Supporting information.

C-N bond formation between alcohols and amines using an iron cyclopentadienone catalyst

Andrew J. Rawlings,[a] Louis J. Diorazio[b] and Martin Wills[a]*

a Department of Chemistry, The University of Warwick, Coventry, CV4 7AL, UK.
b Pharmaceutical Development, AstraZeneca, Silk Road Business Park, Macclesfield, Cheshire, SK10 2NA, UK.

Index:

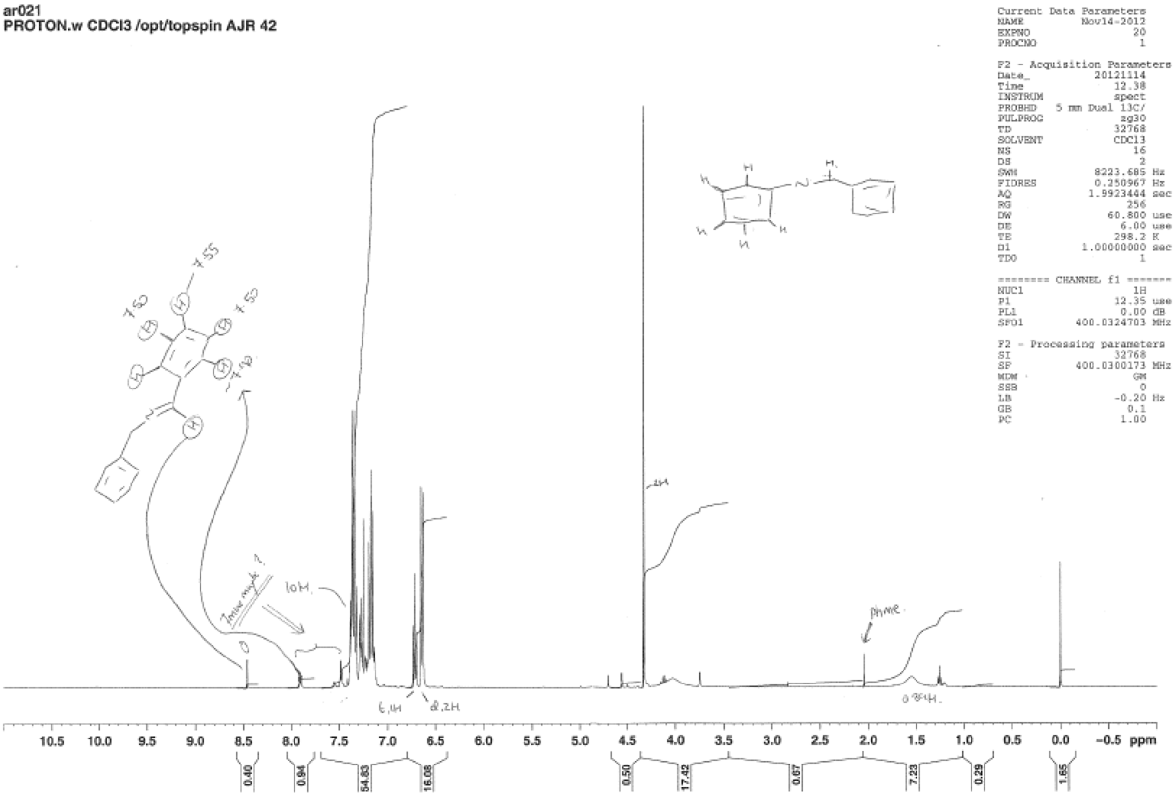
General Procedure for the alkylation of amines with alcohols.

A typical procedure is as follows: Aniline **6** (0.069 mL, 0.76 mmol), benzyl alcohol **5** (0.157 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were placed in a pressure tube which was flushed with nitrogen. Degassed toluene or xylene (0.40 mL) was added and the pressure tube was sealed and heated at 110 ^{o}C (in toluene) or 140 ^{o}C (in xylene) for the time indicated. At the end of this time, an additional excess of trimethylamine *N*-oxide dihydrate was added and reacted for a further 0.5 hours. The mixture was then filtered through celite using 100% EtOAc and the solvent was removed under reduced pressure. For the data in Table 1, the conversion was determined by GC (details are given below). In representative examples, the solvent was removed under vacuum and the mass balance was confirmed to match that expected. In addition, the ratio of reagents/products was confirmed by ^{1}H NMR in order to calibrate the GC result. In cases where compounds were isolated, the purification methods and yields are as described below for each product.

For the data in Table 1, conversion was determined by chiral GC analysis: Chrompac cyclodextrin-β-236M-19, 50 m x 0.25 mm x 0.25 μM, start T = 140 ^{o}C, 10 min, 5 ^{o}C /min, end T=180 ^{o}C, 40 min (AR035). P = 15 psi H_2, det = FID 220 ^{o}C, inj = 220 ^{o}C, aniline 5.8 min, benzyl alcohol 7.9 min, imine 31.2 min, amine 39.9 min. The retention times of aniline, benzyl alcohol and other starting materials were established by running these independently. The retention time of the imine formed between benzaldehyde and aniline was established through the preparation of an authentic standard (described below).

For example in Table 1 entry 14 (AR021) the reaction was carried out using aniline (0.070 mL, 0.76 mmol), benzyl alcohol (0.078 mL, 0.76 mmol), iron catalyst **1** (40 mg, 0.076 mmol) and trimethylamine N-oxide dehydrate (6 mg, 0.08 mmol). The recovered mass after filtration of the decomposed iron catalysts was 119 mg, indicating that product volatility is not significant (this was also confirmed in the isolated product yields). The ^{1}H-NMR spectrum of the crude mixture shows the required product to be the major component (90% conversion) of the mixture along with imine (8%) visible as indicated (this were confirmed by the synthesis of an authentic sample of imine as described in a later section). The ratio of aniline:imine:product amine was then directly measured by GC. As the alcohol was generally used in excess, it was not necessary to calibrate this in the GC measurement.

^{1}H NMR of the crude product from Table 1, entry 14, with imine peaks highlighted. There is a trace of benzyl alcohol (s from CH_2 at ca δ4.6):



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D1            1.00000000 sec
TD0                    1

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F2 - Processing parameters
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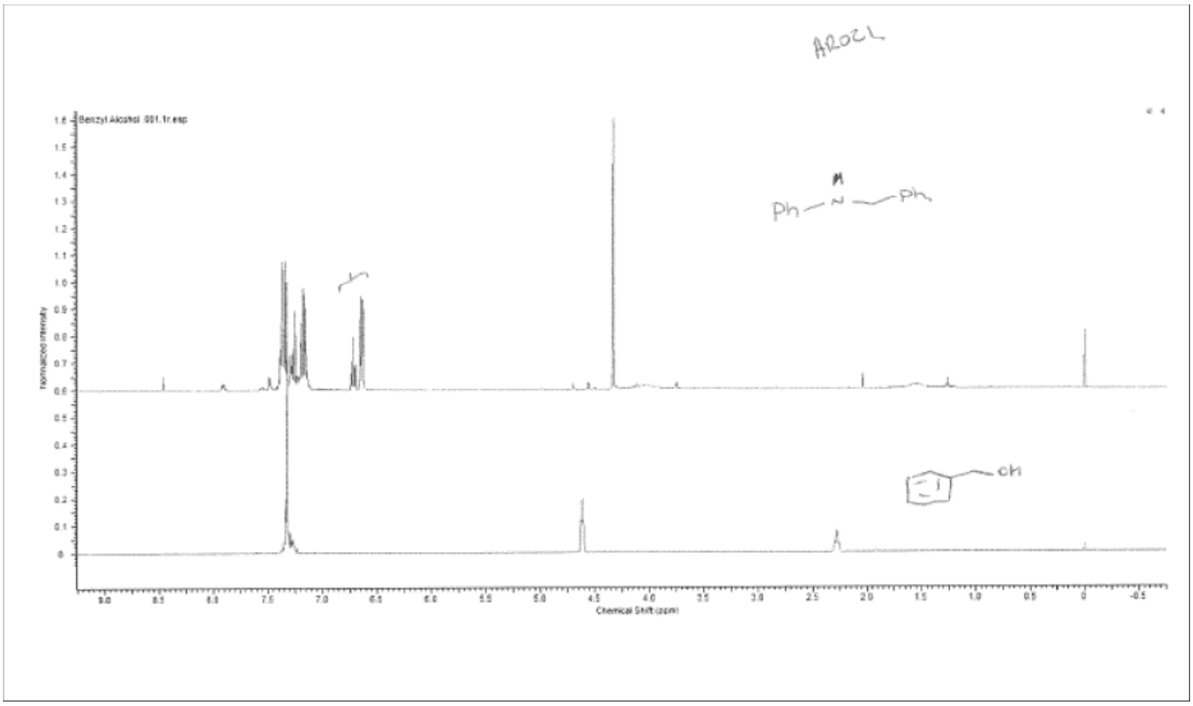
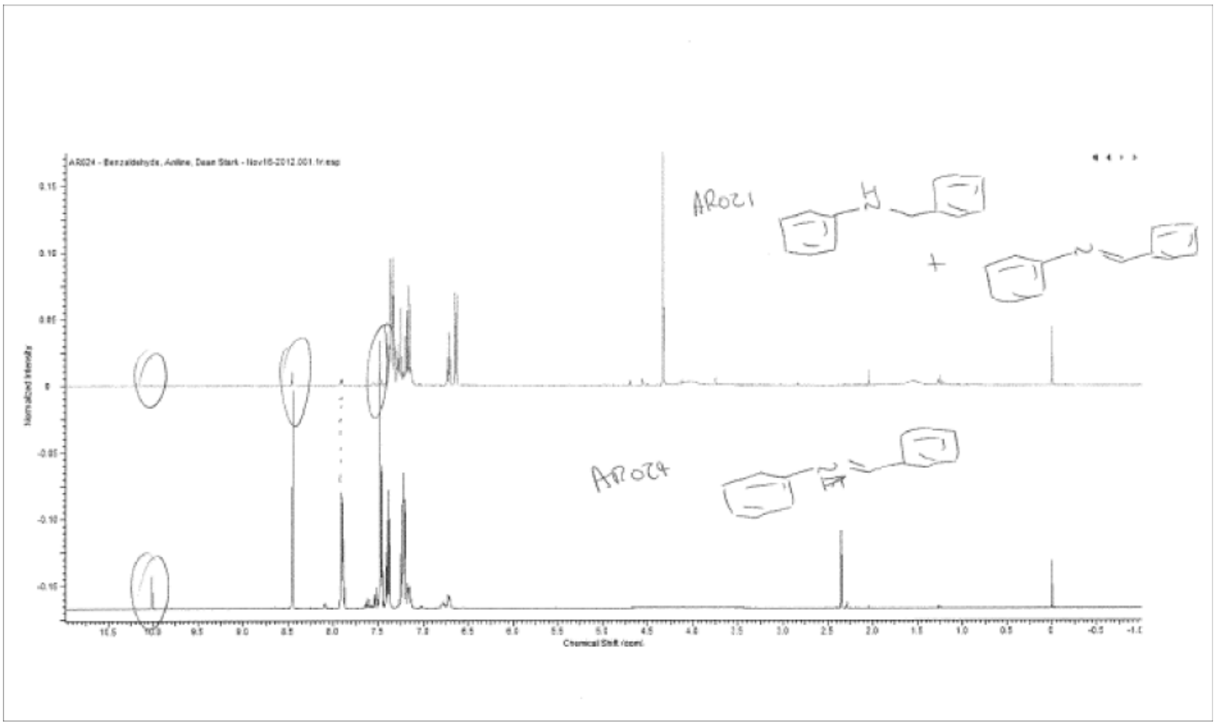
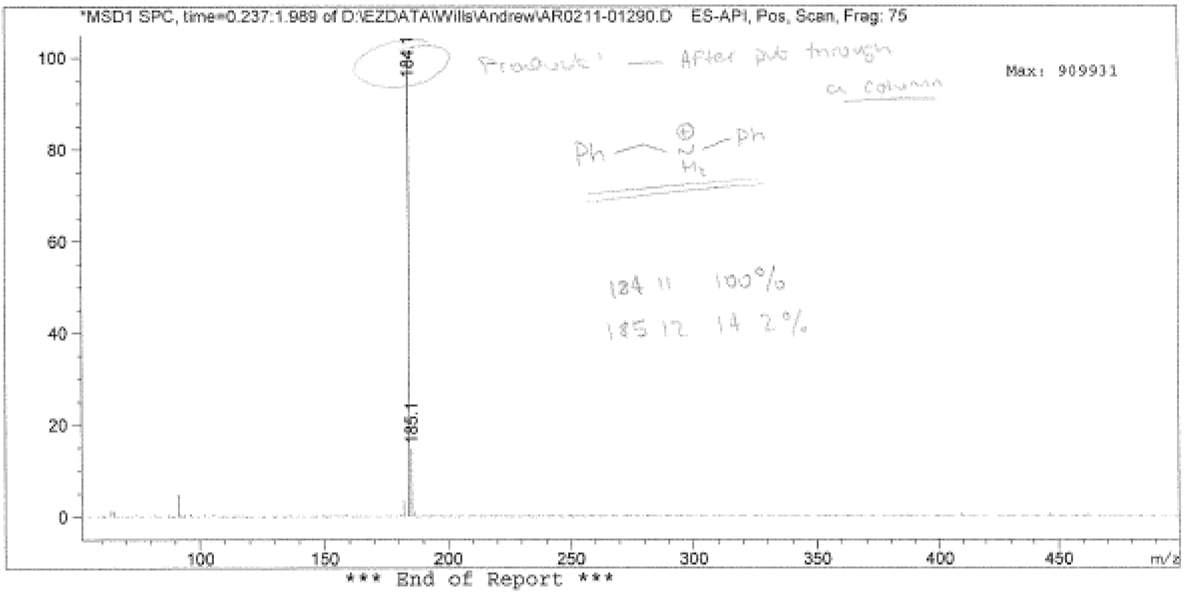
Overlay of ^{1}H NMR with benzyl alcohol ^{1}H NMR to identify peaks:



Overlay of product ^{1}H NMR with imine ^{1}H NMR to identify peaks (there is some benzaldehyde in the imine standard – see later section for synthesis of a standard):

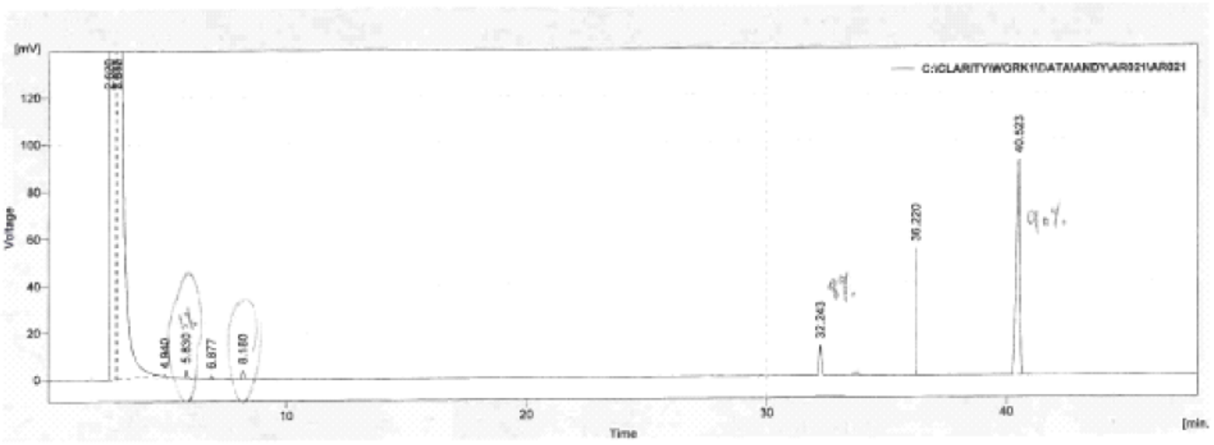


Mass spectrum of **7** from reaction in Table 1 entry 14:



GC of the crude product from Table 1, entry 14, with conversions to product (40.5 min) and imine (32.2.min) indicated. There is a trace of aniline at 5.83 min and alcohol at 6.16 min:

07/12/2012 10:21 Chromatogram C:\CLARITY\WORK1\DATA\ANDY\AR021\AR021.PRM Page 2 of 2



Result Table (Uncal - C:\CLARITY\WORK1\DATA\ANDY\AR021\AR021)

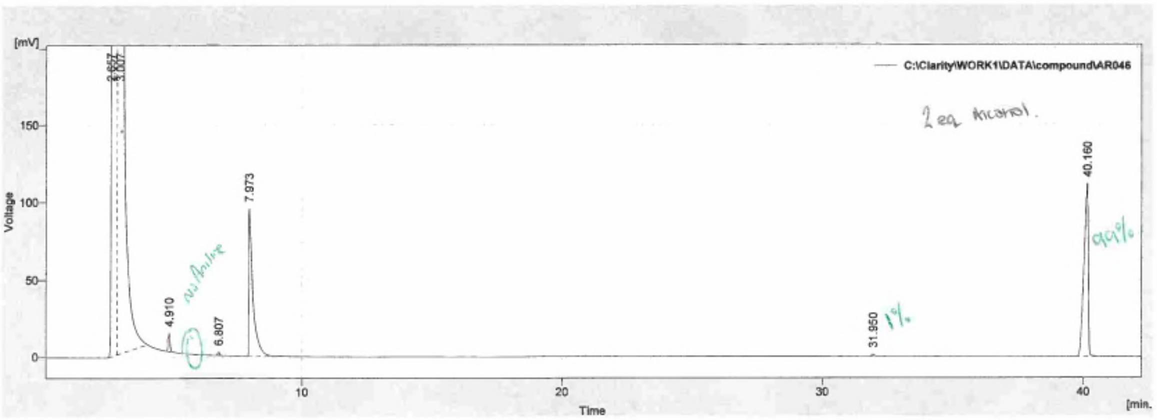
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.620	20949.288	1250.355	62.4	40.4	0.28
2	2.937	2761.044	762.516	8.2	24.7	0.07
3	3.010	8713.715	912.638	25.9	29.5	0.14
4	4.940	3.300	0.494	9.824e-03	1.598e-02	0.10
5	5.830	22.488	3.509	0.1	0.1	0.11
6	6.877	9.700	1.588	2.888e-02	0.1	0.10
7	8.180	26.914	3.585	0.1	0.1	0.12
8	32.243	92.111	12.942	0.3	0.4	0.12
9	36.220	11.343	54.099	3.377e-02	1.7	0.01
10	40.523	1002.604	91.252	3.0	3.0	0.18
	Total	33592.478	3092.977	100.0	100.0	

Re-processed.

Other runs from Table 1.

GC spectrum of crude product following filtration of the reaction in Table 1, entry 1 (AR046) - note BnOH is visible as it was used in excess, but aniline is not:

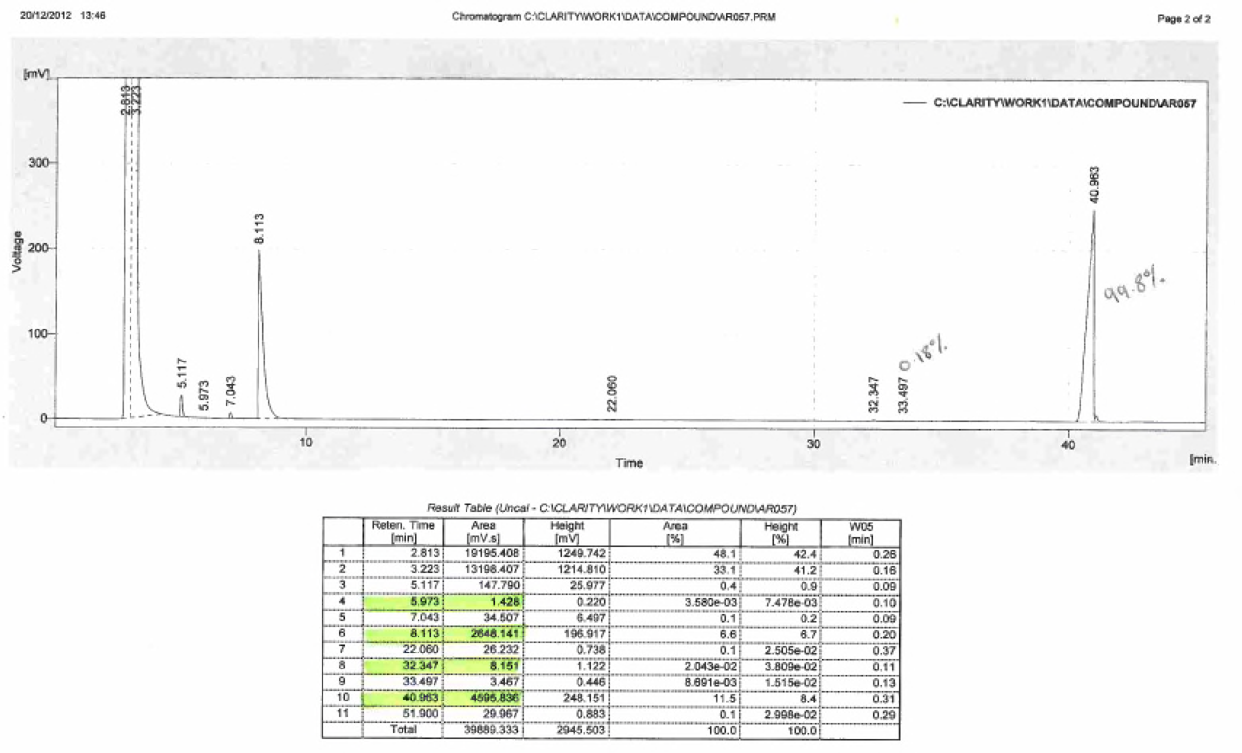
10/12/2012 11:24 Chromatogram C:\Clarity\WORK1\DATA\compound\AR046.PRM Page 2 of 2



Result Table (Uncal - C:\Clarity\WORK1\DATA\compound\AR046)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.657	17631.099	1249.814	55.4	51.2	0.25
2	3.007	11764.775	968.334	37.0	39.7	0.20
3	4.910	63.589	12.174	0.2	0.5	0.09
4	6.807	11.622	2.188	3.651e-02	0.1	0.09
5	7.973	1063.665	95.209	3.3	3.9	0.15
6	31.950	9.862	1.397	3.098e-02	0.1	0.11
7	40.160	1290.520	111.463	4.1	4.6	0.19
	Total	31835.131	2440.579	100.0	100.0	

GC spectrum of crude product following filtration of reaction in Table 1, entry 2 (AR057) - note BnOH is visible (8.13 min) as it was used in excess and a very small trace of aniline (5.97 min., < 0.04%) may be present:

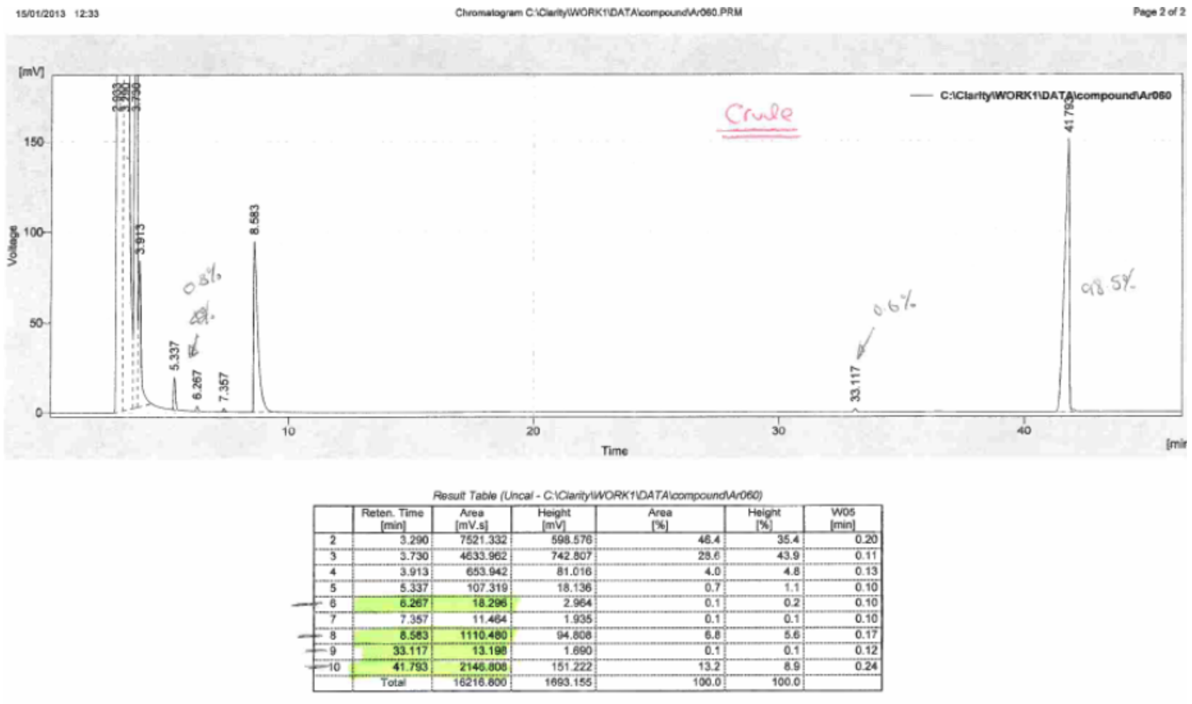


20/12/2012 13:46 Chromatogram C:\CLARITY\WORK1\DATA\COMPOUND\AR057.PRM Page 2 of 2

Result Table (Uncal - C:\CLARITY\WORK1\DATA\COMPOUND\AR057)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.813	19195.408	1249.742	48.1	42.4	0.26
2	3.223	13198.407	1214.810	33.1	41.2	0.16
3	5.117	147.790	25.977	0.4	0.9	0.09
4	5.973	1.428	0.220	3.580e-03	7.478e-03	0.10
5	7.043	34.507	6.497	0.1	0.2	0.09
6	8.113	2648.141	196.917	6.6	6.7	0.20
7	22.060	26.232	0.738	0.1	2.505e-02	0.37
8	32.347	8.151	1.122	2.043e-02	3.809e-02	0.11
9	33.497	3.467	0.446	8.691e-03	1.515e-02	0.13
10	40.963	4595.836	248.151	11.5	8.4	0.31
11	51.900	29.967	0.883	0.1	2.998e-02	0.29
	Total	39889.333	2945.503	100.0	100.0	

GC spectrum of crude product following filtration of reaction in Table 1, entry 16 (AR060) - note BnOH is visible as it was used in excess, as is a trace of aniline (0.8 %):



15/01/2013 12:33 Chromatogram C:\Clarity\WORK1\DATA\compound\Ar060.PRM Page 2 of 2

Result Table (Uncal - C:\Clarity\WORK1\DATA\compound\Ar060)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
2	3.290	7521.332	598.576	46.4	35.4	0.20
3	3.730	4633.962	742.807	28.6	43.9	0.11
4	3.913	653.942	81.016	4.0	4.8	0.13
5	5.337	107.319	18.136	0.7	1.1	0.10
6	6.267	18.296	2.964	0.1	0.2	0.10
7	7.357	11.464	1.935	0.1	0.1	0.10
8	8.583	1110.480	94.808	6.8	5.6	0.17
9	33.117	13.198	1.690	0.1	0.1	0.12
10	41.793	2146.808	151.222	13.2	8.9	0.24
	Total	16216.800	1693.155	100.0	100.0	

Table 1 is reproduced below with experiment numbers which provided the data:

Entry	Reaction code	mol % **1**	equiv **5**	temp /°C	*T* /h	convn /%	imine/ %	*N_2 or Ar*
1	046	10	2.0	110	48	99.0	1	Ar
2	057	10	2.0	110	48	99.8	0.2	N_2
3	051	10	2.5	110	48	99.5	0.5	Ar
4	048	10	3.0	110	48	99.6	0.3	Ar
5	052	10	5.0	110	48	99.7	0.3	Ar
6	045	10	1.8	110	48	99	1	Ar
7	044	10	1.6	110	48	89	6	Ar
8	040	10	1.5	110	48	97	3	Ar
9	149	10	1.5	110	48	95	5	N_2
10	035	10	1.3	110	48	81	7	N_2
11	034	10	1.2	110	48	88	8	N_2
12	036	10	1.1	110	48	78	7	Ar
13	033	10	1.1	110	48	89	8	N_2
14	021	10	1.0	110	48	90	8	N_2
15	162	10	2.0	110	24	94.4	0.3	Ar
16	060	10	2.0	140[b]	24	98.6	0.6	N_2
17	083	10	2.0	140[b,c]	48	96	2	N_2
18	028	15	2.0	110	48	98.8	0.2	N_2
19	056	5	2.0	110	48	90.5	0.4	Ar
20	037	2	1.1	110	48	52	5	Ar
21	038	2	1.1	110	48	21	2	Ar

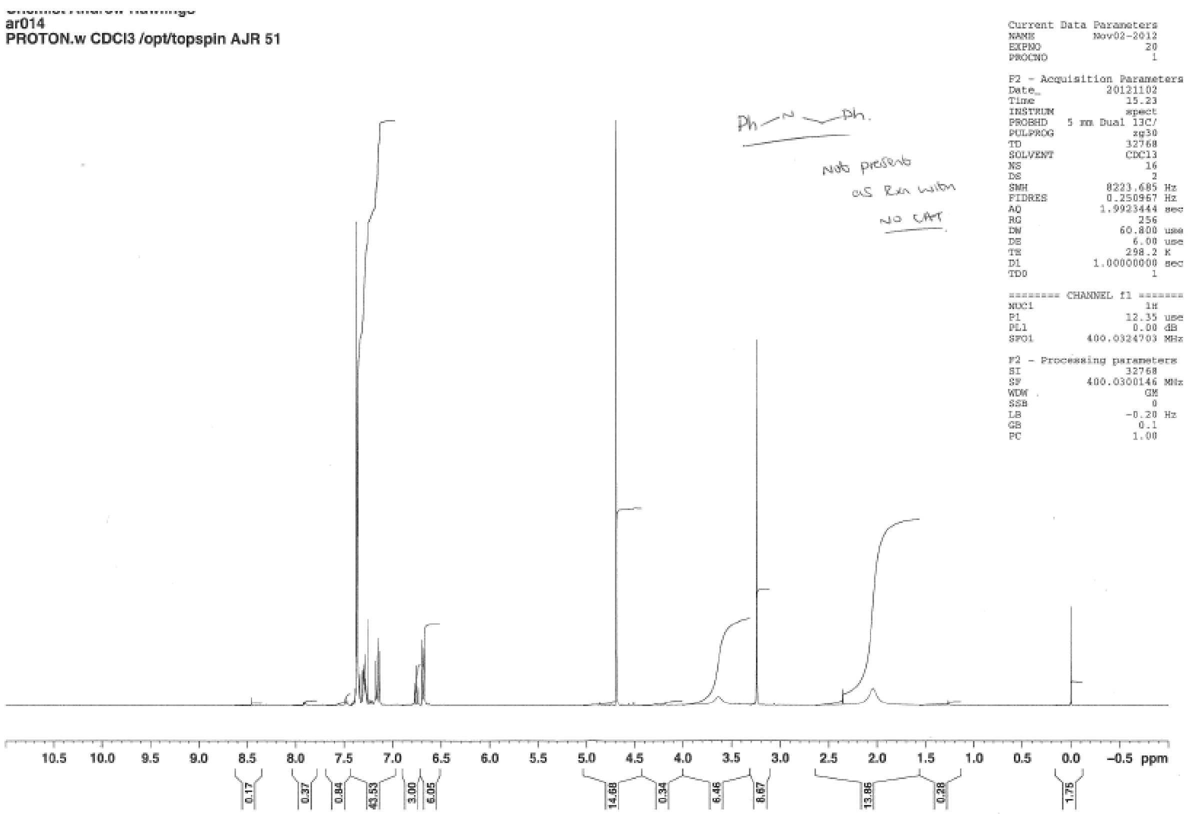
a. 1.0 equiv aniline, 1 eq Me_3NO relative to Fe complex, [aniline] = 0.5 M, b. conducted in xylene. c. Catalyst was first formed in situ by combination of dicyclopentadiene and $Fe(CO)_5$ then addition of aniline and benzylalcohol. Conversion by mass recovery and GC ratio, calibrated.

Control reactions:

Reaction without catalyst (AR014).

Aniline (0.091 mL, 1.0 mmol), benzyl alcohol (0.103 mL, 1.0 mmol) and trimethylamine N-oxide dihydrate (11.1 mg, 0.10 mmol) were combined in degassed toluene (0.5 mL) in a nitrogen-flushed pressure tube which was heated to 110 °C for 48h. At the end of this the reaction was allowed to cool and worked up following the general procedure and analyzed by GC which showed the formation of ca 10% imine and no amine. The imine may have been formed by oxidation of alcohol by the N-oxide.

^{1}H NMR (400 MHz, $CDCl_3$) – benzyl alcohol (s of CH_2 at δ 4.6) and aniline are present, but no coupling product is visible:



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DS                     2
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FIDRES          0.250967 Hz
AQ             1.9923444 sec
RG                   256
DW                60.800 use
DE                  6.00 use
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

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NUC1                  1H
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PL1                 0.00 dB
SFO1         400.0324703 MHz

F2 - Processing parameters
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SF           400.0300146 MHz
WDW                   GM
SSB                    0
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GB                   0.1
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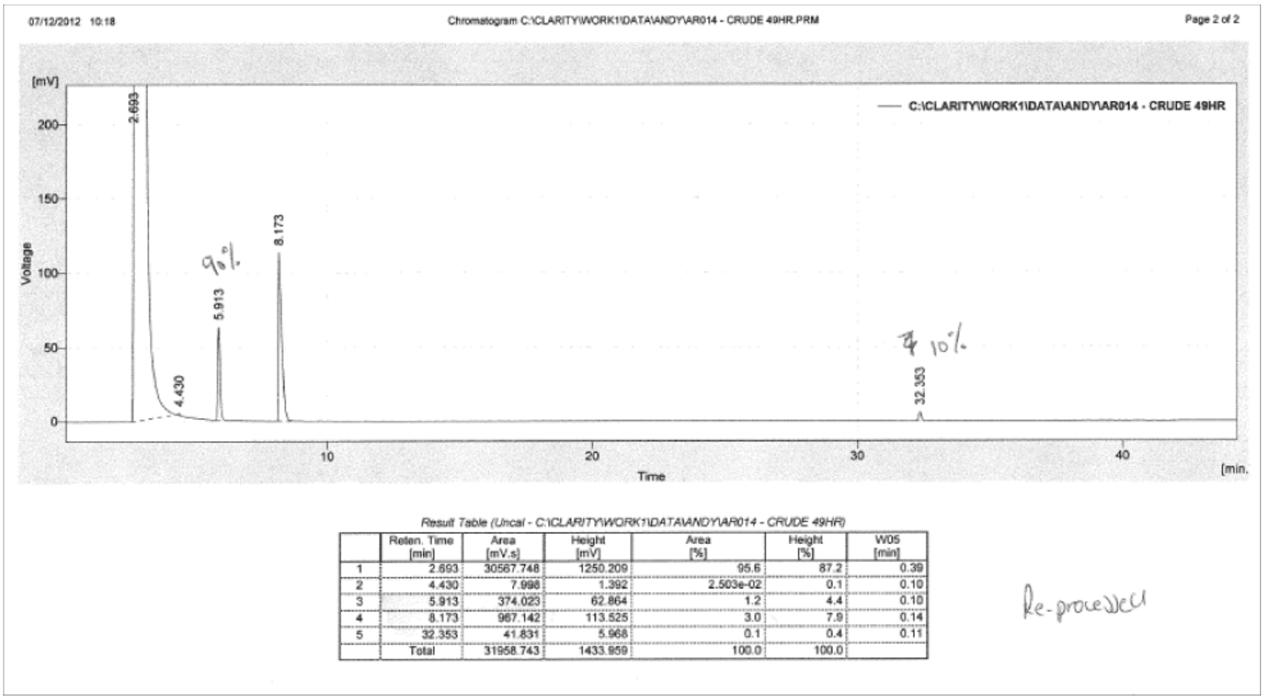
GC spectrum (aniline at 5.91 min., benzyl alcohol at 8.17 min., imine at 32.3 min.):


07/12/2012 10:18 Chromatogram C:\CLARITY\WORK1\DATA\ANDY\AR014 - CRUDE 49HR.PRM Page 2 of 2

Result Table (Uncal - C:\CLARITY\WORK1\DATA\ANDY\AR014 - CRUDE 49HR)

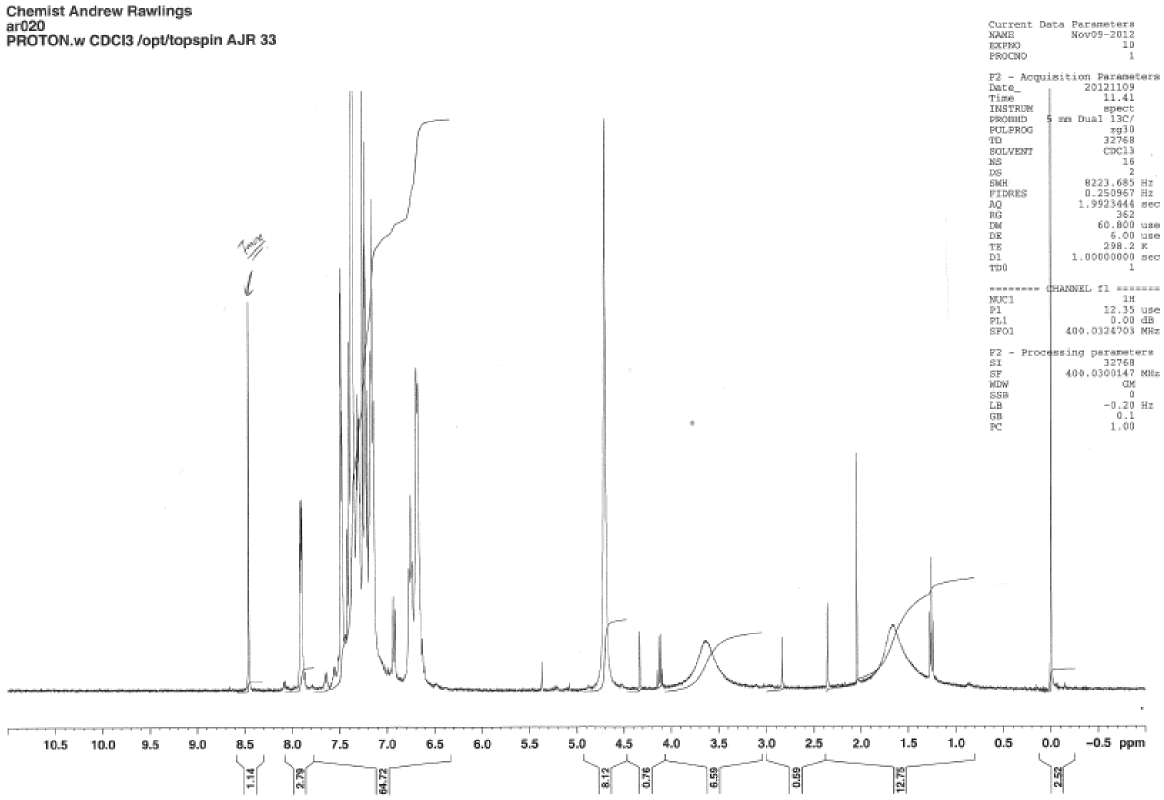
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.693	30567.748	1250.209	95.6	87.2	0.39
2	4.430	7.998	1.392	2.503e-02	0.1	0.10
3	5.913	374.023	62.864	1.2	4.4	0.10
4	8.173	967.142	113.525	3.0	7.9	0.14
5	32.353	41.831	5.968	0.1	0.4	0.11
	Total	31958.743	1433.959	100.0	100.0	

Re-processed

Reaction without degassing (AR020): A reaction was carried out without degassing and under air in a sealed tube using aniline **6** (0.069 mL, 0.76 mmol), benzyl alcohol **5** (0.157 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076

mmol) were placed in a pressure tube which was flushed with nitrogen. Undegassed toluene (0.40 mL) was added and the pressure tube was sealed (without flushing with nitrogen or argon) and heated at 110 °C (in toluene) for the 48h. At the end of this the reaction was allowed to cool and worked up following the general procedure and analyzed by GC which indicated the formation of ca 5% amine and ca. 40% imine.

^{1}H NMR (400 MHz, $CDCl_3$):



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FIDRES          0.250967 Hz
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DE                  6.00 use
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

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PL1                 0.00 dB
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F2 - Processing parameters
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WDW                   GM
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PC                  1.00
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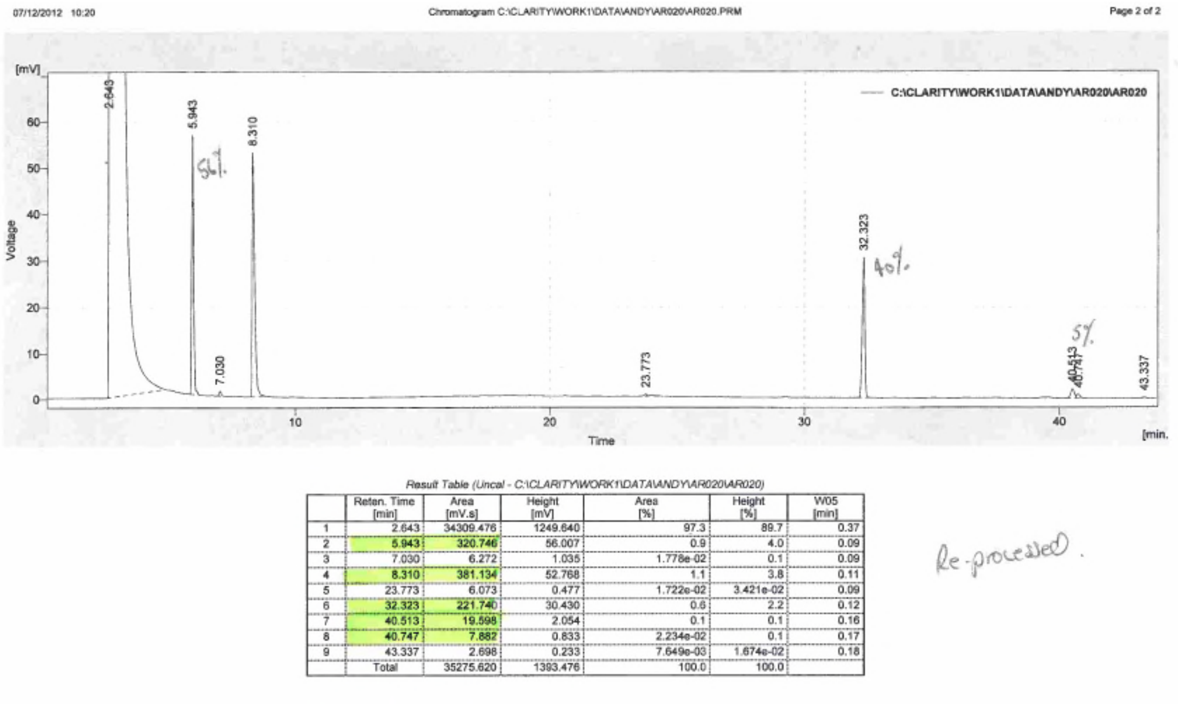
GC spectrum – peaks for aniline (5.94 min), benzyl alcohol (8.31 min), imine (32.3 min) and amine (4.75 min) are indicated:



07/12/2012 10:20 Chromatogram C:\CLARITY\WORK1\DATA\ANDY\AR020\AR020.PRM Page 2 of 2

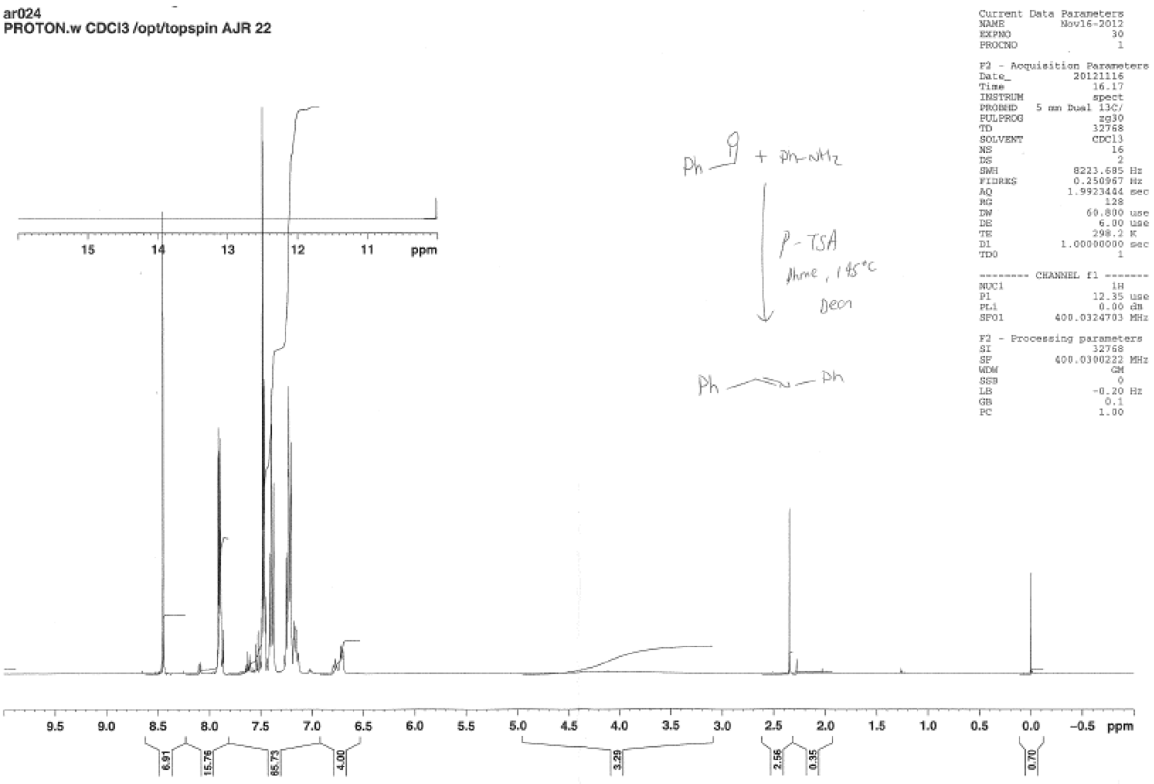
Result Table (Uncal - C:\CLARITY\WORK1\DATA\ANDY\AR020\AR020)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.643	34309.476	1249.640	97.3	89.7	0.37
2	5.943	320.746	56.007	0.9	4.0	0.09
3	7.030	6.272	1.035	1.778e-02	0.1	0.09
4	8.310	381.134	52.768	1.1	3.8	0.11
5	23.773	6.073	0.477	1.722e-02	3.421e-02	0.09
6	32.323	221.740	30.430	0.6	2.2	0.12
7	40.513	19.598	2.054	0.1	0.1	0.16
8	40.747	7.882	0.833	2.234e-02	0.1	0.17
9	43.337	2.698	0.233	7.649e-03	1.674e-02	0.18
	Total	35275.620	1393.476	100.0	100.0	

Re-processed.

Preparation of a standard of the imine intermediate (AR024)**:** Aniline (0.46 mL, 5.0 mmol), benzaldehyde (0.508 mL, 5.0 mml) and p-toluenesulfonicacid (38 mg, 0.2 mmol) were combined in toluene (12.8 mL) and the mixture was heated at 145 ^{o}C for four hours in a Dean-Stark apparatus to remove water. The solution was cooled to room temperature and the solvents removed under reduced pressure. The ^{1}H NMR spectrum indicated formation of the product and this was used as a standard for GC analysis.

^{1}H NMR (400 MHz, $CDCl_3$):



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PROCNO                 1

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SOLVENT            CDCl3
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DS                     2
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ             1.9923444 sec
RG                   128
DW                60.800 use
DE                  6.00 use
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

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P1                 12.35 use
PL1                 0.00 dB
SFO1         400.0324703 MHz

F2 - Processing parameters
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SF           400.0300222 MHz
WDW                   GM
SSB                    0
LB                 -0.20 Hz
GB                   0.1
PC                  1.00
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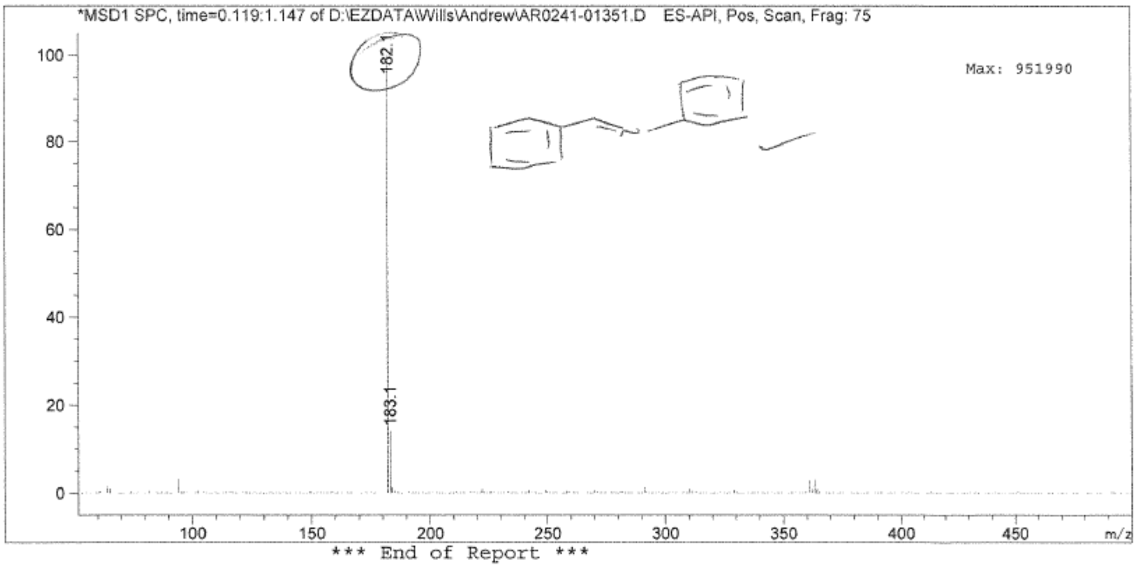
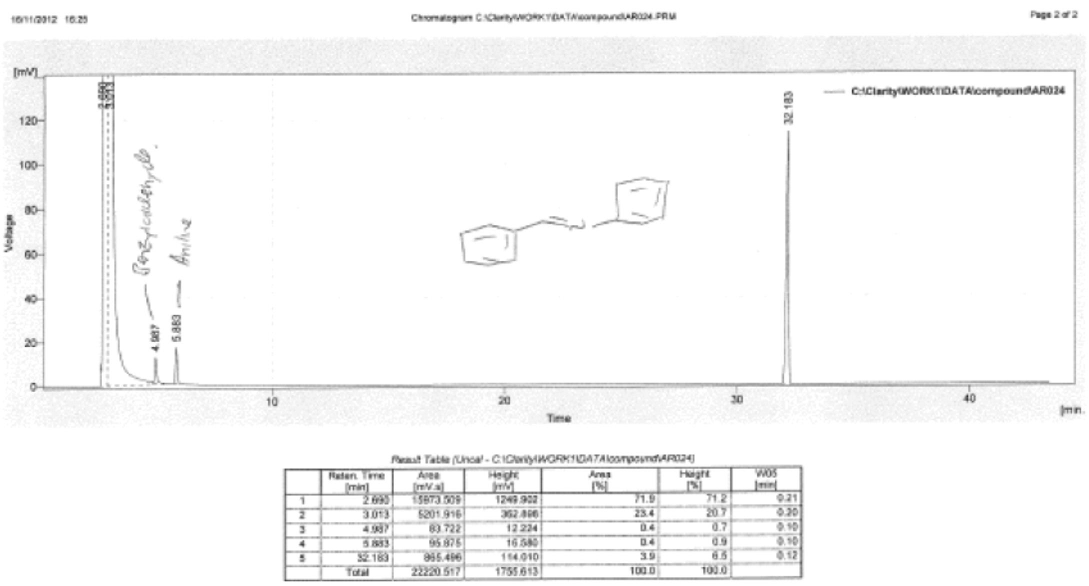
Mass spectrum:



GC of the imine to establish retention time:



16/11/2012 16:25

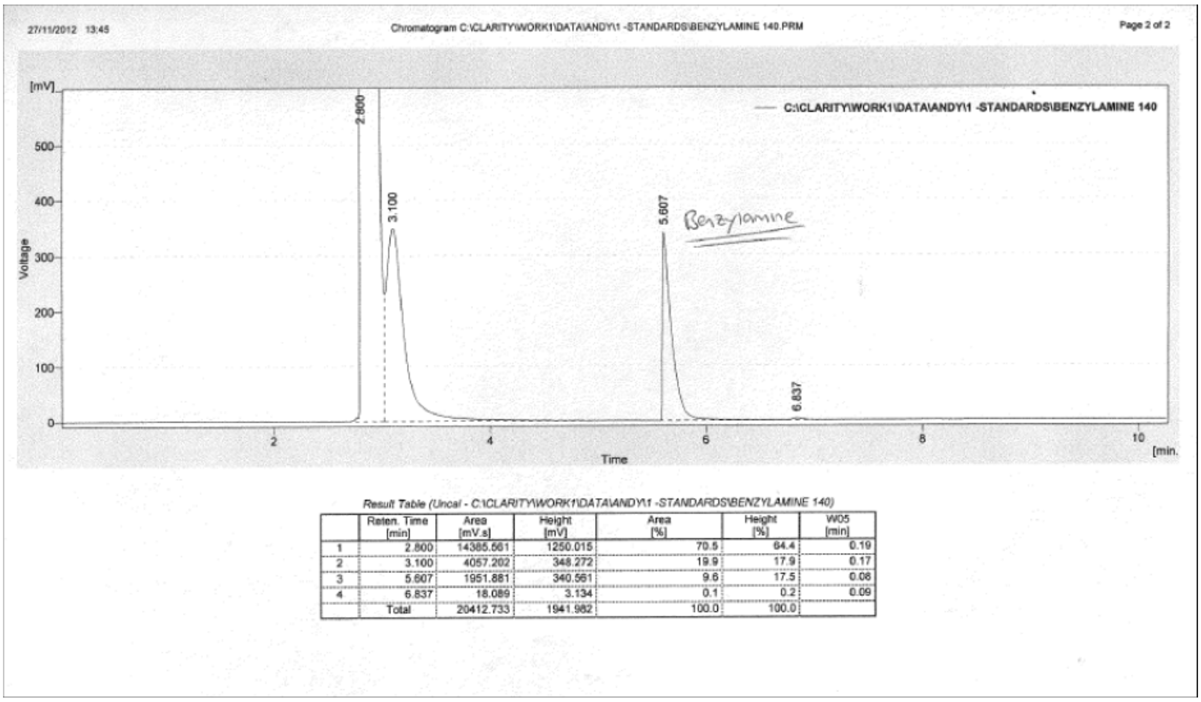
Chromatogram C:\Clarity\WORK1\DATA\compound\AR024.PRM

Page 2 of 2

Result Table (Uncal - C:\Clarity\WORK1\DATA\compound\AR024)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.690	15873.509	1249.902	71.9	71.2	0.21
2	3.013	5201.916	362.896	23.4	20.7	0.20
3	4.987	83.722	12.224	0.4	0.7	0.10
4	5.883	95.875	16.580	0.4	0.9	0.10
5	32.183	865.496	114.010	3.9	6.5	0.12
	Total	22220.517	1755.613	100.0	100.0	

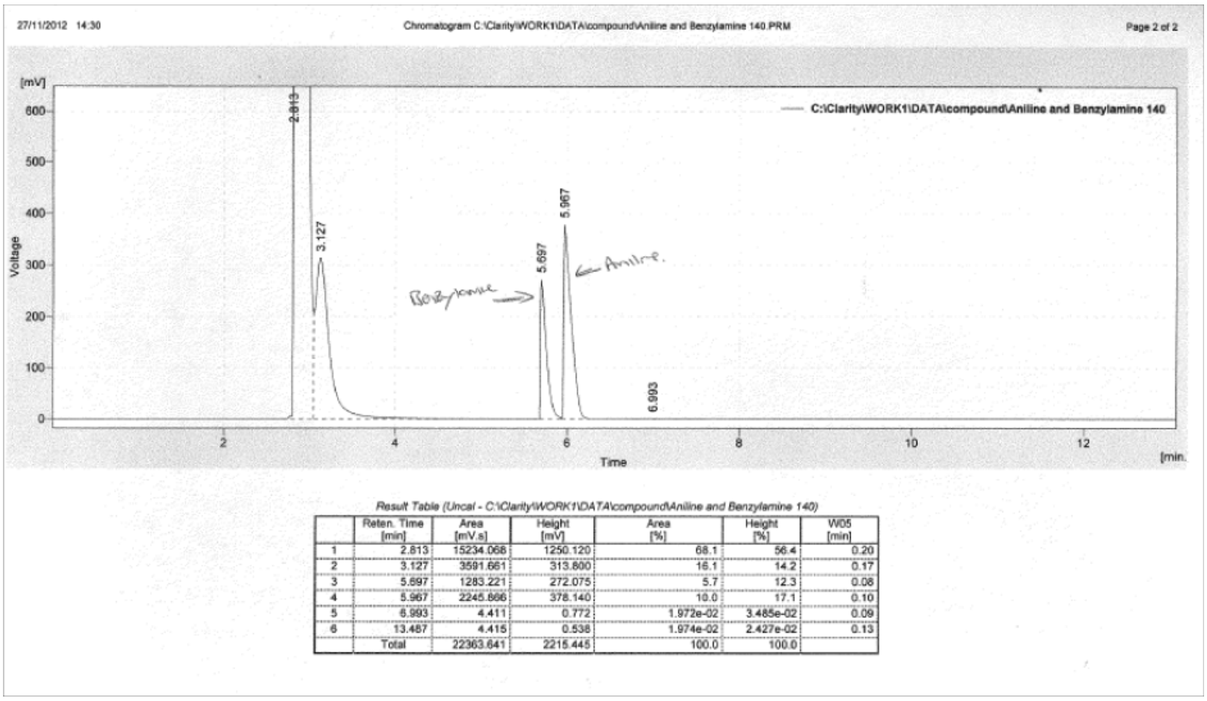
Inhibition of the reaction using benzylamine (AR025): Aniline (0.070 mL, 0.76 mmol), benzyl alcohol (0.078 mL, 0.76 mmol), benzylamine (0.042 mL, 0.38 mmol), triemethylamine N-oxide dehydrate (6 mg, 0.08 mmol) and iron catalyst **1** (40 mg, 0.076 mmol) were combined in a pressure tube along with degassed toluene (0.4 mL). The pressure tube was flushed with nitrogen and heated at 110 ^{o}C for 48h. At the end of this time the reaction was allowed to cool and worked up following the general procedure and analyzed by GC which showed the formation of ca 1% imine and 1% amine (indicated). Speculated, but unconfirmed, products from benzylamine are indicated. Attempts at the coupling of benzylamine alone with benzyl alcohol were also unsuccessful.



27/11/2012 13:45 Chromatogram C:\CLARITY\WORK1\DATA\ANDY\1 -STANDARDS\BENZYLAMINE 140.PRM Page 2 of 2

Result Table (Uncal - C:\CLARITY\WORK1\DATA\ANDY\1 -STANDARDS\BENZYLAMINE 140)

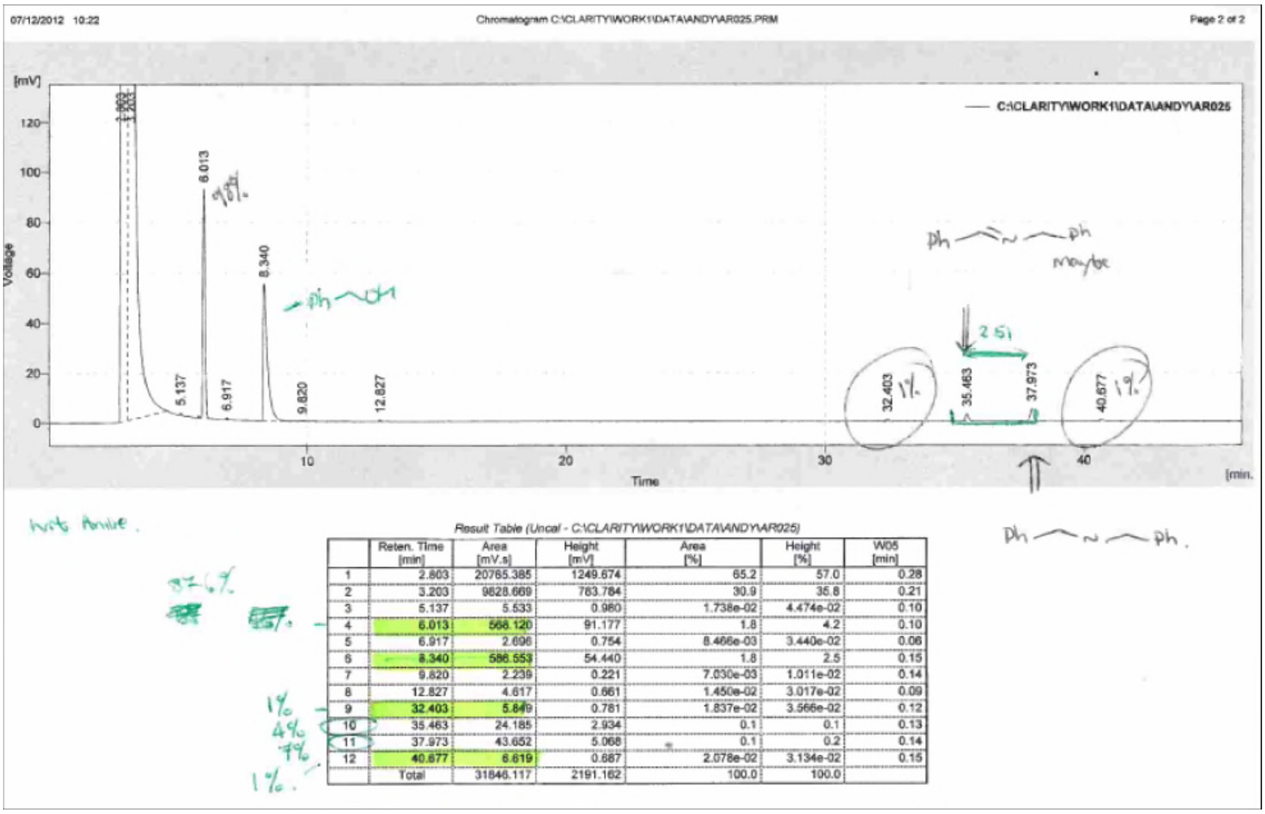
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.800	14385.561	1250.015	70.5	64.4	0.19
2	3.100	4057.202	348.272	19.9	17.9	0.17
3	5.607	1951.881	340.561	9.6	17.5	0.08
4	6.837	18.089	3.134	0.1	0.2	0.09
	Total	20412.733	1941.982	100.0	100.0	



27/11/2012 14:30 Chromatogram C:\Clarity\WORK1\DATA\compound\Aniline and Benzylamine 140.PRM Page 2 of 2

Result Table (Uncal - C:\Clarity\WORK1\DATA\compound\Aniline and Benzylamine 140)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.813	15234.068	1250.120	68.1	56.4	0.20
2	3.127	3591.661	313.800	16.1	14.2	0.17
3	5.697	1283.221	272.075	5.7	12.3	0.08
4	5.967	2245.866	378.140	10.0	17.1	0.10
5	6.993	4.411	0.772	1.972e-02	3.485e-02	0.09
6	13.487	4.415	0.538	1.974e-02	2.427e-02	0.13
	Total	22363.641	2215.445	100.0	100.0	



07/12/2012 10:22 Chromatogram C:\CLARITY\WORK1\DATA\ANDY\AR025.PRM Page 2 of 2

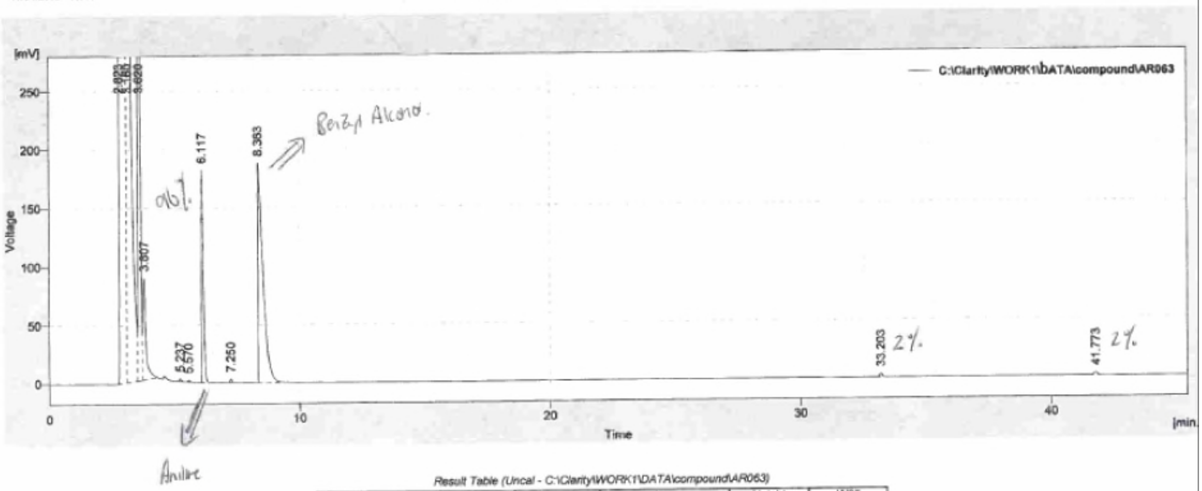
Result Table (Uncal - C:\CLARITY\WORK1\DATA\ANDY\AR025)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.803	20765.385	1249.674	65.2	57.0	0.28
2	3.203	9828.669	763.784	30.9	35.8	0.21
3	5.137	5.533	0.980	1.738e-02	4.474e-02	0.10
4	6.013	568.120	91.177	1.8	4.2	0.10
5	6.917	2.696	0.754	8.466e-03	3.440e-02	0.06
6	8.340	586.553	54.440	1.8	2.5	0.15
7	9.820	2.239	0.221	7.030e-03	1.011e-02	0.14
8	12.827	4.617	0.661	1.450e-02	3.017e-02	0.09
9	32.403	5.849	0.781	1.837e-02	3.566e-02	0.12
10	35.463	24.185	2.934	0.1	0.1	0.13
11	37.973	43.652	5.068	0.1	0.2	0.14
12	40.677	6.619	0.687	2.078e-02	3.134e-02	0.15
	Total	31846.117	2191.162	100.0	100.0	

Reaction carried out using Fe(CO)$_5$ alone (AR063): Aniline (0.069 mL, 0.76 mmol), benzyl alcohol (0.157 mL, 1.52 mmol), trimethylamine N-oxide dehydrate (6 mg, 0.076 mmol) and Fe(CO)$_5$ (38 mg, 0.076 mmol) were combined in degassed xylene in a nitrogen-flushed pressure tube and heated to 140 ^{o}C for 24h. At the end of this time the reaction was allowed to cool and worked up following the general procedure and analyzed by GC which showed the formation of ca. 2% imine and 2% amine.

GC spectrum:

17/01/2013 19:44 Chromatogram C:\Clarity\WORK1\DATA\compound\AR063.PRM Page 2 of 2



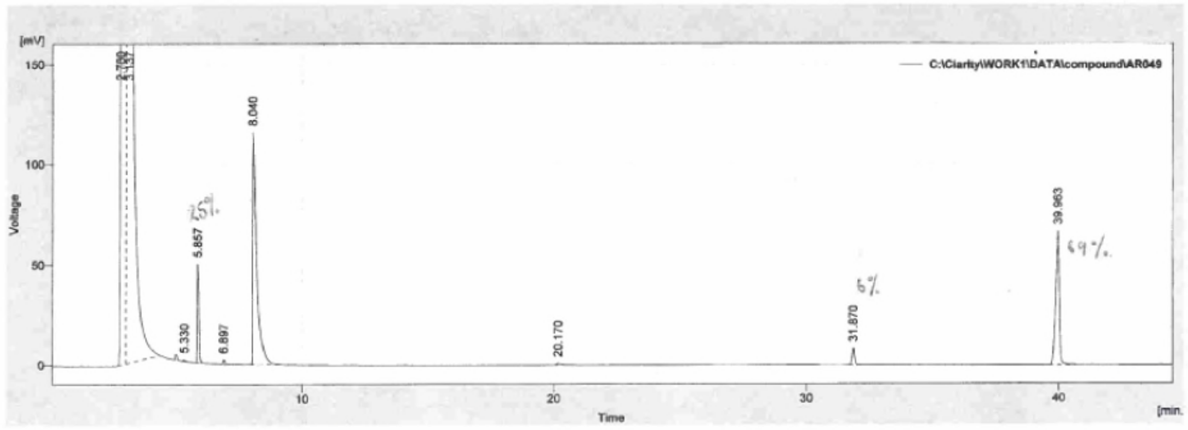
Result Table (Uncal - C:\Clarity\WORK1\DATA\compound\AR063)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.823	20117.507	1250.072	53.4	39.4	0.27
2	3.160	8692.170	753.117	23.1	23.7	0.18
3	3.620	4422.504	704.555	11.7	22.2	0.11
4	3.807	732.607	87.037	1.9	2.7	0.12
5	5.237	13.450	2.317	3.572e-02	0.1	0.10
6	5.570	8.393	1.368	2.229e-02	4.307e-02	0.10
7	6.117	1039.102	181.114	2.8	5.7	0.09
8	7.250	16.336	2.980	4.338e-02	0.1	0.09
9	8.363	2568.889	187.405	6.8	5.9	0.20
10	33.203	23.159	3.066	0.1	0.1	0.12
11	41.773	23.391	2.293	0.1	0.1	0.16
	Total	37657.509	3175.323	100.0	100.0	

Reactions at lower temperatures: Reactions were carried out for 48h following the general procedure above but at lower temperatures; at 100 ^{o}C the conversion was 69% (AR049), at 90 ^{o}C, the conversion was 37% (AR053), and at 80 ^{o}C the conversion was 5% (AR055).

AR049 (100 ^{o}C).

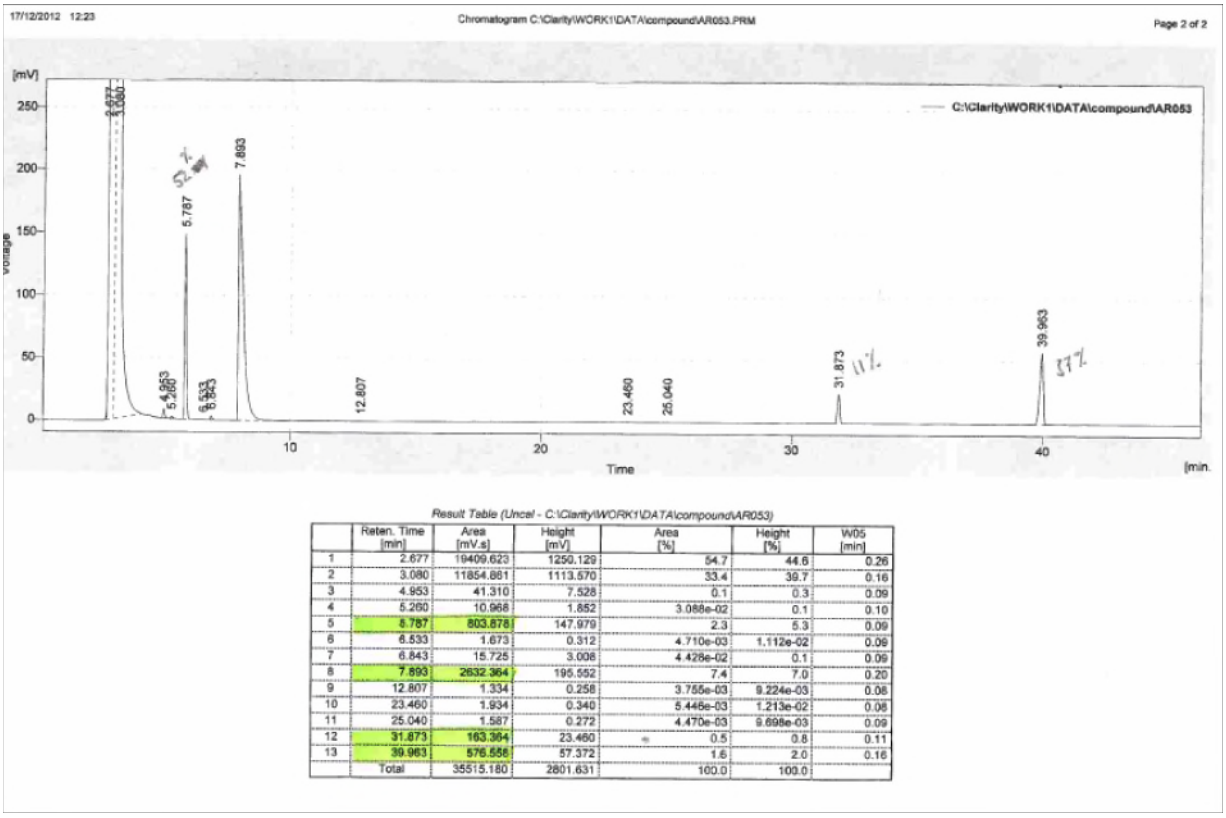
12/12/2012 16:01 Chromatogram C:\Clarity\WORK1\DATA\compound\AR049.PRM Page 2 of 2



Result Table (Uncal - C:\Clarity\WORK1\DATA\compound\AR049)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.780	17411.575	1249.955	52.7	46.9	0.24
2	3.137	13292.758	1173.766	40.3	44.0	0.20
3	5.330	4.426	0.749	1.340e-02	2.808e-02	0.09
4	5.857	255.070	49.195	0.8	1.8	0.09
5	6.897	10.102	2.013	3.059e-02	0.1	0.08
6	8.040	1290.104	115.400	3.9	4.3	0.15
7	20.170	10.946	0.799	3.315e-02	2.997e-02	0.24
8	31.870	60.471	8.302	0.2	0.3	0.11
9	39.963	686.566	66.404	2.1	2.5	0.17
	Total	33022.019	2666.584	100.0	100.0	

AR053 (90 ^{o}C):



17/12/2012 12:23

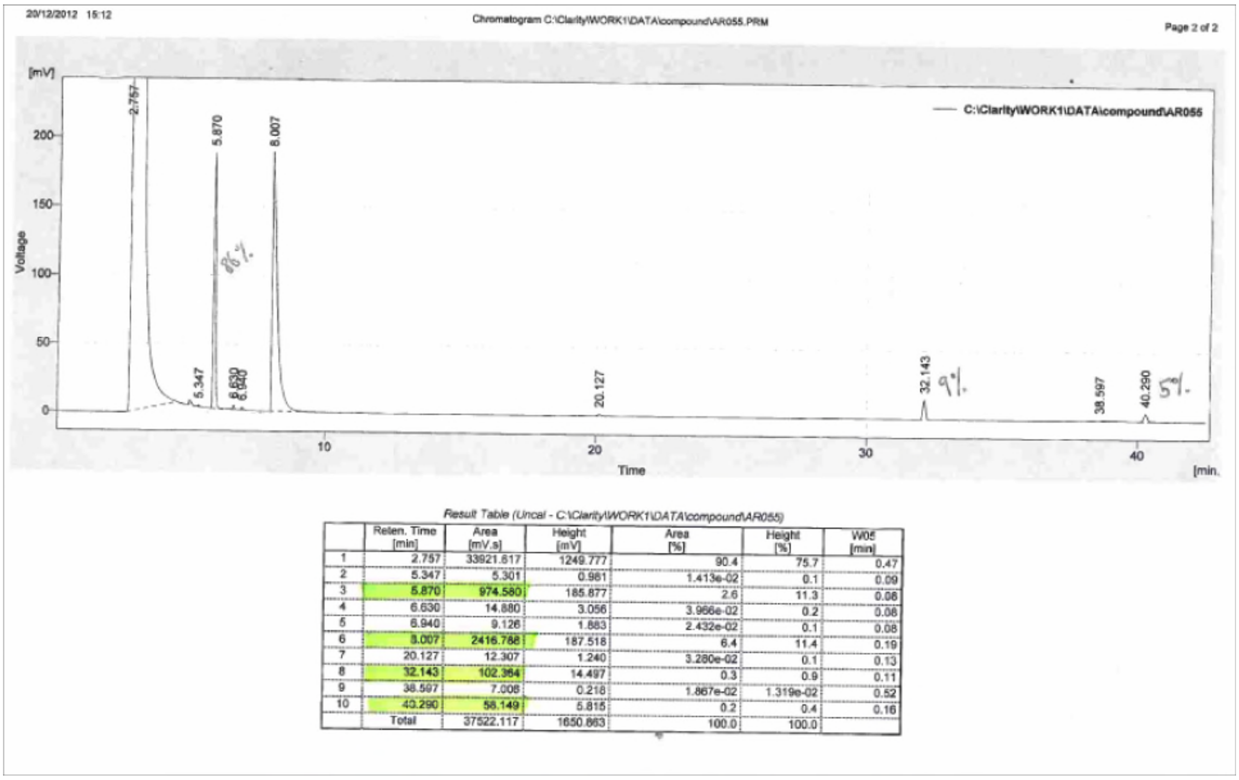
Chromatogram C:\Clarity\WORK1\DATA\compound\AR053.PRM

Page 2 of 2

Result Table (Uncal - C:\Clarity\WORK1\DATA\compound\AR053)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.677	19409.623	1250.129	54.7	44.6	0.26
2	3.080	11854.861	1113.570	33.4	39.7	0.16
3	4.953	41.310	7.528	0.1	0.3	0.09
4	5.260	10.968	1.852	3.088e-02	0.1	0.10
5	5.787	803.878	147.979	2.3	5.3	0.09
6	6.533	1.673	0.312	4.710e-03	1.112e-02	0.09
7	6.843	15.725	3.008	4.428e-02	0.1	0.09
8	7.893	2632.364	195.552	7.4	7.0	0.20
9	12.807	1.334	0.258	3.755e-03	9.224e-03	0.08
10	23.460	1.934	0.340	5.446e-03	1.213e-02	0.08
11	25.040	1.587	0.272	4.470e-03	9.698e-03	0.09
12	31.873	163.364	23.460	0.5	0.8	0.11
13	39.963	576.556	57.372	1.6	2.0	0.16
	Total	35515.180	2801.631	100.0	100.0	

AR055 (80 ^{o}C):



20/12/2012 15:12

Chromatogram C:\Clarity\WORK1\DATA\compound\AR055.PRM

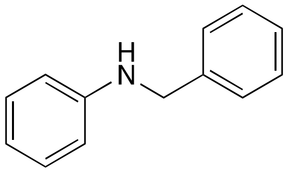
Page 2 of 2

Result Table (Uncal - C:\Clarity\WORK1\DATA\compound\AR055)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	2.757	33921.617	1249.777	90.4	75.7	0.47
2	5.347	5.301	0.981	1.413e-02	0.1	0.09
3	5.870	974.580	185.877	2.6	11.3	0.08
4	6.630	14.880	3.056	3.966e-02	0.2	0.08
5	6.940	9.126	1.883	2.432e-02	0.1	0.08
6	8.007	2416.788	187.518	6.4	11.4	0.19
7	20.127	12.307	1.240	3.280e-02	0.1	0.13
8	32.143	102.364	14.497	0.3	0.9	0.11
9	38.597	7.008	0.218	1.867e-02	1.319e-02	0.52
10	40.290	58.149	5.815	0.2	0.4	0.16
	Total	37522.117	1650.863	100.0	100.0	

Experimental data for isolated products.

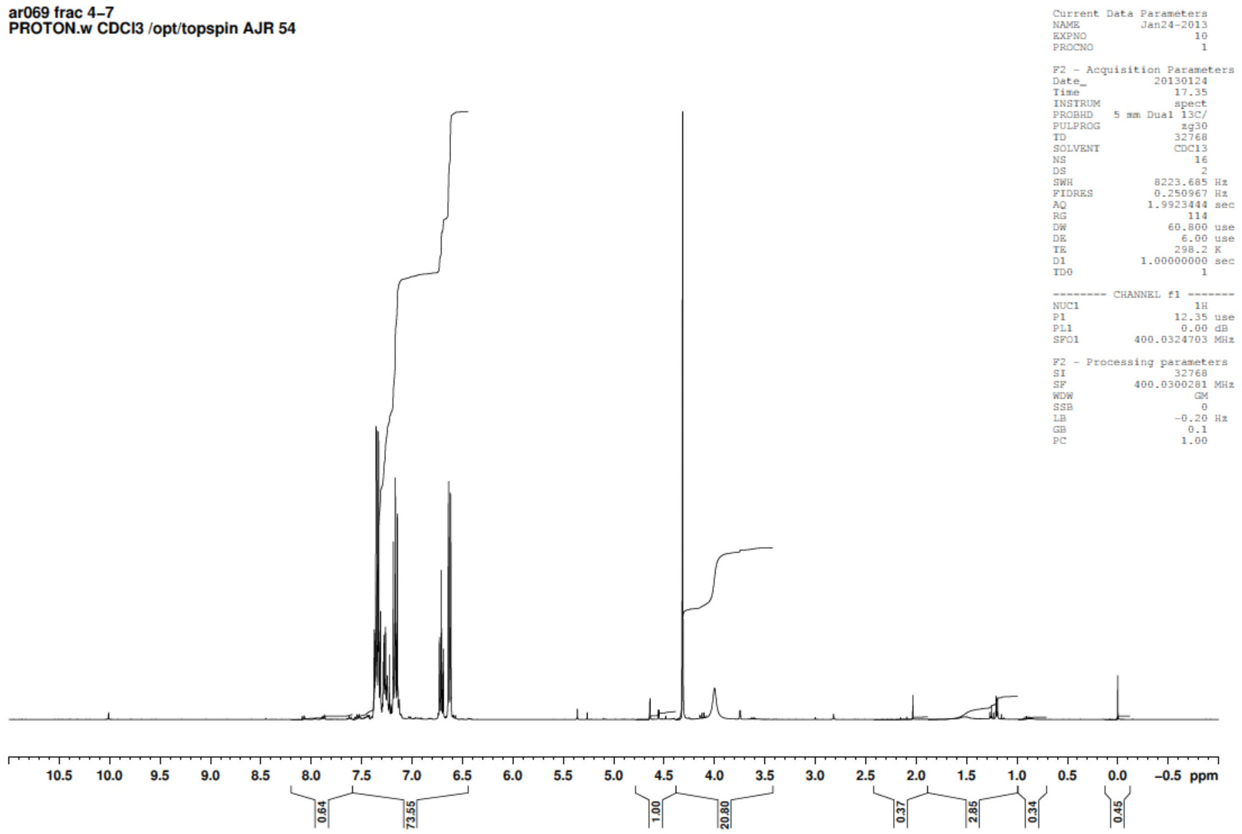
N-Benzylaniline 7.



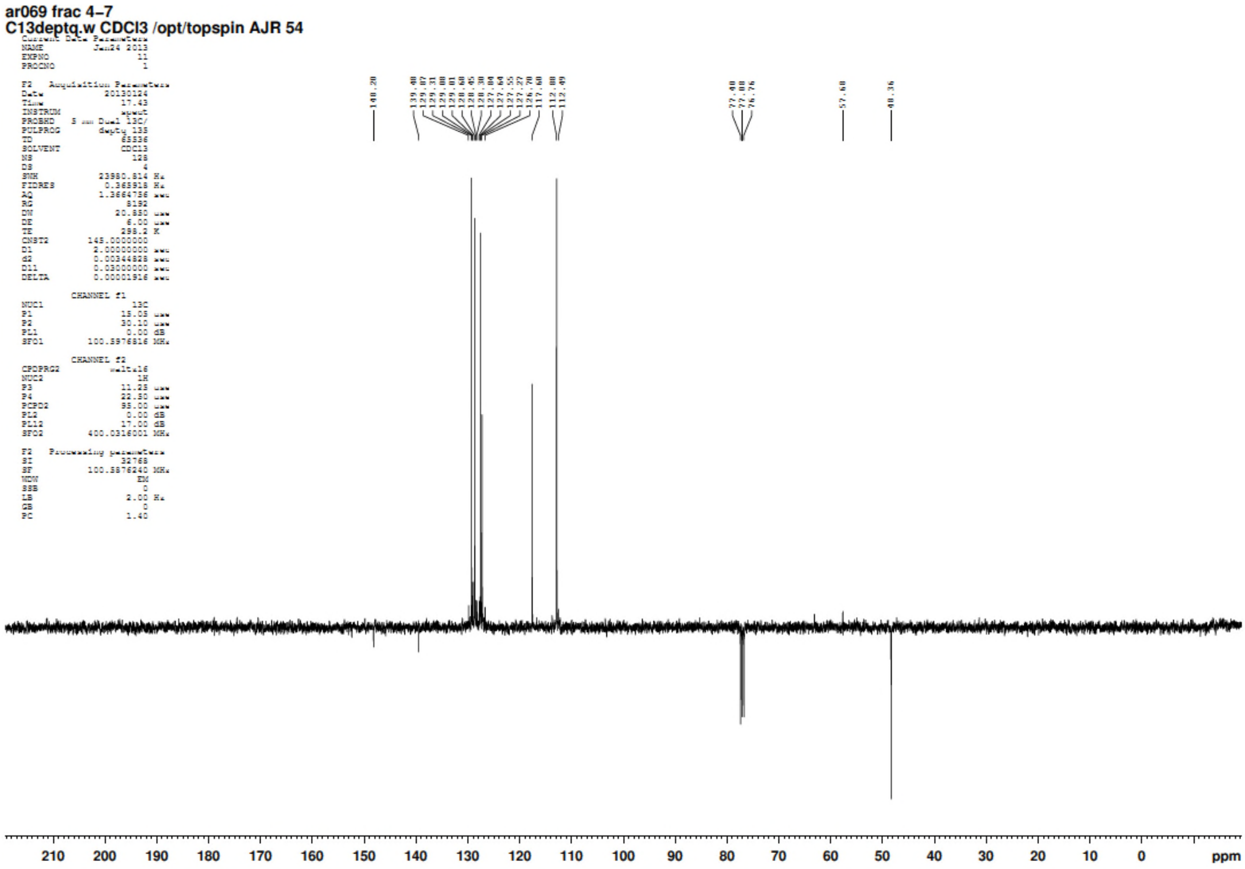
(Toluene, 110 °C, 48h, AR069).

This compound has been reported and fully characterized, and the data matched that reported and of an authentic sample (see end of this file).[1] Aniline **6** (0.069 mL, 0.76 mmol) benzyl alcohol **5** (0.157 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a pale yellow oil (133.7 mg, 0.731 mmol, 95 %). δ_H (400 MHz, $CDCl_3$) 7.30-7.40 (4H, m, Ar*H*), 7.24-7.29 (1H, m, Ar*H*), 7.12-7.20 (2H, m, Ar*H*), 6.68-6.74 (1H, m, Ar*H*), 6.61-6.65 (2H, m, Ar*H*), 4.32 (2H, s, $NHCH_2$), 4.00 (1H, s, N*H*); δ_C (100 MHz, $CDCl_3$) 148.20 (C), 139.48 (C), 129.30 (CH), 128.67 (CH), 127.55 (CH), 127.27 (CH), 117.60 (CH), 112.49 (CH), 48.36 (CH_2); *m/z* (ESMS+) $[M+H]^+$ 184.1. $C_{13}H_{14}N^+$.

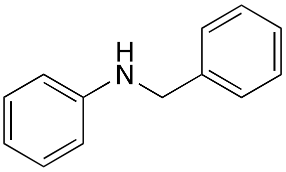
^1H NMR δ_H (400 MHz, $CDCl_3$):



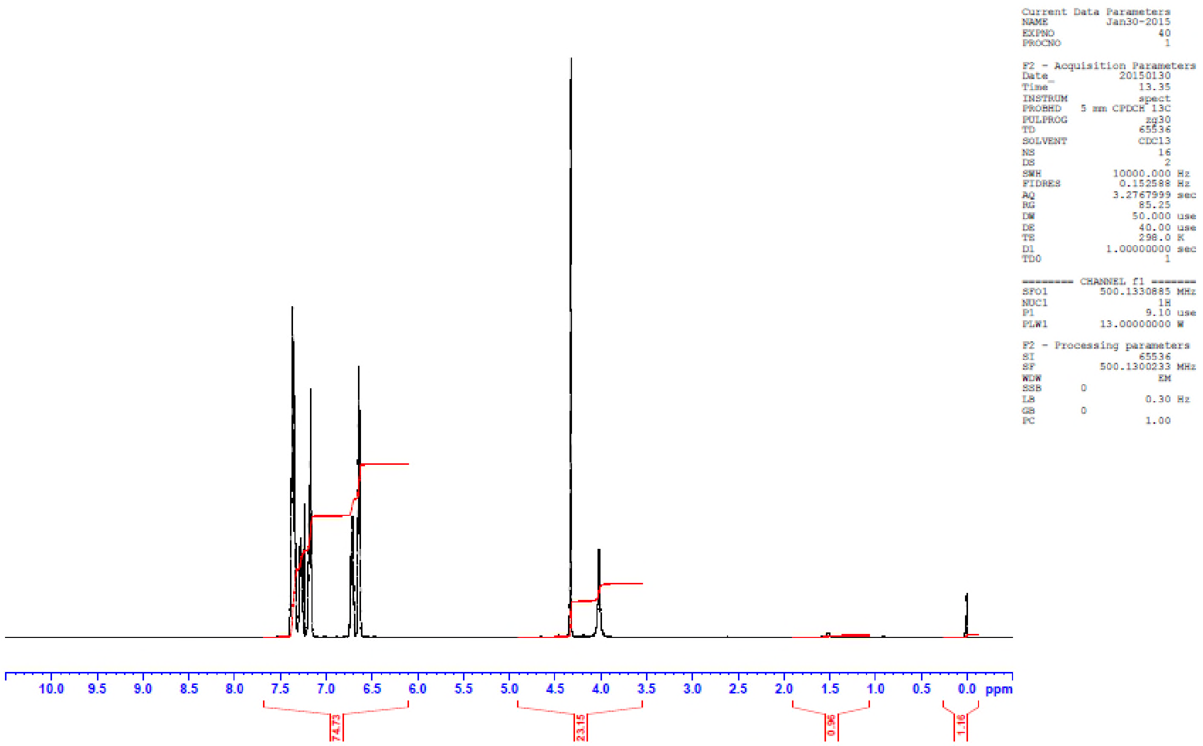
^{13}C NMR δ_C (100 MHz, $CDCl_3$):



***Commercial standard of* N-Benzylaniline 7 for comparison:**



^{1}H NMR δ_H (500 MHz, $CDCl_3$, cryoprobe):



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PROCNO                    1

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PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2767999 sec
RG                    85.25
DW                   50.000 use
DE                    40.00 use
TE                    298.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 =======
SFO1           500.1330885 MHz
NUC1                     1H
P1                     9.10 use
PLW1           13.00000000 W

F2 - Processing parameters
SI                    65536
SF             500.1300233 MHz
WDW                      EM
SSB        0
LB                     0.30 Hz
GB         0
PC                     1.00
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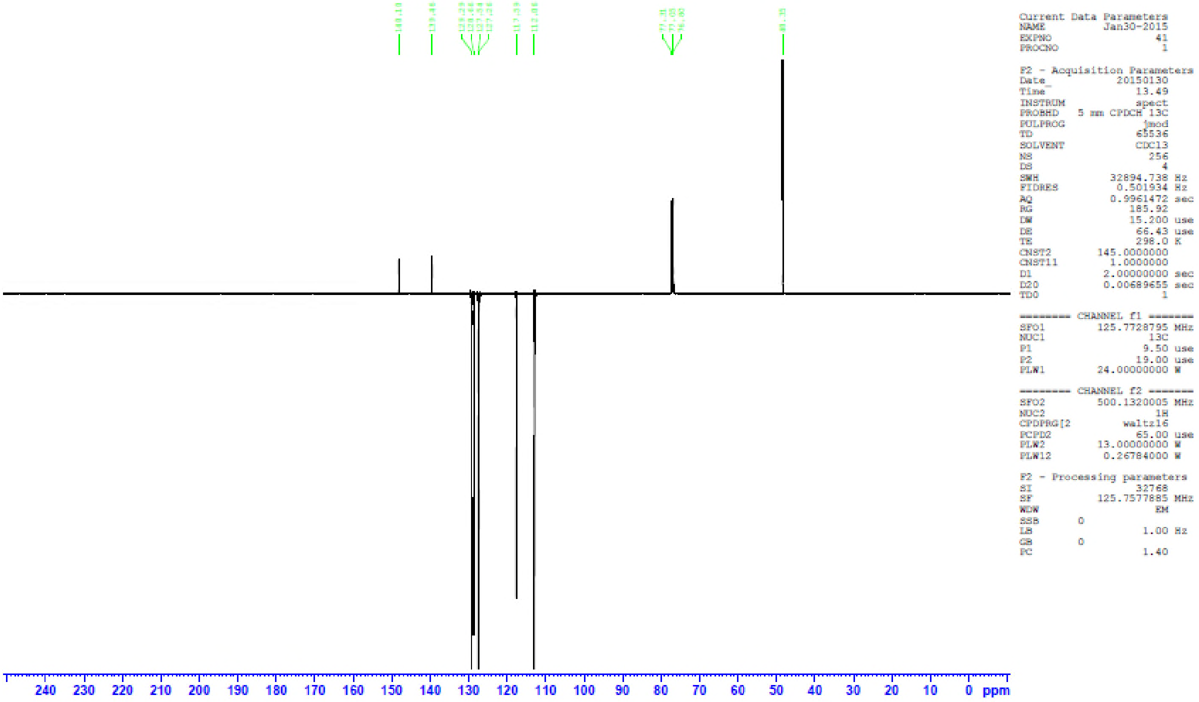
^{13}C NMR δ_C (125 MHz, $CDCl_3$, cryoprobe):



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EXPNO                     41
PROCNO                     1

F2 - Acquisition Parameters
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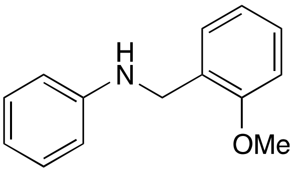
PULPROG                 jmod
TD                     65536
SOLVENT                CDCl3
NS                       256
DS                         4
SWH             32894.738 Hz
FIDRES           0.501934 Hz
AQ              0.9961472 sec
RG                    185.92
DW                15.200 use
DE                 66.43 use
TE                 298.0 K
CNST2         145.0000000
CNST11          1.0000000
D1             2.00000000 sec
D20            0.00689655 sec
TD0                        1

======== CHANNEL f1 =======
SFO1          125.7728795 MHz
NUC1                     13C
P1                   9.50 use
P2                  19.00 use
PLW1          24.00000000 W

======== CHANNEL f2 =======
SFO2          500.1320005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2               65.00 use
PLW2          13.00000000 W
PLW12          0.26784000 W

F2 - Processing parameters
SI                     32768
SF            125.7577885 MHz
WDW                       EM
SSB         0
LB                   1.00 Hz
GB          0
PC                      1.40
```

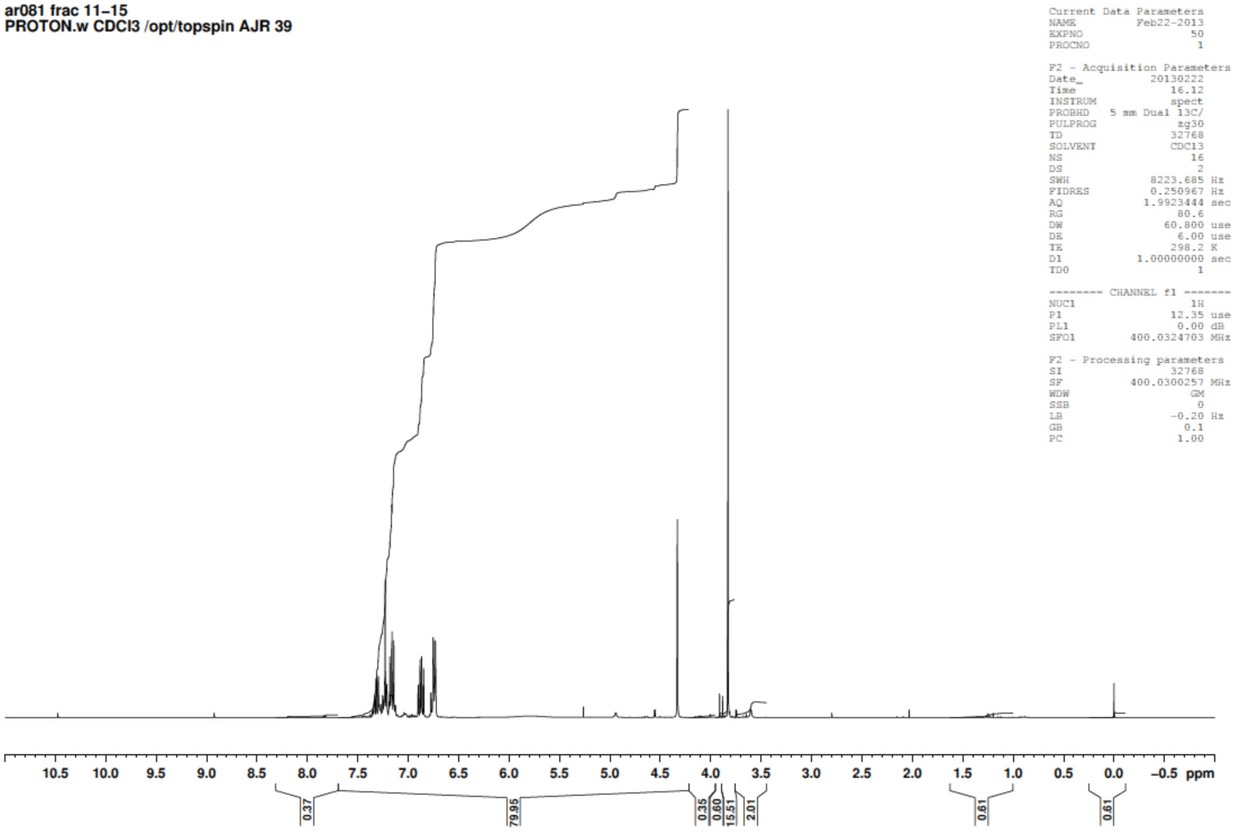
_N_-(2-Methoxybenzyl)aniline 9.



(Xylene, 140 °C, 24h AR081).

This compound has been reported and fully characterized, and the data matched that of an authentic sample (see end of this file).[2] Aniline **6** (0.069 mL, 0.76 mmol) 2-methoxybenzyl alcohol (0.202 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give a pale yellow oil (136.6 mg, 0.641 mmol, 84 %). δ_H (400 MHz, $CDCl_3$) 7.27-7.36 (2H, m, Ar*H*), 7.12-7.20 (2H, m, Ar*H*), 6.84-6.91 (2H, m, Ar*H*), 6.71-6.78 (3H, m, Ar*H*), 5.35-6.17 (1H, br s, N*H*), 4.33 (2H, s, NHCH_2), 3.83 (3H, s, OCH_3); δ_C (100 MHz, $CDCl_3$) 157.52 (C), 146.61 (C), 129.40 (CH), 129.22 (CH), 128.69 (CH), 126.18 (C), 120.55 (CH), 118.89 (CH), 114.53 (CH), 110.28 (CH), 55.35 (CH_3), 44.48 (CH_2); *m/z* (ESMS+) $[M+H]^+$ 214.1. $C_{14}H_{16}NO^+$.

^{1}H NMR δ_H (400 MHz, $CDCl_3$):



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Current Data Parameters
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PROCNO                  1

F2 - Acquisition Parameters
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Time                16.12
INSTRUM             spect
PROBHD   5 mm Dual 13C/
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ              1.9923444 sec
RG                   80.6
DW                 60.800 use
DE                   6.00 use
TE                  298.2 K
D1             1.00000000 sec
TD0                     1

-------- CHANNEL f1 -------
NUC1                   1H
P1                  12.35 use
PL1                  0.00 dB
SFO1          400.0324703 MHz

F2 - Processing parameters
SI                  32768
SF            400.0300257 MHz
WDW                    GM
SSB                     0
LB                  -0.20 Hz
GB                    0.1
PC                   1.00
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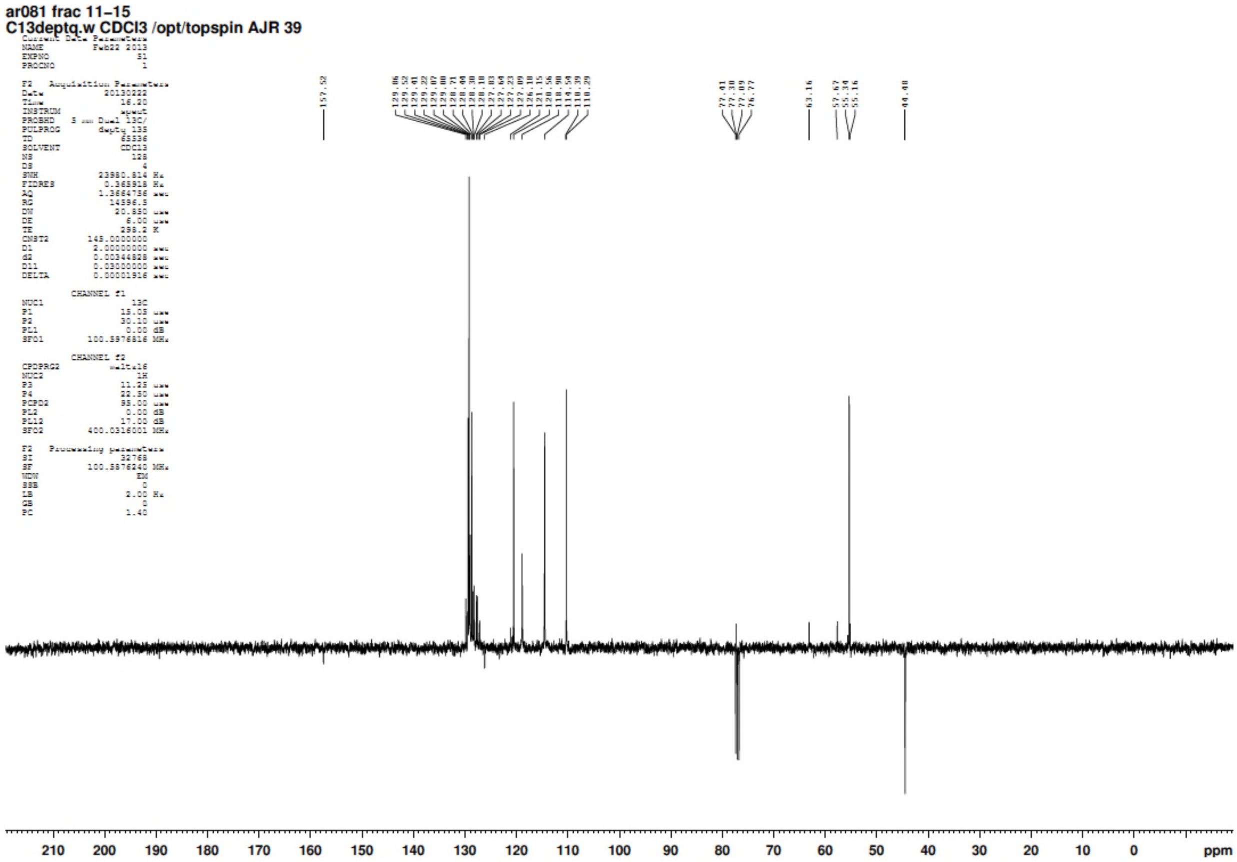
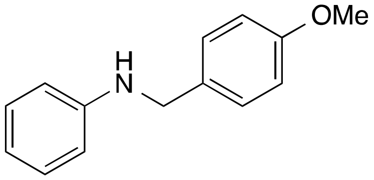
^{13}C NMR δ_C (100 MHz, $CDCl_3$):



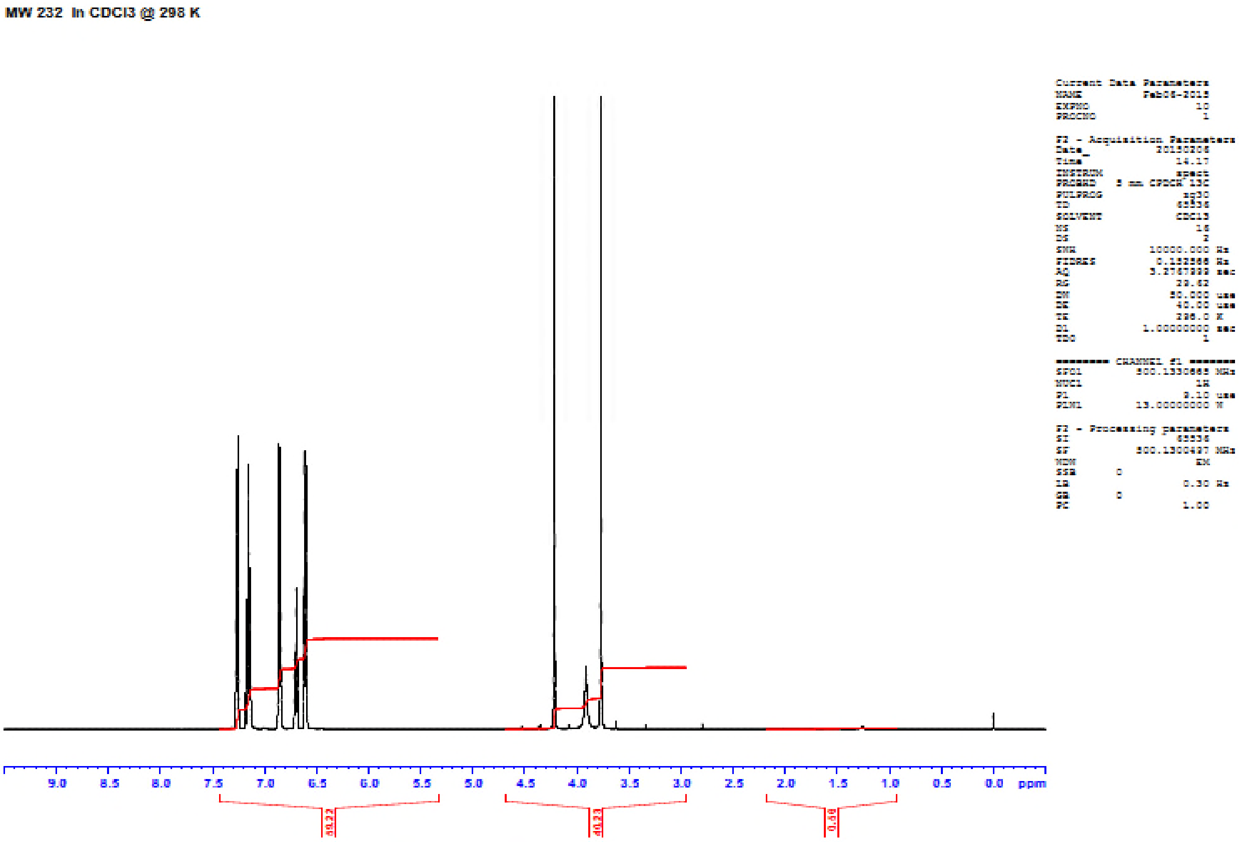
N-(4-Methoxybenzyl)aniline 10.



(Xylene, 140 °C, 24h, MW232).

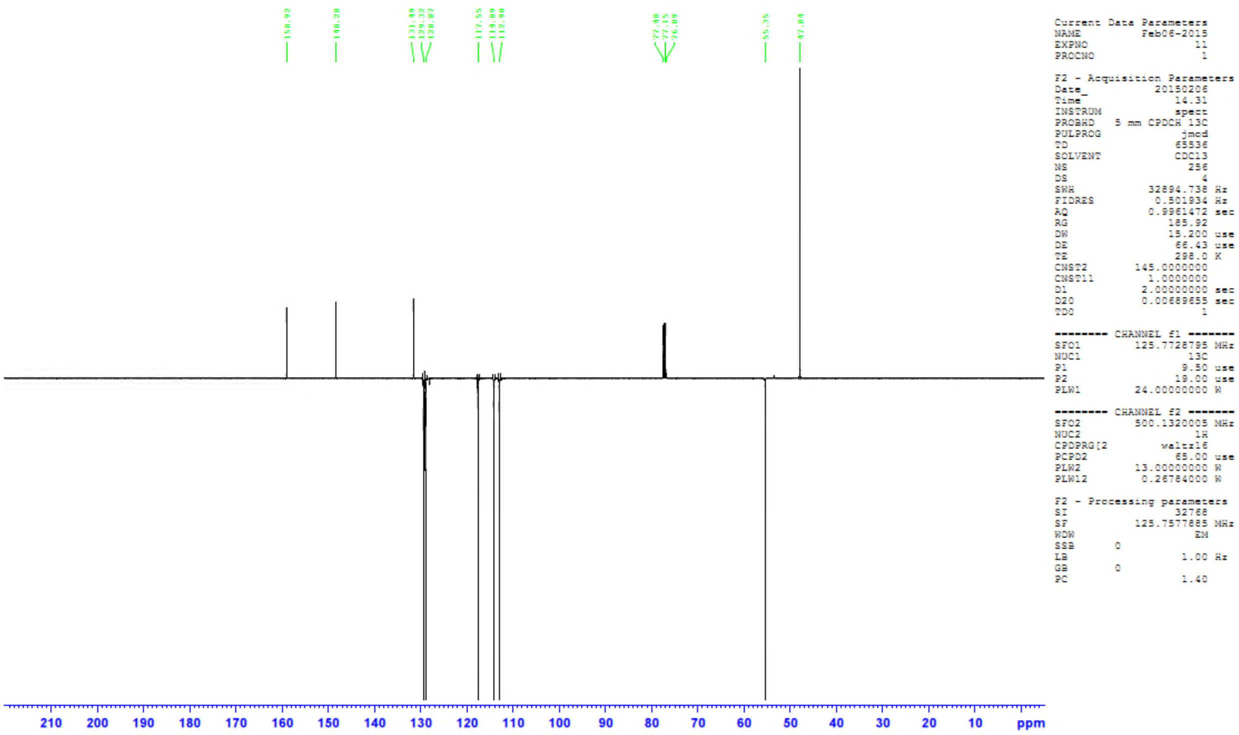
This compound has been reported and fully characterized.[1] Aniline **6** (0.069 mL, 0.76 mmol) 4-methoxybenzyl alcohol (0.189 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. Purification was attempted by column chromatography on silica with a gradient elution 0-30% EtOAc in pet. ether to give the product as a brown oil (124.1 mg, 0.58 mmol, 77 %). ^{1}H NMR. δ_H (500 MHz, $CDCl_3$) 7.15-7.23 (2H, m, Ar*H*), 7.10-7.15 (2H, m, Ar*H*), 6.80-6.85 (2H, m, Ar*H*), 6.65-6.70 (1H, m, Ar*H*), 6.68-6.62 (2H, m, Ar*H*), 4.22 (2H, S, CH_2), 90 (1H, br s, N*H*), 3.75 (3H, s, OC*H*$_3$); δ_C (125 MHz, $CDCl_3$) 158.92 (C), 148.28 (C), 131.49 (C), 129.32 (CH), 128.87 (CH), 117.55 (CH), 114.09 (CH), 112.90 (CH), 55.36 (CH_3), 47.84 (CH_2); *m/z* (ESMS+) $[M+H]^+$ 214.1. $C_{13}H_{13}ClN^+$.

^1H NMR δ_H (500 MHz with cryoprobe, $CDCl_3$):



^{13}C NMR δ_C (125 MHz with cryoprobe, $CDCl_3$):

MW 232 in CDCl3 @ 298 K



```
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EXPNO                 11
PROCNO                 1

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Date_           20150206
Time               14.31
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            32894.738 Hz
FIDRES          0.501934 Hz
AQ             0.9961472 sec
RG                185.92
DW                15.200 use
DE                 66.43 use
TE                 298.0 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
D20           0.00689655 sec
TD0                    1

======== CHANNEL f1 =======
SFO1        125.7728795 MHz
NUC1                 13C
P1                  9.50 use
P2                 19.00 use
PLW1         24.00000000 W

======== CHANNEL f2 =======
SFO2        500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              65.00 use
PLW2         13.00000000 W
PLW12         0.26784000 W

F2 - Processing parameters
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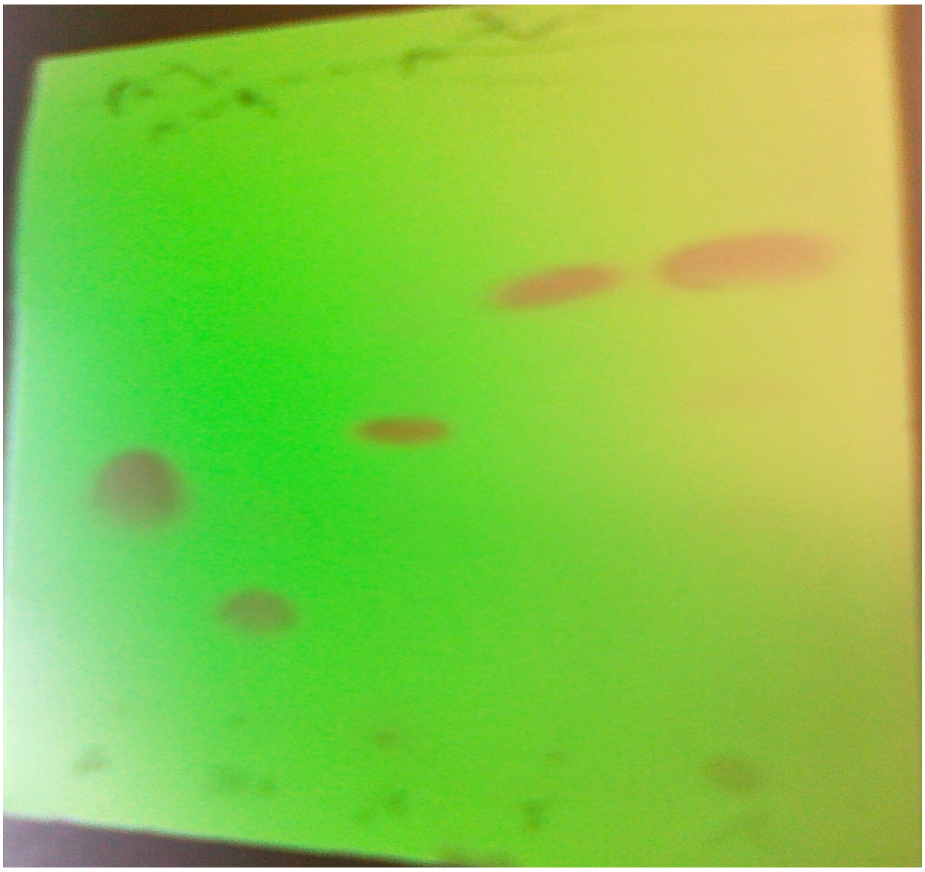
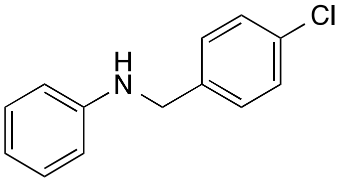
GB        0
PC                  1.40
```

TLC of crude reaction:



The TLC above shows the crude and purified product from the above reaction after dilution of a sample in DCM. In order the lanes show i) aniline, ii) pMeO)$C_6H_4CH_2OH$, iii) Iron catalyst **1**, iv) purified sample of **12**, v) crude reaction mixture. Visualisation by uv, spots can also be visualized using $KMnO_4$. Solvent: hexane:EtOAc 4:1.

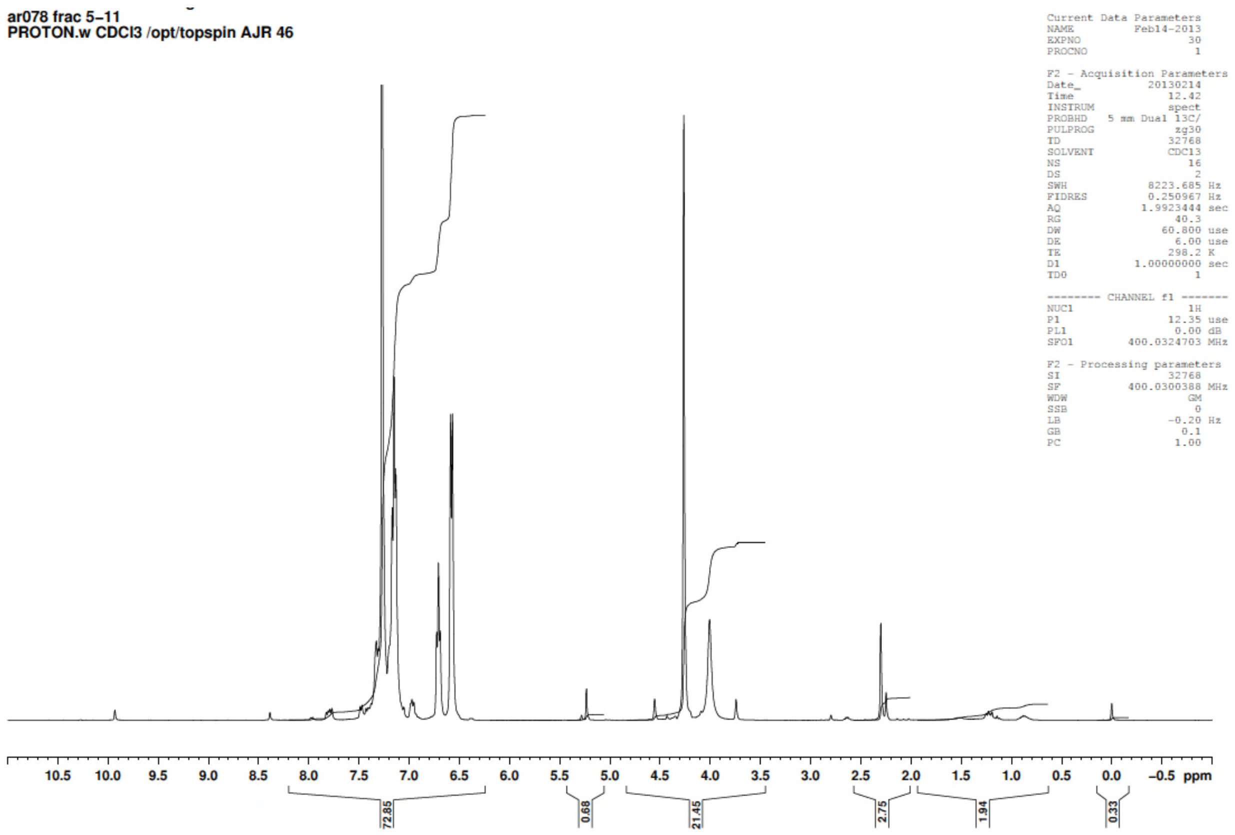
***N*-(4-Chlorobenzyl)aniline 11.**



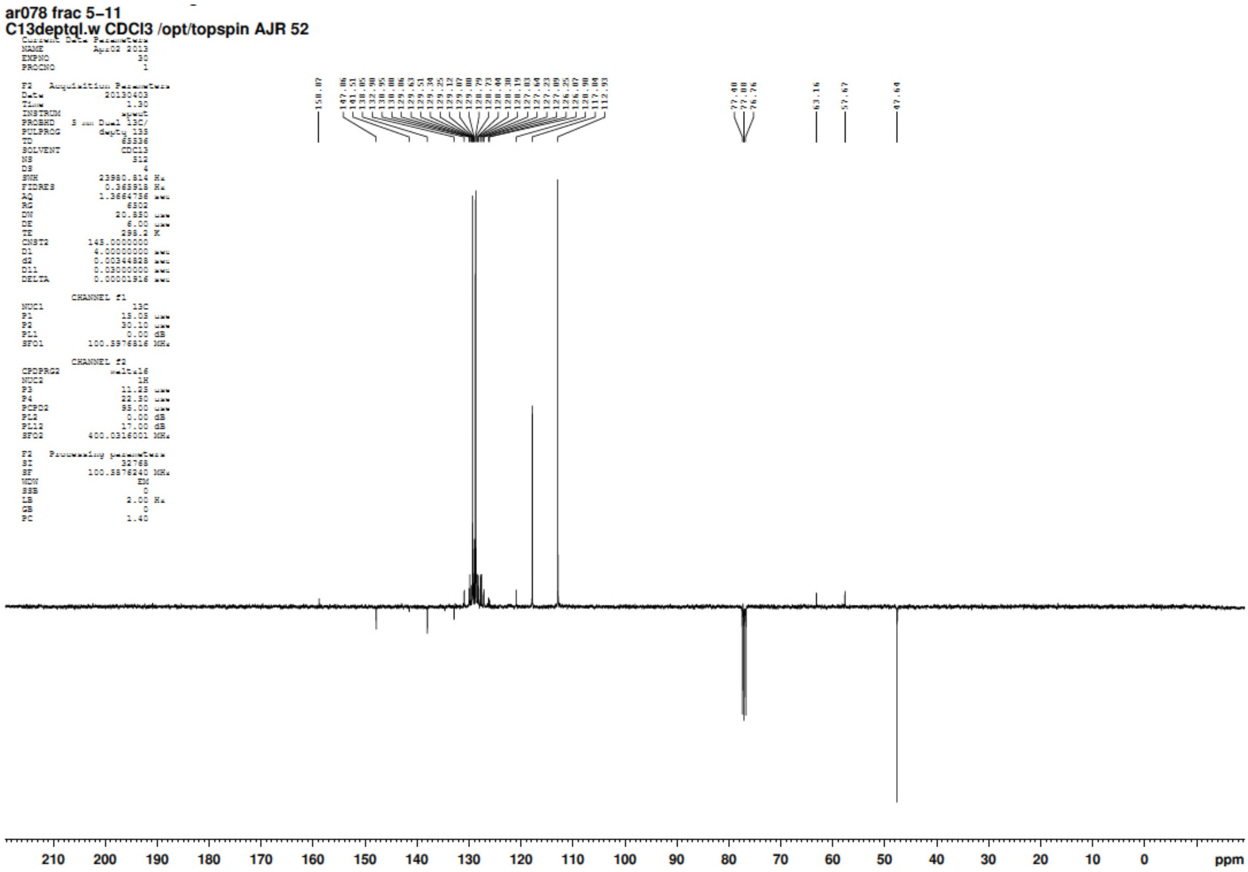
(Xylene, 140 °C, 24h AR078).

This compound has been reported and fully characterised.[1] Aniline **6** (0.069 mL, 0.76 mmol) 4-chlorobenzyl alcohol (0.217 mg, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. Ether to give the product as a pale yellow oil (100.0 mg, 0.461 mmol, 60 %). δ_H (400 MHz, $CDCl_3$) 7.22-7.36 (4H, m, Ar*H*), 7.09-7.19 (2H, m, Ar*H*), 6.67-6.75 (1H, m, Ar*H*), 6.53-6.61 (2H, m, Ar*H*), 4.26 (2H, s, NHCH_2), 4.01 (1H, br s, N*H*); δ_C (100 MHz, $CDCl_3$) 147.86 (C), 138.05 (C), 132.90 (C), 129.34 (CH), 128.79 (CH), 128.73 (CH), 117.84 (CH), 112.93 (CH), 47.64 (CH_2); *m/z* (ESMS+) $[M+H]^+$ 218.1. $C_{13}H_{13}ClN^+$.

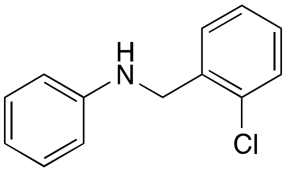
^{1}H NMR δ_H (400 MHz, $CDCl_3$):



^{13}C NMR δ_C (100 MHz, $CDCl_3$):



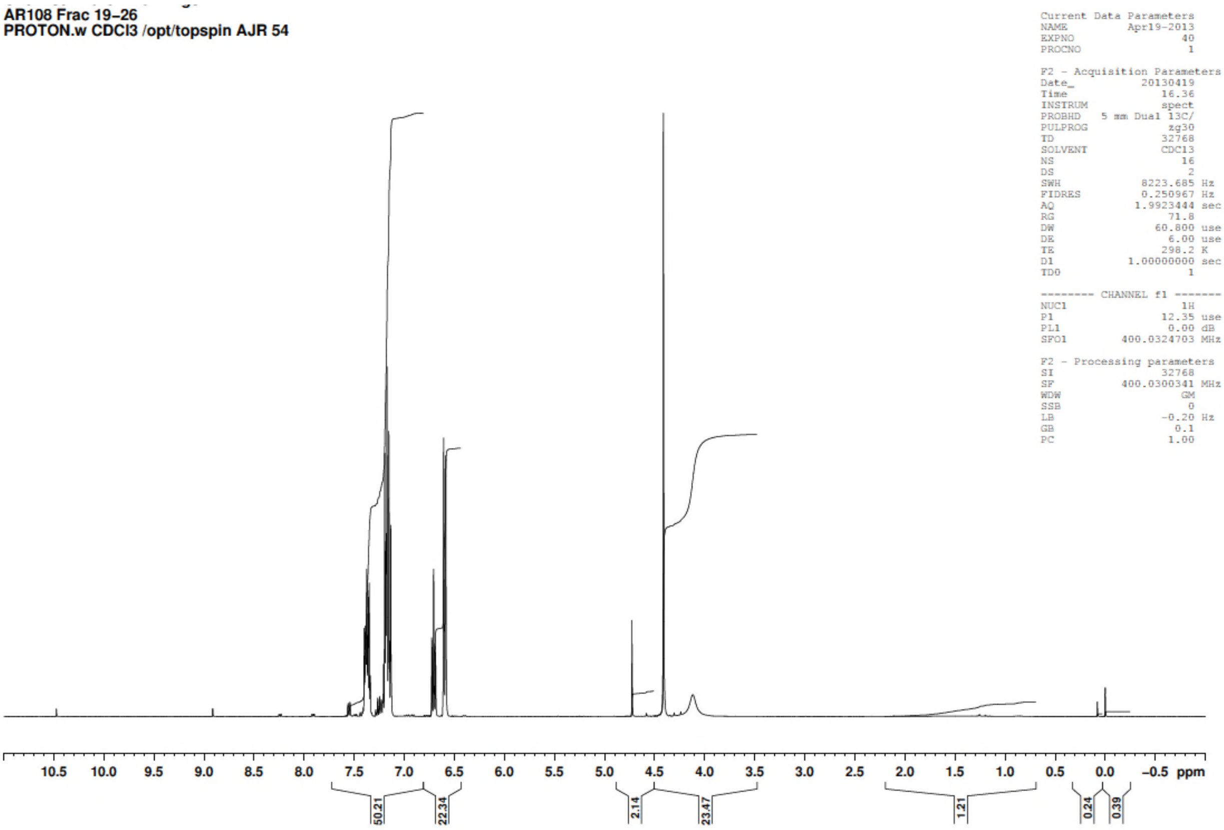
N-(2-Chlorobenzyl)aniline 12.



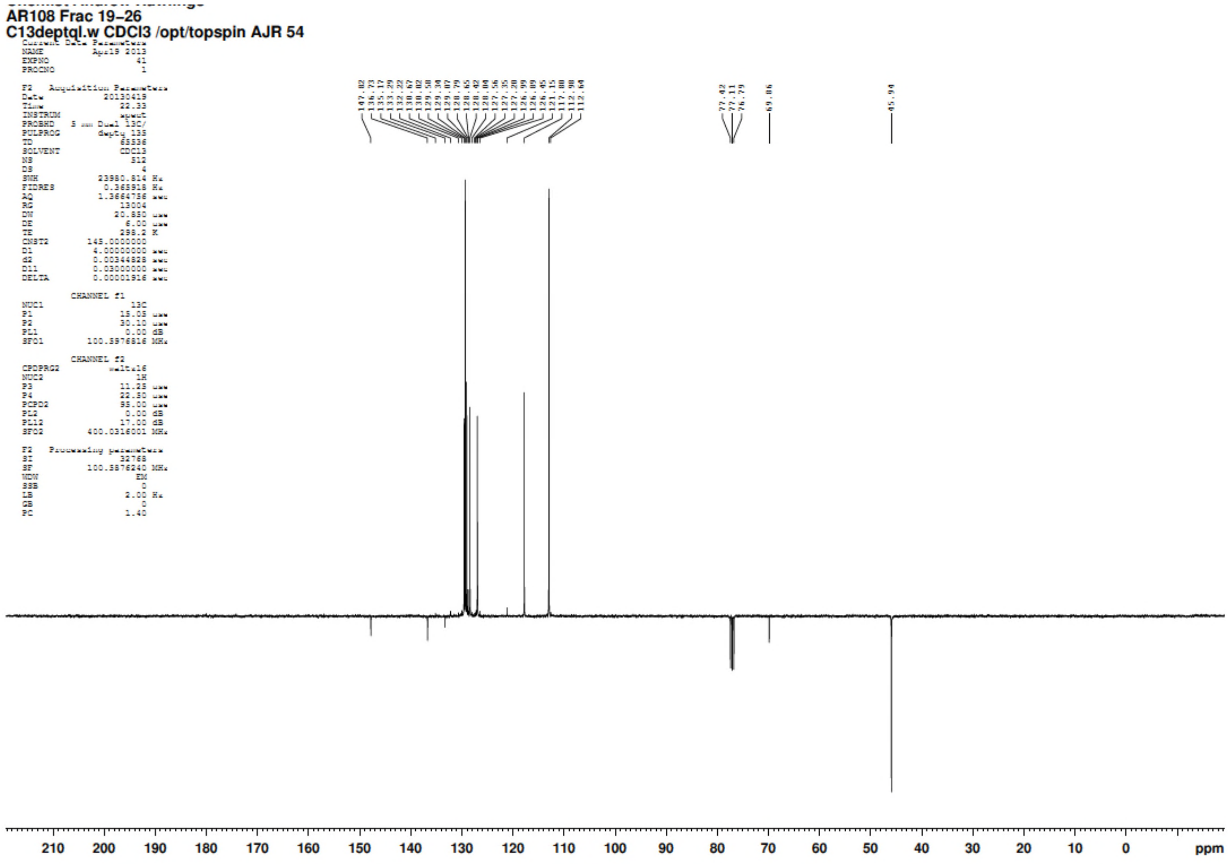
(Xylene, 140 °C, 24h, AR108).

This compound has been reported and fully characterized.[2] Aniline **6** (0.069 mL, 0.76 mmol) o-chlorobenzyl alcohol (0.157 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a light brown oil (93.0 mg, 0.429 mmol, 56 %). δ_H (400 MHz, $CDCl_3$) 7.34-7.42 (2H, m, Ar*H*), 7.11-7.20 (4H, m, Ar*H*), 6.68-6.73 (1H, m, Ar*H*), 6.57-6.62 (2H, m, Ar*H*), 4.41 (2H, s, NHCH_2), 4.12 (1H, br s, N*H*); δ_C (100 MHz, $CDCl_3$) 147.81 (C), 136.72 (C), 133.28 (C), 129.57 (CH), 129.33 (CH), 129.06 (CH), 128.41 (CH), 126.97 (CH), 117.79 (CH), 112.97 (CH), 45.94 (CH_2); *m/z* (ESMS+) $[M+H]^+$ 218.1. $C_{13}H_{13}ClN^+$.

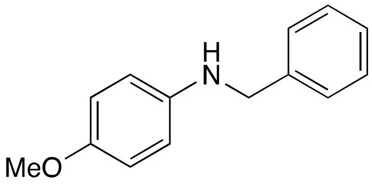
^{1}H NMR δ_H (400 MHz, $CDCl_3$):



^{13}C NMR δ_C (100 MHz, CDCl$_3$):



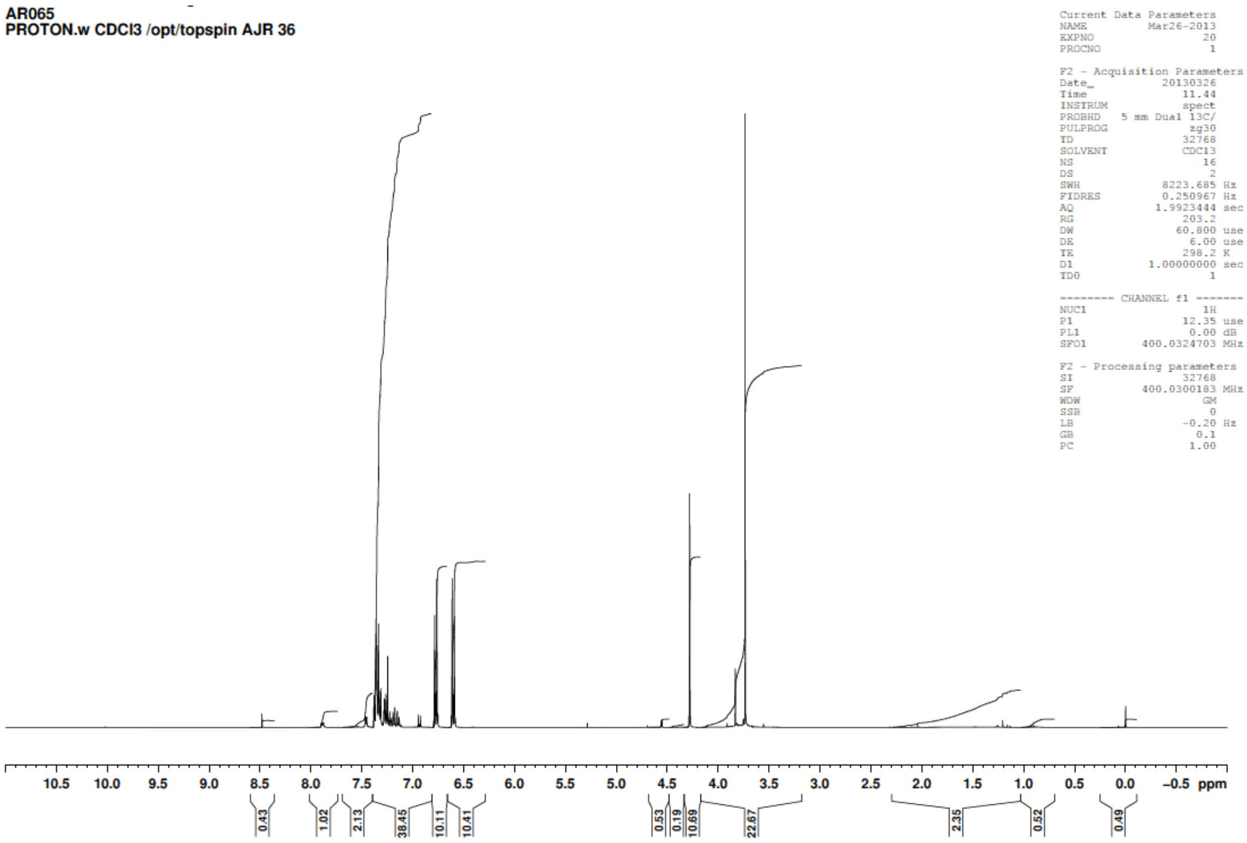
_N_-Benzyl-4-methoxyaniline 13.



(Xylene, 140 °C, 24h AR065).

This compound has been reported and fully characterized, and the data matched that of an authentic sample (see end of this file).[3] 4-Methoxyaniline (94 mg, 0.76 mmol) benzyl alcohol **5** (0.157 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a brown oil (140.6 mg, 0.660 mmol, 87 %). δ_H (400 MHz, $CDCl_3$) 7.31-7.39 (3H, m, Ar*H*), 7.11-7.29 (1H, m, Ar*H*), 6.75-6.80 (2H, m, Ar*H*), 6.57-6.63 (2H, m, Ar*H*), 4.28 (2H, s, NHCH_2), 3.74 (3H, s, OCH_3), NH not observed; δ_C (100 MHz, $CDCl_3$) 152.22 (C), 142.48 (C), 139.71 (C), 128.62 (CH), 127.57 (CH), 127.19 (CH), 114.94 (CH), 114.13 (CH), 55.84 (CH_3), 49.27 (CH_2); *m/z* (ESMS+)$[M+H]^+$ 214.1. $C_{14}H_{16}NO^+$.

^{1}H NMR δ_H (400 MHz, $CDCl_3$):



AR065
PROTON.w CDCl3 /opt/topspin AJR 36

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D1            1.00000000 sec
TD0                    1

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PL1                 0.00 dB
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F2 - Processing parameters
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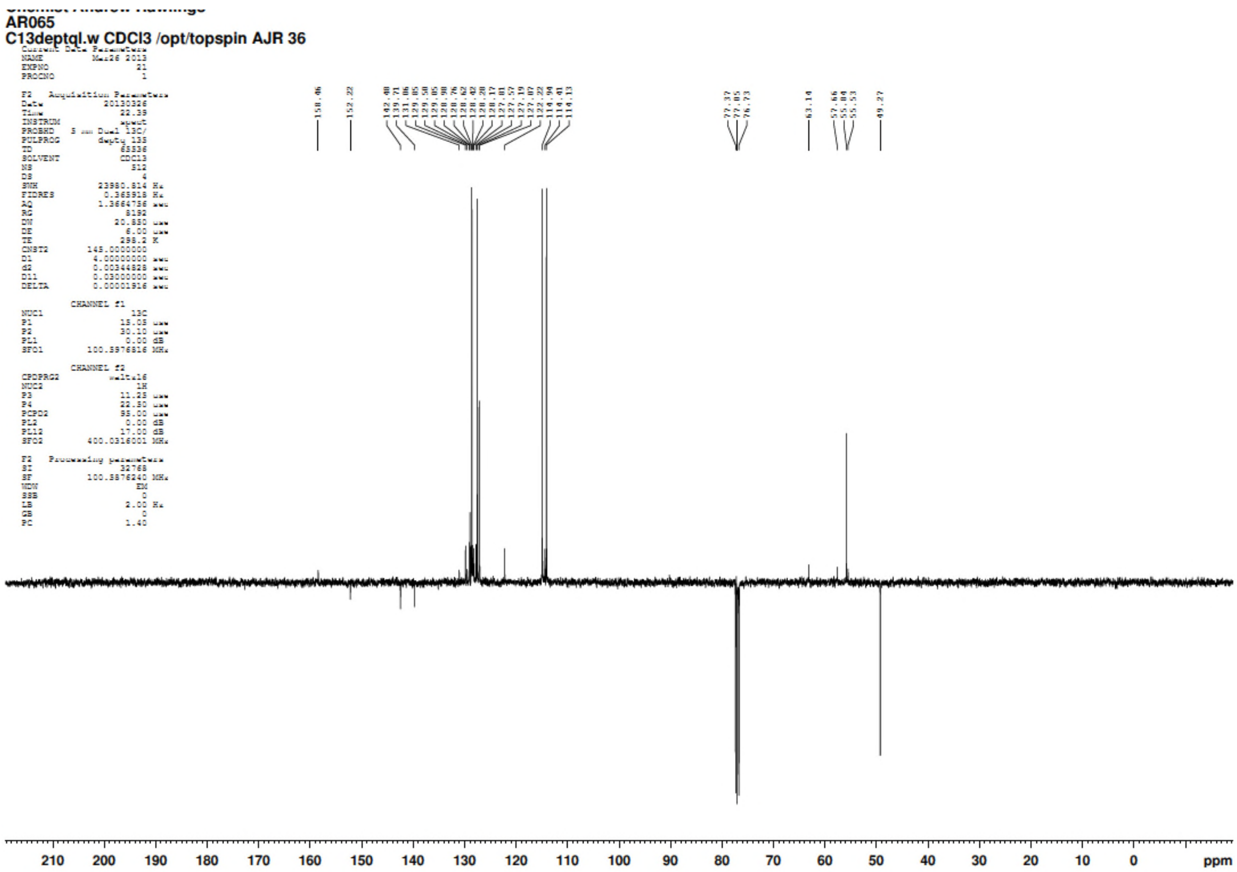
^{13}C NMR δ_C (100 MHz, $CDCl_3$):



Chemist Andrew Rawlings
AR065
C13deptql.w CDCl3 /opt/topspin AJR 36

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D11           0.03000000 sec
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PL1                 0.00 dB
SFO1         100.5976816 MHz

         CHANNEL f2
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P4                 22.50 usec
PCPD2              95.00 usec
PL2                 0.00 dB
PL12               17.00 dB
SFO2         400.0316001 MHz

F2   Processing parameters
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GB                     0
PC                  1.40
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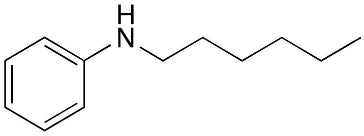
_N_-Hexylaniline 14 and di(n-hexyldiamine) 15.

(Xylene, 140 °C)

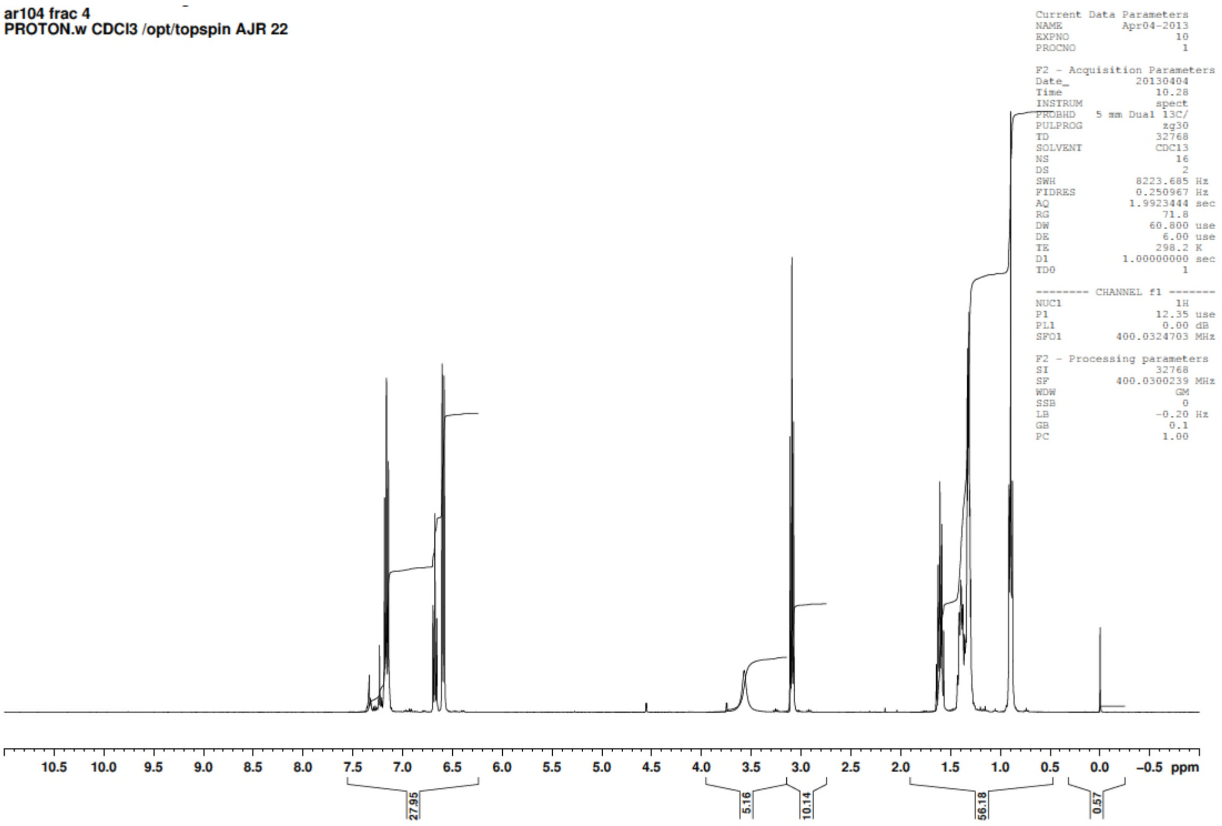
Experiment	Mol% catalyst	Time/ h	Eq amine	Eq. Alcohol	Monoalkylated **14**	Dialkylated **15**	Comments
AR088	10	24	1	2	51%	Not determined	Isolated yield.
AR100	10	24	1	3	72%	13%	Isolated yield.
AR104	10	24	1	1.1	67%	0%	Isolated yield, no dialkylation seen.
AR105	10	48	1	3	96%	4%	Ratio in crude 1H NMR only.
AR134	20	24	1	3	87.5%	12.5%	Ratio in crude 1H NMR only.
AR138	20	48	1	3	72%	28%	Ratio in crude 1H NMR only.



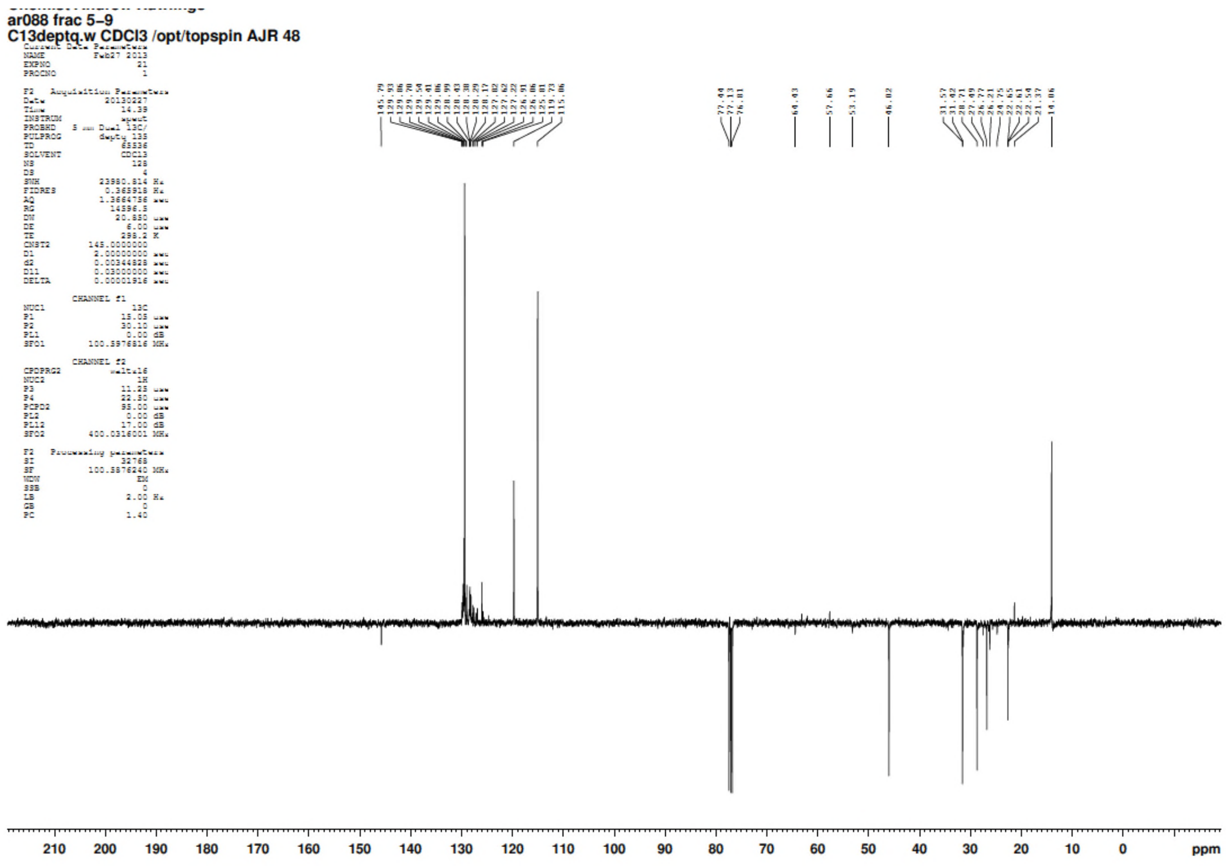
AR104

This compound has been reported and fully characterised.[4] Aniline **6** (0.069 mL, 0.76 mmol) 1-hexanol (0.105 mL, 0.84 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a pale yellow oil (90.2 mg, 0.51 mmol, 67 %). δ_H (400 MHz, $CDCl_3$) 7.13-7.19 (2H, m, Ar*H*), 6.65-6.70 (1H, m, Ar*H*), 6.56-6.61 (2H, m, Ar*H*), 3.57 (1H, br s, N*H*), 3.09 (2H, t, *J* 8.0 $NHCH_2$), 1.61 (2H, quin, *J* 8.0 $NHCH_2CH_2$), 1.26-1.44 (6H, m, hex), 0.85-0.94 (3H, m, CH_2CH_3); δ_C (100 MHz, $CDCl_3$) 148.58 (C), 129.24 (CH), 117.08 (CH), 112.71 (CH), 44.04 (CH_2), 31.69 (CH_2), 29.59 (CH_2), 26.90 (CH_2), 22.67 (CH_2), 14.08 (CH_3); *m/z* (ESMS+) $[M+H]^+$ 178.1. $C_{12}H_{19}N^+$.

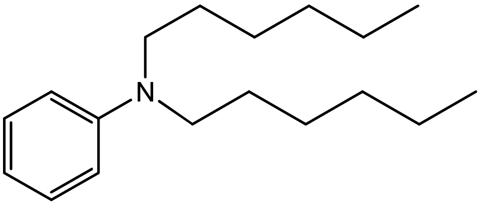
^1H NMR δ_H (400 MHz, $CDCl_3$):



^{13}C NMR δ_C (100 MHz, $CDCl_3$):

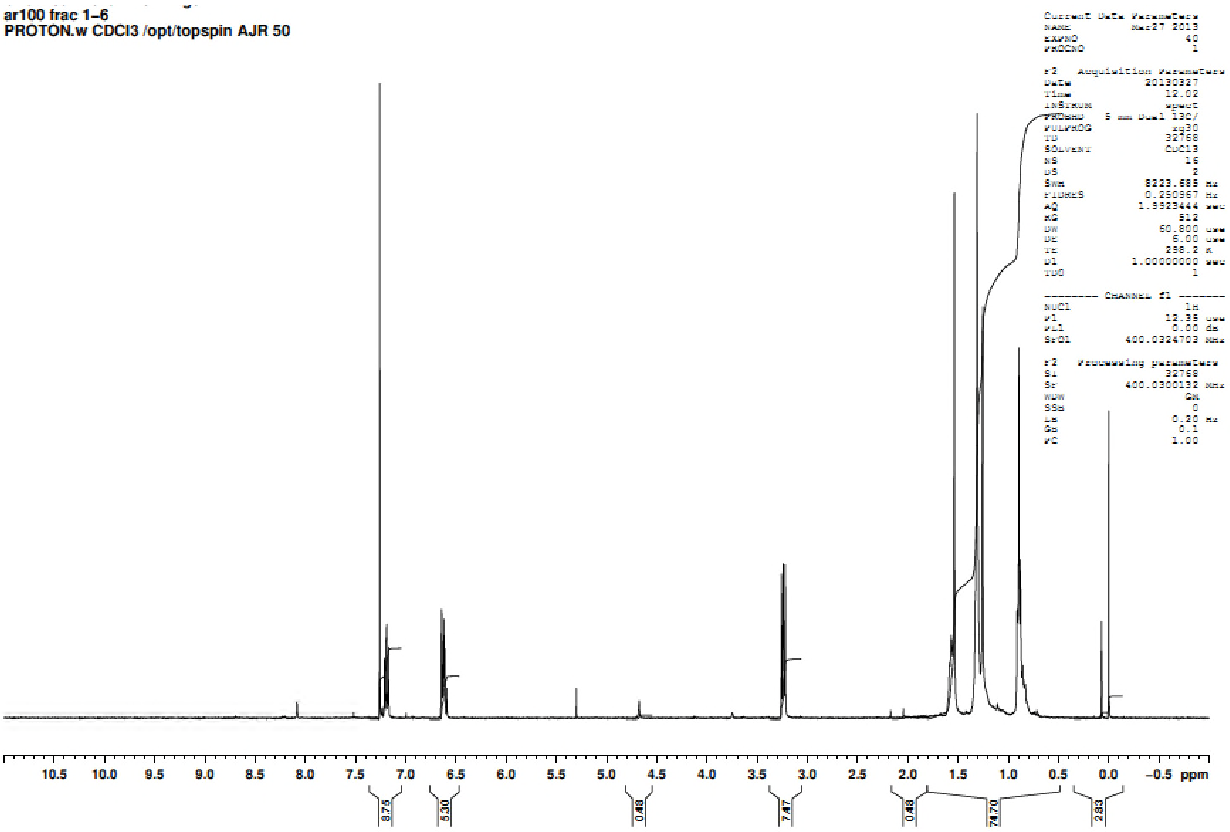


The dialkylation product **15** was formed in low conversion as a mixture alongside **14** however sufficient could be isolated to confirm the structure of the product by 1H NMR[5]:

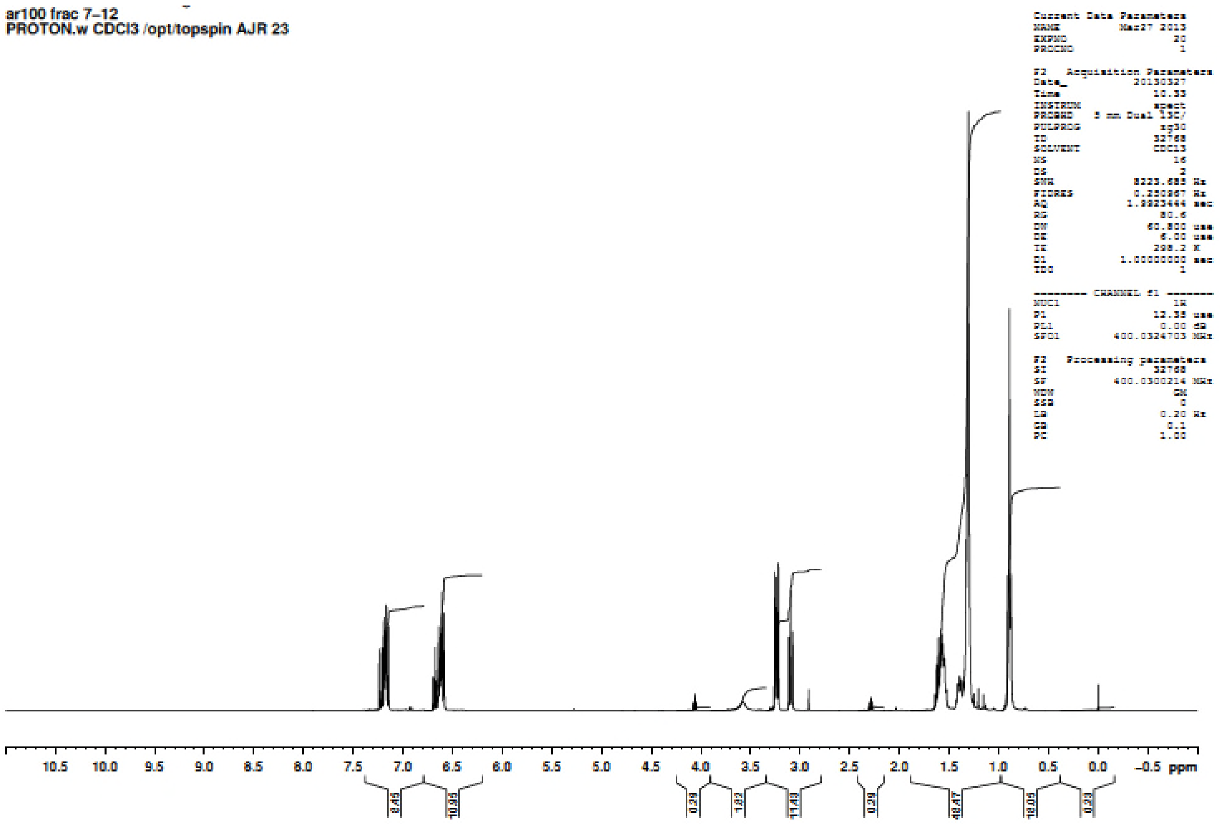


δ_H (400 MHz, $CDCl_3$) 7.25-7.15 (2H,M,Ar*H*), 6.65-6.55 (3H, m, Ar*H*), 3.22 (4H, t, *J* = 6.5, 2 x NCH_2), 1.60-1.50 (4H, m, 2 x CH_2), 1.30-1.20 (12H, m, 6 x CH_2), 0.85 (6H, t, *J* = 6.5, 2 x CH_3).

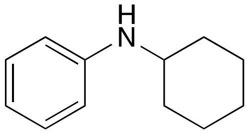
^1H NMR δ_H (400 MHz, $CDCl_3$):



Sample containing 16% mono and 11% dialkylated:



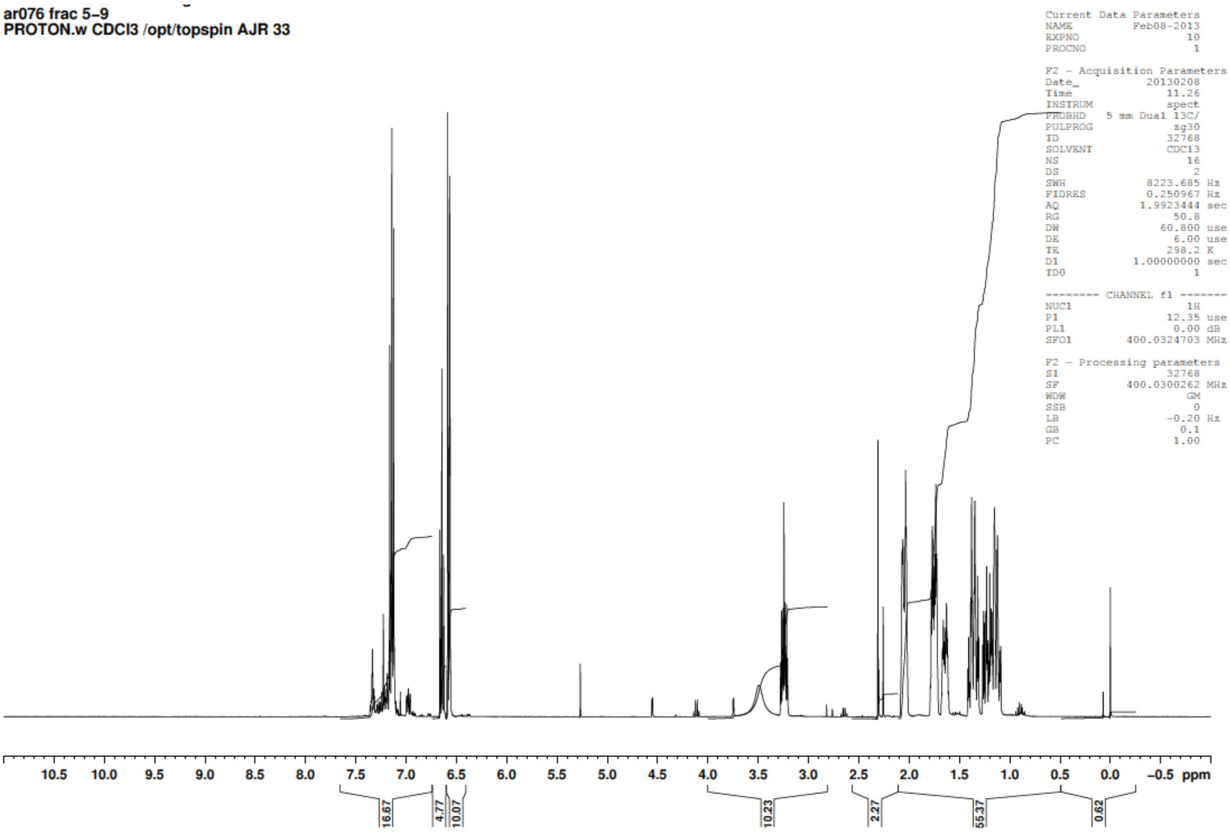
N-Cyclohexylaniline 16.



(Xylene, 140 °C, 24h, AR076).

This compound has been reported and fully characterised.[1] Aniline **6** (0.069 mL, 0.76 mmol) cyclohexanol (0.161 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. Ether to give the product as a pale yellow oil (102.8 mg, 0.587 mmol, 77 %). δ_H (400 MHz, $CDCl_3$) 7.11-7.18 (2H, m, Ar*H*), 6.62-6.67 (1H, m, Ar*H*), 6.55-6.60 (2H, m, Ar*H*), 3.49 (1H, br s, N*H*), 3.20-3.28 (1H, m, NHC*H*CH_2), 2.01-2.09 (2H, m, *c*-Hex), 1.70-1.80 (2H, m, *c*-Hex), 1.60-1.69 (1H, m, *c*-Hex), 1.29-1.43 (2H, m, *c*-Hex), 1.08-1.28 (3H, m, *c*-Hex); δ_C (100 MHz, $CDCl_3$) 147.43 (C), 129.28 (CH), 116.84 (CH), 113.16 (CH), 51.71 (CH), 33.54 (CH_2), 25.98 (CH_2), 25.07 (CH_2); *m/z* (ESMS+) $[M+H]^+$ 176.1. $C_{12}H_{18}N^+$.

^{1}H NMR δ_H (400 MHz, CDCl$_3$):



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TE                 298.2 K
D1            1.00000000 sec
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PL1                 0.00 dB
SFO1         400.0324703 MHz

F2 - Processing parameters
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GB                   0.1
PC                  1.00
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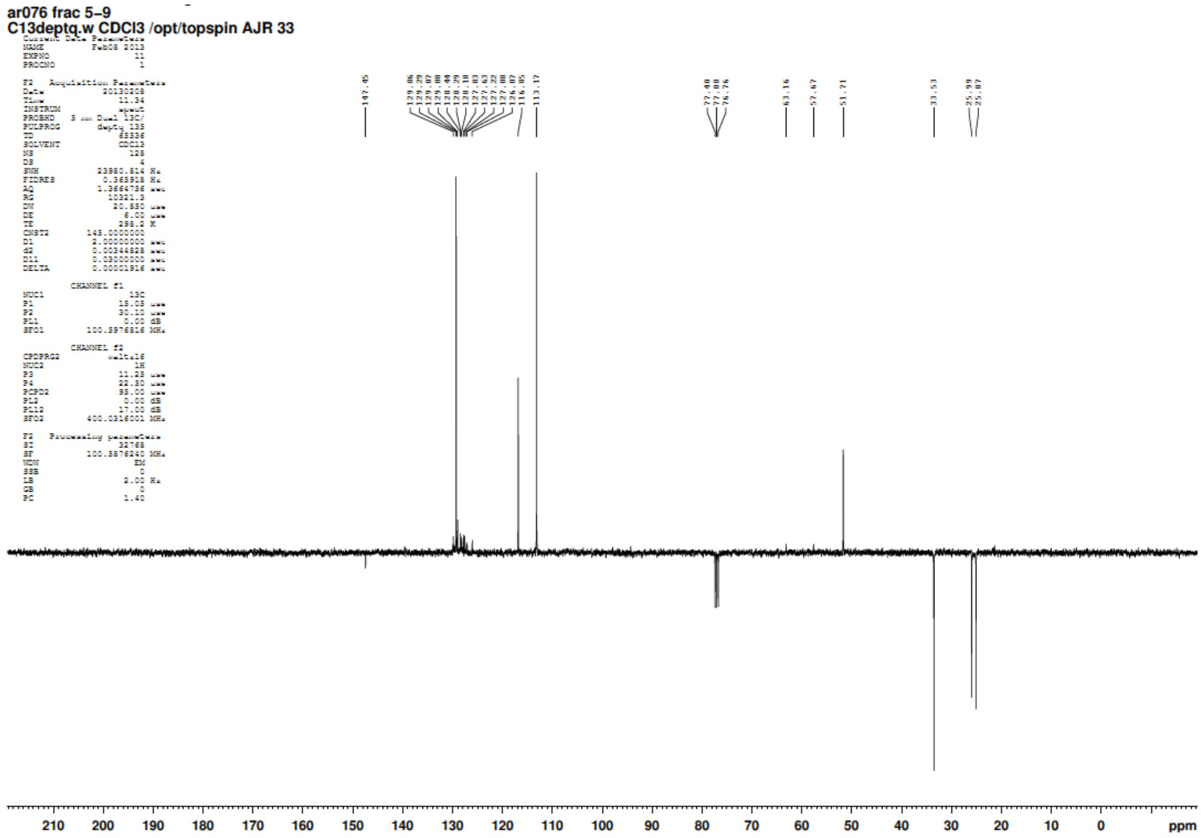
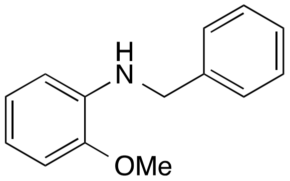
^{13}C NMR δ_C (100 MHz, CDCl$_3$):



Examples which gave poor results:

Included to provide context; product could be observed in ^{1}H NMR spectra but the ^{13}C NMR spectra were too complex to interpret.

Benzyl(2-methoxyphenyl)amine.

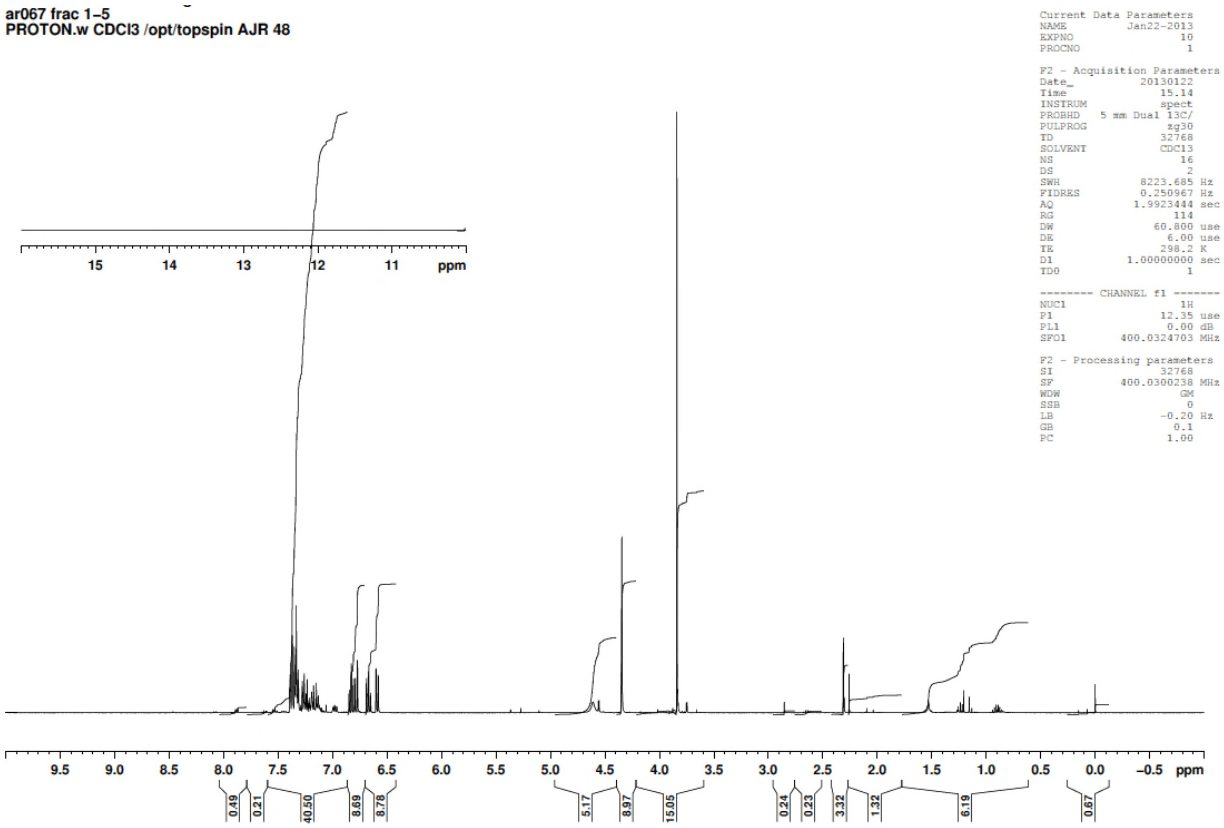


(Xylene, 140 °C, 24h, AR067).

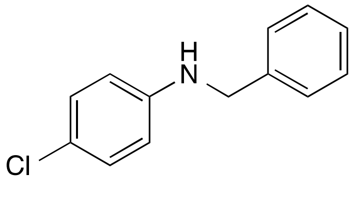
This compound has been reported and fully characterised.[3] 4-methoxyaniline (0.086 mL, 0.76 mmol) benzyl alcohol **5** (0.157 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a pale brown oil (37.3 mg, 0.175 mmol, 23 %, ca 90% pure). δ_H (400 MHz, $CDCl_3$) 7.20-7.40 (5H, m, Ar*H*), 6.65-6.80 (2H, m, Ar*H*), 6.65 (1H, t, J = 6.0, Ar*H*), 6.60 (1H, d, J = 6.0, Ar*H*), 4.57-4.69 (1H, br s, N*H*), 4.35 (2H, s, $NHCH_2$), 3.84 (3H, s, OCH_3); δ_C (100 MHz, $CDCl_3$) 139.62 (C), 138.18

(C), 129.86 (CH), 127.55 (CH), 126.86 (CH), 121.31 (CH), 116.66 (CH), 110.10 (CH), 109.43 (CH), 55.44 (CH_2), 48.08 (CH_3), one ipso C not observed; *m/z* (ESMS+) $[M+H]^+$ 214.1. $C_{14}H_{16}NO^+$.

^1H NMR δ_H (400 MHz, $CDCl_3$):



N-Benzyl-3-chloroaniline.

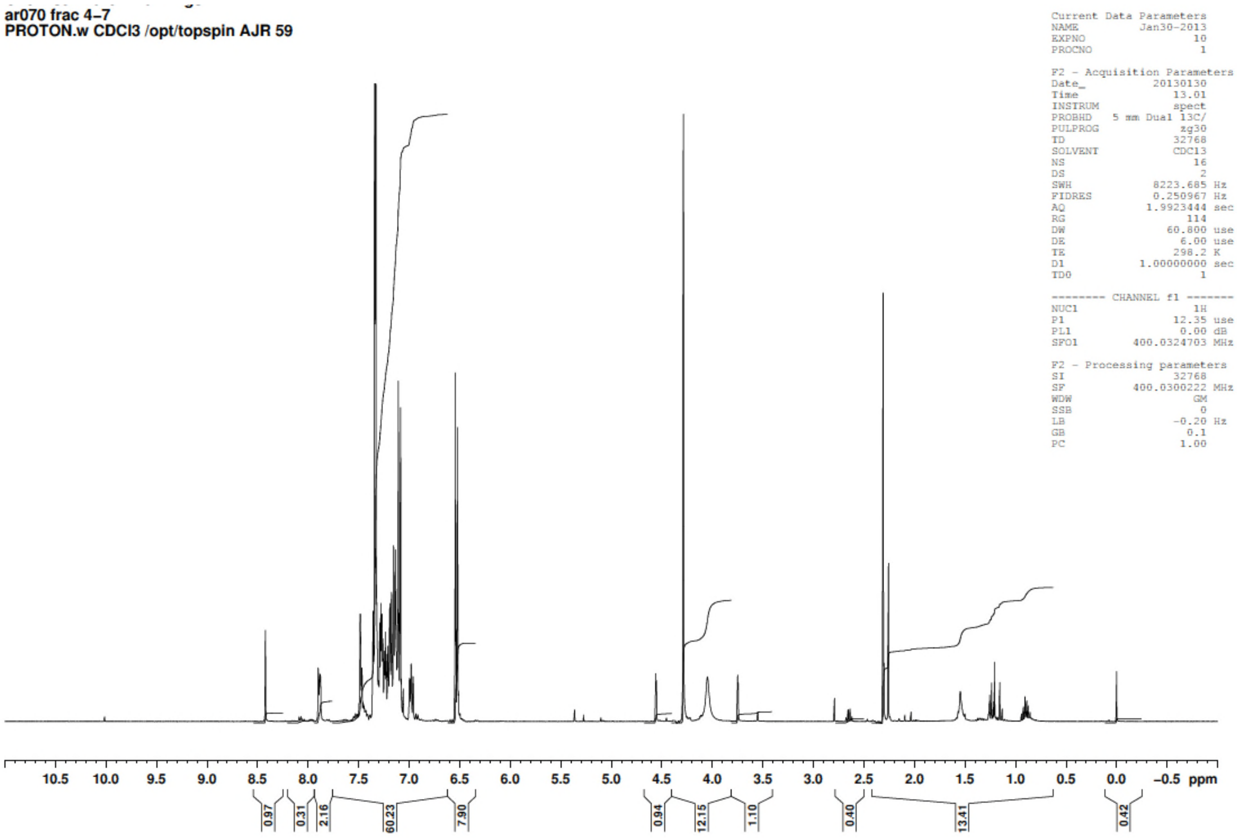


(Xylene, 140 °C, 24h, AR070).

This compound has been reported and fully characterised.[1] 4-Chloroaniline (0.097 mL, 0.76 mmol) benzyl alcohol **5** (0.157 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. Ether to give the product as a brown oil (57.7 mg, 0.266 mmol, 35 %, ca 50% pure). δ_H (400 MHz, $CDCl_3$) 7.15-7.30 (5H, m, Ar*H*), 7.07-7.12

(2H, m, Ar*H*), 6.50-6.56 (2H, m, Ar*H*), 4.29 (2H, s, NHCH_2), 3.96-4.14 (1H, br s, N*H*); *m/z* (ESMS+) $[M+H]^+$ 218.1. $C_{13}H_{13}ClN^+$.

^{1}H NMR δ_H (400 MHz, $CDCl_3$):



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FIDRES          0.250967 Hz
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RG                   114
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DE                  6.00 use
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 =======
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PL1                 0.00 dB
SFO1         400.0324703 MHz

F2 - Processing parameters
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PC                  1.00
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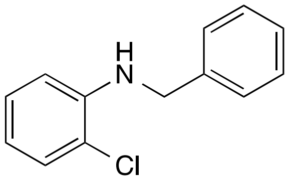
N-Benzyl-2-chloroaniline.

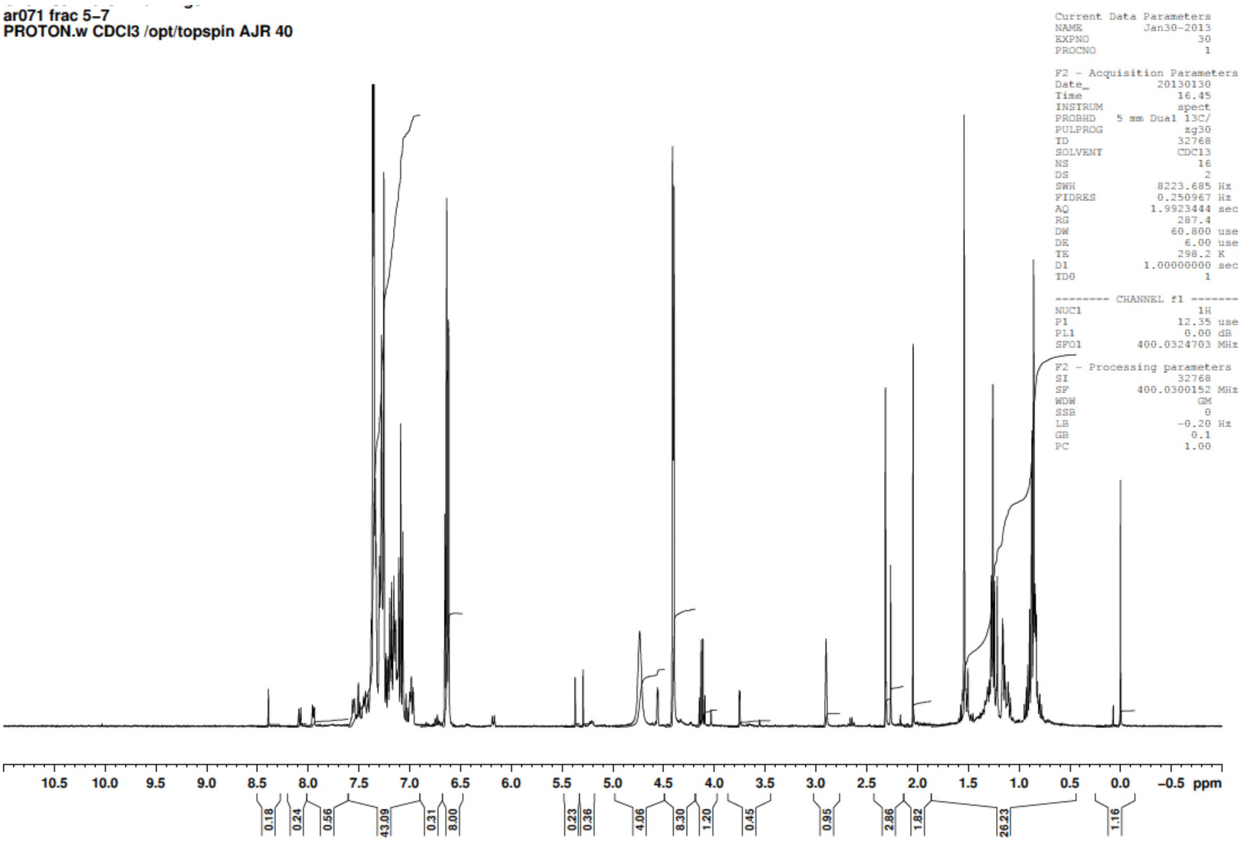


(Xylene, 140 °C, 24h, AR071).

This compound has been reported and fully characterised.[2] 2-Chloroaniline (0.080 mL, 0.76 mmol) benzyl alcohol **5** (0.157 mL, 1.52 mmol), trimethylamine *N*-oxide dihydrate (6 mg, 0.08 mmol) and **1** (40 mg, 0.076 mmol) were combined and reacted under the conditions described above. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a brown oil (6.6 mg, 0.03 mmol, 4 %, <40% pure). *After purification there was still presence of starting material but most of the characteristic peaks could be identified from 1H NMR.* δ_H (400 MHz, $CDCl_3$)

7.32-7.39 (4H, m, Ar*H*), 7.24-7.31 (2H, m, Ar*H*), 7.06-7.12 (1H, m, Ar*H*), 6.60-6.67 (2H, m, Ar*H*), 4.67-4.81 (1H, br s, N*H*), 4.38-4.43 (2H, s, NHC*H*$_2$); *m/z* (ESMS+) $[M+H]^+$ 218.1. $C_{13}H_{13}ClN^+$.

^{1}H NMR δ_H (400 MHz, $CDCl_3$):



References.

1) Bagal, D. B.; Watile, R. A.; Khedkar, M. V.; Dhake, K. P.; Bhanage, B. M. *Catal. Sci. Tech*. **2012**, *2*, 354-358.

2) Zhang, M.; Yang, H.; Zhang, Y.; Zhu, C.; Li, W.; Cheng, Y.; Hu, H. *Chem. Commun.* **2011**, *47*, 6605-6607.

3) Martinez, R.; Ramon, D. J.; Yus, Y. *Org. Biomol. Chem.* **2009**, *7*, 2176-2181.

4) Wang, D.; Ding, K. *Chem. Commun.* **2009**, 1891-1893.

5) (a) Slotta, K. H.; Franke, W. Ber. 1933, 66, 104-108. (b) Döpp, D. *ARCHIVOC* **2000**, 939-944.