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Supporting Information

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Palladium-Catalyzed Stereoselective Oxidation of Methyl Groups by Inexpensive Oxidants under Mild Conditions: a Dual Role for Carboxylic Anhydrides in Catalytic C-H Bond Oxidation

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General Information: Solvents were obtained from Acros and used directly without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light and Vogel's permanganate.

^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively) and internally referenced to $SiMe_4$ signal. Exact mass spectra for new compounds were recorded on a VG 7070 high resolution mass spectrometer. Analytical GC-MS was performed on a Hewlett-Packard G1800C instrument connected to an electron ionization detector using a MS-5 GC column (30 × 0.25 mm). Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrometer. Data Collection for crystal structure of complex **1a** and **16a** was carried out at room temperature on an Enraf-Nonius CAD-4 Turbo diffractometer equipped with MoKα radiation.

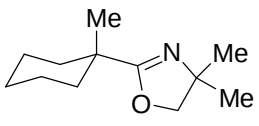
Peroxyesters and peroxides were obtained from Aldrich. Carboxylic acids were purchased from Aldrich and Acros and were used as received. $Pd(OAc)_2$ was procured from Acros. Carboxylic acids for oxazolines **2** and **5** were prepared by methylation [1] of cyclopentanecarboxylic acid and 2-ethylbutyric acid, respectively. In the carboxylic acid for substrates **7** and **12**, the amino group was protected as *N*-phthalimide[2] by heating a mixture of 2-aminoisobutyric acid and phthalic anhydride at 180 °C. For substrates **8** and **13**, methyl ester of 2, 2-dimethylglutaric acid was prepared by selectively methylating the less hindered carboxylic group, first converting it into acid chloride with oxalyl chloride and then reacting the acid chloride with methanol. For substrate **15**, the carboxylic acid was prepared by alkylation of methyl trimethylsilyl dimethylketene acetal[3] and subsequent hydrolysis.[4]

Preparation of oxazoline

Carboxylic acids were converted to their acid chlorides using either oxalyl chloride[1] (oxazolines **1**, **2**, **4**, **6**, **8**, **10**, **11**, **13** and **17**) or thionyl chloride[5] (oxazolines **5**, **7**, **12** and **15**). The acid chlorides were then reacted with 2-amino-2-methyl-1-propanol or (*S*)-*tert*-leucinol to form amides [6] which were subsequently cyclized to oxazolines using triphenylphosphine.[7] Oxazoline **9** was prepared from oxazoline **8** by reducing the ester group with $LiAlH_4$. Oxazoline **14** was prepared by heating 2-hydroxyisobutyric acid with

(*S*)-*tert*-leucinol under reflux[8] and protecting the free hydroxyl group with a TBS group using *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf).[9]

Substrate structure



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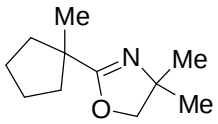

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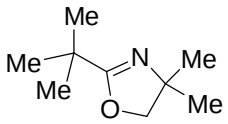

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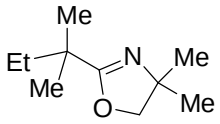

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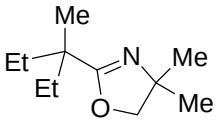

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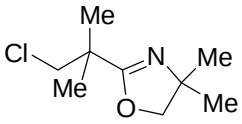

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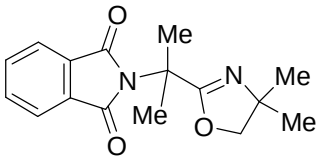

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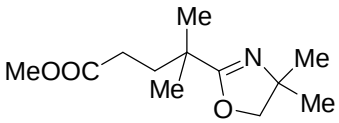

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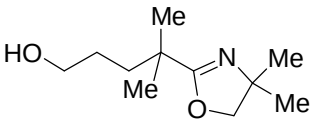

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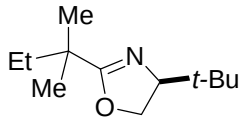

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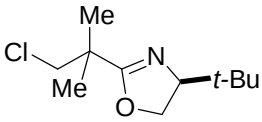

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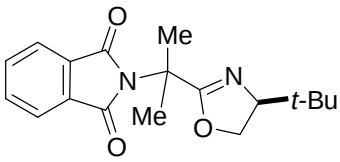

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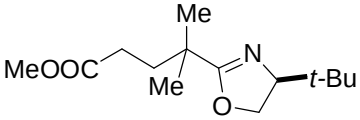

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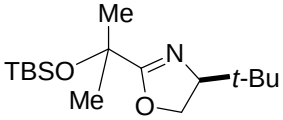

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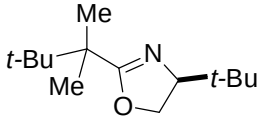

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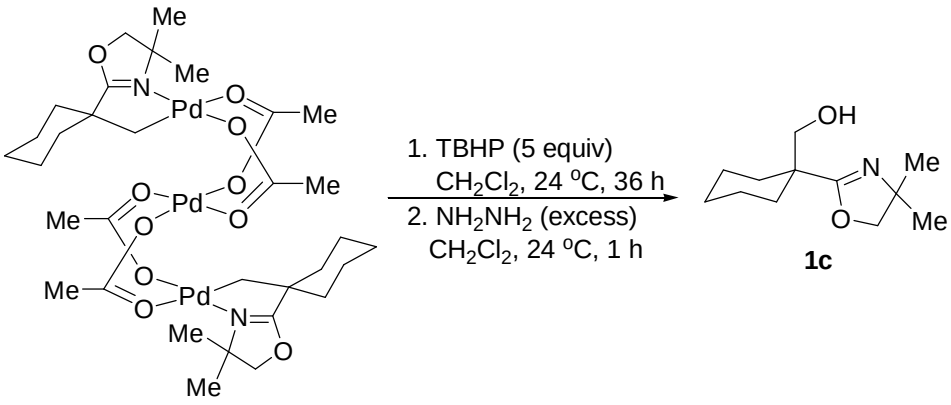
Experimental Section

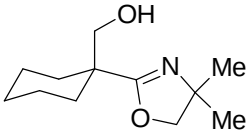
The reaction was carried out under atmospheric air. Methylene chloride and anhydrides were used as received without further distillation.

Stoichiometric hydroxylation with *tert*-butyl hydroperoxide



1a **1c**

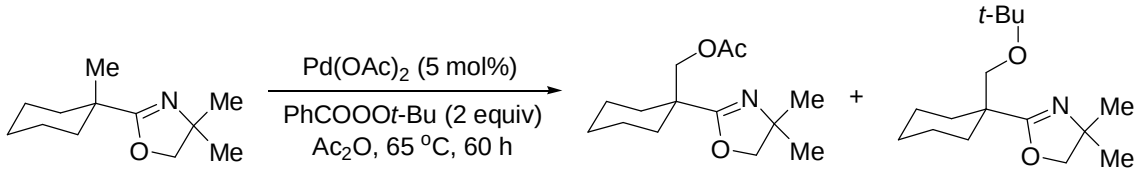
Complex **1a** (94.4 mg, 0.1 mmol) (*vide infra*) was placed in a 20 mL scintillation vial and dissolved in CH_2Cl_2 (2 mL). *tert*-Butyl hydroperoxide (90% solution in water) (54 μL, 0.5 mmol) was added to the solution. The vial was tightly capped and the resulting solution was stirred at 24 °C for 36 h. The reaction mixture was then reduced with excess hydrazine monohydrate at 24 °C for 1 h and the solvent removed in a rotary evaporator. The product was purified by silica gel column chromatography using ethylacetate:hexane /1:5.



1c

(1-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)cyclohexyl)methanol (1c): 1c was obtained as a colorless oil (74 mg, 35% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 6H), 1.42-1.57 (m, 7H), 1.83-1.88 (m, 3H), 3.44 (s, br, 1H), 3.58 (s, br, 2H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.23, 26.12, 28.74, 30.87, 42.35, 67.07, 67.63, 78.81, 170.43; HRMS (EI) Calcd for $C_{12}H_{21}NO_2$ (M^+) 211.1572, found 211.1565.

Catalytic oxidation with *tert*-butyl peroxybenzoate

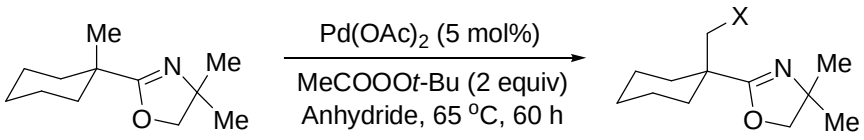


1 **1d** (9%) **1k** (65%)

Oxazoline **1** (97.5 mg, 0.5 mmol) was placed in a 40 mL pressure tube and dissolved in acetic anhydride (5 mL). Palladium acetate (5.6 mg, 0.025 mmol) and *tert*-butyl peroxybenzoate (187 µL, 1 mmol) were added to the solution and the solution flushed with oxygen. The tube was tightly capped and the resulting solution was heated at 65°C for 60 h. The reaction mixture was cooled to room temperature and then the acetic anhydride was hydrolyzed with saturated aqueous sodium bicarbonate at 24 °C for 1 h. The crude product was extracted with methylene chloride (3 × 5 mL), dried over sodium sulfate and the solvent was removed in a rotary evaporator. The product was purified by silica gel column chromatography eluting with ethylacetate:hexane /1:20.

2-(1-*tert*-Butoxymethyl)cyclohexyl)-4,5-dihydro-4,4-dimethyloxazole (1k): 1k was obtained as a colorless oil (87 mg, 65% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.27 (s, 6H), 1.21-1.56 (m, 8H), 1.99 (d, br, *J* = 12.8 Hz, 2H), 3.26 (s, 2H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.08, 26.48, 27.76, 28.75, 31.94, 42.29, 67.33, 69.16, 72.50, 78.75, 168.87; IR (neat) ν 2972, 2857, 1759, 1661, 1452, 1363, 1197 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{29}NO_2$ (M^+) 267.2198, found 267.2192.

<u>Catalytic carboxylation with *tert*-butyl peroxyacetate using various carboxylic anhydrides</u>



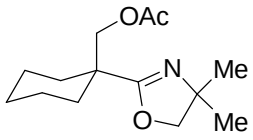
1 **1d, 1i-j, 1l-m**

Oxazoline **1** (97.5 mg, 0.5 mmol) was placed in a 40 mL pressure tube and dissolved in anhydride (5 mL). Palladium acetate (5.6 mg, 0.025 mmol) and *tert*-butyl peroxyacetate (75 wt. % in aliphatic hydrocarbons) (199 µL, 1 mmol) were added to the solution and the solution was flushed with oxygen. The tube was tightly capped and the resulting solution was heated at 65°C for 60 h. The reaction mixture was cooled to room temperature and then the carboxylic anhydride was hydrolyzed at 24 °C with saturated aqueous sodium bicarbonate for 1 h (entries 1-2) or 2N potassium hydroxide (entries 3-5) for 5 h. The crude product was extracted with methylene chloride (3 × 5 mL), dried over sodium sulfate and

the solvent was removed in a rotary evaporator. The product was purified by silica gel column chromatography eluting with ethylacetate:hexane /1:10.

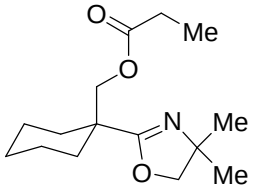
Entry	Anhydride	X	Product yield (%)
1	$(MeCO)_2O$	MeCOO (**1d**)	71
2	$(EtCO)_2O$	EtCOO (**1i**)	73
3	$(i\text{-}PrCO)_2O$	*i*-PrCOO (**1j**)	49
4	$(t\text{-}BuCO)_2O$	*t*-BuCOO (**1l**)	0
5	$(PhCO)_2O$[1]	PhCOO (**1m**)	0

[1]$(PhCO)_2O$ (10 equiv) was dissolved in CH_2Cl_2 (5 mL).



1d

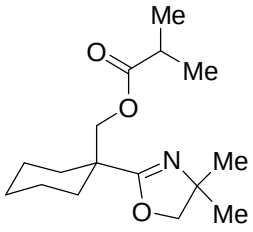
(1-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)cyclohexyl)methyl acetate (1d): [10] **1d** was obtained as a colorless oil (90 mg, 71% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 6H), 1.22-1.57 (m, 8H), 2.03 (s, 3H), 2.05 (d, br, *J* = 14 Hz, 2H), 3.88 (s, 2H), 4.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.14, 22.68, 26.13, 28.56, 31.64, 41.62, 67.53, 70.08, 78.97, 167.31, 171.21; IR (neat) ν 2933, 2858, 1745, 1659, 1453, 1365, 1232 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{23}NO_3$ (M^+) 253.1678, found 253.1684.



1i

(1-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)cyclohexyl)methyl propionate (1i): 1i was obtained as a colorless oil (98 mg, 73% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, *J* = 7.3 Hz, 3H), 1.26 (s, 6H), 1.22-1.35 (m, 3H), 1.41-1.48 (m, 2H), 1.57-1.60 (m, 3H), 2.05 (d, br, *J* = 14 Hz, 2H), 2.31

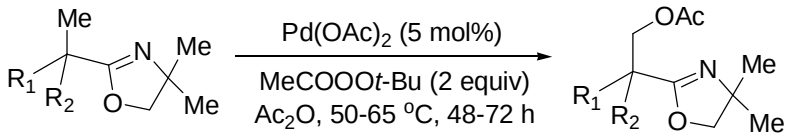
(q, *J* = 7.3 Hz, 2H), 3.87 (s, 2H), 4.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.44, 22.66, 26.18, 27.86, 28.57, 41.61, 67.52, 69.94, 78.95, 167.34, 174.46; IR (neat) ν 2937, 2860, 1743, 1659, 1463, 1364, 1178 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{25}NO_3$ (M^+) 267.1834, found 267.1838.



1j

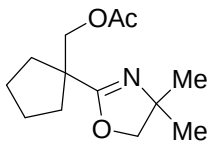
(1-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)cyclohexyl)methyl isobutyrate (1j): 1j was obtained as a colorless oil (69 mg, 49% yield) after purification by column chromatography.^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, *J* = 7.3 Hz, 6H), 1.27 (s, 6H), 1.25-1.59 (m, 8H), 2.04 (d, br, *J* = 13.4 Hz, 2H), 2.53 (sp, *J* = 7.3 Hz, 1H), 3.87 (s, 2H), 4.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.32, 22.66, 26.22, 28.65, 31.69, 34.44, 41.59, 67.55, 69.99, 78.98, 167.50, 177.07; IR (neat) ν 2934, 1738, 1658, 1466, 1196, 1157 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{27}NO_3$ (M^+) 281.1991, found 281.1983.

Catalytic acetoxylation with *tert*-butyl peroxyacetate



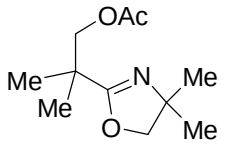
2-9 **2a-9a**

Oxazoline (0.5 mmol) was placed in a 40 mL pressure tube and dissolved in acetic anhydride (5 mL). Palladium acetate (0.025-0.05 mmol) and *tert*-butyl peroxyacetate (75 wt. % in aliphatic hydrocarbons) (199 µL, 1 mmol) were added to the solution and the solution was flushed with oxygen. The tube was tightly capped and the resulting solution was heated at 48-65 °C for 48-72 h. The reaction mixture was cooled to room temperature and then the acetic anhydride was hydrolyzed with saturated aqueous sodium bicarbonate at 24 °C for 1 h. The crude product was extracted with methylene chloride (3 × 5 mL), dried over sodium sulfate and the solvent was removed in a rotary evaporator. The product was purified by silica gel column chromatography eluting with ethylacetate:hexane /1:10.



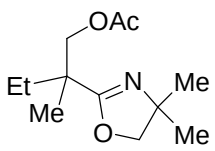
2a

(1-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)cyclopentyl)methyl acetate (2a): The reaction was carried out using 5 mol% $Pd(OAc)_2$. The reaction mixture was heated at 65 °C for 60 h and then subjected to the standard workup procedure as described. **2a** was obtained as a colorless oil (74 mg, 62% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 6H), 1.63-1.70 (m, 6H), 2.04 (s, 3H), 2.04-2.07 (m, 2H), 3.89 (s, 2H), 4.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.22, 25.34, 28.48, 33.88, 48.15, 67.28, 68.56, 79.46, 169.07, 171.41; IR (neat) ν 2963, 1746, 1660, 1463, 1365, 1237 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{22}NO_3$ (MH^+) 240.1600, found 240.1597.

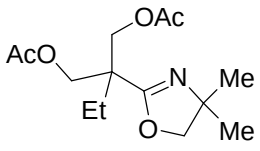


3a

2-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-2-methylpropyl acetate (3a): The reaction was carried out using 5 mol% $Pd(OAc)_2$. The reaction mixture was heated at 65 °C for 60 h and then subjected to the standard workup procedure as described. **3a** was obtained as a colorless oil (74 mg, 69% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 6H), 1.25 (s, 6H), 2.04 (s, 3H), 3.88 (s, 2H), 4.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.15, 23.14, 28.55, 37.27, 67.33, 70.42, 79.34, 169.07, 171.18; IR (neat) ν 2974, 1746, 1662, 1463, 1376, 1245 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{20}NO_3$ (MH^+) 214.1443, found 214.1449.



4a

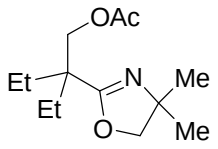


4b

2-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-2-methylbutyl acetate (4a): The reaction was carried out using 5 mol% $Pd(OAc)_2$. The reaction mixture was heated at 65 °C for 60 h and

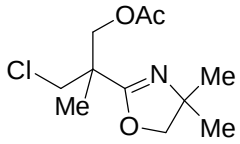
then subjected to the standard workup procedure as described. **4a** and **4b** were obtained as colorless oils (**4a**, 53 mg, 47% yield; **4b**, 60 mg, 42% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.3 Hz, 3H), 1.20 (s, 3H), 1.26 (s, 6H), 1.42-1.53 (m, 1H), 1.65-1.74 (m, 1H), 2.04 (s, 3H), 3.88 (s, 2H), 4.07 (d, *J* = 11 Hz, 1H), 4.16 (d, *J* = 11 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.66, 20.02, 21.16, 28.68, 28.70, 28.79, 41.00, 67.42, 69.25, 79.18, 168.03, 171.21; IR (neat) ν 2771, 2935, 1747, 1660, 1463, 1365, 1236 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{22}NO_3$ (MH^+) 228.1600, found 228.1598.

2-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-3-acetoxy-2-ethylpropyl acetate (4b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.3 Hz, 3H), 1.25 (s, 6H), 1.61 (q, *J* = 7.3 Hz, 2H), 2.04 (s, 3H), 3.88 (s, 2H), 4.22 (d, *J* = 11 Hz, 1H), 4.30 (d, *J* = 11 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.18, 21.12, 23.70, 28.64, 44.50, 63.38, 67.71, 78.86, 164.40, 170.89; IR (neat) ν 2971, 1748, 1663, 1464, 1367, 1230 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{24}NO_5$ (MH^+) 286.1654, found 286.1664.



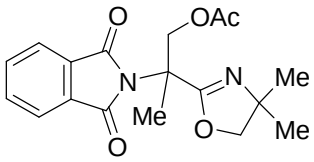
5a

2-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-2-ethylbutyl acetate (5a): The reaction was carried out using 5 mol% $Pd(OAc)_2$. The reaction mixture was heated at 65 °C for 60 h and then subjected to the standard workup procedure as described. **5a** was obtained as a colorless oil (109 mg, 90% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.9 Hz, 3H), 1.26 (s, 6H), 1.61 (q, *J* = 7.3 Hz, 2H), 2.04 (s, 3H), 3.87 (s, 2H), 4.19 s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.35, 21.20, 25.64, 28.80, 44.18, 64.50, 67.46, 78.86, 167.35, 171.53. GC-MS (MH^+) 242.



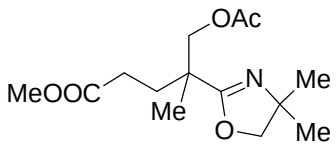
6a

2-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-3-chloro-2-methylpropyl acetate (6a): The reaction was carried out using 10 mol% $Pd(OAc)_2$. The reaction mixture was heated at 65 °C for 60 h and then subjected to the standard workup procedure as described. **6a** was obtained as a colorless oil (84 mg, 68% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 3H), 1.26 (s, 3H), 1.29 (s, 3H), 2.05 (s, 3H), 3.71 (d, *J* = 11 Hz, 1H), 3.78 (d, *J* = 11 Hz, 1H0, 3.90 (s, 2H), 4.19 (d, *J* = 11 Hz, 1H), 4.32 (d, *J* = 11 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.22, 21.08, 28.49, 42.34, 48.01, 65.87, 67.74, 79.29, 165.67, 170.76; IR (neat) ν 2971, 2896, 1749, 1665, 1465, 1375, 1234 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{19}ClNO_3$ (MH^+) 248.1053, found 248.1057.



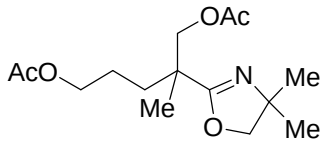
7a

2-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-2-(1,3-dioxoisoindolin-2-yl)propyl acetate (7a): The reaction was carried out using 10 mol% $Pd(OAc)_2$. The reaction mixture was heated at 65 °C for 72 h and then subjected to the standard workup procedure as described. **7a** was obtained as a colorless oil (86 mg, 50% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.33 (s, 3H), 1.92 (s, 3H), 2.00 (s, 3H), 3.93 (d, *J* = 7.9 Hz, 1H), 3.96 (d, *J* = 7.9 Hz, 1H), 4.69 (d, *J* = 11 Hz, 1H), 4.93 (s, *J* = 11 Hz, 1H), 7.69-7.12 (m, 2H), 7.77-7.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.09, 21.47, 28.13, 28.14, 59.00, 66.04, 67.92, 79.74, 123.49, 132.03, 134.42, 164.44, 168.50, 170.80; IR (neat) ν 2973, 2896, 1781, 1715, 1670, 1612, 1467, 1372, 1231 cm^{-1}; HRMS (EI) Calcd for $C_{18}H_{20}N_2O_5$ (M^+) 344.1372, found 344.1364. 40% starting material was recovered.



8a

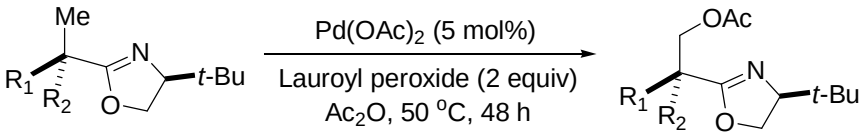
2-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-4-carbomethoxy-2-methylbutyl acetate (8a): The reaction was carried out using 10 mol% $Pd(OAc)_2$. The reaction mixture was heated at 65 °C for 60 h and then subjected to the standard workup procedure as described. **8a** was obtained as a colorless oil (100 mg, 70% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 3H), 1.25 (s, 6H), 1.78-1.85 (m, 2H), 2.04 (s, 3H), 2.29-2.35 (m, 2H), 3.66 (s, 3H), 3.88 (s, 2H), 4.09 (d, *J* = 11 Hz, 1H), 4.14 (d, *J* = 11 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.44, 21.13, 28.66, 29.44, 30.79, 40.11, 52.05, 67.54, 68.97, 79.26, 167.19, 171.06, 173.97; IR (neat) ν 2969, 1743, 1660, 1438, 1376, 1236 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{24}NO_5$ (MH^+) 286.1654, found 286.1658.



9a

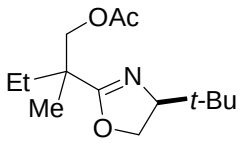
2-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)- 5-acetoxy-2-methylpentyl acetate (9a): Oxazoline **9** (99.7 mg, 0.5 mmol) was dissolved in Ac_2O (5 mL) in a 40 mL pressure tube and heated at 50 °C. After 1 h, the reaction mixture was cooled to room temperature and $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and *tert*-butyl peroxyacetate (75 wt. % in aliphatic hydrocarbons) (199 µL, 1 mmol) were added to it. Heating was continued at 50 °C for 48 h and then subjected to the standard workup procedure as described. **9a** was obtained as a colorless oil (75 mg, 50% yield) after purification by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 3H), 1.25 (s, 6H), 1.47-1.72 (m, 4H), 2.04 (s, 3H), 2.05 (s, 3H), 3.89 (s, 2H), 4.03 (t *J* = 6.7 Hz, 2H), 4.08 (d, *J* = 11 Hz, 1H), 4.16 (d, *J* = 11 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.51, 21.15, 21.33, 23.70, 28.66, 32.20, 40.39, 64.82, 67.51, 69.09, 79.26, 167.75, 171.12, 171.47; IR (neat) ν 2968, 1743, 1660, 1466, 1367, 1240 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{26}NO_5$ (MH^+) 300.1811, found 300.1813.

Diastereoselective acetoxylation using lauroyl peroxide

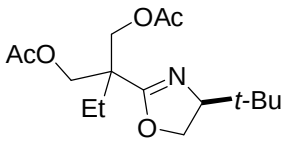


10-15 **10a-15a**

Oxazoline (0.5 mmol) was placed in a 40 mL pressure tube and dissolved in acetic anhydride (5 mL). Palladium acetate (5.6 mg, 0.025 mmol) and lauroyl peroxide (199.3 mg, 0.5 mmol) were added to the solution and the solution was flushed with oxygen. The tube was tightly capped and the resulting solution was heated at 50°C. After 24 h, the reaction mixture was cooled to room temperature and one equivalent of lauroyl peroxide (199.3 mg, 0.5 mmol) was added to it. Heating was continued at 50 °C for another 24 h. The reaction mixture was cooled to room temperature and then the acetic anhydride was hydrolyzed with saturated aqueous sodium bicarbonate at 24 °C for 1 h. The crude product was extracted with methylene chloride (3 × 5 mL), dried over sodium sulfate and the solvent was removed in a rotary evaporator. The product was purified by silica gel column chromatography eluting with ethylacetate:hexane /1:10.



10a

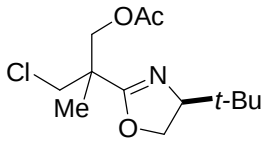


10b

2-((*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl)-2-methylbutyl acetate (10a), mixture of diastereomers: 10a and **10b** were obtained as light yellow oils (**10a**, 86 mg, 67% yield; **10b**, 36 mg, 23% yield) after purification by column chromatography. **10a** was a mixture of diastereomers with 18% de as measured by ^{1}H NMR and GC-MS; 50 °C (50 min) to 280 °C (550 min), oven ramp rate: 0.5 °C/min, helium flow rate: 1 mL/min, t_r (major) = 162.1 min, t_r (minor) = 162.7 min. The diastereomers were not further separated. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85-0.89 (m, 2H), 0.87 (s, 9H × 0.59), 0.88 (s, 9H × 0.41), 1.20 (s, 3H × 0.59), 1.22 (s, 3H × 0.41), 1.45-1.73 (m, 3H), 2.03 (s, 3H × 0.41), 2.04 (s, 3H × 0.59), 3.83 (dd, *J* = 11, 7.3 Hz, 1H), 4.02-4.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.83, 8.86, 20.34, 20.45, 21.21, 21.25, 26.07, 26.10, 28.76, 29.04, 34.01, 41.00, 41.09, 68.65, 68.71,

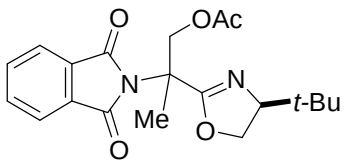
69.05, 69.36, 75.91, 169.31, 169.45, 171.31; IR (neat) ν 2965, 1747, 1665, 1478, 1365, 1241 cm^{-1}; HRMS (CI) Calcd for $C_{14}H_{26}NO_3$ (MH^+) 256.1913, found 256.1916.

2-((*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl)-3-acetoxy-2-ethylpropyl acetate (10b): ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (s, 12H), 1.59 (q, *J* = 7.3 Hz, 2H), 2.01 (s, 3H), 2.03 (s, 3H), 3.85 (dd, *J* = 10.4, 7.9 Hz, 1H), 7.3 (t, *J* = 7.3 Hz, 1H), 4.11 (dd, *J* = 10.4, 8.5 Hz, 1H), 4.22 (s, 2H), 4.24 (d, *J* = 11 Hz, 1H), 4.33 (d, *J* = 11 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.34, 21.13, 21.18, 23.98, 26.03, 33.89, 44.56, 63.30, 63.84, 68.46, 75.90, 165.76, 170.99, 171.02; IR (neat) ν 2959, 1748, 1667, 1466, 1367, 1240 cm^{-1}.



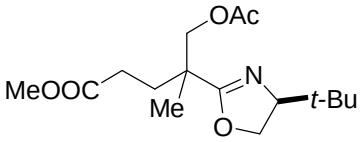
11a

2-((*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl)-3-chloro-2-methylpropyl acetate (11a), mixture of diastereomers: 11a was obtained as a light yellow oil (91 mg, 66% yield) after purification by column chromatography. **11a** was a mixture of diastereomers with 38% de as measured by ^1H NMR and GC-MS; 50 °C (4 min) to 280 °C (30 min), oven ramp rate: 10 °C/min, helium flow rate: 1 mL/min, t_r (major) = 17.6 min, t_r (minor) = 17.7 min. The diastereomers were not further separated. ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 9H), 1.29 (s, 3H × 0.31), 1.30 (s, 3H × 0.69), 2.03 (s, 3H × 0.31), 2.05 (s, 3H × 0.69), 3.72 (d, *J* = 11 Hz, 1H × 0.69), 3.74 (d, *J* = 11 Hz, 1H × 0.31), 3.79 (d, *J* = 11 Hz, 1H × 0.69), 3.83 (dd, *J* = 11, 6.7 Hz, 1H), 4.05 (dd, *J* = 8.5, 7.3 Hz, 1H × 0.31), 4.06 (dd, , *J* = 8.5, 7.3 Hz, 1H × 0.69), 4.14 (dd, *J* = 10.4, 8.5 Hz, 1H), 4.21 (d, *J* = 11 Hz, 1H × 0.69), 4.24 (d, *J* = 11 Hz, 1H × 0.31), 4.28 (d, *J* = 11 Hz, 1H × 0.31), 4.35 (d, *J* = 11 Hz, 1H × 0.69); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.53, 19.67, 21.14, 25.98, 26.02, 34.01, 42.27, 42.45, 47.83, 47.95, 65.85, 66.04, 68.96, 75.99, 166.93, 170.79, 170.84; IR (neat) ν 2958, 2906, 1748, 1668, 1479, 1468, 1365, 1237 cm^{-1}; HRMS (CI) Calcd for $C_{13}H_{23}ClNO_3$ (MH^+) 276.1366, found 276.1362.



12a

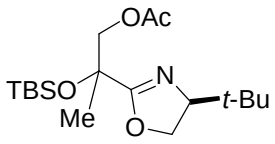
2- ((*S*)-4- *tert*-Butyl -4, 5-dihydrooxazol -2- yl)- 2- (1,3- dioxoisoindolin- 2- yl) propyl acetate (12a), mixture of diastereomers: 12a was obtained as a light yellow oil (71 mg, 38% yield) after purification by column chromatography. **12a** was a mixture of diastereomers with 12% de as measured by ^{1}H NMR. The diastereomers were not further separated. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9H × 0.56), 0.93 (s, 9H × 0.44), 1.99 (s, 3H), 2.00 (s, 3H × 0.44), 2.01 (s, 3H × 0.56), 3.89-3.97 (m, 1H), 4.02-4.10 (m, 1H), 4.15-4.25 (m, 1H), 4.63 (d, *J* = 11.6 Hz, 1H × 0.44), 4.72 (d, *J* = 11.6 Hz, 1H × 0.56), 4.89 (d, *J* = 11.6 Hz, 1H × 0.56), 4.96 (d, *J* = 11.6 Hz, 1H × 0.44); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.62, 21.13, 21.70, 21.81, 26.17, 26.38, 33.99, 34.16, 59.24, 59.27, 66.21, 66.43, 66.52, 69.33, 69.53, 76.06, 76.40, 123.49, 132.06, 134.40, 165.69, 165.74, 168.50, 168.63, 170.86, 170.95; IR (neat) ν 2956, 2871, 1783, 1719, 1674, 1613, 1468, 1368, 1326, 1230 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{25}N_2O_5$ (MH^+) 373.1763, found 373.1757. 50% starting material was recovered.



13a

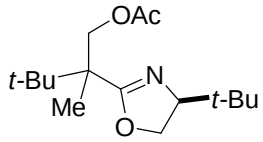
2-((*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl)-4-carbomethoxy-2-methylbutyl acetate (13a), mixture of diastereomers: 13a was obtained as a light yellow oil (115 mg, 73% yield) after purification by column chromatography. **13a** was a mixture of diastereomers with 24% de as measured by ^{1}H NMR. The diastereomers were not further separated. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 9H), 1.22 (s, 3H × 0.62), 1.23 (s, 3H × 0.38), 1.79-2.02 (m, 2H), 2.03 (s, 3H × 0.38), 2.04 (s, 3H × 0.62), 3.66 (s, 3H), 3.82 (dd, *J* = 9.8, 7.3 Hz, 1H), 4.00-4.05 (m, 1H), 4.08-4.14 (m, 1H), 4.11 (d, *J* = 11 Hz, 1H), 4.17 (d, *J* = 11 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.71, 21.01, 21.17, 21.19, 26.05, 26.07, 29.63, 29.68, 30.83, 31.10, 33.97, 40.16, 40.25, 52.02, 68.77, 68.85, 69.20, 75.95, 168.48, 168.53,

171.11, 174.08, 174.12; IR (neat) ν 2955, 2907, 1744, 1665, 1478, 1438, 1365, 1239 cm^{-1}; HRMS (CI) Calcd for $C_{16}H_{28}NO_5$ (MH^+) 314.1967, found 314.1968.



14a

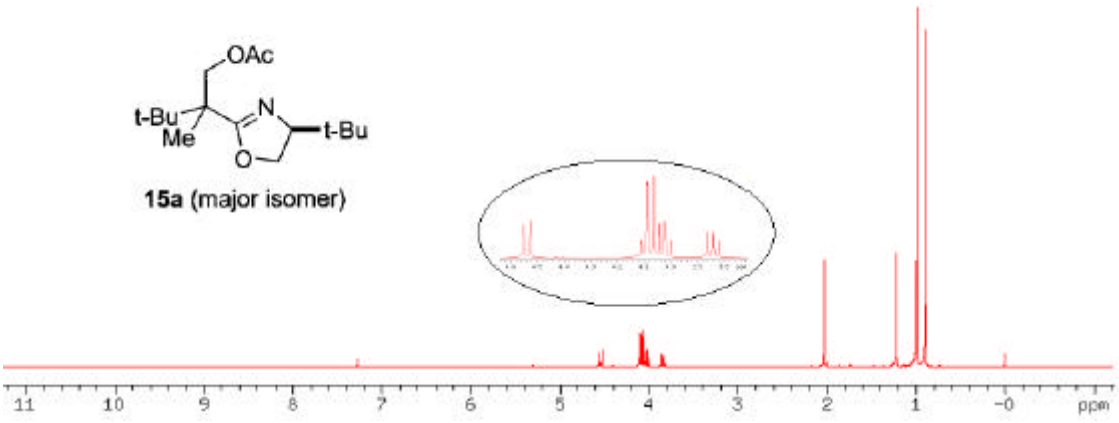
2- ((*S*)-4-*tert*- Butyl- 4,5-dihydrooxazol-2 -yl) -2 -(*tert* - butyldimethylsilyloxy) propyl acetate (14a), mixture of diastereomers: 14a was obtained as a light yellow oil (77 mg, 43% yield) after purification by column chromatography. **14a** was a mixture of diastereomers with 62% de as measured by ^{1}H NMR and GC-MS; 50 °C (50 min) to 280 °C (550 min), oven ramp rate: 0.5 °C/min, helium flow rate: 1 mL/min, t_r (major) = 223.9 min, t_r (minor) = 222.8 min. The diastereomers were not further separated. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.09 (s, 3H), 0.86 (s, 9H), 0.88 (s, 9H), 1.47 (s, 3H × 0.19), 1.51 (s, 3H × 0.81), 2.04 (s, 3H × 0.81), 2.05 (s, 3H × 0.19), 3.86 (dd, *J* = 8.4, 7.6 Hz, 1H), 4.08 (t, *J* = 8.0 Hz, 1H), 4.14-4.18 (m, 3H), 4.28 (d, *J* = 11 Hz, 1H × 0.19); ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.15, -2.60, 18.40, 21.04, 24.37, 25.80, 25.83, 25.93, 25.99, 68.93, 69.84, 72.47, 75.99, 167.51, 170.73; IR (neat) ν 3426, 2957, 1749, 1668, 1474, 1369, 1250 cm^{-1}; HRMS (CI) Calcd for $C_{18}H_{36}NO_4Si$ (MH^+) 358.2414, found 358.2417. 50% starting material was recovered.



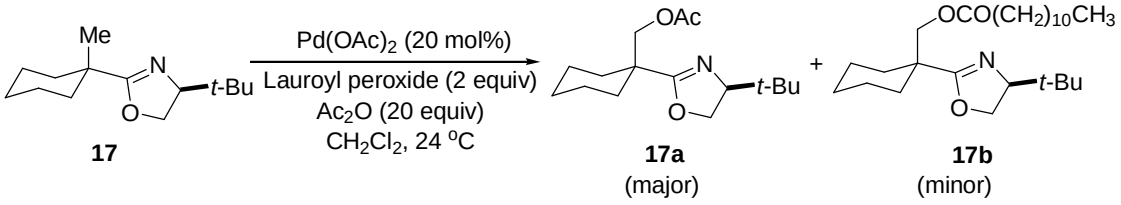
15a

2- ((*S*)- 4- *tert*- Butyl -4, 5- dihydrooxazol- 2- yl) -2, 3, 3- trimethylbutyl acetate (15a), mixture of diastereomers: 15a was obtained as a light yellow oil (70 mg, 49% yield) after purification by column chromatography. **15a** was a mixture of diastereomers with 82% de as measured by ^{1}H NMR and GC-MS; 50 °C (50 min) to 280 °C (550 min), oven ramp rate: 0.5 °C/min, helium flow rate: 1 mL/min, t_r (major) = 191.0 min, t_r (minor) = 192.2 min. The major diastereomer was isolated in 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s,

9H), 0.98 (s, 9H), 1.21 (s, 3H), 2.01 (s, 3H), 3.81 (m, 1H), 4.00-4.13 (m, 3H), 4.52 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.58, 20.98, 25.91, 26.57, 33.72, 35.16, 45.92, 67.95, 67.93, 75.55, 168.59, 171.11; IR (neat) ν 2958, 1743, 1655, 1479, 1385, 1243 cm^{-1}; HRMS (CI) Calcd for $C_{16}H_{30}NO_3$ (MH^+) 284.2226, found 284.2230. 47% starting material was recovered.



Effects of acetic anhydride and oxygen on acetoxylation reaction

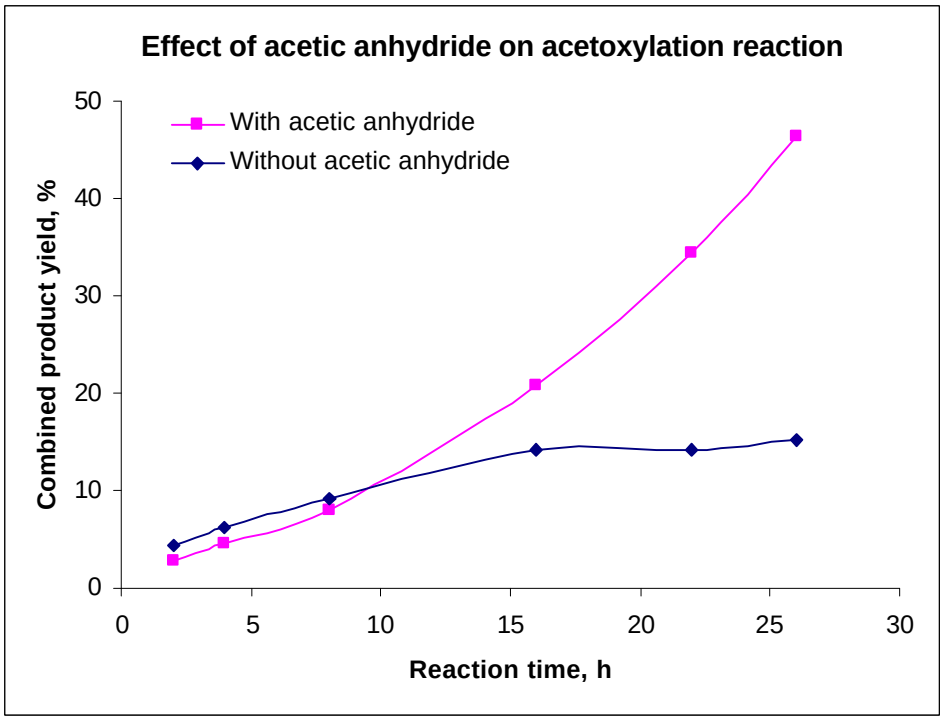


Effect of Ac_2O on acetoxylation reaction: Stock solutions of oxazoline **17** (223 mg/mL), $Pd(OAc)_2$ (44.8 mg/mL), lauroyl peroxide (199.3 mg/mL) and Ac_2O (102 mg/mL) were prepared in CH_2Cl_2. Oxazoline **17** (100 µL, 0.1 mmol), lauroyl peroxide (400 µL, 0.2 mmol), Ac_2O (200 µL, 2 mmol) and CH_2Cl_2 (200 µL) were placed in a 20 mL scintillation vial. $Pd(OAc)_2$ (100 µL, 0.02 mmol) was added to it (final volume: 1 mL) and the reaction mixture was stirred at 24 °C. A parallel reaction was also carried out in absence of acetic anhydride. Reactions were performed in triplicates and aliquots of the reaction mixture were taken at 2, 4, 8, 16, 22 and 26 hours for GC-MS analysis. Percentage yields of the products (acetate as a major and laurate as a minor product) were determined relative to the starting oxazoline **17** and the values in the table 1 represent the average of three reactions.

The combined product yields of acetate and laurate were plotted against the reaction time to acquire the graph.

Table 1: Product formation in presence and absence of Ac_2O

Reaction time, h	Combined product yield, %	
	With Ac_2O	Without Ac_2O
2	2.9	4.4
4	4.6	6.2
8	8.1	9.2
16	20.7	14.2
22	34.4	14.3
26	46.3	15.1

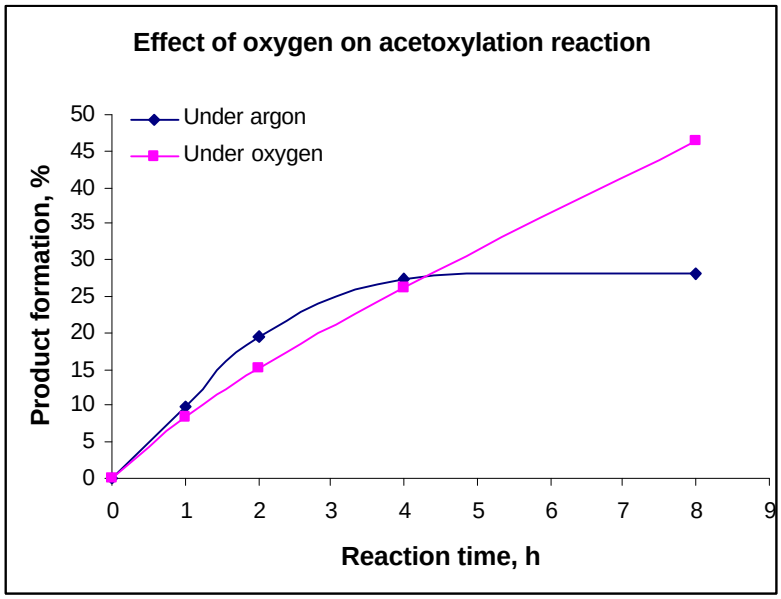


Effect of oxygen on acetoxylation reaction: Stock solutions of oxazoline **17** (223 mg/mL), $Pd(OAc)_2$ (22.4 mg/mL) and lauroyl peroxide (199.3 mg/mL) were prepared in CH_2Cl_2. Oxazoline **17** (100 µL, 0.1 mmol), lauroyl peroxide (200 µL, 0.1 mmol) and $Pd(OAc)_2$ (50 µL, 0.005 mmol)) were placed in a 20 mL pressure tube. CH_2Cl_2 was

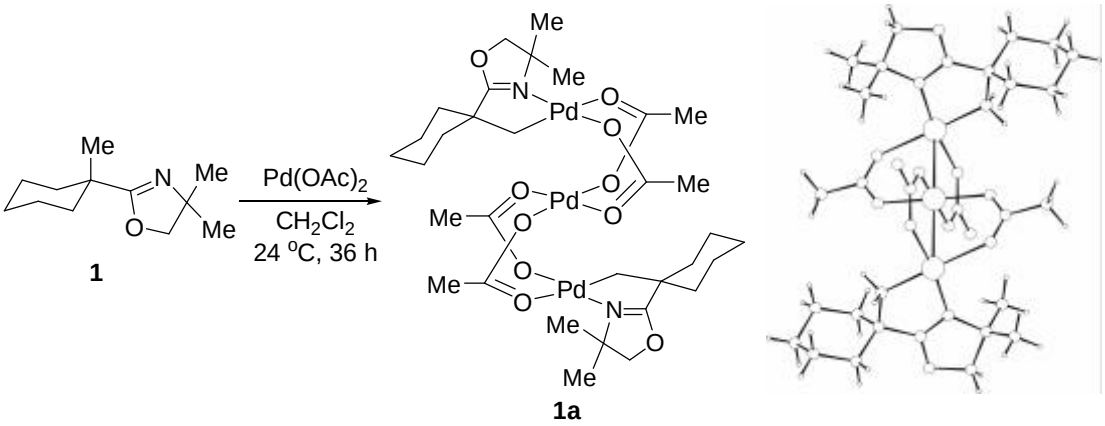
removed by fridge-thaw process. Ac_2O (1 mL) was added to the reaction mixture and oxygen was removed by fridge-thaw process under argon (3 cycles of vacuum/Ar). The reaction was heated at 50 °C. A parallel reaction was also carried out under oxygen. Reactions were performed in triplicates and aliquots of the reaction mixture were taken at 1, 2, 4 and 8 hours for GC-MS analysis. Percentage yields of the products (acetate as a major and laurate as a minor product) were determined relative to the starting oxazoline **17** and the values in the table 2 represent the average of three reactions. The combined product yields of acetate and laurate were plotted against the reaction time to acquire the graph.

Table 2: Product formation in presence and absence of oxygen

Reaction time, h	Combined product yield, %	
	Under Argon	Under oxygen
0	0	0
1	9.8	8.3
2	19.4	15.2
4	27.3	26.1
8	28.1	46.5

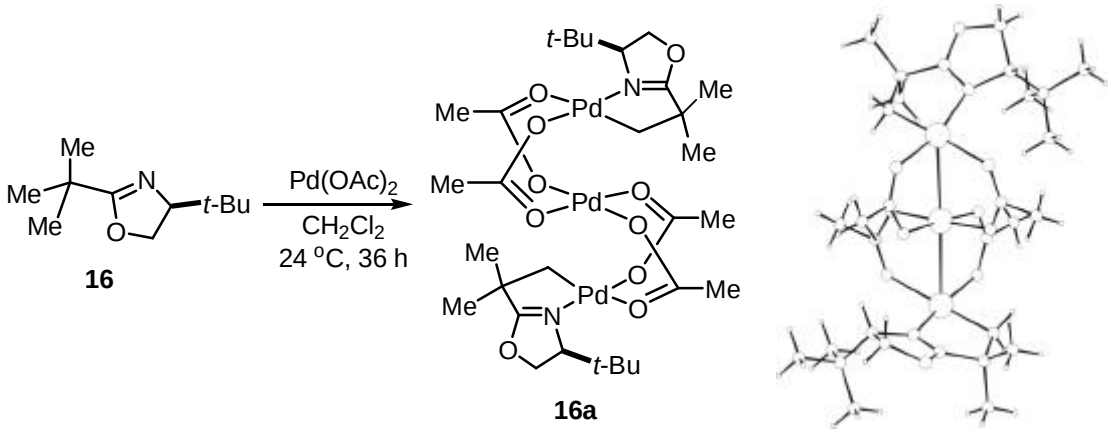


Mechanistic studies using trinuclear palladium complex



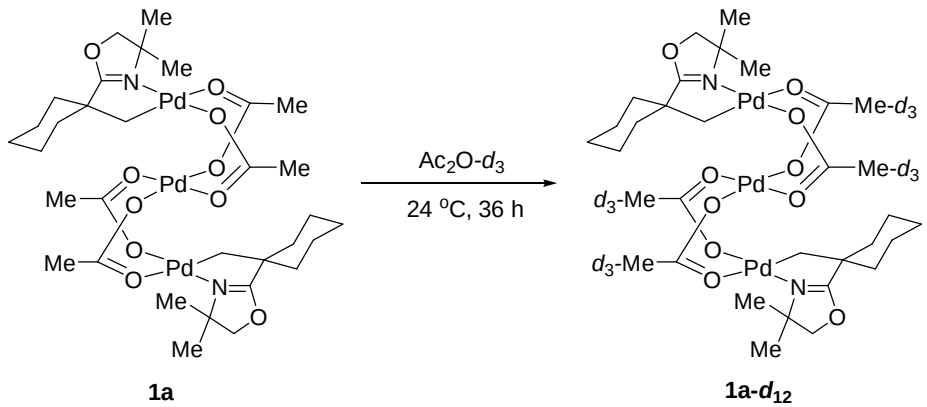
Formation of trinuclear bis-*m*-acetato palladium complex (1a): Oxazoline **1** (195 mg, 1 mmol) was stirred with palladium acetate (336 mg, 1.5 mmol) in CH_2Cl_2 (10 ml) at 24 °C for 36 h. The solvent was removed in a rotary evaporator to give a brown residue. The residue was repeatedly washed with diethyl ether, centrifuged and dried under high vacuum to yield a brown complex **1a** (755 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 3H × 0.67), 1.21 (s, 3H × 0.33), 1.46 (s, 3H × 0.67), 1.47 (s, 3H × 0.33), 1.46-1.83 (m, 8H), 1.72 (s, 3H × 0.33), 1.78 (s, 3H × 0.67), 1.79 (s, 3H × 0.67), 1.83 (s, 3H × 0.33), 2.01 (d, br, *J* = 9.8 Hz, 2H), 2.16 (d, *J* = 8.5 Hz, 1H × 0.33), 2.20 (d, *J* = 7.9 Hz, 1H × 0.67), 2.74 (d, *J* = 8.5 Hz, 1H × 0.33), 2.79 (d, *J* = 7.9 Hz, 1H × 0.67), 4.11 (dd, *J* = 12.2, 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.23, 21.92, 21.94, 22.17, 23.29, 23.39, 23.65, 23.78, 25.99, 27.47, 27.50, 27.55, 33.69, 33.75, 34.43, 44.55, 65.62, 65.66, 80.04, 181.81, 182.02, 183.35, 183.58.

Crystallization of 1a: Complex **1a** (47.2 mg) was dissolved in CH_2Cl_2 (2 mL) and diluted with hexane (2 mL). The solution was filtered through a Cameo 3N syringe filter (0.45 μ, 3 mm) (Osmonics Inc.) in a glass sample vial. The complex was crystallized as brown prisms in 16 days at 24 °C.

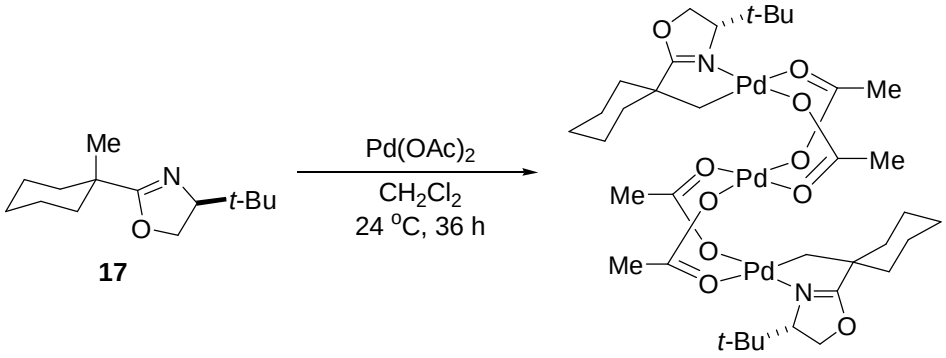


Formation of trinuclear bis-*m*-acetato palladium complex (16a): Oxazoline **16** (183 mg, 1 mmol) was stirred with palladium acetate (336 mg, 1.5 mmol) in CH_2Cl_2 (10 ml) at 24 °C for 36 h. The solvent was removed in a rotary evaporator to give a green residue. The residue was repeatedly washed with diethyl ether, centrifuged and dried under high vacuum to yield a green complex **16a** (689 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.25 (s, 3H), 1.30 (s, 3H), 1.76 (s, 3H), 1.79 (s, 3H), 2.28 (d, *J* = 7.9 Hz, 1H), 2.67 (d, *J* = 7.9 Hz, 1H), 3.55 (dd, *J* = 9.2, 3.0 Hz, 1H), 4.22 (t, *J* = 9.2 Hz, 1H), 4.43 (dd, *J* = 8.5, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.43, 23.49, 24.33, 26.00, 26.06, 28.17, 34.53, 40.92, 70.69, 70.95, 181.30, 183.97, 184.00; TOF MS (ES) (MNH_4^+) 939.1.

Crystallization of 16a: Complex **16a** (45.9 mg) was dissolved in CH_2Cl_2 (0.2 mL) and diluted with hexane (1.8 mL). The solution was filtered through a Cameo 3N syringe filter (0.45 µ, 3 mm) (Osmonics Inc.) in a glass sample vial. The complex was crystallized as brown prisms in 20 days at 24 °C.



Exchange of bridge acetate of complex 1a with Ac_2O-d_6: Complex **1a** (47.2 mg, 0.05 mmol) was mixed with Ac_2O-d_6 (1 mL) in a 20 mL scintillation vial. The vial was capped and the mixture was stirred at 24 °C. After 36 h, the mixture was centrifuged and acetic anhydride was removed. The complex was repeatedly washed with excess diethyl ether, centrifuged and the ether was removed. After drying under high vacuum for 1 h, the complex **1a**-d_{12} was obtained as a brown powder (38.3 mg, 80% yield). ^{1}H NMR of the complex showed the disappearance of peaks at d 1.72, 1.78, 1.79 and 1.83 ppm corresponding to the bridge acetates of syn- and anti-isomers of the complex **1a**.



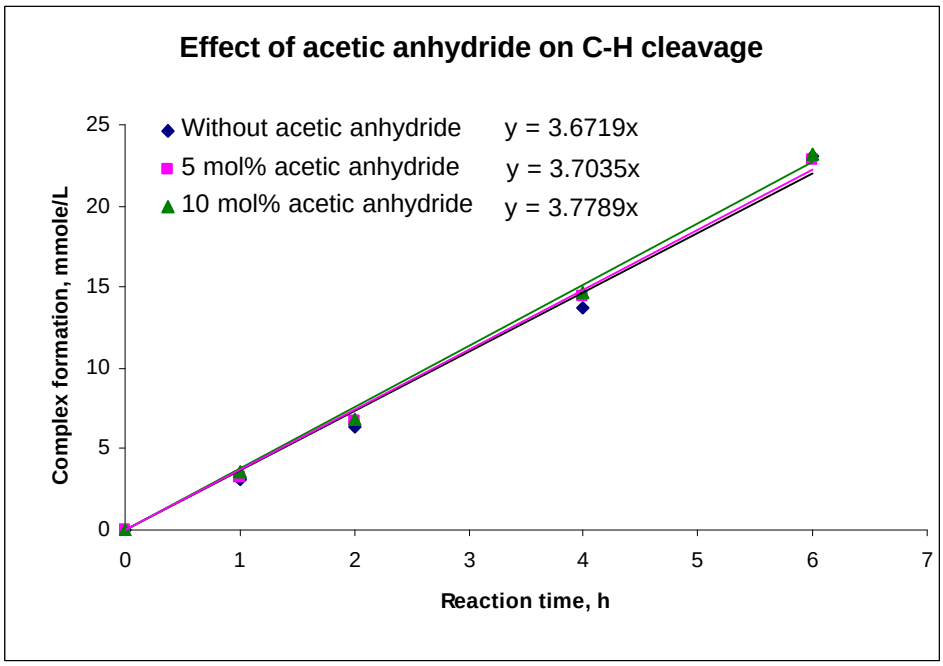
Formation of trinuclear bis-*m*-acetato palladium complex (17c): Oxazoline **17** (223 mg, 1 mmol) was stirred with palladium acetate (336 mg, 1.5 mmol) in CH_2Cl_2 (10 ml) at 24 °C for 36 h. The solvent was removed in a rotary evaporator to give a brown residue. The residue was repeatedly washed with diethyl ether, centrifuged and dried under high vacuum to yield a brown complex **17c** (709 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 9H), 1.38-1.68 (m, 8H), 1.75 (s, 3H), 1.79 (s, 3H), 2.11 (d, br, 2H), 2.23 (d, J = 7.9 Hz, 1H), 2.91 (d, J = 7.9 Hz, 1H), 3.50 (dd, J = 9.2, 3.1 Hz, 1H), 4.21 (t, J = 9.2 Hz, 1H), 4.41 (dd, J = 9.2, 3.1 Hz, 1H).

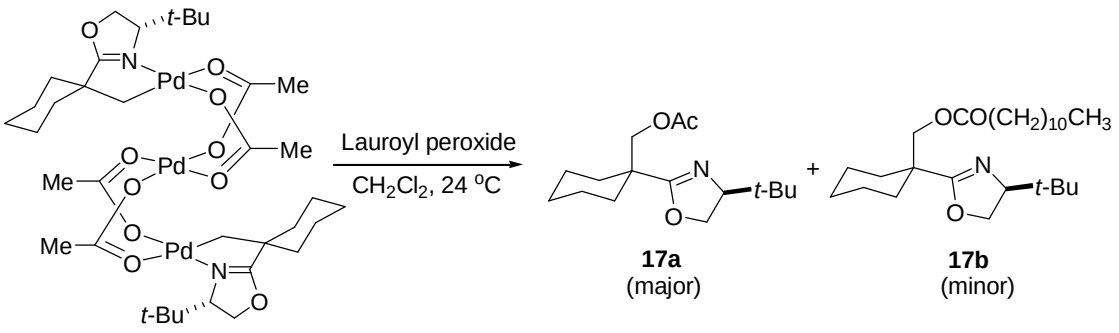
Effect of acetic anhydride on C-H cleavage: Stock solutions of oxazoline **17** (223 mg/mL), Ac_2O (408 mg/mL) and $Pd(OAc)_2$ (44.8 mg/mL) were prepared in CD_2Cl_2. Oxazoline **17** (100 µL, 0.1 mmol) and CD_2Cl_2 (400 µL) were placed in an NMR tube. $Pd(OAc)_2$ (500 µL, 0.1 mmol) was added to it (final volume: 1 mL), the NMR tube was tightly screw-capped and the reaction mixture stirred at 24 °C. Parallel reactions were carried out in presence of 5 equivalents (125 µL, 0.5 mmol) and 10 equivalents (250 µL, 1

mmol) of acetic anhydride keeping the final reaction volume at 1 mL with CD_2Cl_2. Reactions were carried out in triplicates. Formation of the complex **17c** was followed by ^1H NMR at 1, 2, 4 and 6 hours. Percentage of the complex formation was determined by measuring the ratio of *t*-butyl peak of the complex **17c** at d 1.04 ppm and *t*-butyl peak of oxazoline **17** at d 0.89 ppm. Rate of complex formation in presence of acetic anhydride was found to be the same as the rate of complex formation in absence of acetic anhydride (3.7 mmole L^{-1} h^{-1}).

Table 3: Complex formation in presence and absence of acetic anhydride

Reaction time, h	Complex formation, mmole/L		
	Without Ac_2O	Ac_2O (5 mol%)	Ac_2O (10 mol%)
1	31	3.3	3.6
2	6.4	6.7	6.9
4	13.7	14.4	14.7
6	23.1	22.8	23.2

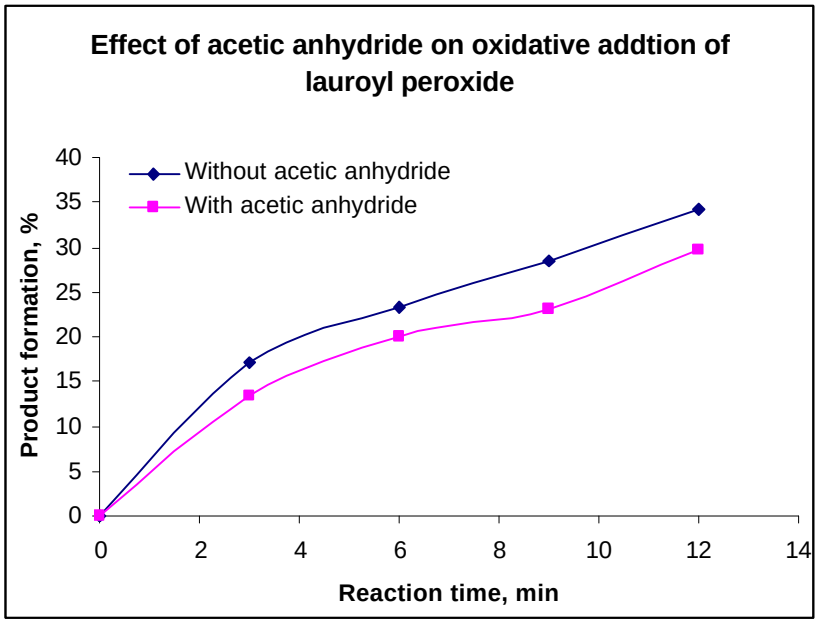




Reaction of lauroyl peroxide with the trinuclear Pd complex in presence and absence of acetic anhydride: Stock solutions of complex **17c** (65.6 mg/mL), lauroyl peroxide (262.7 mg/mL) and Ac_2O (336.6 mg/mL) were prepared in CH_2Cl_2. Complex **17c** (500 µL, 0.033 mmol), Ac_2O (100 µL, 0.33 mmol) and lauroyl peroxide (250 µL, 0.165 mmol) were placed in a 20 mL scintillation vial (final volume: 1 mL) and tightly capped. The reaction mixture was stirred at 24 °C. A parallel reaction was also carried out in absence of Ac_2O. Reactions were performed in triplicates and aliquots of the reaction mixture were taken at 1, 2, 3, 6, 9 and 12 minutes and the unreacted complex **17c** was quenched with I_2 (I_2 instantly reacts with the trinuclear complex **17c** giving iodinated product). Percentage yields of the products (acetate as a major and laurate as a minor product) were determined relative to the iodinated product by GC-MS. The values in the table 3 represent the average of three reactions. The combined product yields of acetate and laurate were plotted against the reaction time to acquire the graph.

Table 4: Product formation in presence and absence of acetic anhydride

Reaction time, min	Combined product yield, %	
	Without Ac_2O	With Ac_2O
0	0	0
3	17.1	13.3
6	23.2	20
9	28.4	23.1
12	34.3	29.6



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10. Oxidation of the substrate **1** using peroxyester carbonate i-PrOCOOOt-Bu as an oxidant in acetic anhydride gives the acetoxylated product **1d** in 68% isolated yield.