SUPPORTING INFORMATION
For
An Efficient Synthesis of Iminoquinones by Chemoseletive Domino ortho-hydroxylation/oxidation/imidation sequence of 2-aminoaryl ketone

S. Chandrasekar, and G. Sekar*

Department of Chemistry, Indian Institute of Technology Madras
Chennai-600 036, Tamil Nadu India
E-mail: gsekar@iitm.ac.in

Table of Contents

- Synthesis of 2-amino benzophenone 2
- Synthesis of secondary alcohol 2
- References 3
- $^1$H and $^{13}$C spectra for all compounds 4
Synthesis of 2-amino benzophenone derivatives\(^1\) (1i-k)

Magnesium turnings were placed in an oven dried two neck 50 mL round bottom flask and the flask was further dried by hot air gun with applying vacuum. Then the setup was allowed to room temperature, refilled with nitrogen. Under nitrogen flow, a catalytic amount of iodine was added, followed by freshly distilled THF. Then followed by corresponding aryl halide was added by drop wise. After the disappearance of the iodine color, the reaction was allowed to stir at room temperature for 2 hours. Once all the magnesium turnings were dissolved. The Grignard reagent was added to solution of 2-amino benzonitrile dissolved in THF at 0 °C over 40 min. Then the reaction was allowed to warm to ambient temperature and allowed to stir at this temperature for 6h. The reaction was quenched by slow addition of 10 % HCl and made basic nature by the addition of NaOH at 0 °C. The organic layer was extracted with ethyl acetate. The combined organic layers were dried over Na\(_2\)SO\(_4\) and the solvent was evaporated under vacuum. The residue was purified by column chromatography with ethyl acetate/hexanes solvents to provide pure products (1i-1k).

\[
\text{CN} \quad \text{R} \quad \text{RMgBr (3 equiv.)} \quad \text{THF, 0°C} \quad \text{NH}_2 \quad \text{R} \\
\]

Synthesis of secondary alcohols\(^1\) (5a-5c)

Grignard reagent was added to solution of 2-aminobenzaldehyde dissolved in THF at 0 °C over 40 min. Then the reaction was allowed to warm to ambient temperature and allowed to stir at this temperature for 6h. The reaction was quenched by slow addition of saturated NH\(_4\)Cl at 0 °C. The organic layer was extracted with ethyl acetate. The combined organic layers were dried over Na\(_2\)SO\(_4\) and the solvent was evaporated under vacuum. The residue was purified by column chromatography with ethyl acetate/hexanes solvents to provide pure products (5a-5c).

\[
\text{NH}_2 \quad \text{H} \quad \text{RMgBr (3 equiv.)} \quad \text{THF, 0°C} \quad \text{OH} \quad \text{NH}_2 \quad \text{R} \\
5a-5c
\]
Reference:

400 MHz $^1$H NMR spectrum of 2a in DMSO-d$_6$
100 MHz $^{13}$C NMR spectrum of 2a in DMSO-d$_6$
400 MHz $^1$H NMR spectrum of 2b in CDCl$_3$
$100$ MHz $^{13}$C NMR spectrum of 2b in DMSO-d$_6$
400 MHz $^1$H NMR spectrum of 2c in DMSO-$d_6$
100 MHz $^{13}$C NMR spectrum of $2c$ in DMSO-$d_6$
400 MHz $^1$HNMR spectrum of 2d in DMSO-d$_6$
100 MHz $^{13}$C NMR spectrum of 2d in DMSO-d$_6$
400 MHz $^1$H NMR spectrum of 2e in DMSO-$d_6$
100 MHz $^{13}$C NMR spectrum of 2e in CDCl$_3$
400 MHz $^1$H NMR spectrum of 2f in CDCl$_3$
100 MHz $^{13}$C NMR spectrum of 2f in CDCl$_3$
400 MHz $^1$H NMR spectrum of 2g in DMSO-d$_6$
100 MHz $^{13}$C NMR spectrum of 2g in CDCl$_3$: DMSO-d$_6$
400 MHz $^1$H NMR spectrum of 2h in DMSO-d$_6$
100 MHz $^{13}$C NMR spectrum of 2h in DMSO-$d_6$
$400 \text{ MHz } ^{13}\text{H NMR spectrum of 2i in CDCl}_3$
$100 \text{ MHz } ^{13}\text{C NMR spectrum of 2i in CDCl}_3$
400 MHz $^1$H NMR spectrum of 2j in CDCl$_3$
100 MHz $^{13}$C NMR spectrum of 2j in CDCl$_3$
400 MHz $^1$H NMR spectrum of 2k in DMSO-d$_6$
100 MHz $^{13}$C NMR spectrum of 2k in DMSO-$d_6$
400 MHz $^{13}$C NMR spectrum of 21 in CDCl$_3$
100 MHz $^{13}$C NMR spectrum of 2I in DMSO-d$_6$
$400 \text{ MHz } ^1\text{H NMR spectrum of 2m in DMSO-d}_6$
100 MHz $^{13}$C NMR spectrum of 2m in DMSO-d$_6$
400 MHz $^1$H NMR spectrum of 4a in DMSO-d$_6$
100 MHz $^{13}$C NMR spectrum of 4a in DMSO-d$_6$
400 MHz $^1$H NMR spectrum of 4b in CDCl$_3$
100 MHz $^{13}$C NMR spectrum of $4b$ in CDCl$_3$
400 MHz $^1$H NMR spectrum of 4c in DMSO-d$_6$
100 MHz $^{13}$CNMR spectrum of 4c in DMSO-d$_6$
100 MHz $^1$H NMR spectrum of 4d in CDCl$_3$
100 MHz $^{13}$C NMR spectrum of $4d$ in CDCl$_3$
400 MHz $^1$H NMR spectrum of 6a in DMSO-$d_6$
$100\text{ MHz }^{13}\text{C NMR spectrum of }6\text{a in DMSO-}d_6$
400 MHz $^1$H NMR spectrum of 6b in CDCl$_3$
100 MHz $^{13}$C NMR spectrum of 6b in CDCl$_3$
400 MHz $^1$H NMR spectrum of 8a in CDCl$_3$
100 MHz $^{13}$C NMR spectrum of 8a in CDCl$_3$
400 MHz $^1$H NMR spectrum of 8b in CDCl$_3$
100 MHz $^{13}$C NMR spectrum of $8b$ in CDCl$_3$
400 MHz $^1$H NMR spectrum of 9 in DMSO-d$_6$
$100 \text{ MHz } ^{13}\text{C NMR spectrum of 9 in DMSO-d}_6$
H NMR spectrum of 3b in CDCl₃