Supplementary Material (ESI) for Organic and Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2010

# Convenient and Clean Synthesis of Imines from Primary Benzylamines

**Guobiao Chu and Chunbao Li,***

Department of Chemistry, College of Science, Tianjin University, Tianjin 300072, P. R. of China.
Fax: +862227403475, E-mail: lichunbao@tju.edu.cn.

## Contents

General experimental information (Page 1)

General procedure for the synthesis of imines in water (Page 1)

General procedure for the synthesis of aromatic aldehydes in water (Page 2)

$^{1}$H NMR and $^{13}$C NMR spectra of imines and aromatic aldehydes (Pages 3-13)

### General experimental information

All of the chemicals were obtained from commercial sources or prepared according to standard methods. The $^{1}$H-NMR (400 MHz) and $^{13}$C-NMR (100 MHz) were recorded on a Bruker AM-400 spectrometer. Chemical shifts (δ) are reported relative to TMS ($^{1}$H) or $CDCl_3$ ($^{13}$C). Mass spectra (ESI) were obtained on a Finnigan LCQ Advantage MAX spectrometer. Elemental analyses for C, H and N were performed on a Yanaco CHNCORNER MF-3 elemental analyzer, and the analytical results were within ±0.4% of the theoretical values.

### General procedure for the preparation of imines in water

In a round bottom flask, benzylamine (200 mg, 1 equiv.), $V_2O_5$ (0.08 equiv) was suspended in water (5 ml) with vigorous stirring. $H_2O_2$ (30% solution in water) (3 equiv.) was added to the reaction mixture. The solid imine was filtered to afford pure product when the reaction completed (monitored by TLC). The oily product was extracted with EtOAc (2 × 5 mL). The extract was washed with water (2 × 3 mL), dried over anhydrous $Na_2SO_4$. The solvent was concentrated in vacuum to give pure product without further purification.

This journal is © The Royal Society of Chemistry 2010

N-(4-Chlorobenzyl) 4-chlorobenzaldimine (2a): $^1$H NMR ($d_6$-DMSO, 400 MHz) δ 8.52 (s, 1H), 7.81 (d, J= 8.0 Hz, 2H), 7.55-7.35 (m, 6H), 4.77 (s, 2H).

N-Benzylbenzaldimine (2b): $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.41 (s, 1H), 7.80-7.78 (m, 2H), 7.44-7.35 (m, 8H), 4.84 (s, 2H).

N-(3-Fluorobenzyl) 3-fluorobenzaldimine (2c): $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.39 (s, 1H), 7.58-7.28 (m, 4H), 7.18-6.95 (m, 4H), 4.84 (s, 2H).

N-(2-Chlorobenzyl) 2-chlorobenzaldimine (2d): $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.89 (s, 1H), 8.14 (d, J= 9.2 Hz, 1H), 7.46-7.23 (m, 7H), 4.97 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 159.8, 136.8, 135.3, 133.4, 133.1, 131.7, 129.8, 129.7, 129.4, 128.5, 128.3, 127.0, 126.9, 62.2; MS (ESI): *m/z* (%) $[M + H]^+$=264 (100), 265 (18), 266 (60); Anal. Calcd. For $C_{14}H_{11}Cl_2N$: C, 63.66; H, 4.20; N, 5.30 Found: C, 63.74; H, 4.10; N, 5.22.

N-(3-Chlorobenzyl) 3-chlorobenzaldimine (2e): $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.36 (s, 1H), 7.84 (s, 1H), 7.65 (d, J= 7.6 Hz , 1H), 7.45-7.23 (m, 6H), 4.81 (s, 2H).

N-(3-Bromobenzyl) 3-bromobenzaldimine (2f): $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.34 (s, 1H), 7.99 (s, 1H), 7.69 (d, J= 8.0 Hz , 1H), 7.58 (d, J= 8.0 Hz, 1H), 7.50 (s, 1H), 7.42 (d, J= 7.6 Hz , 1H), 7.34-7.22 (m, 3H), 4.80 (s, 2H).

N-(2,3-Dichlorobenzyl) 2,3-dichlorobenzaldimine (2g): $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.91 (s, 1H), 8.05 (d, J= 7.6 Hz, 1H), 7.56 (d, J= 7.6 Hz, 1H), 7.42 (d, J= 8.0 Hz, 1H), 7.37 (d, J= 7.2 Hz, 1H), 7.30-7.21 (m, 2H), 4.99 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz ): δ 159.9, 139.0, 135.1, 133.5, 133.4, 133.1, 132.4, 131.6, 129.1, 127.6, 127.4, 127.3, 126.7, 62.7; MS (ESI): *m/z* (%) $[M + H]^+$ = 332 (78), 334 (100), 336 (47); Anal. Calcd. For $C_{14}H_9Cl_4N$: C, 50.49; H, 2.72; N, 4.21 Found: C, 50.61; H, 2.67; N, 4.30.

N-(2,4-Dichlorobenzyl) 2,4-dichlorobenzaldimine (2h): $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.82 (s, 1H), 8.07 (d, J= 8.4 Hz, 1H), 7.45-7.26 (m, 5H), 4.90 (s, 2H).

N-(4-Ethoxycarbonylbenzyl) 4-ethoxycarbonylbenzaldimine (2i): $^1$H NMR ($CDCl_3$, 400 MHz) δ8.48 (s, 1H), 8.12 (d, J= 8.0 Hz, 2H), 8.05 (d, J= 8.0 Hz，2H), 7.87 (d, J= 8.0 Hz, 2H), 7.44 (d, J= 8.0 Hz, 2H), 4.92 (s, 2H), 4.42 (m, 4H), 1.42 (m, 6H).

N-(3-Nitrobenzyl) 3-nitrobenzaldimine (2j): $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.65 (s, 1H), 8.56 (s, 1H), 8.33 (d, J= 8.4 Hz, 1H), 8.25 (s, 1H),8.18 (d, J= 7.6 Hz, 2H), 7.75 (d, J= 7.6 Hz, 1H), 7.65 (t, J= 8.0 Hz, 1H), 7.56 (t, J= 8.0 Hz, 1H), 4.98 (s, 2H).

This journal is © The Royal Society of Chemistry 2010

**General procedure for the preparation of aromatic aldehydes in water**

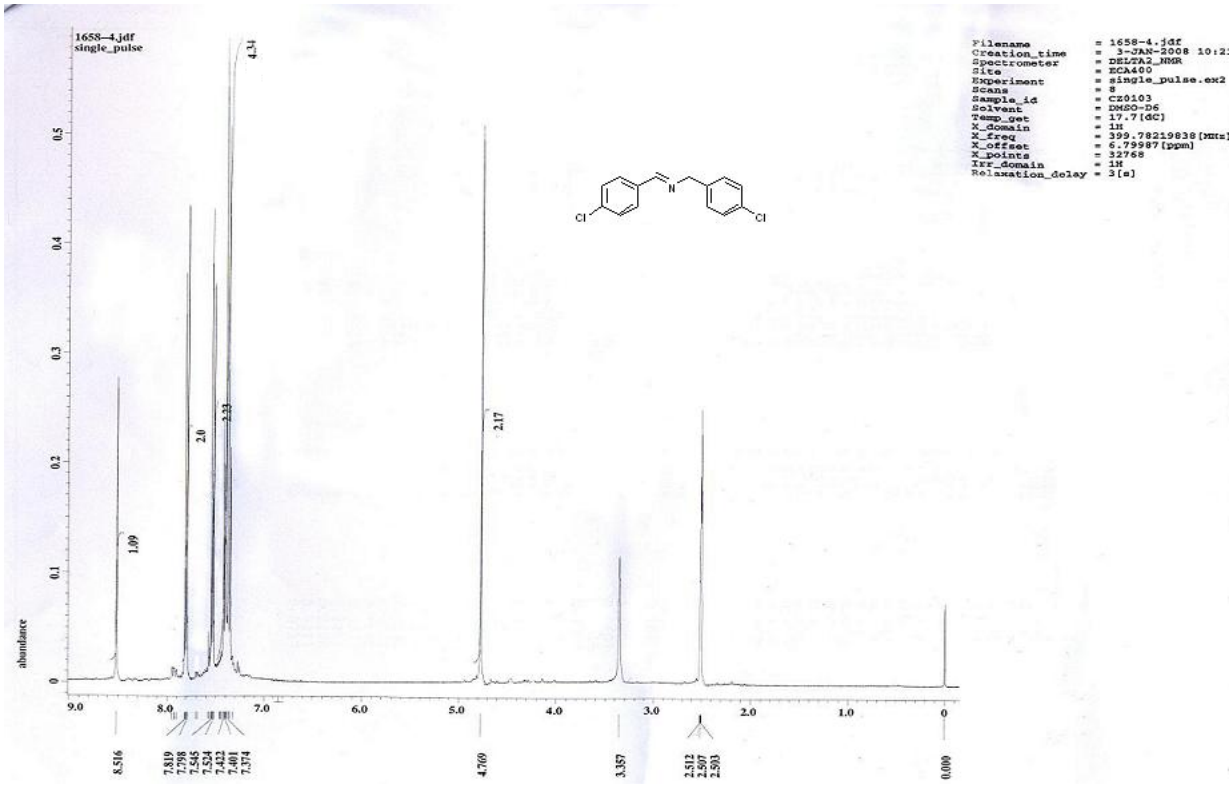
In a round bottom flask, benzylamine (200 mg, 1 equiv.), $V_2O_5$ (0.08 equiv) was suspended in water (5 ml) with vigorous stirring. $H_2O_2$ (30% solution in water) (3 equiv.) was added to the reaction mixture. The system was heated to 50℃ and monitored by TLC to completion. The mixture was extracted with EtOAc (2 × 5 mL). The extract was washed with water (2 × 3 mL), dried over anhydrous $Na_2SO_4$. The solvent was concentrated in vacuum to give crude product, which was then filtered through a silica gel pad with petroleum ether to afford aromatic aldehydes.

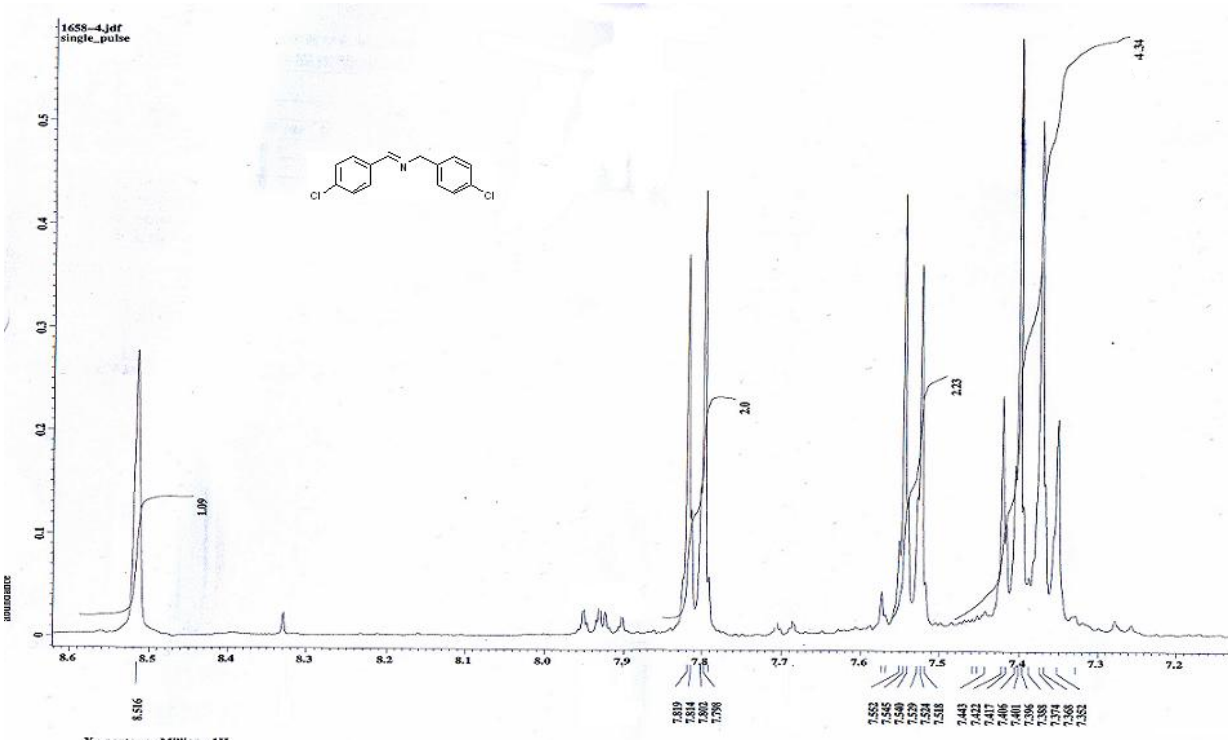
4-Methylbenzaldehyde (3k): $^1$H NMR ($CDCl_3$, 400 MHz) δ 9.98 (s, 1H), 7.79 (d, J= 7.6 Hz, 2H), 7.35 (d, J= 7.6 Hz, 2H), 2.46 (s, 3H).

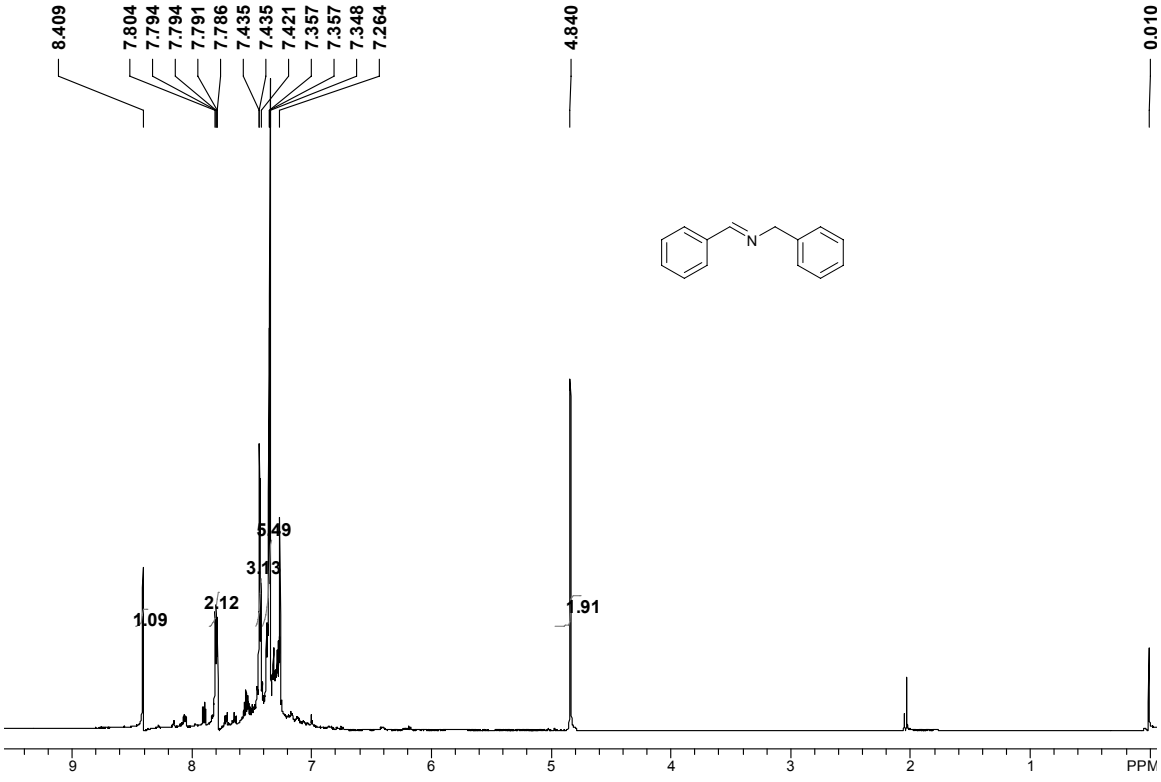
4-Methoxybenzaldehyde (3l): $^1$H NMR ($CDCl_3$, 400 MHz) δ 9.65 (s, 1H), 7.61 (d, J= 7.2 Hz, 2H), 6.79 (d, J= 7.2 Hz, 2H), 3.67(s, 3H).

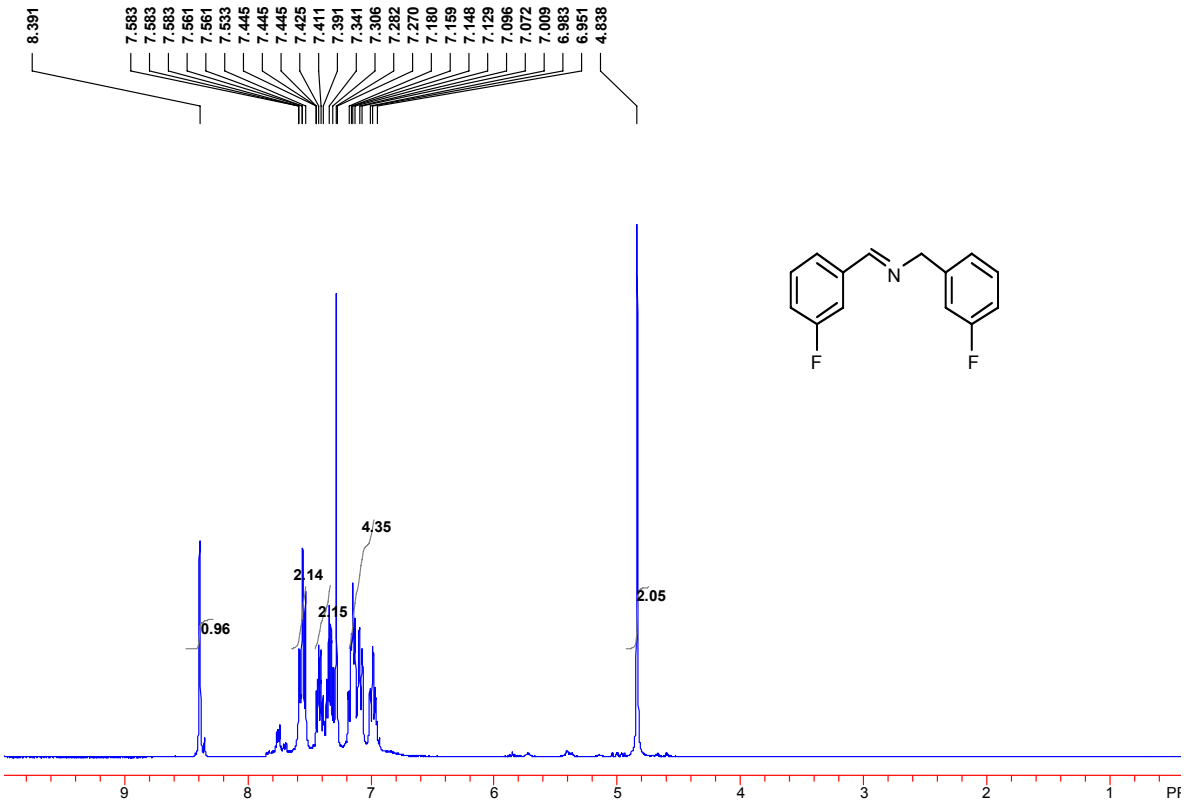
5-Formyl-2-methoxyphenyl acetate (3m): $^1$H NMR ($CDCl_3$, 400 MHz) δ 9.88 (s, 1H), 7.78 (dd, J= 2.0 Hz, J= 8.4 Hz, 1H), 7.60 (d, J= 2.0 Hz, 1H), 7.09 (d, J= 8.4 Hz, 1H), 3.93 (s, 3H), 2.35 (s, 3H).

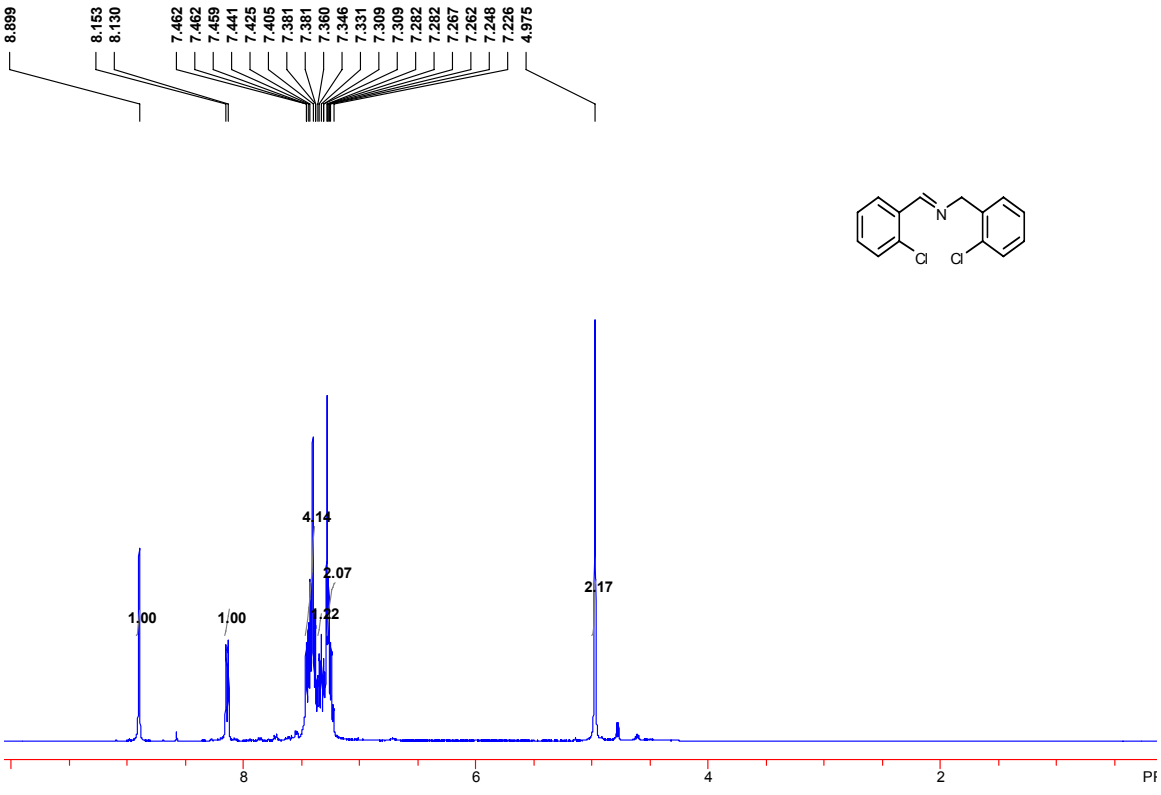
1-Naphthaldehyde (3n): $^1$H NMR ($CDCl_3$, 400 MHz) δ 9.88 (s, 1H), 9.28 (d, J= 8.8 Hz, 1H), 8.11(d, J= 8.0 Hz, 1H), 8.00 (d, J= 7.2 Hz, 1H), 7.94 (d, J= 8.0 Hz, 1H), 7.74-7.60 (m, 3H).



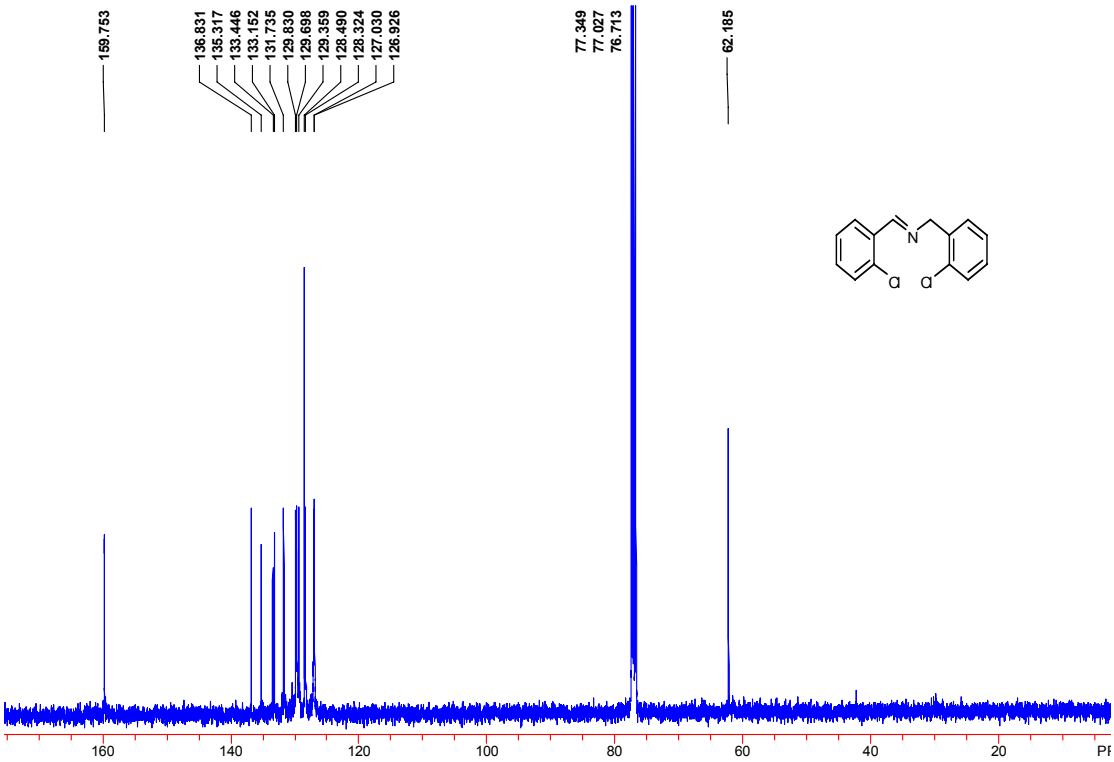

1658-4.jdf
single_pulse
Cl
Cl
4.34
2.23
2.0
1.09
8.516
7.819
7.814
7.803
7.798
7.552
7.545
7.540
7.529
7.524
7.518
7.443
7.432
7.417
7.406
7.401
7.396
7.388
7.374
7.368
7.352

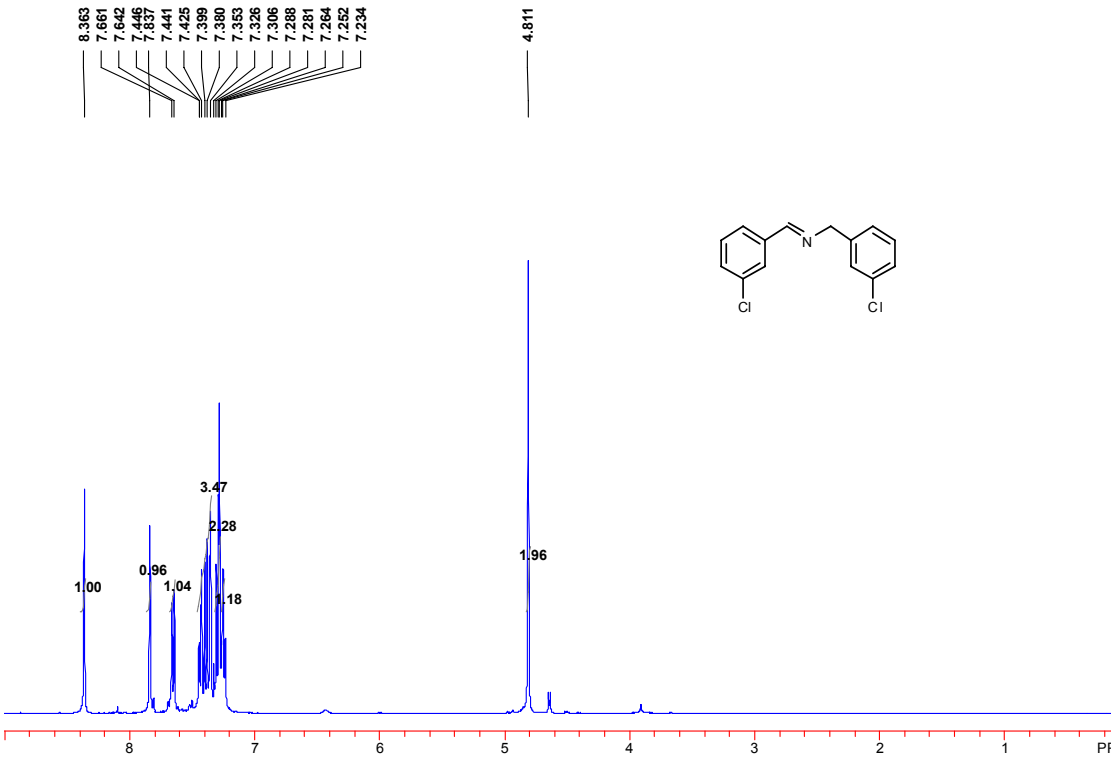

8.409
7.804
7.794
7.794
7.791
7.786
7.435
7.435
7.421
7.357
7.357
7.348
7.264
4.840
0.010
N
5.49
3.13
2.12
1.09
1.91
PPM

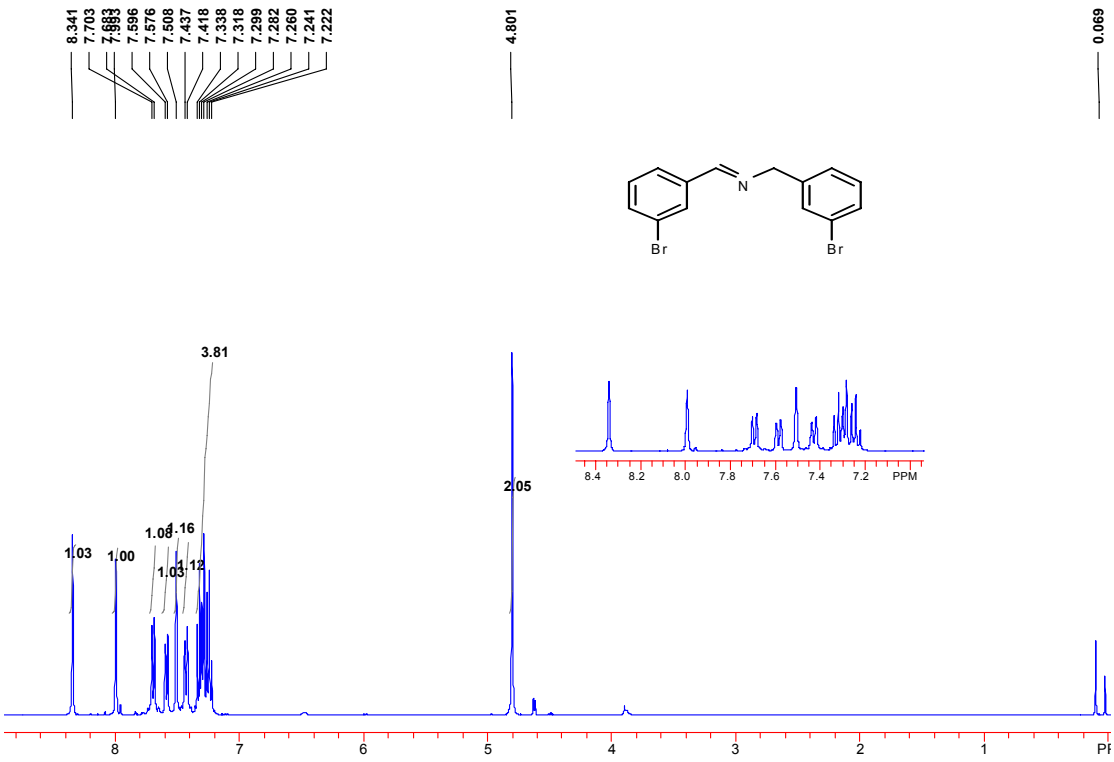

8.391
7.583
7.583
7.583
7.561
7.561
7.533
7.445
7.445
7.445
7.425
7.411
7.391
7.341
7.306
7.282
7.270
7.180
7.159
7.148
7.129
7.096
7.072
7.009
6.983
6.951
4.838
N
F
F
0.96
2.14
2.15
4.35
2.05
9
8
7
6
5
4
3
2
1
PF

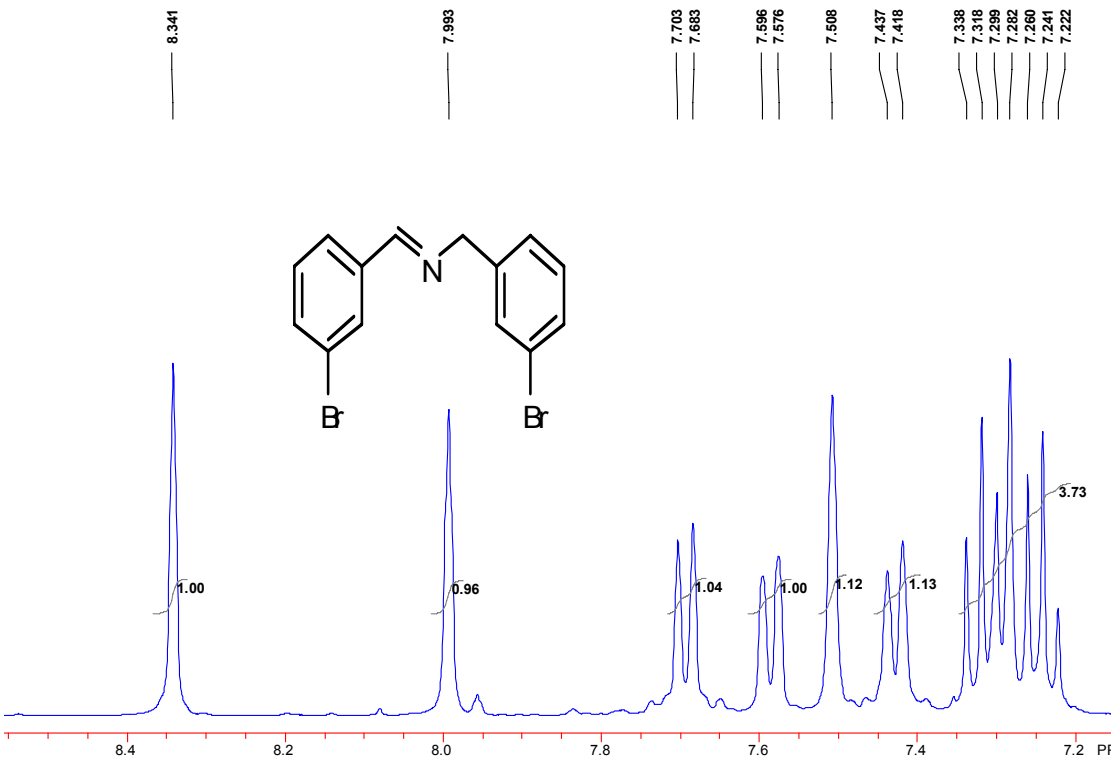

8.899
8.153
8.130
7.462
7.462
7.459
7.441
7.425
7.405
7.381
7.381
7.360
7.346
7.331
7.309
7.309
7.282
7.282
7.267
7.262
7.248
7.226
4.975
N
Cl
Cl
1.00
1.00
4.14
2.07
1.22
2.17
8
6
4
2
PF

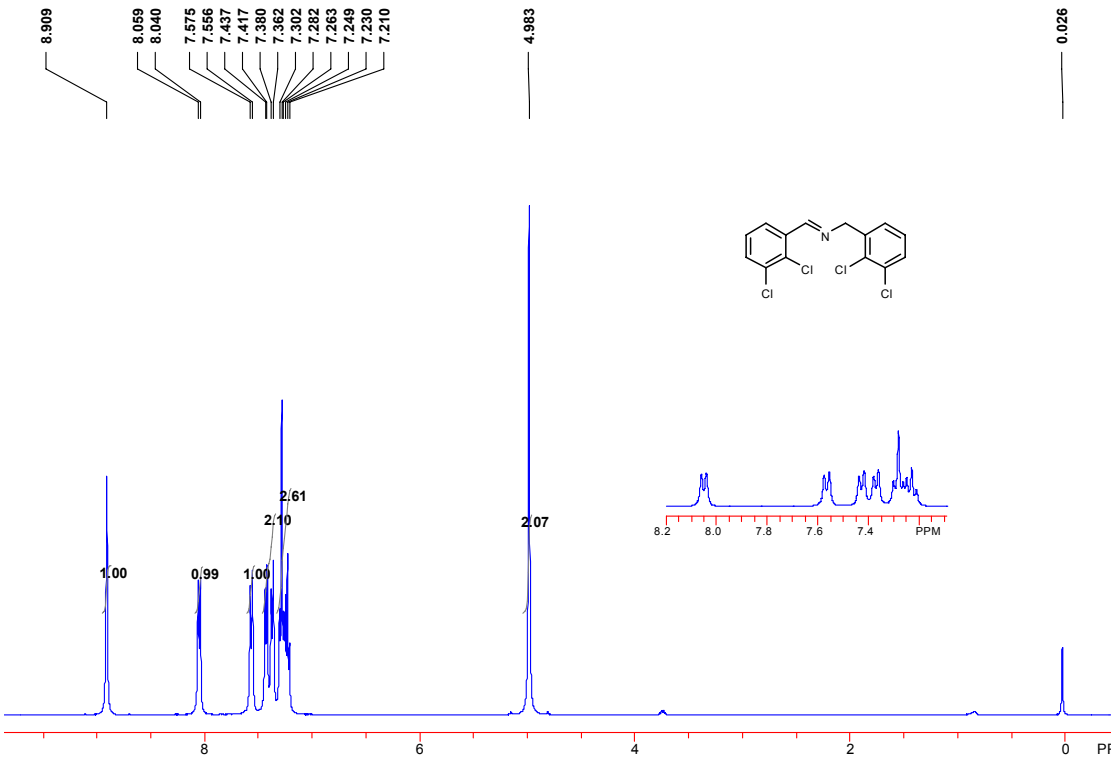
This journal is © The Royal Society of Chemistry 2010

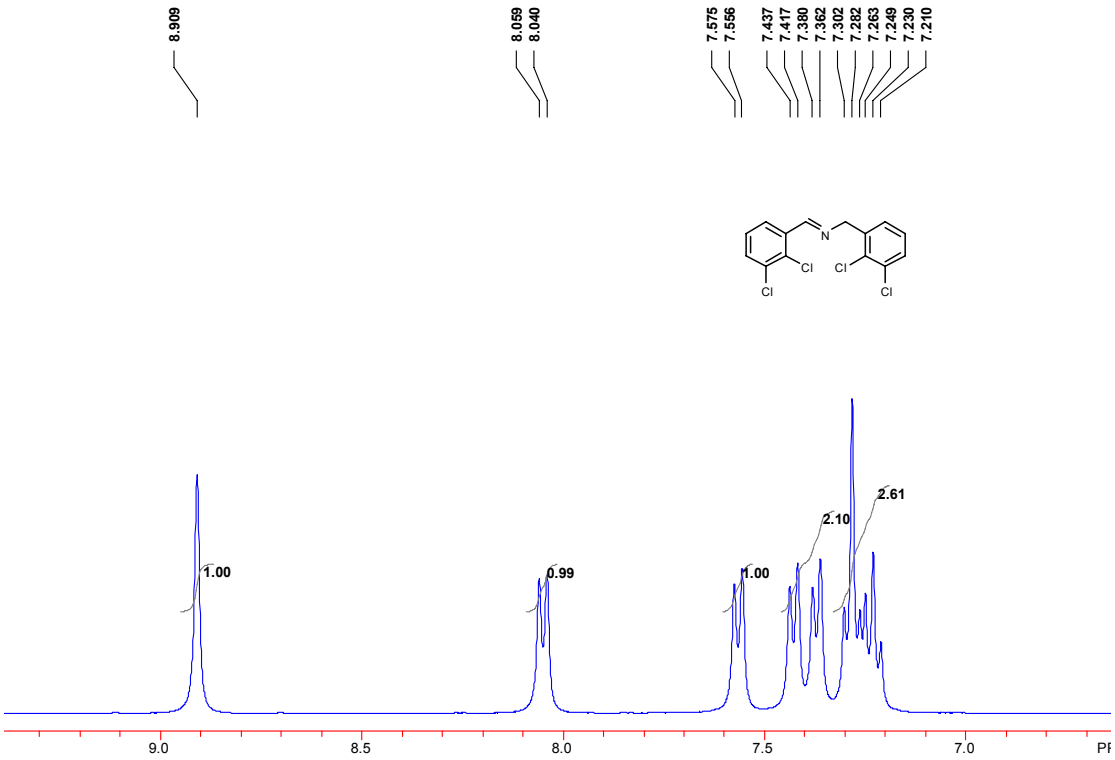



8.341
7.703
7.683
7.596
7.576
7.508
7.437
7.418
7.338
7.318
7.299
7.282
7.260
7.241
7.222
4.801
0.069
N
Br
Br
3.81
2.05
1.03
1.00
1.08
1.16
1.03
1.12
8.4
8.2
8.0
7.8
7.6
7.4
7.2
PPM
8
7
6
5
4
3
2
1


8.341
7.993
7.703
7.683
7.596
7.576
7.508
7.437
7.418
7.338
7.318
7.299
7.282
7.260
7.241
7.222
N
Br
Br
1.00
0.96
1.04
1.00
1.12
1.13
3.73
8.4
8.2
8.0
7.8
7.6
7.4
7.2


8.909
8.059
8.040
7.575
7.556
7.437
7.417
7.380
7.362
7.302
7.282
7.263
7.249
7.230
7.210
4.983
0.026
N
Cl
Cl
Cl
Cl
2.61
2.10
2.07
1.00
0.99
1.00
8.2
8.0
7.8
7.6
7.4
PPM
8
6
4
2
0
PPM


8.909
8.059
8.040
7.575
7.556
7.437
7.417
7.380
7.362
7.302
7.282
7.263
7.249
7.230
7.210
N
Cl
Cl
Cl
Cl
2.61
2.10
1.00
0.99
1.00
9.0
8.5
8.0
7.5
7.0
PPM