

Supporting Information

Catalytic Allylic C-H Acetoxylation and Benzoyloxylation via Suggested (η^3 -Allyl)palladium(IV) Intermediates

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1. General Information

Palladium pincer complex **1b**¹, deuterated substrate **2f-1d**^{2,3} and iodonium salt **3b**⁴ were prepared according to literature procedures. Glacial acetic acid was distilled prior to use. All other chemicals were obtained from commercial sources and used as received. All reactions were carried out under air. Unless otherwise stated ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ (internal standard: 7.26 ppm, ¹H; 77.00 ppm, ¹³C) using a Bruker 400 or 500 MHz spectrometer. ²H NMR spectrum was recorded in CDCl₃ (internal standard: 7.26 ppm, ¹H) using a Bruker 500 MHz spectrometer. High resolution mass data (HRMS) were obtained using ESI technique. For column chromatography, silica gel (35-70 microns) was used.

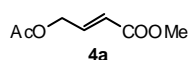
2. Experimental Procedures and Spectral Data

General Procedures:

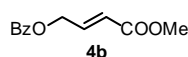
Procedure A: Acetoxylation of Alkenes (Table 1). To a 2 mL screw-top glass vial equipped with a magnetic stirring bar were added sequentially: the indicated palladium salt (0.015 mmol, 5 mol%), **3a** (193.3 mg, 0.60 mmol), substrate (0.30 mmol), potassium acetate (29.4 mg, 0.30 mmol) and appropriate solvent (1 mL). The mixture was stirred for 18 h at 40 °C. The crude reaction mixture was diluted with Et₂O (5 mL), washed with water (3 × 5 mL) and dried (MgSO₄). The solid residues were washed with Et₂O (2 × 5 mL) and the combined liquors concentrated under reduced pressure to give the crude products (**4a**, **4c** and **4e-4h**), which were further purified by silica gel chromatography.

Procedure B: Benzoyloxylation of Alkenes (Table 1). To a 2 mL screw-top glass vial equipped with a magnetic stirring bar were added sequentially: the indicated

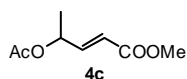
palladium salt (0.015 mmol, 5 mol%), **3b** (267.7 mg, 0.60 mmol), substrate (0.30 mmol), lithium benzoate (38.4 mg, 0.30 mmol) and CH₃CN (1 mL). The mixture was stirred for 18 h at 40 °C. The crude reaction mixture was diluted with Et₂O (5 mL), washed sequentially with water (3 × 5 mL) and aqueous NaHCO₃ (0.4 M, 3 mL), and then dried (MgSO₄). The solid residues were washed with Et₂O (2 × 5 mL) and the combined liquors concentrated under reduced pressure to give the crude products (**4b** and **4d**), which were further purified by silica gel chromatography.



(E)-Methyl 4-acetoxybut-2-enoate (4a). General Procedure A. Isolated in 59% yield (27.3 mg) using pentane/Et₂O 10:1 as eluent for silica gel chromatography. The NMR data obtained for **4a** are in agreement with literature values.⁵ **¹H NMR** (400 MHz, CDCl₃): δ 6.94 (td, *J* = 4.6, 15.7 Hz, 1H), 6.03 (td, *J* = 2.0, 15.7 Hz, 1H), 4.74 (dd, *J* = 2.0, 4.6 Hz, 2H), 3.76 (s, 3H), 2.12 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃): δ 170.3, 166.2, 141.4, 121.8, 62.5, 51.7, 20.7; **HRMS** (pos. ESI) *m/z*: calcd for C₇H₁₀NaO₄ [M+Na]⁺ 181.0471, found 181.0476.

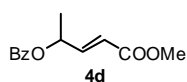


(E)-Methyl 4-benzoyloxybut-2-enoate (4b). General Procedure B. Isolated in 64% yield (42.0 mg) using pentane/Et₂O 10:1 as eluent for silica gel chromatography. **¹H NMR** (400 MHz, CDCl₃): δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.07 (td, *J* = 4.5, 15.8 Hz, 1H), 6.14 (td, *J* = 2.0, 15.8 Hz, 1H), 5.00 (dd, *J* = 2.0, 4.5 Hz, 2H), 3.76 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃): δ 166.2, 165.8, 141.5, 133.3, 129.7, 129.5, 128.5, 121.8, 62.9, 51.8; **HRMS** (pos. ESI) *m/z*: calcd for C₁₂H₁₂NaO₄ [M+Na]⁺ 243.0628, found 243.0630.



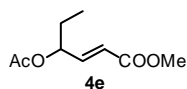
(E)-Methyl 4-acetoxypent-2-enoate (4c). General Procedure A.

Isolated in 62% yield (32.0 mg) using pentane/Et₂O 6:1 as eluent for silica gel chromatography. The NMR data obtained for **4c** are in agreement with literature values.⁵ **¹H NMR** (400 MHz, CDCl₃): δ 6.88 (dd, J = 5.0, 15.8 Hz, 1H), 5.96 (dd, J = 1.6, 15.8 Hz, 1H), 5.49 (ddq, J = 1.6, 5.0, 6.6 Hz, 1H), 3.75 (s, 3H), 2.09 (s, 3H), 1.36 (d, J = 6.6 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃): δ 170.0, 166.5, 146.6, 120.6, 68.8, 51.7, 21.1, 19.6; **HRMS** (pos. ESI) m/z : calcd for C₈H₁₂NaO₄ [M+Na]⁺ 195.0628, found 195.0627.



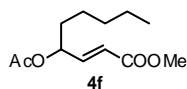
(E)-Methyl 4-benzoyloxypent-2-enoate (4d). General Procedure

B. Isolated in 61% yield (42.8 mg) using pentane/Et₂O 10:1 as eluent for silica gel chromatography. **¹H NMR** (400 MHz, CDCl₃): δ 8.07 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.01 (dd, J = 4.9, 15.8 Hz, 1H), 6.07 (dd, J = 1.7, 15.8 Hz, 1H), 5.75 (ddq, J = 1.7, 4.9, 6.7 Hz, 1H), 3.75 (s, 3H), 1.50 (d, J = 6.7 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃): δ 166.5, 165.5, 146.6, 133.2, 129.9, 129.7, 128.4, 120.6, 69.3, 51.7, 19.7; **HRMS** (pos. ESI) m/z : calcd for C₁₃H₁₄NaO₄ [M+Na]⁺ 257.0784, found 257.0782.



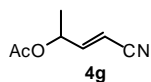
(E)-Methyl 4-acetoxylhex-2-enoate (4e). General Procedure A.

Isolated in 61% yield (34.0 mg) using pentane/Et₂O 10:1 as eluent for silica gel chromatography. The NMR data obtained for **4e** are in agreement with literature values.⁵ **¹H NMR** (400 MHz, CDCl₃): δ 6.85 (dd, J = 5.3, 15.8 Hz, 1H), 5.95 (dd, J = 1.6, 15.8 Hz, 1H), 5.34 (ddt, J = 1.6, 5.3, 6.4 Hz, 1H), 3.75 (s, 3H), 2.10 (s, 3H), 1.70 (dq, J = 6.4, 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃): δ 170.1, 166.5, 145.5, 121.3, 73.5, 51.7, 26.8, 21.0, 9.2; **HRMS** (pos. ESI) m/z : calcd for C₉H₁₄NaO₄ [M+Na]⁺ 209.0784, found 209.0793.



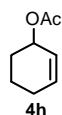
(E)-Methyl 4-acetoxynon-2-enoate (4f). General Procedure A.

Isolated in 70% yield (47.9 mg) using pentane/Et₂O 10:1 as eluent for silica gel chromatography. ¹H NMR (400 MHz, CDCl₃): δ 6.85 (dd, *J* = 5.4, 15.7 Hz, 1H), 5.94 (dd, *J* = 1.6, 15.7 Hz, 1H), 5.39 (ddt, *J* = 1.6, 5.4, 6.5 Hz, 1H), 3.74 (s, 3H), 2.09 (s, 3H), 1.69-1.61 (m, 2H), 1.36-1.23 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 170.1, 166.5, 145.8, 121.0, 72.5, 51.7, 33.7, 31.4, 24.6, 22.4, 21.0, 13.9; HRMS (pos. ESI) *m/z*: calcd for C₁₂H₂₀NaO₄ [M+Na]⁺ 251.1254, found 251.1256.



4-Acetoxypent-2-enenitrile (4g). General Procedure A. Isolated as a mixture of *trans*-**4g** and *cis*-**4g** (1:1 ratio) in 51% yield (21.6 mg) using

pentane/Et₂O 10:1 as eluent for silica gel chromatography. The NMR data obtained for **4g** are in agreement with literature values.^{6,7} *trans*-**4g**: ¹H NMR (400 MHz, CDCl₃): δ 6.65 (dd, *J* = 5.0, 16.4 Hz, 1H), 5.54 (dd, *J* = 1.8, 16.4 Hz, 1H), 5.44 (ddq, *J* = 1.8, 5.0, 6.7 Hz, 1H), 2.10 (s, 3H), 1.36 (d, *J* = 6.7 Hz, 3H) ¹³C NMR (101 MHz, CDCl₃): δ 169.7, 152.6, 116.5, 100.2, 68.6, 20.9, 19.3; HRMS (pos. ESI) *m/z*: calcd for C₇H₉NNaO₂ [M+Na]⁺ 162.0525, found 162.0526. *cis*-**4g**: ¹H NMR (400 MHz, CDCl₃): δ 6.40 (dd, *J* = 6.7, 11.5 Hz, 1H), 5.65 (ddq, *J* = 1.4, 6.7, 6.7 Hz, 1H), 5.41 (dd, *J* = 1.4, 11.5 Hz, 1H), 2.11 (s, 3H), 1.42 (d, *J* = 6.7 Hz, 3H) ¹³C NMR (101 MHz, CDCl₃): δ 170.0, 152.3, 114.8, 99.6, 68.9, 20.9, 19.6.



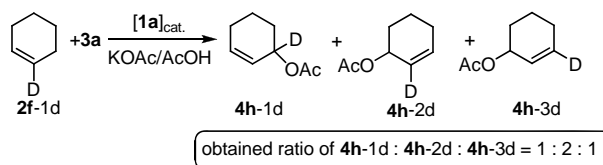
Cyclohex-2-enyl acetate (4h). General Procedure A. Isolated in 66% yield (27.6 mg) using pentane/Et₂O 20:1 as eluent for silica gel chromatography.

The NMR data obtained for **4h** are in agreement with literature values.⁸ ¹H NMR (400 MHz, CDCl₃): δ 5.94 (dtd, *J* = 1.3, 3.8, 10.0 Hz, 1H), 5.72-5.66 (m, 1H), 5.27-5.22 (m, 1H), 2.14-1.93 (m, 2H), 2.04 (s, 3H), 1.91-1.82 (m, 1H), 1.78-1.57 (m, 3H);

^{13}C NMR (101 MHz, CDCl_3): δ 170.8, 132.6, 125.7, 68.1, 28.3, 24.8, 21.4, 18.8;

HRMS (pos. ESI) m/z : calcd for $\text{C}_8\text{H}_{12}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 163.0730, found 163.0732.

3. Catalytic Acetoxylation of Deuterated Cyclohexene



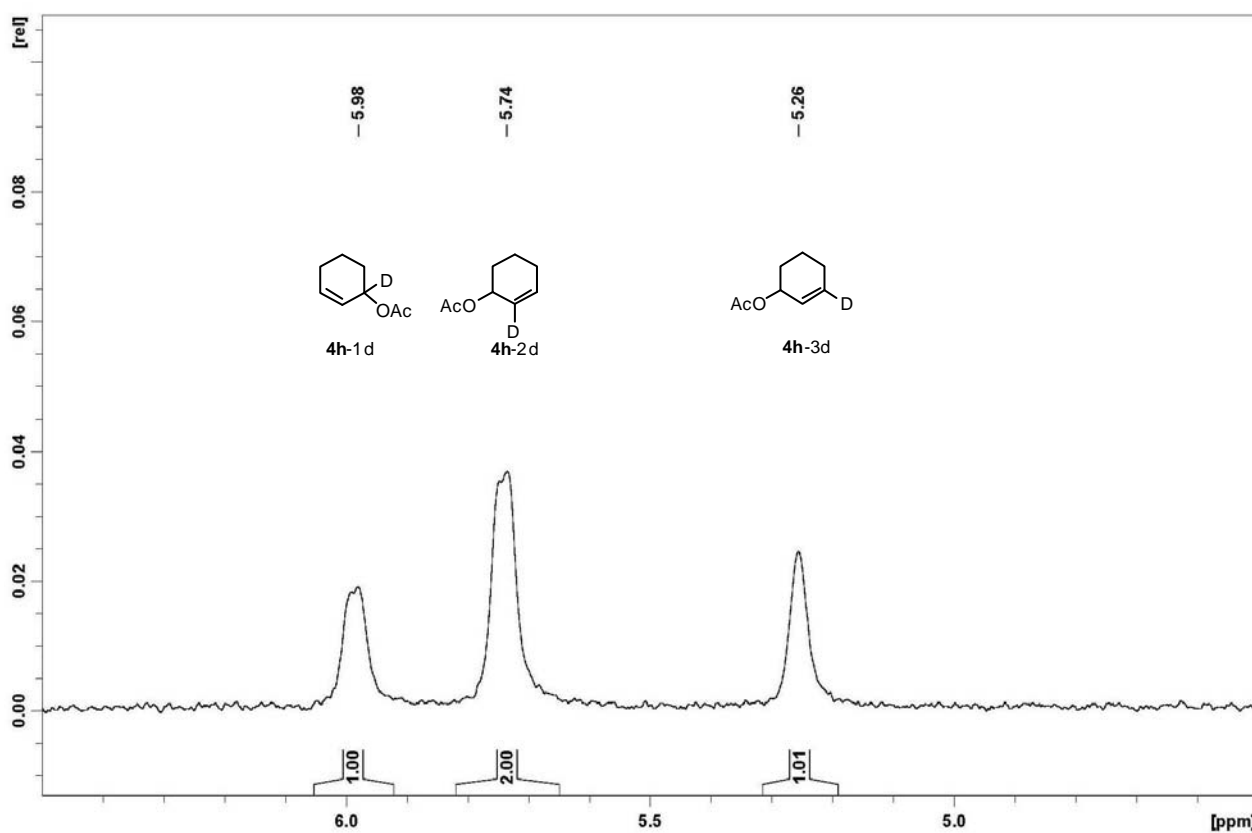
The acetoxylation of **2f-1d** was performed according to General Procedure A. The isotope distribution in product **4h** was determined by integration of the peaks in the ^2H NMR spectrum shown below. No other deuterated species were detected.

Spectral data for the three isomers:

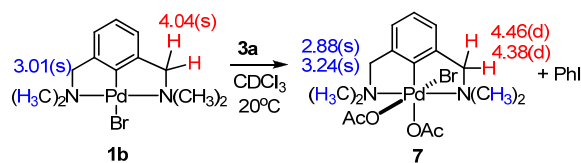
4h-1d: ^2H NMR (76.8 MHz, CDCl_3): δ 6.03-5.93 (br s, 1D).

4h-2d: ^2H NMR (76.8 MHz, CDCl_3): δ 5.80-5.67 (br s, 1D).

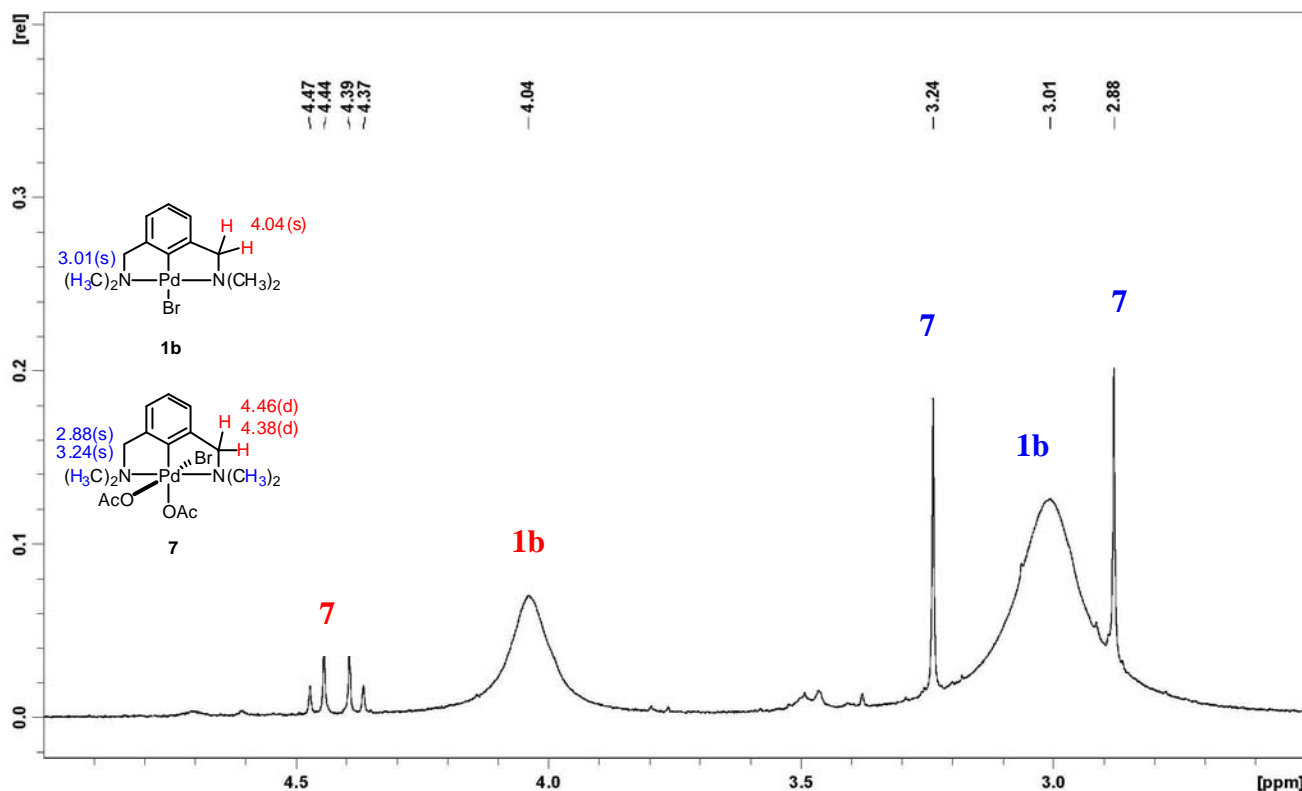
4h-3d: ^2H NMR (76.8 MHz, CDCl_3): δ 5.30-5.20 (br s, 1D).



4. Oxidation of Palladium Complex **1b** Monitored by ^1H NMR



A NMR tube was charged with a solution of palladium complex **1b** (7.6 mg, 0.02 mmol) in CDCl_3 (0.3 mL). To this solution, iodonium salt **3a** (19.3 mg, 0.06 mmol) was added in CDCl_3 (0.1 mL). The sample was vigorously shaken to give a homogeneous solution and five minutes thereafter a ^1H NMR spectrum (shown below) was recorded at room temperature. Approximately 10 minutes later (at room temperature), a second ^1H NMR spectrum was recorded, showing no peaks assigned to complex **7**. Spectral data for the benzyl and methyl protons of proposed complex **7**: ^1H NMR (500 MHz, CDCl_3): δ 4.46 (d, $J = 13.9$ Hz, 2H, Ar- CH_2), 4.38 (d, $J = 13.9$ Hz, 2H, Ar- CH_2), 3.24 (s, 6H, NCH_3), 2.88 (s, 6H, NCH_3).



5. Oxidation of **2a** using $\text{PhI}(\text{OAc})_2$ and LiOBz

To a 2 mL screw-top glass vial equipped with a magnetic stirring bar were added sequentially: $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol, 5 mol%), **3a** (64.4 mg, 0.20 mmol), **2a** (10.0 mg, 0.10 mmol), lithium benzoate (12.8 mg, 0.10 mmol) and CD_3CN (0.3 mL). The mixture was stirred for 18 h at 40 °C, filtered through a cotton wool plug and additional CD_3CN (0.2 mL) was added. The product ratio was determined by ^1H NMR and found to be **4a:4b** 2:1.

6. References

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7. ^1H and ^{13}C NMR spectra of 4a-4h