Supporting Information
for DOI: 10.1055/s-0034-1378895
© Georg Thieme Verlag KG Stuttgart · New York 2014
Supporting Information for

A Novel Efficient Route for Acid-catalyzed Synthesis of
$\alpha,\beta$-Alkynyl/Alkenyl ketones

Xu Zhang,* Xuefeng Xu, Lintao Yu, Zhiqiang Wang, Qiang Zhao

School of Chemistry and Pharmacony Engineering, Nanyang Normal University,
Nanyang 473061, China

E-mail: zhangxuedu@126.com.
General Methods:

$^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ or DMSO-d$_6$ solutions on a Bruker AVANCE 400 MHz spectrometer. High resolution mass spectra were obtained on a Waters Micromass GCT facility. HOTf was purchased from Alfa Aesar. All other reagents and solvents were used as is from commercial sources. Unless noted below, all other compounds have been reported in the literature or are commercially available.

General AgOTf-Catalyzed reaction Procedure:

A round bottom flask (25 mL) was charged with imine (1 mmol, 1 equiv), phenylacetylene, AgOTf (5 mmol %), HOTf (5 mmol %), as in toluene (5 mL). The mixture was stirred at 120 °C for 4 hours, the reaction was cooled down to room temperature, diluted with 10 ml dichloromethane and washed with 10 ml H$_2$O. The aqueous layer was extracted twice with dichloromethane (10 ml) and the combined organic phase was dried over CaCl$_2$. After evaporation of the solvents, the residue was stirred with silica gel in methylene dichloride at room temperature overnight. The resulting mixture was filtered and concentrated, and then the crude product was purified by silica gel chromatography (dichloromethane/pet. ether).

General HOTf-Catalyzed reaction Procedure:

A round bottom flask (25 mL) was charged with imine (1 mmol, 1 equiv), phenylacetylene, HOTf (5 mmol %), as in toluene (5 mL). The mixture was stirred at 120 °C for 4 hours, the reaction was cooled down to room temperature, diluted with 10 ml dichloromethane and washed with 10 ml H$_2$O. The aqueous layer was extracted twice with dichloromethane (10 ml) and the combined organic phase was dried over CaCl$_2$. After evaporation of the solvents, the residue was stirred with silica gel in methylene dichloride at room temperature overnight. The resulting mixture was filtered and concentrated, and then the crude product was purified by silica gel chromatography.
(dichloromethane/pet. ether).
The data of selected spectra

**(Z)-2,6-Dimethyl-N-(3-phenyl-1-p-tolylprop-2-ynylidene)-aniline.** $^1$H NMR (400 MHz, CDCl$_3$) δ ppm: 7.79 (m, 1H), 7.53 (m, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.10 (t, 4H), 6.94-6.99 (m, 2H), 6.60-6.63 (d, $J = 16.5$ Hz, 1H), 2.34 (s, 3H), 2.13 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm: 167.2, 148.5, 141.7, 139.9, 132.9, 129.6, 129.0, 128.3, 127.9, 127.6, 126.2, 123.0, 120.1, 21.3, 18.1; HRMS (EI) Calcd. for C$_{24}$H$_{21}$N: [M$^+$], 323.1674. Found: m/z 323.1671.

**1,3-Diphenylprop-2-yn-1-one** (4a). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, $J = 7.8$ Hz, 2H), 7.71-7.66 (m, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.47 (d, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 177.9, 136.7, 134.0, 133.0, 130.7, 129.5, 128.6, 128.5, 120.0, 93.0, 86.8; HRMS (EI) Calcd. for C$_{15}$H$_{10}$O: [M$^+$], 206.0712. Found: m/z 206.0714.

**3-Phenyl-1-p-tolylprop-2-yn-1-one** (4b). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.07 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 7.6$ Hz, 2H), 7.42-7.35 (m, 3H), 7.25 (d, $J = 8.4$ Hz, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 177.9, 145.5, 134.8, 133.3, 131.0, 129.9, 129.6, 128.9, 120.4, 92.9, 87.2, 22.1; HRMS (EI) Calcd. for C$_{16}$H$_{12}$O: [M$^+$], 239.1067. Found: m/z 239.1064.

**1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-one** (4c). Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.25 (dd, $J = 8.1$, 5.7 Hz, 2H), 7.68 (d, $J = 7.4$ Hz, 2H), 7.53-7.39 (m, 3H), 7.19 (t, $J = 8.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 176.3, 167.7, 165.1, 133.3, 133.0, 132.2, 132.1, 130.9, 128.7, 119.7, 115.9, 115.7, 93.3, 86.5; HRMS (EI) Calcd. for C$_{15}$H$_{9}$FO: [M$^+$], 224.0632. Found: m/z 224.0628.

**1-(4-Nitrophenyl)-3-phenylprop-2-yn-1-one** (4d). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.37 (s, 4H), 7.71 (d, $J = 7.3$ Hz, 2H), 7.58-7.50 (m, 1H), 7.46 (t, $J = 7.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 175.9, 150.8, 140.9, 133.3, 131.4, 130.4, 128.8, 123.8, 119.3, 95.4, 86.5; HRMS (EI) Calcd. for C$_{15}$H$_{9}$NO$_3$: [M$^+$], 223.0521. Found: m/z 223.0519.
**3-Phenyl-1-o-tolylprop-2-yn-1-one (4e)**. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.31 (d, $J = 7.5$ Hz, 1H), 7.65 (d, $J = 7.0$ Hz, 2H), 7.50-7.33 (m, 5H), 7.28 (d, $J = 7.2$ Hz, 1H), 2.68 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 179.7, 140.5, 135.6, 133.2, 132.9, 132.1, 130.6, 128.6, 125.8, 120.3, 91.8, 88.3, 22.0; HRMS (EI) Calcd. for C$_{16}$H$_{12}$O: [M$^+$], 220.0885. Found: m/z 223.0880.

**3-phenyl-1-m-tolylprop-2-yn-1-one (4f)**. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.04-7.99 (m, 2H), 7.68-7.66 (m, 2H), 7.47-7.39 (m, 5H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 178.5, 138.7, 137.1, 135.2, 133.3, 131.0, 130.0, 128.9, 128.7, 127.4, 120.4, 93.1, 87.2, 21.6; HRMS (EI) Calcd. for C$_{16}$H$_{12}$O: [M$^+$], 220.0885. Found: m/z 223.0880.

**3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-one (4g)**. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.22 (d, $J = 7.5$ Hz, 2H), 7.67-7.59 (m, 3H), 7.51 (t, $J = 7.5$ Hz, 2H), 6.93 (d, $J = 8.5$ Hz, 2H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 178.0, 161.7, 137.0, 135.1, 133.9, 129.4, 128.5, 114.4, 111.8, 94.3, 86.8, 55.4. HRMS (EI) Calcd. for C$_{16}$H$_{12}$O$_2$: [M$^+$], 236.0835. Found: m/z 236.0832.

**1-phenylhex-2-yn-1-one (4h)**: $^1$H NMR (400 MHz, CDCl$_3$) δ 1.09 (t, $J = 7.5$ Hz, 3H), 1.66-1.78 (m, 2H), 7.48 (t, $J = 7.2$ Hz, 2H), 7.48-7.51 (m, 2H), 7.57-7.63 (m, 1H), 8.13-8.17 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.61, 21.16, 21.37, 79.79, 96.65, 128.47, 129.53, 133.85, 136.92, 178.25; HRMS (EI) Calcd. for C$_{12}$H$_{12}$O: [M$^+$], 172.0889. Found: m/z 172.0886.

**1-phenylnon-2-yn-1-one (4i)** $^1$H NMR (400 MHz, CDCl$_3$): δ 8.09 (d, $J = 8.0$ Hz, 2H), 7.54 (t, $J = 7.6$Hz, 1H), 7.42 (t, $J = 8.0$Hz, 2H), 2.44 (t, $J = 6.8$Hz, 2H), 1.64-1.58 (m, 2H), 1.46-1.40 (m, 2H), 1.29-1.25 (m, 4H), 0.85 (t, $J = 6.8$Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 178.4, 137.1, 134.1, 129.7, 128.7, 97.1, 79.9, 31.4, 28.8, 28.0, 22.7, 19.4, 14.2; HRMS (EI) Calcd. for C$_{15}$H$_{18}$O: [M$^+$], 214.1358. Found: m/z 214.1360.

**(E)-Chalcone (4j)**. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.91-7.98 (d, 2H, $J = 7.0$ Hz), 7.58 (d, 1H, $J = 16.0$ Hz), 7.49-7.61 (m, 3H), 7.44-7.47 (m, 1H), 7.46 (d, 1H, $J = 16.0$ Hz), 7.38-7.43 (m, 1H), 7.29-7.37 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 190.5, 144.8,
138.2, 134.8, 132.8, 130.5, 128.9, 128.6, 128.5, 128.4, 122.0; HRMS (EI) Calcd. for C₁₅H₁₂O: [M⁺], Calcd. for 208.0889: Found: m/z 208.0886.

(E)-4-Methylchalcone (4k). ¹H NMR (400 MHz, CDCl₃) δ 3.08 (s, 3H), 7.23 (d, J = 7.8 Hz, 2H), 7.48-7.61 (m, 6H), 7.80 (d, J = 15.6 Hz, 1H), 8.00-8.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 121.1, 128.52, 128.54, 128.6, 129.8, 131.2, 132.7, 138.4, 141.2, 145.0, 190.7; HRMS (EI) Calcd. for C₁₆H₁₄O: [M⁺], Calcd. for: 222.1045; Found: m/z 222.1047.

(E)-3-Phenyl-1-p-tolylprop-2-en-1-one (4q). ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, 2H, J = 8.1Hz), 7.70 (d, 1H, J = 15.8Hz), 7.48-7.56 (m, 2H), 7.43 (d, 1H, J = 15.8 Hz), 7.25-7.33 (m, 3H), 7.18 (d, 2H, J = 8.1 Hz), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 189.9, 144.4, 143.7, 135.7, 135.0, 130.5, 129.4, 129.0, 128.7, 128.5, 122.1, 21.8; HRMS (EI) Calcd. for C₁₆H₁₄O: [M⁺], Calcd. for: 222.1045; Found: m/z 222.1047.

(E)-4-Methoxychalcone (4l). ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H), 6.92-6.95 (m, 2H), 7.42 (d, J = 15.6 Hz, 1H), 7.48-7.62 (m, 5H), 7.79 (d, J = 16.0 Hz, 1H), 8.00-8.02 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.5, 114.5, 119.8, 127.7, 128.5, 128.6, 130.3, 132.6, 138.6, 144.8, 161.7, 190.7; HRMS (EI) Calcd. for C₁₆H₁₄O₂: [M⁺], Calcd. for: 238.0994; Found: m/z 238.0992.

References
$^1$H and $^{13}$C spectra of selected spectra