Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Metallic Reductant-Free Synthesis of α-Substituted Propionic Acid Derivatives through Hydrocarboxylation of Alkenes with Formate Salt

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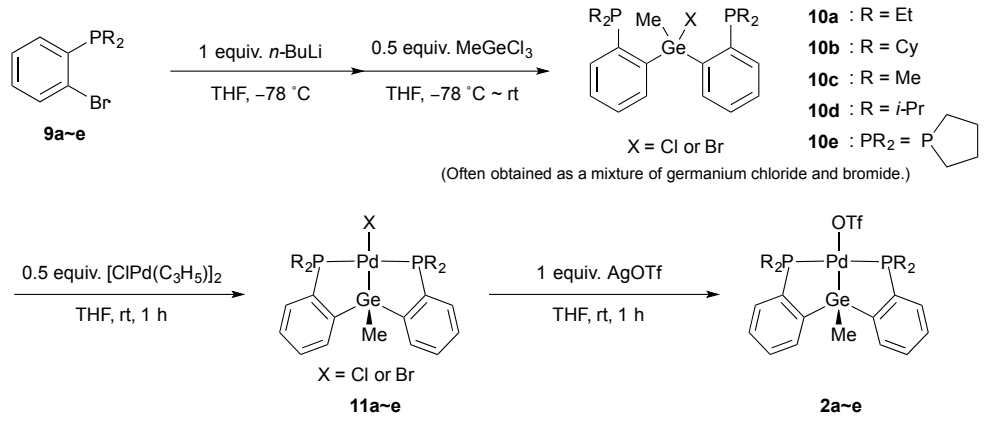
General: All operations were performed under an argon atmosphere. ^{1}H and ^{31}P NMR and ^{13}C spectra were recorded on a JEOL ECX-500 (500 MHz for ^{1}H, 125 MHz for ^{13}C and 202 MHz for ^{31}P) or JEOL ECX-400 (400 MHz for ^{1}H and 160 MHz for ^{31}P) or JEOL ECS-400 (400 MHz for ^{1}H and 160 MHz for ^{31}P) or Burker DRX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrometer in $CDCl_3$, CD_2Cl_2, CD_3OD, or C_6D_6. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane (δ_H 0.00), 85% H_3PO_4 aq. (δ_P 0.00) and are referenced to residual solvents (δ_H 7.26 and δ_C 77.0 for chloroform, δ_H 5.32 and δ_C 53.8 for dichloromethane, δ_H 3.31 and δ_C 49.0 for methanol, δ_H 7.15 and δ_C 128.6 for benzene). IR spectra were recorded on an FT/IR-460 plus (JASCO Co., Ltd.) with ATR PRO450-S accessory (JASCO Co., Ltd.). Mass spectra were recorded on a JEOL JMS-T100. Elemental analyses were performed on an elemental vario MICRO. Silica Gel 60 (Kanto Chemical Co., Inc.) was used for flash column chromatography. Merck Kieselgel 60 F_{254} (0.25 mm thickness, coated on glass 20×20 cm^2) plate was used for analytical thin layer chromatography (TLC), and Wakogel B-5F coated on glass in a thickness of 0.9 mm was used for preparative TLC. GC analysis was performed using a Shimadzu GC-2010 equipped with DB-WAXETR column.

Dehydrated DMF was purchased from Kanto Chemicals and degassed by freeze-dry technique. Dehydrated 1,4-dioxane was purchased from Kanto Chemicals and degassed by Ar bubbling. THF, Et_2O, pentane and toluene were purified by solvent purification system of Glass-Contour. Benzene-d_6 was purchased from ACROS chemicals, and dried and degassed by benzophenone ketyl.

1 was synthesized according to the procedure reported in our previous paper.[1] Dialkyl(2-bromophenyl)phosphines **9** were prepared according to literature procedures.[2-6] Carboxylation products **4b**[7], **4c**[8], **4e**[9], **4f**[9], **4g**[10], **4h**[8], **4i**[11], **6b**[12], and **6c**[13] were known compounds and their spectral data were in good agreement with literature values.

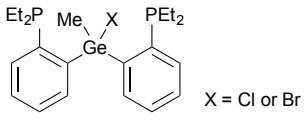
Procedures for the preparation of palladium complexes

Scheme S1



Preparation of germanium chloride (bromide) **10a**

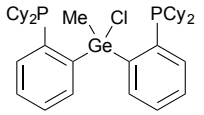
To a stirred solution of diethyl(2-bromophenyl)phosphine **9a** (2.4 g, 10.0 mmol) in THF (40 ml) was added *n*-BuLi (1.57 M in *n*-hexane, 6.4 mL, 10.0 mmol) at −78 ºC. After 1 h, $MeGeCl_3$ (0.57 ml, 5.0 mmol) was added to the solution at −78 ºC, and the mixture was allowed to stand at room temperature. After 24 h, the mixture was concentrated under reduced pressure. Toluene was added, and the solution was filtered through a short pad of Celite to remove inorganic salts. Removal of the solvent under reduced pressure gave crude product **10a** as yellow oil, which was used for next step without further purification. The diarylgermaniums **10** were often obtained as a mixture of germanium chloride and bromide, the latter of which was possibly formed through substitution reaction of the former. The mixture was used for the next step, thus giving palladium complex **11** as a mixture of chloride and bromide, which were converted to the same triflate complex **2** by salt exchange with AgOTf.



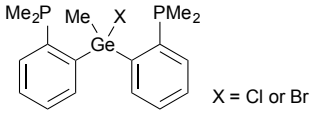
10a (obtained as a mixture of germanium chloride and bromide): ^{1}H NMR (500 MHz, C_6D_6) δ = 8.12-8.08 (m, 2H), 7.30-7.25 (m, 2H), 7.20-7.10 (m, 4H), 1.90 (t, *J* = 4.1 Hz, 0.43H), 1.74 (t, *J* = 3.7 Hz, 2.57H), 1.45-1.30 (m, 8H), 0.86-0.72 (m, 12H); ^{31}P NMR (C_6D_6, 202 MHz) δ = −22.9 (s, 83%), −23.3 (s, 17%).

10c, **10d**, and **10e** were prepared according to the same procedure using corresponding dialkyl(2-bromophenyl)phosphine **9c~e**. In the case of **10b**, the aryllithium intermediate, 2-(dicyclohexylphosphino)phenyllithium•Et_2O, was isolated and used for the reaction, giving germanium chloride **10b** selectively without contamination of bromide derivative. **10b** was isolated as an analytically pure form by

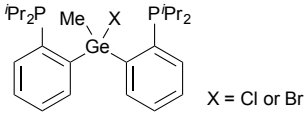
recrystallization from pentane.



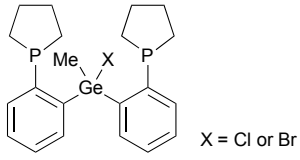
10b: (3.2 mmol, 54%) : ^{1}H NMR (500 MHz, C_6D_6) δ = 8.14-8.10 (m, 2H), 7.41-7.38 (m, 2H), 7.16-7.08 (m, 4H), 1.92 (t, *J* = 4.3 Hz, 3H), 1.96-1.90 (m, 2H), 1.88-1.72 (m, 6H), 1.72-1.62 (m, 4H), 1.60-1.44 (m, 12H), 1.34-0.92 (m, 20H); ^{13}C-NMR (125 MHz, C_6D_6) δ = 151.0 (d, *J* = 51.3 Hz), 142.2 (d, *J* = 14.3 Hz), 136.2 (d, *J* = 16.7 Hz), 132.7, 129.1 (d, *J* = 13.1 Hz), 128.3, 36.0 (d, *J* = 14.3 Hz), 35.9 (t, *J* = 13.1 Hz), 31.2 (d, *J* = 16.7 Hz), 30.9 (d, *J* = 11.9 Hz), 30.6-30.3 (m), 27.7-27.3 (m), 26.8, 26.7, 17.1 (t, *J* = 21.5 Hz); ^{31}P NMR (C_6D_6, 202 MHz) δ = −4.1 (s); IR (ATR) 2926, 2848, 1445, 1264, 1178, 1100, 1029 cm^{-1}; Anal. Calcd for $C_{37}H_{55}ClGeP_2$: C, 66.34; H, 8.28; Found: C, 66.19; H, 7.90.



10c (obtained as a mixture of germanium chloride and bromide): For major compound; ^{1}H NMR (400 MHz, C_6D_6) δ = 8.03 (d, *J* = 7.3 Hz, 2H), 7.32-7.27 (m, 2H), 7.20-7.05 (m, 4H), 1.83 (t, *J* = 3.6 Hz, 3H), 1.05 (d, *J* = 3.7 Hz, 6H), 0.94 (d, *J* = 3.6 Hz, 6H); ^{31}P NMR (C_6D_6, 160 MHz) δ = −51.4 (s)



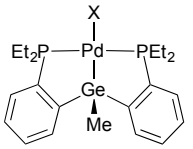
10d (obtained as a mixture of germanium chloride and bromide): ^{1}H NMR (400 MHz, C_6D_6) δ = 8.12-8.06 (m, 2H), 7.34-7.26 (m, 2H), 7.19-7.06 (m, 4H), 2.05 (t, *J* = 4.6 Hz, 0.54H), 1.94-1.80 (m, 6.46H), 1.10-1.02 (m, 6H), 1.02-0.88 (m, 6H), 0.88-0.73 (m, 12H); ^{31}P NMR (C_6D_6, 160 MHz) δ = 4.1 (s, 84%), 3.6 (s, 16%).



10e (obtained as a mixture of germanium chloride and bromide): ^{1}H NMR (500 MHz, C_6D_6) δ = 8.13-8.06 (m, 2H), 7.25-7.20 (m, 2H), 7.13-7.08 (m, 4H), 1.89 (t, *J* = 3.7 Hz, 0.61H), 1.74 (t, *J* = 3.7 Hz, 2.39H), 1.70-1.47 (m, 12H), 1.40-1.23 (m, 4H); ^{31}P NMR (C_6D_6, 202 MHz) δ = −20.6 (s, 85%), −20.8 (s, 15%).

Preparation of palladium chloride (bromide) complex **11a**

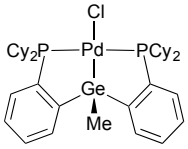
To a stirred solution of germanium chloride (bromide) **10a** (2.17 g) in THF (25 mL) was added $[ClPd(C_3H_5)]_2$ (874 mg, 2.39 mmol) at room temperature. After 1 h, the solvent was removed under reduced pressure, and the resulting solid was washed with pentane to give **11a** as a pale yellow powder (2.50 g). The obtained product was a mixture of two compounds, which were thought to be palladium chloride and bromide, and this mixture was used for the next step.



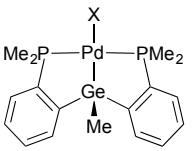
X = Cl or Br

11a (obtained as a mixture of palladium chloride and bromide): ^{1}H NMR (500 MHz, C_6D_6) δ = 7.80-7.77 (m, 2H), 7.24-7.18 (m, 2H), 7.13-7.05 (m, 4H), 2.89-2.75 (m, 2H), 1.98-1.84 (m, 2H), 1.80-1.66 (m, 2H), 1.66-1.57 (m, 2H), 1.03-0.85 (m, 12H), 0.75 (s, 2.5H), 0.73 (s, 0.5H); ^{31}P NMR (C_6D_6, 202 MHz) δ = 54.5 (s, 15%), 54.1 (s, 85%).

11b, **11c**, **11d**, and **11e** were prepared according to the same procedure using corresponding diarylgermanium compounds **10b~e**. In the case of **11b**, the crude compound was washed with Et_2O to give **11b** as an analytically pure form.



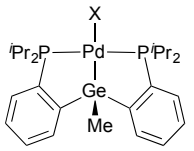
11b (2.97 mmol, 99%): ^{1}H NMR (500 MHz, C_6D_6) δ = 7.92 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 3.16 (t, *J* = 12.3 Hz, 2H), 2.38-2.26 (m, 4H), 2.18 (d, *J* = 12.9 Hz, 2H), 2.09-1.98 (m, 2H), 1.76-1.34 (m, 24H), 1.29-1.07 (m, 6H), 1.07-0.94 (m, 2H), 0.94-0.84 (m, 2H), 0.82 (s, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ = 158.7 (t, *J* = 27.4 Hz), 139.3 (t, *J* = 20.3 Hz), 132.9 (t, *J* = 11.9 Hz), 131.8, 130.6, 128.7, 37.1 (t, *J* = 10.7 Hz), 36.5 (t, *J* = 10.7 Hz), 30.0, 29.9, 28.9, 27.7-27.0 (m), 26.7, 26.0, 8.7; ^{31}P NMR (C_6D_6, 202 MHz) δ = 63.5 (s); IR (ATR) 2928, 2850, 1446, 1101, 1004 cm^{-1}; Anal. Calcd for $C_{37}H_{55}ClGeP_2Pd$: C, 57.25; H, 7.14; Found: C, 57.31; H, 6.87.



X = Cl or Br

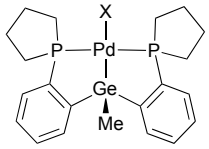
11c (obtained as a mixture of palladium chloride and bromide): ^{1}H NMR (400 MHz, C_6D_6) δ = 7.74 (d, *J* = 7.4 Hz,

2H), 7.21-7.17 (m, 2H), 7.07-6.98 (m, 4H), 1.80-1.65 (br, 6H), 1.36-1.26 (br, 6H), 0.66 (s, 3H); ^{31}P NMR (C_6D_6, 160 MHz) δ = 26.3 (s).



X = Cl or Br

11d (obtained as a mixture of palladium chloride and bromide): ^{1}H NMR (400 MHz, C_6D_6) δ = 7.83 (d, *J* = 7.4 Hz, 2H), 7.30-7.21 (m, 4H), 7.13-7.08 (m, 2H), 3.32-3.15 (m, 2H), 2.38-2.22 (m, 2H), 1.52-1.41 (m, 6H), 1.38-1.24 (m, 6H), 1.10-1.00 (m, 6H), 0.94-0.85 (m, 6H), 0.72 (s, 2.5H), 0.70 (s, 0.5 H); ^{31}P NMR (C_6D_6, 160 MHz) δ = 71.6 (s, 17%), 71.2 (s, 83%).

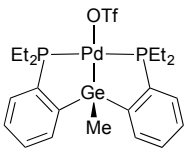


X = Cl or Br

11e (obtained as a mixture of palladium chloride and bromide): ^{1}H NMR (500 MHz, C_6D_6) δ = 7.76 (d, *J* = 7.4 Hz, 2H), 7.23-7.18 (m, 2H), 7.08-7.02 (m, 4H), 3.38-3.29 (m, 2H), 2.26-2.18 (m, 2H), 2.05-1.98 (m, 2H), 1.90-1.80 (m, 2H), 1.80-1.72 (m, 2H), 1.65-1.47 (m, 6H), 0.80 (s, 3H); ^{31}P NMR (C_6D_6, 202 MHz) δ = 49.8 (s).

Preparation of palladium triflate complex **2a**

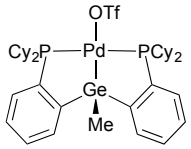
To a stirred solution of palladium chloride (bromide) complex **11a** (1.0 g) in THF (15 mL) was added AgOTf (459 mg, 1.79 mmol) at room temperature. After 1 h, the solvent was removed under reduced pressure. Toluene was added to the mixture, and the solution was filtered through a short pad of Celite to remove inorganic salts. Removal of the solvent from the filtrate under reduced pressure gave solid, which was purified by recrystallization from toluene/pentane to give **2a** as an orange-yellow solid (946 mg, 1.4 mmol) in 70% yield (3 steps from aryl bromide **9a**).



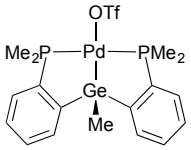
2a: ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.93 (d, *J* = 8.3 Hz, 2H), 7.60-7.55 (m, 4H), 7.54-7.49 (m, 2H), 2.50-2.41 (m, 2H), 2.25-2.13 (m, 4H), 2.07-1.97 (m, 2H), 1.13-1.05 (m, 6H), 1.03-0.95 (m, 6H), 0.72 (s, 3H); ^{13}C-NMR (125 MHz, CD_2Cl_2) δ = 155.7 (t, *J* = 27.3 Hz), 138.1 (t, *J* = 22.7 Hz), 132.6 (t, *J* = 11.9 Hz), 131.6, 130.14, 130.08, 23.5

(t, J = 11.9 Hz), 19.9 (t, J = 13.1 Hz), 9.8, 9.4, 7.8; ^{31}P NMR (CD_2Cl_2, 202 MHz) δ = 52.4 (s); IR (ATR) 2971, 2931, 1455, 1305, 1230, 1207, 1158 cm^{-1}; Anal. Calcd for $C_{22}H_{31}F_3GeO_3P_2PdS$: C, 39.23; H, 4.64; S, 4.76; Found: C, 38.94; H, 4.64; S, 4.58.

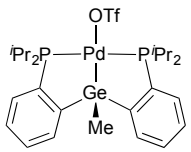
Other palladium triflate complexes **2b**, **2c**, **2d**, and **2e** were also prepared according to the same procedure using corresponding palladium chloride (bromide) complexes **11b-e**.



2b (1.11 mmol, 85%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.91 (d, J = 7.5 Hz, 2H), 7.63 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 2.64-2.54 (m, 2H), 2.50-2.41 (m, 2H), 2.14-2.02 (br, 4H), 1.84-1.74 (br, 8H), 1.70-1.55 (m, 8H), 1.50-1.26 (m, 12H), 1.25-1.08 (m, 8H), 0.70 (s, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ = 157.0 (t, J = 16.2 Hz), 137.4 (t, J = 29.1 Hz), 132.5 (t, J = 17.9 Hz), 132.3, 130.9, 129.0, 36.2 (t, J = 10.7 Hz), 35.5 (t, J = 9.5 Hz), 30.8, 29.8, 29.4, 29.0, 27.4 (t, J = 4.8 Hz), 27.2-27.0 (m), 26.8, 26.0, 8.9; ^{31}P NMR (CD_2Cl_2, 202 MHz) δ = 63.7 (s); IR (ATR) 2930, 1446, 1302, 1231, 1209, 1160, 1106, 1017 cm^{-1}; Anal. Calcd for $C_{38}H_{55}F_3GeO_3P_2PdS$: C, 51.29; H, 6.23; S, 3.60; Found: C, 51.00; H, 6.26; S, 3.42.

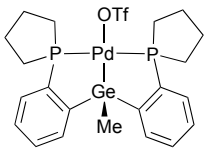


2c (0.45 mmol, 21% (3 steps)) : ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.89 (d, J = 7.2 Hz, 2H), 7.67-7.62 (m, 2H), 7.58-7.49 (m, 4H), 1.88-1.82 (m, 6H), 1.77-1.71 (m, 6H), 0.72 (s, 3H); ^{13}C-NMR (125 MHz, CD_2Cl_2) δ = 152.9 (t, J = 28.6 Hz), 142.0 (t, J = 26.2 Hz), 132.5 (t, J = 11.9 Hz), 131.7, 130.3, 129.9, 16.9 (t, J = 11.9 Hz), 12.8 (t, J = 13.1 Hz), 7.4; ^{31}P NMR (CD_2Cl_2, 202 MHz) δ = 24.8 (s); IR (ATR) 2961, 1417, 1301, 1232, 1212, 1159, 1108, 1023 cm^{-1}; Anal. Calcd for $C_{18}H_{23}F_3GeO_3P_2PdS$: C, 35.01; H, 3.75; S, 5.19; Found: C, 35.36; H, 3.87; S, 4.98.



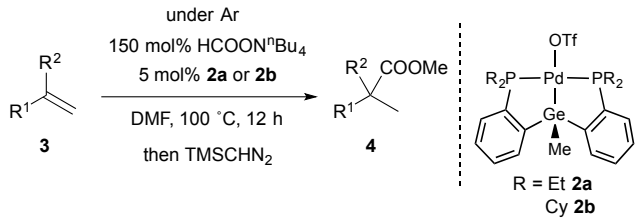
2d (1.22 mmol, 29% (3 steps)) : ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.95 (d, J = 7.2 Hz, 2H), 7.64-7.55 (m, 4H), 7.48 (td, J = 7.2 Hz, 1.4 Hz, 2H), 2.86-2.78 (m, 2H), 2.74-2.68 (m, 2H), 1.39-1.33 (m, 6H), 1.26-1.14 (m, 12H),

1.10-1.04 (m, 6H), 0.74 (s, 3H); ^{13}C-NMR (125 MHz, CD_2Cl_2) δ = 156.6 (t, *J* = 26.2 Hz), 136.7 (t, *J* = 21.5 Hz), 132.5 (t, *J* = 10.7 Hz), 132.2, 131.5, 129.4, 26.9 (t, *J* = 10.7 Hz), 26.6 (t, *J* = 10.7 Hz), 20.6, 19.6, 18.5, 18.2, 9.0; ^{31}P NMR (CD_2Cl_2, 202 MHz) δ = 70.2 (s); IR (ATR) 2931, 1446, 1304, 1231, 1207, 1159, 1107, 1025, 1015 cm^{-1}; Anal. Calcd for $C_{26}H_{39}F_3GeO_3P_2PdS$: C, 42.80; H, 5.39; S, 4.39; Found: C, 42.55; H, 5.42; S, 4.50.

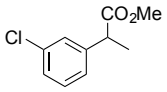


2e (0.55 mmol, 73% (3 steps)) : ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.87 (d, *J* = 7.5 Hz, 2H), 7.56-7.50 (m, 4H), 7.50-7.45 (m, 2H), 2.84-2.75 (m, 2H), 2.53-2.45 (m, 2H), 2.27-2.11 (m, 8H), 2.09-1.97 (m, 4H), 0.78 (s, 3H); ^{13}C-NMR (125 MHz, CD_2Cl_2) δ = 153.0 (t, *J* = 28.6 Hz), 143.5 (t, *J* = 21.5 Hz), 132.2 (t, *J* = 11.9 Hz), 131.1, 130.6, 130.3, 31.4 (t, *J* = 13.1 Hz), 28.2, 27.9, 26.9 (t, *J* = 11.9 Hz), 7.7; ^{31}P NMR (CD_2Cl_2, 202 MHz) δ = 48.3 (s); IR (ATR) 2952, 1444, 1414, 1299, 1233, 1212, 1159, 1106, 1020 cm^{-1}; Anal. Calcd for $C_{22}H_{27}F_3GeO_3P_2PdS$: C, 39.47; H, 4.06; S, 4.79; Found: C, 39.50; H, 4.10; S, 4.66.

Procedures for hydrocarboxylation of styrene derivatives (Table 2)

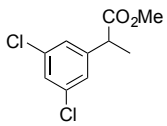


Catalyst (0.01 mmol) and $HCO_2N(n\text{-}Bu)_4$ (86.2 mg, 0.3 mmol) were placed in a 30 mL test tube, and a solution of alkene (0.2 mmol) in DMF (1.0 mL) was added under Ar. The mixture was stirred at 100 °C for 12 h, and then quenched with 1N HCl aq. The resulting mixture was extracted with diethyl ether three times. The combined organic layers were washed with water twice and sat. NaCl aq., and dried over magnesium sulfate. After removal of solvent under reduced pressure, the residue was treated with $TMSCHN_2$ (2.0 M sol. in Et_2O, 0.4 mL, 0.80 mmol) in Et_2O-MeOH (2:1, 2.4 mL) at 0 °C. After 30 min, the solvent was removed under reduced pressure, and the residue was purified by preparative TLC (hexane:ethyl acetate = 10:1 ~ 2:1) to afford carboxylation product as its methyl ester.



methyl 2-(3-chlorophenyl)propionate 4a

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32-7.29 (m, 1H), 7.29-7.22 (m, 2H), 7.22-7.16 (m, 1H), 3.74-3.63 (m, 4H), 1.49 (d, *J* = 7.2 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 174.4, 142.4, 134.4, 129.9, 127.7, 127.4, 125.7, 52.2, 45.1, 18.4; IR (ATR) 2983, 2952, 1739, 1596, 1575, 1478, 1458, 1433, 1377, 1334, 1251, 1208, 1166, 1085, 1066, 1012 cm^{-1}; HR-MS (FD$^+$): Calcd for $C_{10}H_{11}ClO_2$ [M$^+$]: 198.04476; Found: 198.04517.



methyl 2-(3,5-dichlorophenyl)propionate 4d

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.28 (t, *J* = 1.8 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 2H), 3.71-3.65 (m, 4H), 1.47 (d, *J* = 7.2 Hz, 3H); ^{13}C-NMR (125 MHz, CD_2Cl_2) δ = 174.0, 144.4, 135.3, 127.6, 126.8, 52.6, 45.3, 18.5; IR (ATR) 3080, 2984, 2953, 1735, 1576, 1560, 1437, 1332, 1210, 1168, 1089 cm^{-1}; HR-MS (FD$^+$): Calcd for $C_{10}H_{10}Cl_2O_2$ [M$^+$]: 232.00578; Found: 232.00632.

Screening of PGeP-palladium catalysts and reaction conditions

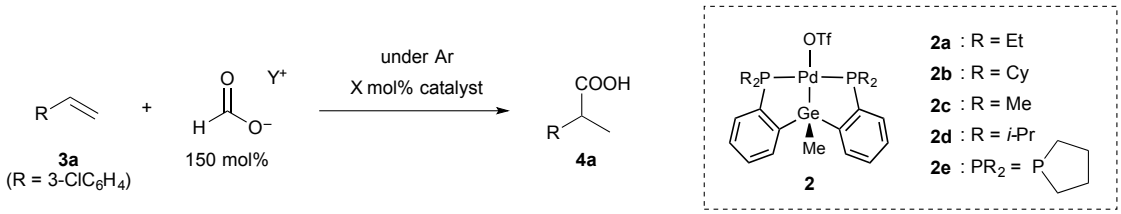


Table S1

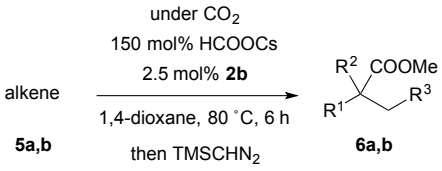
Entry	Catalyst	X	Y	Solvent	Temp. / ˚C	Time	Concentration of [**3a**] / mol/L	Yield[a] /%
1	**2a**	2.5	Cs	DMF	100	6	0.05	3
2	**2b**	2.5	Cs	DMF	100	6	0.05	Not detected
3	**2c**	2.5	Cs	DMF	100	6	0.05	Not detected
4	**2d**	2.5	Cs	DMF	100	6	0.05	Not detected
5	**2e**	2.5	Cs	DMF	100	6	0.05	Not detected
6	**2a**	2.5	K	DMF	100	6	0.05	3
7	**2a**	2.5	Na	DMF	100	6	0.05	Trace
8	**2a**	2.5	Li	DMF	100	6	0.05	Not detected
9	**2a**	2.5	NMe_3Bn	DMF	100	6	0.05	9
10	**2a**	2.5	NMe_4	DMF	100	6	0.05	24
11	**2a**	2.5	NEt_4	DMF	100	6	0.05	16
12	**2a**	2.5	N^nBu_4	DMF	100	6	0.05	36
13	**2a**	2.5	N^nBu_4	DMA	100	6	0.05	20
14	**2a**	2.5	N^nBu_4	NMP	100	6	0.05	24
15	**2a**	2.5	N^nBu_4	THF	100	6	0.05	4
16	**2a**	2.5	N^nBu_4	1,4-dioxane	100	6	0.05	Trace
17	**2a**	2.5	N^nBu_4	Toluene	100	6	0.05	8
18	**2a**	2.5	N^nBu_4	DMF	80	6	0.05	5
19	**2a**	2.5	N^nBu_4	DMF	110	6	0.05	33
20	**2a**	2.5	N^nBu_4	DMF	120	6	0.05	40[b]
21	**2a**	2.5	N^nBu_4	DMF	140	6	0.05	Trace[c]
22	**2a**	2.5	N^nBu_4	DMF	100	6	0.025	12
23	**2a**	2.5	N^nBu_4	DMF	100	6	0.10	45
24	**2a**	2.5	N^nBu_4	DMF	100	6	0.20	50
25	**2a**	5.0	N^nBu_4	DMF	100	12	0.20	73

[a] NMR yield. [b] Unidentified by-product was formed (ca. 20%). [c] 3-(Chloro)ethylbenzene was formed in 24% by hydrogenation of **3a**.

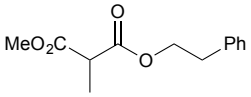
Table S1 shows the results of initial screening of catalyst and reaction conditions for the hydrocarboxylation of **3a**. The results are summarized as follows.

1) Among the palladium complexes **2a-e** with different substituents on the phosphorous atoms, only the palladium complex **2a** having diethylphosphine side arms afforded the desired carboxylation product **4a** under the reaction conditions in entries 1-5.
2) Ammonium formates gave better results than cesium, potassium, sodium, and lithium formates due to their poor solubility, and tetrabutylammonium formate turned out to be the best (Entries 1, 6-12).
3) Polar solvents, in particular DMF, were superior to THF, 1,4-dioxane, and toluene (Entries 12-17).
4) 100 ˚C is necessary to promote the reaction efficiently. However, unidentified by-product was formed at 120 ˚C although the yield of **4a** slightly increased, and the reaction at 140 ˚C afforded hydrogenation product mainly (Entries 12, 18-21).
5) Higher concentration of **3a** resulted in a better yield of **4a** (Entries 12, 22-24).
6) Finally, the reaction conditions in entry 25 turned out to be the best conditions (5 mol% **2a**, 0.20 M **3a**, in DMF, 100 ˚C, 12 h).

Procedure for the hydrocarboxylation of acrylate and vinylsulfone (Table 3, conditions A)



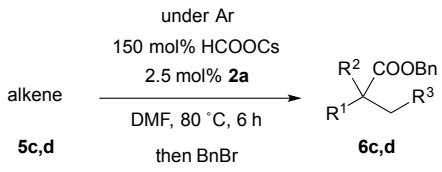
Catalyst (0.0025 mmol) and HCO_2Cs (26.7 mg, 0.15 mmol) were placed in a test tube, and a solution of alkene (0.1 mmol) in 1,4-dioxane (2.0 mL) was added under Ar. After the Ar atmosphere was replaced by carbon dioxide using a balloon, the mixture was stirred at 80 °C for 6 h. After 1N HCl aq. was added, the mixture was extracted with diethyl ether three times. The combined organic layers were washed with water twice and sat. NaCl aq., and dried over magnesium sulfate. After removal of solvent under reduced pressure, the residue was treated with $TMSCHN_2$ (2.0 M sol. in Et_2O, 0.2 mL, 0.40 mmol) in Et_2O-MeOH (2:1, 1.2 mL) at 0 °C. After 30 min, the solvent was removed under reduced pressure, and the residue was purified by preparative TLC (hexane:ethyl acetate = 3:1) to afford carboxylation product as its methyl ester. **6b** was obtained as an inseparable mixture with ethyl phenyl sulfone (30.1 mg, **6b**:$EtSO_2Ph$ = 86:14), and the yield of **6b** was calculated to be 59%.



methyl phenethyl 2-methylmalonate 6a

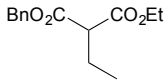
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30 (t, *J* = 7.5 Hz, 2H), 7.24-7.18 (m, 3H), 4.40-4.31 (m, 2H), 3.68 (s, 3H), 3.43 (q, *J* = 7.4 Hz, 1H), 2.95 (t, *J* = 7.2 Hz, 2H), 1.39 (d, *J* = 7.4 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 170.4, 169.9, 137.5, 128.9, 128.4, 126.6, 65.7, 52.4, 46.0, 34.9, 13.5; IR (ATR) 3029, 2992, 2955, 1735, 1457, 1380, 1334, 1222, 1160, 1082, 1034 cm^{-1}; HR-MS (FD^+): Calcd for $C_{13}H_{16}O_4$ [M^+]: 236.10486; Found: 236.10413.

Procedure for the hydrocarboxylation of methacrylate and crotonate (Table 3, conditions B)



Catalyst (0.0025 mmol) and HCO_2Cs (26.7 mg, 0.15 mmol) were placed in a test tube, and a solution of alkene (0.1 mmol) in DMF (2.0 mL) was added under Ar. The mixture was stirred at 80 °C for 6 h. After 1N HCl aq. was added, the mixture was extracted with diethyl ether three times. The combined organic layers were washed with water twice and sat. NaCl aq., and dried over magnesium sulfate. After removal of solvent under reduced pressure,

the residue was treated with BnBr (24 μL, 0.20 mmol), K_2CO_3 (28.0 mg, 0.2 mmol) and NaI (3.0 mg, 0.02 mmol) in DMF (2.0 mL) at room temperature. After 12 h, water was added, and the mixture was extracted with diethyl ether three times. The combined organic layers were washed with water twice and sat. NaCl aq., and dried over magnesium sulfate. After solvent was removed under reduced pressure, the residue was purified by preparative TLC (hexane:ethyl acetate = 3:1) to afford carboxylation product.

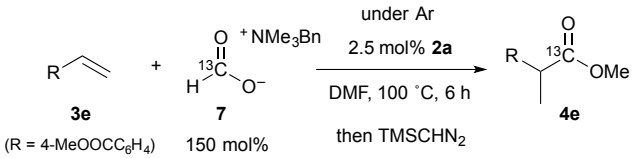


benzyl ethyl 2-ethylmalonate 6c

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38-7.30 (m, 5H), 5.21-5.15 (m, 2H), 4.16 (q, *J* = 7.3 Hz, 2H), 3.31 (t, *J* = 7.3 Hz, 1H), 1.95 (quintet, *J* = 7.3 Hz, 2H), 1.21 (t, *J* = 7.3 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 169.3, 169.2, 135.6, 128.5, 128.3, 128.1, 66.9, 61.3, 53.5, 22.2, 14.0, 11.8; IR (ATR) 2969, 2942, 1259, 1153, 1088, 1046, 1024 cm^{-1}; HR-MS (FD$^+$): Calcd for $C_{14}H_{18}O_4$ [M$^+$]: 250.12051; Found: 250.12149.

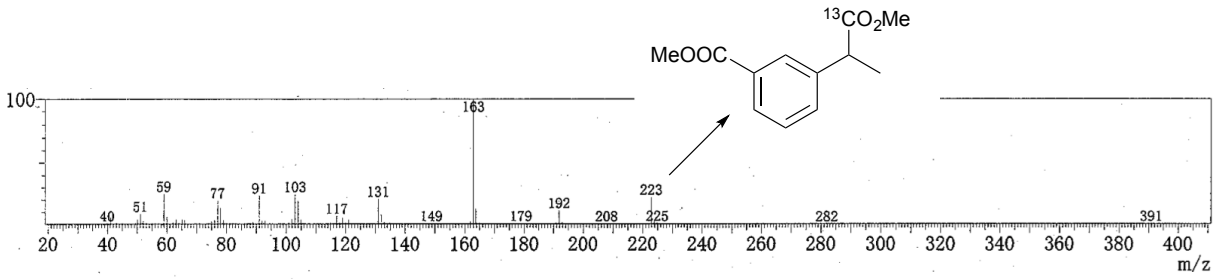
Procedure for ^{13}C labeling experiment (Table 4)

Under Ar (Entry 1)



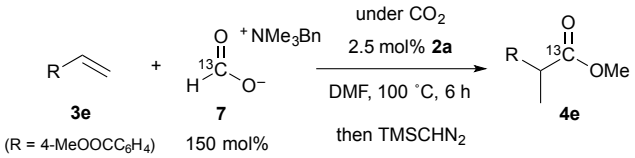
2a (1.7 mg, 0.0025 mmol) and H^{13}COONBnMe$_3$ **7** (29.4 mg, 0.15 mmol) were placed in a test tube, and a solution of **3e** (16.2 mg, 0.10 mmol) in DMF (1 mL) was added under Ar. The reaction mixture was stirred at 100 °C for 6 h and then quenched with 2 mL 1N HCl aq. The resulting mixture was extracted with diethyl ether three times. The combined organic layers were washed with water and sat. NaCl aq., and then dried over $MgSO_4$. After removal of solvent under reduced pressure, the crude residue was dissolved in Et_2O (0.8 mL) and MeOH (0.4 mL) and cooled to 0 °C. To the solution was added $TMSCHN_2$ (2.0 mol/L in Et_2O, 0.2 mL). The resulting mixture was stirred at 0 °C for 0.5 h. Solvent was removed under reduced pressure, and the crude residue was purified by PTLC (hexane:ethyl acetate = 2:1) to afford colorless oil **4e** (18.3 mg, 0.082 mmol) in 82% yield. The ^{13}C-content was determined to be >98% by EI-MS, in which the relative abundance of non-labeled **4e** fragment (*m*/*z* 222) to ^{13}C-labeled fragment (*m*/*z* 223) is 1.61%.

Figure S1. EI-MS spectra of **4e** obtained under Ar atmosphere.



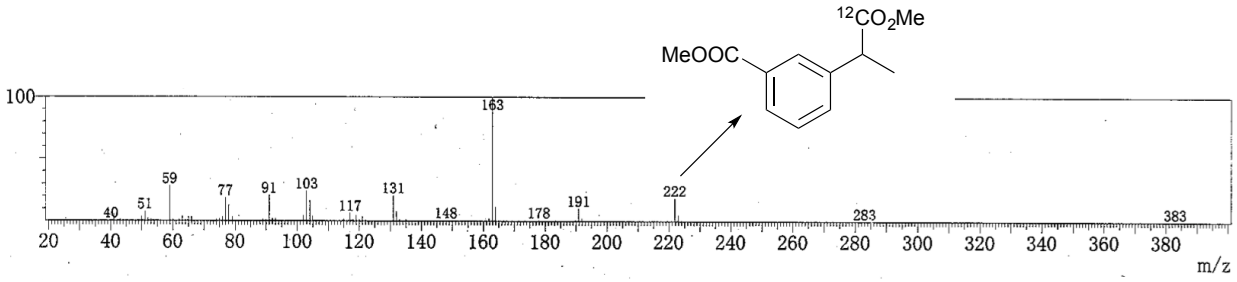
#	m/z	Abundance	#	m/z	Abundance	#	m/z	Abundance	#	m/z	Abundance
45	93.00	2.51	59	119.95	1.05	73	147.90	0.22	87	192.80	1.26
46	94.00	0.23	60	120.95	3.50	74	148.80	0.57	88	193.80	0.26
47	98.00	0.22	61	121.90	0.27	75	159.80	0.30	89	207.80	0.25
48	101.00	0.96	62	128.90	0.16	76	160.80	0.46	90	209.80	0.05
49	102.00	4.11	63	129.90	0.18	77	161.85	1.91	91	221.90	0.36
50	102.95	24.66	64	130.90	20.64	78	162.85	100.00	92	222.90	22.06
51	104.00	19.37	65	131.90	7.71	79	163.85	12.66	93	223.90	2.64
52	104.95	3.95	66	132.90	1.23	80	164.90	1.15	94	224.90	0.44
53	105.90	0.54	67	133.95	0.56	81	175.90	0.22	95	281.90	0.01
54	114.95	1.33	68	134.90	1.23	82	176.90	0.11	96	389.90	0.18
55	115.95	0.48	69	135.90	0.35	83	177.90	0.47	97	390.90	0.20
56	116.95	6.75	70	144.90	0.20	84	178.90	0.62	98	391.90	0.17
57	117.95	1.21	71	145.90	0.39	85	190.75	0.63			
58	118.95	4.96	72	146.90	0.24	86	191.85	11.10			

Under CO_2 (Entry 2)



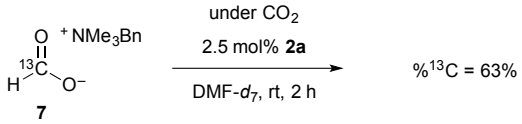
2a (1.7 mg, 0.0025 mmol) and $H^{13}COONBnMe_3$ (29.4 mg, 0.15 mmol) were placed in a test tube (φ = 20 mm), and a solution of **3e** (16.2 mg, 0.10 mmol) in DMF (1 mL) was added under Ar. The Ar atmosphere was replaced by CO_2 by using a balloon, and then the reaction tube was closed. The volume of the closed test tube is ca. 40 cm^3, and the amount of CO_2 inside is calculated to be ca. 1.8 mmol. The reaction mixture was stirred at 100 °C for 6 h, and then quenched with 1N HCl aq. The resulting mixture was extracted with diethyl ether three times. The combined organic layers were washed with water and sat. NaCl aq., and then dried over $MgSO_4$. After removal of solvent under reduced pressure, the crude residue was dissolved in Et_2O (0.8 mL) and MeOH (0.4 mL) and cooled to 0 °C. To the solution was added $TMSCHN_2$ (2.0 mol/L in Et_2O, 0.2 mL). The resulting mixture was stirred at 0 °C for 0.5 h. Solvent was removed under reduced pressure, and the crude residue was purified by PTLC (hexane:ethyl acetate = 2:1) to afford colorless oil **4e** (14.5 mg, 0.065 mmol) in 65% yield. The ^{13}C-content was determined to be ca. 12% by EI-MS, in which the relative abundance of ^{13}C-labeled **4e** fragment (*m*/*z* 223) to non-labeled fragment (*m*/*z* 222) is 20.7%.

Figure S2. EI-MS spectra of **4e** obtained under CO_2 atmosphere.



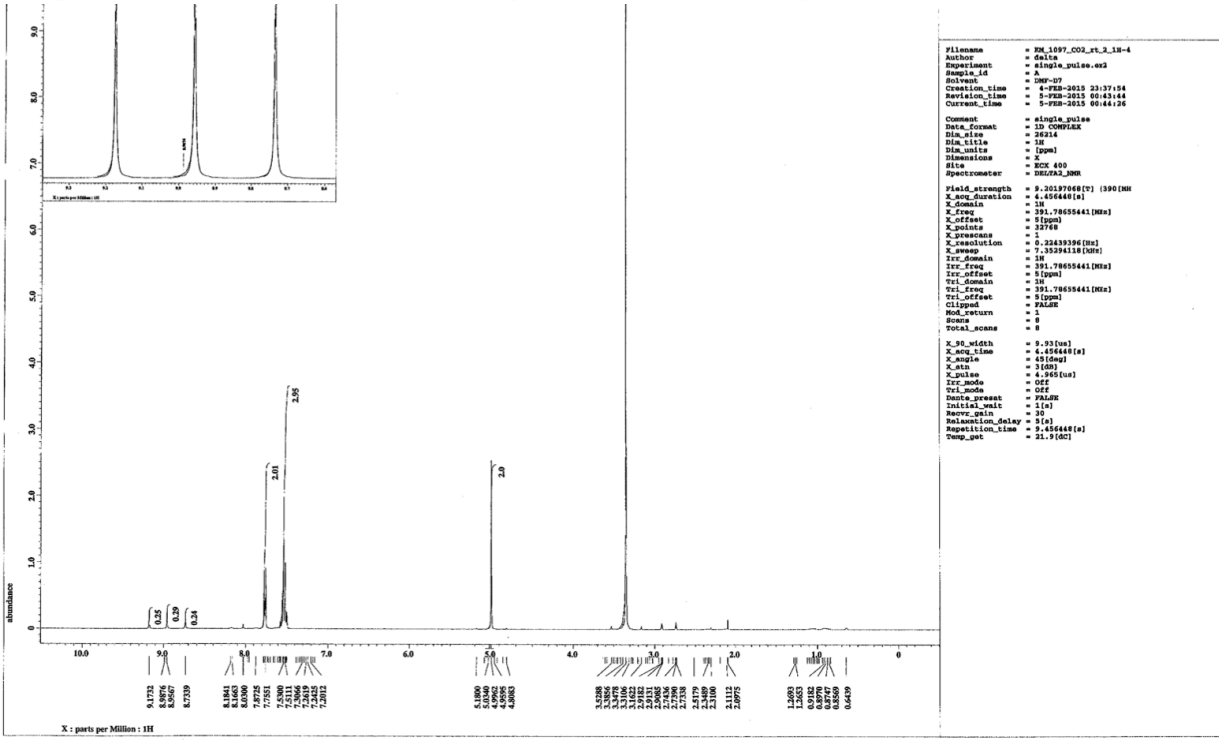
#	m/z	Abundance	#	m/z	Abundance	#	m/z	Abundance	#	m/z	Abundance
45	100.95	0.80	56	118.95	4.74	67	148.00	0.41	78	189.75	0.69
46	101.95	4.14	57	120.00	0.90	68	149.00	0.36	79	190.80	10.17
47	102.95	24.10	58	120.95	3.35	69	159.00	0.34	80	191.85	2.08
48	104.00	16.71	59	122.00	0.42	70	160.90	0.23	81	192.80	0.31
49	104.95	3.79	60	130.90	20.69	71	161.85	1.95	82	193.80	0.20
50	106.00	0.37	61	131.90	7.63	72	162.85	100.00	83	220.90	0.31
51	107.00	0.33	62	132.90	1.28	73	163.85	11.20	84	221.90	18.64
52	115.00	1.20	63	133.90	0.23	74	164.90	0.80	85	222.90	4.86
53	116.00	0.31	64	135.00	1.44	75	175.90	0.17	86	223.90	0.54
54	116.95	6.22	65	138.00	0.25	76	177.90	0.86	87	283.00	0.03
55	117.95	1.28	66	147.00	0.30	77	178.90	0.31	88	383.00	0.22

The reaction of $H^{13}COONMe_3Bn$ with **2a** under CO_2 (additional information, Ref 16)

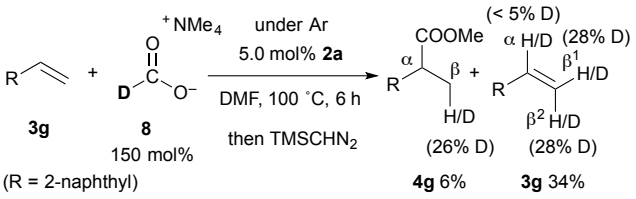


A solution of **2a** (1.7 mg, 0.0025 mmol) and $H^{13}COONBnMe_3$ (19.6 mg, 0.1 mmol) in DMF (0.5 mL) was placed in an NMR tube under Ar, and the Ar atmosphere was replaced by CO_2. After the reaction mixture was allowed to stand at rt for 2 h, the ^{13}C content of **7** was measured by ^1H NMR, in which the formyl proton of **7-^{13}C** appeared as a doublet coupled with ^{13}C whereas that of non-labeled **7-^{12}C** appeared as a singlet. The ^{13}C content was determined to be 63%, demonstrating reversibility of decarboxylation step of formate salt promoted by **2a**.

Figure S3. ^1H NMR spectra of **7** with **2a** after 2 h at room temperature under CO_2 atmosphere.



Procedure for deuterium labeling experiment (Scheme 2)



2a (3.4 mg, 0.005 mmol) and $DCOONMe_4$ (18.0 mg, 0.15 mmol) were placed in a test tube, and a solution of **3g** (15.4 mg, 0.10 mmol) in DMF (1 mL) was added under Ar. The reaction mixture was stirred at 100 °C for 6 h and then quenched with H_2O and 1N NaOH aq. The resulting mixture was extracted with diethyl ether three times. The combined organic layers were washed with sat. NaCl aq., and dried over $MgSO_4$. After removal of solvent under reduced pressure, the crude residue was purified by PTLC (hexane:ethyl acetate = 10:1) to afford partially deuterated **3g-*d*** (5.2 mg, 0.034 mmol) in 34% yield. The aqueous layer was acidified with 4M HCl aq., and then the resulting mixture was extracted with diethyl ether three times. The combined organic layers were washed with sat. NaCl aq. and dried over $MgSO_4$. After removal of solvent under reduced pressure, the crude residue was dissolved in Et_2O (0.8 mL) and MeOH (0.4 mL) and cooled to 0 °C. To the solution was added $TMSCHN_2$ (2.0 mol/L in Et_2O, 0.2 mL). The resulting mixture was stirred at 0 °C for 0.5 h. Solvent was removed under reduced pressure, and the crude residue was purified by PTLC (hexane:ethyl acetate = 10:1) to afford colorless oil **4g** (1.3 mg, 0.006 mmol) in 6% yield. The D-content of **4g** was determined to be 26% by H-NMR. The D-content of **3g** was determined to be α-H = 6%, β^1-H = 28%, β^2-H = 28% by ^{1}H-NMR.

Figure S4. ^{1}H NMR spectra of **4g**

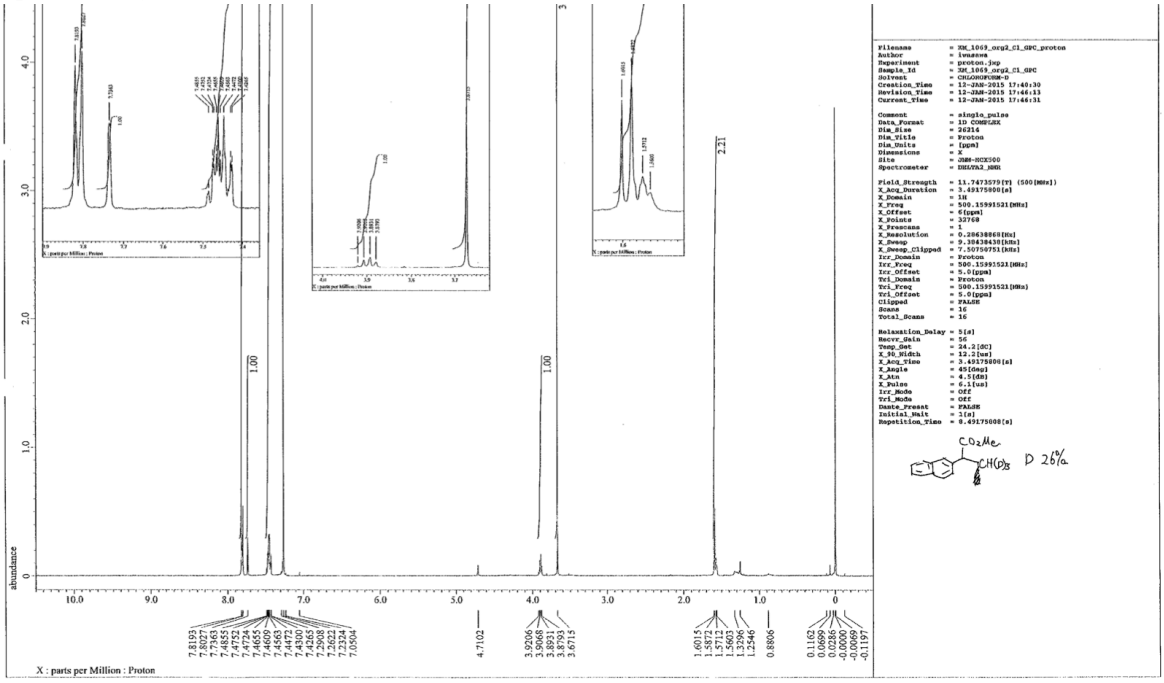
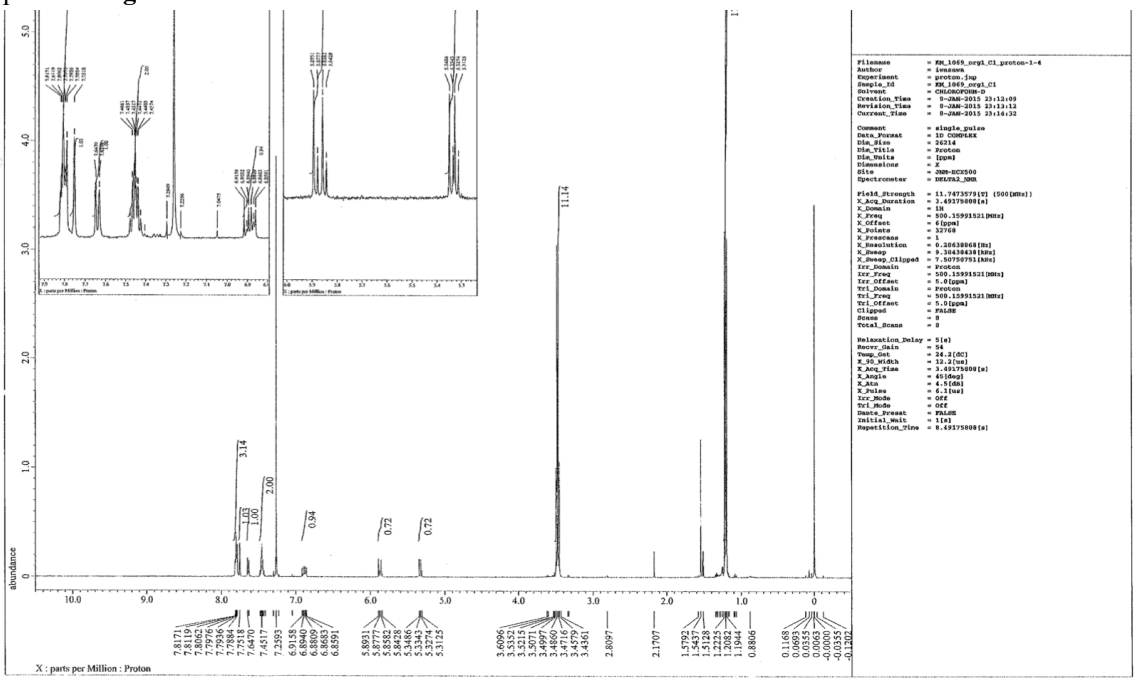
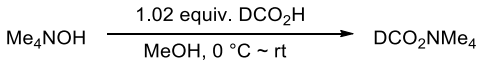


Figure S5. ^{1}H NMR spectra of **3g**



Preparation of DCO_2NMe_4



To a solution of tetramethylammonium hydroxide (25 wt% in methanol, 2.1 mL, 5.0 mmol) was added DCOOH (0.20 mL, 5.1 mmol) dropwise at 0 °C. The resulting mixture was stirred at room temperature for 2 h. Solvent was removed under reduced pressure to give white solid, which was washed with pentane and dried under vacuum to afford DCO_2NMe_4 as a white solid (600 mg, 5.0 mmol) in 100% yield.

^{1}H NMR (500 MHz, CD_3OD) δ = 3.20 (s, 12H); ^{13}C-NMR (125 MHz, CD_3OD) δ = 170.1 (t, J = 28.6 Hz), 55.9 (t, J = 4.2 Hz). The D-content was determined to be ca. 100% by ^{1}H NMR.

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