A Sulfoxide-Promoted, Catalytic Method for the Regioselective Synthesis of Allylic Acetates from Monosubstituted Olefins *via* C-H Oxidation.

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General Information. Unless stated otherwise, reactions were conducted with stirring in 2mL (0.2 mmol reactions) or 40mL (1.0 mmol reactions) VWRbrand borosilicate glass vials with red PTFE-faced silicone lined plastic screw caps or teflon-lined solid caps (respectively) under an air atmosphere. Vials were used as received (no cleansing or drying was done prior to reaction). All commercially obtained reagents (Sigma-Aldrich Chemical Company, unless stated otherwise) were used as received: anhydrous (Sure/Seal) DMSO; 4Å (powered, <5 micron) activated molecular sieves; 1,4-benzoquinone; glacial acetic acid (Mallinckrodt Chemicals); Pd(OAc)₂ (Strem Chemicals); Pd(O₂CCF₃)₂ (Strem Chemicals). Both palladium sources were stored in a glove box under a nitrogen atmosphere. Pd(OAc)₂ was weighed in the air whereas Pd(O₂CCF₃)₂ [Pd(TFA)₂] was weighed in the glove box. Solvents tetrahydrofuran (THF), diethyl ether (Et₂O), ethylene glycol dimethyl ether (DME), methylene chloride (CH₂Cl₂), toluene, benzene were purified prior to use by passage through a bed of activated alumina (Glass Contour, Laguna Beach, California). Acetonitrile (CH₃CN) was distilled from CaH₂. Gas chromatographic (GC) analyses were performed on Agilent Technologies 6890N Series instrument equipped with FID detectors using a HP-5 (5%-Phenyl)-methylpolysiloxane column (30m, 0.32mm, 0.25µm). GC yields reported relative to an internal standard (nitrobenzene) and corrected for response factor variations. Unless otherwise noted, linear to branched allylic acetate ratios [L:B] were determined by GC analysis of the crude and were not corrected for small response factor variations. Retention times for the branched isomers were determined by independent synthesis using catalyst **1** (see general procedure for catalyst **1**, equations 2 and 3) which gave the branched as the major products for substrates constituting entries 3-9 in Table 1 or as mixtures for entry 1 and 10 ([L:B] = 4:1, [L:B] = 2:1, respectively). Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized with UV and potassium permanganate staining. Reaction progression was monitored by both GC and TLC analysis. Flash column chromatography was performed as described by Still et al.¹ using EM reagent silica gel 60 (230-400 mesh). ¹H NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent; coupling constant(s) in Hz; integration. Ratios of *E* to *Z* isomers were determined by ¹H NMR analysis of the crude upon workup and are based on integration of the allylic hydrogens of the acetoxy-bearing carbon of the two isomers. Assignments of all isomers were confirmed by gCOSY experiments. Proton-decoupled ¹³C NMR spectra were recorded on a Varian Mercury-400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.0 ppm). IR spectra were recorded as thin films on NaCl plates on a Matterson FTIR 3000 and are reported in frequency of absorption (cm⁻¹). High resolution mass spectra were obtained at the Harvard University Mass Spectrometry Laboratory. Elemental analysis was conducted at Desert Analytics, Tucson, Arizona.

I. Synthesis and Analytical Data for Catalyst **1**.

1,2-bis(benzylthio)ethane²:

A flame-dried 500 mL round bottom flask was charged sequentially with a stir bar, NaOEt (2.94g, 43.2 mmol), and EtOH (105 mL) under a N₂ atmosphere. 1,2-ethanedithiol (1.8 mL, 21.4 mmol) was added dropwise *via* syringe to the NaOEt solution and the mixture was allowed to stir for 20 min. A solution of benzyl bromide (5 mL, 42.0 mmol) in benzene (63 mL) was added dropwise *via* cannula. The reaction was allowed to stir overnight. Solvents were removed under house vacuum (~25 torr) with mild heating (40°C). The residue was diluted with CHCl₃ (400 mL) and washed with brine (150 mL). The brine was extracted three times with CHCl₃ (3 x 150 mL). The organic layers

were combined, dried over MgSO_4 , filtered and concentrated *in vacuo* to give a yellow oil. The yellow oil was suspended in EtOH (40 mL) and allowed to sit at 0°C for $\sim 1\text{h}$. A white solid crashed out and was washed with EtOH until the supernatant was clear (3 x 30 mL). The solid was dried under high vacuum for 7 h to give 1,2-bis(benzylthio)ethane in 80% yield (4.7g, 17.1 mmol). ^1H NMR (400 MHz, CDCl_3) δ 7.28 (m, 10H), 3.69 (s, 4H), 2.58 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 128.8, 128.5, 127.0, 36.2, 30.9. HRMS (EI^+) m/z calc'd for $[\text{C}_{16}\text{H}_{18}\text{S}_2]^+$: 274.0850, found 274.0842.

1,2-bis(benzylsulfinyl)ethane³:

A 100 mL round bottom flask was charged with a stir bar, 2.5g (9.1 mmol) of 1,2-bis(benzylthio)ethane, and 22 mL of glacial acetic acid. The mixture was allowed to stir at room temperature until it became homogeneous at which time it was cooled to 0°C and H_2O_2 (50 wt% solution, 1.05 mL, 18.22 mmol) was added dropwise. The reaction was allowed to come to room temperature and was stirred overnight. The acetic acid was removed with mild heating (50°C) under high vacuum and the white solid was washed with EtOH until the washings were clear (3 x 40 mL). The white solid was dried under high vacuum overnight to give 2.71g (8.84 mmol) of 1,2-bis(benzylsulfinyl)ethane in 97% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.36 (m, 5H), 7.27 (m, 5H), 4.03 (app dq, $J = 3.6, 13.2\text{ Hz}$, 4H), 3.03 (m, 2H), 2.87 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 130.1, 129.1, 128.9, 128.8, 128.7, 128.69, 58.9, 58.5, 43.5, 42.7; IR (film, cm^{-1}): 2959, 2913, 1454, 1024, 768, 698; HRMS (EI) m/z calc'd for $[\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}_2]^+$: 306.0748, found 306.0751.

Catalyst 1⁴:

A flame dried 250 mL flask was charged with 1.5 g (4.89 mmol) of 1,2-bis(benzylsulfinyl)ethane, 70 mL of CH_2Cl_2 , and 1.1g (4.89 mmol) of $\text{Pd}(\text{OAc})_2$. The mixture was stirred at reflux under a nitrogen atmosphere for 22h. During this time the reaction was observed to turn from a heterogeneous orange brown mixture to a homogeneous, dark red solution. The solution was concentrated *in vacuo* and dried over a N_2 stream for 12 h to give a dark red solid that was used without further purification. IR (film, cm^{-1}): 3032, 1736, 1555, 1495, 1454, 1413, 1231, 1070, 1045, 1030, 766, 698. MS (ESI) m/z 413 ($[\text{M} - (\text{OAc})_2 + \text{H}]^+$, center of isotope cluster); Anal. Calcd for $[\text{C}_{20}\text{H}_{24}\text{O}_6\text{PdS}_2]$ (%): C, 45.24; H, 4.56; Pd, 20.04; S, 12.08. Found (%): C, 45.61; H, 4.53; Pd, 20.63; S, 12.81.

Table 1. The effect of DMSO and bis-sulfoxide ligation on Pd(II) catalyzed oxidations of terminal olefins

10 mol%
Pd(OAc)₂
or
 $\text{Ph}-\text{O}-\text{S}(\text{CH}_2)_2-\text{S}(\text{O})-\text{Ph}$
 $\text{Pd}(\text{OAc})_2$
catalyst 1
 BQ (2 eq),
 AcOH, 40°C
conditions
 R = *n*-C₇H₁₅

Elusive C-H oxidation products:

$\text{R}-\text{CH}=\text{CH}-\text{CH}_2-\text{OAc}$
L

$\text{R}-\text{CH}(\text{OAc})-\text{CH}=\text{CH}_2$
B

Classical Wacker oxidation products:

$\text{R}-\text{CH}_2-\text{CH}(\text{OAc})-\text{CH}_3$
va

$\text{R}-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3$
mk

entry	conditions	% yield (GC) ^a , 48h				[L:B]
		L ^b	B ^c	va ^d	mk ^e	
1	AcOH	3%	5%	17%	14%	1:2
2	DMSO:AcOH (1:1)	40%	2%	3%	6%	20:1
3	1 (10 mol%) CH ₂ Cl ₂ :AcOH (1:1)	8%	66%	<1%	<1%	1:8

^aYields determined by GC for an average of 2-3 runs from reactions carried out on a 0.2 mmol scale. Yields are corrected for response factor variations. ^bMajor linear allylic acetate product observed (*E:Z* selectivity, Table 2). ^cMajor vinyl acetate product observed.

General procedure for Tables 1, S1-S8: Vials (2 mL, borosilicate) were sequentially charged with the following solids: Pd(OAc)₂ (4.5 mg, 0.02 mmol, 10 mol%) or Pd(TFA)₂ (6.6 mg, 0.02 mmol, 10 mol%) or catalyst **1** (10.6 mg, 0.02 mmol, 10 mol%), benzoquinone (43.2 mg, 0.4 mmol, 2 eq), and when indicated 4Å MS (43 mg). Separate vials (2 mL, borosilicate) were sequentially charged with the following liquids: 1-decene (28 mg, 38 µL, 0.2 mmol, 1 eq), nitrobenzene (9.9 mg, 8 µL, 0.08 mmol, 40 mol%), 1.2 mL AcOH or 0.6 mL DMSO/ 0.6 mL AcOH or 0.6 mL solvent/ 0.6 mL AcOH. Aliquots were taken from the liquid vials (~ 10 µL filtered with Et₂O through a short pipette plug of silica) to determine GC initial ratios of 1-decene to the nitrobenzene internal standard. The liquids were transferred *via* pipette into the appropriate solids vials, charged with a stir bar, capped and allowed to heat at 40°C with stirring. Aliquots were taken (as above) at t= 24h, t= 48h (shown) and t= 72h to determine GC yields. Each product was independently synthesized *via* known methods (**L**: Horner-Wadsworth-Emmons olefination of octyl aldehyde followed by reduction and acetylation, **B**: vinyl magnesium bromide alkylation of octyl aldehyde followed by acetylation, **va**: 2-decanone, isopropenyl acetate, *p*-toluenesulfonic acid⁵, **mk**: Aldrich). Response factors relative to decene were determined for each product. Note: Table S4 done on half the scale indicated above (*i.e.* 1-decene: 14.0 mg, 19 µL, 0.1 mmol, etc.).

Table S1. 4Å MS screen with 10 mol% Pd(OAc)₂.

entry	conditions	% yield (GC), 48h			
		L	B	va	mk
1	AcOH	3%	5%	17%	14%
2	AcOH/4Å MS	15%	5%	11%	21%
3	DMSO:AcOH (1:1)	40%	2%	3%	6%
4	DMSO:AcOH (1:1)/ 4Å MS	47%	2%	2%	5%

Table S2. 4Å MS screen with 10 mol% Pd(TFA)₂

entry	conditions	% yield (GC), 48h			
		L	B	va	mk
1	AcOH	3%	4%	11%	29%
2	DMSO:AcOH (1:1)	25%	3%	4%	16%
3	DMSO:AcOH (1:1)/ 4Å MS	46%	2%	2%	6%

Table S3. Solvent screen (solvent:AcOH, 1:1) with 10 mol% Pd(OAc)₂, BQ (2 eq), 40°C.

entry	solvent	% yield (GC), 48h			
		L	B	va	mk
1	AcOH	3%	4%	18%	12%
2	DMSO	40%	2%	3%	4%
3	DMF	3%	<1%	3%	<1%
4	dioxane	<1%	2%	20%	6%
5	CH ₃ CN	8%	5%	2%	2%
6	THF	<1%	1%	13%	3%
7	Et ₂ O	<1%	1%	14%	5%
8	DME	<1%	2%	16%	6%
9	CH ₂ Cl ₂	<1%	2%	10%	3%
10	Benzene	<1%	1%	10%	2%
11	Toluene	2%	2%	10%	2%

Table S4. Solvent screen (solvent:AcOH, 1:1) with 10 mol% catalyst **1**, BQ (2 eq), 40°C.

entry	solvent	% yield (GC), 48h			
		L	B	va	mk
1	AcOH	17%	59%	<1%	<1%
2	DMSO	12%	7%	<1%	<1%
3	DMF	13%	50%	<1%	<1%
4	CH ₃ CN	6%	3%	2%	<1%
5	dioxane	9%	61%	<1%	<1%
6	THF	7%	53%	<1%	<1%
7	Et ₂ O	8%	54%	<1%	<1%
8	DME	8%	57%	<1%	<1%
9	CH ₂ Cl ₂	9%	68%	<1%	<1%
10	Benzene	8%	63%	<1%	<1%
11	Toluene	9%	59%	<1%	<1%

Table S5. Oxidant screen with 10 mol% Pd(OAc)₂, 4Å MS, DMSO:AcOH (1:1), 40°C.

entry	[O]	% yield (GC), 48h			
		L	B	va	mk
1	BQ (2 eq)	47%	2%	2%	4%
2	Cu(OAc) ₂ (2 eq)	2%	1%	<1%	1%
3	BQ (20 mol%) MnO ₂ (2 eq)	31%	2%	1%	4%
4	Cu(OAc) ₂ (5 mol%) O ₂	17%	3%	1%	3%
5	Cu(OAc) ₂ (5 mol%) BQ (10 mol%) O ₂	32%	3%	1%	4%
6	O ₂	6%	2%	<1%	1%

Table S6. Benzoquinone equivalents screen with 10 mol% Pd(OAc)₂, 4Å MS, DMSO:AcOH (1:1), 40°C.

entry	BQ (eq)	% yield (GC), 48h			
		L	B	va	mk
1	1.0	36%	4%	1%	4%
2	1.5	43%	2%	2%	4%
3	2.0	46%	2%	2%	4%
4	2.5	44%	2%	2%	4%
5	3.0	43%	2%	2%	4%

Table S7. DMSO:AcOH ratio with 10 mol% Pd(OAc)₂, 4Å MS, BQ (2eq), 40°C.

entry	DMSO: AcOH	% yield (GC), 48h			
		L	B	va	mk
1	5:1	5%	<1%	<1%	---
2	2:1	24%	1%	1%	2%
3	1:1	44%	2%	1%	4%
4	1:2	55%	5%	2%	6%
5	1:5	50%	7%	4%	7%

Table S8. Reaction temperature screen with 10 mol% Pd(OAc)₂, BQ (2 eq), 4Å MS, and DMSO:AcOH (1:1).

entry	temperature	% yield (GC), 48h			
		L	B	va	mk
1	25°C	13%	<1%	<1%	1%
2	40°C	45%	2%	2%	4%
3	50°C	27%	9%	2%	4%
4	60°C	21%	9%	2%	4%

Table 2. Allylic oxidation of terminal olefins to (*E*)-allylic acetates.^a

entry	major product	linear: branched ^c	<i>E</i> : <i>Z</i> ^d	yield ^e
1		>99:1	>20:1	50% (72h)
2 ^b		>20:1 ^d	13:1	54% (48h)
3		24:1	12:1	52% (48h)
4 ^b		31:1	11:1	50% (72h)
5 ^b		31:1	11:1	57% (48h)
6		14:1	11:1	61% (72h)
7		17:1	13:1	56% (72h)
8		13:1	12:1	64% (72h)
9		23:1	12:1	62% (48h)
10		>99:1	13:1	65% (48h)

^aAll data reported ([L:B], [E:Z] ratios, yields) based on an average of two runs. ^b10mol% Pd(TFA)₂.^cratio based on GC analysis of crude. Not corrected for small response factor variations. ^dratio based on¹H NMR analysis of the crude. ^eIsolated yields after chromatography, from reactions carried out on a 1.0

mmol scale (0.17M). Unpurified commercial DMSO and glacial acetic acid were used, without inert

atmosphere techniques. [L:B] and [E:Z] ratios obtained after chromatography were generally higher. See

Supporting Information for details.

Terminal olefin substrates: The following terminal olefin substrates used were obtained from commercial sources: 1-decene (entry 3); allylbenzene (entry 10); ethyl 4-pentenoate (entry 2, Lancaster Synthesis). The remainder of the substrates were prepared *via* previously reported literature routes: 2-allylcyclohexanone ethylene ketal (entry 1)⁶, 5-(*tert*-butyldiphenylsiloxy)-1-pentene (entry 4)⁷, 1-benzyloxy-4-pentene (entry 5)⁸, 2-hydroxy-benzoic acid hex-5-enyl ester (entry 6/7)⁹, phenyl-carbamic acid hex-5-enyl ester (entry 8)⁹, *N,N*-diethyl-6-heptenamide (entry 9)¹⁰.

General procedure for Table 2: A 40 mL borosilicate glass vial was charged with the following solids: Pd(OAc)₂ (22.4 mg, 0.1 mmol, 10 mol%) or Pd(TFA)₂ (33.2 mg, 0.1 mmol, 10 mol%), benzoquinone (217 mg, 2.0 mmol, 2 eq), and 4 Å MS (217 mg). In cases (entries 2, 4, 5) where Pd(TFA)₂ was used, Pd(OAc)₂ gave slightly lower yields and/or [L:B] selectivities. To the solids vial was sequentially added the following: DMSO (3 mL), olefin substrate (1.0 mmol, 1 eq), AcOH (3 mL). The vial was charged with a stir bar, capped and allowed to heat at 40°C. Aliquots were taken (~ 10 µL filtered through a silica plug with Et₂O) at t= 24h, 48h, and 72h to determine linear:branched ratios [L:B]. For the majority of substrates examined (entries 3-9), the general trend observed was that of a slight decrease in [L:B] ratios over the course of the reaction (see below). The reaction was quenched with saturated NH₄Cl (10 mL) and extracted with CH₂Cl₂ (3 x 100 mL). The combined organic layers were washed with H₂O (2 x 100 mL), dried over MgSO₄, filtered and concentrated *in vacuo* to give a brown oil. A crude ¹H NMR was taken to determine [E:Z] ratios. Purification of the crude by flash chromatography afforded the linear *E*-allylic acetates as the major products with trace amounts of the linear *Z*-allylic acetates and the branched acetates. All data reported in Table 1 is based on an average of 2 runs.

Entry 1: 72h. run 1,2: [L:B] = >99:1, [E:Z] = >20:1 (branched or *Z* isomers were not observed by GC or ¹H NMR). Purification by flash chromatography (10% EtOAc/hexanes eluent) provided pure linear (*E*)-allylic acetate (run 1: 119mg, 0.49 mmol, 49% yield; run 2: 120.5mg, 0.5 mmol, 50% yield; average yield: 50%).

¹H NMR (400 MHz, CDCl₃) δ 5.80 (dd, *J* = 15.6, 7.6 Hz, 1H), 5.61 (dt, *J* = 15.6, 6.0 Hz, 1H), 4.52 (d, *J* = 6.8 Hz, 2H), 3.90 (m, 4H), 2.31 (m, 1H), 2.05 (s, 3H), 1.78-1.2 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 135.2, 125.1, 109.9, 65.3, 65.1, 64.9, 48.2, 35.2, 30.0, 24.3, 23.8, 21.0; IR (film, cm⁻¹): 2936, 2884, 2864, 1740, 1447, 1233; HRMS (EI) *m/z* calc'd for [C₁₃H₂₀O₄]⁺: 240.1362, found 240.1369.

Entry 2: 48h. run 1,2: [L:B] = >20:1, [E:Z] = 13:1. Both ratios determined by ¹H NMR. Purification by flash chromatography (15% EtOAc/hexanes eluent) provided the desired linear (*E*)-allylic acetate as the major product (run 1: 102.4 mg, 0.55 mmol, 55%; run 2: 96.8 mg, 0.52 mmol, 52%; average yield: 54%). After column: [L:B] = >20:1; [E:Z] = 16:1.

¹H NMR (400 MHz, CDCl₃) δ 5.88 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.70 (dt, *J* = 15.6, 6.4 Hz, 1H), 4.55 (dd, *J* = 6.4, 1.2 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 3H), 3.09 (dd, *J* = 6.8, 0.8 Hz, 2H), 2.06 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 170.7, 127.8, 127.1, 64.4, 60.8, 37.6, 20.9, 14.1; IR (film, cm⁻¹): 2984, 2943, 2911, 1740, 1447, 1383, 1367, 1233, 1175; HRMS (EI) *m/z* calc'd for [C₉H₁₄O₄]⁺: 186.0892, found 186.0898.

Entry 3: 48h. run 1: [L:B] = 24:1, [E:Z] = 12:1; run 2: [L:B] = 24:1, [E:Z] = 11:1; average: [L:B] = 24:1, [E:Z] = 12:1 (24 h, [L:B] = 40:1). Purification by flash chromatography (3% EtOAc/hexanes eluent) provided the desired linear (*E*)-allylic acetate as the major product (run 1: 108 mg, 0.54 mmol; 54%; run 2: 101 mg, 0.51 mmol, 51%; average yield: 52%). After column: [L:B] = 22:1, [E:Z] = 13:1.

¹H NMR (400 MHz, CDCl₃) δ 5.77 (dt, *J* = 15.2, 6.8 Hz, 1H), 5.56 (dt, *J* = 15.6, 6.8 Hz, 1H), 4.50 (d, *J* = 6.4 Hz, 2H), 2.06 (s, 3H), 1.4-1.2 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 136.8, 123.6, 65.3, 32.2, 31.8, 29.1, 28.8, 22.6, 21.0, 14.1; IR (film, cm⁻¹): 3021, 2957, 2928, 2857, 1744, 1460, 1231. HRMS (EI) *m/z* calc'd for [C₁₂H₂₂O₂]⁺: 198.1620, found 198.1623.

Entry 4: 72h. run 1: [L:B] = 33:1, [E:Z] = 10:1; run 2: [L:B] = 28:1, [E:Z] = 11:1; average: [L:B] = 31:1, [E:Z] = 11:1 (24h, [L:B] = 71:1, 48h, [L:B] = 43:1). Purification by flash chromatography (3% EtOAc/hexanes eluent) provided the desired linear (*E*)-allylic acetate as the major product (run 1: 191.2 mg, 0.50 mmol, 50%; run 2: 191.4, 0.50 mmol, 50%; average yield: 50%). After column: [L:B] = 87:1, [E:Z] = 12:1.

^1H NMR (400 MHz, CDCl_3) δ 7.66 (m, 4H), 7.40 (m, 6H), 5.77 (dt, $J = 14$, 6.8 Hz, 1H), 5.61 (dt, $J = 14$, 6.4 Hz, 1H), 4.5 (d, $J = 6.4$ Hz, 2H), 3.7 (t, $J = 6.4$ Hz, 2H), 2.31 (brq, $J = 5.6$ Hz, 2H), 2.05 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 135.6, 133.8, 132.8, 129.6, 127.6, 125.8, 65.1, 63.1, 35.6, 26.8, 21.0, 19.2; IR (film, cm^{-1}): 3071, 3050, 2999, 2957, 2932, 2893, 2859, 1742, 1472, 1427, 1111, 1231; HRMS (CI, NH_3) m/z calc'd for $\text{C}_{23}\text{H}_{34}\text{NO}_3\text{Si}$ $[\text{M}+\text{NH}_4]^+$: 400.2308, found 400.2306.

Entry 5: 48h. run 1: [L:B] = 31:1, [E:Z] = 11:1, run 2: [L:B] = 31:1, [E:Z] = 10:1; average: [L:B] = 31:1, [E:Z] = 11:1 (24h, [L:B] = 52:1). Purification by flash chromatography (5% EtOAc/hexanes eluent) provided the desired linear (*E*)-allylic acetate as the major product (run 1: 133.0 mg, 0.57 mmol, 57%; run 2: 133.2 mg, 0.57 mmol, 57%; average yield: 57%). After column: [L:B] = 41:1; [E:Z] = 12:1.

^1H NMR (400 MHz, CDCl_3) δ 7.37-7.26 (m, 5H), 5.8 (dt, $J = 15.2$, 6.8 Hz, 1H), 5.66 (dt, $J = 15.6$, 6.4 Hz, 1H), 4.52 (d, $J = 4.8$ Hz, 2H), 4.51 (s, 2H), 3.52 (t, $J = 6.4$ Hz, 2H), 2.39 (brq, $J = 6.4$ Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 138.3, 132.5, 128.4, 127.64, 127.58, 125.8, 72.9, 69.3, 65.0, 32.7, 21.0; IR (film, cm^{-1}): 3088, 3063, 3030, 2936, 2859, 2793, 1740, 1454, 1364, 1233; HRMS (CI, NH_3) m/z calc'd for $\text{C}_{14}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 252.1600, found 252.1593.

Entry 6: 72 h. run 1,2: [L:B] = 14:1, [E:Z] = 11:1 (24h, [L:B] = 39:1, 48h, [L:B] = 20:1). Purification by flash chromatography (5% EtOAc/hexanes eluent) provided the desired linear (*E*)-allylic acetate as the major product (run 1: 172.0 mg, 0.62 mmol, 62%; run 2: 166.0 mg, 0.60 mmol, 60%; average yield: 61%). After column: [L:B] = 14:1, [E:Z] = 12:1.

^1H NMR (400 MHz, CDCl_3) δ 10.8 (s, 1H), 7.83 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.46 (ddd, $J = 8.6$, 7.2, 2.0 Hz, 1H), 6.98 (dd, $J = 8.4$, 0.8 Hz, 1H), 6.88 (ddd, $J = 8.2$, 8.0, 1.2 Hz, 1H), 5.8 (dt, $J = 15.2$, 6.8 Hz, 1H), 5.64 (dt, $J = 15.2$, 6.4 Hz, 1H), 4.52 (dd, $J = 6.2$, 0.8 Hz, 2H), 4.36 (t, $J = 6.4$ Hz, 2H), 2.24 (bq, $J = 7.6$ Hz, 2H), 2.06 (s, 3H), 1.90 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 170.1, 161.7, 135.7, 134.4, 129.8, 125.1, 124.9, 119.1, 117.6, 112.5, 64.9, 64.6, 28.6, 27.7, 21.0; IR (film, cm^{-1}): 3187, 3156, 2953, 1740, 1674, 1615, 1485, 1302, 1250. HRMS (EI) m/z calc'd for $[\text{C}_{15}\text{H}_{18}\text{O}_5]^+$: 278.1154, found 278.1152.

Entry 7: 72h. run 1: [L:B] = 16:1, [E:Z] = 12:1; run 2: [L:B] = 17:1, [E:Z] = 13:1; average: [L:B] = 17:1, [E:Z] = 13:1 (24h, [L:B] = 40:1, 48h, [L:B] = 22:1). Purification by flash chromatography (15% EtOAc/hexanes eluent) provided the desired linear (*E*)-allylic acetate as the major product (run 1: 160.2 mg, 0.55 mmol, 55%; run 2: 162.9 mg, 0.56 mmol, 56%; average yield: 56%). After column: [L:B] = 18:1, [E:Z] = 13:1.

^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 8.0$, 2.0 Hz, 1H), 7.46 (ddd, $J = 8.4$, 7.6, 1.6 Hz, 1H), 6.97 (m, 2H), 5.80 (dt, $J = 15.6$, 6.8 Hz, 1H), 5.63 (dt, $J = 15.2$, 6.4 Hz, 1H), 4.51 (dd, $J = 6.4$, 0.8 Hz, 2H), 4.30 (t, $J = 6.4$ Hz, 2H), 3.9 (s, 3H), 2.23 (q, $J = 8.0$ Hz, 2H), 2.05 (s, 3H), 1.85 (m, 2H); ^{13}C NMR (400 MHz, CDCl_3) δ 170.8, 166.2, 159.1, 134.9, 133.4, 131.5, 124.7, 120.2, 120.1, 112.0, 65.0, 64.0, 55.9, 28.7, 27.9, 21.0; IR (film, cm^{-1}): 3079, 3003, 2949, 2841, 1736 (br), 1601, 1493, 1302, 1250; HRMS (EI) m/z calc'd for $[\text{C}_{16}\text{H}_{20}\text{O}_5]^+$: 292.1311, found 292.1318.

Entry 8: 72h. run 1: [L:B] = 13:1, [E:Z] = 12:1; run 2: [L:B] = 12:1, [E:Z] = 12:1; average: [L:B] = 13:1, [E:Z] = 12:1 (24h, [L:B] = 37:1, 48h, [L:B] = 21:1). Purification by flash chromatography (15% EtOAc/hexanes eluent) provided the desired linear (*E*)-allylic acetate as the major product (run 1: 183.0 mg, 0.66 mmol, 66%; run 2: 170.2 mg, 0.61 mmol, 61%; average yield: 64%). After column: [L:B] = 14:1; [E:Z] = 12:1.

^1H NMR (400 MHz, CDCl_3) δ 7.38 (bd, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.69 (brs, 1H), 5.78 (dt, $J = 15.2$, 6.4 Hz, 1H), 5.6 (dt, $J = 15.6$, 7.2 Hz, 1H), 4.52 (dd, $J = 6.0$, 0.4 Hz), 4.17 (t, $J = 6.4$ Hz, 2H), 2.18 (brq, $J = 7.2$ Hz, 2H), 2.06 (s, 3H), 1.78 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 153.5, 137.9, 134.9, 129.0, 124.7, 123.4, 118.6, 65.0, 64.6, 28.7, 28.1, 21.0; IR (film, cm^{-1}): 3329 (br), 3138, 3080, 3044, 2953, 2851, 1736 (br, shoulder 1715), 1601, 1539, 1445, 1225; HRMS (EI) m/z calc'd for $[\text{C}_{15}\text{H}_{19}\text{NO}_4]^+$: 277.1314, found 277.1315.

Entry 9: 48h. run 1: [L:B] = 24:1, [E:Z] = 12:1; run 2: [L:B] = 21:1, [E:Z] = 12:1; average: [L:B] = 23:1, [E:Z] = 12:1 (24h, [L:B] = 44:1). Purification by flash chromatography (35% EtOAc/hexanes eluent) provided the desired linear (*E*)-allylic acetate as the major product (run 1: 148.0 mg, 0.61 mmol, 61%; run 2: 150.5 mg, 0.62 mmol, 62% yield; average yield: 62%). After column: [L:B] = 21:1, [E:Z] = 12:1.

^1H NMR (400 MHz, CDCl_3) δ 5.75 (dt, $J = 16$, 6.4 Hz, 1H), 5.58 (dt, $J = 15.2$, 6.0 Hz, 1H), 4.5 (d, $J = 6.4$ Hz, 2H), 3.36 (q, $J = 7.6$ Hz, 2H), 3.28 (q, $J = 7.6$ Hz, 2H), 2.28 (t, $J = 7.6$ Hz, 2H), 2.11 (brq, $J = 7.2$

Hz, 2H), 2.04 (s, 3H), 1.75 (q, $J = 7.6$ Hz, 2H), 1.15 (t, $J = 7.2$ Hz, 3H), 1.09 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 172.0, 171.1, 135.9, 124.8, 65.4, 42.2, 40.3, 32.4, 32.0, 24.7, 21.2, 14.6, 13.3; IR (film, cm^{-1}): 2974, 2936, 2878, 1740, 1641, 1433, 1233; HRMS (ESI) m/z calc'd for $\text{C}_{13}\text{H}_{23}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 242.1756, found 242.1747.

Entry 10: 48h. run 1: [L:B] = >99:1, [E:Z] = 13:1; run 2: [L:B] = >99:1, [E:Z] = 12:1; average: [L:B] = >99:1, [E:Z] = 13:1. Purification by flash chromatography (15% EtOAc/hexanes eluent) provided the desired linear acetate as the major product (run 1: 114.1 mg, 0.65 mmol, 65%; run 2: 112.1 mg, 0.64 mmol, 64%; average yield: 65%). After column: [L:B] = >99:1; [E:Z] = 13:1.

^1H NMR (400 MHz, CDCl_3) δ 7.39 (m, 2H), 7.32 (m, 2H), 7.27 (m, 1H), 6.65 (d, $J = 15.6$ Hz, 1H), 6.29 (dt, $J = 15.8, 6.4$ Hz, 1H), 4.73 (dd, $J = 6.8, 1.6$ Hz, 2H), 2.1 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 136.2, 134.2, 128.6, 128.0, 126.6, 123.1, 65.0, 21.0; IR (film, cm^{-1}): 3082, 3059, 3028, 2943, 2882, 1738, 1495, 1449, 1379, 1364, 1233; HRMS (EI) m/z calc'd for $[\text{C}_{11}\text{H}_{12}\text{O}_2]^+$: 176.0837, found 176.0841.

General procedure for catalyst 1 (equations 2, 3): A 40 mL borosilicate glass vial was charged with the following solids: catalyst **1** (53.2 mg, 0.1 mmol, 10 mol%), benzoquinone (217 mg, 2.0 mmol, 2 eq). A separate 4 mL borosilicate glass vial was charged with olefin substrate (0.1 mmol) which was diluted with CH_2Cl_2 and transferred to the solids vial *via* pipette (3 x 1 mL, total volume of CH_2Cl_2 was always 3 mL). The 40 mL vial was charged with AcOH (3 mL), a stir bar, capped and allowed to heat at 40°C . Aliquots were taken (~50 μL filtered through a silica plug with Et_2O) at $t = 24\text{h}$, 48h , and 72h to determine linear:branched ratios [L:B]. The reaction was quenched with saturated NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with H_2O (2 x 100 mL), dried over MgSO_4 , filtered and concentrated *in vacuo* to give a brown/red oil. Purification of the crude by flash chromatography afforded a mixture of the branched and linear (*E*)-allylic acetates (trace amounts of the *Z* isomer was detected by ^1H NMR) with the branched allylic acetate as the major product.

Equation 2: 72h. run 1: [L:B] = 1:6, run 2: [L:B] = 1:5.5, average reported: [L:B] = 1:6 (24h, [L:B] = 1:7, 48h, [L:B] = 1:6). Purification by flash chromatography (3% EtOAc/hexanes eluent) provided the branched allylic acetate as the major product (run 1: 256.5 mg, 0.67 mmol, 67%; run 2: 240.8 mg, 0.63 mmol, 63%; average yield reported: 65%). After column [L:B] = 1:6.

^1H NMR (400 MHz, CDCl_3) δ 7.65 (m, 4H), 7.40 (m, 6H), 5.78 (ddd, $J = 17.0, 10.4, 6.0$ Hz, 1H), 5.46 (m, 1H), 5.23 (app dt, $J = 17.2, 1.2$ Hz, 1H), 5.15 (app dt, $J = 10.0, 1.6$ Hz, 1H), 3.69 (t, $J = 6.4$ Hz, 2H), 2.0 (s, 3H), 1.87 (m, 2H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 136.4, 135.56 and 135.53 (d), 133.68 and 133.6 (d), 129.6, 127.6, 116.5, 71.9, 59.7, 37.0, 26.8, 21.2, 19.1; IR (film, cm^{-1}): 3073, 3050, 3000, 2957, 2932, 2891, 2859, 1742, 1474, 1427, 1371, 1236, 1111; HRMS (CI, NH_3) m/z calc'd for $\text{C}_{23}\text{H}_{34}\text{NO}_3\text{Si}$ $[\text{M}+\text{NH}_4]^+$: 400.2308, found 400.2308.

Equation 3: 72h. run 1,2: [L:B] = 1:5 (24h, [L:B] = 1:7; $t = 48\text{h}$, [L:B] = 1:7). Purification by flash chromatography (12% EtOAc/hexanes eluent) provided the branched allylic acetate as the major product (run 1: 190.4 mg, 0.69 mmol, 69%; run 2: 189.9 mg, 0.68 mmol, 68%; average yield reported: 69%). After column [L:B] = 1:5.

^1H NMR (400 MHz, CDCl_3) δ 7.38 (brd, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.05 (t, $J = 7.2$ Hz, 1H), 6.71 (brs, 1H), 5.78 (ddd, $J = 17.4, 10.4, 6.4$ Hz, 1H), 5.32 (m, 1H), 5.25 (app dt, $J = 17.2, 1.6$ Hz, 1H), 5.19 (app dt, $J = 10.4, 1.2$ Hz, 1H), 4.17 (t, $J = 6.0$ Hz, 2H), 2.07 (s, 3H), 1.73 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 153.4, 137.8, 136.1, 129.0, 123.4, 118.6, 117.0, 74.2, 64.8, 30.8, 24.6, 21.2; IR (film, cm^{-1}): 3329

(br), 3196, 3138, 3063, 2957, 2859, 1734 (br, shoulder 1716), 1601, 1539, 1225; HRMS (EI) m/z calc'd for $[C_{15}H_{19}NO_4]^+$: 277.1314, found 277.1318.

Synthesis of bis[chloro(1,2,3-trihapto-1-decene)palladium(II)].¹¹

An oven dried 50 mL flask was charged with Pd(TFA)_2 (472mg, 1.42 mmol) and a stir bar under N_2 . To this was added 12 mL of freshly distilled acetone (distilled over K_2CO_3) and 1-decene (200 mg, 270 μL , 1.42 mmol). The reaction was allowed to stir for 40 min at rt under an atmosphere of Ar, at which time an acetone solution (3 mL) of $n\text{-Bu}_4\text{NCl}$ (434 mg, 1.56 mmol) was added *via* syringe. The anion exchange proceeded at rt for 15 min. The mixture was filtered over a plug of Celite (to remove metallic Pd), concentrated and purified *via* column chromatography (50 % EtOAc/hexanes eluent) to afford bis[chloro(1,2,3-trihapto-1-decene)palladium (II)] as a yellow, oily solid (277mg, 0.98 mmol, 69%).

¹H NMR (400 MHz, CCl_4 doped with C_6D_6) δ 4.92 (td, $J = 11.6, 6.8$ Hz, 1H, H-2), 3.59 (d, $J = 6.4$ Hz, 1H, anti H-1), 3.51 (m, 1H, H-3), 2.5 (d, $J = 11.6$, 1 H, syn H-1), 1.6-1.1 (m, 12 H), 0.79 (t, $J = 6.4$ Hz, 3H).

A 2 mL borosilicate vial was charged with 28 mg (0.1 mmol) of bis[chloro(1,2,3-trihapto-1-decene)palladium (II)] and a magnetic stir bar. A separate 2 mL vial was charged with the following: BQ (21.7 mg, 0.2 mmol), 4 Å MS (22 mg), DMSO (0.3 mL), and AcOH (0.3 mL). The liquid mixture was transferred *via* pipette into the vial charged with bis[chloro(1,2,3-trihapto-1-decene)palladium (II)] and the solution was heated at 40°C. Aliquots were taken in (~10 μL filtered with Et_2O through a short pipette plug of silica) at $t = 1, 3$ and 24h. Linear (*E*)-allylic acetate and branched allylic acetate were formed at 24h in 24 % and 18 % yields, respectively, based on GC analysis using standard curves with authentic acetates and nitrobenzene.

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