Supplementary Material for New Journal of Chemistry

SUPPLEMENTARY MATERIAL

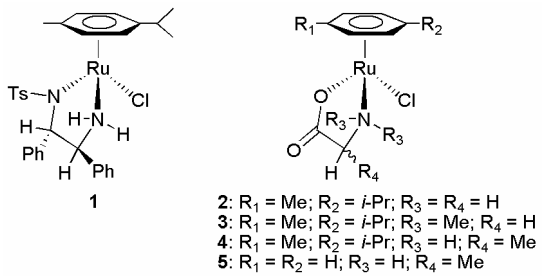
Aggregation in solution of neutral half-sandwich Ru(II) precatalysts for transfer hydrogenation

Daniele Zuccaccia,[a] Eric Clot*[b] and Alceo Macchioni*[a]

[a] *Dipartimento di Chimica, Università di Perugia, via Elce di Sotto, 8 - 06123 Perugia, Italy.*
E-mail: alceo@unipg.it

[b] *L.S.D.S.M.S. (UMR 5636), Case Courrier 14, Université de Montpellier 2, 34095 Montpellier Cedex 5 France.*
E-mail: clot@univ-montp2.fr

Catalysts **1**,[1] **2-5**[2] (Scheme 1)and *trans*-[Ru(COMe)(CO){(pz_2)BH_2}(PMe_3)$_2$] (**6**)[3] were synthesized by the reaction of [Ru_2(η^6-arene)$_2Cl_2$(μ-Cl)$_2$] with the appropriate N, X-ligand according to the literature. [Ru_2(η^6-arene)$_2Cl_2$(μ-Cl)$_2$] were prepared as described by Benneth *et al.*[4] Deuterated solvents were purchased from Sigma and used without further purification.



1

2: R_1 = Me; R_2 = *i*-Pr; R_3 = R_4 = H
3: R_1 = Me; R_2 = *i*-Pr; R_3 = Me; R_4 = H
4: R_1 = Me; R_2 = *i*-Pr; R_3 = H; R_4 = Me
5: R_1 = R_2 = H; R_3 = H; R_4 = Me

Scheme 1

PGSE Measurements

All the PGSE NMR measurements were performed by using the standard stimulated echo pulse sequence [5] on a Bruker AVANCE DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil, at 296 K without spinning. The shape of the gradients was rectangular, their duration (δ) was 4-5 ms, and their strength (G) was varied during the experiments. All the spectra were acquired using 32K points, a spectral width of 5000 (^{1}H), and processed with a line broadening of 1.0 Hz. After having checked

that the change of total relaxation time (from 5 to 15 s) does not affect the measurement results, standard experiments were carried out with a total recycle time of 5 s. The semi-logarithmic plots of $\ln(I/I_0)$ *vs* G^2 were fitted using a standard linear regression algorithm obtaining an *R* factor always better than 0.99. Different values of Δ, "nt" (number of transients) and number of different gradient strengths (G) were used for different samples. For example, for the measurements of solution of catalysts **1** in 2-propanol-d_8, the "nt" was 48 (^{1}H). The arene resonances (methyl and isopropyl for cymene) and methyl of Ts group for compound **1** were usually investigated.

The dependence of the resonance intensity (I) on a constant waiting time and on a varied gradient strength (G) is described by the equation 1:

$$\ln\frac{I}{I_0} = -(\gamma\delta)^2 D_t\left(\Delta - \frac{\delta}{3}\right)G^2 \qquad (1)$$

where I = intensity of the observed spin echo, I_0 = intensity of the spin echo without gradients, D = diffusion coefficient, Δ = delay between the midpoints of the gradients, δ = length of the gradient pulse, and γ = magnetogyric ratio. The diffusion coefficient D_t is directly proportional to the slope of the regression line (-m) divided by Δ - δ/3 and its value was estimated by measuring the -m/(Δ - δ/3) parameter for a sample of HDO (5%) in D_2O (known diffusion coefficient: $1.902\cdot10^{-9}$ m^2/s at 298 K)[6] under the same conditions as those for compounds.

According to the Stokes-Einstein equation 2, D_t is proportional to $1/r_H$ (where r_H represents the hydrodynamic radius of the diffusing particle).

$$D_t = \frac{kT}{c\pi\eta r_H} \qquad (2)$$

k is the Boltzmann constant, T is the absolute temperature, c is a numerical factor that depends on the size and shape of the solute and the hydrodynamic behavior of the solute-solvent system[7], and η is the viscosity of the pure solvent. By applying equations (2) to samples of catalyst containing TMSS as internal standard, the average hydrodynamic radii and c factors for the catalysts were estimated (Table 1).[8]

From the average hydrodynamic radii of the aggregates, assumed to be spherical, their volumes were obtained. The ratios of these volumes and the Van der Waals volumes of catalysts afforded the aggregation numbers N (Table 1). Van der Waals volumes of catalysts

were computed from the crystal structures using the software package WebLab ViewerLite 4.0.

The measurement uncertainty was estimated by determining the standard deviation of *m* by performing experiments with different Δ values. Standard propagation of errors analysis yielded a standard deviation of approximately 8-9 % in the volume.

Supplementary Material for New Journal of Chemistry

Table 1S Diffusion coefficients ($10^{10}D_t$ m^2s^{-1}), hydrodynamic radii (r_H. Å), c factors, hydrodynamic volumes ($Å^3$) and aggregation numbers (N) as a function of concentration (C, mM) in isopropanol-d_8

Entry	Comp.	D_t	r_H	c	V_H	N	C
1	**1**	1.6	5.8	5.2	833	1.8	0.05
2	**1**	1.6	5.8	5.2	842	1.8	0.2
3	**1**	1.6	6.2	5.2	988	2.1	1.0
4	**1**	1.5	6.3	5.3	1051	2.3	4.0
5	**1**	1.4	6.7	5.4	1264	2.8	12.0
6	**1**	1.1	7.6	5.5	1823	4.0	42.0[a]
7	**1**[b]	6.1	6.4	5.5	1087	2.4	2.0
8	**1**[b]	4.6	8.1	5.7	2242	4.9	12.0
9	**1**[c]	11.4	5.8	5.3	815	1.8	2.0
10	**1**[d]	6.3	5.8	5.5	834	1.8	2.0
11	**1**[e]	1.6	6.6	5.5	1204	2.6	2.0
12	**2**	2.0	5.1	4.9	572	2.6	0.5
13	**2**	1.9	5.3	5.0	623	2.8	1.5
14	**2**	1.9	5.3	5.0	630	2.8	4.0[a]
15	**3**	2.4	4.7	4.7	443	1.7	0.2
16	**3**	2.1	4.9	4.8	492	1.9	4.0
17	**3**	2.1	4.9	4.8	501	2.0	7.0[a]
18	**3**[e]	2.5	4.6	5.0	415	1.7	2.6
19	**4**	1.9	5.3	5.0	613	2.6	9.0
20	**4**	1.6	5.9	5.2	847	3.6	50.0
21	**5**	2.1	4.9	4.8	480	2.7	0.5[a]
22	**5**[e]	2.2	4.9	5.1	498	2.7	60.0
23	**6**	2.5	4.6	4.7	410	1.1	2.0
24	**6**[b]	9.2	4.7	5.1	470	1.2	2.0
25	**6**[b]	8.5	4.7	5.1	448	1.2	16.0
26	**6**[d]	8.6	4.7	5.0	451	1.2	2.0
27	**6**[f]	8.2	4.4	4.9	368	1.0	2.0

[a] Saturated solution. [b] In $CDCl_3$. [c] In acetone-d_6. [d] In methanol-d_4. [e] In DMSO-d_6. [f] In benzene-d_6.

Table 2S Ln(I/I_0) vs. G^2 for solution of **1** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 1)

G^2	**0.05 10^{-3} M. Δ = 90 ms** catalyst	TMSS	2-propanol
1.00E-04	0	0	0
9.00E-02	-	-1.5563	-0.94655
0.49	-2.89137	-7.55481	-
0.36	-1.86033	-5.62525	-
0.25	-1.33026	-3.91975	-
0.16	-0.74297	-2.50939	-1.42582
0.0064	-	-0.10528	-

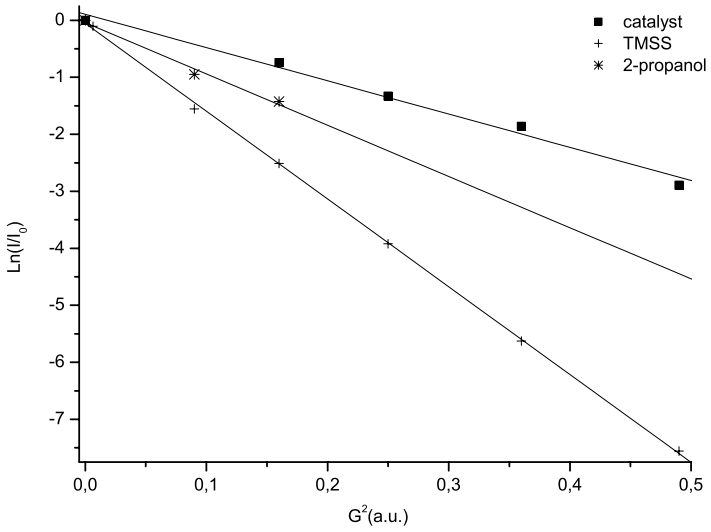


Table 3S Ln(I/I_0) vs. G^2 for solution of **1** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 2).

	0.2 10^{-3} M. Δ = 90 ms		
G^2	**catalyst**	**TMSS**	**2-propanol**
1.00E-04	0	0	0
4.00E-04	-0.01229	-6.08E-05	-0.01471
0.0016	0.01043	-0.01725	-0.01622
0.0036	-0.00787	-0.04621	-0.03414
0.0064	-0.11504	-0.09501	-0.06277
0.01	-0.15879	-0.14922	-0.08562
0.0225	-0.26156	-0.35351	-0.21291
0.04	-0.35896	-0.62781	-0.38065
0.0625	-0.54226	-0.99347	-0.58992
0.09	-0.73631	-1.42655	-0.85006
0.1225	-0.89355	-1.94254	-1.14284
0.16	-1.10894	-2.534	-1.49377
0.25	-1.61733	-3.97364	-2.38153
0.36	-2.26242	-5.66799	-3.39704
0.49	-2.90008	-7.58887	-4.64136
0.64	-3.79639	-	-6.05554
0.81	-4.93338	-	-

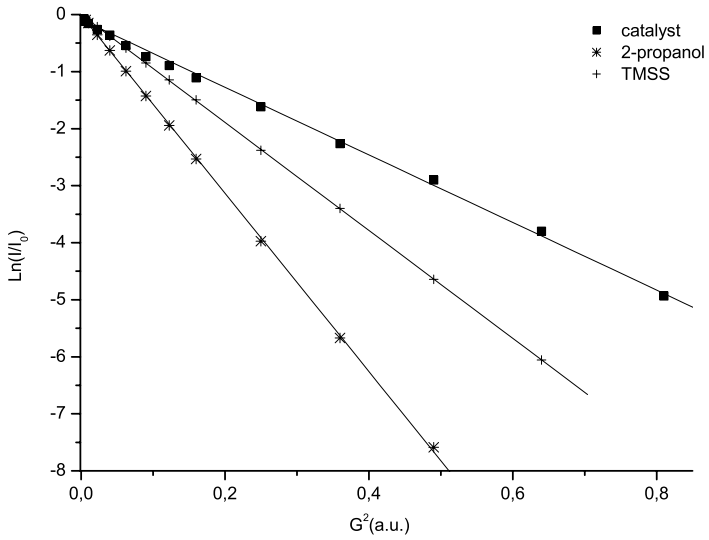


Table 4S Ln(I/I_0) vs. G^2 for solution of **1** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 3)

G^2	**1 10^{-3} M. Δ = 90 ms** catalyst	TMSS	2-propanol
1.00E-04	0	0	0
4.00E-04	-0.00484	-7.84E-03	-3.28E-05
0.0016	-9.03E-04	-0.0179	0.00859
0.0036	-0.01874	-0.05013	-0.02399
0.0064	-0.03587	-0.10063	-0.04405
0.01	-0.05994	-0.15706	-0.07661
0.0225	-0.13052	-0.35247	-0.20759
0.04	-0.22317	-0.62075	-0.39194
0.36	-1.90911	-5.58584	-3.33753
0.0625	-0.33356	-0.98187	-0.56539
0.09	-0.48626	-1.41017	-0.83493
0.16	-0.89468	-2.50991	-1.48727
0.25	-1.37198	-3.89411	-2.34043
0.49	-2.63794	-	-4.57413
0.64	-3.54932	-	-
0.81	-4.50717	-	-

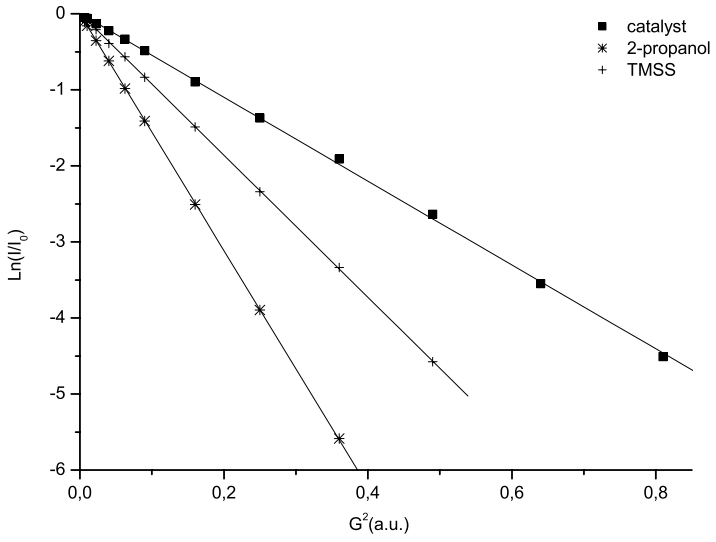


Table 5S $Ln(I/I_0)$ vs. G^2 for solution of **1** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 4)

	4 10^{-3} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**2-propanol**	**TMSS**
1.00E-04	0	0	0	0
4.00E-04	5.12E-04	5.17E-03	1.09E-04	0.00934
0.0016	-9.98E-03	-0.00233	-0.0205	-0.01497
0.0064	-0.04077	-0.03645	-0.09804	-0.09289
0.0144	-0.08659	-0.08157	-0.22244	-0.17538
0.04	-0.22953	-0.22441	-0.62693	-0.42454
0.09	-0.48937	-0.47832	-1.40146	-0.88196
0.16	-0.83002	-0.81738	-2.47887	-1.49329
0.25	-1.30522	-1.28295	-3.8666	-2.30905
0.36	-1.88415	-1.86895	-5.53617	-3.36802
0.49	-2.61075	-2.5515	-	-4.58015
0.64	-3.43188	-3.37886	-	-5.99427

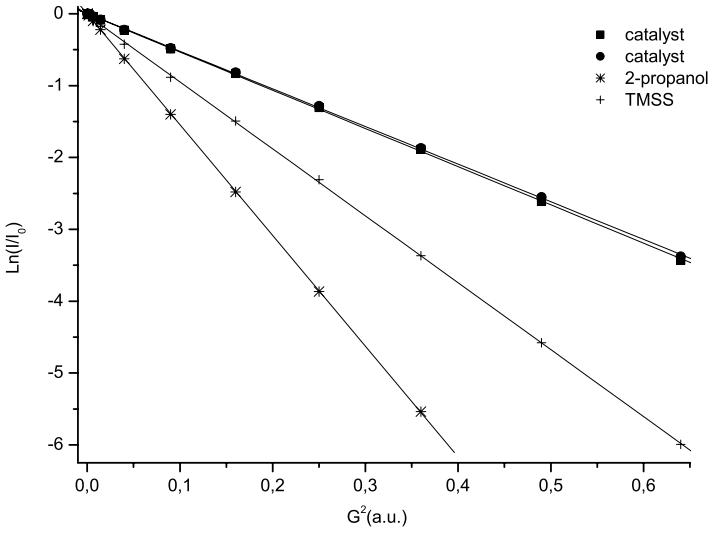


Table 6S Ln(I/I_0) vs. G^2 for solution of **1** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 5)

	1.2 10^{-2} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**2-propanol**	**TMSS**
1.00E-04	0	0	0	0
4.00E-04	3.13E-03	1.05E-02	1.34E-02	0.00142
0.0016	1.26E-02	0.02392	0.00763	0.00429
0.0064	-0.03169	-0.0195	-0.05613	-0.06538
0.0144	-0.06016	-0.04586	-0.17767	-0.11294
0.0256	-0.082	-0.06451	-0.34046	-0.16375
0.04	-0.13206	-0.12052	-0.56578	-0.26776
0.0625	-0.26028	-0.24093	-0.90442	-0.49002
0.09	-0.38837	-0.3653	-1.32313	-0.73261
0.16	-0.74943	-0.7225	-2.37844	-1.3934
0.25	-1.15934	-1.13022	-3.71964	-2.17318
0.36	-1.65795	-1.63519	-5.24904	-3.11094
0.49	-2.29983	-2.24742	-	-4.26381
0.64	-3.01421	-2.97573	-	-5.58289
0.81	-3.86922	-3.80605	-	-

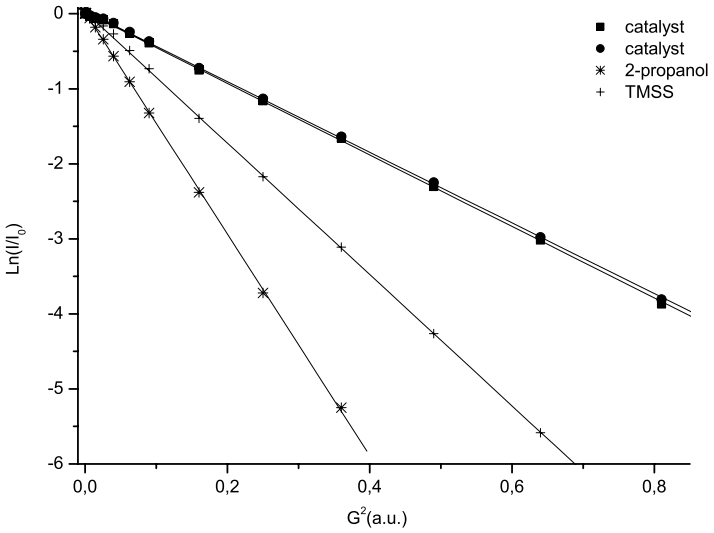


Table 7S Ln(I/I_0) vs. G^2 for solution of **1** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 6)

	4.2 10^{-2} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**2-propanol**	**TMSS**
1.00E-04	0	0	0	0
4.00E-04	7.72E-03	1.41E-02	-5.78E-03	0.03556
0.0016	1.34E-02	0.02438	-0.01365	0.02985
0.0144	-0.03249	-0.02023	-0.19795	-0.07138
0.04	-0.14044	-0.12186	-0.57282	-0.28323
0.09	-0.3411	-0.32817	-1.32018	-0.69037
0.16	-0.60734	-0.59012	-2.33458	-1.29722
0.25	-0.97369	-0.9533	-3.63555	-2.05986
0.36	-1.4093	-1.39011	-5.17014	-2.97907
0.49	-1.93844	-1.90885	-	-4.07833
0.64	-2.53055	-2.50646	-	-5.52773
0.9025	-3.55993	-3.5717	-	-

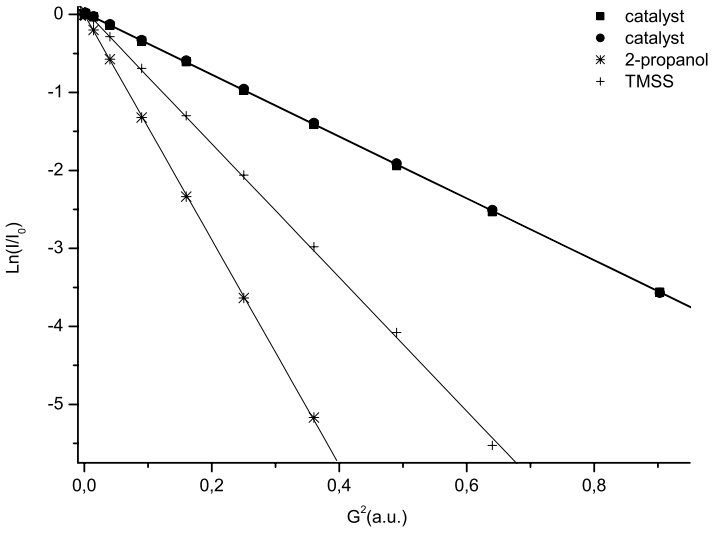


Table 8S Ln(I/I_0) vs. G^2 for solution of **1** in chloroform-d at 296 K using TMSS as internal standard (entry 7)

	2.0 10^{-3} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**TMSS**	**chloroform**
0,0001	0	0	0	0
0,0004	0,00306	0,02218	0,05798	0,04497
0,0016	-0,01405	0,00824	0,04095	-0,00133
0,0036	-0,06107	-0,02801	-0,01258	-0,14367
0,0064	-0,12869	-0,10137	-0,15732	-0,41475
0,0144	-0,30889	-0,27859	-0,47232	-1,06451
0,0256	-0,53672	-0,49337	-0,83387	-1,88316
0,04	-0,84552	-0,79244	-1,32201	-2,95868
0,0576	-1,20316	-1,15385	-1,94731	-4,23713
0,0784	-1,65603	-1,59942	-2,7244	-
0,1024	-2,18621	-2,11565	-3,53579	-
0,16	-3,311	-3,32981	-	-

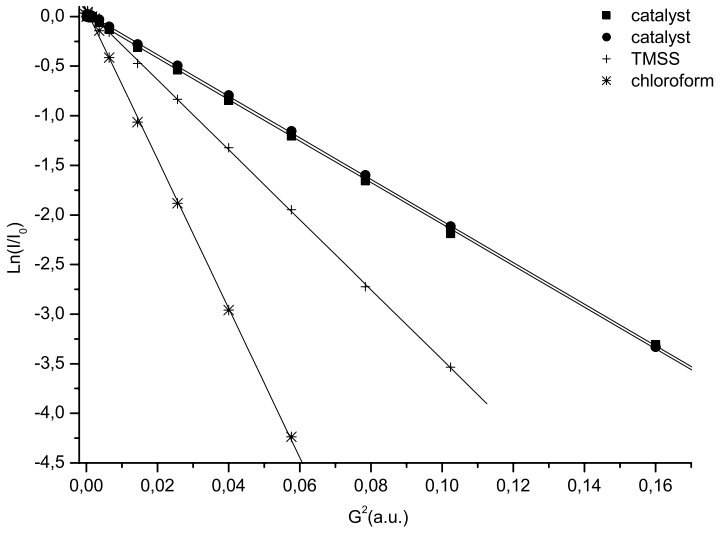


Table 9S Ln(I/I_0) vs. G^2 for solution of **1** in chloroform-d at 296 K using TMSS as internal standard (entry 8)

	1.2 10^{-2} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**TMSS**	**chloroform**
1.00E-04	0	0	0	0
4.00E-04	-0.02124	-0.00622	0.00247	-0.01571
0.0016	-0.12196	-0.02093	-0.02221	-0.05842
0.0036	-0.26987	-0.05014	-0.04499	-0.13132
0.0064	-0.48903	-0.09015	-0.09193	-0.23027
0.01	-0.77268	-0.14712	-0.14793	-0.35845
0.0144	-1.09897	-0.21365	-0.20944	-0.52301
0.0256	-1.94019	-0.39586	-0.38606	-0.93076
0.04	-2.99177	-0.6249	-0.61829	-1.45762
0.0576	-4.1224	-0.8971	-0.8898	-2.09028
0.09	-	-1.40995	-1.39284	-3.23912
0.16	-	-2.513	-2.48622	-5.67286
0.25	-	-4.02691	-3.9586	-

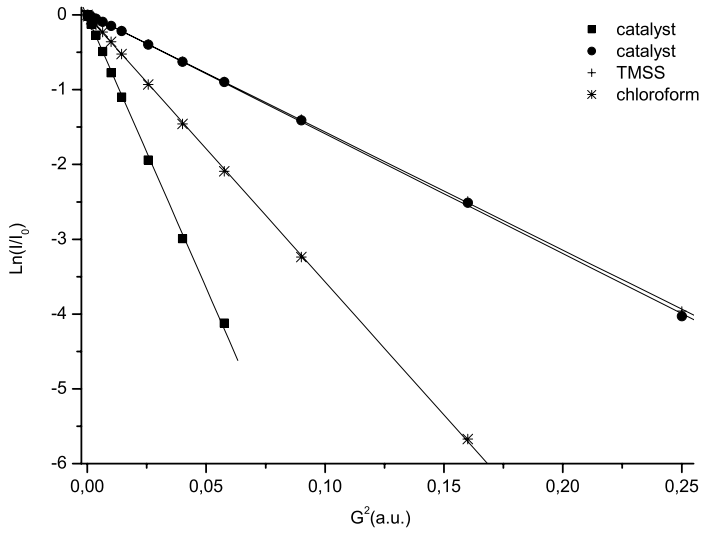


Table 10S Ln(I/I_0) vs. G^2 for solution of **1** in acetone-d_6 at 296 K using TMSS as internal standard (entry 9)

	2 10^{-3} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**acetone**	**TMSS**
1.00E-04	0	0	0	0
4.00E-04	1.15E-01	5.32E-02	-2.99E-02	0.10968
0.0016	3.65E-02	0.04287	-0.14919	0.12967
0.0036	-0.058	-0.0448	-0.4347	-0.02354
0.0064	-0.15953	-0.15493	-0.82201	-0.16727
0.0144	-0.45575	-0.45417	-1.92052	-0.64068
0.0256	-0.90498	-0.90128	-3.46093	-1.32701
0.04	-1.48751	-1.47456	-5.39326	-2.20225
0.0576	-2.17205	-2.18044	-	-3.28098
0.0784	-3.07313	-3.02152	-	-4.53595
0.1024	-3.98588	-3.94766	-	-

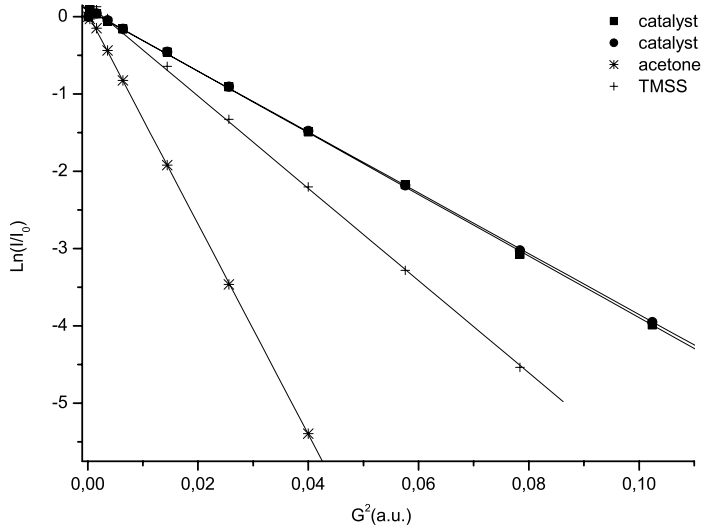


Table 11S Ln(I/I_0) vs. G^2 for solution of **1** in methanol-d_4 at 296 K using TMSS as internal standard (entry 10)

		2 10^{-3} M. Δ = 90 ms		
G^2	**catalyst**	**catalyst**	**TMSS**	**methanol**
1.00E-04	0	0	0	0
4.00E-04	-9.14E-03	-3.66E-02	-7.81E-02	-0.04423
0.0016	-1.82E-02	-0.0052	-0.01807	-0.08428
0.0036	-0.05859	-0.05837	-0.10735	-0.22752
0.0064	-0.10312	-0.08298	-0.14042	-0.38961
0.01	-0.17865	-0.16171	-0.27499	-0.64738
0.0144	-0.29297	-0.28339	-0.45861	-0.97484
0.0196	-0.41797	-0.40797	-0.65112	-1.35386
0.0256	-0.53906	-0.52902	-0.83677	-1.75785
0.04	-0.84791	-0.81788	-1.29297	-2.74322
0.0576	-1.2216	-1.19174	-1.887	-3.94996
0.0784	-1.69967	-1.6723	-2.60275	-5.39856
0.1024	-2.22433	-2.18915	-3.44864	-
0.16	-3.44615	-3.44823	-5.34343	-

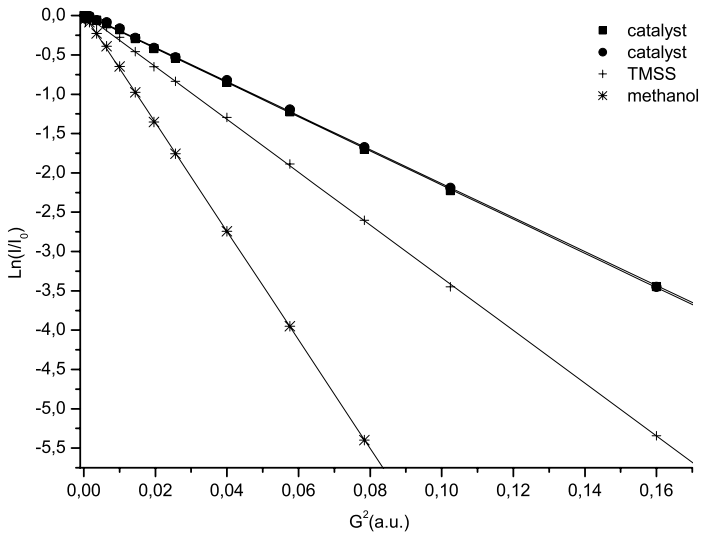


Table 12S Ln(I/I_0) vs. G^2 for solution of **1** in dimethylsulfoxide-d_6 at 296 K using TMSS as internal standard (entry 11)

	2 10^{-3} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**TMSS**	**DMSO**
1.00E-04	0	0	0	0
4.00E-04	3.10E-02	3.32E-02	2.75E-02	0.01734
0.0016	6.34E-02	0.06529	0.07482	0.01796
0.0064	0.05928	0.06691	0.07266	-0.06161
0.0144	0.03405	0.04253	0.03403	-0.2154
0.04	-0.1026	-0.09222	-0.19903	-0.74035
0.09	-0.39336	-0.38209	-0.67179	-1.7712
0.16	-0.80046	-0.78624	-1.35968	-3.21406
0.25	-1.32988	-1.3271	-2.24403	-5.04055
0.36	-1.97863	-1.97101	-3.31671	-6.93813
0.49	-2.74908	-2.71056	-4.57379	-
0.64	-3.63552	-3.63568	-	-

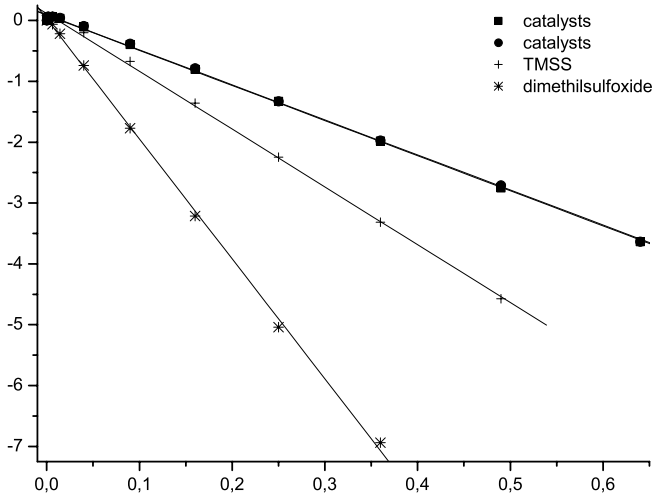


Table 13S Ln(I/I_0) vs. G^2 for solution of **2** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 12)

	0.5 10^{-3} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**TMSS**	**2-propanol**
1.00E-04	0	0	0	0
0.04	-2.95E-01	-0.32045	-0.40843	-0.66379
0.09	-0.65768	-0.65636	-0.91983	-1.50288
0.16	-1.1623	-1.172	-1.60662	-2.65472
0.25	-1.80352	-1.78212	-2.46123	-4.09429
0.49	-3.29725	-3.45511	-4.64449	-7.86385

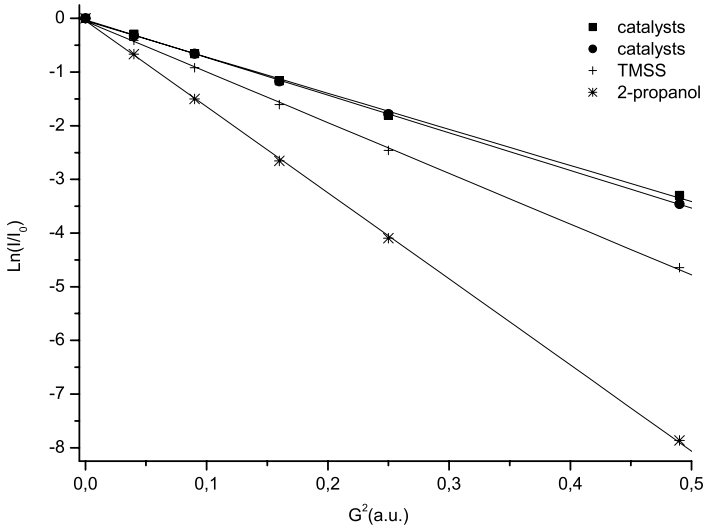


Table 14S Ln(I/I_0) vs. G^2 for solution of **2** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 13).

G^2	**$1.5\ 10^{-3}$ M. Δ = 90 ms** catalyst	2-propanol	TMSS
1.00E-04	0	0	0
4.00E-04	-9.21E-03	-0.0074	-0.01837
0.04	-0.24015	-0.62881	-0.32349
0.0064	0.00776	-0.09621	0.00719
0.0144	-0.08803	-0.22582	-0.11198
0.49	-3.21254	-7.5717	-4.55423
0.09	-0.57691	-1.41198	-0.80809
0.16	-0.99958	-2.49904	-1.40483
0.25	-1.63157	-3.88923	-2.27444
0.36	-2.38045	-5.62307	-3.34894
0.0016	-0.00211	-0.02512	-0.01273
0.64	-4.18106	-	-5.87202

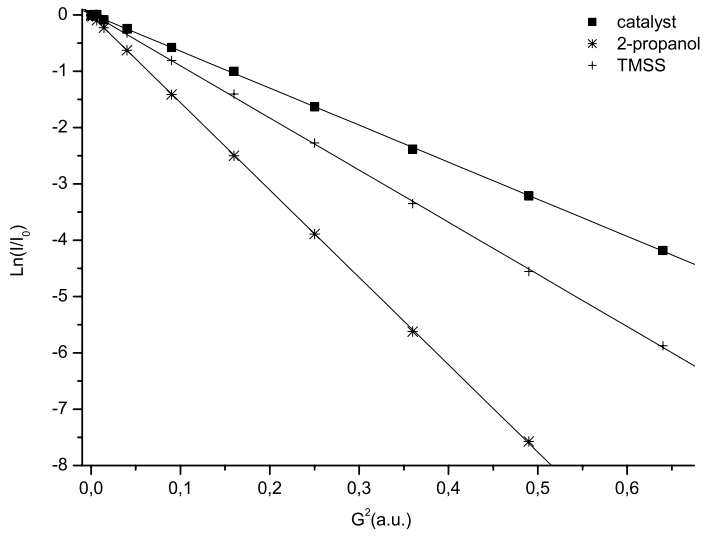


Table 15S Ln(I/I_0) vs. G^2 for solution of **2** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 14)

G^2	**4 10^{-3} M. Δ = 90 ms** catalyst	2-propanol	TMSS
1.00E-04	0	0	0
4.00E-04	8.26E-03	-0.01177	0.05636
0.0016	0.02344	-0.02665	0.06001
0.0064	-0.01146	-0.10489	0.01505
0.0144	-0.0722	-0.22848	-0.05467
0.04	-0.26049	-0.63157	-0.3396
0.09	-0.61388	-1.4168	-0.82006
0.16	-1.08435	-2.51535	-1.50613
0.25	-1.68967	-3.91953	-2.33362
0.36	-2.39849	-5.6327	-3.32341
0.49	-3.28996	-	-4.50527

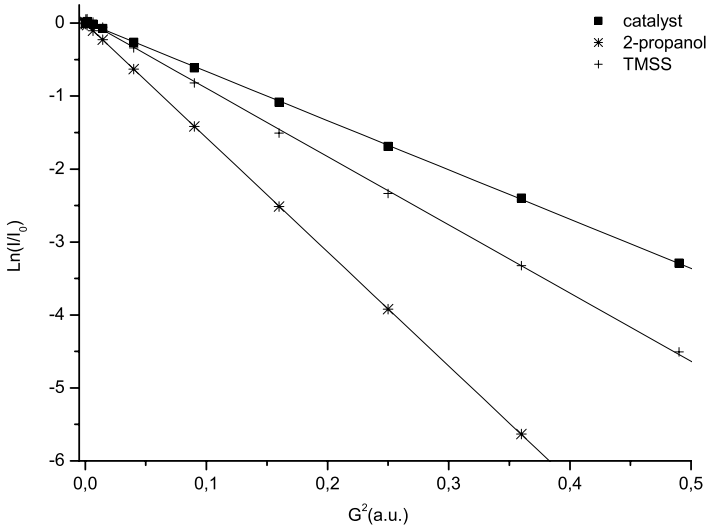


Table 16S Ln(I/I_0) vs. G^2 for solution of **3** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 15)

G^2	**$0.2\ 10^{-3}$ M. Δ = 90 ms** catalyst	2-propanol	TMSS
4.00E-04	3.63E-02	0.00425	0.03279
0.04	-0.28686	-0.64287	-0.36375
0.16	-1.20191	-2.56746	-1.54071
0.49	-3.96063	-7.65503	-4.73396
0.0064	-0.01464	-0.09966	-0.00267
0.0144	-0.09221	-0.22769	-0.09327
0.0256	-0.18094	-0.40628	-0.20906
0.09	-0.69712	-1.44566	-0.85309
0.2025	-1.62176	-3.2527	-1.97863
0.25	-1.98961	-4.01784	-2.47542
0.36	-2.87146	-5.76652	-3.57125

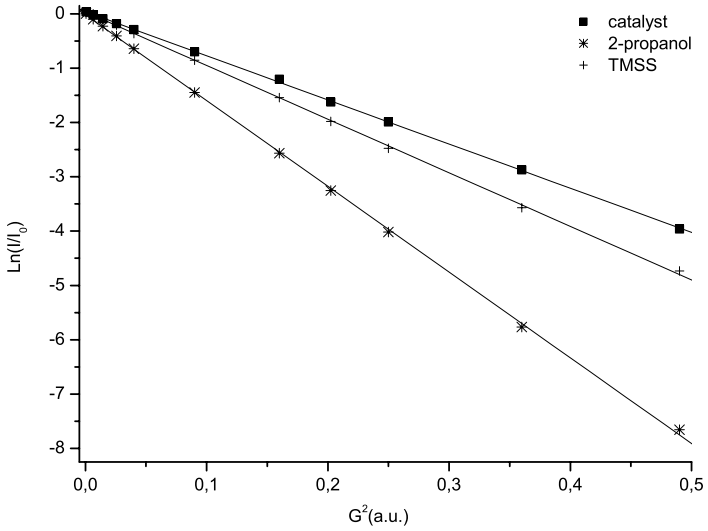


Table 17S Ln(I/I_0) vs. G^2 for solution of **3** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 16)

	4 10^{-3} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**2-propanol**	**TMSS**
1.00E-04	0	0	0	0
4.00E-04	0.0117	0.02	0.01484	0.05361
0.0016	0.02232	0.01776	9.93E-04	0.04796
0.0064	-0.02545	-0.02116	-0.07583	-0.01325
0.0144	-0.08027	-0.08195	-0.20417	-0.08378
0.04	-0.23044	-0.25381	-0.58847	-0.28967
0.09	-0.5858	-0.60402	-1.35571	-0.73496
0.16	-1.14392	-1.13103	-2.44361	-1.37239
0.25	-1.7684	-1.8024	-3.84162	-2.19771
0.36	-2.63611	-2.65684	-5.55453	-3.23372
0.49	-3.49875	-3.52919	-	-4.41864
0.64	-4.58626	-4.49371	-	-

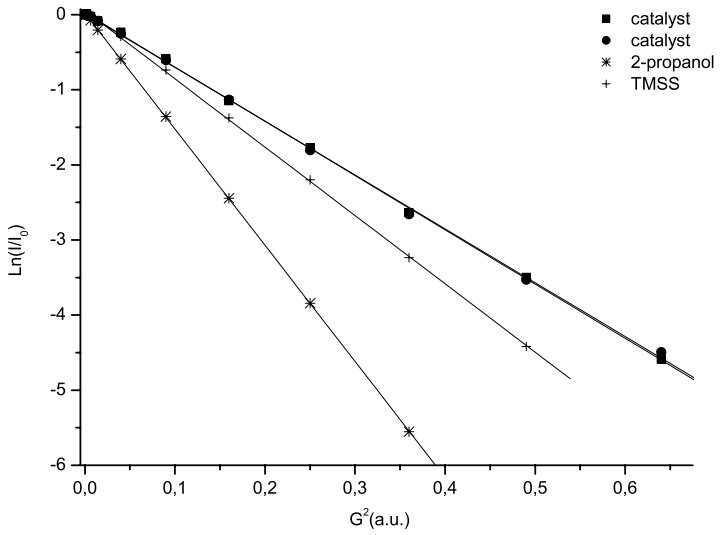


Table 18S Ln(I/I_0) vs. G^2 for solution of **3** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 17)

	7 10^{-3} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**2-propanol**	**TMSS**
1.00E-04	0	0	0	0
4.00E-04	0.00355	0.00242	-0.01045	-0.00354
0.0016	-0.00584	-0.04012	-3.19E-02	-0.04507
0.0144	-0.10859	-0.12315	-0.24353	-0.15427
0.04	-0.30432	-0.32607	-0.6529	-0.40707
0.09	-0.69354	-0.67196	-1.4398	-0.85048
0.16	-1.212	-1.20221	-2.5372	-1.5054
0.25	-1.85751	-1.87098	-3.92912	-2.3498
0.36	-2.69951	-2.67577	-	-3.37442
0.49	-3.67303	-3.63206	-	-4.57756
0.64	-	-	-	-

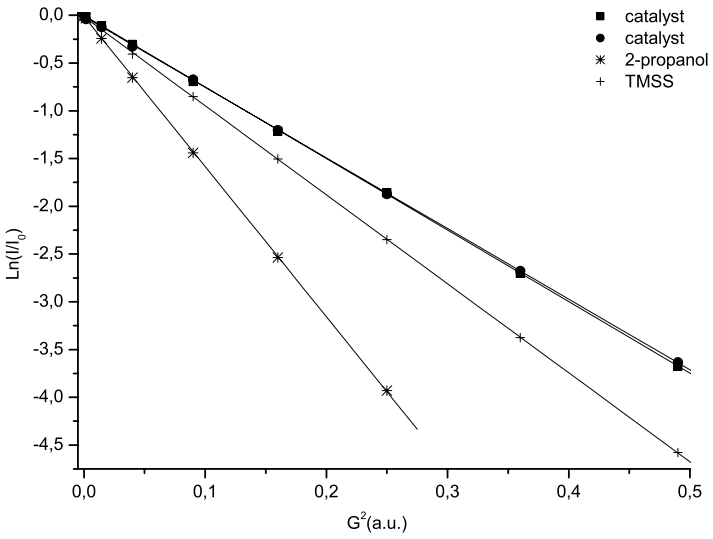


Table 19S Ln(I/I0) vs. G^2 for solution of **3** in dimethylsulfoxide-d_6 at 296 K using TMSS as internal standard (entry 18)

	2.6 10^{-3} M. Δ = 90 ms			
G^2	**catalyst**	**catalyst**	**TMSS**	**DMSO**
1.00E-04	0	0	0	0
4.00E-04	0.01197	0.02169	0.01309	0.005
0.0016	0.00284	0.03285	-0.00216	-0.01323
0.0064	-0.03984	-0.01163	-0.04267	-0.11094
0.0256	-0.18179	-0.16021	-0.22165	-0.51071
0.0576	-0.46177	-0.43303	-0.52342	-1.1824
0.1024	-0.83166	-0.80543	-0.98507	-2.11852
0.16	-1.32473	-1.27471	-1.52421	-3.30232
0.25	-2.04391	-2.02674	-2.34735	-5.16049

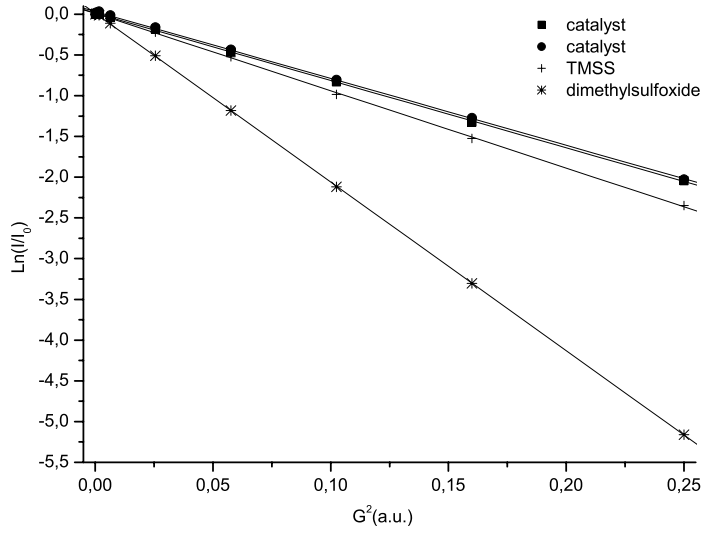


Table 20S Ln(I/I_0) vs. G^2 for solution of **4** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 19)

		$9\ 10^{-3}$ M. Δ = 90 ms		
G^2	catalyst	catalyst	TMSS	2-propanol
1.00E-04	0	0	0	0
4.00E-04	-0.02739	-0.02912	-0.00513	-0.00947
0.0016	-0.0303	-0.01752	-0.02005	-0.01695
0.0144	-0.08983	-0.08584	-0.11826	-0.21733
0.04	-0.27531	-0.25702	-0.35437	-0.61488
0.09	-0.60164	-0.55979	-0.81672	-1.39221
0.16	-1.048	-1.0095	-1.46155	-2.47399
0.25	-1.63339	-1.59438	-2.29688	-3.86593
0.36	-2.36364	-2.30559	-3.33015	-
0.49	-3.13711	-3.17842	-	-

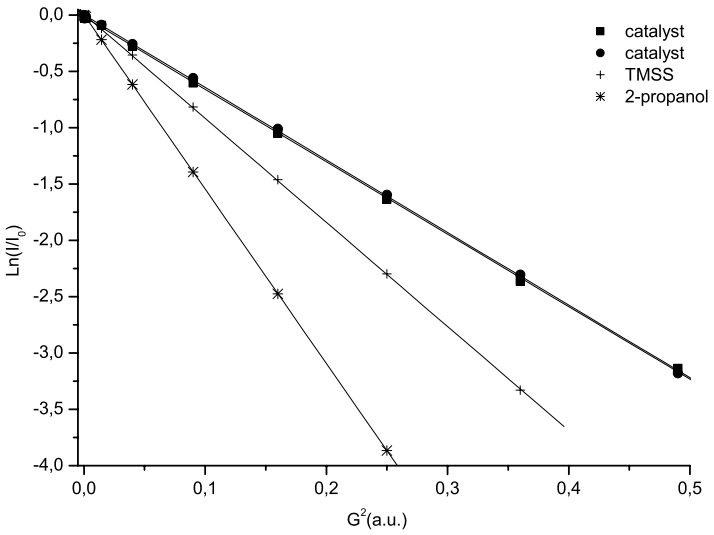


Table 21S Ln(I/I_0) vs. G^2 for solution of **4** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 20)

G^2	**5.0 10^{-2} M. Δ = 90 ms** catalyst	catalyst	TMSS	2-propanol
1.00E-04	0	0	0	0
4.00E-04	0.03077	0.03153	0.05432	0.01017
0.0016	0.06332	0.02578	0.07239	-0.00724
0.0144	-0.0115	-0.04322	-0.04815	-0.19104
0.04	-0.15896	-0.20246	-0.29321	-0.58747
0.09	-0.42511	-0.46889	-0.71866	-1.32158
0.16	-0.81606	-0.85039	-1.33693	-2.37598
0.25	-1.32974	-1.36302	-2.16976	-3.61863
0.36	-1.928	-1.9583	-3.12368	-
0.49	-2.63792	-2.6632	-	-

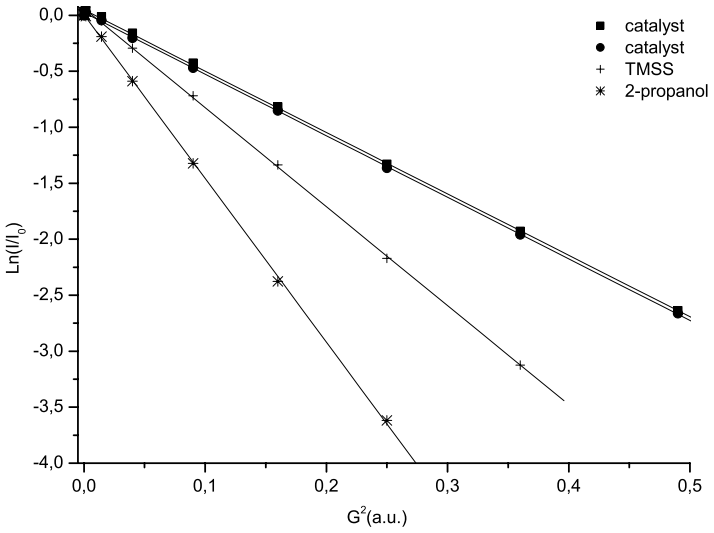


Table 22S Ln(I/I_0) vs. G^2 for solution of **5** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 21)

G^2	**0.5 10^{-3} M. Δ = 90 ms** catalyst	2-propanol	TMSS
1.00E-04	0	0	0
4.00E-04	-0.01328	4.25E-04	0.00195
0.0016	-0.03588	-0.01096	-0.00174
0.0144	-0.13687	-0.20493	-0.12053
0.04	-0.29662	-0.60209	-0.34971
0.09	-0.64848	-1.38342	-0.81798
0.16	-1.17806	-2.45591	-1.46401
0.25	-1.84147	-3.83025	-2.29938
0.36	-2.6753	-5.35123	-3.28736

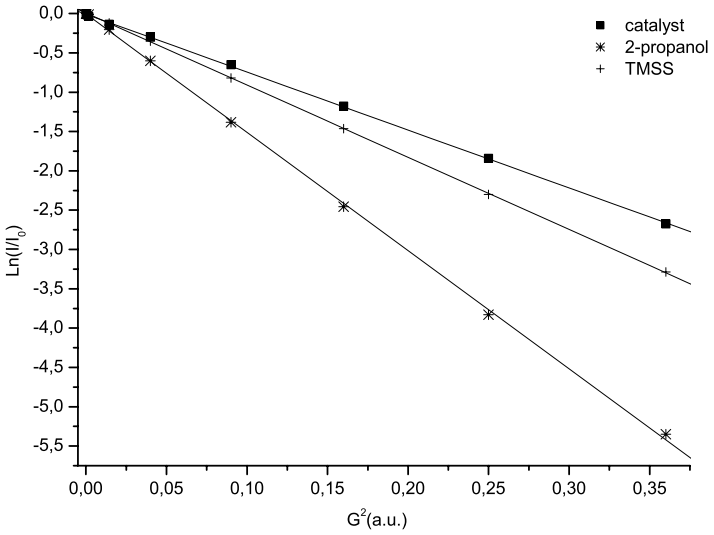


Table 23S $Ln(I/I_0)$ vs. G^2 for solution of **5** in dimethylsulfoxide-d_6 at 296 K using TMSS as internal standard (entry 22)

	6.0 10^{-2} M. Δ = 90 ms		
G^2	**catalyst**	**catalyst**	**DMSO**
1.00E-04	0	0	0
4.00E-04	0.0149	1.57E-02	-0.00585
0.0016	0.0386	0.0632	-0.09195
0.0144	-0.09136	-0.09978	-0.38019
0.04	-0.28866	-0.29336	-1.05069
0.0784	-0.5846	-0.57481	-2.03604
0.1296	-0.98645	-0.94799	-3.33862
0.25	-1.90846	-1.84193	-
0.36	-2.74425	-2.6556	-
0.49	-3.72207	-3.60368	-

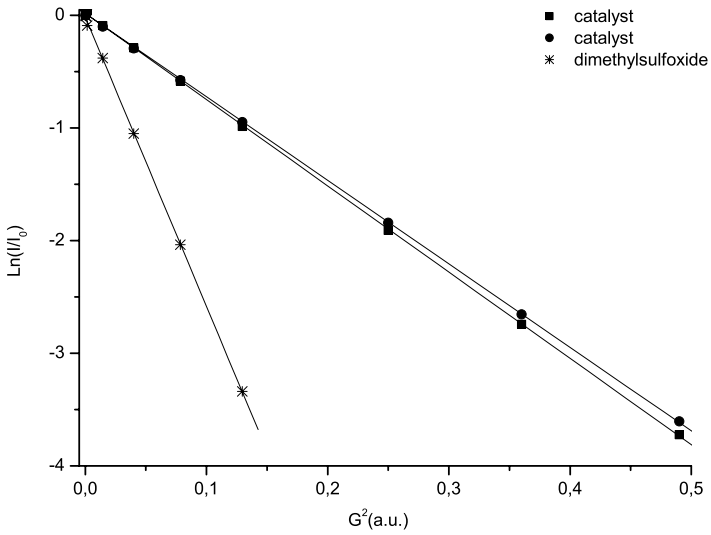


Table 24S Ln(I/I_0) vs. G^2 for solution of **6** in 2-propanol-d_8 at 296 K using TMSS as internal standard (entry 23)

	2 10^{-3} M. Δ = 90 ms		
G^2	**Ru-complex**	**Ru-complex**	**TMSS**
1.00E-04	0	0	0
4.00E-04	-0.02057	-0.03239	-0.04151
0.0016	-0.01819	-0.0364	-0.04554
0.0144	-0.12369	-0.14715	-0.17865
0.04	-0.34057	-0.36363	-0.46962
0.09	-0.77973	-0.78923	-0.94449
0.16	-1.39279	-1.39173	-1.61328
0.25	-2.17166	-2.14406	-2.4769
0.36	-3.11238	-3.08225	-3.57111

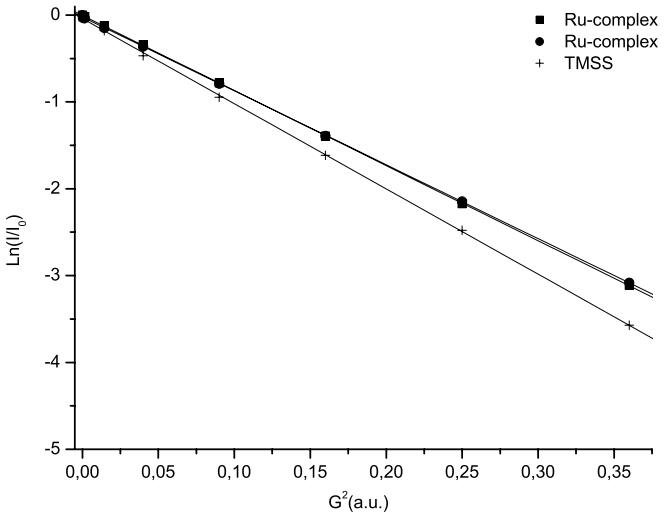


Table 25S Ln(I/I_0) vs. G^2 for solution of **6** in chloroform-d at 296 K using TMSS as internal standard (entry 24)

G^2	**2 10^{-3} M. Δ = 90 ms** Ru-complex	TMSS	chloroform
1.00E-04	0	0	0
4.00E-04	-0.01753	-0.03378	-0.03878
0.0016	-0.06305	-0.07464	-0.13081
0.0064	-0.2111	-0.24904	-0.5233
0.0144	-0.47876	-0.5795	-1.17798
0.0256	-0.83847	-0.95295	-2.06708
0.04	-1.28493	-1.50077	-3.16109
0.0576	-1.85822	-2.16118	-4.60439
0.0784	-2.47985	-2.90973	-
0.1024	-3.21744	-3.78372	-

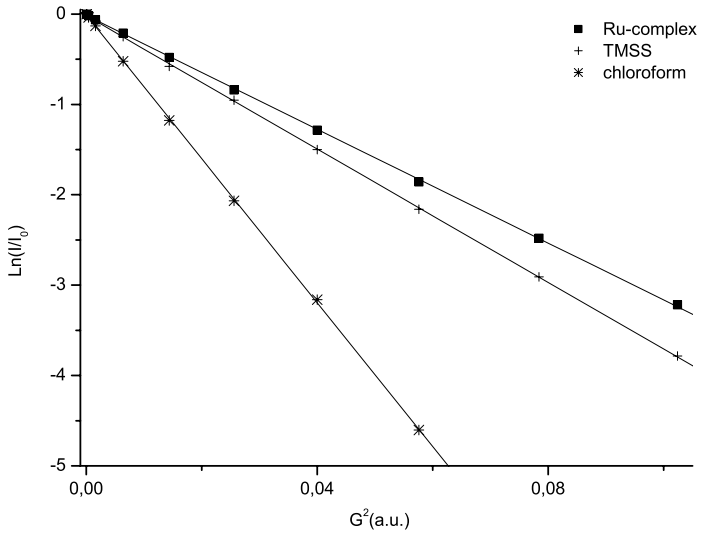


Table 26S Ln(I/I_0) vs. G^2 for solution of **6** in chloroform-d at 296 K using TMSS as internal standard (entry 25)

	1.6 10^{-2} M. Δ = 90 ms			
G^2	**Ru-complex**	**Ru-complex**	**TMSS**	**chloroform**
1.00E-04	0	0	0	0
4.00E-04	-0.01532	-0.00298	-0.0164	-0.01729
0.0016	-0.02145	-0.01774	-0.04443	-0.10407
0.0064	-0.16716	-0.20883	-0.22007	-0.50216
0.0144	-0.40696	-0.41237	-0.50278	-1.08323
0.0256	-0.74034	-0.74384	-0.88859	-1.93148
0.04	-1.17639	-1.17729	-1.40614	-3.01977
0.0576	-1.69966	-1.67812	-1.99621	-4.11522
0.0784	-2.30865	-2.28608	-2.70991	-
0.1024	-3.02291	-2.99872	-3.53476	-
0.16	-4.68471	-4.6671	-	-

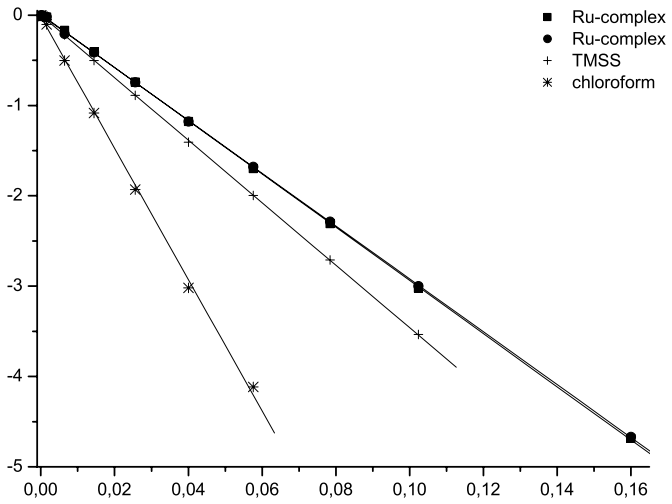


Table 27S Ln(I/I_0) vs. G^2 for solution of **6** in methanol-d_4 at 296 K using TMSS as internal standard (entry 26)

G^2	**2 10^{-3} M. Δ = 90 ms** Ru-complex	Ru-complex	TMSS
1.00E-04	0	0	0
4.00E-04	-0.00408	0.01387	-0.00751
0.0016	-0.04098	-0.03396	-0.03479
0.0036	-0.10661	-0.10621	-0.10818
0.0064	-0.17785	-0.18957	-0.20754
0.0144	-0.43163	-0.41323	-0.48804
0.0256	-0.76641	-0.75008	-0.88013
0.04	-1.21573	-1.19296	-1.3851
0.09	-2.65972	-2.67297	-3.15293
0.16	-4.70842	-4.71575	-

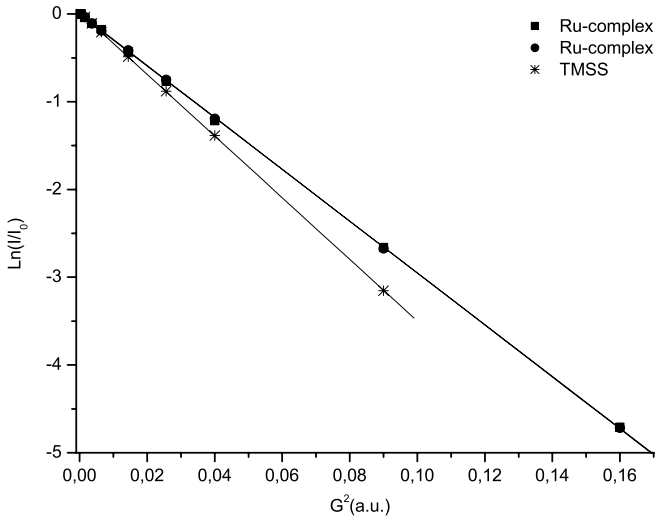
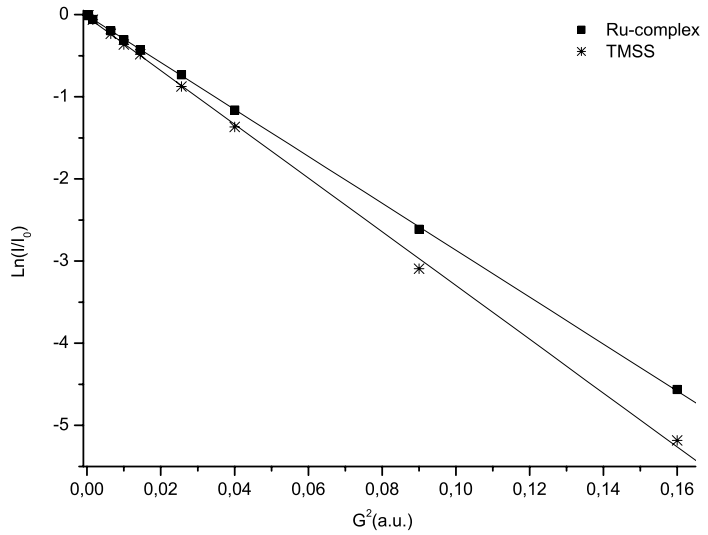


Table 28S Ln(I/I0) vs. G^2 for solution of **6** in benzene-d_6 at 296 K using TMSS as internal standard (entry 27)

G^2	**2 10^{-3} M. Δ = 90 ms** **Ru-complex**	**TMSS**
1.00E-04	0	0
4.00E-04	-0.01157	-0.0073
0.0016	-0.05848	-0.0619
0.0064	-0.19709	-0.23489
0.01	-0.30418	-0.36486
0.0144	-0.42857	-0.48246
0.0256	-0.73144	-0.87475
0.04	-1.16132	-1.36738
0.09	-2.61135	-3.09297
0.16	-4.56239	-5.18187



[1] K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 285.

[2] D. F. Dersnah, M. C. Baird, *J. Organomet. Chem.*, 1977, **127**, C55; R. Krämer, K. Polborn, H. Wanjek, I. Zahn, W. Beck, *Chem. Ber.*, 1990, **123**, 767; D. Carmona, A. Mendoza, F. J. Lahoz, L. A. Oro, M. P. Lamata, E. San José, *J. Organomet. Chem.*, 1990, **396**, C17.

[3] G. Bellachioma, G. Cardaci, V. Gramlich, A. Macchioni, L. M. Venanzi, *J. Chem. Soc., Dalton Trans.*, 1998, 947.

[4] M. A. Benneth, A. K. Smith, A., K. *J. Chem. Soc., Dalton Trans.*, 1974**,** 233.

[5] M. Valentini, H. Rüegger, P. S. Pregosin, *Helv. Chim. Acta* 2001, **84**, 2833 and references therein.

[6] H. J. W. Tyrrell, K. R. Harris, *Diffusion in Liquid*s; Butter-worth: London, 1984.

[7] A. Gierer, A.; K. Wirtz, *Z. Naturforsch. A*, 1953, **8**, 522. A. Spernol, K. Wirtz, *Z. Naturforsch. A* **1953**, *8*, 532. P. J. Espinosa, J. G. de la Torre, *J. Phys. Chem.*, 1987, **91**, 3612. H. –C. Chen, S. -H. Chen, *J. Phys. Chem.*, 1984, **88**, 5118.

[8] D. Zuccaccia, S. Sabatini, G. Bellachioma, G. Cardaci, E. Clot, A. Macchioni, *Inorg. Chem.*, 2003, **42**, 5465.