Supporting Information

for

Cobalt bis(acetylacetonate)–tert-butyl hydroperoxide–triethylsilane:

a general reagent combination for the Markovnikov-selective
hydrofunctionalization of alkenes by hydrogen atom transfer

Xiaoshen Ma¹ and Seth B. Herzon*¹,²

Address: ¹Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States and
²Department of Pharmacology, Yale School of Medicine, New Haven, Connecticut 06520, United States

Email: Seth B. Herzon - seth.herzon@yale.edu

* Corresponding author

Detailed experimental procedures and characterization data

for all new compounds

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**Table S1.** Condition optimization of the Markovnikov-selective hydrofunctionalization.

| entry | x (equiv) | y (equiv) | SOMOphile | z (equiv) | solvent | atm. | product | conv. | yield |
|-------|-----------|-----------|-----------|-----------|---------|------|---------|-------|-------|
| 1     | 5.00      | 5.00      | –         | –         | n-propanol | air  | 4a      | >95%  | 86%   |
| 2     | 5.00      | 5.00      | SelectFluor® | 5.00      | n-propanol | argon| 4b      | <5%   | <5%   |
| 3     | 5.00      | 5.00      | DAST      | 5.00      | n-propanol | argon| 4b      | <5%   | <5%   |
| 4     | 5.00      | 5.00      | TsF       | 5.00      | n-propanol | argon| 4b      | <5%   | <5%   |
| 5     | 5.00      | 5.00      | NFSI      | 5.00      | n-propanol | argon| 4b      | 60%   | 22%   |
| 6     | 2.50      | 10.0      | NFSI      | 2.50      | CH₂Cl₂   | argon| 4b      | 71%   | 36%   |
| 7     | 2.50      | 10.0      | TsCl      | 2.50      | n-propanol | argon| 4c      | >95%  | 92%   |
| 8     | 3.75      | 10.0      | TsBr      | 2.50      | n-propanol | argon| 4d      | >95%  | 95%   |
| 9     | 3.75      | 10.0      | TsI       | 5.00      | CH₂Cl₂   | argon| 4e      | <5%   | <5%   |
| 10    | 3.75      | 10.0      | NIS       | 5.00      | CH₂Cl₂   | argon| 4e      | <5%   | <5%   |
| 11    | 3.75      | 10.0      | I₂        | 5.00      | CH₂Cl₂   | argon| 4e      | <5%   | <5%   |
| 12    | 3.75      | 10.0      | CH₃I      | 15.0      | CH₂Cl₂   | argon| 4e      | >95%  | 89%   |
| 13    | 3.75      | 10.0      | CH₃CO₂Et | 15.0      | CH₂Cl₂   | argon| 4e      | 51%   | 49%   |
| 14    | 3.75      | 10.0      | CH₃CN    | 15.0      | CH₂Cl₂   | argon| 4e      | 44%   | 36%   |
| 15    | 3.75      | 10.0      | (CH₃)₂Cl | 15.0      | CH₂Cl₂   | argon| 4e      | <5%   | <5%   |
| 16    | 10.0      | 10.0      | O₂        | –         | n-propanol | O₂   | 4f      | >95%  | 69%   |
| 17    | 2.50      | 10.0      | PhSO₂SPh | 2.50      | n-propanol | argon| 4g      | >95%  | 96%   |
| 18    | 2.50      | 10.0      | TsSePh   | 2.50      | n-propanol | argon| 4h      | >95%  | 93%   |
| 19    | 5.00      | 10.0      | p-ABSA   | 2.50      | n-propanol | argon| 4i      | >95%  | 36%   |
| 20    | 5.00      | 10.0      | DPPA     | 2.50      | n-propanol | argon| 4i      | 55%   | <5%   |
| 21    | 5.00      | 10.0      | p-ABSA   | 5.00      | n-propanol | argon| 4i      | >95%  | 52%   |
| 22    | 5.00      | 10.0      | p-ABSA   | 7.50      | n-propanol | argon| 4i      | >95%  | 57%   |
| 23    | 5.00      | 10.0      | p-ABSA   | 5.00      | CH₂Cl₂   | argon| 4i      | 79%   | 44%   |
| 24    | 5.00      | 10.0      | p-ABSA   | 5.00      | THF      | argon| 4i      | >95%  | 62%   |
| 25    | 5.00      | 10.0      | p-ABSA   | 5.00      | CH₂CN   | argon| 4i      | >95%  | 71%   |
| 26    | 0         | 10.0      | p-ABSA   | 5.00      | CH₂CN   | argon| 4i      | >95%  | 76%   |
| 27    | 1.00      | 10.0      | p-ABSA   | 5.00      | CH₂CN   | argon| 4i      | >95%  | 79%   |
| 28    | 2.50      | 10.0      | p-ABSA   | 5.00      | CH₂CN   | argon| 4i      | 95%   | 78%   |
| 29    | 0         | 6.25      | 5a        | 1.50      | CH₂Cl₂   | argon| 7a      | >95%  | 92%   |
| 30    | 3.75      | 10.0      | 6a        | 2.50      | n-propanol | argon| 4j      | >95%  | 60%   |
| 31    | 3.75      | 10.0      | 6b        | 2.50      | n-propanol | argon| 4k      | >95%  | 48%   |
| 32    | 0         | 5.00      | 6c        | 5.00      | CH₂Cl₂   | argon| 4l      | >95%  | 66%   |
| 33    | 0         | 5.00      | 6d        | 1.00      | CH₂CN   | argon| 4m      | >95%  | 50%   |
**General experimental procedures.** All reactions were performed in single-neck, flame-dried, round-bottomed flask filled with rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula, or were handled in a nitrogen-filled drybox (working oxygen level <5 ppm). Organic solutions were concentrated by rotary evaporation at 30–33 °C. Intermediates were purified using a Biotage Isolera system, employing polypropylene cartridges preloaded with silica gel (60 Å, 40–63 μm particle size, purchased from Silicycle, Quebec City, Canada). Alternatively, intermediates were purified using a Teledyne ISEO system, employing RediSep RF High Performance Gold cartridges (RediSep RF Gold Silica, 20–40 um spherical, purchased from Teledyne ISEO, Dallas, Texas). Samples were eluted using a flow rate of 12–50 mL/min, with detection by UV (254 nm). Analytical thin-layered chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or submersion in aqueous ceric ammonium molybdate solution (CAM), or aqueous potassium permanganate solution (KMnO₄), followed by brief heating on a hot plate (120 °C, 10–15 s).

**Materials.** Commercial solvents and reagents were used as received with the following exceptions. Acetonitrile was purified according to the method of Pangborn et al[1]. Pyridine was distilled from calcium hydride under an atmosphere of nitrogen immediately before use. Methanol was distilled from magnesium shavings under an atmosphere of nitrogen immediately before use. Commercial anhydrous ethanol was stored over 4 Å MS under an atmosphere of nitrogen before use. Tetrahydrofuran was distilled from sodium–benzophenone 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. Triethyliosilane 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. Tosyl iodide[2], (η⁶-benzene) manganese tricarbonyl hexafluorophosphate[3], N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide sodium salt[4], and phenyl N-benzyloxymethanimidodithioate[4] were prepared according to published procedures. p-Toluenesulfonyl chloride was recrystallized from chloroform–pentane immediately before use. N-Iodosuccinimide was recrystallized from 1,4-dioxane–tetrachloromethane immediately before use. m-Chloroperbenzoic acid was recrystallized from dichloromethane immediately before use.

**Instrumentation.** Proton nuclear magnetic resonance spectra (¹H NMR) were recorded at 400, 500, or 600 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃, δ 7.26; CH₂Cl₂, δ 5.32). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad), integration, coupling constant in Hertz, and assignment. Proton-decoupled carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 100, 125, or 150 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl₃, δ 77.0; CD₂Cl₂, δ 54.0). Distortionless enhancement by polarization transfer spectra [DEPT (135)] were recorded at 100, 125, or 150 MHz at 24 °C, unless otherwise noted. ¹³C NMR and DEPT (135) data are combined and represented as follows: chemical shift, carbon type [obtained from DEPT (135) experiments]. Proton-decoupled fluorine nuclear magnetic resonance spectra (¹⁹F NMR) were recorded at 375 MHz or 470 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from fluorotrichloromethane. Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were obtained using a Thermo Electron Corporation Nicolet 6700 FTIR spectrometer referenced to a polystyrene standard. Data are represented as follows: frequency of absorption (cm⁻¹), intensity of absorption (s = strong, m = medium, w = weak, br = broad). High-resolution mass spectrometry (HRMS) were obtained on a Waters UPLC/HRMS.
instrument equipped with a dual API/ESI high-resolution mass spectrometry detector and photodiode array detector. Unless otherwise noted, samples were eluted over a reverse-phase C18 column (1.7 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 (I):**

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 (I) as a clear oil (1.20 g, 98%).

R<sub>f</sub> = 0.52 (10% ethyl acetate–hexanes; UV, KMnO<sub>4</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (d, 2H, J = 9.0 Hz, H<sub>3</sub>), 6.94 (d, 2H, J = 9.0 Hz, H<sub>2</sub>), 5.55–5.53 (m, 1H, H<sub>5</sub>), 5.45–5.42 (m, 1H, H<sub>6</sub>), 4.87 (br s, 2H, H<sub>4</sub>), 3.87 (s, 3H, H<sub>1</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 165.0 (C), 163.4 (C), 135.9 (C), 131.6 (CH), 121.5 (C), 114.4 (CH<sub>2</sub>), 113.5 (CH), 65.8 (CH<sub>2</sub>), 55.2 (CH<sub>3</sub>).

<sup>1</sup>H and <sup>13</sup>C NMR data for 2-chloroallyl 4-methoxybenzoate (I) prepared in this way were in agreement with those previously described<sup>[5]</sup>.
Preparation of 2-methylallyl 4-methoxybenzoate (3a):

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

R_f = 0.55 (20% ethyl acetate–hexanes; UV, KMnO_4). \(^1^H\) NMR (600 MHz, CDCl_3) δ 8.02 (d, 2H, J = 8.4 Hz, H_2), 6.92 (d, 2H, J = 8.4 Hz, H_3), 5.05 (s, 1H, H_6), 4.96 (s, 1H, H_6), 4.71 (s, 2H, H_4), 3.87 (s, 3H, H_1), 1.82 (s, 3H, H_1). \(^1^C\) NMR (150 MHz, CDCl_3) δ 166.0 (C), 163.4 (C), 140.2 (C), 131.6 (CH), 122.6 (C), 113.6 (CH), 112.7 (CH_2), 67.8 (CH_2), 55.4 (CH_3), 19.6 (CH_3).

\(^1^H\) and \(^1^C\) NMR data for 2-methylallyl 4-methoxybenzoate (3a) prepared in this way were in agreement with those previously described\(^6\).
Preparation of allyl 4-methoxybenzoate (3b):

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

R_f = 0.55 (20% ethyl acetate–hexanes; UV, KMnO_4). ¹H NMR (600 MHz, CDCl₃) δ 8.02 (d, 2H, J = 8.4 Hz, H₃), 6.92 (d, 2H, J = 8.4 Hz, H₂), 6.03 (ddt, J = 16.8, 10.2, 4.2 Hz, 1H, H₅), 5.40 (d, J = 16.8 Hz, 1H, H₆), 5.27 (d, J = 10.2 Hz, 1H, H₆), 4.80 (d, J = 4.2 Hz, 2H, H₄), 3.86 (s, 3H, H₁). ¹³C NMR (150 MHz, CDCl₃) δ 166.0 (C), 163.4 (C), 132.5 (CH), 131.6 (CH), 122.5 (C), 117.9 (CH₂), 113.6 (CH), 65.2 (CH₂), 55.4 (CH₃).

¹H and ¹³C NMR data for 2-methylallyl allyl 4-methoxybenzoate (3b) prepared in this way were in agreement with those previously described⁷. 
Preparation of 3-methylbut-2-en-1-yl 4-methoxybenzoate (3c):

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

R<sub>f</sub> = 0.55 (20% ethyl acetate–hexanes; UV, KMnO<sub>4</sub>). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.98 (d, 2H, J = 8.5 Hz, H<sub>3</sub>), 6.94 (d, 2H, J = 9.0 Hz, H<sub>2</sub>), 5.47 (t, J = 7.0 Hz, 1H, H<sub>5</sub>), 4.78 (d, J = 7.5 Hz, 2H, H<sub>4</sub>), 3.86 (s, 3H, H<sub>1</sub>), 1.80 (s, 3H, H<sub>7</sub>), 1.78 (s, 3H, H<sub>8</sub>). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 166.6 (C), 163.9 (C), 139.4 (C), 131.9 (CH), 123.6 (C), 119.5 (CH), 114.1 (CH), 62.0 (CH<sub>2</sub>), 56.0 (CH<sub>3</sub>), 26.0 (CH<sub>3</sub>), 18.4 (CH<sub>3</sub>). IR (ATR-FTIR), cm<sup>−1</sup>: 2935 (w), 1707 (s), 1606 (s), 1251 (s), 1096 (s). HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>12</sub>NaO<sub>3</sub>, 243.0997; found, 243.1003.
Preparation of \( p \)-toluenesulfonyl bromide (\( S1 \)):

A solution of sodium bromide (815 mg, 7.92 mmol, 0.333 equiv) and sodium bromate (2.43 g, 16.1 mmol, 0.667 equiv) in water (14 mL) was added dropwise to a suspension of \( p \)-toluenesulfonyl hydrazide (4.47 g, 24.0 mmol, 1 equiv) in an aqueous solution of hydrochloric acid (10% w/w, 80 mL) at 24 \( ^\circ \)C. The product mixture was stirred for 10 min and filtered immediately. The residue obtained was recrystallized from petroleum ether to afford \( p \)-toluenesulfonyl bromide (\( S1 \)) as a white crystalline solid (3.99 g, 71%).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.88 (d, 2H, \( J = 8.5 \) Hz, H\(_3\)), 7.39 (d, 2H, \( J = 8.5 \) Hz, H\(_2\)), 2.49 (s, 3H, H\(_1\)).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 146.7 (C), 144.6 (C), 130.1 (CH), 126.4 (CH), 21.8 (CH\(_3\)).

\(^1\)H and \(^{13}\)C NMR data for \( p \)-toluenesulfonyl bromide (\( S1 \)) prepared in this way were in agreement with those previously described\(^8\).
**Preparation of Se-phenyl seleno-\textit{p}-toluenesulfonate (S2):**

A suspension of \textit{p}-toluenesulfonyl hydrazide (1.86 g, 10.0 mmol, 1 equiv) in methanol (8.0 mL) was added dropwise over 15 min to a suspension of benzeneseleninic acid (1.89 g, 10.0 mmol, 1.00 equiv) in methanol (8.0 mL) at 0 °C. Vigorous evolution of nitrogen gas was observed and a yellow precipitate was formed. The reaction mixture was cooled to −5 °C overnight. The suspension was filtered to afford Se-phenyl seleno-\textit{p}-toluenesulfonate (S2) as a light yellow solid (2.83 g, 91%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.51 (d, J = 8.0 Hz, 2H, H$_4$), 7.46 (t, J = 7.5 Hz, 1H, H$_6$), 7.39 (d, J = 7.0 Hz, 2H, H$_3$), 7.34 (t, J = 7.5 Hz, 2H, H$_5$), 7.18 (d, J = 8.0 Hz, 2H, H$_2$), 2.41 (s, 3H, H$_1$). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.5 (C), 142.7 (C), 137.2 (CH), 130.8 (CH), 129.5 (CH), 128.2 (CH), 128.0 (C), 127.0 (CH), 21.6 (CH$_3$).

$^1$H and $^{13}$C NMR data for Se-phenyl seleno-\textit{p}-toluenesulfonate (S2) prepared in this way were in agreement with those previously described$^{[9]}$. 

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$\text{CH}_2\text{O}, 0 \rightarrow -5 \degree C \rightarrow \text{S2}$

91%
Preparation of N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (6a):

Benzyl bromide (615 μL, 5.17 mmol, 1.20 equiv) was added to a suspension of N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide sodium salt (1.00 g, 4.31 mmol, 1 equiv) in ethanol (10 mL). The resulting suspension was heated to reflux for 1 h. The product was concentrated to dryness and the residue was suspended with ether (100 mL). The resulting mixture was filtered through a pad of celite and the pad was rinsed with ether (50 mL). The filtrates were combined and the combined filtrates were concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 20% ethyl acetate–hexanes) to afford N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (6a) as a white solid (1.15 g, 89%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.97 (d, $J = 7.5$ Hz, 2H, H$_3$), 7.76 (t, $J = 7.5$ Hz, 1H, H$_1$), 7.62 (t, $J = 8.0$ Hz, 2H, H$_2$), 7.39–7.35 (m, 3H, 2 × H$_5$, 1 × H$_7$), 7.33–7.29 (m, 2H, H$_6$), 5.43 (s, 2H, H$_4$). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 136.5 (C), 135.5 (CH), 134.8 (C), 133.7 (CH), 130.8 (C), 129.9 (CH), 129.4 (CH), 129.2 (CH), 128.8 (CH), 105.7 (C), 81.6 (CH$_2$).

$^1$H and $^{13}$C NMR data for N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (6a) prepared in this way were in agreement with those previously described$^{[4]}$. 
Preparation of (phenylsulfonyl)methanal O-benzyl oxime (6b):

Six equal portions of m-chloroperbenzoic acid (4.40 g, 25.5 mmol, 2.20 equiv) were added over 1 h to a suspension of phenyl N-(benzylxy)methanimidothioate (2.82 g, 11.6 mmol, 1 equiv) and sodium bicarbonate (2.00 g, 23.8 mmol, 2.05 equiv) in dichloromethane (50 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 15 min. The reaction vessel was then placed in an oil bath that had been previously heated to 40 °C. The reaction mixture was stirred and heated at 40 °C for 1 h. The product mixture was allowed to cool down to 24 °C over 30 min and the cooled product mixture was transferred to a separatory funnel that had been charged with dichloromethane (100 mL) and a saturated aqueous sodium bicarbonate solution (50 mL). The layers that formed was separated and the organic layer was washed with aqueous saturated sodium thiosulfate solution (3 × 50 mL). The organic layer was dried and the dried solution was filtered. The filtrate was concentrated to dryness and the residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–hexanes initially, grading to 20% ethyl acetate–hexanes, linear gradient) to afford (phenylsulfonyl)methanal O-benzyl oxime (6b) as a white solid (3.03 g, 95%).

1H NMR (500 MHz, CDCl₃) δ 7.91 (d, J = 7.8 Hz, 2H, H₃), 7.63 (t, J = 7.2 Hz, 1H, H₁), 7.49–7.35 (m, 3H, 2 × H₂, 1 × H₆), 7.29–7.23 (m, 3H, 2 × H₅, 1 × H₇), 7.02 (d, J = 8.4 Hz, 2H, H₈), 5.11 (s, 2H, H₄). 13C NMR (125 MHz, CDCl₃) δ 143.8 (CH), 139.1 (C), 135.3 (C), 134.3 (CH), 129.1 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 78.7 (CH₂).

1H and 13C NMR data for (phenylsulfonyl)methanal O-benzyl oxime (6b) prepared in this way were in agreement with those previously described⁴. 
Preparation of \(N\)-methoxypyridinium methyl sulfate (6c):

A 25-mL round-bottomed flask fitted with a rubber septum was charged with pyridine \(N\)-oxide (2.17 g, 22.8 mmol, 1 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. The reaction vessel was then cooled to 0 °C. Dimethyl sulfate (2.16 mL, 22.8 mmol, 1.00 equiv) was added to the reaction vessel dropwise via syringe over 5 min. The reaction vessel was placed in an oil bath that had been preheated to 100 °C. The reaction mixture was stirred and heated for 5 h at 100 °C. The product mixture was concentrated in vacuo (0.1 Torr) overnight to afford \(N\)-methoxypyridinium methyl sulfate (6c) as a colorless low-melting solid (4.99 g, 99%).

\(^{1}\text{H NMR}\) (400 MHz, (CD\(_3\))\(_2\)SO) \(\delta\) 9.44 (d, \(J = 6.8\) Hz, 2H, H\(_3\)), 8.61 (t, \(J = 8.0\) Hz, 1H, H\(_1\)), 8.23 (t, \(J = 7.2\) Hz, 2H, H\(_2\)), 4.42 (s, 3H, H\(_4\)), 3.37 (s, 3H, H\(_5\)). \(^{13}\text{C NMR}\) (100 MHz, (CD\(_3\))\(_2\)SO) \(\delta\) 145.5 (CH), 141.3 (CH), 129.8 (CH), 69.9 (CH\(_3\)), 53.4 (CH\(_3\)). \(\text{IR (ATR-FTIR)}\), cm\(^{-1}\): 3041 (w), 1479 (m), 1220 (s), 1001 (s), 730 (s), 668 (m), 576 (s). \(\text{HRMS-ESI (m/z): [M – CH\(_2\)OSO\(_3\)]}^+\) calcd for C\(_6\)H\(_8\)NO, 110.0600; found, 110.0604.
Preparation of 4-methoxybenzenediazonium tetrafluoroborate (5a):

A solution of tetrafluoroboric acid in water (48% w/w, 6.15 mL, 33.6 mmol, 2.00 equiv) was added to a solution of p-anisidine (2.07 g, 16.8 mmol, 1 equiv) in water (8.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (1.16 g, 16.8 mmol, 1.00 equiv) in water (2.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 4-methoxybenzenediazonium tetrafluoroborate (5a) as white needles (2.95 g, 79%).

\[ \text{NH}_2 \quad \text{OCH}_3 \quad \overset{\text{NaNO}_2, \text{HCl}}{\text{H}_2\text{O}, 0 ^\circ \text{C}} \quad \text{N}_2^+ \quad \text{BF}_4^- \]

5a

1H NMR (500 MHz, (CD$_3$)$_2$SO) δ 8.60 (d, J = 9.0 Hz, 2H, H$_1$), 7.48 (d, J = 9.0 Hz, 2H, H$_2$), 4.04 (s, 3H, H$_3$). 13C NMR (125 MHz, (CD$_3$)$_2$SO) δ 169.2 (C), 136.5 (CH), 117.9 (CH), 103.7 (C), 57.9 (CH$_3$). $^{19}$F NMR (470 MHz, (CD$_3$)$_2$SO) δ −148.2.

$^1$H and $^{13}$C NMR data for 4-methoxybenzenediazonium tetrafluoroborate (5a) prepared in this way were in agreement with those previously described$^{[10]}$. 

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S14
Preparation of 4-fluorobenzenediazonium tetrafluoroborate (5b):

A solution of tetrafluoroboric acid in water (48% w/w, 3.66 mL, 17.6 mmol, 2.00 equiv) was added to a solution of 4-fluoroaniline (947 μL, 10.0 mmol, 1 equiv) in water (2.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (690 mg, 1.0 mmol, 1.00 equiv) in water (1.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 4-fluorobenzenediazonium tetrafluoroborate (5b) as an off-white solid (1.76 g, 84%).

$^1$H NMR (500 MHz, (CD$_3$)$_2$SO) $\delta$ 8.86–8.75 (m, 2H, H$_1$), 7.93–7.84 (m, 2H, H$_2$). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO) $\delta$ 168.4 (d, J = 265.3 Hz, C), 137.0 (d, J = 12.4 Hz, CH), 119.4 (d, J = 25.1 Hz, CH), 111.8 (d, J = 2.9 Hz, C). $^{19}$F NMR (470 MHz, (CD$_3$)$_2$SO) $\delta$ –78.2 (1F), –148.3 (4F).

$^1$H and $^{13}$C NMR data for 4-fluorobenzenediazonium tetrafluoroborate (5b) prepared in this way were in agreement with those previously described$^{[11]}$. 
Preparation of 4-(trifluoromethyl)benzenediazonium tetrafluoroborate (5c):

A solution of tetrafluoroboric acid in water (48% w/w, 3.66 mL, 20.0 mmol, 2.00 equiv) was added to a solution of 4-(trifluoromethyl)aniline (1.26 mL, 10.0 mmol, 1 equiv) in water (2.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (690 mg, 10.0 mmol, 1.00 equiv) in water (1.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 4-(trifluoromethyl)benzenediazonium tetrafluoroborate (5c) as a light yellow solid (2.76 g, 99%).

\[ ^1H \text{ NMR (} 500 \text{ MHz, (CD}_3\text{)}_2\text{SO} \delta 8.90 \text{ (d, } J = 8.5 \text{ Hz, 2H, } H_1), 8.41 \text{ (d, } J = 9.0 \text{ Hz, 2H, } H_2) \]. \[ ^13C \text{ NMR (} 125 \text{ MHz, (CD}_3\text{)}_2\text{SO} \delta 138.2 \text{ (q, } J = 33.4 \text{ Hz, C), 133.8 \text{ (CH), 128.3 (q, } J = 3.8 \text{ Hz, CH), 122.3 (q, } J = 272.4 \text{ Hz, C), 121.3 (C) \]. \[ ^19F \text{ NMR (} 470 \text{ MHz, (CD}_3\text{)}_2\text{SO} \delta -62.7 \text{ (3F), } -148.2 \text{ (4F) \]. IR (ATR-FTIR), cm\(^{-1}\): 3571 (br w), 3120 (w), 2307 (w), 1427 (w), 1318 (m), 1180 (m), 1139 (m), 1026 (s), 1009 (s), 853 (s), 724 (m), 585 (m), 524 (m). HRMS-ESI (m/z): [M – BF\(_4\)]\(^+\) calcd for C\(_7\)H\(_4\)F\(_3\)N\(_2\)^+ , 173.0321; found, 173.0320.
Preparation of 4-bromobenzenediazonium tetrafluoroborate (5d):

A solution of tetrafluoroboric acid in water (48% w/w, 3.66 mL, 20.0 mmol, 2.00 equiv) was added to a solution of 4-(trifluoromethyl)aniline (1.72 g, 10.0 mmol, 1 equiv) in water (2.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (690 mg, 10.0 mmol, 1.00 equiv) in water (1.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 4-bromobenzenediazonium tetrafluoroborate (5d) as a white solid (2.41 g, 89%).

$^1$H NMR (500 MHz, (CD$_3$)$_2$SO) δ 8.58 (d, J = 9.0 Hz, 2H, H$_1$), 8.26 (d, J = 9.0 Hz, 2H, H$_2$). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO) δ 136.5 (C), 134.5 (CH), 134.0 (CH), 116.2 (C). $^{19}$F NMR (470 MHz, (CD$_3$)$_2$SO) δ –148.2.

$^1$H and $^{13}$C NMR data for 4-bromobenzenediazonium tetrafluoroborate (5d) prepared in this way were in agreement with those previously described$^{[12]}$. 
Preparation of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (5e):

A solution of tetrafluoroboric acid in water (48% w/w, 3.66 mL, 20.0 mmol, 2.00 equiv) was added to a solution of methyl 4-aminobenzoate (1.51 g, 10.0 mmol, 1 equiv) in water (2.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (690 mg, 10.0 mmol, 1.00 equiv) in water (1.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (5e) as an orange solid (1.89 g, 76%).

\[ \text{1H NMR (500 MHz, (CD)}_3\text{SO)} \delta 8.79 (d, J = 8.5 Hz, 2H, H}_1\text{), 8.44 (d, J = 8.5 Hz, 2H, H}_2\text{), 3.95 (s, 3H, H}_3\text{).} \]

\[ \text{13C NMR (125 MHz, (CD)}_3\text{SO)} \delta 163.9 (C), 139.3 (C), 133.2 (CH), 131.3 (CH), 120.2 (C), 53.4 (CH}_3\text{).} \]

\[ \text{19F NMR (470 MHz, (CD)}_3\text{SO)} \delta -148.2. \]

\[ \text{1H and 13C NMR data for 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (5e) prepared in this way were in agreement with those previously described}^{13}. \]
Preparation of 2-methylbenzenediazonium tetrafluoroborate (5f):

A solution of tetrafluoroboric acid in water (48% w/w, 3.66 mL, 20.0 mmol, 2.00 equiv) was added to a solution of 2-methylaniline (1.06 mL, 10.0 mmol, 1 equiv) in water (2.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (690 mg, 10.0 mmol, 1.00 equiv) in water (1.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 2-methylbenzenediazonium tetrafluoroborate (5f) as a light yellow solid (1.76 g, 85%).

$^1$H NMR (500 MHz, (CD$_3$)$_2$SO) $\delta$ 8.64 (d, $J = 8.0$ Hz, 1H, $H_1$), 8.15 (t, $J = 7.8$ Hz, 1H, $H_3$), 7.84 (d, $J = 8.0$ Hz, 1H, $H_4$), 7.80 (t, $J = 8.0$ Hz, 1H, $H_5$), 2.74 (s, 3H, $H_6$). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO) $\delta$ 143.8 (C), 140.7 (CH), 132.6 (CH), 132.5 (CH), 128.8 (CH), 116.0 (C), 18.2 (CH$_3$). $^{19}$F NMR (470 MHz, (CD$_3$)$_2$SO) $\delta$ –148.3.

$^1$H and $^{13}$C NMR data for 2-methylbenzenediazonium tetrafluoroborate (5f) prepared in this way were in agreement with those previously described.$^{[12]}$
Preparation of 3-phenoxybenzenediazonium tetrafluoroborate (5g):
A solution of tetrafluoroboric acid in water (48% w/w, 3.66 mL, 20.0 mmol, 2.00 equiv) was added to a solution of 3-phenoxyaniline (1.85 g, 10.0 mmol, 1 equiv) in water (2.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (690 mg, 10.0 mmol, 1.00 equiv) in water (1.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 3-phenoxybenzenediazonium tetrafluoroborate (5g) as a beige solid (2.58 g, 91%).

$^1$H NMR (500 MHz, (CD$_3$)$_2$SO) δ 8.44–8.40 (m, 1H, H$_1$), 8.20 (s, 1H, H$_4$), 8.00–7.94 (m, 2H, 1 × H$_2$, 1 × H$_3$), 7.55 (t, J = 8.0 Hz, 2H, H$_6$), 7.36 (t, J = 7.5 Hz, 1H, H$_7$), 7.23 (d, J = 7.5 Hz, 2H, H$_5$). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO) δ 157.9 (C), 153.9 (C), 132.9 (CH), 130.9 (CH), 130.6 (CH), 127.4 (CH), 125.9 (CH), 120.3 (CH), 118.9 (CH), 117.0 (C). $^{19}$F NMR (470 MHz, (CD$_3$)$_2$SO) δ –148.3. IR (ATR-FTIR), cm$^{-1}$: 3109 (m), 2302 (m), 1585 (m), 1476 (m), 1326 (w), 1283 (w), 1240 (m), 1019 (s), 926 (m), 873 (m), 807 (m), 775 (s), 692 (m), 663 (m), 522 (m), 466 (m). HRMS-ESI (m/z): [M – BF$_4$]$^+$ calcd for C$_{12}$H$_9$N$_2$O, 197.0709; found, 197.0705.
Preparation of 3,4-methylenedioxybenzenediazonium tetrafluoroborate (5h):

A solution of tetrafluoroboric acid in water (48% w/w, 3.66 mL, 20.0 mmol, 2.00 equiv) was added to a solution of 3,4-methylenedioxyaniline (1.37 g, 10.0 mmol, 1 equiv) in water (2.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (690 mg, 10.0 mmol, 1.00 equiv) in water (1.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 3,4-methylenedioxybenzenediazonium tetrafluoroborate (5h) as a black solid (1.90 g, 81%).

$^1$H NMR (500 MHz, (CD$_3$)$_2$SO) δ 8.42 (dd, J = 8.5, 2.0 Hz, 1H, H$_1$), 8.05 (d, J = 2.0 Hz, 1H, H$_4$), 7.49 (d, J = 8.5 Hz, 1H, H$_2$), 6.45 (s, 2H, H$_3$). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO) δ 158.8 (C), 148.5 (C), 134.2 (CH), 110.6 (CH), 109.4 (CH), 105.5 (CH$_2$), 104.4 (C). $^{19}$F NMR (470 MHz, (CD$_3$)$_2$SO) δ −148.3.

$^1$H and $^{13}$C NMR data for 3,4-methylenedioxybenzenediazonium tetrafluoroborate (5h) prepared in this way were in agreement with those previously described.$^{[12]}$
**Preparation of 1-naphthlenediazonium tetrafluoroborate (5i):**

A solution of tetrafluoroboric acid in water (48% w/w, 3.66 mL, 20.0 mmol, 2.00 equiv) was added to a solution of naphthylamine (1.43 g, 10.0 mmol, 1 equiv) in water (2.0 mL) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C. A solution of sodium nitrite (690 mg, 10.0 mmol, 1.00 equiv) in water (1.0 mL) was added dropwise to the reaction vessel over 2 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and the resulting mixture was filtered immediately. The residue obtained was recrystallized with acetone–ether to afford 1-naphthlenediazonium tetrafluoroborate (5i) as a purple solid (1.31 g, 54%).

$^1$H NMR (500 MHz, (CD$_3$)$_2$SO) δ 9.20 (d, J = 8.0 Hz, 1H, H$_4$), 8.94 (d, J = 8.5 Hz, 1H, H$_3$), 8.51 (d, J = 8.5 Hz, 1H, H$_7$), 8.43 (d, J = 8.5 Hz, 1H, H$_1$), 8.12 (t, J = 7.8 Hz, 1H, H$_2$), 8.06 (t, J = 8.0 Hz, 1H, H$_5$), 7.98 (t, J = 7.5 Hz, 1H, H$_6$). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO) δ 142.6 (CH), 137.2 (CH), 132.6 (C), 132.2 (CH), 130.3 (CH), 129.9 (CH), 127.3 (C), 126.4 (CH), 122.4 (CH), 111.1 (C). $^{19}$F NMR (470 MHz, (CD$_3$)$_2$SO) δ –148.3.

$^1$H and $^{13}$C NMR data for 1-naphthlenediazonium tetrafluoroborate (5i) prepared in this way were in agreement with those previously described$^{[14]}$. 
Selective reduction of 2-chloroallyl 4-methoxybenzoate (1) to 2-chloropropyl 4-methoxybenzoate (2, Scheme 1)

A 10-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-chloroallyl 4-methoxybenzoate (1, 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 keep 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 added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C until the consumption of 1 was complete (as determined by TLC analysis, 40 min for 1). 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) as a clear oil (35.5 mg, 62%).

Rf = 0.52 (20% ethyl acetate–hexanes; UV). ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, 2H, J = 9.0 Hz, H₃), 6.93 (d, 2H, J = 9.0 Hz, H₂), 4.42–4.38 (m, 2H, H₄), 4.34–4.27 (m, 1H, H₅), 3.87 (s, 3H, H₁), 1.60 (d, 3H, J = 6.5 Hz, H₆). ¹³C NMR (150 MHz, CDCl₃) δ 165.6 (C), 163.4 (C), 131.7 (CH), 121.9 (C), 113.6 (CH), 68.6 (CH₂), 55.3 (CH₃), 54.1 (CH), 21.5 (CH₃). IR (ATR-FTIR), cm⁻¹: 2936 (w), 1712 (m), 1605 (m), 1252 (s), 1167 (s). HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₁H₁₄ClO₃, 229.0631/231.0602; found, 229.0638/231.0614.
Hydrogenation of 2-methylallyl 4-methoxybenzoate (3a) to isobutyl 4-methoxybenzoate (4a, Table 1, entry 1)

A 25 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). A 16-gauge needle was penetrated through the septum. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred at 24 °C for 3.5 h. 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 isobutyl 4-methoxybenzoate (4a) as a clear oil (44.6 mg, 86%).

R_f = 0.54 (20% ethyl acetate–hexanes; UV). 1H NMR (400 MHz, CDCl_3) δ 8.01 (d, 2H, J = 8.8 Hz, H_3), 6.92 (d, 2H, J = 8.8 Hz, H_2), 4.07 (d, J = 6.8 Hz, 2H, H_4), 3.86 (s, 3H, H_1), 2.12–2.02 (m, H_5), 1.02 (d, J = 6.8 Hz, 6H, H_6). 13C NMR (100 MHz, CDCl_3) δ 166.4 (C), 163.2 (C), 131.5 (CH), 123.0 (C), 113.5 (CH), 70.7 (CH_2), 55.4 (CH_3), 27.9 (CH), 19.2 (CH_3).

1H and 13C NMR data for isobutyl 4-methoxybenzoate (4a) prepared in this way were in agreement with those previously described\(^{13}\).
Hydrofluorination of 2-methylallyl 4-methoxybenzoate (3a) to 2-fluoro-2-methylpropyl 4-methoxybenzoate (4b, Table 1, entry 2)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), N-fluorobenzenesulfonimide (197 mg, 625 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (833 μL), 1,4-dihydrobenzene (57.4 μL, 938 μmol, 2.50 equiv), triethylsilane (400 μL, 2.50 mmol, 10.0 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 purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 5% ethyl acetate–hexanes, linear gradient) to afford separately 2-fluoro-2-methylpropyl 4-methoxybenzoate (4b, clear oil, 20.5 mg, 36%) and 2-methylallyl 4-methoxybenzoate (3a, clear oil, 14.8 mg, 29%).

2-Fluoro-2-methylpropyl 4-methoxybenzoate (4b): R_f = 0.47 (20% ethyl acetate–hexanes; UV). ^1H NMR (500 MHz, CD₂Cl₂) δ 8.01 (d, J = 8.5 Hz, 2H, H₂), 6.95 (d, J = 8.5 Hz, 2H, H₂), 4.28 (d, J = 20.0 Hz, 2H, H₄), 3.86 (s, 3H, H₁), 1.46 (d, J = 21.0 Hz, 6H, H₅). ^13C NMR (125 MHz, CD₂Cl₂) δ 166.2 (C), 164.2 (C), 132.1 (CH), 122.9 (C), 114.2 (CH), 94.1 (d, J = 168.5 Hz, C), 69.8 (d, J = 25.1 Hz, CH₂), 56.1 (CH₃), 24.2 (d, J = 24.0 Hz, CH₃). ^19F NMR (470 MHz, CD₂Cl₂) δ −146.4. IR (ATR-FTIR), cm⁻¹: 2983 (w), 1713 (s), 1606 (s), 1581 (w), 1512 (m), 1462 (w), 1379 (m), 1278 (s), 1250 (s), 1165 (s), 1100 (s), 1027 (s), 885 (m), 847 (s), 769 (s), 696 (m), 635 (w), 613 (m). HRMS-ESI (m/z): [M + H]^+ calcd for C₁₂H₁₆F₃O₃, 227.1083; found, 227.1083.
**Hydrochlorination of 2-methylallyl 4-methoxybenzoate (3a) to 2-chloro-2-methylpropyl 4-methoxybenzoate (4c, Table 1, entry 3)**

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), p-toluenesulfonyl chloride (119 mg, 625 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (833 μL), 1,4-dihydrobenzene (57.4 μL, 938 μmol, 2.50 equiv), triethylsilane (400 μL, 2.50 mmol, 10.0 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 purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 5% ethyl acetate–hexanes, linear gradient) to afford 2-chloro-2-methylpropyl 4-methoxybenzoate (4c) as a clear oil (55.7 mg, 92%).

R<sub>f</sub> = 0.47 (20% ethyl acetate–hexanes; UV). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.03 (d, J = 8.8 Hz, 2H, H<sub>3</sub>), 6.96 (d, J = 8.8 Hz, 2H, H<sub>2</sub>), 4.35 (s, 2H, H<sub>4</sub>), 3.86 (s, 3H, H<sub>1</sub>), 1.68 (s, 6H, H<sub>5</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 166.0 (C), 164.2 (C), 132.2 (CH), 122.8 (C), 114.3 (CH), 72.7 (CH<sub>2</sub>), 67.5 (C), 56.1 (CH<sub>3</sub>), 29.8 (CH<sub>3</sub>). IR (ATR-FTIR), cm<sup>−1</sup>: 2983 (w), 1713 (s), 1606 (s), 1581 (w), 1512 (m), 1462 (w), 1379 (m), 1278 (s), 1250 (s), 1165 (s), 1100 (s), 1027 (s), 885 (m), 847 (s), 769 (s), 696 (m), 635 (w), 613 (m). HRMS-ESI (m/z): [M + H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>16</sub>FO<sub>3</sub>, 227.1083; found, 227.1083.
**Hydrobromination of 2-methylallyl 4-methoxybenzoate (3a) to 2-bromo-2-methylpropyl 4-methoxybenzoate (4d, Table 1, entry 4)**

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), tosyl bromide (147 mg, 625 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (86.0 μL, 938 μmol, 3.75 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 4.0 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) to 2-bromo-2-methylpropyl 4-methoxybenzoate (4d) as a clear oil (71.5 mg, 95%).

Rf = 0.47 (20% ethyl acetate–hexanes; UV). \(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)) δ 8.03 (d, J = 8.5 Hz, 2H, H\(_3\)), 6.96 (d, J = 8.5 Hz, 2H, H\(_2\)), 4.40 (s, 2H, H\(_4\)), 3.87 (s, 3H, H\(_1\)), 1.85 (s, 6H, H\(_5\)). \(^{13}\)C NMR (125 MHz, CD\(_2\)Cl\(_2\)) δ 165.9 (C), 164.2 (C), 132.2 (CH), 122.7 (C), 114.3 (CH), 73.5 (CH\(_2\)), 62.3 (C), 56.1 (CH\(_3\)), 31.4 (CH\(_3\)). IR (ATR-FTIR), cm\(^{-1}\): 2970 (w), 1713 (m), 1605 (m), 1252 (s), 1096 (s). HRMS-ESI (m/z): [M + H]\(^+\) calcd for C\(_{12}\)H\(_{16}\)\(^{79/83}\)BrO\(_3\), 287.0283/289.0262; found, 287.0280/289.0261.
Hydroiodination of 2-methylallyl 4-methoxybenzoate (3a) to 2-iodo-2-methylpropyl 4-methoxybenzoate (4e, Table 2, entry 5)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. The reaction vessel was protected from light with aluminum foil. Dichloromethane (830 μL), diiodomethane (302 μL, 3.75 mmol, 15.0 equiv), 1,4-dihydrobenzene (115 μL, 1.25 mmol, 5.00 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 50 h at 24 °C. The product mixture was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) to 2-iodo-2-methylpropyl 4-methoxybenzoate (4e) as a clear oil (74.3 mg, 89%).

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

A 25 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv) and cobalt bis(acetylacetonate) (16.1 mg, 62.5 μmol, 0.250 equiv). The reaction vessel was left open to air. n-Propanol (830 μL), 1,4-dihydrobenzene (238 μL, 2.50 mmol, 10.0 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 11.4 μL, 62.5 μmol, 0.250 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction vessel was evacuated and refilled using a balloon of oxygen. This process was repeated twice. The reaction mixture was stirred at 24 °C until the consumption of 3a was complete (as determined by TLC analysis, 180 min for 3a). The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with 2% ether–hexanes initially, grading to 20% ether–hexanes, linear gradient) to afford 2-hydroxy-2-methylpropyl 4-methoxybenzoate (4f, clear oil, 38.5 mg, 69%).

\[ R_f = 0.29 \text{ (20\% ether–hexanes; UV).} \]

\[ ^1H \text{ NMR (400 MHz, CD}_2\text{Cl}_2) \delta 9.46 \text{ (s, 1H, OH), 8.03 (d, J = 8.8 Hz, 2H, H}_3\text{), 6.96 (d, J = 9.2 Hz, 2H, H}_3\text{), 4.36 (s, 2H, H}_4\text{), 3.87 (s, 3H, H}_1\text{), 1.27 (s, 6H, H}_5\text{).} \]

\[ ^13C \text{ NMR (100 MHz, CD}_2\text{Cl}_2) \delta 168.4 \text{ (C), 164.5 (C), 132.5 (CH), 122.4 (C), 114.3 (CH), 82.1 (C), 67.0 (CH}_2\text{), 56.1 (CH}_3\text{), 21.7 (CH}_3\text{).} \]

IR (ATR-FTIR), cm\(^{-1}\): \(3342 \text{ (w), 2983 (m), 1688 (m), 1255 (m), 1167 (s).} \)

HRMS-ESI (m/z): [M + Na]\(^+\) calcd for C\(_{12}\)H\(_{16}\)NaO\(_4\), 247.0946; found, 247.0942.
Hydrothioetherification of 2-methylallyl 4-methoxybenzoate (3a) to 2-methyl-2-(phenylthio)propyl 4-methoxybenzoate (4g, Table 2, entry 7)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 28.2 mg, 125 μmol, 1 equiv) and cobalt bis(acetylacetonate) (32.1 mg, 125 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. The reaction vessel was protected from light with aluminum foil. n-Propanol (400 μL), S-phenyl benzenesulfonothioate (78.2 mg, 313 μmol, 2.50 equiv), 1,4-dihydrobenzene (28.7 μL, 313 μmol, 2.50 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 12 h at 24 °C. The product mixture was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to 2-phenylthio-2-methylpropyl 4-methoxybenzoate (4g) as a clear oil (38.1 mg, 96%).

R_f = 0.45 (20% ethyl acetate–hexanes; UV). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.98 (d, J = 8.8 Hz, 2H, H₃), 7.58–7.56 (m, 2H, H₇), 7.40–7.32 (m, 3H, 2 × H₆, 1 × H₅), 6.94 (d, J = 8.8 Hz, 2H, H₂), 4.17 (s, 2H, H₄), 3.86 (s, 3H, H₁), 1.36 (s, 6H, H₅). ¹³C NMR (100 MHz, CD₂Cl₂) δ 166.3 (C), 164.1 (C), 138.2 (CH), 132.1 (CH), 131.7 (C), 129.7 (CH), 129.3 (CH) 123.1 (C), 114.2 (CH), 71.5 (CH₂), 56.0 (CH₂), 48.1 (C), 29.8 (CH₃). IR (ATR-FTIR), cm⁻¹: 2966 (w), 1709 (m), 1605 (m), 1250 (s), 1098 (s). HRMS-ESI (m/z): [M + Na]⁺ calcd for C₁₈H₂₀NaSO₃, 339.1031; found, 339.1035.
Hydroselenation of 2-methylallyl 4-methoxybenzoate (3a) to 2-methyl-2-(phenylselanyl)propyl 4-methoxybenzoate (4h, Table 1, entry 8)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), Se-phenyl 4-methylbenzenesulfonoselenoate (195 mg, 625 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (830 μL), 1,4-dihydrobenzene (86.0 μL, 938 μmol, 3.75 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 45.5 μL, 250 μmol, 1.00 equiv), and triethylsilane (400 μL, 2.50 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 4.0 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 6% ethyl acetate–hexanes, linear gradient) to 2-methyl-2-(phenylselanyl)propyl 4-methoxybenzoate (4h) as a clear oil (83.9 mg, 89%).

R_f = 0.47 (20% ethyl acetate–hexanes; UV, CAM). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.98–7.95 (m, 2H, H₃), 7.69–7.66 (m, 2H, H₇), 7.42–7.38 (m, 1H, H₈), 7.34–7.30 (m, 2H, H₆), 6.95–6.92 (m, 2H, H₂), 4.24 (s, 2H, H₄), 3.86 (s, 3H, H₁), 1.46 (s, 6H, H₅). ¹³C NMR (100 MHz, CD₂Cl₂) δ 166.2 (C), 164.1 (C), 138.9 (CH), 132.1 (CH), 129.4 (CH), 129.4 (CH), 127.4 (C), 123.1 (C), 114.2 (CH), 72.7 (CH₂), 56.0 (CH₃), 45.0 (C), 27.0 (CH₃). IR (ATR-FTIR), cm⁻¹: 2960 (w), 1712 (m), 1606 (m), 1256 (s), 1167 (m). HRMS-ESI (m/z): [M + H]⁺ calcd for C₁₈H₂₁SeO₃, 365.0656; found, 365.0648.
Hydroazidation of 2-methylallyl 4-methoxybenzoate (3a) to 2-azido-2-methylpropyl 4-methoxybenzoate (4i, Table 1 entry 9)

\[
\text{CH}_3\text{O} \quad \text{O} \quad \text{Co(acac)}_3, \text{TBHP, Et}_3\text{SiH, DHB, p-ABSA} \quad \text{CH}_3\text{CN, argon, 24 °C} \quad \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \quad \text{79%} \]

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 25.8 mg, 125 μmol, 1 equiv), 4-acetamidobenzenesulfonyl azide (150 mg, 625 μmol, 5.00 equiv), and cobalt bis(acetylacetonate) (32.1 mg, 125 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Acetonitrile (400 μL), 1,4-dihydrobenzene (11.5 μL, 125 μmol, 1.00 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 1.00 equiv), and triethylsilane (200 μL, 1.25 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 1.5 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 3% ethyl acetate–hexanes initially, grading to 7% ethyl acetate–hexanes, linear gradient) to 2-azido-2-methylpropyl 4-methoxybenzoate (4i) as a clear oil (24.6 mg, 79%).

R_f = 0.42 (20% ethyl acetate–hexanes; UV). 1H NMR (600 MHz, CD_2Cl_2) δ 8.02 (d, J = 9.0 Hz, 2H, H_3), 6.95 (d, J = 9.0 Hz, 2H, H_2), 4.21 (s, 2H, H_4), 3.86 (s, 3H, H_1), 1.37 (s, 6H, H_5). 13C NMR (100 MHz, CD_2Cl_2) δ 166.1 (C), 164.2 (C), 132.2 (CH), 122.6 (C), 114.2 (CH), 71.4 (CH_2), 60.9 (C), 56.0 (CH_3), 23.6 (CH_3). IR (ATR-FTIR), cm⁻¹: 2977 (w), 2095 (m), 1715 (m), 1606 (m), 1255 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C_{12}H_{15}N_3NaO_3, 272.1011; found, 272.0998.
Hydrooximation of 2-methylallyl 4-methoxybenzoate (3a) to 3-((benzyloxy)imino)-3-cyano-2,2-dimethylpropyl 4-methoxybenzoate (4j)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 25.8 mg, 125 μmol, 1 equiv), N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (6a, 93.9 mg, 313 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (32.1 mg, 125 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (400 μL), 1,4-dihydrobenzene (43.0 μL, 470 μmol, 3.75 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 1.00 equiv), and triethylsilane (200 μL, 1.25 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 8.0 h at 24 °C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to 3-((benzyloxy)imino)-3-cyano-2,2-dimethylpropyl 4-methoxybenzoate (4j) as a clear oil (27.5 mg, 60%).

\[ R_f = 0.35 \ (20\% \ \text{ethyl acetate–hexanes; UV, CAM}) \]

\[ ^1H \ \text{NMR} \ (600 MHz, CD}_2\text{Cl}_2 \ \delta \ 7.92 \ (d, J = 8.4 \ \text{Hz}, 2H, H_3), \ 7.36–7.32 \ (m, 5H, 2 \times H_7, 2 \times H_8, 1 \times H_9), \ 6.91 \ (d, J = 8.4 \ \text{Hz}, 2H, H_2), \ 5.26 \ (s, 2H, H_6), \ 4.21 \ (s, 2H, H_4), \ 3.86 \ (s, 3H, H_1), \ 1.36 \ (s, 6H, H_5). \]

\[ ^13C \ \text{NMR} \ (100 MHz, CD}_2\text{Cl}_2 \ \delta \ 166.1 \ (C), \ 164.2 \ (C), \ 138.1 \ (C), \ 136.6 \ (C), \ 132.1 \ (CH), \ 129.1 \ (CH), \ 129.0 \ (CH), \ 128.9 \ (CH), \ 122.7 \ (C), \ 114.2 \ (CH), \ 109.9 \ (C), \ 78.7 \ (CH_2), \ 70.2 \ (CH_2), \ 56.0 \ (CH_3), \ 40.5 \ (C), \ 23.2 \ (CH_3). \]

IR (ATR-FTIR), cm\(^{-1}\): 2973 (w), 1713 (m), 1605 (m), 1511 (m), 1254 (s).

HRMS-ESI (m/z): [M + H]\(^+\) calcd for C\(_{21}\)H\(_{23}\)N\(_2\)O\(_4\), 367.1658; found, 367.1653.
**Hydrooximation of 2-methylallyl 4-methoxybenzoate (3a) to 3-((benzyloxy)imino)-2,2-dimethylpropyl 4-methoxybenzoate (4k)**

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 25.8 mg, 125 μmol, 1 equiv), (phenylsulfonyl)methanal O-benzyl oxime (6b, 86.0 mg, 313 μmol, 2.50 equiv), and cobalt bis(acetylacetonate) (32.1 mg, 125 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. n-Propanol (400 μL), 1,4-dihydrobenzene (43.0 μL, 470 μmol, 3.75 equiv), a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 22.8 μL, 125 μmol, 1.00 equiv), and triethylsilane (200 μL, 1.25 mmol, 10.0 equiv) were added sequentially to the reaction vessel via syringe. The reaction mixture was stirred for 6.0 h at 24°C. The product mixture was filtered through a short column of silica gel and the short column was rinsed with 20% ethyl acetate–hexanes (100 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, linear gradient) to 3-((benzyloxy)imino)-2,2-dimethylpropyl 4-methoxybenzoate (4k) as a clear oil (20.4 mg, 48%).

R_f = 0.40 (20% ethyl acetate–hexanes; UV, CAM). \(^1\)H NMR (500 MHz, CD_2Cl_2) 𝛿 7.96 (d, J = 8.5 Hz, 2H, H_3), 7.47 (s, 1H, H_10), 7.35–7.28 (m, 5H, 2 × H_7, 2 × H_8, 1 × H_9), 6.93 (d, J = 8.5 Hz, 2H, H_2), 5.04 (s, 2H, H_6), 4.17 (s, 2H, H_4), 3.86 (s, 3H, H_1), 1.21 (s, 6H, H_5). \(^{13}\)C NMR (125 MHz, CD_2Cl_2) 𝛿 166.4 (C), 164.0 (C), 155.6 (CH), 138.5 (C), 132.0 (CH), 128.8 (CH), 128.7 (CH), 128.2 (CH), 123.1 (C), 114.2 (CH), 76.2 (CH_2), 71.1 (CH_2), 56.0 (CH_2), 38.1 (C), 23.2 (CH_3). IR (ATR-FTIR), cm\(^{-1}\): 2969 (w), 2969 (w), 2969 (w), 2969 (w), 2969 (w), 2969 (w), 2969 (w), 2969 (w), 2969 (w), 2969 (w). HRMS-ESI (m/z): [M + Na]^+ calcd for C_{20}H_{23}NNaO_4, 364.1525; found, 364.1517.
Hydropyridylation of 2-methylallyl 4-methoxybenzoate (3a) to 2-methyl-2-(pyridin-4-yl)propyl 4-methoxybenzoate (4l) and 2-methyl-2-(pyridin-2-yl)propyl 4-methoxybenzoate (4la)

A 25-mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 206 mg, 1.00 mmol, 1 equiv), N-methoxy pyridinium methylsulfate (6c, 1.11 g, 5.00 mmol, 5.00 equiv), and cobalt bis(acetylacetonate) (257 mg, 1.00 mmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. The reaction vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 16 h. The product mixture was transfer to a separatory funnel that had been charged with ethyl acetate (200 mL). The diluted product mixture was washed with 3 M aqueous ammonium hydroxide solution (3 × 50 mL). The organic layer was isolated and the isolated organic layer was 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 dichloromethane initially, grading to 10% methanol–dichloromethane, linear gradient). The mixture containing the minor regioisomer was further purified by flash-column chromatography (eluting with 10% ethyl acetate–10% dichloromethane–10% triethylamine–hexanes) to afford 2-methyl-2-(pyridin-4-yl)propyl 4-methoxybenzoate (4l) as a colorless oil (189 mg, 66%). The mixture containing the minor regioisomer was further purified three times by automated flash-column chromatography (eluting with hexanes initially, grading to 33% ether–hexanes, linear gradient) to afford 2-methyl-2-(pyridin-2-yl)propyl 4-methoxybenzoate (4la) as a colorless oil (38.9 mg, 14%).

2-Methyl-2-(pyridin-4-yl)propyl 4-methoxybenzoate (4l): Rf = 0.55 (10% methanol–dichloromethane; UV). 1H NMR (400 MHz, CDCl3) δ 8.36 (br s, 2H, H2), 7.85 (d, J = 8.8 Hz, 2H, H2), 7.33 (d, J = 5.2 Hz, 2H, H6), 6.87 (d, J = 8.8 Hz, 2H, H2), 4.35 (s, 2H, H4), 3.83 (s, 3H, H3), 1.43 (s, 6H, H8). 13C NMR (100 MHz, CDCl3) δ 166.0 (C), 163.4 (C), 155.4 (C), 149.9 (CH), 131.5 (CH), 122.2 (C), 121.3 (CH), 113.6 (CH), 72.1 (CH2), 55.4 (CH3), 38.5 (CH3). IR (ATR-FTIR), cm⁻¹: 2970 (w), 1709 (m), 1605 (m), 1271 (s), 1254 (s), 1166 (m), 1101 (m), 769 (m). HRMS-ESI (m/z): [M + H]+ calcld for C17H20NO3, 286.1443; found, 286.1434.

2-Methyl-2-(pyridin-2-yl)propyl 4-methoxybenzoate (4la): Rf = 0.61 (40% ether–hexanes; UV). 1H NMR (400 MHz, CDCl3) δ 8.59 (d, J = 4.8 Hz, 1H, H9), 7.85 (d, J = 8.4 Hz, 2H, H2), 7.64 (t, J = 7.4 Hz, 1H, H7), 7.38 (d, J = 8.4 Hz, 1H, H6), 7.12 (dd, J = 6.4, 5.2 Hz, 1H, H8), 6.86 (d, J = 8.4 Hz, 2H, H2), 4.50 (s, 2H, H4), 3.82 (s, 3H, H3), 1.48 (s, 6H, H8). 13C NMR (100 MHz, CDCl3) δ 166.1 (C), 165.3 (C), 163.2 (C), 148.9 (CH), 136.2 (CH), 131.5 (CH), 122.7 (C), 121.2 (CH), 120.0 (CH), 113.5 (CH), 72.5 (CH2), 55.4 (CH3), 41.2 (C), 25.1 (CH3). IR (ATR-FTIR), cm⁻¹: 2971 (w), 1709 (s), 1606 (s), 1512 (m), 1273 (m), 1256 (s), 1167 (s), 1102 (w), 1029 (s), 770 (m). HRMS-ESI (m/z): [M + H]+ calcld for C17H20NO3, 286.1443; found, 286.1440.
Hydrofunctionalization of 2-methylallyl 4-methoxybenzoate (3a) to the manganese(I) complex 4m

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 51.5 mg, 250 μmol, 1 equiv), (η⁶-benzene) manganese tricarbonyl hexafluorophosphate (6d, 90.5 mg, 250 μmol, 1.00 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Acetonitrile (1.25 mL) was added to the reaction vessel via syringe and the reaction vessel was cooled to 0 °C. Triethylsilane (200 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred for 12 h at 0 °C. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 33% ethyl acetate–hexanes, linear gradient) to afford 4-(1-((4-methoxybenzoyl)oxy)-2-methylpropan-2-yl)cyclohexa-2,5-dien-1-yl tricarbonyl manganese(I) (4m) as a pale yellow oil (53.6 mg, 50%).

R_f = 0.29 (33% ether–hexanes; UV). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.4 Hz, 2H, H₂), 6.93 (d, J = 8.4 Hz, 2H, H₂), 5.68 (t, J = 4.6 Hz, 1H, H₆); 4.92 (t, J = 6.0 Hz, 2H, H₇), 3.87 (s, 3H, H₁), 3.82 (s, 2H, H₄), 3.21 (t, J = 6.0 Hz, 2H, H₈), 2.80 (t, J = 5.4 Hz, 1H, H₉), 0.69 (s, 6H, H₅). ¹³C NMR (100 MHz, CDCl₃) δ 222.8 (C), 166.2 (C), 163.4 (C), 131.5 (CH), 122.6 (C), 113.7 (CH), 97.8 (CH), 78.8 (CH), 69.4 (CH₂), 56.2 (CH₃), 55.5 (CH), 42.5 (CH), 41.4 (C), 20.7 (CH₃). IR (ATR-FTIR), cm⁻¹: 2964 (w), 2961 (w), 2008 (s), 1907 (s), 1708 (m), 1606 (m), 1253 (s), 1166 (m), 1101 (m), 1029 (m), 658 (m), 636 (s), 613 (s). HRMS-ESI (m/z): [M + H]⁺ calcd for C₂₁H₂₂MnO₆, 425.0797; found, 425.0772.
Hyrdadiazeniaen of 2-methylallyl 4-methoxybenzoate (3a) to 2-((4-methoxyphenyl)diazenzyl)-2-methylpropyl 4-methoxybenzoate (7a)

A 25 mL round-bottomed flask fitted with a rubber septum was charged sequentially with 2-methylallyl 4-methoxybenzoate (3a, 206 mg, 1.00 mmol, 1 equiv), 4-methoxybenzenediazonium tetrafluoroborate (5a, 333 mg, 1.50 mmol, 1.50 equiv), and cobalt bis(acetylacetonate) (257 mg, 1.00 mmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (5.0 mL), triethylsilane (998 μL, 6.25 mmol, 6.25 equiv), and a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 182 μL, 1.00 mmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 25% ether–hexanes, linear gradient) to afford 2-((4-methoxyphenyl)diazenzyl)-2-methylpropyl 4-methoxybenzoate (7a) as a bright yellow oil (316 mg, 92%).

R_f = 0.33 (25% ether–hexanes; UV). 1H NMR (400 MHz, CDCl3) δ 7.95 (d, J = 8.8 Hz, 2H, H_2), 7.69 (d, J = 8.4 Hz, 2H, H_6), 6.94 (d, J = 8.8 Hz, 2H, H_7), 6.88 (d, J = 8.8 Hz, 2H, H_5), 4.60 (s, 2H, H_4), 3.85 (s, 3H, H_3), 3.83 (s, 3H, H_1), 1.41 (s, 6H, H_8). 13C NMR (100 MHz, CDCl3) δ 166.2 (C), 163.3 (C), 161.5 (C), 146.3 (C), 131.6 (CH), 123.9 (CH), 122.7 (C), 113.9 (CH), 113.6 (CH), 70.1 (CH_2), 69.1 (C), 55.5 (CH_3), 55.4 (CH_3), 22.4 (CH_3). IR (ATR-FTIR), cm⁻¹: 2952 (w), 1719 (s), 1607 (m), 1512 (w), 1436 (w), 1365 (w), 1275 (s), 1257 (s), 1167 (m), 1103 (m), 1030 (w), 848 (w), 770 (m). HRMS-ESI (m/z): [M + H]⁺ calcd for C_{19}H_{23}N_2O_4, 343.1658; found, 343.1661.
Hydrodiazenation of allyl 4-methoxybenzoate (3b) to 2-((4-methoxyphenyl)diazenyl)propyl 4-methoxybenzoate (7b)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3b, 48.1 mg, 250 μmol, 1 equiv), 4-methoxybenzenediazonium tetrafluoroborate (5a, 83.2 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 20% ethyl acetate–hexanes, linear gradient) to afford 2-((4-methoxyphenyl)diazenyl)propyl 4-methoxybenzoate (7b) as a bright yellow oil (63.2 mg, 77%).

R_f = 0.45 (20% ethyl acetate–hexanes; UV). 1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 8.8 Hz, 2H, H_2), 7.69 (d, J = 8.4 Hz, 2H, H_2), 6.95 (d, J = 8.8 Hz, 2H, H_2), 6.87 (d, J = 8.8 Hz, 2H, H_2), 4.75 (dd, J = 11.2, 8.4 Hz, 1H, 1 × H_4), 4.63 (dd, J = 11.2, 4.4 Hz, 1H, 1 × H_4), 4.16–4.10 (m, 1H, H_3), 3.86 (s, 3H, H_3), 3.83 (s, 3H, H_3), 1.42 (d, J = 6.8 Hz, 3H, H_3). 13C NMR (100 MHz, CDCl_3) δ 166.1 (C), 163.3 (C), 146.2 (C), 131.6 (CH), 124.1 (CH), 122.5 (C), 114.0 (CH), 113.5 (CH), 71.0 (CH), 66.6 (CH_2), 55.5 (CH_3), 55.5 (CH_3), 15.5 (CH_3). IR (ATR-FTIR), cm⁻¹: 2977 (w), 1719 (s), 1606 (m), 1512 (w), 1436 (w), 1315 (w), 1275 (s), 1256 (s), 1167 (m), 1103 (m), 1030 (w), 849 (w), 770 (m). HRMS-ESI (m/z): [M + H]^+ calcd for C_{18}H_{21}N_2O_4, 329.1501; found, 329.1500.
Hydrodiazenation of prenyl 4-methoxybenzoate (3c) to 3-((4-methoxyphenyl)diazenyl)-3-methylbutyl 4-methoxybenzoate (7c)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with prenyl 4-methoxybenzoate (3c, 48.1 mg, 250 μmol, 1 equiv), 4-methoxybenzenediazonium tetrafluoroborate (5a, 83.2 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 20% ethyl acetate–hexanes, linear gradient) to afford 3-((4-methoxyphenyl)diazenyl)-3-methylbutyl 4-methoxybenzoate (7c) as a bright yellow oil (63.2 mg, 91%).

R_f = 0.45 (20% ethyl acetate–hexanes; UV). 1H NMR (500 MHz, CDCl_3) δ 7.93 (d, J = 8.5 Hz, 2H, H_2), 7.66 (d, J = 8.5 Hz, 2H, H_7), 6.92 (d, J = 8.5 Hz, 2H, H_8), 6.85 (d, J = 8.5 Hz, 2H, H_3), 4.41 (t, J = 7.0 Hz, 2H, H_4), 3.85 (s, 3H, H_6), 3.84 (s, 3H, H_9), 2.28 (t, J = 7.0 Hz, 2H, H_5), 1.37 (s, 6H, H_3). 13C NMR (125 MHz, CDCl_3) δ 166.3 (C), 163.2 (C), 161.3 (C), 146.2 (C), 131.5 (CH), 123.8 (CH), 122.8 (C), 113.9 (CH), 113.5 (CH), 68.3 (C), 61.5 (CH_2), 55.5 (CH_3), 55.4 (CH_3), 39.2 (CH_2), 25.3 (CH_3). IR (ATR-FTIR), cm⁻¹: 2966 (w), 1708 (m), 1605 (s), 1461 (w), 1315 (w), 1274 (m), 1247 (s), 1166 (s), 1101 (s), 1028 (s), 836 (s), 769 (s), 696 (m), 613 (m). HRMS-ESI (m/z): [M + H]^+ calcd for C_{20}H_{25}N_2O_4, 357.1814; found, 357.1815.
Hydrodiazenation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((4-fluorophenyl)diazyl)-2-methylpropyl 4-methoxybenzoate (7d)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), 4-fluorobenzenediazonium tetrafluoroborate (5b, 78.7 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 20% ethyl acetate–hexanes, linear gradient) to afford 2-((4-fluorophenyl)diazyl)-2-methylpropyl 4-methoxybenzoate (7d) as a bright yellow oil (67.9 mg, 82%).

R_f = 0.45 (20% ethyl acetate–hexanes; UV). ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, J = 8.0 Hz, 2H, H_2), 7.70 (dd, J = 8.0, 5.5 Hz, 2H, H_6), 7.12 (t, J = 8.5 Hz, 2H, H_7), 6.89 (d, J = 8.0 Hz, 2H, H_3), 4.61 (s, 2H, H_4), 3.84 (s, 3H, H_1), 1.42 (s, 6H, H_5). ^13C NMR (125 MHz, CDCl_3) δ 166.1 (C), 164.0 (d, J = 249.0 Hz, C), 163.4 (C), 148.5 (d, J = 3.0 Hz, C), 131.6 (CH), 124.1 (d, J = 8.8 Hz, CH), 122.6 (CH), 115.7 (d, J = 22.6 Hz, CH), 113.6 (C), 69.9 (CH_2), 69.7 (C), 55.4 (CH_3), 22.3 (CH_3). ^19F NMR (470 MHz, CDCl_3) δ = -110.8. IR (ATR-FTIR), cm⁻¹: 2977 (w), 1714 (m), 1607 (m), 1152 (w), 1316 (w) 1274 (m), 1256 (s), 1167 (s), 1102 (m), 844 (m), 769 (m). HRMS-ESI (m/z): [M + H]^+ calcd for C_{18}H_{20}F_{N}O_{3}, 331.1458; found, 331.1451.
Hydrodiazenation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((4-(trifluoromethyl)phenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7e)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), 4-(trifluoromethyl)benzenediazonium tetrafluoroborate (5c, 97.5 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 12% ethyl acetate–hexanes, linear gradient) to afford 2-((4-(trifluoromethyl)phenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7e) as a bright yellow oil (67.5 mg, 71%).

R<sub>f</sub> = 0.43 (33% ethyl acetate–hexanes; UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (d, J = 9.0 Hz, 2H, H<sub>2</sub>), 7.75 (d, J = 8.0 Hz, 2H, H<sub>6</sub>), 7.71 (d, J = 8.5 Hz, 2H, H<sub>7</sub>), 6.89 (d, J = 9.0 Hz, 2H, H<sub>3</sub>), 4.64 (s, 2H, H<sub>4</sub>), 3.84 (s, 3H, H<sub>1</sub>), 1.44 (s, 6H, H<sub>5</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.0 (C), 163.4 (C), 154.0 (C), 131.9 (q, J = 21.7 Hz, CH), 131.6 (CH), 126.2 (q, J = 4.2 Hz, CH), 123.9 (q, J = 270.8 Hz, C), 122.4 (C), 122.3 (CH), 113.6 (C), 70.7 (C), 69.6 (CH<sub>2</sub>), 55.4 (CH<sub>3</sub>), 22.2 (CH<sub>3</sub>). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ –62.6. IR (ATR-FTIR), cm<sup>–1</sup>: 1715 (m), 1678 (w), 1508 (m), 1512 (w), 1323 (s), 1302 (m), 1257 (s), 1167 (s), 1110 (s), 1064 (m), 845 (m), 770 (w). HRMS-ESI (m/z): [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>, 381.1426; found, 381.1429.
Hydrodiazenation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((4-bromophenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7f)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), 4-bromobenzenediazonium tetrafluoroborate (5d, 102 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 ºC for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 12% ethyl acetate–hexanes, linear gradient) to afford 2-((4-bromophenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7f) as a bright yellow oil (63.2 mg, 65%).

R_f = 0.42 (33% ethyl acetate–hexanes; UV). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.8 Hz, 2H, H₂), 7.60–7.53 (m, 4H, 2 × H₆, 2 × H₇), 6.88 (d, J = 8.8 Hz, 2H, H₃), 4.61 (s, 2H, H₄), 3.84 (s, 3H, H₁), 1.42 (s, 6H, H₅). ¹³C NMR (100 MHz, CDCl₃) δ 166.0 (C), 163.4 (C), 150.8 (C), 132.1 (CH), 131.6 (CH), 124.7 (C), 123.7 (CH), 122.5 (C), 113.6 (CH), 70.1 (CH₂), 69.8 (C), 55.4 (CH₃), 22.2 (CH₃). IR (ATR-FTIR), cm⁻¹: 2976 (w), 1713 (s), 1606 (m), 1580 (w), 1511 (w), 1470 (w), 1364 (w), 1316 (w), 1273 (m), 1255 (s), 1167 (s), 1102 (m), 1031 (w), 1009 (w), 847 (w), 832 (w), 769 (w). HRMS-ESI (m/z): [M + H]⁺ calc'd for C₁₈H₂₀Br₇N₂O₃, 391.0657/393.0637; found, 391.0652/393.0637.
Hydrodiazенation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((4-(methoxycarbonyl)phenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7g)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (5e, 93.7 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 20% ethyl acetate–hexanes, linear gradient) to afford 2-((4-(methoxycarbonyl)phenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7g) as a bright yellow oil (47.8 mg, 52%).

R_f = 0.32 (20% ethyl acetate–hexanes; UV). ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, J = 8.4 Hz, 2H, H_6), 7.92 (d, J = 8.8 Hz, 2H, H_3), 7.67 (d, J = 8.4 Hz, 2H, H_2), 6.88 (d, J = 8.8 Hz, 2H, H_5), 4.63 (s, 2H, H_4), 3.93 (s, 3H, H_8), 3.83 (s, 3H, H_1), 1.42 (s, 6H, H_5). ^13C NMR (100 MHz, CDCl_3) δ 166.5 (C), 166.0 (C), 163.4 (C), 154.7 (C), 131.6 (CH), 131.4 (C), 130.5 (CH), 122.4 (C), 121.9 (CH), 113.6 (CH), 70.7 (CH_2), 69.7 (C), 55.4 (CH_3), 52.3 (CH_3), 22.2 (CH_3). IR (ATR-FTIR), cm[^-1]: 2951 (w), 1714 (s), 1606 (m), 1459 (w), 1435 (w), 1315 (w), 1272 (s), 1252 (s), 1165 (s), 1096 (s), 1028 (m), 1013 (m), 847 (m), 767 (s), 696 (m), 634 (w), 612 (w), 510 (w). HRMS-ESI (m/z): [M + H]^+ calcd for C_{20}H_{23}N_2O_5, 371.1607; found, 371.1605.
Hydrodiazenation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((2-methylphenyl)diazeyl)-2-methylpropyl 4-methoxybenzoate (7h)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), 2-methylbenzenediazonium tetrafluoroborate (5f, 77.2 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 20% ethyl acetate–hexanes, linear gradient) to afford 2-((2-methylphenyl)diazeyl)-2-methylpropyl 4-methoxybenzoate (7h) as a bright yellow oil (79.5 mg, 97%).

Rf = 0.37 (20% ethyl acetate–hexanes; UV). 1H NMR (500 MHz, CD2Cl2) δ 7.94 (d, J = 8.0 Hz, 2H, H2), 7.33–7.26 (m, 3H, 1 × H6, 1 × H7, 1 × H8), 7.22–7.17 (m, 1H, 1 × H9), 6.90 (d, J = 8.0 Hz, 2H, H3), 4.61 (s, 2H, H4), 3.84 (s, 3H, H1), 2.56 (s, 3H, H10), 1.44 (s, 6H, H5). 13C NMR (125 MHz, CD2Cl2) δ 165.8 (C), 163.4 (C), 150.4 (C), 136.2 (C), 131.4 (CH), 130.9 (CH), 130.0 (CH), 126.2 (CH), 122.6 (C), 115.5 (CH), 113.5 (CH), 70.2 (CH2), 69.7 (C), 55.4 (CH3), 22.1 (CH3), 16.8 (CH3). IR (ATR-FTIR), cm⁻¹: 2975 (w), 1714 (s), 1607 (m), 1512 (w), 1316 (w), 1274 (m), 1256 (s), 1167 (s), 1102 (m), 1031 (w), 847 (w), 769 (m), 696 (w). HRMS-ESI (m/z): [M + H]^+ calcd for C19H23N2O3, 327.1709; found, 327.1704.
Hydro diazenation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((3-phenox yphenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7i)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 51.6 mg, 250 µmol, 1 equiv), 3-phenox ybenzenediazonium tetrafluoroborate (5g, 107 mg, 375 µmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 µmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 µL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 12% ethyl acetate–hexanes, linear gradient) to afford 2-((3-phenox yphenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7i) as a bright yellow oil (78.1 mg, 77%).

R_f = 0.32 (20% ethyl acetate–hexanes; UV). ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, J = 9.0 Hz, 2H, H_2), 7.44–7.38 (m, 2H, 1 × H_6, 1 × H_9), 7.37–7.32 (m, 3H, 1 × H_6, 2 × H_11), 7.13 (t, J = 5.0 Hz, 1H, H_12), 7.09–7.01 (m, 3H, 1 × H_7, 2 × H_10), 6.88 (d, J = 9.0 Hz, 2H, H_4), 4.59 (s, 2H, H_3), 3.85 (s, 3H, H_1), 1.41 (s, 6H, H_5). ^13C NMR (125 MHz, CDCl_3) δ 166.1 (C), 163.3 (C), 157.9 (C), 156.8 (C), 153.6 (C), 131.5 (CH), 123.0 (CH), 129.8 (CH), 123.5 (CH), 122.6 (C), 120.5 (CH), 119.0 (CH), 117.3 (CH), 113.6 (CH), 112.1 (CH), 70.0 (CH_2), 69.8 (C), 55.4 (CH_3), 22.2 (CH_3). IR (ATR-FTIR), cm⁻¹: 2974 (w), 1713 (s), 1586 (m), 1511 (m), 1490 (m), 1473 (m), 1315 (w), 1254 (s), 1209 (w), 1167 (s), 1102 (m), 1030 (w), 847 (w), 769 (m), 694 (m). HRMS-ESI (m/z): [M + H]^+ calcd for C_{24}H_{35}N_2O_4, 405.1814; found, 405.1814.
Hydrodiazenation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((3,4-methyleneoxyphenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7j)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), 3,4-methyleneoxybenzenediazonium tetrafluoroborate (5h, 88.5 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 12% ethyl acetate–hexanes, linear gradient) to afford 2-((3,4-methyleneoxyphenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7j) as a bright yellow oil (72.4 mg, 81%).

Rf = 0.34 (20% ethyl acetate–hexanes; UV). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.94 (d, J = 9.0 Hz, 2H, H$_2$), 7.38 (d, J = 9.5 Hz, 1H, H$_6$), 7.18 (s, 1H, H$_8$), 6.89–6.87 (m, 3H, 1 × H$_7$, 2 × H$_3$), 6.01 (s, 2H, H$_9$), 4.58 (s, 2H, H$_4$), 3.84 (s, 3H, H$_1$), 1.40 (s, 6H, H$_5$). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.1 (C), 163.3 (C), 149.6 (C), 148.5 (C), 147.8 (C), 131.6 (CH), 122.6 (C), 121.7 (CH), 113.6 (CH), 107.7 (CH), 101.7 (CH$_3$), 99.1 (CH), 70.0 (CH$_2$), 69.1 (C), 55.4 (CH$_3$), 22.4 (CH$_3$). IR (ATR-FTIR), cm$^{-1}$: 2974 (w), 1710 (s), 1606 (s), 1511 (m), 1473 (s), 1364 (w), 1473 (s), 1316 (m), 1250 (s), 1165 (s), 1100 (s), 1031 (m), 931 (m), 846 (m), 810 (m), 769 (s), 634 (w), 612 (m), 526 (w). HRMS-ESI (m/z): [M + H]$^+$ calcd for C$_{19}$H$_{21}$N$_2$O$_5$, 357.1450; found, 357.1451.
Hydrodiazenation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((1-naphthyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7k)

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 51.6 mg, 250 μmol, 1 equiv), 1-naphthylendiazionium tetrafluoroborate (5i, 90.7 mg, 375 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (64.3 mg, 250 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (1.3 mL), triethylsilane (250 μL, 1.56 mmol, 6.25 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 vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained was purified by automated flash-column chromatography (eluting with hexanes initially, grading to 12% ethyl acetate–hexanes, linear gradient) to afford 2-((1-naphthyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7k) as a bright orange oil (62.3 mg, 69%).

R_f = 0.31 (20% ethyl acetate–hexanes; UV). ^1H NMR (500 MHz, CDCl₃) δ 8.67–8.65 (m, 1H, H₁₂), 7.96–7.89 (m, 4H, 2 × H₃, 1 × H₅, 1 × H₈), 7.59–7.53 (m, 2H, 1 × H₇, 1 × H₉), 7.50 (t, J = 7.8 Hz, 1H, H₁₀), 7.44 (d, J = 9.0 Hz, 1H, H₉), 6.86 (d, J = 8.5 Hz, 2H, H₃), 4.72 (s, 2H, H₁₅), 3.83 (s, 3H, H₁₆), 1.54 (s, 6H, H₁₇). ^13C NMR (125 MHz, CDCl₃) δ 166.1 (C), 163.4 (C), 147.6 (C), 134.1 (C), 131.6 (CH), 130.4 (CH), 130.3 (C), 127.8 (CH), 126.6 (CH), 126.4 (CH), 125.6 (CH), 123.2 (CH), 122.5 (C), 113.6 (CH), 111.8 (CH), 70.9 (CH₂), 69.8 (C), 55.4 (CH₃), 22.5 (CH₃). IR (ATR-FTIR), cm⁻¹: 2977 (w), 1711 (s), 1606 (s), 1511 (m), 1459 (w), 1364 (w), 1316 (w), 123 (s), 1165 (s), 1100 (s), 1029 (m), 1010 (w), 846 (w), 801 (m), 769 9s), 696 (w), 612 (m). HRMS-ESI (m/z): [M + H]^+ calcd for C₂₂H₂₃N₂O₃, 363.1709; found, 363.1710.
**Attempted hydrodiazeneation of 2-methylallyl 4-methoxybenzoate (3a) to 2-((4-nitrophenyl)diazenyl)-2-methylpropyl 4-methoxybenzoate (7l)**

A 10 mL round-bottomed flask fitted with a rubber septum was charged sequentially with allyl 4-methoxybenzoate (3a, 20.6 mg, 100 μmol, 1 equiv), 4-nitrobenzenediazonium tetrafluoroborate (5k, 35.5 mg, 150 μmol, 1.50 equiv), and cobalt bis(acetylacetonate) (25.7 mg, 100 μmol, 1.00 equiv). The reaction vessel was evacuated and refilled using a balloon of argon. This process was repeated twice. Dichloromethane (500 μL), triethylsilane (79.9 μL, 625 μmol, 6.25 equiv), and a solution of tert-butyl hydroperoxide in nonane (~5.5 M, 18.2 μL, 100 μmol, 1.00 equiv) were added sequentially to the reaction vessel via syringe. The reaction vessel was protected from light with aluminum foil. The reaction mixture was stirred at 24 °C for 30 min. The product mixture was concentrated to dryness and the residue obtained filtered through a short column of silica gel. The column was rinsed with ether (100 mL). The filtrates were combined and the combined filtrates were concentrated to dryness. $^1$H NMR analysis of the unpurified mixture showed complex decomposition of 3a.
Catalog of nuclear magnetic resonance and infrared spectra

$^1$H NMR (CD$_2$Cl$_2$, 500 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz)
$^1$H NMR, (CD$_3$)$_2$SO, 400 MHz
$^{13}$C NMR, (CD$_3$)$_2$SO, 100 MHz
$^1$H NMR (CD$_3$)$_2$SO, 500 MHz

5c

$\text{CF}_3$

$\text{BF}_2^-$

$\text{N}_2^+$

f$_1$ (ppm)
$^{19}$F NMR ((CD$_3$)$_2$SO, 470 MHz)

![NMR Spectrum]

$^{5c}$
$^1$H NMR (CD$_3$)SO, 500 MHz
$^{13}$C NMR ((CD)$_2$SO, 125 MHz)
$^{19}$F NMR ((CD$_3$)$_2$SO, 470 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 150 MHz)
$^{19}\text{F NMR (CD}_2\text{Cl}_2, 470 \text{ MHz)}$
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)

\[ \text{Formula Image} \]

\[ f_1 \text{ (ppm)} \]

\[ \text{Diagram Image} \]
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)
$^{13}\text{C NMR (CD}_2\text{Cl}_2, 100 \text{ MHz)}$
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz)

4h

CH$_3$O

CH$_3$

CH$_3$
$^{13}$C NMR (CD$_2$Cl$_2$, 150 MHz)
$^{13}$C NMR (CD$_2$Cl$_2$, 150 MHz)
$^1\text{H NMR (CD}_2\text{Cl}_2$, 500 MHz)

4k
\[^{13}\text{C} \text{ NMR (CD}_2\text{Cl}_2, 125 \text{ MHz)}\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{H} & \quad \text{N} \\
\text{CH}_3 & \quad \text{O} \\
\text{CH}_3 & 
\end{align*}
\]

\(4k\)
$^{13}$C NMR, CDCl$_3$, 100 MHz
$^{13}$C NMR, CDCl$_3$, 100 MHz

4la
$^{13}$C NMR, CDCl$_3$, 100 MHz
$^{13}$C NMR (CDCl$_3$, 100 MHz)

![13C NMR spectrum with chemical structure 7a](image)
$^1$H NMR, CDCl₃, 400 MHz
$^1$H NMR, CDCl$_3$, 500 MHz
$^1$H NMR, CDCl$_3$, 500 MHz

[Chemical structure image]
$^{13}$C NMR, CDCl$_3$, 125 MHz

![NMR Spectrum Image]
$^{13}$C NMR, CDCl$_3$, 125 MHz
$^{17}$F NMR, CDCl$_3$, 470 MHz
$^{13}$C NMR, CDCl$_3$, 100 MHz

![NMR spectrum of a chemical compound](image)
$^1$H NMR, CDCl$_3$, 400 MHz
$^1$H NMR, CD$_2$Cl$_2$, 500 MHz
$^{13}$C NMR, CD$_2$Cl$_2$, 125 MHz
$^1$H NMR, CDCl$_3$, 500 MHz
$^{13}\text{C NMR, CDCl}_3$, 125 MHz

$\text{CDCl}_3$

$f_1$ (ppm)

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
$^1$H NMR, CDCl$_3$, 500 MHz
$^1$H NMR, CDCl$_3$, 500 MHz
$^1$H NMR, CDCl$_3$, 125 MHz
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