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Synthesis of Ketones and Esters from Heteroatom-Functionalized Alkenes by Cobalt-Mediated Hydrogen Atom Transfer

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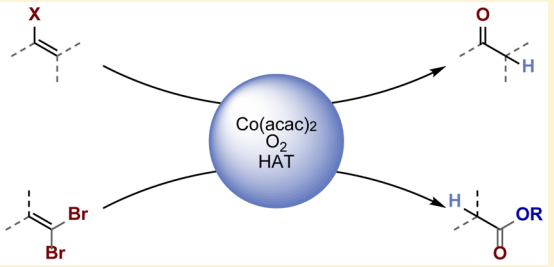
Supporting Information

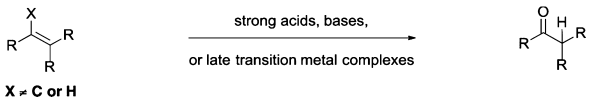
ABSTRACT: Cobalt bis(acetylacetonate) is shown to mediate hydrogen atom transfer to a broad range of functionalized alkenes; in situ oxidation of the resulting alkylradical intermediates, followed by hydrolysis, provides expedient access to ketones and esters. By modification of the alcohol solvent, different alkyl ester products may be obtained. The method is compatible with a number of functional groups including alkenyl halides, sulfides, triflates, and phosphonates and provides a mild and practical alternative to the Tamao−Fleming oxidation of vinylsilanes and the Arndt−Eistert homologation.



INTRODUCTION

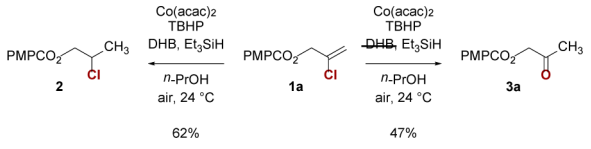
Ketones and esters are among the central functional groups in organic chemistry.[1] They are most frequently accessed by oxidation of the corresponding alcohols.[2] Although heteroatom-substituted alkenes are at the carbonyl or carboxylic acid oxidation state, their application as synthetic equivalents of ketones or esters is limited.[3] Classical methods to convert heteroatom-substituted alkenes to carbonyl compounds typically employ Lewis acids or bases or late transition metals (Scheme 1).[4]

Scheme 1. Classical Methods for the Conversion of Functionalized Alkenes to Ketones Typically Employ Strong Acids or Bases or Late-Transition-Metal Complexes



We have previously reported the reduction of 2-chloroallyl 4-methoxybenzoate (**1a**) by a hydrogen atom transfer pathway (Scheme 2).[5] Under optimized conditions, treatment of **1a** with the hydrogen atom donors triethylsilane (Et_3SiH) and 1,4-dihydrobenzene (DHB) in the presence of cobalt bis(acetylacetonate) [$Co(acac)_2$] and *tert*-butyl hydroperoxide (TBHP) formed the reduction product **2** in 62% yield.[5f]

Scheme 2. Hydrogenation (Left) and Oxydechlorination (Right) of 1a



Surprisingly, when DHB was omitted from the reaction mixture, the formal hydrolysis product **3a** was obtained in 47% yield. None of the reduction product **2** was observed (^1H NMR analysis). Given the facility of hydrogen atom transfer to functionalized alkenes,[5e,f,6] this result suggested a potentially general method. As shown below, this formal hydrolysis proceeds under near-neutral conditions and is amenable to a range of functionalized alkenes. Trimethylsilylalkenes undergo a novel oxidative desilylation to the corresponding ketone derivatives, thereby establishing a useful and mild alternative to the Tamao−Fleming oxidation.[7] When used in conjunction with the Ramirez alkenylation,[8] the oxydehalogenation of *gem*-dihaloalkenes provides a useful alternative to the Arndt−Eistert homologation.[9]

RESULTS AND DISCUSSION

Synthesis of Ketones by the Formal Hydrolysis of Heteroatom-Functionalized Alkenes. We optimized the conversion of 2-bromoallyl 4-methoxybenzoate (**1b**) to 2-oxopropyl 4-methoxybenzoate (**3a**, Table 1). In the presence of 1 equiv of $Co(acac)_2$, 1 equiv TBHP, and 5 equiv of Et_3SiH in *n*-propanol under 1 atm of air, a 68% isolated yield of the desired product **3a** and an 8% yield (by NMR) of 2,2-dibromopropyl 4-methoxybenzoate (**4**) were obtained. Use of *N*,*N*-dimethylformamide (DMF) as solvent increased the yield of **3a** to 76% (entry 2). Attempts to decrease the catalyst loading to 25 mol % resulted in lower conversion (52%, entry 3). We attributed this reduction in conversion to the hydrobromic acid generated in the reaction. Attempts to neutralize the acid with isoamylene (entry 4) or lithium acetylacetonate [Li(acac)] (entry 5) in DMF were not successful. After some experimentation, an 81% isolated yield

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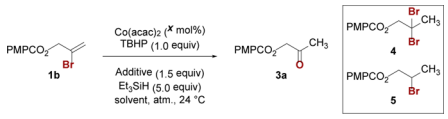
Table 1. Optimization of the $Co(acac)_2$-Mediated Formal Hydrolysis of 1b[a]



entry	x (mol %)	additive	solvent	atm	conv of 1b (%)	yield (%) 3a	4	5
1	100		*n*-PrOH	air	>95	(68)[b]	8	<1
2	100		DMF	air	>95	(76)	3	(10)
3	25		DMF	air	52	46	<1	<1
4	25	isoamylene	DMF	air	55	41	<1	<1
5	25	Li(acac)	DMF	air	16	15	<1	<1
6	25	Li(acac)	CH_3OH	O_2	>95	(81)	<1	<1
7	100		CH_3OH	O_2	>95	(85)	<1	5
8[c]	10		THF	O_2	62	(20)	(39)	<1

[a]Reactions employed 250 μmol of **1b**. Conversions and yields were determined by ^1H NMR spectroscopy using mesitylene as an internal standard. [b]Yields in parentheses are isolated yields after purification by flash column chromatography. [c]$PhSiH_3$ was employed instead of Et_3SiH.

of **3a** was obtained when methanol was used as solvent under 1 atm of dioxygen and in the presence of 1.5 equiv of Li(acac) as the acid scavenger (entry 6). Consistent with our analysis, stoichiometric quantities of $Co(acac)_2$ afforded an 85% yield of **3a** in the absence of added Li(acac) (entry 7). As the conditions of entry 6 enabled transformation with a substoichiometric amount of $Co(acac)_2$ and those of entry 7 afforded the highest yield, both were employed in our investigation of the scope. Mukaiyama hydration conditions were also applied to the hydrolysis of **3a** (entry 8);[6b] however, the conversion was low and the major product was the *gem*-dibromide **4** (39%); the ketone **3a** was obtained in 20% yield.

In its present form, the scope of the reaction encompasses a wide range of heteroatom-functionalized alkenes (Table 2). The alkenyl fluoride **1c**, chloride **1a**, and bromide **1b** all underwent smooth conversion to the ketone **3a** in 81−99% yield (entries 1−3). The alkenyl iodide **1d** was also converted to **3a**, but the conversion was incomplete (45% or 85% conversion, 40% or 63% yield, entry 4). We have previously observed that styrene derivatives undergo decomposition in the hydrogen atom transfer reduction,[5f,g] but the styryl bromide **1e** was efficiently transformed in 88% yield under these conditions (entry 5). The trisubstituted alkenyl bromide **1f** was also converted to the ketone **3c** in 50% yield, with concomitant oxidation of the C−Si bond (entry 6). The cyclic alkenyl bromide **1g** was transformed to α-benzoyloxyl cyclohexanone (**3d**) in 91% yield (entry 7). The alkenyl alkyl ether **1h** was converted to **3d** in 73% yield (entry 8). The alkenyl phenyl ether **1i** provided the ketone **3e** in 47% yield (entry 9).

The addition of Li(acac) renders the reaction conditions slightly basic, and control experiments (Table S1) demonstrated that the alkenyl ester **1j** underwent formal hydrolysis without $Co(acac)_2$, presumably by base-catalyzed methanolysis of the ester. However, a separate experiment demonstrated that the ester was stable in the absence of cobalt and in the absence of both cobalt and Li(acac) (Table S1), and under the more neutral stoichiometric conditions, **1j** was converted to the ketone **3f** in 90% yield (entry 10). The alkenyl triflate **1k** was cleanly converted to the corresponding ketone **3g** in 78% yield (entry 11). Reaction of the alkenyl phosphonate **1l** proceeded in 50% yield under stoichiometric conditions; catalytic conditions led to an 81% recovery of starting material (entry 12). The enoxysilane **1m** was also cleaved under the neutral stoichiometric conditions to provide the ketone **3i** in 74% yield (entry 13).

Classical methods for the hydrolysis of alkenyl sulfides usually require stoichiometric quantities of mercury salts.[4c,10] Cobalt-mediated hydrolysis of the alkenyl sulfides **1n**, **1o**, and **1p** proceeded smoothly to provide the ketones **3a** and **3d** in 41−93% yield (entries 14−16). The alkenyl sulfone **1q** was also converted cleanly to the ketone **3d** in 89% yield (entry 17). The stoichiometric conditions allowed efficient transformation of the alkenyl selenide **1r** to the ketone **3d** (66%), but low conversion (22%) of **1r** was observed when catalytic conditions were applied (entry 18). Although the hydrolysis of enamides typically require strong Brønsted acids,[4h,11] the enamide **1s** underwent cobalt-mediated hydrolysis in 79% yield (entry 19). The alkenyl boronic ester **1t** was transformed to 2′-chloroacetophenone (**3k**) in 79% yield under stoichiometric conditions (entry 20), and control experiments demonstrated that the cobalt reagent was required for this transformation (Table S1). The stoichiometric conditions allowed efficient conversion of the alkenyl silanes **1u** and **1v** to the ketones **3a** (89%) and **3e** (88%). Although the mechanism of this reaction is not known, it provides a useful and mild alternative to the Tamao−Fleming oxidation, which typically requires installation of a heteroatom substituent at silicon.[7] Interestingly, when propargyl 4-methoxybenzoate (**1w**) was used as substrate, 88% of the starting material was recovered using substoichiometric quantities of cobalt. When stoichiometric conditions were applied, significant decomposition was observed and the ketone **3a** was obtained in only 32% yield (entry 23).

To gain insight into the mechanism of the reaction, the conversion of the alkenyl chloride **1a** in *n*-propanol was terminated after 4 h (Scheme 3). Purification of the mixture by flash column chromatography provided a 42% yield of the ketone **3a** and 57% of the alkyl hydroperoxide **6**. Resubjection of the alkyl hydroperoxide **6** to the reaction conditions afforded 74% of the desired ketone **3a**.

Based on these results and literature precedent, we propose that hydrogen atom transfer from a cobalt(III)hydride intermediate occurs to generate the more stable α-heteroatom-substituted radical **7** (Scheme 4).[5d,f,6q] Addition of dioxygen may form a peroxycobalt(III) intermediate **8**, which undergoes exchange with methanol to form the acetal **9**. Silylation of the cobalt peroxide intermediate to provide **10**,

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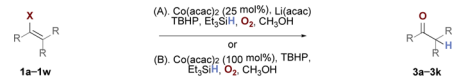
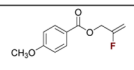
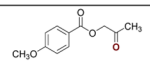
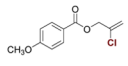
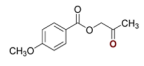
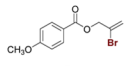
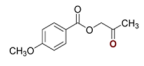
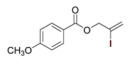
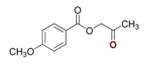
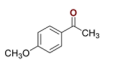
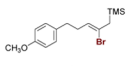
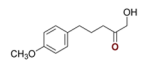
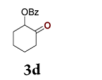
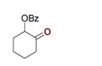
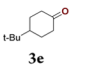
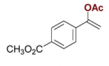
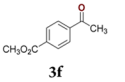
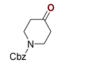
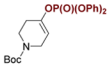
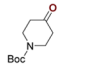
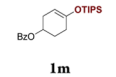
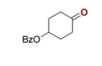
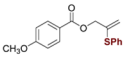
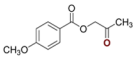
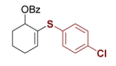
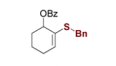
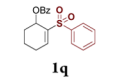
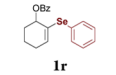
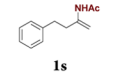
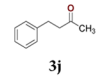
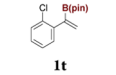
Table 2. Preliminary Scope of the Formal Hydrolysis Reaction[a]



entry	substrate	conv.[b]	product	yield[c]
1	 **1c**	A:>95% B:>95%	 **3a**	A:99% B:99%
2	 **1a**	A:>95% B:>95%	 **3a**	A:92% B:89%
3	 **1b**	A:>95% B:>95%	 **3a**	A:81% B:85%
4	 **1d**	A:85% B:45%	 **3a**	A:63% B:40%
5	 **1e**	A:>95% B:>95%	 **3b**	A:88% B:78%
6	 **1f**	A:>95% B:>95%	 **3c**	A:0% B:50%
7	 **1g**	A:>95% B:>95%	 **3d**	A:80% B:91%
8	 **1h**	A:>95% B:>95%	 **3d**	A:61% B:73%
9	 **1i**	A:29% B:95%	 **3e**	A:0% B:47%
10	 **1j**	A:– B:>95%	 **3f**	A:– B:90%
11	 **1k**	A:>95% B:>95%	 **3g**	A:78% B:64%
12	 **1l**	A:19% B:>95%	 **3h**	A:0% B:50%
13	 **1m**	A:9% B:>95%	 **3i**	A:0% B:74%
14	 **1n**	A:>95% B:>95%	 **3a**	A:41% B:82%
15	 **1o**	A:>95% B:>95%	 **3d**	A:80% B:92%
16	 **1p**	A:>95% B:>95%	 **3d**	A:93% B:87%
17	 **1q**	A:>95% B:>95%	 **3d**	A:83% B:89%
18	 **1r**	A:22% B:>85%	 **3d**	A:18% B:66%
19	 **1s**	A:>95% B:>95%	 **3j**	A:64% B:79%
20	 **1t**	A:– B:>95%	**3k**	A:– B:79%
21	**1u**	A:66% B:>95%	**3a**	A:63% B:89%
22	**1v**	A:10% B:>95%	**3e**	A:7% B:88%
23	**1w**	A:12% B:>95%	**3a**	A:0% B:32%

[a]Conditions A: $Co(acac)_2$ (25 mol %), Li(acac) (1.50 equiv), TBHP (1.00 equiv), Et_3SiH (5.00 equiv), CH_3OH (0.3 M), O_2, 24 °C. Conditions B: $Co(acac)_2$ (1.0 equiv), TBHP (1.0 equiv), Et_3SiH (5.0 equiv), CH_3OH (0.3 M), O_2, 24 °C. [b]Conversions determined by ^1H NMR spectroscopy using mesitylene as an internal standard. [c]Isolated yield after purification by flash column chromatography.

Scheme 3. Synthesis and Reaction of the Alkyl Hydroperoxide 6

Scheme 4. Proposed Mechanism

followed by hydrolysis on silica gel or reduction in situ, may then generate the observed product. The mechanism of oxidation of the vinyl boronate **1t** and the vinylsilanes **1u** and **1v** is likely to be distinct.

As further evidence of the near-neutral hydrolysis conditions, we prepared the enantiomerically enriched (*R*)-**1g** (94:6 er, Scheme 5). The yields of both conditions are comparable to those obtained with racemic **3d**, and no racemization of the allylic stereocenter was observed.

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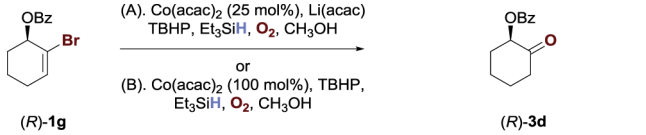
Scheme 5. Allylic Stereocenter Can Be Preserved during Formal Hydrolysis Process



(*R*)-**1g** (94:6 e.r.)

(*R*)-**3d** condition (A): 77% yield, 95:5 e.r. condition (B): 89% yield, 95:5 e.r.

Synthesis of Esters from *gem*-Dibromoalkenes. We then applied the optimized conditions to the transformation of *gem*-dihaloalkenes to esters (Table 3).[12] These substrates are readily accessible by Ramirez alkenylation of the corresponding aldehydes or ketones.[8b] The *gem*-dichloride **11a** and *gem*-dibromide **11b** both underwent formal hydrolysis to the methyl ester **12a** in 87−98% yield (entries 1 and 2). The *gem*-diiodide **11c** was also converted to **12a**, but the conversion was incomplete (41 or 54% conversion, 38 or 47% yield, entry 3). Though the *gem*-dichloroalkene **11a** transformed more efficiently than *gem*-dibromoalkene **11b**, the latter was preferred due to its ease of preparation. The formal hydrolysis conditions are compatible with a broad range of functional groups including methyl aryl ethers (entry 4, 85%), methyl benzoates (entry 5, 92%), aryl bromides (entry 6, 98%), nitrile substituents (entry 7, 91%), nitro substituents (entry 8, 96%), aryl boronic esters (entry 9, 51%), and trifluoromethyl groups (entry 10, 86%). The stoichiometric conditions appeared to be less sensitive to steric hindrance than the substoichiometric conditions (entry 11−13). The α-amino acid derivative **11n** can be transformed to the β-amino acid derivative **12l** in 82% yield (entry 14). The tetrasubstituted *gem*-dibromoalkene **11o** derived from the corresponding ketone was transformed to the ester **12m** in 89% yield (entry 15).

Interestingly, *gem*-dibromoalkenes **11d−m** derived from arylaldehydes can also be converted to the corresponding methyl esters **12b−k** under optimized conditions despite the fact that benzylic radical has been reported to be more stable than *gem*-dibromoalkyl radical.[13] We attribute this result to the steric hindrance created by the *gem*-dibromo group, which biases the first hydrogen atom transfer to the less-hindered benzylic position.

When conducted in different alcoholic solvents, the isopropyl ester **12n** and *tert*-butyl ester **12o** can both be accessed in 41−79% yield (Table 4, entry 1 and 2). The *gem*-dibromoalkene **11d** could also be transformed to the carboxylic acid **12p** with 71% yield when using tetrahydrofuran (THF) containing 10.0 equiv of water as the solvent.

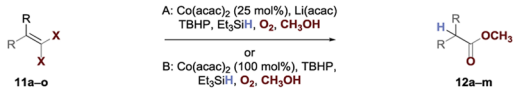
CONCLUSION

In summary, we have shown that in situ oxidation of alkylradical intermediates derived from heteroatom-functionalized alkenes provides access to ketones or esters from a broad range of starting materials. The methodology provides a simple alternative to the Tamao−Fleming oxidation of alkenyl silanes and the Arndt−Eistert homologation. This reaction constitutes a useful addition to the burgeoning area of alkene functionalization by hydrogen atom transfer.

EXPERIMENTAL SECTION

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) or neutral aluminum oxide (60 Å, 50−200 μm particle size). Alternatively, intermediates were purified using a Teledyne ISCO system, employing RediSep Rf High Performance Gold cartridges (RediSep Rf Gold Silica, 20−40 μm spherical). Samples were eluted using a flow rate of 12−50 mL/min, with detection by UV (254 nm). Analytical thin-layer chromatography (TLC) was performed using glass plates precoated

Table 3. Preliminary Scope of *gem*-Dihalides



entry	substrate	Product	yield[a]
1	**11a**	**12a**	A:92%[b] B:98%[c]
2	**11b**	**12a**	A:87%[b] B:88%[c]
3	**11c**	**12a**	A:47%[b,d] B:38%[c,e]
4	**11d**	**12b**	A:61%[b] B:85%[c]
5	**11e**	**12c**	A:86%[b] B:92%[c]
6	**11f**	**12d**	A:91%[b] B:98%[c]
7	**11g**	**12e**	A:91%[b] B:70%[c]
8	**11h**	**12f**	A:89%[b] B:96%[c]
9	**11i**	**12g**	A:0%[b] B:51%[c]
10	**11j**	**12h**	A:81%[b] B:86%[c]
11	**11k**	**12i**	A:0%[b] B:49%[c]
12	**11l**	**12j**	A:0%[b] B:77%[c]
13	**11m**	**12k**	A:0%[b] B:31%[c]
14	**11n**	**12l**	A:0%[b] B:82%[c]
15	**11o**	**12m**	A:83%[b] B:89%[c]

[a]Isolated yield after purification by flash column chromatography. [b]Conditions: $Co(acac)_2$ (25 mol %), Li(acac) (1.50 equiv), TBHP (1.00 equiv), Et_3SiH (5.00 equiv), CH_3OH (0.3 M), O_2, 24 °C. [c]Conditions: $Co(acac)_2$ (1.0 equiv), TBHP (1.0 equiv), Et_3SiH (5.0 equiv), CH_3OH (0.3 M), O_2, 24 °C. [d]46% of **1c** was recovered. [e]59% of **1c** was recovered.

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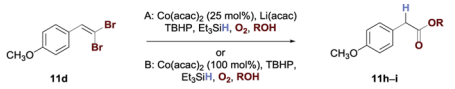
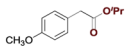
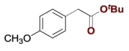
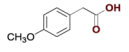
Table 4. Variation of the Nucleophilic Component



entry	product	yield[a]
1	 **12n**	A:41%[b] B:79%[c]
2	 **12o**	A:49%[b] B:68%[c]
3	 **12p**	A:32%[b,d] B:71%[c,d]

[a]Isolated yield after purification by flash column chromatography. [b]Conditions: $Co(acac)_2$ (25 mol %), Li(acac) (1.50 equiv), TBHP (1.00 equiv), Et_3SiH (5.00 equiv), ^{i}PrOH or ^{t}BuOH (0.3 M), O_2, 24 °C. [c]Conditions: $Co(acac)_2$ (1.0 equiv), TBHP (1.0 equiv), Et_3SiH (5.0 equiv), ^{i}PrOH or ^{t}BuOH (0.3 M), O_2, 24 °C. [d]Reaction conducted in THF (0.3 M) with H_2O (10.0 equiv).

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), acidic *p*-anisaldehyde solution (PAA), or aqueous potassium permanganate solution ($KMnO_4$), 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, dichloromethane, ether, and toluene were purified according to the method of Pangborn et al.[14] Pyridine was distilled from calcium hydride under an atmosphere of nitrogen immediately before use. Commercial anhydrous *N*,*N*-dimethylformamide was degassed by three freeze–pump–thaw cycles and stored over activated 4 Å MS under an atmosphere of nitrogen before use. Tetrahydrofuran 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. Methanol was distilled from magnesium 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-Dihydrobenzene 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,[15] 2-fluoro-2-propen-1-ol alcohol,[5f] 2-iodo-2-propen-1-ol alcohol,[16] 3-(4-methoxyphenyl)propanal,[17] 2-bromocyclohex-2-en-1-ol,[18] 2-((2-bromobenzyl)oxy)cyclohex-2-en-1-ol,[19] 4-*tert*-butylcyclohex-1-en-1-yl trifluoromethanesulfonate,[20] 4-oxocyclohexyl benzoate,[21] 2-(phenylthio)prop-2-en-1-ol,[22] 2-(phenylthio)cyclohex-2-en-1-ol,[23] 2-(phenylselanyl)cyclohex-2-en-1-one,[24] and 4-*tert*-butyl-1-chlorocyclohex-1-ene[25] were prepared according to published procedures. The concentration of *tert*-butyllithium in hexanes was determined by titration against a standard solution of diphenylacetic acid (average of three determinations).[26]

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H 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 ($CHCl_3$, δ 7.26; $CHDCl_2$, δ 5.32; C_6HD_5, 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 (^{13}C 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 ($CDCl_3$, δ 77.0; CD_2Cl_2, δ 54.0; C_6D_6, 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; ^{13}C 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 or 470 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from fluorotrichloromethane. Proton-decoupled phosphine nuclear magnetic resonance spectra (^{31}P NMR) were recorded at 200 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from trimethyl phosphate. Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were obtained using an 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 UPLC/HRMS instrument equipped with a photodiode array detector, a dual API/ESI ionizer and quadrupole time-of-flight (Q-TOF) mass detector. Unless otherwise noted, samples were eluted over a reversed-phase C18 column (1.7 μm particle size, 2.1 × 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 μL/min.

Synthetic Procedures. *Preparation of 2-Chloroallyl 4-Methoxybenzoate (**1a**).* 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 (**1a**) as a colorless oil (1.20 g, 98%): R_f = 0.52 (10% ethyl acetate–hexanes; UV, $KMnO_4$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, 2H, J = 9.0 Hz), 6.94 (d, 2H, J = 9.0 Hz), 5.55–5.53 (m, 1H), 5.45–5.42 (m, 1H), 4.87 (br s, 2H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.0 (C), 163.4 (C), 135.9 (C), 131.6 (CH), 121.5 (C), 114.4 (CH_2), 113.5 (CH), 65.8 (CH_2), 55.2 (CH_3). ^{1}H and ^{13}C NMR data for 2-chloroallyl 4-methoxybenzoate (**1a**) prepared in this way were in agreement with those previously described.[5f]

*Preparation of 2-Bromoallyl 4-Methoxybenzoate (**1b**).* 4-Methoxybenzoyl chloride (938 mg, 5.50 mmol, 1.10 equiv) was added dropwise via syringe to a solution of 2-bromo-2-propen-1-ol (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

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initially, grading to 10% ethyl acetate–hexanes, linear gradient) to afford 2-bromoallyl 4-methoxybenzoate (**1b**) as a colorless oil (1.26 g, 93%): R_f = 0.51 (20% ethyl acetate–hexanes; UV, $KMnO_4$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (d, 2H, J = 8.8 Hz), 6.96 (d, 2H, J = 8.8 Hz), 6.00 (br s, 1H), 5.70 (br s, 1H), 4.92 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 165.6 (C), 164.3 (C), 132.2 (CH), 127.2 (C), 122.4 (C), 119.3 (CH_2), 114.3 (CH), 68.1 (CH_2), 56.0 (CH_3); IR (ATR-FTIR), cm^{-1} 1714 (s), 1604 (s), 1510 (m), 1249 (s), 1165 (s); HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{11}H_{12}{}^{79/81}BrO_3$, 270.9970/272.9949, found 270.9975/272.9943.

*Preparation of 2-Fluoroallyl 4-Methoxybenzoate (**1c**).* 4-Methoxybenzoyl chloride (1.24 g, 7.24 mmol, 1.10 equiv) was added dropwise via syringe to a solution of 2-fluoro-2-propen-1-ol (500 mg, 6.58 mmol, 1 equiv) in pyridine (26 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-fluoroallyl 4-methoxybenzoate (**1c**) as a colorless oil (1.20 g, 86%): R_f = 0.52 (20% ethyl acetate–hexanes; UV, $KMnO_4$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 2H, J = 8.8 Hz), 6.92 (d, 2H, J = 8.8 Hz), 4.87–4.63 (m, 4H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (d, C, J = 188 Hz), 161.8 (C), 159.2 (C), 131.8 (CH), 121.8 (C), 113.7 (CH), 94.2 (d, CH_2, J = 170 Hz), 61.4 (d, CH_2, J = 340 Hz), 55.4 (CH_3); ^{19}F NMR (375 MHz, $CDCl_3$) δ −105.4; IR (ATR-FTIR), cm^{-1} 1715 (s), 1605 (s), 1511 (m), 1250 (s), 1166 (s); HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{11}H_{12}FO_3$, 211.0770, found 211.0776.

*Preparation of 2-Iodoallyl 4-Methoxybenzoate (**1d**).* 4-Methoxybenzoyl chloride (1.29 g, 7.58 mmol, 1.10 equiv) was added dropwise via syringe to a solution of freshly purified 2-iodo-2-propen-1-ol (1.27 g, 6.89 mmol, 1 equiv) in pyridine (28 mL) at 0 °C. The reaction vessel was covered with foil to exclude light. 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-iodoallyl 4-methoxybenzoate (**1d**) as a colorless oil (2.18 g, 98%): R_f = 0.53 (20% ethyl acetate–hexanes; UV, $KMnO_4$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (d, 2H, J = 8.8 Hz), 6.96 (d, 2H, J = 8.8 Hz), 6.43 (br s, 1H), 5.98 (br s, 1H), 4.88 (br s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 164.9 (C), 163.7 (C), 131.7 (CH), 127.0 (CH_2), 121.9 (C), 113.7 (CH), 102.8 (C), 70.8 (CH_2), 55.5 (CH_3); IR (ATR-FTIR), cm^{-1} 1713 (s), 1604 (s), 1510 (m), 1248 (s), 1165 (s); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{11}H_{11}INaO_3$ 340.9651, found 340.9659.

*Preparation of 1-(1-Bromovinyl)-4-methoxybenzene (**1e**).* This experiment was adapted from the work of Rovis and co-workers.[27] A solution of hydrobromic acid in acetic acid (33%, w/w, 1.00 mL) was added dropwise via syringe to 4-ethynylanisol (736 mg, 5.57 mmol, 1 equiv) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. The product mixture was transferred to a separatory funnel that had been charged with dichloromethane (100 mL). The diluted product mixture was washed with water (20 mL). The aqueous layer was isolated, and the isolated aqueous layer was extracted with dichloromethane (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 10% ether–hexanes, linear gradient) to afford 1-(1-bromovinyl)-4-methoxybenzene (**1e**) as a white solid (1.14 g, 96%): R_f = 0.15 (hexanes; UV, $KMnO_4$); mp 34–37 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.55 (d, 2H, J = 8.5 Hz), 6.89 (d, 2H, J = 8.5 Hz), 6.04 (br s, 1H), 5.69 (br s, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.4 (C), 131.0 (C), 130.6 (C), 128.6 (CH), 115.7 (CH_2), 113.5 (CH), 55.3 (CH_3). ^{1}H and ^{13}C NMR data for 1-(1-bromovinyl)-4-methoxybenzene (**1e**) prepared in this way were in agreement with those previously described.[27]

*Preparation of 1-(4,4-Dibromobut-3-en-1-yl)-4-methoxybenzene (**11b**).* Carbon tetrabromide (9.95 g, 30.0 mmol, 4.00 equiv) and zinc dust (1.96 g, 30.0 mmol, 4.00 equiv) were added sequentially to a solution of 3-(4-methoxyphenyl)propanal (1.23 g, 7.50 mmol, 1 equiv) in dichloromethane (90 mL) at 24 °C. Triphenylphosphine (7.87 g, 60.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 24 °C. The reaction mixture was stirred for 1 h at 24 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel and the pad was rinsed with 50% ether–pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with hexanes initially, grading to 10% ether–hexanes, linear gradient) to afford 1-(4,4-dibromobut-3-en-1-yl)-4-methoxybenzene (**11b**) as a white solid (2.19 g, 91%): R_f = 0.56 (5% ether–hexanes; UV, CAM); mp 33–36 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 2H, J = 8.4 Hz), 6.85 (d, 2H, J = 8.4 Hz), 6.42 (t, 1H, J = 7.2 Hz), 3.81 (s, 3H), 2.70 (t, 2H, J = 7.2 Hz), 2.43–2.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2 (C), 137.7 (CH), 132.6 (C), 129.3 (CH), 114.0 (CH), 89.3 (C), 55.3 (CH_3), 34.9 (CH_2), 33.0 (CH_2); IR (ATR-FTIR), cm^{-1} 2953 (w), 1511 (s), 1244 (s), 801 (m), 729 (s); HRMS-EI (m/z) $[M + H]^+$ calcd for $C_{11}H_{13}{}^{79}Br^{81}BrO$ 320.9313, found 320.9323.

*Preparation of (Z)-(2-Bromo-5-(4-methoxyphenyl)pent-2-en-1-yl)trimethylsilane (**1f**).* This experiment was adapted from the work of Uenishi and Ohmi.[28] A 50 mL round-bottomed flask that had been fused to a Teflon-coated valve was charged sequentially with 1-(4,4-dibromobut-3-en-1-yl)-4-methoxybenzene (**7b**, 368 mg, 1.15 mmol, 1 equiv) and dichloro(1,3-bis(diphenylphosphino)propane)nickel (62.3 mg, 115 μmol, 0.100 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated two times. Ether (20 mL) was added to the reaction vessel, and the resulting mixture was degassed by three freeze–pump–thaw cycles. A solution of (trimethylsilyl)methylmagnesium chloride in ether (1.00 M, 4.60 mL, 4.60 mmol, 4.00 equiv) was added dropwise via syringe to the reaction mixture. The reaction vessel was sealed, and the reaction mixture was stirred for 72 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 ammonium chloride 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 1% ether–hexanes initially, grading to 7% ether–hexanes, linear gradient) to afford (*Z*)-(2-bromo-5-(4-methoxyphenyl)pent-2-en-1-yl)trimethylsilane (**1f**) as a colorless oil (334 mg, 88%): R_f = 0.75 (10% ether–hexanes; UV, CAM); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.12 (d, 2H, J = 8.4 Hz), 6.82 (d, 2H, J = 8.4 Hz), 5.43 (t, 1H, J = 6.8 Hz), 3.77 (s, 3H), 2.64 (t, 2H, J = 7.8 Hz), 2.44–2.38 (m, 2H), 2.09 (br s, 2H), 0.07 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 157.9 (C), 133.7 (C), 129.2 (CH), 125.1 (C), 125.0 (CH), 113.6 (CH), 55.1 (CH_3), 33.9 (CH_2), 33.6 (CH_2), 32.6 (CH_2), −1.2 (CH_3); IR (ATR-FTIR), cm^{-1} 2952 (w), 1511 (s), 1244 (s), 839 (s); HRMS-EI (m/z) $[M + H]^+$ calcd for $C_{15}H_{24}{}^{79}BrOSi$ 327.0780, found 327.0779.

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*Preparation of 2-Bromocyclohex-2-en-1-yl Benzoate (**1g**).* Benzoyl chloride (310 mg, 2.20 mmol, 1.10 equiv) was added dropwise via syringe to a solution of 2-bromocyclohex-2-en-1-ol (354 mg, 2.00 mmol, 1 equiv) in pyridine (8.0 mL) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 5 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 20% ethyl acetate−hexanes, linear gradient) to afford 2-bromocyclohex-2-en-1-yl benzoate (**1g**) as a colorless oil (515 mg, 92%): R_f = 0.63 (20% ethyl acetate−hexanes; UV); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, 2H, J = 7.6 Hz), 7.57 (t, 1H, J = 7.4 Hz), 7.45 (t, 2H, J = 7.6 Hz), 6.41 (br s, 1H), 5.66 (br s, 1H), 2.29−2.19 (m, 1H), 2.17−2.01 (m, 3H), 1.83−1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (C), 135.4 (CH), 133.0 (CH), 130.1 (C), 129.7 (CH), 128.3 (CH), 119.9 (C), 71.8 (CH), 30.1 (CH_2), 27.6 (CH_2), 17.4 (CH_2); IR (ATR-FTIR), cm^{-1} 2948 (w), 1715 (s), 1264 (s), 1106 (m), 709 (s); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{13}H_{13}{}^{79/81}BrNaO_2$ 302.9997/304.9976, found 303.0001/304.9993. ^{1}H and ^{13}C NMR data for 2-bromocyclohex-2-en-1-yl benzoate (**1g**) prepared in this way were in agreement with those previously described.[5f]

*Preparation of (R)-2-Bromocyclohex-2-en-1-yl Benzoate [(**R**)-**1g**].* A 100 mL round-bottomed flask that had been fused to a Teflon-coated valve was charged with a solution of the (*S*)-Corey−Bakshi−Shibata catalyst in toluene (1.0 M, 0.297 mL, 297 μmol, 0.100 equiv). The solution was concentrated to dryness in vacuo. The residue obtained was dissolved in tetrahydrofuran (15 mL), and the resulting solution was cooled to −20 °C. A solution of borane dimethylsulfide complex (5.0 M, 1.19 mL, 5.94 mmol, 2.00 equiv) was added to the cooled solution, and the resulting clear, colorless mixture was stirred for 10 min at −20 °C. A solution of 2-bromocyclohex-2-en-1-one [520 mg, 2.97 mmol, 1 equiv; dried by azeotropic distillation with benzene (6.0 mL)] in tetrahydrofuran (12 mL) was then added dropwise via cannula to the cold catalyst solution. The flask containing 2-bromocyclohex-2-en-1-one was rinsed three times with tetrahydrofuran (1.0 mL), and the rinses were transferred to the reaction mixture via cannula. The reaction mixture was stirred for 12 h at −20 °C. Methanol (15 mL) was added slowly to the product mixture at −20 °C. The diluted product mixture was washed with saturated aqueous sodium chloride 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 suspended in dichloromethane (100 mL), and the product mixture was filtered through a pad of Celite. The pad was rinsed with dichloromethane (3 × 20 mL). The filtrates were combined, and the combined filtrate was concentrated to dryness. The (*R*)-2-bromocyclohex-2-en-1-ol prepared in this way was immediately used in the following step without further purification.

Benzoyl chloride (447 mg, 3.17 mmol, 1.10 equiv) was added dropwise via syringe to a solution of (*R*)-2-bromocyclohex-2-en-1-ol (nominally 2.88 mmol, 1 equiv) in pyridine (12 mL) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 5 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 20% ethyl acetate−hexanes, linear gradient) to afford (*R*)-2-bromocyclohex-2-en-1-yl benzoate [(***R***)-**1g**] as a colorless oil (661 mg, 79%, two steps). The enantiomeric ratio of (***R***)-**1g** was determined to be 94:6 by chiral stationary phase HPLC analysis (Chiralpak AD-H: 1% ethanol−hexanes, 24 °C, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 15.5 min, $t_{R(minor)}$ = 17.3 min).

^{1}H and ^{13}C NMR data for (*R*)-2-bromocyclohex-2-en-1-yl benzoate [(***R***)-**1g**] prepared in this way were in agreement with the racemic form.

*Preparation of 2-((2-Bromobenzyl)oxy)cyclohex-2-en-1-yl Benzoate (**1h**).* Benzoyl chloride (122 mg, 866 μmol, 1.05 equiv) was added dropwise via syringe to a solution of 2-((2-bromobenzyl)oxy)-cyclohex-2-en-1-ol (182 mg, 825 μmol, 1 equiv) in pyridine (3.3 mL) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred overnight 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 1% ether−hexanes initially, grading to 15% ether−hexanes, linear gradient) to afford 2-((2-bromobenzyl)oxy)cyclohex-2-en-1-yl benzoate (**1h**) as a colorless oil (315 mg, 98%): R_f = 0.33 (20% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.05 (d, 2H, J = 8.4 Hz), 7.56 (t, 1H, J = 7.4 Hz), 7.50 (d, 1H, J = 8.0 Hz), 7.46−7.41 (m, 3H), 7.24 (t, 1H, J = 7.6 Hz), 7.14−7.10 (m, 1H), 5.86 (t, 1H, J = 4.0 Hz), 5.09 (dd, 1H, J = 5.2, 3.2 Hz), 4.83 (s, 2H), 2.28−2.20 (m, 1H), 2.16−2.10 (m, 1H), 2.09−2.01 (m, 1H), 1.94−1.86 (m, 1H), 1.80−1.72 (m, 1H), 1.71−1.63 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 165.9 (C), 151.1 (C), 136.5 (C), 132.7 (CH), 132.3 (CH), 130.8 (C), 129.5 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 127.4 (CH), 122.0 (C), 101.4 (CH), 68.6 (CH), 68.1 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 18.2 (CH_2); IR (ATR-FTIR), cm^{-1} 2938 (w), 1714 (s), 1269 (s), 1109 (m), 710 (s); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{20}H_{19}{}^{79/81}BrNaO_3$ 409.0415/411.0395, found 409.0429/411.0388.

*Preparation of ((4-tert-Butylcyclohex-1-en-1-yl)oxy)benzene (**1i**).* This experiment was adapted from the work of Willis and co-workers.[29] A 25 mL round-bottomed flask that had been fused to a Teflon-coated valve was charged sequentially with phenol (197 mg, 2.10 mmol, 1.50 equiv), tris(dibenzylideneacetone)dipalladium (38.4 mg, 42.0 μmol, 0.03 equiv), JohnPhos (37.5 mg, 126 μmol, 0.09 equiv), and sodium *tert*-butoxide (235 mg, 2.45 mg, 1.75 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated two times. Toluene (10 mL) was added to the reaction vessel, and the resulting mixture was degassed by three freeze−pump−thaw cycles. 4-*tert*-Butylcyclohex-1-en-1-yl trifluoromethanesulfonate (400 mg, 1.40 mmol, 1 equiv) was added dropwise to the reaction vessel at 24 °C. The reaction vessel was sealed, and the sealed reaction vessel was placed in an oil bath that had been preheated to 100 °C. The reaction mixture was stirred and heated for 24 h at 100 °C. The product mixture was allowed to cool over 20 min to 24 °C. The cooled product mixture was filtered through a pad of Celite, and the pad was rinsed with hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography on neutral aluminum oxide (eluting with 3% ether−hexanes, isocratic gradient) to afford ((4-*tert*-butylcyclohex-1-en-1-yl)oxy)-benzene (**1i**) as a light yellow oil (235 mg, 73%): R_f = 0.23 (3% ether−hexanes; CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, 2H, J = 8.0 Hz), 7.04 (t, 1H, J = 7.4 Hz), 7.00−6.97 (m, 2H), 5.07−5.04 (m, 1H), 2.26−2.08 (m, 3H), 1.96−1.89 (m, 2H), 1.40−1.34 (m, 2H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9 (C), 152.2 (C), 128.7 (CH), 121.7 (CH), 117.8 (CH), 106.7 (CH), 43.4 (CH), 31.4 (C), 26.9 (CH_2) 26.4 (CH_3), 24.3 (CH_2), 23.5 (CH_2). ^{1}H and ^{13}C

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NMR data for ((4-*tert*-butylcyclohex-1-en-1-yl)oxy)benzene (**1i**) prepared in this way were in agreement with those previously described.[29]

*Preparation of Methyl 4-(1-Acetoxyvinyl)benzoate (**1j**).* This experiment was adapted from the work of Jacobi von Wangelin and co-workers.[30] A solution of methyl 4-acetylbenzoate (891 mg, 5.00 mmol, 1 equiv) in tetrahydrofuran (5 mL) was added dropwise via syringe over 30 min via syringe to a solution of lithium hexamethyldisilazide (920 mg, 5.50 mmol, 1.10 equiv) in tetrahydrofuran (10 mL) at −78 °C. The resulting mixture was stirred for 30 min at −78 °C. A solution of acetic anhydride (562 mg, 5.50 mmol, 1.10 equiv) in tetrahydrofuran (6 mL) was added dropwise via syringe over 15 min to the reaction mixture at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, and then the cold bath was removed. The reaction was stirred overnight 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 ammonium chloride 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 20% ethyl acetate−hexanes, isocratic gradient) to afford methyl 4-(1-acetoxyvinyl)benzoate (**1j**) as a white solid (978 mg, 89%): R_f = 0.31 (20% ethyl acetate−hexanes; UV, CAM). mp 69−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 2H, J = 7.2 Hz), 7.52 (d, 2H, J = 7.2 Hz), 5.58 (br s, 1H), 5.14 (br s, 1H), 3.91 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (C), 166.5 (C), 152.0 (C), 138.5 (C), 130.3 (C), 129.8 (CH), 124.8 (CH), 104.3 (CH_2), 52.2 (CH_3), 20.9 (CH_3). ^{1}H and ^{13}C NMR data for 4-(1-acetoxyvinyl)benzoate (**1j**) prepared in this way were in agreement with those previously described.[30]

*Preparation of Benzyl 4-(((Trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2H)-carboxylate (**1k**).* This experiment was adapted from the work of Patel and co-workers.[31] A solution of benzyl 4-oxopiperidine-1-carboxylate (1.17 g, 5.00 mmol, 1 equiv) in tetrahydrofuran (11 mL) was added dropwise via syringe over 10 min to a solution of lithium hexamethyldisilazide (920 mg, 5.50 mmol, 1.10 equiv) in tetrahydrofuran (22 mL) at −78 °C. The reaction mixture was stirred for 30 min at −78 °C. A solution of *N*-phenylbis(trifluoromethanesulfonimide) (1.96 g, 5.50 mmol, 1.10 equiv) in tetrahydrofuran (11 mL) was added dropwise via syringe over 10 min to the reaction mixture at −78 °C. The reaction mixture was stirred for 2 h at −78 °C, and then the cold bath was removed. The reaction was stirred for 2 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 ammonium chloride 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 20% ether−hexanes, isocratic gradient) to afford benzyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1k**) as a colorless oil (1.50 g, 95%): R_f = 0.24 (33% ether−hexanes; UV, $KMnO_4$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.31 (m, 5H), 5.77 (br s, 1H), 5.16 (s, 2H), 4.12 (br s, 2H), 3.71 (br s, 2H), 2.46 (br s, 2H); ^{19}F NMR (375 MHz, $CDCl_3$) δ −73.8. ^{1}H and ^{19}F NMR data for benzyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1k**) prepared in this way were in agreement with those previously described.[31]

*Preparation of tert-Butyl 4-((Diphenoxyphosphoryl)oxy)-3,6-dihydropyridine-1(2H)-carboxylate (**1l**).* This experiment was adapted from the work of Begtrup and co-workers.[32] A solution of potassium hexamethyldisilazide (1.21 g, 6.06 mmol, 1.27 equiv) in toluene (12 mL) was added dropwise via syringe over 15 min to a solution of *tert*-butyl 4-oxopiperidine-1-carboxylate (1.17 g, 5.00 mmol, 1 equiv), diphenyl chlorophosphate (1.21 mL, 5.82 mmol, 1.22 equiv), and hexamethylphosphoramide (1.18 mL, 6.77 mmol, 1.42 equiv) in tetrahydrofuran (20 mL) at −78 °C. The reaction mixture was stirred for 2 h at −78 °C, and then the cold bath was removed. The reaction was stirred for another 2 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 ammonium chloride 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 10% ether−hexanes initially, grading to 30% ether−hexanes, linear gradient) to afford *tert*-butyl 4-((diphenoxyphosphoryl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1l**) as a colorless oil (2.04 g, 82%): R_f = 0.24 (15% ether−hexanes; UV, $KMnO_4$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.36 (m, 4H), 7.25−7.22 (m, 6H), 5.56 (br s, 1H), 3.94 (br s, 2H), 3.55 (br s, 2H), 2.31 (br s, 2H), 1.44 (s, 9H); ^{31}P NMR (200 MHz, $CDCl_3$) δ −17.6. ^{1}H and ^{31}P NMR data for *tert*-butyl 4-((diphenoxyphosphoryl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1l**) prepared in this way were in agreement with those previously described.[32]

*Preparation of 4-((Triisopropylsilyl)oxy)cyclohex-3-en-1-yl Benzoate (**1m**).* This experiment was adapted from the work of Corey and co-workers.[33] Triisopropylsilyl trifluoromethanesulfonate (434 μL, 2.40 mmol, 1.20 equiv) was added dropwise via syringe to a solution of 4-oxocyclohexyl benzoate (437 mg, 2.00 mmol, 1 equiv) and trimethylamine (502 μL, 3.60 mmol, 1.80 equiv) in dichloromethane (6.0 mL) at 24 °C. The reaction mixture was stirred for 2 h at 24 °C. The product mixture was transferred to a separatory funnel that had been charged with ether (50 mL) and pentane (50 mL). The diluted product mixture was washed with saturated aqueous ammonium chloride solution (20 mL). The aqueous layer was isolated, and the isolated aqueous layer was extracted with ether (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% ether hexane, isocratic gradient) to afford 4-((triisopropylsilyl)oxy)cyclohex-3-en-1-yl benzoate (**1m**) as a colorless oil (749 mg, 98%): R_f = 0.83 (20% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, 2H, J = 6.8 Hz), 7.54 (t, 1H, J = 7.0 Hz), 7.42 (t, 2H, J = 7.6 Hz), 5.30−5.24 (m, 1H), 4.81−4.79 (m, 1H), 2.52−2.45 (m, 1H), 2.32−2.26 (m, 3H), 2.06−1.98 (m, 2H), 1.26−1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (C), 150.1 (C), 132.8 (CH), 130.7 (C), 129.6 (CH), 128.2 (CH), 99.6 (CH), 69.5 (CH), 29.4 (CH_2), 27.6 (CH_2), 27.1 (CH_2), 18.0 (CH_3), 12.6 (CH); IR (ATR-FTIR), cm^{-1} 2944 (w), 2866 (w), 1718 (s), 1274 (s), 1114 (m), 711 (m); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{22}H_{34}NaO_3Si$ 397.2175, found 397.2163.

*Preparation of 2-(Phenylthio)allyl 4-Methoxybenzoate (**1n**).* 4-Methoxybenzoyl chloride (210 mg, 1.23 mmol, 1.10 equiv) was added dropwise via syringe to a solution of 2-(phenylthio)prop-2-en-1-ol (186 mg, 1.12 mmol, 1 equiv) in pyridine (4.5 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 7.5% ethyl acetate−hexanes, isocratic gradient) to afford 2-(phenylthio)allyl 4-methoxybenzoate (**1n**) as a colorless oil (322 mg, 96%): R_f = 0.80 (30% ethyl acetate−hexanes; UV, CAM); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.00 (d, 2H, J = 8.0 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.38−7.20 (m, 3H), 6.95 (d, 2H, J = 8.0 Hz), 5.64 (br s, 1H), 5.36 (br s, 1H), 4.84 (br s, 2H), 3.86 (s, 3H);

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^{13}C NMR (100 MHz, CD_2Cl_2) δ 165.9 (C), 164.2 (C), 140.2 (C), 133.0 (C), 132.8 (CH), 132.2 (CH), 129.8 (CH), 128.4 (CH), 122.8 (C), 118.1 (CH_2), 114.2 (CH), 66.2 (CH_2), 56.0 (CH_3); IR (ATR-FTIR), cm^{-1} 2936 (w), 1714 (s), 1605 (s), 1510 (m), 1254 (s), 1167 (s), 1098 (s); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{17}H_{16}NaO_3S$ 323.0729, found 323.0718.

*Preparation of 2-((4-Chlorophenyl)thio)cyclohex-2-en-1-yl Benzoate (**1o**).* This experiment was adapted from the work of Fringuelli and co-workers.[34] An aqueous solution of sodium hydroxide (0.100 M, 0.600 mL, 60.0 μmol, 0.03 equiv) was added dropwise to a suspension of 4-chlorothiophenol (224 mg, 2.00 mmol, 1.00 equiv) in water (3.4 mL) at 30 °C. The resulting mixture was stirred for 5 min at 30 °C. 7-Oxabicyclo[4.1.0]heptan-2-one (198 μL, 2.00 mmol, 1 equiv) was added dropwise to the reaction mixture. The resulting mixture was stirred for 2 h at 30 °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 15% aqueous sodium hydroxide solution (6 × 20 mL). The organic layer was dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated. The 2-((4-chlorophenyl)thio)cyclohex-2-en-1-one prepared in this way was immediately used in the following step without further purification.

Cerium(III) chloride heptahydrate (553 mg, 1.49 mmol, 1.10 equiv) was added to a solution of 2-((4-chlorophenyl)thio)cyclohex-2-en-1-one (nominally, 1.35 mmol) in methanol (6.8 mL) at 0 °C. Sodium borohydride (51.1 mg, 1.35 mmol, 1.00 equiv) was added to the reaction mixture portionwise over 30 min at 0 °C. The resulting mixture was stirred for 1 h at 0 °C. Acetone (5 mL) was added dropwise via syringe, and the resulting mixture was stirred for 10 min at 0 °C. The product mixture was concentrated, the residue obtained was filtered through a pad of silica gel, and the pad was rinsed with ether (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The 2-((4-chlorophenyl)thio)cyclohex-2-en-1-ol prepared in this way was immediately used in the following step without further purification.

Benzoyl chloride (197 mg, 1.40 mmol, 1.05 equiv) was added dropwise via syringe to a solution of 2-((4-chlorophenyl)thio)-cyclohex-2-en-1-ol (nominally 1.33 mmol) in pyridine (5.3 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 hexanes initially, grading to 5% ethyl acetate−hexanes, linear gradient) to afford 2-((4-chlorophenyl)thio)cyclohex-2-en-1-yl benzoate (**1o**) as a colorless oil (388 mg, 57%, three steps): R_f = 0.71 (20% ethyl acetate−hexanes; UV, CAM); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.87 (d, 2H, J = 8.4 Hz), 7.58−7.53 (m, 1H), 7.41 (t, 2H, J = 7.6 Hz), 7.28−7.19 (m, 4H), 6.52 (t, 1H, J = 4.0 Hz), 5.53−5.51 (m, 1H), 2.41−2.30 (m, 1H), 2.29−2.21 (m, 1H), 2.06−1.99 (m, 1H), 1.96−1.88 (m, 1H), 1.85−1.69 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 165.5 (C), 141.9 (CH), 134.1 (C), 132.8 (CH), 132.4 (C), 131.4 (CH), 130.4 (C), 130.1 (C), 129.4 (CH), 128.9 (CH), 128.2 (CH), 69.5 (CH), 29.6 (CH_2), 27.1 (CH_2), 17.4 (CH_2); IR (ATR-FTIR), cm^{-1} 2945 (w), 1715 (s), 1475 (s), 1266 (s), 1108 (m), 817 (m), 710 (s); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{19}H_{17}{}^{35/37}ClNaO_2S$ 367.0535/369.0506, found 367.0539/369.0531.

*Preparation of 2-(Benzylthio)cyclohex-2-en-1-yl Benzoate (**1p**).* This experiment was adapted from the work of Fringuelli and co-workers.[34] An aqueous solution of sodium hydroxide (0.100 M, 0.600 mL, 60.0 μmol, 0.03 equiv) was added dropwise to a suspension of benzyl mercaptan (235 μL, 2.00 mmol, 1.00 equiv) in water (3.4 mL) at 30 °C. The reaction mixture was stirred for 5 min at 30 °C. 7-Oxabicyclo[4.1.0]heptan-2-one (198 μL, 2.00 mmol, 1 equiv) was added dropwise. The resulting mixture was stirred for 2 h at 30 °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 15% aqueous sodium hydroxide solution (6 × 20 mL). The organic layer was dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated. The 2-(benzylthio)cyclohex-2-en-1-one prepared in this way was immediately used in the following step without further purification.

Cerium(III) chloride heptahydrate (693 mg, 1.86 mmol, 1.10 equiv) was added to a solution of 2-(benzylthio)cyclohex-2-en-1-one (nominally, 1.69 mmol) in methanol (8.5 mL) at 0 °C. Sodium borohydride (63.9 mg, 1.69 mmol, 1.00 equiv) was added to the reaction mixture portionwise over 30 min at 0 °C. The resulting mixture was stirred for 1 h at 0 °C. Acetone (10 mL) was added dropwise via syringe, and the resulting mixture was stirred for 10 min at 0 °C. The product mixture was concentrated, the residue obtained was filtered through a pad of silica gel, and the pad was rinsed with ether (200 mL). The filtrates were combined, and the combined filtrates were concentrated. The 2-(benzylthio)cyclohex-2-en-1-ol prepared in this way was immediately used in the following step without further purification.

Benzoyl chloride (213 mg, 1.51 mmol, 1.05 equiv) was added dropwise via syringe to a solution of 2-(benzylthio)cyclohex-2-en-1-ol (nominally 1.44 mmol) in pyridine (5.8 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 2% ethyl acetate−hexanes initially, grading to 15% ethyl acetate−hexanes, linear gradient) to afford 2-(benzylthio)cyclohex-2-en-1-yl benzoate (**1p**) as a colorless oil (450 mg, 73%, three steps): R_f = 0.47 (15% ethyl acetate−hexanes; UV, CAM); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.05 (d, 2H, J = 8.4 Hz), 7.59−7.55 (m, 1H), 7.44 (t, 2H, J = 7.6 Hz), 7.28−7.20 (m, 5H), 6.04 (t, 1H, J = 4.2 Hz), 5.63−5.61 (m, 1H), 3.89 (q, 2H, J = 12.7 Hz), 2.24−2.06 (m, 1H), 2.03−2.01 (m, 1H), 2.00−1.97 (m, 1H), 1.92−1.87 (m, 1H), 1.85−1.61 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 165.8 (C), 137.8 (C), 134.7 (CH), 132.8 (CH), 130.8 (C), 130.6 (C), 129.5 (CH), 128.9 (CH), 128.3 (CH), 128.3 (CH), 126.9 (CH), 69.6 (CH), 37.2 (CH_2), 29.4 (CH_2), 26.7 (CH_2), 17.6 (CH_2); IR (ATR-FTIR), cm^{-1} 2942 (w), 1712 (s), 1452 (w), 1266 (s), 1108 (m), 710 (s); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{20}H_{20}NaO_2S$ 347.1082, found 347.1079.

*Preparation of 2-(Phenylsulfonyl)cyclohex-2-en-1-yl Benzoate (**1q**).* Benzoyl chloride (144 mg, 1.02 mmol, 1.05 equiv) was added dropwise via syringe to a solution of 2-(phenylthio)cyclohex-2-en-1-ol (200 mg, 969 μmol, 1 equiv) in pyridine (3.9 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 2-(phenylthio)cyclohex-2-en-1-yl benzoate prepared in this way was immediately used in the following step without further purification.

3-Chloroperoxybenzoic acid (70% purity, 567 mg, 2.30 mmol, 2.50 equiv) was added to a solution of 2-(phenylthio)cyclohex-2-en-1-yl benzoate (nominally 918 μmol) in dichloromethane (9.7 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 2 h at 24 °C. The

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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 30% ethyl acetate−hexanes, isocratic gradient) to afford 2-(phenylsulfonyl)cyclohex-2-en-1-yl benzoate (**1q**) as a white solid (296 mg, 89%, two steps): R_f = 0.54 (40% ethyl acetate−hexanes; UV, CAM); mp 135−136 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.74 (d, 2H, J = 8.0 Hz), 7.56 (t, 2H, J = 8.4 Hz), 7.52−7.48 (m, 2H), 7.35−7.27 (m, 5H), 5.95 (br s, 1H), 2.58−2.51 (m, 1H), 2.34−2.29 (m, 1H), 2.09−2.00 (m, 1H), 1.76−1.65 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 164.8 (C), 145.9 (CH), 140.5 (C), 138.3 (C), 132.9 (CH), 132.9 (CH), 129.7 (C), 129.4 (CH), 129.0 (CH), 128.0 (CH), 127.7 (CH), 63.7 (CH), 28.4 (CH_2), 26.0 (CH_2), 15.9 (CH_2); IR (ATR-FTIR), cm^{-1} 2951 (w), 1714 (s), 1447 (w), 1263 (s), 1148 (s), 1095 (m), 710 (s); HRMS-ESI (m/z) $[M + K]^+$ calcd for $C_{19}H_{18}KO_4S$, 381.0563, found 381.0559.

*Preparation of 2-(Phenylselanyl)cyclohex-2-en-1-yl Benzoate (**1r**).* Cerium(III) chloride heptahydrate (553 mg, 1.49 mmol, 1.10 equiv) was added to a solution of 2-(phenylselanyl)cyclohex-2-en-1-one (339 mg, 1.35 mmol, 1 equiv) in methanol (13.5 mL) at 0 °C. Sodium borohydride (51.1 mg, 1.35 mmol, 1.00 equiv) was added to the reaction mixture portionwise over 30 min at 0 °C. The resulting mixture was stirred for 1 h at 0 °C. Acetone (5 mL) was added dropwise via syringe, and the resulting mixture was stirred for 10 min at 0 °C. The product mixture was concentrated, the residue obtained was filtered through a pad of silica gel, and the pad was rinsed with ether (150 mL). The filtrates were combined, and the combined filtrates were concentrated. The 2-(phenylselanyl)cyclohex-2-en-1-ol prepared in this way was immediately used in the following step without further purification.

Benzoyl chloride (185 mg, 1.31 mmol, 1.05 equiv) was added dropwise via syringe to a solution of 2-(phenylselanyl)cyclohex-2-en-1-ol (nominally 1.25 mmol) in pyridine (5.0 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% ether−hexanes, isocratic gradient) to afford 2-(phenylselanyl)cyclohex-2-en-1-yl benzoate (**1r**) as a colorless oil (421 mg, 87%, two steps): R_f = 0.65 (20% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.90 (d, 2H, J = 8.0 Hz), 7.58−7.53 (m, 1H), 7.48−7.44 (m, 2H), 7.41 (t, 2H, J = 7.6 Hz), 7.27−7.22 (m, 3H), 6.52 (t, 1H, J = 4.0 Hz), 5.58−5.55 (m, 1H), 2.37−2.19 (m, 2H), 2.05−1.93 (m, 2H), 1.85−1.69 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 165.6 (C), 141.4 (CH), 132.7 (CH), 132.6 (CH), 130.5 (C), 130.3 (C), 129.5 (CH), 129.1 (CH), 128.2 (CH), 127.6 (C), 127.0 (CH), 70.9 (CH), 29.8 (CH_2), 27.6 (CH_2), 17.6 (CH_2); IR (ATR-FTIR), cm^{-1} 2943 (w), 1714 (s), 1451 (w), 1266 (s), 1108 (m), 710 (w); HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{18}NaO_2Se$ 381.0370, found 381.0373.

*Preparation of N-(4-Phenylbut-1-en-2-yl)acetamide (**1s**).* This experiment was adapted from the work of Reeves and co-workers.[35] A solution of ammonia in methanol (7.00 M, 2.14 mL, 15.0 mmol, 1.50 equiv) and titanium(IV) isopropoxide (5.92 mL, 20.0 mmol, 2.00 equiv) were added sequentially to a solution of 4-phenyl-2-butanone (1.50 mL, 10.0 mmol, 1 equiv) in toluene (6.0 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 resulted mixture was cooled again to 0 °C. Triethylamine (5.58 mL, 40.0 mmol, 4.00 equiv) and acetic anhydride (1.89 mL, 20.0 mmol, 2.00 equiv) were added sequentially to the cooled reaction mixture. The reaction mixture was stirred for 30 min at 0 °C, and then the ice bath was removed. The reaction mixture was stirred for 6 h at 24 °C. *N*,*N*,*N*′,*N*′-Tetrakis(2-hydroxyethyl)ethylenediamine (4.51 mL, 21.0 mmol, 2.10 equiv) was added dropwise to the product mixture. The resulting mixtue was placed in an oil bath that had been preheated to 55 °C. The product mixture was stirred and heated for 15 min at 55 °C. The product mixture was allowed to cool over 20 min to 24 °C. The cooled product mixture was transferred to a separatory funnel that had been charged with ethyl acetate (20 mL). The diluted product mixture was washed with 10% aqueous ammonium hydroxide solution (20 mL). The aqueous layer was isolated, and the isolated aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layer 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 10% ethyl acetate−hexanes initially, grading to 50% ethyl acetate−hexanes, linear gradient) to afford *N*-(4-phenylbut-1-en-2-yl)acetamide (**1s**) as a white solid (110 mg, 12%): R_f = 0.52 (40% ether−hexanes; UV, PAA). mp 86−90 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.32−7.26 (m, 2H), 7.23−7.19 (m, 3H), 6.84 (br s, 1H), 5.46 (s, 1H), 4.48 (s, 1H), 2.82 (t, 2H, J = 7.8 Hz), 2.46 (t, 2H, J = 7.8 Hz), 1.95 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 168.6 (C), 141.4 (C), 141.2 (C), 128.4 (CH), 128.3 (CH), 126.1 (CH), 98.2 (CH_2), 37.4 (CH_2). 34.4 (CH_2), 24.3 (CH_3). ^{1}H and ^{13}C NMR data for *N*-(4-phenylbut-1-en-2-yl)acetamide (**1s**) prepared in this way were in agreement with those previously described.[35]

*Preparation of 2-(Trimethylsilyl)allyl 4-Methoxybenzoate (**1u**).* A solution of *tert*-butyllithium in pentane (1.63 M, 3.42 mL, 5.59 mmol, 2.00 equiv) was added dropwise via syringe over 15 min to a solution of (1-bromovinyl)trimethylsilane (501 mg, 2.80 mmol, 1 equiv) in ether (10 mL) at −78 °C. The resulting mixture was stirred for 2.5 h at −78 °C. The cold mixture was transferred over 15 min via cannula to a suspension of paraformaldehyde (83.9 mg, 2.80 mmol, 1.00 equiv) in ether (5 mL) at −78 °C. The resulting mixture was allowed to warm to 24 °C over 15 min. The reaction mixture was stirred for 2.5 h at 24 °C. The product mixture was cooled to 0 °C, and water (5 mL) was added to quench the reaction. The resulting mixture was transferred to a separatory funnel that had been charged with pentane (10 mL). The diluted product mixture was washed with water (50 mL). The aqueous layer was isolated, and the isolated aqueous layer was extracted with ether (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 (150 Torr, 0 °C). The 2-(trimethylsilyl)prop-2-en-1-ol prepared in this way was immediately used in the following step.

4-Methoxybenzoyl chloride (525 mg, 3.08 mmol, 1.10 equiv) was added dropwise via syringe to a solution of freshly prepared 2-(trimethylsilyl)prop-2-en-1-ol (nominally 2.80 mmol) in pyridine (9 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 hexanes initially, grading to 20% ether−hexanes, linear gradient) to afford 2-(trimethylsilyl)allyl 4-methoxybenzoate (**1u**) as a colorless oil (491 mg, 66%, two steps): R_f = 0.52 (10% ether−hexanes; UV, $KMnO_4$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 2H, J = 7.6 Hz), 6.92 (d, 2H, J = 7.6 Hz), 5.87 (br s, 1H), 5.50 (br s, 1H), 4.92 (br s, 2H), 3.86 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (C), 163.3 (C), 146.7 (C), 131.6 (CH), 125.6 (CH_2), 122.7 (C), 113.6 (CH), 68.2 (CH_2), 55.4 (CH_3), −1.6 (CH_3); IR (ATR-FTIR), cm^{-1} 2955

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(w), 1711 (m), 1606 (m), 1251 (s), 1166 (s), 1098 (m), 837 (s); HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{14}H_{21}O_3Si$ 265.1260, found 265.1273.

*Preparation of (4-tert-Butylcyclohex-1-en-1-yl)trimethylsilane (**1v**).* This experiment was adapted from the work of Adam and Richter.[25] Chlorotrimethylsilane (3.43 mL, 27.0 mmol, 1.50 equiv) was added dropwise to a suspension of sodium (1.03 g, 45 mmol, 2.5 equiv) in toluene (36 mL) at 24 °C. The resulting mixture was stirred at 24 °C for 15 min. 4-*tert*-Butyl-1-chlorocyclohex-1-ene (3.12 mL, 18.0 mmol, 1 equiv) was added dropwise to the reaction mixture. The reaction vessel was placed in an oil bath that had been preheated to 115 °C. The reaction mixture was stirred and heated for 10 min at 115 °C. The reaction mixture was allowed to cool over 2 h to 24 °C. The cooled product mixture was filtered through a pad of silica gel, and the pad was rinsed with pentane (5 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by reduced pressure distillation (~50 °C, ~300 mTorr) to afford (4-*tert*-butylcyclohex-1-en-1-yl)trimethylsilane (**1v**) as colorless oil that solidifies at room temperature (757 mg, 20%): R_f = 0.81 (hexanes; $KMnO_4$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (br s, 1H), 2.21−2.16 (m, 1H), 2.11−2.01 (m, 2H), 1.87−1.79 (m, 2H), 1.29−1.22 (m, 1H), 1.14−1.06 (m, 1H), 0.86 (s, 9H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2 (C), 135.9 (CH), 44.0 (CH), 32.2 (C), 28.6 (CH_2), 28.4 (CH_2), 27.1 (CH_3), 24.3 (CH_2), −2.2 (CH_3). ^{1}H and ^{13}C NMR data for (4-(*tert*-butyl)cyclohex-1-en-1-yl)-trimethylsilane (**1v**) prepared in this way were in agreement with those previously described.[25]

*Preparation of Propargyl 4-Methoxybenzoate (**1w**).* 4-Methoxybenzoyl chloride (938 mg, 5.50 mmol, 1.10 equiv) was added dropwise via syringe to a solution of propargyl alcohol (280 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, isocratic gradient) to afford propargyl 4-methoxybenzoate (**1w**) as a white solid (955 mg, 96%): R_f = 0.49 (20% ethyl acetate−hexanes; UV, $KMnO_4$). mp 34−38 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 2H, J = 9.0 Hz), 6.92 (d, 2H, J = 9.0 Hz), 4.89 (br s, 2H), 3.87 (s, 3H), 2.51 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (C), 163.6 (C), 131.9 (CH), 121.7 (C), 113.7 (CH), 78.0 (C), 74.8 (CH), 55.4 (CH_3), 52.1 (CH_2). ^{1}H and ^{13}C NMR data for propargyl 4-methoxybenzoate (**1w**) prepared in this way were in agreement with those previously described.[36]

*Preparation of 1-(4,4-Dichlorobut-3-en-1-yl)-4-methoxybenzene (**11a**).* This experiment was adapted from the work of Ichikawa and co-workers.[37] Sodium trichloroacetate (1.06 g, 5.70 mmol, 1.50 equiv) was added portionwise to a solution of trichloroacetic acid (931 mg, 5.70 mmol, 1.50 equiv) and 3-(4-methoxyphenyl)propanal (624 mg, 3.80 mmol, 1 equiv) in *N*,*N*-dimethylformamide (5.5 mL) over 30 min at 24 °C. The reaction mixture was stirred for 4 h at 24 °C, and the resulting mixture was cooled to 0 °C. Acetic anhydride (718 μL, 7.60 mmol, 2.00 equiv) was added dropwise at 0 °C, and the reaction mixture was slowly warmed to 24 °C over 4 h. Acetic acid (5.0 mL) and zinc powder (497 mg, 7.60 mmol, 2.00 equiv) were added to the reaction mixture at 24 °C. The reaction vessel was placed in an oil bath that had been preheated to 60 °C. The reaction mixture was stirred and heated for 2 h at 60 °C. The product mixture was allowed to cool over 20 min to 24 °C. The cooled product mixture was filtered through a pad of Celite, and the pad was rinsed with hexanes (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 initially, grading to 5% ether−hexanes, linear gradient) to afford 1-(4,4-dichlorobut-3-en-1-yl)-4-methoxybenzene (**11a**) as a light yellow oil (480 mg, 55%): R_f = 0.56 (5% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, 2H, J = 8.4 Hz), 6.84 (d, 2H, J = 8.4 Hz), 5.86 (t, 1H, J = 7.2 Hz), 3.80 (s, 3H), 2.67 (t, 2H, J = 7.8 Hz), 2.48−2.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (C), 132.7 (C), 129.3 (CH), 129.0 (CH), 120.4 (C), 113.9 (CH), 55.3 (CH_3), 33.3 (CH_2), 31.5 (CH_2); IR (ATR-FTIR), cm^{-1} 2933 (w), 1613 (w), 1511 (s), 1245 (s), 1037 (m), 878 (m), 818 (m); HRMS-EI (m/z) $[M + Na]^+$ calcd for $C_{11}H_{12}Na^{35}Cl_2O$ 253.0163, found 253.0154.

*Preparation of 1-(4,4-Diiodobut-3-en-1-yl)-4-methoxybenzene (**11c**).* This experiment was adapted from the work of Charette and Cloarec.[38] Potassium *tert*-butoxide (525 mg, 4.68 mmol, 2.00 equiv) was added portionwise to a solution of iodoform (1.84 mg, 4.68 mmol, 2.00 equiv) and triphenylphosphine (1.23 g, 4.68 mmol, 2.00 equiv) in toluene (12 mL) over 30 min at −20 °C. The reaction mixture was stirred for 30 min at −20 °C. 3-(4-Methoxyphenyl)propanal (384 mg, 2.34 mmol, 1 equiv) was added dropwise at −20 °C, and the reaction mixture was stirred for 30 min at −20 °C. The product mixture was filtered through a pad of Celite, and the pad was rinsed with hexanes (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 initially, grading to 5% ether−hexanes, linear gradient) to afford 1-(4,4-diiodobut-3-en-1-yl)-4-methoxybenzene (**11c**) as a white solid (91.0 mg, 9%): R_f = 0.55 (5% ether−hexanes; UV, CAM). mp 52−56 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.11 (d, 2H, J = 8.0 Hz), 6.99 (t, 1H, J = 7.0 Hz), 6.84 (d, 2H, J = 8.0 Hz), 3.78 (s, 3H), 2.68 (t, 2H, J = 8.5 Hz), 2.24−2.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7 (C), 153.0 (CH), 133.1 (C), 129.8 (CH), 114.3 (CH), 55.7 (CH_3), 42.0 (CH_2), 33.0 (CH_2), 12.8 (C); IR (ATR-FTIR), cm^{-1} 2931 (w), 1611 (w), 1511 (s), 1246 (s), 1177 (m), 1035 (m), 828 (m); HRMS-EI (m/z) $[M + Na]^+$ calcd for $C_{11}H_{12}I_2NaO$ 436.8875, found 436.8862.

*Preparation of 1-(2,2-Dibromovinyl)-4-methoxybenzene (**11d**).* Carbon tetrabromide (3.32 g, 10.0 mmol, 2.00 equiv) was added to a solution of *p*-anisaldehyde (681 mg, 5.00 mmol, 1 equiv) in dichloromethane (12 mL) at 0 °C. Triphenylphosphine (5.25 g, 20.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with hexanes initially, grading to 5% ether−hexanes, linear gradient) to afford 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**) as an off-white solid (1.37 g, 94%): R_f = 0.57 (10% ether−hexanes; UV, CAM). mp 36−38 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, 2H, J = 8.8 Hz), 7.41 (s, 1H), 6.89 (d, 2H, J = 8.8 Hz), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (C), 136.3 (CH), 129.9 (CH), 127.8 (C), 113.8 (CH), 87.3 (C), 55.3 (CH_3). ^{1}H and ^{13}C NMR data for 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**) prepared in this way were in agreement with those previously described.[39]

*Preparation of Methyl 4-(2,2-Dibromovinyl)benzoate (**11e**).* Carbon tetrabromide (3.32 g, 10.0 mmol, 2.00 equiv) was added to a solution of methyl 4-formylbenzoate (821 mg, 5.00 mmol, 1 equiv) in dichloromethane (12 mL) at 0 °C. Triphenylphosphine (5.25 g, 20.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 2.5% ether−hexanes, isocratic gradient) to afford methyl 4-(2,2-dibromovinyl)benzoate (**11e**) as a white solid (1.37 g, 86%): R_f = 0.35 (10% ether−hexanes; UV). mp 67−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 2H, J = 8.4 Hz), 7.59 (d, 2H, J = 8.4 Hz), 7.51 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (C), 139.6 (C), 136.0 (CH), 129.8 (C), 129.6

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(CH), 128.3 (CH), 91.9 (C), 52.2 (CH_3). ^1H and ^{13}C NMR data for methyl 4-(2,2-dibromovinyl)benzoate (**11e**) prepared in this way were in agreement with those previously described.[40]

*Preparation of 1-Bromo-4-(2,2-dibromovinyl)benzene (**11f**).* Carbon tetrabromide (2.32 g, 7.00 mmol, 2.00 equiv) was added to a solution of 4-bromobenzaldehyde (648 mg, 3.50 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. Triphenylphosphine (3.67 g, 14.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 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-bromo-4-(2,2-dibromovinyl)benzene (**11f**) as an off-white solid (1.21 g, 95%): R_f = 0.76 (10% ether−hexanes; UV). mp 28−30 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, 2H, J = 8.4 Hz), 7.41−7.39 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7 (CH), 134.1 (C), 131.6 (CH), 129.9 (CH), 122.6 (C), 90.5 (C). ^1H and ^{13}C NMR data for 1-bromo-4-(2,2-dibromovinyl)benzene (**11f**) prepared in this way were in agreement with those previously described.[41]

*Preparation of 1-Cyano-4-(2,2-dibromovinyl)benzene (**11g**).* Carbon tetrabromide (2.32 g, 7.00 mmol, 2.00 equiv) was added to a solution of 4-cyanobenzaldehyde (459 mg, 3.50 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. Triphenylphosphine (3.67 g, 14.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 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-cyano-4-(2,2-dibromovinyl)benzene (**11g**) as an off-white solid (594 mg, 59%): R_f = 0.76 (10% ether−hexanes; UV); mp 82−86 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67−7.62 (m, 4H), 7.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6 (C), 135.2 (CH), 132.2 (CH), 128.9 (CH), 118.5 (C), 112.0 (C), 93.4 (C). ^1H and ^{13}C NMR data for 1-cyano-4-(2,2-dibromovinyl)benzene (**11g**) prepared in this way were in agreement with those previously described.[41]

*Preparation of 1-Nitro-4-(2,2-dibromovinyl)benzene (**11h**).* Carbon tetrabromide (2.32 g, 7.00 mmol, 2.00 equiv) was added to a solution of 4-nitrobenzaldehyde (529 mg, 3.50 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. Triphenylphosphine (3.67 g, 14.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 10% ether−hexanes, isocratic gradient) to afford 1-nitro-4-(2,2-dibromovinyl)benzene (**11h**) as a light yellow solid (563 mg, 58%): R_f = 0.70 (10% ether−hexanes; UV); mp 87−90 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, 2H, J = 8.8 Hz), 7.69 (d, 2H, J = 8.8 Hz), 7.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2 (C), 141.4 (C), 134.9 (CH), 129.2 (CH), 123.7 (CH), 94.1 (C). ^1H and ^{13}C NMR data for 1-nitro-4-(2,2-dibromovinyl)benzene (**11h**) prepared in this way were in agreement with those previously described.[41]

*Preparation of 2-(4-(2,2-Dibromovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11i**).* Carbon tetrabromide (1.16 g, 3.50 mmol, 2.00 equiv) was added to a solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (406 mg, 1.75 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. Triphenylphosphine (1.84 g, 7.00 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 2.5% ether−hexanes, isocratic gradient) to afford 2-(4-(2,2-dibromovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11i**) as an off-white solid (583 mg, 86%): R_f = 0.76 (10% ether−hexanes; UV); mp 34−35 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, 2H, J = 8.8 Hz), 7.53−7.50 (m, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.9 (C), 136.9 (CH), 134.8 (CH), 127.6 (C, CH), 90.4 (C), 83.9 (C), 24.9 (CH_3); IR (ATR-FTIR), cm^{-1} 2978 (w), 1608 (w), 1356 (s), 1142 (s), 1089 (s), 857 (m), 654 (m); HRMS-EI (m/z) $[M + Na]^+$ calcd for $C_{14}H_{17}B^{79}Br_2NaO_2$ 408.9586, found 408.9584.

*Preparation of 1-(2,2-Dibromovinyl)-4-(trifluoromethyl)benzene (**11j**).* Carbon tetrabromide (2.32 g, 7.00 mmol, 2.00 equiv) was added to a solution of 4-nitrobenzaldehyde (529 mg, 3.50 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. Triphenylphosphine (3.67 g, 14.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 10% ether−hexanes, isocratic gradient) to afford 1-(2,2-dibromovinyl)-4-(trifluoromethyl)benzene (**11j**) as a light yellow solid (869 mg, 75%): R_f = 0.73 (10% ether−hexanes; UV); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 4H), 7.51 (s, 1H). ^{19}F NMR (375 MHz, $CDCl_3$) δ −62.8. ^1H and ^{19}F NMR data for 1-(2,2-dibromovinyl)-4-(trifluoromethyl)benzene (**11j**) prepared in this way were in agreement with those previously described.[39]

*Preparation of 1-(2,2-Dibromovinyl)naphthalene (**11k**).* Carbon tetrabromide (2.32 g, 7.00 mmol, 2.00 equiv) was added to a solution of 1-naphthaldehyde (547 mg, 3.50 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. Triphenylphosphine (3.67 g, 14.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 10% ether−hexanes, isocratic gradient) to afford 1-(2,2-dibromovinyl)naphthalene (**11k**) as a light yellow solid (815 mg, 75%): R_f = 0.70 (10% ether−hexanes; UV); mp 45−47 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.87 (m, 4H), 7.63−7.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9 (CH), 133.5 (C), 133.2 (C), 130.7 (C), 128.9 (CH), 128.6 (CH), 126.8 (CH), 126.6 (CH), 126.2 (CH), 125.3 (CH), 124.2 (CH), 92.9 (C). ^1H and ^{13}C NMR data for 1-(2,2-dibromovinyl)naphthalene (**11k**) prepared in this way were in agreement with those previously described.[41]

*Preparation of 1-(2,2-Dibromovinyl)-2-iodobenzene (**11l**).* Carbon tetrabromide (2.32 g, 7.00 mmol, 2.00 equiv) was added to a solution of 1-naphthaldehyde (547 mg, 3.50 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. Triphenylphosphine (3.67 g, 14.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 10% ether−hexanes, isocratic gradient) to afford 1-(2,2-dibromovinyl)-2-iodobenzene (**11l**) as a light yellow oil (626 mg, 81%): R_f = 0.70 (10% ether−hexanes; UV); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, 1H, J = 8.0 Hz), 7.60 (d, 1H, J = 7.8 Hz), 7.41 (s, 1H), 7.37 (t, 1H, J = 7.8 Hz), 7.04 (t, 1H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8 (CH), 139.9 (C), 139.0 (CH), 130.0 (CH), 129.9 (CH), 128.0 (CH), 98.4 (C), 93.3 (C). ^1H and ^{13}C NMR data for 1-(2,2-dibromovinyl)-2-iodobenzene (**11l**)

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prepared in this way were in agreement with those previously described.[42]

*Preparation of 2-(2,2-Dibromovinyl)-1,3,5-trimethylbenzene (**11m**).* Carbon tetrabromide (2.32 g, 7.00 mmol, 2.00 equiv) was added to a solution of mesitaldehyde (516 μL, 3.50 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. Triphenylphosphine (3.67 g, 14.0 mmol, 4.00 equiv) was added portionwise to the reaction mixture over 1 h at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The product mixture was diluted sequentially with ether (200 mL) and pentane (200 mL). The diluted product mixture was filtered through a pad of silica gel, and the pad was rinsed with 50% ether−pentane (500 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 10% ether−hexanes, isocratic gradient) to afford 2-(2,2-dibromovinyl)-1,3,5-trimethylbenzene (**11m**) as a white solid (740 mg, 69%): R_f = 0.70 (10% ether−hexanes; UV); mp 53−54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 6.90 (s, 2H), 2.30 (s, 3H), 2.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8 (C), 137.5 (CH), 135.6 (C), 132.9 (C), 128.2 (CH), 92.7 (C), 21.1 (CH_3), 19.9 (CH_3). ^{1}H and ^{13}C NMR data for 2-(2,2-dibromovinyl)-1,3,5-trimethylbenzene (**11m**) prepared in this way were in agreement with those previously described.[43]

*Preparation of Benzyl (4,4-Dibromo-1-phenylbut-3-en-2-yl)-carbamate (**11n**).* Triphenylphosphine (2.62 g, 10.0 mmol, 4.00 equiv) was added portionwise to a solution of carbon tetrabromide (1.66 g, 5.00 mol, 2.00 equiv) in dichloromethane (15 mL) over 1 h at 0 °C. The ice bath was removed, and the resulting mixture was stirred for 1 h at 24 °C. The ylide solution was cooled to −78 °C and a solution of benzyl (1-oxo-3-phenylpropan-2-yl)carbamate (708 mg, 2.50 mmol, 1 equiv) in dichloromethane (5.0 mL) was added dropwise via syringe over 15 min at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, and the resulting mixture was allowed to warm 24 °C over 2 h. 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 water (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 30% ether−hexanes, isocratic gradient) to afford benzyl (4,4-dibromo-1-phenylbut-3-en-2-yl)carbamate (**11n**) as an off-white solid (599 mg, 64%): R_f = 0.23 (30% ether−hexanes; UV). mp 102−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.16 (m, 10H), 6.41 (br s, 1H), 5.08 (s, 2H), 4.91 (br s, 1H), 4.59−4.56 (m, 1H), 2.92−2.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.4 (C), 138.0 (CH), 136.2 (C), 136.1 (C), 129.5 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.0 (CH), 91.6 (C), 66.9 (CH_2), 54.9 (CH), 39.6 (CH_2); IR (ATR-FTIR), cm^{-1} 3363 (w), 1689 (s), 1523 (m), 1236 (m), 1021 (m), 706 (m); HRMS-EI (*m*/*z*) [M + Na]$^+$ calcd for $C_{18}H_{17}{}^{79}Br_2NNaO_2$ 459.9524, found 459.9557.

*Preparation of Benzyl 4-(1-Bromo-2,2-dimethylpropylidene)-piperidine-1-carboxylate (**11o**).* Triphenylphosphine (2.62 g, 10.0 mmol, 4.00 equiv) was added portionwise to a solution of carbon tetrabromide (1.66 g, 5.00 mol, 2.00 equiv) in dichloromethane (15 mL) over 1 h at 0 °C. The ice bath was removed, and the resulting mixture was stirred for 1 h at 24 °C. The ylide solution was cooled to −78 °C, and a solution of benzyl 4-oxopiperidine-1-carboxylate (583 mg, 2.50 mmol, 1 equiv) in dichloromethane (5.0 mL) was added dropwise via syringe over 15 min at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, and the resulting mixture was allowed to warm to 24 °C over 2 h. 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 water (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 10% ether−hexanes, isocratic gradient) to afford benzyl 4-(1-bromo-2,2-dimethylpropylidene)-piperidine-1-carboxylate (**11o**) as a light yellow oil (941 mg, 97%): R_f = 0.23 (10% ether−hexanes; UV); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.31 (m, 5H), 5.15 (s, 2H), 3.53 (t, 4H, *J* = 5.8 Hz), 2.50 (t, 4H, *J* = 5.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 155.1 (C), 140.1 (CH), 136.6 (C), 133.8 (C), 128.5 (CH), 127.9 (CH), 85.3 (C), 67.3 (CH_2), 43.3 (CH_2), 33.9 (CH_2); IR (ATR-FTIR), cm^{-1} 2903 (w), 1695 (s), 1422 (m), 1279 (m), 1213 (s), 1110 (m), 990 (m); HRMS-EI (*m*/*z*) [M + Na]$^+$ calcd for $C_{14}H_{15}{}^{79}Br_2NNaO_2$ 409.9367, found 409.9368.

*Hydrogenation of 2-Chloroallyl 4-Methoxybenzoate (**1a**, Scheme 2).* A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-chloroallyl 4-methoxybenzoate (**1a**, 56.7 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1 equiv). A 16-gauge needle was penetrated through the septum to maintain the reaction mixture under air (atmospheric pressure). *n*-Propanol (830 μL), 1,4-cyclohexadiene (119 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 (200 μL, 1.25 mmol, 5.00 equiv) were then 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, 40 min for **1a**). The product mixture was concentrated to dryness, and 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-chloropropyl 4-methoxybenzoate (**2**, colorless oil, 35.5 mg, 62%): 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), 6.93 (d, 2H, *J* = 9.0 Hz), 4.42−4.38 (m, 2H), 4.34−4.27 (m, 1H), 3.87 (s, 3H), 1.60 (d, 3H, *J* = 6.5 Hz); ^{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); IR (ATR-FTIR), cm^{-1} 2936 (w), 1712 (m), 1605 (m), 1252 (s), 1167 (s); HRMS-ESI (*m*/*z*) [M + H]$^+$ calcd for $C_{11}H_{14}{}^{35/37}ClO_3$ 229.0631/231.0602, found 229.0638/231.0614.

*Hydrogenation of 2-Chloroallyl 4-Methoxybenzoate (**1a**) in n-Propanol (Scheme 2).* A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-chloroallyl 4-methoxybenzoate (**1a**, 56.7 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1 equiv). A 16-gauge needle was penetrated through the septum to maintain the reaction mixture under air (atmospheric pressure). *n*-Propanol (830 μL), a solution of *tert*-butyl hydroperoxide in nonane (∼5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (200 μL, 1.25 mmol, 5.00 equiv) were then 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, 40 min for **1a**). The product mixture was concentrated to dryness, and 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-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 24.6 mg, 47%).

Condition Optimization for Hydrolysis (Table 1, Entry 1). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 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), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (∼5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C until the consumption of **1b** was complete (as determined by TLC analysis, 3.5 h for **1b**). The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% 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 an 8% yield of 2,2-dibromopropyl 4-methoxybenzoate (**4**). The NMR sample was concentrated to dryness, and the residue obtained was purified by automated flash column chromatography (eluting with 2% ethyl

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acetate−hexanes initially, grading to 40% ethyl acetate−hexanes, linear gradient) to afford 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 35.4 mg, 68%). 2-Oxopropyl 4-methoxybenzoate (**3a**): R_f = 0.27 (20% ethyl acetate−hexanes; UV); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (d, 2H, J = 8.8 Hz), 6.96 (d, 2H, J = 8.8 Hz), 4.83 (s, 2H), 3.86 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 202.2 (C), 165.9 (C), 164.4 (C), 132.3 (CH), 122.2 (C), 114.3 (CH), 69.1 (CH_2), 56.1 (CH_3), 26.5 (CH_3); IR (ATR-FTIR), cm^{-1} 2937 (w), 1714 (s), 1606 (m), 1256 (s), 1167 (m); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{11}H_{12}NaO_4$ 231.0633, found 231.0632.

Condition Optimization for Hydrolysis (Table 1, Entry 2). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 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*,*N*-Dimethylformamide (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C until the consumption of **1b** was complete (as determined by TLC analysis, 3 h for **1b**). The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% 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 3% yield of 2,2-dibromopropyl 4-methoxybenzoate (**4**). The NMR sample was concentrated to dryness, and the residue obtained was purified by automated flash column chromatography (eluting with 2% ethyl acetate−hexanes initially, grading to 40% ethyl acetate−hexanes, linear gradient) to afford separately 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 39.5 mg, 76%) and 2-bromopropyl 4-methoxybenzoate (**5**, cleaer oil, 6.8 mg, 10%). 2-Bromopropyl 4-methoxybenzoate (**5**): R_f = 0.45 (20% ethyl acetate−hexanes; UV); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.01 (d, 2H, J = 9.0 Hz), 6.95 (d, 2H, J = 9.0 Hz), 4.49−4.35 (m, 3H), 3.86 (s, 3H), 1.77 (d, 3H, J = 6.5 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 166.0 (C), 164.3 (C), 132.2 (CH), 122.7 (C), 114.3 (CH), 69.5 (CH_2), 56.1 (CH_3), 46.1 (CH), 23.0 (CH_3); IR (ATR-FTIR), cm^{-1} 2931 (w), 1714 (m), 1605 (m), 1254 (s), 1167 (s); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{11}H_{13}{}^{79/81}BrNaO_3$ 294.9946/296.9925, found 294.9944/296.9909.

Condition Optimization for Hydrolysis (Table 1, Entry 3). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.25 equiv). A 16-gauge needle was penetrated through the septum. *N*,*N*-Dimethylformamide (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% 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 48% yield of 2-bromoallyl 4-methoxybenzoate (**1b**) and a 46% yield of 2-oxopropyl 4-methoxybenzoate (**3a**).

Condition Optimization for Hydrolysis (Table 1, Entry 4). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.25 equiv). A 16-gauge needle was penetrated through the septum. *N*,*N*-Dimethylformamide (830 μL), isoamylene (132 μL, 1.25 mmol, 5.00 equiv), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% 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 45% yield of 2-bromoallyl 4-methoxybenzoate (**1b**) and a 41% yield of 2-oxopropyl 4-methoxybenzoate (**3a**).

Condition Optimization for Hydrolysis (Table 1, Entry 5). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 mg, 250 μmol, 1 equiv), lithium acetylacetoante (39.8 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.25 equiv). A 16-gauge needle was penetrated through the septum. *N*,*N*-Dimethylformamide (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% 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 an 84% yield of 2-bromoallyl 4-methoxybenzoate (**1b**) and a 15% yield of 2-oxopropyl 4-methoxybenzoate (**3a**).

Condition Optimization for Hydrolysis (Table 1, Entry 6). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 mg, 250 μmol, 1 equiv), lithium acetylacetonate (39.8 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.25 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C until the consumption of **1b** was complete (as determined by TLC analysis, 24 h for **1b**). The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 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−hexane initially, grading to 40% ethyl acetate−hexanes, linear gradient) to afford 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 42.2 mg, 81%).

Condition Optimization for the Hydrolysis (Table 1, Entry 7). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 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 dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C until the consumption of **1b** was complete (as determined by TLC analysis, 12 h for **1b**). The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 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−hexane initially, grading to 40% ethyl acetate−hexanes, linear gradient) to afford 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 44.3 mg, 85%).

Condition Optimization for Hydrolysis (Table 1, Entry 8). This experiment was adapted from the work of Mukaiyama and co-workers.[44] A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (6.4 mg, 25 μmol, 0.100 equiv). The reaction vessel was evacuated and refilled

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using a balloon of dioxygen. This process was repeated two times. Tetrahydrofuran (1.25 mL) and phenylsilane (154 μL, 1.25 mmol, 5.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 24 h at 24 °C. The product mixture was concentrated to dryness, and the residue obtained was filtered through a short column of silica gel and the short column was rinsed with 50% 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 38% yield of 2-bromoallyl 4-methoxybenzoate (**1b**). The residue obtained was purified by automated flash column chromatography (eluting with 5% ethyl acetate−hexane initially, grading to 40% ethyl acetate−hexanes, linear gradient) to afford separately 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 10.4 mg, 20%) and 2,2-dibromopropyl 4-methoxybenzoate (**4**, colorless oil, 34.4 mg, 39%). 2,2-Dibromopropyl 4-methoxybenzoate (**4**): R_f = 0.43 (20% ethyl acetate−hexanes; UV); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.05 (d, 2H, J = 8.5 Hz), 6.97 (d, 2H, J = 8.5 Hz), 4.75 (s, 2H), 3.87 (s, 3H), 2.56 (s, 3H); ^{13}C 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]$^+$ calcd for $C_{11}H_{13}{}^{79/81}Br_2O_3$ 350.9231/352.9211/354.9191, found 350.9240/352.9212/354.9185.

Representative Formal Hydrolysis Procedure A (Tables 2−4). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with the substrate (250 μmol, 1 equiv), lithium acetylacetoante (39.8 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.25 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C until the consumption of substrate was complete (as determined by TLC analysis). The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. Conversions were judged based on ^{1}H NMR analyses of the unpurified product mixtures using mesitylene as an internal standard. The NMR sample was concentrated to dryness. The residue obtained was purified by automated flash column chromatography to afford the hydrolysis product.

Representative Formal Hydrolysis Procedure B (Tables 2−4). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with the 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 dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C until the consumption of substrate was complete (as determined by TLC analysis). The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. Conversions were judged based on ^{1}H NMR analyses of the unpurified product mixtures using mesitylene as an internal standard. The NMR sample was concentrated to dryness. The residue obtained was purified by automated flash column chromatography to afford the hydrolysis product.

*Hydrolysis of 2-Fluoroallyl 4-Methoxybenzoate (**1c**; Table 2, Entry 1).* Following general procedure A using 2-fluoroallyl 4-methoxybenzoate (**1c**, 52.6 mg, 250 μmol, 1 equiv). Reaction time was 24 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 33% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 51.5 mg, 99%).

Following general procedure B using 2-fluoroallyl 4-methoxybenzoate (**1c**, 52.6 mg, 250 μmol, 1 equiv). Reaction time was 36 h. Purification by automated flash column chromatography (eluting with 10% ethyl acetate−hexanes initially, grading to 40% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 51.6 mg, 99%).

*Hydrolysis of 2-chloroallyl 4-methoxybenzoate (**1a**; Table 2, entry 2).* Following the general procedure A using 2-chloroallyl 4-methoxybenzoate (**1a**, 56.7 mg, 250 μmol, 1 equiv). Reaction time was 24 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 33% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 47.7 mg, 92%).

Following general procedure B using 2-chloroallyl 4-methoxybenzoate (**1a**, 56.7 mg, 250 μmol, 1 equiv). Reaction time was 48 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 33% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 47.1 mg, 89%).

*Hydrolysis of 2-Bromoallyl 4-Methoxybenzoate (**1b**; Table 2, Entry 3).* Following general procedure A using 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 mg, 250 μmol, 1 equiv). Reaction time was 24 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 40% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 42.2 mg, 81%).

Following general procedure B using 2-bromoallyl 4-methoxybenzoate (**1b**, 67.8 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 40% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 44.3 mg, 85%).

*Hydrolysis of 2-Iodoallyl 4-Methoxybenzoate (**1d**; Table 2, Entry 4).* Following general procedure A using 2-iodoallyl 4-methoxybenzoate (**1d**, 79.5 mg, 250 μmol, 1 equiv). The reaction vessel was covered with foil to exclude light. Reaction time was 60 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 33% ethyl acetate−hexanes, linear gradient) afforded separately 2-iodoallyl 4-methoxybenzoate (**1d**, colorless oil, 12.0 mg, 15%) and 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 32.8 mg, 63%).

Following general procedure B using 2-iodoallyl 4-methoxybenzoate (**1d**, 79.5 mg, 250 μmol, 1 equiv). The reaction vessel was covered with foil to exclude light. Reaction time was 60 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 33% ethyl acetate−hexanes, linear gradient) afforded separately 2-iodoallyl 4-methoxybenzoate (**1d**, colorless oil, 43.7 mg, 55%) and 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 20.9 mg, 40%).

*Hydrolysis of 1-(1-Bromovinyl)-4-methoxybenzene (**1e**; Table 2, entry 5).* Following general procedure A using 1-(1-bromovinyl)-4-methoxybenzene (**1e**, 53.3 mg, 250 μmol, 1 equiv). The reaction vessel was covered with foil to exclude light. Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 15% ether−hexanes, isocratic gradient) afforded 1-(4-methoxyphenyl)-ethan-1-one (**3b**, white solid, 33.0 mg, 88%).

Following general procedure B using 1-(1-bromovinyl)-4-methoxybenzene (**1e**, 53.3 mg, 250 μmol, 1 equiv). The reaction vessel was covered with foil to exclude light. Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 15% ether−hexanes, isocratic gradient) afforded 1-(4-methoxyphenyl)ethan-1-one (**3b**, white solid, 29.1 mg, 78%): R_f = 0.31 (20% ether−hexanes; UV, PAA). mp 37−38 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, 2H, J = 8.8 Hz), 6.87 (d, 2H, J = 8.8 Hz), 3.81 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7 (C), 163.4 (C), 130.5 (CH), 130.3 (C), 113.6 (CH), 55.4 (CH_3), 26.3 (CH_3). ^{1}H and ^{13}C NMR data for 1-(4-methoxyphenyl)ethan-1-one (**3b**) prepared in this way were in agreement with those previously described.[45]

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*Hydrolysis of (Z)-(2-Bromo-5-(4-methoxyphenyl)pent-2-en-1-yl)-trimethylsilane (**1f**; Table 2, entry 6).* Following general procedure A using (*Z*)-(2-bromo-5-(4-methoxyphenyl)pent-2-en-1-yl)-trimethylsilane (**1f**, 81.8 mg, 250 μmol, 1 equiv). Reaction time was 12 h; ^{1}H NMR analysis of the unpurified product mixture revealed a complex mixture of unidentified decomposition products.

Following general procedure B using (*Z*)-(2-bromo-5-(4-methoxyphenyl)pent-2-en-1-yl)trimethylsilane (**1f**, 81.8 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 15% ether−hexanes, isocratic gradient) afforded 1-hydroxy-5-(4-methoxyphenyl)pentan-2-one (**3c**, colorless oil, 26.3 mg, 50%): R_f = 0.10 (20% ethyl acetate−hexanes; UV, CAM); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.10 (d, 2H, *J* = 8.8 Hz), 6.83 (d, 2H, *J* = 8.4 Hz), 4.18 (d, 2H, *J* = 4.4 Hz), 3.77 (s, 3H), 3.01 (t, 1H, *J* = 4.8 Hz), 2.58 (t, 2H, *J* = 7.6 Hz), 2.40 (t, 2H, *J* = 7.6 Hz), 1.95−1.87 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 209.7 (C), 158.0 (C), 133.3 (C), 129.3 (CH), 113.7 (CH), 68.0 (CH_2), 55.1 (CH_3), 37.4 (CH_2), 34.0 (CH_2), 25.3 (CH_2); IR (ATR-FTIR), cm^{-1} 3483 (w), 2929 (m), 1721 (s), 1513 (s), 1246 (s), 1123 (m), 1073 (m); HRMS-ESI (*m*/*z*) $[M + Na]^+$ calcd for $C_{12}H_{16}NaO_3$ 231.0997, found 231.0989.

*Hydrolysis of 2-Bromocyclohex-2-en-1-yl Benzoate (**1g**; Table 2, Entry 7).* Following general procedure A using 2-bromocyclohex-2-en-1-yl benzoate (**1g**, 70.3 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 43.8 mg, 80%).

Following general procedure B using 2-bromocyclohex-2-en-1-yl benzoate (**1g**, 70.3 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 49.5 mg, 91%): R_f = 0.41 (20% ethyl acetate−hexanes; UV, CAM); mp 67−72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, 2H, *J* = 7.5 Hz), 7.57 (t, 1H, *J* = 7.5 Hz), 7.45 (t, 2H, *J* = 8.0 Hz), 5.41 (dd, 1H, *J* = 12.3, 6.2 Hz), 2.59−2.55 (m, 1H), 2.50−2.41 (m, 2H), 2.15−2.11 (m, 1H), 2.05−2.03 (m, 1H), 1.96−1.90 (m, 1H), 1.88−1.80 (m, 1H), 1.74−1.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2 (C), 165.5 (C), 133.1 (CH), 129.8 (CH), 129.6 (C), 128.3 (CH), 76.9 (CH), 40.7 (CH_2), 33.1 (CH_2), 27.1 (CH_2), 23.7 (CH_2). ^{1}H and ^{13}C NMR data for 2-oxocyclohexyl benzoate (**3d**) prepared in this way were in agreement with those previously described.[46]

*Hydrolysis of 2-((2-Bromobenzyl)oxy)cyclohex-2-en-1-yl Benzoate (**1h**; Table 2, Entry 8).* Following general procedure A using 2-((2-bromobenzyl)oxy)cyclohex-2-en-1-yl benzoate (**1h**, 96.8 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 33.3 mg, 61%).

Following general procedure B using 2-((2-bromobenzyl)oxy)-cyclohex-2-en-1-yl benzoate (**1h**, 96.8 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 40.1 mg, 73%).

*Hydrolysis of ((4-tert-Butylcyclohex-1-en-1-yl)oxy)benzene (**1i**; Table 2, Entry 9).* Following general procedure A using ((4-*tert*-butylcyclohex-1-en-1-yl)oxy)benzene (**1i**, 57.6 mg, 250 μmol, 1 equiv). Reaction time was 48 h. Purification by automated flash column chromatography on neutral aluminum oxide (eluting with 5% ether−hexanes, isocratic gradient) recovered ((4-(*tert*-butyl)cyclohex-1-en-1-yl)oxy)benzene (**1i**, colorless oil, 40.8 mg, 71%).

Following general procedure B using ((4-*tert*-butylcyclohex-1-en-1-yl)oxy)benzene (**1i**, 57.6 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 15% ethyl acetate−hexanes, isocratic gradient) afforded 4-*tert*-butylcyclohexan-1-one (**3e**, white solid, 18.2 mg, 47%): R_f = 0.59 (20% ethyl acetate−hexanes; UV, I_2). mp 38−41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38−2.23 (m, 4H), 2.08−2.02 (m, 2H), 1.46−1.38 (m, 3H), 0.88 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.5 (C), 46.7 (CH), 41.3 (CH_2), 32.4 (C), 27.6 (CH_2, CH_3). ^{1}H and ^{13}C NMR data for 4-*tert*-butylcyclohexan-1-one (**3e**) prepared in this way were in agreement with those previously described.[47]

*Hydrolysis of methyl 4-(1-acetoxyvinyl)benzoate (**1j**; Table 2, Entry 10).* Following general procedure B using methyl 4-(1-acetoxyvinyl)benzoate (**1j**, 55.1 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 12% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded methyl 4-acetylbenzoate (**3f**, white solid, 40.3 mg, 90%): R_f = 0.45 (20% ethyl acetate−hexanes; UV). mp 82−84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 2H, *J* = 8.0 Hz), 7.90 (d, 2H, *J* = 8.0 Hz), 3.93 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5 (C), 166.2 (C), 140.2 (C), 133.9 (C), 129.8 (CH), 128.2 (CH), 52.4 (CH_3), 26.9 (CH_3). ^{1}H and ^{13}C NMR data for methyl 4-acetylbenzoate (**3f**) prepared in this way were in agreement with those previously described.[48]

*Hydrolysis of Benzyl 4-(((Trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2H)-carboxylate (**1k**; Table 2, Entry 11).* Following general procedure A using benzyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1k**, 91.3 mg, 250 μmol, 1 equiv). Reaction time was 60 h. Purification by automated flash column chromatography on neutral aluminum oxide (eluting with 20% ethyl acetate−hexanes, isocratic gradient) afforded benzyl 4-oxopiperidine-1-carboxylate (**3g**, colorless oil, 46.0 mg, 78%).

Following general procedure B using benzyl 4-(((trifluoromethyl)-sulfonyl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1k**, 91.3 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 20% ethyl acetate−hexanes, isocratic gradient) afforded benzyl 4-oxopiperidine-1-carboxylate (**3g**, colorless oil, 37.3 mg, 64%): R_f = 0.59 (20% ethyl acetate−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.30 (m, 5H), 5.16 (br s, 2H), 3.77 (t, 4H, *J* = 6.4 Hz), 2.43 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1 (C), 155.1 (C), 136.3 (C), 128.6 (CH), 128.2 (CH), 128.0 (CH), 67.6 (CH_2), 43.1 (CH_2), 41.0 (CH_2). ^{1}H and ^{13}C NMR data for benzyl 4-oxopiperidine-1-carboxylate (**3g**) prepared in this way were in agreement with those previously described.[49]

*Hydrolysis of Benzyl tert-Butyl 4-((Diphenoxyphosphoryl)oxy)-3,6-dihydropyridine-1(2H)-carboxylate (**1l**; Table 2, Entry 12).* Following general procedure A using *tert*-butyl 4-((diphenoxyphosphoryl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1l**, 107 mg, 250 μmol, 1 equiv). Reaction time was 60 h. Purification by automated flash column chromatography (eluting with 20% ether−hexanes, isocratic gradient) recovered *tert*-butyl 4-((diphenoxyphosphoryl)-oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1l**, colorless oil, 87.8 mg, 81%).

Following general procedure B using *tert*-butyl 4-((diphenoxyphosphoryl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1l**, 107 mg, 250 μmol, 1 equiv). Reaction time was 36 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 33% ether−hexanes, linear gradient) afforded *tert*-butyl 4-oxopiperidine-1-carboxylate (**3h**, white solid, 24.9 mg, 50%): R_f = 0.24 (20% ethyl acetate−hexanes; UV, CAM). mp 64−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (t, 4H, *J* = 6.2 Hz), 2.40 (t, 4H, *J* = 6.2 Hz), 1.45 (s, 9H_1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7 (C), 154.4 (C), 80.3 (CH_2), 43.0 (C), 41.1 (CH_2), 28.3 (CH_3). ^{1}H and ^{13}C NMR data for *tert*-butyl 4-oxopiperidine-1-carboxylate (**3h**) prepared in this way were in agreement with those previously described.[50]

*Hydrolysis of 4-((Triisopropylsilyl)oxy)cyclohex-3-en-1-yl Benzoate (**1m**; Table 2, Entry 13).* Following general procedure A using 4-((triisopropylsilyl)oxy)cyclohex-3-en-1-yl benzoate (**1m**, 93.7 mg, 250 μmol, 1 equiv). Reaction time was 60 h. Purification by automated flash column chromatography (eluting with 5% ether−hexanes, isocratic gradient) recovered 4-((triisopropylsilyl)oxy)cyclohex-3-en-1-yl benzoate (**1m**, colorless oil, 85.2 mg, 91%).

Following general procedure B using 4-((triisopropylsilyl)oxy)-cyclohex-3-en-1-yl benzoate (**1m**, 93.7 mg, 250 μmol, 1 equiv). Reaction time was 24 h. Purification by automated flash column chromatography (eluting with 20% ethyl acetate−hexanes, isocratic

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gradient) afforded 4-oxocyclohexyl benzoate (**3i**, white solid, 40.4 mg, 74%): R_f = 0.31 (20% ethyl acetate−hexanes; UV, CAM). mp 45−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, 2H, J = 7.6 Hz), 7.56 (t, 1H, J = 7.4 Hz), 7.44 (t, 2H, J = 7.8 Hz), 5.43−5.38 (m, 1H), 2.66−2.59 (m, 2H), 2.44−2.38 (m, 2H), 2.26−2.12 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7 (C), 165.7 (C), 133.2 (CH), 130.2 (C), 129.5 (CH), 128.4 (CH), 69.0 (CH), 37.3 (CH_2), 30.5 (CH_2). ^{1}H and ^{13}C NMR data for 4-oxocyclohexyl benzoate (**3i**) prepared in this way were in agreement with those previously described.[21]

*Hydrolysis of 2-(Phenylthio)allyl 4-Methoxybenzoate (**1n**; Table 2, Entry 14).* Following general procedure A using 2-(phenylthio)allyl 4-methoxybenzoate (**1n**, 75.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 33% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 21.3 mg, 41%).

Following general procedure B using 2-(phenylthio)allyl 4-methoxybenzoate (**1n**, 75.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 33% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 42.6 mg, 82%).

*Hydrolysis of 2-((4-Chlorophenyl)thio)cyclohex-2-en-1-yl Benzoate (**1o**; Table 2, Entry 15).* Following general procedure A using 2-((4-chlorophenyl)thio)cyclohex-2-en-1-yl benzoate (**1o**, 86.2 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 43.8 mg, 80%).

Following general procedure B using 2-((4-chlorophenyl)thio)-cyclohex-2-en-1-yl benzoate (**1o**, 86.2 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 50.4 mg, 92%).

*Hydrolysis of 2-(Benzylthio)cyclohex-2-en-1-yl Benzoate (**1p**; Table 2, Entry 16).* Following general procedure A using 2-(benzylthio)cyclohex-2-en-1-yl benzoate (**1p**, 81.1 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 50.7 mg, 93%).

Following general procedure B using 2-(benzylthio)cyclohex-2-en-1-yl benzoate (**1p**, 81.1 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 47.7 mg, 87%).

*Hydrolysis of 2-(Phenylsulfonyl)cyclohex-2-en-1-yl Benzoate (**1q**; Table 2, Entry 17).* Following general procedure A using 2-(phenylsulfonyl)cyclohex-2-en-1-yl benzoate (**1q**, 85.6 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 45.4 mg, 83%).

Following general procedure B using 2-(phenylsulfonyl)cyclohex-2-en-1-yl benzoate (**1q**, 85.6 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 48.7 mg, 89%).

*Hydrolysis of 2-(Phenylselanyl)cyclohex-2-en-1-yl benzoate (**1r**; Table 2, Entry 18).* Following general procedure A using 2-(phenylselenyl)cyclohex-2-en-1-yl benzoate (**1r**, 86.2 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 2% ethyl acetate−hexanes initially, grading to 35% ethyl acetate−hexanes, linear gradient) afforded separately 2-(phenylselanyl)cyclohex-2-en-1-yl benzoate (**1r**, colorless oil, 69.9 mg, 78%) and 2-oxocyclohexyl benzoate (**3d**, white solid, 9.8 mg, 18%).

Following general procedure B using 2-(phenylselenyl)cyclohex-2-en-1-yl benzoate (**1r**, 86.2 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate (**3d**, white solid, 36.1 mg, 66%).

*Hydrolysis of N-(4-Phenylbut-1-en-2-yl)acetamide (**1s**; Table 2, Entry 19).* Following general procedure A using *N*-(4-phenylbut-1-en-2-yl)acetamide (**1s**, 47.3 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 10% ether−hexanes, isocratic gradient) afforded 4-phenylbutan-2-one (**3j**, colorless oil, 23.8 mg, 64%).

Following general procedure B using *N*-(4-phenylbut-1-en-2-yl)acetamide (**1s**, 47.3 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 10% ether−hexanes, isocratic gradient) afforded 4-phenylbutan-2-one (**3j**, colorless oil, 29.3 mg, 79%): R_f = 0.55 (20% ethyl acetate−hexanes; UV, PAA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.26 (m, 2H), 7.21−7.17 (m, 3H), 2.90 (t, 2H, J = 7.6 Hz), 2.76 (t, 2H, J = 7.8 Hz), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9 (C), 141.0 (C), 128.5 (CH), 128.3 (CH), 126.1 (CH), 45.1 (CH_2), 30.1 (CH_3), 29.7 (CH_2). ^{1}H and ^{13}C NMR data for 4-phenylbutan-2-one (**3j**) prepared in this way were in agreement with those previously described.[51]

*Hydrolysis of 2-(1-(2-Chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1t**; Table 2, Entry 20).* Following general procedure B using 2-(1-(2-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1t**, 66.1 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 30% ether−hexanes, linear gradient) afforded 1-(2-chlorophenyl)ethan-1-one (**3k**, colorless oil, 30.5 mg, 79%): R_f = 0.6 (20% ethyl acetate−hexanes; UV, PAA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.51 (m, 1H), 7.40−7.25 (m, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4 (C), 139.1 (C), 132.0 (CH), 131.2 (C), 130.6 (CH), 129.4 (CH), 126.9 (CH), 30.7 (CH_3). ^{1}H and ^{13}C NMR data for 1-(2-chlorophenyl)ethan-1-one (**3k**) prepared in this way were in agreement with those previously described.[52]

*Hydrolysis of 2-(Trimethylsilyl)allyl 4-Methoxybenzoate (**1u**; Table 2, Entry 21).* Following general procedure A using 2-(trimethylsilyl)allyl 4-methoxybenzoate (**1u**, 66.1 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 2% ethyl acetate−hexanes initially, grading to 40% ethyl acetate−hexanes, linear gradient) afforded separately 2-(trimethylsilyl)allyl 4-methoxybenzoate (**1u**, colorless oil, 22.7 mg, 34%) and 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 33.2 mg, 63%).

Following general procedure B using 2-(trimethylsilyl)allyl 4-methoxybenzoate (**1u**, 66.1 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 2% ethyl acetate−hexanes initially, grading to 40% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 46.5 mg, 89%).

*Hydrolysis of (4-tert-Butylcyclohex-1-en-1-yl)trimethylsilane (**1v**; Table 2, Entry 22).* Following general procedure A using (4-*tert*-butylcyclohex-1-en-1-yl)trimethylsilane (**1v**, 52.6 mg, 250 μmol, 1 equiv). Reaction time was 12 h; ^{1}H NMR study of the unpurified product mixture using mesitylene as an internal standard revealed a 90% yield of **1v**. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 33% ether−hexanes, linear gradient) afforded 4-*tert*-butylcyclohexan-1-one (**3e**, white solid, 2.8 mg, 7%). The mixture containing starting material was repurified by flash column chromatography (silver nitrate impregnated silica gel; eluting with hexanes initially, grading to 5% ether−hexanes, linear gradient) afforded (4-*tert*-butylcyclohex-1-en-1-yl)trimethylsilane(**1v**, clear oil, 46.5 mg, 88%).

Following general procedure B using(4-*tert*-butylcyclohex-1-en-1-yl)trimethylsilane (**1v**, 52.6 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting

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with hexanes initially, grading to 33% ether−hexanes, linear gradient) afforded 4-*tert*-butylcyclohexan-1-one (**3e**, white solid, 34.1 mg, 88%).

*Hydration of Propargyl 4-Methoxybenzoate (**1w**; Table 2, entry 23).* Following general procedure A using propargyl 4-methoxybenzoate (**1w**, 47.6 mg, 250 μmol, 1 equiv). Reaction time was 60 h. Purification by automated flash column chromatography (eluting with 2% ethyl acetate−hexanes initially, grading to 15% ethyl acetate−hexanes, linear gradient) recovered propargyl 4-methoxybenzoate (**1w**, white solid, 41.6 mg, 88%).

Following general procedure B using propargyl 4-methoxybenzoate (**1w**, 47.6 mg, 250 μmol, 1 equiv). Reaction time was 24 h. Purification by automated flash column chromatography (eluting with 5% ethyl acetate−hexanes initially, grading to 33% ethyl acetate−hexanes, linear gradient) afforded 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 16.4 mg, 32%).

Mechanistic Studies (Scheme 3). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-chloroallyl 4-methoxybenzoate (**1a**, 56.7 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.250 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. *n*-Propanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 4 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (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 initially, grading to 50% ethyl acetate−hexanes, linear gradient) to afford separately 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 25.1 mg, 42%) and 2-hydroperoxy-2-propoxypropyl 4-methoxybenzoate (**6**, clear oil, 40.2 mg, 57%). 2-Hydroperoxy-2-propoxypropyl 4-methoxybenzoate (**6**): R_f = 0.36 (20% ethyl acetate−hexanes; UV); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.01 (d, 2H, J = 8.5 Hz), 6.92 (d, 2H, J = 8.5 Hz), 4.92 (d, 1H, J = 12.0 Hz), 3.93 (d, 1H, J = 12.0 Hz), 3.91 (s, 3H), 3.68−3.63 (m, 1H), 3.52−3.47 (m, 1H), 1.67−1.60 (m, 2H), 1.37 (s, 3H), 0.95 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4 (C), 163.9 (C), 132.0 (CH), 121.7 (C), 113.8 (CH), 104.5 (C), 64.2 (CH_2), 63.0 (CH_2), 55.5 (CH_3), 23.0 (CH_2), 17.5 (CH_3), 10.6 (CH_3); IR (ATR-FTIR), cm^{-1} 3357 (br), 2963 (w), 1716 (m), 1605 (s), 1258 (s), 1167 (s), 1105 (m), 848 (m), 770 (m); HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{14}H_{20}NaO_6$ 307.1158, found 307.1153.

Mechanistic Studies (Scheme 3). A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-hydroperoxy-2-propoxypropyl 4-methoxybenzoate (**6**, 10.0 mg, 35.0 μmol, 1 equiv) and cobalt bis(acetylacetonate) (2.2 mg, 8.75 μmol, 0.250 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. *n*-Propanol (117 μL), triethylsilane (28.0 μL, 175 μmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 6.4 μL, 35.0 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 15% ethyl acetate−hexanes, isocratic gradient) to afford 2-oxopropyl 4-methoxybenzoate (**3a**, colorless oil, 5.4 mg, 74%).

*Hydrolysis of 1-(4,4-Dichlorobut-3-en-1-yl)-4-methoxybenzene (**11a**; Table 3, Entry 1).* Following general procedure A using 1-(4,4-dichlorobut-3-en-1-yl)-4-methoxybenzene (**11a**, 57.8 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded methyl 4-(4-methoxyphenyl)butanoate (**12a**, colorless oil, 48.0 mg, 92%).

Following general procedure B using 1-(4,4-dichlorobut-3-en-1-yl)-4-methoxybenzene (**11a**, 57.8 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded methyl 4-(4-methoxyphenyl)butanoate (**12a**, colorless oil, 50.8 mg, 98%): R_f = 0.30 (20% ether−hexanes; UV); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, 2H, J = 8.0 Hz), 6.83 (d, 2H, J = 8.0 Hz), 3.79 (s, 3H), 3.66 (s, 3H), 2.65 (t, 2H, J = 7.8 Hz), 2.32 (t, 2H, J = 7.5 Hz), 1.95−1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0 (C), 157.9 (C), 113.4 (C), 129.3 (CH), 113.8 (CH), 55.2 (CH_3), 51.5 (CH_3), 34.2 (CH_2), 33.3 (CH_2), 26.7 (CH_2); IR (ATR-FTIR), cm^{-1} 2951 (w), 1734 (s), 1152 (s), 1243 (s), 1175 (s), 1034 (s), 811 (m); HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{12}H_{17}O_3$, 209.1178, found 209.1185.

*Hydrolysis of 1-(4,4-Dibromobut-3-en-1-yl)-4-methoxybenzene (**11b**; Table 3, Entry 2).* Following general procedure A using 1-(4,4-dibromobut-3-en-1-yl)-4-methoxybenzene (**11b**, 80.0 mg, 250 μmol, 1 equiv). Reaction time was 7 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded methyl 4-(4-methoxyphenyl)butanoate (**12a**, colorless oil, 45.5 mg, 87%).

Following general procedure B using 1-(4,4-dibromobut-3-en-1-yl)-4-methoxybenzene (**11b**, 80.0 mg, 250 μmol, 1 equiv). Reaction time was 8 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded methyl 4-(4-methoxyphenyl)butanoate (**12a**, colorless oil, 45.9 mg, 88%).

*Hydrolysis of 1-(4,4-diiodobut-3-en-1-yl)-4-methoxybenzene (**11c**; Table 3, Entry 3).* Following general procedure A using 1-(4,4-dichlorobut-3-en-1-yl)-4-methoxybenzene (**11c**, 45.5 mg, 110 μmol, 1 equiv). Reaction time was 60 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded separately 1-(4,4-dichlorobut-3-en-1-yl)-4-methoxybenzene (**11c**, white solid, 20.9 mg, 46%) and methyl 4-(4-methoxyphenyl)butanoate (**12a**, colorless oil, 10.8 mg, 47%).

Following general procedure B using 1-(4,4-dichlorobut-3-en-1-yl)-4-methoxybenzene (**11c**, 45.5 mg, 110 μmol, 1 equiv). Reaction time was 60 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded separately 1-(4,4-dichlorobut-3-en-1-yl)-4-methoxybenzene (**11c**, white solid, 26.8 mg, 59%) and methyl 4-(4-methoxyphenyl)butanoate (**12a**, colorless oil, 8.7 mg, 38%).

*Hydrolysis of 1-(2,2-Dibromovinyl)-4-methoxybenzene (**11d**; Table 3, Entry 4).* Following general procedure A using 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**, 73.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded methyl 2-(4-methoxyphenyl)acetate (**12b**, colorless oil, 27.6 mg, 61%).

Following general procedure B using 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**, 80.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded methyl 2-(4-methoxyphenyl)acetate (**12b**, colorless oil, 38.2 mg, 85%): R_f = 0.51 (20% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 2H, J = 8.8 Hz), 6.86 (d, 2H, J = 8.8 Hz), 3.79 (s, 3H), 3.68 (s, 3H), 3.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3 (C), 158.6 (C), 130.2 (CH), 126.0 (C), 113.9 (CH), 55.2 (CH_3), 51.9 (CH_3), 40.2 (CH_2). ^{1}H and ^{13}C NMR data for methyl 2-(4-methoxyphenyl)acetate (**12b**) prepared in this way were in agreement with those previously described.[53]

*Hydrolysis of Methyl 4-(2,2-Dibromovinyl)benzoate (**11e**; Table 3, Entry 5).* Following general procedure A using methyl 4-(2,2-dibromovinyl)benzoate (**11e**, 80.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 40% ether−hexanes, linear gradient) afforded methyl 4-(2-methoxy-2-oxoethyl)benzoate (**12c**, colorless oil, 44.7 mg, 86%).

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Following general procedure B using methyl 4-(2,2-dibromovinyl)-benzoate (**11e**, 80.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 40% ether−hexanes, linear gradient) afforded methyl 4-(2-methoxy-2-oxoethyl)benzoate (**12c**, colorless oil, 47.8 mg, 92%): R_f = 0.31 (33% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, 2H, J = 8.0 Hz), 7.35 (d, 2H, J = 8.0 Hz), 3.91 (s, 3H), 3.71 (s, 3H), 3.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1 (C), 166.7 (C), 139.0 (C), 129.7 (CH), 129.2(CH), 129.0 (C), 52.1 (CH_3), 52.0 (CH_3), 41.0 (CH_2). ^{1}H and ^{13}C NMR data for methyl 2-(4-methoxyphenyl)acetate (**12c**) prepared in this way were in agreement with those previously described.[54]

*Hydrolysis of 1-Bromo-4-(2,2-dibromovinyl)benzene (**11f**; Table 3, Entry 6).* Following general procedure A using 1-bromo-4-(2,2-dibromovinyl)benzene (**11f**, 85.2 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded methyl 2-(4-bromophenyl)acetate (**12d**, colorless oil, 52.3 mg, 91%).

Following general procedure B using 1-bromo-4-(2,2-dibromovinyl)benzene (**11f**, 85.2 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 25% ether−hexanes, linear gradient) afforded methyl 2-(4-bromophenyl)acetate (**12d**, colorless oil, 56.9 mg, 98%): R_f = 0.72 (20% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, J = 8.0 Hz), 7.15 (d, 2H, J = 8.0 Hz), 3.66 (s, 3H), 3.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4 (C), 132.9 (C), 131.6 (CH), 131.0 (CH), 121.1 (C), 52.1 (CH_3), 40.5 (CH_2). ^{1}H and ^{13}C NMR data for methyl 2-(4-bromophenyl)acetate (**12d**) prepared in this way were in agreement with those previously described.[54]

*Hydrolysis of 4-(2,2-Dibromovinyl)benzonitrile (**11g**; Table 3, Entry 7).* Following general procedure A using 4-(2,2-dibromovinyl)-benzonitrile (**11g**, 71.7 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 33% ether−hexanes, linear gradient) afforded methyl 2-(4-cyanophenyl)acetate (**12e**, colorless oil, 39.8 mg, 91%).

Following general procedure B using 4-(2,2-dibromovinyl)-benzonitrile (**11g**, 71.7 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 33% ether−hexanes, linear gradient) afforded methyl 2-(4-cyanophenyl)acetate (**12e**, colorless oil, 30.6 mg, 70%): R_f = 0.59 (33% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 8.0 Hz, H_1), 7.38 (d, 2H, J = 8.0 Hz, H_2), 3.69 (s, 3H, H_4), 3.68 (s, 2H, H_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7 (C), 139.3 (C), 132.3 (CH), 130.2 (CH), 118.8 (C), 111.1 (C), 52.3 (CH_3), 41.0 (CH_2). ^{1}H and ^{13}C NMR data for methyl 2-(4-cyanophenyl)acetate (**12e**) prepared in this way were in agreement with those previously described.[55]

*Hydrolysis of 1-(2,2-Dibromovinyl)-4-nitrobenzene (**11h**; Table 3, Entry 8).* Following general procedure A using 1-(2,2-dibromovinyl)-4-nitrobenzene (**11h**, 76.7 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 33% ether−hexanes, linear gradient) afforded methyl 2-(4-nitrophenyl)acetate (**12f**, light yellow oil, 43.4 mg, 89%).

Following general procedure B using 1-(2,2-dibromovinyl)-4-nitrobenzene (**11h**, 76.7 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 33% ether−hexanes, linear gradient) afforded methyl 2-(4-nitrophenyl)acetate (**12f**, light yellow oil, 46.7 mg, 96%): R_f = 0.47 (33% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, 2H, J = 8.4 Hz), 7.45 (d, 2H, J = 8.4 Hz), 3.73 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6 (C), 147.2 (C), 141.2 (C), 130.28 (CH), 123.7 (CH), 52.4 (CH_3), 40.7 (CH_2). ^{1}H and ^{13}C NMR data for methyl 2-(4-nitrophenyl)acetate (**12f**) prepared in this way were in agreement with those previously described.[56]

*Hydrolysis of 2-(4-(2,2-Dibromovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11i**; Table 3, Entry 9).* Following general procedure A using 2-(4-(2,2-dibromovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11i**, 97.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h; ^{1}H NMR analysis of the unpurified sample showed complicated decomposition of unidentified products.

Following general procedure B using 2-(4-(2,2-dibromovinyl)-phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11i**, 97.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 15% ether−hexanes, linear gradient) afforded methyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetate (**12g**, white solid, 35.5 mg, 51%): R_f = 0.52 (20% ether−hexanes; UV, CAM). mp 42−45 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.0 Hz), 7.29 (d, 2H, J = 8.0 Hz), 3.67 (s, 3H), 3.64 (s, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (C), 137.1 (C), 135.0 (CH), 128.6 (CH), 83.7 (C), 52.0 (CH_3), 41.4 (CH_2), 24.8 (CH_3). ^{1}H and ^{13}C NMR data for methyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-acetate (**12g**) prepared in this way were in agreement with those previously described.[57]

*Hydrolysis of 1-(2,2-Dibromovinyl)-4-(trifluoromethyl)benzene (**11j**; Table 3, Entry 10).* Following general procedure A using 1-(2,2-dibromovinyl)-4-(trifluoromethyl)benzene (**11j**, 82.5 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 15% ether−hexanes, linear gradient) afforded methyl 2-(4-(trifluoromethyl)phenyl)acetate (**12h**, colorless oil, 44.1 mg, 81%).

Following general procedure B using 1-(2,2-dibromovinyl)-4-(trifluoromethyl)benzene (**11j**, 82.5 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 15% ether−hexanes, linear gradient) afforded methyl 2-(4-(trifluoromethyl)phenyl)acetate (**12h**, colorless oil, 47.1 mg, 86%): R_f = 0.54 (20% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J = 8.0 Hz), 7.40 (d, 2H, J = 8.0 Hz), 3.71 (s, 3H), 3.69 (s, 2H). ^{19}F NMR (375 MHz, $CDCl_3$) δ −62.6. ^{1}H and ^{13}C NMR data for methyl 2-(4-(trifluoromethyl)phenyl)acetate (**12h**) prepared in this way were in agreement with those previously described.[58]

*Hydrolysis of 1-(2,2-Dibromovinyl)naphthalene (**11k**; Table 3, Entry 11).* Following general procedure A using 1-(2,2-dibromovinyl)-naphthalene (**11k**, 78.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h; ^{1}H NMR analysis of the unpurified sample showed complicated decomposition of unidentified products.

Following general procedure B using 1-(2,2-dibromovinyl)-naphthalene (**11k**, 78.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 15% ether−hexanes, linear gradient) afforded methyl 2-(naphthalen-1-yl)acetate (**12i**, colorless oil, 24.4 mg, 49%): R_f = 0.63 (20% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, 1H, J = 8.8 Hz), 7.89 (d, 1H, J = 8.8 Hz), 7.82 (d, 1H, J = 7.6 Hz), 7.59−7.43 (m, 4H), 4.11 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0 (C), 133.8 (C), 132.1 (C), 130.5 (C), 128.8 (CH), 128.1 (CH), 128.0 (CH), 126.4 (CH), 125.8 (CH), 125.5 (CH), 123.8 (CH), 52.2 (CH_3), 39.1 (CH_2). ^{1}H and ^{13}C NMR data for methyl 2-(naphthalen-1-yl)acetate (**12i**) prepared in this way were in agreement with those previously described.[59]

*Hydrolysis of 1-(2,2-Dibromovinyl)-2-iodobenzene (**11l**; Table 3, Entry 12).* Following general procedure A using 1-(2,2-dibromovinyl)-2-iodobenzene (**11l**, 97.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h; ^{1}H NMR analysis of the unpurified sample showed complicated decomposition of unidentified products.

Following general procedure B using 1-(2,2-dibromovinyl)-2-iodobenzene (**11l**, 97.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 20% ether−hexanes, linear gradient) afforded methyl 2-(2-iodophenyl)acetate (**12j**, colorless oil, 53.2 mg, 77%): R_f = 0.57 (20% ether−hexanes; UV, CAM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 1H, J = 8.0 Hz), 7.34−7.27 (m, 2H), 6.98−6.94 (m, 1H), 3.81 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz,

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$CDCl_3$) δ 170.9 (C), 139.5 (CH), 137.7 (C), 130.6 (CH), 128.9 (CH), 128.4 (CH), 101.0 (C), 52.2 (CH_3), 46.1 (CH_2). ^1H and ^{13}C NMR data for methyl 2-(2-iodophenyl)acetate (**12j**) prepared in this way were in agreement with those previously described.[60]

*Hydrolysis of 2-(2,2-Dibromovinyl)-1,3,5-trimethylbenzene (**11m**; Table 3, Entry 13).* Following general procedure A using 2-(2,2-dibromovinyl)-1,3,5-trimethylbenzene (**11m**, 76.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h; ^1H NMR analysis of the unpurified sample showed complicated decomposition of unidentified products.

Following general procedure B using 2-(2,2-dibromovinyl)-1,3,5-trimethylbenzene (**11m**, 76.0 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 15% ether−hexanes, linear gradient) afforded methyl 2-mesitylacetate (**12k**, colorless oil, 14.9 mg, 31%): R_f = 0.59 (20% ether−hexanes; UV, CAM); ^1H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 3.70 (s, 3H), 3.69 (s, 2H), 2.32 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0 (C), 137.0 (C), 136.5 (C), 128.9 (CH), 128.5 (C), 51.9 (CH_3), 34.9 (CH_2), 20.9 (CH_3), 20.2 (CH_3). ^1H and ^{13}C NMR data for methyl 2-mesitylacetate (**12k**) prepared in this way were in agreement with those previously described.[61]

*Hydrolysis of Benzyl (4,4-Dibromo-1-phenylbut-3-en-2-yl)-carbamate (**11n**; Table 3, Entry 14).* Following general procedure A using benzyl (4,4-dibromo-1-phenylbut-3-en-2-yl)carbamate (**11n**, 110 mg, 250 μmol, 1 equiv). Reaction time was 12 h; ^1H NMR analysis of the unpurified sample showed complicated decomposition of unidentified products.

Following general procedure B using benzyl (4,4-dibromo-1-phenylbut-3-en-2-yl)carbamate (**11n**, 110 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 20% ethyl acetate−hexanes, linear gradient) afforded methyl 3-(((benzyloxy)-carbonyl)amino)-4-phenylbutanoate (**12l**, colorless oil, 67.2 mg, 82%): R_f = 0.47 (20% ethyl acetate−hexanes; UV, CAM); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.41−7.22 (m, 10H), 5.38 (d, 1H, J = 9.2 Hz), 5.08 (s, 2H), 4.29−4.20 (m, 1H), 3.68 (s, 3H), 2.98−2.85 (m, 2H), 2.60−2.47 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 171.8 (C), 155.5 (C), 137.8 (C), 136.9 (C), 129.3 (CH), 127.5 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 126.6 (CH), 66.3 (CH_2), 51.6 (CH_3), 49.5 (CH), 40.3 (CH_2), 37.8 (CH_2); IR (ATR-FTIR), cm^{-1} 3334 (br), 2952 (w), 1720 (s), 1527 (m), 1249 (m), 1046 (m), 743 (m), 699 (m); HRMS-EI (m/z) $[M + H]^+$ calcd for $C_{19}H_{22}NO_4$ 328.1549, found 328.1544.

*Hydrolysis of Benzyl 4-(Dibromomethylene)piperidine-1-carboxylate (**11o**; Table 3, entry 15).* Following general procedure A using benzyl 4-(dibromomethylene)piperidine-1-carboxylate (**11o**, 97.3 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 15% ethyl acetate−hexanes, linear gradient) afforded 1-benzyl 4-methylpiperidine-1,4-dicarboxylate (**12m**, colorless oil, 57.4 mg, 83%).

Following general procedure B using benzyl 4-(dibromomethylene)piperidine-1-carboxylate (**11o**, 97.3 mg, 250 μmol, 1 equiv). Reaction time was 12 h. Purification by automated flash column chromatography (eluting with hexanes initially, grading to 15% ethyl acetate−hexanes, linear gradient) afforded 1-benzyl 4-methylpiperidine-1,4-dicarboxylate (**12m**, colorless oil, 61.9 mg, 89%): R_f = 0.45 (20% ethyl acetate−hexanes; UV, CAM); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (m, 5H), 5.12 (s, 2H), 4.11 (br s), 3.69 (s, 3H), 2.93 (t, 2H, J = 12.6 Hz), 2.50−2.45 (m, 1H), 1.91−1.88 (m, 2H), 1.70−1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8 (C), 155.2 (C), 136.7 (C), 128.5 (CH), 128.0 (CH), 127.8 (CH), 67.1 (CH_2), 51.8 (CH_3), 43.2 (CH_2), 40.8 (CH), 27.9 (CH_2). ^1H and ^{13}C NMR data for 1-benzyl 4-methylpiperidine-1,4-dicarboxylate (**12m**) prepared in this way were in agreement with those previously described.[62]

*Hydrolysis of 1-(2,2-Dibromovinyl)-4-methoxybenzene (**11d**) with 2-Propanol (Table 4, Entry 1).* A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**, 73.0 mg, 250 μmol, 1 equiv), lithium acetylacetoante (39.8 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.25 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. 2-Propanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with hexane initially, grading to 20% ether−hexanes, linear gradient) to afford 2-propyl 2-(4-methoxyphenyl)acetate (**12n**, colorless oil, 21.2 mg, 41%).

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**, 73.0 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 dioxygen. This process was repeated two times. 2-Propanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, and the residue obtained was filtered through a short column of silica gel and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with hexane initially, grading to 20% ether−hexanes, linear gradient) to afford 2-propyl 2-(4-methoxyphenyl)acetate (**12n**, colorless oil, 41.0 mg, 79%): R_f = 0.55 (20% ether−hexanes; UV, CAM); ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, 2H, J = 8.5 Hz), 6.85 (d, 2H, J = 8.5 Hz), 5.02−4.99 (m, 1H), 3.79 (s, 3H), 3.52 (s, 2H), 1.22 (d, 6H, J = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4 (C), 158.6 (C), 130.2 (CH), 126.4 (C), 113.9 (CH), 68.0 (CH), 55.3 (CH_3), 40.8 (CH_2), 21.8 (CH_3). ^1H and ^{13}C NMR data for *iso*-propyl 2-(4-methoxyphenyl)acetate (**12n**) prepared in this way were in agreement with those previously described.[53]

*Hydrolysis of 1-(2,2-Dibromovinyl)-4-methoxybenzene (**11d**) with 2-Methyl-2-propanol (Table 4, Entry 2).* A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**, 73.0 mg, 250 μmol, 1 equiv), lithium acetylacetoante (39.8 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.25 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. *tert*-Butanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with hexane initially, grading to 20% ether−hexanes, linear gradient) to afford *tert*-butyl 2-(4-methoxyphenyl)acetate (**12o**, colorless oil, 27.6 mg, 49%).

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**, 73.0 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 dioxygen. This process was repeated two times. 2-Methyl-2-propanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−

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hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with hexane initially, grading to 20% ether−hexanes, linear gradient) to afford *tert*-butyl 2-(4-methoxyphenyl)acetate (**12o**, colorless oil, 37.7 mg, 68%): R_f = 0.55 (20% ether−hexanes; UV, CAM); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, 2H, J = 8.5 Hz), 6.86 (d, 2H, J = 8.5 Hz), 3.80 (s, 3H), 3.46 (s, 2H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0 (C), 158.5 (C), 130.2 (CH), 127.0 (C), 113.7 (CH), 80.4 (C), 55.1 (CH_3), 41.5 (CH_2), 27.7 (CH_3). ^{1}H and ^{13}C NMR data for *tert*-butyl 2-(4-methoxyphenyl)acetate (**12o**) prepared in this way were in agreement with those previously described.[63]

*Hydrolysis of 1-(2,2-Dibromovinyl)-4-methoxybenzene (**11d**) with Water (Table 4, Entry 3).* A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**, 73.0 mg, 250 μmol, 1 equiv), lithium acetylacetoante (39.8 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.25 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. Tetrahydrofuran (830 μL), water (45.0 μL, 2.50 mmol, 10.0 equiv), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 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 1 N aqueous hydrochloric acid 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 20% ether−1% acetic acid−hexanes, isocratic gradient) to afford 2-(4-methoxyphenyl)acetic acid (**12p**, off-white solid, 13.3 mg, 32%).

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 1-(2,2-dibromovinyl)-4-methoxybenzene (**11d**, 73.0 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 dioxygen. This process was repeated two times. Tetrahydrofuran (830 μL), water (45.0 μL, 2.50 mmol, 10.0 equiv), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 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 1 N aqueous hydrochloric acid 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 20% ether−1% acetic acid−hexanes, isocratic gradient) to afford 2-(4-methoxyphenyl)acetic acid (**12p**, off-white solid, 29.5 mg, 71%): R_f = 0.19 (20% ethyl acetate−1% acetic acid−hexanes; UV, CAM); mp 66−68 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.8 (br s, 1H), 7.21 (d, 2H, J = 8.4 Hz), 6.88 (d, 2H, J = 8.4 Hz), 3.80 (s, 3H), 3.59 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4 (C), 158.9 (C), 130.4 (CH), 125.3 (C), 114.1 (CH), 55.3 (CH_3), 40.2 (CH_2). ^{1}H and ^{13}C NMR data for 2-(4-methoxyphenyl)acetic acid (**12p**) prepared in this way were in agreement with those previously described.[64]

*Hydrolysis of (R)-2-Bromocyclohex-2-en-1-yl benzoate [(**R**)-**1g**; Scheme 5].* Following general procedure A using (*R*)-2-bromocyclohex-2-en-1-yl benzoate [(***R***)-**1g**, 70.3 mg, 250 μmol, 1 equiv]. Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate [(***R***)-**3d**, white solid, 42.2 mg, 77%]. The enantiomeric ratio of (***R***)-**3d** prepared this way was determined to be 95:5 by chiral stationary phase HPLC analysis (Chiralpak OD-H: 10% 2-propanol−hexanes, 24 °C, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 7.5 min, $t_{R(minor)}$ = 10.5 min).

Following general procedure B using 2-bromocyclohex-2-en-1-yl benzoate [(***R***)-**1g**, 70.3 mg, 250 μmol, 1 equiv]. Reaction time was 12 h. Purification by automated flash column chromatography (eluting with 7.5% ethyl acetate−10% dichloromethane−hexanes, isocratic gradient) afforded 2-oxocyclohexyl benzoate [(***R***)-**3d**, white solid, 48.6 mg, 89%]. The enantiomeric ratio of (***R***)-**3d** prepared this way was determined to be 95:5 by chiral stationary phase HPLC analysis (Chiralpak OD-H: 10% 2-propanol−hexanes, 24 °C, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 7.5 min, $t_{R(minor)}$ = 10.5 min).

^{1}H and ^{13}C NMR data for (*R*)-2-oxocyclohexyl benzoate [(***R***)-**3d**] prepared in this way were in agreement with its racemic form.

*Control Studies for the Hydrolysis of Methyl 4-(1-Acetoxyvinyl)-benzoate (**1j**, Table S1, Entry 1).* A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with methyl 4-(1-acetoxyvinyl)benzoate (**1j**, 55.1 mg, 250 μmol, 1 equiv) and lithium acetylacetoante (39.8 mg, 375 μmol, 1.50 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 20% ethyl acetate−hexane, isocratic gradient) to afford methyl 4-acetylbenzoate (**3f**, white solid, 43.3 mg, 97%).

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with methyl 4-(1-acetoxyvinyl)benzoate (**1j**, 55.1 mg, 250 μmol, 1 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 20% ethyl acetate−hexane, isocratic gradient) to afford methyl 4-(1-acetoxyvinyl)benzoate (**1j**, white solid, 52.5 mg, 95%).

*Control Studies for the Hydrolysis of Benzyl 4-(((Trifluoromethyl)-sulfonyl)oxy)-3,6-dihydropyridine-1(2H)-carboxylate (**1k**, Table S1, Entry 2).* A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with benzyl 4-(((trifluoromethyl)sulfonyl)-oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1k**, 91.3 mg, 250 μmol, 1 equiv) and lithium acetylacetoante (39.8 mg, 375 μmol, 1.50 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate−hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 20% ether−hexane, isocratic gradient) to afford benzyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (1k, colorless oil, 87.9 mg, 96%).

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with benzyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1k**, 91.3 mg, 250 μmol, 1 equiv). The reaction vessel was evacuated and refilled using a balloon

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of dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 20% ether–hexane, isocratic gradient) to afford benzyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (**1k**, colorless oil, 86.8 mg, 95%).

*Control Studies for the Hydrolysis of 2-(1-(2-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1t**, Table S1, Entry 3).* A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-(1-(2-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1t**, 66.1 mg, 250 μmol, 1 equiv) and lithium acetylacetoante (39.8 mg, 375 μmol, 1.50 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate–hexanes (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 initially, grading to 12% ether–hexanes, linear gradient) to afford separately 2-(1-(2-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1t**, white solid, 27.4 mg, 41%) and 1-(2-chlorophenyl)ethan-1-one (**3k**, colorless oil, 18.9 mg, 49%).

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-(1-(2-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1t**, 66.1 mg, 250 μmol, 1 equiv). The reaction vessel was evacuated and refilled using a balloon of dioxygen. This process was repeated two times. Methanol (830 μL), triethylsilane (199 μL, 1.25 mmol, 5.00 equiv), and a solution of *tert*-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated to dryness, the residue obtained was filtered through a short column of silica gel, and the short column was rinsed with 50% ethyl acetate–hexanes (100 mL). The filtrates were combined, and the combined filtrates were concentrated. The residue obtained was purified by automated flash column chromatography (eluting with 5% ether–hexane, isocratic gradient) to afford 2-(1-(2-chlorophenyl)-vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1t**, white solid, 63.9 mg, 97%): R_f = 0.42 (20% ether–hexanes; UV, $KMnO_4$); mp 34–36 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, 1H, J = 7.6 Hz), 7.25–7.17 (m, 3H), 6.12 (d, 1H, J = 4.0 Hz), 5.85 (d, 1H, J = 3.2 Hz), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (C), 132.6 (CH_2), 132.5 (C), 129.6 (CH), 129.0 (CH), 128.2 (CH), 126.9 (CH), 83.9 (C), 24.7 (CH_3). ^{1}H and ^{13}C NMR data for 2-(1-(2-chlorophenyl)-vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1t**) prepared in this way were in agreement with those previously described.[65]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01709.

Table S1 and spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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