Amino acid ionic liquids as catalysts in a solvent-free Morita–Baylis–Hillman reaction

Mathias Prado Pereira, a Rafaela de Souza Martins a, Marcone Augusto Leal de Oliveira a and Fernanda Irene Bombonato* a

Nucleus of studies in organic synthesis and catalysis, Department of Chemistry, University of Juiz de Fora, São Pedro 36036-900, Juiz de Fora, Brazil.

fernanda.bombonato@ufjf.edu.br

Table of contents

1. 1H and 13C NMR spectra of intermediate compounds (S1)
2. 1H and 13C NMR spectra of amino acid ionic liquids (S4)
3. 1H and 13C NMR spectra of Morita-Baylis-Hillman compounds (S14)
4. 1H NMR spectra of recycle experiments of amino acid ionic liquid 4c (S26)
5. 1H NMR spectra of recycle experiments of amino acid ionic liquid 4d (S27)
5. ESI(−)/MS spectra of recycle experiments of amino acid ionic liquid 4d (S27)
$^1$H and $^{13}$C NMR spectra compounds.

$^1$H NMR of 2 (300 MHz, D$_2$O)
$^{13}$C NMR of 2 (75 MHz, D$_2$O)

**Current Data Parameters**

- **SNR**
- **DEPDC**
- **PROCNO**

**FT - Acquisition Parameters**

- **Date**
- **Time**
- **SPECTRAL**
- **PEAKPROG**
- **SOLVENT**
- **DEPOL**
- **D2O**

**FT - Processing parameters**

- **D2O**
- **D1**
- **D1**
- **D1**

---

**CHANNEL**

- **CH1**
- **CH2**

---

**C6H13**

- **MIX**
- **F1L**
- **F1L**
- **F1L**
- **F1L**
- **F1L**
- **F1L**

---

**S3**
**1H NMR of 3 (300 MHz, D₂O)**

![1H NMR of 3 (300 MHz, D₂O)](image)

**13C NMR of 3 (75 MHz, D₂O)**

![13C NMR of 3 (75 MHz, D₂O)](image)

**1H NMR of 4a (300 MHz, D₂O)**

![1H NMR of 4a (300 MHz, D₂O)](image)
$^{13}$C NMR of 4a (75 MHz, D$_2$O)

Current Data Parameters
NAME MAT021
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters:
Date 20121221
Time 15.23
INSTRUM spect
PROCDB 5 mm QNP18/13
PULPDB zggp30
TD 65536
SOLVENT D2O
NS 16
DS 2
SNR 6172.839 Hz
FIDRES 0.09499 Hz
AQ 5.3084860 sec
RG 143.3
DM 81.000 usec
DE 6.00 usec
TE 380.8 K
DT 1.0000000 sec
TQ0 1

-------- CHANNEL 1 --------
NUC1 1H
P1 12.50 usec
PL1 -3.50 dB
SFO1 300.1318934 MHz

F2 - Processing parameters:
SF 32768
SF 300.1299702 MHz

$^{1}$H NMR of 4b (300 MHz, D$_2$O)

Current Data Parameters
NAME MAT021
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters:
Date 20121221
Time 15.23
INSTRUM spect
PROCDB 5 mm QNP18/13
PULPDB zggp30
TD 65536
SOLVENT D2O
NS 16
DS 2
SNR 6172.839 Hz
FIDRES 0.09499 Hz
AQ 5.3084860 sec
RG 143.3
DM 81.000 usec
DE 6.00 usec
TE 380.8 K
DT 1.0000000 sec
TQ0 1

-------- CHANNEL 1 --------
NUC1 1H
P1 12.50 usec
PL1 -3.50 dB
SFO1 300.1318934 MHz

F2 - Processing parameters:
SF 32768
SF 300.1299702 MHz

S5
$^{13}$C NMR of 4b (75 MHz, D$_2$O)

$^1$H NMR of 4c (300 MHz, D$_2$O)
$^{13}\text{C NMR of 4c (75 MHz, D}_2\text{O)}$

$^1\text{H NMR of 4d (500 MHz, D}_2\text{O)}$
$^{13}$C NMR of 4d (125 MHz, D$_2$O)
$^1$H NMR of 4e (300 MHz, D$_2$O)

Current Data Parameters
NAME  mat026
EXPNO  6
PROCNO  1

F2 - Acquisition Parameter
Date  20130221
Time  10.46
INSTRUM  spect
PROCBD  5 mm QNP 1H/13
PULPROG  zg50
TD  65.58
SOLVENT  D2O
DS  2
SNR  6172.839 Hz
FIDRES  0.094190 Hz
AQ  945060.000000 sec
DG  88.6
DM  81.000 usec
DE  6.000 usec
TE  305.0 K
TD  1.000000000 sec

------- CHANNEL F1 -------
Nuci1  118
P1  12.50 usec
PL1  -3.50 dB
SHF1  300.13185354 MHz

F2 - Processing parameters
SI  2766
SF  300.1299700 MHz
MDW  EM
LDS  2.000 Hz
GB  0
PC  1.00

$^{13}$C NMR of 4e (75 MHz, D$_2$O)

Current Data Parameters
NAME  mat029
EXPNO  6
PROCNO  1

F2 - Acquisition Parameter
Date  20130221
Time  10.46
INSTRUM  spect
PROCBD  5 mm QNP 1H/13
PULPROG  zg50
TD  65.58
SOLVENT  D2O
DS  2
SNR  6172.839 Hz
FIDRES  0.094190 Hz
AQ  945060.000000 sec
DG  88.6
DM  81.000 usec
DE  6.000 usec
TE  305.0 K
TD  1.000000000 sec

------- CHANNEL F1 -------
Nuci1  118
P1  12.50 usec
PL1  -3.50 dB
SHF1  300.13185354 MHz

F2 - Processing parameters
SI  2766
SF  300.1299700 MHz
MDW  EM
LDS  2.000 Hz
GB  0
PC  1.00
$^{1}$H NMR of 5a (300 MHz, D$_2$O)

|$\text{H NMR of 5a (300 MHz, D}_2\text{O)}$

|$\text{C NMR of 5a (75 MHz, D}_2\text{O)}$

|$^{13}\text{C NMR of 5a (75 MHz, D}_2\text{O)}$
$^1$H NMR of 5b (300 MHz, D$_2$O)

Current Data Parameters
NAME: mat031
EXP NO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date: 20130504
Time: 11:39
INSTRUM: spact
PFBIND: 5 mm QNP In/13
PFBPOW: zg30
TD: 65536
NS: 16
DS: 2
SMN: 6172,839 Hz
FIDRES: 0.94186 Hz
AQ: 5.3884660 sec
RG: 90.5
DM: 81,000 usec
DE: 6.00 usec
TE: 300.0 K
DS: 1.00000000 sec
TD: 1

F2 - Processing parameters
SI: 32768
SF: 300.1318934 MHz

$^{13}$C NMR of 5b (75 MHz, D$_2$O)

Current Data Parameters
NAME: mat031
EXP NO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date: 20130504
Time: 11:39
INSTRUM: spact
PFBIND: 5 mm QNP In/13
PFBPOW: zg30
TD: 65536
NS: 16
DS: 2
SMN: 6172,839 Hz
FIDRES: 0.94186 Hz
AQ: 5.3884660 sec
RG: 90.5
DM: 81,000 usec
DE: 6.00 usec
TE: 300.0 K
DS: 1.00000000 sec
TD: 1

F2 - Processing parameters
SI: 32768
SF: 300.1318934 MHz
$^1$H NMR of 5c (300 MHz, D$_2$O)

$^{13}$C NMR of 5c (75 MHz, D$_2$O)
$^1$H NMR of 5d (D$_2$O, 500 MHz)

$^{13}$C NMR of 5d (125 MHz, D$_2$O)
\[ ^{1}H \text{NMR of 5e (300 MHz, D}_{2}\text{O)} \]

\[ ^{13}C \text{NMR of 5e (75 MHz, D}_{2}\text{O)} \]
$^1$H NMR of 8a (500 MHz, CDCl$_3$)

$^{13}$C NMR of 8a (125 MHz, CDCl$_3$)
$^1$H NMR of $8b$ (500 MHz, CDCl$_3$)

$^{13}$C NMR of $8b$ (125 MHz, CDCl$_3$)
$\text{H NMR of } 8c (500 \text{ MHz, CDCl}_3)$

$\text{C NMR of } 8c (125 \text{ MHz, CDCl}_3)$
$^1$H NMR of 8d (500 MHz, CDCl$_3$)

$^{13}$C NMR of 8d (125 MHz, CDCl$_3$)
\[ ^{1}H \text{ NMR of } 8e (500 \text{ MHz, CDCl}_3) \]

\[ ^{13}C \text{ NMR of } 8e (125 \text{ MHz, CDCl}_3) \]
$^1$H NMR of 8f (500 MHz, CDCl$_3$)

$^{13}$C NMR of 8f (125 MHz, CDCl$_3$)
$\text{H NMR of } 8g \ (500 \text{ MHz, CDCl}_3)$

$\text{C NMR of } 8g \ (125 \text{ MHz, CDCl}_3)$
**H NMR of 8h (500 MHz, CDCl₃)**

**13C NMR of 8h (125 MHz, CDCl₃)**
$^1$H NMR of 8i (500 MHz, CDCl$_3$)

$^{13}$C NMR of 8i (125 MHz, CDCl$_3$)
$^1$H NMR of 8j (500 MHz, CDCl$_3$)

$^{13}$C NMR of 8j (125 MHz, CDCl$_3$)
H NMR of 8k (500 MHz, CDCl$_3$)

$^1$H NMR of 8k (500 MHz, CDCl$_3$)

C NMR of 8k (125 MHz, CDCl$_3$)

$^{13}$C NMR of 8k (125 MHz, CDCl$_3$)
$^1$H NMR of recycle AAIL 4c (500 MHz, D$_2$O): a) AAIL fresh before reaction; b) after the reaction.
$^1$H NMR of recycle AAIL 4d (500 MHz, D$_2$O): a) AAIL fresh before reaction; b) second cycle; c) third cycle; d) fourth cycle.

ESI-(−)MS of the recycle AAIL 4d after the MBH reaction.