Cu-catalyzed stereoselective conjugate addition of arylboronic acids to alkynoates

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Supplementary Information

General Considerations.

Column chromatography was performed with silica gel (Cica silica gel 60N or Fuji Silysia FL100D) eluted with mixed solvents [hexane / ethyl acetate]. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini 2000 NMR spectrometer as $CDCl_3$ solutions at 25 °C. ^{1}H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at 7.26 ppm for chloroform. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.0 ppm for $CDCl_3$. EI mass measurements were performed with a Shimadzu GCMS-QP2010 plus mass spectrometer. Elemental analyses were performed at Center for Advanced Materials Analysis of Tokyo Institute of Technology. Melting points were obtained in capillary tubes and are uncorrected. Alkynoates **1a**,**e**, arylboronic acids **2**, CuOAc, and MeOH were purchased and used as received. Alkynoates **1b**-**g** and alkynyl ketone **6** were reported in the literature (A. B. Smith, III, J. W. Leahy, I. Noda, S. W. Remiszewski, N. J. Liverton and R. Zibuck, *J. Am. Chem. Soc.*, 1992, **114**, 2995; A. Covarrubias-Zúñiga, L. S. Germán-Sánchez, L. A. Maldonado, M. Romero-Ortega and J. G. Ávila-Zárraga, *Synthesis*, **2005**, 2293; R. A. Earl and L. B. Townsend, *Org. Synth.* 1981, **60**, 81; T. Sakamoto, F. Shiga, A. Yasuhara, D. Uchiyama, Y. Kondo and H. Yamanaka, *Synthesis*, **1992**, 746; U. Appelberg, N. Mohell and U. Hacksell,

Bioorg. Med. Chem. Lett., 1996, **6**, 415; L. Dufková, M. Kotora and I. Císařová, *Eur. J. Org. Chem.*, **2005**, 2491; R. J. Cox, D. J. Ritson, T. A. Dane, J. Berge, J. P. H. Charmant and A. Kantacha, *Chem. Commun.*, **2005**, 1037.).

Representative Procedure for Cu-catalyzed Addition of Arylboronic Acids to Alkynoates: Synthesis of Cinnamate 3aa from Alkynoate 1a and Phenylboronic acid 2a. To a solution of methyl 2-octynoate (**1a**) (168 μL, 1.0 mmol) and phenylboronic acid (**2a**) (366 mg, 3.0 mmol) in methanol (2.0 mL) was added CuOAc (1.23 mg, 0.01 mmol). The reaction mixture was degassed at -78 ˚C, and then stirred at 28 ˚C under Ar atmosphere for 5 h. After filtration through a pad of celite to remove insoluble materials, the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane-AcOEt 150:1) to give **3aa** (214 mg, 94%) as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 1.25-1.45 (m, 6 H), 3.09 (t, *J* = 7.2 Hz, 2 H), 3.75 (s, 3 H), 6.02 (s, 1 H), 7.34-7.45 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.3, 28.6, 30.9, 31.8, 51.0, 116.8, 126.8, 128.6, 128.9, 141.6, 161.5, 167.1; MS (EI): *m/z* (%): 232 (22) [M^+], 201 (25) [M^+ - OMe], 189 (24) [M^+ - $(CH_2)_2CH_3$], 176 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{15}H_{20}O_2$ (232.32): C 77.55, H 8.68; found: C 77.53, H 8.45.

The stereochemistry was determined by comparison of the ^{1}H NMR data with those reported for known ethyl ester analogues (A. R. Katritzky, D. Feng and H. Lang, *J. Org. Chem.*, 1997, **62**, 715.) as shown below.

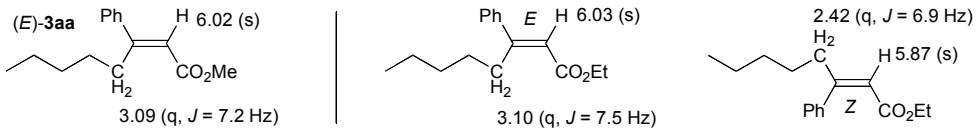
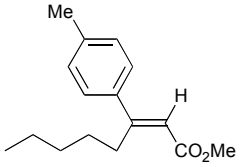
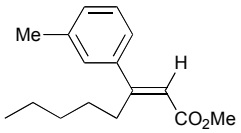


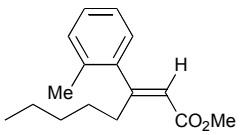
Fig. S1



3ab: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 1.25-1.45 (m, 6 H), 2.37 (s, 3 H), 3.08 (t, *J* = 7.2 Hz, 2 H), 3.74 (s, 3 H), 6.02 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 21.0, 22.3, 28.7, 30.7, 31.8, 50.9, 116.0, 126.7, 129.3, 138.5, 139.1, 161.4, 167.2; MS (EI): *m/z* (%): 246 (11) [M^+], 215 (15) [M^+ - OMe], 203 (7) [M^+ - $(CH_2)_2CH_3$], 190 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{16}H_{22}O_2$ (246.34): C 78.01, H 9.00; found: C 78.00, H 9.13.

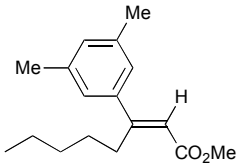


3ac: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 1.24-1.46 (m, 6 H), 2.37 (s, 3 H), 3.07 (t, *J* = 7.2 Hz, 2 H), 3.74 (s, 3 H), 6.00 (s, 1 H), 7.15-7.23 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 21.2, 22.2, 28.6, 30.8, 31.7, 50.8, 116.5, 123.8, 127.4, 128.4, 129.6, 138.1, 141.5, 161.7, 167.0; MS (EI): *m/z* (%): 246 (24) [M^+], 215 (21) [M^+ - OMe], 203 (10) [M^+ - $(CH_2)_2CH_3$], 190 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{16}H_{22}O_2$ (246.34): C 78.01, H 9.00; found: C 77.79, H 9.19.

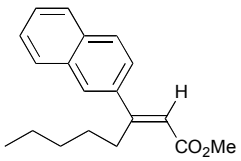


3ad: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (t, *J* = 7.2 Hz, 3 H), 1.22-1.39 (m, 6 H), 2.27 (s, 3 H), 2.93 (t, *J* = 7.2 Hz, 2 H), 3.74 (s, 3 H), 5.70 (s, 1 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 7.13-7.22 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 19.6, 22.3, 27.6, 31.9, 33.4, 50.9, 118.7,

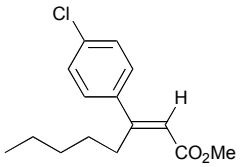
125.5, 127.6, 127.7, 130.4, 134.3, 142.6, 163.2, 166.9; MS (EI): *m/z* (%): 246 (67) [M^+], 231 (42) [M^+ - Me], 215 (100) [M^+ - OMe], 203 (38) [M^+ - $(CH_2)_2CH_3$], 190 (15) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{16}H_{22}O_2$ (246.34): C 78.01, H 9.00; found: C 77.91, H 8.83.



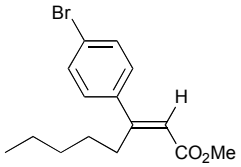
3ae: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.2 Hz, 3 H), 1.25-1.44 (m, 6 H), 2.33 (s, 6 H), 3.06 (t, *J* = 7.2 Hz, 2 H), 3.74 (s, 3 H), 5.99 (s, 1 H), 7.00 (s, 1 H), 7.03 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 21.3, 22.4, 28.7, 31.0, 31.9, 60.0, 116.3, 124.5, 130.5, 137.9, 141.5, 161.9, 167.0; MS (EI): *m/z* (%): 260 (22) [M^+], 229 (20) [M^+ - OMe], 204 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{17}H_{24}O_2$ (260.37): C 78.42, H 9.29; found: C 78.35, H 9.29.



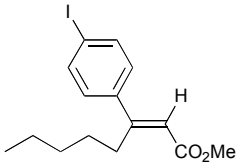
3af: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 1.25-1.50 (m, 6 H), 3.21 (t, *J* = 7.5 Hz, 2 H), 3.77 (s, 3 H), 6.16 (s, 1 H), 7.50 (d, *J* = 9.3 Hz, 1 H), 7.51 (dd, *J* = 3.0, 0.6 Hz, 1 H), 7.55 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.82-7.91 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.3, 28.7, 30.8, 31.8, 51.0, 117.2, 124.5, 126.2, 126.5, 126.7, 127.7, 128.3, 128.5, 133.3, 133.6, 138.8, 161.4, 167.1; MS (EI): *m/z* (%): 282 (27) [M^+], 251 (9) [M^+ - OMe], 226 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{19}H_{22}O_2$ (282.38): C 80.82, H 7.85; found: C 80.49, H 8.03.



3ag: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 1.25-1.45 (m, 6 H), 3.06 (t, *J* = 7.2 Hz, 2 H), 3.75 (s, 3 H), 5.99 (s, 1 H), 7.35 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.3, 28.5, 30.8, 31.7, 51.1, 117.2, 128.1, 128.8, 135.0, 139.9, 160.0, 166.8; MS (EI): *m*/*z* (%): 266 (21) [M^+], 235 (15) [M^+ - OMe], 210 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{15}H_{19}ClO_2$ (266.76): C 67.54, H 7.18; found: C 67.54, H 6.89.

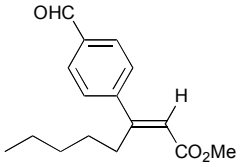


3ah: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 1.24-1.42 (m, 6 H), 3.05 (t, *J* = 7.2 Hz, 2 H), 3.74 (s, 3 H), 5.99 (s, 1 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 7.50 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.3, 28.5, 30.7, 31.7, 51.1, 117.2, 123.1, 128.3, 131.8, 140.3, 160.1, 166.8; MS (EI): *m*/*z* (%): 310 (9) [M^+], 279 (11) [M^+ - OMe], 267 (10) [M^+ - $(CH_2)_2CH_3$], 254 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{15}H_{19}BrO_2$ (311.21): C 57.89, H 6.15; found: C 57.97, H 6.40.

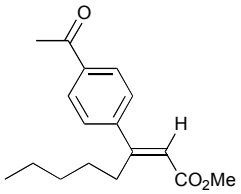


3ai: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.2 Hz, 3 H), 1.24-1.40 (m, 6 H), 3.04 (t, *J* = 7.5 Hz, 2 H), 3.74 (s, 3 H), 5.99 (s, 1 H), 7.16 (d, *J* = 8.5 Hz, 2 H), 7.70 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.2, 28.5, 30.6, 31.7, 51.1, 94.8, 117.2, 128.5,

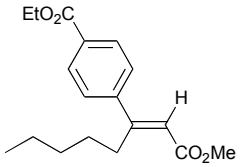
137.7, 140.9, 160.2, 166.7; MS (EI): *m/z* (%): 358 (13) [M^+], 327 (6) [M^+ - OMe], 315 (6) [M^+ - $(CH_2)_2CH_3$], 302 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{15}H_{19}IO_2$ (358.21): C 50.29, H 5.35; found: C 50.27, H 5.47.



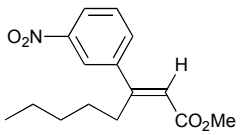
3aj: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.2 Hz, 3 H), 1.24-1.45 (m, 6 H), 3.10 (t, *J* = 7.2 Hz, 2 H), 3.77 (s, 3 H), 6.06 (s, 1 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 10.04 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.2, 28.4, 30.8, 31.6, 51.1, 118.6, 127.2, 129.8, 136.3, 147.4, 159.6, 166.3, 191.4; MS (EI): *m/z* (%): 260 (31) [M^+], 229 (18) [M^+ - OMe], 217 (25) [M^+ - $(CH_2)_2CH_3$], 204 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{16}H_{20}O_3$ (260.33): C 73.82, H 7.74; found: C 73.46, H 8.09.



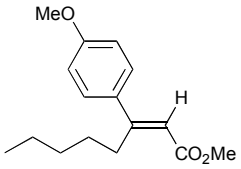
3ak: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.2 Hz, 3 H), 1.24-1.44 (m, 6 H), 2.62 (s, 3 H), 3.10 (t, *J* = 7.2 Hz, 2 H), 3.76 (s, 3 H), 6.05 (s, 1 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 7.96 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.2, 26.5, 28.4, 30.7, 31.6, 51.1, 118.2, 126.8, 128.5, 137.0, 145.9, 159.8, 166.4, 197.2; MS (EI): *m/z* (%): 274 (35) [M^+], 259 (11) [M^+ - Me], 243 (11) [M^+ - OMe], 231 (15) [M^+ - $(CH_2)_2CH_3$], 218 (59) [M^+ - CH_2=$CHCH_2CH_3$], 203 (100) [M^+ - $(CH_2)_3CH_3$]; EA calcd (%) for $C_{17}H_{22}O_3$ (274.35): C 74.42, H 8.08; found: C 74.13, H 8.36.



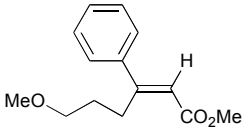
3al: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.2 Hz, 3 H), 1.24-1.44 (m, 6 H), 1.40 (t, *J* = 7.2 Hz, 3 H), 3.10 (t, *J* = 7.2 Hz, 2 H), 3.76 (s, 3 H), 4.39 (q, *J* = 7.2 Hz, 2 H), 6.04 (s, 1 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 8.04 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.3, 22.3, 28.5, 30.9, 31.7, 51.2, 61.1, 118.1, 126.7, 129.7, 130.7, 145.8, 160.1, 166.1, 166.5; MS (EI): *m/z* (%): 304 (15) [M^+], 275 (17) [M^+ - Et], 273 (14) [M^+ - OMe], 259 (17) [M^+ - OEt], 248 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{18}H_{24}O_4$ (304.38): C 71.03, H 7.95; found: C 70.81, H 8.17.



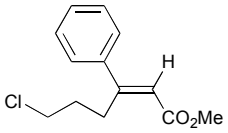
3am: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 1.24-1.45 (m, 6 H), 3.12 (t, *J* = 7.2 Hz, 2 H), 3.78 (s, 3 H), 6.08 (s, 1 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.74 (ddd, *J* = 8.0, 1.8, 1.2 Hz, 1 H), 8.22 (ddd, *J* = 8.0, 2.1, 0.9 Hz, 1 H), 8.28 (t, *J* = 2.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 22.2, 28.3, 30.7, 31.6, 51.2, 119.0, 121.6, 123.5, 129.7, 132.6, 143.2, 148.5, 158.4, 166.3; MS (EI): *m/z* (%): 277 (12) [M^+], 260 (100) [M^+ - OH], 246 (20) [M^+ - OMe], 221 (55) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{15}H_{19}NO_4$ (277.32): C 64.97, H 6.91, N 5.05; found: C 64.77, H 7.16, N 4.97.



3an: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2 Hz, 3 H), 1.25-1.46 (m, 6 H), 3.07 (t, *J* = 7.2 Hz, 2 H), 3.74 (s, 3 H), 3.83 (s, 3 H), 6.00 (s, 1 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.4, 28.9, 30.6, 31.9, 50.9, 55.2, 113.8, 114.9, 127.9, 133.3, 160.3, 160.7, 167.0; MS (EI): *m*/*z* (%): 262 (16) [M^+], 231 (13) [M^+ - OMe], 206 (100) [M^+ - CH_2=$CHCH_2CH_3$]; EA calcd (%) for $C_{16}H_{22}O_3$ (262.34): C 73.25, H 8.45; found: C 73.22, H 8.64.

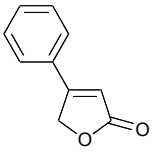


3ba: colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.67-1.77 (m, 2 H), 3.16 (t, *J* = 7.5 Hz, 2 H), 3.28 (s, 3 H), 3.40 (t, *J* = 6.6 Hz, 2 H), 3.75 (s, 3 H), 6.06 (s, 1 H), 7.34-7.47 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.6, 28.8, 51.0, 58.3, 72.2, 116.9, 126.6, 128.5, 128.9, 140.9, 160.4, 166.7; MS (EI): *m*/*z* (%): 234 (0.4) [M^+], 202 (9) [M^+ - HOMe], 189 (6) [M^+ - CH_2OMe], 176 (100) [M^+ - CH_2=CHOMe]; EA calcd (%) for $C_{14}H_{18}O_3$ (234.29): C 71.77, H 7.74; found: C 71.71, H 7.85

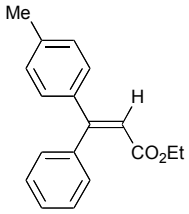


3ca: colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87-1.98 (m, 2 H), 3.25 (t, *J* = 7.5 Hz, 2 H), 3.56 (t, *J* = 6.6 Hz, 2 H), 3.76 (s, 3 H), 6.10 (s, 1 H), 7.37-7.45 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.5, 31.8, 44.7, 51.1, 117.6, 126.6, 128.6, 129.2, 140.5, 159.1, 166.7; MS (EI): *m*/*z*

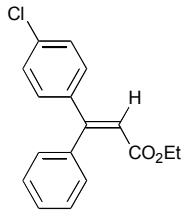
(%): 238 (91) [M^+], 207 (35) [M^+ - OMe], 189 (100) [M^+ - CH_2Cl], 176 (81) [M^+ - CH_2=CHCl]; EA calcd (%) for $C_{13}H_{15}ClO_2$ (238.71): C 65.41, H 6.33; found: C 65.59, H 6.15.



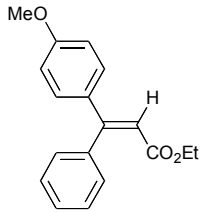
5: colorless solid (mp. 92-93 °C, lit. mp. 91-93 °C: T. Taniguchi, H. Nagata, R. M. Kanada, K. Kadota, M. Tekeuchi and K. Ogasawara, *Heterocycles*, 2000, **52**, 67.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.24 (d, *J* = 1.8 Hz, 2 H), 6.39 (t, *J* = 1.8 Hz, 1 H), 7.46-7.52 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 71.0, 113.0, 126.4, 129.3, 129.6, 131.7, 163.9, 173.8.



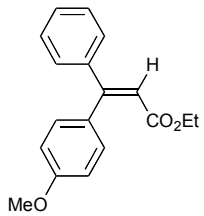
3eb: colorless oil (known compound: N. Kamigata, A. Satoh and M. Yoshida, *Phosphorus, Sulfur, and Silicon*, 1989, **46**, 121.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.2 Hz, 3 H), 2.35 (s, 3 H), 4.04 (q, *J* = 7.2 Hz, 2 H), 6.35 (s, 1 H), 7.12-7.39 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 55.2, 59.8, 113.8, 115.4, 127.9, 128.0, 129.1, 129.8, 133.2, 139.4, 156.3, 160.9, 166.4.



3eg: colorless solid (mp. 40-42 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.2 Hz, 3 H), 4.05 (q, *J* = 7.2 Hz, 2 H), 6.33 (s, 1 H), 7.17-7.40 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 60.0, 117.7, 127.9, 128.2, 128.5, 129.0, 129.4, 135.4, 138.4, 139.2, 154.9, 165.7.; MS (EI): *m*/*z* (%): 286 (69) [M^+], 257 (19) [M^+ - Et], 241 (100) [M^+ - OEt], 214 (77) [M^+ - CH_2=CH_2 - CO_2]; EA calcd (%) for $C_{17}H_{15}ClO_2$ (286.75): C 71.20, H 5.27; found: C 71.22, H 5.00.



(*E*)-**3en**: colorless oil (known compound: N. Kamigata, A. Satoh and M. Yoshida, *Phosphorus, Sulfur, and Silicon*, 1989, **46**, 121.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.2 Hz, 3 H), 3.81 (s, 3 H), 4.03 (q, *J* = 7.2 Hz, 2 H), 6.31 (s, 1 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 7.25 (d, *J* = 8.7 Hz, 2 H), 7.18-7.40 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 55.3, 59.8, 113.7, 115.3, 127.8, 127.9, 129.0, 129.7, 133.1, 139.2, 156.2, 160.7, 166.2.



(*Z*)-**3fa**: colorless oil (known compound: N. Kamigata, A. Satoh and M. Yoshida, *Phosphorus, Sulfur, and Silicon*, 1989, **46**, 121.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (t, *J* = 7.2 Hz, 3 H),

3.84 (s, 3 H), 4.09 (q, *J* = 7.2 Hz, 2 H), 6.27 (s, 1 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 7.16 (d, *J* = 8.8 Hz, 2 H), 7.28-7.37 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 55.1, 59.9, 113.2, 116.9, 128.3, 128.6, 129.3, 131.0, 131.1, 141.6, 156.6, 159.8, 166.4.

The spectral data for (*E*)-**3en** and (*Z*)-**3fa** were in good agreement with those reported for the known compounds (N. Kamigata, A. Satoh and M. Yoshida, *Phosphorus, Sulfur, and Silicon*, 1989, **46**, 121.) as shown below.

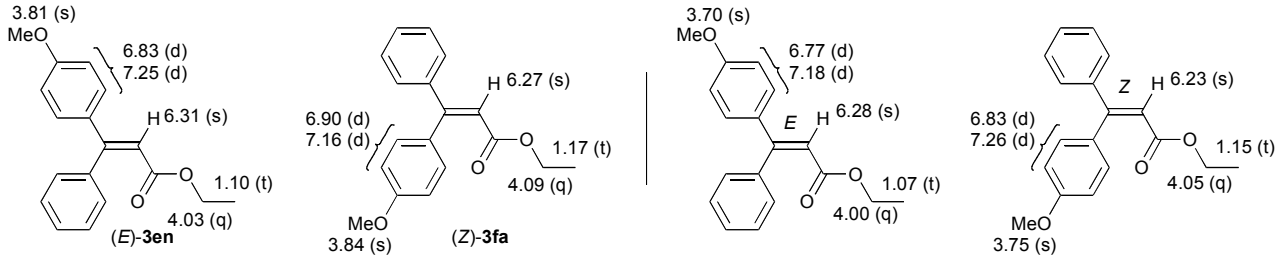
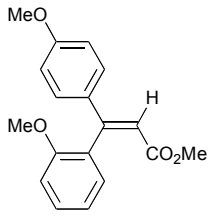
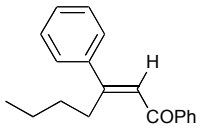


Fig. S2



3gn: colorless solid (mp. 109-111 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.58 (s, 3 H), 3.70 (s, 3 H), 3.80 (s, 3 H), 6.41 (s, 1 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 6.94-7.10 (m, 2 H), 7.28 (d, *J* = 9.0 Hz, 2 H), 7.33-7.40 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.0, 55.2, 55.6, 111.0, 113.7, 115.4, 120.3, 128.2, 128.8, 129.2, 129.9, 132.3, 153.1, 156.5, 160.6, 166.3.; MS (EI): *m*/*z* (%): 298 (60) [M^+], 267 (83) [M^+ - OMe], 252 (15) [M^+ - OMe - Me], 225 (100) [MH^+ - Me - CO_2Me]; EA calcd (%) for $C_{18}H_{18}O_4$ (298.33): C 72.47, H 6.08; found: C 72.46, H 6.14.



7: pale-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): (*E*)-isomer: 0.88 (t, *J* = 7.2 Hz, 3 H), 1.34-1.49 (m, 4 H), 3.06 (t, *J* = 7.2 Hz, 2 H), 7.04 (s, 1 H), 7.39-7.58 (m, 8 H), 7.97-8.00 (m, 2 H): (*Z*)-isomer: 0.91 (t, *J* = 7.2 Hz, 3 H), 1.34-1.51 (m, 4 H), 2.59 (t, *J* = 7.2 Hz, 2 H), 6.66 (s, 1 H), 7.12-7.47 (m, 8 H), 7.80-7.84 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): (*E*)-isomer: δ 13.7, 22.8, 31.1, 31.4, 122.4, 126.9, 128.3, 128.6, 128.7, 129.0, 132.6, 139.5, 142.1, 160.4, 191.7: (*Z*)-isomer: δ 13.7, 22.2, 29.8, 39.6, 123.6, 127.7, 127.8, 128.1, 128.3, 128.8, 132.5, 138.3, 140.2, 157.2, 193.5; MS (EI): *m*/*z* (%): 264 (35) [M^+], 235 (20) [M^+ - CH_2CH_3], 221 (100) [M^+ - $(CH_2)_2CH_3$], 207 (50) [M^+ - $(CH_2)_3CH_3$]; EA calcd (%) for $C_{19}H_{20}O$ (264.36): C 86.32, H 7.63; found: C 86.35, H 7.26.

The stereochemistry of (*E*)- and (*Z*)-**7** was assigned by comparison of their ^{1}H NMR data with those reported for both stereoisomers of dypnone (L. E. Friedrich, N. L. de Vera and Y.-S. P. Lam, *J. Org. Chem.*, 1978, **43**, 34.) as shown below. The allylic and vinylic protons of the (*E*)-isomers resonate at lower fields than those of the corresponding *(Z)*-isomers.

Fig. S3

Procedure for Cu-catalyzed Addition of Phenylboronic Acid 2a to Alkynoate 1a in MeOD. To a solution of methyl 2-octynoate (**1a**) (168 μL, 1.0 mmol) and phenylboronic acid (**2a**) (183 mg, 1.5 mmol) in methanol-d_1 (2.0 mL) was added CuOAc (1.23 mg, 0.01 mmol). The reaction mixture was degassed at -78 ˚C, and then stirred at 28 ˚C under Ar atmosphere for 24 h. After

filtration through a pad of celite to remove insoluble materials, the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane-AcOEt 150:1) to give **3aa**/**3aa**-d_1 (175 mg, 74%) as colorless oil. The reaction of **1a** with 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (**10**) was carried out with a catalyst loading of 5 mol% otherwise under the same conditions to give **3aa**/**3aa**-d_1 (181 mg, 78%). The D contents were estimated from the integral ratio of the singlet at δ 6.02 ppm corresponding to the residual vinylic proton relative to that of the singlet of the methoxy group at δ 3.75 ppm in the ^{1}H NMR spectra. The vinylic carbon bearing a D atom was observed at δ 116.4 ppm as a triplet ($J_{C\text{-}D}$ = 24.2 Hz) in the ^{13}C NMR spectra.

Procedure for Cu-catalyzed Addition of Triphenylboroxin to Alkynoate 1a. To a solution of methyl 2-octynoate (**1a**) (168 μL, 1.0 mmol) and triphenylboroxin (312 mg, 1.0 mmol) in methanol (2.0 mL) was added CuOAc (1.25 mg, 0.01 mmol). The reaction mixture was degassed at -78 ˚C, and then stirred at 28 ˚C under Ar atmosphere for 10 h. After filtration through a pad of celite to remove insoluble materials, the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane-AcOEt 150:1) to give **3aa** (215 mg, 94%) as colorless oil.