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Supporting Information

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Regio- and Stereoselective Decarbonylative Carbostannylation of Propargyl 2-Furoates Catalyzed by Pd/C

Yoshiaki Nakao,[†] Jun Satoh,[†] Eiji Shirakawa,*[,‡] and Tamejiro Hiyama*[,†]

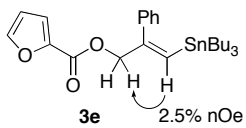
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510 Japan and Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502 Japan

General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Flush column chromatography was performed using Merck silica gel 60 (230–400 mesh). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz), JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz; ^{119}Sn, 101 MHz), or Varian Mercury 200 (^{1}H, 200 MHz; ^{13}C, 50.3 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm) or Me_4Sn (^{119}Sn NMR, at 0 ppm) as the external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, br t = broad triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI and CI) or JEOL JMS-HX110A (FAB+) spectrometer.

Chemicals. Unless otherwise noted, commercially available reagents were used without purification. Dibutyl ether and THF were distilled from sodium/benzophenone ketyl. Anhydrous NMP was purchased from Aldrich and used without further purification. Acylstannanes[1] and dimethyl (2-chloromethyl-2-propenyl)malonate[2] were prepared according to the respective literature procedure.

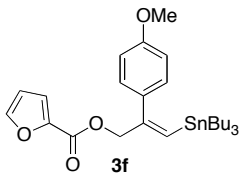
Decarbonylative carbostannylation of propargyl esters. ***A general procedure.*** To a solution of an acylstannane (0.10 mmol) and a propargyl ester (0.20 mmol) in dibutyl ether (0.15 mL) was added Pd/C (10 wt%, 0.2 mg), and the resulting mixture was stirred at 50 °C for the time specified in Table 1 and Table 2. The mixture was filtered through a Florisil pad, concentrated in vacuo, and purified by flash chromatography (hexane–ethyl acetate) on silica gel to give carbostannylation products.



(*E*)-2-Phenyl-3-(tributylstannyl)-2-propenyl 2-furoate (entry 7 of Table 1). A yellowish oil, R_f 0.34 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.35–7.24 (m, 5H), 7.15 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.29 (t, *J* = 1.5 Hz, 1H), 5.08 (d, *J* = 1.5 Hz, 2H), 1.42–1.14 (m, 12H), 0.82 (t, *J* = 7.2 Hz, 9H), 0.71–0.52 (m,

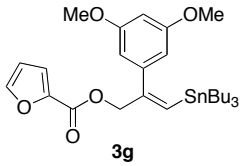
[†] Graduate School of Engineering
[‡] Graduate School of Science

6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 152.6, 146.4, 144.6, 142.0, 130.5, 128.2, 128.0, 127.7, 117.9, 111.8, 69.2, 29.0, 27.2, 13.6, 10.4; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ –56.6; Anal. Calcd for $C_{26}H_{38}O_3Sn$; C, 60.37; H, 7.40. Found: C, 60.24; H, 7.40.



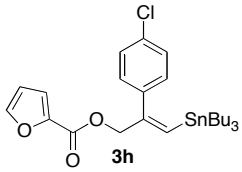
3f

(*E*)-2-(4-Methoxyphenyl)-3-(tributylstannyl)-2-propenyl 2-furoate (entry 1 of Table 2). A yellowish oil, R_f 0.37 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.6, 0.9 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.15 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.49 (dd, *J* = 3.5, 1.6 Hz, 1H), 6.22 (t, *J* = 1.3 Hz, 1H), 5.06 (d, *J* = 1.3 Hz, 2H), 3.81 (s, 3H), 1.42–1.14 (m, 12H), 0.82 (t, *J* = 7.2 Hz, 9H), 0.72–0.55 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 158.3, 152.1, 146.3, 144.7, 134.5, 129.8, 129.1, 117.9, 113.5, 111.8, 69.2, 55.3, 29.0, 27.2, 13.6, 10.4; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ –56.8; Anal. Calcd for $C_{27}H_{40}O_4Sn$; C, 59.25; H, 7.37. Found: C, 59.15; H, 7.43.



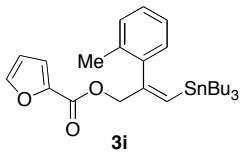
3g

(*E*)-2-(3,5-Dimethoxyphenyl)-3-(tributylstannyl)-2-propenyl 2-furoate (entry 2 of Table 2). A yellowish oil, R_f 0.17 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) 7.58 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.17 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.41 (d, *J* = 2.1 Hz, 2H), 6.39 (t, *J* = 2.1 Hz, 1H), 6.25 (t, *J* = 1.4 Hz, 1H), 5.05 (d, *J* = 1.5 Hz, 2H), 3.78 (s, 6H), 1.38–1.16 (m, 12H), 0.83 (t, *J* = 7.2 Hz, 9H), 0.75–0.58 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 158.2, 152.4, 146.3, 144.7, 144.1, 130.3, 117.9, 111.8, 106.2, 99.8, 69.0, 55.3, 29.0, 27.3, 13.6, 10.4; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ –57.4; Anal. Calcd for $C_{28}H_{42}O_5Sn$; C, 58.25; H, 7.33. Found: C, 58.37; H, 7.20.



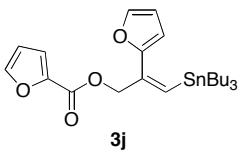
3h

(*E*)-2-(4-Chlorophenyl)-3-(tributylstannyl)-2-propenyl 2-furoate (entry 3 of Table 2). A yellowish oil, R_f 0.26 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) 7.58 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.13 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.32 (t, *J* = 1.3 Hz, 1H), 5.05 (d, *J* = 1.3 Hz, 2H), 1.41–1.15 (m, 12H), 0.83 (t, *J* = 7.2 Hz, 9H), 0.73–0.55 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 151.4, 146.4, 144.5, 140.5, 133.6, 132.2, 129.4, 128.4, 118.0, 111.8, 69.1, 29.0, 27.2, 13.6, 10.5; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ –56.7; Anal. Calcd for $C_{26}H_{37}ClO_3Sn$; C, 56.60; H, 6.76. Found: C, 56.65; H, 6.65.



3i

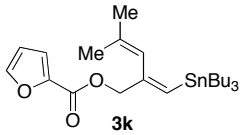
(*E*)-2-(2-Methylphenyl)-3-(tributylstannyl)-2-propenyl 2-furoate (entry 4 of Table 2). A yellowish oil, R_f 0.31 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.22–7.11 (m, 4H), 7.06 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.36 (t, *J* = 1.5 Hz, 1H), 4.95 (br s, 2H), 2.32 (s, 3H), 1.39–1.13 (m, 12H), 0.82 (t, *J* = 7.1 Hz, 9H), 0.65–0.46 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 152.5, 146.3, 144.7, 140.9, 135.8, 130.0, 129.6, 129.5, 127.7, 125.6, 117.9, 111.8, 68.8, 29.0, 27.3, 19.4, 13.6, 9.6; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ –59.3; Anal. Calcd for $C_{27}H_{40}O_3Sn$; C, 61.04; H, 7.59. Found: C, 61.14; H, 7.67.



3j

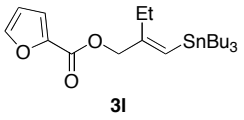
(*E*)-2-(2-Furyl)-3-(tributylstannyl)-2-propenyl 2-furoate (entry 5 of Table 2). A yellowish oil, R_f 0.29 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.33 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.6 Hz, 1H), 6.43 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.39 (d, *J* = 3.5 Hz, 1H), 6.35 (s, 1H), 5.10 (s, 2H), 1.55–1.41 (m, 6H), 1.29–1.23 (m, 6H), 1.03–0.84 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 153.7, 146.4, 144.5, 141.4, 138.7, 132.8, 118.1, 111.8, 111.7, 107.0, 67.6, 29.0, 27.3, 13.7, 11.6; ^{119}Sn{^{1}H} NMR

(101 MHz, $CDCl_3$) δ –55.8; Anal. Calcd for $C_{24}H_{36}O_4Sn$; C, 56.83; H, 7.15. Found: C, 56.59; H, 7.27.



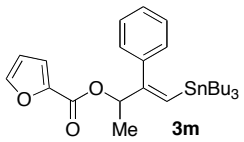
3k

(*E*)-4-Methyl-2-(tributylstannyl)methylidene-3-pentenyl 2-furoate (entry 6 of Table 2). A yellowish oil, R_f 0.29 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.19 (dd, *J* = 3.4, 0.9 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.14 (q, *J* = 1.5 Hz, 1H), 5.73 (br d, *J* = 1.3 Hz, 1H), 4.79 (dd, *J* = 1.5, 0.7 Hz, 2H), 1.75 (d, *J* = 1.3 Hz, 3H), 1.65 (d, *J* = 0.9 Hz, 3H), 1.53–1.24 (m, 12H), 0.94–0.76 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 149.4, 146.3, 144.8, 137.0, 128.9, 124.9, 117.8, 111.8, 68.5, 29.1, 27.3, 25.6, 19.4, 13.7, 9.8; $^{119}Sn\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ –58.5; Anal. Calcd for $C_{24}H_{40}O_3Sn$; C, 58.20; H, 8.14. Found: C, 58.20; H, 7.98.



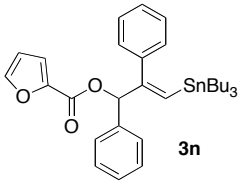
3l

(*E*)-2-Ethyl-3-(tributylstannyl)-2-propenyl 2-furoate (entry 7 of Table 2). A yellowish oil, R_f 0.33 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.20 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.6 Hz, 1H), 5.87 (t, *J* = 1.2 Hz, 1H), 4.84 (d, *J* = 1.3 Hz, 2H), 2.16 (q, *J* = 7.6 Hz, 2H), 1.55–1.40 (m, 6H), 1.36–1.22 (m, 6H), 1.08 (t, *J* = 7.6 Hz, 3H), 1.02–0.82 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 153.1, 146.3, 144.8, 126.3, 117.8, 111.8, 68.2, 29.8, 29.1, 27.3, 13.9, 13.7, 10.1; $^{119}Sn\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ –61.4; Anal. Calcd for $C_{22}H_{38}O_3Sn$; C, 56.31; H, 8.16. Found: C, 56.10; H, 8.14.



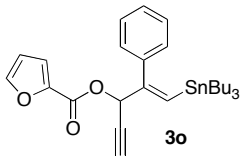
3m

(*E*)-1-Methyl-2-phenyl-3-(tributylstannyl)-2-propenyl 2-furoate (entry 8 of Table 2). A yellowish oil, R_f 0.34 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.34–7.25 (m, 5H), 7.17 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.6 Hz, 1H), 6.28 (d, *J* = 1.1 Hz, 1H), 5.80 (qd, *J* = 6.6, 1.1 Hz, 1H), 1.39 (d, *J* = 6.6 Hz, 3H), 1.35–1.12 (m, 12H), 0.80 (t, *J* = 7.2 Hz, 9H), 0.80–0.47 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 157.9, 146.2, 145.1, 142.4, 128.6, 128.2, 128.1, 127.4, 117.6, 111.7, 75.4, 29.0, 27.2, 20.1, 13.6, 10.2; $^{119}Sn\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ –56.0; Anal. Calcd for $C_{27}H_{40}O_3Sn$; C, 61.04; H, 7.59. Found: C, 61.27; H, 7.50.



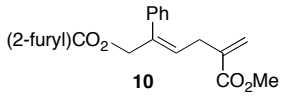
3n

(*E*)-1,2-Diphenyl-3-(tributylstannyl)-2-propenyl 2-furoate (entry 9 of Table 2). A yellowish oil, R_f 0.23 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 1.6, 0.9 Hz, 1H), 7.35–7.19 (m, 9H), 7.09–7.05 (m, 2H), 6.70 (d, *J* = 1.0 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.45 (d, *J* = 1.1 Hz, 1H), 1.36–1.12 (m, 12H), 0.81 (t, *J* = 7.2 Hz, 9H), 0.58–0.53 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 156.1, 146.4, 144.8, 142.0, 138.0, 129.5, 128.8, 128.2, 128.0, 127.9, 127.6, 127.4, 118.0, 111.8, 80.2, 29.0, 27.2, 13.6, 10.3; $^{119}Sn\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ –55.1; Anal. Calcd for $C_{32}H_{42}O_3Sn$; C, 64.77; H, 7.13. Found: C, 64.71; H, 7.20.



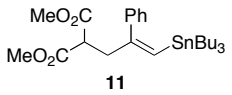
3o

(*E*)-1-Ethynyl-2-phenyl-3-(tributylstannyl)-2-propenyl 2-furoate (entry 10 of Table 2). A yellowish oil, R_f 0.31 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.32–7.24 (m, 5H), 7.16 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.67 (d, *J* = 1.1 Hz, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.36 (dd, *J* = 2.2, 1.3 Hz, 1H), 2.61 (d, *J* = 2.2 Hz, 1H), 1.35–1.14 (m, 12H), 0.82 (t, *J* = 7.2 Hz, 9H), 0.67–0.52 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 151.8, 146.7, 144.1, 141.0, 134.2, 128.7, 128.0, 127.8, 118.6, 111.8, 79.4, 76.1, 68.5, 28.9, 27.2, 13.6, 10.2; $^{119}Sn\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ –55.3; Anal. Calcd for $C_{28}H_{38}O_3Sn$; C, 62.13; H, 7.08. Found: C, 62.11; H, 6.90.



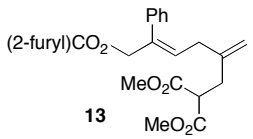
10

Reaction of 3e with methyl 2-(bromomethyl)acrylate. To a solution of **3e** (52 mg, 0.10 mmol) and methyl 2-(bromomethyl)acrylate (18 mg, 0.10 mmol) in NMP (0.2 mL) was added $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), and the resulting mixture was stirred for 3 h at 50 °C. The mixture was filtered through a Florisil pad, concentrated in vacuo, and purified by flash chromatography (hexane–ethyl acetate = 5:1) on silica gel to give methyl (*E*)-6-(2-Furoyloxy)-5-phenyl-1,4-hexadiene-2-carboxylate (**10**: 32 mg, 99%) as a yellowish oil, R_f 0.19 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.37–7.22 (m, 5H), 7.11 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.48 (dd, *J* = 3.5, 1.6 Hz, 1H), 6.19 (q, *J* = 1.1 Hz, 1H), 5.92 (tt, *J* = 7.5, 1.2 Hz, 1H), 5.56 (q, *J* = 1.5 Hz, 1H), 5.01 (d, *J* = 1.5 Hz, 2H), 3.72 (s, 3H), 3.02 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 158.3, 146.4, 144.5, 138.9, 137.6, 137.3, 128.37, 128.35, 127.7, 127.5, 125.5, 118.0, 111.8, 68.8, 51.9, 30.9; Anal. Calcd for $C_{19}H_{18}O_5$; C, 69.93; H, 5.56. Found: C, 69.67; H, 5.64.



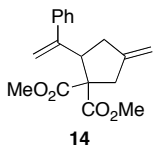
11

Reaction of 3e with sodium dimethyl malonate. To a solution of dimethyl malonate (15 mg, 0.11 mmol) in THF (0.3 mL) was added NaH (60% dispersion in mineral oil, 4.4 mg, 0.11 mmol) at room temperature, and the mixture was stirred for 15 min. To this were added **3e** (52 mg, 0.1 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.9 mg, 2.5 μmol), and PPh_3 (26 mg, 10 μmol). After stirred for 5.5 h at ambient temperature, the mixture was diluted with diethyl ether, washed with water and brine, dried over anhydrous $MgSO_4$, concentrated in vacuo, and purified by flash chromatography (hexane–ethyl acetate = 5:1) on silica gel to give dimethyl (*Z*)-2-phenyl-3-(tributylstannyl)-2-propenylmalonate (**11**: 40 mg, 74%) as a yellowish oil, R_f 0.19 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 3H), 7.17–7.15 (m, 2H), 5.95 (s, 1H), 3.68 (s, 6H), 3.48 (t, *J* = 7.8 Hz, 1H), 3.12 (d, *J* = 7.9 Hz, 2H), 1.38–1.13 (m, 12H), 0.83 (t, *J* = 7.2 Hz, 9H), 0.63–0.46 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 155.3, 143.9, 130.6, 128.1, 127.8, 127.4, 52.4, 50.9, 41.0, 29.0, 27.2, 13.6, 10.3; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ –58.4; Anal. Calcd for $C_{26}H_{42}O_4Sn$; C, 58.12; H, 7.88. Found: C, 58.33; H, 7.80.



13

Reaction of 3e with 12. To a solution of **3e** (52 mg, 0.10 mmol) and dimethyl 2-(chloromethyl)propen-3-ylmalonate (**12**) (22 mg, 0.10 mmol) in NMP (0.1 mL) was added $Pd_2(dba)_3$ (2.3 mg, 2.5 μmol), and the resulting mixture was stirred for 2 h at 50 °C. The reaction was quenched with an aqueous 1 M KF solution, and the organic layer was concentrated in vacuo and purified by flash chromatography (hexane–ethyl acetate = 2:1) on silica gel to give dimethyl (*E*)-[6-(2-furoyloxy)-2-methylidene-5-phenyl-4-hexenyl]malonate (**13**: 32 mg, 99%) as a yellowish oil, R_f 0.29 (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 1.8, 0.9 Hz,1H), 7.38–7.21 (m, 5H), 7.12 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.48 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.89 (tt, *J* = 7.5, 1.0 Hz, 1H), 5.01 (d, *J* = 1.0 Hz, 2H), 4.86 (d, *J* = 0.9 Hz, 1H), 4.81 (d, *J* = 0.9 Hz, 1H), 3.69 (s, 6H), 3.46 (t, *J* = 7.9 Hz, 1H), 2.73 (d, *J* = 7.5 Hz, 2H), 2.58 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 158.3, 146.4, 144.5, 144.0, 137.34, 137.33, 128.39, 128.33, 127.5, 118.0, 112.4, 111.8, 68.8, 52.5, 50.2, 35.2, 35.0; Anal. Calcd for $C_{23}H_{24}O_7$; C, 66.98; H, 5.87. Found: C, 67.08; H, 5.74.



14

Intramolecular cyclization of 13. To a solution of 13 (21.1 mg, 50 μmol) in THF (0.5 mL) was added NaH (60% dispersion in mineral oil, 2.2 mg, 55 μmol) at room temperature, and the mixture was stirred for 10 min. To this were added $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.5 mg, 1.4 μmol), and PPh_3 (1.3 mg, 5.0 μmol). After stirred for 3.5 h at ambient temperature, the mixture was diluted with diethyl ether, washed with water and brine, dried over anhydrous $MgSO_4$, concentrated in vacuo, and purified by flash chromatography (hexane–ethyl acetate = 5:1) on silica gel to give dimethyl

4-methylene-2-(1-phenylvinyl)cyclopentane-1,1-dicarboxylate (**14**, 10.1 mg, 67%) as a yellowish oil, R_f 0.37 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.18 (m, 5H), 5.30 (s, 1H), 5.14 (s, 1H), 4.98 (br s, 2H), 4.11 (dd, *J* = 8.0, 3.4 Hz, 1H), 3.62 (s, 3H), 3.38 (dq, *J* = 17.5, 2.6 Hz, 1H), 3.10 (s, 3H), 2.96 (ddq, *J* = 16.8, 8.0, 2.6 Hz, 1H), 2.83 (br d, *J* = 17.4 Hz, 1H), 2.66 (br dq, *J* = 16.9, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 169.4, 149.2, 147.2, 142.2, 127.9, 127.3, 126.9, 115.3, 107.3, 63.9, 52.7, 51.6, 47.2, 39.3, 38.9; Anal. Calcd for $C_{18}H_{20}O_4$; C, 71.98; H, 6.71. Found: C, 71.94; H, 6.48.

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