Supplementary Material

Formal allene insertion into amides. Reaction of propargyl magnesium bromide with morpholine amides

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General experimentation

All reactions were performed in round-bottom flasks fitted with rubber septa. Reactions sensitive to air and/or moisture were performed under a positive pressure of argon. Air- and moisture-sensitive liquids were transferred by syringe. Analytical thin-layer chromatography (TLC) was performed using aluminum plates pre-coated with silica gel (silica gel 60 F254, Sorbfil). TLC plates were visualized by exposure to 254 nm ultraviolet light (UV) or were stained by submersion in acidic ethanolic solution of vanillin followed by brief heating (vanillin) or submersion in aqueous potassium permanganate solution followed by extensive washing with water (KMnO4). Flash-column chromatography was carried out on silica gel (60 Å, 230–400 mesh, Merck). All solvents for chromatography and extractions were technical grade and distilled prior use.

All reagents were obtained from commercial suppliers and were used without further purification. Et2O and THF were stored over sodium benzophenone ketyl and were distilled directly prior use.

Nuclear magnetic resonance spectra were recorded using Bruker Furier 300, Bruker Avance 800 instruments at indicated temperature. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant (J) in Hertz, integration. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvents (CHCl3, δ 7.26 ppm). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonances of the NMR solvents (CDCl3, δ 77.16 ppm).

High-resolution mass spectra were recorded on a Bruker microTOF-Q II mass spectrometer using electrospray ionization (ESI-TOF). Melting points were determined on Kofler melting point apparatus and are uncorrected.
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Copies of NMR spectra

1H NMR (300 MHz, CDCl₃)
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$^{13}$C NMR (75 MHz, CDCl$_3$)
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4a

92:8 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

\[ \text{4a} \]

\(^{13}\text{C NMR (75 MHz, CDCl}_3\)
Issue in honor of Professor Samir Zard

$^1$H NMR (300 MHz, CDCl$_3$)
3b

$^{13}$C NMR (75 MHz, CDCl₃)
Issue in honor of Professor Samir Zard

4b

95.5 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

4b

$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

^1H NMR (300 MHz, CDCl₃)
Issue in honor of Professor Samir Zard

\[ ^{13}C \text{NMR (75 MHz, CDCl}_3) \]

\[ \text{O} \quad \text{Me} \]

[Chemical structure image]

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4c

95:5 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
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$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

\[ ^{13}\text{C NMR (75 MHz, CDCl}_3 \text{)} \]
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4d

93:7 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

4e

90:10 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

\[
\text{OH} \quad \text{O} \\
\text{Me}
\]

MeO

4f

88:12 enol/keto forms

\(^1\)H NMR (300 MHz, CDCl\(_3\))
$^{13}$C NMR (75 MHz, CDCl$_3$)
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4g

92:8 enol/keto forms

^H NMR (300 MHz, CDCl3)
Issue in honor of Professor Samir Zard

\[ \text{MeO} \begin{array}{c} \text{Me} \\ \text{OH} \end{array} \begin{array}{c} \text{O} \\ \text{4g} \end{array} \]

\(^{13}\text{C} \text{NMR (75 MHz, } \text{CDCl}_3)\)
Issue in honor of Professor Samir Zard

80:20 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

4i

80:20 enol/keto forms

\[ ^{13}C \text{ NMR (75 MHz, CDCl}_3 \]
Issue in honor of Professor Samir Zard

3j

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

\[
\begin{align*}
&\text{OH} & \text{O} \\
&\text{Me} & \text{Me}
\end{align*}
\]

\[4k\]

\(^1\text{H NMR (800 MHz, CDCl}_3\)\]

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4k

$^{13}$C NMR (201 MHz, CDCl$_3$)
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4I

87:13 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$\text{4l}$

$87:13 \text{ enol/keto forms}$

$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

\[ \text{H NMR (800 MHz, CDCl}_3\text{)} \]
Issue in honor of Professor Samir Zard

$^{13}$C NMR (201 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

OH

\[ \text{Me} \]

\[ 4m \]

97:3 enol/keto forms

\[ ^1H \text{ NMR (300 MHz, CDCl}_3 \) \]
Issue in honor of Professor Samir Zard

$\overset{13}{\text{C}}$ NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

3n
(ca. 90% purity)

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

\[ \text{3n} \]

(ca. 90% purity)

\(^{13}\text{C NMR (75 MHz, CDCl}_3\))
Issue in honor of Professor Samir Zard

OH
\[ \text{Me} \]

4n

84:16 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

84:16 enol/keto forms

$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

\[
\begin{align*}
3o \\
(\text{ca. } 85\% \text{ purity}) \\
^1\text{H NMR (300 MHz, CDCl}_3) 
\end{align*}
\]
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3o
(ca. 85% purity)

$^{13}$C NMR (75 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

4o

88:12 enol/keto forms

$^1$H NMR (300 MHz, CDCl$_3$)
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$\text{OH} \quad \text{O} \quad \text{Me}$

$4o$

88:12 enol/keto forms

$^{13}\text{C NMR (75 MHz, CDCl}_3)$
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4p
90:10 enol/keto forms

^H NMR (300 MHz, CDCl₃)
Issue in honor of Professor Samir Zard

$\text{Me}\xrightarrow{4p}\text{Me}$

$90:10$ enol/keto forms

$^{13}\text{C NMR (75 MHz, CDCl}_3)$
$^{1}\text{H NMR (300 MHz, CDCl}_3\text{)}$
Issue in honor of Professor Samir Zard

$^{13}$C NMR (75 MHz, CDCl$_3$)

$3r$
Issue in honor of Professor Samir Zard

$^1$H NMR (800 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^{13}$C NMR (201 MHz, CDCl$_3$)
Issue in honor of Professor Samir Zard

$^{13}$C NMR (75 MHz, CDCl$_3$)


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\[
\text{Me-}^7\text{N-Ph}
\]

\(^1\text{H NMR (800 MHz, CDCl}_3\text{)}\)
7

$^{13}$C NMR (201 MHz, CDCl$_3$)