Supplementary Material (ESI) for Chemical Communications

Supporting Information

Ruthenium-catalysed Regioselective Allylic Alkylation of Allyl Acetates: High Linear Selectivity by $Ru_3(CO)_{12}$ with 2-(Diphenylphosphino)benzoic acid

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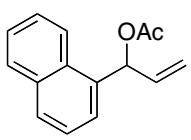
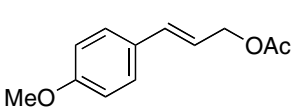
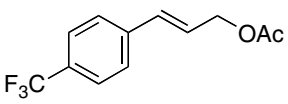
General and Materials: All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. NMR spectra were recorded on a JEOL JNM MH400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) or JNM MH-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal SiMe4 standard for ^{1}H NMR, and to an external 85% H_3PO_4 standard for ^{31}P NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 ˚C unless otherwise noted. $Ru_3(CO)_{12}$ and 2-(diphenylphosphino)benzoic acid were purchased from Aldrich, and were used without further purification. Allyl acetates **1a**,[1] **1b**,[2] **1c**,[2] **1e**,[3] **1f**[2] and **2e**[4] were prepared according to the literatures. Other allyl acetates **1d**,[5] **2b**,[6] **2c**,[7] **2d**[8] and **2f**[9] were prepared by reaction of corresponding alcohols[1,10,11] with acetic anhydride. Other reagents and solvents were purchased from common commercial sources and were used as received or purified by distillation from appropriate drying agents.



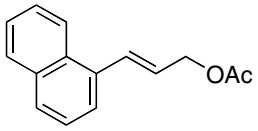
Allyl Acetate **1d:** ^{1}H NMR (500 MHz, $CDCl_3$) 2.08 (s, 3H), 5.28-5.33 (m, 2H), 6.19 (ddd, *J* = 5.5, 10.5, 16.9 Hz, 1H), 7.00 (d, *J* = 5.5 Hz, 1H), 7.45–7.55 (m, 3H), 7.59 (d, *J* = 6.8, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.86–7.88 (m, 1H), 8.12 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 20.98, 73.43, 117.05, 123.61, 125.11, 125.26, 125.60, 126.17, 128.66, 128.84, 130.56, 133.75, 134.33, 135.78, 169.79.



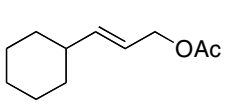
Allyl Acetate **2b**: ^{1}H NMR (500 MHz, $CDCl_3$) 2.09 (s, 3H), 3.80 (s, 3H), 4.70 (dd, *J* = 1.4 Hz, 6.4, 2H), 6.15 (dt, *J* = 6.7, 15.6 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.85 (m, 2H), 7.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 20.94, 55.17, 65.28, 113.91, 120.75, 127.79, 128.86, 133.97, 159.51, 170.83



Allyl Acetate **2c**: ^{1}H NMR (500 MHz, $CDCl_3$) 2.13 (s, 3H), 4.76 (dd, *J* = 1.25, 6.25 Hz, 2H), 6.38 (dt, *J* = 6.25, 15.5 Hz, 1H), 6.68 (d, *J* = 15.5 Hz, 1H), 7.48 (d, *J* = 8 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 20.71, 64.42, 125.43, 125.46, 126.00, 126.63, 129.66 (q, J = 32.68), 132.12, 139.64, 170.58.



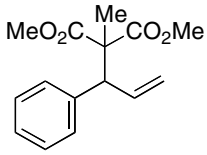
Allyl Acetate **2d**: ^{1}H NMR (500 MHz, $CDCl_3$) 2.14 (s, 3H), 4.84 (dd, *J* = 1.25, 6.25 Hz, 2H), 6.32 (dt, *J* = 6.25, 15.75 Hz, 1H), 7.42 (d, *J* = 16.5 Hz, 1H), 7.45 (d, *J* = 8.00 Hz, 1H), 7.48–7.54 (m, 2H), 7.60 (d, *J* = 7.00 Hz, 1H), 7.79 (d, *J* = 8.00 Hz, 1H), 7.84–7.86 (m, 1H), 8.19 (d, *J* = 8.00 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 20.74, 64.91, 123.40, 123.83, 125.31, 125.60, 125.93, 126.14, 128.14, 128.31, 130.85, 130.99, 133.33, 133.68, 170.51



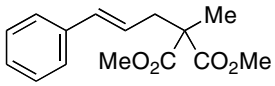
Allyl Acetate **2f**: ^{1}H NMR (500 MHz, $CDCl_3$) 1.04–1.11 (m, 2H), 1.16 (tt, *J* = 3.21, 12.37 Hz, 1H), 1.22–1.31 (m, 2H), 1.63–1.67 (m, 1H), 1.71–1.74 (m, 4H), 1.93–2.00 (m, 1H), 2.06 (s, 3H), 4.50 (d, *J* = 6.4 Hz, 2H), 5.48–5.54 (m, 1H), 5.71 (dd, *J* = 6.9, 15.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 20.99, 25.90, 26.06, 32.49, 40.28, 65.49, 121.22, 142.09, 170.82.

General Procedure of Catalytic Allylic Alkylation. The reaction conditions and results are shown in Table 1. A typical procedure is given for the reaction of 1-phenyl-2-propenyl acetate (**1a**) (entry 6). To a solution of $Ru_3(CO)_{12}$ (21.1 mg, 0.033 mmol), 2-(diphenylphosphino)benzoic acid (30.6 mg, 0.10 mmol) in THF (1 mL) was added 1-phenyl-2-propenyl acetate (**1a**) (176 mg, 1.0 mmol) and dimethyl methylmalonate (219 mg, 1.5 mmol). LiHMDS (1.4 mmol. 1.4 mL of 1.0M in THF) was slowly added at 0 ˚C, and stirred at 60 ˚C for 12 h. The reaction mixture was quenched with 1*N* HCl (0.5 mL), then extracted with ether (3 x 2 mL). The combined organic

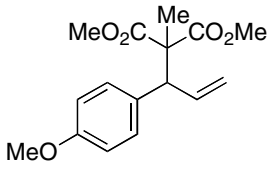
layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/EtOAc = 10/1) to give 255 mg (97%) of a mixture of branch isomer **3a** and linear isomer **4a**. The ratio of **3a** and **4a** was determined to be 1 : 99 by 1H NMR of the crude materials.



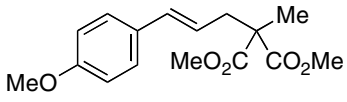
branch **3a**[6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) 1.43 (s, 3H), 3.62 (s, 3H), 3.71 (s, 3H), 4.15 (d, *J* = 8.70 Hz, 1H), 5.09–5.15 (m, 2H), 6.32 (ddd, *J* = 16.96, 10.10, 8.7 Hz, 1H), 7.22–7.28 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) 18.37, 52.35, 54.49, 58.83, 117.75, 127.11, 128.14, 129.46, 136.84, 139.03, 171.25, 171.45.



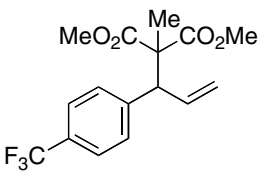
linear **4a**[6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) 1.46 (s, 3H), 2.77 (dd, *J* = 1.40, 7.33Hz, 2H), 3.74 (s, 6H), 6.05–6.11 (m, 1H), 6.45 (d, *J* = 15.55 Hz, 1H), 7.20–7.34 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) 20.05, 39.47, 52.53, 53.97, 124.12, 126.12, 127.39, 128.47, 134.12, 137.08, 172.32.



branch **3b**[6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) 1.42 (s, 3H), 3.63 (s, 3H), 3.71 (s, 3H), 3.78 (s, 3H), 4.10 (d, *J* = 8.70 Hz, 1H), 5.07–5.13 (m, 2H), 6.28 (ddd, *J* = 8.70, 8.48, 5.28 Hz, 1H), 6.80–6,82 (m, 2H), 7.15–7.17 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 18.23, 52.29, 53.66, 53.95, 55.06, 58.86, 113.48, 117.39, 130.43, 130.94, 137.05, 158.52, 171.27, 171.46.

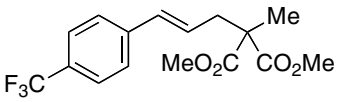


linear **4b**[6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) 1.45 (s, 3H), 2.74 (dd, *J* = 15.0, 7.75 Hz, 2H), 3.73 (s, 6H), 3.80 (s, 3H), 5.90–5.96 (m, 1H), 6.38 (d, *J* = 15.55 Hz, 1H), 6.81–6.84 (m, 2H), 7.25–7.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 19.88, 39.35, 52.37, 53.90, 55.11, 113.78, 121.65, 127.23, 129.79, 133.39, 158.96, 172.25.

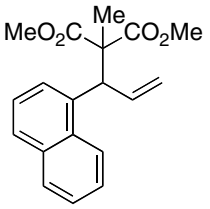


branch **3c:** ^{1}H NMR (500 MHz, $CDCl_3$) 1.44 (s, 3H), 3.64 (s, 3H), 3.71 (s, 3H), 4.20 (d, *J* = 8.70 Hz, 1H), 5.09–5.19 (m, 2H), 6.30 (ddd, *J* = 16.96, 10.05, 8.70 Hz, 1H), 7.39 (d, *J* = 8.25 Hz,

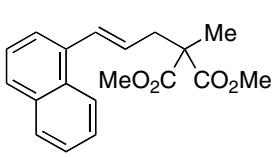
2H), 7.54 (d, J = 8.25 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 18.52, 52.46, 52.54, 54.28, 58.60, 118.59, 123.00, 125.01, 129.33 (d, J_{CF} = 32.63 Hz), 129.71, 136.01, 143.35, 170.97, 171.17. EI-HRMS m/z: 330.1081 (Calcd for $C_{16}H_{17}F_3O_4$: 330.1079)



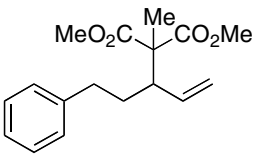
linear **4c:** ^{1}H NMR (500 MHz, $CDCl_3$) 1.46 (s, 3H), 2.79 (dd, J = 7.33, 1.35 Hz, 2H), 3.74 (s, 6H), 6.18–6.24 (m, 1H), 6.48 (d, J = 16.06 Hz, 1H), 7.42 (d, J = 8.25 Hz, 2H), 7.54 (d, J = 8.25 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 20.11, 39.45, 52.56, 53.84, 125.40, 125.43, 126.33, 127.16, 129.18 (d, J_{CF} = 32.31 Hz), 132.73, 140.45, 172.13. HR-MS m/z: 330.1071 (Calcd for $C_{16}H_{17}F_3O_4$: 330.1079).



branch **3d**: ^{1}H NMR (500 MHz, $CDCl_3$) 1.48 (s, 1H), 3.40 (s, 3H), 3.75 (s, 3H), 5.09–5.14 (m, 2H), 5.20 (d, J = 8.25 Hz, 1H), 6.42 (ddd, J = 16.96, 10.00, 8.25 Hz, 1H), 7.41–7.54 (m, 4H), 7.74 (dd, J = 7.30, 1.80 Hz, 1H), 7.83 (dd, J = 8.25, 1.35 Hz, 1H), 8.25 (d, J = 8.70 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 19.21, 47.08, 52.26, 52.42, 59.04, 117.45, 123.26, 125.07, 125.38, 125.95, 126.17, 127.67, 128.92, 132.30, 133.97, 135.40, 137.80, 171.74, 171.76. HR-MS m/z: 312.1358 (Calcd for $C_{19}H_{20}O_4$: 312.1361).

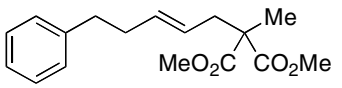


linear **4d**: ^{1}H NMR (500 MHz, $CDCl_3$) 1.53 (s, 3H), 2.90 (dd, J = 7.55, 1.15 Hz, 2H), 3.75 (s, 6H), 6.08–6.14 (m, 1H), 7.19 (d, J = 15.56 Hz, 1H), 7.41–7.52 (m, 4H), 7.76 (d, J = 8.25 Hz, 1H), 7.83–7.85 (m, 1H), 8.05–8.07 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 20.48, 39.69, 52.58, 54.07, 65.84, 123.63, 123.98, 125.60, 125.71, 125.93, 127.52, 127.79, 128.47, 131.60, 133.51, 134.97, 172.35. HR-MS m/z: 312.1365 (Calcd for $C_{19}H_{20}O_4$: 312.1361).

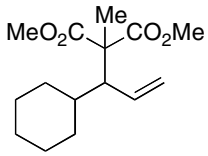


branch **3e**: ^{1}H NMR (500 MHz, $CDCl_3$) 1.38 (s, 3H), 2.46-2.52 (m, 1H), 2.68-2.72 (m, 1H), 2.76 (dt, J = 2.05, 11.45 Hz, 1H), 3.66 (s, 3H), 3.68(s, 3H), 5.12 (dd, J = 1.80, 16.96 Hz, 1H), 5.19 (dd, J = 1.80, 10.10 Hz, 1H), 5.64 (dt, J = 10.10, 16.96 Hz, 1H), 7.16-7.19 (m, 2H), 7.26-7.29 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) 17.18, 31.86, 34.01, 48.85,

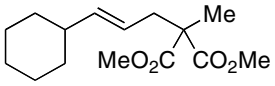
52.36, 57.80, 119.04, 125.76, 128.27, 128.46, 136.84, 142.04, 171.70. EI-HRMS m/z: 290.1521 (Calcd for $C_{17}H_{22}O_4$: 290.1518).



linear **4e**: ^{1}H NMR (500 MHz, $CDCl_3$) 1.34 (s, 3H), 2.31 (dd, *J* = 14.68, 6.88 Hz, 2H), 2.54 (d, *J* = 7.30 Hz, 2H), 2.65 (dd, *J* = 8.25, 7.30 Hz, 2H), 3.70 (s, 6H), 5.27–5.35 (m, 1H), 5.51–5.58 (m, 1H), 7.15–7.19 (m, 3H), 7.25–7.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 19.73, 34.29, 35.83, 38.93, 52.42, 53.78, 124.42, 125.76, 128.26, 128.38, 134.50, 141.72, 172.45. HR-MS m/z: 290.1521 (Calcd for $C_{17}H_{22}O_4$: 290.1518)



branch **3f**: ^{1}H NMR (500 MHz, $CDCl_3$) 1.58 (s, 3H), 2.67 (dd, J = 4.00, 10.50 Hz, 1H), 3.66 (s, 3H), 3.72 (s, 3H), 5.02 (dd, J = 2.01, 17.50 Hz, 1H), 5.07 (dd, J = 2.01, 10.50 Hz, 1H), 5.66 (dt, J = 10.50, 17.50 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) 17.57, 54.04, 54.36, 57.92, 60.42, 118.36, 135.85, 171.95, 172.19. EI-HRMS m/z: 268.1668 (Calcd for $C_{17}H_{22}O_4$: 268.1675).



linear **4f**: ^{1}H NMR (500 MHz, $CDCl_3$) 0.98–1.07 (m, 2H), 1.08–1.17 (m, 1H), 1.38 (s, 3H), 1.60–1.71 (m, 5H), 1.87–1.93 (m, 1H), 2.53 (d, *J* = 7.30 Hz, 2H), 3.71 (s, 6H), 5.21–5.27 (m, 1H), 5.44 (dd, *J* = 15.10, 6.85 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 19.77, 25.92, 26.08, 32.99, 38.99, 40.73, 52.32, 53.98, 121.01, 141.55, 172.46.

Preparation of π-allylruthenium complex 5 [Ru(1-phenyl-allyl)(L1)(CO)$_2$] and 5'

$Ru_3(CO)_{12}$ (1.0 g, 1.56 mmol), 2-(diphenylphosphino)benzoic acid (**L1**) (1.4 g, 4.69 mmol), 1-phenyl-2-propenyl acetate (**1a**) (3.3 g, 18.7 mmol) and dimethyl methylmalonate (2.1 g, 14.0 mmol) were suspended in 15 mL of THF in a screw-capped vial. The mixture was stirred at 0 ˚C for 5 min, then LiHMDS (14.0 mmol. 14 mL of 1.0M in THF) was slowly added at same temperature. The reaction mixture was then stirred at 60 ˚C for 2 h. The mixture was absorbed onto silica gel and chromatographed with ethyl acetate/hexane (50/50~100/0), then evaporated. The gummy residue was dissolved in a minimum amount of ethyl acetate and recrystallized by slow diffusion of pentane into the concentrated ethyl acetate solution at room

temperature, yielding orange prismatic crystals; yield 660 mg (71% as ethyl acetate co-crystals). A suitable crystal was selected for the X-ray study. On the other hands, the mother liquor was concentrated and gave ruthenium complex **5'** as a yellow powder; ca.100 mg. The ^{1}H NMR and ^{31}P NMR revealed that the ruthenium complex **5** (28.22 ppm in ^{31}P NMR) slowly converts to ruthenium complex **5'** (34.59 ppm in ^{31}P NMR). **Ruthenium complex 5**: ^{1}H NMR (500 MHz, $CDCl_3$) 2.58 (dd, *J* = 4.55, 12.90 Hz, 1H), 3.12 (d, *J* = 12.90 Hz, 1H), 4.42 (dd, *J* = 4.55, 7.80 Hz, 1H), 5.94 (dt, *J* = 7.80, 12.90 Hz, 1H), 6.32–6.37 (m, 3H), 6.50–6.54 (m, 2H), 7.07–7.13 (m, 5H), 7.32–7.40 (m, 4H), 7.44–7.48 (m, 3H), 7.65–7.68 (m, 1H), 8.38 (ddd, *J* = 1.35, 4.6, 7.8 Hz, 1H). selected ^{13}C NMR (125 MHz, $CDCl_3$) 14.16, 21.00, 61.64 (d, *J* = 17.30), 80.53 (d, *J* = 4.80), 102.96, 139.51, 140.37 (d, *J* = 11.54), 169.28 (d, *J* = 7.69), 171.09, 195.36 (d, *J* = 4.81), 197.76 (d, *J* = 11.54). ^{31}P NMR (202MHz, $CDCl_3$) 28.22. mp 144-147 ˚C (decomp). **Ruthenium complex 5'**: selected ^{1}H NMR (500 MHz, $CDCl_3$) 1.74 (d, *J* = 12.58 Hz, 1H), 3.60 (d, *J* = 7.80 Hz, 1H), 4.48 (dd, *J* = 12.58 Hz, J_{HP} = 5.50 Hz, 1H), 5.88 (dt, *J* = 7.80, 12.58 Hz, 1H). selected ^{13}C NMR (125 MHz, $CDCl_3$) 14.20, 21.06, 57.07, 60.41, 89.12, 89.32, 104.76, 139.65, 139.68, 140.36. ^{31}P NMR (202MHz, $CDCl_3$) 34.59. mp 174-176 ˚C (decomp).

Stoichiometric reaction of 5: To a solution of ruthenium complex **5** (30 mg, 0.050 mmol) in THF (1.0 mL) was added dimethyl methylmalonate (10 mg, 0.070 mmol). LiHMDS (0.07 mmol, 70 μL of 1.0M in THF) was slowly added at 0 ˚C, and stirred at room temperature for 26 h. The reaction mixture was quenched with 1*N* HCl (50 μL), and extracted with ether (1.0 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The 1H NMR of the crude materials indicated the 100% conversion and the ratio of **3a** and **4a** to be 1:99.

Stoichiometric reaction of 5': To a solution of ruthenium complex **5'** (26 mg, 0.044 mmol) in THF (1.0 mL) was added dimethyl methylmalonate (9.0 mg, 0.061 mmol). LiHMDS (0.066 mmol, 66 μL of 1.0M in THF) was slowly added at 0 ˚C, and stirred at room temperature for 26 h. The reaction mixture was quenched with 1*N* HCl (50 μL), and extracted with ether (1.0 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The ^{1}H NMR of the crude materials indicated the 80% conversion and the ratio of **3a** and **4a** to be 79:21.

Supplementary Material (ESI) for Chemical Communications

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