Supplementary Information

for

Mechanistic investigation of the iridium-catalysed alkylation of amines with alcohols

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GC retention times

Injector temperature 300 °C, detector temperature 350 °C.

Table A. Programmed oven temperature: start 100 °C, ramp 20 °C/min to 300 °C, 5 min @ 300 °C.

Compound	***Retention Time***
aniline	1.52 min
benzyl alcohol	1.70 min
1,2,4,5-tetramethylbenzene	2.11 min
naphthalene	2.47 min
p-anisalcohol	2.92 min

Table B. Programmed oven temperature: start 100 °C, ramp 20 °C/min to 200 °C, 5 min @ 200 °C, ramp 20 °C/min to 300 °C, 5 min @ 300 °C.

Compound	***Retention Time***
p-toluidine	1.84 min
p-(trifluoromethyl)aniline	1.85 min
p-(trifluoromethyl)benzyl alcohol	1.91 min
p-methylbenzyl alcohol	2.14 min
p-chloroaniline	2.43 min
p-anisidine	2.51 min
p-chlorobenzyl alcohol	2.64 min
p-(dimethylamino)aniline	3.31 min
p-(hydroxymethyl)benzonitrile	3.52 min
p-aminobenzonitrile	3.76 min
p-(dimethylamino)benzyl alcohol	3.98 min
methyl *p*-(hydroxymethyl)benzoate	4.08 min
methyl *p*-aminobenzoate	4.18 min
p-nitrobenzyl alcohol	4.21 min

Table C. Programmed oven temperature: start 100 °C, ramp 5 °C/min to 130 °C, 20 °C/min to 200 °C, 5 min @ 200 °C, ramp 20 °C to 300 °C, 5 min @ 300 °C.

Compound	***Retention Time***
aniline	1.73 min
benzyl alcohol	2.05 min
1,2,4,5-tetramethylbenzene	2.85 min
naphthalene	3.53 min
p-chloroaniline	3.39 min
p-aminobenzonitrile	6.72 min

Competition experiment 1, *p*-methoxybenzyl alcohol vs. benzyl alcohol

K_2CO_3 (14 mg, 0.10 mmol)

aniline (180 µL, 2 mmol)

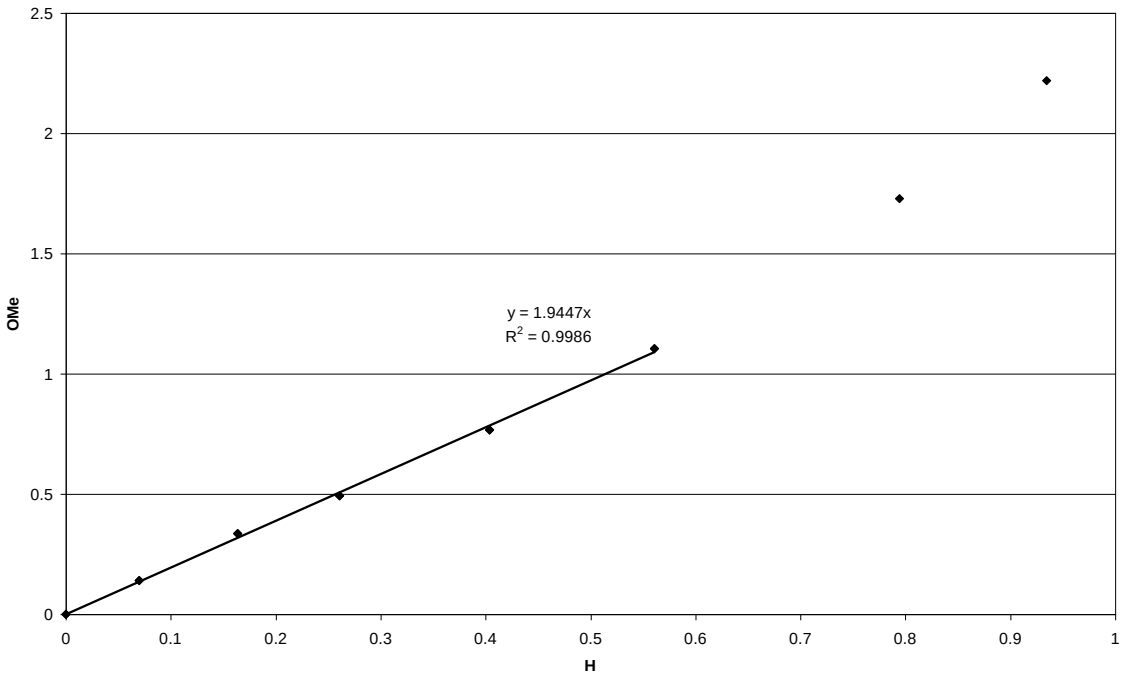
benzyl alcohol (105 µL, 1 mmol)

p-methoxybenzyl alcohol (125 µL, 1 mmol)

naphthalene (129 mg, 1 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas				Conversion		
Time	$PhNH_2$	BnOH	*p*-MeO-BnOH	Naphthalene	$PhNH_2$	BnOH	*p*-MeO-BnOH
0 - no cat.	58363	33031	27709	52420	0.0024	0.0082	-0.0045
0 - cat.	89360	50868	42134	80064	0.0000	0.0000	0.0000
30 min	62112	35090	27070	59223	0.0603	0.0674	0.1314
1h	33934	19358	13487	35878	0.1526	0.1508	0.2857
2h	70544	44593	29264	91116	0.3063	0.2297	0.3897
3h	84513	57311	33053	135093	0.4395	0.3323	0.5351
4h	66124	47585	22871	131233	0.5485	0.4293	0.6688
6h	50356	41146	13398	143293	0.6851	0.5480	0.8223
8h	51889	42795	9803	171480	0.7282	0.6072	0.8914
24h	12822	3046	0	161975	0.9289	0.9704	1.0000



Competition experiment 2, *p*-methylbenzyl alcohol vs. benzyl alcohol

K_2CO_3 (14 mg, 0.10 mmol)

aniline (180 µL, 2 mmol)

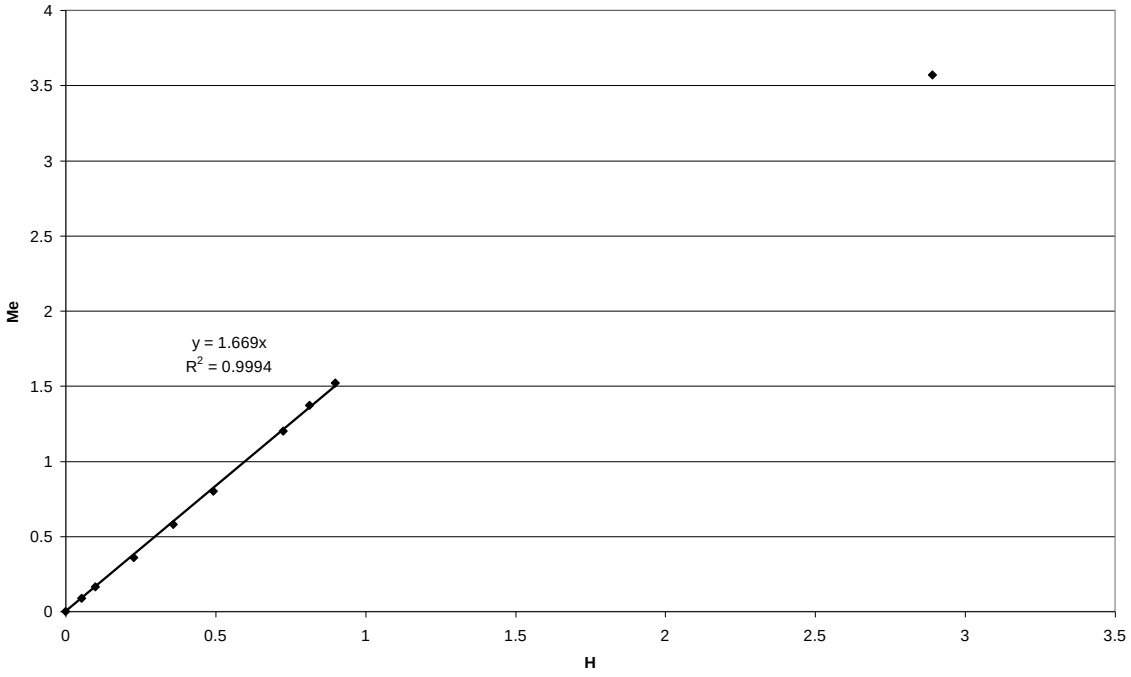
benzyl alcohol (105 µL, 1 mmol)

p-methylbenzyl alcohol (122 mg, 1 mmol)

naphthalene (126 mg, 1 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas				Conversion		
time	PhNH2	BnOH	p-Me-BnOH	Naphthalene	PhNH2	BnOH	p-Me-BnOH
0 - no cat.	717745	424429	470110	625773	0.0071	-0.0164	-0.0298
0 - cat.	445759	261196	285530	391417	0.0000	0.0000	0.0000
30 min	465851	271063	286663	428255	0.0448	0.0515	0.0824
1 h	307854	180906	185579	299271	0.0967	0.0941	0.1499
2 h	269225	163497	156588	307424	0.2310	0.2030	0.3018
3 h	106058	65690	57578	140889	0.3390	0.3013	0.4398
4 h	83940	53727	43248	131790	0.4407	0.3891	0.5501
6 h	63474	44218	30041	136795	0.5926	0.5156	0.6990
7 h	61753	45149	28244	152627	0.6472	0.5567	0.7463
8 h	202196	152689	89591	562404	0.6865	0.5932	0.7816
26 h	6387	7795	4327	210311	0.9735	0.9445	0.9718



Competition experiment 3, *p*-(trifluoromethyl)benzyl alcohol vs. benzyl alcohol

K_2CO_3 (15 mg, 0.11 mmol)

aniline (180 µL, 2 mmol)

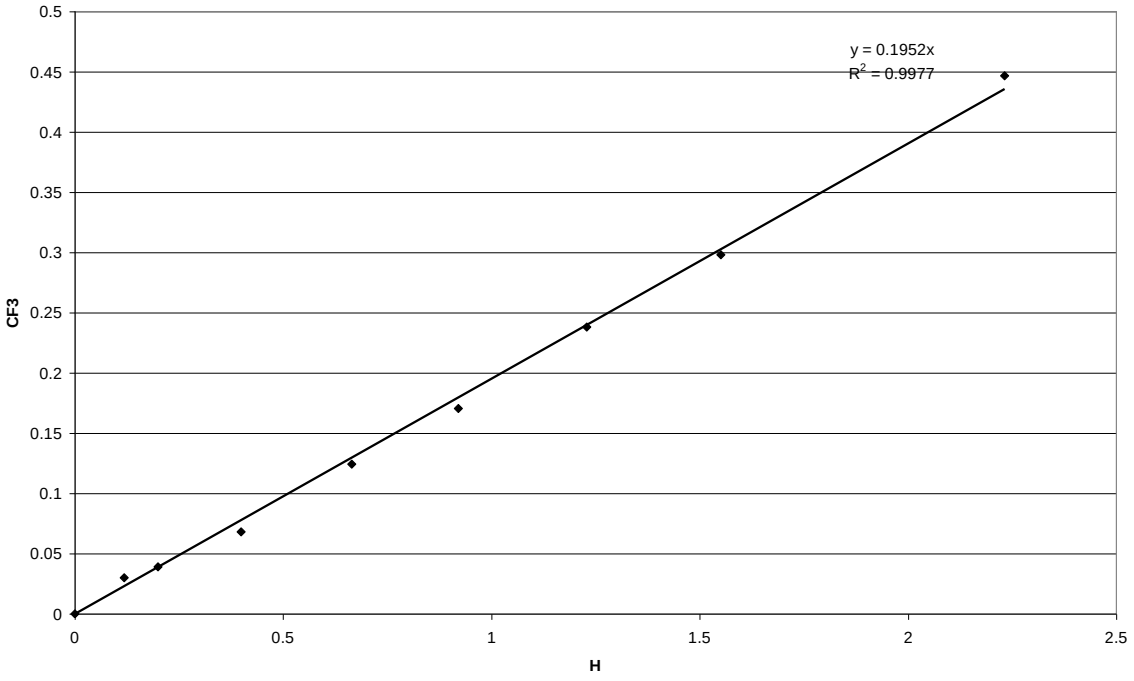
benzyl alcohol (105 µL, 1 mmol)

p-(trifluoromethyl)benzyl alcohol (135 µL, 0.99 mmol)

naphthalene (127 mg, 1 mmol)

$[Cp^*IrCl_2]_2$ (39 mg, 0.049 mmol)

	Areas				Conversion		
time	$PhNH_2$	BnOH	*p*-CF_3-BnOH	Naphthalene	$PhNH_2$	BnOH	*p*-CF_3-BnOH
0 - no cat.	157965	89809	95716	136593	-0.0121	-0.0368	-0.0259
0 - cat.	174293	96726	104192	152533	0.0000	0.0000	0.0000
30 min	168967	89463	102363	151947	0.0268	0.0715	0.0138
1 h	119507	61467	75025	113259	0.0766	0.1442	0.0302
2 h	204569	96720	140437	219523	0.1845	0.3052	0.0635
3 h	114162	46925	84758	139837	0.2855	0.4708	0.1127
5 h	109765	39957	88195	152176	0.3687	0.5859	0.1515
6 h	124374	28462	120277	239791	0.5461	0.8128	0.2657
24 h	12946	0	19788	178546	0.9365	1.0000	0.8378



Competition experiment 4, *p*-chlorobenzyl alcohol vs. benzyl alcohol

K_2CO_3 (14 mg, 0.10 mmol)

aniline (180 µL, 2 mmol)

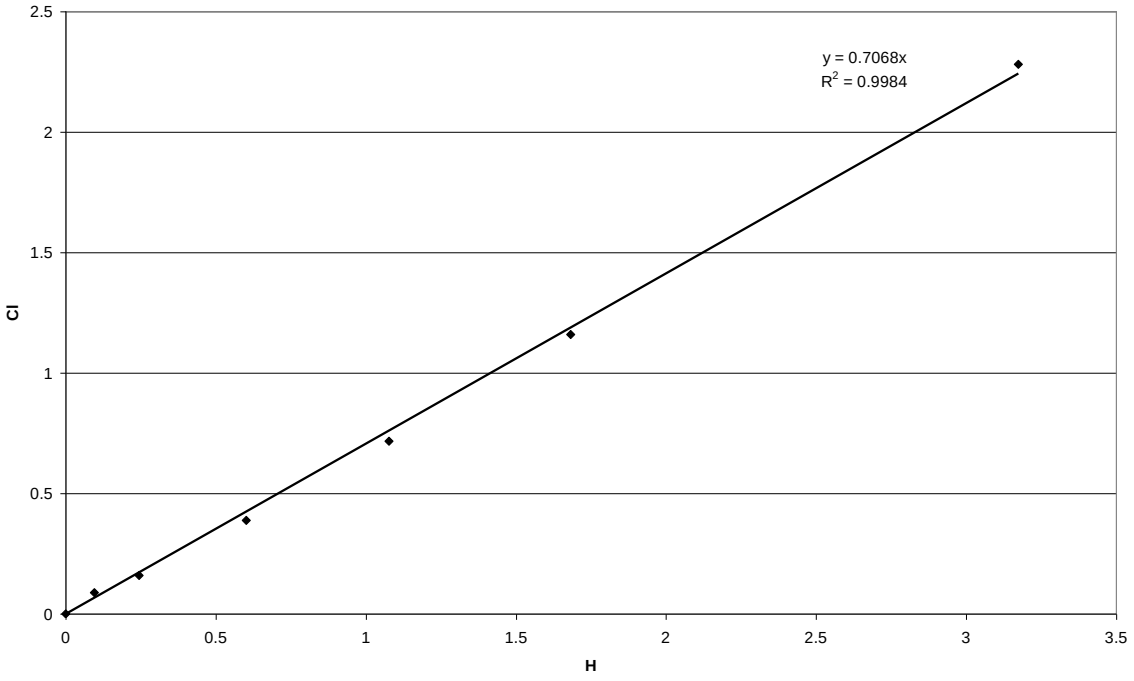
benzyl alcohol (105 µL, 1 mmol)

p-chlorobenzyl alcohol (143 mg, 1 mmol)

naphthalene (128 mg, 1 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas				Conversion		
time	PhNH2	BnOH	p-Cl-BnOH	Naphthalene	PhNH2	BnOH	p-Cl-BnOH
0 - no cat.	99611	56266	46300	89186	-0.0123	-0.0878	-0.0516
0 - cat.	89255	46913	39933	80893	0.0000	0.0000	0.0000
30 min	62807	33772	28970	64089	0.1118	0.0914	0.0843
1 h	78890	41633	38611	91734	0.2206	0.2174	0.1474
2 h	88375	44380	46788	139776	0.4270	0.4525	0.3219
3 h	63734	29365	35887	148703	0.6116	0.6595	0.5111
4 h	36608	15073	21644	139784	0.7626	0.8141	0.6863
6 h	12715	3999	8300	164598	0.9300	0.9581	0.8979
18 h	1223	0	1072	181903	0.9940	1.0000	0.9881



Competition experiment 5, methyl *p*-(hydroxymethyl)benzoate vs. benzyl alcohol

K_2CO_3 (15 mg, 0.11 mmol)

aniline (180 µL, 2 mmol)

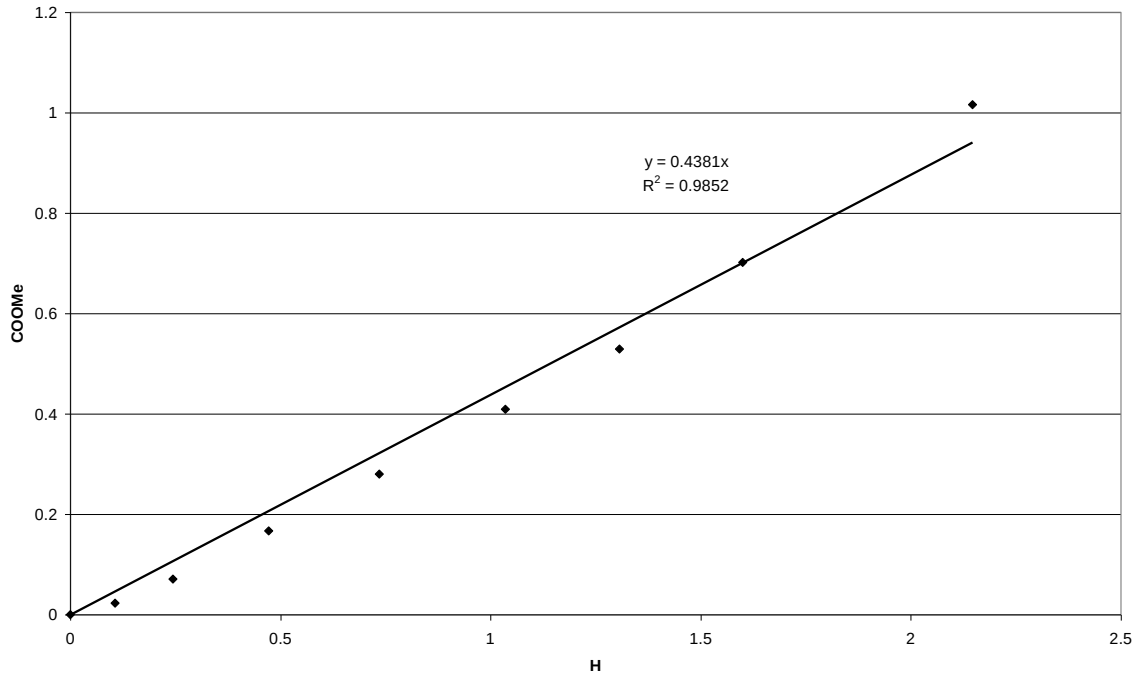
benzyl alcohol (105 µL, 1 mmol)

methyl *p*-(hydroxymethyl)benzoate (165 mg, 0.99 mmol)

naphthalene (128 mg, 1 mmol)

$[Cp^*IrCl_2]_2$ (39 mg, 0.049 mmol)

	Areas				Conversion		
time	PhNH2	BnOH	p-COOMe-BnOH	Naphthalene	PhNH2	BnOH	p-COOMe-BnOH
0 - no cat.	149311	78395	58713	127031	-0.0089	-0.0396	-0.0554
0 - cat.	206242	105095	77526	177035	0.0000	0.0000	0.0000
30 min	141927	69644	55831	130416	0.0659	0.1004	0.0224
1 h	148095	68740	60272	147716	0.1394	0.2161	0.0682
2 h	120747	51527	51569	139089	0.2548	0.3760	0.1533
3 h	103203	39140	45545	137564	0.3560	0.5207	0.2440
4 h	99813	32690	45105	155033	0.4474	0.6448	0.3356
5 h	90074	25861	41549	160990	0.5197	0.7294	0.4106
6 h	78559	19559	35409	163113	0.5866	0.7980	0.5043
8 h	63949	11928	27265	171960	0.6808	0.8832	0.6379
26 h	46563	3743	14776	237079	0.8314	0.9734	0.8577



Competition experiment 6, *p*-(hydroxymethyl)benzonitrile vs. benzyl alcohol

K_2CO_3 (14 mg, 0.10 mmol)

aniline (180 µL, 2 mmol)

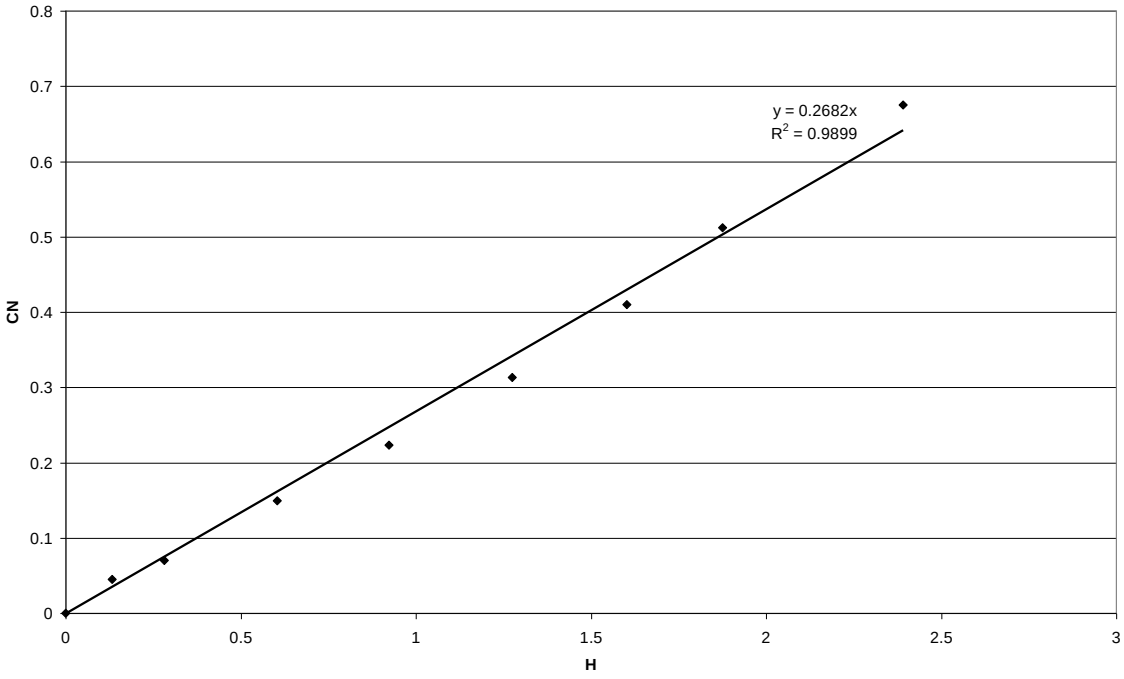
benzyl alcohol (105 µL, 1 mmol)

p-(hydroxymethyl)benzonitrile (132 mg, 0.99 mmol)

naphthalene (127 mg, 1 mmol)

$[Cp^*IrCl_2]_2$ (39 mg, 0.049 mmol)

	Areas				Conversion		
time	$PhNH_2$	BnOH	*p*-CN-BnOH	Naphthalene	$PhNH_2$	BnOH	*p*-CN-BnOH
0 - no cat.	149709	86415	81164	129097	0.0065	-0.0217	-0.0499
0 - cat.	231764	130082	118897	198548	0.0000	0.0000	0.0000
30 min	179791	95674	95399	166665	0.0758	0.1238	0.0441
1 h	144854	72163	81544	146009	0.1501	0.2456	0.0674
2 h	141770	62334	89792	174040	0.3022	0.4533	0.1384
3 h	98940	37233	68475	142925	0.4070	0.6024	0.1999
4 h	79275	25041	59880	136787	0.5035	0.7206	0.2690
5 h	81792	21816	65654	165216	0.5759	0.7985	0.3364
6 h	62498	14644	52365	145869	0.6330	0.8468	0.4005
8 h	64211	11503	58439	191729	0.7131	0.9084	0.4910
26 h	41001	3633	45939	249599	0.8593	0.9778	0.6926



Competition experiment 7, *p*-(dimethylamino)benzyl alcohol vs. benzyl alcohol

K_2CO_3 (14 mg, 0.10 mmol)

aniline (180 µL, 2 mmol)

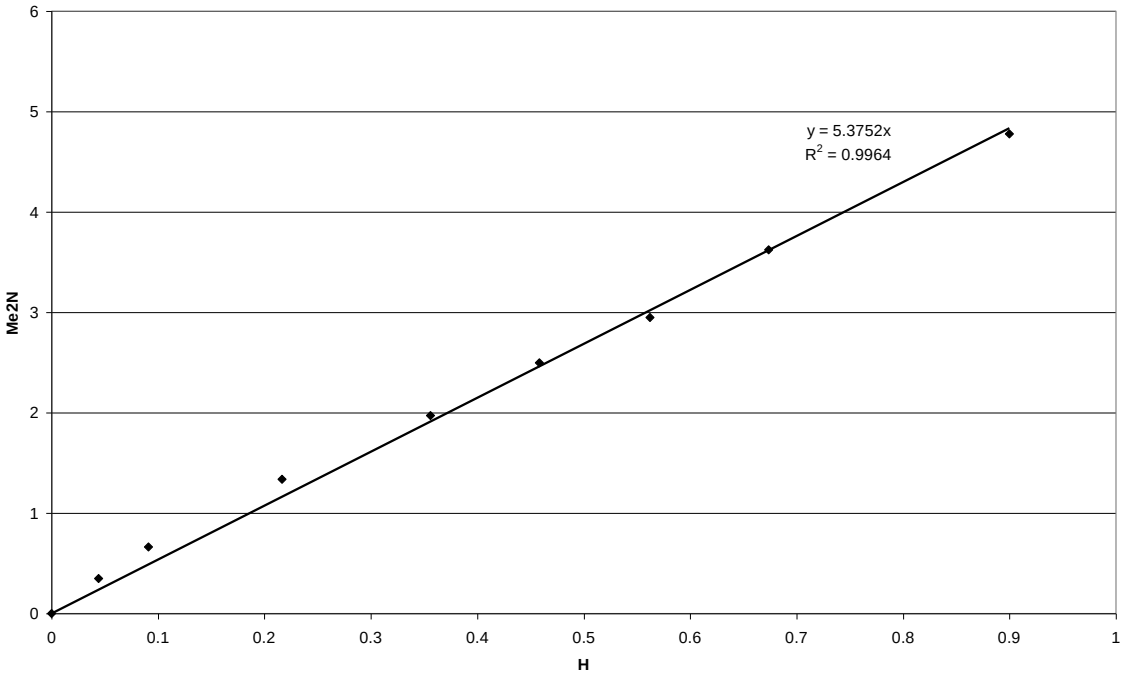
benzyl alcohol (105 µL, 1 mmol)

p-(dimethylamino)benzyl alcohol (156 mg, 1.03 mmol)

naphthalene (126 mg, 1 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas				Conversion		
time	$PhNH_2$	BnOH	*p*-NMe_2-BnOH	Naphthalene	$PhNH_2$	BnOH	*p*-NMe_2-BnOH
0 - no cat.	209125	121875	117043	181156	-0.0013	-0.0055	-0.0813
0 - cat.	218138	126593	113049	189206	0.0000	0.0000	0.0000
30 min	144087	88655	58560	138510	0.0977	0.0434	0.2924
1 h	158873	104275	52523	170665	0.1926	0.0868	0.4849
2 h	126122	91434	26633	169650	0.3552	0.1945	0.7373
3 h	107588	85496	15213	182405	0.4884	0.2995	0.8604
4 h	84270	71699	8315	169416	0.5686	0.3675	0.9179
5 h	88457	76599	6273	200827	0.6180	0.4299	0.9477
6 h	63133	53784	2523	157699	0.6528	0.4903	0.9732
8 h	95615	80366	1489	295368	0.7192	0.5933	0.9916



Competition experiment 8, *p*-nitrobenzyl alcohol vs. *p*-chlorobenzyl alcohol

K_2CO_3 (14 mg, 0.10 mmol)

aniline (180 µL, 2 mmol)

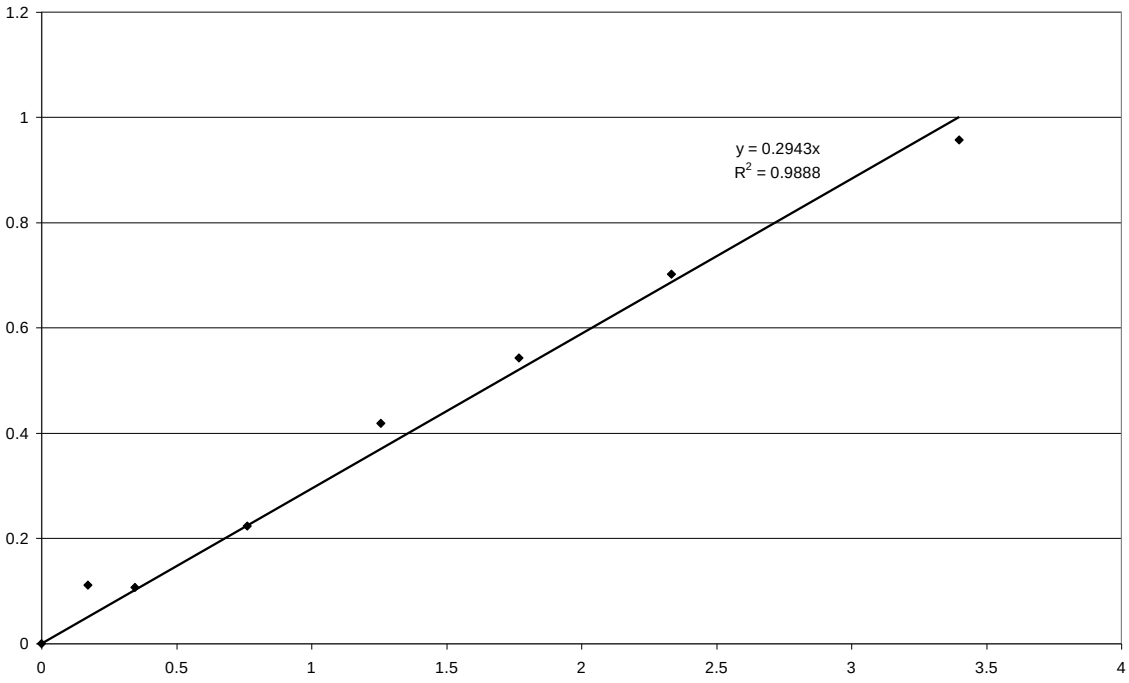
p-chlorobenzyl alcohol (144 mg, 1.01 mmol)

p-nitrobenzyl alcohol (154 mg, 1.02 mmol)

naphthalene (130 mg, 1.01 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas				Conversion		
time	aniline	*p*-Cl-BnOH	*p*-NO_2-BnOH	Naphthalene	$PhNH_2$	*p*-Cl-BnOH	*p*-NO_2-BnOH
0 - no cat.	163482	85109	63816	150191	0.0087	-0.0116	-0.0219
0 - cat.	213004	108662	80655	193979	0.0000	0.0000	0.0000
30 min	119982	56846	44856	120605	0.0940	0.1586	0.1055
1 h	165550	72359	68134	182402	0.1735	0.2918	0.1016
2 h	134663	47881	60983	183316	0.3310	0.5337	0.1999
3 h	81317	22524	38640	141190	0.4755	0.7152	0.3418
4 h	96742	19581	49538	205067	0.5704	0.8295	0.4190
5 h	75060	10498	39788	193123	0.6461	0.9030	0.5045
6 h	67887	4324	36922	231096	0.7325	0.9666	0.6157



Competition experiment 9, *p*-toluidine vs. aniline

K_2CO_3 (15 mg, 0.11 mmol)

aniline (90 µL, 1 mmol)

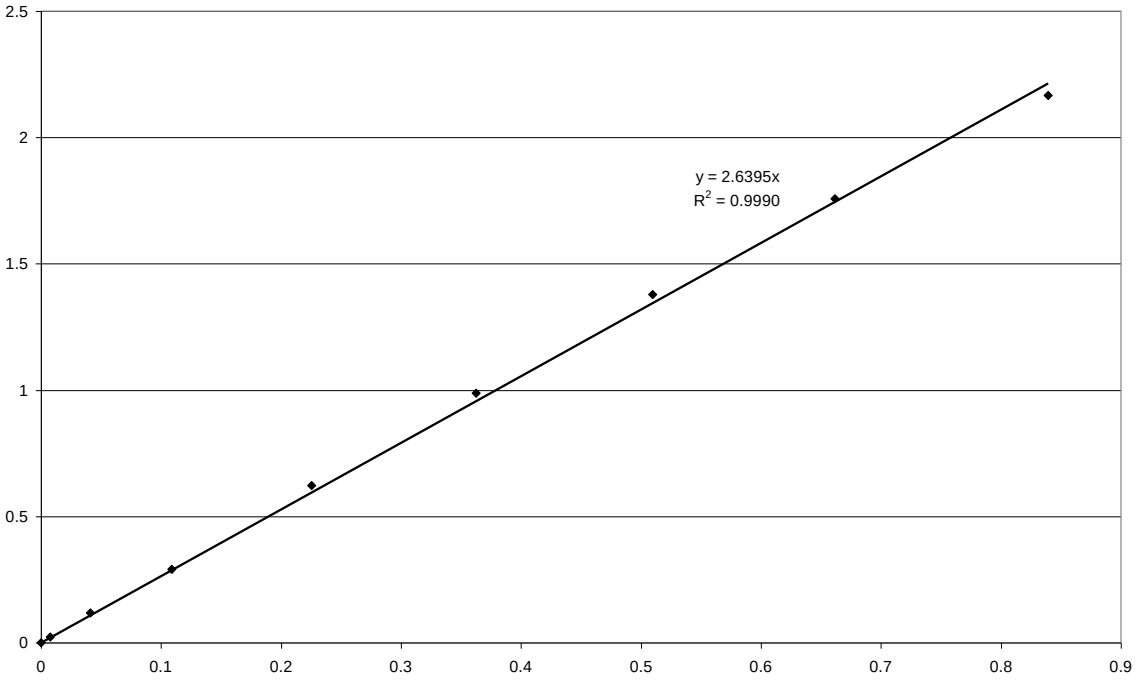
p-toluidine (107 mg, 1.0 mmol)

benzyl alcohol (210 µL, 2.03 mmol)

naphthalene (126 mg, 0.98 mmol)

$[Cp^*IrCl_2]_2$ (41 mg, 0.051 mmol)

	Areas				Conversion		
time	BnOH	*p*-H-aniline	*p*-Me-aniline	Naphthalene	BnOH	*p*-H-aniline	*p*-Me-aniline
0 - no cat.	285154	123435	138575	219133	-0.0099	0.0075	0.0218
0 - cat.	380537	167625	190922	295339	0.0000	0.0000	0.0000
30 min	275236	126766	133758	232700	0.0820	0.0402	0.1108
1 h	196237	94492	89722	185673	0.1797	0.1033	0.2525
2 h	239260	128024	98125	282659	0.3431	0.2020	0.4630
3 h	168770	98359	59964	249005	0.4740	0.3040	0.6275
4 h	136298	86445	41337	253530	0.5828	0.3993	0.7478
5 h	121028	82521	31423	281709	0.6666	0.4839	0.8275
6 h	84128	61049	18463	248942	0.7377	0.5679	0.8853
8 h	41953	32764	6403	197281	0.8350	0.7074	0.9498



Competition experiment 10, *p*-anisidine vs. aniline

K_2CO_3 (14 mg, 0.10 mmol)

aniline (90 µL, 1 mmol)

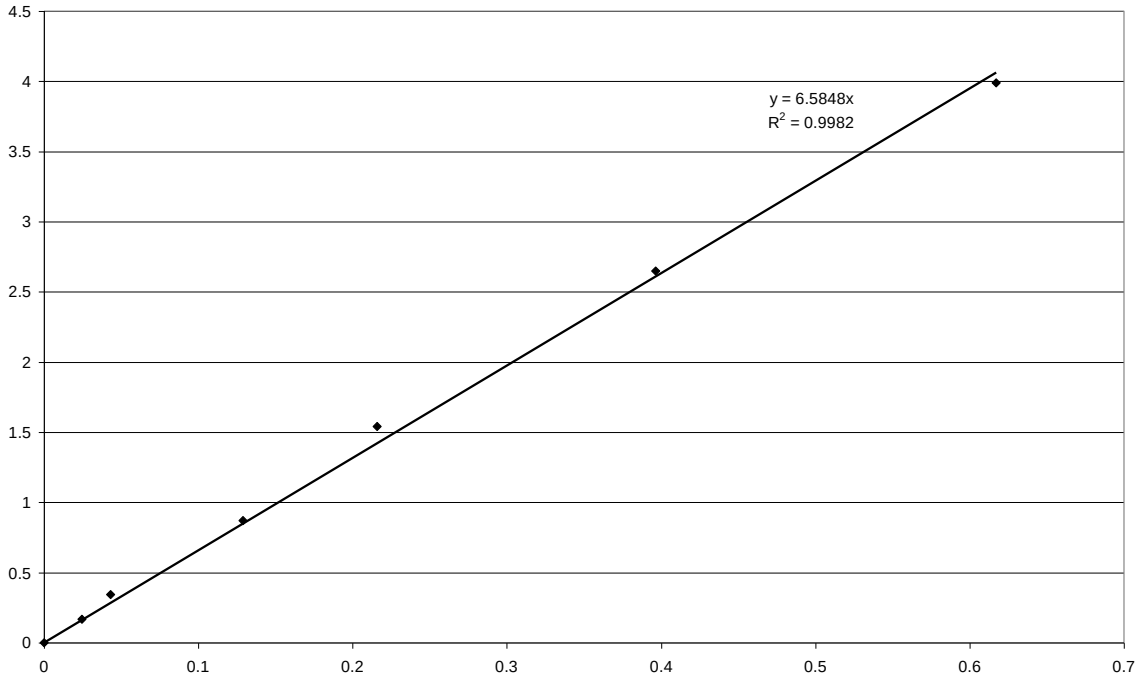
p-anisidine (122 mg, 0.99 mmol)

benzyl alcohol (210 µL, 2.03 mmol)

naphthalene (126 mg, 0.98 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas				Conversion		
time	BnOH	*p*-H-aniline	*p*-MeO-aniline	Naphthalene	BnOH	*p*-H-aniline	*p*-MeO-aniline
0 - no cat.	343599	150659	138236	264187	-0.0122	-0.0043	-0.0102
0 - cat.	329652	145678	132887	256548	0.0000	0.0000	0.0000
30 min	265783	126448	100102	228199	0.0936	0.0242	0.1531
1 h	323116	166186	112462	305549	0.1770	0.0422	0.2894
2 h	187718	113165	49157	226687	0.3555	0.1209	0.5814
3 h	223473	158426	38374	346160	0.4976	0.1940	0.7860
4 h	103434	82922	7967	217062	0.6292	0.3272	0.9291
5 h	76477	66151	2073	215921	0.7244	0.4605	0.9815
6 h	64130	56295	0	234453	0.7871	0.5771	1.0000
8 h	25236	21225	0	176175	0.8885	0.7878	1.0000



Competition experiment 11, *p*-(trifluoromethyl)aniline vs. aniline

K_2CO_3 (14 mg, 0.10 mmol)

aniline (90 µL, 1 mmol)

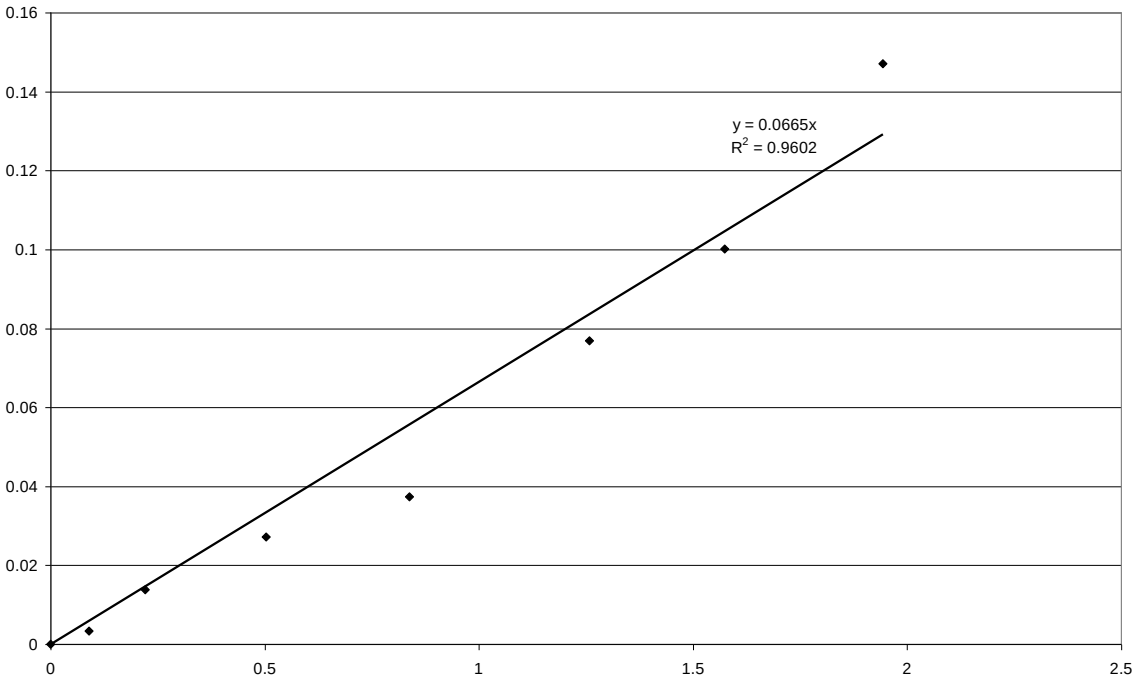
p-(trifluoromethyl)aniline (125 µL, 1.0 mmol)

benzyl alcohol (210 µL, 2.03 mmol)

naphthalene (126 mg, 0.98 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas				Conversion		
time	BnOH	*p*-H-aniline	*p*-CF_3-aniline	Naphthalene	BnOH	*p*-H-aniline	*p*-CF_3-aniline
0 - no cat.	210026	90846	107115	168150	-0.0127	-0.0028	0.0029
0 - cat.	191996	83874	99455	155674	0.0000	0.0000	0.0000
30 min	234622	97912	126553	198747	0.0428	0.0856	0.0033
1 h	169951	66518	97037	154009	0.1053	0.1984	0.0138
2 h	146850	49756	95014	152816	0.2208	0.3957	0.0268
3 h	140662	38164	100703	163620	0.3029	0.5671	0.0366
4 h	125541	26412	102073	172529	0.4100	0.7159	0.0739
5 h	125630	21416	110818	191722	0.4687	0.7927	0.0953
6 h	105803	14126	101013	183163	0.5316	0.8569	0.1368
8 h	91915	6395	96242	195842	0.6195	0.9394	0.2308



Competition experiment 12, *p*-chloroaniline vs. aniline

K_2CO_3 (14 mg, 0.10 mmol)

aniline (90 µL, 1 mmol)

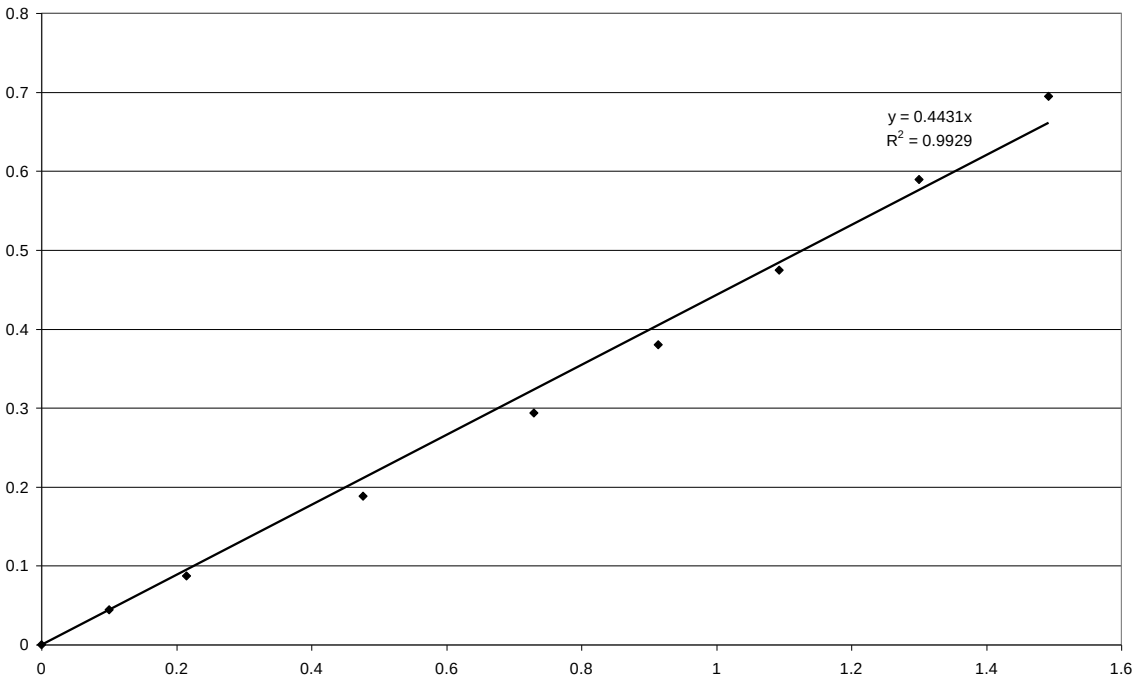
p-chloroaniline (129 mg, 1.01 mmol)

benzyl alcohol (210 µL, 2.03 mmol)

1,2,4,5-tetramethylbenzene (126 mg, 0.94 mmol)

$[Cp^*IrCl_2]_2$ (39 mg, 0.049 mmol)

	Areas				Conversion		
time	BnOH	*p*-H-aniline	*p*-Cl-aniline	Tetramethylbenzene	BnOH	*p*-H-aniline	*p*-Cl-aniline
0 - no cat.	209006	88519	88270	144515	-0.0126	0.0060	0.0015
0 - cat.	232327	100245	99506	162671	0.0000	0.0000	0.0000
30 min	213482	89702	94107	160869	0.0708	0.0951	0.0437
1 h	175181	71243	80309	143274	0.1439	0.1931	0.0837
2 h	144877	54172	71734	141569	0.2835	0.3791	0.1716
3 h	149759	51815	79557	174394	0.3987	0.5179	0.2542
4 h	117712	39141	66249	158382	0.4796	0.5990	0.3162
5 h	109630	34877	64241	168820	0.5453	0.6648	0.3779
6 h	101105	30170	60989	179698	0.6061	0.7276	0.4452
7 h	63000	17900	39426	129122	0.6584	0.7750	0.5008



Competition experiment 13, methyl *p*-aminobenzoate vs. aniline

K_2CO_3 (15 mg, 0.11 mmol)

aniline (90 µL, 1 mmol)

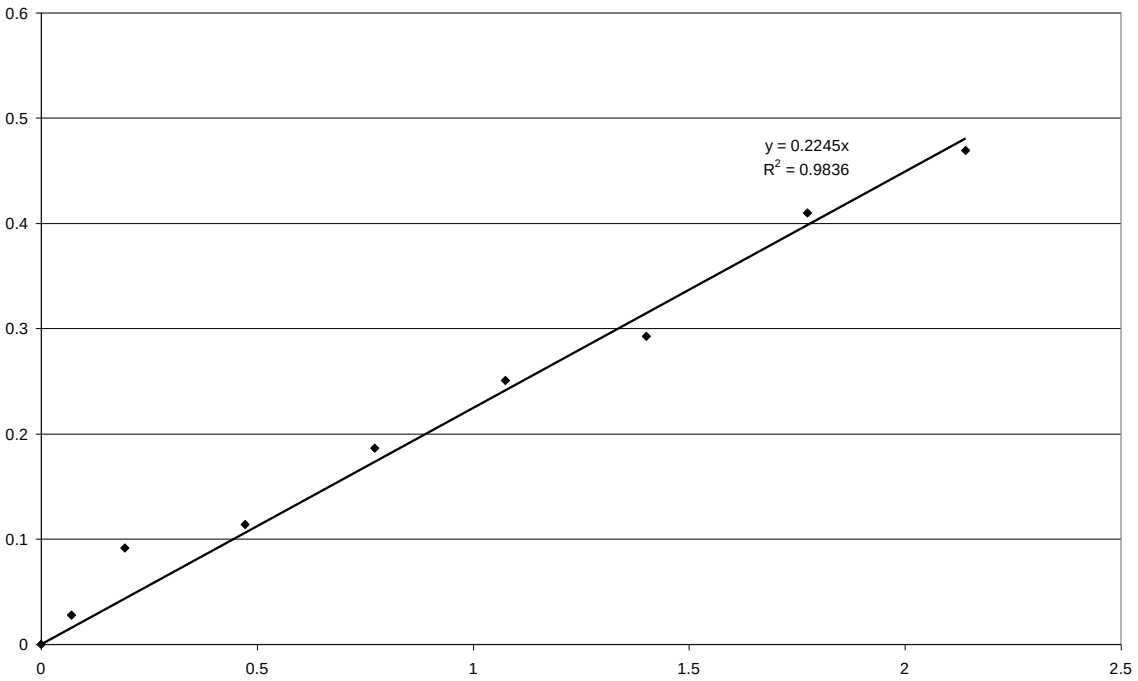
methyl *p*-aminobenzoate (152 mg, 1.0 mmol)

benzyl alcohol (210 µL, 2.03 mmol)

naphthalene (125 mg, 0.98 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas				Conversion		
time	BnOH	*p*-H-aniline	*p*-COOMe-aniline	Naphthalene	BnOH	*p*-H-aniline	*p*-COOMe-aniline
0 - no cat.	493982	206935	218743	370208	-0.0259	-0.0058	-0.0206
0 - cat.	297596	127156	132455	228796	0.0000	0.0000	0.0000
30 min	252779	107859	117237	208190	0.0665	0.0678	0.0273
1 h	150220	62258	71807	135941	0.1504	0.1759	0.0876
2 h	193466	71720	106919	206935	0.2812	0.3764	0.1075
3 h	127141	41371	77424	161178	0.3935	0.5381	0.1702
4 h	93886	26075	61894	137378	0.4746	0.6585	0.2218
5 h	106262	24251	76572	177230	0.5390	0.7538	0.2537
6 h	83955	15578	63510	165311	0.6095	0.8304	0.3364
7 h	158634	23359	129457	357468	0.6588	0.8824	0.3744
8 h	65853	8194	51799	179693	0.7182	0.9180	0.5021



Competition experiment 14, *p*-aminobenzonitrile vs. *p*-chloroaniline

K_2CO_3 (14 mg, 0.10 mmol)

p-chloroaniline (124 mg, 0.97 mmol)

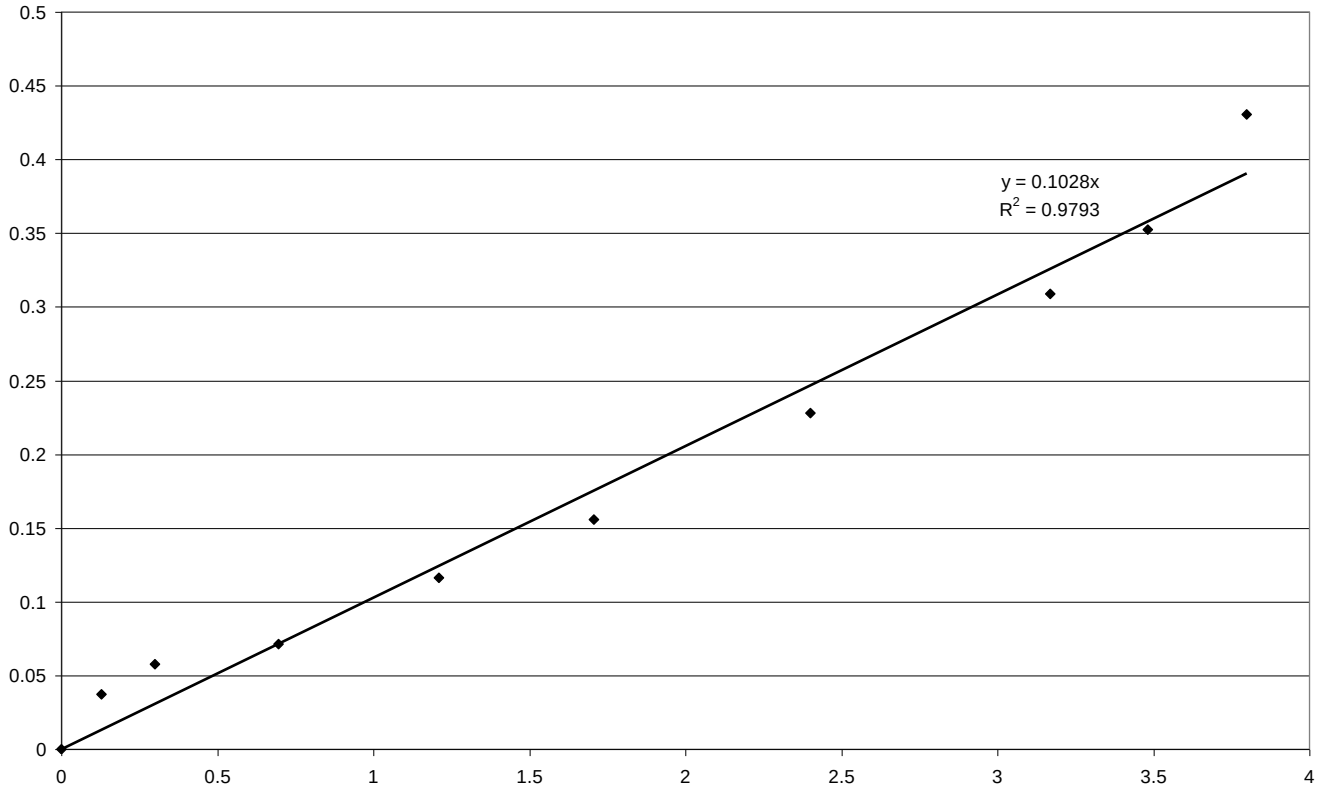
p-aminobenzonitrile (119 mg, 1.0 mmol)

benzyl alcohol (210 µL, 2.03 mmol)

1,2,4,5-tetramethylbenzene (132 mg, 0.98 mmol)

$[Cp^*IrCl_2]_2$ (39 mg, 0.049 mmol)

	Areas				Conversion		
time	BnOH	*p*-Cl-aniline	*p*-CN-aniline	Tetramethylbenzene	BnOH	*p*-Cl-aniline	*p*-CN-aniline
0 - no cat.	233314	93183	103012	166550	-0.0034	0.0058	0.0001
0 - cat.	178896	72108	79263	128135	0.0000	0.0000	0.0000
30 min	214225	82386	99233	166475	0.0783	0.1206	0.0364
1 h	201588	71375	99824	170991	0.1556	0.2583	0.0562
2 h	118369	33458	68688	119250	0.2890	0.5014	0.0688
3 h	116703	23827	78155	141923	0.4110	0.7017	0.1098
4 h	113251	16425	85178	160923	0.4959	0.8186	0.1443
5 h	97388	8353	80651	163787	0.5741	0.9094	0.2040
6 h	68706	3219	61793	136057	0.6383	0.9580	0.2658
7 h	74327	2888	72650	167028	0.6813	0.9693	0.2969
8 h	63142	1989	63461	157813	0.7134	0.9776	0.3499



Competition experiment 15, *p*-(dimethylamino)aniline vs. *p*-anisidine

K_2CO_3 (14 mg, 0.10 mmol)

p-anisidine (122 mg, 0.99 mmol)

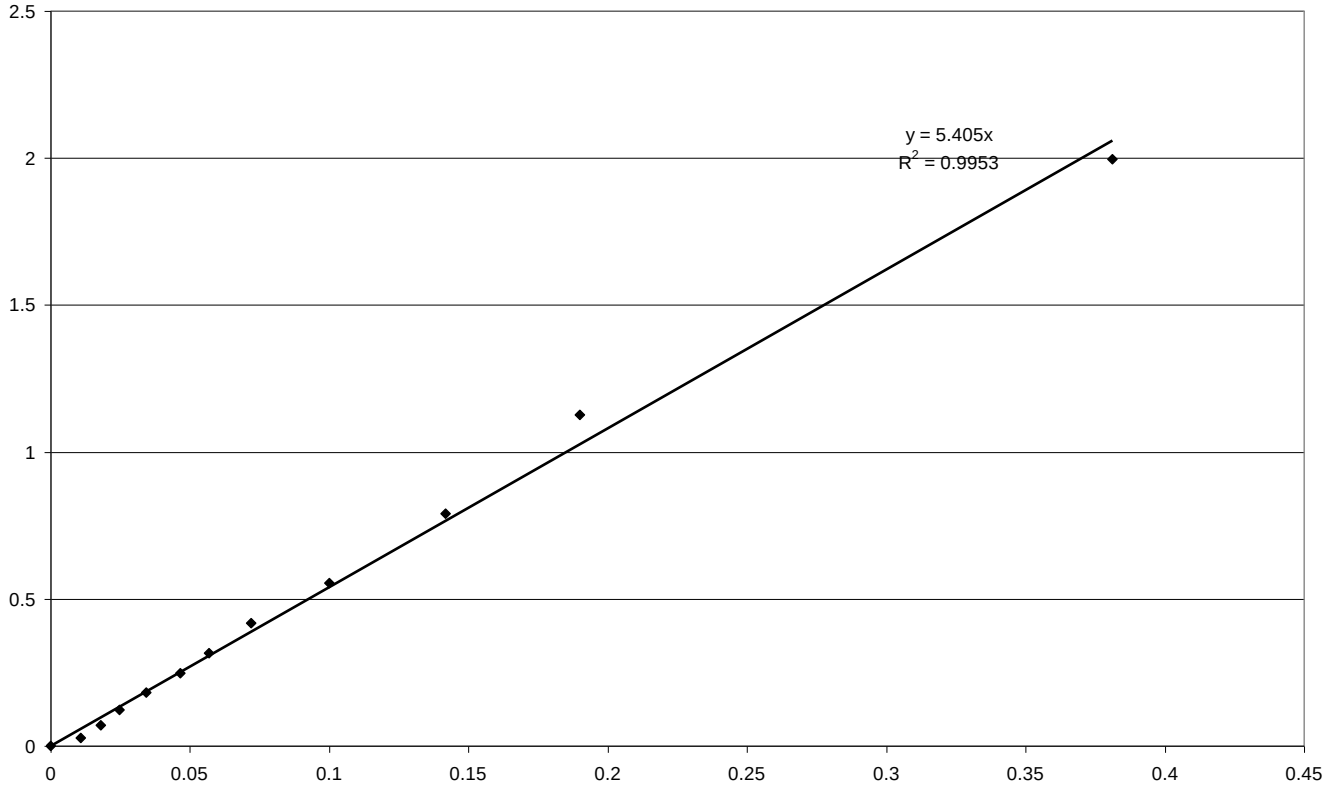
p-(dimethylamino)aniline (135 mg, 0.99 mmol)

benzyl alcohol (210 µL, 2.03 mmol)

1,2,4,5-tetramethylbenzene (132 mg, 0.98 mmol)

$[Cp^*IrCl_2]_2$ (39 mg, 0.049 mmol)

	Areas				Conversion		
time	BnOH	*p*-MeO-aniline	*p*-NMe_2-aniline	Tetramethylbenzene	BnOH	*p*-MeO-aniline	*p*-NMe_2-aniline
0 - no cat.	194107	81284	93998	140054	-0.0199	0.0060	-0.0213
0 - cat.	146101	62771	70648	107509	0.0000	0.0000	0.0000
15 min	231065	100203	111051	173475	0.0199	0.0107	0.0258
30 min	196023	86241	92017	150397	0.0409	0.0179	0.0689
45 min	234581	104980	107067	184316	0.0635	0.0245	0.1160
1 h	185058	84790	82286	150286	0.0939	0.0337	0.1668
75 min	174824	81623	75079	146444	0.1215	0.0454	0.2198
90 min	210558	100370	87288	181959	0.1485	0.0553	0.2700
105 min	135580	67000	53411	123328	0.1910	0.0695	0.3410
2 h	170809	88012	62926	166598	0.2455	0.0952	0.4252
150 min	170965	93984	55340	185493	0.3218	0.1322	0.5460
3 h	102274	61037	26934	126408	0.4046	0.1730	0.6758
4 h	89794	60893	13643	152671	0.5672	0.3169	0.8640
5 h	83232	60963	6097	202967	0.6982	0.4856	0.9543
6 h	42241	30267	1720	140723	0.7791	0.6316	0.9814



Primary KIE determination

Compounds loads:

K_2CO_3 (15 mg, 0.11 mmol)

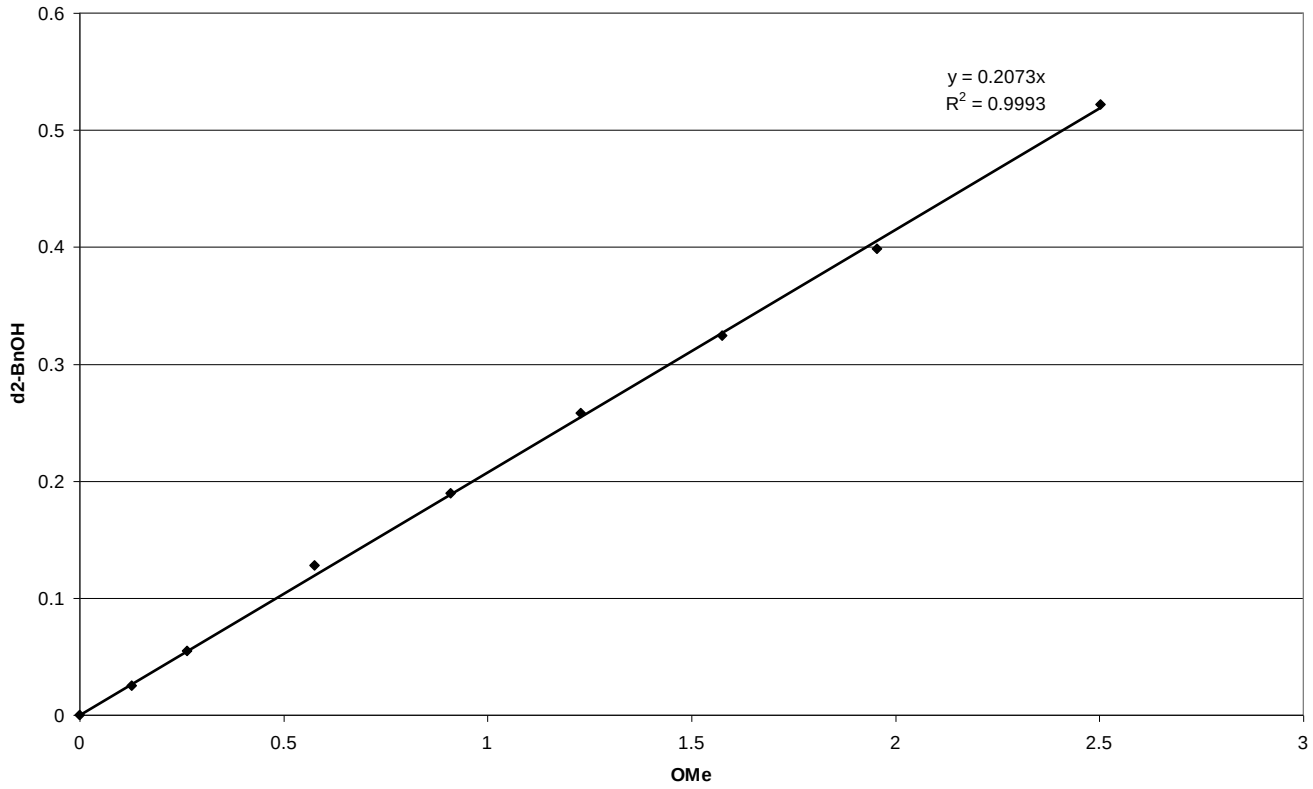
aniline (180 µL, 2 mmol)

benzyl alcohol (105 µL, 1 mmol)

p-methoxybenzyl alcohol (125 µL, 1 mmol)

naphthalene (125 mg, 0.98 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)



$k_D/k_{OMe} = 0.207$

$k_{OMe}/k_H = 1.944$

$k_H/k_D = 2.48$

Primary KIE determination with benzyl alcohol α,α-d_2 vs. *p*-chlorobenzyl alcohol

K_2CO_3 (14 mg, 0.10 mmol)

aniline (186 mg, 2 mmol)

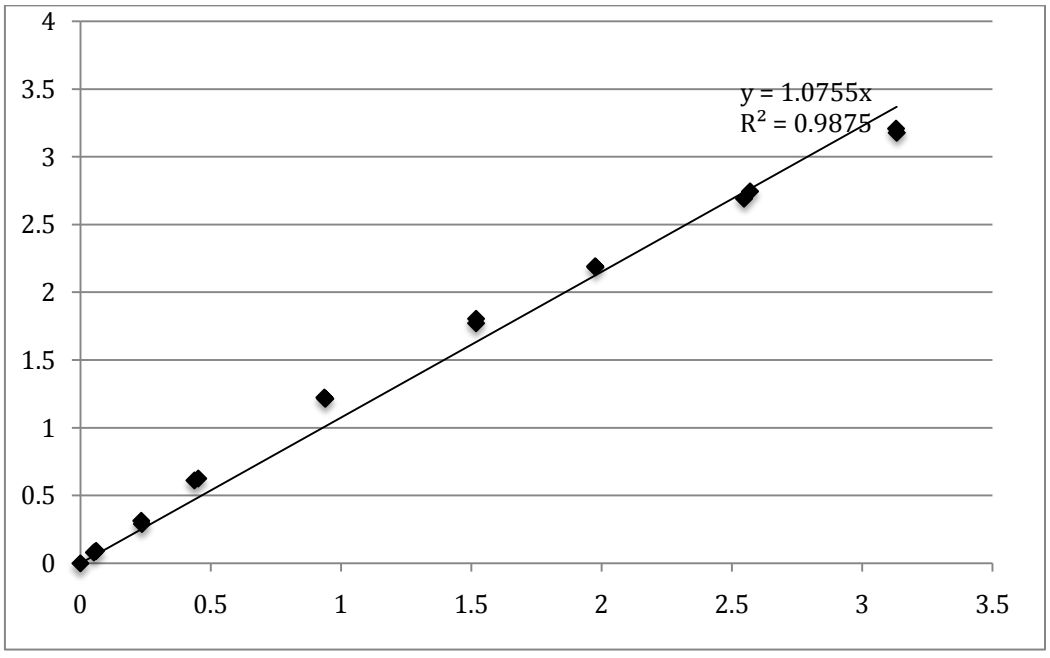
benzyl alcohol α,α-d_2 (110 mg, 1 mmol)

p-chlorobenzyl alcohol (142 mg, 1 mmol)

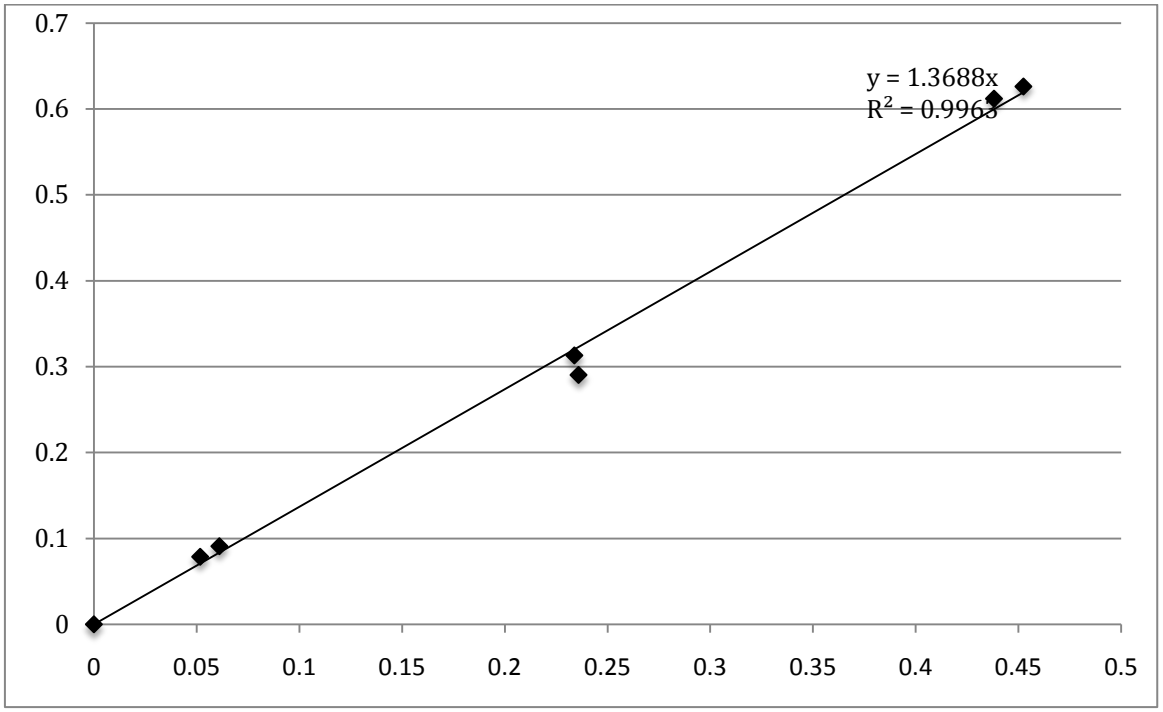
naphthalene (129 mg, 1 mmol)

$[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol)

	Areas			Conversion	
Time	*d2*-BnOH	*p*-Cl-BnOH	Naphthalene	*d2*-BnOH	*p*-Cl-BnOH
0 - no cat.	154477	104752	217235	0	0
30 min	188203	124221	278685	0.0503	0.0756
1h	98966	63562	176199	0.2101	0.2519
2h	91076	51902	198512	0.3548	0.4578
3h	52796	27193	190094	0.6094	0.7033
4h	36222	19047	232507	0.7809	0.8301
6h	21170	11555	214654	0.8613	0.8884
	13724	7816	252091	0.9234	0.9357
8h	8135	5101	261655	0.9563	0.9596



There seems to be a slight curvature which may arise from loss of deuterium from benzyl alcohol α,α-d_2. When only the first part of the curve is plotted the difference in reactivity is significantly higher (1.37).



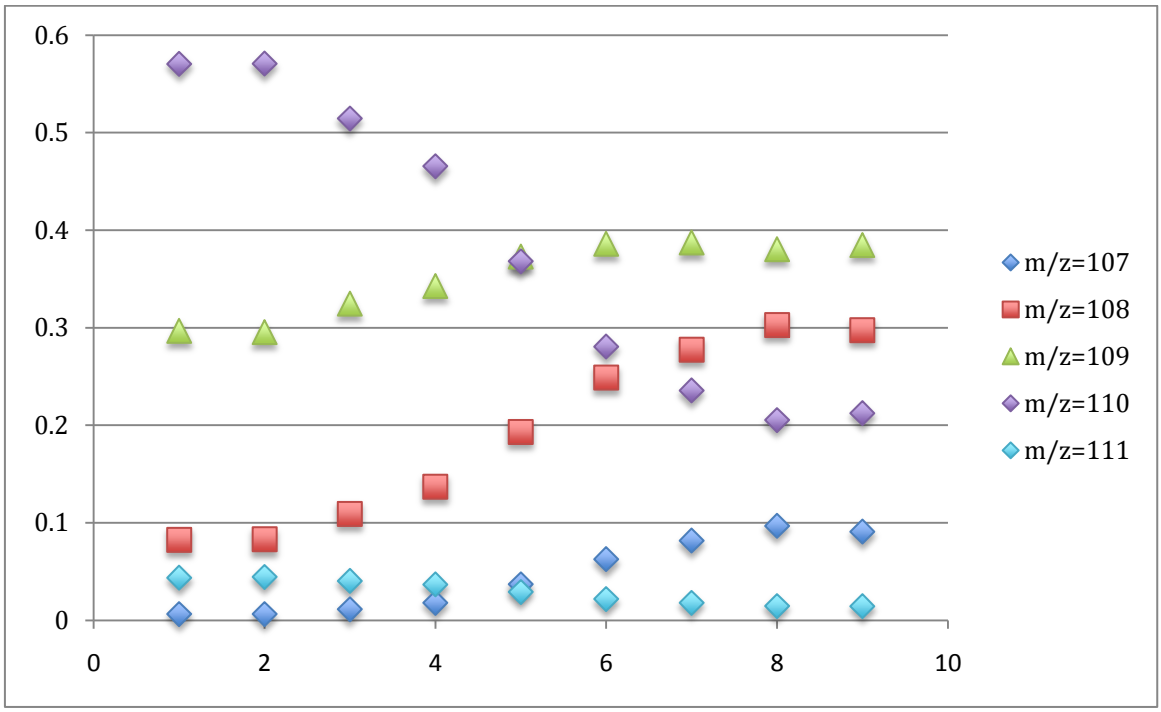
Using these data one can again determine the kinetic isotope effect (KIE) as follows:

$k_{Cl}/k_D = 1.37$

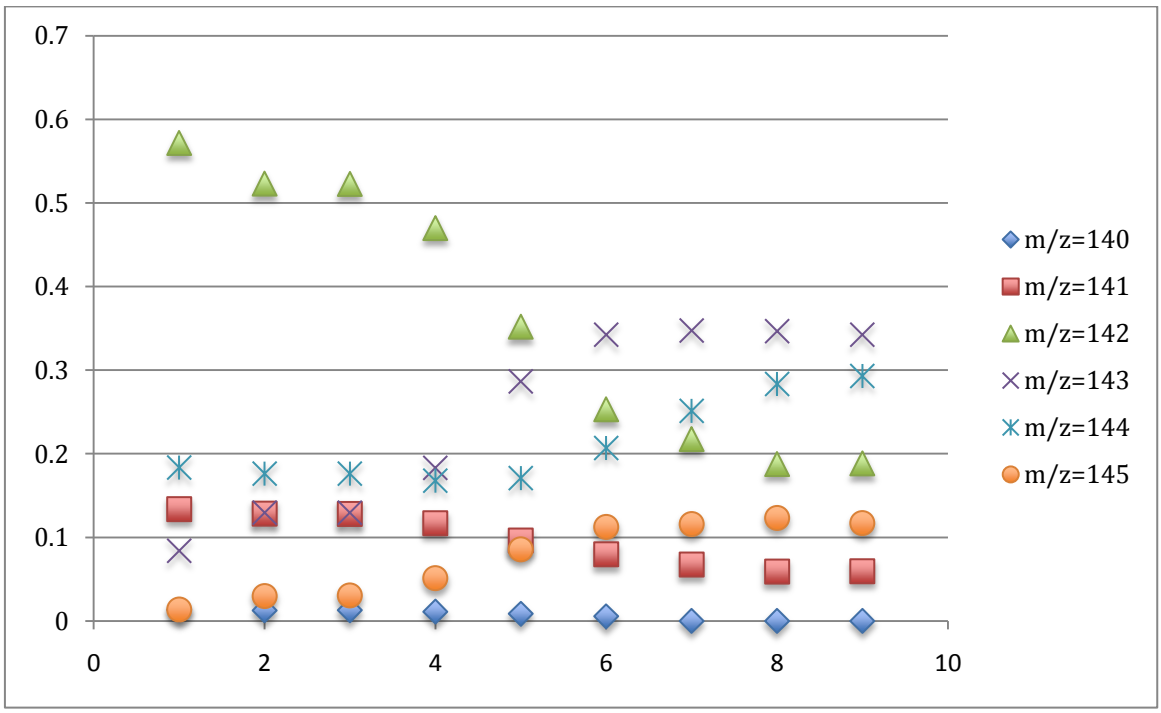
$k_{Cl}/k_H = 0.71$

$k_H/\ k_D = 1.94$

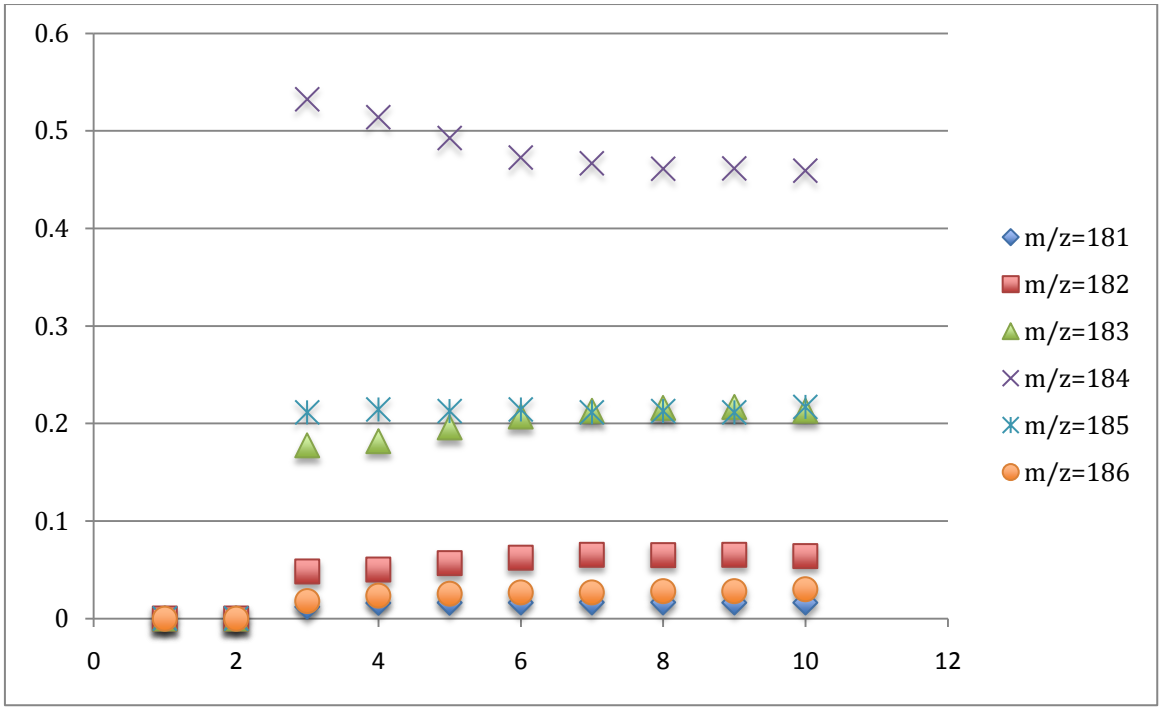
GC-MS data from primary KIE determination, benzyl alcohol α,α-d_2 vs. *p*-chlorobenzyl alcohol



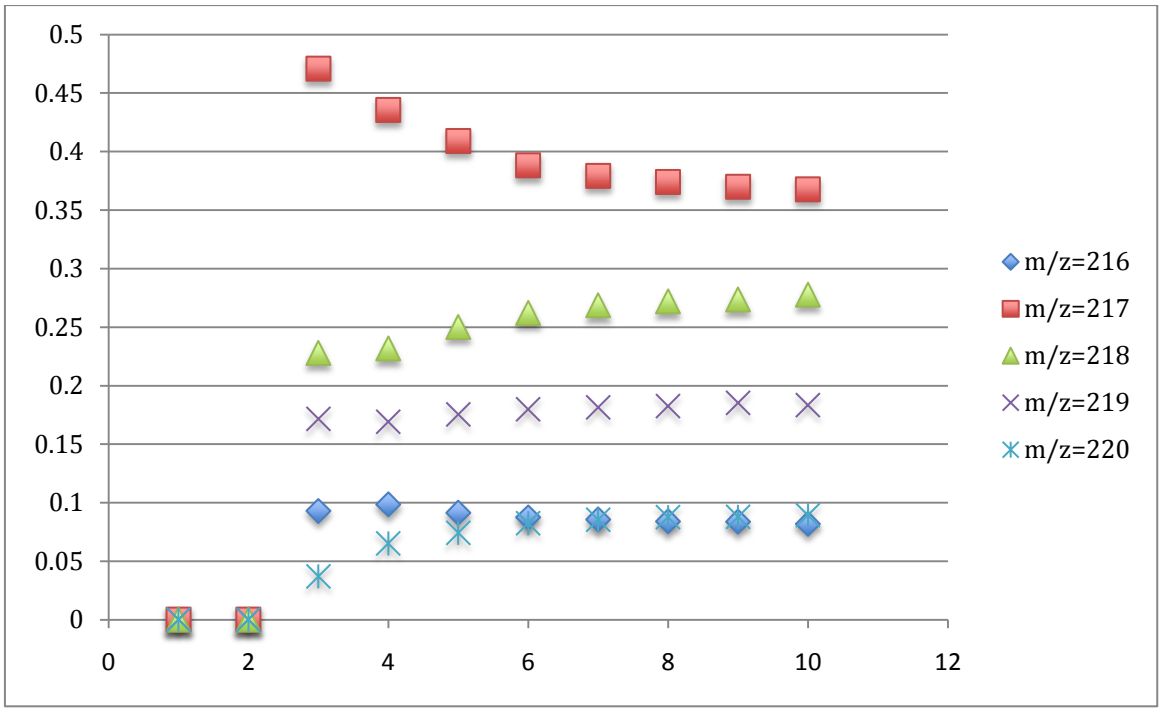
GC-MS data showing that the benzyl alcohol α,α-d_2 (m/z=110) loses its deuterium content during the reaction.



GC-MS data showing that the undeuterated *p*-chlorobenzyl alcohol (m/z=142) increases its deuterium content during the reaction (m/z=144).

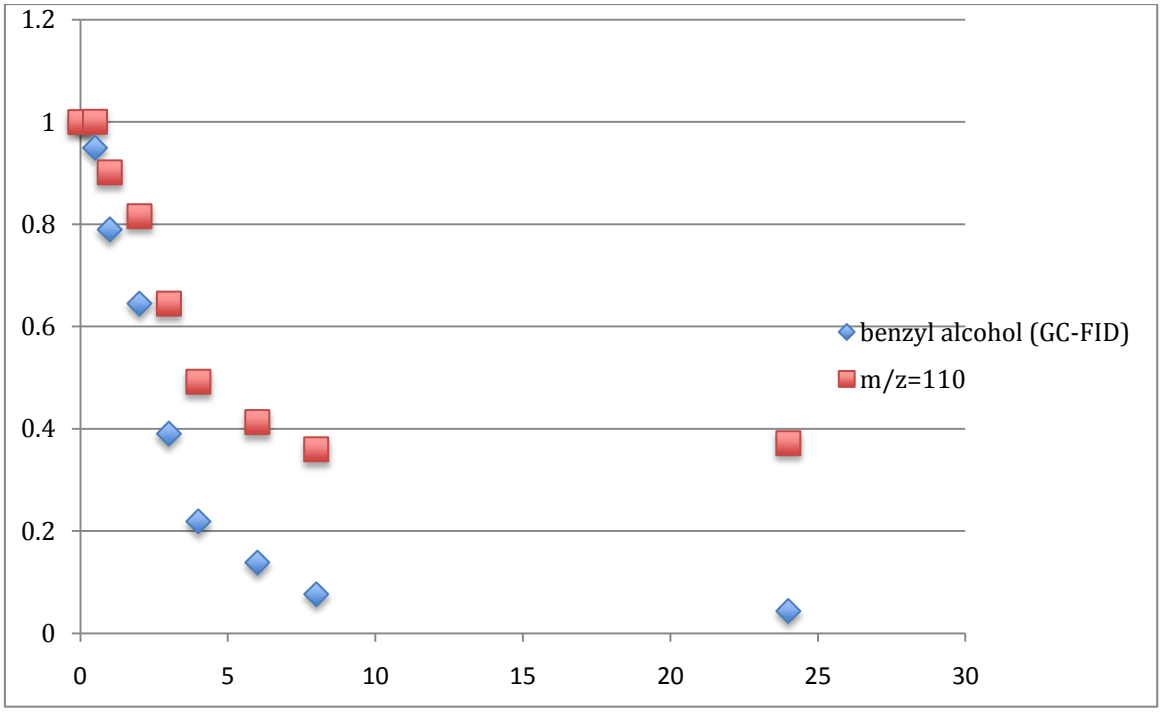


GC-MS data showing the data for the unsubstituted product. Here, the deuterium content is high (m/z=184) and also remains relatively high during the reaction which illustrates that the final reduction to the amine is virtually irreversible.



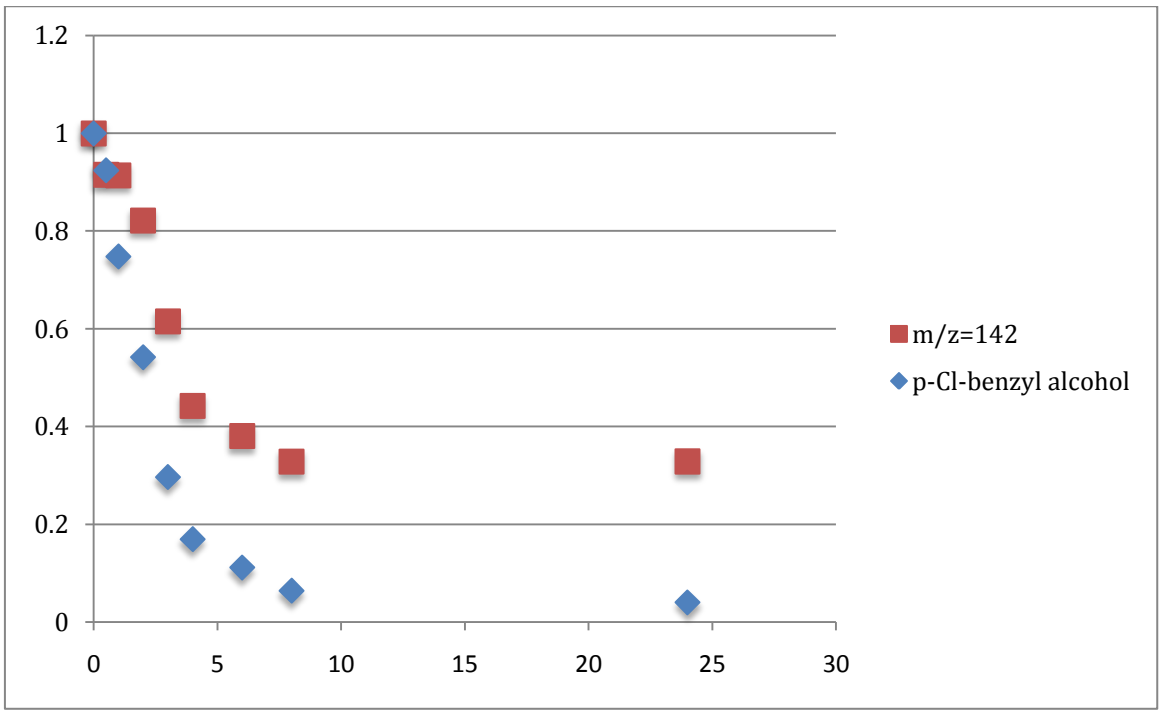
GC-MS data for the chloro-substituted amine product. Here, the deuterium content is low in the beginning (m/z=217), but gradually increases (m/z=218).

To estimate the degree of reversibility of the initial alcohol oxidation we decided to plot the conversion of benzyl alcohol measured by GC-FID (i.e. total amount irrespective of deuterium content) versus the decrease of the m/z=110 signal.



Since the experiment was run under competetion conditions one will not obtain absolute kinetics or reaction orders, but it is still clear that the disappearance of the benzyl alcohol is faster than the deuterium exchange of the unreacted benzyl alcohol α,α-d_2.

The same type of analysis was carried out for *p*-chlorobenzyl alcohol.



Also here the disappearance of the total amount of *p*-chlorobenzyl alcohol is significantly faster than the proton/deuterium exchange.

Racemisation experiment

In an oven-dried Schlenk tube were placed K_2CO_3 (4 mg, 0.03 mmol), (*R*)-1-deutero-1-phenylethanol (29 mg, 0.24 mmol, 81% *ee*), acetophenone (30 mg, 0.24 mmol) and dry toluene (0.5 mL). The mixture was placed in an oil bath preheated to 110 °C and a GC sample was taken out. Then, $[Cp^*IrCl_2]_2$ (10 mg, 0.0125 mmol) was added. After addition of the catalyst, a GC sample was taken out immediately. Then, GC samples were taken out after 30 min, 1h, 2h, 3h, 4h, 5h. At that time, GC analysis showed 8% *ee* (Column: Chrompack CP Chirasil-Dex CB 0.25 mm x 25 m column), the reaction mixture was cooled down to rt and subjected to column chromatography (hexane/Et_2O 4/1), which yielded 10 mg of 1-phenylethanol. The ^1H content was determined by NMR to be 6%.

Computational study

The description of the computational method is included in the main text of the manuscript.

Two available crystal structures (Refcode: DCPMIR, ARADAY01)[1] were used to access the accuracy of the applied computational method (B3LYP in combination with an effective core potential for iridium). Below is shown an overlay of the crystal structure (blue) with the calculated structure (red) (figure S1 and S2). The superimposition was performed for atoms heavier than hydrogen to avoid the otherwise dominating influence of the methyl rotation. For the DCPMIR structure the RMSD was 0.0951 Å, indicating an acceptable overall structural similarity. The largest errors in the computational structure was found to be overly long Ir-Cl and Ir-Cpstar bonds, in both cases on the order of 0.04-0.05Å which we are confident will not influence the overall conclusions reached in this study. For ARADAY01 structure the RMSD was calculated to 0.1112 Å, slightly higher than for the DCPMIR structure, which to some degree can be assigned to the lack of symmetry in the crystal structure, resulting in three slightly different experimental Ir-Cl bond lengths.

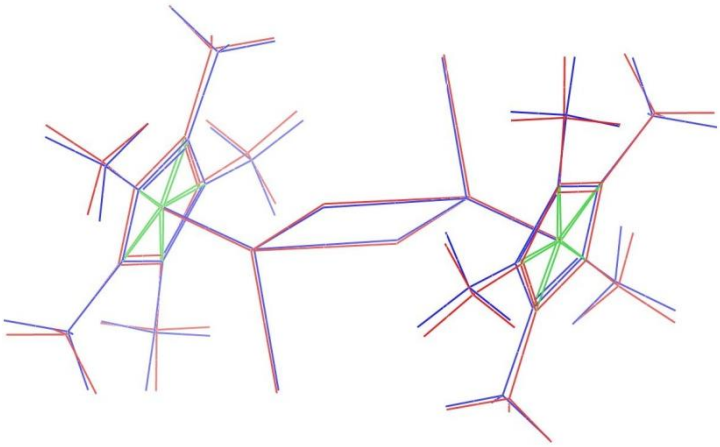


Figure S1 Overlay of X-ray structure (blue, DCPMIR) with a structure energy minimized using DFT/B3LYP (red). RMSD for non-hydrogen atoms were 0.0951 Å.

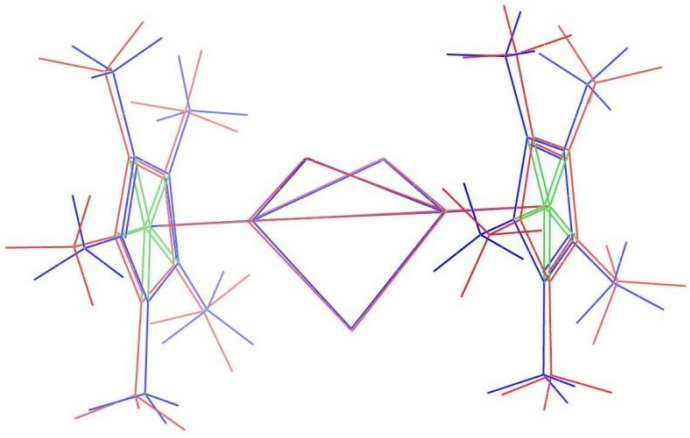


Figure S2 Overlay of X-ray structure (blue, ARADAY01) with a structure energy minimized using DFT/B3LYP (red). RMSD for non-hydrogen atoms were 0.1112 Å.

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(1) (*a*) DCPMIR: M. R. Churchill, S. A. Julis, *Inorg. Chem.*, 1977, **16**, 1488-1494; (*b*) ARADAY01: M. Maekawa, Y. Suenaga, T. Kuroda-Sowa, M. Munakata, *Anal. Sci.*, 2004, **20**, x11-x12.

XYZ Coordinates and energies for calculated complexes.

Ir2_Cpstar2_Cl4_dimer
E_scf (B3LYP/6-31G*) = -2830.59978674074 a.u.
E_scf (M06/6-31G*) = -2829.81044552623 a.u.
E_Gibbs = -2830.216703 a.u.
E_solv = -2830.61290539357 a.u.
ZPE = 284.281 kcal/mol

Ir	1.40005	0.37059	1.23409
Cl	0.89402	0.65138	-1.21286
Cl	2.29532	-1.82983	0.72157
C	1.62705	2.52420	1.59077
C	0.85782	1.95299	2.65529
C	1.67389	0.92366	3.30701
C	2.96791	0.91049	2.65687
C	2.93350	1.85913	1.56464
C	1.17530	3.62153	0.67575
C	-0.53458	2.35245	3.04001
C	1.28292	0.13599	4.52097
C	4.13877	0.06023	3.04173
C	4.07428	2.20625	0.65664
Cl	-0.89402	-0.65138	1.21286
Ir	-1.40005	-0.37059	-1.23409
Cl	-2.29532	1.82983	-0.72157
C	-1.62705	-2.52420	-1.59077
C	-0.85782	-1.95299	-2.65529
C	-1.67389	-0.92366	-3.30701
C	-2.96791	-0.91049	-2.65687
C	-2.93350	-1.85913	-1.56464
C	-1.17530	-3.62153	-0.67575
C	0.53458	-2.35245	-3.04001
C	-1.28292	-0.13599	-4.52097
C	-4.13877	-0.06023	-3.04173
C	-4.07428	-2.20625	-0.65664
H	1.34367	4.59826	1.14913
H	1.72316	3.60239	-0.26907
H	0.11269	3.52498	0.43770
H	-0.50400	3.22553	3.70612
H	-1.13063	2.60464	2.15875
H	-1.05086	1.54395	3.56257
H	1.50616	0.70201	5.43575
H	0.21320	-0.08966	4.51680
H	1.82221	-0.81338	4.56793
H	4.78769	0.61343	3.73455
H	3.81757	-0.86185	3.53054
H	4.72744	-0.22290	2.16648
H	4.65888	3.03834	1.07261
H	4.74401	1.35356	0.52142
H	3.71507	2.50709	-0.33115
H	-1.34367	-4.59826	-1.14913
H	-0.11269	-3.52498	-0.43770
H	-1.72316	-3.60239	0.26907
H	0.50400	-3.22553	-3.70612
H	1.05086	-1.54395	-3.56257
H	1.13063	-2.60464	-2.15875
H	-1.50616	-0.70201	-5.43575
H	-1.82221	0.81338	-4.56793
H	-0.21320	0.08966	-4.51680
H	-4.78769	-0.61343	-3.73455
H	-4.72744	0.22290	-2.16648
H	-3.81757	0.86185	-3.53054
H	-4.65888	-3.03834	-1.07261
H	-3.71507	-2.50709	0.33115
H	-4.74401	-1.35356	-0.52142

Ir_Cpstar_Cl2_monomer
E_scf (B3LYP/6-31G*) = -1415.28792421121 a.u.
E_scf (M06/6-31G*) = -1414.88095256718 a.u.
E_solv = -1415.30056115991 a.u.
E_Gibbs = -1415.106428 a.u.
ZPE = 141.716 kcal/mol

Ir	0.39820	-1.01633	2.61002
Cl	-0.63653	1.05498	2.99589
Cl	-1.46621	-1.75061	1.38498
C	1.45057	-2.18357	4.08374
C	1.54926	-2.88281	2.81052
C	2.19672	-1.99446	1.88771
C	2.55569	-0.76390	2.60715
C	2.12572	-0.89802	3.96951
C	0.84485	-2.73833	5.33588
H	0.02626	-3.42662	5.11200
H	0.45216	-1.94357	5.97481
H	1.60580	-3.28870	5.90648
C	1.05554	-4.26603	2.51486
H	1.86512	-4.99771	2.63636
H	0.67524	-4.33866	1.49280
H	0.23986	-4.54860	3.18488
C	2.52100	-2.28716	0.45522
H	2.50047	-1.37841	-0.15204
H	1.80840	-2.99368	0.02373
H	3.52638	-2.72302	0.37747
C	3.30575	0.39444	2.02503
H	3.06854	1.32364	2.54808
H	3.06557	0.53495	0.96781
H	4.38766	0.22175	2.10580
C	2.32407	0.10408	5.06568
H	3.31164	-0.02268	5.52850
H	1.56763	-0.00544	5.84662
H	2.25040	1.12540	4.68360

Ir_Cpstar_PhNH2_PhCO_alcohol (**1a**)
E_scf (B3LYP/6-31G*) = -1128.41741204488 a.u.
E_scf (B3LYP/6-31G+*) = -1128.44109688036 a.u.
E_scf (M06/6-31G*) = -1127.60152790116 a.u.
E_scf (M06/6-31G+*) = -1127.62253578181 a.u.
E_solv = -1128.45406105785 a.u.
E_Gibbs = -1128.006407 a.u.
ZPE = 294.228 kcal/mol

C	0.00000	0.00000	0.00000
C	0.00000	0.00000	1.43103
C	1.40146	0.00000	1.86230
C	2.24660	0.07147	0.69317
C	1.39718	0.02007	-0.45977
C	-1.20377	0.03132	-0.89094
H	-2.07611	-0.41383	-0.40673
H	-1.02458	-0.49969	-1.82974
H	-1.45053	1.07215	-1.14035
C	-1.20178	0.02521	2.32562
H	-1.54442	1.05736	2.47263
H	-0.97736	-0.39750	3.30828
H	-2.02708	-0.55056	1.89831
C	1.86661	0.05002	3.28395
H	2.88131	-0.34161	3.39256
H	1.20618	-0.51528	3.94706
H	1.87273	1.09276	3.63048
C	3.73735	0.22634	0.68986
H	4.19438	-0.24346	-0.18385

H	4.19553	-0.21122	1.58130
H	3.99767	1.29308	0.67377
C	1.83180	0.13100	-1.88939
H	1.86230	1.18775	-2.18829
H	1.13880	-0.38088	-2.56210
H	2.82812	-0.28984	-2.04364
H	0.40988	-4.94895	1.69834
Ir	0.98652	-1.81531	0.70769
C	-0.39297	-4.53738	1.04253
O	-0.42352	-3.11818	1.08343
H	-1.35621	-4.85830	1.46247
C	0.04611	-6.23867	-2.92054
C	0.67145	-6.84106	-1.82925
C	0.53594	-6.28763	-0.55202
C	-0.22743	-5.12803	-0.35162
C	-0.85892	-4.53463	-1.45654
C	-0.72124	-5.08578	-2.73064
H	0.15067	-6.66628	-3.91422
H	1.26670	-7.73933	-1.96840
H	1.01982	-6.76956	0.29673
H	-1.46220	-3.64338	-1.30808
H	-1.22102	-4.62288	-3.57778
N	2.35352	-3.46136	0.33430
H	1.81993	-4.14065	-0.22295
H	2.50895	-3.91469	1.23905
C	6.08289	-2.80145	-1.57363
C	6.02375	-2.92750	-0.18475
C	4.79890	-3.13995	0.45179
C	3.63510	-3.22284	-0.31120
C	3.68248	-3.10354	-1.70182
C	4.91140	-2.89375	-2.32905
H	7.03752	-2.64069	-2.06627
H	6.93205	-2.86795	0.40795
H	4.75630	-3.24887	1.53394
H	2.77058	-3.19029	-2.28816
H	4.95286	-2.81096	-3.41159

Ir_Cpstar_PhNH2_PhCO_E_TS (**1b**)
E_scf (B3LYP/6-31G*) = -1128.39698846890 a.u.
E_scf (B3LYP/6-31G+*) = -1128.4220149877 a.u.
E_scf (M06/6-31G*) = -1127.58421739353 a.u.
E_scf (M06/6-31G+*) = -1127.60561866302 a.u.
E_solv = -1128.433844 a.u.
E_Gibbs = -1127.991528 a.u.
ZPE = 291.649 kcal/mol

C	0.00000	0.00000	0.00000
C	0.00000	0.00000	1.45266
C	1.38333	0.00000	1.89458
C	2.23456	-0.06653	0.73801
C	1.36631	-0.06655	-0.44219
C	-1.22213	0.05248	-0.86412
H	-2.02942	-0.56000	-0.45253
H	-1.01717	-0.29656	-1.87902
H	-1.58474	1.08622	-0.93156
C	-1.21483	0.14123	2.32189
H	-1.48711	1.19942	2.42715
H	-1.04278	-0.25532	3.32631
H	-2.07420	-0.38262	1.89418
C	1.84535	0.09821	3.31746
H	2.80761	-0.39808	3.46523
H	1.12327	-0.34050	4.01040
H	1.96784	1.15434	3.59155
C	3.73143	0.03020	0.72396
H	4.16781	-0.53573	-0.10298
H	4.16791	-0.34901	1.65136

H	4.03920	1.07846	0.61263
C	1.84627	-0.00288	-1.86064
H	2.04107	1.04130	-2.13915
H	1.10527	-0.39818	-2.56036
H	2.78057	-0.55467	-1.99439
H	1.06027	-3.04056	2.08487
Ir	0.94801	-1.86274	0.77350
C	-0.12315	-3.70175	1.84727
O	-0.54630	-3.35689	0.62769
H	-0.69249	-3.28700	2.69269
C	1.25583	-7.72502	2.49595
C	1.32932	-6.78483	3.52941
C	0.87935	-5.48408	3.32059
C	0.35756	-5.11120	2.07326
C	0.27447	-6.05709	1.04305
C	0.72251	-7.36269	1.25888
H	1.60680	-8.73979	2.66092
H	1.73455	-7.06953	4.49635
H	0.93328	-4.75479	4.12735
H	-0.17992	-5.77470	0.09746
H	0.64567	-8.09820	0.46308
N	2.01155	-3.45437	-0.32296
H	1.62146	-3.42902	-1.26558
H	1.67796	-4.33435	0.08301
C	6.25030	-3.46448	-0.47075
C	5.58386	-3.79305	0.71276
C	4.19109	-3.78458	0.76400
C	3.46342	-3.45273	-0.38065
C	4.11891	-3.13599	-1.57068
C	5.51599	-3.13791	-1.61049
H	7.33573	-3.47119	-0.50499
H	6.15052	-4.05946	1.60039
H	3.67133	-4.03923	1.68427
H	3.54882	-2.90912	-2.46946
H	6.02555	-2.89552	-2.53855

Ir_Cpstar_PhNH2_PhCO_aldehyde (**1c**)
E_scf (B3LYP/6-31G*) = -1128.41630452236 a.u.
E_scf (B3LYP/6-31G+*) = -1128.43996372608 a.u.
E_scf (M06/6-31G*) = -1127.59885490471 a.u.
E_scf (M06/6-31G+*) = -1127.60753286739 a.u.
E_solv = -1128.45181701163 a.u.
E_Gibbs = -1128.009846 a.u.
ZPE = 292.452 kcal/mol

C	0.00000	0.00000	0.00000
C	0.00000	0.00000	1.46722
C	1.36388	0.00000	1.92223
C	2.20920	-0.16661	0.74513
C	1.33988	-0.08622	-0.43728
C	-1.24291	0.05303	-0.83507
H	-1.95309	-0.72174	-0.52699
H	-1.02741	-0.08829	-1.89665
H	-1.74091	1.02382	-0.72028
C	-1.22897	0.17840	2.30948
H	-1.55524	1.22598	2.28339
H	-1.04656	-0.08453	3.35459
H	-2.05853	-0.43273	1.93982
C	1.83686	0.22282	3.32920
H	2.79673	-0.26488	3.51463
H	1.12005	-0.15264	4.06393
H	1.96619	1.29841	3.50692
C	3.70713	-0.07174	0.71398
H	4.13411	-0.67821	-0.08905
H	4.14795	-0.40871	1.65560
H	4.01665	0.96906	0.55234

C	1.83753	-0.06602	-1.85020
H	2.19863	0.94063	-2.10054
H	1.05187	-0.32255	-2.56550
H	2.67505	-0.75464	-1.99376
H	1.82749	-2.63973	2.13159
Ir	0.96507	-1.93958	0.98050
C	-0.58636	-3.38314	1.98110
O	-0.83842	-3.12305	0.74322
H	-1.02107	-2.73401	2.75304
C	0.74695	-7.21562	3.33635
C	0.69662	-6.13348	4.22097
C	0.25770	-4.88965	3.77629
C	-0.12176	-4.71096	2.43663
C	-0.09152	-5.80743	1.55742
C	0.34326	-7.05352	2.00881
H	1.08684	-8.18657	3.68577
H	0.99713	-6.26384	5.25654
H	0.21997	-4.04752	4.46416
H	-0.45540	-5.68680	0.54051
H	0.35335	-7.90186	1.33013
N	1.71312	-3.63296	-0.18199
H	1.03837	-3.75209	-0.93922
H	1.58425	-4.44103	0.43278
C	5.66630	-3.63400	-1.71566
C	5.44185	-3.81606	-0.34839
C	4.14426	-3.80680	0.16146
C	3.06752	-3.62167	-0.70816
C	3.27990	-3.44977	-2.07644
C	4.58453	-3.45199	-2.57684
H	6.67929	-3.64100	-2.10705
H	6.28005	-3.96697	0.32575
H	3.96837	-3.93939	1.22584
H	2.43592	-3.33245	-2.75328
H	4.74931	-3.32310	-3.64263

Ir_Cpstar_H_Hemiaminal_bidentate (**1d**)
E_scf (B3LYP/6-31G*) = -1128.39961212675 a.u.
E_scf (B3LYP/6-31G+*) = -1128.424523 a.u.
E_scf (M06/6-31G*) = -1127.583319 a.u.
E_scf (M06/6-31G+*) = -1127.604427 a.u.
E_solv = -1128.43749216801 a.u.
E_Gibbs = -1127.989254 a.u.
ZPE = 293.273 kcal/mol

C	0.32580	-0.24470	2.00260
O	0.05070	1.06630	2.55900
H	1.37710	-0.31040	1.72130
H	0.87680	1.56330	2.67680
N	-0.49080	-0.25740	0.73910
C	1.43860	-1.64840	-2.77970
C	2.04660	-0.66370	-1.99860
C	1.42060	-0.18920	-0.84600
C	0.18680	-0.72090	-0.46100
C	-0.42460	-1.70800	-1.23670
C	0.19940	-2.16350	-2.39910
H	1.92780	-2.01090	-3.67870
H	3.01010	-0.25560	-2.28980
H	1.88990	0.60000	-0.26420
H	-1.38280	-2.12560	-0.93430
H	-0.28200	-2.93050	-2.99850
C	-0.78400	-3.51520	4.55150
C	-1.52900	-2.33410	4.58350
C	-1.16680	-1.25220	3.78220
C	-0.04840	-1.35450	2.94370
C	0.70280	-2.53690	2.91930

C	0.33320	-3.61580	3.72100
H	-1.07050	-4.35460	5.17860
H	-2.39220	-2.25320	5.23780
H	-1.73930	-0.32990	3.81490
H	1.57700	-2.61530	2.27620
H	0.91990	-4.52950	3.70090
H	-1.29610	-0.86180	0.89680
Ir	-1.33730	1.79790	0.85990
C	-0.89380	2.97030	-1.15500
C	-2.29240	2.58320	-0.89270
C	-2.75010	3.32910	0.26940
C	-1.59400	3.96930	0.83440
C	-0.46390	3.78820	-0.09790
C	-0.12320	2.55460	-2.36960
H	-0.28420	1.50070	-2.61350
H	0.95140	2.71260	-2.25140
H	-0.45280	3.14430	-3.23570
C	-3.16100	1.83630	-1.86190
H	-3.50440	2.50670	-2.66150
H	-4.04480	1.42230	-1.37020
H	-2.61740	1.01140	-2.33220
C	-4.16650	3.44370	0.74930
H	-4.21670	3.61260	1.82770
H	-4.74300	2.54360	0.52250
H	-4.65500	4.29140	0.25100
C	-1.57740	4.87790	2.02780
H	-0.62540	4.82380	2.56500
H	-2.37450	4.62870	2.73240
H	-1.71870	5.92080	1.71370
C	0.88470	4.42100	0.07380
H	0.85300	5.47600	-0.22870
H	1.64570	3.92700	-0.53540
H	1.21490	4.40080	1.11780
H	-2.43190	1.06260	1.77820

Ir_Cpstar_H_Hemiaminal_Hshift (**1e**)
E_scf (B3LYP/6-31G*) = -1128.39958012802 a.u.
E_scf (B3LYP/6-31G+*) = -1128.42452349778 a.u.
E_scf (M06/6-31G*) = -1127.60442655919 a.u.
E_scf (M06/6-31G+*) = -1127.60442655919 a.u.
E_solv = -1128.43546989413 a.u.
E_Gibbs = -1127.995229 a.u.
ZPE = 291.117 kcal/mol

C	-0.05830	-1.34080	1.29040
O	0.04640	1.45230	2.80840
H	0.55710	-2.11540	0.82700
H	-0.25010	2.17740	3.38410
N	-0.34880	-0.33280	0.52650
C	1.17820	-0.99760	-3.36900
C	1.99410	-0.43500	-2.38550
C	1.48850	-0.18650	-1.10790
C	0.15960	-0.50690	-0.82220
C	-0.66400	-1.07450	-1.79660
C	-0.14890	-1.31610	-3.07240
H	1.57670	-1.19480	-4.35990
H	3.03020	-0.19580	-2.60780
H	2.11810	0.24410	-0.33390
H	-1.68780	-1.33920	-1.54850
H	-0.78360	-1.76810	-3.82940
C	-0.77460	-2.40130	5.36890
C	-1.73500	-1.63180	4.70620
C	-1.53990	-1.24380	3.38130
C	-0.37110	-1.63310	2.69630

C	0.56830	-2.44550	3.36520
C	0.37780	-2.80980	4.69440
H	-0.93310	-2.69660	6.40200
H	-2.64880	-1.34460	5.21820
H	-2.30430	-0.67560	2.86480
H	1.45610	-2.78290	2.83580
H	1.11920	-3.42260	5.19820
Ir	-1.22980	1.59850	0.91180
C	-0.80690	2.91770	-1.07550
C	-2.18310	2.43850	-0.85270
C	-2.68940	3.10190	0.34060
C	-1.57370	3.76210	0.95490
C	-0.42380	3.68670	0.03290
C	-0.01270	2.66100	-2.31700
H	-0.17020	1.65220	-2.70340
H	1.05840	2.80150	-2.15710
H	-0.32810	3.36470	-3.10020
C	-3.02660	1.75290	-1.88840
H	-3.42070	2.48600	-2.60550
H	-3.87800	1.23960	-1.43350
H	-2.44840	1.01600	-2.45140
C	-4.11920	3.13510	0.79520
H	-4.20000	3.26960	1.87690
H	-4.64760	2.21620	0.52980
H	-4.63880	3.97350	0.31250
C	-1.61580	4.61910	2.18730
H	-0.66550	4.59520	2.73290
H	-2.41330	4.31020	2.86880
H	-1.79790	5.66780	1.91870
C	0.89230	4.36870	0.26110
H	0.80990	5.44370	0.05240
H	1.67560	3.96480	-0.38490
H	1.22910	4.26610	1.29790
H	-2.36510	0.81830	1.70720
H	-0.21180	0.63120	3.27270

Ir_Cpstar_PhNH2_PhCNPh_imine (**1f**)
E_scf (B3LYP/6-31G*) = -1339.58902420953 a.u.
E_scf (B3LYP/6-31G+*) = -1339.6042702536 a.u.
E_scf (M06/6-31G*) = -1338.58214250675 a.u.
E_scf (M06/6-31G+*) = -1338.60723679592 a.u.
E_solv = -1339.62324053399 a.u.
E_Gibbs = -1339.092519 a.u.
ZPE = 351.163 kcal/mol

C	0.00000	0.00000	0.00000
C	0.00000	0.00000	1.46035
C	1.36893	0.00000	1.91410
C	2.21078	-0.16407	0.74080
C	1.34296	-0.11348	-0.43396
C	-1.21643	0.18715	-0.85041
H	-2.06062	-0.40740	-0.49289
H	-1.03356	-0.08279	-1.89319
H	-1.52355	1.24189	-0.82952
C	-1.21215	0.24399	2.31117
H	-1.46320	1.31309	2.30389
H	-1.04138	-0.04545	3.35151
H	-2.08349	-0.30302	1.94032
C	1.83773	0.26027	3.31646
H	2.81509	-0.18882	3.50824
H	1.13570	-0.13063	4.05708
H	1.92727	1.34225	3.48068
C	3.70883	-0.05999	0.70407
H	4.13992	-0.67747	-0.08808
H	4.15634	-0.37335	1.65069
H	4.01023	0.97988	0.52111

C	1.83857	-0.09343	-1.84799
H	2.18025	0.91781	-2.10603
H	1.05752	-0.36873	-2.56083
H	2.68833	-0.76658	-1.98895
H	1.99580	-2.52464	2.13016
Ir	0.98745	-1.97612	1.03586
C	-0.30328	-3.34274	2.25955
N	-0.64040	-3.46871	0.95114
H	-0.91054	-2.71568	2.92074
C	1.77520	-6.52732	4.25996
C	1.59114	-5.29452	4.89501
C	0.91719	-4.26536	4.24418
C	0.42112	-4.44925	2.94408
C	0.58188	-5.69915	2.32480
C	1.26263	-6.72859	2.97851
H	2.30108	-7.32970	4.76959
H	1.97320	-5.13930	5.90016
H	0.78279	-3.30627	4.74061
H	0.13196	-5.87127	1.35083
H	1.37479	-7.69395	2.49212
C	-4.47380	-2.72108	-0.65124
C	-3.36479	-2.90433	-1.48290
C	-2.10399	-3.10748	-0.93276
C	-1.92076	-3.12249	0.46161
C	-3.04203	-2.95173	1.29255
C	-4.30500	-2.75033	0.73321
H	-5.46070	-2.57590	-1.07996
H	-3.48660	-2.90207	-2.56270
H	-1.24370	-3.26980	-1.57780
H	-2.94428	-3.02878	2.37087
H	-5.16414	-2.63644	1.38838
N	1.86161	-3.67995	-0.04955
H	1.15849	-3.92242	-0.74705
H	1.82274	-4.42945	0.64630
C	5.72612	-3.50065	-1.77702
C	5.57930	-3.68504	-0.39997
C	4.30963	-3.73609	0.17390
C	3.18212	-3.60748	-0.63984
C	3.31862	-3.43273	-2.01808
C	4.59456	-3.37653	-2.58338
H	6.71731	-3.46209	-2.21898
H	6.45639	-3.79318	0.23149
H	4.19469	-3.87866	1.24548
H	2.43681	-3.35863	-2.65123
H	4.69974	-3.24699	-3.65658

Ir_Cpstar_PhNH2_PhCNPh_E_TS (**1g**)
E_scf (B3LYP/6-31G*) = -1339.56853055598 a.u.
E_scf (B3LYP/6-31G+*) = -1339.59760521943 a.u.
E_scf (M06/6-31G*) = -1338.57672797674 a.u.
E_scf (M06/6-31G+*) = -1338.60229782931 a.u.
E_solv = -1339.60311545421 a.u.
E_Gibbs = -1339.073762 a.u.
ZPE = 349.900 kcal/mol

C	0.00000	0.00000	0.00000
C	0.00000	0.00000	1.45166
C	1.38334	0.00000	1.89360
C	2.23166	-0.09170	0.73703
C	1.36013	-0.10728	-0.43542
C	-1.21345	0.15165	-0.86109
H	-2.02984	-0.49750	-0.53164
H	-1.00141	-0.07586	-1.90883
H	-1.57211	1.18857	-0.81171
C	-1.21461	0.19635	2.31025

H	-1.50731	1.25449	2.31734
H	-1.03128	-0.10060	3.34647
H	-2.06320	-0.38437	1.93841
C	1.84626	0.14868	3.31311
H	2.81352	-0.33305	3.47671
H	1.12882	-0.27397	4.02108
H	1.95880	1.21388	3.55422
C	3.72906	0.00797	0.71134
H	4.16319	-0.58903	-0.09485
H	4.17177	-0.33297	1.65089
H	4.03660	1.05118	0.55786
C	1.84168	-0.06428	-1.85469
H	2.05000	0.97510	-2.14153
H	1.09627	-0.45539	-2.55200
H	2.76813	-0.62953	-1.98391
H	1.35955	-2.85449	2.17995
Ir	0.94683	-1.91375	0.85186
C	0.10085	-3.64197	2.16230
N	-0.48600	-3.52730	0.90772
H	-0.40621	-3.17407	3.01450
C	2.04101	-7.34151	3.21062
C	2.17033	-6.22204	4.03973
C	1.55442	-5.02317	3.69349
C	0.80128	-4.92902	2.51262
C	0.66471	-6.05591	1.69078
C	1.28611	-7.25753	2.04183
H	2.52193	-8.27671	3.48288
H	2.74906	-6.28811	4.95670
H	1.65533	-4.15505	4.34299
H	0.04378	-5.99288	0.80185
H	1.16874	-8.12977	1.40502
C	-4.64687	-3.03511	0.35602
C	-3.75277	-2.92794	-0.71362
C	-2.38451	-3.06242	-0.50264
C	-1.87435	-3.30284	0.78698
C	-2.78056	-3.42658	1.85568
C	-4.15226	-3.28937	1.63444
H	-5.71566	-2.94013	0.18934
H	-4.12499	-2.75112	-1.71935
H	-1.68775	-3.00310	-1.33513
H	-2.43207	-3.67929	2.85257
H	-4.83743	-3.40130	2.47046
N	1.93928	-3.52223	-0.30688
H	1.40046	-3.57636	-1.17083
H	1.70632	-4.37637	0.20648
C	6.09508	-3.45089	-1.13997
C	5.63833	-3.73275	0.15027
C	4.27260	-3.74672	0.42838
C	3.35962	-3.48521	-0.59595
C	3.80605	-3.21510	-1.89018
C	5.17724	-3.19361	-2.15784
H	7.16026	-3.44044	-1.35097
H	6.34825	-3.94558	0.94442
H	3.91531	-3.96649	1.43138
H	3.09149	-3.04325	-2.69264
H	5.52262	-2.98810	-3.16690

Ir_Cpstar_PhNH2_PhCNPh_amine (**1h**)
E_scf (B3LYP/6-31G*) = -1339.59766182466 a.u.
E_scf (B3LYP/6-31G+*) = -1339.62566981375 a.u.
E_scf (M06/6-31G*) = -1338.6045756043 a.u.
E_scf (M06/6-31G+*) = -1338.63014721474 a.u.
E_solv = -1339.63171811230 a.u.
E_Gibbs = -1339.095999 a.u.
ZPE = 353.329 kcal/mol

C	0.00000	0.00000	0.00000
C	0.00000	0.00000	1.45548
C	1.37919	0.00000	1.87782
C	2.22336	0.01709	0.69854
C	1.36768	0.02960	-0.45654
C	-1.21640	0.08212	-0.87054
H	-2.07988	-0.39939	-0.40543
H	-1.05068	-0.37986	-1.84751
H	-1.47646	1.13578	-1.04304
C	-1.18722	0.21799	2.34371
H	-1.31632	1.29326	2.52607
H	-1.06847	-0.27513	3.31162
H	-2.10693	-0.15945	1.89479
C	1.85385	0.06723	3.29668
H	2.83858	-0.39177	3.41731
H	1.15590	-0.43070	3.97433
H	1.93500	1.11687	3.61123
C	3.71844	0.13630	0.69481
H	4.16280	-0.31769	-0.19420
H	4.16618	-0.34056	1.57046
H	4.00688	1.19604	0.70892
C	1.81848	0.12763	-1.88459
H	1.93554	1.17957	-2.17527
H	1.09401	-0.31955	-2.57193
H	2.78557	-0.35997	-2.03728
H	1.85631	-4.68324	1.92692
Ir	0.99683	-1.85706	0.74760
C	0.77785	-4.75548	1.75562
N	0.19500	-3.39334	1.64754
H	0.36401	-5.21530	2.66054
C	0.12640	-7.53783	-1.50563
C	1.31250	-7.56350	-0.77205
C	1.51297	-6.64708	0.26179
C	0.53006	-5.69621	0.57999
C	-0.65931	-5.68086	-0.16246
C	-0.85713	-6.59555	-1.19733
H	-0.03210	-8.24856	-2.31180
H	2.08361	-8.29317	-1.00330
H	2.43933	-6.67559	0.83309
H	-1.43528	-4.96156	0.07750
H	-1.78574	-6.57630	-1.76162
C	-3.36139	-2.98769	3.92232
C	-3.38514	-2.83036	2.53594
C	-2.20846	-2.94523	1.79599
C	-0.99119	-3.23092	2.43186
C	-0.97420	-3.39217	3.82665
C	-2.15164	-3.26372	4.56352
H	-4.27777	-2.90065	4.49866
H	-4.32312	-2.62755	2.02576
H	-2.22113	-2.83382	0.71504
H	-0.03563	-3.60645	4.33193
H	-2.12311	-3.38316	5.64312
N	2.10075	-3.25798	-0.53593
H	1.75722	-3.04255	-1.47303
H	1.77260	-4.21470	-0.35736
C	6.34911	-3.25435	-0.63285
C	5.67475	-3.47709	0.57018
C	4.28114	-3.46063	0.61190
C	3.55874	-3.23563	-0.56171
C	4.22545	-3.01828	-1.76828
C	5.62223	-3.02100	-1.79964
H	7.43471	-3.26278	-0.65894
H	6.23526	-3.65850	1.48292
H	3.75896	-3.60629	1.55327
H	3.66219	-2.86365	-2.68674
H	6.13705	-2.85073	-2.74070

Calculation of theoretical KIE

The calculation of the theoretical KIE was performed using the Hessian calculated in gas phase for the complexes **1a** and **1b.** To allow comparison with experimental results the Gibbs free energy was evaluated at T=383 K (=110 ˚C, bp. of toluene).

This gave the following results:

Ir_Cpstar_PhNH2_PhCO_E_TS_freq_D_383K	-1128.020753 a.u.
Ir_Cpstar_PhNH2_PhCO_E_TS_alcohol_min_full_freq_D_383K	-1128.036312 a.u.
Ir_Cpstar_PhNH2_PhCO_E_TS_freq_H_383K	-1128.018455 a.u.
Ir_Cpstar_PhNH2_PhCO_E_TS_alcohol_min_full_freq_H_383K	-1128.032809 a.u.

From this we find an activation energy of 37.7 kJ/mol (proton) and 40.9 kJ/mol (deuterium). This difference in energy of 3.2 kJ/mol corresponds to a difference in reaction rate of 2.70 when using a Boltzmann expression evaluated at T=383K.

Performing a similar analysis using differences in zero-point energies (ZPE) resulted in a calculated KIE of 2.73, thus documenting that the observed effect arises mainly from differences in bond strengths, as expected.

IRC scan calculations

An IRC scan calculations was carried out for a representative beta-hydride elimination. Below are shown three structures, one close to the TS and one from either end of the IRC scan.

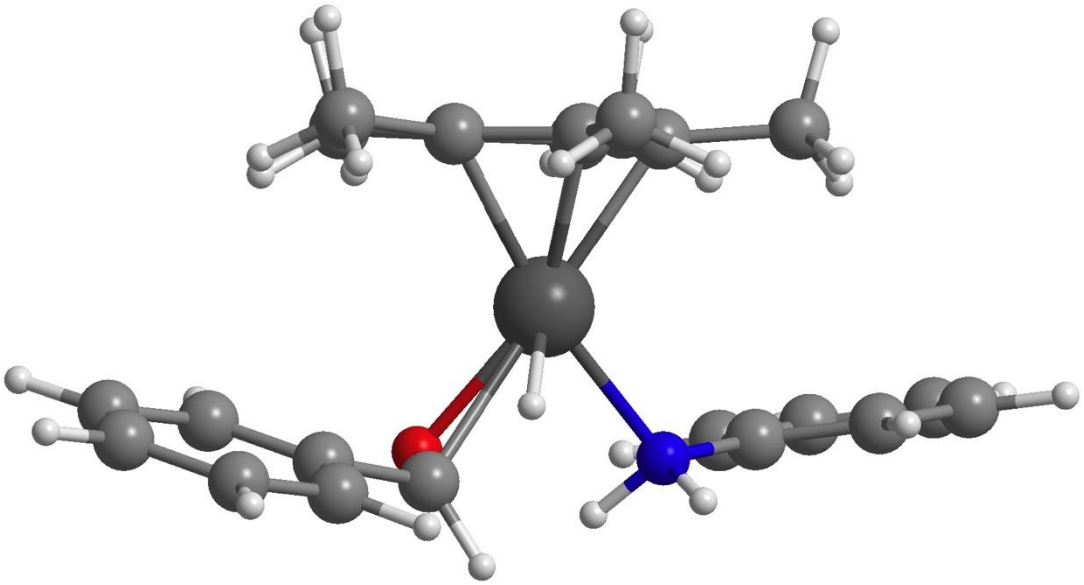

Figure 1 IRC step close to TS (forward1)

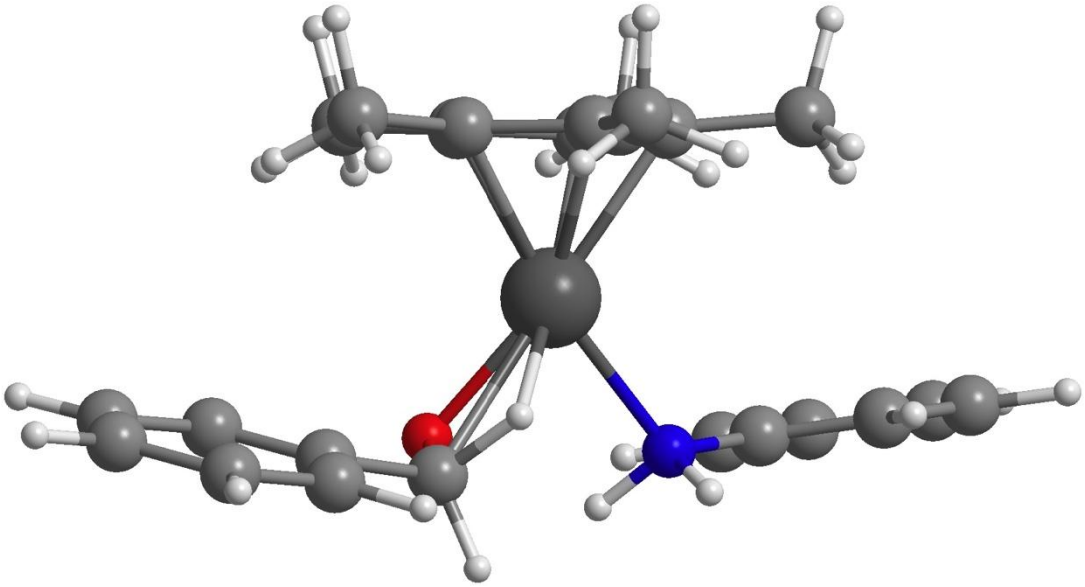

Figure 2 IRC step close to alcohol (reverse 8)

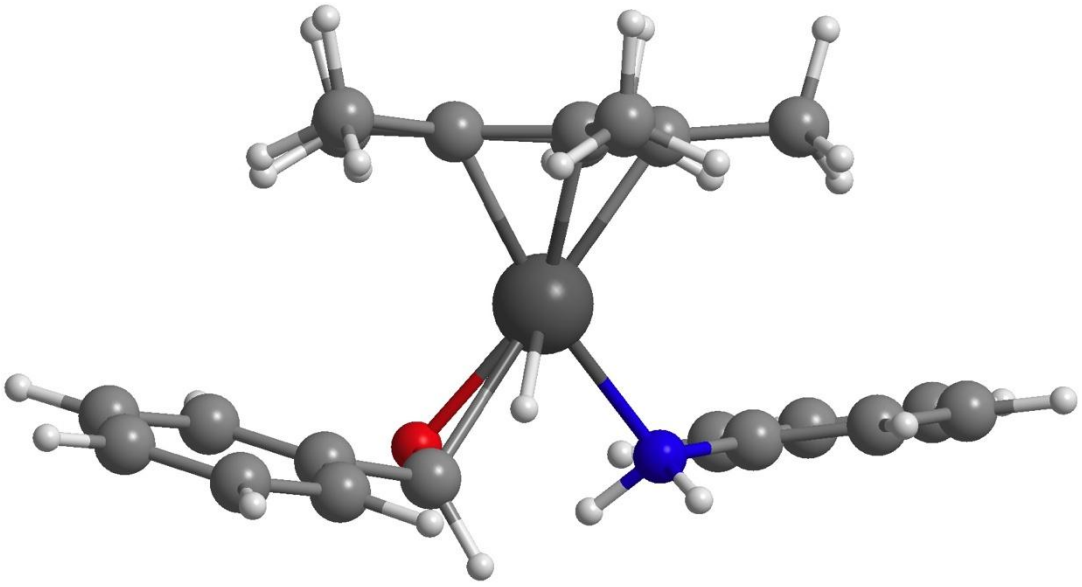

Figure 3 IRC step close to aldehyde (forward 10)

Table 1 Data from the IRC scan of a representative beta-hydride abstraction

Ir_Cpstar_PhNH2_PhCO_Z_TS_freq_IRC				
point #	Rxn. Coord	Energy (Hartree)	Relative Energy (kJ/mol)	C-H distance (Å)
1	-0.73626	-1128.396029	-3.056082	1.2255
2	-0.65277	-1128.395951	-2.851293	1.2328
3	-0.56745	-1128.395834	-2.5441095	1.2465
4	-0.47493	-1128.395753	-2.331444	1.2628
5	-0.38124	-1128.395566	-1.8404755	1.2836
6	-0.28677	-1128.395292	-1.1210885	1.3122
7	-0.19188	-1128.395147	-0.740391	1.3447
8	-0.09845	-1128.394992	-0.3334385	1.3787
9	0	-1128.394865	0	1.4168
10	0.0985	-1128.394939	-0.194287	1.4576
11	0.19593	-1128.395221	-0.934678	1.4977
12	0.29299	-1128.395594	-1.9139895	1.5393
13	0.39092	-1128.396177	-3.444656	1.5819
14	0.49	-1128.396882	-5.2956335	1.6257
15	0.58962	-1128.39782	-7.7583525	1.6702
16	0.68936	-1128.398881	-10.544008	1.7151
17	0.78924	-1128.400004	-13.4924445	1.7601
18	0.88913	-1128.401199	-16.629917	1.8053
19	0.98897	-1128.4024	-19.7831425	1.8503

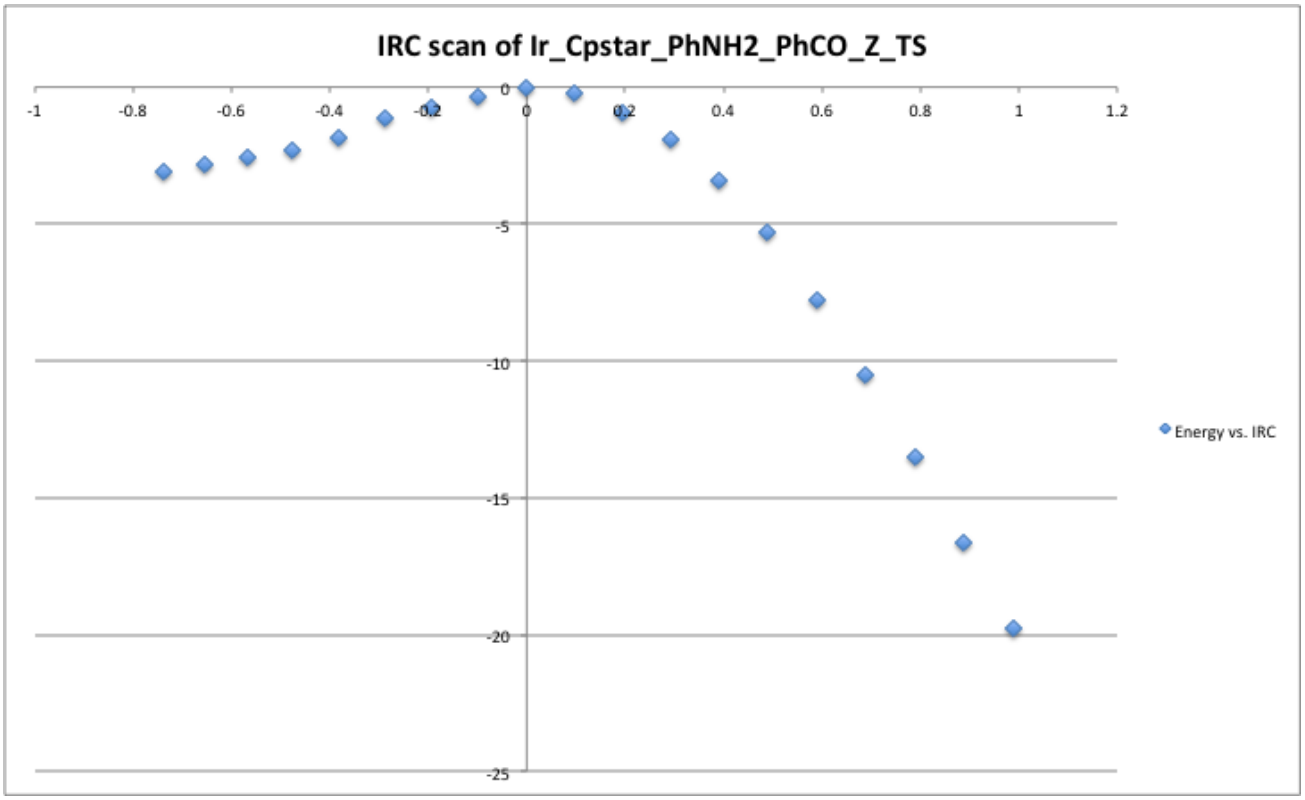

Figure 4 Relative energy vs. IRC coordinate for beta-hydride elimination

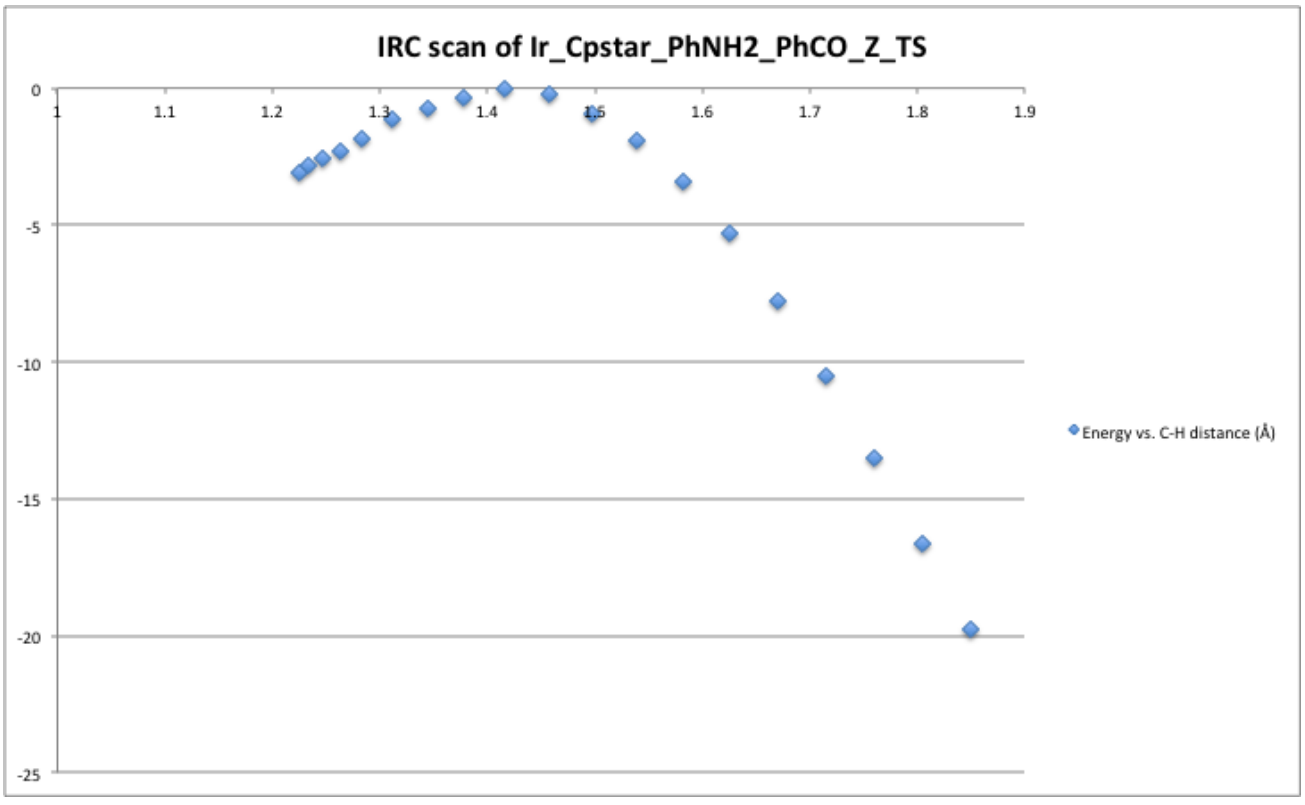

Figure 5 Relative energy vs. C-H distance (Å) for the C-H bond which is being broken/formed.

An IRC scan calculations was also carried out for a representative imine reduction. Below are shown three structures, one close to the TS and one from either end of the IRC scan.

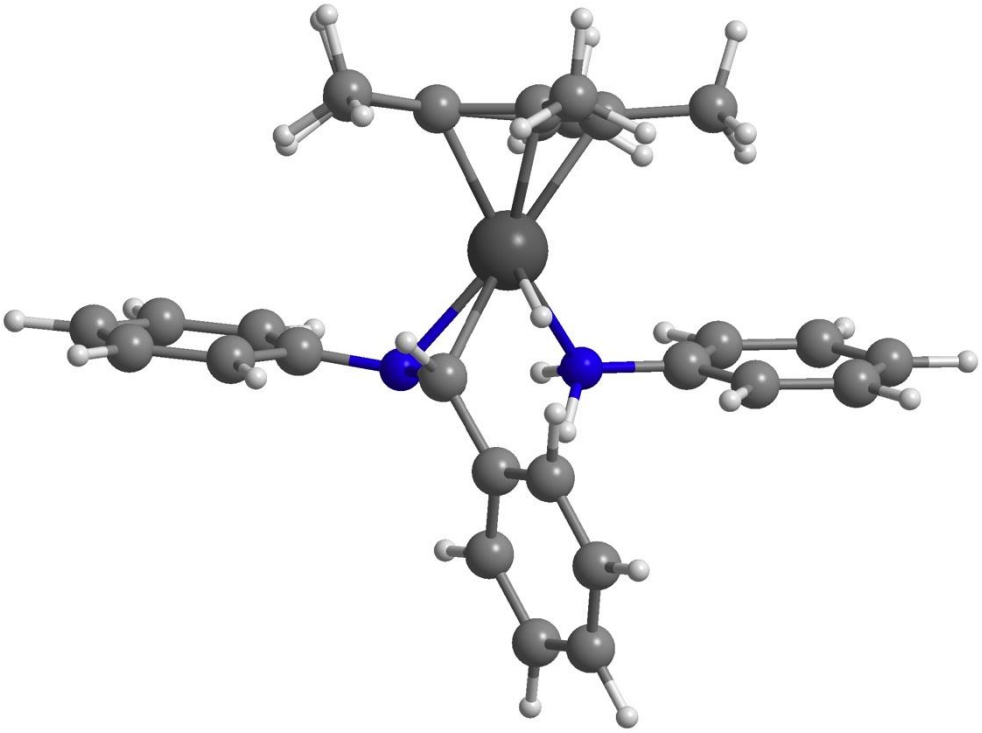

Figure 6 IRC step close to TS (forward1)

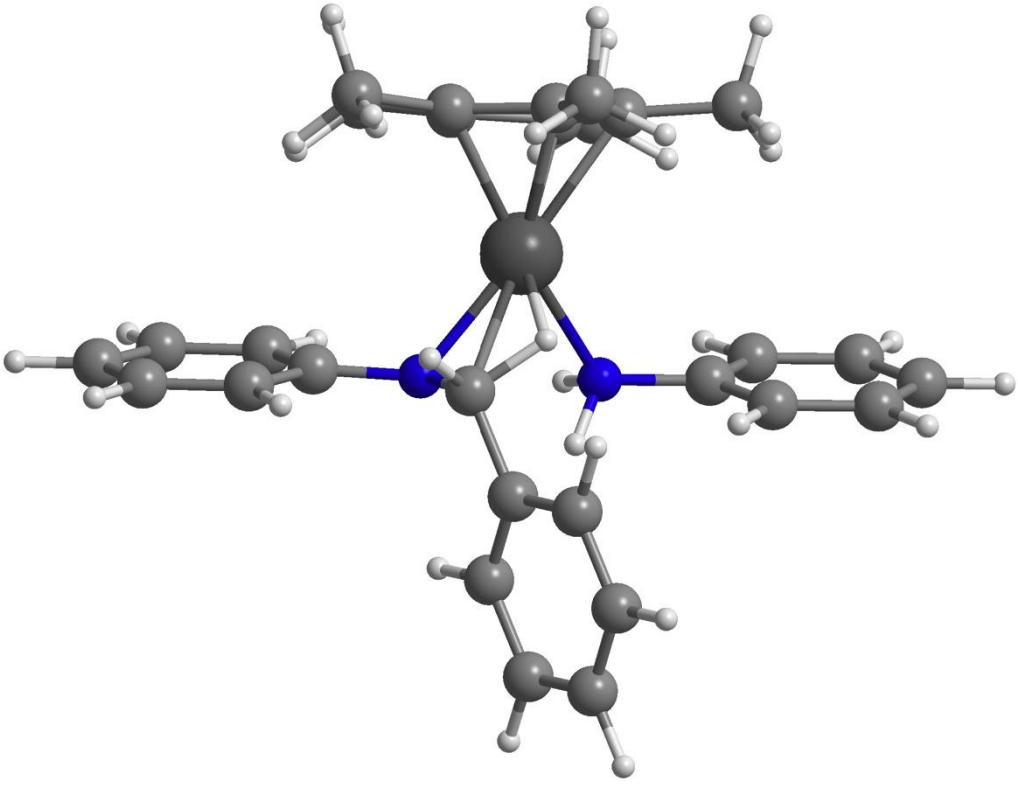

Figure 7 IRC step close to amine (reverse 10)

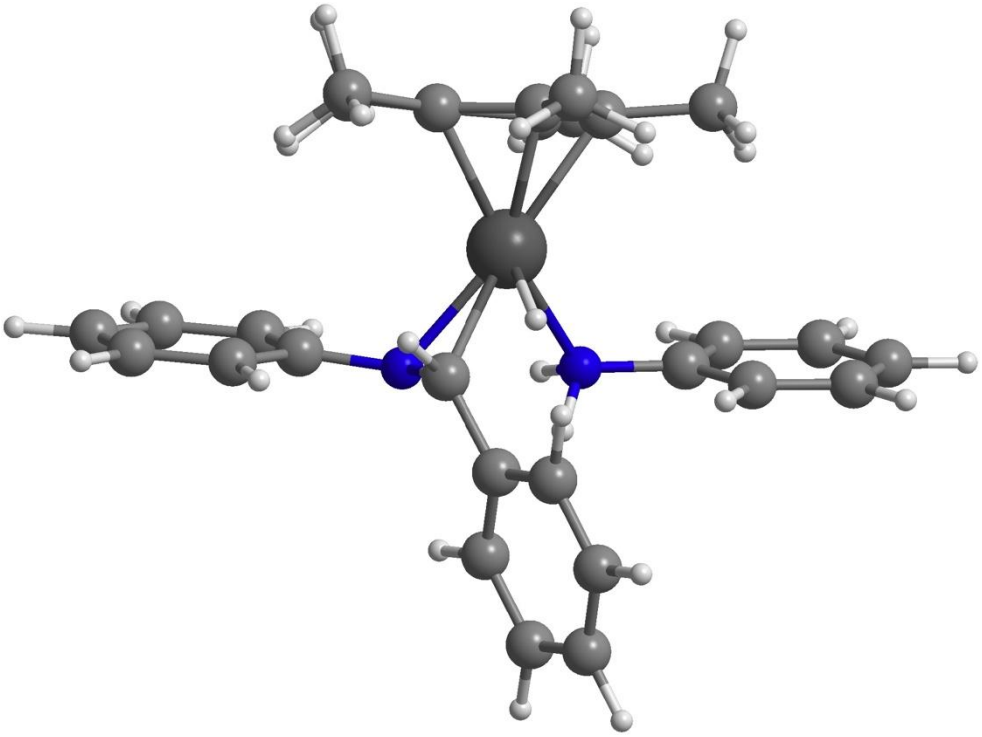

Figure 8 IRC step close to imine (forward 10)

Table 2 Data from the IRC scan of a representative imine reduction.

Ir_Cpstar_PhNH2_PhCNPh_E_TS_freq_IRC				
point #	Rxn. Coord	Energy	Relative Energy (kJ/mol)	C-H distance (Å)
1	-0.98799	-1339.57239	-10.13443	1.1959
2	-0.88993	-1339.572094	-9.357282	1.2075
3	-0.79105	-1339.571785	-8.5460025	1.2223
4	-0.69218	-1339.571285	-7.2332525	1.2436
5	-0.5929	-1339.570842	-6.070156	1.2699
6	-0.49347	-1339.570255	-4.5289875	1.3008
7	-0.39442	-1339.569458	-2.436464	1.3351
8	-0.29581	-1339.568979	-1.1788495	1.371
9	-0.19697	-1339.568619	-0.2336695	1.4082
10	-0.09925	-1339.568471	0.1549045	1.4459
11	0	-1339.56853	0	1.4848
12	0.09949	-1339.568723	-0.5067215	1.5245
13	0.19774	-1339.569016	-1.275993	1.5633
14	0.29625	-1339.569574	-2.741022	1.6028
15	0.39577	-1339.570303	-4.6550115	1.6429
16	0.49535	-1339.571208	-7.031089	1.6829
17	0.595	-1339.572316	-9.940143	1.7232
18	0.6947	-1339.573534	-13.138002	1.7631
19	0.79414	-1339.574751	-16.3332355	1.8032
20	0.89404	-1339.575982	-19.565226	1.8434
21	0.99404	-1339.577239	-22.8654795	1.8833

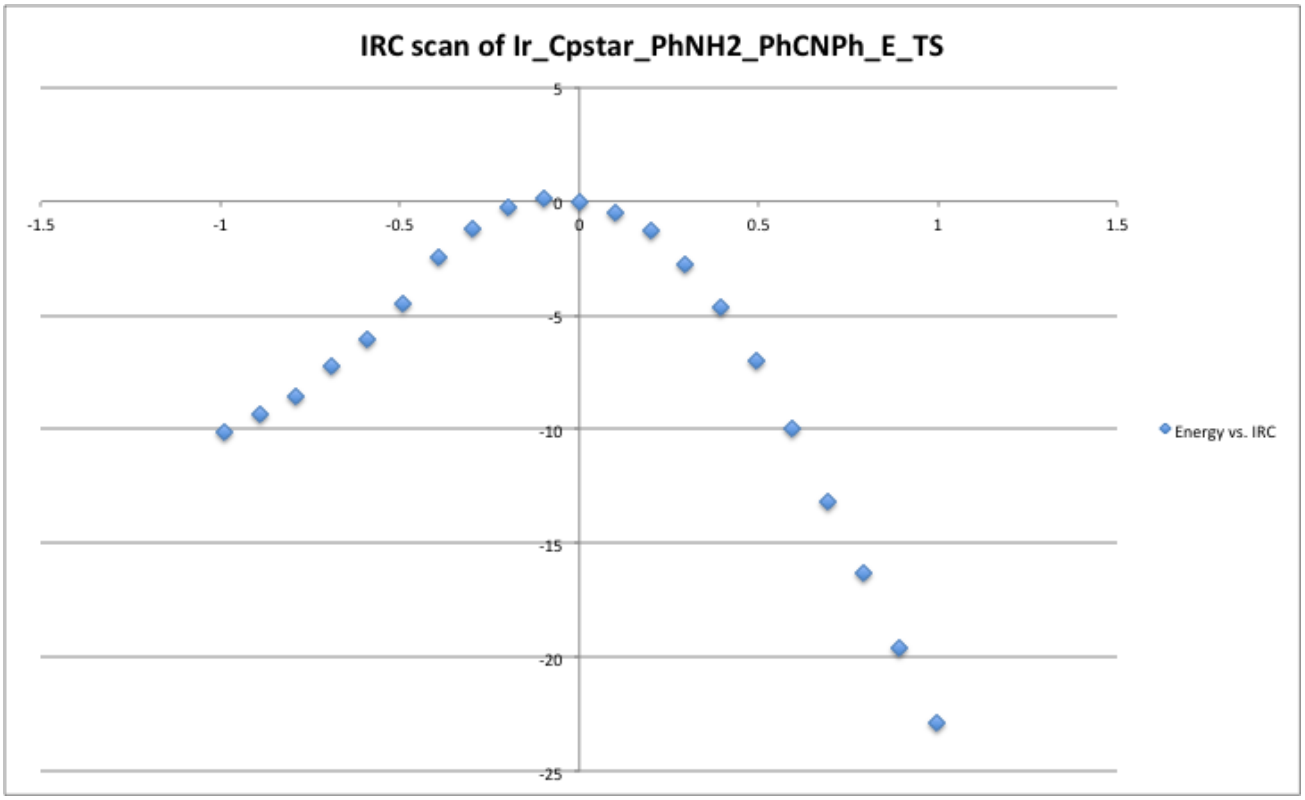

Figure 9 Relative energy vs. IRC coordinate for imine reduction.

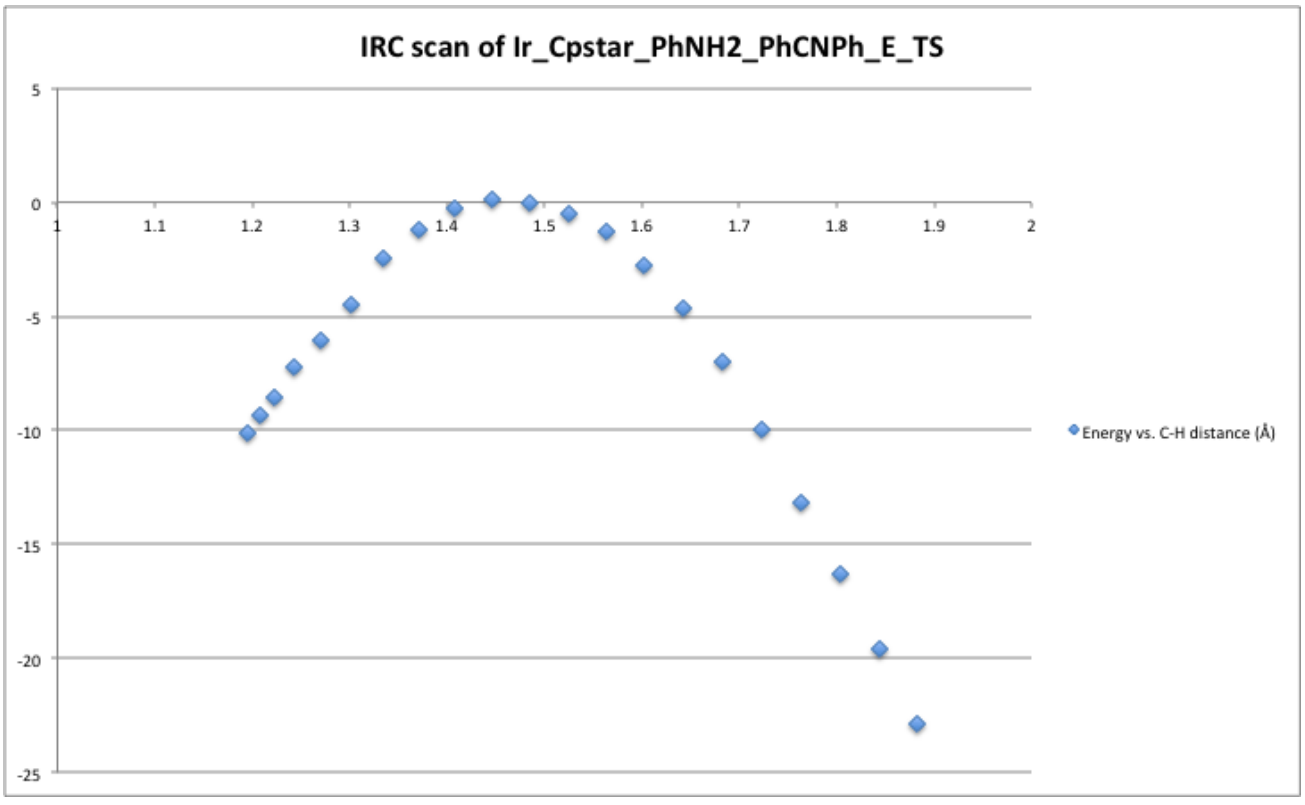

Figure 10 Relative energy vs. C-H distance (Å) for the C-H bond which is being broken/formed.

Dihedral scan, *cis*-imine to *trans*-imine

To estimate the possibility of *cis* to *trans* isomerization of the intermediate imine, a dihedral scan calculation was carried out (B3LYP/6-31G*, gas phase). It is clear that the barrier is very high, which can be ascribed to the very strong electrostatic interaction between the hydride and the proton on the phenyl group of the imine.

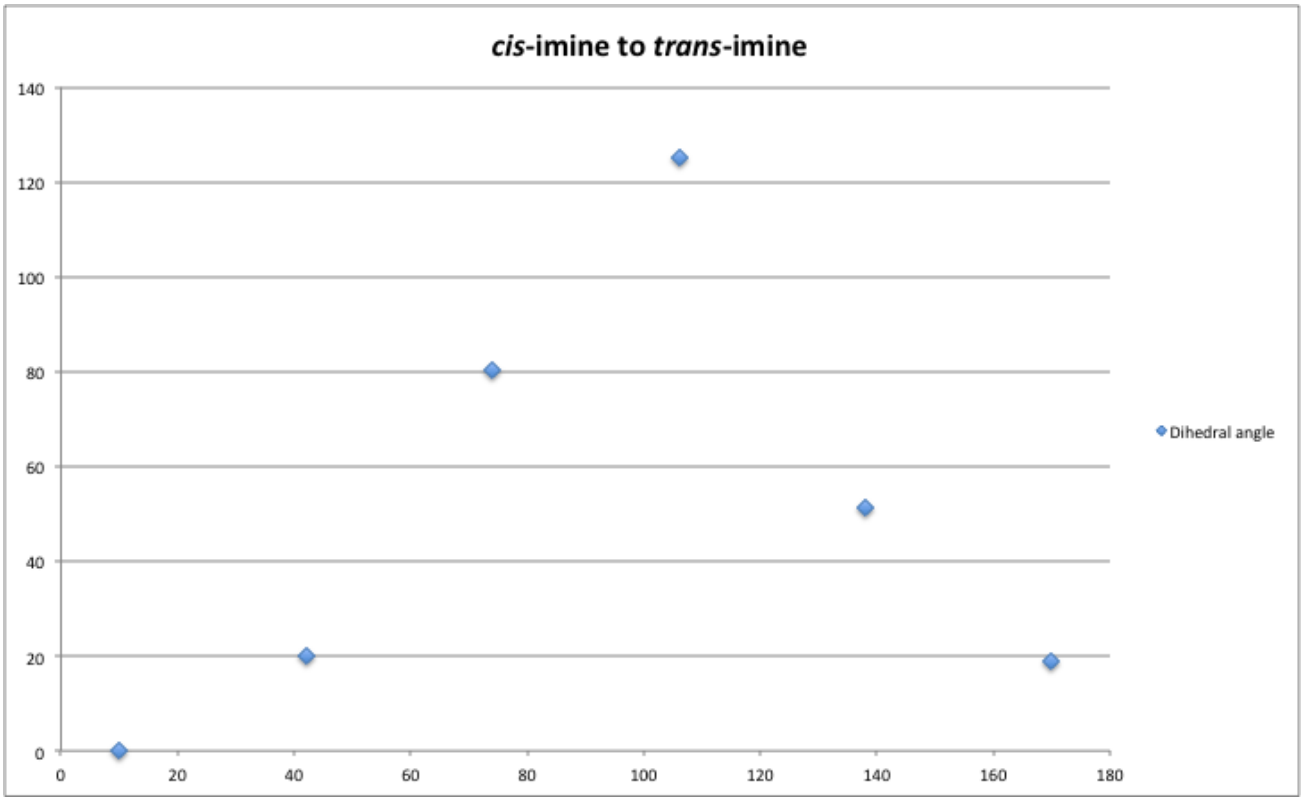

Figure 11 Energy profile for the dihedral scan.

Table 3 The data obtained from the dihedral scan.

dihedral angle	Energy (Ha)	Relative Energy
10.00	-1128.41	0.00
42.00	-1128.40	19.96
74.00	-1128.38	80.27
106.00	-1128.36	125.03
138.00	-1128.39	51.14
170.00	-1128.40	18.84

Below are shown the structures obtained during the scan from *cis*-imine to *trans*-imine:

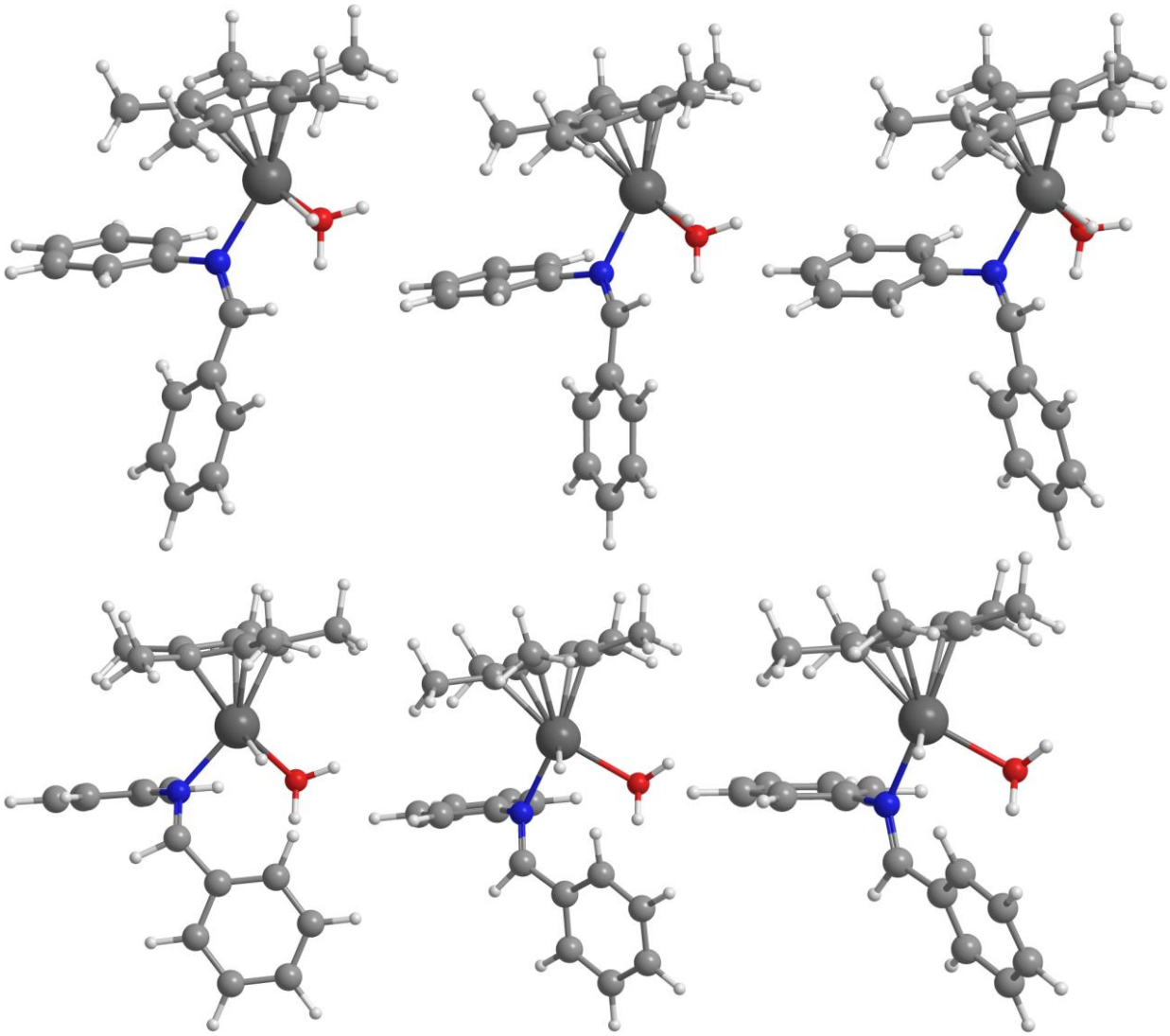

Figure 12 Structures obtained in the dihedral scan from *cis*-imine (top-left) to *trans*-imine (bottom right).