Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer

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Table S1. The influence of hydrogen atom donor to the reaction. 

| entry | variation from the conditions above | time  | conv. 1a | yield 2a | conv. 1b | yield 2b | 2a:2b |
|-------|-----------------------------------|-------|----------|----------|----------|----------|--------|
| 1     | cyclohexa-2,5-diene-1-carboxylic acid (10 equiv) instead of DHB | 280 min | >95%     | 13% (60% 3y) | 32%      | 3%       | 4.3:1.0 |
| 2     | methyl cyclohexa-2,5-diene-1-carboxylate (10 equiv) instead of DHB | 40 min  | 33%     | 15% (18% 3y) | 11%      | 4%       | 3.8:1.0 |
| 3     | 1-methoxycyclohexa-1,4-diene (10 equiv) instead of DHB | 380 min | 5%      | 5%       | 8%       | 3%       | 1.7:1.0 |

*aReactions employed 250 μmol each of 1a and 1b. All conversions and yields were calculated by 1H NMR spectroscopy using mesitylene as an internal standard.*
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Table S2. Relative reactivity of different unsaturated substrates.

| entry | target substrate | conditions and yield$^a$ | competition substrate | conversion$^b$ | yield$^b$ | ratio of reduction products |
|-------|------------------|--------------------------|-----------------------|--------------|----------|---------------------------|
| 1     | PMPCO$_2$        | A: 79%$^8$               | PMPCO$_2$            | 17%          | 14%      | 5.6:1.0                   |
|       | $^1$a            | B: 91%$^8$               | $^1$c                 | 29%          | 24%      | 3.8:1.0                   |
| 2     | PMPCO$_2$        | A: 86%                   | $^4$a                 | 17%          | 12%      | 7.2:1.0                   |
|       | $^1$a            | B: 92%                   | $^4$c                 | 17%          | 17%      | 5.4:1.0                   |
| 3     | PMPCO$_2$        | A: 79%                   | $^4$a                 | 15%          | 15%      | 5.3:1.0                   |
|       | $^1$d            | B: 87%                   | $^4$a                 | 29%          | 28%      | 3.1:1.0                   |
| 4     | PMPCO$_2$        | A: 71%                   | $^4$a                 | 5%           | 2%       | 2.8:1.0                   |
| 5     | Cbz-$\equiv$N-   | A: 78%                   | $^4$a                 | 17%          | 17%      | 4.6:1.0                   |
|       | $^1$e            | B: 88%                   | $^4$a                 | 38%          | 39%      | 2.3:1.0                   |
| 6     | PMPCO$_2$        | A: 96%                   | $^4$b                 | 11%          | 11%      | 8.7:1.0                   |
| 7     | PMPCO$_2$        | A: 72%                   | $^4$c                 | 12%          | 8%       | 8.8:1.0                   |
| 8     | PMPCO$_2$        | A: 93%                   | $^4$d                 | 12%          | 12%      | 7.8:1.0                   |
| 9     | PMPCO$_2$        | A: 77%                   | $^4$e                 | 26%          | 22%      | 3.0:1.0                   |
| 10    | PMPCO$_2$        | A: 64%                   | $^4$f                 | 31%$^e$      | 31%$^e$ | 2.1:1.0                   |
| 11    | PMPCO$_2$        | A: 92%                   | $^4$g                 | 46%          | 46%      | 2.0:1.0                   |
| 12    | PMPCO$_2$        | A: 95%                   | $^4$h                 | 64%          | 64%      | 1.5:1.0                   |
| 13    | PMPCO$_2$        | A: 86%                   | $^4$i                 | 22%          | 18%      | 4.8:1.0                   |
| 14    | PMPCO$_2$        | A: 90%                   | $^4$j                 | 35%          | 28%      | 3.2:1.0                   |
| 15    | PMPCO$_2$        | A: 95%                   | $^4$k                 | 31%$^e$      | 31%$^e$ | 3.1:1.0                   |
| 16    | PMPCO$_2$        | A: 95%                   | $^4$l                 | > 95%$^e$    | > 95%$^e$| 1.0:1.0$^d$               |
| 17    | PMPCO$_2$        | A: 55%                   | $^4$m                 | > 95%$^e$    | > 95%$^e$| 1.0:1.7$^d$               |

$^a$Reactions employed 250 μmol of each substrate. Yields refer to purified products isolated by flash-column chromatography, unless otherwise noted. $^b$Determined by $^1$H NMR spectroscopy using mesytilene as an internal standard. $^c$Competition substrate was converted to unidentified products. $^d$Ratios are calculated as the yield of the target substrate versus the conversion of the competition substrate. $^e$Conversion determined by $^{19}$F-NMR with hexafluorobenzene as an internal standard. $^f$Decomposition was observed.
**Table S3. Evaluation of heterogeneous, directed homogeneous, and hydrogen atom transfer reduction of 1a and 1c.**

| entry | conditions                      | time  | conv. 1a | yield 2a | conv. 1c | yield 2c | 2a:2b  |
|-------|--------------------------------|-------|----------|----------|----------|----------|--------|
| 1     | 1 mol% Pd/C, 1 atm H₂, CH₃OH, 24 °C | 5 min | 13%      | 13%      | 70%      | 57%      | 1.0:4.4|
| 2     | 0.5 mol% Pt/C, 1 atm H₂, CH₃OH, 24 °C | 3 min | 24%      | 13%      | 56%      | 25%      | 1.0:1.9|
| 3     | 2 mol% [Ir(COD)(PCy₃)py], 1 atm H₂, CH₂Cl₂, 24 °C | 180 min | 8%       | 5%       | 43%      | 28%      | 1.0:5.6|
| 4     | Mn(dpm)₃, TBHP, PhSiH₃, i-PrOH, 24 °C | 10 min | 59%      | 24%      | 53%      | 25%      | 1.0:1.0|

*Reactions employed 250 μmol each of 1a and 1b. All conversions and yields were calculated by ¹H NMR spectroscopy using mesitylene as an internal standard.*

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Table S4. Optimization of hydrobromination, hydroiodination, and hydroselenation reactions.¹

| entry | radical trap | variation from conditions above | yieldb | yield of reductionc |
|-------|--------------|---------------------------------|--------|---------------------|
| 1     | TsBr         | DHB omitted                     | <1%    | <1%                 |
| 2     | TsBr         | —                               | 95%    | <1%                 |
| 3     | I₂           | DCM as solvent                  | <1%    | <1%                 |
| 4     | TsI          | DCM as solvent                  | <1%    | <1%                 |
| 5     | NIS          | DCM as solvent                  | <1%    | <1%                 |
| 6     | (CH₂I)₂      | DCM as solvent                  | <1%    | <1%                 |
| 7     | CH₂I₂        | DCM as solvent, 15 equiv of CH₂I₂ | 89%    | <1%                 |
| 8     | CH₂I₂        | DCM as solvent, 7.5 equiv of CH₂I₂ | 52%    | <1%                 |
| 9     | CH₂CO₂Et     | DCM as solvent                  | 49%    | <1%                 |
| 10    | ICH₂CN       | DCM as solvent                  | 36%    | <1%                 |
| 11    | TsSePh       | —                               | 89%    | <1%                 |

¹Conditions: Co(acac)₂ (100 mol%), TBHP (100 mol%), DHB (3.75 equiv), Et₃SiH (10 equiv), radical trap (2.5 equiv), n-PrOH (0.3 M), argon, 24 °C.
²Isolated yield after purification by flash-column chromatography. ³Determined by ¹H NMR analysis against an internal standard. ⁴The silyl ether (X = OTES) was isolated in 47% yield.
General Experimental Procedures. All reactions were performed in single-neck, flame-dried, round-bottomed flasks fitted with rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula, or were handled in a nitrogen-filled drybox (working oxygen level <5 ppm). Organic solutions were concentrated by rotary evaporation at 30–33 °C. Intermediates were purified using a Biotage Isolera system, employing polypropylene cartridges preloaded with silica gel (60 Å, 40–63 µm particle size, purchased from Silicycle, Quebec City, Canada). Alternatively, intermediates were purified using a Teledyne ISCO system, employing RediSep RF High Performance Gold cartridges (RediSep RF Gold Silica, 20–40 um spherical, purchased from Teledyne ISCO, Dallas, Texas). Samples were eluted using a flow rate of 12–50 mL/min, with detection by UV (254 nm). Analytical thin-layered chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or submersion in aqueous ceric ammonium molybdate solution (CAM), or aqueous potassium permanganate solution (KMnO₄), followed by brief heating on a hot plate (120 °C, 10–15 s).

Materials. Commercial solvents and reagents were used as received with the following exceptions. Acetonitrile was purified according to the method of Pangborn et al. Pyridine was distilled from calcium hydride under an atmosphere of nitrogen immediately before use. Commercial anhydrous N,N-dimethylformamide (Sigma-Aldrich Corporation, St. Louis, MO) was degassed by three freeze–pump–thaw cycles and stored over activated 4Å MS under an atmosphere of nitrogen before use. 1,4-Dioxane was degassed by three freeze-pump-thaw cycles, and was stored under an atmosphere of nitrogen before use. Tetrahydropyran was distilled from sodium–benzophenone under an atmosphere of nitrogen immediately before use. Triethylamine was distilled from calcium hydride under an atmosphere of nitrogen immediately before use. n-Propanol was dried over calcium hydride for 12 h at 24 °C, degassed by three freeze–pump–thaw cycles, vacuum transferred, and stored under an atmosphere of argon before use. Triethylsilane was degassed by three freeze–pump–thaw cycles and stored under an atmosphere of argon before use. 1,4-Dihydribenzenzene was degassed by three freeze–pump–thaw cycles, vacuum transferred, and stored under an atmosphere of argon at −10 °C before use. Cobalt bis(acetylacetonate) was dried by heating overnight in vacuo (70 °C, 200 mTorr), and stored under an atmosphere of argon before use. Benzyl 4-oxopiperidine-1-carboxylate, (E)-2-methylbut-2-en-1-ol, cyclohexa-2,5-diene-1-carboxylic acid, methyl cyclohexa-2,5-diene-1-carboxylate, manganese tris(dipivaloylmethane), tosyl bromide, tosyl iodide, Se-phenyl 4-methylbenzenesulfonoselenoate, N-(benzoyloxy)-1-(phenylsulfonyl) methanemimidoyl cyanide, and phenylsulfonyl) methanal O-benzyl oxime were prepared according to published procedures. p-Toluenesulfonyl chloride was recrystallized from chloroform–pentane immediately before use. N-Iodosuccinimide was recrystallized from 1,4-dioxane–tetrachloromethane immediately before use. 1,2-Diidoethane was recrystallized from diethyl ether–pentane immediately before use. The concentration of n-butyllithium in hexanes was determined by titration against a standard solution of diphenylacetic acid (average of three determinations).

Instrumentation. Proton nuclear magnetic resonance spectra (¹H NMR) were recorded at 400, 500, or 600 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl₃, δ 7.26; CHDCl₃, δ 5.32; C₆D₆, δ 7.16). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad), integration, coupling constant in Hertz, and assignment. Proton-decoupled carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 100, 125, or 150 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl₃, δ 77.0; CD₂Cl₂, δ 54.0; C₆D₆, δ 128.1). Distortionless enhancement by polarization transfer spectra [DEPT (135)] were recorded at 100, 125, or 150 MHz at 24 °C, unless otherwise noted. ¹³C NMR and DEPT (135) data are combined and represented as follows: chemical shift, carbon type [obtained from DEPT (135) experiments]. Proton-decoupled
fluorine nuclear magnetic resonance spectra ($^{19}$F NMR) were recorded at 375 MHz or 470 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, $\delta$ scale) downfield from fluorotrichloromethane. Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were obtained using a Thermo Electron Corporation Nicolet 6700 FTIR spectrometer referenced to a polystyrene standard. Data are represented as follows: frequency of absorption (cm$^{-1}$), intensity of absorption (s = strong, m = medium, w = weak, br = broad). High-resolution mass spectrometry (HRMS) were obtained on a Waters UPLC/HRMS instrument equipped with a dual API/ESI high-resolution mass spectrometry detector and photodiode array detector. Unless otherwise noted, samples were eluted over a reverse-phase C18 column (1.7 $\mu$m particle size, 2.1 $\times$ 50 mm) with a linear gradient of 5% acetonitrile–water containing 0.1% formic acid→95% acetonitrile–water containing 0.1% formic acid over 1.6 min, followed by 100% acetonitrile containing 0.1% formic acid for 1 min, at a flow rate of 600 $\mu$L/min.
**Synthetic Procedures.**

![Chemical Structure](image)

Preparation of 2-methylallyl 4-methoxybenzoate (1a):

4-Methoxybenzoyl chloride (1.50 g, 8.80 mmol, 1.10 equiv) was added dropwise via syringe to a solution of 2-methyl-2-propen-1-ol (576 mg, 8.00 mmol, 1 equiv) in pyridine (32 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (50 mL). The diluted product mixture was washed with saturated aqueous sodium bicarbonate solution (50 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford 2-methylallyl 4-methoxybenzoate (1a) as a clear oil (1.60 g, 97%).

R_f = 0.55 (20% ethyl acetate–hexanes; UV, KMnO_4). ¹H NMR (600 MHz, CDCl_3) δ 8.02 (d, 2H, J = 8.4 Hz, H_3), 6.92 (d, 2H, J = 8.4 Hz, H_2), 5.05 (s, 1H, H_6), 4.96 (s, 1H, H_6), 4.71 (s, 2H, H_4), 3.87 (s, 3H, H_1), 1.82 (s, 3H, H_5).

¹³C NMR (150 MHz, CDCl_3) δ 166.0 (C), 163.4 (C), 140.2 (C), 131.6 (CH), 122.6 (C), 113.6 (CH), 112.7 (CH_2), 67.8 (CH_2), 55.4 (CH_3), 19.6 (CH_3).

¹H and ¹³C NMR data for 2-methylallyl 4-methoxybenzoate (1a) prepared in this way were in agreement with those previously described.[11]
Preparation of 1-((allyloxy)methyl)-4-methoxybenzene (1b):

A 250-mL round-bottomed flask that had been fused to a Teflon-coated valve was charged with sodium hydride (300 mg, 7.50 mmol, 1.50 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Tetrahydrofuran (24 mL) was added to the reaction vessel via syringe and the resulting mixture was cooled to 0 °C. A 250-mL round-bottomed flask was charged with 4-methoxybenzyl alcohol (691 mg, 5.00 mmol, 1 equiv). The vessel containing the starting material was evacuated and refilled using a balloon of argon. This process was repeated twice. Tetrahydrofuran (100 mL) was added to the vessel containing the starting material and the resulting solution was transferred via cannula to the sodium hydride suspension. The reaction mixture was stirred at 0 °C for 45 min. Tetrabutylammonium iodide (92.3 mg, 250 μmol, 0.0500 equiv) and allyl bromide (786 mg, 6.50 mmol, 1.30 equiv) were then added in sequence. The reaction mixture was allowed to warm over 30 min to 24 °C. The warmed reaction mixture was stirred for 12 h at 24 °C. The product mixture was filtered through a pad of silica gel and the pad was rinsed with ethyl acetate (50 mL). The filtrates were collected and combined and the combined filtrates were concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) to afford 1-((allyloxy)methyl)-4-methoxybenzene (1b) as a light yellow oil (890 mg, 99%).

$R_f = 0.39$ (20% ether–hexanes; UV, KMnO$_4$). $^1$H NMR (600 MHz, CDCl$_3$) δ 7.27 (d, 2H, $J = 7.8$ Hz, H$_3$), 6.88 (d, 2H, $J = 7.2$ Hz, H$_2$), 5.94 (ddt, $J = 16.8$, 10.2, 5.4 Hz, 1H, H$_6$), 5.29 (d, $J = 16.8$ Hz, 1H, H$_7$), 5.19 (d, $J = 10.2$ Hz, 1H, H$_2$), 4.45 (s, 2H, H$_4$), 4.00 (d, $J = 5.4$ Hz, 2H, H$_5$), 3.80 (s, 3H, H$_1$). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 159.2 (C), 134.8 (CH), 130.3 (C), 129.3 (CH), 117.0 (CH$_2$), 113.7 (CH), 71.8 (CH$_2$), 70.8 (CH$_2$), 55.2 (CH$_3$).

$^1$H and $^{13}$C NMR data for 1-((allyloxy)methyl)-4-methoxybenzene (1b) prepared in this way were in agreement with those previously described.$^{[12]}$
Preparation of allyl 4-methoxybenzoate (1c):

4-Methoxybenzoyl chloride (1.50 g, 8.80 mmol, 1.10 equiv) was added dropwise via syringe to a solution of allyl alcohol (464 mg, 8.00 mmol, 1 equiv) in pyridine (32 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (50 mL). The diluted product mixture was washed with saturated aqueous sodium bicarbonate solution (50 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford allyl 4-methoxybenzoate (1c) as a clear oil (1.54 g, 99%).

R_f = 0.55 (20% ethyl acetate–hexanes; UV, KMnO_4). \(^1^H\) NMR (600 MHz, CDCl_3) \(\delta\) 8.02 (d, 2H, \(J = 8.4\) Hz, \(H_3\)), 6.92 (d, 2H, \(J = 8.4\) Hz, \(H_2\)), 6.03 (ddt, \(J = 16.8, 10.2, 4.2\) Hz, 1H, \(H_5\)), 5.40 (d, \(J = 16.8\) Hz, 1H, \(H_6\)), 5.27 (d, \(J = 10.2\) Hz, 1H, \(H_6\)), 4.80 (d, \(J = 4.2\) Hz, 2H, \(H_4\)), 3.86 (s, 3H, \(H_1\)). \(^{13}\)C NMR (150 MHz, CDCl_3) \(\delta\) 166.0 (C), 163.4 (C), 132.5 (CH), 131.6 (CH), 122.5 (CH), 117.9 (CH_2), 113.6 (CH), 65.2 (CH_2), 55.4 (CH_3).

\(^1\)H and \(^{13}\)C NMR data for 2-methylallyl allyl 4-methoxybenzoate (1c) prepared in this way were in agreement with those previously described.\(^{[13]}\)
Preparation of 2-chloroallyl 4-methoxybenzoate (1d):

4-Methoxybenzoyl chloride (1.02 g, 5.96 mmol, 1.10 equiv) was added dropwise via syringe to a solution of 2-chloro-2-propen-1-ol (500 mg, 5.41 mmol, 1 equiv) in pyridine (22 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (20 mL). The diluted product mixture was washed with saturated aqueous sodium bicarbonate solution (20 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford 2-chloroallyl 4-methoxybenzoate (1d) as a clear oil (1.20 g, 98%).

Rf = 0.52 (10% ethyl acetate–hexanes; UV, KMnO4). ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, 2H, J = 9.0 Hz, H₂), 6.94 (d, 2H, J = 9.0 Hz, H₂), 5.55–5.53 (m, 1H, H₆), 5.45–5.42 (m, 1H, H₆), 4.87 (br s, 2H, H₄), 3.87 (s, 3H, H₁). ¹³C NMR (150 MHz, CDCl₃) δ 165.0 (C), 163.4 (C), 135.9 (C), 131.6 (CH), 121.5 (C), 114.4 (CH₂), 113.5 (CH), 65.8 (CH₂), 55.2 (CH₃).

¹H and ¹³C NMR data for 2-chloroallyl 4-methoxybenzoate (1d) prepared in this way were in agreement with those previously described.[14]
Preparation of 3-bromobut-3-en-1-yl (4-methoxyphenyl)carbamate (1e):

1-Methylimidazole (71.4 μL, 900 μmol, 0.300 equiv) and 4-methoxyphenyl isocyanate (386 μL, 3.00 mmol, 1.00 equiv) were added in sequence to a solution of 3-bromo-3-buten-1-ol (298 μL, 3.00 mmol, 1 equiv) in acetonitrile (7.5 mL) at 24 °C. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated and the residue obtained was purified by automated flash-column chromatography (eluting with 10% ethyl acetate–hexanes initially, grading to 33% ethyl acetate–hexanes, linear gradient) to afford 3-bromobut-3-en-1-yl (4-methoxyphenyl)carbamate (1e) as a white solid (809 mg, 90%).

R<sub>f</sub> = 0.34 (20% ethyl acetate–hexanes; UV, KMnO<sub>4</sub>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.34–7.26 (m, 2H, H<sub>3</sub>), 6.85 (d, 2H, J = 9.0 Hz, H<sub>2</sub>), 6.57 (br s, 1H, NH), 5.69 (br s, 1H, H<sub>7</sub>), 5.52 (s, 1H, H<sub>7</sub>), 4.34 (t, 2H, J = 6.3 Hz, H<sub>4</sub>), 3.78 (s, 3H, H<sub>1</sub>), 2.79 (t, 2H, J = 6.3 Hz, H<sub>5</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 155.9 (C), 153.5 (C), 130.7 (C), 129.5 (C), 120.5 (CH), 119.1 (CH<sub>2</sub>), 114.2 (CH), 62.3 (CH<sub>2</sub>), 55.5 (CH<sub>3</sub>), 40.8 (CH<sub>2</sub>).

<sup>1</sup>H and <sup>13</sup>C NMR data for 3-bromobut-3-en-1-yl (4-methoxyphenyl)carbamate (1e) prepared in this way were in agreement with those previously described. [14]
Preparation of benzyl 4-methyleneepiperidine-1-carboxylate (1f):

A 250-mL round-bottomed flask that had been fused to a Teflon-coated valve was charged with methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol, 1.20 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Tetrahydrofuran (60 mL) was added to the reaction vessel via syringe and the resulting mixture was cooled to 0 °C. A solution of n-butyllithium in hexanes (2.42 M, 4.96 mL, 12.0 mmol, 1.20 equiv) was added dropwise via syringe to the cold mixture. The reaction mixture was stirred for 1 h at 0 °C. A 25-mL round-bottomed flask was charged with benzyl 4-oxopiperidine-1-carboxylate (2.33 g, 10.0 mmol, 1 equiv). The vessel containing the starting material was evacuated and refilled using a balloon of argon. This process was repeated twice. Tetrahydrofuran (10 mL) was added to the vessel containing the starting material and the resulting solution was transferred via cannula to the ylide solution. The reaction mixture was stirred at 0 °C for 1 h and then was allowed to warm over 30 min to 24 °C. The warmed product mixture was filtered through a pad of silica gel and the pad was rinsed with ethyl acetate (50 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford benzyl 4-methyleneepiperidine-1-carboxylate (1f) as a clear oil (1.78 g, 77%).

R<sub>f</sub> = 0.27 (20% ethyl acetate–hexanes; UV, KMnO<sub>4</sub>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.36–7.30 (m, 5H, ArH), 5.14 (s, 2H, H<sub>5</sub>), 4.75 (s, 2H, H<sub>1</sub>), 3.50 (br s, 4H, H<sub>2</sub>), 2.19 (br s, 4H, H<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 155.1 (C), 144.8 (C), 136.8 (C), 128.4 (CH), 127.9 (CH), 127.8 (CH), 109.4 (CH<sub>2</sub>), 67.1 (CH<sub>2</sub>), 45.5 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>).

<sup>1</sup>H and <sup>13</sup>C NMR data for benzyl 4-methyleneepiperidine-1-carboxylate (1f) prepared in this way were in agreement with those previously described.<sup>[15]</sup>
Preparation of 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g):

1-Methylimidazole (71.4 μL, 900 μmol, 0.300 equiv) and 4-methoxyphenyl isocyanate (386 μL, 3.00 mmol, 1.00 equiv) were added in sequence to a solution of 3-methylbut-2-en-1-ol (284 mg, 3.00 mmol, 1 equiv) in acetonitrile (7.5 mL) at 24 °C. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated and the residue obtained was purified by automated flash-column chromatography (eluting with 10% ethyl acetate–hexanes initially, grading to 33% ethyl acetate–hexanes, linear gradient) to afford 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g) as a white solid (705 mg, 99%).

R_f = 0.25 (20% ethyl acetate–hexanes; UV, CAM). ¹H NMR (600 MHz, CDCl₃) δ 7.28–7.26 (m, 2H, H₃), 6.84 (d, 2H, J = 9.0 Hz, H₂), 6.49 (br s, NH), 5.41–5.37 (m, 1H, H₅), 4.65 (d, 2H, J = 7.0 Hz, H₄), 3.78 (s, 3H, H₁), 1.77 (s, 3H, H₇), 1.74 (s, 3H, H₈). ¹³C NMR (150 MHz, CDCl₃) δ 155.6 (C), 153.7 (C), 138.9 (C), 130.8 (C), 120.4 (CH), 118.6 (CH), 114.0 (CH), 61.7 (CH₂), 55.2 (CH₃), 25.5 (CH₃), 17.8 (CH₃). IR (ATR-FTIR), cm⁻¹: 3315 (w), 1696 (s), 1511 (s), 1209 (s), 826 (s). HRMS-ESI (m/z): [M + H]⁺ calcd for C₁₃H₁₈NO₃, 236.1287; found, 236.1278.
Preparation of (E)-2-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1h):

1-Methylimidazole (71.4 μL, 900 μmol, 0.300 equiv) and 4-methoxyphenyl isocyanate (386 μL, 3.00 mmol, 1.00 equiv) were added in sequence to a solution of (E)-2-methylbut-2-en-1-ol (284 mg, 3.00 mmol, 1 equiv) in acetonitrile (7.5 mL) at 24 °C. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated and the residue obtained was purified by automated flash-column chromatography (eluting with 10% ethyl acetate–hexanes initially, grading to 33% ethyl acetate–hexanes, linear gradient) to afford (E)-2-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1h) as a white solid (654 mg, 93%).

R_f = 0.25 (20% ethyl acetate–hexanes; UV, CAM). 1H NMR (400 MHz, CD₂Cl₂) δ 7.31 (d, 2H, J = 8.0 Hz, H₃), 6.87-6.85 (m, 3H, 2 × H₂, 1 × NH), 5.60 (t, 1H, J = 6.6 Hz, H₆), 4.54 (s, 2H, H₄), 3.78 (s, 3H, H₁), 1.70 (s, 3H, H₇), 1.66 (d, 3H, J = 6.8 Hz, H₈). 13C NMR (150 MHz, CD₂Cl₂) δ 156.4 (C), 154.5 (C), 131.9 (C), 131.8 (C), 124.2 (CH), 121.1 (CH), 114.6 (CH), 71.2 (CH₂), 55.9 (CH₃), 13.9 (CH₃), 13.5 (CH₃). IR (ATR-FTIR), cm⁻¹: 3320 (s), 1689 (s), 1525 (s), 1232 (m), 1028 (m). HRMS-ESI (m/z): [M + H]⁺ calcd for C₁₃H₁₈NO₅, 236.1287; found, 236.1284.
Preparation of 2-fluoroallyl (4-methoxyphenyl)carbamate (1i):

1-Methylimidazole (238 μL, 3.00 mmol, 0.300 equiv) and 4-methoxyphenyl isocyanate (1.29 mL, 10.0 mmol, 1.00 equiv) were added in sequence to a solution of 2-fluoroprop-2-en-1-ol (761 mg, 10.0 mmol, 1 equiv) in acetonitrile (25 mL) at 24 °C. The reaction mixture was stirred for 36 h at 24 °C. The product mixture was concentrated and the residue obtained was purified by automated flash-column chromatography (eluting with 8% ethyl acetate–hexanes initially, grading to 33% ethyl acetate–hexanes, linear gradient) to afford 2-fluoroallyl (4-methoxyphenyl)carbamate (1i) as a white solid (1.30 g, 58%).

R_f = 0.65 (33% ethyl acetate–hexanes; UV, KMnO_4). \(^1^H\) NMR (600 MHz, CDCl_3) δ 7.29 (d, 2H, J = 7.2 Hz, H_3), 6.94 (br s, 1H, NH), 6.84 (d, 2H, J = 8.1 Hz, H_2), 4.81 (dd, 1H, J = 15.9, 3.3 Hz, H_6), 4.71–4.60 (m, 3H, 2 × H_4, 1 × H_6), 3.77 (s, 3H, H_1). \(^1^9^F\) NMR (375 MHz, CDCl_3) δ –105.36.

\(^1^H\) and \(^1^9^F\) NMR data for 2-fluoroallyl (4-methoxyphenyl)carbamate (1i) prepared in this way were in agreement with those previously described.\(^{[14]}\)
Preparation of (allyloxy)(tert-butyl)diphenylsilane (4a):

Imidazole (1.02 g, 15.0 mmol, 1.50 equiv) and tert-butyl(chloro)diphenylsilane (3.02 g, 11.0 mmol, 1.10 equiv) were added in sequence to a solution of allyl alcohol (580 mg, 10.0 mmol, 1 equiv) in N,N-dimethylformamide (8.0 mL) at 24 °C. The reaction mixture was stirred for 4 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (50 mL). The diluted product mixture was washed with saturated aqueous ammonium chloride solution (50 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The residue obtained was purified by automated flash-column chromatography (eluting with 1% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) to afford (allyloxy)(tert-butyl)diphenylsilane (4a) as a clear oil (2.96 g, 99%).

R<sub>f</sub> = 0.75 (5% ether–hexanes; UV, KMnO<sub>4</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72–7.69 (m, 4H, H<sub>3</sub>), 7.46–7.37 (m, 6H, 4 × H<sub>2</sub>, 2 × H<sub>2</sub>), 5.99–5.90 (m, 1H, H<sub>6</sub>), 5.42–5.37 (m, 1H, H<sub>7</sub>), 5.15–5.12 (m, 1H, H<sub>7</sub>), 4.24–4.22 (m, 2H, H<sub>5</sub>), 1.09 (s, 9H, H<sub>1</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.0 (C), 135.5 (CH), 133.7 (CH), 129.6 (CH), 127.6 (CH), 113.9 (CH<sub>2</sub>), 64.6 (CH<sub>2</sub>), 26.8 (CH<sub>3</sub>), 19.3 (C).

<sup>1</sup>H and <sup>13</sup>C NMR data for (allyloxy)(tert-butyl)diphenylsilane (4a) prepared in this way were in agreement with those previously described.<sup>[16]</sup>
Preparation of (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b):

Imidazole (510 mg, 7.50 mmol, 1.50 equiv) and tert-butyl(chloro)diphenylsilane (1.51 g, 5.50 mmol, 1.10 equiv) were added in sequence to a solution of (E)-pent-2-en-1-ol (430 mg, 5.00 mmol, 1 equiv) in N,N-dimethylformamide (4.0 mL) at 24 °C. The reaction mixture was stirred for 4 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (25 mL). The diluted product mixture was washed with saturated aqueous ammonium chloride solution (25 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 1% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) to afford (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b) as a clear oil (1.62 g, 99%).

R_f = 0.75 (5% ether–hexanes; UV, KMnO_4). ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.72 (m, 4H, H₃), 7.45–7.40 (m, 6H, 4 × H₂, 2 × H₄), 5.75–5.70 (m, 1H, H₇), 5.61–5.59 (m, 1H, H₆), 4.22–4.19 (m, 2H, H₅), 2.11–2.05 (m, 2H, H₈), 1.12–1.09 (m, 9H, H₁), 1.06–0.99 (m, 3H, H₀). ¹³C NMR (100 MHz, CDCl₃) δ 135.6 (CH), 133.9 (C), 132.9 (CH), 129.5 (CH), 127.7 (CH), 127.6 (CH), 64.7 (CH₂), 26.9 (CH₃), 25.2 (CH₂), 19.2 (C), 13.5 (CH₃). IR (ATR-FTIR), cm⁻¹: 2960 (m), 1428 (m), 1105 (s), 699 (s), 502 (m). HRMS-ESI (m/z): [M + H]^+ calcd for C₂₁H₂₉OSi, 325.1988; found, 325.1983.
Preparation of (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c):

Imidazole (510 mg, 7.50 mmol, 1.50 equiv) and tert-butyl(chloro)diphenylsilane (1.51 g, 5.50 mmol, 1.10 equiv) were added in sequence to a solution of (Z)-pent-2-en-1-ol (430 mg, 5.00 mmol, 1 equiv) in N,N-dimethylformamide (4.0 mL) at 24 °C. The reaction mixture was stirred for 4 h at 24 °C. The diluted product mixture was washed with saturated aqueous ammonium chloride solution (25 mL). The aqueous layer was isolated and the isolated aqueous layers were extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 1% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) to afford (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c) as a clear oil (1.57 g, 97%).

R<sub>f</sub> = 0.75 (5% ether–hexanes; UV, KMnO<sub>4</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74–7.72 (m, 4H, H<sub>3</sub>), 7.44–7.41 (m, 6H, 4 × H<sub>2</sub>, 2 × H<sub>4</sub>), 5.64–5.58 (m, 1H, H<sub>7</sub>), 5.47–5.42 (m, 1H, H<sub>6</sub>), 4.30–4.29 (m, 2H, H<sub>5</sub>), 1.94–1.89 (m, 2H, H<sub>8</sub>), 1.10–1.08 (m, 9H, H<sub>1</sub>), 0.94–0.89 (m, 3H, H<sub>9</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.6 (CH), 133.9 (C), 132.7 (CH), 129.5 (CH), 128.4 (CH), 127.6 (CH), 60.2 (CH<sub>2</sub>), 26.8 (CH<sub>3</sub>), 20.8 (CH<sub>2</sub>), 19.1 (C), 14.2 (CH<sub>3</sub>). IR (ATR-FTIR), cm<sup>-1</sup>: 2961 (m), 1428 (s), 1070 (m), 698 (s), 502 (m). HRMS-ESI (m/z): [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>29</sub>OSi, 325.1988; found, 325.1986.
Preparation of (but-2-yn-1-yloxy)(tert-butyl)diphenylsilane (4d):

Imidazole (510 mg, 7.50 mmol, 1.50 equiv) and tert-butyl(chloro)diphenylsilane (1.51 g, 5.50 mmol, 1.10 equiv) were added in sequence to a solution of 2-butyn-1-ol (350 mg, 5.00 mmol, 1 equiv) in N,N-dimethylformamide (4.0 mL) at 24 °C. The reaction mixture was stirred for 4 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (25 mL). The diluted product mixture was washed with saturated aqueous ammonium chloride solution (25 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 1% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) to afford (but-2-yn-1-yloxy)(tert-butyl)diphenylsilane (4d) as a clear oil (1.52 g, 99%).

Rf = 0.75 (5% ether–hexanes; UV, KMnO4). 1H NMR (400 MHz, CDCl3) δ 7.73–7.72 (m, 4H, H3), 7.44–7.39 (m, 6H, 4 × H2, 2 × H4), 4.30 (s, 2H, H5), 1.81 (s, 3H, H8), 1.07 (s, 9H, H1). 13C NMR (100 MHz, CDCl3) δ 135.6 (CH), 133.3 (C), 129.7 (CH), 127.6 (CH), 81.2 (C), 77.5 (C), 52.9 (CH2), 26.7 (CH3), 19.2 (C), 3.6 (CH3). IR (ATR-FTIR), cm⁻¹: 2930 (m), 1428 (s), 1062 (s), 698 (s), 500 (m). HRMS-ESI (m/z): [M + Na]+ calcd for C20H24NaOSi, 331.1494; found, 331.1498.
Preparation of tert-butyldiphenyl(prop-2-yn-1-yloxy)silane (4e):

Imidazole (510 mg, 7.5 mmol, 1.50 equiv) and tert-butyldiphenylchlorosilane (1.51 g, 5.50 mmol, 1.10 equiv) were added in sequence to a solution of propargyl alcohol (280 mg, 5.00 mmol, 1 equiv) in N,N-dimethylformamide (4.0 mL) at 24 °C. The reaction mixture was stirred for 4 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (25 mL). The diluted product mixture was washed with saturated aqueous ammonium chloride solution (25 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 1% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) to afford tert-butyldiphenyl(prop-2-yn-1-yloxy)silane (4e) as a colorless solid (1.29 g, 88%).

R<sub>f</sub> = 0.75 (5% ether–hexanes; UV, KMnO<sub>4</sub>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.74–7.72 (m, 4H, H<sub>3</sub>), 7.47–7.40 (m, 6H, 4 × H<sub>2</sub>, 2 × H<sub>4</sub>), 4.33 (d, J = 2.4 Hz, 2H, H<sub>5</sub>), 2.40 (t, J = 2.4 Hz, 1H, H<sub>7</sub>), 1.09 (s, 9H, H<sub>1</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 135.6 (CH), 132.9 (C), 129.8 (CH), 127.7 (CH), 82.0 (C), 73.0 (CH), 52.5 (CH<sub>2</sub>), 26.7 (CH<sub>3</sub>), 19.1 (C)

<sup>1</sup>H and <sup>13</sup>C NMR data for tert-butyldiphenyl(prop-2-yn-1-yloxy)silane (4e) prepared in this way were in agreement with those previously described.\textsuperscript{[17]}
Preparation of 1-fluoro-4-(hex-1-yn-1-yl)benzene (4f):

A 25-mL round-bottomed flask that had been fused to a Teflon-coated valve was charged sequentially with 1-fluoro-4-iodobenzene (1.11 g, 5.00 mmol, 1 equiv), bis(triphenylphosphine)palladium dichloride (175 mg, 250 μmol, 0.0500 equiv), and copper iodide (95.2 mg, 500 μmol, 0.100 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Triethylamine (10.0 mL) and 1-hexyne (860 μL, 7.50 mmol, 1.50 equiv) were added sequentially to the reaction vessel. The reaction vessel was sealed and the sealed vessel was placed in an oil bath that had been preheated to 50 °C. The reaction mixture was stirred and heated for 4 h at 50 °C. The product mixture was allowed to cool over 20 min to 24 °C. The cooled product mixture was filtered through a pad of silica gel and the pad was rinsed with ethyl acetate (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with hexanes, isocratic gradient) to afford 1-fluoro-4-(hex-1-yn-1-yl)benzene (4f) as a light yellow oil (723 mg, 82%).

R_f = 0.40 (hexanes; UV, KMnO_4). _^1_H NMR (500 MHz, CDCl_3) δ 7.34 (dd, J = 8.4, 5.5 Hz, 2H, H_1), 6.98–6.47 (m, 2H, H_2), 2.39 (t, J = 7.3 Hz, 2H, H_3), 1.61–1.55 (m, 2H, H_7), 1.51–1.44 (m, 2H, H_6), 0.95 (t, J = 7.5 Hz, 3H, H_8). _^19_F NMR (470 MHz, CDCl_3) δ -112.5.

_^1_H and _^19_F NMR data for 1-fluoro-4-(hex-1-yn-1-yl)benzene (4f) prepared in this way were in agreement with those previously described.[18]
Preparation of (E)-pent-2-en-1-yl 4-methoxybenzoate (S1):

4-Methoxybenzoyl chloride (563 mg, 3.30 mmol, 1.10 equiv) was added dropwise via syringe to a solution of (E)-pent-2-en-1-ol (258 mg, 3.00 mmol, 1 equiv) in pyridine (12 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (20 mL). The diluted product mixture was washed with saturated aqueous sodium bicarbonate solution (20 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford (E)-pent-2-en-1-yl 4-methoxybenzoate (S1) as a clear oil (621 mg, 94%).

Rf = 0.55 (20% ethyl acetate–hexanes; UV, KMnO⁴). ¹H NMR (500 MHz, CD₂Cl₂) δ 7.99 (d, 2H, J = 8.5 Hz, H₃), 6.92 (d, 2H, J = 9.0 Hz, H₂), 5.93–5.88 (m, 1H, H₅), 5.71–5.66 (m, 1H, H₆), 4.72 (d, J = 6.5 Hz, 2H, H₄), 3.85 (s, 3H, H₁), 2.14–2.08 (m, 2H, H₇), 1.03 (t, J = 7.5 Hz, 3H, H₈). ¹³C NMR (125 MHz, CD₂Cl₂) δ 166.4 (C), 164.0 (C), 138.1 (CH), 132.0 (C), 123.8 (C), 123.5 (CH), 114.1 (CH), 65.9 (CH₂), 56.0 (CH₃), 25.9 (CH₂), 13.6 (CH₃). IR (ATR-FTIR), cm⁻¹: 2966 (m), 1708 (s), 1605 (s), 1511 (s), 1249 (s), 1096 (s). HRMS-ESI (m/z): [M + Na]+ calcd for C₁₃H₁₆NaO₃, 243.0997; found, 243.0996.
Preparation of (Z)-pent-2-en-1-yl 4-methoxybenzoate (S2):

4-Methoxybenzoyl chloride (563 mg, 3.30 mmol, 1.10 equiv) was added dropwise via syringe to a solution of (Z)-pent-2-en-1-ol (258 mg, 3.00 mmol, 1 equiv) in pyridine (12 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (20 mL). The diluted product mixture was washed with saturated aqueous sodium bicarbonate solution (20 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford (Z)-pent-2-en-1-yl 4-methoxybenzoate (S2) as a clear oil (661 mg, 99%).

R_f = 0.55 (20% ethyl acetate–hexanes; UV, KMnO_4). \(^1^H\) NMR (500 MHz, CD_2Cl_2) \(\delta\) 7.99 (d, 2H, J = 9.0 Hz, H_3), 6.94 (d, 2H, J = 9.0 Hz, H_2), 5.73–5.68 (m, 1H, H_6), 5.66–5.61 (m, 1H, H_5), 4.82 (d, J = 7.0 Hz, 2H, H_4), 3.86 (s, 3H, H_1), 2.23–2.17 (m, 2H, H_7), 1.03 (t, J = 7.5 Hz, 3H, H_8). \(^1^C\) NMR (125 MHz, CD_2Cl_2) \(\delta\) 166.6 (C), 164.0 (C), 137.4 (CH), 132.0 (CH), 123.6 (C), 123.4 (CH), 114.1 (CH), 61.0 (CH_2), 56.0 (CH_3), 21.5 (CH_2), 14.5 (CH_3). IR (ATR-FTIR), cm\(^{-1}\): 2965 (m), 1708 (m), 1605 (s), 1249 (s), 1096 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C_{13}H_{16}NaO_3, 243.0997; found, 243.1002. 

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Preparation of 3-methylbut-2-en-1-yl 4-methoxybenzoate (S3):

4-Methoxybenzoyl chloride (563 mg, 3.30 mmol, 1.10 equiv) was added dropwise via syringe to a solution of 3-methylbut-2-en-1-ol (258 mg, 3.00 mmol, 1 equiv) in pyridine (12 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (20 mL). The diluted product mixture was washed with saturated aqueous sodium bicarbonate solution (20 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford 3-methylbut-2-en-1-yl 4-methoxybenzoate (S3) as a clear oil (661 mg, 99%).

R<sub>f</sub> = 0.55 (20% ethyl acetate–hexanes; UV, KMnO<sub>4</sub>). ¹H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.98 (d, 2H, J = 8.5 Hz, H<sub>3</sub>), 6.94 (d, 2H, J = 9.0 Hz, H<sub>2</sub>), 5.47 (t, J = 7.0 Hz, 1H, H<sub>5</sub>), 4.78 (d, J = 7.5 Hz, 2H, H<sub>4</sub>), 3.86 (s, 3H, H<sub>1</sub>), 1.80 (s, 3H, H<sub>7</sub>), 1.78 (s, 3H, H<sub>8</sub>). ¹³C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 166.6 (C), 163.9 (C), 139.4 (C), 131.9 (CH), 123.6 (C), 119.5 (CH), 114.1 (CH), 62.0 (CH<sub>2</sub>), 56.0 (CH<sub>3</sub>), 26.0 (CH<sub>3</sub>), 18.4 (CH<sub>3</sub>). IR (ATR-FTIR), cm<sup>-1</sup>: 2935 (w), 1707 (s), 1606 (s), 1251 (s), 1096 (s). HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>12</sub>NaO<sub>3</sub>, 243.0997; found, 243.1003.
Preparation of but-2-yn-1-yl 4-methoxybenzoate (S4):

4-Methoxybenzoyl chloride (563 mg, 3.30 mmol, 1.10 equiv) was added dropwise via syringe to a solution of but-2-yn-1-ol (210 mg, 3.00 mmol, 1 equiv) in pyridine (12 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (20 mL). The diluted product mixture was washed with saturated aqueous sodium bicarbonate solution (20 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford but-2-yn-1-yl 4-methoxybenzoate (S4) as a clear oil (612 mg, 99%).

R_f = 0.55 (20% ethyl acetate–hexanes; UV, KMnO_4). ^1H NMR (500 MHz, CD_2Cl_2) δ 7.99 (d, 2H, J = 9.0 Hz, H_3), 6.94 (d, 2H, J = 9.0 Hz, H_2), 4.83 (s, 2H, H_4), 3.86 (s, 3H, H_1), 1.87 (s, 3H, H_7). ^13C NMR (125 MHz, CD_2Cl_2) δ 166.0 (C), 164.2 (C), 132.2 (CH), 122.7 (C), 114.2 (CH), 83.4 (C), 74.0 (C), 56.0 (CH_3), 53.4 (CH_2), 3.9 (CH_3). IR (ATR-FTIR), cm⁻¹: 2938 (w), 1710 (m), 1605 (s), 1248 (s), 1091 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C_{12}H_{12}NaO_3, 227.0684; found, 227.0685.
**Preparation of 2-bromoallyl 4-methoxybenzoate (1k):**

4-Methoxybenzoyl chloride (938 mg, 5.50 mmol, 1.10 equiv) was added dropwise via syringe to a solution of 2-bromoallyl alcohol (685 mg, 5.00 mmol, 1 equiv) in pyridine (20 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (20 mL). The diluted product mixture was washed with saturated aqueous sodium bicarbonate solution (20 mL). The aqueous layer was isolated and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by automated flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford 2-bromoallyl 4-methoxybenzoate (1k) as a clear oil (1.26g, 93%).

R_f = 0.51 (20% ethyl acetate–hexanes; UV, KMnO_4). ¹H NMR (400 MHz, CD_2Cl_2) δ 8.03 (d, 2H, J = 8.8 Hz, H_3), 6.96 (d, 2H, J = 8.8 Hz, H_2), 6.00 (br s, 1H, H_6), 5.70 (br s, 1H, H_5), 4.92 (s, 2H, H_4), 3.86 (s, 3H, H_1). ¹³C NMR (100 MHz, CD_2Cl_2) δ 165.6 (C), 164.3 (C), 132.2 (C), 127.2 (C), 122.4 (C), 119.3 (CH₂), 114.3 (CH), 68.1 (CH₂), 56.0 (CH₃). IR (ATR-FTIR), cm⁻¹: 1714 (s), 1604 (s), 1510 (m), 1249 (s), 1165 (s). HRMS-ESI (m/z): [M + H]^+ calcd for C_{11}H_{12}BrO₃, 270.9970/272.9949; found, 270.9975/272.9943.
Preparation of (E)-2-methylallyl pent-2-en-1-yl terephthalate (9):

**N,N’-Diisopropylallylcarbodiimide (1.55 mL, 10.0 mmol, 2.00 equiv) and 4-dimethylaminopyrididine (122 mg, 1.00 mmol, 0.200 equiv) were added sequentially to a suspension of 2-methylallyl alcohol (371 mg, 5.00 mmol, 1 equiv) and 4-formylnbenzoic acid (750 mg, 5.00 mmol, 1 equiv) in dichloromethane (25 mL) at 24 °C. The reaction mixture was stirred for 2 h at 24 °C. The product mixture was concentrated and the residue obtained was diluted with a mixture of ethyl acetate and hexanes (1:4, v/v, 100 mL). The diluted product mixture was filtered through a pad of celite and the pad was rinsed with a mixture of ethyl acetate and hexanes (1:4, v/v, 100 mL). The filtrates were collected and combined. The combined filtrate was concentrated. The 2-methylallyl 4-formylnbenzoate prepared in this way was immediately used in the following step without further purification.

2-Methyl-2-butene (6.36 mL, 60.0 mmol, 12.0 equiv) and a solution of sodium chlorite (3.00 g, 33.3 mmol, 6.65 equiv) and sodium phosphate monobasic (3.68 g, 26.7 mg, 5.34 equiv) in water (22.7 mL) were added sequentially to a suspension of 2-methylallyl 4-formylnbenzoate (nominally, 5.00 mmol) in t-butanol (71.4 mL) at 24 °C. The reaction mixture was stirred for 30 min at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (250 mL). The diluted product mixture was washed with saturated ammonium chloride (3 x 50 mL). The organic layer was combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The 4-((2-methylallyloxy)carbonyl)benzoic acid prepared in this way was immediately used in the following step without further purification.

**N,N’-Diisopropylcarbodiimide (1.55 mL, 10.0 mmol, 2.00 equiv) and 4-dimethylaminopyrididine (122 mg, 1.00 mmol, 0.200 equiv) were added sequentially to a suspension of (E)-2-penten-1-ol (517 mg, 6.00 mmol, 1.20 equiv) and 4-(((2-methylallyloxy)carbonyl)benzoic acid (nominally, 5.00 mmol) in dichloromethane (25 mL) at 24 °C. The reaction mixture was stirred at 24 °C for 24 h at 24 °C. The product mixture was concentrated and the residue obtained was mixed with a mixture of ethyl acetate and hexanes (1:4, v/v, 200 mL). The diluted product mixture was filtered through a pad of celite and the pad was rinsed with a mixture of ethyl acetate and hexanes (1:4, v/v, 250 mL). The filtrates were collected and combined. The combined filtrate was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–hexanes, isocratic gradient) to afford (E)-2-methylallyl pent-2-en-1-yl terephthalate (9) as a light yellow oil (579 mg, 40%).

$R_f = 0.47$ (10% ethyl acetate–hexanes; UV, KMnO₄)

$^1$H NMR (500 MHz, CDCl₃) δ 8.11–8.10 (m, 4H, 2 × H₆, 2 × H₇), 5.94–5.87 (m, 1H, H₃), 5.70–5.63 (m, 1H, H₄), 5.07 (s, 1H, H₁₀), 4.98 (s, 1H, H₁₀), 4.78–4.75 (m, 4H, 2 × H₅, 2 × H₆), 2.11–2.08 (m, 2H, H₂), 1.83 (s, 3H, H₃), 1.01 (t, 3H, J = 10.0 Hz, H₃). $^{13}$C NMR (125 MHz, CDCl₃) δ 165.5 (C), 165.3 (C), 139.6 (C), 138.4 (CH), 134.2 (C), 133.8 (C), 129.5 (CH), 129.4 (CH), 122.5 (CH), 113.2 (CH), 68.4 (CH₂), 66.1 (CH₂), 25.2 (CH₂), 19.5 (CH₃), 13.0 (CH₃). IR (ATR-FTIR), cm⁻¹: 2964 (w), 1717 (s), 1262 (s), 1242 (s), 1099 (s). HRMS-ESI (m/z): [M + H]+ calc for C₁₇H₂₁O₄, 289.1440; found, 289.1439.
Condition Optimization for the Hydrogenation (Table 1, Entry 1).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). A 16-gauge needle was penetrated through the septum. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C and tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.500 equiv) was added every hour until the consumption of 1a was complete (as determined by TLC analysis, 135 min for 1a, 2.00 equiv of TBHP in total). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (25.4 mg, 212 μmol, 0.848 equiv) revealed a < 5% yield of 2-methylallyl 4-methoxybenzoate (1a), a 71% yield of isobutyl 4-methoxybenzoate (2a), an 86% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a 14% yield of 1-methoxy-4-(propoxymethyl)benzene (2b).
Condition Optimization for the Hydrogenation (Table 1, Entry 2).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was equipped with a balloon of dry air and the reaction vessel was cooled to 0 °C. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 0 °C for 300 min. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using 1,3,5-trimethoxybenzene as an internal standard (35.7 mg, 241 μmol, 0.964 equiv) revealed a 95% yield of 2-methylallyl 4-methoxybenzoate (1a), a <5% yield of isobutyl 4-methoxybenzoate (2a), a 93% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a < 1% yield of 1-methoxy-4-(propoxymethyl)benzene (2b).
Condition Optimization for the Hydrogenation (Table 1, Entry 3).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). A 16-gauge needle was penetrated through the septum. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C and tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.500 equiv) was added every hour until the consumption of 1a was complete (as determined by TLC analysis, 180 min for 1a, 2.50 equiv of TBHP in total). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using 1,3,5-trimethoxybenzene as an internal standard (46.8 mg, 278 μmol, 1.11 equiv) revealed a 28% yield of 2-methylallyl 4-methoxybenzoate (1a), a 31% yield of isobutyl 4-methoxybenzoate (2a), an 82% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a < 1% yield of 1-methoxy-4-(propoxymethyl)benzene (2b).
Condition Optimization for the Hydrogenation (Table 1, Entry 4).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was open to the atmosphere. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (32.2 mg, 268 μmol, 1.07 equiv) revealed a < 5% yield of 2-methylallyl 4-methoxybenzoate (1a), a 63% yield of isobutyl 4-methoxybenzoate (2a), an 44% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a 17% yield of 1-methoxy-4-(propoxymethyl)benzene (2b).
Condition Optimization for the Hydrogenation (Table 1, Entry 5).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.250 equiv). The reaction vessel was left open to air. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 11.4 μL, 62.5 μmol, 0.250 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C until the consumption of 1a was complete (as determined by TLC analysis, 180 min for 1a). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (21.9 mg, 183 μmol, 0.730 equiv) revealed a 94% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a <1% yield of 1-methoxy-4-(propoxymethyl)benzene (2b). The NMR sample was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 20% ether–hexanes, linear gradient) to afford 2-hydroxy-2-methylpropyl 4-methoxybenzoate (3, clear oil, 38.6 mg, 69%).

Rf = 0.29 (20% ether–hexanes; UV). 1H NMR (400 MHz, CD2Cl2) δ 9.46 (s, 1H, OH), 8.03 (d, J = 8.8 Hz, 2H, H5), 6.96 (d, J = 9.2 Hz, 2H, H2), 4.36 (s, 2H, H4), 3.87 (s, 3H, H1), 1.27 (s, 6H, H5). 13C NMR (100 MHz, CD2Cl2) δ 168.4 (C), 164.5 (C), 132.5 (CH), 122.4 (C), 114.3 (CH), 82.1 (C), 67.0 (CH2), 56.1 (CH3), 21.7 (CH3). IR (ATR-FTIR), cm⁻¹: 3342 (w), 2983 (m), 1688 (m), 1255 (m), 1167 (s). HRMS-ESI (m/z): [M + Na]⁺ calcd for C12H18NaO4, 247.0946; found, 247.0942.
Condition Optimization for the Hydrogenation (Table 1, Entry 6).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C and tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.500 equiv) was added every hour until the consumption of 1a was complete (as determined by TLC analysis, 360 min for 1a, 3.50 equiv of TBHP in total). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using 1,3,5-trimethoxybenzene as an internal standard (41.4 mg, 246 μmol, 0.948 equiv) revealed a 19% yield of 2-methylallyl 4-methoxybenzoate (1a), a 69% yield of isobutyl 4-methoxybenzoate (2a), an 67% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a 14% yield of 1-methoxy-4-(propoxymethyl)benzene (2b).
Condition Optimization for the Hydrogenation (Table 1, Entry 7).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction vessel was placed in an oil bath that had been preheated to 50 °C. The reaction mixture was stirred at 50 °C and tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.500 equiv) was added every hour until the consumption of 1a was complete (as determined by TLC analysis, 120 min for 1a, 1.50 equiv of TBHP in total). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (29.3 mg, 244 μmol, 0.977 equiv) revealed a < 5% yield of 2-methylallyl 4-methoxybenzoate (1a), a 80% yield of isobutyl 4-methoxybenzoate (2a), an 75% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a 18% yield of 1-methoxy-4-(propoxymethyl)benzene (2b).
Condition Optimization for the Hydrogenation (Table 1, Entry 8).

A 10-mL two-neck round-bottomed flask fitted with a rubber septum and a reflux condenser was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.5 mmol, 10.0 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction vessel was placed in an oil bath that had been preheated to 40 °C. A solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) was added dropwise over 60 min via syringe pump to the reaction vessel. The reaction mixture was stirred and heated at 40 °C until the consumption of 1a was complete (as determined by TLC analysis, 60 min for 1a). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (28.7 mg, 239 μmol, 0.956 equiv) revealed a < 5% yield of 2-methylallyl 4-methoxybenzoate (1a), a 91% yield of isobutyl 4-methoxybenzoate (2a), a 72% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a 20% yield of 1-methoxy-4-(propoxymethyl)benzene (2b).
Condition Optimization for the Hydrogenation (Table S1, Entry 1).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). A 16-gauge needle was penetrated through the septum. n-Propanol (830 μL), cyclohexa-2,5-diene-1-carboxylic acid (310 mg, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C and tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.500 equiv) was added every hour until the consumption of 1a was complete (as determined by TLC analysis, 280 min for 1a, 3.50 equiv of TBHP in total). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (61.9 mg, 516 μmol, 2.06 equiv) revealed a < 5% yield of 2-methylallyl 4-methoxybenzoate (1a), a 13% yield of isobutyl 4-methoxybenzoate (2a), an 68% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a 3% yield of 1-methoxy-4-(propoxymethyl)benzene (2b). The NMR sample was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 20% ether–hexanes, linear gradient) to afford 2-hydroxy-2-methylpropyl 4-methoxybenzoate (3, clear oil, 33.6 mg, 60%).
Condition Optimization for the Hydrogenation (Table S1, Entry 2).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). A 16-gauge needle was penetrated through the septum. n-Propanol (830 μL), methyl cyclohexa-2,5-diene-1-carboxylate (345 mg, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C 40 min. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (29.9 mg, 249 μmol, 1.06 equiv) revealed a 67% yield of 2-methylallyl 4-methoxybenzoate (1a), a 15% yield of isobutyl 4-methoxybenzoate (2a), an 89% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a 4% yield of 1-methoxy-4-(propoxymethyl)benzene (2b). The NMR sample was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 20% ether–hexanes, linear gradient) to afford 2-hydroxy-2-methylpropyl 4-methoxybenzoate (3, clear oil, 10.0 mg, 18%).
**Condition Optimization for the Hydrogenation (Table S1, Entry 3).**

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), 1-((allyloxy)methyl)-4-methoxybenzene (1b, 44.5 mg, 250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). A 16-gauge needle was penetrated through the septum. *n*-Propanol (830 μL), 1-methoxycyclohexa-1,4-diene (275 mg, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C and tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.500 equiv) was added every hour until the consumption of 1a was complete (as determined by TLC analysis, 380 min for 1a, 4.00 equiv of TBHP in total). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (29.1 mg, 243 μmol, 0.970 equiv) revealed a < 5% yield of 2-methylallyl 4-methoxybenzoate (1a), a < 1% yield of isobutyl 4-methoxybenzoate (2a), a 92% yield of 1-((allyloxy)methyl)-4-methoxybenzene (1b), and a < 5% yield of 1-methoxy-4-(propoxymethyl)benzene (2b).
Representative Procedure for Competition Experiments (Table S2, Condition A).

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with the target substrate (250 μmol, 1 equiv), the competition substrate (250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). A 16-gauge needle was penetrated through the septum. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C and a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.50 equiv) was added every hour until the consumption of the target substrate was complete (as determined by TLC analysis). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The conversion of the competition substrate and the yield of the competition product were determined by 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard. The NMR sample was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography to afford the target hydrogenation product.
Representative Procedure for Competition Experiments (Table S2, Condition B).

A 10-mL round-bottomed flask fitted with a reflux condenser was charged sequentially with the target substrate (250 μmol, 1 equiv), the competition substrate (250 μmol, 1 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.5 mmol, 10.0 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction vessel was placed in an oil bath that had been preheated to 40 °C. A solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) was added dropwise via syringe pump to the reaction vessel. The reaction mixture was stirred and heated at 40 °C until the consumption of the target substrate was complete (as determined by TLC analysis). The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The conversion of the competition substrate and the yield of the competition product were determined by 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard. The NMR sample was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography to afford the target hydrogenation product.
2-Methylallyl 4-methoxybenzoate (1a) versus allyl 4-methoxybenzoate (1c)

Condition A
Following the general procedure A using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and allyl 4-methoxybenzoate (1c, 48.1 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP were employed. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (24.1 mg, 201 μmol, 0.803 equiv) revealed a 79% yield of isobutyl 4-methoxybenzoate, an 83% yield of allyl 4-methoxybenzoate (1c) and a 14% yield of propyl 4-methoxybenzoate (2c).

Condition B:
Following the general procedure B using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and allyl 4-methoxybenzoate (1c, 48.1 mg, 250 μmol, 1 equiv). Reaction time was 60 min and 1.00 equiv of TBHP was added in total. $^1$H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (28.7 mg, 239 μmol, 0.957 equiv) revealed a 91% yield of isobutyl 4-methoxybenzoate (2a), a 71% yield of allyl 4-methoxybenzoate (1c) and a 24% yield of propyl 4-methoxybenzoate (2c).
2-Methylallyl 4-methoxybenzoate (1a) versus (allyloxy)(tert-butyl)diphenylsilane (4a)

\[
\begin{align*}
\text{CH}_3 \text{O} & \quad \text{CH}_3 \\
\text{1a} & \quad \text{Co(acac)}_2, \text{TBHP}, \text{Et}_3\text{SiH}, \text{DHB} \\
\text{CH}_3 & \quad \text{n-ProH, 16-GA, 24 °C} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{1} & \quad \text{2} \\
\text{2a} & \quad \text{Co(acac)}_2, \text{TBHP (syringe pump)}, \text{Et}_3\text{SiH}, \text{DHB} \\
\text{CH}_3 & \quad \text{n-ProH, argon, 40 °C} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{3} & \quad \text{4} \\
\text{4a} & \quad \text{86\% (2a), 83\% (4a), 12\% (SS), 2a:SS = 7.2:1.0} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{2} & \quad \text{5} \\
\text{5} & \quad \text{2a, SS = 5.4:1.0} \\
\end{align*}
\]

**Condition A**

Following the general procedure A using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP were employed. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (24.7 mg, 206 μmol, 0.823 equiv) revealed an 83% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 12% yield of tert-butyldiphenyl(propoxy)silane (SS). The NMR sample was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) to afford isobutyl 4-methoxybenzoate (2a, clear oil, 44.6 mg, 86%).

Isobutyl 4-methoxybenzoate (2a): $R_f = 0.54$ (20% ethyl acetate–hexanes; UV). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, 2H, $J = 8.8$ Hz, H$_3$), 6.92 (d, $J = 8.8$ Hz, H$_2$), 4.07 (d, $J = 6.8$ Hz, 2H, H$_4$), 3.86 (s, 3H, H$_1$), 2.12–2.02 (m, H, H$_5$), 1.02 (d, $J = 6.8$ Hz, 6H, H$_6$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.4 (C), 163.2 (C), 131.5 (C), 123.0 (C), 113.5 (C), 70.7 (CH$_2$), 55.4 (CH$_3$), 27.9 (CH$_3$), 19.2 (CH$_3$).

$^1$H and $^{13}$C NMR data for isobutyl 4-methoxybenzoate (2a) prepared in this way were in agreement with those previously described.$^{[19]}$

**Condition B**

Following the general procedure B using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 60 min and 1.00 equiv of TBHP was added in total. $^1$H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (30.8 mg, 257 μmol, 1.03 equiv) revealed a 83% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 17% yield of tert-butyldiphenyl(propoxy)silane (SS). The NMR sample was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) to afford isobutyl 4-methoxybenzoate (2a, clear oil, 47.8 mg, 92%).

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2-Chloroallyl 4-methoxybenzoate (1d) versus (allyloxy)(tert-butyl)diphenylsilane (4a)

\[
\begin{align*}
\text{CH}_3O & & \text{Cl} & & \text{O} & & \text{CH}_2=\text{CH}_2 \quad \text{Co(\text{acac})}_2, \text{TBHP, Et}_3\text{SiH, DHB} \\
\text{CH}_3O & & \text{Cl} & & \text{O} & & \text{CH}_2=\text{CH}_2
\end{align*}
\]

**Condition A:**

Following the general procedure A using 2-chloroallyl 4-methoxybenzoate (1d, 56.7 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 40 min and 1.00 equiv of TBHP were employed. \(^1\)H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (28.5 mg, 238 μmol, 0.950 equiv) revealed an 85% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 15% yield of tert-butyl(diphenyl)(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) afforded 2-chloroallyl 4-methoxybenzoate (S6) as a clear oil (45.3 mg, 79%).

R_f = 0.52 (20% ethyl acetate–hexanes; UV). \(^1\)H NMR (500 MHz, CDCl_3) δ 8.02 (d, 2H, J = 9.0 Hz, H_3), 6.93 (d, 2H, J = 9.0 Hz, H_2), 4.42–4.38 (m, 2H, H_4), 4.34–4.27 (m, 1H, H_5), 3.87 (s, 3H, H_1), 1.60 (d, 3H, J = 6.5 Hz, H_6). \(^{13}\)C NMR (150 MHz, CDCl_3) δ 165.6 (C), 163.4 (C), 131.7 (CH), 121.9 (C), 113.6 (CH), 68.6 (CH_2), 55.3 (CH_3), 54.1 (CH), 21.5 (CH_3).

\(^1\)H and \(^{13}\)C NMR data for 2-chloroallyl 4-methoxybenzoate (S6) prepared in this way were in agreement with those previously described.\(^{[14]}\)

\[
\begin{align*}
\text{CH}_3O & & \text{Cl} & & \text{O} & & \text{CH}_2=\text{CH}_2 & & \text{Co(\text{acac})}_2, \text{TBHP (syringe pump), Et}_3\text{SiH, DHB} \\
\text{CH}_3O & & \text{Cl} & & \text{O} & & \text{CH}_2=\text{CH}_2
\end{align*}
\]

**Condition B:**

Following the general procedure B using 2-chloroallyl 4-methoxybenzoate (1d, 56.7 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 60 min and 1.00 equiv of TBHP was added in total. \(^1\)H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (28.7 mg, 239 μmol, 0.957 equiv) revealed a 71% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 28% yield of tert-butyl(diphenyl)(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 5% ether–hexanes, linear gradient) afforded 2-chloroallyl 4-methoxybenzoate (S6) as a clear oil (49.8 mg, 87%).
3-Bromobut-3-en-1-yl (4-methoxyphenyl)carbamate (1e) versus (allyloxy)(tert-butyl)diphenylsilane (4a)

**Condition A:**
Following the general procedure A using 3-bromobut-3-en-1-yl (4-methoxyphenyl)carbamate (1e, 75.0 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 20 min and 1.00 equiv of TBHP were employed. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (33.2 mg, 277 μmol, 1.11 equiv) revealed a 95% yield of (allyloxy)(tert-butyl)diphenylsilane (4a). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded 3-bromobutyl (4-methoxyphenyl)carbamate (S7) as a white solid (53.6 mg, 71%).

$\text{R}_f = 0.34$ (33% ether–hexanes; UV, CAM). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33–7.22 (m, 2H, H$_3$), 6.83 (d, 2H, J = 8.8 Hz, H$_2$), 6.74 (br s, 1H, NH), 4.40–4.31 (m, 1H, H$_4$), 4.30–4.15 (m, 2H, H$_6$, 1×H$_4$), 3.77 (s, 3H, H$_1$), 2.19–2.05 (m, 2H, H$_5$), 1.74 (d, 3H, J = 6.8 Hz, H$_7$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.8 (C), 153.6 (C), 130.7 (C), 120.5 (CH), 114.1 (CH), 63.1 (CH$_2$), 55.4 (CH$_3$), 47.0 (CH), 39.9 (CH$_2$), 26.4 (CH$_3$).

$^1$H and $^{13}$C NMR data for 3-bromobutyl (4-methoxyphenyl)carbamate (S7) prepared in this way were in agreement with those previously described.[14]

**Condition B:**
Following the general procedure B using 2-chloroallyl 4-methoxybenzoate (1e, 75.0 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 60 min and 1.00 equiv of TBHP was added in total. $^1$H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (29.1 mg, 243 μmol, 0.971 equiv) revealed a 62% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 30% yield of tert-butyldiphenyl(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) afforded 3-bromobutyl (4-methoxyphenyl)carbamate (S7) as a white solid (62.8 mg, 83%).
**Benzyl 4-methyleneepiperidine-1-carboxylate (1f) versus (allyloxy)(tert-butyl)diphenylsilane (4a)**

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**Condition A:**

Following the general procedure A using benzyl 4-methyleneepiperidine-1-carboxylate (1f, 57.8 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 120 min and 1.50 equiv of TBHP were employed. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (30.3 mg, 253 μmol, 1.01 equiv) revealed an 83% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 17% yield of tert-butyldiphenyl(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded benzyl 4-methyleneepiperidine-1-carboxylate (S8) as a clear oil (45.4 mg, 78%).

$R_f = 0.29$ (20% ethyl acetate–hexanes; UV, CAM). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.37–7.29 (m, 5H, ArH), 5.11 (s, 2H, H$_1$), 4.12 (br d, J = 12.4 Hz, 2H, H$_2$), 2.77 (br s, 2H, H$_2$), 1.63 (br d, J = 12.4 Hz, 2H, H$_3$), 1.57–1.52 (m, 1H, H$_4$), 1.10 (qd, J = 12.4, 4.0 Hz, 2H, H$_3$), 0.95 (d, 3H, J = 6.8 Hz, H$_5$). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $\delta$ 155.6 (C), 138.0 (C), 128.9 (CH), 128.3 (CH), 128.2 (CH), 67.2 (CH$_2$), 44.8 (CH$_2$), 34.5 (CH$_2$), 31.5 (CH), 22.2 (CH$_3$).

$^1$H and $^{13}$C NMR data for benzyl 4-methyleneepiperidine-1-carboxylate (S8) prepared in this way were in agreement with those previously described.[20]

**Condition B:**

Following the general procedure B using benzyl 4-methyleneepiperidine-1-carboxylate (1f, 57.8 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 90 min and 1.52 equiv of TBHP was added in total. $^1$H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (37.9 mg, 316 μmol, 1.26 equiv) revealed a 62% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 39% yield of tert-butyldiphenyl(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially,
grading to 10% ethyl acetate–hexanes, linear gradient) afforded benzyl 4-methylpiperidine-1-carboxylate (S8) as a white solid (51.3 mg, 88%).
2-Methallyl 4-methoxybenzoate (1a) versus (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b)

**Condition A:**
Following the general procedure A using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b, 81.1 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP was added in total. $^1$H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (27.7 mg, 231 μmol, 0.923 equiv) revealed a 88% yield of (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b) and a 9% yield of tert-butyl(pentyloxy)diphenylsilane (S9). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (35.8 mg, 69%).

**Condition B:**
Following the general procedure B using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b, 81.1 mg, 250 μmol, 1 equiv). Reaction time was 60 min and 1.00 equiv of TBHP were employed. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (27.7 mg, 231 μmol, 0.923 equiv) revealed an 89% yield of (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b) and an 11% yield of tert-butyl(pentyloxy)diphenylsilane (S9). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (50.2 mg, 96%).
2-Methallyl 4-methoxybenzoate (1a) versus (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c)

**Condition A:**

Following the general procedure A using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c, 81.1 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP were employed. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (27.7 mg, 231 μmol, 0.923 equiv) revealed an 86% yield of (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c) and an 8% yield of tert-butyl(pentyloxy)diphenylsilane (S9). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (36.5 mg, 70%).

**Condition B:**

Following the general procedure B using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c, 81.1 mg, 250 μmol, 1 equiv). Reaction time was 60 min and 1.00 equiv of TBHP was added in total. $^1$H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (27.9 mg, 233 μmol, 0.930 equiv) revealed an 88% yield of (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c) and a 11% yield of tert-butyl(pentyloxy)diphenylsilane (S9). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (47.8 mg, 92%).
2-Methallyl 4-methoxybenzoate (1a) versus (but-2-yn-1-yloxy)(tert-butyl)diphenylsilane (4d)

Condition A:
Following the general procedure A using 2-methallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and (but-2-yn-1-yloxy)(tert-butyl)diphenylsilane (4d, 77.1 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP was added in total. ^1H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (29.0 mg, 242 μmol, 0.967 equiv) revealed a 88% yield of (but-2-yn-1-yloxy)(tert-butyl)diphenylsilane (4d). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (37.4 mg, 72%).

Condition B:
Following the general procedure B using 2-methallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and (but-2-yn-1-yloxy)(tert-butyl)diphenylsilane (4d, 77.1 mg, 250 μmol, 1 equiv). Reaction time was 58 min and 0.97 equiv of TBHP were employed. ^1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (30.7 mg, 256 μmol, 1.02 equiv) revealed an 88% yield of (but-2-yn-1-yloxy)(tert-butyl)diphenylsilane (4d). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (48.4 mg, 93%).
2-Methallyl 4-methoxybenzoate (1a) versus tert-butyldiphenyl(prop-2-yn-1-yloxy)silane (4e)

Condition A:
Following the general procedure A using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and tert-butyldiphenyl(prop-2-yn-1-yloxy)silane (4e, 73.6 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP was added in total. \(^1\)H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (28.9 mg, 241 μmol, 0.963 equiv) revealed a 74% yield of tert-butyldiphenyl(prop-2-yn-1-yloxy)silane (4e). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (40.1 mg, 77%).

Condition B:
Following the general procedure B using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and tert-butyldiphenyl(prop-2-yn-1-yloxy)silane (4e, 73.6 mg, 250 μmol, 1 equiv). Reaction time was 100 min and 1.28 equiv of TBHP were employed. \(^1\)H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (30.9 mg, 258 μmol, 1.03 equiv) revealed a 70% yield of tert-butyldiphenyl(prop-2-yn-1-yloxy)silane (4e). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (46.3 mg, 89%).
**2-Methallyl 4-methoxybenzoate (1a) versus 1-fluoro-4-(hex-1-yn-1-yl)benzene (4f)**

![Chemical structure](image)

**Condition A:**
Following the general procedure A using 2-methallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and 1-fluoro-4-(hex-1-yn-1-yl)benzene (4f, 44.1 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP was added in total. \(^{19}\)F NMR analysis of the unpurified product mixture with hexafluorobenzene as an internal standard (46.6 mg, 251 μmol, 1.00 equiv) revealed a 69% yield of 1-fluoro-4-(hex-1-yn-1-yl)benzene (4f). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (33.3 mg, 64%).

![Chemical structure](image)

**Condition B:**
Following the general procedure B using 2-methallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and 1-fluoro-4-(hex-1-yn-1-yl)benzene (4f, 44.1 mg, 250 μmol, 1 equiv). Reaction time was 70 min and 1.00 equiv of TBHP were employed. \(^{19}\)F NMR analysis of the unpurified product mixture using hexafluorobenzene as an internal standard (46.3 mg, 249 μmol, 0.996 equiv) revealed a 78% yield of 1-fluoro-4-(hex-1-yn-1-yl)benzene (4f). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (46.8 mg, 90%).
3-Methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g) versus (allyloxy)(tert-butyl)diphenylsilane (4a)

**Condition A:**
Following the general procedure A using 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g, 57.8 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). A solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.50 equiv) was added every half an hour. Reaction time was 420 min and 8.00 equiv of TBHP were employed. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (29.9 mg, 249 μmol, 0.998 equiv) revealed a 54% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 46% yield of tert-butyl diphenyl(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isopentyl (4-methoxyphenyl)carbamate (S10) as a white solid (54.4 mg, 92%).

R$_f$ = 0.52 (33% ethyl acetate–hexanes; UV, CAM). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.28 (d, J = 8.4 Hz, 2H, H$_3$), 6.89 (d, J = 8.8 Hz, 2H, H$_2$), 6.60 (br s, 1H, NH), 4.16 (t, J = 7.0 Hz, 2H, H$_4$), 3.77 (s, 3H, H$_1$), 1.76–1.69 (m, 1H, H$_6$), 1.60–1.53 (m, 2H, H$_5$), 0.94 (d, 6H, $J$ = 6.4 Hz, H$_7$). $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) δ 156.4 (C), 154.5 (C), 131.8 (C), 121.0 (CH), 114.6 (CH), 64.2 (CH$_2$), 56.0 (CH$_3$), 38.2 (CH$_2$), 25.6 (CH), 22.8 (CH$_3$). IR (ATR-FTIR), cm$^{-1}$: 3317 (w), 2959 (m), 1698 (s), 1512 (s), 1213 (s). HRMS-ESI (m/z): [M + H]$^+$ calecd for C$_{13}$H$_{19}$NO$_3$, 238.1443; found, 238.1441.

**Condition B:**
Following the general procedure B using 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g, 57.8 mg, 250 μmol, 1 equiv) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 180 min and 3.00 equiv of TBHP was added in total. $^1$H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (32.4 mg, 270 μmol, 1.08 equiv) revealed a 16% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 82% yield of tert-butyl diphenyl(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isopentyl (4-methoxyphenyl)carbamate (S10) as a white solid (59.5 mg, >99%).

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(E)-2-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1h) versus (allyloxy)(tert-butyl)diphenylsilane (4a)

Condition A:
Following the general procedure A using (E)-2-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1h, 57.8 mg, 250 μmol) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). A solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.50 equiv) was added every half an hour. Reaction time was 420 min and 8.00 equiv of TBHP were employed. ¹H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (33.8 mg, 282 μmol, 1.13 equiv) revealed a 36% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 64% yield of tert-butyldiphenyl(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded 2-methylbutyl (4-methoxyphenyl)carbamate (S11) as a white solid (55.9 mg, 95%).

Rₚ = 0.52 (33% ethyl acetate–hexanes; UV, CAM). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (br d, J = 8.4 Hz, 2H, H₃), 6.85 (d, J = 8.8 Hz, 2H, H₂), 6.48 (br s, 1H, NH), 4.07–4.02 (m, 1H, 1 × H₄), 3.97–3.93 (m, 1H, 1 × H₄), 3.79 (s, 3H, H₁), 1.78–1.70 (m, 1H, H₅), 1.50–1.43 (m, 1H, 1 × H₆), 1.26–1.15 (m, 1H, 1 × H₆), 0.96–0.91 (m, 6H, 3 × H₇, 3 × H₈). ¹³C NMR (150 MHz, CDCl₃) δ 155.9 (C), 154.1 (C), 131.0 (C), 120.5 (CH), 114.2 (CH), 69.8 (CH₂), 565.5 (CH₃), 34.4 (CH), 26.0 (CH₂), 16.4 (CH₃), 11.2 (CH₃). IR (ATR-FTIR), cm⁻¹: 3315 (w), 2961 (m), 1699 (s), 1512 (s), 1216 (s). HRMS-ESI (m/z): [M + H]⁺ calcd for C₁₃H₁₉NO₃, 238.1443; found, 238.1432.
3-Methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g) versus (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b)

Condition A:
Following the general procedure A using 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g, 57.8 mg, 250 μmol, 1 equiv) and (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b, 81.1 mg, 250 μmol, 1 equiv). A solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.50 equiv) was added every half an hour. Reaction time was 360 min and 5.00 equiv of TBHP were employed. Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isopentyl (4-methoxyphenyl)carbamate (S10) as a white solid (51.1 mg, 86%). All the other fractions are combined and concentrated. 1H NMR analysis of the residue using mesitylene as an internal standard (24.5 mg, 204 μmol, 0.817 equiv) revealed a 78% yield of (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b) and an 18% yield of tert-butyl(pentyloxy)diphenylsilane (S9).

Condition B:
Following the general procedure B using 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g, 57.8 mg, 250 μmol, 1 equiv) and (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b, 81.1 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.20 equiv of TBHP was added in total. Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isopentyl (4-methoxyphenyl)carbamate (S10) as a white solid (54.5 mg, 92%). All the other fractions are combined and concentrated. 1H NMR analysis of the residue using mesitylene as an internal standard (22.1 mg, 184 μmol, 0.737 equiv) revealed a 75% yield of (E)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4b) and a 25% yield of tert-butyl(pentyloxy)diphenylsilane (S9).
3-Methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g) versus (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c)

**Condition A:**
Following the general procedure A using 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g, 57.8 mg, 250 μmol, 1 equiv) and (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c, 81.1 mg, 250 μmol, 1 equiv). A solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 0.50 equiv) was added every half an hour. Reaction time was 360 min and 6.50 equiv of TBHP were employed. 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (28.6 mg, 238 μmol, 0.953 equiv) revealed a 65% yield of (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c) and a 28% yield of tert-butyl(pentyloxy)diphenylsilane (S9). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isopentyl (4-methoxyphenyl)carbamate (S10) as a white solid (53.2 mg, 90%).

**Condition B:**
Following the general procedure B using 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1g, 57.8 mg, 250 μmol, 1 equiv) and (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c, 81.1 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.20 equiv of TBHP was added in total. 1H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (51.3 mg, 428 μmol, 1.71 equiv) revealed a 69% yield of (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (4c) and a 29% yield of tert-butyl(pentyloxy)diphenylsilane (S9). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isopentyl (4-methoxyphenyl)carbamate (S10) as a white solid (52.9 mg, 89%).
2-Methallyl 4-methoxybenzoate (1a) versus 1-fluoro-3-vinylbenzene (4g)

Condition A:
Following the general procedure A using 2-methallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and 1-fluoro-3-vinylbenzene (4g, 30.5 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP were employed. $^{19}$F NMR analysis of the unpurified product mixture using hexafluorobenzene as an internal standard revealed (34.0 mg, 183 μmol, 0.732 equiv) a 7% yield of 1-fluoro-3-vinylbenzene (4g). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (49.6 mg, 95%).

Condition B:
Following the general procedure B using 2-methallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and 1-fluoro-3-vinylbenzene (4g, 30.5 mg, 250 μmol, 1 equiv). Reaction time was 70 min and 1.00 equiv of TBHP was added in total. $^{19}$F NMR analysis of the unpurified product mixture with hexafluorobenzene as an internal standard (39.0 mg, 210 μmol, 0.839 equiv) revealed a <5% yield of 1-fluoro-3-vinylbenzene (4g). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (50.1 mg, 96%).
2-Methallyl 4-methoxybenzoate (1a) versus 1-ethynyl-4-(trifluoromethyl)benzene (4h)

Condition A:
Following the general procedure A using 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and 1-ethynyl-4-(trifluoromethyl)benzene (4h, 42.5 mg, 250 μmol, 1 equiv). Reaction time was 135 min and 2.00 equiv of TBHP were employed. $^{19}$F NMR analysis of the unpurified product mixture using hexafluorobenzene as an internal standard (49.8 mg, 268 μmol, 1.07 equiv) revealed a <5% yield of 1-ethynyl-4-(trifluoromethyl)benzene (4h). Purification by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) afforded isobutyl 4-methoxybenzoate (2a) as a clear oil (28.6 mg, 55%).
2-Fluoroallyl (4-methoxyphenyl)carbamate (1i) versus (allyloxy)(tert-butyl)diphenylsilane (4a)

Condition A:

Following the general procedure A using 2-fluoroallyl (4-methoxyphenyl)carbamate (1i, 56.3 mg, 250 μmol) and (allyloxy)(tert-butyl)diphenylsilane (4a, 74.0 mg, 250 μmol, 1 equiv). Reaction time was 19 h but only 1.00 equiv of TBHP was added to initially activate the catalyst. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard revealed a 28% yield of (allyloxy)(tert-butyl)diphenylsilane (4a) and a 67% yield of tert-butyldiphenyl(propoxy)silane (S5). Purification by automated flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) afforded 2-fluoropropyl (4-methoxyphenyl)carbamate (S12) as a white solid (35.5 mg, 62%).

R_f = 0.58 (33% ethyl acetate–hexanes; UV, CAM). $^1$H NMR (400 MHz, CDCl_3) $\delta$ 7.27 (br d, 2H, J = 8.0 Hz, H_3), 6.85 (d, 2H, J = 8.8 Hz, H_2), 6.74 (br s, 1H, NH), 4.99–4.78 (m, 1H, H_5), 4.35–4.11 (m, 2H, H_4), 3.78 (s, 3H, H_1), 1.37 (dd, 3H, J = 23.6, 6.4 Hz, H_6). $^{19}$F NMR (375 MHz, CDCl_3) $\delta$ –47.71.

$^1$H and $^{19}$F NMR data for 2-fluoropropyl (4-methoxyphenyl)carbamate (S12) prepared in this way were in agreement with those previously described.[20]
Competitive hydrogenation employing palladium on carbon (Table S3, Entry 1 and Table 3, Entry 2, $H_2/Pd-C$)

Palladium on carbon (10 wt. % loading, 1.1 mg, 1.0 μmol, 0.01 equiv) was added to a solution of 2-methylallyl 4-methoxybenzoate ($1a$, 20.6 mg, 100 μmol, 1 equiv) and allyl 4-methoxybenzoate ($1c$, 19.2 mg, 100 μmol, 1 equiv) in methanol (10 mL) at 24 °C. The reaction vessel was evacuated and re-filled using a balloon of dihydrogen. This process was repeated four times. The reaction mixture was stirred for 5 min at 24 °C. The product mixture was filtered through a short column of celite and the short column was rinsed with ether (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (5.0 mg, 42.0 μmol, 0.420 equiv) revealed an 87% yield of 2-methallyl 4-methoxybenzoate ($1a$), a 13% yield of isobutyl 4-methoxybenzoate ($2a$), a 30% yield of allyl 4-methoxybenzoate ($1c$), and a 57% yield of propyl 4-methoxybenzoate ($2c$).
Competitive hydrogenation employing platinum on carbon (Table S3, Entry 2)

Palladium on carbon (10 wt. % loading, 1.0 mg, 0.5 μmol, 0.005 equiv) was added to a solution of 2-methylallyl 4-methoxybenzoate (1a, 20.6 mg, 100 μmol, 1 equiv) and allyl 4-methoxybenzoate (1c, 19.2 mg, 100 μmol, 1 equiv) in methanol (10 mL) at 24 °C. The reaction vessel was evacuated and re-filled using a balloon of dihydrogen. This process was repeated four times. The reaction mixture was stirred for 3 min at 24 °C. The product mixture was filtered through a short column of celite and the short column was rinsed with ether (100 mL). The filtrates were combined and the combined filtrates were concentrated. 

$^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (7.7 mg, 6.43 μmol, 0.643 equiv) revealed an 76% yield of 2-methallyl 4-methoxybenzoate (1a), a 13% yield of isobutyl 4-methoxybenzoate (2a), a 44% yield of allyl 4-methoxybenzoate (1c), and a 25% yield of propyl 4-methoxybenzoate (2c).
Competitive hydrogenation employing Crabtree’s catalyst (Table S3, Entry 3)

Crantree’s catalyst (2.5 mol%, 2.0 mg, 0.25 μmol, 0.0025 equiv) was added to a solution of 2-methylallyl 4-methoxybenzoate (1a, 20.6 mg, 100 μmol, 1 equiv) and allyl 4-methoxybenzoate (1c, 19.2 mg, 100 μmol, 1 equiv) in dichloromethane (500 μL) at 24 °C. The reaction vessel was evacuated and refilled using a balloon of dihydrogen. This process was repeated four times. The reaction mixture was stirred for 3 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with dichloromethane (200 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (6.9 mg, 5.73 μmol, 0.573 equiv) revealed a 92% yield of 2-methallyl 4-methoxybenzoate (1a), a 5% yield of isobutyl 4-methoxybenzoate (2a), a 57% yield of allyl 4-methoxybenzoate (1c), and a 28% yield of propyl 4-methoxybenzoate (2c).
Competitive hydrogenation employing manganese tris(dipivaloylmethane) (Table S3, Entry 4)

This experiment followed the procedure of Shenvi and co-workers. Phenylsilane (64.5 µL, 600 µmol, 6.00 equiv) and a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 36.4 µL, 200 µmol, 2.00 equiv) were added sequentially to a solution of 2-methylallyl 4-methoxybenzoate (1a, 20.6 mg, 100 µmol, 1 equiv), allyl 4-methoxybenzoate (1c, 19.2 mg, 100 µmol, 1 equiv) in i-propanol (200 µL) under argon at 24 °C. The resulting mixture was degassed by bubbling argon through the solution for 10 min. Manganese tris(dipivaloylmethane) (9.0 mg, 15.0 µmol, 0.15 equiv) was added and the resulting mixture was degassed by bubbling argon through the solution for 30 s. The reaction mixture was stirred for 10 min at 24 °C. The reaction was quenched by filtering the product mixture through a plug of silica gel and the plug was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture with mesitylene as an internal standard (9.4 mg, 78.4 µmol, 0.784 equiv) revealed a 41% yield of 2-methylallyl 4-methoxybenzoate (1a), a 24% yield of isobutyl 4-methoxybenzoate (2a), a 47% yield of allyl 4-methoxybenzoate (1c), and a 25% yield of propyl 4-methoxybenzoate (2c).
Competitive hydrogenation employing palladium on carbon (Table 3, Entry 2, H$_2$/Pd-C)

Palladium on carbon (10 wt. % loading, 1.1 mg, 1.0 μmol, 0.01 equiv) was added to a solution of 2-methylallyl 4-methoxybenzoate (1a, 20.6 mg, 100 μmol, 1 equiv) and (E)-pent-2-en-1-yl 4-methoxybenzoate (S1, 22.6 mg, 100 μmol, 1 equiv) in methanol (10 mL) at 24 °C. The reaction vessel was evacuated and re-filled using a balloon of dihydrogen. This process was repeated four times. The reaction mixture was stirred for 5 min at 24 °C. The product mixture was filtered through a short column of celite and the short column was rinsed with ether (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (9.8 mg, 82.0 μmol, 0.820 equiv) revealed a 63% yield of 2-methylallyl 4-methoxybenzoate (1a), a 34% yield of isobutyl 4-methoxybenzoate (2a), a 36% yield of (E)-pent-2-en-1-yl 4-methoxybenzoate (S1), and a 63% yield of pentyl 4-methoxybenzoate (S13).
Competitive hydrogenation employing palladium on carbon (Table 3, Entry 3, H₂/Pd-C)

Palladium on carbon (10 wt. % loading, 1.1 mg, 1.0 μmol, 0.01 equiv) was added to a solution of 2-methylallyl 4-methoxybenzoate (1a, 20.6 mg, 100 μmol, 1 equiv) and (Z)-pent-2-en-1-yl 4-methoxybenzoate (S2, 22.6 mg, 100 μmol, 1 equiv) in methanol (10 mL) at 24 °C. The reaction vessel was evacuated and re-filled using a balloon of dihydrogen. This process was repeated four times. The reaction mixture was stirred for 5 min at 24 °C. The product mixture was filtered through a short column of celite and the short column was rinsed with ether (100 mL). The filtrates were combined and the combined filtrates were concentrated. ¹H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (15.6 mg, 130 μmol, 1.30 equiv) revealed a 39% yield of 2-methylallyl 4-methoxybenzoate (1a), a 61% yield of isobutyl 4-methoxybenzoate (2a), a 20% yield of (Z)-pent-2-en-1-yl 4-methoxybenzoate (S2), and a 77% yield of pentyl 4-methoxybenzoate (S13).
Competitive hydrogenation employing palladium on carbon (Table 3, Entry 4, H$_2$/Pd-C)

Palladium on carbon (10 wt. % loading, 1.1 mg, 1.0 μmol, 0.01 equiv) was added to a solution of 3-methylbut-2-en-1-yl 4-methoxybenzoate (S3, 22.6 mg, 100 μmol, 1 equiv) and (E)-pent-2-en-1-yl 4-methoxybenzoate (S1, 22.6 mg, 100 μmol, 1 equiv) in methanol (10 mL) at 24 °C. The reaction vessel was evacuated and re-filled using a balloon of dihydrogen. This process was repeated four times. The reaction mixture was stirred for 5 min at 24 °C. The product mixture was filtered through a short column of celite and the short column was rinsed with ether (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (10.9 mg, 90.3 μmol, 0.903 equiv) revealed a 80% yield of 3-methylbut-2-en-1-yl 4-methoxybenzoate (S3), a 7% yield of isopentyl 4-methoxybenzoate (S14), a 37% yield of (E)-pent-2-en-1-yl 4-methoxybenzoate (S1), and a 56% yield of pentyl 4-methoxybenzoate (S13).
Competitive hydrogenation employing palladium on carbon (Table 3, Entry 5, H₂/Pd-C)

Palladium on carbon (10 wt. % loading, 1.1 mg, 1.0 μmol, 0.01 equiv) was added to a solution of 3-methylbut-2-en-1-yl 4-methoxybenzoate (S₃, 22.6 mg, 100 μmol, 1 equiv) and (E)-pent-2-en-1-yl 4-methoxybenzoate (S₂, 22.6 mg, 100 μmol, 1 equiv) in methanol (10 mL) at 24 °C. The reaction vessel was evacuated and re-filled using a balloon of dihydrogen. This process was repeated four times. The reaction mixture was stirred for 5 min at 24 °C. The product mixture was filtered through a short column of celite and the short column was rinsed with ether (100 mL). The filtrates were combined and the combined filtrates were concentrated. ¹H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (9.7 mg, 80.3 μmol, 0.803 equiv) revealed a 70% yield of 3-methylbut-2-en-1-yl 4-methoxybenzoate (S₃), a 23% yield of isopentyl 4-methoxybenzoate (S₁₄), a 24% yield of (E)-pent-2-en-1-yl 4-methoxybenzoate (S₂), and a 75% yield of pentyl 4-methoxybenzoate (S₁₃).
Competitive hydrogenation employing palladium on carbon (Table 3, Entry 6, H$_2$/Pd-C)

Palladium on carbon (10 wt. % loading, 1.1 mg, 1.0 μmol, 0.01 equiv) was added to a solution of 2-methylallyl 4-methoxybenzoate (1a, 22.6 mg, 100 μmol, 1 equiv) and but-2-yn-1-yl 4-methoxybenzoate (S4, 20.4 mg, 100 μmol, 1 equiv) in methanol (10 mL) at 24 °C. The reaction vessel was evacuated and refilled using a balloon of dihydrogen. This process was repeated four times. The reaction mixture was stirred for 5 min at 24 °C. The product mixture was filtered through a short column of celite and the short column was rinsed with ether (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (11.5 mg, 96.0 μmol, 0.960 equiv) revealed a 71% yield of 2-methylallyl 4-methoxybenzoate (1a), a 30% yield of isobutyl 4-methoxybenzoate (2a), and a 24% yield of but-2-yn-1-yl 4-methoxybenzoate (S4).
Hydrobromination of 2-methylallyl 4-methoxybenzoate (1a) to 2-bromo-2-methylpropyl 4-methoxybenzoate (5a, Table S4, entry 2)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), tosyl bromide (147 mg, 625 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (86.0 μL, 938 μmol, 3.75 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 4.0 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) to 2-bromo-2-methylpropyl 4-methoxybenzoate (5a) as a clear oil (71.5 mg, 95%).

R_f = 0.47 (20% ethyl acetate–hexanes; UV). 1H NMR (500 MHz, CD2Cl2) δ 8.03 (d, J = 8.5 Hz, 2H, H3), 6.96 (d, J = 8.5 Hz, 2H, H2), 4.40 (s, 2H, H4), 3.87 (s, 3H, H1), 1.85 (s, 6H, H5). 13C NMR (125 MHz, CD2Cl2) δ 165.9 (C), 164.2 (C), 132.2 (CH), 122.7 (C), 114.3 (CH), 73.5 (CH2), 62.3 (C), 56.1 (CH3), 31.4 (CH3). IR (ATR-FTIR), cm⁻¹: 2970 (w), 1713 (m), 1605 (m), 1252 (s), 1096 (s). HRMS-ESI (m/z): [M + H]^+ calcd for C12H1679/81BrO3, 287.0283/289.0262; found, 287.0280/289.0261.
Hydroiodination of 2-methylallyl 4-methoxybenzoate (1a) to 2-iodo-2-methylpropyl 4-methoxybenzoate (5b, Table S4, entry 7)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. The reaction vessel was protected from light with aluminum foil. Dichoromethane (830 μL), diiodomethane (302 μL, 3.75 mmol, 15.0 equiv), 1,4-dihydrobenzene (115 μL, 1.25 mmol, 5.00 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 50 h at 24 °C. The product mixture was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) to 2-iodo-2-methylpropyl 4-methoxybenzoate (5b) as a clear oil (74.3 mg, 89%).

R_f = 0.47 (20% ethyl acetate–hexanes; UV). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.04 (d, J = 8.8 Hz, 2H, H₃), 6.96 (d, J = 8.8 Hz, 2H, H₂), 4.32 (s, 2H, H₄), 3.87 (s, 3H, H₁), 2.01 (s, 6H, H₅). ¹³C NMR (100 MHz, CD₂Cl₂) δ 165.8 (C), 164.3 (C), 132.2 (CH), 122.7 (C), 114.3 (CH), 76.1 (CH₂), 56.1 (CH₃), 43.5 (C), 34.8 (CH₃). IR (ATR-FTIR), cm⁻¹: 2963 (w), 1714 (m), 1605 (m), 1254 (s), 1099 (s). HRMS-ESI (m/z): [M + H]+ calcd for C₁₂H₁₆IO₃, 335.0144; found, 335.0148.
Hydroiodination of 2-methylallyl 4-methoxybenzoate (1a) to 2-iodo-2-methylpropyl 4-methoxybenzoate (5b, Table S4, entry 9)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. The reaction vessel was protected from light with aluminum foil. Dichloromethane (830 μL), diiodomethane (156 μL, 1.88 mmol, 7.50 equiv), 1,4-dihydrobenzene (115 μL, 1.25 mmol, 5.00 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 50 h at 24 °C. The product mixture was concentrated and the residue obtained was purified by flash-column chromatography (eluting with hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) to 2-iodo-2-methylpropyl 4-methoxybenzoate (5b) as a clear oil (43.4 mg, 52%) and 2-methyl-2-((triethylsilyl)oxy)propyl 4-methoxybenzoate (S15) as a clear oil (39.7 mg, 47%).

2-Methyl-2-((triethylsilyl)oxy)propyl 4-methoxybenzoate (S15) Rf = 0.57 (20% ethyl acetate–hexanes; UV). 1H NMR (400 MHz, CD2Cl2) δ 8.00 (d, J = 8.8 Hz, 2H, H3), 6.94 (d, J = 8.8 Hz, 2H, H2), 4.30 (s, 2H, H4), 3.86 (s, 3H, H1), 1.30 (s, 6H, H5), 0.97 (t, J = 8.0 Hz, 9H, H7), 0.68 (q, J = 8.0 Hz, 6H, H6). 13C NMR (100 MHz, CD2Cl2) δ 166.4 (C), 164.0 (C), 132.0 (CH), 123.4 (C), 114.1 (CH), 81.7 (C), 67.9 (CH2), 56.0 (CH3), 22.3 (CH3), 7.1 (CH3), 4.3 (CH2). IR (ATR-FTIR), cm⁻¹: 2955(w), 1714 (m), 1275 (m), 1253 (s), 1101 (s). HRMS-ESI (m/z): [M + H]+ calcd for C18H31SiO4, 339.1992; found, 339.1989.

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General procedure for the hydroselenation of 2-methylallyl 4-methoxybenzoate (1a) to 2-methyl-2-(phenylselanyl)propyl 4-methoxybenzoate (5c, Table S4, entry 11)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (1a, 51.6 mg, 250 μmol, 1 equiv), Se-phenyl 4-methylbenzenesulfonoselenoate (195 mg, 625 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (86.0 μL, 938 μmol, 3.75 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 4.0 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 6% ethyl acetate–hexanes, linear gradient) to 2-methyl-2-(phenylselanyl)propyl 4-methoxybenzoate (5c) as a clear oil (83.9 mg, 89%).

Rf = 0.47 (20% ethyl acetate–hexanes; UV, CAM). 1H NMR (400 MHz, CD2Cl2) δ 7.98–7.95 (m, 2H, H3), 7.69–7.66 (m, 2H, H7), 7.42–7.38 (m, 1H, H8), 7.34–7.30 (m, 2H, H6), 6.95–6.92 (m, 2H, H2), 4.24 (s, 2H, H4), 3.86 (s, 3H, H1), 1.46 (s, 6H, H5). 13C NMR (100 MHz, CD2Cl2) δ 166.2 (C), 164.1 (C), 138.9 (CH), 132.1 (CH), 129.4 (CH), 129.4 (CH), 127.4 (C), 123.1 (C), 114.2 (CH), 72.7 (CH2), 56.0 (CH3), 45.0 (C), 27.0 (CH3). IR (ATR-FTIR), cm⁻¹: 2960 (w), 1712 (m), 1606 (m), 1256 (s), 1167 (m). HRMS-ESI (m/z): [M + H]+ calcd for C18H21SeO3, 365.0656; found, 365.0648.
2-Bromopropyl 4-methoxybenzoate (6a)

Following the general hydrobromination procedure using allyl 4-methoxybenzoate (1c, 48.1 mg, 250μmol, 1 equiv). Reaction time was 4.0 h. Purification by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) afforded 2-bromopropyl 4-methoxybenzoate (6a) as a clear oil (60.1 mg, 88%).

R_f = 0.48 (20% ethyl acetate–hexanes; UV). 1H NMR (500 MHz, CD2Cl2) δ 8.01 (d, J = 9.0 Hz, 2H, H3), 6.95 (d, J = 9.0 Hz, 2H, H2), 4.49–4.35 (m, 3H, 2×H4, 1×H5), 3.86 (s, 3H, H1), 1.77 (d, J = 6.5 Hz, 3H, H6). 13C NMR (125 MHz, CD2Cl2) δ 166.0 (C), 164.3 (C), 132.2 (CH), 122.7 (C), 114.3 (CH), 69.5 (CH2), 56.1 (CH3), 46.1 (CH), 23.0 (CH3). IR (ATR-FTIR), cm⁻¹: 2931 (w), 1714 (m), 1605 (m), 1254 (s), 1167 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C11H13BrNaO3, 294.9946/296.9925; found, 294.9944/296.9909.

2-Iodopropyl 4-methoxybenzoate (6b)

Following the general hydroiodination procedure using allyl 4-methoxybenzoate (1c, 48.1 mg, 250μmol, 1 equiv). Reaction time was 168 h. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. 1H NMR analysis of the unpurified product mixture using mesitylene as an internal standard revealed a 69% yield of allyl 4-methoxybenzoate (9c) and a 23% yield of 2-iodopropyl 4-methoxybenzoate (6b). An inseparable 1.2:1.0 mixture of 1c versus 6b was obtained for characterization by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 6% ethyl acetate–hexanes, linear gradient).

R_f = 0.55 (20% ethyl acetate–hexanes; UV). 1H NMR (500 MHz, C6D6) δ 8.18–8.15 (m, 2H, H3), 6.64–6.62 (m, 2H, H2), 4.24–4.22 (m, 1H, 1×H4), 4.12–4.08 (m, 1H, 1×H4), 3.88–3.84 (m, 1H, H5), 3.15–3.13 (m, 3H, H1), 1.45 (d, J = 7.0 Hz, 3H, H6). 13C NMR (125 MHz, C6D6) δ 165.3 (C), 164.9 (C), 131.8 (CH), 122.4 (C), 113.7 (CH), 70.2 (CH2), 54.5 (CH3), 24.1 (CH3), 21.8 (CH). IR (ATR-FTIR), cm⁻¹: 2931 (w), 1714 (m), 1605 (m), 1254 (s), 1167 (s). HRMS-ESI (m/z): [M + H]^+ calcd for C11H13INaO3, 342.9807; found, 342.9805.

2-(Phenylselanyl)propyl 4-methoxybenzoate (6c)

Following the general hydroselenation procedure using allyl 4-methoxybenzoate (1c, 48.1 mg, 250μmol, 1 equiv). Reaction time was 4.0 h. Purification by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) afforded 2-(phenylselanyl)propyl 4-methoxybenzoate (6c) as a clear oil (75.9 mg, 87%).
$R_f = 0.48$ (20% ethyl acetate–hexanes; UV, CAM). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.92 (d, $J = 8.8$ Hz, 2H, $H_3$), 7.63–7.60 (m, 2H, $H_3$), 7.31–7.29 (m, 3H, 2 × $H_7$, 1 × $H_8$), 6.91 (d, $J = 8.8$ Hz, 2H, $H_2$), 4.46–4.41 (m, 1H, 1 × $H_6$), 4.31–4.26 (m, 1H, 1 × $H_8$), 3.85 (s, 3H, $H_3$), 3.67–3.57 (m, 1H, $H_5$), 1.50 (d, $J = 6.8$ Hz, 3H, $H_9$). $^{13}$C NMR (10 MHz, CD$_2$Cl$_2$) δ 166.2 (C), 164.0 (C), 135.5 (CH), 132.0 (CH), 129.6 (CH), 128.8 (C), 128.3 (CH), 123.0 (C), 114.1 (CH), 69.3 (CH$_2$), 56.0 (CH$_3$), 37.3 (CH), 19.0 (CH$_3$). IR (ATR-FTIR), cm$^{-1}$: 2963 (w), 1709 (m), 1605 (m), 1510 (w), 1253 (s). HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{12}$H$_{18}$SeO$_3$, 351.0499; found, 351.0513.

**3-Bromo-3-methylbutyl 4-methoxybenzoate (7a)**

Following the general hydrobromination procedure using 3-methylbut-2-en-1-yl 4-methoxybenzoate (1j, 55.0 mg, 250 μmol, 1 equiv). Reaction time was 4.0 h. Purification by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) afforded 3-bromo-3-methylbutyl 4-methoxybenzoate (7a) as a clear oil (63.7 mg, 88%).

$R_f = 0.46$ (20% ethyl acetate–hexanes; UV). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.98 (d, $J = 9.0$ Hz, 2H, $H_3$), 6.94 (d, $J = 9.0$ Hz, 2H, $H_3$), 4.52 (t, $J = 6.8$ Hz, 2H, $H_4$), 3.85 (s, 3H, $H_3$), 2.31 (t, $J = 6.8$ Hz, 2H, $H_5$), 1.77 (s, 6H, $H_9$). $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$) δ 166.5 (C), 164.0 (C), 132.0 (CH), 123.2 (C), 114.2 (CH), 65.6 (C), 63.3 (CH$_2$), 56.0 (CH$_3$), 46.0 (CH$_2$), 35.1 (CH$_3$). IR (ATR-FTIR), cm$^{-1}$: 2965 (w), 1710 (m), 1605 (m), 1253 (s), 1166 (m). HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{13}$H$_{17}$BrNaO$_3$, 323.0259/325.0238; found, 323.0266/325.0243.

**3-iodo-3-methylbutyl 4-methoxybenzoate (7b)**

Following the general hydroiodination procedure using 3-methylbut-2-en-1-yl 4-methoxybenzoate (1j, 55.0 mg, 250 μmol, 1 equiv). Reaction time was 125 h. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. $^1$H NMR analysis of the unpurified product mixture using mesitylene as an internal standard revealed a 58% yield of 3-methylbut-2-en-1-yl 4-methoxybenzoate (1j) and a 29% yield of 3-iodo-3-methylbutyl 4-methoxybenzoate (7b). An analytically pure sample of 7b was obtained for characterization by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 5% ethyl acetate–hexanes, linear gradient).

$R_f = 0.49$ (20% ethyl acetate–hexanes; UV). $^1$H NMR (500 MHz, C$_6$D$_6$) δ 8.15 (d, $J = 8.0$ Hz, 2H, $H_3$), 6.67 (d, $J = 8.0$ Hz, 2H, $H_3$), 4.45 (t, $J = 6.8$ Hz, 2H, $H_4$), 3.16 (m, 3H, $H_3$), 1.81 (t, $J = 6.8$ Hz, 2H, $H_5$), 1.63 (s, 6H, $H_9$). $^{13}$C NMR (125 MHz, C$_6$D$_6$) δ 165.9 (C), 163.8 (C), 132.0 (CH), 123.4 (C), 114.0 (CH), 64.7 (CH$_2$), 54.9 (CH$_3$), 48.5 (CH$_2$), 46.2 (C), 38.3 (CH$_3$). IR (ATR-FTIR), cm$^{-1}$: 2962 (w), 1710 (m), 1605 (m), 1256 (s), 1167 (m). HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{13}$H$_{17}$I NaO$_3$, 371.0120; found, 371.0131.
3-Methyl-3-(phenylselanyl)butyl 4-methoxybenzoate (7c)

Following the general hydroselenation procedure using 3-methylbut-2-en-1-yl 4-methoxybenzoate (1j, 55.0 mg, 250μmol, 1 equiv). Reaction time was 4.0 h. Purification by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) afforded 3-methyl-3-(phenylselanyl)butyl 4-methoxybenzoate (7c) as a clear oil (76.4 mg, 81%).

R_f = 0.48 (20% ethyl acetate–hexanes; UV, CAM). 1H NMR (500 MHz, CD2Cl2) δ 7.98 (d, J = 7.5 Hz, 2H, H3), 7.68–7.66 (m, 2H, H8), 7.41–7.39 (m, 1H, H9), 7.35–7.32 (m, 2H, H7), 6.94 (d, J = 7.5 Hz, 2H, H2), 4.51 (t, J = 6.8 Hz, 2H, H5), 3.87 (s, 3H, H1), 2.01 (t, J = 6.8 Hz, 2H, H3), 1.47 (s, 6H, H6). 13C NMR (125MHz, CD2Cl2) δ 166.6 (C), 164.0 (C), 138.8 (CH), 132.0 (CH), 129.3 (CH), 129.2 (CH), 128.2 (C), 123.4 (C), 114.1 (CH), 63.1 (CH2), 56.0 (CH3), 45.7 (C), 42.1 (CH2), 30.5 (CH3). IR (ATR-FTIR), cm⁻¹: 2960 (w), 1708 (m), 1605 (m), 1511 (w), 1254 (s). HRMS-ESI (m/z): [M + K]^+ calcd for C19H22SeKO3, 417.0371; found, 417.0366.
Hydrobromination of 2-chloroallyl 4-methoxybenzoate (1d) to 2-bromo-2-chloropropyl 4-methoxybenzoate (8a)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-chloroallyl 4-methoxybenzoate (1d, 28.3 mg, 125 μmol, 1 equiv), tosyl bromide (73.5 mg, 313 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (32.1 mg, 125 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (400 μL), 1,4-dihydrobenzene (43.0 μL, 469 μmol, 3.75 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 1.00 equiv), and triethylsilane (200 μL, 1.25 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 3.0 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes, grading to 5% ethyl acetate–hexanes, linear gradient) to 2-bromo-2-chloropropyl 4-methoxybenzoate (8a) as a clear oil (35.6 mg, 93%).

R_f = 0.53 (20% ethyl acetate–hexanes; UV). ^1H NMR (500 MHz, CD_2Cl_2) δ 8.05 (d, J = 8.5 Hz, 2H, H_3), 6.97 (d, J = 8.5 Hz, 2H, H_2), 4.73–4.68 (m, 2H, H_4), 3.87 (s, 3H, H_1), 2.38 (s, 3H, H_5). ^13C NMR (150 MHz, CD_2Cl_2) δ 165.4 (C), 164.6 (C), 132.4 (CH), 122.1 (C), 114.4 (CH), 74.9 (C), 73.8 (CH_2), 56.1 (CH_3), 36.2 (CH_3). IR (ATR-FTIR), cm^-1: 2931 (w), 1721 (m), 1606 (m), 1255 (m), 557 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C_{11}H_{12}^{35/37}Cl^{79/81}BrNaO_3, 328.9556/330.9536/330.9527/332.9506; found, 328.9560/330.9528/330.9518/332.9510.
Hydrobromination of 2-bromoallyl 4-methoxybenzoate (1k) to 2,2-dibromopropyl 4-methoxybenzoate (8b)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (1k, 33.9 mg, 125 μmol, 1 equiv), tosyl bromide (147 mg, 625 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (86.0 μL, 938 μmol, 3.75 equiv), a solution of tert-butyl hydroperoxide in nonane (∼5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 5.0 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 5% ethyl acetate–hexanes, linear gradient) to 2,2-dibromopropyl 4-methoxybenzoate (8b) as a clear oil (39.9 mg, 93%).

R_f = 0.51 (20% ethyl acetate–hexanes; UV). ^1H NMR (500 MHz, CD_2Cl_2) δ 8.05 (d, J = 8.5 Hz, 2H, H_3), 6.97 (d, J = 8.5 Hz, 2H, H_2), 4.75 (s, 2H, H_4), 3.87 (s, 3H, H_1), 2.56 (s, 3H, H_5). ^13C NMR (125 MHz, CD_2Cl_2) δ 165.3 (C), 164.5 (C), 132.4 (CH), 122.1 (C), 114.4 (CH), 74.7 (CH_2), 61.7 (C), 56.1 (CH_3), 37.8 (CH_3). IR (ATR-FTIR), cm^{-1}: 2933 (w), 1719 (m), 1605 (m), 1254 (m), 1091 (m). HRMS-ESI (m/z): [M + H]^+ calcld for C_{11}H_{12}Br_2O_3, 350.9231/352.9211/354.9191; found, 350.9240/352.9212/354.9185.
Intramolecular Competition Experiment (Scheme 2):

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CH_3-CH=CH-\(\text{O}\)\(\text{O}\)-CH_3
B

\(\begin{array}{c}
\text{Co(acac)}_3, \text{TBHP (syringe pump), Et}_3\text{SiH, DHB}
\text{n-PrOH, argon, 40 °C}
\text{20% (A), 90% (B), 72% (A-H_2), 9% (B-H_2)}
A-H_2:B-H_2 = 8.0:1.0
\end{array}\)
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Following the general procedure B using (E)-2-methylallyl pent-2-en-1-yl terephthalate (9, 72.0 mg, 250 μmol, 1 equiv). Reaction time was 40 min and 0.667 equiv of TBHP were employed. \(^1\)H NMR analysis of the unpurified product mixture using mesitylene as an internal standard (28.2 mg, 235 μmol, 0.940 equiv) revealed a 20% yield of alkene (A), a 90% yield of alkene (B), a 72% yield of alkene (A) hydrogenation, and a 9% yield of alkene (B) hydrogenation. An analytically pure sample of (E)-isobutyl pent-2-en-1-yl terephthalate (10) was obtained by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 10% ether–hexanes, linear gradient) followed by five iterations of preparative thin-layer chromatography on silver nitrate impregnated silica gel plates.

\(R_f = 0.47\) (10% ethyl acetate–hexanes; UV, KMnO_4). \(^1\)H NMR (500 MHz, CDCl_3) \(\delta\) 8.13–8.08 (m, 4H, 2 × H_6, 2 × H_7), 5.95–5.89 (m, 1H, H_3), 5.71–5.65 (m, 1H, H_4), 4.79 (d, 2H, J = 5 Hz, H_5), 4.12 (d, 2H, J = 5 Hz, H_6), 2.14–2.06 (m, 3H, 2 × H_2, 1 × H_9), 1.04–1.01 (m, 9H, 3 × H_1, 9 × H_10). \(^1\)C NMR (125 MHz, CDCl_3) \(\delta\) 165.8 (C), 165.6 (C), 138.5 (CH), 134.2 (C), 134.1 (C), 129.6 (CH), 129.4 (CH), 122.5 (CH), 71.4 (CH_2), 66.2 (CH_2), 27.9 (CH), 25.2 (CH_2), 19.2 (CH_3), 13.1 (CH_3). IR (ATR-FTIR), cm\(^{-1}\): 2964 (w), 1716 (S), 1263 (s), 1244 (s), 1115 (s). HRMS-ESI (m/z): [M + H]^+ calcd for C_{17}H_{23}O_4, 291.1596; found, 291.1587.
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$^{13}$C NMR (CDCl$_3$, 150 MHz)
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$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)
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$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)
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$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
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Ma and Herzon. "Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer." Chem. Sci. S102
Ma and Herzon. "Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer." Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
$^1$H NMR (CD$_2$Cl$_2$, 500 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz)
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$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz)
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$^1$H NMR ($\text{CD}_2\text{Cl}_2$, 400 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” *Chem. Sci.*
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
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$^1$H NMR (CD$_2$Cl$_2$, 500 MHz)
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” *Chem. Sci.*
$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz)
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Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
$^1$H NMR Spectra of Unpurified Product Mixtures Containing Added Internal Standard

Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Table 1, Entry 2
$^1$H NMR (CDCl$_3$, 400 MHz)

Ma and Herzon "Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer" Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Table 1, Entry 4

$^1$H NMR (CDCl$_3$, 400 MHz)
Table 1, Entry 5

$^1$H NMR (CDCl$_3$, 400 MHz)

| Compound | NMR Spectrum |
|----------|--------------|
| 1a       | ![NMR Spectrum of 1a](image) |
| 1b       | ![NMR Spectrum of 1b](image) |
| 2a       | ![NMR Spectrum of 2a](image) |
| 2b       | ![NMR Spectrum of 2b](image) |
Table 1, Entry 6

^1^H NMR (CDCl₃, 400 MHz)
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Table S1. Entry 1
\(^1\text{H} \text{NMR (CDCl}_3, 400 \text{ MHz)}\)

Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Table S1, Entry 2
^1^H NMR (CDCl$_3$, 400 MHz)

Ma and Herzon. "Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer." Chem. Sci.
Table S1, Entry 3
\(^1\)H NMR (CDCl\(_3\), 400 MHz)

| Compound | Structure |
|----------|-----------|
| 1a       | ![Structure 1a](image1) |
| 1b       | ![Structure 1b](image2) |
| 2a       | ![Structure 2a](image3) |
| 2b       | ![Structure 2b](image4) |

NMR spectrum showing peaks for different hydrogen atoms.

- H\(_{1a}\)
- H\(_{1b}\)
- H\(_{2a}\)
- H\(_{2b}\)
Ma and Herzon "Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer" Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” *Chem. Sci.*
Table S2, Entry 2-B
$^1$H NMR (CDCl$_3$, 400 MHz)

| Compound | Structure |
|----------|-----------|
| 1a       | ![Structure 1a](image1) |
| 2a       | ![Structure 2a](image2) |
| 4a       | ![Structure 4a](image3) |
| S5       | ![Structure S5](image4) |

![NMR Spectrum](image5)
Table S2, Entry 3-A

$^1$H NMR (CDCl$_3$, 400 MHz)

| Compound | NMR Spectrum |
|----------|--------------|
| 1d       | ![1d NMR Spectrum](image1) |
| S6       | ![S6 NMR Spectrum](image2) |
| 4a       | ![4a NMR Spectrum](image3) |
| S5       | ![S5 NMR Spectrum](image4) |

Hydrogen Atom Transfer Chem. Sci.
Table S2, Entry 3-B

$^1$H NMR (CDCl$_3$, 400 MHz)

| Compound | Chemical Structure |
|----------|--------------------|
| 1d       | ![1d](image)       |
| S6       | ![S6](image)       |
| 4a       | ![4a](image)       |
| S5       | ![S5](image)       |

- **5.87 ppm**: $H_{4a}$
- **7.10 ppm**: $H_{1d}$
- **0.56 ppm**: $H_{5a}$
- **0.55 ppm**: $H_{5b}$
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Table S2, Entry 7-A
\(^1\)H NMR (CDCl\(_3\), 400 MHz)

| Compound | Structure |
|----------|-----------|
| 1a       | ![Structure 1a] |
| 2a       | ![Structure 2a] |
| 4c       | ![Structure 4c] |
| S9       | ![Structure S9] |

**Chem. Sci.** S183
Table S2, Entry 7-B
$^1$H NMR (CDCl$_3$, 400 MHz)
Table S2, Entry 8-A
$^1$H NMR (CDCl$_3$, 400 MHz)

![NMR spectrum image]
Table S2, Entry 8-B

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz)} \]

| Compound | Structure |
|----------|-----------|
| 1a       | ![Structure 1a](image) |
| 2a       | ![Structure 2a](image) |
| 4d       | ![Structure 4d](image) |

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**Chem. Sci.** S186
Table S2, Entry 9-B

$^1$H NMR (CDCl$_3$, 400 MHz)

| Compound | Structure |
|----------|-----------|
| 1a (not observed) | ![1a](image) |
| 2a | ![2a](image) |
| 4e | ![4e](image) |

![NMR Spectrum](image)
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Table S2, Entry 11-A

°H NMR (CDCl₃, 400 MHz)

1g (not observed) S10 (not resolved from impurities)

4a
Table S2, Entry 11-B

$^1$H NMR (CDCl$_3$, 400 MHz)
Table S2, Entry 12

$^1$H NMR (CDCl$_3$, 400 MHz)

| Compound | Structure |
|----------|-----------|
| 1h (not observed) | ![Structure 1h](image) |
| S11 (not resolved from impurities) | ![Structure S11](image) |
| 4a | ![Structure 4a](image) |
| S5 | ![Structure S5](image) |

![NMR Spectrum](image)
Table S2, Entry 13-A
\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz)
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Table S2, Entry 14-A

$^1$H NMR (CDCl$_3$, 400 MHz)

![Chemical structures](image-url)
Table S2, Entry 14-B

$^1$H NMR (CDCl$_3$, 400 MHz)

| Compound | Structure |
|----------|-----------|
| 1g (not observed) | ![Image] |
| S10 | ![Image] |
| 4c | ![Image] |
| S9 | ![Image] |

| Peak | Assignment |
|------|------------|
| H$_{4d}$ | 6.8 ppm |
| H$_{69}$ | 6.1 ppm |
| H$_{510}$ | 6.6 ppm |
| H$_{59}$ | 7.0 ppm |
| H$_{4d}$ | 8.0 ppm |
| H$_{69}$ | 7.5 ppm |
| H$_{510}$ | 7.8 ppm |
| H$_{59}$ | 8.5 ppm |
Table S2, Entry 15-A
$^{19}$F NMR (CDCl$_3$, 375 MHz)
Table S2, Entry 15-B

$^{19}$F NMR (CDCl$_3$, 375 MHz)

4g (not observed)

F$_{std}$
Table S2, Entry 16

$^{19}$F NMR (CDCl$_3$, 375 MHz)

4h (not observed)
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” *Chem. Sci.*
| Compound | Structure | 
|----------|-----------| 
| 1a       | ![Structure 1a](image1.png) | 
| 2a       | ![Structure 2a](image2.png) | 
| 1c       | ![Structure 1c](image3.png) | 
| 2c       | ![Structure 2c](image4.png) | 

**Table S3, Entry 1**

$^1$H NMR (CDCl$_3$, 400 MHz)
Table S3, Entry 3
$^1$H NMR (CDCl$_3$, 400 MHz)

| Compound | Structure |
|----------|-----------|
| 1a       | ![Structure 1a](image) |
| 2a       | ![Structure 2a](image) |
| 1c       | ![Structure 1c](image) |
| 2c       | ![Structure 2c](image) |
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Ma and Herzon “Non-Classical Selectivities in the Reduction of Alkenes by Cobalt-Mediated Hydrogen Atom Transfer” Chem. Sci.
Table 3, Entry 5 (H₂/Pd-C)

\(^1\)H NMR (CDCl₃, 400 MHz)
Table 3, Entry 6 (H2/Pd-C)

\( ^1\text{H} \) NMR (CDCl3, 400 MHz)
Scheme 2

$^1$H NMR (CDCl$_3$, 400 MHz)

![Chemical Structures and NMR spectrum](Image)
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