Supplementary information

Morita-Baylis-Hillman reaction in eutectic solvent under aqueous medium

Sanhu Zhao, Hangyu Zhi, Mi Zhang, Qin Yan, Jianfeng Fan and Jinchang Guo

Department of Chemistry, Xinzhou Teachers University, Xinzhou 034000, Shanxi, China

Corresponding author. e-mail: sanhuzhao@163.com

1. NMR spectra of all M-B-H products;
2. $^1$H NMR spectra of the product of benzene-1,4-dicarbaldehyde with acrylonitrile;
3. $^1$H NMR spectra of the crude product and the water purified product;
4. FT-IR spectra of the whole M-B-H reaction of 4-chloro-benzaldehyde with acrylonitrile in the green solvent system $1\text{ChCl} / 2\text{Gly DES–H}_2\text{O}$. 
1. The NMR spectra for the M-B-H products

2-(Hydroxy-phenyl-methyl)-acrylonitrile (Table 2, entry 1).
2-[(4-fluoro-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 2).
2-[(4-chloro-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 3).
2-[(2-chloro-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 4).
2-[Hydroxy-(4-nitro-phenyl)-methyl]-acrylonitrile (Table 2, entry 5).
2-[Hydroxy-(3-nitro-phenyl)-methyl]-acrylonitrile (Table 2, entry 6).
2-[Hydroxy-(2-methoxy-phenyl)-methyl]-acrylonitrile (Table 2, entry 7).
2-[Hydroxy-(4-methyl-phenyl)-methyl]-acrylonitrile (Table 2, entry 8).
2-(hydroxy-naphthalen-1-yl-methyl)-acrylonitrile (Table 2, entry 9).
2-(Hydroxy-pyridin-2-yl-methyl)-acrylonitrile (Table 2, entry 10).
2-(Furan-2-yl-hydroxy-methyl)-acrylonitrile (Table 2, entry 11).
2-[Hydroxy-(1H-pyrazol-4-yl)-methyl]-acrylonitrile (Table 2, entry 12).
2-(Hydroxy-quinolin-4-yl-methyl)-acrylonitrile (Table 2, entry 13).
2-[Hydroxy-[4-hydroxy-3-methoxy-phenyl]-methyl]-acrylonitrile (Table 2, entry 14).
2-[Hydroxy-(4-chloro-3-nitrophenyl)-methyl]-acrylonitrile (Table 2, entry 15).
2-[[3,4-Dichloro-phenyl]-hydroxy-methyl]-acrylonitrile (Table 2, entry 16).
2-[(2,4-Dichloro-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 17).
2-[(4-(2-cyano-1-hydroxy-allyl)-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 18).
3-Hydroxy-2-methylene-hexanenitrile (Table 2, entry 19).
2-(Hydroxy-phenyl-methyl)-acrylic acid methyl ester (Table 2, entry 20).

2-[(4-Chloro-phenyl)-hydroxy-methyl]-acrylic acid methyl ester (Table 2, entry 21).
2-[Hydroxy-(4-nitro-phenyl)-methyl]-acrylic acid methyl ester (Table 2, entry 22).
2-[(4-Chloro-3-nitro-phenyl)-hydroxy-methyl]-acrylic acid methyl ester (Table 2, entry 23).
2-[Hydroxy-(3-hydroxy-phenyl)-methyl]-acrylic acid methyl ester (Table 2, entry 24).
2-(Hydroxy-quinolin-4-yl-methyl)-acrylic acid ethyl ester (Table 2, entry 25).
2-(Hydroxy-quinolin-4-yl-methyl)-acrylic acid butyl ester (Table 2, entry 26).
2. H\textsuperscript{1} NMR spectra of the product of benzene-1,4-dicarbaldehyde with acrylonitrile

For the reaction of benzene-1,4-dicarbaldehyde with acrylonitrile, when the reaction time is 40 min, we obtained a mixture of the M–B–H adducts of one aldehyde group with two aldehyde group, when the reaction time is 90 min, only the product of two aldehyde group was obtained. Their H\textsuperscript{1} NMR spectra are as follows.
3. H\textsuperscript{1} NMR spectra of the crude product and the water purified product;

For the DABCO catalyzed M-B-H reaction of 4-chloro-benzaldehyde with acrylonitrile in the green solvent system 1ChCl/2Gly DES–H\textsubscript{2}O, the crude product and the water purified product were characterized by H\textsuperscript{1} NMR spectra (400 MHz, CDCl\textsubscript{3}), the spectra are as follows:
4. FT-IR spectra of the whole M-B-H reaction of 4-chloro-benzaldehyde with acrylonitrile in the green solvent system 1ChCl/2Gly DES–H$_2$O.

a. FT-IR spectra of the glycerol

b. the FT-IR spectra of the solvent system 1ChCl/2Gly DES–H$_2$O
c. the FT-IR spectra of the mixture of 1ChCl/2Gly DES–H2O, 4-chloro-benzaldehyde, acrylonitrile and DABCO

d. 10 minutes later, the FT-IR spectra of the reaction system.
e. 20 minutes later, the FT-IR spectra of the reaction system.

f. 30 minutes later, the FT-IR spectra of the reaction system.
g. 40 minutes later, the FT-IR spectra of the reaction system.

h. 50 minutes later, the FT-IR spectra of the reaction system.
i. 60 minutes later, the FT-IR spectra of the reaction system.

J. 70 minutes later, the FT-IR spectra of the reaction system.

k. 80 minutes later, the FT-IR spectra of the reaction system.