Supporting Information

Rhodium Catalyzed Three-Component Reaction of Diazoacetates, Titanium(IV) Alkoxides and Aldehydes

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In addition, ^{1}H and ^{13}C NMR spectra for all compounds listed above to support it's purity, this material is available free of charge from authors (E-mail:chongdaolu@yahoo.com).

General methods. HRMS (ESI) Mass spectra were recorded on BRUCKER FT-MS. NMR spectra were recorded on a Brucker-300MHz spectrometer. Dichloromethane was distilled over calcium hydride. All reactions were handled under Ar unless otherwise indicated.

General procedure for the three-component reaction of aryl diazoacetates, titanium(IV) alkoxides and aldehydes: To a 8 mL CH_2Cl_2 solution of Rh(II) catalyst (0.01 mmol), titanium alkoxide (1.1 mmol) and aldehyde (1.1 mmol) was added diazoacetate (1.0 mmol) in 4 mL of CH_2Cl_2 via a syringe pump over 10 min under refluxing. After completed addition, the reaction mixture was cooled to room temperature and the solvent was removed, then 30 mL ethyl acetate was added, the reaction mixture was washed with 20 mL saturated aqueous NH_4Cl and the aqueous phase was extracted with 20 mL of EtOAc (2×). The combined organic phase was washed with 20 mL water, then washed with saturated brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed, and a portion of crude product was subjected to ^1H NMR analysis for determination of the product ratio. The crude product was purified by flash chromatography on silica gel by using petroleum ether:EtOAc=10:1 as eluent to give three-component products **4**+**5**.

Table 1. The diagnostic ^{13}C NMR assignments (δ_{COOMe}) of compounds **4a-m** and **5a-m:** δ_{COOMe}(**5**)> δ_{COOMe}(**4**)

	4 (δ_{COOMe} ppm) **erythro-**	**5** (δ_{COOMe} ppm) **threo-**
a	171.5	172.9
b	172.4	172.8
c	172.1	172.6
d	172.3 (X-ray structure available)	173.2
e	172.0	172.9
f	172.6	173.5
g	173.5	No detection[a]
h	173.5	174.0
i	173.1	174.0
j	171.7	172.4
k	171.7	172.4
l	172.2	172.6
m	171.9	172.4

[a] **4g**:**5g** ≥ 20:1.

(2S*,3S*) and (2S*,3R*) Methyl 3-hydroxy-2-isopropoxy-3-(4-methoxy-phenyl)-2-phenyl-propionate (**4a**+**5a**) (mixture of diastereomers) ^1H NMR (300 MHz, $CDCl_3$) δ 7.39-7.14 (m, 5 H; erythro-, **4a**), (7.39-7.14 (m, 5 H); threo-, **5a**), (7.04-7.01 (m, 2 H)), 6.98-6.94 (m, 2 H), (6.71-6.68 (m, 2 H)), 6.70-6.66 (m, 2 H), (5.33 (d, *J* = 6.0 Hz, 1 H)), 5.23 (d, *J* = 6.6 Hz, 1 H), 3.98-3.94 (m, 1 H), (3.98-3.94 (m, 1 H)), (3.74 (s, 3 H)), 3.73 (s, 3 H), (3.72 (s, 3 H)), 3.62 (s, 3H), 3.54 (d, *J* = 6.6 Hz, 1 H), (3.36 (d, *J* = 6.0 Hz, 1 H)), 1.23 (d, *J* = 6.0 Hz, 3 H), (1.20 (d, *J* = 6.0 Hz, 3 H)), (0.97 (d, *J* = 6.0 Hz, 3 H)), 0.86 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (172.9), 171.5, (159.1), 159.0, 137.0, (136.5), 131.6, (130.8), (129.3), 129.2, 129.0, (128.6), 128.2, (128.1), 127.5, (127.5), 112.7, (112.7), (88.1), 87.3, 77.8, (77.6), (69.8), 69.1, (55.14), 55.13, (52.0), 51.8, (24.0), 23.8, (23.7), 23.6. HRMS: calcd for $C_{20}H_{24}O_5$: 344.1624; found: 344.1612 $[M+ NH_4]^+$.

(2S*,3S*) and (2S*,3R*) Methyl 3-hydroxy-2-isopropoxy-2,3- diphenyl-propionate (**4b**+**5b**) (mixture of diastereomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.01 (m, 10 H; erythro-, **4b**), (7.35-7.01 (m, 10 H); threo-, **5b**), (5.36 (d, *J* = 4.5 Hz, 1 H)), 5.28 (d, *J* = 5.7 Hz, 1 H), 3.98-3.90 (m, 1 H), (3.98-3.90 (m, 1 H)), (3.67 (s, 3 H)), 3.61 (d, *J* = 5.7 Hz, 1 H), 3.60 (s, 3 H), 3.46 (d, *J* = 4.5 Hz, 1 H), 1.22 (d, *J* = 6.0 Hz, 3 H), (1.19 (d, *J* = 6.0 Hz, 3 H)), (0.94 (d, *J* = 6.0 Hz, 3 H)), 0.87 (d, *J* = 6.0 Hz, 3 H),; ^{13}C NMR (75 MHz, $CDCl_3$) δ (172.8), 172.4, 139.3, (138.7), 136.8, (136.5), 128.9, (128.5), 128.2, (128.2), (128.1), 128.0, 127.62, (127.56), (127.50), 127.4, (127.23), 127.20, (88.0), 87.2, 78.1, (77.6), (69.8), 69.1, (52.0), 51.8, (24.0), 23.9, (23.7), 23.6. HRMS: calcd for $C_{19}H_{22}O_4$: 314.1518; found: 314.1520 $[M+ Na]^+$.

(2S*,3S*) and (2S*,3R*) Methyl 3-hydroxy-2-isopropoxy-3-(4-nitro-phenyl)-2-phenyl-propionate (**4c**+**5c**) (mixture of diastereomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ (7.99 (d, *J* = 8.7 Hz, 2 H); threo-, **5c**), 7.94 (d, *J* = 8.7 Hz, 2 H; erythro-, **4c**), 7.33-7.11 (m, 7 H), (7.33-7.11 (m, 7 H)), 5.42 (s, 1H), (5.42 (s, 1H)), 4.01-3.91 (m, 1 H), (4.01-3.91 (m, 1 H)), 3.75 (s, 3 H), (3.72 (s, 3 H)), 1.19 (d, *J* = 6.0 Hz, 3 H), (1.19 (d, *J* = 6.0 Hz, 3 H)), 0.99 (d, *J* = 6.0 Hz, 3 H), (0.97 (d, *J* = 6.0 Hz, 3 H)); ^{13}C NMR (75 MHz, $CDCl_3$) δ (172.6), 172.1, (147.2), 147.1, 146.4, (146.3), (136.1), 135.3, (129.0), 128.8, 128.5, 128.3, (128.3), (127.9), (127.8), 127.2, (122.1), 121.9, (87.5), 87.1, (77.0), 76.9, (70.2), 69.3, 52.2, (52.2), 23.9, (23.8), (23.6), 23.3. HRMS: calcd for $C_{19}H_{21}NO_6$: 359.1369; found: 359.1363 $[M+ NH_4]^+$.

(2S*,3S*) Methyl 3-hydroxy-2-isopropoxy-3-(2-nitro-phenyl) -2-phenyl-propionate (erythro-, **4d**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 1 H), 7.31-7.12 (m, 5 H), 6.93 (d, *J* = 8.1 Hz, 2 H), 6.73 (d, *J* = 8.1 Hz, 1 H), 6.46 (s, 1 H), 3.90-3.81 (m. 1 H), 3.81 (s, 3 H), 3.24 (br, 1 H), 1.04 (d, *J* = 6.0 Hz, 3 H), 0.98 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 150.2, 134.8, 132.6, 130.7, 129.5, 128.6, 128.0, 127.8, 126.7, 123.1, 87.2, 70.4, 69.2, 52.5, 23.6, 22.7; HRMS: calcd for $C_{19}H_{20}NO_6$: 359.1369; found: 359.1359 $[M+ Na]^+$.

(2S*,3R*) Methyl 3-hydroxy-2-isopropoxy-3-(2-nitro-phenyl) -2-phenyl-propionate (threo-, **5d**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.75 (m, 1 H), 7.57-7.36 (m, 8 H), 6.48 (d, *J* = 7.8 Hz, 1 H), 3.87 (d, *J* = 7.8 Hz, 1 H), 3.66 (s, 3 H), 3.66-3.59 (m, 1 H), 1.02 (d, *J* =

6.0 Hz, 3 H), 0.68 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 150.8, 136.2, 133.8, 131.4, 128.9, 128.6, 128.3 (overlap), 128.2, 123.9, 87.9, 71.7, 70.4, 52.0, 23.3, 23.0; HRMS: calcd for $C_{19}H_{20}NO_6$: 359.1369; found: 359.1367 $[M+ Na]^+$.

(2S*,3S*) Methyl 3-(2,4-dinitro-phenyl)-3-hydroxy-2-isopropoxy-2-phenyl-propionate (erythro-, **4e**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.4 Hz, 1 H), 7.94 (dd, *J* = 8.7, 2.4 Hz, 1 H), 7.28-7.14 (m, 3 H), 6.87-6.83 (m. 3 H), 6.57 (s, 1 H), 3.93-3.85 (m. 1 H), 3.89 (s, 3 H), 3.36 (br, 1 H), 1.04 (d, *J* = 6.0 Hz, 3 H), 1.02 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 150.0, 146.7, 139.6, 134.0, 131.3, 128.4, 128.3, 126.9, 124.5, 118.5, 87.3, 70.4, 69.7, 52.9, 23.6, 22.6; HRMS: calcd for $C_{19}H_{20}N_2O_8$: 404.12197; found: 404.1212 $[M+ NH_4]^+$.

(2S*,3R*) Methyl 3-(2,4-dinitro-phenyl)-3-hydroxy-2-isopropoxy-2-phenyl-propionate (threo-, **5e**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.4 Hz, 1 H), 8.35 (dd, *J* = 8.7, 2.4 Hz, 1 H), 7.84 (d, *J* = 8.7 Hz, 1 H), 7.43-7.36 (m, 5 H), 6.50 (d, *J* = 7.5 Hz, 1 H), 4.03 (d, *J* = 7.5 Hz, 1 H), 3.72-3.61 (m. 1 H), 3.70 (s, 3 H), 1.01 (d, *J* = 6.0 Hz, 3 H), 0.72 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 150.6, 147.0, 141.1, 135.6, 130.2, 129.4 (overlap), 128.5, 125.5, 119.2, 87.6, 72.0, 70.9, 52.3, 23.2, 23.0; HRMS: calcd for $C_{19}H_{20}N_2O_8$: 404.12197; found: 404.1209 $[M+ NH_4]^+$.

(2S*,3S*) and (2S*,3R*) Methyl 3-hydroxy-2-isopropoxy-2,5-diphenyl-pent-4-enoate (**4f**+**5f**) (mixture of diastereomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.13 (m, 10 H; erythro-, **4f**), (7.50-7.13 (m, 10 H); threo-, **5f**), (6.59 (d, *J* = 16.2 Hz, 1 H)), 6.50 (d, *J* = 15.9 Hz, 1 H), (6.25 (dd, *J* = 16.2, 5.1 Hz, 1 H)), 6.11 (dd, *J* = 15.9, 5.7 Hz, 1 H), 5.00-4.98 (m, 1 H), (5.00-4.98 (m, 1 H)), 3.74 (s, 3 H), (3.73 (s, 3 H)), 3.29 (d, *J* = 8.1 Hz, 1 H), (3.27 (d, *J* = 9.6 Hz, 1 H)), (1.26 (d, *J* = 6.0 Hz, 3 H)), 1.25 (d, *J* = 6.0 Hz, 3 H), (1.00 (d, *J* = 6.0 Hz, 3 H)), 0.93 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (173.5), 172.6, 137.4, (137.08), 137.05, 137.00, 132.2, (132.1), (128.50), 128.45, 128.34, (128.31), 128.2, (128.0), 127.8, (127.54), (127.50), 127.50, (127.0), 126.7, 126.5, (126.5), 87.1, (87.0), (76.1), 76.0, (69.9), 69.4, (52.2), 52.1, 24.1, (23.8). HRMS: calcd for $C_{21}H_{24}O_4$: 340.1675; found: 340.1671 $[M+ Na]^+$.

(2S*,3S*) Methyl 3-hydroxy-2-isopropoxy-2-phenyl-caproate (erythro-, **4g**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2 H), 7.34-7.31 (m, 3 H), 4.26 (d, *J* = 10.5 Hz, 1 H),

3.88-3.81 (m, 1 H), 3.78 (s, 3 H), 3.07 (br, 1 H), 1.56-1.23 (m, 3 H), 1.22 (d, *J* = 6.0 Hz, 3 H), 0.99-0.94 (m 1 H), 0.95 (d, *J* = 6.0 Hz, 3 H), 0.85 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 137.2, 127.9, 127.6, 127.5, 86.6, 74.8, 68.9, 51.9, 32.5, 24.0, 23.6, 19.6, 13.9; HRMS: calcd for $C_{16}H_{24}O_4$: 280.1675; found: 280.1669 $[M+ Na]^+$.

(2S*,3S*) and (2S*,3R*) Methyl 3-hydroxy-2-isopropoxy-4-methyl-2-phenyl-valerate (**4h**+**5h**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.56 (m, 2 H; erythro-, **4h**), (7.42-7.41 (m, 2 H); threo-, **5h**), 7.36-7.29 (m, 3 H), (7.36-7.29 (m, 3 H)), 4.10 (d, *J* = 6.6 Hz, 1 H), (4.09 (d, *J* = 7.5 Hz, 1 H)), 3.92-3.82 (m, 1 H), (3.92-3.82 (m, 1 H)), (3.81 (s, 3 H)), 3.77 (s, 3 H), 3.12 (d, *J* = 6.6 Hz, 1 H), (2.82 (d, *J* = 7.5 Hz, 1 H)), 1.82-1.70 (m, 1 H), (1.82-1.70 (m, 1 H)), 1.24 (d, *J* = 6.0 Hz, 3 H), (1.18 (d, *J* = 6.0 Hz, 3 H)), (0.92 (d, *J* = 6.0 Hz, 6 H)), 0.90 (d, *J* = 6.0 Hz, 3 H), (0.82 (d, *J* = 6.0 Hz, 3 H)), 0.80 (d, *J* = 6.0 Hz, 3 H),0.62 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (174.0), 173.5, 138.3, (138.1), (128.1), 127.99, 127.96, (127.96), 127.8, (127.7), (86.5), 86.3, (79.5), 78.6, (69.4), 68.8, (52.0), 51.8, 29.5, (29.4), 23.9, (23.9), (23.8), 23.6, 22.2, (22.0). HRMS: calcd for $C_{16}H_{24}O_4$: 280.1675; found: 280.1677 $[M+ Na]^+$.

(2S*,3S*) Methyl 3-hydroxy-2-isopropoxy-4,4-dimethyl-2-phenyl- valerate (**4i**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2 H), 7.35-7.29 (m, 3 H), 4.08 (d, *J* = 5.4 Hz, 1 H), 3.91-3.83 (m, 1 H), 3.76 (s, 3 H), 3.19 (d, *J* = 5.4 Hz, 1 H), 1.18 (d, *J* = 6.0 Hz, 3 H), 0.91 (d, *J* = 6.0 Hz, 3 H), 0.76 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 138.2, 128.6, 127.8, 127.5, 86.3, 81.7, 68.8, 51.7, 35.8, 27.3, 23.8, 23.5; HRMS: calcd for $C_{17}H_{26}O_4$: 294.1831; found: 294.1831 $[M+ Na]^+$.

(2S*,3R*) Methyl 3-hydroxy-2-isopropoxy-4,4-dimethyl-2-phenyl- valerate (**5i**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2 H), 7.38-7.32 (m, 3 H), 4.07 (d, *J* = 9.0 Hz, 1 H), 3.85 (s, 3 H), 3.77-3.69 (m, 1 H), 2.89 (d, *J* = 9.0 Hz, 1 H), 1.20 (d, *J* = 6.0 Hz, 3 H), 0.95 (s, 9 H), 0.58 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 138.3, 128.6, 128.2, 127.8, 86.5, 81.8, 69.2, 51.7, 36.1, 27.7, 23.8, 23.7; HRMS: calcd for $C_{17}H_{26}O_4$: 294.1831; found: 294.1830 $[M+ Na]^+$.

(2S*,3S*) and (2S*,3R*) Methyl 2-ethoxy-3-hydroxy-2,3-diphenyl- propionate (**4j**+**5j**) (mixture of diastereomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-6.90 (m, 10 H; erythro-, **4j**), (7.23-6.90 (m, 10 H); threo-, **5j**), 5.24 (s, 1 H), (5.24 (s, 1 H)), (3.85-3.82 (m,

1 H)), (3.74 (s, 3 H)), 3.70 (s, 3 H), (3.60-3.52 (m, 1 H)), 3.54 (br, 1 H), (3.54 (br, 1 H)), 3.44-3.35 (m, 2 H), 1.21 (t, *J* = 6.9 Hz, 3 H), (1.20 (t, *J* = 6.9 Hz, 3 H)); ^{13}C NMR (75 MHz, $CDCl_3$) δ (172.4), 171.7, 138.2, (138.1), (135.7), 135.0, 128.1, (127.9), (127.8), 127.7, 127.6, (127.5), (127.4), 127.32, (127.28), 127.1, (127.0), 126.8, (87.9), 87.4, (79.3), 77.9, (62.2), 61.4, (52.0), 51.8, (15.4), 15.3. HRMS: calcd for $C_{18}H_{20}O_4$: 300.1362; found: 300.1359 $[M+ NH_4]^+$.

(2S*,3S*) and (2S*,3R*) Methyl 3-hydroxy-2,3-diphenyl-2- propoxy-pionate (**4k**+**5k**) (mixture of diastereomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-6.88 (m, 10 H; erythro-, **4k**), (7.22-6.88 (m, 10 H); threo-, **5k**), 5.26 (s, 1 H), (5.26 (s, 1 H)), (3.72 (s, 3 H)), 3.69 (s, 3 H), 3.48 (br, 1 H), (3.48 (br, 1 H)), (3.46-3.41 (m, 2 H)), 3.33-3.27 (m, 2 H), 1.65-1.59 (m, 2 H), (1.65-1.59 (m, 2 H)), 0.94-0.88 (m, 3 H), (0.94-0.88 (m, 3 H)); ^{13}C NMR (75 MHz, $CDCl_3$) δ (172.4), 171.7, 138.2, (138.2), (135.8), 134.9, 128.2, (127.9), (127.8), 127.71, 127.65, (127.5), 127.4, (127.4), (127.3), 127.1, (127.0), 126.8, (87.7), 87.2, (79.3), 77.8, (68.1), 67.2, (51.9), 51.8, (23.3), 23.1, (10.4), 10.4. HRMS: calcd for $C_{19}H_{22}O_4$: 314.1518; found: 314.1512 $[M+ Na]^+$.

(2S*,3S*) and (2S*,3R*) Methyl 3-hydroxy-2-isopropoxy-2-(4-methoxy-phenyl)-3-phenyl-propionate (**4l**+**5l**) (mixture of diastereomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 9.0 Hz, 2 H; erythro-, **4l**), 7.20-7.04 (m, 5 H), (7.20-7.04 (m, 7 H); threo-, **5l**), 6.77 (d, *J* = 9.0 Hz, 2 H), (6.77 (d, *J* = 9.0 Hz, 2 H)), (5.31 (s, 1 H)), 5.24 (s, 1 H), 3.94-3.86 (m, 1 H), (3.94-3.86 (m, 1 H)), 3.73 (s, 3 H), (3.73 (s, 3 H)), (3.66 (s, 3 H)), 3.66 (br, 1 H), 3.56 (s, 3 H), (3.46 (br, 1 H)), 1.21 (d, *J* = 6.0 Hz, 3 H), (1.17 (d, *J* = 6.0 Hz, 3 H)), (0.92 (d, *J* = 6.0 Hz, 3 H)), 0.85 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (172.6), 172.2, 159.1, (159.1), 139.3, (138.7), 130.1, (129.7), 128.7, (128.1), (127.9), 127.8, 127.33, (127.28), 127.0, (127.0), (112.6), 112.5, (87.6), 86.6, 78.0, (77.4), (69.2), 68.6, 54.9, (54.9), (51.6), 51.4, (23.7), 23.6, (23.4), 23.3. HRMS: calcd for $C_{20}H_{24}O_5$: 344.1624; found: 344.1625 $[M+ NH_4]^+$.

(2S*,3S*) and (2S*,3R*) Methyl 2-(hydroxy-phenyl-methyl)-2-isopropoxy-4-phenyl-but-3-enoate (**4m**+**5m**) (mixture of diastereomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.22 (m, 10 H; erythro-, **4m**), (7.39-7.22 (m, 10 H); threo-, **5m**), (6.62 (d, *J* = 16.5 Hz, 1 H)), 6.58 (d, *J* = 16.5 Hz, 1 H), 6.48 (d, *J* = 16.5 Hz, 1 H), (5.91 (d,

J = 16.5 Hz, 1 H)), (5.06 (d, *J* = 6.3 Hz, 1 H)), 4.93 (d, *J* = 4.8 Hz, 1 H), 4.01-3.92 (m, 1 H), (4.01-3.92 (m, 1 H)), (3.81 (s, 3 H)), 3.65 (s, 3 H), 3.55 (d, *J* = 4.8 Hz, 1 H), (3.39 (d, *J* = 6.3 Hz, 1 H)), (1.26 (d, *J* = 6.0 Hz, 3 H)), 1.24 (d, *J* = 6.0 Hz, 3 H), 1.12 (d, *J* = 6.0 Hz, 3 H), (1.05 (d, *J* = 6.0 Hz, 3 H)); ^{13}C NMR (75 MHz, $CDCl_3$) δ (172.4), 171.9, 138.61, (138.58), 136.25, (136.22), 134.4, (134.1), (128.7), (128.2), 128.1, 128.0, (127.7), 127.6, 126.70, (126.65), 125.7, (124.7), (86.4), 85.9, 79.6, (79.0), 69.4, (69.2), (52.2), 51.8, (24.74), 24.66, 23.4, (23.4). HRMS: calcd for $C_{21}H_{24}O_4$: 340.1675; found: 340.1678 $[M+Na]^+$.

The reaction of methyl phenyldiazoacetate with $Rh_2(OAc)_4$ under Ar

Under Ar, to a 8 mL CH_2Cl_2 solution of $Rh_2(OAc)_4$ 4.4 mg (0.01 mmol) was added methyl phenyldiazoacetate (1.0 mmol) in 4 mL of CH_2Cl_2 in one portion at room temperature. After 5 minute, the solvent was removed, and a portion of crude product was subjected to ^1H NMR analysis for determination of the product ratio. The crude NMR shown that the ratio of *trans*-dimer:*cis*-dimer is 58:42. The crude product was purified by flash chromatography on silica gel by using petroleum ether:EtOAc=20:1 as eluent to give *trans*-dimer dimethyl 2,3-diphenyl fumarate and *cis*-dimer dimethyl 2,3-diphenyl maleate in 70% total yield.

Dimethyl 2,3-diphenyl fumarate (*trans*-dimer) ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.36 (m, 5 H), 3.54 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 137.7, 135.5, 129.0, 128.6, 128.1, 52.4.

Dimethyl 2,3-diphenyl maleate (*cis*-dimer) ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.15 (m, 3 H), 7.10-7.07 (m, 2 H), 3.82 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 138.9, 134.5, 129.8, 128.5, 128.3, 52.8.

The reaction of methyl phenyldiazoacetate with $Rh_2(OAc)_4$ under O_2

Under 1 atm O_2, to a 8 mL CH_2Cl_2 solution of $Rh_2(OAc)_4$ 4.4 mg (0.01 mmol) was added methyl phenyldiazoacetate (1.0 mmol) in 4 mL of CH_2Cl_2 via a syringe pump over 1.0 h at room temperature. After completed addition, the solvent was removed, and a portion of crude product was subjected to ^1H NMR analysis for determination of the product ratio. From the crude NMR spectra, no trace amount of dimmers was detected. The crude product was purified by flash chromatography on silica gel by using petroleum ether:EtOAc=30:1 as eluent to give methyl benzoylformate in 26% yield. The structure of the other byproducts is now unclear.

methyl benzoylformate ^1H NMR (300 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2 H), 7.70-7.64 (m, 1 H), 7.55-7.50 (m, 2 H), 3.99 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.2, 164.2, 135.1, 132.6, 130.2, 129.0, 52.9.

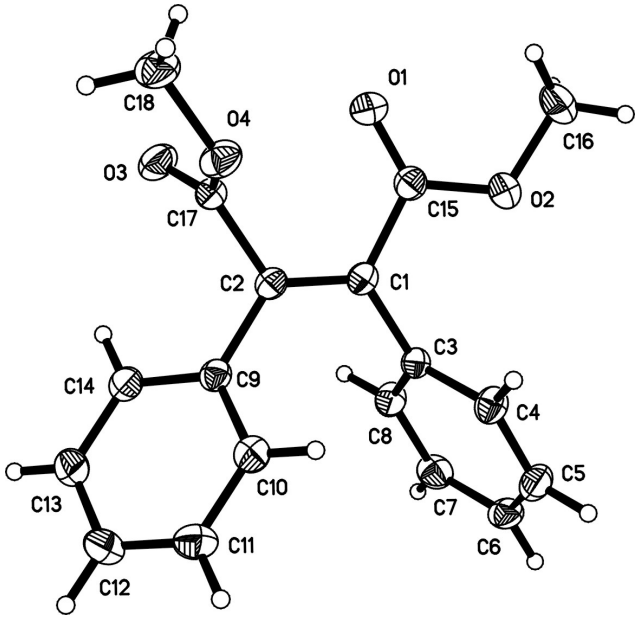

Figure 1. ORTEP representation of the crystal structure of Dimethyl 2,3-diphenyl maleate

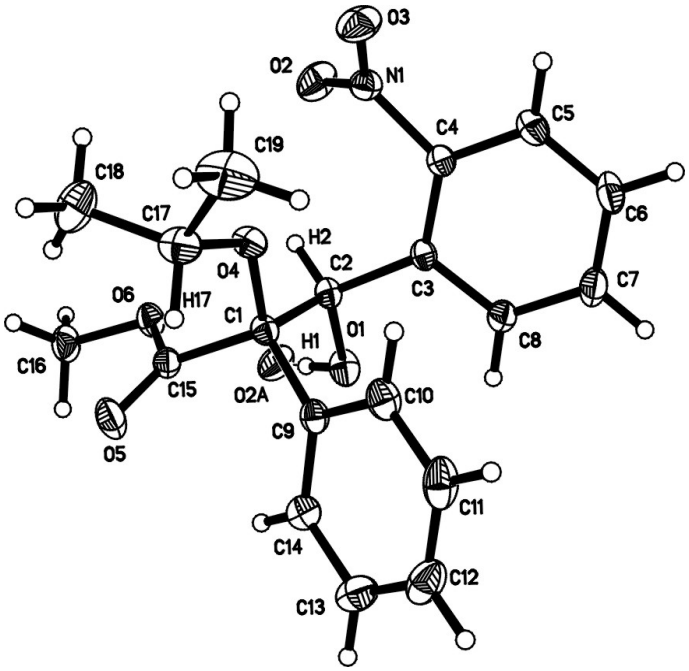

Figure 2. ORTEP representation of the crystal structure of **4d**