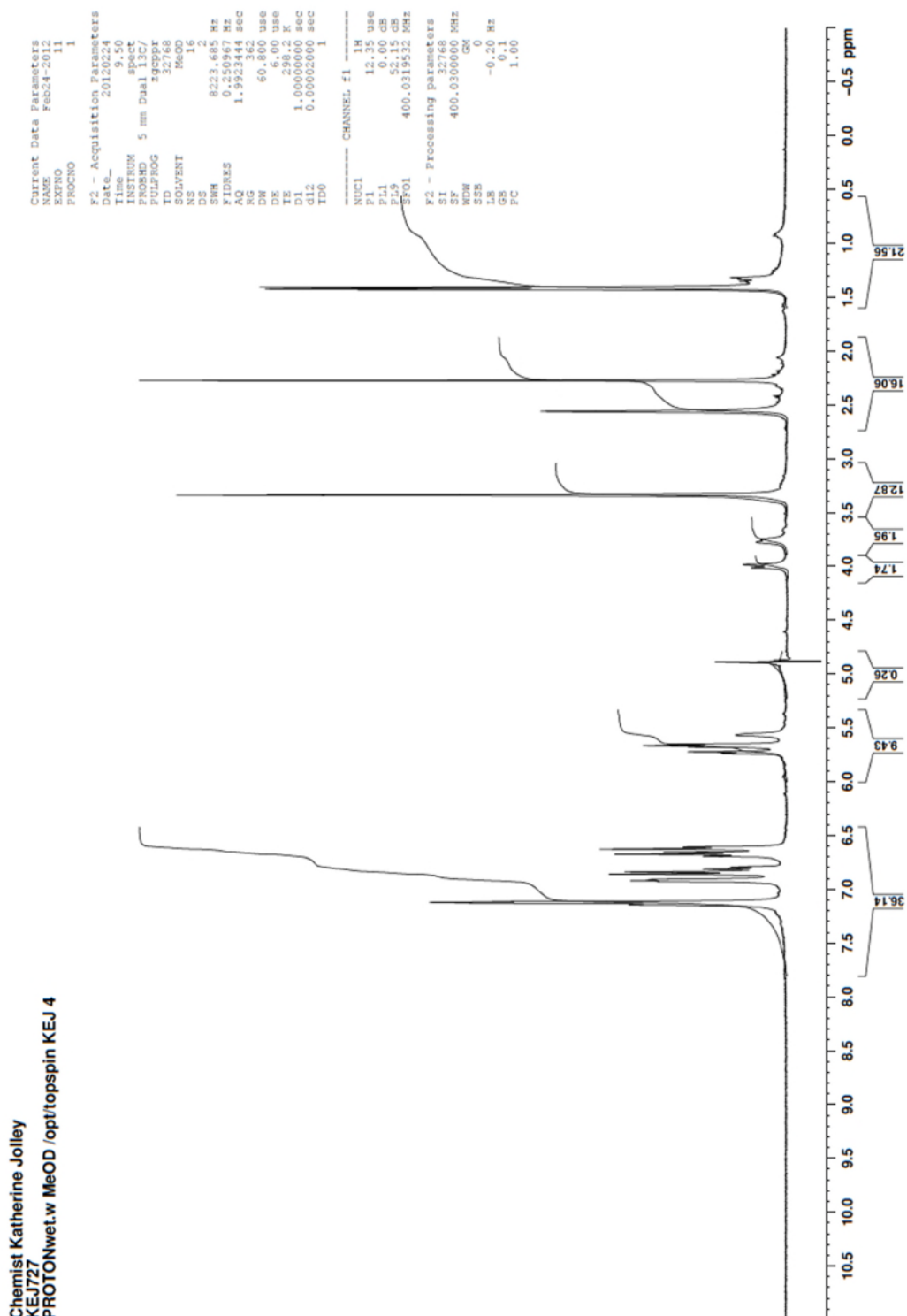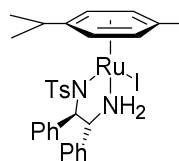**Tethered Ru(II) catalysts containing a Ru-I bond.**

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Supplementary Information.

Index:

N-[(1R,2R)-2-(Amino)-1,2-diphenylethyl]-4-methylbenzenesulfonamide(p-

cymene)ruthenium(II)iodide monomer 8.

^{1}H NMR (water peak suppressed) in MeOH, 400 MHz.

^{1}H NMR (water peak unsuppressed) in MeOH, 400 MHz.

Chemist Katherine Jolley
KEJ727
PROTON.w MeOD /opt/topspin KEJ 4

¹³H NMR in DMSO, 150 MHz.

KEJ117 in d-DMSO @ 298°K 13C APT Spectrum

N-[(1S,   2S)-1,   2-Diphenyl-2-(3-phenypropylamino)ethyl)-4-

*methylbenzenesulfonamide)ruthenium(II)iodide monomer **7.***

^{1}H NMR in CDCl$_3$, 400 MHz.

<superscript>13</superscript>H NMR in CDCl₃, 100 MHz.

^{13}H NMR in CDCl$_3$, 100 MHz.

*X-ray crystallographic data for (S,S)-3C-tethered-RuI catalysts **7** (CCDC 1016062) and (b) (R,R)-**8** (CCDC 1016063).*

*(S,S)-**7** (CCDC 1016062)*

Solid state structure of *CCDC 1016062* with atom numbering (disordered solvent removed for clarity).

Experimental data for *CCDC 1016062*: The asymmetric unit contained a complex composed of an iodide and a tosyl diphenyldiamine with a propylphenyl chain about ruthenium. There was some electron density refined as disordered methanol solvent. This was modelled as disordered over two 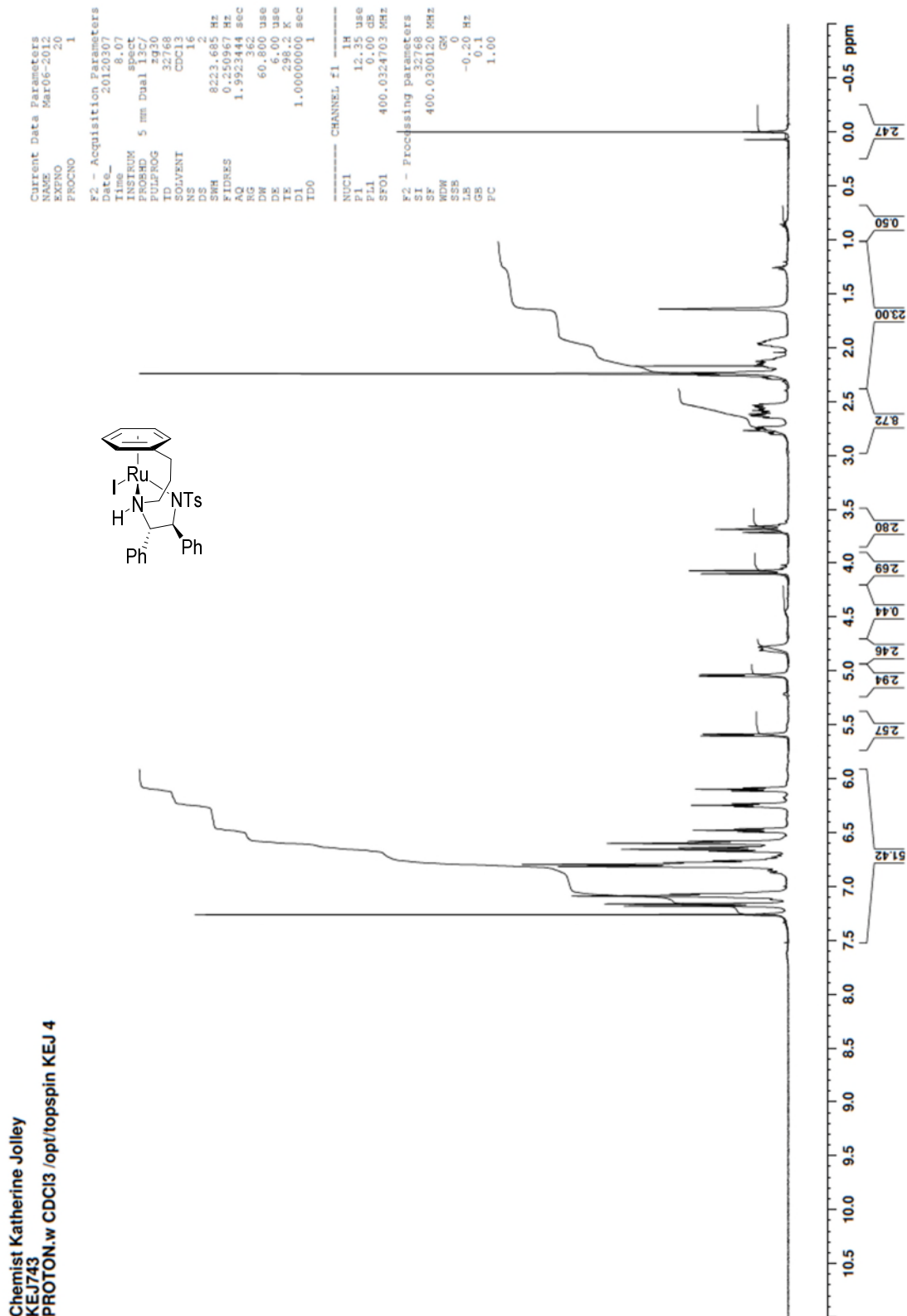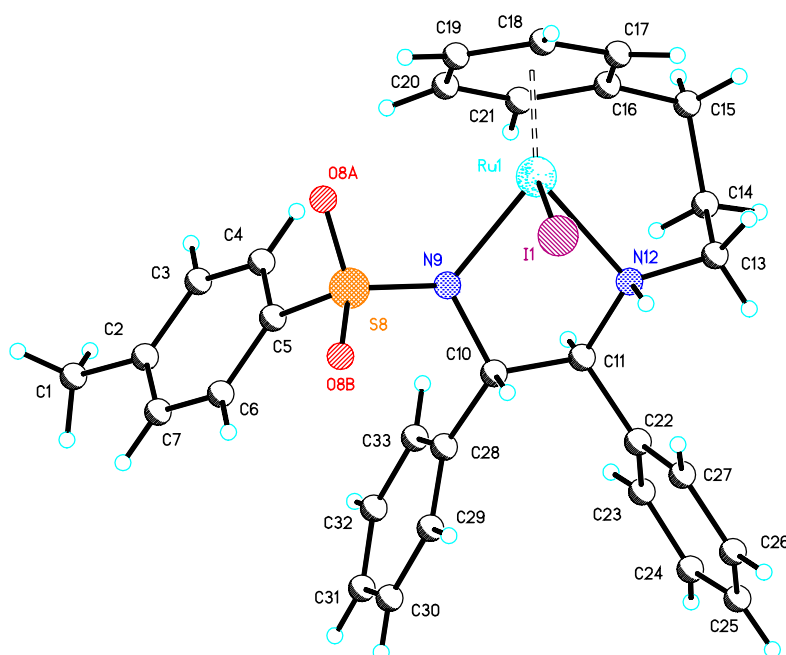positions and refined to 50:50 occupancy. Distance restraints were used to give one of the disordered methanol molecules a reasonable C-O bond length. No hydrogens were located for these solvent molecules but were included in the formula for completeness. The solvent atoms were refined isotropically. The NH could not be located and was placed at a calculated position. It lies parallel to the Ru-I bond which may be some sort of dipole dipole interaction. There is an internal pi stacking interaction between the tosyl and one of the phenyl rings. This is characterised as the atoms used to define mean planes through the two pi

systems, the angle between these mean planes and the closest atomic contact. Angle between C2 C3 C4 C5 C6 C7 to C28 C29 C30 C31 C32 C33 is 20.47 (0.24) degrees. Closest atomic contact C5 - C33 3.1122 (0.0047)   Angstroms. The Flack parameter refined to 0.038(16). The Hooft y parameter refined to 0.039(8) (Olex2). These numbers reflect the confidence in the assignment of the handedness of the crystal chosen and are good (a small number with an equivalent small esd)

Crystal Data: $C_{31}H_{35}IN_2O_3RuS$, M = 743.64, Monoclinic, space group P2(1), a = 11.7063(2), b = 9.65672(16), c = 13.5915(3) Å, alpha = 90 deg., beta = 98.9689(17) deg., gamma = 90 deg., U = 1517.66(5) Å^3 (by least squares refinement on 8297 reflection positions), T =298(2)K, lambda = 0.71073 A, Z = 2, D(cal) = 1.627 Mg/m^3, F(000) = 744. mu(MoK-alpha) = 1.636 mm^{-1}. Crystal character:brown block. Crystal dimensions 0.24 x 0.12 x 0.12 mm.

Structure Analysis and Refinement: Systematic absences indicated space group P2(1) or P2(1)m. The former was chosen on the basis of intensity statistics and shown to be correct by successful refinement. The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. R1[for 8157 reflections with I>2sigma(I)] = 0.0415, wR2 = 0.0855. Data / restraints/parameters 9644/2/352. Largest difference Fourier peak and hole 0.853 and -0.530 e.A^{-3}. Refinement used SHELXL 97 (Sheldrick, 1997). Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

*(R,R)-**8** (CCDC 1016063).*
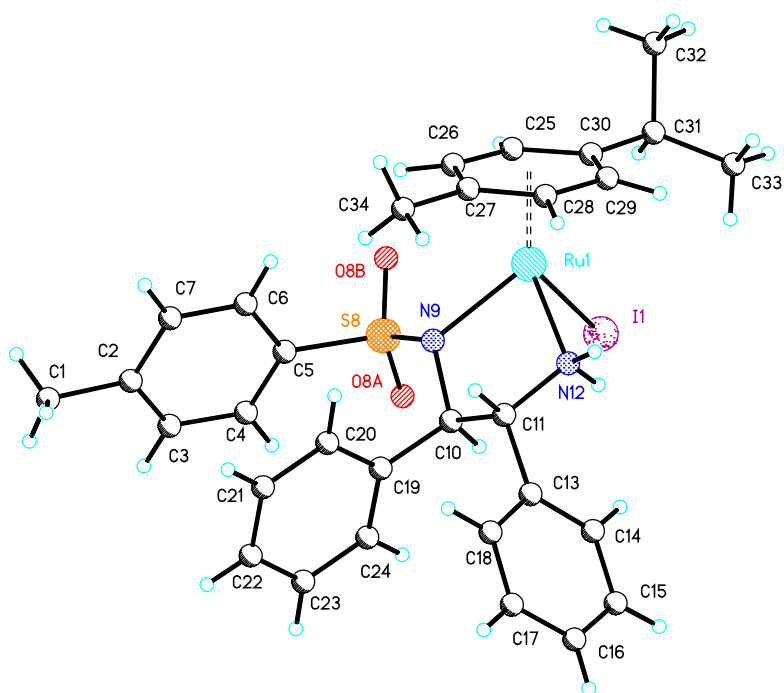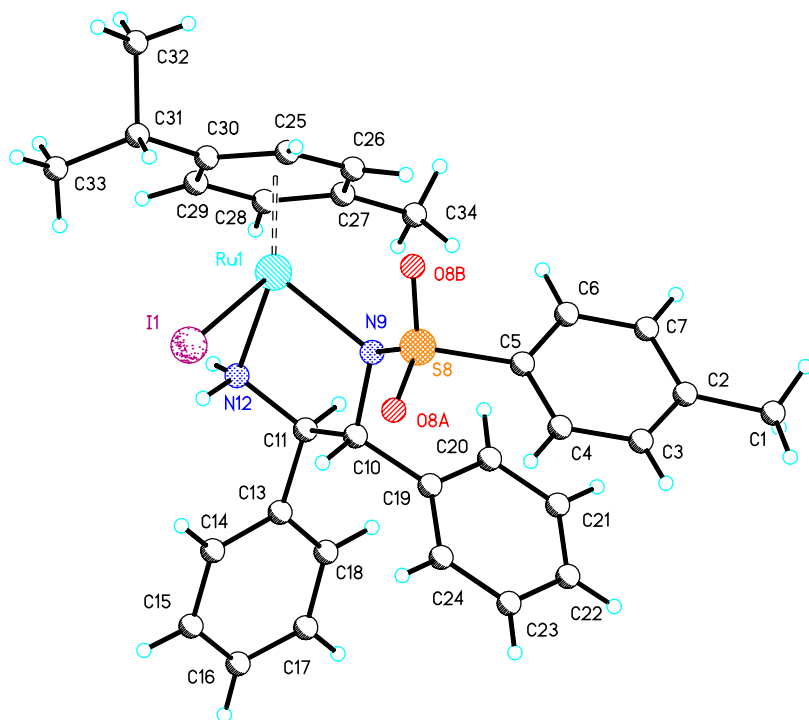
Two pictures of the solid state structure of *CCDC 1016063* with atom labelling (different views)

Experimental data for *CCDC 1016063*: The asymmetric unit contained the complex. There were 4 complexes in the unit cell. The hydrogens on N12 were located in a difference map and refined with DFIX restraint to give them equivalent N-H distances and given isotropic displacement parameter equal 1.5 times the equivalent isotropic displacement parameter of N12. There is an internal pi stacking interaction between the tosyl and one of the phenyl rings. This is characterised as the atoms used to define mean planes through the two pi systems, the angle between these mean planes and the closest atomic contact angle between C2 C3 C4 C5 C6 C7 to C19 C20 C21 C22 C23 C24 is 14.69 (0.26) degrees. Closest atomic contact C5 - C19 3.1243 (0.0059) Angstroms The Flack parameter refined to 0.04(2). The Hooft y parameter refined to 0.031(9) (Olex2). These numbers reflect the confidence in the assignment of the handedness of the crystal chosen and are good (a small number with an equivalent small esd).

Crystal Data: $C_{31}H_{35}IN_2O_2RuS$, M = 727.64, Orthorhombic, space group P2(1)2(1)2(1), a = 8.8762(6), b = 13.4321(7), c = 26.712(3) Å , alpha = 90 deg., beta = 90 deg., gamma = 90 deg., U = 3184.7(4) $Å^3$ (by least squares refinement on 9388 reflection positions), T =298(2)K, lambda = 0.71073 A, Z = 4, D(cal) = 1.518 Mg/m^3, F(000) = 1456. mu(MoK-alpha) = 1.555 mm^{-1}. Crystal character:brown block. Crystal dimensions 0.24 x 0.12 x 0.04 mm.

Structure Analysis and Refinement: Systematic absences indicated space group P2(1)2(1)2(1) and shown to be correct by successful refinement. The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached. The absolute structure of the individual crystal chosen was checked by refinement of a delta-f" multiplier. Absolute structure parameter x = 0.04(2). R1[for 6883 reflections with I>2sigma(I)] = 0.0541, wR2 = 0.0931. Data/restraints/parameters 9078/2/353. Largest difference Fourier peak and hole 0.928 and -0.664 $e.A^{-3}$. Refinement used SHELXL 97 (Sheldrick, 1997). Additional material available from the Cambridge Crystallographic Data Centre comprises H-

atom coordinates, thermal parameters and the remaining bond lengths and angles.

X-ray References. For relevant information for the SHELXTL suite of programmes used to solve, refine and produce the files for this structure, please refer to "A Short History of Shelx, G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122" Use Mercury (Free from CCDC at www.ccdc.cam.ac.uk/products/mercury) to view the structure.
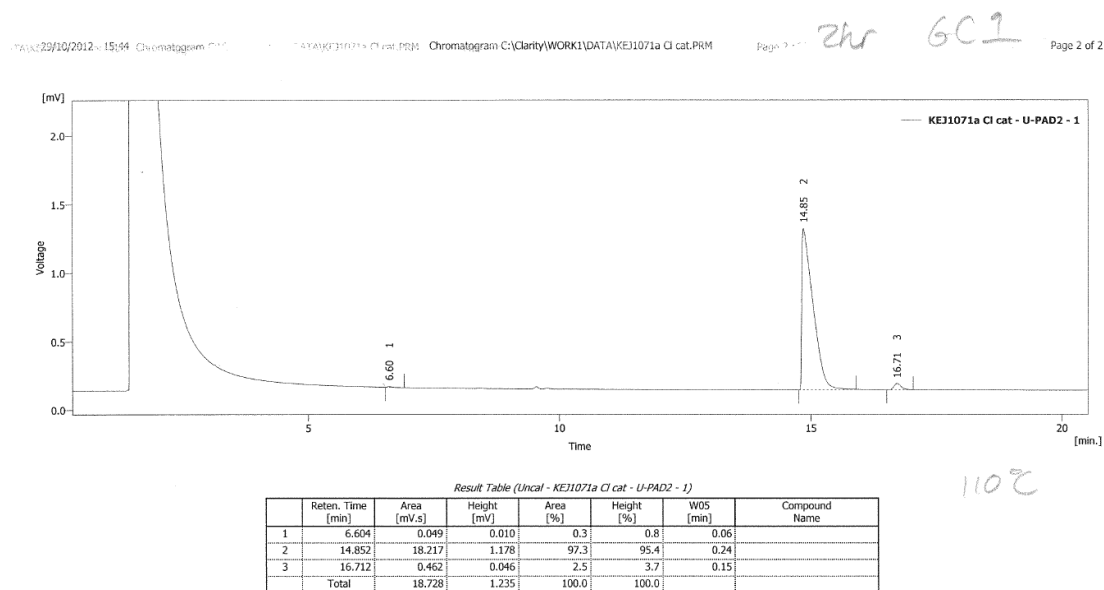
(R)-1-Phenylethanol.

OH
|
Ph   Me
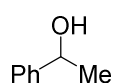
The conditions for the ee determination for this compound are well established using chiral Gas Chromatography, and a typical set of conditions are as follows: Chrompac cyclodextrin-β-236M-19 50m x 0.25 mm x 0.25 μm, T = 115°C, P = 15psi H_2, det = FID 220°C, inj = 220°C, ketone 9.2 min., *R* isomer 14.2 min., *S* isomer 15.6 min. Other data: $[\alpha]_D^{24}$ +64.5 (*c* 1.0 in $CHCl_3$) 96.7% ee (*R*)); δ_H (400 MHz, $CDCl_3$) 7.37-7.31 (4H, m, C*H*Ar), 7.28-7.24 (1H, m, C*H*Ar), 4.87 (1H, q *J* 6.5 Hz, C*H*), 2.00 (1H, br s, O*H*), 1.48 (3H, d *J* 6.5 Hz, C*H₃*). Taken from; Jolley, K. E.; Zanotti-Gerosa, A.; Hancock, F.; Dyke, A.; Grainger, D. M.; Medlock, J. A.; Nedden, H. G.; Le Paih, J. J. M.; Roseblade, S. J.; Seger, A.; Sivakumar, V.; Morris, D. J.; Prokes, I.; M. Wills, M. *Adv. Synth. Catal.* **2012**, *354*, 2545-2555.

In each analysis the retention times can vary slightly, as illustrated by the two examples below (run on the same column as the example but at 110 °C):

i) Table 2 entry 3, reduction of acetophenone using the tethered Cl catalyst (*R,R*)-**6**, which gives the *R*-configuration product:

110 ℃

Result Table (Uncal - KEJ1071a Cl cat - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.604	0.049	0.010	0.3	0.8	0.06	
2	14.852	18.217	1.178	97.3	95.4	0.24	
3	16.712	0.462	0.046	2.5	3.7	0.15	
	Total	18.728	1.235	100.0	100.0		

i) Table 2 entry 4, reduction of acetophenone using the tethered Cl catalyst (*S,S*)-**7**, which gives the *S*-configuration product:

Result Table (Uncal - C:\Clarity\WORK1\DATA\Katie\KEJ1071b iodo 3C teth cat 500 to 1 60degr - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.612	0.107	0.027	0.6	2.4	0.06	
2	15.180	0.445	0.056	2.3	4.8	0.13	
3	16.352	18.673	1.068	97.1	92.8	0.28	
	Total	19.225	1.151	100.0	100.0		