Supporting Information
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Supporting information for

Simple and General Procedure for the Synthesis of α,β-Alkynyl Ketones from Nitriles using Alkynyldimethylaluminum Reagents

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General remarks:

All chemicals were obtained from commercial supplier and were used without purification. Thin layer chromatography (TLC) was carried out using Merck 60 F254 plates with a 0.25 mm thickness. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh) using ethyl acetate/hexanes as eluent. $^1$H NMR (400 MHz or 600 MHz) and $^{13}$C NMR (100 MHz or 150 MHz) spectra were recorded using Varian INOVA-399 (400 MHz) and Agilent VNMR (600 MHz) calibrated using tetramethylsilane as an internal reference. High resolution mass data were obtained from Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. MS spectra were recorded on an Agilent Technologies GC-MS instrument equipped with a 7890 injector, 5975 mass selective detector. The mass spectrometer was operated in EI mode at 70 eV and MS spectra were recorded from $m/z$ 50 to 650.
General experimental procedure:

General experimental procedure for the synthesis of ketone 4aa (Table 2, entry 1) and N-H ketimine 3aa (Table 3, entry 1): The alane (alkynylidimethylaluminum) solution 2 was prepared according to the procedure described.\textsuperscript{1} Alane 2a solution (1.42 mL, 1.4 M in toluene, 2.0 mmol) was added drop-wise to a solution of nitrile 1a (0.103 g, 1.0 mmol) in toluene (4 mL). The resulting reaction mixture was stirred at 60 °C for 6 h and progress of the reaction was monitored by TLC. After cooling, the reaction was quenched by pouring of the reaction mixture into a slurry of Merck silica gel 60 (10 g, 230-400 mesh) in CHCl₃ (100 mL). After being stirred for 12 h, the resultant mixture was filtered and washed with CHCl₃. The combined filtrate was evaporated in vacuo to provide the crude residue. This was then purified by column chromatography on silica gel using ethyl acetate/hexanes (1:20) as eluent to provide the ketone 4aa (0.170 g, 0.85 mmol, 85%) as colorless oil.

To synthesize N-H ketimine 3aa as product, the reaction was performed under same reaction condition as described above. Then, the reaction mixture was diluted with THF (5 mL), and quenched with careful addition of THF-water mixture (5 mL, 8:2). Then the resulting mixture was stirred for 20 min, filtered through Celite® and washed with THF. The combined filtrate was evaporated to dryness to provide the crude product, which then purified by column chromatography on silica gel using ethyl acetate/hexanes (1:9) containing 3% triethylamine as eluent to provide the N-H ketimine 3aa (0.180 g, 0.90 mmol, 90%) as colorless oil.
Characterization of the compounds:

1-Phenyloct-2-yn-1-one \(^2\) (4aa):

\[
\text{1H NMR (400 MHz, CDCl}_3\text{): } \delta = \begin{align*} 
8.18-8.09 & \text{ (m, 2H)}, \\
7.63-7.54 & \text{ (m, 1H)}, \\
7.51-7.41 & \text{ (m, 2H),} \\
2.49 & \text{ (t, } J = 7.2 \text{ Hz, 2H),} \\
1.68 & \text{ (quint, } J = 7.2 \text{ Hz, 2H),} \\
1.50-1.32 & \text{ (m, 4H),} \\
0.93 & \text{ (t, } J = 7.2 \text{ Hz, 3H).} 
\end{align*}
\]

\[
\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } \delta = \begin{align*} 
178.5, \\
137.2, \\
134.1, \\
129.8, \\
128.7, \\
97.1, \\
79.9, \\
31.3, \\
27.7, \\
22.3, \\
19.4, \\
14.1. 
\end{align*}
\]

HRMS (EI\(^+\)): \(m/z\) [M\(^+\)] calcd for C\(_{14}\)H\(_{16}\)O: 200.1201; found: 200.1198.

1,3-Diphenylprop-2-yn-1-one \(^3\) (4ab):

\[
\text{1H NMR (600 MHz, CDCl}_3\text{): } \delta = \begin{align*} 
8.24-8.16 & \text{ (m, 2H),} \\
7.68-7.63 & \text{ (m, 2H),} \\
7.62-7.57 & \text{ (m, 1H),} \\
7.52-7.35 & \text{ (m, 5H).} 
\end{align*}
\]

\[
\text{\textsuperscript{13}C NMR (150 MHz, CDCl}_3\text{): } \delta = \begin{align*} 
178.0, \\
136.9, \\
134.1, \\
133.1, \\
130.8, \\
129.6, \\
128.7, \\
128.6, \\
120.1, \\
93.1, \\
86.9. 
\end{align*}
\]

HRMS (EI\(^+\)): \(m/z\) [M\(^+\)] calcd for C\(_{15}\)H\(_{10}\)O: 206.0732; found: 206.0732.

1-(3-Methoxyphenyl)oct-2-yn-1-one \(^4\) (4ba):

\[
\text{1H NMR (600 MHz, CDCl}_3\text{): } \delta = \begin{align*} 
7.73-7.68 & \text{ (m, 1H),} \\
7.60-7.56 & \text{ (m, 1H),} \\
7.33 & \text{ (t, } J = 8.1 \text{ Hz,} \\
1H), \\
7.11-7.05 & \text{ (m, 1H),} \\
3.79 & \text{ (s, 3H),} \\
2.44 & \text{ (t, } J = 6.9 \text{ Hz, 2H),} \\
1.62 & \text{ (quint, } J = 7.2 \text{ Hz, 2H),} \\
1.44-1.37 & \text{ (m, 2H),} \\
1.35-1.26 & \text{ (m, 2H),} \\
0.87 & \text{ (t, } J = 7.2 \text{ Hz, 3H).} 
\end{align*}
\]

\[
\text{\textsuperscript{13}C NMR (150 MHz, CDCl}_3\text{): } \delta = \begin{align*} 
177.8, \\
159.6, \\
138.2, \\
129.4, \\
122.5, \\
120.5, \\
112.8, \\
96.6, \\
79.6, \\
55.3, \\
30.9, \\
27.4, \\
21.9, \\
19.0, \\
13.7. 
\end{align*}
\]

HRMS (EI\(^+\)): \(m/z\) [M\(^+\)] calcd for C\(_{15}\)H\(_{19}\)O\(_2\): 230.1307; found: 230.1307.

1-(3-Methoxyphenyl)-3-phenylprop-2-yn-1-one \(^4\) (4bb):
$^1$H NMR (600 MHz, CDCl$_3$): δ = 7.86-7.80 (m, 1H), 7.69-7.61 (m, 3H), 7.47-7.42 (m, 1H), 7.41-7.35 (m, 3H), 7.16-7.11 (m, 1H), 3.84 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 177.6, 159.7, 138.1, 132.9, 130.7, 129.5, 128.6, 122.7, 120.8, 119.9, 112.8, 92.8, 86.9, 55.3. HRMS (EI$^+$): m/z [M]$^+$ calcd for C$_{16}$H$_{12}$O$_2$: 236.0837; found: 236.0836.

1-(3-Methoxyphenyl)-5-phenylpent-2-yn-1-one (4bc):

![Chemical Structure](image)

$^1$H NMR (600 MHz, CDCl$_3$): δ = 7.64-7.54 (m, 2H), 7.36-7.29 (m, 3H), 7.28-7.22 (m, 3H), 7.14-7.07 (m, 1H), 3.79 (s, 3H), 2.96 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 177.8, 159.7, 139.7, 138.2, 129.6, 128.7, 128.5, 126.7, 123.0, 120.8, 112.7, 95.4, 80.3, 55.4, 33.9, 21.3. HRMS (EI$^+$): m/z [M]$^+$ calcd for C$_{18}$H$_{16}$O$_2$: 264.1150; found: 264.1150.

1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-one$^4$ (4cb):

![Chemical Structure](image)

$^1$H NMR (600 MHz, CDCl$_3$): δ = 8.15-8.07 (m, 2H), 7.68-7.59 (m, 2H), 7.51-7.42 (m, 3H), 7.41-7.34 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 176.4, 140.6, 135.2, 132.9, 130.9, 130.7, 128.9, 128.6, 119.7, 93.5, 86.5. HRMS (EI$^+$): m/z [M]$^+$ calcd for C$_{15}$H$_9$ClO: 240.0342; found: 240.0343.

1-(4-Chlorophenyl)-5-phenylpent-2-yn-1-one (4cc):

![Chemical Structure](image)

$^1$H NMR (600 MHz, CDCl$_3$): δ = 7.93-7.84 (m, 2H), 7.42-7.33 (m, 4H), 7.32-7.24 (m, 3H), 2.99 (t, J = 7.2 Hz, 2H), 2.83 (m, J = 7.2 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 176.8, 140.5, 139.7, 135.3, 130.9, 128.9, 128.8, 128.6, 126.9, 96.1, 80.1, 33.9, 21.3. HRMS (EI$^+$): m/z [M]$^+$ calcd for C$_{17}$H$_{13}$ClO: 268.0655; found: 268.0656.

3-Phenyl-1-(thiophen-2-yl)prop-2-yn-1-one$^4$ (4db):

![Chemical Structure](image)

S5
$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.97$ (dd, $J = 1.2$, 4.2 Hz, 1H), 7.69 (dd, $J = 1.2$, 4.8 Hz, 1H), 7.65-7.58 (m, 2H), 7.49-7.42 (m, 1H), 7.41-7.34 (m, 2H), 7.18-7.11 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 169.7$, 144.8, 135.2, 135.0, 132.9, 130.8, 128.6, 128.3, 119.8, 91.6, 86.4. HRMS (EI$^+$): $m/z$ [M]$^+$ calcd for C$_{13}$H$_8$SO: 212.0296; found: 212.0298.

**1-Phenylnon-3-yn-2-one** $^2$ (4ea):

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36$-7.17 (m, 5H), 3.79 (s, 2H), 2.28 (t, $J = 7.2$ Hz, 2H), 1.55-1.40 (m, 2H). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36$-7.17 (m, 5H), 3.79 (s, 2H), 2.28 (t, $J = 7.2$ Hz, 2H), 1.55-1.40 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 185.5$, 133.6, 129.9, 128.8, 127.5, 96.8, 80.9, 52.5, 31.1, 27.5, 22.3, 19.1, 14.1. HRMS (EI$^+$): $m/z$ [M]$^+$ calcd for C$_{15}$H$_{18}$O: 214.1358; found: 214.1355.

**1,4-Diphenylbut-3-yn-2-one** (4eb):

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.46$-7.26 (m, 10H), 3.92 (s, 2H). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.46$-7.26 (m, 10H), 3.92 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 185.4$, 133.5, 133.3, 131.1, 130.1, 128.9, 128.8, 127.6, 120.1, 93.2, 87.9, 52.4. HRMS (EI$^+$): $m/z$ [M]$^+$ calcd for C$_{16}$H$_{12}$O: 220.0888; found: 220.0890.

**1,6-Diphenylhex-3-yn-2-one** (4ec):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.39$-7.17 (m, 10H), 3.80 (s, 2H), 2.84 (t, $J = 7.2$ Hz, 2H), 2.63 (t, $J = 7.2$ Hz, 2H). $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.39$-7.17 (m, 10H), 3.80 (s, 2H), 2.84 (t, $J = 7.2$ Hz, 2H), 2.63 (t, $J = 7.2$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 185.2$, 139.7, 133.3, 129.9, 128.8, 128.7, 128.5, 127.4, 126.8, 95.2, 81.4, 52.3, 33.9, 21.2. HRMS (EI$^+$): $m/z$ [M]$^+$ calcd for C$_{18}$H$_{16}$O: 248.1201; found: 248.1200.
1-Phenyldec-3-yn-5-one (4fc):

![Chemical Structure]

$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.19$-$7.06$ (m, 5H), 2.89 (t, $J = 7.2$ Hz, 2H), 2.66 (t, $J = 7.2$ Hz, 2H), 2.48 (t, $J = 7.8$ Hz, 2H), 1.68-1.55 (m, 2H), 1.38-1.09 (m, 4H), 0.90 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 188.3$, 139.6, 128.4, 128.3, 126.5, 92.8, 81.3, 45.4, 33.9, 31.0, 23.7, 22.3, 20.9, 13.8. HRMS (EI$^+$): m/z [M$^+$] calcd for C$_{16}$H$_{20}$O: 228.1514; found: 228.1512.

1-Phenyl oct-2-yn-1-imine (3aa):

![Chemical Structure]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.12$ (br s, 1H), 8.07 (s, 2H), 7.50-7.30 (m, 3H), 2.43 (t, $J = 7.2$ Hz, 2H), 1.64 (quint, $J = 7.2$ Hz, 2H), 1.45-1.27 (m, 4H), 0.928 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 160.5$, 136.7, 131.2, 128.2, 127.5, 95.1, 78.0, 31.0, 27.8, 22.1, 19.1, 13.9. MS (EI): m/z (%) calcd. for C$_{14}$H$_{17}$N: 199; found: 199 ([M$^+$], 10), 198 (84), 156 (100), 143 (77), 115 (38), 77 (25).

1,3-Diphenylpro-2-yn-1-imine (3ab):

![Chemical Structure]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.35$ (br s, 1H), 8.15 (s, 2H), 7.64-7.56 (m, 2H), 7.54-7.34 (m, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 160.0$, 136.4, 132.1, 131.4, 129.7, 128.5, 128.3, 127.5, 121.1, 92.4, 85.4. MS (EI): m/z (%) calcd. for C$_{15}$H$_{11}$N: 205; found: 205 ([M$^+$], 28), 204 (50), 178 (11), 128 (11), 77 (11).

1-(4-Chlorophenyl)oct-2-yn-1-imine (3ca):

![Chemical Structure]
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.13 (br s, 1H), 7.99 (s, 2H), 7.36 (d, $J$ = 8.4 Hz, 2H), 2.41 (t, $J$ = 7.2 Hz, 2H), 1.60 (quint, $J$ = 7.2 Hz, 2H), 1.44-1.28 (m, 4H), 0.90 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 159.3, 137.5, 135.4, 129.2, 128.6, 95.8, 77.7, 31.2, 27.9, 22.3, 19.3, 14.1. MS (EI): $m/z$ (%) cacl. for C$_{14}$H$_{16}$ClN: 233; found: 233 ([M$^+$], 10), 204 (30), 190 (100), 177 (77), 115 (22).

1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-imine (3cb):

1H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.37 (br s, 1H), 8.08 (s, 2H), 7.57 (d, 2H), 7.48-7.33 (m, 5H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 158.5, 137.4, 134.8, 131.9, 129.7, 128.83, 128.82, 128.4, 120.7, 92.7, 84.6. MS (EI): $m/z$ (%) cacl. for C$_{15}$H$_{10}$ClN: 239; found: 239 ([M$^+$], 44), 204 (100), 176 (10), 128 (36).

References:
