Supporting Information
for DOI: 10.1055/s-0030-1259930
© Georg Thieme Verlag KG Stuttgart · New York 2011
Indium-catalyzed synthesis of furans and pyrroles via cyclization of
\(\alpha\)-propargyl-\(\beta\)-ketoesters

Hayato Tsuji,* Ken-ichi Yamagata, Yasuyuki Ueda, and Eiichi Nakamura*

Department of Chemistry, School of Science, The University of Tokyo, Hongo 7-3-1,
Bunkyo-ku, Tokyo 113-0033, Japan
Fax: +81-3-5800-6889
E-mail: nakamura@chem.s.u-tokyo.ac.jp
Experimental

General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. The water content of the solvent was confirmed with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 20 ppm. Analytical thin-layer chromatography (TLC) was performed using glass plates coated with 0.25-mm, 230–400 mesh silica gel containing a fluorescent indicator (Merck). Thin layer chromatography plates were visualized by exposure to ultraviolet light (UV) and/or immersion in an ethanol solution of p-anisaldehyde followed by heating on hot plate. Organic solutions were concentrated by rotary evaporation at ca. 15 Torr (evacuated with a diaphragm pump). Flash silica gel chromatography was performed on silica gel 60N (Kanto, spherical, neutral, 140–325 mesh) as described by Still et al.\(^1\)

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and used after appropriate purification before use. Anhydrous tetrahydrofuran (THF) was purchased from Wako Pure Chemical and purified by a solvent purification system (GlassContour)\(^2\) equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use. Toluene was purified by distillation and was stored over molecular sieves 4A. Indium(III) trifluoromethanesulfonate (indium triflate, In(OTf)\(_3\)) was purchased from Aldrich Inc., and used as purchased. Indium(III) tris(trifluoromethanesulfonimide) (indium triflylamide, In(NTf\(_2\))\(_3\)) was prepared as described in the literature.\(^3\)

Instruments. Melting points of solid materials were determined on a Mel-Temp II capillary melting-point apparatus and were uncorrected. Proton nuclear magnetic resonance (\(^1\)H NMR) and carbon nuclear magnetic resonance (\(^{13}\)C NMR) spectra were recorded using a JEOL ECA-500 (500 MHz) NMR spectrometer and JEOL ECX-400

(400 MHz) NMR spectrometer. Chemical shift data for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent (CDCl₃; δ 7.26). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 125 MHz and 100 MHz: chemical shift data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent (CDCl₃; δ 77.0). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), and integration. Mass spectra were acquired by atmospheric pressure ionization (APCI) using a time-of-flight mass analyzer on JEOL JMS-T100LC (AccuTOF) spectrometer.

Substrate synthesis

Procedure A: Synthesis via substitution reaction of enolates and halides.

**Ethyl 2-(4-methoxybenzoyl)pent-4-ynoate (1e)**

\[ \text{MeO} \quad \text{O} \quad \text{O} \quad \text{H} \]

To a suspension of sodium hydride (0.91 g, 24 mmol, 63% dispersed in oil) in THF (50 mL) was added ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (5.30 g, 24 mmol) dropwise via syringe for 15 min at 0 °C. After 10 min stirring, propargyl bromide (3.39 g, 27.8 mmol) was added in one portion, and then the reaction mixture was allowed to warm to room temperature. After stirring for 14 h, aqueous ammonium chloride (50 mL) was added, and the mixture was extracted three times with diethyl ether (50 mL). The combined organic layers were washed with brine (50 mL) and dried over magnesium sulfate. After concentration *in vacuo*, purification by silica gel column chromatography (5% ethyl acetate in hexane) afforded title compound (5.93 g, 96% yield). Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.19 (t, J = 14.0 Hz, 3H, CO₂C₃H₅), 1.98 (t, J = 5.6 Hz, 1H, CH₂C≡CH), 2.83 (ddd, J = 2.8, 7.5, 17.2 Hz, 1H, CH₃C≡CH), 2.94 (ddd, J = 2.8, 7.5, 17.2 Hz, 1H, CH₂C≡CH), 3.88 (s, 3H, ArOCH₃), 4.14–4.20 (dq, J = 1.6, 21.6 Hz, 2H, CO₂CH₃CH₂), 4.53 (t, J = 15.2 Hz, 1H, C(=O)CHC(=O)), 6.96 (dt, J = 5.2, 9.2 Hz, 2H, ArH), 8.03 (dt, J = 5.2, 9.2 Hz, 2H, ArH).
ArH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.9, 19.3, 53.8, 56.5, 62.7, 71.1, 81.7, 114.9 (2C), 129.7, 132.2 (2C), 165.0, 169.4, 192.5; MS (APCI+) 260 (M$^+$). Anal. Calcd for C$_{15}$H$_{16}$O$_4$: C, 69.22; H, 6.20. Found C, 68.99; H, 6.26.

**Ethyl 3-oxo-2-(prop-2-yn-1-yl)butanoate (1a)**

Analytical data were in good accordance with those reported in the literature.$^4$

**Ethyl 2-pivaloylpent-4-ynoate (1b)**

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.21 (s, 9H, C(CH$_3$)$_3$), 1.25 (t, $J$ = 14.3 Hz, 3H, CO$_2$CH$_2$CH$_3$), 1.98 (t, $J$ = 5.2 Hz, 1H, CH$_2$C≡CH), 2.68 (ddd, $J$ = 2.3, 8.1, 16.6 Hz, 1H, CH$_2$C≡CH), 2.77 (ddd, $J$ = 2.3, 8.1, 16.6 Hz, 1H, CH$_2$C≡CH), 4.14 (d, $J$ = 6.9 Hz, 1H, C(=O)CHC(=O)), 4.17 (q, $J$ = 23.5 Hz, 2H, CO$_2$CH$_2$CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 13.7, 18.9, 25.9 (3C), 44.8, 51.1, 61.3, 70.0, 80.6, 167.9, 208.2; MS (APCI–) 209 ([M – H$^+$]). Anal. Calcd for C$_{12}$H$_{18}$O$_3$: C, 68.54; H, 8.63. Found C, 68.17; H, 8.62.

**Ethyl 10-(benzyloxy)-3-oxo-2-(prop-2-yn-1-yl)decanoate (1c)**

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.26–1.36 (m, 6H, alkyl H), 1.27 (t, $J$ = 14.3 Hz, 3H, C(=O)CH$_2$CH$_2$CH$_3$), 1.56–1.63 (m, 4H, alkyl H), 1.98 (t, $J$ = 5.2 Hz, 1H, CH$_2$C≡CH), 2.52–2.57 (m, 1H, CH$_2$C≡CH), 2.60–2.66 (m, 1H, CH$_2$C≡CH), 2.70–2.73 (m, 2H, C(=O)CH$_2$CH$_2$CH$_3$), 3.46 (t, $J$ = 15.5 Hz, 2H, alkyl H), 3.69 (t, $J$ = 15.5 Hz, 1H, C(=O)CHC(=O)), 4.21 (dq, $J$ = 1.7, 21.8 Hz, 2H, CO$_2$CH$_2$CH$_3$), 4.50 (s, 2H, OCH$_2$Ph),

7.26–7.29 (m, 1H, ArH), 7.33–7.34 (m, 4H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) 14.0, 17.4, 23.2, 25.9, 28.8, 29.1, 29.6, 42.5, 57.4, 61.6, 70.1, 70.3, 72.8, 80.5, 127.4, 127.5 (2C), 128.2 (2C), 138.6, 168.0, 203.3; MS (APCI–) 357 ([M – H$^-$]). Anal. Calcd for C$_{22}$H$_{30}$O$_4$: C, 73.71; H, 8.44. Found C, 73.42; H, 8.30.

**Ethyl 2-benzoylpent-4-ynoate (1d)**

Analytical data were in good accordance with those reported in the literature.$^5$

**Ethyl 2-[4-(trifluoromethyl)benzoyl]pent-4-ynoate (1f)**

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.18 (t, J = 14.4 Hz, 3H, CO$_2$CH$_2$CH$_3$), 1.99 (t, J = 5.2 Hz, 1H, CH$_2$C≡CH), 2.88–2.97 (m, 2H, CH$_2$C≡CH), 4.17 (dq, J = 1.7, 22.9 Hz, 2H, CO$_2$CH$_2$CH$_3$), 4.56 (t, J = 14.9 Hz, 1H, C(=O)CHC(=O)), 7.76 (dt, J = 8.6 Hz, 2H, ArH), 8.14 (dt, J = 8.6 Hz, 2H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 13.7, 18.1, 53.3, 61.9, 70.5, 80.1, 123.4 ($^3$J$_{C,F}$ = 813.2 Hz), 125.7 ($^3$J$_{C,F}$ = 10.7 Hz, 2C), 129.1 (2C), 134.7 ($^3$J$_{C,F}$ = 96.6 Hz), 138.6, 167.7, 192.6; MS (APCI–) 297 ([M – H$^-$]). Anal. Calcd for C$_{15}$H$_{13}$F$_3$O$_3$: C, 60.40; H, 4.39. Found C, 60.38; H, 4.38.

**Ethyl 2-(4-bromobenzoyl)pent-4-ynoate (1g)**

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.18 (t, J = 14.4 Hz, 3H, CO$_2$CH$_2$CH$_3$), 1.98 (t, J = 5.2 Hz, 1H, CH$_2$C≡CH), 2.85 (ddd, J = 2.9, 7.5, 17.2 Hz, 1H, CH$_2$C≡CH), 2.92 (ddd, J = 2.9, 7.5, 17.2 Hz, 1H, CH$_2$C≡CH), 4.16 (dq, J = 2.3, 21.2 Hz, 2H, 5. Imagawa, H.; Kurisaki, T.; Nishizawa, M. *Org. Lett.* **2004**, *6*, 3679–3681.
CO\sub{2}CH\sub{2}CH\sub{3}), 4.51 (t, J = 14.9 Hz, 1H, C(=O)CHC(=O)), 7.64 (dt, J = 4.6, 8.6 Hz, 2H, Ar\textit{H}), 7.90 (dt, J = 4.6, 8.6 Hz, 2H, Ar\textit{H}); \textsuperscript{13}C NMR (125 MHz, CDCl\sub{3}) δ 13.6, 17.9, 52.7, 61.6, 70.4, 80.2, 128.7, 130.0 (2C), 131.7 (2C), 134.4, 167.6, 192.0; MS (APCI–) 309 ([M – H]\textsuperscript{+} for C\sub{14}H\sub{13}\textsubscript{81}BrO\sub{3}), 307 ([M – H]\textsuperscript{+} for C\sub{14}H\sub{13}\textsubscript{79}BrO\sub{3}). Anal. Calcd for C\sub{14}H\sub{13}BrO\sub{3}: C, 54.39; H, 4.24. Found C, 54.75; H, 4.40.

**Ethyl 2-benzoylnon-4-ynoate (1h)**

![Ethyl 2-benzoylnon-4-ynoate (1h)](image)

Colorless oil; \textsuperscript{1}H NMR (500 MHz, CDCl\sub{3}) δ 0.84 (t, J = 14.0 Hz, 3H, CH\sub{2}CH\sub{2}CH\sub{2}CH\sub{3}), 1.20 (t, J = 14.4 Hz, 3H, CO\sub{2}CH\sub{2}CH\sub{2}CH\sub{3}), 1.27–1.38 (m, 4H, alkyl H), 2.04–2.08 (m, 2H, alkyl H), 2.85 (tdd, J = 3.6, 7.7, 17.2 Hz, 1H, CH\sub{2}C≡CH), 2.98 (tdd, J = 3.6, 7.7, 17.2 Hz, 1H, CH\sub{2}C≡CH), 4.11–4.19 (m, 2H, CO\sub{2}CH\sub{2}CH\sub{2}CH\sub{3}), 4.53 (t, J = 14.5 Hz, 1H, C(=O)CHC(=O)), 7.49 (t, J = 15.0 Hz, 2H, Ar\textit{H}), 7.60 (t, J = 15.0 Hz, 1H, Ar\textit{H}), 8.03 (d, J = 7.5 Hz, 2H, Ar\textit{H}); \textsuperscript{13}C NMR (100 MHz, CDCl\sub{3}) δ 13.5, 14.0, 18.3, 18.9, 21.7, 30.8, 53.7, 61.6, 76.0, 82.6, 128.6 (2C), 128.8 (2C), 133.6, 136.1, 168.6, 194.0; MS (APCI–) 285 ([M – H]\textsuperscript{+}). Anal. Calcd for C\sub{18}H\sub{22}O\sub{3}: C, 75.50; H, 7.74. Found C, 75.26; H, 7.75.

**Ethyl 2-benzoyl-5-(tert-butyldimethylsilyl)pent-4-ynoate (1i)**

![Ethyl 2-benzoyl-5-(tert-butyldimethylsilyl)pent-4-ynoate (1i)](image)

Colorless solid; mp 42–43 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\sub{3}) δ 0.00 (s, 6H, Si(CH\sub{3})\sub{2}), 0.83 (s, 9H, SiC(CH\sub{3})\sub{3}), 1.18 (t, J = 14.0 Hz, 3H, CO\sub{2}CH\sub{2}CH\sub{2}CH\sub{3}), 2.85 (dd, J = 7.7, 17.2 Hz, 1H, CH\sub{2}C≡CH), 2.98 (dd, J = 7.7, 17.2 Hz, 1H, CH\sub{2}C≡CH), 4.11–4.18 (m, 2H, CO\sub{2}CH\sub{2}CH\sub{2}CH\sub{3}), 4.58 (t, J = 15.2 Hz, 1H, C(=O)CHC(=O)), 7.48 (t, J = 15.2 Hz, 2H, Ar\textit{H}), 7.60 (t, J = 14.4 Hz, 1H, Ar\textit{H}), 8.03 (d, J = 7.2 Hz, 2H, Ar\textit{H}); \textsuperscript{13}C NMR (100 MHz, CDCl\sub{3}) δ −4.7 (2C), 14.0, 16.3, 20.0, 25.9 (3C), 53.3, 61.7, 85.3, 103.4, 128.7 (2C), 128.9 (2C), 133.7, 136.1, 168.3, 193.8; MS (APCI–) 343 ([M – H]\textsuperscript{+}). Anal. Calcd for C\sub{20}H\sub{28}O\sub{3}Si: C, 69.72; H, 8.19. Found C, 69.42; H, 8.19.
**Ethyl 2-benzoyl-5-phenylpent-4-ynoate (1j)**

![Ethyl 2-benzoyl-5-phenylpent-4-ynoate](image)

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.19 (t, $J = 13.7$ Hz, 3H, CO$_2$CH$_2$CH$_3$), 3.07 (dd, $J = 7.5, 17.2$ Hz, 1H, CH$_2$C≡CPh), 3.16 (dd, $J = 7.5, 17.2$ Hz, 1H, CH$_2$C≡CPh), 4.16–4.21 (m, 2H, CO$_2$CH$_2$CH$_3$), 4.66 (t, $J = 14.9$ Hz, 1H, C(=O)CHC(=O)), 7.23–7.28 (m, 5H, ArH), 7.50 (t, $J = 15.5$ Hz, 2H, ArH), 7.61 (t, $J = 16.1$ Hz, 1H, ArH), 8.06 (d, $J = 7.5$ Hz, 2H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 13.8, 19.3, 53.2, 61.6, 82.4, 85.9, 123.0, 127.7, 128.0 (2C), 128.6 (2C), 128.7 (2C), 131.3 (2C), 133.6, 135.9, 168.3, 193.6; MS (APCI–) 305 ([M – H]). Anal. Calcd for C$_{20}$H$_{18}$O$_3$: C, 78.41; H, 5.92. Found C, 78.32; H, 6.14.

**Procedure B: Synthesis via Sonogashira Cross-Coupling Reaction**

**Ethyl 2-benzoyl-5-(4-methoxyphenyl)pent-4-ynoate (1k)**

![Ethyl 2-benzoyl-5-(4-methoxyphenyl)pent-4-ynoate](image)

To a solution of ethyl 2-benzoylpent-4-ynoate (0.67 g, 2.9 mmol), 4-iodotoluene (0.68 g, 3.1 mmol), dichlorobis(triphenylphosphine)palladium(II) (43 mg, 0.06 mmol), copper(I) iodide (23 mg, 0.12 mmol) in THF (6.0 mL) was added triethylamine (0.62 mL) dropwise. After stirring for 7 h at room temperature, the reaction mixture was extracted three times with diethyl ether (5 mL). The combined organic layers were passed through a pad of silica gel with an elution of ether. After concentration in vacuo, purification by silica gel column chromatography (5% ethyl acetate in hexane) afforded the title compound (0.73 g, 79% yield). Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.19 (t, $J = 14.3$ Hz, 3H, CO$_2$CH$_2$CH$_3$), 2.31 (s, 3H, ArCH$_3$), 3.05 (dd, $J = 7.5, 17.2$ Hz, 1H, CH$_2$C≡CAr), 3.15 (dd, $J = 7.5, 17.2$ Hz, 1H, CH$_2$C≡CAr), 4.14–4.22 (m, 2H, CO$_2$CH$_2$CH$_3$), 4.65 (t, $J = 14.9$ Hz, 1H, C(=O)CHC(=O)), 7.04 (d, $J = 8.0$ Hz, 2H, ArH), 7.16 (dt, $J = 8.0$ Hz, 2H, ArH), 7.49 (t, $J = 15.5$ Hz, 2H, ArH), 7.60 (t, $J = 14.9$ Hz, 1H, ArH), 8.06 (d, $J = 7.0$ Hz, 2H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 13.9, 19.4, 21.3, 53.3, 61.6, 82.6, 85.2, 120.0, 128.6 (2C), 128.76 (2C), 128.80 (2C), 131.3 (2C), 133.6, 135.9, 168.3, 193.6; MS (APCI–) 305 ([M – H]).
136.0, 137.8, 168.4, 193.7; MS (APCI–) 319 ([M – H]⁻). Anal. Calcd for C₂₁H₂₀O₃: C, 78.73; H, 6.29. Found C, 78.58; H, 6.42.

**Ethyl 2-benzoyl-5-(4-trifluoromethylphenyl)pent-4-ynoate (1l)**

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 1.19 (t, J = 14.3 Hz, 3H, CO₂CH₂CH₃), 3.09 (dd, J = 7.4, 17.2 Hz, 1H, CH₂C=CAr), 3.17 (dd, J = 7.4, 17.2 Hz, 1H, CH₂C=CAr), 3.19 (dq, J = 2.9, 21.2 Hz, 2H, CO₂CH₂CH₃), 4.66 (t, J = 14.9 Hz, 1H, C(=O)CHC(=O)), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.49–7.52 (m, 4H, ArH), 7.62 (t, J = 14.9 Hz, 1H, ArH), 8.06 (d, J = 8.1 Hz, 2H, ArH); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 19.3, 53.0, 61.8, 81.3, 88.9, 123.2 (¹J_{C-F} = 810.8 Hz), 125.0 (¹J_{C-F} = 11.9 Hz, 2C), 127.0, 128.7 (2C), 128.8 (2C), 129.5 (¹J_{C-F} = 97.8 Hz), 131.7 (2C), 133.7, 135.9, 168.3, 194.3; MS (APCI–) 373 ([M – H]⁻). Anal. Calcd for C₂₁H₁₇F₃O₃: C, 67.38; H, 4.58. Found C, 67.65; H, 4.72.

**Ethyl 2-benzoyl-5-(2-trifluoromethylphenyl)pent-4-ynoate (1m)**

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 1.18 (t, J = 14.4 Hz, 3H, CO₂CH₂CH₃), 3.10 (dd, J = 6.9, 17.2 Hz, 1H, CH₂C=CAr), 3.22 (dd, J = 6.9, 17.2 Hz, 1H, CH₂C=CAr), 4.18 (dq, J = 2.3, 24.1 Hz, 2H, CO₂CH₂CH₃), 4.68 (t, J = 14.9 Hz, 1H, C(=O)CHC(=O)), 7.35 (t, J = 14.4 Hz, 1H, ArH), 7.40–7.44 (m, 2H, ArH), 7.50 (t, J = 15.5 Hz, 2H, ArH), 7.58–7.62 (m, 2H, ArH), 8.07 (d, J = 8.0 Hz, 2H, ArH); ¹³C NMR (125 MHz, CDCl₃) δ 13.8, 19.4, 53.0, 61.7, 78.4, 92.2, 121.3, 123.4 (¹J_{C-F} = 815.5 Hz), 125.5 (¹J_{C-F} = 14.3 Hz), 127.6, 128.6 (2C), 128.8 (2C), 131.2, 131.3 (¹J_{C-F} = 89.4 Hz), 133.7, 133.9, 135.7, 168.1, 193.3; MS (APCI–) 373 ([M – H]⁻). Anal. Calcd for C₂₁H₁₇F₃O₃: C, 67.38; H, 4.58. Found C, 67.59; H, 4.81.
**Ethyl 2-benzoyl-5-(4-bromophenyl)pent-4-ynoate (1n)**

Colorless solid; mp 58–59 °C; \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 1.18 (t, \(J = 14.3\) Hz, 3H, CO\(_2\)CH\(_2\)CH\(_3\)), 3.05 (dd, \(J = 7.5, 17.2\) Hz, 1H, CH\(_3\)C=CAr), 3.13 (dd, \(J = 7.5, 17.2\) Hz, 1H, CH\(_2\)C=CAr), 4.18 (dq, \(J = 2.9, 14.3\) Hz, 2H, CO\(_2\)CH\(_2\)CH\(_3\)), 4.64 (t, \(J = 14.9\) Hz, 1H, C(=O)CHC(=O)), 7.12 (dt, \(J = 8.6, 4.0\) Hz, 2H, Ar\(H\)), 7.37 (dt, \(J = 8.6, 4.0\) Hz, 2H, Ar\(H\)), 7.50 (t, \(J = 15.5\) Hz, 2H, Ar\(H\)), 7.61 (t, \(J = 14.9\) Hz, 1H, Ar\(H\)), 8.05 (d, \(J = 7.5\) Hz, 2H, Ar\(H\)); \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 13.9, 19.3, 53.0, 61.7, 81.5, 87.3, 121.9, 122.0, 128.6 (2C), 128.7 (2C), 131.3 (2C), 132.9 (2C), 133.7, 135.9, 168.3, 193.5; MS (APCI−) 385 ([M − H]\(^−\) for C\(_{20}\)H\(_{17}\)BrO\(_3\)), 383 ([M − H]\(^−\) for C\(_{20}\)H\(_{17}\)\(^{79}\)BrO\(_3\)). Anal. Calcd for C\(_{20}\)H\(_{17}\)BrO\(_3\): C, 62.35; H, 4.45. Found C, 62.47; H, 4.61.

**Representative procedure for In-catalyzed synthesis of trisubstituted furans**

**Ethyl 5-methyl-2-phenylfuran-3-carboxylate (2d)**

To a solution of ethyl 2-benzoylpent-4-ynoate (1.45 g, 6.3 mmol) in toluene (12.5 mL) was added In(OTf)\(_3\) (35.8 mg, 64 \(\mu\)mol). After stirring for 4 h at room temperature, the resulting reaction mixture was passed through a pad of silica gel with an elution of ether. After concentration in vacuo, purification by silica gel column chromatography (3% ethyl acetate in hexane) afforded the title compound (1.43 g, 99% yield). Analytical data were good accordance with the literature data.\(^5\)

**Ethyl 2,5-dimethylfuran-3-carboxylate (2a)**

---

S9
Analytical data were in good accordance with those reported in the literature.\(^6\)

**Ethyl 2-tert-butyl-5-methylfuran-3-carboxylate (2b)**

![Chemical structure](image)

Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.33 (t, \(J = 14.3\) Hz, 3H, CO\(_2\)CH\(_2\)CH\(_3\)), 1.41 (s, 9H, C(CH\(_3\))\(_3\)), 2.23 (s, 3H, ArCH\(_3\)), 4.25 (q, \(J = 21.8\) Hz, 2H, CO\(_2\)CH\(_2\)CH\(_3\)), 6.26 (s, 1H, ArH); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 12.9, 14.2, 28.2 (3C), 34.2, 59.9, 108.1, 112.5, 147.8, 163.9, 166.6; MS (APCI–) 209 ([M – H]\(^+\)). Anal. Calcd for C\(_{12}\)H\(_{18}\)O\(_3\): C, 68.54; H, 8.63. Found C, 68.26; H, 8.71.

**Ethyl 2-[7-(benzyloxy)heptyl]-5-methylfuran-3-carboxylate (2c)**

![Chemical structure](image)

Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.31–1.38 (m, 9H, Alkyl H), 1.57–1.65 (m, 4H, Alkyl H), 2.24 (s, 3H, ArH), 2.92 (t, \(J = 15.5\) Hz, 2H, Alkyl H), 3.46 (t, \(J = 15.5\) Hz, 2H, Alkyl H), 4.25 (q, \(J = 21.8\) Hz, 2H, CO\(_2\)CH\(_2\)CH\(_3\)), 4.50 (s, 2H, C\(_2\)H\(_2\)Ph), 6.21 (s, 1H, ArH), 7.26–7.35 (m, 5H, ArH); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 13.2, 14.3, 26.1, 27.6, 28.1, 29.1, 29.2, 29.7, 59.8, 70.4, 72.8, 106.1, 113.6, 127.4, 127.6 (2C), 128.3 (2C), 138.7, 149.8, 161.6, 164.2; MS (APCI–) 357 ([M – H]\(^+\)). Anal. Calcd for C\(_{22}\)H\(_{30}\)O\(_4\): C, 73.71; H, 8.44. Found C, 73.36; H, 8.46.

**Ethyl 2-(4-methoxyphenyl)-5-methylfuran-3-carboxylate (2e)**

![Chemical structure](image)

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.33 (t, \(J = 14.4\) Hz, 3H, CO\(_2\)CH\(_2\)CH\(_3\)), 2.34 (d, \(J = 0.8\) Hz, 3H, ArCH\(_3\)), 3.85 (s, 3H, ArOCH\(_3\)), 4.27 (q, \(J = 21.6\) Hz, 2H, CO\(_2\)CH\(_2\)CH\(_3\)), 6.41 (d, \(J = 0.8\) Hz, 1H, ArH), 6.94 (dt, \(J = 5.2, 8.8\) Hz, 2H, ArH), 7.94

---

(dt, $J = 5.2, 8.4$ Hz, 2H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.3, 14.3, 55.3, 60.2, 108.5, 113.2, 113.4 (2C), 122.8, 129.6 (2C), 150.4, 156.2, 160.1, 163.9; MS (APCI+) 260 (M$^+$). Anal. Calcd for C$_{15}$H$_{16}$O$_4$: C, 69.2; H, 6.20. Found C, 69.00; H, 6.48.

**Ethyl 5-methyl-2-(4-trifluoromethylphenyl)furan-3-carboxylate (2f)**

![Chemical Structure](image)

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.34 (t, $J = 14.3$ Hz, 3H, CO$_2$CH$_2$CH$_3$), 2.37 (s, 3H, ArCH$_3$), 4.29 (q, $J = 21.2$ Hz, 2H, CO$_2$CH$_2$CH$_3$), 6.47 (s, 1H, ArH), 7.65 (d, $J = 8.6$ Hz, 2H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 13.1, 14.1, 60.5, 109.2, 116.1, 124.0 ($^3J_{C-F} = 810.8$ Hz), 124.9 ($^3J_{C-F} = 10.7$ Hz, 2C), 128.1 (2C), 130.2 ($^3J_{C-F} = 96.6$ Hz), 133.2, 152.0, 153.8, 163.4; MS (APCI–) 297 ([M – H$^-$]). Anal. Calcd for C$_{15}$H$_{13}$F$_3$O$_3$: C, 60.40; H, 4.39. Found C, 60.44; H, 4.48.

**Ethyl 2-(4-bromophenyl)-5-methylfuran-3-carboxylate (2g)**

![Chemical Structure](image)

White solid; mp 49–50 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.33 (t, $J = 14.4$ Hz, 3H, CO$_2$CH$_2$CH$_3$), 2.35 (s, 3H, ArCH$_3$), 4.28 (q, $J = 21.2$ Hz, 2H, CO$_2$CH$_2$CH$_3$), 6.44 (s, 1H, ArH), 7.53 (dt, $J = 3.4, 8.6$ Hz, 2H, ArH), 7.88 (dt, $J = 3.4, 8.6$ Hz, 2H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.2, 14.2, 60.4, 109.0, 111.5, 123.0, 128.8, 129.4 (2C), 131.1 (2C), 151.3, 154.6, 163.5; MS (APCI+) 310 (M$^+$ for C$_{14}$H$_{13}$BrO$_3$), 308 (M$^+$ for C$_{14}$H$_{13}$BrO$_3$). Anal. Calcd for C$_{14}$H$_{13}$BrO$_3$: C, 54.39; H, 4.24. Found C, 54.37; H, 4.28.

**Ethyl 5-pentyl-2-phenylfuran-3-carboxylate (2h)**

![Chemical Structure](image)

Analytical data were in good accordance with those reported in the literature. 7

---

Ethyl 5-(tert-butyldimethylsilyl)methyl-2-phenylfuran-3-carboxylate (2i)

Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.05 (s, 6H, Si(CH\(_3\))\(_2\)), 0.91 (s, 9H, SiC(CH\(_3\))\(_3\)), 1.33 (t, \(J = 14.3\) Hz, 3H, CO\(_2\)CH\(_2\)CH\(_3\)), 2.12 (s, 2H, ArCH\(_2\)Si), 2.67 (s, 1H, ArH), 3.48 (d, \(J = 7.5\) Hz, 1H, ArH), 7.40 (t, \(J = 7.4\) Hz, 2H, ArH); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) –6.0 (2C), 14.2, 14.3, 16.6, 26.3 (3C), 60.3, 106.9, 114.7, 127.8 (2C), 127.9 (2C), 128.6, 130.2, 153.9, 154.9, 163.9; MS (APCI–) 343 ([M – H]+). Anal. Calcd for C\(_{20}\)H\(_{28}\)O\(_3\): C, 69.72; H, 8.19. Found C, 69.49; H, 8.07.

Ethyl 5-benzyl-2-phenylfuran-3-carboxylate (2j)

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.30 (t, \(J = 14.0\) Hz, 3H, CO\(_2\)CH\(_2\)CH\(_3\)), 2.34 (s, 3H, ArC(CH\(_3\))\(_3\)), 3.97 (s, 2H, ArCH\(_2\)Ar), 4.26 (q, \(J = 21.6\) Hz, 2H, CO\(_2\)CH\(_2\)CH\(_3\)), 6.44 (s, 1H, ArH), 6.42 (s, 1H, ArH), 7.13 (d, \(J = 7.5\) Hz, 2H, ArH), 7.25–7.43 (m, 8H, ArH), 7.94 (d, \(J = 7.4\) Hz, 2H, ArH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.2, 34.3, 60.4, 109.4, 114.5, 126.7, 128.0 (2C), 128.2 (2C), 128.6 (2C), 128.8, 129.0 (2C), 129.9, 137.2, 153.5, 156.4, 163.7; MS (APCI–) 305 ([M – H]+). Anal. Calcd for C\(_{20}\)H\(_{18}\)O\(_3\): C, 78.41; H, 5.92. Found C, 78.50; H, 6.01.

Ethyl 2-phenyl-5-(4-tolylmethyl)furan-3-carboxylate (2k)

Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.30 (t, \(J = 14.4\) Hz, 3H, CO\(_2\)CH\(_2\)CH\(_3\)), 2.34 (s, 3H, ArCH\(_3\)), 2.97 (s, 2H, ArCH\(_2\)Ar), 4.26 (q, \(J = 21.2\) Hz, 2H, CO\(_2\)CH\(_2\)CH\(_3\)), 6.42 (s, 1H, ArH), 7.13 (d, \(J = 7.5\) Hz, 2H, ArH), 7.18 (d, \(J = 7.5\) Hz, 2H, ArH), 7.35 (t, \(J = 13.7\) Hz, 1H, ArH), 7.40 (t, \(J = 14.9\) Hz, 2H, ArH), 7.94 (d, \(J = 8.0\) Hz, 2H, ArH); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 14.2, 21.0, 33.8, 60.3, 109.2, 114.4, 127.9 (2C), 128.2 (2C), 128.6 (2C), 129.0, 129.3 (2C), 129.9, 134.1, 136.3, 153.8, 156.4, 163.7; MS (APCI–) 319 ([M – H]+). Anal. Calcd for C\(_{21}\)H\(_{20}\)O\(_3\): C, 78.73; H, 6.29. Found C, 78.41; H, 6.48.
Ethyl 2-phenyl-5-[4-(trifluoromethyl)phenyl]methylfuran-3-carboxylate (2l)

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.31 (t, $J$ = 14.3 Hz, 3H, CO$_2$CH$_2$CH$_3$), 4.07 (s, 2H, ArCH$_2$Ar), 4.27 (dq, $J$ = 1.2, 21.2 Hz, 2H, CO$_2$CH$_2$CH$_3$), 6.48 (s, 1H, ArH), 7.37–7.43 (m, 5H, ArH), 7.59 (d, $J$ = 8.0 Hz, 2H, ArH), 7.92 (d, $J$ = 8.0 Hz, 2H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.2, 34.0, 60.5, 109.9, 114.5, 104.1 ($^1$J$_{C,F}$ = 790.5 Hz), 125.6 ($^3$J$_{C,F}$ = 10.7 Hz, 2C), 128.0 (2C), 128.2 (2C), 129.0 (2C), 129.1 ($^2$J$_{C,F}$ = 95.4 Hz), 129.2, 129.7, 141.2, 152.2, 156.8, 163.5; MS (APCI–) 373 ([M – H]$^-$). Anal. Calcd for C$_{21}$H$_{17}$F$_3$O$_3$: C, 67.38; H, 4.58. Found C, 67.38; H, 4.73.

Ethyl 2-phenyl-5-[2-(trifluoromethyl)phenyl]methylfuran-3-carboxylate (2m)

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.31 (t, $J$ = 14.3 Hz, 3H, CO$_2$CH$_2$CH$_3$), 4.07 (s, 2H, ArCH$_2$Ar), 4.27 (q, $J$ = 21.2 Hz, 2H, CO$_2$CH$_2$CH$_3$), 6.46 (s, 1H, ArH), 7.33–7.42 (m, 5H, ArH), 7.49 (t, $J$ = 14.9 Hz, 1H, ArH), 7.67 (d, $J$ = 8.0 Hz, 1H, ArH), 7.94 (d, $J$ = 7.5 Hz, 2H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.2, 30.7, 60.4, 110.2, 114.6, 124.4 ($^1$J$_{C,F}$ = 815.6 Hz), 126.1 ($^2$J$_{C,F}$ = 15.5 Hz), 126.9, 128.0 (2C), 128.2 (2C), 128.6 ($^3$J$_{C,F}$ = 89.4 Hz), 129.1, 129.8, 131.3, 132.0, 135.8, 152.0, 156.6, 163.6; MS (APCI–) 373 ([M – H]$^-$). Anal. Calcd for C$_{21}$H$_{17}$F$_3$O$_3$: C, 67.38; H, 4.58. Found C, 67.38; H, 4.78.

Ethyl 5-(4-bromophenyl)methyl-2-phenylfuran-3-carboxylate (2n)

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.31 (t, $J$ = 14.3 Hz, 3H, CO$_2$CH$_2$CH$_3$), 3.96 (s, 2H, ArCH$_2$Ar), 4.27 (q, $J$ = 21.2 Hz, 2H, CO$_2$CH$_2$CH$_3$), 6.44 (s, 1H, ArH), 7.16 (d, $J$ = 8.6 Hz, 2H, ArH), 7.37–7.42 (m, 3H, ArH), 7.45 (d, $J$ = 8.6 Hz, 2H, ArH), 7.92 (d, $J$ = 8.6 Hz, 2H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.2, 33.6, 60.4, 109.6, 114.4, 120.6, 128.0 (2C), 128.1 (2C), 129.1, 129.7, 130.4 (2C), 131.6 (2C), 136.1, 152.7, 156.6,
163.5; MS (APCI–) 385 ([M – H]− for C_{20}H_{17}{^81}BrO_{3}) 383 ([M – H]− for C_{20}H_{17}{^79}BrO_{3}).
Anal. Calcd for C_{20}H_{17}BrO_{3}: C, 62.35; H, 4.45. Found C, 62.28; H, 4.53.

Representative procedure for In-catalyzed synthesis of trisubstituted pyrroles

**Ethyl 1-benzyl-2,5-dimethyl-1H-pyrrole-3-carboxylate (3)**

![Chemical structure of ethyl 1-benzyl-2,5-dimethyl-1H-pyrrole-3-carboxylate (3)](image)

To the solution of In(OTf)₃ (35 mg, 62 µmol) and benzylamine (0.77 g, 7.2 mmol) in toluene (12.0 mL) was added ethyl 3-oxo-2-(prop-2-yn-1-yl)butanoate (1a, 1.04 g, 6.2 mmol). After stirring 6 h at 60 °C, the reaction mixture was warmed to reflux temperature and then stirred for the additional 12 h. After reaction mixture was cooled to room temperature, it was filtrated through a pad of silica gel with an elution of diethyl ether. After concentration in vacuo, purification by silica gel column chromatography (5% ethyl acetate in hexane) afforded 3 (1.51 g, 95% yield). Analytical data were in good accordance with those reported in the literature.⁸

**Ethyl 1-butyl-2,5-dimethyl-1H-pyrrole-3-carboxylate (4)**

![Chemical structure of ethyl 1-butyl-2,5-dimethyl-1H-pyrrole-3-carboxylate (4)](image)

Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 0.95 (t, J = 14.3 Hz, 3H, CH₂CH₂CH₂CH₃), 1.32 (t, J = 14.9 Hz, 3H, CH₂CH₂CH₂CH₃), 1.34–1.40 (m, 2H, CH₂CH₂CH₂CH₃), 1.54–1.62 (m, 2H, CH₂CH₂CH₂CH₃), 2.19 (s, 3H, ArCH₃), 2.51 (s, 3H, ArCH₃), 3.74 (q, J = 21.2 Hz, 2H, CO₂CH₂CH₃), 6.24 (s, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃) δ 11.3, 12.1, 13.7, 14.5, 20.0, 32.6, 43.4, 58.9, 107.3, 110.5, 127.2, 134.8, 165.7; MS (APCI+) 224 ([M + H]^+). Anal. Calcd for C_{13}H_{21}NO₂: C, 69.92; H, 9.48; N, 6.27. Found C, 69.76; H, 9.38; N, 6.00.

---

Ethyl 2,5-dimethyl-1-phenyl-1H-pyrrole-3-carboxylate (5)

![Chemical structure of ethyl 2,5-dimethyl-1-phenyl-1H-pyrrole-3-carboxylate](image)

Analytical data were in good accordance with those reported in the literature.\(^8\)

Diethyl 1,1′-(butane-1,4-diyl)bis(2,5-dimethyl-1H-pyrrole-3-carboxylate) (6)

Colorless solid; mp 146–147 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta \) 1.32 (t, \(J = 14.3\) Hz, 6H, CO\(_2\)C\(_2\)H\(_2\)C\(_3\)), 1.64 (t, \(J = 14.3\) Hz, 4H, ArCH\(_2\)CH\(_2\)CH\(_2\)Ar), 2.17 (s, 6H, ArCH\(_3\)), 2.49 (s, 6H, ArCH\(_3\)), 3.75 (t, \(J = 14.3\) Hz, 4H, ArCH\(_2\)CH\(_2\)CH\(_2\)Ar), 4.24 (q, \(J = 21.2\) Hz, 4H, CO\(_2\)C\(_2\)H\(_2\)C\(_3\)), 6.25 (s, 2H, ArH); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta \) 11.2 (2C), 12.1 (2C), 14.3 (2C), 27.6 (2C), 42.9 (2C), 58.9 (2C), 107.6 (2C), 110.8 (2C), 126.9 (2C), 134.5 (2C), 165.4 (2C); MS (APCI+) 389 ([M + H]\(^+\)). Anal. Calcd for C\(_{22}\)H\(_{32}\)N\(_2\)O\(_4\): C, 68.01; H, 8.30; N, 7.21. Found C, 67.75; H, 8.33; N, 6.95.

Ethyl 5-methyl-1,2-diphenyl-1H-pyrrole-3-carboxylate (7)

![Chemical structure of ethyl 5-methyl-1,2-diphenyl-1H-pyrrole-3-carboxylate](image)

Analytical data were in good accordance with those reported in the literature.\(^9\)

Ethyl 5-benzyl-1,2-diphenyl-1H-pyrrole-3-carboxylate (8)

Colorless solid; mp 90–91 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta \) 1.15 (t, \(J = 14.4\) Hz, 3H, CO\(_2\)C\(_2\)H\(_2\)C\(_3\)), 3.75 (s, 2H, ArCH\(_2\)Ph), 4.13 (q, \(J = 21.2\) Hz, 2H, CO\(_2\)C\(_2\)H\(_2\)C\(_3\)), 6.53 (s,

---

1H, ArH), 6.91 (d, J = 6.9 Hz, 2H, ArH), 6.99 (d, J = 6.9 Hz, 2H, ArH), 7.14–7.22 (m, 11H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 14.1, 33.3, 59.3, 109.6, 113.1, 126.1, 127.1 (2C), 127.4, 127.9, 128.1 (2C), 128.5 (2C), 128.6 (2C), 128.7 (2C), 131.0 (2C), 131.6, 133.4, 137.5, 138.6, 138.9, 164.8; MS (APCI+) 382 ([M + H]$^+$). Anal. Calcd for C$_{26}$H$_{23}$NO$_2$: C, 81.86; H, 6.08; N, 3.67. Found C, 81.90; H, 6.27; N, 3.68.