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Article

Sequential Ag-catalyzed carboxylative coupling/Ru-catalyzed cross-metathesis reactions for the synthesis of functionalized 2-alkynoates

ZHANG Linlin, ZHANG Wenzhen*, SHI Linglong, REN Xiang, LÜ Xiaobing[#]

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, Liaoning China

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ABSTRACT

Sequential reactions can provide efficient access to a variety of important organic compounds that would be otherwise difficult to obtain using conventional methods and readily available starting materials. Based on the importance of 2-alkynoates in organic synthesis, the current research aimed to develop a method for the convenient synthesis of functionalized 2-alkynoates from terminal alkynes, CO₂, terminal alkene-derived bromides, and methyl acrylate using a combination of the carboxylative coupling and cross-metathesis reactions. The initial ligand-free silver-catalyzed carboxylative coupling reactions of a variety of different aryl-substituted terminal alkynes and CO₂ with 5-bromopentene and 6-bromohexene provided a series of 4-pentenyl 2-alkynoates and 5-hexenyl 2-alkynoates, respectively, in good yield. These resulting 2-alkynoates were further transformed into methyl (*E*)-6-acetylenecarboxy-2-hexenoates and (*E*)-7-acetylenecarboxy-2-heptenoates in moderate to good yields by their cross-metathesis reactions with methyl acrylate in the presence of the Grubbs-Hoveyda catalyst. All of the new products characterized spectroscopically.

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1. Introduction

Methods for the synthesis of high value-added fine chemicals using carbon dioxide as a raw material have been the subject of increasing levels of attention during the course of the last two decades, because carbon dioxide is an abundant, inexpensive, and nontoxic renewable C₁ feedstock [1–7]. In the presence of suitable homogeneous transition-metal catalysts, carbon dioxide can be efficiently transformed into a variety of different functionalized carboxylic acids and related derivatives [8–22]. The copper- and silver-catalyzed direct carboxylation reactions of terminal alkynes using CO₂ as the carboxylative agent have recently been established as efficient and straight-

forward methods for the synthesis of functionalized propiolic acids and 2-alkynoates [23,34]. In 2010, we reported the highly selective synthesis of allylic 2-alkynoates according to the carboxylative coupling reaction of terminal alkynes, CO₂, and allylic chlorides using a 10 mol% loading of (IPr)CuCl (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as the catalyst [28]. In a later publication, we also disclosed a convenient method for the selective synthesis of functionalized propiolic acids via the direct carboxylation of terminal alkynes with CO₂ under ligand-free conditions using only a 1 mol% loading of AgI as the catalyst [30]. More recently, this simple silver-based catalytic system has also been used as a catalyst for the highly efficient and selective carboxylative coupling reaction of a vari-

* Corresponding author. Tel: +86-411-84986257; Fax: +86-411-84986256; E-mail: zhangwz@dlut.edu.cn

[#] Corresponding author. Tel: +86-411-84986255; Fax: +86-411-84986256; E-mail: lxb-1999@163.com

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ety of different terminal alkynes, CO₂, and chloride compounds to yield 2-alkynoates exclusively. Furthermore, the ligand-free silver catalyst system showed significantly enhanced levels of activity and selectivity at much lower catalyst loadings than the corresponding copper catalyst system [34].

Over the past two decades, olefin metathesis has become one of the most powerful and broadly applicable tools for the construction of carbon-carbon double bonds in organic synthesis [35–39]. In contrast, the cross-metathesis reaction has not been developed to the same extent because of the lack of efficient catalysts capable of controlling the chemoselectivity and stereoselectivity of the reaction [40–44]. Interestingly, however, as a convenient method to gain functionalized and higher olefins from simple alkene precursors, cross-metathesis has emerged as a powerful synthetic strategy and played a crucial role in the total syntheses of many natural products and biologically active compounds, with the utility of technique being significantly enhanced by the development of highly active and selective catalysts [45–50].

Based on the importance of 2-alkynoates in organic synthesis [51–55] and the success of olefin metathesis in a recent study [56], our attentions became focused on the development of a sequential carboxylative coupling/cross-metathesis reaction sequence for the synthesis of functionalized 2-alkynoates from CO₂, and other simple and readily available starting materials. With this goal in mind, it was envisaged that the carboxylative coupling of terminal alkynes, CO₂, and terminal alkene-derived halides would provide access to terminal alkene-derived 2-alkynoates that could then be subjected to the conditions of the cross-metathesis reactions with an olefin of lower reactivity to give functionalized 2-alkynoates, which would be otherwise difficult to obtain using conventional methods (Scheme 1). Herein, we present an efficient and convenient synthetic protocol for the selective synthesis of functionalized 2-alkynoates in good yields from terminal alkynes, CO₂, terminal alkene-derived bromides, and methyl acrylate. The two-steps of this synthetic procedure involved the silver-catalyzed carboxylative coupling and ruthenium-catalyzed cross-metathesis reactions.

2. Experimental

Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry argon or CO₂ atmosphere. *N,N*-Dimethylformamide (DMF) was dis-

tilled from CaH₂ at 60 °C under reduced pressure and stored over 4A molecular sieves. NMR spectra (¹H NMR, 400 MHz; ¹³C NMR, 100 MHz) were recorded on a Bruker AvanceII 400M type spectrometer (Bruker). Multiplicity abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometer (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared (IR) spectra were measured using a Nicolet NEXUS FT-IR spectrophotometer. The second-generation Grubbs catalyst **5** [57,58] and Grubbs-Hoveyda catalyst **6** [59] were synthesized according to the reported procedures. Carbon dioxide (99.999%), commercially available terminal alkynes, bromide compounds, silver(I) salt, methyl acrylate, and other all of the other reagents were used without further purification.

2.1. General procedure for the Ag-catalyzed carboxylative coupling of terminal alkynes, CO₂, and bromides

A 70 ml oven dried autoclave containing a stirrer bar was charged the AgI (0.5 mg, 0.002 mmol) and Cs₂CO₃ (978 mg, 3.0 mmol). The autoclave was purged three time with CO₂ and the terminal alkynes **1** (2.0 mmol), bromides **2** (3.0 mmol), and dry DMF (20 ml) were then added sequentially via a syringe. The autoclave was then sealed and pressurized to the appropriate pressure with CO₂. The reaction mixture was then stirred at 60 °C for 24 h and the autoclave was cooled to room temperature and the remaining CO₂ slowly vented from the system. The reaction mixture was diluted with water (30 ml) and extracted with ethyl acetate (30 ml × 3). The combined organic layers were washed with water and brine, dried over Na₂SO₄, and filtered. The solvent was removed under vacuum. The product was isolated by column chromatography on silica gel.

All new products prepared by the above procedure were characterized spectroscopically as shown below.

4-Pentenyl phenylpropiolate (**3a**). 69% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.61–7.36 (m, 5H, 5CH), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH=CH₂), 5.08 (d, *J* = 16.9 Hz, 1H, *trans* CH=CH₂), 5.02 (d, *J* = 10.2 Hz, 1H, *cis* CH=CH₂), 4.25 (t, *J* = 6.7 Hz, 2H, OCH₂), 2.21–2.16 (m, 2H, CHCH₂), 1.86–1.79 (m, 2H, CH₂CH₂CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 154.10 (C=O), 137.16 (vinyl C), 132.97 (aromatic C), 130.62 (aromatic C), 128.57 (aromatic C), 119.64 (aromatic C), 115.56 (vinyl C), 86.16 (alkynyl C), 80.68 (alkynyl C), 65.42 (OCH₂), 29.89 (CH₂), 27.60 (CH₂). IR (neat, cm⁻¹): 2959, 2223, 1709, 1640, 1490, 1285,

Scheme 1. Synthesis of functionalized 2-alkynoates via the sequential carboxylative coupling/cross-metathesis reactions.

758, 689. HRMS (ESI, m/z) calcd. for $C_{14}H_{14}O_2Na$ $[M+Na]^+$: 237.0891; found: 237.0892.

4-Pentenyl 4-methylphenylpropiolate (**3b**). 87% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.0 Hz, 2H, 2CH), 7.18 (d, J = 8.0 Hz, 2H, 2CH), 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 5.07 (d, J = 16.9 Hz, 1H, *trans* $CH=CH_2$), 5.02 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.24 (t, J = 6.7 Hz, 2H, OCH_2), 2.38 (s, 2H, CH_3), 2.21–2.16 (m, 2H, $CHCH_2$), 1.86–1.79 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.25 (C-O), 141.27 (aromatic C), 137.19 (vinyl C), 132.98 (aromatic C), 129.36 (aromatic C), 116.51 (aromatic C), 115.53 (vinyl C), 86.72 (alkynyl C), 80.33 (alkynyl C), 65.35 (OCH_2), 29.90 (CH_2), 27.62 (CH_2), 21.69 (CH_3). IR (neat, cm^{-1}): 2957, 2217, 1708, 1641, 1508, 1290, 817, 748. HRMS (ESI, m/z) calcd. for $C_{15}H_{16}O_2Na$ $[M+Na]^+$: 251.1048; found: 251.1046.

4-Pentenyl 4-methoxyphenylpropiolate (**3c**). 91% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.7 Hz, 2H, 2CH), 6.88 (d, J = 8.7 Hz, 2H, 2CH), 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 5.07 (d, J = 16.9 Hz, 1H, *trans* $CH=CH_2$), 5.02 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.23 (t, J = 6.7 Hz, 2H, OCH_2), 3.82 (s, 2H, CH_3), 2.20–2.15 (m, 2H, $CHCH_2$), 1.85–1.78 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.50 (aromatic C), 154.37 (C-O), 137.22 (vinyl C), 134.92 (aromatic C), 115.52 (vinyl C), 114.28 (aromatic C), 111.36 (aromatic C), 87.02 (alkynyl C), 80.10 (alkynyl C), 65.27 (OCH_2), 55.37 (OCH_3), 29.91 (CH_2), 27.62 (CH_2). IR (neat, cm^{-1}): 2959, 2210, 1705, 1605, 1510, 1286, 834, 747. HRMS (ESI, m/z) calcd. for $C_{15}H_{16}O_3Na$ $[M+Na]^+$: 267.0997; found: 267.0993.

4-Pentenyl 4-tert-butylphenylpropiolate (**3d**). 87% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.2 Hz, 2H, 2CH), 7.40 (d, J = 8.2 Hz, 2H, 2CH), 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 5.08 (d, J = 16.9 Hz, 1H, *trans* $CH=CH_2$), 5.02 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.25 (t, J = 6.7 Hz, 2H, OCH_2), 2.21–2.16 (m, 2H, $CHCH_2$), 1.85–1.79 (m, 2H, $CH_2CH_2CH_2$), 1.32 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.26 (aromatic C), 154.23 (C-O), 137.18 (vinyl C), 132.89 (aromatic C), 125.64 (aromatic C), 116.53 (aromatic C), 115.55 (vinyl C), 86.65 (alkynyl C), 80.35 (alkynyl C), 65.32 (OCH_2), 35.01 ($C(CH_3)_3$), 31.04 (CH_3), 29.92 (CH_2), 27.61 (CH_2). IR (neat, cm^{-1}): 2964, 2220, 1709, 1290, 1200, 1117, 837, 748. HRMS (ESI, m/z) calcd. for $C_{18}H_{22}O_2Na$ $[M+Na]^+$: 293.1517; found: 293.1519.

4-Pentenyl 4-trifluoromethylphenylpropiolate (**3e**). 85% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.1 Hz, 2H, 2CH), 7.64 (d, J = 8.1 Hz, 2H, 2CH), 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 5.08 (d, J = 16.9 Hz, 1H, *trans* $CH=CH_2$), 5.02 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.27 (t, J = 6.7 Hz, 2H, OCH_2), 2.21–2.16 (m, 2H, $CHCH_2$), 1.87–1.80 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.78 (C-O), 137.19 (vinyl C), 133.29 (aromatic C), 132.49 (aromatic C), 132.14 (aromatic C), 125.67 (aromatic C), 123.63 (CF_3), 115.78 (vinyl C), 84.06 (alkynyl C), 82.40 (alkynyl C), 65.87 (OCH_2), 30.01 (CH_2), 27.70 (CH_2). IR (neat, cm^{-1}): 2960, 2232, 1715, 1324, 1288, 1197, 1178, 1132, 1067, 844, 748. HRMS (ESI, m/z) calcd. for $C_{15}H_{13}O_2F_3Na$ $[M+Na]^+$: 305.0765; found: 305.0774.

4-Pentenyl 5-phenyl-2-pentynoate (**3f**). 65% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.21 (m, 5H, 5CH), 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 5.05 (d, J = 16.9 Hz, 1H,

trans $CH=CH_2$), 5.00 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.16 (t, J = 6.7 Hz, 2H, OCH_2), 2.90 (t, J = 7.6 Hz, 2H, CH_2), 2.62 (t, J = 7.6 Hz, 2H, CH_2), 2.17–2.12 (m, 2H, $CHCH_2$), 1.81–1.74 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.76 (C-O), 139.63 (aromatic C), 137.21 (vinyl C), 128.59 (aromatic C), 128.38 (aromatic C), 126.67 (aromatic C), 115.53 (vinyl C), 88.40 (alkynyl C), 73.74 (alkynyl C), 65.16 (OCH_2), 33.85 (CH_2), 29.91 (CH_2), 27.56 (CH_2), 20.88 (CH_2). IR (neat, cm^{-1}): 2954, 2237, 1709, 1258, 1070, 750, 699. HRMS (ESI, m/z) calcd. for $C_{16}H_{18}O_2Na$ $[M+Na]^+$: 265.1204; found: 265.1211.

4-Pentenyl 2-nonynoate (**3g**). 64% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 5.04 (d, J = 16.9 Hz, 1H, *trans* $CH=CH_2$), 5.00 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.17 (t, J = 6.7 Hz, 2H, OCH_2), 2.33 (t, J = 7.2 Hz, 2H, CH_2), 2.17–2.12 (m, 2H, $CHCH_2$), 1.81–1.74 (m, 2H, $CH_2CH_2CH_2$), 1.61–1.29 (m, 8H, 4 CH_2), 0.89 (t, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.93 (C-O), 137.17 (vinyl C), 115.43 (vinyl C), 89.60 (alkynyl C), 73.07 (alkynyl C), 65.09 (OCH_2), 31.17 (CH_2), 29.86 (CH_2), 28.48 (CH_2), 27.53 (CH_2), 27.47 (CH_2), 22.42 (CH_2), 18.65 (CH_2), 13.96 (CH_3). IR (neat, cm^{-1}): 2959, 2236, 1713, 1642, 1258, 1083. HRMS (ESI, m/z) calcd. for $C_{14}H_{22}O_2Na$ $[M+Na]^+$: 245.1517; found: 245.1521.

5-Hexenyl phenylpropiolate (**4a**). 75% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 7.60–7.36 (m, 5H, 5CH), 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 5.04 (d, J = 16.9 Hz, 1H, *trans* $CH=CH_2$), 4.98 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.25 (t, J = 6.7 Hz, 2H, OCH_2), 2.14–2.11 (m, 2H, $CHCH_2$), 1.76–1.72 (m, 2H, $CH_2CH_2CH_2$), 1.54–1.50 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.17 (C-O), 138.19 (vinyl C), 132.98 (aromatic C), 130.63 (aromatic C), 128.58 (aromatic C), 119.63 (aromatic C), 115.00 (vinyl C), 86.12 (alkynyl C), 80.70 (alkynyl C), 65.99 (OCH_2), 33.24 (CH_2), 27.88 (CH_2), 25.07 (CH_2). IR (neat, cm^{-1}): 2936, 2221, 1709, 1640, 1490, 1286, 758, 689. HRMS (ESI, m/z) calcd. for $C_{15}H_{16}O_2Na$ $[M+Na]^+$: 251.1048; found: 251.1045.

5-Hexenyl 4-methylphenylpropiolate (**4b**). 76% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 2H, 2CH), 7.19 (d, J = 8.0 Hz, 2H, 2CH), 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 5.04 (d, J = 16.9 Hz, 1H, *trans* $CH=CH_2$), 4.99 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.24 (t, J = 6.7 Hz, 2H, OCH_2), 2.39 (s, 2H, CH_3), 2.15–2.09 (m, 2H, $CHCH_2$), 1.76–1.71 (m, 2H, $CH_2CH_2CH_2$), 1.56–1.50 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.25 (C-O), 141.23 (aromatic C), 138.17 (vinyl C), 132.95 (aromatic C), 129.35 (aromatic C), 116.52 (aromatic C), 114.95 (vinyl C), 86.62 (alkynyl C), 80.38 (alkynyl C), 65.85 (OCH_2), 33.23 (CH_2), 27.90 (CH_2), 25.08 (CH_2), 21.66 (CH_3). IR (neat, cm^{-1}): 2937, 2218, 1709, 1641, 1509, 1290, 817, 748. HRMS (ESI, m/z) calcd. for $C_{16}H_{18}O_2Na$ $[M+Na]^+$: 265.1204; found: 265.1211.

5-Hexenyl 4-methoxyphenylpropiolate (**4c**). 86% isolated yield. Oil. 1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.7 Hz, 2H, 2CH), 6.79 (d, J = 8.7 Hz, 2H, 2CH), 5.72 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, $CH=CH_2$), 4.95 (d, J = 16.9 Hz, 1H, *trans* $CH=CH_2$), 4.89 (d, J = 10.2 Hz, 1H, *cis* $CH=CH_2$), 4.14 (t, J = 6.7 Hz, 2H, OCH_2), 3.74 (s, 2H, CH_3), 2.05–1.99 (m, 2H, $CHCH_2$), 1.67–1.60 (m, 2H, $CH_2CH_2CH_2$), 1.46–1.38 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.49 (aromatic C), 154.39 (C-O), 138.20 (vinyl C),

134.90 (aromatic C), 114.94 (vinyl C), 114.27 (aromatic C), 111.37 (aromatic C), 86.94 (alkynyl C), 80.14 (alkynyl C), 65.78 (OCH₂), 55.35 (OCH₃), 33.23 (CH₂), 27.91 (CH₂), 25.08 (CH₂). IR (neat, cm⁻¹): 2937, 2214, 1705, 1604, 1510, 1288, 834, 747. HRMS (ESI, *m/z*) calcd. for C₁₆H₁₈O₃Na [M+Na]⁺: 281.1154; found: 281.1162.

5-Hexenyl 4-tert-butylphenylpropiolate (**4d**). 88% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.53 (d, *J* = 8.5 Hz, 2H, 2CH), 7.39 (d, *J* = 8.5 Hz, 2H, 2CH), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH=CH₂), 5.04 (d, *J* = 16.9 Hz, 1H, *trans* CH=CH₂), 4.98 (d, *J* = 10.2 Hz, 1H, *cis* CH=CH₂), 4.24 (t, *J* = 6.6 Hz, 2H, OCH₂), 2.14–2.09 (m, 2H, CHCH₂), 1.77–1.70 (m, 2H, CH₂CH₂CH₂), 1.56–1.48 (m, 2H, CH₂), 1.32 (s, 9H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 154.18 (aromatic C), 154.16 (C-O), 138.11 (vinyl C), 132.85 (aromatic C), 125.60 (aromatic C), 116.58 (aromatic C), 114.97 (vinyl C), 86.49 (alkynyl C), 80.43 (alkynyl C), 65.78 (OCH₂), 34.96 (C(CH₃)₃), 33.24 (CH₃), 31.01 (CH₂), 27.91 (CH₂), 25.08 (CH₂). IR (neat, cm⁻¹): 2964, 2220, 1709, 1290, 1201, 1175, 837, 748. HRMS (ESI, *m/z*) calcd. for C₁₉H₂₄O₂Na [M+Na]⁺: 307.1674; found: 307.1678.

5-Hexenyl 4-trifluoromethylphenylpropiolate (**4e**). 83% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 8.1 Hz, 2H, 2CH), 7.64 (d, *J* = 8.1 Hz, 2H, 2CH), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH=CH₂), 5.03 (d, *J* = 16.9 Hz, 1H, *trans* CH=CH₂), 4.99 (d, *J* = 10.2 Hz, 1H, *cis* CH=CH₂), 4.26 (t, *J* = 6.7 Hz, 2H, OCH₂), 2.14–2.09 (m, 2H, CHCH₂), 1.78–1.71 (m, 2H, CH₂CH₂CH₂), 1.56–1.48 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 153.68 (C-O), 138.11 (vinyl C), 133.14 (aromatic C), 132.33 (aromatic C), 132.00 (aromatic C), 125.51 (aromatic C), 123.50 (CF₃), 115.02 (vinyl C), 83.87 (alkynyl C), 82.29 (alkynyl C), 66.27 (OCH₂), 33.21 (CH₂), 27.85 (CH₂), 25.06 (CH₂). IR (neat, cm⁻¹): 2938, 2228, 1716, 1324, 1289, 1197, 1177, 1133, 1068, 844, 748. HRMS (ESI, *m/z*) calcd. for C₁₆H₁₅O₂F₃Na [M+Na]⁺: 319.0922; found: 319.0926.

5-Hexenyl 5-phenyl-2-pentynoate (**4f**). 66% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.33–7.21 (m, 5H, 5CH), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH=CH₂), 5.03 (d, *J* = 16.9 Hz, 1H, *trans* CH=CH₂), 4.98 (d, *J* = 10.2 Hz, 1H, *cis* CH=CH₂), 4.16 (t, *J* = 6.6 Hz, 2H, OCH₂), 2.90 (t, *J* = 7.6 Hz, 2H, CH₂), 2.63 (t, *J* = 7.7 Hz, 2H, CH₂), 2.12–2.06 (m, 2H, CHCH₂), 1.72–1.65 (m, 2H, CH₂CH₂CH₂), 1.51–1.44 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 153.80 (C-O), 139.64 (aromatic C), 138.21 (vinyl C), 128.58 (aromatic C), 128.37 (aromatic C), 126.66 (aromatic C), 114.97 (vinyl C), 88.34 (alkynyl C), 73.77 (alkynyl C), 65.71 (OCH₂), 33.86 (CH₂), 33.24 (CH₂), 27.85 (CH₂), 25.08 (CH₂), 20.88 (CH₂). IR (neat, cm⁻¹): 2934, 2236, 1709, 1252, 1070, 750, 699. HRMS (ESI, *m/z*) calcd. for C₁₇H₂₀O₂Na [M+Na]⁺: 279.1361; found: 279.1372.

5-Hexenyl 2-nonynoate (**4g**). 59% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH=CH₂), 5.02 (d, *J* = 16.9 Hz, 1H, *trans* CH=CH₂), 4.97 (d, *J* = 10.2 Hz, 1H, *cis* CH=CH₂), 4.16 (t, *J* = 6.7 Hz, 2H, OCH₂), 2.33 (t, *J* = 7.1 Hz, 2H, CH₂), 2.11–2.06 (m, 2H, CHCH₂), 1.72–1.30 (m, 12H, 6CH₂), 0.89 (t, *J* = 6.5 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 153.95 (C-O), 138.15 (vinyl C), 114.87 (vinyl C), 89.50 (alkynyl C), 73.09 (alkynyl C), 65.61 (OCH₂), 33.20 (CH₂), 31.17 (CH₂), 28.48 (CH₂), 27.80 (CH₂), 27.47 (CH₂), 25.02 (CH₂), 22.42

(CH₂), 18.63 (CH₂), 13.96 (CH₃). IR (neat, cm⁻¹): 2954, 2236, 1713, 1641, 1250, 1083. HRMS (ESI, *m/z*) calcd. for C₁₅H₂₄O₂Na [M+Na]⁺: 259.1674; found: 259.1683.

2.2. General procedure for the cross-metathesis reaction of the terminal alkene-derived 2-alkynoates with methyl acrylate

To a solution of the terminal alkene-derived 2-alkynoates **3** or **4** (0.2 mmol) in toluene (0.1 mol/L) in a Schlenk tube containing a stirrer bar were added methyl acrylates (50 equiv) and the Grubbs-Hoveyda catalyst (5 mol%). The resulting reaction mixtures were heated under an argon atmosphere at 60 °C for 12 h. The mixtures were then quickly filtered through silica and the solvent removed under reduced pressure to give the crude residues, which were purified by flash column chromatography on silica gel to provide the cross-metathesis products **8** or **9**.

All new products prepared by the above procedure were characterized spectroscopically as shown below.

Methyl (*E*)-6-phenylacetylenecarboxy-2-hexenoate (**8a**). 31% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.60–7.36 (m, 5H, 5CH), 6.97 (dt, *J* = 15.6, 6.9 Hz, 1H, CHCH₂), 5.89 (d, *J* = 15.6, 1H, CHCO), 4.26 (t, *J* = 6.9 Hz, 2H, OCH₂), 3.73 (s, 3H, OCH₃), 2.38–2.32 (m, 2H, CHCH₂), 1.93–1.86 (m, 2H, CH₂CH₂CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 166.84 (C-O), 154.00 (C-O), 147.51 (alkenyl C), 133.01 (aromatic C), 130.69 (aromatic C), 128.58 (aromatic C), 121.89 (alkenyl C), 119.55 (aromatic C), 86.54 (alkynyl C), 80.47 (alkynyl C), 64.98 (OCH₂), 51.47 (OCH₃), 28.52 (CH₂), 26.91 (CH₂). IR (neat, cm⁻¹): 2956, 2924, 2219, 1716, 1660, 1463, 1278, 1261, 1024, 757, 689. HRMS (ESI, *m/z*) calcd. for C₁₆H₁₆O₄Na [M+Na]⁺: 295.0946; found: 295.0935.

Methyl (*E*)-6-(4-methylphenyl)acetylenecarboxy-2-hexenoate (**8b**). 63% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, *J* = 8.0 Hz, 2H, 2CH), 7.19 (d, *J* = 8.0 Hz, 2H, 2CH), 6.98 (dt, *J* = 15.7, 6.4 Hz, 1H, CHCH₂), 5.89 (d, *J* = 15.7, 1H, CHCO), 4.25 (t, *J* = 6.4 Hz, 2H, OCH₂), 3.73 (s, 3H, OCH₃), 2.39 (s, 3H, CH₃), 2.39–2.33 (m, 2H, CHCH₂), 1.93–1.86 (m, 2H, CH₂CH₂CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 167.01 (C-O), 154.30 (C-O), 147.74 (alkenyl C), 141.54 (aromatic C), 133.18 (aromatic C), 129.53 (aromatic C), 122.01 (alkenyl C), 116.54 (aromatic C), 87.26 (alkynyl C), 80.29 (alkynyl C), 65.07 (OCH₂), 51.68 (OCH₃), 29.87 (CH₂), 28.70 (CH₂), 27.07 (CH₃). IR (neat, cm⁻¹): 2950, 2924, 2214, 1709, 1659, 1436, 1382, 1289, 1168, 1034, 817, 747. HRMS (ESI, *m/z*) calcd. for C₁₇H₁₈O₄Na [M+Na]⁺: 309.1103; found: 309.1102.

Methyl (*E*)-6-(4-methoxyphenyl)acetylenecarboxy-2-hexenoate (**8c**). 68% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, *J* = 8.9 Hz, 2H, 2CH), 6.97 (dt, *J* = 15.6, 6.9 Hz, 1H, CHCH₂), 6.89 (d, *J* = 8.9 Hz, 2H, 2CH), 5.88 (d, *J* = 15.6, 1H, CHCO), 4.24 (t, *J* = 6.9 Hz, 2H, OCH₂), 3.84 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃), 2.38–2.32 (m, 2H, CHCH₂), 1.92–1.85 (m, 2H, CH₂CH₂CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 167.00 (C-O), 161.72 (aromatic C), 154.41 (C-O), 147.76 (alkenyl C), 135.13 (aromatic C), 121.98 (alkenyl C), 114.45 (aromatic C), 111.43 (aromatic C), 87.55 (alkynyl C), 80.09 (alkynyl C), 64.98 (OCH₂), 55.56 (OCH₃), 51.64 (OCH₃), 28.70 (CH₂), 27.08 (CH₂). IR (neat,

cm⁻¹): 2955, 2922, 2212, 1708, 1658, 1604, 1462, 1288, 1165, 1026, 835, 746. HRMS (ESI, *m/z*) calcd. for C₁₇H₁₈O₅Na [M+Na]⁺: 325.1052; found: 325.1058.

Methyl (*E*)-6-(4-*tert*-butylphenyl)acetylenecarboxy-2-hexenoate (**8d**). 89% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.53 (d, *J* = 8.2 Hz, 2H, 2CH), 7.40 (d, *J* = 8.2 Hz, 2H, 2CH), 6.97 (dt, *J* = 15.7, 6.4 Hz, 1H, CHCH₂), 5.89 (d, *J* = 15.7, 1H, CHCO), 4.25 (t, *J* = 6.4 Hz, 2H, OCH₂), 3.73 (s, 3H, OCH₃), 2.38–2.33 (m, 2H, CHCH₂), 1.93–1.86 (m, 2H, CH₂CH₂CH₂), 1.32 (s, 9H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 166.97 (C-O), 154.54 (C-O), 154.29 (aromatic C), 147.70 (alkenyl C), 133.04 (aromatic C), 125.77 (aromatic C), 121.98 (alkenyl C), 116.52 (aromatic C), 87.21 (alkynyl C), 80.23 (alkynyl C), 65.03 (OCH₂), 51.59 (OCH₃), 35.19 (C(CH₃)₃), 31.17 (CH₃), 28.67 (CH₂), 27.04 (CH₂). IR (neat, cm⁻¹): 2960, 2219, 1716, 1658, 1436, 1290, 1201, 1171, 1040, 838, 748. HRMS (ESI, *m/z*) calcd. for C₂₀H₂₄O₄Na [M+Na]⁺: 351.1572; found: 351.1581.

Methyl (*E*)-6-(4-trifluoromethyl)acetylenecarboxy-2-hexenoate (**8e**). 49% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 7.7 Hz, 2H, 2CH), 7.65 (d, *J* = 7.7 Hz, 2H, 2CH), 6.97 (dt, *J* = 15.5, 6.9 Hz, 1H, CHCH₂), 5.89 (d, *J* = 15.5, 1H, CHCO), 4.27 (t, *J* = 6.9 Hz, 2H, OCH₂), 3.73 (s, 3H, OCH₃), 2.38–2.32 (m, 2H, CHCH₂), 1.93–1.88 (m, 2H, CH₂CH₂CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 166.98 (C-O), 153.67 (C-O), 147.56 (alkenyl C), 133.34 (aromatic C), 132.59 (aromatic C), 132.26 (aromatic C), 125.70 (aromatic C), 123.52 (CF₃), 122.10 (alkenyl C), 84.42 (alkynyl C), 82.19 (alkynyl C), 65.43 (OCH₂), 51.67 (OCH₃), 28.66 (CH₂), 27.01 (CH₂). IR (neat, cm⁻¹): 2953, 2927, 2230, 1716, 1660, 1324, 1287, 1172, 1067, 845, 747. HRMS (ESI, *m/z*) calcd. for C₁₇H₁₅O₄NaF₃ [M+Na]⁺: 363.0820; found: 363.0814.

Methyl (*E*)-7-phenylacetylenecarboxy-2-heptenoate (**9a**). 30% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.61–7.36 (m, 5H, 5CH), 6.97 (dt, *J* = 15.6, 7.0 Hz, 1H, CHCH₂), 5.86 (d, *J* = 15.6, 1H, CHCO), 4.24 (t, *J* = 6.9 Hz, 2H, OCH₂), 3.73 (s, 3H, OCH₃), 2.30–2.24 (m, 2H, CHCH₂), 1.79–1.56 (m, 4H, 2CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 166.98 (C-O), 154.10 (C-O), 148.53 (alkenyl C), 133.00 (aromatic C), 130.65 (aromatic C), 128.57 (aromatic C), 121.51 (alkenyl C), 119.61 (aromatic C), 86.36 (alkynyl C), 80.57 (alkynyl C), 65.59 (OCH₂), 51.43 (OCH₃), 31.63 (CH₂), 27.92 (CH₂), 24.37 (CH₂). IR (neat, cm⁻¹): 2958, 2924, 2201, 1722, 1701, 1660, 1460, 1259, 1024, 800, 745. HRMS (ESI, *m/z*) calcd. for C₁₇H₁₈O₄Na [M+Na]⁺: 309.1103; found: 309.1091.

Methyl (*E*)-7-(4-methylphenyl)acetylenecarboxy-2-heptenoate (**9b**). 49% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, *J* = 7.9 Hz, 2H, 2CH), 7.18 (d, *J* = 7.9 Hz, 2H, 2CH), 6.97 (dt, *J* = 15.7, 6.4 Hz, 1H, CHCH₂), 5.86 (d, *J* = 15.7, 1H, CHCO), 4.24 (t, *J* = 6.4 Hz, 2H, OCH₂), 3.73 (s, 3H, OCH₃), 2.38 (s, 3H, CH₃), 2.30–2.24 (m, 2H, CHCH₂), 1.78–1.56 (m, 4H, 2CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 167.15 (C-O), 154.40 (C-O), 148.76 (alkenyl C), 141.48 (aromatic C), 133.16 (aromatic C), 129.51 (aromatic C), 121.61 (alkenyl C), 116.58 (aromatic C), 87.07 (alkynyl C), 80.38 (alkynyl C), 65.68 (OCH₂), 51.63 (OCH₃), 31.81 (CH₂), 29.86 (CH₂), 28.08 (CH₂), 24.52 (CH₃). IR (neat, cm⁻¹): 2957, 2925, 2217, 1708, 1658, 1435, 1382, 1290, 1169, 1038, 817, 747. HRMS (ESI, *m/z*) calcd. for C₁₈H₂₀O₄Na [M+Na]⁺: 323.1259; found: 323.1247.

Methyl (*E*)-7-(4-methoxyphenyl)acetylenecarboxy-2-heptenoate (**9c**). 56% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 8.8 Hz, 2H, 2CH), 6.97 (dt, *J* = 15.6, 7.0 Hz, 1H, CHCH₂), 6.89 (d, *J* = 8.8 Hz, 2H, 2CH), 5.86 (d, *J* = 15.6, 1H, CHCO), 4.23 (t, *J* = 7.0 Hz, 2H, OCH₂), 3.84 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃), 2.30–2.25 (m, 2H, CHCH₂), 1.78–1.56 (m, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 167.16 (C-O), 161.68 (aromatic C), 154.53 (C-O), 148.78 (alkenyl C), 135.12 (aromatic C), 121.61 (alkenyl C), 114.44 (aromatic C), 111.49 (aromatic C), 87.38 (alkynyl C), 80.17 (alkynyl C), 65.60 (OCH₂), 55.56 (OCH₃), 51.62 (OCH₃), 31.82 (CH₂), 28.10 (CH₂), 24.53 (CH₂). IR (neat, cm⁻¹): 2924, 2850, 2212, 1705, 1657, 1604, 1510, 1460, 1286, 1163, 1029, 835, 747. HRMS (ESI, *m/z*) calcd. for C₁₈H₂₀O₅Na [M+Na]⁺: 339.1208; found: 339.1216.

Methyl (*E*)-7-(4-*tert*-butylphenyl)acetylenecarboxy-2-heptenoate (**9d**). 77% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 8.7 Hz, 2H, 2CH), 7.39 (d, *J* = 8.7 Hz, 2H, 2CH), 6.97 (dt, *J* = 15.6, 6.4 Hz, 1H, CHCH₂), 5.86 (d, *J* = 15.6, 1H, CHCO), 4.24 (t, *J* = 6.4 Hz, 2H, OCH₂), 3.73 (s, 3H, OCH₃), 2.30–2.24 (m, 2H, CHCH₂), 1.77–1.72 (m, 2H, CH₂CH₂CH₂), 1.63–1.56 (m, 2H, CH₂), 1.32 (s, 9H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 167.08 (C-O), 154.47 (C-O), 154.37 (aromatic C), 148.70 (alkenyl C), 133.02 (aromatic C), 125.75 (aromatic C), 121.60 (alkenyl C), 116.58 (aromatic C), 87.02 (alkynyl C), 80.33 (alkynyl C), 65.64 (OCH₂), 51.55 (OCH₃), 35.17 (C(CH₃)₃), 31.77 (CH₂), 31.16 (CH₃), 28.05 (CH₂), 24.50 (CH₂). IR (neat, cm⁻¹): 2962, 2216, 1716, 1660, 1436, 1290, 1201, 1170, 1034, 838, 747. HRMS (ESI, *m/z*) calcd. for C₂₁H₂₆O₄Na [M+Na]⁺: 365.1729; found: 365.1717.

Methyl (*E*)-7-(4-trifluoromethyl)acetylenecarboxy-2-heptenoate (**9e**). 44% isolated yield. Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.2 Hz, 2H, 2CH), 7.65 (d, *J* = 8.2 Hz, 2H, 2CH), 6.97 (dt, *J* = 15.5, 7.0 Hz, 1H, CHCH₂), 5.86 (d, *J* = 15.5, 1H, CHCO), 4.26 (t, *J* = 7.0 Hz, 2H, OCH₂), 3.73 (s, 3H, OCH₃), 2.31–2.25 (m, 2H, CHCH₂), 1.78–1.59 (m, 2H, 2CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 166.98 (C-O), 153.62 (C-O), 148.49 (alkenyl C), 133.17 (aromatic C), 132.38 (aromatic C), 132.06 (aromatic C), 125.53 (aromatic C), 123.43 (CF₃), 121.54 (alkenyl C), 84.10 (alkynyl C), 82.15 (alkynyl C), 65.90 (OCH₂), 51.47 (OCH₃), 31.62 (CH₂), 29.71 (CH₂), 27.88 (CH₂). IR (neat, cm⁻¹): 2951, 2228, 1717, 1658, 1324, 1288, 1174, 1067, 845, 748. HRMS (ESI, *m/z*) calcd. for C₁₈H₁₇O₄NaF₃ [M+Na]⁺: 377.0977; found: 377.0972.

3. Results and discussion

Sequential reactions can offer efficient methods for the synthesis of a variety of different important organic compounds that would be otherwise difficult to prepare using conventional methods. Our recent studies on the carboxylative coupling [34] and olefin metathesis [56] reactions provided a platform for the synthesis of functionalized 2-alkynoates from CO₂, and other simple and readily available starting materials via the combination of these two reactions. Considering the high reaction efficiency of the carboxylative coupling reaction and the use of the relatively costly Grubbs-Hoveyda catalyst in the cross-metathesis reaction, the carboxylative coupling reaction was conducted prior to the cross-metathesis reaction.

Ag-catalyzed carboxylative coupling of terminal alkynes, CO₂, and bromides.

Reaction conditions: 2.0 mmol terminal alkyne **1**, 3.0 mmol bromide **2**, 3.0 mmol Cs₂CO₃, 0.002 mmol AgI, 2.0 MPa CO₂, 20 ml DMF, 60 °C, 24 h.

Scheme 2. The second-generation Grubbs catalyst **5** and Grubbs-Hoveyda catalyst **6**.

Table 2

Cross-metathesis reaction of terminal alkene-derived 2-alkynoates with methyl acrylate.

Entry	3 or 4		Product	Isolated yield (%)
	R	n		
1	Ph	1	3a	8a
2	4-MeC ₆ H ₄	1	3b	8b
3	4-MeOC ₆ H ₄	1	3c	8c
4	4- ^t BuC ₆ H ₄	1	3d	8d
5 ^a	4- ^t BuC ₆ H ₄	1	3d	8d
6	4-CF ₃ C ₆ H ₄	1	3e	8e
7	PhCH ₂ CH ₂	1	3f	8f
8	<i>n</i> -hexyl	1	3g	8g
9	Ph	2	4a	9a
10	4-MeC ₆ H ₄	2	4b	9b
11	4-MeOC ₆ H ₄	2	4c	9c
12	4- ^t BuC ₆ H ₄	2	4d	9d
13	4-CF ₃ C ₆ H ₄	2	4e	9e
14	PhCH ₂ CH ₂	2	4f	9f
15	<i>n</i> -hexyl	2	4g	9g

Reaction conditions: 0.2 mmol 2-alkynoates **3** or **4**, 10 mmol methyl acrylate **7**, 0.01 mmol Grubbs-Hoveyda catalyst **6**, 2 ml toluene, 60 °C, 12 h. ^a 0.01 mmol **5** as catalyst. ^b Yield was determined by ¹H NMR.

dene complex as a catalytically active intermediate. The occurrence of chelate coordination would become possible in this newly formed complex because of the existence of carbonyl and alkyne group in 2-alkynoates substrate. Aryl-substituted 2-alkynoate substrates with longer chains gave lower yields likely because their chelate intermediates showed higher levels of stability and their catalytic activities were inhibited. Alkyl-substituted 4-pentenyl (**3f** and **3g**) and 5-hexenyl (**4f** and **4g**) propiolates failed to undergo the cross-metathesis reactions with methyl acrylate even at elevated temperatures, with higher catalyst loadings and with prolonged reaction times, which might be attributed to the preponderantly competitive coordination of the alkyne moiety in alkyl-substituted propiolate substrates to the ruthenium center (Table 2, entries 7, 8, 14, and 15). Other cross-metathesis partners such as acrolein, acrylonitrile and *t*-butyl acrylate gave the corresponding cross-metathesis products in very low yields (< 5%).

4. Conclusions

A silver-catalyzed carboxylative coupling reaction was successfully developed for the coupling of a variety of different aryl-substituted terminal alkynes and CO₂ with 5-bromopentene or 6-bromohexene to give a series of 4-pentenyl 2-alkynoates or 5-hexenyl 2-alkynoates in good yields. The resulting 2-alkynoates were further transformed into methyl (*E*)-6-acetylenecarboxy-2-hexenoates or (*E*)-7-acetylenecarboxy-2-heptenoates in moderate to good yields via their cross-metathesis reaction with methyl acrylate in the presence of the Grubbs-Hoveyda catalyst. This carboxylative coupling/cross-metathesis reaction sequence offers an efficient and convenient method for the synthesis of functionalized 2-alkynoates from CO₂, and other simple and readily available starting materials.

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Graphical Abstract

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Sequential Ag-catalyzed carboxylative coupling/Ru-catalyzed cross-metathesis reactions for the synthesis of functionalized 2-alkynoates

ZHANG Linlin, ZHANG Wenzhen*, SHI Linglong, REN Xiang, LÜ Xiaobing*

Dalian University of Technology

An efficient and convenient method has been developed for the synthesis of functionalized 2-alkynoates in good yield from terminal alkynes, CO₂, terminal alkene-derived bromides, and methyl acrylate via the combination of silver-catalyzed carboxylative coupling and ruthenium-catalyzed cross-metathesis reactions.

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银催化羧化偶联反应及钌催化交叉复分解反应串联合成官能团炔酸酯

张琳琳, 张文珍*, 石凌龙, 任 祥, 吕小兵[#]

大连理工大学精细化工国家重点实验室, 辽宁大连116024

摘要: 通过将Ag催化的羧化偶联反应与Ru催化的交叉复分解反应串联, 用端炔、二氧化碳、端烯基取代的溴代物和甲基丙烯酸甲酯高效高产率地合成了一系列官能团化的炔酸酯。

关键词: 二氧化碳; 羧化偶联反应; 银催化剂; 交叉复分解反应; Grubbs-Hoveyda催化剂; 均相催化

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*通讯联系人. 电话: (0411)84986257; 传真: (0411)84986256; 电子信箱: zhangwz@dlut.edu.cn

[#]通讯联系人. 电话: (0411)84986255; 传真: (0411)84986256; 电子信箱: lxb-1999@163.com

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