Supplementary Material (ESI) for Chemical Communications

A reductase-mimicking thiourea organocatalyst incorporating a covalently bound NADH analogue: efficient 1,2-diketone reduction with *in situ* prosthetic group generation and recycling

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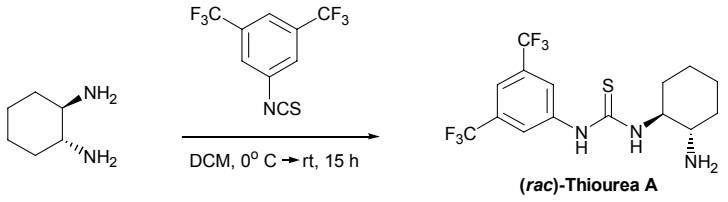
1.0 General

Proton Nuclear Magnetic Resonance spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ referenced relative to residual $CHCl_3$ (δ = 7.26 ppm). Chemical shifts are reported in ppm and coupling constants in Hertz. Carbon NMR spectra were recorded on the same instrument (100 MHz) with total proton decoupling. All melting points are uncorrected. Infrared spectra were obtained on a Perkin Elmer spectrophotometer. Flash chromatography was carried out using silica gel, particle size 0.04-0.063 mm. TLC analysis was performed on precoated $60F_{254}$ slides, and visualised by either UV irradiation or $KMnO_4$ staining. Dichloromethane and triethylamine were distilled from calcium hydride. Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. Unless otherwise specified, all reactions were carried out in oven-dried glassware with magnetic stirrers under an atmosphere of argon.

2.0 Synthesis of catalyst (*rac*)-10a

(*rac*)-Thiourea A

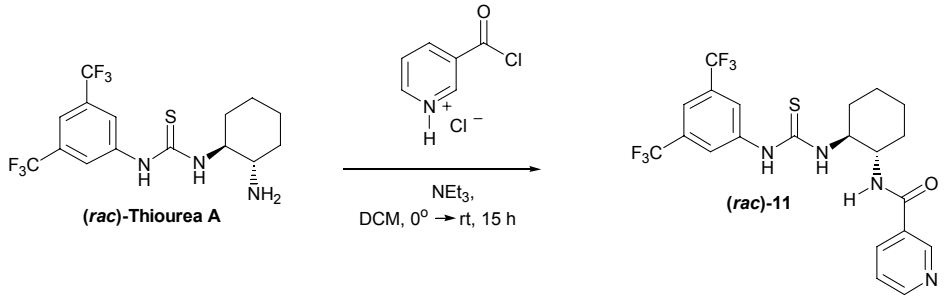


(*rac*)-Thiourea A

(*rac*)-Thiourea A. A 100 cm^3 oven dried round bottom flask charged with (*trans*)-1,2-diamino-cyclohexane (1.05 mL, 8.74 mmol) and dry DCM (15 cm^3) was placed under an atmosphere of N_2 and cooled to 0 ^oC. Subsequently, a solution of 3,5-*bis*(trifluoromethyl)-phenyl isothiocyanate (1.60 mL, 8.74 mmol) in dry DCM (15 cm^3) was added dropwise *via* syringe over 6 h. The resulting yellow solution was left to stir overnight. The reaction mixture was concentrated *in*

vacuo and the yellow residue purified by column chromatography (4:1 EtOAc-CH_2Cl_2) to afford **(*rac*)-Thiourea A** (1.662 g, 49%) as a yellow solid, mp 70-72 ^oC; δ_H (DMSO-d_6) 1.03-1.40 (4H, m), 1.54-1.73 (2H, m), 1.80-2.18 (2H, m), 2.52-2.64 (1H, m), 3.78-3.99 (1H, m), 7.69 (1H, s), 8.24 (2H, s) – (**Note**: thiourea and amino resonances not observed); δ_C (DMSO-d_6) 24.4, 24.5, 30.7, 34.7, 53.7, 60.1, 115.6, 121.6, 123.3 (2C, q, J 273.4), 130.0 (2C, q, J 34.2), 142.2, 180.2; ν_{max} (nujol)/cm^{-1} 1272, 1172, 1166, 1136, 964, 886, 721; *m/z* (ES) 386.1133 (M^+ $C_{15}H_{18}N_3F_6S$ requires 386.1126).

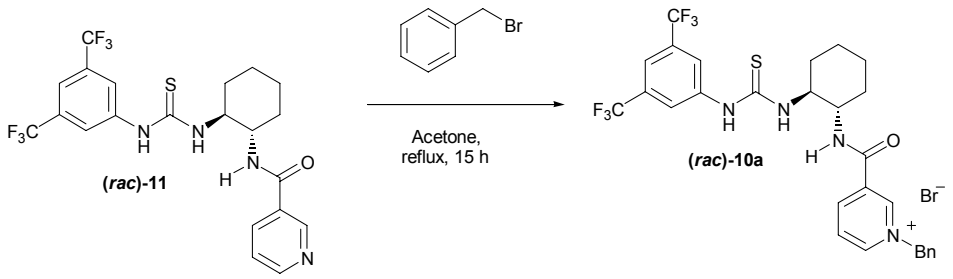
(*rac*)-11



(*rac*)-11. A 50 cm^3 oven dried round bottom flask charged with **(*rac*)-thiourea A** (1.662 g, 4.21 mmol), NEt_3 (1.90 mL, 13.5 mmol) and dry DCM (20 cm^3) was placed under an atmosphere of N_2 and cooled to 0 ^oC. Subsequently, nicotinoyl chloride hydrochloride (801 mg, 4.49 mmol) was added. The resulting yellow solution was left to stir overnight. CH_2Cl_2 (100 cm^3) was then added and the resulting solution washed with $NaHCO_3$ (2 x 40 cm^3), and brine (2 x 40 cm^3). Upon separation of the organic extracts precipitation of a **(*rac*)-11** as a white solid is often observed. In this case the suspension was filtered and the white precipitate was washed with DCM (*ca*. 20 cm^3) to give **(*rac*)-11** as a white solid (748 mg). The mother liquor was then concentrated *in vacuo* and the resulting yellow solid washed with DCM (*ca*. 20 cm^3) to afford a further crop of pure **(*rac*)-11** (494 mg) to give an overall combined yield of 60%, mp 204-206 ^oC; δ_H (DMSO-d_6) 1.21-1.59 (4H, m), 1.74 (2H, m), 1.92 (1H, m), 2.09-2.22 (1H, m), 3.92-4.05 (1H, m), 4.28-4.44 (1H, m), 7.47 (1H, dd, J 5.0 and 8.5), 7.69 (1H, s), 8.05-8.22 (4H, m), 8.59 (1H, d, J 8.5), 8.67 (1H, d, J 5.0), 8.99 (1H, s), 10.11 (1H, s); δ_C (DMSO-d_6) 24.4, 24.5, 31.2, 31.7, 52.5, 57.1, 116.2, 122.0, 121.9 (2C, q, J 273.1), 129.9, 130.0, 130.1 (2C, q, J 33.5), 135.0,

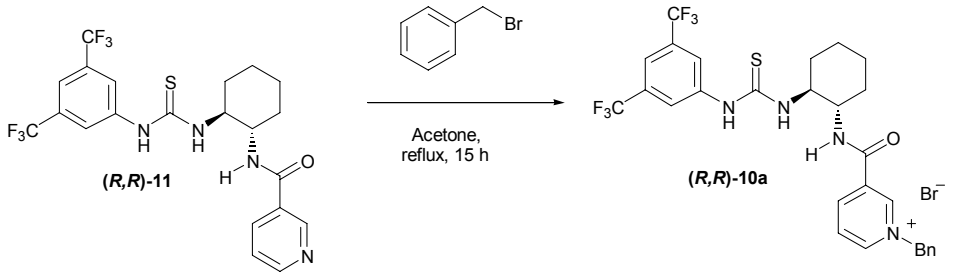
141.7, 148.6, 151.8, 164.8, 180.1; ν_{max} (nujol)/cm^{-1} 3311, 3069, 1618, 1552, 1332, 1278, 1175, 1121, 883, 712; *m/z* (ES) 491.1361 (M^+ $C_{21}H_{21}N_4OF_6S$ requires 491.1340).

(*rac*)-10a



(*rac*)-10a. A 25 cm^3 oven dried round bottom flask charged with **(*rac*)-11** (350 mg, 0.71 mmol), and acetone (8.0 cm^3) was placed under an atmosphere of N_2. Subsequently, benzyl bromide (90 μL, 0.71 mmol) was added *via* syringe. The flask was then fitted with a reflux condenser and the solution was heated under reflux at 65 ^{o}C for 15 h. The reaction mixture was then cooled to rt and the resulting suspension was filtered. The white precipitate was washed with acetone (*ca*. 5 cm^3) and hexane (*ca*. 10 cm^3) to afford **(*rac*)-10a** as a white solid (370 mg, 79%), mp 289-291 ^{o}C (dec.); δ_H (DMSO-d_6) 1.19-1.39 (2H, m), 1.42-1.64 (2H, m), 1.67-1.82 (2H, m), 1.92-2.16 (2H, m), 3.97-5.23 (2H, m), 5.99 (2H, s), 7.01-8.02 (10H, m), 8.28 (1H, s), 9.13 (1H, d, J 7.2), 9.38 (1H, d, J 6.3), 9.61 (1H, s), 9.91 (1H, s); δ_C (DMSO-d_6) 24.0, 24.2, 30.7, 31.0, 52.6, 61.6, 63.4, 122.9 (2C, q, J 272.7), 127.8, 128.2, 128.6, 129.0, 129.1, 129.2, 129.5, 130.8 (2C, q, J 35.2), 133.7, 133.9, 135.5, 144.8, 146.4, 160.9, 184.2; ν_{max} (nujol)/cm^{-1} 1660, 1609, 1558, 1278, 1178, 1139.

(*R,R*)-10a



(*R,R*)-10a. Prepared exactly as per **(*rac*)-10a** using (*R,R*)-*trans*-1,2-diamino-cyclohexane. 49% yield. $[\alpha]^{16}_{589} = +75$ ($c = 0.428$, $CHCl_3$).

3.0 Reduction protocol

3.1 General procedure

In a 10 cm^3 round bottom flask equipped with a stirring bar and a rubber septum, Na_2CO_3 (49 mg, 0.47 mmol) and **(*rac*)-10b** (39 mg, 0.07 mmol) were dissolved in degassed water (1.0 cm^3) under an atmosphere of N_2. Subsequently, a solution of the substrate (0.35 mmol) in Et_2O (3.0 cm^3) was added *via* syringe. $Na_2S_2O_4$ (64 mg, 0.38 mmol) was then added quickly and the rubber septum was substituted with a glass stopper. The resulting biphasic solution was vigorously stirred over 48 h in the dark. When ^1H NMR analysis indicated complete consumption of the starting material, the reaction mixture was extracted with EtOAc (3 x 5 cm^3). The organic extracts were combined, dried ($MgSO_4$) and concentrated *in vacuo* to afford crude product which was purified by column chromatography.

3.2 Determination of conversion by HPLC analysis.

In three cases involving reactions outlined in Table 1, conversion was also analysed by HPLC to confirm the accuracy of the NMR spectroscopic methodology. This was carried out as follows: A solution of benzil and benzoin (in a 1:1 ratio) in DCM (approximate concentration of 1 mg mL^{-1} benzoin) was analysed by HPLC (CSP-HPLC (Chiralpak AD-H 250 x 46 mm column), solvent: 90:10 Hexane:IPA, flow-rate: 1.0 mL/min, λ = 220 nm, retention times: 6.9 min (benzil), 20.9 and 27.9 min (benzoin – both enantiomers). This resulted in an integral ratio of 1.72: 1. The

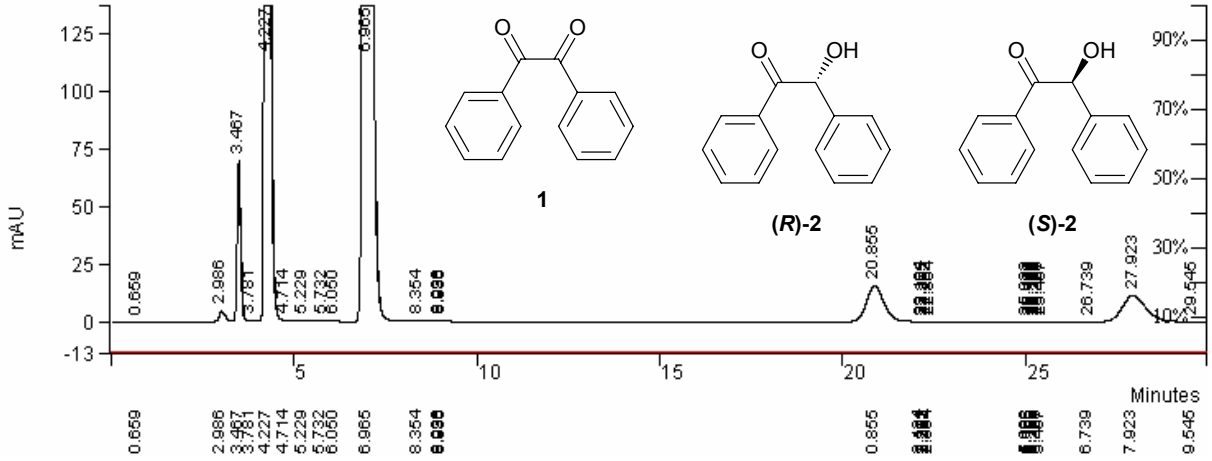
crude reaction mixtures from entries 1, 2 and 11 (Table 1) after filtration through a short pad of silica gel (to remove the catalyst) were then injected sequentially and the molar ratio's of the starting material and product were determined by dividing the integral associated with benzil by 1.72.

The level of conversion for these reactions as determined by HPLC analysis are as follows (conversion by ^{1}H NMR in parenthesis)

Entry 1 8% (6%)
Entry 2 14% (13%)
Entry 11 78% (71%)

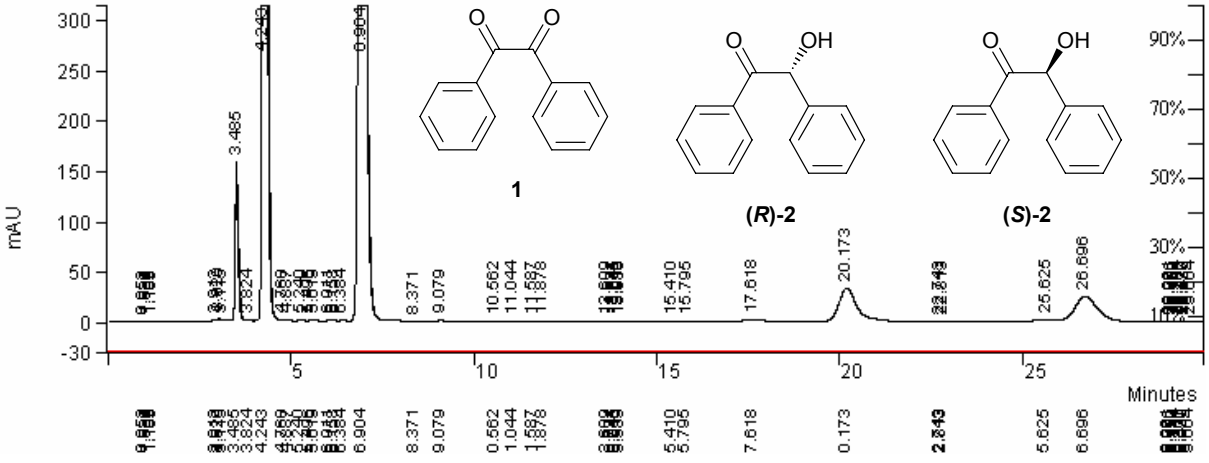
The chromatograms associated with these experiments are below.

Entry 1



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
6		0.0019	4.714	0.000	6334	0.00	TS	0.0		0
7		0.0074	5.229	0.000	24773	0.00	BP	7.1		0
8		0.0014	5.732	0.000	4516	0.00	VB	0.0		0
9		0.0028	6.050	0.000	9165	0.00	BB	8.3		0
10		58.2551	6.965	0.000	193936736	0.00	PP	10.1		0
11		0.0135	8.354	0.000	44834	0.00	TS	0.0		0
12		0.0015	8.936	0.000	4871	0.00	TF	0.0		0
13		0.0010	8.986	0.000	3181	0.00	TF	0.0		0
14		1.5487	20.855	0.000	5155626	0.00	VV	0.0		0
15		0.0005	22.124	0.000	1802	0.00	VV	0.0		0
16		0.0005	22.203	0.000	1672	0.00	VV	0.0		0
17		0.0005	22.282	0.000	1548	0.00	VV	0.0		0
18		0.0003	22.364	0.000	1133	0.00	VV	0.0		0
19		0.0005	25.033	0.000	1621	0.00	VV	0.0		0
20		0.0006	25.106	0.000	2143	0.00	VV	0.0		0
21		0.0006	25.182	0.000	1953	0.00	VV	0.0		0
22		0.0005	25.252	0.000	1744	0.00	VV	0.0		0
23		0.0005	25.329	0.000	1635	0.00	VV	0.0		0
24		0.0003	25.407	0.000	1160	0.00	VV	0.0		0
25		0.0003	26.739	0.000	1039	0.00	VV	0.0		0
26		1.5500	27.923	0.000	5160177	0.00	VV	0.0		0
27		0.0004	29.545	0.000	1325	0.00	VV	0.0		0
	Totals	**61.3888**		**0.000**	**204368976**					

Entry 2



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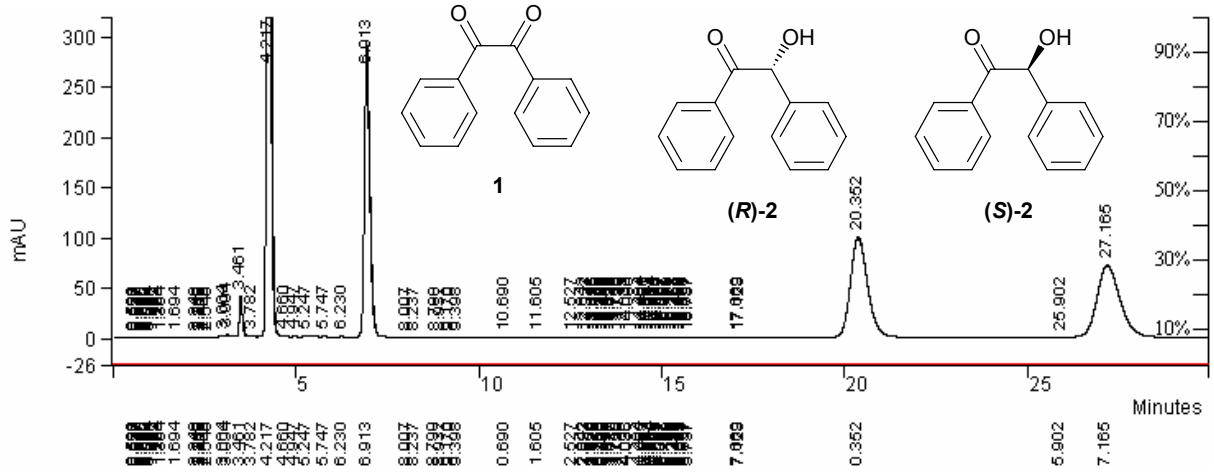
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
6		0.0282	3.020	0.000	125590	0.00	VV	0.0		0
7		0.0391	3.115	0.000	174076	0.00	VV	13.8		0
8		1.9716	3.485	0.000	8772988	0.00	VV	5.0		0
9		0.0093	3.824	0.000	41540	0.00	TS	0.0		0
10		41.1254	4.243	0.000	182990304	0.00	VV	5.8		0
11		0.0034	4.760	0.000	15035	0.00	TS	0.0		0
12		0.0021	4.887	0.000	9330	0.00	TS	0.0		0
13		0.0203	5.240	0.000	90428	0.00	TF	0.0		0
14		0.0036	5.496	0.000	15857	0.00	TF	0.0		0
15		0.0074	5.619	0.000	32898	0.00	TF	0.0		0
16		0.0045	6.011	0.000	19817	0.00	TF	0.0		0
17		0.0092	6.158	0.000	41151	0.00	TF	0.0		0
18		0.0121	6.384	0.000	53977	0.00	TF	0.0		0
19		51.4665	6.904	0.000	229003872	0.00	VB	9.1		0
20		0.0028	8.371	0.000	12303	0.00	TS	0.0		0
21		0.0135	9.079	0.000	60137	0.00	TS	0.0		0
22		0.0129	10.562	0.000	57445	0.00	TF	0.0		0
23		0.0048	11.044	0.000	21462	0.00	TF	0.0		0
24		0.0003	11.587	0.000	1221	0.00	TF	0.0		0
25		0.0098	11.878	0.000	43556	0.00	TF	0.0		0
26		0.0003	13.609	0.000	1286	0.00	PV	3.5		0
27		0.0007	13.771	0.000	2954	0.00	VV	0.0		0
28		0.0006	13.845	0.000	2449	0.00	VV	0.0		0
29		0.0006	13.916	0.000	2797	0.00	VV	0.0		0
30		0.0008	13.983	0.000	3585	0.00	VB	17.8		0
31		0.0002	15.410	0.000	1048	0.00	VV	4.3		0
32		0.0115	15.795	0.000	50955	0.00	VB	26.2		0
33		0.1373	17.618	0.000	611137	0.00	VB	27.9		0
34		2.5375	20.173	0.000	11290735	0.00	VB	29.2		0
35		0.0005	22.743	0.000	2296	0.00	VV	20.1		0
36		0.0008	22.813	0.000	3428	0.00	VP	23.1		0
37		0.1445	25.625	0.000	642813	0.00	VV	38.1		0
38		2.3911	26.696	0.000	10639535	0.00	VP	38.9		0
39		0.0006	29.001	0.000	2846	0.00	VV	0.0		0
40		0.0005	29.076	0.000	2032	0.00	VV	0.0		0
41		0.0006	29.150	0.000	2785	0.00	VV	0.0		0
42		0.0006	29.214	0.000	2511	0.00	VV	0.0		0
43		0.0006	29.303	0.000	2794	0.00	VV	0.0		0
44		0.0008	29.377	0.000	3629	0.00	VV	0.0		0
45		0.0010	29.430	0.000	4442	0.00	VV	0.0		0
46		0.0007	29.604	0.000	3084	0.00	VV	0.0		0
	Totals	**99.9786**		**0.000**	**444862016**					

Entry 3


mAU
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200
150
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15
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50%
30%
10%
1
(R)-2
(S)-2
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5.247
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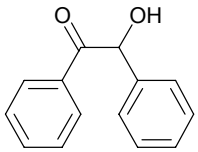
11.605

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
22		45.8265	4.217	0.000	84712664	0.00	VV	5.8		0
23		0.0111	4.660	0.000	20507	0.00	TS	0.0		0
24		0.0122	4.947	0.000	22569	0.00	TS	0.0		0
25		0.1458	5.247	0.000	269582	0.00	TF	0.0		0
26		0.0261	5.747	0.000	48323	0.00	TF	0.0		0
27		0.0169	6.230	0.000	31163	0.00	TF	0.0		0
28		16.9328	6.913	0.000	31301236	0.00	VV	9.2		0
29		0.0008	8.007	0.000	1489	0.00	TF	0.0		0
30		0.0031	8.237	0.000	5687	0.00	TF	0.0		0
31		0.0060	8.790	0.000	11105	0.00	TF	0.0		0
32		0.0009	8.932	0.000	1724	0.00	TF	0.0		0
33		0.0101	9.170	0.000	18579	0.00	TF	0.0		0
34		0.0007	9.398	0.000	1208	0.00	TF	0.0		0
35		0.0278	10.690	0.000	51351	0.00	TF	0.0		0
36		0.0190	11.605	0.000	35125	0.00	TF	0.0		0
37		0.0251	12.527	0.000	46331	0.00	TF	0.0		0
38		0.0007	12.842	0.000	1327	0.00	TF	0.0		0
39		0.0006	12.923	0.000	1120	0.00	TF	0.0		0
40		0.0007	13.095	0.000	1270	0.00	TF	0.0		0
41		0.0013	13.175	0.000	2345	0.00	TF	0.0		0
42		0.0020	13.253	0.000	3647	0.00	TF	0.0		0
43		0.0027	13.318	0.000	4931	0.00	TF	0.0		0
44		0.0024	13.393	0.000	4479	0.00	TF	0.0		0
45		0.0020	13.466	0.000	3777	0.00	TF	0.0		0
46		0.0017	13.550	0.000	3162	0.00	TF	0.0		0
47		0.0015	13.627	0.000	2811	0.00	TF	0.0		0
48		0.0015	13.710	0.000	2770	0.00	TF	0.0		0
49		0.0014	13.796	0.000	2579	0.00	TF	0.0		0
50		0.0127	14.033	0.000	23428	0.00	TF	0.0		0
51		0.0146	14.086	0.000	26933	0.00	TF	0.0		0
52		0.0013	14.404	0.000	2453	0.00	TF	0.0		0
53		0.0010	14.485	0.000	1819	0.00	TF	0.0		0
54		0.0011	14.567	0.000	1953	0.00	TF	0.0		0
55		0.0010	14.643	0.000	1895	0.00	TF	0.0		0
56		0.0010	14.724	0.000	1845	0.00	TF	0.0		0
57		0.0011	14.798	0.000	1966	0.00	TF	0.0		0
58		0.0010	14.879	0.000	1883	0.00	TF	0.0		0
59		0.0010	14.967	0.000	1938	0.00	TF	0.0		0
60		0.0016	15.037	0.000	3004	0.00	TF	0.0		0
61		0.0009	15.105	0.000	1747	0.00	TF	0.0		0
62		0.0009	15.186	0.000	1684	0.00	TF	0.0		0
63		0.0008	15.271	0.000	1434	0.00	TF	0.0		0
64		0.0008	15.351	0.000	1425	0.00	TF	0.0		0
65		0.0009	15.429	0.000	1654	0.00	TF	0.0		0
66		0.0011	15.505	0.000	2047	0.00	TF	0.0		0
67		0.0009	15.578	0.000	1687	0.00	TF	0.0		0
68		0.0008	15.657	0.000	1414	0.00	TF	0.0		0
69		0.0006	15.737	0.000	1063	0.00	TF	0.0		0
70		0.0301	17.069	0.000	55610	0.00	TF	0.0		0
71		0.0392	17.128	0.000	72388	0.00	TF	0.0		0
72		17.8762	20.352	0.000	33045130	0.00	VV	29.9		0
73		0.0014	25.902	0.000	2669	0.00	TF	0.0		0
74		17.0807	27.165	0.000	31574628	0.00	VP	41.4		0
	Totals	**98.1561**		**0.000**	**181446528**					

3.3 Characterisation data for 2 and 19-23

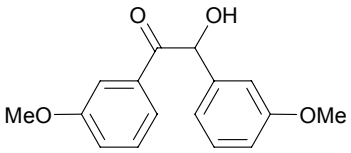
Benzoin (2)



2

Isolated **2** exhibited spectral characteristics identical to those in the literature.[1] mp 134-136 ^{o}C, Lit.[1] 133-134 ^{o}C. δ_H ($CDCl_3$) 7.94 (2H, d, J 7.7), 7.52-7.58 (1H, m), 7.30-7.46 (7H, m), 5.98 (1H, d, J 6.0), 4.58 (1H, d, J 6.0).

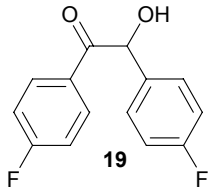
3,3'-dimethoxybenzoin (18)



18

Isolated **18** exhibited spectral characteristics identical to those in the literature.[1] mp 56-58 ^{o}C, Lit.[1] 55 ^{o}C. δ_H ($CDCl_3$) 7.46-7.54 (2H, m), 7.23-7.36 (2H, m), 7.09 (1H, d, J 7.9), 6.95 (1H, d, J 6.4), 6.84 (2H, m), 5.91 (1H, d, J 5.6), 4.54 (1H, d, J 5.6), 3.82 (3H, s), 3.78 (3H, s).

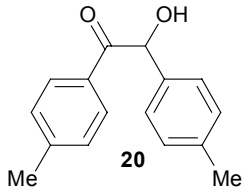
4,4'-difluorobenzoin (19)



19

Isolated **19** exhibited spectral characteristics identical to those in the literature.[2] mp 84-86 ^{o}C, Lit.[1] 81-82 ^{o}C. δ_H ($CDCl_3$) 7.90-8.00 (2H, dd, J 8.7, 4.8), 7.30 (2H, dd, J 8.7, 4.8), 7.11 (2H, dd, J 8.5, 8.5), 7.05 (2H, dd, J 8.5, 8.5), 5.92 (1H, d, J 6.0), 4.53 (1H, d, J 6.0).

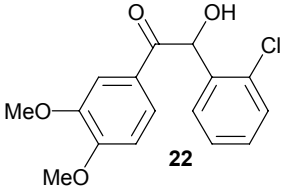
4,4'-dimethylbenzoin (20)



20

Isolated **20** exhibited spectral characteristics identical to those in the literature.[1] mp 91-93 ^{o}C, Lit.[1] 89 ^{o}C. δ_H ($CDCl_3$) 7.84 (2H, d, J 7.9), 7.18-7.26 (4H, m), 7.14 (2H, d, J 7.9), 5.92 (1H, d, J 5.9), 4.57 (1H, d, 5.9), 2.37 (3H, s), 2.31 (3H, s).

2-chloro-3',4'-dimethoxybenzoin (22)

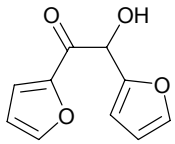


22

mp 144-146 ^{o}C; δ_H ($CDCl_3$) 3.91 (3H, s), 3.92 (3H, s), 4.69 (1H, d, J 5.6), 6.37 (1H, d, J 5.6), 6.85 (1H, d, J 8.5), 7.14 (1H, dd, J 2.0 and 7.5), 7.18-7.26 (2H, m), 7.45 (1H, dd, J 1.5 and 8.0), 7.51 (1H, d, J 2.0), 7.59 (1H, dd, J 2.0 and 8.5); δ_C ($CDCl_3$) 55.5, 55.6, 71.8, 109.9, 110.4, 123.4,

127.4, 128.7, 129.5, 129.8, 131.7, 132.9, 136.9, 148.5, 153.6, 196.5; ν_{max} (nujol)/cm^{-1} 3462, 3426, 1660, 1594, 1576, 1272, 1172, 1151, 1088, 1028, 1010, 769, 727*; m/z* (ES) 329.0540 (M^+ + Na. $C_{16}H_{15}O_4ClNa$ requires 329.0557).

Furoin (23)



23

Isolated **23** exhibited spectral characteristics consistent with those in the literature.[1] mp 135-137 ^oC, Lit.[1] 135-136 ^oC. δ_H ($CDCl_3$) 7.61-7.66 (1H, m), 7.37-7.41 (1H, m), 7.25-7.30 (1H, m), 6.56 (1H, dd, J 1.5 and 3.5), 6.43 (1H, d, J 3.5), 6.36-6.39 (1H, m) 5.82 (1H, bs), 4.21 (1H, d, J 5.6).

3.4 Attempted enantioselective reduction of benzil using (*R,R*)-10a

Procedure

In a 10 cm^3 round bottom flask equipped with a stirring bar and a rubber septum, Na_2CO_3 (88 mg, 0.83 mmol) and **(*R,R*)-10a** (44 mg, 0.07 mmol) were dissolved in degassed water (2.5 cm^3) under an atmosphere of N_2. Subsequently, a solution of the substrate (0.33 mmol) in Et_2O (1.0 cm^3) was added *via* syringe. $Na_2S_2O_4$ (116 mg, 0.67 mmol) was then added quickly and the rubber septum was substituted with a glass stopper. The resulting biphasic solution was vigorously stirred over 24 h in the dark. Samples were taken periodically and analyzed by ^1H

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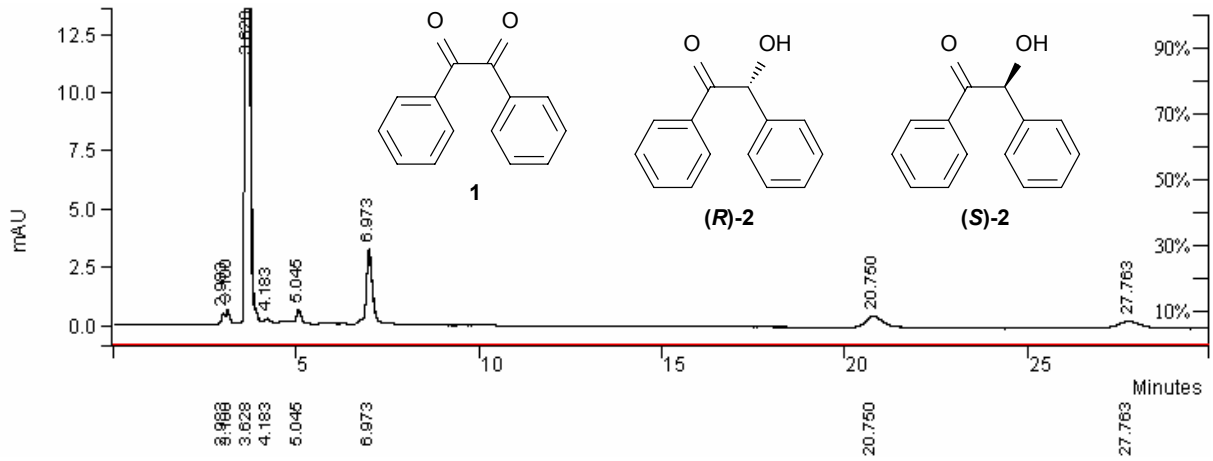
NMR spectroscopy and CSP-HPLC (Chiralpak AD-H 250 x 46 mm column, solvent: 90:10 Hexane:IPA, flow-rate: 1.0 mL/min, λ = 220 nm, retention times: 20.8 min (*R*), 27.7 min (*S*).[1]

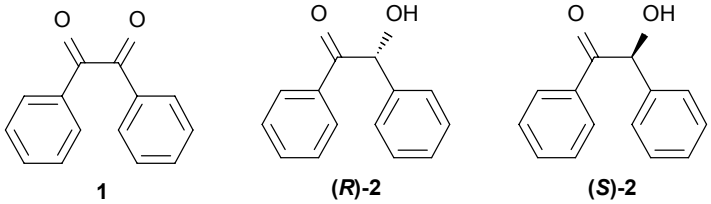
The chromatograms associated with this experiment are presented below.

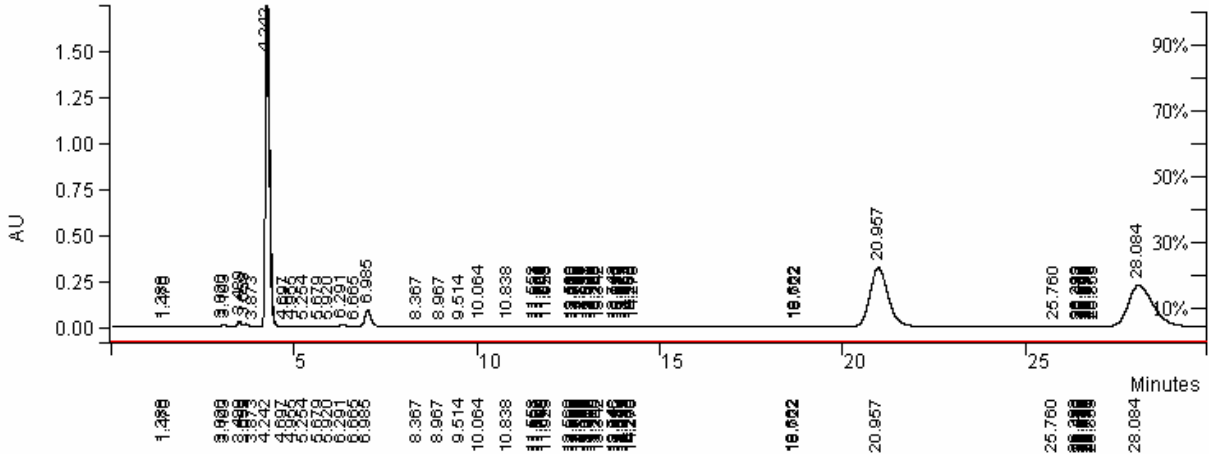
Sample taken after 15 h (29% conversion – 25% *ee*)



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
6		3.5410	6.973	0.000	32498	0.00	BB	9.6		0
7		0.5247	20.750	0.000	4815	0.00	BB	30.2		0
8		0.3058	27.763	0.000	2807	0.00	BB	38.4		0
	Totals	**4.3715**		**0.000**	**40120**					

Sample taken after 24 h (97% conversion 2% *ee*)




AU
1.50
1.25
1.00
0.75
0.50
0.25
0.00
90%
70%
50%
30%
10%
5
10
15
20
25
Minutes
20.957
28.084
25.760
8.367
8.967
9.514
10.064
10.838
6.985

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
6		0.2752	3.659	0.000	1041617	0.00	VV	7.1		0
7		0.0462	3.873	0.000	174810	0.00	VV	11.7		0
8		37.8465	4.242	0.000	143271248	0.00	VV	6.5		0
9		0.0224	4.697	0.000	84780	0.00	TS	0.0		0
10		0.0324	4.955	0.000	122728	0.00	TS	0.0		0
11		0.0134	5.254	0.000	50687	0.00	TS	0.0		0
12		0.0029	5.679	0.000	11101	0.00	TF	0.0		0
13		0.0034	5.920	0.000	12771	0.00	TF	0.0		0
14		0.3193	6.291	0.000	1208899	0.00	TF	0.0		0
15		0.0195	6.665	0.000	73667	0.00	TF	0.0		0
16		2.8414	6.985	0.000	10756375	0.00	TF	0.0		0
17		0.0292	8.367	0.000	110693	0.00	TF	0.0		0
18		0.0026	8.967	0.000	9844	0.00	TF	0.0		0
19		0.0155	9.514	0.000	58733	0.00	TF	0.0		0
20		0.0494	10.064	0.000	187004	0.00	TF	0.0		0
21		0.0186	10.838	0.000	70331	0.00	TF	0.0		0
22		0.0003	11.553	0.000	1172	0.00	TF	0.0		0
23		0.0005	11.627	0.000	1742	0.00	TF	0.0		0
24		0.0005	11.702	0.000	1890	0.00	TF	0.0		0
25		0.0005	11.780	0.000	1989	0.00	TF	0.0		0
26		0.0005	11.845	0.000	2037	0.00	TF	0.0		0
27		0.0003	11.923	0.000	1269	0.00	TF	0.0		0
28		0.0003	12.560	0.000	1150	0.00	TF	0.0		0
29		0.0003	12.639	0.000	1146	0.00	TF	0.0		0
30		0.0003	12.720	0.000	1324	0.00	TF	0.0		0
31		0.0003	12.792	0.000	1260	0.00	TF	0.0		0
32		0.0003	12.865	0.000	1062	0.00	TF	0.0		0
33		0.0003	13.027	0.000	1198	0.00	TF	0.0		0
34		0.0003	13.108	0.000	1322	0.00	TF	0.0		0
35		0.0004	13.186	0.000	1589	0.00	TF	0.0		0
36		0.0004	13.266	0.000	1673	0.00	TF	0.0		0
37		0.0005	13.342	0.000	2018	0.00	TF	0.0		0
38		0.0066	13.743	0.000	25163	0.00	TF	0.0		0
39		0.0023	13.816	0.000	8842	0.00	TF	0.0		0
40		0.0024	13.888	0.000	9159	0.00	TF	0.0		0
41		0.0022	13.971	0.000	8335	0.00	TF	0.0		0
42		0.0024	14.053	0.000	9223	0.00	TF	0.0		0
43		0.0027	14.133	0.000	10308	0.00	TF	0.0		0
44		0.0033	14.205	0.000	12460	0.00	TF	0.0		0
45		0.0097	14.270	0.000	36820	0.00	TF	0.0		0
46		0.2103	18.662	0.000	796134	0.00	TF	0.0		0
47		0.2115	18.722	0.000	800554	0.00	TF	0.0		0
48		29.0976	20.957	0.000	110151592	0.00	VP	31.7		0
49		0.0003	25.760	0.000	1005	0.00	VV	0.0		0
50		0.0003	26.393	0.000	1223	0.00	VV	0.0		0
51		0.0004	26.472	0.000	1399	0.00	VV	0.0		0
52		0.0004	26.552	0.000	1649	0.00	VV	0.0		0
53		0.0006	26.619	0.000	2103	0.00	VV	0.0		0
54		0.0004	26.696	0.000	1691	0.00	VV	0.0		0
55		0.0004	26.777	0.000	1620	0.00	VV	0.0		0
56		0.0003	26.859	0.000	1317	0.00	VV	0.0		0
57		28.1034	28.084	0.000	106387976	0.00	VB	44.8		0
	Totals	**99.2014**		**0.000**	**375537728**					

4.0 References

1. A. S. Demir, O. Sesenoglu, E. Eren, B. Hosrik, M. Pohl, E. Janzen, D. Kolter, R. Feldmann, P. Dunkelmann and M. Muller, *Adv. Synth. Catal.,* 2002*,* **344**, 96.

2. A. Waldemar, S.-M. R. Chantu and C.-G. Zhao, *J. Org. Chem.* 1999, **64**, 7492.