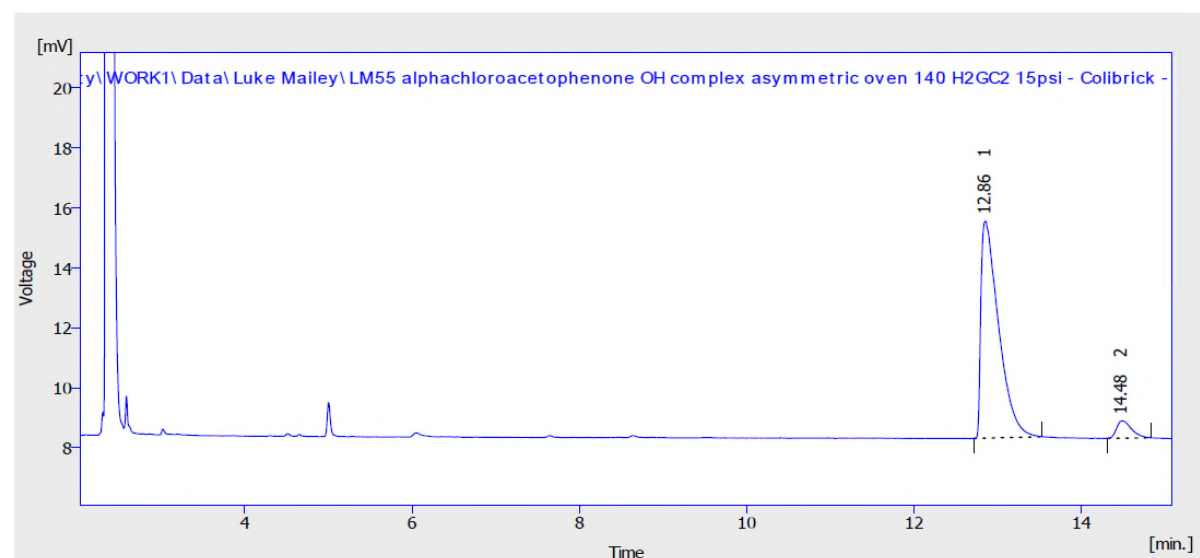
GC trace of (±)-1-(2-Chlorophenyl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM55 alphachloroacetophenone racemic oven 140 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.872	45.642	3.984	50.0	52.5	0.18	
2	14.352	45.575	3.610	50.0	47.5	0.20	
	Total	91.218	7.594	100.0	100.0		

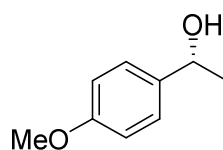
GC trace of (R)-1-(2-Chlorophenyl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM55 alphachloroacetophenone OH complex asymmetric oven 140 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.856	106.194	7.237	93.7	92.6	0.23	
2	14.480	7.154	0.581	6.3	7.4	0.19	
	Total	113.348	7.818	100.0	100.0		

(R)-1-(4-Methoxyphenyl)ethan-1-ol

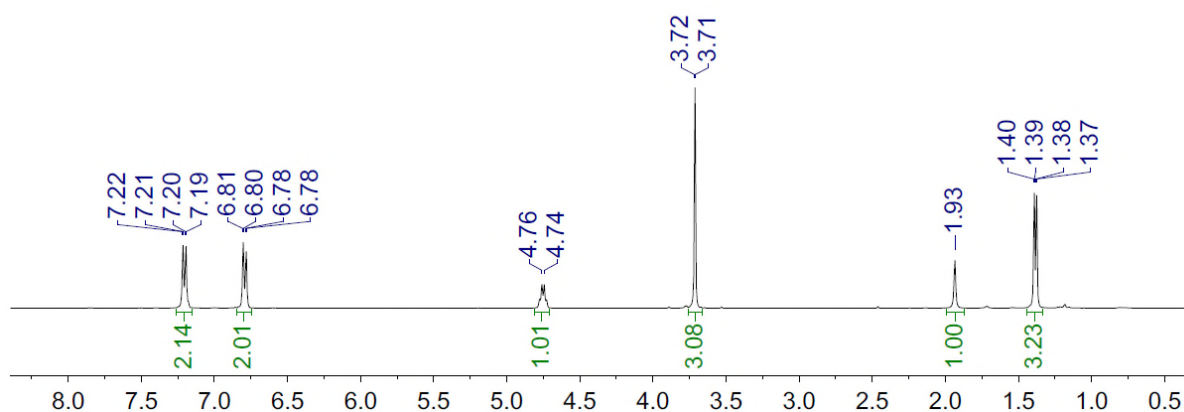


This compound was prepared by the general procedure for ATH in FA/TEA using 1-(4-methoxyphenyl)ethanone (0.112 g, 0.73 mmol, 1.0 eq), catalyst (0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give (*R*)-1-(4-Methoxyphenyl)ethan-1-ol as a colourless oil (0.042g, 37%);

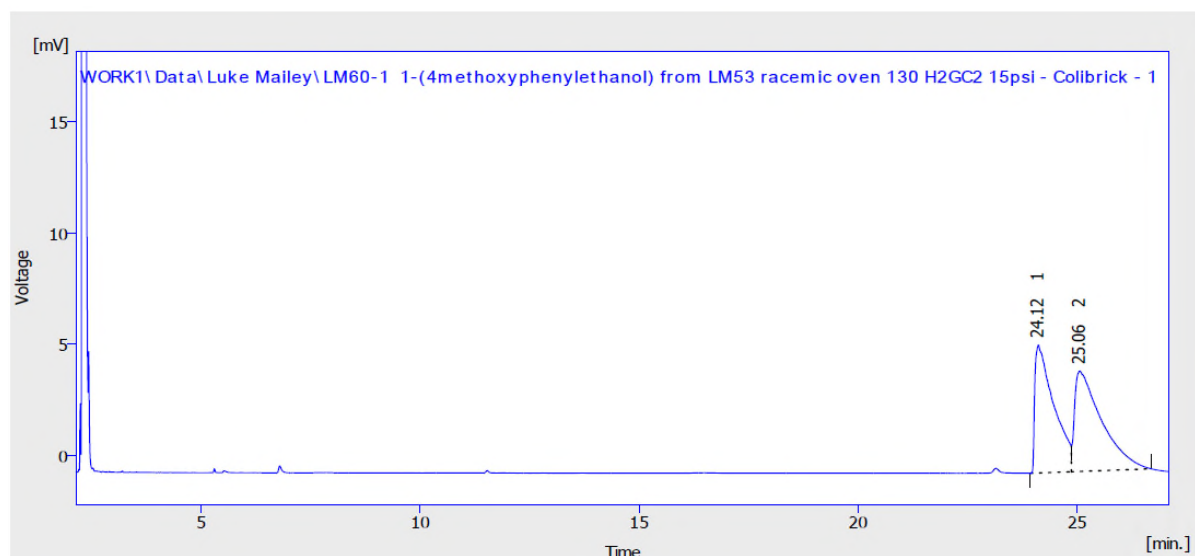
δ_{H} (400 MHz, CDCl_3) 7.20 (2 H, d, J 8.0, ArH), 6.80 (2 H, d, J 8.4, ArH), 4.81 (1 H, q, J 6.3 CHO), 3.72 (3 H, s, OCH_3), 1.93 (1 H, s, OH) and 1.39 (3 H, d, J 6.4, CH_3).

Conversion and enantiomeric excess were determined by chiral GC analysis (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μm , gas hydrogen, $T = 130^\circ\text{C}$, $P = 15$ psi, FID temp 250°C , injector temp 220°C): ketone 23.6 min, R isomer 24.1 min, S isomer 25.1 min.

^1H NMR spectrum (400 MHz, CDCl_3)



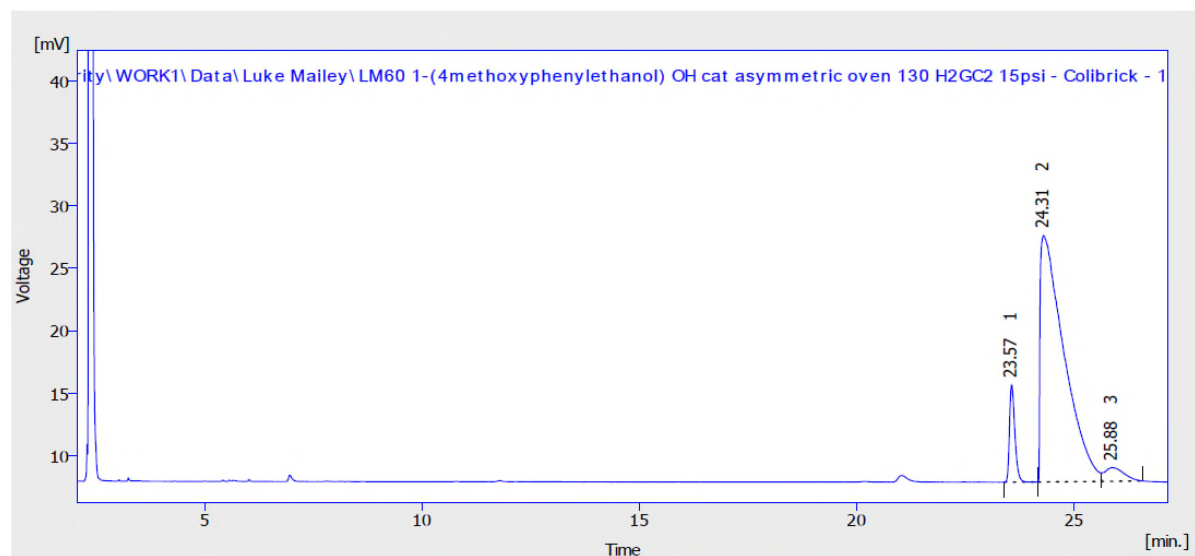
GC trace of (±)-1-(4-Methoxyphenyl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM60-1 1-(4methoxyphenylethanol) from LM53 racemic oven 130 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	24.116	172.405	5.756	47.1	56.0	0.48	
2	25.064	193.702	4.516	52.9	44.0	0.65	
Total		366.107	10.272	100.0	100.0		

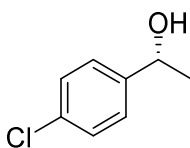
GC trace of (R)-1-(4-Methoxyphenyl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM60 1-(4methoxyphenylethanol) OH cat asymmetric oven 130 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	23.572	66.899	7.789	7.9	27.2	0.13	
2	24.308	749.490	19.750	88.1	69.0	0.58	
3	25.884	34.236	1.098	4.0	3.8	0.56	
Total		850.625	28.637	100.0	100.0		

(*R*)-1-(4-Chlorophenyl)ethan-1-ol

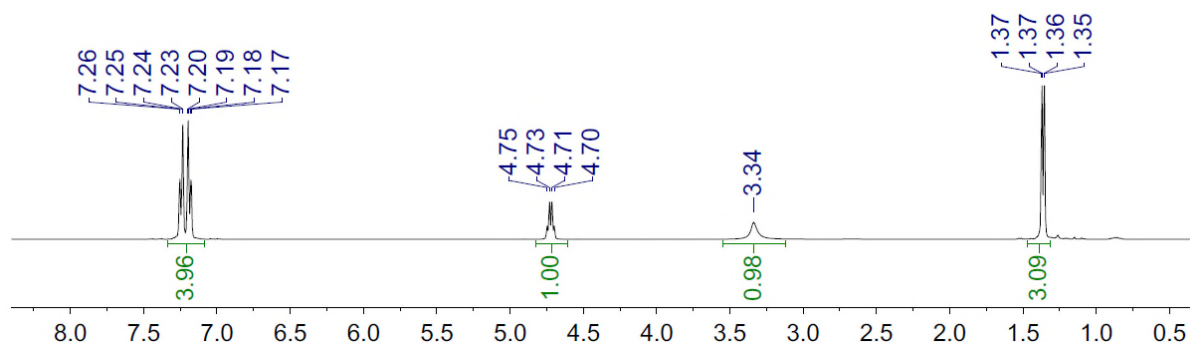


This compound was prepared by the general procedure for ATH in FA/TEA using 1-(4-chlorophenyl)ethanone (0.110 g, 0.73 mmol, 1.0 eq), catalyst (0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give (*R*)-1-(4-Chlorophenyl)ethan-1-ol as a colourless oil (0.064 g, 57%);

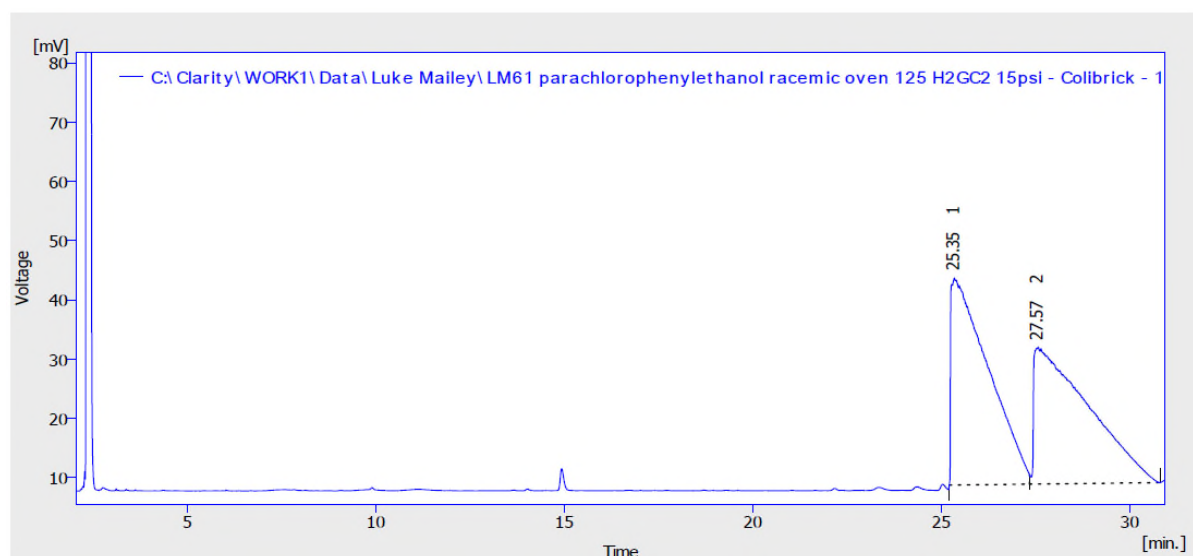
δ_{H} (400 MHz, CDCl_3) 7.27 – 7.15 (4 H, m, ArH), 4.72 (1 H, q, J 6.2, CHOH), 3.34 (1 H, s, OH) and 1.37 (3 H, d, J 6.3, CH_3)

Conversion and enantiomeric excess were determined by chiral GC analysis (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μm , gas hydrogen, $T = 125^\circ\text{C}$, $P = 15$ psi, FID temp 250°C , injector temp 220°C): ketone 14.9 min, R isomer 25.4 min, S isomer 27.6 min.

^1H NMR spectrum (400 MHz, CDCl_3)



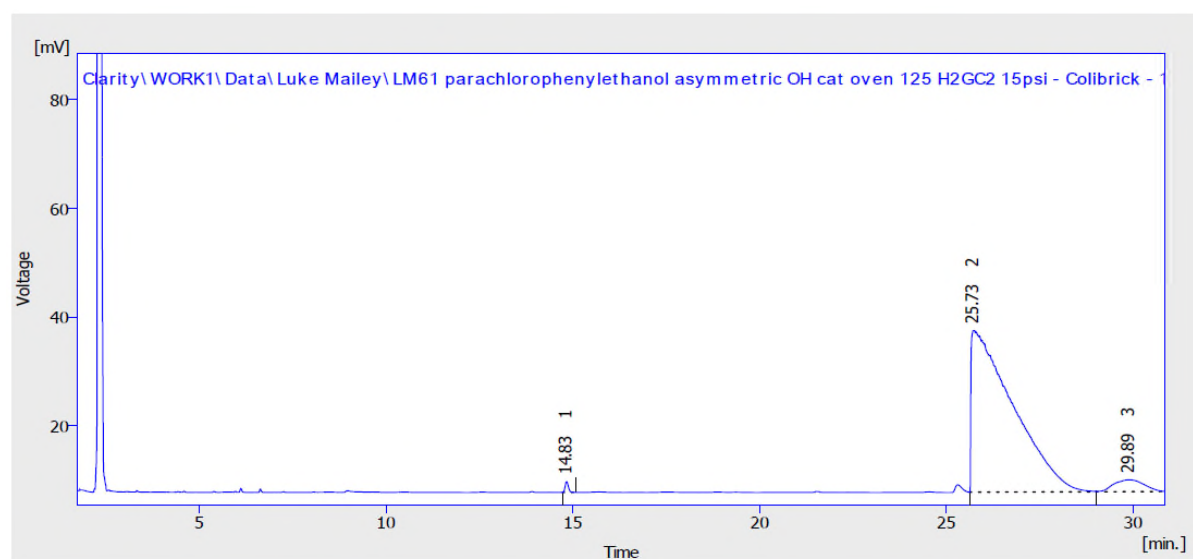
GC trace of (±)-1-(4-Chlorophenyl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM61 parachlorophenylethanol racemic oven 125 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	25.352	2396.366	34.975	50.8	60.2	1.14	
2	27.568	2317.505	23.103	49.2	39.8	1.68	
Total		4713.871	58.077	100.0	100.0		

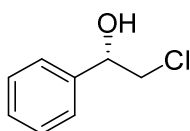
GC trace of (R)-1-(4-Chlorophenyl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM61 parachlorophenylethanol asymmetric OH cat oven 125 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.832	11.819	1.973	0.5	5.8	0.10	
2	25.728	2306.347	29.726	94.5	87.7	1.22	
3	29.888	123.010	2.188	5.0	6.5	0.95	
Total		2441.176	33.887	100.0	100.0		

(S)-2-Chloro-1-phenylethan-1-ol

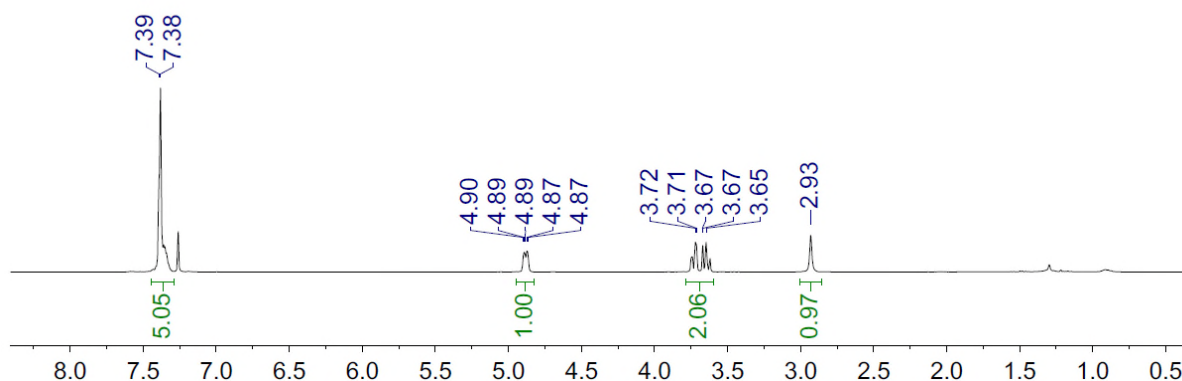


This compound was prepared by the general procedure for ATH in FA/TEA using 2-chloro-1-phenylethanone (0.112 g, 0.73 mmol, 1.0 eq), catalyst .. (R,R) (5 mg, 0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give 2-chloro-1-phenylethan-1-ol as a colourless oil (0.078 g, 69% yield);

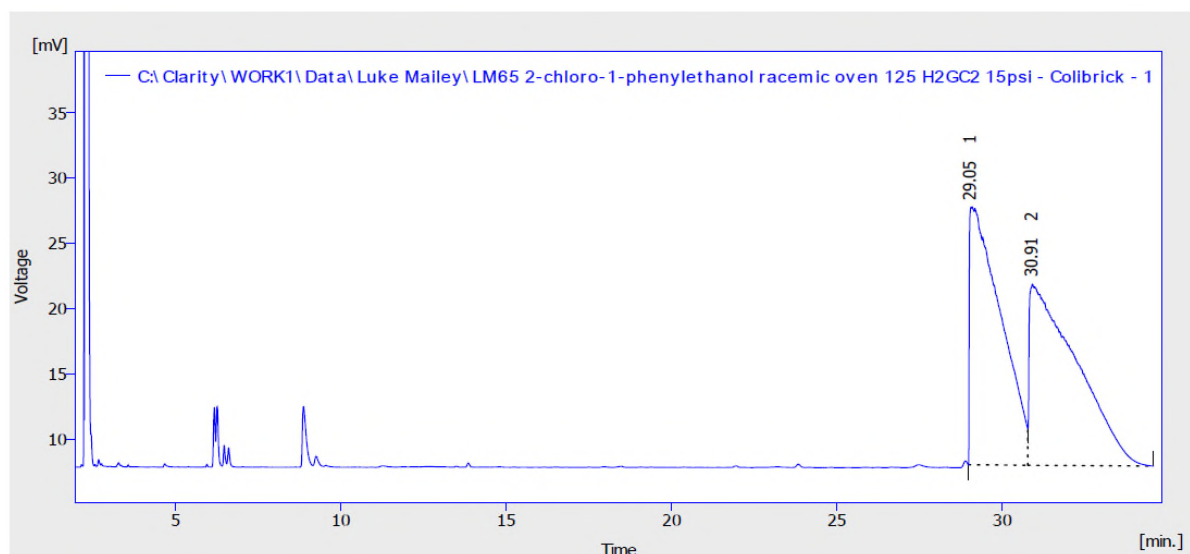
δ_{H} (400 MHz, CDCl_3) 7.43 – 7.29 (5 H, m, ArH), 4.91 – 4.84 (1 H, m, CHOH), 3.77 – 3.58 (2 H, m, CH_2Cl) and 2.93 (1 H, s, OH).

Conversion and enantiomeric excess were determined by chiral GC analysis (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μm , gas hydrogen, T = 110 $^{\circ}\text{C}$, P = 18 psi, FID temp 220 $^{\circ}\text{C}$, injector temp 220 $^{\circ}\text{C}$): ketone 13.9 min, S isomer 29.1 min, R isomer 30.9 min.

^1H NMR spectrum (400 MHz, CDCl_3)



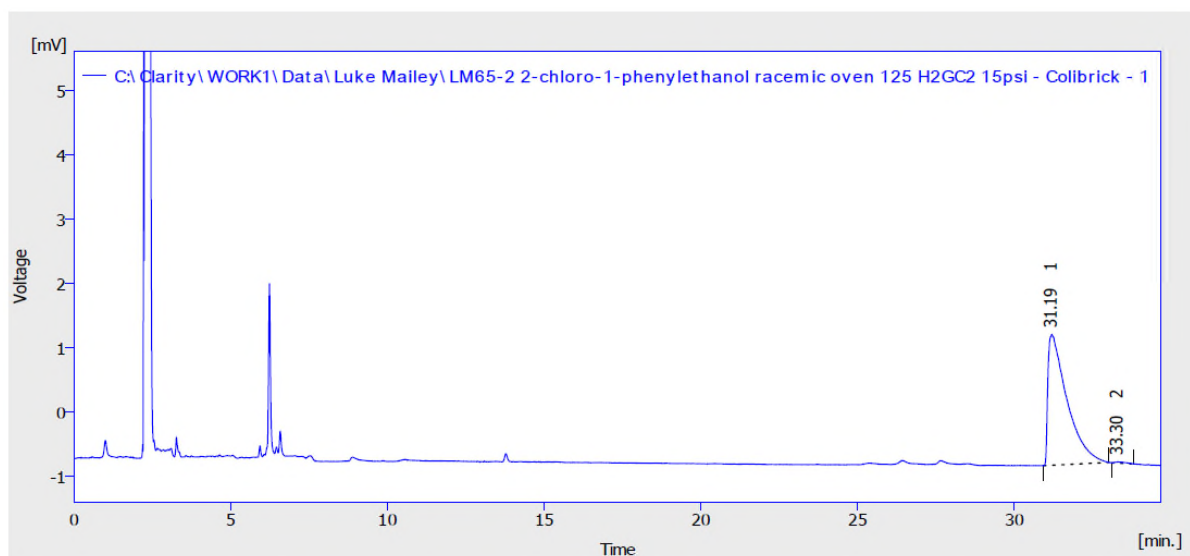
GC trace of (±)-2-Chloro-1-phenylethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM65 2-chloro-1-phenylethan-1-ol racemic oven 125 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	29.052	1287.195	19.726	48.5	58.7	1.11	
2	30.908	1368.614	13.860	51.5	41.3	1.68	
	Total	2655.809	33.586	100.0	100.0		

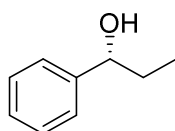
GC trace of (S)-2-Chloro-1-phenylethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM65-2 2-chloro-1-phenylethan-1-ol racemic oven 125 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	31.192	86.275	2.039	99.4	98.8	0.64	
2	33.300	0.550	0.024	0.6	1.2	0.28	
	Total	86.825	2.063	100.0	100.0		

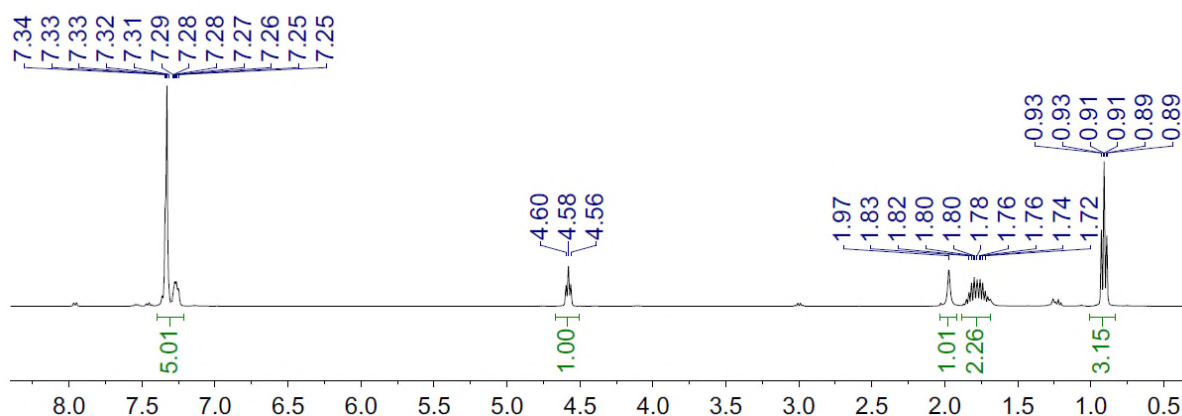
(R)-1-Phenylpropan-1-ol



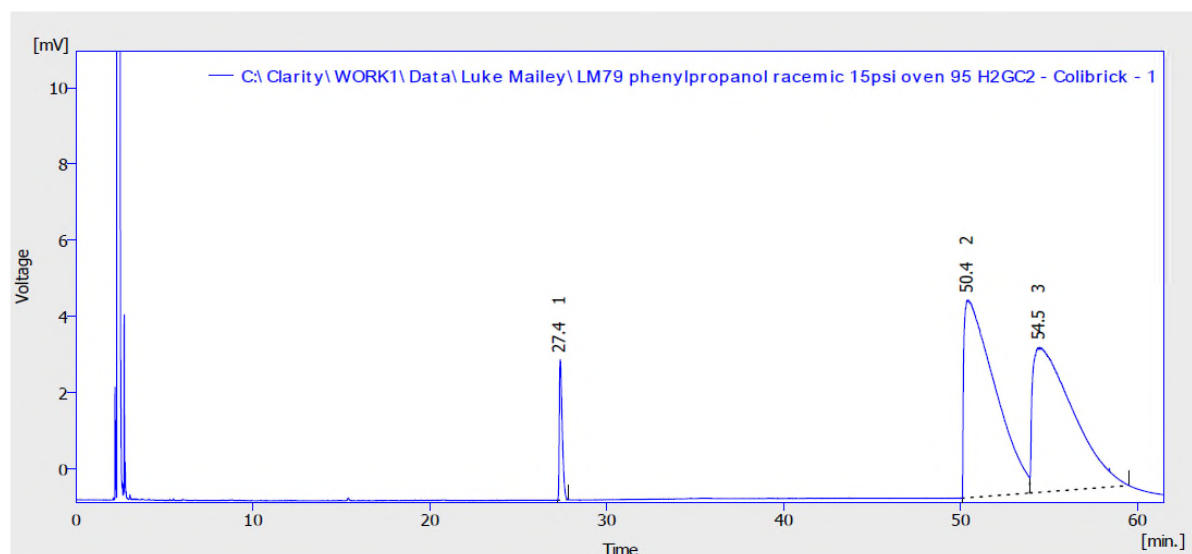
This compound was prepared by the general procedure for ATH in FA/TEA using propiophenone (0.098 g, 0.73 mmol, 1.0 eq), catalyst (R,R) (5 mg, 0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give (*R*)-1-Phenylpropan-1-ol (0.071 g, 0.50 mmol, 68 %) as a colourless oil; δ_{H} (400 MHz, CDCl₃) 7.35 – 7.29 (5 H, m, ArH), 4.58 (1 H, t, *J* 6.5, CHOH), 1.97 (1 H, s, OH), 1.84 – 1.72 (2 H, m, CH₂CH₃) and 0.91 (3 H, t, *J* 7.4, CH₃).

Conversion and enantiomeric excess were determined by chiral GC analysis (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μ m, gas hydrogen, T = 95 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C): ketone 27.4 min, R isomer 50.4 min, S isomer 54.5 min.

¹H NMR spectrum (400 MHz, CDCl₃)



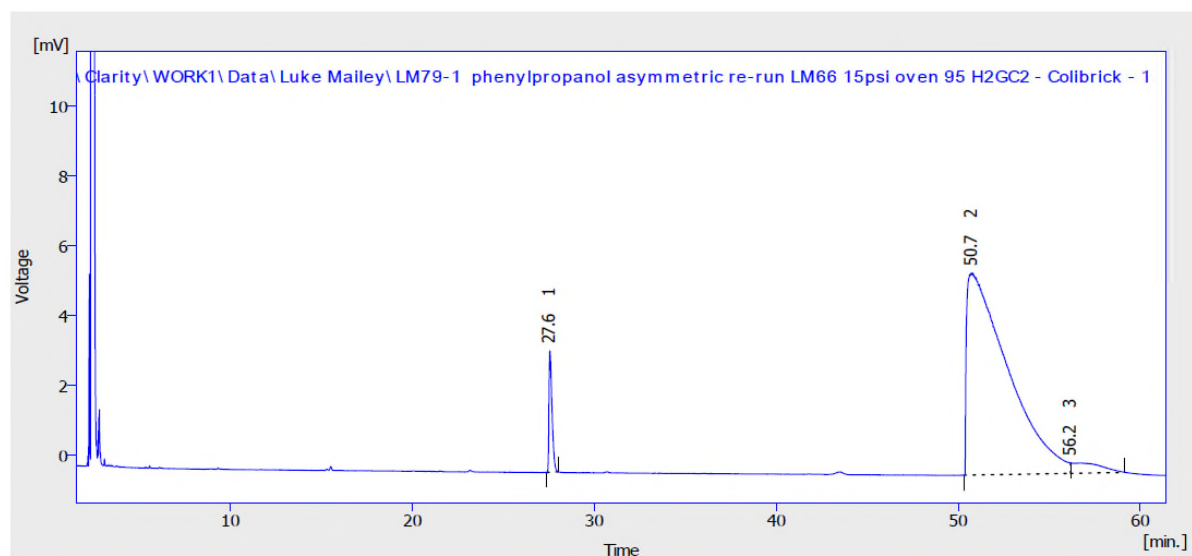
GC trace of (±)-1-Phenylpropan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM79 phenylpropanol racemic 15psi oven 95 H2GC2 - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	27.368	41.973	3.685	3.3	29.1	0.18	
2	50.396	629.719	5.191	49.5	40.9	2.00	
3	54.464	599.302	3.802	47.2	30.0	2.59	
	Total	1270.994	12.678	100.0	100.0		

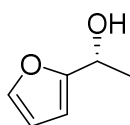
GC trace of (R)-1-Phenylpropan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM79-1 phenylpropanol asymmetric re-run LM66 15psi oven 95 H2GC2 - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	27.556	40.321	3.480	4.1	36.3	0.18	
2	50.744	909.972	5.797	92.5	60.5	2.42	
3	56.188	33.681	0.302	3.4	3.2	2.01	
	Total	983.973	9.579	100.0	100.0		

(R)-1-(Furan-2-yl)ethan-1-ol

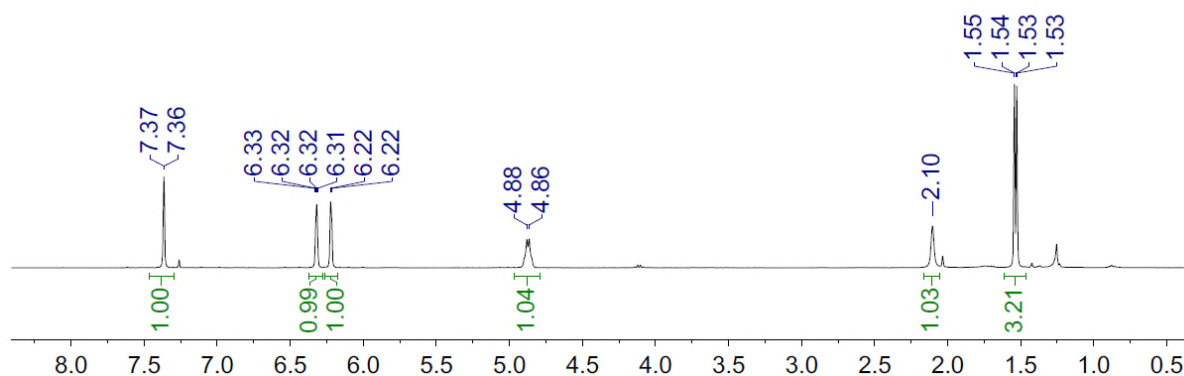


This compound was prepared by the general procedure for ATH in FA/TEA using 1-furan-2-yl methyl ketone (0.081 g, 0.73 mmol, 1 eq), catalyst (0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give (*R*)-1-(Furan-2-yl)ethan-1-ol as a colourless oil (0.043 g, 53%);

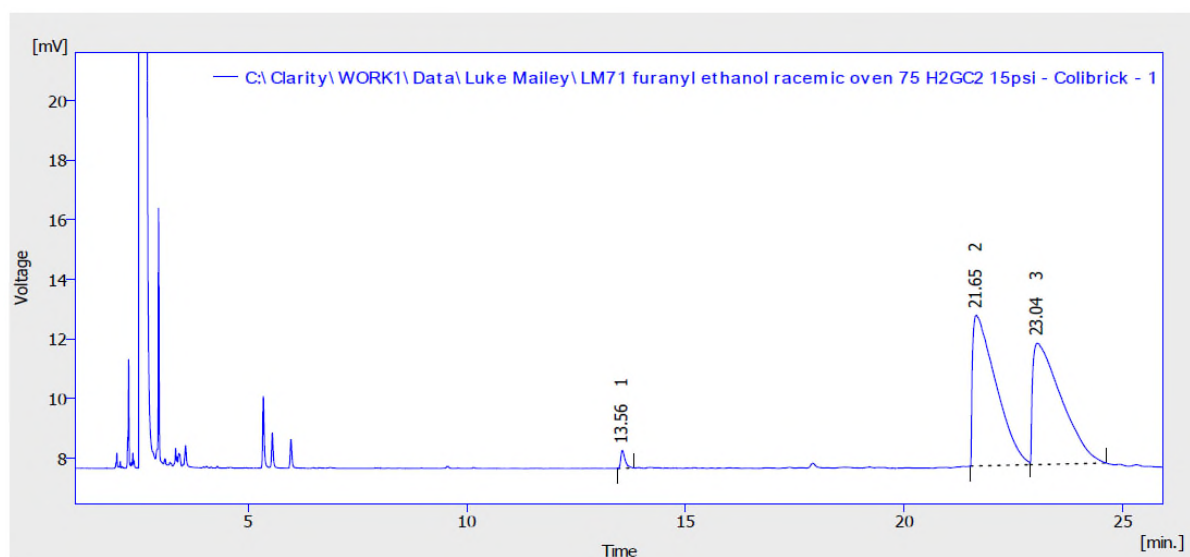
δ_{H} (400 MHz, CDCl_3) 7.37 (1 H, s, ArH), 6.32 (1 H, s, ArH), 6.22 (1 H, s, ArH), 4.87 (1 H, q, J 6.3, CHOH), 2.10 (1 H, s, OH) and 1.54 (3 H, d, J 6.6, CH_3).

Conversion and enantiomeric excess were determined by chiral GC analysis (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μm , gas hydrogen, $T = 75^\circ\text{C}$, $P = 15$ psi, FID temp 250°C , injector temp 220°C): ketone 13.6 min, *R* isomer 21.7 min, *S* isomer 23.0 min.

^1H NMR spectrum (400 MHz, CDCl_3)



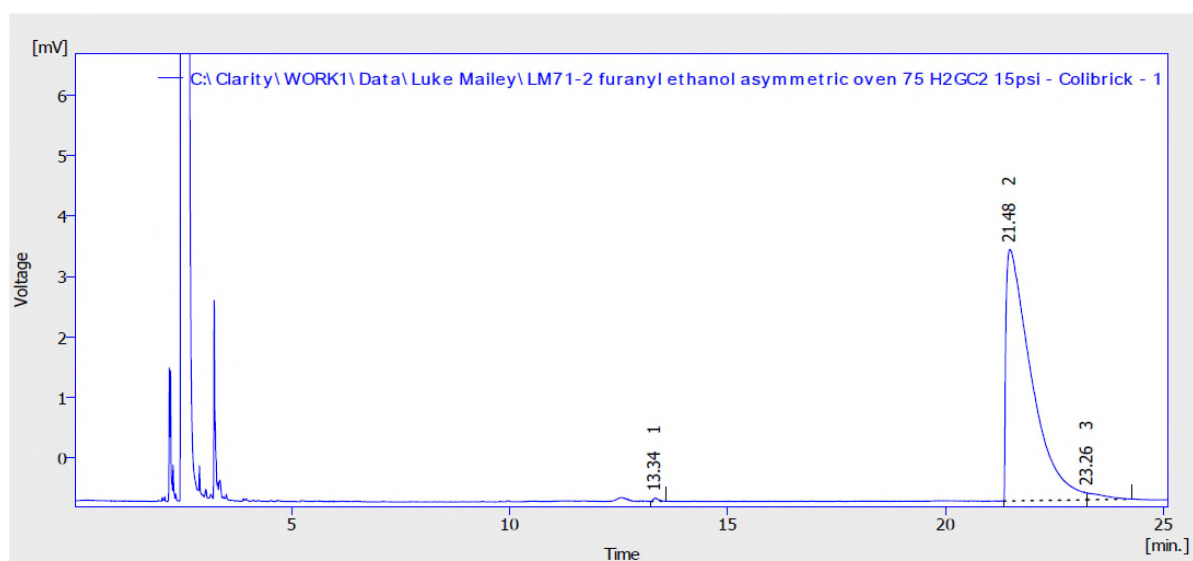
GC trace of (±)-1-(Furan-2-yl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM71 furanyl ethanol racemic oven 75 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	13.556	4.100	0.601	1.1	6.2	0.10	
2	21.648	187.255	5.063	49.7	52.0	0.60	
3	23.044	185.547	4.071	49.2	41.8	0.73	
Total		376.902	9.735	100.0	100.0		

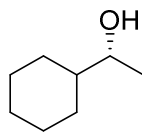
GC trace of (R)-1-(Furan-2-yl)ethan-1-ol



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM71-2 furanyl ethanol asymmetric oven 75 H2GC2 15psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	13.340	0.466	0.058	0.3	1.3	0.12	
2	21.484	168.078	4.155	98.0	96.1	0.60	
3	23.260	3.040	0.112	1.8	2.6	0.46	
Total		171.584	4.324	100.0	100.0		

(R)-1-Cyclohexylethan-1-ol

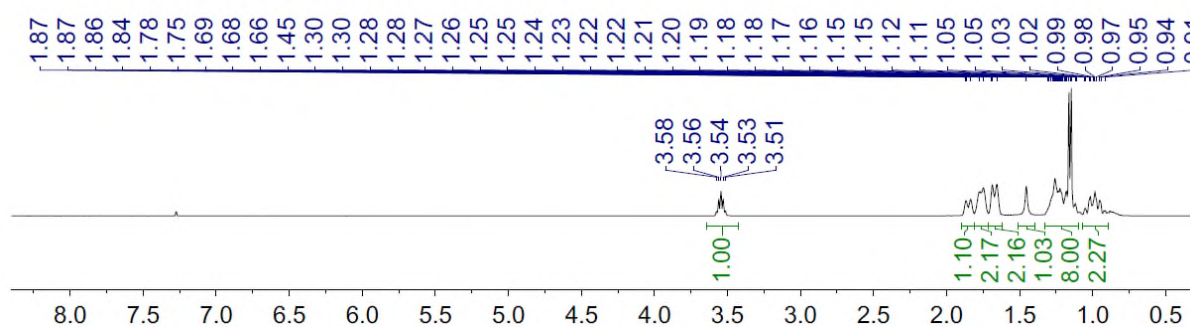


This compound was prepared by the general procedure for ATH in FA/TEA using cyclohexylmethyl ketone (0.092 g, 0.73 mmol, 1.0 eq), catalyst (R,R) (5 mg, 0.0073 mmol, 0.01 eq) and FA/TEA (0.5 mL) to give (R)-1-Cyclohexylethan-1-ol (0.081 g, 0.63 mmol, 86 %) as a colourless oil.

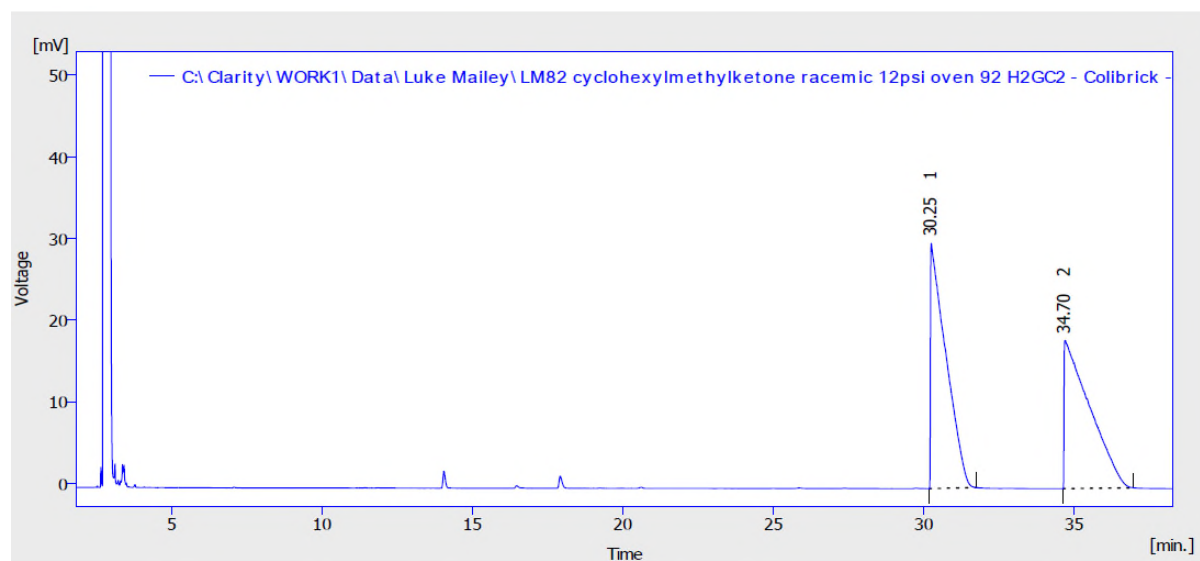
δ_{H} (400 MHz, CDCl_3) 3.54 (1 H, quin, J 6.1, CHOH), 1.85 (1 H, d, J 12.6, CH), 1.79 – 1.74 (2 H, m, CH_2), 1.67 (2 H, d, J 12.1, CH_2), 1.45 (1 H, s, OH), 1.27 – 1.18 (3 H, m, CH_2 + CH), 1.15 (3 H, d, J 6.2, CH_3) and 1.05 – 0.95 (2 H, m, CH_2).

Conversion and enantiomeric excess were determined by chiral GC analysis after conversion to the acetate derivative (CROMPAC CYCLODEXTRIN- β - 236M-19, 50 m \times 0.25 mm \times 0.25 μm , gas hydrogen, $T = 92^\circ\text{C}$, $P = 15$ psi, FID temp 250 $^\circ\text{C}$, injector temp 220 $^\circ\text{C}$): ketone 40.0 min, R isomer 30.3 min, S isomer 34.7 min.

^1H NMR spectrum (400 MHz, CDCl_3)



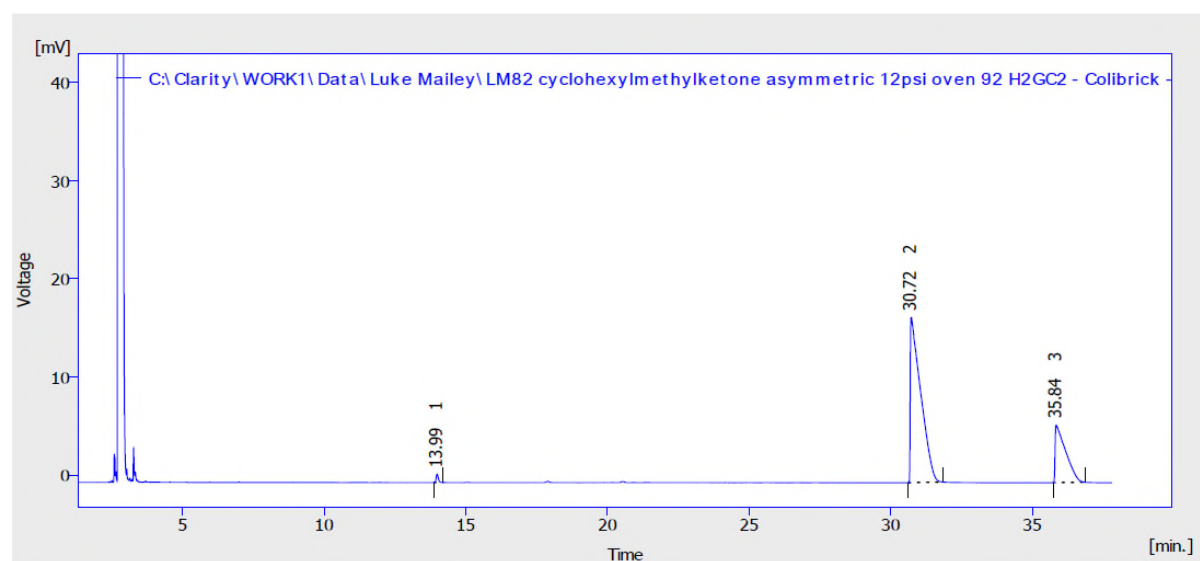
GC trace of (±)-1-cyclohexylethyl acetate



Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM82 cyclohexylmethylketone racemic 12psi oven 92 H2GC2 - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	30.252	1067.513	30.023	50.0	62.3	0.58	
2	34.696	1069.279	18.137	50.0	37.7	0.96	
	Total	2136.791	48.159	100.0	100.0		

GC trace of (R)-1-cyclohexylethyl acetate

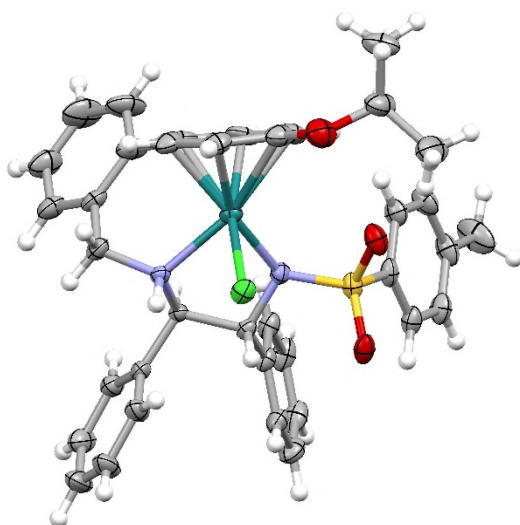


Result Table (Uncal - C:\Clarity\WORK1\Data\Luke Mailey\LM82 cyclohexylmethylketone asymmetric 12psi oven 92 H2GC2 - Colibrick - 1)

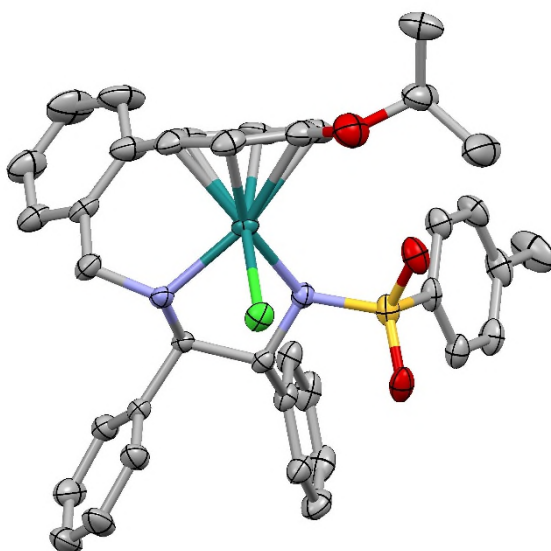
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	13.988	4.790	0.869	0.8	3.7	0.09	
2	30.720	431.881	16.831	73.4	71.5	0.41	
3	35.844	151.514	5.849	25.8	24.8	0.42	
	Total	588.185	23.549	100.0	100.0		

3. Single crystal X-ray crystallography

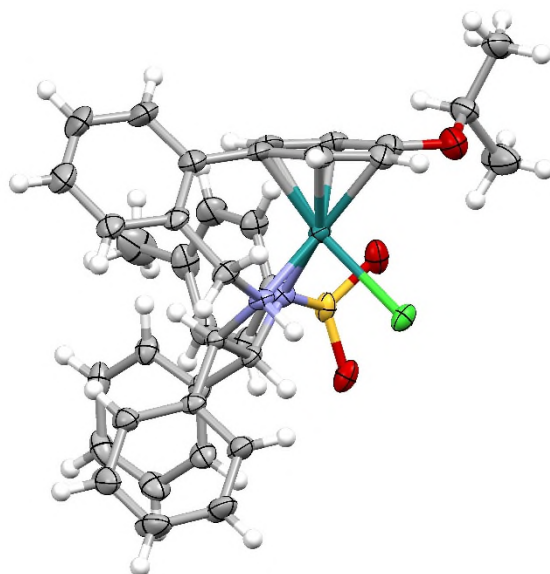
4-Isopropoxy RR-TsDPENRuCl complex (CCDC 1828153)



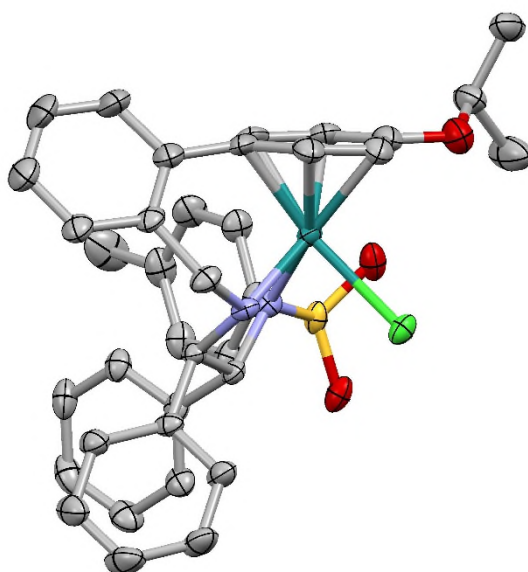
Single crystal x-ray structure of 4-isopropoxy RR-TsDPENRuCl complex (ellipsoids are plotted at the 50% probability level; minor disordered component omitted for clarity)



Single crystal x-ray structure of 4-isopropoxy RR-TsDPENRuCl complex (ellipsoids are plotted at the 50% probability level; minor disordered component and hydrogen atoms omitted for clarity)



Single crystal x-ray structure of 4-isopropoxy RR-TsDPENRuCl complex (ellipsoids are plotted at the 50% probability level; minor disordered component omitted for clarity)



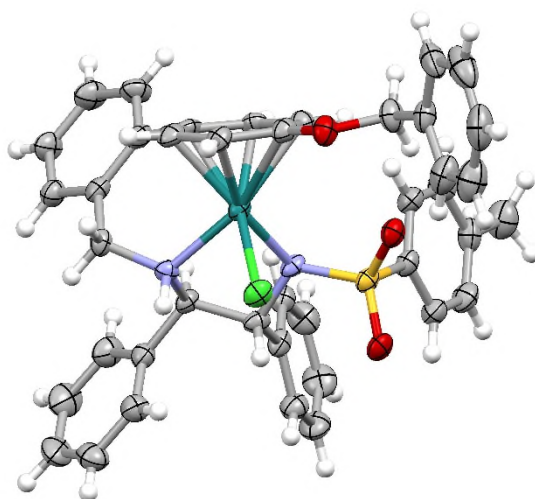
Single crystal x-ray structure of 4-isopropoxy RR-TsDPENRuCl complex (ellipsoids are plotted at the 50% probability level; minor disordered component and hydrogen atoms omitted for clarity)

CCDC 1828153 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

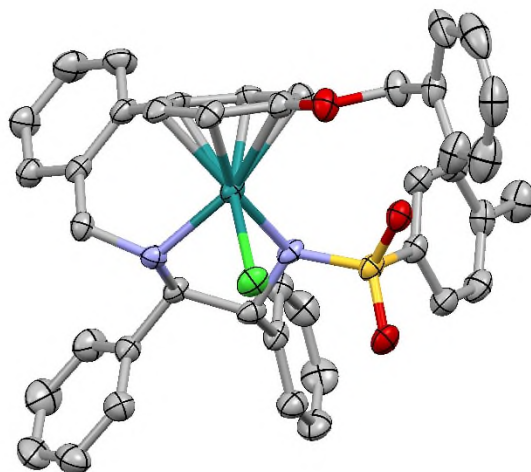
Single crystals of were grown from vapour diffusion of *n*-hexane into a chloroform solution of the compound over several days. Rigaku Oxford Diffraction SuperNova diffractometer with a duel source (Cu at zero) equipped with an AtlasS2 CCD area detector at 150(2) K. The structure was solved using Olex2[1] and the ShelXT[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares refinement.

Compound Reference	4-OiPr RR-TsDPENRuCl complex 2
Chemical Formula	C ₃₇ H ₃₇ ClN ₂ O ₃ RuS
Formula Mass	726.26
Crystal system	monoclinic
<i>a</i> / Å	12.84674(10)
<i>b</i> / Å	10.21786(8)
<i>c</i> / Å	12.94691(10)
α / °	90
β / °	107.1026(8)
γ / °	90
Unit cell volume/ Å ³	1624.34(2)
Temperature/ K	100(2) K
Space group	P 2 ₁ b
Crystal size/ mm	0.08 × 0.16 × 0.20
Radiation	Cu K α
Goodness-of-fit on <i>F</i> ²	1.060
No. of formula units per unit cell, <i>Z</i>	2
No. of reflections measured	33429
No. of independent reflections	6865
Final <i>R</i> ₁ vaules (<i>I</i> > 2 σ (<i>I</i>))	0.0453
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.1196
Final <i>R</i> ₁ values (all data)	0.0458
Final <i>wR</i> (<i>F</i> ²) (all data)	0.1201

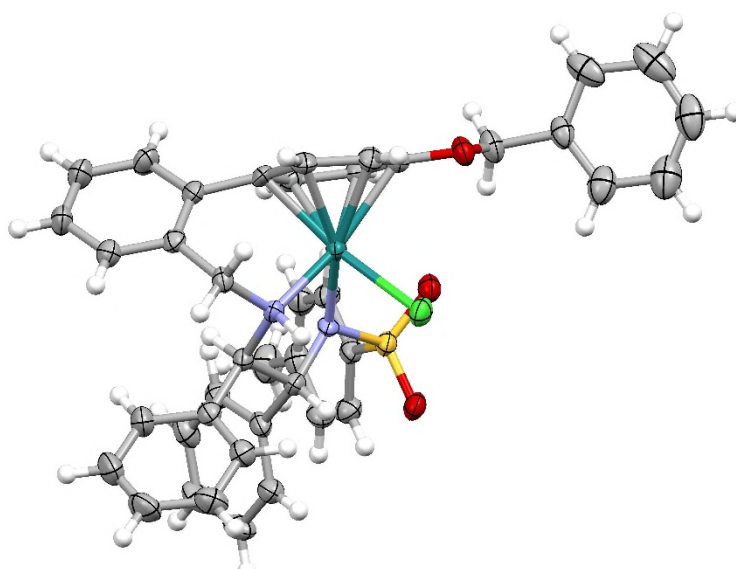
4-benzyloxy RR-TsDPENRuCl complex (CCDC 1828154)



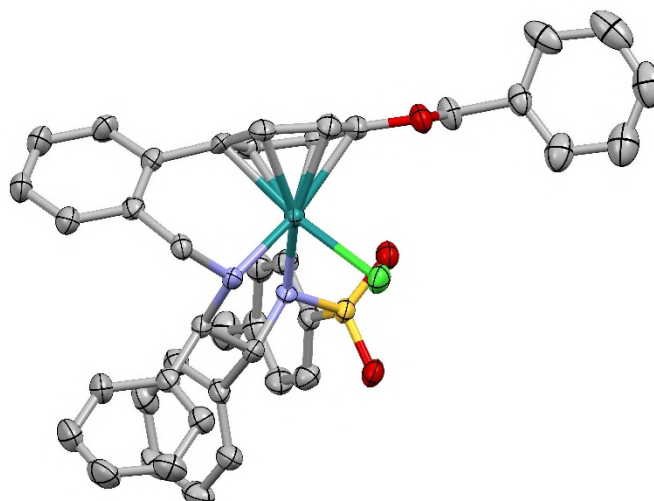
Single crystal x-ray structure of 4-benzyloxy RR-TsDPENRuCl complex (ellipsoids are plotted at the 50% probability level; solvent omitted for clarity)



Single crystal x-ray structure of 4-benzyloxy RR-TsDPENRuCl complex (ellipsoids are plotted at the 50% probability level; solvent and hydrogen atoms omitted for clarity)



Single crystal x-ray structure of 4-benzyloxy RR-TsDPENRuCl complex (ellipsoids are plotted at the 50% probability level; solvent omitted for clarity)



Single crystal x-ray structure of 4-benzyloxy RR-TsDPENRuCl complex (ellipsoids are plotted at the 50% probability level; solvent and hydrogen atoms omitted for clarity)

CCDC 1828154 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Single crystals of were grown from vapour diffusion of *n*-hexane into a chloroform solution of the compound over several days. A suitable crystal was mounted on a Mitegen head with Fomblin oil and collected on an Xcalibur Gemini diffractometer with a Ruby CCD area detector at 150(2) K. The structure was solved using Olex2[1] and the ShelXT[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares refinement.

Compound Reference	4-OBn RR-TsDPENRuCl complex 3
Chemical Formula	C ₄₂ H ₃₈ Cl ₄ N ₂ O ₃ RuS
Formula Mass	893.67
Crystal system	orthorhombic
<i>a</i> / Å	11.01638(12)
<i>b</i> / Å	15.7699(2)
<i>c</i> / Å	22.9663(3)
α / °	90
β / °	90
γ / °	90
Unit cell volume/ Å ³	3989.88(9)
Temperature/ K	150(2) K
Space group	P 2ac 2ab
Crystal size/ mm	0.03 × 0.04 × 0.70
Radiation	Cu K/α
Goodness-of-fit on F ²	1.073
No. of formula units per unit cell, Z	4
No. of reflections measured	18321
No. of independent reflections	7531
Final R ₁ vaules (<i>I</i> > 2σ(<i>I</i>))	0.0357

Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0806
Final R_1 values (all data)	0.0400
Final $wR(F^2)$ (all data)	0.0853

4. References

- [1] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. of Appl. Crystallogr. 42 (2009) 339-341.
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