Supporting Information
Aerobic Linear Allylic C−H Amination: Overcoming Benzoquinone Inhibition

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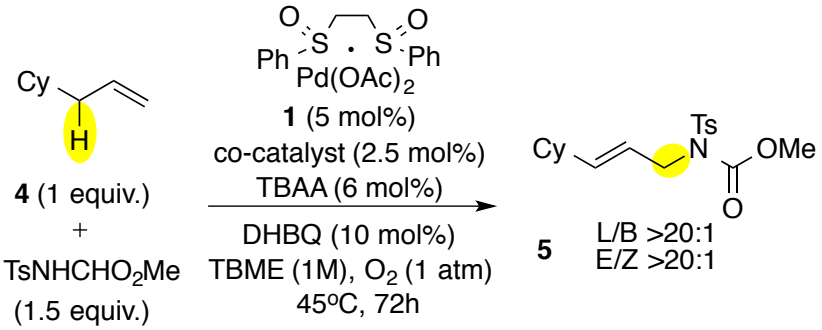
General Information: All commercially obtained reagents were used as received: 1,4-dihydroquinone (DHBQ, Aldrich); White Catalyst (1,2-Bis(phenylsulfinyl)ethanepalladium(II) acetate), CAS: 858971-43-4, Aldrich). Catalyst **1** was stored in a refrigerator at 0°C, and weighed out on the bench at room temperature. Tetra *n*-butylammonium acetate (Aldrich) was stored in a glove box under an argon atmosphere and weighed out in a vial in the glove box prior to use. All other reagents where purchased from least expensive supplier and used directly unless otherwise stated. The cobalt(II) salophen catalyst **2** was prepared using the procedure developed by Bäckvall and coworkers.[1] We have also observed no difference in reactivity when using commercially available cobalt(II) salophen monohydrate (Aldrich). Solvents: diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), and N, N-dimethylformamide (DMF) were purified prior to use by passage through a bed of activated alumina (Glass Contour, Laguna Beach, California). All allylic amination reactions were run under oxygen balloon atmosphere with no precautions taken to exclude moisture. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized with UV, potassium permanganate, and ceric ammonium molybdate staining. Flash column chromatography was performed as described by Still et al.[2] using EM reagent silica gel 60 (230-400 mesh). ^{1}H NMR spectra were recorded on a Varian Unity 500 (500 MHz) or a Varian Unity Inova 500NB spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration, corresponding carbon atom. Proton-decoupled ^{13}C-NMR spectra were recorded on a Varian Unity-500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.2 ppm). IR spectra were recorded as thin films on NaCl plates on a Mattson Galaxy Series FTIR 5000 and are reported in frequency of absorption (cm^{-1}). All optical rotations were determined on a Perkin Elmer 341 Polarimeter using the sodium D line (589 nm). High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory. Medium pressure liquid chromatography (MPLC) was used in cases with difficult silica chromatography separations and consists of a Teledyne ISCO CombiFlash Rf with 12, 24, or 40g RediSep Rf Silica columns. Optical rotations were measured using a 1 mL cell with a 100 mm path length on a Jasco P-1020 polarimeter. Optical rotations were obtained with a sodium lamp and are reported as follows: $[\alpha]_\lambda^{T°C}$ (c = g/100 mL, solvent).

A. General procedure for the Co(II) (salophen) system: To a 10 mL, oven dried round bottom flask containing a PTFE-covered stir bar was added tetra *n*-butyl ammonium acetate (7.2 mg, 0.024 mmol, 6 mol%) in a glove box. The following solids were all weighed outside of the glovebox and sequentially added to the reaction flask containing TBAA: carbamate nucleophile (137.6 mg, 0.6 mmol, 1.5 equiv.), DHBQ (4.4 mg, 0.04 mmol, 10 mol%), Co(II)(salophen) (3.7 mg, 0.01 mmol, 2.5 mol%) and Pd^{II}/bis-sulfoxide catalyst **1** (5 mg, 0.01 mmol, 2.5 mol% or 10 mg, 0.02 mmol, 5 mol% according to Tables 2 and 3). *(NOTE: Because of the hygroscopic nature of TBAA, the reaction flask was not opened until all the other solids were ready to be transferred into the flask; in some cases, we have seen lower reactivity when the TBAA is exposed to air for longer periods of time).* The terminal olefin (0.4 mmol, 1 equiv., preweighed in a ½ dram vial) was diluted with 0.1 mL TBME and then added to the reaction flask using TBME for the transfer (0.3 mL – total of 0.4 mL solvent). The top of a condenser was sealed with a rubber septum, a balloon of oxygen was attached with a needle, and the condenser was briefly purged with oxygen. The flask was attached to this cold-water condenser using a PTFE sleeve as a seal, with no additional support of the flask required and the joint was wrapped in teflon tape. The reaction was allowed to stir at 400 rpm in a 45°C oil bath under a balloon of oxygen for 24-72 hours or until completed by TLC. The reaction mixture was diluted with ethyl acetate and transferred to a 125 mL separatory funnel, washed with 5% aq. K_2CO_3 (3 x 10 mL), and the aqueous rinses back-extracted with ethyl acetate (2 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered through Celite, and evaporated to dryness (ca. 30-40°C, 30 torr). *Generally this workup leads to higher purity of isolated products by removing remaining nucleophile and water-soluble impurities.* Alternatively, the reaction may be diluted with dichloromethane and flushed through a 3-5 cm silica gel plug with an 80% ethyl acetate/20% hexanes mixture. If no work-up is necessary, the reaction mixture may also be directly loaded onto a silica gel column using dichloromethane or toluene. Purification of the products is done using flash column chromatography - in general, with a gradient of 10-30% EtOAc/hexanes. We have also found that 10-30% acetone/hexanes or 10-50% ether/pentane gradients are also effective solvent systems for purification.

B. General procedure for the $VO(acac)_2$ system: To a 10 mL, oven dried round bottom flask containing a PTFE-covered stir bar was added tetra *n*-butyl ammonium acetate (7.2 mg, 0.024 mmol, 6 mol%) in a glove box. The following solids were all weighed outside of the glovebox and sequentially added to the reaction flask containing TBAA: carbamate nucleophile (183.6 mg, 0.8 mmol, 2 equiv.), DHBQ (4.4 mg, 0.04 mmol, 10 mol%), $VO(acac)_2$ (2.7 mg, 0.01 mmol, 2.5 mol%) and Pd^{II}/bis-sulfoxide catalyst **1** (10 mg, 0.02 mmol, 5 mol%). *(NOTE: Because of the hygroscopic nature of TBAA, the reaction flask was not opened until all the other solids were ready to be transferred into the flask; in some cases, we have seen lower reactivity when the TBAA is exposed to air for longer periods of time).* The terminal olefin (0.4 mmol, 1 equiv., preweighed in a ½ dram vial) was diluted with 0.1 mL THF and then added to the reaction flask using THF for the transfer (0.3 mL – total of 0.4 mL solvent). The top of a condenser was sealed with a rubber septum, a balloon of oxygen was attached with a needle, and the condenser was briefly purged with oxygen. The flask was attached to this cold-water condenser using a PTFE sleeve as a seal, with no additional support of the flask required and the joint was wrapped in teflon tape. The reaction was allowed to stir at 400 rpm in a 45°C oil bath under a balloon of oxygen for 72 hours or until completed by TLC. The reaction mixture was diluted with ethyl acetate and transferred to a 125 mL separatory funnel, washed with 5% aq. K_2CO_3 (3 x 10 mL), and the aqueous rinses back-extracted with ethyl acetate (2 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered through Celite, and evaporated to dryness (ca. 30-40°C, 30 torr). *Generally this workup leads to higher purity of isolated products by removing remaining nucleophile and water-soluble impurities.* Alternatively, the reaction my be diluted with dichloromethane and flushed through a 3-5 cm silica gel plug with an 80% ethyl acetate/20% hexanes mixture. If no work-up is necessary, the reaction mixture may also be directly loaded onto a silica gel column using dichloromethane or toluene. Purification of the products is done using flash column chromatography - in general, with a gradient of 10-30% EtOAc/hexanes. We have also found that 10-30% acetone/hexanes or 10-50% ether/pentane gradients are also effective solvent systems for purification.

Table S1. Optimization of the Intermolecular Allylic C−H Amination.



Entry[a]	catalyst/co-catalyst	Oxidant	Yield of 5[b]
1[c]	10 mol% **1**/--	BQ (2 equiv.)	84%
2[c]	5 mol% **1**/--	BQ (2 equiv.)	20%
3[d]	**1**/Co(II)(salophen) **2**	O_2 (1atm)	68%
4	**1**/Co(II)(salophen) **2**	O_2 (1atm)	79%(78%)[e]
5	**1**/Co(II)(TPP)	O_2 (1atm)	60%
6	**1**/Co(II)(salen)	O_2 (1atm)	74%
7	**1**/Mn(III)(salen)	O_2 (1atm)	8%
8	**1**/Fe(II)Pc	O_2 (1atm)	39%
9	**1**/$VO(acac)_2$ **3**	O_2 (1atm)	48%
10[f]	**1**/$VO(acac)_2$ **3**	O_2 (1atm)	75% (80%)[g]
11[f]	**1**/VO(TPP)	O_2 (1atm)	53%
12[f]	**1**/VO(Salophen)	O_2 (1atm)	54%
13[f,h]	**1**/$VOSO_4$	O_2 (1atm)	65%
14	**1**/--	O_2 (1atm)	17%
15[i]	$Pd(OAc)_2$/DAF	O_2 (1 atm)	*trace*
16[c]	**1**/--	2,5-DMBQ (1 equiv.)	72%

[a] Conditions are as listed above unless noted. Co(II)(salophen) = N,N'-Bis(salicylidene)-1,2-phenylenediamino cobalt(II); Co(II)(TPP) = 5,10,15, 20-Tetraphenyl-21H,23H-porphine cobalt (II); Co(II)(salen) = (R,R)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II); Mn(III)(salen) = (R,R)-(-)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride; Fe(II)Pc = Iron(II) phthalocyanine; $VO(acac)_2$ = vanadyl acetylacetonate; VO(TPP) = 5,10,15,20-Tetraphenyl-21H, 23H-porphinevanadium(IV)oxide; VO(salophen) = N,N'-bis(salicylidene)-1,2-phenylenediaminovanadium(IV) oxide. [b] Isolated yield; average of at least 2 runs at 0.4 mmol scale. [c] Conditions from ref. 7b. [d] 1M TBME, 2 equiv. $TsNHCO_2Me$. [e] Number in parenthesis is yield at 24h. [f] 2 equiv. $TsNHCO_2Me$, 1M THF. [g] Number in parentheses is yield with 1 mol% co-catalyst on a 0.8 mmol scale for accurate co-catalyst weight. [h] 1 mmol scale used for accurate co-catalyst weights. [i] 5 mol% $Pd(OAc)_2$, 5 mol% 4,5-diazafluorene-9-one (DAF), with identical conditions to entries 4-9.

Entry 1: See reference 10.

Entry 2: The reaction was set up following the procedure described in reference 10; however, 5 mol% **1** was used. Run 1 (23.9 mg, 0.068 mmol, 17% yield); run 2 (30.9 mg, 0.088 mmol, 22% yield). **Average:** 20% yield. When TBAA was used as a base instead of DIPEA, product yield was 25% (35.1 mg, 0.1 mmol).

Entry 3: The reaction was set up according to general procedure **A**, using Co(II)salophen **2** (3.7 mg, 0.01 mmol) as the reoxidation catalyst, 2-equiv. $TsNHCO_2Me$ and 1M TBME as solvent. Run 1 (94.6 mg, 0.272 mmol, 68% yield); run 2 (94.6 mg, 0.272 mmol, 68% yield). **Average:** 68% yield.

Entry 4: The reaction was set up according to general procedure **A**, using Co(II)salophen **2** (3.7 mg, 0.01 mmol) as the reoxidation catalyst, 1.5 equiv. $TsNHCO_2Me$ (0.6 mmol, 137.6 mg) and 1M TBME as the solvent. Run 1 (109.6 mg, 0.312 mmol, 78% yield); run 2 (112.5 mg, 0.320 mmol, 80% yield). **Average:** 79% yield.

The reaction was set up according to general procedure **A**, using Co(II)salophen **2** (3.7 mg, 0.01 mmol) as the reoxidation catalyst, 1.5 equiv. $TsNHCO_2Me$ (0.6 mmol, 137.6 mg), 1M TBME as the solvent, and a 24 hour reaction time. Run 1 (105.4 mg, 0.300 mmol, 75% yield); run 2 (113.9 mg, 0.324 mmol, 81% yield). **Average:** 78% yield.

Entry 5: The reaction was set up according to general procedure **A**. Co(II)(TPP) (6.7 mg, 0.01 mmol) was used as the reoxidation catalyst. Run 1 (84.4 mg, 0.240 mmol, 60% yield); run 2 (82.9 mg, 0.236 mmol, 59% yield). **Average:** 60% yield.

Entry 6: The reaction was set up according to general procedure **A**. Co(II)salen (3.3 mg, 0.01 mmol) was used as the reoxidation catalyst. Run 1 (108.2 mg, 0.308 mmol, 77% yield); run 2 (99.8 mg, 0.284 mmol, 71% yield). **Average:** 74% yield.

Entry 7: The reaction was set up according to general procedure **A**. Mn(III)salen (6.4 mg, 0.01 mmol) was used as the reoxidation catalyst. Run 1 (11.2 mg, 0.032 mmol, 8% yield); run 2 (11.2 mg, 0.032 mmol, 8% yield). **Average:** 8% yield

Entry 8: The reaction was set up according to general procedure **A**. Fe(II)Pc was used as the reoxidation catalyst (5.7 mg, 0.01 mmol). Run 1 (54.8 mg, 0.156 mmol, 39% yield); run 2 (54.8 mg, 0.156 mmol, 39% yield). **Average:** 39% yield.

Entry 9: The reaction was set up according to general procedure **A**. $VO(acac)_2$ (2.7 mg, 0.01 mmol) was used as the reoxidation catalyst. Run 1 (66.1 mg, 0.188 mmol, 47% yield); run 2 (67.5 mg, 0.192 mmol, 48% yield). **Average:** 48% yield.

Entry 10: The reaction was set up according to general procedure **B**. $VO(acac)_2$ (2.7 mg, 0.01 mmol) was used as the reoxidation catalyst. Run 1 (104.0 mg, 0.296 mmol, 74% yield); run 2 (105.4 mg, 0.300 mmol, 75% yield). **Average:** 75% yield.

The reaction was set up according to general procedure **B**, but on a 0.8 mmol scale in order to accurately weigh 1 mol% of the vanadium co-catalyst. $VO(acac)_2$ (2.12 mg, 0.008 mmol) was used as the reoxidation catalyst. Run 1 (112.5 mg, 0.320 mmol, 80% yield); run 2 (111.1 mg, 0.316 mmol, 79% yield). **Average:** 80% yield.

Entry 11: The reaction was set up according to general procedure **B**. VO(TPP) (6.8 mg, 0.01 mmol) was used as the reoxidation catalyst. Run 1 (84.4 mg, 0.240 mmol, 60% yield); run 2 (63.3 mg, 0.180 mmol, 45% yield). **Average:** 53% yield.

Entry 12: The reaction was set up according to general procedure **B**, using VO(salophen) (3.8 mg, 0.01 mmol) as the reoxidation catalyst. Run 1 (89.9 mg, 0.256 mmol, 64% yield); run 2 (68.9 mg, 0.196 mmol, 49% yield), run 3 (68.9 mg, 0.196 mmol, 49%). **Average:** 54% yield.

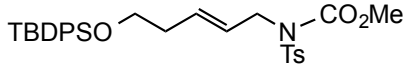
Entry 13: The reaction was set up according to general procedure **B**, but on a 1 mmol scale in order to accurately weigh 2.5 mol% of the vanadium co-catalyst. $VOSO_4$ (6.3 mg, 0.025 mmol) was used as the reoxidation catalyst. Run 1 (231.9 mg, 0.660 mmol, 66% yield); run 2 (224.9 mg, 0.640 mmol, 64% yield). **Average:** 65% yield.

Entry 14: The reaction was set up according to general procedure **A**, with no co-catalyst added. Run 1 (21.1 mg, 0.060 mmol, 15% yield); run 2 (26.7 mg, 0.076 mmol, 19% yield). **Average:** 17% yield.

Entry 15: The reaction was set up according to general procedure **A**, using $Pd(OAc)_2$ (0.01 mmol, 2.2 mg) and 4,5-diazafluorene-9-one (0.01 mmol, 1.8 mg) and no reoxidation catalyst. Additionally, 1.5 equiv. $TsNHCO_2Me$ were used (0.6 mmol, 137.6 mg) and 1M TBME was used as the solvent. For two runs, trace product was observed.

Entry 16: The reaction was set up following the procedure described in reference 10. 1 equiv. 2,5-DMBQ (0.4 mmol, 54.5 mg) was used in place of 2 equiv. BQ. Run 1 (101.2 mg, 0.288 mmol, 72% yield); run 2 (101.2 mg, 0.288 mmol, 72% yield). **Average:** 72% yield.

Scope of the Linear Allylic Amination Reaction



methyl(*E*)-(5-((*tert*-butyldiphenylsilyl)oxy)pent-2-en-1-yl)(tosyl)carbamate (6): *tert*-butyl(pent-4-en-1-yloxy)diphenylsilane[3] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results: Run 1 (165.36 mg, 0.3 mmol, 75% yield); run 2 (172 mg, 0.312 mmol, 78% yield). **Average:** 77% yield, 20:1 L:B. Additionally, 4% branched product and approximately 11% isomerized starting material were isolated.

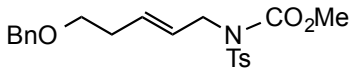
$VO(acac)_2$ results: Run 1 (112.6 mg, 0.204 mmol, 51% yield); run 2 (92.7 mg, 0.168 mmol, 42% yield); run 3 (101.5 mg, 0.184 mmol, 46% yield). **Average:** 46% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.67 - 7.65 (m, 4H), 7.39 (dddd, *J* = 14.2, 8.3, 5.8, 2.1 Hz, 6H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.79 (dt, *J* = 14.5, 6.9 Hz, 1H), 5.57 (dt, *J* = 14.4, 6.5 Hz, 1H), 4.39 (d, *J* = 6.3 Hz, 2H), 3.70 (t, *J* = 6.8 Hz, 2H), 3.66 (s, 3H), 2.39 (s, 3H), 2.31 (q, *J* = 6.6 Hz, 2H), 1.04 (s, 9H)

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 144.6, 136.7, 135.7, 134.0, 132.2, 129.7, 129.4, 128.6, 127.8, 126.6, 63.4, 53.9, 48.7, 35.7, 27.0, 21.7, 19.3.

HRMS (ESI) m/z calc'd for $C_{30}H_{38}NO_5SSi$ $[M+H^+]$: 552.224, found 552.2234.

IR (film, cm^{-1}): 3367 (broad), 2956, 2931, 2857, 1734, 1597, 1443, 1428, 1359, 1169, 1107, 1089.



methyl(*E*)-(5-(benzyloxy)pent-2-en-1-yl)(tosyl)carbamate (7):

((pent-4-en-1-yloxy)methyl)benzene[4] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results (72 hours): Run 1 (87.2 mg, 0.216 mmol, 54% yield); run 2 (90.4 mg, 0.224 mmol, 56% yield); run 3 (82.2 mg, 0.204 mmol, 51%); run 4 (85.5 mg, 0.212 mmol, 53% yield). **Average:** 54% Yield. Additionally, 4% branched allylic amination product was observed (L:B, 14:1). **Standard Deviation:** 2%

Co(II) salophen results (24 hours): Run 1 (59.9 mg, 0.148 mmol, 37% yield); run 2 (35.5 mg, 0.088 mmol, 22% yield). **Average:** 30% yield

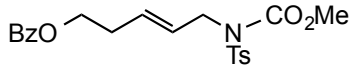
$VO(acac)_2$ results: Run 1 (88.8 mg, 0.22 mmol, 55% yield); run 2 (91.9 mg, 0.228 mmol, 57% yield); run 3 (48.4 mg, 0.12 mmol, 30% yield); run 4 (53.3 mg, 0.132 mmol, 33% yield). **Average:** 44% Yield. **Standard Deviation:** 14%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.36 - 7.22 (m, 7H), 5.82 (dt, *J*=15.0, 6.7 Hz, 1H), 5.62 (dt, *J*=13.0, 6.1 Hz,1H), 4.53 (s, 2H), 4.42 (d, *J* = 6.4, 1.3 Hz, 2H), 3.67 (s, 3H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.46 - 2.35 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 144.6, 138.5, 136.6, 132.2, 129.4, 128.6, 128.5, 127.8, 127.7,126.4, 73.1, 69.5, 53.9, 48.7, 32.8, 21.8.

HRMS (ESI) m/z calc'd for $C_{21}H_{26}NO_5S$ [M+H$^+$]: 404.1532, found 404.1528.

IR (film, cm^{-1}): 2857, 1733, 1597, 1444, 1354, 1239, 1167, 1089.



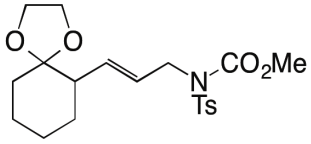
(*E*)-5-((*N*-(methoxycarbonyl)-4-methylphenyl)sulfonamido)pent-3-en-1-yl benzoate (8): pent-4-en-1-yl benzoate[5] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results (72 hours): Run 1 (123.5 mg, 0.296 mmol, 74% yield); run 2 (125.1 mg, 0.3 mmol, 75% yield). **Average:** 75% Yield, 15:1 L:B. Additionally, 5% of the branched product was observed. Approximately 4% isomerized starting material was isolated.

Co(II) salophen results (24 hours): Run 1 (116.9 mg, 0.280 mmol, 70%); run 2 (115.2 mg, 0.276 mmol, 69%). **Average**: 70% yield.

$VO(acac)_2$ results: Run 1 (141.9 mg, 0.34 mmol, 85% yield); run 2 (125.2 mg, 0.300 mmol, 75% yield); run 3 (136.9 mg, 0.328 mmol, 82% yield). **Average:** 81% Yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 5.84 (dt, *J* = 14.1, 6.7 Hz, 1H), 5.71 (dt, *J* = 12.3, 6.2 Hz, 1H), 4.43 (d, *J* = 6.2 Hz, 2H), 4.36 (t, *J* = 6.7 Hz, 2H), 3.66 (s, 3H), 2.54 (q, *J* = 6.7 Hz, 2H), 2.41 (s, 3H). Spectroscopic data for the amination product matched that which was reported previously.[6]



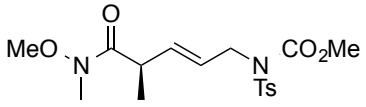
methyl(*E*)-(3-(1,4-dioxaspiro[4.5]decan-6-yl)allyl)(tosyl)carbamate (9):

6-allyl-1,4-dioxaspiro[4.5]decane[7] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results: Run 1 (117.9 mg, 0.288 mmol, 72% yield); run 2 (101.5 mg, 0.248 mmol, 62% yield). **Average:** 67% Yield.

$VO(acac)_2$ results: Run 1 (101.6 mg, 0.248 mmol, 62% yield); run 2 (95.0 mg, 0.232 mmol, 58% yield); run 3 (88.5 mg, 0.216 mmol, 54% yield). **Average:** 58% Yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.87 (dd, *J* = 15.7, 7.8 Hz, 1H), 5.56 (ddd, *J* = 15.3, 6.9, 5.9 Hz, 1H), 4.42 (d, *J* = 6.3 Hz, 2H), 3.97 - 3.85 (m, 4H), 3.66 (s, 3H), 2.43 (s, 3H), 2.31 (ddd, *J* = 11.6, 7.7, 3.8 Hz, 1H), 1.79 - 1.72 (dt, *J* = 12.9, 3.2 Hz, 1H), 1.68 (m, *J* = 10.6, 3.2 Hz, 3H), 1.58 - 1.46 (m, 2H), 1.42 (td, *J* = 12.7, 3.6 Hz, 1H), 1.32 - 1.21 (m, 1H). Spectroscopic data for the amination product matched that which was reported previously. [6]



methyl(*R*,*E*)-(5-(methoxy(methyl)amino)-4-methyl-5-oxopent-2-en-1-yl)(tosyl)carbamate (10): (*R*)-*N*-methoxy-*N*,2-dimethylpent-4-enamide[8] (1.0 equiv., 0.4 mmol) was reacted according to the general

procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results (run with opposite enantiomer shown): Run 1 (78.4 mg, 0.204 mmol, 51% yield); run 2 (89.2 mg, 0.232 mmol, 58% yield). **Average:** 55% Yield.

$VO(acac)_2$ results: Run 1 (34.6 mg, 0.09 mmol, 23%).

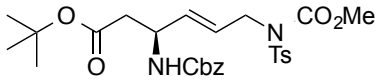
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.90 (dd, *J* = 15.5, 7.6 Hz, 1H), 5.64 (dt, *J* = 13.0, 6.7 Hz, 1H), 4.42 (d, *J* = 6.4, 1.2 Hz, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.65 - 3.57 (m, 1H), 3.18 (s, 3H), 2.42 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 144.7, 136.6, 135.1, 129.5, 128.7, 125.8, 61.7, 53.9, 48.5, 38.6, 21.8, 17.4

HRMS (ESI) m/z calc'd for $C_{17}H_{25}N_2O_6S$ $[M+H^+]$: 385.14, found 385.1433.

IR (film, cm^{-1}): 2937, 1733, 1654, 1597, 1443, 1356, 1168, 1088, 992, 765, 676.

$[\alpha]_D^{27}$= +4.9° (c = 0.98, $CHCl_3$)



***tert*-butyl(*S*,*E*)-3-(((benzyloxy)carbonyl)amino)-6-((*N*-(methoxycarbonyl)-4-methylphenyl)sulfonamido)hex-4-enoate [(+)-11]:**

tert-butyl (*R*)-3-(((benzyloxy)carbonyl)amino)hex-5-enoate[8] (1.0 equiv., 0.5 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results: Run 1 (183.6 mg, 0.336 mmol, 84% yield); run 2 (190.2 mg, 0.348 mmol, 87% yield). **Average:** 86% yield.

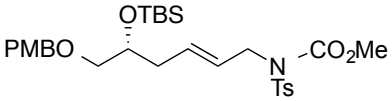
$VO(acac)_2$ results: Run 1 (32.8 mg, 0.06 mmol, 15% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 8.5 Hz, 2H), 7.31 (m, 7H), 5.79 (dd, J = 16.0, 5.5 Hz, 1H), 5.72 (dt, J = 15.3, 5.5 Hz, 1H), 5.55 (broad d, J = 8.0 Hz, 1H), 5.11 (m, 2H), 4.57 (m, 1H), 4.43 (d, J = 5.5 Hz, 2H), 3.66 (s, 3H), 2.56 (app qd, J = 15.5, 5.0 Hz, 2H), 2.41 (s, 3H), 1.41 (s, 9H).

$[\alpha]_D^{27}$ = +6.8° (c = 0.94, $CHCl_3$)

Spectroscopic data for the amination product matched that which was reported previously.[8]

Note: this compound displays rotamers.



methyl(*R*,*E*)-(5-((*tert*-butyldimethylsilyl)oxy)-6-((4-methoxybenzyl)oxy)hex-2-en-1-yl)(tosyl)carbamate [(+)-12]:

(*R*)-*tert*-butyl((1-((4-methoxybenzyl)oxy)hex-5-en-2-yl)oxy)dimethylsilane[8] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results: Run 1 (0.2 mmol scale) (82.0 mg, 0.142 mmol, 71% yield). Approximately 10% isomerically pure starting material was recovered as a mixture with 9% isomerized starting material.

Run 2 (180.1 mg, 0.312 mmol, 78% yield). Approximately 10% isomerized starting material was recovered.

Run 3 (178.0 mg, 0.308 mmol, 77% yield). **Average:** 75% Yield.

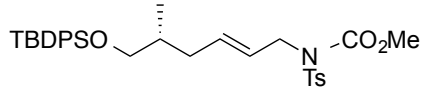
Co(II) salophen results (24 hours): Run 1 (143.3 mg, 0.248 mmol, 62% yield); run 2 (152.5 mg, 0.264 mmol, 66% yield). **Average:** 64% yield.

$VO(acac)_2$ results: Run 1 (161.8 mg, 0.280 mmol, 70% yield); run 2 (154.9 mg, 0.268 mmol, 67% yield); **Average:** 69% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.31 (dd, *J* = 16.5, 8.5 Hz, 4H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.82 (dt, 1H), 5.63 (dt, 1H), 4.48 (s, 2H), 4.44 (dd, *J* = 6.3, 1.3 Hz, 2H), 3.90 (t, *J* = 5.7 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.39 (dd, *J* = 5.5, 3.7 Hz, 2H), 2.46 (s, 3H), 2.41 - 2.34 (m, 1H), 2.29 - 2.22 (m, 1H), 0.92 (s, 9H), 0.09 (s, 6H).

$[\alpha]_D^{26}$= +2.1^o (c = 0.95, $CHCl_3$)

Spectroscopic data for the amination product matched that which was reported previously. [8]



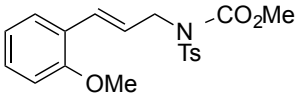
methyl(*R*,*E*)-(6-((*tert*-butyldiphenylsilyl)oxy)-5-methylhex-2-en-1-yl)(tosyl)carbamate [(+)-13]: (*R*)-*tert*-butyl((2-methylhex-5-en-1-yl)oxy)diphenylsilane[8] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results: Run 1 (178.6 mg, 0.308 mmol, 77% yield); run 2 (178.6 mg, 0.308 mmol, 77% yield). **Average:** 77% yield.

$VO(acac)_2$ results: Run 1 (206.4 mg, 0.356 mmol, 89% yield); run 2 (180.9 mg, 0.312 mmol, 78% yield); run 3 (136.8 mg, 0.236 mmol, 59% yield); run 4 (153.1 mg, 0.264 mmol, 66% yield); run 5 (146.1mg, 0.252 mmol, 63% yield); run 6 (109.0 mg, 0.188 mmol, 47% yield). **Average:** 67% Yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 6.2 Hz, 4H), 7.46 -7.36 (m, 6H), 7.30 - 7.26 (m, 2H), 5.74 (dt, *J* = 14.7, 7.2 Hz, 1H), 5.54 (dt, *J*= 13.1, 6.4 Hz, 1H), 4.40 (d, *J* = 6.2 Hz, 2H), 3.67 (s, 3H), 3.49 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.29 (dt, *J* = 12.9, 6.0 Hz, 1H), 1.94 - 1.87 (m, 1H), 1.81 - 1.72 (m, 1H), 1.07 (s, 9H), 0.91 (d, *J* = 6.7 Hz, 3H).
$[\alpha]_D^{25}$= +4.6^o (c=1.0, $CHCl_3$).

Spectroscopic data for the amination product matched that which was reported previously.[8]



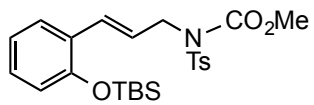
methyl (*E*)-(3-(2-methoxyphenyl)allyl)(tosyl)carbamate (14): 1-Allyl-2-methoxybenzene (Aldrich) (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II)salophen results (2.5 mol% of catalyst 1): Run 1 (103.6 mg, 0.276 mmol, 69% yield); run 2 (102.1 mg, 0.272 mmol, 68% yield). **Average:** 69% yield.

Co(II)salophen results (5 mol% of catalyst 1): Run 1 (145.7 mg, 0.388 mmol, 97% yield); run 2 (141.2 mg, 0.376 mmol, 94% yield). **Average:** 96% yield.

$VO(acac)_2$ results: Run 1 (138.2 mg, 0.368 mmol, 92% yield); run 2 (120.1 mg, 0.320 mmol, 80% yield); run 3 (130.7 mg, 0.348 mmol, 87% yield). **Average:** 86% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.01 (d, *J* = 16.0 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.7 Hz, 1H), 4.63 (dd, *J* = 6.7, 1.1 Hz, 2H), 3.85 (s, 3H), 3.72 (s, 3H), 2.41 (s, 3H). Spectroscopic data for the amination product matched that which was reported previously.[6]



methyl(*E*)-(3-(2-((*tert*-butyldimethylsilyl)oxy)phenyl)allyl)(tosyl)carbamate (15): (2-allylphenoxy)(*tert*-butyl)dimethylsilane[9] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results (2.5 mol% of catalyst 1): Run 1 (89.4 mg, 0.188 mmol, 47% yield); run 2 (87.5 mg, 0.184 mmol, 46% yield). **Average:** 47% yield.

Co(II) salophen results (5 mol% of catalyst 1): Run 1 (171.2 mg, 0.360 mmol, 90% yield); run 2 (173.1 mg, 0.364 mmol, 91% yield). **Average**: 91% yield.

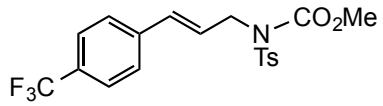
$VO(acac)_2$ results: Run 1 (169.3 mg, 0.356 mmol, 89% yield); run 2 (97.0 mg, 0.204 mmol, 51% yield); run 3 (89.4 mg, 0.188 mmol, 47% yield). **Average:** 62% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.27 (d, 2H), 7.16 (td, *J* = 8.1, 1.7 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 6.94 (t, 7.5 Hz, 1H), 6.82 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.20 (dt, *J* = 16.0, 6.6 Hz, 1H), 4.63 (dd, *J* = 6.6, 1.2 Hz, 2H), 3.72 (s, 3H), 2.42 (s, 3H), 1.02 (s, 9H), 0.23 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 152.8, 144.6, 136.7, 129.7, 129.4, 129.0, 128.7, 127.8, 126.8, 123.8, 121.5, 119.8, 53.9, 49.3, 25.9, 21.7, 18.4, -4.1.

HRMS (ESI) m/z calc'd for $C_{24}H_{34}NO_5SSi$ [M+H$^+$]: 476.1927, found 476.1925.

IR (film, cm^{-1}): 3367 (broad), 2956, 2930, 2858, 1735, 1597, 1484, 1443, 1359, 1251, 1169, 1089.



methyl (*E*)-tosyl(3-(4-(trifluoromethyl)phenyl)allyl)carbamate (16): 1-allyl-4-trifluoromethylbenzene (Aldrich) (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results (2.5 mol% of catalyst 1): Run 1 (95.9 mg, 0.232 mmol, 58% yield); run 2 (100.9 mg, 0.244 mmol, 61% yield). **Average:** 60% yield.

Co(II) salophen results (5 mol% of catalyst 1): Run 1 (137.3 mg, 0.332 mmol, 83% yield); run 2 (122.4 mg, 0.296 mmol, 74% yield). **Average:** 79% yield.

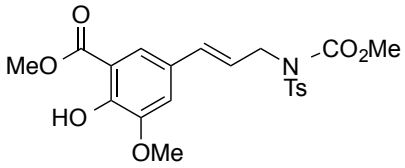
$VO(acac)_2$ results: Run 1 (24.8 mg, 0.060 mmol, 15% yield); run 2 (26.5 mg, 0.064 mmol, 16% yield). **Average:** 16% Yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.64 (d, *J* = 6.3 Hz, 2H), 3.72 (s, 3H), 2.42 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7, 144.9, 139.9, 136.4, 132.5, 129.8 (d, *J*=32 Hz), 129.5, 128.6, 126.8, 126.8, 125.6 (q, *J*=3.8 Hz), 124.2 (d, *J*=272.1 Hz), 54.1, 48.7, 21.7.

HRMS (ESI): m/z calc'd for $C_{19}H_{18}F_3NO_4SNa$ [M+Na$^+$]: 436.0806, found 436.0807.

IR (film, cm^{-1}): 2964, 1747, 1613, 1446, 1332, 1242, 1156, 1118, 1070.



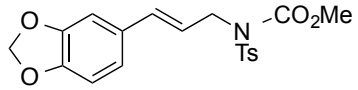
methyl(*E*)-2-hydroxy-3-methoxy-5-(3-((*N*-(methoxycarbonyl)-4 methylphenyl)sulfonamido)prop-1-en-1-yl)benzoate (17) : methyl 5-allyl-2-hydroxy-3-methoxybenzoate (Aldrich) (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results (2.5 mol% of catalyst 1): *The reaction was complete at 24h.* Run 1 (107.9 mg, 0.24 mmol, 60% yield); run 2 (118.7 mg, 0.264 mmol, 66% yield). **Average:** 63% yield.

Co(II) salophen results (5% of catalyst 1): *The reaction mixture became heterogeneous when the reaction was complete (approximately 12 hours).* Run 1 (163.6 mg, 0.364 mmol, 91%); run 2 (170.8 mg, 0.38 mmol, 96% yield). **Average:** 94% yield.

$VO(acac)_2$ results: Run 1 (167.2 mg, 0.372 mmol, 93% yield); run 2 (128.9 mg, 0.28 mmol, 70% yield); run 3 (140.2 mg, 0.312 mmol, 78% yield); run 4 (149.2 mg, 0.332 mmol, 83% yield). **Average:** 81% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.01 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.40 (s, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.04 (s, 1H), 6.55 (d, J = 16.0 Hz, 1H), 6.10 (dt, J = 15.5, 6.5 Hz, 1H), 4.57 (d, J = 6.5 Hz, 2H), 3.93 (s, 3H), 3.88 (s, 3H), 3.69 (s, 3H), 2.38 (s, 3H). Spectroscopic data for the amination product matched that which was reported previously.[10]



methyl (*E*)-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)(tosyl)carbamate (18): 5-allylbenzo[*d*][1,3]dioxole (Aldrich,1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

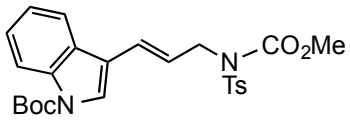
Co(II) salophen results (2.5 mol% of catalyst 1): Run 1 (113.7 mg, 0.292 mmol, 73% yield); run 2 (99.7 mg, 0.256 mmol, 64% yield); run 3 (114.1 mg, 0.293 mmol, 73% yield) **Average:** 70% yield.

Co(II) salophen results (24 hours, 2.5 mol% of catalyst 1): Run 1 (112.2 mg, 0.288 mmol, 72% yield); run 2 (113.7 mg, 0.292 mmol, 73% yield); run 3 (99.7 mg, 0.256 mmol, 64% yield); run 4 (102.8 mg, 0.264 mmol, 66% yield). **Average:** 69% yield.

Co(II)salophen results (5 mol% of catalyst 1): Run 1 (139.0 mg, 0.357 mmol, 89% yield); run 2 (142.9 mg, 0.367 mmol, 92% yield). **Average:** 91% yield.

$VO(acac)_2$ results: Run 1 (148.0 mg, 0.38 mmol, 95% yield); run 2 (132.4 mg, 0.34 mmol, 85% yield). **Average:** 90% Yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 1.5 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.06 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.96 (s, 2H), 4.59 (dd, *J* = 6.6, 1.0 Hz, 2H), 3.71 (s, 3H), 2.42 (s, 3H). Spectroscopic data for the amination product matched that which was reported previously.[8]



***tert*-butyl (*E*)-3-(3-((*N*-(methoxycarbonyl)-4-methylphenyl)sulfonamido)prop-1-en-1-yl)-1*H*-indole-1-carboxylate (19):** *tert*-butyl 3-allyl-1*H*-indole-1-carboxylate[11] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results (5 mol% of catalyst 1): Run 1 (114.4 mg, 0.236 mmol, 59% yield); run 2 (100.8 mg, 0.208 mmol, 52% yield). **Average:** 56% yield.

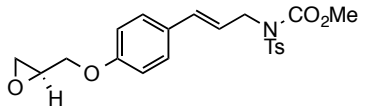
$VO(acac)_2$ results: Run 1 (21.3 mg, 0.044 mmol, 11% yield); run 2 (15.5 mg, 0.032 mmol, 8% yield); **Average:** 10% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.24 (m, 4H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 16.0, 6.5 Hz, 1H), 4.66 (d, *J* = 6.5 Hz, 2H), 3.74 (s, 3H), 2.40 (s, 3H), 1.68 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.9, 149.6, 144.7, 136.7, 136.1, 129.5, 128.7, 128.7, 125.9, 124.9, 124.6, 124.0, 123.1, 120.1, 117.9, 115.5, 84.1, 54.1, 49.5, 28.4, 21.8.

HRMS (ESI) m/z calc'd for $C_{25}H_{28}N_2O_6SNa$ $[M+Na]^+$: 507.1566, found 507.1571.

IR (film, cm^{-1}): 2977, 1732, 1451, 1356, 1251, 1160, 1087.



methyl (*S*,*E*)-(3-(4-(oxiran-2-ylmethoxy)phenyl)allyl)(tosyl)carbamate [(+)-20]: A 1/2 dram vial was charged with (*S*)-2-((4-allylphenoxy)methyl)oxirane[10] (1.0 equiv., 0.3 mmol), followed by 0.45 mL TBME. To this vial was then added 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate (0.015 mmol, 0.05 equiv), 2,5-dimethylbenzoquinone (0.3 mmol, 1.0 equiv), methyl tosylcarbamate (0.6 mmol, 2.0 equiv), and a stir bar. Finally, N,N-Diisopropylethylamine (0.018 mmol, 0.06 equiv) was added *via* micro-syringe, and the mixture instantly became cloudy. The vial was fitted with a Teflon cap, and heated to 45°C (with magnetic stirring) in an oil bath for 24 h. The vial was removed, allowed to cool to room temperature, and thoroughly rinsed into a 125 mL separatory funnel with ether (ca. 30 mL). The organic phase was washed with 5% aq. K_2CO_3 (6 x 10 mL), and the aqueous rinses back-extracted with ether (2 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered through Celite, and evaporated to dryness (ca. 30-40°C, 30 torr). Column chromatography (30-50% ethyl acetate/hexanes) afforded the product clear oil that crystallized after drying under high vacuum.

Results: Run 1 (75.1 mg, 0.184 mmol, 60% yield); run 2 (92.4 mg, 0.221 mmol, 74% yield); run 3 (89.8 mg, 0.215 mmol, 71% yield). **Average:** 68% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.59 (d, *J* = 6.6 Hz, 2H), 4.24 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.95 (dd, *J* = 11.0, 5.7 Hz, 1H), 3.71 (s, 3H), 3.36 (dq, *J* = 5.7, 2.9 Hz, 1H), 2.91 (t, *J* = 4.5 Hz, 1H), 2.76 (dd, *J* = 4.9, 2.6 Hz, 1H), 2.41 (s, 3H).

$[\alpha]_D^{26}$= +5.4^o (c=1.01, CH_2Cl_2).

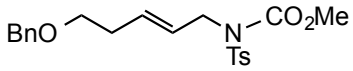
Note: the previously reported rotation was measured in $CHCl_3$ giving $[\alpha]_D^{22}$= -0.26^o (c=1.0, $CHCl_3$)[10]

Spectroscopic data for the amination product matched that which was reported previously.[10]

Allylic C-H Amination Using Air

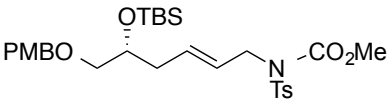
General procedure: To a 10 mL round bottom flask containing a PTFE-covered stir bar was added tetra *n*-butyl ammonium acetate (7.2 mg, 0.024 mmol, 6 mol%) in a glove box. The following solids were all weighed outside of the glovebox and sequentially added to the reaction flask containing TBAA: carbamate nucleophile (137.6 mg, 0.6 mmol, 1.5 equiv), DHBQ (4.4 mg, 0.04 mmol, 10 mol%), Co(II)(salophen) (3.7 mg, 0.01 mmol, 2.5 mol%) and Pd^{II}/bis-sulfoxide catalyst **1** (5 mg, 0.01 mmol, 2.5 mol% or 10 mg, 0.02 mmol, 5 mol%). *(NOTE: Because of the hygroscopic nature of TBAA, the reaction flask was not opened until all the other solids were ready to be transferred into the flask; in some cases, we have seen lower reactivity when the TBAA is exposed to air for longer periods of time).* The terminal olefin (0.4 mmol, 1 equiv, preweighed in a ½ dram vial) was diluted with 0.1 mL TBME and then added to the reaction flask using TBME for the transfer (0.3 mL – total of 0.4 mL solvent). The flask was attached to a cold-water condenser using a PTFE sleeve as a seal, with no additional support of the flask required and the joint was wrapped in teflon tape. The top of the condenser was sealed with a rubber septum, and a balloon of air was attached with a needle. While the reaction condenser may be left opened to air, we have noted rapid and continual loss of the very volatile TBME solvent under this scenario and recommend the use of an air balloon. The reaction was allowed to stir at 400rpm in a 45°C oil bath for 24-72 hours or until completed by TLC. The reaction mixture was diluted with ethyl acetate and transferred to a 125 mL separatory funnel, washed with 5% aq. K_2CO_3 (6 x 10 mL), and the aqueous rinses back-extracted with ethyl acetate (2 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered through Celite, and evaporated to dryness (ca. 30-40°C, 30 torr). *Generally this workup leads to higher purity of isolated products by removing remaining nucleophile and water-soluble impurities.* Alternatively, the reaction may be diluted with dichloromethane and flushed through a 3-5 cm silica gel plug with an 80% ethyl acetate/20% hexanes mixture. If no work-up is necessary, the reaction mixture may also be directly loaded onto a silica gel

column using dichloromethane or toluene. Purification of the products is done using flash column chromatography - in general, with a gradient of 10-30% EtOAc/hexanes. We have also found that 10-30% acetone/hexanes or 10-50% ether/pentane gradients are also effective solvent systems for purification.

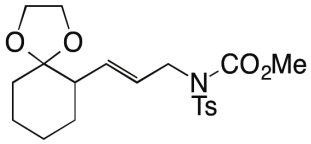


methyl(*E*)-(5-(benzyloxy)pent-2-en-1-yl)(tosyl)carbamate: ((pent-4-en-1-yloxy)methyl)benzene (1.0 equiv, 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Results (5 mol% of catalyst 1): Run 1 (80.7 mg, 0.2 mmol, 50% yield); run 2 (87.2 mg, 0.216 mmol, 54% yield). **Average:** 52% yield. E/Z 11:1.

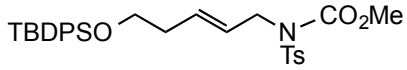


methyl(*R*,*E*)-(5-((*tert*-butyldimethylsilyl)oxy)-6-((4-methoxybenzyl)oxy)hex-2-en-1-yl)(tosyl)carbamate: (*R*)-*tert*-butyl((1-((4-methoxybenzyl)oxy)hex-5-en-2-yl)oxy)dimethylsilane (1.0 equiv, 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil. **Results (5 mol% of catalyst 1):** Run 1 (143.3 mg, 0.248 mmol, 62% yield); run 2 (127.1 mg, 0.22 mmol, 55% yield). **Average:** 59% yield.

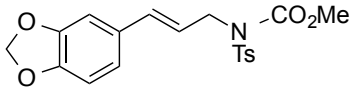


methyl(*E*)-(3-(1,4-dioxaspiro[4.5]decan-6-yl)allyl)(tosyl)carbamate: 6-allyl-1,4-dioxaspiro[4.5]decane (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Results (5 mol% of catalyst 1): Run 1 (91.73 mg, 0.224 mmol, 56% yield); run 2 (93.37 mg, 0.228 mmol, 57% yield). **Average:** 57% yield.



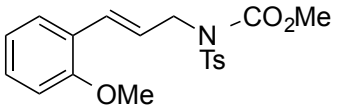
methyl (*E*)-(5-((*tert*-butyldiphenylsilyl)oxy)pent-2-en-1-yl)(tosyl)carbamate: *tert*-butyl(pent-4-en-1-yloxy)diphenylsilane (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil. **Results (2.5 mol% of catalyst 1):** Run 1 (145.66 mg, 0.264 mmol, 66% yield); run 2 (143.46 mg, 0.26 mmol, 65% yield). **Average:** 66% yield.



methyl (*E*)-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)(tosyl)carbamate: 5-allylbenzo[*d*][1,3]dioxole (Aldrich) (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

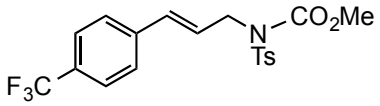
Results: (2.5 mol% of catalyst 1): Run 1 (119.94 mg, 0.308 mmol, 77%); run 2 (113.71 mg, 0.292 mmol, 73%); run 3 (116.83 mmol, 0.3 mmol, 75%). **Average:** 75% yield.

Results (5 mol% of catalyst 1): Run 1 (140.19 mg, 0.36 mmol, 90%); run 2 (140.19, 0.36, 90%). **Average:** 90% yield.



methyl (*E*)-(3-(2-methoxyphenyl)allyl)(tosyl)carbamate: 1-Allyl-2-methoxybenzene (1.0 equiv, 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Results (2.5 mol% of catalyst 1): Run 1 (88.6 mg, 0.236 mmol, 59% yield); run 2 (94.6 mg, 0.252 mmol, 63% yield); run 3 (97.61 mg, 0.26 mmol, 65% yield). **Average:** 62% yield.

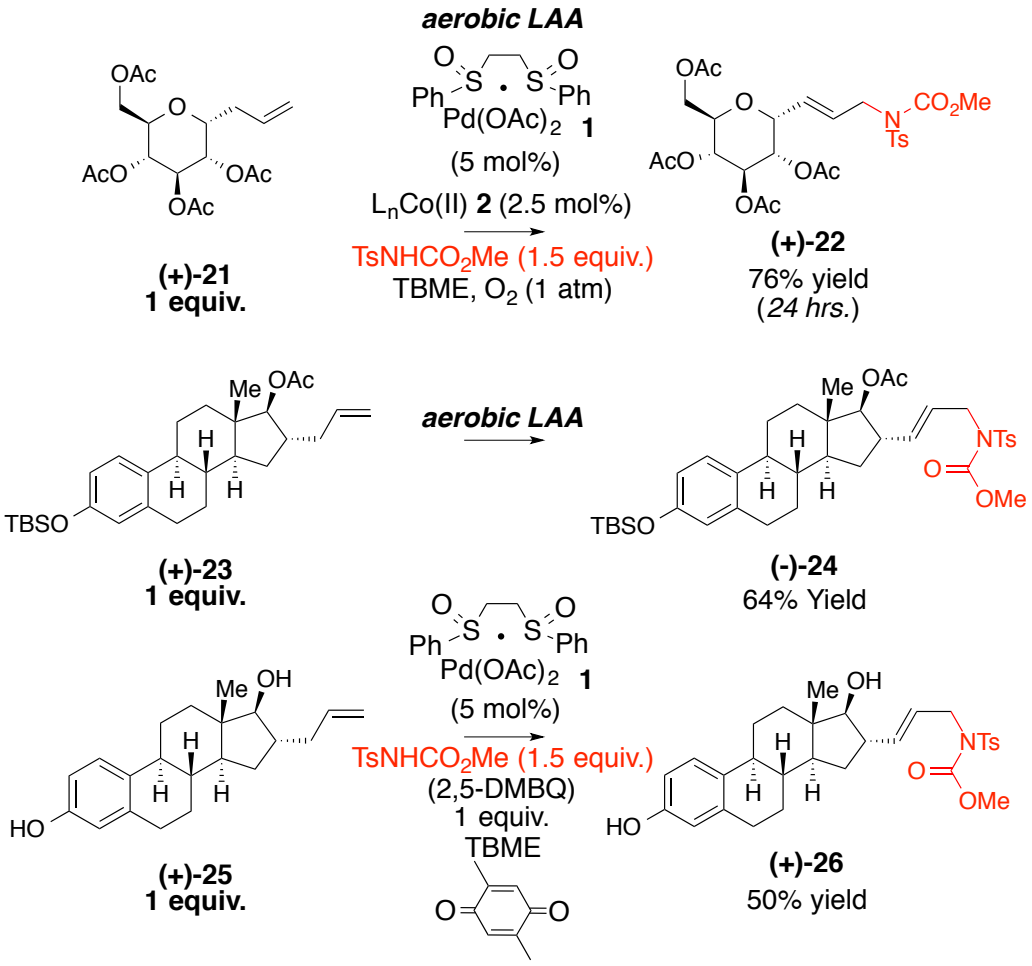


methyl (*E*)-tosyl(3-(4-(trifluoromethyl)phenyl)allyl)carbamate: 1-allyl-4-trifluoromethylbenzene (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes or 10-30% acetone/hexanes) provided the linear allylic amine as a clear oil.

Results (2.5 mol% of catalyst 1): Run 1 (62.8 mg, 0.152 mmol, 38% yield); run 2 (91.0 mg, 0.22 mmol, 55% yield); run 3 (71.1 mg, 0.172 mmol, 43%). **Average:** 45% yield.

Results (5 mol% of catalyst 1): Run 1 (122.0 mg, 0.295 mmol, 74% yield); run 2 (110.8 mg, 0.268 mmol, 67% yield). **Average:** 71% yield.

Scheme S1. Reactivity of Functionally Diverse Substrates.



(2*R*,3*R*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-((*E*)-3-((*N*-(methoxycarbonyl)-4-methylphenyl)sulfonamido)prop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate [(+)-22]:

(2*R*,3*R*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-allyltetrahydro-2*H*-pyran-3,4,5-triyl triacetate[12] (1.0 equiv., 0.2 mmol or 0.3 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.

Co(II) salophen results (24 hours, reaction run on a 0.2 mmol scale): Run 1 (98.3 mg, 0.164 mmol, 82% yield); run 2 (87.5 mg, 0.146 mmol, 73% yield); run 3 (0.3 mmol scale) (133 mg, 0.222 mmol, 74% yield). **Average:** 76% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.00 - 5.91 (m, 2H), 5.28 (t, *J* = 9.5 Hz, 1H), 5.10 - 4.97 (m, 2H), 4.76 (dd, *J* = 5.2, 2.3 Hz, 1H), 4.54 - 4.46 (m, 2H), 4.19 (dd, *J* = 12.3, 4.9 Hz, 1H), 4.07 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.94 (ddd, *J* = 10.0, 5.0, 2.3 Hz, 1H), 3.70 (s, 3H), 2.43 (s, 3H), 2.06 (s, 3H), 2.02 (s, 6H), 2.00 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.8, 170.1, 169.8, 169.6, 152.6, 144.9, 136.4, 132.4, 129.6, 128.6, 126.3, 72.4, 70.7, 70.4, 69.7, 69.0, 62.4, 54.1, 48.2, 21.8, 20.8 (broad).

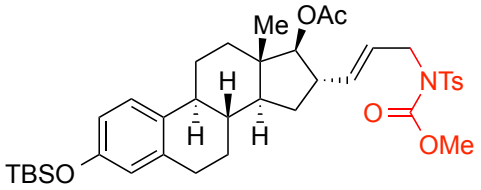
HRMS (ESI) m/z calc'd for $C_{26}H_{34}NO_{13}S$ [M+H$^+$]: 600.1751, found 600.1752.

IR (film, cm^{-1}): 2959, 2259, 1740, 1597, 1444, 1365, 1219, 1170, 1089, 1033, 908, 727

$[\alpha]_D^{26}$= +77.6° (c=1.08, CH_2Cl_2).

(8*R*,9*S*,13*S*,14*S*,16*S*,17*S*)-3-((*tert*-butyldimethylsilyl)oxy)-16-((*E*)-3-((*N*-(methoxycarbonyl)-4-methylphenyl)sulfonamido)prop-1-en-1-yl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl acetate [(-)-24].

(8*R*,9*S*,13*S*,14*S*,16*R*,17*S*)-16-allyl-3-((*tert*-butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl acetate[10] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure using Co(II)salophen **2** as the reoxidation co-catalyst. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a white solid.



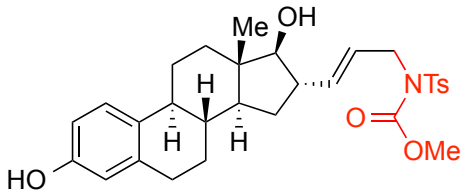
Results: Run 1 (172.6 mg, 0.248 mmol, 62% yield); run 2 (180.9 mg, 0.260 mmol 65% yield). **Average:** 64% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.61 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 5.79 (dd, *J* = 15.3, 8.3 Hz, 1H), 5.53 (dt, *J* = 15.4, 6.4 Hz, 1H), 4.71 (d, *J* = 8.0 Hz, 1H), 4.40 (dt, *J* = 6.4, 1.5 Hz, 2H), 3.70 (s, 3H), 2.81 (dd, *J* = 6.7, 3.3 Hz, 2H), 2.69 (dtd, *J* = 11.7, 8.1, 3.6 Hz, 1H), 2.43 (s, 3H), 2.31 - 2.15 (m, 2H), 2.05 (s, 3H), 1.89 - 1.69 (m, 3H), 1.52 - 1.20 (m, 5H), 0.97 (s, 9H), 0.84 (s, 3H), 0.18 (s, 6H).
$[\alpha]_D^{25}$ = -1.5° (c = 1.0, $CHCl_3$).

Spectroscopic data for the amination product matched that which was reported previously.[10]

methyl((*E*)-3-((8*R*,9*S*,13*S*,14*S*,16*S*,17*S*)-3,17-dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-16-yl)allyl)(tosyl)carbamate [(+)-26].

A 1 dram vial was charged with (8*R*,9*S*,13*S*,14*S*,16*R*,17*S*)-16-allyl-3-((*tert*-butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol[10] (1.0 equiv., 0.2 mmol), 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate (0.01 mmol, 0.05 equiv), 2,5-dimethylbenzoquinone (0.2 mmol, 1.0 equiv), methyl tosylcarbamate (0.4 mmol, 2.0 equiv), and a stir bar. TBME (0.66M) was then added, followed by N,N-Diisopropylethylamine (0.012 mmol, 0.06 equiv) and the reaction mixture instantly became cloudy. The vial was fitted with a Teflon cap, and heated to 45°C (with magnetic stirring) in an oil bath for 72 h. The vial was removed, allowed to cool to room temperature, and vigorously rinsed into a 125 mL separatory funnel with ether (ca. 30 mL). The organic phase was washed with 5% aq. K_2CO_3 (6 x 10 mL), and the aqueous rinses back-extracted with ether (2 x 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered through Celite, and evaporated to dryness (ca. 30-40°C, 30 torr). Column chromatography (30-50% ethyl acetate/hexanes) afforded the product as a white solid.



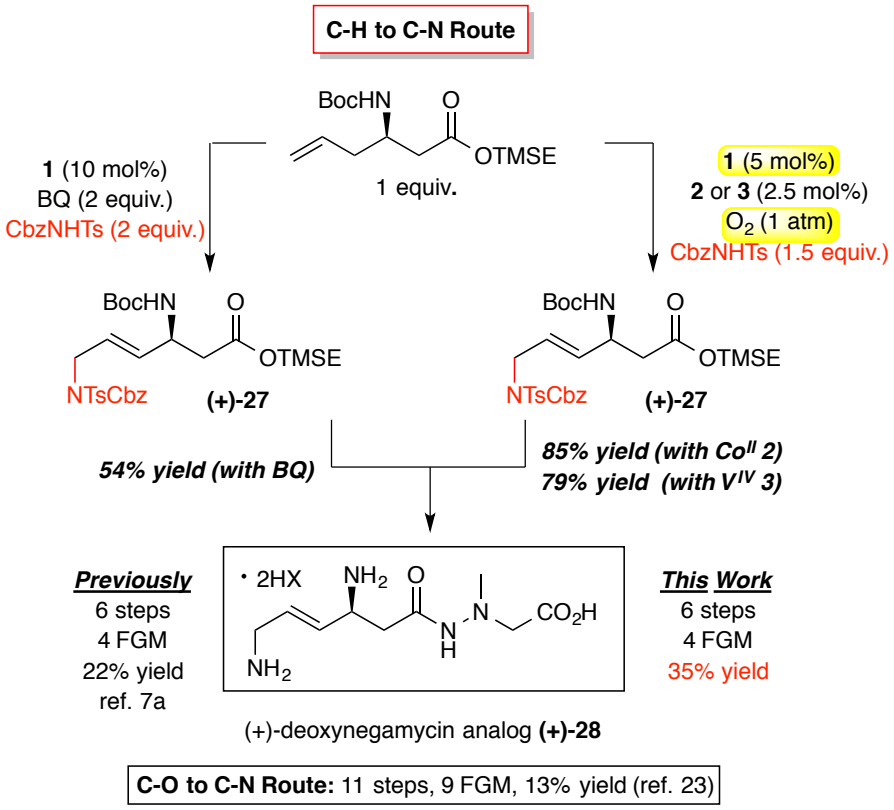
Results: Run 1 (52.9 mg, 0.098 mmol, 49%); run 2 (54.97 mg, 0.102 mmol, 51%).

Average: 50% yield

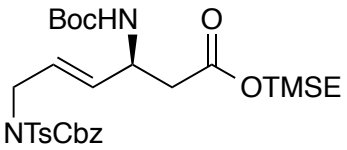
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 5.85 (dd, *J* = 15.2, 8.6 Hz, 1H), 5.59 (dt, *J* = 15.2, 6.3 Hz, 1H), 5.23 (s, 1H), 4.45 (d, *J* = 6.3 Hz, 2H), 3.69 (s, 3H), 3.42 (d, *J* = 7.9 Hz, 1H), 2.85 - 2.75 (m, 2H), 2.47 (ddt, *J* = 12.7, 8.4, 4.3 Hz, 1H), 2.43 (s, 3H), 2.29 (dt, *J* = 13.9, 3.7 Hz, 1H), 2.17 (ddd, *J* = 15.2, 10.6, 4.4 Hz, 1H), 1.94 (dt, *J* = 12.7, 3.3 Hz, 1H), 1.86 - 1.66 (m, 2H), 1.59 - 1.19 (m, 7H), 0.83 (s, 3H).
$[\alpha]_D^{27}$= +25.6° (c = 0.99, $CHCl_3$)

Spectroscopic data for the amination product matched that which was reported previously.[10]

Scheme S2. Streamlining of a Deoxynegamycin Analog.



2-(trimethylsilyl)ethyl(*S*,*E*)-6-((*N*-((benzyloxy)carbonyl)-4-methylphenyl)sulfonamido)-3-((*tert*-butoxycarbonyl)amino)hex-4-enoate [(+)-27]: 2-(trimethylsilyl)ethyl (*R*)-3-((*tert*-butoxycarbonyl)amino)hex-5-enoate[8] (1.0 equiv., 0.4 mmol) was reacted according to the general procedure. Purification by flash column chromatography (gradient 10%-25% EtOAc/hexanes) provided the linear allylic amine as a clear oil.



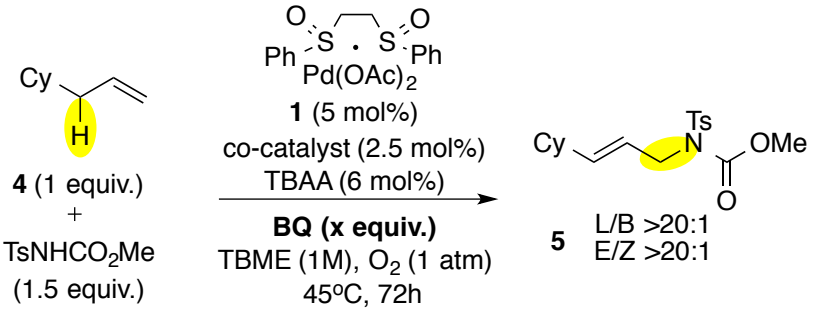
Co(II)salophen results (5 mol% of catalyst 1): Run 1 (212.6 mg, 0.336 mmol, 84% yield); run 2 (217.7 mg, 0.344 mmol, 86% yield). **Average:** 85% yield.

$VO(acac)_2$ results: Run 1 (192.4 mg, 0.304 mmol, 76% yield); run 2 (13.0 mg, 81% yield). **Average:** 79% Yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (dd, *J* = 4.8, 2.1 Hz, 3H), 7.22 - 7.16 (m, 4H), 5.81 - 5.67 (m, 2H), 5.17 (br. s, 1H), 5.07 (s, 2H), 4.53 (br. s, 1H), 4.45 (d, *J* = 4.9 Hz, 2H), 4.16 (ddd, *J* = 11.3, 5.8, 2.4 Hz, 2H), 2.54 (qd, *J* = 15.8, 5.7 Hz, 2H), 2.40 (s, 3H), 1.44 (s, 9H), 1.01 - 0.96 (m, 2H), 0.03 (s, 9H).

Spectroscopic data for the amination product matched that which was reported previously.[8]

Table S2. Effect of BQ Loading on Overall Reaction Yields



Entry[a]	co-catalyst	BQ equivalents	Yield of 5[b]
1	Co(II)(salophen) **2**	0.1 equiv.	81%
2	Co(II)(salophen) **2**	0.5 equiv.	56%
3	Co(II)(salophen) **2**	1 equiv.	50%
4	$VO(acac)_2$ **3**	0.1 equiv.	70%
5	$VO(acac)_2$ **3**	0.5 equiv.	40%
6	$VO(acac)_2$ **3**	1 equiv.	25%

[a] Conditions are as listed above unless otherwise noted.
[b] Isolated yield; average of two runs at a 0.4 mmol scale.

Entry 1: The reaction was set up according to general procedure **A**. 10 mol% BQ was used in place of 10 mol% DHBQ. Run 1 (113.9 mg, 0.324 mmol, 81% yield); run 2 (112.5 mg, 0.320 mmol, 80% yield). **Average:** 81% yield.

Entry 2: The reaction was set up according to general procedure **A**. 50 mol% BQ was used in place of 10 mol% DHBQ. Run 1 (81.5 mg, 0.232 mmol, 58% yield); run 2 (74.5 mg, 0.212 mmol, 53% yield). **Average:** 56% yield.

Entry 3: The reaction was set up according to general procedure **A**. 100 mol% BQ was used in place of 10 mol% DHBQ. Run 1 (70.3 mg, 0.200 mmol, 50% yield); run 2 (70.3 mg, 0.200 mmol, 50% yield). **Average:** 50% yield.

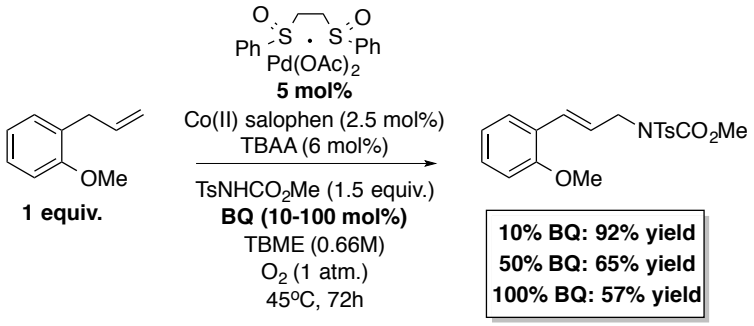
Entry 4: The reaction was set up according to general procedure **B**. 10 mol% BQ was used in place of 10 mol% DHBQ. Run 1 (106.8 mg, 0.304 mmol, 76% yield); run 2 (88.6 mg, 0.252 mmol, 63% yield). **Average:** 70% yield.

Entry 5: The reaction was set according to general procedure **B.** 50 mol% BQ was used in place of 10 mol% DHBQ. Run 1 (57.6 mg, 0.164 mmol, 41% yield); run 2 (53.4 mg, 0.152 mmol, 38% yield). **Average:** 40% yield.

Entry 6: The reaction was set up according to general procedure **B**. 100 mol% BQ was used in place of 10 mol% DHBQ. Run 1 (35.1 mg, 0.100 mmol, 25% yield); run 2 (33.7 mg, 0.096 mmol, 24% yield). **Average:** 25% yield.

Rate Experiments

Scheme S3. Reaction Conditions Used for Rate Measurments



General Procedure for Obtaining Rate Data for 10 and 20 mol% BQ: To an oven-dried 15 mL, 3-necked round bottom flask containing a PTFE-covered stir bar was added tetra *n*-butyl ammonium acetate (18.1 mg, 0.06 mmol, 6 mol%) in a glove box. To the reaction flask containing TBAA was then added carbamate nucleophile (343.8 mg, 1.5 mmol, 1.5 equiv.) and Co(II) (salophen) (9.7 mg, 0.025 mmol, 2.5 mol%). To these solids was then added 1 mL TBME, and the solution was stirred at 45°C for 15 minutes. The flask was removed from heat and briefly cooled to room temperature. *Note: TBAA, nucleophile and Co(II)-salophen were briefly pre-stirred to improve homogeneity for any kinetic experiment in which time-points were removed earlier than 30 minutes into the reaction. A reaction concentration of 0.66 M was used to maximize reaction homogeneity.* The terminal olefin substrate (1 mmol, 148.2 mg, 1 equiv.) and nitrobenzene (41.1 uL, 40 mol%), both pre-mixed in a 1-dram vial, were then added using the remaining 0.5 mL of TBME (1.5 mL total volume, 0.66 M) to ensure quantitative transfer. Benzoquinone (10 or 20 mol%) was then added, followed by the Pd(II)-catalyst. The reaction was immediately attached to a cold-water condenser (purged for ca. 30 seconds with O_2) fitted with an O_2 balloon and stirred at 45°C. Aliquots (ca. 30 μL) were removed by from the reaction at time intervals shown below. Aliquots were removed through the neck of the flask without disrupting the atmosphere of the reaction, diluted with 0.6 mL of THF and filtered through a small plug of silica gel. Samples were analyzed by normal phase HPLC (Zorbax CN 4.6 x 250 nm column, 10% isopropyl alcohol/90% hexanes, 1 mL/min, λ=280 nm). Rate data is reported as the average of three experiments, with error bars representing standard deviation. *Note: for the measurement of the rate of reaction for 10% BQ, an HPLC calibration curve calibrated for a 0.5-20% yield was used. For the remaining kinetic measurements, a calibration curve calibrated for a 2-100% yield was used.*

General Procedure for Obtaining Rate Data for 30, 50, 75, and 100 mol% BQ: To an oven-dried 15 mL, 3-necked round bottom flask containing a PTFE-covered stir bar was added tetra *n*-butyl ammonium acetate (18.1 mg, 0.06 mmol, 6 mol%) in a glove box. To the reaction flask containing TBAA was then added carbamate nucleophile (343.8 mg, 1.5 mmol, 1.5 equiv.), Co(II) (salophen) (9.7 mg, 0.025 mmol, 2.5 mol%), and benzoquinone (varying equivalents, see below). The terminal olefin substrate (1 mmol, 148.2 mg, 1 equiv.) and nitrobenzene (41.1 uL, 40 mol%), both pre-mixed in a 1-dram vial, were then added using 1.5 mL of TBME (0.66 M) to ensure quantitative transfer. *A reaction concentration of 0.66 M was used to maximize reaction homogeneity.* The Pd(II) catalyst was then added, and the reaction was immediately attached to a cold-water condenser (purged for ca. 30 seconds with O_2) fitted with an O_2 balloon and stirred at 45°C. Aliquots (ca. 30 μL) were removed by from the reaction according to the times shown below. Aliquots were removed through the neck of the flask without disrupting the atmosphere of the reaction, diluted with 0.6 mL THF and filtered through a small plug of silica gel. Samples were analyzed by normal phase HPLC (Zorbax CN 4.6 x 250 nm column, 10% isopropyl alcohol/90% hexanes, 1 mL/min, λ=280 nm). Rate data is reported as the average of three experiments, with error bars representing standard deviation.

Figure S1. Effect of BQ Concentration on Rate

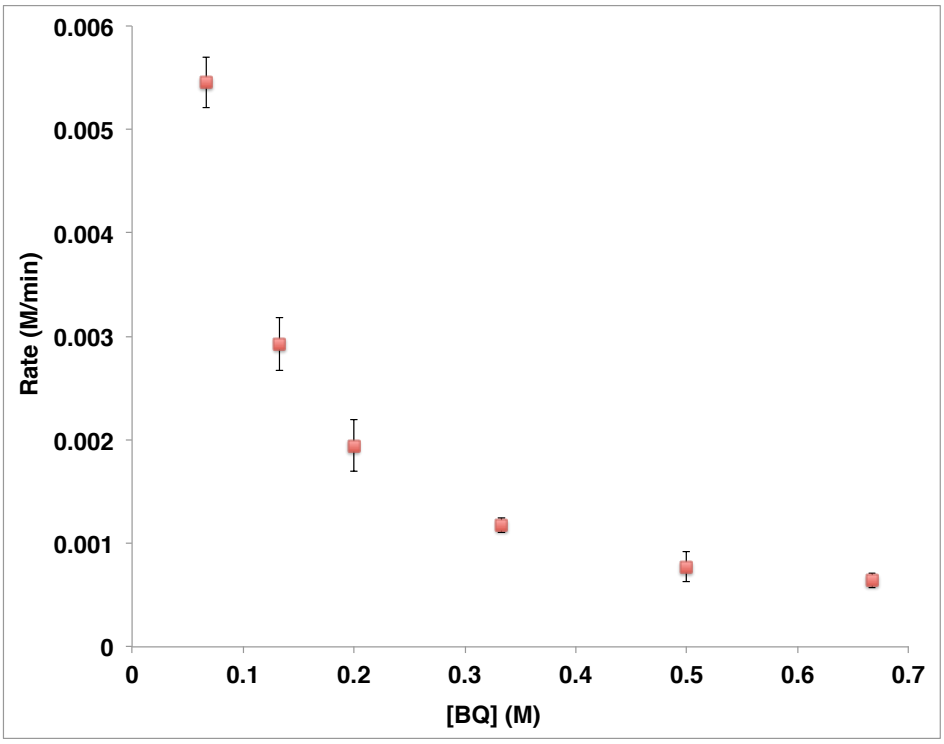
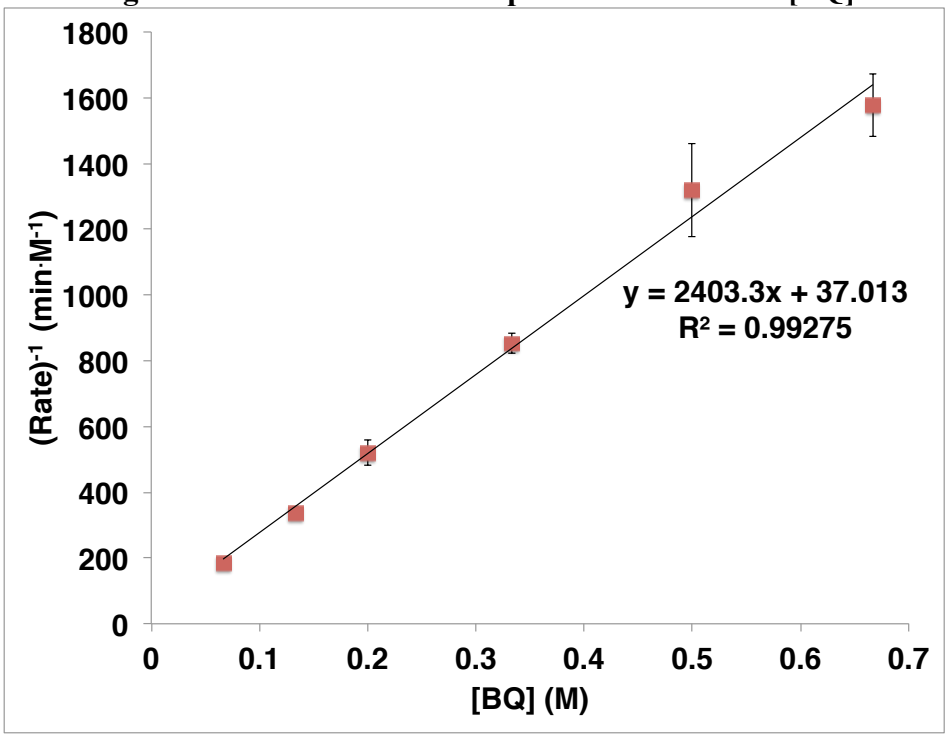


Figure S2. Inverse Relationship Between Rate and [BQ]



Note: error bars for Figure S2 determined via propagation of percent error

Figure S3. Rate of Reaction—10 mol% Benzoquinone

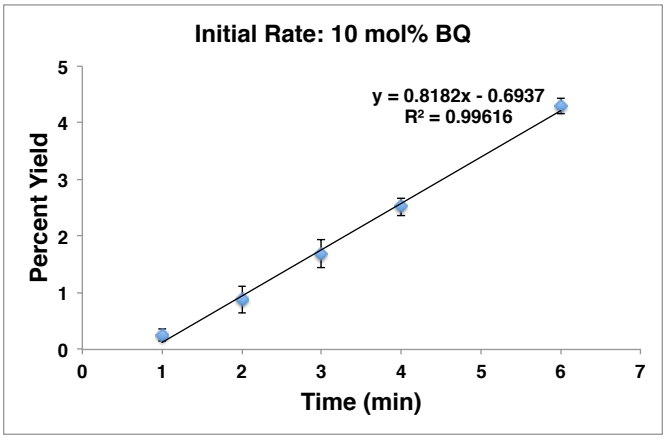


Figure S4. Rate of Reaction—20 mol% Benzoquinone

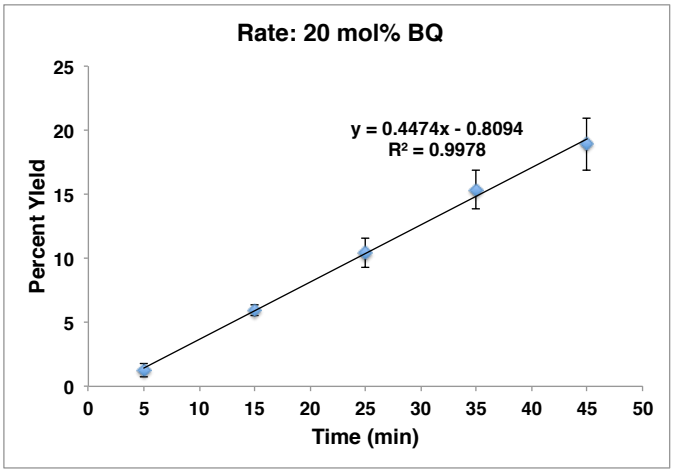


Figure S5. Rate of Reaction—30 mol% Benzoquinone

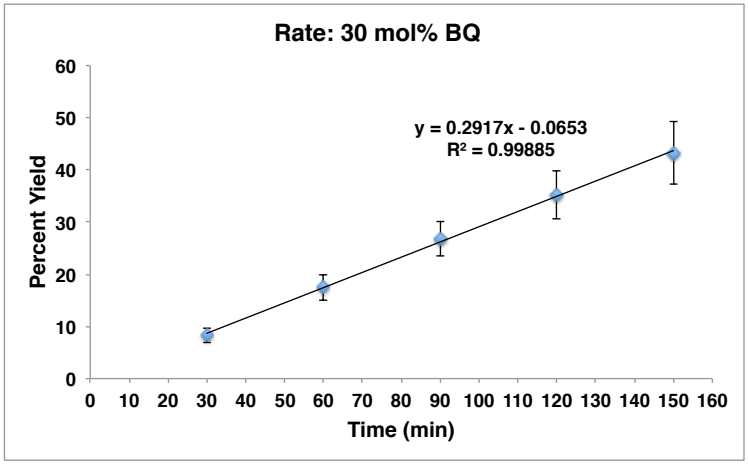


Figure S6. Rate of Reaction—50 mol% Benzoquinone

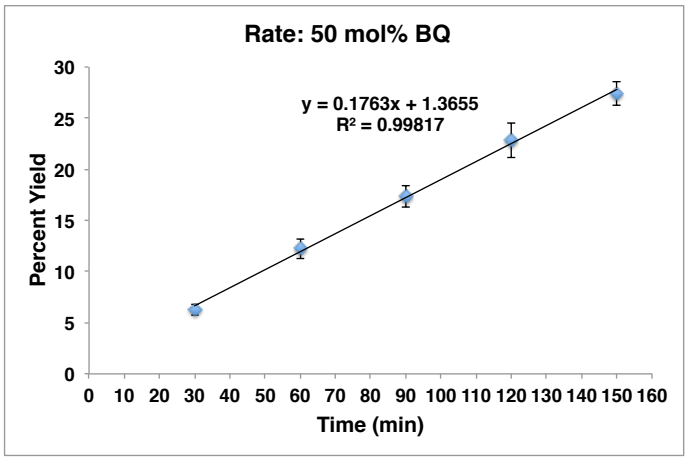


Figure S7. Rate of Reaction—75 mol% Benzoquinone

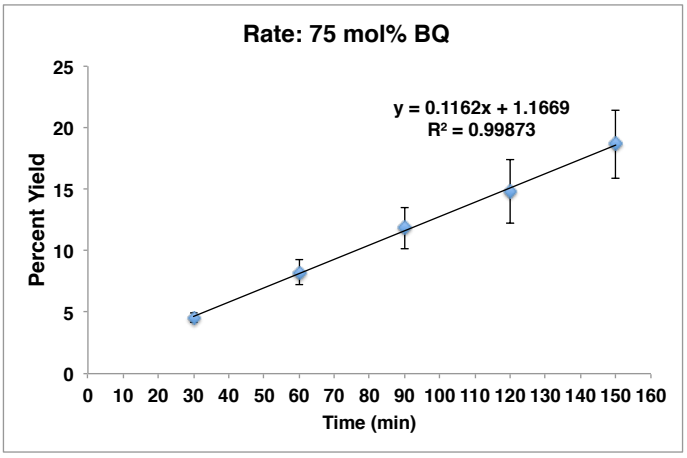
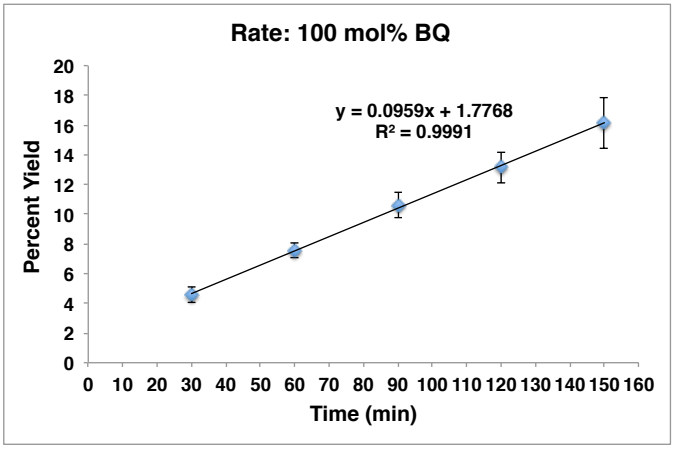


Figure S8. Rate of Reaction—100 mol% Benzoquinone



References:

1. Bäckvall, J.E.; Hopkins, R.B.; Grennberg, H.; Mader, M.M.; Awasthi, A.K. *J. Am. Chem. Soc.* **1990**, *112*, 5160.
2. Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923
3. Nemoto, H.; Shiraki, M; Fukumoto, K. *J. Org. Chem.* **1996**, *61*, 1347.
4. Lowik, D.W.P.M.; Liskamp, R.M.J. *Eur. J. Org. Chem.* **2000**, 1219.
5. Clavier, H.; Nolan, S.P.; Mauduit, M. *Organometallics*, **2008**, *27*, 2287
6. Liu, G.; Yin, G.; Wu, L. *Angew. Chem. Int. Ed.* **2008**, 4733.
7. Knust, H.; Hoffmann, R.W. *Helv. Chim. Acta.* **2003***, 86*, 1871.
8. Reed, S. A.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130,* 3316.
9. Pelly, S.C.; Govender, S.; Fernandes, M.A.; Schmalz, H.G.; de Konig, C.B. *J. Org. Chem.* **2006**, *72*, 2857.
10. Reed, S. A.; Mazzotti, A. R.; White, M. C. *J. Am. Chem. Soc.* **2009**, *131,* 11701.
11. Tomakinian, T.; Guillot, R.; Kouklovsky, C.; Vincent, G. *Angew. Chem. Int. Ed.* **2014**, *53*, 11881.
12. McGarvey, G. J.; LeCLair, C. A.; Schmidtmann, B. A. *Org. Lett.* **2008**, *10*, 4727.