Supporting Information

Easy Access to Esters with a Benzylic Quaternary Carbon Center from Diallyl Malonates by Palladium-Catalyzed Decarboxylative Allylation

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General. ^1H NMR spectra are recorded at 300 MHz. Chemical shifts are reported in ppm from tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra are recorded at 75 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (CDCl_3 : δ 77.0). High resolution mass spectrometry is performed by the means of FAB-MS (matrix m-NBA, reference PEG-400). Optical rotation was measured with spectrophotometer. Liquid chromatographic analyses were conducted under conditions (Chiralcel OJ-H, 0.25 m, 0.5 mL/min, UV 254 nm) and simultaneous detection of optical rotation sign of each separated compound with HPLC chiral column (assignment of optical rotation sign for peaks obtained was determined by authentic optically pure samples; (*R*)-(+)-1-phenylethyl alcohol and (*S*)-(-)-1-phenylethyl alcohol) was also conducted.

All reactions were carried out under an inert atmosphere of argon by standard Schlenk techniques. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ precursor was prepared according to a reported method.¹ All phosphine ligands, $\text{Pd}(\text{PPh}_3)_4$, Phenylmalonic acid were purchased and used without further purification. $\text{PPh}_2(\text{OPh})$ was prepared according to a reported method.² A dried tetrahydrofuran (THF) was prepared by distilling from a blue solution of sodium benzophenone ketyl and stored under argon atmosphere. The other solvents were distilled using standard procedures.

1) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, 65, 253.

2) van der Slot, S. C.; Duran, J.; Luten, J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **2002**, 21, 3873.

Syntheses of substrates

Diallyl 2-phenylmalonate (1f)

Phenylmalonic acid (15 g, 83 mmol), allyl alcohol (45 mL, 660 mmol) and *p*-toluenesulfonic acid monohydrate (1.7 g, 9.0 mmol) was dissolved in Benzene (800 mL) and H₂O was azeotropically removed. After the reaction was complete, the apparatus was cooled to ambient temperature. The benzene solution was washed with saturated NaHCO₃ aq. and saturated NaCl aq. and was dried over anhydrous Na₂SO₄. Yellow oil was remained after concentration and was purified by silica gel column chromatography (Hexane:AcOEt = 4 : 1), affording **1f** (colorless oil) in 94% yield (20 g). ¹H NMR (CDCl₃, 300 MHz) δ 4.62 (ddd, A of AB system, *J* = 15, 5.7, 1.5, 2H), 4.67 (ddd, B of AB system, *J* = 15, 5.7, 1.5, 2H), 4.69 (s, 1H), 5.21 (dq, *J* = 10.5, 1.5, 2H), 5.27 (dq, *J* = 17.1, 1.5, 2H), 5.87 (ddt, *J* = 17.1, 10.5, 5.7, 2H), 7.32-7.43 (m, 5H); ¹³C NMR (CDCl₃, 75 MHz) δ 57.8, 66.3, 118.6, 128.2, 128.5, 129.2, 131.2, 131.3, 132.4, 167.5; HRMS (FAB⁺) calcd for C₁₅H₁₇O₄ 261.1127 [M+H]⁺; found: 261.1127.

Diallyl 2-methyl-2-phenylmalonate (1a)

1f (8.0 g, 31 mmol) in anhydrous THF (80 mL) was added drop-wise to NaH (1.1 g, 45 mmol) dissolved in ice-cooled anhydrous THF (80 mL). After the evolution of H₂ gas was complete, the apparatus was warmed to ambient temperature. To the reaction mixture was slowly added methyl iodide (4.5 mL, 72 mmol). The resulting mixture was stirred at 60 °C overnight. After the apparatus was cooled to ambient temperature, the reaction was quenched by adding 1M HCl aq. and was extracted with Hexane. The collected organic layers was washed with dilute Na₂S₂O₃ aq. saturated NaCl aq. and was dried over anhydrous Na₂SO₄. Yellow oil was remained after concentration and was purified by silica gel column chromatography (Hexane:AcOEt = 5:1), affording colorless oil in 94% yield (7.9 g). ¹H NMR (CDCl₃, 300 MHz) δ 1.91 (s, 3H), 4.66 (dt, *J* = 5.7, 1.5, 4H), 5.20 (dq, *J* = 10.2, 5.7, 2H), 5.26 (dq, *J* = 17.1, 5.7, 2H), 5.87 (ddt, *J* = 17.1, 10.2, 5.7, 2H), 7.29-7.40 (m, 5H); ¹³C NMR (CDCl₃, 75 MHz) δ 22.4, 58.9, 66.2, 118.4, 127.3, 127.6, 128.1, 131.4, 137.9, 170.9; HRMS (FAB⁺) calcd for C₁₆H₁₉O₄ 275.1283 [M+H]⁺; Found: 275.1265.

Diallyl 2-ethyl-2-phenylmalonate (1b)

1b was prepared by the same procedure for **1a**, using ethyl iodide instead of methyl iodide (Yield 91%, colorless oil). ¹H NMR (CDCl₃, 300 MHz) δ 0.90 (t, *J* = 7.5, 3H), 2.39 (q, *J* = 7.5, 2H), 4.64 (dt, *J* = 5.7, 1.5, 4H),

5.17-5.28 (m, 4H), 5.86 (ddt, $J = 17.1, 10.5, 5.7, 2\text{H}$), 7.24-7.44 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 9.4, 28.9, 63.2, 65.9, 118.4, 127.4, 128.0, 131.4, 136.5, 170.1; HRMS (FAB^+) calcd for $\text{C}_{17}\text{H}_{21}\text{O}_4$ 289.1440 $[\text{M}+\text{H}]^+$; found: 289.1444.

Diallyl 2-benzyl-2-phenylmalonate (1c)

1c was prepared by the same procedure for **1a**, using benzyl bromide instead of methyl iodide (Yield 86%, colorless oil). ^1H NMR (CDCl_3 , 300 MHz) δ 3.64 (s, 2H), 4.58 (ddt, $J = 13.2, 5.7, 1.5, 2\text{H}$), 4.63 (ddt, $J = 13.2, 5.7, 1.5, 2\text{H}$), 5.18 (dq, $J = 10.5, 1.5, 2\text{H}$), 5.23 (dq, $J = 17.1, 1.5, 2\text{H}$), 5.81 (ddt, $J = 17.1, 10.5, 2\text{H}$), 6.88-6.91 (m, 2H), 7.10-7.27 (m, 8H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 43.0, 64.4, 66.2, 118.6, 126.8, 127.7, 128.1, 130.3, 131.3, 135.8, 136.7, 169.5; HRMS (FAB^+) calcd for $\text{C}_{22}\text{H}_{23}\text{O}_4$ 351.1596 $[\text{M}+\text{H}]^+$; found: 351.1607.

Diallyl 2-(2-methoxycarbonyl)ethyl-2-phenylmalonate (1d)

DBU (0.2 g, 1.3 mmol) was added to a solution of **1f** (3.0 g, 12 mmol) in anhydrous THF (3 mL). To the solution was added methyl acrylate (1.3 mL, 16 mmol). The resulting mixture was stirred at r.t. for 2 d. The reaction was quenched by adding 1N HCl aq. CH_2Cl_2 (15 mL) was added and washed with distilled water, saturated NaCl aq. dried by anhydrous Na_2SO_4 . Yellow oil was remained after evaporation and was purified by silica gel column chromatography (Hexane:AcOEt = 5:1), affording **1d** in 82% yield (colorless oil). ^1H NMR (CDCl_3 , 300 MHz) δ 2.30-2.35 (m, 2H), 2.65-2.70 (m, 2H), 3.63 (s, 3H), 4.66 (dt, $J = 5.7, 1.5, 4\text{H}$), 5.18-5.29 (m, 4H), 5.86 (ddt, $J = 17.1, 10.5, 5.7, 2\text{H}$), 7.28-7.39 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 29.9, 30.9, 51.7, 62.0, 66.2, 118.7, 127.7, 128.3, 131.2, 136.0, 169.7, 173.0; HRMS (FAB^+) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_6$ 347.1495 $[\text{M}+\text{H}]^+$; found: 347.1492.

Diallyl 2-(2-cyanoethyl)-2-phenylmalonate (1e)

1e was prepared by the same method described for **1d** using acrylonitrile instead of methyl acrylate, and $t\text{-BuOK}$ as a base and the reaction was carried out for 20 h. Yield 90% (colorless oil). ^1H NMR (CDCl_3 , 300 MHz) δ 2.33-2.38 (m, 2H), 2.64-2.69 (m, 2H), 4.67-4.70 (dt, $J = 5.7, 1.9, 4\text{H}$), 5.23 (dq, $J = 10.5, 1.5, 2\text{H}$), 5.27 (dq, $J = 17.1, 1.5, 2\text{H}$), 5.86 (ddt, $J = 17.1, 10.5, 5.7, 2\text{H}$), 7.26-7.40 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 13.5, 32.4, 61.8, 66.6, 118.9, 119.2, 127.4, 128.2, 128.6, 130.8, 130.9, 135.1, 169.0; HRMS (FAB^+) calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_4$ 314.1392 $[\text{M}+\text{H}]^+$; found: 314.1374.

1g was prepared by the same method for **1a** using Diallyl 2-methylmalonate (*vide infra*) instead of **1f** and using benzyl bromide instead of methyl iodide. The product was purified by (Hexane:AcOEt = 5:1). Yield: 82% (pale yellow oil). ¹H NMR (s, 3H), 3.25 (s, 2H), 4.61 (dt, *J* = 1.5, 5.7, 4H), 5.22 (dt, *J* = 10.5, 1.5, 2H), 5.87 (ddt, *J* = 17.1, 10.5, 1.5, 1H); ¹³C NMR (CDCl₃, 75.55.9, 118.4, 126.8, 128.0, 130.1, 131.4, 135.8, 171.2; HRMS (FAB⁺) 40 [M+H]⁺; found: 289.1428

1h was prepared through the same methods to **1a** using 1,1-dideuterioallyl alcohol³ instead of allyl alcohol. ¹H NMR (CDCl₃, 300 MHz) δ 1.90 (s, 3H), 5.21 (dd, *J* = 10.5, 1.5, 2H), 5.86 (dd, *J* = 17.1, 10.5, 2H), 7.28-7.40 (m, 5H); ¹³C NMR 4, 58.9, 118.5, 127.3, 127.6, 128.1, 131.2, 137.9, 170.9; HRMS 4O₄ 279.1534 [M+H]⁺; found: 279.1531.

To prepare **1i**, Dicrotyl 2-phenylmalonate was synthesized by the same method for **1f** using crotyl alcohol (a *cis-trans* mixture) instead of allyl alcohol (85% Yield from 3.0 g

phenylmalonic acid). The purified dicrotyl 2-phenylmalonate (column chromatography; Hexane:AcOEt = 4:1) was applied to the same methylation procedure described for **1a**. Purification by column chromatography (Hexane:AcOEt = 4:1) gave **1i** in 81% yield as colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 1.66-1.72 (m, 6H), 1.87 (s, 3H), 4.58, (d, *J* = 6.3, 3.12H), 4.72 (d, *J* = 6.3, 0.88H), 5.46-5.59 (m, 2H), 5.65-5.81 (m, 2H), 7.25-7.38 (m, 5H); ¹³C NMR (CDCl₃, 75 MHz) δ 13.3 (=CHCH₃, minor), 17.9 (=CHCH₃, major), 22.5 (Cq-CH₃), 58.8 (Ph-Cq, minor), 58.9 (Ph-Cq, major), 61.3 (O-CH₂-CH=, minor), 66.3 (O-CH₂-CH=, major), 123.6 (=CHCH₃, minor), 124.4 (=CHCH₃, major), 127.3, 127.5, 128.0 (phenyl:-CH=CH-), 129.6 (-OCH₂CH=, minor), 131.3, (-OCH₂CH=, major), 138.1 (phenyl:-CH=C(-Cq)-CH=) 171.1 (-COO-, major), 171.2 (-COO-, minor); HRMS (FAB⁺) calcd for C₁₈H₂₃O₄ 303.1596 [M+H]⁺; found: 303.1600.

3) (a) Anderson, R. J.; Ashwell, S.; Garnett, I.; Golding, B. T. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 4488. (b) Schuetz, R. D.; Millard, W. F. *J. Org. Chem.* **1959**, 24, 297.

Diallyl malonate

1j was prepared by the same method for **1f** using malonic acid instead of phenylmalonic acid. (Yield 97%, colorless oil). ^1H NMR (CDCl_3 , 300 MHz) δ 3.44 (s, 2H), 4.65 (dt, $J = 5.7, 1.5$, 4H), 5.23-5.38 (m, 4H), 5.84-5.98 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ 41.7, 66.4, 119.0, 131.6, 166.2; GCMS m/z 185.

Diallyl 2-(2-nitrophenyl)malonate

To solution of NaH (2.2 eq.) in DMF (4 mL) at 0 °C was added drop-wise diallyl malonate (2.0 g, 10.9 mmol) in DMF (2 mL) for 20 min. After cease of hydrogen gas evolution, 2-fluoronitrobenzene (0.77 g, 5.4 mmol) in DMF (2 mL) was added drop-wise at 0 °C for 10 min. The mixture was stirred at 55 °C overnight. At ambient temperature CH_2Cl_2 and saturated NH_4Cl solution were added to the mixture. Extracted CH_2Cl_2 was washed with distilled water and brine and was dried over anhydrous Na_2SO_4 . After condensation under reduced pressure, the remained oil was purified with column chromatography (Hexane:AcOEt = 9:1). (Yield 88%, yellow oil). ^1H -NMR (CDCl_3 , 300MHz) δ 4.70 (dt, $J = 5.7, 1.2$, 4H), 5.25 (dq, $J = 10.5, 1.2$, 2H), 5.32 (dq, $J = 17.1, 1.2$, 2H), 5.37 (s, 1H), 5.83-5.96 (ddt, $J = 17.1, 10.5, 5.7$, 2H), 7.50-7.56 (m, 2H), 7.63-7.68 (m, 1H), 8.06-8.09 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 54.3, 66.7, 119.0, 125.2, 127.8, 129.2, 131.0, 131.2, 133.5, 148.5, 166.6; HRMS (FAB^+) calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_6$ 306.0977 $[\text{M}+\text{H}]^+$; found: 306.0974.

Diallyl 2-methyl-2-(2-nitrophenyl)malonate (1k)

To solution of NaH (1.1 eq.) in DMF (10 mL) at 0 °C was added drop-wise diallyl malonate (1.0 g, 3.3 mmol) in DMF (10 mL) for 10 min. After cease of hydrogen gas evolution at room temperature, methyl iodide (0.47mL, 7.5 mmol) in DMF (10 mL) was added drop-wise. The mixture was stirred at 55 °C overnight. At ambient temperature, ethyl acetate and saturated NH_4Cl solution were added to the mixture. The organic phase was washed with brine and was dried over anhydrous Na_2SO_4 . After condensation, the remained oil was purified with column chromatography (Hexane:AcOEt = 9:1). (Yield 88%; yellow oil. ^1H -NMR (CDCl_3 , 300MHz) δ 2.04 (s, 3H), 4.57-4.71 (m, 4H), 5.18-5.29 (m, 4H), 5.78-5.91 (m, 2H), 7.34 (dd, $J = 7.8, 1.2$, 1H), 7.45-7.63 (m, 2H), 8.03 (dd, $J = 7.8, 1.2$, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 23.6, 59.4, 66.7, 118.9, 125.9, 128.5, 129.1, 131.0, 133.2, 134.1, 148.4, 169.0; HRMS (FAB^+) calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_6$ 320.1134 $[\text{M}+\text{H}]^+$; found: 320.1130.

Diallyl 2-methylmalonate

This compound was prepared by the same method for **1f** using methylmalonic acid instead of phenylmalonic acid (Yield 92%; colorless oil). ^1H NMR (CDCl_3 , 300 MHz) δ 1.45 (d, $J = 7.5$, 3H), 3.51 (q, $J = 5.1$, 1H), 4.62-4.66 (m, 4H), 5.21-5.36 (m, 4H), 5.83-5.97 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 13.7, 46.1, 65.9, 118.4, 131.4, 169.5; HRMS (FAB^+) calcd for $\text{C}_{10}\text{H}_{15}\text{O}_4$ 199.0970 $[\text{M}+\text{H}]^+$; found: 199.0968.

Diallyl 2-methyl-2-(4-nitrophenyl)malonate (1i)

To solution of NaH (1.1 eq.) in DMF (8 mL) at 0 °C was added drop-wise a mixture of diallyl 2-methylmalonate (2.0 g, 10.3 mmol) and 4-fluoronitrobenzene (1.6 g, 11.3 mmol) in DMF (8 mL) was added drop-wise at 0 °C for 1 h. The mixture was stirred at 70 °C overnight. At ambient temperature ethyl acetate and saturated NH_4Cl solution were added to the mixture. The organic phase was subsequently washed with distilled water and brine and was dried over anhydrous Na_2SO_4 . After condensation under reduced pressure, the remained oil was purified with column chromatography (Hexane:AcOEt = 7:1), affording yellow oil (Yield 75%; yellow oil). ^1H -NMR (CDCl_3 , 300MHz) δ 1.94 (m, 3H), 4.68 (dt, $J = 5.7$, 1.5, 4H), 5.22-5.32 (m, 4H), 5.80-5.93 (m, 2H), 7.55-7.60 (m, 2H), 8.18-8.23 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 22.2, 58.8, 66.7, 119.0, 123.2, 128.6, 130.9, 144.8, 147.1, 169.8; HRMS (FAB^+) calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_6$ 320.1134 $[\text{M}+\text{H}]^+$; found: 320.1143

Products of Catalyses

Allyl 2-methyl-2-phenyl-4-pentenoate (3a)

The product was obtained as a colorless oil: The value of enantiomeric excess was measured by HPLC. [Chiralcell OJ-H column, *n*-hexane/*i*PrOH = 70:30, 0.5 mL/min, 254 nm, t_R = 13.6 min ((+)-rotation) and 20.3 min ((-)-rotation)]. ^1H NMR (CDCl_3 , 300 MHz) δ 1.55 (s, 3H), 2.67 and 2.85 (dd, AB system, J = 13.8, 7.2, 2H), 4.55-4.58 (m, 2H), 5.02-5.21 (m, 4H), 5.54-5.68 (m, 1H), 5.76-5.89 (m, 1H), 7.20-7.32 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 22.6, 43.7, 49.9, 65.3, 117.8, 118.4, 125.9, 126.7, 128.3, 131.9, 133.8, 143.0, 175.2; HRMS (FAB^+) calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2$ 231.1385 $[\text{M}+\text{H}]^+$; found: 231.1397.

Allyl 2-ethyl-2-phenyl-4-pentenoate (3b)

This compound was obtained as colorless oil, ^1H NMR (CDCl_3 , 300 MHz) δ 0.77 (t, J = 7.5, 3H), 2.06 (m, 2H), 2.10 (qd, J = 7.2, 15.0, 1H), 2.75 (dd, A of AB system, J = 14.1, 6.6, 1H), 2.85 (dd, B of AB system, J = 14.1, 7.5, 1H), 4.51-4.62 (m, 2H), 4.99-5.20 (m, 4H), 5.44-5.57 (m, 1H), 5.75-5.90 (m, 1H), 7.15-7.34 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 8.4, 27.0, 38.5, 54.0, 65.2, 118.0, 118.1, 126.4, 126.6, 128.1, 131.9, 133.5, 141.9, 174.9; HRMS (FAB^+) calcd for $\text{C}_{16}\text{H}_{21}\text{O}_2$ 245.1541 $[\text{M}+\text{H}]^+$; found: 245.1560.

Allyl 2-benzyl-2-phenyl-4-pentenoate (3c)

This compound was obtained as colorless oil, ^1H NMR (CDCl_3 , 300 MHz) δ 2.64-2.79 (m, 2H), 3.32 (ABq, J = 13.5, ν_{AB} = 29.4, 2H), 4.51-4.64 (m, 2H), 5.10-5.21 (m, 4H), 5.65-5.89 (m, 2H), 6.78-6.81 (m, 2H), 7.07-7.32 (m, 8H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 37.8, 41.1, 55.2, 65.5, 118.2, 118.9, 126.3, 126.6, 126.8, 127.6, 128.1, 130.4, 131.8, 133.6, 136.7, 141.7, 174.5; HRMS (FAB^+) calcd for $\text{C}_{21}\text{H}_{23}\text{O}_2$ 307.1698 $[\text{M}+\text{H}]^+$; found: 307.1714

Allyl 2-(2-methoxycarbonyl-ethyl)-2-phenyl-4-pentenoate (3d)

This compound was obtained as colorless oil, ^1H NMR (CDCl_3 , 300 MHz) δ 2.07-2.46 (m, 4H), 2.72 and 2.88 (AB system, J = 14.1, 7.2, 2H), 3.61 (s, 3H), 4.58 (dm, J = 6.0, 2H), 5.05-5.21 (m, 4H), 5.51-5.65 (m, 1H), 5.76-5.89 (m, 1H), 7.20-7.35 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 29.2, 29.9, 39.6, 51.6, 53.1, 65.5, 118.3, 118.8, 126.2, 126.9, 128.4, 131.7, 132.8, 140.9, 173.4, 174.2; HRMS (FAB^+) calcd for $\text{C}_{18}\text{H}_{23}\text{O}_4$ 303.1596 $[\text{M}+\text{H}]^+$; found: 303.1600.

Allyl 2-(2-cyanoethyl)-2-phenyl-4-pentenoate (3d)

This compound was obtained as colorless oil, ^1H NMR (CDCl_3 , 300 MHz) δ 2.00-2.51 (m, 4H), 2.72 (ddm, A of AB system, $J = 14.1$, 7.5, 1H), 2.72 (ddm, B of AB system, $J = 14.1$, 6.9, 1H), 4.65 (dt, $J = 5.7$, 1.4, 2H), 5.14-5.25 (m, 4H), 5.53-5.67 (m, 1H), 5.77-5.90 (m, 1H), 7.18-7.39 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 12.7, 31.4, 39.6, 53.2, 65.8, 118.9, 119.5, 119.6, 126.1, 127.5, 128.8, 131.3, 132.2, 139.7, 173.4; HRMS (FAB^+) calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_2$ 270.1494 $[\text{M}+\text{H}]^+$; found: 270.1473.

Allyl 2-phenyl-4-pentenoate (3f)

This compound was obtained as colorless oil, ^1H NMR (CDCl_3 , 300 MHz) δ 2.47-2.57 (m, A of AB system, 1H), 2.78-2.89 (m, B of AB system 1H), 3.66 (dd, $J = 8.4$, 6.9, 1H), 4.49-4.62 (m, 2H), 4.97-5.23 (m, 4H), 5.65-5.90 (m, 2H), 7.21-7.32 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 37.6, 51.5, 65.3, 116.9, 117.9, 127.2, 127.8, 128.2, 128.5, 131.9, 135.1, 138.3, 172.8; HRMS (FAB^+) calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2$ 217.1229 $[\text{M}+\text{H}]^+$; found: 217.1239.

Allyl 2-methyl-2-(2-nitrophenyl)-4-pentenoate (3k)

This compound was obtained as yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 1.68 (s, 3H), 2.82-2.96 (m, 2H), 4.55 (ddd, AB system, $J = 13.2$, 6.0, 1.4, $\nu_{\text{AB}} = 15.9$, 2H), 4.99-5.06 (m, 2H), 5.18 (dq, $J = 11.4$, 1.2, 1H), 5.23 (dq, $J = 17.1$, 1.7, 2H), 5.41-5.55 (m, 1H), 5.85 (ddt, $J = 17.1$, 10.2, 6.0, 1H), 7.39-7.62 (m, 3H), 7.91 (dd $J = 8.1$, 1.5, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 25.4, 42.5, 49.6, 65.7, 118.4, 119.0, 125.5, 127.7, 129.1, 131.8, 132.6, 132.8, 136.8, 148.9, 173.8; HRMS (FAB^+) calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_4$ 276.1236 $[\text{M}+\text{H}]^+$; found: 276.1232.

Allyl 2-methyl-2-(4-nitrophenyl)-4-pentenoate (3l)

This compound was obtained as yellow oil, ^1H NMR (CDCl_3 , 300 MHz) δ 1.60 (s, 3H), 2.77 (dd, AB system, $J = 13.8$, 7.2, $\nu_{\text{AB}} = 42.3$, 2H), 4.57-4.59 (m, 2H), 5.03-5.11 (m, 2H), 5.16-5.24 (m, 2H), 5.49-5.63 (m, 1H), 5.82 (ddt, $J = 17.1$, 10.5, 5.7, 1H), 7.44-7.50 (m, 2H), 8.15-8.20 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 22.6, 43.6, 50.4, 65.8, 118.5, 119.4, 123.4, 127.1, 131.4, 132.6, 146.6, 150.3, 174.0; HRMS (FAB^+) calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_4$ 276.1236 $[\text{M}+\text{H}]^+$; found: 276.1248.

4-Methyl-4-(4-nitrophenyl)-1,7-heptadiene (8)

This compound was obtained as pale yellow oil. ^1H NMR (CDCl_3 , 300 MHz) δ 1.35 (s, 3H), 2.34 (dd, A of AB system, $J = 14.1, 7.5$, 2H), 2.53 (dd, A of AB system, $J = 14.1, 6.9$, 2H), 4.94-5.01 (m, 4H), 5.41-5.55 (m, 2H), 7.43-7.48 (m, 2H), 8.13-8.18 (m, 2H); GCMS (m/z) 231.

Catalysis in Ionic Liquid (IL)

1-*n*-Butyl-3-methyl-imidazolium tetrafluoroborate, [bmim][BF₄], was purchased and was used after dehydration under vacuum at 50 °C for 5 h. [bdmim][BF₄] was used after the same procedure.

Catalysis with Pd(PPh₃)₄

To the solution of Pd(PPh₃)₄ (2 mol%) dissolved in IL (1 mL) was added **1a** (0.5 mmol). The mixture was stirred at 30 °C. After reaction was complete product was extracted several times with hexane under air. Combined hexane phases were condensed and the product was purified by silica gel column chromatography (Hexane:AcOEt = 1:5).

Recycling procedure

In order to prepare an active phosphine complex before a first run, Pd₂(dba)₃•CHCl₃ (1 mol %) and xantphos (2.4 mol %) was first put in the reaction vessel and dissolved in CH₂Cl₂ (1 mL) and stirred for 30 min. After removal of CH₂Cl₂ under reduced pressure, IL and substrate were added. After extraction with hexane under air, the reaction vessel was set under argon after evacuation and substrate was added at 30 °C again.

1-*n*-Butyl-2,3-dimethylimidazolium tetrafluoroborate: [bdmim][BF₄]^{4a}

This compound was prepared by the same method previously reported^{4b} using sodium tetrafluoroborate (instead of sodium hexafluorophosphate as used in literature) for anion exchange (total yield; 58% from 1,2-dimethylimidazole). ^1H NMR (CDCl_3 , 300 MHz) δ 0.95 (t, $J = 7.5$, 3H), 1.37 (sext, $J = 7.2$, 2H), 1.72-1.82 (m, 2H), 2.61 (s, 3H), 3.80 (s, 3H), 4.06 (t, $J = 7.5$, 2H), 7.22, 7.23 (d $\times$ 2, $J = 2.1$, 1H $\times$ 2); ^{13}C NMR (CDCl_3 , 75 MHz) δ 0.11, 0.54, 13.5, 19.6, 31.6, 35.2, 48.4, 120.7, 122.5, 143.8; HRMS (FAB⁺) calcd for C₉H₁₇N₂ 153.1392 [M]⁺; found: 153.1390.

4) (a) Ho, K.-P.; Wong, K.-G.; Chan, T. H. *Tetrahedron* **2006**, 62, 6650. (b) Webb, P. B.; Sellin, M. F.; Thulani E. Kunene, T. E.; Williamson, S.; Slawin, A. M. Z.; and Cole-Hamilton, D. J. *J. Am. Chem. Soc.* **2003**, 125, 15577-15588.

Catalysis using Several Chiral Phosphines

These reaction was carried out with general procedure using several commercially available bidentate chiral phosphine ligands. The results were summarized beneath.

Catalysis using Tetradeuterated Substrate **1h**

Catalysis with **1h** to **3h**

The reaction was carried out with general procedure in CH_2Cl_2 . The product was purified with silica gel column chromatography (Hexane:AcOEt = 5:1), affording **3h** in 91% isolated yield as a colorless oil. A delay of 25 s in ^1H NMR analysis was established between pulses to allow complete relaxation. ^1H NMR (CDCl_3 , 300 MHz) δ 1.55 (s, 3H, $-\text{CH}_3$), 2.67 and 2.85 (dd, AB system, $J = 13.8, 7.2, 0.98\text{H}$, $-\text{CqCH}_2\text{CH}=\text{CH}_2$), 4.56 (dd, $J = 5.4, 0.9, 0.75\text{H}$, $-\text{OCH}_2\text{CH}=\text{CH}_2$), 5.03 (dd, $J = 4.5, 2.1, 0.49\text{H}$), 5.08 (dd, $J = 11.4, 2.1, 0.56\text{H}$), 5.14 (dd, $J = 5.7, 1.5, 0.55\text{H}$), 5.29 (dd, $J = 12.3, 1.5, 0.55\text{H}$), (total 2.23H for $-\text{XCH}_2\text{CH}=\text{CH}_2$, X = O or Cq), 5.56-5.65 (m, 1H, $\text{CqCH}_2\text{CH}=\text{CH}_2$), 5.77-5.87 (m, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 7.20-7.32 (m, 5H, $-\text{C}_6\text{H}_5$).

Catalysis with **1d** and **1h**

The reaction was carried out with **1d** (0.25 mmol) and **1h** (0.25 mmol) with general procedure with some changes. Catalyst was added to the vigorously stirred solution of both substrates and after ca. 30 s, hexane (10 mL) was added and immediately filtered through a thin silica gel pad for the removal of catalyst. A delay of 25 s in ^1H NMR analysis was established between pulses to allow complete relaxation. ^1H NMR (CDCl_3 , 300 MHz) δ 1.91 (s, 3H, $-\text{CH}_3$), 4.65-4.67 (m, 2.25H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), 5.18-5.29 (m, 3.25H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), 5.81-5.93 (m, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 7.28-7.40 (m, 5H, $-\text{C}_6\text{H}_5$).

The total number of protons at ($-\text{OCH}_2\text{CH}=\text{CH}_2$ and $-\text{OCH}_2\text{CH}=\text{CH}_2$), should be 4.00 (8.00 for non-deuterated substrate) if there were no intermolecular allylic scrambling, however, the measured sum of them was found to be 5.53. It means ca. 38% of non-deuterated allyl moieties should be exchanged between **1d** and **1h** within only 30 s.

Synthesis of Enantioenriched Substrate 5 **Allyl hydrogen 2-methyl-2-phenylmalonate (4)**

This compound was prepared with the method previously reported.⁵ PLE (50 mg, Porcine Liver Esterase, 1200Unit) was dissolved in buffer solution (30 mL, 0.2 M NaH₂PO₄ aq. adjusted to pH 7 with using NaOH solution). To the solution was added **1a** (1.0 g, 3.8 mmol) at ambient temperature. The mixture was stirred for 3 d. During the reaction pH was checked and adjusted to 7 with NaOH solution. The mixture was acidified with 6 M HCl aq. to pH 2 and extracted with ether. Organic phase was dried over MgSO₄ and was condensed under reduced pressure. Purification by silica gel column chromatography (Hexane:AcOEt = 5:1 → ether) gave **4** in 80% yield as colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 1.92 (s, 3H), 4.67 (dt, *J* = 1.5, 5.4, 2H), 5.18-5.30 (m, 2H), 5.81-5.93 (m, 1H), 7.26-7.42 (m, 5H), 9.74 (br, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 21.9, 58.6, 66.5, 118.6, 127.2, 127.9, 128.2, 131.1, 137.1, 171.1, 176.8; HRMS (FAB⁺) calcd for C₁₃H₁₅O₄ 235.0970 [M+H]⁺; found: 235.0976.

3-hydroxy-2-methyl-2-phenylpropanoic acid⁶

This compound was synthesized from **4** to determine the absolute configuration by the method previously reported.⁷ To the solution of **4** (0.12 g, 0.54 mmol) in THF (1.5 mL) at 10 °C in an Ar atmosphere was added Me₂S·BH₃ (0.3 mL, 1.2 eq. 2 M in THF) drop-wise. The mixture was stirred for 5 h at 20 °C and then acidified with 2 M HCl aq. at 0 °C. The mixture was extracted with ethyl acetate and was dried over Na₂SO₄. An oil was remained after evaporation and was purified by PTLC (CH₂Cl₂:AcOEt = 4:1). Yield 37%. [α]_D²⁵ – 19.4 (*c* 1.65, CHCl₃). ¹H NMR (CDCl₃, 300 MHz) δ 1.68 (s, 3H), 3.66 (AB quartet, *J* = 11.4, 1H), 4.10 (AB quartet, *J* = 11.4, 1H), 6.18 (br, 2H), 7.25-7.38 (m, 5H); ¹³C NMR (CDCl₃, 75 MHz) δ 20.5, 52.7, 69.4, 126.5, 127.8, 128.9, 139.8, 180.7. This compound dissolved in CHCl₃ exhibited (-)-rotation in measurement with spectrophotometer, which means this compound possesses *S* configuration⁶ ([α]_D²⁵ – 19.0 (*c* 5.0, CHCl₃, 81% *ee*)^{5b} as depicted above in square and consequently means **4** possesses *R* configuration which is accord with the results with using 2-methyl-2-phenylmalonic acid methyl^{5b} or ethyl esters.^{5a}

5) (a) Dominguez de María, P.; Kossmann, B.; Potgrave, N.; Buchholz, S.; Trauthwein, H.; May, O.; Gröger, H. *Synlett* **2005**, 11, 1749. (b) Toone, E. J.; Jones, J. B. *Tetrahedron: Asymmetry* **1991**, 10, 1041.

6) Hiratake, J.; Shibata, K.; Baba, N.; Oda, J.-i. *Synthesis* **1988**, 281.

7) Fadel, A.; Garcia-Argote, S. *Tetrahedron: Asymmetry* **1996**, 7, 1159.

Allyl methyl 2-methyl-2-phenylmalonate (5)

To an ice-cooled solution of DCC (0.22 g, 1.1 mmol) in CH_2Cl_2 (2 mL) was added drop-wise the acid **4** (0.23 g, 1.0 mmol) in methanol (5 mL). The mixture was stirred at ambient temperature for 7 d. After filtration through a thin silica gel pad, the mixture was condensed over reduced pressure. Purification by silica gel column chromatography (Hexane:AcOEt = 5:1) gave **5** in 43% yield as colorless oil. The value of enantiomeric excess was measured by HPLC. 83% ee [Chiralcell OJ-H column, *n*-hexane/EtOH = 70:30, 0.5 mL/min, 254 nm, t_R = 43.82 min (major, (+)-rotation) and 57.52 min (minor, (-)-rotation)]. $[\alpha]_D^{25}$ 1.7 (*c* 2.9, CHCl_3). ^1H NMR (CDCl_3 , 300 MHz) δ 1.53 (s, 3H), 2.65 (AB quartet, J = 13.8, 7.2, 1H), 2.83 (AB quartet, J = 13.8, 7.2, 1H), 3.65 (s, 3H), 5.01-5.10 (m, 2H), 5.53-5.68 (m, 1H), 7.20-7.35 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 22.7, 43.7, 50.0, 52.2, 118.3, 125.8, 126.7, 128.3, 133.9, 143.2, 176.1; HRMS (FAB^+) calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2$ 205.1229 $[\text{M}+\text{H}]^+$; found: 205.1222.

Methyl 2-methyl-2-phenyl-4-pentenoate (6)

Catalysis with **5** was carried out with the general procedure in CH_2Cl_2 . The product was purified with silica gel column chromatography (Hexane:AcOEt = 5:1), affording **6** in 88% isolated yield as colorless oil. The value of enantiomeric excess was measured with HPLC (racemate). [Chiralcell OJ-H column, *n*-hexane/*i*PrOH = 90:10, 0.5 mL/min, 254 nm, t_R = 20.42 min and 24.07 min] ^1H NMR (CDCl_3 , 300 MHz) δ 1.53 (s, 3H), 2.65 (AB quartet, J = 13.8, 7.2, 1H), 2.83 (AB quartet, J = 13.8, 7.2, 1H), 3.65 (s, 3H), 5.01-5.10 (m, 2H), 5.53-5.68 (m, 1H), 7.20-7.35 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 22.7, 43.7, 50.0, 52.2, 118.3, 125.8, 126.7, 128.3, 133.9, 143.2, 176.1; HRMS (FAB^+) calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2$ 205.1229 $[\text{M}+\text{H}]^+$; found: 205.1222.

Scrambling Experiment using 1e and 1i**Catalytic decarboxylative allylic alkylation**

The reaction was carried out with **1e** (0.25 mmol) and **1i** (0.25 mmol) in benzene with general procedure. It took 3 h to complete monitored by TLC. The newly formed two spots were separated by column chromatography (Hexane:AcOEt = 6:1). The oily products corresponding to both **3e'** (0.07 g: 104% yield if no scrambling takes place) and **3i'** (0.06 g: 93% yield if no scrambling takes place) were obtained. Both mixtures were subjected to catalytic deallylation conditions.

Catalytic deallylation reactions with 3e' and 3i'

These reactions were separately carried out for each compounds with the following method; To the solution of each substrate in CH₂Cl₂ (1 mL) under argon was added Pd(PPh₃)₄ (2 mol% for each) and morpholine (0.5 mmol, 0.045 mL) at rt and was stirred for about 2 h monitored by TLC analysis. After reaction was complete, the mixture was extracted with CH₂Cl₂ (20 mL) and (saturated Na₂CO₃aq. /water = 50 v/v%, 10 mL × 3). The combined aqueous phase was acidified with 2 M HCl aq. to pH 2. The acidified phase was washed with ethyl acetate four times. The collected organic phase was dried over anhydrous Na₂SO₄, concentrated under vacuum, purified by filtration through a thin silica gel pad (ethyl acetate as an eluent). Both products were analyzed by ¹H NMR. We obtained pale yellow viscous oil (0.057 g) from **3e'** and colorless oil (0.039 g) from **3i'**.

¹H NMR analysis of product from **3e'**

¹H NMR analysis revealed it contained only allylated compound **2e**. No crotylated compounds (**2j-b** or **2j-l**) were observed. We separately prepared **2e** and compared the ¹H NMR charts of both compounds (*vide infra*).

¹H NMR analysis of product from **3i'**

The ¹H NMR analysis revealed a main compound contained in the mixture of products from **3i** was allylated compound **2a**. A mixture of crotylated compounds (**2i-b** and **2i-l**) was separately prepared (*vide infra*). At the same time, **2a** was also prepared and they were compared with the products from **3i'** (*vide infra*). Both results using **3i** contained 2-phenylpropionic acid as an impurity (its ¹H NMR chemical shifts were identical to the one observed with an authentic compound; ¹H NMR (CDCl₃, 300 MHz) δ 1.51 (d, J = 7.2, 3H), 3.72 (q, J = 7.2, 1H), 7.23-7.35 (m, 5H), 10.1 (br, 1H)), probably caused by decarboxylation of 2-phenyl-2-methylmalonic acid generated by catalytic hydrolysis of **1i** or its derivatives which did not react in catalytic decarboxylative alkylation. The (allylated/crotylated) ratio among alkylated products was found to be ca. 84:16 from NMR analysis.

2-(2-Cyanoethyl)-2-phenyl-4-pentenoic acid (**2e**)

This compound was prepared from **3e** with the catalytic deallylation method already described (S14) using morpholine. (Pale yellow oil). ¹H NMR (CDCl₃, 300 MHz) δ 2.02-2.49 (m, 4H), 2.73 (ddm, A of AB system, J = 14.4, 4.5, 1H), 2.93 (ddm, B of AB system, J = 14.1, 6.9, 1H), 5.16-5.23 (m, 2H), 5.58-5.72 (m, 1H), 7.26-7.41 (m and br, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 12.7, 31.0, 39.4, 53.1, 119.3, 119.5, 119.8, 126.2, 127.8, 128.9, 132.0, 138.9, 179.3; HRMS (FAB⁺) calcd for C₁₄H₁₆NO₂ 230.1181 [M+H]⁺; found: 230.1182.

2-methyl-2-phenyl-4-pentenoic acid (**2a**)⁸

This compound was prepared with the same method for **2e** using **3a**. (colorless oil). ¹H NMR (CDCl₃, 300 MHz) δ 1.56 (s, 3H), 2.67 and 2.81 (dd, AB system, J = 13.8, 7.2, 2H), 5.02-5.10 (m, 2H), 5.54-5.67 (m, 1H), 7.22-7.39 (m, 5H), 10.84 (br, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 22.2, 43.5, 49.7, 118.6, 126.1, 127.0, 128.4, 133.6, 142.2, 182.1; HRMS (FAB⁺) calcd for C₁₂H₁₅O₂ 191.1072 [M+H]⁺; found: 191.1078.

8) Miller, R. D.; Goelitz, P. J. *Org. Chem.* **1981**, 46, 1616.

A mixture of **2i-b** and **2i-l**

To a solution of **1i** (0.5 mmol) in benzene (1 mL) was added Pd(PPh₃)₄ (2 mol%). The mixture was stirred for 4 h (**1i** or its derivatives were yet remained after 4 h, judging from TLC analysis). To the mixture was added morpholine (1.0 mmol, 0.09 mL). The mixture was stirred for additional 2 h. After reaction was complete, the mixture was extracted with CH₂Cl₂ (20 mL) and (saturated Na₂CO₃ aq. /water = 50 v/v%, 10 mL × 3). The combined aqueous phase was acidified with 2 M HCl aq. to pH 2. The acidified phase was washed with ethyl acetate four times. The organic phase was dried over anhydrous Na₂SO₄, concentrated under vacuum, purified by filtration through a thin silica gel pad (ethyl acetate as an eluent). The mixture was analyzed by ¹H NMR and H-H COSY methods.

Supporting Information : Imao, Itoi, Yamazaki, Shirakura, Ohtoshi, Ogata, Ohmori, Ohta, and Ito

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as a main product from reaction with 31'

Supporting Information : Imao, Itoi, Yamazaki, Shirakura, Ohtoshi, Ogata, Ohmori, Ohta, and Ito

Supporting Information : Imao, Itoi, Yamazaki, Shirakura, Ohtoshi, Ogata, Ohmori, Ohta, and Ito